STRAIN-ENABLED PHOSPHINATION AND FLUORINATION REACTIONS

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Chapter one of this thesis discusses the hydrophosphination of carbodiimides with secondary phosphine boranes. These reactions provide access to phosphaguanidine boranes, which have previously not been studied. A cyclic carbodiimide was also prepared, and hydrophosphination of this substrate provided access to structurally unique phosphaguanidines that bear resemblance to cyclophanes.

Chapter two delineates the extension of this hydrophosphination method to functionalize strained carbocycles, namely bicyclo[1.1.0]butanes. The scope and stereoselectivity of this transformation was investigated, and further transformations of the cyclobutyl phosphine products were conducted. Studies on the addition of aromatic and heteroaromatic thiols to bicyclo[1.1.0]butanes are also described in this chapter.

Chapter three describes a strain-relieving deoxyfluorination of bicyclo[1.1.0]butyl alcohols. The products of these transformations are fluorinated methylenecyclobutanes, which can be oxidatively transformed into cyclobutanones. Bicyclo[1.1.0]butyl amides were also subjected to fluorination with a high degree of diastereoselectivity.

Chapter four details the development of bicyclo[1.1.0]butyl amides as potential androgen receptor antagonists for the treatment of castration-resistant prostate cancer. In the course of these medicinal chemistry studies, an acid-mediated isomerization of bicyclo[1.1.0]butanes to cyclobutenes was discovered.

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LIST OF ABBREVIATIONS

Å..... angstrom (10^{-10} meter)

Ac..... acetyl

AR..... androgen receptor

ATR..... attenuated total reflectance

aq..... aqueous

BHT..... butylated hydroxytoluene

BINAP..... (2,2'-bis(diphenylphosphino)-1,1'-binaphthyl

BINOL ..... 1,1'-bi-2-naphthol

BIPI..... Boehringer Ingelheim Phosphine-Imidazole

BPE ..... 1,2-bis((2,5)-diphenylphospholano)ethane

Boc ..... *t*-butyloxycarbonyl

Bn..... benzyl

Bz..... benzoyl

calcd..... calculated

CCDC..... Cambridge Crystallographic Data Centre

centrimide ..... cetyltrimethyl ammonium bromide

COD 1,5-cyclooctadiene

CRPC ..... castration-resistant prostate cancer

CSA..... 10-camphorsulfonic acid

Cy..... cyclohexyl

d..... days

DAST ..... diethylaminosulfur trifluoride

DABCO..... 1,4-diazabicyclo[2.2.2]octane

Deoxo-Fluor®. bis(2-methoxyethyl)aminosulfur trifluoride

DIBAL ..... diisobutylaluminum hydride

DBU ..... 1,8-diazabicyclo[5.4.0]undec-7-ene

DCC ..... dicyclohexylcarbodiimide

DCE..... 1,2-dichloroethane

DCE-d_4..... deuterated 1,2-dichloroethane

DEPT..... distortionless enhancement by polarization transfer (NMR method)

DHP..... 3,4-dihydro-2*H*-pyran

DMAc ..... dimethylacetamide

DMAP 4-dimethylaminopyridine

DMF ..... dimethylformamide

DMP ..... Dess-Martin periodinane

DMPU ..... 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone

DMSO ..... dimethylsulfoxide

dppe..... 1,2-*bis*(diphenylphosphino)ethane

ee ..... enantiomeric excess

eq..... equivalents

EC_{50}..... effective concentration for 50% inhibition

EtOAc ..... ethyl acetate

ESI..... electrospray ionization

FDA..... United States Food and Drug Administration

Fluolead..... 4-*tert*-butyl-2,6-dimethylphenylsulfur trifluoride

HFIP ..... hexafluoroisopropanol

HMBC..... heteronuclear multiple bond correlation (NMR method)

HPLC ..... high performance liquid chromatography

HRMS ..... high resolution mass spectrometry

HSQC ..... heteronuclear single quantum coherence spectroscopy (NMR method)

Hz ..... hertz

IR ..... infrared

k_{rel} ..... relative rate

LAH ..... lithium aluminum hydride

M ..... molar (mol/L, concentration unit)

m-CPBA ..... *meta*-chloroperbenzoic acid

Me ..... methyl

min ..... minutes

mp ..... melting point

Ms ..... mesyl; methanesulfonyl

MS ..... mass spectrometry

NBS ..... *N*-bromosuccinimide

NfF ..... nonafluorobutyl sulfonyl fluoride

NFSI ..... *N*-fluorobenzenesulfonimide

NMO ..... *N*-methylmorpholine-*N*-oxide

NMP *N*-methyl-2-pyrrolidone

NMR ..... nuclear magnetic resonance

NOESY ..... nuclear Overhauser effect spectroscopy (NMR method)

NTTL ..... *N*-1,2-naphthaloyl-(*S*)-*tert*-leucine

PCC ..... pyridinium chlorochromate

PPTS ..... pyridinium *p*-toluenesulfonate

Ph ..... phenyl

PyFluor 2-pyridinesulfonylfluoride

R_f ..... retardation factor

rt ..... room temperature

RSM ..... recovered starting material

s-Bu ..... secondary butyl

SFC ..... supercritical fluid chromatography

Skewphos ..... 2,4-bis(diphenylphosphino)pentane

$t_{1/2}$ ..... half life

T3P 2,4,6-tripropyl-1,3,5,2,4,6-trixatriphosphorinane-2,4,6-trioxide

t-Bu ..... tertiary butyl

THF ..... tetrahydrofuran

TLC ..... thin layer chromatography

Ts..... *p*-toluenesulfonyl

UV ..... ultraviolet

ACKNOWLEDGEMENTS

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development of the androgen receptor antagonists described in Chapter 4 (with Dr. James Johnson, Dr. Keita Takubo, Serene Tai, Taber Maskrey, and numerous other collaborators from outside the group). I also acknowledge the NMR, MS, and X-ray crystallography facility directors (Dr. Damodaran Achary, Dr. Bhaskar Godugu, and Dr. Steve Geib, respectively) for maintaining these essential resources for the research described herein.

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1.0 HYDROPHOSPHINATION OF CARBODIIMIDES WITH PHOSPHINE BORANES

1.1 INTRODUCTION

1.1.1 Hydrophosphination of Carbodiimides

The hydrophosphination of carbon-carbon and carbon-heteroatom multiple bonds is a highly atom economical means to prepare substituted phosphines. The earliest hydrophosphinations, which were reported in the 1950's, involved reacting alkenes with primary phosphines under harsh conditions.[1] An array of catalytic methods for alkene and alkyne hydrophosphination have since been developed, including methods that are mediated by bases[2], organocatalysts,[3] radical initiators,[4] or Lewis acids.[5] Hydrophosphinations have also been catalyzed by late transition metals[6] or lanthanides.[7] More recently, overarching efforts to develop more sustainable catalytic methods have produced hydrophosphination catalysts derived from coinage[8] and alkali earth[9] metals. The development of catalytic, asymmetric hydrophosphinations of hydrocarbons is also an area of ongoing research.[10]

Although carbodiimides are most prominently known as peptide coupling agents,[11] they too can been subjected to hydrophosphination. Early protocols for these transformations involved harsh conditions such as heating a neat mixture of a secondary phosphine with a carbodiimide.[12] In modern practice, various methods using base, transition metal, or lanthanide catalysts are available for the hydrophosphination of carbodiimides.[13] Deprotonated secondary phosphines can be used to formally hydrophosphinate carbodiimides through attack of the phosphide anion onto

the carbodiimide followed by aqueous workup.[14] The hydrophosphination of other electrophiles such as isocyanates, isothiocyanates, and aldehydes has also been investigated (Figure 1).[15]

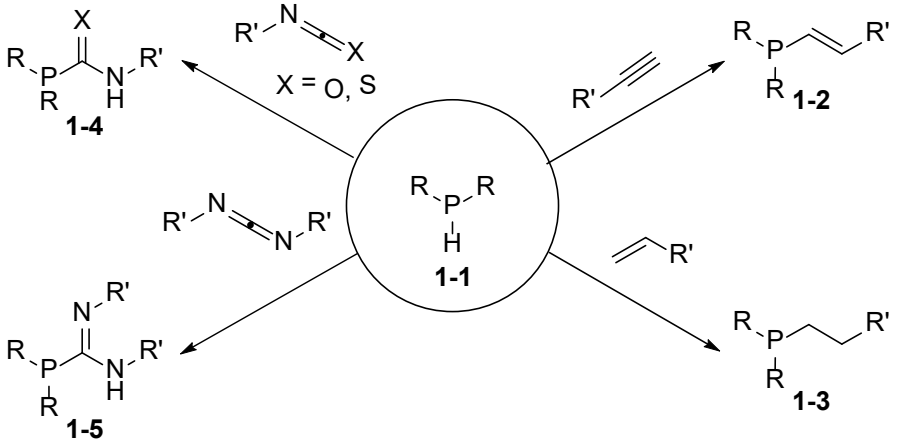


Figure 1. General overview of hydrophosphination chemistry.

1.1.2 Hydrophosphination with Phosphine Boranes

Phosphine boranes are Lewis acid/base adducts that have been known for over a century, but interest in the chemistry of these molecules has increased in recent decades.[16] Aside from serving as air-stable precursors of functionalized phosphines, these adducts have been used as hydrogen atom donors in Barton-McCombie deoxygenations[17] and as polyphosphinoborane monomers.[18] A marked advantage of phosphine boranes is their tendency to be air-stable crystalline solids, whereas the parent phosphines (particularly primary and secondary alkyl phosphines) are often air sensitive, pyrophoric, and/or malodorous. These adducts are generally synthesized from the corresponding phosphines with BH_3•THF or BH_3•SMe_2 as the borane donor, although alternative methods for their preparation have been described, such as a one-pot reduction/boron complexation of phosphine oxides.[19]

In addition to protecting the phosphine against oxidation, the borane decreases the magnitude of the pKa of hydrogens adjacent to phosphorus (as with tertiary phosphine boranes) or directly attached to phosphorus (in the case of secondary phosphine boranes).[20] This property enables phosphine boranes to be convenient, air-stable reagents that can be readily elaborated into more complex phosphines. For example, dimethylphenyl tertiary phosphine boranes can be subjected to an enantioselective deprotonation using *s*-BuLi and (–)-sparteine. Subsequent addition of a copper (II) salt promotes oxidative anion dimerization to provide access to *P*-chiral dppe derivatives.[21] The P–H bond in secondary phosphine boranes (**1-6**) can be deprotonated with *n*-BuLi, NaH, or *t*-BuOK, and the resulting anion can be subjected to a hydrophosphination or alkylation reaction.

Imamoto and co-workers first reported in 1990 that secondary phosphine boranes (**1-6**) can hydrophosphinate Michael acceptors in the presence of substoichiometric potassium hydroxide.[22] Since Imamoto's pioneering work, Gaumont and co-workers have found that hydrophosphinations of alkenes and alkynes can be conducted with secondary phosphine boranes by simply heating a neat mixture of the two reactants (Figure 2).[23] For example, terminal alkynes were hydrophosphinated to afford vinyl phosphines (**1-8**) with high regioselectivity and *E/Z* selectivity.[24] Similar selectivity was observed in the thermal hydrophosphination of vinyl ethers[25] (**1-9**) and 1,1-disubstituted alkenes.[26] A thermal hydrophosphination of β-pinene afforded the limonene-derived product **1-10** through a ring opening, which suggests that these thermal transformations proceed through a radical mechanism.[26]

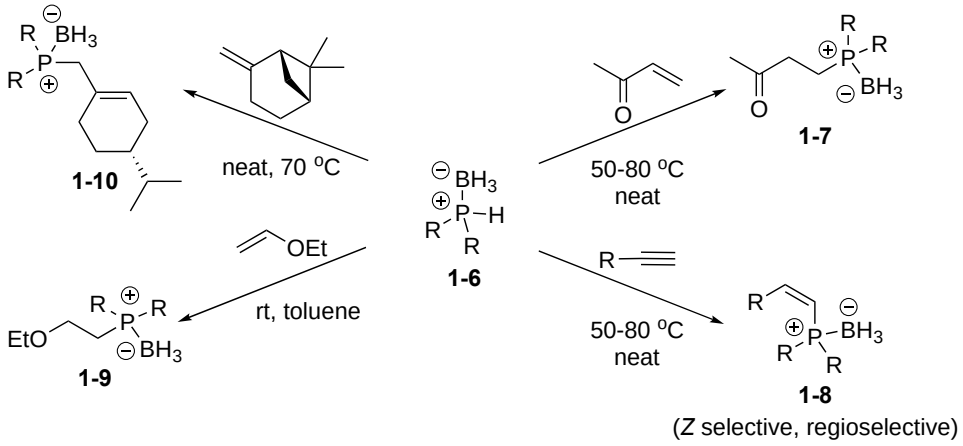
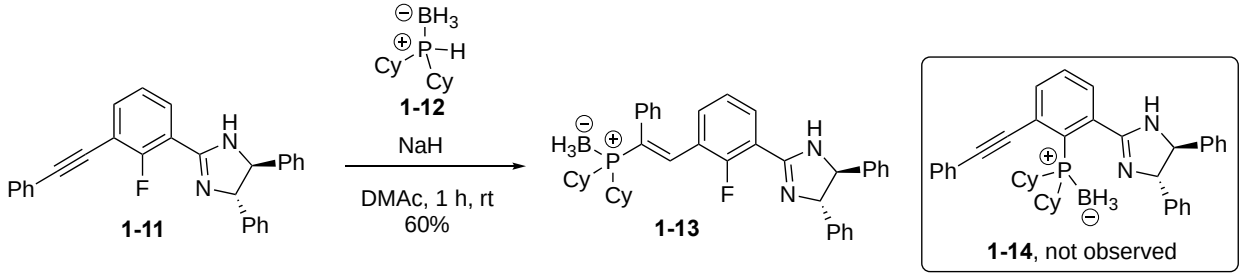


Figure 2. Thermal hydrophosphinations of secondary phosphine boranes.

In 2009, Busacca and co-workers serendipitously discovered a base-mediated hydrophosphination of alkynes using secondary phosphine boranes. This unprecedented reaction was discovered while attempting to prepare ligand **1-14** through nucleophilic aromatic substitution of imidazoline **1-11** (Scheme 1). Further investigation revealed that the hydrophosphination is general for a range of substituted alkynes. Vinyl phosphine boranes such as **1-13** with are obtained in good yields and *E:Z* ratios ranging from 3:1 to >20:1.[27] In cases where differentially substituted alkynes were used, complete regioselectivity was attained based on the electronic parameters of the alkyne substituents. This method offers advantages over Gaumont's thermal hydrophosphination in that it is effective on internal alkynes, proceeds at ambient temperature, and does not require a large excess of the alkyne.



Scheme 1. Discovery of a base-mediated hydrophosphination of internal alkynes.

This operationally simple hydrophosphination method enables access to phosphines that are potentially useful for catalytic applications. The vinyl phosphines derived from alkyne hydrophosphination (**1-15**) were enantioselectively hydrogenated with cationic rhodium and (*R, R*)-Skewphos[28] to afford chiral monodentate phosphine boranes with >99% ee.[27] Alkyne derivatives such as propargyl amines, and propargyl alcohols, allenyl phosphine oxides also effectively undergo this hydrophosphination (**1-16** and **1-17**, Figure 3).[29] These more highly functionalized hydrophosphination products can also serve as ligand precursors. For example, the allene hydrophosphination products (**1-16**) are protected equivalents of bis-phosphine monooxides, which are a useful class of ligands for catalysis.[30] The products of propargyl amine or alcohol hydrophosphination are also precursors to P–N or P–O bidentate ligands. The bidentate binding mode of **1-17** (X = NHPh) was confirmed by preparing an ^{15}N labeled substrate and evaluating the ^{15}N and ^{31}P coupling constants of Pt or Rh complexes.[29]

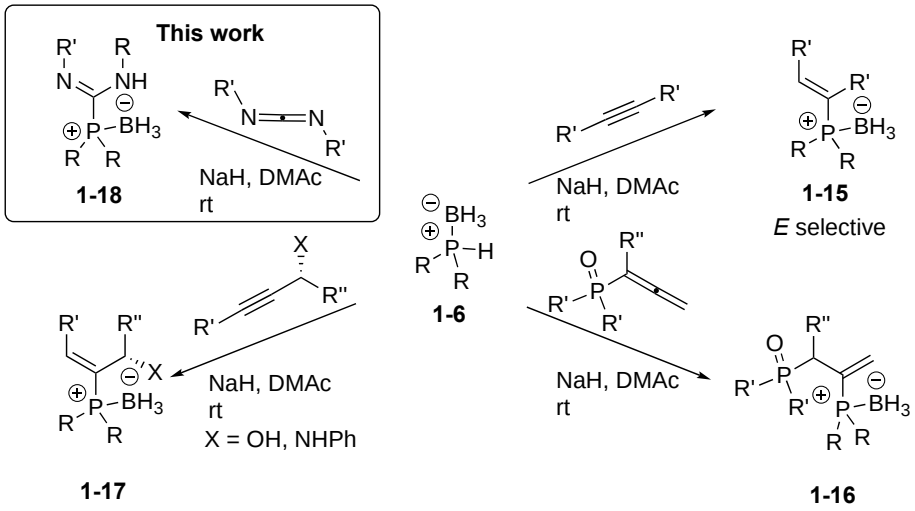
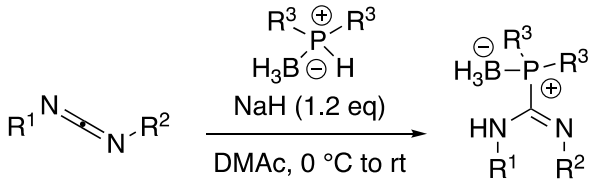


Figure 3. Base-mediated hydrophosphinations with phosphine boranes.

Given the simplicity of this base-mediated hydrophosphination protocol, it became of interest to extend this method to the hydrophosphination of heterocumulenes such as carbodiimides. In an initial screening effort, Busacca and co-workers found that secondary

phosphine boranes do indeed hydrophosphinate carbodiimides to provide phosphaguanidine boranes **1-19 – 1-24** (Table 1). Carbodiimides with *N,N'*-dialkyl, *N,N'*-diaryl and *N*-alkyl, *N*'-aryl substituents undergo this transformation equally well (entry 1 vs. entry 3). Di-*t*-butyl and dicyclohexyl phosphine boranes were also similarly effective in the reaction. The products of the reaction were typically crystalline solids that were easily purified by chromatography on SiO_2. X-ray crystal structures of two representative phosphaguanidine boranes (**1-21** and **1-23**) were obtained (Figure 4).[31]

Table 1. Preliminary results from Busacca *et al*. on the hydrophosphination of carbodiimides.



entry	R^1	R^2	R^3	product	yield (%)
1	Cy	Cy	Cy	**1-19**	71
2	Cy	Cy	t-Bu	**1-20**	58
3	Ph	Ph	Cy	**1-21**	69
4	Ph	Ph	t-Bu	**1-22**	77
5	Cy	Ph	Cy	**1-23**	63
6	Cy	Ph	t-Bu	**1-24**	58

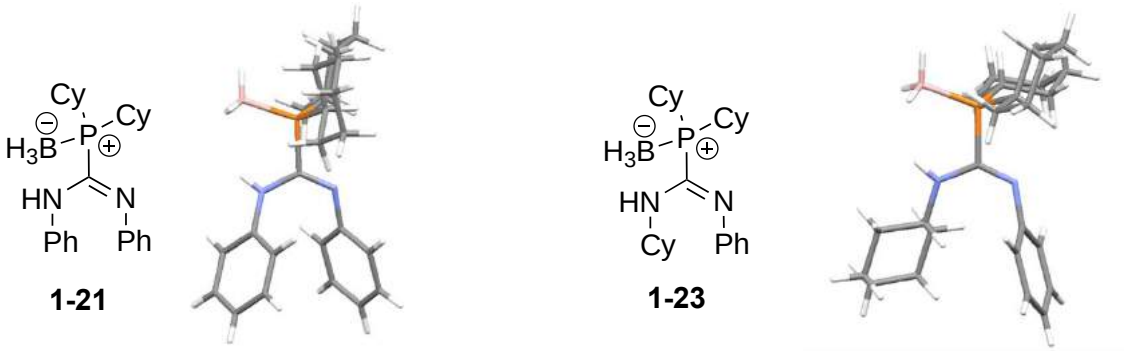


Figure 4. Phosphaguanidine boranes crystallized by Busacca *et al*.

1.1.3 Structure and Utility of Phosphaguanidines

Guanidines have long been of interest to the chemistry community due to their structure, reactivity, and occurrence in biologically active natural products.[32] The guanidine structure is well-represented among common nucleophilic organocatalysts,[33] and a significant number of chiral guanidines have been designed to accomplish various asymmetric catalytic transformations.[34] Phosphaguanidines, wherein one nitrogen from the guanidine unit is substituted for a phosphine, have received significantly less attention. These molecules are typically prepared by the hydrophosphination of carbodiimides with secondary phosphines.[13a]

An extensive NMR, computational, and crystallographic study of phosphaguanidines was undertaken by Coles and co-workers.[35] Their research demonstrated that phosphaguanidines have distinct conformational preferences that are governed by the nature of the *P* and *N* substituents. A nomenclature system was developed to define the eight possible conformations of a given phosphaguanidine that arise from three binary factors: *E* vs *Z* stereochemistry about the C=N bond, *syn* vs *anti* orientation of the *N*–R substituents and α vs β alignment of the guanidine *N–H* with the *P–R* substituents (Figure 5). It was found that these orientations are dependent on the nature of the *P–R* substituent: *P*-diphenyl phosphines appear only in the E_{syn} α conformation, whereas *P*-cyclohexylphosphines show a mixture of E_{syn} α and Z_{anti} α/β isomers. When the phosphines were transformed to the corresponding phosphine sulfides or selenides, a mixture of E_{syn} β and Z_{syn} β conformers were observed, with the former being preferred in *P*-diphenyl phosphines and the latter in *P*-dicyclohexyl phosphines.

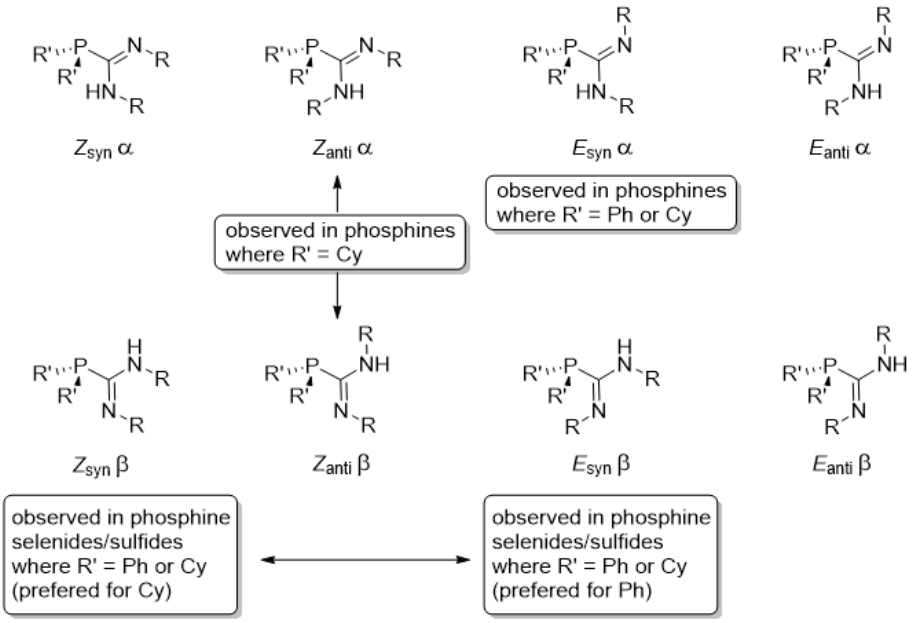


Figure 5. Eight possible conformations of phosphaguanidines annotated with the observations of Coles *et al*.[32]

The Z_{syn} β conformation allows for an interaction between the guanidine N–H and the chalcogen atom in the phosphine sulfides and selenides. In the case of the phosphine selenide **1-25**, the interaction was evident through a J_{SeH} NMR coupling of 6 Hz. A similar alignment between the N–H and the borane was observed in the crystal structures of phosphaguanidine boranes **1-21** and **1-23**, as illustrated in Figure 6. The distances between the phosphaguanidine N–H and boron/selenium atoms are comparable between the two structures (2.68 Å H–Se distance vs. 2.57 Å H–B distance).

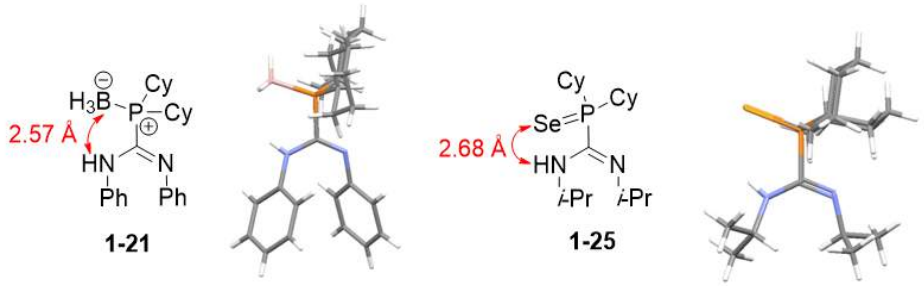
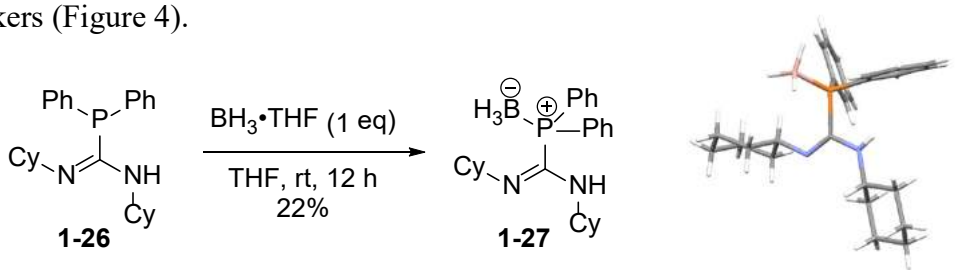


Figure 6. Comparison between the conformations of phosphine borane **1-21** and phosphine selenide **1-25**.

As part of their study, Coles and co-workers prepared the first example of a phosphaguanidine borane (**1-27**) by treating **1-26** with BH_3•THF (Scheme 2).[35] While this synthesis was successful in providing crystals of **1-27** suitable for X-ray diffraction, the yield of the transformation was low, and the product was reported to be unstable in solution. Interestingly, **1-26** adopted an E_{syn} (pseudo) α conformation in the solid state, which stands in contrast to the Z_{syn} β conformation observed in the phosphaguanidine boranes **1-21** and **1-23** prepared by Busacca and co-workers (Figure 4).



Scheme 2: Phosphaguanidine borane **1-27** prepared by Coles *et al*.[35]

Despite these studies on the preparation and structure of phosphaguanidines, no examples of their use in catalysis have been reported to date. This is somewhat surprising considering that phosphaguanidines have been shown to exhibit either mono- or bidentate binding modes to metals such as molybdenum.[14b] Upon deprotonation of the phosphaguanidine *N–H*, the resulting anion has exhibited a wide array of binding modes to lithium,[14a] aluminum,[36] titanium,[36] zirconium,[36] thallium,[37] and rhodium.[38] Similarly, there have been no reports on the application of phosphaguanidines or their borane-protected analogs as organocatalysts, where the nitrogen atoms could plausibly participate in nucleophilic[33] or hydrogen bonding[39] catalysis. The opportunity to identify new types of catalysts provided further motivation to develop a convenient method for the hydrophosphination of carbodiimides to produce phosphaguanidine boranes.

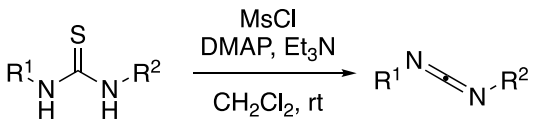
1.2 RESULTS AND DISCUSSION

1.2.1 Hydrophosphination of Acyclic Carbodiimides

Given the previous success with using deprotonated secondary phosphine boranes to conduct hydrophosphination reactions,[27, 29] we sought to extend the scope of this method to include the hydrophosphination of carbodiimides. Preliminary studies by collaborators at Boehringer Ingelheim suggested that under the previously developed conditions (NaH in DMAc), hydrophosphination of alkyl and aryl carbodiimides could be conducted with aliphatic phosphine boranes (Table 1). However, it remained to be explored as to whether aromatic phosphine boranes or other carbodiimides would be tolerated in the transformation.

Thus, a series of carbodiimides containing both electron-rich and electron-poor aryl substituents was prepared by desulfurization of the corresponding disubstituted thioureas.[40] In cases where the necessary thioureas were not commercially available or obtained from collaborators, they were prepared by reacting the appropriate primary amine with an isothiocyanate. This approach provided convenient access to carbodiimides **1-28**–**1-31** (Table 2).

Table 2. Preparation of carbodiimides through desulfurization of the corresponding thioureas.

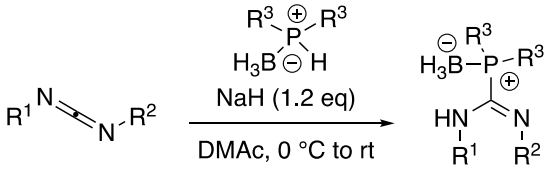


entry	R^1	R^2	product	yield (%)
1	$(3,5\text{-}CF_3)_2C_6H_3$	Cy	**1-28**	83
2	$(2\text{-}OMe)C_6H_4$	Cy	**1-29**	72
3	$(4\text{-}OMe)C_6H_4$	Ph	**1-30**	87
4	allyl	allyl	**1-31**	58

These carbodiimides, along with commercially available dicyclohexylcarbodiimide (DCC), were tested in the hydrophosphination reaction (Table 3).[31] Both electron-rich and

electron-poor aryl carbodiimides were effective substrates (entries 1–3), although a diallyl carbodiimide gave a somewhat lower yield (entry 4). Aryl secondary phosphine boranes showed poor reactivity, regardless of the nature of the carbodiimide (entry 5). Commercially available *N, N*'-bistrimethylsilyl carbodiimide could not be hydrophosphinated with either cyclohexyl or *t*-butyl phosphine boranes, perhaps due to the high steric encumbrance of this substrate (entry 6).

Table 3. Hydrophosphination of carbodiimides.

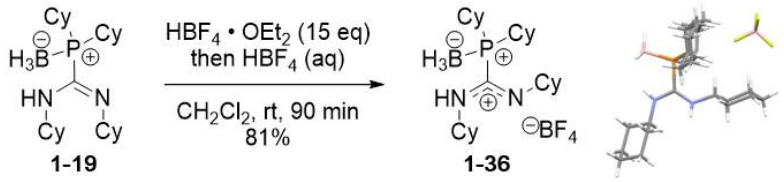


entry	R^1	R^2	R^3	product	yield (%)
1	Ph	(4-OMe)C_6H_4	*t*-Bu	**1-32**	78
2	Cy	(3,5-CF_3)$_2C_6H_3$	Cy	**1-33**	55
3	Cy	(2-OMe)C_6H_4	Cy	**1-34**	58
4	allyl	allyl	Cy	**1-35**	37
5	Cy	Cy	(4-Me)C_6H_4	(—)	<10
6	$SiMe_3$	$SiMe_3$	Cy or *t*-Bu	(—)	0

While the borane motif on products **1-32–1-35** prevents oxidation of the phosphaguanidine, it must ultimately be removed to enable ligation of the phosphine to a metal center. Heating a toluene solution of a phosphine borane with DABCO is an effective approach for the deboronation of aromatic phosphine boranes.[31] Alternatively, removal of the borane can be conducted with HBF_4 to provide a tralkylphosphonium tetrafluoroborate salt. These phosphonium salts can be free-based *in situ*, and thus serve as convenient air-stable surrogates of alkyl phosphines for use in catalysis.[41]

Phosphaguanidine **1-19** was subjected to this acid-mediated deboronation. These conditions, however, did not cleave the alkyl phosphaguanidine boranes, but rather protonated the guanidine functionality to afford phosphaguanidinium borane tetrafluoroborate salt **1-36** (Scheme 4). In contrast to generic trialkylphosphines, the protonation of the guanidine apparently deactivates the phosphine borane and consequently prevents deboronation. The structure of **1-36**,

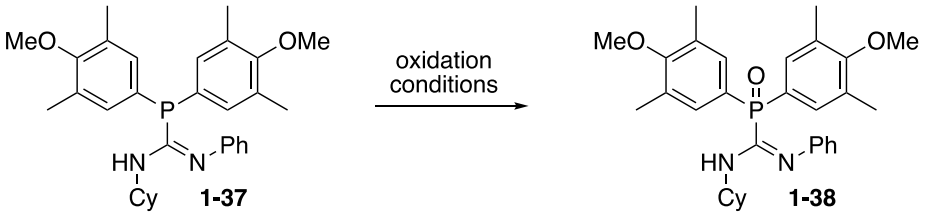
which was confirmed by X-ray crystallography, features an unmodified borane and a phosphaguanidinium core with identical C–N bond lengths of 1.316 Å. The guanidinium substituents of **1-36** crystallized in an E_{syn}/Z_{anti} conformation, much like a similar phosphaguanidinium salt that was previously crystallized by Mansfield *et al*.[42]



Scheme 3. Attempted acidic deboronation with HBF_4 results in tetrafluoroborate salt **1-36**.

The oxidation of the free phosphaguanidines to the phosphaguanidine oxides was also explored. Interestingly, Hitchcock and co-workers reported that phosphaguanidines undergo C–P bond cleavage when treated with *t*-BuOOH to afford an amidinium phosphinate salt.[42] In agreement with this result, treatment of phosphine **1-37** with *t*-BuOOH using Hitchcock's procedure resulted in a complex mixture that likely contains an analogous species (Table 4). A cleaner oxidation occurred when *m*-CPBA was used as the oxidant, and the desired phosphine oxide **1-38** was isolated in 33% yield after chromatography on SiO_2. Dilute aqueous hydrogen peroxide, however, provided phosphine oxide **1-38** in nearly quantitative yield. This series of experiments suggests that despite their relative paucity in the literature,[43] phosphaguanidine oxides are stable entities that can be prepared through the oxidation of phosphaguanidines with the appropriate oxidizing agent.

Table 4. Oxidation of phosphaguanidine **1-37**.



oxidant	solvent	yield (%)
3% H_2O_2	acetone	99
m-CPBA	CH_2Cl_2	30
t-BuOOH	CH_2Cl_2	0

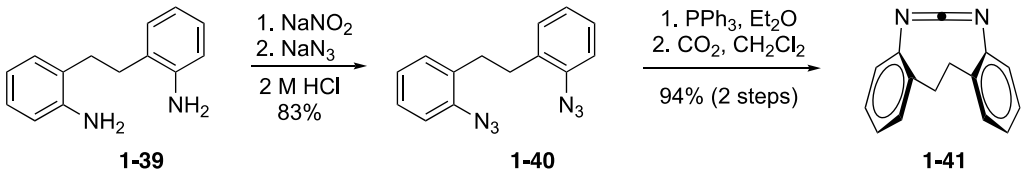
1.2.2 Preparation and Hydrophosphination of a Cyclic Carbodiimide

While this base-mediated hydrophosphination of acyclic carbodiimides is operationally convenient, the method has limitations. Aryl phosphine boranes showed poor reactivity, which significantly limits the scope of the phosphaguanidines that can be obtained. In addition, the products have a congested steric environment around the phosphorous center that disfavors the binding of metals and reduces the ability of the guanidine motif to act as an organocatalyst. Attempts to use the deprotected phosphaguanidines in Cu-catalyzed conjugate additions, Rh-catalyzed hydrogenation, and organocatalytic transformations were unsuccessful. These results may suggest that the phosphine center of these molecules is poorly accessible for metal binding. Further complicating this structural issue is the fact that some phosphaguanidine products are a mixture of *E/Z* isomers in solution (for example, tetracyclohexyl product **1-19** is a 2:1 mixture of Z_{syn}/E_{syn} isomers as judged by ^{13}C NMR).[31] This isomerism suboptimal for the design of phosphaguanidine ligands for use in stereoselective catalysis.

To produce phosphaguanidines with a greater potential for catalytic applications, analogs with a well-defined rigid structure and a more accessible phosphorus center were pursued. The

most intriguing approach toward this end is to constrain the nitrogen substituents in a Z_{syn} conformation by embedding them in a medium-sized ring. Efficient access to such a scaffold could be achieved through the hydrophosphination of a cyclic carbodiimide. Although seven-membered or smaller cyclic carbodiimides are unprecedented, eight-membered carbodiimides have been prepared from cyclic thioureas or amidooximes.[44] These cyclic molecules are useful tools for experimental studies of the nitrogen inversion barrier in carbodiimides.[45]

Molina and co-workers have reported an efficient preparation of cyclic carbodiimide **1-41** from commercially available 2,2'-ethylenedianiline **1-39** (Scheme 4).[46] A diazotization/azidation sequence, formation of a bis-iminophosphorane, and double Staudinger-aza-Wittig ring closure with CO_2 provided an efficient access to the cyclic carbodiimide **1-41**. Although the originally reported preparation used stoichiometric DMAP and Boc_2O to form a CO_2 equivalent *in situ*,[47] bubbling CO_2 gas through the solution with a balloon was found to be a more convenient and equally effective means to conduct this ring closure. The three-step sequence is operationally straightforward, uses inexpensive reagents, and requires only one chromatographic purification.



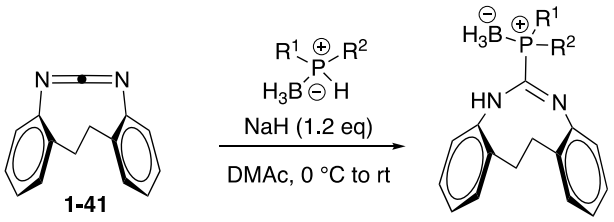
Scheme 4. Preparation of cyclic carbodiimide **1-41**.

The nine-membered cyclic carbodiimide **1-41** is a strain-activated molecule. Although this ring strain has not been experimentally quantified, the strained nature of **1-41** and related derivatives has been verified spectroscopically.[46, 48] For example, the abnormally high carbodiimide IR stretch of **1-41** (2186 cm^{-1}, as compared to the typical range of 2120-2145 cm^{-1}) is suggestive of a strain-induced weakening of the carbodiimide C=N bonds. This strain activation may render **1-41** more reactive than DCC and other acyclic carbodiimides in hydrophosphination

chemistry. Nonetheless, carbodiimide **1-41** is a bench-stable solid that showed no detectable decomposition after several months of storage at room temperature under air.

The hydrophosphination of carbodiimide **1-41** was conducted with a variety of phosphine boranes (Table 5). In contrast to acyclic carbodiimides, consistent yields were obtained for both aliphatic (entries 1, 2) and aromatic (entries 3, 4) secondary phosphine boranes using the standard hydrophosphination conditions. A mixed phenylcyclohexyl phosphine borane also performed well (entry 5). This improved reaction scope may be attributed to the enhanced reactivity of carbodiimide **1-41**, which benefits from strain-activated C=N bonds and high accessibility of the central *sp*-hybridized carbon. The products resulting from hydrophosphination of **1-41** (**1-42**–**1-46**) constitute the first examples of a phosphaguanidines that are embedded in a medium ring system.

Table 5. Hydrophosphinations on cyclic carbodiimide **1-41**.



entry	R^1	R^2	product	yield (%)
1	*t*-Bu	*t*-Bu	**1-42**	67
2	Cy	Cy	**1-43**	72
3	(4-Me)C_6H_4	(4-Me)C_6H_4	**1-44**	78
4	(3,5-Me-4-OMe)C_6H_3	(3,5-Me-4-OMe)C_6H_3	**1-45**	83
5	Ph	Cy	**1-46**	69

The cyclic phosphaguanidines were typically colorless, crystalline solids that could be purified by chromatography on SiO_2 or by recrystallization. Single crystal X-ray diffraction was conducted on suitable crystals of phosphaguanidines **1-42** and **1-44**. Interestingly, in both cases, the nine-membered ring adopts a compact boat-like conformation (Figure 7). This produces a tight dihedral angle (17–24°) for the H-C-C-H bonds of the ethylene bridge. Consequently, the aromatic

rings of the guanidine sit nearly aligned, with an average inter-ring distance of about 4 Å. Although the shortest inter-ring distances (2.8 Å) are comparable to those of [2,2]-*p*-cyclophanes (2.7–3.2 Å) and graphite (3.4 Å), the rings angle outward to give much longer maximal inter-ring distances (5.2–5.3 Å) (Table 6).[49]

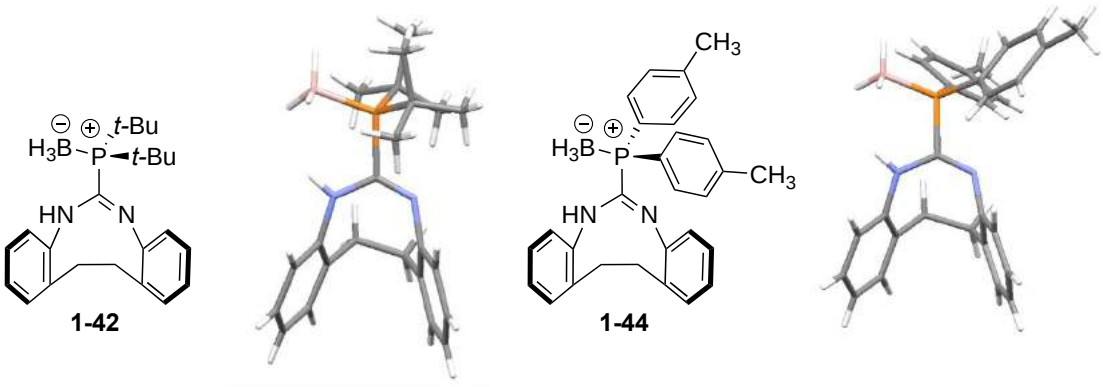
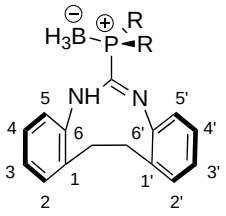


Figure 7. Crystal structures for compounds **1-42** and **1-44**.

Table 6. Pertinent data from the crystal structures of **1-42** and **1-44**.



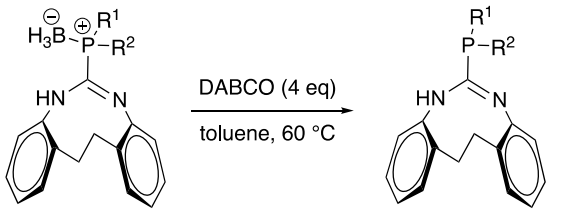
R	ethylene bridge H-C-C-H dihedral angle (°)	B-P-C-*N*H dihedral angle (°)	C_1-C_1' distance (Å)	C_4-C_4' distance (Å)	C_n-C_n' average distance (Å)
t-Bu	22	4	2.80	5.15	3.98
4-MeC_6H_4	24	21	2.83	5.33	4.07

In addition, **1-42** and **1-44** were found to have an α (eclipsed) orientation between the N–H and BH_3 in the solid state. This phenomenon was also observed in the acyclic phosphaguanidines **1-21** and **1-23** that were crystallized by Busacca and co-workers (Figure 6). Modeling studies of *t*-butyl phosphine borane **1-42** at the HF/6-311+G** level of theory revealed that the

α (N–H eclipsed) orientation is preferred over the β orientation by 10 kcal/mol, although the exact origin of this preference is not known.

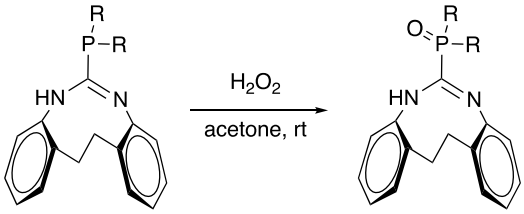
Deprotection of the aromatic cyclic phosphaguanidine boranes using DABCO in toluene proceeded smoothly to provide phosphines **1-47** and **1-48** (Table 7). The mixed aromatic/aliphatic phosphaguanidine borane **1-46** also successfully underwent deprotection to afford racemic phosphine **1-49**. The free phosphines **1-47** and **1-48** were oxidized using dilute hydrogen peroxide to provide phosphine oxides **1-50** and **1-51** in high yield with no evidence of phosphaguanidine cleavage (Table 8).

Table 7. Deprotection of cyclic phosphaguanidine boranes.



R^1	R^2	product	yield (%)
(4-Me)C_6H_4	(4-Me)C_6H_4	**1-47**	81
(3,5-Me-4-OMe)C_6H_3	(3,5-Me-4-OMe)C_6H_3	**1-48**	65
Ph	Cy	**1-49**	94

Table 8. Oxidation of cyclic phosphaguanidines.



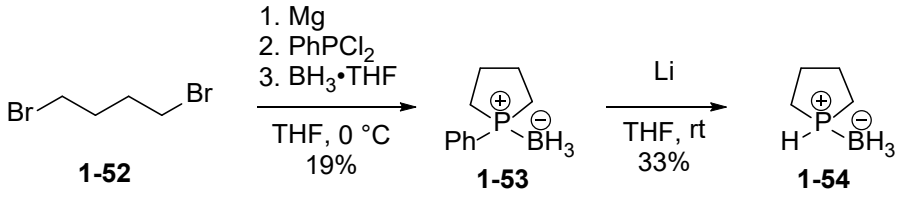
R	product	yield (%)
(4-Me)C_6H_4	**1-50**	86
(3,5-Me-4-OMe)C_6H_3	**1-51**	91

1.2.3 Hydrophosphination with Phospholane Boranes and Attempted Catalytic Applications

The use of strained cyclic carbodiimide **1-41** as a hydrophosphination substrate enabled the preparation of both aromatic and aliphatic phosphaguanidine boranes in good yield (Table 5). As evidenced by crystallography studies on cyclic phosphaguanidine boranes **1-42** and **1-44** (Figure 7), these products adopt predictable, well-defined geometries that can enable the rational design of ligands and organocatalysts. Moreover, the ability to readily remove the borane and expose the free phosphines **1-47**–**1-49** (which can be manipulated on the benchtop using standard precautions) also bodes well for the application of the molecules as phosphine ligands in catalytic applications.

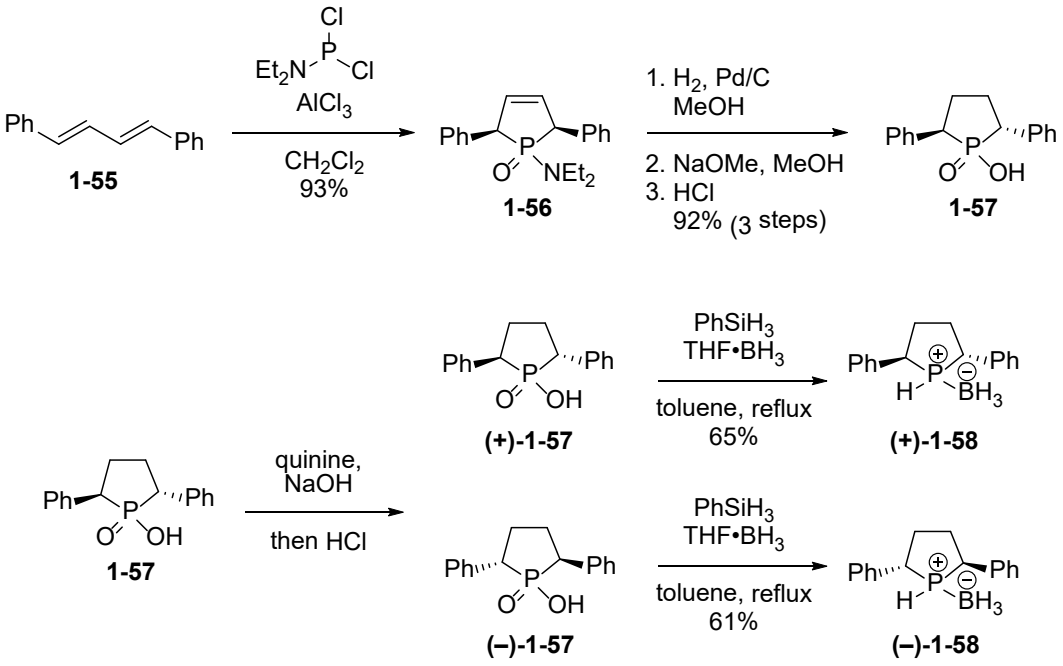
Ideally, chirality could be introduced into cyclic phosphaguanidine scaffold to provide access to molecules that can catalyze enantioselective transformations. Attempts were made to produce a chiral derivative of cyclic carbodiimide **1-41** by installing a cyclic acetal on the ethylene backbone, but these efforts were unsuccessful. Alternatively, chirality can be introduced by conducting the hydrophosphinations with a chiral secondary phosphine borane. If the chiral secondary phosphine borane was also cyclic in nature, this approach could provide a phosphaguanidine core with a highly accessible phosphine center.

Five-membered phospholane boranes have the greatest precedent among cyclic secondary phosphine boranes, and were the primary targets of this study. Phospholane borane **1-54** was prepared from 1,4-dibromobutane **1-52** through double Grignard formation, trapping with a dichlorophosphine, formation of a tertiary phosphine borane, and reduction with lithium metal (Scheme 5).[50] This preparation was low yielding, but the inexpensive reagents allowed the reactions to be sufficiently scaled to provide >200 mg of **1-54**.



Scheme 5. Preparation of phospholane borane **1-54**.

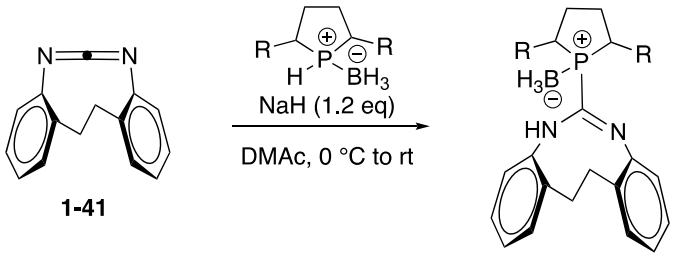
Chiral *C2* symmetric phospholanes have been prepared by introducing phenyl substituents at the 2- and 5-positions of the phospholane ring. These chiral phospholanes are the basis of the BPE ligand class, which are useful for asymmetric hydrogenation and other transformations.[51] Several methods to prepare these phospholanes have been reported; however, the method previously used by Busacca proved to be the most effective.[27] The phospholane scaffold was accessed from diene **1-55** by using a McCormack [4+1] cyclization.[52] Subsequent hydrogenation and epimerization/hydrolysis afforded phosphinic acid **1-57**, which was subjected to a classical resolution with quinine. Reduction with phenylsilane and borane complexation then afforded each enantiomer of phospholane borane **1-58** (Scheme 6).



Scheme 6. Preparation of chiral phospholane borane **1-58**.

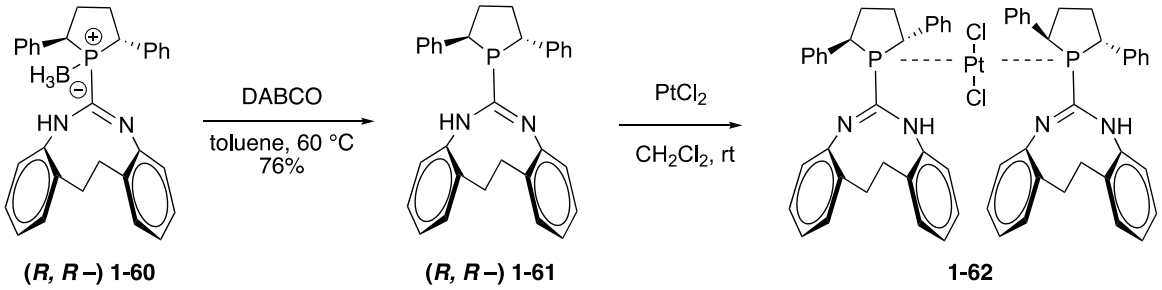
The phospholanes **1-54** and **1-58** were used in hydrophosphination reactions with cyclic carbodiimide **1-41** (Table 9). While unsubstituted phospholane borane **1-54** was less effective in the transformation, each of the **1-58** enantiomers underwent hydrophosphination in moderate to good yield to afford chiral phospholane borane **1-60**. It was found that the sign of the specific rotation for **1-60** is opposite of that of the corresponding secondary phosphine borane precursor (**1-58**).

Table 9. Hydrophosphination of cyclic carbodiimide **1-41** with phospholane boranes.



R	enantiomer	product	yield (%)
H	(—)	**1-59**	35
Ph	(*R, R*)	**(–)-1-60**	79
Ph	(*S, S*)	**(+)-1-60**	61

Like the other phosphaguanidines, **1-60** can be deprotected by heating in the presence of excess DABCO (Scheme 7). The resulting phosphine **1-61** is sufficiently air-stable to be briefly manipulated in air, but the material was placed under an inert atmosphere for storage. The potential of this phosphine to bind to transition metals was evaluated by forming a complex with platinum (II) chloride. When a solution of **1-61** in CH_2Cl_2 was treated with 0.5 equivalents of $PtCl_2$ and left undisturbed, the *trans*-$PtCl_2$(phosphine)$_2$ complex **1-62** formed as light yellow prisms. The structure of this complex was confirmed by X-ray crystallography (Figure 8). The observed Pt–P bond length (2.305 Å) and J_{PtP} coupling constant (2352 Hz) of **1-62** is consistent with similar $PtCl_2$ complexes with sterically bulky phosphines.[53]



Scheme 7. Deprotection and platinum complex formation with chiral phosphine borane **1-61**.

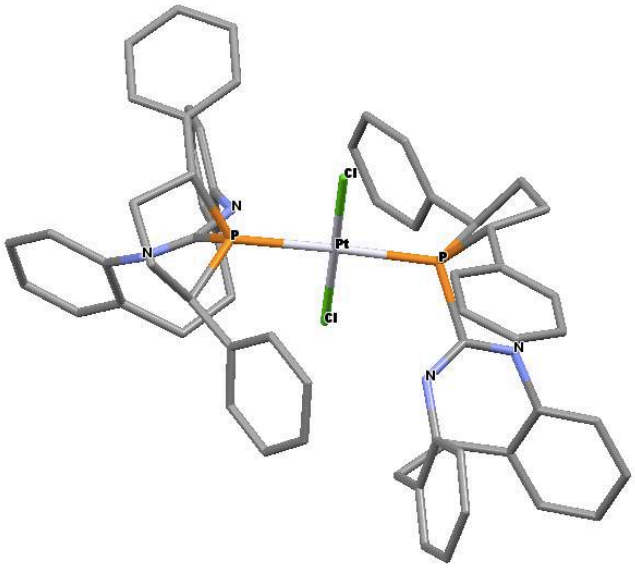


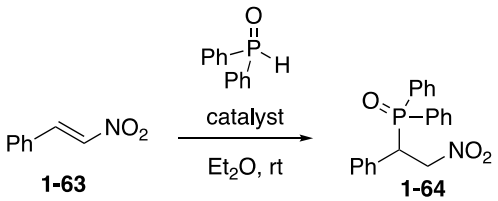
Figure 8. X-ray crystal structure of platinum complex **1-62**. Hydrogens are omitted for clarity.

Despite the success in forming complex **1-62**, the application of **1-61** in asymmetric catalysis did not yield successful results. For example, enantioselective borylation[54] or Heck reactions[55] were **1-61** was used as a ligand either showed poor conversion or gave extensive decomposition of the substrate. Rhodium-catalyzed hydrogenation was successfully carried out using **1-61**; however, the hydrogenated product had no detectable enantiomeric excess.

Attempts to use the either the free phosphaguanidines or their borane complexes as guanidine-type hydrogen bonding catalysts were similarly unsuccessful. The addition of diphenylphosphite to nitrostyrene (**1-63**), for example, is reported to proceed in excellent yield and enantioselectivity using a chiral, bicyclic guanidine catalyst (Table 10).[56] However, 20 mol% of

achiral phosphine borane **1-59** was required to get similarly high yields in this transformation. Disappointingly, when the same catalyst loading of the chiral derivative **1-60** was used, a much lower yield was obtained. This is possibly due to the steric encumbrance of the phosphaguanidine motif imparted by the phenyl rings on the phospholane. In general, the poor catalytic activity of these molecules suggests that alternative phosphaguanidine architectures will need to be considered for the preparation of phosphaguanidines with high utility in catalysis.

Table 10. Attempted hydrogen bonding catalysis with phosphaguanidine boranes.



catalyst	loading (mol %)	yield (%)
1-59	5	47
1-59	20	81
1-60	20	23

1.3 CONCLUSIONS

A method for the hydrophosphination of carbodiimides using air-stable secondary phosphine boranes was developed. Various aromatic and aliphatic substituents were tolerated on the carbodiimide substrate in the transformation. However, aryl phosphine boranes were less effective than alkyl phosphine boranes. An acidic deboronation protocol was attempted on the alkyl phosphaguanidine products, but protonation of the guanidine occurred and phosphaguanidinium borane salts were isolated. The free phosphines could, however, be oxidized to phosphine oxides in good yield without cleavage of the C–P bond.

A cyclic carbodiimide was prepared, which underwent a facile hydrophosphination with a wider scope of phosphine boranes. Thus, a series of nine-membered cyclic phosphaguanidines were prepared, which were found to have interesting boat-like structures that were elucidated by X-ray crystallography. Chiral derivatives of the cyclic phosphaguanidines were prepared through hydrophosphination with chiral, cyclic phospholane boranes. The chiral phospholane borane was deprotected, and a crystalline platinum (II) complex was prepared with this material. Unfortunately, attempts to use this chiral phosphaguanidine either as a ligand in asymmetric catalysis or as an organocatalyst were not fruitful.

2.0 NUCLEOPHILIC ADDITIONS TO BICYCLO[1.1.0]BUTYL NITRILES

2.1 INTRODUCTION

2.1.1 Bicyclo[1.1.0]butanes: Structure and Reactivity

The concept of molecular strain has a storied history that dates back to the proclamations of Adolf von Baeyer in the late ninetieth century.[57] Indeed, strain activation underlies many aspects of modern synthetic chemistry, such as strategic design in total synthesis,[58] strain-enabled reaction methods,[59] and bioorthogonal tranformations.[60] Numerous strained molecules containing three- and four-membered rings have been designed and applied in target-oriented synthesis.[61]

Among these strained rings, bicyclo[1.1.0]butanes are distinguished by their high strain energy (64 kcal/mol) and unique structural properties.[57] Though they are quite strained, many derivatives are readily prepared and are bench-stable. The first synthesis of an authentic bicyclo[1.1.0]butane derivative was published by Wiberg in 1959, who prepared methyl bicyclo[1.1.0]butanoate by ring contraction of 3-bromocyclobutane methyl ester.[62] The parent bicyclo[1.1.0]butane hydrocarbon, which is a gas at room temperature (boiling point 8 °C), can be synthesized in a similar fashion through intramolecular Wurtz coupling of 1,3-dihalocyclobutanes.[63] More versatile synthetic methods to access functionalized bicyclo[1.1.0]butanes have since been developed, including those based on Simmons-Smith chemistry,[64] intramolecular carbenoid cyclizations,[65] or ring closures of appropriately substituted cyclopropanes.[66]

Studies of the structure and bonding in bicyclo[1.1.0]butanes have elucidated several unique features of these molecules. For example, bicyclo[1.1.0]butanes adopt a "butterfly" like geometry, with an interflap angle of about 123° (Figure 9). The C–C bond distances of both the lateral and central bonds are 1.507 Å, which is slightly shorter than those of typical cyclopropanes (1.512 Å).[67] The C–H bonds range in length from 1.142 Å (methine) to 1.194 Å (*exo* methylene).

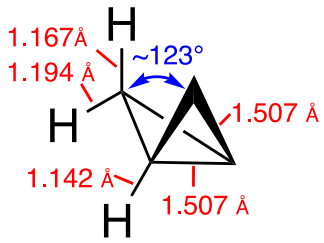


Figure 9. Key structural parameters of bicyclo[1.1.0]butanes.[67a]

Although the C–C bonds of bicyclo[1.1.0]butanes are equal in length, the central bond is distinguished from the lateral bonds by its substantial π character.[68] Experimental verification of this character was reported by Moore and co-workers, who found that bicyclo[1.1.0]butane dimer **2-1** has a substantial UV absorption at 195 nm that is characteristic of a conjugated π system (Figure 10).[69] The nature of this central bond imparts a high *s* character to the methine C–H bonds, which is manifested by an unusually large ^{13}C–H coupling constant (202 Hz) that is intermediate between ethylene (156 Hz) and acetylene (249 Hz).[62b]

Much like cyclopropanes,[70] the central bond of bicyclo[1.1.0]butanes can impact the reactivity of adjacent carbinols through hyperconjugative stabilization. In fact, the hydrolysis of bicyclo[1.1.0]butane ester **2-3** was found to be 3 orders of magnitude faster than the corresponding cyclopropane ester **2-2** (Figure 10).[62b] In contrast to cyclopropane **2-2**, which formed the expected cyclopropylmethanol upon hydrolysis, bicyclobutane **2-3** reacted preferentially at the central bond to produce cyclobutanols.

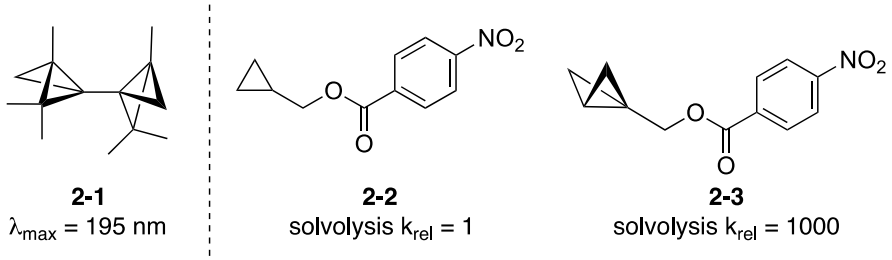
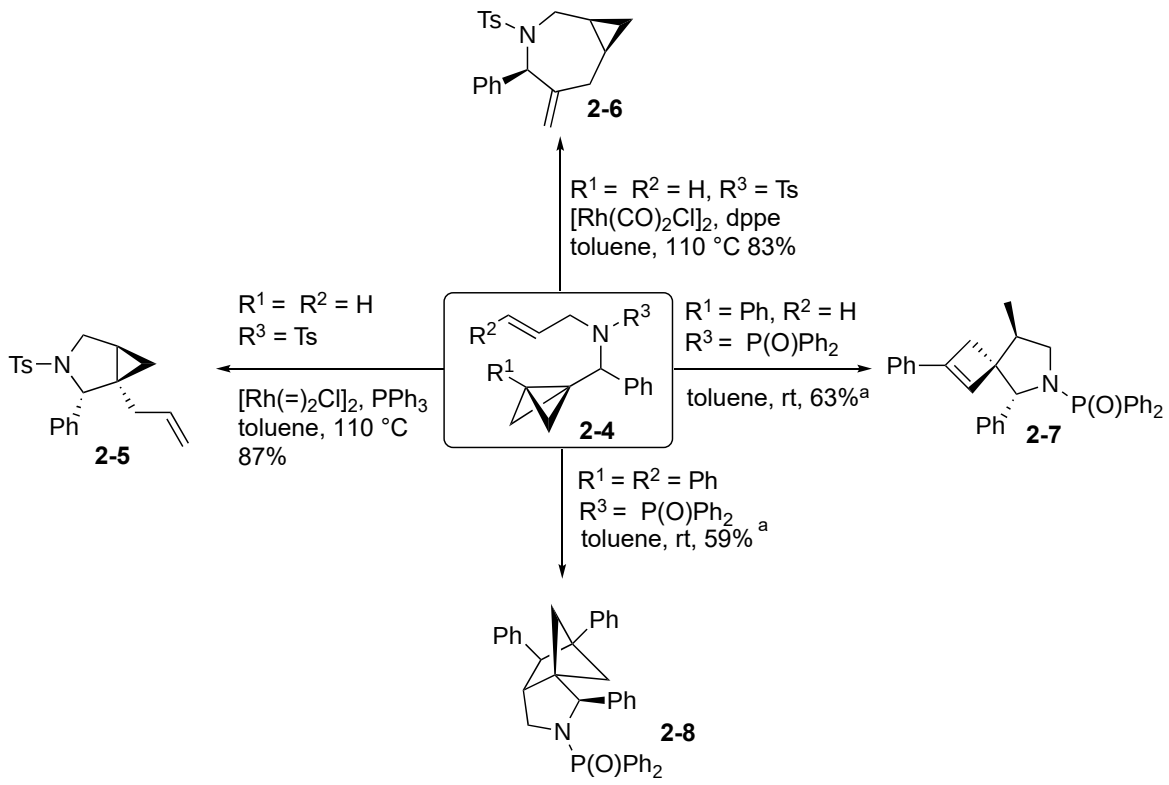


Figure 10. Experimental verifications of the unusual π character of the central bond of bicyclo[1.1.0]butanes.

Despite the very interesting structure and reactivity of bicyclo[1.1.0]butanes, their application in preparative organic synthesis has been limited. Most synthetic studies of these strained hydrocarbons have focused on their solvolysis and transition-metal mediated isomerizations to dienes and related structures, which was a popular research focus in the 1970's and early 1980's.[71] Various metals were studied in this context, including palladium, nickel, rhodium, silver, and platinum.[72]

More recently, Walczak and Wipf have demonstrated the value of bicyclo[1.1.0]butanes as precursors of structurally novel heterocycles (Scheme 8).[73] For example, an intramolecular Rh-mediated isomerization of alkene-tethered bicyclo[1.1.0]butanes (**2-4**) can selectively provide pyrrolidine **2-5** or azepine **2-6** in good yield, depending on the ligand and rhodium source employed.[74] When phenyl-substituted bicyclo[1.1.0]butyl phosphinamides are alkylated with allyl and propargyl electrophiles using phase-transfer catalysis, the intermediate alkylated products spontaneously rearrange to spirocyclic cyclobutenes such as **2-7** through an Alder-ene reaction. In contrast, the use of cinnamyl bromide derivatives enables the synthesis of pyrrrolidines such as **2-8** through a formal [2+2] reaction pathway.[75] Studies of these thermal transformations using electron spin resonance spectroscopy suggest that they occur through biradical intermediates.[76] The unique heterocycles that can be obtained from bicyclo[1.1.0]butanes have been applied in medicinal chemistry studies[77] and in a synthetic approach toward the daphniglaucin family of polycyclic alkaloids.[78]

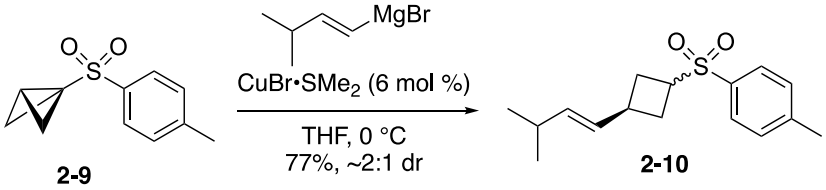


Scheme 8. Intramolecular transformations of bicyclo[1.1.0]butanes developed by Walczak and Wipf.[74-75]
[a]The thermal rearrangements were conducted through phase-transfer allylations of the bicyclobutyl phosphinamides with the appropriate allyl bromide. The intermediate allylated materials (i.e., **2-4**) underwent rearrangement *in situ* at rt.

2.1.2 Nucleophilic Additions to Bicyclo[1.1.0]butanes

Both the highly-strained nature of the bicyclo[1.1.0]butane scaffold and the substantial π character of its central bond enable ring-opening transformations to provide cyclobutanes. In fact, the ability of bicyclo[1.1.0]butanes to undergo facile hydrolysis to cyclobutanol derivatives was recognized soon after the initial discovery of these carbocycles.[62b, 79] Bicyclo[1.1.0]butanes have been converted into functionalized cyclobutanes through acidic solovolysis,[80] electrophilic halogenation,[81] and photochemical irradiation.[82] These reactions provide an intriguing alternative to [2+2] cyclizations for the selective synthesis of 1,3-difunctionalized cyclobutane derivatives.

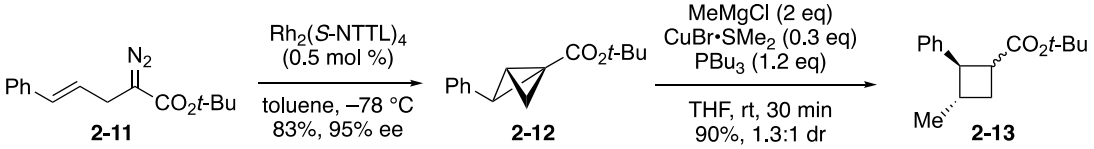
The importance of these studies notwithstanding, the addition of carbon-based nucleophiles through an anionic pathway provides a more versatile and synthetically useful method for the synthesis of cyclobutanes from bicyclo[1.1.0]butanes. The high π character of the strained central bond enables bicyclo[1.1.0]butanes to be functional equivalents of Michael acceptors, especially when substituted with an electron withdrawing group at the ring junction. Gaoni and co-workers were the first to study this mode of reactivity by investigating the addition of organocuprates to sulfones such as **2-9** (Scheme 9).[83] These additions were found to be quite facile, but the cyclobutane products such as **2-10** were typically formed as inseparable mixtures of *cis/trans*-diastereomers.[84] However, the researchers later designed a series of constrained polycyclic bicyclo[1.1.0]butane derivatives that underwent diastereoselective organocuprate additions.[83b, 83c] This synthetic method was also applied to the total synthesis of citrilol acetate, a cyclobutane-containing monoterpene natural product.[83b]



Scheme 9. Nucleophilic addition to bicyclo[1.1.0]butane sulfones developed by Gaoni *et al.*

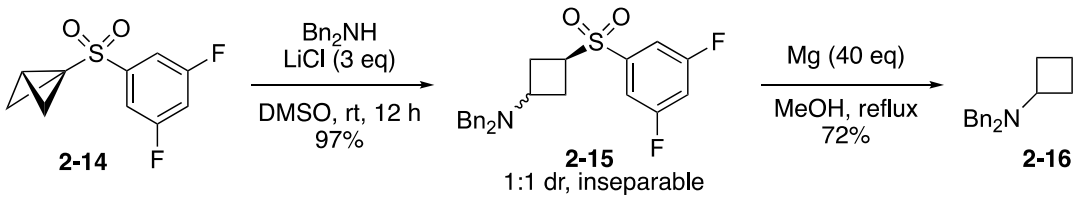
Fox and co-workers have developed a tandem approach to functionalized cyclobutanes through an enantioselective bicyclo[1.1.0]butane formation and nucleophilic addition sequence.[65a] Upon treatment of diazo ester **2-11** with a chiral rhodium carboxylate complex, bicyclo[1.1.0]butane ester **2-12** is formed with good enantioselectivity (typically >90% ee, Scheme 10). The ester can be either isolated or subjected to an *in situ* nucleophilic attack by an organocuprate. Unfortunately, the nucleophilic addition proceeds with negligible diastereoselectivity. An epimerization method was therefore developed whereby **2-13** can be

deprotonated and treated with a bulky proton source (BHT) to provide the desired cyclobutanes with >20:1 diastereoselectivity.



Scheme 10. Enantioselective bicyclo[1.1.0]butane synthesis/nucleophilic addition sequence.

Until recently, the nucleophilic addition of heteroatomic nucleophiles to bicyclo[1.1.0]butanes was typically limited to solvolysis-type reactions.[80] However, Baran and co-workers realized the potential of bicyclo[1.1.0]butyl sulfones (along with related strained molecules such as aza-bicyclo[1.1.0]butane and [1.1.1]propellane) to enable the late-stage derivation of biologically relevant amines, which is a synthetic paradigm they dubbed "strain-release amination" (Scheme 11).[85] Upon heating a secondary amine with sulfone **2-14**, for example, an excellent yield of aminocyclobutane **2-15** was obtained. Various sulfones were screened in this transformation, and it was found that electron-deficient sulfones such as the difluorophenyl derivative **2-14** are necessary to promote efficient nucleophilic attack of the amine. This addition lacked diastereoselectivity. However, this was inconsequential as the sulfonyl group was typically removed under reductive conditions to provide the cyclobutyl amine (**2-16**). This method was successfully used for many amine substrates, as well as for the selective cyclobutylation of cysteine residues of peptides.



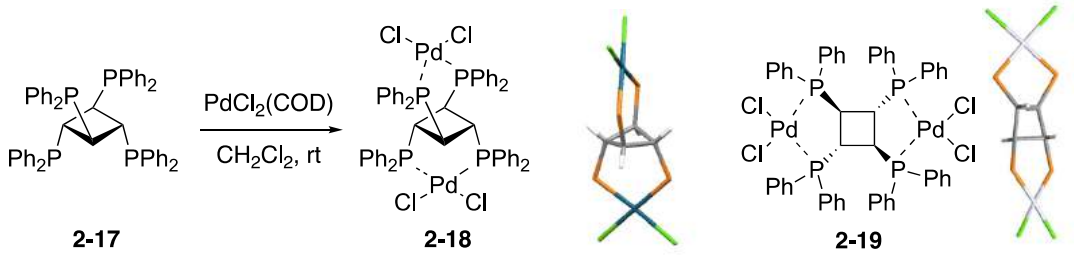
Scheme 11. "Strain-release amination" protocol developed by Baran *et al*.

2.1.3 Cyclobutyl Phosphines: Synthesis and Utility

Phosphines have played an indispensable role in the development of organometallic chemistry and asymmetric catalysis. Many of the most frequently employed phosphines are bidentate derivatives that are supported by a chiral backbone, such as BINAP.[86] The ability of chiral, monodentate phosphines to effectively moderate catalytic transformations has more recently come to be appreciated.[87] Perhaps the most widely employed of the monodentate phosphines are the Buchwald biaryl ligands. Extensive structural analyses of this ligand class have revealed that steric bulk at phosphorus, often provided through cyclohexyl phosphine substituents, is essential for their effective performance in Suzuki-Miyaura cross-couplings.[88] Therefore, the design of novel phosphines with bulky, cyclic substituents may give rise to ligands that are useful for transition-metal mediated transformations.

A cyclobutane is an intriguing substituent to consider for the development of phosphine ligands. Aside from providing some degree of steric bulk, the cyclobutane architecture allows for the introduction of substituents adjacent to the phosphine center with a well-defined spatial relationship. One of the few phosphine derivatives that is based on this architecture is tetraphosphine **2-17**, which was prepared through photochemical [2+2] dimerization of an alkenyl diphosphine.[89] Treatment of **2-17** with (cylcooctadiene)palladium (II) chloride affords a mixture of complexes **2-18** and **2-19**, both of which were studied by X-ray crystallography (Scheme 12). Although the catalytic applications of these tetraphosphines have been limited to CO-ethylene copolymerization reactions, these studies illustrate the potential of cyclobutanes to be effective scaffolds on which to design phosphines with specific structural parameters. Modulating the bite angle of bidentate ligands is known to have a major effect on their performance in catalysis,[90] thus,

bidentate ligands derived from this underexplored cyclobutane scaffold may find unique catalytic applications in organic synthesis.



Scheme 12. Cyclobutyl tetraphosphines as ligands in palladium complexes.

Aside from this example, few other cyclobutyl phosphines have been prepared to date, and many of them are highly unusual structures that lack functional handles for further diversification. For example, phosphine oxide **2-20**[91] and phosphine **2-21**[92] have been prepared from pre-formed phosphinane or carbohydrate scaffolds, respectively (Figure 11). Functionalization of cubane and [1.1.1]-propellane has been exploited to produce phosphines **2-22**,[93] **2-23**,[94] and **2-24**.[95] Intramolecular cyclization of phosphine borane **2-25** has recently been used to prepare cyclobutylphosphine borane **2-26**, but this approach is not amenable to the synthesis of functionalized cyclobutyl phosphines (Scheme 13).[96] To the best of our knowledge, none of these phosphines based on the cyclobutane architecture have been applied in catalysis.

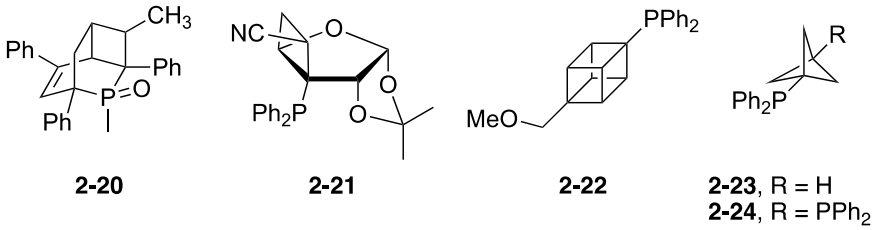
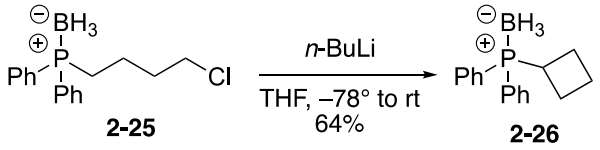


Figure 11. Examples of cyclobutylphosphines.



Scheme 13. Preparation of cyclobutyl phosphine borane **2-26** through intramolecular cyclization.

As these examples illustrate, a general method to produce functionalized cyclobutylphosphines is lacking, as are studies on their utility in catalytic transformations. This prompted the development of a hydrophosphination reaction of bicyclo[1.1.0]butanes with secondary phosphine boranes to produce cyclobutylphosphines. Unlike existing methods, the preparation of cyclobutylphosphines through a hydrophosphination approach would allow for a modular synthesis and would provide products with functional handles for further diversification. Although hydrophosphination with secondary phosphine boranes has been successfully conducted on carbodiimides[31] and alkynes,[27] extension of the method to include strained carbocycles would provide access to novel phosphines that are rich in sp^3 carbons. Moreover, while the addition of carbon and nitrogen nucleophiles to bicyclo[1.1.0]butanes have been demonstrated (Section 2.1.2), the development of a method to add phosphorus nucleophiles would further expand the synthetic utility of these strained rings.

2.2 RESULTS AND DISCUSSION

2.2.1 Hydrophosphination of Bicyclo[1.1.0]butyl Nitriles

Studies on the hydrophosphination of strained rings commenced with a screening of potential reaction substrates. It was initially anticipated that the relief of ring strain would be a driving force to enable the synthesis of a wide variety of phosphine derivatives through hydrophosphination.

Unfortunately, this was not the case. As shown in Figure 12, bicyclo[1.1.0]butyl alcohols (**2-27**, **2-28**), methylenecyclopropanes (**2-29**), cyclopropenes (**2-30**), bicyclic ethers (**2-31**), and activated cyclobutanes (**2-32**) were all inert to the standard hydrophosphination conditions.

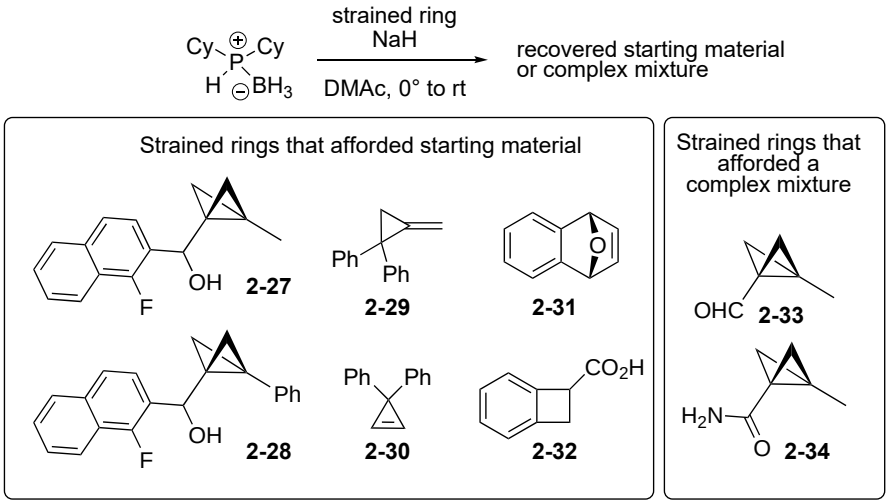
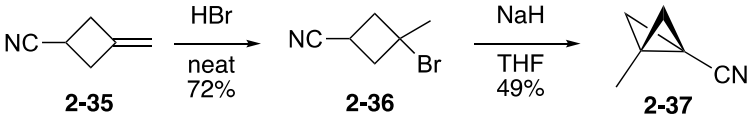


Figure 12. Initial screening studies for the hydrophosphination of strained rings.

In contrast, bicyclo[1.1.0]butanes substituted with an electron withdrawing group at the ring junction (**2-33**, **2-34**) reacted to afford a complex mixture of products. This result suggests that the "hydrophosphination" reaction is, to some degree, a Michael addition of a deprotonated phosphine borane nucleophile onto the electron deficient central bond of the bicyclo[1.1.0]butane. As previously noted (Section 2.1.1), the central bond of this strained ring has substantial π character that presumably facilitates such an addition. This finding is also consistent with previous studies of nucleophilic addition to the central bond of bicyclo[1.1.0]butanes, where sulfone[83, 85] or ester[65a] substituents were found to be necessary for effective cyclobutane formation (Section 2.1.2).

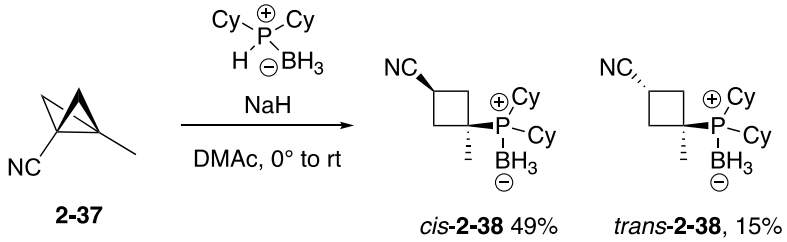
Based on this hypothesis, a nitrile was selected as the optimal activating group to promote the hydrophosphination. Unlike aldehydes (**2-33**) or primary amides (**2-34**), nitriles are not affected by deprotonated secondary phosphine boranes. The bicyclo[1.1.0]butyl nitrile of choice

for these studies was **2-37**, which can be efficiently accessed in two steps from commercially available methylenecyclobutane **2-35** (Scheme 14).[80] Using this protocol, **2-35** was subjected to HBr addition to afford **2-36** as a mixture of diastereomers. Treatment of **2-36** with NaH in THF at reflux affords bicyclobutane **2-37** as a liquid that can be purified by bulb-to-bulb distillation. In this manner, nitrile **2-37** was prepared on decagram scale. Differential scanning calorimetry studies of **2-37** showed that this strained molecule is a moderate explosion hazard upon heating, with a decomposition energy of 1600 J/g at an onset temperature of ~100 °C. Nitrile **2-37** was therefore stored in a –20 °C freezer and handled with appropriate personal protective equipment.



Scheme 14. Synthesis of bicyclo[1.1.0]butyl nitrile **2-37**.

When **2-37** was subjected to the previously developed hydrophosphination conditions with dicyclohexylphosphine borane, a ~2:1 mixture of cyclobutane diastereomers *cis*-**2-38** and *trans*-**2-38** was obtained upon workup (Scheme 15).[97] Notably, and in contrast to previous bicyclo[1.1.0]butane nucleophilic addition studies, these two phosphine borane diastereomers had significantly distinct R_f values on SiO_2 and could be readily separated by chromatography.



Scheme 15. Hydrophosphination of nitrile **2-37** with dicyclohexylphosphine borane.

The identity of the major *cis*-diastereomer was assigned by NOESY (Figure 13). The characteristic correlation between the methyl doublet at 1.52 ppm ($^3J_{HP}$ = 9.2 Hz) and the methine at 3.39 ppm, along with the correlation of both peaks to a single methylene at 2.05 ppm, provides

strong spectroscopic evidence for this assignment of relative stereochemistry. This assignment was later confirmed by obtaining an X-ray crystal structure of a *cis*-cyclobutane derivative (Section 2.2.3).

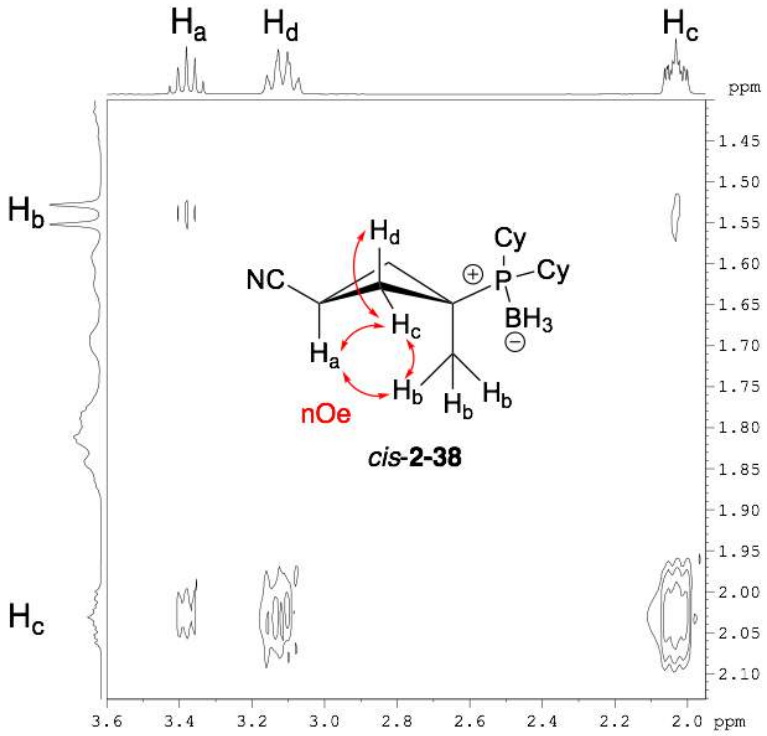
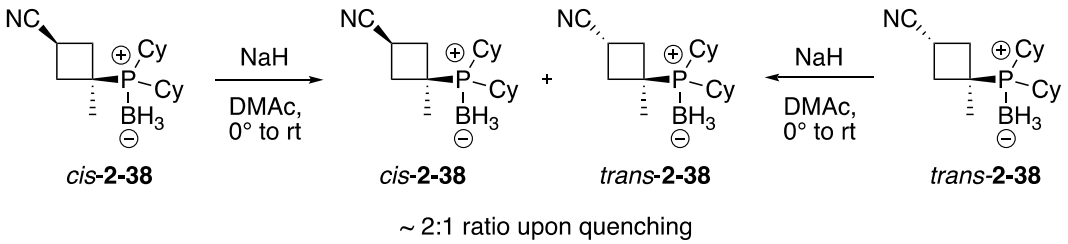


Figure 13. NOESY spectrum of *cis*-**2-38**.

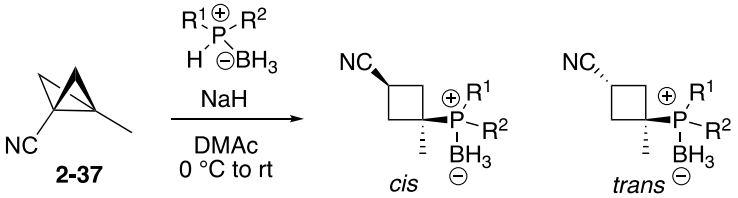
An isomerization study was conducted to investigate the nature of the diastereoselectivity in the transformation. When either pure diastereomer of **2-38** was subjected to the reaction conditions (1.2 eq NaH in DMAc), HPLC analysis of a quenched aliquot showed formation of the original 2:1 mixture of isomers (Scheme 16). This suggests that the diastereoselectivity is thermodynamic in origin. Therefore, a higher yield of the *cis*-isomer (which is potentially more valuable for the preparation of bidentate phosphine ligands) can be achieved by iterative "recycling" of the minor *trans*-isomer through isomerization and purification by chromatography on SiO_2.



Scheme 16. Isomerization studies of **2-38**.

The hydrophosphination of nitrile **2-37** was conducted with various phosphine boranes (Table 11). A variety of aliphatic and aromatic phosphine boranes were effective in the transformation, each giving a ~2:1 mixture of readily separable diastereomers. A generally consistent yield was obtained for all the substrates except for furyl derivative **2-41**. In each case, the identity of the major *cis*-isomer was confirmed by NOESY and by the similarity of the ^{1}H NMR shifts to other analogs.

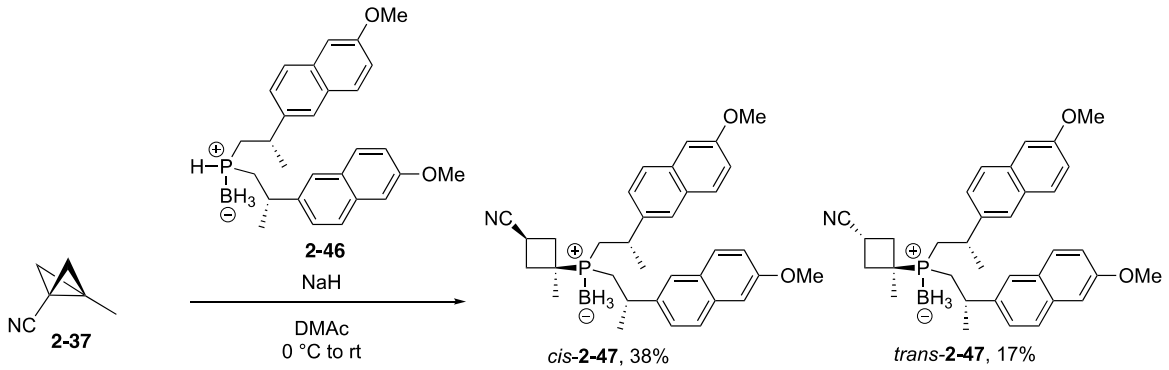
Table 11. Hydrophosphinations of nitrile **2-37**.



R^1	R^2	product	*cis* yield (%)	*trans* yield (%)
Cy	Cy	**2-38**	49	15
t-Bu	*t*-Bu	**2-39**	57	26
Cy	Ph	**2-40**	47	23
n-Bu	2-furyl	**2-41**	28	13
4-(Me)C_6H_4	4-(Me)C_6H_4	**2-42**	48	28
3,5-(Me)C_6H_3	3,5-(Me)C_6H_3	**2-43**	48	24
4-(MeO)C_6H_4	4-(MeO)C_6H_4	**2-44**	43	16
4-(Ph)C_6H_4	4-(Ph)C_6H_4	**2-45**	42	22

A chiral cyclobutylphosphine borane was also prepared using this method. Secondary phosphine borane **2-46** (which was prepared by collaborators at Boehringer Ingelheim over several steps from naproxen) was used to prepare cyclobutane **2-47** in the typical ~2:1 ratio of readily

separable diastereomers (Scheme 17). The hydrophosphination was also attempted with chiral phospholane borane **1-58**. However, unlike in the previous carbodiimide studies, the phospholane underwent epimerization under the reaction conditions to afford a mixture of 4 products (*cis*-and *trans*-cyclobutane isomers, each with a pair of *C2*-symmetric or *meso* phospholanes).



Scheme 17. Preparation of chiral phosphine borane **2-47**.

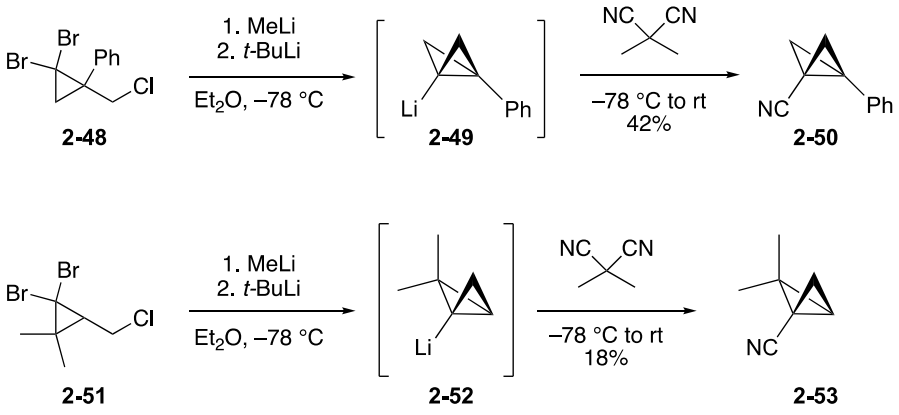
2.2.2 Preparation and Hydrophosphination of other Bicyclo[1.1.0]butane Nitriles

Nitrile **2-37** was suitably reactive in hydrophosphination reactions, convenient to prepare, and stable upon storage. Despite these advantages, the exclusive use of **2-37** as the hydrophosphination substrate only provides access to phosphines with a methyl substituent on the cyclobutane. Access to bicyclo[1.1.0]butyl nitriles with other substituents at the ring junction would enable the preparation of a wider range of cyclobutyl phosphines. However, published methods for the synthesis of bicyclo[1.1.0]butyl nitriles require multiple steps and lack generality.[98]

A more versatile approach to bicyclo[1.1.0]butane nitriles was envisioned to proceed through the direct installation of a nitrile onto a bicyclo[1.1.0]butane scaffold rather than a ring contraction of a cyclobutylnitrile. In practice, this could be accomplished by trapping a bicyclo[1.1.0]butyllithium species with an electrophilic "CN^+" source rather than an imine or

aldehyde (the method commonly used for the synthesis of bicyclo[1.1.0]butyl amines and alcohols by Wipf and co-workers).[73a] Coincidentally, our collaborators at Boehringer Ingelheim had recently developed a convenient method that could enable such a transformation. As part of a research effort to develop new methods for the process-scale preparation of aryl nitriles, it was found that dimethylmalononitrile is a safe and inexpensive reagent for the electrophilic cyanation of aryl lithiums and Grignard reagents.[99] The cyanation reaction is proposed to proceed through the addition of an organometallic reagent to this dinitrile reagent followed by a retro-Thorpe collapse of the anionic intermediate to afford the desired aryl nitrile.

When dibromocyclopropane **2-48** was subjected to the previously reported dilithiation sequence,[66a, 73b] the resulting anion **2-49** underwent this "transnitrilation" to afford nitrile **2-50** (Scheme 18). The analogous bicyclo[1.1.0] butyllithium species **2-52** also underwent this transformation to provide nitrile **2-53**, albeit in a low yield of 18%. This poor yield may be attributed to the lack of an aryl substituent to provide conjugative stabilization of the central bicyclo[1.1.0]butane bond. Nonetheless, this approach provided efficient access to these alternative bicyclo[1.1.0]butane nitriles for hydrophosphination studies.

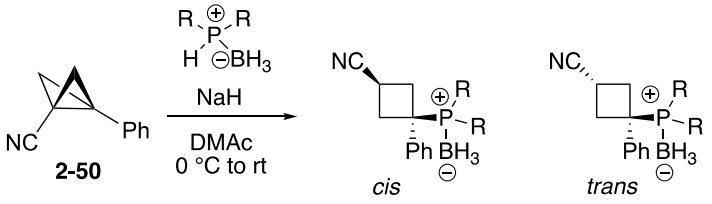


Scheme 18. Preparation of bicyclobutane nitriles **2-50** and **2-53**.

The hydrophosphination of nitriles **2-50** and **2-53** was conducted with dicyclohexyl and di-*p*-tolyl phosphine boranes using the established protocol.[97] Hydrophosphinations of **2-50** afforded

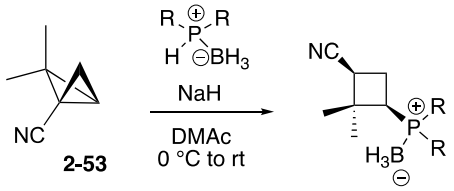
a nearly 1:1 mixture of diastereomers that were readily separable on SiO_2 (Table 12). In contrast, hydrophosphinations of unsubstituted nitrile **2-53** afforded only the *cis*-cyclobutane products, albeit in modest yield (Table 13). These lower yields may be a consequence of the somewhat unstable nature of **2-53**, which showed significant decomposition and polymerization after several days at –20 °C.

Table 12. Hydrophosphination of bicyclobutane nitrile **2-50**.



R	product	*cis* yield (%)	*trans* yield (%)
Cy	**2-54**	38	28
4-(Me)C_6H_4	**2-55**	32	40

Table 13. Hydrophosphination of bicyclobutane nitrile **2-53**.



R	product	yield (%)
Cy	**2-56**	34
4-(Me)C_6H_4	**2-57**	27

These studies suggest that the ratio of *cis/trans*-isomers obtained through this hydrophosphination is heavily influenced by the substituent at the bicyclo[1.1.0]butane ring junction. This can be rationalized in light of the extensive studies on the stereochemical course of nucleophilic additions to bicyclo[1.1.0]butanes conducted by Hoz and co-workers.[100] Both theoretical and experimental evidence suggests that upon equatorial attack by a nucleophile, the incipient nitrile anion will adopt the thermodynamically *less* favored tetrahedral conformation wherein the nitrile is *trans* to the nucleophile.[100b] The anion will equilibrate between two

diastereomeric species prior to workup, presumably through the intermediacy of a planar keteneimine tautomer.[100a] The isomerization study shown in Scheme 16 demonstrates that the thermodynamically favored *cis*- isomer, wherein both substituents sit in equatorial positions, is preferentially formed under thermodynamic equilibration (Figure 14). As the A-value of the R^2 substituent increases from 1.7 (methyl) to 3 (phenyl), the thermodynamic differentiation between the two anionic forms is less pronounced. Thus, a mixture of diastereomers is obtained upon aqueous workup of the reaction.

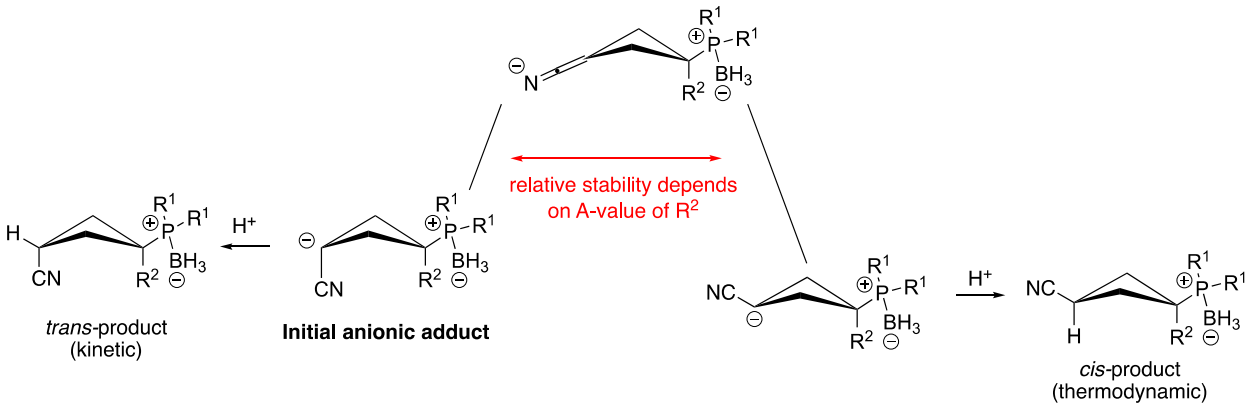
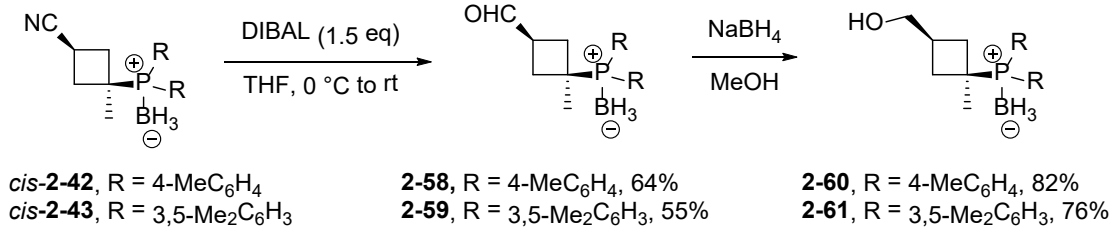


Figure 14. Explanation for the diastereoselectivity observed in the hydrophosphination of bicyclo[1.1.0]butyl nitriles.

2.2.3 Utility of Cyclobutylphosphine Products

An advantage of using nitriles as hydrophosphination substrates is the potential to diversify the cyclobutyl phosphine products. This strategy can be leveraged to enable the synthesis of an array of diversified phosphines. Attempts were made to enact this strategy by converting the cyclobutylnitrile to an imidazoline through a Pinner reaction. This would provide access to cyclobutyl analogs of the bidentate phosphine/imidazoline "BIPI" ligands,[101] but unfortunately, this effort was unsuccessful. However, the cyclobutyl nitriles could be readily be reduced. A two-

step reduction of **2-42** and **2-43** using DIBAL and $NaBH_4$ afforded the corresponding primary alcohols **2-60** and **2-61** (Scheme 19).



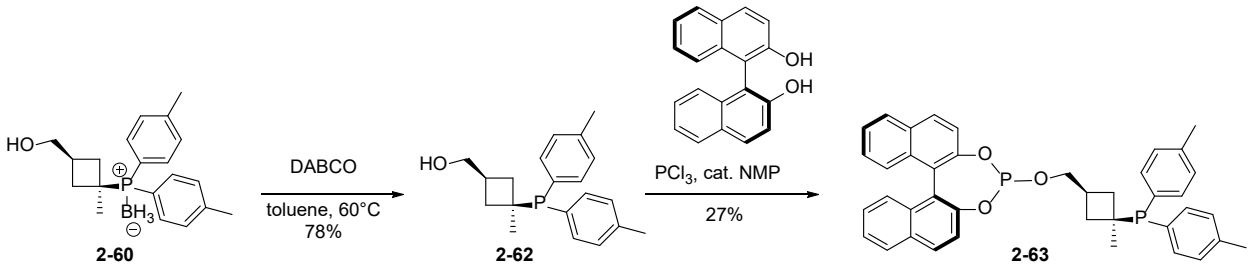
cis-**2-42**, R = 4-MeC_6H_4
cis-**2-43**, R = 3,5-$Me_2C_6H_3$

2-58, R = 4-MeC_6H_4, 64%
2-59, R = 3,5-$Me_2C_6H_3$, 55%

2-60, R = 4-MeC_6H_4, 82%
2-61, R = 3,5-$Me_2C_6H_3$, 76%

Scheme 19. Reduction of cyclobutyl nitriles.

The alcohols **2-60** and **2-61** are versatile precursors of bidentate ligands. For example, the primary alcohol could be treated with a $(RO)_2PCl$ reagent to produce a phosphine/phosphite bidentate system. This class of ligands has been used in asymmetric catalysis, most frequently in asymmetric hydrogenations and hydroformylations.[102] To prepare this type of ligand on the *cis*-cyclobutane scaffold, phosphine borane **2-60** was first deprotected using the standard DABCO method. The free phosphine was then subjected to the chlorophosphite derived from PCl_3 and *S*-BINOL to afford ligand **2-63** (Scheme 20).

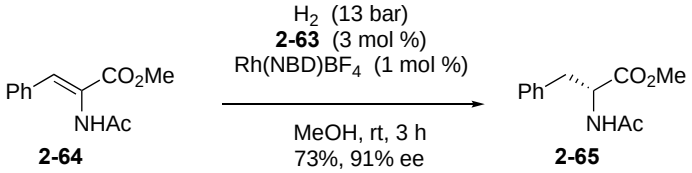


2-60 **2-62** **2-63**

Scheme 20. Synthesis of phosphine/phosphite **2-63**.

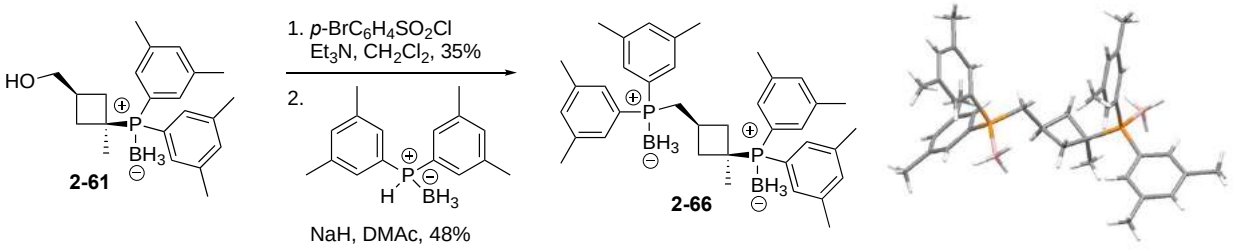
When ligand **2-63** was treated with $[Rh(COD)Cl]_2$ in DCE-d_4, evidence of bidentate Rh binding was observed by ^{31}P NMR: the phosphite shifted upfield from 144.9 to 134.7 ppm and a $J_{Rh\text{-}P}$ of 262 Hz was observed, while the phosphine shifted downfield from 11.2 to 45.7 ppm and a $J_{Rh\text{-}P}$ of 151 Hz was observed. Encouraged by this data, **2-63** was applied in several asymmetric catalytic transformations. The asymmetric hydrogenation of dehydrophenylalanine derivative **2-**

64 with ligand **2-63** and a cationic rhodium source provided the unnatural enantiomer of *N*-phenylalanine methyl ester (**2-65**) in 91% ee (Scheme 21). The absolute configuration of **2-65** was confirmed by optical rotation, and the ee was determined using chiral SFC. Unfortunately, ligand **2-63** did not provide high reactivity or selectivity in the asymmetric hydrogenation of more challenging alkene substrates or in the asymmetric hydrocyanation of alkenes.



Scheme 21. Application of **2-63** in enantioselective hydrogenation.

The preparation of diphosphines from alcohol **2-61** was also explored through formation of a sulfonate ester and treatment with a phosphine borane nucleophile. While the mesylation of alcohol **2-61** was effective, the resulting mesylate was an insufficiently reactive electrophile. The more reactive *p*-bromosulfonate of **2-61** was thus prepared (Scheme 22). Treatment of the sulfonate with a diaryl phosphine borane and base afforded diphosphine borane **2-66**. The structure of this diphosphine borane was secured by X-ray crystallography, which confirms the assignment of relative stereochemistry on the cyclobutane (which was previously based on NOESY).



Scheme 22. Synthesis and X-ray crystal structure of diphosphine borane **2-66**.

The application of **2-66** and monophosphines such as **2-42** and **2-43** (as HBF_4 salts) in catalysis proved difficult. For example, application of these ligands in challenging C–H activations resulted in low conversion and/or extensive substrate decomposition.

While these cyclobutyl phosphines were effective some Suzuki cross-couplings, the yields of the reactions were no better than those employing other more accessible ligands.[104] Future studies should be conducted to identify transformations where the structural rigidity of this cyclobutylphosphine scaffold would be particularly advantageous in facilitating catalysis.

2.2.4 Addition of Thiols to Bicyclo[1.1.0]butanes

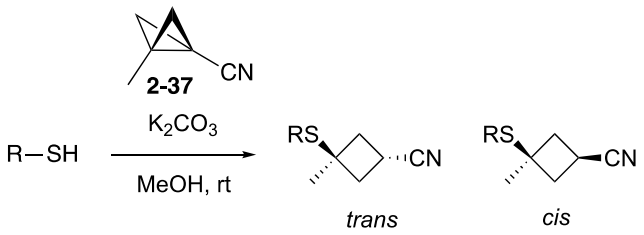
The success of phosphine borane additions to bicyclo[1.1.0]butyl nitriles raised the question of whether thiols, which are similarly good nucleophiles, could add to these strained rings to afford 1,3-difunctionalized cyclobutyl thioethers. Other approaches to cyclobutyl thioethers and their oxidized analogs (sulfoxides and sulfones) include [2+2] cycloaddtions,[105] additions of thiol nucleophiles to cyclobutyl bromides,[106] or additions to pre-formed sulfonyl bicyclo[1.1.0]butanes.[107] In contrast, the nucleophilic addition of thiols to readily obtained bicyclo[1.1.0]butyl nitriles offers a straightforward access to versatile 1,3-difunctionalized cyclobutyl thioethers. Moreover, this operationally simple approach is a viable alternative to photochemical irradiation, which has previously been used to add thiols across bicyclo[1.1.0]butanes.[82]

Interestingly, early reports on the reactivity of nitrile **2-37** noted that hydrolysis and aminolysis reactions of the central bond occur with complete *trans*-diastereoselectivity.[108] This selectivity was also observed when thiophenol was added to **2-37** in methanol. Experimental and theoretical studies of this addition concluded that the *trans* diastereomer is kinetically favored, and fast protonation of the anionic intermediate in protic solvents selectively provides the *trans* product.[100b]

Despite these insightful mechanistic studies, the addition of thiols to bicyclobutanes appears to have gained limited traction from a preparative standpoint. No systematic study has investigated the scope, yield, and selectivity for the addition of a range of thiophenol nucleophiles, nor have additions of heterocyclic thiols been studied. We were therefore encouraged to develop this addition as a method to access stereodefined cyclobutylthioethers as potentially useful synthetic building blocks. There is also an increasing interest in the development of small molecules that are capable of selective covalent modification of cysteine residues in enzyme active sites.[109] Bicyclo[1.1.0] butanes are bench-stable, strain activated electrophiles that are well suited for this purpose. In fact, the bioconjugation of peptides with a sulfonyl bicyclo[1.1.0]butane bearing an ^{131}I radiolabel has quite recently been described.[110] Further investigation of the scope and parameters of thiol additions to bicyclo[1.1.0]butanes will enable a better understanding of the potential of these strained rings to be used as tools for medicinal chemistry and chemical biology applications.

In contrast to the studies with phosphine boranes, treatment of a mixture of thiophenol and **2-37** with NaH in DMAc afforded only a modest yield of adduct **2-67** with low diastereoselectivity. However, in agreement with previous studies,[100b] treatment of the mixture with K_2CO_3 at room temperature cleanly afforded the desired cyclobutane with high *trans*-diastereoselectivity. A series of thiophenol derivatives were then employed in the reaction, all of which reacted with similarly high yield and diastereoselectivity (Table 14). Like the cyclobutylphosphine boranes, the mixture of diastereomers obtained upon workup were quite separable by chromatography on SiO_2.

Table 14. Addition of thiophenol derivatives to bicyclobutane **2-37**.

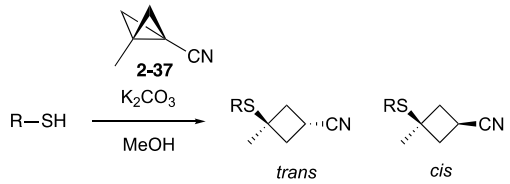


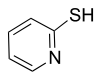
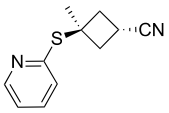
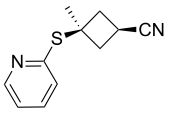
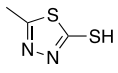
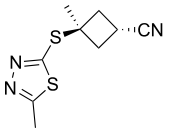
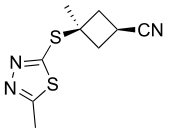
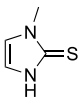
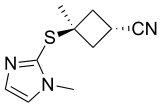
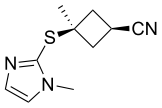
entry	R	product	*trans* yield	*cis* yield
1	Ph	**2-67**	70	11
2	2-naphthyl	**2-68**	62	17
3	2-(Me)C_6H_4	**2-69**	79	8
4	2-(Br)C_6H_4	**2-71**	69	13
5	3-(F)C_6H_4	**2-72**	51	16

Various heterocyclic thiols were tested in the addition reaction (Table 15). Except for an electron-rich indole-based thiol (entry 5), these substrates required heating and longer reaction times (usually 12–24 h) to reach completion. The yields of these transformations were slightly lower than those with thiophenols, however, the *trans*-diastereoselectivity remained high. An exception to this trend was the poorly nucleophilic tetrazole-based thiol (entry 4). In this case, a non-nucleophilic alcohol solvent (CF_3CH_2OH) was necessary to prevent degradation of the tetrazole product **2-75**.

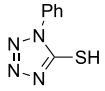
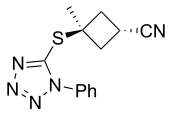
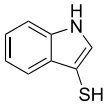
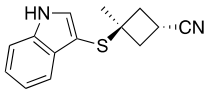
The fact that bicyclo[1.1.0]butyl nitriles only react with heterocyclic thiols at elevated temperature suggests that they may be stable and selective bioconjugation agents. These studies, along with the related bioconjugation studies by Baran and co-workers,[85] bodes well for the potential of bicyclo[1.1.0]butanes as components of targeted covalent inhibitors that are not prone to attack by glutathione and other off-target nucleophiles.

Table 15. Addition of heterocyclic thiols to bicyclobutane **2-37**.



thiol	temperature (°C)	*trans* product	*cis* product
	70	 *trans*-**2-72**, 51%	 *cis*-**2-72**, 14%
	60	 *trans*-**2-73**, 52%	 *cis*-**2-73**, 10%
	60		

2-74, 75%, 5:1 anti:syn (inseparable)

thiol	temperature (°C)	product
	60[a]	 *trans*-**2-75**, 19%
	25	 *trans*-**2-76**, 41%

[a]CF_3CH_2OH was used as the solvent for the synthesis of **2-75**

2.3 CONCLUSIONS

The ability of bicyclo[1.1.0]butyl nitriles to undergo addition by phosphorous and sulfur nucleophiles has been demonstrated. Most these studies were conducted with methyl-substituted bicyclo[1.1.0]butyl nitrile **2-37**. To expand the reaction scope, the transnitrilation method developed by Reeves and co-workers[99] was applied to access bicyclo[1.1.0]butyl nitriles **2-50** and **2-53**, and the previously developed hydrophosphination conditions were used to hydrophosphinate these substrates. Modifications of the resulting cyclobutyl nitrile products were conducted, which provided access to phosphine/phosphite **2-63** and diphosphine borane **2-66**. The addition of

thiophenols and heterocyclic thiols to **2-37** was also investigated. These transformations were found to proceed with high *trans*-diastereoselectivity.

3.0 FLUORINATION OF BICYCLO[1.1.0]BUTANES

3.1 INTRODUCTION

3.1.1 Overview of Selective Monofluorination in Organic Chemistry

With a bond dissociation energy of 105 kcal/mol, the carbon-fluorine bond is the strongest of those commonly encountered in organic chemistry. Fluorine is also the most electronegative of the elements, therefore, C–F bonds can induce a substantial dipole moment in fluorinated molecules. However, the poor polarizability of the fluorine atom renders these strong bonds inert in many transformations such as oxidative addition and nucleophilic substitution. This feature, along with the similarity of the C–O and C–F bond lengths (1.43 Å and 1.35 Å, respectively) and atomic radii (1.52 Å and 1.47 Å, respectively), make the C–F bond an effective isostere of ethers and other polar functional groups.[111] Strategic incorporation of C–F bonds in organic molecules has become a popular way to modulate the conformation, solubility, reactivity, and intermolecular interactions of molecules. Consequently, fluorinated molecules are well represented in the pharmaceutical, agrochemical, and material industries.[112]

Due to this demand, the development of methods to selectively fluorinate organic molecules has been a subject of intensive research efforts.[113] These methods can be broadly divided into three categories: electrophilic fluorination, where a carbon nucleophile attacks an F^+ equivalent; radical fluorination, where carbon and fluorine radicals join; and nucleophilic fluorination, where an F^- source attacks an organic molecule, often with the aid of H^+ or another activator (Figure 15).

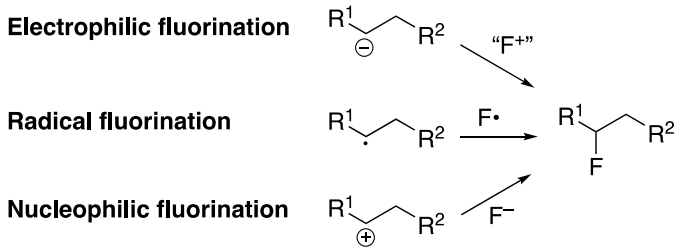


Figure 15. General overview of fluorination methods.

Electrophilic fluorination is very commonly employed.[114] Historically, F^+ sources such as F_2 gas, CF_3OF, and XeF_2 have been used in these transformations, although the drawbacks associated with their handling (F_2, CF_3OF) and expense (XeF_2) have limited their widespread adoption. Most electrophilic fluorinations are now conducted with N–F reagents such as Selectfluor®, NFSI, and fluoropyridinium salts. A wide range of substrates have been employed in electrophilic fluorination, including alkenes, arenes, heterocycles, glycals, and enol ethers.[114] The wide scope of electrophilic fluorination with N–F reagents enables access to fluorinated organic molecules for a variety of applications.

Radical fluorination is a less developed methodology. Recent studies by Boger[115] and Hiroya[116] have demonstrated that N–F reagents can be used to conduct radical fluorinations of alkenes in the presence of an iron or cobalt catalyst. Radial fluorination has also been investigated in the context of the burgeoning field of photoredox catalysis. For example, MacMillan and co-workers have developed a photocatalytic method for the conversion of carboxylic acids to the corresponding alkyl fluorides.[117] The activation of SF_6 gas through photoredox catalysis has also been recently used as a method for alcohol deoxyfluorination.[118]

Nucleophilic fluorination is a well-studied field that has several variations. Direct S_N2 reactions with inexpensive and easily handled fluoride salts is an ideal approach for fluorine introduction. However, the poor solubility and low nucleophilicty of F^- (~1600-fold less reactive toward CH_3I than Br^- in MeOH[119]) make this approach less effective. In certain cases, anhydrous

tetraalkylammonium fluorides can affect the nucleophilic fluorination of good electrophiles, but the generality of this transformation is limited.[120]

A more effective approach to nucleophilic fluorination is the use of HF to activate a Lewis basic substrate, which is then attacked by F^- to provide a fluorinated product. Anhydrous HF has been used for this purpose, but its low boiling point (19.6 °C) and extreme toxicity significantly deter its use. In the 1970's, Olah and co-workers discovered that HF can be dissolved in pyridine to provide poly(hydrogen fluoride, pyridine • 9 HF), a much more easily handled source of HF that is now widely known as Olah's reagent.[121] Pyridine • 9 HF can effectively fluorinate alkenes, alcohols, and isocyanates, among other functional groups. Alternative reagents have been developed where HF is dissolved in solvents such as DPMU.[122] Quite recently, it has been reported that HF can be condensed with solid $KHSO_4$ to yield a stable liquid HF reagent.[123] These alternative HF reagents are reported to be superior to Olah's reagent in some nucleophilic fluorinations.

The concept of using a single reagent to both activate a substrate and conduct a nucleophilic attack with fluoride is also the basis of the deoxyfluorination of alcohols, which is a widely popular fluorination method. The most commonly employed reagents for deoxyfluorination are sulfur trifluoride reagents such as diethylaminosulfur trifluoride (DAST) and the closely related Deoxofluor®.[124] Despite their utility, the toxicity and explosive potential of these reagents have prompted the development of innocuous and bench stable deoxyfluorination reagents. Examples of deoxyfluorination reagents that have recently gained popularity include the pyridine sulfonyl fluoride (PyFluor) developed by Doyle and co-workers,[125] the fluoroimidiazolium salts (PhenoFluor™/AlkylFluor™) developed by Ritter and co-workers,[126] and the bench-stable sulfur trifluoride (Fluolead™) developed by Umemoto and co-workers (Figure 16).[127]

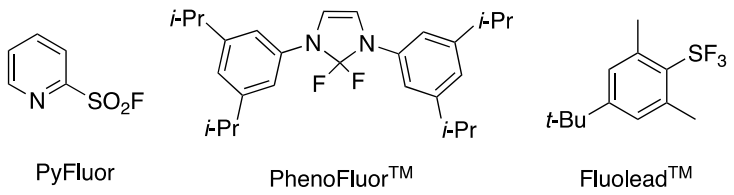


Figure 16. Recently developed deoxyfluorination reagents.

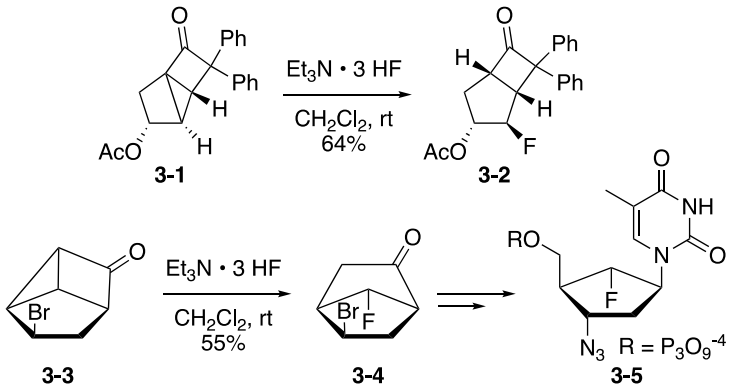
The fluorination of organic molecules through activation by transition metal catalysis is also a growing area of research.[128] The fluorination of alkenes and alkynes can be enabled by late transition metals such as palladium[129] or gold.[130] Palladium catalysis has been used to form allylic fluorides by attack of F^- onto π-allyl complexes.[131] A few examples of Pd-catalyzed C–H fluorination have also been reported,[132] however, these transformations require directing groups and/or are limited in scope. The development of selective, widely applicable C–H fluorination methods (and C–H activation methods in general) is a major unsolved challenge in organic synthesis.

3.1.2 Fluorinations Involving the Opening of Strained Rings

Although many classes of molecules have been subjected to nucleophilic and electrophilic fluorination reactions, the fluorination of molecules containing strained rings is somewhat underdeveloped. By leveraging the inherent strain energy of small carbocyclic rings and heterocycles, efficient and selective fluorinations can lead to structurally novel fluorinated chemotypes.

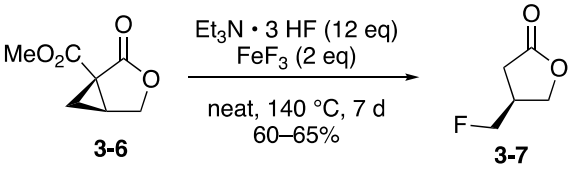
Illustrative examples of unique fluorinated products that can be accessed through the fluorination of strained rings of can be found in the work of Roberts and co-workers (Scheme 23). Upon treatment with $Et_3N \bullet 3$ HF, ketone **3-1** undergoes diastereoselective fluorination to provide cyclobutanone **3-2** in good yield.[133] A similar approach was also used to prepare a fluorinated

analog of 3'-azidothymidine (AZT), the antiretroviral molecule that is one of the great triumphs of 20th century medicinal chemistry. This AZT analog was prepared from ketone **3-3** through a diastereoselective fluorination with $Et_3N \bullet 3\ HF$ to afford **3-4**. Through a series of steps, **3-4** was converted into the carbocyclic AZT analog **3-5**. Unfortunately, **3-5** had much weaker antiretroviral activity than the parent compound (AZT).[134]



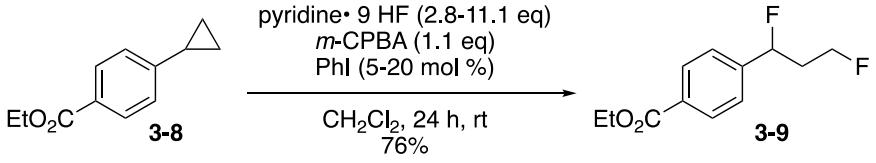
Scheme 23. Nucleophilic fluorination of strained cyclopropanes **3-1** and **3-3**.

Not all cyclopropanes undergo such facile nucleophilic fluorination. Despite being activated by diester substituents, cyclopropyl lactone **3-6** was inert to fluorination under a variety of standard conditions (Scheme 24). Only upon prolonged heating of **3-6** with excess $Et_3N \bullet 3\ HF$ and FeF_3 did sufficient conversion to primary fluoride **3-7** occur. This transformation was investigated while developing a process-scale route to the antidiabetic agent carmegliptin, but the harsh nature of this fluorination prompted the researchers to develop an alternative route involving the deoxyfluorination of a primary alcohol.[135]



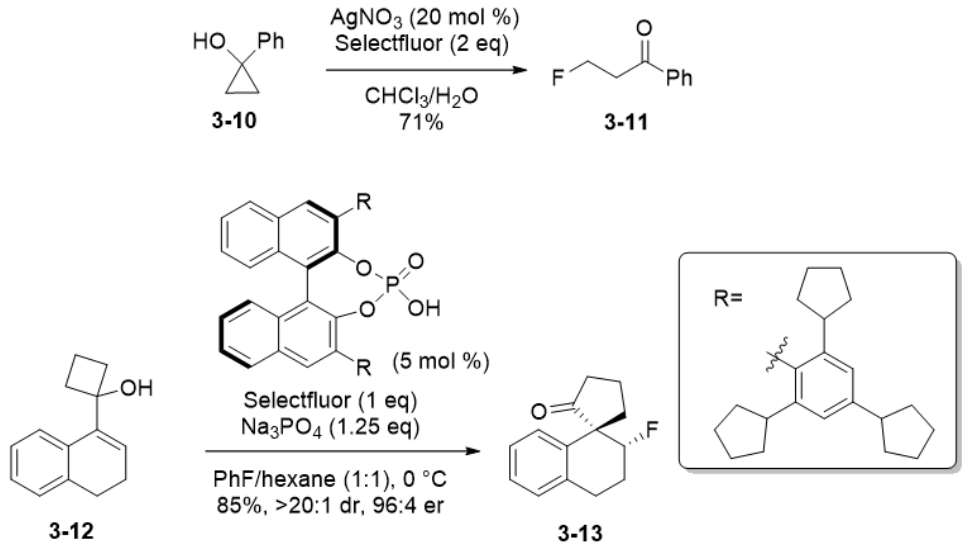
Scheme 24. Nucleophilic fluorination of lactone **3-6**.

Alternatively, cyclopropanes can be subjected to nucleophilic difluorination through an oxidative ring-opening (Scheme 25).[136] This method was recently developed by Jacobsen and co-workers as an extension of similar oxidative fluorinations of alkenes[137] and alkenyl lactones.[138] The transformation is presumed to occur through the catalytic formation of a hypervalent iodonium fluoride, which facilitates ring-opening of the cyclopropane. Variations of the reaction were developed to provide access to other 1,3-difunctionalized products from **3-8**.



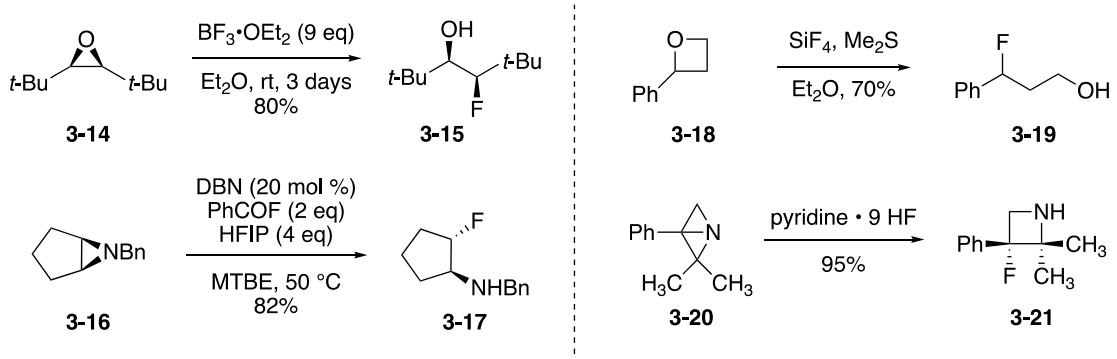
Scheme 25. Oxidative difluorination of cyclopropanes developed by Jacobsen and co-workers.

Electrophilic N–F reagents have been used to conduct fluorinations of cyclopropyl or cyclobutyl carbinols with concomitant ring expansion (Scheme 26). In the presence of catalytic silver nitrate, Selectfluor® promotes a radical-based ring opening fluorination of cyclopropane **3-10** to afford ketone **3-11**.[139] Photocatalysis has also been used to conduct similar transformations.[140] Alexakis and co-workers have used chiral phosphoric acids to prepare enantioenriched fluorinated ketones through this approach. A representative transformation of this type is the conversion of cyclobutane carbinol **3-12** to spirocyclic ketone **3-13**.[141]



Scheme 26. Ring expansion of carbinols using electrophilic fluorination.

The ring-opening fluorination of three- and four-membered heterocycles has been explored, and many of these transformations do not require the use of HF complexes (Scheme 27).[142] For example, the symmetrical epoxide **3-14** undergoes diastereoselective fluorination when treated with excess $BF_3 \bullet OEt_2$ at room temperature for an extended time.[143] Aziridines can be fluorinated under similar conditions, or alternatively, through nucleophilic catalysis by using an acyl fluoride as a fluorine source. This method was used for the conversion of aziridine **3-16** to **3-17**.[144] Although oxetanes are less strained than their epoxide counterparts, fluorination of oxetane **3-18** was accomplished with SiF_4 and Me_2S.[145] In contrast, fluorination of the highly strained azabicyclo[1.1.0]butane heterocycle **3-20** is reported to occur in excellent yield upon treatment with Olah's reagent.[146] However, no method for the fluorination of the carbocyclic analogs (bicyclo[1.1.0]butanes) has been reported.

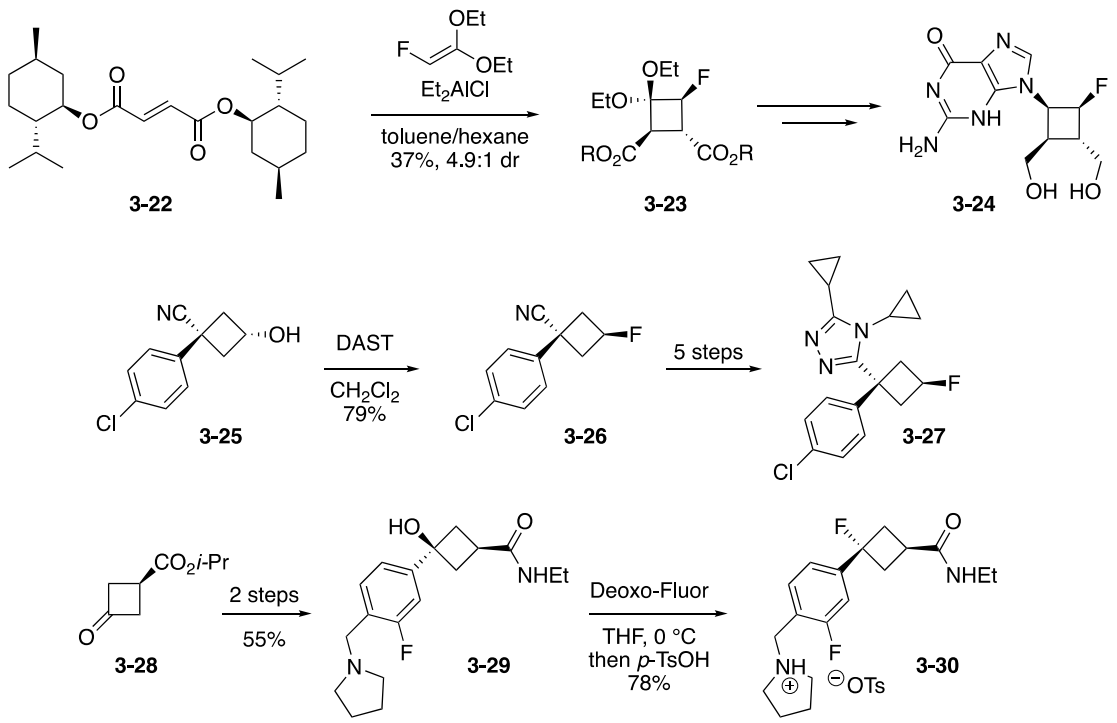


Scheme 27. Fluorination of 3- and 4-membered heterocycles**.**

3.1.3 Synthesis and Utility of Fluorinated Cyclobutanes

The introduction of fluorine substituents can modulate the reactivity and conformational preferences of cyclobutanes.[147] For example, perfluorocyclobutanes and related carbocycles exhibit unique isomerization behavior, and studies of this reactivity have broadened modern understanding of fluorine substitution effects in organic molecules.[148] In the context of medicinal chemistry, fluorinated carbocycles have been leveraged to improve the potency and pharmacokinetic properties of lead compounds.[149] The structural rigidity of the cyclobutane scaffold makes fluorinated cyclobutanes particularly intriguing for the exploitation of carbon-fluorine bond interactions with specific residues in enzyme active sites.[147]

Three examples of monofluorinated cyclobutanes that have been developed by pharmaceutical companies for various indications are shown in Scheme 28. The cyclobutyl nucleoside analog **3-24** was developed by Bristol-Myers Squibb as a treatment for herpes infections.[150] This fluorinated cyclobutane was prepared through a diastereoselective [2+2] cycloaddition between fumarate **3-22** and a fluorinated ketene acetal. However, cycloaddition product **3-23** was obtained in modest yield and with low diastereoselectivity.

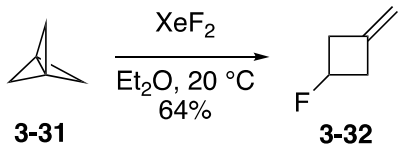


Scheme 28. Synthetic approaches to monofluorinated cyclobutanes of medicinal interest.

Deoxyfluorination of cyclobutyl alcohols has more commonly been used to access monofluorinated cyclobutanes. For example, deoxyfluorination of secondary alcohol **3-25** with DAST afforded **3-26** as a single diastereomer in 79% yield (Scheme 29). This intermediate was carried forward through 5 steps to triazole **3-27**, which is a hydroxysteroid dehydrogenase inhibitor for the treatment of cardiovascular ailments.[151] Deoxyfluorination was also used in the last step of a process-scale route to cyclobutane **3-30**, an H_3 receptor antagonist developed by Pfizer for the treatment of neurological disorders.[152]

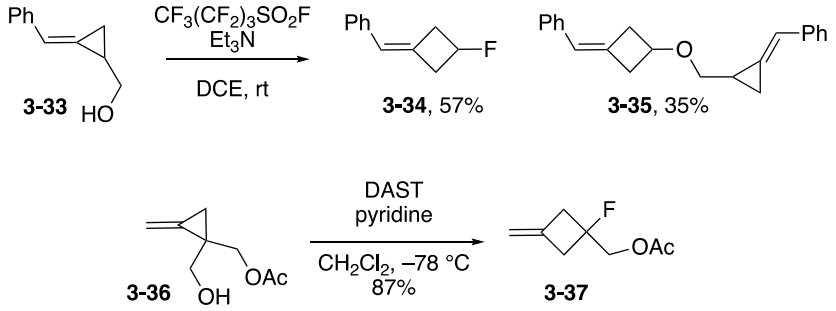
The preparation of fluorinated cyclobutanes through fluorinations that involve the opening of strained rings is a mechanistically intriguing alternative to [2+2] or deoxyfluorination approaches. An early example of such a transformation was reported as a side reaction by Adcock and co-workers. As part of a studies on the isomerization behavior of bicyclo[1.1.1]pentanes, it was found that [1.1.1] propellane (**3-31**) undergoes rearrangement to 3-

fluoromethylenecyclobutane **3-32** in the presence of XeF_2 (Scheme 29).[153] The transformation is presumably mediated by trace amounts of HF generated under the reaction conditions.



Scheme 29. Rearrangement of [1.1.1]-propellane.

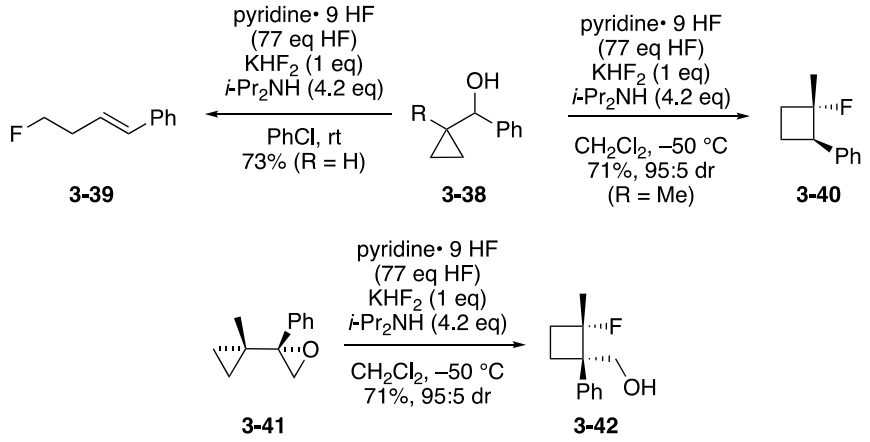
Substituted 3-fluoromethylenecyclobutanes can be prepared through the ring expansion of methylenecyclopropyl alcohols. When treated with nonafluorobutanesulfonyl fluoride, alcohol **3-33** underwent ring expansion to provide a mixture of fluorinated product **3-34** and ether **3-35** (Scheme 30).[154] Similarly, alcohol **3-36** underwent DAST-mediated ring expansion to provide fluorocyclobutane **3-37** in good yield.[155] These transformations are proposed to proceed through formation of a non-classical bicyclobutonium carbocation,[156] which is then trapped with a fluoride nucleophile to afford the cyclobutane product. The conversion of **3-33** to a cyclobutyl amide has also been accomplished through a Ritter reaction on this putative non-classical carbocation intermediate.[157]



Scheme 30. Expansions of methylenecyclopropanes to fluorinated methylenecyclobutanes.

A series of conceptually similar fluorinations involving cyclopropane ring expansion were developed by Yoshioka and co-workers (Scheme 31).[158] These transformations are conducted with Olah's reagent that is modified with KHF_2 and diisopropyl amine to provide a more nucleophilic

and monomeric source of fluoride. When alcohol **3-38** (R = H) is treated with this reagent, **3-39** is obtained in good yield as a single alkene isomer.[159] This method provides superior access to the homoallylic fluoride motif, as the direct treatment of homoallylic alcohols with deoxyfluorination reagents is often complicated by side reactions. When derivatives of **3-38** where R is an alkyl or aryl substituent were employed, a ring expansion occurred to provide tertiary fluorocyclobutane **3-40** in good yield with high diastereoselectivity.[160] Electrophilic ring opening of an epoxide can also be used to trigger the ring expansion and fluorination. This is exemplified by the conversion of **3-41** to primary alcohol **3-42**.[160] An extension of this method was developed that provides access to fluorinated cyclopentenones.[161] The method also was used as a key step in the total synthesis of a fluorinated analog of grandisol, a cyclobutane-containing monoterpene.[162]

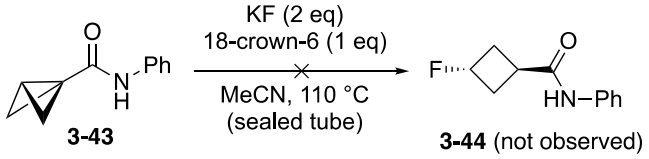


Scheme 31. Fluorinations involving cyclopropane ring expansion developed by Yoshioka *et al.*[158]

3.2 RESULTS AND DISCUSSION

3.2.1 Deoxyfluorination of Bicyclo[1.1.0]butyl Alcohols

The successful development of methods to add phosphorus and sulfur nucleophiles to bicyclo[1.1.0]butanes prompted consideration as to whether poor nucleophiles could also be used in these strain-releasing transformations. The addition of fluoride, a prototypical poor nucleophile, would provide an intriguing access to monofluorinated cyclobutane products. However, despite the substantial strain energy of bicyclo[1.1.0]butanes, preliminary attempts to use fluoride salts to fluorinate bicyclobutyl amides, sulfones, and nitriles were unsuccessful. In the representative transformation shown in Scheme 32, potassium fluoride fails to fluorinate amide **3-43** even with extensive heating in the presence of 18-crown-6. When heated above 110 °C, **3-43** began to decompose.



Scheme 32. Attempted direct fluorination of bicyclo[1.1.0]butyl amide **3-43** with KF/18-crown-6.

Since the direct addition of fluoride salts appeared unfeasible, a fluorination method involving the activation of bicyclo[1.1.0]butyl alcohols was developed. The work of Yoshioka and co-workers on the deoxyfluorination of cyclopropanes[158] (Scheme 31) was an inspiration toward this end, and the modified reagent that they developed (KHF_2/*i*-Pr_2NH/pyridine • 9 HF) was expected to fluorinate the structurally related bicyclo[1.1.0]butyl alcohols. Some accounts from the literature also suggested that bicyclo[1.1.0]butyl alcohols could be converted to methylenecyclobutanes through deoxygenation and nucleophilic attack. Wiberg and co-workers

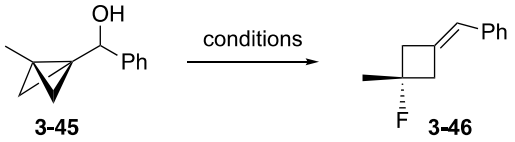
noted in the original full paper on bicyclo[1.1.0]butanes that treatment of bicyclo[1.1.0]butyl methanol with HBr resulted in a rearrangement to form 3-bromomethylenecyclobutane.[62b] Additionally, Szeimies and co-workers prepared a 3-chloromethylenecyclobutane from the corresponding bicyclo[1.1.0]butyl methanol using *N*-chlorosuccinimide and dimethyl sulfide.[163]

Alcohol **3-45** was successfully converted to methylenecyclobutane **3-46** in moderate yield when subjected to the HF reagent developed by Yoshioka (Table 16). A substantial increase in yield was realized by adding the substrate to the pre-mixed reagent, as opposed to adding reagents to a solution of the substrate (entry 1 vs entry 2). The yield was also found to be correlated to the stoichiometry of pyridine • 9 HF: the yield dropped when less than 50 equivalents of HF was used (entry 1 vs entry 3), but no advantage was observed with >70 equivalents. The use of a large excess of pyridine • 9 HF (100 eq HF) is also required for the difluorination chemistry recently developed by Jacobsen and co-workers.[136-138] Despite this high stoichiometric excess, only 1.8 mL of pyridine • 9 HF (1 mL reagent = 38 mmol HF) is required to fluorinate 1 mmol of a bicyclobutyl alcohol using this newly developed method. While the hazardous and corrosive nature of pyridine • 9 HF necessitates the use of a plastic reaction vessel (typically a polypropylene syringe sealed on one end), the reagent can be safely quenched upon workup with aqueous NaOH. Unfortunately, less reactive and more easily handled sources of HF such as Et_3N • 3 HF or KHF_2 alone did not enable this fluorination (entries 4 and 5).

Standard deoxyfluorination reagents such as DAST and Deoxofluor® also successfully converted alcohol **3-45** to the fluorinated methylenecyclobutane **3-46** (Table 16, entries 6 and 7). However, the yields of these transformations tended to be lower and their purification was often complicated by side products. Sulfonyl fluoride-based deoxyfluorination reagents such as nonfluorobutanesulfonyl fluoride (NfF) and PyFluor[125] provided only modest amounts of **3-46**

(entries 8-11). The use of alkali fluoride salts in combination with various Lewis or Bronsted acids was also ineffective (entry 12).

Table 16. Screening of deoxyfluorination conditions.

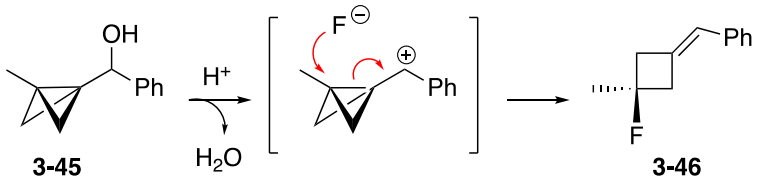


3-45 **3-46**

entry	conditions	solvent	temperature (°C)	yield (%)
1	KHF_2 (1 eq), *i*-Pr_2NH (4 eq), pyridine • 9 HF (70 eq HF)[a]	CH_2Cl_2	–78	57
2	KHF_2 (1 eq), *i*-Pr_2NH (4 eq), pyridine • 9 HF (70 eq HF)	CH_2Cl_2	–78	38
3	KHF_2 (1 eq), *i*-Pr_2NH (4 eq), pyridine • 9 HF (10.5 eq HF)	CH_2Cl_2	–78	33
4	KHF_2 (1 eq), *i*-Pr_2NH (4 eq), Et_3N • 3 HF (3 eq)	CH_2Cl_2	25	0
5	KHF_2 (1 eq)	DCE	80	0
6	DAST (1 eq)	CH_2Cl_2	0	51[b]
7	Deoxo-fluor (1 eq)	CH_2Cl_2	0	32
8	Fluolead (1 eq)	CH_2Cl_2	25	0
9	NfF (1.5 eq), DBU (3 eq)	toluene	25	23
10	same as entry 9, w/ CsF (3 eq)	toluene	25	26
11	PyFluor (1.1 eq), DBU (2.0 eq)	toluene	25	14
12	NaF (3 eq)	CH_2Cl_2/HFIP (10:1)	25	0

a = substrate added to the pre-mixed reagent, as opposed to addition of reagents to substrate
b = contaminated with inseparable DAST-derived impurities

The conversion of alcohol **3-45** to methylenecyclobutane **3-46** likely proceeds through an acid-mediated dehydration to form a cationic intermediate (Scheme 33). This putative cation is highly stabilized, as it has both benzylic and non-classical bicyclobutonium character.[156] Evidence for the non-classical character of the bicyclo[1.1.0]butyl-1-carbinyl cation was found through spectroscopic and computational studies by Wiberg and co-workers.[164] Attack of this stable cationic intermediate by the fluoride nucleophile at the ring junction results in an opening of the bicyclic system to relieve ~17 kcal/mol of ring strain and provide product **3-46**.

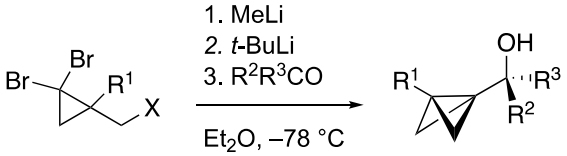


Scheme 33. Proposed mechanism for the deoxyfluorination of **3-45**.

A mechanistic alternative is that the benzylic cation rearranges to a tertiary 3-methylenecyclobutyl cation prior to fluoride attack. However, the computational studies conducted by Wiberg and co-workers at the MP4/6-31G* level of theory suggest that the 3-methylenecyclobutyl cation is 16.6 kcal/mol less stable than the non-classical bicyclo[1.1.0]butyl-1-carbinyl cation.[164] This bicyclo[1.1.0]butane/methylenecyclobutane isomerization is a rare instance in which one isomeric form (the bicyclobutane) is strongly favored as the cationic intermediate, while the other (the methylenecyclobutane) is preferred as the product.

To evaluate the scope of this deoxyfluorination, a series of bicyclo[1.1.0]butyl alcohols were prepared (Table 17). This was accomplished using the method discovered by Brinker[66a] and adapted by Walczak and Wipf,[73b] where a trihalocyclopropane is dilithiated and trapped with an aldehyde or ketone electrophile. The R^2 substituent on the alcohol products was easily varied by trapping with various benzaldehyde derivatives (entries 1–6). Acetophenone (entry 7) and 3-pentanone (entries 16 and 17) were also successfully trapped to provide tertiary alcohols. The R^1 substituent was varied by using several trihalocyclopropane precursors, which were in turn prepared through dibromocyclopropanation of the appropriate allylic halides (entries 8–17).

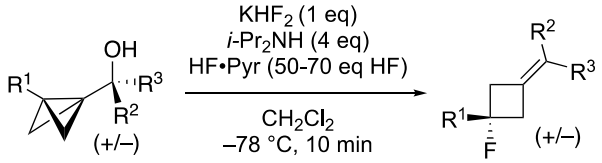
Table 17. Preparation of bicyclo[1.1.0]butyl alcohol substrates.



entry	R^1	R^2	R^3	X	product	yield (%)
1	CH_3	H	Ph	Cl	**3-45**	80
2	CH_3	H	4-$CF_3C_6H_4$	Cl	**3-47**	64
3	CH_3	H	4-ClC_6H_4	Cl	**3-48**	56
4	CH_3	H	4-$OMeC_6H_4$	Cl	**3-49**	46
5	CH_3	H	2-(allyloxy)C_6H_4	Cl	**3-50**	36
6	CH_3	H	2-pyridyl	Cl	**3-51**	49
7	CH_3	CH_3	Ph	Cl	**3-52**	77
8	*n*-Pr	H	Ph	Br	**3-53**	34
9	*i*-Pr	H	Ph	Br	**3-54**	40
10	$Ph(CH_2)_2$	H	Ph	Br	**3-55**	47
11	Ph	H	*n*-Bu	Br	**3-56**	81
12	Ph	H	*t*-Bu	Br	**3-57**	38
13	4-$CF_3C_6H_4$	H	*t*-Bu	Br	**3-58**	27
14	4-$CF_3C_6H_4$	H	Ph	Br	**3-59**	54
15	4-ClC_6H_4	H	Ph	Br	**3-60**	67
16	4-$CF_3C_6H_4$	Et	Et	Br	**3-61**	63
17	4-ClC_6H_4	Et	Et	Br	**3-62**	71

The deoxyfluorination of these bicyclo[1.1.0]butyl alcohols was evaluated using the pyridine • 9 HF/KHF_2/*i*-Pr_2NH reagent (Table 18). The yields for these transformations generally ranged from 40–65%. Tertiary (entries 7, 14, and 15) and secondary alcohols performed equally well in the deoxyfluorination. Although the presence of a benzylic alcohol presumably facilitates the transformation by providing a more stabilized cationic intermediate, benzylic activation is not required as evidenced by the successful preparation of **3-71**, albeit with a reduced yield (entry 11). Appended functional groups appeared detrimental to the reaction, as evidenced by the lower yield of allyloxy-substituted derivative **3-66**. The only heterocyclic alcohol attempted, pyridine **3-51**, afforded a complex mixture under the reaction conditions.

Table 18. Deoxyfluorination of bicyclo[1.1.0]butyl alcohols.



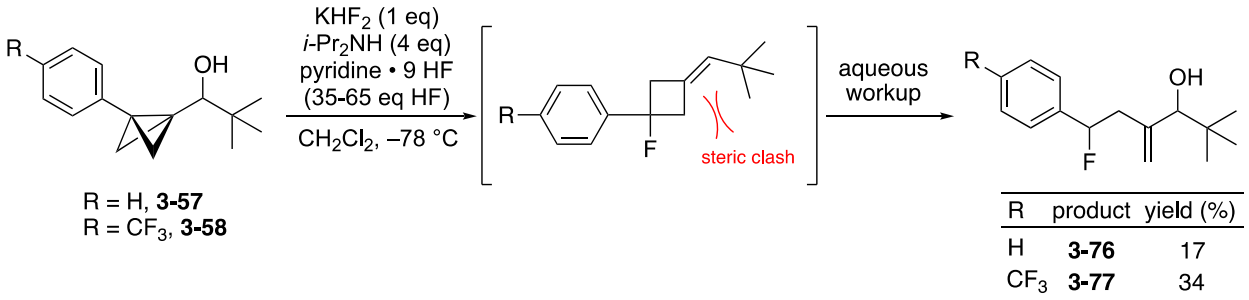
entry	R^1	R^2	R^3	product	yield (%)
1	CH_3	H	Ph	**3-46**	57
2	CH_3	H	4-$CF_3C_6H_4$	**3-63**	46
3	CH_3	H	4-ClC_6H_4	**3-64**	58
4	CH_3	H	4-$OMeC_6H_4$	**3-65**	46
5	CH_3	H	2-(allyloxy)C_6H_4	**3-66**	34
6	CH_3	H	2-pyridyl	—	0
7	CH_3	CH_3	Ph	**3-67**	63
8	*n*-Pr	H	Ph	**3-68**	60
9	*i*-Pr	H	Ph	**3-69**	47
10	$Ph(CH_2)_2$	H	Ph	**3-70**	58
11	Ph	H	*n*-Bu	**3-71**	31
12	4-$CF_3C_6H_4$	H	Ph	**3-72**	62
13	4-ClC_6H_4	H	Ph	**3-73**	41
14	4-$CF_3C_6H_4$	Et	Et	**3-74**	51
15	4-ClC_6H_4	Et	Et	**3-75**	48

No side products were isolated upon purification of these reactions. However, the fact that some yellow/brown material is typically adsorbed to the base of the SiO_2 column suggests that some degree of polymerization or decomposition occurs. Despite moderate yields obtained in these transformations, this method is the first example of a bicyclo[1.1.0]butane fluorination and is one of the only means available for the synthesis of substituted 3-fluoromethylenecyclobutanes.[154]

3.2.2 Anomalous Deoxyfluorination Substrates

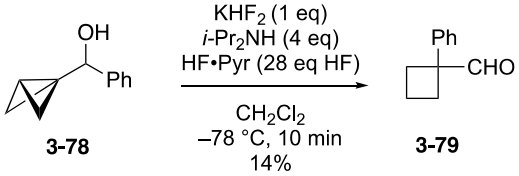
Not all the bicyclo[1.1.0]butyl alcohols that were tested in the deoxyfluorination reaction provided the expected methylenecyclobutane product. These limitations revealed some interesting aspects of the deoxyfluorination mechanism and the stability of the methylenecyclobutane products. For example, when *t*-butyl-substituted alcohols **3-57** and **3-58** were subjected to the deoxyfluorination conditions, allylic alcohols **3-76** and **3-77** (respectively) were obtained in low yield (Scheme 34).

The structure of these alcohols was assigned using a combination of one- and two-dimensional NMR experiments. It is hypothesized that **3-76** and **3-77** originate from the expected 3-methylenecyclobutane, but the unfavorable stearic clash between the *t*-butyl group and the cyclobutane render the products unstable. Upon aqueous workup, hydrolytic alkene transposition would relieve both this interaction and the cyclobutane ring strain to afford the observed allylic alcohol product.



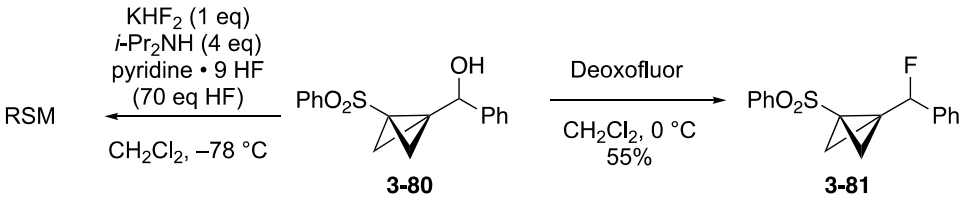
Scheme 34. Deoxyfluorination of **3-57** and **3-58** affords rearranged allylic alcohol products.

The deoxyfluorination was also impacted by substitution at the bicyclo[1.1.0]butane ring junction. As Table 18 shows, a variety of alkyl and aryl substituents are tolerated in the transformation. In contrast, the attempted deoxyfluorination of bicyclobutane **3-78** (which does not bear a substituent at the ring junction) afforded aldehyde **3-79** in low yield (Scheme 35). This aldehyde may arise from protonation of the bicyclo[1.1.0]butane at the less substituted ring junction, which would trigger a semipinicol rearrangement (1,2-arene shift) of the resulting tertiary carbocation to afford **3-79**. Although products resulting from alternative reaction pathways are presumably formed, **3-79** was the only tractable product isolated from the crude reaction mixture.



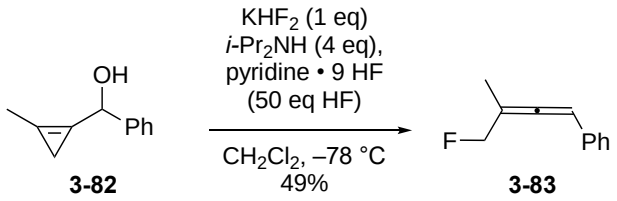
Scheme 35. Attempted deoxyfluorination of bicyclobutanes without a ring junction substituent.

Sulfonyl-substituted bicyclo[1.1.0]butane **3-80** was completely inert to the pyridine • 9 HF reagent (Scheme 36). When treated with Deoxofluor®, however, a deoxfluorination occurred to provide bicyclo[1.1.0]butyl fluoride **3-81** with no formation of a methylenecyclobutane or other rearranged product. The failure of **3-80** to undergo rearrangement supports the hypothesis that the fluorination proceeds through a delocalized carbocation intermediate. The formation of such an intermediate would be strongly disfavored by the strong electron withdrawing capacity of the sulfone at the ring junction.



Scheme 36. Deoxyfluorination of sulfonyl bicyclobutane **3-80**.

It was hypothesized that cyclopropenyl carbinols, inasmuch as they are structurally and functionally similar to the bicyclo[1.1.0]butyl alcohols previously studied, would form fluorinated methylenecyclopropanes when subjected to the deoxyfluorination conditions. Encouragingly, cyclopropene **3-82** has been converted to metheylenecyclopropanes through organocuprate addition or [2,3]-sigmatropic rearrangement.[165] However, when **3-82** was subjected to the deoxyfluorination conditions, allene **3-83** was the only product obtained (Scheme 37). This allene product is presumably formed though activation of the alcohol and attack of the fluoride nucleophile on the cyclopropyl methylene. While the rearrangement of similar cyclopropene carbinols to allenes has been accomplished using perchloric acid[166] or silica gel,[167] this is the first example of a rearrangement of this type involving fluorination. A potentially fruitful line of future research would identify divergent conditions that provide selective access to either fluorinated allenes or methylenecyclopropanes with various substitution patterns.

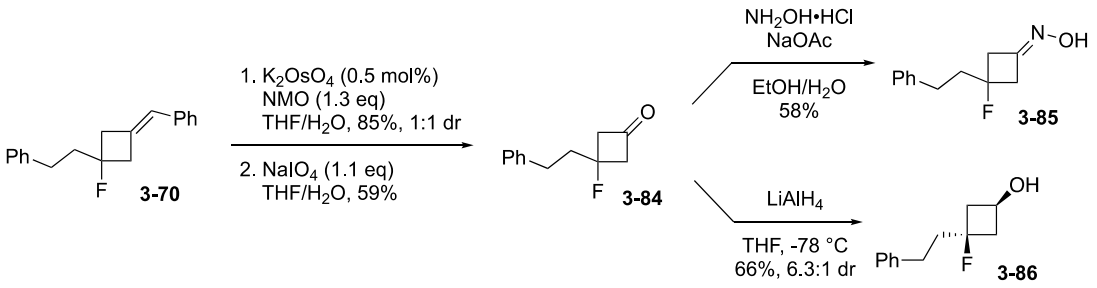


Scheme 37. Deoxyfluorination of cyclopropene alcohol **3-82** provides allene **3-83**.

3.2.3 Transformations of Fluorinated Methylenecyclobutanes

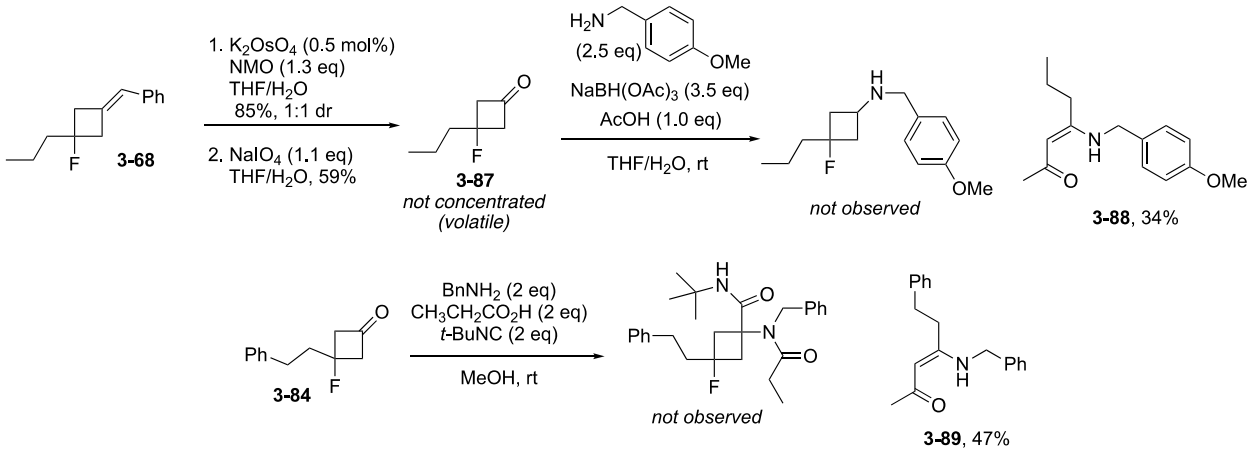
With a method to access 3-fluoromethylenecyclobutanes established, the utility of these products was explored. A prime objective along these lines was to convert the methylenecyclobutanes into 3-fluorocyclobutanones through oxidative scission of the exocyclic alkene. These cyclobutanone products were envisioned to be versatile precursors to more complex fluorinated carbocycles. Moreover, there are only a few scattered reports of 3-fluorocyclobutanones in the patent literature, and their utility remains unexplored.

A problematic aspect of this oxidative scission was the loss of material due to the generation of volatile, low molecular weight ketones in small quantities. Thus, the larger phenethylamine substituted methylenecyclobutane **3-70** was the primary substrate used in these studies. When subjected to a two-step sequence of dihydroxylation and oxidative diol cleavage, cyclobutanone **3-84** was obtained (Scheme 38). Ketone **3-84** was converted into oxime **3-85**, which is a potential precursor of fluorinated cyclobutyl amines[168] or fluorinated spirocycles through [3+2] dipolar cycloaddition.[169] Reduction of ketone **3-84** occurred with moderate diastereoselectivity to afford alcohol **3-86** in 66% yield and a 6.3:1 diastereomeric ratio, and the relative stereochemistry of the major alcohol isomer was tentatively assigned by NOESY.

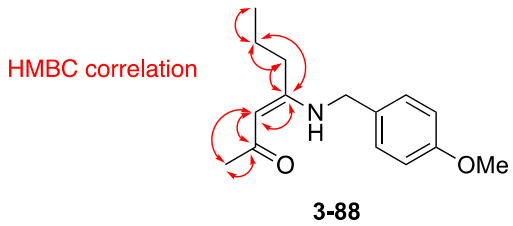


Scheme 38. Transformations of ketone **3-84**.

Unfortunately, ketone **3-84** and analogs thereof appear to be unstable to acid-mediated transformations. When an oxidative alkene cleavage was conducted on *n*-propyl substituted methylenecyclobutane **3-68**, the cyclobutanone product **3-87** was carried directly forward to a reductive amination due to concerns of volatility (Scheme 39). No secondary amine was isolated from this reaction, but rather, the unexpected vinylogous amide product **3-88** was obtained in 34% yield. Similarly, when ketone **3-84** was subjected to an Ugi multicomponent reaction, vinylogous amide **3-89** was obtained in 47% yield, with no evidence of Ugi product formation. The structure of these vinylogous amides was assigned by ^{1}H NMR, ^{13}C NMR, DEPT 135, and HMBC. The connectivity of the molecule was confirmed by analysis of HMBC correlations (Figure 17). The alkene geometry was assigned on the basis of the high N–H ^{1}H NMR shift (11.17 ppm) that is indicative of intramolecular hydrogen bonding in these systems.[170]



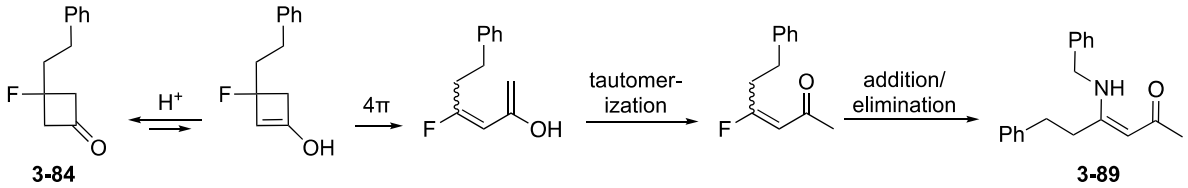
Scheme 39. Attempted acid-mediated transformations of cyclobutanones result in vinylogous amides.



3-88

Figure 17. Key HMBC correlations of **3-88**.

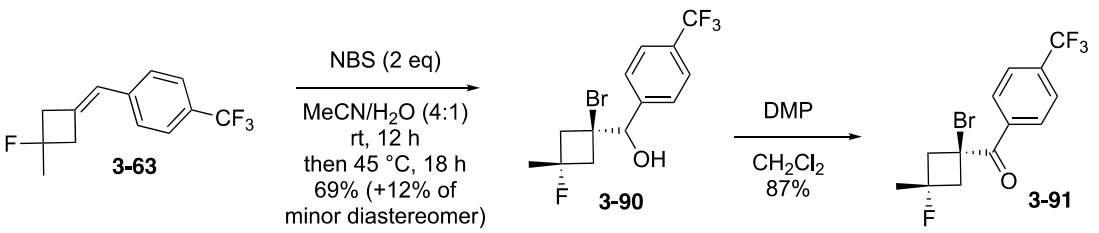
The formation of these vinylogous amides likely occurs by enol formation, 4π electrocyclic ring opening, and addition/elimination of the amine nucleophile into the β–fluoroenone (Scheme 40). Alternatively, an initial elimination of fluoride from **3-84** would provide a reactive cyclobuteneone that undergoes nucleophilic attack by the amine, 4π electrocyclic ring opening, and tautomerization to afford **3-89**.



3-84 **3-89**

Scheme 40. Possible mechanism for the conversion of **3-84** to **3-89**.

Other transformations were investigated that retain the aryl substituent of the deoxyfluorination products. Bromohydrin formation of **3-63** proceeded with regio- and diastereoselectivity to provide **3-90** as a single regioisomer and as a separable 5.8:1 mixture of diastereomers (69% and 12% isolated yields, Scheme 41). The structure and relative stereochemistry of **3-90** was assigned using ^{1}H NMR, ^{13}C NMR, NOESY, and HSQC. The secondary alcohol of the bromohydrin was converted to the corresponding ketone **3-91** in 87% yield using Dess-Martin periodinane. Attempted Bayer-Villager oxidation of **3-91** was unsuccessful, as this ketone was resilient to *m*-chloroperbenzoic acid and other oxidation conditions.



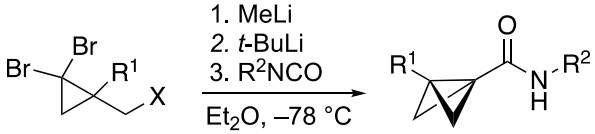
Scheme 41. Regio- and diastereoselective bromohydrin formation from **3-63**.

3.2.4 Diastereoselective Fluorination of Bicyclo[1.1.0]butyl amides

With the demonstrated ability of the pyridine • 9 HF/KHF_2/*i*-Pr_2NH reagent to conduct deoxyfluorination reactions, the fluorination of other bicyclo[1.1.0]butane derivatives was considered. Specifically, a bicyclo[1.1.0]butane substituted with a Lewis basic functional group such as an amide was expected to undergo a ring-opening fluorination when treated with this HF reagent. This transformation would provide access to fluorinated cyclobutyl amides, which are useful structures in medicinal chemistry and other applications (Section 3.1.3).

To test this hypothesis, a series of bicyclo[1.1.0]butyl amides were prepared through dilithiation of the appropriate trihalocyclopropane precursor and trapping with an isocyanate (Table 19). The yields of isocyanate trapping tend to be lower than those of aldehyde or imine trapping. In the case where R^1 was an *n*-propyl substituent, the yield was poor (entry 4). Nonetheless, amides **3-92**–**3-96** were obtained in sufficient quantity to test their feasibility in fluorination reactions.

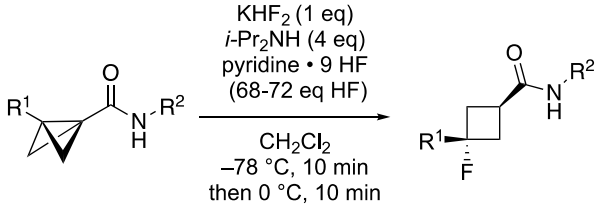
Table 19. Preparation of bicyclo[1.1.0] butyl amides.



entry	R^1	R^2	X	product	yield (%)
1	CH_3	Ph	Cl	**3-92**	49
2	CH_3	4-$OMeC_6H_4$	Cl	**3-93**	66
3	CH_3	allyl	Cl	**3-94**	45
4	*n*-Pr	Ph	Br	**3-95**	16
5	Ph	Ph	Br	**3-96**	50

Treatment of the bicyclo[1.1.0]butyl amides with the modified pyridine • 9 HF reagent afforded 3-fluoro-3-alkylcyclobutyl amides (Table 20). The reaction tended to be slower than the alcohol deoxyfluorination, thus, an additional time period at 0 °C was added to ensure full conversion. The products were obtained as single regioisomers, and the diastereoselectivity of the transformation was also high. In cases where $R^1 = CH_3$ (entries 1–3) only one diastereomer (with the methyl and amide in a *cis* relationship) was isolated after chromatography. Larger substituents at the ring junction, however, resulted in attenuated diastereoselectivity. This was most pronounced in the fluorination of **3-96** (R^1 = Ph), which yielded **3-101** as separable diastereomers in isolated yields of 39 and 25%. The poor diastereoselectivity in this case may be the consequence of the more planar stabilized benzylic cation that is a putative intermediate in the conversion of **3-96** to **3-101**.

Table 20. Diastereoselective fluorination of bicyclo[1.1.0]butyl amides.



entry	R^1	R^2	product	yield (%)
1	CH_3	Ph	**3-97**	58
2	CH_3	4-$OMeC_6H_4$	**3-98**	50
3	CH_3	allyl	**3-99**	43
4	*n*-Pr	Ph	**3-100**	37[a]
5	Ph	Ph	**3-101**	39[b]

a = 9% of the minor diastereomer also isolated
b = 25% of the minor diastereomer also isolated

The relative stereochemistry of each of the major amide isomers was assigned by NOESY (in **3-97**, for example, the methyl and methine protons each correlate to methylene protons on opposite faces of the cyclobutane). To confirm these assignments, a single crystal of amide **3-98** was grown and analyzed by X-ray crystallography. The crystal structure obtained for **3-98** confirms the regio- and stereochemical assignments of the cyclobutane products (Figure 18).

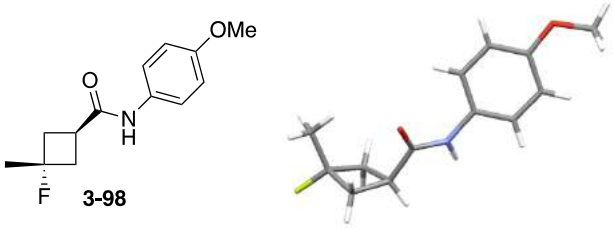
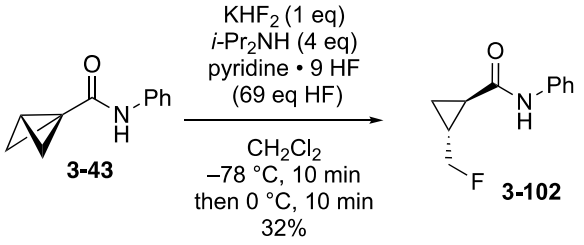


Figure 18. X-ray crystal structure of amide **3-98**.

As observed in bicyclo[1.1.0]butyl alcohol deoxyfluorinations, attempted fluorination of a bicyclobutane derivative without a ring junction substituent resulted in an unexpected product. When amide **3-43** was treated under the typical reaction conditions, attack of the fluoride nucleophile at the bicyclobutane methylene afforded racemic cyclopropane **3-102** as the major product in 32% yield (Scheme 42). An inseparable mixture of byproducts was also obtained upon purification, a component of which appears to be the expected 3-fluorocyclobutyl amide. While the acidic methanolysis of bicyclo[1.1.0]butanes is known to produce a mixture of 3-

methoxycyclobutane and *trans*-cyclopropane products,[79-80] the origin of the preference for the cyclopropane product in this case is not obvious.

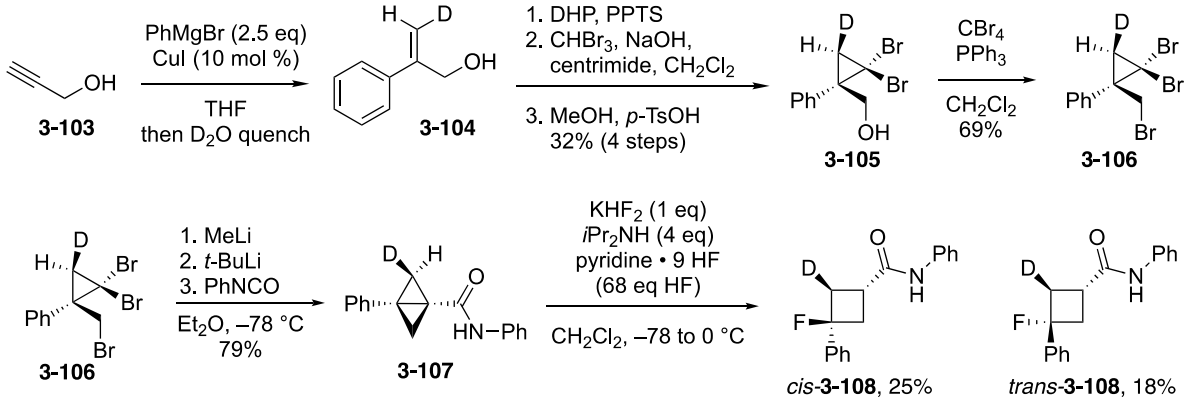


Scheme 42. Fluorination of amide **3-43** affords cyclopropane **3-102**.

This amide fluorination reaction is interesting from a methodological and mechanistic perspective, but unlike the alcohol deoxyfluorination, viable alternatives exist to access the fluorinated products. Commercially available 3-oxocyclobutanecarboxylic acid can be used as a synthetic building block to access fluorinated amides such as **3-88**–**3-93**. For example, a three-step sequence of amide coupling, treatment with a Grignard reagent, and deoxyfluorination with Deoxofluor® was used to access the fluorinated amide **3-30** on process scale (Scheme 28).[152]

However, the *de novo* preparation of the cyclobutane ring *via* a bicyclo[1.1.0]butane provides opportunities for unique modifications such as isotopic labelling. As a demonstration of this potential, deuterium-labeled bicyclo[1.1.0]butyl amide **3-107** was prepared and fluorinated to afford the labeled and fluorinated cyclobutane **3-108** (Scheme 43). Substrate **3-107** was accessed through copper-catalyzed addition of phenyl magnesium bromide to propargyl alcohol (**3-103**), which upon quenching with D_2O provides allylic alcohol **3-104** as a single alkene isomer.[171] This alcohol was then protected, subjected to dibromocyclopropanation, and deprotected to afford racemic alcohol **3-105**. Conversion to bromide **3-106** and subjection of the resulting tribromide to the dilithiation/isocyanate trapping procedure afforded racemic bicyclo[1.1.0]butane **3-107** in good yield. Like the non-labeled material **3-96**, fluorination of **3-107** proceeded with very little diastereoselectivity. However, the **3-108** diastereomers were readily separable on SiO_2, and each

has a *trans*-relationship between the deuterium and amide substituents. One could envision using a similar strategy to produce fluorinated cyclobutanes with other substitution patterns or isotopic labels (such as ^{13}C).



Scheme 43. Preparation and fluorination of a deuterium labeled bicyclo[1.1.0]butane.

3.3 CONCLUSIONS

A method to convert bicyclo[1.1.0]butyl alcohols to fluorinated methylenecyclobutanes has been developed. Screening of a variety of deoxyfluorination conditions revealed that a modified version of Olah's reagent (pyridine • 9 HF with KHF_2 and *i*-Pr_2NH additives) was most effective in this reaction. A series of bicyclo[1.1.0]butyl alcohols with various substitution patterns was prepared and subjected to the optimized deoxyfluorination conditions. Many of these alcohols reacted smoothly to form the expected methylenecyclobutane products, but derivatives with sterically demanding appendages or alternative ring junction substituents gave unexpected products. The utility of the fluorinated methylenecyclobutane products was explored through oxidative cleavage of the exocyclic alkene or diastereoselective bromohydrin formation. Preliminary studies on the

fluorination of bicyclo[1.1.0]butyl amides were also undertaken, and a deuterium-labelled cyclobutyl amide was prepared using this method.

4.0 SYNTHESIS OF ANDROGEN RECEPTOR ANTAGONISTS CONTAINING STRAINED CARBOCYCLES

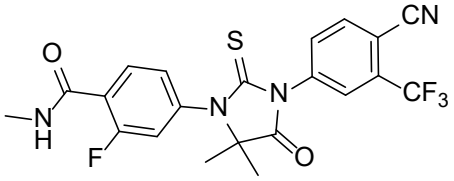
4.1 INTRODUCTION

4.1.1 Androgen Receptor Antagonists as Prostate Cancer Therapeutics

Prostate cancer is the third most common type of cancer diagnosed in the United States. Approximately 12% of men will be diagnosed with prostate cancer in their lifetime, and an estimated 161,000 new cases were diagnosed in the United States in 2017 alone. Fortunately, current treatment technologies limit the fatality rate from prostate cancer to 20.1 per 100,000 men in the U.S.[172] A common method to treat high-risk prostate cancer is radiation therapy (with or without prostatectomy) followed by androgen deprivation therapy, including chemical castration. While this approach is an effective short-term treatment, 10-20% of prostate cancer treated by castration progresses to castration-resistant prostate cancer (CRPC) within 5 years. The estimated period of survival for individuals living with CRPC is 14 months.[173]

A key player in the development of CRPC is the androgen receptor (AR), a nuclear transcription factor that regulates the growth of healthy prostate cells. Upon binding to endogenous 5α–dihydrotestosterone, the androgen receptor translocates into the prostate cell nucleus.[174] It has been demonstrated that excessive AR localized in the cell nucleus enables the progression of CRPC.[175] Thus, treatment with a small-molecule AR antagonist is a viable strategy to slow CRPC progression. Enzalutamide (**4-1**, Figure 19) is an FDA-approved AR antagonist for the treatment of CRPC, but it is not completely effective and enables an extension

of patient lifespan by just 3–5 months.[176] Therefore, there is a need for new AR antagonists that show an improved ability to slow the progression of CRPC, perhaps through a novel mechanism of action.



4-1 (enzalutamide)

Figure 19. Enzalutamide, an FDA-approved treatment for castration-resistant prostate cancer.

4.1.2 Previous Medicinal Chemistry Efforts in the Wipf group

In an effort to identify new small molecule AR antagonists for the potential treatment of CRPC, a library of 219,055 compounds was screened for suppression of AR activity in the prostate cell nucleus.[177] The compounds were tested in a castration-resistant prostate cancer cell line (C4-2) transfected with an AR expression vector containing a green fluorescent protein tag (2GFP-AR). A promising hit from this screening was isoxazole thioether **4-2** (Figure 19). In a similar luciferase reporter assay using C4-2 CRPC cells transfected with luciferase-tagged AR vector (C4-2-PSA-rl), **4-2** showed promising inhibition of AR activity with an EC_{50} of 7.3 μM.

An extensive structure-activity relationship study of **4-2** was conducted in the Wipf group with the aim of developing more potent analogs.[178] Specific features of **4-2** that were evaluated include the isoxazole appendage, thioether and amide linkages, piperazine heterocycle, and arene appendage (Figure 20). These studies revealed the importance of the *o*-methyl aniline and piperazine features. The isoxazole and thioether, however, were found to be replaceable. More potent analogs were attained by substituting the flexible thioether with a more rigid cyclopropane. The most successful compound in this series was **4-3** (known as JJ-450). Aside from having a >2

fold improvement in activity over **4-2**, cyclopropane **4-3** has a higher drug-likeness score and eliminates the metabolically liable thioether motif. Extensive evaluations of the capability of **4-3** to treat CRPC *in vivo* is ongoing.

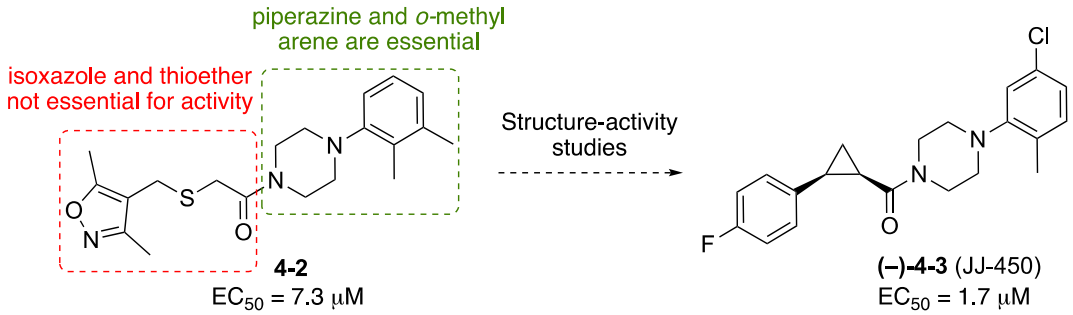


Figure 20. Optimization of high-throughput screening hit **4-2** yielded lead **4-3**.

4.2 RESULTS AND DISCUSSION

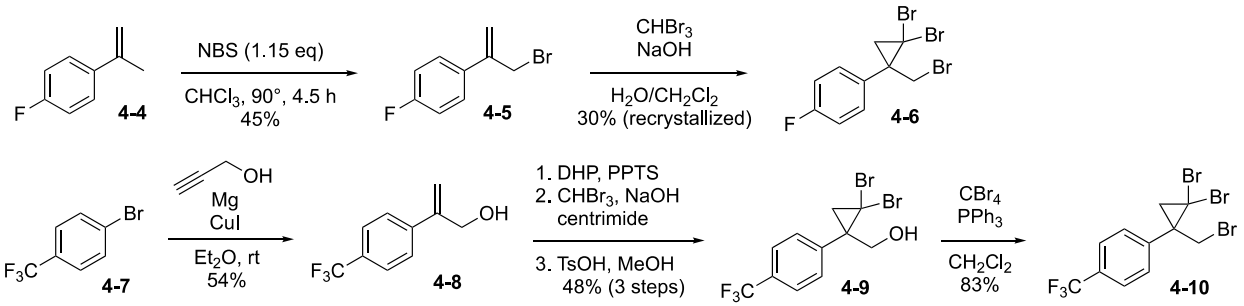
4.2.1 Synthesis of Androgen Receptor Antagonists Containing Bicyclo[1.1.0]butanes

Despite the high potency (EC_{50} = 1.7 μM) of (–)-**4-3** in the luciferase reporter assay, the metabolic stability of this compound is suboptimal. When tested in human, mouse, and dog liver microsomes, (–)-**4-3** displayed poor stability with half-lives of 31.7, 5.3, and 5.6 min, respectively. The aryl cyclopropane, piperazine heterocycle, and *o*-methyl arene substituent are each features of **4-3** that may contribute to this fast metabolic degradation by cytochrome P450 enzymes.[179] Mass spectrometry analyses of the degradation products from these microsomal stability assays affirmed that oxidative cleavage of the cyclopropane is a major metabolic pathway.

To mitigate these metabolic shortcomings and discover compounds with even greater potency, modifications and replacements of the cyclopropane core of **4-3** were developed.

Alternative carbocycles such as bicyclo[1.1.0]butanes were envisioned to be structurally novel cyclopropane replacements. Others have found that unusual carbocycles such as bicyclo[1.1.1]pentanes and cubanes can be used to enhance the properties of lead compounds.[180] Despite the structural rigidity and novelty of bicyclo[1.1.0]butanes, to our knowledge, they have not been exploited for this purpose. While the potential for undesired reactivity of bicyclobutanes substituted with an electron withdrawing group (such as an amide) may raise concerns of off-target reactivity, previous thiol addition studies (Section 2.2.4) suggest that endogenous nucleophiles such as glutathione would only add to these systems at elevated temperature or in the presence of base.

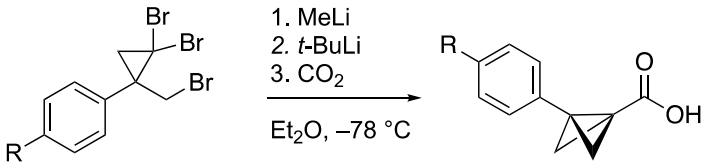
In order to prepare bicyclo[1.1.0]butane-derived analogs of **4-3**, it was necessary to prepare the appropriate tribromide precursors with electron deficient arenes (Scheme 44). The *p*-fluorophenyl tribromide **4-6** was prepared through allylic bromination of commercially available methyl styrene **4-4** and dibromocyclopropanation of the resulting allylic bromide product (**4-5**). The same approach has been used to prepare the parent phenyl tribromide,[73b] however, the presence of the fluoride substituent decreased the yield for this transformation. Bromination of more highly deactivated trifluoromethyl styrene was completely ineffective. An alternative procedure involving the Cu-mediated addition of *p*-trifluoromethyl magnesium bromide to propargyl alcohol was therefore used to access allylic alcohol **4-8**.[181] The alcohol **4-8** was then subjected to a protection/dibromocyclopropanation/deprotection sequence to provide alcohol **4-9**. Bromination of **4-9** afforded the tribromide **4-10**.



Scheme 44. Preparation of tribromides **4-6** and **4-10**.

With the necessary tribromides in hand, a dilithiation and trapping sequence was proposed to access the amide targets. As outlined in Section 3.2.4, bicyclo[1.1.0]butyl amides can be accessed by trapping the bicyclo[1.1.0]butyl lithium species with isocyanates, but this transformation cannot provide direct access to the tertiary amides needed for these studies. Attempts were made to trap electrophiles (such as 1,1-carbonyldiimidazole (CDI) or chloroformates) that would provide a bicyclobutyl amide precursor at the correct oxidation state. Ultimately, the most successful approach was trapping of the bicyclobutane anion with CO_2 to form a carboxylic acid (Table 21). By conducting a pH-controlled workup of this reaction, bicyclo[1.1.0]butyl acids **4-11** and **4-12** were obtained in acceptable purity without purification by chromatography. Although some reports describe the preparation of certain bicyclo[1.1.0]butyl carboxylic acids through anionic trapping of CO_2,[83c, 182] this work is the first example of a general approach to aryl-substituted bicyclo[1.1.0]butyl carboxylic acids.

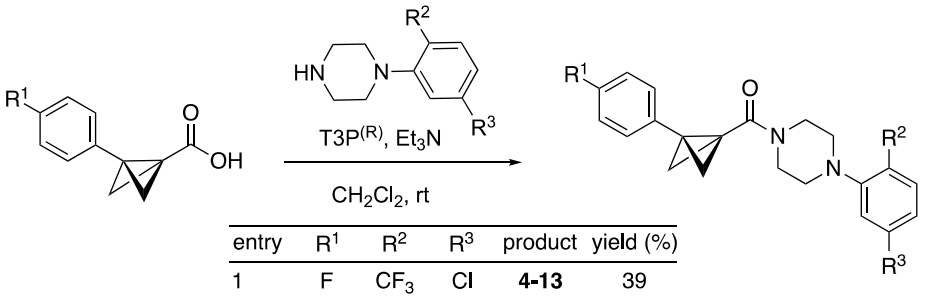
Table 21. Preparation of carboxylic acids **4-11** and **4-12**.



R	product	yield (%)
F	**4-11**	57
CF_3	**4-12**	50

The bicyclo[1.1.0]butane carboxylic acids **4-11** and **4-12** were coupled to the appropriate aryl piperizines using the T3P® reagent (Table 22).[183] These piperazine coupling partners were prepared by collaborators through Buchwald-Hartwig coupling of *N*-Boc piperazine with an aryl bromide.[178] The carbamate protecting group was then removed with HCl in dioxane to afford the piperazine HCl salts, which were typically free-based before amide coupling. In this manner, three bicyclobutyl amide analogs **4-13**, **4-14**, and **4-15** were prepared for testing of their AR antagonist activity.

Table 22. Amide coupling of carboxylic acids **4-11** and **4-12**.



entry	R^1	R^2	R^3	product	yield (%)
1	F	CF_3	Cl	**4-13**	39
2	CF_3	CF_3	Cl	**4-14**	55
3	CF_3	CH_3	CF_3	**4-15**	72

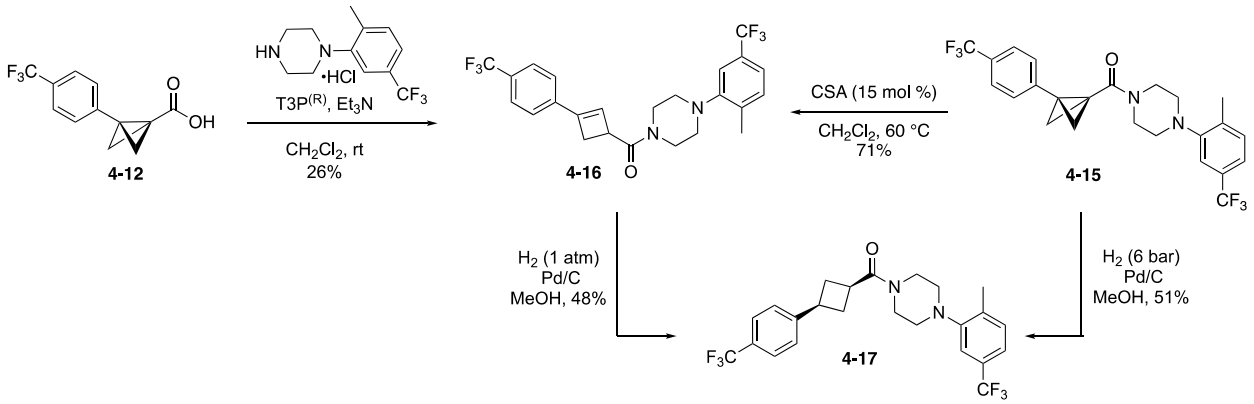
4.2.2 Rearrangement of Bicyclo[1.1.0]butyl Amides to Cyclobutenes

Initially, the amide couplings described in Table 22 were conducted by pre-mixing a solution of bicyclo[1.1.0]butane carboxylic acid with piperazine HCl salt, treating with excess Et_3N, and then adding the T3P® coupling reagent. This approach gave perplexingly inconsistent results. While the expected bicyclo[1.1.0]butyl amides were isolated in some cases, in many others an unexpected cyclobutene product was obtained in low yield (as in the conversion of **4-12** to **4-16**, Scheme 45). Through a systematic evaluation of reaction parameters, it was determined that this cyclobutene formation was triggered by excess HCl in the piperazine HCl salt, possibly resulting from

incomplete washing of the solid during large-scale preparations. When the piperazine HCl salt was partitioned between CH_2Cl_2 and 1 M NaOH before use in the coupling, bicyclobutyl amides such as **4-15** could be reliably prepared.

With this knowledge, several acids were screened for their effectiveness in promoting the isomerization of bicyclobutane **4-15** to cyclobutene **4-16**. The optimally clean and high yielding protocol was found to be treatment of a CH_2Cl_2 solution of **4-15** with a catalytic (15 mol %) amount of camphorsulfonic acid followed by heating at 60 °C. Camphorsulfonic acid is an advantageous acid source in that it is an easily weighed solid that does not exist as a hydrate. Acids with appreciable water content tended to promote the competitive formation of a cyclobutanol hydration product in addition to cyclobutene formation.

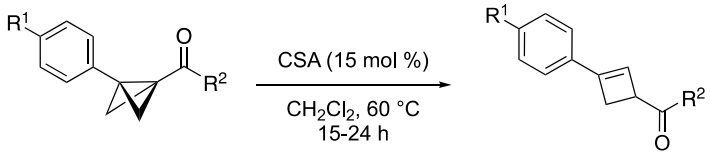
To confirm the structure of cyclobutene **4-16**, it was subjected to hydrogenation to afford cyclobutane **4-17** as a single diastereomer (Scheme 45). Bicyclo[1.1.0]butyl amide **4-15** was also subjected to hydrogenation across the strained central bond at elevated pressure to afford the same cyclobutane product (**4-17**), which affirms the structural assignment of **4-16**. The relative stereochemistry of cyclobutane **4-17** was confirmed by NOESY, wherein a correlation is observed from both methines to one of the two methylenes.



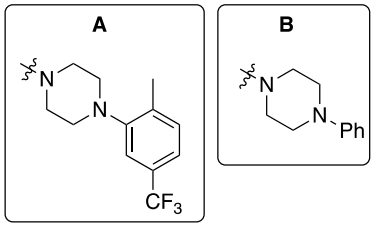
Scheme 45. Preparation of cyclobutane **4-16** and confirmation of structure through conversion to **4-17**.

The isomerization of bicyclo[1.1.0]butanes to cyclobutenes has been conducted with cobalt (II) porphyrin complexes,[184] photochemical irradiation,[185] or reduction over lithium metal.[186] However, no general method for the isomerization of functionalized bicyclobutanes under mild conditions has been described. The scope of this catalytic acid-mediated isomerization was therefore investigated (Table 23). Both secondary (NHPh) and tertiary (piperazine) amides were well tolerated in the isomerization (entries 1–5). The electronic nature of the arene ring was unimportant, as evidenced by the similar yields obtained in entries 4 (R^1 = H) and 5 (R^1 = CF_3). A ketone substrate (obtained through DMP oxidation of the corresponding bicyclo[1.1.0]butyl alcohol) afforded the expected cyclobutane in modest yield (entry 6). The lower yield may be attributed to the poor stability of bicyclo[1.1.0]butyl ketones, which are more susceptible to decomposition than other bicyclobutane derivatives.

Table 23. Conversion of bicyclo[1.1.0]butyl amides to cyclobutenes.

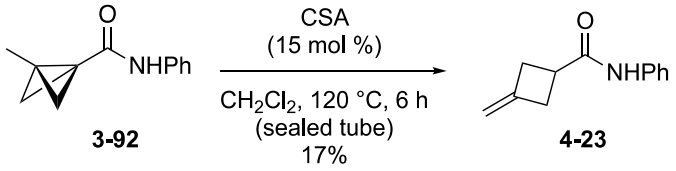


entry	R^1	R^2	product	yield (%)
1	CF_3	**A**	**4-16**	71
2	H	NHPh	**4-18**	66
3	Cl	NHPh	**4-19**	84
4	H	**B**	**4-20**	75
5	CF_3	**B**	**4-21**	76
6	CF_3	Ph	**4-22**	30



An arene substituent at the ring junction is necessary for this isomerization. When methyl-substituted amide **3-92** was subjected to the optimized conditions, no conversion occurred. More vigorous heating at 120 °C eventually triggered formation of methylenecyclobutane **4-23** in 17% yield (Scheme 46). This result is consistent with an isomerization mechanism whereby amide protonation results in a cyclobutyl cation that is stabilized by the aryl substituent. Elimination then

affords the racemic cyclobutene product. In the case of **4-23**, thermodynamic formation of the less strained methylenecyclobutane is favored over cyclobutene formation.

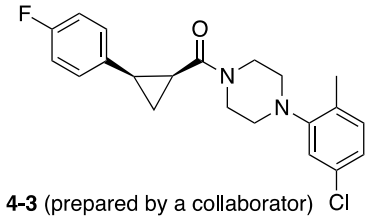


Scheme 46. Conversion of amide **3-92** to methylenecyclobutane **4-23**.

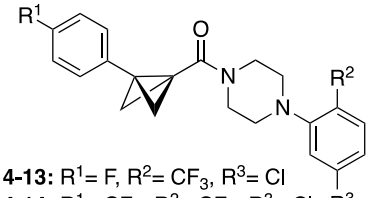
4.2.3 Biological Activity of Amide Analogs

Bicyclo[1.1.0]amides **4-13**, **4-14**, and **4-15**, as well as cyclobutane **4-17** (all of which are achiral) were tested for their ability to inhibit AR activity in the prostate cell nucleus using the AR luciferase dual-reporter assay.[177] Select analogs were subjected to additional microsome stability tests and cell proliferation assays in both AR positive (22Rv1) and AR negative (PC3) CRPC cell lines (Table 24). The respective enantiomers of cyclobutane **4-16** (which is chiral due to the desymmetrization from the cyclic olefin) were separated by preparative chiral SFC and evaluated separately in the assays. Although many other analogs were prepared by collaborators and tested in these assays, only one (oxetane **4-24**) contained a four-membered ring. The biological data for both enantiomers of **4-24** are shown in Table 24 to enable comparison to cyclobutane **4-17**. Assay data for both enantiomers of the lead compound **4-3** (JJ-450) are also shown for comparison.

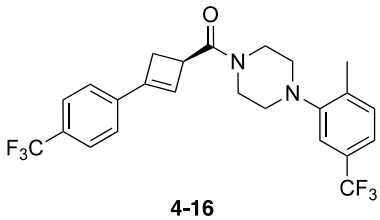
Table 24. Biological testing of androgen receptor antagonist analogs.



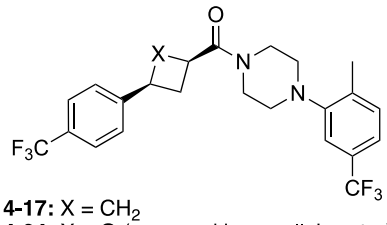
4-3 (prepared by a collaborator)



4-13: R^1= F, R^2= CF_3, R^3= Cl
4-14: R^1= CF_3, R^2= CF_3, R^3= Cl
4-15: R^1= CF_3, R^2= CH_3, R^3= CF_3



4-16



4-17: X = CH_2
4-24: X = O (prepared by a collaborator)

entry	compound	luciferase assay EC_{50} (μM)	human liver microsome $t_{1/2}$ (min)	mouse liver microsome $t_{1/2}$ (min)	22Rv1 cell assay (% inibition at 30 μM)	PC3 cell assay (% inibition at 30 μM)
1	(–)-**4-3**	1.7	31.7	5.3	88	44
2	(+)-**4-3**	14.8	16.3	7.3	78	33
3	**4-13**	>25	not tested	not tested	not tested	not tested
4	**4-14**	2.8	36.5	43.1	70	30
5	**4-15**	12.3	26.9	31.2	83	49
6	(–)-**4-16**	8.2	not tested	not tested	not tested	not tested
7	(+)-**4-16**	>25	not tested	not tested	not tested	not tested
8	**4-17**	>25	>1000	178.7	24	10
9	(–)-**4-24**	15.1	21.3	16.0	78	46
10	(+)-**4-24**	12.7	129.0	88.4	82	35

While the *p*-fluoro bicyclo[1.1.0]butyl amide **4-13** showed >25 μM activity in the luciferase dual-reporter assay and was not considered for cell-based evaluation (entry 3), *p*-trifluoromethyl substrates **4-14** and **4-15** were comparable in activity to lead structure (–)-**4-3** (entries 4 and 5 vs 1 and 2). Like (–)-**4-3**, these bicyclobutanes showed strong and selective growth inhibition of the human 22Rv1 (androgen receptor positive) CRPC cell line over the PC3 (androgen receptor negative) CRPC cell line. The stability of these bicyclo[1.1.0]butane substrates in human liver microsomes was comparable to lead compound (–)-**4-3**. In the case of mice liver microsomes, however, the half-life was nearly an order of magnitude greater. These results suggest

that despite their high strain energy, bicyclo[1.1.0]butanes can serve as cyclopropane, cyclobutane, or *cis*-alkene substitutes that are stable to metabolic degradation *in vivo*.

Cyclobutane **4-17** was significantly less potent than many other analogs (including oxetane **4-24**) in both the luciferase reporter and cell growth assays (entry 8). However, **4-17** exhibited dramatically higher microsomal stability than any of the comparison substrates. Others have observed that cyclobutane derivatives of lead structures have an enhanced metabolic stability,[180a] and molecules containing cyclobutanes have shown effective pharmacokinetic performance in human clinical trials.[187] Taken together, these results encourage continued studies of these and other small carbocyclic ring systems in medicinal chemistry.

4.3 CONCLUSIONS

Several bicyclo[1.1.0]butyl amides were prepared as part of a medicinal chemistry to identify androgen receptor antagonists for the treatment of castration-resistant prostate cancer. A method for the synthesis of aryl bicyclo[1.1.0]butane carboxylic acids was developed to attain the necessary synthetic targets. These new analogs had comparable androgen receptor antagonist activity and greater microsomal stability than the previous lead compound **4-3** (JJ-450). During these studies, an acid-mediated isomerization of bicyclo[1.1.0]butanes to cyclobutenes was discovered. The scope of this transformation was investigated.

5.0 EXPERIMENTAL

5.1 GENERAL EXPERIMENTAL

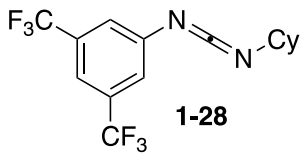
All glassware was oven dried and cooled in a desiccator prior to use. All moisture sensitive reactions were performed under an atmosphere of dry N_2 or Ar. Reactions carried out below 0 °C employed an acetone/dry ice bath. Reagents obtained from commercial sources were used as received unless otherwise specified. THF and Et_2O were distilled from sodium/benzophenone ketyl and CH_2Cl_2 and toluene were distilled over CaH_2. Concentrating under reduced pressure refers to the use of a rotary evaporator connected to a PIAB Lab Vac H40, followed by a 1–1.5 torr high vacuum pump to remove residual solvent.

Melting points were determined using a Laboratory Devices Mel-Temp II in open capillary tubes and are uncorrected. Infrared spectra were determined as neat solids or oils on a Smiths Detection IdentifyIR FT-IR spectrometer. ^{1}H NMR, ^{13}C NMR, ^{11}B NMR, ^{19}F NMR and ^{31}P NMR spectra were recorded on a Bruker Advance 300 MHz, 400 MHz, or 500 MHz instruments. ^{1}H NMR and ^{13}C NMR chemical shifts (δ) were reported in parts per million with the residual solvent peak used as an internal standard δ and are tabulated as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), number of protons, and coupling constant(s). ^{13}C NMR spectra were obtained using a proton-decoupled pulse sequence and are tabulated by observed peak. ^{11}B NMR, ^{19}F NMR, and ^{31}P NMR spectra were taken without an internal standard. Thin-layer chromatography was performed using pre-coated silica gel 60 F254 plates (EMD, 250 μm thickness) and visualization was accomplished with a 254 nm UV light and by staining with a $KMnO_4$ solution (1.5 g of $KMnO_4$ and 1.5 g of K_2CO_3 in 100 mL of a 0.1%

NaOH solution). Flash chromatography on SiO_2 (Silicycle, Silia-P Flash Silica Gel or SiliaFlash® P60, 40-63 μm) was used to purify crude reaction mixtures.

Unless otherwise stated, starting materials were purchased from commercial sources and used without further purification. Thiourea starting materials were either obtained from commercial sources, from collaborators, or were prepared from the corresponding primary amine and isocyanate. Secondary phosphine boranes were supplied from Boehringer-Ingelheim (Ridgefield, CT) or were prepared according to the referenced procedure.

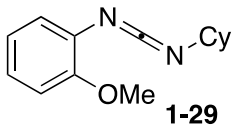
5.2 CHAPTER 1 EXPERIMENTAL PART



1-28

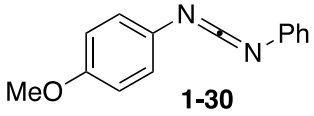
General Procedure A (Carbodiimide formation from the corresponding thiourea): *N*-(3, 5-Bistrifluoromethyl)phenyl *N'*-cyclohexylcarbodiimide (1-28). A 25 mL round bottom flask was charged with the corresponding thiourea (0.263 g, 0.710 mmol), triethylamine (0.30 mL, 1.4 mmol, 2.0 eq), DMAP (0.004 g, 0.03 mmol, 5 mol %) and CH_2Cl_2 (5 mL). The reaction mixture was cooled to 0 ºC and mesyl chloride (0.10 mL, 1.4 mmol, 2.0 eq) was added via syringe over 5 min. The solution was stirred at room temperature for 1 h then was concentrated under reduced pressure. The crude material was slurried in hexane and filtered through a plug of Celite®. The filtrate was concentrated under reduced pressure and purified by chromatography on SiO_2 (hexanes) under N_2 pressure to afford **1-28** (0.197 g, 0.585 mmol, 83%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (s, 1 H), 7.46 (s, 2 H), 3.63-3.58 (m, 1 H), 2.03-2.00 (m, 2 H), 1.77 (dd, 2 H, J = 9.6, 4.0 Hz), 1.60-1.49 (m, 3 H), 1.43-1.40 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.8, 133.4 (q, $^2J_{CF}$

= 33 Hz), 123.2 ($^3J_{CF}$ = 3 Hz), 123.0 (q, $^1J_{CF}$ = 271 Hz), 117.6 ($^3J_{CF}$ = 4 Hz), 56.8, 34.7, 25.2, 24.1; MS (ESI)$^+$ *m/z* 337 (100); HRMS (ESI)$^+$ *m/z* calcd for $C_{15}H_{15}N_2F_6$ [M+H] 337.1139, found 337.1141.



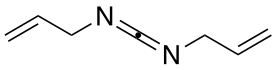
1-29

***N*-2-Methoxyphenyl *N'*-cyclohexylcarbodiimide (1-29)**. Prepared according to General Procedure A from the corresponding thiourea (0.327 g, 1.23 mmol), DMAP (0.008 g, 0.06 mmol), triethylamine (0.52 mL, 3.7 mmol) and mesyl chloride (0.19 mL, 2.5 mmol) in CH_2Cl_2 (15 mL). Purification by chromatography on SiO_2 afforded **1-29** (0.204 g, 0.885 mmol, 72%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.12-6.97 (m, 2 H), 6.91-6.81 (m, 2 H), 3.88 (s, 3 H), 3.49-3.36 (m, 1 H), 2.08-1.93 (m, 2 H), 1.84-1.68 (m, 2 H), 1.62-1.08 (m, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.0, 136.4, 129.3, 125.2, 124.6, 121.0, 111.2, 56.5, 55.7, 34.6, 25.5, 24.5; IR (ATR) 3027, 2134, 1593, 1485, 1232, 1192, 827, 769, 692 cm^{-1}; MS (ESI)$^+$ *m/z* 249 (100, M + H_2O), 231 (10), 149 (7); HRMS (ESI)$^+$ *m/z* calcd for $C_{14}H_{19}N_2O_2$ [M+H+H_2O] 249.1603, found 249.1655.



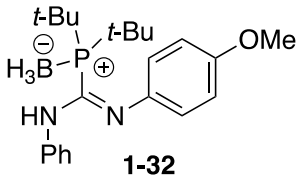
1-30

***N*-4-Methoxyphenyl *N'*-phenylcarbodiimide (1-30)**.[188] Prepared according to General Procedure A from the corresponding thiourea (1.63 g, 6.31 mmol), triethylamine (2.66 mL, 18.9 mmol, 3.00 eq), mesyl chloride (0.97 mL, 13 mmol, 2.0 eq) and DMAP (0.039 g, 0.32 mmol, 5 mol%) in CH_2Cl_2 (60 mL). Purification by chromatography on SiO_2 (5% EtOAc/hexanes) afforded **1-30** (1.23 g, 5.49 mmol, 87%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35-7.30 (m, 2 H), 7.19-7.13 (m, 5 H), 6.85 (dd, 2 H, *J* = 6.9 Hz, 2.4 Hz), 3.80 (s, 3 H).



1-31

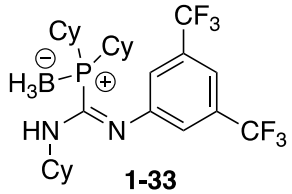
***N, N′*-Diallylcarbodiimide (1-31**). Prepared according to General Procedure A from the corresponding thiourea (1.00 g, 6.40 mmol), DMAP (0.039 g, 0.32 mmol), triethylamine (2.69 mL, 19.2 mmol), and mesyl chloride (1.00 mL, 12.8 mmol) in CH_2Cl_2 (30 mL). Purification by filtration through Celite afforded carbodiimide **1-31** (0.456 g, 3.73 mmol, 58%) as a clear oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.90, 5.27, 5.18 (ABX, 2 x 3 H, J_{AX} = 17.2 Hz, J_{BX} = 10.0 Hz, J_{AB} = 1.6 Hz), 3.82 (d, 2 x 2 H, J = 4.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.0, 134.6, 116.4, 48.8.



1-32

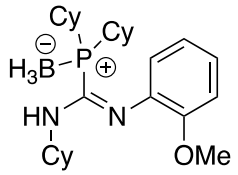
General Procedure B (Hydrophosphination of Carbodiimides): (*N*-Cyclohexyl, *N'*-(3, 5-trifluoromethyl) phenylcarbamimidoyl)-dicyclohexylphosphine borane (1-32). A 5 mL vial was flushed with Ar and charged with di-tert-butyl phosphine borane (0.064 g, 0.40 mmol) and carbodiimide **1-30** (0.075 g, 0.33 mmol). These materials were dissolved in dimethylacetamide (2 mL) and sparged with Ar for 10 min. The flask was then cooled in an ice bath. Sodium hydride (0.016 g, 0.40 mmol, 60% dispersion) was then added at once, causing immediate gas evolution, and foaming to a white suspension. After 15 min, the ice bath was removed and then the reaction mixture allowed to warm to rt. After 15 min at rt, the reaction was stirred vigorously while open to the air for 30 minutes (the solution had a distinct green color). The reaction mixture was treated with sat aq NH_4Cl (2 mL), and extracted with diethyl ether (2 x 30 mL). The combined organic phases were then washed with water (30 mL), dried (Na_2SO_4), and concentrated to give a crude sticky oil. Purification by chromatography on SiO_2 (5% EtOAc/hexane) afforded **1-32** (0.100 g,

0.260 mmol, 78%) as a clear oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (s, 0.5 H), 7.86 (s, 0.5 H), 6.96-6.86 (m, 2 H), 6.82 (t, 0.5 H, J = 7.5 Hz), 6.69 (t, 0.5 H, J = 7.5 Hz), 6.61-6.46 (m, 4 H), 6.44 (dd, 1 H, J = 7.0 Hz, 2.0 Hz), 3.65 (s, 3 H), 1.53 (s, 9 H), 1.51 (s, 9 H), 1.1-0.3 (br, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, $^{1}J_{CP}$ not resolved) δ 128.0, 127.9, 124.1, 123.7, 122.1, 121.8, 121.3, 120.4, 113.4 ($^{3}J_{CP}$ = 14 Hz), 55.5, 33.8, 28.4, 27.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ 52.1; ^{11}B NMR (128 MHz, $CDCl_3$) δ –43; HRMS (ESI)$^{+}$ *m/z* calcd for $C_{22}H_{32}N_2OP$ [M+H–BH_3] 371.2252, found 371.2265. This compound exhibits rotomers and/or *E*-*Z* isomers by NMR.



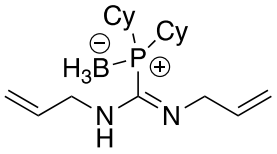
1-33

(3,5-Bis(trifluoromethyl)phenyl)-*N*-cyclohexylcarbamimidoyldicyclohexyl phosphine borane (**1-33**).[31] Prepared according to General Procedure B from dicyclohexylphosphine borane (0.080 g, 0.38 mmol), carbodiimide **1-28** (0.106 g, 0.315 mmol) and sodium hydride (0.015 g, 0.38 mmol, 60%) in DMAc (1.2 mL). Purification by chromatography on SiO_2 (5% EtOAc/hexane) afforded phosphine borane **1-33** (0.095 g, 0.17 mmol, 55%) as a clear oil that solidified to a colorless solid on standing: Mp 97.5–98.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.43 (t, 1 H, J = 9.2 Hz), 6.30 (d, 2 H, J = 6.8 Hz), 5.84 (br s, 1 H), 3.07 (br s, 1 H), 2.10-2.00 (m, 2 H), 1.90-0.75 (m, 30 H), 1.0-0.0 (br, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, CF_3 not resolved) δ 164.5, 164.3, 162.0, 161.9, 153.2, 147.9 (d, $^{1}J_{CP}$ = 68 Hz), 103.5 (d, $^{3}J_{CP}$ = 25 Hz), 97.2 (t, $^{3}J_{CP}$ = 27 Hz), 52.0, 33.1, 32.3, 31.9, 26.9, 26.69, 26.66, 25.9, 25.2, 24.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 41.1; ^{11}B NMR (128 MHz, $CDCl_3$) δ –44; HRMS (ESI)$^{+}$ *m/z* calcd for $C_{27}H_{38}F_6N_2P$ [M+H–BH_3] 535.2677, found 535.2661.



1-34

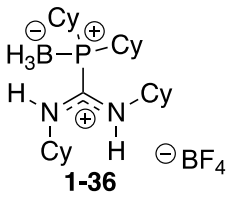
(*N*-Phenyl, *N*'-2-methoxylphenylylcarbamimidoyl)-dicyclohexylphosphine borane (1-34). Prepared according to general Procedure B from dicyclohexylphosphine borane (0.536 g, 2.53 mmol), carbodiimide **1-29** (0.485 g, 2.10 mmol) and sodium hydride (0.101 g, 1.06 mmol, 60%) in DMAc (10 mL). Purification by chromatography on SiO_2 (5% EtOAc/hexane) afforded phosphine borane **1-34** (0.540 g, 1.22 mmol, 58%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.93 (t, 1 H, J = 7.6 Hz), 6.86-6.71 (m, 3 H), 5.67 (t, 3 H, J = 3.2 Hz), 3.75 (s, 3 H), 2.95-2.79 (m, 1 H), 2.23-2.07 (m, 2 H), 1.95-1.48 (m, 18 H), 1.45-0.70 (m, 13 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.2, 147.0 ($^1J_{CP}$ = 77 Hz), 139.6 ($^3J_{CP}$ = 13 Hz), 122.8, 121.1, 120.5, 110.6, 55.1, 51.5 ($^3J_{CP}$ = 6 Hz), 34.7, 33.7, 32.1, 31.8, 31.6, 26.8, 26.82, 26.77, 26.69, 26.65, 26.63, 26.61, 25.29, 25.26, 24.4, 14.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 39.1; ^{11}B NMR (128 MHz, $CDCl_3$) δ –45; HRMS (ESI)$^+$ *m/z* calcd for $C_{26}H_{45}N_2OPB$ [M+H] 443.3362, found 433.3353.



1-35

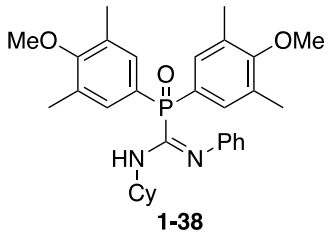
(*N*, *N*'-Diallylcarbamimidoyl)-dicyclohexylphosphine borane (1-35). Prepared according to General Procedure B from carbodiimide **1-31** (0.150 g, 1.23 mmol), dicyclohexylphosphine borane (0.312 g, 1.47 mmol), and NaH dispersion (0.059 g, 1.47 mmol) in DMAc (6 mL). Purification by chromatography on SiO_2 (5% EtOAc in hexane) to afforded **1-35** (0.153 g, 0.458 mmol, 37%) as a yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.08-5.70 (m, 2 H), 5.35-5.04 (m, 4 H), 4.14 (s, 2 H), 3.95 (s, 2 H), 2.40-1.05 (m, 22 H), 0.90-0.05 (br, 3 H); IR (ATR): 3368, 2934, 2376, 1629, 1450,

1077, 982, 917 cm^{-1}; ^{31}P NMR (162 MHz, $CDCl_3$) δ 38.4; ^{11}B NMR (128 MHz, $CDCl_3$) δ –44; HRMS m/z calcd for $C_{19}H_{34}N_2P$ [M+H–BH_3] 321.2454, found 321.2432. Significant broadening was observed in the ^1H and ^{13}C NMR spectra.



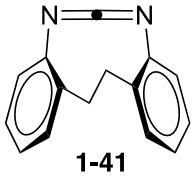
1-36

(*N, N'*-Dicyclohexylcarbamimidoylium)- dicyclohexylphosphine borane tetrafluoroborate (1-36).[31] A solution of phosphine borane **1-19** (0.077 g, 0.18 mmol) in CH_2Cl_2 (1.5 mL) was cooled to 0 °C under Ar and treated with HBF_4 diethyl ether complex (0.37 mL, 2.8 mmol, 15 eq). After 30 min at 0 °C, the reaction was warmed to rt over 30 min. The solution was opened to air, treated with aq HBF_4 (1.5 mL), and stirred for 30 min more. The solution was then diluted with water (5 mL) and extracted with CH_2Cl_2 (2 x 15 mL). The combined extracts were washed with brine, dried (Na_2SO_4) and were concentrated to afford **1-36** (0.075 g, 0.15 mmol, 81%) as a colorless crystalline solid: Mp 259–261 ºC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.46-7.34 (br s, 1 H), 4.75-4.65 (m, 1 H), 3.62-3.38 (m, 2 H), 2.40-2.25 (m, 2 H), 1.95-1.10 (m, 41 H); ^{13}C NMR (100 MHz, $CDCl_3$,) δ 158.1 ($^1J_{CP}$ = 30 Hz), 156.2 ($^1J_{CP}$ = 27 Hz), 58.6, 53.3 ($^3J_{CP}$ = 3 Hz), 34.9, 34.7, 32.8, 32.6, 32.1, 31.8, 31.2, 28.3, 27.8, 27.7, 27.2, 26.42, 26.38, 26.3, 26.0, 25.9, 25.8, 25.7, 25.42, 25.40, 25.1, 25.0, 24.4, 24.2, 23.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 60.0, 56.9; ^{11}B NMR (128 MHz, $CDCl_3$, measured without lock) δ –0.9, –45.4. A single crystal suitable for X-ray analysis was grown from hexanes/acetone (1:1). The X-ray crystal structure data for the compound has been deposited with CCDC #997593.



1-38

***N*-Cyclohexyl, *N*'-phenylcarbamimidoyl)-di-(3, 5-dimethyl-4-methoxyphenyl) phosphine oxide (1-38)**.[31] A solution of phosphine **1-37** (0.052 g, 0.10 mmol, obtained from collaborators) in acetone (1 mL) was treated with hydrogen peroxide (0.12 mL, 0.11 mmol, 3% aq. solution). The reaction mixture was stirred for 1 h at rt; TLC analysis (10% EtOAc/hexanes) showed a clean and quantitative oxidation. The solution was diluted with water (5 mL) and extracted with Et_2O (2 x10 mL). The combined organic extracts were washed with water (10 mL), brine (10 mL), dried (Na_2SO_4), and concentrated to afford phosphine oxide **1-38** (0.053 g, 0.10 mmol, 99%) as a sticky colorless gum: ^{1}H NMR (400 MHz, $CDCl_3$) (significant broadening) δ 7.60-7.41 (m, 4 H), 7.22-6.60 (m, 5 H), 6.30-6.20 (br s, 1 H), 3.74 (s, 6 H), 2.28 (s, 12 H), 1.78-0.95 (m, 11 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4 (s), 132.9, 132.8, 131.3, 131.2, 128.2, 126.3, 125.3, 122.0, 120.8, 59.6, 33.3, 25.4, 24.7, 16.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.0; HRMS $(ESI)^+$ *m/z* calcd for $C_{31}H_{40}N_2O_3P$ [M+H] 519.2777, found 519.2764.



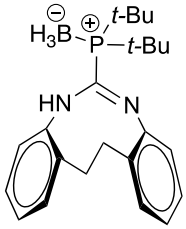
1-41

5, 6-Didehydro-12, 13-dihydrodibenzodiazonine (1-41).[46] A solution of dianiline **1-39** (3.50 g, 16.4 mmol) in 2 M HCl (60 mL) was cooled to 0 °C and treated dropwise with a solution of sodium nitrite (3.41 g, 49.5 mmol, 3.00 eq) in H_2O (30 mL). The yellow solution was stirred for 1 h at 0 °C, then was treated dropwise with a solution of sodium azide (4.29 g, 65.0 mmol, 4.00 eq) in water (35 mL), which caused considerable foaming. The mixture warmed to rt and stirred for 24

h, which resulted in formation of a tan precipitate. After addition of CH_2Cl_2 (75 mL) and water (10 mL), the layers were separated and the organic layer was dried (Na_2SO_4) and concentrated in *vacuo*. The crude material was filtered through a short plug of SiO_2 with 30% EtOAc in hexanes. Concentration of the eluent afforded diazide **1-40** (3.61 g, 13.7 mmol, 83%) as a tan solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (td, 2 H, J = 9.0 Hz, 1.8 Hz), 7.12 (t, 4 H, J = 6.6 Hz), 7.04 (app t, 2 H, J = 7.2 Hz), 2.82 (s, 4 H); IR (ATR) 3085, 2993, 2115, 1485, 1286, 1163, 751 cm^{-1}.

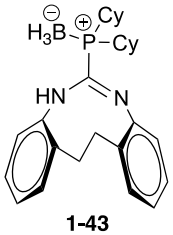
A solution of diazide **1-40** (3.61 g, 13.7 mmol) in Et_2O (100 mL) under N_2 at rt was treated with triphenylphosphine (7.17 g, 27.3 mmol). The opaque brown solution was stirred at rt for 20 h and developed a brown precipitate. The solvent was removed *in vacuo* to afford the iminophosphorane (10.1 g) as a buff solid that was used without further purification: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85-7.23 (m, 32 H), 7.12-7.01 (d, 3 H, J = 6.6 Hz), 6.80-6.45 (m, 6 H), 3.23-3.05 (s, 4 H); IR (ATR) 3026, 1594, 1479, 1450, 1340, 1103, 726, 691cm^{-1}.

A suspension of the iminophosphorane (2.40 g, 3.27 mmol) in CH_2Cl_2 (200 mL) was sparged with a balloon CO_2 at rt for 4 h, over which period the reaction mixture turned from opaque to transparent yellow/brown. The reaction mixture was concentrated, and the concentrate was purified by chromatography on SiO_2 (10% EtOAc/hexane) to afford carbodiimide **1-41** (0.68 g, 3.1 mmol, 94%) as a colorless solid: Mp 141.9–142.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.20 (m, 4 H), 7.16-7.01 (m, 4 H), 3.41-3.27 (m, 2 H), 3.12-2.97 (m, 2 H); IR (ATR) 2974, 2104, 2091, 1737, 1595, 1450, 1140, 734 cm^{-1}. This material contained ca. 10% of dimeric bis-carbodiimide that was readily removed in subsequent transformations.



1-42

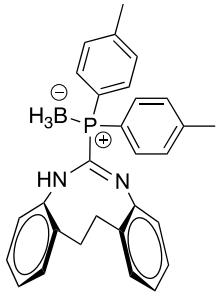
6-(Di-*t*-butylphosphanyl)-12, 13-dihydrodibenzodiazonine borane (1-42).[31] Prepared according to General Procedure B from carbodiimide **1-41** (0.065 g, 0.30 mmol), di-*t*-butyl phosphine borane (0.057 g, 0.35 mmol) and NaH (0.014 g, 0.35 mmol, 60% dispersion) in DMAc (1.2 mL). Purification by chromatography on SiO_2 (5% EtOAc/hexanes) afforded **1-42** (0.075 g, 0.20 mmol, 67%) as a colorless crystalline solid: Mp 174–177 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (s, 1 H), 6.92-6.73 (m, 5 H), 6.69 (d, 1 H, J = 7.2 Hz), 6.63 (t, 1 H, J = 7.2 Hz), 6.49 (d, 1 H, J = 7.6 Hz), 3.45-3.26 (m, 2 H), 2.97-2.83 (m, 2 H), 1.58 (s, 9 H), 1.54 (s, 9 H), 1.2-0.1 (br, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.9 ($^3J_{CP}$ = 11 Hz), 146.3 ($^1J_{CP}$ = 75 Hz), 137.7, 137.5 ($^3J_{CP}$ = 8 Hz), 130.9, 130.2, 128.4, 127.0, 126.7, 126.6, 126.5, 122.3, 120.3, 34.3 ($^1J_{CP}$ = 27 Hz), 33.6 ($^1J_{CP}$ = 26 Hz), 30.4 ($^2J_{CP}$ = 7 Hz), 28.8, 28.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 52.6; ^{11}B NMR (128 MHz, $CDCl_3$) δ –42; HRMS (ESI)$^+$ *m/z* calcd for $C_{23}H_{34}N_2PB$ [M+H] 381.2631, found 381.2622. The X-ray crystal structure data for this compound has been deposited (CCDC #1008171).



1-43

6-(Dicyclohexylphosphanyl)-12, 13-dihydrodibenzodiazonine borane (1-43). Prepared according to General Procedure B from carbodiimide **1-41** (0.15 g, 0.68 mmol), dicyclohexylphosphine borane (0.173 g, 0.817 mmol), and NaH (0.032 g, 0.82 mmol, 60% dispersion) in DMAc (3 mL). Purification by chromatography on SiO_2 (10% EtOAc/hexane)

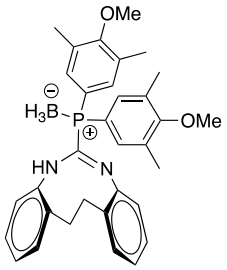
afforded phosphine borane **1-43** (0.212 g, 0.049 mmol, 72%), with a trace amount of inseparable phosphine borane starting material, as a clear oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.20 (s, 1 H), 6.91-6.73 (m, 5 H), 6.67 (d, 1 H, J = 7.2 Hz), 6.60 (t, 1 H, J = 7.2 Hz), 6.42 (d, 1 H, J = 7.6 Hz), 3.36-3.23 (m, 2 H), 3.02-2.80 (m, 2 H), 2.47-2.20 (m, 2 H), 2.15-1.18 (m, 20 H), 0.9-0.1 (br, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.0 (d, $^{3}J_{CP}$ = 12 Hz), 145.9 (d, $^{1}J_{CP}$ = 78 Hz), 137.4 (d, $^{3}J_{CP}$ = 8 Hz), 130.8, 130.4, 128.5, 126.9, 126.7, 126.6, 126.1, 122.5, 120.2, 32.0, 31.63, 31.57, 31.2, 30.7, 30.0, 29.4, 29.3, 29.1, 28.7, 27.7, 27.0, 26.83, 26.76, 26.72, 26.67, 26.65, 26.6, 26.5, 26.4, 26.3, 26.1, 26.1, 25.8; ^{31}P NMR (162 MHz, $CDCl_3$) δ 38.3; ^{11}B NMR (128 MHz, $CDCl_3$) δ –43.1; IR (ATR) 3334, 2933, 2862, 2378, 1629, 1480, 1325, 1215, 1077, 767, 734 cm^{-1}; HRMS (ESI)$^{+}$ *m/z* calcd for $C_{27}H_{39}N_2PB$ [M+H] 433.2944, found 433.2930.



1-44

6-(Ditolylphosphanyl)-12, 13-dihydrodibenzodiazonine borane (1-44).[31] Prepared according to General Procedure B from carbodiimide **1-41** (0.200 g, 0.907 mmol), di-tolyl phosphine borane (0.249 g, 1.09 mmol) and NaH (0.022 g, 0.55 mmol, 60% dispersion) in DMAc (5 mL). Purification by chromatography on SiO_2 (10% EtOAc/hexanes) afforded phosphine borane **1-44** (0.319 g, 0.712 mmol, 78%) as a colorless crystalline solid: Mp 189.7–191.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, 1 H, J = 8.0 Hz), 7.98 (d, 1 H, J = 8.4 Hz), 7.85 (d, 1 H, J = 8.0 Hz), 7.82 (d, 1 H, J = 8.4 Hz), 7.42 (s, 1 H), 7.31 (td, 4 H, J = 6.4 Hz, 2.0 Hz), 6.86-6.80 (m, 3 H), 6.79-6.72 (m, 2 H), 6.63-6.54 (m, 2 H), 6.42 (d, 1 H, J = 7.6 Hz), 3.23-3.15 (m, 1 H), 2.97-2.86 (m, 1 H), 2.78-2.66 (m, 2 H), 2.43 (s, 3 H), 2.41 (s, 3 H), 1.5-0.8 (br, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ

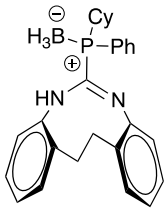
148.7 ($^1J_{CP}$ = 91 Hz), 148.0 ($^3J_{CP}$ = 13 Hz), 142.7 ($^4J_{CP}$ = 2 Hz), 142.1 ($^4J_{CP}$ = 2 Hz), 137.3 ($^3J_{CP}$ = 10 Hz), 136.9, 133.6 ($^2J_{CP}$ = 10 Hz), 133.2 ($^2J_{CP}$ = 10 Hz), 130.7, 130.4, 129.6 ($^3J_{CP}$ = 11 Hz), 128.4, 126.6, 126.5, 125.4, 124.2 ($^1J_{CP}$ = 64 Hz), 123.3 ($^1J_{CP}$ = 61 Hz), 122.6, 119.6, 31.1, 29.2, 21.7, 21.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.4; ^{11}B NMR (128 MHz, $CDCl_3$) δ –40.4; IR (ATR) 3340, 3026, 2378, 1637, 1486, 1356, 1128, 1045, 908, 802, 734 cm^{-1}; HRMS (ESI)$^+$ *m/z* calcd for $C_{29}H_{28}N_2P$ [M+H–BH_3] 435.1990, found 435.1975. An X-ray crystal structure was obtained for this molecule.



1-45

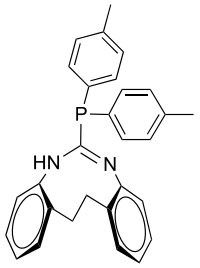
6-(Di-(3, 5-dimethyl-4-methyoxy)phenylphosphanyl)-12, 13-dihydrodibenzodiazonine borane (1-45).[31] Prepared according to General Procedure B from carbodiimide **1-41** (0.084 g, 0.38 mmol), di-(3,5-dimethyl-4-methoxy)phosphine borane (0.133 g, 0.545 mmol) and NaH (0.018 g, 0.46 mmol, 60% dispersion) in DMAc (3 mL). Purification by chromatography on SiO_2 (10% EtOAc/hexanes) afforded phosphine borane **1-45** (0.171 g, 0.319 mmol, 83%) as a colorless foam: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, 2 H, *J* = 10.8 Hz), 7.54 (d, 2 H, *J* = 11.2 Hz), 7.43 (s, 1 H), 6.89-6.83 (m, 3 H), 6.80-6.74 (m, 2 H), 6.63-6.55 (m, 2 H), 6.44 (d, 1 H, *J* = 7.6 Hz), 3.79 (s, 3 H), 3.76 (s, 3 H), 3.27-3.18 (m, 1 H), 2.92-2.81 (m, 1 H), 2.79-2.68 (m, 2 H), 2.36 (s, 6 H), 2.33 (s, 6 H), 1.5-0.2 (br, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.5 ($^4J_{CP}$ = 2 Hz), 159.9 ($^4J_{CP}$ = 2 Hz), 149.2 ($^1J_{CP}$ = 91 Hz), 148.0 ($^3J_{CP}$ = 13 Hz), 137.3 ($^3J_{CP}$ = 10 Hz), 136.6, 134.3 ($^2J_{CP}$ = 11 Hz), 133.8 ($^2J_{CP}$ = 10 Hz), 131.8 ($^3J_{CP}$ = 24 Hz), 131.8, 130.6 ($^3J_{CP}$ = 17 Hz), 128.4, 126.7, 126.5, 126.4, 125.1, 122.6, 122.0 ($^1J_{CP}$ = 65 Hz), 120.9 ($^1J_{CP}$ = 60 Hz), 119.4, 59.8, 59.7, 31.2, 28.8, 16.4,

16.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.8; ^{11}B NMR (128 MHz, $CDCl_3$) δ –38.3; IR (ATR) 3345, 2934, 2378, 1637, 1480, 1278, 1114, 917, 734 cm^{-1}; HRMS $(ESI)^+$ *m/z* calcd for $C_{33}H_{36}N_2O_2P$ $[M+H–BH_3]$ 523.2514, found 523.2494.



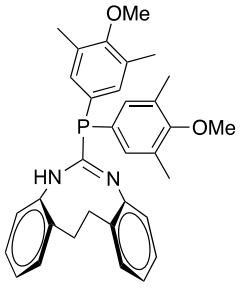
1-46

6-(Cyclohexylphenylphosphanyl)-12, 13-dihydrodibenzodiazonine borane (1-46).[31] Prepared according to general Procedure B from carbodiimide **1-41** (0.100 g, 0.454 mmol), phenylcyclohexyl phosphine borane (0.112 g, 0.545 mmol) and NaH (0.022 g, 0.55 mmol, 60% dispersion) in DMAc (2 mL). Purification by chromatography on SiO_2 (hexanes) to afforded phosphine borane **1-46** (0.134 g, 0.314 mmol, 69%) as a colorless solid that is an equilibrating mixture of rotomers/isomers in solution: Mp 164–166 ºC; IR (ATR) 3353, 2934, 2385, 1644, 1474, 1435, 1260, 726, 692 cm^{-1};^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18-8.09 (m, 2 H), 7.63-7.48 (m, 3 H), 7.28 (s, 0.7 H), 7.13 (s, 0.3 H), 6.93-6.74 (m, 4 H), 6.69 (d, 1 H, *J* = 7.6 Hz), 6.65-6.54 (m, 2 H), 6.49 (d, 1 H, *J* = 7.6 Hz), 3.20-3.09 (m, 0.5 H), 3.10 (dd, 1 H, *J* = 9.6 Hz, 2.4 Hz), 3.04-2.71 (m, 1.5 H), 2.69-2.60 (m, 1 H), 2.58-2.43 (m, 1.5 Hz), 2.30-2.15 (m, 1 H), 1.97-1.86 (m, 1 H), 1.80-1.65 (m, 3 H), 1.48-1.17 (m, 6 H), 1.1-0.4 (br, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1, 148.0, 147.4 ($^1J_{CP}$ = 57 Hz), 137.2, 137.1, 133.0, 132.9, 132.1, 130.7, 130.5, 130.4, 128.8, 128.7, 128.7, 128.6, 128.5, 127.1, 126.8, 126.5, 126.4, 126.3, 125.5, 124.9, 122.6, 119.9, 119.8, 33.5, 33.2, 33.1, 31.1, 30.7, 30.2, 28.4, 26.7, 26.5, 26.4, 25.9, 25.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.1, 25.3; ^{11}B NMR (128 MHz, $CDCl_3$) δ –44.3; HRMS $(ESI)^+$ *m/z* calcd for $C_{27}H_{33}N_2PB$ [M+H] 427.2474, found 427.2466.



1-47

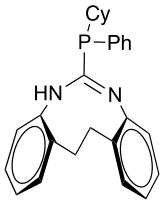
General Procedure C (Phosphine borane deprotection): 6-(Di-tolylphosphanyl)-12, 13-dihydrodibenzodiazonine (1-47).[31] A solution of phosphine borane **1-44** (0.071 g, 0.16 mmol) in toluene (2 mL) was treated under an Ar atmosphere with DABCO (0.025 g, 0.22 mmol) and stirred at 60 ºC for 90 min. After cooling to rt, the reaction mixture was purified by chromatography on SiO_2 (5% EtOAc/hexanes) to afford phosphine **1-47** (0.056 g, 0.13 mmol, 81%) as clear sticky oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72-7.48 (m, 4 H), 7.25-7.19 (m, 3 H), 6.88-6.76 (m, 3 H), 6.76-6.59 (m, 4 H), 6.54 (d, 2 H, J = 7.6 Hz), 3.38 (d, 2 H, J = 8.8 Hz), 2.83 (d, 2 H, J = 9.2 Hz), 2.38 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.5, 139.9, 134.3 (d, $^3J_{CP}$ = 19 Hz), 131.3 (d, $^3J_{CP}$ = 11 Hz), 130.4, 129.9, 129.8, 126.3, 30.5, 21.4; ^{31}P NMR (162 MHz, $CDCl_3$) δ –3.7; HRMS (ESI)$^+$ *m/z* calcd for $C_{29}H_{28}N_2P$ [M+H] 435.1990, found 435.1991.



1-48

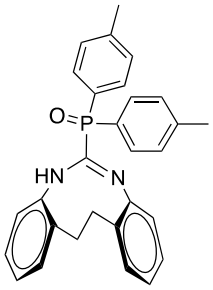
6-(Di-(3, 5-dimethyl-4-methoxy)phenylphosphanyl)-12, 13-dihydrodibenzo]diazonine (1-48).[31] Prepared according to General Procedure C from phosphine borane **1-45** (0.176 g, 0.328 mmol) and DABCO (0.147 g, 1.31 mmol) in toluene (2 mL). Purification by chromatography on SiO_2 (5% EtOAc/hexanes) afforded phosphine **1-48** (0.112 g, 0.214 mmol, 65%) as a sticky oil:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60-7.29 (br m, 4 H), 6.89-6.50 (br m, 8 H), 6.25-6.10 (br s, 1 H), 3.80 (s, 6 H), 3.65-3.15 (br m, 2 H), 3.00-2.68 (br m, 2 H), 2.35 (s, 12 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 156.7, 156.6, 135.2, 135.0, 131.7, 130.5, 129.5, 129.4, 126.3, 59.7, 31.4, 29.5, 16.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ –3.2; HRMS (ESI)$^{+}$ *m/z* calcd for $C_{33}H_{36}N_2O_2P$ [M+H] 523.2514, found 523.2494.



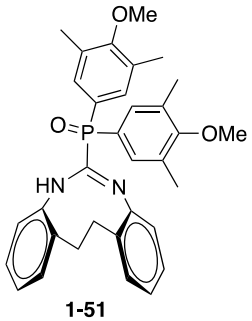
1-49

6-(Cyclohexylphenylphosphanyl)-12, 13-dihydrodibenzodiazonine (1-49).[31] Prepared according to General Procedure C from phosphine borane **1-46** (0.099 g, 0.23 mmol) and DABCO (0.104 g, 0.929 mmol) in toluene (2 mL). Purification by chromatography on SiO_2 (5% EtOAc/hexanes) afforded phosphine **1-49** (0.090 g, 0.22 mmol, 94%) as a colorless oil that is an equilibrating mixture of diastereomers in solution: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98-7.75 (m, 2 H), 7.51-7.38 (m, 3 H), 6.94-6.73 (m, 4 H), 6.74-6.63 (m, 2 H), 6.63-6.51 (m, 2 H), 6.51-6.43 (m, 2 H), 6.03-6.08 (s, 0.3 H), 3.52-3.23 (m, 1.5 H), 3.04-2.57 (m, 2.5 H), 2.49 (d, 1 H, J = 7.6 Hz), 2.39-2.24 (m, 1 H), 1.95-1.28 (m, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 149.5, 138.6, 136.4, 135.1, 135.0, 134.7, 134.6, 133.9, 133.8, 130.6, 130.4, 130.1, 128.8, 128.4, 126.6, 126.4, 126.1, 125.5, 125.1, 124.1, 121.7, 120.3, 119.6, 35.8, 34.8, 31.6, 31.1, 30.7, 30.2, 29.9, 29.8, 28.6, 28.2, 27.7, 27.6, 26.8, 26.5, 26.3, 26.1, 25.9; ^{31}P NMR (162 MHz, $CDCl_3$) δ 3.6, 2.5; HRMS (ESI)$^{+}$ *m/z* calcd for $C_{27}H_{30}N_2P$ [M+H] 413.2147, found 413.2144.



1-50

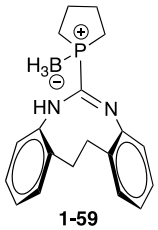
6-(Di-tolylphosphanyloxide)-12, 13-dihydrodibenzodiazonine (1-50). A solution of phosphine **1-47** (0.019 g, 0.044 mmol) in acetone (1 mL) was treated with hydrogen peroxide (0.05 mL, 0.04 mmol, 3% aq. soln) at rt. After stirring for 15 min, the reaction mixture was partitioned between water and EtOAc (10 mL each). The phases were separated, and the aqueous phase was re-extracted with EtOAc (10 mL). The combined organic phases were washed with water (15 mL), brine (15 mL), dried (Na_2SO_4) and concentrated to afford phosphine oxide **1-50** (0.017 g, 0.038 mmol, 86%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10-7.91 (m, 5 H), 7.33 (dd, 4 H, *J* = 7.6 Hz, 2.4 Hz), 6.91-6.72 (m, 5 H), 6.67-6.54 (m, 2 H), 6.42 (d, 1 H, *J* = 7.6 Hz), 3.16-3.04 (m, 1 H), 3.02-2.90 (m, 1 H), 2.81-2.65 (m, 2 H), 2.43 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 149.1, 147.7, 147.5, 142.9, 142.9, 142.8, 142.8, 137.0, 137.0, 136.9, 132.3, 132.2, 132.1, 132.0, 130.7, 130.3, 129.3, 129.3, 129.2, 129.2, 128.6, 128.3, 128.1, 127.2, 127.0, 126.6, 126.6, 126.5, 125.8, 122.5, 120.0, 30.9, 29.4, 21.7; ^{31}P NMR (162 MHz, $CDCl_3$) δ 18.2.



1-51

6-(Di-(3, 5-dimethyl-4-methoxy)phenylphosphanyloxide)-12, 13-dihydrodibenzo-

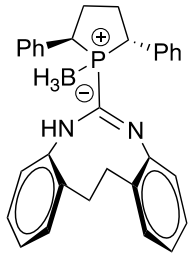
diazonine (1-51).[31] A solution of phosphine **1-48** (0.094 g, 0.16 mmol) in acetone (1 mL) was treated with hydrogen peroxide (0.2 mL, 0.2 mmol, 3% aq. soln) at rt. After stirring for 15 min, the reaction mixture was partitioned between water and EtOAc (20 mL each). The phases were separated, and the aqueous phase was extracted with EtOAc (20 mL). The combined organic phases were washed with water (25 mL) and brine (25 mL), then were dried (Na_2SO_4) and concentrated to afford phosphine oxide **1-51** (0.088 g, 0.16 mmol, 91%) as a colorless crystalline solid: Mp 236–238 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, 1 H, J = 2.8 Hz), 7.81 (d, 2 H, J = 12.0 Hz), 7.76 (d, 2 H, J = 12.0 Hz), 6.89-6.73 (m, 5 H), 6.66-6.56 (m, 2 H), 6.43 (d, 1 H, J = 7.6 Hz), 3.79 (s, 3 H), 3.78 (s, 3 H), 3.21-3.09 (m, 1 H), 2.98-2.87 (m, 1 H), 2.81-2.66 (m, 2 H), 2.34 (s, 12 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 160.6, 160.5, 160.5, 150.6, 149.1, 147.8, 147.6, 137.1, 137.0, 136.7, 133.1, 133.0, 132.8, 132.6, 131.6, 131.5, 131.5, 131.4, 130.7, 130.4, 128.7, 126.7, 126.5, 126.5, 126.1, 125.9, 125.6, 125.0, 124.9, 122.6, 119.9, 59.7, 59.7, 31.0, 29.0, 16.3, 16.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 18.5; IR (ATR) 3202, 2934, 1627, 1480, 1286, 1215, 1163, 1115, 994, 758 cm^{-1}; HRMS (ESI)$^+$ *m/z* calcd for $C_{33}H_{36}N_2PO_3$ [M+H] 539.2458, found 539.2443.



1-59

6-(Phospholan-1-yl)-12,13-dihydro-5H-dibenzo[1,3]diazonine borane (1-59). Prepared according to General Procedure B from phospholane borane **1-54** (0.080 g, 0.78 mmol), carbodiimide **1-41** (0.207 g, 0.942 mmol) and sodium hydride (0.037 g, 0.94 mmol, 60% dispersion) in DMAc (3 mL). Purification by was chromatography on SiO_2 (hexanes to 15% EtOAc/hexanes) afforded **1-59** (0.153 g, 0.475 mmol, 35%) as a colorless solid: Mp 118–121 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (s, 1 H), 6.92-6.75 (m, 5 H), 6.64 (d, 1 H, J = 6.4 Hz), 6.60 (t,

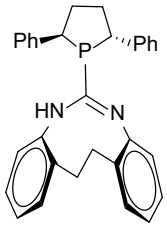
1 H, J = 7.2 Hz), 6.42 (d, 1 H, J = 7.6 Hz), 3.26 (td, 1 H, J = 10.0 Hz, 2.8 Hz), 3.20-3.10 (m, 1 H), 2.95 (t, 1 H, J = 10.4 Hz, 2.8 Hz), 2.83 (ddd, 1 H, J = 12.8 Hz, 10.0 Hz, 6.4 Hz), 2.57 (ddd, 1 H, J = 14.4 Hz, 6.8 Hz, 6.8 Hz), 2.51-2.40 (m, 1 H), 2.21-1.97 (m, 4 H), 0.83 (q, 3 H, $^1J_{BH}$ = 82 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.5 ($^1J_{CP}$ = 78 Hz), 147.7 ($^3J_{CP}$ = 12 Hz), 137.2, 137.1, 136.6, 130.7, 130.4, 128.1, 126.8, 126.7, 126.6, 125.5, 122.6, 119.9, 30.8, 29.8, 27.6, 27.5 ($^3J_{CP}$ = 8 Hz), 29.9 ($^1J_{CP}$ = 36 Hz), 26.1 ($^1J_{CP}$ = 36 Hz), 24.2 ($^1J_{CP}$ = 38 Hz); ^{31}P NMR (161 MHz, $CDCl_3$) δ 40.1; ^{11}B NMR (128 MHz, $CDCl_3$) δ –39; IR (ATR) 3358, 2951, 2365, 1629, 1474, 1053, 751 cm^{-1}; MS (ESI)$^+$ m/z 321, 309, 221; HRMS (ESI)$^+$ m/z calcd for $C_{19}H_{22}N_2P$ [M+H–BH_3] 309.1521, found 309.1514.



1-60

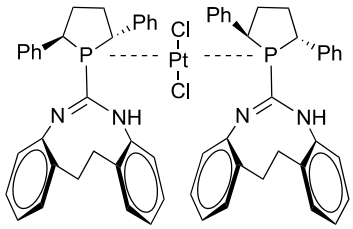
6-(2,5-Diphenylphospholan-1-yl)-12,13-dihydro-5H-dibenzo[1,3]diazonine borane (1-60). Prepared according to General Procedure B from phosphine borane (*S, S*)-**1-58**[27] (0.119 g, 0.468 mmol), carbodiimide **1-41** (0.086 g, 0.39 mmol), and sodium hydride (0.019 g, 0.47 mmol, 60%) in DMAc (2 mL). Purification by chromatography on SiO_2 (5% EtOAc/hexane) afforded **1-60** (0.113 g, 0.238 mmol, 61%) as a colorless solid: $[\alpha]_D$ +22 (c = 0.5, CH_2Cl_2); Mp 184–188 ºC; IR (ATR) 3340, 3026, 3058, 2951, 2378, 1629, 1485, 907, 727 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67-7.53 (m, 2 H), 7.52-7.21 (m, 8 H), 6.89-6.73 (m, 2 H), 6.71-6.48 (m, 4 H), 6.34 (d, 0.5 H, J = 7.6 Hz), 5.56 (d, 0.5 H, J = 7.2 Hz), 4.89-4.73 (m, 1 H), 3.96-3.75 (m, 1 H), 3.19 (app d, 1 H, J = 8.4 Hz), 2.91-2.73 (m, 1 H), 2.74-2.15 (m, 6 H), 1.35-1.15 (m, 2 H), 1.1-0.1(br q, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.9 ($^2J_{CP}$ = 12 Hz), 147.5 ($^2J_{CP}$ = 12 Hz), 146.8 ($^1J_{CP}$ = 72 Hz), 146.3 ($^1J_{CP}$

= 74 Hz), 138.0, 137.1, 137.0, 136.9, 136.7, 136.5, 136.4, 135.8 (J_{CP} = 5 Hz), 136.7 (J_{CP} = 5 Hz), 130.4 ($^1J_{CP}$ = 73 Hz), 130.5, 130.4, 130.0, 129.0, 128.8, 128.7, 128.61, 128.59, 128.54, 128.49, 128.3 (J_{CP} = 4 Hz), 128.0 (J_{CP} = 4 Hz), 127.6, 127.5, 127.3, 127.1, 126.7, 126.6, 126.5, 126.4, 126.3, 125.4, 122.8, 122.5, 120.5, 120.3, 120.3, 48.0 ($^1J_{CP}$ = 29 Hz), 47.5 ($^1J_{CP}$ = 29 Hz), 45.6 ($^1J_{CP}$ = 32 Hz), 43.4 ($^1J_{CP}$ = 32 Hz), 38.8, 32.8 ($^2J_{CP}$ = 5 Hz), 32.5 ($^2J_{CP}$ = 6 Hz), 30.9, 30.8, 30.5 ($^2J_{CP}$ = 6 Hz), 29.9, 29.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ 51.7; HRMS (ESI)$^+$ *m*/*z* calcd for $C_{31}H_{33}N_2PB$ [M+H] 475.2469, found 475.2473.



1-61

6-(2,5-Diphenylphospholan-1-yl)-12,13-dihydro-5H-dibenzo[1,3]diazonine (1-61). Prepared according to General Procedure C from phosphine borane **1-60** (0.050 g, 0.11 mmol) and DABCO (0.047 g, 0.42 mmol) in toluene (1.5 mL). Purification by chromatography on SiO_2 (5% EtOAc/hexane) afforded phosphine **1-61** (0.037 g, 0.080 mmol, 76%) as a colorless oil: ^{31}P NMR (202 MHz, $CDCl_3$) δ 28.0.



1-62

Bis[6-(2,5-Diphenylphospholan-1-yl)-12,13-dihydro-5H-dibenzo[1,3]diazonine] platinum chloride complex (1-62). A solution of phosphine **1-61** (0.169 g, 0.38 mmol) in CH_2Cl_2 (3 mL) was treated with $PtCl_2$ (0.102 g, 0.380 mmol). The vial was sealed under Ar and stirred at rt for 1

h, at which point NMR indicated formation of a complex. The heterogeneous reaction mixture was filtered through a syringe filter, and the eluent was placed in a vapor diffusion chamber with methyl *t*-butyl ether (30 mL). After standing for 9 days, yellow rectangular crystals Pt complex **1-62** formed: ^{31}P NMR (202 MHz, $CDCl_3$) δ 52.9 (J_{PtP} = 2532 Hz). An X-ray crystal structure was obtained for this complex.

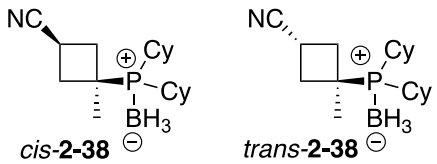
5.3 CHAPTER 2 EXPERIMENTAL PART

2-37

3-Methylbicyclo[1.1.0]butane-1-carbonitrile (2-37).[97] A mixture of 3-methylenecyclobutanecarbonitrile **2-35** (10.0 g, 0.107 mol) and 48% HBr (21 mL, 0.376 mol, 3.5 eq) was vigorously stirred at room temperature for 24 h. The reaction mixture was partitioned between water and ether (100 mL), the phases were separated, and the aqueous layer was extracted with ether (2 x 75 mL). The combined ethereal solution was washed with water (100 mL) then sat. aq. $NaHCO_3$ (100 mL). The organic layer was dried ($MgSO_4$), filtered, and concentrated to afford the bromocyclobutane **2-36** (13.44 g, 77.20 mmol, 72%) as a colorless liquid with a *dr* of 1.7:1. Characteristic signal for the major isomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.95 (s, 3 H). Characteristic signal for the minor isomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.89 (s, 3 H).

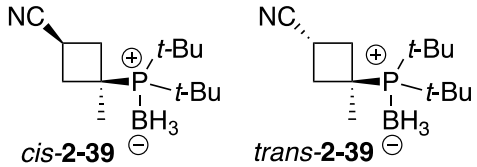
A solution of bromide **2-36** (13.43 g, 77.17 mmol) in THF (70 mL) in a dry 3-necked 250-mL round bottom flask fitted with a stopper, septum, and N_2 inlet was treated with NaH (3.06 g, 77.2 mmol) in portions over 5 min. The flask was stirred at 35 °C for 12 h, then at reflux for 5 h. After cooling, the grey/brown reaction mixture was quenched with sat. aq. NH_4Cl (25 mL). The

reaction mixture was then partitioned between diethyl ether (100 mL) and water (100 mL), the layers were separated, and the aqueous layer was re-extracted with ether (75 mL). The combined organic layers were washed with water (100 mL) and brine (100 mL), dried (Na_2SO_4) and concentrated to afford a yellow-tinted cloudy liquid. The crude material was purified by bulb-to-bulb distillation (bath temp 75 °C, 2 mmHg)) to afford bicyclobutane **2-37** (3.54 g, 38.0 mmol, 49%) as a colorless liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.97 (s, 2 H), 1.71 (s, 3 H), 1.28 (s, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 120.2, 40.5, 37.0, 23.1, 12.7, -3.4. SAFETY NOTE: The distillation should be conducted using the strongest accessible vacuum source and the minimum possible temperature. Although we encountered no difficulty conducting this distillation, differential scanning calorimetry analysis suggests that it is unsafe to heat this material above ~100 °C.



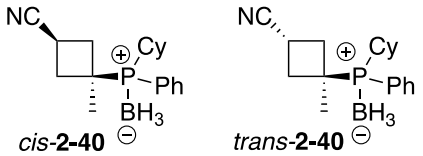
General Procedure D (Bicyclo[1.1.0]butane hydrophosphination): 3-(Dicyclohexylphosphanyl)-3-methylcyclobutane-1-carbonitrile borane (2-38).[97] A solution of bicyclobutane **2-37** (0.472 g, 5.07 mmol, 1.2 eq) and dicyclohexyl phosphine borane (0.896 g, 4.22 mmol) in DMAc (20 mL) was sparged with Ar for 10 min, cooled to 0 °C, and treated with NaH (0.203 g, 5.07 mmol, 60% in oil) in one portion. The reaction mixture was stirred for 10 min at 0 °C, then the bath was removed and the solution was warmed to rt over 2 h. The orange/brown reaction mixture was quenched with sat. aq. NH_4Cl (5 mL), and the material was partitioned between water (30 mL) and diethyl ether (30 mL). The aqueous layer was extracted with ether (30 mL). The combined extracts were washed with water (40 mL) and brine (40 mL), then were dried (Na_2SO_4) and concentrated. The crude residue was purified by chromatography on SiO_2 (15%

EtOAc/hexane) to afford *cis*-**2-38** (0.634 g, 2.08 mmol, 49%) and *trans*-**2-38** (0.197 g, 0.645 g, 15%), both as colorless solids. ***cis*-2-38**: Mp 193–195 °C; IR (ATR) 2933, 2386, 1450, 1070, 840 cm^{-1}; MS (ESI^+) *m/z* 306, 245, 215, 172; ^1H NMR (400 MHz, $CDCl_3$) δ 3.37 (pent, 1 H, J = 9.6 Hz), 3.22-3.09 (m, 2 H), 2.08-2.01 (m, 2 H), 1.91-1.77 (m, 8 H), 1.77-1.67 (br s, 2 H), 1.66-1.58 (m, 2 H), 1.55 (d, 3 H, $^3J_{PH}$ = 9.2 Hz), 1.48-1.31 (m, 4 H), 1.30-1.15 (m, 6 H), 0.9-0.1 (br q, 3 H); ^{31}P NMR (162 MHz, $CDCl_3$) δ 35.8; ^{13}C NMR (125 MHz, $CDCl_3$) δ 120.5 ($^4J_{CP}$ = 2.5 Hz), 36.3, 32.7 ($^1J_{CP}$ = 26 Hz), 31.5 ($^1J_{CP}$ = 29 Hz), 27.69, 27.67, 27.66, 27.65, 27.2, 27.11, 27.08, 27.0, 25.95, 25.94, 22.1, 22.1, 19.7 (J_{CP} = 17 Hz); HRMS (ESI^+) *m/z* calcd for $C_{18}H_{34}BNP$ [M+H] 306.2516, found 306.2506. ***trans*-2-38**: Mp 165–168 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 3.32-3.23 (m, 1 H), 3.11 (dd, 2 H, J = 10.8 Hz, 2.4 Hz), 2.16-2.07 (m, 2 H), 1.88-1.75 (m, 8 H), 1.75-1.61 (m, 2 H), 1.67 (d, 3 H, $^3J_{PH}$ = 9.6 Hz), 1.47-1.32 (m, 4 H), 1.30-1.14 (m, 8 H), 0.7-0.0 (br q, 3 H); ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.3; ^{13}C NMR (100 MHz, $CDCl_3$) δ 122.9 ($^4J_{CP}$ = 1.0 Hz), 36.4, 33.0 ($^1J_{CP}$ = 26 Hz), 31.3 ($^1J_{CP}$ = 29 Hz), 27.9, 27.1, 27.03, 26.98, 26.9, 25.8, 25.1 (J_{CP} = 3 Hz), 17.8 (J_{CP} = 9 Hz); IR (ATR) 2933, 2390, 1442, 1072, 734 cm^{-1}; HRMS (ESI^+) *m/z* calcd for $C_{18}H_{34}BNP$ [M+H] 306.2516, found 306.2502.



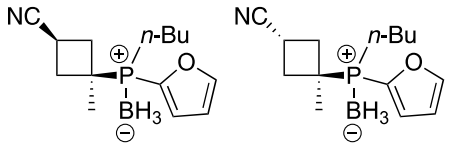
3-(Di-*t*-butylphosphanyl)-3-methylcyclobutane-1-carbonitrile borane (2-39).[97] Prepared according to General Procedure D from di-*t*-butyl phosphine borane (0.363 g, 2.27 mmol), bicyclobutane **2-37** (0.264 g, 2.84 mmol), and NaH (0.100 g, 2.49 mmol, 60% dispersion in oil) in DMAc (8 mL). Purification by chromatography on SiO_2 (10-30% EtOAc in hexanes) afforded *cis*-**2-39** (0.327 g, 1.29 mmol, 57%) and *trans*-**2-39** (0.147 g, 0.58 mmol, 26%), both as colorless

solids. *cis*-**2-39**: Mp 125–127 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.47-3.31 (m, 3 H), 2.14-2.02 (m, 2 H), 1.83 (d, 3 H, $^{3}J_{PH}$ = 8.8 Hz), 1.33 (s, 9 H), 1.30 (s, 9 H), 0.61 (br q, 3 H, $^{1}J_{BH}$ = 98 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 120.6 ($^{4}J_{CP}$ = 3 Hz), 38.1, 35.8 ($^{1}J_{CP}$ = 20 Hz), 35.1 ($^{1}J_{CP}$ = 23 Hz), 29.6, 23.7 (J_{CP} = 4 Hz), 20.1 (J_{CP} = 18 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 54.7; IR (ATR) 2974, 2378, 2235, 1480, 1072 cm^{-1}; MS (ESI^{+}) *m/z* 240, 223, 208, 196, 162, 142, 114; HRMS (ESI^{+}) *m/z* calcd for $C_{14}H_{30}BNP$ [M+H] 254.2203, found 254.2197. *trans*-**2-39**: Mp 53–56 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.48 (app q, 2 H, *J* = 12.4 Hz), 3.27-3.17 (m, 1 H), 2.09 (d, 3 H, $^{3}J_{PH}$ = 9.2), 2.13-2.05 (m, 2 H), 1.35 (s, 9 H), 1.32 (s, 9 H), 0.53 (br q, 3 H, $^{1}J_{BH}$ = 98 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 123.5, 37.5, 36.9 ($^{1}J_{CP}$ = 20 Hz), 35.1 ($^{1}J_{CP}$ = 23 Hz), 29.6, 26.5 (J_{CP} = 4 Hz), 19.3 (J_{CP} = 15 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 53.6.



3-(Cyclohexyl(phenyl)phosphanyl)-3-methylcyclobutane-1-carbonitrile borane (2-40).[97] Prepared according to General Procedure D from racemic phenyl cyclohexyl phosphine borane (0.275 g, 1.33 mmol), bicyclobutane **2-37** (0.136 g, 1.47 mmol, 1.20 eq), and NaH (0.059 g, 1.5 mmol, 1.2 eq) in DMAc (8 mL). Purification by chromatography on SiO_2 (15-40% EtOAc/hexane) afforded *cis*-**2-40** (0.189 g, 0.632 mmol, 47%) as a colorless solid and *trans*-**2-40** (0.092 g, 0.31 mmol, 23%) as a colorless oil. *cis*-**2-40**: Mp 137–139 °C; IR (ATR) 2934, 2397, 1448, 1072, 751 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (td, 2 H, *J* = 8.4, 1.6 Hz), 7.55-7.42 (m, 3 H), 3.30 (pent, 1 H, *J* = 9.2 Hz), 3.13 (ddd, 1 H, *J* = 12.8 Hz, 10.0 Hz, 7.6 Hz), 2.90 (ddd, 1 H, *J* = 13.6 Hz, 11.6 Hz, 9.6 Hz), 2.41-2.28 (m, 1 H), 2.10 (ddd, 1 H, *J* = 16.0 Hz, 4.4 Hz, 3.2 Hz), 1.93-1.83 (m, 1 H), 1.79-1.55 (m, 5 H), 1.51-1.18 (m, 5 H), 1.42 (d, 3 H, $^{3}J_{PH}$ = 11.2 Hz), 1.1-0.3 (br m, 3 H); ^{13}C

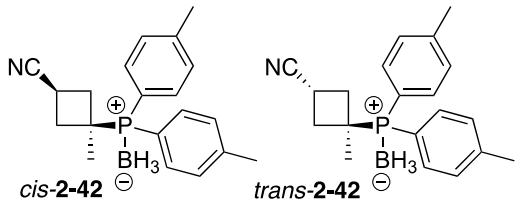
NMR (100 MHz, $CDCl_3$) δ 132.9 (J_{CP} = 7 Hz), 131.5 (J_{CP} = 3 Hz), 128.8, 128.7, 125.0, 124.5, 120.7, 34.8, 34.2, 32.2 ($^1J_{CP}$ = 30 Hz), 30.3 ($^1J_{CP}$ = 33 Hz), 26.6, 26.5, 26.4, 26.3, 25.7, 20.9, 18.3 ($^2J_{CP}$ = 18 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.0; MS (ESI^+) *m/z* 300, 286, 231, 209, 173, 150; HRMS (ESI^+) *m/z* calcd for $C_{18}H_{28}BNP$ [M+H], 300.2047, found 300.2060. ***trans*-2-40**: IR (ATR) 2939, 2858, 2384, 2239, 1437, 1109, 1066, 742 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (td, 2 H, *J* = 8.0 Hz, 1.2 Hz), 7.54-7.41 (m, 3 H), 3.32 (dddd, 1 H, *J* = 9.6 Hz, 9.6 Hz, 7.2 Hz, 7.2 Hz), 3.15 (app q, 1 H, *J* = 12.0 Hz), 2.71 (td, 1 H, *J* = 13.2 Hz, 11.2 Hz), 2.42-2.29 (m, 1 H), 2.23 (ddd, 1 H, *J* = 12.4 Hz, 6.8 Hz, 6.4 Hz), 1.91-1.78 (m, 2 H), 1.77-1.62 (m, 3 H), 1.53 (d, 3 H, $^3J_{PH}$ = 10.4 Hz), 1.49-1.38 (m, 1 H), 1.38-1.15 (m, 5 H), 1.2-0.2 (br m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.1 (J_{CP} = 8 Hz), 131.7 (J_{CP} = 2 Hz), 128.8, 128.7, 124.7, 124.2, 122.6, 35.7 (J_{CP} = 3 Hz), 34.9, 32.3 ($^1J_{CP}$ = 28 Hz), 30.6 ($^1J_{CP}$ = 33 Hz), 26.6 (J_{CP} = 5 Hz), 26.5, 26.4, 26.3, 26.2, 25.6, 24.0 (J_{CP} = 3 Hz), 17.0 (J_{CP} = 7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.2; IR (ATR) 2939, 2858, 2384, 2239, 1437, 1109, 1066, 742 cm^{-1}



cis-**2-41** *trans*-**2-41**

3-(*n*-Butyl(furan-2-yl)phosphanyl)-3-methylcyclobutane-1-carbonitrile borane (2-41).[97] Prepared according to General Procedure D from racemic furyl butyl phosphine borane (0.261 g, 1.54 mmol), bicyclobutane **2-37** (0.172 g, 1.8 mmol, 1.20 eq), and NaH (0.074 g, 1.8 mmol, 1.2 eq, 60% in oil) in DMAc (8 mL). Purification by chromatography on SiO_2 (15-40% EtOAc/hexane) afforded *cis*-**2-41** (0.115 g, 0.437 mmol, 28%) and *trans*-**2-41** (0.052 g, 0.20 mmol, 13%), both as colorless oils. ***cis*-2-41**: IR (ATR) 2956, 2933, 2386, 2240, 1456, 1128, 1072, 757 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (s, 1 H), 7.18-7.15 (m, 1 H), 6.53-6.50 (m, 1 H), 3.28

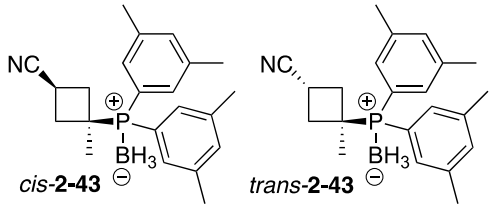
(pent, 1 H, J = 9.2 Hz), 2.88 (td, 1 H, 13.2 Hz, 9.2 Hz), 2.69 (td, 1 H, 13.6 Hz, 9.2 Hz), 2.19-1.98 (m, 3 H), 1.77-1.66 (m, 1 H), 1.60-1.47 (m, 1 H), 1.44 (d, 3 H, $^3J_{PH}$ = 14.4 Hz), 1.35 (sextet, 2 H, J = 7.2 Hz), 1.28-1.13 (m, 1 H), 0.87 (t, 3 H, J = 7.2 Hz), 1.1-0.0 (br q, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.1 ($^3J_{CP}$ = 3 Hz), 143.2 ($^1J_{CP}$ = 61 Hz), 125.8 ($^2J_{CP}$ = 18 Hz), 121.1 ($^4J_{CP}$ = 2 Hz), 111.3 ($^3J_{CP}$ = 8 Hz), 34.1, 33.9, 32.7 ($^1J_{CP}$ = 35 Hz), 25.0, 24.1 ($^2J_{CP}$ = 14 Hz), 22.1, ($^3J_{CP}$ = 3 Hz), 19.0 ($^1J_{CP}$ = 36 Hz), 17.1 ($^2J_{CP}$ = 16 Hz), 13.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 18.6; MS (ESI^+) *m/z* 264, 250, 228, 200, 184, 154, 110; HRMS (ESI^+) *m/z* calcd for $C_{14}H_{24}BNOP$ [M+H] 264.1683, found 264.1685. ***trans*-2-41**: IR (ATR) 2958, 2380, 2238, 1555, 1458, 1212, 1128, 1071, 1049, 1007, 909, 732 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (s, 1 H), 7.16 (d, 1 H, J = 1.2 Hz), 6.51 (t, 1 H, J = 1.6 Hz), 2.98 (pent, 1 H, J = 7.6 Hz), 2.89-2.77 (m, 2 H), 2.32-2.12 (m, 2 H), 2.08 (dd, 1 H, J = 14.8, 4.0 Hz), 1.76-1.63 (m, 1 H), 1.58-1.44 (m, 1 H), 1.53 (d, 3 H, $^3J_{PH}$ = 12.0 Hz), 1.35 (pent, 2 H, J = 7.2 Hz), 1.29-1.18 (m, 1 H), 0.86 (t, 3 H, J = 7.2 Hz), 1.1-0.1 (br q, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9 ($^3J_{CP}$ = 3 Hz), 143.2 ($^1J_{CP}$ = 61 Hz), 125.5 ($^2J_{CP}$ = 18 Hz), 122.1, 111.4 ($^3J_{CP}$ = 8 Hz), 35.0, 34.9 ($^3J_{CP}$ = 3 Hz), 33.2 ($^1J_{CP}$ = 33 Hz), 25.0, 24.1 ($^2J_{CP}$ = 13 Hz), 18.8 ($^1J_{CP}$ = 36 Hz), 16.2 ($^3J_{CP}$ = 5 Hz), 13.6; ^{31}P NMR (202 MHz, $CDCl_3$) δ 17.6.



cis-**2-42** *trans*-**2-42**

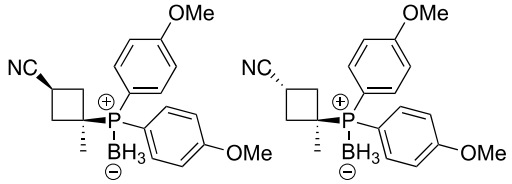
3-(Di-*p*-tolylphosphanyl)-3-methylcyclobutane-1-carbonitrile borane (2-42).[97] Prepared according to General Procedure D from di-*p*-tolylphosphine borane (0.500 g, 2.19 mmol), bicyclobutane **2-37** (0.245 g, 2.63 mmol), and NaH (0.105 g, 2.63 mmol) in DMAc (10 mL). Purification by chromatography on SiO_2 (20-40% EtOAc/hexane) afforded *cis*-**2-42** (0.341 g, 1.06 mmol, 48%) as a colorless solid and *trans*-**2-42** (0.199 g, 0.620 mmol, 28%) as a colorless foam.

cis-**2-42**: Mp 162–163 °C; IR (ATR) 2392, 1429, 1066, 807 cm^{-1};^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, 2 H, *J* = 8.4 Hz), 7.51 (d, 2 H, *J* = 8.0 Hz), 7.29 (d, 2 H, *J* = 8.0 Hz), 7.28 (d, 2 H, *J* = 8.0 Hz), 3.31 (pent, 1 H, *J* = 9.2 Hz), 2.88-2.78 (m, 2 H), 2.40 (s, 6 H), 2.34-2.26 (m, 2 H), 1.54 (d, 3 H, $^3J_{PH}$ = 14.0 Hz), 1.2-0.5 (br q, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.2 (J_{CP} = 2 Hz), 133.4 (J_{CP} = 7 Hz), 129.8 (J_{CP} = 8 Hz), 123.3, 122.8, 120.5 ($^4J_{CP}$ = 2 Hz), 34.7, 33.4 ($^1J_{CP}$ = 34 Hz), 22.1 (J_{CP} = 5 Hz), 21.5, 18.2 ($^2J_{CP}$ = 17 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 27.7; MS (ESI^+) *m/z* 240, 219, 167, 139, 122; HRMS (ESI^+) *m/z* calcd for $C_{20}H_{26}BNP$ [M+H] 322.1890, found 322.1879. *trans*-**2-42**: IR (ATR) 2956, 2386, 1498, 1066, 814 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, 2 H, *J* = 8.4 Hz), 7.49 (d, 2 H, *J* = 8.0 Hz), 7.28 (d, 2 H, *J* = 8.0 Hz), 7.27 (d, 2 H, *J* = 8.0 Hz), 3.07 (ddd, 2 H, *J* = 13.6 Hz, 13.6 Hz, 10.0 Hz), 2.80 (ddd, 1 H, *J* = 17.0 Hz, 9.6 Hz, 7.6 Hz), 2.46-2.36 (m, 2 H), 2.39 (s, 6 H), 1.60 (d, 3 H, $^3J_{PH}$ = 12.8 Hz), 1.4-0.5 (br q, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.10, 142.08, 133.2, 133.1, 129.8, 129.7, 123.6, 123.2, 122.1 ($^4J_{CP}$ = 0.5 Hz), 35.7, 33.2 ($^1J_{CP}$ = 31 Hz), 25.7 (J_{CP} = 1.5 Hz), 21.5 (J_{CP} = 1.0 Hz), 16.9 ($^2J_{CP}$ = 6 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 28.2.



3-(Bis(3,5-dimethylphenyl)phosphanyl)-3-methylcyclobutane-1-carbonitrile borane (2-43). Prepared according to General Procedure D from di-*m*-xylyl phosphine borane (5.00 g, 19.5 mmol), bicyclobutane **2-37** (3.1 mL, 29 mmol), and sodium hydride (0.780 g, 19.5 mmol, 60% dispersion) in DMAc (100 mL). Purification by chromatography on SiO_2 (10-15-20-25% EtOAc in hexane) afforded *cis*-**2-43** (3.24 g, 9.28 mmol, 48%) and *trans*-**2-43** (1.66 g, 4.76 mmol, 24%), both as colorless solids: *cis*-**2-43**: Mp 162–165 °C; IR (ATR) 2932, 2390, 1448, 1128, 1066, 692

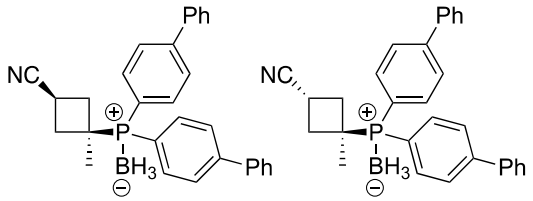
cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (s, 2 H), 7.21 (s, 2 H), 7.16 (s, 2 H), 3.31 (pent, 1 H, J = 9.5 Hz), 2.85 (td, 2 H, J = 10.0 Hz, 2.5 Hz), 2.35 (s, 12 H), 2.24-2.37 (m, 2 H), 1.53 (d, 3 H, $^{3}J_{PH}$ = 14.5 Hz), 1.2-0.5 (br q, 3 H); ^{31}P NMR (202 MHz, $CDCl_3$) δ 29.0; ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.1 (J_{CP} = 10 Hz), 137.8, 133.4 (J_{CP} = 8 Hz), 131.6 (J_{CP} = 8 Hz), 129.0 (J_{CP} = 4 Hz), 128.7, 127.6, 127.4, 125.4 ($^{1}J_{CP}$ = 53 Hz), 120.2, 43.8 ($^{3}J_{CP}$ = 25 Hz), 36.9, 35.8, 21.4, 19.2 ($^{3}J_{CP}$ = 19 Hz), 13.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.6; MS (ESI^{+}) *m/z* 350, 259, 212, 155; HRMS (ESI^{+}) *m/z* calcd for $C_{22}H_{30}BNP$ [M+H] 350.2203, found 350.2190. ***trans*-2-43**: Mp 130–134 °C; IR (ATR) 2937, 2386, 1450, 1128, 852, 692 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 (s, 2 H), 7.17 (s, 2 H), 7.14 (s, 2 H), 3.08 (td, 2 H, J = 13.5 Hz, 10.0 Hz), 2.83-2.75 (m, 1 H), 2.46-2.37 (m, 2 H), 2.33 (s, 12 H), 1.62 (d, 3 H, $^{3}J_{PH}$ = 13.0 Hz), 1.4-0.5 (br q, 3 H); ^{31}P NMR (202 MHz, $CDCl_3$) δ 26.8; ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.6, 138.5, 133.4, 133.4, 130.8, 130.7, 126.7, 126.3, 122.2 ($^{4}J_{CP}$ = 1 Hz), 35.8, 33.1 ($^{1}J_{CP}$ = 31 Hz), 25.8 (J_{CP} = 1 Hz), 21.4, 21.4, 16.9 (J_{CP} = 6 Hz).



cis-**2-44** *trans*-**2-44**

(3-(Bis(4-methoxyphenyl)phosphanyl)-3-methylcyclobutane-1-carbonitrile borane (2-44).[97] Prepared according to General Procedure D from di-*p*-methoxy phosphine borane (0.222 g, 0.854 mmol), and bicyclobutane **2-37** (0.254 g, 2.73 mmol) and NaH (0.038 g, 0.94 mmol) in DMAc (6 mL). Purification by chromatography on SiO_2 (10-30% EtOAc/hexane) afforded *cis*-**2-44** (0.130 g, 0.368 mmol, 43%) as a colorless foam and *trans*-**2-44** (0.048 g, 0.14 mmol, 16%) as a colorless oil. ***cis*-2-44**: IR (ATR) 2394, 2385, 1600, 1499, 1245, 1109, 1021, 798 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (t, 4 H, J = 9.2 Hz), 6.99 (dd, 4 H, J = 8.8 Hz, 1.6 Hz), 3.84 (s, 6 H), 3.31 (pent, 1 H, J = 9.2 Hz), 2.79 (qd, 2 H, J = 10.0 Hz, 2.0 Hz), 2.34-2.24 (m, 2 H), 1.50 (d, 3 H, $^{3}J_{PH}$ = 14.4

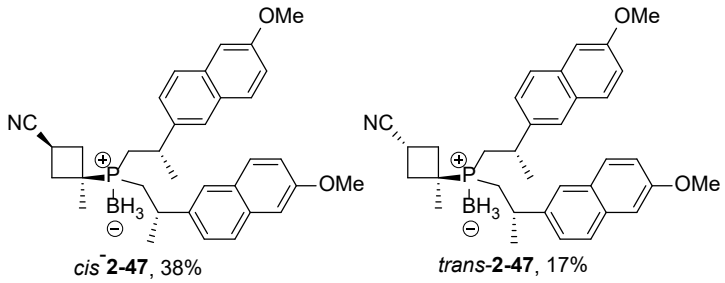
Hz), 1.2-0.3 (br m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.23, 162.21, 135.1, 135.0, 120.6 ($^4J_{CP}$ = 2 Hz), 117.6, 117.0, 114.7, 114.6, 55.4, 34.6, 33.6 ($^1J_{CP}$ = 34 Hz), 22.1 (J_{CP} = 5 Hz), 18.2 (J_{CP} = 17 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.2; MS (ESI^+) *m/z* 318, 316, 259, 247; HRMS (ESI^+) *m/z* calcd for $C_{20}H_{26}BNO_2P$ [M+H] 354.1789, found 354.1793. <u>*trans*-**2-44**</u>: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (tt, 4 H, *J* = 9.2 Hz, 2.0 Hz), 6.96 (dd, 4 H, *J* = 8.8 Hz, 1.6 Hz), 3.84 (s, 6 H), 3.04 (td, 2 H, 13.6 Hz, 10.0 Hz), 2.74 (ddd, 1 H, *J* = 17.6 Hz, 9.6 Hz, 7.6 Hz), 2.39 (td, 2 H, *J* = 13.2 Hz, 7.6 Hz), 1.59 (d, 3 H, $^3J_{PH}$ = 12.8 Hz), 1.4-0.5 (br m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.09, 162.07, 134.8, 134.7, 122.1, 117.8, 117.2, 114.6, 114.5, 55.3, 35.6, 33.4 ($^1J_{CP}$ = 32 Hz), 25.7 (J_{CP} = 2 Hz), 16.8 (J_{CP} = 6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.3; IR (ATR) 2940, 2379, 2237, 1902, 1594, 1501, 1289, 1253, 1180, 1061, 1024, 801 cm^{-1}



cis-**2-45** *trans*-**2-45**

3-(Di([1,1'-biphenyl]-4-yl)phosphanyl)-3-methylcyclobutane-1-carbonitrile borane (2-45).[97] Prepared according to General Procedure D from biphenylphosphine borane (0.300 g, 0.850 mmol), bicyclobutane **2-37** (0.095 g, 1.0 mmol), NaH (0.036 g, 0.89 mmol) in DMAc (4 mL). Purification by chromatography on SiO_2 (15-30% EtOAc/hexane) afforded *cis*-**2-45** (0.158 g, 0.35 mmol, 42%) and *trans*-**2-45** (0.083 g, 0.186 mmol, 22%), both as sticky waxes. <u>*cis*-**2-45**</u>: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79-7.70 (m, 8 H), 7.64-7.59 (m, 4 H), 7.48 (t, 4 H, *J* = 7.5 Hz), 7.40 (t, 2 H, *J* = 7.2 Hz), 3.38 (pent, 1 H, *J* = 9.2 Hz), 2.94 (dd, 2 H, *J* = 12.8 Hz, 9.6 Hz), 2.42-2.35 (m, 2 H), 1.61 (d, 3 H, $^3J_{PH}$ = 14.4 Hz), 1.4-0.7 (br q, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6 (J_{CP} = 2 Hz), 139.7, 134.0, 129.1, 128.3, 127.7, 127.3, 125.3, 124.7, 120.5, 34.8, 33.5 ($^1J_{CP}$

= 33 Hz), 22.3 (J_{CP} = 5 Hz), 18.3 ($^2J_{CP}$ = 17 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 29.0; IR (ATR) 3027, 2384, 1077, 911, 726 cm^{-1}; MS (ESI^+) *m/z* 423, 324, 292, 224, 124; HRMS (ESI^+) *m/z* calcd for $C_{30}H_{30}BNP$ [M+H] 446.2203, found 446.2211. ***trans*-2-45**: IR (ATR) 3029, 2980, 2374, 2236, 1597, 1483, 1389, 1109, 1061, 1006, 909, 834, 736, 695 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76-7.68 (m, 8 H),7.61 (d, 4 H, *J* = 7.5 Hz), 7.49 (t, 4 H, *J* = 7.5 Hz), 7.42 (t, 2 H, *J* = 7.5 Hz), 3.20 (dd, 2 H, *J* = 13.6 Hz, 10.0 Hz), 3.03-2.90 (m, 1 H), 2.49 (td, 2 H, *J* = 14.0 Hz, 7.0 Hz), 1.71 (d, 3 H, $^3J_{PH}$ = 12.8 Hz), 1.4-0.7 (br m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.5 (J_{CP} = 2 Hz), 139.6, 133.8, 129.1, 128.4, 127.6, 127.2, 125.5, 125.0, 122.1, 35.7, 33.4 ($^1J_{CP}$ = 31 Hz), 25.8, 17.1 ($^2J_{CP}$ = 6 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 29.1.



cis-**2-47**, 38% *trans*-**2-47**, 17%

3-(Bis((*S*)-2-(6-methoxynaphthalen-2-yl)propyl)phosphanyl)-3-methylcyclobutane-1-carbonitrile (2-47).[97] Prepared according to General Procedure D from di-(*S*)-naproxen phosphine borane (3.77 g, 8.49 mmol), bicyclobutane nitrile **2-37** (0.790 g, 8.49 mmol) and NaH (0.340 g, 8.49 mmol, 60% dispersion) in DMAc (40 mL). Purification by automated chromatography (120 g SiO_2 cartridge, 5-10-15-50% EtOAc in hexane) afforded *cis*-**2-47** (1.73 g, 3.22 mmol, 38%) and *trans*-**2-47** (0.773 g, 1.43 mmol, 17%), both as colorless solids. ***cis*-2-47**: Mp 162–163 °C; $[\alpha]_D$ –24.1 (*c* 0.220, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (app t, 3 H, *J* = 9.2 Hz), 7.52 (d, 2 H, *J* = 8.4 Hz), 7.36 (dd, 1 H, *J* = 8.4 Hz, 2.0 Hz), 7.22-7.16 (m, 2 H), 7.14 (d, 1 H, *J* = 2.4 Hz), 7.09 (dd, 1 H, *J* = 8.8 Hz, 2.4 Hz), 7.02 (d, 1 H, *J* = 2.4 Hz), 6.92 (dd, 1 H, *J* = 8.4, 1.6 Hz), 3.95 (s, 3 H), 3.89 (s, 3 H), 3.51-3.40 (m, 1 H), 3.10 (pent, 1 H, *J* = 9.2 Hz), 2.97-2.86 (m, 1 H), 2.79 (app

q, 1 H, J = 12.0 Hz), 2.66 (td, 1 H, J = 13.2 Hz, 10.0 Hz), 1.98-1.87 (m, 2 H), 1.70-1.59 (m, 2 H), 1.46 (d, 3 H, J = 7.2 Hz), 1.21 (d, 3 H, $^3J_{PH}$ = 11.0 Hz), 1.26-1.14 (m, 1 H), 1.08 (ddd, 1 H, J = 15.2 Hz, 9.2 Hz, 6.4 Hz), 0.92 (d, 3 H, J = 6.8 Hz), 1.0-0.3 (br m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 157.5, 141.5, 141.4, 141.04, 141.00, 133.6, 133.3, 129.2, 129.03, 128.98, 128.8, 127.5, 127.2, 126.0, 125.6, 125.5, 124.9, 120.6 ($^4J_{CP}$ = 2 Hz), 105.67, 105.57, 55.4, 55.3, 35.2, 35.0, 33.6, 31.9 ($^1J_{CP}$ = 31 Hz), 30.0 ($^1J_{CP}$ = 31 Hz), 29.3 ($^1J_{CP}$ = 27 Hz), 25.6, 25.0, 20.5, 17.8 ($^2J_{CP}$ = 18 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.7; IR (ATR) 2933, 2386, 1603, 1450, 1215, 837 cm^{-1}; MS (ESI^+) *m/z* 538, 500, 447, 338; HRMS (ESI^+) *m/z* calcd for $C_{34}H_{42}BNO_2P$ [M+H] 538.3041, found 538.3025. ***trans*-2-47**: $[\alpha]_D$ +27.1 (c = 0.240, CH_2Cl_2); IR (ATR) 2933, 2395, 1605, 1028, 857 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78-7.72 (m, 3 H), 7.53 (dd, 2 H, J = 8.4 Hz, 6.0 Hz), 7.38 (dd, 1 H, J = 8.4 Hz, 1.6 Hz), 7.24-7.15 (m, 3 H), 7.11 (dd, 1 H, J = 8.8 Hz, 2.4 Hz), 7.05 (d, 1 H, J = 2.4 Hz), 6.89 (dd, 1 H, J = 8.4, 2.4 Hz), 3.96 (s, 3 H), 3.90 (s, 3 H), 3.53-3.43 (m, 1 H), 3.21-3.13 (m, 1 H), 2.94-2.80 (m, 2 H), 2.49 (dd, 1 H, J = 13.2 Hz, 10.4 Hz), 2.11 (td, 1 H, J = 12.4 Hz, 7.2 Hz), 1.94 (td, 1 H, J = 14.0 Hz, 9.6 Hz), 1.70-1.55 (m, 3 H), 1.47 (d, 3 H, J = 6.4 Hz), 1.35 (d, 3 H, $^3J_{PH}$ = 10.4 Hz), 1.13-1.04 (m, 1 H), 0.93 (d, 3 H, J = 7.2 Hz), 1.0-0.3 (br m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 157.5, 141.6, 141.5, 140.9, 140.9, 133.7, 133.3, 129.2, 129.0, 128.8, 127.6, 127.2, 126.1, 125.6, 125.3, 124.8, 122.5, 119.3, 105.7, 105.6, 55.4, 55.3, 35.2, 35.0, 34.7, 34.3, 34.2, 34.2, 32.1 ($^1J_{CP}$ = 31 Hz), 30.4 ($^1J_{CP}$ = 32 Hz), 29.6 ($^1J_{CP}$ = 27 Hz), 25.7 (J_{CP} = 11 Hz), 24.9 (J_{CP} = 7 Hz), 23.6 (J_{CP} = 3 Hz), 16.5 ($^2J_{CP}$ = 7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.5.

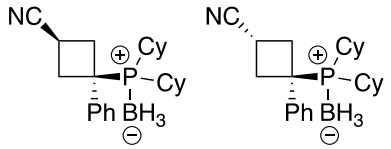
2-50

General Procedure E (Bicyclobutane nitrile synthesis through transnitrilation): 3-Phenylbicyclo[1.1.0]butane-1-carbonitrile (2-50).[189] A solution of dibromocyclopropane (8.28 g, 25.5 mmol) in diethyl ether (60 mL) was cooled to –78 °C under N_2 in a 250-mL round bottom flask. Methyl lithium (15.6 mL, 25.5 mmol, 1.63 M in Et_2O) was added dropwise via syringe over 15 min. After stirring for 1 h at –78 °C, *t*-butyl lithium (15.0 mL, 25.5 mmol, 1.70 M in pentane) was added dropwise via syringe over 15 min. After stirring for an additional 1 h at –78 °C, dimethyl malononitrile (2.40 g, 25.5 mmol) was added as a solution in THF (10 mL), and the reaction mixture turned from a clear orange into an opaque yellow solution. The cooling bath was removed and the solution was warmed to rt over 1.5 h, affording an orange/brown suspension. The mixture was quenched with sat. aq. NH_4Cl (20 mL), and partitioned between water (30 mL) and diethyl ether (50 mL). The aqueous layer was extracted with ether (50 mL). The combined organic extracts were washed with water (60 mL) and brine (60 mL), dried (Na_2SO_4) and concentrated. Chromatography of the crude black residue on SiO_2 (5-20% EtOAc/hexane) afforded bicyclobutane **2-50** (1.71 g, 11.0 mmol, 43%) as a yellow oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45-7.29 (m, 5 H), 2.71 (s, 2 H), 1.68 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.8, 128.9, 128.5, 128.0, 126.5, 118.8, 37.9, 29.5, 5.8.

2-53

2,2-Dimethylbicyclo[1.1.0]butane-1-carbonitrile (2-53).[98] Prepared according to General

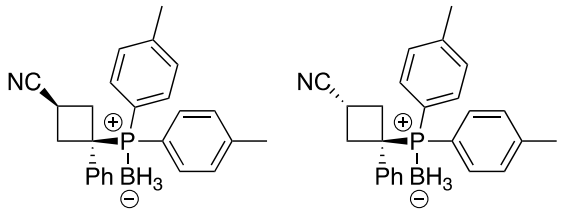
Procedure E from dibromocyclopropane (10.0 g, 18.1 mmol), methyl lithium (22.2 mL, 36.2 mmol, 1.63 M in Et_2O), *t*-butyl lithium (21.3 mL, 36.2 mmol, 1.70 M in pentane), and dimethylmalononitrile (4.43 g, 47.0 mmol, 1.30 eq) in Et_2O (80 mL). Purification by chromatography on SiO_2 (5-20% EtOAc in hexanes) afforded **2-53** (0.694 g, 6.48 mmol, 18%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.30 (dd, 1 H, J = 3.0 Hz, 3.0 Hz), 2.21 (t, 1 H, J = 3.0 Hz), 1.86 (t, 1 H, J = 3.0 Hz), 1.35 (s, 3 H), 0.96 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 120.6, 53.8, 35.3, 24.9, 22.0, 13.8, 2.6.



cis-**2-54** *trans*-**2-54**

3-(Dicyclohexylphosphanyl)-3-phenylcyclobutane-1-carbonitrile (2-54).[97] Prepared according to General Procedure D from nitrile **2-50** (0.083 g, 0.54 mmol, 1.3 eq), dicyclohexyl phosphine borane (0.087 g, 0.41 mmol) and NaH (0.016 g, 0.41 mmol, 60% in oil) in DMAc (2 mL). Purification by chromatography on SiO_2 (15% EtOAc/hexane) afforded less polar *cis*-**2-54** (0.043 g, 0.117 mmol, 28%) and the more polar *trans*-**2-54** (0.058 g, 0.158 mmol, 38%), both as colorless solids. ***cis*-2-54**: Mp 198–201 °C; IR (ATR) 2934, 2844, 2391, 1448, 1072 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 (t, 2 H, J = 6.9 Hz), 7.35 (t, 3 H, J = 7.8 Hz), 3.64-3.48 (m, 2 H), 3.07 (pent, 1 H, J = 9.2 Hz), 2.76 (tt, 2 H, J = 8.7 Hz, 3.0 Hz), 1.95-1.53 (m, 11 H), 1.32-1.05 (m, 11 H), 1.1-0.1 (br m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.1 (J_{CP} = 5 Hz), 128.9, 128.5, 127.8 (J_{CP} = 2 Hz), 127.6, 127.6, 124.5, 120.2 ($^4J_{CP}$ = 3 Hz), 42.1 ($^1J_{CP}$ = 21 Hz), 36.9, 36.6, 31.5 ($^1J_{CP}$ = 28 Hz), 27.4, 27.2, 27.1, 27.0, 26.9, 26.8, 25.9, 20.6 ($^2J_{CP}$ = 18 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 39.6; MS (ESI$^+$) *m/z* 385 (M+NH_4^+), 368, 273, 215; HRMS (ESI$^+$) *m/z* calcd for $C_{23}H_{36}BNP$ [M+H] 368.2673, found 368.2696. ***trans*-2-54**: Mp 205–207 °C; IR (ATR) 2930, 2856, 2377, 2239, 1446,

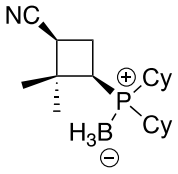
1064, 760 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (t, 2 H, J = 7.2 Hz), 7.33 (app t, 1 H, J = 7.6 Hz), 7.13 (d, 2 H, J = 8.0 Hz), 3.67 (pent, 1 H, J = 9.2 Hz), 3.38 (td, 2 H, J = 13.2 Hz, 10.0 Hz), 2.98-2.86 (m, 2 H), 1.95-1.49 (m, 10 H), 1.47-1.32 (m, 2 H), 1.32-1.02 (m, 10 H), 0.9-0.0 (br m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.0 ($^{2}J_{CP}$ = 6 Hz), 128.8, 127.4, 126.3 ($^{3}J_{CP}$ = 3 Hz), 121.8, 41.4 ($^{1}J_{CP}$ = 21 Hz), 37.3, 31.3 ($^{1}J_{CP}$ = 29 Hz), 28.6, 27.6, 27.2, 27.1, 26.7, 26.6, 25.8, 17.6 ($^{2}J_{CP}$ = 3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 35.9.



cis-**2-55** *trans*-**2-55**

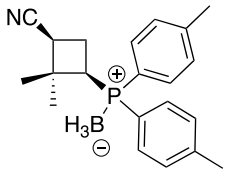
3-(Di-*p*-tolylphosphanyl)-3-phenylcyclobutane-1-carbonitrile (2-55).[97] Prepared according to General Procedure D from nitrile **2-50** (0.621 g, 4.01 mmol), di-*p*-tolyl phosphine borane (0.684 g, 3.00 mmol) and NaH (0.120 g, 3.0 mmol) in DMAc (15 mL). Purification by automated chromatography (80 g SiO_2 cartridge, 5-10-50% EtOAc in hexane) afforded *cis*-**2-55** (0.365 g, 0.95 mmol, 32%) as a light yellow solid and *trans*-**2-55** (0.457 g, 1.19 mmol, 40%) as a white crystalline solid. ***cis*-2-55**: Mp 68–72 °C; IR (ATR) 2368, 1600, 1497, 1446, 1190, 1063, 806, 655 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, 2 H, J = 8.4 Hz), 7.45 (d, 2 H, J = 8.4 Hz), 7.24-7.13 (m, 7 H), 7.09-7.02 (m, 2 H), 3.30 (ddd, 2 H, J = 13.2 Hz, 10.0 Hz, 2.4 Hz), 3.03 (pent, 1 H, J = 9.2 Hz), 2.91-2.84 (m, 2 H), 2.38 (s, 6 H), 1.5-0.5 (br m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2 (J_{CP} = 2 Hz), 137.6, 133.9 (J_{CP} = 6 Hz), 129.4 (J_{CP} = 11 Hz), 128.9 (J_{CP} = 3 Hz), 127.8, 127.8, 127.7, 127.5, 127.4, 122.6, 122.1, 120.2 ($^{4}J_{CP}$ = 3 Hz), 43.7 ($^{1}J_{CP}$ = 27 Hz), 35.8, 21.5, 19.1 (J_{CP} = 19 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 29.0. ***trans*-2-55**: Mp 172–174 °C; IR (ATR) 2933, 2391, 1604, 1450, 1064 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, 2 H, J = 8.4 Hz), 7.42 (d, 2

H, J = 8.0 Hz), 7.25-7.13 (m, 7 H), 6.66 (dd, 2 H, J = 6.4 Hz, 1.6 Hz), 3.55 (pent, 1 H, J = 9.2 Hz), 3.45-3.34 (m, 2 H), 2.96-2.87 (m, 2 H), 2.38 (s, 6 H), 1.3-0.7 (br m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3 (J_{CP} = 3 Hz), 142.2 (J_{CP} = 5 Hz), 134.2 (J_{CP} = 98 Hz), 129.2, 129.1, 128.0 (J_{CP} = 2 Hz), 127.6 (J_{CP} = 2 Hz), 127.1, 122.1, 121.7, 121.5, 42.9 ($^1J_{CP}$ = 24 Hz), 36.7, 21.5, 17.7; ^{31}P NMR (162 MHz, $CDCl_3$) δ 25.7; IR (ATR) 2933, 2383, 1437, 1065, 757, 744 cm^{-1}; MS (ESI$^+$) *m/z* 384, 370, 345, 155; HRMS (ESI$^+$) *m/z* calcd for $C_{25}H_{28}BNP$ [M+H] 384.2047, found 384.2038.



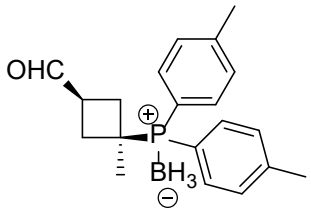
2-56

3-(Dicyclohexylphosphanyl)-2,2-dimethylcyclobutane-1-carbonitrile (2-56).[97] Prepared according to General Procedure D from bicyclobutane **2-53** (0.148 g, 1.37 mmol), dicyclohexyl phosphine borane (0.225 g, 1.06 mmol), NaH (0.055 g, 1.37 mmol, 60% in mineral oil) in DMAc (7.5 mL). Purification by chromatography on SiO_2 (10-30% EtOAc/hexane) afforded **2-56** (0.144 g, 0.339 mmol, 34%) as a colorless solid: Mp 135–139 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.90 (app t, 1 H, J = 8.8 Hz), 2.68 (pent, 1 H, J = 10.8 Hz), 2.50 (td, 1 H, J = 10.8 Hz, 8.0 Hz), 2.31 (dtd, 1 H, J = 10.4 Hz, 8.0 Hz, 2.0 Hz), 2.05-1.96 (m, 1 H), 1.94-1.55 (m, 11 H), 1.51 (s, 3 H), 1.28 (s, 3 H), 1.37-1.14 (m, 10 H), 1.1-0.0 (br m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 118.4 ($^4J_{CP}$ = 6 Hz), 45.3 ($^3J_{CP}$ = 1 Hz), 36.3 ($^1J_{CP}$ = 25 Hz), 34.3 ($^1J_{CP}$ = 23 Hz), 33.6 (J_{CP} = 10 Hz), 33.3 (J_{CP} = 9 Hz), 31.2, 27.8, 27.53, 27.46, 27.4, 27.3, 27.14, 27.05, 27.00, 26.95, 26.9, 26.0, 25.9 (J_{CP} = 19 Hz), 25.4, 21.9 (J_{CP} = 4 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.7; IR (ATR) 2924, 2365, 1448, 1066 cm^{-1}; MS (ESI$^+$) *m/z* 320, 306, 268, 241, 215, 273, 152; HRMS (ESI$^+$) *m/z* calcd for $C_{19}H_{36}BNP$ [M+H] 320.2673, found 320.2684.



2-57

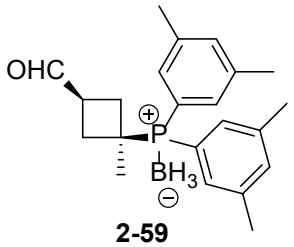
(3-(Di-*p*-tolylphosphanyl)-2,2-dimethylcyclobutane-1-carbonitrile borane (2-57).[97] Prepared according to General Procedure D from bicyclobutane **2-53** (0.049 g, 0.46 mmol), di-*p*-tolylphosphine borane (0.081 g, 0.36 mmol), and NaH (0.018 g, 0.46 mmol, 60% in mineral oil) in DMAc (2.5 mL). Purification by chromatography on SiO_2 (5-25% EtOAc/hexane) afforded 0.032 g (0.095 mmol, 27%) of **2-57** as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, 1 H, J = 8.0 Hz), 7.56 (d, 1 H, J = 8.4 Hz), 7.45 (d, 1 H, J = 8.0 Hz), 7.42 (d, 1 H, J = 8.4 Hz), 7.27 (dd, 2 H, J = 8.0 Hz, 2.0 Hz), 7.22 (dd, 2 H, J = 8.0 Hz, 1.6 Hz), 3.04 (ddd, 1 H, J = 11.2 Hz, 8.4 Hz, 8.4 Hz), 2.93 (td, 1 H, J = 10.0 Hz, 0.8 Hz), 2.73 (pent, 1 H, J = 11.2 Hz), 2.48 (ddd, 1 H, J = 19.2 Hz, 8.4 Hz, 2.4 Hz), 2.39 (s, 3 H), 2.37 (s, 3 H), 1.27 (s, 3 H), 1.16 (s, 3 H), 1.2-0.6 (br m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.9 ($^1J_{CP}$ = 35 Hz), 141.9 ($^1J_{CP}$ = 35 Hz), 132.5 ($^2J_{CP}$ = 15 Hz), 132.4 ($^2J_{CP}$ = 14 Hz), 129.7, 129.7, 129.6, 129.6, 126.3, 125.8, 125.3, 124.7, 118.5 ($^4J_{CP}$ = 6 Hz), 45.3, 39.9 ($^1J_{CP}$ = 28 Hz), 33.8 (J_{CP} = 25 Hz), 30.9, 24.9, 21.5, 21.5, 20.9 ($^3J_{CP}$ = 5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 13.7; IR (ATR) 2974, 2391, 2235, 1450, 1103, 1059, 734 cm^{-1}; MS (ESI$^+$) *m/z* 336, 322, 282, 249, 228, 209; HRMS (ESI$^+$) *m/z* calcd for $C_{21}H_{28}BNP$ [M+H] 336.2047, found 336.2061.



2-58

3-(Ditolylphosphanyl)-3-methylcyclobutane-1-carbaldehyde borane (2-58).[97] A solution of

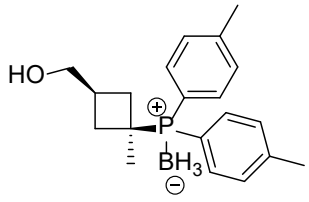
nitrile *cis*-**2-42** (0.755 g, 2.35 mmol) in THF (12 mL) was cooled to 0 °C under N_2. DIBAL (3.5 mL, 3.5 mmol, 1.5 eq, 1 M in hexanes) was added via syringe over 2 min. The ice bath was removed, and the resulting solution was stirred at rt for 16 h, then was quenched with 2 M H_2SO_4 (10 mL). The solution was stirred for 1 h and gradually became an opaque white suspension. The suspension was partitioned between water (40 mL) and Et_2O (40 mL), and the aqueous layer was extracted with Et_20 (40 mL). The combined extracts were washed with water (40 mL), brine (40 mL), dried (Na_2SO_4) and concentrated. The crude oil was purified by chromatography on SiO_2 (20% EtOAc in hexanes) to afford aldehyde **2-58** (0.484 g, 1.49 mmol, 64%) as a colorless foam: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.24 (d, 1 H, J = 2.0 Hz), 7.54 (d, 2 H, J = 8.4 Hz), 7.52 (d, 2 H, J = 8.4 Hz), 7.26 (d, 2 H, J = 8.0 Hz), 7.25 (d, 2 H, J = 7.6 Hz), 3.26 (pent d, 1 H, J = 9.2 Hz, 2.4 Hz), 2.88-2.74 (m, 2 H), 2.41 (s, 6 H), 2.13-2.04 (m, 2 H), 1.61 (d, 3 H, $^3J_{PH}$ = 14.8 Hz), 1.2-0.4 (br q, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.1, 141.8, 133.5, 133.4, 129.6, 129.5, 124.0, 123.5, 40.3 (J_{CP} = 12 Hz), 31.9 ($^1J_{CP}$ = 32 Hz), 30.6, 23.6 (J_{CP} = 5 Hz), 21.5; MS (ESI$^+$) *m/z* 324, 311, 295, 213; ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.1; HRMS (ESI$^+$) *m/z* calcd for $C_{20}H_{27}BOP$ [M+H] 325.1887, found 325.1892.



2-59

3-(Di-*m*-xylylphosphanyl)-3-methylcyclobutane-1-carbaldehyde borane (2-59). A solution of *cis*-**2-43** (1.00 g, 2.86 mmol) in THF (25 mL) was cooled to 0 °C under N_2 in a 100 mL flask. The solution was treated with DIBAL (4.29 mL, 4.29 mmol, 1 M in hexane, 1.5 eq) via syringe over 20 s. The cooling bath was removed, and the resulting colorless solution was stirred at rt for 24 h.

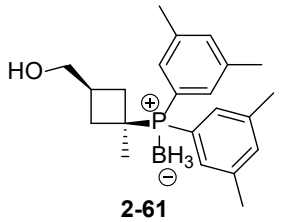
The reaction was quenched with 2 M H_2SO_4 (15 mL). The resulting solution was stirred for 30 min, was extracted with ether (2 x 50 mL). The combined extracts were washed with water (30 mL), brine (30 mL), dried (Na_2SO_4), and concentrated. The crude material was purified by chromatography on SiO_2 (15-25% EtOAc/hexane) to afford aldehyde **2-59** (0.556 g, 1.58 mmol, 55%) as a colorless solid: Mp 133–134 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.24 (d, 1 H, J = 2.0 Hz), 7.25 (s, 2 H), 7.22 (s, 2 H), 7.13 (s, 2 H), 3.24 (pent, 1 H, J = 8.8 Hz), 2.87-2.75 (m, 2 H), 2.33 (s, 12 H), 2.14-2.05 (m, 2 H), 1.60 (d, 3 H, $^3J_{PH}$ = 14.0 Hz), 1.2-0.3 (br q, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.2, 138.4, 138.3, 133.18, 133.16, 131.1, 131.0, 127.1, 126.6, 40.3 (J_{CP} = 11 Hz), 31.7 ($^1J_{CP}$ = 31 Hz), 30.8, 23.8 (J_{CP} = 5 Hz), 21.6, 13.8; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.4 IR (ATR) 2933, 2373, 1713, 1128, 1069, 839, 692 cm^{-1}; MS (ESI$^+$) *m/z* 367, 353, 341, 241, 212; HRMS (ESI$^+$) *m/z* calcd for $C_{22}H_{31}BOP$ [M+H] 353.2200, found 353.2180.



2-60

3-(Ditolyl-3-methylcyclobutyl)methanol borane (2-60).[97] A solution of aldehyde **2-58** (0.608 g, 1.88 mmol, 1.00 eq) in MeOH (10 mL) was cooled to 0 °C. Sodium borohydride (0.074 g, 2.0 mmol, 1.1 eq) was added to the colorless solution in one portion. Bubbling ensued, and then subsided after ca. 10 min. The reaction mixture was stirred at rt for 2 h, and quenched with 1 M HCl (5 mL). The contents of the flask were then partitioned between ether (30 mL) and water (30 mL), and the aqueous phase was extracted with ether (30 mL). The combined organic phases were washed with water (30 mL) and brine (30 mL), were (Na_2SO_4) and concentrated. The residue was purified by chromatography on SiO_2 (25% EtOAc/hexane) to afford alcohol **2-60** (0.503 g, 1.54

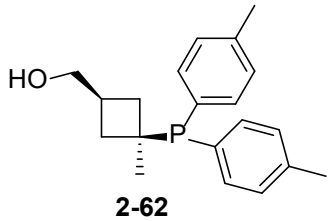
mmol, 82%) as a colorless solid: Mp 108–110 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, 2 H, *J* = 8.0 Hz), 7.52 (d, 2 H, *J* = 8.8 Hz), 7.23 (d, 4 H, *J* = 6.8 Hz), 3.19 (d, 2 H, *J* = 6.4 Hz), 2.74 (pent, 1 H, *J* = 8.0 Hz), 2.37 (s, 6 H), 2.38-2.23 (m, 2 H), 2.01-1.89 (m, 2 H), 1.54 (d, 3 H, $^{3}J_{PH}$ = 14.8 Hz), 1.2-0.3 (br q, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.49, 141.47, 133.54, 133.45, 129.4, 129.3, 124.7, 124.2, 66.2, 33.1, 32.2 ($^{2}J_{CP}$ = 13 Hz), 31.0 ($^{1}J_{CP}$ = 32 Hz), 23.5 (J_{CP} = 3 Hz), 21.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.3.



2-61

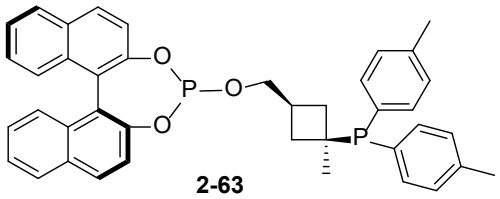
3-((Di-*m*-xylylphosphanyl)-3-methylcyclobutyl)methanol borane (2-61). A solution of aldehyde **2-59** (0.414 g, 1.18 mmol) in MeOH (8 mL) and THF (3 mL) was treated with sodium borohydride (0.049 g, 1.3 mmol) at 0 °C. The ice bath was removed, and the colorless reaction mixture was stirred at rt for 1.25 h. The reaction was quenched with 1 M HCl (5 mL), then was partitioned between water (40 mL) and CH_2Cl_2 (40 mL), and the aqueous phase was re-extracted with CH_2Cl_2 (40 mL). The combined extracts were washed with water (30 mL), 1:1 water/brine (30 mL), dried (Na_2SO_4) and were concentrated. Chromatography on SiO_2 (15-30% EtOAc/hexane) afforded alcohol **2-61** (0.318 g, 0.897 mmol, 76%) as a colorless solid: Mp 142–144 °C; IR (ATR) 3360 (br), 2934, 2384, 1450, 1127, 911, 726 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (s, 2 H), 7.25 (s, 2 H), 7.13 (s, 2 H), 3.25 (d, 2 H, *J* = 6.4 Hz), 2.75 (pent, 1 H, *J* = 7.6 Hz), 2.42-2.24 (m, 2 H), 2.35 (s, 12 H), 2.03-1.92 (m, 2 H), 1.58 (d, 3 H, $^{3}J_{PH}$ = 14.4 Hz), 1.45 (br s, 1 H), 1.3-0.5 (br q, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.2, 138.1, 132.89, 132.87, 131.13, 131.05, 127.8, 127.3, 66.2, 33.3, 32.2, (J_{CP} = 12 Hz), 31.0 ($^{1}J_{CP}$ = 30 Hz), 23.6 ($^{3}J_{CP}$ = 3 Hz), 21.4; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.4; HRMS (ESI^{+}) *m/z* calcd for $C_{22}H_{31}BOP$ [M–H] 353.2200,

found 353.2188.



2-62

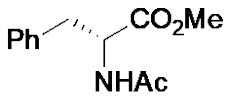
3-(Ditolyl-3-methylcyclobutyl)methanol (2-62). Prepared according to General Procedure C from phosphine borane **2-60** (0.160 g, 0.512 mmol) and DABCO (0.230 g, 2.05 mmol) in toluene (2 mL) to afford phosphine **2-62** (0.119 g, 0.381 mmol, 78%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, 4 H, J = 7.2 Hz), 7.15 (d, 4 H, J = 9.6 Hz), 3.21 (d, 2 H, J = 6.4 Hz), 2.68 (pent, 1 H, J = 8.0 Hz), 2.35 (s, 6 H), 2.07 (d, 1 H, J = 12.4 Hz), 2.02 (d, 1 H, J = 11.2 Hz), 2.00-1.91 (m, 2 H), 1.48 (d, 3 H, $^{3}J_{PH}$ = 12.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 7.7.



2-63

(11*S*)-4-((3-(Di-*p*-tolylphosphanyl)-3-methylcyclobutyl)methoxy)dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine (2-63).[97] *S*-BINOL (0.223 g, 0.778 mmol) was placed under N_2 into a 50-mL flask and treated with PCl_3 (1.1 mL, 12 mmol, 17 eq) and *N*-methylpyrrolidone (1 drop). The mixture was stirred at 60 °C for 15 min, cooled, and slowly concentrated under high vacuum to give a semi-solid. The residue was azeotroped with toluene (5 mL) and dissolved in THF (5 mL). An NMR of an aliquot showed the clean chlorophosphite (^{31}P NMR δ 174). In a separate 50-mL flask, a solution of phosphine **2-62** (0.221 g, 0.707 mmol) in THF (3 mL) was cooled to 0 °C under N_2. NaH (0.031 g, 0.79 mmol, 1.1 eq, 60% in oil) was added in one portion. The resulting alkoxide was stirred for 10 min at 0 °C. The chlorophosphine solution was then transferred to the

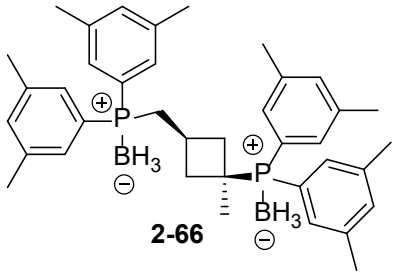
alkoxide solution via syringe at 0 °C. The cooling bath was removed, and the reaction mixture was stirred for 19 h at rt, concentrated, and purified by chromatography on SiO_2 (5-40% EtOAc/hexane) to afford **2-63** (0.121 g, 0.193 mmol, 27%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, 1 H, J = 8.8 Hz), 7.95-7.86 (m, 3 H), 7.47 (d, 1 H, J = 8.8 Hz), 7.42 (td, 2 H, J = 6.8 Hz, 1.2 Hz), 7.37-7.22 (m, 9 H), 7.18-7.12 (m, 4 H), 3.55 (app dd, 1 H, $^3J_{PH}$ = 17.2 Hz, J = 7.6 Hz), 3.37 (app dd, 1 H, $^3J_{PH}$ = 17.6 Hz, J = 7.6 Hz), 2.72 (pent, 1 H, J = 8.0 Hz), 2.34 (s, 6 H), 2.05 (dd, 2 H, J = 20 Hz, 12 Hz), 1.96-1.88 (m, 2 H), 1.45 (d, 3 H, $^3J_{PH}$ = 12.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.5 (J_{CP} = 5 Hz), 147.5, 138.5 (J_{CP} = 5 Hz), 134.3 (J_{CP} = 6 Hz), 134.1 (J_{CP} = 6 Hz), 133.1, 133.0, 132.8, 132.6, 131.5, 131.0, 130.3, 129.9, 129.1 (J_{CP} = 7 Hz), 128.3 (J_{CP} = 6 Hz), 127.0, 126.2 (J_{CP} = 9 Hz), 125.0, 124.9, 124.1 (J_{CP} = 5 Hz), 122.7 (J_{CP} = 2 Hz), 121.9, 121.7, 68.5 ($^2J_{CP}$ = 7 Hz), 34.73, 34.69, 34.63, 34.55, 31.8 ($^1J_{CP}$ = 18 Hz), 31.2, (J_{CP} = 10 Hz), 26.9, 25.4, 25.3 (J_{CP} = 4 Hz), 21.4, 20.7, 14.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 142.8, 7.2; HRMS (ESI$^+$) *m/z* calcd for $C_{40}H_{37}O_3P_2$ [M+H] 627.2212, found 627.2206.



2-65

Methyl acetyl-*D*-phenylalaninate (**2-65**).[97] A solution of **2-64** (0.116 g, 0.532 mmol) in MeOH (1 mL) in a stainless steel pressure vessel was charged with a solution of phosphine-phosphite **2-63** (0.010 g, 0.016 mmol, 3 mol%) in MeOH (0.3 mL) and a solution of Rh(NBD)BF_4 (0.002 g, 0.005 mmol, 1 mol%) in MeOH (0.3 mL) under an Ar blanket provided by an inverted funnel. The resulting yellow solution was sealed in the Parr autoclave and placed under 13.99 bar of H_2. After 3.5 h, the remaining 13.96 bar was vented. The solution was concentrated, re-dissolved in CH_2Cl_2 (1 mL), and filtered through neutral Al_2O_3 to afford **2-65** (0.086 g, 0.39 mmol, 73%) as a colorless solid: $[\alpha]_D$ –0.855 (c = 1.0, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38-7.21 (m 3 H), 7.16-7.07

(m, 2 H), 6.09 (d, 1 H, J = 6.6 Hz), 4.90 (ddd, 1 H, J = 7.8 Hz, 6.0 Hz, 5.7 Hz), 3.74 (s, 3 H), 3.21-3.04 (m, 2 H), 1.99 (s, 3 H); Chiral SFC (Chiralpak IA, 5-15% *i*-PrOH modifier gradient) T_r 8.48 min (major, *D*-isomer), 11.42 min (minor, *L*-isomer).

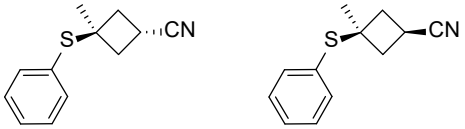


2-66

((3-(Bis(3,5-dimethylphenyl)phosphanyl)-3-methylcyclobutyl)methyl)bis(3,5-dimethylphenyl)phosphane diborane (2-66). A solution of alcohol **2-61** (0.119 g, 0.336 mmol) and Et_3N (0.05 mL, 0.03 mmol) in CH_2Cl_2 (2 mL) was cooled to 0 °C under N_2. Brosyl chloride (0.086 g, 0.34 mmol) was added in one portion. The solution was warmed to rt over 2.5 h, then was directly placed on an SiO_2 column and purified by chromatography (10% EtOAc/hexane) to afford the corresponding *p*-bromosulfonate (0.068 g, 0.119 mmol, 35%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76-7.66 (m, 4 H), 7.20 (s, 2 H), 7.16 (s, 2 H), 7.11 (s, 2 H), 3.64 (d, 2 H, J = 7.2 Hz), 2.85 (pent, 1 H, J = 8.1 Hz), 2.32 (s, 12 H), 2.35-2.22 (m, 2 H), 2.02-1.91 (m, 2 H), 1.52 (d, 3 H, $^3J_{PH}$ = 14.1 Hz), 1.3-0.1 (br q, 3 H).

A solution of this brosylate (0.068 g, 0.119 mmol) and di-*m*-xylyl phosphine borane (0.046 g, 0.178 mmol) in DMAc (1 mL) under N_2 was treated with sodium hydride (0.007 g, 0.2 mmol, 60% in oil) in one portion. The reaction was stirred for 19 h at rt, then was quenched with sat aq NH_4Cl (10 mL). The material was partitioned between ether and water (30 mL each), the layers were separated, and the aqueous layer was extracted with ether (30 mL). The combined extracts were washed with water (30 mL), brine (30 mL), then were dried (Na_2SO_4) and concentrated. Two iterations of chromatography on SiO_2 (10% EtOAc/hexane)

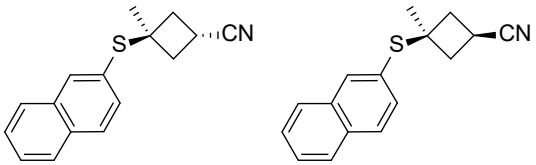
afforded diphosphine borane **2-66** (0.034 g, 0.057 mmol, 48%) as a colorless solid: Mp 225–227 °C; IR (ATR) 2933, 2378, 1737, 1461, 1128, 1066, 915, 734 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 (s, 2 H), 7.16 (s, 4 H), 7.14 (s, 2 H), 7.09 (s, 4 H), 2.85-2.74 (m, 1 H), 2.35-2.26 (m, 2 H), 2.33 (s, 12 H), 2.31 (s, 12 H), 1.97 (dd, 2 H, J = 11.0 Hz, 7.0 Hz), 1.94-1.87 (m, 2 H), 1.42 (d, 3 H, $^{3}J_{PH}$ = 14.0 Hz), 1.1-0.4 (br q, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.3, 138.2, 138.1, 138.0, 132.9, 132.8, 131.1, 131.0, 129.7, 129.6, 129.1, 127.7, 127.2, 38.0 (J_{CP} = 9 Hz), 31.5 (J_{CP} = 5 Hz), 31.2 ($^{1}J_{CP}$ = 31 Hz), 25.4 (J_{CP} = 14 Hz), 23.3, 21.4, 21.3; ^{31}P NMR (202 MHz, $CDCl_3$) δ 29.5, 11.8. An X-ray crystal structure was obtained for this compound.



trans **2-67** *cis* **2-67**

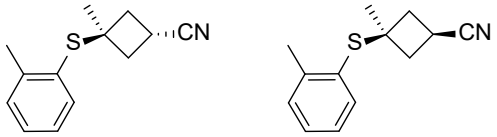
General Procedure F (Thiol additions to bicyclo[1.1.0]butyl nitriles): 3-Methyl-3-(phenylthio)cyclobutane-1-carbonitrile (2-67). A 50 mL flask under N_2 was charged with a solution of thiophenol (0.19 mL, 1.8 mmol) in MeOH (10 mL). This solution was treated with anhydrous K_2CO_3 (0.251 g, 1.82 mmol, 1.00 eq) and stirred 10 min at rt. Nitrile **2-37** (0.203 g, 2.18 mmol, 1.20 eq) was then added neat by syringe over 1 min. The solution was stirred at rt for 21 h, at which point it was concentrated. The crude, cloudy liquid was purified by chromatography on SiO_2 (10-20% EtOAc/hexanes) to afford the less polar *trans*-**2-67** (0.260 g, 1.27 mmol, 70%) and the more polar *cis*-**2-67** (0.042 g, 0.21 mmol, 11%), both as colorless oils: *trans*-**2-67**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.44 (m, 2 H), 7.39-7.32 (m, 3 H), 3.23 (pent, 1 H, J = 8.8 Hz), 2.60 (ddd, 2 H, J = 10.8 Hz, 8.4 Hz, 2.4 Hz), 2.41 (ddd, 2 H, J = 10.4 Hz, 8.4 Hz, 2.4 Hz), 1.55 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.5, 132.3, 129.0, 128.9, 122.2, 48.2, 39.6, 29.7, 16.7. *cis*-**2-67**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49-7.45 (m, 2 H), 7.40-7.34 (m, 3 H), 3.05 (pent, 1 H, J =

8.5 Hz), 2.64 (app dt, 2 H, J = 9.5 Hz, 2.5 Hz), 2.34 (ddd, 2 H, J = 10.5 Hz, 8.0Hz, 2.5 Hz), 1.49 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.7, 131.9, 129.1, 129.0, 121.4, 46.3, 39.8, 39.6, 26.9, 16.5; IR (ATR) 2956, 2235, 1720, 1474, 917, 745, 695 cm^{-1}; MS (ESI$^+$) *m/z* 204, 159, 118; HRMS (ESI$^+$) *m/z* calcd for $C_{12}H_{14}NS$ [M+H] 204.0842, found 204.0842.



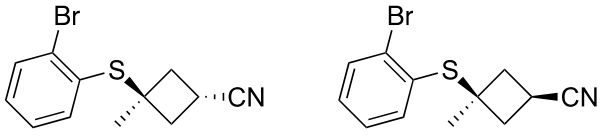
trans **2-68** *cis* **2-68**

3-Methyl-3-(naphthalen-2-ylthio)cyclobutane-1-carbonitrile (2-68). Prepared according to General Procedure F from 2-naphthlenethiol (0.122 g, 0.761 mmol), K_2CO_3 (0.105 g, 0.761 mmol, 1.00 eq), and nitrile **2-37** (0.203 g, 2.18 mmol, 1.20 eq) **in** MeOH (5 mL). Purification by chromatography on SiO_2 (10-20% EtOAc/hexanes) afforded *trans*-**2-68** (0.119 g, 0.470 mmol, 62%) as a colorless solid and *cis*-**2-68** (0.032 g, 0.13 mmol, 17%) as a colorless oil: ***trans*-2-68**: Mp 61–64 °C; IR (ATR) 2970, 2236, 1583, 1375, 1196, 1114, 863, 827, 749 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1 H), 7.88-7.77 (m, 3 H), 7.57-7.48 (m, 3 H), 3.27 (pent, 1 H, J = 8.8 Hz), 2.67 (ddd, 2 H, J = 11.2 Hz, 8.8 Hz, 2.4 Hz), 2.43 (ddd, 2 H, J = 10.8 Hz, 8.0 Hz, 2.4 Hz), 1.60 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.0, 133.5, 133.0, 132.1, 129.8, 128.6, 127.82, 127.76, 127.0, 126.8, 122.2, 48.6, 39.7, 29.8, 16.8. ***cis*-2-68**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, 1 H, J = 1.2 Hz), 7.88-7.75 (m, 3 H), 7.56-7.46 (m, 3 H), 3.08 (pent, 1 H, J = 8.8 Hz), 2.73 (dd, 2 H, J = 8.8 Hz, 2.4 Hz), 2.43 (ddd, 2 H, J = 10.4 Hz, 8.0 Hz, 2.0 Hz), 1.52 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.2, 133.6, 133.1, 132.1, 129.3, 128.7, 127.82, 127.76, 126.9, 126.7, 121.5, 46.6, 40.0, 27.0, 16.7; HRMS (ASAP) *m/z* calcd for $C_{16}H_{16}NS$ [M+H] 254.1003, found 254.1035.



trans **2-69** *cis* **2-69**

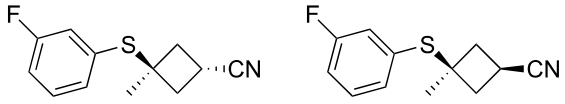
3-Methyl-3-(*o*-tolylthio)cyclobutane-1-carbonitrile (2-69). Prepared according to General Procedure F from nitrile **2-37** (0.050 g, 0.54 mmol), *o*-thiocresol (0.06 mL, 0.49 mmol), and K_2CO_3 (0.074 g, 0.54 mmol) in MeOH (3 mL). Purification by chromatography on SiO_2 (10-20% EtOAc/hexanes) to afford the less polar *trans*-**2-69** (0.084 g, 0.39 mmol, 79%) and the more polar *cis*-**2-69** (0.008 g, 0.04 mmol, 8%), both as colorless oils. ***trans*-2-69**: IR (ATR): 2940, 2238, 1732, 1589, 1487, 1263, 1114, 1063, 748 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.36 (dd, 1 H, J = 7.2 Hz, 0.8 Hz), 7.29-7.20 (m, 2 H), 7.17 (td, 1 H, J = 7.2 Hz, 1.2 Hz), 3.25 (pent, 1 H, J = 8.8 Hz), 2.63 (ddd, 2 H, J = 11.2 Hz, 9.2 Hz, 2.0 Hz), 2.48-2.39 (m, 2 H), 2.45 (s, 3 H), 1.60 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7, 134.7, 132.2, 130.8, 128.5, 126.4, 122.3, 48.7, 39.8, 29.5, 21.4, 17.0; HRMS $(ESI)^+$ calcd for $C_{13}H_{16}NS$ [M+H] 218.1003, found 218.0991. ***cis*-2-69**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, 1 H, J = 7.2 Hz), 7.32-7.23 (m, 2 H), 7.19 (td, 1 H, J = 7.2 Hz, 2.4 Hz), 3.05 (pent, 1 H, J = 8.8 Hz), 2.63 (td, 2 H, J = 9.6 Hz, 2.4 Hz), 2.48-2.35 (m, 2 H), 2.44 (s, 3 H), 1.49 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3, 136.1, 131.6, 130.8, 129.0, 126.5, 45.8, 40.1, 26.5, 21.5, 16.8.



trans-**2-70** *cis*-**2-70**

3-((2-Bromophenyl)thio)-3-methylcyclobutane-1-carbonitrile (**2-70**). Prepared according to General Procedure F from bicyclobutane **2-37** (0.210 g, 2.25 mmol, 1.20 eq), 2-bromothiophenol (0.22 mL, 1.87 mmol) and K_2CO_3 (0.286 g, 2.07 mmol, 1.10 eq) in MeOH (5 mL). Purification by

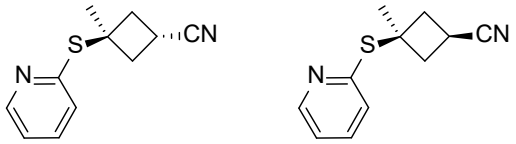
chromatography on SiO_2 (20-30% EtOAc/hexanes) afforded *trans*-**2-70** (0.367 g, 1.30 mmol, 69%) and *cis*-**2-70** (0.067 g, 0.24 mmol, 13%), both as colorless oils. ***trans*-2-70**: IR (ATR) 2940, 2238, 1731, 1445, 1426, 1103, 1019, 712 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.65 (dd, 1 H, *J* = 8.0 Hz, 1.6 Hz), 7.39 (dd, 1 H, *J* = 8.0 Hz, 1.6 Hz), 7.29 (td, 1 H, *J* = 7.6 Hz, 1.2 Hz), 7.16 (td, 1 H, *J* = 7.6 Hz, 1.6 Hz), 3.37 (pent, 1 H, *J* = 8.8 Hz), 2.70 (ddd, 2 H, *J* = 10.8 Hz, 9.2 Hz, 2.4 Hz), 2.48 (ddd, 2 H, *J* = 10.8 Hz, 8.4 Hz, 2.4 Hz), 1.66 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.5, 134.4, 133.8, 129.3, 128.7, 122.0, 49.1, 39.8, 29.4, 17.2; MS $(ESI)^+$ *m/z* 281, 261, 233, 212, 199, 144, 127, 114; HRMS $(ESI)^+$ calcd for $C_{12}H_{13}NSBr$ [M+H] 281.9947, found 281.9938. ***cis*-2-70**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.68 (dd, 1 H, *J* = 8.0 Hz, 1.6 Hz), 7.47 (dd, 1 H, *J* = 7.6 Hz, 1.6 Hz), 7.31 (td, 1 H, *J* = 7.6 Hz, 1.2 Hz), 7.20 (td, 1 H, *J* = 7.6 Hz, 1.6 Hz), 3.08 (pent, 1 H, *J* = 8.8 Hz), 2.72 (td, 2 H, *J* =9.6 Hz, 2.4 Hz), 2.54-2.43 (m, 2 H), 1.53 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.3, 133.9, 133.8, 130.0, 127.9, 121.3, 47.1, 40.3, 26.3, 17.0.



trans-**2-71** *cis*-**2-71**

3-((3-Fluorophenyl)thio)-3-methylcyclobutane-1-carbonitrile (2-71). Prepared according to General Procedure F from 3-fluorothiophenol (0.06 mL, 0.49 mmol), nitrile **2-37** (0.067 g, 0.72 mmol, 1.1 eq) and K_2CO_3 (0.099 g, 0.72 mmol, 1.1 eq) in MeOH (3 mL). Purification by chromatography on SiO_2 (10-20% EtOAc/hexanes) afforded the less polar *trans*-**2-71** (0.074 g, 0.33 mmol, 51%) and the more polar *cis*-**2-71** (0.023 g, 0.10 mmol, 16%), both as colorless oils. ***trans*-2-71**: IR (ATR) 2942, 2262, 1597, 1578, 1472, 1261, 1215, 1112, 863 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.31 (td, 1 H, *J* = 8.0 Hz, 6.0 Hz), 7.20 (d, 1 H, *J* = 7.6 Hz), 7.14 (dt, 1 H, *J* = 8.0 Hz, 2.0 Hz), 7.05 (td, 1 H, *J* = 8.0 Hz, 2.0 Hz), 3.28 (pent, 1 H, *J* = 8.4 Hz), 2.60 (ddd, 2 H, *J* = 10.8 Hz, 9.2 Hz, 2.0 Hz), 2.44 (ddd, 2 H, *J* = 10.8 Hz, 8.4 Hz, 2.4 Hz), 1.60 (s, 3 H); ^{13}C NMR

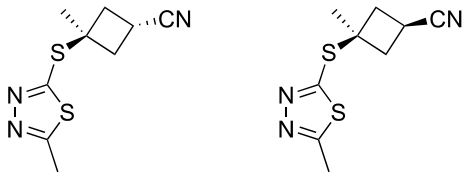
(100 MHz, $CDCl_3$) δ 162.5 ($^1J_{CF}$ = 248 Hz), 134.6 ($^3J_{CF}$ = 7 Hz), 130.4 ($^4J_{CF}$ = 3 Hz), 130.3 ($^3J_{CF}$ = 9 Hz), 122.0, 121.3 ($^2J_{CF}$ = 21 Hz), 115.8 ($^2J_{CF}$ = 21 Hz), 48.4, 39.6, 29.6, 16.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ –111.7; HRMS (ESI)$^+$ calcd for $C_{12}H_{13}NSF$ [M+H] 222.0723, found 222.0753. *cis*-**2-71**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (td, 1 H, *J* = 8.0 Hz, 6.0 Hz), 7.22 (dt, 1 H, *J* = 7.6 Hz, 1.2 Hz), 7.15 (dt, 1 H, *J* = 8.8 Hz, 2.0 Hz), 7.08 (tdd, 1 H, *J* = 8.4 Hz, 2.8 Hz, 0.8 Hz), 3.09 (pent, 1 H, *J* = 8.8 Hz), 2.67 (ddd, 2 H, *J* = 10.4 Hz, 8.8 Hz, 2.0 Hz), 2.43 (ddd, 2 H, *J* = 10.8 Hz, 8.8 Hz, 2.0 Hz), 1.50 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5 ($^1J_{CF}$ = 248 Hz), 134.2 ($^3J_{CF}$ = 8 Hz), 130.8 ($^4J_{CF}$ = 3 Hz), 130.4 ($^3J_{CF}$ = 8 Hz), 121.8 ($^2J_{CF}$ = 22 Hz), 121.3, 116.0 ($^2J_{CF}$ = 21 Hz), 46.4, 40.0, 26.9, 16.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ –111.7.



trans **2-72** *cis* **2-72**

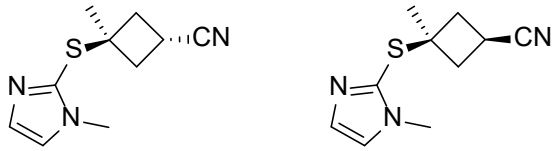
3-Methyl-3-(pyridin-2-ylthio)cyclobutane-1-carbonitrile (2-72). Prepared according to General Procedure F from 2-mercaptopyridine (0.093 g, 0.84 mmol), nitrile **2-37** (0.086 g, 0.92 mmol) and K_2CO_3 (0.116 g, 0.839 mmol) in MeOH (4 mL) with heating at 70 °C. Purification by chromatography on SiO_2 (25% EtOAc/hexanes) afforded *trans*-**2-72** (0.088 g, 0.43 mmol, 51%) as a colorless oil that solidified upon standing and *cis*-**2-72** (0.024 g, 0.12 mmol, 14%) as a colorless oil. *trans*-**2-72**: Mp 55–57 °C; IR (ATR) 2957, 2240, 1578, 1564, 1457, 1416, 1111, 760, 723 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (dt, 1 H, *J* = 4.0 Hz, 0.8 Hz), 7.48 (ddt, 1 H, *J* = 7.6 Hz, 2.0 Hz, 0.8 Hz), 7.14 (dd, 1 H, *J* = 8.4 Hz, 0.8 Hz), 7.04-6.98 (m, 1 H), 3.38 (pent, 1 H, *J* = 8.4 Hz), 2.91-2.81 (m, 2 H), 2.60-2.51 (m, 2 H), 1.79 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 149.6, 136.1, 123.9, 122.4, 120.1, 47.9, 40.0, 29.8, 17.4; MS (ESI)$^+$ *m/z* 205, 171, 144, 112 (5); HRMS (ESI)$^+$ calcd for $C_{11}H_{13}N_2S$ [M+H] 205.0799, found 205.0781. *cis*-**2-72**: ^{1}H NMR (400

MHz, $CDCl_3$) δ 8.48 (d, 1 H, *J* = 4.0 Hz), 7.51 (td, 1 H, *J* = 7.6 Hz, 1.2 Hz), 7.16 (d, 1 H, *J* = 8.0 Hz), 7.03 (t, 1 H, *J* = 6.0 Hz), 3.19 (pent, 1 H, *J* = 8.0 Hz), 3.13-3.04 (m, 2 H), 2.58 (ddd, 2 H, *J* = 10.4 Hz, 8.8 Hz, 2.0 Hz), 1.69 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 149.6, 136.2, 123.9, 122.4, 122.0, 45.8, 40.0, 27.7, 17.3.



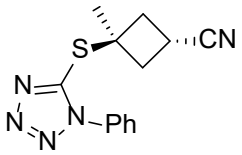
trans-**2-73** *cis*-**2-73**

3-Methyl-3-((5-methyl-1,3,4-thiadiazol-2-yl)thio)cyclobutane-1-carbonitrile (**2-73)**. Prepared according to General Procedure F from 5-methylthiadiazole-2-thiol (0.084 g, 0.63 mmol), nitrile **2-37** (0.065 g, 0.70 mmol, 1.1 eq), and K_2CO_3 (0.096 g, 0.70 mmol, 1.1 eq) in MeOH (3 mL) with heating at 60 °C. Purification by chromatography on SiO_2 (10-20% EtOAc/hexanes) afforded the less polar *trans*-**2-73** (0.075 g, 0.33 mmol, 52%) and the more polar *cis*-**2-37** (0.015 g, 0.07 mmol, 10%), both as colorless oils. ***trans*-2-73**: IR (ATR) 2963, 2239, 1426, 1383, 1190, 1039, 911, 726 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.37 (pent, 1 H, *J* = 8.8 Hz), 2.87 (ddd, 2 H, *J* = 12.0 Hz, 9.2 Hz, 2.4 Hz), 2.72 (s, 3 H), 2.56 (ddd, 2 H, *J* = 11.6 Hz, 8.4 Hz, 2.8 Hz), 1.77 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.2, 161.8, 121.6, 50.7, 39.7, 29.3, 16.9, 15.5; HRMS $(ESI)^+$ calcd for $C_9H_{12}N_3S_2$ [M+H] 226.0473, found 226.0479. ***cis*-2-73**: ^1H NMR (400 MHz, $CDCl_3$) δ 3.19 (pent, 1 H, *J* = 8.8 Hz), 2.95-2.85 (m, 2 H), 2.75 (s, 3 H), 2.66 (ddd, 2 H, *J* = 11.2 Hz, 8.8 Hz, 2.4 Hz), 1.75 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.3, 161.7, 121.2, 48.4, 40.2, 27.1, 17.2, 15.6.



2-74, 5:1 anti:syn (inseparable)

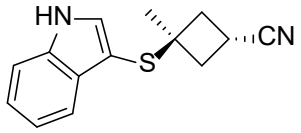
3-Methyl-3-((1-methyl-1*H*-imidazol-2-yl)thio)cyclobutane-1-carbonitrile (2-74). Prepared according to General Procedure F from bicyclobutane **2-37** (0.070 g, 0.75 mmol, 1.20 eq), 1-methyl-2-mercaptoimidazole (0.072 g, 0.063 mmol) and K_2CO_3 (0.095 g, 0.69 mmol, 1.10 eq) in MeOH (3 mL) with heating at 60 °C. Purification by chromatography on SiO_2 (5% MeOH/CH_2Cl_2) afforded **2-74** (0.097 g, 0.467 mmol, 75%) as a colorless oil. The material is an inseparable 5:1 mixture of *trans* (major) and *cis* diastereomers: *trans*-**2-74**: IR (ATR) 3378, 2945, 2337, 1637, 1453, 1310, 1214, 1112, 753 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.14 (d, 1 H, *J* = 1.2 Hz), 7.04 (d, 1 H, *J* = 1.2 Hz), 3.71 (s, 3 H), 3.28 (pent, 1 H, *J* = 8.4 Hz), 2.82 (ddd, 2 H, *J* = 11.2 Hz, 9.2 Hz, 2.8 Hz), 2.44 (ddd, 2 H, *J* = 10.8 Hz, 8.0 Hz, 2.8 Hz), 1.56 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.8, 130.1, 123.3, 122.1, 50.8, 39.6, 34.0, 29.6, 16.6; HRMS $(ESI)^+$ calcd for $C_{10}H_{14}N_3S$ [M+H] 208.0908, found 208.0902.



trans **2-75**

***trans*-3-Methyl-3-((1-phenyl-1*H*-tetrazol-5-yl)thio)cyclobutane-1-carbonitrile (2-75)**. Prepared according to General Procedure F from bicyclobutane **2-37** (0.064 g, 0.69 mmol, 1.1 eq), *N*-phenyl 2-mercaptotetrazole (0.112 g, 0.063 mmol) and K_2CO_3 (0.087 g, 0.63 mmol, 1.0 eq) in CF_3CH_2OH (3 mL) with heating at 60 °C. After stirring at 60 °C for 13 h, the reaction was concentrated and purified by chromatography on SiO_2 (30% EtOAc/hexanes) to afford tetrazole **2-75** (0.032 g, 0.118 mmol, 19%) as a colorless solid: Mp 119–120 °C; IR (ATR) cm^{-1} 3064, 2962,

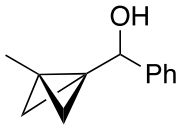
2240, 1596, 1499, 1459, 1387, 1239, 1015, 762, 695; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61-7.50 (m, 5 H), 3.42 (pent, 1 H, *J* = 8.8 Hz), 2.99 (ddd, 2 H, *J* = 12.0 Hz, 9.6 Hz, 2.4 Hz), 2.68 (ddd, 2 H, *J* = 11.6 Hz, 8.4 Hz, 2.8 Hz), 1.89 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.2, 133.4, 130.4, 129.9, 124.2, 121.6, 50.7, 39.9, 29.4, 17.2; MS $(ESI)^+$ *m/z* 272, 262, 179, 151, 83; HRMS $(ESI)^+$ calcd for $C_{13}H_{14}N_5S$ [M+H] 272.0964, found 272.0954.



trans **2-76**

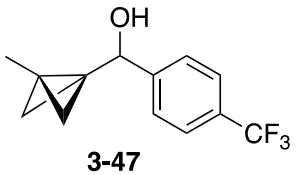
3-((1*H*-Indol-3-yl)thio)-3-methylcyclobutane-1-carbonitrile (2-76). Prepared according to General Procedure F from indole-3-thiol (0.327 g, 2.20 mmol) nitrile **2-37** (0.225 g, 2.42 mmol, 1.10 eq), and K_2CO_3 (0.304 g, 2.19 mmol, 1.00 eq) in MeOH (10 mL). Purification by chromatography on SiO_2 (10-20% EtOAc/hexanes) afforded *trans*-**2-76** (0.218 g, 0.900 mmol, 41%) as a colorless solid in ~80-90% purity. The *cis* isomer co-eluted with several impurities and was not characterized. ***trans*-2-76**: IR (ATR) 3321, 2956, 2245, 1492, 1452, 1416, 1266, 1110, 1009, 739 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.71 (s, 1 H), 7.82 (d, 1 H, *J* = 6.6 Hz), 7.51-7.46 (m, 1 H), 7.37 (d, 1 H, *J* = 2.7 Hz), 7.34-7.23 (m, 2 H), 3.32-3.16 (m, 1 H), 2.61 (ddd, 2 H, *J* = 11.4 Hz, 9.6 Hz, 1.8 Hz), 2.35 (ddd, 2 H, *J* = 11.1 Hz, 8.1 Hz, 2.1 Hz), 1.57 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.2, 131.7, 130.5, 122.9, 122.7, 121.0, 119.4, 111.8, 103.2, 49.0, 39.3, 29.7, 16.6; HRMS $(ESI)^+$ calcd for $C_{14}H_{15}N_2S$ [M+H] 243.0951, found 243.0940.

5.4 CHAPTER 3 EXPERIMENTAL PART



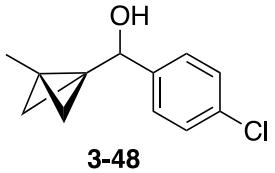
3-45

General Procedure G (Preparation of Bicyclo[1.1.0butyl alcohols/amides): (3-Methylbicyclo[1.1.0]butan-1-yl)(phenyl)methanol (3-45).[73b] A solution of 1-chloromethyl-1-methyl-2,2-dibromocyclopropane (10 g, 38 mmol) in Et_2O (50 mL) was cooled to –78 °C under N_2. A solution of MeLi (25 mL, 38 mmol, c = 1.3 M in Et_2O) was added via syringe over 15 min. After 1 h at –78 °C, a solution of *t*-BuLi (25 mL, 38 mmol, c = 1.5 M in pentane) was added via syringe over 15 min. The reaction mixture was stirred for an additional 1 h at –78 °C, then neat benzaldehyde (1.5 mL, 15 mmol) was added in one portion. The reaction mixture was quenched at –78 °C with sat aq NH_4Cl (20 mL), warmed up to rt, and extracted (3 x 50 mL) with Et_2O. The combined organic layers were washed with water (50 mL), brine (50 mL), dried (Na_2SO4), and concentrated. The crude product was purified by Kugelrohr distillation (1 mmHg, fractions collected at 105-115 °C oven temperature) to afford alcohol **3-45** (2.13 g, 12.2 mmol, 80 %) as colorless liquid: IR (ATR) 3383, 1493, 1450, 1088 cm; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42-7.26 (m, 5 H), 5.05 (d, *J* = 4.2 Hz, 1 H), 1.96 (d, 1 H, *J* = 4.2 Hz,), 1.48 (d, 1 H, *J* = 6.6 Hz,), 1.46 (s, 3 H), 1.13 (d, *J* = 6.6 Hz, 1 H), 0.73 (s, 1 H), 0.64 (s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.1, 128.2, 127.5, 126.5, 73.3, 32.8, 32.6, 16.1, 11.1, 10.5; MS (EI) *m/z* 174 (71), 159 (66), 141 (53), 115 (76), 105 (100), 91 (77), 77 (90); HRMS (EI) calcd for $C_{12}H_{14}O$ [M^+] 174.1045, found 174.1042.



3-47

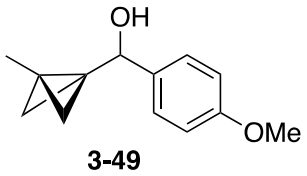
(3-Methylbicyclo[1.1.0]butan-1-yl)(4-(trifluoromethyl)phenyl)methanol (3-47). Prepared according to General Procedure G using 1-chloromethyl-1-methyl-2,2-dibromocyclopropane (2.00 g, 7.62 mmol, 2.50 eq), MeLi (4.7 mL, 7.6 mmol, 2.5 eq), *t*-BuLi (4.5 mL, 7.6 mmol, 2.5 eq), and *p*-trifluoromethylbenzaldehyde (0.42 mL, 3.0 mmol, 1.0 eq). Purification by chromatography on SiO_2 (15% EtOAc/hexanes) afforded **3-47** (0.472 g, 1.95 mmol, 64%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, 2 H, J = 8.0 Hz), 7.50 (d, 2 H, J = 8.0 Hz), 5.11 (d, 1 H, J = 4.0 Hz), 2.05 (d, 1 H, J = 3.2 Hz), 1.47 (s, 3 H), 1.10 (d, 1 H, J = 6.4 Hz), 0.71 (s, 1 H), 0.64 (s, 1 H); ^{13}C NMR (100MHz, $CDCl_3$) δ 147.0, 129.8 (q, $^2J_{CF}$ = 32 Hz), 126.8, 125.5, 125.3, 122.8, 72.8, 32.9, 32.6, 16.4, 11.3, 11.2.



3-48

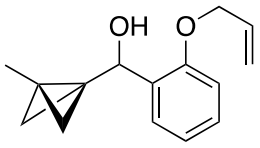
(4-Chlorophenyl)(3-methylbicyclo[1.1.0]butan-1-yl)methanol (3-48). Prepared according to General Procedure G using 1-chloromethyl-1- methyl-2,2-dibromocyclopropane (1.20 g, 4.57 mmol, 2.50 eq), MeLi (2.9 mL, 4.6 mmol, 2.5 eq), *t*-BuLi (2.7 mL, 4.6 mmol, 2.5 eq) and *p*-chlorobenzaldehyde (0.257 g, 1.83 mmol) in diethyl ether (8 mL). Purification by chromatography on SiO_2 afforded **3-48** (0.215 g, 1.03 mmol, 56%) as a colorless oil: IR (ATR) 3358, 2923, 1489, 1091, 1013, 967, 815 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (s, 4 H), 5.02 (d, 1 H, J = 4.0 Hz), 1.97 (d, 1 H, J = 3.6 Hz), 1.44 (d, 1 H, J = 6.0 Hz) 1.44 (s, 3 H), 1.09 (d, 1 H, J = 6.4 Hz), 0.70 (s, 1 H), 0.62 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.6, 133.3, 128.5, 127.9, 72.9, 32.8, 32.6,

16.3, 11.2, 11.0; MS (ESI^+) 191 (70), 177 (100), 146 (30), 133 (90); HRMS (ESI^+) calcd for $C_{12}H_{12}Cl$ [M+H–H_2O] 191.0628, found 191.0622.



3-49

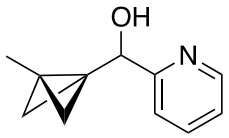
(4-Methoxyphenyl)(3-methylbicyclo[1.1.0]butan-1-yl)methanol (3-49). Prepared according to General Procedure G using 1-chloromethyl-1-methyl-2,2-dibromocyclopropane (2.00 g, 7.62 mmol, 2.50 eq), MeLi (4.8 mL, 7.6 mmol, 2.5 eq), *t*-BuLi (4.5 mL, 7.6 mmol, 2.5 eq), and *p*-anisaldehyde (0.37 mL, 3.0 mmol, 1.0 eq). Purification by chromatography on SiO_2 afforded **3-49** (0.284 g, 1.30 mmol, 46%) as a colorless oil: IR (ATR) 3393, 2921, 1612, 1511, 1246, 1172, 1034, 832 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.31 (d, 2 H, J = 8.7 Hz), 6.88 (d, 2 H, J = 8.7 Hz), 4.38 (d, 1 H, J = 3.9 Hz), 3.81 (s, 3 H), 1.86 (d, 1 H, J = 3.9 Hz), 1.47 (d, 1 H, J = 6.6 Hz), 1.43 (s, 3 H), 1.12 (d, 1 H, J = 6.6 Hz), 0.71 (s, 1 H), 0.62 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 135.6, 127.8, 113.9, 73.1, 55.3, 33.0, 32.6, 16.2, 11.2, 10.4; MS [ESI^+] *m/z* 187 (100), 172 (40), 139 (10), 121 (5); HRMS [ESI^+] *m/z* calcd for $C_{13}H_{15}O$ [M+H–H_2O] 187.1117, found 187.1117.



3-50

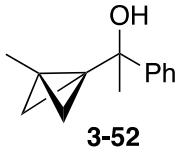
(2-(Allyloxy)phenyl)(3-methylbicyclo[1.1.0]butan-1-yl)methanol (3-50). Prepared according to General Procedure G using 1-chloromethyl-1-methyl-2,2-dibromocyclopropane (1.21 g, 4.62 mmol, 2.50 eq), MeLi (2.9 mL, 4.6 mmol, 2.5 eq), *t*-BuLi (2.7 mL, 4.6 mmol, 2.5 eq), and a solution of *O*-allylsalicyaldehyde (0.300 g, 1.85 mmol, 1.00 eq) in THF (1 mL). Purification by chromatography on SiO_2 afforded **3-50** (0.154 g, 0.669 mmol, 36%) as a colorless oil: IR (ATR)

3418, 2920, 1601, 1489, 1454, 1237, 998, 753 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.38 (dd, 1 H, *J* = 7.5 Hz, 1.8 Hz), 7.22 (td, 1 H, *J* = 7.5 Hz, 1.5 Hz), 6.96 (app t, 1 H, *J* = 7.2 Hz), 6.87 (d, 1 H, *J* = 8.1 Hz), 6.06, 5.42, 5.30 (ABX, 3 H, J_{AB} = 1.5 Hz, J_{AX} = 15.9 Hz, J_{BX} = 10.5 Hz), 5.22 (d, 1 H, *J* = 6.6 Hz), 4.58 (dt, 2 H, *J* = 5.1 Hz, 1.5 Hz), 2.90 (d, 1 H, *J* = 6.6 Hz), 1.51 (d, 1 H, *J* = 6.3 Hz), 1.42 (s, 3 H), 1.12 (d, 1 H, *J* = 6.6 Hz), 0.73 (s, 1 H), 0.64 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6, 133.0, 131.6, 128.5, 128.2, 120.9, 117.7, 111.8, 70.0, 68.9, 33.4, 32.8, 15.3, 11.1, 10.7; MS [ESI^+] *m/z* 213 (100), 172 (35), 131 (15), 118 (20); HRMS [ESI^+] calcd for $C_{15}H_{17}O$ [M+H–H_2O] 213.1274, found 213.1273.



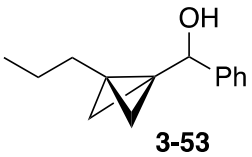
3-51

(3-Methylbicyclo[1.1.0]butan-1-yl)(pyridin-2-yl)methanol (3-51). Prepared according to General Procedure G from 1-chloromethyl-1-methyl-2,2-dibromocyclopropane (1.50 g, 5.72 mmol), MeLi (3.6 mL, 5.7 mmol, c = 1.6 M in Et_2O), *t*-BuLi (3.4 mL, 5.7 mmol, c = 1.7 M in pentane), and 2-pyridinecarboxaldehyde (0.22 mL, 2.3 mmol) in Et_2O (12 mL). Purification by chromatography on SiO_2 (15% EtOAc/hexanes) afforded alcohol **3-51** (0.198 g, 1.13 mmol, 49%) as a yellow oil: ^1H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, 1 H, *J* = 4.4 Hz), 7.70 (td, 1 H, *J* = 7.6 Hz, 1.6 Hz), 7.35 (d, 1 H, *J* = 8.0 Hz), 7.21 (dd, 1 H, *J* = 6.8 Hz, 5.2 Hz), 5.01 (d, 1 H, *J* = 4.0 Hz), 4.45 (d, 1 H, *J* = 4.0 Hz), 1.58 (s, 3 H), 1.47 (d, 1 H, *J* = 6.4 Hz), 1.35 (d, 1 H, *J* = 6.4 Hz), 0.71 (s, 1 H), 0.53 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3, 148.0, 136.6, 122.4, 121.0, 71.1, 34.1, 31.3, 16.1, 10.5.



3-52

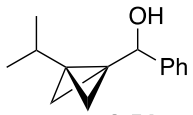
1-(3-Methylbicyclo[1.1.0]butan-1-yl)-1-phenylethan-1-ol (3-52). Prepared according to General Procedure G from 1-chloromethyl-1-methyl-2,2-dibromocyclopropane (2.00 g, 7.62 mmol, 2.50 eq), MeLi (4.8 mL, 7.6 mmol, c = 1.6 M in Et_2O), *t*-BuLi (4.5 mL, 7.6 mmol, c = 1.7 M in pentane) and acetophenone (0.36 mL, 3.0 mmol). Purification by chromatography on SiO_2 (15% EtOAc/hexanes) to afforded **3-52** (0.440 g, 2.34 mmol, 77%) as a colorless oil: IR (ATR) 3432, 2921, 1446, 1372, 1088, 961, 760, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, 2 H, *J* = 7.6 Hz), 7.34 (t, 2 H, *J* = 7.6 Hz), 7.25 (t, 1 H, *J* = 7.2 Hz), 1.89 (s, 1 H), 1.61 (s, 3 H), 1.60 (s, 3 H), 1.34 (d, 1 H, *J* = 6.8 Hz), 1.26 (d, 1 H, *J* = 6.8 Hz), 0.58 (s, 1 H), 0.47 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.0, 128.0, 126.8, 125.2, 73.9, 32.2, 30.3, 28.6, 20.7, 12.6, 10.8; MS [ESI^+] *m/z* 171 (60), 154 (30), 143 (100), 129 (50); HRMS [ESI^+] *m/z* calcd for $C_{13}H_{15}$ [M+H–H_2O] 171.1174, found 171.1169.



3-53

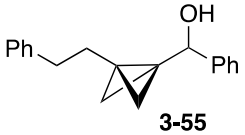
Phenyl(3-propylbicyclo[1.1.0]butan-1-yl)methanol (3-53). Prepared according to General Procedure G using the corresponding tribromide (2.03 g, 6.06 mmol, 2.54 eq), MeLi (3.8 mL, 6.1 mmol, c = 1.6 M in Et_2O), *t*-BuLi (3.6 mL, 6.1 mmol, c = 1.7 M in pentane), and benzaldehyde (0.25 mL, 2.4 mmol) in Et_2O (15 mL). Purification by chromatography on SiO_2 (15-25% EtOAc/hexanes) afforded alcohol **3-53** (0.165 g, 0.816 mmol, 34% over 3 steps) as a colorless oil: IR (ATR) 3353, 2926, 1453, 1085, 1002, 964, 754, 698 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.44-7.27 (m, 5 H), 5.05 (d, 1 H, *J* = 3.9 Hz), 1.93 (d, 1 H, *J* = 4.2 Hz), 1.80-1.59 (m, 2 H), 1.52-1.38

(m, 2 H), 1.48 (d, 1 H, J = 6.6 Hz), 1.14 (d, 1 H, J = 6.6 Hz), 0.95 (t, 3 H, J = 7.2 Hz), 0.68 (s, 1 H), 0.61 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 128.4, 128.3, 127.6, 127.1, 126.6, 73.4, 31.9, 31.5, 28.0, 22.7, 16.7, 15.0, 14.0; MS (ESI)$^+$ *m/z* 185 (75), 143 (90), 129 (100); HRMS (ESI)$^+$ *m/z* calcd for $C_{14}H_{17}$ [M+H–H_2O] 185.1325, found 185.1325.



3-54

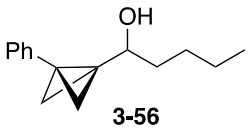
(3-Isopropylbicyclo[1.1.0]butan-1-yl)(phenyl)methanol (3-54). Prepared according to General Procedure G using from the corresponding tribromide (3.30 g, 9.86 mmol, 2.17 eq), MeLi (7.1 mL, 11.4 mmol, c = 1.6 M in Et_2O), *t*-BuLi (6.7 mL, 11.4 mmol, c = 1.7 M in pentane), and benzaldehyde (0.46 mL, 4.5 mmol) in Et_2O (20 mL). Purification by chromatography on SiO_2 (15-25% EtOAc/hexanes) afforded alcohol **3-54** (0.372 g, 1.84 mmol, 40%) as a colorless oil: IR (ATR) 3379, 2959, 1453, 1083, 1002, 963, 891, 751, 698 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.27 (m, 5 H), 5.12 (d, 1 H, J = 4.0 Hz), 2.04 (pent, 1 H, J = 6.8 Hz), 1.89 (d, 1 H, J = 4.4 Hz), 1.51 (d, 1 H, J = 6.8 Hz), 1.18 (d, 1 H, J = 6.8 Hz), 1.01 (d, 3 H, J = 6.8 Hz), 0.95 (d, 3 H, J = 6.8 Hz), 0.53 (s, 1 H), 0.48 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 128.4, 127.7, 126.6, 72.7, 29.3, 28.3, 24.6, 21.8, 21.2, 18.8; MS (ESI)$^+$ *m/z* 203, 201 (20), 185 (100), 157 (3); HRMS (ESI)$^+$ *m/z* cald for $C_{14}H_{19}O$ [M+H] 203.1430, found 203.1433.



3-55

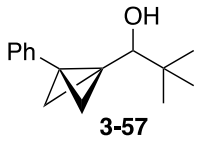
(3-Phenethylbicyclo[1.1.0]butan-1-yl)(phenyl)methanol (3-55). Prepared using General Procedure G from the corresponding tribromide (0.968 g, 2.44 mmol, 2.00 eq), MeLi (1.5 mL, 2.4 mmol, c = 1.6 M in Et_2O), *t*-BuLi (1.4 mL, 2.4 mmol, c = 1.7 M in pentane), and benzaldehyde (0.12 mL, 1.2 mmol) in Et_2O (8 mL). Purification by chromatography on SiO_2 (15-25%

EtOAc/hexanes) afforded alcohol **3-55** (0.153 g, 0.579 mmol, 47%) as a yellow tinted oil: IR (ATR) 3376, 3026, 2922, 1603, 1495, 1453, 1013, 699 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.31 (m, 4 H), 7.30-7.26 (m, 3 H), 7.21-7.15 (m, 3 H), 5.02 (d, 1 H, *J* = 4.4 Hz), 2.82-2.66 (m, 2 H), 2.18-2.08 (m, 1 H), 2.07-1.97 (m, 1 H), 1.86 (d, 1 H, *J* = 4.0 Hz), 1.48 (d, 1 H, *J* = 6.4 Hz), 1.18 (d, 1 H, *J* = 6.8 Hz), 0.67 (s, 1 H), 0.60 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 142.1, 128.5, 128.4, 128.3, 127.7, 126.5, 125.8, 73.2, 35.7, 31.8, 31.4, 28.2, 17.5, 15.1.



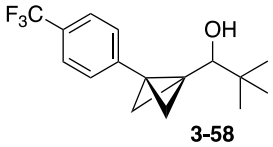
3-56

1-(3-Phenylbicyclo[1.1.0]butan-1-yl)pentan-1-ol (3-56). Prepared according to General Procedure G from the corresponding tribromide (0.957 g, 2.59 mmol, 2.50 eq), MeLi (1.6 mL, 2.6 mmol, c = 1.62 M in Et_2O), *t*-BuLi (1.5 mL, 2.6 mmol, c = 1.7 M in pentane), and valeraldehyde (0.11 mL, 1.0 mmol, 1.0 eq) in Et_2O (6 mL). Purification by chromatography on SiO_2 (10% EtOAc/hexanes) afforded alcohol **3-56** (0.181 g, 0.837 mmol, 81%) as a yellow-tinted oil: IR (ATR) 3396, 2929, 1602, 1446, 1104, 1026, 761, 695 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.21 (m, 4 H), 7.14 (tt, 1 H, *J* = 6.8 Hz, 1.6 Hz), 3.81 (ddd, 1 H, *J* = 4.0 Hz, 4.0 Hz, 4.0 Hz), 2.35 (d, 1 H, *J* = 6.8 Hz), 2.19 (dd, 1 H, *J* = 6.8 Hz, 0.8 Hz), 1.67-1.21 (m, 6 H), 1.15 (s, 1 H), 1.13 (d, 1 H, *J* = 4.0 Hz), 1.09 (s, 1 H), 0.85 (t, 3 H, *J* = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.0, 128.6, 125.3, 125.2, 125.1, 70.2, 36.3, 12.2, 30.2, 27.6, 22.5, 17.4, 14.0; MS $(ESI)^+$ *m/z* 217 (10), 199 (100), 177 (15), 143 (40), 117 (10); HRMS $(ESI)^+$ *m/z* calcd for $C_{15}H_{21}O$ [M+H] 217.1587, found 217.1586.



3-57

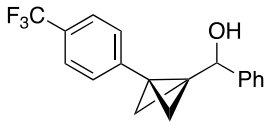
2,2-Dimethyl-1-(3-phenylbicyclo[1.1.0]butan-1-yl)propan-1-ol (3-57). Prepared according to General Procedure G from the corresponding tribromide (2.24 g, 6.05 mmol, 1.75 eq), MeLi (4.31 mL, 6.91 mmol, c = 1.6 M in Et_2O), *t*-BuLi (4.07 mL, 6.91 mmol, c = 1.7 M in pentane), and neat trimethylacetaldehyde (0.40 mL, 3.5 mmol) in Et_2O (12 mL). Purification by chromatography on SiO_2 (25% EtOAc/hexanes) followed by a second chromatography on neutral Al_2O_3 (10% EtOAc/hexanes) to afford alcohol **3-57** (0.282 g, 1.30 mmol, 38%) as a light yellow oil: IR (ATR) 3562, 2951, 2866, 1602, 1479, 1362, 1107, 1007, 950, 773, 695 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.37-7.23 (m, 4 H), 7.21-7.13 (m, 1 H), 3.41 (d, 1 H, *J* = 3.3 Hz), 2.51 (d, 1 H, *J* = 6.3 Hz), 2.20 (d, 1 H, *J* = 6.3 Hz), 1.28 (s, 1 H), 1.13 (s, 1 H), 1.01 (s, 9 H), 0.94 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.4, 128.7, 125.2, 125.1, 77.7, 36.6, 35.2, 29.6, 25.9, 25.7, 14.1; MS $(ESI)^+$ *m/z* 217, 215, 213, 247 (20), 231 (30), 215 (30), 199 (100), 143 (20); HRMS $(ESI)^+$ *m/z* calcd for $C_{15}H_{21}O$ [M+H] 217.1587, found 217.1586.



3-58

2,2-Dimethyl-1-(3-(4-(trifluoromethyl)phenyl)bicyclo[1.1.0]butan-1-yl)propan-1-ol (3-58). Prepared according to General Procedure G from the corresponding tribromide (0.822 g, 1.88 mmol, 2.00 eq), MeLi (1.2 mL, 1.9 mmol, c = 1.62 M in Et_2O), *t*-BuLi (1.1 mL, 1.9 mmol, c = 1.7 M in pentane), and trimethylacetaldehyde (0.11 mL, 0.94 mmol) in Et_2O (5 mL). Purification by two iterations of chromatography on SiO_2 (5-10% EtOAc/hexanes) afforded alcohol **3-58** (0.071 g, 0.25 mmol, 27%) as a colorless solid: Mp 80–84 °C; IR (ATR) 2955, 1614, 1324, 1163, 1109,

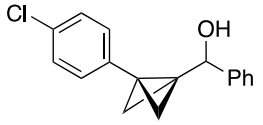
1062, 1013, 951, 841, 688 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, 2 H, J = 8.4 Hz), 7.32 (d, 2 H, J = 8.4 Hz), 3.34 (d, 1 H, J = 4.4 Hz), 2.53 (d, 1 H, J = 6.4 Hz), 2.21 (dd, 1 H, J = 6.8 Hz, 1.2 Hz), 1.34 (s, 1 H), 1.18 (s, 1 H), 1.01 (s, 1 H), 0.98 (s, 9 H), 0.95 (d, 1 H, J = 4.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 129.4, 126.9 (q, $^2J_{CF}$ = 32 Hz), 125.4, 125.3 (q, $^3J_{CF}$ = 3 Hz), 124.4 (q, $^1J_{CF}$ = 270 Hz), 80.8, 36.8, 35.5, 30.2, 28.1, 25.8, 14.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.1; MS $(ESI)^+$ *m/z* 267 (100), 189 (40), 137 (50); HRMS $(ESI)^+$ *m/z* calcd for $C_{16}H_{18}F_3$ [M+H–H_2O] 267.1361, found 267.1354.



3-59

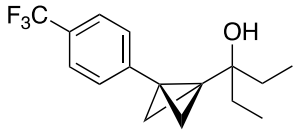
Phenyl(3-(4-(trifluoromethyl)phenyl)bicyclo[1.1.0]butan-1-yl)methanol (3-59). Prepared according to General Procedure G the corresponding tribromide (1.49 g, 3.41 mmol, 2.00 eq), MeLi (2.1 mL, 3.4 mmol, c = 1.6 M in Et_2O), *t*-BuLi (2.0 mL, 341 mmol, c = 1.7 M in pentane), and benzaldehyde (0.17 mL, 1.7 mmol, 1.0 eq) in Et_2O (8 mL). Purification by chromatography on SiO_2 (15% EtOAc/hexanes) afforded alcohol **3-59** (0.281 g, 54%) as a yellow tinted solid. ^1H NMR revealed that the material was contaminated with minor impurities, so the material was recrystallized from hexanes (~20 mL) to afford 0.132 g (25%) of the product as light yellow crystals: Mp 99–102 °C; IR (ATR) 3327, 2922, 1617, 1324, 1106, 1065, 1006, 835 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, 2 H, J = 8.4 Hz), 7.29-7.23 (m, 3 H), 7.19 (d, 2 H, J = 8.0 Hz), 7.15-7.09 (m, 2 H), 4.85 (s, 1 H), 2.49 (d, 1 H, J = 6.8 Hz), 2.10 (dd, 1 H, J = 6.8 Hz, 0.8 Hz), 1.81 (d, 1 H, J = 2.0 Hz), 1.31 (s, 1 H), 1.25 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7, 141.3, 128.4, 128.0, 127.2 ($^2J_{CF}$ = 32 Hz), 126.5, 125.7, 125.1 ($^3J_{CF}$ = 4 Hz), 124.5 ($^1J_{CF}$ = 270), 123.1, 72.6,

32.6, 31.7, 29.8, 18.4; MS (ESI)$^+$ *m/z* 287 (100), 238 (10), 200 (10), 159 (10); HRMS (ESI)$^+$ *m/z* calcd for $C_{18}H_{14}F_3$ [M+H–H_2O] 287.1048, found 287.1038.



3-60

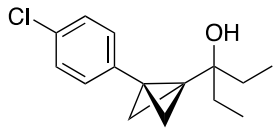
(3-(4-Fhlorophenyl)bicyclo[1.1.0]butan-1-yl)(phenyl)methanol (3-60). Prepared according to General Procedure G from the corresponding tribromide (0.860 g, 2.13 mmol, 2.00 eq), MeLi (1.3 mL, 2.1 mmol, c = 1.6 M in Et_2O), *t*-BuLi (1.3 mL, 2.1 mmol, c = 1.7 M in pentane), and benzaldehyde (0.11 mL, 1.1 mmol, 1.0 eq) in Et_2O (5 mL). Purification by chromatography on SiO_2 (10-25% EtOAc/hexanes) afforded alcohol **3-60** (0.193 g, 0.713 mmol, 67%) as a red-tinted oil: ^{1}H NMR (400 MHz, $CDCl_3$) 7.30-7.24 (m, 3 H), 7.22, 7.04 (AA'BB', 4 H), 7.17-7.12 (m, 2 H), 4.85 (s, 1 H), 2.40 (d, 1 H, *J* = 6.4 Hz), 2.01 (d, 1 H, *J* = 6.8 Hz), 1.76 (s, 1 H), 1.24 (s, 1 H), 1.18 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.8, 135.1, 130.9, 128.4, 128.3, 127.9, 126.9, 126.5, 72.7, 32.4, 31.3, 28.3, 18.0, 14.2.



3-61

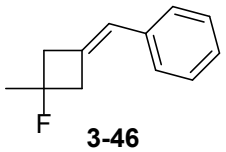
3-(3-(4-(Trifluoromethyl)phenyl)bicyclo[1.1.0]butan-1-yl)pentan-3-ol (3-61). Prepared according to General Procedure G from the corresponding tribromide (0.911 g, 2.09 mmol, 2.50 eq), MeLi (1.3 mL, 2.1 mmol, c = 1.6 M in Et_2O), *t*-BuLi (1.2 mL, 2.1 mmol, c = 1.7 M in pentane), and 3-pentanone (0.09 mL, 0.83 mmol, 1.0 eq) in Et_2O (5 mL). Purification by chromatography on SiO_2 (15% EtOAc/hexanes) afforded alcohol **3-61** (0.149 g, 0.524 mmol, 63%) (OH not visible) as a colorless oil: IR (ATR) 3469, 2971, 1616, 1321, 1162, 1106, 841 cm^{-1}; ^{1}H NMR (400 MHz,

$CDCl_3$) δ 7.51 (d, 2 H, J = 8.4 Hz), 7.37 (d, 2 H, J = 8.0 Hz), 2.31 (s, 2 H), 1.65, 1.40, 0.85 (ABX_3, 2+2+6 H, J_{AB} = 7.6 Hz, ∂_{AB} = 0.15 ppm), 1.02 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 126.9 ($^2J_{CF}$ = 32 Hz), 126.0, 125.3 ($^3J_{CF}$ = 4 Hz), 124.5 ($^1J_{CF}$ = 269), 74.5, 34.1, 30.6, 30.5, 19.1, 7.9; MS (ESI)$^+$ *m/z* 267 (100), 225 (10), 173 (5); HRMS (ESI)$^+$ *m/z* calcd for $C_{16}H_{18}F_3$ [M+H-H_2O] 267.1361, found 267.1352.



3-62

3-(3-(4-Chlorophenyl)bicyclo[1.1.0]butan-1-yl)pentan-3-ol (3-62). Prepared according to General Procedure G from the corresponding tribromide (1.14 g, 2.83 mmol, 2.50 eq), MeLi (1.8 mL, 2.8 mmol, c = 1.6 M in Et_2O), *t*-BuLi (1.7 mL, 2.8 mmol, c = 1.7 M in pentane), and 3-pentanone (0.12 mL, 1.1 mmol, 1.0 eq) in Et_2O (6 mL). Purification by chromatography on SiO_2 (10% EtOAc/hexanes) afforded alcohol **3-62** (0.202 g, 0.806 mmol, 71%) as a colorless oil: IR (ATR) 3469, 2971, 1616, 1321, 1162, 1106, 841 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) (OH not visible) δ 7.25-7.17 (m, 4 H), 2.23 (s, 2 H), 1.63, 1.41, 0.84 (ABX_3, 2+2+6 H, J_{AB} = 7.6 Hz, ∂_{AB} = 0.24 ppm), 0.96 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.9, 130.6, 128.6, 127.2, 74.5, 32.3, 30.6, 30.2, 18.7, 8.0; MS (ESI)$^+$ *m/z* 233 (100), 191 (20), 167 (20), 1491 (10), 135 (40); HRMS (ESI)$^+$ *m/z* calcd for $C_{15}H_{18}Cl$ [M+H-H_2O] 233.1097, found 233.1090.



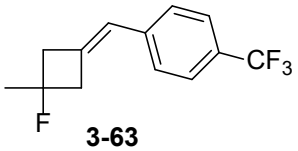
3-46

General Procedure H (Alcohol Deoxyfluorination): ((3-Fluoro-3-methylcyclobutylidene)methyl)benzene (3-46). To a suspension of KHF_2 (0.070 g, 0.90 mmol) in dichloromethane (1 mL) was added diisopropylamine (0.51 mL, 3.6 mmol, 4.0 eq) in a polypropylene reaction vessel. The suspension was cooled under N_2 to –78 °C, then pyridine • 9 HF (1.2 mL, 46 mmol HF, 51 eq HF) was added. The suspension was stirred for 5 min at –78 °C, then a solution of alcohol **3-45** (0.157 g, 0.90 mmol) in CH_2Cl_2 (1 mL) was added over ~30 s. After stirring at –78 °C for 10 min, the mixture was quenched at –78 °C with sat aq. KF (5 mL), then the reaction was warmed to rt and diluted with water (25 mL). The material was extracted with ether (2 x 20 mL). The organic layers were washed with saturated aq. $NaHCO_3$ (30 mL) and brine (30 mL), then were dried (Na_2SO_4) and concentrated. Chromatography on SiO_2 (2.5% EtOAc/hexanes) afforded methylenecyclobutane **3-46** (0.090 g, 0.51 mmol, 57%) as a colorless oil: IR (ATR) 2794, 1602, 1490, 1448, 1381, 1241, 1145, 914, 738 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.32 (dd, 2 H, J = 8.0 Hz, 7.2 Hz), 7.20 (d, 3 H, J = 7.2 Hz), 6.31 (t, 1 H, J = 2.4 Hz), 3.39 (tdd, 1 H, $^3J_{HF}$ = 18.0 Hz, J = 3.2 Hz, 3.2 Hz), 3.26 (tdd, 1 H, $^3J_{HF}$ = 18.4 Hz, J = 3.2 Hz, 3.2 Hz), 3.11-3.00 (m, 1 H), 2.95-2.84 (m, 1 H), 1.56 (d, 3 H, $^4J_{CF}$ = 21.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.4, 131.9 ($^3J_{CF}$ = 16 Hz), 128.5, 127.2, 126.5, 123.8, 123.7, 92.8 ($^1J_{CF}$ = 206 Hz), 46.1 ($^3J_{CF}$ = 24 Hz), 45.7 ($^2J_{CF}$ = 24 Hz), 24.2 ($^2J_{CF}$ = 25 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ –131.2; HRMS [ES^+] calcd for $C_{12}H_{13}F$ [M^+] 176.1001, found 175.0056.

Notes on pyridine • 9 HF: For simplicity, the pyridine • 9 HF stoichiometry was initially calculated based on a molecular formula of C_5H_6FN (molecular weight = 99.11), which is

*typically shown on data sheets for this reagent. However, it is more appropriate to consider stoichiometry in terms of equivalents of HF. The equivalents of HF can be calculated in the following manner: X mL reagent * 1.1 g/mL (density) * 0.7 (percentage HF by weight) / 20 g/mol (HF molecular weight)* * 1000 = *mmol HF. For reference, 1 mmol of pyridine • 9 HF (as calculated by a molecular weight of 99.11) = 3.5 mmol of HF.*

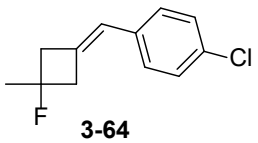
This reagent should be handled with great care using appropriate personal protective equipment. If skin contact with this reagent occurs, apply calcium gluconate gel immediately and liberally. After quenching the fluorinations with aqueous NaOH, the basicity of the aqueous layer should be confirmed by pH paper during the extraction step.



3-63

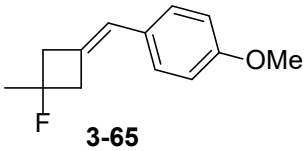
1-((3-Fluoro-3-methylcyclobutylidene)methyl)-4-(trifluoromethyl)benzene (3-63). Prepared according to General Procedure H using KHF_2 (0.051 g, 0.65 mmol, 1.0 eq), diisopropylamine (0.37 mL, 2.6 mmol, 4.0 eq), pyridine • 9 HF (1.2 mL, 46 mmol HF, 71 eq HF), and alcohol **3-47** (0.158 g, 0.652 mmol, 1.00 eq) in CH_2Cl_2 (4 mL). Purification by chromatography on SiO_2 (5% EtOAc in hexanes) afforded methylenecyclobutane **3-63** (0.073 g, 0.30 mmol, 46%) as a colorless oil: IR (ATR) 2977, 2919, 1617, 1415, 1382, 1323, 1243, 1164, 1121, 1067 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, 2 H, J = 8.5 Hz), 7.28 (d, 2 H, J = 8.0 Hz), 6.34 (t, 1 H, J = 2.0 Hz), 3.41 (ddt, 1 H, $^3J_{FH}$ = 19.5 Hz, J = 17.0 Hz, 3.0 Hz), 3.41 (ddt, 1 H, $^3J_{FH}$ = 19.0 Hz, J = 17.0 Hz, 3.0 Hz), 3.10-3.01 (m, 1 H), 2.97-2.87 (m, 1 H), 1.56 (d, 3 H, $^3J_{FH}$ = 21.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.8, 135.4 ($^3J_{CF}$ = 15 Hz), 128.2 (q, $^1J_{CF}$ = 32 Hz), 127.2, 125.6, 125.4 (q, $^2J_{CF}$ = 4 Hz), 122.9, 122.8, 92.6 (d, $^1J_{CF}$ = 207 Hz), 46.2 (d, $^2J_{CF}$ = 23 Hz), 45.8 (d, $^2J_{CF}$ = 24 Hz), 24.2 (d,

$^{2}J_{CF}$ = 25 Hz); ^{19}F NMR δ (471 MHz, $CDCl_3$) –131.4, –62.4; HRMS [ES] calcd for $C_{13}H_{12}F_4$ [M] 244.0875, found 244.0854.



3-64

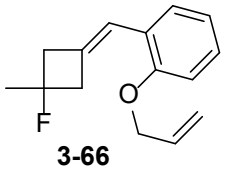
1-Chloro-4-((3-fluoro-3-methylcyclobutylidene)methyl)benzene (3-64). Prepared according to General Procedure H using KHF_2 (0.035 g, 0.45 mmol, 1.0 eq), diisopropylamine (0.25 mL, 1.8 mmol, 4.0 eq), pyridine • 9 HF (0.81 mL, 31 mmol HF, 69 eq HF), and alcohol **3-48** (0.094 g, 0.45 mmol, 1.0 eq) in CH_2Cl_2 (3 mL). Purification by chromatography on SiO_2 (5% EtOAc in hexanes) afforded methylenecyclobutane **3-64** (0.055 g, 0.26 mmol, 58%) as a colorless oil: IR (ATR) 2975, 2913, 1655, 1492, 1405, 1381, 1242, 1146, 1092, 915, 827 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27, 7.11 (AA'BB', 4 H, J_{AB} = 8.4 Hz, ∂_{AB} = 0.13 ppm), 6.26 (t, 1 H, J = 2.4 Hz), 3.36 (ddt, 1 H, $^{3}J_{HF}$ = 19.2 Hz, J = 16.4 Hz, 2.8 Hz), 3.25 (ddt, 1 H, $^{3}J_{HF}$ = 19.2 Hz, J = 16.8 Hz, 2.4 Hz), 3.07-2.96 (m, 1 H), 2.95-2.84 (m, 1 H), 1.55 (d, 3 H, $^{3}J_{HF}$ = 21.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.9, 132.7 ($^{3}J_{CF}$ = 15 Hz), 132.0, 128.6, 128.3, 122.7 ($^{4}J_{CF}$ = 7 Hz), 92.7 ($^{1}J_{CF}$ = 207 Hz), 46.1 ($^{2}J_{CF}$ = 24 Hz), 45.6 ($^{2}J_{CF}$ = 24 Hz), 24.2 ($^{2}J_{CF}$ = 25 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ –131.3; HRMS (ESI^{+}) *m/z* calcd for $C_{12}H_{11}ClF$ [M–H] 209.0533, found 209.0803.



3-65

1-((3-Fluoro-3-methylcyclobutylidene)methyl)-4-methoxybenzene (3-65). Prepared according to General Procedure H using KHF_2 (0.050 g, 0.64 mmol, 1.0 eq), diisopropylamine (0.36 mL, 2.6 mmol, 4.0 eq), pyridine • 9 HF (1.16 mL, 44.7 mmol, 69.7 eq HF), and alcohol **3-49** (0.131 g, 0.641 mmol, 1.00 eq) in CH_2Cl_2 (4 mL). Purification by chromatography on SiO_2 (5% EtOAc in

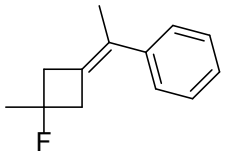
hexanes) afforded methylenecyclobutane **3-65** (0.061 g, 0.30 mmol, 46%) as a colorless oil: IR (ATR) cm^{-1} 2972, 1607, 1511, 1296, 1246, 1175, 1144, 1034, 830 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.14 (app d, 2 H, J = 8.7 Hz), 6.87 (app d, 2 H, J = 9.0 Hz), 6.25 (t, 1 H, J = 2.1 Hz), 3.81 (s, 3 H), 3.44-3.16 (m, 2 H), 3.09-2.95 (m, 1 H), 2.95-2.80 (m, 1 H), 1.56 (d, 3 H, $^{3}J_{HF}$ = 21.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 130.5, 129.2, 129.0, 128.3, 123.2 ($^{3}J_{CF}$ = 7 Hz), 114.0, 92.8 ($^{1}J_{CF}$ = 206 Hz), 55.3, 46.0 ($^{2}J_{CF}$ = 24 Hz), 45.4 ($^{2}J_{CF}$ = 23 Hz), 24.3 ($^{2}J_{CF}$ = 25 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ –131.1; MS (ESI^{+}) *m/z* 207 (100), 187 (90), 171 (20), 140 (20); HRMS (ESI^{+}) *m/z* calcd for $C_{13}H_{16}OF$ [M+H] 207.1185, found 207.1179.



3-66

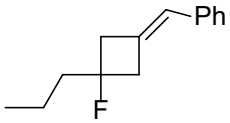
1-(Allyloxy)-2-((3-fluoro-3-methylcyclobutylidene)methyl)benzene (3-66). Prepared according to General Procedure H using KHF_2 (0.019 g, 0.24 mmol, 1.0 eq), diisopropylamine (0.14 mL, 0.96 mmol, 4.0 eq), pyridine • 9 HF (0.43 mL, 17 mmol HF, 69 eq HF), and alcohol **3-50** (0.155 g, 0.239 mmol, 1.00 eq) in CH_2Cl_2 (1.5 mL). Purification by chromatography on SiO_2 (5-20% EtOAc in hexanes) afforded methylenecyclobutane **3-66** (0.019 g, 0.082 mmol, 34%) as a colorless oil: IR (ATR) 2973, 2912, 1597, 1487, 1451, 1240, 1144, 997, 917, 748 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24-7.13 (m, 2 H), 6.92 (t, 1 H, J = 7.2 Hz), 6.86 (d, 1 H, J = 8.0 Hz), 6.69 (app s, 1 H), 6.08, 5.42, 5.29 (ABX, 3 H, J_{AB} = 1.2, J_{AX} = 17.2, J_{BX} = 10.4 Hz), 4.56 (d, 2 H, J = 4.8 Hz), 3.44-3.18 (m, 2 H), 3.05-2.85 (m, 2 H), 1.55 (d, 3 H, $^{3}J_{HF}$ = 21.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 133.5, 131.4 ($^{3}J_{CF}$ = 16 Hz), 127.5, 127.4, 126.7, 120.6, 117.9 ($^{4}J_{CF}$ = 7 Hz), 117.4, 112.2, 92.9 ($^{1}J_{CF}$ = 207 Hz), 69.2, 46.2 ($^{2}J_{CF}$ = 23 Hz), 45.7 ($^{2}J_{CF}$ = 24 Hz), 24.2 ($^{2}J_{CF}$ = 25 Hz); ^{19}F NMR

(376 MHz, $CDCl_3$) δ –131.0; MS (ESI^+) *m/z* 233 (15), 213 (100), 172 (30), 140 (30), 128 (30); HRMS (ESI^+) *m/z* calcd for $C_{15}H_{18}OF$ [M+H] 213.1342, found 213.1335.



3-67

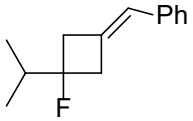
(1-(3-Fluoro-3-methylcyclobutylidene)ethyl)benzene (3-67). Prepared according to General Procedure H using KHF_2 (0.069 g, 0.88 mmol, 1.0 eq), diisopropylamine (0.50 mL, 3.5 mmol, 4.0 eq), pyridine • 9 HF (1.59 mL, 61.2 mmol HF, 69.4 eq HF), and alcohol **3-52** (0.166 g, 0.882 mmol, 1.00 eq) in CH_2Cl_2 (4 mL). Purification by chromatography on SiO_2 (2.5% EtOAc in hexanes) afforded methylenecyclobutane **3-67** (0.106 g, 0.557 mmol, 63%) as a colorless oil: IR (ATR) cm^{-1} 2974, 1599, 1496, 1444, 1379, 1241, 1168, 912, 759, 697 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.34 (t, 2 H, *J* = 7.6), 7.29 (t, 2 H, *J* = 7.2 Hz), 7.22 (td, 1 H, *J* = 6.8 Hz, 1.2 Hz), 3.29 (t, 1 H, *J* = 18.8 Hz), 3.23 (t, 1 H, *J* = 19.6 Hz), 2.87 (app q, 2 H, *J* = 12.4 Hz), 1.96 (s, 3 H), 1.52 (d, 3 H, $^3J_{HF}$ = 21.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.8, 128.9, 128.1, 128.0, 126.54, 126.51, 126.4, 125.8 ($^3J_{CF}$ = 15 Hz), 92.1 ($^1J_{CF}$ = 205 Hz), 45.4 ($^2J_{CF}$ = 24 Hz), 44.5 ($^2J_{CF}$ = 24 Hz), 24.4 ($^2J_{CF}$ = 25 Hz), 17.5; ^{19}F NMR (470 MHz, $CDCl_3$) δ –132.4; HRMS (EI^+) *m/z* calcd for $C_{13}H_{15}F$ [M^+] 190.1158, found 190.1192.



3-68

((3-Fluoro-3-propylcyclobutylidene)methyl)benzene (3-68). Prepared according to General Procedure H using KHF_2 (0.029 g, 0.38 mmol, 1.0 eq), diisopropylamine (0.21 mL, 1.5 mmol, 4.0 eq), pyridine • 9 HF (0.68 mL, 26.2 mmol HF, 68.9 eq HF), and alcohol **3-53** (0.076 g, 0.38 mmol,

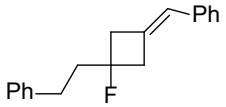
1.0 eq) in CH_2Cl_2 (2 mL). Purification by chromatography on SiO_2 (5% EtOAc in hexanes) afforded methylenecyclobutane **3-68** (0.046 g, 0.23 mmol, 60%) as a colorless oil: IR (ATR) 2959, 1598, 1449, 1254, 1128, 1028, 912, 735, 692 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.22 (app t, 2 H, J = 7.6 Hz), 7.14-7.06 (m, 3 H), 6.20 (s, 1 H), 3.31 (ddt, 1 H, $^3J_{FH}$ = 20.0 Hz, J = 16.8 Hz, 2.8 Hz), 3.18 (ddt, 1 H, $^3J_{FH}$ = 20.0 Hz, J = 17.2 Hz, 2.8 Hz), 3.14-3.02 (m, 1 H), 2.91-2.86 (m, 1 H), 1.81-1.68 (m, 2 H), 1.47 (pent, 2 H, J = 7.6 Hz), 0.95 (t, 3 H, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.6, 132.7, 132.6, 128.5, 127.2, 126.4, 123.6, 95.1 ($^1J_{CF}$ = 208 Hz), 44.5 ($^2J_{CF}$ = 41 Hz), 44.2 ($^2J_{CF}$ = 41 Hz), 39.4 ($^2J_{CF}$ = 22 Hz), 16.8 ($^3J_{CF}$ = 3 Hz), 14.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ –140.6; HRMS (ASAP) *m/z* calcd for $C_{14}H_{18}F$ [M+H] 205.1393, found 205.1409.



3-69

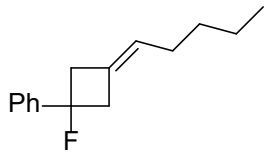
((3-Fluoro-3-isopropylcyclobutylidene)methyl)benzene (3-69). Prepared according to General Procedure H using KHF_2 (0.060 g, 0.77 mmol, 1.0 eq), diisopropylamine (0.43 mL, 3.1 mmol, 4.0 eq), pyridine • 9 HF (1.4 mL, 53.9 mmol HF, 70 eq HF), and alcohol **3-54** (0.155 g, 0.77 mmol) in CH_2Cl_2 (2 mL). Purification by chromatography on SiO_2 (5% EtOAc in hexanes) afforded methylenecyclobutane **3-69** (0.073 g, 0.36 mmol, 47%) as a colorless oil: IR (ATR) 2966, 1599, 1471, 1448, 1240, 1113, 1017, 913, 693 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.38-7.29 (m, 2 H), 7.25 (m, 3 H), 6.29 (t, 1 H, J = 2.4 Hz), 3.35-2.94 (m, 4 H), 1.92 (d heptet, 1 H, $^3J_{FH}$ = 25 Hz, J = 6.8 Hz), 0.99 (d, 6 H, J = 6.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.6, 132.88, 132.75, 128.5, 127.2, 126.4, 123.4 ($^3J_{CF}$ = 6 Hz), 98.0 ($^1J_{CF}$ = 210 Hz), 42.7 ($^2J_{CF}$ = 25 Hz), 42.4 ($^2J_{CF}$ = 24 Hz), 34.9 (d,$^2J_{CF}$ = 22 Hz), 15.73 ($^3J_{CF}$ = 4 Hz), 15.71 ($^3J_{CF}$ = 5 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ –

152.6; GC-MS (ESI)$^+$ *m/z* 204, 161, 129, 115, 91, 63, 51; HRMS (ASAP) *m/z* calcd for $C_{14}H_{17}F$ [M^+] 204.1314, found 204.1304.



3-70

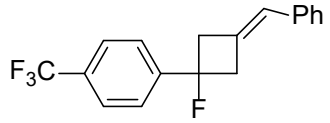
(2-(3-Benzylidene-1-fluorocyclobutyl)ethyl)benzene (3-70). Prepared according to General Procedure H using KHF_2 (0.058 g, 0.75 mmol, 1.0 eq), diisopropylamine (0.42 mL, 3.0 mmol, 4.0 eq), pyridine • 9 HF (1.4 mL, 52 mmol HF, 69 eq HF), and alcohol **3-55** (0.198 g, 0.75 mmol) in CH_2Cl_2 (3 mL). Purification by chromatography on SiO_2 (5% EtOAc in hexanes) afforded methylenecyclobutane **3-70** (0.160 g, 0.601 mmol, 48%) as a colorless oil: IR (ATR) 2915, 1599, 1496, 1453, 1305, 1237, 1059, 913, 738, 692 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.27 (m, 4 H), 7.25-7.17 (m, 6 H), 6.33 (t, 1 H, J = 2.0 Hz), 3.39 (ddt, 1 H, $^3J_{HF}$ = 19.6 Hz, J = 16.8 Hz, 3.2 Hz), 3.25 (ddt, 1 H, $^3J_{HF}$ = 20.0 Hz, J = 16.8 Hz, 2.8 Hz), 3.45-3.32 (m, 1 H), 3.02-2.91 (m, 1 H), 2.79, 2.13 (AA'BB', 4 H, J = 5.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.6, 137.5, 132.2, 128.51, 128.49, 128.4, 127.2, 126.0, 124.0, 123.9, 94.8 (d, $^1J_{CF}$ = 210 Hz), 44.5 (d, $^2J_{CF}$ = 37 Hz), 44.2 (d, $^2J_{CF}$ = 37 Hz), 39.2 (d, $^2J_{CF}$ = 23 Hz), 29.8 (d, $^3J_{CF}$ = 3 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ –141.7; HRMS (ES^+) *m/z* calcd for $C_{19}H_{19}F$ [M^+] 266.1471, found 266.1465.



3-71

(1-Fluoro-3-pentylidenecyclobutyl)benzene (3-71). Prepared according to General Procedure H using KHF_2 (0.040 g, 0.51 mmol, 1.0 eq), diisopropylamine (0.28 mL, 2.0 mmol, 4.0 eq), pyridine • 9 HF (0.46 mL, 18 mmol HF, 34.7 eq HF), and alcohol **3-56** (0.110 g, 0.509 mmol) in CH_2Cl_2 (2 mL). Purification by chromatography on SiO_2 (5% EtOAc in hexanes) afforded

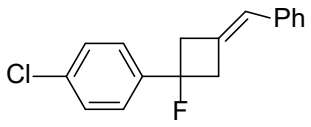
methylenecyclobutane **3-71** (0.034 g, 0.16 mmol, 31%) as a colorless oil: IR (ATR) 2957, 2924, 1449, 1301, 1229, 1065, 755, 697 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.45 (m, 2 H), 7.39 (app t, 2 H, J = 7.6), 7.35-7.28 (m, 1 H), 5.44-5.36 (m, 1 H), 3.41-3.23 (m, 2 H), 3.22-3.10 (m, 2 H), 1.97 (q, 2 H, J = 7.2 Hz), 1.41-1.26 (m, 4 H), 0.92 (t, 3 H, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.8 (d, $^{2}J_{CF}$ = 22 Hz), 128.4, 127.71, 127.69, 125.6, 124.3 (d, $^{3}J_{CF}$ = 6 Hz), 124.0 (d, $^{3}J_{CF}$ = 8 Hz), 94.2 (d, $^{1}J_{CF}$ = 207 Hz), 45.5 (d, $^{2}J_{CF}$ = 24 Hz), 44.0 (d, $^{2}J_{CF}$ = 25 Hz), 31.7, 28.5, 22.3, 14.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ –138.2; HRMS (ASAP) *m/z* calcd for $C_{15}H_{18}F$ [M–H] 217.1414, found 217.1393.



3-72

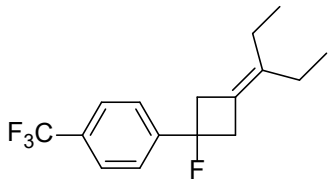
1-(3-Benzylidene-1-fluorocyclobutyl)-4-(trifluoromethyl)benzene (3-72). Prepared according to General Procedure H using KHF_2 (0.029 g, 0.37 mmol, 1.0 eq), diisopropylamine (0.21 mL, 1.5 mmol, 4.0 eq), pyridine • 9 HF (0.68 mL, 26 mmol HF, 71 eq HF), and alcohol **3-59** (0.114 g, 0.375 mmol, 1.00 eq) in CH_2Cl_2 (1 mL). Purification by chromatography on SiO_2 (5% EtOAc in hexanes) afforded methylenecyclobutane **3-72** (0.071 g, 0.023 mmol, 62%) as a colorless oil: IR (ATR) 2967, 1622, 1324, 1165, 1122, 1069, 841, 693 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (AB q, 4 H, J_{AB} = 8.8 Hz, ∂_{AB} = 0.04 ppm), 7.37 (app t, 2 H, J = 6.8 Hz), 7.30-7.21 (m, 3 H), 6.45 (t, 1 H, J = 2.4 Hz), 3.79 (ddt, 1 H, $^{3}J_{HF}$ = 20.8 Hz, J = 17.2 Hz, 3.2 Hz), 3.65 (ddt, 1 H, $^{3}J_{HF}$ = 21.6 Hz, J = 17.2 Hz, 2.8 Hz), 3.58-3.46 (m, 1 H), 3.41-3.30 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.4, (d, $^{2}J_{CF}$ = 23 Hz), 137.1, 130.6 (d, $^{3}J_{CF}$ = 14 Hz), 130.1 (q, $^{2}J_{CF}$ = 32 Hz), 128.6, 127.3, 126.8, 125.5 (q, $^{3}J_{CF}$ = 4 Hz), 124.4 (d, $^{4}J_{CF}$ = 6 Hz), 124.3, 124.2 (d, $^{3}J_{CF}$ = 9 Hz), 124.1 (q, $^{1}J_{CF}$ = 271 Hz), 94.0 (d, $^{1}J_{CF}$ = 211 Hz), 47.5 (d, $^{2}J_{CF}$ = 25 Hz), 47.2 (d, $^{2}J_{CF}$ = 25 Hz); ^{19}F NMR (376

MHz, $CDCl_3$) δ –62.6, –140.5; MS (ESI^+) *m/z* 287 (100), 201 (20), 171 (45), 140 (60); HRMS (ESI^+) *m/z* calcd for $C_{18}H_{14}F_3$ [M–F] 287.1040, found 287.1048.



3-73

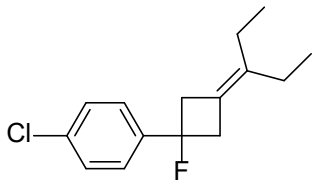
1-(3-Benzylidene-1-fluorocyclobutyl)-4-chlorobenzene (3-73). Prepared according to General Procedure H using KHF_2 (0.053 g, 0.68 mmol, 1.0 eq), diisopropylamine (0.38 mL, 2.7 mmol, 4.0 eq), pyridine • 9 HF (1.2 mL, 46 mmol HF, 70 eq HF), and alcohol **3-60** (0.183 g, 0.676 mmol, 1.00 eq). Purification by chromatography on SiO_2 (2.5% EtOAc in hexanes) afforded methylenecyclobutane **3-73** (0.076 g, 0.28 mmol, 41%) as a yellow-tinted oil: IR (ATR) 2961, 2913, 1599, 1493, 1398, 1301, 1242, 1092, 1010, 826, 692 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.41 (app d, 2 H, J = 8.8 Hz), 7.38-7.31 (m, 4 H), 7.25-7.20 (m, 3 H), 6.41 (t, 1 H, J = 2.0 Hz), 3.74 (ddt, 1 H, $^3J_{HF}$ = 20.8 Hz, J = 17.6 Hz, 3.2 Hz), 3.67-3.43 (m, 2 H), 3.33 (dddd, 1 H, J = 16.8 Hz, 13.2 Hz, 5.2 Hz, 3.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8 ($^2J_{CF}$ = 23 Hz), 137.2, 133.8 ($^4J_{CF}$ = 1 Hz), 131.1, 131.0, 128.61, 128.59, 127.3, 126.7, 125.5 ($^3J_{CF}$ = 8 Hz), 124.2 ($^3J_{CF}$ = 5 Hz), 94.2 ($^1J_{CF}$ = 209 Hz), 47.3 ($^2J_{CF}$ = 25 Hz), 47.0 ($^2J_{CF}$ = 25 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ –137.8; GC-MS (EI^+) 272, 752, 217, 202, 116. HRMS (ASAP) *m/z* calcd for $C_{17}H_{14}FCl$ [M] 272.0768, found 272.0361.



3-74

1-(1-Fluoro-3-(pentan-3-ylidene)cyclobutyl)-4-(trifluoromethyl)benzene (3-74). Prepared according to General Procedure H using KHF_2 (0.041 g, 0.52 mmol, 1.0 eq), diisopropylamine

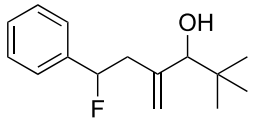
(0.30 mL, 2.1 mmol, 4.0 eq), pyridine • 9 HF (0.94 mL, 36 mmol HF, 70 eq HF), and alcohol **3-61** (0.149 g, 0.524 mmol, 1.00 eq). Purification by chromatography on SiO_2 (5% EtOAc in hexanes) afforded methylenecyclobutane **3-74** (0.077 g, 0.27 mmol, 51%) as a colorless oil: IR (ATR) cm^{-1} 2966, 1622, 1462, 1408, 1325, 1165, 1125, 1069, 843 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.63, 7.56 (AA'BB', 4 H, J_{AB} = 8.4 Hz, ∂_{AB} = 0.07 ppm), 3.39-3.25 (m, 2 H), 3.11 (ddd, 2 H, J = 14.4 Hz, 14.4 Hz, 3.6 Hz), 2.02 (q, 4 H, J = 7.6 Hz), 1.00 (t, 6 H, J = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.4 (d, $^2J_{CF}$ = 23 Hz), 137.8 (d, $^4J_{CF}$ = 6 Hz), 129.8 (q, $^2J_{CF}$ = 31 Hz), 125.3 (q, $^3J_{CF}$ = 4 Hz), 124.1 (d, $^3J_{CF}$ = 4 Hz), 124.1 (q, $^1J_{CF}$ = 270 Hz), 118.9 (d, $^3J_{CF}$ = 13 Hz), 93.2 (d, $^1J_{CF}$ = 209 Hz), 43.5 (d, $^2J_{CF}$ = 24 Hz), 23.5, 12.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ – 62.6, –142.5; MS (ASAP) *m/z* 267 (100), 237 (75), 225 (75), 211 (70); HRMS (ASAP) *m/z* calcd for $C_{16}H_{17}F_3$ [M–HF] 266.1282, found 266.1298.



3-75

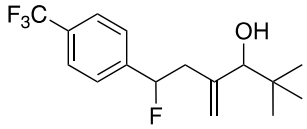
1-Chloro-4-(1-fluoro-3-(pentan-3-ylidene)cyclobutyl)benzene (3-75). Prepared according to General Procedure H using KHF_2 (0.063 g, 0.80 mmol, 1.0 eq), diisopropylamine (0.45 mL, 3.2 mmol, 4.0 eq), pyridine • 9 HF (1.4 mL, 54 mmol HF, 67 eq HF), and alcohol **3-62** (0.201 g, 0.802 mmol, 1.00 eq). Purification by chromatography on SiO_2 (2.5% EtOAc in hexanes) afforded methylenecyclobutane **3-75** (0.097 g, 0.38 mmol, 48%) as a colorless oil: IR (ATR) 2963, 1491, 1300, 1093, 1013, 829 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.40-7.31 (m, 4 H), 3.35-3.20 (m, 2 H), 3.14-3.02 (m, 2 H), 2.00 (q, 4 H, J = 7.6 Hz), 1.00 (t, 6 H, J = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.8 ($^2J_{CF}$ = 24 Hz), 137.5 ($^4J_{CF}$ = 6 Hz), 133.4, 128.5, 125.4 ($^3J_{CF}$ = 9 Hz), 119.2 ($^3J_{CF}$ = 13 Hz), 93.4 ($^1J_{CF}$ = 208 Hz), 44.5 ($^2J_{CF}$ = 25 Hz), 23.5, 12.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ –

139.7; MS (ASAP) *m/z* 233 (80), 232 (55), 217 (30), 209 (20); HRMS (ASAP) *m/z* calcd for $C_{15}H_{18}Cl$ [M–F] 233.1097, found 233.1089.



3-76

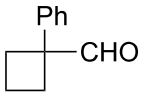
6-Fluoro-2,2-dimethyl-4-methylene-6-phenylhexan-3-ol (3-76). Prepared according General Procedure H from KHF_2 (0.044 g, 0.56 mmol, 1.2 eq), diisopropylamine (0.32 mL, 2.3 mmol, 5.0 eq), pyridine • 9 HF (0.76 mL, 29 mmol HF, 65 eq HF), and alcohol **3-58** (0.098 g, 0.45 mmol) in CH_2Cl_2 (1 mL). Purification by chromatography on SiO_2 (2.5% EtOAc/hexanes) afforded allylic alcohol **3-77** (0.018 g, 0.076 mmol, 17%) as a colorless oil: IR (ATR) 3598, 2955, 1480, 1455, 1362, 1059, 1004, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.41-7.31 (m, 5 H), 5.57 (ddd, 1 H, $^2J_{HF}$ = 48.0 Hz, *J* = 8.4 Hz, 4.0 Hz), 5.20 (s, 1 H), 5.18 (s, 1 H), 3.75 (s, 1 H), 2.87 (td, 1 H, *J* = 15.2 Hz, 9.2 Hz), 2.48 (ddd, 1 H,$^3J_{HF}$ = 32.4 Hz, *J* = 14.8 Hz, 4.0 Hz), 1.64 (s, 1 H), 0.92 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.8 (d, $^3J_{CF}$ = 2 Hz), 139.9 (d, $^2J_{CF}$ = 20 Hz), 125.7 (d, $^3J_{CF}$ = 11 Hz), 125.6 (d, $^3J_{CF}$ = 10 Hz), 116.0, 94.8 (d, $^1J_{CF}$ = 171 Hz), 82.3, 41.2 (d, $^2J_{CF}$ = 24 Hz), 35.5, 26.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ –172.5; HRMS (ESI^+) *m/z* calcd for $C_{15}H_{19}$ [M–H_2O–F] 199.1487, found 199.1482.



3-77

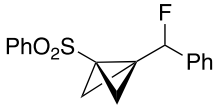
6-Fluoro-2,2-dimethyl-4-methylene-6-(4-(trifluoromethyl)phenyl)hexan-3-ol (3-77). Prepared according to General Procedure H from KHF_2 (0.010 g, 0.13 mmol, 1.0 eq), diisopropylamine (0.07 mL, 0.51 mmol, 4.0 eq), pyridine • 9 HF (0.12 mL, 4.6 mmol HF, 36 eq HF), and alcohol **3-57** (0.039 g, 0.13 mmol) in dichloromethane (1 mL). Purification by chromatography on SiO_2

(2.5% EtOAc/hexanes) afforded **3-77** (0.014 g, 0.046 mmol, 34%) as a colorless oil: IR (ATR) 3598, 2957, 1623, 1325, 1166, 1127, 1069, 1007, 841 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, 2 H, J = 8.4 Hz), 7.47 (d, 2 H, J = 8.0 Hz), 5.66 (ddd, 1 H, $^2J_{HF}$ = 47.6 Hz, J = 8.8 Hz, 4.4 Hz), 5.17 (s, 1 H), 5.15 (s, 1 H), 3.80 (s, 1 H), 2.85 (td, 1 H, J = 15.2 Hz, 8.8 Hz), 2.48 (ddd, 1 H, $^3J_{HF}$ = 32.0 Hz, J = 15.2 Hz, 4.4 Hz), 1.65 (s, 1 H), 0.92 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0 (d, $^3J_{CF}$ = 3 Hz), 143.9 (d, $^2J_{CF}$ = 20 Hz), 130.9 (q, $^2J_{CF}$ = 32 Hz), 125.9 (d, $^3J_{CF}$ = 7 Hz), 125.5 (q, $^3J_{CF}$ = 4 Hz), 123.7 (q, $^1J_{CF}$ = 270 Hz), 116.3, 93.8 (d, $^1J_{CF}$ = 173 Hz), 82.4, 41.1 (d, $^2J_{CF}$ = 24 Hz), 35.6, 26.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ –176.1, –62.6; MS (ESI^+) *m/z* 267 (100), 173 (10), 137 (35); HRMS (ESI^+) *m/z* calcd for $C_{16}H_{18}F_3$ [M–H_2O–F] 267.1361, found 267.1353.



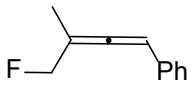
3-79

1-Phenylcyclobutane-1-carbaldehyde (3-79). Prepared according to General Procedure H from KHF_2 (0.100 g, 1.29 mmol), diisopropylamine (0.73 mL, 5.1 mmol, 4.0 eq), alcohol **3-78**[73b] (0.206 g, 1.29 mmol), and pyridine • 9 HF (0.93 mL, 35.8 mmol HF, 28 eq HF) in dichloromethane (6 mL). Purification by chromatography on SiO_2 (2.5% EtOAc/hexanes) afforded aldehyde **3-79** (0.028 g, 0.17 mmol, 14%) as a colorless oil: ^1H NMR (400 MHz, $CDCl_3$) δ 9.46 (s, 1 H), 7.27 (t, 2 H, J = 7.6 Hz), 7.17 (t, 1 H, J = 7.6 Hz), 7.05 (dd, 2 H, J = 8.4 Hz, 1.2 Hz), 2.68-2.59 (m, 2 H), 2.31 (ddd, 2 H, J = 19.2 Hz, 9.6 Hz, 2.4 Hz), 1.97-1.76 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.5, 141.0, 128.8, 128.5, 126.4, 57.6, 28.4, 15.9.



3-81

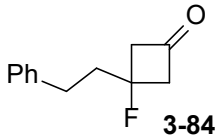
1-(Fluoro(phenyl)methyl)-3-(phenylsulfonyl)bicyclo[1.1.0]butane (3-81). A solution of alcohol **3-80**[83b] (0.049 g, 0.16 mmol) in CH_2Cl_2 (2 mL) was treated with Deoxofluor® (0.03 mL, 0.16 mmol) at 0 °C. The reaction was stirred at 0 °C for 2 h, then it was quenched with sat aq $NaHCO_3$ (5 mL). The mixture was extracted with CH_2Cl_2 (5 mL), and the combined extracts were washed with water (30 mL) and brine (30 mL), then were dried (Na_2SO_4) and concentrated. Chromatography on SiO_2 (25% EtOAc/hexanes) afforded bicyclobutane **3-81** (0.027 g, 0.089 mmol, 55%) as a colorless oil: IR (ATR) 3065, 2958, 1447, 1317, 1307, 1146, 1084, 945, 724 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.98-7.91 (m, 2 H), 7.63 (tt, 1 H, J = 7.2 Hz, 1.2 Hz), 7.60-7.49 (m, 4 H), 7.48-7.37 (m, 3 H), 6.15 (d, 1 H, $^2J_{HF}$ = 46.8 Hz), 2.77 (d, 1 H, J = 6.4 Hz), 2.36 (dd, 1 H, J = 6.4 Hz, 0.8 Hz), 1.50 (t, 1 H, J = 0.8 Hz), 1.43 (d, 1 H, J = 4.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.0, 137.4 ($^2J_{CF}$ = 22 Hz), 133.3, 129.3 ($^4J_{CF}$ = 2 Hz), 129.2, 128.6, 127.3, 127.0 ($^3J_{CF}$ = 5 Hz), 89.7 ($^1J_{CF}$ = 174 Hz), 36.9, 36.1, 30.7 ($^2J_{CF}$ = 39 Hz), 28.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ –163.5; HRMS (ES^+) *m/z* calcd for $C_{17}H_{15}SO_2F$ [M^+] 302.0777, found 302.0785.



3-83

(4-Fluoro-3-methylbuta-1,2-dien-1-yl)benzene (3-83). Prepared according to General Procedure H from KHF_2 (0.060 g, 0.77 mmol), diisopropylamine (0.44 mL, 3.1 mmol, 4.0 eq), pyridine • 9 HF (1.0 mL, 12 mmol, 15 eq), and cyclopropene **3-82**[190] (0.124 g, 0.77 mmol) in CH_2Cl_2 (2 mL). Purification by chromatography on SiO_2 (hexanes) afforded fluorinated allene **3-83** (0.062 g, 0.38 mmol, 49%) as a colorless oil: IR (ATR) 2984, 2885, 1956, 1599, 1497, 1464, 1374, 978, 693 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.32-7.07 (m, 5 H), 6.21 (ddd, 1 H, J = 4.8 Hz, 4.8 Hz, 2.8 Hz), 4.84 (dd, 2 H, $^2J_{HF}$ = 47.6 Hz, J = 2.0 Hz), 1.91 (d, 3 H, J = 2.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$)

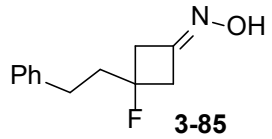
δ 204.1 ($^3J_{CF}$ = 10 Hz), 134.1, 128.7, 127.2, 127.0, 100.3 ($^2J_{CF}$ = 19 Hz), 95.2 ($^4J_{CF}$ = 2 Hz), 84.4 ($^1J_{CF}$ = 170 Hz), 15.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ –213.0.



3-84

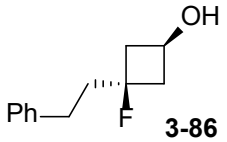
3-Fluoro-3-phenethylcyclobutan-1-one (3-84). To a solution of **3-70** (0.025 g, 0.094 mmol) in THF/H_2O (10:1, 1 mL total) was added potassium osmate(VI) dihydrate (0.3 mg, ~1 μmol, 0.5 mol%) and NMO (0.016 g, 0.12 mmol, 1.3 eq). The reaction mixture was stirred at room temperature for 19 h, then it was directly placed on an SiO_2 column and purified by chromatography (25-50% EtOAc/hexanes) to afford the corresponding diol (0.024 g, 0.080 mmol, 85%) as a colorless oil. The material is a ~1:1 mixture of diastereomers: ^{19}F NMR (376 MHz, $CDCl_3$) δ – 137.8, – 143.9.

A solution of this diol (0.024 g, 0.080 mmol, 1.0 eq) in THF (0.5 mL) and water (0.5 mL) was treated with sodium periodate (0.019 g, 0.088 mmol, 1.1 eq). The reaction was stirred at rt for 3 h. The reaction mixture was then directly placed on an SiO_2 column and purified by chromatography (10% EtOAc/hexanes) to afford cyclobutanone **3-84** (0.009 g, 0.047 mmol, 59%) as a colorless film. The material contained a trace of benzaldehyde byproduct but was used without further purification: IR (ATR) 2918, 1792, 909, 730 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.28 (m, 2 H), 7.25-7.19 (m, 3 H), 3.45-3.32 (m, 2 H), 3.15-3.04 (m, 2 H), 2.87-2.81 (m, 2 H), 2.34-2.22 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.9 (d, $^3J_{CF}$ = 12 Hz), 140.6, 128.6, 128.4, 128.3, 126.3, 89.6 (d, $^1J_{CF}$ = 202 Hz), 57.9 (d, $^2J_{CF}$ = 25 Hz), 39.2 (d, $^2J_{CF}$ = 23 Hz), 30.4 (d, $^3J_{CF}$ = 4 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ –151.7.



3-85

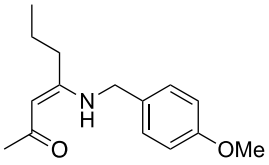
3-Fluoro-3-phenethylcyclobutan-1-one oxime (**3-85)**. A solution of ketone **3-84** (0.016 g, 0.08 mmol) in EtOH (0.25 mL) and water (0.25 mL) was treated with hydroxylamine hydrochloride (0.007 g, 0.11 mmol) and sodium acetate (0.016 g, 0.19 mmol). The reaction mixture was sealed in a microwave vial and was heated at 60 °C for 4.5 h. The reaction mixture was then cooled to rt and purified by chromatography on SiO_2 (30% EtOAc/hexanes) to afford oxime **3-85** (0.010 g, 0.05 mmol, 58%) as a colorless oil: IR (ATR) 3262, 2925, 1466, 1710, 1455, 1238, 929, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.30 (app t, 2 H, J = 7.6 Hz), 7.24-7.18 (m, 3 H), 3.28-2.92 (m, 4 H), 2.77 (ddd, 2 H, J = 5.6 Hz, 5.6 Hz, 5.6 Hz), 2.20-2.07 (m, 2 H), 1.8-1.4 (br s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.9, 128.6, 128.4, 126.2, 92.4 (d, $^1J_{CF}$ = 206 Hz), 43.7 (d, $^2J_{CF}$ = 26 Hz), 42.7 (d, $^2J_{CF}$ = 26 Hz), 39.2 (d, $^2J_{CF}$ = 23 Hz), 29.8 (d, $^3J_{CF}$ = 4 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ –146.1; MS (ESI^+) *m/z* 208 (60), 188 (100), 170 (40), 129 (65); HRMS (ESI^+) *m/z* calcd for $C_{12}H_{15}FNO$ [M+H] 208.1138, found 208.1131.



3-86

3-Fluoro-3-phenethylcyclobutan-1-ol (3-86). A solution of cyclobutanone **3-84** (0.012 g, 0.062 mmol) in THF (1 mL) was cooled to –78 °C under N_2 and treated with LAH (1 drop of 4 M solution in ether). The reaction was slowly warmed to rt over 4 h, then it was quenched with water (5 mL) and extracted with CH_2Cl_2 (2 x 25 mL). The organic layers were dried (Na_2SO_4) and concentrated. Purification by chromatography on SiO_2 afforded alcohol **3-86** (0.008 g, 0.041 mmol, 66%) as a colorless film. The material is a ~6.5:1 mixture of diastereomers: IR (ATR) 3344, 2936, 1603,

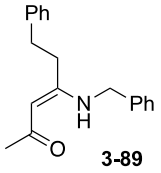
1496, 1455, 1238, 1040, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.33-7.24 (m, 2 H), 7.22-7.13 (m, 3 H), 3.64 (q, 1 H, J = 6.8 Hz), 2.72, 1.94, 1.88 (AA'BB', 4 H, J_{AB} = 5.2 Hz), 2.62 (dtd, 2 H, J = 10.4 Hz, 7.2 Hz, 3.2 Hz), 2.31 (dddd, 2 H, $^3J_{HF}$ = 23.2 Hz, J = 10.0 Hz, 7.2 Hz, 3.2 Hz), 1.62 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.3, 128.5, 128.4, 128.3, 126.0, 89.3 ($^1J_{CF}$ = 211 Hz), 58.9, 44.5 ($^2J_{CF}$ = 20 Hz), 40.4 ($^2J_{CF}$ = 23 Hz), 29.6 ($^3J_{CF}$ = 3 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ –133.8.



3-88

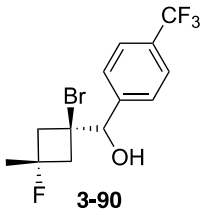
(***E*)-4-((4-Methoxybenzyl)amino)hept-3-en-2-one (3-88)**. Ketone **3-87** was prepared by the dissolving the corresponding diol (0.091 g, 0.38 mmol, 1.0 eq) in THF (1.5 mL) and water (0.5 mL) and treating with sodium periodate (0.090 g, 0.42 mmol, 1.1 eq). The reaction was stirred at rt for 2 h, then was filtered through a 1" pipette column of SiO_2 that was then flushed with THF (1 mL). The filtrate was directly used without concentration or further purification. The filtrate was treated with 4-methoxybenzylamine (0.13 mL, 0.95 mmol, 2.5 eq), acetic acid (0.02 mL, 0.38 mmol, 1.0 eq) and sodium triacetoxyborohydride (0.283 g, 1.34 mmol, 3.50 eq). The reaction was stirred at rt for 15 h, then was quenched with 1 M NaOH (5 mL) and partitioned between water (30 mL) and EtOAc (30 mL). The combined extracts were washed with water (30 mL), then were dried (Na_2SO_4) and concentrated. Chromatography on SiO_2 (20-30% EtOAc in hexanes) afforded vinylogous amide **3-88** (0.032 g, 0.13 mmol, 34%) as a colorless oil: IR (ATR) 2961, 1602, 1568, 1517, 1302, 1245, 1175, 1032, 811, 746; ^1H NMR (300 MHz, $CDCl_3$) δ 11.17 (br s, 1 H), 7.16 (d, 2 H, J = 8.7 Hz), 6.85 (d, 2 H, J = 8.7 Hz), 5.02 (s, 1 H), 4.38 (d, 2 H, J = 6.0 Hz), 3.78 (s, 3 H), 2.17 (t, 2 H, J = 7.5 Hz), 2.02 (s, 3 H), 1.54 (pent, 2 H, J = 7.5 Hz), 0.96 (t, 3

H, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.3, 166.7, 159.0, 130.1, 128.1, 114.2, 94.7, 55.3, 45.9, 33.9, 29.1, 21.4, 14.0; MS (ESI^+) *m/z* 248 (2), 121 (100); HRMS (ESI^+) *m/z* calcd for $C_{15}H_{22}NO_2$ [M+H] 248.1642, found 248.1645.



3-89

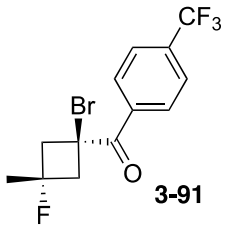
(*E*)-4-(Benzylamino)-6-phenylhex-3-en-2-one (3-89). A solution of crude ketone **3-84** (0.030 g, 0.023 mmol) in MeOH (0.5 mL) was treated sequentially with benzylamine (0.02 mL, 0.17 mmol), *t*-butyl isonitrile (0.02 mL, 0.17 mmol), and propionic acid (0.01 mL, 0.17 mmol). The reaction was stirred at rt for 16 h, then was directly placed on an SiO_2 column and chromatographed (30% EtOAc/hexanes) to afford vinylogous amide **3-89** (0.011 g, 49%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 11.29 (s, 1 H), 7.48-7.20 (m, 8 H), 7.20-7.11 (m, 2 H), 5.13 (s, 1 H), 4.43 (d, 2 H, J = 6.3 Hz), 2.83, 2.53 (AA'BB', 4 H, J_{AB} = 7.5 Hz, $J_{A'B'}$ = 5.7 Hz), 2.09 (s, 3 H).



3-90

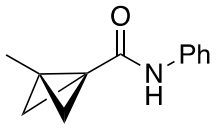
1-Bromo-3-fluoro-3-methylcyclobutyl)(4-(trifluoromethyl)phenyl)methanol (3-90). A solution of methylenecyclobutane **3-46** (0.025 g, 0.10 mmol) in MeCN (0.75 mL) and water (0.25 mL) was treated with NBS (0.037 g, 0.20 mmol, 2.0 eq). The reaction was stirred at 45 °C for 18 h. After cooling, the material was directly chromatographed on SiO_2 to afford bromohydrin **3-90** (0.024 g, 0.070 mmol, 69%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63, 7.55 (ABq, 4 H, J_{AB} = 8.4 Hz), 4.88 (s, 1 H), 3.13 (app q, 2 H, J = 16.8 Hz), 2.79 (dddd, 1 H, J = 14.2 Hz, 13.6 Hz, 4.4 Hz, 1.2 Hz), 2.65 (dddd, 1 H, J = 13.6 Hz, 13.2 Hz, 4.4 Hz, 1.2 Hz), 2.50 (br s, 1 H, 1.71

(d, 3 H, $^{3}J_{HF}$ = 22.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 130.6 (q, $^{2}J_{CF}$ = 32 Hz), 127.9, 125.0 (q, $^{3}J_{CF}$ = 4 Hz), 124.0 (q, $^{1}J_{CF}$ = 270 Hz), 91.6 (d, $^{1}J_{CF}$ = 202 Hz), 79.2, 60.7 (q, $^{3}J_{CF}$ = 14 Hz), 50.2 (d, $^{2}J_{CF}$ = 23 Hz), 48.7 (d, $^{2}J_{CF}$ = 24 Hz), 26.4 (d, $^{2}J_{CF}$ = 25 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ –62.6, –127.5.



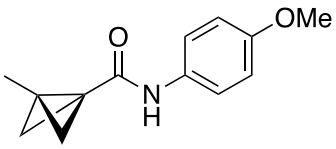
3-91

1-Bromo-3-fluoro-3-methylcyclobutyl)(4-(trifluoromethyl)phenyl)methanone (3-91). A solution of alcohol **3-90** (0.015 g, 0.044 mmol) in CH_2Cl_2 (1 mL) was cooled to 0 °C under N_2. Dess-Martin periodinane (0.028 g, 0.032 mmol, 1.1 eq) was added in one portion. The reaction was stirred at rt for 2 h, then it was diluted with CH_2Cl_2 (10 mL) and sat aq $NaHCO_3$ (10 mL). The organic layer was dried (Na_2SO_4) and concentrated. Purification by chromatography on SiO_2 afforded ketone **3-91** (0.013 g, 0.048 mmol, 87%) as a colorless semi-solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, 2 H, *J* = 8.4 Hz), 7.74 (d, 2 H, *J* = 8.0 Hz), 3.45, 2.94 (AA'BB', 4 H, $^{3}J_{HF}$ = 19.6 Hz, *J* = 16.0 Hz, 12.0 Hz), 1.83 (d, 3 H, $^{3}J_{HF}$ = 22.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.0, 134.8 (q, $^{2}J_{CF}$ = 25 Hz), 130.5, 125.6 (q, $^{3}J_{CF}$ = 4 Hz), 123.4 (q, $^{1}J_{CF}$ = 271 Hz), 91.1 (d, $^{1}J_{CF}$ = 204 Hz), 49.6 (d, $^{2}J_{CF}$ = 25 Hz), 49.3 (d, $^{3}J_{CF}$ = 14 Hz), 26.4 (d, $^{3}J_{CF}$ = 25 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ –63.3, –127.3; HRMS (ASAP) *m/z* calcd for $C_{13}H_{12}BrOF_4$ [M+H] 339.0008, found 339.0029.



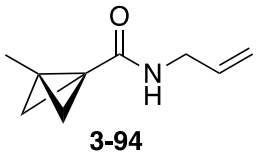
3-92

3-Methyl-*N*-phenylbicyclo[1.1.0]butane-1-carboxamide (3-92).[73b] Prepared according to General Procedure G from A solution of 1-chloromethyl-2,2-dibromocyclopropane (3.85 g, 14.7 mmol), MeLi (9.8 mL, 14.7 mmol, 1.5 M in Et_2O), *t*-BuLi (9.8 mL, 14.7 mmol, 1.5 M in pentane), and phenyl isocyanate (0.70 mL, 7.38 mmol) in Et_2O (25 mL). Purification by chromatography on SiO_2 (15% EtOAc/hexane) afforded amide **3-92** (0.538 g, 2.87 mmol, 49%) as a colorless solid: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.53 (d, *J* = 7.8 Hz, 2 H), 7.44 (br s, 1 H), 7.30 (t, *J* = 7.9 Hz, 2 H), 7.08 (t, *J* = 7.4 Hz, 1 H), 2.22 (s, 2 H), 1.59 (s, 3 H), 1.24 (s, 2 H).



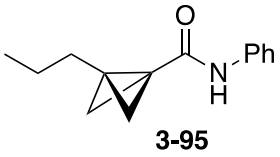
3-93

***N*-(4-Methoxyphenyl)-3-methylbicyclo[1.1.0]butane-1-carboxamide (3-93)**. Prepared according to General Procedure G from 1-chloromethyl-2,2-dibromocyclopropane (3.50 g, 13.3 mmol), MeLi (8.3 mL, 13.3 mmol, 1.6 M in Et_2O), *t*-BuLi (7.8 mL, 13.4 mmol, 1.7 M in pentane), and 4-methoxyphenyl isocyanate (0.87 mL, 6.7 mmol) in Et_2O (25 mL). Purification by chromatography on SiO_2 (30-50% EtOAc/hexane) to afford amide **3-93** (0.961 g, 4.42 mmol, 66%) as a colorless solid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (d, 2 H, *J* = 9.0 Hz), 7.11 (s, 1 H), 6.85 (d, 2 H, *J* = 9.0 Hz), 3.78 (s, 3 H), 2.12 (s, 2 H), 1.58 (s, 3 H), 1.22 (s, 2 H).



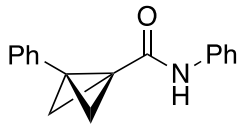
3-94

***N*-Allyl-3-methylbicyclo[1.1.0]butane-1-carboxamide (3-94)**. Prepared according to General Procedure G from 1-chloromethyl-2,2-dibromocyclopropane (1.00 g, 3.81 mmol), MeLi (2.4 mL, 3.8 mmol, 1.6 M in Et_2O), *t*-BuLi (2.2 mL, 13.4 mmol, 1.7 M in pentane), and allyl isocyanate (0.17 mL, 1.9 mmol) in Et_2O (8 mL). Purification by chromatography on SiO_2 (30-50% EtOAc/hexane) afforded amide **3-94** (0.129 g, 0.853 mmol, 45%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.03 (s, 1 H), 5.76, 5.08, 5.02 (ABX, 3 H, J_{AB} = 17.2, J_{AX} = 10.4 Hz), 3.82 (t, 2 H, J = 5.6 Hz), 2.02 (s, 2 H), 1.43 (s, 3 H), 1.04 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 134.9, 115.7, 42.0, 37.0, 23.7, 14.2, 12.2.



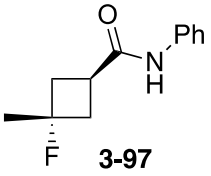
3-95

***N*-Phenyl-3-propylbicyclo[1.1.0]butane-1-carboxamide (3-95)**. Prepared according to General Procedure G from the corresponding tribromide (2.42 g, 7.23 mmol), MeLi (4.5 mL, 7.2 mmol, 1.6 M in Et_2O), *t*-BuLi (4.3 mL, 7.2 mmol, 1.7 M in pentane), and phenyl isocyanate (0.39 mL, 1.8 mmol). Purification by two iterations chromatography on SiO_2 (30% EtOAc/hexane) afforded amide **3-95** (0.127 g 0.590 mmol, 16%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60-7.35 (m, 3 H), 7.30-7.15 (m, 2 H), 7.11-7.02 (m, 1 H), 2.21 (s, 2 H), 1.85 (t, 2 H, J = 7.6 Hz), 1.49 (pent, 2 H, J = 7.6 Hz), 1.18 (s, 2 H), 0.98 (t, 3 H, J = 7.2 Hz). The material was contaminated with ~12% (by mass) of inseparable *N*-phenyl acetamide (MeLi addition product).



3-96

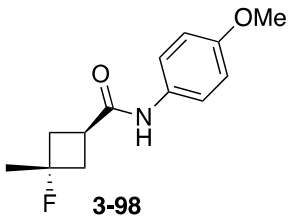
***N*, 3-Diphenylbicyclo[1.1.0]butane-1-carboxamide (3-96)**. Prepared according to General Procedure G from the corresponding tribromide (1.31 g, 3.55 mmol), MeLi (2.2 mL, 3.6 mmol, 1.6 M in Et_2O), *t*-BuLi (2.1 mL, 3.6 mmol, 1.7 M in pentane), and phenyl isocyanate (0.15 mL, 1.4 mmol) in Et_2O (8 mL). Purification by chromatography on SiO_2 (15-40% EtOAc/hexanes) afforded amide **3-96** (0.176 g, 0.71 mmol, 50%) as a tan crystalline solid: Mp 150–152 °C; ^{1}H NMR (300 MHz, CD_3OD) (N–H absent) δ 7.39-7.33 (m, 2 H), 7.33-7.24 (m, 4 H), 7.24-7.15 (m, 3 H), 7.01 (tt, 1 H, *J* = 7.2 Hz, 1.2 Hz), 3.07 (s, 2 H), 1.62 (t, 2 H, *J* = 1.2 Hz); ^{13}C NMR (100 MHz, CD_3OD) δ 168.6, 138.1, 133.8, 128.14, 128.06, 126.4, 125.6, 123.8, 120.7, 34.0, 31.5, 24.7; MS (ESI$^+$) *m/z* 250 (100), 227 (5), 185 (5), 129 (5); HRMS (ESI$^+$) *m/z* calcd for $C_{17}H_{16}NO$ [M+H] 250.1226, found 250.1225.



3-97

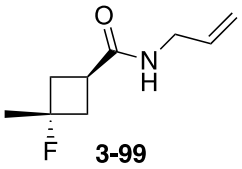
General Procedure I (Bicyclo[1.1.0]butyl amide fluorination): 3-Fluoro-3-methyl-*N*-phenylcyclobutane-1-carboxamide (3-97). To a suspension of KHF_2 (0.012 g, 0.15 mmol) in CH_2Cl_2 (0.5 mL) in a polypropylene reaction vessel was added diisopropylamine (0.08 mL, 0.60 mmol, 4.0 eq). The suspension was cooled under N_2 to –78 °C, then pyridine • 9 HF (0.27 mL, 10 mmol HF, 69 eq HF) was added. The mixture was stirred for 5 min at –78 °C, then a solution of the amide **3-92**[73b] (0.028 g, 0.15 mmol) in CH_2Cl_2 (0.5 mL) was slowly added. After stirring at –78 °C for 10 min, the mixture was warmed to 0 °C for 10 min and then quenched with sat aq. KF (2 mL), warmed to rt, and diluted with 2 M NaOH (50 mL). The material was extracted with ether

(2 X 20 mL). The organic layers were washed with saturated aq. $NaHCO_3$ (30 mL) and brine (30 mL), then were dried (Na_2SO_4) and concentrated. Chromatography on SiO_2 (25% EtOAc/hexanes) afforded amide **3-97** (0.018 g, 0.09 mmol, 58%) as a colorless solid: Mp 159–161 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, 2 H, J = 6.4 Hz), 7.32 (t, 2 H, J = 6.4 Hz), 7.17 (br s, 1 H), 7.11 (t, 1 H, J = 7.5 Hz), 3.20 (ddd, 1 H, J = 16.0 Hz, 9.0 Hz, 7.0 Hz), 2.65-2.46 (m, 4 H), 1.53 (d, 3 H, $^3J_{HF}$ = 22.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.5, 137.8, 129.1, 124.4, 119.8, 95.6 ($^1J_{CF}$ = 195 Hz), 37.8 ($^2J_{CF}$ = 24 Hz), 32.8 ($^3J_{CF}$ = 4 Hz), 25.0 ($^2J_{CF}$ = 25 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ –133.2; MS (ESI$^+$) *m/z* 208 (100), 195 (10); HRMS (ESI$^+$) *m/z* calcd for $C_{12}H_{15}NOF$ [M+H] 208.1138, found 208.1132 .



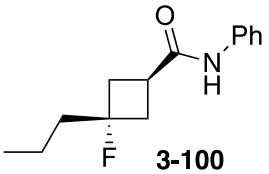
3-98

3-Fluoro-*N*-(4-methoxyphenyl)-3-methylcyclobutane-1-carboxamide (3-98). Prepared according to General Procedure I from KHF_2 (0.032 g, 0.41 mmol), diisopropylamine (0.23 mL, 1.6 mmol, 4.0 eq), pyridine • 9 HF (0.73 mL, 28 mmol HF, 69 eq HF), and amide **3-93** (0.088 g, 0.41 mmol) in CH_2Cl_2 (2.5 mL). Chromatography on SiO_2 (20-50% EtOAc/hexanes) afforded amide **3-98** (0.048 g, 0.20 mmol, 50%) as a colorless solid: Mp 104–107 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, 2 H, J = 8.0 Hz), 7.35-7.20 (br s, 1 H), 6.83 (d, 2 H, J = 8.5 Hz), 3.78 (s, 3 H), 3.16 (ddd, 1 H, J = 16.0 Hz, 9.0 Hz, 7.0 Hz), 2.64-2.38 (m, 4 H), 1.51 (d, 3 H, $^3J_{HF}$ = 22.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 156.5, 130.9, 121.8, 114.1, 95.8 ($^1J_{CF}$ = 195 Hz), 55.5, 37.8 ($^2J_{CF}$ = 24 Hz), 32.6 ($^3J_{CF}$ = 4 Hz), 25.1 ($^2J_{CF}$ = 25 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ –133.2; MS (ESI$^+$) *m/z* 238 (100), 200 (5), 195 (5), 184 (5); HRMS (ESI$^+$) *m/z* calcd for $C_{13}H_{17}NO_2F$ [M+H] 238.1243, found 238.1236. An X-ray crystal structure was obtained for this compound.



3-99

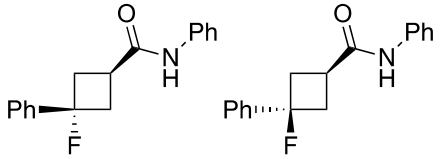
***N*-Allyl-3-fluoro-3-methylcyclobutane-1-carboxamide (3-99)**. Prepared according to General Procedure I from KHF_2 (0.066 g, 0.85 mmol), diisopropylamine (0.48 mL, 3.4 mmol, 4.0 eq), pyridine • 9 HF (1.5 mL, 58 mmol HF, 68 eq HF), and the corresponding amide (0.129 g, 0.853 mmol) in CH_2Cl_2 (4 mL). Purification by chromatography on SiO_2 (20-50% EtOAc/hexanes) afforded amide **3-99** (0.063 g, 0.37 mmol, 43%) as a colorless semi-solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.86-5.62 (br s, 1 H), 5.78, 5.13, 5.09 (ABX, 3 H, J_{AX} = 18.4 Hz, J_{BX} = 10.0 Hz), 3.84 (t, 2 H, J = 5.6 Hz), 3.04 (ddd, 1 H, J = 16.0 Hz, 9.6 Hz, 6.8 Hz), 2.57-2.32 (m, 4 H), 1.47 (d, 3 H, $^3J_{HF}$ = 22.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1, 134.2, 116.4, 95.8 ($^1J_{CF}$ = 195 Hz), 42.0, 37.8 ($^2J_{CF}$ = 24 Hz), 31.6 ($^3J_{CF}$ = 4 Hz), 25.0 ($^2J_{CF}$ = 25 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ –133.3; MS (ESI$^+$) *m/z* 172 (100), 152 (5), 115 (2); HRMS (ESI$^+$) *m/z* calcd for $C_9H_{15}NOF$ [M+H] 172.1138, found 172.1132.



3-100

3-Fluoro-*N*-phenyl-3-propylcyclobutane-1-carboxamide (3-100). Prepared according to General Procedure I from KHF_2 (0.046 g, 0.59 mmol), diisopropylamine (0.33 mL, 2.3 mmol, 4.0 eq), pyridine • 9 HF (1.1 mL, 42 mmol, 72 eq HF), and amide **3-95** (0.127 g, 0.59 mmol) in CH_2Cl_2 (3 mL). Chromatography on SiO_2 (25% EtOAc/hexanes) afforded amide **3-100** (0.051 g, 0.22 mmol, 37%) as a colorless oil that partially solidified on standing. The minor diastereomer was isolated (0.013 g, 9 %) but was contaminated with an elimination/diene product. Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, 2 H, J = 7.6 Hz), 7.32 (t, 2 H, J = 7.6 Hz), 7.25-7.14 (br s, 1

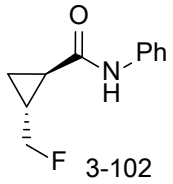
H), 7.11 (t, 1 H, J = 7.6 Hz), 3.24 (pent, 1 H, J = 8.4 Hz), 2.54 (d, 2 H, J = 8.0 Hz), 2.48 (d, 2 H, J = 8.4 Hz), 1.74 (AA'BB', 2 H, J_{AB} = 8.0 Hz, ∂_{AB} = 0.05 ppm), 1.47-1.35 (m, 2 H), 0.93 (t, 3 H, J = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.6, 137.8, 129.1, 124.4, 119.8, 97.9 ($^1J_{CF}$ = 196 Hz), 40.3 ($^2J_{CF}$ = 23 Hz), 36.4 ($^2J_{CF}$ = 24 Hz), 33.5, 16.1 ($^3J_{CF}$ = 3 Hz), 14.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ –144.5; MS (ESI^+) *m/z* 236 (100), 216 (15); HRMS (ESI^+) *m/z* calcd for $C_{14}H_{19}NOF$ [M+H] 236.1451, found 236.1443.



cis **3-101** *trans* **3-101**

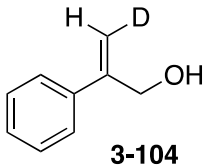
3-Fluoro-*N*,3-diphenylcyclobutane-1-carboxamide (3-101). Prepared according to General Procedure I from KHF_2 (0.013 g, 0.16 mmol), diisopropylamine (0.09 mL, 0.64 mmol, 4.0 eq), pyridine • 9 HF (0.29 mL, 11 mmol HF, 70 eq HF), and amide **3-96** (0.040 g, 0.16 mmol) in CH_2Cl_2 (1.5 mL). Chromatography on SiO_2 (25% EtOAc/hexanes) afforded *cis* **3-101** (17 mg, 0.063 mmol, 39%) as a colorless oil and *trans* **3-101** (11 mg, 0.041 mmol, 25%) as a colorless semi-solid. Major product *cis* **3-101**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, 2 H, J = 7.5 Hz), 7.50 (d, 2 H, J = 8.0 Hz), 7.40 (t, 2 H, J = 7.5 Hz), 7.36-7.29 (m, 3 H), 7.24 (br s, 1 H), 7.12 (t, 1 H, J = 7.6 Hz), 3.46 (AB_2X (app q), 1 H, J = 8.4 Hz), 3.12-2.93 (AB_2X (m), 2 H), 2.88-2.75 (AB_2X (m), 2 H); ^{19}F NMR (470 MHz, $CDCl_3$) δ –146.0. Minor product *trans* **3-101**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, 2 H, J = 8.0 Hz), 7.50 (d, 2 H, J = 8.0 Hz), 7.43 (t, 2 H, J = 7.5 Hz), 7.40-7.27 (m, 4 H), 7.12 (t, 1 H, J = 7.5 Hz), 3.12-3.01 (AMX (m), 2 H), 2.91-2.82 (AMX (m), 2 H), 2.75 (AMX (app pent), 1 H, J = 8.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.2, 140.9 ($^2J_{CF}$ = 23 Hz), 137.8, 129.1, 128.6, 128.5, 124.8 ($^3J_{CF}$ = 6 Hz), 124.5, 119.8, 92.0 ($^1J_{CF}$ = 211 Hz), 38.7 ($^2J_{CF}$ = 25 Hz), 31.1 ($^3J_{CF}$ =

13 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ –119.3. MS (ESI^+) *m/z* 250 (100), 225 (10), 184 (30), 128 (20); HRMS (ESI^+) *m/z* calcd for $C_{17}H_{16}NO$ [M+H–HF] 250.1226, found 250.1225.



3-102

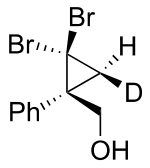
2-(Fluoromethyl)-*N*-phenylcyclopropane-1-carboxamide (3-102). Prepared according to General Procedure I from KHF_2 (0.032 g, 0.40 mmol), diisopropylamine (0.23 mL, 1.6 mmol, 4.0 eq), pyridine • 9 HF (0.72 mL, 28 mmol HF, 69 eq HF), and amide **3-43** (0.070 g, 0.40 mmol) in CH_2Cl_2 (3 mL). Chromatography on SiO_2 (20-50% EtOAc/hexanes) afforded a less polar minor product (10 mg), which appears to be a ~ 1:1 mixture of a cyclopropane diastereomer and an unidentified product. The major product was identified as primary fluoride **3-102** (25 mg, 0.13 mmol, 32%), a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (br s, 1 H), 7.50 (d, 2 H, J = 8.0 Hz), 7.35-7.24 (m, 3 H), 7.10 (t, 1 H, J = 7.2 Hz), 4.54 (ddd, 1 H, $^2J_{HF}$ = 48.4 Hz, J = 9.6 Hz, 5.6 Hz), 4.17 (ddd, 1 H, $^2J_{HF}$ = 48.4 Hz, J = 8.4 Hz, 8.4 Hz), 1.97-1.84 (m, 1 H), 1.63-1.54 (m, 1 H), 1.42-1.33 (m, 1 H), 0.95-0.86 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.9, 129.1, 129.0, 124.3, 119.8, 84.9 ($^1J_{CF}$ = 167 Hz), 21.0 ($^2J_{CF}$ = 24 Hz), 11.74, 11.67; ^{19}F NMR (376 MHz, $CDCl_3$) δ –214.4.



3-104

(*Z*)-2-Phenylprop-2-en-3-*d*-1-ol (3-104). A 500 mL 3-neck flask affixed with an internal thermometer, septum, and condenser with N_2 inlet was charged with magnesium turnings (2.25 g, 92.8 mmol, 2.6 eq) and THF (120 mL). Bromobenzene (9.5 mL, 89 mmol, 2.5 eq) was added in

~1 mL portions. The system was heated with a heat gun to initiate Grignard formation. Upon complete formation of the Grignard reagent, the reaction was stirred until it cooled to rt. In a separate 500 mL 3-neck flask affixed with a septum, internal thermometer, and N_2 inlet. Under an N_2 atmosphere, CuI (0.679 g, 3.57 mmol, 0.100 eq), THF (80 mL), and propargyl alcohol (2.1 mL, 36 mmol, 1.0 eq) were added sequentially. The solution was cooled to –78 °C. The Grignard solution was cannulated to this alcohol solution over a period of 1.5 h. After complete transfer, the cooling bath was removed and the reaction was warmed to rt and stirred for 17 h. The reaction was then cooled to –78 °C and treated with D_2O (6.5 mL, 0.36 mol, 10 eq). After warming to rt, 1 M HCl (300 mL) was added. The material was extracted with ether (2 x 100 mL). The combined extracts were washed with water (70 mL) and brine (70 mL), then were dried (Na_2SO_4) and concentrated. Purification by chromatography on SiO_2 (30% EtOAc/hexanes) afforded labelled alcohol (4.26 g, 35.8 mmol, 100%) as a yellow-tinted oil. The material contained trace EtOAc but was carried forward without further purification. ^{1}H NMR suggests ~90% D incorporation at the alkene: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52-7.18 (m, 5 H), 5.46 (s, 1 H), 4.55 (s, 2 H).



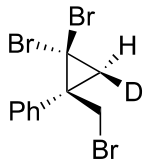
3-105

2,2-Dibromo-1-phenylcyclopropyl-3-*d*)methanol (3-105). A solution of alcohol **3-104** (4.26 g, 31.5 mmol) in CH_2Cl_2 (60 mL) was treated with 3,4-dihydro-2H-pyran (2.9 mL, 32 mmol, 1.2 eq) followed by PPTS (0.791 g, 3.15 mmol, 0.10 eq). The resulting solution was stirred at rt for 4 h. The reaction mixture was then concentrated on the rotovap. The residue was partitioned between ether and water (75 mL each). The layers were separated, and the organic layer was washed with

sat aq $NaHCO_3$ (75 mL). The organic layer was then dried (Na_2SO_4) and concentrated to afford the protected alcohol (7.304 g). The material was used without further purification, and a 100% yield was assumed.

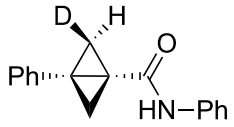
A solution of protected alcohol (6.91 g, 31.5 mmol) and cetyltrimethyl ammonium bromide (0.116 g, 0.315 mmol, 1 mol %) in CH_2Cl_2 (10 mL) in a 250 mL 3-neck flask was affixed with an N_2 inlet, mechanical stirrer, and septum. Bromoform (8.3 mL, 95 mmol, 3.00 eq) was added, and the solution was cooled to 0 °C. Sodium hydroxide (15.1 g, 0.378 mol, 12.0 eq) was added as a solution in water (30 mL, ~50 g/100 mL) via syringe over 10 min. The ice bath was removed and the flask was stirred for 25 h at 300 rpm. The reaction mixture became very dark and thick. The material was partitioned between water (50 mL) and CH_2Cl_2 (50 mL), filtered through Celite, and the layers were separated. The aqueous phase was extracted with CH_2Cl_2 (50 mL). The combined extracts were washed with water (25 mL), 1:1 water/brine (25 mL), then was dried ($MgSO_4$), filtered through a pad of SiO_2, and concentrated.

This crude dark red oil was dissolved in MeOH (30 mL) and treated with *p*-toluenesulfonic acid monohydrate (0.599 g, 3.15 mmol, 10 mol %). After stirring at rt for 5 h, the reaction mixture was concentrated. The residue was partitioned between water and ether (75 mL each). The layers were separated and the organic layer was washed with water (75 mL), sat aq $NaHCO_3$ (75 mL), and brine (75 mL). The organic layer was then dried (Na_2SO_4) and concentrated. Purification by chromatography on SiO_2 (15-50% EtOAc/hexanes) afforded alcohol **3-105** (3.14 g, 10.2 mmol, 32% over 4 steps) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.28 (m, 5 H), 4.05, 3.95 (AB q, 2 H, J_{AB} = 11.6 Hz), 2.09 (app s, 1 H), 1.72 (br s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.3, 129.7, 128.6, 128.0, 126.1, 70.3, 40.8, 32.4, 31.5 ($^1J_{CD}$ = 27 Hz).



3-106

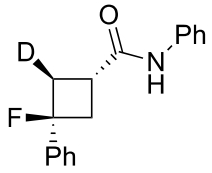
2,2-Dibromo-1-(bromomethyl)cyclopropyl-3-*d*)benzene (3-106). A solution of alcohol **3-105** (3.14 g, 10.2 mmol) in CH_2Cl_2 (50 mL) at 0 °C was treated with triphenylphosphine (2.95 g, 11.3 mmol, 1.10 eq) followed by carbon tetrabromide (3.73 g, 11.3 mmol, 1.10 eq). The reaction was warmed to rt for 4 h. The solution was then concentrated, and the residue was purified by chromatography on SiO_2 to afford tribromide **3-106** (2.62 g, 7.08 mmol, 69%) as a colorless oil. The material contained ~20% of allylic bromide (from unreacted cyclopropane in the previous step). After standing overnight, the material solidified. This solid was recrystallized from hexanes to afford 0.962 g (0.962 g, 25%) of material as a colorless solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.31 (m, 5 H), 3.97, 3.84 (AB q, 2 H, J_{AB} = 10.4 Hz), 2.25 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.2, 129.8, 128.4, 128.2, 42.5, 40.0, 34.7, 34.4 ($^1J_{CD}$ = 25 Hz).



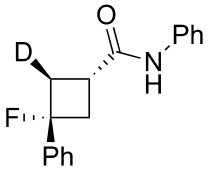
3-107

***N*, 3-Diphenylbicyclo[1.1.0]butane-2-*d*-1-carboxamide (3-107)**. Prepared according to General Procedure G from tribromide **3-106** (0.898 g, 2.43 mmol, 2.00 eq), MeLi (1.5 mL, 2.4 mmol, 1.6 M in Et_2O), *t*-BuLi (1.4 mL, 2.4 mmol, 1.7 M in pentane), and phenyl isocyanate (0.13 mL, 1.2 mmol) in Et_2O (10 mL). Purification by chromatography on SiO_2 (15-40% EtOAc/hexanes) afforded amide **3-107** (0.241 g, 0.963 mmol, 79%) as a colorless solid: ^{1}H NMR (400 MHz, acetone-D_6) δ 8.95 (br s, 1 H), 7.50 (d, 2 H, *J* = 7.6 Hz), 7.38 (d, 2 H, *J* = 7.2 Hz), 7.27 (t, 2 H, *J*

= 7.6 Hz), 7.18 (t, 3 H, *J* = 7.2 Hz), 6.94 (t, 1 H, *J* = 7.2 Hz), 3.06 (d, 2 H, *J* = 2.4 Hz), 1.53 (d, 1 H, *J* = 1.2 Hz); ^{13}C NMR (100 MHz, acetone-D_6) δ 166.9, 140.3, 135.4, 129.3, 129.1, 127.3, 126.9, 123.9, 120.4, 35.0, 34.7 ($^1J_{CD}$ = 25 Hz), 31.3, 26.1.



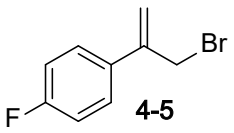
cis **3-108**, 24%



trans **3-108**, 18%

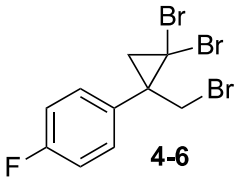
3-Fluoro-*N*,3-diphenylcyclobutane-2-*d*-1-carboxamide (3-108). Prepared according to General Procedure I from KHF_2 (0.044 g, 0.57 mmol), diisopropylamine (0.32 mL, 2.3 mmol, 4.0 eq), pyridine • 9 HF (1.0 mL, 39 mmol HF, 68 eq HF) and amide **3-107** (0.142 g, 0.567 mmol) in CH_2Cl_2 (4 mL). Chromatography on SiO_2 (25% EtOAc/hexanes) afforded less polar *cis* **3-108** (38 mg, 0.14 mmol, 25%) as a colorless solid and the more polar *trans* **3-108** (28 mg, 0.15 mmol, 18%) as a colorless solid. *cis* **3-108**: Mp 107–110 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, 2 H, *J* = 7.6 Hz), 7.50 (d, 2 H, *J* = 8.0 Hz), 7.40 (t, 2 H, *J* = 7.6 Hz), 7.36-7.29 (m, 3 H), 7.24 (br s, 1 H), 7.12 (t, 1 H, *J* = 7.6 Hz), 3.46 (AB*X* (app q), 1 H, *J* = 8.4 Hz), 3.12-2.93 (A*B*X (m), 2 H), 2.88-2.75 (*A*BX (m), 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 141.4 ($^2J_{CF}$ = 23 Hz), 137.7, 129.1, 128.4, 128.2, 124.64, 124.56, 124.51, 119.8, 97.4 ($^1J_{CF}$ = 192 Hz), 38.7 ($^2J_{CF}$ = 25 Hz), 34.2 ($^1J_{CD}$ not resolved); ^{19}F NMR (470 MHz, $CDCl_3$) δ –146.3; *trans* **3-108**: Mp 146–148 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (br s, 1 H), 7.54 (d, 2 H, *J* = 7.6 Hz), 7.49 (d, 2 H, *J* = 7.6 Hz), 7.45-7.34 (m, 3 H), 7.31 (t, 2 H, *J* = 7.6 Hz), 7.11 (t, 1 H, *J* = 7.6 Hz), 3.12-2.93 (m, 2 H), 2.88-2.72 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6, 140.8 ($^2J_{CF}$ = 22 Hz), 137.8, 129.1, 128.7, 128.5, 124.9 ($^3J_{CF}$ = 6 Hz), 124.5, 120.0, 91.3 ($^1J_{CF}$ = 211 Hz), 38.7 ($^1J_{CD}$ = 21 Hz, $^2J_{CF}$ = 25 Hz), 30.9 ($^3J_{CF}$ = 13 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ –119.2; MS (ESI$^+$) *m/z* 251 (100), 158 (5), 130 (5); HRMS (ESI$^+$) *m/z* calcd for $C_{17}H_{15}NOD$ [M+H–HF] 251.1295, found 251.1285.

5.5 CHAPTER 4 EXPERIMENTAL PART



4-5

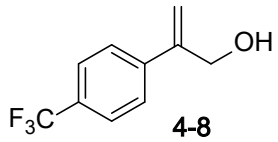
1-(3-Bromoprop-1-en-2-yl)-4-fluorobenzene (4-5).[171] A solution of methylstyrene **4-4** (4.78 g, 35.1 mmol) in $CHCl_3$ (7 mL) was treated with NBS (8.50 g, 47.7 mmol, 1.36 eq). The reaction was heated to reflux (~90 °C) for 6 h then it was cooled and filtered through Celite. The filter cake was washed with hexane (50 mL) and the eluent was concentrated. The residue was purified by chromatography on SiO_2 (hexane) to afford bromide **4-5** (3.38 g, 15.7 mmol, 45%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.43 (m, 2 H), 7.13-7.01 (m, 2 H), 5.50 (s, 1 H), 5.48 (s, 1 H), 4.36 (s, 2 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ –113.7.



4-6

1-(2,2-Dibromo-1-(bromomethyl)cyclopropyl)-4-fluorobenzene (4-6). A solution of allylic bromide **4-5** (3.17 g, 14.7 mmol) and cetyltrimethyl ammonium bromide (0.054 g, 0.15 mmol, 1 mol %) in CH_2Cl_2 (4 mL) was charged to a 100 mL 3-neck flask affixed with an N_2 inlet, mechanical stirrer, and septum. Bromoform (3.9 mL, 44 mmol, 3.0 eq) was added by syringe, and the solution was cooled to 0 °C. Sodium hydroxide (7.07 g, 0.177 mol) was added as a solution in water (15 mL, ~50 g/100 mL) via syringe over 5 min. The ice bath was removed and the flask stirred for 26 h at 300 rpm (color changed from clear to a dark, opaque brown). The reaction mixture was then partitioned between water (50 mL) and CH_2Cl_2 (50 mL). The layers were separated, and the aqueous phase was extracted with CH_2Cl_2 (50 mL). The combined extracts were

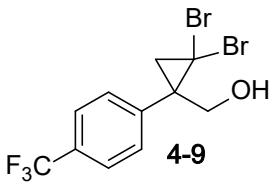
washed with water (25 mL), 1:1 water/brine (25 mL), then were dried (Na_2SO_4) and concentrated. The residue was purified by column chromatography on SiO_2 (10% EtOAc in hexane). Upon concentration of the product-containing fractions, a solid mass formed. This material was then recrystallized from ~1:1 EtOAc/hexanes (~15 mL), and the crystals were washed with cold hexanes (30 mL). After drying under vacuum, tribromide **4-6** (1.68 g, 4.35 mmol, 30%) was obtained as a colorless crystalline solid: Mp 101–103 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.30 (m, 2 H), 7.08 (app t, 2 H, *J* = 8.8 Hz), 3.91 (dd, 2 H, *J* = 10.8 Hz, 1.6 Hz), 3.82 (d, 1 H, *J* = 10.4 Hz), 2.21 (dd, 1 H, *J* = 8.0 Hz, 1.2 Hz), 2.01 (d, 1 H, *J* = 8.4 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ –113.2.



4-8

2-(4-(Trifluoromethyl)phenyl)prop-2-en-1-ol (4-8).[181] Magnesium turnings (2.71 g, 0.111 mol) were charged to a 500 mL 3-neck round bottomed flask fitted with a reflux condenser, septum, and internal thermometer. After flushing with N_2, the turnings were suspended in ether (120 mL). Neat aryl bromide **4-7** (15.8 mL, 0.111 mol) was added by syringe in ~1 mL portions over ~15 min, which caused the formation of a dark brown Grignard solution and spontaneous heating of the reaction to reflux. After ~1 h, the reaction has cooled from reflux to rt. To the freshly prepared Grignard reagent was added CuI (1.27 g, 6.67 mmol) and the black suspension was stirred for 15 min. A solution of propargyl alcohol (2.60 mL, 44.6 mmol) in ether (50 mL) was added via cannula over 1.75 h, causing an exotherm to 29 °C. The reaction was stirred at rt for 18 h, at which point a quenched aliquot showed consumption of propargyl alcohol by ^{1}H NMR. The reaction was then cooled to 0 °C and quenched with sat aq NH_4Cl (100 mL). The layers were separated and the aqueous layer was extracted with ether (2 x 100 mL). The organic extracts were washed with water

(100 mL) and brine (100 mL), then they were dried ($MgSO_4$), filtered, and concentrated. The crude product was purified by chromatography on SiO_2 (25% EtOAc/hexanes) to afford alcohol **4-8** (4.86 g, 24.0 mmol, 54%) as a red-tinted oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 (AB q, 4 H, J = 8.4 Hz, ∂_{AB} = 0.05 ppm), 5.55 (s, 1 H), 5.46 (s, 1 H), 4.56 (s, 2 H), 1.62 (s, 1 H).



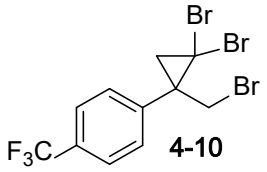
4-9

(2,2-Dibromo-1-(4-(trifluoromethyl)phenyl)cyclopropyl)methanol (4-9). A solution of alcohol **4-8** (4.86 g, 24.0 mmol) in CH_2Cl_2 (40 mL) was treated with 3,4-dihydro-2H-pyran (3.1 mL, 34 mmol, 1.4 eq) followed by PPTS (0.604 g, 2.40 mmol, 0.10 eq). The resulting solution was stirred at rt for 2.5 h. The reaction mixture was then concentrated on the rotovap. The residue was partitioned between ether and water (75 mL each). The layers were separated, and the organic layer was washed with sat aq $NaHCO_3$ (75 mL). The organic layer was then dried (Na_2SO_4) and concentrated to afford the protected alcohol (7.11 g) as a red-tinted oil. The material contained residual solvents and was carried on without further purification.

A solution of protected alcohol (7.11 g, 24.8 mmol) and cetyltrimethyl ammonium bromide (0.091 g, 0.25 mmol, 1 mol %) in CH_2Cl_2 (12 mL) in a 250 mL 3-neck flask was affixed with an N_2 inlet, mechanical stirrer, and septum. Bromoform (6.5 mL, 75 mmol, 3.0 eq) was added, and the solution was cooled to 0 °C. Sodium hydroxide (11.9 g, 298 mmol, 12.0 eq) was added as a solution in water (24 mL, ~50 g/100 mL) via syringe over 10 min. The ice bath was removed and the flask stirred for 24 h at 300 rpm. ^{1}H NMR of an aliquot showed consumption of the alkene. The reaction mixture was partitioned between water (50 mL) and CH_2Cl_2 (50 mL), the layers were separated, and the aqueous phase was extracted with CH_2Cl_2 (50 mL). The combined extracts were

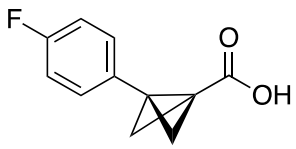
washed with water (25 mL), 1:1 water/brine (25 mL), then were dried (Na_2SO_4) and concentrated.

This crude dark red oil was dissolved in MeOH (25 mL) and treated with *p*-toluenesulfonic acid monohydrate (0.472 g, 2.48 mmol, 10 mol %). After stirring at rt for 3 h, the reaction mixture was concentrated. The residue was partitioned between water and ether (75 mL each). The layers were separated and the organic layer was washed with water (75 mL), sat aq $NaHCO_3$ (75 mL), and brine (75 mL). The organic layer was then dried (Na_2SO_4) and concentrated. Purification by chromatography on SiO_2 afforded **4-9** (4.45 g, 11.9 mmol, 48% over 3 steps) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (app d, 2 H, J = 8.4 Hz), 7.52 (app d, 2 H, J = 8.0 Hz), 4.01 (AB q, J = 12.0 Hz, ∂_{AB} = 0.04 ppm), 2.11 (AB q, 4 H, J = 7.6 Hz, ∂_{AB} = 0.03 ppm); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 130.2, 125.4 (q, $^3J_{CF}$ = 4 Hz), 70.1, 40.7, 31.9, 31.3, 21.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.6.



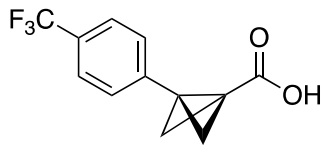
4-10

1-(2,2-Dibromo-1-(bromomethyl)cyclopropyl)-4-(trifluoromethyl)benzene **(4-10)**. A solution of alcohol **4-9** (4.45 g, 11.9 mmol) in CH_2Cl_2 (35 mL) was cooled to 0 °C under N_2. PPh_3 (3.75 g, 13.1 mmol, 1.20 eq) was then charged, followed by CBr_4 (4.34 g, 13.1 mmol, 1.10 eq). The reaction was warmed to rt and stirred for 20 h, then it was concentrated. Purification by chromatography on SiO_2 (0-15% EtOAc in hexanes) afforded bromide **4-10** (4.31 g, 9.85 mmol, 83%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, 2 H, J = 8.0 Hz), 7.49 (d, 2 H, J = 8.0 Hz), 3.93 (dd, 1 H, J = 10.8 Hz, 1.2 Hz), 3.83 (d, 1 H, J = 10.8 Hz), 2.27 (dd, 1 H, J = 8.0 Hz, 1.2 Hz), 2.06 (d, 1 H, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.0, 130.6, 130.3, 125.4 (q, $^3J_{CF}$ = 4 Hz), 41.7, 39.8, 34.8, 34.7, 33.4, 31.6, 14.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.6.



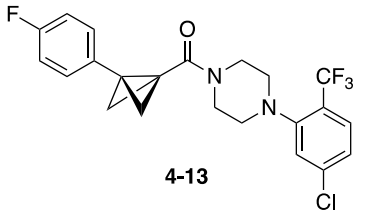
4-11

General Procedure J (Bicyclo[1.1.0]butyl carboxylic acid synthesis): 3-(4-Fluorophenyl)bicyclo[1.1.0]butane-1-carboxylic acid (4-11). A solution of dibromocyclopropane **4-8** (0.880 g, 2.57 mmol) in Et_2O (7 mL) and THF (3 mL) in a 50 mL round bottom flask was placed under N_2 and cooled to –78 °C. MeLi (1.6 mL, 2.6 mmol, 1.0 eq) was added via syringe over 10 min. After 1.75 h at –78 °C, *t*-BuLi (1.5 mL, 2.6 mmol, 1.0 eq) was added via syringe over 10 min. After an additional 1 h at –78 °C, a balloon of dry CO_2 was bubbled through the solution via a needle for 10 min (an external bubbler was used, providing a continuous stream of CO_2 through the flask). The cooling bath was then removed, and the opaque grey reaction mixture was warmed to 0 °C over 20 min. The reaction mixture was then quenched with 1 M NaOH (10 mL), then it was partitioned between ether and 1 M NaOH (50 mL each). The light brown aqueous layer was acidified to litmus with conc HCl, which caused formation of a light brown precipitate. This suspension was then extracted with ether (40 mL). The organic layer was dried (Na_2SO_4) and concentrated to afford acid **4-11** (0.228 g, 1.19 mmol, 57%) as a buff solid: Mp 158–160 °C; IR (ATR) 1646, 1527, 1226, 841 cm^{-1}; ^1H NMR (300 MHz, CD_3OD) δ 7.41-7.32 (m, 2 H), 7.05 (app t, 2 H, J = 9.0 Hz), 2.88 (t, 2 H, J = 1.2 Hz), 1.60 (s, 2 H); ^{13}C NMR (100 MHz, CD_3OD) ($^1J_{CF}$ not resolved) δ 172.2, 127.5 (d, $^3J_{CF}$ = 8 Hz), 114.9 (d, $^2J_{CF}$ = 21 Hz), 34.9, 31.8, 22.4; ^{19}F NMR (376 MHz, CD_3OD) δ –117.7; HRMS *m/z* calcd for $C_{11}H_{10}FO_2$ [M+H] 193.0665, found 193.0660.



4-12

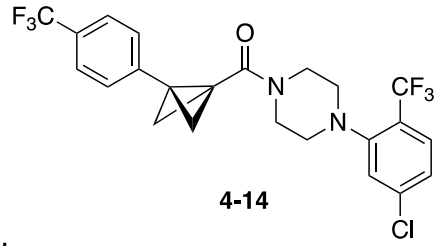
3-(4-(Trifluoromethyl)phenyl)bicyclo[1.1.0]butane-1-carboxylic acid (4-12). Prepared according to General Procedure J from tribromocyclopropane **4-12** (1.50 g, 3.43 mmol), MeLi (2.1 mL, 3.4 mmol, 1.6 M in Et_2O), and *t*-BuLi (2.0 mL, 3.4 mmol, 1.7 M in pentane, 1.0 eq) to afford acid **4-12** (0.416 g, 1.72 mmol, 50%) as a colorless solid: Mp 146–148 °C; IR (ATR) 2980, 1648, 1616, 1463, 1318, 1167, 1116, 1061, 907, 842, 689 cm^{-1}; ^1H NMR (400 MHz, CD_3OD) δ 7.61 (d, 2 H, J = 8.4 Hz), 7.52 (d, 2 H, J = 8.4 Hz), 4.88 (s, 1 H), 2.99 (t, 2 H, J = 1.2 Hz), 1.68 (s, 2 H); ^{13}C NMR (100 MHz, CD_3OD) δ 171.5, 140.0, 128.4 (q, $^2J_{CF}$ = 32 Hz), 126.2, 124.9 (q, $^3J_{CF}$ = 4 Hz), 124.4 (q, $^1J_{CF}$ = 269 Hz), 35.0, 31.0, 24.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ –64.0; MS $(ESI)^+$ *m/z* 243 (80), 233 (50), 231 (50), 197 (60), 177 (40), 155 (100); HRMS $(ESI)^+$ *m/z* calcd for $C_{12}H_{10}F_3O_2$ [M+H] 243.0633, found 243.0626.



4-13

(4-(5-chloro-2-(trifluoromethyl)phenyl)piperazin-1-yl)(3-(4-fluorophenyl)bicyclo[1.1.0] butan-1-yl)methanone (4-13). A solution of bicyclobutane acid **4-11** (0.018 g, 0.096 mmol, 1.1 eq) and piperazine free base (0.023 g, 0.087 mmol) in CH_2Cl_2 (1 mL) was cooled to 0°C and treated with Et_3N (0.02 mL, 0.2 mmol, 2 eq). The transparent beige solution was then treated with T3P (50% solution in EtOAc) (0.09 mL, 0.13 mmol, 1.5 eq) dropwise via syringe over ~1 min. The reaction was stirred at 0°C for 30 min, then the ice bath was removed and the reaction was warmed to rt for 19.5 h. The reaction mixture was then directly purified by chromatography on SiO_2 (15-

25% EtOAc/hexanes) without workup to afford amide **4-13** (0.015 g, 0.038 mmol, 39%) as a colorless oil: IR (ATR) 2923, 1620, 1596, 1434, 1307, 1221, 1120, 1027, 906, 933, 725 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, 1 H, J = 8.4 Hz), 7.34-7.27 (m, 2 H), 7.25-7.19 (m, 2 H), 7.01 (app t, 2 H, J = 8.8 Hz), 4.1-3.5 (br m, 4 H), 2.9-2.7 (br m, 4 H), 2.75 (s, 2 H), 1.63 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) (piperazine carbons broadened and are not clearly visible) δ 167.7, 161.9 (d, $^{1}J_{CF}$ = 243 Hz), 152.9, 138.8, 135.1, 129.7 (d, $^{4}J_{CF}$ = 3 Hz), 128.6 (q, $^{3}J_{CF}$ = 5 Hz), 128.0 (d, $^{3}J_{CF}$ = 8 Hz), 126.3 (q, $^{1}J_{CF}$ = 272 Hz), 125.4 (q, $^{2}J_{CF}$ = 30 Hz), 115.4 (d, $^{2}J_{CF}$ = 21 Hz), 36.9, 30.6, 30.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ –60.3, –115.9; MS $(ESI)^+$ *m/z* 439 (100), 265 (3), 175 (5), 147 (45); HRMS $(ESI)^+$ *m/z* calcd for $C_{22}H_{20}ClF_4N_2O$ [M+H] 439.1195, found 439.1193.



4-14

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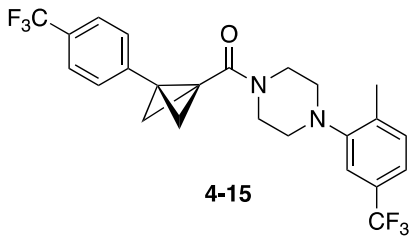
(4-(5-Chloro-2-(trifluoromethyl)phenyl)piperazin-1-yl)(3-(4(trifluoromethyl)phenyl)bicyclo [1.1.0]butan-1-yl)methanone (4-14). A solution of bicyclobutane acid **4-12** (0.046 g, 0.19 mmol, 1.0 eq) and piperazine HCl (0.057 g, 0.19 mmol) in CH_2Cl_2 (4 mL) cooled to 0 °C was treated Et_3N (0.08 mL, 0.6 mmol, 3 eq). The transparent beige solution was then treated with T3P (50% solution in EtOAc) (0.2 mL, 0.28 mmol, 1.5 eq) dropwise via syringe over ~1 min. The reaction was stirred at 0 °C for 30 min, then the ice bath was removed and the reaction was warmed to rt for 22 h. The reaction mixture was then partitioned between water and CH_2Cl_2 (30 mL each). The layers were separated, and the aqueous layer was extracted with additional CH_2Cl_2 (30 mL). The combined extracts were washed with water (30 mL) and sat aq $NaHCO_3$ (30 mL), then were dried (Na_2SO_4) and concentrated. Purification by chromatography on SiO_2 (15-25% EtOAc/hexanes)

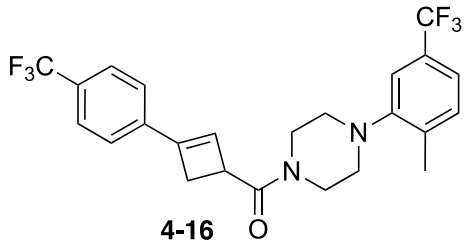
afforded amide **4-14** (0.051 g, 0.10 mmol, 55%) as a colorless solid: Mp 137–139 °C; IR (ATR) 2902, 1604, 1466, 1438, 1312, 1100, 1027, 924, 838, 825 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (app d, 3 H, J = 8.4 Hz), 7.43 (app d, 2 H, J = 8.4 Hz), 7.23 (app q, 2 H, J = 8.4 Hz), 4.1-3.5 (br, 4 H), 3.0-2.7 (br, 4 H), 2.83 (s, 2 H), 1.69 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) (piperazine carbons broadened and are not clearly visible) δ 167.1, 152.8, 138.8, 138.6, 128.5 (q, $^{2}J_{CF}$ = 32 Hz), 128.5 (q, $^{3}J_{CF}$ = 4 Hz), 126.6, 125.7 (q, $^{2}J_{CF}$ = 29 Hz), 125.5, 125.3 (q, $^{3}J_{CF}$ = 3 Hz), 124.6, 124.3 (q, $^{1}J_{CF}$ = 270 Hz), 123.6 (q, $^{1}J_{CF}$ = 272 Hz), 37.0, 30.0, 29.7, 22.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ –60.3, –62.4; MS $(ESI)^+$ *m/z* 489, 256 (5); HRMS $(ESI)^+$ *m/z* calcd for $C_{23}H_{20}F_6ClN_2O$ [M+H] 489.1168, found 489.1158.



4-15

(4-(2-Methyl-5-(trifluoromethyl)phenyl)piperazin-1-yl)(3-(4-(trifluoromethyl)phenyl) bicyclo[1.1.0]butan-1-yl)methanone (4-15). A solution of bicyclobutane acid **4-12** (0.052 g, 0.21 mmol) and piperazine free base (1.1 eq, HCl salt washed with NaOH, dried and concentrated before use) in CH_2Cl_2 (2 mL) cooled to 0 °C and treated with Et_3N (0.06 mL, 0.43 mmol, 2.0 eq). The transparent beige solution was treated with T3P (0.23 mL, 0.32 mmol, 1.5 eq, 50% solution in EtOAc) dropwise via syringe. The reaction was stirred at 0 °C for 30 min, then the ice bath was removed and the reaction was warmed to rt for 17 h. The reaction mixture was partitioned between water and CH_2Cl_2 (50 mL each). The layers were separated, and the aqueous layer was extracted with additional CH_2Cl_2 (30 mL). The combined extracts were washed with water (50 mL) and sat aq $NaHCO_3$ (40 mL), then were dried (Na_2SO_4) and concentrated. Purification by chromatography on SiO_2 (15-25% EtOAc/hexanes) afforded amide **4-15** (0.072 g, 0.154 mmol, 72%) as a colorless

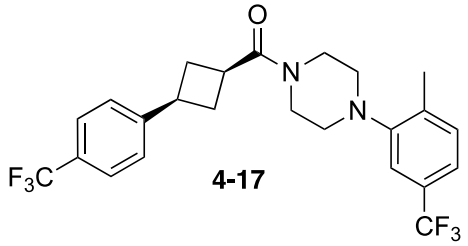
oil: IR (ATR) 2821, 1618, 1435, 1418, 1323, 1162, 1114, 1030, 840, 732 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, 2 H, J = 8.0 Hz), 7.43 (d, 2 H, J = 8.4 Hz), 7.28 (app q, 2 H, J = 8.0 Hz), 7.18 (s, 1 H), 4.1-3.5 (br, 4 H), 3.0-2.7 (br, 4 H), 2.84 (s, 2 H), 2.36 (s, 3 H), 1.70 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) (piperazine carbons broadened and are not clearly visible) δ 167.1, 151.2, 138.6, 136.8, 131.6, 129.1 (q, $^{2}J_{CF}$ = 32 Hz), 128.5 (q, $^{2}J_{CF}$ = 32 Hz), 126.6, 125.3 (q, $^{3}J_{CF}$ = 4 Hz), 124.3 (q, $^{1}J_{CF}$ = 270 Hz), 124.2 (q, $^{1}J_{CF}$ = 271 Hz), 120.4 (q, $^{3}J_{CF}$ = 3 Hz), 116.0 (q, $^{3}J_{CF}$ = 4 Hz), 37.0, 30.0, 22.8, 18.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.2, –62.4; MS $(ESI)^{+}$ *m/z* 469 (100), 197 (5); HRMS $(ESI)^{+}$ *m/z* calcd for $C_{24}H_{23}F_6N_2O$ [M+H] 469.1709, found 469.1705.



4-16

General Procedure K (Rearrangement of Bicyclo[1.1.0[butyl amides): ((*E*)-(4-(2-methyl-5-(trifluoromethyl)phenyl)piperazin-1-yl)(2-(4-(trifluoromethyl) benzylidene) cyclopropyl)methanone (4-16). A solution of amide **4-13** (0.680 g, 1.45 mmol) in CH_2Cl_2 (8 mL) was treated with camphorsulfonic acid (0.050 g, 0.22 mmol, 15 mol %). The vial was sealed and heated at 50 °C for 18 h. After cooling, the solution was partitioned between CH_2Cl_2 at sat aq $NaHCO_3$ (20 mL each). The organic layer was dried (Na_2SO_4) and concentrated. Purification by chromatography on SiO_2 afforded methylenecyclopropane **4-16** (0.484 g, 1.03 mmol, 71%) as an off-white foam: IR (ATR) 2921, 1638, 1417, 1324, 1116, 1069, 825, 729 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, 2 H, J = 8.0 Hz), 7.46 (d, 2 H, J = 8.4 Hz), 7.33-7.27 (m, 2 H), 7.21 (s, 1 H), 6.53 (d, 1 H, J = 0.8 Hz), 3.87 (app s, 1 H), 3.80 (q, 2 H, J = 5.2 Hz), 3.69 (t, 2 H, J = 4.8 Hz), 3.17-3.07 (m, 2 H), 2.99 (t, 2 H, J = 4.8 Hz), 2.91 (t, 2 H, J = 4.4 Hz), 2.39 (s, 3 H); ^{13}C NMR (100

MHz, $CDCl_3$) δ 170.7, 151.2, 145.7, 136.94, 136.88, 131.6, 129.9 (q, $^2J_{CF}$ = 33 Hz), 129.1 (q, $^2J_{CF}$ = 32 Hz), 128.1, 126.6, 126.4, 125.4 (q, $^3J_{CF}$ = 4 Hz), 124.9, 124.2 (q, $^1J_{CF}$ = 271 Hz), 124.1 (q, $^1J_{CF}$ = 271 Hz), 120.4 (q, $^3J_{CF}$ = 4 Hz), 116.0 (q, $^3J_{CF}$ = 4 Hz), 51.9, 51.7, 45.6, 42.1, 40.8, 32.7, 29.7, 21.0, 18.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.2, –62.5; MS (ESI)$^+$ *m/z* 469 (100), 371 (1), 225 (2); HRMS (ESI)$^+$ *m/z* calcd for $C_{24}H_{23}F_6N_2O$ [M+H] 469.1709, found 469.1715.

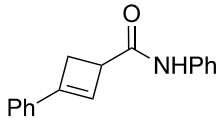


4-17

(4-(2-Methyl-5-(trifluoromethyl)phenyl)piperazin-1-yl)(3-(4-(trifluoromethyl)phenyl) cyclobutyl)methanone (4-17). A solution of amide **4-13** (0.072 g, 0.153 mmol) in MeOH (3 mL) was placed under N_2 and treated with Pd/C (3 mg, ~20 mol %). A hydrogen atmosphere of 6.43 bar was then established on the Parr hydrogenator. The reaction was stirred at rt for 18 h, at which point the hydrogen was vented and the solution was purified by chromatography on SiO_2 (25-40% EtOAc/hexanes) afforded cyclobutane **4-17** (0.037 g, 0.079 mmol, 51%) as a colorless oil.

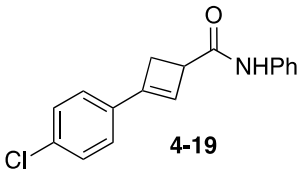
Alternatively, **4-17** was prepared by dissolving a solution of amide **4-16** (0.031 g, 0.080 mmol, 1.0 eq) in MeOH (2 mL) and treating with Pd/C (2 mg, 20 mol%). A hydrogen atmosphere was then established with a balloon. After stirring at rt for 2 h, the reaction mixture was filtered through Celite and concentrated to afford cyclobutane **4-17** (0.015 g, 0.039 mmol, 48%) as a colorless oil: IR (ATR) 2939, 1641, 1618, 1417, 1324, 1308, 1161, 1112, 1067, 834, 732 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, 2 H, *J* = 8.4 Hz), 7.36 (d, 2 H, *J* = 8.4 Hz), 7.32-7.24 (m, 2 H, *J* = 8.0 Hz), 7.19 (s, 1 H), 3.79 (t, 2 H, *J* = 4.8 Hz), 3.60 (t, 2 H, *J* = 5.2 Hz), 3.57-3.48 (m, 1 H), 3.37-3.26 (m, 1 H), 2.95-2.86 (m, 4 H), 2.68-2.59 (m, 2 H), 2.53 (ddd, 2 H, *J* = 19.2 Hz, 9.6 Hz,

2.4 Hz), 2.37 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 151.2, 148.7, 136.8, 131.6, 129.1 (q, $^2J_{CF}$ = 32 Hz), 128.5 (q, $^2J_{CF}$ = 32 Hz), 126.9, 125.3 (q, $^3J_{CF}$ = 4 Hz), 124.3 (q, $^1J_{CF}$ = 270 Hz), 124.2 (q, $^1J_{CF}$ = 270 Hz), 120.4 (q, $^3J_{CF}$ = 4 Hz), 116.0 (q, $^3J_{CF}$ = 5 Hz), 51.9, 51.7, 45.5, 42.2, 35.5, 33.1, 32.6, 18.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.3; MS (ESI)$^+$ *m/z* 471 (100), 355 (1), 246 (3), 179 (3); HRMS (ESI)$^+$ *m/z* calcd for $C_{24}H_{25}F_6N_2O$ [M+H] 471.1871, found 471.1865.



4-18

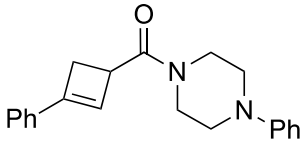
(*E*)-2-Benzylidene-*N*-phenylcyclopropane-1-carboxamide (4-18). Prepared according to General Procedure K from amide **3-96** (0.041 g, 0.16 mmol) and camphorsulfonic acid (6 mg, 0.025 mmol, 15 mol %) in CH_2Cl_2 (1 mL). Purified by chromatography on SiO_2 to afford amide **4-18** (0.027 g, 0.011 mmol, 66%) as a colorless solid: Mp 149–152 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, 2 H, *J* = 8.0 Hz), 7.46-7.28 (m, 8 H), 7.10 (t, 1 H, *J* = 7.2 Hz), 6.41 (s, 1 H), 3.71 (d, 1 H, *J* = 4.8 Hz), 3.24 (dd, 1 H, *J* = 13.6 Hz, 4.8 Hz), 3.00 (dd, 1 H, *J* = 13.6 Hz, 1.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 150.9, 137.8, 133.4, 129.0, 128.9, 128.5, 124.9, 124.3, 123.8, 119.8, 44.5, 34.1; MS (ESI$^+$) *m/z* 250 (100), 185 (20), 129 (5); HRMS (ESI$^+$) *m/z* calcd for $C_{17}H_{16}NO$ [M+H] 250.1226, found 250.1224.



4-19

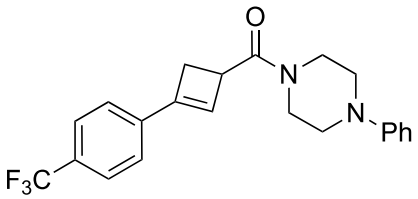
(*E*)-2-(4-Chlorobenzylidene)-*N*-phenylcyclopropane-1-carboxamide (4-19). Prepared according to General Procedure K from the corresponding bicyclobutane (0.043 g, 0.15 mmol, crystallized material) and camphorsulfonic acid (5 mg, 0.023 mmol, 15 mol %) in CH_2Cl_2 (1 mL). Purification by chromatography on SiO_2 afforded amide **4-19** (0.036 g, 0.13 mmol, 84%) as a

colorless semi-solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, 2 H, *J* = 8.0 Hz), 7.33-7.15 (m, 7 H), 7.02 (t, 1 H, *J* = 7.2 Hz), 6.32 (s, 1 H), 3.61 (d, 1 H, *J* = 3.6 Hz), 3.12 (dd, 1 H, *J* = 12.8 Hz, 4.8 Hz), 2.91 (d, 1 H, *J* = 13.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 149.5, 137.7, 129.1, 128.8, 126.2, 124.6, 124.4, 119.8, 44.4, 33.9; MS (ESI^+) *m/z* 284 (100), 195 (10); HRMS (ESI^+) *m/z* calcd for $C_{17}H_{15}ClNO$ [M+H] 284.0842, found 284.0836.



4-20

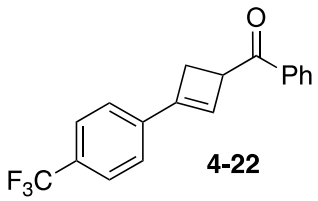
(*E*)-(2-Benzylidenecyclopropyl)(4-phenylpiperazin-1-yl)methanone (4-20). Prepared according to General Procedure K from the corresponding bicyclobutane (0.057 g, 0.18 mmol) and camphorsulfonic acid (0.006 g, 0.03 mmol, 15 mol%) in CH_2Cl_2 (2 mL). Purification by chromatography on SiO_2 (25-60% EtOAc/hexanes) afforded **4-20** (0.043 g, 0.14 mmol, 75%) as a colorless solid: Mp 138–142 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.26 (m, 7 H), 7.10-6.92 (m, 3 H), 6.42 (d, 1 H, *J* = 1.2 Hz), 3.88-3.77 (m, 3 H), 3.71 (dd, 2 H, *J* = 4.8 Hz, 4.8 Hz), 3.28-3.17 (m, 4 H), 3.14-3.11 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 151.0, 147.1, 133.8, 129.3, 128.4, 128.2, 125.0, 124.7, 120.6, 116.8, 50.0, 49.5, 45.1, 41.6, 40.7, 32.6; MS (ESI^+) *m/z* 319 (100), 157 (10); HRMS (ESI^+) *m/z* calcd for $C_{21}H_{23}N_2O$ [M+H] 319.1805, found 319.1802.



4-21

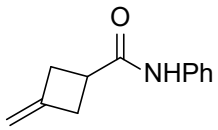
(*E*)-(4-Phenylpiperazin-1-yl)(2-(4-(trifluoromethyl)benzylidene)cyclopropyl)methanone (4-21). Prepared according to General Procedure K from the corresponding amide (0.067 g, 0.17 mmol) and camphorsulfonic acid (0.006 g, 0.03 mmol, 15 mol%) in CH_2Cl_2 (2 mL). Purification

by chromatography on SiO_2 afforded **4-21** (0.051 g, 0.013 mmol, 76%) as a colorless solid: Mp 152–155 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58, 7.45 (ABq, 4 H, J_{AB} = 8.0 Hz), 7.30 (app t, 2 H, J = 8.0 Hz), 6.99-6.89 (m, 3 H), 6.53 (s, 1 H), 3.90-3.86 (m, 1 H), 3.80 (dd, 2 H, J = 9.6 Hz, 4.0 Hz), 3.72-3.65 (m, 2 H), 3.27-3.15 (m, 4 H), 3.12 (d, 2 H, J = 3.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 151.0, 145.8, 136.9, 129.9 ($^2J_{CF}$ = 32 Hz), 129.3, 125.4 ($^3J_{CF}$ = 4 Hz), 124.9, 124.1 ($^1J_{CF}$ = 271 Hz), 120.7, 116.8, 50.0, 49.5, 45.1, 41.7, 40.8, 32.6; MS (ESI$^+$) *m/z* 387 (100), 225 (5); HRMS (ESI$^+$) *m/z* calcd for $C_{22}H_{22}N_2OF_3$ [M+H] 387.1684, found 387.1674.



4-22

(*E*)-Phenyl(2-(4-(trifluoromethyl)benzylidene)cyclopropyl)methanone (4-22). Prepared according to General Procedure K from the corresponding amide (0.027 g, 0.089 mmol) and camphorsulfonic acid (3 mg, 0.013 mmol ~15 mol%) in CH_2Cl_2 (1.5 mL). Purification by chromatography on SiO_2 (30% EtOAc/hexanes) afforded amide **4-22** (0.008 g, 0.026 mol, 30%) as a colorless semi-solid:^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 (d, 2 H, J = 7.2 Hz), 7.65-7.56 (m, 3 H), 7.56-7.41 (m, 4 H), 6.62 (s, 1 H), 4.53 (app s, 1 H), 3.28-3.13 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) ($^1J_{CF}$ not resolved) δ 198.7, 146.3, 136.9, 135.9, 133.3, 130.0 ($^2J_{CF}$ = 32 Hz), 128.8, 128.2, 125.4 ($^3J_{CF}$ = 4 Hz), 124.9, 46.0, 32.6; MS (ESI$^+$) *m/z* 303 (100), 225 (10), 167 (30); HRMS (ESI$^+$) *m/z* calcd for $C_{18}H_{14}OF_3$ [M+H] 303.0997, found 303.0989.

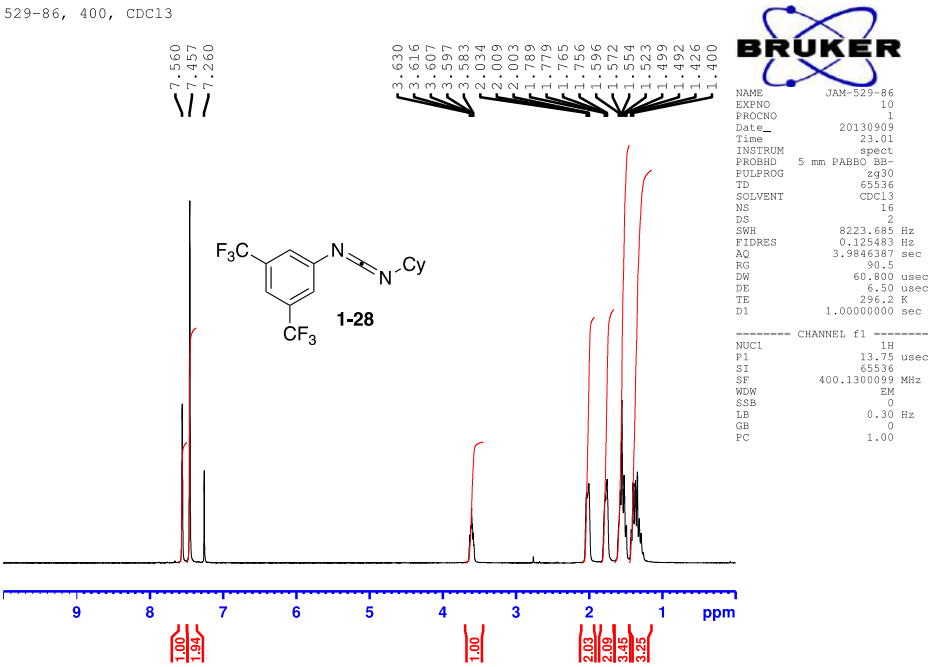


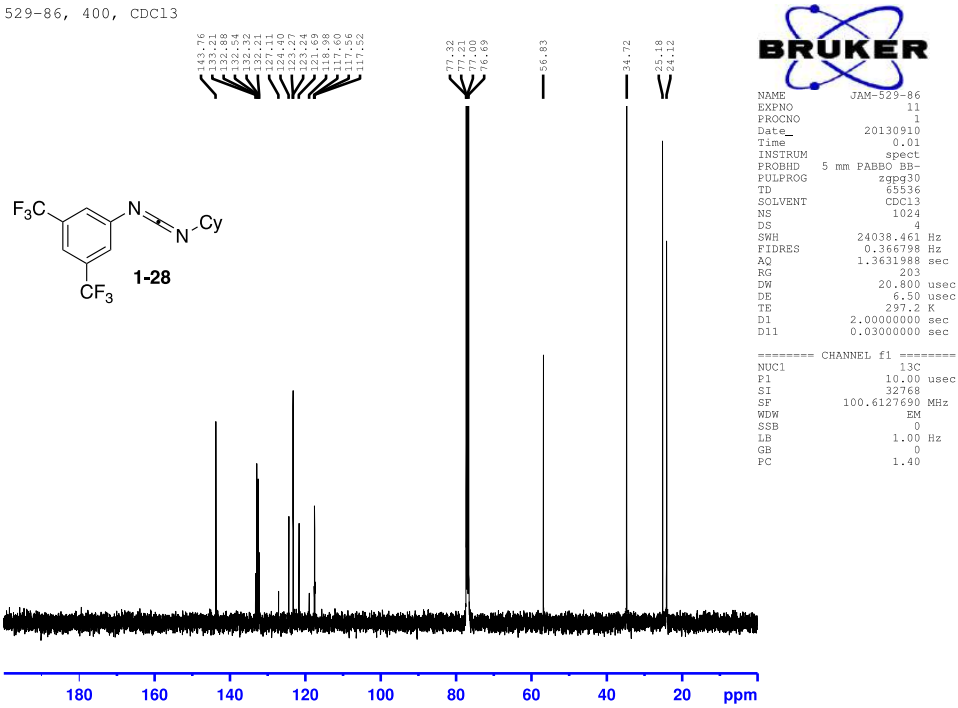
4-23

3-Methylene-*N*-phenylcyclobutane-1-carboxamide (4-23). A solution of amide **3-92** (0.042 g, 0.22 mmol) in CH_2Cl_2 (1 mL) was treated with camphorsulfonic acid (0.008 g, 0.034 mmol, 15 mol %). The reaction was stirred at rt for 3 h, then at 60 °C for 14 h, and then 120 °C for 6 h. The reaction mixture was directly purified by chromatography on SiO_2 to afford methylenecyclobutane **4-23** (7 mg, 0.04 mmol, 17%) as a colorless semi-solid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 (d, 2 H, J = 8.1 Hz), 7.32 (app t, 2 H, J = 7.8 Hz), 7.21-7.04 (m, 2 H), 4.84 (s, 2 H), 3.22-3.04 (m, 3 H), 3.02-2.84 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.6 (s), 143.9 (s), 137.9 (s), 129.0 (d), 124.3 (d), 119.7 (d), 106.8 (t), 35.9 (d), 35.6 (t).

APPENDIX A

^{1}H, ^{13}C, ^{19}F, AND ^{31}P NMR SPECTRA FOR NEW COMPOUNDS


529-86, 400, CDCl3
7.560
7.457
7.260
3.630
3.616
3.607
3.597
3.583
2.034
2.009
2.003
1.789
1.779
1.765
1.756
1.596
1.572
1.554
1.523
1.499
1.492
1.426
1.400
F3C
N
N
Cy
CF3
1-28
9
8
7
6
5
4
3
2
1
ppm
1.00
1.94
1.00
2.03
2.09
3.45
3.25
BRUKER
NAME JAM-529-86
EXPNO 10
PROCNO 1
Date_ 20130909
Time 23.01
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 90.5
DW 60.800 usec
DE 6.50 usec
TE 296.2 K
D1 1.00000000 sec
-------- CHANNEL f1 --------
NUC1 1H
P1 13.75 usec
SI 65536
SF 400.1300099 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


529-86, 400, CDCl3
143.76
133.21
132.88
132.54
132.20
131.21
127.11
124.40
123.27
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121.49
118.98
117.60
117.56
117.52
77.32
77.21
77.00
76.69
56.83
34.72
25.18
24.12
F3C
N
N
Cy
CF3
1-28
180
160
140
120
100
80
60
40
20
ppm
BRUKER
NAME JAM-529-86
EXPNO 11
PROCNO 1
Date_ 20130910
Time 0.01
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 297.2 K
D1 2.00000000 sec
D11 0.03000000 sec
======== CHANNEL f1 ========
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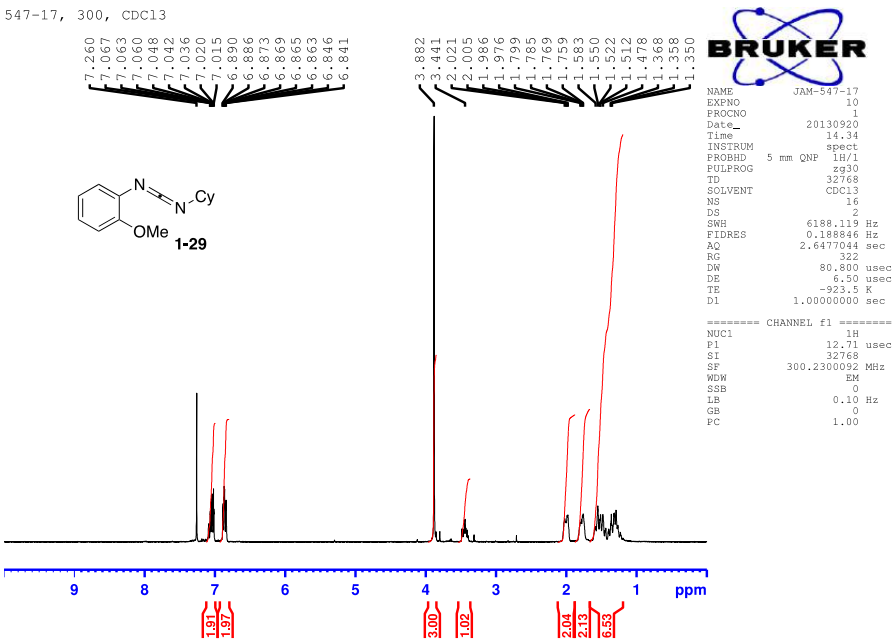
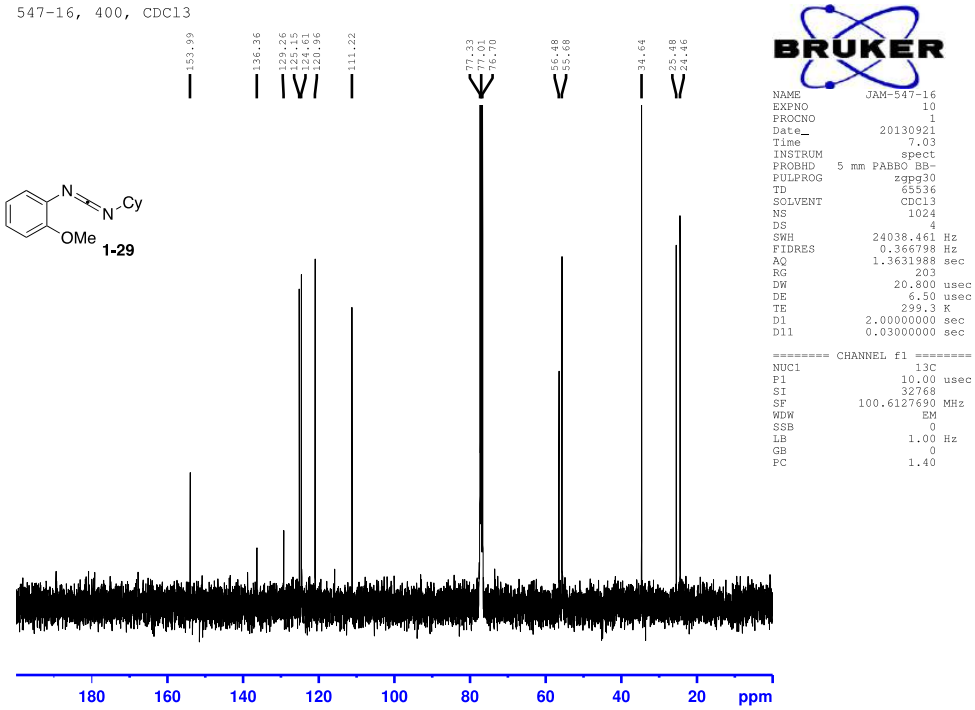
P1 10.00 usec
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40


547-17, 300, CDCl3
7.260
7.067
7.063
7.060
7.048
7.042
7.036
7.020
7.015
6.890
6.886
6.873
6.869
6.865
6.863
6.846
6.841
3.882
3.441
2.021
2.005
1.986
1.976
1.799
1.785
1.769
1.759
1.583
1.550
1.522
1.512
1.478
1.368
1.358
1.350
N
N
Cy
OMe
1-29
BRUKER
NAME JAM-547-17
EXPNO 10
PROCNO 1
Date_ 20130920
Time 14.34
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.188846 Hz
AQ 2.6477044 sec
RG 322
DW 80.800 usec
DE 6.50 usec
TE -923.5 K
D1 1.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 12.71 usec
SI 32768
SF 300.2300092 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00
9
8
7
6
5
4
3
2
1
ppm
1.91
1.97
3.00
1.02
2.04
2.13
6.53


547-16, 400, CDCl3
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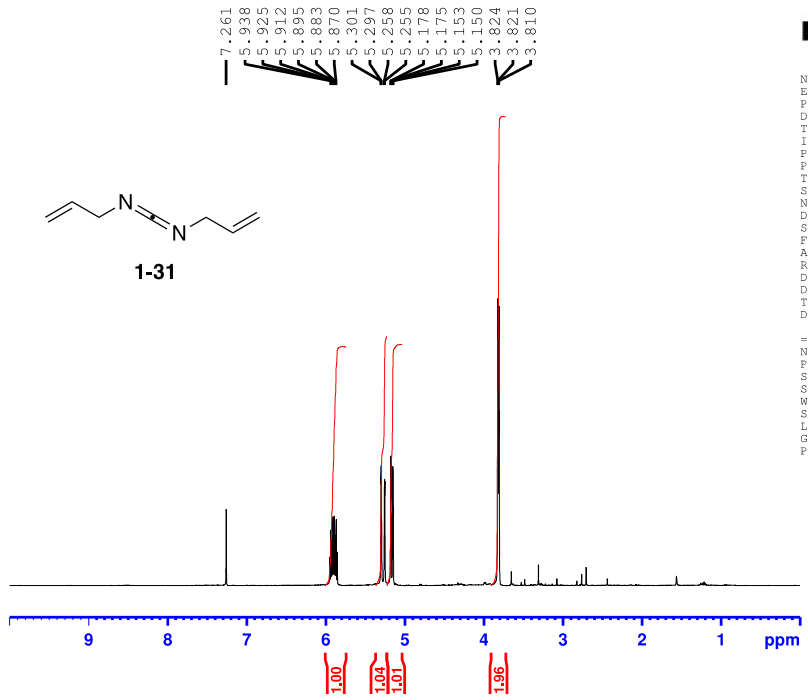
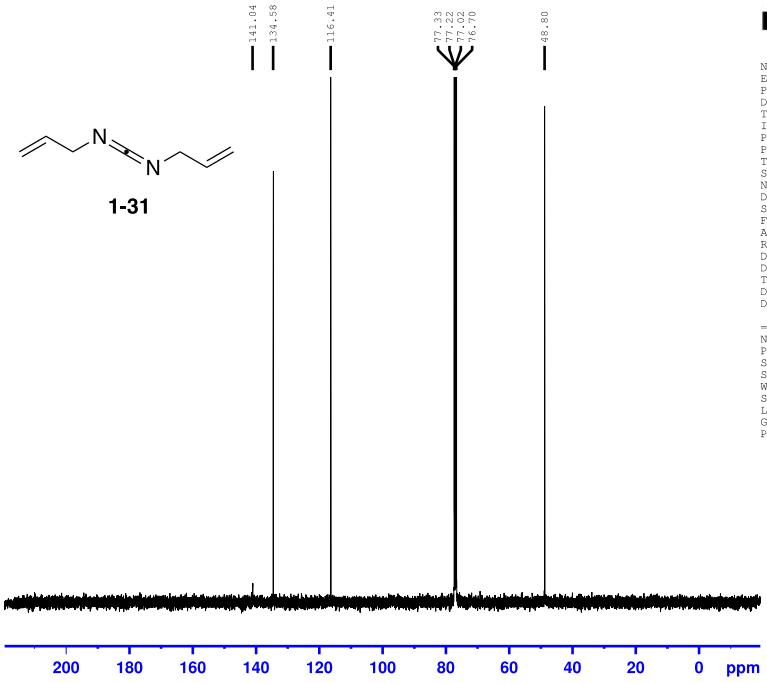
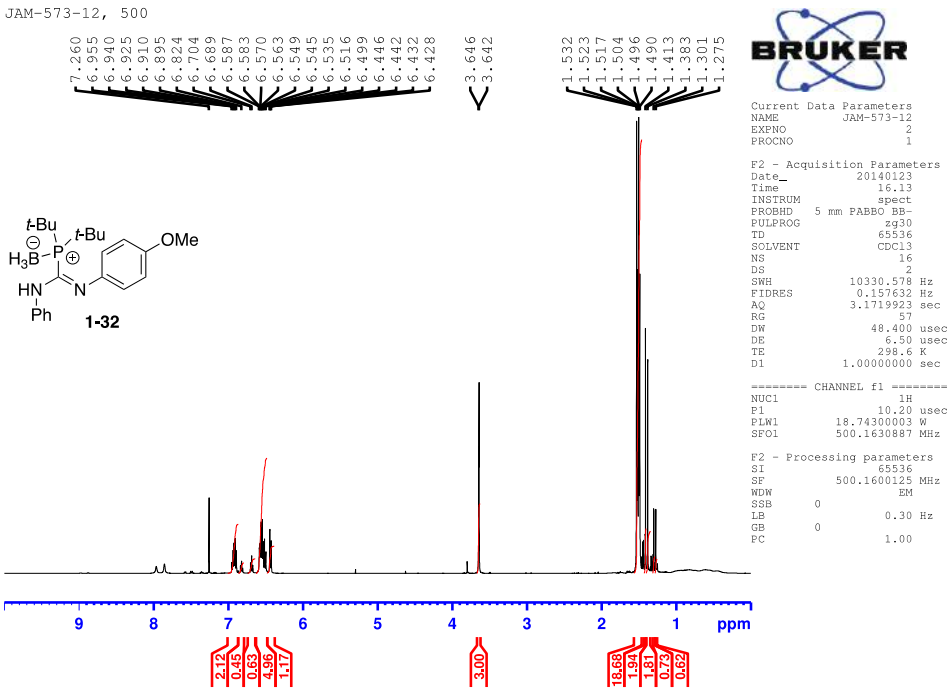
136.36
129.26
125.15
124.61
120.96
111.22
77.33
77.01
76.70
56.48
55.68
34.64
25.48
24.46
N
N
Cy
OMe
1-29
BRUKER
NAME JAM-547-16
EXPNO 10
PROCNO 1
Date_ 20130921
Time 7.03
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 299.3 K
D1 2.00000000 sec
D11 0.03000000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
180
160
140
120
100
80
60
40
20
ppm

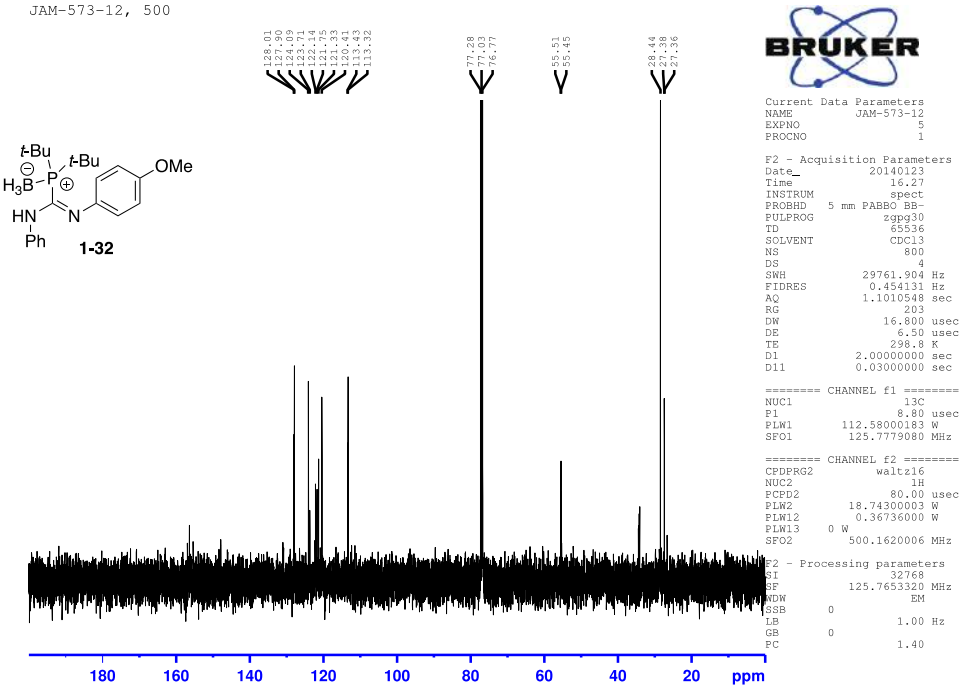



```
NAME                JAM-573-85
EXPNO                       10
PROCNO                       1
Date_                 20140315
Time                     20.45
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG                  zg30
TD                      65536
SOLVENT                 CDCl3
NS                         16
DS                          2
SWH                 8223.685 Hz
FIDRES               0.125483 Hz
AQ                3.9846387 sec
RG                        114
DW                   60.800 usec
DE                    6.50 usec
TE                    33.3 K
D1                 1.00000000 sec

======== CHANNEL f1 ========
NUC1                       1H
P1                    13.75 usec
SI                      65536
SF             400.1300096 MHz
WDW                        EM
SSB                         0
LB                     0.30 Hz
GB                          0
PC                     1.00
```

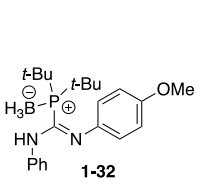



```
NAME                JAM-573-85
EXPNO                       11
PROCNO                       1
Date_                 20140316
Time                     3.28
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG                zgpg30
TD                      65536
SOLVENT                 CDCl3
NS                       1024
DS                          4
SWH                24038.461 Hz
FIDRES              0.366798 Hz
AQ                 1.3631988 sec
RG                       203
DW                   20.800 usec
DE                    6.50 usec
TE                  1896.1 K
D1                 2.00000000 sec
D11                0.03000000 sec

======== CHANNEL f1 ========
NUC1                       13C
P1                    10.00 usec
SI                      32768
SF             100.6127690 MHz
WDW                        EM
SSB                         0
LB                     1.00 Hz
GB                          0
PC                     1.40
```


JAM-573-12, 500
7.260
6.955
6.940
6.925
6.910
6.895
6.824
6.704
6.689
6.587
6.583
6.570
6.563
6.549
6.545
6.535
6.516
6.499
6.446
6.442
6.432
6.428
3.646
3.642
1.532
1.523
1.517
1.504
1.496
1.490
1.413
1.383
1.301
1.275
t-Bu
t-Bu
OMe
H3B
P
HN
N
Ph
1-32
9
8
7
6
5
4
3
2
1
ppm
2.12
0.45
0.63
4.96
1.17
3.00
18.68
1.94
1.81
0.73
0.62
BRUKER
Current Data Parameters
NAME JAM-573-12
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20140123
Time 16.13
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 57
DW 48.400 usec
DE 6.50 usec
TE 298.6 K
D1 1.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 10.20 usec
PLW1 18.74300003 W
SFO1 500.1630887 MHz
F2 - Processing parameters
SI 65536
SF 500.1600125 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


JAM-573-12, 500
128.01
127.90
124.09
123.71
122.14
121.75
121.33
120.41
113.45
113.32
77.28
77.03
76.77
55.51
55.45
28.44
27.38
27.36
t-Bu
t-Bu
OMe
H3B
P
HN
N
Ph
1-32
180
160
140
120
100
80
60
40
20
ppm
BRUKER
Current Data Parameters
NAME JAM-573-12
EXPNO 5
PROCNO 1
F2 - Acquisition Parameters
Date_ 20140123
Time 16.27
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 800
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010548 sec
RG 203
DW 16.800 usec
DE 6.50 usec
TE 298.8 K
D1 2.00000000 sec
D11 0.03000000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 8.80 usec
PLW1 112.58000183 W
SFO1 125.7779080 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PLW2 18.74300003 W
PLW12 0.36736000 W
PLW13 0 W
SFO2 500.1620006 MHz
F2 - Processing parameters
SI 32768
SF 125.7653320 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

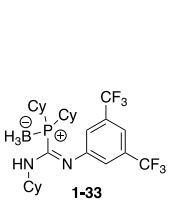
JAM-573-12, 500



1-32

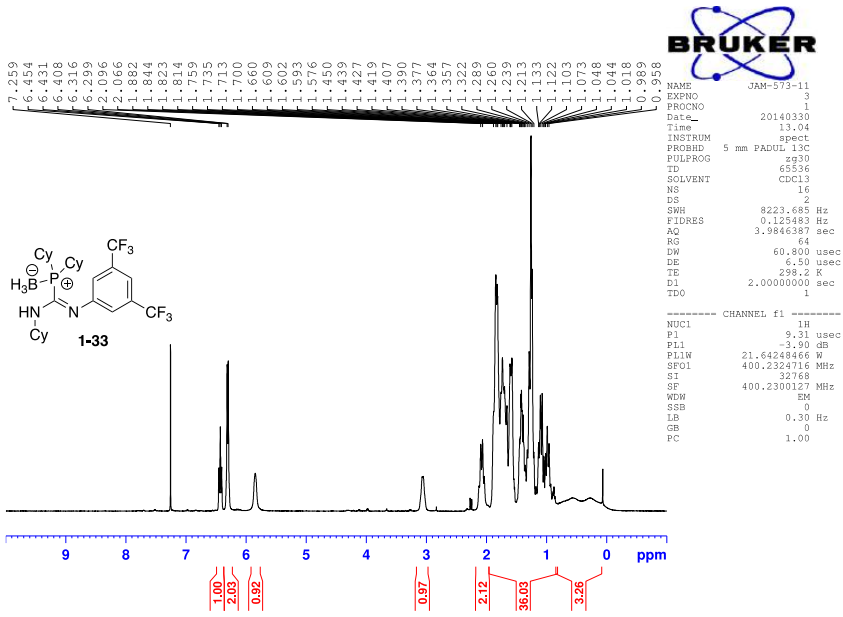

```
Current Data Parameters
NAME            JAM-573-12
EXPNO                    3
PROCNO                   1

F2 - Acquisition Parameters
Date_          20140123
Time             16.20
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   64
DS                    4
SWH           40760.871 Hz
FIDRES         0.621962 Hz
AQ             0.8039582 sec
RG                 203
DW                12.267 usec
DE                 6.50 usec
TE                298.7 K
D1           2.00000000 sec
D11          0.03000000 sec

======== CHANNEL f1 ========
NUC1                31P
P1                10.80 usec
PLW1         95.32399750 W
SFO1        202.4790173 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                1H
PCPD2             80.00 usec
PLW2         18.74300003 W
PLW12         0.36736000 W
PLW13    0 W
SFO2         500.1620006 MHz

F2 - Processing parameters
SI                32768
SF           202.4684790 MHz
WDW                  EM
SSB                  0
LB                2.00 Hz
GB                   0
PC                1.40
```

573-11, 400, CDCl3

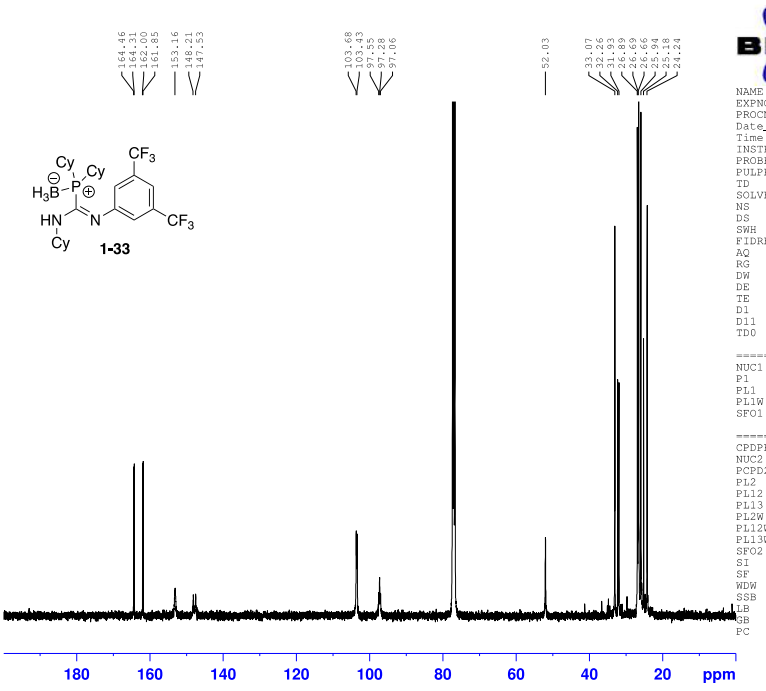


1-33

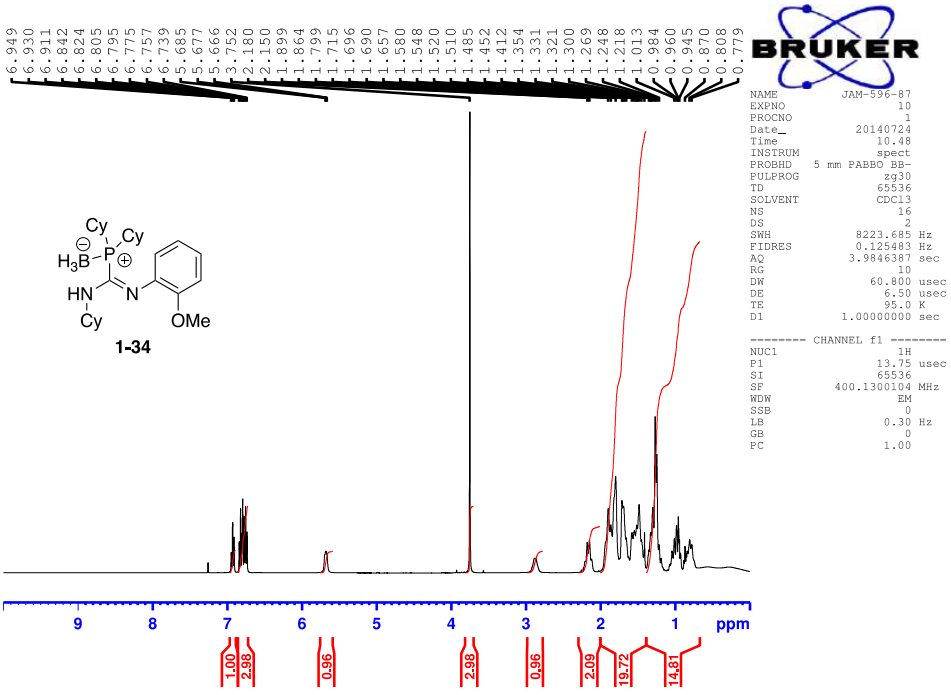

```
NAME            JAM-573-11
EXPNO                   11
PROCNO                   1
Date_          20140122
Time             16.22
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  100
DS                    4
SWH           64102.563 Hz
FIDRES         0.978127 Hz
AQ             0.5112308 sec
RG                 203
DW                7.800 usec
DE                 6.50 usec
TE               2243.5 K
D1           2.00000000 sec
D11          0.03000000 sec

-------- CHANNEL f1 --------
NUC1                31P
P1                13.30 usec
SI                32768
SF           161.9755930 MHz
WDW                  EM
SSB                  0
LB                1.00 Hz
GB                   0
PC                1.40
```




```
NAME                JAM-573-11
EXPNO                        3
PROCNO                       1
Date_                 20140330
Time                     13.04
INSTRUM                  spect
PROBHD   5 mm PADUL 13C
PULPROG                  zg30
TD                      65536
SOLVENT                  CDCl3
NS                          16
DS                           2
SWH                 8223.685 Hz
FIDRES              0.125483 Hz
AQ                  3.9846387 sec
RG                          64
DW                     60.800 usec
DE                      6.50 usec
TE                     298.2 K
D1                  2.00000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                        1H
P1                       9.31 usec
PL1                     -3.90 dB
PL1W               21.64248466 W
SFO1               400.2324716 MHz
SI                        32768
SF                 400.2300127 MHz
WDW                          EM
SSB                           0
LB                       0.30 Hz
GB                            0
PC                       1.00
```




```
NAME                JAM-573-11
EXPNO                        6
PROCNO                       1
Date_                 20140330
Time                     16.01
INSTRUM                  spect
PROBHD   5 mm PADUL 13C
PULPROG                zgpg30
TD                      65536
SOLVENT                  CDCl3
NS                       16314
DS                           4
SWH                24038.461 Hz
FIDRES              0.366798 Hz
AQ                  1.3631988 sec
RG                        50.8
DW                     20.800 usec
DE                      6.50 usec
TE                     298.2 K
D1                  3.00000000 sec
D11                 0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                       13C
P1                      10.00 usec
PL1                     -0.44 dB
PL1W               39.19395828 W
SFO1               100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                        1H
PCPD2                   90.00 usec
PL2                     -3.90 dB
PL12                    15.81 dB
PL13                   120.00 dB
PL2W               21.64248466 W
PL12W               0.23137002 W
PL13W               0.00000000 W
SFO2               400.2316009 MHz
SI                        32768
SF                 100.6379140 MHz
WDW                          EM
SSB                           0
LB                       1.00 Hz
GB                            0
PC                       1.40
```

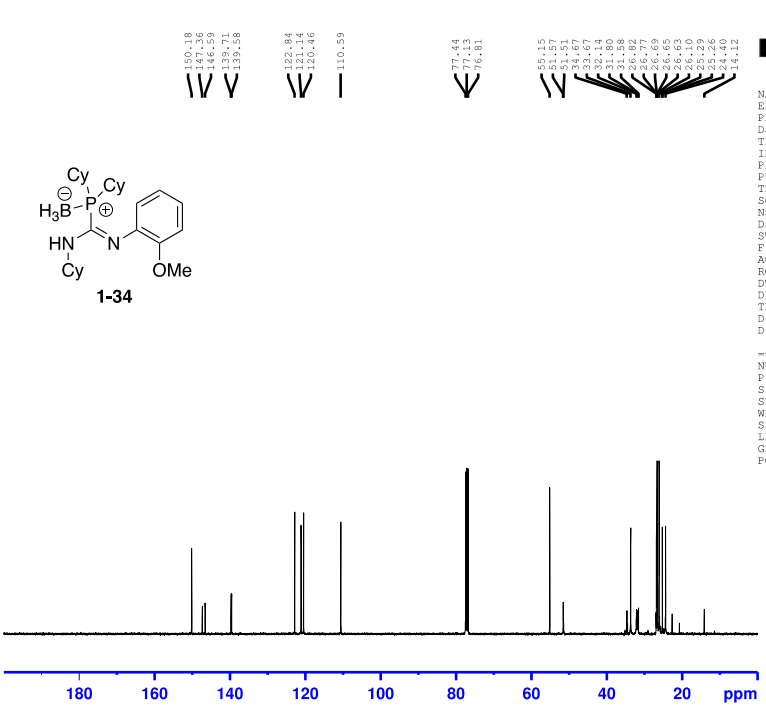


BRUKER

NAME	JAM-596-87
EXPNO	10
PROCNO	1
Date_	20140724
Time	10.48
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	8223.685 Hz
FIDRES	0.125483 Hz
AQ	3.9846387 sec
RG	10
DW	60.800 usec
DE	6.50 usec
TE	95.0 K
D1	1.00000000 sec

-------- CHANNEL f1 --------

NUC1	1H
P1	13.75 usec
SI	65536
SF	400.1300104 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

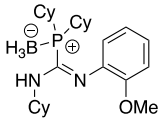


BRUKER

NAME	JAM-596-87
EXPNO	13
PROCNO	1
Date_	20140724
Time	21.08
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	1024
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	94.1 K
D1	2.00000000 sec
D11	0.03000000 sec

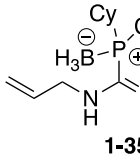
-------- CHANNEL f1 --------

NUC1	13C
P1	10.00 usec
SI	32768
SF	100.6127690 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

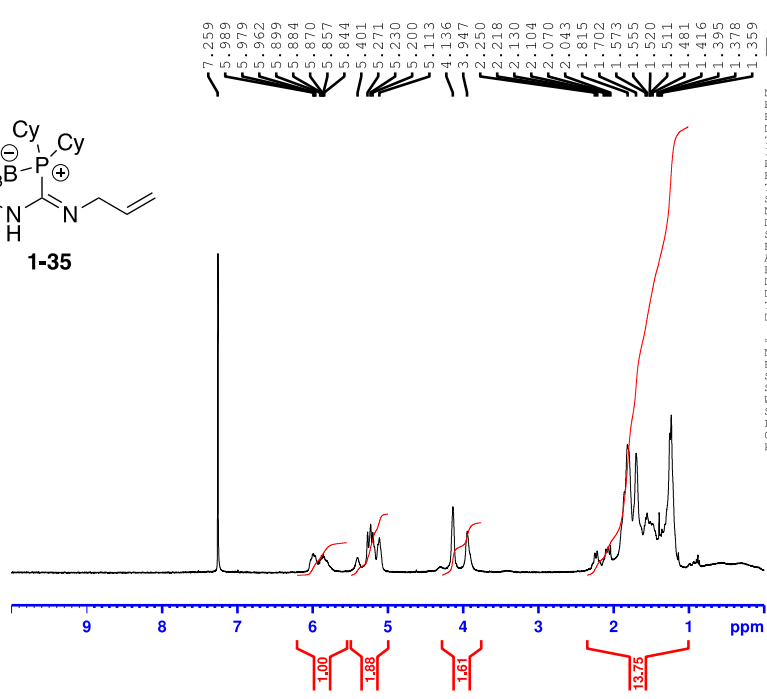


1-34

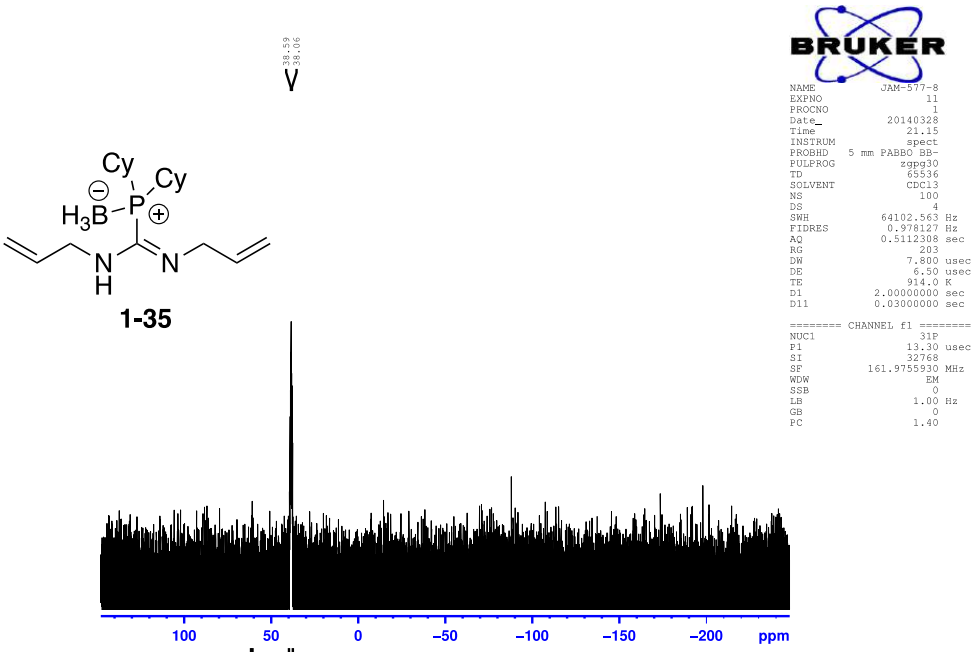

```
NAME                JAM-596-87
EXPNO                       11
PROCNO                       1
Date_             20140724
Time                     10.50
INSTRUM                  spect
PROBHD     5 mm PABBO BB-
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                          16
DS                           4
SWH                  64102.563 Hz
FIDRES                0.978127 Hz
AQ                    0.5112308 sec
RG                         203
DW                       7.800 usec
DE                       6.50 usec
TE                       94.9 K
D1                    2.00000000 sec
D11                   0.03000000 sec

======== CHANNEL f1 ========
NUC1                       31P
P1                       13.30 usec
SI                       32768
SF                 161.9755930 MHz
WDW                         EM
SSB                          0
LB                        1.00 Hz
GB                           0
PC                        1.40
```



1-35

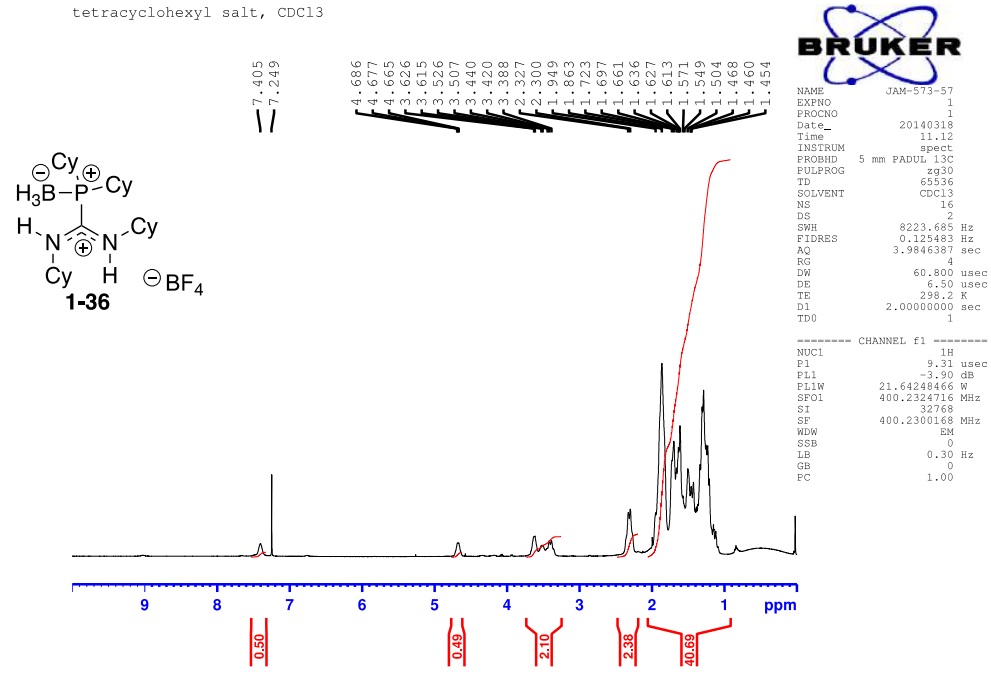



```
NAME                JAM-577-8
EXPNO                       10
PROCNO                       1
Date_             20140328
Time                     21.09
INSTRUM                  spect
PROBHD     5 mm PABBO BB-
PULPROG                   zg30
TD                       65536
SOLVENT                  CDCl3
NS                          16
DS                           2
SWH                   8223.685 Hz
FIDRES                0.125483 Hz
AQ                    3.9846387 sec
RG                         128
DW                       60.800 usec
DE                        6.50 usec
TE                       913.0 K
D1                    1.00000000 sec

======== CHANNEL f1 ========
NUC1                        1H
P1                       13.75 usec
SI                       65536
SF                 400.1300108 MHz
WDW                         EM
SSB                          0
LB                        0.30 Hz
GB                           0
PC                        1.00
```

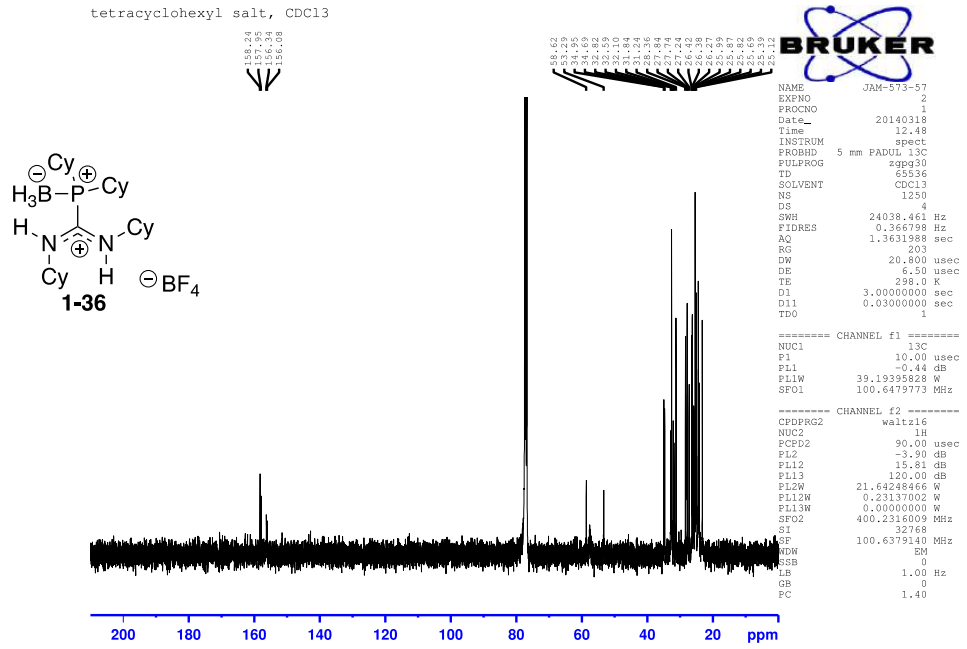


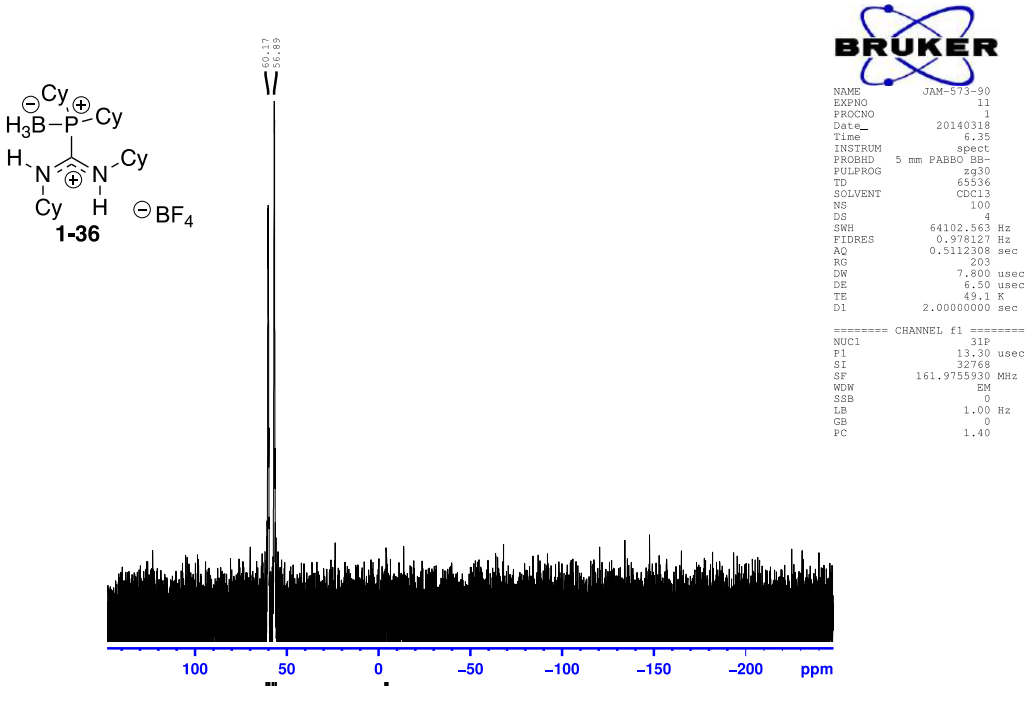

```
NAME                JAM-577-8
EXPNO                      11
PROCNO                      1
Date_                20140328
Time                    21.15
INSTRUM                 spect
PROBHD   5 mm PABBO BB-
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                         100
DS                           4
SWH                 64102.563 Hz
FIDRES              0.978127 Hz
AQ                  0.5112308 sec
RG                         203
DW                     7.800 usec
DE                     6.50 usec
TE                     914.0 K
D1                 2.00000000 sec
D11                0.03000000 sec

======== CHANNEL f1 ========
NUC1                       31P
P1                       13.30 usec
SI                       32768
SF                 161.9755930 MHz
WDW                         EM
SSB                          0
LB                        1.00 Hz
GB                           0
PC                        1.40
```

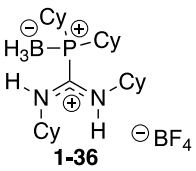
tetracyclohexyl salt, CDCl3




```
NAME                JAM-573-57
EXPNO                       1
PROCNO                      1
Date_                20140318
Time                    11.12
INSTRUM                 spect
PROBHD   5 mm PADUL 13C
PULPROG                 zg30
TD                       65536
SOLVENT                  CDCl3
NS                          16
DS                           2
SWH                  8223.685 Hz
FIDRES               0.125483 Hz
AQ                   3.9846387 sec
RG                           4
DW                      60.800 usec
DE                       6.50 usec
TE                      298.2 K
D1                 2.00000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                        1H
P1                        9.31 usec
PL1                      -3.90 dB
PL1W               21.64248466 W
SFO1               400.2324716 MHz
SI                       32768
SF                 400.2300168 MHz
WDW                         EM
SSB                          0
LB                        0.30 Hz
GB                           0
PC                        1.00
```


tetracyclohexyl salt, CDCl3
158.24
157.95
156.34
156.08
58.62
53.29
34.95
34.69
32.82
32.59
32.10
31.84
31.24
28.36
27.94
27.78
27.24
26.42
26.28
26.27
25.99
25.87
25.82
25.65
25.39
25.12
Cy
H3B–P–Cy
H
N
N
Cy
Cy
H
BF4
1-36
BRUKER
NAME JAM-573-57
EXPNO 2
PROCNO 1
Date_ 20140318
Time 12.48
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1250
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 298.0 K
D1 3.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 -0.44 dB
PL1W 39.19395828 W
SFO1 100.6479773 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.90 dB
PL12 15.81 dB
PL13 120.00 dB
PL2W 21.64248466 W
PL12W 0.23137002 W
PL13W 0.00000000 W
SFO2 400.2316009 MHz
SI 32768
SF 100.6379140 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200
180
160
140
120
100
80
60
40
20
ppm

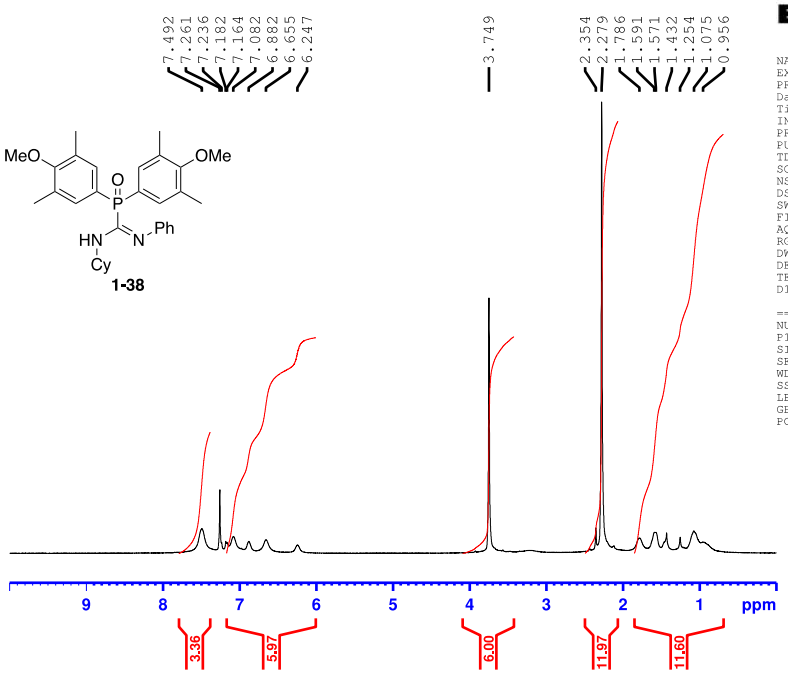

60.17
56.89
Cy
H3B–P–Cy
H
N
N
Cy
Cy
H
BF4
1-36
BRUKER
NAME JAM-573-90
EXPNO 11
PROCNO 1
Date_ 20140318
Time 6.35
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 100
DS 4
SWH 64102.563 Hz
FIDRES 0.978127 Hz
AQ 0.5112308 sec
RG 203
DW 7.800 usec
DE 6.50 usec
TE 49.1 K
D1 2.00000000 sec
======== CHANNEL f1 ========
NUC1 31P
P1 13.30 usec
SI 32768
SF 161.9755930 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
100
50
0
-50
-100
-150
-200
ppm



1-36


```
NAME                JAM-573-90
EXPNO                       12
PROCNO                       1
Date_             20140318
Time                      6.37
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG                  zgbs
TD                      65536
SOLVENT                 CDCl3
NS                          4
DS                          2
SWH                 25510.203 Hz
FIDRES                0.389255 Hz
AQ                    1.2845556 sec
RG                          203
DW                     19.600 usec
DE                      6.50 usec
TE                      63.4 K
D1                  5.00000000 sec

======== CHANNEL f1 ========
NUC1                       11B
P1                     11.00 usec
P2                     22.00 usec
SI                        6272
SF                128.3776050 MHz
WDW                         EM
SSB                          0
LB                     1.00 Hz
GB                           0
PC                     1.40
```

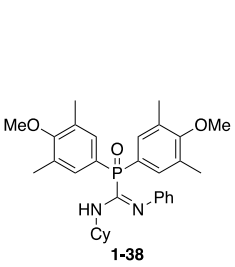
555-37.2, 400, CDCl3



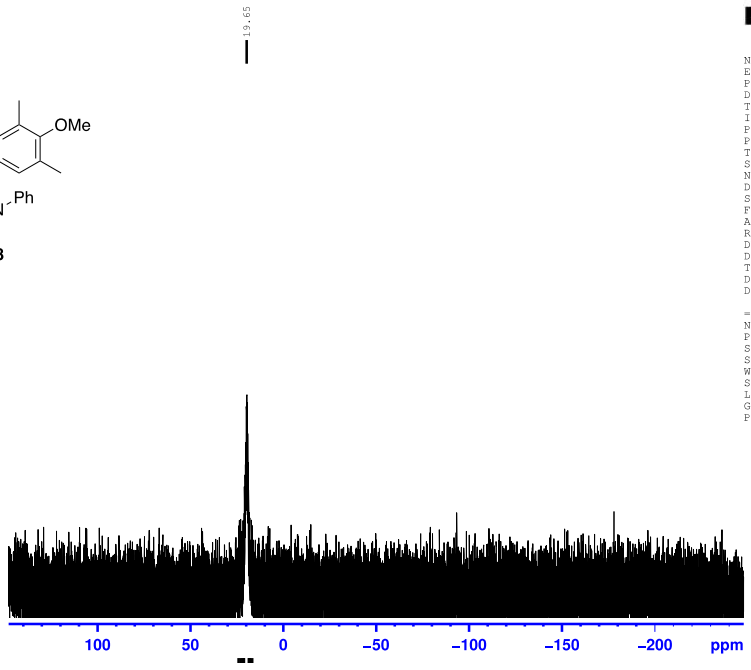
1-38

```
NAME              JAM-555-37.2
EXPNO                       10
PROCNO                       1
Date_             20131211
Time                     15.28
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG                  zg30
TD                      65536
SOLVENT                 CDCl3
NS                          16
DS                          2
SWH                  8223.685 Hz
FIDRES                0.125483 Hz
AQ                    3.9846387 sec
RG                          101
DW                     60.800 usec
DE                      6.50 usec
TE                      298.6 K
D1                  1.00000000 sec

======== CHANNEL f1 ========
NUC1                        1H
P1                     13.75 usec
SI                        65536
SF                400.1300102 MHz
WDW                         EM
SSB                          0
LB                     0.30 Hz
GB                           0
PC                     1.00
```

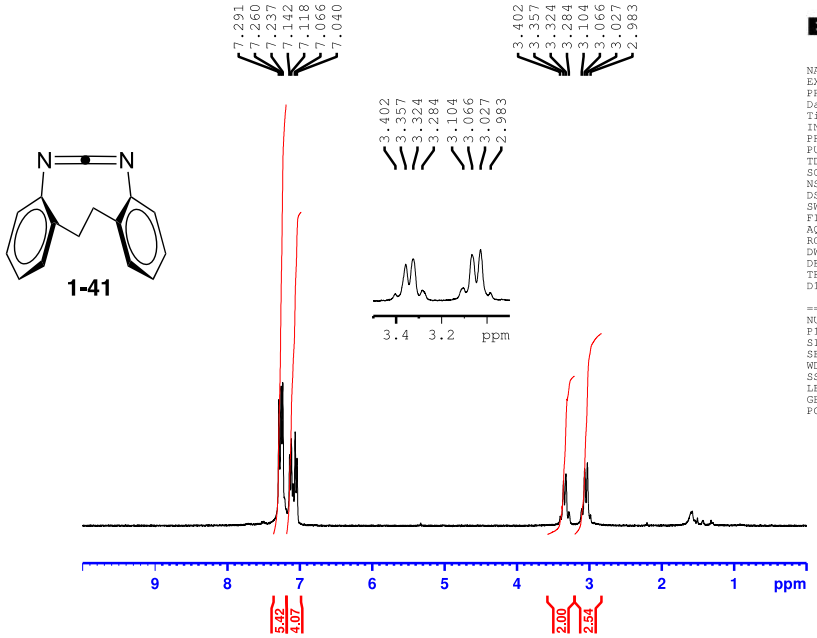
555-37.2, 400, CDCl3



1-38

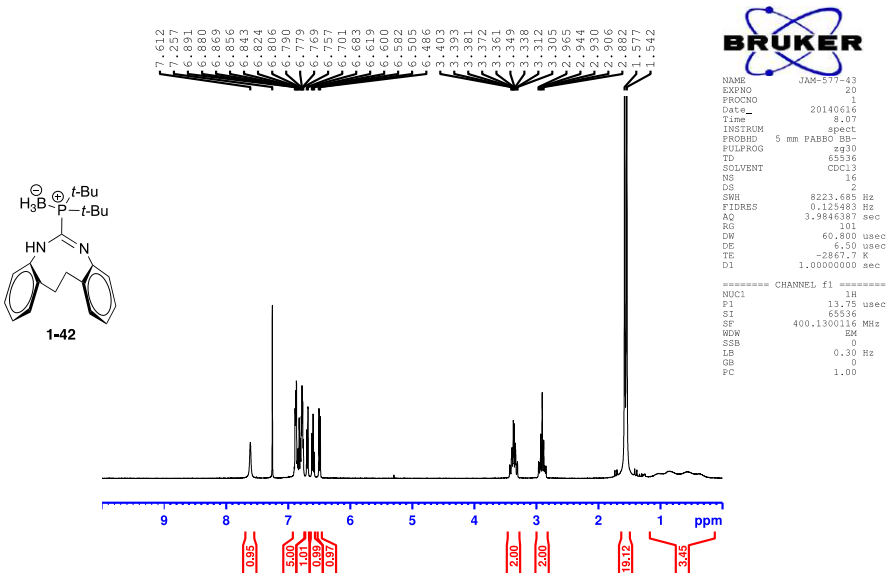



```
NAME            JAM-555-37.2
EXPNO                     11
PROCNO                     1
Date_           20131211
Time                   15.34
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      100
DS                        4
SWH              64102.563 Hz
FIDRES           0.978127 Hz
AQ               0.5112308 sec
RG                      203
DW                   7.800 usec
DE                   6.50 usec
TE                   298.8 K
D1             2.00000000 sec
D11            0.03000000 sec

======== CHANNEL f1 ========
NUC1                   31P
P1                  13.30 usec
SI                    32768
SF            161.9755930 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```



1-41

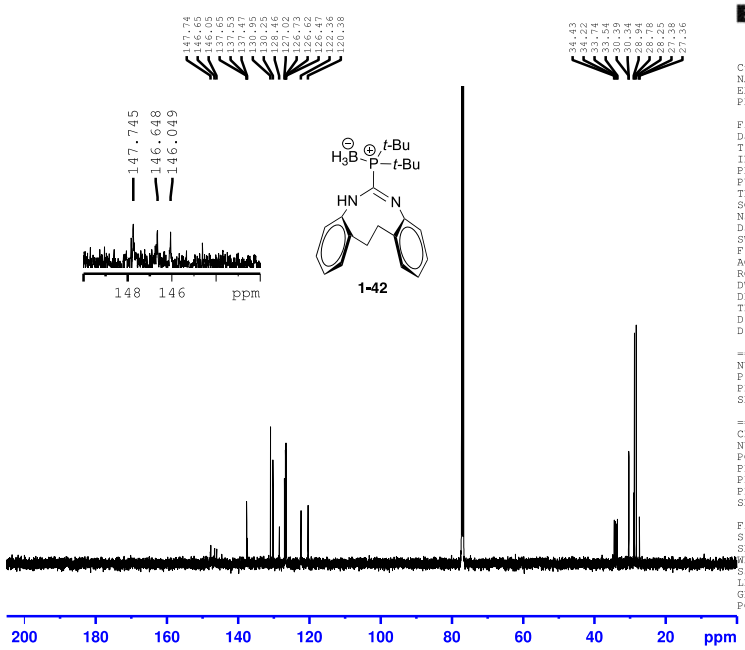
```
NAME            JAM-577-31.2
EXPNO                     10
PROCNO                     1
Date_           20140417
Time                   20.26
INSTRUM                spect
PROBHD    5 mm QNP   1H/1
PULPROG                zg30
TD                    32768
SOLVENT               CDCl3
NS                       16
DS                        2
SWH              6188.119 Hz
FIDRES           0.188846 Hz
AQ               2.6477044 sec
RG                      322
DW                  80.800 usec
DE                   6.50 usec
TE                  -927.8 K
D1             1.00000000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                  12.71 usec
SI                    32768
SF            300.2300000 MHz
WDW                    EM
SSB                     0
LB                   0.10 Hz
GB                      0
PC                   1.00
```



BRUKER

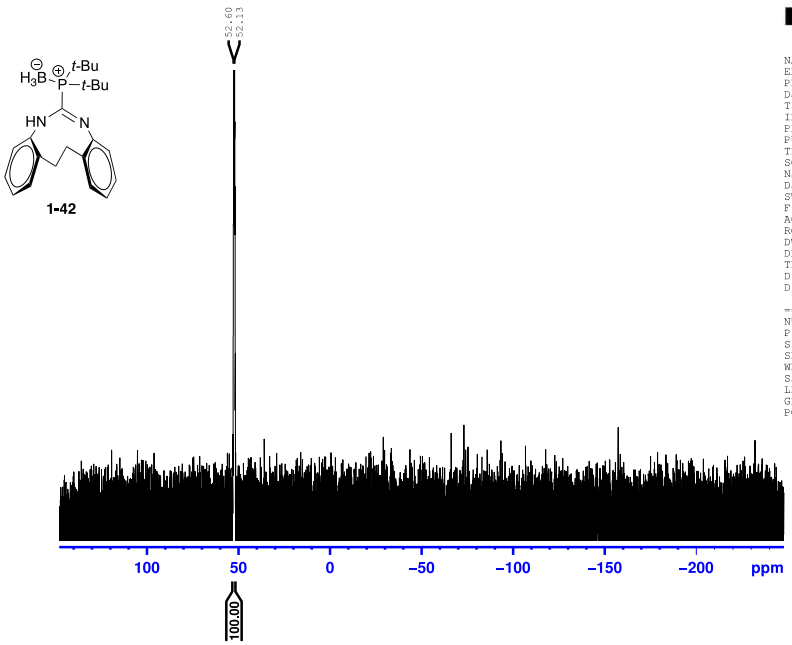
```
NAME              JAM-577-43
EXPNO                 20
PROCNO                 1
Date_           20140616
Time                8.07
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8223.685 Hz
FIDRES             0.125483 Hz
AQ              3.9846387 sec
RG                   101
DW                60.800 usec
DE                 6.50 usec
TE               -2867.7 K
D1              1.00000000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 13.75 usec
SI                 65536
SF           400.1300116 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

JAM-577-43



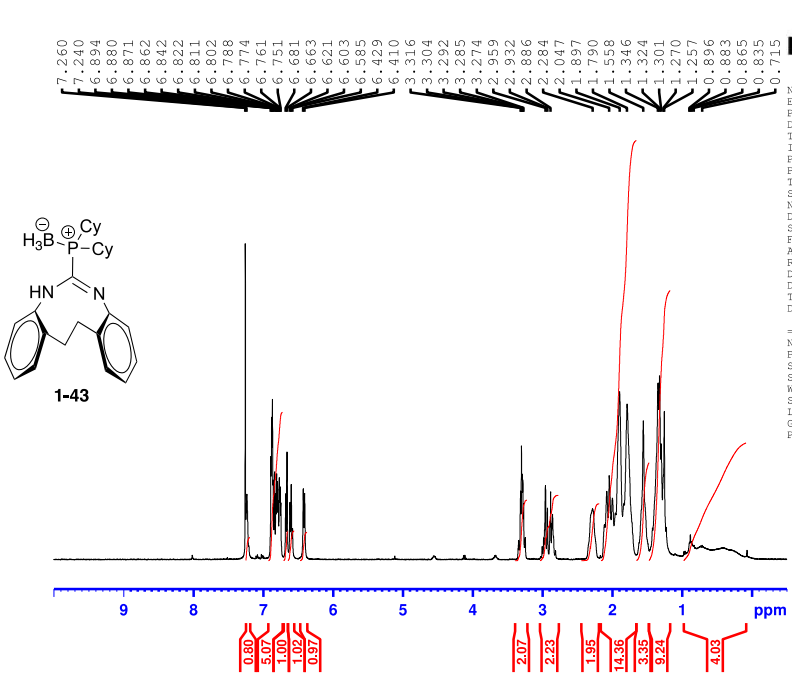
BRUKER

```
Current Data Parameters
NAME            JAM-577-43
EXPNO                    5
PROCNO                   1

F2 - Acquisition Parameters
Date_             20140428
Time                 20.51
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                    1829
DS                       4
SWH              29761.904 Hz
FIDRES             0.454131 Hz
AQ               1.1010548 sec
RG                     203
DW                  16.800 usec
DE                   6.50 usec
TE                  298.0 K
D1               2.00000000 sec
D11              0.03000000 sec

======== CHANNEL f1 ========
NUC1                   13C
P1                    8.80 usec
PLW1          112.58000183 W
SFO1          125.7779080 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                   1H
PCPD2                80.00 usec
PLW2          18.74300003 W
PLW12          0.36736000 W
PLW13     0 W
SFO2          500.1620006 MHz

F2 - Processing parameters
SI                   32768
SF            125.7653320 MHz
WDW                     EM
SSB          0
LB                    1.00 Hz
GB           0
PC                    1.40
```



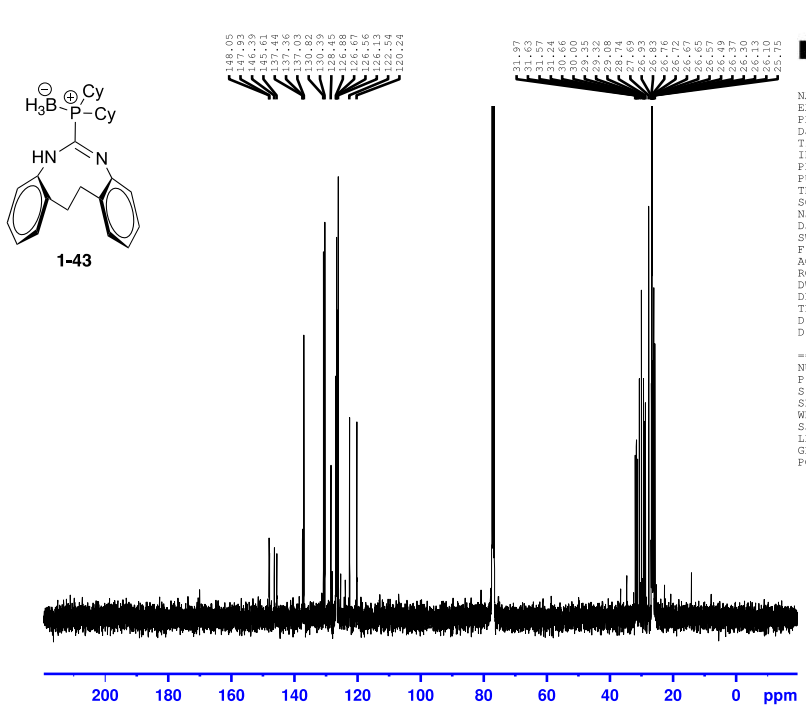
1-42

```
NAME                JAM-577-43
EXPNO                       21
PROCNO                       1
Date_                 20140616
Time                      8.11
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                          50
DS                           4
SWH                 64102.563 Hz
FIDRES              0.978127 Hz
AQ                  0.5112308 sec
RG                         203
DW                     7.800 usec
DE                     6.50 usec
TE                     320.2 K
D1                  2.00000000 sec
D11                 0.03000000 sec

======== CHANNEL f1 ========
NUC1                       31P
P1                      13.30 usec
SI                       32768
SF                 161.9755930 MHz
WDW                         EM
SSB                          0
LB                      1.00 Hz
GB                           0
PC                      1.40
```



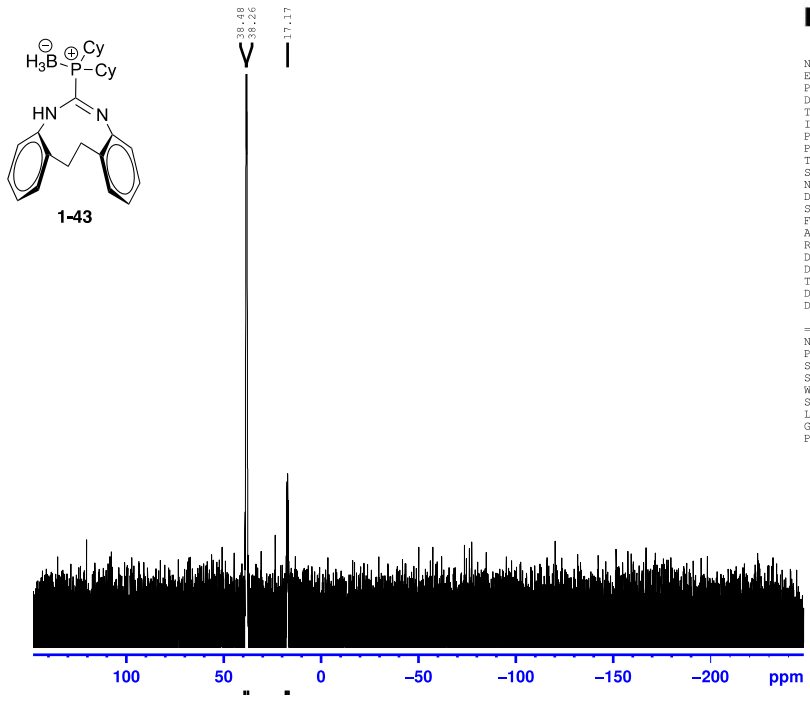
1-43

```
NAME              JAM-577-27.4
EXPNO                       10
PROCNO                       1
Date_                 20140422
Time                     18.44
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG                  zg30
TD                       65536
SOLVENT                  CDCl3
NS                          16
DS                           2
SWH                 8223.685 Hz
FIDRES              0.125483 Hz
AQ                  3.9846387 sec
RG                        90.5
DW                     60.800 usec
DE                      6.50 usec
TE                     -1250.2 K
D1                  1.00000000 sec

======== CHANNEL f1 ========
NUC1                        1H
P1                      13.75 usec
SI                       65536
SF                 400.1300104 MHz
WDW                         EM
SSB                          0
LB                      0.30 Hz
GB                           0
PC                      1.00
```



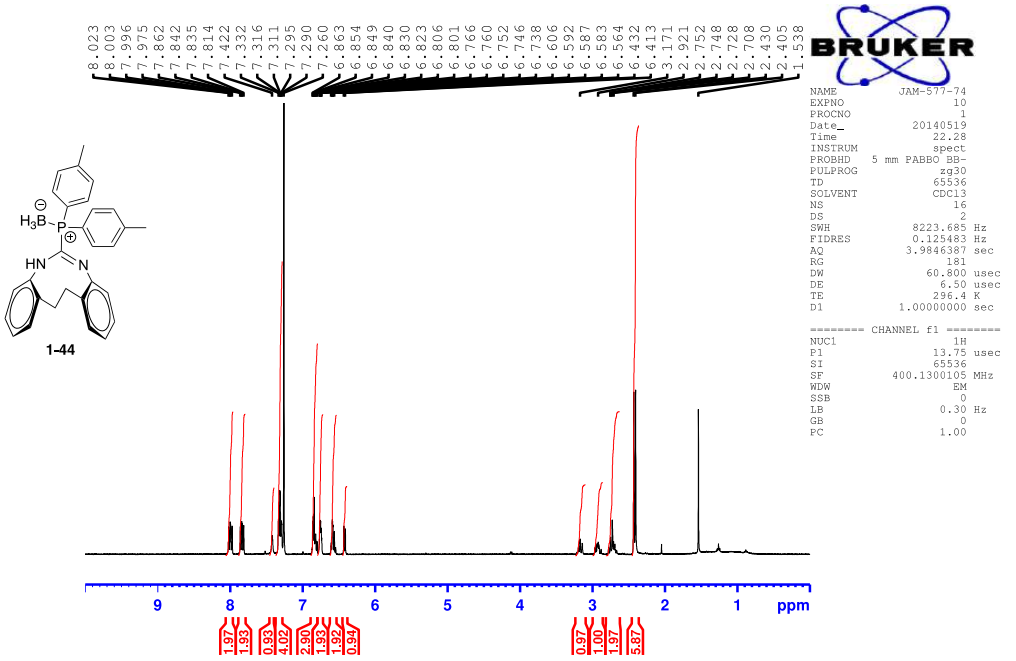
BRUKER

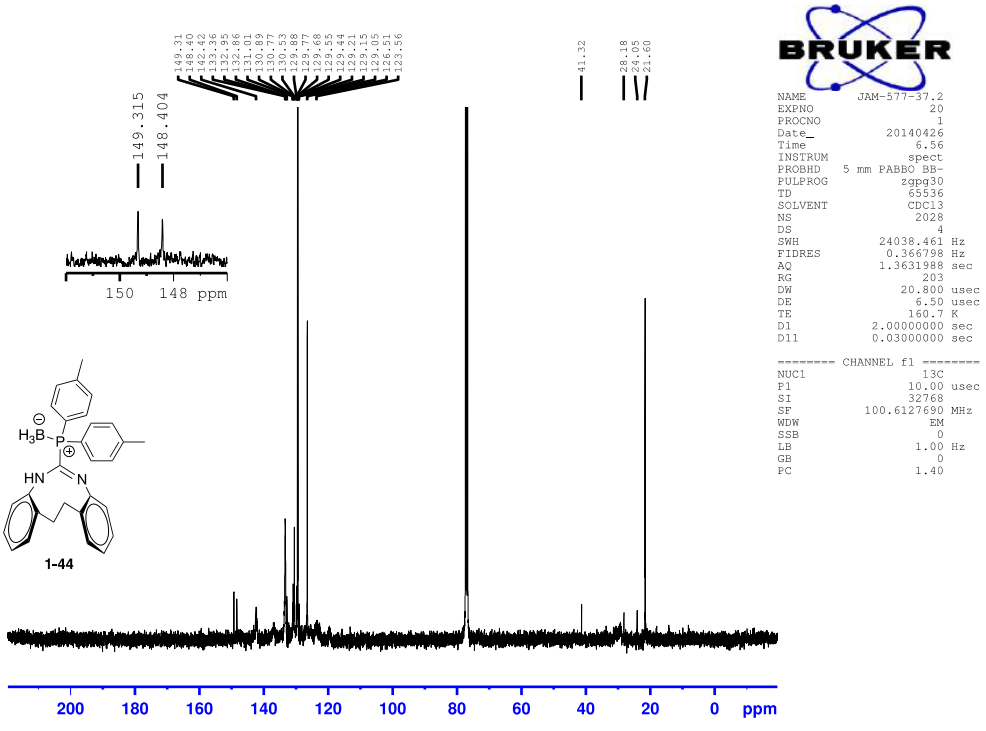
```
NAME            JAM-577-26.2
EXPNO                     12
PROCNO                     1
Date_           20140421
Time                 22.01
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG             zgpg30
TD                  65536
SOLVENT             CDCl3
NS                   2028
DS                      4
SWH             24038.461 Hz
FIDRES          0.366798 Hz
AQ              1.3631988 sec
RG                    203
DW                20.800 usec
DE                 6.50 usec
TE                3207.1 K
D1              2.00000000 sec
D11             0.03000000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                 10.00 usec
SI                 32768
SF            100.6127690 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

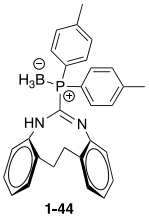


BRUKER

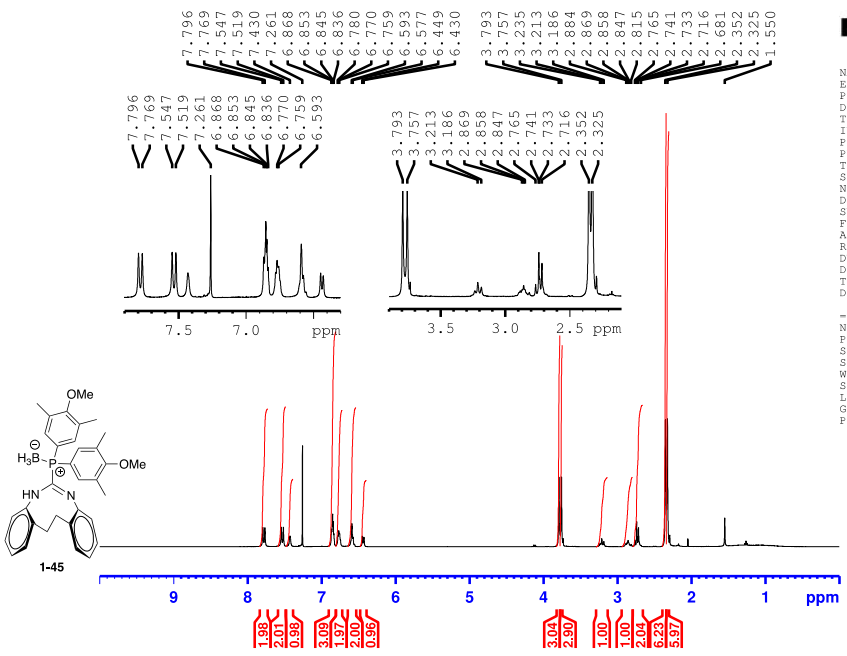
```
NAME            JAM-577-27.4
EXPNO                     11
PROCNO                     1
Date_           20140422
Time                 18.48
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG             zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     75
DS                      4
SWH             64102.563 Hz
FIDRES          0.978127 Hz
AQ              0.5112308 sec
RG                    203
DW                 7.800 usec
DE                 6.50 usec
TE                -1969.1 K
D1              2.00000000 sec
D11             0.03000000 sec

======== CHANNEL f1 ========
NUC1                  31P
P1                 13.30 usec
SI                 32768
SF            161.9755930 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```


8.023
8.003
7.996
7.975
7.862
7.842
7.835
7.814
7.422
7.332
7.316
7.311
7.295
7.290
7.260
6.863
6.854
6.849
6.840
6.830
6.823
6.806
6.801
6.766
6.760
6.752
6.746
6.738
6.606
6.592
6.587
6.583
6.564
6.432
6.413
3.171
2.921
2.752
2.748
2.728
2.708
2.430
2.405
1.538
BRUKER
NAME JAM-577-74
EXPNO 10
PROCNO 1
Date_ 20140519
Time 22.28
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 181
DW 60.800 usec
DE 6.50 usec
TE 296.4 K
D1 1.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 13.75 usec
SI 65536
SF 400.1300105 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
H3B
HN
N
1-44
9
8
7
6
5
4
3
2
1
ppm
1.97
1.93
0.93
4.02
2.90
1.93
1.82
0.94
0.97
1.00
1.97
5.87

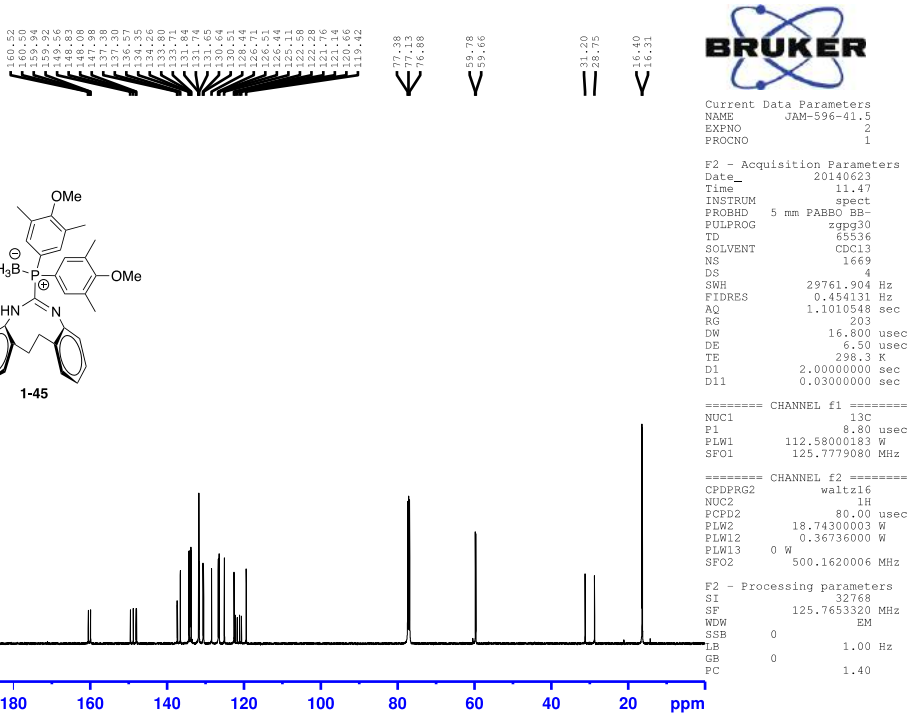

149.31
148.40
142.42
133.36
132.95
132.86
131.01
130.89
130.77
130.53
129.88
129.77
129.68
129.55
129.44
129.21
129.15
129.05
128.51
128.36
41.32
28.18
24.05
21.60
149.315
148.404
150
148 ppm
BRUKER
NAME JAM-577-37.2
EXPNO 20
PROCNO 1
Date_ 20140426
Time 6.56
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2028
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 160.7 K
D1 2.00000000 sec
D11 0.03000000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
H3B
HN
N
1-44
200
180
160
140
120
100
80
60
40
20
0
ppm




```
NAME                JAM-577-74
EXPNO                       11
PROCNO                       1
Date_             20140519
Time                     22.32
INSTRUM                  spect
PROBHD     5 mm PABBO BB-
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                          75
DS                           4
SWH                  64102.563 Hz
FIDRES               0.978127 Hz
AQ                   0.5112308 sec
RG                         203
DW                     7.800 usec
DE                     6.50 usec
TE                     296.6 K
D1                  2.00000000 sec
D11                 0.03000000 sec

======== CHANNEL f1 ========
NUC1                       31P
P1                      13.30 usec
SI                         32768
SF                161.9755930 MHz
WDW                        EM
SSB                         0
LB                      1.00 Hz
GB                          0
PC                      1.40
```

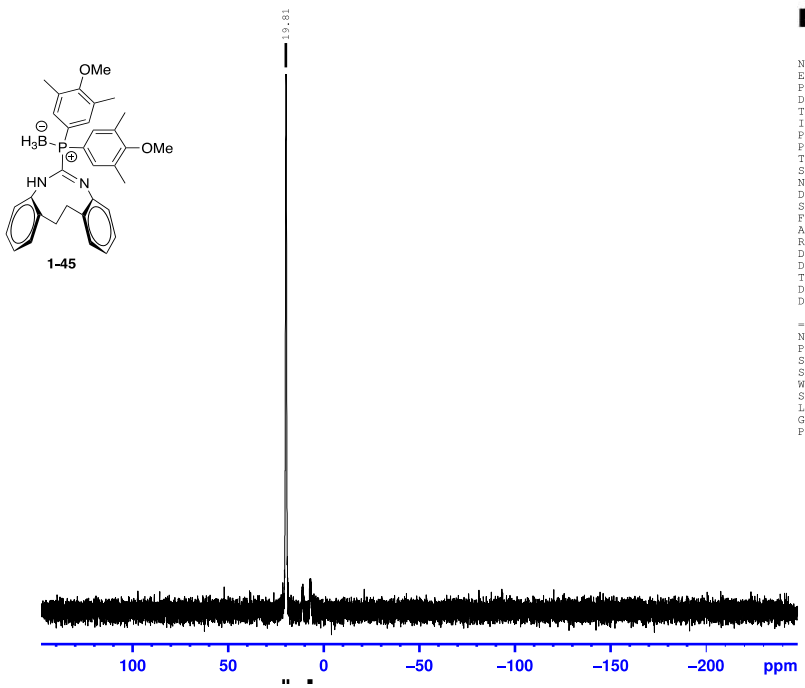



```
NAME                JAM-596-41.5
EXPNO                       10
PROCNO                       1
Date_             20140623
Time                     8.16
INSTRUM                  spect
PROBHD     5 mm PABBO BB-
PULPROG                  zg30
TD                       65536
SOLVENT                  CDCl3
NS                          16
DS                           2
SWH                  8223.685 Hz
FIDRES               0.125483 Hz
AQ                   3.9846387 sec
RG                         114
DW                     60.800 usec
DE                     6.50 usec
TE                     94.8 K
D1                  1.00000000 sec

======== CHANNEL f1 ========
NUC1                        1H
P1                      13.75 usec
SI                         65536
SF                400.1300096 MHz
WDW                        EM
SSB                         0
LB                      0.30 Hz
GB                          0
PC                      1.00
```



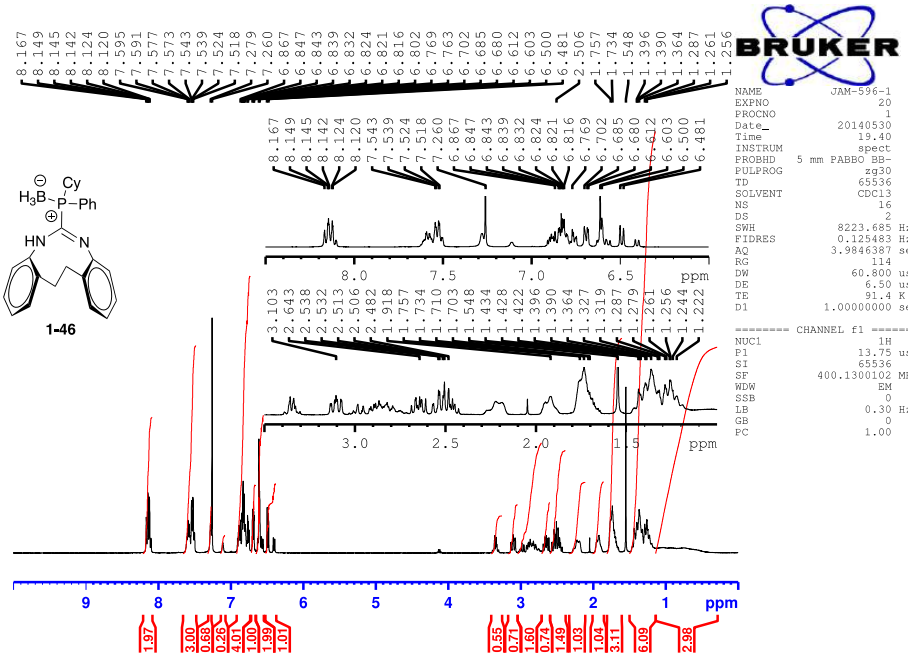
BRUKER

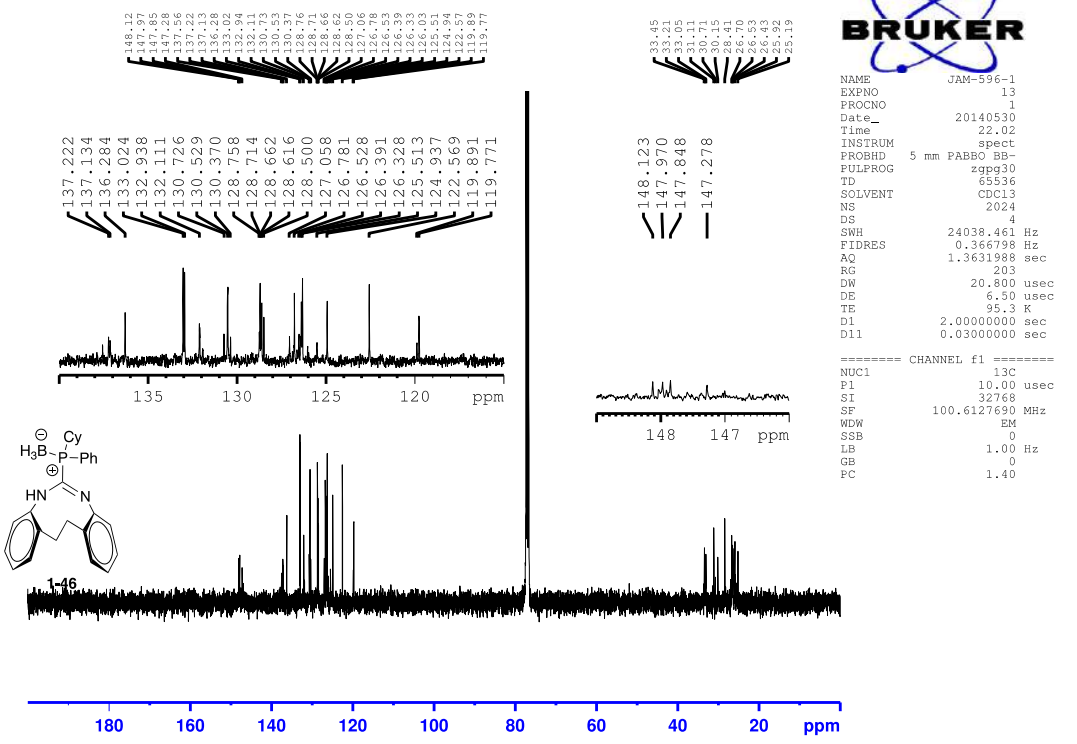
```
Current Data Parameters
NAME          JAM-596-41.5
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_          20140623
Time              11.47
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG         zgpg30
TD               65536
SOLVENT          CDC13
NS                1669
DS                   4
SWH          29761.904 Hz
FIDRES         0.454131 Hz
AQ           1.1010548 sec
RG                 203
DW              16.800 usec
DE               6.50 usec
TE              298.3 K
D1           2.00000000 sec
D11          0.03000000 sec

======== CHANNEL f1 ========
NUC1               13C
P1              8.80 usec
PLW1      112.58000183 W
SFO1       125.7779080 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2               1H
PCPD2          80.00 usec
PLW2       18.74300003 W
PLW12       0.36736000 W
PLW13    0 W
SFO2        500.1620006 MHz

F2 - Processing parameters
SI               32768
SF         125.7653320 MHz
WDW                EM
SSB       0
LB              1.00 Hz
GB        0
PC              1.40
```

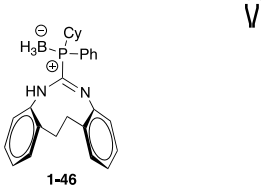


BRUKER

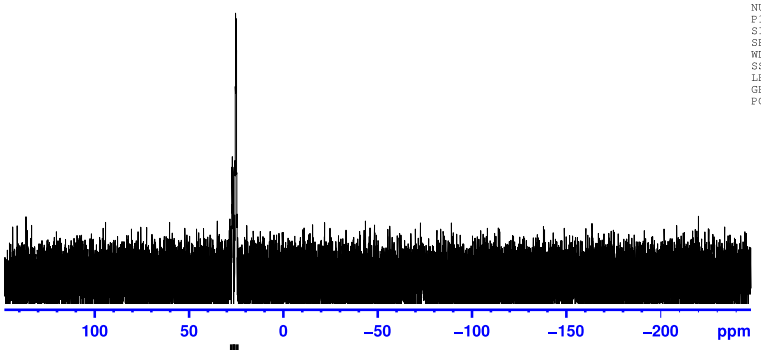
```
NAME          JAM-577-75
EXPNO                 12
PROCNO                 1
Date_          20140519
Time              22.50
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG         zgpg30
TD               65536
SOLVENT          CDC13
NS                 100
DS                   4
SWH          64102.563 Hz
FIDRES         0.978127 Hz
AQ           0.5112308 sec
RG                 203
DW              7.800 usec
DE               6.50 usec
TE              296.7 K
D1           2.00000000 sec
D11          0.03000000 sec

======== CHANNEL f1 ========
NUC1               31P
P1              13.30 usec
SI               32768
SF         161.9755930 MHz
WDW                EM
SSB                 0
LB              1.00 Hz
GB                  0
PC              1.40
```


BRUKER
NAME JAM-596-1
EXPNO 20
PROCNO 1
Date_ 20140530
Time 19.40
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 114
DW 60.800 usec
DE 6.50 usec
TE 91.4 K
D1 1.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 13.75 usec
SI 65536
SF 400.1300102 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1-46
ppm

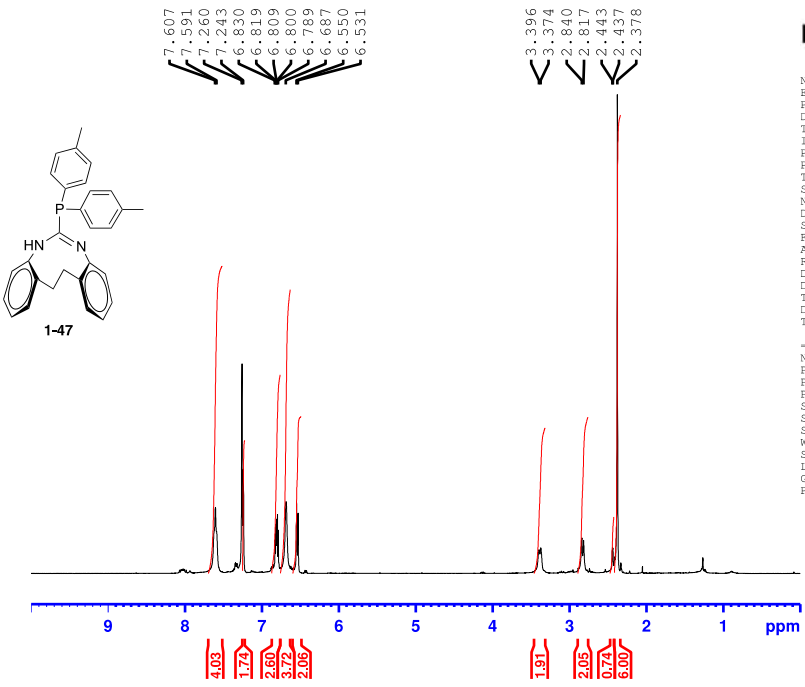

BRUKER
NAME JAM-596-1
EXPNO 13
PROCNO 1
Date_ 20140530
Time 22.02
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2024
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 95.3 K
D1 2.00000000 sec
D11 0.03000000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1-46
ppm



1-46

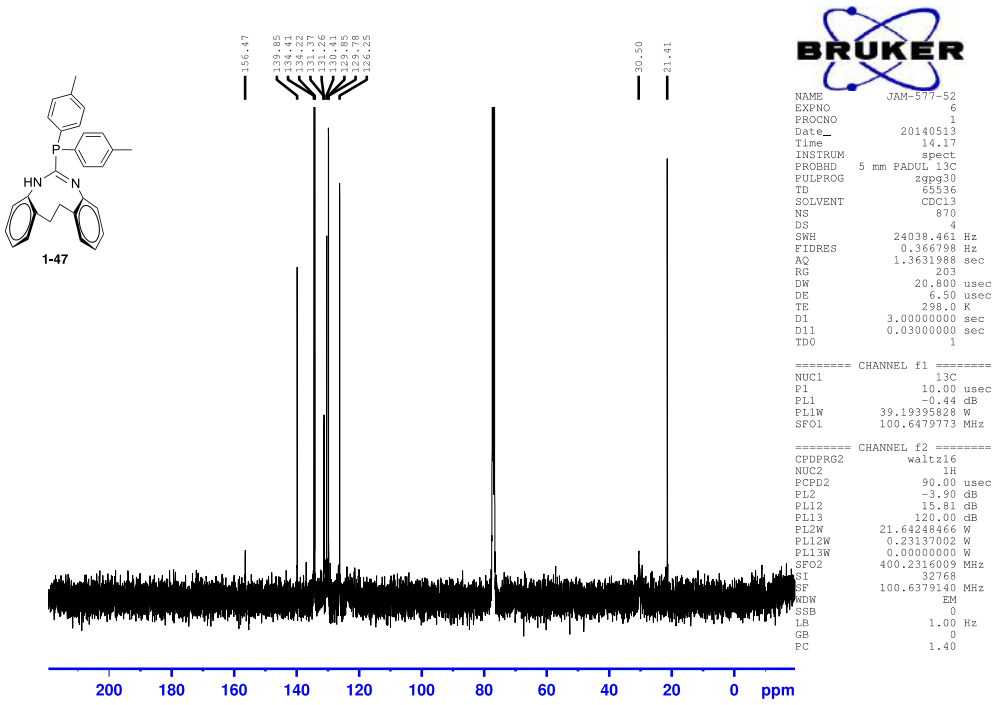



```
NAME                JAM-596-1
EXPNO                      21
PROCNO                      1
Date_                20140530
Time                    19.44
INSTRUM                 spect
PROBHD    5 mm PABBO BB-
PULPROG                zgpg30
TD                      65536
SOLVENT                 CDCl3
NS                         50
DS                          4
SWH                64102.563 Hz
FIDRES             0.978127 Hz
AQ                 0.5112308 sec
RG                        203
DW                    7.800 usec
DE                    6.50 usec
TE                     91.5 K
D1                2.00000000 sec
D11               0.03000000 sec

======== CHANNEL f1 ========
NUC1                      31P
P1                     13.30 usec
SI                        32768
SF               161.9755930 MHz
WDW                        EM
SSB                         0
LB                     1.00 Hz
GB                          0
PC                     1.40
```



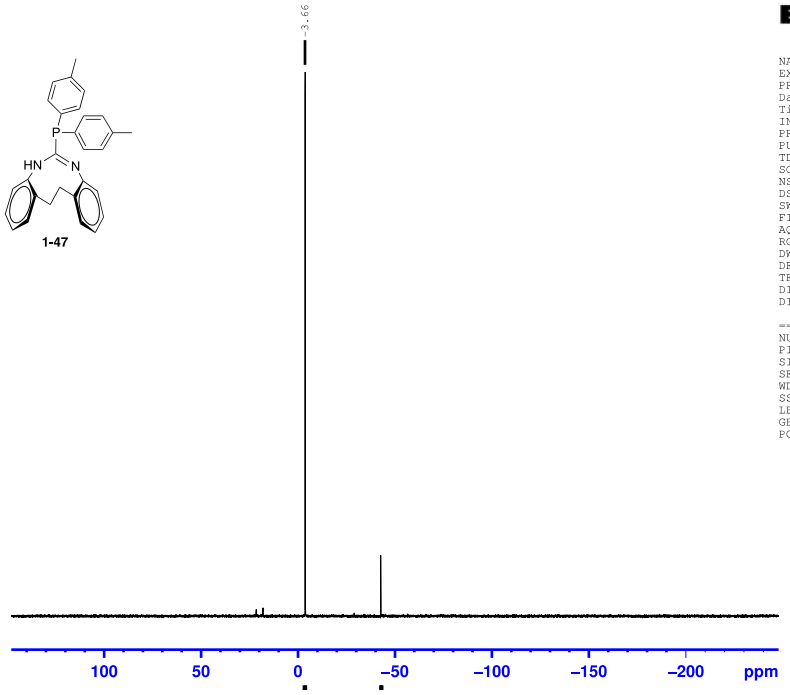
1-47

```
NAME                JAM-577-52
EXPNO                       5
PROCNO                      1
Date_                20140513
Time                    13.09
INSTRUM                 spect
PROBHD    5 mm PADUL 13C
PULPROG                 zg30
TD                      65536
SOLVENT                 CDCl3
NS                         16
DS                          2
SWH                8223.685 Hz
FIDRES             0.125483 Hz
AQ                 3.9846387 sec
RG                        114
DW                   60.800 usec
DE                    6.50 usec
TE                     298.0 K
D1                2.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                     9.31 usec
PL1                   -3.90 dB
PL1W              21.64248466 W
SFO1              400.2324716 MHz
SI                        32768
SF                400.2300121 MHz
WDW                        EM
SSB                         0
LB                     0.30 Hz
GB                          0
PC                     1.00
```



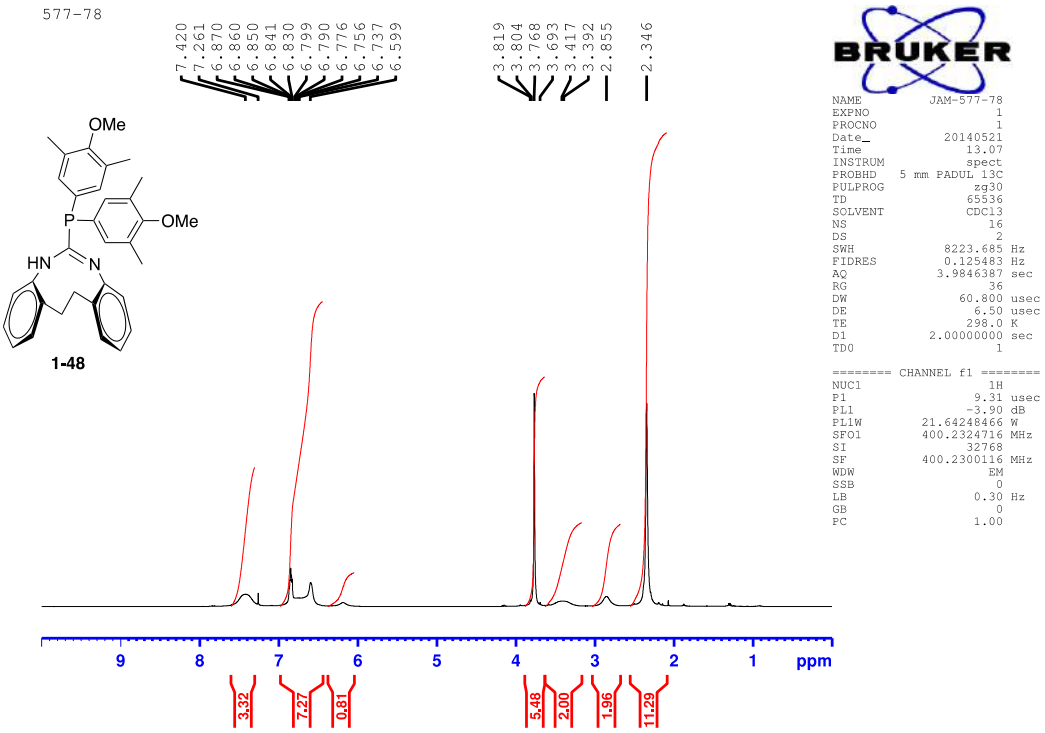
BRUKER

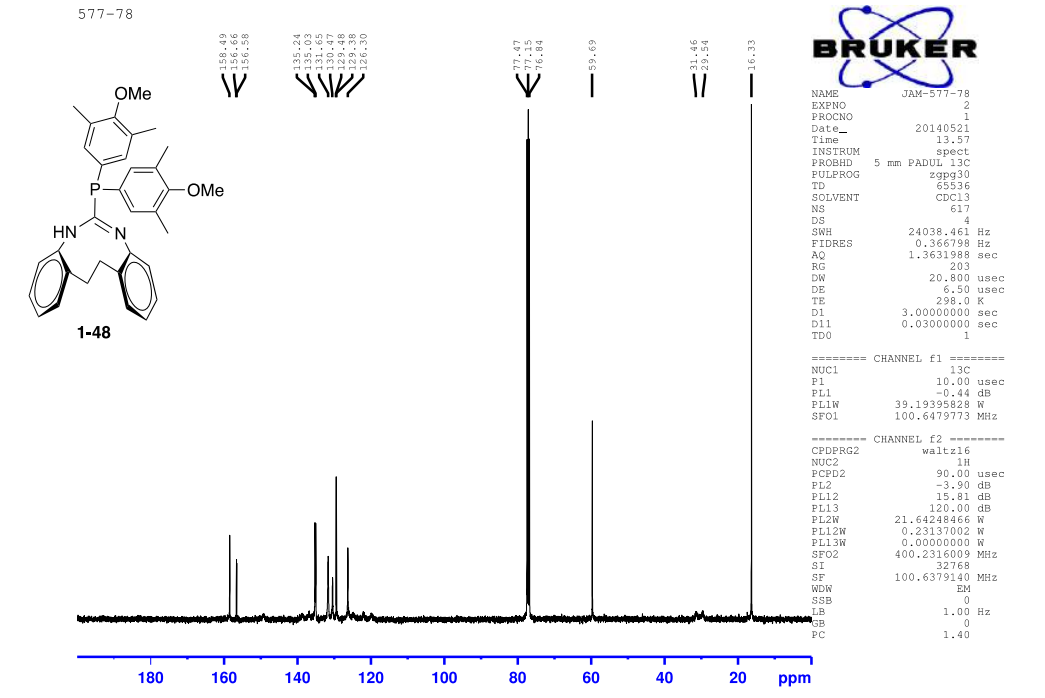
```
NAME              JAM-577-52
EXPNO                      6
PROCNO                     1
Date_               20140513
Time                   14.17
INSTRUM                spect
PROBHD    5 mm PADUL 13C
PULPROG                zgpg30
TD                      65536
SOLVENT                 CDCl3
NS                        870
DS                          4
SWH                24038.461 Hz
FIDRES             0.366798 Hz
AQ                 1.3631988 sec
RG                        203
DW                    20.800 usec
DE                     6.50 usec
TE                    298.0 K
D1                 3.00000000 sec
D11                0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                     13C
P1                     10.00 usec
PL1                    -0.44 dB
PL1W            39.19395828 W
SFO1           100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2               waltz16
NUC2                      1H
PCPD2                 90.00 usec
PL2                   -3.90 dB
PL12                  15.81 dB
PL13                 120.00 dB
PL2W            21.64248466 W
PL12W            0.23137002 W
PL13W            0.00000000 W
SFO2           400.2316009 MHz
SI                     32768
SF             100.6379140 MHz
WDW                       EM
SSB                        0
LB                      1.00 Hz
GB                         0
PC                      1.40
```

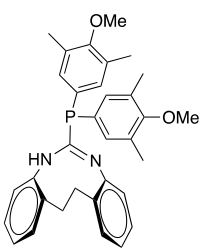


BRUKER

```
NAME              JAM-577-56
EXPNO                     11
PROCNO                     1
Date_               20140506
Time                   18.28
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG                zgpg30
TD                      65536
SOLVENT                 CDCl3
NS                         75
DS                          4
SWH                64102.563 Hz
FIDRES             0.978127 Hz
AQ                 0.5112308 sec
RG                        203
DW                     7.800 usec
DE                     6.50 usec
TE                     90.9 K
D1                 2.00000000 sec
D11                0.03000000 sec

======== CHANNEL f1 ========
NUC1                     31P
P1                     13.30 usec
SI                     32768
SF             161.9755930 MHz
WDW                       EM
SSB                        0
LB                      1.00 Hz
GB                         0
PC                      1.40
```

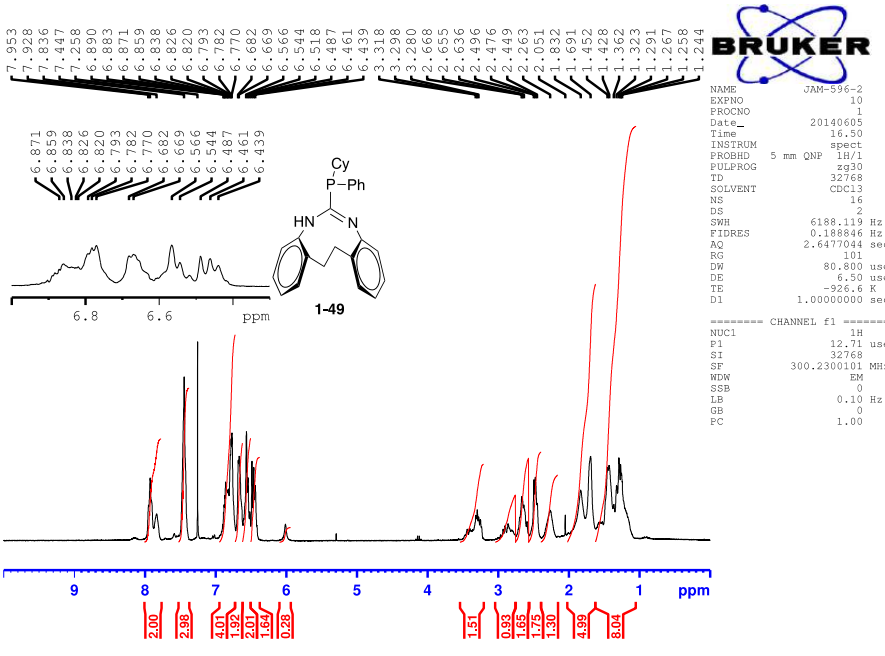

577-78
7.420
7.261
6.870
6.860
6.850
6.841
6.830
6.799
6.790
6.776
6.756
6.737
6.599
3.819
3.804
3.768
3.693
3.417
3.392
2.855
2.346
OMe
OMe
P
HN
N
1-48
9
8
7
6
5
4
3
2
1
ppm
3.32
7.27
0.81
5.48
2.00
1.96
11.29
BRUKER
NAME JAM-577-78
EXPNO 1
PROCNO 1
Date_ 20140521
Time 13.07
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 36
DW 60.800 usec
DE 6.50 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.31 usec
PL1 -3.90 dB
PL1W 21.64248466 W
SFO1 400.2324716 MHz
SI 32768
SF 400.2300116 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


577-78
158.49
156.66
156.58
135.24
135.03
131.65
130.47
129.48
129.38
126.30
77.47
77.15
76.84
59.69
31.46
29.54
16.33
OMe
OMe
P
HN
N
1-48
180
160
140
120
100
80
60
40
20
ppm
BRUKER
NAME JAM-577-78
EXPNO 2
PROCNO 1
Date_ 20140521
Time 13.57
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 617
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 298.0 K
D1 3.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 -0.44 dB
PL1W 39.19395828 W
SFO1 100.6479773 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.90 dB
PL12 15.81 dB
PL13 120.00 dB
PL2W 21.64248466 W
PL12W 0.23137002 W
PL13W 0.00000000 W
SFO2 400.2316009 MHz
SI 32768
SF 100.6379140 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



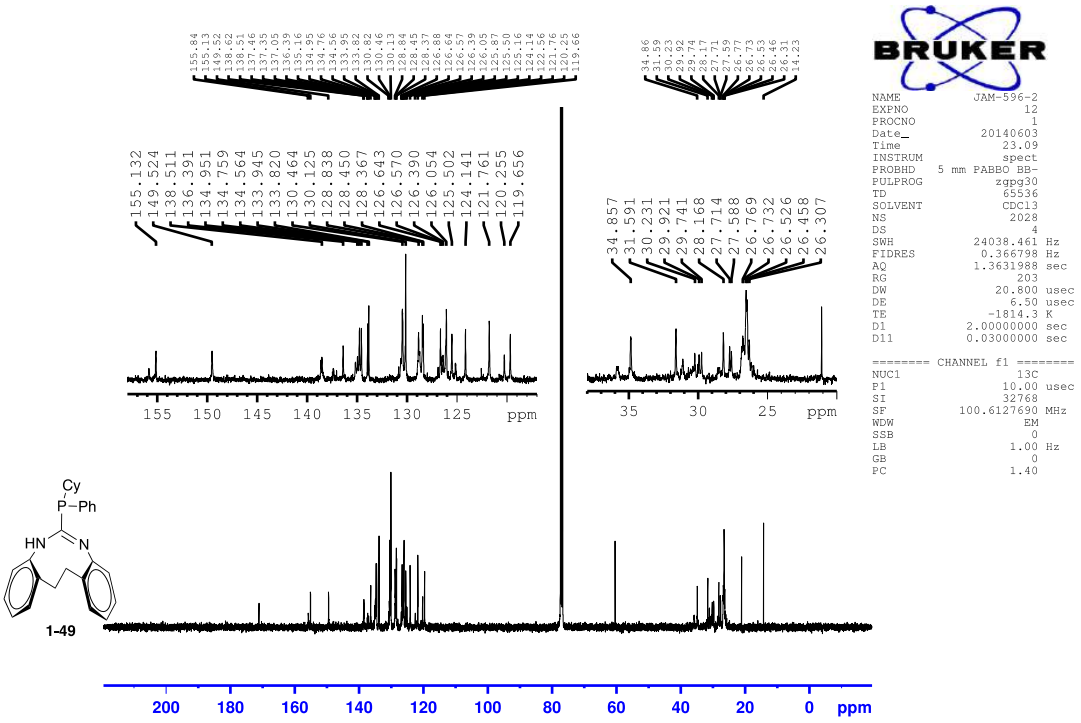
1-48


```
NAME                JAM-577-78
EXPNO                       11
PROCNO                       1
Date_             20140521
Time                      7.57
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                          16
DS                           4
SWH                 64102.563 Hz
FIDRES              0.978127 Hz
AQ                  0.5112308 sec
RG                         203
DW                     7.800 usec
DE                     6.50 usec
TE                     297.0 K
D1                  2.00000000 sec
D11                 0.03000000 sec

======== CHANNEL f1 ========
NUC1                       31P
P1                      13.30 usec
SI                       32768
SF                 161.9755930 MHz
WDW                         EM
SSB                          0
LB                      1.00 Hz
GB                           0
PC                      1.40
```

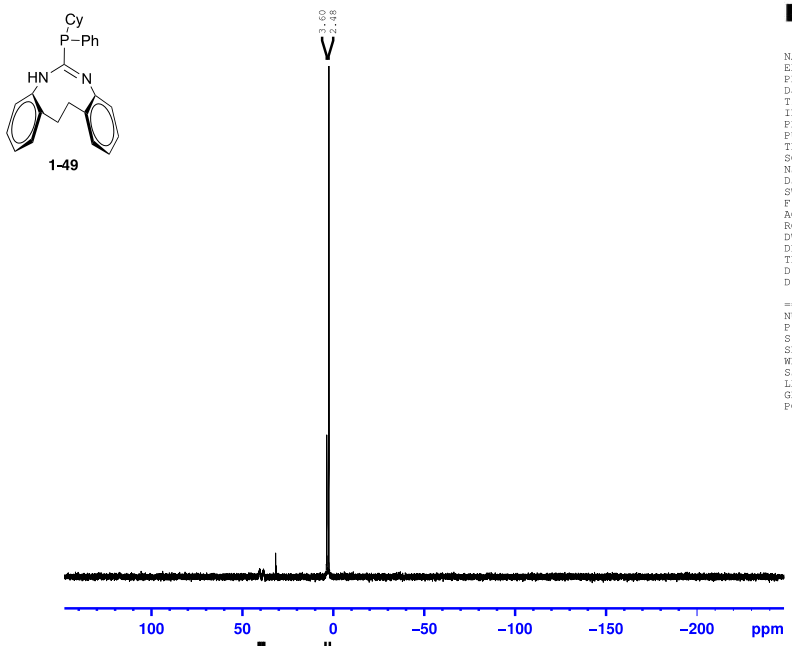


1-49

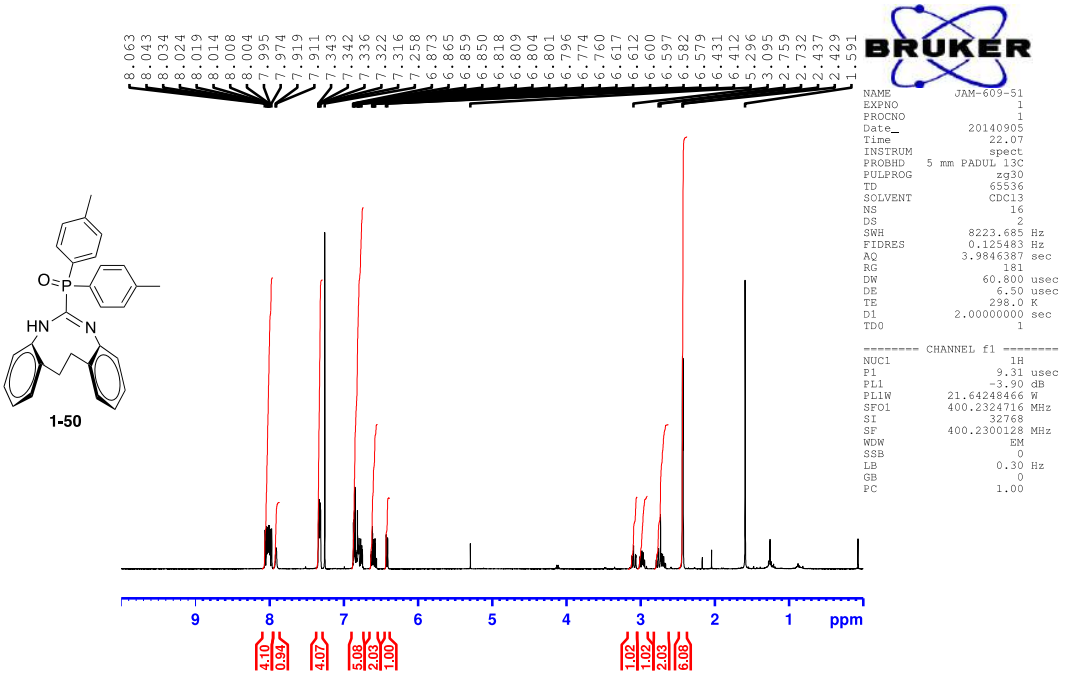
```
NAME                JAM-596-2
EXPNO                       10
PROCNO                       1
Date_             20140605
Time                     16.50
INSTRUM                  spect
PROBHD    5 mm QNP  1H/1
PULPROG                  zg30
TD                       32768
SOLVENT                  CDCl3
NS                          16
DS                           2
SWH                 6188.119 Hz
FIDRES              0.188846 Hz
AQ                  2.6477044 sec
RG                         101
DW                     80.800 usec
DE                     6.50 usec
TE                    -926.6 K
D1                  1.00000000 sec

======== CHANNEL f1 ========
NUC1                        1H
P1                      12.71 usec
SI                       32768
SF                 300.2300101 MHz
WDW                         EM
SSB                          0
LB                      0.10 Hz
GB                           0
PC                      1.00
```

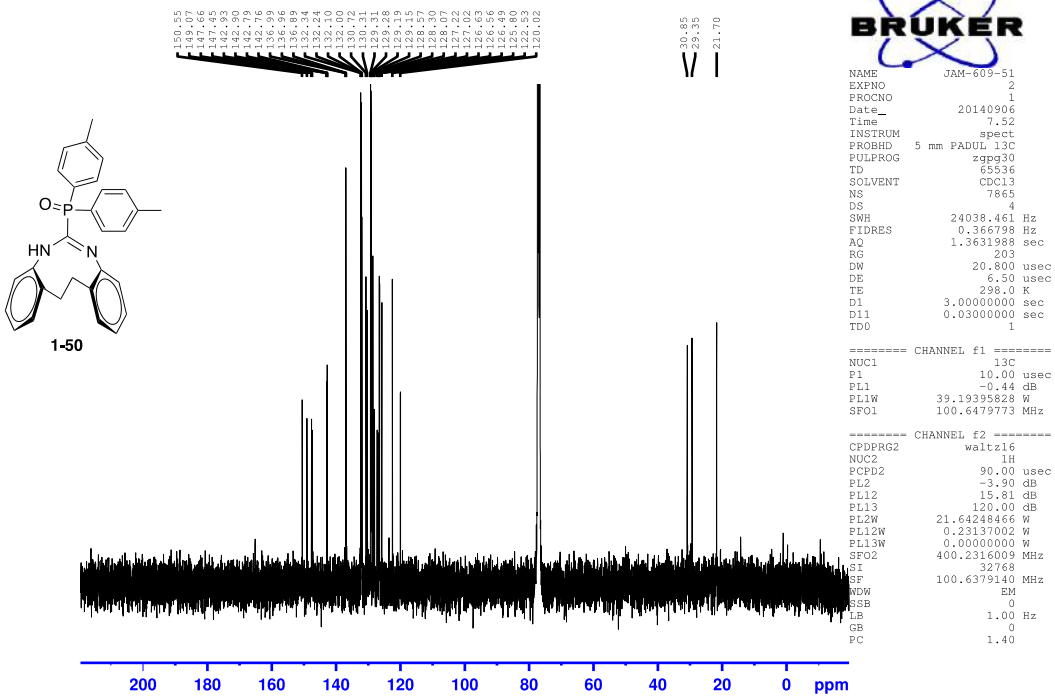


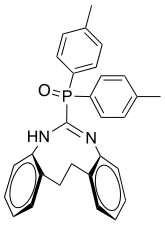

```
NAME                JAM-596-2
EXPNO                      12
PROCNO                      1
Date_                20140603
Time                    23.09
INSTRUM                 spect
PROBHD   5 mm PABBO BB-
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                        2028
DS                           4
SWH                  24038.461 Hz
FIDRES                0.366798 Hz
AQ                    1.3631988 sec
RG                         203
DW                      20.800 usec
DE                       6.50 usec
TE                     -1814.3 K
D1                  2.00000000 sec
D11                 0.03000000 sec

======== CHANNEL f1 ========
NUC1                       13C
P1                      10.00 usec
SI                        32768
SF                100.6127690 MHz
WDW                          EM
SSB                           0
LB                       1.00 Hz
GB                            0
PC                       1.40
```




```
NAME                JAM-596-2
EXPNO                      11
PROCNO                      1
Date_                20140602
Time                    19.01
INSTRUM                 spect
PROBHD   5 mm PABBO BB-
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                           32
DS                           4
SWH                  64102.563 Hz
FIDRES                0.978127 Hz
AQ                    0.5112308 sec
RG                         203
DW                       7.800 usec
DE                       6.50 usec
TE                     -365.5 K
D1                  2.00000000 sec
D11                 0.03000000 sec

======== CHANNEL f1 ========
NUC1                       31P
P1                      13.30 usec
SI                        32768
SF                161.9755930 MHz
WDW                          EM
SSB                           0
LB                       1.00 Hz
GB                            0
PC                       1.40
```

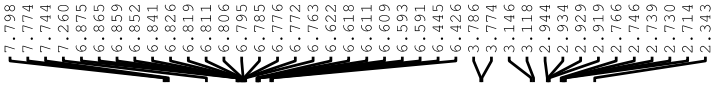

8.063
8.043
8.034
8.024
8.019
8.014
8.008
8.004
7.995
7.974
7.919
7.911
7.343
7.342
7.336
7.322
7.316
7.258
6.873
6.865
6.859
6.850
6.818
6.809
6.804
6.801
6.796
6.774
6.760
6.617
6.612
6.600
6.597
6.582
6.579
6.431
6.412
5.296
3.095
2.759
2.732
2.437
2.429
1.591
BRUKER
NAME JAM-609-51
EXPNO 1
PROCNO 1
Date_ 20140905
Time 22.07
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 181
DW 60.800 usec
DE 6.50 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.31 usec
PL1 -3.90 dB
PL1W 21.64248466 W
SFO1 400.2324716 MHz
SI 32768
SF 400.2300128 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
O
P
HN
N
1-50
9
8
7
6
5
4
3
2
1
ppm
4.10
0.94
4.07
5.08
2.03
1.00
1.02
1.02
2.03
6.08

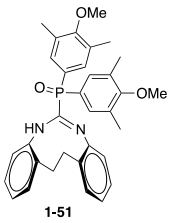

150.55
149.07
147.66
147.45
142.93
142.90
142.79
142.76
136.99
136.96
136.89
132.34
132.24
132.10
132.00
130.72
130.31
130.11
129.28
129.19
129.15
128.57
128.30
128.07
127.22
127.02
126.63
126.56
126.49
126.00
125.90
122.53
120.02
30.85
29.35
21.70
BRUKER
NAME JAM-609-51
EXPNO 2
PROCNO 1
Date_ 20140906
Time 7.52
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 7865
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 298.0 K
D1 3.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 -0.44 dB
PL1W 39.19395828 W
SFO1 100.6479773 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.90 dB
PL12 15.81 dB
PL13 120.00 dB
PL2W 21.64248466 W
PL12W 0.23137002 W
PL13W 0.00000000 W
SFO2 400.2316009 MHz
SI 32768
SF 100.6379140 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
O
P
HN
N
1-50
200
180
160
140
120
100
80
60
40
20
0
ppm



1-50

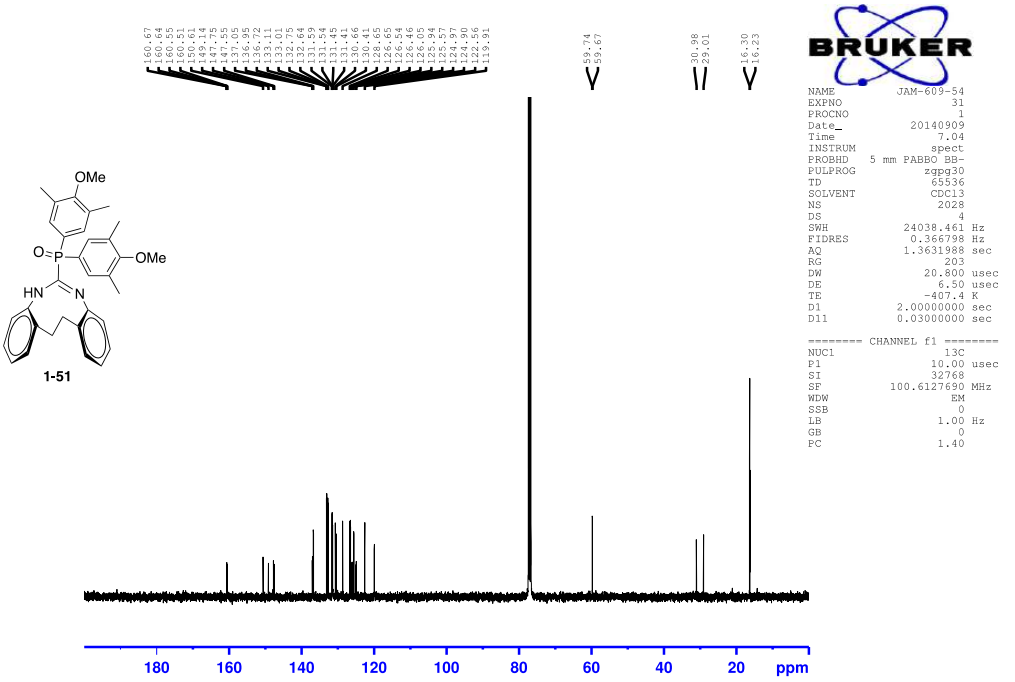

```
NAME                JAM-609-51
EXPNO                       11
PROCNO                       1
Date_                 20140905
Time                     16.32
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                          32
DS                           4
SWH                 64102.563 Hz
FIDRES              0.978127 Hz
AQ                  0.5112308 sec
RG                         203
DW                     7.800 usec
DE                     6.50 usec
TE                     369.0 K
D1                  2.00000000 sec
D11                 0.03000000 sec

======== CHANNEL f1 ========
NUC1                       31P
P1                     13.30 usec
SI                        32768
SF                161.9755930 MHz
WDW                        EM
SSB                         0
LB                      1.00 Hz
GB                          0
PC                       1.40
```





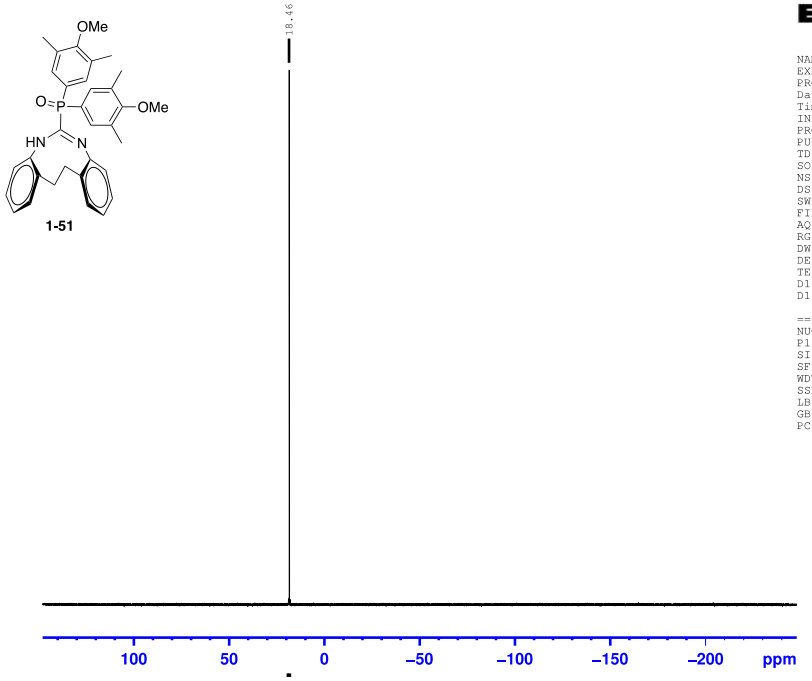
1-51


```
NAME                JAM-609-54
EXPNO                       30
PROCNO                       1
Date_                 20140908
Time                     14.50
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG                  zg30
TD                       65536
SOLVENT                  CDCl3
NS                          16
DS                           2
SWH                 8223.685 Hz
FIDRES              0.125483 Hz
AQ                  3.9846387 sec
RG                        90.5
DW                    60.800 usec
DE                     6.50 usec
TE                     81.6 K
D1                  1.00000000 sec

======== CHANNEL f1 ========
NUC1                        1H
P1                     13.75 usec
SI                        65536
SF                400.1300100 MHz
WDW                        EM
SSB                         0
LB                      0.30 Hz
GB                          0
PC                       1.00
```



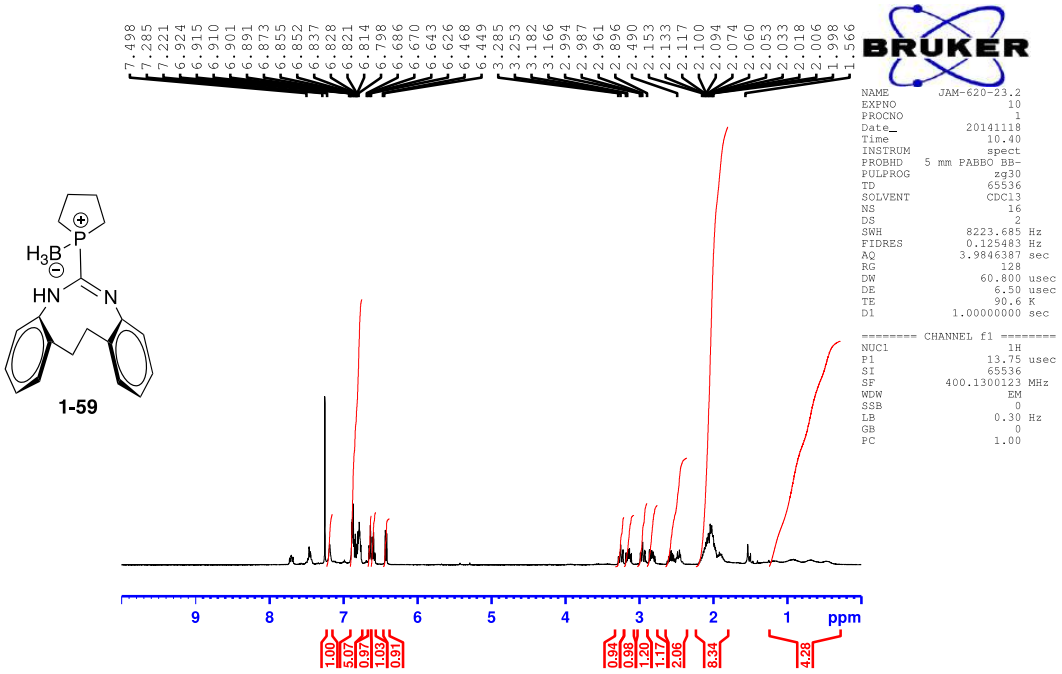
BRUKER

```
NAME                JAM-609-54
EXPNO                       31
PROCNO                       1
Date_                 20140909
Time                      7.04
INSTRUM                 spect
PROBHD    5 mm PABBO BB-
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDC13
NS                        2028
DS                           4
SWH                 24038.461 Hz
FIDRES               0.366798 Hz
AQ                   1.3631988 sec
RG                         203
DW                      20.800 usec
DE                       6.50 usec
TE                     -407.4 K
D1                  2.00000000 sec
D11                 0.03000000 sec

======== CHANNEL f1 ========
NUC1                       13C
P1                      10.00 usec
SI                       32768
SF                100.6127690 MHz
WDW                         EM
SSB                          0
LB                      1.00 Hz
GB                           0
PC                      1.40
```



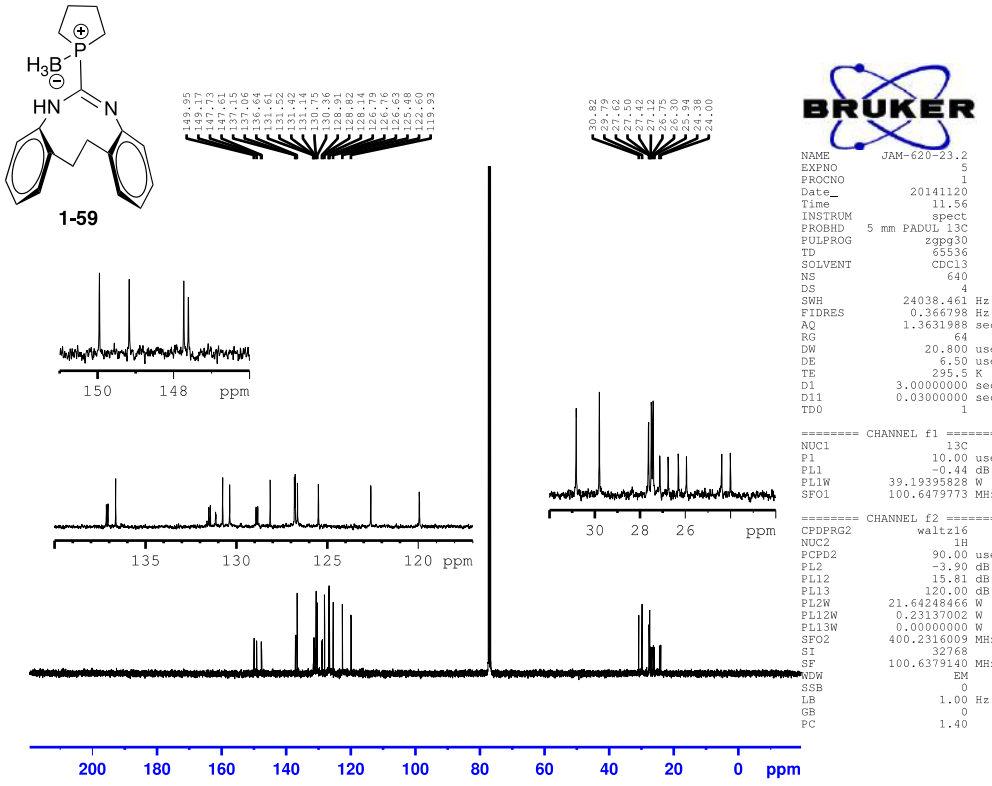
BRUKER

```
NAME                JAM-609-54
EXPNO                       21
PROCNO                       1
Date_                 20140908
Time                      7.52
INSTRUM                 spect
PROBHD    5 mm PABBO BB-
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDC13
NS                          32
DS                           4
SWH                 64102.563 Hz
FIDRES               0.978127 Hz
AQ                   0.5112308 sec
RG                         203
DW                       7.800 usec
DE                       6.50 usec
TE                     3024.8 K
D1                  2.00000000 sec
D11                 0.03000000 sec

======== CHANNEL f1 ========
NUC1                       31P
P1                      13.30 usec
SI                       32768
SF                161.9755930 MHz
WDW                         EM
SSB                          0
LB                      1.00 Hz
GB                           0
PC                      1.40
```



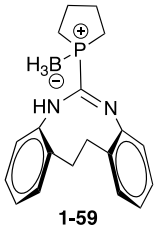
BRUKER

```
NAME          JAM-620-23.2
EXPNO                   10
PROCNO                   1
Date_             20141118
Time                 10.40
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              8223.685 Hz
FIDRES           0.125483 Hz
AQ               3.9846387 sec
RG                    128
DW                60.800 usec
DE                 6.50 usec
TE                 90.6 K
D1              1.00000000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                 13.75 usec
SI                  65536
SF            400.1300123 MHz
WDW                    EM
SSB                     0
LB                 0.30 Hz
GB                      0
PC                   1.00
```



BRUKER

```
NAME          JAM-620-23.2
EXPNO                    5
PROCNO                   1
Date_             20141120
Time                 11.56
INSTRUM              spect
PROBHD   5 mm PADUL 13C
PULPROG             zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    640
DS                      4
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ               1.3631988 sec
RG                     64
DW                20.800 usec
DE                 6.50 usec
TE                 295.5 K
D1              3.00000000 sec
D11             0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                10.00 usec
PL1                -0.44 dB
PL1W            39.19395828 W
SFO1           100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              90.00 usec
PL2                -3.90 dB
PL12               15.81 dB
PL13              120.00 dB
PL2W           21.64248466 W
PL12W           0.23137002 W
PL13W           0.00000000 W
SFO2           400.2316009 MHz
SI                  32768
SF             100.6379140 MHz
WDW                    EM
SSB                     0
LB                 1.00 Hz
GB                      0
PC                   1.40
```

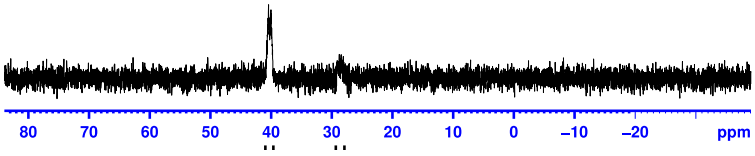


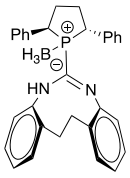
1-59

40.41
40.01

BRUKER

```
NAME            JAM-620-23.2
EXPNO                     11
PROCNO                     1
Date_           20141118
Time                 10.43
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                      32
DS                       4
SWH              64102.563 Hz
FIDRES           0.978127 Hz
AQ               0.5112308 sec
RG                     203
DW                  7.800 usec
DE                  6.50 usec
TE                  90.8 K
D1              2.00000000 sec
D11             0.03000000 sec

======== CHANNEL f1 ========
NUC1                   31P
P1                  13.30 usec
SI                   32768
SF            161.9755930 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

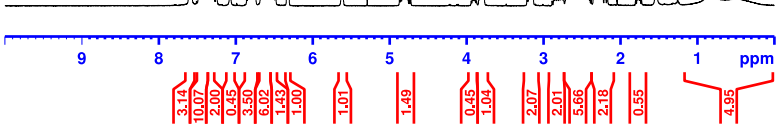


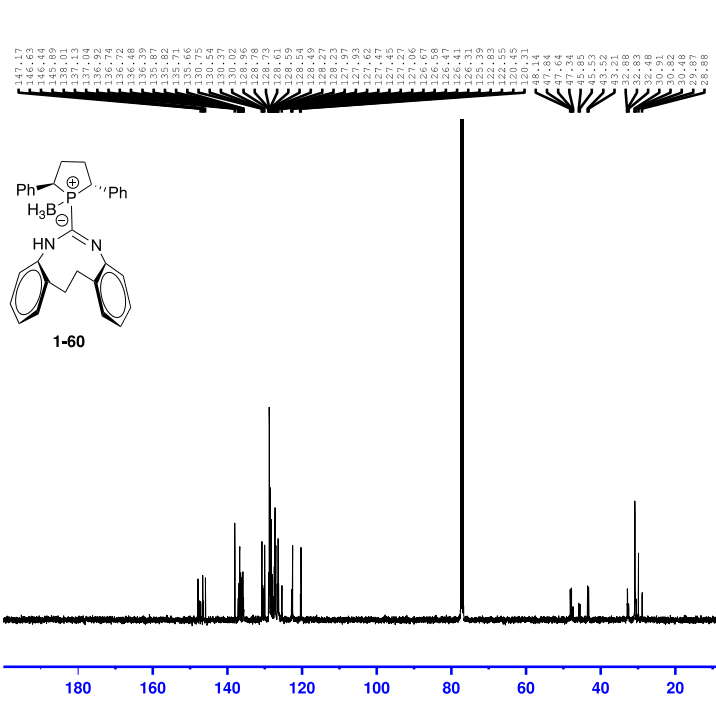


1-60

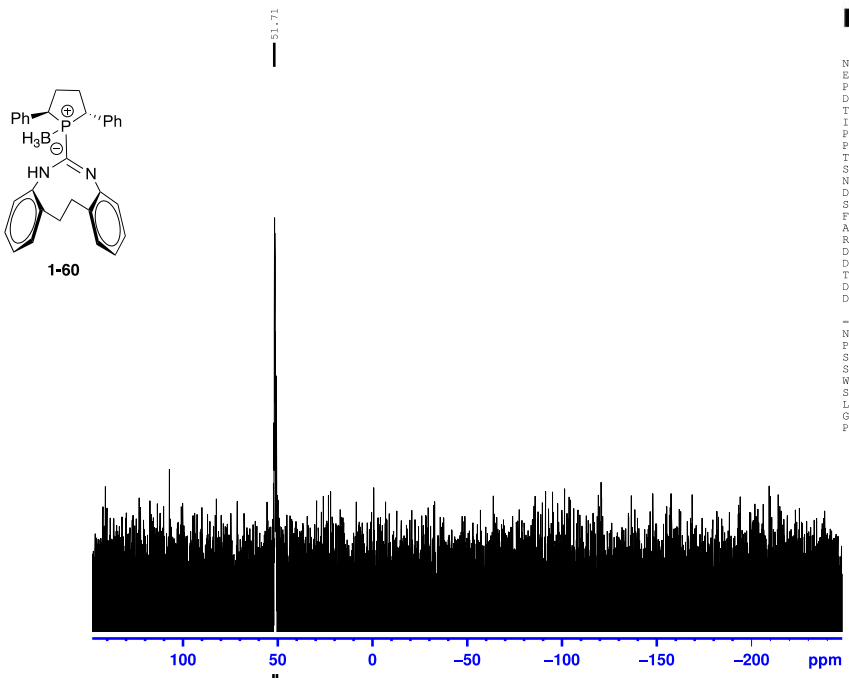
BRUKER

```
NAME            JAM-647-37
EXPNO                   10
PROCNO                   1
Date_           20150501
Time                 10.31
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH               8223.685 Hz
FIDRES           0.125483 Hz
AQ               3.9846387 sec
RG                     114
DW                 60.800 usec
DE                  6.50 usec
TE                  95.3 K
D1              1.00000000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                  13.75 usec
SI                   65536
SF            400.1300128 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

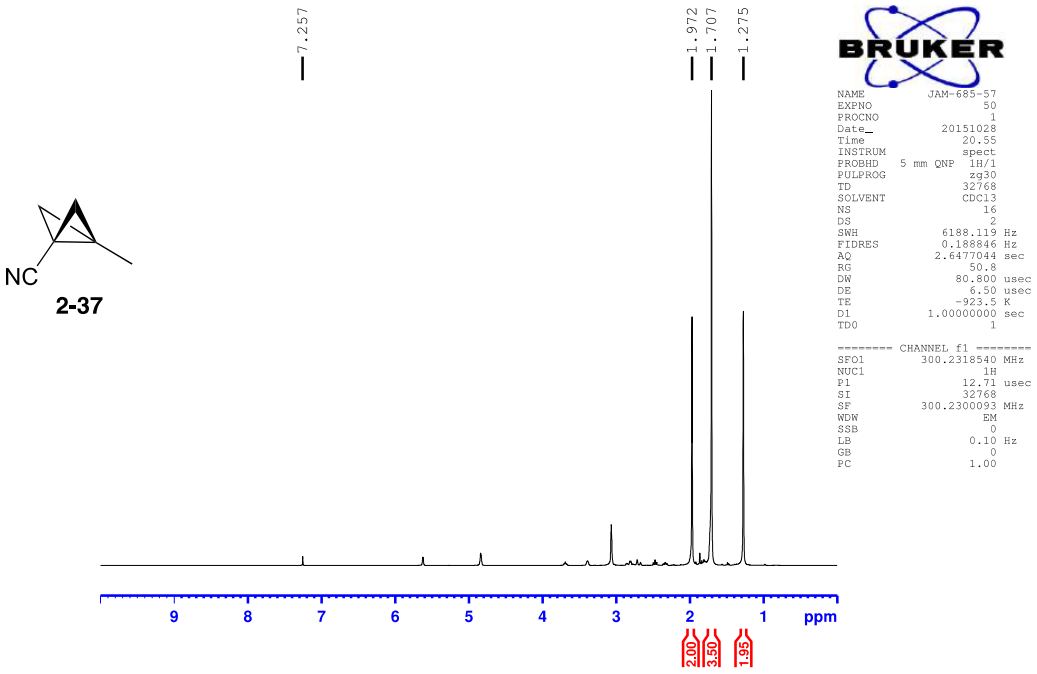


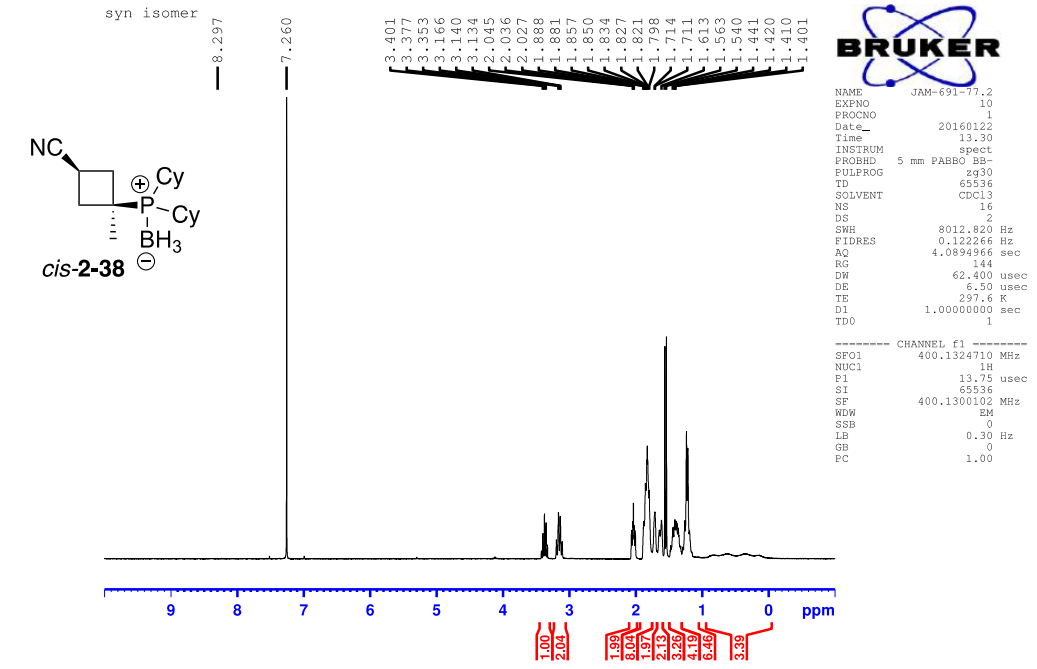


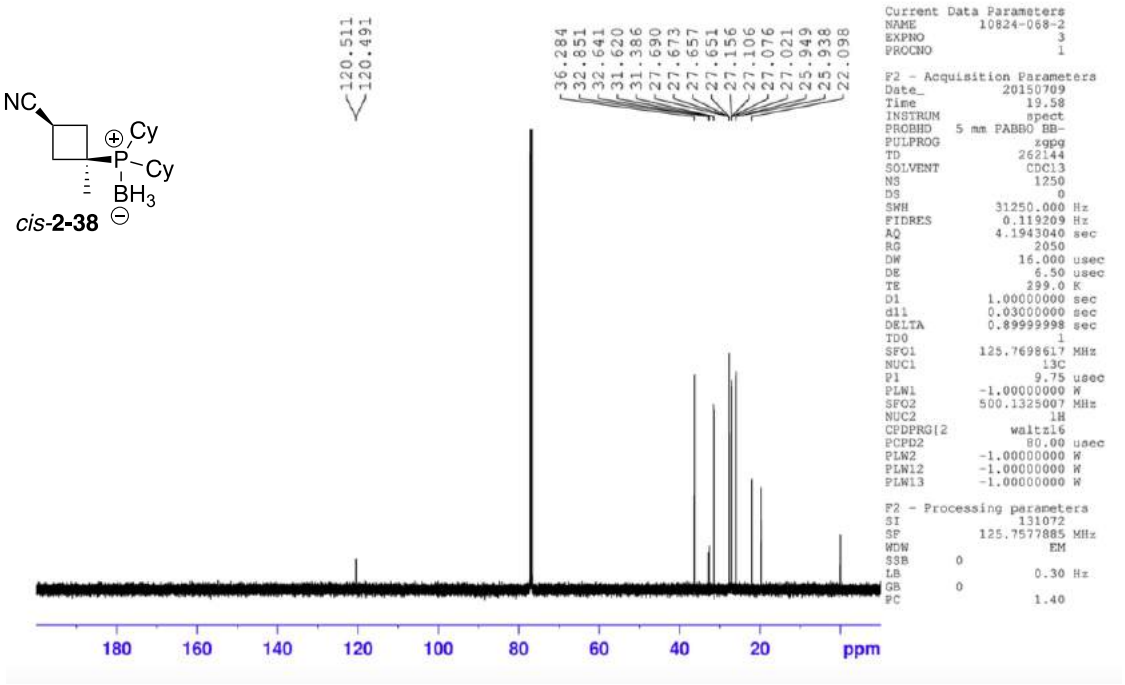

```
NAME                JAM-647-37
EXPNO                        2
PROCNO                       1
Date_                 20150501
Time                     15.56
INSTRUM                  spect
PROBHD    5 mm PADUL 13C
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                         612
DS                           4
SWH                 24038.461 Hz
FIDRES               0.366798 Hz
AQ                   1.3631988 sec
RG                        50.8
DW                      20.800 usec
DE                       6.50 usec
TE                      296.8 K
D1                  3.00000000 sec
D11                 0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                       13C
P1                       10.00 usec
PL1                      -0.44 dB
PL1W               39.19395828 W
SFO1              100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                        1H
PCPD2                    90.00 usec
PL2                      -3.90 dB
PL12                     15.81 dB
PL13                    120.00 dB
PL2W               21.64248466 W
PL12W               0.23137002 W
PL13W               0.00000000 W
SFO2              400.2316009 MHz
SI                       32768
SF                100.6379140 MHz
WDW                         EM
SSB                          0
LB                       1.00 Hz
GB                           0
PC                       1.40
```




```
NAME                JAM-647-37
EXPNO                       11
PROCNO                       1
Date_                 20150501
Time                     10.33
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                          16
DS                           4
SWH                 64102.563 Hz
FIDRES               0.978127 Hz
AQ                   0.5112308 sec
RG                         203
DW                       7.800 usec
DE                       6.50 usec
TE                      95.3 K
D1                  2.00000000 sec
D11                 0.03000000 sec

======== CHANNEL f1 ========
NUC1                       31P
P1                       13.30 usec
SI                       32768
SF                161.9755930 MHz
WDW                         EM
SSB                          0
LB                       1.00 Hz
GB                           0
PC                       1.40
```

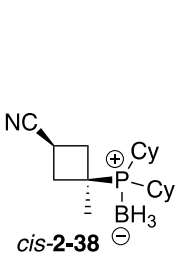

7.257
1.972
1.707
1.275
NC
2-37
BRUKER
NAME JAM-685-57
EXPNO 50
PROCNO 1
Date_ 20151028
Time 20.55
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.188846 Hz
AQ 2.6477044 sec
RG 50.8
DW 80.800 usec
DE 6.50 usec
TE -923.5 K
D1 1.00000000 sec
TD0 1
-------- CHANNEL f1 --------
SFO1 300.2318540 MHz
NUC1 1H
P1 12.71 usec
SI 32768
SF 300.2300093 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00
9 8 7 6 5 4 3 2 1 ppm
2.00 3.50 1.95


syn isomer
8.297
7.260
3.401
3.377
3.353
3.166
3.140
3.134
2.045
2.036
2.027
1.888
1.881
1.857
1.850
1.834
1.827
1.821
1.798
1.714
1.711
1.613
1.563
1.540
1.441
1.420
1.410
1.401
NC
Cy
P
Cy
BH3
cis-2-38
BRUKER
NAME JAM-691-77.2
EXPNO 10
PROCNO 1
Date_ 20160122
Time 13.30
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 144
DW 62.400 usec
DE 6.50 usec
TE 297.6 K
D1 1.00000000 sec
TD0 1
-------- CHANNEL f1 --------
SFO1 400.1324710 MHz
NUC1 1H
P1 13.75 usec
SI 65536
SF 400.1300102 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9 8 7 6 5 4 3 2 1 0 ppm
1.00 2.04 1.99 3.04 1.97 2.13 3.26 4.19 6.46 3.39

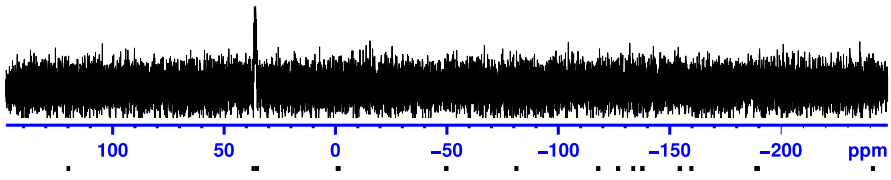


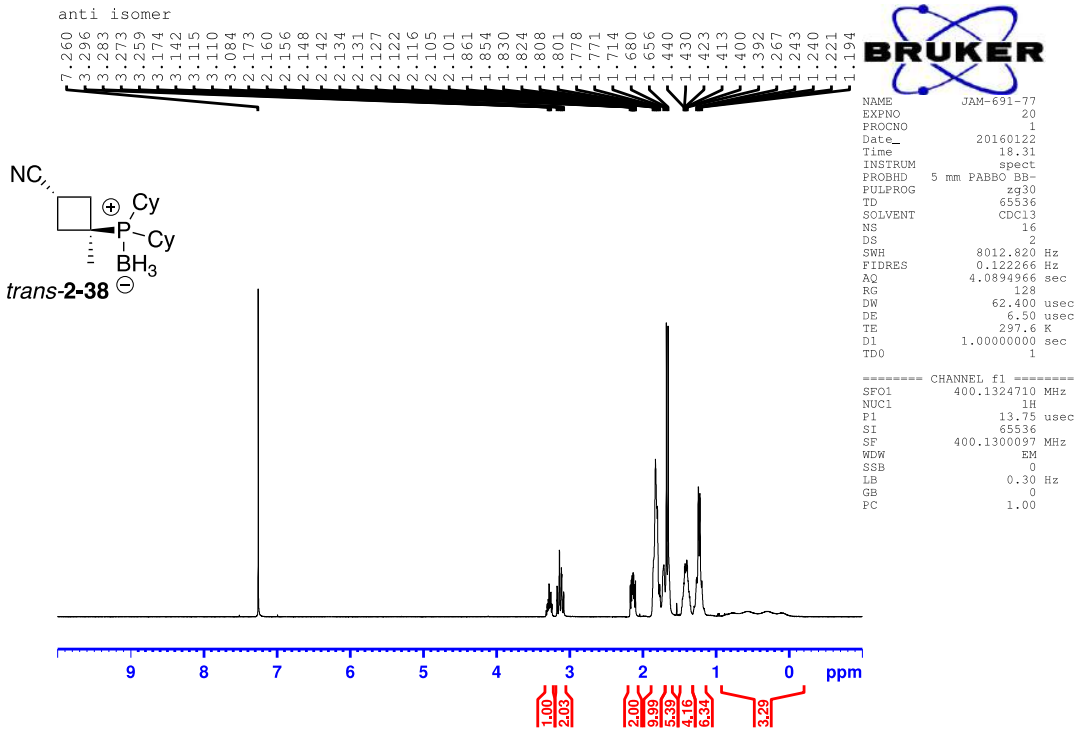

```
Current Data Parameters
NAME          10824-068-2
EXPNO                   3
PROCNO                  1

F2 - Acquisition Parameters
Date_            20150709
Time                19.58
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG             zgpg
TD                262144
SOLVENT             CDCl3
NS                    1250
DS                       0
SWH           31250.000 Hz
FIDRES        0.119209 Hz
AQ            4.1943040 sec
RG                    2050
DW              16.000 usec
DE               6.50 usec
TE                299.0 K
D1           1.00000000 sec
d11          0.03000000 sec
DELTA        0.89999998 sec
TD0                     1
SFO1        125.7698617 MHz
NUC1                  13C
P1               9.75 usec
PLW1        -1.00000000 W
SFO2        500.1325007 MHz
NUC2                  1H
CPDPRG[2          waltz16
PCPD2            80.00 usec
PLW2        -1.00000000 W
PLW12       -1.00000000 W
PLW13       -1.00000000 W

F2 - Processing parameters
SI                 131072
SF          125.7577885 MHz
WDW                    EM
SSB                     0
LB               0.30 Hz
GB                      0
PC                  1.40
```

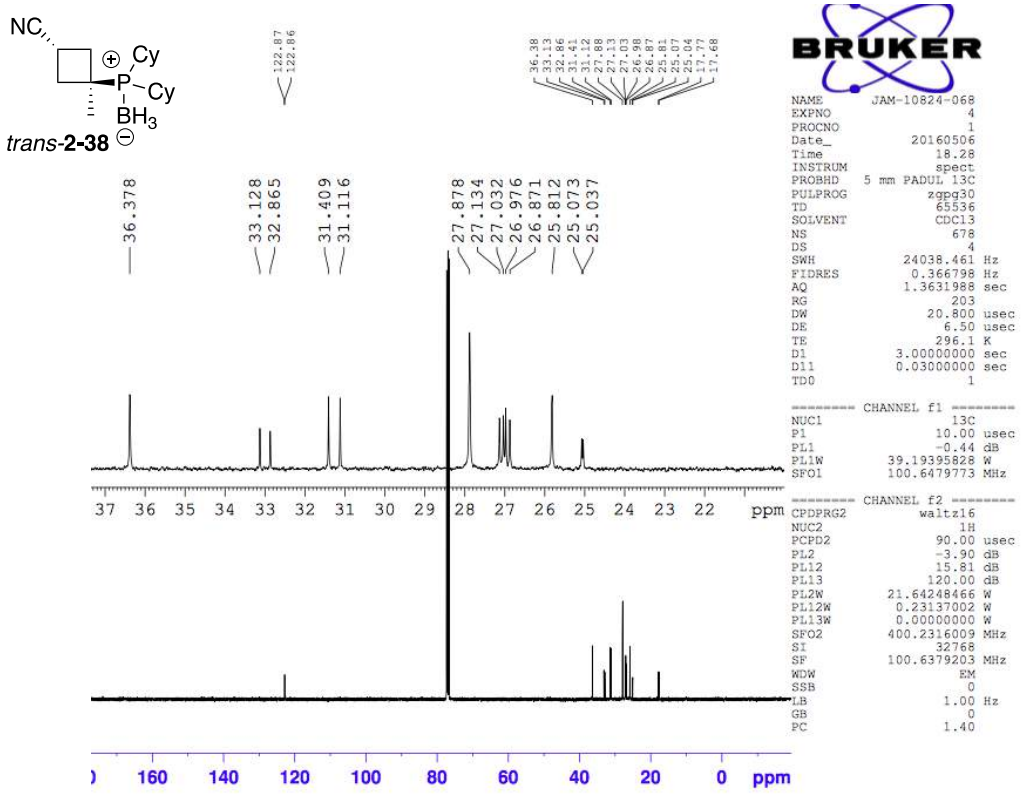
syn isomer



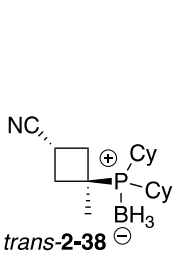

```
NAME          JAM-691-77.2
EXPNO                   11
PROCNO                   1
Date_             20160122
Time                13.32
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                  65536
SOLVENT             CDCl3
NS                      16
DS                       4
SWH           64102.563 Hz
FIDRES        0.978127 Hz
AQ            0.5112308 sec
RG                    203
DW              7.800 usec
DE               6.50 usec
TE                297.7 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1        161.9674942 MHz
NUC1                  31P
P1              13.30 usec
SI                  32768
SF          161.9755930 MHz
WDW                    EM
SSB                     0
LB               1.00 Hz
GB                      0
PC                  1.40
```




anti isomer
7.260 3.296 3.283 3.273 3.259 3.174 3.142 3.115 3.110 3.084 2.173 2.160 2.156 2.148 2.142 2.134 2.131 2.127 2.122 2.116 2.105 2.101 1.861 1.854 1.830 1.824 1.808 1.801 1.778 1.771 1.714 1.680 1.656 1.440 1.430 1.423 1.413 1.400 1.392 1.267 1.243 1.240 1.221 1.194
BRUKER
NAME JAM-691-77
EXPNO 20
PROCNO 1
Date_ 20160122
Time 18.31
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 128
DW 62.400 usec
DE 6.50 usec
TE 297.6 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 13.75 usec
SI 65536
SF 400.1300097 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
NC
Cy
P
Cy
BH3
trans-2-38
9 8 7 6 5 4 3 2 1 0 ppm
1.00 2.03 2.00 9.98 5.39 4.16 6.34 3.29

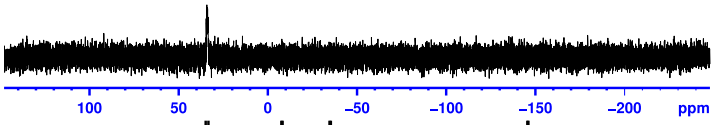

NC
Cy
P
Cy
BH3
trans-2-38
122.87 122.86
36.38 33.13 32.86 31.41 31.12 27.88 27.13 27.03 26.98 26.87 25.81 25.07 25.04 17.77 17.68
36.378 33.128 32.865 31.409 31.116 27.878 27.134 27.032 26.976 26.871 25.812 25.073 25.037
37 36 35 34 33 32 31 30 29 28 27 26 25 24 23 22 ppm
160 140 120 100 80 60 40 20 0 ppm
BRUKER
NAME JAM-10824-068
EXPNO 4
PROCNO 1
Date_ 20160506
Time 18.28
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 678
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 296.1 K
D1 3.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 -0.44 dB
PL1W 39.19395828 W
SFO1 100.6479773 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.90 dB
PL12 15.81 dB
PL13 120.00 dB
PL2W 21.64248466 W
PL12W 0.23137002 W
PL13W 0.00000000 W
SFO2 400.2316009 MHz
SI 32768
SF 100.6379203 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

anti isomer

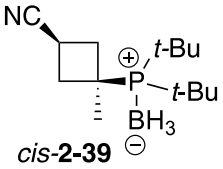


trans-**2-38**


```
NAME                JAM-691-77
EXPNO                       21
PROCNO                       1
Date_                 20160122
Time                     18.34
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG                zgpg30
TD                      65536
SOLVENT                 CDCl3
NS                         16
DS                          4
SWH                 64102.563 Hz
FIDRES              0.978127 Hz
AQ                  0.5112308 sec
RG                        203
DW                     7.800 usec
DE                     6.50 usec
TE                     297.7 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1             161.9674942 MHz
NUC1                     31P
P1                     13.30 usec
SI                      32768
SF                161.9755930 MHz
WDW                        EM
SSB                         0
LB                      1.00 Hz
GB                          0
PC                      1.40
```

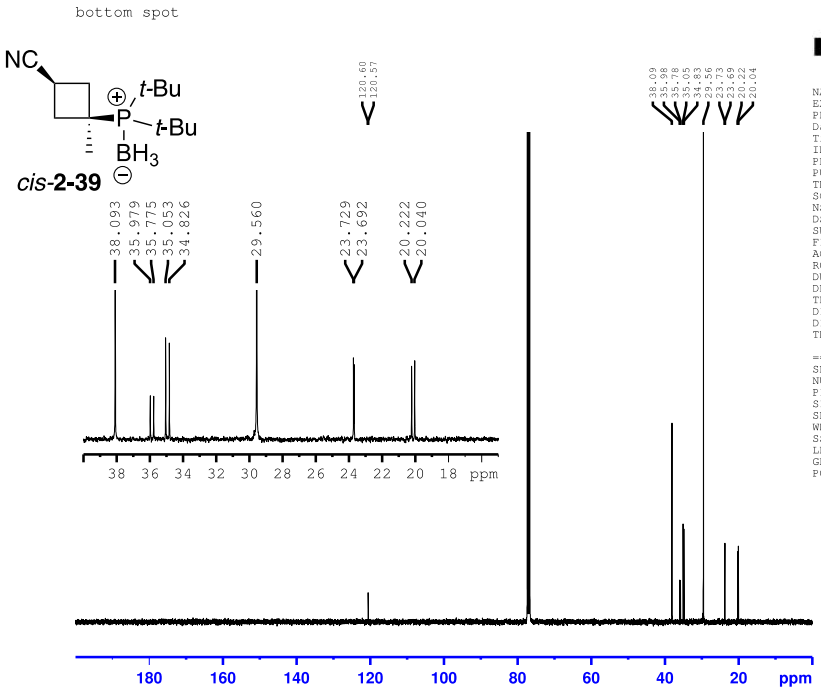


bottom spot



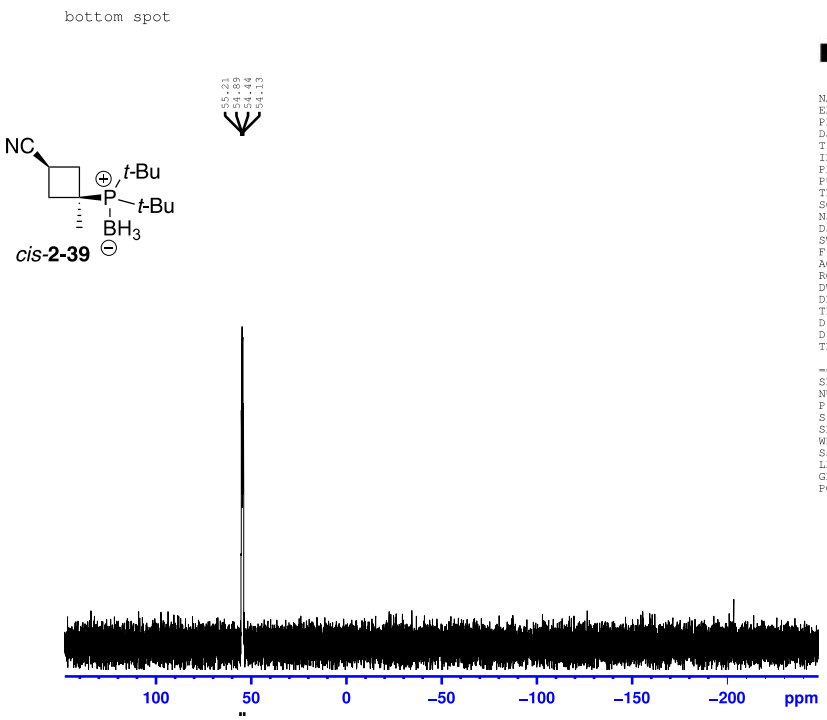
cis-**2-39**


```
NAME                JAM-685-87.2
EXPNO                       10
PROCNO                       1
Date_                 20151116
Time                     16.00
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG                  zg30
TD                      65536
SOLVENT                 CDCl3
NS                         16
DS                          2
SWH                  8012.820 Hz
FIDRES               0.122266 Hz
AQ                   4.0894966 sec
RG                         57
DW                     62.400 usec
DE                      6.50 usec
TE                      95.3 K
D1                1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1             400.1324710 MHz
NUC1                     1H
P1                     13.75 usec
SI                      65536
SF                400.1300116 MHz
WDW                        EM
SSB                         0
LB                      0.30 Hz
GB                          0
PC                      1.00
```



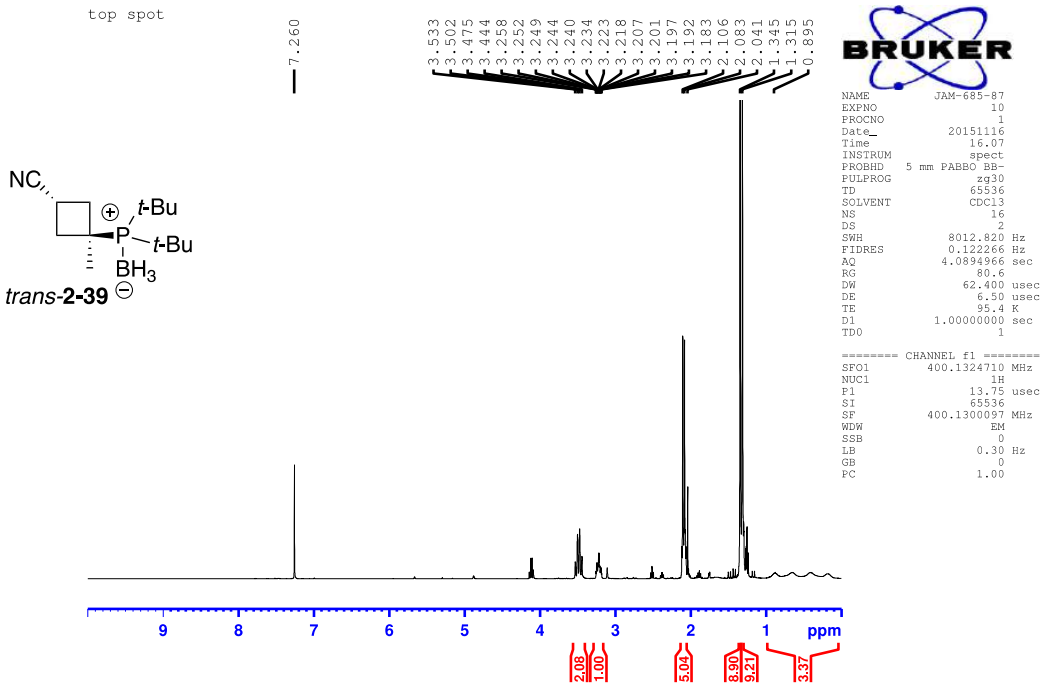
BRUKER

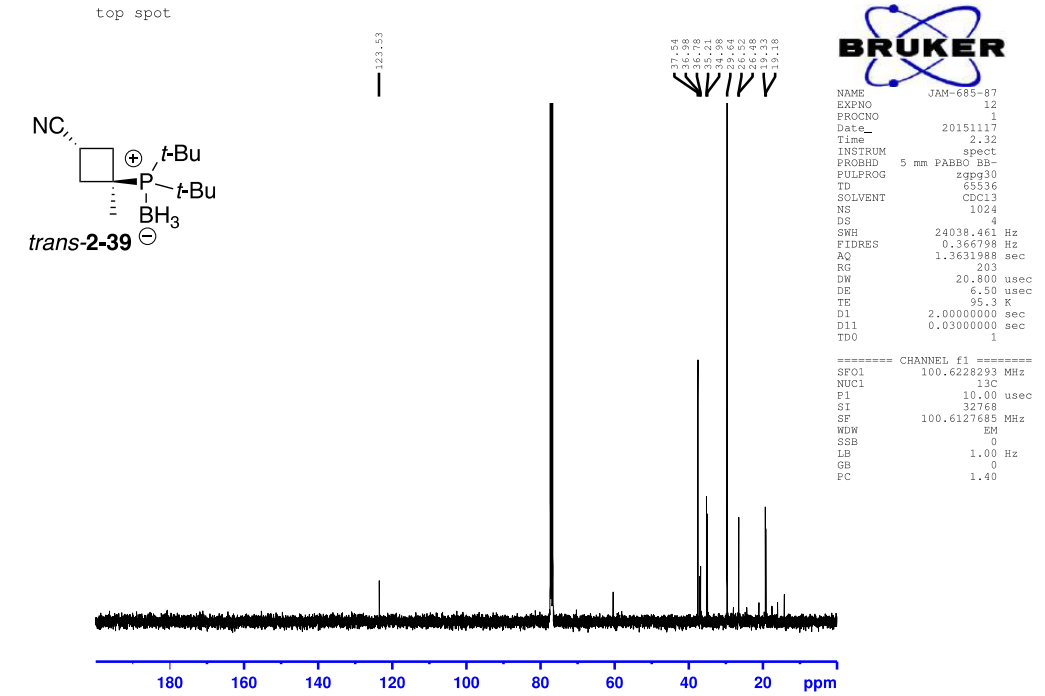
```
NAME                JAM-685-87.2
EXPNO                         12
PROCNO                         1
Date_                 20151117
Time                      0.42
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                        1024
DS                           2
SWH                 24038.461 Hz
FIDRES               0.366798 Hz
AQ                  1.3631988 sec
RG                         203
DW                    20.800 usec
DE                     6.50 usec
TE                     96.0 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                           1

======== CHANNEL f1 ========
SFO1           100.6228298 MHz
NUC1                     13C
P1                     10.00 usec
SI                      32768
SF             100.6127685 MHz
WDW                        EM
SSB                         0
LB                     1.00 Hz
GB                          0
PC                     1.40
```



BRUKER

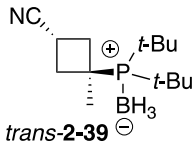
```
NAME                JAM-685-87.2
EXPNO                         11
PROCNO                         1
Date_                 20151116
Time                     16.02
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                          16
DS                           4
SWH                 64102.563 Hz
FIDRES               0.978127 Hz
AQ                  0.5112308 sec
RG                         203
DW                     7.800 usec
DE                     6.50 usec
TE                     95.3 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                           1

======== CHANNEL f1 ========
SFO1           161.9674942 MHz
NUC1                     31P
P1                     13.30 usec
SI                      32768
SF             161.9755930 MHz
WDW                        EM
SSB                         0
LB                     1.00 Hz
GB                          0
PC                     1.40
```


top spot
7.260
3.533
3.502
3.475
3.444
3.258
3.252
3.249
3.244
3.240
3.234
3.223
3.218
3.207
3.201
3.197
3.192
3.183
3.106
2.083
2.041
1.345
1.315
0.895
NC
t-Bu
P
t-Bu
BH3
trans-2-39
BRUKER
NAME JAM-685-87
EXPNO 10
PROCNO 1
Date_ 20151116
Time 16.07
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 80.6
DW 62.400 usec
DE 6.50 usec
TE 95.4 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 13.75 usec
SI 65536
SF 400.1300097 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9
8
7
6
5
4
3
2
1
ppm
2.08
1.00
5.04
8.90
9.21
3.37


top spot
123.53
37.54
36.98
36.78
35.21
34.88
29.64
26.52
26.48
24.43
19.18
NC
t-Bu
P
t-Bu
BH3
trans-2-39
BRUKER
NAME JAM-685-87
EXPNO 12
PROCNO 1
Date_ 20151117
Time 2.32
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 95.3 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6228293 MHz
NUC1 13C
P1 10.00 usec
SI 32768
SF 100.6127685 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
180
160
140
120
100
80
60
40
20
ppm

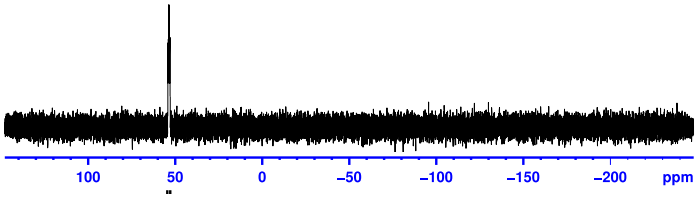
top spot

54.22
53.83
53.41
53.06



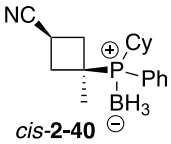
trans-**2-39**

```
NAME            JAM-685-87
EXPNO               11
PROCNO               1
Date_            20151116
Time                16.09
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    4
SWH           64102.563 Hz
FIDRES        0.978127 Hz
AQ            0.5112308 sec
RG                  203
DW                7.800 usec
DE                6.50 usec
TE                95.4 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
SFO1        161.9674942 MHz
NUC1              31P
P1                13.30 usec
SI                32768
SF          161.9755930 MHz
WDW                EM
SSB                 0
LB                1.00 Hz
GB                  0
PC                1.40
```



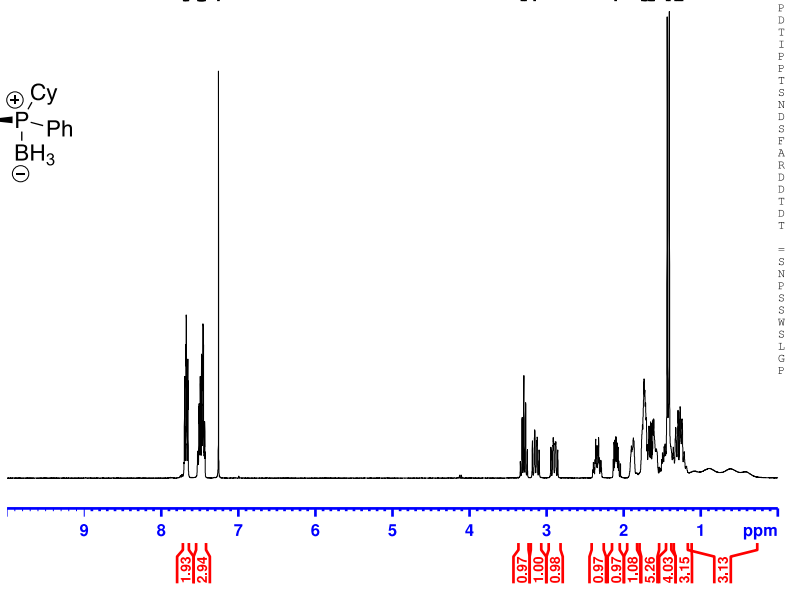
syn isomer

7.700
7.697
7.693
7.680
7.676
7.657
7.653
7.513
7.509
7.499
7.495
7.492
7.488
7.478
7.474
7.473
7.470
7.463
7.458
7.454
7.442
7.437
7.258
3.317
3.295
3.272
3.155
2.102
1.756
1.736
1.725
1.716
1.706
1.671
1.649
1.640
1.619
1.609
1.435
1.407
1.323
1.294
1.266
1.243

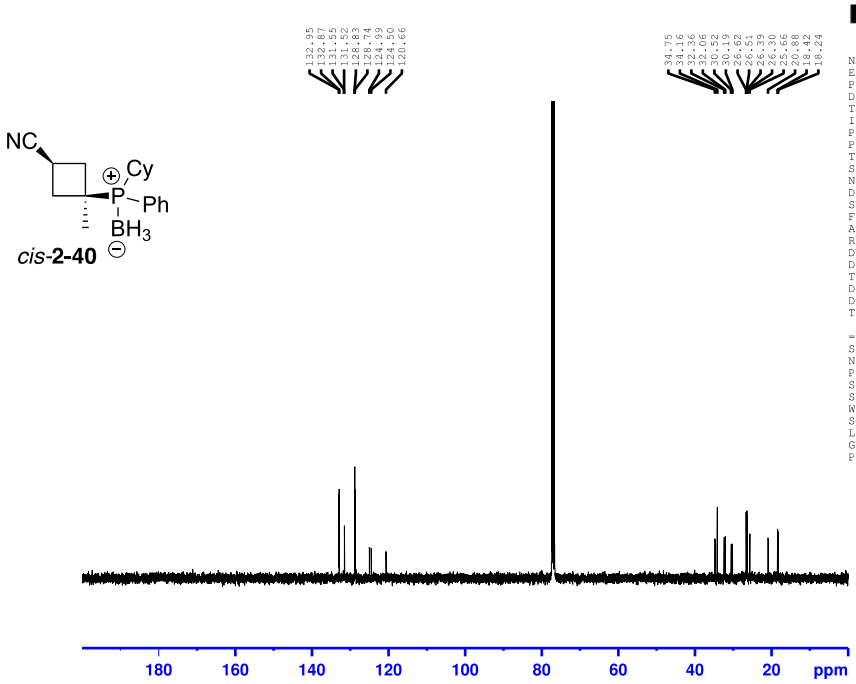


cis-**2-40**

```
NAME          JAM-704-82.2
EXPNO               10
PROCNO               1
Date_            20160328
Time                11.15
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            8012.820 Hz
FIDRES         0.122266 Hz
AQ             4.0894966 sec
RG                  101
DW                62.400 usec
DE                6.50 usec
TE                96.6 K
D1            1.00000000 sec
TD0                  1

======== CHANNEL f1 ========
SFO1        400.1324710 MHz
NUC1               1H
P1                13.75 usec
SI                65536
SF          400.1300110 MHz
WDW                EM
SSB                 0
LB                0.30 Hz
GB                  0
PC                1.00
```



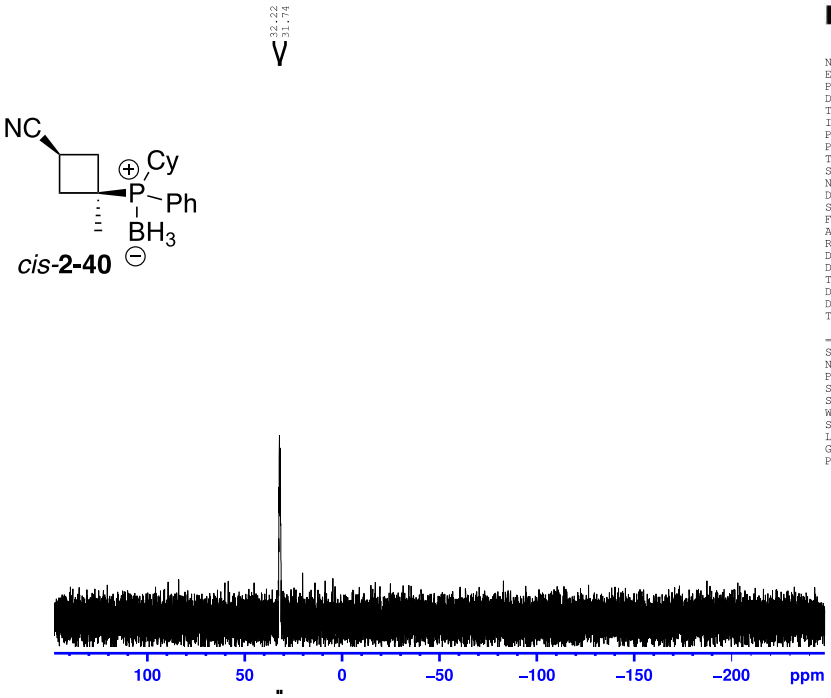
syn isomer



BRUKER

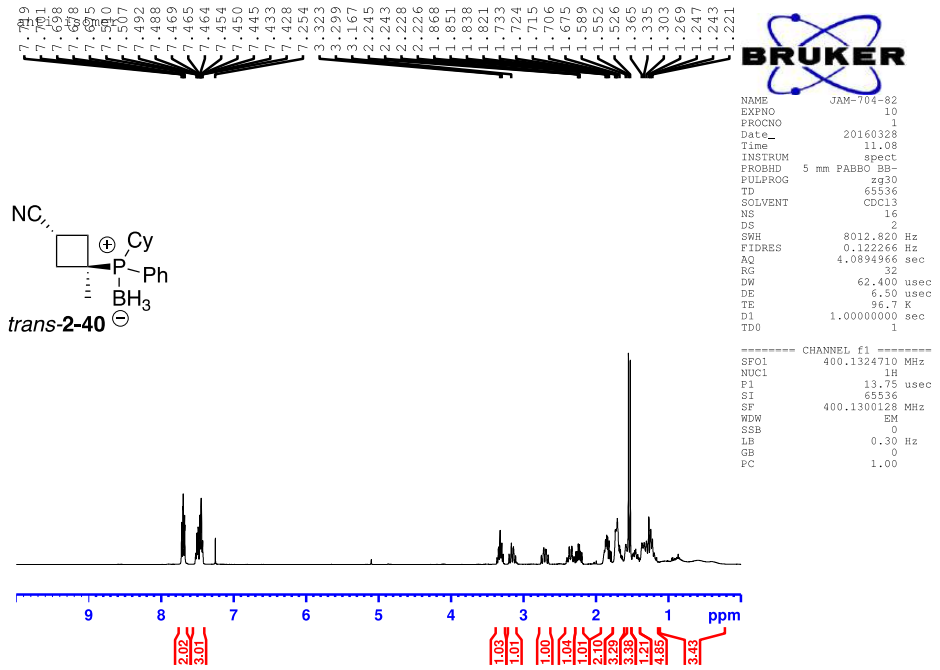
```
NAME            JAM-704-82.2
EXPNO                     12
PROCNO                     1
Date_               20160328
Time                   22.05
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     1024
DS                        4
SWH               24038.461 Hz
FIDRES             0.366798 Hz
AQ                1.3631988 sec
RG                      203
DW                  20.800 usec
DE                   6.50 usec
TE                   95.0 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1             100.6228293 MHz
NUC1                    13C
P1                   10.00 usec
SI                    32768
SF               100.6127685 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40
```

syn isomer

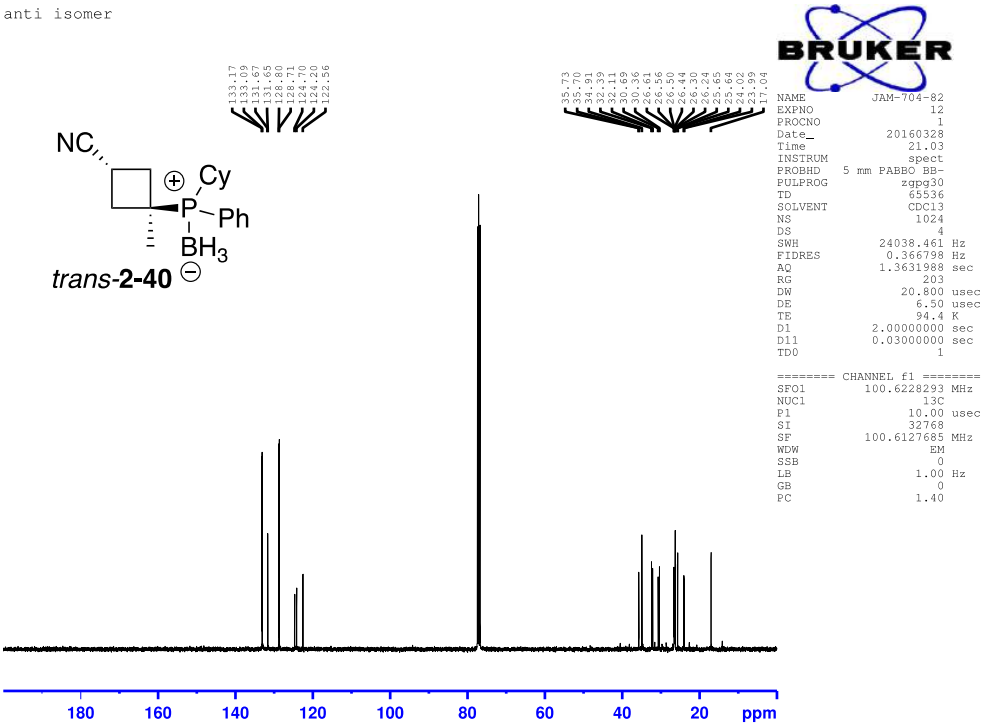


BRUKER

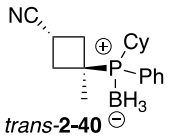
```
NAME            JAM-704-82.2
EXPNO                     11
PROCNO                     1
Date_               20160328
Time                   11.17
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        4
SWH               64102.563 Hz
FIDRES             0.978127 Hz
AQ                0.5112308 sec
RG                      203
DW                   7.800 usec
DE                   6.50 usec
TE                   96.6 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1             161.9674942 MHz
NUC1                    31P
P1                   13.30 usec
SI                    32768
SF               161.9755930 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40
```


7.729
7.701
7.698
7.678
7.675
7.507
7.492
7.488
7.469
7.465
7.464
7.454
7.450
7.445
7.433
7.428
7.254
3.323
3.299
3.167
2.245
2.243
2.228
2.226
1.868
1.851
1.838
1.821
1.733
1.724
1.715
1.706
1.675
1.589
1.552
1.526
1.365
1.335
1.303
1.269
1.247
1.243
1.221
NC
Cy
P
Ph
BH3
trans-2-40
NAME JAM-704-82
EXPNO 10
PROCNO 1
Date_ 20160328
Time 11.08
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 32
DW 62.400 usec
DE 6.50 usec
TE 96.7 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 13.75 usec
SI 65536
SF 400.1300128 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9
8
7
6
5
4
3
2
1
ppm
2.02
3.01
1.03
1.01
1.00
1.04
1.01
2.10
3.29
3.38
1.21
4.85
3.43

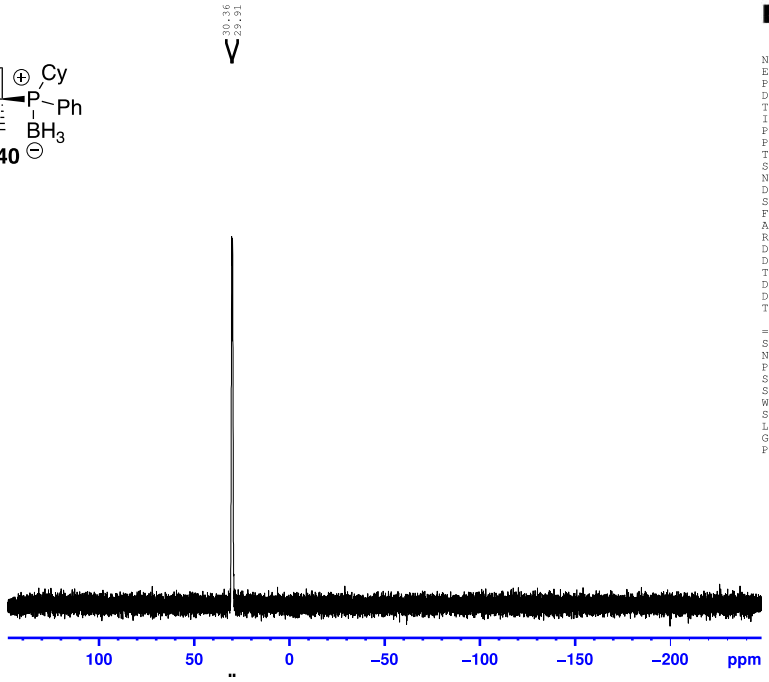
anti isomer


133.17
133.09
131.67
131.65
128.80
128.71
124.70
124.20
122.56
35.73
35.70
34.91
32.39
32.11
30.69
30.36
26.61
26.56
26.50
26.44
26.30
26.24
25.65
25.64
24.02
23.99
17.04
NC
Cy
P
Ph
BH3
trans-2-40
NAME JAM-704-82
EXPNO 12
PROCNO 1
Date_ 20160328
Time 21.03
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 94.4 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6228293 MHz
NUC1 13C
P1 10.00 usec
SI 32768
SF 100.6127685 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
180
160
140
120
100
80
60
40
20
ppm

anti isomer

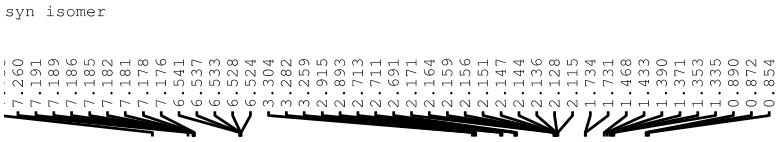


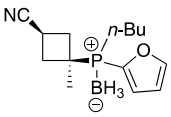
trans-**2-40**



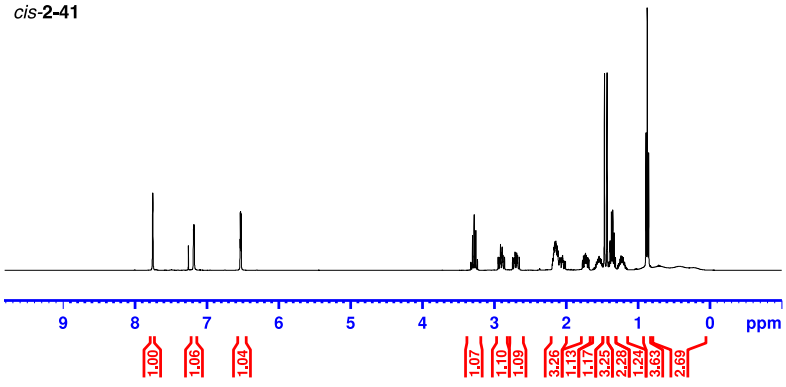

```
NAME                JAM-704-82
EXPNO                       11
PROCNO                       1
Date_                 20160328
Time                     11.10
INSTRUM                  spect
PROBHD     5 mm PABBO BB-
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                          16
DS                           4
SWH                  64102.563 Hz
FIDRES                0.978127 Hz
AQ                    0.5112308 sec
RG                         203
DW                       7.800 usec
DE                       6.50 usec
TE                       96.6 K
D1                    2.00000000 sec
D11                   0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1                161.9674942 MHz
NUC1                        31P
P1                        13.30 usec
SI                         32768
SF                  161.9755930 MHz
WDW                           EM
SSB                            0
LB                          1.00 Hz
GB                             0
PC                          1.40
```

syn isomer



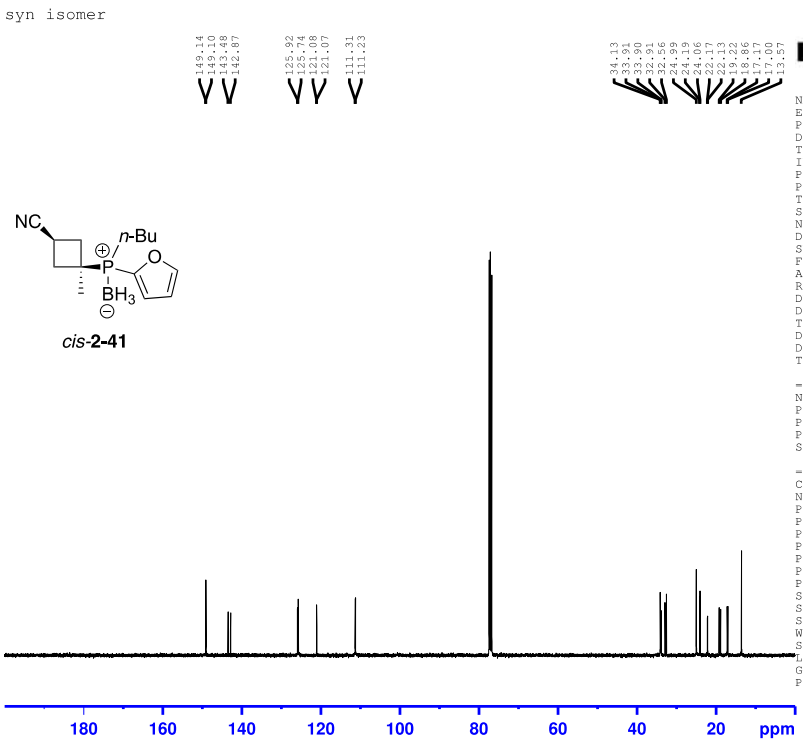


cis-**2-41**




```
NAME                JAM-704-32.2
EXPNO                         20
PROCNO                         1
Date_                 20160229
Time                     13.04
INSTRUM                  spect
PROBHD     5 mm PABBO BB-
PULPROG                   zg30
TD                       65536
SOLVENT                  CDCl3
NS                          16
DS                           2
SWH                   8012.820 Hz
FIDRES                0.122266 Hz
AQ                    4.0894966 sec
RG                          32
DW                       62.400 usec
DE                       6.50 usec
TE                       298.4 K
D1                    1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1                400.1324710 MHz
NUC1                        1H
P1                        13.75 usec
SI                         65536
SF                  400.1300100 MHz
WDW                           EM
SSB                            0
LB                          0.30 Hz
GB                             0
PC                          1.00
```

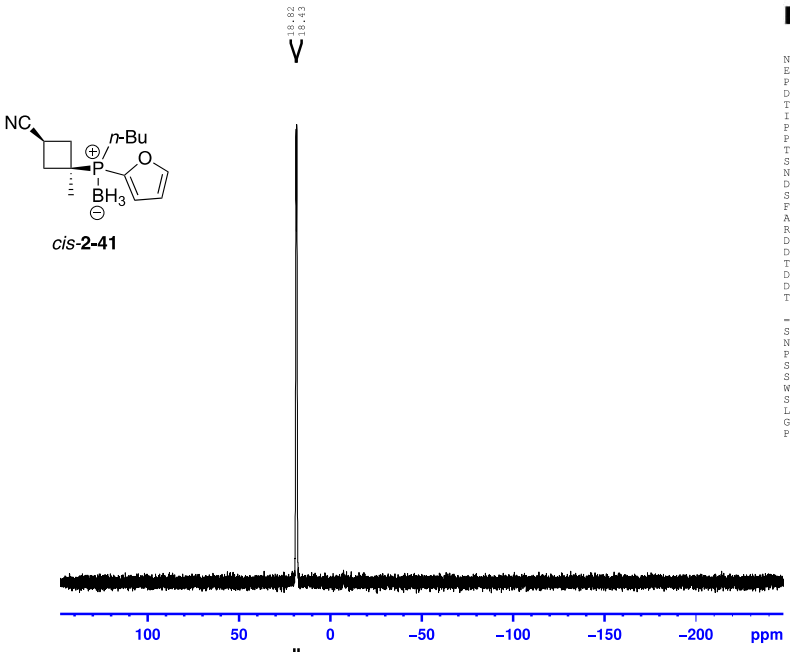
syn isomer



cis-**2-41**

```
NAME            JAM-704-32.2
EXPNO                      6
PROCNO                     1
Date_           20160229
Time                   17.42
INSTRUM                spect
PROBHD    5 mm PADUL 13C
PULPROG             zgpg30
TD                     65536
SOLVENT                CDCl3
NS                       434
DS                         4
SWH              24038.461 Hz
FIDRES               0.366798 Hz
AQ                1.3631988 sec
RG                      71.8
DW                   20.800 usec
DE                    6.50 usec
TE                   295.8 K
D1                3.00000000 sec
D11               0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                     13C
P1                    10.00 usec
PL1                   -0.44 dB
PL1W            39.19395828 W
SFO1           100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                     1H
PCPD2                 90.00 usec
PL2                   -3.90 dB
PL12                  15.81 dB
PL13                 120.00 dB
PL2W            21.64248466 W
PL12W            0.23137002 W
PL13W            0.00000000 W
SFO2           400.2316009 MHz
SI                     32768
SF             100.6379140 MHz
WDW                       EM
SSB                        0
LB                      1.00 Hz
GB                         0
PC                      1.40
```

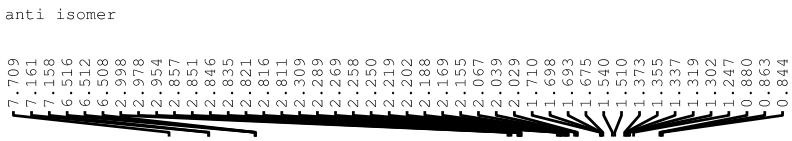
syn isomer

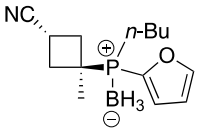


cis-**2-41**

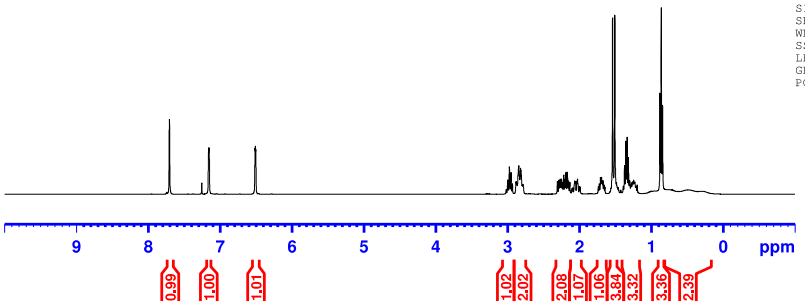
```
NAME            JAM-704-32.2
EXPNO                     11
PROCNO                     1
Date_           20160228
Time                   15.01
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG             zgpg30
TD                     65536
SOLVENT                CDCl3
NS                        16
DS                         4
SWH              64102.563 Hz
FIDRES               0.978127 Hz
AQ                0.5112308 sec
RG                       203
DW                    7.800 usec
DE                    6.50 usec
TE                   299.1 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1           161.9674942 MHz
NUC1                     31P
P1                    13.30 usec
SI                     32768
SF             161.9755930 MHz
WDW                       EM
SSB                        0
LB                      1.00 Hz
GB                         0
PC                      1.40
```

anti isomer



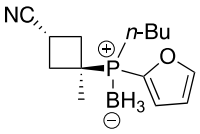


trans-**2-41**




```
NAME                JAM-704-32
EXPNO                       10
PROCNO                       1
Date_                 20160228
Time                     14.52
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG                  zg30
TD                      65536
SOLVENT                 CDCl3
NS                         16
DS                          2
SWH                 8012.820 Hz
FIDRES                0.122266 Hz
AQ                    4.0894966 sec
RG                         18
DW                     62.400 usec
DE                      6.50 usec
TE                     299.6 K
D1                  1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1           400.1324710 MHz
NUC1                       1H
P1                     13.75 usec
SI                      65536
SF             400.1300106 MHz
WDW                        EM
SSB                         0
LB                       0.30 Hz
GB                          0
PC                       1.00
```

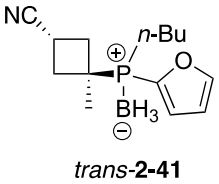
anti isomer



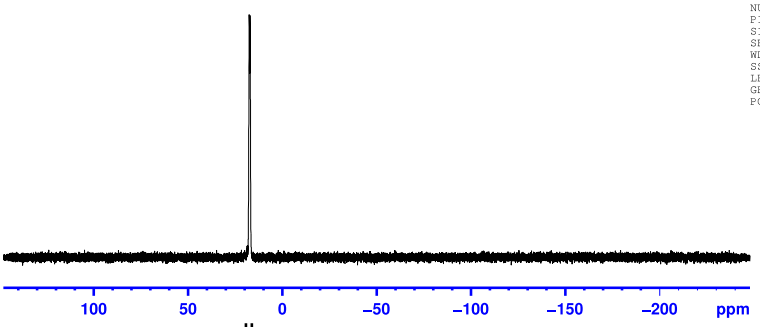
trans-**2-41**


```
NAME                JAM-704-32
EXPNO                       12
PROCNO                       1
Date_                 20160228
Time                     17.17
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG                 zgpg30
TD                      65536
SOLVENT                 CDCl3
NS                       1024
DS                          4
SWH                24038.461 Hz
FIDRES                0.366798 Hz
AQ                    1.3631988 sec
RG                        203
DW                     20.800 usec
DE                      6.50 usec
TE                     298.2 K
D1                  2.00000000 sec
D11                 0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1           100.6228293 MHz
NUC1                       13C
P1                     10.00 usec
SI                      32768
SF             100.6127685 MHz
WDW                        EM
SSB                         0
LB                       1.00 Hz
GB                          0
PC                       1.40
```

anti isomer

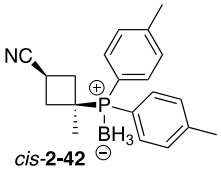


trans-**2-41**

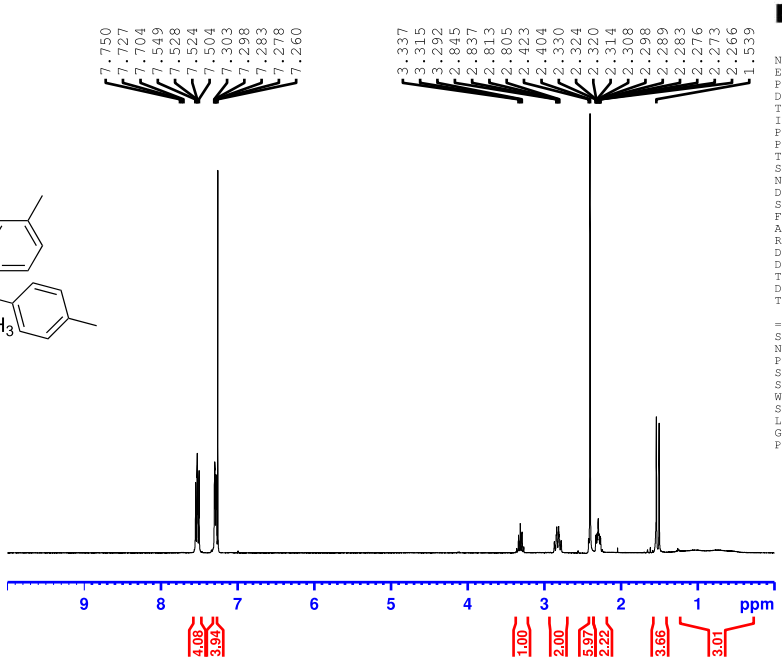



```
NAME                JAM-704-32
EXPNO                       11
PROCNO                       1
Date_                 20160228
Time                     14.54
INSTRUM                  spect
PROBHD     5 mm PABBO BB-
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                          16
DS                           4
SWH                 64102.563 Hz
FIDRES              0.978127 Hz
AQ                  0.5112308 sec
RG                         203
DW                     7.800 usec
DE                     6.50 usec
TE                     299.6 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1               161.9674942 MHz
NUC1                       31P
P1                      13.30 usec
SI                       32768
SF                 161.9755930 MHz
WDW                         EM
SSB                          0
LB                      1.00 Hz
GB                           0
PC                      1.40
```

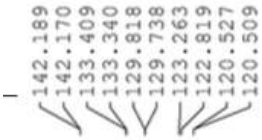
syn isomer

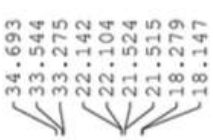


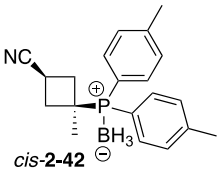
cis-**2-42**




```
NAME              JAM-704-28.2
EXPNO                       10
PROCNO                       1
Date_                 20160225
Time                     14.18
INSTRUM                  spect
PROBHD     5 mm PABBO BB-
PULPROG                  zg30
TD                       65536
SOLVENT                  CDCl3
NS                          16
DS                           2
SWH                  8012.820 Hz
FIDRES              0.122266 Hz
AQ                  4.0894966 sec
RG                         144
DW                    62.400 usec
DE                     6.50 usec
TE                     298.1 K
D1                 1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1               400.1324710 MHz
NUC1                        1H
P1                      13.75 usec
SI                       65536
SF                 400.1300104 MHz
WDW                         EM
SSB                          0
LB                      0.30 Hz
GB                           0
PC                      1.00
```

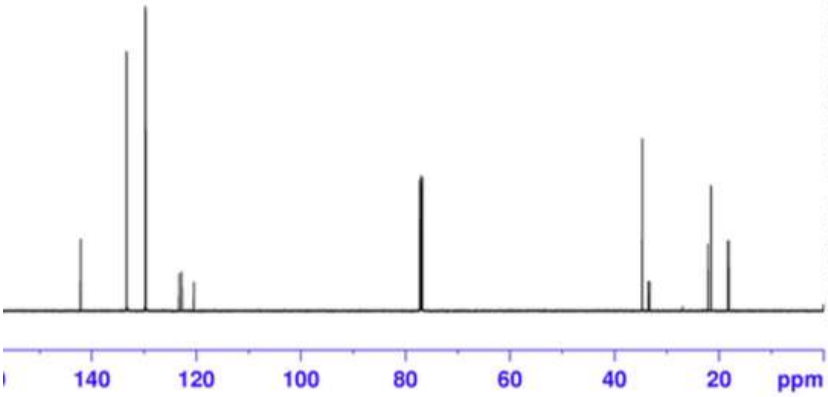




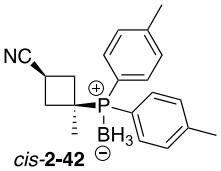


cis-**2-42**

```
Current Data Parameters
NAME                 10824-141
EXPNO                        4
PROCNO                       1

F2 - Acquisition Parameters
Date_               20150820
Time                   19.41
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG                zgpg
TD                   262144
SOLVENT                CDCl3
NS                        1024
DS                           0
SWH                31250.000 Hz
FIDRES             0.119209 Hz
AQ                 4.1943040 sec
RG                        2050
DW                   16.000 usec
DE                    6.50 usec
TE                   299.0 K
D1                 1.00000000 sec
d11                0.03000000 sec
DELTA              0.89999998 sec
TD0                          1
SFO1             125.7698617 MHz
NUC1                      13C
P1                    9.75 usec
PLW1              -1.00000000 W
SFO2             500.1325007 MHz
NUC2                       1H
CPDPRG[2               waltz16
PCPD2                80.00 usec
PLW2              -1.00000000 W
PLW12             -1.00000000 W
PLW13             -1.00000000 W

F2 - Processing parameters
SI                       131072
SF                125.7577899 MHz
WDW                        EM
SSB                  0
LB                    0.30 Hz
GB                   0
PC                    1.40
```



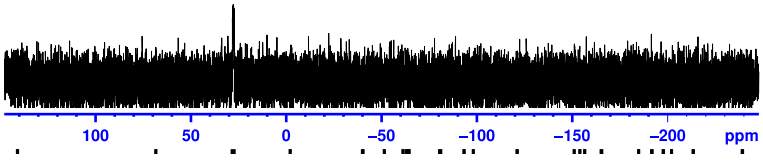
syn isomer

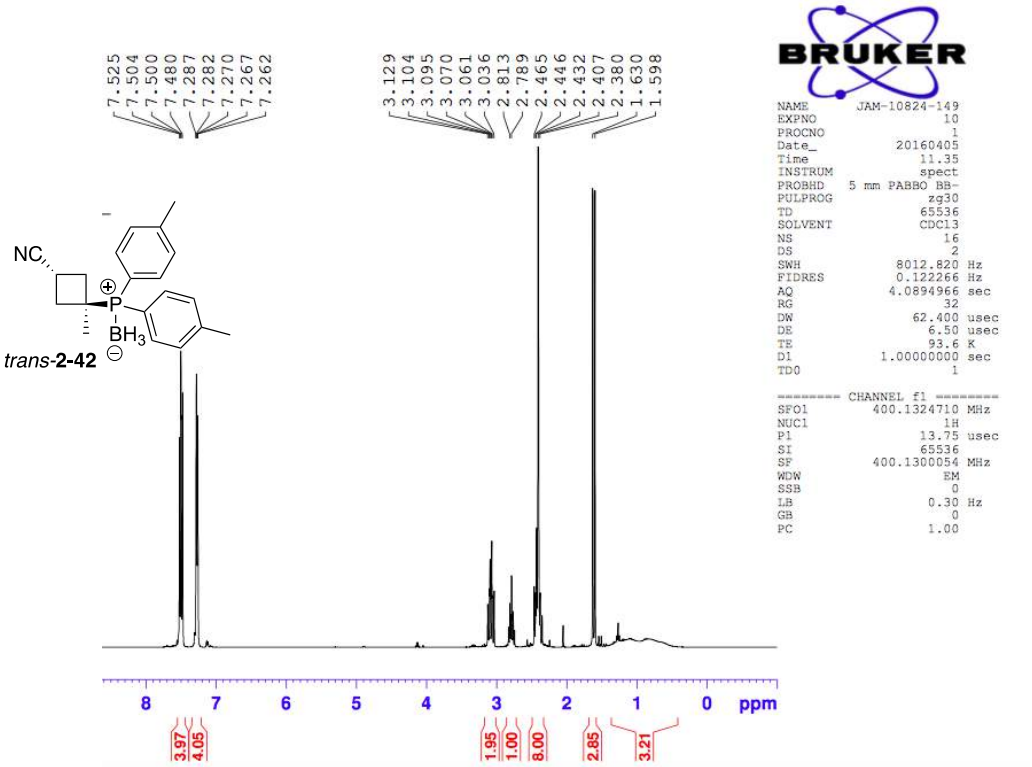


cis-**2-42**

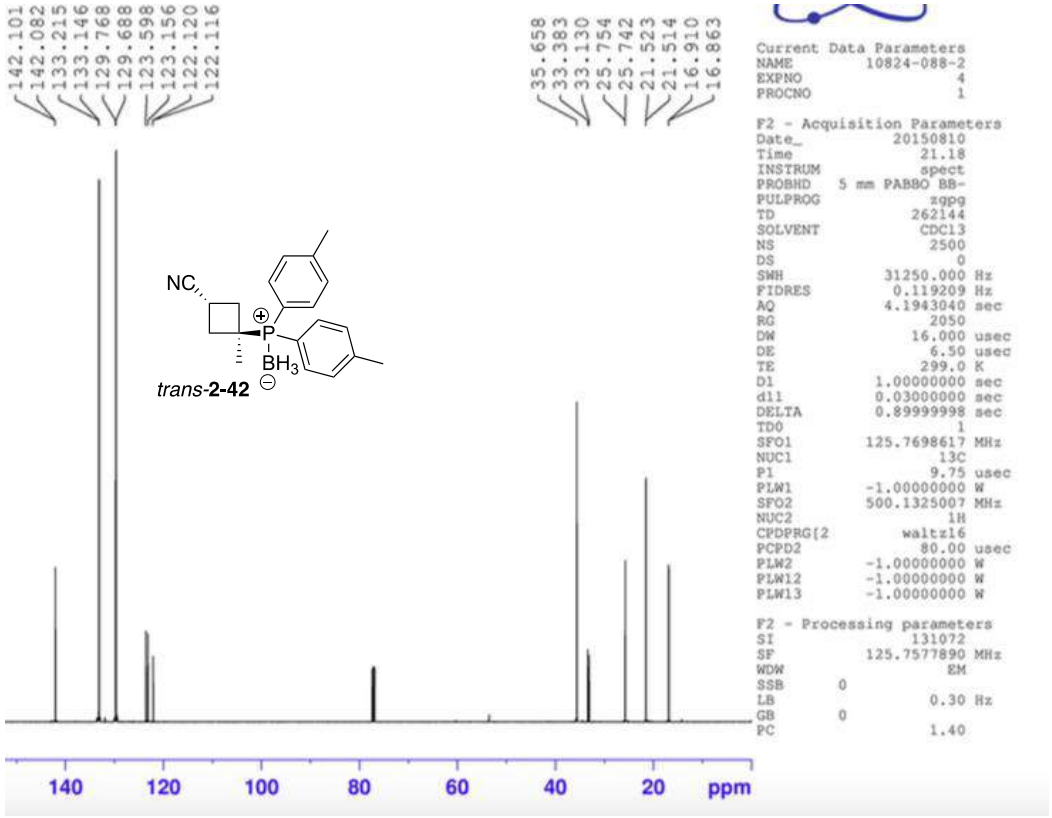
BRUKER

```
NAME              JAM-704-28.2
EXPNO                       11
PROCNO                       1
Date_               20160225
Time                   14.20
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG              zgpg30
TD                        65536
SOLVENT                CDCl3
NS                           16
DS                            4
SWH                64102.563 Hz
FIDRES             0.978127 Hz
AQ                 0.5112308 sec
RG                         203
DW                   7.800 usec
DE                    6.50 usec
TE                   298.2 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1             161.9674942 MHz
NUC1                      31P
P1                   13.30 usec
SI                        32768
SF                161.9755930 MHz
WDW                        EM
SSB                          0
LB                    1.00 Hz
GB                           0
PC                    1.40
```



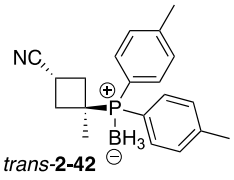



```
NAME            JAM-10824-149
EXPNO                      10
PROCNO                      1
Date_                20160405
Time                    11.35
INSTRUM                 spect
PROBHD    5 mm PABBO BB-
PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                        16
DS                         2
SWH                 8012.820 Hz
FIDRES              0.122266 Hz
AQ                  4.0894966 sec
RG                        32
DW                    62.400 usec
DE                     6.50 usec
TE                     93.6 K
D1                1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1             400.1324710 MHz
NUC1                       1H
P1                      13.75 usec
SI                         65536
SF               400.1300054 MHz
WDW                        EM
SSB                         0
LB                       0.30 Hz
GB                          0
PC                       1.00
```

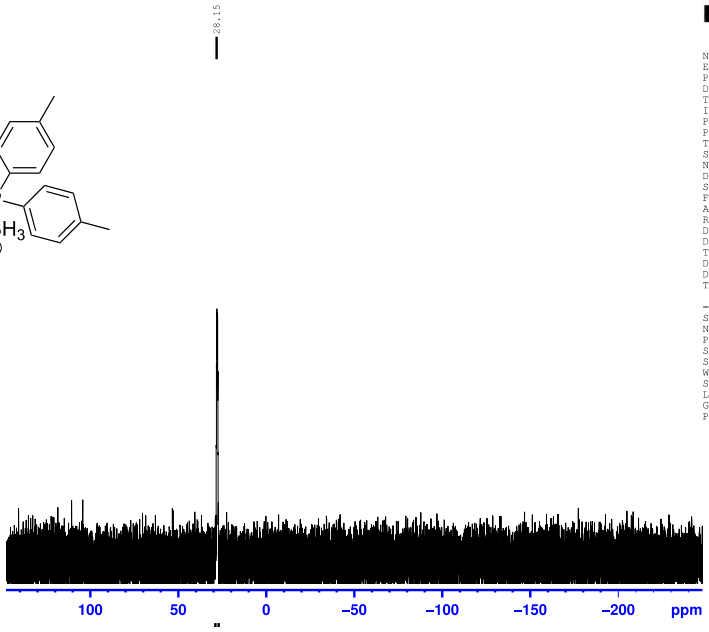



```
Current Data Parameters
NAME            10824-088-2
EXPNO                     4
PROCNO                    1

F2 - Acquisition Parameters
Date_                20150810
Time                    21.18
INSTRUM                 spect
PROBHD    5 mm PABBO BB-
PULPROG                 zgpg
TD                     262144
SOLVENT                CDCl3
NS                       2500
DS                          0
SWH                31250.000 Hz
FIDRES              0.119209 Hz
AQ                  4.1943040 sec
RG                       2050
DW                    16.000 usec
DE                     6.50 usec
TE                     299.0 K
D1                1.00000000 sec
d11               0.03000000 sec
DELTA             0.89999998 sec
TD0                        1
SFO1             125.7698617 MHz
NUC1                      13C
P1                      9.75 usec
PLW1             -1.00000000 W
SFO2             500.1325007 MHz
NUC2                       1H
CPDPRG[2                waltz16
PCPD2                  80.00 usec
PLW2             -1.00000000 W
PLW12            -1.00000000 W
PLW13            -1.00000000 W

F2 - Processing parameters
SI                       131072
SF               125.7577890 MHz
WDW                        EM
SSB                         0
LB                       0.30 Hz
GB                          0
PC                       1.40
```

anti isomer



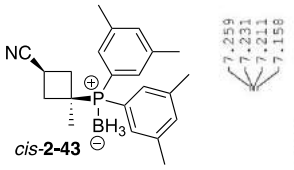
trans-**2-42**



BRUKER

```
NAME                JAM-704-28
EXPNO                       11
PROCNO                       1
Date_                 20160225
Time                     14.12
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG                zgpg30
TD                      65536
SOLVENT                 CDCl3
NS                         16
DS                          4
SWH                 64102.563 Hz
FIDRES              0.978127 Hz
AQ                  0.5112308 sec
RG                        203
DW                    7.800 usec
DE                    6.50 usec
TE                    298.2 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1               161.9674942 MHz
NUC1                       31P
P1                    13.30 usec
SI                        32768
SF                 161.9755930 MHz
WDW                        EM
SSB                         0
LB                    1.00 Hz
GB                          0
PC                    1.40
```

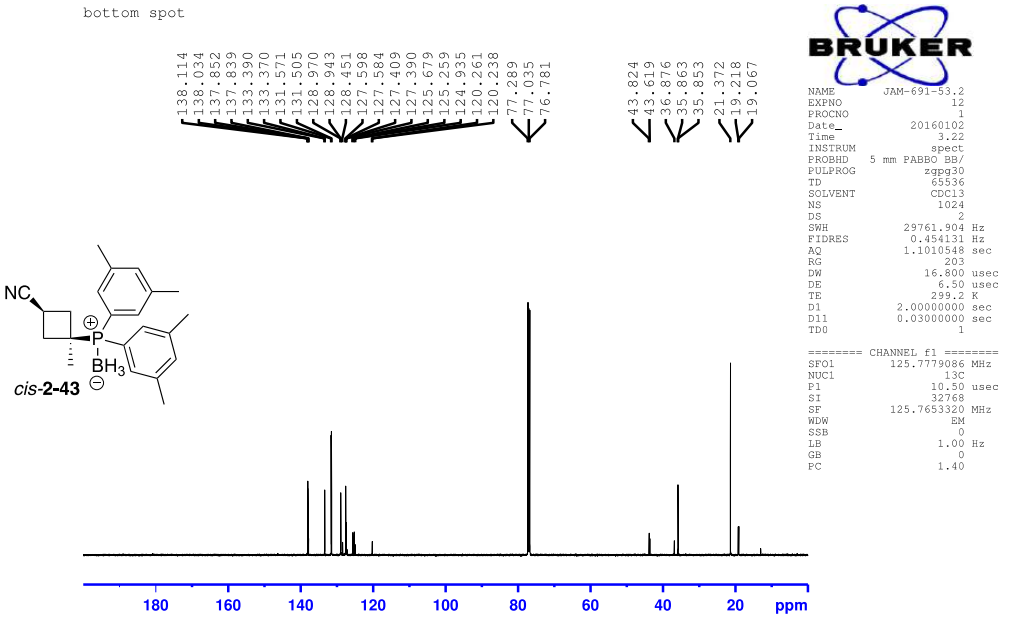
syn isomer m-xylyl HPN dried

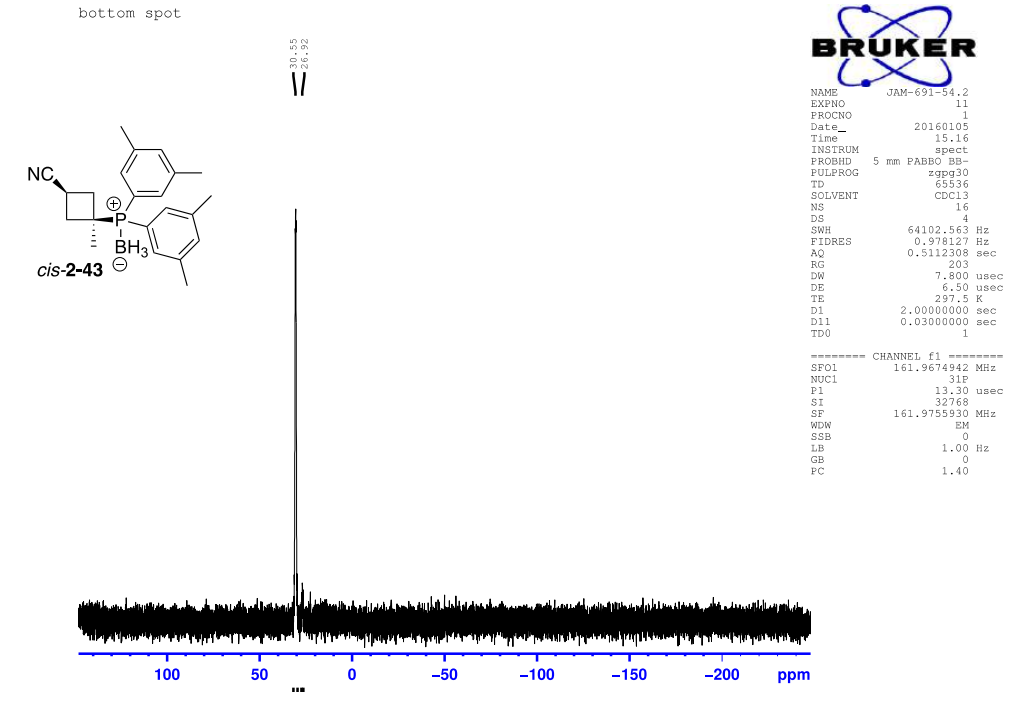


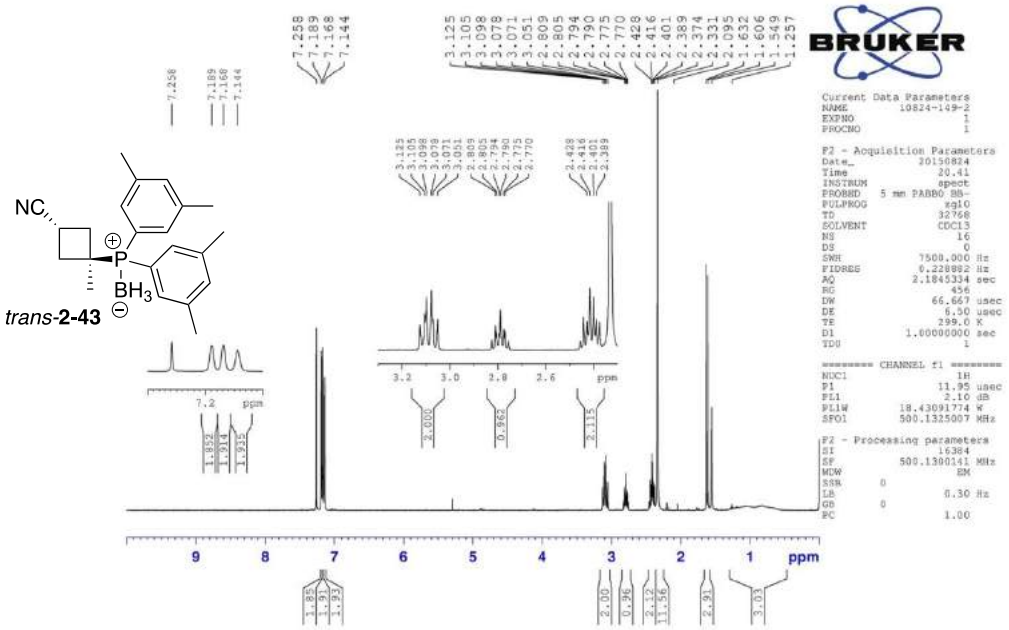
cis-**2-43**

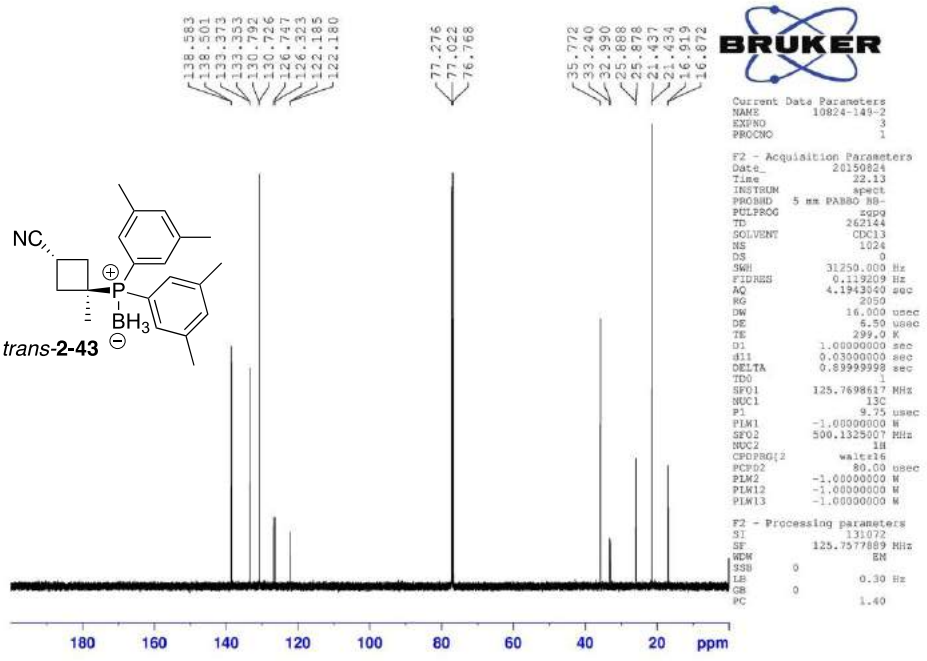
BRUKER

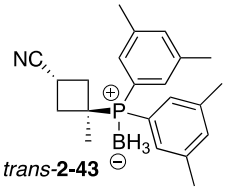
```
Current Data Parameters
NAME                10824-149
EXPNO                       4
PROCNO                      1

F2 - Acquisition Parameters
Date_                20150825
Time                    13.45
INSTRUM                 spect
PROBHD    5 mm PABBO BB-
PULPROG                 zg10
TD                      32768
SOLVENT                 CDCl3
NS                         16
DS                          0
SWH                 7500.000 Hz
FIDRES              0.228882 Hz
AQ                  2.1845334 sec
RG                        287
DW                   66.667 usec
DE                    6.50 usec
TE                    299.0 K
D1                 1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                        1H
P1                   11.95 usec
PL1                   2.10 dB
PL1W               18.43091774 W
SFO1               500.1325007 MHz

F2 - Processing parameters
SI                        16384
SF                 500.1300136 MHz
WDW                        EM
SSB                         0
LB                    0.30 Hz
GB                          0
PC                    1.00
```


bottom spot
138.114
138.034
137.852
137.839
133.390
133.370
131.571
131.505
128.970
128.943
128.451
127.598
127.584
127.409
127.390
125.679
125.259
124.935
120.261
120.238
77.289
77.035
76.781
43.824
43.619
36.876
35.863
35.853
21.372
19.218
19.067
NC
P
BH3
cis-2-43
180
160
140
120
100
80
60
40
20
ppm
BRUKER
NAME JAM-691-53.2
EXPNO 12
PROCNO 1
Date_ 20160102
Time 3.22
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 2
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010548 sec
RG 203
DW 16.800 usec
DE 6.50 usec
TE 299.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 125.7779086 MHz
NUC1 13C
P1 10.50 usec
SI 32768
SF 125.7653320 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

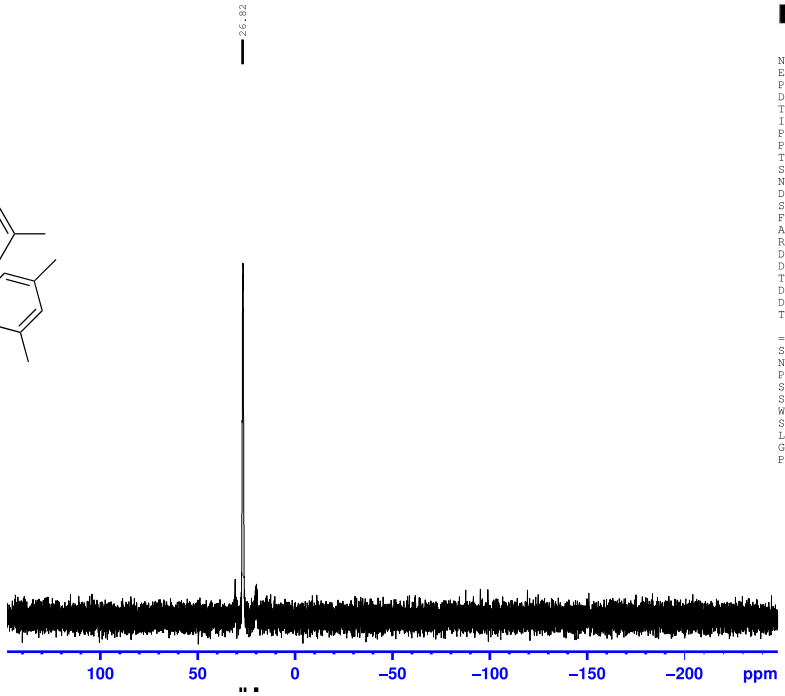

bottom spot
30.55
26.92
NC
P
BH3
cis-2-43
100
50
0
-50
-100
-150
-200
ppm
BRUKER
NAME JAM-691-54.2
EXPNO 11
PROCNO 1
Date_ 20160105
Time 15.16
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 16
DS 4
SWH 64102.563 Hz
FIDRES 0.978127 Hz
AQ 0.5112308 sec
RG 203
DW 7.800 usec
DE 6.50 usec
TE 297.5 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 161.9674942 MHz
NUC1 31P
P1 13.30 usec
SI 32768
SF 161.9755930 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40


trans-2-43
NC
P
BH3
BRUKER
ppm

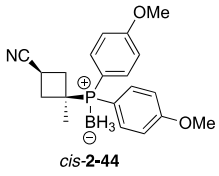

trans-2-43
NC
P
BH3
BRUKER
ppm



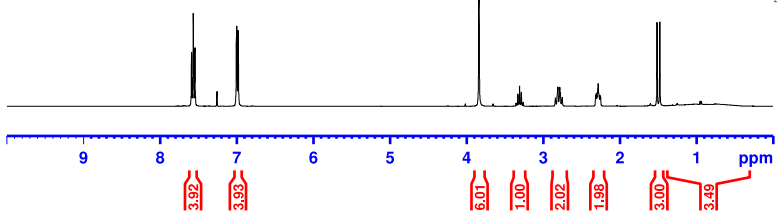
trans-**2-43**




```
NAME                JAM-691-53
EXPNO                       11
PROCNO                       1
Date_             20160105
Time                    15.01
INSTRUM                 spect
PROBHD    5 mm PABBO BB-
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                          16
DS                           4
SWH                 64102.563 Hz
FIDRES              0.978127 Hz
AQ                  0.5112308 sec
RG                         203
DW                      7.800 usec
DE                      6.50 usec
TE                      297.6 K
D1                  2.00000000 sec
D11                 0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1               161.9674942 MHz
NUC1                       31P
P1                      13.30 usec
SI                       32768
SF                 161.9755930 MHz
WDW                         EM
SSB                          0
LB                      1.00 Hz
GB                           0
PC                      1.40
```

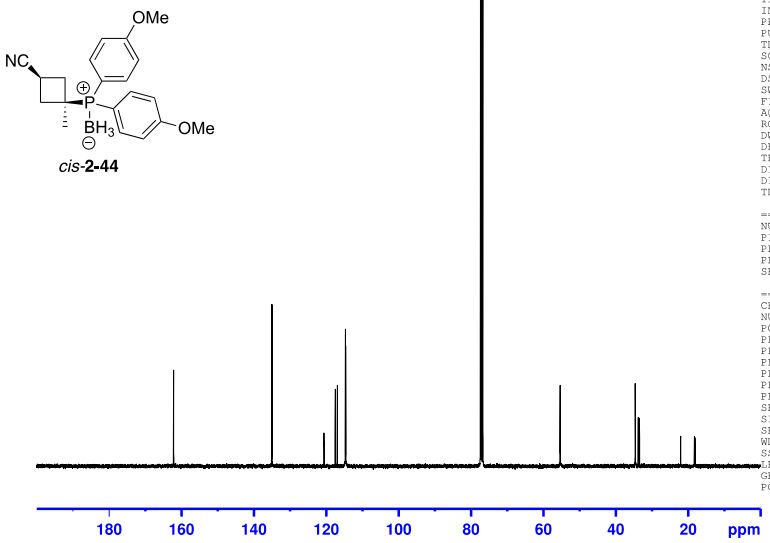


cis-**2-44**

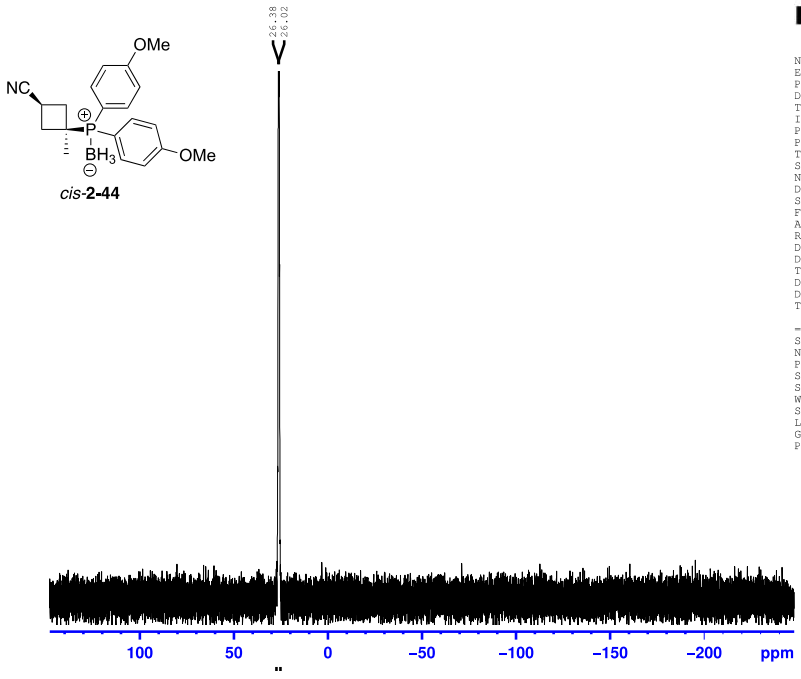



```
NAME             JAM-685-89.3
EXPNO                      20
PROCNO                      1
Date_            20151120
Time                   11.29
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG                 zg30
TD                      65536
SOLVENT                 CDCl3
NS                         16
DS                          2
SWH                8012.820 Hz
FIDRES             0.122266 Hz
AQ                 4.0894966 sec
RG                         32
DW                     62.400 usec
DE                     6.50 usec
TE                     96.0 K
D1                 1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1              400.1324710 MHz
NUC1                       1H
P1                     13.75 usec
SI                      65536
SF                400.1300099 MHz
WDW                        EM
SSB                         0
LB                     0.30 Hz
GB                          0
PC                     1.00
```

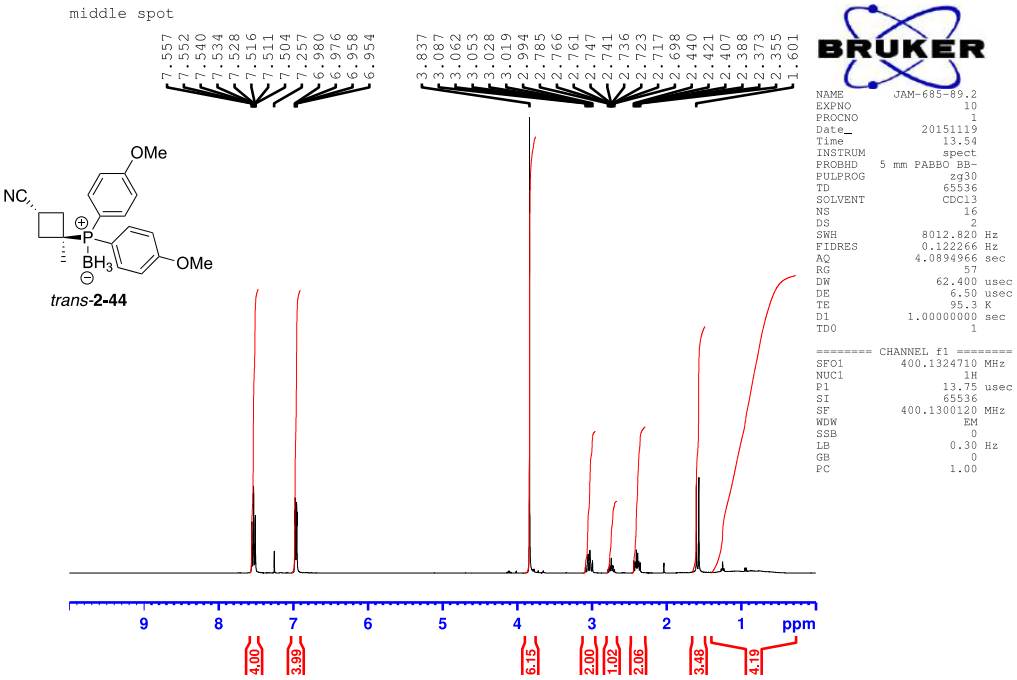
syn isomer

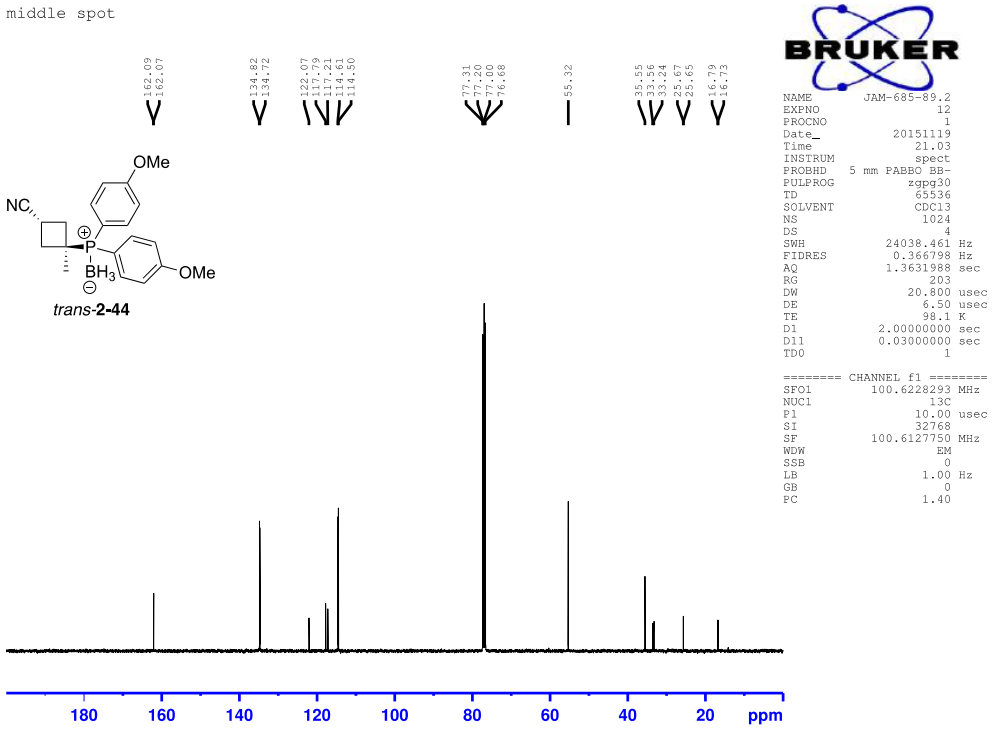



```
NAME          JAM-685-89.3
EXPNO                    2
PROCNO                   1
Date_             20151120
Time                 16.20
INSTRUM              spect
PROBHD   5 mm PADUL 13C
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     639
DS                       4
SWH              24038.461 Hz
FIDRES           0.366798 Hz
AQ               1.3631988 sec
RG                    71.8
DW                20.800 usec
DE                 6.50 usec
TE                 296.1 K
D1             3.00000000 sec
D11            0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                  10.00 usec
PL1                 -0.44 dB
PL1W          39.19395828 W
SFO1          100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                   1H
PCPD2               90.00 usec
PL2                 -3.90 dB
PL12                15.81 dB
PL13               120.00 dB
PL2W          21.64248466 W
PL12W          0.23137002 W
PL13W          0.00000000 W
SFO2          400.2316009 MHz
SI                   32768
SF            100.6379140 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

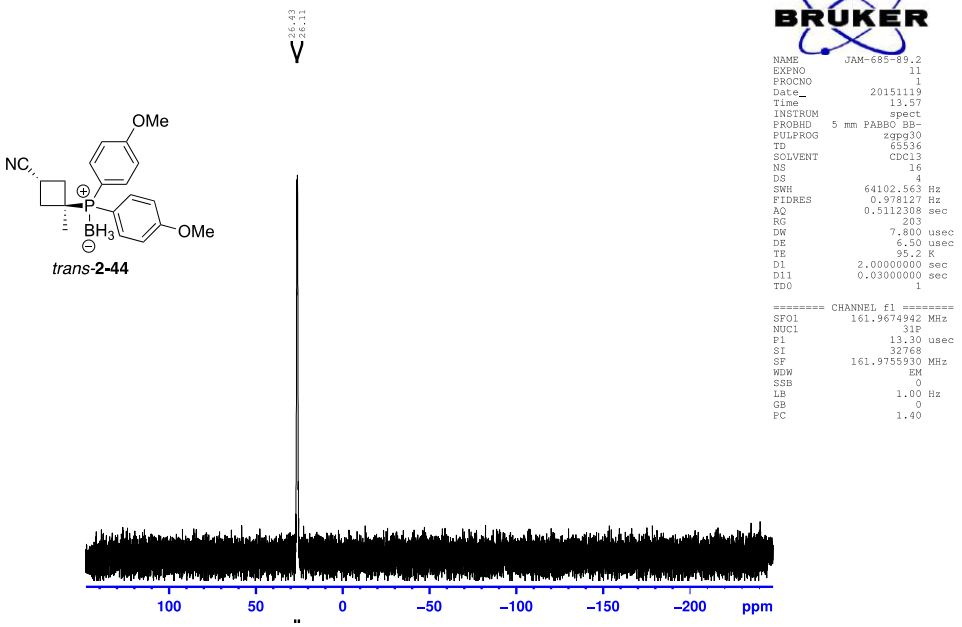



```
NAME          JAM-685-89.3
EXPNO                   11
PROCNO                   1
Date_             20151119
Time                 14.04
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       4
SWH              64102.563 Hz
FIDRES           0.978127 Hz
AQ               0.5112308 sec
RG                     203
DW                 7.800 usec
DE                 6.50 usec
TE                 95.5 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1          161.9674942 MHz
NUC1                   31P
P1                  13.30 usec
SI                   32768
SF            161.9755930 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```


middle spot
7.557
7.552
7.540
7.534
7.528
7.516
7.511
7.504
7.257
6.980
6.976
6.958
6.954
3.837
3.087
3.062
3.053
3.028
3.019
2.994
2.785
2.766
2.761
2.747
2.741
2.736
2.723
2.717
2.698
2.440
2.421
2.407
2.388
2.373
2.355
1.601
OMe
NC
P
BH3
OMe
trans-2-44
NAME JAM-685-89.2
EXPNO 10
PROCNO 1
Date_ 20151119
Time 13.54
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 57
DW 62.400 usec
DE 6.50 usec
TE 95.3 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 13.75 usec
SI 65536
SF 400.1300120 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9
8
7
6
5
4
3
2
1
ppm
4.00
3.99
6.15
2.00
1.02
2.06
3.48
4.19


middle spot
162.09
162.07
134.82
134.72
122.07
117.79
117.21
114.61
114.50
77.31
77.20
77.00
76.68
55.32
35.55
33.56
33.24
25.67
25.65
16.79
16.73
OMe
NC
P
BH3
OMe
trans-2-44
NAME JAM-685-89.2
EXPNO 12
PROCNO 1
Date_ 20151119
Time 21.03
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 98.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6228293 MHz
NUC1 13C
P1 10.00 usec
SI 32768
SF 100.6127750 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
180
160
140
120
100
80
60
40
20
ppm

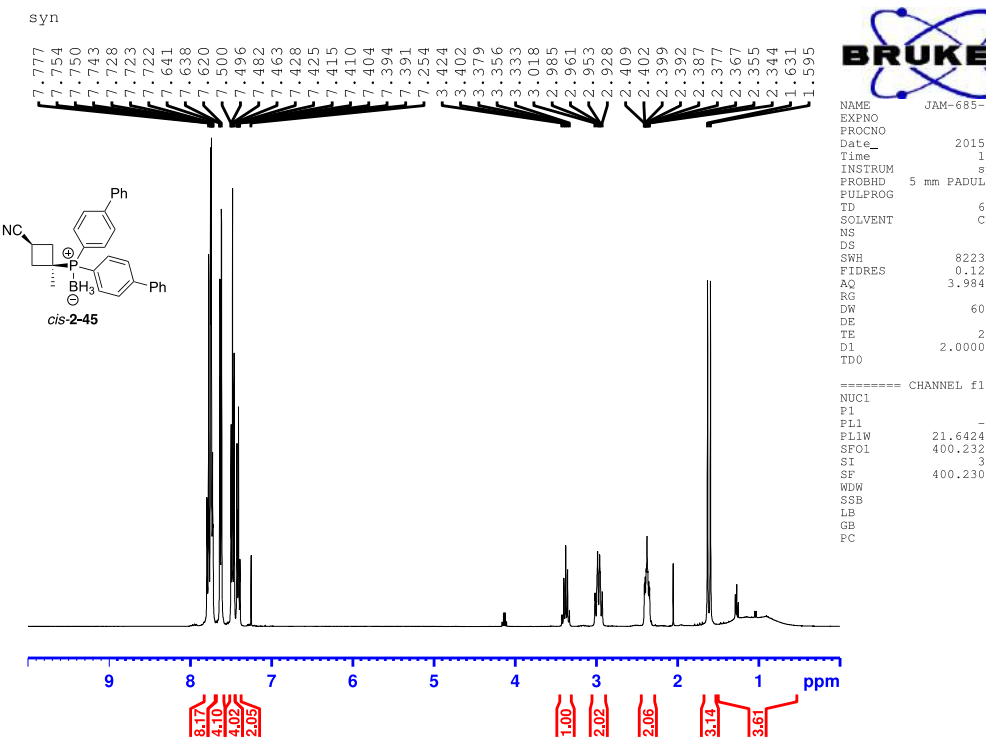
middle spot



trans-**2-44**

```
NAME          JAM-685-89.2
EXPNO               11
PROCNO               1
Date_         20151119
Time              13.57
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    4
SWH           64102.563 Hz
FIDRES        0.978127 Hz
AQ            0.5112308 sec
RG                  203
DW                7.800 usec
DE                6.50 usec
TE                95.2 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
SFO1        161.9674942 MHz
NUC1              31P
P1              13.30 usec
SI                32768
SF          161.9755930 MHz
WDW               EM
SSB                0
LB              1.00 Hz
GB                 0
PC              1.40
```

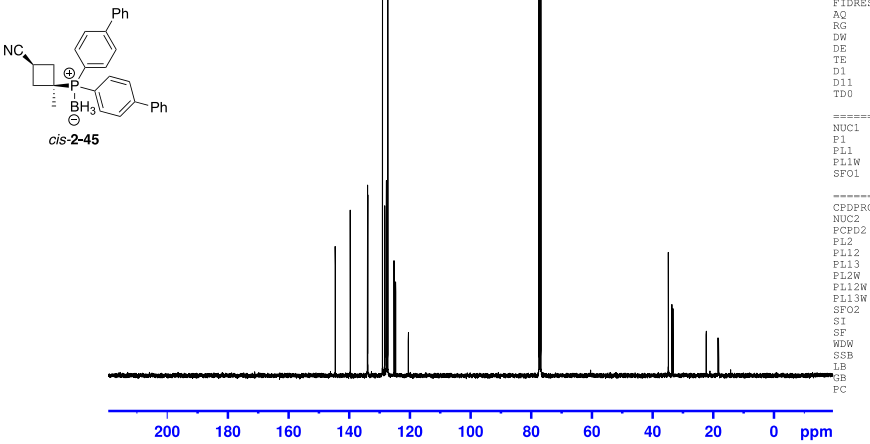
syn



cis-**2-45**

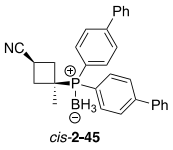
```
NAME          JAM-685-61.2
EXPNO                1
PROCNO               1
Date_         20151031
Time              13.06
INSTRUM           spect
PROBHD   5 mm PADUL 13C
PULPROG           zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            8223.685 Hz
FIDRES        0.125483 Hz
AQ            3.9846387 sec
RG                 45.2
DW                60.800 usec
DE                 6.50 usec
TE                298.0 K
D1           2.00000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1                 1H
P1                9.31 usec
PL1               -3.90 dB
PL1W         21.64248466 W
SFO1         400.2324716 MHz
SI                32768
SF           400.2300145 MHz
WDW                EM
SSB                 0
LB              0.30 Hz
GB                  0
PC              1.00
```

syn



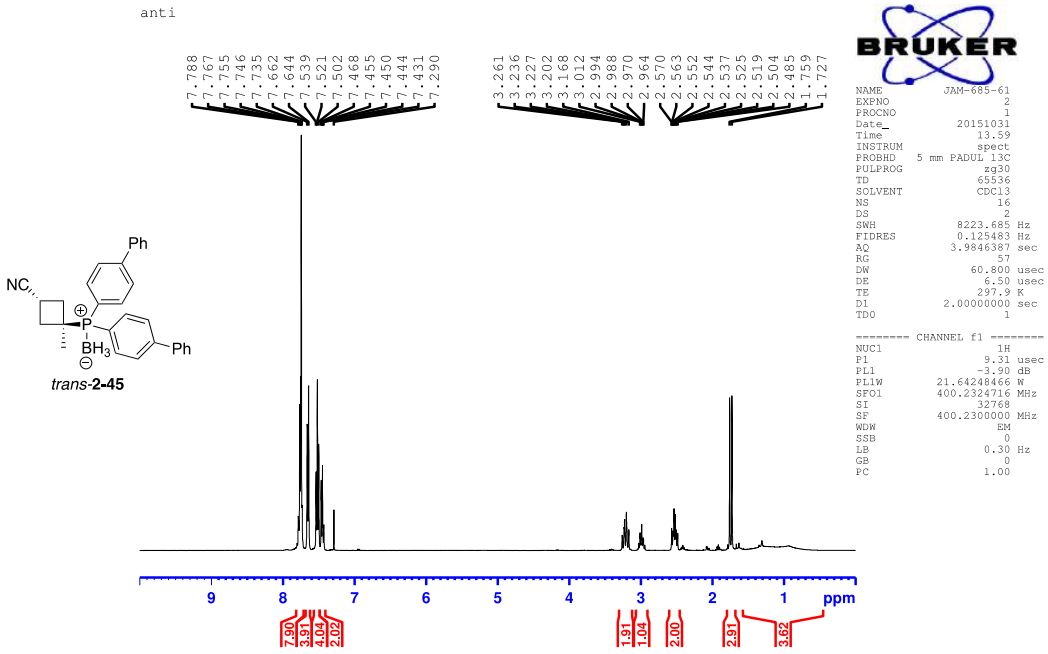
cis-**2-45**

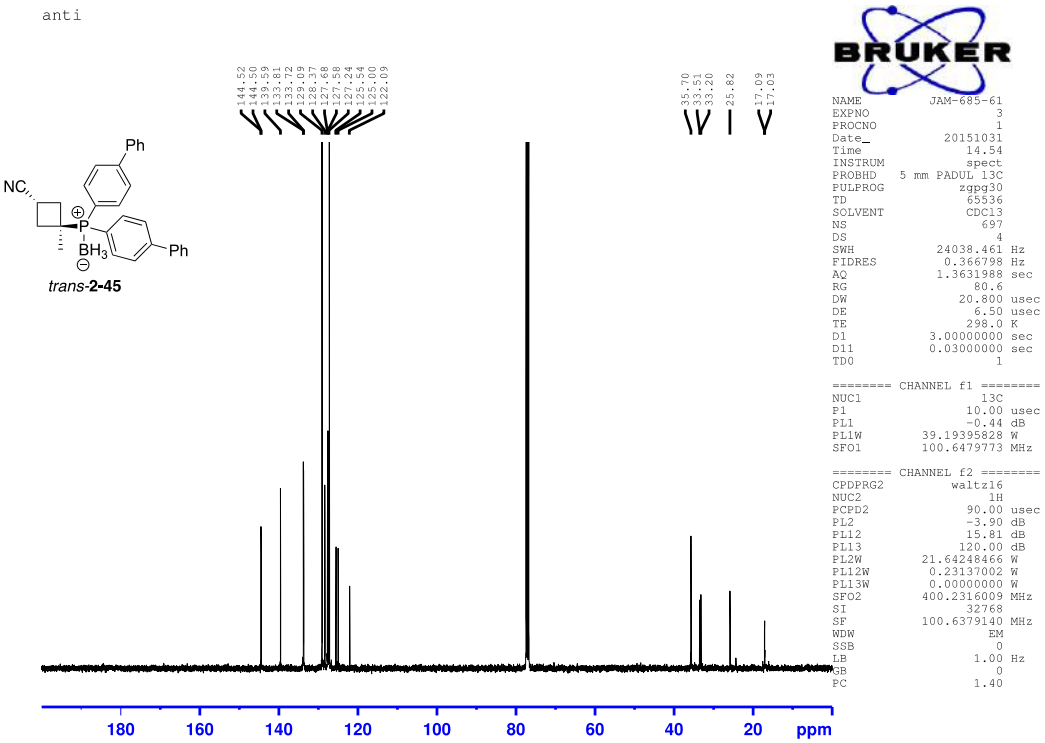
```
NAME            JAM-685-61.2
EXPNO                      2
PROCNO                     1
Date_               20151031
Time                   13.52
INSTRUM                spect
PROBHD    5 mm PADUL 13C
PULPROG             zgpg30
TD                      65536
SOLVENT                CDCl3
NS                       572
DS                         4
SWH                24038.461 Hz
FIDRES             0.366798 Hz
AQ                 1.3631988 sec
RG                       114
DW                    20.800 usec
DE                     6.50 usec
TE                   298.0 K
D1                 3.00000000 sec
D11                0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                     13C
P1                     10.00 usec
PL1                    -0.44 dB
PL1W            39.19395828 W
SFO1            100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                     1H
PCPD2                 90.00 usec
PL2                   -3.90 dB
PL12                  15.81 dB
PL13                 120.00 dB
PL2W            21.64248466 W
PL12W            0.23137002 W
PL13W            0.00000000 W
SFO2            400.2316009 MHz
SI                     32768
SF              100.6379140 MHz
WDW                       EM
SSB                        0
LB                      1.00 Hz
GB                         0
PC                      1.40
```

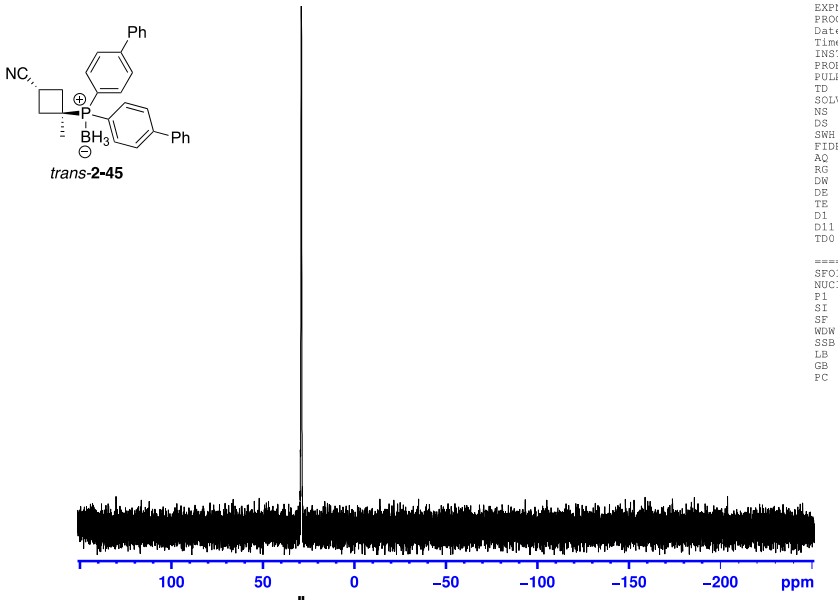


cis-**2-45**

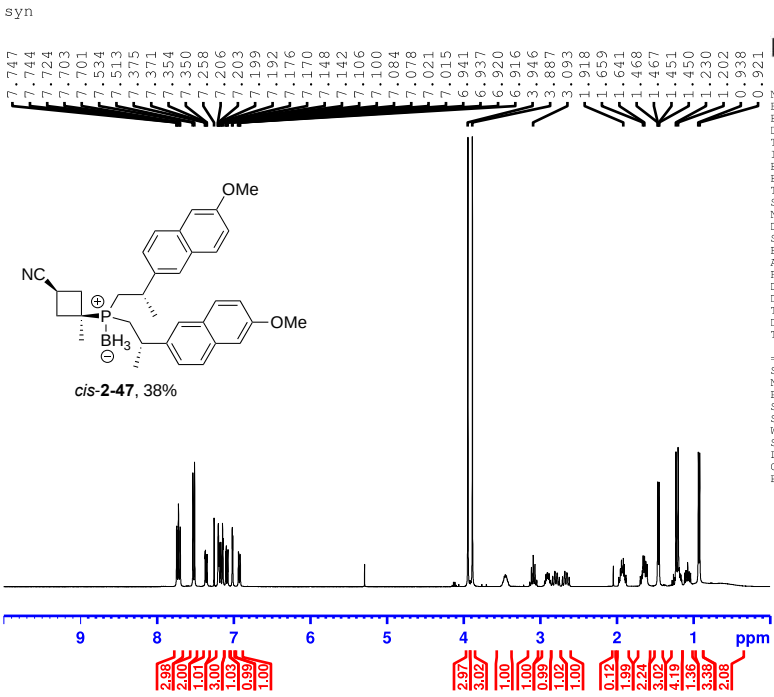

```
NAME            JAM-685-61.2
EXPNO                     22
PROCNO                     1
Date_               20151030
Time                   18.59
INSTRUM                spect
PROBHD    5 mm PABBO BB/
PULPROG             zgpg30
TD                      65536
SOLVENT                CDCl3
NS                       16
DS                         4
SWH                81521.742 Hz
FIDRES             1.243923 Hz
AQ                 0.4020041 sec
RG                       203
DW                     6.133 usec
DE                     6.50 usec
TE                   298.1 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1            202.4583558 MHz
NUC1                     31P
P1                     11.50 usec
SI                     32768
SF              202.4684792 MHz
WDW                       EM
SSB                        0
LB                      1.00 Hz
GB                         0
PC                      1.40
```


anti
7.788
7.767
7.755
7.746
7.735
7.662
7.644
7.539
7.521
7.502
7.468
7.455
7.450
7.444
7.431
7.290
3.261
3.236
3.227
3.202
3.168
3.012
2.994
2.988
2.970
2.964
2.570
2.563
2.552
2.544
2.537
2.525
2.519
2.504
2.485
1.759
1.727
Ph
NC
P
BH3
Ph
trans-2-45
9
8
7
6
5
4
3
2
1
ppm
7.90
3.91
4.04
2.02
1.91
1.04
2.00
2.91
3.62
BRUKER
NAME JAM-685-61
EXPNO 2
PROCNO 1
Date_ 20151031
Time 13.59
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 57
DW 60.800 usec
DE 6.50 usec
TE 297.9 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.31 usec
PL1 -3.90 dB
PL1W 21.64248466 W
SFO1 400.2324716 MHz
SI 32768
SF 400.2300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

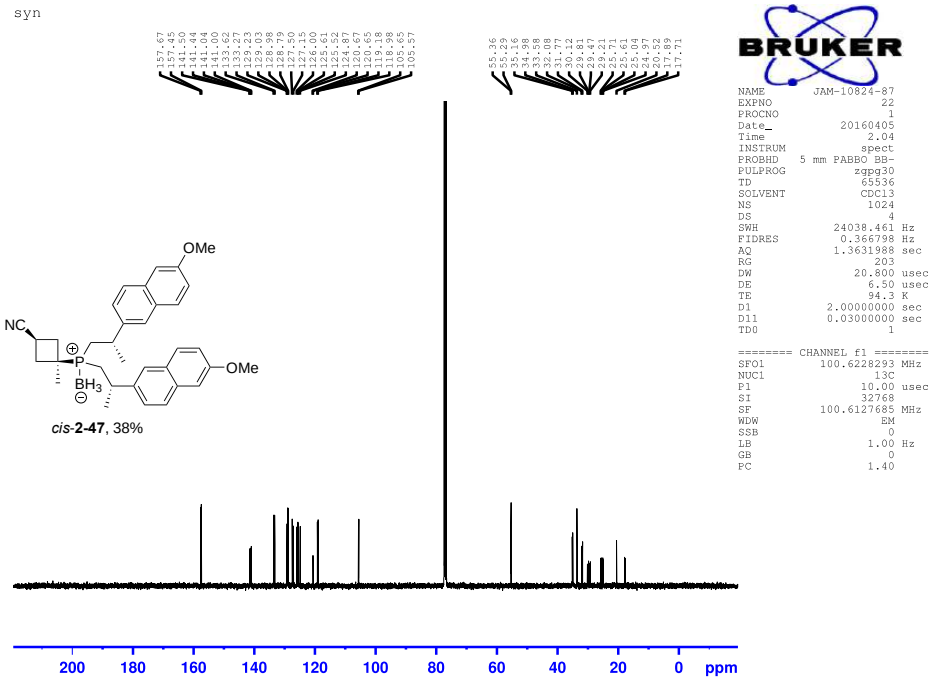

anti
144.52
144.50
134.59
133.81
133.72
129.09
128.37
127.68
127.58
127.24
125.54
125.00
122.09
35.70
33.51
33.20
25.82
17.09
17.03
Ph
NC
P
BH3
Ph
trans-2-45
180
160
140
120
100
80
60
40
20
ppm
BRUKER
NAME JAM-685-61
EXPNO 3
PROCNO 1
Date_ 20151031
Time 14.54
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 697
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 80.6
DW 20.800 usec
DE 6.50 usec
TE 298.0 K
D1 3.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 -0.44 dB
PL1W 39.19395828 W
SFO1 100.6479773 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.90 dB
PL12 15.81 dB
PL13 120.00 dB
PL2W 21.64248466 W
PL12W 0.23137002 W
PL13W 0.00000000 W
SFO2 400.2316009 MHz
SI 32768
SF 100.6379140 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40




```
NAME                JAM-685-61
EXPNO                       21
PROCNO                       1
Date_                 20151030
Time                     18.36
INSTRUM                  spect
PROBHD    5 mm PABBO BB/
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                          16
DS                           4
SWH                 81521.742 Hz
FIDRES              1.243923 Hz
AQ                  0.4020041 sec
RG                         203
DW                     6.133 usec
DE                     6.50 usec
TE                     298.1 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1             202.4583558 MHz
NUC1                     31P
P1                     11.50 usec
SI                       32768
SF               202.4684792 MHz
WDW                         EM
SSB                          0
LB                      1.00 Hz
GB                           0
PC                      1.40
```

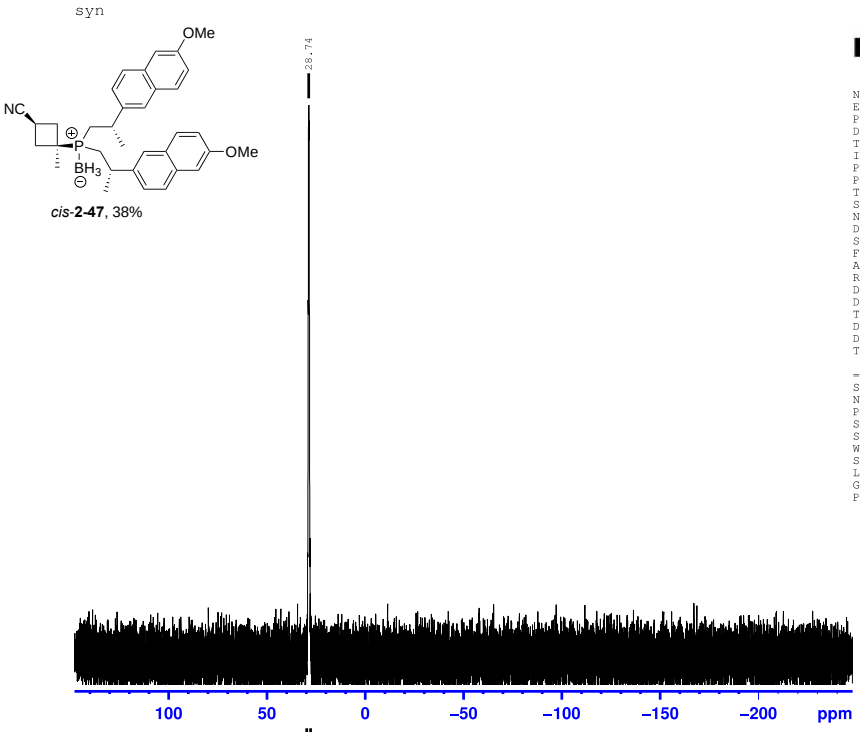



```
NAME              JAM-10824-87
EXPNO                       20
PROCNO                       1
Date_                 20160404
Time                     14.20
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG                  zg30
TD                       65536
SOLVENT                  CDCl3
NS                          16
DS                           2
SWH                  8012.820 Hz
FIDRES               0.122266 Hz
AQ                   4.0894966 sec
RG                        50.8
DW                      62.400 usec
DE                      6.50 usec
TE                      95.8 K
D1                 1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1             400.1324710 MHz
NUC1                     1H
P1                     13.75 usec
SI                       65536
SF               400.1300104 MHz
WDW                         EM
SSB                          0
LB                      0.30 Hz
GB                           0
PC                      1.00
```



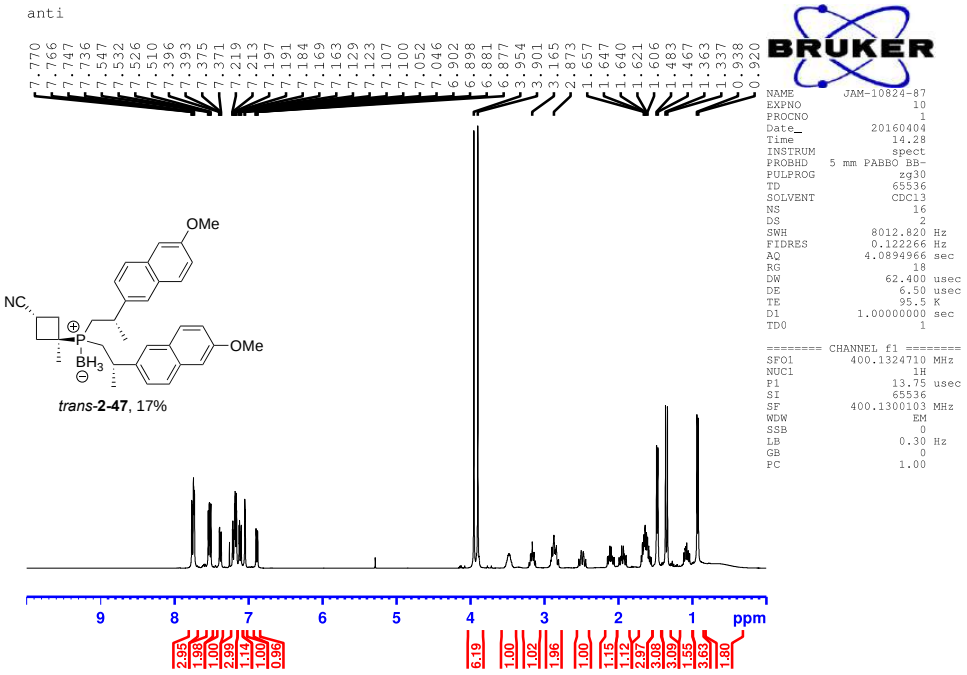
BRUKER

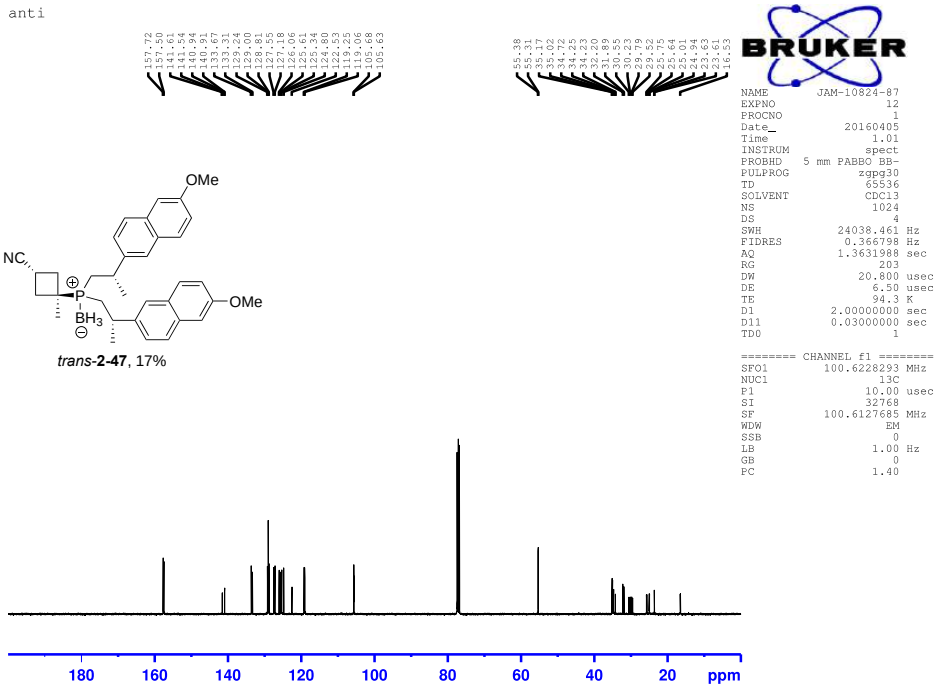
```
NAME          JAM-10824-87
EXPNO                   22
PROCNO                   1
Date_             20160405
Time                 2.04
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  1024
DS                     4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG                   203
DW                20.800 usec
DE                 6.50 usec
TE                 94.3 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         100.6228293 MHz
NUC1               13C
P1               10.00 usec
SI                32768
SF           100.6127685 MHz
WDW                EM
SSB                 0
LB               1.00 Hz
GB                  0
PC               1.40
```



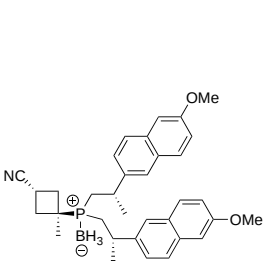
BRUKER

```
NAME          JAM-10824-87
EXPNO                   21
PROCNO                   1
Date_             20160404
Time                14.22
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     4
SWH           64102.563 Hz
FIDRES         0.978127 Hz
AQ            0.5112308 sec
RG                   203
DW                7.800 usec
DE                 6.50 usec
TE                 95.7 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         161.9674942 MHz
NUC1               31P
P1               13.30 usec
SI                32768
SF           161.9755930 MHz
WDW                EM
SSB                 0
LB               1.00 Hz
GB                  0
PC               1.40
```


anti
7.770
7.766
7.747
7.736
7.547
7.532
7.526
7.510
7.396
7.393
7.375
7.371
7.219
7.213
7.197
7.191
7.184
7.169
7.163
7.129
7.123
7.107
7.100
7.052
7.046
6.902
6.898
6.881
6.877
3.954
3.901
3.165
2.873
1.657
1.647
1.640
1.621
1.606
1.483
1.467
1.363
1.337
0.938
0.920
OMe
NC
P
BH3
OMe
trans-2-47, 17%
9
8
7
6
5
4
3
2
1
ppm
2.95
1.98
1.00
2.99
1.14
1.09
0.96
6.19
1.00
1.02
1.96
1.00
1.15
1.12
2.97
3.08
3.09
1.55
3.83
1.80
BRUKER
NAME JAM-10824-87
EXPNO 10
PROCNO 1
Date_ 20160404
Time 14.28
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 18
DW 62.400 usec
DE 6.50 usec
TE 95.5 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 13.75 usec
SI 65536
SF 400.1300103 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

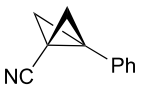

anti
157.72
157.50
141.61
141.54
140.94
140.91
133.67
133.31
133.28
129.00
128.81
127.55
127.18
126.06
125.61
125.34
124.80
124.55
119.25
119.06
105.68
105.63
55.38
55.31
35.17
35.02
34.72
34.55
34.23
32.20
31.89
30.33
30.23
29.79
29.52
25.75
25.64
25.01
24.94
23.63
23.61
16.53
OMe
NC
P
BH3
OMe
trans-2-47, 17%
180
160
140
120
100
80
60
40
20
ppm
BRUKER
NAME JAM-10824-87
EXPNO 12
PROCNO 1
Date_ 20160405
Time 1.01
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 94.3 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6228293 MHz
NUC1 13C
P1 10.00 usec
SI 32768
SF 100.6127685 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

anti

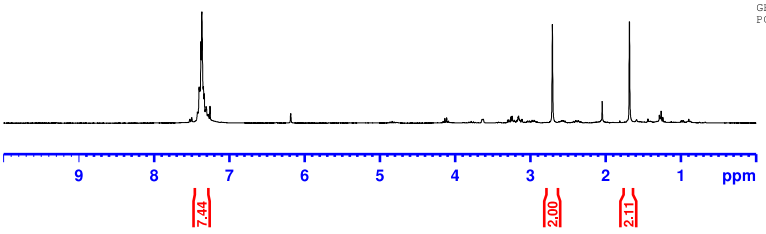


trans-**2-47**, 17%

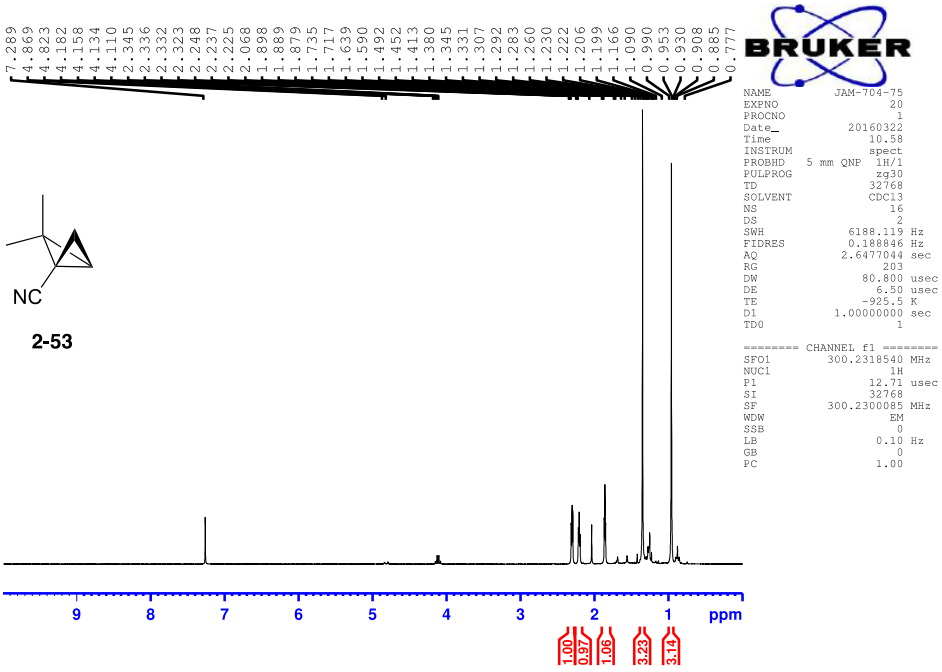

```
NAME          JAM-10824-87
EXPNO               11
PROCNO               1
Date_           20160404
Time               14.30
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    4
SWH           64102.563 Hz
FIDRES         0.978127 Hz
AQ            0.5112308 sec
RG                  203
DW                7.800 usec
DE                6.50 usec
TE                95.5 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
SFO1        161.9674942 MHz
NUC1              31P
P1               13.30 usec
SI               32768
SF          161.9755930 MHz
WDW                EM
SSB                 0
LB               1.00 Hz
GB                  0
PC               1.40
```

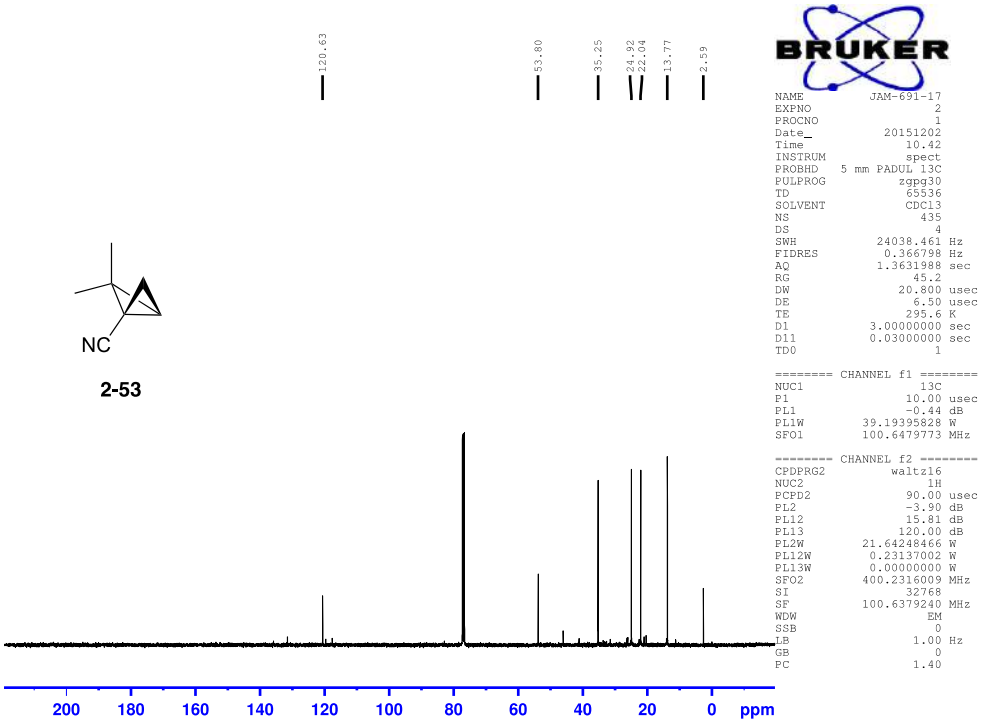


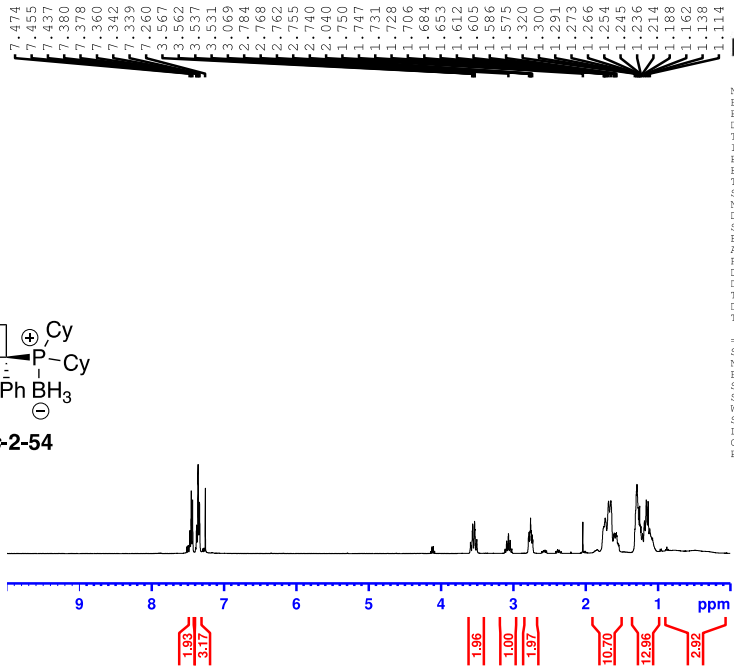
2-50

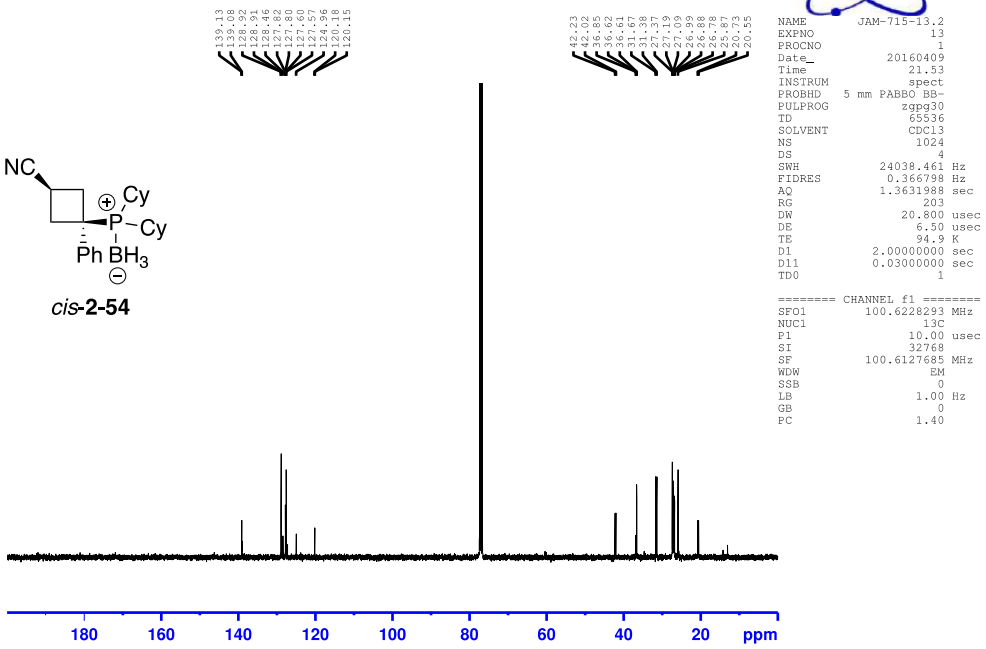


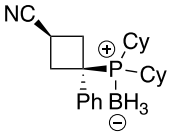

```
NAME          JAM-691-49
EXPNO               10
PROCNO               1
Date_           20151229
Time               19.17
INSTRUM            spect
PROBHD   5 mm QNP  1H/1
PULPROG          zg30
TD                32768
SOLVENT           CDCl3
NS                   16
DS                    2
SWH           6188.119 Hz
FIDRES        0.188846 Hz
AQ            2.6477044 sec
RG                 90.5
DW               80.800 usec
DE                6.50 usec
TE              -926.4 K
D1           1.00000000 sec
TD0                  1

======== CHANNEL f1 ========
SFO1        300.2318540 MHz
NUC1              1H
P1               12.71 usec
SI               32768
SF          300.2300092 MHz
WDW                EM
SSB                 0
LB               0.10 Hz
GB                  0
PC               1.00
```


7.289
4.869
4.823
4.182
4.158
4.134
4.110
2.345
2.336
2.332
2.323
2.248
2.237
2.225
2.068
1.898
1.889
1.879
1.735
1.717
1.639
1.590
1.492
1.452
1.413
1.380
1.345
1.331
1.307
1.292
1.283
1.260
1.230
1.222
1.206
1.199
1.166
1.090
0.990
0.953
0.930
0.908
0.885
0.777
NC
2-53
NAME JAM-704-75
EXPNO 20
PROCNO 1
Date_ 20160322
Time 10.58
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.188846 Hz
AQ 2.6477044 sec
RG 203
DW 80.800 usec
DE 6.50 usec
TE -925.5 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 300.2318540 MHz
NUC1 1H
P1 12.71 usec
SI 32768
SF 300.2300085 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00
9
8
7
6
5
4
3
2
1
ppm
1.00
0.97
1.06
3.23
3.14


120.63
53.80
35.25
24.92
22.04
13.77
2.59
NC
2-53
NAME JAM-691-17
EXPNO 2
PROCNO 1
Date_ 20151202
Time 10.42
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 435
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 45.2
DW 20.800 usec
DE 6.50 usec
TE 295.6 K
D1 3.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 -0.44 dB
PL1W 39.19395828 W
SFO1 100.6479773 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.90 dB
PL12 15.81 dB
PL13 120.00 dB
PL2W 21.64248466 W
PL12W 0.23137002 W
PL13W 0.00000000 W
SFO2 400.2316009 MHz
SI 32768
SF 100.6379240 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200
180
160
140
120
100
80
60
40
20
0
ppm

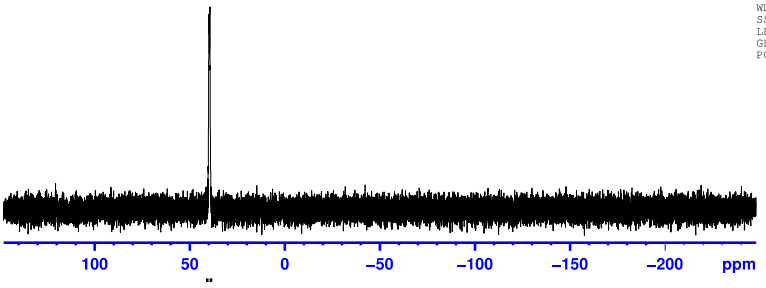

7.474
7.455
7.437
7.380
7.378
7.360
7.342
7.339
7.260
3.567
3.562
3.537
3.531
3.069
2.784
2.768
2.762
2.755
2.740
2.040
1.750
1.747
1.731
1.728
1.706
1.684
1.653
1.612
1.605
1.586
1.575
1.320
1.300
1.291
1.273
1.266
1.254
1.245
1.236
1.214
1.188
1.162
1.138
1.114
BRUKER
NAME JAM-715-13.2
EXPNO 10
PROCNO 1
Date_ 20160409
Time 20.05
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDC13
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 57
DW 62.400 usec
DE 6.50 usec
TE 94.8 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 13.75 usec
SI 65536
SF 400.1300100 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
NC
Cy
P
Cy
Ph
BH3
cis-2-54
9
8
7
6
5
4
3
2
1
ppm
1.93
3.17
1.96
1.00
1.97
10.70
12.96
2.92

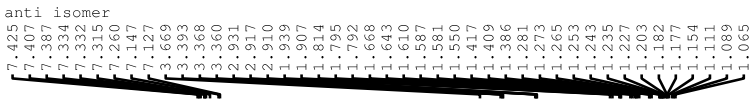

130.13
133.08
128.92
128.91
128.46
127.82
127.80
127.60
121.57
124.96
120.18
120.15
42.23
42.02
36.85
36.82
36.61
31.67
31.38
27.37
27.19
27.09
26.99
26.88
26.78
25.87
25.73
20.55
BRUKER
NAME JAM-715-13.2
EXPNO 13
PROCNO 1
Date_ 20160409
Time 21.53
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDC13
NS 1024
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 94.9 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6228293 MHz
NUC1 13C
P1 10.00 usec
SI 32768
SF 100.6127685 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
NC
Cy
P
Cy
Ph
BH3
cis-2-54
180
160
140
120
100
80
60
40
20
ppm



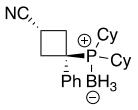
cis-**2-54**

```
NAME            JAM-715-13.2
EXPNO                     11
PROCNO                     1
Date_           20160409
Time                  20.07
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG               zgpg30
TD                     65536
SOLVENT                CDCl3
NS                        16
DS                         4
SWH               64102.563 Hz
FIDRES            0.978127 Hz
AQ                0.5112308 sec
RG                       203
DW                   7.800 usec
DE                   6.50 usec
TE                    94.9 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1            161.9674942 MHz
NUC1                     31P
P1                   13.30 usec
SI                      32768
SF              161.9755930 MHz
WDW                        EM
SSB                         0
LB                       1.00 Hz
GB                          0
PC                       1.40
```

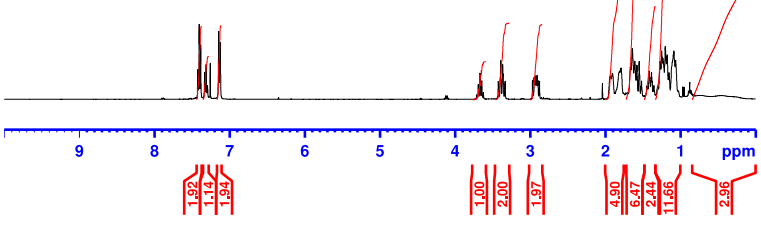




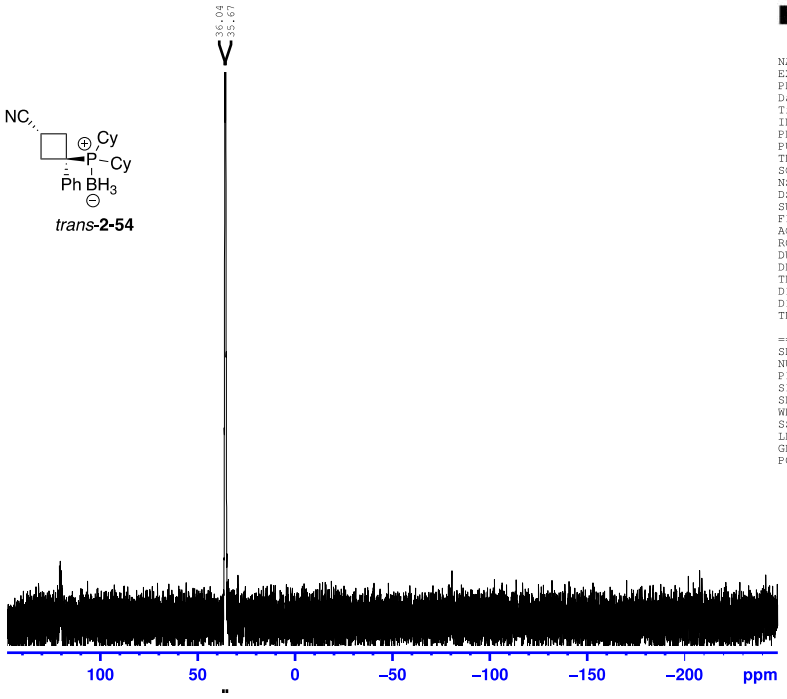
```
NAME            JAM-691-72
EXPNO                     20
PROCNO                     1
Date_           20160120
Time                  17.59
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                     65536
SOLVENT                CDCl3
NS                        16
DS                         2
SWH                8012.820 Hz
FIDRES            0.122266 Hz
AQ                4.0894966 sec
RG                        32
DW                   62.400 usec
DE                   6.50 usec
TE                    297.6 K
D1                1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1            400.1324710 MHz
NUC1                     1H
P1                   13.75 usec
SI                      65536
SF              400.1300103 MHz
WDW                        EM
SSB                         0
LB                       0.30 Hz
GB                          0
PC                       1.00
```



trans-**2-54**



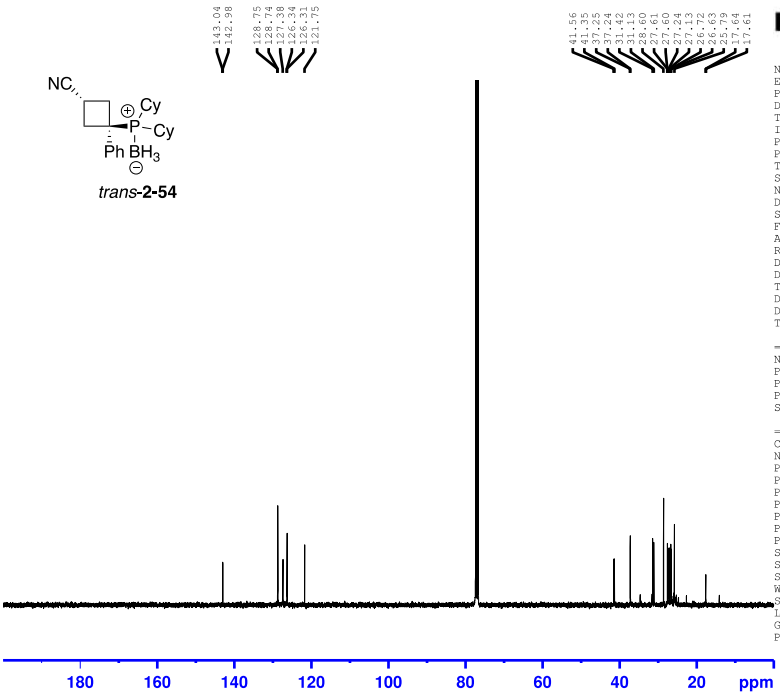
anti isomer



trans-**2-54**

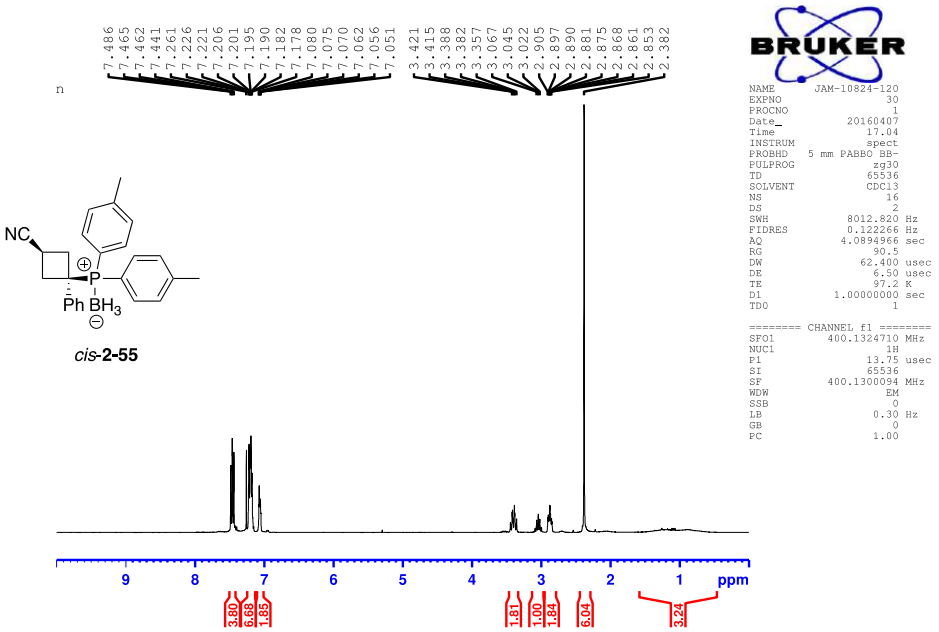
```
NAME                JAM-691-72
EXPNO                       21
PROCNO                       1
Date_                 20160120
Time                     17.57
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                          16
DS                           4
SWH                 64102.563 Hz
FIDRES               0.978127 Hz
AQ                   0.5112308 sec
RG                         203
DW                       7.800 usec
DE                       6.50 usec
TE                       297.7 K
D1                   2.00000000 sec
D11                  0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1               161.9674942 MHz
NUC1                       31P
P1                       13.30 usec
SI                       32768
SF                 161.9755930 MHz
WDW                         EM
SSB                          0
LB                        1.00 Hz
GB                           0
PC                        1.40
```

anti isomer



trans-**2-54**

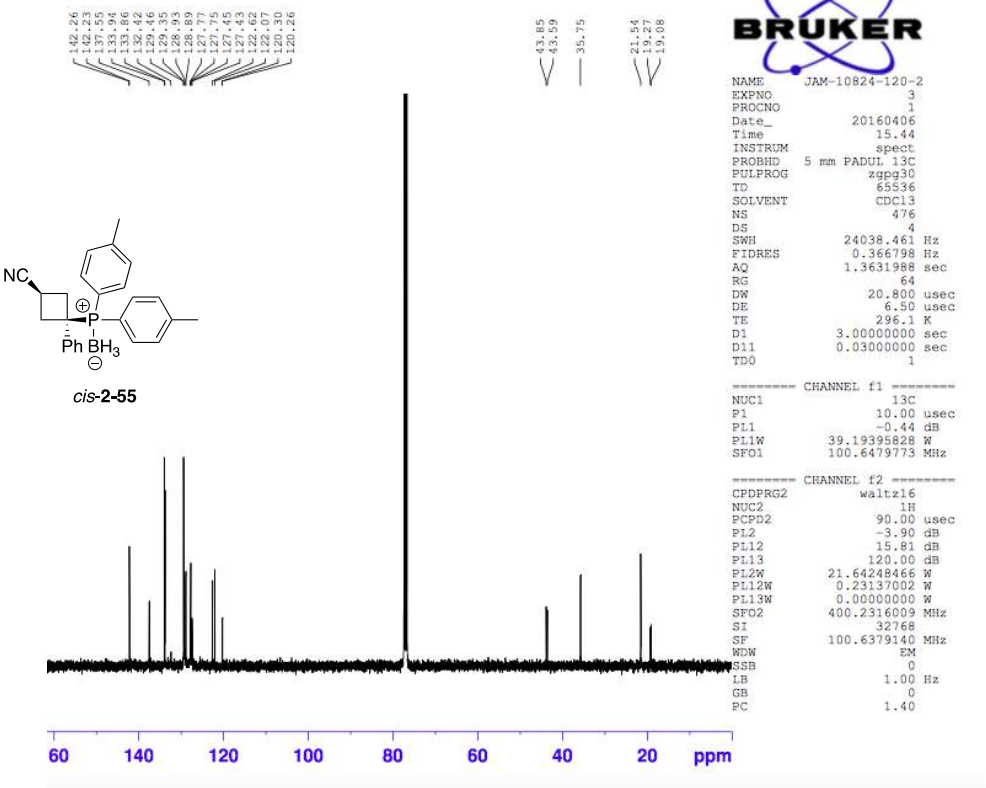
```
NAME                JAM-691-72
EXPNO                        1
PROCNO                       1
Date_                 20160120
Time                     19.01
INSTRUM                  spect
PROBHD    5 mm PADUL 13C
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                         640
DS                           4
SWH                 24038.461 Hz
FIDRES               0.366798 Hz
AQ                   1.3631988 sec
RG                          32
DW                      20.800 usec
DE                       6.50 usec
TE                       295.8 K
D1                   3.00000000 sec
D11                  0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                        13C
P1                       10.00 usec
PL1                      -0.44 dB
PL1W                39.19395828 W
SFO1                100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                        1H
PCPD2                    90.00 usec
PL2                      -3.90 dB
PL12                     15.81 dB
PL13                    120.00 dB
PL2W                21.64248466 W
PL12W                0.23137002 W
PL13W                0.00000000 W
SFO2                400.2316009 MHz
SI                       32768
SF                  100.6379140 MHz
WDW                         EM
SSB                          0
LB                        1.00 Hz
GB                           0
PC                        1.40
```



cis-**2-55**

BRUKER

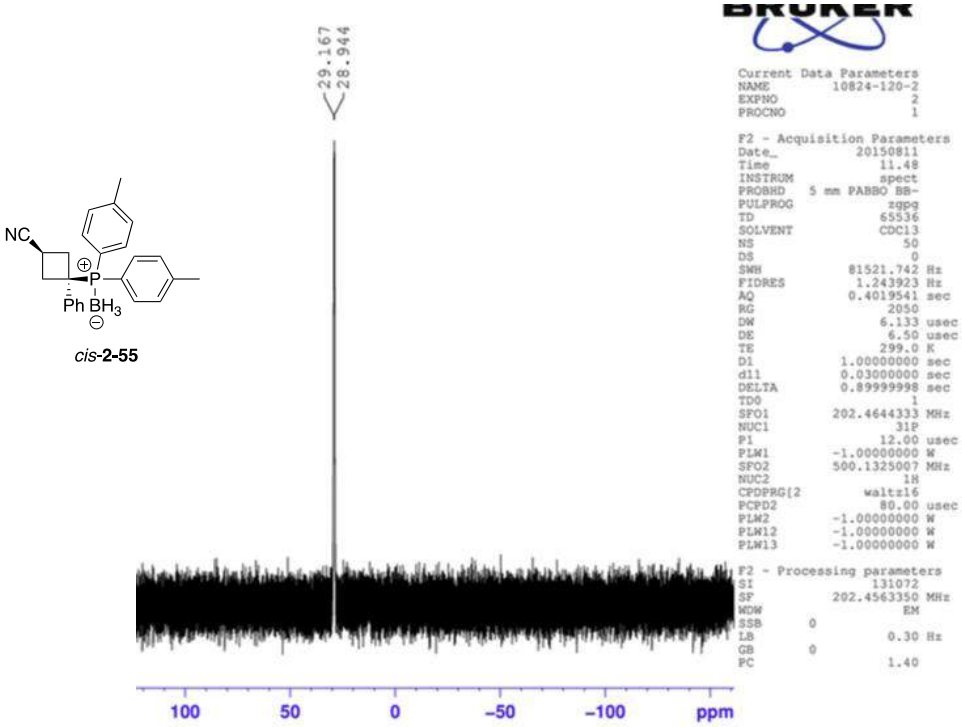
NAME	JAM-10824-120
EXPNO	30
PROCNO	1
Date_	20160407
Time	17.04
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	8012.820 Hz
FIDRES	0.122266 Hz
AQ	4.0894966 sec
RG	90.5
DW	62.400 usec
DE	6.50 usec
TE	97.2 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
SFO1	400.1324710 MHz
NUC1	1H
P1	13.75 usec
SI	65536
SF	400.1300094 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00



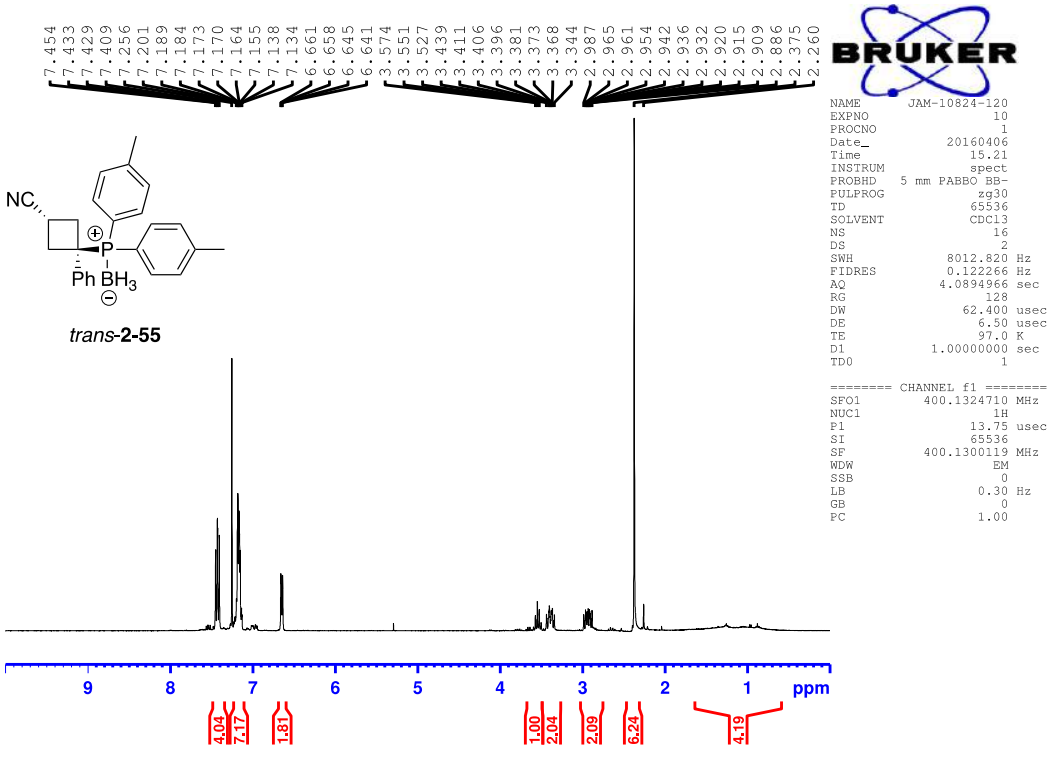
cis-**2-55**

BRUKER

NAME	JAM-10824-120-2
EXPNO	3
PROCNO	1
Date_	20160406
Time	15.44
INSTRUM	spect
PROBHD	5 mm PADUL 13C
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	476
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	64
DW	20.800 usec
DE	6.50 usec
TE	296.1 K
D1	3.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	10.00 usec
PL1	-0.44 dB
PL1W	39.19395828 W
SFO1	100.6479773 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	90.00 usec
PL2	-3.90 dB
PL12	15.81 dB
PL13	120.00 dB
PL2W	21.64248466 W
PL12W	0.23137002 W
PL13W	0.00000000 W
SFO2	400.2316009 MHz
SI	32768
SF	100.6379140 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40



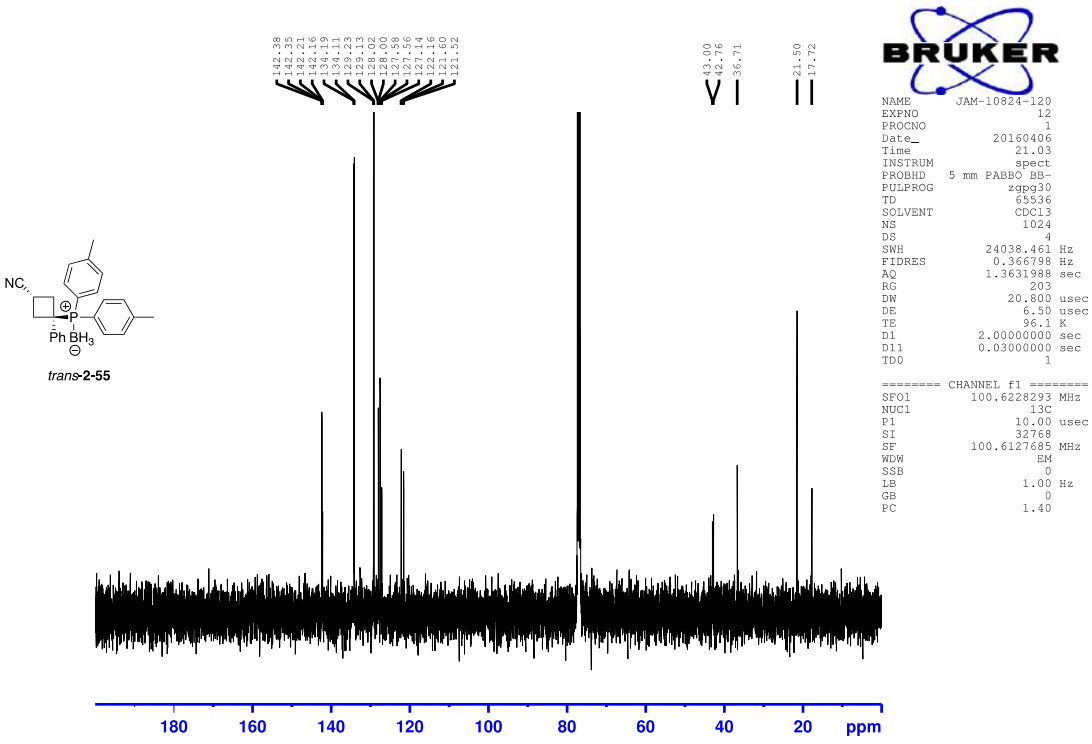
cis-**2-55**



trans-**2-55**

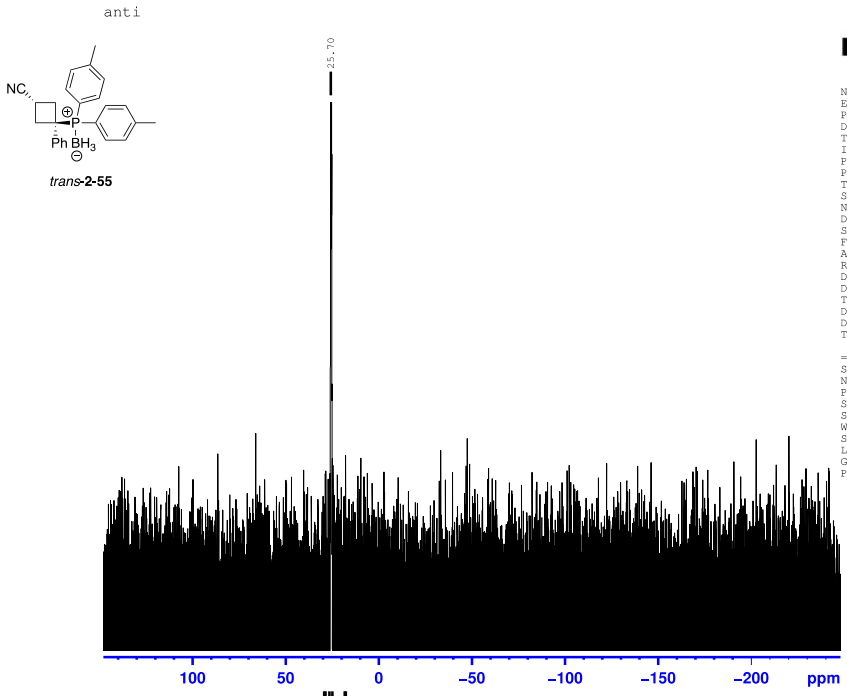

```
Current Data Parameters
NAME         10824-120-2
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_          20150811
Time              11.48
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg
TD               65536
SOLVENT          CDCl3
NS                  50
DS                   0
SWH          81521.742 Hz
FIDRES        1.243923 Hz
AQ            0.4019541 sec
RG                2050
DW               6.133 usec
DE               6.50 usec
TE               299.0 K
D1            1.00000000 sec
d11           0.03000000 sec
DELTA         0.89999998 sec
TD0                  1
SFO1         202.4644333 MHz
NUC1               31P
P1               12.00 usec
PLW1         -1.00000000 W
SFO2         500.1325007 MHz
NUC2               1H
CPDPRG[2         waltz16
PCPD2            80.00 usec
PLW2         -1.00000000 W
PLW12        -1.00000000 W
PLW13        -1.00000000 W

F2 - Processing parameters
SI               131072
SF         202.4563350 MHz
WDW                EM
SSB                 0
LB              0.30 Hz
GB                  0
PC              1.40
```

```
NAME        JAM-10824-120
EXPNO                  10
PROCNO                  1
Date_           20160406
Time               15.21
INSTRUM            spect
PROBHD    5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES             0.122266 Hz
AQ              4.0894966 sec
RG                   128
DW                62.400 usec
DE                 6.50 usec
TE                 97.0 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1          400.1324710 MHz
NUC1                  1H
P1                13.75 usec
SI                65536
SF           400.1300119 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



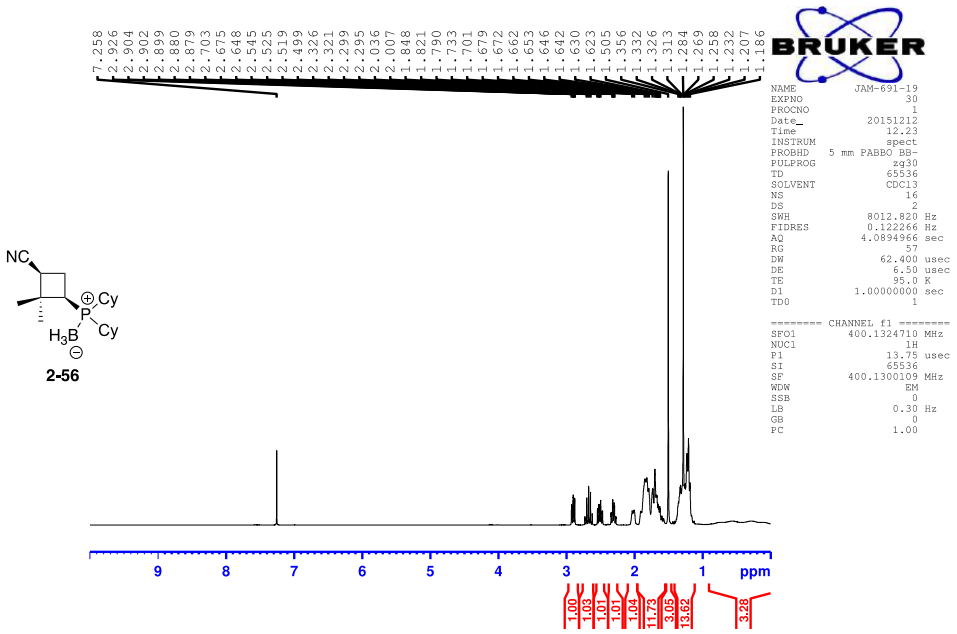
BRUKER

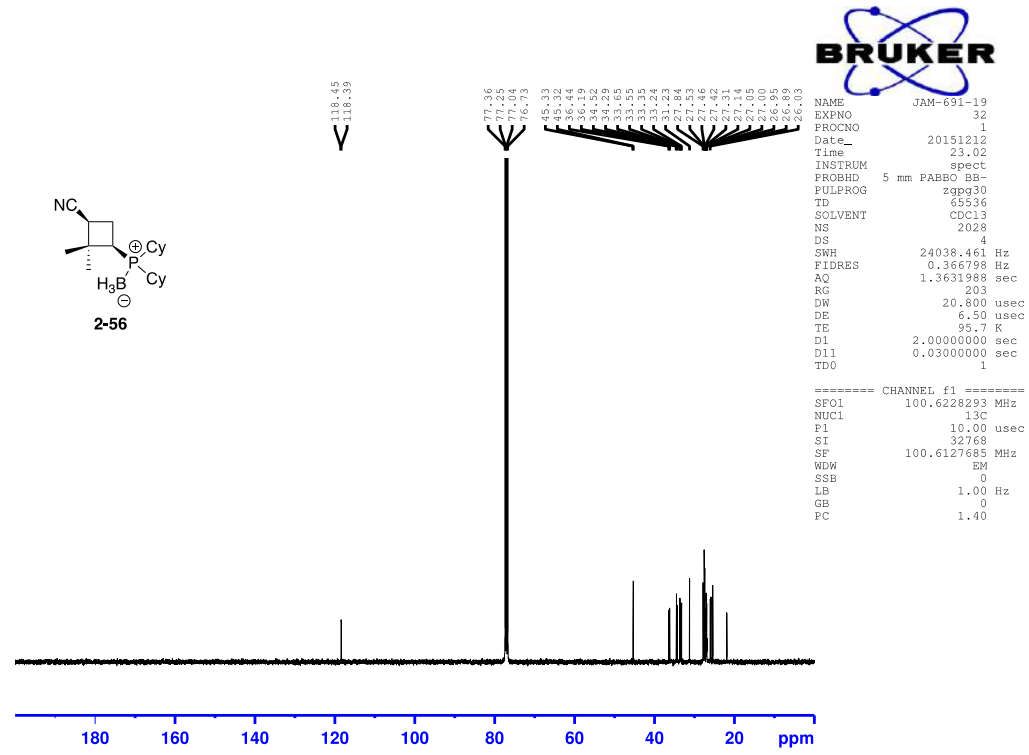
NAME	JAM-10824-120
EXPNO	12
PROCNO	1
Date_	20160406
Time	21.03
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	1024
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	96.1 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
SFO1	100.6228293 MHz
NUC1	13C
P1	10.00 usec
SI	32768
SF	100.6127685 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

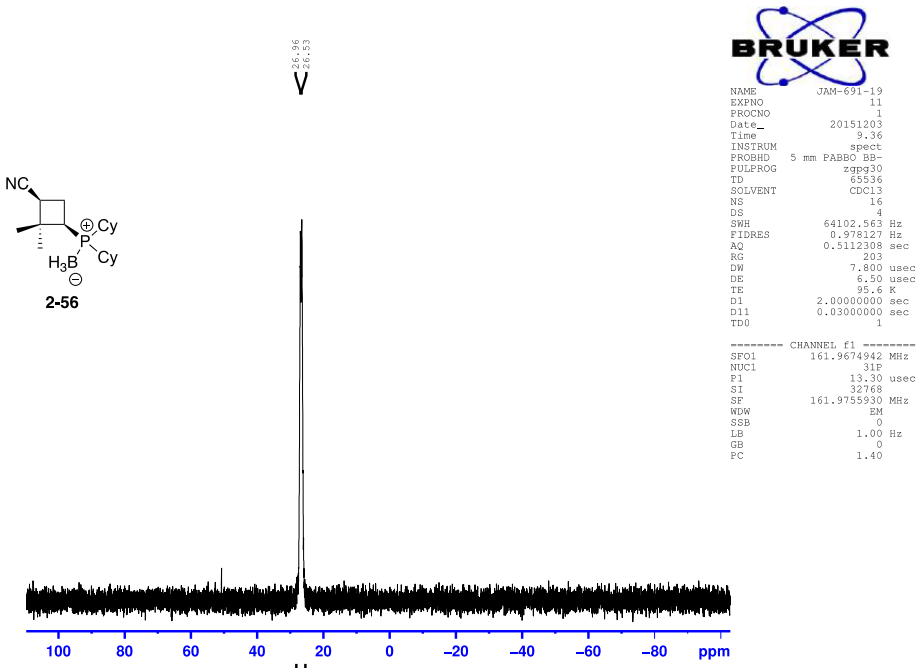


BRUKER

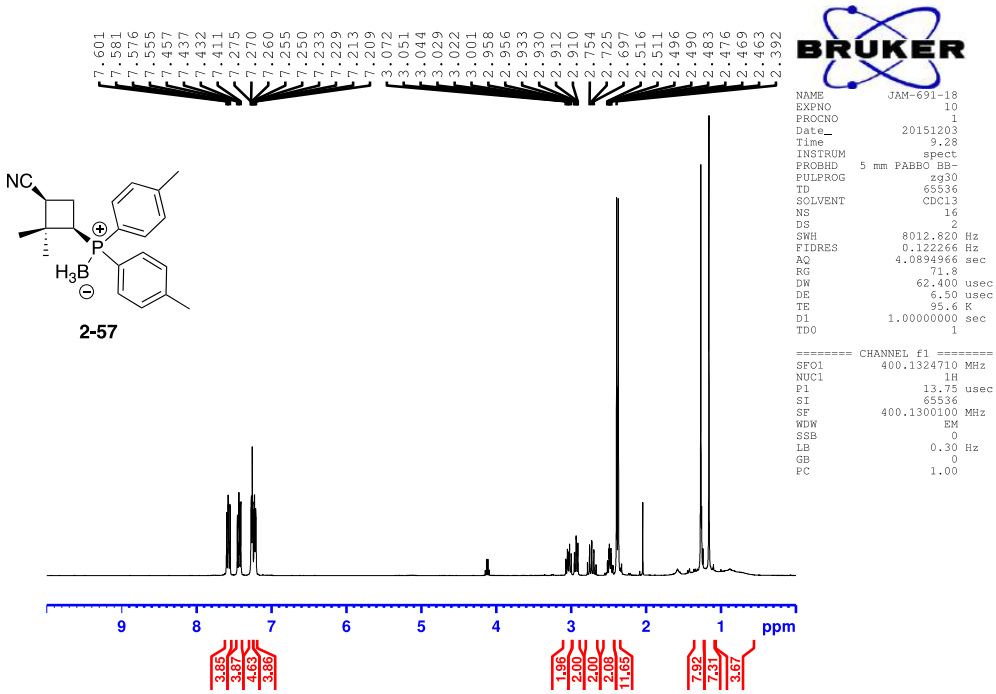
NAME	JAM-10824-120
EXPNO	21
PROCNO	1
Date_	20160407
Time	11.06
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	32
DS	4
SWH	64102.563 Hz
FIDRES	0.978127 Hz
AQ	0.5112308 sec
RG	203
DW	7.800 usec
DE	6.50 usec
TE	96.8 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
SFO1	161.9674942 MHz
NUC1	31P
P1	13.30 usec
SI	32768
SF	161.9755930 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40


7.258 2.926 2.904 2.902 2.899 2.880 2.879 2.703 2.675 2.648 2.545 2.525 2.519 2.499 2.326 2.321 2.299 2.295 2.036 2.007 1.848 1.821 1.790 1.733 1.701 1.679 1.672 1.662 1.653 1.646 1.642 1.630 1.623 1.505 1.356 1.332 1.326 1.313 1.284 1.269 1.258 1.232 1.207 1.186
BRUKER
NAME JAM-691-19
EXPNO 30
PROCNO 1
Date_ 20151212
Time 12.23
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDC13
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 57
DW 62.400 usec
DE 6.50 usec
TE 95.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 13.75 usec
SI 65536
SF 400.1300109 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
NC
Cy
P
Cy
H3B
2-56
9 8 7 6 5 4 3 2 1 ppm
1.00 1.03 1.01 1.01 1.04 11.73 3.05 13.62 3.28

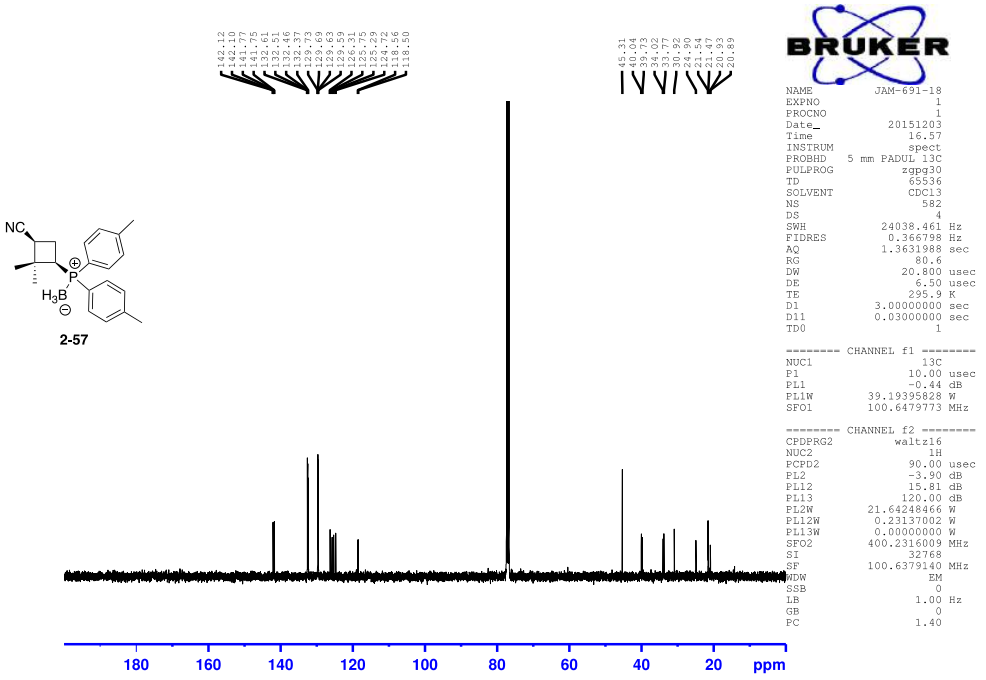

118.45 118.39
77.36 77.25 77.04 76.73
45.33 45.32 36.44 36.19 34.52 34.29 33.65 33.55 33.35 33.24 31.23 31.04 27.53 27.46 27.42 27.31 27.14 27.05 27.00 26.95 26.89 26.03
BRUKER
NAME JAM-691-19
EXPNO 32
PROCNO 1
Date_ 20151212
Time 23.02
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDC13
NS 2028
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 95.7 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6228293 MHz
NUC1 13C
P1 10.00 usec
SI 32768
SF 100.6127685 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
NC
Cy
P
Cy
H3B
2-56
180 160 140 120 100 80 60 40 20 ppm



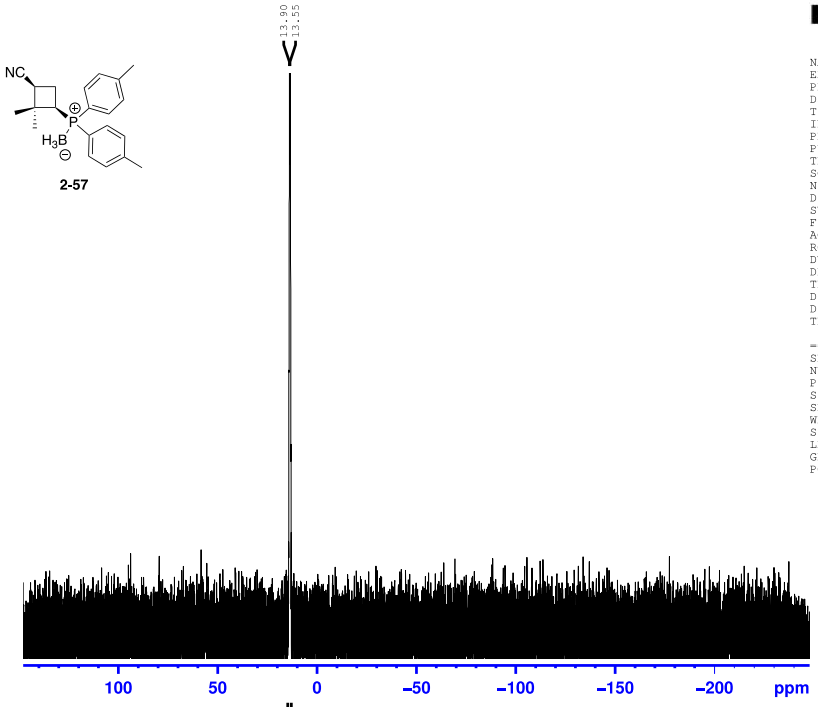

```
BRUKER
NAME                JAM-691-19
EXPNO                       11
PROCNO                       1
Date_                 20151203
Time                      9.36
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG                zgpg30
TD                      65536
SOLVENT                 CDCl3
NS                         16
DS                          4
SWH                 64102.563 Hz
FIDRES               0.978127 Hz
AQ                   0.5112308 sec
RG                        203
DW                     7.800 usec
DE                     6.50 usec
TE                      95.6 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1              161.9674942 MHz
NUC1                      31P
P1                     13.30 usec
SI                        32768
SF                161.9755930 MHz
WDW                        EM
SSB                         0
LB                       1.00 Hz
GB                          0
PC                       1.40
```



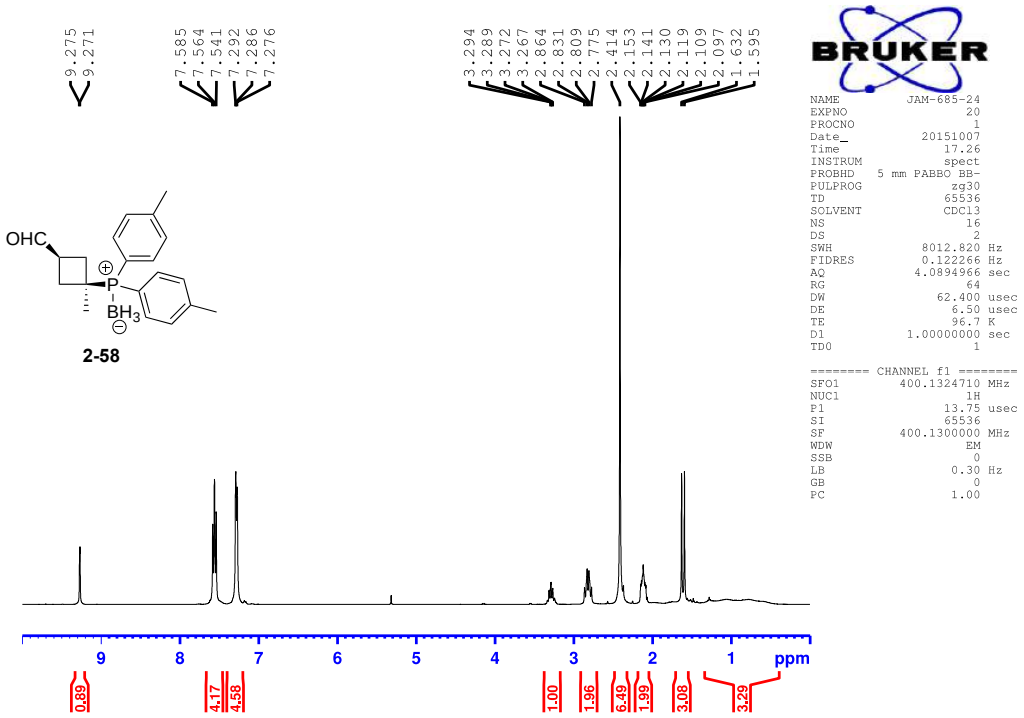

```
BRUKER
NAME                JAM-691-18
EXPNO                       10
PROCNO                       1
Date_                 20151203
Time                      9.28
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG                  zg30
TD                      65536
SOLVENT                 CDCl3
NS                         16
DS                          2
SWH                  8012.820 Hz
FIDRES               0.122266 Hz
AQ                   4.0894966 sec
RG                         71.8
DW                     62.400 usec
DE                      6.50 usec
TE                      95.6 K
D1                1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1              400.1324710 MHz
NUC1                       1H
P1                     13.75 usec
SI                        65536
SF                400.1300100 MHz
WDW                        EM
SSB                         0
LB                       0.30 Hz
GB                          0
PC                       1.00
```

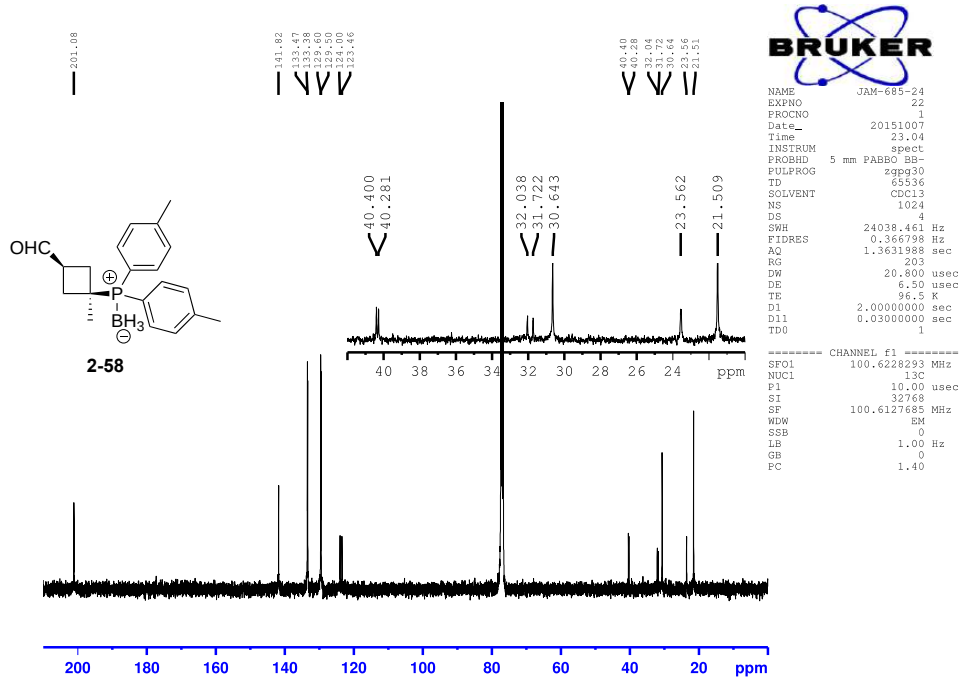


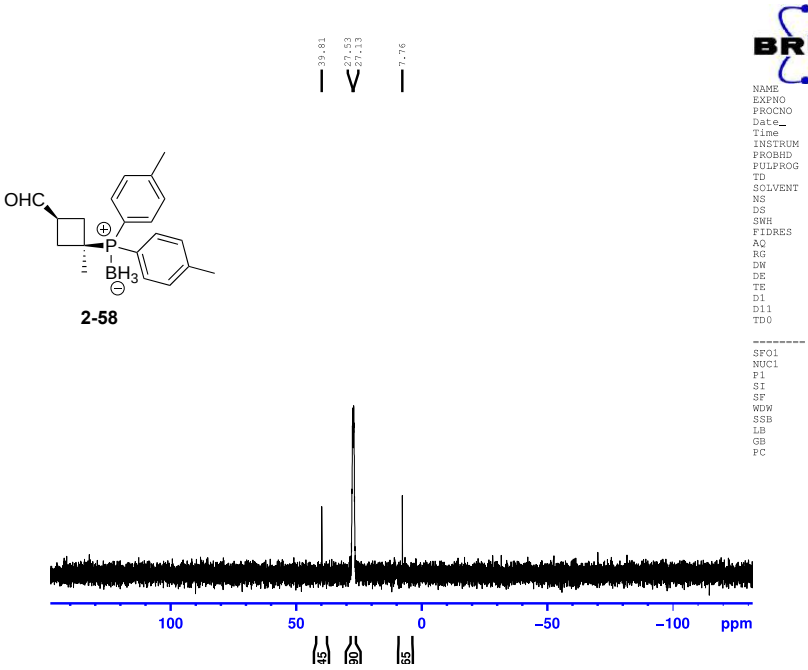

```
BRUKER
NAME                JAM-691-18
EXPNO                        1
PROCNO                       1
Date_                 20151203
Time                     16.57
INSTRUM                  spect
PROBHD   5 mm PADUL 13C
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                         582
DS                           4
SWH                 24038.461 Hz
FIDRES                0.366798 Hz
AQ                    1.3631988 sec
RG                        80.6
DW                       20.800 usec
DE                        6.50 usec
TE                       295.9 K
D1                    3.00000000 sec
D11                   0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                       13C
P1                       10.00 usec
PL1                      -0.44 dB
PL1W               39.19395828 W
SFO1              100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                        1H
PCPD2                    90.00 usec
PL2                      -3.90 dB
PL12                     15.81 dB
PL13                    120.00 dB
PL2W               21.64248466 W
PL12W               0.23137002 W
PL13W               0.00000000 W
SFO2              400.2316009 MHz
SI                       32768
SF                100.6379140 MHz
WDW                         EM
SSB                          0
LB                        1.00 Hz
GB                           0
PC                        1.40
```



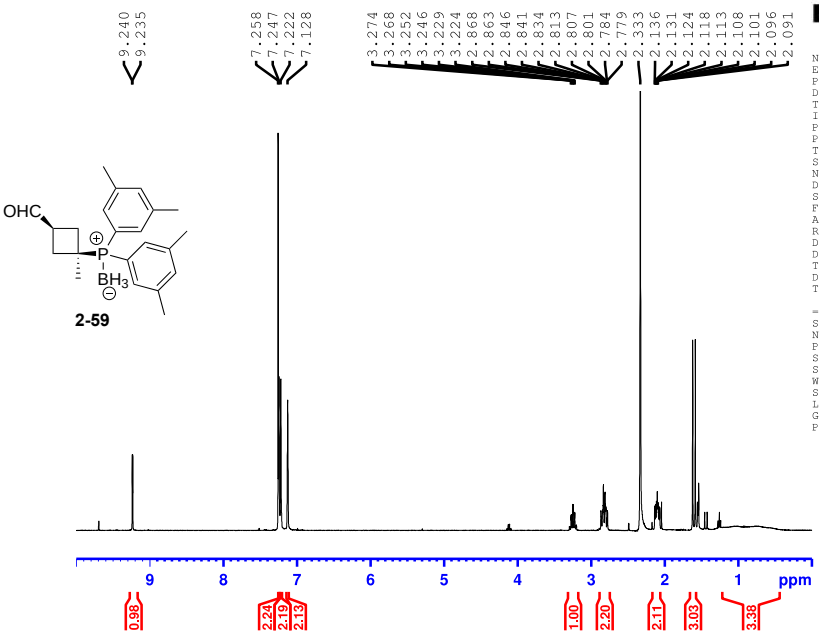

```
BRUKER
NAME                JAM-691-18
EXPNO                       11
PROCNO                       1
Date_                 20151203
Time                     9.30
INSTRUM                  spect
PROBHD   5 mm PABBO BB-
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                          16
DS                           4
SWH                 64102.563 Hz
FIDRES                0.978127 Hz
AQ                    0.5112308 sec
RG                         203
DW                        7.800 usec
DE                        6.50 usec
TE                        95.6 K
D1                    2.00000000 sec
D11                   0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1              161.9674942 MHz
NUC1                       31P
P1                       13.30 usec
SI                       32768
SF                161.9755930 MHz
WDW                         EM
SSB                          0
LB                        1.00 Hz
GB                           0
PC                        1.40
```


9.275
9.271
7.585
7.564
7.541
7.292
7.286
7.276
3.294
3.289
3.272
3.267
2.864
2.831
2.809
2.775
2.414
2.153
2.141
2.130
2.119
2.109
2.097
1.632
1.595
OHC
P
BH3
2-58
9
8
7
6
5
4
3
2
1
ppm
0.89
4.17
4.58
1.00
1.96
6.49
1.99
3.08
3.29
BRUKER
NAME JAM-685-24
EXPNO 20
PROCNO 1
Date_ 20151007
Time 17.26
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 64
DW 62.400 usec
DE 6.50 usec
TE 96.7 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 13.75 usec
SI 65536
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

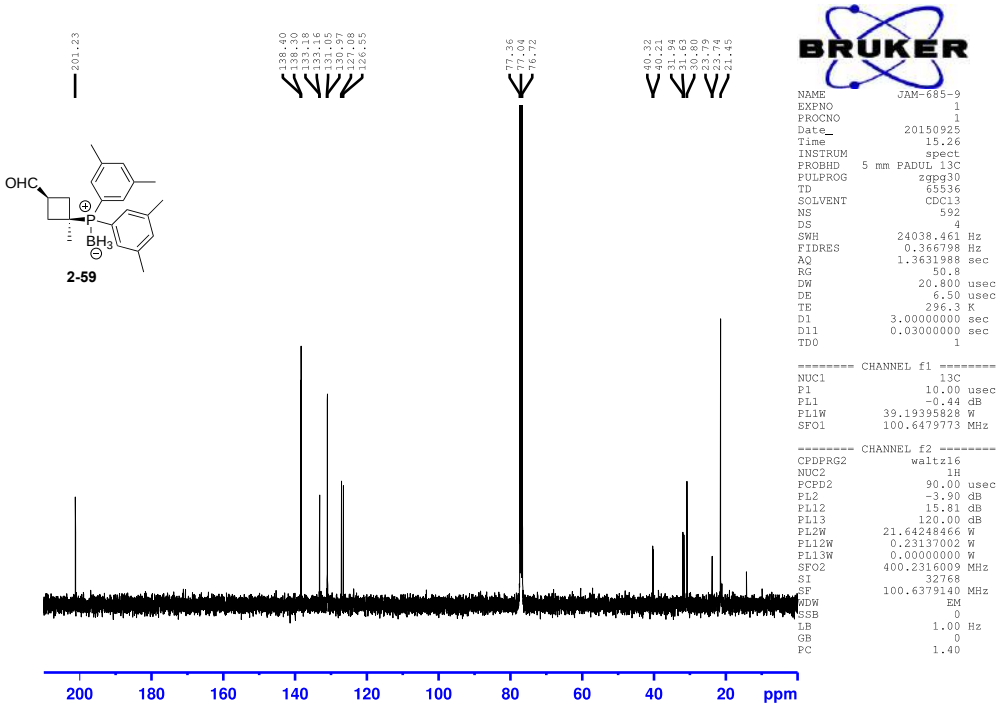

201.08
141.82
133.47
133.38
129.60
129.50
124.00
123.46
40.40
40.28
32.04
31.72
30.64
23.56
21.51
40.400
40.281
32.038
31.722
30.643
23.562
21.509
OHC
P
BH3
2-58
40
38
36
34
32
30
28
26
24
ppm
200
180
160
140
120
100
80
60
40
20
ppm
BRUKER
NAME JAM-685-24
EXPNO 22
PROCNO 1
Date_ 20151007
Time 23.04
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 96.5 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6228293 MHz
NUC1 13C
P1 10.00 usec
SI 32768
SF 100.6127685 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40




```
NAME                JAM-685-24
EXPNO                       21
PROCNO                       1
Date_             20151007
Time                    17.28
INSTRUM                 spect
PROBHD   5 mm PABBO BB-
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                          16
DS                           4
SWH                 64102.563 Hz
FIDRES               0.978127 Hz
AQ                   0.5112308 sec
RG                         203
DW                      7.800 usec
DE                      6.50 usec
TE                      96.7 K
D1                  2.00000000 sec
D11                 0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1               161.9674942 MHz
NUC1                       31P
P1                      13.30 usec
SI                       32768
SF                 161.9755930 MHz
WDW                         EM
SSB                          0
LB                      1.00 Hz
GB                           0
PC                      1.40
```

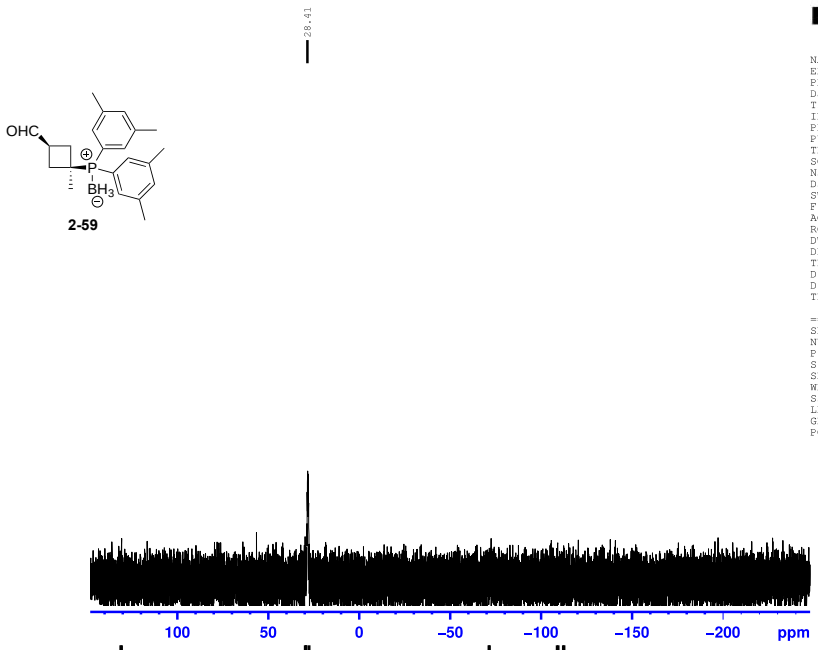



```
NAME                JAM-685-47
EXPNO                       10
PROCNO                       1
Date_             20151023
Time                    16.14
INSTRUM                 spect
PROBHD   5 mm PABBO BB-
PULPROG                 zg30
TD                       65536
SOLVENT                  CDCl3
NS                          16
DS                           2
SWH                  8012.820 Hz
FIDRES               0.122266 Hz
AQ                   4.0894966 sec
RG                         128
DW                      62.400 usec
DE                      6.50 usec
TE                      93.7 K
D1                  1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1               400.1324710 MHz
NUC1                        1H
P1                      13.75 usec
SI                       65536
SF                 400.1300105 MHz
WDW                         EM
SSB                          0
LB                      0.30 Hz
GB                           0
PC                      1.00
```



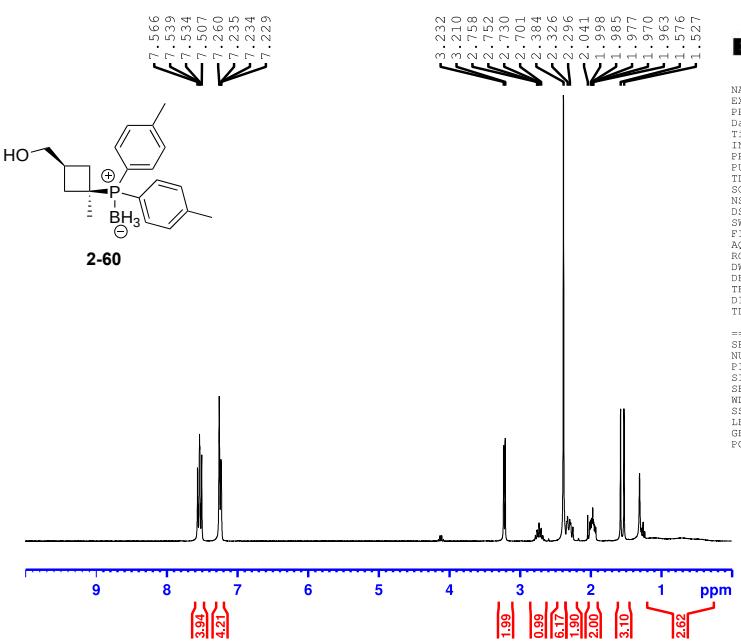
BRUKER

NAME	JAM-685-9
EXPNO	1
PROCNO	1
Date_	20150925
Time	15.26
INSTRUM	spect
PROBHD	5 mm PADUL 13C
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	592
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	50.8
DW	20.800 usec
DE	6.50 usec
TE	296.3 K
D1	3.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	10.00 usec
PL1	-0.44 dB
PL1W	39.19395828 W
SFO1	100.6479773 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	90.00 usec
PL2	-3.90 dB
PL12	15.81 dB
PL13	120.00 dB
PL2W	21.64248466 W
PL12W	0.23137002 W
PL13W	0.00000000 W
SFO2	400.2316009 MHz
SI	32768
SF	100.6379140 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40



BRUKER

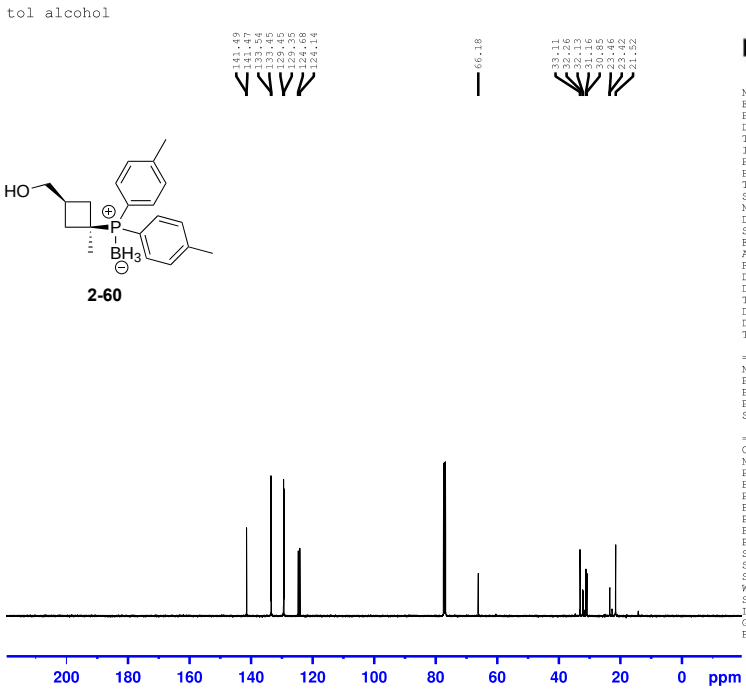
NAME	JAM-685-47
EXPNO	11
PROCNO	1
Date_	20151023
Time	16.16
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	4
SWH	64102.563 Hz
FIDRES	0.978127 Hz
AQ	0.5112308 sec
RG	203
DW	7.800 usec
DE	6.50 usec
TE	93.8 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
SFO1	161.9674942 MHz
NUC1	31P
P1	13.30 usec
SI	32768
SF	161.9755930 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40



BRUKER

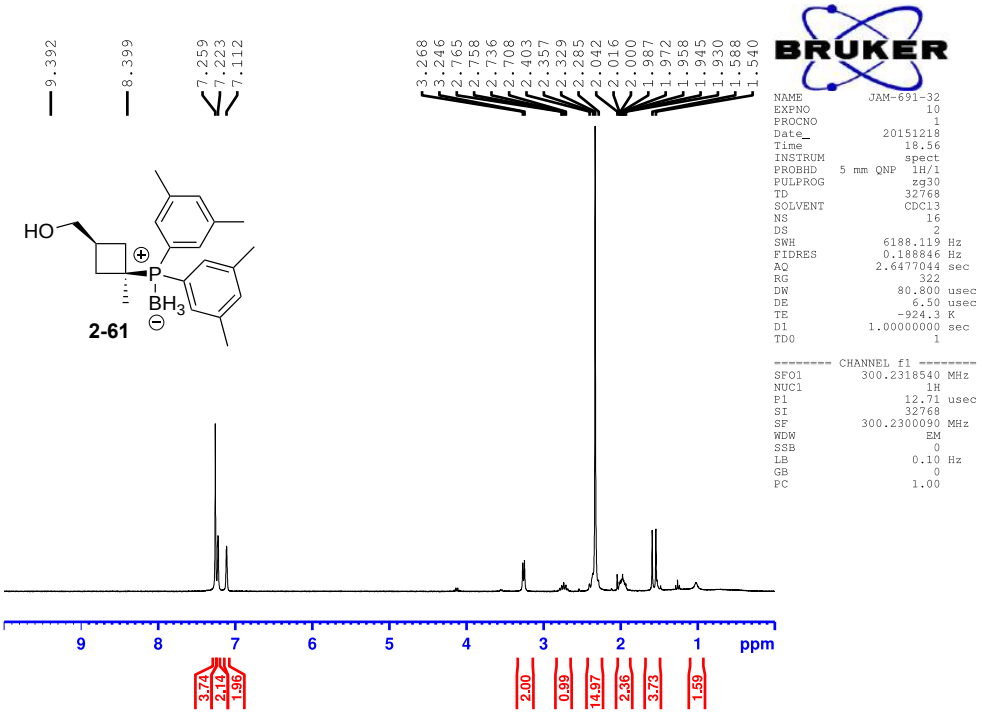
NAME	JAM-704-47
EXPNO	10
PROCNO	1
Date_	20160307
Time	12.36
INSTRUM	spect
PROBHD	5 mm QNP 1H/1
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	6188.119 Hz
FIDRES	0.188846 Hz
AQ	2.6477044 sec
RG	101
DW	80.800 usec
DE	6.50 usec
TE	-928.6 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
SFO1	300.2318540 MHz
NUC1	1H
P1	12.71 usec
SI	32768
SF	300.2300086 MHz
WDW	EM
SSB	0
LB	0.10 Hz
GB	0
PC	1.00

tol alcohol



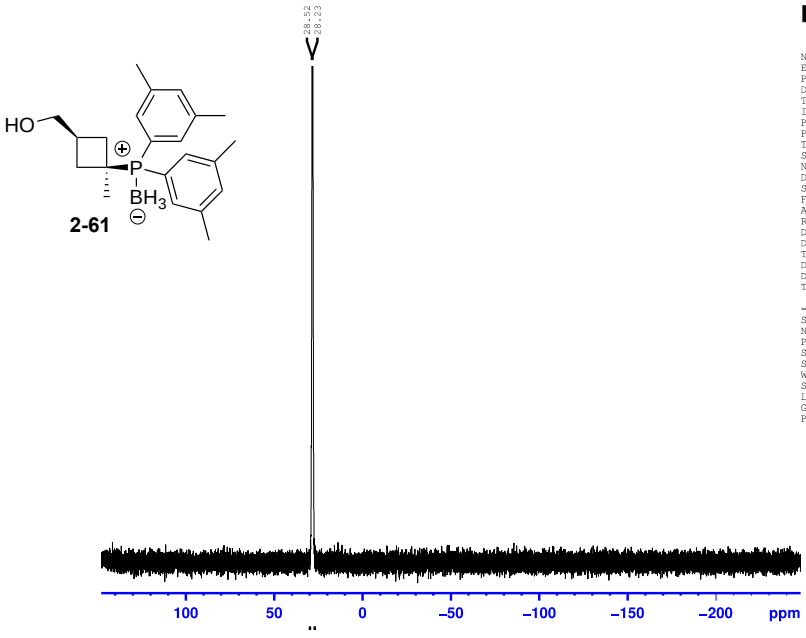
BRUKER

NAME	JAM-715-12
EXPNO	2
PROCNO	1
Date_	20160409
Time	13.03
INSTRUM	spect
PROBHD	5 mm PADUL 13C
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	700
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	71.8
DW	20.800 usec
DE	6.50 usec
TE	295.8 K
D1	3.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	10.00 usec
PL1	-0.44 dB
PL1W	39.19395828 W
SFO1	100.6479773 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	90.00 usec
PL2	-3.90 dB
PL12	15.81 dB
PL13	120.00 dB
PL2W	21.64248466 W
PL12W	0.23137002 W
PL13W	0.00000000 W
SFO2	400.2316009 MHz
SI	32768
SF	100.6379140 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40



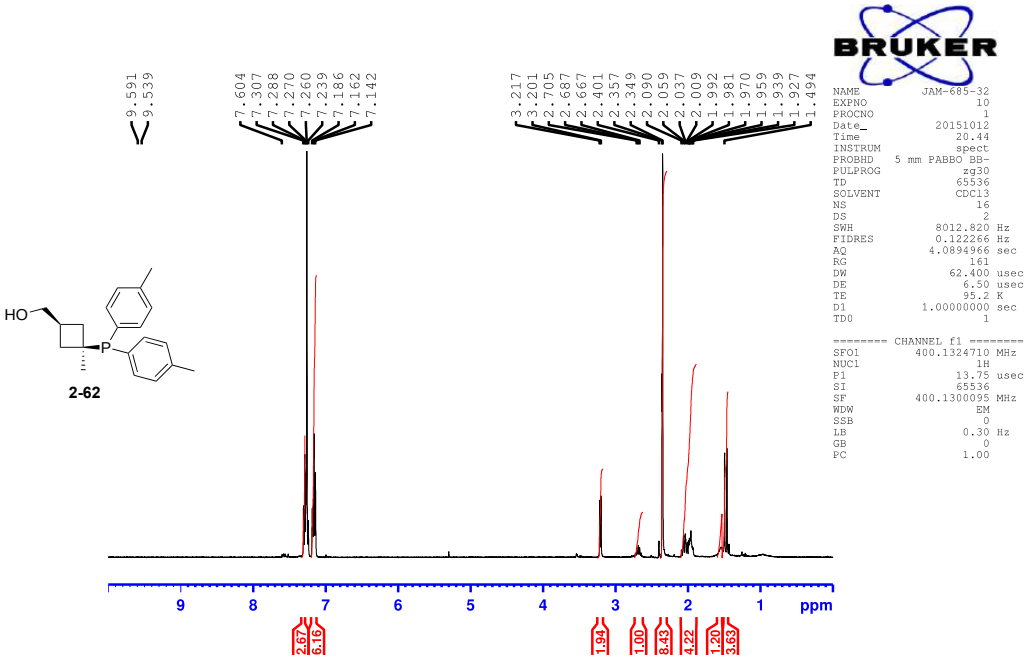
BRUKER

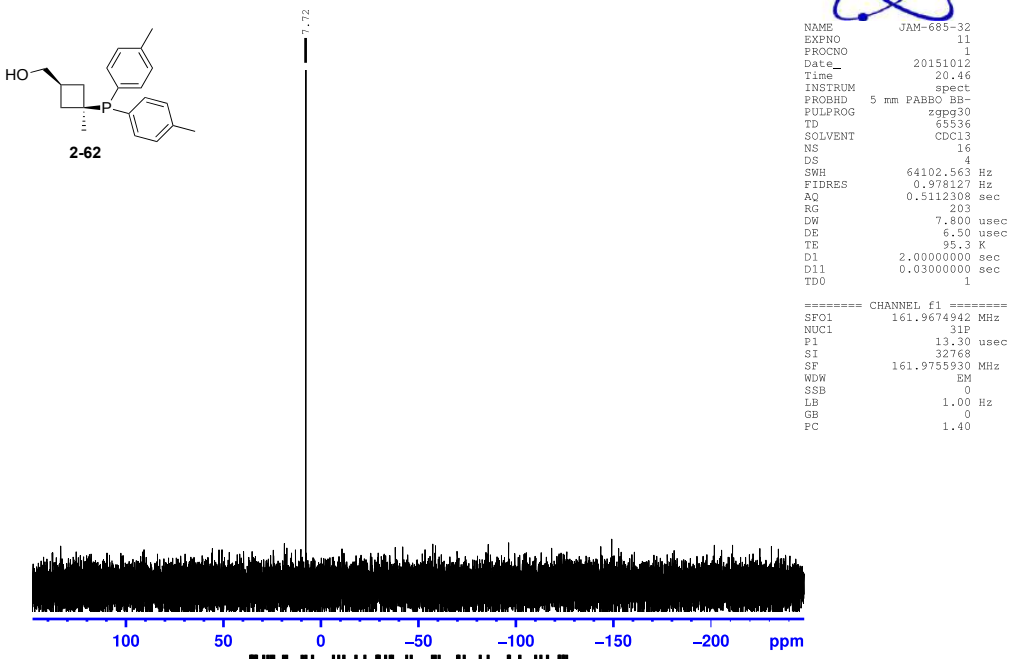
```
NAME                JAM-691-32
EXPNO                       10
PROCNO                       1
Date_                 20151218
Time                     18.56
INSTRUM                  spect
PROBHD     5 mm QNP   1H/1
PULPROG                  zg30
TD                      32768
SOLVENT                 CDCl3
NS                         16
DS                          2
SWH                  6188.119 Hz
FIDRES               0.188846 Hz
AQ                  2.6477044 sec
RG                        322
DW                     80.800 usec
DE                      6.50 usec
TE                     -924.3 K
D1                  1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1           300.2318540 MHz
NUC1                     1H
P1                    12.71 usec
SI                     32768
SF             300.2300090 MHz
WDW                       EM
SSB                        0
LB                      0.10 Hz
GB                         0
PC                      1.00
```

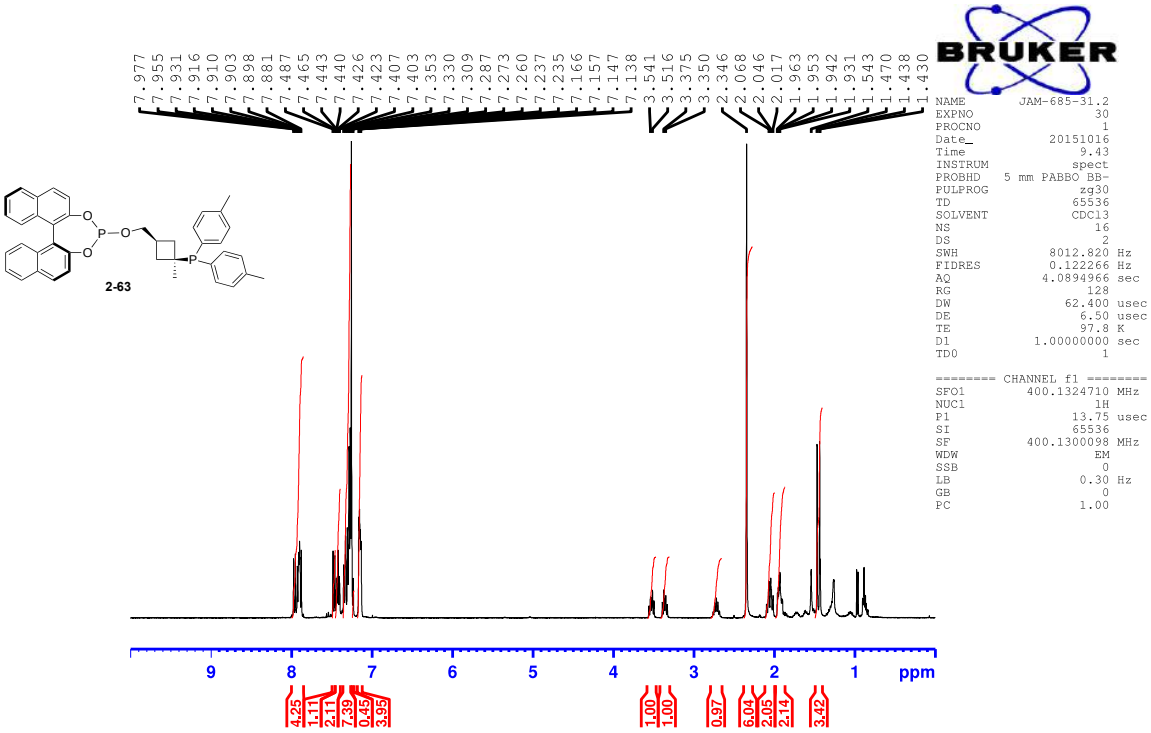


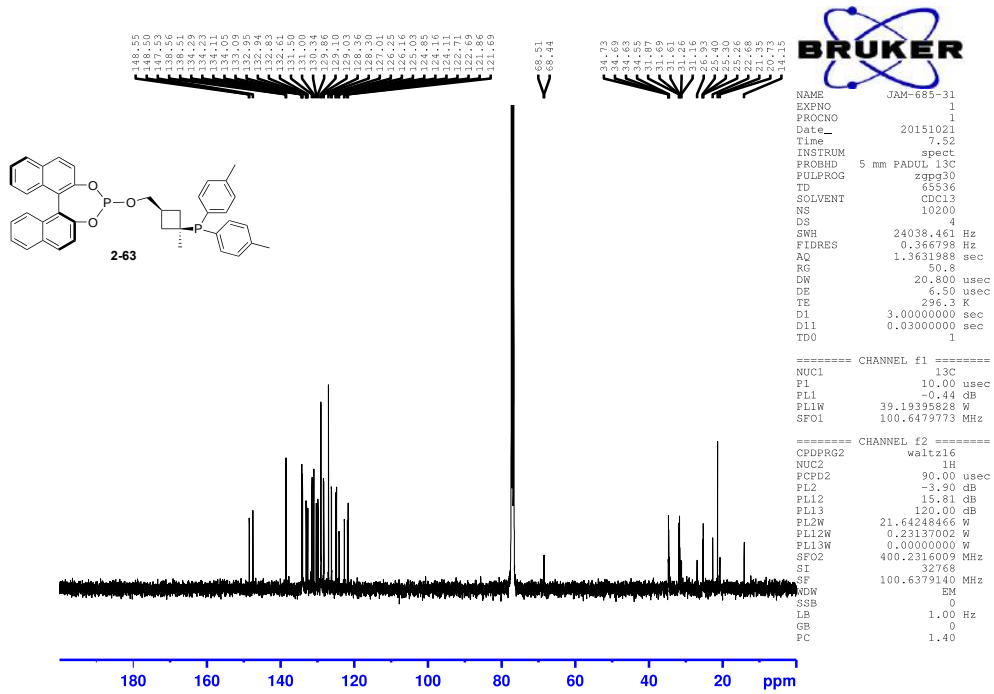
BRUKER

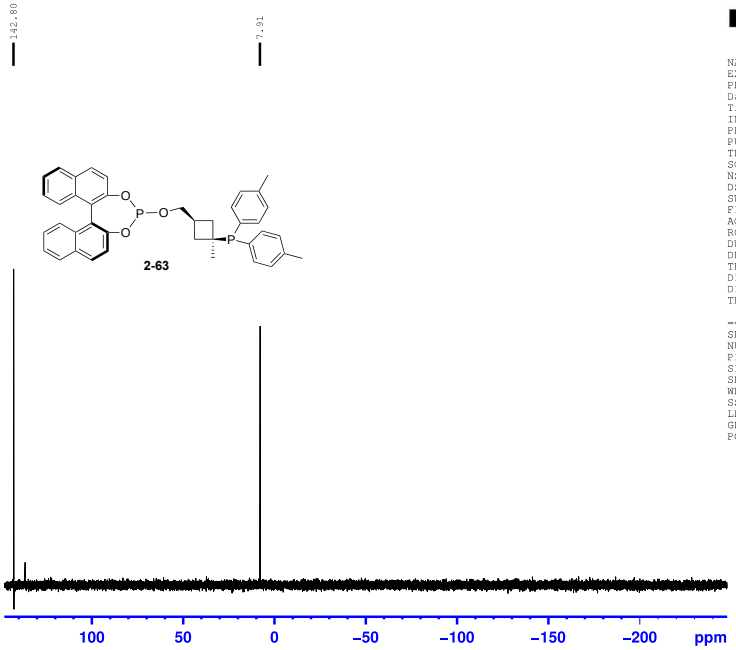
```
NAME                JAM-647-91
EXPNO                       11
PROCNO                       1
Date_                 20150914
Time                     15.57
INSTRUM                  spect
PROBHD     5 mm PABBO BB-
PULPROG                zgpg30
TD                      65536
SOLVENT                 CDCl3
NS                         16
DS                          4
SWH                 64102.563 Hz
FIDRES               0.978127 Hz
AQ                  0.5112308 sec
RG                        203
DW                     7.800 usec
DE                      6.50 usec
TE                      95.0 K
D1                  2.00000000 sec
D11                 0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1           161.9674942 MHz
NUC1                     31P
P1                    13.30 usec
SI                     32768
SF             161.9755930 MHz
WDW                       EM
SSB                        0
LB                      1.00 Hz
GB                         0
PC                      1.40
```


9.591
9.539
7.604
7.307
7.288
7.270
7.260
7.239
7.186
7.162
7.142
3.217
3.201
2.705
2.687
2.667
2.401
2.357
2.349
2.090
2.059
2.037
2.009
1.992
1.981
1.970
1.959
1.939
1.927
1.494
HO
P
2-62
9
8
7
6
5
4
3
2
1
ppm
2.67
6.16
1.94
1.00
8.43
4.22
1.20
3.63
BRUKER
NAME JAM-685-32
EXPNO 10
PROCNO 1
Date_ 20151012
Time 20.44
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 161
DW 62.400 usec
DE 6.50 usec
TE 95.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 13.75 usec
SI 65536
SF 400.1300095 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


7.72
HO
P
2-62
100
50
0
–50
–100
–150
–200
ppm
BRUKER
NAME JAM-685-32
EXPNO 11
PROCNO 1
Date_ 20151012
Time 20.46
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 16
DS 4
SWH 64102.563 Hz
FIDRES 0.978127 Hz
AQ 0.5112308 sec
RG 203
DW 7.800 usec
DE 6.50 usec
TE 95.3 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 161.9674942 MHz
NUC1 31P
P1 13.30 usec
SI 32768
SF 161.9755930 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

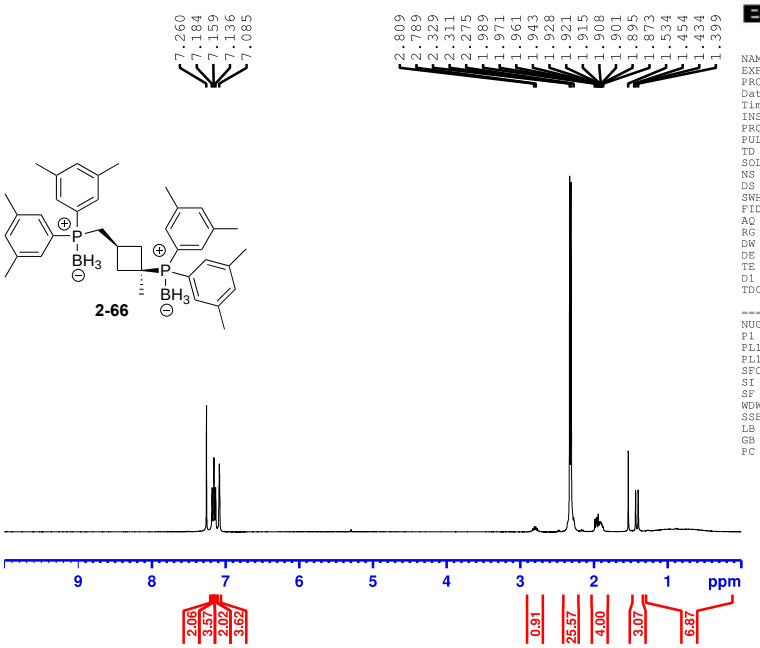

7.977
7.955
7.931
7.916
7.910
7.903
7.898
7.881
7.487
7.465
7.443
7.440
7.426
7.423
7.407
7.403
7.353
7.330
7.309
7.287
7.273
7.260
7.237
7.235
7.166
7.157
7.147
7.138
3.541
3.516
3.375
3.350
2.346
2.068
2.046
2.017
1.963
1.953
1.942
1.931
1.543
1.470
1.438
1.430
2-63
BRUKER
NAME JAM-685-31.2
EXPNO 30
PROCNO 1
Date_ 20151016
Time 9.43
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 128
DW 62.400 usec
DE 6.50 usec
TE 97.8 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 13.75 usec
SI 65536
SF 400.1300098 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9
8
7
6
5
4
3
2
1
ppm
4.25
1.11
2.11
7.39
0.45
3.95
1.00
1.00
0.97
6.04
2.05
2.14
3.42


148.55
148.50
147.53
138.56
138.51
134.73
134.23
134.11
134.05
133.99
132.95
132.94
132.83
132.61
132.50
131.00
130.34
129.86
129.10
128.83
128.36
128.30
127.01
126.25
126.16
125.03
124.85
124.16
124.11
122.71
122.69
121.86
121.69
68.51
68.44
34.73
34.69
34.63
34.55
31.87
31.69
31.61
31.46
31.16
26.93
25.40
25.30
25.26
22.68
21.35
20.73
14.15
2-63
BRUKER
NAME JAM-685-31
EXPNO 1
PROCNO 1
Date_ 20151021
Time 7.52
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 10200
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 50.8
DW 20.800 usec
DE 6.50 usec
TE 296.3 K
D1 3.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 -0.44 dB
PL1W 39.19395828 W
SFO1 100.6479773 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.90 dB
PL12 15.81 dB
PL13 120.00 dB
PL2W 21.64248466 W
PL12W 0.23137002 W
PL13W 0.00000000 W
SFO2 400.2316009 MHz
SI 32768
SF 100.6379140 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
180
160
140
120
100
80
60
40
20
ppm



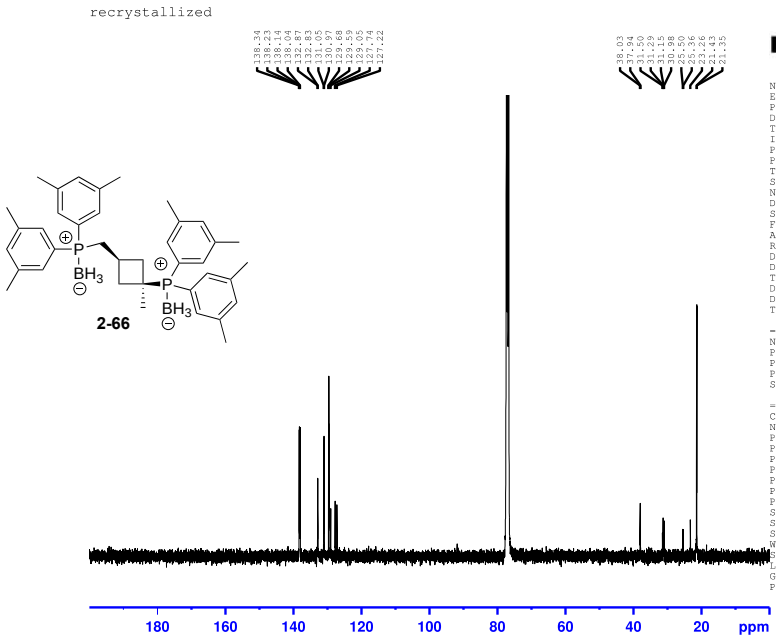

```
NAME            JAM-685-31.2
EXPNO                     31
PROCNO                     1
Date_               20151016
Time                    9.45
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG               zgpg30
TD                     65536
SOLVENT                CDCl3
NS                        16
DS                         4
SWH                64102.563 Hz
FIDRES             0.978127 Hz
AQ                 0.5112308 sec
RG                       203
DW                   7.800 usec
DE                    6.50 usec
TE                    97.8 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1             161.9674942 MHz
NUC1                     31P
P1                    13.30 usec
SI                     32768
SF               161.9755930 MHz
WDW                       EM
SSB                        0
LB                    1.00 Hz
GB                         0
PC                    1.40
```

recrystallized



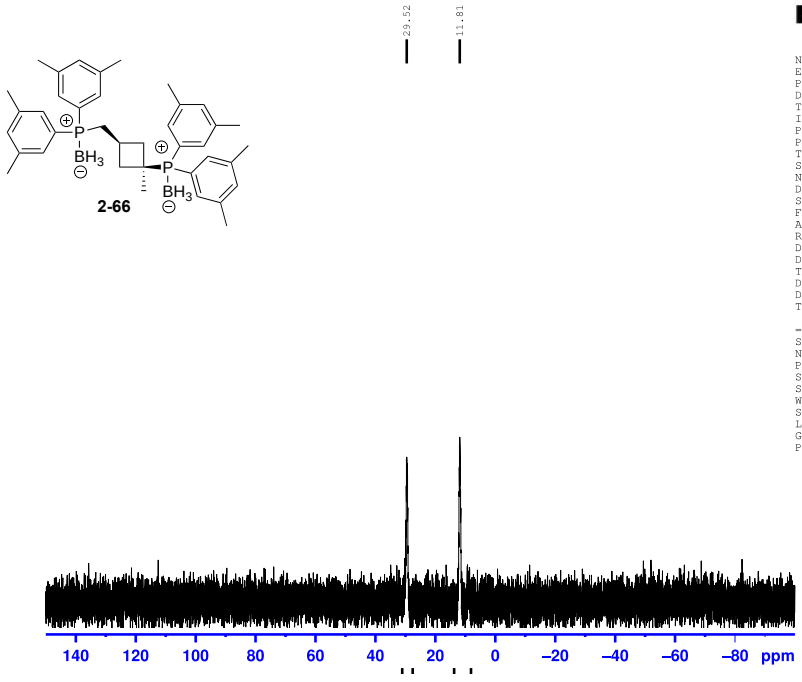

```
NAME            JAM-691-43
EXPNO                     1
PROCNO                    1
Date_               20160109
Time                   14.51
INSTRUM                spect
PROBHD    5 mm PADUL 13C
PULPROG                zg30
TD                     65536
SOLVENT                CDCl3
NS                        16
DS                         2
SWH                8223.685 Hz
FIDRES             0.125483 Hz
AQ                 3.9846387 sec
RG                       144
DW                   60.800 usec
DE                    6.50 usec
TE                    299.9 K
D1                2.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                    9.31 usec
PL1                  -3.90 dB
PL1W            21.64248466 W
SFO1            400.2324716 MHz
SI                     32768
SF              400.2300095 MHz
WDW                       EM
SSB                        0
LB                    0.30 Hz
GB                         0
PC                    1.00
```

recrystallized



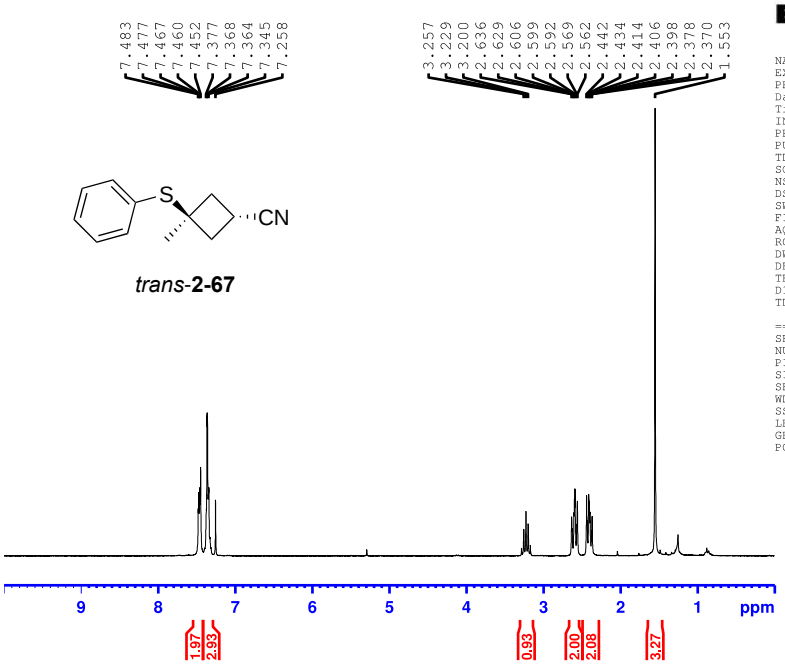
BRUKER

```
NAME                JAM-691-43
EXPNO                        2
PROCNO                       1
Date_             20160110
Time                      8.11
INSTRUM                  spect
PROBHD     5 mm PADUL 13C
PULPROG                  zgpg30
TD                        65536
SOLVENT                   CDCl3
NS                        14000
DS                           4
SWH                  24038.461 Hz
FIDRES                0.366798 Hz
AQ                    1.3631988 sec
RG                           64
DW                       20.800 usec
DE                        6.50 usec
TE                       295.4 K
D1                    3.00000000 sec
D11                   0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                       13C
P1                       10.00 usec
PL1                      -0.44 dB
PL1W                39.19395828 W
SFO1                100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                    90.00 usec
PL2                      -3.90 dB
PL12                     15.81 dB
PL13                    120.00 dB
PL2W                21.64248466 W
PL12W                0.23137002 W
PL13W                0.00000000 W
SFO2                400.2316009 MHz
SI                        32768
SF                  100.6379140 MHz
WDW                          EM
SSB                           0
LB                         1.00 Hz
GB                            0
PC                         1.40
```



BRUKER

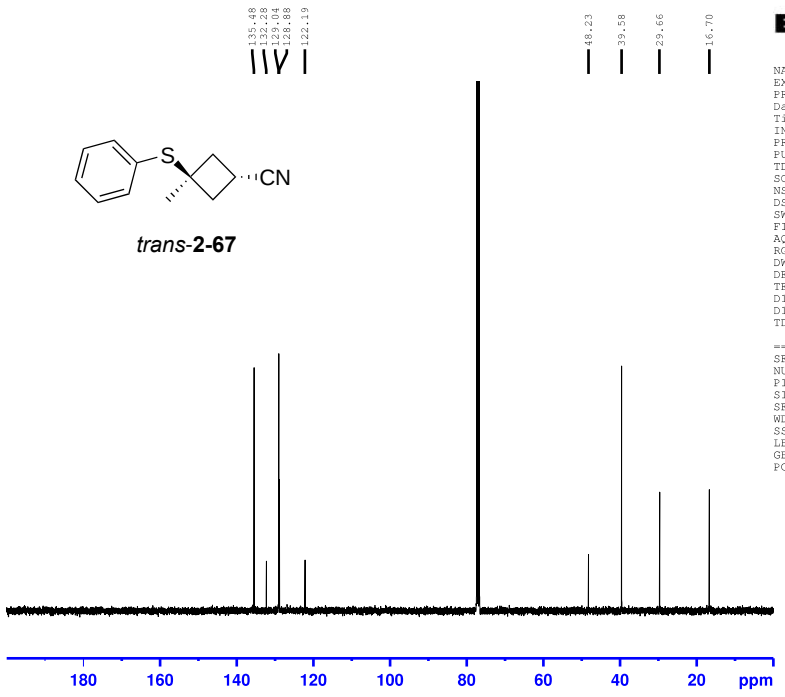
```
NAME                JAM-691-43
EXPNO                       11
PROCNO                       1
Date_             20151225
Time                      1.41
INSTRUM                  spect
PROBHD     5 mm PABBO BB/
PULPROG                  zgpg30
TD                        65536
SOLVENT                   CDCl3
NS                           16
DS                            4
SWH                  81521.742 Hz
FIDRES                1.243923 Hz
AQ                    0.4020041 sec
RG                          203
DW                        6.133 usec
DE                        6.50 usec
TE                       297.8 K
D1                    2.00000000 sec
D11                   0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1                202.4583558 MHz
NUC1                       31P
P1                       11.50 usec
SI                        32768
SF                  202.4684792 MHz
WDW                          EM
SSB                           0
LB                         1.00 Hz
GB                            0
PC                         1.40
```



trans-**2-67**

BRUKER

```
NAME                JAM-704-71
EXPNO                       20
PROCNO                       1
Date_             20160321
Time                     16.09
INSTRUM                  spect
PROBHD    5 mm QNP  1H/1
PULPROG                  zg30
TD                      32768
SOLVENT                 CDCl3
NS                         16
DS                          2
SWH                 6188.119 Hz
FIDRES              0.188846 Hz
AQ                  2.6477044 sec
RG                        144
DW                     80.800 usec
DE                      6.50 usec
TE                     -925.6 K
D1                  1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1             300.2318540 MHz
NUC1                       1H
P1                      12.71 usec
SI                      32768
SF               300.2300091 MHz
WDW                        EM
SSB                         0
LB                       0.10 Hz
GB                          0
PC                       1.00
```

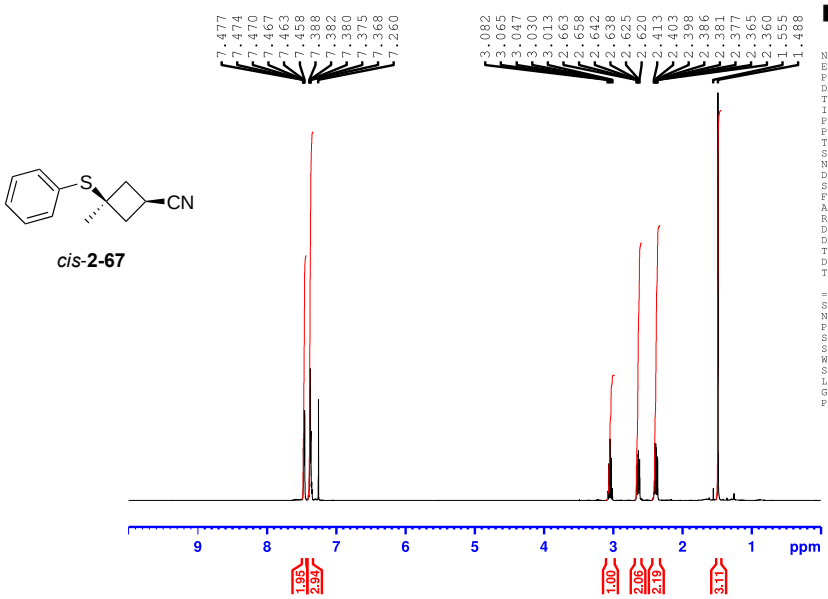


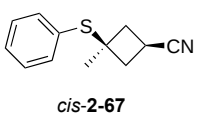
trans-**2-67**

BRUKER

```
NAME                JAM-704-71
EXPNO                       11
PROCNO                       1
Date_             20160322
Time                      1.20
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG                zgpg30
TD                      65536
SOLVENT                 CDCl3
NS                        700
DS                          4
SWH                24038.461 Hz
FIDRES              0.366798 Hz
AQ                  1.3631988 sec
RG                        203
DW                     20.800 usec
DE                      6.50 usec
TE                      94.6 K
D1                  2.00000000 sec
D11                 0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1             100.6228293 MHz
NUC1                       13C
P1                      10.00 usec
SI                      32768
SF               100.6127685 MHz
WDW                        EM
SSB                         0
LB                       1.00 Hz
GB                          0
PC                       1.40
```

more polar isomer

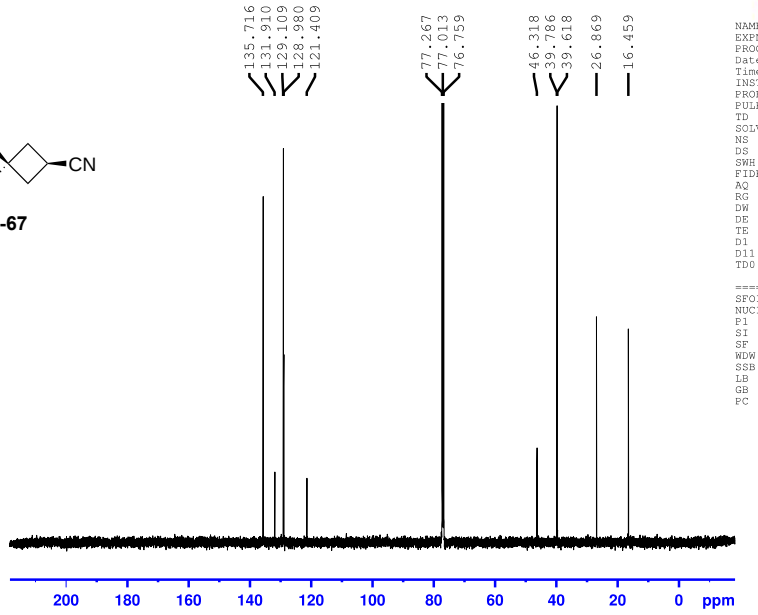




cis-**2-67**

```
NAME              JAM-704-71.2
EXPNO                       10
PROCNO                       1
Date_             20160321
Time                     23.53
INSTRUM                  spect
PROBHD   5 mm PABBO BB/
PULPROG                  zg30
TD                      65536
SOLVENT                 CDCl3
NS                         16
DS                          2
SWH                10000.000 Hz
FIDRES                 0.152588 Hz
AQ                 3.2768500 sec
RG                        161
DW                     50.000 usec
DE                      6.50 usec
TE                     300.2 K
D1                 1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1               500.1630887 MHz
NUC1                       1H
P1                      11.45 usec
SI                      65536
SF                 500.1600129 MHz
WDW                        EM
SSB                         0
LB                      0.30 Hz
GB                          0
PC                      1.00
```

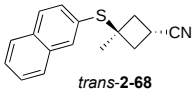
more polar isomer



cis-**2-67**

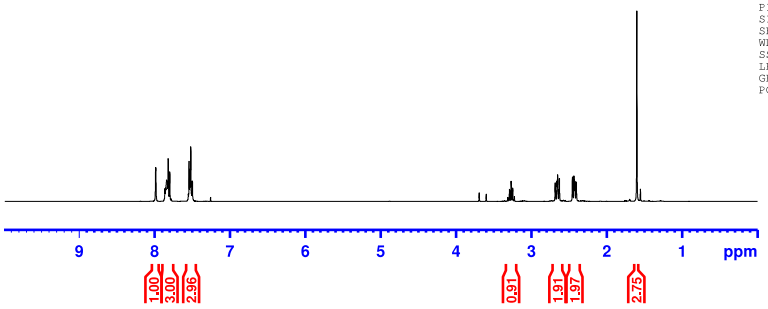
```
NAME              JAM-704-71.2
EXPNO                       11
PROCNO                       1
Date_             20160322
Time                      0.31
INSTRUM                  spect
PROBHD   5 mm PABBO BB/
PULPROG                zgpg30
TD                      65536
SOLVENT                 CDCl3
NS                        700
DS                          2
SWH                29761.904 Hz
FIDRES                 0.454131 Hz
AQ                 1.1010548 sec
RG                        203
DW                     16.800 usec
DE                      6.50 usec
TE                     299.6 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1               125.7779086 MHz
NUC1                       13C
P1                      10.50 usec
SI                      32768
SF                 125.7653320 MHz
WDW                        EM
SSB                         0
LB                      1.00 Hz
GB                          0
PC                      1.40
```

anti isomer

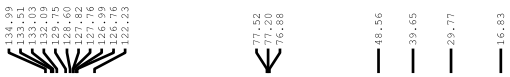


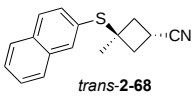
trans-**2-68**

```
NAME                JAM-715-49
EXPNO                       10
PROCNO                       1
Date_                 20160430
Time                     11.26
INSTRUM                  spect
PROBHD     5 mm PABBO BB-
PULPROG                  zg30
TD                      65536
SOLVENT                 CDCl3
NS                         16
DS                          2
SWH                  8012.820 Hz
FIDRES               0.122266 Hz
AQ                   4.0894966 sec
RG                         18
DW                     62.400 usec
DE                      6.50 usec
TE                      95.5 K
D1                  1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1            400.1324710 MHz
NUC1                       1H
P1                      13.75 usec
SI                      65536
SF              400.1300104 MHz
WDW                        EM
SSB                         0
LB                       0.30 Hz
GB                          0
PC                       1.00
```



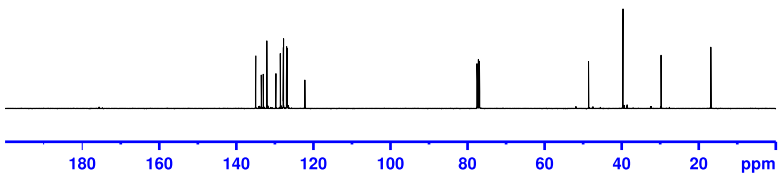
anti isomer



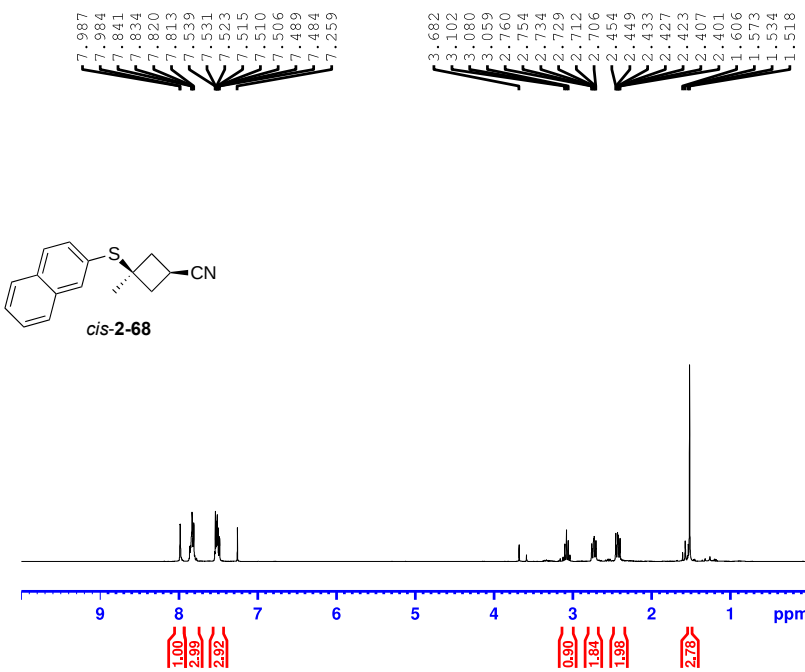


trans-**2-68**

```
NAME                JAM-715-49
EXPNO                       11
PROCNO                       1
Date_                 20160430
Time                     21.04
INSTRUM                  spect
PROBHD     5 mm PABBO BB-
PULPROG                 zgpg30
TD                      65536
SOLVENT                 CDCl3
NS                       1024
DS                          4
SWH                 24038.461 Hz
FIDRES               0.366798 Hz
AQ                   1.3631988 sec
RG                        203
DW                     20.800 usec
DE                      6.50 usec
TE                      95.5 K
D1                  2.00000000 sec
D11                 0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1            100.6228293 MHz
NUC1                       13C
P1                      10.00 usec
SI                      32768
SF              100.6127685 MHz
WDW                        EM
SSB                         0
LB                       1.00 Hz
GB                          0
PC                       1.40
```



syn isomer

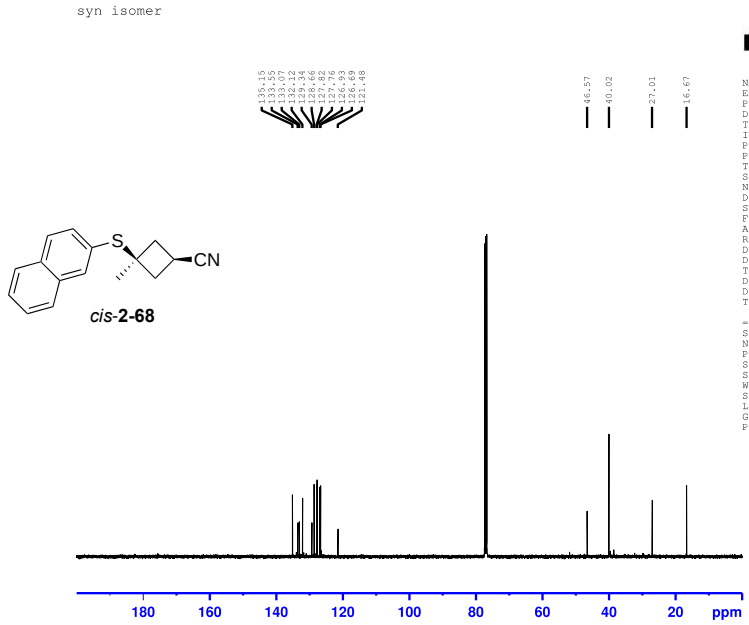


cis-**2-68**

BRUKER

```
NAME            JAM-715-49.2
EXPNO                     10
PROCNO                     1
Date_           20160430
Time                   11.33
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG                zg30
TD                     65536
SOLVENT                CDCl3
NS                        16
DS                         2
SWH                8012.820 Hz
FIDRES                0.122266 Hz
AQ                 4.0894966 sec
RG                      80.6
DW                     62.400 usec
DE                      6.50 usec
TE                      95.6 K
D1                 1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1             400.1324710 MHz
NUC1                       1H
P1                     13.75 usec
SI                     65536
SF               400.1300106 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      1.00
```

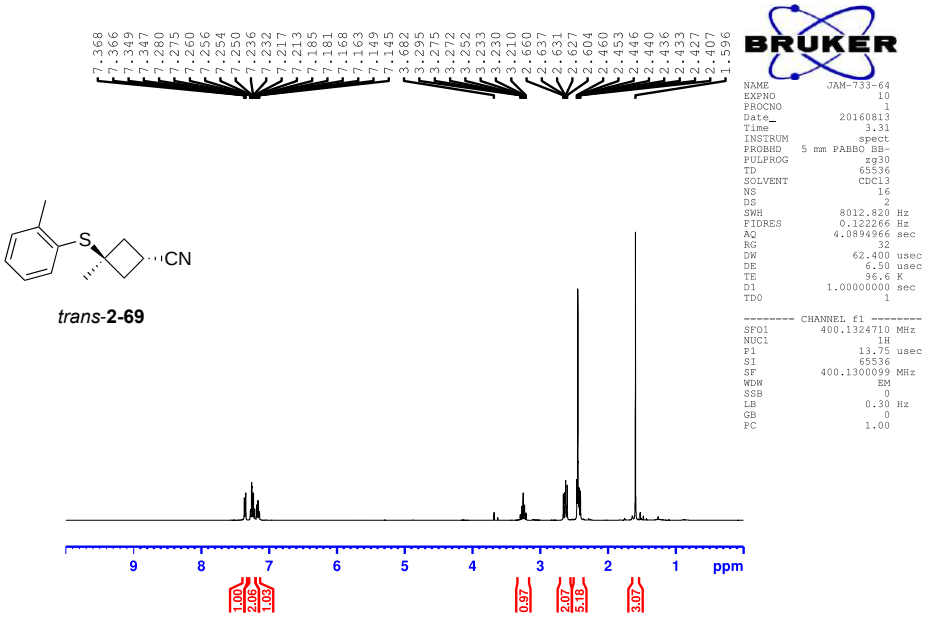
syn isomer

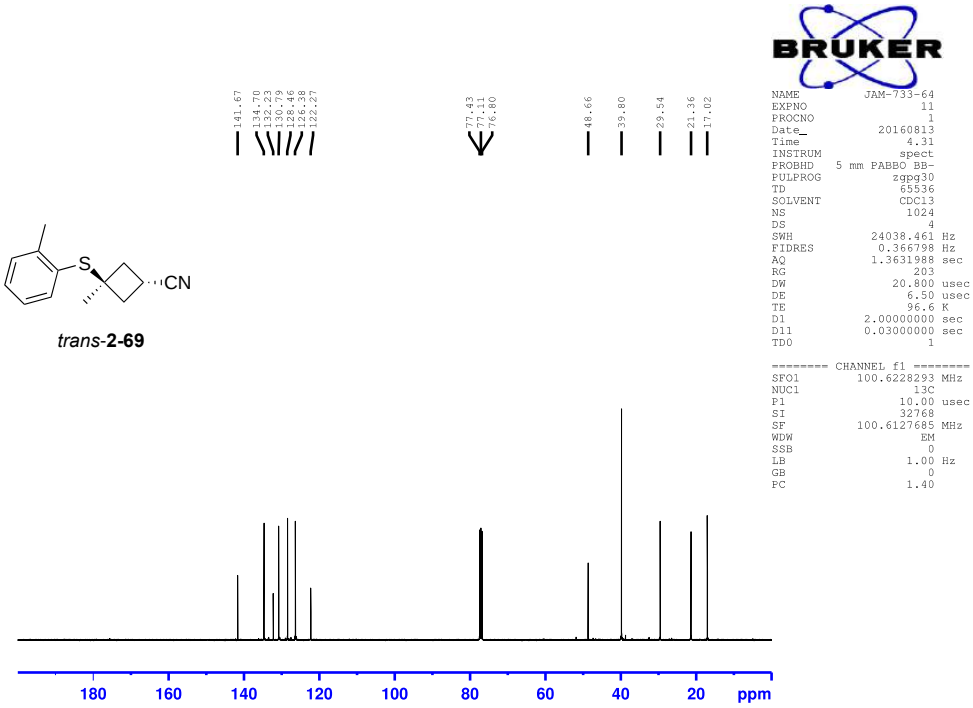


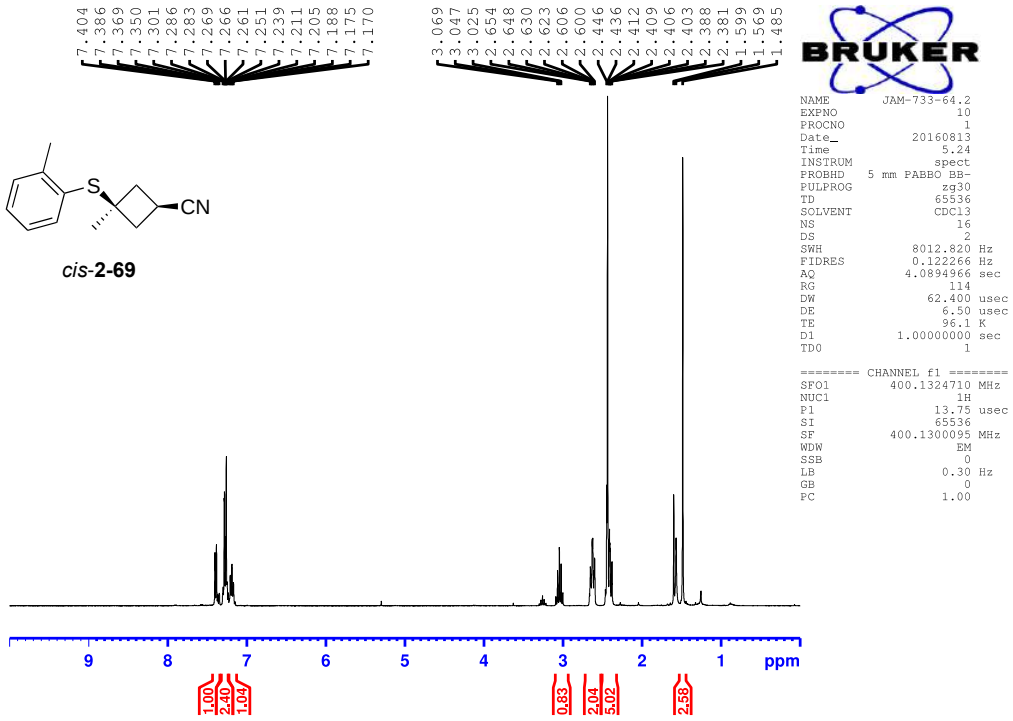
cis-**2-68**

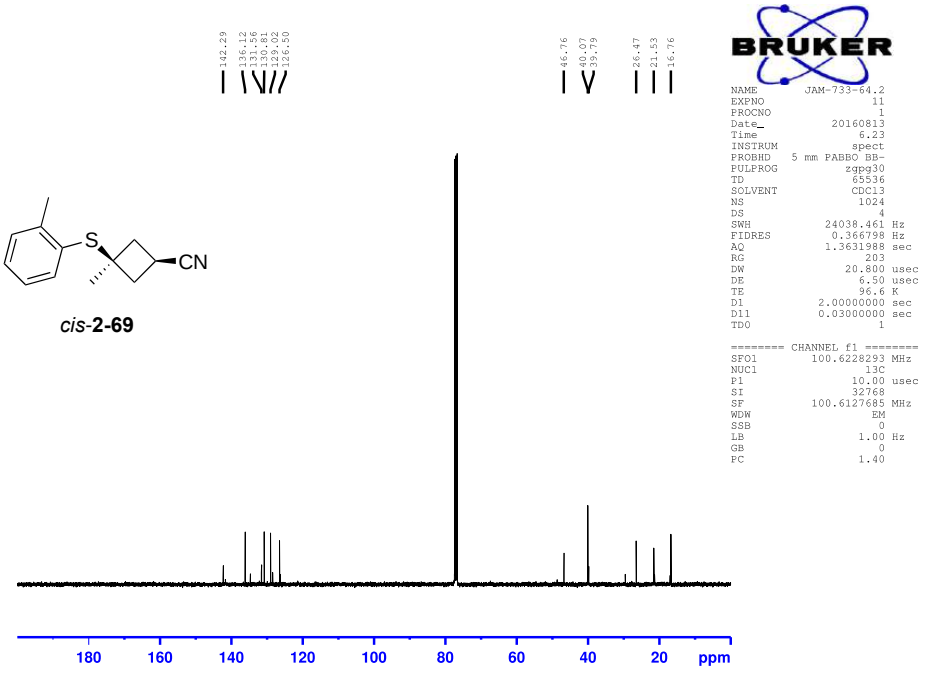
BRUKER

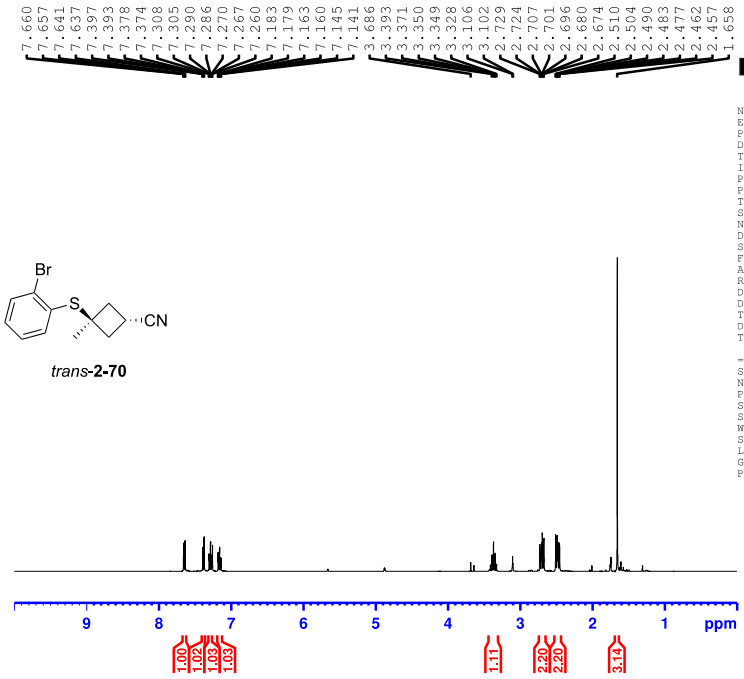
```
NAME            JAM-715-49.2
EXPNO                     11
PROCNO                     1
Date_           20160430
Time                   22.09
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG            zgpg30
TD                     65536
SOLVENT                CDCl3
NS                      1024
DS                         4
SWH               24038.461 Hz
FIDRES                0.366798 Hz
AQ                 1.3631988 sec
RG                       203
DW                     20.800 usec
DE                      6.50 usec
TE                      96.2 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1             100.6228293 MHz
NUC1                       13C
P1                     10.00 usec
SI                     32768
SF               100.6127685 MHz
WDW                       EM
SSB                        0
LB                      1.00 Hz
GB                         0
PC                      1.40
```

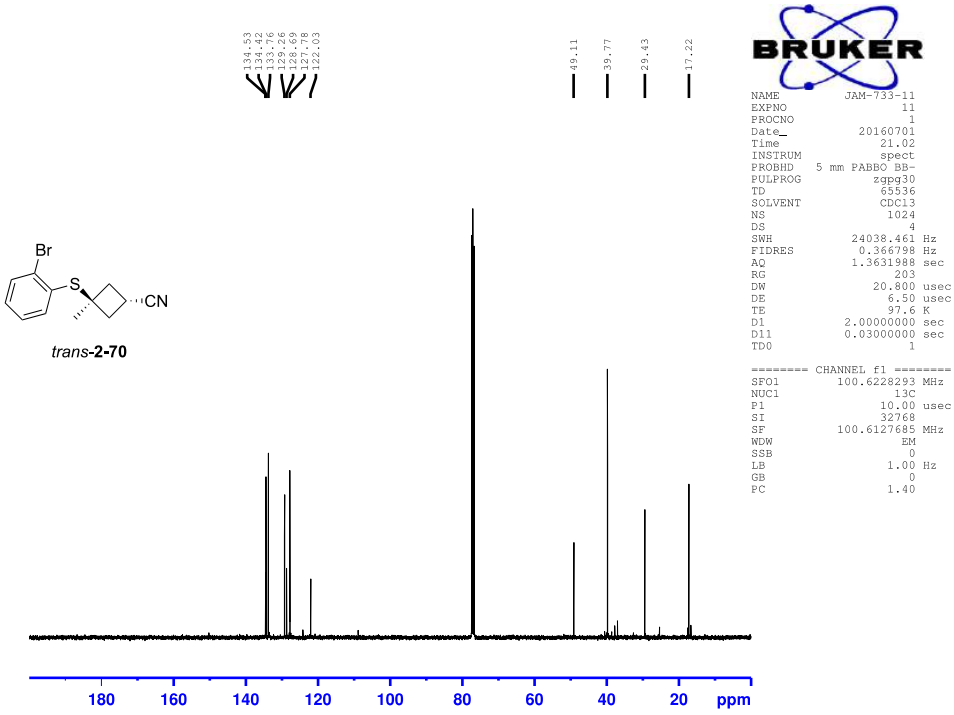

7.368
7.366
7.349
7.347
7.280
7.275
7.260
7.256
7.254
7.250
7.236
7.232
7.217
7.213
7.185
7.181
7.168
7.163
7.149
7.145
3.682
3.295
3.275
3.272
3.252
3.233
3.230
3.210
2.660
2.637
2.631
2.627
2.604
2.460
2.453
2.446
2.440
2.436
2.433
2.427
2.407
1.596
BRUKER
NAME JAM-733-64
EXPNO 10
PROCNO 1
Date_ 20160813
Time 3.31
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 32
DW 62.400 usec
DE 6.50 usec
TE 96.6 K
D1 1.00000000 sec
TD0 1
-------- CHANNEL f1 --------
SFO1 400.1324710 MHz
NUC1 1H
P1 13.75 usec
SI 65536
SF 400.1300099 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
S
CN
trans-2-69
9
8
7
6
5
4
3
2
1
ppm
1.00
2.06
1.03
0.97
2.07
5.18
3.07

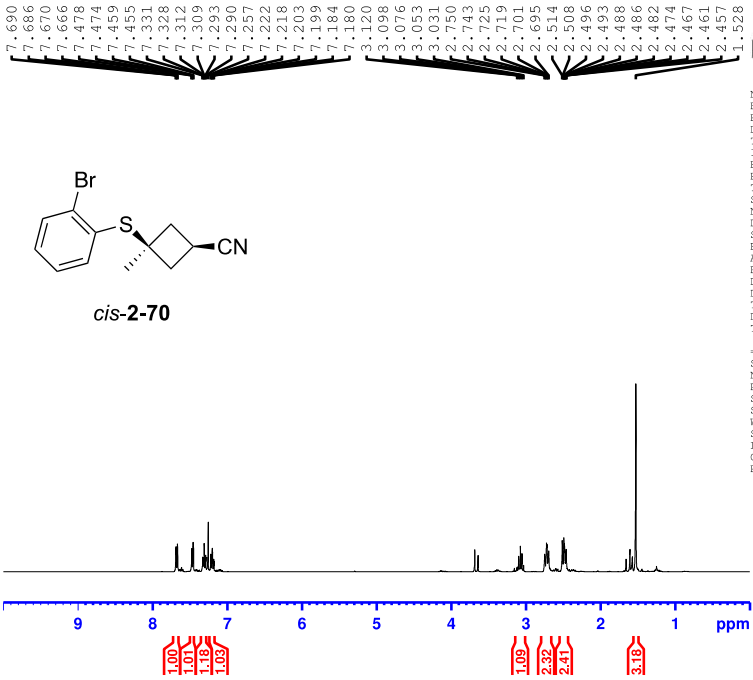

141.67
134.70
132.23
130.79
128.46
128.38
122.27
77.43
77.11
76.80
48.66
39.80
29.54
21.36
17.02
BRUKER
NAME JAM-733-64
EXPNO 11
PROCNO 1
Date_ 20160813
Time 4.31
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 96.6 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
-------- CHANNEL f1 --------
SFO1 100.6228293 MHz
NUC1 13C
P1 10.00 usec
SI 32768
SF 100.6127685 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
S
CN
trans-2-69
180
160
140
120
100
80
60
40
20
ppm

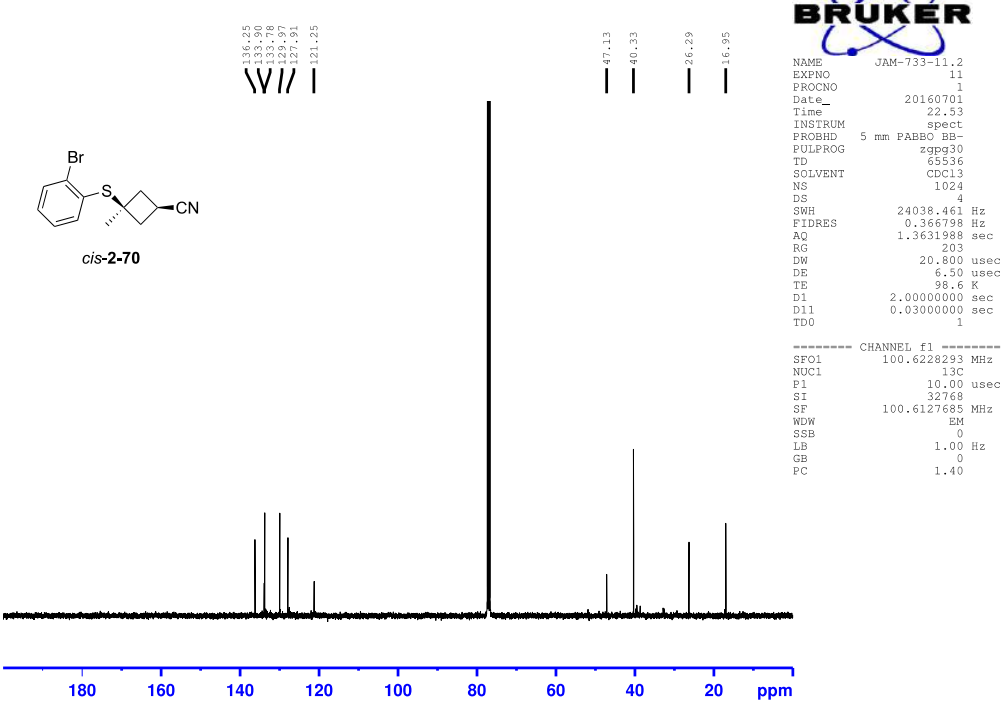

7.404
7.386
7.369
7.350
7.301
7.286
7.283
7.269
7.266
7.261
7.251
7.239
7.211
7.205
7.188
7.175
7.170
3.069
3.047
3.025
2.654
2.648
2.630
2.623
2.606
2.600
2.446
2.436
2.412
2.409
2.406
2.403
2.388
2.381
1.599
1.569
1.485
S
CN
cis-2-69
BRUKER
NAME JAM-733-64.2
EXPNO 10
PROCNO 1
Date_ 20160813
Time 5.24
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 114
DW 62.400 usec
DE 6.50 usec
TE 96.1 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 13.75 usec
SI 65536
SF 400.1300095 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9
8
7
6
5
4
3
2
1
ppm
1.00
2.40
1.04
0.83
2.04
5.02
2.58

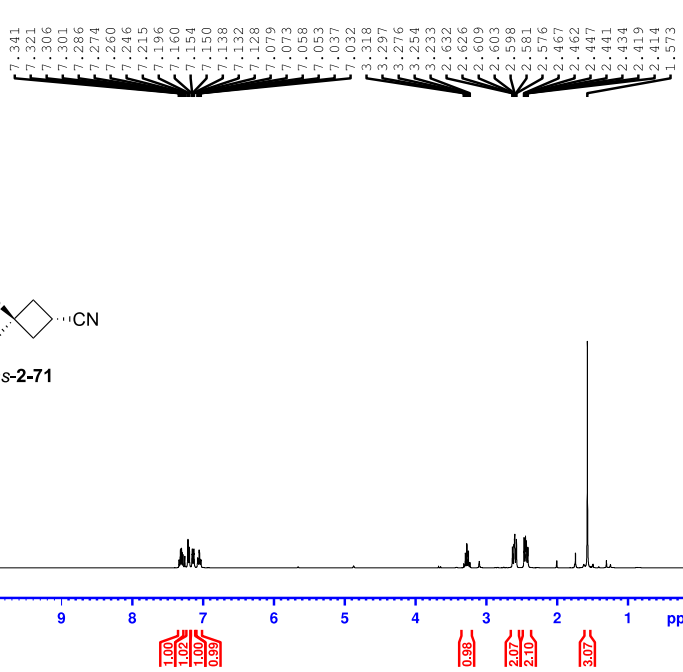

142.29
136.12
131.56
130.81
128.02
126.50
46.76
40.07
39.79
26.47
21.53
16.76
S
CN
cis-2-69
BRUKER
NAME JAM-733-64.2
EXPNO 11
PROCNO 1
Date_ 20160813
Time 6.23
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 96.6 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6228293 MHz
NUC1 13C
P1 10.00 usec
SI 32768
SF 100.6127685 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
180
160
140
120
100
80
60
40
20
ppm


7.660
7.657
7.641
7.637
7.397
7.393
7.378
7.374
7.308
7.305
7.290
7.286
7.270
7.267
7.260
7.183
7.179
7.163
7.160
7.145
7.141
3.686
3.393
3.371
3.350
3.349
3.328
3.106
3.102
2.729
2.724
2.707
2.701
2.696
2.680
2.674
2.510
2.504
2.490
2.483
2.477
2.462
2.457
1.658
BRUKER
NAME JAM-733-11
EXPNO 10
PROCNO 1
Date_ 20160701
Time 16.33
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 80.6
DW 62.400 usec
DE 6.50 usec
TE 96.5 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 13.75 usec
SI 65536
SF 400.1300097 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
Br
S
CN
trans-2-70
9
8
7
6
5
4
3
2
1
ppm
1.00
1.02
1.03
1.09
1.11
2.20
2.26
3.14


134.53
134.42
133.76
129.26
128.60
127.78
122.03
49.11
39.77
29.43
17.22
BRUKER
NAME JAM-733-11
EXPNO 11
PROCNO 1
Date_ 20160701
Time 21.02
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 97.6 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6228293 MHz
NUC1 13C
P1 10.00 usec
SI 32768
SF 100.6127685 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
Br
S
CN
trans-2-70
180
160
140
120
100
80
60
40
20
ppm


7.690
7.686
7.670
7.666
7.478
7.474
7.459
7.455
7.331
7.328
7.312
7.309
7.293
7.290
7.257
7.222
7.218
7.203
7.199
7.184
7.180
3.120
3.098
3.076
3.053
3.031
2.750
2.743
2.725
2.719
2.701
2.695
2.514
2.508
2.496
2.493
2.488
2.486
2.482
2.474
2.467
2.461
2.457
1.528
Br
S
CN
cis-2-70
BRUKER
NAME JAM-733-11.2
EXPNO 10
PROCNO 1
Date_ 20160701
Time 16.38
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 114
DW 62.400 usec
DE 6.50 usec
TE 96.6 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 13.75 usec
SI 65536
SF 400.1300112 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9
8
7
6
5
4
3
2
1
ppm
1.00
1.01
1.18
1.03
1.09
2.32
2.41
3.18

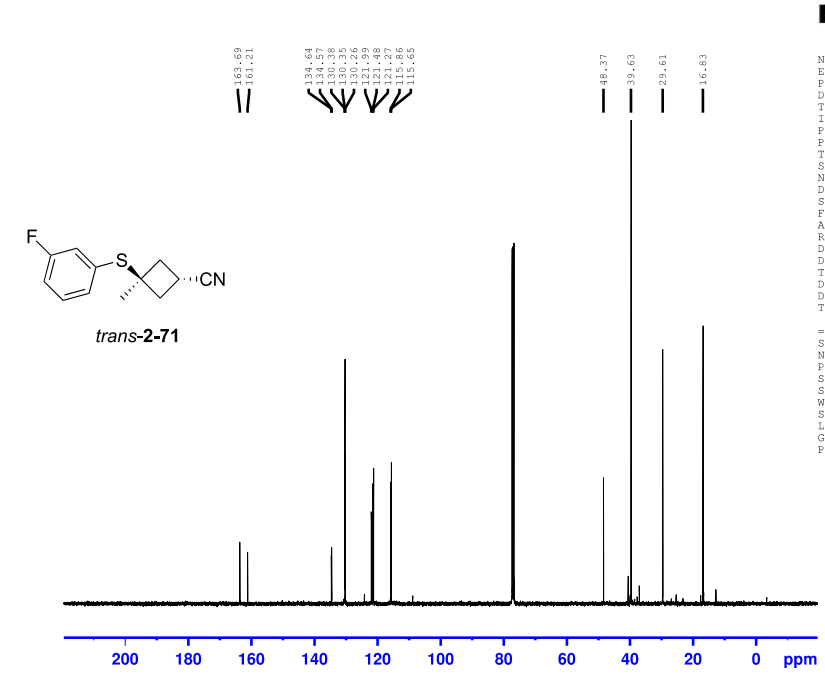

136.25
133.90
133.78
130.07
127.91
121.25
47.13
40.33
26.29
16.95
Br
S
CN
cis-2-70
BRUKER
NAME JAM-733-11.2
EXPNO 11
PROCNO 1
Date_ 20160701
Time 22.53
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 98.6 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6228293 MHz
NUC1 13C
P1 10.00 usec
SI 32768
SF 100.6127685 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
180
160
140
120
100
80
60
40
20
ppm



trans-**2-71**

BRUKER

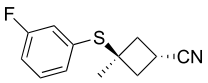
NAME	JAM-733-67
EXPNO	20
PROCNO	1
Date_	20160813
Time	16.33
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	8012.820 Hz
FIDRES	0.122266 Hz
AQ	4.0894966 sec
RG	32
DW	62.400 usec
DE	6.50 usec
TE	95.6 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
SFO1	400.1324710 MHz
NUC1	1H
P1	13.75 usec
SI	65536
SF	400.1300099 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00



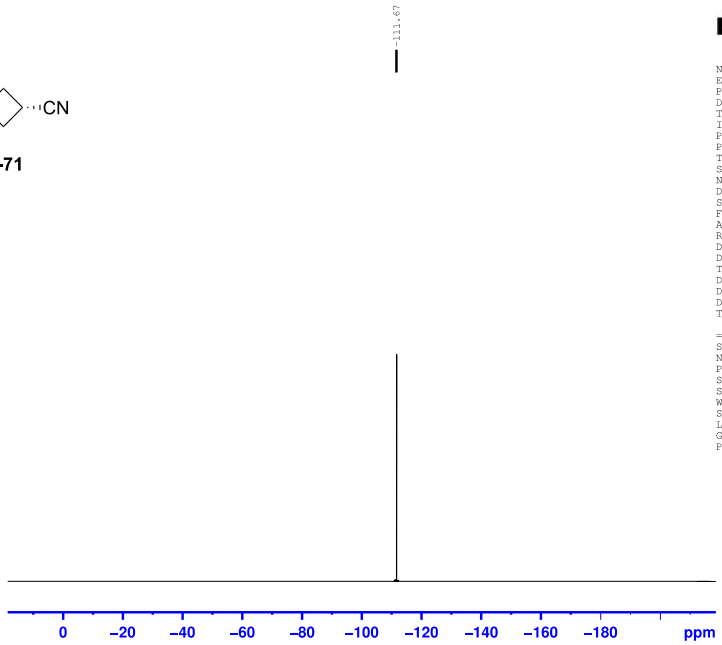
trans-**2-71**

BRUKER

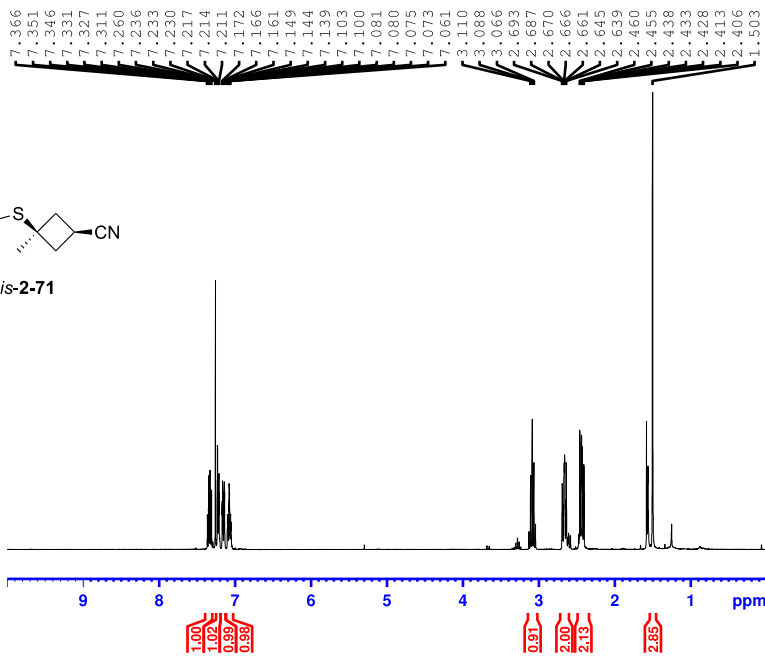
NAME	JAM-733-67
EXPNO	21
PROCNO	1
Date_	20160813
Time	22.56
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	1024
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	96.0 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
SFO1	100.6228293 MHz
NUC1	13C
P1	10.00 usec
SI	32768
SF	100.6127685 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40



trans-**2-71**

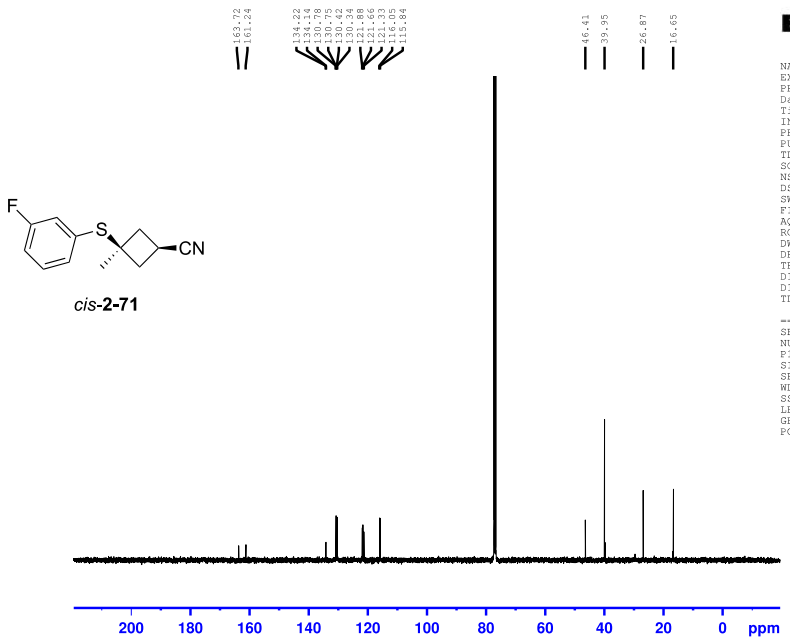



```
NAME                JAM-733-67
EXPNO                       23
PROCNO                       1
Date_                 20160813
Time                     23.45
INSTRUM                  spect
PROBHD     5 mm PABBO BB-
PULPROG           zgfhigqn.2
TD                      131072
SOLVENT                 CDCl3
NS                          16
DS                           4
SWH                  89285.711 Hz
FIDRES               0.681196 Hz
AQ                   0.7340532 sec
RG                         203
DW                     5.600 usec
DE                     6.50 usec
TE                      95.7 K
D1                1.00000000 sec
D11               0.03000000 sec
D12               0.00002000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1               376.4607164 MHz
NUC1                       19F
P1                       14.20 usec
SI                        65536
SF                 376.4983662 MHz
WDW                          EM
SSB                           0
LB                       0.30 Hz
GB                            0
PC                         1.00
```



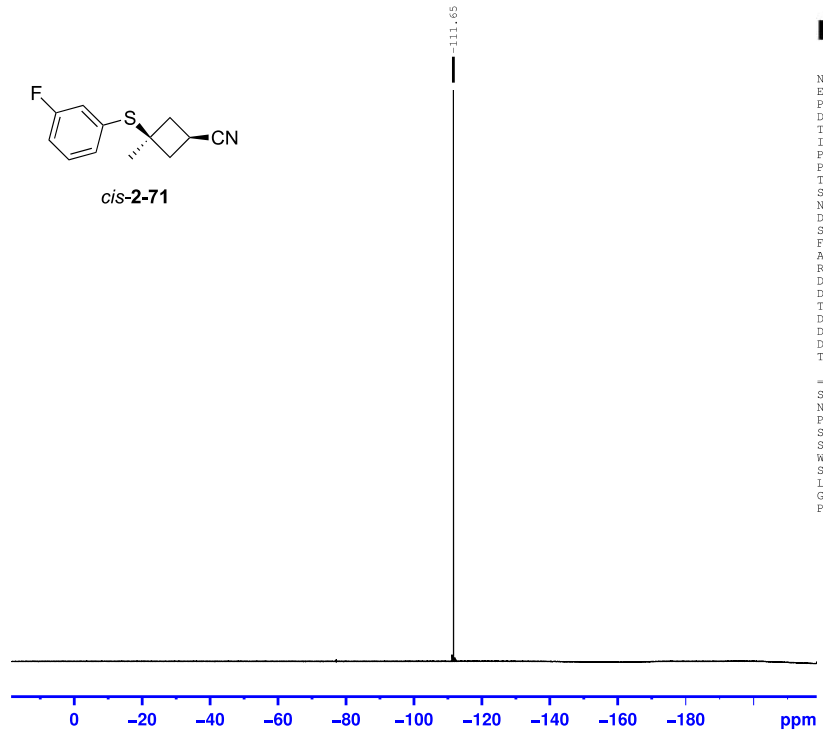
cis-**2-71**

```
NAME                JAM-733-67.2
EXPNO                         10
PROCNO                         1
Date_                   20160813
Time                       16.38
INSTRUM                    spect
PROBHD     5 mm PABBO BB-
PULPROG                    zg30
TD                        65536
SOLVENT                   CDCl3
NS                            16
DS                             2
SWH                    8012.820 Hz
FIDRES                 0.122266 Hz
AQ                     4.0894966 sec
RG                           128
DW                       62.400 usec
DE                        6.50 usec
TE                         95.8 K
D1                  1.00000000 sec
TD0                           1

======== CHANNEL f1 ========
SFO1                 400.1324710 MHz
NUC1                         1H
P1                        13.75 usec
SI                        65536
SF                   400.1300097 MHz
WDW                          EM
SSB                           0
LB                       0.30 Hz
GB                            0
PC                         1.00
```



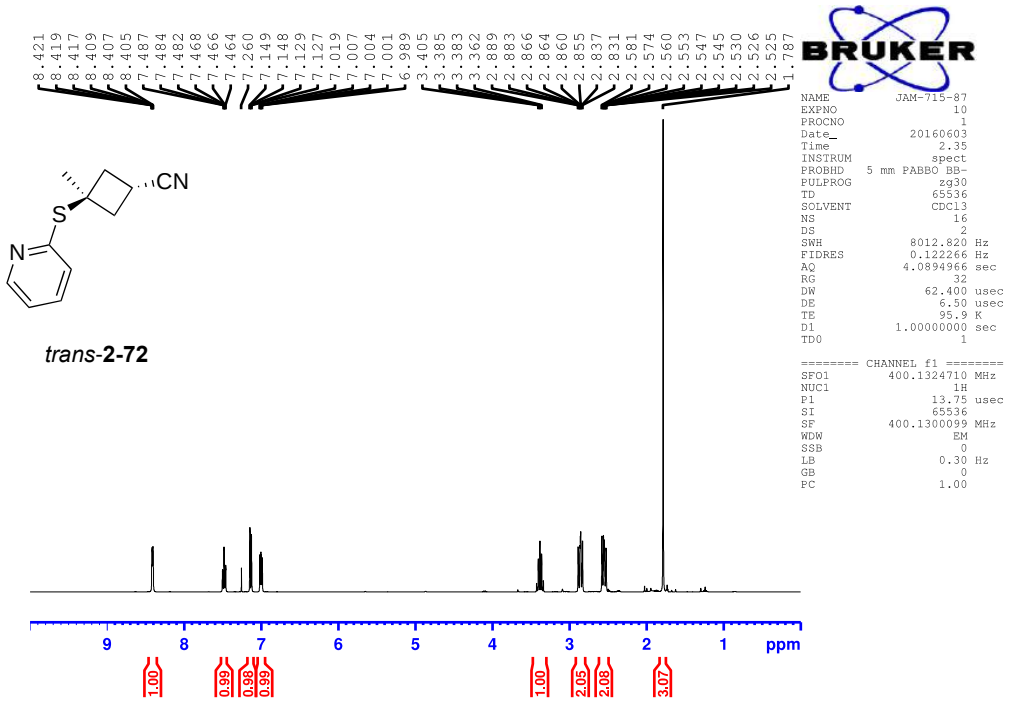
cis-**2-71**

```
NAME            JAM-733-67.2
EXPNO                     11
PROCNO                     1
Date_               20160813
Time                   21.04
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG                zgpg30
TD                      65536
SOLVENT                 CDCl3
NS                       1024
DS                          4
SWH                 24038.461 Hz
FIDRES              0.366798 Hz
AQ                  1.3631988 sec
RG                        203
DW                     20.800 usec
DE                      6.50 usec
TE                     95.6 K
D1                  2.00000000 sec
D11                 0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1               100.6228293 MHz
NUC1                       13C
P1                       10.00 usec
SI                       32768
SF                 100.6127685 MHz
WDW                         EM
SSB                          0
LB                        1.00 Hz
GB                           0
PC                        1.40
```



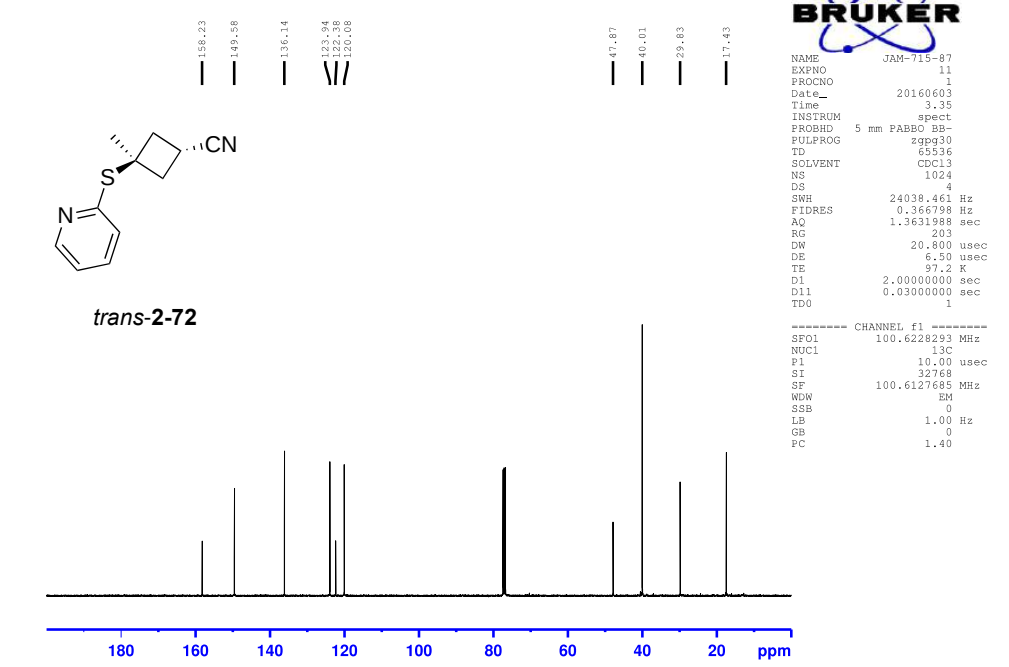
cis-**2-71**

```
NAME            JAM-733-67.2
EXPNO                     13
PROCNO                     1
Date_               20160813
Time                   21.53
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG            zgfhigqn.2
TD                     131072
SOLVENT                 CDCl3
NS                       16
DS                          4
SWH                 89285.711 Hz
FIDRES              0.681196 Hz
AQ                  0.7340532 sec
RG                        203
DW                     5.600 usec
DE                      6.50 usec
TE                     95.6 K
D1                  1.00000000 sec
D11                 0.03000000 sec
D12                 0.00002000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1               376.4607164 MHz
NUC1                       19F
P1                       14.20 usec
SI                       65536
SF                 376.4983662 MHz
WDW                         EM
SSB                          0
LB                        0.30 Hz
GB                           0
PC                        1.00
```



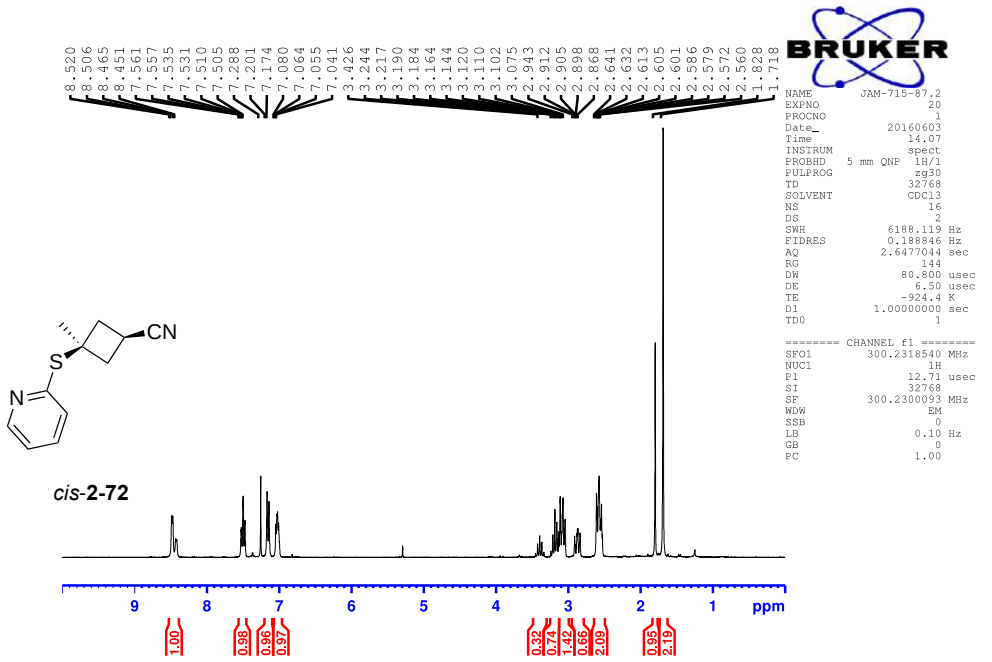
BRUKER

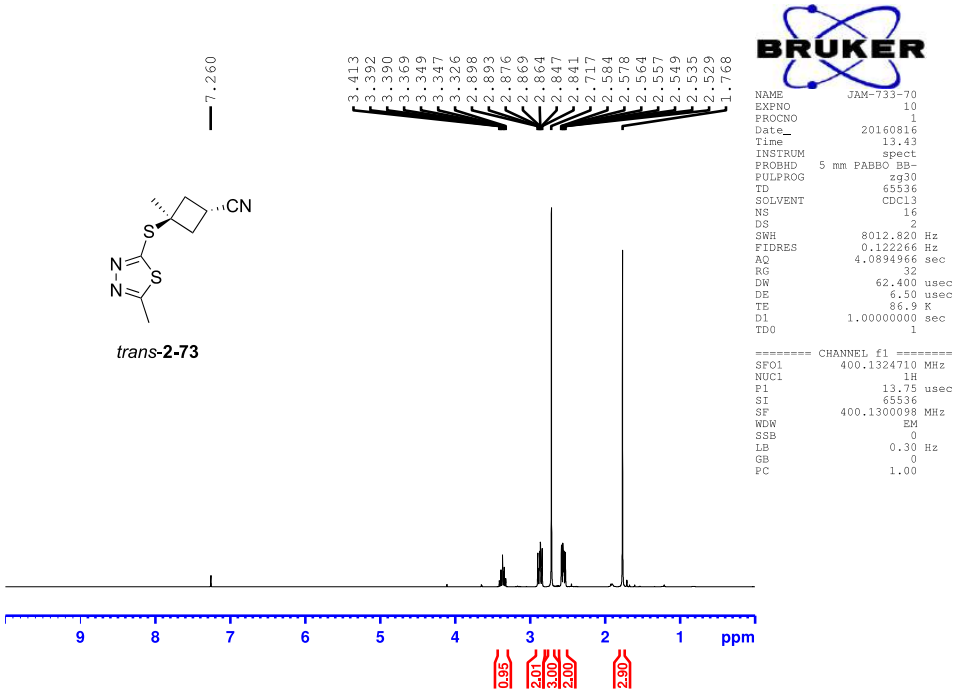
```
NAME                JAM-715-87
EXPNO                       10
PROCNO                       1
Date_             20160603
Time                     2.35
INSTRUM                 spect
PROBHD    5 mm PABBO BB-
PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                        16
DS                         2
SWH                8012.820 Hz
FIDRES                0.122266 Hz
AQ                 4.0894966 sec
RG                        32
DW                    62.400 usec
DE                     6.50 usec
TE                     95.9 K
D1                 1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1             400.1324710 MHz
NUC1                       1H
P1                      13.75 usec
SI                     65536
SF               400.1300099 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      1.00
```

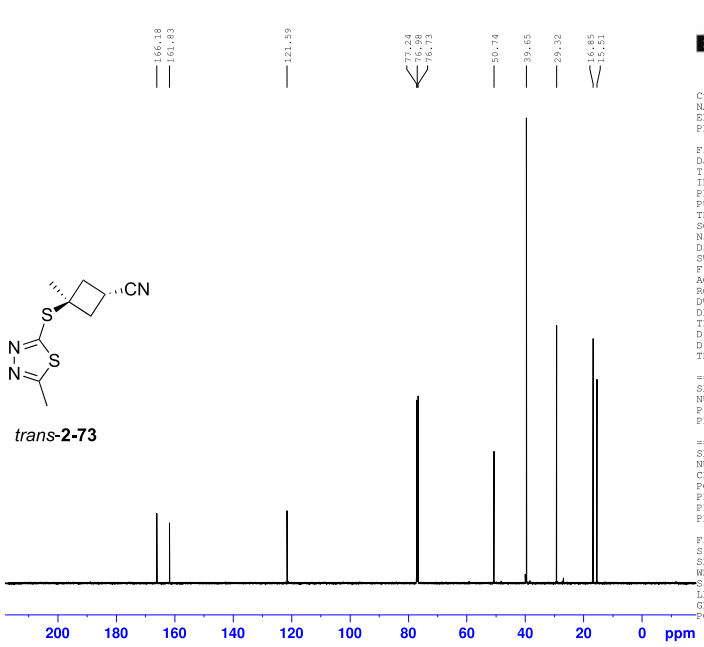


BRUKER

```
NAME                JAM-715-87
EXPNO                       11
PROCNO                       1
Date_             20160603
Time                     3.35
INSTRUM                 spect
PROBHD    5 mm PABBO BB-
PULPROG              zgpg30
TD                     65536
SOLVENT                CDCl3
NS                      1024
DS                         4
SWH               24038.461 Hz
FIDRES                0.366798 Hz
AQ                 1.3631988 sec
RG                       203
DW                    20.800 usec
DE                     6.50 usec
TE                     97.2 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1             100.6228293 MHz
NUC1                       13C
P1                      10.00 usec
SI                     32768
SF               100.6127685 MHz
WDW                       EM
SSB                        0
LB                      1.00 Hz
GB                         0
PC                      1.40
```

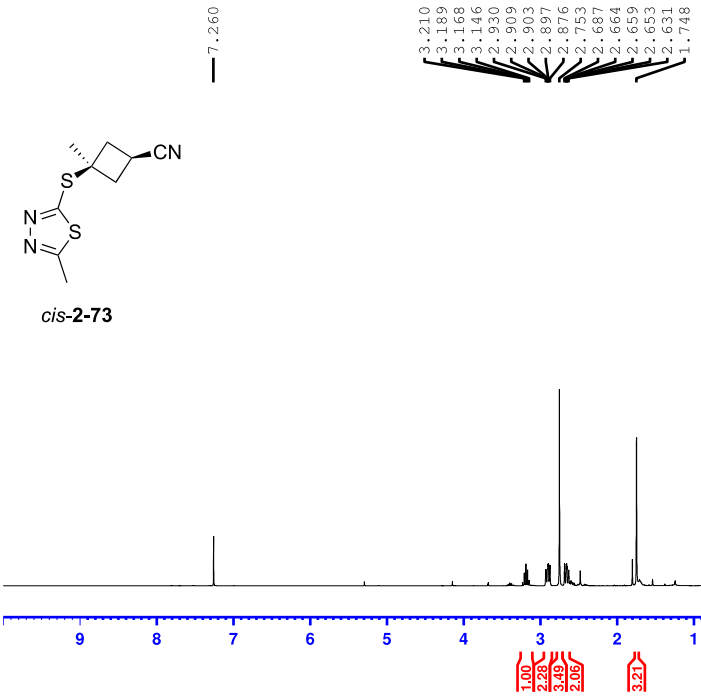

8.520
8.506
8.465
8.451
7.561
7.557
7.535
7.531
7.510
7.505
7.288
7.201
7.174
7.080
7.064
7.055
7.041
3.426
3.244
3.217
3.190
3.184
3.164
3.144
3.120
3.110
3.102
3.075
2.943
2.912
2.905
2.898
2.868
2.641
2.632
2.613
2.605
2.601
2.586
2.579
2.572
2.560
1.828
1.718
CN
S
N
cis-2-72
9
8
7
6
5
4
3
2
1
ppm
1.00
0.98
0.96
0.97
0.32
0.74
1.42
0.66
2.09
0.95
2.19
BRUKER
NAME JAM-715-87.2
EXPNO 20
PROCNO 1
Date_ 20160603
Time 14.07
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.188846 Hz
AQ 2.6477044 sec
RG 144
DW 80.800 usec
DE 6.50 usec
TE -924.4 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 300.2318540 MHz
NUC1 1H
P1 12.71 usec
SI 32768
SF 300.2300093 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00


7.260
3.413
3.392
3.390
3.369
3.349
3.347
3.326
2.898
2.893
2.876
2.869
2.864
2.847
2.841
2.717
2.584
2.578
2.564
2.557
2.549
2.535
2.529
1.768
CN
S
N
N
S
trans-2-73
9
8
7
6
5
4
3
2
1
ppm
0.95
2.01
3.00
2.00
2.90
BRUKER
NAME JAM-733-70
EXPNO 10
PROCNO 1
Date_ 20160816
Time 13.43
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 32
DW 62.400 usec
DE 6.50 usec
TE 86.9 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 13.75 usec
SI 65536
SF 400.1300098 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



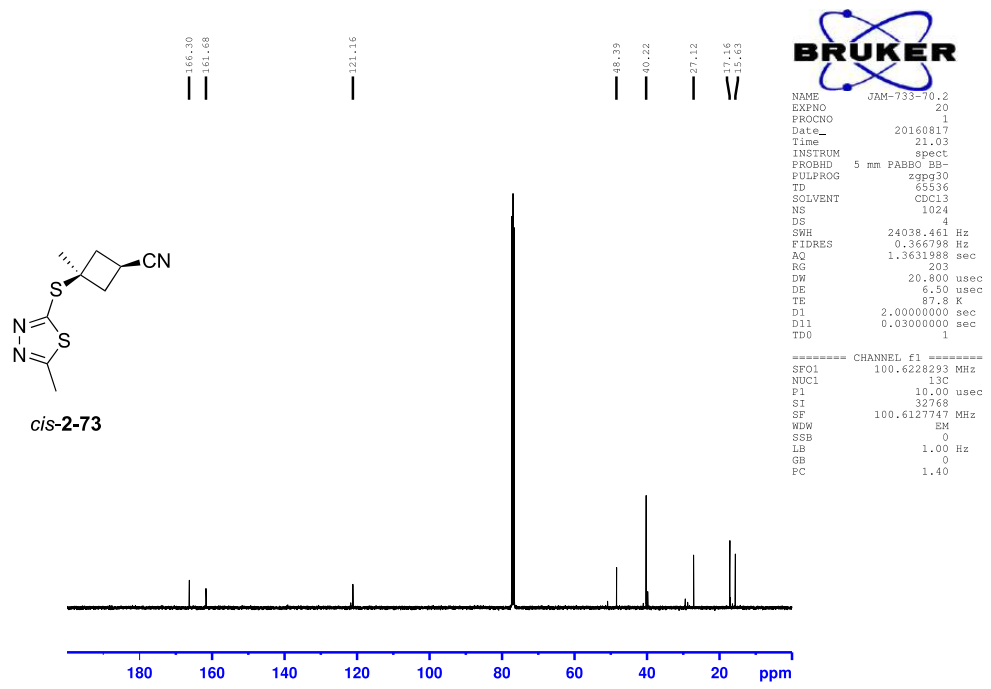
trans-**2-73**

```
Current Data Parameters
NAME          JAM-733-70
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160817
Time                1.55
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  650
DS                    2
SWH           29761.904 Hz
FIDRES         0.454131 Hz
AQ            1.1010048 sec
RG                  203
DW               16.800 usec
DE                6.50 usec
TE               296.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        125.7779086 MHz
NUC1                13C
P1                10.50 usec
PLW1       110.00000000 W

======== CHANNEL f2 ========
SFO2        500.1620006 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             80.00 usec
PLW2        18.00000000 W
PLW12        0.37195000 W
PLW13        0.23805000 W

F2 - Processing parameters
SI                 32768
SF          125.7653521 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```



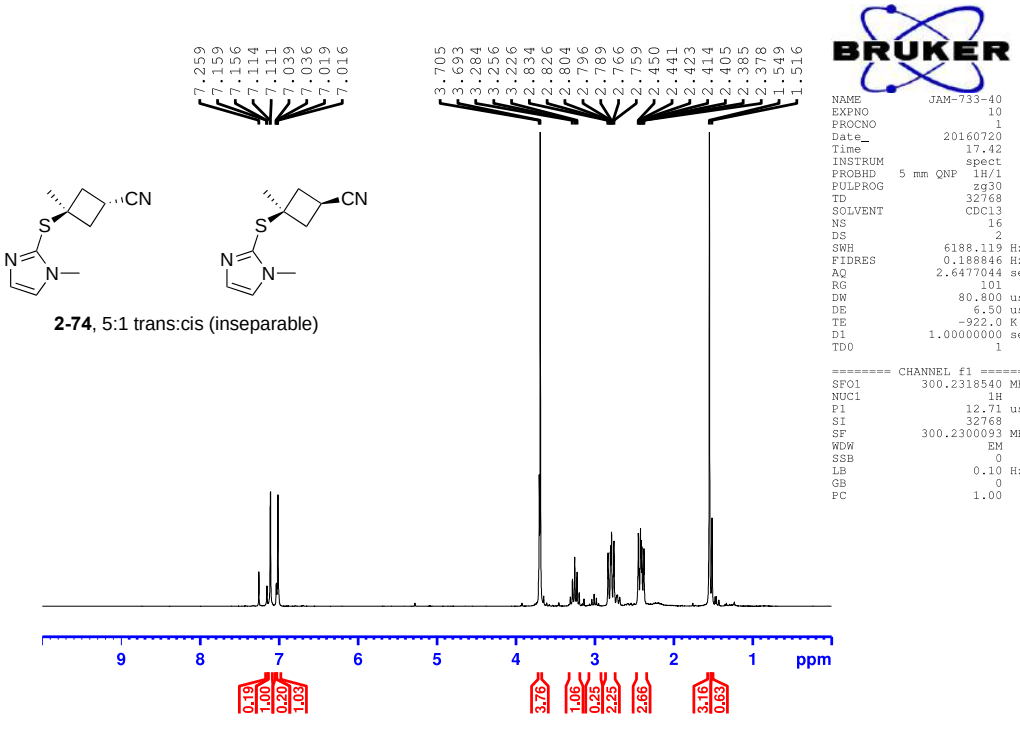
cis-**2-73**

```
NAME          JAM-733-70.2
EXPNO                 10
PROCNO                 1
Date_           20160816
Time               13.48
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            8012.820 Hz
FIDRES         0.122266 Hz
AQ             4.0894966 sec
RG                  114
DW               62.400 usec
DE                6.50 usec
TE                86.8 K
D1             1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        400.1324710 MHz
NUC1                1H
P1                13.75 usec
SI                65536
SF          400.1300098 MHz
WDW                   EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```



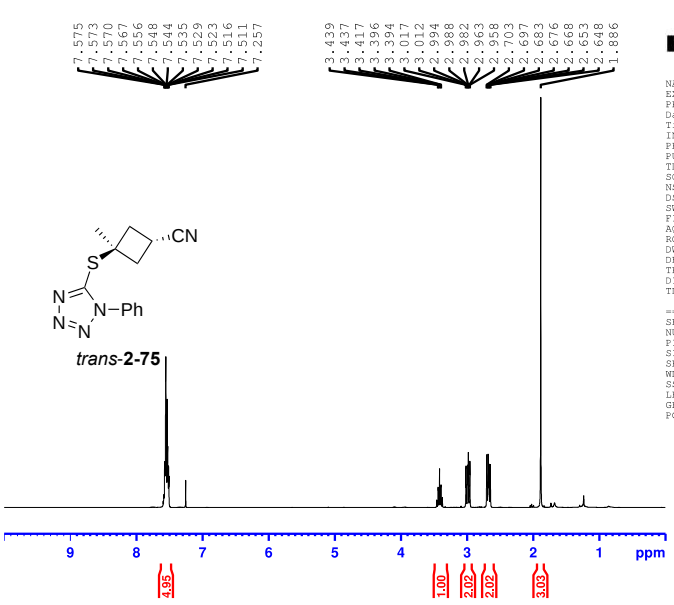
cis-**2-73**

```
NAME            JAM-733-70.2
EXPNO                     20
PROCNO                     1
Date_               20160817
Time                   21.03
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG             zgpg30
TD                     65536
SOLVENT                CDCl3
NS                      1024
DS                         4
SWH                24038.461 Hz
FIDRES                 0.366798 Hz
AQ                 1.3631988 sec
RG                       203
DW                    20.800 usec
DE                     6.50 usec
TE                     87.8 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1             100.6228293 MHz
NUC1                     13C
P1                    10.00 usec
SI                       32768
SF               100.6127747 MHz
WDW                       EM
SSB                        0
LB                      1.00 Hz
GB                         0
PC                      1.40
```



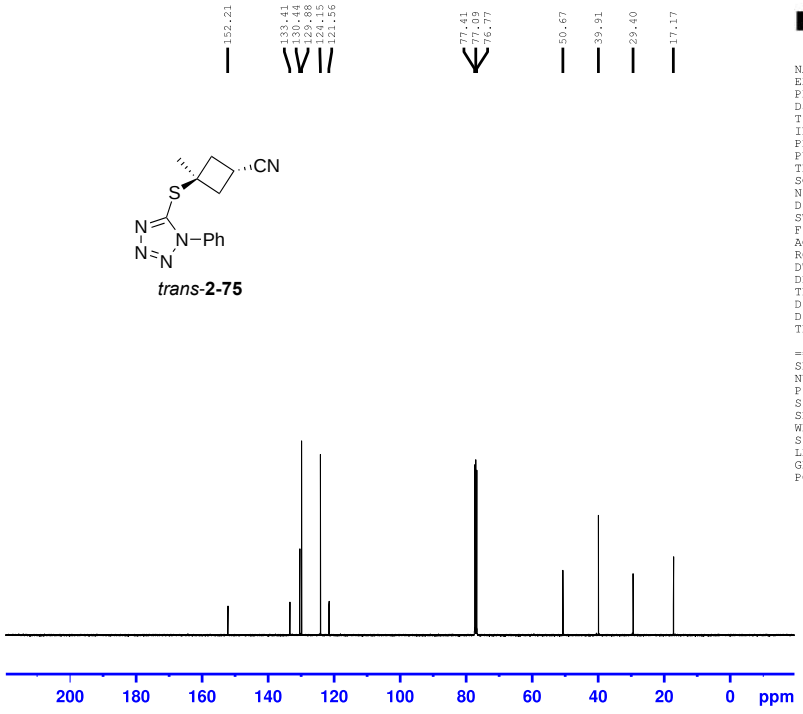
2-74, 5:1 trans:cis (inseparable)

```
NAME            JAM-733-40
EXPNO                     10
PROCNO                     1
Date_               20160720
Time                   17.42
INSTRUM                spect
PROBHD    5 mm QNP  1H/1
PULPROG                zg30
TD                     32768
SOLVENT                CDCl3
NS                        16
DS                         2
SWH                6188.119 Hz
FIDRES                 0.188846 Hz
AQ                 2.6477044 sec
RG                       101
DW                    80.800 usec
DE                     6.50 usec
TE                    -922.0 K
D1                 1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1             300.2318540 MHz
NUC1                      1H
P1                    12.71 usec
SI                       32768
SF               300.2300093 MHz
WDW                       EM
SSB                        0
LB                      0.10 Hz
GB                         0
PC                      1.00
```



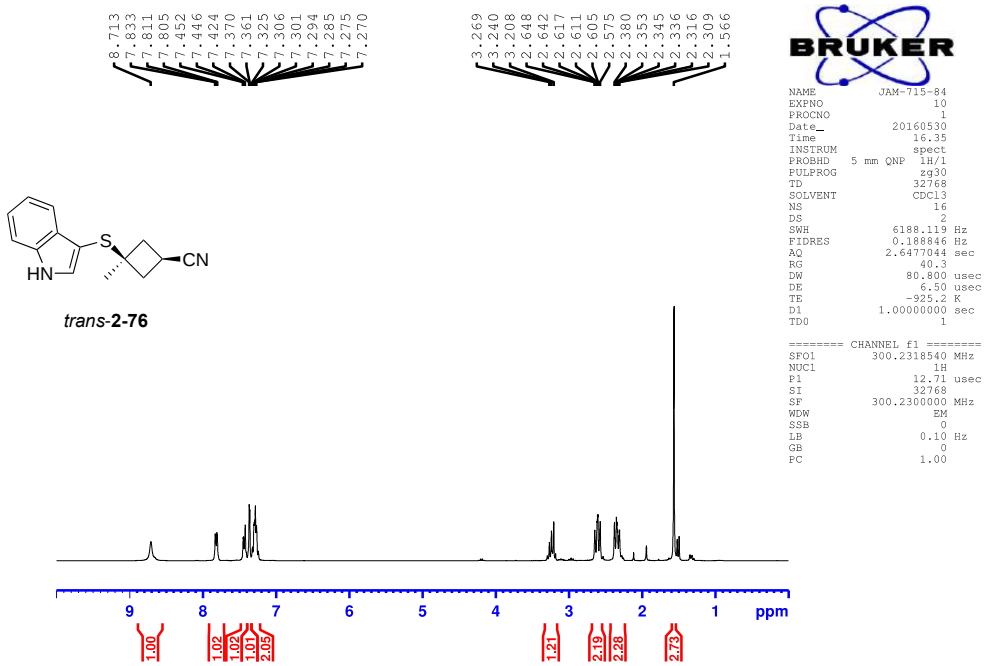
BRUKER

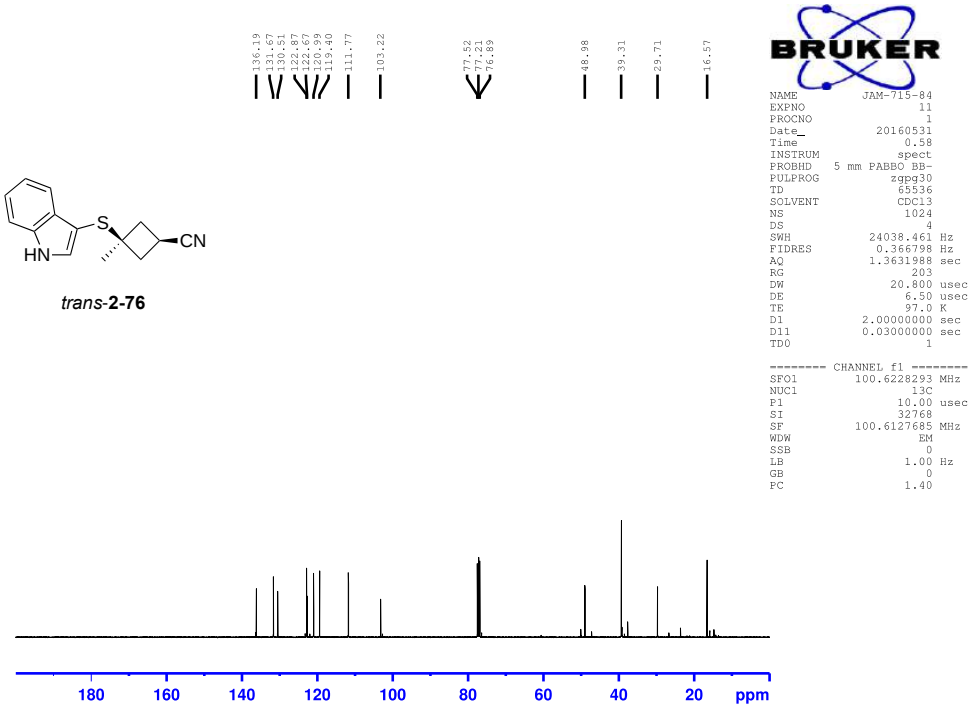
```
NAME              JAM-733-52
EXPNO                 10
PROCNO                 1
Date_           20160804
Time                13.49
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ              4.0894966 sec
RG                    64
DW                62.400 usec
DE                 6.50 usec
TE                 96.2 K
D1              1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1          400.1324710 MHz
NUC1                  1H
P1                13.75 usec
SI                 65536
SF            400.1300110 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

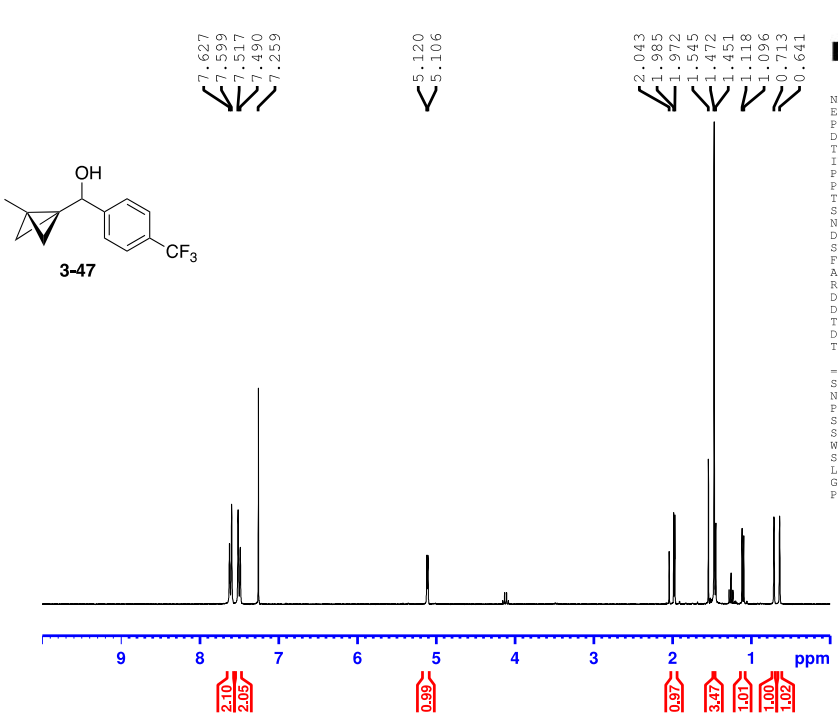


BRUKER

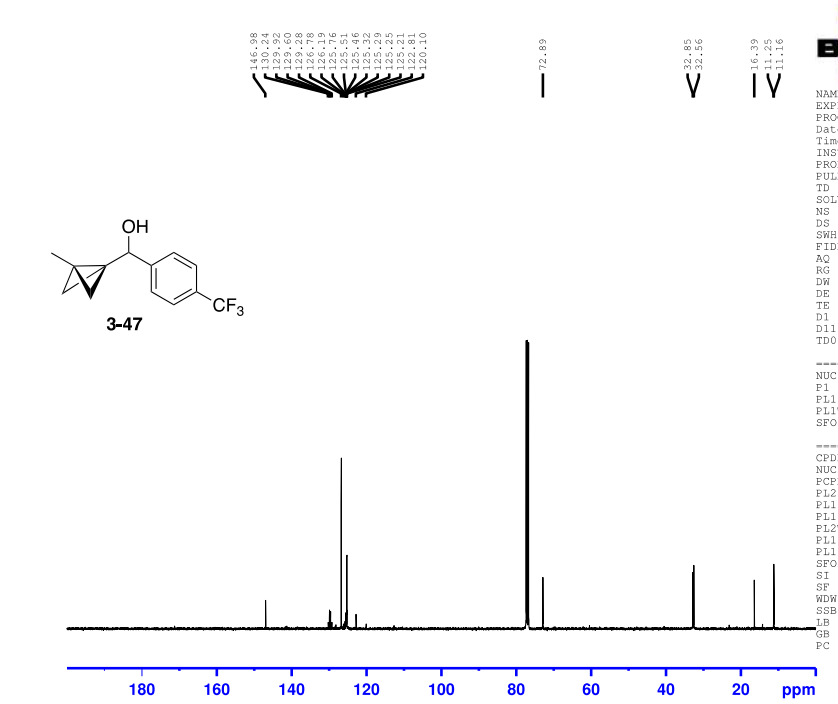
```
NAME              JAM-733-52
EXPNO                 12
PROCNO                 1
Date_           20160804
Time                21.50
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  1024
DS                     4
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ              1.3631988 sec
RG                   203
DW                20.800 usec
DE                 6.50 usec
TE                 97.4 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1          100.6228293 MHz
NUC1                  13C
P1                10.00 usec
SI                 32768
SF            100.6127685 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```


8.713
7.833
7.811
7.805
7.452
7.446
7.424
7.370
7.361
7.325
7.306
7.301
7.294
7.285
7.275
7.270
3.269
3.240
3.208
2.648
2.642
2.617
2.611
2.605
2.575
2.380
2.353
2.345
2.336
2.316
2.309
1.566
BRUKER
NAME JAM-715-84
EXPNO 10
PROCNO 1
Date_ 20160530
Time 16.35
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.188846 Hz
AQ 2.6477044 sec
RG 40.3
DW 80.800 usec
DE 6.50 usec
TE -925.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 300.2318540 MHz
NUC1 1H
P1 12.71 usec
SI 32768
SF 300.2300000 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00
HN
S
CN
trans-2-76
9
8
7
6
5
4
3
2
1
ppm
1.00
1.02
1.02
1.01
2.05
1.21
2.19
2.28
2.73

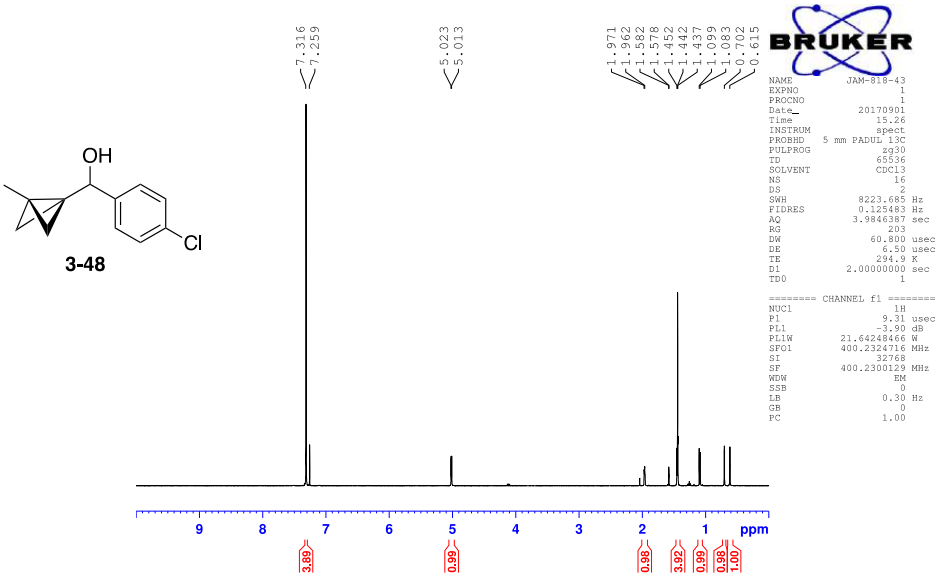

136.19
131.67
130.51
122.87
122.67
120.99
119.40
111.77
103.22
77.52
77.21
76.89
48.98
39.31
29.71
16.57
BRUKER
NAME JAM-715-84
EXPNO 11
PROCNO 1
Date_ 20160531
Time 0.58
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 97.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6228293 MHz
NUC1 13C
P1 10.00 usec
SI 32768
SF 100.6127685 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
HN
S
CN
trans-2-76
180
160
140
120
100
80
60
40
20
ppm

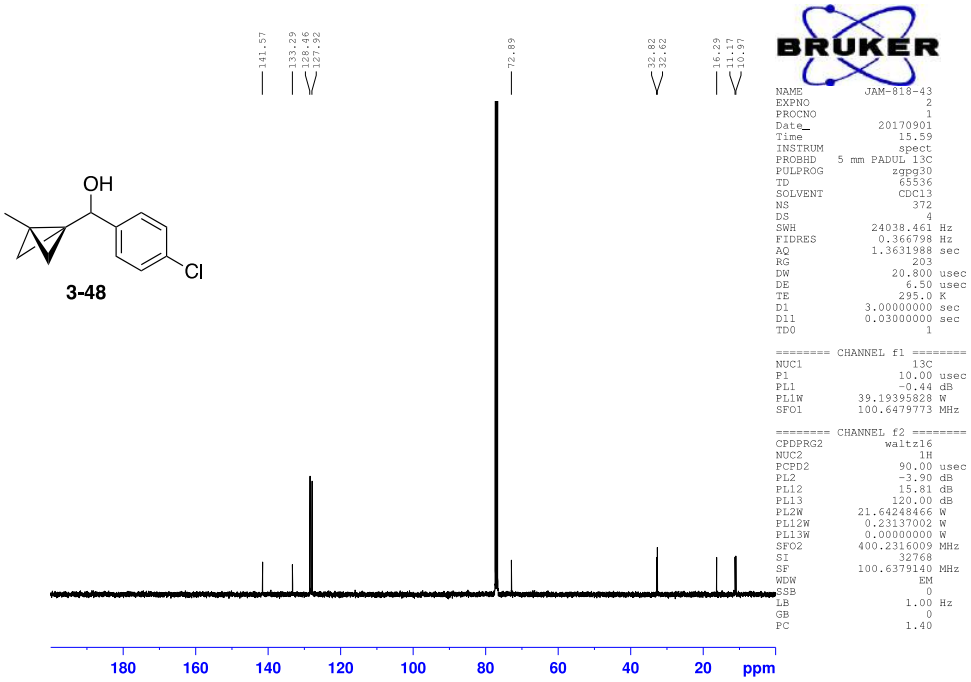


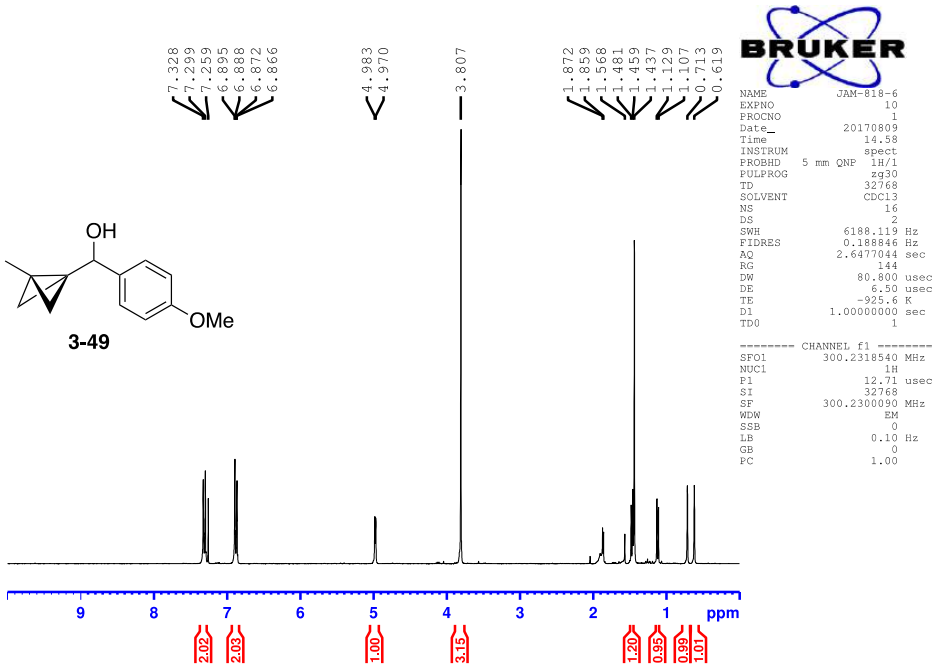

```
NAME                JAM-818-5
EXPNO                      30
PROCNO                      1
Date_              20170809
Time                   14.53
INSTRUM                spect
PROBHD    5 mm QNP   1H/1
PULPROG                 zg30
TD                     32768
SOLVENT                CDCl3
NS                        16
DS                         2
SWH                6188.119 Hz
FIDRES                0.188846 Hz
AQ                 2.6477044 sec
RG                       322
DW                    80.800 usec
DE                     6.50 usec
TE                    -926.0 K
D1                 1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1               300.2318540 MHz
NUC1                       1H
P1                     12.71 usec
SI                     32768
SF                 300.2300086 MHz
WDW                       EM
SSB                        0
LB                      0.10 Hz
GB                         0
PC                      1.00
```

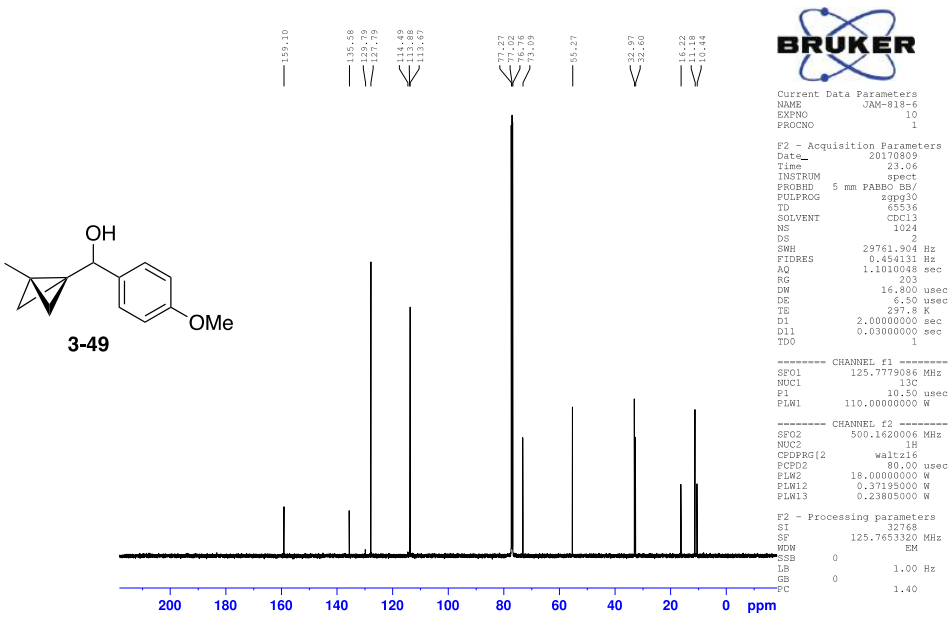


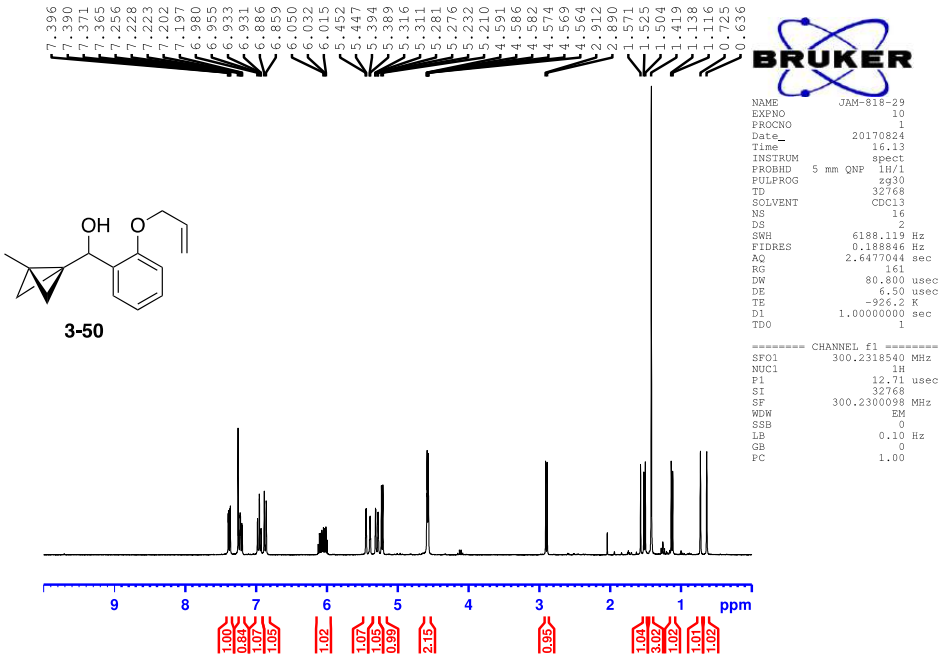

```
NAME                JAM-749-10
EXPNO                       2
PROCNO                      1
Date_              20160916
Time                   17.23
INSTRUM                spect
PROBHD    5 mm PADUL 13C
PULPROG                zgpg30
TD                     65536
SOLVENT                CDCl3
NS                       897
DS                         4
SWH               24038.461 Hz
FIDRES                0.366798 Hz
AQ                 1.3631988 sec
RG                       203
DW                    20.800 usec
DE                     6.50 usec
TE                    294.8 K
D1                 3.00000000 sec
D11                0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      13C
P1                     10.00 usec
PL1                    -0.44 dB
PL1W              39.19395828 W
SFO1              100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                  90.00 usec
PL2                    -3.90 dB
PL12                   15.81 dB
PL13                  120.00 dB
PL2W              21.64248466 W
PL12W              0.23137002 W
PL13W              0.00000000 W
SFO2              400.2316009 MHz
SI                     32768
SF                100.6379140 MHz
WDW                       EM
SSB                        0
LB                      1.00 Hz
GB                         0
PC                      1.40
```

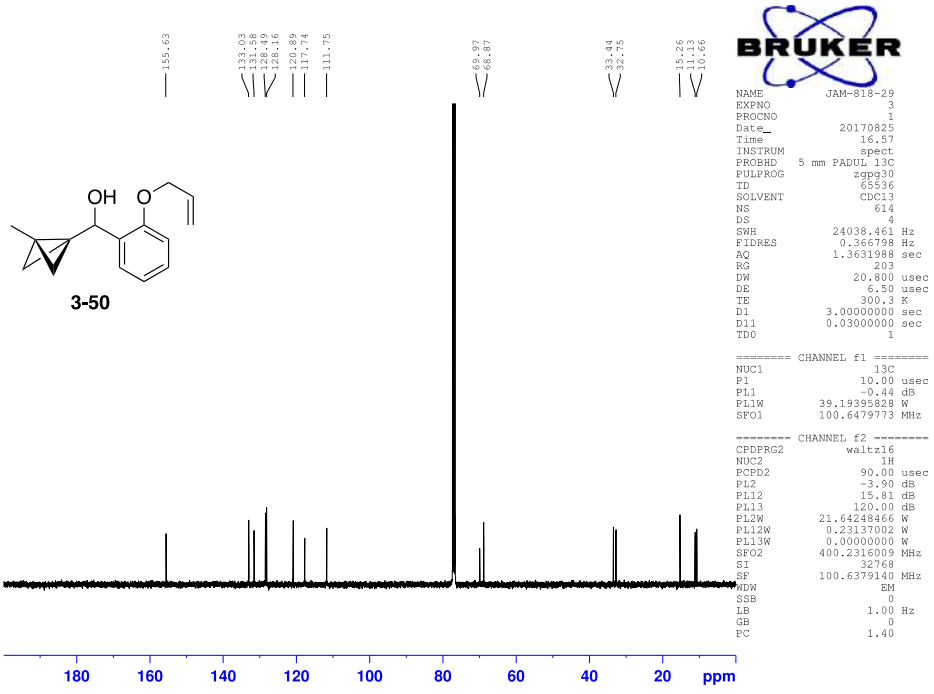

OH
Cl
3-48
7.316
7.259
5.023
5.013
1.971
1.962
1.582
1.578
1.452
1.442
1.437
1.099
1.083
0.702
0.615
9
8
7
6
5
4
3
2
1
ppm
3.89
0.99
0.98
3.92
0.99
0.98
1.00
BRUKER
NAME JAM-818-43
EXPNO 1
PROCNO 1
Date_ 20170901
Time 15.26
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 203
DW 60.800 usec
DE 6.50 usec
TE 294.9 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.31 usec
PL1 -3.90 dB
PL1W 21.64248466 W
SFO1 400.2324716 MHz
SI 32768
SF 400.2300129 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

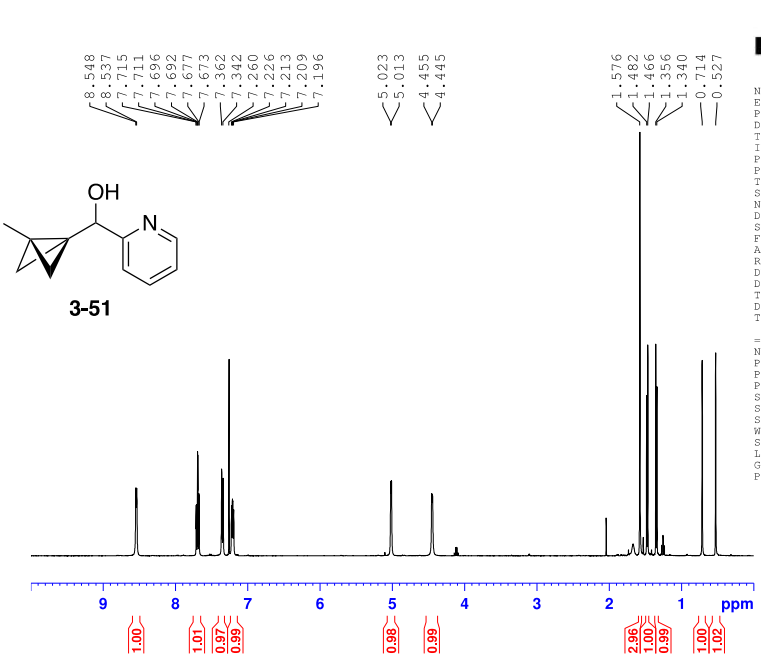

OH
Cl
3-48
141.57
133.29
128.46
127.92
72.89
32.82
32.62
16.29
11.17
10.97
180
160
140
120
100
80
60
40
20
ppm
BRUKER
NAME JAM-818-43
EXPNO 2
PROCNO 1
Date_ 20170901
Time 15.59
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 372
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 295.0 K
D1 3.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 -0.44 dB
PL1W 39.19395828 W
SFO1 100.6479773 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.90 dB
PL12 15.81 dB
PL13 120.00 dB
PL2W 21.64248466 W
PL12W 0.23137002 W
PL13W 0.00000000 W
SFO2 400.2316009 MHz
SI 32768
SF 100.6379140 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40


7.328
7.299
7.259
6.895
6.888
6.872
6.866
4.983
4.970
3.807
1.872
1.859
1.568
1.481
1.459
1.437
1.129
1.107
0.713
0.619
OH
OMe
3-49
9
8
7
6
5
4
3
2
1
ppm
2.02
2.03
1.00
3.15
1.20
0.95
0.98
1.07
BRUKER
NAME JAM-818-6
EXPNO 10
PROCNO 1
Date_ 20170809
Time 14.58
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.188846 Hz
AQ 2.6477044 sec
RG 144
DW 80.800 usec
DE 6.50 usec
TE -925.6 K
D1 1.00000000 sec
TD0 1
-------- CHANNEL f1 --------
SFO1 300.2318540 MHz
NUC1 1H
P1 12.71 usec
SI 32768
SF 300.2300090 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00


159.10
135.58
129.79
127.79
114.49
113.88
113.67
77.27
77.02
76.76
73.09
55.27
32.97
32.60
16.22
11.18
10.44
OH
OMe
3-49
200
180
160
140
120
100
80
60
40
20
0
ppm
BRUKER
Current Data Parameters
NAME JAM-818-6
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20170809
Time 23.06
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 2
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010048 sec
RG 203
DW 16.800 usec
DE 6.50 usec
TE 297.8 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
-------- CHANNEL f1 --------
SFO1 125.7779086 MHz
NUC1 13C
P1 10.50 usec
PLW1 110.00000000 W
-------- CHANNEL f2 --------
SFO2 500.1620006 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 18.00000000 W
PLW12 0.37195000 W
PLW13 0.23805000 W
F2 - Processing parameters
SI 32768
SF 125.7653320 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

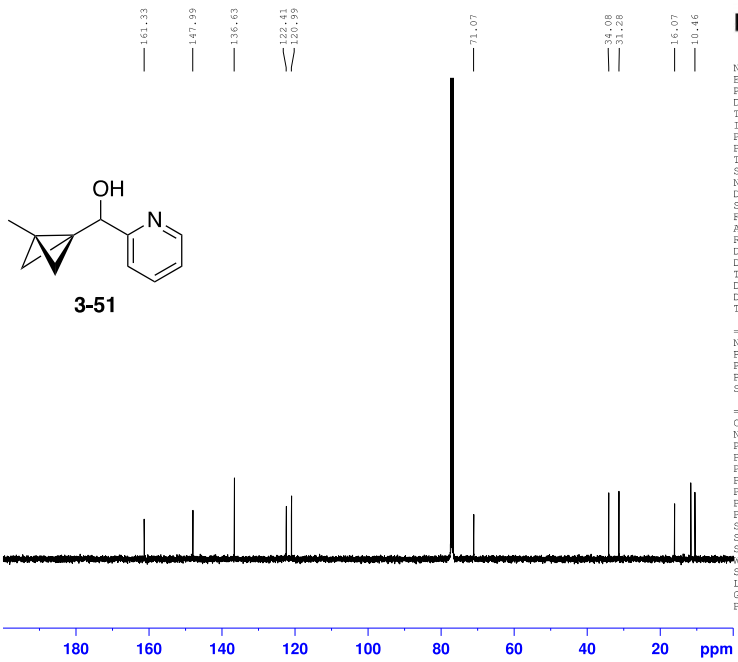

7.396
7.390
7.371
7.365
7.256
7.228
7.223
7.202
7.197
6.980
6.955
6.933
6.931
6.886
6.859
6.050
6.032
6.015
5.452
5.447
5.394
5.389
5.316
5.311
5.281
5.276
5.232
5.210
4.591
4.586
4.582
4.574
4.569
4.564
2.912
2.890
1.571
1.525
1.504
1.419
1.138
1.116
0.725
0.636
OH
O
3-50
9
8
7
6
5
4
3
2
1
ppm
1.00
0.84
1.07
1.05
1.02
1.07
1.05
0.99
2.15
0.95
1.04
3.02
1.02
1.01
1.02
BRUKER
NAME JAM-818-29
EXPNO 10
PROCNO 1
Date_ 20170824
Time 16.13
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.188846 Hz
AQ 2.6477044 sec
RG 161
DW 80.800 usec
DE 6.50 usec
TE -926.2 K
D1 1.00000000 sec
TDO 1
======== CHANNEL f1 ========
SFO1 300.2318540 MHz
NUC1 1H
P1 12.71 usec
SI 32768
SF 300.2300098 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00


155.63
133.03
131.58
128.49
128.16
120.89
117.74
111.75
69.97
68.87
33.44
32.75
15.26
11.13
10.66
OH
O
3-50
180
160
140
120
100
80
60
40
20
ppm
BRUKER
NAME JAM-818-29
EXPNO 3
PROCNO 1
Date_ 20170825
Time 16.57
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 614
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 300.3 K
D1 3.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 -0.44 dB
PL1W 39.19395828 W
SFO1 100.6479773 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.90 dB
PL12 15.81 dB
PL13 120.00 dB
PL2W 21.64248466 W
PL12W 0.23137002 W
PL13W 0.00000000 W
SFO2 400.2316009 MHz
SI 32768
SF 100.6379140 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



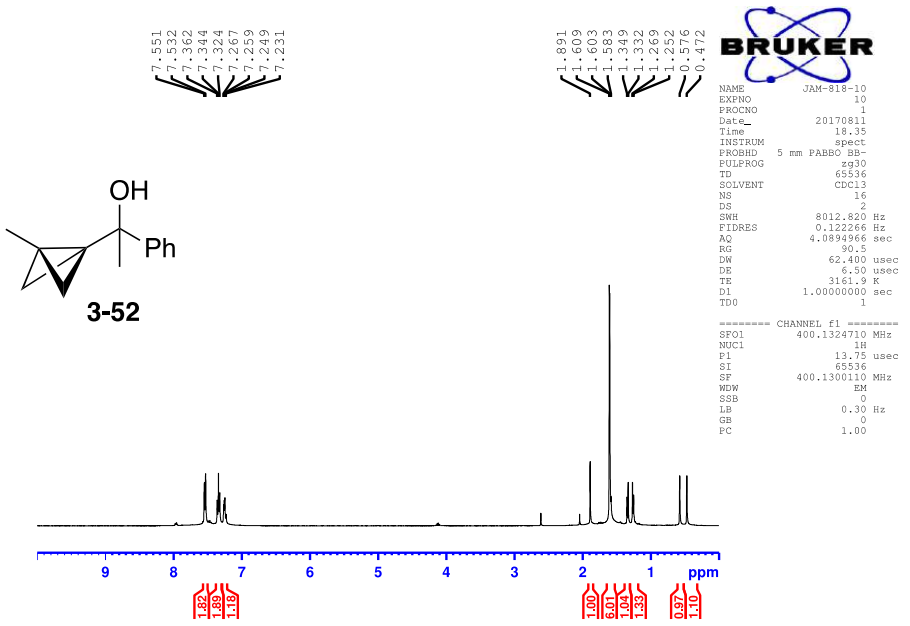
BRUKER

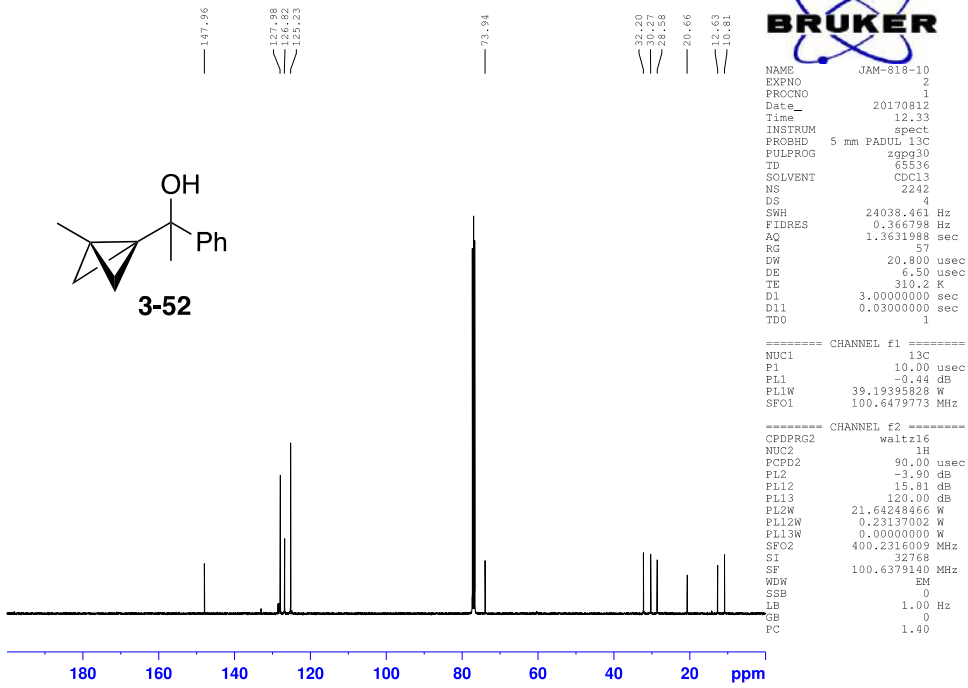
```
NAME              JAM-818-22
EXPNO                      1
PROCNO                     1
Date_               20170822
Time                   15.05
INSTRUM                spect
PROBHD    5 mm PADUL 13C
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                        16
DS                         2
SWH                8223.685 Hz
FIDRES             0.125483 Hz
AQ                 3.9846387 sec
RG                       128
DW                  60.800 usec
DE                   6.50 usec
TE                  294.5 K
D1                 2.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                     9.31 usec
PL1                   -3.90 dB
PL1W              21.64248466 W
SFO1             400.2324716 MHz
SI                      32768
SF               400.2300125 MHz
WDW                        EM
SSB                         0
LB                   0.30 Hz
GB                          0
PC                       1.00
```

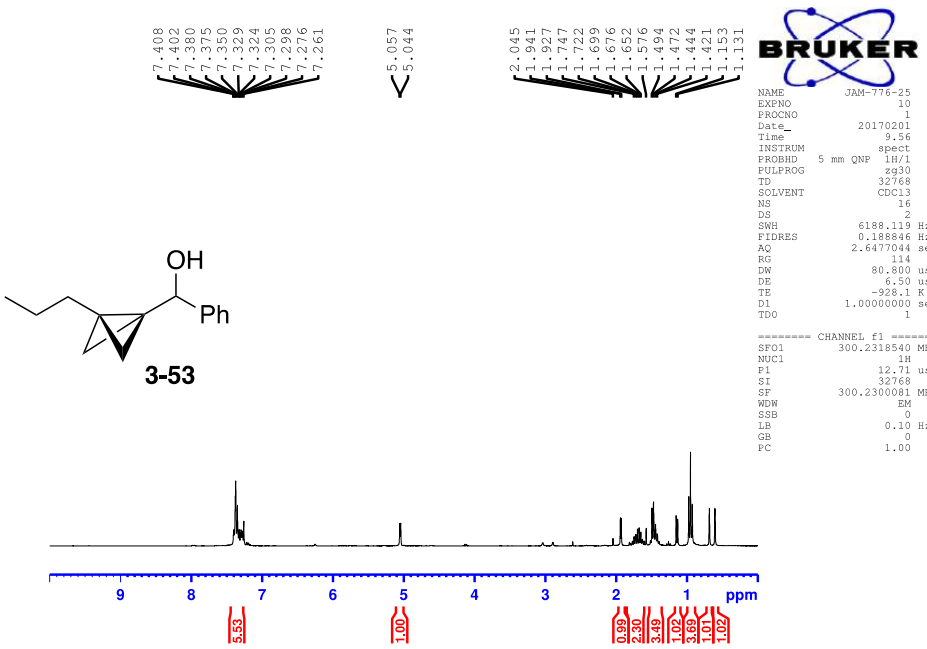


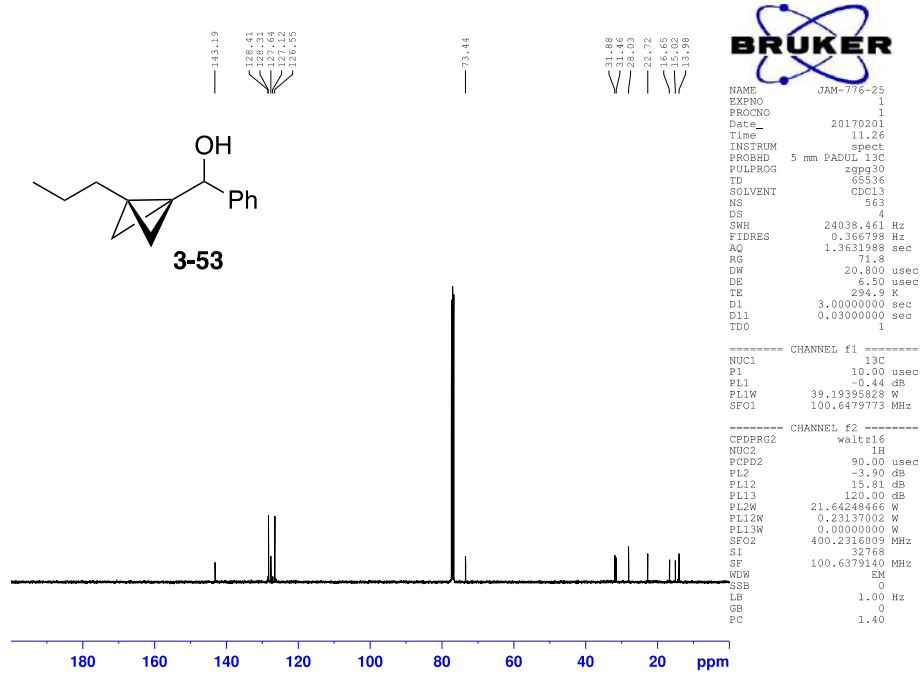
BRUKER

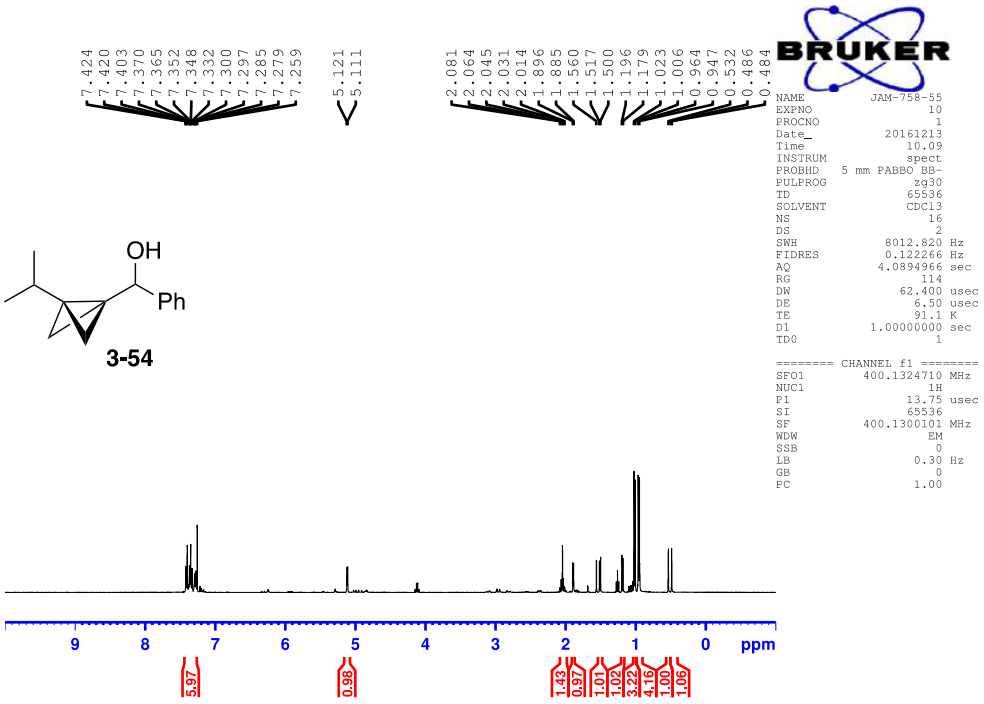
```
NAME              JAM-818-22
EXPNO                      2
PROCNO                     1
Date_               20170822
Time                   15.48
INSTRUM                spect
PROBHD    5 mm PADUL 13C
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                       531
DS                         4
SWH               24038.461 Hz
FIDRES             0.366798 Hz
AQ                 1.3631988 sec
RG                       203
DW                  20.800 usec
DE                   6.50 usec
TE                  294.7 K
D1                 3.00000000 sec
D11                0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                     13C
P1                    10.00 usec
PL1                   -0.44 dB
PL1W              39.19395828 W
SFO1             100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                      1H
PCPD2                 90.00 usec
PL2                   -3.90 dB
PL12                  15.81 dB
PL13                 120.00 dB
PL2W              21.64248466 W
PL12W              0.23137002 W
PL13W              0.00000000 W
SFO2             400.2316009 MHz
SI                      32768
SF               100.6379140 MHz
WDW                        EM
SSB                         0
LB                    1.00 Hz
GB                          0
PC                       1.40
```


7.551
7.532
7.362
7.344
7.324
7.267
7.259
7.249
7.231
1.891
1.609
1.603
1.583
1.349
1.332
1.269
1.252
0.576
0.472
OH
Ph
3-52
BRUKER
NAME JAM-818-10
EXPNO 10
PROCNO 1
Date_ 20170811
Time 18.35
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDC13
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 90.5
DW 62.400 usec
DE 6.50 usec
TE 3161.9 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 13.75 usec
SI 65536
SF 400.1300110 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9 8 7 6 5 4 3 2 1 ppm
1.82 1.89 1.18
1.00 6.01 1.04 1.33 0.97 1.10


147.96
127.98
126.82
125.23
73.94
32.20
30.27
28.58
20.66
12.63
10.81
OH
Ph
3-52
BRUKER
NAME JAM-818-10
EXPNO 2
PROCNO 1
Date_ 20170812
Time 12.33
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG zgpg30
TD 65536
SOLVENT CDC13
NS 2242
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 57
DW 20.800 usec
DE 6.50 usec
TE 310.2 K
D1 3.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 -0.44 dB
PL1W 39.19395828 W
SFO1 100.6479773 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.90 dB
PL12 15.81 dB
PL13 120.00 dB
PL2W 21.64248466 W
PL12W 0.23137002 W
PL13W 0.00000000 W
SFO2 400.2316009 MHz
SI 32768
SF 100.6379140 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
180 160 140 120 100 80 60 40 20 ppm

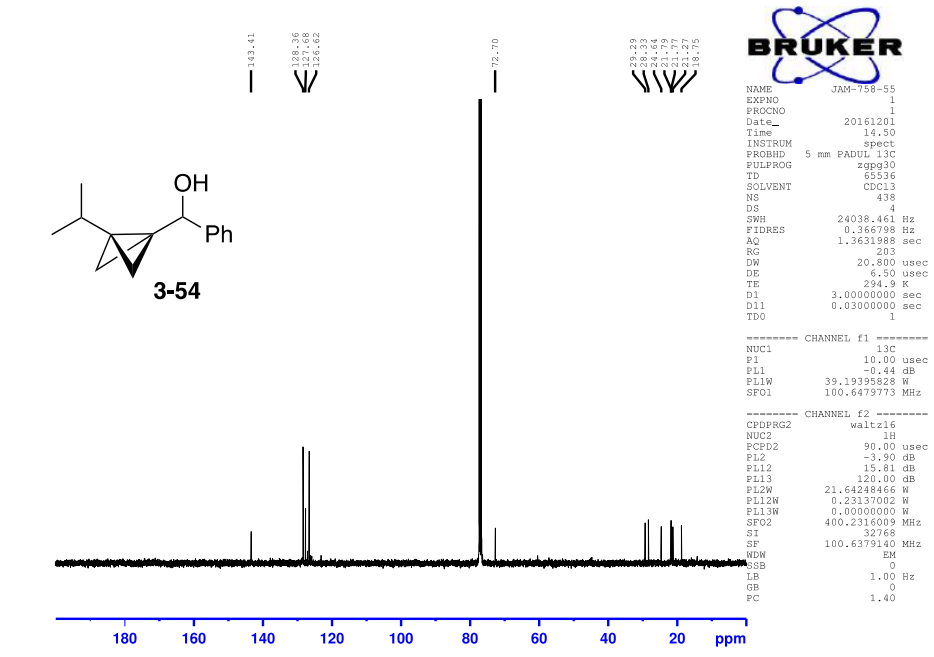

7.408
7.402
7.380
7.375
7.350
7.329
7.324
7.305
7.298
7.276
7.261
5.057
5.044
2.045
1.941
1.927
1.747
1.722
1.699
1.676
1.652
1.576
1.494
1.472
1.444
1.421
1.153
1.131
BRUKER
NAME JAM-776-25
EXPNO 10
PROCNO 1
Date_ 20170201
Time 9.56
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.188846 Hz
AQ 2.6477044 sec
RG 114
DW 80.800 usec
DE 6.50 usec
TE -928.1 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 300.2318540 MHz
NUC1 1H
P1 12.71 usec
SI 32768
SF 300.2300081 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00
OH
Ph
3-53
9
8
7
6
5
4
3
2
1
ppm
5.53
1.00
0.99
2.30
2.49
1.02
3.69
1.01
1.02


143.19
128.41
128.31
127.64
127.12
126.55
73.44
31.88
31.46
28.03
22.72
16.65
15.02
13.98
BRUKER
NAME JAM-776-25
EXPNO 1
PROCNO 1
Date_ 20170201
Time 11.26
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 563
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 71.8
DW 20.800 usec
DE 6.50 usec
TE 294.9 K
D1 3.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 -0.44 dB
PL1W 39.19395828 W
SFO1 100.6479773 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.90 dB
PL12 15.81 dB
PL13 120.00 dB
PL2W 21.64248466 W
PL12W 0.23137002 W
PL13W 0.00000000 W
SFO2 400.2316009 MHz
SI 32768
SF 100.6379140 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
OH
Ph
3-53
180
160
140
120
100
80
60
40
20
ppm



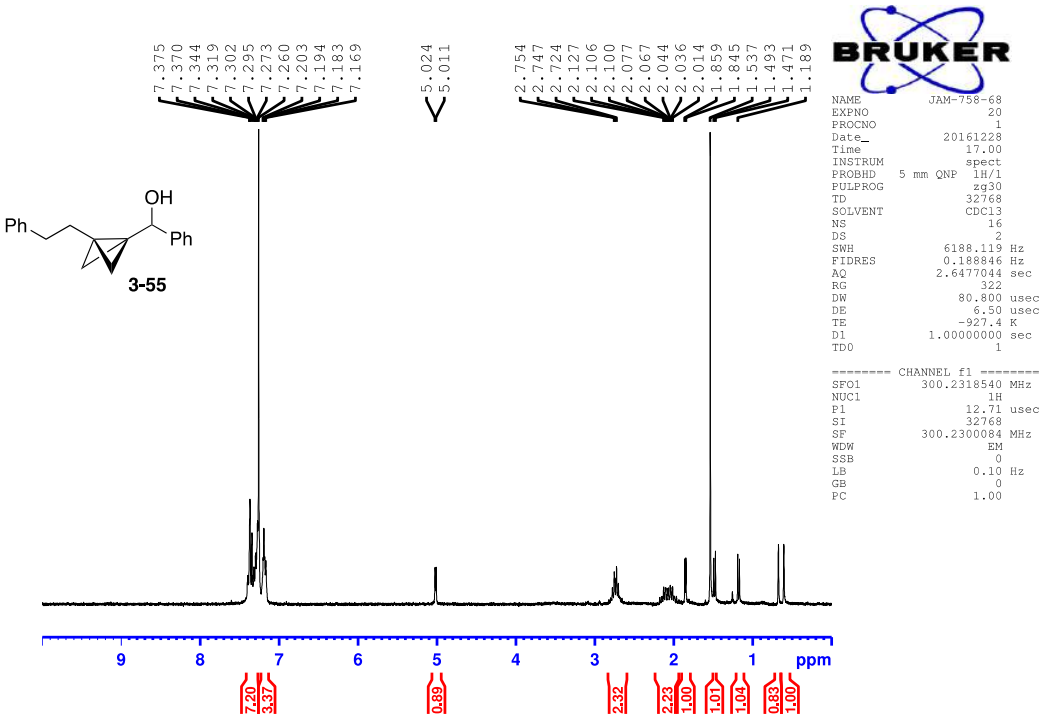
BRUKER

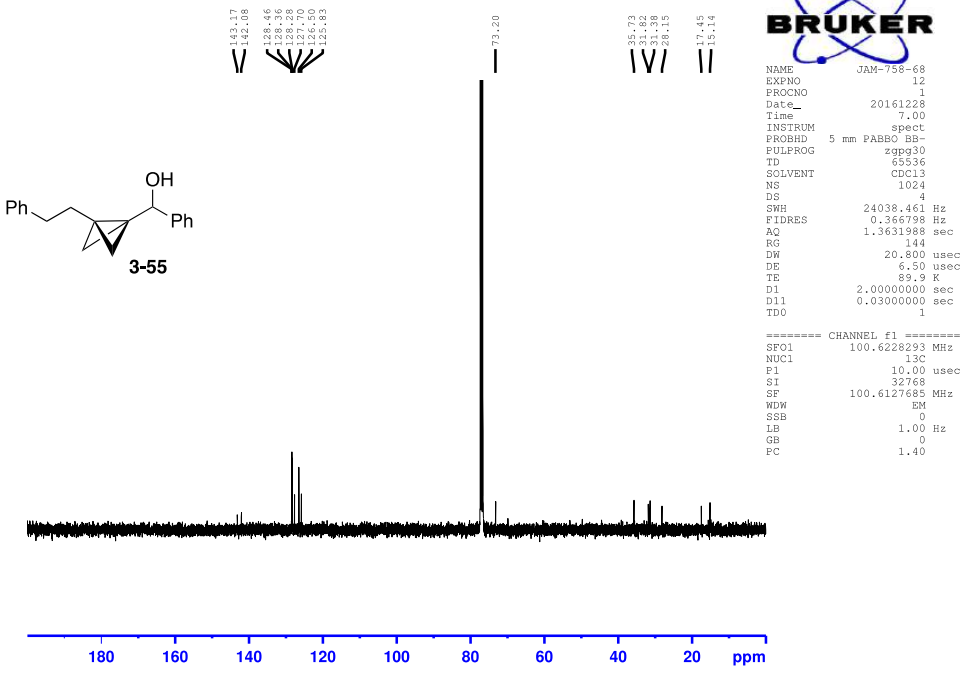
```
NAME              JAM-758-55
EXPNO                 10
PROCNO                 1
Date_           20161213
Time                10.09
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES             0.122266 Hz
AQ              4.0894966 sec
RG                   114
DW                62.400 usec
DE                 6.50 usec
TE                 91.1 K
D1              1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1          400.1324710 MHz
NUC1                  1H
P1                 13.75 usec
SI                 65536
SF            400.1300101 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

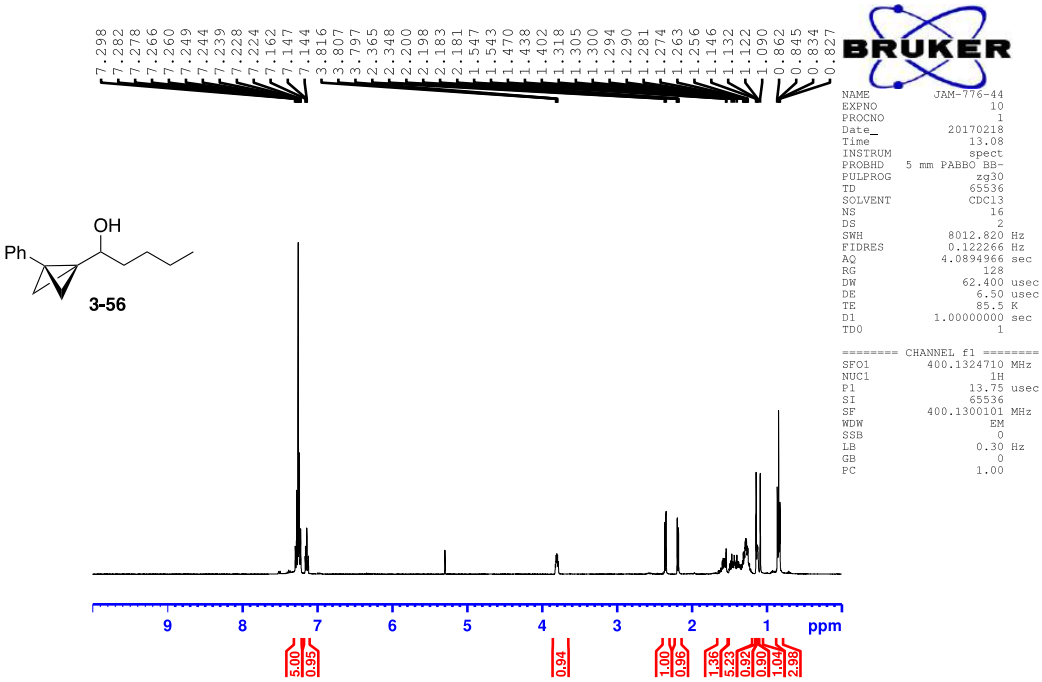


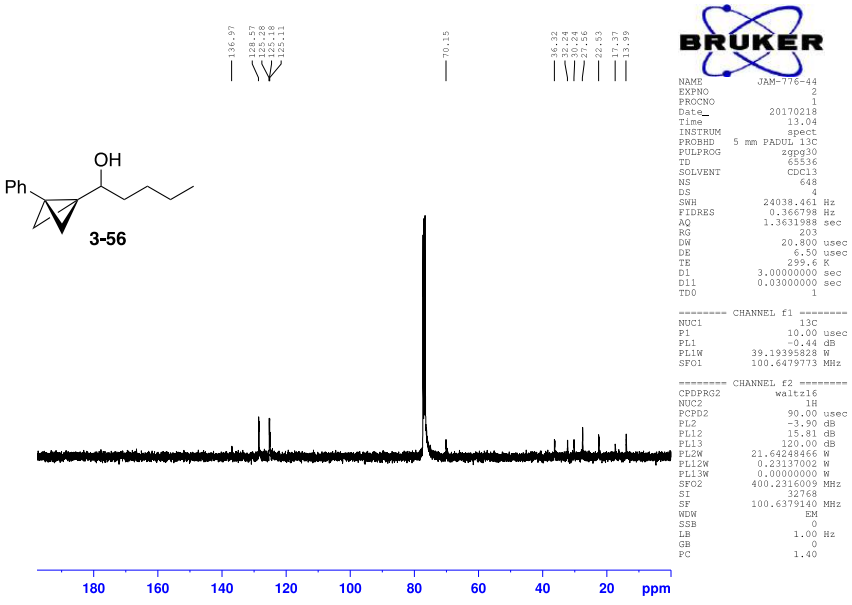
BRUKER

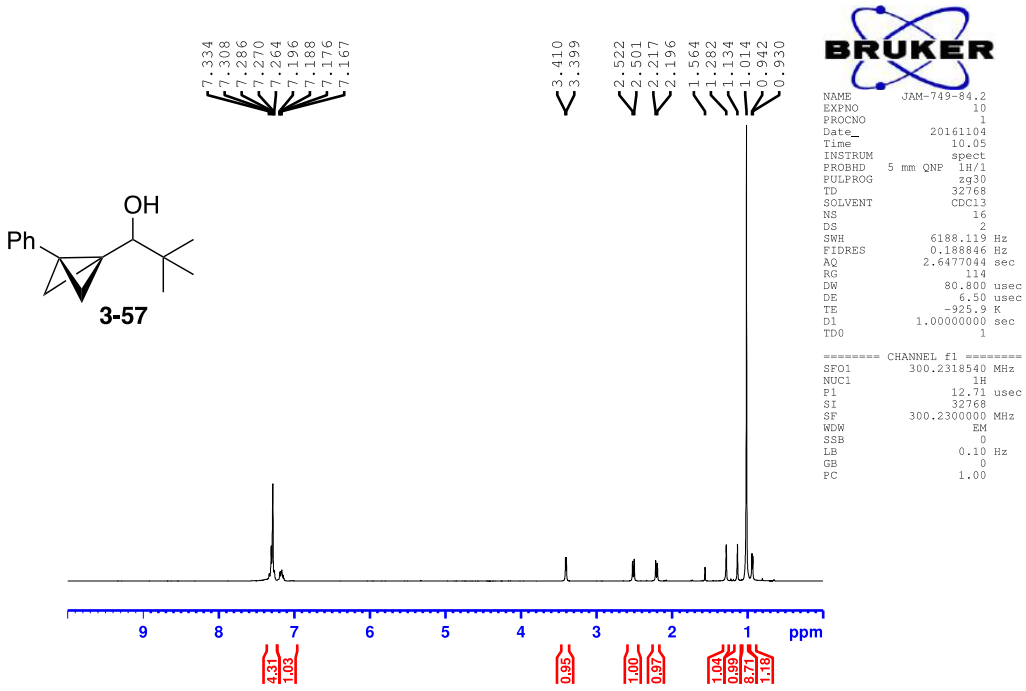
```
NAME              JAM-758-55
EXPNO                  1
PROCNO                 1
Date_           20161201
Time                14.50
INSTRUM             spect
PROBHD   5 mm PADUL 13C
PULPROG            zgpg30
TD                 65536
SOLVENT             CDCl3
NS                   438
DS                     4
SWH            24038.461 Hz
FIDRES             0.366798 Hz
AQ              1.3631988 sec
RG                   203
DW                20.800 usec
DE                 6.50 usec
TE                 294.9 K
D1              3.00000000 sec
D11             0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  13C
P1                 10.00 usec
PL1                -0.44 dB
PL1W           39.19395828 W
SFO1          100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                  1H
PCPD2              90.00 usec
PL2                -3.90 dB
PL12               15.81 dB
PL13              120.00 dB
PL2W           21.64248466 W
PL12W           0.23137002 W
PL13W           0.00000000 W
SFO2          400.2316009 MHz
SI                 32768
SF            100.6379140 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

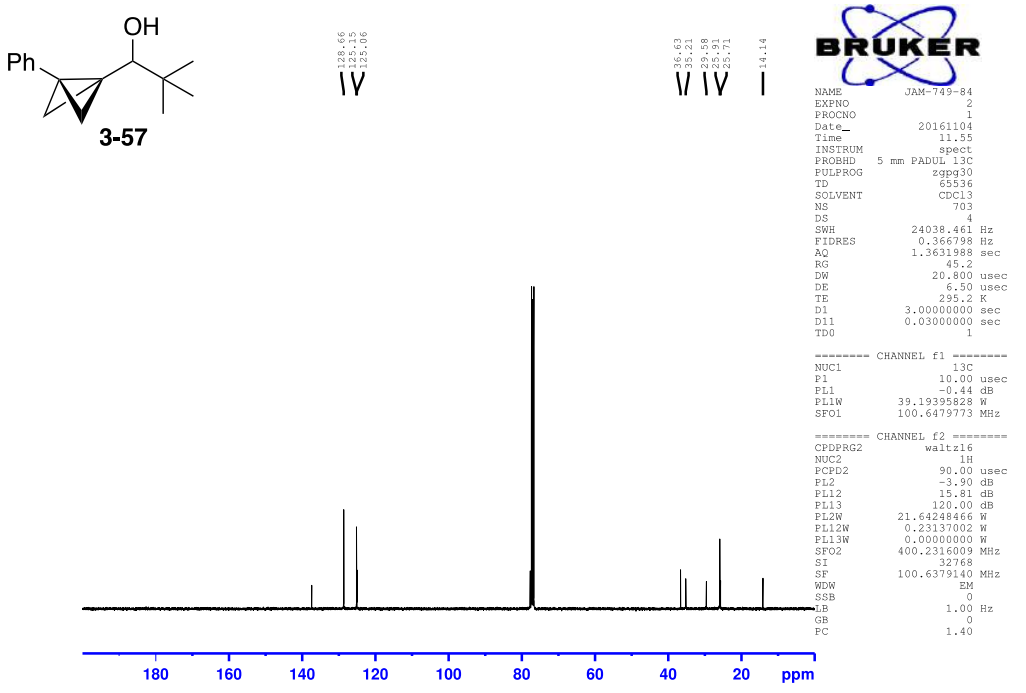

7.375
7.370
7.344
7.319
7.302
7.295
7.273
7.260
7.203
7.194
7.183
7.169
5.024
5.011
2.754
2.747
2.724
2.127
2.106
2.100
2.077
2.067
2.044
2.036
2.014
1.859
1.845
1.537
1.493
1.471
1.189
OH
Ph
Ph
3-55
9
8
7
6
5
4
3
2
1
ppm
7.20
5.37
0.89
2.32
2.23
1.00
1.01
1.04
0.83
1.00
BRUKER
NAME JAM-758-68
EXPNO 20
PROCNO 1
Date_ 20161228
Time 17.00
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.188846 Hz
AQ 2.6477044 sec
RG 322
DW 80.800 usec
DE 6.50 usec
TE -927.4 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 300.2318540 MHz
NUC1 1H
P1 12.71 usec
SI 32768
SF 300.2300084 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

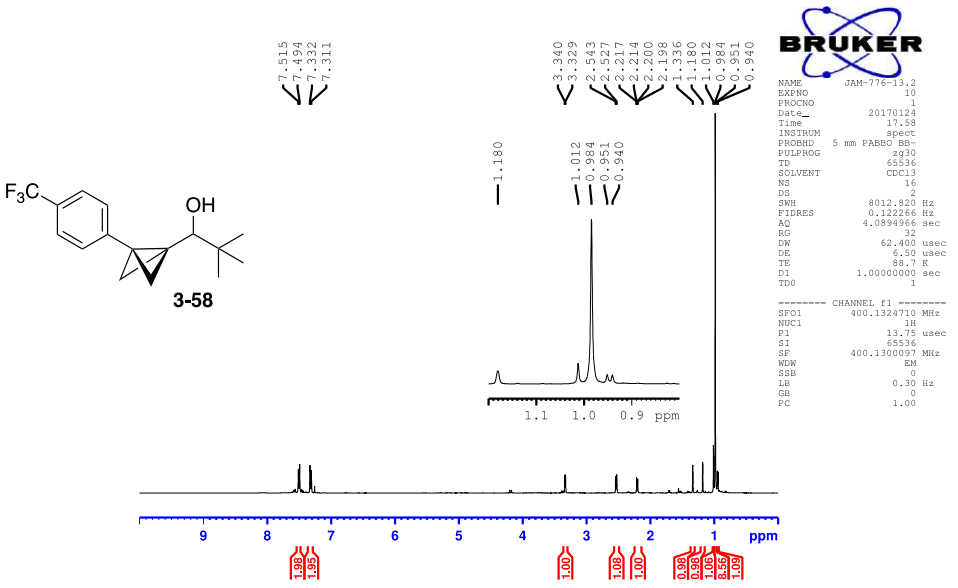

143.17
142.08
128.46
128.36
128.28
127.70
126.50
125.83
73.20
35.73
31.82
31.38
28.15
17.45
15.14
OH
Ph
Ph
3-55
180
160
140
120
100
80
60
40
20
ppm
BRUKER
NAME JAM-758-68
EXPNO 12
PROCNO 1
Date_ 20161228
Time 7.00
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 144
DW 20.800 usec
DE 6.50 usec
TE 89.9 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6228293 MHz
NUC1 13C
P1 10.00 usec
SI 32768
SF 100.6127685 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40


7.298
7.282
7.278
7.266
7.260
7.249
7.244
7.239
7.228
7.224
7.162
7.147
7.144
3.816
3.807
3.797
2.365
2.348
2.200
2.198
2.183
2.181
1.547
1.543
1.470
1.438
1.402
1.318
1.305
1.300
1.294
1.290
1.281
1.274
1.263
1.256
1.146
1.132
1.122
1.090
0.862
0.845
0.834
0.827
OH
Ph
3-56
9
8
7
6
5
4
3
2
1
ppm
5.00
0.95
0.94
1.00
0.96
1.36
5.23
0.92
0.90
1.04
2.98
BRUKER
NAME JAM-776-44
EXPNO 10
PROCNO 1
Date_ 20170218
Time 13.08
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 128
DW 62.400 usec
DE 6.50 usec
TE 85.5 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 13.75 usec
SI 65536
SF 400.1300101 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


136.97
128.57
128.28
125.18
125.11
70.15
36.32
32.24
30.24
27.58
22.53
17.37
13.99
OH
Ph
3-56
180
160
140
120
100
80
60
40
20
ppm
BRUKER
NAME JAM-776-44
EXPNO 2
PROCNO 1
Date_ 20170218
Time 13.04
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 648
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 299.6 K
D1 3.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 -0.44 dB
PL1W 39.19395828 W
SFO1 100.6479773 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.90 dB
PL12 15.81 dB
PL13 120.00 dB
PL2W 21.64288466 W
PL12W 0.23137002 W
PL13W 0.00000000 W
SFO2 400.2316009 MHz
SI 32768
SF 100.6379140 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

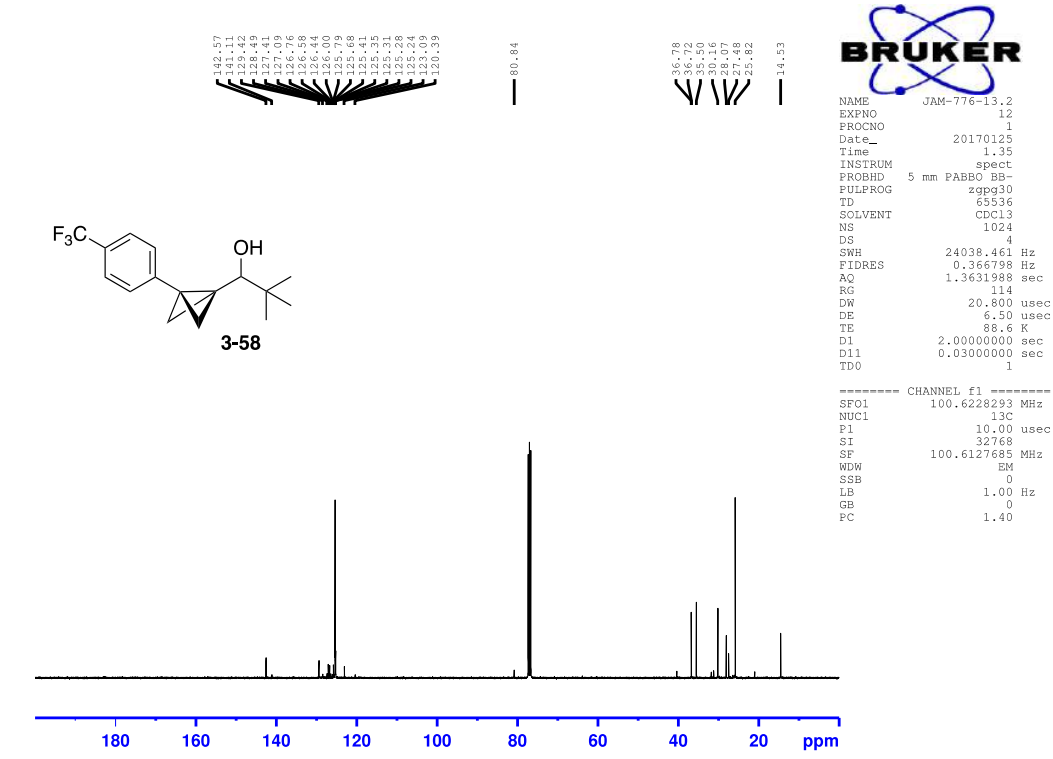

7.334
7.308
7.286
7.270
7.264
7.196
7.188
7.176
7.167
3.410
3.399
2.522
2.501
2.217
2.196
1.564
1.282
1.134
1.014
0.942
0.930
OH
Ph
3-57
9
8
7
6
5
4
3
2
1
ppm
4.31
1.03
0.95
1.00
0.97
1.04
0.99
8.71
1.18
BRUKER
NAME JAM-749-84.2
EXPNO 10
PROCNO 1
Date_ 20161104
Time 10.05
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.188846 Hz
AQ 2.6477044 sec
RG 114
DW 80.800 usec
DE 6.50 usec
TE -925.9 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 300.2318540 MHz
NUC1 1H
P1 12.71 usec
SI 32768
SF 300.2300000 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00


OH
Ph
3-57
128.66
125.15
125.06
36.63
35.21
29.38
29.31
25.71
14.14
180
160
140
120
100
80
60
40
20
ppm
BRUKER
NAME JAM-749-84
EXPNO 2
PROCNO 1
Date_ 20161104
Time 11.55
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 703
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 45.2
DW 20.800 usec
DE 6.50 usec
TE 295.2 K
D1 3.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 -0.44 dB
PL1W 39.19395828 W
SFO1 100.6479773 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.90 dB
PL12 15.81 dB
PL13 120.00 dB
PL2W 21.64248466 W
PL12W 0.23137002 W
PL13W 0.00000000 W
SFO2 400.2316009 MHz
SI 32768
SF 100.6379140 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



BRUKER

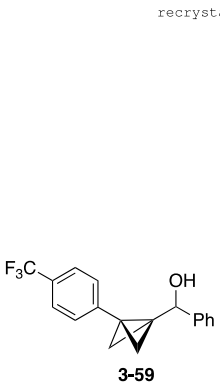
```
NAME            JAM-776-13.2
EXPNO                     10
PROCNO                     1
Date_               20170124
Time                   17.58
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8012.820 Hz
FIDRES                0.122266 Hz
AQ                 4.0894966 sec
RG                       32
DW                    62.400 usec
DE                     6.50 usec
TE                     88.7 K
D1                1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1             400.1324710 MHz
NUC1                       1H
P1                    13.75 usec
SI                     65536
SF               400.1300097 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      1.00
```



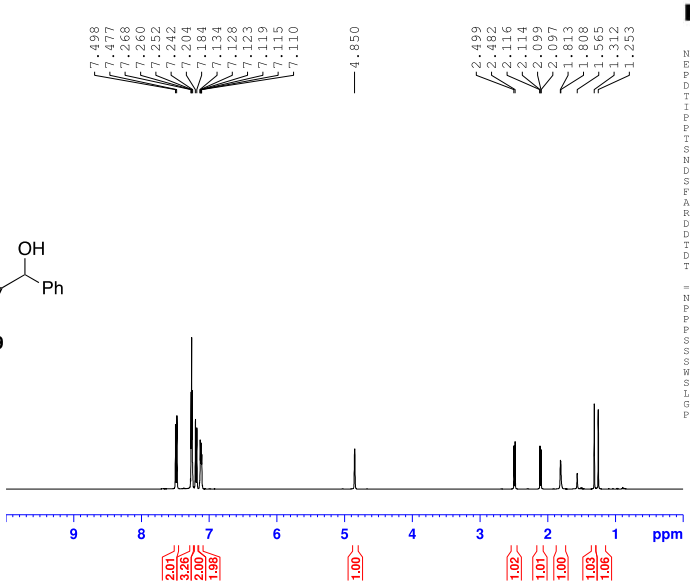
BRUKER

```
NAME            JAM-776-13.2
EXPNO                     12
PROCNO                     1
Date_               20170125
Time                   1.35
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     1024
DS                        4
SWH               24038.461 Hz
FIDRES                0.366798 Hz
AQ                 1.3631988 sec
RG                      114
DW                    20.800 usec
DE                     6.50 usec
TE                     88.6 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1             100.6228293 MHz
NUC1                      13C
P1                    10.00 usec
SI                     32768
SF               100.6127685 MHz
WDW                       EM
SSB                        0
LB                      1.00 Hz
GB                         0
PC                      1.40
```

recrystallized

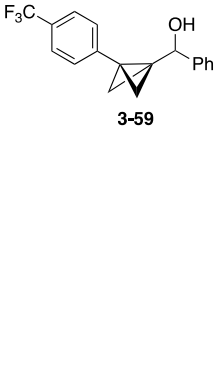


3-59

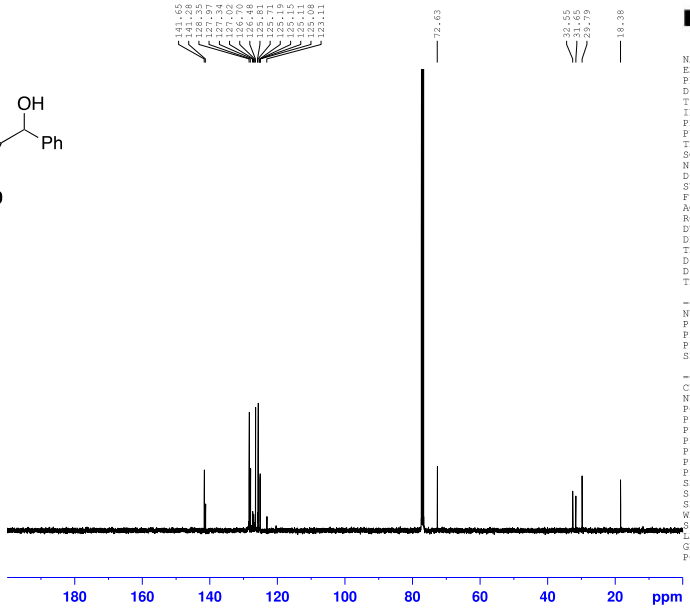



```
NAME                JAM-818-39
EXPNO                        2
PROCNO                       1
Date_                 20170831
Time                      9.20
INSTRUM                 spect
PROBHD    5 mm PADUL 13C
PULPROG                  zg30
TD                      65536
SOLVENT                 CDC13
NS                         16
DS                          2
SWH                  8223.685 Hz
FIDRES               0.125483 Hz
AQ                   3.98466387 sec
RG                         181
DW                    60.800 usec
DE                     6.50 usec
TE                     294.7 K
D1                   2.00000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                       1H
P1                      9.31 usec
PL1                     -3.90 dB
PL1W                21.64248466 W
SFO1                400.2324716 MHz
SI                        32768
SF                  400.2300125 MHz
WDW                          EM
SSB                           0
LB                       0.30 Hz
GB                            0
PC                         1.00
```

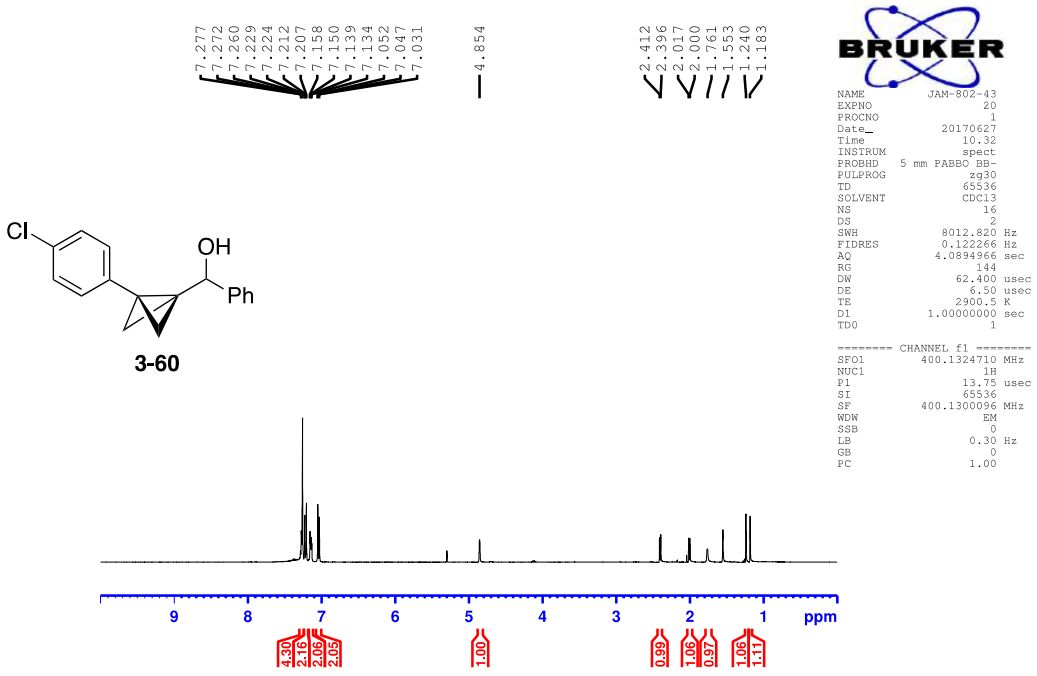
recrystallized

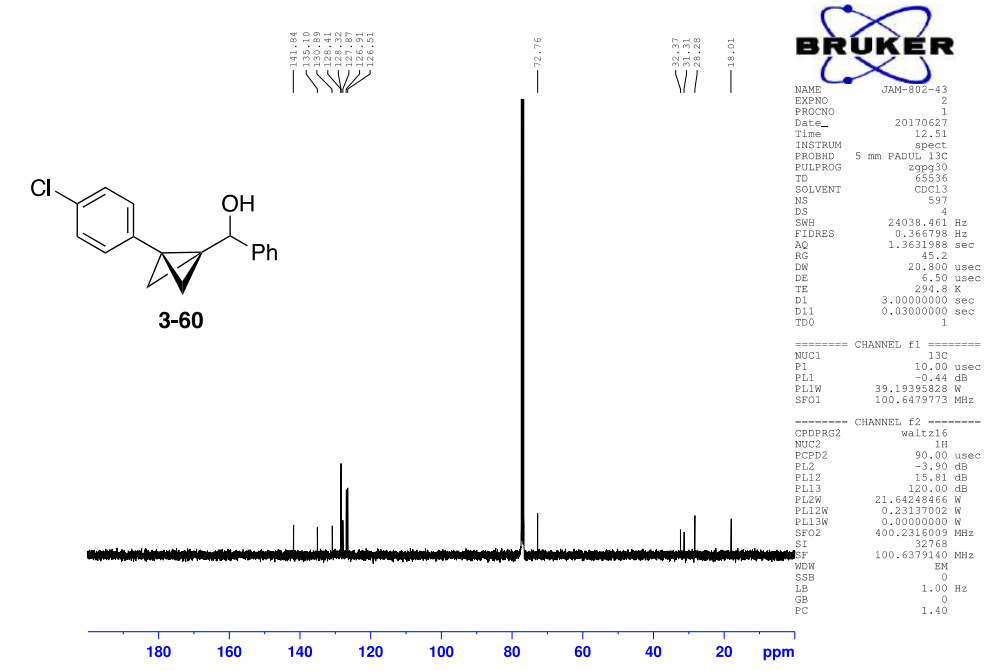


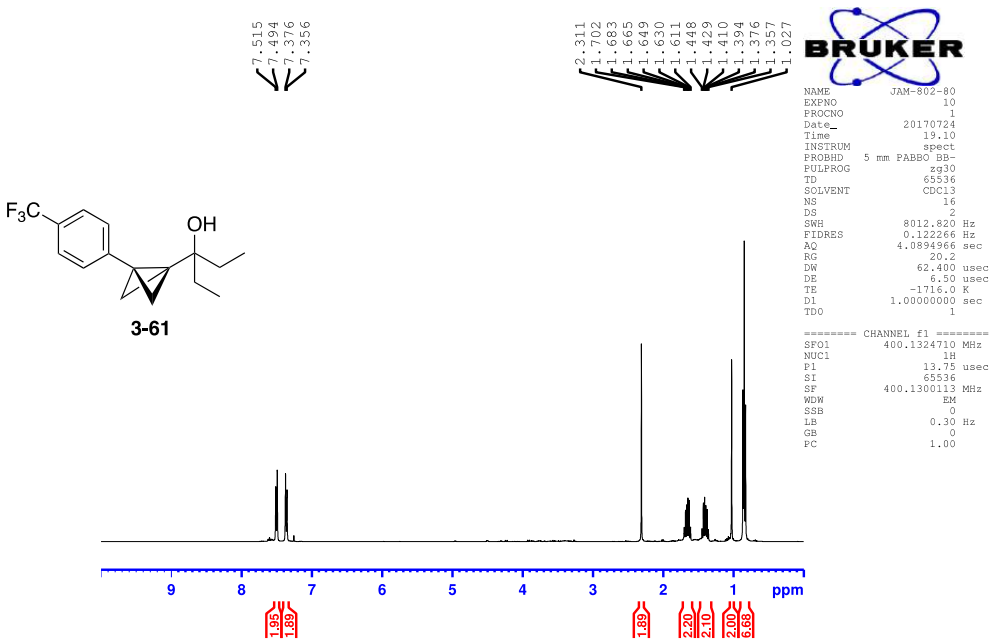
3-59

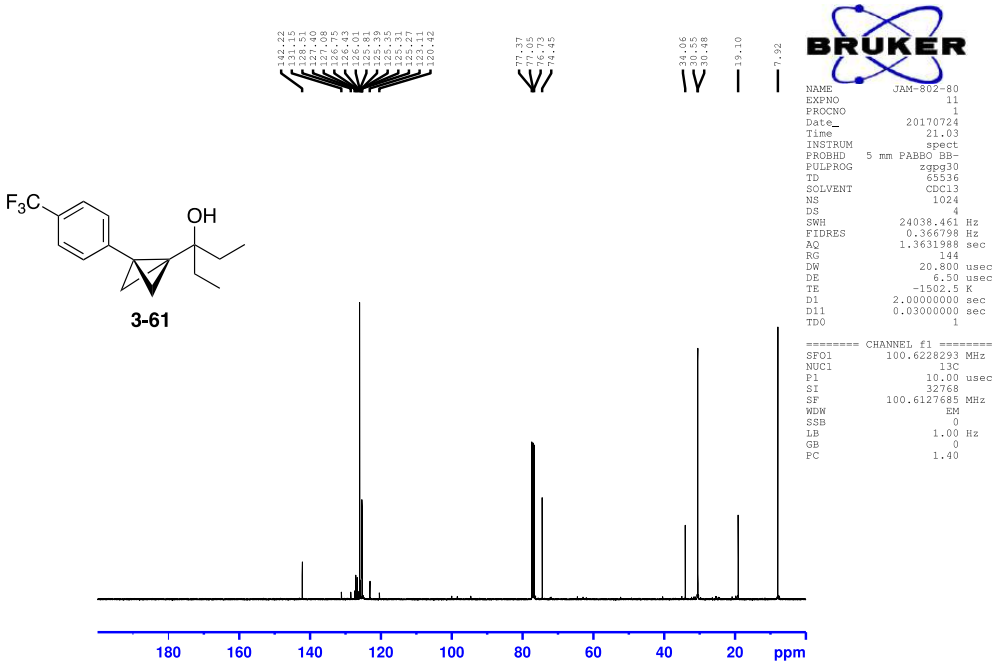


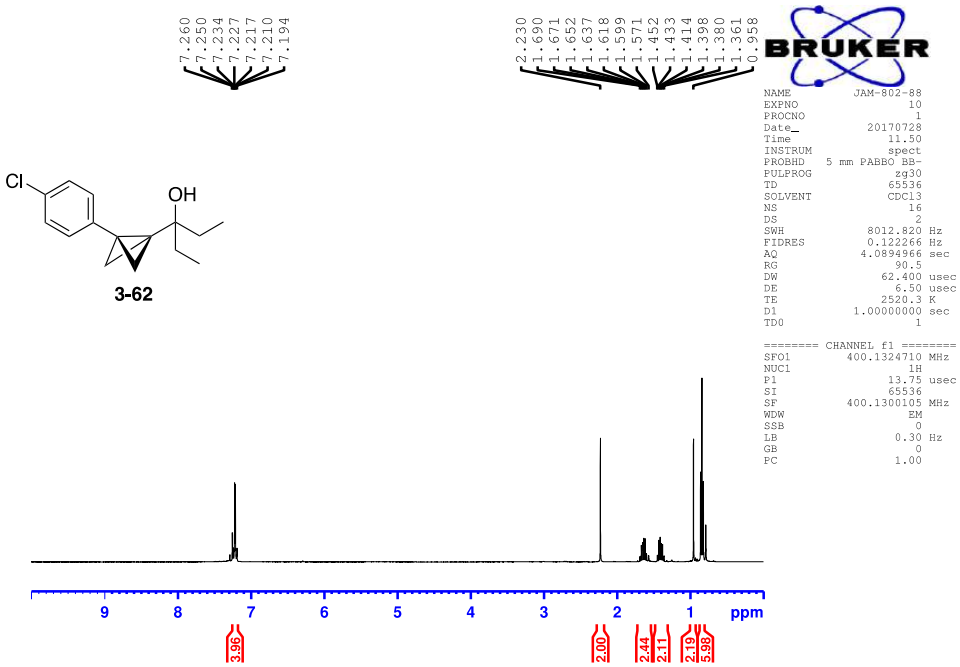

```
NAME                JAM-818-39
EXPNO                        3
PROCNO                       1
Date_                 20170831
Time                      9.55
INSTRUM                 spect
PROBHD    5 mm PADUL 13C
PULPROG                zgpg30
TD                      65536
SOLVENT                 CDC13
NS                        437
DS                          4
SWH                 24038.461 Hz
FIDRES               0.366798 Hz
AQ                   1.3631988 sec
RG                         203
DW                    20.800 usec
DE                     6.50 usec
TE                     295.0 K
D1                   3.00000000 sec
D11                  0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                      13C
P1                     10.00 usec
PL1                     -0.44 dB
PL1W                39.19395828 W
SFO1                100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                  90.00 usec
PL2                     -3.90 dB
PL12                    15.81 dB
PL13                   120.00 dB
PL2W                21.64248466 W
PL12W                0.23137002 W
PL13W                0.00000000 W
SFO2                400.2316009 MHz
SI                        32768
SF                  100.6379140 MHz
WDW                          EM
SSB                           0
LB                       1.00 Hz
GB                            0
PC                         1.40
```

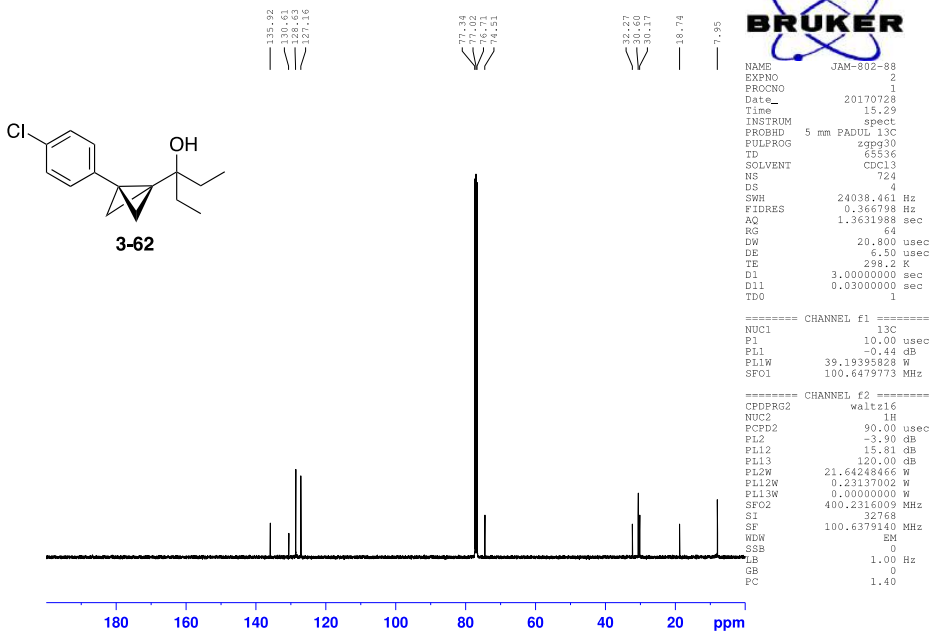

7.277
7.272
7.260
7.229
7.224
7.212
7.207
7.158
7.150
7.139
7.134
7.052
7.047
7.031
4.854
2.412
2.396
2.017
2.000
1.761
1.553
1.240
1.183
BRUKER
NAME JAM-802-43
EXPNO 20
PROCNO 1
Date_ 20170627
Time 10.32
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 144
DW 62.400 usec
DE 6.50 usec
TE 2900.5 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 13.75 usec
SI 65536
SF 400.1300096 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
Cl
OH
Ph
3-60
9
8
7
6
5
4
3
2
1
ppm
4.30
2.19
2.06
2.05
1.00
0.99
1.06
0.97
1.06
1.17

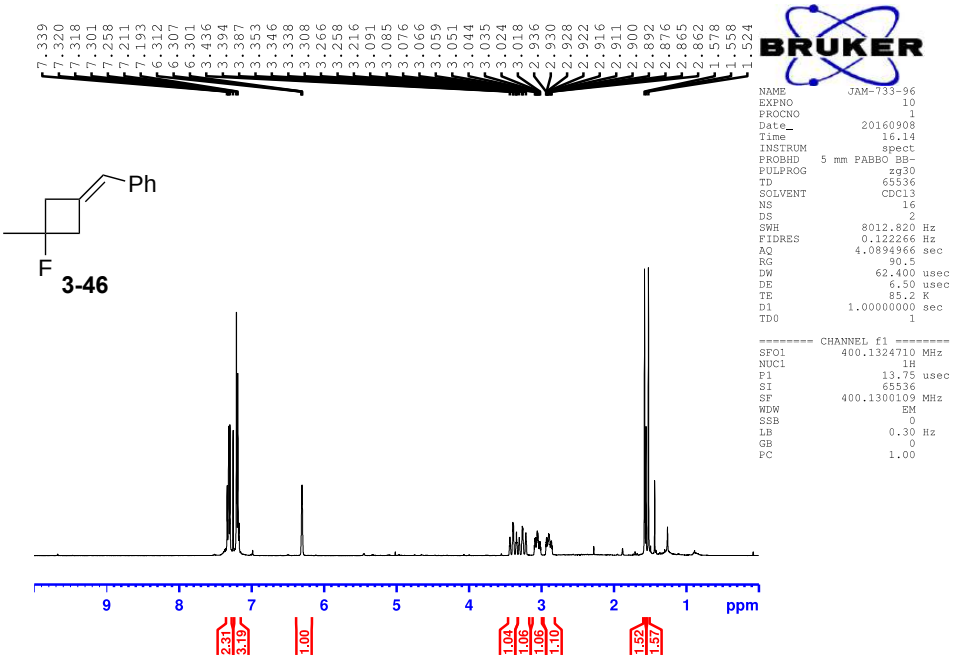

141.84
135.10
130.89
128.41
128.32
127.87
126.91
126.51
72.76
32.37
31.31
28.28
18.01
BRUKER
NAME JAM-802-43
EXPNO 2
PROCNO 1
Date_ 20170627
Time 12.51
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 597
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 45.2
DW 20.800 usec
DE 6.50 usec
TE 294.8 K
D1 3.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 -0.44 dB
PL1W 39.19395828 W
SFO1 100.6479773 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.90 dB
PL12 15.81 dB
PL13 120.00 dB
PL2W 21.64248466 W
PL12W 0.23137002 W
PL13W 0.00000000 W
SFO2 400.2316009 MHz
SI 32768
SF 100.6379140 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
Cl
OH
Ph
3-60
180
160
140
120
100
80
60
40
20
ppm

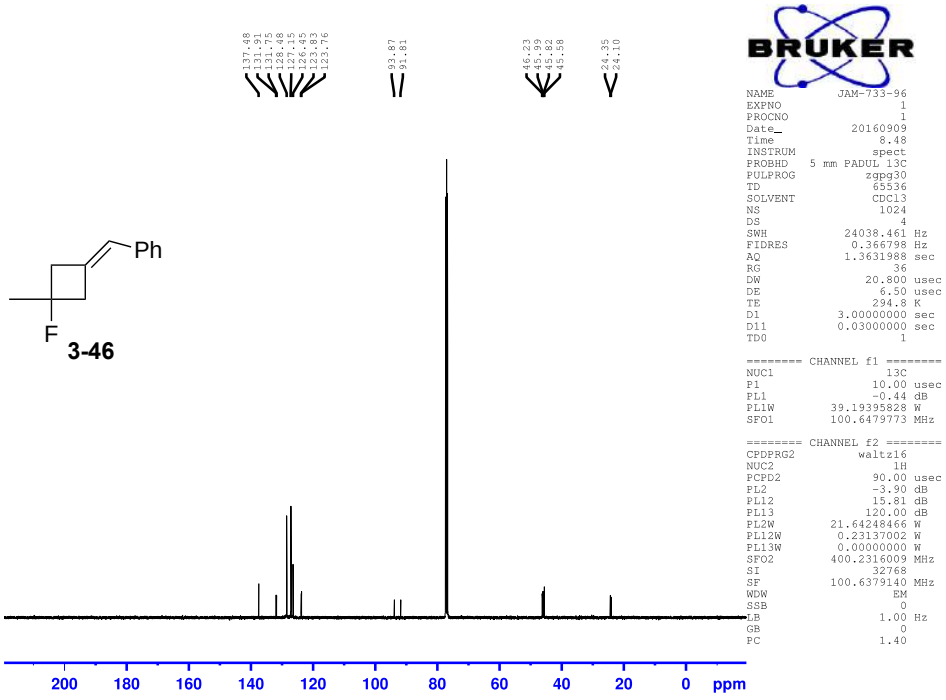

7.515
7.494
7.376
7.356
2.311
1.702
1.683
1.665
1.649
1.630
1.611
1.448
1.429
1.410
1.394
1.376
1.357
1.027
F3C
OH
3-61
NAME JAM-802-80
EXPNO 10
PROCNO 1
Date_ 20170724
Time 19.10
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 20.2
DW 62.400 usec
DE 6.50 usec
TE -1716.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 13.75 usec
SI 65536
SF 400.1300113 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9
8
7
6
5
4
3
2
1
ppm
1.95
1.89
1.89
2.20
2.10
2.00
6.68

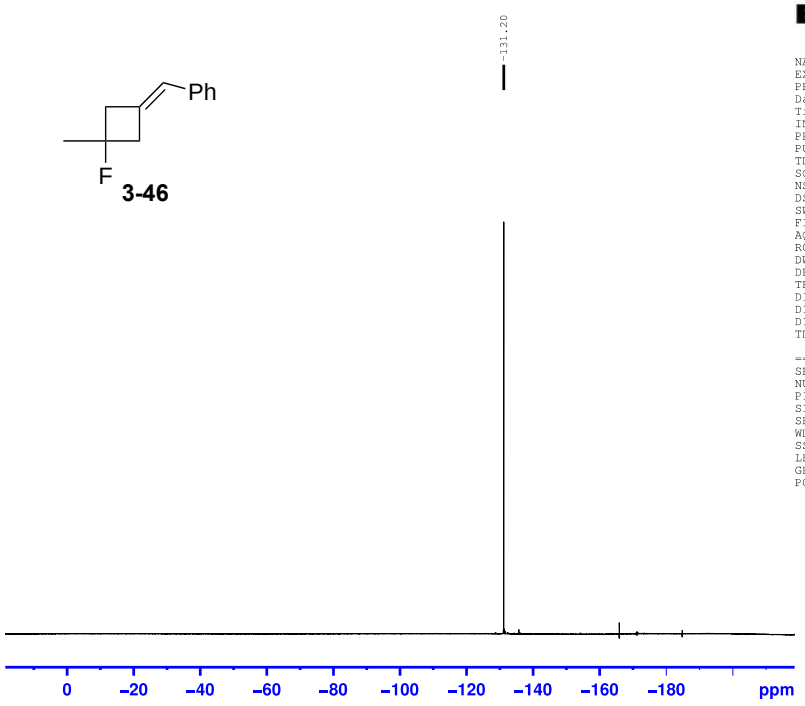

142.22
131.15
128.51
127.40
127.08
126.75
126.43
126.01
125.81
125.39
125.35
125.31
125.27
123.11
120.42
77.37
77.05
76.73
74.45
34.06
30.55
30.48
19.10
7.92
F3C
OH
3-61
NAME JAM-802-80
EXPNO 11
PROCNO 1
Date_ 20170724
Time 21.03
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 144
DW 20.800 usec
DE 6.50 usec
TE -1502.5 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6228293 MHz
NUC1 13C
P1 10.00 usec
SI 32768
SF 100.6127685 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
180
160
140
120
100
80
60
40
20
ppm


7.260
7.250
7.234
7.227
7.217
7.210
7.194
2.230
1.690
1.671
1.652
1.637
1.618
1.599
1.571
1.452
1.433
1.414
1.398
1.380
1.361
0.958
BRUKER
NAME JAM-802-88
EXPNO 10
PROCNO 1
Date_ 20170728
Time 11.50
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 90.5
DW 62.400 usec
DE 6.50 usec
TE 2520.3 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 13.75 usec
SI 65536
SF 400.1300105 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
Cl
OH
3-62
9
8
7
6
5
4
3
2
1
ppm
3.96
2.00
2.44
2.11
2.19
5.98

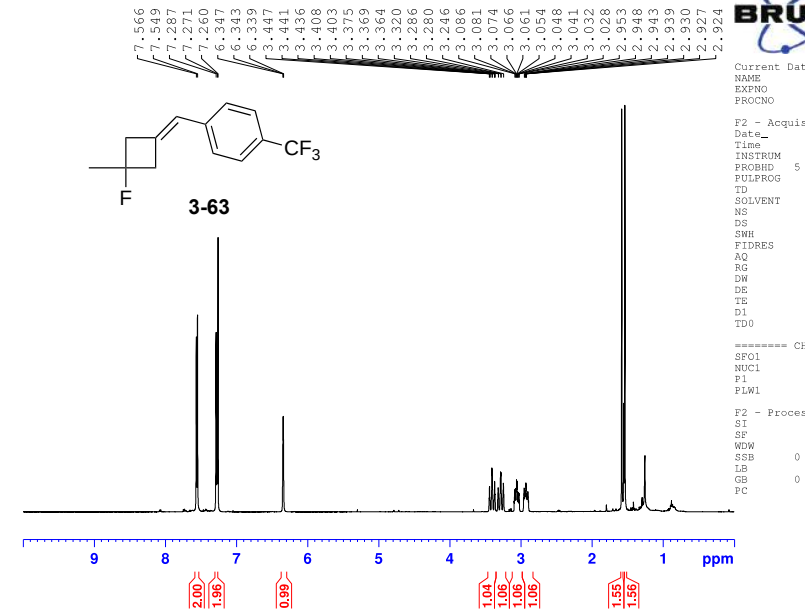

135.92
130.63
128.63
127.16
77.34
77.02
76.71
74.51
32.27
30.60
30.17
18.74
7.95
BRUKER
NAME JAM-802-88
EXPNO 2
PROCNO 1
Date_ 20170728
Time 15.29
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 724
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 64
DW 20.800 usec
DE 6.50 usec
TE 298.2 K
D1 3.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 -0.44 dB
PL1W 39.19395828 W
SFO1 100.6479773 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.90 dB
PL12 15.81 dB
PL13 120.00 dB
PL2W 21.64248466 W
PL12W 0.23137002 W
PL13W 0.00000000 W
SFO2 400.2316009 MHz
SI 32768
SF 100.6379140 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
Cl
OH
3-62
180
160
140
120
100
80
60
40
20
ppm


7.339
7.320
7.318
7.301
7.258
7.211
7.193
6.312
6.307
6.301
3.436
3.394
3.387
3.353
3.346
3.338
3.308
3.266
3.258
3.216
3.091
3.085
3.076
3.066
3.059
3.051
3.044
3.035
3.024
3.018
2.936
2.930
2.928
2.922
2.916
2.911
2.900
2.892
2.876
2.865
2.862
1.578
1.558
1.524
Ph
F
3-46
9
8
7
6
5
4
3
2
1
ppm
2.31
3.19
1.00
1.04
1.06
1.06
1.10
1.52
1.57
BRUKER
NAME JAM-733-96
EXPNO 10
PROCNO 1
Date_ 20160908
Time 16.14
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 90.5
DW 62.400 usec
DE 6.50 usec
TE 85.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 13.75 usec
SI 65536
SF 400.1300109 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

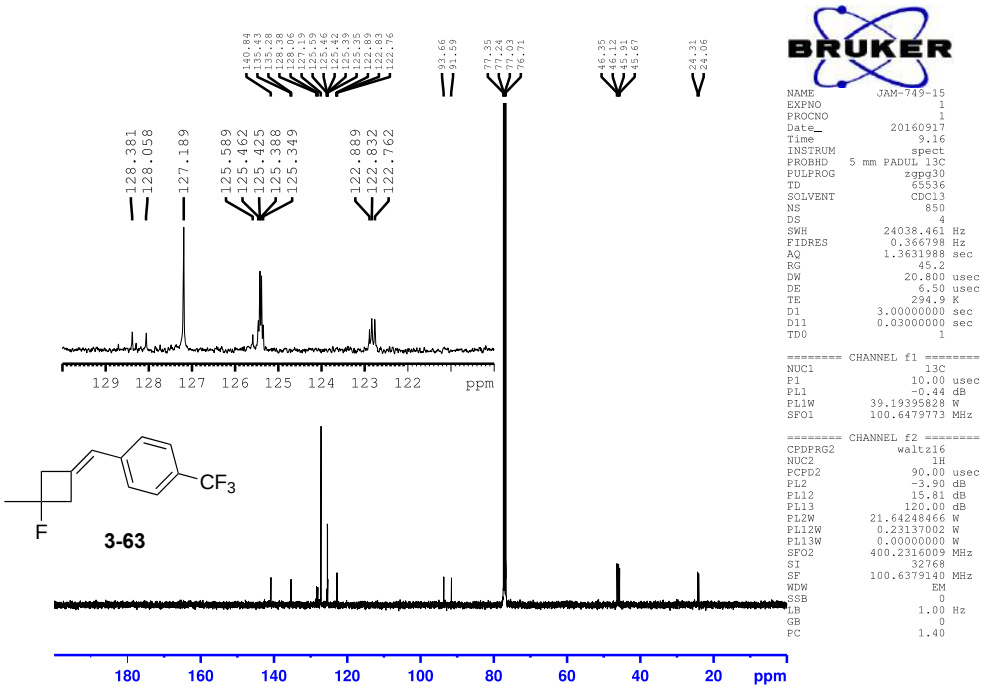

137.48
131.91
128.75
128.48
127.15
126.45
123.83
123.76
93.87
91.81
46.23
45.99
45.82
45.58
24.35
24.10
Ph
F
3-46
200
180
160
140
120
100
80
60
40
20
0
ppm
BRUKER
NAME JAM-733-96
EXPNO 1
PROCNO 1
Date_ 20160909
Time 8.48
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 36
DW 20.800 usec
DE 6.50 usec
TE 294.8 K
D1 3.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 -0.44 dB
PL1W 39.19395828 W
SFO1 100.6479773 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.90 dB
PL12 15.81 dB
PL13 120.00 dB
PL2W 21.64248466 W
PL12W 0.23137002 W
PL13W 0.00000000 W
SFO2 400.2316009 MHz
SI 32768
SF 100.6379140 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40




```
NAME                JAM-733-96
EXPNO                       11
PROCNO                       1
Date_             20160908
Time                     16.16
INSTRUM                  spect
PROBHD     5 mm PABBO BB-
PULPROG          zgfhigqn.2
TD                      131072
SOLVENT                 CDCl3
NS                          16
DS                           4
SWH                89285.711 Hz
FIDRES                 0.681196 Hz
AQ                 0.7340532 sec
RG                         203
DW                     5.600 usec
DE                      6.50 usec
TE                      85.2 K
D1                 1.00000000 sec
D11                0.03000000 sec
D12                0.00002000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1            376.4607164 MHz
NUC1                     19F
P1                     14.20 usec
SI                      65536
SF              376.4983662 MHz
WDW                        EM
SSB                         0
LB                      0.30 Hz
GB                          0
PC                      1.00
```

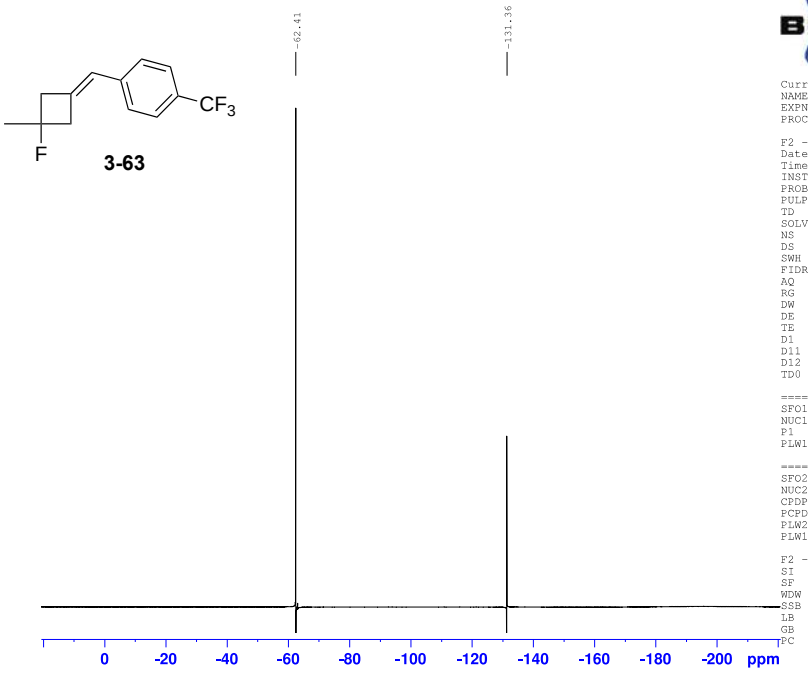



```
Current Data Parameters
NAME              JAM-749-15
EXPNO                     10
PROCNO                     1

F2 - Acquisition Parameters
Date_           20160916
Time                 15.48
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH             10000.000 Hz
FIDRES              0.152588 Hz
AQ                3.2767999 sec
RG                    101
DW                 50.000 usec
DE                  6.50 usec
TE                 494.2 K
D1              1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1            500.1630887 MHz
NUC1                       1H
P1                     11.50 usec
PLW1           18.00000000 W

F2 - Processing parameters
SI                      65536
SF              500.1600128 MHz
WDW                        EM
SSB                 0
LB                      0.30 Hz
GB                  0
PC                      1.00
```



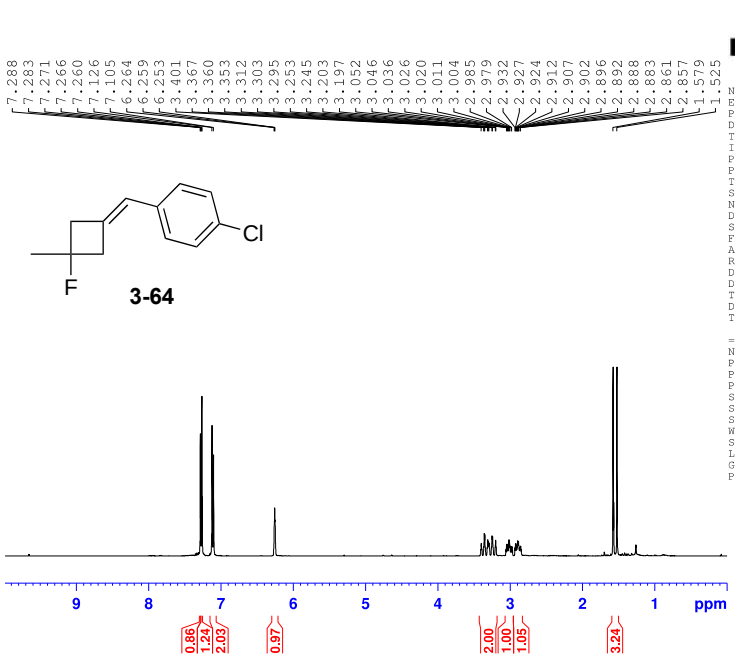
BRUKER

```
NAME                JAM-749-15
EXPNO                        1
PROCNO                       1
Date_                 20160917
Time                      9.16
INSTRUM                  spect
PROBHD    5 mm PADUL 13C
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                         850
DS                           4
SWH                 24038.461 Hz
FIDRES                0.366798 Hz
AQ                    1.3631988 sec
RG                         45.2
DW                       20.800 usec
DE                        6.50 usec
TE                       294.9 K
D1                  3.00000000 sec
D11                 0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                        13C
P1                        10.00 usec
PL1                       -0.44 dB
PL1W               39.19395828 W
SFO1              100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2                 waltz16
NUC2                        1H
PCPD2                     90.00 usec
PL2                       -3.90 dB
PL12                      15.81 dB
PL13                     120.00 dB
PL2W               21.64248466 W
PL12W               0.23137002 W
PL13W               0.00000000 W
SFO2              400.2316009 MHz
SI                        32768
SF                100.6379140 MHz
WDW                          EM
SSB                           0
LB                         1.00 Hz
GB                            0
PC                         1.40
```



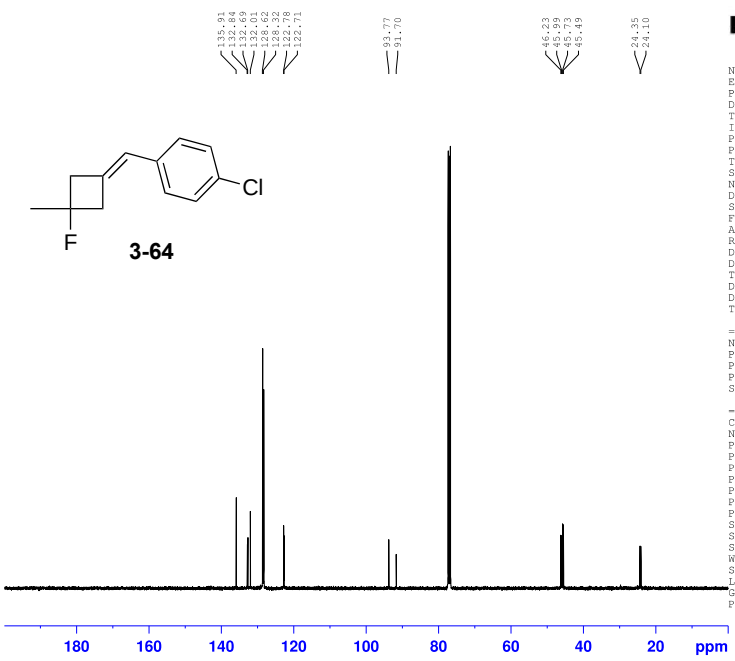
BRUKER

```
Current Data Parameters
NAME                JAM-749-15
EXPNO                       11
PROCNO                       1

F2 - Acquisition Parameters
Date_                 20160916
Time                     15.50
INSTRUM                  spect
PROBHD    5 mm PABBO BB/
PULPROG              zgfhigqn.2
TD                       131072
SOLVENT                  CDCl3
NS                          16
DS                           4
SWH                 113636.367 Hz
FIDRES                0.866977 Hz
AQ                    0.5767168 sec
RG                         203
DW                       4.400 usec
DE                        6.50 usec
TE                       494.2 K
D1                  1.00000000 sec
D11                 0.03000000 sec
D12                 0.00002000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1              470.5735434 MHz
NUC1                        19F
P1                         5.00 usec
PLW1               10.00000000 W

======== CHANNEL f2 ========
SFO2              500.1620006 MHz
NUC2                        1H
CPDPRG[2                waltz16
PCPD2                     80.00 usec
PLW2               18.00000000 W
PLW12               0.37195000 W

F2 - Processing parameters
SI                        65536
SF                470.6206054 MHz
WDW                          EM
SSB                   0
LB                         0.30 Hz
GB                    0
PC                         1.00
```



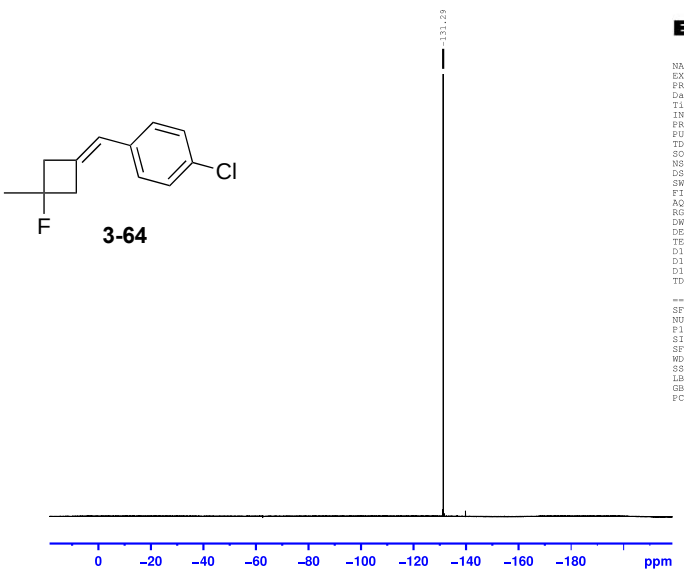
BRUKER

```
NAME                JAM-818-44
EXPNO                        1
PROCNO                       1
Date_                 20170902
Time                     15.58
INSTRUM                  spect
PROBHD    5 mm PADUL 13C
PULPROG                  zg30
TD                      65536
SOLVENT                  CDCl3
NS                          16
DS                           2
SWH                 8223.685 Hz
FIDRES              0.125483 Hz
AQ                  3.9846387 sec
RG                        90.5
DW                    60.800 usec
DE                     6.50 usec
TE                    294.9 K
D1                  2.00000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                        1H
P1                       9.31 usec
PL1                     -3.90 dB
PL1W               21.64248466 W
SFO1              400.2324716 MHz
SI                       32768
SF                400.23001125 MHz
WDW                         EM
SSB                          0
LB                    0.30 Hz
GB                           0
PC                        1.00
```

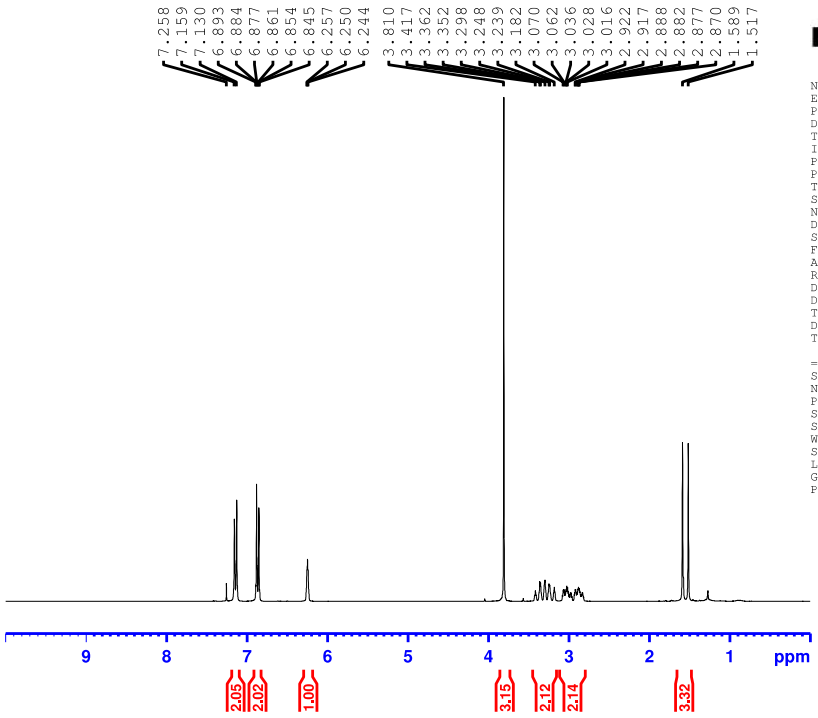


BRUKER

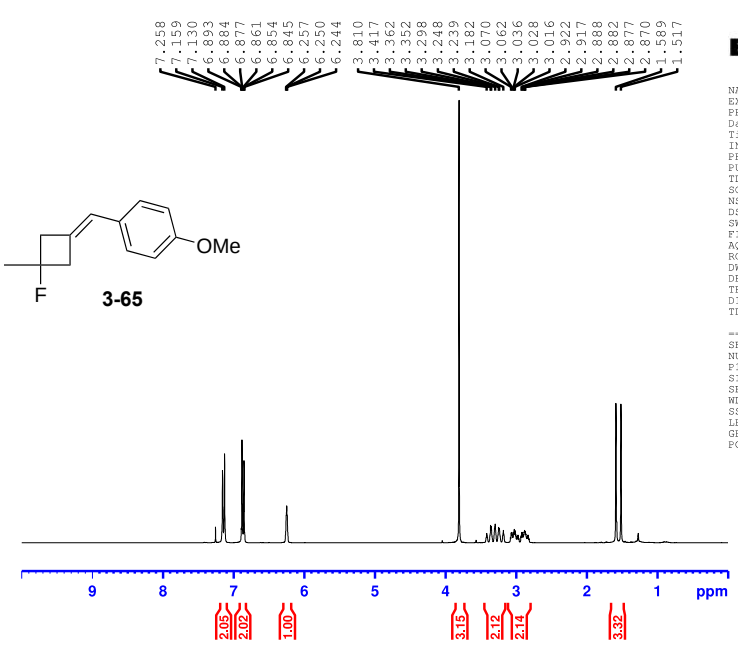
```
NAME                JAM-818-44
EXPNO                        2
PROCNO                       1
Date_                 20170902
Time                     17.04
INSTRUM                  spect
PROBHD    5 mm PADUL 13C
PULPROG                zgpg30
TD                      65536
SOLVENT                  CDCl3
NS                         848
DS                           4
SWH                24038.461 Hz
FIDRES              0.366798 Hz
AQ                  1.3631988 sec
RG                         203
DW                    20.800 usec
DE                     6.50 usec
TE                    295.1 K
D1                  3.00000000 sec
D11                 0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                       13C
P1                      10.00 usec
PL1                     -0.44 dB
PL1W               39.19395828 W
SFO1              100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                        1H
PCPD2                   90.00 usec
PL2                     -3.90 dB
PL12                    15.81 dB
PL13                   120.00 dB
PL2W               21.64248466 W
PL12W               0.23137002 W
PL13W               0.00000000 W
SFO2              400.2316009 MHz
SI                       32768
SF                100.6379140 MHz
WDW                         EM
SSB                          0
LB                    1.00 Hz
GB                           0
PC                        1.40
```



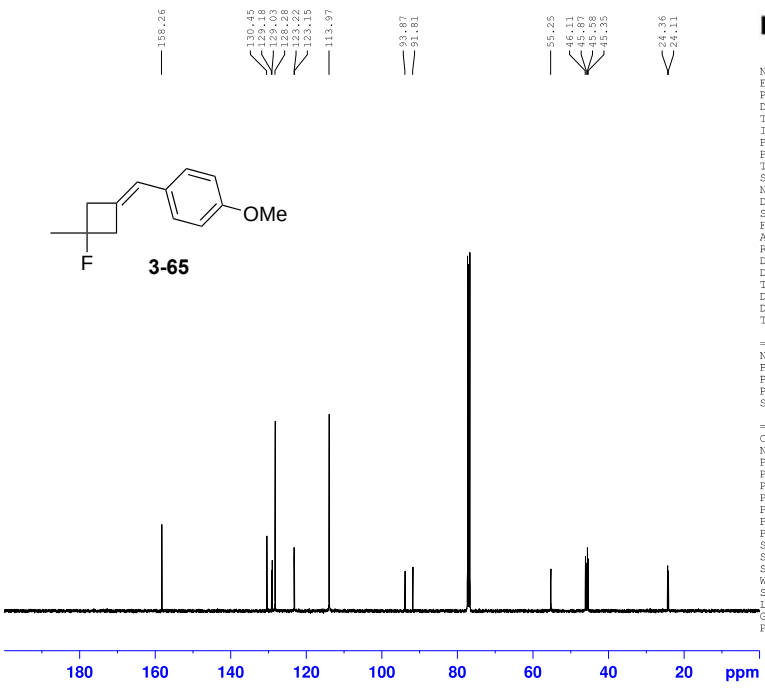

```
NAME                JAM-818-44
EXPNO                       11
PROCNO                       1
Date_                 20170904
Time                     11.32
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG          zgfhigqn.2
TD                       131072
SOLVENT                  CDCl3
NS                          16
DS                           4
SWH                  89285.711 Hz
FIDRES               0.681196 Hz
AQ                   0.7340532 sec
RG                         203
DW                     5.600 usec
DE                     6.50 usec
TE                    -3200.8 K
D1                 1.00000000 sec
D11                0.03000000 sec
D12                0.00002000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1                376.4607164 MHz
NUC1                        19F
P1                       14.20 usec
SI                         65536
SF                  376.4983662 MHz
WDW                          EM
SSB                           0
LB                       0.30 Hz
GB                            0
PC                         1.00
```



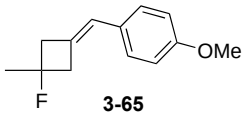

```
NAME                JAM-818-8
EXPNO                      10
PROCNO                      1
Date_                20170809
Time                    22.04
INSTRUM                 spect
PROBHD    5 mm QNP  1H/1
PULPROG                 zg30
TD                      32768
SOLVENT                 CDCl3
NS                         16
DS                          2
SWH                 6188.119 Hz
FIDRES              0.188846 Hz
AQ                  2.6477044 sec
RG                       71.8
DW                    80.800 usec
DE                     6.50 usec
TE                    -925.3 K
D1                 1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1           300.2318540 MHz
NUC1                       1H
P1                      12.71 usec
SI                      32768
SF             300.2300092 MHz
WDW                        EM
SSB                         0
LB                      0.10 Hz
GB                          0
PC                       1.00
```



```
NAME                JAM-818-8
EXPNO                      10
PROCNO                      1
Date_                20170809
Time                    22.04
INSTRUM                 spect
PROBHD    5 mm QNP  1H/1
PULPROG                 zg30
TD                      32768
SOLVENT                 CDCl3
NS                         16
DS                          2
SWH                6188.119 Hz
FIDRES                0.188846 Hz
AQ                 2.6477044 sec
RG                       71.8
DW                     80.800 usec
DE                      6.50 usec
TE                    -925.3 K
D1                 1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1            300.2318540 MHz
NUC1                      1H
P1                     12.71 usec
SI                     32768
SF              300.2300092 MHz
WDW                       EM
SSB                        0
LB                      0.10 Hz
GB                         0
PC                      1.00
```

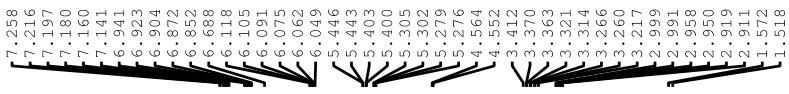


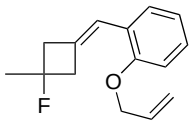
```
NAME                JAM-818-8
EXPNO                       1
PROCNO                      1
Date_                20170810
Time                    10.54
INSTRUM                 spect
PROBHD   5 mm PADUL 13C
PULPROG                 zgpg30
TD                      65536
SOLVENT                 CDCl3
NS                        595
DS                          4
SWH               24038.461 Hz
FIDRES                0.366798 Hz
AQ                 1.3631988 sec
RG                       71.8
DW                     20.800 usec
DE                      6.50 usec
TE                    310.2 K
D1                 3.00000000 sec
D11                0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                      13C
P1                     10.00 usec
PL1                    -0.44 dB
PL1W              39.19395828 W
SFO1              100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                      1H
PCPD2                  90.00 usec
PL2                    -3.90 dB
PL12                   15.81 dB
PL13                  120.00 dB
PL2W              21.64248466 W
PL12W              0.23137002 W
PL13W              0.00000000 W
SFO2              400.2316009 MHz
SI                     32768
SF              100.6379140 MHz
WDW                       EM
SSB                        0
LB                      1.00 Hz
GB                         0
PC                      1.40
```



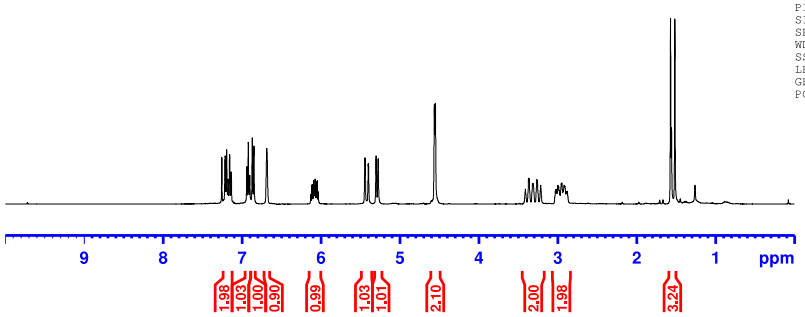
3-65


```
NAME                JAM-818-8
EXPNO                      11
PROCNO                      1
Date_                20170810
Time                    10.00
INSTRUM                 spect
PROBHD    5 mm PABBO BB-
PULPROG          zgfhigqn.2
TD                     131072
SOLVENT                 CDCl3
NS                         16
DS                          4
SWH                89285.711 Hz
FIDRES             0.681196 Hz
AQ                 0.7340532 sec
RG                       203
DW                     5.600 usec
DE                     6.50 usec
TE                   3079.3 K
D1                 1.00000000 sec
D11                0.03000000 sec
D12                0.00002000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1            376.4607164 MHz
NUC1                     19F
P1                     14.20 usec
SI                      65536
SF              376.4983662 MHz
WDW                        EM
SSB                         0
LB                      0.30 Hz
GB                          0
PC                       1.00
```

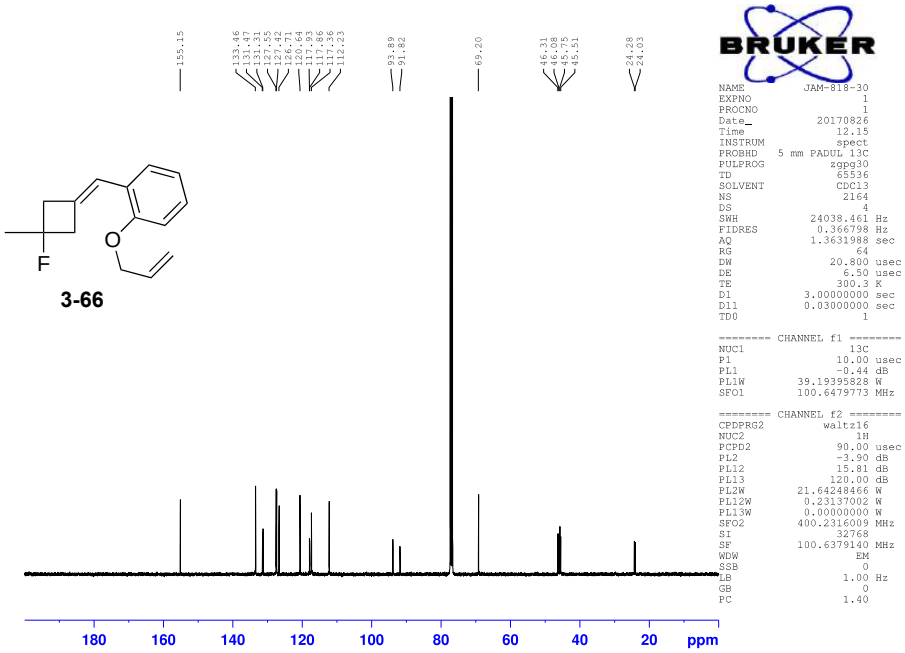




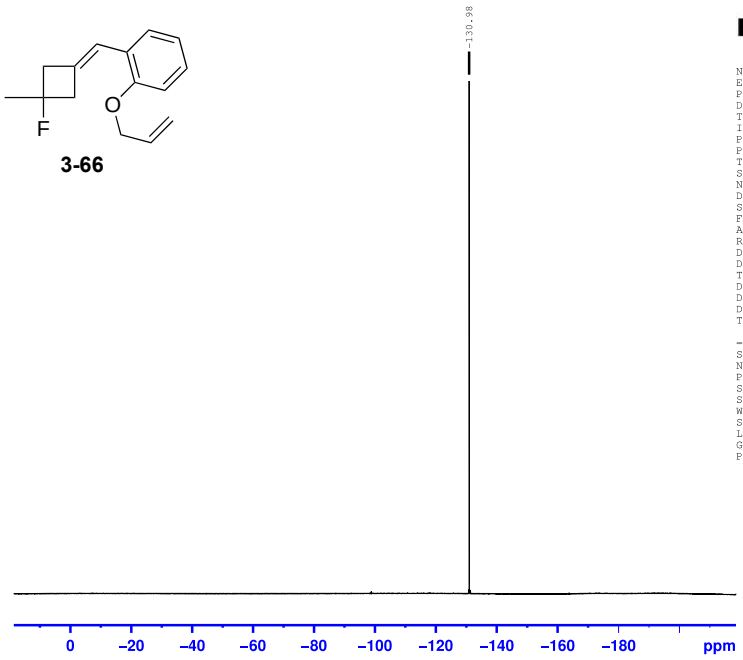
3-66



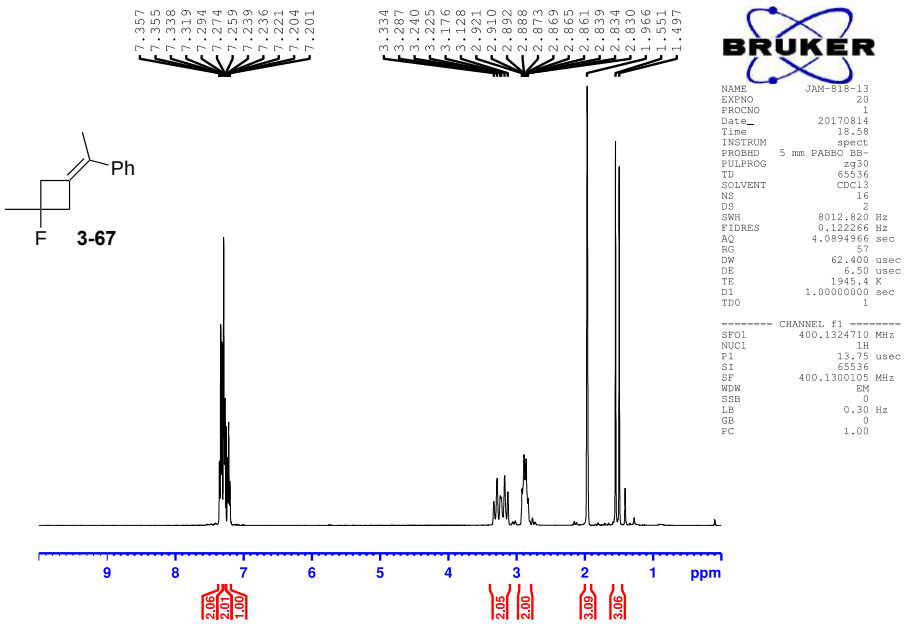

```
NAME                JAM-818-30
EXPNO                       10
PROCNO                       1
Date_                20170825
Time                    14.01
INSTRUM                 spect
PROBHD    5 mm PABBO BB-
PULPROG                  zg30
TD                      65536
SOLVENT                 CDCl3
NS                         16
DS                          2
SWH                8012.820 Hz
FIDRES             0.122266 Hz
AQ                 4.0894966 sec
RG                       71.8
DW                    62.400 usec
DE                     6.50 usec
TE                   2961.8 K
D1                 1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1            400.1324710 MHz
NUC1                     1H
P1                     13.75 usec
SI                      65536
SF              400.1300103 MHz
WDW                        EM
SSB                         0
LB                      0.30 Hz
GB                          0
PC                       1.00
```

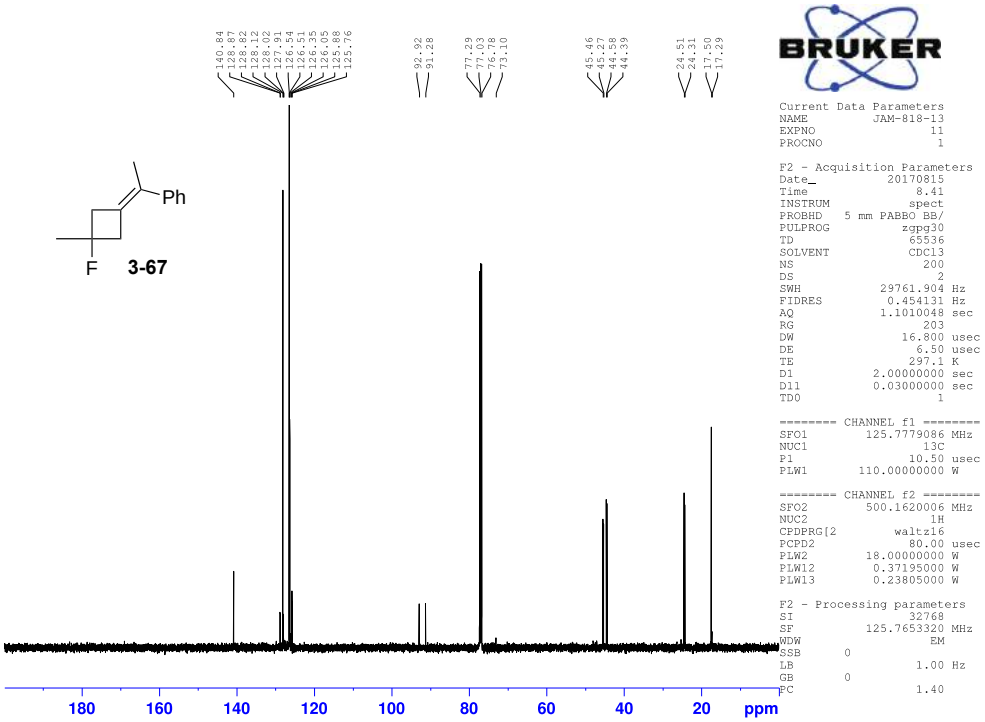


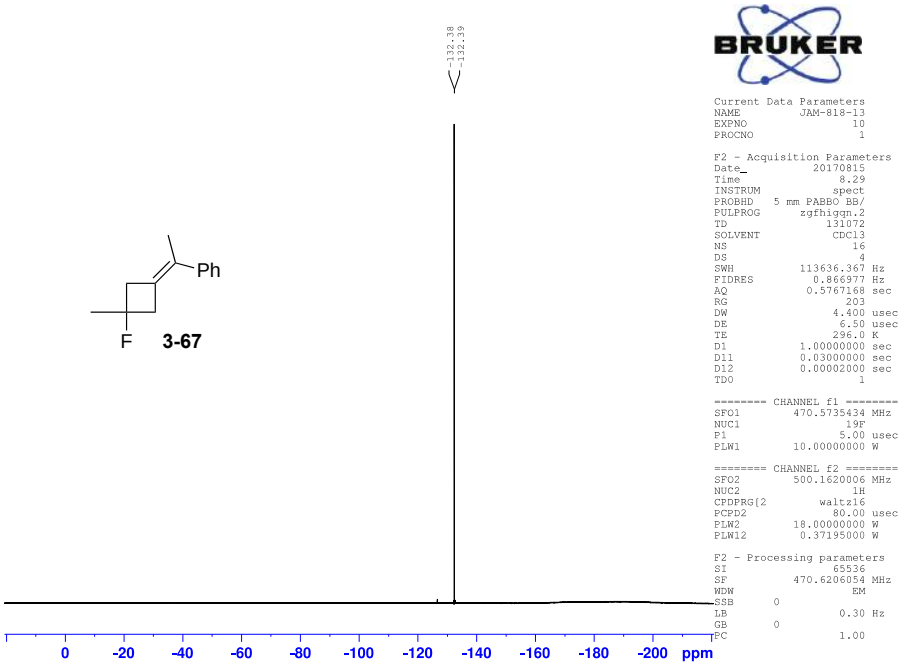

```
NAME              JAM-818-30
EXPNO                      1
PROCNO                     1
Date_               20170826
Time                  12.15
INSTRUM               spect
PROBHD    5 mm PADUL 13C
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     2164
DS                        4
SWH               24038.461 Hz
FIDRES             0.366798 Hz
AQ                1.3631988 sec
RG                       64
DW                  20.800 usec
DE                   6.50 usec
TE                  300.3 K
D1               3.00000000 sec
D11              0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    13C
P1                   10.00 usec
PL1                  -0.44 dB
PL1W          39.19395828 W
SFO1         100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                90.00 usec
PL2                  -3.90 dB
PL12                 15.81 dB
PL13                120.00 dB
PL2W          21.64248466 W
PL12W          0.23137002 W
PL13W          0.00000000 W
SFO2         400.2316009 MHz
SI                    32768
SF           100.6379140 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```



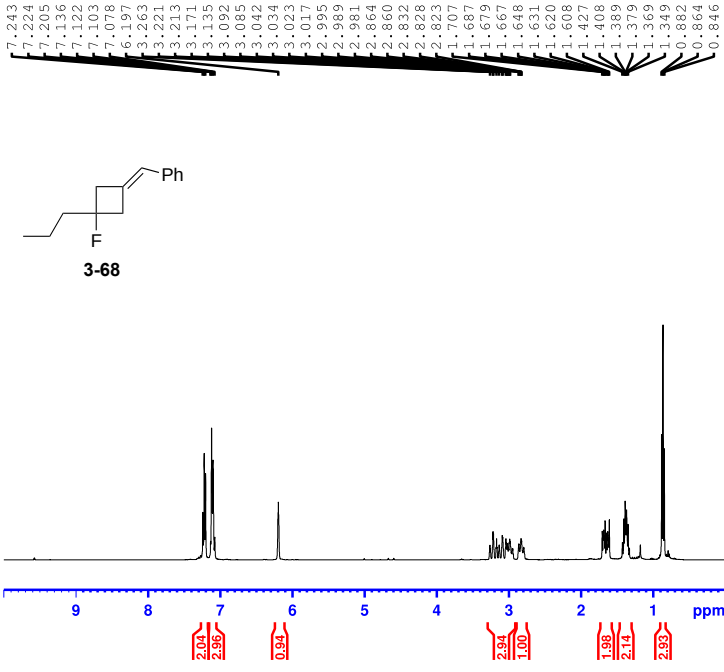

```
NAME              JAM-818-30
EXPNO                     11
PROCNO                     1
Date_               20170825
Time                  14.03
INSTRUM               spect
PROBHD    5 mm PABBO BB-
PULPROG          zgfhigqn.2
TD                   131072
SOLVENT               CDCl3
NS                        16
DS                         4
SWH               89285.711 Hz
FIDRES             0.681196 Hz
AQ                0.7340532 sec
RG                       203
DW                   5.600 usec
DE                   6.50 usec
TE                  2698.5 K
D1               1.00000000 sec
D11              0.03000000 sec
D12              0.00002000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1         376.4607164 MHz
NUC1                   19F
P1                   14.20 usec
SI                    65536
SF           376.4983662 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```


7.357
7.355
7.338
7.319
7.294
7.274
7.259
7.239
7.236
7.221
7.204
7.201
3.334
3.287
3.240
3.225
3.176
3.128
2.921
2.910
2.892
2.888
2.873
2.869
2.865
2.861
2.839
2.834
2.830
1.966
1.551
1.497
Ph
F
3-67
9
8
7
6
5
4
3
2
1
ppm
2.06
2.01
1.00
2.05
2.00
3.09
3.06
BRUKER
NAME JAM-818-13
EXPNO 20
PROCNO 1
Date_ 20170814
Time 18.58
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 57
DW 62.400 usec
DE 6.50 usec
TE 1945.4 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 13.75 usec
SI 65536
SF 400.1300105 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


140.84
138.87
128.82
128.12
128.02
127.91
126.54
126.51
126.35
126.05
125.88
125.76
92.92
91.28
77.29
77.03
76.78
73.10
45.46
45.27
44.58
44.39
24.51
24.31
17.50
17.29
Ph
F
3-67
180
160
140
120
100
80
60
40
20
ppm
BRUKER
Current Data Parameters
NAME JAM-818-13
EXPNO 11
PROCNO 1
F2 - Acquisition Parameters
Date_ 20170815
Time 8.41
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 200
DS 2
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010048 sec
RG 203
DW 16.800 usec
DE 6.50 usec
TE 297.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 125.7779086 MHz
NUC1 13C
P1 10.50 usec
PLW1 110.00000000 W
======== CHANNEL f2 ========
SFO2 500.1620006 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 18.00000000 W
PLW12 0.37195000 W
PLW13 0.23805000 W
F2 - Processing parameters
SI 32768
SF 125.7653320 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

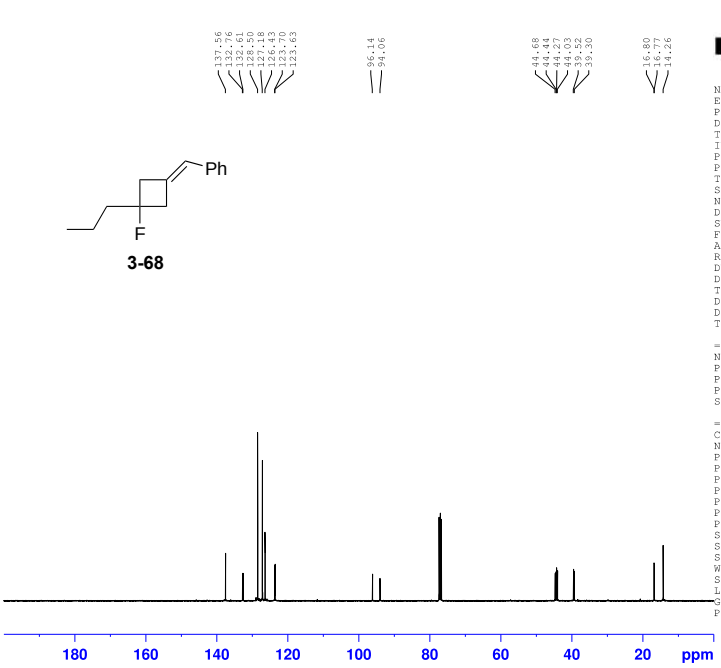



```
Current Data Parameters
NAME                  JAM-818-13
EXPNO                         10
PROCNO                         1

F2 - Acquisition Parameters
Date_                   20170815
Time                        8.29
INSTRUM                    spect
PROBHD    5 mm PABBO BB/
PULPROG            zgfhigqn.2
TD                        131072
SOLVENT                   CDCl3
NS                            16
DS                             4
SWH                  113636.367 Hz
FIDRES                 0.866977 Hz
AQ                    0.5767168 sec
RG                          203
DW                        4.400 usec
DE                        6.50 usec
TE                       296.0 K
D1                  1.00000000 sec
D11                 0.03000000 sec
D12                 0.00002000 sec
TD0                            1

======== CHANNEL f1 ========
SFO1                470.5735434 MHz
NUC1                        19F
P1                         5.00 usec
PLW1               10.00000000 W

======== CHANNEL f2 ========
SFO2                500.1620006 MHz
NUC2                        1H
CPDPRG[2                waltz16
PCPD2                     80.00 usec
PLW2               18.00000000 W
PLW12               0.37195000 W

F2 - Processing parameters
SI                         65536
SF                  470.6206054 MHz
WDW                           EM
SSB                 0
LB                         0.30 Hz
GB                  0
PC                         1.00
```

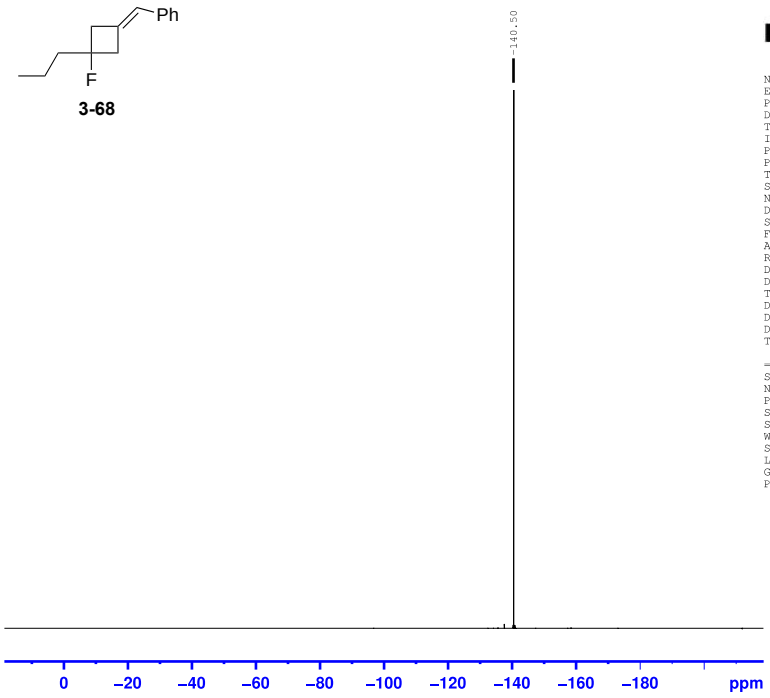



```
NAME                  JAM-776-28
EXPNO                         10
PROCNO                         1
Date_                   20170201
Time                       17.55
INSTRUM                    spect
PROBHD    5 mm PABBO BB-
PULPROG                     zg30
TD                         65536
SOLVENT                   CDCl3
NS                            16
DS                             2
SWH                   8012.820 Hz
FIDRES                0.122266 Hz
AQ                    4.0894966 sec
RG                          20.2
DW                       62.400 usec
DE                        6.50 usec
TE                        89.9 K
D1                  1.00000000 sec
TD0                            1

======== CHANNEL f1 ========
SFO1                400.1324710 MHz
NUC1                        1H
P1                        13.75 usec
SI                         65536
SF                  400.1300593 MHz
WDW                           EM
SSB                            0
LB                         0.30 Hz
GB                             0
PC                         1.00
```

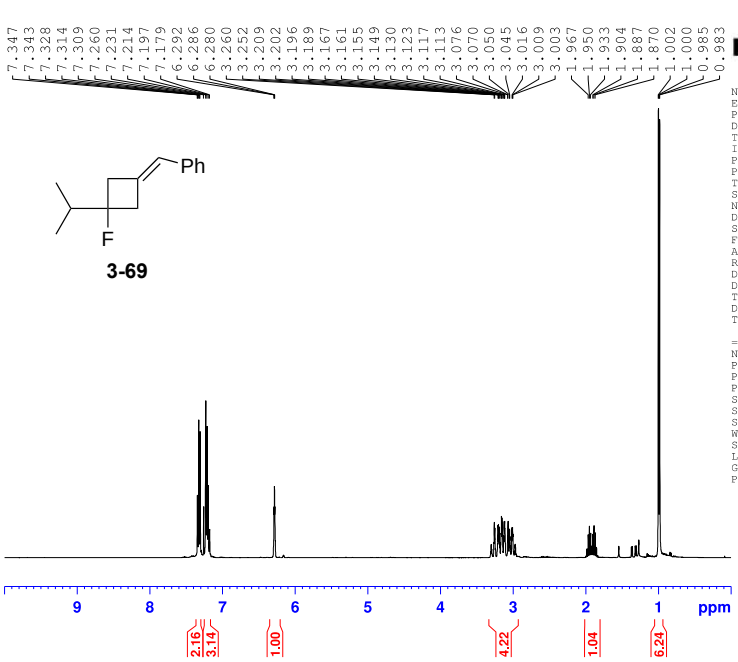
,



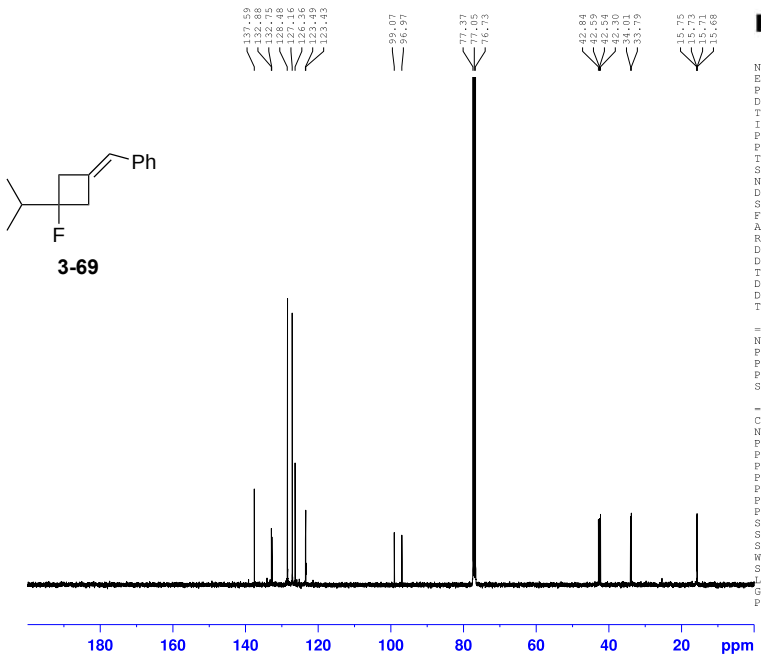

```
BRUKER
NAME                JAM-776-28
EXPNO                        2
PROCNO                       1
Date_                 20170202
Time                      8.54
INSTRUM                  spect
PROBHD    5 mm PADUL 13C
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                         836
DS                           4
SWH                 24038.461 Hz
FIDRES                0.366798 Hz
AQ                    1.3631988 sec
RG                         50.8
DW                       20.800 usec
DE                        6.50 usec
TE                       294.7 K
D1                  3.00000000 sec
D11                 0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                       13C
P1                       10.00 usec
PL1                      -0.44 dB
PL1W               39.19395828 W
SFO1              100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                    90.00 usec
PL2                      -3.90 dB
PL12                     15.81 dB
PL13                    120.00 dB
PL2W               21.64248466 W
PL12W               0.23137002 W
PL13W               0.00000000 W
SFO2              400.2316009 MHz
SI                         32768
SF                100.6379140 MHz
WDW                          EM
SSB                           0
LB                        1.00 Hz
GB                            0
PC                         1.40
```



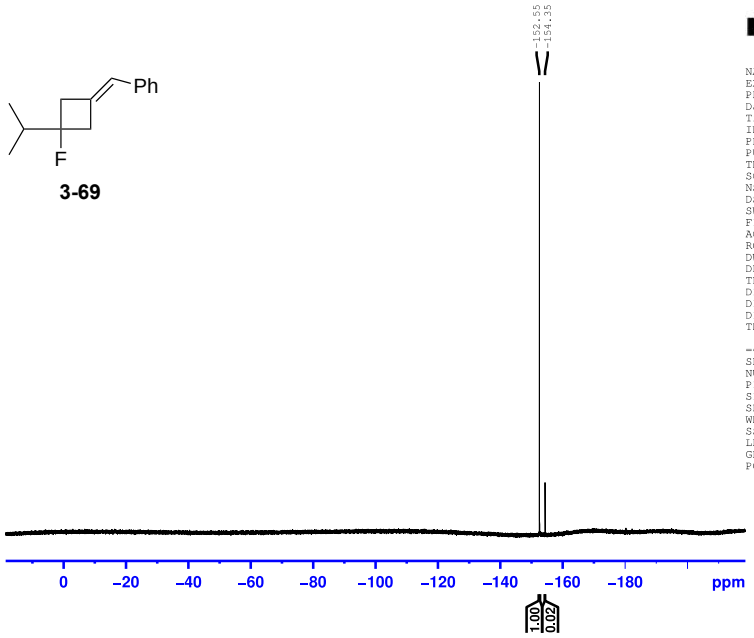

```
BRUKER
NAME                JAM-776-28
EXPNO                       11
PROCNO                       1
Date_                 20170201
Time                     17.57
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG             zgfhigqn.2
TD                      131072
SOLVENT                  CDCl3
NS                          16
DS                           4
SWH                 89285.711 Hz
FIDRES                0.681196 Hz
AQ                    0.7340532 sec
RG                         203
DW                       5.600 usec
DE                        6.50 usec
TE                        90.0 K
D1                  1.00000000 sec
D11                 0.03000000 sec
D12                 0.00002000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1              376.4607164 MHz
NUC1                       19F
P1                       14.20 usec
SI                        65536
SF                376.4983662 MHz
WDW                          EM
SSB                           0
LB                        0.30 Hz
GB                            0
PC                         1.00
```



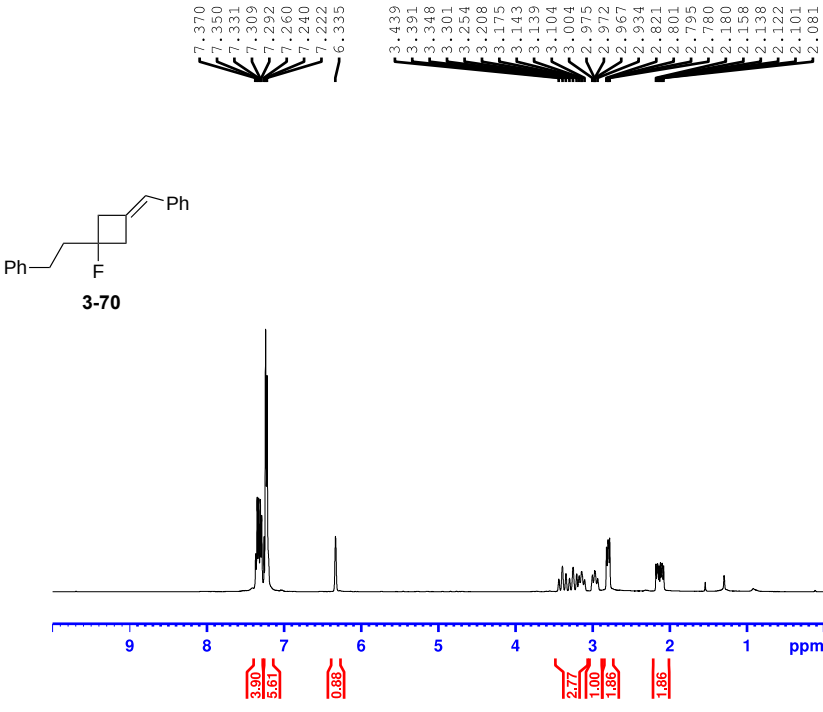

```
NAME            JAM-758-S7
EXPNO                    1
PROCNO                   1
Date_             20161214
Time                 10.50
INSTRUM              spect
PROBHD   5 mm PADUL 13C
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      16
DS                       2
SWH               8223.685 Hz
FIDRES           0.125483 Hz
AQ                3.9846387 sec
RG                    71.8
DW                60.800 usec
DE                 6.50 usec
TE                 294.3 K
D1              2.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   1H
P1                  9.31 usec
PL1                -3.90 dB
PL1W         21.64248466 W
SFO1         400.2324716 MHz
SI                   32768
SF           400.2300121 MHz
WDW                    EM
SSB                     0
LB                 0.30 Hz
GB                      0
PC                   1.00
```



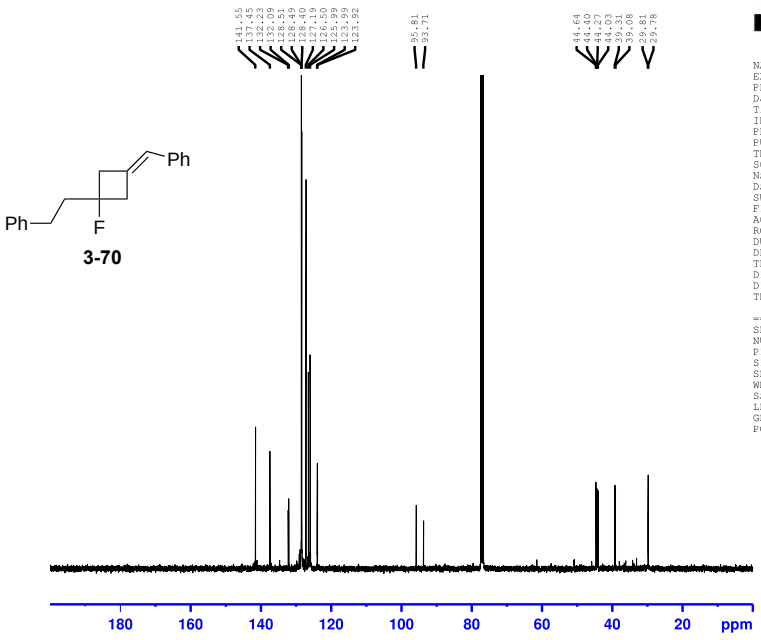

```
NAME            JAM-758-S7
EXPNO                    2
PROCNO                   1
Date_             20161214
Time                 12.09
INSTRUM              spect
PROBHD   5 mm PADUL 13C
PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    1024
DS                       4
SWH              24038.461 Hz
FIDRES           0.366798 Hz
AQ                1.3631988 sec
RG                      64
DW                20.800 usec
DE                 6.50 usec
TE                 294.8 K
D1              3.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                 10.00 usec
PL1                -0.44 dB
PL1W         39.19395828 W
SFO1         100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                   1H
PCPD2              90.00 usec
PL2                -3.90 dB
PL12               15.81 dB
PL13              120.00 dB
PL2W         21.64248466 W
PL12W         0.23137002 W
PL13W         0.00000000 W
SFO2         400.2316009 MHz
SI                   32768
SF           100.6379140 MHz
WDW                    EM
SSB                     0
LB                 1.00 Hz
GB                      0
PC                   1.40
```




```
NAME            JAM-758-57
EXPNO                   11
PROCNO                   1
Date_             20161213
Time                19.32
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG       zgfhigqn.2
TD                  131072
SOLVENT              CDCl3
NS                      16
DS                       4
SWH             89285.711 Hz
FIDRES          0.681196 Hz
AQ              0.7340532 sec
RG                     203
DW                 5.600 usec
DE                 6.50 usec
TE                  90.7 K
D1            1.00000000 sec
D11           0.03000000 sec
D12           0.00002000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1          376.4607164 MHz
NUC1                  19F
P1                 14.20 usec
SI                 65536
SF            376.4983662 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

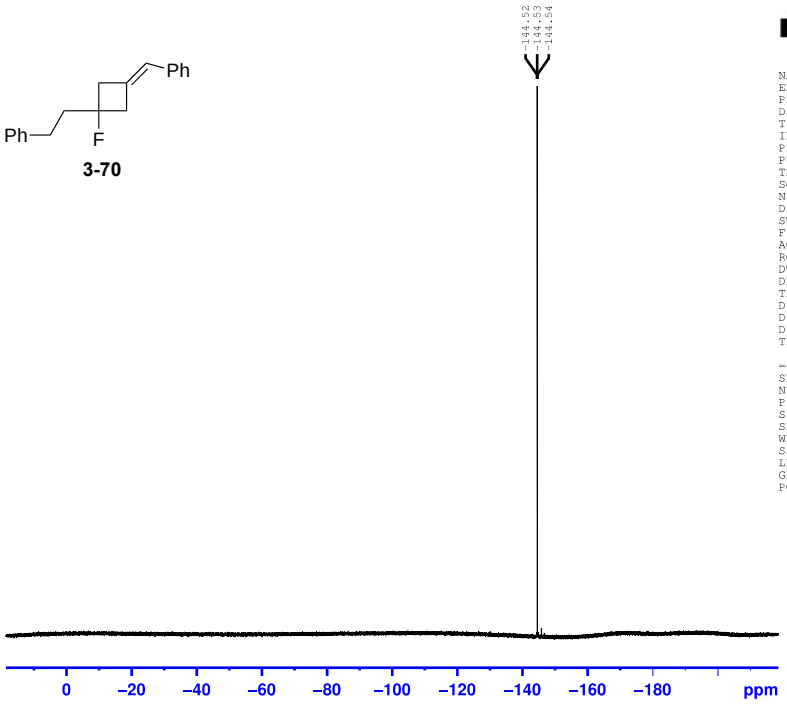



```
NAME            JAM-776-1
EXPNO                  10
PROCNO                  1
Date_            20170114
Time               17.03
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH            8012.820 Hz
FIDRES         0.122266 Hz
AQ             4.0894966 sec
RG                     32
DW                62.400 usec
DE                 6.50 usec
TE                 88.0 K
D1           1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1         400.1324710 MHz
NUC1                   1H
P1                13.75 usec
SI                65536
SF           400.1300092 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



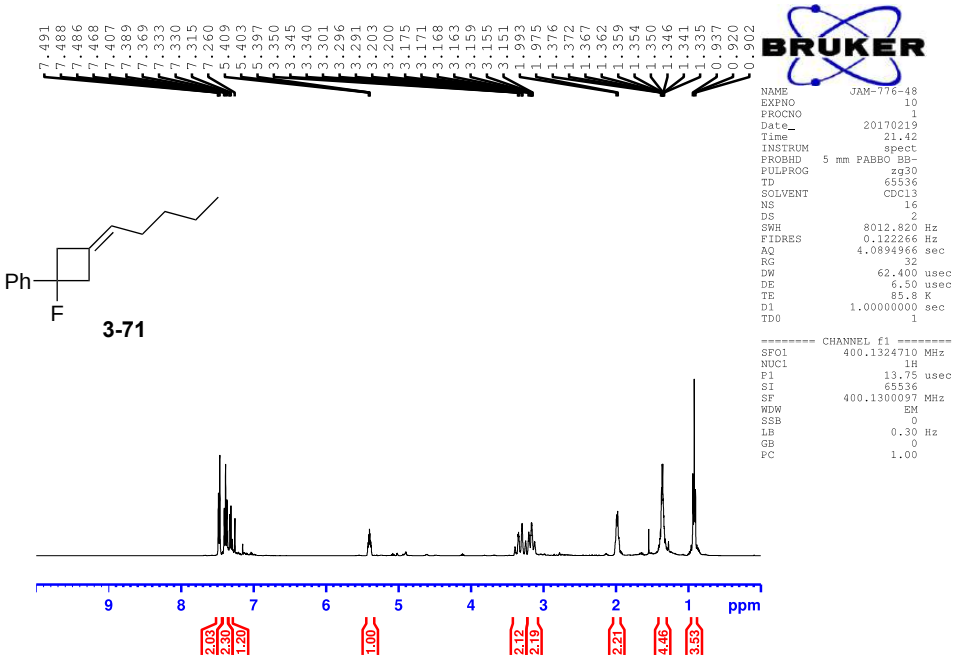
BRUKER

```
NAME                JAM-758-75
EXPNO                       11
PROCNO                       1
Date_             20161230
Time                     22.49
INSTRUM                  spect
PROBHD     5 mm PABBO BB-
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                        1024
DS                           4
SWH                 24038.461 Hz
FIDRES              0.366798 Hz
AQ                  1.3631988 sec
RG                         161
DW                  20.800 usec
DE                   6.50 usec
TE                   91.7 K
D1                  2.00000000 sec
D11                 0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1               100.6228293 MHz
NUC1                        13C
P1                  10.00 usec
SI                       32768
SF                 100.6127685 MHz
WDW                         EM
SSB                          0
LB                   1.00 Hz
GB                           0
PC                   1.40
```



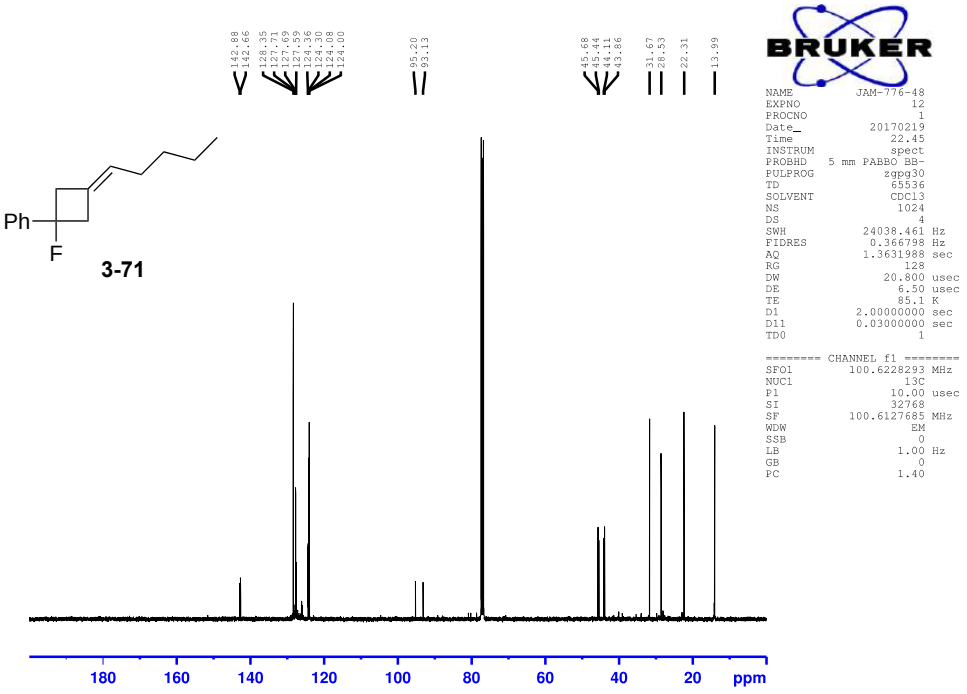
BRUKER

```
NAME                JAM-834-7
EXPNO                       11
PROCNO                       1
Date_             20171013
Time                     18.55
INSTRUM                  spect
PROBHD     5 mm PABBO BB-
PULPROG             zgfhigqn.2
TD                      131072
SOLVENT                  CDCl3
NS                          16
DS                           4
SWH                 89285.711 Hz
FIDRES              0.681196 Hz
AQ                  0.7340532 sec
RG                         203
DW                  5.600 usec
DE                   6.50 usec
TE                  -2530.9 K
D1                  1.00000000 sec
D11                 0.03000000 sec
D12                 0.00002000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1               376.4607164 MHz
NUC1                        19F
P1                  14.20 usec
SI                       65536
SF                 376.4983662 MHz
WDW                         EM
SSB                          0
LB                   0.30 Hz
GB                           0
PC                   1.00
```



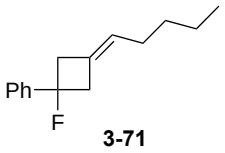
BRUKER

NAME	JAM-776-48
EXPNO	10
PROCNO	1
Date_	20170219
Time	21.42
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	8012.820 Hz
FIDRES	0.122266 Hz
AQ	4.0894966 sec
RG	32
DW	62.400 usec
DE	6.50 usec
TE	85.8 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
SFO1	400.1324710 MHz
NUC1	1H
P1	13.75 usec
SI	65536
SF	400.1300097 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00



BRUKER

NAME	JAM-776-48
EXPNO	12
PROCNO	1
Date_	20170219
Time	22.45
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	1024
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	128
DW	20.800 usec
DE	6.50 usec
TE	85.1 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
SFO1	100.6228293 MHz
NUC1	13C
P1	10.00 usec
SI	32768
SF	100.6127685 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40



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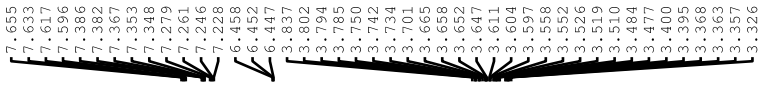
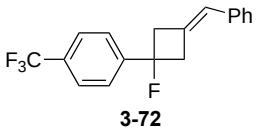
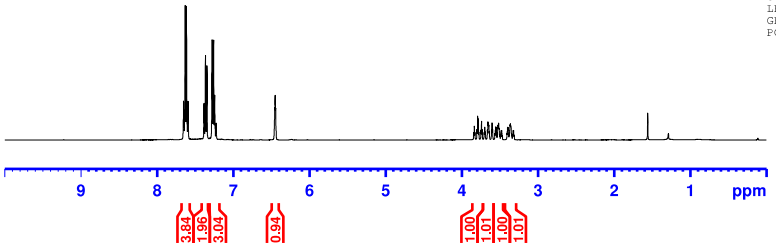
```
NAME                JAM-776-48
EXPNO                       11
PROCNO                       1
Date_                 20170219
Time                     21.44
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG          zgfhigqn.2
TD                       131072
SOLVENT                  CDCl3
NS                          16
DS                           4
SWH                  89285.711 Hz
FIDRES               0.681196 Hz
AQ                   0.7340532 sec
RG                         203
DW                       5.600 usec
DE                       6.50 usec
TE                       85.7 K
D1                1.00000000 sec
D11               0.03000000 sec
D12               0.00002000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1               376.4607164 MHz
NUC1                       19F
P1                       14.20 usec
SI                       65536
SF                376.4983662 MHz
WDW                        EM
SSB                         0
LB                       0.30 Hz
GB                          0
PC                       1.00
```

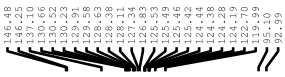


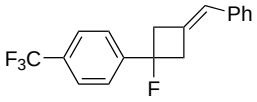


3-72

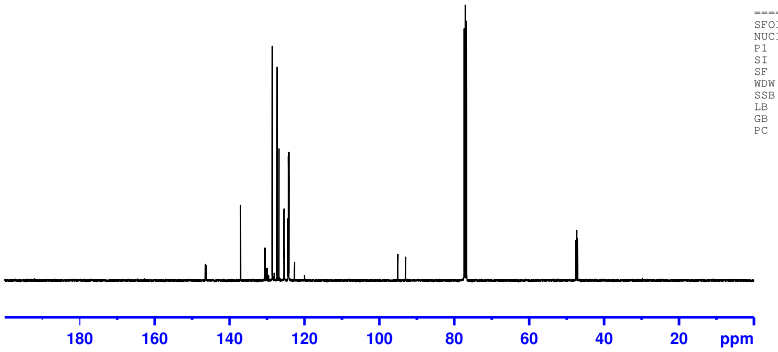



```
NAME                JAM-818-41
EXPNO                       10
PROCNO                       1
Date_                 20170831
Time                     16.58
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG                  zg30
TD                       65536
SOLVENT                  CDCl3
NS                          16
DS                           2
SWH                  8012.820 Hz
FIDRES               0.122266 Hz
AQ                   4.0894966 sec
RG                        50.8
DW                       62.400 usec
DE                       6.50 usec
TE                       2389.8 K
D1                1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1               400.1324710 MHz
NUC1                       1H
P1                       13.75 usec
SI                       65536
SF                400.1300092 MHz
WDW                        EM
SSB                         0
LB                       0.30 Hz
GB                          0
PC                       1.00
```

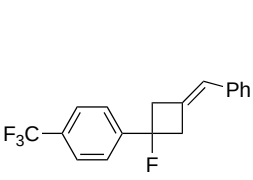




3-72

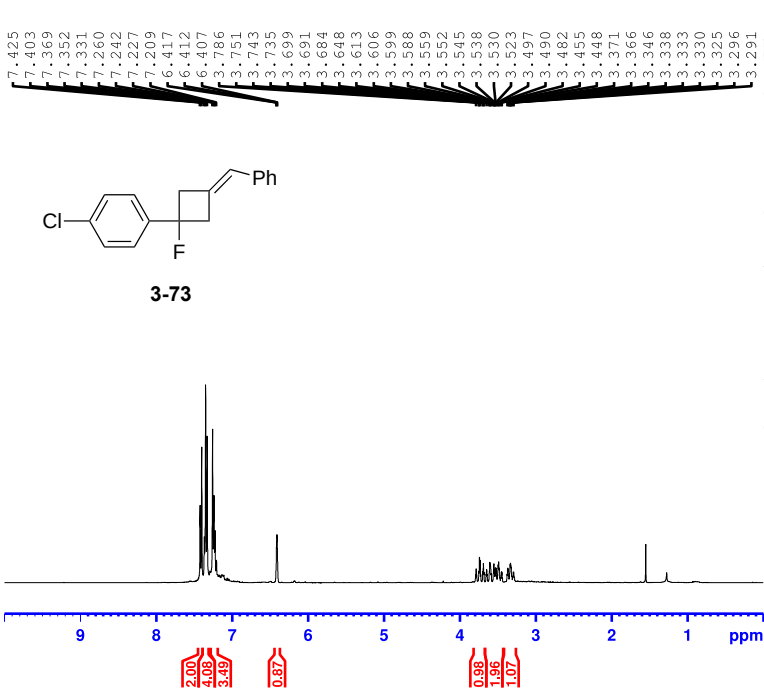


```
NAME                JAM-818-41
EXPNO                       12
PROCNO                       1
Date_                 20170901
Time                      2.36
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                        1024
DS                           4
SWH                 24038.461 Hz
FIDRES              0.366798 Hz
AQ                  1.3631988 sec
RG                         203
DW                    20.800 usec
DE                     6.50 usec
TE                    2632.5 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1               100.6228293 MHz
NUC1                       13C
P1                       10.00 usec
SI                       32768
SF                 100.6127685 MHz
WDW                         EM
SSB                          0
LB                        1.00 Hz
GB                           0
PC                        1.40
```



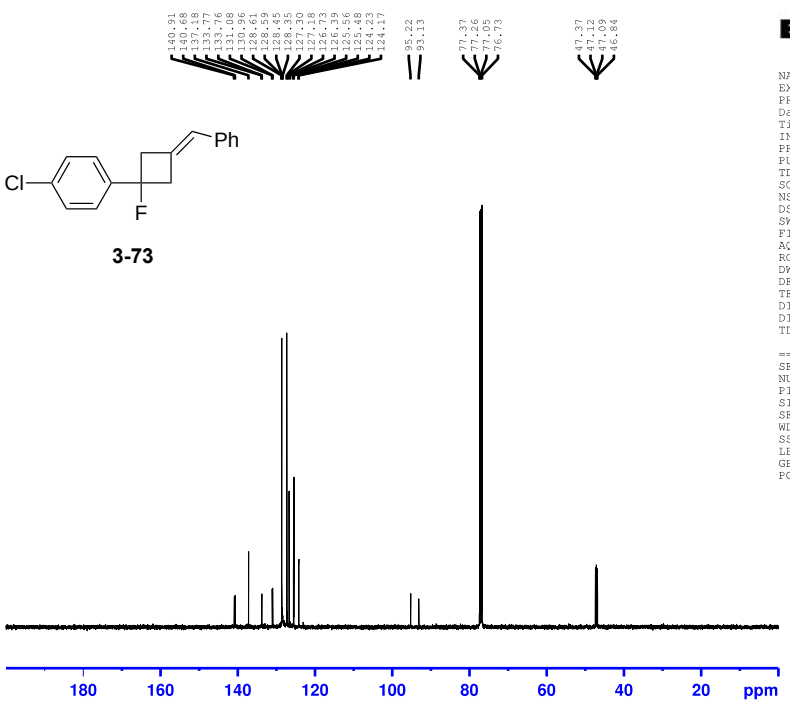
3-72

```
NAME                JAM-818-41
EXPNO                       11
PROCNO                       1
Date_                 20170831
Time                     17.00
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG              zgfhigqn.2
TD                      131072
SOLVENT                  CDCl3
NS                           16
DS                           4
SWH                 89285.711 Hz
FIDRES              0.681196 Hz
AQ                  0.7340532 sec
RG                         203
DW                     5.600 usec
DE                     6.50 usec
TE                    2467.0 K
D1                 1.00000000 sec
D11                0.03000000 sec
D12                0.00002000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1               376.4607164 MHz
NUC1                       19F
P1                       14.20 usec
SI                       65536
SF                 376.4983662 MHz
WDW                         EM
SSB                          0
LB                        0.30 Hz
GB                           0
PC                        1.00
```



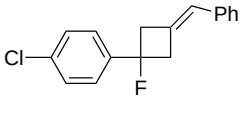
BRUKER

```
NAME                JAM-802-47
EXPNO                       10
PROCNO                       1
Date_                 20170627
Time                     18.59
INSTRUM                  spect
PROBHD     5 mm PABBO BB-
PULPROG                  zg30
TD                      65536
SOLVENT                 CDCl3
NS                         16
DS                          2
SWH                  8012.820 Hz
FIDRES               0.122266 Hz
AQ                   4.0894966 sec
RG                         64
DW                     62.400 usec
DE                      6.50 usec
TE                    2694.3 K
D1                 1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1           400.1324710 MHz
NUC1                       1H
P1                     13.75 usec
SI                      65536
SF           400.1300092 MHz
WDW                        EM
SSB                         0
LB                       0.30 Hz
GB                          0
PC                       1.00
```



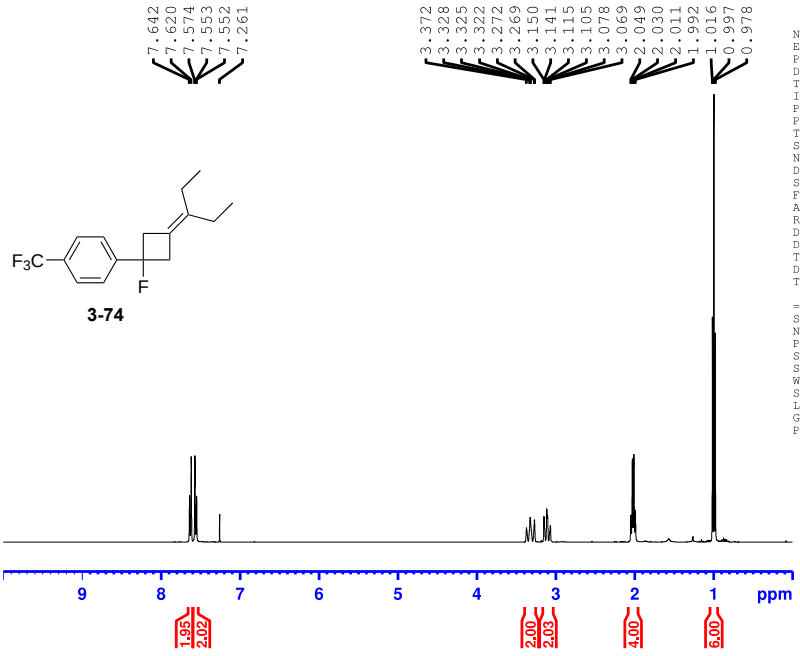
BRUKER

```
NAME                JAM-802-47
EXPNO                       12
PROCNO                       1
Date_                 20170627
Time                     21.04
INSTRUM                  spect
PROBHD     5 mm PABBO BB-
PULPROG                 zgpg30
TD                      65536
SOLVENT                 CDCl3
NS                       1024
DS                          4
SWH                 24038.461 Hz
FIDRES               0.366798 Hz
AQ                   1.3631988 sec
RG                        203
DW                     20.800 usec
DE                      6.50 usec
TE                    2336.9 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1           100.6228293 MHz
NUC1                      13C
P1                     10.00 usec
SI                      32768
SF           100.6127685 MHz
WDW                        EM
SSB                         0
LB                       1.00 Hz
GB                          0
PC                       1.40
```



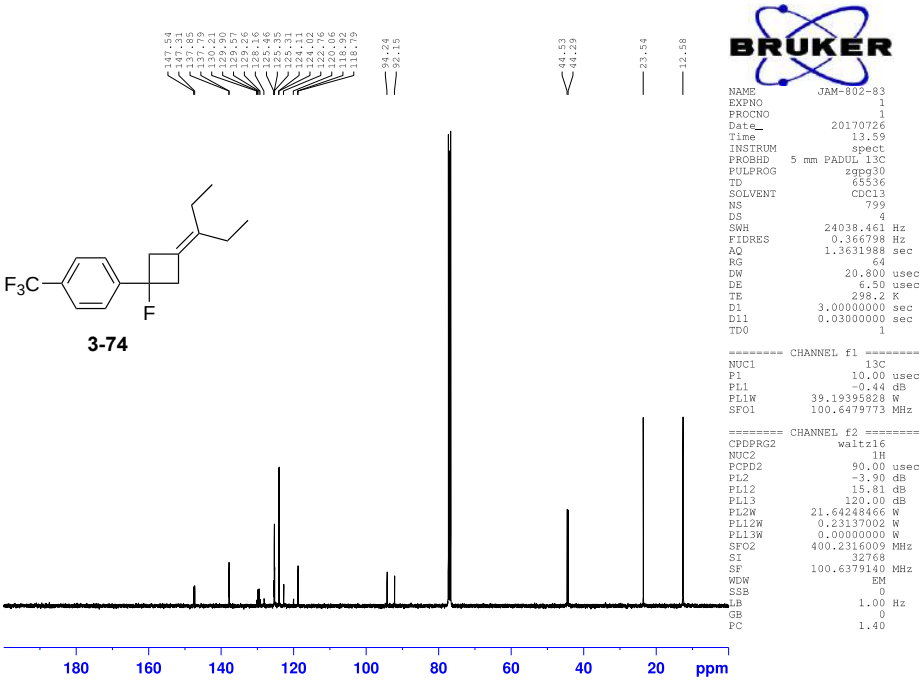
3-73


```
NAME                JAM-802-47
EXPNO                       11
PROCNO                       1
Date_                 20170627
Time                     19.02
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG          zgfhigqn.2
TD                      131072
SOLVENT                 CDCl3
NS                          16
DS                           4
SWH                89285.711 Hz
FIDRES                 0.681196 Hz
AQ                    0.7340532 sec
RG                          203
DW                      5.600 usec
DE                      6.50 usec
TE                     2506.8 K
D1                  1.00000000 sec
D11                 0.03000000 sec
D12                 0.00002000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1           376.4607164 MHz
NUC1                     19F
P1                     14.20 usec
SI                      65536
SF             376.4983662 MHz
WDW                        EM
SSB                         0
LB                     0.30 Hz
GB                          0
PC                      1.00
```



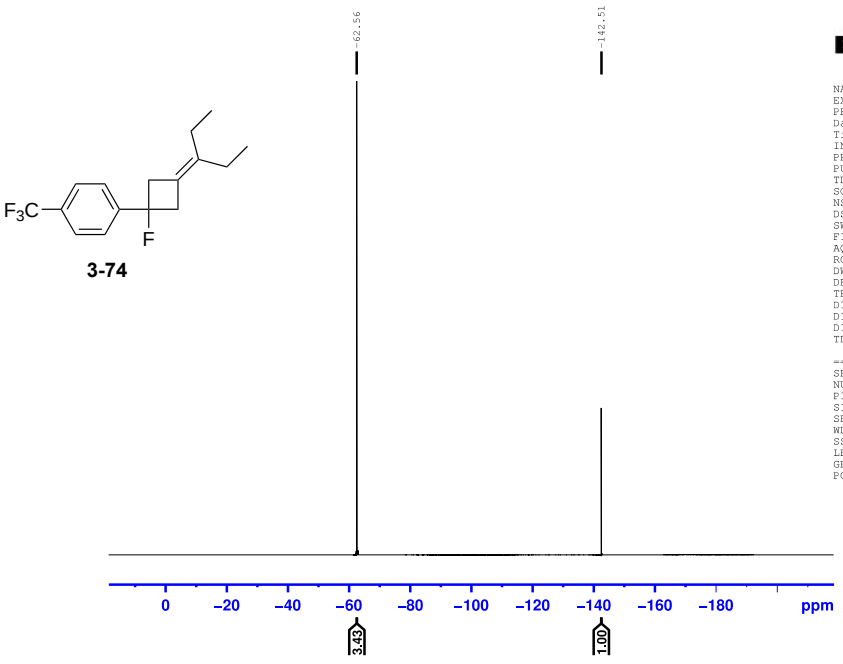
3-74

```
NAME                JAM-802-83
EXPNO                       10
PROCNO                       1
Date_                 20170726
Time                     11.05
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG                  zg30
TD                      65536
SOLVENT                 CDCl3
NS                          16
DS                           2
SWH                 8012.820 Hz
FIDRES                 0.122266 Hz
AQ                    4.0894966 sec
RG                         50.8
DW                     62.400 usec
DE                      6.50 usec
TE                    -3141.0 K
D1                  1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1           400.1324710 MHz
NUC1                     1H
P1                     13.75 usec
SI                      65536
SF             400.1300094 MHz
WDW                        EM
SSB                         0
LB                     0.30 Hz
GB                          0
PC                      1.00
```



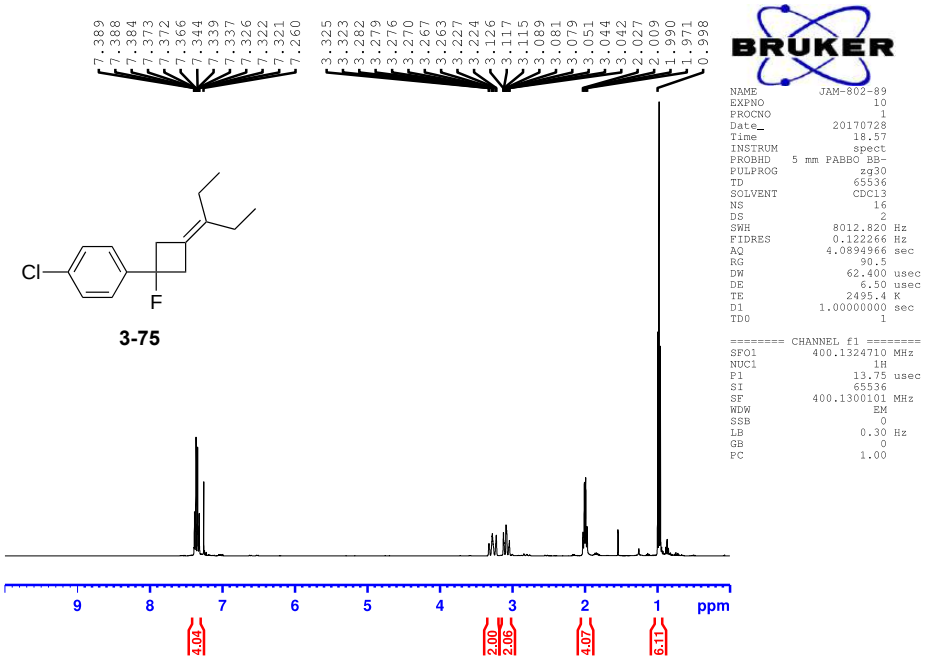
BRUKER

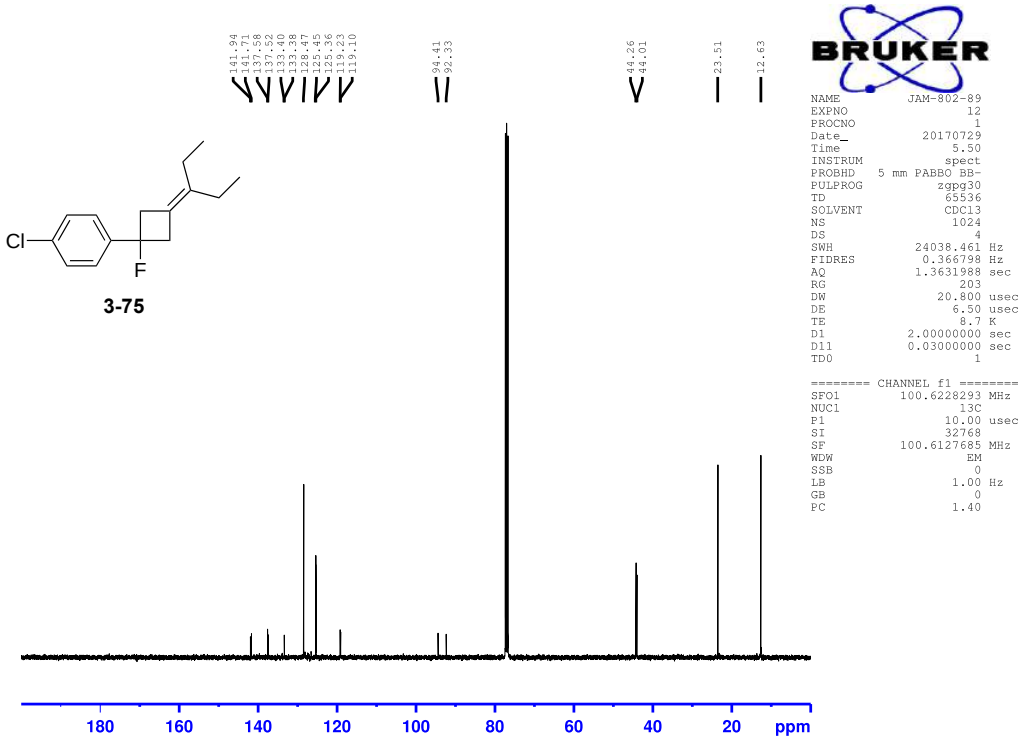
NAME	JAM-802-83
EXPNO	1
PROCNO	1
Date_	20170726
Time	13.59
INSTRUM	spect
PROBHD	5 mm PADUL 13C
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	799
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	64
DW	20.800 usec
DE	6.50 usec
TE	298.2 K
D1	3.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	10.00 usec
PL1	-0.44 dB
PL1W	39.19395828 W
SFO1	100.6479773 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	90.00 usec
PL2	-3.90 dB
PL12	15.81 dB
PL13	120.00 dB
PL2W	21.64248466 W
PL12W	0.23137002 W
PL13W	0.00000000 W
SFO2	400.2316009 MHz
SI	32768
SF	100.6379140 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

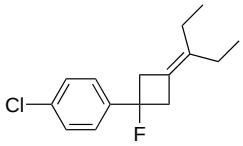


BRUKER

NAME	JAM-802-83
EXPNO	11
PROCNO	1
Date_	20170726
Time	11.07
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgfhigqn.2
TD	131072
SOLVENT	CDCl3
NS	16
DS	4
SWH	89285.711 Hz
FIDRES	0.681196 Hz
AQ	0.7340532 sec
RG	203
DW	5.600 usec
DE	6.50 usec
TE	-2833.3 K
D1	1.00000000 sec
D11	0.03000000 sec
D12	0.00002000 sec
TD0	1
======== CHANNEL f1 ========	
SFO1	376.4607164 MHz
NUC1	19F
P1	14.20 usec
SI	65536
SF	376.4983662 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

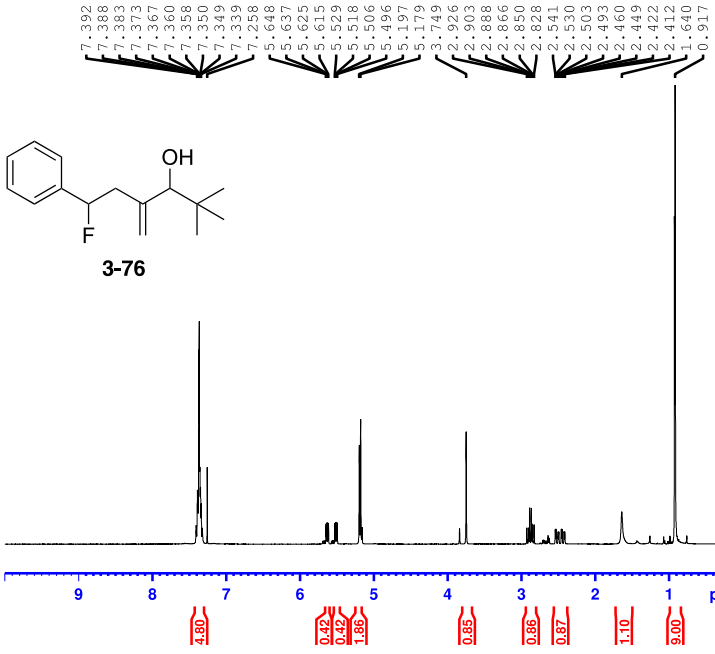

7.389
7.388
7.384
7.373
7.372
7.366
7.344
7.339
7.337
7.326
7.322
7.321
7.260
3.325
3.323
3.282
3.279
3.276
3.270
3.267
3.263
3.227
3.224
3.126
3.117
3.115
3.089
3.081
3.079
3.051
3.044
3.042
2.027
2.009
1.990
1.971
0.998
Cl
F
3-75
9
8
7
6
5
4
3
2
1
ppm
4.04
2.00
2.06
4.07
6.11
BRUKER
NAME JAM-802-89
EXPNO 10
PROCNO 1
Date_ 20170728
Time 18.57
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 90.5
DW 62.400 usec
DE 6.50 usec
TE 295.4 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 13.75 usec
SI 65536
SF 400.1300101 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


141.94
141.71
137.68
137.52
133.40
133.38
128.47
125.45
125.26
123.23
119.10
94.41
92.33
44.26
44.01
23.51
12.63
Cl
F
3-75
180
160
140
120
100
80
60
40
20
ppm
BRUKER
NAME JAM-802-89
EXPNO 12
PROCNO 1
Date_ 20170729
Time 5.50
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 8.7 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6228293 MHz
NUC1 13C
P1 10.00 usec
SI 32768
SF 100.6127685 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



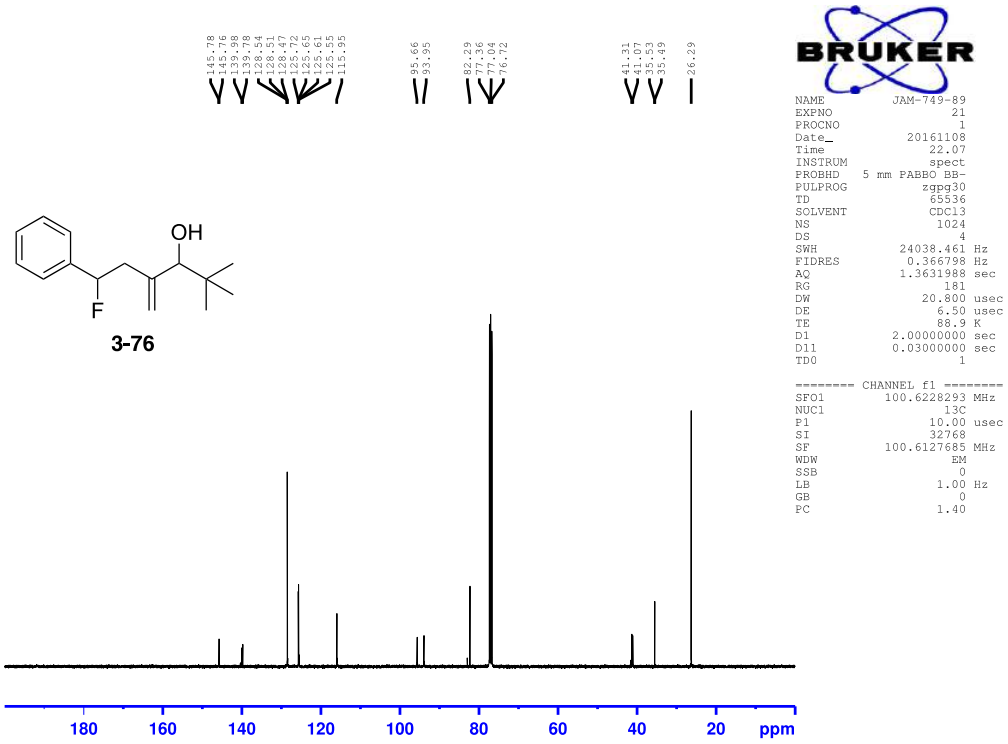
3-75


```
NAME                JAM-802-89
EXPNO                       11
PROCNO                       1
Date_             20170728
Time                     18.59
INSTRUM                  spect
PROBHD     5 mm PABBO BB-
PULPROG           zgfhigqn.2
TD                      131072
SOLVENT                 CDCl3
NS                          16
DS                           4
SWH                  89285.711 Hz
FIDRES               0.681196 Hz
AQ                   0.7340532 sec
RG                         203
DW                       5.600 usec
DE                       6.50 usec
TE                     2521.7 K
D1                   1.00000000 sec
D11                  0.03000000 sec
D12                  0.00002000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1                376.4607164 MHz
NUC1                       19F
P1                       14.20 usec
SI                       65536
SF                  376.4983662 MHz
WDW                         EM
SSB                          0
LB                        0.30 Hz
GB                           0
PC                        1.00
```

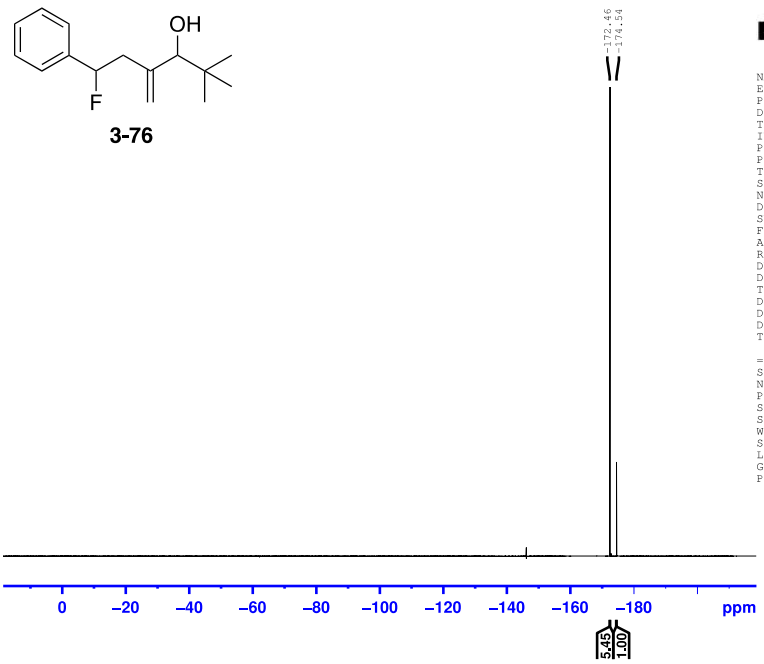


3-76

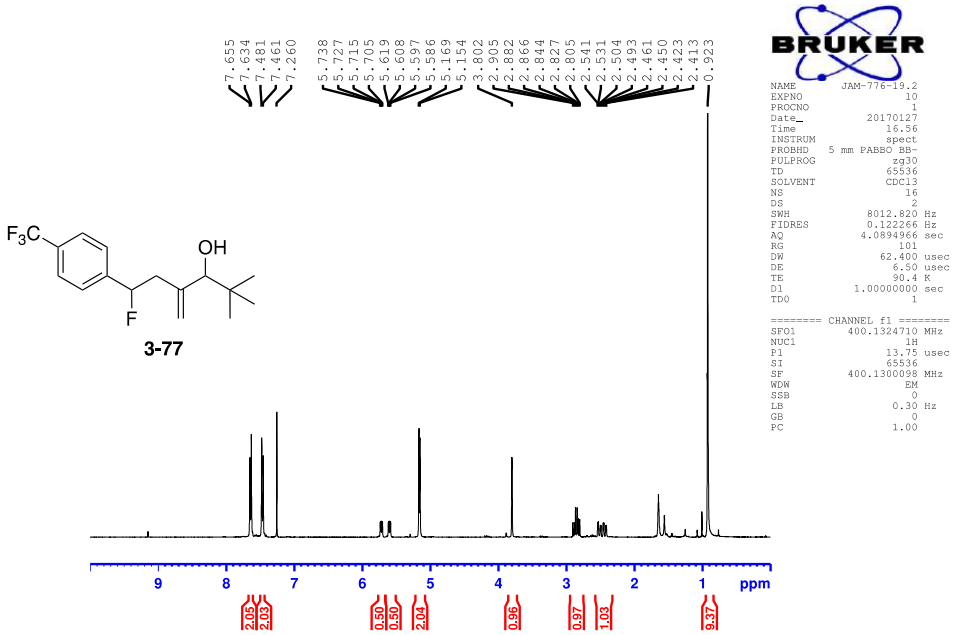
```
NAME                JAM-749-89
EXPNO                       20
PROCNO                       1
Date_             20161108
Time                     21.07
INSTRUM                  spect
PROBHD     5 mm PABBO BB-
PULPROG                  zg30
TD                       65536
SOLVENT                 CDCl3
NS                          16
DS                           2
SWH                  8012.820 Hz
FIDRES               0.122266 Hz
AQ                   4.0894966 sec
RG                          64
DW                       62.400 usec
DE                       6.50 usec
TE                       89.7 K
D1                   1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1                400.1324710 MHz
NUC1                        1H
P1                       13.75 usec
SI                       65536
SF                  400.1300107 MHz
WDW                         EM
SSB                          0
LB                        0.30 Hz
GB                           0
PC                        1.00
```

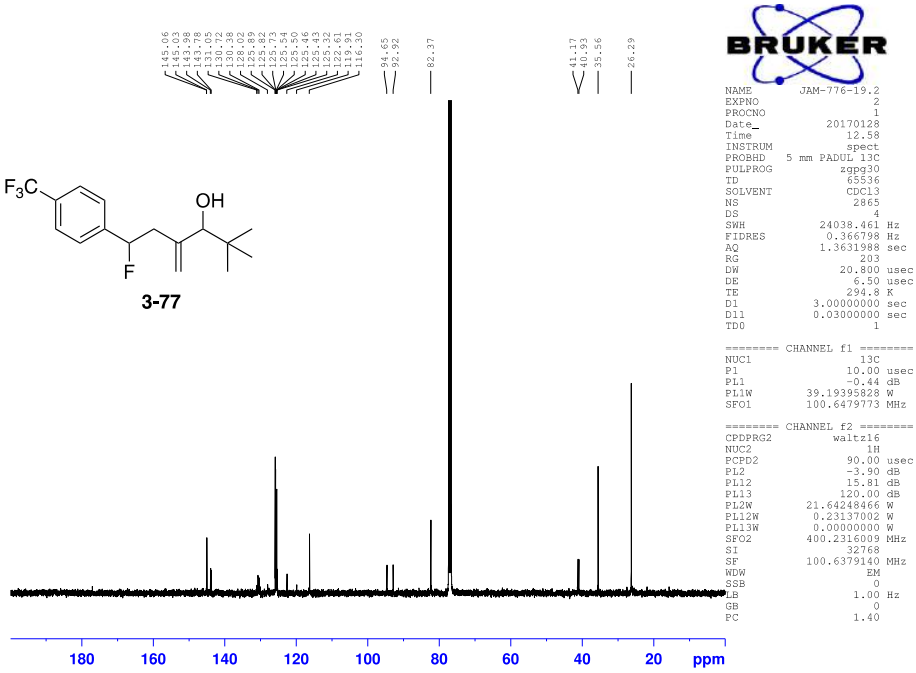


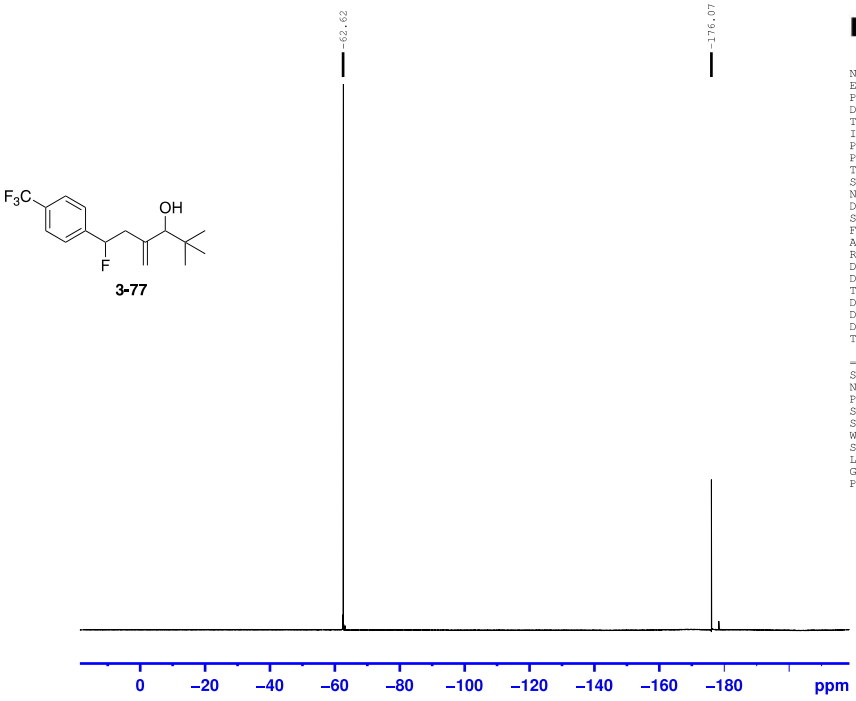

```
NAME                JAM-749-89
EXPNO                       21
PROCNO                       1
Date_             20161108
Time                     22.07
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                        1024
DS                           4
SWH                 24038.461 Hz
FIDRES                0.366798 Hz
AQ                    1.3631988 sec
RG                         181
DW                      20.800 usec
DE                       6.50 usec
TE                       88.9 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1               100.6228293 MHz
NUC1                       13C
P1                       10.00 usec
SI                       32768
SF                100.6127685 MHz
WDW                         EM
SSB                          0
LB                        1.00 Hz
GB                           0
PC                        1.40
```




```
NAME                JAM-749-89
EXPNO                       10
PROCNO                       1
Date_             20161104
Time                     19.35
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG              zgfhigqn.2
TD                      131072
SOLVENT                  CDCl3
NS                          16
DS                           4
SWH                 89285.711 Hz
FIDRES                0.681196 Hz
AQ                    0.7340532 sec
RG                         203
DW                       5.600 usec
DE                       6.50 usec
TE                       88.5 K
D1                 1.00000000 sec
D11                0.03000000 sec
D12                0.00002000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1               376.4607164 MHz
NUC1                       19F
P1                       14.20 usec
SI                       65536
SF                376.4983662 MHz
WDW                         EM
SSB                          0
LB                        0.30 Hz
GB                           0
PC                        1.00
```


7.655
7.634
7.481
7.461
7.260
5.738
5.727
5.715
5.705
5.619
5.608
5.597
5.586
5.169
5.154
3.802
2.905
2.882
2.866
2.844
2.827
2.805
2.541
2.531
2.504
2.493
2.461
2.450
2.423
2.413
0.923
F3C
OH
F
3-77
9
8
7
6
5
4
3
2
1
ppm
2.05
2.03
0.50
0.50
2.04
0.96
0.97
1.03
9.37
BRUKER
NAME JAM-776-19.2
EXPNO 10
PROCNO 1
Date_ 20170127
Time 16.56
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 101
DW 62.400 usec
DE 6.50 usec
TE 90.4 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 13.75 usec
SI 65536
SF 400.1300098 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


145.06
145.03
143.98
143.78
131.05
130.72
130.38
128.02
125.89
125.82
125.73
125.54
125.50
125.46
125.43
125.32
122.61
119.91
116.30
94.65
92.92
82.37
41.17
40.93
35.56
26.29
F3C
OH
F
3-77
180
160
140
120
100
80
60
40
20
ppm
BRUKER
NAME JAM-776-19.2
EXPNO 2
PROCNO 1
Date_ 20170128
Time 12.58
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2865
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 294.8 K
D1 3.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 -0.44 dB
PL1W 39.19395828 W
SFO1 100.6479773 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.90 dB
PL12 15.81 dB
PL13 120.00 dB
PL2W 21.64248466 W
PL12W 0.23137002 W
PL13W 0.00000000 W
SFO2 400.2316009 MHz
SI 32768
SF 100.6379140 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



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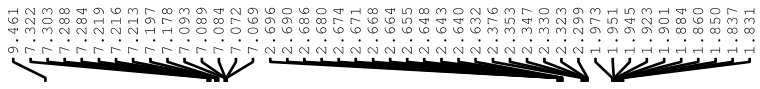
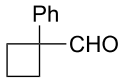
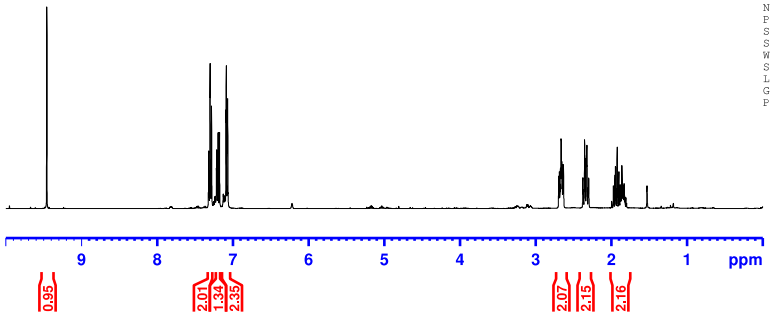
```
NAME                JAM-776-19.2
EXPNO                         11
PROCNO                         1
Date_                   20170127
Time                       16.59
INSTRUM                    spect
PROBHD    5 mm PABBO BB-
PULPROG              zgfhigqn.2
TD                         131072
SOLVENT                    CDCl3
NS                            16
DS                             4
SWH                    89285.711 Hz
FIDRES                 0.681196 Hz
AQ                     0.7340532 sec
RG                           203
DW                         5.600 usec
DE                         6.50 usec
TE                         90.4 K
D1                     1.00000000 sec
D11                    0.03000000 sec
D12                    0.00002000 sec
TD0                            1

======== CHANNEL f1 ========
SFO1                 376.4607164 MHz
NUC1                        19F
P1                        14.20 usec
SI                         65536
SF                   376.4983662 MHz
WDW                           EM
SSB                            0
LB                          0.30 Hz
GB                             0
PC                          1.00
```

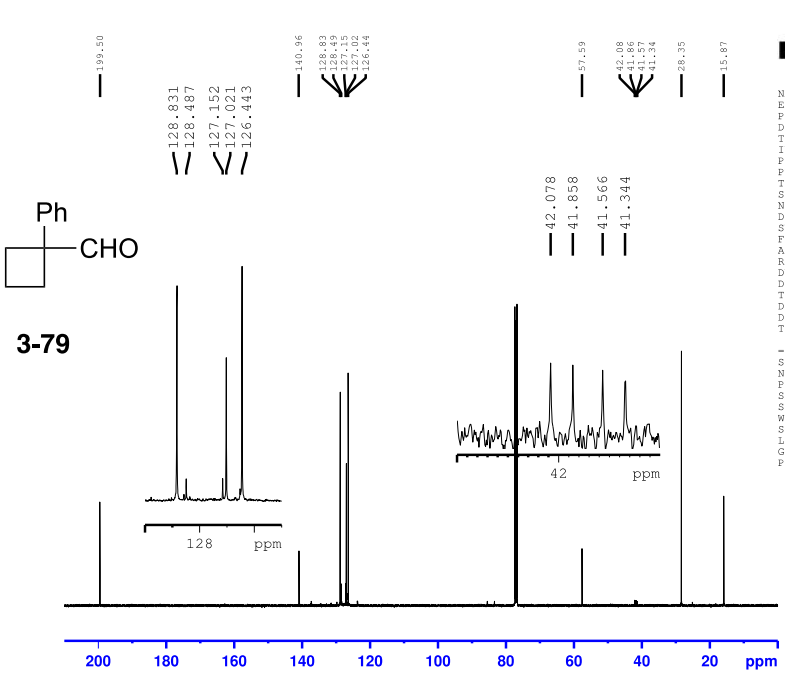




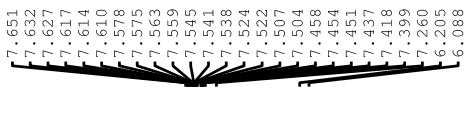
3-79

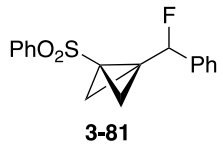



```
NAME                JAM-749-54
EXPNO                         10
PROCNO                         1
Date_                   20161010
Time                       16.51
INSTRUM                    spect
PROBHD    5 mm PABBO BB-
PULPROG                    zg30
TD                         65536
SOLVENT                    CDCl3
NS                            16
DS                             2
SWH                    8012.820 Hz
FIDRES                 0.122266 Hz
AQ                     4.0894966 sec
RG                            57
DW                        62.400 usec
DE                         6.50 usec
TE                         89.1 K
D1                     1.00000000 sec
TD0                            1

======== CHANNEL f1 ========
SFO1                 400.1324710 MHz
NUC1                         1H
P1                        13.75 usec
SI                         65536
SF                   400.1300426 MHz
WDW                           EM
SSB                            0
LB                          0.30 Hz
GB                             0
PC                          1.00
```

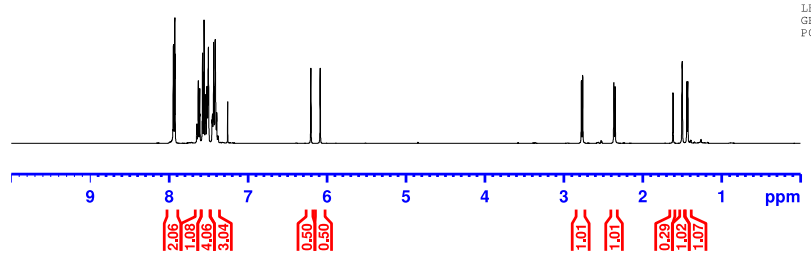


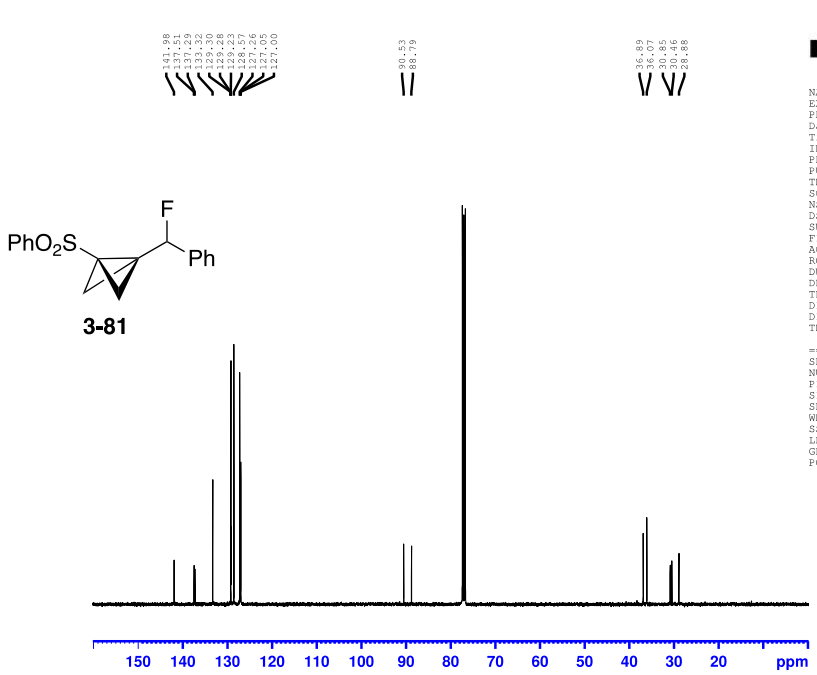
```
NAME                JAM-749-54
EXPNO                       12
PROCNO                       1
Date_             20161010
Time                     21.04
INSTRUM                  spect
PROBHD     5 mm PABBO BB-
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                        1024
DS                           4
SWH                 24038.461 Hz
FIDRES                0.366798 Hz
AQ                    1.3631988 sec
RG                         203
DW                      20.800 usec
DE                       6.50 usec
TE                       88.6 K
D1                    2.00000000 sec
D11                   0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1               100.6228293 MHz
NUC1                       13C
P1                      10.00 usec
SI                       32768
SF                 100.6127685 MHz
WDW                         EM
SSB                          0
LB                      1.00 Hz
GB                           0
PC                        1.40
```





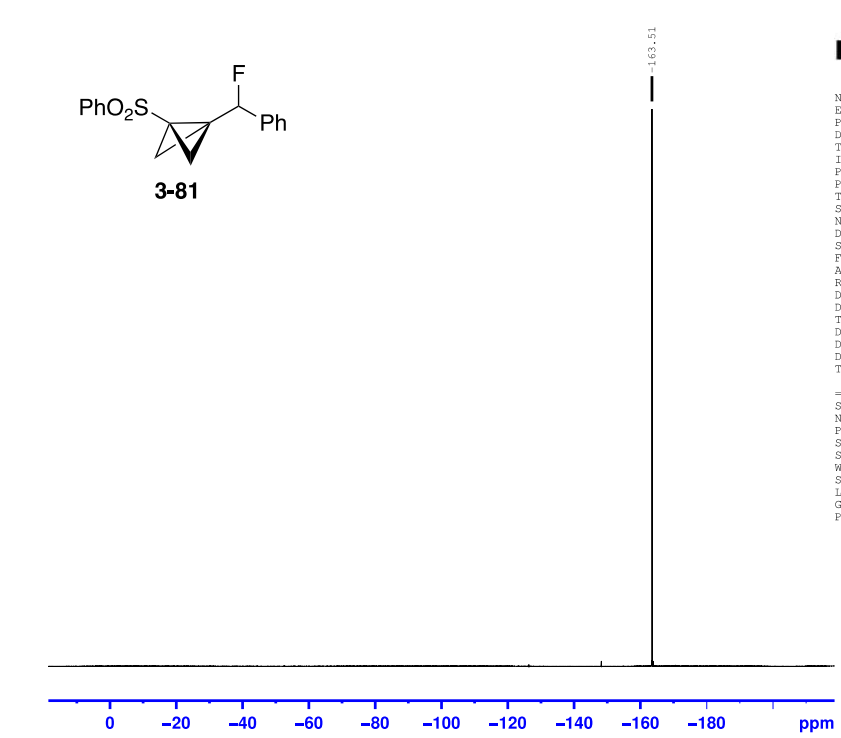
```
NAME                JAM-785-71
EXPNO                       10
PROCNO                       1
Date_             20170523
Time                     10.34
INSTRUM                  spect
PROBHD     5 mm PABBO BB-
PULPROG                  zg30
TD                       65536
SOLVENT                  CDCl3
NS                          16
DS                           2
SWH                  8012.820 Hz
FIDRES                0.122266 Hz
AQ                    4.0894966 sec
RG                         71.8
DW                      62.400 usec
DE                       6.50 usec
TE                       87.9 K
D1                    1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1               400.1324710 MHz
NUC1                       1H
P1                      13.75 usec
SI                       65536
SF                 400.1300102 MHz
WDW                         EM
SSB                          0
LB                      0.30 Hz
GB                           0
PC                        1.00
```





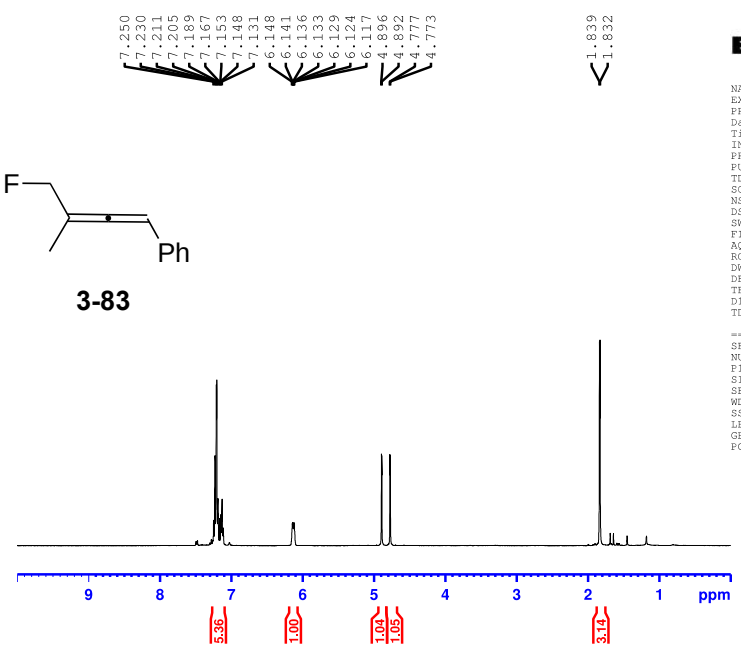
BRUKER

```
NAME                JAM-785-71
EXPNO                       12
PROCNO                       1
Date_                 20170524
Time                      1.26
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG                 zppg30
TD                       65536
SOLVENT                  CDCl3
NS                        1024
DS                           4
SWH                 24038.461 Hz
FIDRES               0.366798 Hz
AQ                   1.3631988 sec
RG                         144
DW                      20.800 usec
DE                       6.50 usec
TE                       87.9 K
D1                  2.00000000 sec
D11                 0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1               100.6228293 MHz
NUC1                       13C
P1                       10.00 usec
SI                       32768
SF                 100.6127685 MHz
WDW                         EM
SSB                          0
LB                       1.00 Hz
GB                           0
PC                       1.40
```



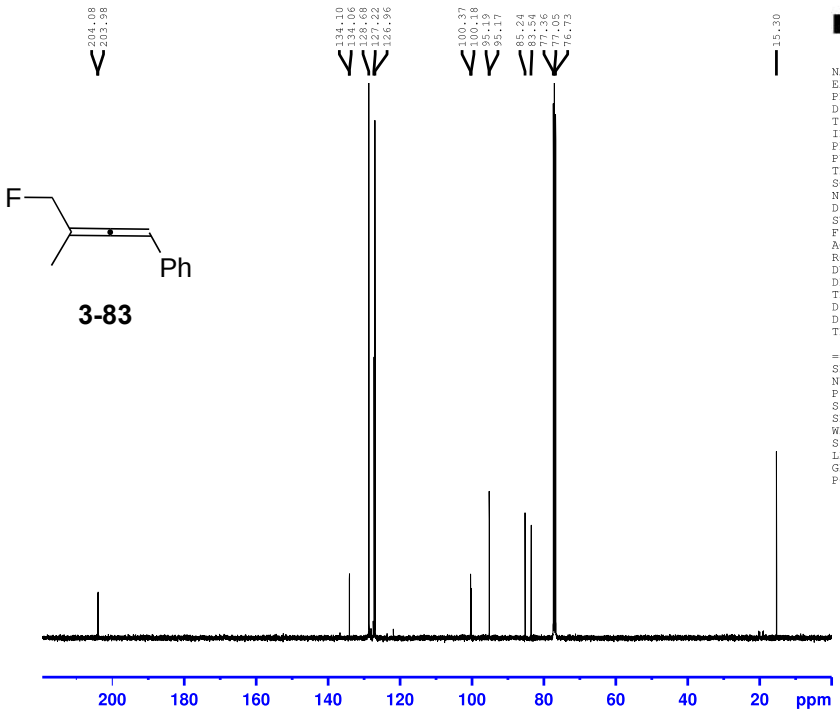
BRUKER

```
NAME                JAM-785-71
EXPNO                       11
PROCNO                       1
Date_                 20170523
Time                     10.37
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG              zgfhigqn.2
TD                       131072
SOLVENT                  CDCl3
NS                           16
DS                            4
SWH                 89285.711 Hz
FIDRES               0.681196 Hz
AQ                   0.7340532 sec
RG                         203
DW                       5.600 usec
DE                       6.50 usec
TE                       88.0 K
D1                  1.00000000 sec
D11                 0.03000000 sec
D12                 0.00002000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1               376.4607164 MHz
NUC1                       19F
P1                       14.20 usec
SI                       65536
SF                 376.4983662 MHz
WDW                         EM
SSB                          0
LB                       0.30 Hz
GB                           0
PC                       1.00
```



BRUKER

```
NAME            JAM-785-47.2
EXPNO                     10
PROCNO                     1
Date_               20170508
Time                   18.26
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8012.820 Hz
FIDRES                0.122266 Hz
AQ                 4.0894966 sec
RG                       64
DW                    62.400 usec
DE                     6.50 usec
TE                     89.3 K
D1                 1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1           400.1324710 MHz
NUC1                     1H
P1                    13.75 usec
SI                    65536
SF             400.1300475 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
```



BRUKER

```
NAME            JAM-785-47.2
EXPNO                     12
PROCNO                     1
Date_               20170509
Time                   4.10
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                       900
DS                         4
SWH               24038.461 Hz
FIDRES                0.366798 Hz
AQ                 1.3631988 sec
RG                       128
DW                    20.800 usec
DE                     6.50 usec
TE                     89.0 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1           100.6228293 MHz
NUC1                     13C
P1                    10.00 usec
SI                    32768
SF             100.6127685 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40
```

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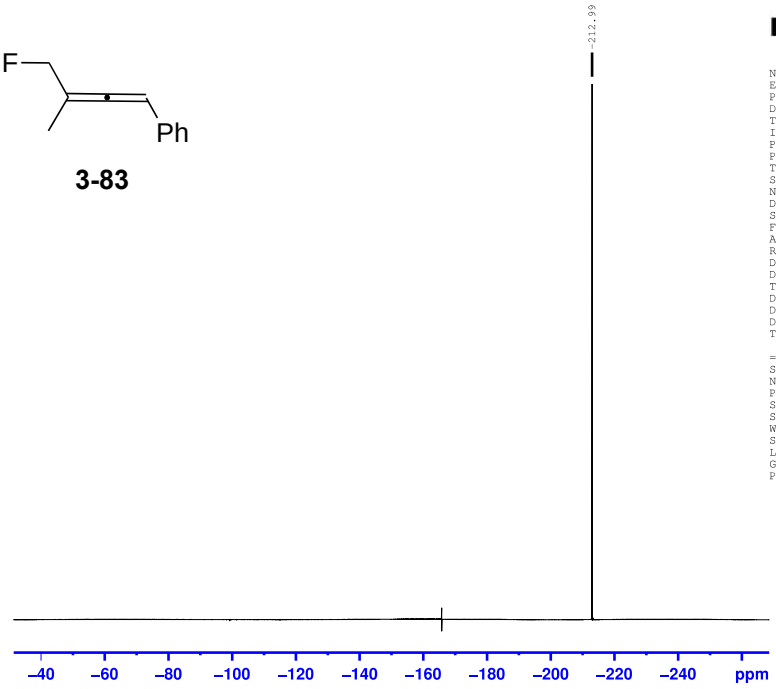
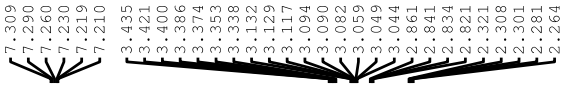
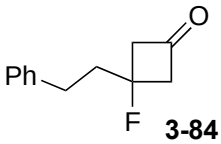



```
NAME                JAM-785-47.2
EXPNO                         11
PROCNO                         1
Date_                   20170508
Time                       18.29
INSTRUM                    spect
PROBHD     5 mm PABBO BB-
PULPROG             zgfhigqn.2
TD                        131072
SOLVENT                   CDCl3
NS                            16
DS                             4
SWH                    89285.711 Hz
FIDRES                 0.681196 Hz
AQ                     0.7340532 sec
RG                          203
DW                        5.600 usec
DE                        6.50 usec
TE                         89.4 K
D1                    1.00000000 sec
D11                   0.03000000 sec
D12                   0.00002000 sec
TD0                            1

======== CHANNEL f1 ========
SFO1                376.4418915 MHz
NUC1                        19F
P1                        14.20 usec
SI                         65536
SF                  376.4983662 MHz
WDW                           EM
SSB                            0
LB                          0.30 Hz
GB                             0
PC                          1.00
```





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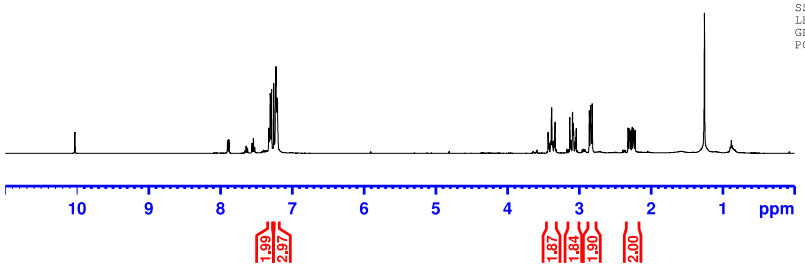
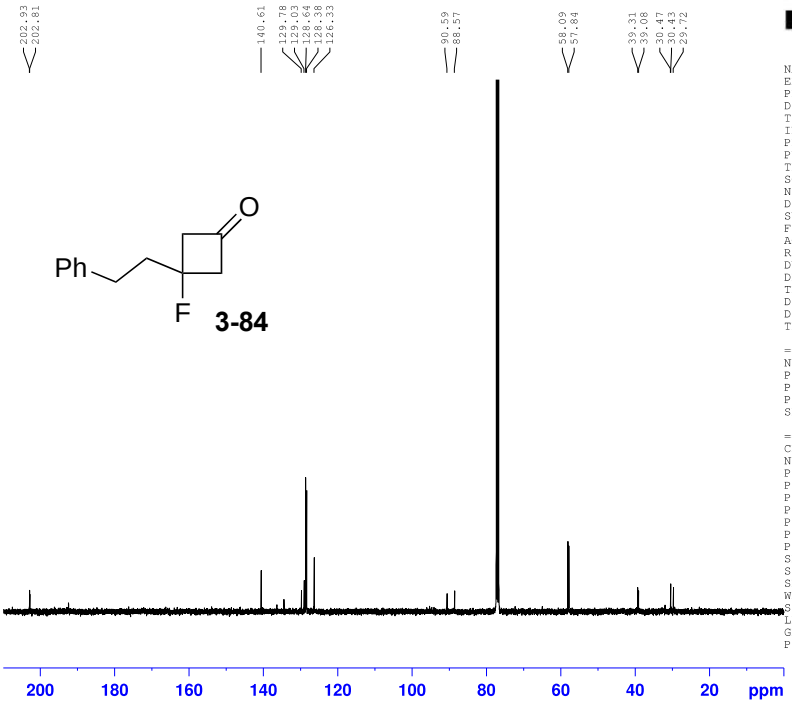
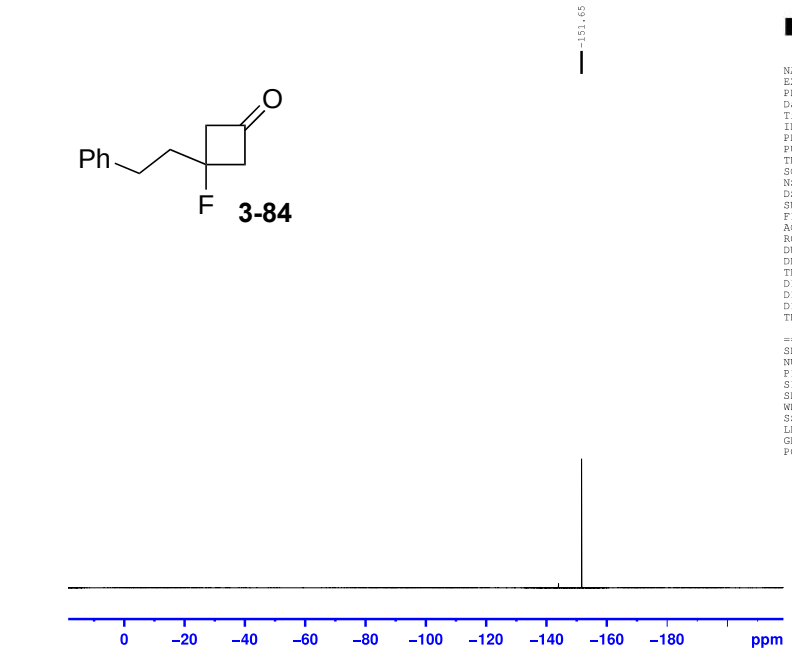


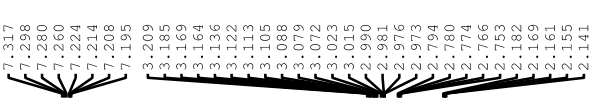

```
NAME                JAM-758-80
EXPNO                         10
PROCNO                         1
Date_                   20170104
Time                       13.17
INSTRUM                    spect
PROBHD     5 mm PABBO BB-
PULPROG                    zg30
TD                         65536
SOLVENT                   CDCl3
NS                            16
DS                             2
SWH                    8012.820 Hz
FIDRES                 0.122266 Hz
AQ                     4.0894966 sec
RG                           101
DW                        62.400 usec
DE                        6.50 usec
TE                         90.5 K
D1                    1.00000000 sec
TD0                            1

======== CHANNEL f1 ========
SFO1                400.1324710 MHz
NUC1                        1H
P1                        13.75 usec
SI                         65536
SF                  400.1300095 MHz
WDW                           EM
SSB                            0
LB                          0.30 Hz
GB                             0
PC                          1.00
```

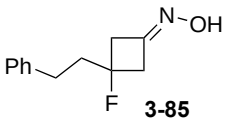



```
NAME                JAM-758-80
EXPNO                        2
PROCNO                       1
Date_                 20170104
Time                     14.52
INSTRUM                  spect
PROBHD    5 mm PADUL 13C
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                         794
DS                           4
SWH                 24038.461 Hz
FIDRES               0.366798 Hz
AQ                   1.3631988 sec
RG                        45.2
DW                      20.800 usec
DE                       6.50 usec
TE                     295.0 K
D1                  3.00000000 sec
D11                 0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                       13C
P1                       10.00 usec
PL1                      -0.44 dB
PL1W                39.19395828 W
SFO1               100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                    90.00 usec
PL2                      -3.90 dB
PL12                     15.81 dB
PL13                    120.00 dB
PL2W                21.64248466 W
PL12W                0.23137002 W
PL13W                0.00000000 W
SFO2               400.2316009 MHz
SI                       32768
SF                 100.6379140 MHz
WDW                         EM
SSB                          0
LB                        1.00 Hz
GB                           0
PC                        1.40
```



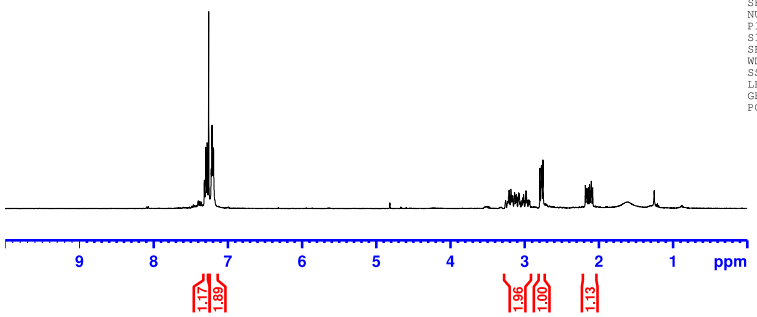

```
NAME                JAM-758-80
EXPNO                       11
PROCNO                       1
Date_                 20170104
Time                     13.19
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG             zgfhigqn.2
TD                      131072
SOLVENT                  CDCl3
NS                          16
DS                           4
SWH                 89285.711 Hz
FIDRES               0.681196 Hz
AQ                   0.7340532 sec
RG                         203
DW                       5.600 usec
DE                       6.50 usec
TE                      90.6 K
D1                  1.00000000 sec
D11                 0.03000000 sec
D12                 0.00002000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1               376.4607164 MHz
NUC1                       19F
P1                       14.20 usec
SI                       65536
SF                 376.4983662 MHz
WDW                         EM
SSB                          0
LB                        0.30 Hz
GB                           0
PC                        1.00
```

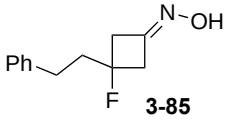




3-85

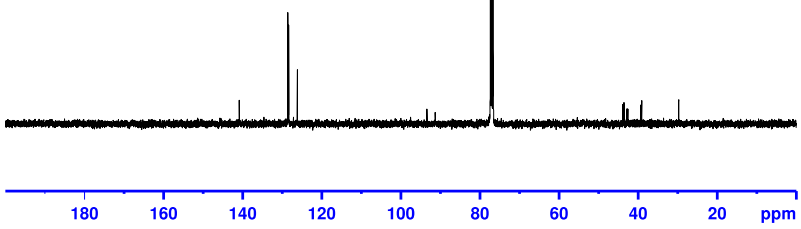
```
NAME                JAM-776-11
EXPNO                       10
PROCNO                       1
Date_                 20170120
Time                     19.17
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG                  zg30
TD                      65536
SOLVENT                 CDCl3
NS                         16
DS                          2
SWH                 8012.820 Hz
FIDRES                 0.122266 Hz
AQ                  4.0894966 sec
RG                        144
DW                     62.400 usec
DE                      6.50 usec
TE                      90.8 K
D1                  1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1             400.1324710 MHz
NUC1                       1H
P1                     13.75 usec
SI                      65536
SF               400.1300094 MHz
WDW                        EM
SSB                         0
LB                      0.30 Hz
GB                          0
PC                       1.00
```

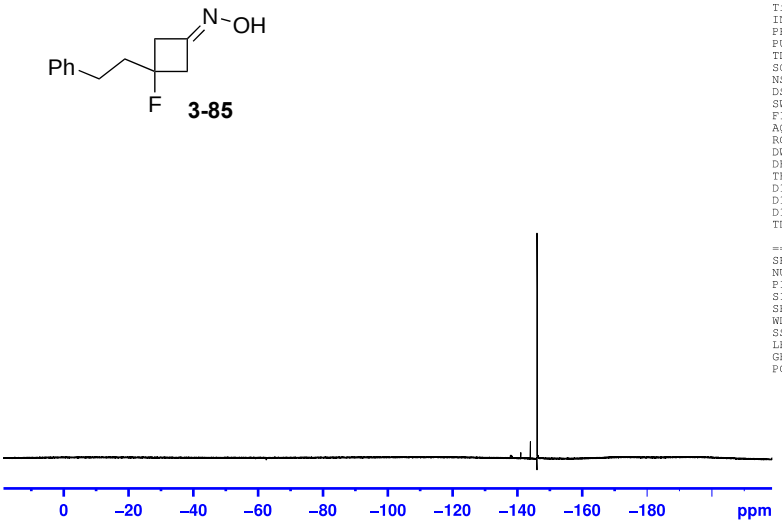




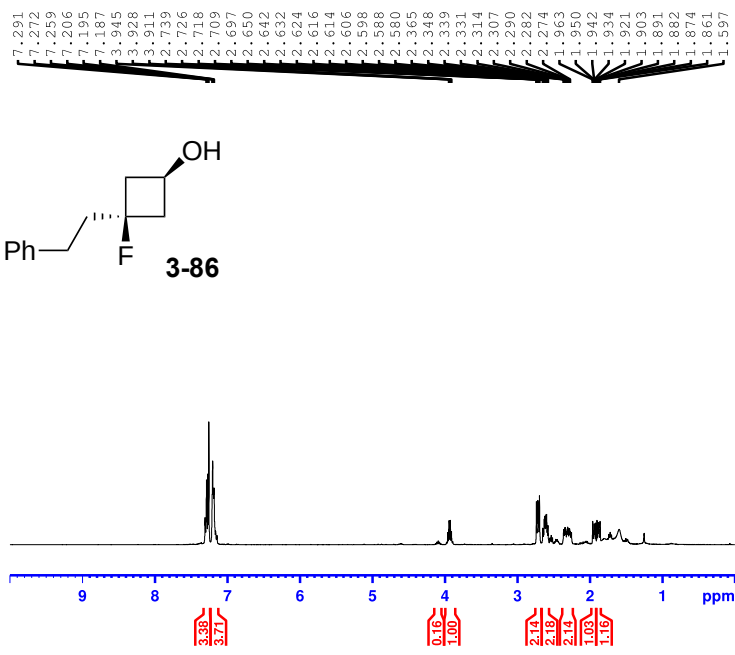
3-85

```
NAME                JAM-776-11
EXPNO                       12
PROCNO                       1
Date_                 20170121
Time                     6.56
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG                 zgpg30
TD                      65536
SOLVENT                 CDCl3
NS                       2028
DS                          4
SWH                24038.461 Hz
FIDRES                 0.366798 Hz
AQ                  1.3631988 sec
RG                        128
DW                     20.800 usec
DE                      6.50 usec
TE                      89.2 K
D1                  2.00000000 sec
D11                 0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1             100.6228293 MHz
NUC1                       13C
P1                     10.00 usec
SI                      32768
SF               100.6127685 MHz
WDW                        EM
SSB                         0
LB                      1.00 Hz
GB                          0
PC                       1.40
```

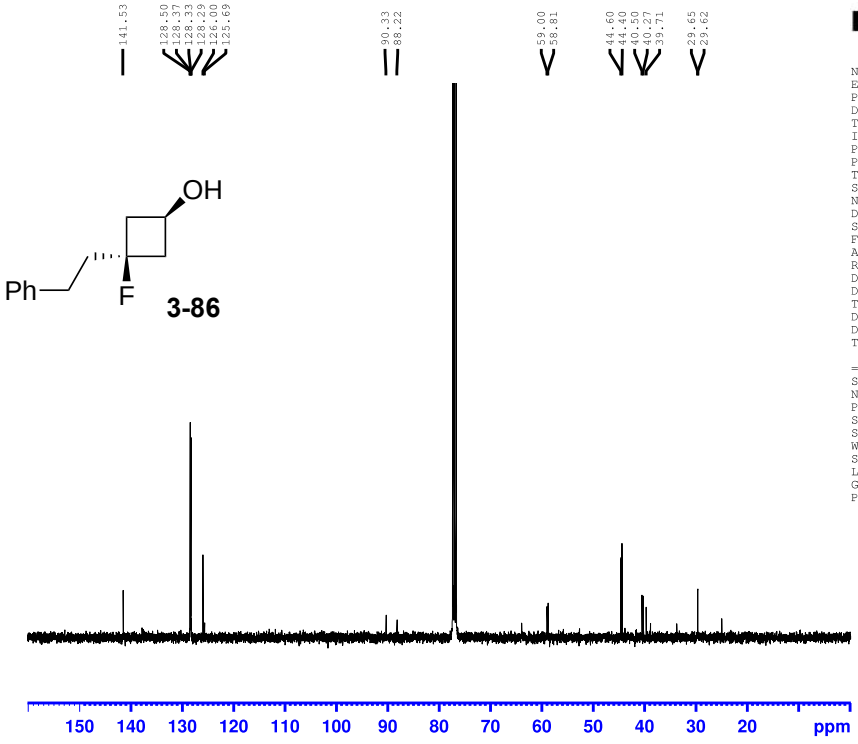




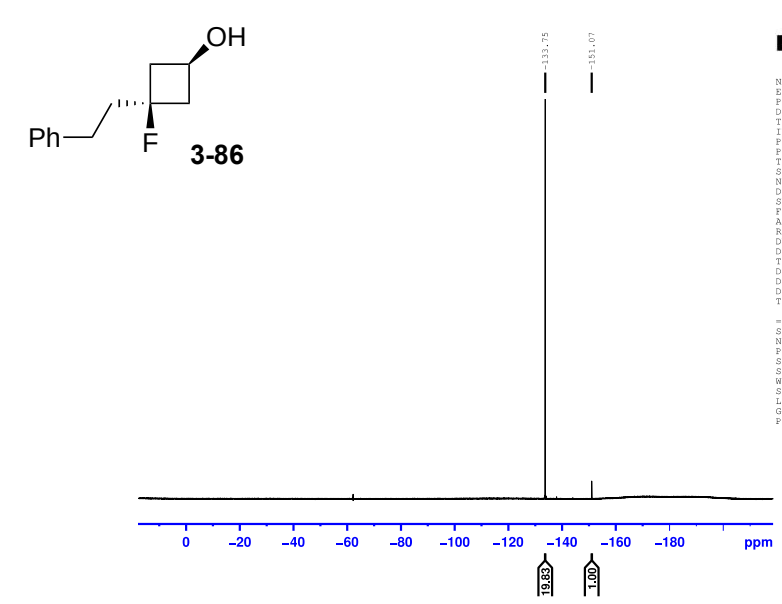

```
NAME                JAM-776-11
EXPNO                       11
PROCNO                       1
Date_                 20170120
Time                     19.19
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG           zgfhigqn.2
TD                       131072
SOLVENT                  CDCl3
NS                          16
DS                           4
SWH                 89285.711 Hz
FIDRES                0.681196 Hz
AQ                    0.7340532 sec
RG                         203
DW                       5.600 usec
DE                       6.50 usec
TE                       90.9 K
D1                    1.00000000 sec
D11                   0.03000000 sec
D12                   0.00002000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1                376.4607164 MHz
NUC1                        19F
P1                       14.20 usec
SI                        65536
SF                  376.4983662 MHz
WDW                          EM
SSB                           0
LB                       0.30 Hz
GB                            0
PC                       1.00
```



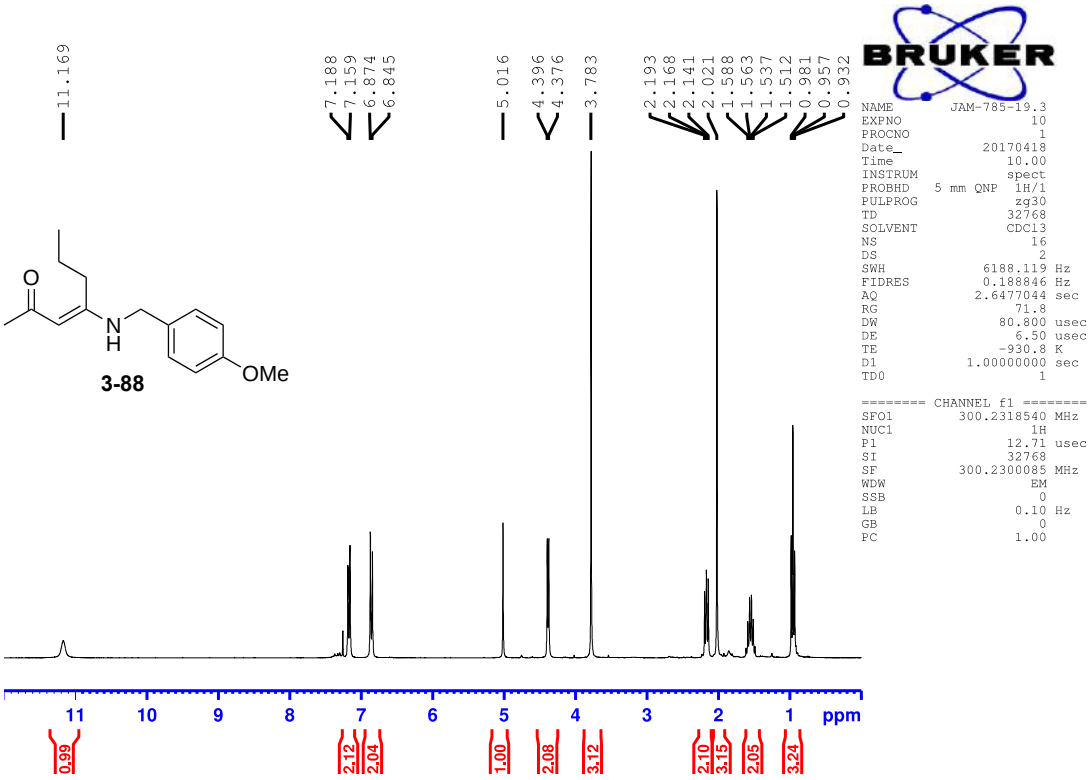

```
NAME                JAM-802-90
EXPNO                       10
PROCNO                       1
Date_                 20170801
Time                      9.15
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG                  zg30
TD                        65536
SOLVENT                  CDCl3
NS                          16
DS                           2
SWH                  8012.820 Hz
FIDRES                0.122266 Hz
AQ                    4.0894966 sec
RG                         128
DW                       62.400 usec
DE                       6.50 usec
TE                       3146.6 K
D1                    1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1                400.1324710 MHz
NUC1                        1H
P1                       13.75 usec
SI                        65536
SF                  400.1300105 MHz
WDW                          EM
SSB                           0
LB                       0.30 Hz
GB                            0
PC                       1.00
```



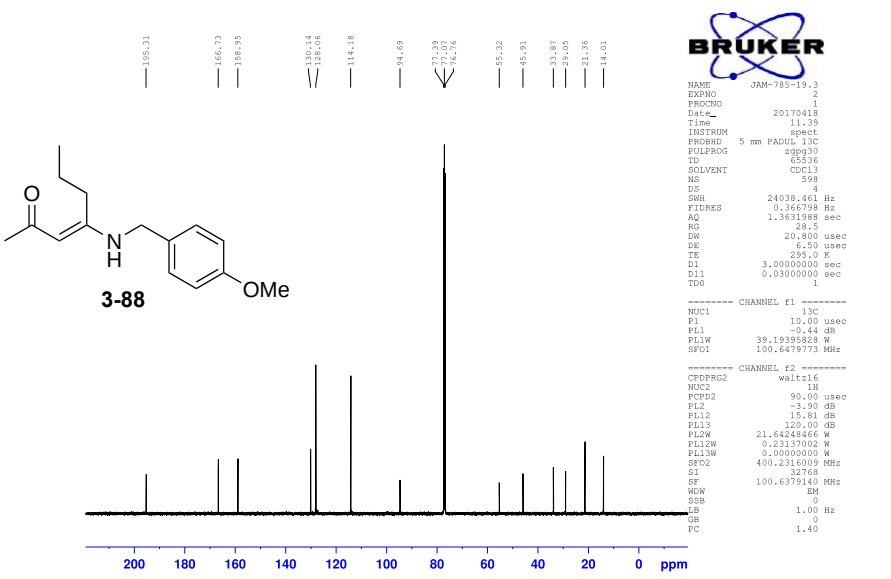

```
NAME                JAM-802-90
EXPNO                       12
PROCNO                       1
Date_                 20170801
Time                     22.05
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                        1024
DS                           4
SWH                  24038.461 Hz
FIDRES                0.366798 Hz
AQ                    1.3631988 sec
RG                         203
DW                      20.800 usec
DE                       6.50 usec
TE                    -2908.3 K
D1                    2.00000000 sec
D11                   0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1                100.6228293 MHz
NUC1                        13C
P1                        10.00 usec
SI                        32768
SF                  100.6127685 MHz
WDW                          EM
SSB                           0
LB                         1.00 Hz
GB                            0
PC                         1.40
```

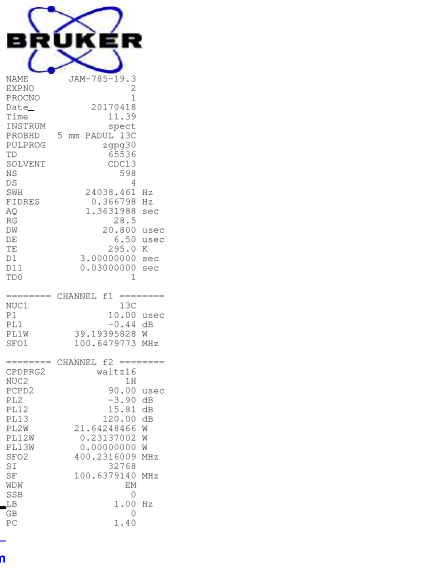


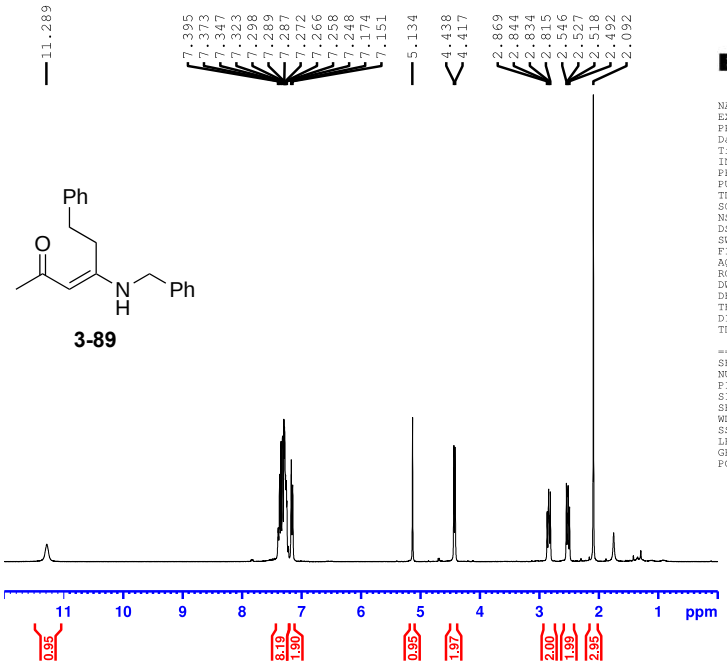

```
NAME                JAM-802-90
EXPNO                       11
PROCNO                       1
Date_                 20170801
Time                      9.17
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG             zgfhigqn.2
TD                      131072
SOLVENT                  CDCl3
NS                          16
DS                           4
SWH                  89285.711 Hz
FIDRES                0.681196 Hz
AQ                    0.7340532 sec
RG                         203
DW                       5.600 usec
DE                       6.50 usec
TE                    -2855.8 K
D1                    1.00000000 sec
D11                   0.03000000 sec
D12                   0.00002000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1                376.4607164 MHz
NUC1                        19F
P1                        14.20 usec
SI                        65536
SF                  376.4983662 MHz
WDW                          EM
SSB                           0
LB                         0.30 Hz
GB                            0
PC                         1.00
```


11.169
7.188
7.159
6.874
6.845
5.016
4.396
4.376
3.783
2.193
2.168
2.141
2.021
1.588
1.563
1.537
1.512
0.981
0.957
0.932
O
N
H
OMe
3-88
11
10
9
8
7
6
5
4
3
2
1
ppm
0.99
2.12
2.04
1.00
2.08
3.12
2.10
3.15
2.05
3.24

BRUKER
NAME JAM-785-19.3
EXPNO 10
PROCNO 1
Date_ 20170418
Time 10.00
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.188846 Hz
AQ 2.6477044 sec
RG 71.8
DW 80.800 usec
DE 6.50 usec
TE -930.8 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 300.2318540 MHz
NUC1 1H
P1 12.71 usec
SI 32768
SF 300.2300085 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

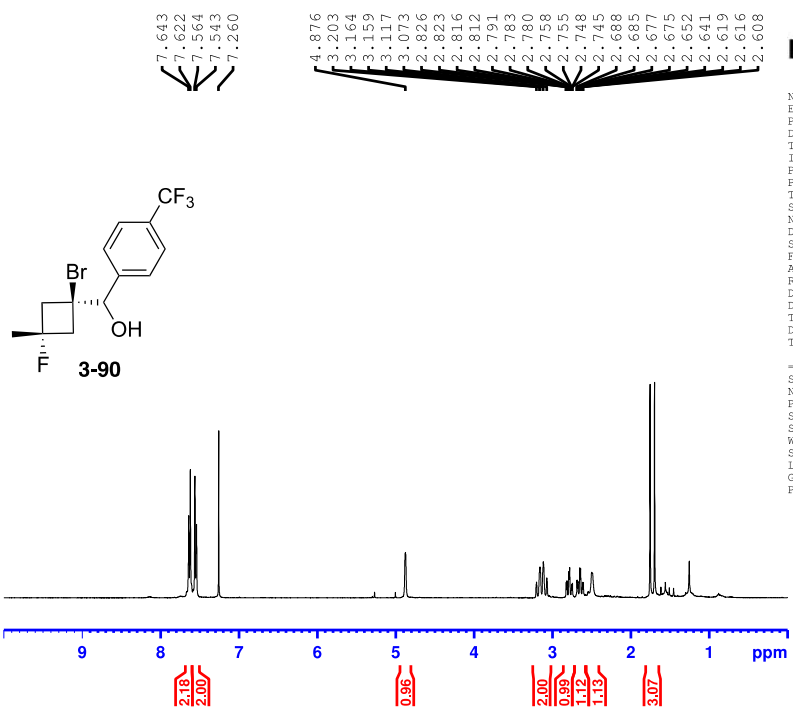

195.31
166.73
158.95
130.54
129.06
114.18
94.69
77.39
77.07
76.76
55.32
45.91
33.87
29.05
21.36
14.01
O
N
H
OMe
3-88
200
180
160
140
120
100
80
60
40
20
0
ppm


BRUKER
NAME JAM-785-19.3
EXPNO 2
PROCNO 1
Date_ 20170418
Time 11.39
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 598
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 28.5
DW 20.800 usec
DE 6.50 usec
TE 295.0 K
D1 3.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 -0.44 dB
PL1W 39.19395828 W
SFO1 100.6479773 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.90 dB
PL12 15.81 dB
PL13 120.00 dB
PL2W 21.64248466 W
PL12W 0.23137002 W
PL13W 0.00000000 W
SFO2 400.2316009 MHz
SI 32768
SF 100.6379140 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



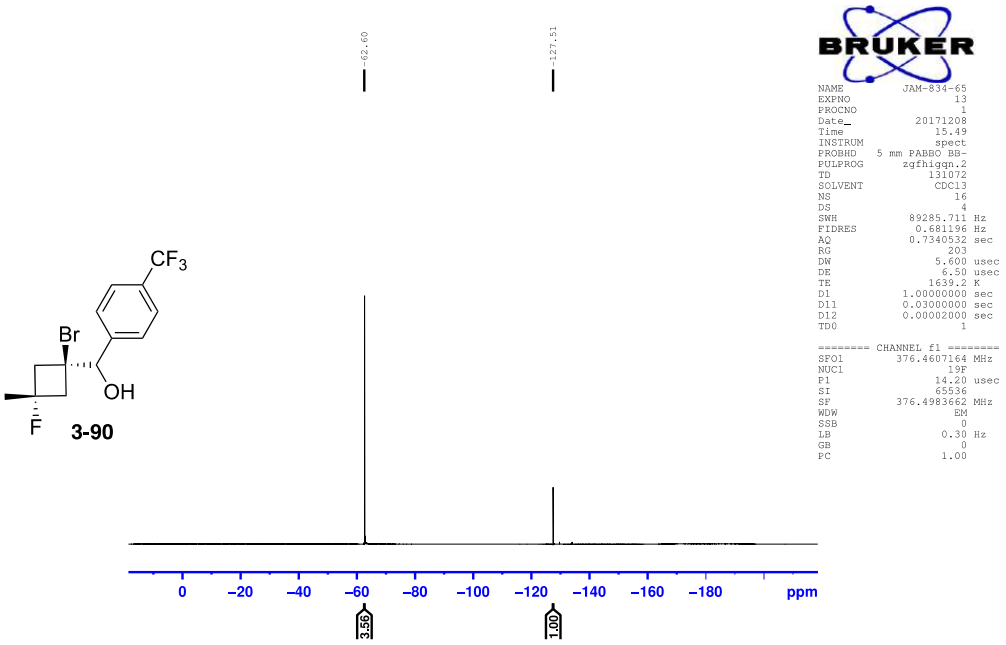
BRUKER

```
NAME                JAM-785-66
EXPNO                       10
PROCNO                       1
Date_                 20170519
Time                     19.26
INSTRUM                  spect
PROBHD     5 mm QNP   1H/1
PULPROG                  zg30
TD                      32768
SOLVENT                 CDCl3
NS                         16
DS                          2
SWH                  6188.119 Hz
FIDRES               0.188846 Hz
AQ                   2.6477044 sec
RG                        114
DW                     80.800 usec
DE                      6.50 usec
TE                    -929.7 K
D1                   1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1          300.2318540 MHz
NUC1                     1H
P1                    12.71 usec
SI                      32768
SF            300.2300000 MHz
WDW                     EM
SSB                      0
LB                    0.10 Hz
GB                       0
PC                    1.00
```

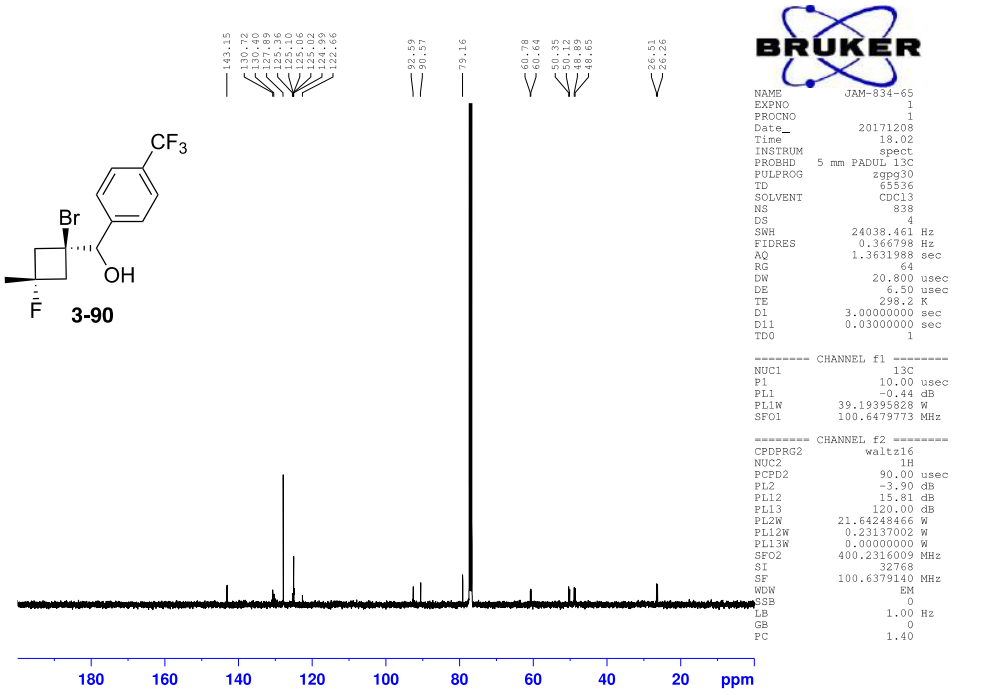


BRUKER

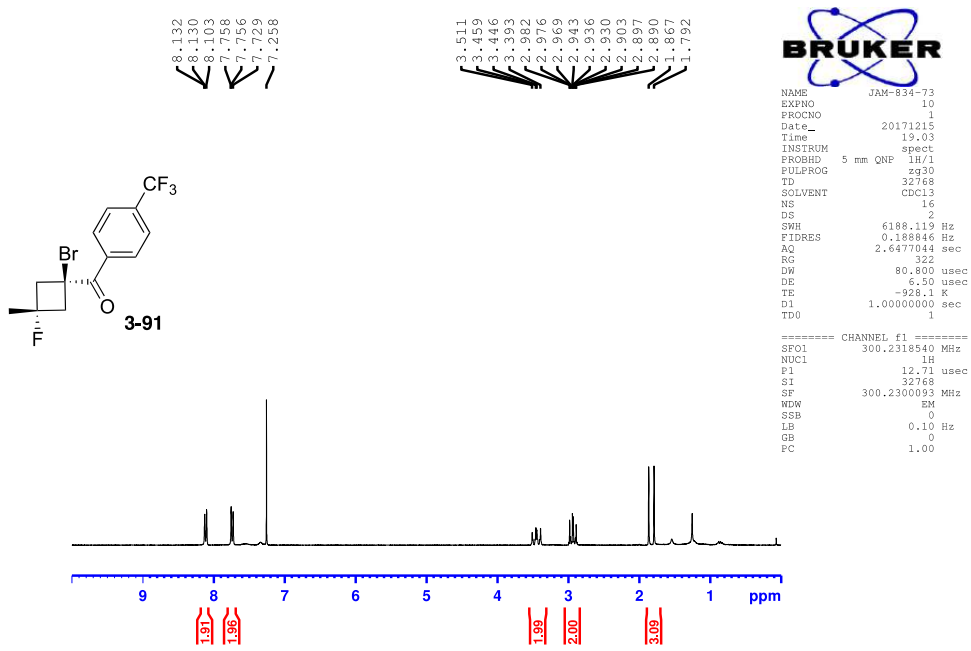
```
NAME                JAM-834-65
EXPNO                       10
PROCNO                       1
Date_                 20171208
Time                     15.29
INSTRUM                  spect
PROBHD     5 mm PABBO BB-
PULPROG                  zg30
TD                      65536
SOLVENT                 CDCl3
NS                         16
DS                          2
SWH                  8012.820 Hz
FIDRES               0.122266 Hz
AQ                   4.0894966 sec
RG                        114
DW                     62.400 usec
DE                      6.50 usec
TE                    1554.5 K
D1                   1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1          400.1324710 MHz
NUC1                     1H
P1                    13.75 usec
SI                      65536
SF            400.1300093 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```




```
NAME                JAM-834-65
EXPNO                       13
PROCNO                       1
Date_                 20171208
Time                     15.49
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG          zgfhigqn.2
TD                       131072
SOLVENT                  CDCl3
NS                          16
DS                           4
SWH                  89285.711 Hz
FIDRES                0.681196 Hz
AQ                   0.7340532 sec
RG                         203
DW                       5.600 usec
DE                       6.50 usec
TE                       1639.2 K
D1                   1.00000000 sec
D11                  0.03000000 sec
D12                  0.00002000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1                376.4607164 MHz
NUC1                        19F
P1                        14.20 usec
SI                        65536
SF                  376.4983662 MHz
WDW                          EM
SSB                           0
LB                         0.30 Hz
GB                            0
PC                         1.00
```

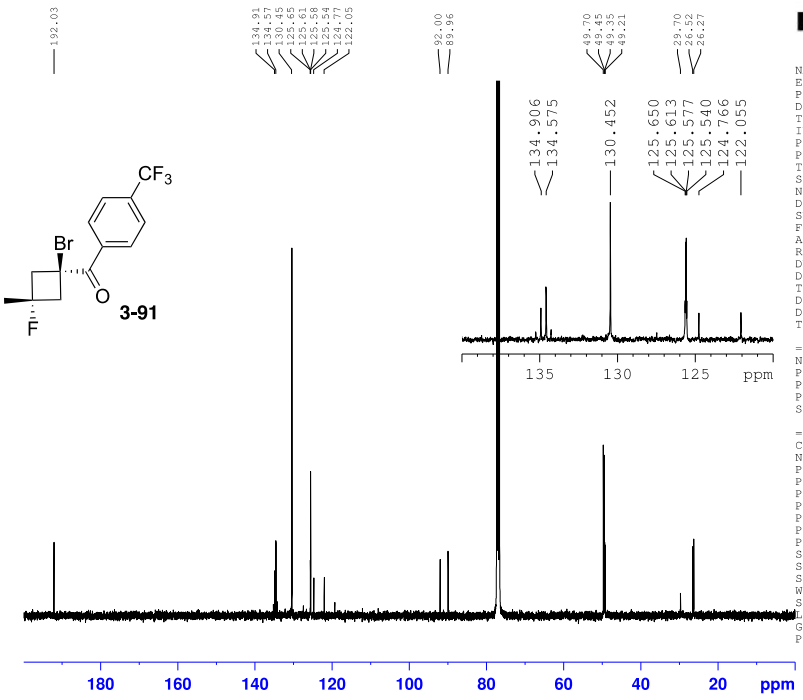



```
NAME                JAM-834-65
EXPNO                        1
PROCNO                       1
Date_                 20171208
Time                     18.02
INSTRUM                  spect
PROBHD    5 mm PADUL 13C
PULPROG             zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                         838
DS                           4
SWH                  24038.461 Hz
FIDRES                0.366798 Hz
AQ                   1.3631988 sec
RG                          64
DW                       20.800 usec
DE                       6.50 usec
TE                       298.2 K
D1                   3.00000000 sec
D11                  0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                        13C
P1                        10.00 usec
PL1                       -0.44 dB
PL1W                39.19395828 W
SFO1                100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                        1H
PCPD2                     90.00 usec
PL2                       -3.90 dB
PL12                      15.81 dB
PL13                     120.00 dB
PL2W                21.64248466 W
PL12W                0.23137002 W
PL13W                0.00000000 W
SFO2                400.2316009 MHz
SI                       32768
SF                  100.6379140 MHz
WDW                          EM
SSB                           0
LB                         1.00 Hz
GB                            0
PC                         1.40
```



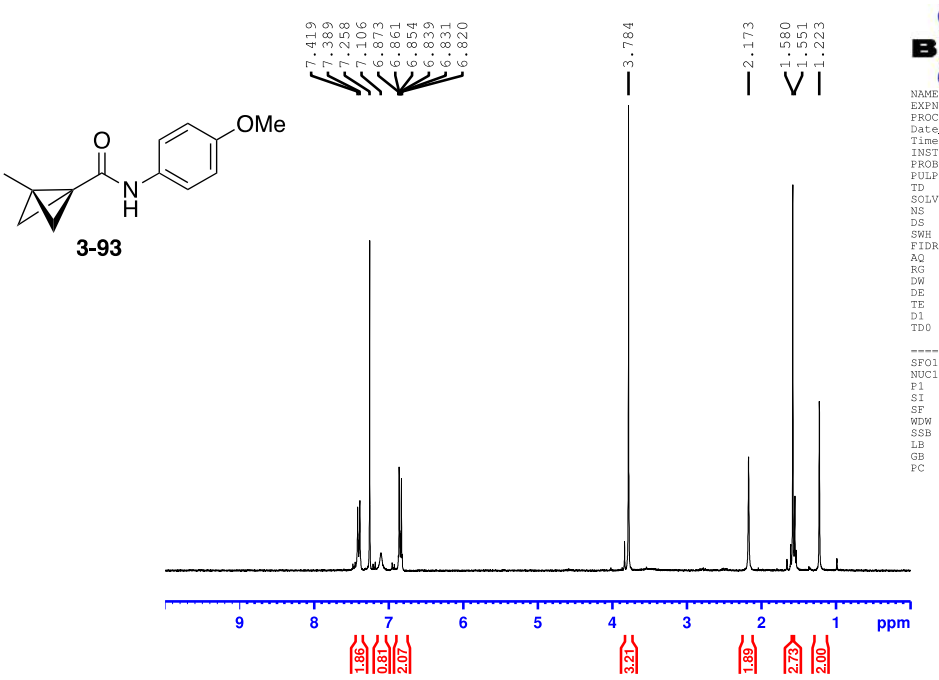
BRUKER

NAME	JAM-834-73
EXPNO	10
PROCNO	1
Date_	20171215
Time	19.03
INSTRUM	spect
PROBHD	5 mm QNP 1H/1
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	6188.119 Hz
FIDRES	0.188846 Hz
AQ	2.6477044 sec
RG	322
DW	80.800 usec
DE	6.50 usec
TE	-928.1 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
SFO1	300.2318540 MHz
NUC1	1H
P1	12.71 usec
SI	32768
SF	300.2300093 MHz
WDW	EM
SSB	0
LB	0.10 Hz
GB	0
PC	1.00

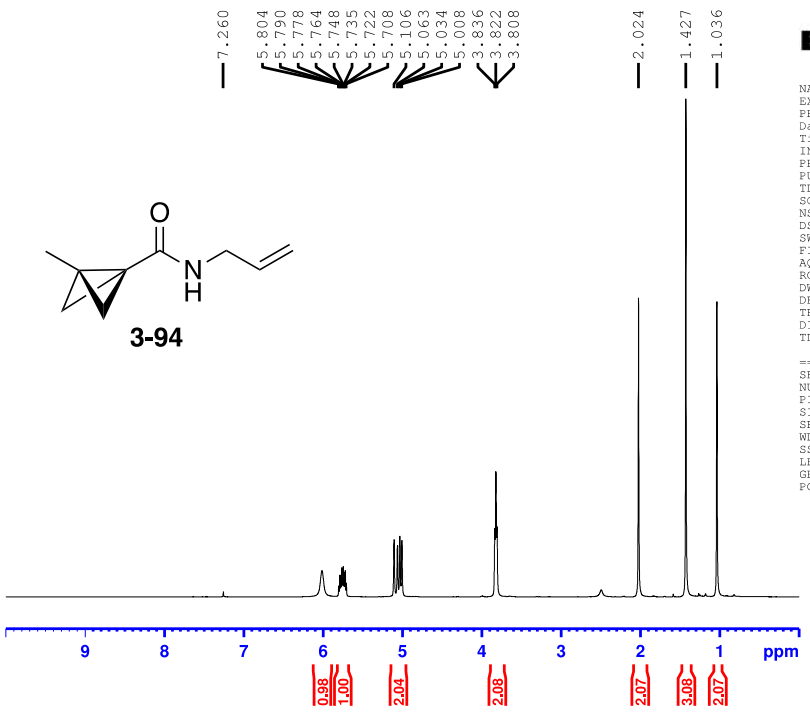


BRUKER

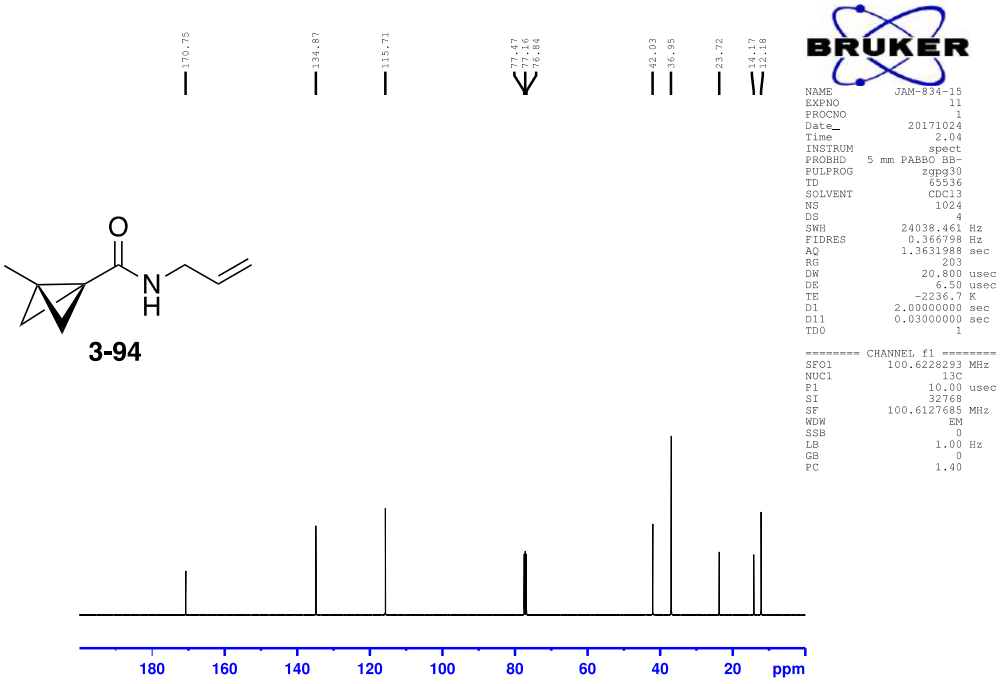
NAME	JAM-834-73
EXPNO	1
PROCNO	1
Date_	20171216
Time	8.36
INSTRUM	spect
PROBHD	5 mm PADUL 13C
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	10719
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	57
DW	20.800 usec
DE	6.50 usec
TE	294.5 K
D1	3.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	10.00 usec
PL1	-0.44 dB
PL1W	39.19395828 W
SFO1	100.6479773 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	90.00 usec
PL2	-3.90 dB
PL12	15.81 dB
PL13	120.00 dB
PL2W	21.64248466 W
PL12W	0.23137002 W
PL13W	0.00000000 W
SFO2	400.2316009 MHz
SI	32768
SF	100.6379172 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40



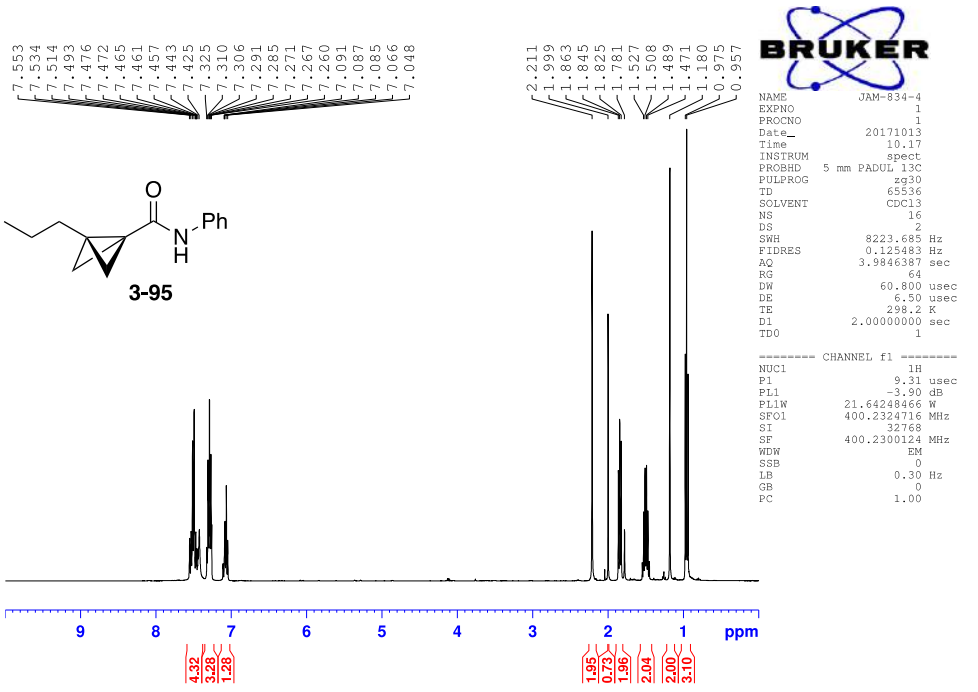

```
NAME            JAM-749-67.2
EXPNO                     10
PROCNO                     1
Date_               20161021
Time                  21.22
INSTRUM               spect
PROBHD    5 mm QNP   1H/1
PULPROG                zg30
TD                    32768
SOLVENT               CDCl3
NS                        16
DS                         2
SWH                6188.119 Hz
FIDRES            0.188846 Hz
AQ                2.6477044 sec
RG                       322
DW                  80.800 usec
DE                   6.50 usec
TE                  -925.4 K
D1                1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1             300.2318540 MHz
NUC1                       1H
P1                    12.71 usec
SI                    32768
SF               300.2300094 MHz
WDW                       EM
SSB                        0
LB                    0.10 Hz
GB                         0
PC                    1.00
```



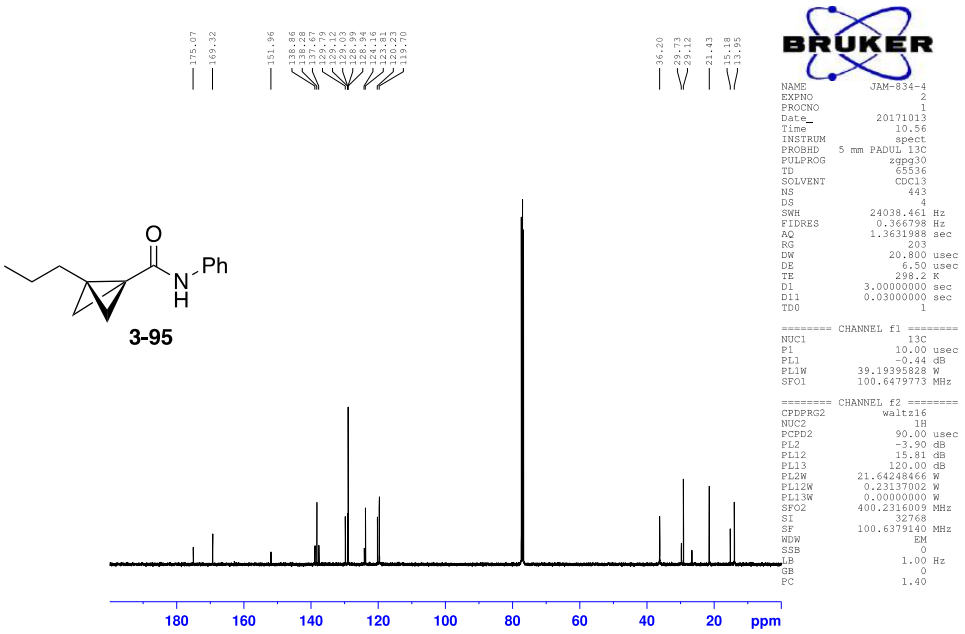

```
NAME            JAM-834-15
EXPNO                     10
PROCNO                     1
Date_               20171023
Time                  16.49
INSTRUM               spect
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                        16
DS                         2
SWH                8012.820 Hz
FIDRES            0.122266 Hz
AQ                4.0894966 sec
RG                        16
DW                  62.400 usec
DE                   6.50 usec
TE                 -2675.6 K
D1                1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1             400.1324710 MHz
NUC1                       1H
P1                    13.75 usec
SI                    65536
SF               400.1300091 MHz
WDW                       EM
SSB                        0
LB                    0.30 Hz
GB                         0
PC                    1.00
```



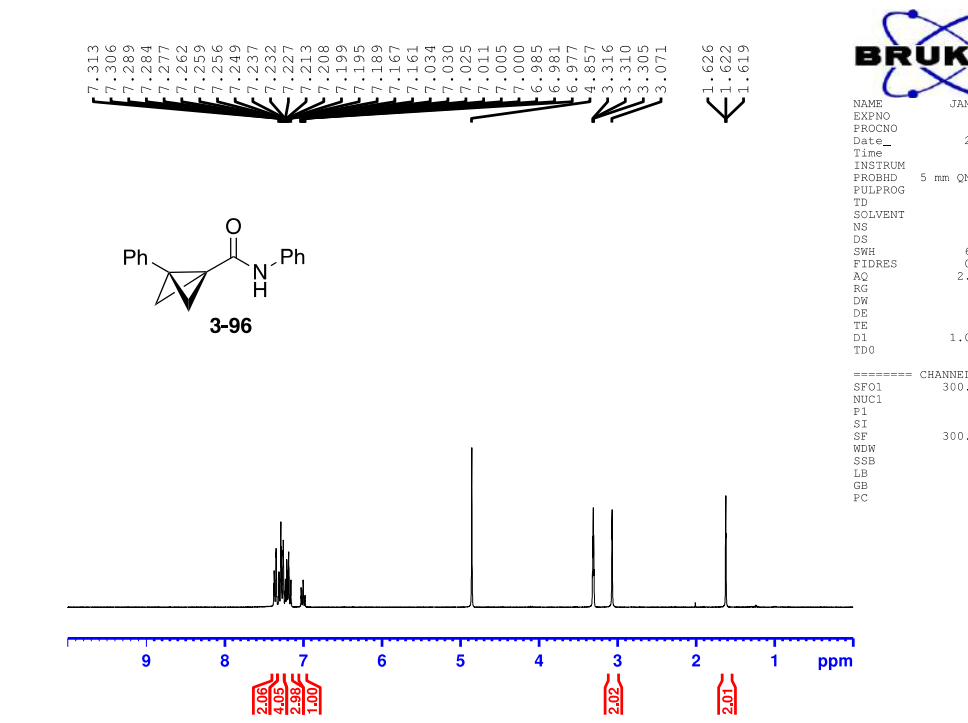

```
NAME                JAM-834-15
EXPNO                       11
PROCNO                       1
Date_                 20171024
Time                      2.04
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                        1024
DS                           4
SWH                 24038.461 Hz
FIDRES               0.366798 Hz
AQ                   1.3631988 sec
RG                         203
DW                      20.800 usec
DE                       6.50 usec
TE                     -2236.7 K
D1                  2.00000000 sec
D11                 0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1               100.6228293 MHz
NUC1                       13C
P1                       10.00 usec
SI                        32768
SF                 100.6127685 MHz
WDW                         EM
SSB                          0
LB                        1.00 Hz
GB                           0
PC                        1.40
```



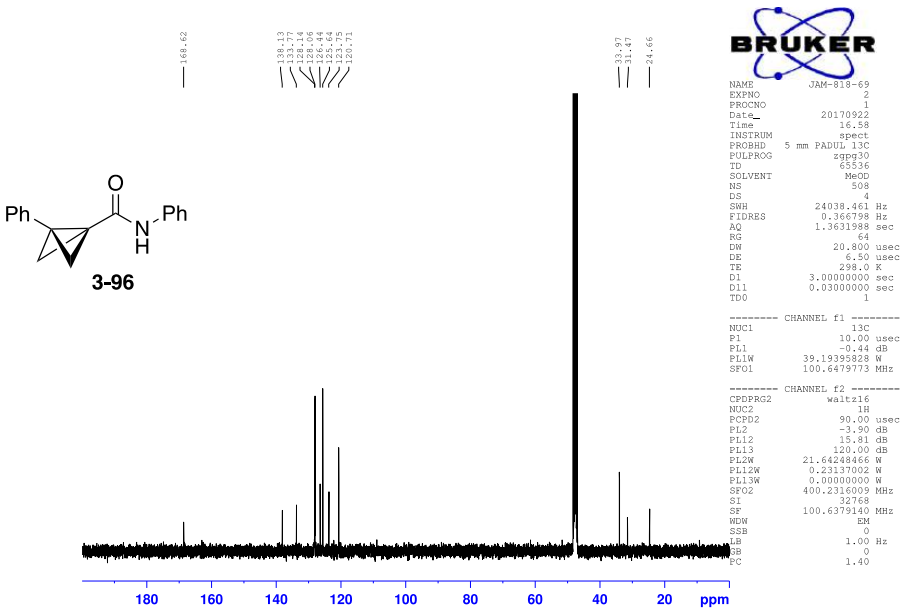

```
NAME                JAM-834-4
EXPNO                       1
PROCNO                      1
Date_                20171013
Time                    10.17
INSTRUM                  spect
PROBHD    5 mm PADUL 13C
PULPROG                  zg30
TD                       65536
SOLVENT                  CDCl3
NS                          16
DS                           2
SWH                  8223.685 Hz
FIDRES               0.125483 Hz
AQ                   3.9846387 sec
RG                          64
DW                      60.800 usec
DE                       6.50 usec
TE                     298.2 K
D1                  2.00000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                        1H
P1                       9.31 usec
PL1                     -3.90 dB
PL1W               21.64248466 W
SFO1               400.2324716 MHz
SI                        32768
SF                 400.2300124 MHz
WDW                         EM
SSB                          0
LB                        0.30 Hz
GB                           0
PC                        1.00
```



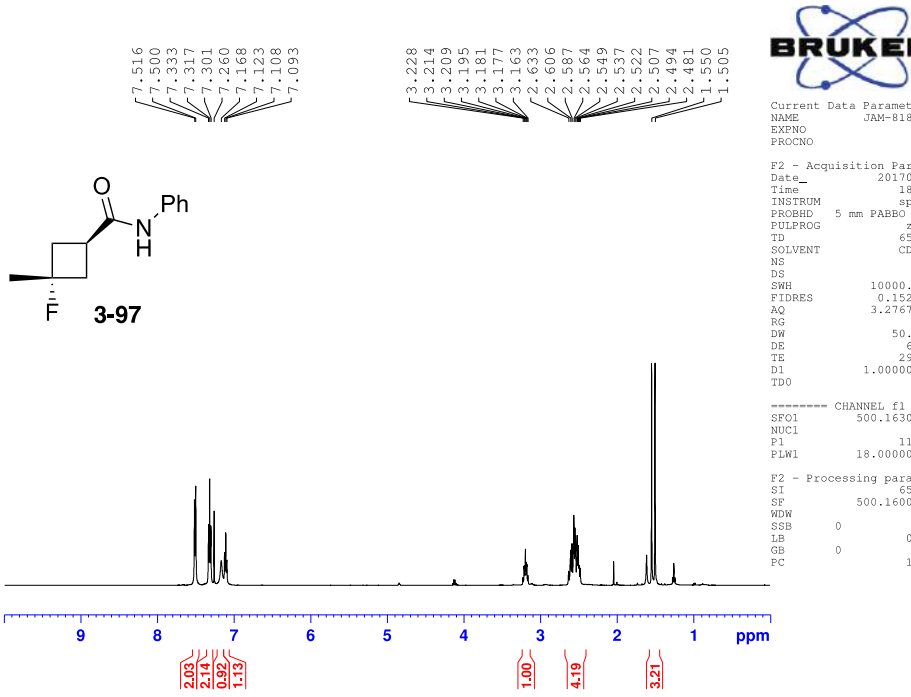

```
BRUKER
NAME                JAM-834-4
EXPNO                       2
PROCNO                      1
Date_                20171013
Time                    10.56
INSTRUM                 spect
PROBHD   5 mm PADUL 13C
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                         443
DS                           4
SWH                 24038.461 Hz
FIDRES              0.366798 Hz
AQ                  1.3631988 sec
RG                         203
DW                    20.800 usec
DE                     6.50 usec
TE                    298.2 K
D1                  3.00000000 sec
D11                 0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                      13C
P1                      10.00 usec
PL1                     -0.44 dB
PL1W               39.19395828 W
SFO1              100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                   90.00 usec
PL2                     -3.90 dB
PL12                    15.81 dB
PL13                   120.00 dB
PL2W               21.64248466 W
PL12W               0.23137002 W
PL13W               0.00000000 W
SFO2              400.2316009 MHz
SI                       32768
SF                100.6379140 MHz
WDW                         EM
SSB                          0
LB                      1.00 Hz
GB                           0
PC                      1.40
```



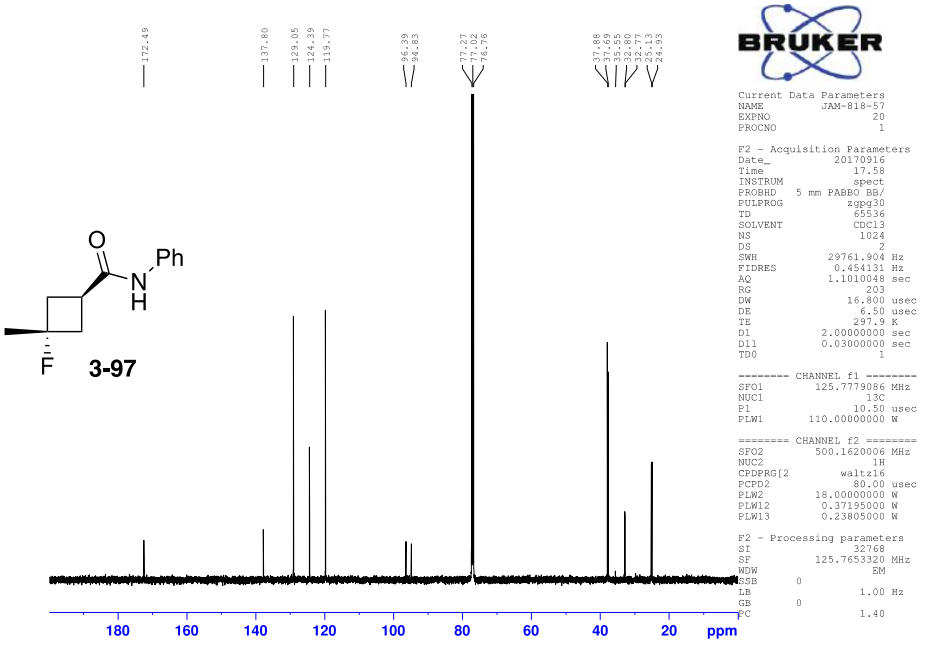

```
BRUKER
NAME                JAM-818-69
EXPNO                       10
PROCNO                       1
Date_                20170922
Time                    10.17
INSTRUM                 spect
PROBHD   5 mm QNP  1H/1
PULPROG                 zg30
TD                       32768
SOLVENT                  CD3OD
NS                          16
DS                           2
SWH                  6188.119 Hz
FIDRES              0.188846 Hz
AQ                  2.6477044 sec
RG                         322
DW                    80.800 usec
DE                     6.50 usec
TE                    -923.3 K
D1                  1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1              300.2318540 MHz
NUC1                       1H
P1                      12.71 usec
SI                       32768
SF                300.2300068 MHz
WDW                         EM
SSB                          0
LB                      0.10 Hz
GB                           0
PC                      1.00
```



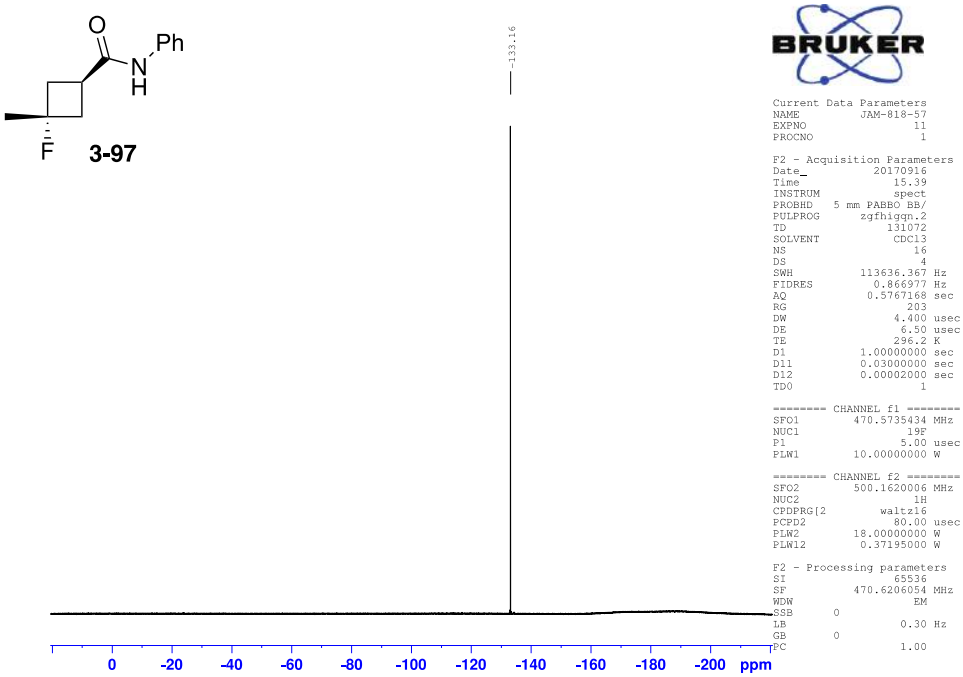

```
BRUKER
NAME            JAM-818-69
EXPNO                    2
PROCNO                   1
Date_             20170922
Time                 16.58
INSTRUM              spect
PROBHD   5 mm PADUL 13C
PULPROG           zgpg30
TD                 65536
SOLVENT              MeOD
NS                    508
DS                      4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631988 sec
RG                     64
DW                20.800 usec
DE                 6.50 usec
TE                298.0 K
D1            3.00000000 sec
D11           0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   13C
P1                   10.00 usec
PL1                  -0.44 dB
PL1W         39.19395828 W
SFO1         100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                90.00 usec
PL2                  -3.90 dB
PL12                 15.81 dB
PL13                120.00 dB
PL2W         21.64248466 W
PL12W         0.23137002 W
PL13W         0.00000000 W
SFO2         400.2316009 MHz
SI                   32768
SF           100.6379140 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```



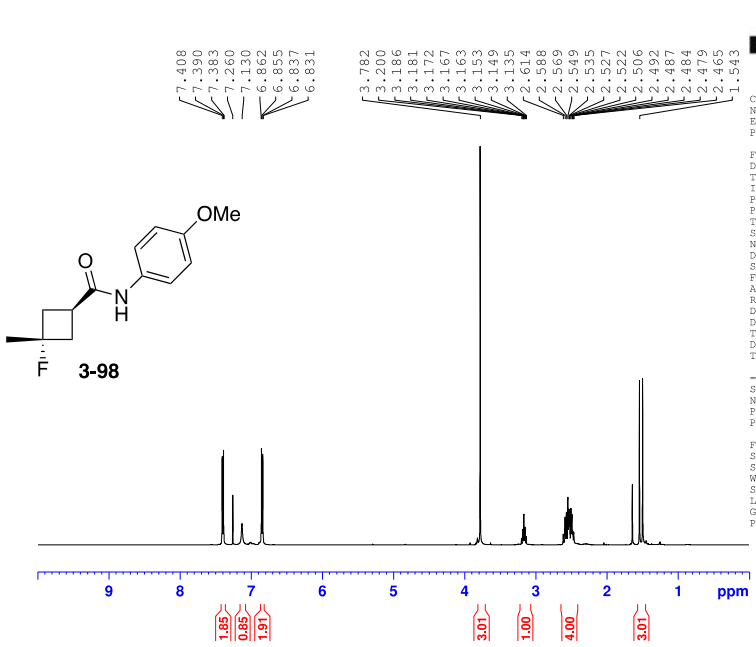

```
BRUKER
Current Data Parameters
NAME            JAM-818-57
EXPNO                   21
PROCNO                   1

F2 - Acquisition Parameters
Date_             20170916
Time                 18.00
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG              zg30
TD                 65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH          10000.000 Hz
FIDRES         0.152588 Hz
AQ             3.2767999 sec
RG                     101
DW                50.000 usec
DE                 6.50 usec
TE                297.5 K
D1            1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1         500.1630887 MHz
NUC1                    1H
P1                  11.50 usec
PLW1         18.00000000 W

F2 - Processing parameters
SI                   65536
SF           500.1600113 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```




```
Current Data Parameters
NAME          JAM-818-57
EXPNO                 20
PROCNO                 1

F2 - Acquisition Parameters
Date_           20170916
Time               17.58
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG         zgpg30
TD              65536
SOLVENT         CDCl3
NS               1024
DS                  2
SWH         29761.904 Hz
FIDRES       0.454131 Hz
AQ           1.1010048 sec
RG                203
DW             16.800 usec
DE              6.50 usec
TE             297.9 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0                1

======== CHANNEL f1 ========
SFO1       125.7779086 MHz
NUC1               13C
P1               10.50 usec
PLW1      110.00000000 W

======== CHANNEL f2 ========
SFO2       500.1620006 MHz
NUC2               1H
CPDPRG[2        waltz16
PCPD2            80.00 usec
PLW2       18.00000000 W
PLW12       0.37195000 W
PLW13       0.23805000 W

F2 - Processing parameters
SI              32768
SF         125.7653320 MHz
WDW                EM
SSB       0
LB               1.00 Hz
GB        0
PC               1.40
```




```
Current Data Parameters
NAME          JAM-818-57
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameters
Date_           20170916
Time               15.39
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG       zgfhiqqn.2
TD             131072
SOLVENT         CDCl3
NS                16
DS                 4
SWH         113636.367 Hz
FIDRES       0.866977 Hz
AQ           0.5767168 sec
RG                203
DW             4.400 usec
DE              6.50 usec
TE             296.2 K
D1          1.00000000 sec
D11         0.03000000 sec
D12         0.00002000 sec
TD0                1

======== CHANNEL f1 ========
SFO1       470.5735434 MHz
NUC1               19F
P1               5.00 usec
PLW1      10.00000000 W

======== CHANNEL f2 ========
SFO2       500.1620006 MHz
NUC2               1H
CPDPRG[2        waltz16
PCPD2            80.00 usec
PLW2       18.00000000 W
PLW12       0.37195000 W

F2 - Processing parameters
SI              65536
SF         470.6206054 MHz
WDW                EM
SSB       0
LB               0.30 Hz
GB        0
PC               1.00
```



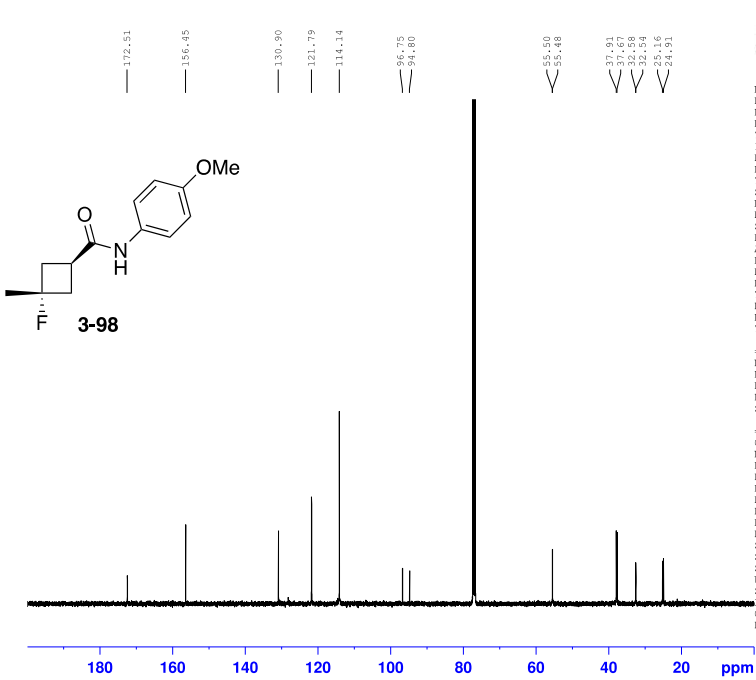
BRUKER

Current Data Parameters
NAME JAM-818-79
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20170930
Time 10.42
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2767999 sec
RG 90.5
DW 50.000 usec
DE 6.50 usec
TE 297.3 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 500.1630887 MHz
NUC1 1H
P1 11.50 usec
PLW1 18.00000000 W

F2 - Processing parameters
SI 65536
SF 500.1600115 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

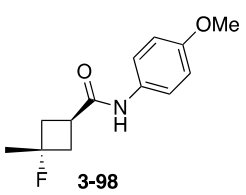


BRUKER

NAME JAM-818-78
EXPNO 2
PROCNO 1
Date_ 20170928
Time 9.59
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 723
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 57
DW 20.800 usec
DE 6.50 usec
TE 295.0 K
D1 3.00000000 sec
D11 0.03000000 sec
TD0 1

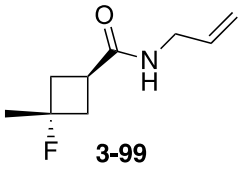
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 -0.44 dB
PL1W 39.19395828 W
SFO1 100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.90 dB
PL12 15.81 dB
PL13 120.00 dB
PL2W 21.64248466 W
PL12W 0.23137002 W
PL13W 0.00000000 W
SFO2 400.2316009 MHz
SI 32768
SF 100.6379140 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

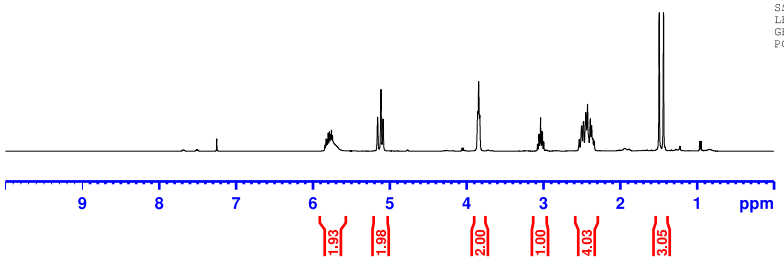


3-98

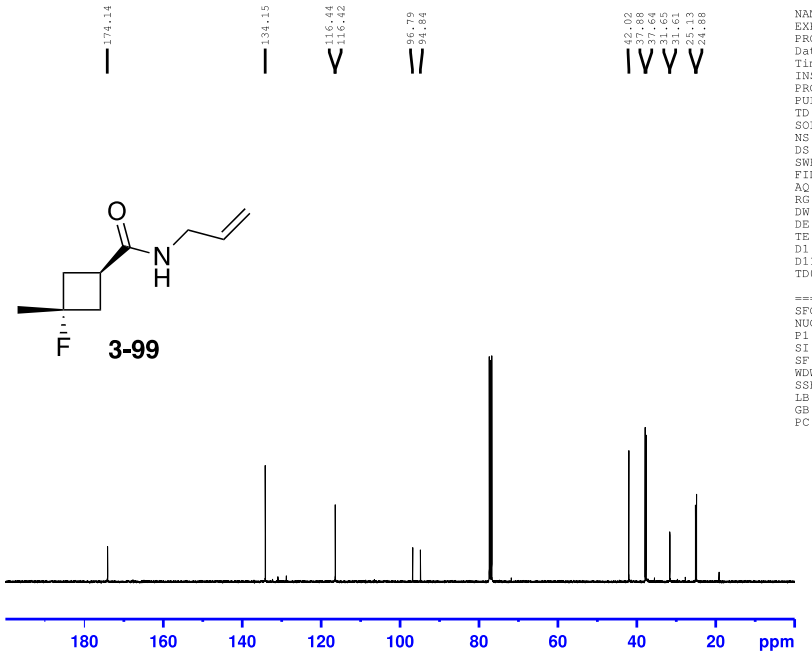

```
Current Data Parameters
NAME          JAM-818-79
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameters
Date_           20170930
Time               10.44
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG      zgfhigqn.2
TD                131072
SOLVENT             CDC13
NS                     16
DS                      4
SWH           113636.367 Hz
FIDRES          0.866977 Hz
AQ             0.5767168 sec
RG                    203
DW                4.400 usec
DE                6.50 usec
TE                297.2 K
D1           1.00000000 sec
D11          0.03000000 sec
D12          0.00002000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         470.5735434 MHz
NUC1                 19F
P1                  5.00 usec
PLW1        10.00000000 W

======== CHANNEL f2 ========
SFO2         500.1620006 MHz
NUC2                 1H
CPDPRG[2          waltz16
PCPD2              80.00 usec
PLW2        18.00000000 W
PLW12        0.37195000 W

F2 - Processing parameters
SI                  65536
SF           470.6206054 MHz
WDW                    EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```



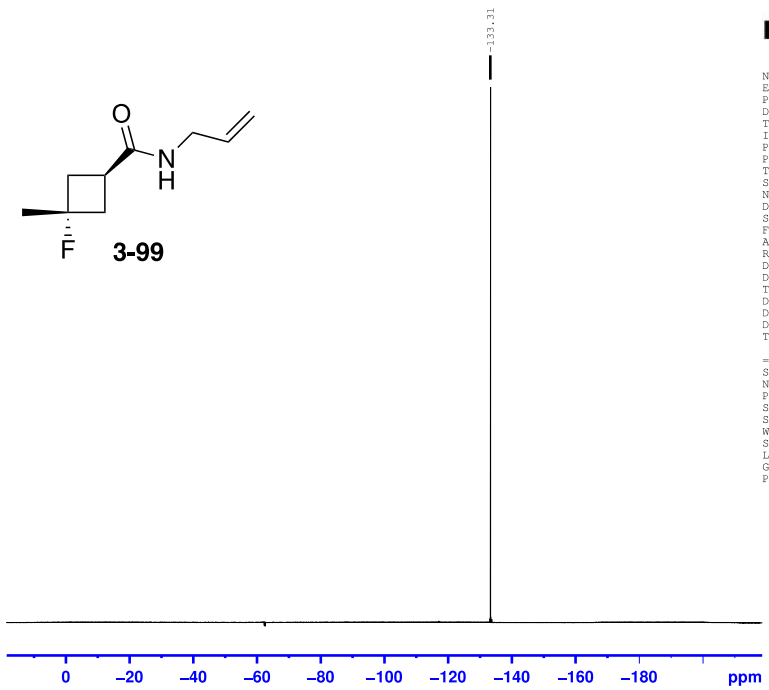
3-99



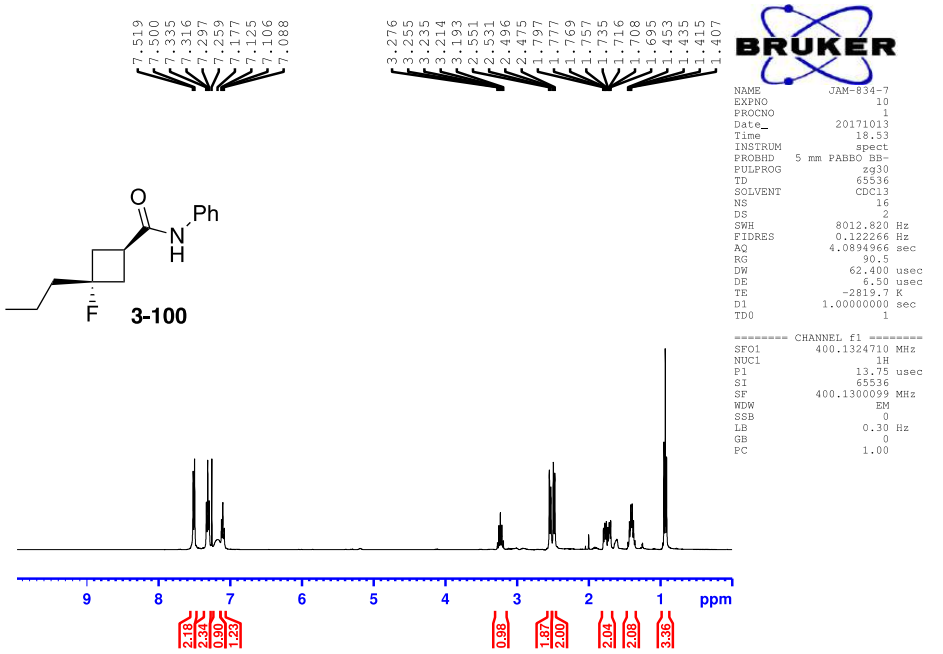

```
NAME          JAM-834-18
EXPNO                 10
PROCNO                 1
Date_           20171024
Time               14.02
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                65536
SOLVENT             CDC13
NS                     16
DS                      2
SWH             8012.820 Hz
FIDRES             0.122266 Hz
AQ              4.0894966 sec
RG                     32
DW                62.400 usec
DE                 6.50 usec
TE                -2478.4 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         400.1324710 MHz
NUC1                 1H
P1                 13.75 usec
SI                 65536
SF           400.1300123 MHz
WDW                    EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

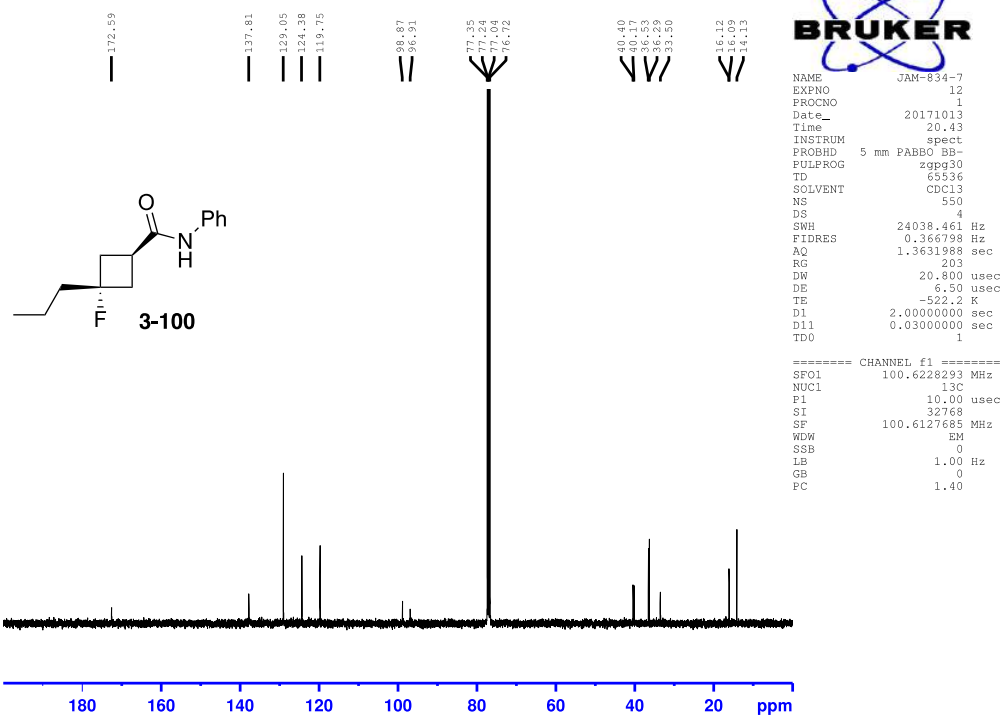


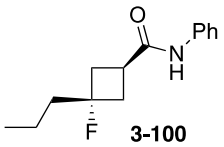

```
NAME                JAM-834-18
EXPNO                       12
PROCNO                       1
Date_                 20171024
Time                     23.00
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                        1024
DS                           4
SWH                 24038.461 Hz
FIDRES              0.366798 Hz
AQ                  1.3631988 sec
RG                         203
DW                    20.800 usec
DE                     6.50 usec
TE                    3122.6 K
D1                  2.00000000 sec
D11                 0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1               100.6228293 MHz
NUC1                       13C
P1                       10.00 usec
SI                       32768
SF                100.6127685 MHz
WDW                         EM
SSB                          0
LB                        1.00 Hz
GB                           0
PC                        1.40
```




```
NAME                JAM-834-18
EXPNO                       11
PROCNO                       1
Date_                 20171024
Time                     14.04
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG              zgfhigqn.2
TD                      131072
SOLVENT                  CDCl3
NS                           16
DS                           4
SWH                 89285.711 Hz
FIDRES              0.681196 Hz
AQ                  0.7340532 sec
RG                         203
DW                     5.600 usec
DE                     6.50 usec
TE                   -2178.2 K
D1                  1.00000000 sec
D11                 0.03000000 sec
D12                 0.00002000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1               376.4607164 MHz
NUC1                       19F
P1                       14.20 usec
SI                       65536
SF                376.4983662 MHz
WDW                         EM
SSB                          0
LB                        0.30 Hz
GB                           0
PC                        1.00
```

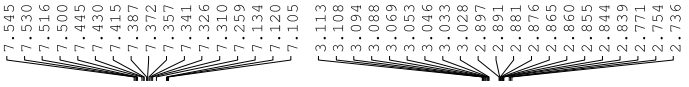

7.519
7.500
7.335
7.316
7.297
7.259
7.177
7.125
7.106
7.088
3.276
3.255
3.235
3.214
3.193
2.551
2.531
2.496
2.475
1.797
1.777
1.769
1.757
1.735
1.716
1.708
1.695
1.453
1.435
1.415
1.407
BRUKER
NAME JAM-834-7
EXPNO 10
PROCNO 1
Date_ 20171013
Time 18.53
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 90.5
DW 62.400 usec
DE 6.50 usec
TE -2819.7 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 13.75 usec
SI 65536
SF 400.1300099 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
O
N
H
Ph
F
3-100
9
8
7
6
5
4
3
2
1
ppm
2.18
2.34
0.90
1.23
0.98
1.87
2.00
2.04
2.08
3.36

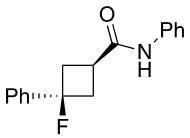

172.59
137.81
129.05
124.38
119.75
98.87
96.91
77.35
77.24
77.04
76.72
40.40
40.17
36.53
36.29
33.50
16.12
16.09
14.13
BRUKER
NAME JAM-834-7
EXPNO 12
PROCNO 1
Date_ 20171013
Time 20.43
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 550
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE -522.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6228293 MHz
NUC1 13C
P1 10.00 usec
SI 32768
SF 100.6127685 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
O
N
H
Ph
F
3-100
180
160
140
120
100
80
60
40
20
ppm



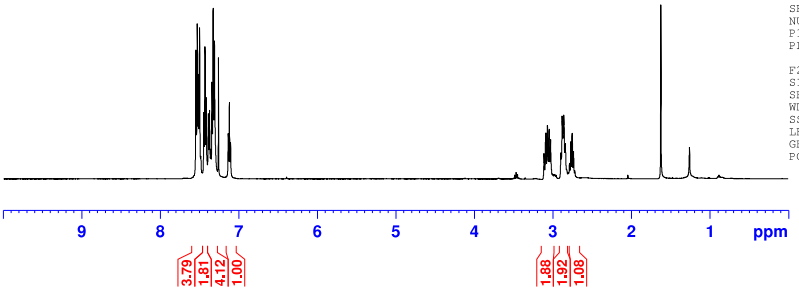
3-100


```
NAME                JAM-834-7
EXPNO                      11
PROCNO                      1
Date_            20171013
Time                    18.55
INSTRUM                 spect
PROBHD    5 mm PABBO BB-
PULPROG          zgfhigqn.2
TD                     131072
SOLVENT                 CDCl3
NS                         16
DS                          4
SWH                89285.711 Hz
FIDRES              0.681196 Hz
AQ                  0.7340532 sec
RG                        203
DW                      5.600 usec
DE                      6.50 usec
TE                   ~2530.9 K
D1                 1.00000000 sec
D11                0.03000000 sec
D12                0.00002000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1            376.4607164 MHz
NUC1                     19F
P1                     14.20 usec
SI                      65536
SF              376.4983662 MHz
WDW                        EM
SSB                         0
LB                       0.30 Hz
GB                          0
PC                       1.00
```

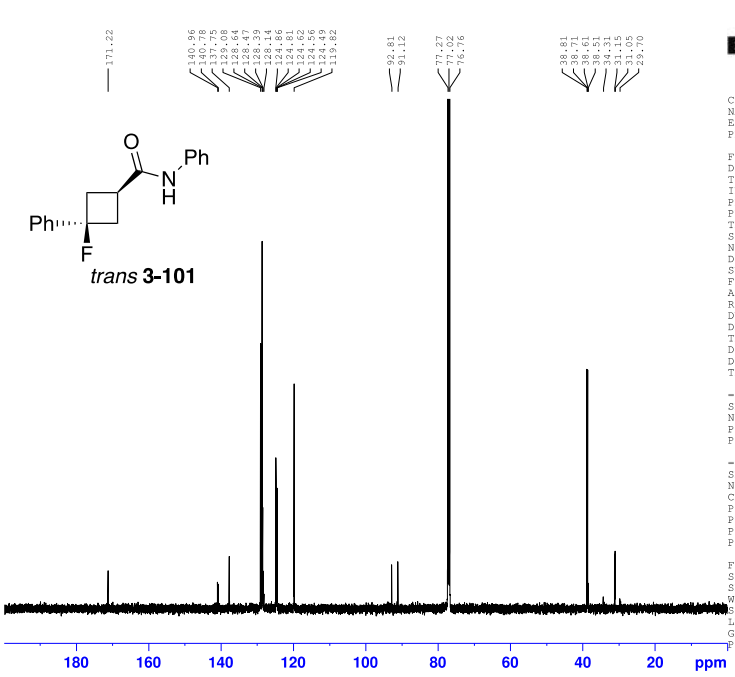




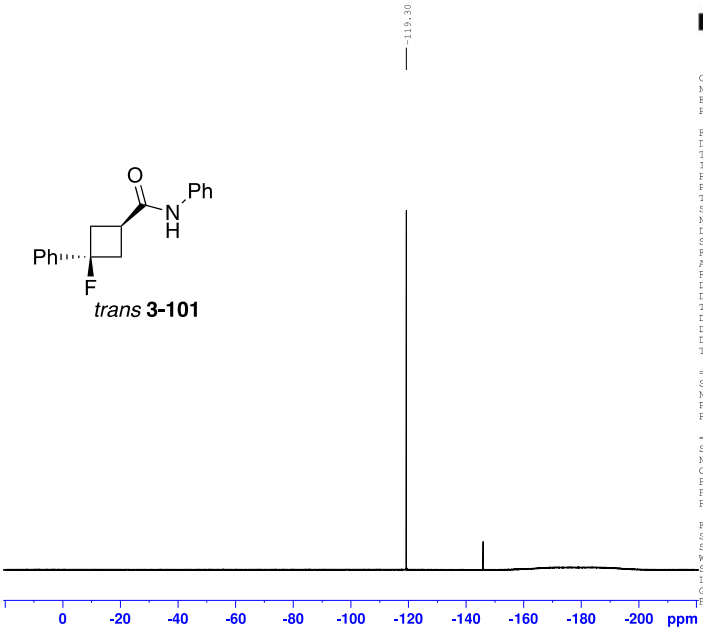
trans **3-101**



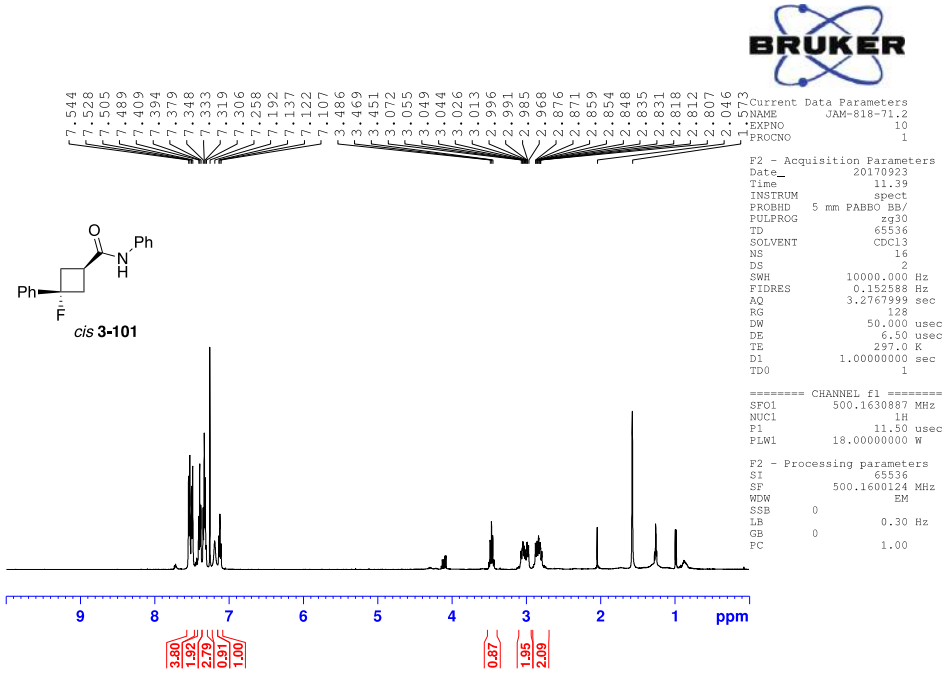

```
Current Data Parameters
NAME                JAM-818-71
EXPNO                       10
PROCNO                       1

F2 - Acquisition Parameters
Date_            20170922
Time                    18.12
INSTRUM                 spect
PROBHD    5 mm PABBO BB/
PULPROG                 zg30
TD                     65536
SOLVENT                 CDCl3
NS                         16
DS                          2
SWH               10000.000 Hz
FIDRES              0.152588 Hz
AQ                  3.2767999 sec
RG                        101
DW                     50.000 usec
DE                      6.50 usec
TE                      296.7 K
D1                 1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1            500.1630887 MHz
NUC1                     1H
P1                     11.50 usec
PLW1           18.00000000 W

F2 - Processing parameters
SI                      65536
SF              500.1600119 MHz
WDW                        EM
SSB                 0
LB                       0.30 Hz
GB                  0
PC                       1.00
```

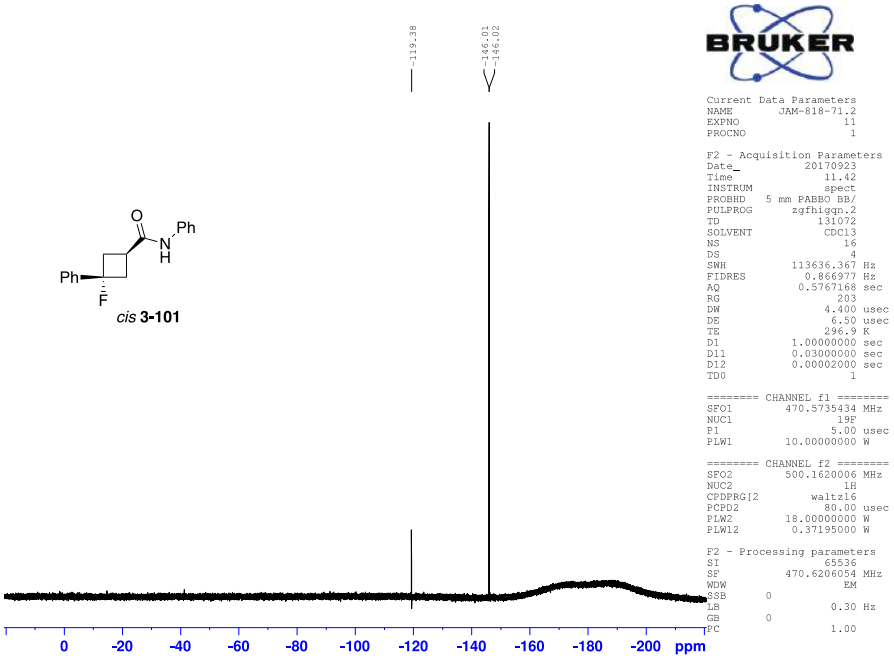


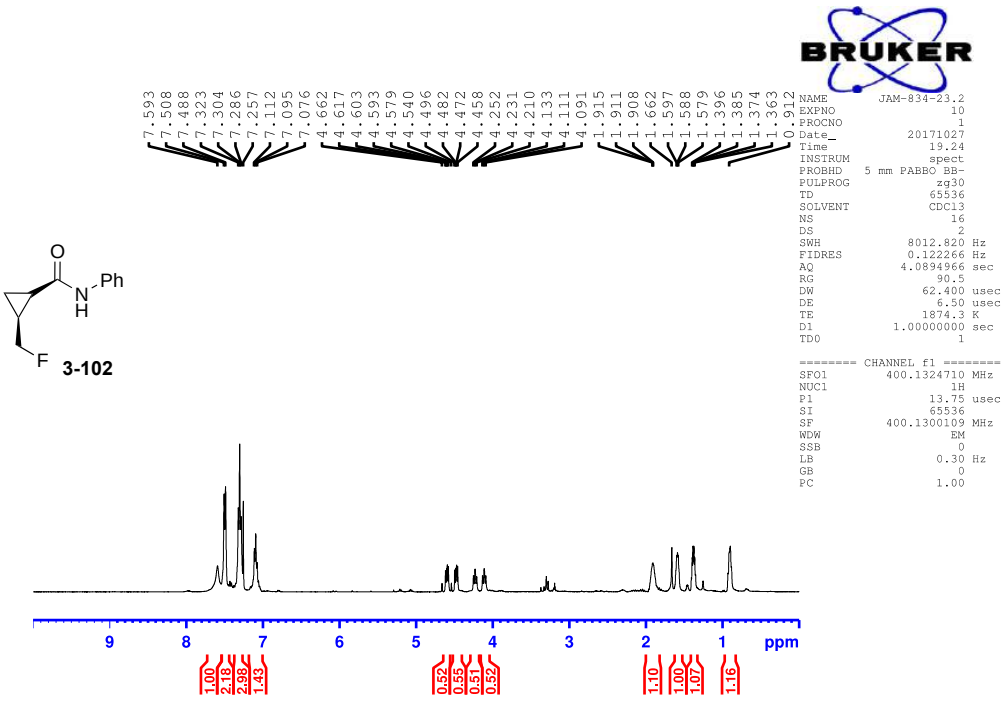

```
Current Data Parameters
NAME                  JAM-818-71
EXPNO                         13
PROCNO                         1

F2 - Acquisition Parameters
Date_                 20170923
Time                      7.52
INSTRUM                  spect
PROBHD     5 mm PABBO BB/
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                        1028
DS                           2
SWH                  29761.904 Hz
FIDRES                0.454131 Hz
AQ                    1.1010048 sec
RG                         203
DW                    16.800 usec
DE                     6.50 usec
TE                     298.6 K
D1                    2.00000000 sec
D11                   0.03000000 sec
TD0                            1

======== CHANNEL f1 ========
SFO1           125.7779086 MHz
NUC1                     13C
P1                    10.50 usec
PLW1          110.00000000 W

======== CHANNEL f2 ========
SFO2           500.1620006 MHz
NUC2                      1H
CPDPRG[2              waltz16
PCPD2                 80.00 usec
PLW2          18.00000000 W
PLW12          0.37195000 W
PLW13          0.23805000 W

F2 - Processing parameters
SI                        32768
SF                 125.7653320 MHz
WDW                          EM
SSB          0
LB                     1.00 Hz
GB           0
PC                     1.40
```



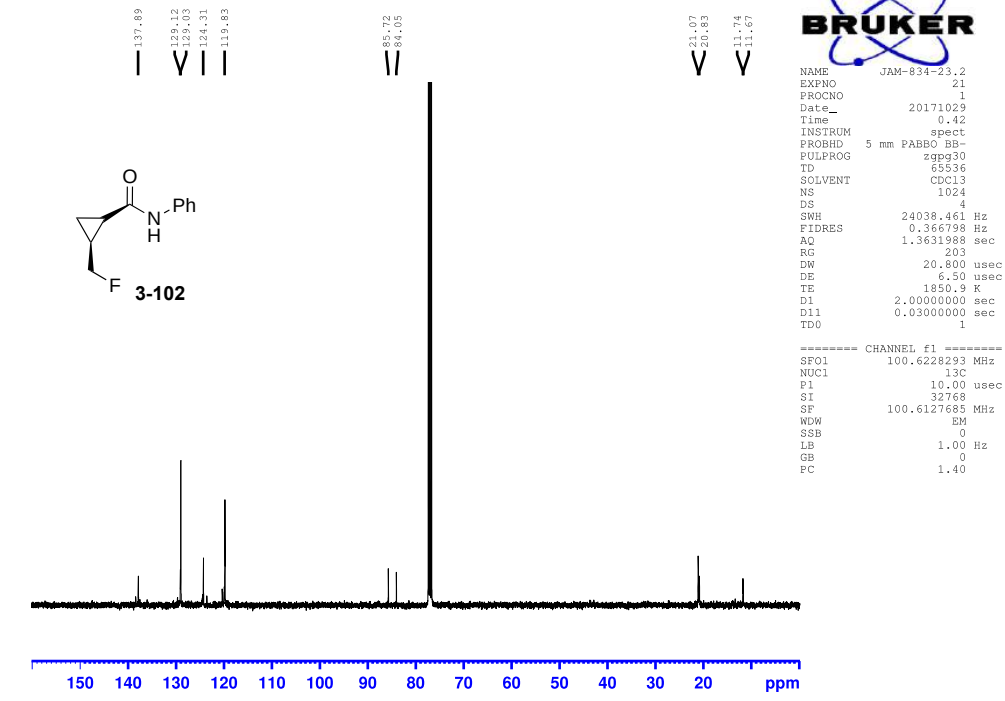

```
Current Data Parameters
NAME                  JAM-818-71
EXPNO                         11
PROCNO                         1

F2 - Acquisition Parameters
Date_                 20170922
Time                     18.14
INSTRUM                  spect
PROBHD     5 mm PABBO BB/
PULPROG             zgfhigqn.2
TD                      131072
SOLVENT                  CDCl3
NS                           16
DS                            4
SWH                 113636.367 Hz
FIDRES                0.866977 Hz
AQ                    0.5767168 sec
RG                         203
DW                     4.400 usec
DE                     6.50 usec
TE                     296.6 K
D1                    1.00000000 sec
D11                   0.03000000 sec
D12                   0.00002000 sec
TD0                            1

======== CHANNEL f1 ========
SFO1           470.5735434 MHz
NUC1                     19F
P1                     5.00 usec
PLW1          10.00000000 W

======== CHANNEL f2 ========
SFO2           500.1620006 MHz
NUC2                      1H
CPDPRG[2              waltz16
PCPD2                 80.00 usec
PLW2          18.00000000 W
PLW12          0.37195000 W

F2 - Processing parameters
SI                        65536
SF                 470.6206054 MHz
WDW                          EM
SSB          0
LB                     0.30 Hz
GB           0
PC                     1.00
```


7.544
7.528
7.505
7.489
7.409
7.394
7.379
7.348
7.333
7.319
7.306
7.258
7.192
7.137
7.122
7.107
3.486
3.469
3.451
3.072
3.055
3.049
3.044
3.026
3.013
2.996
2.991
2.985
2.968
2.876
2.871
2.859
2.854
2.848
2.835
2.831
2.818
2.812
2.807
2.046
1.573
O
N
H
Ph
Ph
F
cis 3-101
9
8
7
6
5
4
3
2
1
ppm
3.80
1.92
2.79
0.91
1.00
0.87
1.95
2.09
Current Data Parameters
NAME JAM-818-71.2
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20170923
Time 11.39
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2767999 sec
RG 128
DW 50.000 usec
DE 6.50 usec
TE 297.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 500.1630887 MHz
NUC1 1H
P1 11.50 usec
PLW1 18.00000000 W
F2 - Processing parameters
SI 65536
SF 500.1600124 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

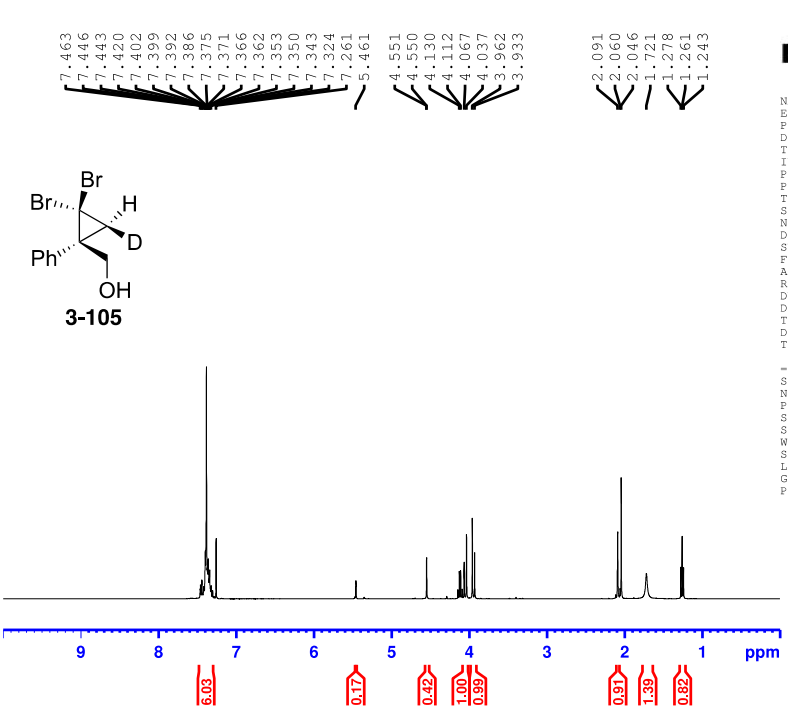

119.38
146.01
146.02
O
N
H
Ph
Ph
F
cis 3-101
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm
Current Data Parameters
NAME JAM-818-71.2
EXPNO 11
PROCNO 1
F2 - Acquisition Parameters
Date_ 20170923
Time 11.42
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgfhigqn.2
TD 131072
SOLVENT CDCl3
NS 16
DS 4
SWH 113636.367 Hz
FIDRES 0.866977 Hz
AQ 0.5767168 sec
RG 203
DW 4.400 usec
DE 6.50 usec
TE 296.9 K
D1 1.00000000 sec
D11 0.03000000 sec
D12 0.00002000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 470.5735434 MHz
NUC1 19F
P1 5.00 usec
PLW1 10.00000000 W
======== CHANNEL f2 ========
SFO2 500.1620006 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 18.00000000 W
PLW12 0.37195000 W
F2 - Processing parameters
SI 65536
SF 470.6206054 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



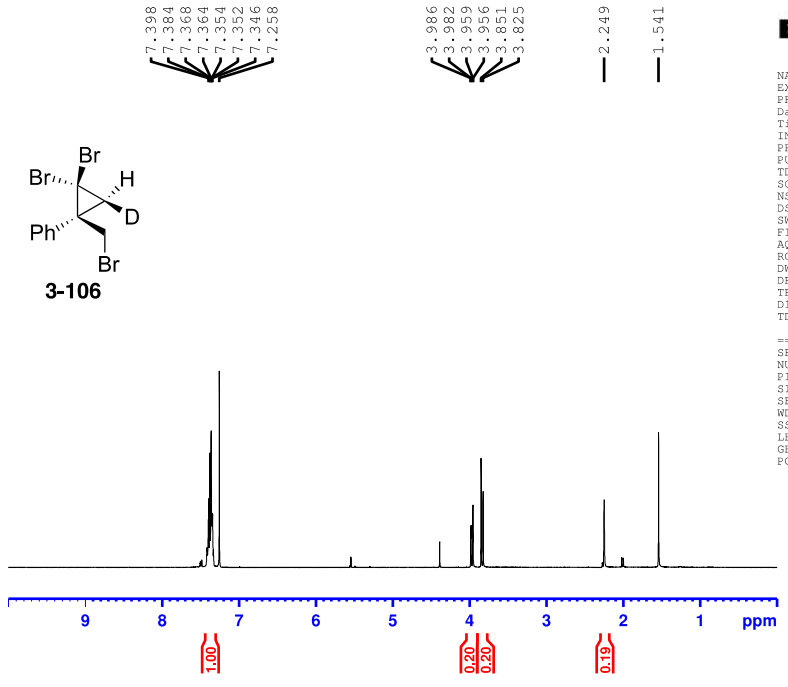

```
NAME          JAM-834-23.2
EXPNO               10
PROCNO               1
Date_         20171027
Time              19.24
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG           zg30
TD               65536
SOLVENT          CDCl3
NS                  16
DS                   2
SWH            8012.820 Hz
FIDRES            0.122266 Hz
AQ             4.0894966 sec
RG                90.5
DW               62.400 usec
DE                6.50 usec
TE              1874.3 K
D1              1.00000000 sec
TD0                  1

======== CHANNEL f1 ========
SFO1          400.1324710 MHz
NUC1               1H
P1               13.75 usec
SI               65536
SF            400.1300109 MHz
WDW                EM
SSB                 0
LB               0.30 Hz
GB                  0
PC                1.00
```



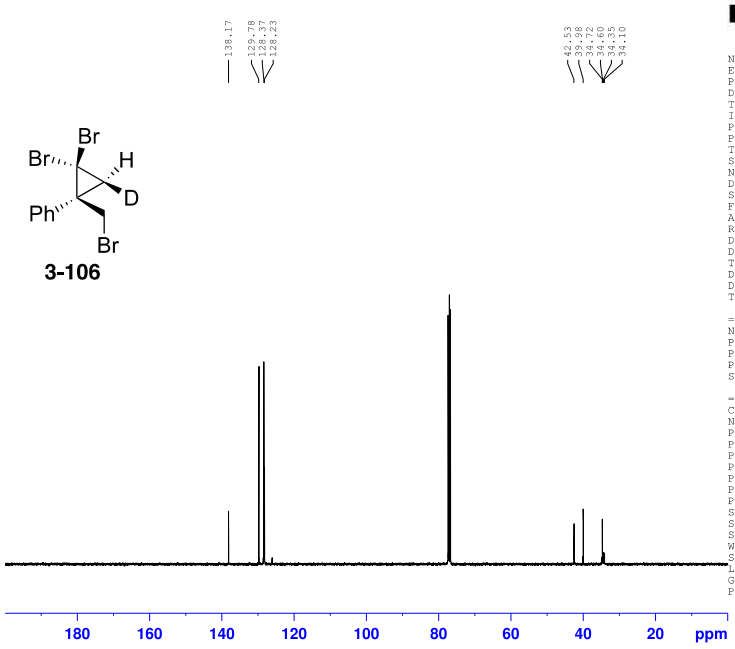

```
NAME          JAM-834-23.2
EXPNO               21
PROCNO               1
Date_         20171029
Time               0.42
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD               65536
SOLVENT          CDCl3
NS                1024
DS                   4
SWH           24038.461 Hz
FIDRES            0.366798 Hz
AQ             1.3631988 sec
RG                 203
DW               20.800 usec
DE                6.50 usec
TE              1850.9 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
SFO1          100.6228293 MHz
NUC1               13C
P1               10.00 usec
SI               32768
SF            100.6127685 MHz
WDW                EM
SSB                 0
LB               1.00 Hz
GB                  0
PC                1.40
```



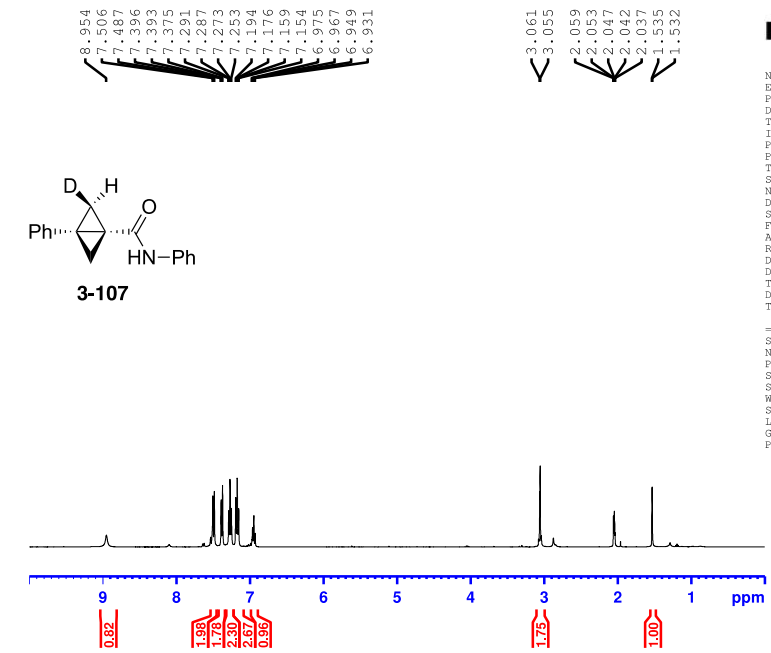

```
NAME                JAM-834-54
EXPNO                       10
PROCNO                       1
Date_                 20171124
Time                     17.27
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG                  zg30
TD                      65536
SOLVENT                 CDCl3
NS                         16
DS                          2
SWH                  8012.820 Hz
FIDRES               0.122266 Hz
AQ                   4.0894966 sec
RG                        101
DW                     62.400 usec
DE                      6.50 usec
TE                     294.7 K
D1                   1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1          400.1324710 MHz
NUC1                     1H
P1                    13.75 usec
SI                    65536
SF            400.1300089 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
```



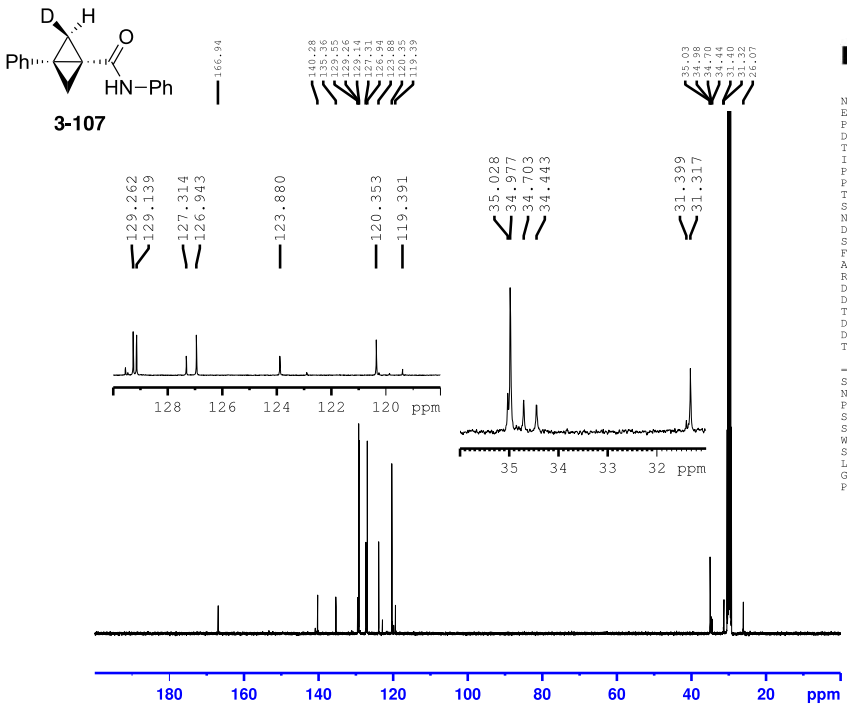

```
NAME                JAM-834-56
EXPNO                       10
PROCNO                       1
Date_                 20171128
Time                     17.46
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG                  zg30
TD                      65536
SOLVENT                 CDCl3
NS                         16
DS                          2
SWH                  8012.820 Hz
FIDRES               0.122266 Hz
AQ                   4.0894966 sec
RG                        144
DW                     62.400 usec
DE                      6.50 usec
TE                     211.9.7 K
D1                   1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1          400.1324710 MHz
NUC1                     1H
P1                    13.75 usec
SI                    65536
SF            400.1300098 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
```



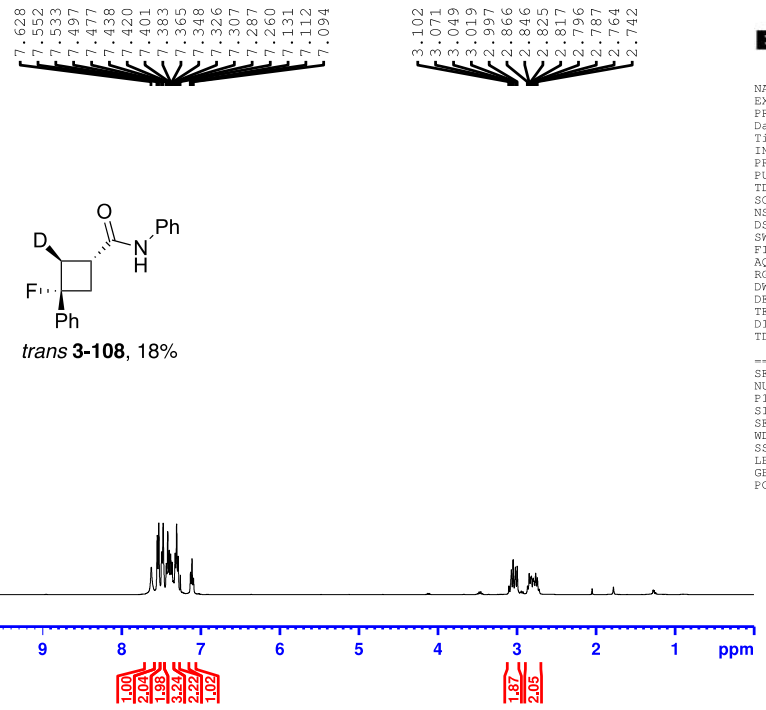

```
NAME                JAM-834-56
EXPNO                        2
PROCNO                       1
Date_                 20171129
Time                      8.57
INSTRUM                  spect
PROBHD    5 mm PADUL 13C
PULPROG                zgpg30
TD                        65536
SOLVENT                 CDCl3
NS                          649
DS                            4
SWH                  24038.461 Hz
FIDRES                0.366798 Hz
AQ                    1.3631988 sec
RG                         50.8
DW                       20.800 usec
DE                        6.50 usec
TE                      298.2 K
D1                    3.00000000 sec
D11                   0.03000000 sec
TD0                           1

======== CHANNEL f1 ========
NUC1                        13C
P1                        10.00 usec
PL1                       -0.44 dB
PL1W                39.19395828 W
SFO1                100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2                 waltz16
NUC2                         1H
PCPD2                     90.00 usec
PL2                       -3.90 dB
PL12                      15.81 dB
PL13                     120.00 dB
PL2W                21.64248466 W
PL12W                0.23137002 W
PL13W                0.00000000 W
SFO2                400.2316009 MHz
SI                        32768
SF                  100.6379140 MHz
WDW                          EM
SSB                           0
LB                         1.00 Hz
GB                            0
PC                         1.40
```




```
NAME                JAM-834-60
EXPNO                       10
PROCNO                       1
Date_                 20171129
Time                     19.29
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG                  zg30
TD                        65536
SOLVENT                Acetone
NS                           16
DS                            2
SWH                  8012.820 Hz
FIDRES                0.122266 Hz
AQ                    4.0894966 sec
RG                         71.8
DW                       62.400 usec
DE                        6.50 usec
TE                      2234.7 K
D1                    1.00000000 sec
TD0                           1

======== CHANNEL f1 ========
SFO1                400.1324710 MHz
NUC1                         1H
P1                        13.75 usec
SI                        65536
SF                  400.1300077 MHz
WDW                          EM
SSB                           0
LB                         0.30 Hz
GB                            0
PC                         1.00
```

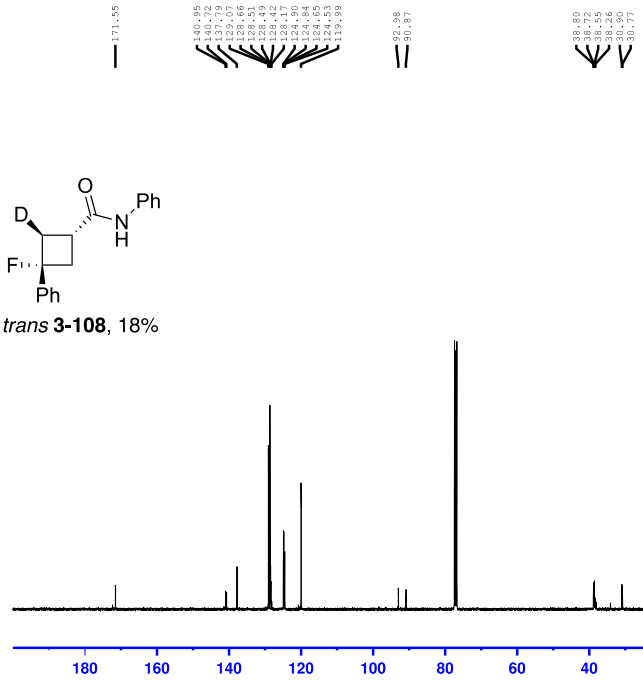



```
NAME                JAM-834-60
EXPNO                       11
PROCNO                       1
Date_                 20171129
Time                     22.02
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG                 zgpg30
TD                       65536
SOLVENT                Acetone
NS                          2028
DS                             4
SWH                 24038.461 Hz
FIDRES               0.366798 Hz
AQ                  1.3631988 sec
RG                           203
DW                      20.800 usec
DE                       6.50 usec
TE                     1988.7 K
D1                  2.00000000 sec
D11                 0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1           100.6228293 MHz
NUC1                     13C
P1                     10.00 usec
SI                      32768
SF             100.6126795 MHz
WDW                        EM
SSB                         0
LB                       1.00 Hz
GB                          0
PC                       1.40
```



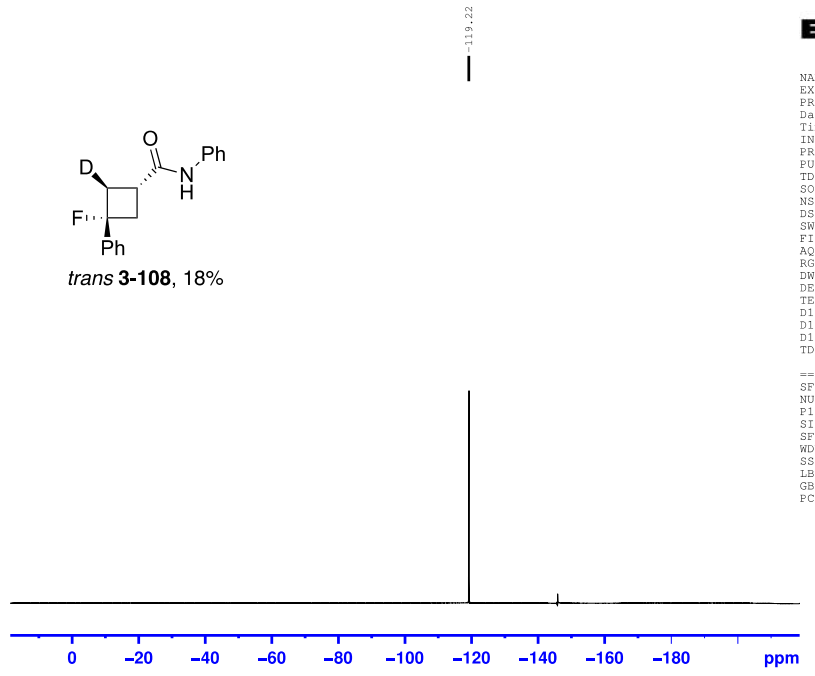
trans **3-108**, 18%

```
NAME              JAM-834-62.2
EXPNO                       10
PROCNO                       1
Date_                 20171202
Time                     3.14
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG                  zg30
TD                       65536
SOLVENT                  CDCl3
NS                          16
DS                           2
SWH                 8012.820 Hz
FIDRES               0.122266 Hz
AQ                  4.0894966 sec
RG                        50.8
DW                      62.400 usec
DE                       6.50 usec
TE                     2140.3 K
D1                  1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1           400.1324710 MHz
NUC1                      1H
P1                     13.75 usec
SI                      65536
SF             400.1300099 MHz
WDW                        EM
SSB                         0
LB                       0.30 Hz
GB                          0
PC                       1.00
```



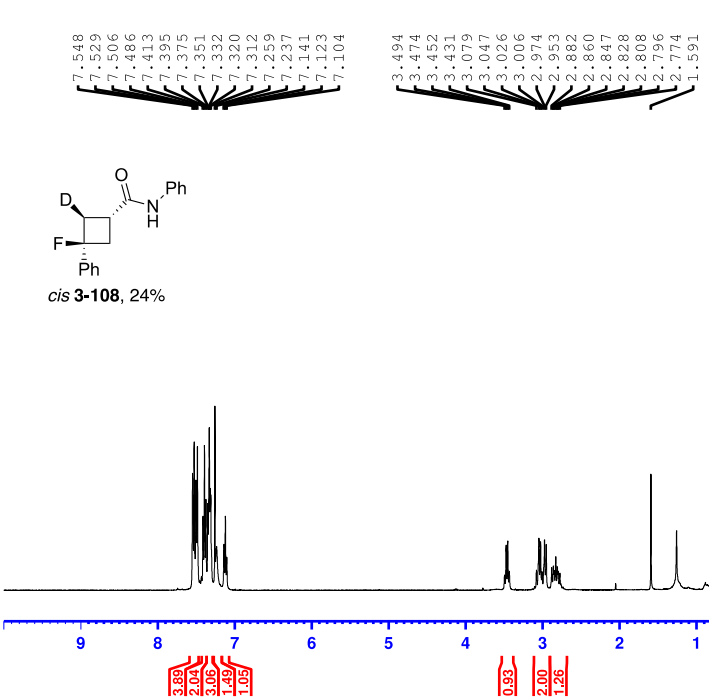
trans **3-108**, 18%

```
NAME            JAM-834-62.2
EXPNO                     11
PROCNO                     1
Date_           20171202
Time                    4.15
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                    1024
DS                       4
SWH             24038.461 Hz
FIDRES          0.366798 Hz
AQ              1.3631988 sec
RG                     203
DW                20.800 usec
DE                 6.50 usec
TE                2226.1 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1          100.6228293 MHz
NUC1                   13C
P1                   10.00 usec
SI                   32768
SF            100.6127685 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```



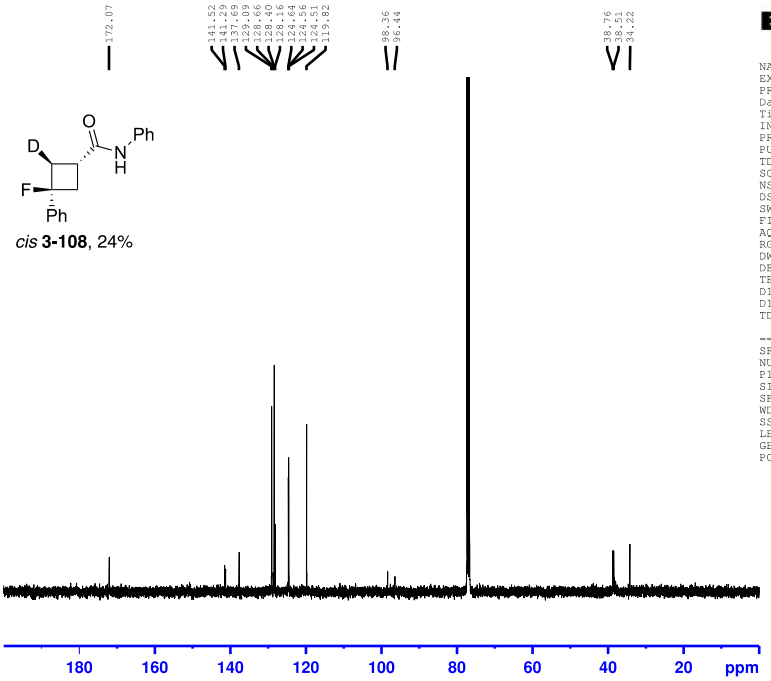
trans **3-108**, 18%

```
NAME            JAM-834-62.2
EXPNO                     13
PROCNO                     1
Date_           20171202
Time                    5.04
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG         zgfhigqn.2
TD                  131072
SOLVENT              CDCl3
NS                      16
DS                       4
SWH             89285.711 Hz
FIDRES          0.681196 Hz
AQ              0.7340532 sec
RG                     203
DW                 5.600 usec
DE                 6.50 usec
TE                2072.6 K
D1             1.00000000 sec
D11            0.03000000 sec
D12            0.00002000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1          376.4607164 MHz
NUC1                   19F
P1                   14.20 usec
SI                   65536
SF            376.4983662 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```



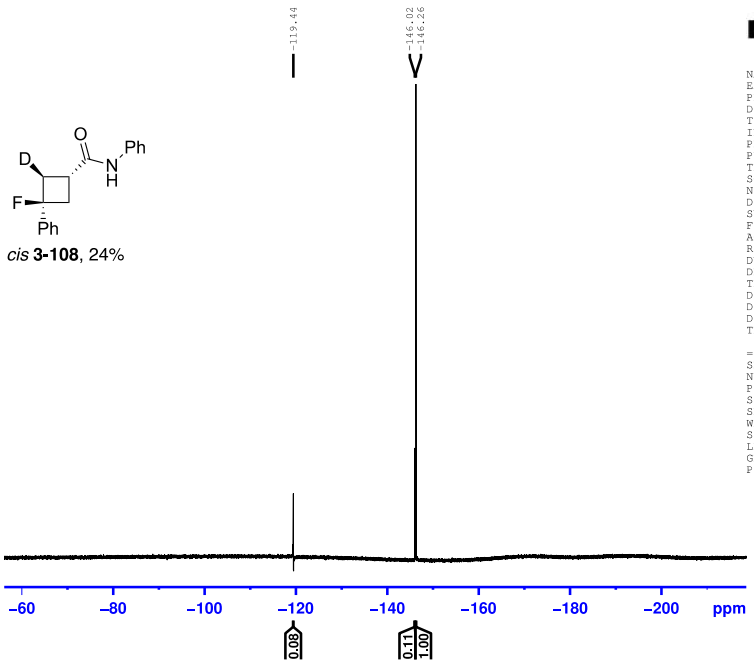
cis **3-108**, 24%

```
NAME                JAM-834-62
EXPNO                       10
PROCNO                       1
Date_                 20171201
Time                     17.32
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG                  zg30
TD                      65536
SOLVENT                 CDCl3
NS                         16
DS                          2
SWH                  8012.820 Hz
FIDRES               0.122266 Hz
AQ                   4.0894966 sec
RG                        101
DW                     62.400 usec
DE                      6.50 usec
TE                    1964.5 K
D1                 1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1           400.1324710 MHz
NUC1                     1H
P1                    13.75 usec
SI                    65536
SF             400.1300105 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
```



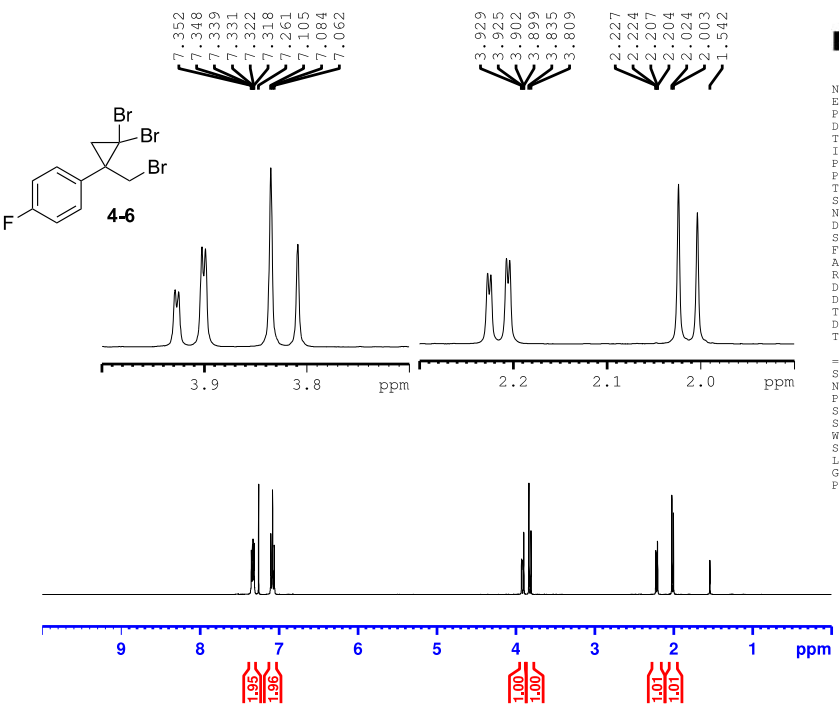
cis **3-108**, 24%

```
NAME              JAM-834-62_2
EXPNO                       10
PROCNO                       1
Date_                 20171202
Time                     22.53
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG                zgpg30
TD                      65536
SOLVENT                 CDCl3
NS                       1024
DS                          4
SWH                24038.461 Hz
FIDRES              0.366798 Hz
AQ                  1.3631988 sec
RG                        203
DW                     20.800 usec
DE                      6.50 usec
TE                    2236.6 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1           100.6228293 MHz
NUC1                     13C
P1                    10.00 usec
SI                    32768
SF             100.6127685 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40
```

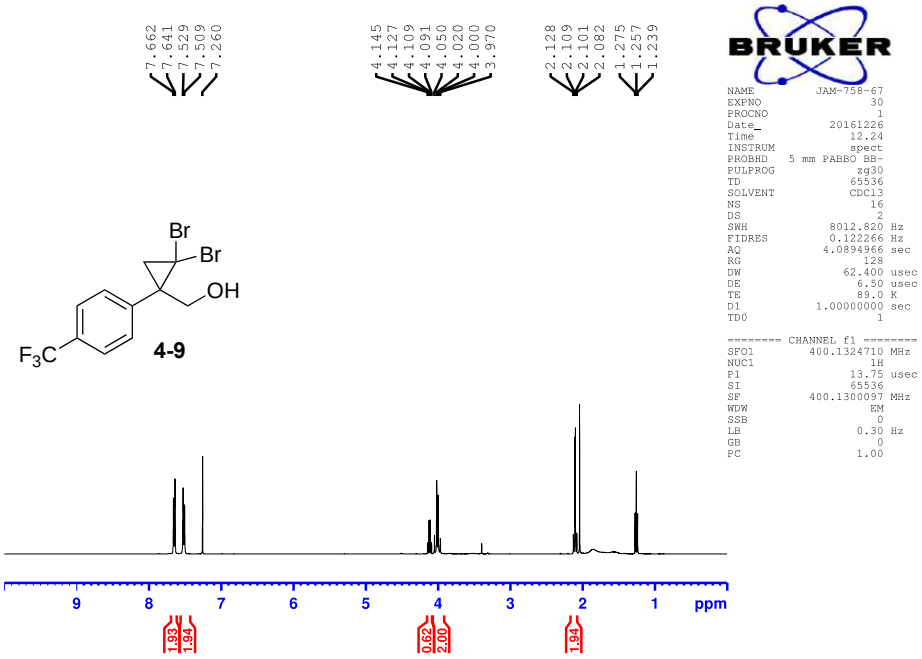


cis **3-108**, 24%

```
NAME                JAM-834-62
EXPNO                       11
PROCNO                       1
Date_                 20171201
Time                     17.34
INSTRUM                  spect
PROBHD     5 mm PABBO BB-
PULPROG             zgfhigqn.2
TD                      131072
SOLVENT                  CDCl3
NS                          16
DS                           4
SWH                 89285.711 Hz
FIDRES                0.681196 Hz
AQ                   0.7340532 sec
RG                         203
DW                       5.600 usec
DE                       6.50 usec
TE                     1919.9 K
D1                  1.00000000 sec
D11                 0.03000000 sec
D12                 0.00002000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1                376.4607164 MHz
NUC1                        19F
P1                       14.20 usec
SI                        65536
SF                  376.4983662 MHz
WDW                          EM
SSB                           0
LB                         0.30 Hz
GB                            0
PC                         1.00
```

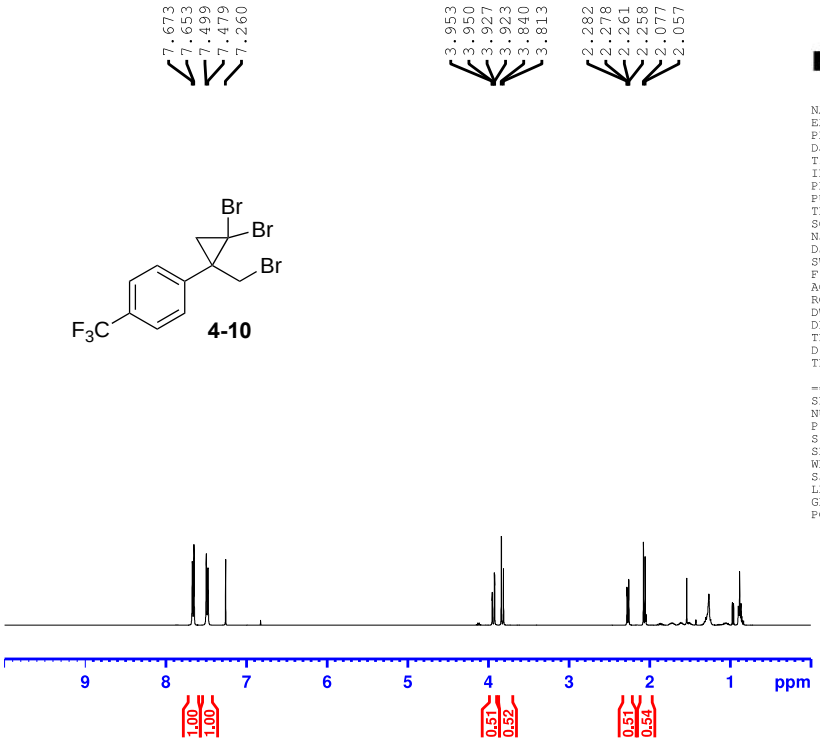



```
NAME                JAM-749-87
EXPNO                       10
PROCNO                       1
Date_                 20161104
Time                     19.56
INSTRUM                  spect
PROBHD     5 mm PABBO BB-
PULPROG                  zg30
TD                        65536
SOLVENT                  CDCl3
NS                          16
DS                           2
SWH                 8012.820 Hz
FIDRES                0.122266 Hz
AQ                   4.0894966 sec
RG                         144
DW                      62.400 usec
DE                       6.50 usec
TE                      88.8 K
D1                  1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1                400.1324710 MHz
NUC1                        1H
P1                       13.75 usec
SI                        65536
SF                  400.1300091 MHz
WDW                          EM
SSB                           0
LB                         0.30 Hz
GB                            0
PC                         1.00
```



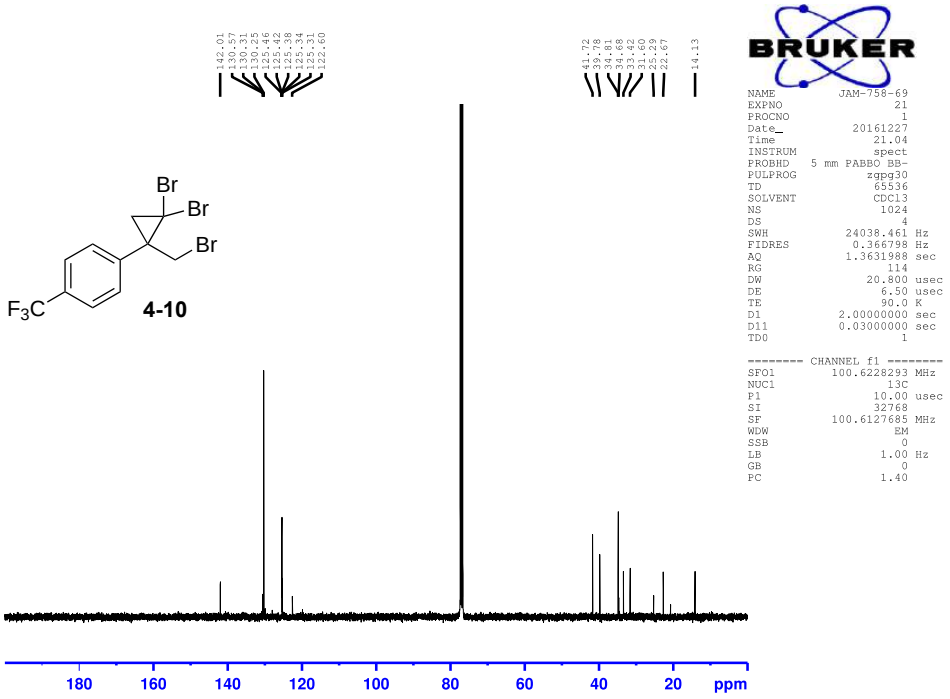
BRUKER

```
NAME                JAM-758-67
EXPNO                       30
PROCNO                       1
Date_                 20161226
Time                     12.24
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG                  zg30
TD                      65536
SOLVENT                 CDCl3
NS                         16
DS                          2
SWH                 8012.820 Hz
FIDRES              0.122266 Hz
AQ                  4.0894966 sec
RG                        128
DW                     62.400 usec
DE                      6.50 usec
TE                      89.0 K
D1                  1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1             400.1324710 MHz
NUC1                       1H
P1                      13.75 usec
SI                      65536
SF               400.1300097 MHz
WDW                        EM
SSB                         0
LB                       0.30 Hz
GB                          0
PC                       1.00
```



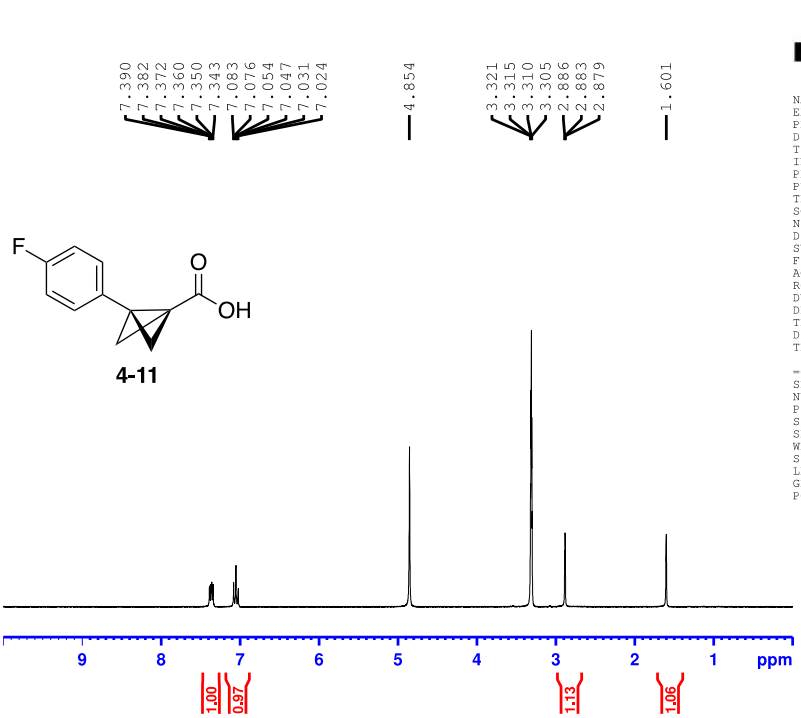
BRUKER

```
NAME                JAM-758-69
EXPNO                       20
PROCNO                       1
Date_                 20161227
Time                     10.55
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG                  zg30
TD                      65536
SOLVENT                 CDCl3
NS                         16
DS                          2
SWH                 8012.820 Hz
FIDRES              0.122266 Hz
AQ                  4.0894966 sec
RG                        114
DW                     62.400 usec
DE                      6.50 usec
TE                      91.2 K
D1                  1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1             400.1324710 MHz
NUC1                       1H
P1                      13.75 usec
SI                      65536
SF               400.1300093 MHz
WDW                        EM
SSB                         0
LB                       0.30 Hz
GB                          0
PC                       1.00
```



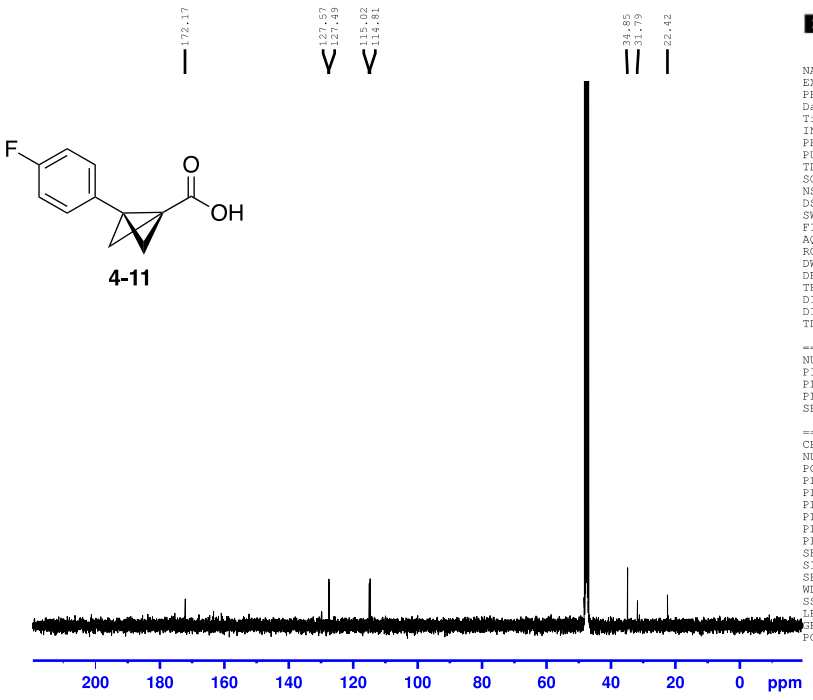
BRUKER

```
NAME              JAM-758-69
EXPNO                     21
PROCNO                     1
Date_              20161227
Time                  21.04
INSTRUM               spect
PROBHD    5 mm PABBO BB-
PULPROG               zgpg30
TD                     65536
SOLVENT                CDCl3
NS                      1024
DS                         4
SWH               24038.461 Hz
FIDRES             0.366798 Hz
AQ                 1.3631988 sec
RG                       114
DW                  20.800 usec
DE                   6.50 usec
TE                   90.0 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1             100.6228293 MHz
NUC1                     13C
P1                   10.00 usec
SI                     32768
SF               100.6127685 MHz
WDW                      EM
SSB                       0
LB                    1.00 Hz
GB                        0
PC                     1.40
```



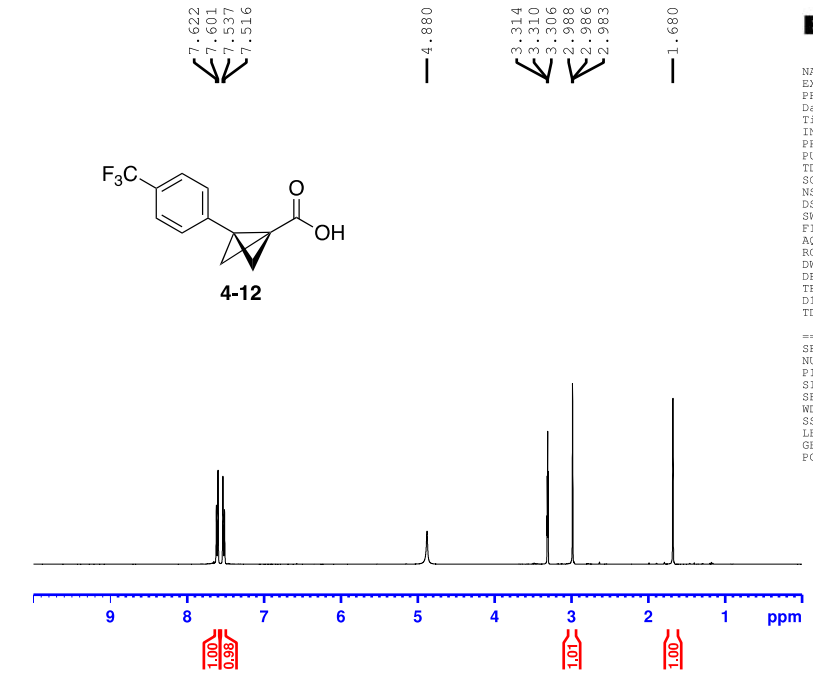
BRUKER

```
NAME              JAM-758-6
EXPNO                    10
PROCNO                    1
Date_             20161110
Time                 14.33
INSTRUM              spect
PROBHD    5 mm QNP   1H/1
PULPROG                zg30
TD                    32768
SOLVENT               CD3OD
NS                       16
DS                        2
SWH               6188.119 Hz
FIDRES            0.188846 Hz
AQ                2.6477044 sec
RG                      322
DW                 80.800 usec
DE                  6.50 usec
TE                  -928.3 K
D1                1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1             300.2318540 MHz
NUC1                     1H
P1                   12.71 usec
SI                    32768
SF               300.2300070 MHz
WDW                      EM
SSB                       0
LB                    0.10 Hz
GB                        0
PC                     1.00
```



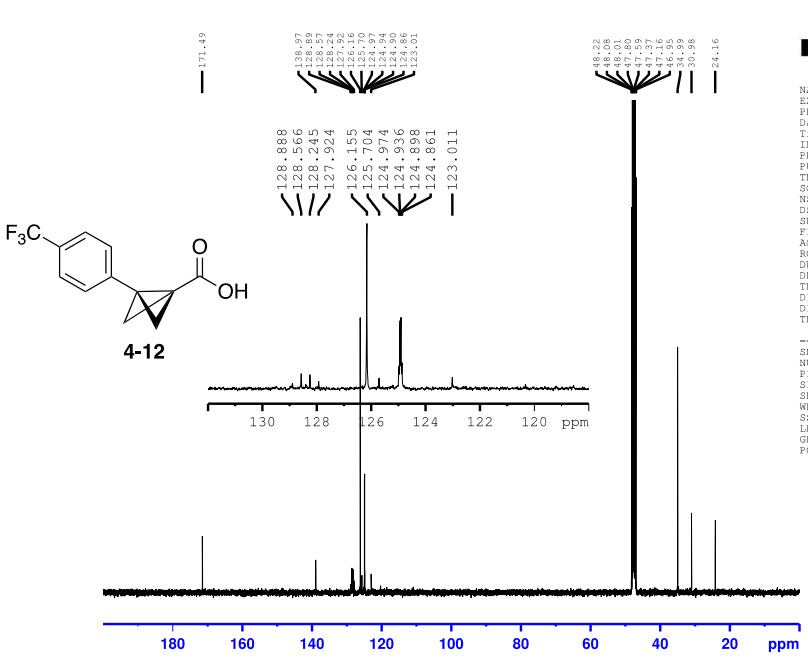
4-11

```
NAME                JAM-758-6
EXPNO                       1
PROCNO                      1
Date_            20161111
Time                     8.59
INSTRUM                spect
PROBHD    5 mm PADUL 13C
PULPROG             zgpg30
TD                      65536
SOLVENT                 MeOD
NS                        842
DS                          4
SWH                24038.461 Hz
FIDRES             0.366798 Hz
AQ                 1.3631988 sec
RG                      45.2
DW                   20.800 usec
DE                    6.50 usec
TE                   295.1 K
D1                3.00000000 sec
D11               0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                      13C
P1                      10.00 usec
PL1                     -0.44 dB
PL1W             39.19395828 W
SFO1            100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                      1H
PCPD2                 90.00 usec
PL2                   -3.90 dB
PL12                  15.81 dB
PL13                 120.00 dB
PL2W             21.64248466 W
PL12W             0.23137002 W
PL13W             0.00000000 W
SFO2            400.2316009 MHz
SI                      32768
SF              100.6379140 MHz
WDW                        EM
SSB                         0
LB                       1.00 Hz
GB                          0
PC                       1.40
```



4-12

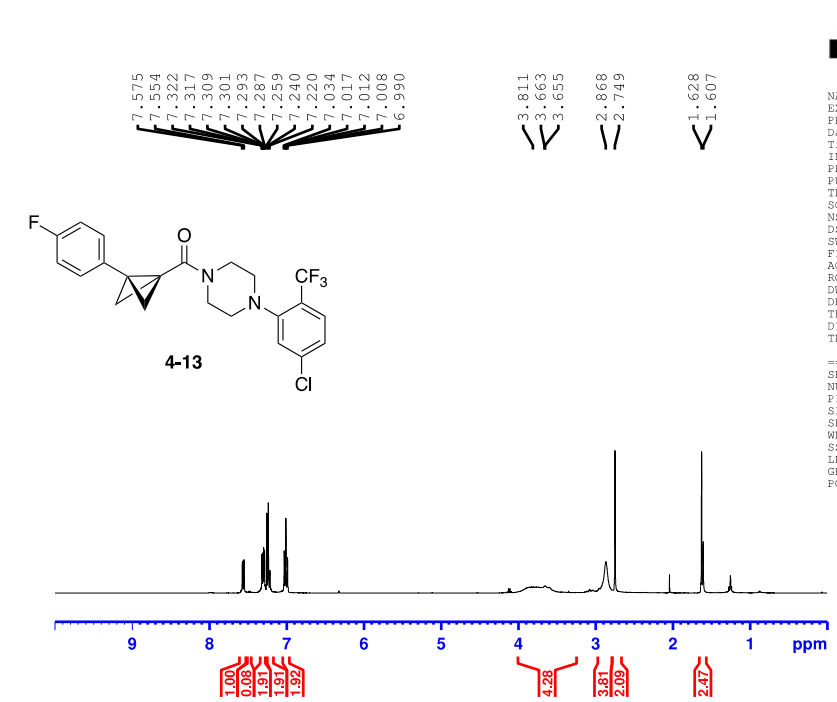
```
NAME                JAM-758-71
EXPNO                       10
PROCNO                      1
Date_            20161228
Time                    12.50
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG                 zg30
TD                      65536
SOLVENT                 MeOD
NS                         16
DS                          2
SWH                 8012.820 Hz
FIDRES              0.122266 Hz
AQ                  4.0894966 sec
RG                        128
DW                    62.400 usec
DE                     6.50 usec
TE                    90.6 K
D1                1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1            400.1324710 MHz
NUC1                      1H
P1                     13.75 usec
SI                      65536
SF              400.1300075 MHz
WDW                        EM
SSB                         0
LB                       0.30 Hz
GB                          0
PC                       1.00
```



BRUKER

NAME JAM-758-71
EXPNO 11
PROCNO 1
Date_ 20161228
Time 22.02
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT MeOD
NS 2048
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 181
DW 20.800 usec
DE 6.50 usec
TE 90.5 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

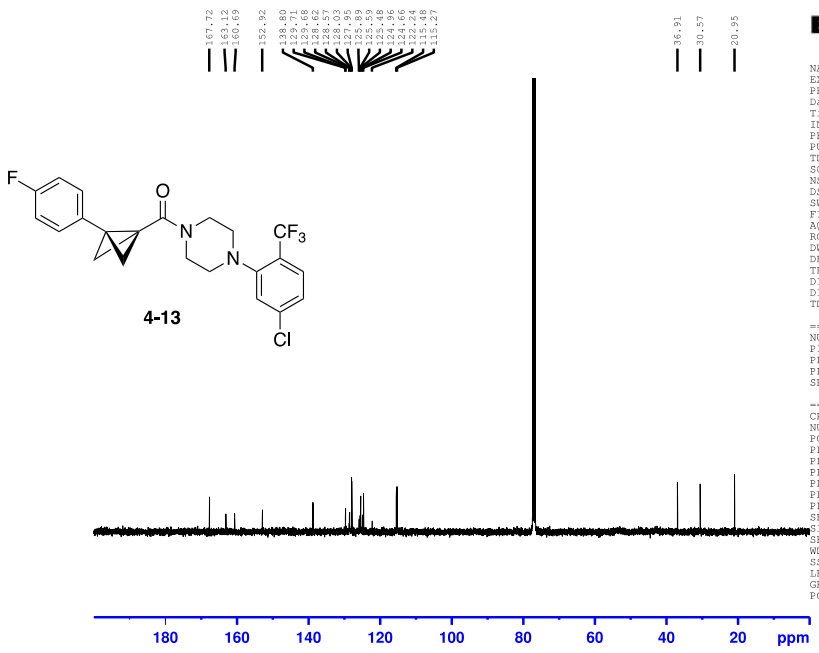
-------- CHANNEL f1 --------
SFO1 100.6228293 MHz
NUC1 13C
P1 10.00 usec
SI 32768
SF 100.6127685 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



BRUKER

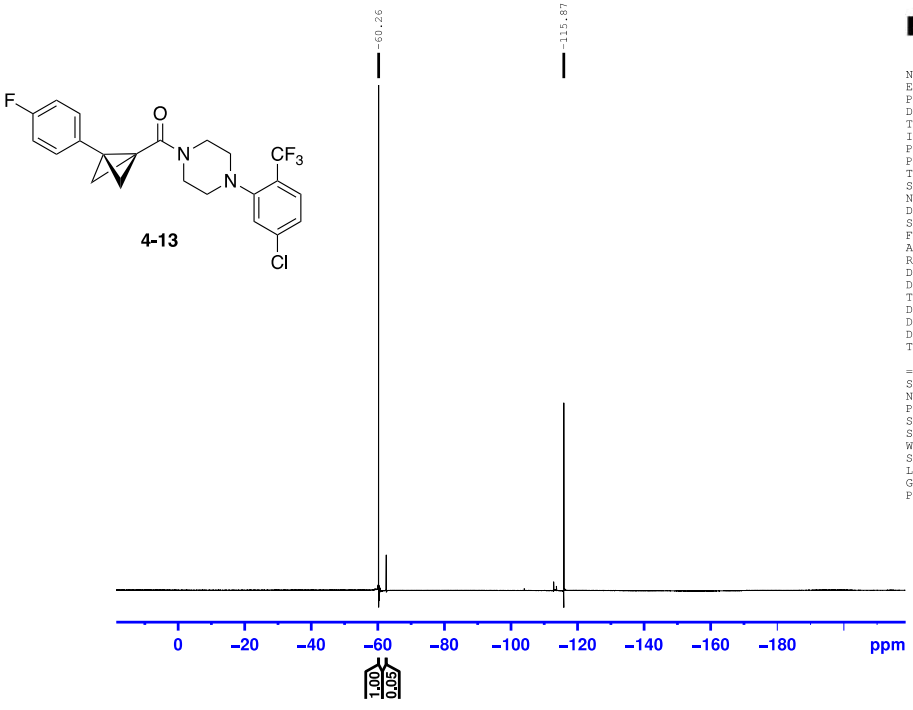
NAME JAM-758-45
EXPNO 10
PROCNO 1
Date_ 20161206
Time 14.59
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 114
DW 62.400 usec
DE 6.50 usec
TE 90.3 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 13.75 usec
SI 65536
SF 400.1300096 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



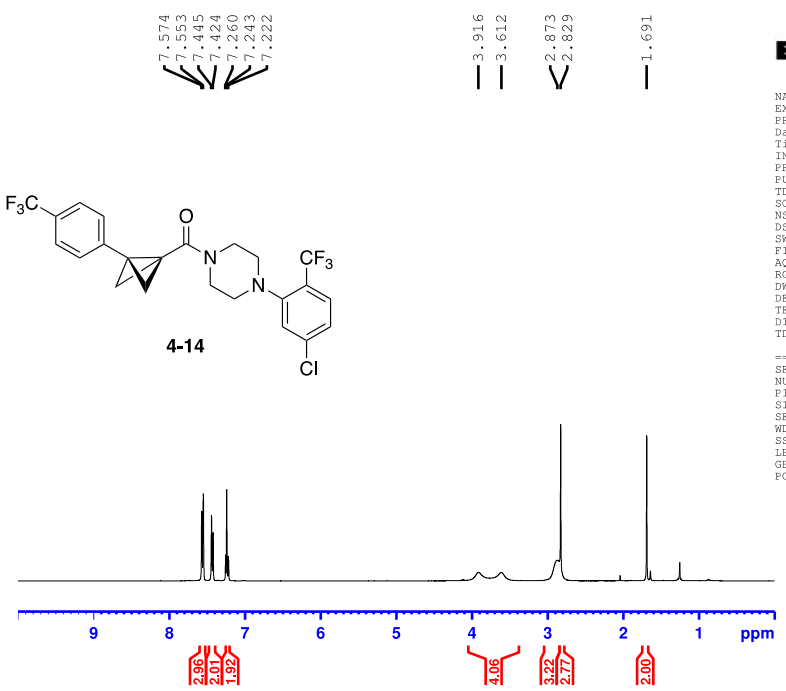
BRUKER

```
NAME                JAM-758-45
EXPNO                        2
PROCNO                       1
Date_             20161206
Time                     17.12
INSTRUM                  spect
PROBHD    5 mm PADUL 13C
PULPROG              zgpg30
TD                        65536
SOLVENT                  CDCl3
NS                         846
DS                           4
SWH                24038.461 Hz
FIDRES              0.366798 Hz
AQ                  1.3631988 sec
RG                          57
DW                     20.800 usec
DE                      6.50 usec
TE                     294.8 K
D1                  3.00000000 sec
D11                 0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                       13C
P1                       10.00 usec
PL1                      -0.44 dB
PL1W             39.19395828 W
SFO1             100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                    90.00 usec
PL2                      -3.90 dB
PL12                     15.81 dB
PL13                    120.00 dB
PL2W             21.64248466 W
PL12W             0.23137002 W
PL13W             0.00000000 W
SFO2             400.2316009 MHz
SI                       32768
SF               100.6379140 MHz
WDW                         EM
SSB                          0
LB                        1.00 Hz
GB                           0
PC                        1.40
```

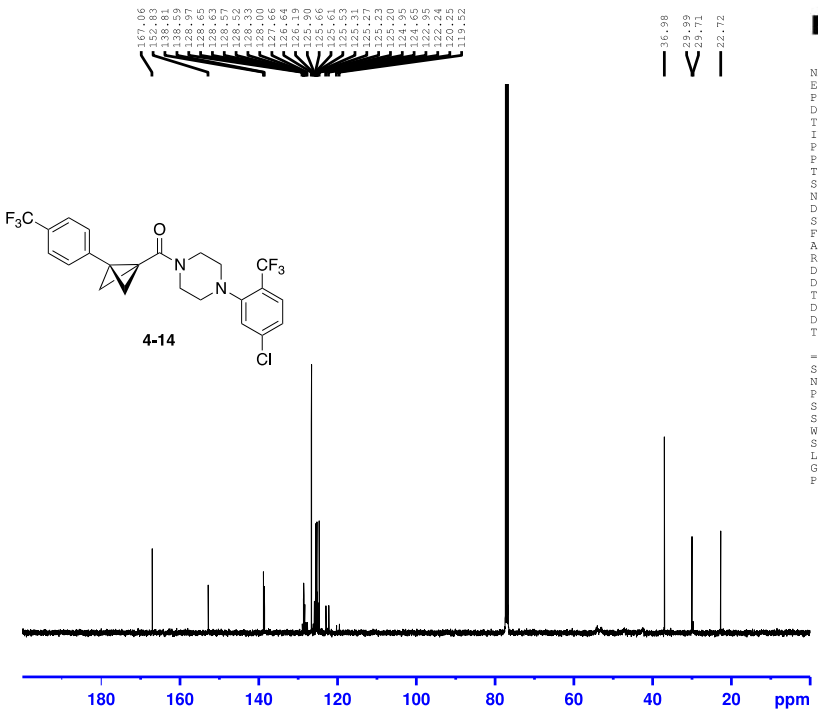


BRUKER

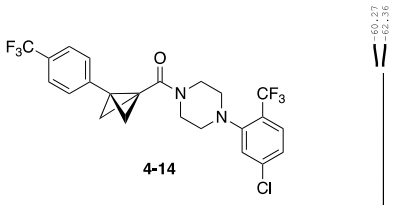
```
NAME                JAM-758-45
EXPNO                       11
PROCNO                       1
Date_             20161206
Time                     15.01
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG             zgfhigqn.2
TD                       131072
SOLVENT                  CDCl3
NS                          16
DS                           4
SWH                89285.711 Hz
FIDRES              0.681196 Hz
AQ                  0.7340532 sec
RG                         203
DW                     5.600 usec
DE                      6.50 usec
TE                      90.3 K
D1                  1.00000000 sec
D11                 0.03000000 sec
D12                 0.00002000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1             376.4607164 MHz
NUC1                       19F
P1                       14.20 usec
SI                       65536
SF               376.4983662 MHz
WDW                         EM
SSB                          0
LB                        0.30 Hz
GB                           0
PC                        1.00
```




```
NAME                JAM-758-73
EXPNO                       10
PROCNO                       1
Date_             20161229
Time                     16.08
INSTRUM                  spect
PROBHD     5 mm PABBO BB-
PULPROG                  zg30
TD                      65536
SOLVENT                 CDCl3
NS                         16
DS                          2
SWH                 8012.820 Hz
FIDRES              0.122266 Hz
AQ                  4.0894966 sec
RG                         64
DW                     62.400 usec
DE                      6.50 usec
TE                      90.9 K
D1                  1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1             400.1324710 MHz
NUC1                       1H
P1                      13.75 usec
SI                      65536
SF               400.1300095 MHz
WDW                        EM
SSB                         0
LB                       0.30 Hz
GB                          0
PC                       1.00
```

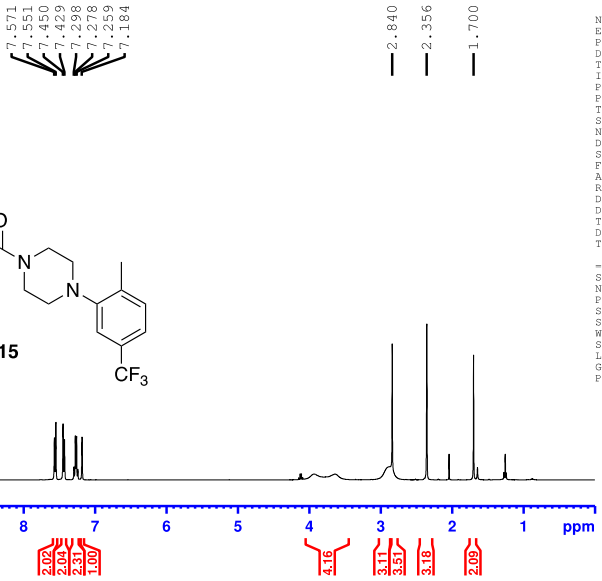



```
NAME                JAM-758-73
EXPNO                       11
PROCNO                       1
Date_             20161229
Time                     21.03
INSTRUM                  spect
PROBHD     5 mm PABBO BB-
PULPROG                zgpg30
TD                      65536
SOLVENT                 CDCl3
NS                       1024
DS                          4
SWH                24038.461 Hz
FIDRES              0.366798 Hz
AQ                  1.3631988 sec
RG                        161
DW                     20.800 usec
DE                      6.50 usec
TE                      90.7 K
D1                  2.00000000 sec
D11                 0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1             100.6228293 MHz
NUC1                      13C
P1                      10.00 usec
SI                      32768
SF               100.6127685 MHz
WDW                        EM
SSB                         0
LB                       1.00 Hz
GB                          0
PC                       1.40
```



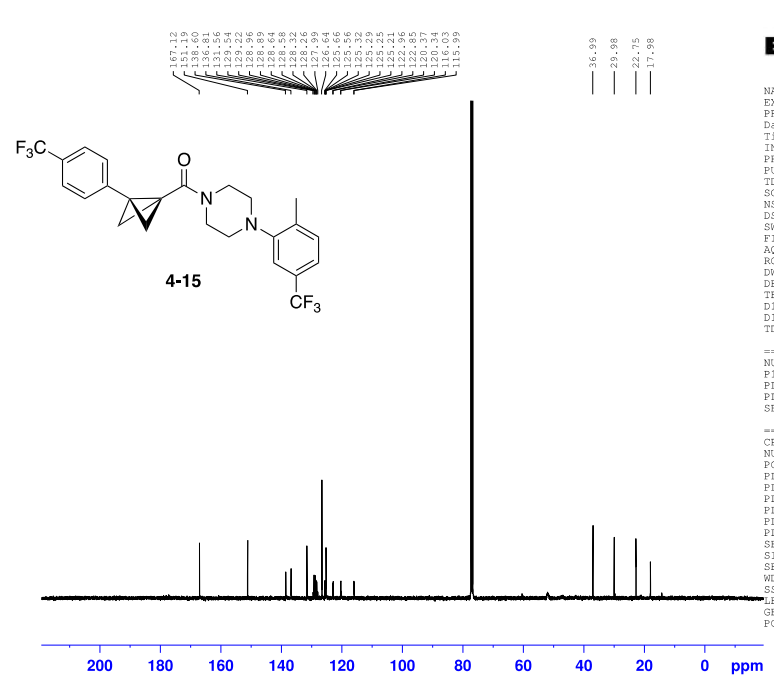
4-14


```
NAME                JAM-758-73
EXPNO                       13
PROCNO                       1
Date_             20161229
Time                     21.24
INSTRUM                  spect
PROBHD     5 mm PABBO BB-
PULPROG          zgfhigqn.2
TD                       131072
SOLVENT                  CDCl3
NS                          16
DS                           4
SWH                  89285.711 Hz
FIDRES               0.681196 Hz
AQ                   0.7340532 sec
RG                         203
DW                       5.600 usec
DE                       6.50 usec
TE                       90.3 K
D1                   1.00000000 sec
D11                  0.03000000 sec
D12                  0.00002000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1              376.4607164 MHz
NUC1                      19F
P1                      14.20 usec
SI                       65536
SF                376.4983662 MHz
WDW                         EM
SSB                          0
LB                        0.30 Hz
GB                           0
PC                        1.00
```



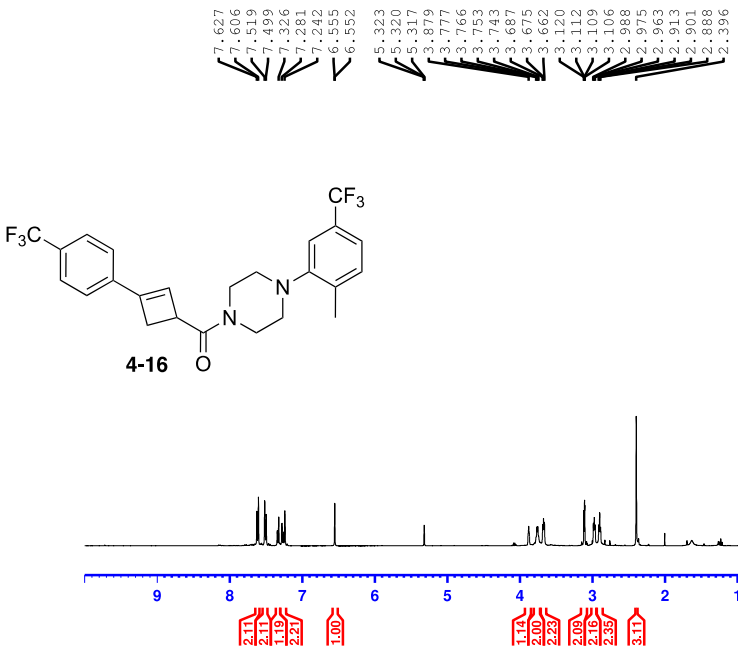
4-15

```
NAME                JAM-758-79
EXPNO                       10
PROCNO                       1
Date_             20170103
Time                     10.41
INSTRUM                  spect
PROBHD     5 mm PABBO BB-
PULPROG                  zg30
TD                       65536
SOLVENT                  CDCl3
NS                          16
DS                           2
SWH                  8012.820 Hz
FIDRES               0.122266 Hz
AQ                   4.0894966 sec
RG                          64
DW                       62.400 usec
DE                       6.50 usec
TE                       92.2 K
D1                   1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1              400.1324710 MHz
NUC1                       1H
P1                      13.75 usec
SI                       65536
SF                400.1300100 MHz
WDW                         EM
SSB                          0
LB                        0.30 Hz
GB                           0
PC                        1.00
```



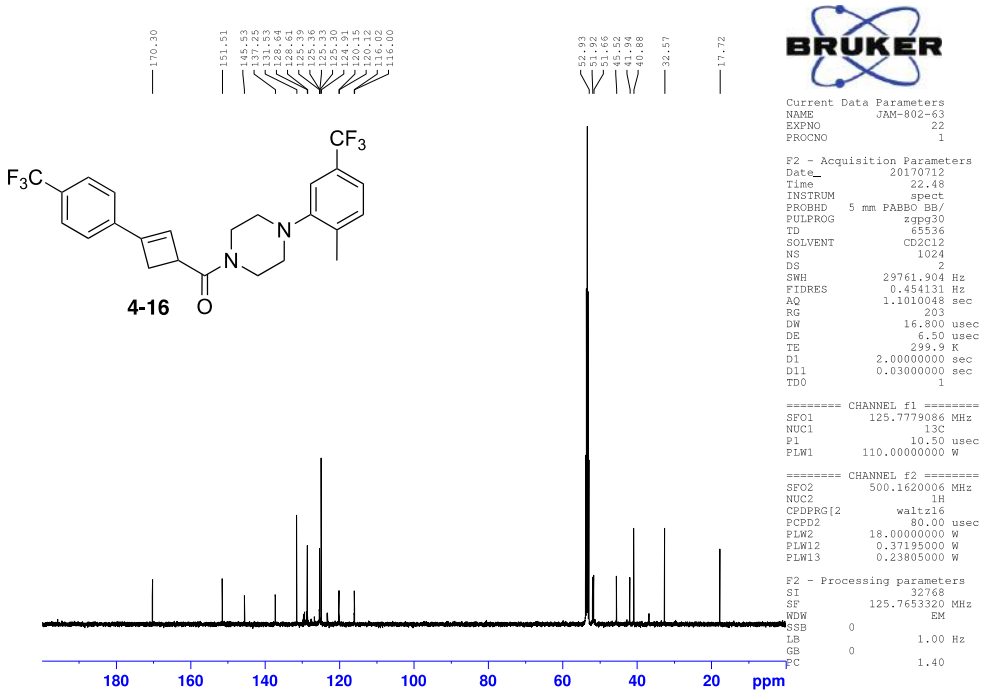
BRUKER

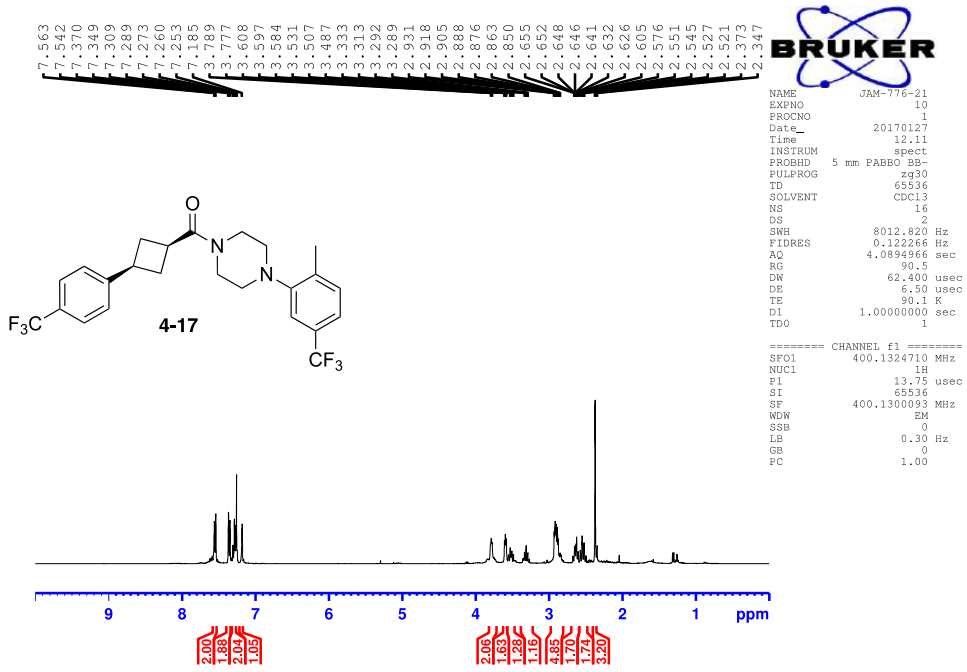
```
NAME                JAM-758-79
EXPNO                        1
PROCNO                       1
Date_             20170103
Time                     12.54
INSTRUM                  spect
PROBHD    5 mm PADUL 13C
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                         848
DS                           4
SWH                 24038.461 Hz
FIDRES                0.366798 Hz
AQ                    1.3631988 sec
RG                          57
DW                      20.800 usec
DE                       6.50 usec
TE                      295.1 K
D1                    3.00000000 sec
D11                   0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                       13C
P1                       10.00 usec
PL1                      -0.44 dB
PL1W                39.19395828 W
SFO1               100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2                 waltz16
NUC2                        1H
PCPD2                    90.00 usec
PL2                      -3.90 dB
PL12                     15.81 dB
PL13                    120.00 dB
PL2W                21.64248466 W
PL12W                0.23137002 W
PL13W                0.00000000 W
SFO2               400.2316009 MHz
SI                       32768
SF                 100.6379140 MHz
WDW                         EM
SSB                          0
LB                        1.00 Hz
GB                           0
PC                        1.40
```



BRUKER

```
NAME                JAM-802-63
EXPNO                       10
PROCNO                       1
Date_             20170711
Time                     18.38
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG                   zg30
TD                       65536
SOLVENT                 CD2Cl2
NS                           16
DS                            2
SWH                  8012.820 Hz
FIDRES                0.122266 Hz
AQ                    4.0894966 sec
RG                         90.5
DW                      62.400 usec
DE                       6.50 usec
TE                      -394.2 K
D1                    1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1               400.1324710 MHz
NUC1                        1H
P1                       13.75 usec
SI                       65536
SF                 400.1300157 MHz
WDW                         EM
SSB                          0
LB                        0.30 Hz
GB                           0
PC                        1.00
```


170.30
151.51
145.53
137.55
131.53
128.64
128.61
125.39
125.36
125.33
125.30
124.91
120.15
116.12
116.02
116.00
52.93
51.92
51.65
45.52
41.94
40.88
32.57
17.72
CF3
F3C
N
N
O
4-16
BRUKER
Current Data Parameters
NAME JAM-802-63
EXPNO 22
PROCNO 1
F2 - Acquisition Parameters
Date_ 20170712
Time 22.48
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CD2C12
NS 1024
DS 2
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010048 sec
RG 203
DW 16.800 usec
DE 6.50 usec
TE 299.9 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 125.7779086 MHz
NUC1 13C
P1 10.50 usec
PLW1 110.00000000 W
======== CHANNEL f2 ========
SFO2 500.1620006 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 18.00000000 W
PLW12 0.37195000 W
PLW13 0.23805000 W
F2 - Processing parameters
SI 32768
SF 125.7653320 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
180
160
140
120
100
80
60
40
20
ppm


7.563
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7.370
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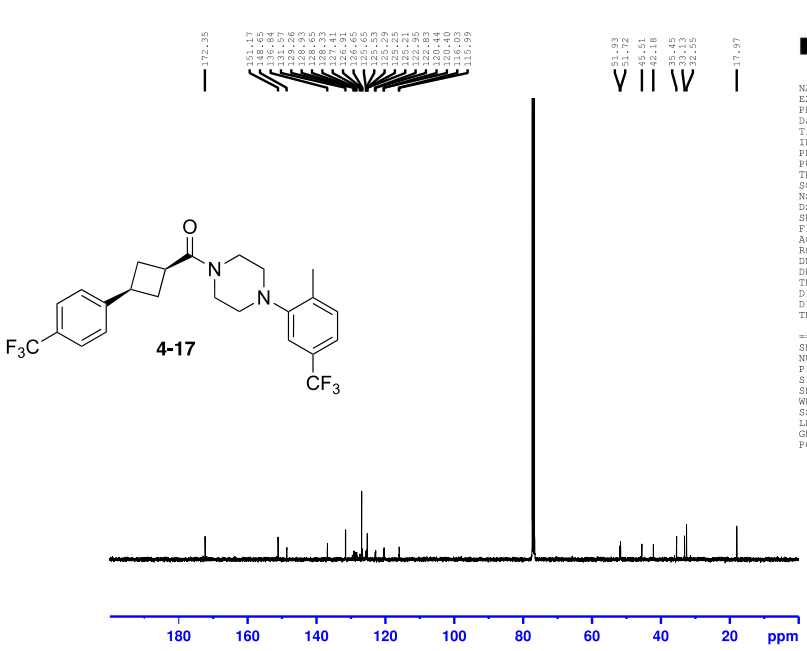
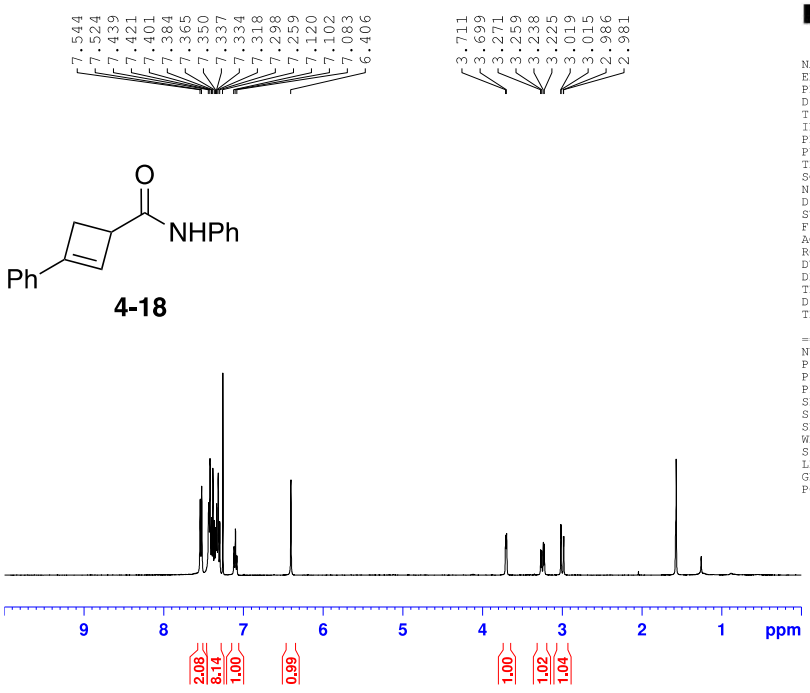
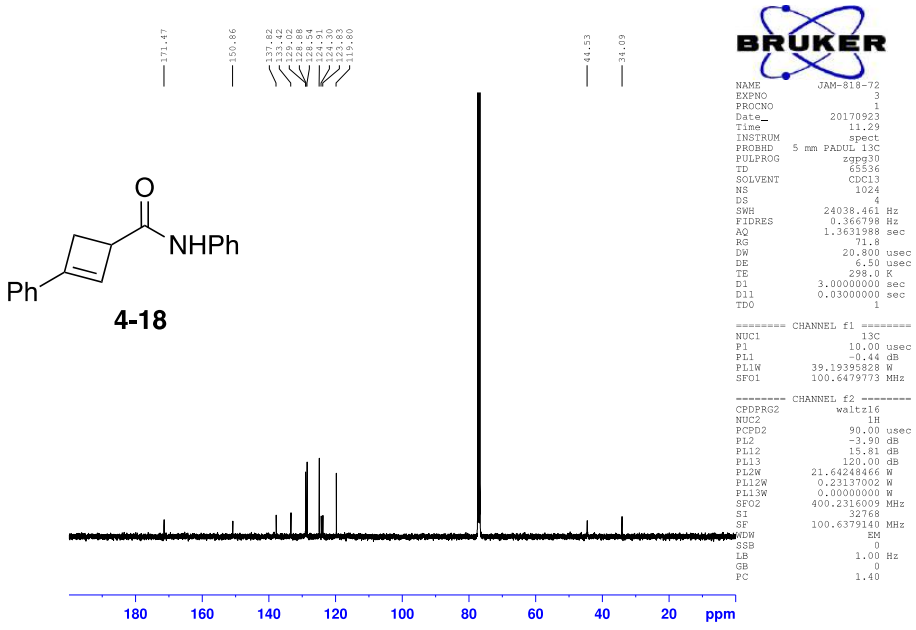
7.309
7.289
7.273
7.260
7.253
7.185
3.789
3.777
3.608
3.597
3.584
3.531
3.507
3.487
3.333
3.313
3.292
3.289
2.931
2.918
2.905
2.888
2.876
2.863
2.850
2.655
2.652
2.648
2.646
2.641
2.632
2.626
2.605
2.576
2.551
2.545
2.527
2.521
2.373
2.347
O
N
N
F3C
CF3
4-17
BRUKER
NAME JAM-776-21
EXPNO 10
PROCNO 1
Date_ 20170127
Time 12.11
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 90.5
DW 62.400 usec
DE 6.50 usec
TE 90.1 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 13.75 usec
SI 65536
SF 400.1300093 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9
8
7
6
5
4
3
2
1
ppm
2.00
1.88
2.04
1.05
2.06
1.63
1.29
1.16
4.85
1.70
1.74
3.20



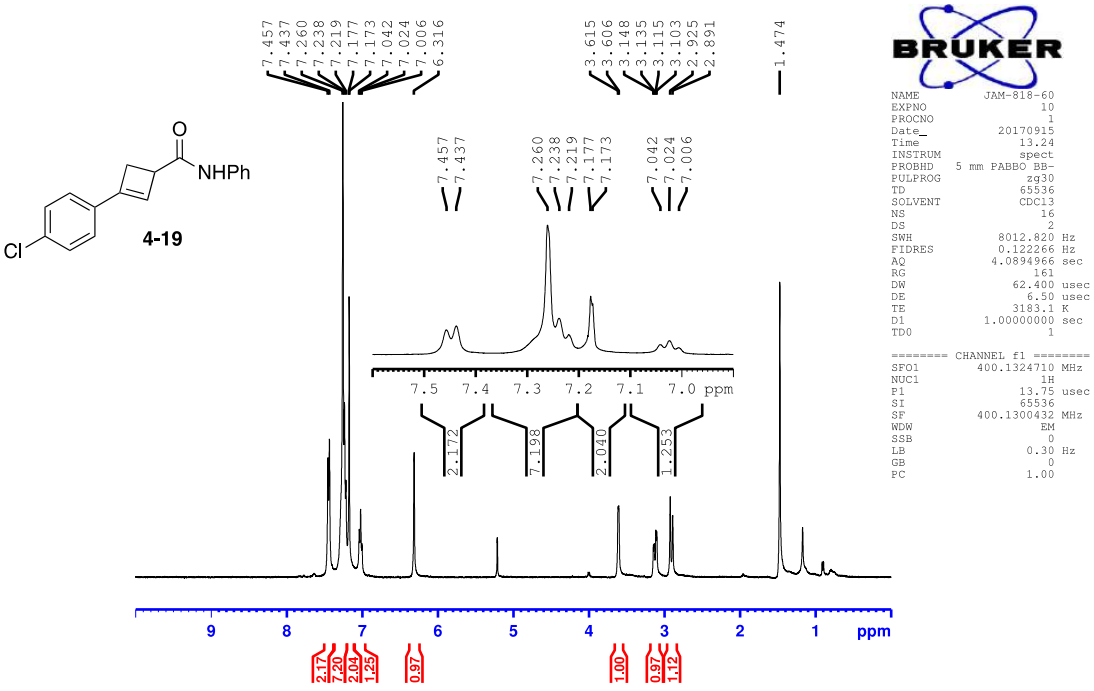

```
NAME                JAM-776-21
EXPNO                       12
PROCNO                       1
Date_                 20170127
Time                     22.07
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                        1024
DS                           4
SWH                 24038.461 Hz
FIDRES              0.366798 Hz
AQ                  1.3631988 sec
RG                         114
DW                    20.800 usec
DE                     6.50 usec
TE                      89.8 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1             100.6228293 MHz
NUC1                     13C
P1                     10.00 usec
SI                       32768
SF               100.6127685 MHz
WDW                        EM
SSB                         0
LB                      1.00 Hz
GB                          0
PC                      1.40
```



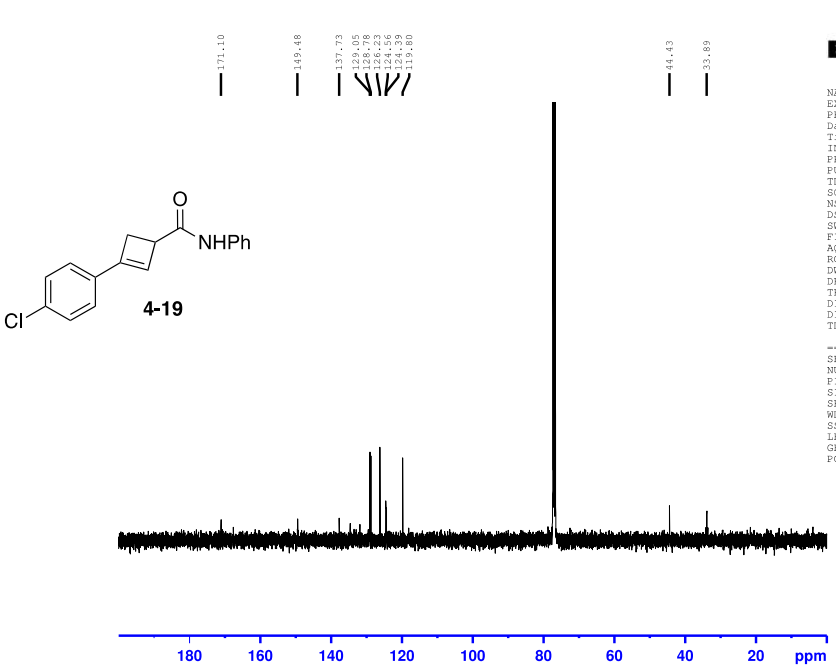

```
NAME                JAM-818-72
EXPNO                        2
PROCNO                       1
Date_                 20170923
Time                     10.09
INSTRUM                  spect
PROBHD    5 mm PADUL 13C
PULPROG                  zg30
TD                       65536
SOLVENT                  CDCl3
NS                          16
DS                           2
SWH                  8223.685 Hz
FIDRES               0.125483 Hz
AQ                   3.9846387 sec
RG                         181
DW                    60.800 usec
DE                     6.50 usec
TE                      298.0 K
D1                 2.00000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                       1H
P1                      9.31 usec
PL1                    -3.90 dB
PL1W              21.64248466 W
SFO1              400.2324716 MHz
SI                       32768
SF                400.2300128 MHz
WDW                        EM
SSB                         0
LB                      0.30 Hz
GB                          0
PC                      1.00
```




```
BRUKER
NAME                JAM-818-72
EXPNO                        3
PROCNO                       1
Date_                 20170923
Time                     11.29
INSTRUM                  spect
PROBHD    5 mm PADUL 13C
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                        1024
DS                           4
SWH                 24038.461 Hz
FIDRES               0.366798 Hz
AQ                   1.3631988 sec
RG                        71.8
DW                      20.800 usec
DE                       6.50 usec
TE                     298.0 K
D1                  3.00000000 sec
D11                 0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                       13C
P1                       10.00 usec
PL1                      -0.44 dB
PL1W                39.19395828 W
SFO1                100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                        1H
PCPD2                    90.00 usec
PL2                      -3.90 dB
PL12                     15.81 dB
PL13                    120.00 dB
PL2W                21.64248466 W
PL12W                0.23137002 W
PL13W                0.00000000 W
SFO2                400.2316009 MHz
SI                         32768
SF                  100.6379140 MHz
WDW                           EM
SSB                            0
LB                          1.00 Hz
GB                             0
PC                          1.40
```

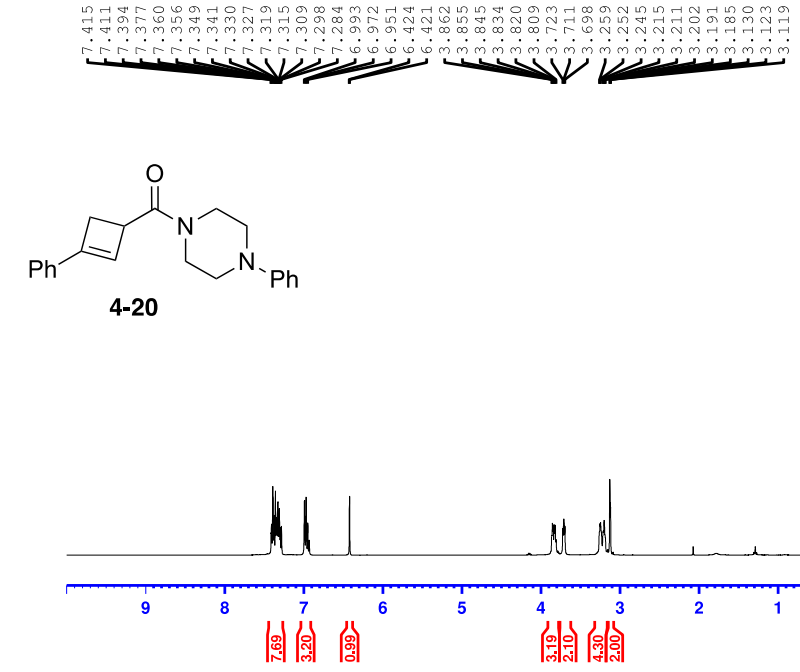



```
BRUKER
NAME                JAM-818-60
EXPNO                       10
PROCNO                       1
Date_                 20170915
Time                     13.24
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG                  zg30
TD                       65536
SOLVENT                  CDCl3
NS                          16
DS                           2
SWH                  8012.820 Hz
FIDRES               0.122266 Hz
AQ                   4.0894966 sec
RG                         161
DW                      62.400 usec
DE                       6.50 usec
TE                     3183.1 K
D1                  1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1                400.1324710 MHz
NUC1                        1H
P1                       13.75 usec
SI                         65536
SF                  400.1300432 MHz
WDW                           EM
SSB                            0
LB                          0.30 Hz
GB                             0
PC                          1.00
```



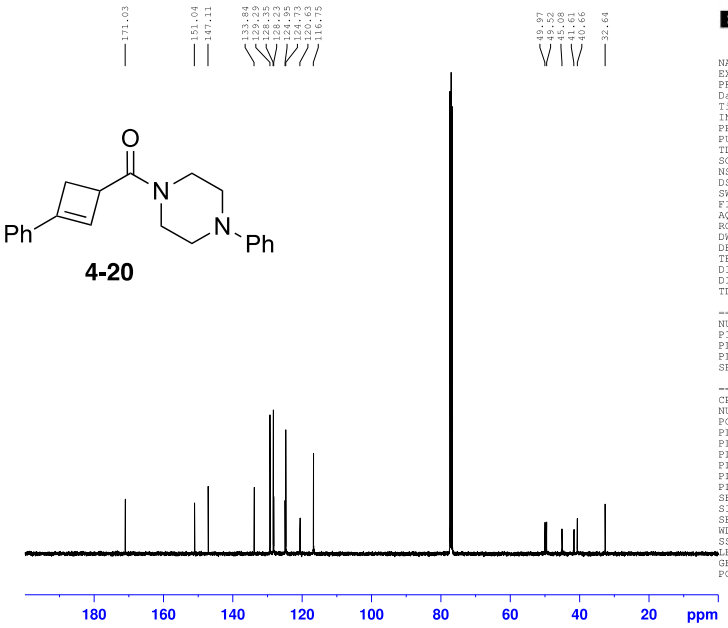
BRUKER

```
NAME                JAM-818-60
EXPNO                       11
PROCNO                       1
Date_             20170915
Time                     21.03
INSTRUM                  spect
PROBHD     5 mm PABBO BB-
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                        1024
DS                           4
SWH                  24038.461 Hz
FIDRES                0.366798 Hz
AQ                    1.3631988 sec
RG                          203
DW                       20.800 usec
DE                        6.50 usec
TE                     -2224.0 K
D1                    2.00000000 sec
D11                   0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1                100.6228293 MHz
NUC1                        13C
P1                        10.00 usec
SI                         32768
SF                  100.6127685 MHz
WDW                          EM
SSB                           0
LB                         1.00 Hz
GB                            0
PC                         1.40
```



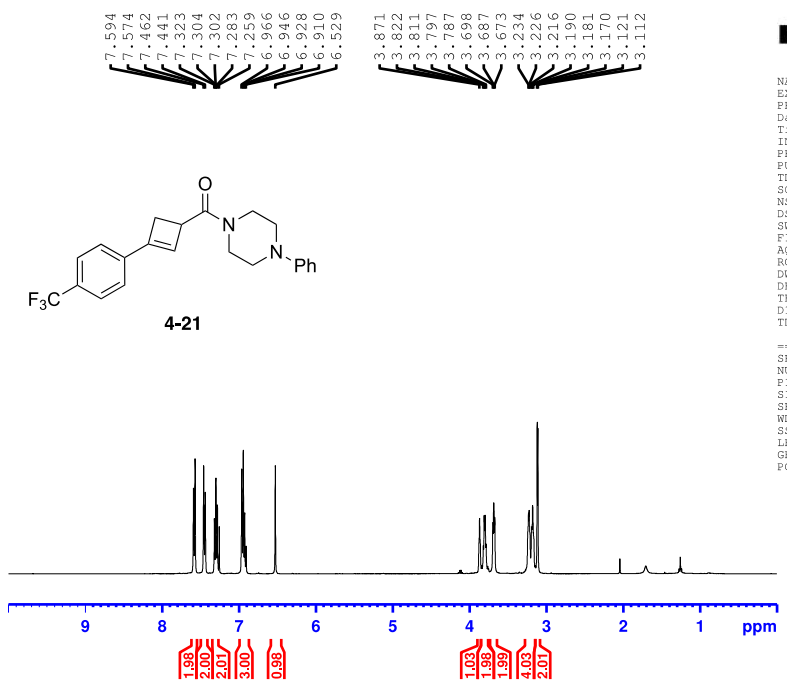
BRUKER

```
NAME                JAM-834-26
EXPNO                       10
PROCNO                       1
Date_             20171101
Time                     11.28
INSTRUM                  spect
PROBHD     5 mm PABBO BB-
PULPROG                   zg30
TD                       65536
SOLVENT                  CDCl3
NS                          16
DS                           2
SWH                   8012.820 Hz
FIDRES                0.122266 Hz
AQ                    4.0894966 sec
RG                          57
DW                       62.400 usec
DE                        6.50 usec
TE                     1849.1 K
D1                    1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1                400.1324710 MHz
NUC1                        1H
P1                        13.75 usec
SI                         65536
SF                  400.1300000 MHz
WDW                          EM
SSB                           0
LB                         0.30 Hz
GB                            0
PC                         1.00
```



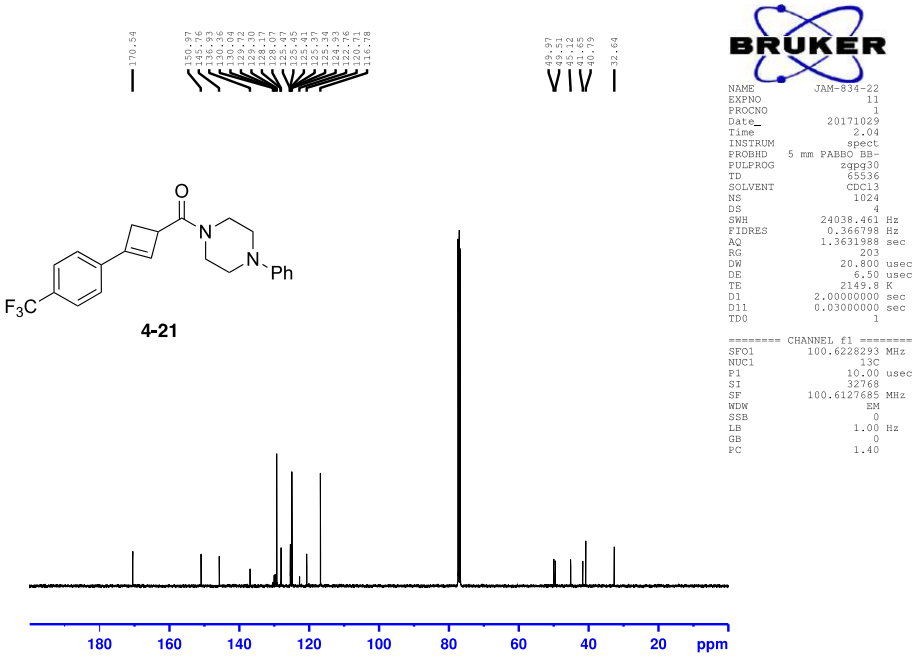
4-20

```
BRUKER
NAME              JAM-834-26
EXPNO                      3
PROCNO                     1
Date_              20171101
Time                  12.52
INSTRUM               spect
PROBHD   5 mm PADUL 13C
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      767
DS                        4
SWH              24038.461 Hz
FIDRES               0.366798 Hz
AQ                1.3631988 sec
RG                     50.8
DW                   20.800 usec
DE                    6.50 usec
TE                  298.2 K
D1                3.00000000 sec
D11               0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                     13C
P1                     10.00 usec
PL1                    -0.44 dB
PL1W            39.19395828 W
SFO1           100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                    1H
PCPD2                90.00 usec
PL2                   -3.90 dB
PL12                  15.81 dB
PL13                 120.00 dB
PL2W            21.64248466 W
PL12W            0.23137002 W
PL13W            0.00000000 W
SFO2           400.2316009 MHz
SI                     32768
SF             100.6379140 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40
```



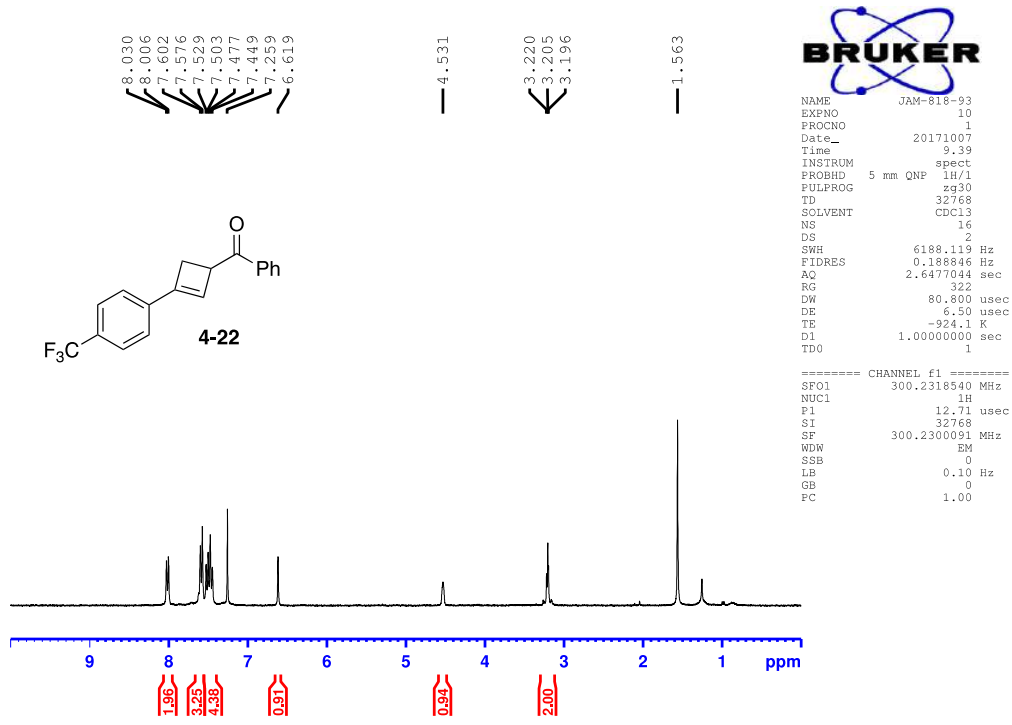
4-21

```
BRUKER
NAME              JAM-834-22
EXPNO                     10
PROCNO                     1
Date_              20171028
Time                  14.19
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH               8012.820 Hz
FIDRES               0.122266 Hz
AQ                4.0894966 sec
RG                       64
DW                   62.400 usec
DE                    6.50 usec
TE                  2906.6 K
D1                1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1           400.1324710 MHz
NUC1                    1H
P1                   13.75 usec
SI                    65536
SF             400.1300096 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
```



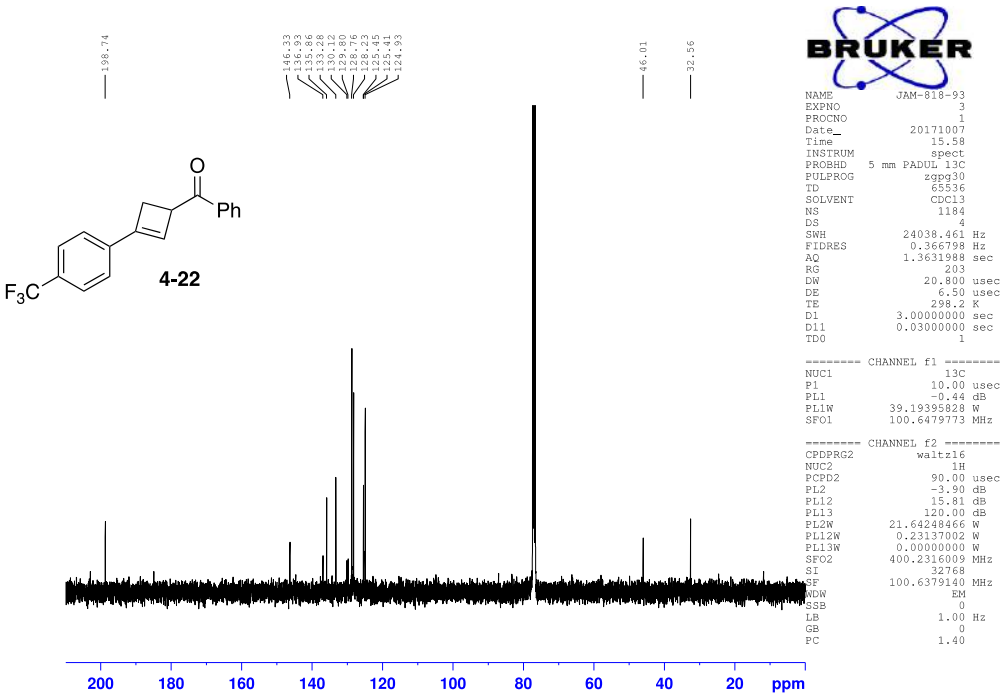
BRUKER

```
NAME              JAM-834-22
EXPNO                 11
PROCNO                 1
Date_           20171029
Time                2.04
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  1024
DS                     4
SWH            24038.461 Hz
FIDRES             0.366798 Hz
AQ                 1.3631988 sec
RG                   203
DW                  20.800 usec
DE                   6.50 usec
TE                2149.8 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1          100.6228293 MHz
NUC1                 13C
P1                  10.00 usec
SI                 32768
SF            100.6127685 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```



BRUKER

```
NAME              JAM-818-93
EXPNO                 10
PROCNO                 1
Date_           20171007
Time                9.39
INSTRUM            spect
PROBHD   5 mm QNP  1H/1
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             6188.119 Hz
FIDRES             0.188846 Hz
AQ                 2.6477044 sec
RG                   322
DW                  80.800 usec
DE                   6.50 usec
TE                -924.1 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1          300.2318540 MHz
NUC1                  1H
P1                  12.71 usec
SI                 32768
SF            300.2300091 MHz
WDW                   EM
SSB                    0
LB                  0.10 Hz
GB                     0
PC                  1.00
```

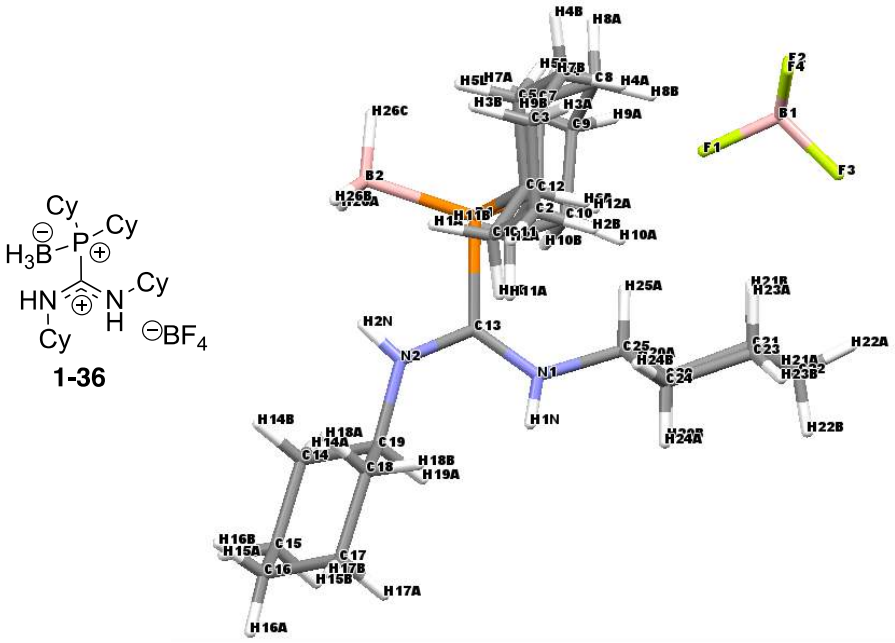


BRUKER

NAME	JAM-818-93
EXPNO	3
PROCNO	1
Date_	20171007
Time	15.58
INSTRUM	spect
PROBHD	5 mm PADUL 13C
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	1184
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	298.2 K
D1	3.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	10.00 usec
PL1	-0.44 dB
PL1W	39.19395828 W
SFO1	100.6479773 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	90.00 usec
PL2	-3.90 dB
PL12	15.81 dB
PL13	120.00 dB
PL2W	21.64248466 W
PL12W	0.23137002 W
PL13W	0.00000000 W
SFO2	400.2316009 MHz
SI	32768
SF	100.6379140 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

APPENDIX B

ATOMIC COORDINATES, BOND LENGTHS, AND BOND ANGLES FOR X-RAY CRYSTAL STRCUCTURES



1-36

The coordinates for **1-36** were deposited in the CCDC (#997593)

Sample and crystal data for 1-36:

Identification code	milligan21314	
Chemical formula	$C_{25}H_{49}B_2F_4N_2P$	
Formula weight	506.25	
Temperature	180(2) K	
Wavelength	1.54178 Å	
Crystal size	0.120 x 0.150 x 0.190 mm	
Crystal habit	translucent colorless chunk	
Crystal system	monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 12.0541(3)	α = 90°
	b = 16.1202(4)	β = 92.0953(12)°
	c = 15.0576(3)	γ = 90°
Volume	2923.95(12)	
Z	4	
Density (calculated)	1.150 g/cm^3	
Absorption coefficient	1.174 mm^{-1}	

Data collection and structure refinement for 1-36:

Diffractometer	Bruker Apex II CCD
Radiation source	IMuS micro-focus source, Cu
Theta range for data collection	4.02 to 68.42°
Reflections collected	9574
Independent reflections	9574 [R(int) = 0.0531]
Coverage of independent reflections	99.9%
Absorption correction	multi-scan
Max. and min. transmission	0.8720 and 0.8080
Structure solution technique	direct methods
Structure solution program	SHELXS-97 (Sheldrick, 2008)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2013 (Sheldrick, 2013)
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	9574 / 0 / 328
Goodness-of-fit on F^2	1.381
Δ/σ_{max}	0.001
Final R indices	8008 data; $I>2\sigma(I)$ R1 = 0.0468, wR2 = 0.1300
	all data R1 = 0.0601, wR2 = 0.1374
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0680P)^2]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	0.414 and -0.281 eÅ^{-3}
R.M.S. deviation from mean	0.044 eÅ^{-3}

Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for 1-36:

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
P1	0.73288(4)	0.20888(3)	0.53514(3)	0.02680(15)
N1	0.75376(14)	0.37049(11)	0.60853(10)	0.0330(4)
C1	0.96303(17)	0.22337(14)	0.55496(18)	0.0452(6)
F1	0.76990(15)	0.13600(10)	0.78558(10)	0.0766(5)
B1	0.7782(3)	0.09909(17)	0.86832(18)	0.0542(8)
N2	0.72945(14)	0.35777(10)	0.45672(11)	0.0325(4)

	x/a	y/b	z/c	U(eq)
C2	0.07055(19)	0.19561(16)	0.6021(2)	0.0595(7)
F2	0.69015(14)	0.04416(9)	0.87708(11)	0.0687(4)
C3	0.08718(18)	0.10302(15)	0.59521(17)	0.0458(6)
F3	0.77869(16)	0.15727(9)	0.93442(11)	0.0794(5)
C4	0.98875(18)	0.05588(16)	0.62831(19)	0.0506(6)
F4	0.87055(18)	0.04995(13)	0.87643(16)	0.1005(7)
C5	0.88235(17)	0.08340(13)	0.57994(19)	0.0459(6)
C6	0.86364(15)	0.17631(12)	0.59062(13)	0.0293(4)
C7	0.5883(2)	0.09087(15)	0.6026(2)	0.0587(8)
C8	0.4942(2)	0.07218(18)	0.6640(2)	0.0656(9)
C9	0.39146(19)	0.12236(18)	0.63972(19)	0.0563(7)
C10	0.41609(19)	0.21424(17)	0.6345(2)	0.0552(7)
C11	0.51084(16)	0.23259(14)	0.57355(16)	0.0397(5)
C12	0.61460(16)	0.18340(12)	0.60323(13)	0.0309(4)
C13	0.73887(15)	0.32474(11)	0.53658(12)	0.0279(4)
C14	0.6671(2)	0.46339(14)	0.34972(16)	0.0455(6)
C15	0.6780(2)	0.55434(15)	0.32248(18)	0.0589(7)
C16	0.7974(2)	0.57870(16)	0.31101(16)	0.0569(7)
C17	0.8682(2)	0.56057(15)	0.39427(17)	0.0526(6)
C18	0.85816(19)	0.46994(14)	0.42199(16)	0.0438(5)
C19	0.73767(17)	0.44611(11)	0.43351(13)	0.0326(4)
C20	0.65632(18)	0.37163(14)	0.74970(14)	0.0389(5)
C21	0.66051(19)	0.33682(15)	0.84361(14)	0.0440(5)
C22	0.7661(2)	0.36165(14)	0.89481(14)	0.0461(6)
C23	0.86914(19)	0.34039(15)	0.84469(15)	0.0445(6)
C24	0.86404(18)	0.37282(14)	0.74934(14)	0.0399(5)
C25	0.75805(16)	0.34242(11)	0.70144(12)	0.0305(4)
B2	0.7180(2)	0.17385(16)	0.41319(17)	0.0408(6)

Bond lengths (Å) for 1-36:

P1-C12	1.8330(19)	P1-C6	1.833(2)
P1-C13	1.8691(19)	P1-B2	1.923(2)
N1-C13	1.318(2)	N1-C25	1.469(2)
N1-H1N	0.80(3)	C1-C2	1.522(4)
C1-C6	1.532(3)	C1-H1A	0.99
C1-H1B	0.99	F1-B1	1.381(3)
B1-F3	1.367(3)	B1-F4	1.369(4)

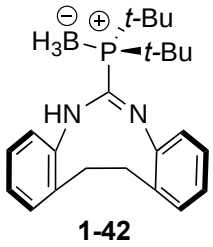
B1-F2	1.392(3)	N2-C13	1.316(2)
N2-C19	1.471(2)	N2-H2N	0.85(3)
C2-C3	1.510(3)	C2-H2A	0.99
C2-H2B	0.99	C3-C4	1.509(3)
C3-H3A	0.99	C3-H3B	0.99
C4-C5	1.518(3)	C4-H4A	0.99
C4-H4B	0.99	C5-C6	1.524(3)
C5-H5A	0.99	C5-H5B	0.99
C6-H6A	1.0	C7-C8	1.519(3)
C7-C12	1.525(3)	C7-H7A	0.99
C7-H7B	0.99	C8-C9	1.512(3)
C8-H8A	0.99	C8-H8B	0.99
C9-C10	1.513(4)	C9-H9A	0.99
C9-H9B	0.99	C10-C11	1.520(3)
C10-H10A	0.99	C10-H10B	0.99
C11-C12	1.534(3)	C11-H11A	0.99
C11-H11B	0.99	C12-H12A	1.0
C14-C19	1.521(3)	C14-C15	1.529(3)
C14-H14A	0.99	C14-H14B	0.99
C15-C16	1.508(4)	C15-H15A	0.99
C15-H15B	0.99	C16-C17	1.519(4)
C16-H16A	0.99	C16-H16B	0.99
C17-C18	1.525(3)	C17-H17A	0.99
C17-H17B	0.99	C18-C19	1.518(3)
C18-H18A	0.99	C18-H18B	0.99
C19-H19A	1.0	C20-C25	1.523(3)
C20-C21	1.520(3)	C20-H20A	0.99
C20-H20B	0.99	C21-C22	1.517(3)
C21-H21A	0.99	C21-H21B	0.99
C22-C23	1.516(3)	C22-H22A	0.99
C22-H22B	0.99	C23-C24	1.527(3)
C23-H23A	0.99	C23-H23B	0.99
C24-C25	1.525(3)	C24-H24A	0.99
C24-H24B	0.99	C25-H25A	1.0
B2-H26A	1.06(3)	B2-H26B	1.07(2)
B2-H26C	1.09(3)		

Bond angles (°) for 1-36:

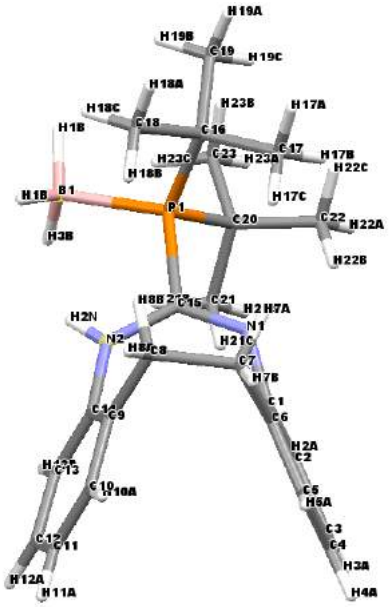
C12-P1-C6	110.75(9)	C12-P1-C13	104.36(9)
C6-P1-C13	104.40(9)	C12-P1-B2	114.88(11)
C6-P1-B2	113.56(11)	C13-P1-B2	107.86(10)
C13-N1-C25	127.55(16)	C13-N1-H1N	116.3(18)
C25-N1-H1N	116.1(18)	C2-C1-C6	110.8(2)
C2-C1-H1A	109.5	C6-C1-H1A	109.5
C2-C1-H1B	109.5	C6-C1-H1B	109.5
H1A-C1-H1B	108.1	F3-B1-F4	110.5(3)
F3-B1-F1	111.1(2)	F4-B1-F1	111.2(2)
F3-B1-F2	110.5(2)	F4-B1-F2	104.1(2)
F1-B1-F2	109.2(2)	C13-N2-C19	127.20(17)
C13-N2-H2N	114.6(16)	C19-N2-H2N	117.8(16)
C3-C2-C1	111.81(19)	C3-C2-H2A	109.3
C1-C2-H2A	109.3	C3-C2-H2B	109.3
C1-C2-H2B	109.3	H2A-C2-H2B	107.9
C2-C3-C4	111.54(19)	C2-C3-H3A	109.3
C4-C3-H3A	109.3	C2-C3-H3B	109.3
C4-C3-H3B	109.3	H3A-C3-H3B	108.0
C3-C4-C5	110.8(2)	C3-C4-H4A	109.5
C5-C4-H4A	109.5	C3-C4-H4B	109.5
C5-C4-H4B	109.5	H4A-C4-H4B	108.1
C4-C5-C6	111.24(19)	C4-C5-H5A	109.4
C6-C5-H5A	109.4	C4-C5-H5B	109.4
C6-C5-H5B	109.4	H5A-C5-H5B	108.0
C5-C6-C1	109.21(16)	C5-C6-P1	111.19(14)
C1-C6-P1	111.65(16)	C5-C6-H6A	108.2
C1-C6-H6A	108.2	P1-C6-H6A	108.2
C8-C7-C12	110.5(2)	C8-C7-H7A	109.6
C12-C7-H7A	109.6	C8-C7-H7B	109.6
C12-C7-H7B	109.6	H7A-C7-H7B	108.1
C9-C8-C7	111.7(2)	C9-C8-H8A	109.3
C7-C8-H8A	109.3	C9-C8-H8B	109.3
C7-C8-H8B	109.3	H8A-C8-H8B	107.9
C8-C9-C10	112.1(2)	C8-C9-H9A	109.2
C10-C9-H9A	109.2	C8-C9-H9B	109.2
C10-C9-H9B	109.2	H9A-C9-H9B	107.9
C9-C10-C11	112.0(2)	C9-C10-H10A	109.2
C11-C10-H10A	109.2	C9-C10-H10B	109.2

C11-C10-H10B	109.2	H10A-C10-H10B	107.9
C10-C11-C12	110.3(2)	C10-C11-H11A	109.6
C12-C11-H11A	109.6	C10-C11-H11B	109.6
C12-C11-H11B	109.6	H11A-C11-H11B	108.1
C7-C12-C11	109.67(17)	C7-C12-P1	112.44(15)
C11-C12-P1	111.34(15)	C7-C12-H12A	107.7
C11-C12-H12A	107.7	P1-C12-H12A	107.7
N1-C13-N2	121.96(17)	N1-C13-P1	124.96(14)
N2-C13-P1	113.05(13)	C19-C14-C15	110.30(19)
C19-C14-H14A	109.6	C15-C14-H14A	109.6
C19-C14-H14B	109.6	C15-C14-H14B	109.6
H14A-C14-H14B	108.1	C16-C15-C14	111.9(2)
C16-C15-H15A	109.2	C14-C15-H15A	109.2
C16-C15-H15B	109.2	C14-C15-H15B	109.2
H15A-C15-H15B	107.9	C15-C16-C17	111.4(2)
C15-C16-H16A	109.3	C17-C16-H16A	109.3
C15-C16-H16B	109.3	C17-C16-H16B	109.3
H16A-C16-H16B	108.0	C16-C17-C18	111.2(2)
C16-C17-H17A	109.4	C18-C17-H17A	109.4
C16-C17-H17B	109.4	C18-C17-H17B	109.4
H17A-C17-H17B	108.0	C19-C18-C17	111.07(19)
C19-C18-H18A	109.4	C17-C18-H18A	109.4
C19-C18-H18B	109.4	C17-C18-H18B	109.4
H18A-C18-H18B	108.0	N2-C19-C18	110.20(16)
N2-C19-C14	109.51(17)	C18-C19-C14	111.53(17)
N2-C19-H19A	108.5	C18-C19-H19A	108.5
C14-C19-H19A	108.5	C25-C20-C21	109.25(17)
C25-C20-H20A	109.8	C21-C20-H20A	109.8
C25-C20-H20B	109.8	C21-C20-H20B	109.8
H20A-C20-H20B	108.3	C22-C21-C20	111.96(19)
C22-C21-H21A	109.2	C20-C21-H21A	109.2
C22-C21-H21B	109.2	C20-C21-H21B	109.2
H21A-C21-H21B	107.9	C21-C22-C23	112.01(19)
C21-C22-H22A	109.2	C23-C22-H22A	109.2
C21-C22-H22B	109.2	C23-C22-H22B	109.2
H22A-C22-H22B	107.9	C22-C23-C24	112.64(18)
C22-C23-H23A	109.1	C24-C23-H23A	109.1
C22-C23-H23B	109.1	C24-C23-H23B	109.1

H23A-C23-H23B	107.8	C25-C24-C23	109.81(17)
C25-C24-H24A	109.7	C23-C24-H24A	109.7
C25-C24-H24B	109.7	C23-C24-H24B	109.7
H24A-C24-H24B	108.2	N1-C25-C20	110.99(16)
N1-C25-C24	110.55(16)	C20-C25-C24	110.50(17)
N1-C25-H25A	108.2	C20-C25-H25A	108.2
C24-C25-H25A	108.2	P1-B2-H26A	105.2(15)
P1-B2-H26B	107.4(14)	H26A-B2-H26B	114.(2)
P1-B2-H26C	103.1(14)	H26A-B2-H26C	110.5(19)
H26B-B2-H26C	115.4(19)		



1-42



The X-ray coordinates for **1-42** have been deposited in the CCDC (#1008171)

Sample and crystal data for 1-42		
Identification code	Milligan57743	
Chemical formula	$C_{23}H_{34}BN_2P$	
Formula weight	380.30	
Temperature	220(2) K	
Wavelength	1.54178 Å	
Crystal size	0.040 x 0.120 x 0.210 mm	
Crystal habit	clear colourless shard	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 11.3394(5) Å	α = 93.950(3)°
	b = 13.9575(7) Å	β = 90.335(2)°
	c = 14.6789(8) Å	γ = 104.560(2)°
Volume	2242.63(19) $Å^3$	
Z	4	
Density (calculated)	1.126 g/cm^3	
Absorption coefficient	1.134 mm^{-1}	
F(000)	824	

Data collection and structure refinement for 1-42:

Diffractometer	Bruker Apex II CCD
Radiation source	IMuS micro-focus, Cu
Theta range for data collection	3.02 to 68.37°
Index ranges	-13<=h<=12, -16<=k<=16, -16<=l<=15
Reflections collected	30798
Independent reflections	7969 [R(int) = 0.0330]
Coverage of independent reflections	96.6%
Absorption correction	multi-scan
Max. and min. transmission	0.9560 and 0.7970
Structure solution technique	direct methods
Structure solution program	direct methods
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2013 (Sheldrick, 2013)
Function minimized	$\Sigma\ w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	7969 / 0 / 519
Goodness-of-fit on F^2	1.904
Δ/σ_{max}	0.012
Final R indices	6625 data; I>2σ(I) R1 = 0.0628, wR2 = 0.1796
	all data R1 = 0.0743, wR2 = 0.1853
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0680P)^2]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	1.684 and -0.696 eÅ^{-3}
R.M.S. deviation from mean	0.050 eÅ^{-3}

Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for 1-42:

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
P1	0.04228(5)	0.27378(5)	0.19476(4)	0.03658(19)
B1	0.0807(3)	0.2623(4)	0.3220(2)	0.0622(10)
N1	0.84027(17)	0.28302(15)	0.10241(13)	0.0379(5)
C1	0.7229(2)	0.29548(19)	0.08021(15)	0.0368(5)
P2	0.30261(6)	0.24570(6)	0.68762(5)	0.0467(2)
B2	0.2561(3)	0.2196(4)	0.8149(2)	0.0649(11)
N2	0.8137(2)	0.2451(2)	0.25756(16)	0.0504(6)
C2	0.7094(3)	0.3913(2)	0.07953(18)	0.0500(7)
N3	0.51351(18)	0.27361(16)	0.59653(14)	0.0393(5)
C3	0.6027(3)	0.4095(3)	0.0480(2)	0.0659(9)
N4	0.5185(2)	0.22477(18)	0.74848(16)	0.0458(5)
C4	0.5082(3)	0.3309(3)	0.0165(2)	0.0707(10)
C5	0.5204(3)	0.2360(3)	0.01772(19)	0.0612(9)
C6	0.6271(2)	0.2154(2)	0.04900(17)	0.0461(6)
C7	0.6374(3)	0.1114(2)	0.0540(2)	0.0676(9)
C8	0.6444(3)	0.0812(2)	0.1510(3)	0.0739(10)
C9	0.6032(3)	0.1471(2)	0.2224(2)	0.0530(7)
C10	0.4806(3)	0.1347(3)	0.2402(3)	0.0711(11)
C11	0.4418(3)	0.1955(4)	0.3033(3)	0.0874(14)
C12	0.5221(3)	0.2709(4)	0.3504(2)	0.0801(12)
C13	0.6448(3)	0.2877(3)	0.33317(19)	0.0595(8)
C14	0.6851(2)	0.2275(2)	0.26948(18)	0.0458(6)
C15	0.8769(2)	0.26534(16)	0.18019(15)	0.0331(5)
C16	0.0720(2)	0.1689(2)	0.12064(18)	0.0463(6)
C17	0.0172(3)	0.1576(3)	0.0236(2)	0.0687(9)
C18	0.0142(4)	0.0749(3)	0.1682(3)	0.0854(12)
C19	0.2089(3)	0.1806(3)	0.1142(3)	0.0829(12)
C20	0.1182(3)	0.3997(2)	0.1590(2)	0.0573(8)
C21	0.0544(3)	0.4723(2)	0.2083(3)	0.0756(10)
C22	0.1134(3)	0.4100(3)	0.0568(3)	0.0818(12)
C23	0.2534(3)	0.4264(3)	0.1934(3)	0.0835(11)
C24	0.6402(2)	0.29546(17)	0.57736(15)	0.0343(5)
C25	0.7057(3)	0.3939(2)	0.58237(18)	0.0485(6)
C26	0.8255(3)	0.4202(2)	0.5566(2)	0.0609(8)
C27	0.8826(3)	0.3477(2)	0.52397(19)	0.0558(8)
C28	0.8167(2)	0.2501(2)	0.51772(16)	0.0439(6)
C29	0.6956(2)	0.22242(18)	0.54304(15)	0.0350(5)

	x/a	y/b	z/c	U(eq)
C30	0.6267(2)	0.11453(19)	0.53692(17)	0.0453(6)
C31	0.5911(2)	0.07151(19)	0.62884(19)	0.0466(6)
C32	0.6682(2)	0.12844(17)	0.70757(16)	0.0366(5)
C33	0.7793(2)	0.1097(2)	0.72948(18)	0.0443(6)
C34	0.8534(2)	0.1631(2)	0.80008(19)	0.0524(7)
C35	0.8195(3)	0.2372(2)	0.84994(19)	0.0529(7)
C36	0.7109(2)	0.2588(2)	0.83046(17)	0.0463(6)
C37	0.6347(2)	0.20477(19)	0.76007(17)	0.0389(6)
C38	0.4661(2)	0.24739(17)	0.67143(16)	0.0349(5)
C39	0.2962(3)	0.3734(3)	0.6635(2)	0.0671(9)
C40	0.4026(4)	0.4444(3)	0.7203(3)	0.0889(13)
C41	0.3069(4)	0.3917(3)	0.5619(3)	0.0809(11)
C42	0.1752(4)	0.3913(3)	0.7022(3)	0.1004(15)
C43	0.2135(2)	0.1441(2)	0.60545(18)	0.0438(6)
C44	0.2623(3)	0.1411(2)	0.50951(19)	0.0572(7)
C45	0.0815(3)	0.1530(3)	0.6005(2)	0.0788(11)
C46	0.2177(3)	0.0470(2)	0.6468(2)	0.0691(9)

Bond lengths (Å) for 1-42:

P1-C15	1.860(2)	P1-C16	1.864(3)
P1-C20	1.865(3)	P1-B1	1.942(3)
B1-H3B	1.11(4)	B1-H1B	1.12(3)
B1-H1B	1.14(4)	N1-C15	1.273(3)
N1-C1	1.423(3)	C1-C2	1.385(4)
C1-C6	1.397(3)	P2-C39	1.861(3)
P2-C38	1.865(2)	P2-C43	1.875(3)
P2-B2	1.978(4)	B2-H2B	1.07(4)
B2-H2C	1.15(4)	B2-H2D	1.04(5)
N2-C15	1.355(3)	N2-C14	1.430(3)
N2-H2N	0.79(4)	C2-C3	1.380(4)
C2-H2A	0.94	N3-C38	1.263(3)
N3-C24	1.425(3)	C3-C4	1.377(5)
C3-H3A	0.94	N4-C38	1.367(3)
N4-C37	1.425(3)	N4-H4N	0.87(4)
C4-C5	1.368(5)	C4-H4A	0.94
C5-C6	1.394(4)	C5-H5A	0.94
C6-C7	1.493(5)	C7-C8	1.520(5)

C7-H7A	0.98	C7-H7B	0.98
C8-C9	1.502(5)	C8-H8A	0.98
C8-H8B	0.98	C9-C10	1.386(4)
C9-C14	1.400(4)	C10-C11	1.362(6)
C10-H10A	0.94	C11-C12	1.352(6)
C11-H11A	0.94	C12-C13	1.379(5)
C12-H12A	0.94	C13-C14	1.371(4)
C13-H13A	0.94	C16-C18	1.529(5)
C16-C19	1.524(4)	C16-C17	1.533(4)
C17-H17A	0.97	C17-H17B	0.97
C17-H17C	0.97	C18-H18A	0.97
C18-H18B	0.97	C18-H18C	0.97
C19-H19A	0.97	C19-H19B	0.97
C19-H19C	0.97	C20-C22	1.519(5)
C20-C21	1.532(5)	C20-C23	1.557(4)
C21-H21A	0.97	C21-H21B	0.97
C21-H21C	0.97	C22-H22A	0.97
C22-H22B	0.97	C22-H22C	0.97
C23-H23A	0.97	C23-H23B	0.97
C23-H23C	0.97	C24-C25	1.385(4)
C24-C29	1.394(3)	C25-C26	1.378(4)
C25-H25A	0.94	C26-C27	1.392(5)
C26-H26A	0.94	C27-C28	1.376(4)
C27-H27A	0.94	C28-C29	1.390(3)
C28-H28A	0.94	C29-C30	1.508(4)
C30-C31	1.530(4)	C30-H30A	0.98
C30-H30B	0.98	C31-C32	1.498(3)
C31-H31A	0.98	C31-H31B	0.98
C32-C33	1.390(3)	C32-C37	1.403(4)
C33-C34	1.380(4)	C33-H33A	0.94
C34-C35	1.361(4)	C34-H34A	0.94
C35-C36	1.373(4)	C35-H35A	0.94
C36-C37	1.392(4)	C36-H36A	0.94
C39-C41	1.531(5)	C39-C40	1.552(5)
C39-C42	1.559(5)	C40-H40A	0.97
C40-H40B	0.97	C40-H40C	0.97
C41-H41A	0.97	C41-H41B	0.97
C41-H41C	0.97	C42-H42A	0.97

C42-H42B	0.97	C42-H42C	0.97
C43-C44	1.518(4)	C43-C46	1.535(4)
C43-C45	1.535(4)	C44-H44A	0.97
C44-H44B	0.97	C44-H44C	0.97
C45-H45A	0.97	C45-H45B	0.97
C45-H45C	0.97	C46-H46A	0.97
C46-H46B	0.97	C46-H46C	0.97

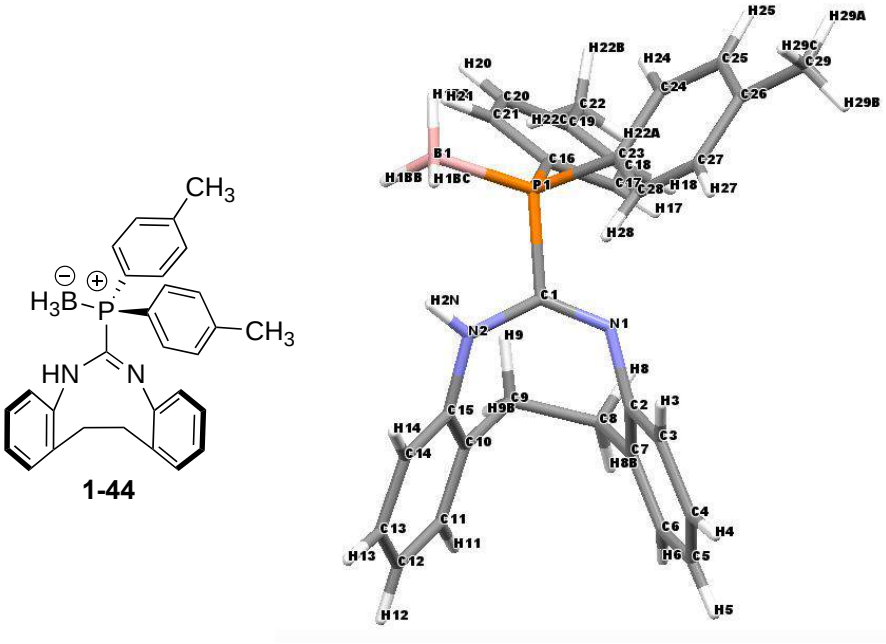
Bond angles (°) for 1-42:

C15-P1-C16	105.90(11)	C15-P1-C20	103.98(12)
C16-P1-C20	114.82(14)	C15-P1-B1	109.86(14)
C16-P1-B1	111.07(16)	C20-P1-B1	110.78(18)
P1-B1-H3B	104.(2)	P1-B1-H1B	103.2(16)
H3B-B1-H1B	118.(3)	P1-B1-H1B	107.1(18)
H3B-B1-H1B	115.(3)	H1B-B1-H1B	108.(3)
C15-N1-C1	126.5(2)	C2-C1-C6	119.7(2)
C2-C1-N1	118.0(2)	C6-C1-N1	121.9(2)
C39-P2-C38	103.44(14)	C39-P2-C43	115.25(14)
C38-P2-C43	105.99(11)	C39-P2-B2	110.39(19)
C38-P2-B2	110.43(13)	C43-P2-B2	110.94(17)
P2-B2-H2B	103.(2)	P2-B2-H2C	110.(2)
H2B-B2-H2C	112.(3)	P2-B2-H2D	105.(2)
H2B-B2-H2D	115.(3)	H2C-B2-H2D	112.(3)
C15-N2-C14	128.2(2)	C15-N2-H2N	113.(3)
C14-N2-H2N	119.(3)	C3-C2-C1	121.2(3)
C3-C2-H2A	119.4	C1-C2-H2A	119.4
C38-N3-C24	126.07(19)	C4-C3-C2	119.4(3)
C4-C3-H3A	120.3	C2-C3-H3A	120.3
C38-N4-C37	129.0(2)	C38-N4-H4N	117.(2)
C37-N4-H4N	113.(2)	C5-C4-C3	119.9(3)
C5-C4-H4A	120.1	C3-C4-H4A	120.1
C4-C5-C6	121.9(3)	C4-C5-H5A	119.0
C6-C5-H5A	119.0	C5-C6-C1	117.9(3)
C5-C6-C7	121.5(3)	C1-C6-C7	120.5(2)
C6-C7-C8	113.7(3)	C6-C7-H7A	108.8
C8-C7-H7A	108.8	C6-C7-H7B	108.8

C8-C7-H7B	108.8	H7A-C7-H7B	107.7
C9-C8-C7	114.4(3)	C9-C8-H8A	108.7
C7-C8-H8A	108.7	C9-C8-H8B	108.7
C7-C8-H8B	108.7	H8A-C8-H8B	107.6
C10-C9-C14	117.0(3)	C10-C9-C8	120.9(3)
C14-C9-C8	121.9(3)	C11-C10-C9	121.5(3)
C11-C10-H10A	119.2	C9-C10-H10A	119.2
C12-C11-C10	120.8(3)	C12-C11-H11A	119.6
C10-C11-H11A	119.6	C11-C12-C13	119.6(4)
C11-C12-H12A	120.2	C13-C12-H12A	120.2
C14-C13-C12	120.2(3)	C14-C13-H13A	119.9
C12-C13-H13A	119.9	C13-C14-C9	120.8(3)
C13-C14-N2	117.9(3)	C9-C14-N2	121.2(3)
N1-C15-N2	129.5(2)	N1-C15-P1	117.10(18)
N2-C15-P1	113.31(16)	C18-C16-C19	109.6(3)
C18-C16-C17	108.3(3)	C19-C16-C17	108.5(3)
C18-C16-P1	105.8(2)	C19-C16-P1	109.7(2)
C17-C16-P1	114.80(19)	C16-C17-H17A	109.5
C16-C17-H17B	109.5	H17A-C17-H17B	109.5
C16-C17-H17C	109.5	H17A-C17-H17C	109.5
H17B-C17-H17C	109.5	C16-C18-H18A	109.5
C16-C18-H18B	109.5	H18A-C18-H18B	109.5
C16-C18-H18C	109.5	H18A-C18-H18C	109.5
H18B-C18-H18C	109.5	C16-C19-H19A	109.5
C16-C19-H19B	109.5	H19A-C19-H19B	109.5
C16-C19-H19C	109.5	H19A-C19-H19C	109.5
H19B-C19-H19C	109.5	C22-C20-C21	109.4(3)
C22-C20-C23	109.5(3)	C21-C20-C23	108.3(3)
C22-C20-P1	114.6(2)	C21-C20-P1	106.7(2)
C23-C20-P1	108.2(2)	C20-C21-H21A	109.5
C20-C21-H21B	109.5	H21A-C21-H21B	109.5
C20-C21-H21C	109.5	H21A-C21-H21C	109.5
H21B-C21-H21C	109.5	C20-C22-H22A	109.5
C20-C22-H22B	109.5	H22A-C22-H22B	109.5
C20-C22-H22C	109.5	H22A-C22-H22C	109.5
H22B-C22-H22C	109.5	C20-C23-H23A	109.5
C20-C23-H23B	109.5	H23A-C23-H23B	109.5
C20-C23-H23C	109.5	H23A-C23-H23C	109.5

H23B-C23-H23C	109.5	C25-C24-C29	119.2(2)
C25-C24-N3	118.4(2)	C29-C24-N3	121.9(2)
C26-C25-C24	121.0(3)	C26-C25-H25A	119.5
C24-C25-H25A	119.5	C25-C26-C27	120.2(3)
C25-C26-H26A	119.9	C27-C26-H26A	119.9
C28-C27-C26	118.6(3)	C28-C27-H27A	120.7
C26-C27-H27A	120.7	C27-C28-C29	121.8(3)
C27-C28-H28A	119.1	C29-C28-H28A	119.1
C28-C29-C24	119.0(2)	C28-C29-C30	120.5(2)
C24-C29-C30	120.5(2)	C29-C30-C31	114.9(2)
C29-C30-H30A	108.6	C31-C30-H30A	108.6
C29-C30-H30B	108.6	C31-C30-H30B	108.6
H30A-C30-H30B	107.5	C32-C31-C30	113.4(2)
C32-C31-H31A	108.9	C30-C31-H31A	108.9
C32-C31-H31B	108.9	C30-C31-H31B	108.9
H31A-C31-H31B	107.7	C33-C32-C37	117.1(2)
C33-C32-C31	120.8(2)	C37-C32-C31	122.1(2)
C34-C33-C32	121.8(2)	C34-C33-H33A	119.1
C32-C33-H33A	119.1	C35-C34-C33	120.3(2)
C35-C34-H34A	119.9	C33-C34-H34A	119.9
C34-C35-C36	120.1(3)	C34-C35-H35A	120.0
C36-C35-H35A	120.0	C35-C36-C37	120.2(3)
C35-C36-H36A	119.9	C37-C36-H36A	119.9
C36-C37-C32	120.6(2)	C36-C37-N4	117.5(2)
C32-C37-N4	121.7(2)	N3-C38-N4	129.8(2)
N3-C38-P2	118.19(17)	N4-C38-P2	111.91(18)
C41-C39-C40	111.1(3)	C41-C39-C42	111.3(3)
C40-C39-C42	107.3(3)	C41-C39-P2	113.0(2)
C40-C39-P2	105.8(2)	C42-C39-P2	108.0(3)
C39-C40-H40A	109.5	C39-C40-H40B	109.5
H40A-C40-H40B	109.5	C39-C40-H40C	109.5
H40A-C40-H40C	109.5	H40B-C40-H40C	109.5
C39-C41-H41A	109.5	C39-C41-H41B	109.5
H41A-C41-H41B	109.5	C39-C41-H41C	109.5
H41A-C41-H41C	109.5	H41B-C41-H41C	109.5
C39-C42-H42A	109.5	C39-C42-H42B	109.5
H42A-C42-H42B	109.5	C39-C42-H42C	109.5
H42A-C42-H42C	109.5	H42B-C42-H42C	109.5

C44-C43-C46	107.8(3)	C44-C43-C45	109.2(2)
C46-C43-C45	109.9(3)	C44-C43-P2	115.82(19)
C46-C43-P2	105.41(19)	C45-C43-P2	108.5(2)
C43-C44-H44A	109.5	C43-C44-H44B	109.5
H44A-C44-H44B	109.5	C43-C44-H44C	109.5
H44A-C44-H44C	109.5	H44B-C44-H44C	109.5
C43-C45-H45A	109.5	C43-C45-H45B	109.5
H45A-C45-H45B	109.5	C43-C45-H45C	109.5
H45A-C45-H45C	109.5	H45B-C45-H45C	109.5
C43-C46-H46A	109.5	C43-C46-H46B	109.5
H46A-C46-H46B	109.5	C43-C46-H46C	109.5
H46A-C46-H46C	109.5	H46B-C46-H46C	109.5



Sample and crystal data for 1-44:

Identification code	milligan62414
Chemical formula	$C_{29}H_{30}BN_2P$
Formula weight	448.33
Temperature	230(2) K
Wavelength	1.54178 Å
Crystal size	0.080 x 0.120 x 0.210 mm
Crystal system	monoclinic
Space group	P 1 21/c 1
Unit cell dimensions	a = 9.9801(4) Å α = 90°
	b = 10.0187(4) β = 96.4999(14)°
	c = 26.0554(9) γ = 90°
Volume	2588.47(17) Å
Z	4
Density (calculated)	1.150 g/cm^3
Absorption coefficient	1.065 mm^{-1}
F(000)	952

Data collection and structure refinement for 1-44:

Diffractometer	Bruker Apex II CCD
Radiation source	IMuS micro-focus, Cu
Theta range for data collection	3.41 to 68.18°
Index ranges	-11<=h<=11, -12<=k<=11, -30<=l<=31
Reflections collected	27146
Independent reflections	4683 [R(int) = 0.0273]
Max. and min. transmission	0.9200 and 0.8070
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2013 (Sheldrick, 2013)
Function minimized	$\Sigma\ w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	4683 / 0 / 396
Goodness-of-fit on F^2	1.551
Δ/σ_{max}	0.006
Final R indices	4271 data; I>2σ(I) R1 = 0.0449, wR2 = 0.1435
	all data R1 = 0.0481, wR2 = 0.1467
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0814P)^2]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	0.416 and -0.225 eÅ^{-3}
R.M.S. deviation from mean	0.047 eÅ^{-3}

Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for 1-44:

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
P1	0.78683(3)	0.88794(4)	0.82935(2)	0.04084(16)
N1	0.00867(11)	0.99504(12)	0.87989(4)	0.0412(3)
B1	0.67095(18)	0.7413(2)	0.84310(8)	0.0527(4)

	x/a	y/b	z/c	U(eq)
C1	0.94348(13)	0.88605(13)	0.87524(5)	0.0393(3)
N2	0.96856(13)	0.76400(13)	0.89692(5)	0.0469(3)
C2	0.12591(13)	0.01970(13)	0.91463(5)	0.0390(3)
C3	0.10990(15)	0.08574(15)	0.96042(6)	0.0448(3)
C4	0.22152(19)	0.12870(18)	0.99293(7)	0.0588(4)
C5	0.3487(2)	0.1050(2)	0.97951(9)	0.0713(5)
C6	0.36415(16)	0.0386(2)	0.93429(8)	0.0660(5)
C7	0.25498(14)	0.99586(16)	0.90045(6)	0.0483(3)
C8	0.2753(2)	0.9232(2)	0.85134(8)	0.0638(5)
C9	0.2194(2)	0.77962(19)	0.84799(7)	0.0621(4)
C10	0.21122(16)	0.71648(15)	0.89977(6)	0.0513(4)
C11	0.3253(2)	0.6611(2)	0.92751(9)	0.0683(5)
C12	0.3200(2)	0.6024(2)	0.97514(9)	0.0791(6)
C13	0.2007(2)	0.59757(19)	0.99694(8)	0.0647(5)
C14	0.08701(17)	0.65459(16)	0.97111(6)	0.0506(4)
C15	0.09211(14)	0.71410(13)	0.92325(6)	0.0440(3)
C16	0.84946(14)	0.88640(14)	0.76717(5)	0.0433(3)
C17	0.93975(19)	0.98334(19)	0.75453(6)	0.0595(4)
C18	0.9923(2)	0.97799(18)	0.70766(6)	0.0617(4)
C19	0.95656(18)	0.87769(15)	0.67220(6)	0.0521(4)
C20	0.86331(19)	0.78416(17)	0.68476(7)	0.0585(4)
C21	0.81089(16)	0.78692(16)	0.73163(6)	0.0512(4)
C22	0.0168(3)	0.8711(2)	0.62182(8)	0.0728(5)
C23	0.71245(13)	0.04943(15)	0.83737(5)	0.0442(3)
C24	0.6542(2)	0.1214(2)	0.79536(8)	0.0725(6)
C25	0.5862(3)	0.2392(2)	0.80269(9)	0.0836(7)
C26	0.57316(17)	0.28717(17)	0.85121(8)	0.0634(5)
C27	0.63216(17)	0.21436(19)	0.89292(7)	0.0601(4)
C28	0.70087(16)	0.09696(17)	0.88646(6)	0.0521(4)
C29	0.4965(3)	0.4136(2)	0.85927(12)	0.0932(8)

Bond lengths (Å) for 1-44:

P1-C16	1.8013(15)	P1-C23	1.8021(15)

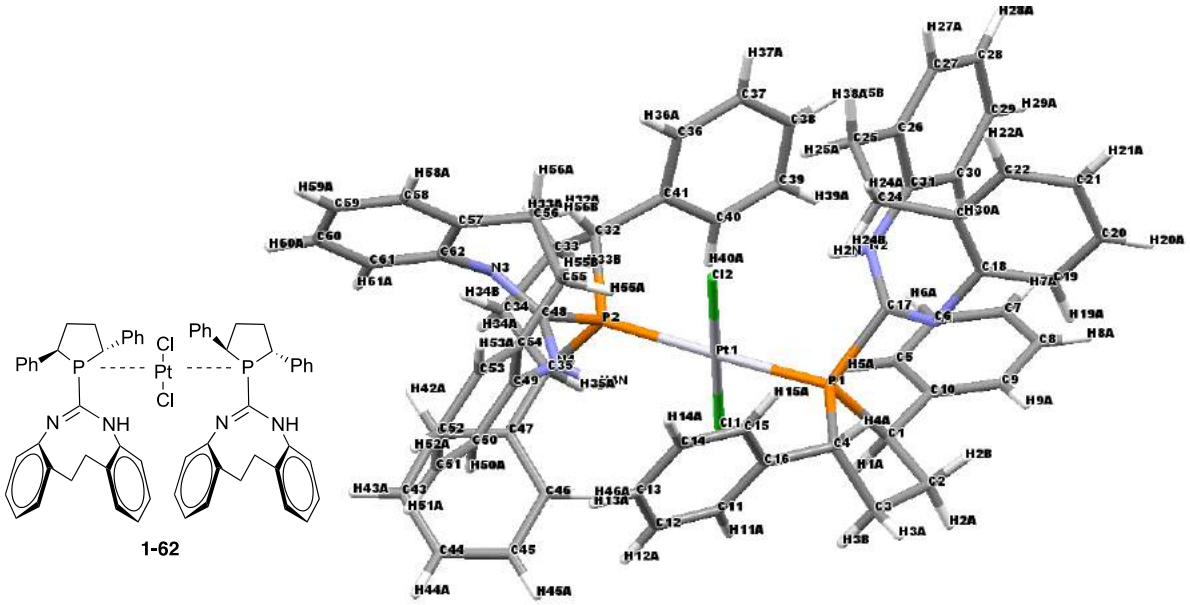
P1-C1	1.8578(14)	P1-B1	1.9279(19)
N1-C1	1.2699(18)	N1-C2	1.4176(17)
B1-H1BC	1.12(2)	B1-H1BB	1.11(2)
B1-H1BA	0.99(2)	C1-N2	1.3582(18)
N2-C15	1.4315(19)	N2-H2N	0.88(2)
C2-C3	1.389(2)	C2-C7	1.400(2)
C3-C4	1.389(2)	C3-H3	0.98(2)
C4-C5	1.375(3)	C4-H4	0.98(2)
C5-C6	1.377(3)	C5-H5	0.97(3)
C6-C7	1.389(2)	C6-H6	0.95(3)
C7-C8	1.506(2)	C8-C9	1.542(3)
C8-H8	1.03(2)	C8-H8B	1.03(3)
C9-C10	1.501(3)	C9-H9B	0.96(2)
C9-H9	1.07(2)	C10-C11	1.393(3)
C10-C15	1.397(2)	C11-C12	1.380(3)
C11-H11	0.94(3)	C12-C13	1.376(3)
C12-H12	0.98(3)	C13-C14	1.376(2)
C13-H13	0.98(2)	C14-C15	1.388(2)
C14-H14	0.98(2)	C16-C21	1.385(2)
C16-C17	1.390(2)	C17-C18	1.384(2)
C17-H17	0.92(2)	C18-C19	1.384(2)
C18-H18	0.98(3)	C19-C20	1.386(3)
C19-C22	1.506(2)	C20-C21	1.382(2)
C20-H20	0.95(2)	C21-H21	0.94(2)
C22-H22A	0.97	C22-H22B	0.97
C22-H22C	0.97	C23-C28	1.382(2)
C23-C24	1.383(2)	C24-C25	1.386(3)
C24-H24	1.02(2)	C25-C26	1.372(3)
C25-H25	0.98(3)	C26-C27	1.384(3)
C26-C29	1.507(3)	C27-C28	1.381(2)
C27-H27	1.01(2)	C28-H28	0.94(2)
C29-H29A	0.97	C29-H29B	0.97
C29-H29C	0.97		

Bond angles (°) for 1-44:

C16-P1-C23	107.54(7)	C16-P1-C1	103.09(6)
C23-P1-C1	105.20(6)	C16-P1-B1	115.92(8)

C23-P1-B1	113.50(8)	C1-P1-B1	110.57(7)
C1-N1-C2	125.99(12)	P1-B1-H1BC	105.5(12)
P1-B1-H1BB	108.6(11)	H1BC-B1-H1BB	111.0(16)
P1-B1-H1BA	109.1(13)	H1BC-B1-H1BA	110.7(17)
H1BB-B1-H1BA	111.6(16)	N1-C1-N2	131.77(12)
N1-C1-P1	115.93(10)	N2-C1-P1	112.27(10)
C1-N2-C15	128.45(12)	C1-N2-H2N	115.2(12)
C15-N2-H2N	116.3(12)	C3-C2-C7	120.44(13)
C3-C2-N1	117.68(12)	C7-C2-N1	121.28(13)
C4-C3-C2	120.59(15)	C4-C3-H3	120.5(11)
C2-C3-H3	118.8(11)	C5-C4-C3	119.42(18)
C5-C4-H4	120.2(13)	C3-C4-H4	120.2(13)
C4-C5-C6	119.81(16)	C4-C5-H5	119.3(15)
C6-C5-H5	120.9(15)	C5-C6-C7	122.42(16)
C5-C6-H6	121.9(15)	C7-C6-H6	115.6(15)
C6-C7-C2	117.31(15)	C6-C7-C8	121.10(16)
C2-C7-C8	121.56(14)	C7-C8-C9	114.60(14)
C7-C8-H8	108.0(12)	C9-C8-H8	108.6(12)
C7-C8-H8B	103.1(13)	C9-C8-H8B	112.0(14)
H8-C8-H8B	110.4(18)	C10-C9-C8	113.49(15)
C10-C9-H9B	108.3(13)	C8-C9-H9B	109.1(13)
C10-C9-H9	109.6(11)	C8-C9-H9	109.2(11)
H9B-C9-H9	107.0(16)	C11-C10-C15	116.88(16)
C11-C10-C9	120.66(16)	C15-C10-C9	122.42(14)
C12-C11-C10	121.58(18)	C12-C11-H11	119.5(15)
C10-C11-H11	118.8(16)	C13-C12-C11	120.64(18)
C13-C12-H12	120.8(17)	C11-C12-H12	118.6(17)
C12-C13-C14	119.16(19)	C12-C13-H13	123.0(13)
C14-C13-H13	117.9(13)	C13-C14-C15	120.35(16)
C13-C14-H14	120.6(13)	C15-C14-H14	119.0(13)
C14-C15-C10	121.33(14)	C14-C15-N2	117.59(13)
C10-C15-N2	120.91(13)	C21-C16-C17	118.88(14)
C21-C16-P1	120.60(12)	C17-C16-P1	120.51(11)
C18-C17-C16	120.21(15)	C18-C17-H17	121.0(14)
C16-C17-H17	118.7(14)	C17-C18-C19	121.47(16)
C17-C18-H18	120.2(14)	C19-C18-H18	118.2(14)
C18-C19-C20	117.55(15)	C18-C19-C22	121.04(16)
C20-C19-C22	121.41(15)	C21-C20-C19	121.78(15)

C21-C20-H20	117.6(14)	C19-C20-H20	120.7(13)
C20-C21-C16	120.05(16)	C20-C21-H21	119.7(12)
C16-C21-H21	120.3(12)	C19-C22-H22A	109.5
C19-C22-H22B	109.5	H22A-C22-H22B	109.5
C19-C22-H22C	109.5	H22A-C22-H22C	109.5
H22B-C22-H22C	109.5	C28-C23-C24	118.78(15)
C28-C23-P1	119.70(12)	C24-C23-P1	121.20(12)
C23-C24-C25	120.24(18)	C23-C24-H24	117.8(13)
C25-C24-H24	121.8(13)	C26-C25-C24	121.62(19)
C26-C25-H25	123.0(19)	C24-C25-H25	115.4(19)
C25-C26-C27	117.56(16)	C25-C26-C29	121.7(2)
C27-C26-C29	120.74(19)	C28-C27-C26	121.73(17)
C28-C27-H27	117.8(12)	C26-C27-H27	120.4(12)
C23-C28-C27	120.06(16)	C23-C28-H28	119.4(12)
C27-C28-H28	120.4(12)	C26-C29-H29A	109.5
C26-C29-H29B	109.5	H29A-C29-H29B	109.5
C26-C29-H29C	109.5	H29A-C29-H29C	109.5
H29B-C29-H29C	109.5		



Sample and crystal data for 1-62:

Identification code	JM1r	
Chemical formula	$C_{63}H_{60}Cl_4N_4P_2Pt$	
Formula weight	1271.98 g/mol	
Temperature	240(2) K	
Wavelength	1.54178 Å	
Crystal size	0.040 x 0.080 x 0.080 mm	
Crystal system	monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 11.2580(16) Å	α = 90°
	b = 12.9240(19) Å	β = 98.888(7)°
	c = 19.447(3) Å	γ = 90°
Volume	2795.5(7) $Å^3$	
Z	2	
Density (calculated)	1.511 g/cm^3	
Absorption coefficient	7.334 mm^{-1}	
F(000)	1284	

Data collection and structure refinement for 1-62:

Diffractometer	Bruker Apex II CCD
Radiation source	IMuS micro-focus source, Cu

Theta range for data collection	2.30 to 70.25°
Index ranges	-13<=h<=13, -15<=k<=15, -23<=l<=23
Reflections collected	35162
Independent reflections	10415 [R(int) = 0.0263]
Absorption correction	multi-scan
Max. and min. transmission	0.7580 and 0.5910
Structure solution technique	direct methods
Structure solution program	SHELXS-97 (Sheldrick, 2008)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-97 (Sheldrick, 2008)
Function minimized	$\Sigma\ w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	10415 / 1 / 675
Goodness-of-fit on F^2	1.003
Δ/σ_{max}	0.002
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0226P)^2]$
Absolute structure parameter	-0.0(0)
Largest diff. peak and hole	0.668 and -0.651 eÅ^{-3}
R.M.S. deviation from mean	0.058 eÅ^{-3}

Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for 1-62:

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
P1	0.82425(9)	0.03999(8)	0.81485(5)	0.0319(2)
Pt1	0.84217(2)	0.21192(2)	0.78668(2)	0.03098(5)
Cl1	0.01676(10)	0.22898(11)	0.86398(6)	0.0489(3)
N1	0.6436(4)	0.9058(3)	0.8170(2)	0.0417(8)
C1	0.9224(4)	0.9794(4)	0.8906(3)	0.0435(10)
P2	0.85031(9)	0.38228(8)	0.75273(5)	0.0320(2)
Cl2	0.66348(9)	0.1981(2)	0.71102(6)	0.0476(5)

	x/a	y/b	z/c	U(eq)
N2	0.6107(3)	0.0774(3)	0.8558(2)	0.0386(8)
C2	0.9448(6)	0.8703(4)	0.8639(3)	0.0607(14)
C3	0.9672(7)	0.8830(5)	0.7900(4)	0.0651(18)
N3	0.7671(4)	0.4938(3)	0.6397(2)	0.0430(8)
C4	0.8647(5)	0.9484(4)	0.7487(3)	0.0455(11)
N4	0.8472(4)	0.3273(3)	0.6195(2)	0.0424(8)
C5	0.8780(5)	0.0845(5)	0.9919(3)	0.0550(12)
C6	0.8330(6)	0.0943(6)	0.0540(3)	0.0652(15)
C7	0.7902(5)	0.0119(6)	0.0851(3)	0.0625(16)
C8	0.7870(5)	0.9167(5)	0.0529(3)	0.0621(15)
C9	0.8290(5)	0.9050(4)	0.9900(3)	0.0536(12)
C10	0.8754(4)	0.9888(4)	0.9586(3)	0.0441(10)
C11	0.0015(7)	0.0451(5)	0.6796(4)	0.0672(16)
C12	0.0262(9)	0.0886(6)	0.6194(5)	0.089(3)
C13	0.9405(11)	0.0892(5)	0.5604(5)	0.091(3)
C14	0.8322(10)	0.0473(7)	0.5636(4)	0.087(3)
C15	0.8074(7)	0.0022(6)	0.6248(4)	0.0687(18)
C16	0.8922(6)	0.9991(4)	0.6837(3)	0.0507(12)
C17	0.6699(5)	0.0000(4)	0.8294(3)	0.0356(11)
C18	0.5285(4)	0.8626(4)	0.8195(2)	0.0417(9)
C19	0.5224(5)	0.7769(4)	0.8615(3)	0.0535(12)
C20	0.4148(5)	0.7234(7)	0.8609(3)	0.0709(17)
C21	0.3138(6)	0.7557(6)	0.8168(4)	0.0710(18)
C22	0.3196(5)	0.8412(5)	0.7751(3)	0.0579(14)
C23	0.4257(5)	0.8958(4)	0.7751(2)	0.0451(10)
C24	0.4259(5)	0.9916(4)	0.7307(3)	0.0504(11)
C25	0.3806(5)	0.0897(4)	0.7653(3)	0.0520(12)
C26	0.3909(4)	0.0836(4)	0.8427(3)	0.0454(10)
C27	0.2900(5)	0.0860(5)	0.8754(3)	0.0594(14)
C28	0.2972(5)	0.0766(5)	0.9461(3)	0.0636(15)
C29	0.4070(5)	0.0601(5)	0.9873(3)	0.0563(13)
C30	0.5099(4)	0.0575(4)	0.9566(3)	0.0456(10)
C31	0.5027(5)	0.0699(4)	0.8853(3)	0.0371(11)
C32	0.7516(5)	0.4704(4)	0.7940(2)	0.0429(10)
C33	0.8381(6)	0.5545(4)	0.8293(3)	0.0577(13)
C34	0.9399(6)	0.5700(4)	0.7865(3)	0.0503(14)
C35	0.9892(4)	0.4614(4)	0.7758(2)	0.0419(10)

	x/a	y/b	z/c	U(eq)
C36	0.5516(6)	0.4101(5)	0.8193(4)	0.0636(15)
C37	0.4769(9)	0.3630(7)	0.8608(5)	0.076(2)
C38	0.5261(8)	0.3201(6)	0.9216(5)	0.080(2)
C39	0.6489(8)	0.3231(5)	0.9437(4)	0.079(2)
C40	0.7242(7)	0.3714(5)	0.9026(3)	0.0653(16)
C41	0.6764(7)	0.4167(5)	0.8397(3)	0.0481(14)
C42	0.1016(5)	0.5297(4)	0.6820(3)	0.0575(13)
C43	0.1887(6)	0.5196(5)	0.6393(4)	0.0701(17)
C44	0.2568(6)	0.4329(6)	0.6417(4)	0.0695(16)
C45	0.2373(6)	0.3537(6)	0.6860(4)	0.0715(17)
C46	0.1496(6)	0.3633(5)	0.7286(3)	0.0610(14)
C47	0.0811(4)	0.4517(4)	0.7271(3)	0.0429(10)
C48	0.8118(4)	0.4056(3)	0.6575(2)	0.0347(9)
C49	0.8527(5)	0.3284(4)	0.5464(2)	0.0389(10)
C50	0.9633(5)	0.3450(4)	0.5254(3)	0.0460(10)
C51	0.9739(5)	0.3361(4)	0.4553(3)	0.0548(13)
C52	0.8740(6)	0.3116(4)	0.4075(3)	0.0575(13)
C53	0.7653(5)	0.2968(4)	0.4283(3)	0.0539(12)
C54	0.7506(5)	0.3031(4)	0.4981(3)	0.0445(10)
C55	0.6303(5)	0.2859(5)	0.5209(3)	0.0571(13)
C56	0.5735(5)	0.3840(5)	0.5488(3)	0.0553(13)
C57	0.6277(4)	0.4841(4)	0.5291(3)	0.0462(11)
C58	0.5818(5)	0.5347(5)	0.4668(3)	0.0582(14)
C59	0.6322(6)	0.6239(5)	0.4460(3)	0.0638(15)
C60	0.7317(6)	0.6665(5)	0.4871(3)	0.0631(15)
C61	0.7772(5)	0.6194(4)	0.5491(3)	0.0524(12)
C62	0.7265(4)	0.5292(4)	0.5712(2)	0.0412(9)
C63	0.6119(8)	0.6943(6)	0.6913(4)	0.086(2)
Cl3	0.4819(2)	0.6166(2)	0.6754(2)	0.1278(10)
Cl4	0.5954(3)	0.80182(18)	0.63711(14)	0.1063(7)

Table 4. Bond lengths (Å) for 1-62.

P1-C4	1.857(5)	P1-C1	1.871(5)
P1-C17	1.875(6)	P1-Pt1	2.3048(11)
Pt1-Cl1	2.2932(11)	Pt1-P2	2.3045(11)
Pt1-Cl2	2.3085(10)	N1-C17	1.267(7)
N1-C18	1.418(6)	C1-C10	1.504(7)

C1-C2	1.538(7)	C1-H1A	0.99
P2-C32	1.858(5)	P2-C48	1.861(5)
P2-C35	1.864(5)	N2-C17	1.347(7)
N2-C31	1.426(7)	N2-H2N	0.83(6)
C2-C3	1.504(9)	C2-H2A	0.98
C2-H2B	0.98	C3-C4	1.551(9)
C3-H3A	0.98	C3-H3B	0.98
N3-C48	1.272(6)	N3-C62	1.415(6)
C4-C16	1.497(7)	C4-H4A	0.99
N4-C48	1.349(6)	N4-C49	1.433(6)
N4-H4N	0.92(7)	C5-C6	1.385(8)
C5-C10	1.394(8)	C5-H5A	0.94
C6-C7	1.350(10)	C6-H6A	0.94
C7-C8	1.378(10)	C7-H7A	0.94
C8-C9	1.387(8)	C8-H8A	0.94
C9-C10	1.383(8)	C9-H9A	0.94
C11-C12	1.366(10)	C11-C16	1.380(9)
C11-H11A	0.94	C12-C13	1.380(15)
C12-H12A	0.94	C13-C14	1.345(14)
C13-H13A	0.94	C14-C15	1.393(11)
C14-H14A	0.94	C15-C16	1.374(10)
C15-H15A	0.94	C18-C19	1.384(7)
C18-C23	1.400(7)	C19-C20	1.393(8)
C19-H19A	0.94	C20-C21	1.379(9)
C20-H20A	0.94	C21-C22	1.378(9)
C21-H21A	0.94	C22-C23	1.387(7)
C22-H22A	0.94	C23-C24	1.510(7)
C24-C25	1.558(8)	C24-H24A	0.98
C24-H24B	0.98	C25-C26	1.494(8)
C25-H25A	0.98	C25-H25B	0.98
C26-C27	1.386(7)	C26-C31	1.407(7)
C27-C28	1.371(9)	C27-H27A	0.94
C28-C29	1.382(9)	C28-H28A	0.94
C29-C30	1.383(7)	C29-H29A	0.94
C30-C31	1.386(8)	C30-H30A	0.94
C32-C41	1.490(8)	C32-C33	1.547(7)
C32-H32A	0.99	C33-C34	1.530(9)
C33-H33A	0.98	C33-H33B	0.98

C34-C35	1.535(7)	C34-H34A	0.98
C34-H34B	0.98	C35-C47	1.512(7)
C35-H35A	0.99	C36-C37	1.392(10)
C36-C41	1.402(10)	C36-H36A	0.94
C37-C38	1.345(13)	C37-H37A	0.94
C38-C39	1.382(13)	C38-H38A	0.94
C39-C40	1.400(10)	C39-H39A	0.94
C40-C41	1.388(9)	C40-H40A	0.94
C42-C47	1.379(7)	C42-C43	1.387(9)
C42-H42A	0.94	C43-C44	1.354(10)
C43-H43A	0.94	C44-C45	1.377(10)
C44-H44A	0.94	C45-C46	1.390(9)
C45-H45A	0.94	C46-C47	1.376(8)
C46-H46A	0.94	C49-C50	1.386(7)
C49-C54	1.405(7)	C50-C51	1.391(8)
C50-H50A	0.94	C51-C52	1.381(9)
C51-H51A	0.94	C52-C53	1.361(9)
C52-H52A	0.94	C53-C54	1.395(7)
C53-H53A	0.94	C54-C55	1.506(7)
C55-C56	1.555(8)	C55-H55A	0.98
C55-H55B	0.98	C56-C57	1.505(8)
C56-H56A	0.98	C56-H56B	0.98
C57-C58	1.403(7)	C57-C62	1.403(7)
C58-C59	1.373(10)	C58-H58A	0.94
C59-C60	1.385(10)	C59-H59A	0.94
C60-C61	1.377(8)	C60-H60A	0.94
C61-C62	1.395(7)	C61-H61A	0.94
C63-Cl4	1.737(9)	C63-Cl3	1.763(9)
C63-H63A	0.98	C63-H63B	0.98

Table 5. Bond angles (°) for 1-62:

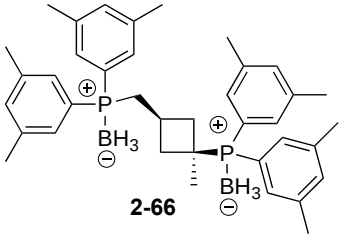
C4-P1-C1	95.8(2)	C4-P1-C17	105.1(2)
C1-P1-C17	102.4(2)	C4-P1-Pt1	114.21(16)
C1-P1-Pt1	121.85(17)	C17-P1-Pt1	114.76(17)
Cl1-Pt1-P2	91.60(4)	Cl1-Pt1-P1	91.98(4)
P2-Pt1-P1	176.37(4)	Cl1-Pt1-Cl2	178.22(7)
P2-Pt1-Cl2	87.75(7)	P1-Pt1-Cl2	88.69(7)

C17-N1-C18	124.0(4)	C10-C1-C2	118.0(4)
C10-C1-P1	114.4(3)	C2-C1-P1	103.0(4)
C10-C1-H1A	106.9	C2-C1-H1A	106.9
P1-C1-H1A	106.9	C32-P2-C48	105.5(2)
C32-P2-C35	95.5(2)	C48-P2-C35	102.0(2)
C32-P2-Pt1	114.14(16)	C48-P2-Pt1	115.26(14)
C35-P2-Pt1	121.61(15)	C17-N2-C31	127.4(4)
C17-N2-H2N	112.(4)	C31-N2-H2N	120.(4)
C3-C2-C1	106.4(5)	C3-C2-H2A	110.4
C1-C2-H2A	110.4	C3-C2-H2B	110.4
C1-C2-H2B	110.4	H2A-C2-H2B	108.6
C2-C3-C4	109.5(5)	C2-C3-H3A	109.8
C4-C3-H3A	109.8	C2-C3-H3B	109.8
C4-C3-H3B	109.8	H3A-C3-H3B	108.2
C48-N3-C62	127.0(4)	C16-C4-C3	116.2(5)
C16-C4-P1	114.2(3)	C3-C4-P1	103.3(4)
C16-C4-H4A	107.5	C3-C4-H4A	107.5
P1-C4-H4A	107.5	C48-N4-C49	126.7(4)
C48-N4-H4N	114.(4)	C49-N4-H4N	119.(4)
C6-C5-C10	120.1(6)	C6-C5-H5A	119.9
C10-C5-H5A	119.9	C7-C6-C5	121.5(6)
C7-C6-H6A	119.3	C5-C6-H6A	119.3
C6-C7-C8	119.1(6)	C6-C7-H7A	120.4
C8-C7-H7A	120.4	C7-C8-C9	120.6(6)
C7-C8-H8A	119.7	C9-C8-H8A	119.7
C10-C9-C8	120.4(6)	C10-C9-H9A	119.8
C8-C9-H9A	119.8	C9-C10-C5	118.2(5)
C9-C10-C1	122.2(5)	C5-C10-C1	119.6(5)
C12-C11-C16	121.9(8)	C12-C11-H11A	119.0
C16-C11-H11A	119.0	C11-C12-C13	120.4(8)
C11-C12-H12A	119.8	C13-C12-H12A	119.8
C14-C13-C12	118.9(7)	C14-C13-H13A	120.6
C12-C13-H13A	120.6	C13-C14-C15	120.7(9)
C13-C14-H14A	119.7	C15-C14-H14A	119.7
C16-C15-C14	121.3(8)	C16-C15-H15A	119.3
C14-C15-H15A	119.3	C15-C16-C11	116.8(6)
C15-C16-C4	120.5(6)	C11-C16-C4	122.7(6)
N1-C17-N2	132.1(5)	N1-C17-P1	115.5(4)

N2-C17-P1	112.2(4)	C19-C18-C23	119.8(5)
C19-C18-N1	117.7(5)	C23-C18-N1	122.0(4)
C18-C19-C20	120.9(6)	C18-C19-H19A	119.5
C20-C19-H19A	119.5	C21-C20-C19	119.2(6)
C21-C20-H20A	120.4	C19-C20-H20A	120.4
C22-C21-C20	119.9(5)	C22-C21-H21A	120.0
C20-C21-H21A	120.0	C21-C22-C23	121.8(5)
C21-C22-H22A	119.1	C23-C22-H22A	119.1
C22-C23-C18	118.3(5)	C22-C23-C24	119.6(5)
C18-C23-C24	122.0(4)	C23-C24-C25	113.0(4)
C23-C24-H24A	109.0	C25-C24-H24A	109.0
C23-C24-H24B	109.0	C25-C24-H24B	109.0
H24A-C24-H24B	107.8	C26-C25-C24	114.3(4)
C26-C25-H25A	108.7	C24-C25-H25A	108.7
C26-C25-H25B	108.7	C24-C25-H25B	108.7
H25A-C25-H25B	107.6	C27-C26-C31	117.0(5)
C27-C26-C25	121.3(5)	C31-C26-C25	121.6(5)
C28-C27-C26	122.2(5)	C28-C27-H27A	118.9
C26-C27-H27A	118.9	C27-C28-C29	120.3(5)
C27-C28-H28A	119.8	C29-C28-H28A	119.8
C28-C29-C30	119.1(5)	C28-C29-H29A	120.4
C30-C29-H29A	120.4	C29-C30-C31	120.4(5)
C29-C30-H30A	119.8	C31-C30-H30A	119.8
C30-C31-C26	120.9(5)	C30-C31-N2	119.3(5)
C26-C31-N2	119.7(5)	C41-C32-C33	116.0(5)
C41-C32-P2	113.9(4)	C33-C32-P2	104.2(4)
C41-C32-H32A	107.4	C33-C32-H32A	107.4
P2-C32-H32A	107.4	C34-C33-C32	108.9(4)
C34-C33-H33A	109.9	C32-C33-H33A	109.9
C34-C33-H33B	109.9	C32-C33-H33B	109.9
H33A-C33-H33B	108.3	C33-C34-C35	105.7(4)
C33-C34-H34A	110.6	C35-C34-H34A	110.6
C33-C34-H34B	110.6	C35-C34-H34B	110.6
H34A-C34-H34B	108.7	C47-C35-C34	117.2(4)
C47-C35-P2	115.7(3)	C34-C35-P2	103.1(3)
C47-C35-H35A	106.7	C34-C35-H35A	106.7
P2-C35-H35A	106.7	C37-C36-C41	122.1(8)

C37-C36-H36A	118.9	C41-C36-H36A	118.9
C38-C37-C36	119.1(9)	C38-C37-H37A	120.5
C36-C37-H37A	120.5	C37-C38-C39	121.2(7)
C37-C38-H38A	119.4	C39-C38-H38A	119.4
C38-C39-C40	120.0(7)	C38-C39-H39A	120.0
C40-C39-H39A	120.0	C41-C40-C39	120.3(7)
C41-C40-H40A	119.8	C39-C40-H40A	119.8
C40-C41-C36	117.3(6)	C40-C41-C32	122.9(7)
C36-C41-C32	119.8(6)	C47-C42-C43	121.1(6)
C47-C42-H42A	119.4	C43-C42-H42A	119.4
C44-C43-C42	120.3(6)	C44-C43-H43A	119.8
C42-C43-H43A	119.8	C43-C44-C45	119.5(6)
C43-C44-H44A	120.2	C45-C44-H44A	120.2
C44-C45-C46	120.2(6)	C44-C45-H45A	119.9
C46-C45-H45A	119.9	C47-C46-C45	120.6(6)
C47-C46-H46A	119.7	C45-C46-H46A	119.7
C46-C47-C42	118.2(5)	C46-C47-C35	119.4(5)
C42-C47-C35	122.4(5)	N3-C48-N4	131.4(5)
N3-C48-P2	116.0(4)	N4-C48-P2	112.4(3)
C50-C49-C54	121.2(5)	C50-C49-N4	118.2(5)
C54-C49-N4	120.3(5)	C49-C50-C51	119.5(5)
C49-C50-H50A	120.2	C51-C50-H50A	120.2
C52-C51-C50	119.6(5)	C52-C51-H51A	120.2
C50-C51-H51A	120.2	C53-C52-C51	120.5(5)
C53-C52-H52A	119.7	C51-C52-H52A	119.7
C52-C53-C54	121.9(5)	C52-C53-H53A	119.1
C54-C53-H53A	119.1	C53-C54-C49	117.1(5)
C53-C54-C55	121.6(5)	C49-C54-C55	121.2(5)
C54-C55-C56	114.8(4)	C54-C55-H55A	108.6
C56-C55-H55A	108.6	C54-C55-H55B	108.6
C56-C55-H55B	108.6	H55A-C55-H55B	107.6
C57-C56-C55	114.0(4)	C57-C56-H56A	108.7
C55-C56-H56A	108.7	C57-C56-H56B	108.7
C55-C56-H56B	108.7	H56A-C56-H56B	107.6
C58-C57-C62	117.6(5)	C58-C57-C56	120.8(5)
C62-C57-C56	121.6(5)	C59-C58-C57	122.1(6)
C59-C58-H58A	118.9	C57-C58-H58A	118.9
C58-C59-C60	119.8(5)	C58-C59-H59A	120.1

C60-C59-H59A	120.1	C61-C60-C59	119.2(6)
C61-C60-H60A	120.4	C59-C60-H60A	120.4
C60-C61-C62	121.6(6)	C60-C61-H61A	119.2
C62-C61-H61A	119.2	C61-C62-C57	119.5(5)
C61-C62-N3	118.2(4)	C57-C62-N3	121.8(4)
Cl4-C63-Cl3	110.0(4)	Cl4-C63-H63A	109.7
Cl3-C63-H63A	109.7	Cl4-C63-H63B	109.7
Cl3-C63-H63B	109.7	H63A-C63-H63B	108.2



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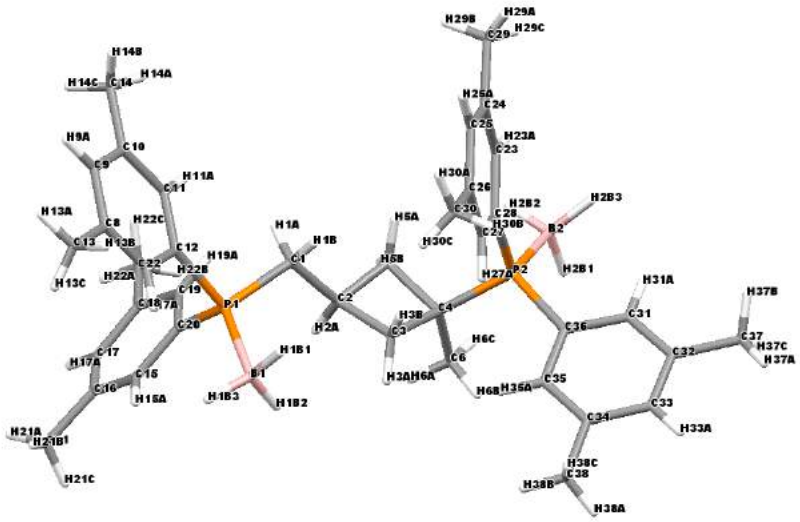


Sample and crystal data for 2-66:

Identification code	milligan5
Chemical formula	$C_{38}H_{52}B_2P_2$
Formula weight	592.35 g/mol
Temperature	230(2) K
Wavelength	1.54178 Å
Crystal size	0.100 x 0.140 x 0.190 mm
Crystal system	triclinic
Space group	P -1
Unit cell dimension	a = 10.7360(2) α = 109.8510(10)°
	b = 12.9572(3) β = 93.0060(10)°
	c = 13.9710(3) γ = 94.6320(10)°
Volume	1815.41(7) Å
Z	2
Density (calculated)	1.084 g/cm^3
Absorption coeffici	1.244 mm^{-1}
F(000)	640

Data collection and structure refinement for 2-66:

Diffractometer	Bruker Apex II CCD
Radiation source	IMuS micro-focus source, Cu
Theta range for data collection	3.38 to 68.26°

Index ranges	-12<=h<=12, -15<=k<=15, -16<=l<=16
Reflections collected	30565
Independent reflections	6499 [R(int) = 0.0247]
Absorption correction	multi-scan
Max. and min. transmission	0.8860 and 0.7980
Structure solution technique	direct methods
Structure solution program	SHELXS-97 (Sheldrick, 2008)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-97 (Sheldrick, 2008)
Function minimized	$\Sigma\ w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	6499 / 0 / 412
Goodness-of-fit on F^2	1.601
Δ/σ_{max}	0.683
Largest diff. peak and hole	0.459 and -0.316 $eÅ^{-3}$
R.M.S. deviation from mean	0.042 $eÅ^{-3}$

Atomic coordinates and equivalent isotropic atomic displacement parameters ($Å^2$) for 2-66:

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
P1	0.19966(3)	0.52444(3)	0.82114(3)	0.03355(13)
P2	0.32664(3)	0.23653(3)	0.38012(2)	0.02806(12)
B1	0.0721(2)	0.40690(18)	0.80845(17)	0.0507(5)
B2	0.4100(2)	0.28633(19)	0.28232(15)	0.0471(5)
C1	0.30086(14)	0.48894(13)	0.71670(11)	0.0369(3)
C2	0.23159(14)	0.45774(12)	0.61122(11)	0.0359(3)
C3	0.17927(14)	0.33626(12)	0.55564(11)	0.0361(3)
C4	0.23208(14)	0.34194(12)	0.45546(11)	0.0326(3)

C5	0.31503(16)	0.44912(12)	0.52218(11)	0.0371(3)
C6	0.13207(18)	0.36468(15)	0.38489(13)	0.0489(4)
C7	0.26700(15)	0.53205(13)	0.01746(12)	0.0392(3)
C8	0.34174(16)	0.56628(14)	0.10964(13)	0.0426(4)
C9	0.45289(16)	0.63279(14)	0.11847(13)	0.0453(4)
C10	0.49153(15)	0.66547(14)	0.03932(13)	0.0426(4)
C11	0.41629(15)	0.63046(13)	0.94792(12)	0.0396(3)
C12	0.30398(14)	0.56373(12)	0.93672(11)	0.0344(3)
C13	0.3023(2)	0.5309(2)	0.19656(15)	0.0641(5)
C14	0.61199(19)	0.7382(2)	0.05089(17)	0.0645(6)
C15	0.03494(14)	0.68418(14)	0.87547(12)	0.0407(4)
C16	0.99422(16)	0.78788(16)	0.89116(13)	0.0474(4)
C17	0.06097(19)	0.85856(15)	0.85328(14)	0.0522(4)
C18	0.1683(2)	0.83074(16)	0.80348(15)	0.0539(5)
C19	0.20836(17)	0.72818(14)	0.79004(13)	0.0444(4)
C20	0.14216(14)	0.65440(13)	0.82583(11)	0.0351(3)
C21	0.8820(2)	0.8215(2)	0.94971(19)	0.0711(6)
C22	0.2421(3)	0.9116(2)	0.7666(2)	0.0907(9)
C23	0.56510(14)	0.24970(13)	0.47283(12)	0.0377(3)
C24	0.65519(15)	0.22992(14)	0.53742(14)	0.0453(4)
C25	0.61727(16)	0.17137(15)	0.59964(13)	0.0473(4)
C26	0.49283(16)	0.13203(13)	0.59825(12)	0.0400(4)
C27	0.40416(14)	0.15100(12)	0.53136(11)	0.0341(3)
C28	0.43931(13)	0.21081(11)	0.46885(10)	0.0311(3)
C29	0.79204(17)	0.2697(2)	0.53894(19)	0.0678(6)
C30	0.4531(2)	0.06822(16)	0.66562(14)	0.0526(4)
C31	0.26691(15)	0.03334(13)	0.23348(12)	0.0399(4)
C32	0.20427(18)	0.92824(14)	0.18698(13)	0.0486(4)
C33	0.10107(19)	0.89866(14)	0.23020(15)	0.0533(5)
C34	0.05788(17)	0.97066(15)	0.31808(14)	0.0488(4)
C35	0.12303(15)	0.07547(13)	0.36388(12)	0.0399(3)
C36	0.22863(14)	0.10699(12)	0.32230(11)	0.0324(3)
C37	0.2503(3)	0.84995(19)	0.09215(17)	0.0764(7)
C38	0.9448(2)	0.9343(2)	0.3628(2)	0.0734(7)

Bond lengths (Å) for 2-66:

P1-C12	1.8113(15)	P1-C1	1.8200(15)
P1-C20	1.8216(16)	P1-B1	1.9184(19)
P2-C36	1.8116(14)	P2-C28	1.8164(14)
P2-C4	1.8340(15)	P2-B2	1.9285(17)
B1-H1B1	1.12(3)	B1-H1B2	1.07(2)
B1-H1B3	1.12(2)	B2-H2B1	1.13(2)
B2-H2B2	1.10(2)	B2-H2B3	1.19(2)
C1-C2	1.523(2)	C1-H1A	0.98
C1-H1B	0.98	C2-C3	1.542(2)
C2-C5	1.550(2)	C2-H2A	0.99
C3-C4	1.5595(19)	C3-H3A	0.98
C3-H3B	0.98	C4-C6	1.533(2)
C4-C5	1.557(2)	C5-H5A	0.98
C5-H5B	0.98	C6-H6A	0.97
C6-H6B	0.97	C6-H6C	0.97
C7-C12	1.391(2)	C7-C8	1.395(2)
C7-H7A	0.94	C8-C9	1.389(3)
C8-C13	1.505(2)	C9-C10	1.383(2)
C9-H9A	0.94	C10-C11	1.389(2)
C10-C14	1.505(2)	C11-C12	1.395(2)
C11-H11A	0.94	C13-H13A	0.97
C13-H13B	0.97	C13-H13C	0.97
C14-H14A	0.97	C14-H14B	0.97
C14-H14C	0.97	C15-C20	1.389(2)
C15-C16	1.396(3)	C15-H15A	0.94
C16-C17	1.377(3)	C16-C21	1.502(3)
C17-C18	1.387(3)	C17-H17A	0.94
C18-C19	1.385(3)	C18-C22	1.506(3)
C19-C20	1.386(2)	C19-H19A	0.94
C21-H21A	0.97	C21-H21B	0.97
C21-H21C	0.97	C22-H22A	0.97
C22-H22B	0.97	C22-H22C	0.97
C23-C24	1.386(2)	C23-C28	1.394(2)
C23-H23A	0.94	C24-C25	1.390(3)
C24-C29	1.514(2)	C25-C26	1.388(3)
C25-H25A	0.94	C26-C27	1.393(2)
C26-C30	1.505(2)	C27-C28	1.397(2)

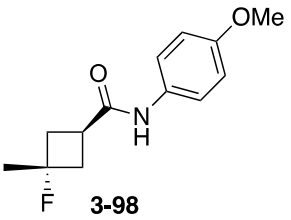
C27-H27A	0.94	C29-H29A	0.97
C29-H29B	0.97	C29-H29C	0.97
C30-H30A	0.97	C30-H30B	0.97
C30-H30C	0.97	C31-C32	1.391(2)
C31-C36	1.390(2)	C31-H31A	0.94
C32-C33	1.378(3)	C32-C37	1.505(3)
C33-C34	1.394(3)	C33-H33A	0.94
C34-C35	1.397(2)	C34-C38	1.507(3)
C35-C36	1.395(2)	C35-H35A	0.94
C37-H37A	0.97	C37-H37B	0.97
C37-H37C	0.97	C38-H38A	0.97
C38-H38B	0.97	C38-H38C	0.97

Bond angles (°) for 2-66:

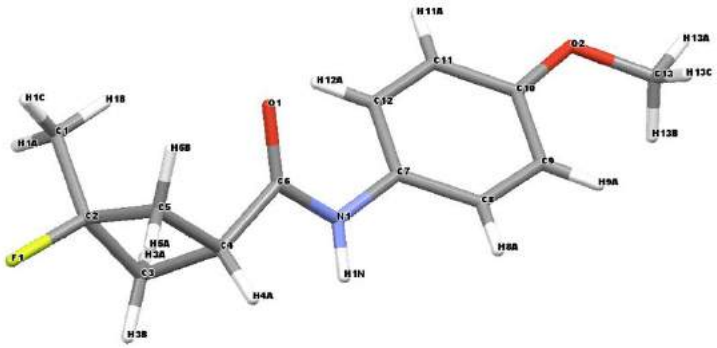
C12-P1-C1	105.45(7)	C12-P1-C20	102.99(7)
C1-P1-C20	106.08(7)	C12-P1-B1	113.92(9)
C1-P1-B1	112.26(9)	C20-P1-B1	115.18(9)
C36-P2-C28	104.87(6)	C36-P2-C4	109.45(7)
C28-P2-C4	107.39(7)	C36-P2-B2	113.35(8)
C28-P2-B2	111.13(8)	C4-P2-B2	110.37(8)
P1-B1-H1B1	102.4(13)	P1-B1-H1B2	104.9(13)
H1B1-B1-H1B2	114.2(18)	P1-B1-H1B3	109.5(12)
H1B1-B1-H1B3	111.8(17)	H1B2-B1-H1B3	113.1(17)
P2-B2-H2B1	104.2(11)	P2-B2-H2B2	102.3(10)
H2B1-B2-H2B2	111.1(16)	P2-B2-H2B3	106.6(10)
H2B1-B2-H2B3	115.3(15)	H2B2-B2-H2B3	115.7(15)
C2-C1-P1	114.11(10)	C2-C1-H1A	108.7
P1-C1-H1A	108.7	C2-C1-H1B	108.7
P1-C1-H1B	108.7	H1A-C1-H1B	107.6
C1-C2-C3	118.42(13)	C1-C2-C5	115.84(13)
C3-C2-C5	88.73(11)	C1-C2-H2A	110.7
C3-C2-H2A	110.7	C5-C2-H2A	110.7
C2-C3-C4	89.55(11)	C2-C3-H3A	113.7
C4-C3-H3A	113.7	C2-C3-H3B	113.7
C4-C3-H3B	113.7	H3A-C3-H3B	111.0
C6-C4-C3	112.14(13)	C6-C4-C5	112.06(13)
C3-C4-C5	87.83(10)	C6-C4-P2	109.88(11)
C3-C4-P2	121.35(10)	C5-C4-P2	111.82(10)

C2-C5-C4	89.36(11)	C2-C5-H5A	113.8
C4-C5-H5A	113.8	C2-C5-H5B	113.8
C4-C5-H5B	113.8	H5A-C5-H5B	111.0
C4-C6-H6A	109.5	C4-C6-H6B	109.5
H6A-C6-H6B	109.5	C4-C6-H6C	109.5
H6A-C6-H6C	109.5	H6B-C6-H6C	109.5
C12-C7-C8	120.42(15)	C12-C7-H7A	119.8
C8-C7-H7A	119.8	C7-C8-C9	118.32(15)
C7-C8-C13	120.36(17)	C9-C8-C13	121.32(17)
C10-C9-C8	122.31(15)	C10-C9-H9A	118.8
C8-C9-H9A	118.8	C9-C10-C11	118.69(15)
C9-C10-C14	121.36(16)	C11-C10-C14	119.94(16)
C10-C11-C12	120.37(15)	C10-C11-H11A	119.8
C12-C11-H11A	119.8	C7-C12-C11	119.89(14)
C7-C12-P1	118.94(12)	C11-C12-P1	121.05(12)
C8-C13-H13A	109.5	C8-C13-H13B	109.5
H13A-C13-H13B	109.5	C8-C13-H13C	109.5
H13A-C13-H13C	109.5	H13B-C13-H13C	109.5
C10-C14-H14A	109.5	C10-C14-H14B	109.5
H14A-C14-H14B	109.5	C10-C14-H14C	109.5
H14A-C14-H14C	109.5	H14B-C14-H14C	109.5
C20-C15-C16	120.91(16)	C20-C15-H15A	119.5
C16-C15-H15A	119.5	C17-C16-C15	118.22(16)
C17-C16-C21	121.28(19)	C15-C16-C21	120.49(18)
C16-C17-C18	121.91(17)	C16-C17-H17A	119.0
C18-C17-H17A	119.0	C17-C18-C19	119.03(17)
C17-C18-C22	120.64(19)	C19-C18-C22	120.32(19)
C20-C19-C18	120.50(17)	C20-C19-H19A	119.7
C18-C19-H19A	119.8	C19-C20-C15	119.40(16)
C19-C20-P1	121.93(12)	C15-C20-P1	118.39(12)
C16-C21-H21A	109.5	C16-C21-H21B	109.5
H21A-C21-H21B	109.5	C16-C21-H21C	109.5
H21A-C21-H21C	109.5	H21B-C21-H21C	109.5
C18-C22-H22A	109.5	C18-C22-H22B	109.5
H22A-C22-H22B	109.5	C18-C22-H22C	109.5
H22A-C22-H22C	109.5	H22B-C22-H22C	109.5
C24-C23-C28	121.15(14)	C24-C23-H23A	119.4
C28-C23-H23A	119.4	C23-C24-C25	118.50(15)

C23-C24-C29	120.72(17)	C25-C24-C29	120.77(17)
C26-C25-C24	121.96(15)	C26-C25-H25A	119.0
C24-C25-H25A	119.0	C25-C26-C27	118.61(15)
C25-C26-C30	121.43(16)	C27-C26-C30	119.96(16)
C26-C27-C28	120.68(14)	C26-C27-H27A	119.7
C28-C27-H27A	119.7	C23-C28-C27	119.09(14)
C23-C28-P2	118.92(11)	C27-C28-P2	121.98(11)
C24-C29-H29A	109.5	C24-C29-H29B	109.5
H29A-C29-H29B	109.5	C24-C29-H29C	109.5
H29A-C29-H29C	109.5	H29B-C29-H29C	109.5
C26-C30-H30A	109.5	C26-C30-H30B	109.5
H30A-C30-H30B	109.5	C26-C30-H30C	109.5
H30A-C30-H30C	109.5	H30B-C30-H30C	109.5
C32-C31-C36	121.45(16)	C32-C31-H31A	119.3
C36-C31-H31A	119.3	C33-C32-C31	118.37(16)
C33-C32-C37	121.76(18)	C31-C32-C37	119.9(2)
C32-C33-C34	122.11(16)	C32-C33-H33A	118.9
C34-C33-H33A	118.9	C33-C34-C35	118.45(17)
C33-C34-C38	120.15(18)	C35-C34-C38	121.39(19)
C36-C35-C34	120.56(16)	C36-C35-H35A	119.7
C34-C35-H35A	119.7	C35-C36-C31	119.04(14)
C35-C36-P2	124.30(12)	C31-C36-P2	116.57(12)
C32-C37-H37A	109.5	C32-C37-H37B	109.5
H37A-C37-H37B	109.5	C32-C37-H37C	109.5
H37A-C37-H37C	109.5	H37B-C37-H37C	109.5
C34-C38-H38A	109.5	C34-C38-H38B	109.5
H38A-C38-H38B	109.5	C34-C38-H38C	109.5
H38A-C38-H38C	109.5	H38B-C38-H38C	109.5



3-98



Sample and crystal data for 3-98:

Identification code	jam81878	
Chemical formula	$C_{13}H_{16}FNO_2$	
Formula weight	237.27 g/mol	
Temperature	230(2) K	
Wavelength	1.54178 Å	
Crystal size	0.008 x 0.030 x 0.160 mm	
Crystal system	orthorhombic	
Space group	P b c a	
Unit cell dimensions	a = 8.9568(11) Å	α = 90°
	b = 11.5358(14) Å	β = 90°
	c = 24.472(3) Å	γ = 90°
Volume	2528.5(6) $Å^3$	
Z	8	
Density (calculated)	1.247 g/cm^3	
Absorption coefficier	0.778 mm^{-1}	
F(000)	1008	

Data collection and structure refinement for 3-98:

Theta range for data collection	3.61 to 68.24°
Index ranges	-10<=h<=10, -13<=k<=13, -29<=l<=24
Reflections collected	19125
Independent reflections	2309 [R(int) = 0.1553]
Max. and min. transmission	0.7500 and 0.3400
Structure soluti technique	direct methods

Structure soluti program	SHELXT 2014/4 (Sheldrick, 2014)	
Refinement meth	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2016/6 (Sheldrick, 2016)	
Function minimiz	$\Sigma\ w(F_o^2 - F_c^2)^2$	
Data / restraints parameters	2309 / 0 / 160	
Goodness-of-fit o	1.000	
Final R indices	1047 data; I>2σ(I)	R1 = 0.0587, wR2 = 0.1453
	all data	R1 = 0.1376, wR2 = 0.1924
Weighting schem	$w=1/[\sigma^2(F_o^2)+(0.0866P)^2]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. pe and hole	0.190 and -0.163 eÅ^{-3}	
R.M.S. deviati from mean	0.036 eÅ^{-3}	

Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for 3-

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	**y/b**	**z/c**	**U(eq)**
O1	0.1658(2)	0.2099(2)	0.20833(11)	0.0881(9)
N1	0.3726(3)	0.2658(3)	0.25405(13)	0.0743(9)
F1	0.4198(3)	0.1106(3)	0.04365(11)	0.1451(12)
C1	0.2177(5)	0.2229(6)	0.0737(2)	0.145(2)
C2	0.3527(4)	0.1543(4)	0.09125(18)	0.0969(13)
O2	0.1180(3)	0.5585(2)	0.40871(14)	0.1059(10)
C3	0.4619(5)	0.2137(4)	0.12880(19)	0.1062(15)
C4	0.4023(4)	0.1408(3)	0.17685(16)	0.0810(11)
C5	0.3238(4)	0.0642(3)	0.13499(19)	0.0930(13)
C6	0.3011(3)	0.2069(3)	0.21450(16)	0.0729(10)
C7	0.3060(3)	0.3389(3)	0.29391(16)	0.0668(9)
C8	0.3536(4)	0.3338(3)	0.34713(17)	0.0789(11)
C9	0.2972(4)	0.4060(3)	0.38702(17)	0.0819(11)
C10	0.1850(4)	0.4842(3)	0.37262(18)	0.0797(11)

	x/a	y/b	z/c	U(eq)
C11	0.1361(4)	0.4887(3)	0.31983(19)	0.0824(11)
C12	0.1951(4)	0.4179(3)	0.28017(16)	0.0745(10)
C13	0.1727(5)	0.5652(5)	0.4624(2)	0.1249(18)

Bond lengths (Å) for 3-98:

O1-C6	1.221(3)	N1-C6	1.345(4)
N1-C7	1.421(4)	N1-H1N	0.89(3)
F1-C2	1.405(4)	C1-C2	1.507(6)
C1-H1A	0.97	C1-H1B	0.97
C1-H1C	0.97	C2-C3	1.507(6)
C2-C5	1.515(6)	O2-C10	1.369(4)
O2-C13	1.404(5)	C3-C4	1.540(5)
C3-H3A	0.98	C3-H3B	0.98
C4-C6	1.501(5)	C4-C5	1.525(5)
C4-H4A	0.99	C5-H5A	0.98
C5-H5B	0.98	C7-C8	1.372(5)
C7-C12	1.390(4)	C8-C9	1.379(5)
C8-H8A	0.94	C9-C10	1.396(5)
C9-H9A	0.94	C10-C11	1.365(5)
C11-C12	1.373(5)	C11-H11A	0.94
C12-H12A	0.94	C13-H13A	0.97
C13-H13B	0.97	C13-H13C	0.97

Bond angles (°) for 3-98:

C6-N1-C7	126.4(3)	C6-N1-H1N	119.(2)
C7-N1-H1N	115.(2)	C2-C1-H1A	109.5
C2-C1-H1B	109.5	H1A-C1-H1B	109.5
C2-C1-H1C	109.5	H1A-C1-H1C	109.5
H1B-C1-H1C	109.5	F1-C2-C1	107.2(4)
F1-C2-C3	113.0(3)	C1-C2-C3	117.1(4)
F1-C2-C5	114.4(4)	C1-C2-C5	115.1(4)
C3-C2-C5	89.5(3)	C10-O2-C13	119.0(4)
C2-C3-C4	89.6(3)	C2-C3-H3A	113.7
C4-C3-H3A	113.7	C2-C3-H3B	113.7
C4-C3-H3B	113.7	H3A-C3-H3B	111.0

C6-C4-C5	115.3(3)	C6-C4-C3	113.6(3)
C5-C4-C3	87.9(3)	C6-C4-H4A	112.6
C5-C4-H4A	112.6	C3-C4-H4A	112.6
C2-C5-C4	89.9(3)	C2-C5-H5A	113.7
C4-C5-H5A	113.7	C2-C5-H5B	113.7
C4-C5-H5B	113.7	H5A-C5-H5B	110.9
O1-C6-N1	123.2(3)	O1-C6-C4	122.5(3)
N1-C6-C4	114.2(3)	C8-C7-C12	118.7(3)
C8-C7-N1	119.8(3)	C12-C7-N1	121.6(3)
C7-C8-C9	122.2(4)	C7-C8-H8A	118.9
C9-C8-H8A	118.9	C8-C9-C10	118.4(4)
C8-C9-H9A	120.8	C10-C9-H9A	120.8
C11-C10-O2	116.5(4)	C11-C10-C9	119.6(4)
O2-C10-C9	123.9(4)	C10-C11-C12	121.5(4)
C10-C11-H11A	119.2	C12-C11-H11A	119.2
C11-C12-C7	119.6(4)	C11-C12-H12A	120.2
C7-C12-H12A	120.2	O2-C13-H13A	109.5
O2-C13-H13B	109.5	H13A-C13-H13B	109.5
O2-C13-H13C	109.5	H13A-C13-H13C	109.5
H13B-C13-H13C	109.5		

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