Studies on the Structure/Reactivity Relationships of Bicyclic Epoxonium Ions and Tethered Nucleophiles. Efforts towards the Total Synthesis of (+)-Lactodehydrothyrsiferol and its Analogs. Multicomponent Approach to the Synthesis of Oxidized Amides through Nitrile Hydrozirconation

by

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Shuangyi Wan, PhD

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A systematic study on the structure/reactivity relationships of bicyclic epoxonium ions towards tethered nucleophiles has been conducted. The cyclization results show that bicyclo[3.1.0] epoxonium ions have a significant to exclusive preference for *exo*-cyclizations while bicyclo[4.1.0] epoxonium ions have a strong preference for *endo*-cyclizations.

A convergent approach towards the total synthesis of polycyclic ether natural product (+)-lactodehydrothyrsiferol and its analogs is currently being pursued. This route includes the stereoselective reduction of the bicyclo[3.2.1] ketal which could be prepared from coupling of the functionalized aldehyde and vinyl iodide. Both enantiopure fragments can be obtained from cyclizations of the diepoxide and the monoepoxide, respectively. Key transformations involve two asymmetric epoxidations, a cascade cyclization of diepoxide, a Cr/Ni-mediated coupling reaction and a stereoselective reduction of bicyclo[3.2.1] ketal.

An efficient one-pot synthesis of oxidized amides from nitrile hydrozirconation has been developed. From the common acylimine intermediates, acyl aminals can be accessed through alcohol addition, acyl hemiaminals can be accessed through water addition and enamides can be accessed through tautomerization.

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1.0 STUDIES ON THE STRUCTURE/REACTIVITY RELATIONSHIPS OF BICYCLIC EPOXONIUM IONS AND TETHERED NUCLEOPHILES

1.1 INTRODUCTION

Polycyclic ether structures (Figure 1), which have been discovered in a number of marine natural products, have gained considerable attention from synthetic community due not only to their intrinsically complex structures but also to their interesting biological activities.[1,2] From a biosynthetic view of point, these compounds have been proposed to arise from cascade cyclizations from the requisite polyepoxide precursors.[3-5] A key issue associated in this process is the strict regiochemical control, i.e., *exo*- vs *endo*-cyclization (Figure 2). As can be envisioned in Figure 1, hemibrevetoxin B[5] could be prepared from the polyepoxide through all *endo*-cyclization, bullatacin[6] could be prepared from the polyepoxide precursor through all *exo*-cyclization and lactodehydrothyrsiferol[7] could be prepared from the polyepoxide through a combination of *exo*- and *endo*-cyclizations.

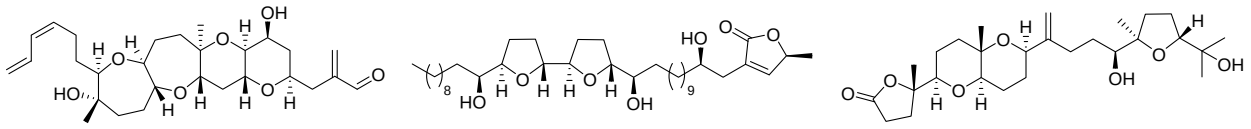


Figure 1. Representative polyether natural products

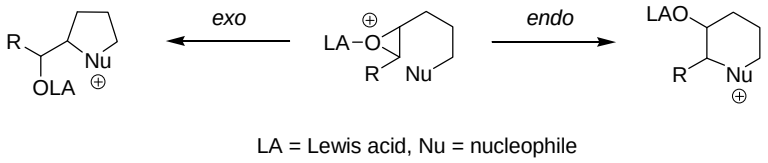


Figure 2. *Exo*- vs *endo*-cyclization

The *exo*-pathway is well known and commonly observed from studies on intramolecular cyclizations through epoxide opening. For example, epoxy alcohol **1.1**, under acidic conditions, afforded tetrahydrofuran derivative **1.3** predominantly through *exo*-pathway transition state **1.2** (Figure 3).[8] However, in the presence of the catalytic antibody IgG26D9 elicited from amine oxide antigen **1.4**, tetrahydropyran **1.6** was isolated as the sole product from *endo*-cyclization,[8] which formally violated the Baldwin's rules[9] for ring closure reactions.

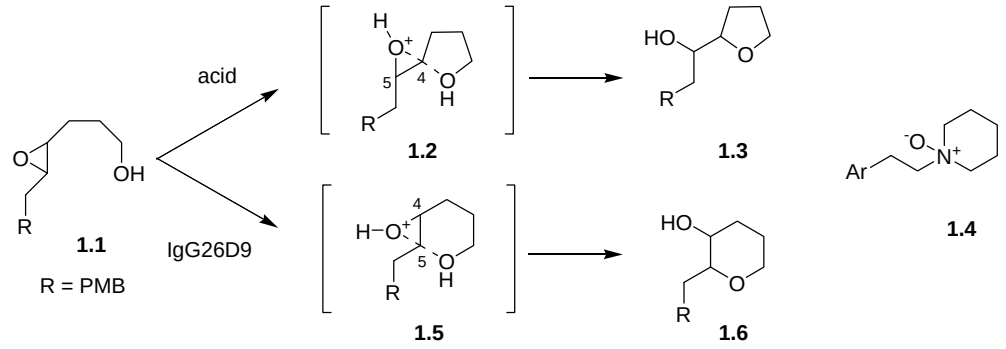


Figure 3. Cyclizations of epoxy alcohol under acid- and antibody-catalyzed conditions

Ab initio calculations performed by Houk[10,11] and Coxon[12,13] showed that under acid-catalyzed conditions, the *exo*-transition structure (TS) has a nearly ideal trajectory for the attack of the hydroxyl oxygen atom via an S_N2 manner and therefore has lower energy than *endo*-TS, resulting in the formation of **1.3** as the major product through a kinetically and chemically

favored process. The exclusive formation of **1.6** under antibody-catalyzed (enzymatic) conditions was attributed to the similarity between *endo*-TS **1.5** and *N*-oxide **1.4**. Calculations showed that *endo*-cyclization proceeds through an S_N1-type transition structure.

Due to the difficulty in the polycyclic ether formation through *endo*-pathway and the high efficiency in increasing complexity in cascade cyclizations of polyepoxides, a number of researchers have been involved in investigating the epoxide opening cascades. Murai and co-workers[14] first reported *endo*-selective cascade cyclizations of polyepoxides (Figure 4). Diepoxy alcohol **1.7**, when treated with $La(OTf)_3$, provided fused bicyclic product **1.8** in 52% yield. Unfortunately, when the conditions were applied to triepoxy alcohol **1.9**, the cyclization efficiency decreased drastically and only 9.3% of the desired tricycle **1.10** was obtained from all *endo*-cyclization. In addition, the proposed mechanism requires the presence of chelation of La(III) ion with the epoxide oxygen and the pendent methoxy oxygen to promote the *endo*-selectivity, which also limits its potential applications in natural product synthesis.

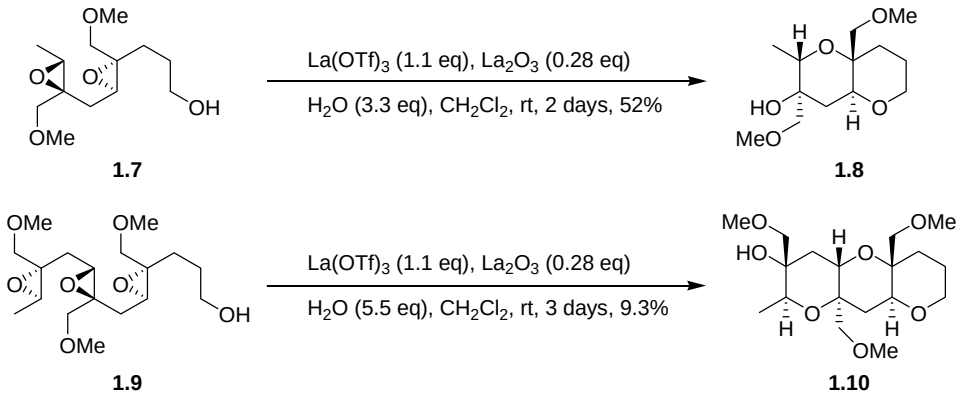


Figure 4. *Endo*-selective cascade cyclizations of polyepoxides in Murai group

At nearly the same time, McDonald and co-workers[15,16] studied epoxide opening cascades under Lewis-acid-promoted conditions, and demonstrated that *endo*-cyclizations could be

achieved in high efficiency with rationally designed substrates. Some representative examples are shown in Figure 5.

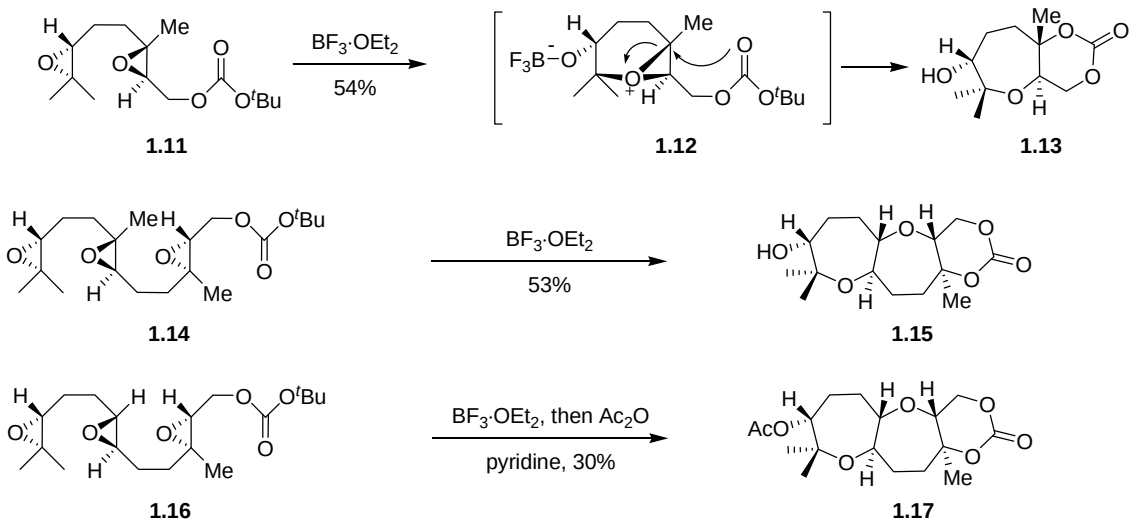


Figure 5. Representative *endo*-selective cyclizations of polyepoxides in McDonald group

McDonald postulated that bicyclic epoxonium ions are key intermediates in cascade cyclizations of epoxides to generate polycyclic ethers and that *endo*-cyclizations were favored over *exo*-cyclizations due to the increased ring strain in *exo*-TSs (bicyclo[3.1.0] epoxonium ions).[15] As illustrated in Figure 6, bicyclo[4.1.0] epoxonium ion **1.20** (from *endo*-cyclization) is presumed to be energetically lower than bicyclo[3.1.0] intermediate **1.19** (from *exo*-cyclization) in the initial cyclization as well as a similar comparison between bicyclo[4.1.0] ion **1.22** and bicyclo[3.1.0] ion **1.21** in the ensuing cyclization, leading to the formation of *trans*-fused tricycle **1.23** with excellent *endo*-selectivity.

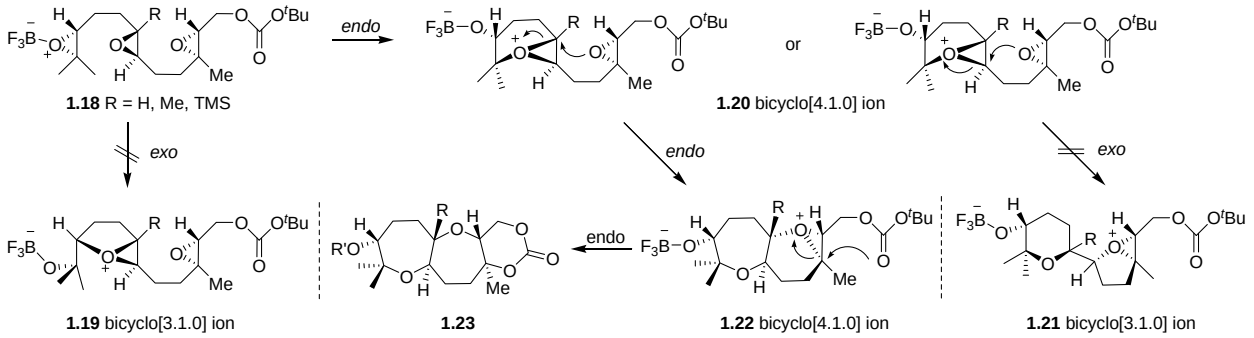


Figure 6. Hypothesis for regioselective cascade cyclizations

McDonald also observed that terminal nucleophiles can also affect the stereochemical outcomes and/or regioselectivity (Figure 7).[17] Cyclization of diepoxide **1.24** with a *t*-butyl carbonate group as the terminal nucleophile provided *cis*-fused bicycle **1.28** which arose from the addition of the carbonate carbonyl to the tertiary carbocation **1.26** via an S_N1 fashion as the predominant product. Alternatively, the cyclization of diepoxide **1.29** with the better terminal nucleophile dimethyl carbamate gave *trans*-fused bicycle **1.27** as the major product which came from direct attack of the carbamate carbonyl to the epoxonium ion **1.25** through an S_N2 pathway. Interestingly, triepoxy *t*-butyl carbonate **1.30**, upon cyclization, afforded mainly tricyclic structure **1.32** which came from a combination of *endo*-cyclization and *exo*-cyclization and has a *cis*-ring fusion between the six- and five-membered cyclic ethers. In this case, only trace amount of all-fused *trans*,*trans*-tricycle **1.31** was obtained. On the other hand, reaction of dimethylcarbamate triepoxide **1.33** produced desired tricycle **1.31** in good yield, with **1.32** not being observed.

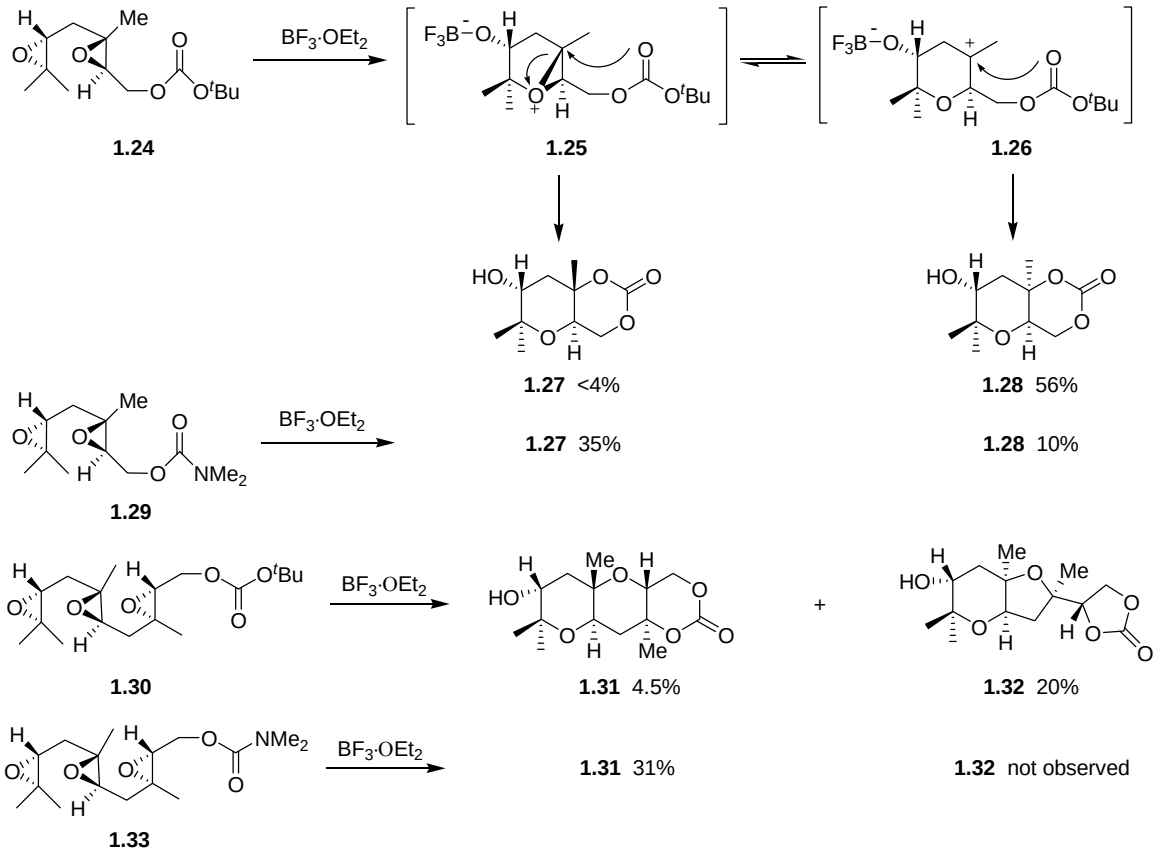


Figure 7. Impact of terminal nucleophiles on stereospecificity and regioselectivity

Besides acidic conditions, cyclizations of epoxides can also be performed under basic[18], neutral[19] and oxidative[20,21] conditions. Jamison and co-workers demonstrated that diepoxide **1.34A** and triepoxide **1.35A**, under basic conditions in the protic solvent MeOH, provided THP triad **1.34B** and tetrad **1.35B**, respectively, in good yields, with the TMS group as a "disappearing" directing group.[18] Without the "disappearing directing groups", the diepoxide **1.36A** and triepoxide **1.37A**, under essentially neutral conditions, delivered triad **1.36B** and tetrad **1.37B**, respectively, in excellent yields.[19] In the total synthesis of hemibrevetoxin B, Holton developed a novel intramolecular epoxide opening cascade initiated by oxidation of the alkene with *N*-(phenylseleno)phthalimide to effect the formation of **1.39** in excellent yield, with

the B and C rings assembled in a single operation (Figure 9).[20] In this process, the highly polar solvent hexafluoroisopropanol was selected for the *endo*-selective epoxide opening through the S_N1-type transition state, which is consistent with the computational analysis.[10,11]

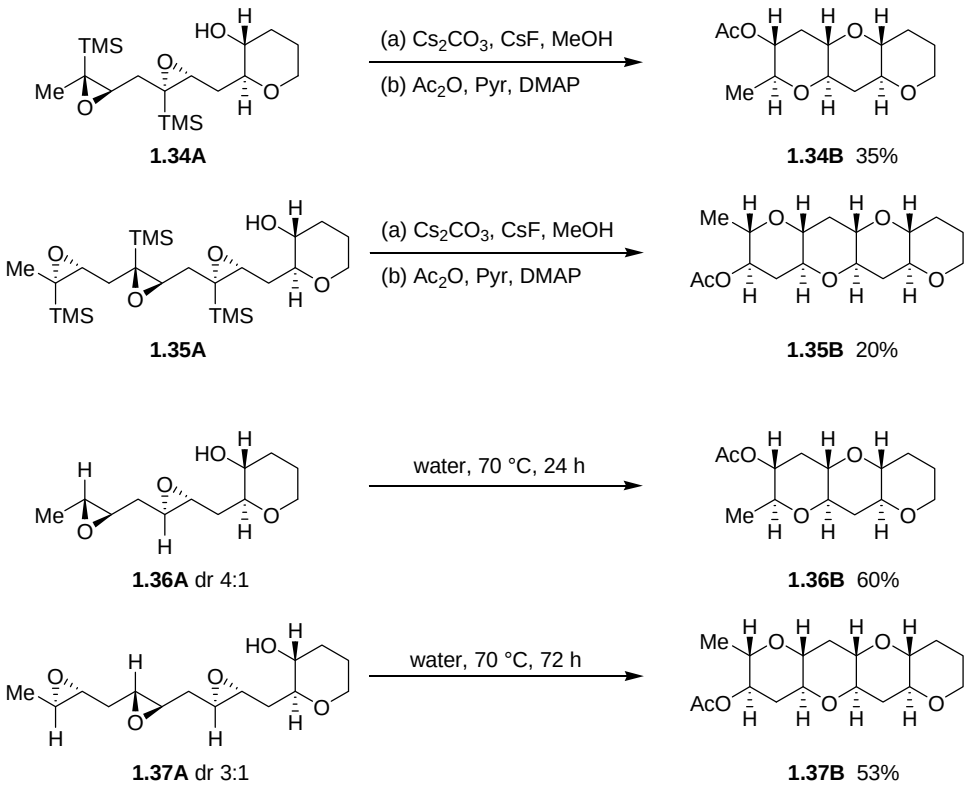


Figure 8. Regioselective epoxide opening cascades under basic and neutral conditions

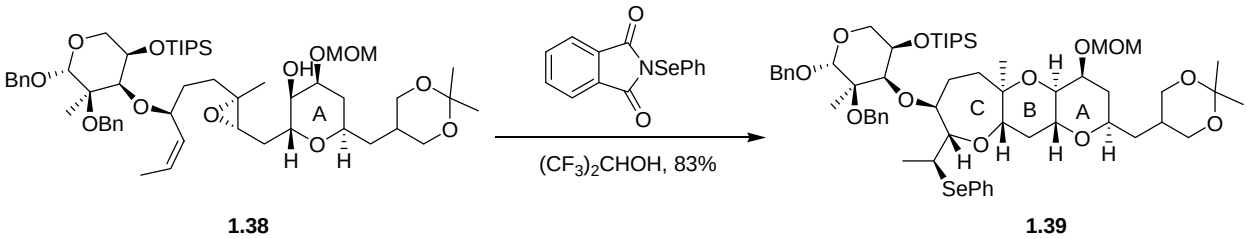
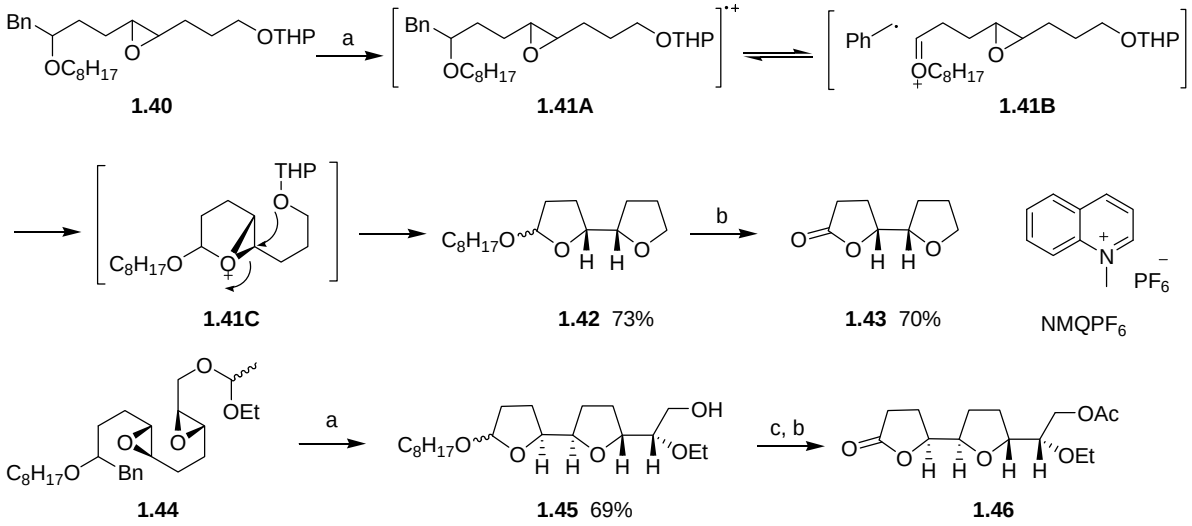


Figure 9. Key transformation in Holton's total synthesis of hemibrevetoxin B

Cascade cyclizations of epoxides/polyepoxides were also studied in my laboratory[22] under electron transfer initiated cyclization (ETIC[23,24]) conditions. These photochemical conditions use medium-pressure mercury lamp as the excitation source, catalytic amount of *N*-methylquinolinium hexafluorophosphate as the sensitizer, O_2 as the ultimate oxidant, 4 Å molecular sieves as moisture scavenger, NaOAc as the base, $Na_2S_2O_3$ as the peroxide remover, 1,2-dichloroethane as the solvent and toluene as the co-sensitizer. Two typical examples are depicted in Figure 10. Under ETIC conditions, homobenzylic ether **1.40** was oxidized to radical cation **1.41A** which fragmented to form the benzyl radical and oxocarbenium ion **1.41B** in a reversible manner. The tethered epoxide attacked the electrophile **1.41B** to generate bicyclic epoxonium ion **1.41C**. The terminal nucleophile THP ether opened the bicyclo[3.1.0] epoxonium ion through *exo*-pathway to deliver bis-THF product **1.42** irreversibly in good yield. Similarly, reaction of diepoxide **1.44** gave rise to the consecutive *exo*,*exo*-cyclization product **1.45** in high efficiency. After removal of the anomeric center with Jones reagent,[25] lactones **1.43** and **1.46** were obtained as single diastereomers, respectively. The regioselectivity observed herein is in accord with Houk and Coxon's computational studies with 5-*exo*-pathway being preferred over 6-*endo*-pathway.



Conditions: (a) *hv*, O_2, $NMQPF_6$ (cat.), NaOAc, $Na_2S_2O_3$, 1,2-dichloroethane (DCE)/PhMe (6:1, v/v). (b) Jones reagent. (c) Ac_2O.

Figure 10. Epoxide opening cascades under electron transfer initiated cyclization conditions

The oxocarbenium ion (Lewis acid) generated under ETIC conditions has the merit that it is able to activate the proximal epoxide specifically so that the complication from possible random activation of epoxides by a Brønsted or Lewis acid can be eliminated, making this method ideal for investigating the reactivity of epoxonium ions with specific structures. In order to examine the factors that can affect the reaction pathways in epoxide opening cascades, a systematic study on the cascade cyclizations of monoepoxides/diepoxides under ETIC conditions has been conducted[26] and details will be discussed in the following context.

1.2 STUDIES ON EPOXIDE OPENING CASCADES UNDER ETIC CONDITIONS

As previously described, regioselectivity in epoxide opening cascades could be influenced by ring strain in the forming bicyclic epoxonium ions, nucleophiles and solvents. Besides these, I was interested in whether other factors such as bicyclic epoxonium structure and Lewis acid selection can also affect the reaction pathways. Towards this end, we prepared substrates shown in Figure 11.

From monoepoxides **1.47-1.50**, oxocarbenium-activated bicyclic epoxonium ion intermediates (bicyclo[3.1.0] epoxonium and bicyclo[4.1.0] epoxonium) with different substitution patterns (disubstituted and trisubstituted) will be formed and compared in terms of their regioselectivity towards terminal nucleophiles. Diepoxides **1.51-1.55** were designed to study the impact of different Lewis acid-activating groups (oxocarbenium ion and non-stabilized carbenium ion) on the regiochemical outcomes as well as the effect of relative stereochemical orientations of epoxides on the cyclization efficiency. Figure 12 shows the corresponding bicyclic epoxonium ion intermediates that will be compared in this study. Also of note is that the more reactive diphenylmethyl group was employed in the monoepoxide substrates **1.47-1.50** instead of benzyl group (*cf*. Figure 10) as the electroauxiliary to initiate the oxocarbenium ion formation due to the reduced nucleophilicity of epoxides by the proximal *t*-butyl carbonate groups. For consistency throughout the studies, the diphenylmethyl group was also incorporated in the diepoxide substrates **1.51-1.55** though benzyl group is sufficiently reactive for this purpose.

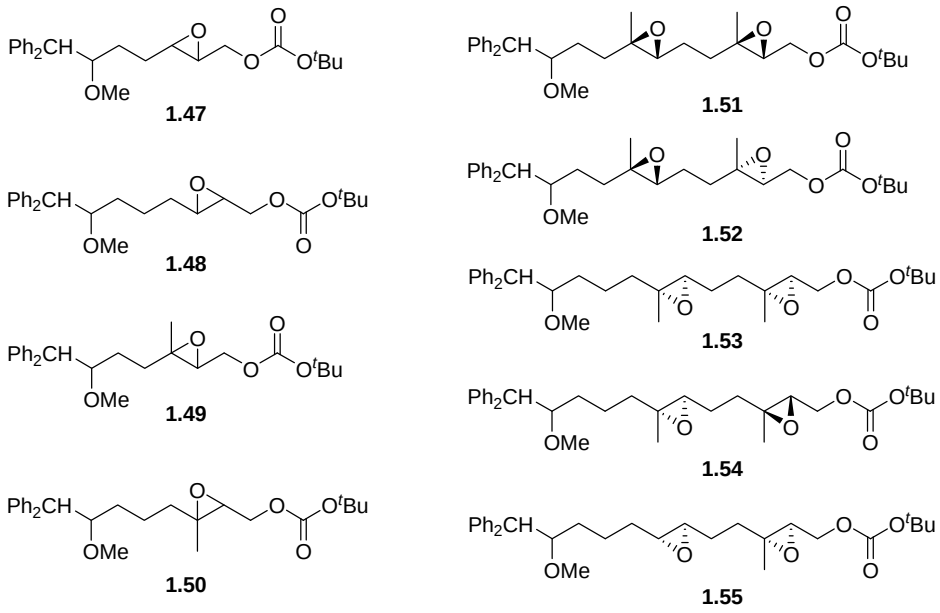


Figure 11. Substrates for cyclizations

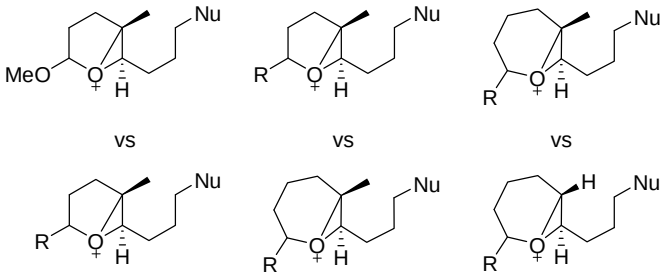


Figure 12. Bicyclic epoxonium ion intermediates to be investigated

1.2.1 Synthesis of epoxide substrates

The synthesis of disubstituted monoepoxide **1.47** proceeded from commercially available 4-pentenal in a straightforward manner (Figure 13). Addition of diphenylmethyllithium to 4-pentenal followed by methylation of the secondary alcohol and cleavage of the terminal alkene afforded aldehyde **1.56**. A sequence of Horner-Emmons olefination, ester reduction, allylic

alcohol epoxidation and primary hydroxyl group protection with Boc_2O[27] provided carbonate **1.47**. Likewise, epoxide **1.48** was prepared from 5-hexenal which was obtained from Swern oxidation of 5-hexen-1-ol.

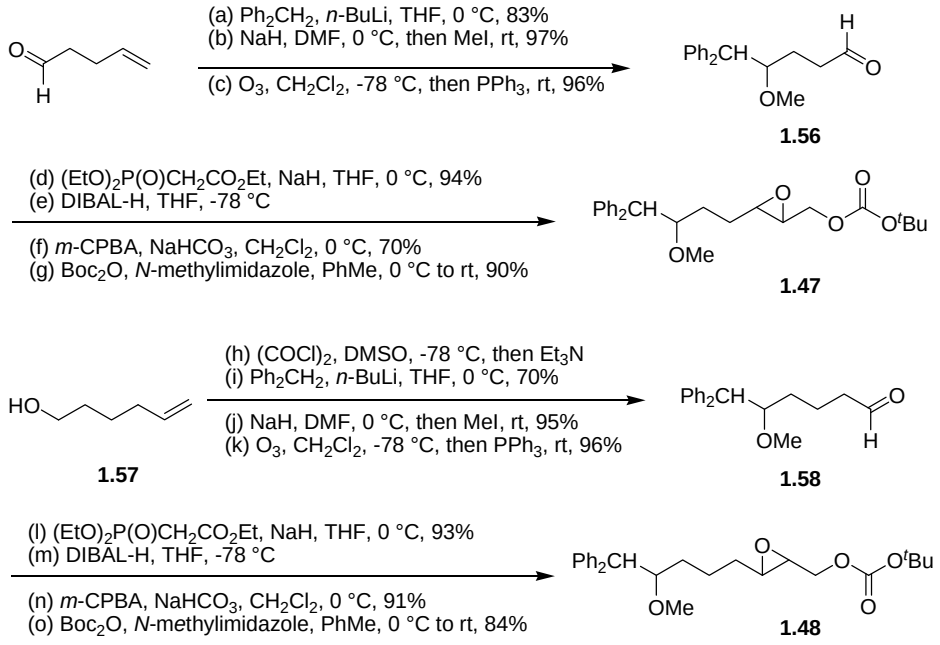


Figure 13. Synthesis of disubstituted monoepoxides **1.47** and **1.48**

The synthesis of trisubstituted monoepoxides **1.49** and **1.50** is illustrated in Figure 14. Opening of epoxide **1.59** using Yamamoto's aluminum-amide promoted protocol[28] followed by Johnson-Claisen rearrangement[29] of the allylic alcohol and reduction of the ethyl ester provided aldehyde **1.60**, which was converted into **1.49** through a sequence of diphenylmethyllithium addition, methylation, silyl ether deprotection, epoxidation and protection of the primary alcohol with Boc_2O. For the synthesis of homologous substrate, aldehyde **1.60** was homologated through Wittig olefination and mercury-mediated enol ether hydrolysis[30] to give the corresponding aldehyde which was further transformed into **1.50** in a similar manner.

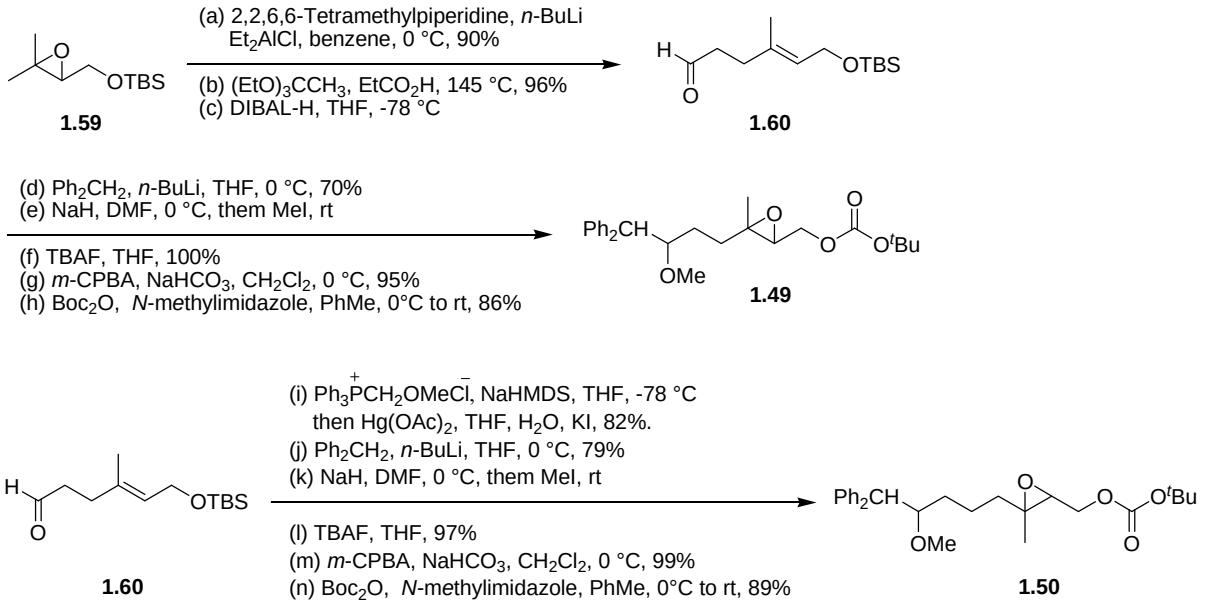


Figure 14. Synthesis of trisubstituted monoepoxides **1.49** and **1.50**

The trisubstituted diepoxides **1.51**-**1.52** were prepared similar to **1.49** and **1.50**. Monoepoxide **1.61** was converted into aldehyde **1.62** in excellent yields through epoxide opening, Johnson-Claisen rearrangement and reduction (Figure 15). Dienol **1.63** was obtained in good yields after a three-step sequence of diphenylmethyllithium addition, methylation and silyl group removal. To ensure the high enantiomeric and diastereomeric control in the epoxidations, asymmetric epoxidation methods were utilized. Dienol **1.63** was converted into diepoxy carbonate **1.51** through double Shi epoxidation[31] and protection of the primary hydroxyl group with Boc_2O in excellent yields. A sequence of Sharpless epoxidation,[32] Shi epoxidation and the primary hydroxyl group protection of **1.63** efficiently provided diastereomeric counterpart **1.52**. The stereochemical orientations of the epoxides in **1.51** and **1.52** were given based on the mechanistic analysis.

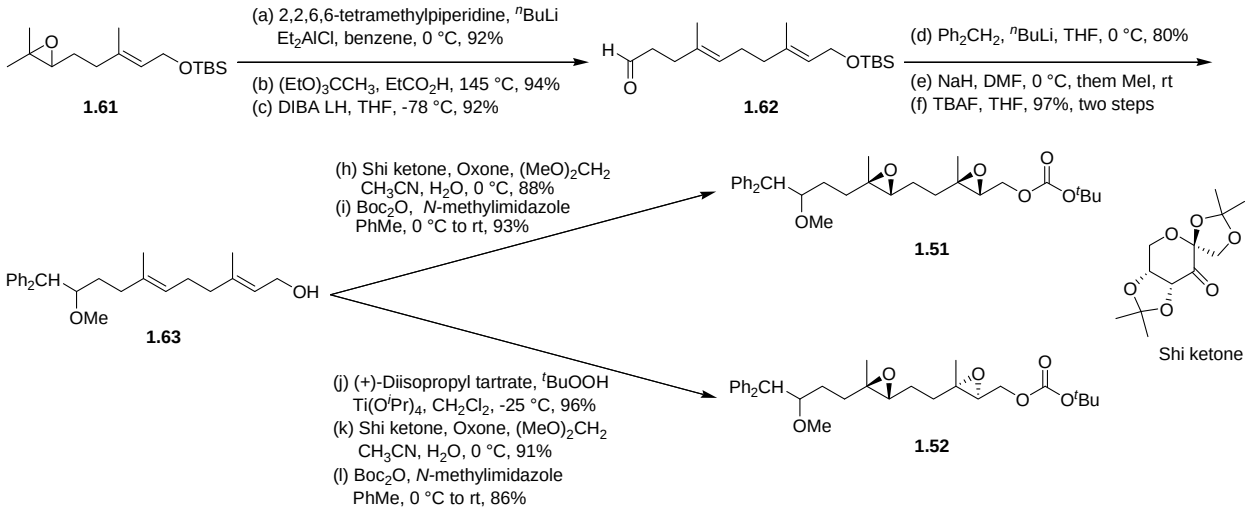


Figure 15. Synthesis of diepoxides **1.51** and **1.52**

Aldehyde **1.62** was homologated to aldehyde **1.64** to prepare diepoxides **1.53** and **1.54** through olefination and mercury-mediated enol ether hydrolysis in 91% yield (Figure 16). Dienol **1.65** was obtained in a similar manner to **1.63** through diphenylmethyllithium addition, methylation and deprotection. Subsequently, dienol **1.65** was converted into carbonate **1.53** through double Shi epoxidation and carbonate formation, or carbonate **1.54** through a sequence of Sharpless epoxidation, Shi epoxidation and carbonate formation.

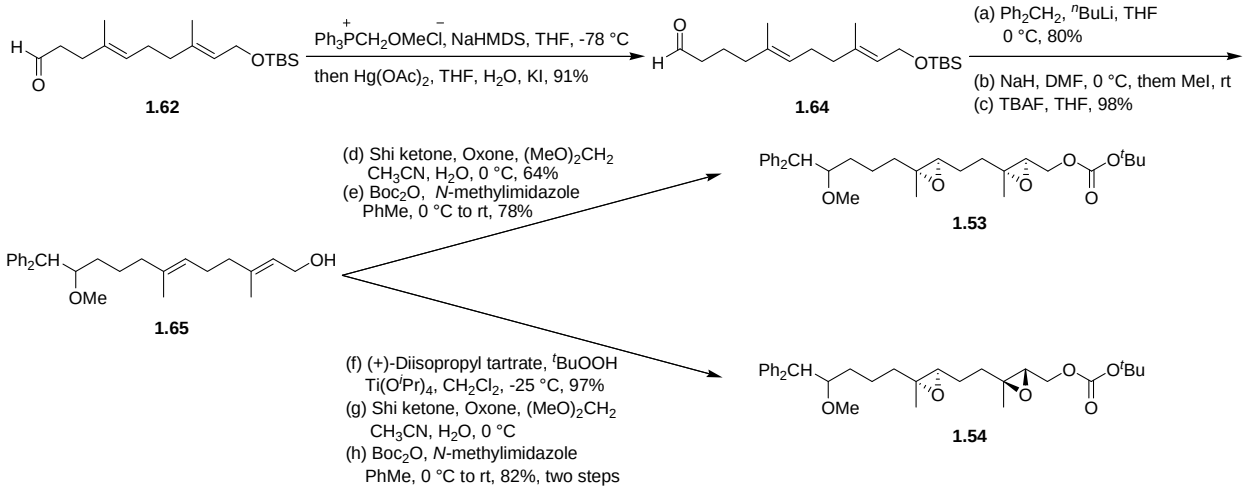


Figure 16. Synthesis of diepoxides **1.53** and **1.54**

Diepoxide **1.55** was prepared in a convergent manner (Figure 17). Reduction of δ-lactone followed by diphenylmethyllithium addition to the crude lactol provided the diol in 82% yield over the two steps, which was converted to sulfone **1.66** through a sequence of Mitsunobu reaction, methylation and oxidation[33] of the resulting sulfide with *m*CPBA. A Kocienski-modified Julia olefination[34] between sulfone **1.66** and aldehyde **1.60** afforded the desired diene in 63% yield. Further operations similar to the synthesis of **1.51** and **1.53** provided carbonate **1.55** in excellent yields.

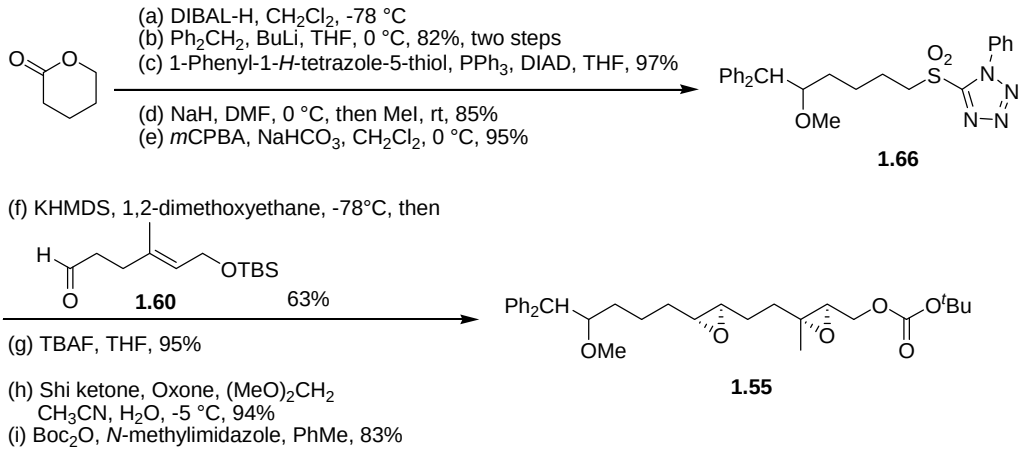


Figure 17. Synthesis of diepoxide **1.55**

1.2.2 Cyclizations of epoxide substrates under ETIC conditions

With these epoxides in hand, I examined their reactions under ETIC conditions to explore the factors that could affect the regioselectivity in the opening of bicyclic epoxonium ions by pendent nucleophiles. First, I carried out the reactions of disubstituted monoepoxides and the cyclization results are illustrated in Figure 18. The reaction of **1.47** exclusively provided 5-*exo*-product **1.68** through a disubstituted bicyclo[3.1.0] epoxonium ion intermediate, which is consistent with the previous observations that disubstituted bicyclo[3.1.0] ions prefer 5-*exo*-cyclization (*cf*. Figure 10).[35] Interestingly, cyclization of the homologated epoxide **1.48** gave a mixture of 5-*exo*- and 6-*endo*-products **1.71** and **1.72,** respectively, with *exo*-pathway being slightly favored. The difference between these two reactions is that the initial cyclization of **1.47** forms a bicyclo[3.1.0] intermediate while the cyclization of **1.48** forms a bicyclo[4.1.0] ion. The *exo*-products were fully characterized by oxidation to the corresponding lactones.[25,36,37]

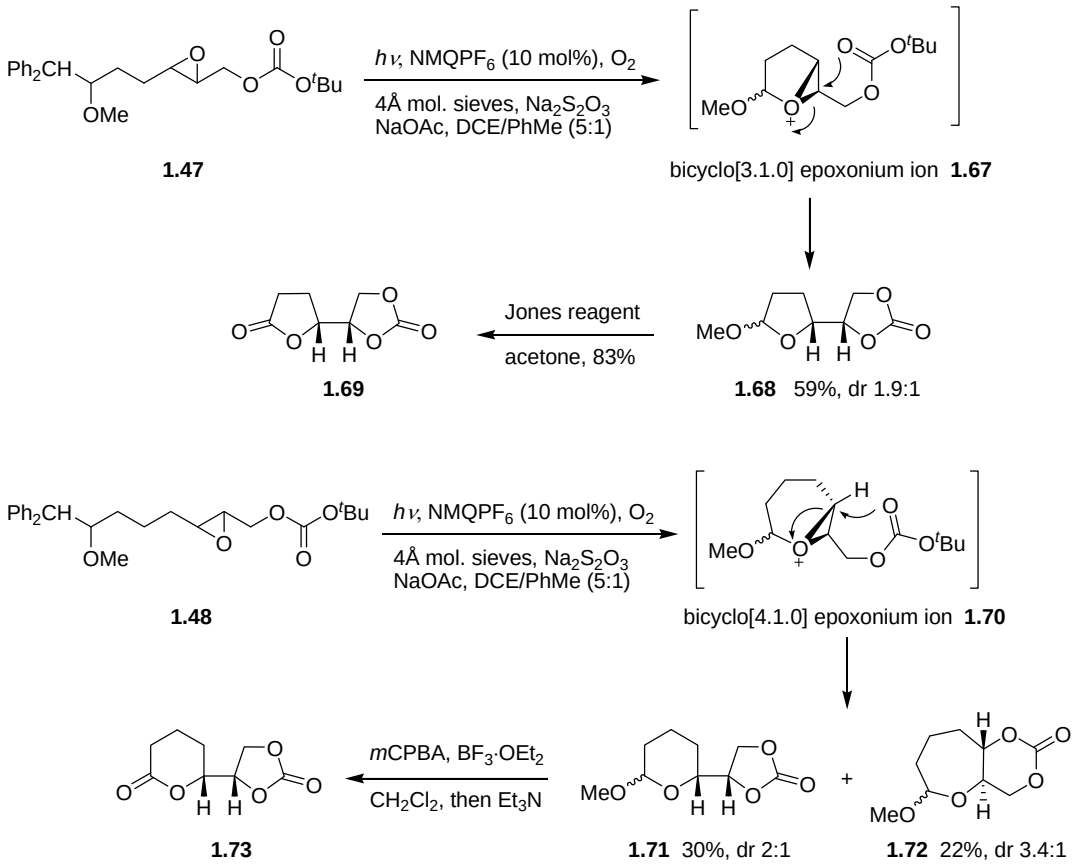


Figure 18. Cyclizations of disubstituted monoepoxides **1.47** and **1.48**

Cyclization of trisubstituted epoxide **1.49** produced a complex mixture of *exo*- and *endo*-products from trisubstituted bicyclo[3.1.0] ion **1.74**. The *trans*-fused *endo*-product **1.77** arose from the S_N2 attack of the carbonate to the epoxonium ion **1.74** while the *syn*-fused *endo*-product **1.78** was from the addition of the carbonate carbonyl oxygen to the tertiary carbocation **1.75** in an S_N1 manner. The formation of **1.78** is in accord with McDonald's observation[17] of *cis*-fused bicycle **1.28** from **1.24** (*cf.* Figure 7). On the contrary, the reaction of **1.50** cleanly afforded *trans*-fused bicycle **1.81** as the only isolable product in excellent yield. These cyclization results clearly demonstrate that the combination of both the methyl substitution and the bicyclo[4.1.0]

epoxonium ion can reverse the regiochemical outcomes from complete *exo*-pathway to exclusive *endo*-pathway.

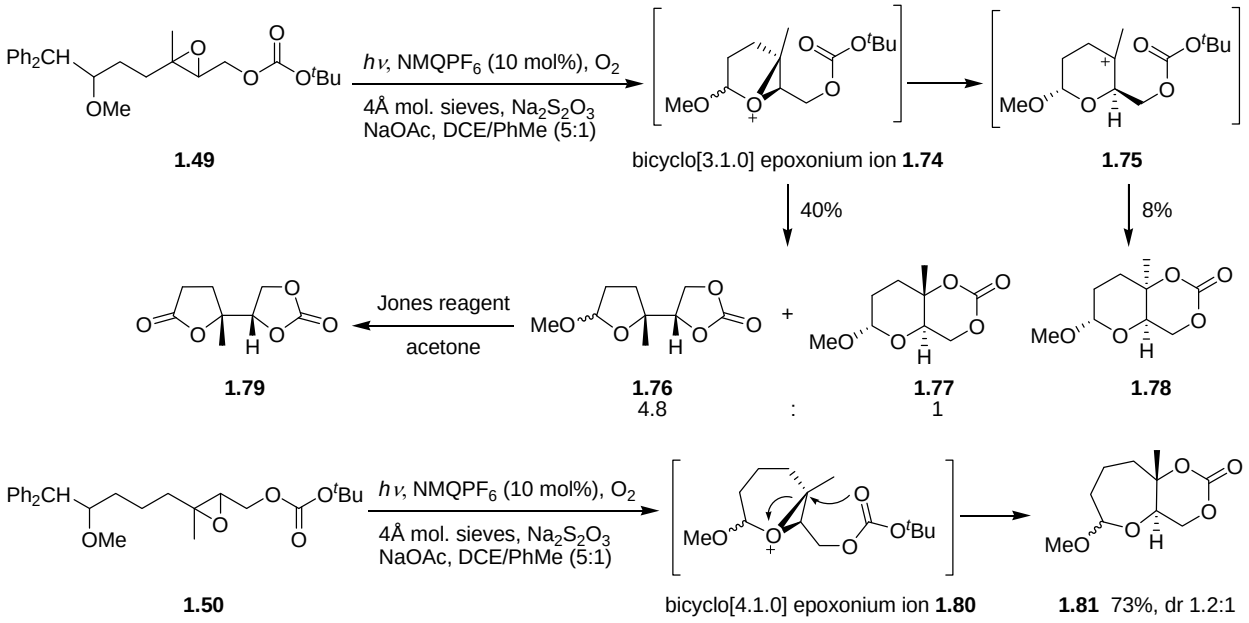


Figure 19. Cyclizations of disubstituted monoepoxides **1.49** and **1.50**

Having obtained the general information on the regioselectivity of monoepoxide opening/cyclization with carbonates as the nucleophile, I next investigated the cyclizations of diepoxides. Diepoxide **1.51**, under ETIC conditions, provided a mixture of consecutive *exo*,*exo*- and *endo*,*endo*-products **1.85** and **1.86**, respectively, in a combined 40% yield and with a 5.5:1 ratio (Figure 20). Mechanistic analysis suggests that initial cyclization formed bicyclo[3.1.0] epoxonium intermediate **1.82**, which could be opened by the epoxide either in an *exo*-mode to form a second bicyclo[3.1.0] epoxonium **1.83**, or in an *endo*-mode to form bicyclo[4.1.0] epoxonium **1.84**. It is noteworthy that no *endo*-cyclization product from **1.83** was isolated, indicating that bicyclo[3.1.0] epoxonium ions activated by non-stabilized carbeniums (stronger

Lewis acids) prefer *exo*-pathway towards tethered nucleophiles. Also of note is that no *cis*-fused *endo*-product was observed from **1.84**, indicating that epoxides are better nucleophiles than carbonates or that the addition of carbonate to the epoxonium ion is reversible before the loss of the *t*-butyl cation. A similar regioselectivity was observed and a better overall yield was obtained when diastereomeric counterpart **1.52** was exposed to the ETIC conditions.

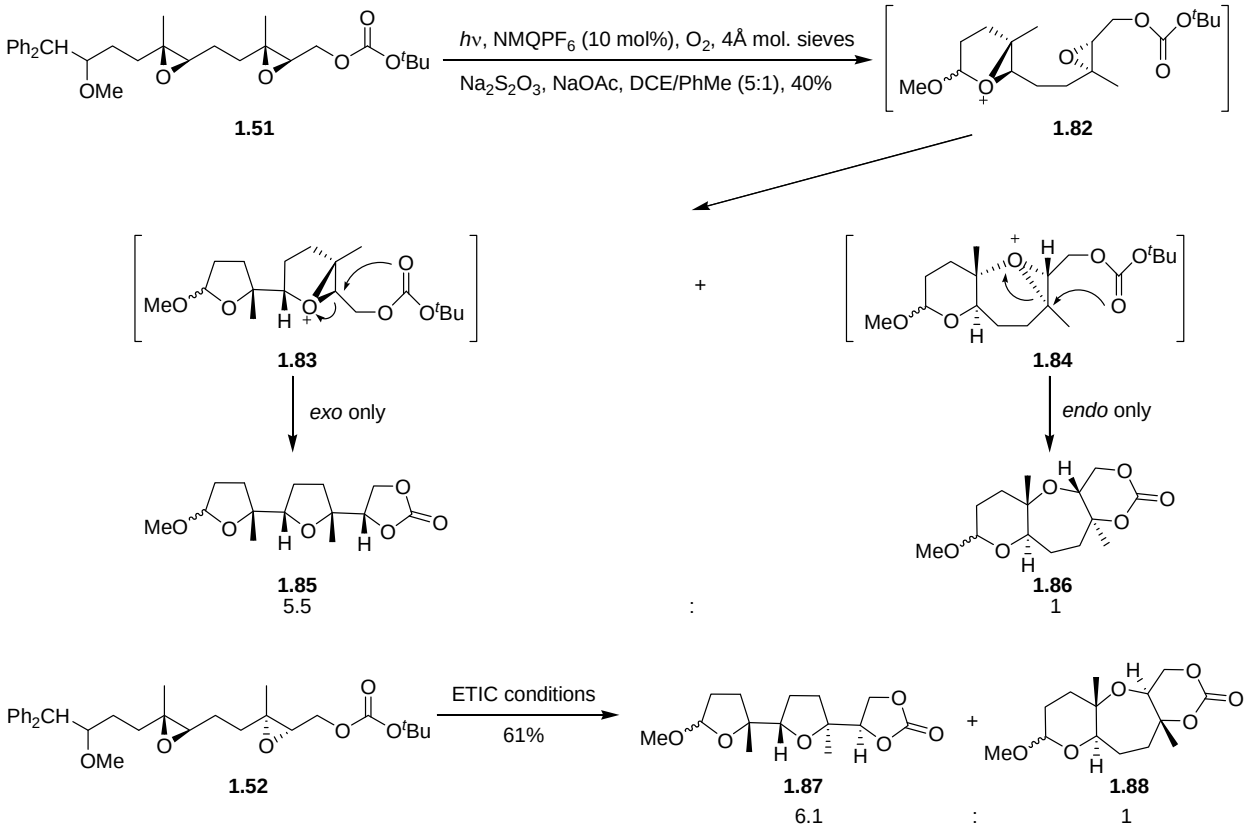


Figure 20. Cyclizations of diepoxides **1.51** and **1.52**

Following the completely *endo*-selective opening of bicyclo[4.1.0] epoxonium ions **1.80** and **1.84**, reaction of diepoxides **1.53** and **1.54** afforded *trans*,*syn*,*trans*-fused tricycles **1.91** and **1.93** in all *endo*-modes as expected since the intermediates were trisubstituted bicyclo[4.1.0]

epoxonium ions. The cyclization of **1.54** is highly efficient in consideration of the product complexity. The higher yield observed in cyclization of **1.54** compared with **1.53** is probably due to the diminished steric interactions in the cyclization processes. To simplify characterizations, acetals **1.91** and **1.93** were oxidized by treatment with *m*CPBA and BF3•OEt_2 followed by addition of Et_3N[36,37] to form lactones **1.92** and **1.94**. The structure of **1.92** was unambiguously confirmed through single crystal X-ray analysis (Figure 22).[38]

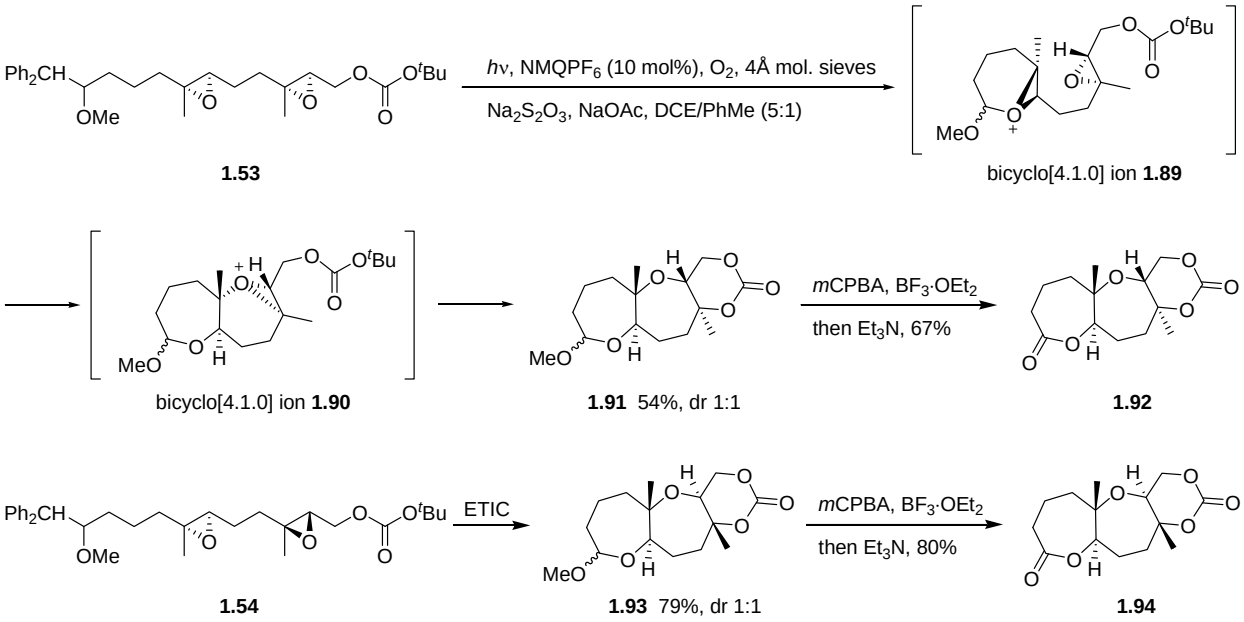


Figure 21. Cyclizations of diepoxides **1.53** and **1.54**

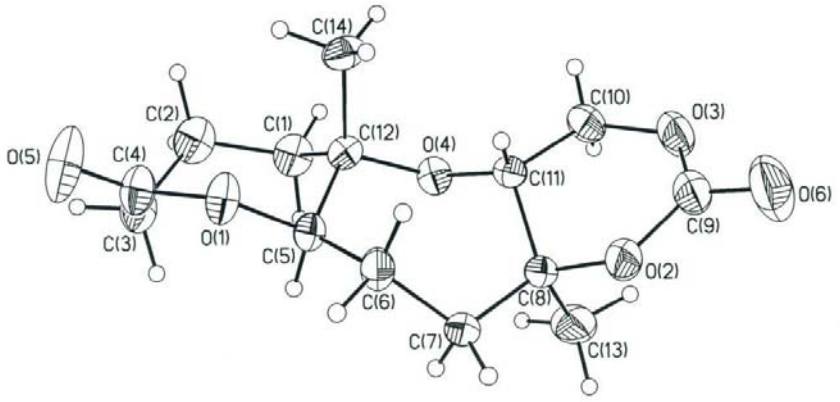


Figure 22. ORTEP structure of lactone **1.92**

Since no selectivity was observed in the cyclization of **1.42**, I was not surprised to observe that when diepoxide **1.55** was subjected to ETIC conditions, consecutive *exo*,*exo*- and *endo*,*endo*-products **1.97** and **1.98** were obtained in comparable yields, with the disubstituted bicyclo[4.1.0] epoxonium **1.95** from initial cyclization being non-regioselective (Figure 23). Tricycle **1.98** was converted into lactone **1.99** and its stereochemical outcomes were established through single crystal X-ray analysis (Figure 24).[39]

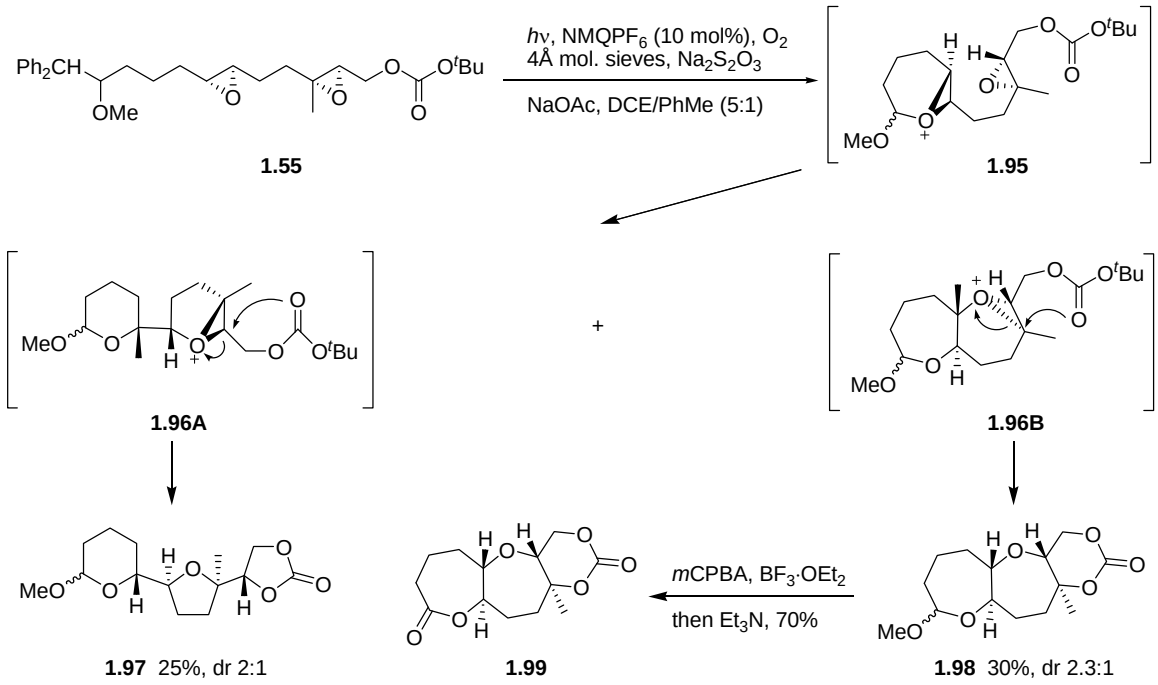


Figure 23. Cyclization of diepoxide **1.55**

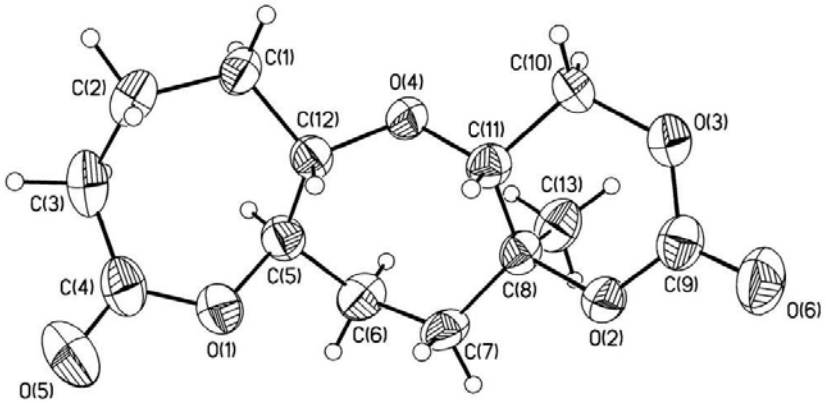


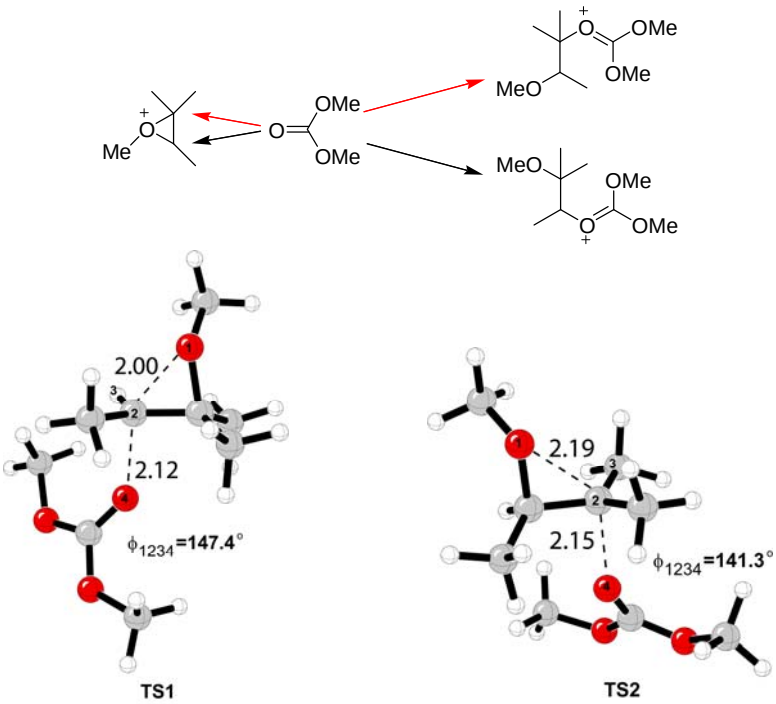
Figure 24. ORTEP structure of lactone **1.99**

1.3 COMPUTATIONAL ANALYSIS

The cyclization results of the epoxide opening cascades under ETIC conditions show that the regioselectivity is highly dependent on the bicyclic epoxonium ion structures. Trisubstituted bicyclo[4.1.0] epoxonium ions prefer exclusive *endo*-pathways while disubstituted bicyclo[4.1.0] epoxonium ions essentially show no preference towards *exo*- or *endo*-pathways. I also found that trisubstituted bicyclo[3.1.0] epoxonium ions, when formed from attack of epoxides to non-stabilized carbenium ions, favor *exo*-selectivity exclusively; when formed from attack of epoxides to oxocarbenium ions, give lower selectivity towards *exo*-cyclization. In order to better understand the origin of the regioselectivity, especially *endo*-selectivity in cascade cyclizations of epoxides, computational analysis was initiated using the B3LYP/6-31G(d) method[40,41] to mimic the cyclization transition structures in the gas phase. This was performed by using Gaussian03[42] program in the Houk group at UCLA.

Initial study was carried out on a model reaction of bimolecular nucleophilic addition of dimethyl carbonate to 1,2,2,3-tetramethyloxiranium ion (Figure 25). The dimethyl carbonate can add to either the tertiary or secondary center of the epoxonium ion, with no geometrical constraints in either case. As shown in Figure 25, **TS1** corresponds to the transition structure for nucleophilic addition to the secondary center and **TS2** corresponds to the transition structure for nucleophilic addition to the tertiary center. In both TSs, the breaking and forming C-O bond distances are within the range of 2.0 and 2.2 Å, indicating that both reactions proceed through S_N1-like transition states. The observation of the longer partial C-O bonds in **TS2** is an indicative of a looser S_N1 transition state, resulting from the formation of a partial tertiary carbocation. The partial tertiary carbocation formation can better stabilize the transition state, making **TS2** lower in energy than **TS1** by 4.3 kcal/mol. The dihedral angles in the absence of geometrical

constraints in **TS1** (O_{ep}-C_{ep}-H-O) and **TS2** (O_{ep}-C_{ep}-C-O) are 141.3° and 147.4°, respectively. The bond distances in **TS1** and **TS2** will be used as the references in the following context, with shorter bond distances being S_N2-like transition structures.

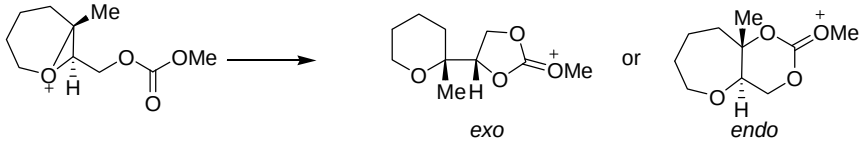


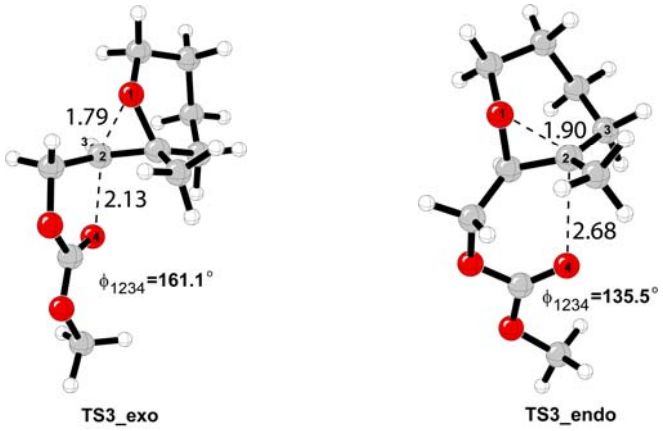
ΔH_{rel} (kcal/mol)	4.3	0.0
ΔG_{rel} (kcal/mol)	5.0	0.0

Figure 25. Transition structures for the addition of dimethyl carbonate to the 1,2,2,3-tetramethyl-oxiranium ion. The distances are given in Å.

A model reaction was studied to elucidate the origin of the exclusive *endo*-selectivity from trisubstituted bicyclo[4.1.0] epoxonium ions. As shown in Figure 26, the difference between the model reaction and the real reaction (**1.50** → **1.81**, Figure 19) is the replacement of the anomeric methoxy group with a hydrogen atom and the *tert*-butyl carbonate with a methyl carbonate. This model reaction can also be employed to account for the formation of **1.86**, **1.88**, **1.91**, **1.93** and **1.98** in the terminal cyclizations of the corresponding substrates.

The methyl carbonate carbonyl can add either to the secondary or tertiary center of bicyclo[4.1.0] epoxonium ion to form 5-*exo*- or 6-*endo*-cyclization products. The transition structure for *endo*-cyclization (**TS3_endo**) has a lower energy than that of *exo*-cyclization (**TS3_exo**) by 4.5 kcal/mol, which is nearly identical to the energy difference in the unconstrained system. The longer forming C-O bond in **TS3_endo** means a looser S_N1-like transition state presumably due to the partial formation of the tertiary carbocation. However, **TS3_exo** has an S_N2-like transition state as evidenced by the shorter breaking and forming C-O bond distances. The dihedral angle in **TS3_exo** has a greater distortion from the unconstrained system (161.1° vs 147.4°) than that in **TS3_endo** (135.5° vs 141.3°). The higher energy and greater distortion of the dihedral angle of **TS3_exo** than those of **TS3_endo** result in the complete preference towards *endo*-cyclization pathway.

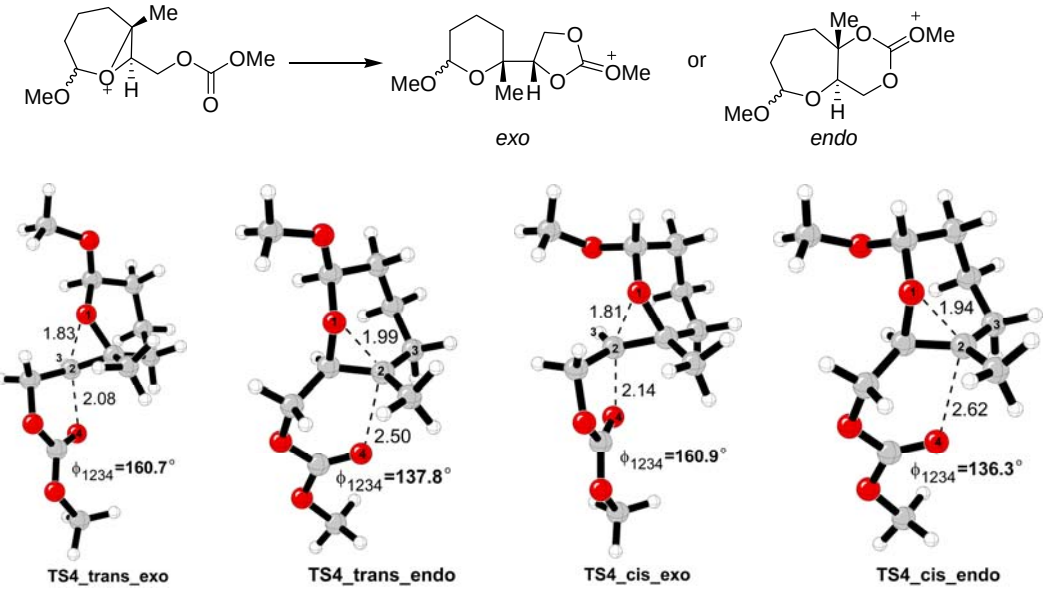




ΔH_{rel} (kcal/mol)	4.5	0.0
ΔG_{rel} (kcal/mol)	4.6	0.0

Figure 26. Transition structures for the 5-*exo*- and 6-*endo*-cyclizations from trisubstituted bicyclo[4.1.0] epoxonium ion. The distances are given in Å.

The effect of the anomeric methoxy group was investigated using the model reaction illustrated in Figure 27. The methoxy group can be either *cis* or *trans* to the epoxonium ion ring, with the *cis*-isomer being more stable than the *trans*-isomer by 0.3 kcal/mol in the gas phase. It is clear that the incorporation of the methoxy group has negligible effect on the geometries of the transition structures, though **TS4_trans_endo** shows a slightly better leaving group departure and enhanced bond formation compared with **TS3_endo**. The *trans*- and *cis*-methoxy isomers favor the *endo*-cyclization pathway by 4.6 and 4.8 kcal/mol relative to the corresponding *exo*-pathway, respectively, which is similar to the energy difference (4.5 kcal/mol) observed between **TS3_endo** and **TS3_exo**.

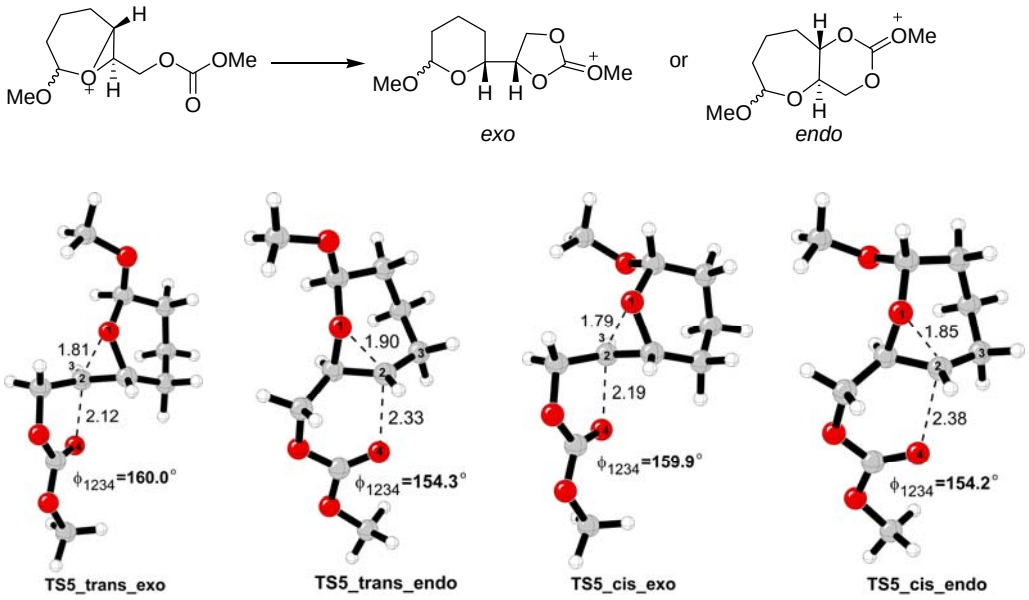


ΔH_{rel} (kcal/mol)	5.8	1.2	4.8	0.0
ΔG_{rel} (kcal/mol)	5.9	1.5	5.2	0.0

Figure 27. Transition structures for 5-*exo*- and 6-*endo*-cyclizations of *cis*- and *trans*-methoxy trisubstituted bicyclo[4.1.0] epoxonium ions. The distances are given in Å.

As depicted in Figure 18, almost no regioselectivity was obtained from the cyclization of disubstituted epoxide **1.48** which does not have the methyl group on the epoxide. To explain the role of the methyl group, an additional model was employed with the angular methyl group being replaced by a hydrogen atom, in which both 5-*exo*- and 6-*endo*-cyclization modes would have partially formed secondary carbocations (Figure 28).

The calculations in the gas phase revealed that the absence of the methyl group has negligible influence on the 5-*exo*-transition structures. However, the two 6-*endo*-transition structures are perturbed substantially, with shorter breaking and forming bond distances being observed, indicating more S_N2-like character in the transition states. The corresponding dihedral angles are also distorted significantly from 137.8° to 154.3°, and from 136.3° to 154.2° for the *trans*- and *cis*-isomers, respectively. The transition structures of *endo*-modes are energetically lower than the corresponding transition structures of *exo*-modes by 1.4 kcal/mol for both *cis*- and *trans*-isomers, meaning that *endo*-cyclization is slightly favored over *exo*-cyclization for disubstituted bicyclo[4.1.0] epoxonium ions. While experimental results show that *exo*- and *endo*-cyclizations are two competitive pathways as illustrated in Figure 18, computational studies still support that bicyclo[4.1.0] epoxonium ions have a strong tendency towards *endo*-cyclizations.

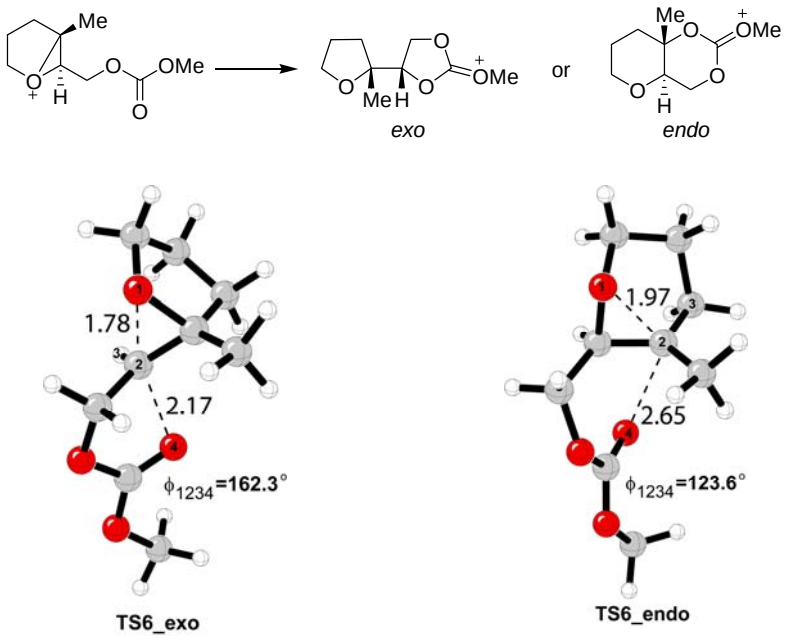


ΔH_{rel} (kcal/mol)	1.4	0.0	1.4	0.0
ΔG_{rel} (kcal/mol)	0.8	0.0	1.2	0.0

Figure 28. Transition structures for 5-*exo*- and 6-*endo*-cyclizations of *cis*- and *trans*-methoxy disubstituted bicyclo[4.1.0] epoxonium ions. The distances are given in Å.

In the terminal annulations of diepoxides **1.51** and **1.52**, the bicyclo[3.1.0] epoxonium ions (activated by non-stabilized carbenium ions) preferentially generated 5-*exo*-cyclization products, which is in accord with Baldwin's ring closure rules. This was mimicked by a model reaction depicted in Figure 29. The transition structure for *exo*-cyclization (**TS6_exo**) is similar to the transition structure for the bicyclo[4.1.0] epoxonium ion (**TS3_exo**) in terms of the forming and breaking bond distances and the dihedral angle. The transition structure for *endo*-cyclization (**TS6_endo**), though having similar bond breaking and forming features to the corresponding transition structure for the bicyclo[4.1.0] epoxonium ion (**TS3_endo**), shows a significant decrease in the dihedral angle (123.6° vs 135.5°). As a result, this perturbation leads to the

increase of the energy for **TS3_endo**, making 5-*exo*-pathway energetically favored over 6-*endo*-pathway by 2.7 kcal/mol.



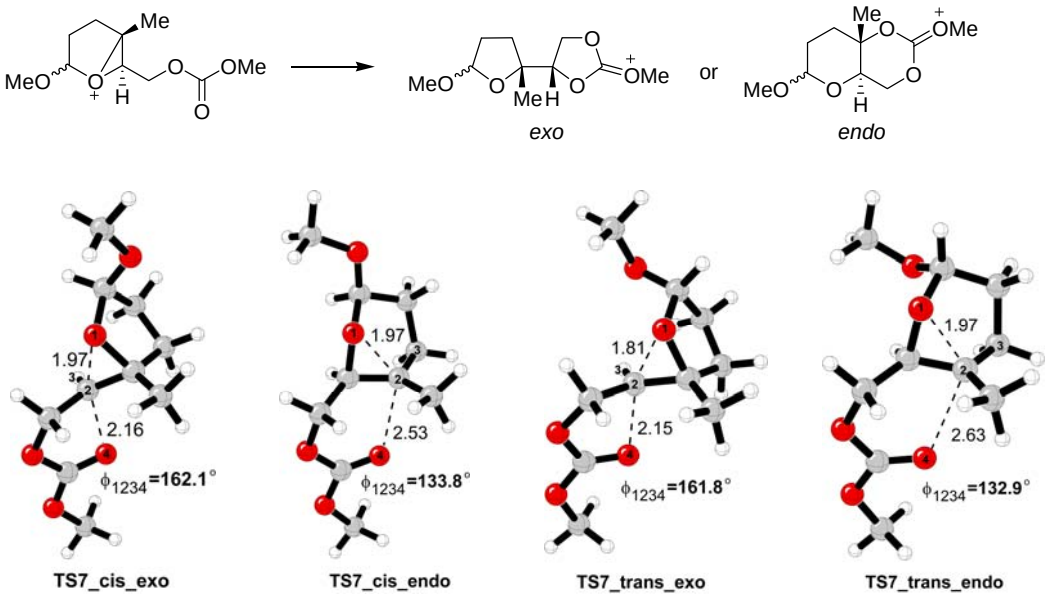
ΔH_{rel} (kcal/mol)	0.0	2.7
ΔG_{rel} (kcal/mol)	0.0	2.4

Figure 29. Transition structures for 5-*exo*- and 6-*endo*-cyclizations of trisubstituted bicyclo[3.1.0] epoxonium ion. The distances are given in Å.

When the epoxide was activated by the oxocarbenium ion instead of a non-stabilized carbenium ion, a small amount of *trans*-fused *endo*-cyclization product **1.78** was also isolated from trisubstituted bicyclo[3.1.0] epoxonium ion **1.74**. To elucidate the impact of the anomeric methoxy group on the regiochemical outcomes, another model reaction was employed, as shown in Figure 30. Similar to the transition structures in Figure 27, the methoxy group could be *cis* or *trans* to the epoxonium ion ring. The *trans*-isomer 1.0 kcal/mol more stable than the *cis*-isomer

because of the stabilization between the lone pair of the epoxide oxygen and the anti-bonding orbital of the C-O (methoxy) bond when they are antiperiplanarly oriented.

For the transition structures for the two *cis*-isomers, **TS7_cis_exo** shows a greater leaving group departure in the presence of the anomeric methoxy group while the bond forming character and the dihedral angle remain approximately the same. **TS7_cis_endo**, however, has enhanced bond formation and a widened dihedral angle which is close to those in the transition structures (**TS3_endo**, **TS4_cis_endo** and **TS4_trans_endo**) of trisubstituted bicyclo[4.1.0] epoxonium ions. For the *trans*-isomers, the geometry of **TS7_trans_exo** is essentially unaffected by the incorporation of the methoxy group. Although the breaking and forming bond distances remain nearly the same in **TS7_trans_endo**, the dihedral angle is distorted from 123.6° to 132.9°, which is similar to that in **TS7_cis_endo**. From an energetic view of point, **TS7_trans_endo** has the lowest energy which is attributed to the stabilization of the anomeric effect when the electronegative methoxy group assumes a pseudoaxial position in the forming tetrahydropyran ring. The two transition structures for *exo*-cyclizations have slightly higher energy. In addition, **TS7_cis_endo**, without benefiting from the developing anomeric effect, is the highest in energy.



ΔH_{rel} (kcal/mol)	0.2	1.7	0.6	0.0
ΔG_{rel} (kcal/mol)	0.6	2.1	0.4	0.0

Figure 30. Transition structures for 5-*exo*- and 6-*endo*-cyclizations of *cis*- and *trans*-methoxy trisubstituted bicyclo[3.1.0] epoxonium ions. The distances are given in Å.

The role of the methoxy group is consistent with the previous observations that the 5-*exo*-regioselectivity decreased when bicyclo[3.1.0] epoxonium ions were generated from combination of epoxides with oxocarbenium ions (**1.74** and **1.82**) rather than non-stabilized carbenium ions (**1.83** and **1.96A**). Also of note is the isolation of *trans*-fused bicycle **1.77** as a single anomer with the methoxy group adopting an axial position.

1.4 CONCLUSIONS

A systematic study has been carried out on the oxocarbenium ion-initiated cascade cyclizations of epoxides under ETIC conditions, in which the impact of the epoxide substitution pattern, ring size of the bicyclic epoxonium ions and the Lewis acidic carbocation structures on regiochemical outcomes was fully investigated. These results clearly revealed that ring size is an important determinant on the regioselectivity of bicyclic epoxonium ion opened by tethered nucleophiles. That is, bicyclo[3.1.0] epoxonium ions show significant to exclusive preference towards *exo*-cyclization pathways while bicyclo[4.1.0] epoxonium ions show a strong tendency towards *endo*-cyclizations. This observation could be explained from the computational studies that larger rings can adopt a looser transition state with more S_N1 character, thereby favoring *endo*-cyclizations. As for smaller rings, *endo*-TSs are more distorted than *exo*-TSs, making *endo*-TSs energetically higher and *exo*-pathways more favorable. In addition, epoxide substitution pattern also has significant influence on the regioselectivity, especially when bicyclo[4.1.0] epoxonium ions serve as the key intermediates. Trisubstituted bicyclo[4.1.0] epoxonium ions prefer exclusive *endo*-cyclization pathways with the cyclization proceeding through an S_N1-like transition state due to the better stabilization from a partially formed tertiary carbocation. However, disubstituted bicyclo[4.1.0] epoxonium ions show almost no preference towards *exo*- or *endo*-cyclizations. Though Lewis acid selection has negligible effect on the regiochemical outcomes of bicyclo[4.1.0] intermediates, it can affect the reaction pathways in a subtle manner when reactions proceed through bicyclo[3.1.0] epoxonium ions. That is, when bicyclo[3.1.0] epoxonium ions are formed from combination of epoxides and non-stabilized carbenium ions, exclusive *exo*-selectivity is observed; when bicyclo[3.1.0] epoxonium ions are formed from combination of epoxides and oxocarbenium ions, *exo*-selectivity decreases to some extent. The

endo-cyclization in this process arises from the anomeric effect that generates from the forming tetrahydropyran ring through *endo*-pathway when the methoxy group adopts a pseudoaxial position, which makes *endo*-transition structure lower in energy. This delicate effect undoubtedly demonstrates that *endo*-cyclization can be achieved to generate tetrahydropyran rings through modification of bicyclic epoxonium ions. The current studies definitely provide a solid base for designing new epoxide substrates to provide polycyclic ether structures efficiently.

2.0 EFFORTS TOWARDS THE TOTAL SYNTHESIS OF (+)-LACTODEHYDROTHYRSIFEROL AND ITS ANALOGS

2.1 INTRODUCTION

(+)-Lactodehydrothyrsiferol (**2.1**), a marine polycyclic ether natural product, was isolated as an amorphous white solid by Fernandez and co-workers in 2002 from seeds of *Laurencia viridis* around the Canary Islands (Figure 31).[7] Spectroscopic analysis shows that it has a central *trans*-fused pyranopyran structure with a pendent 5-membered lactone ring and an aliphatic side chain that connects the central unit to a *trans*-tetrahydrofuran ring. It is interesting to note that the B ring assumes a chair conformation while the C ring adopts a twist-boat-like conformation. This has also been observed in structurally related natural products through X-ray and NMR spectroscopic analyses.[7,43-45]

Biological assay shows that **2.1** has modest inhibitory effect on serine/threonine protein phosphatase (PP2A) with IC_{50} value of 100 μM.[46] The structurally related natural product thyrsiferyl-23-acetate (**TA**) is more potent toward the inhibition of PP2A with IC_{50} values of 4-16 μM depending on the enzyme concentration. It is worth noting that **TA** exhibits specific inhibitory effect on PP2A, and has no effect on protein phosphatase 1 (PP1), 2B (PP2B), 2C (PP2C), or protein tyrosine phosphatases (PTP).[47] Though other structurally diverse natural products, such as polyether okadaic acid, polyketide tautomycin, and terpenoid cantharidin, are

much more potent inhibitors of PP2A (IC_{50} = 0.2 ~ 40 nM) than **2.1** and **TA**, they also show inhibitory effect on PP1 and/or PP2B (Figure 31).[48,49] The exclusive selectivity of **TA** is presumably due to its unique structural features and makes itself an ideal tool to study the cellular processes mediated by PP2A. However, it is unclear whether **2.1** can affect the activity of other protein phosphatases besides PP2A. Up to now, no total synthesis of **2.1** has been reported. I am currently pursuing a convergent approach toward the total synthesis of **2.1** and its analogs to further explore their biological activity.

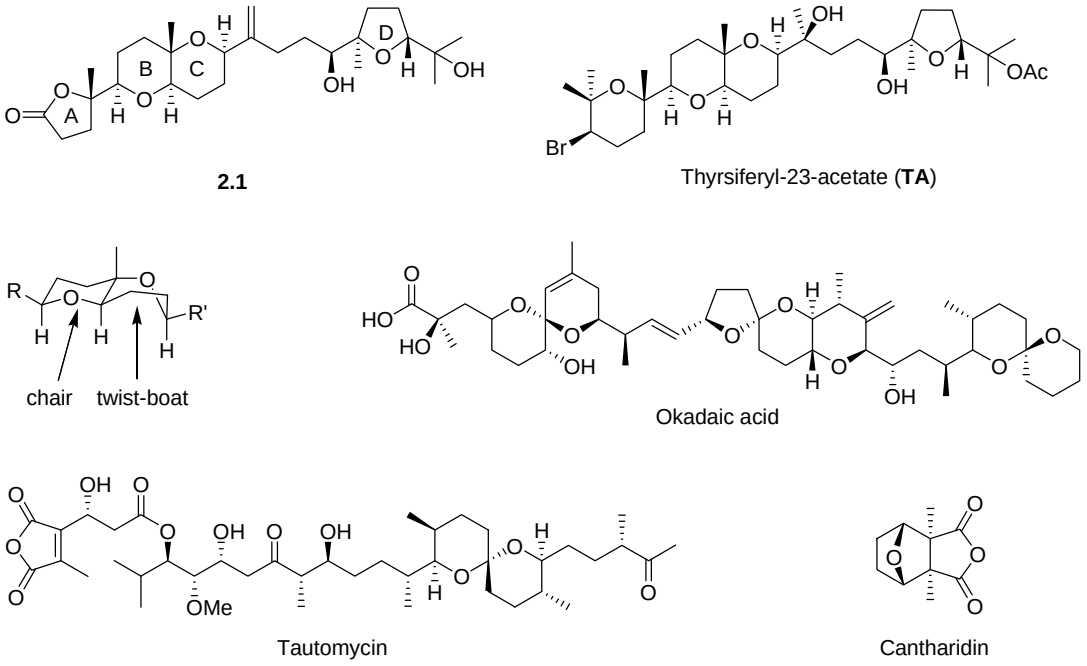


Figure 31. Biologically active natural products and the conformation of the B and C rings in **2.1** and **TA**

2.2 SYNTHETIC PROGRESS

2.2.1 Preliminary results

Previous studies on the cascade cyclizations of epoxides showed that the reaction of diepoxide **2.2** under ETIC conditions gave a mixture of *exo*,*exo*-product **2.3** and *endo*,*endo*-product **2.4** in a combined 61% yield and with a 6.1:1 ratio. In this reaction, tricycle **2.5** from an *exo*-cyclization followed by an *endo*-cyclization was not observed (Figure 32).[26] Therefore, construction of the A, B and C rings of **2.1** in a single operation from the diepoxide similar to **2.2** is difficult and a new strategy is required for this purpose.

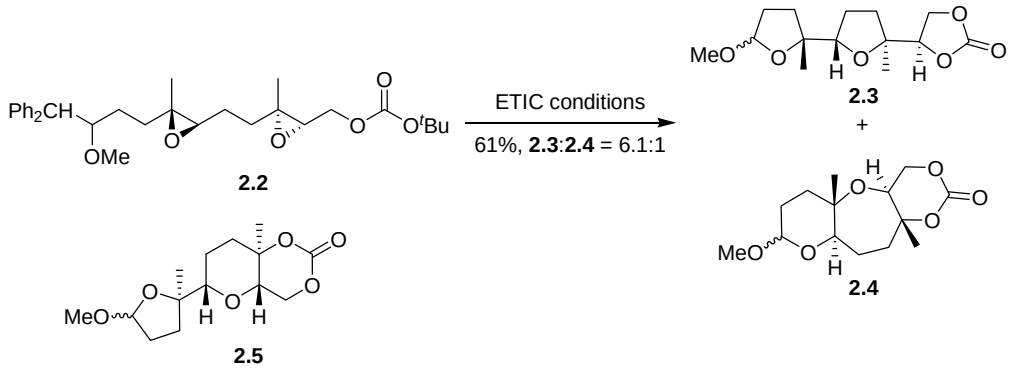


Figure 32. Cyclization of diepoxide **2.2**

As depicted in Figure 33, an alternative approach was proposed. The reaction of diepoxide **2.6** under ETIC conditions is expected to give bicyclic epoxonium ion **2.7** and the terminal cyclization will proceed through addition of carbonate carbonyl to the proximal tertiary center in a kinetically favored fashion to generate tricycle **2.8**. With **2.8** in hand, further elaborations will provide tetracyclic compound **2.9** with the A, B and C rings being installed.

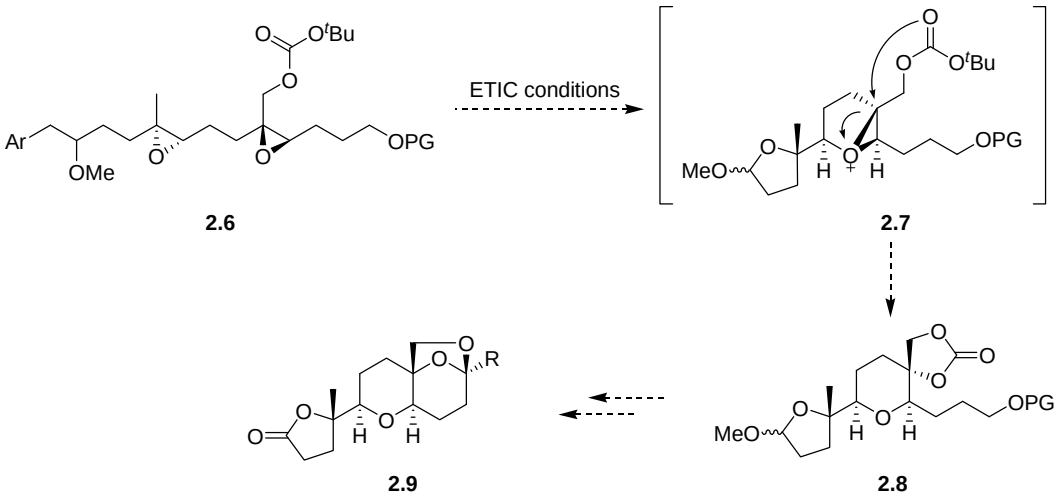


Figure 33. Proposed cyclization of diepoxide **2.6**

To validate the transformation from **2.7** to **2.8**, I prepared epoxy carbonate **2.14**, which will form an epoxonium ion intermediate similar to **2.7** upon cyclization (Figure 34). Oxidation of known alkene **2.10**[26] with $KMnO_4$ afforded α-hydroxyl ketone **2.11** in 57% yield.[50] Olefination of the ketone under Lebel's Rh-catalyzed conditions provided allylic alcohol **2.12** in 72% yield.[51] Epoxidation[52] of **2.12** catalyzed by $VO(acac)_2$ in the presence of *tert*-butyl hydroperoxide followed by protection of the primary hydroxyl group with Boc_2O[27] gave carbonate **2.14** in excellent yield.

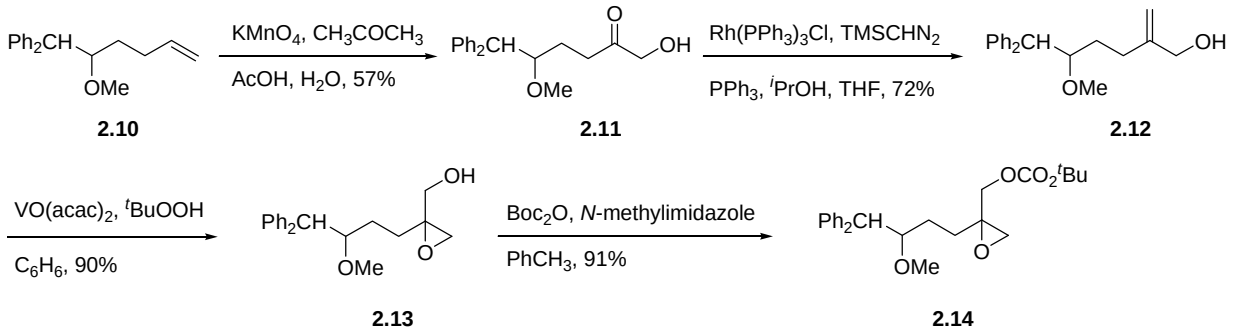


Figure 34. Synthesis of epoxide **2.14**

Reaction of **2.14** under ETIC conditions cleanly afforded the desired spiro product **2.17** in excellent yield through addition of carbonate to the tertiary center of bicyclic epoxonium ion **2.16**, which was completely consistent with my expectations (Figure 35).

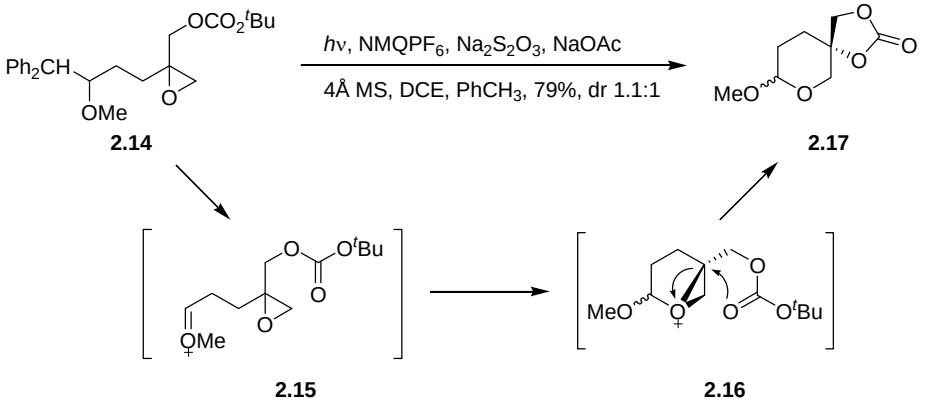


Figure 35. Cyclization of epoxide 2.**14**

2.2.2 Current progress

Following the smooth conversion of **2.14** into bicycle **2.17**, I proposed a retrosynthetic approach toward **2.1**. As shown in Figure 36, **2.1** can be obtained from a stereoselective

reduction of ketal **2.18** which will be prepared from coupling of aldehyde **2.19** and vinyl iodide **2.20**.[53] These two coupling components can be accessed from cyclizations of diepoxide **2.21** and **2.22**, respectively.

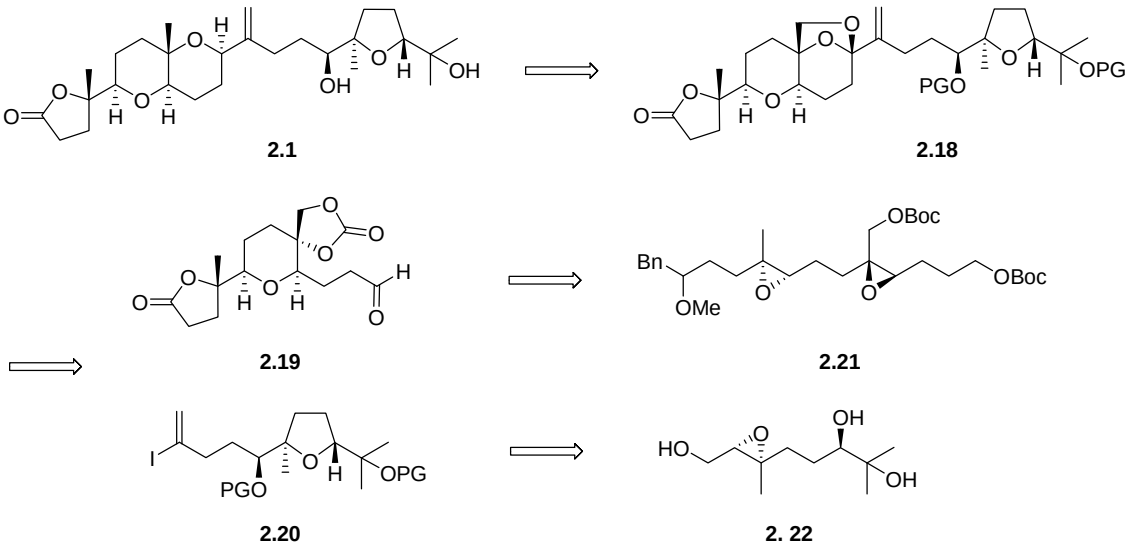


Figure 36. Retrosynthetic analysis of **2.1**

Due to the availability of the chiral reagents for asymmetric epoxidations, *ent*-**2.21** was initially prepared to explore the feasibility of the above route (Figure 37). Coupling of known vinyl bromide **2.23**[54] and aldehyde **2.24** under Fürstner-modified Nozaki-Hiyama-Kishi conditions[53] provided allylic alcohol **2.25** in 85% yield. It was subsequently converted into ethyl ester **2.26** through a Johnson-Claisen rearrangement.[54] Trost[54] emphasized that the rearrangement efficiency of a similar allylic alcohol is highly dependent on the reaction temperature, with higher temperatures leading to decreased *Z*/*E* stereoselectivity and lower temperatures leading to decreased yields. Subsequently, **2.26** was converted into allylic alcohol **2.27** through reduction with DIBAL-H and addition with isopropenylmagnesium bromide. Another Johnson-Claisen rearrangement of **2.27** followed by reduction/addition gave homobenzylic alcohol **2.29** in 65%

yield over two steps. Methylation of the secondary alcohol followed by removal of the two silyl groups provided diol **2.30** in good yield. A sequence of Sharpless asymmetric epoxidation,[32] Shi asymmetric epoxidation,[31] and protection of the two hydroxyl groups with Boc_2O afforded the cyclization substrate *ent*-**2.21**. It is worth noting that the first epoxidation gave modest yield due to the unexpected cyclization through addition of the distal hydroxyl group to the epoxide and the diastereoselectivity after the two epoxidations was low (dr ~ 2:1) based on NMR analysis.

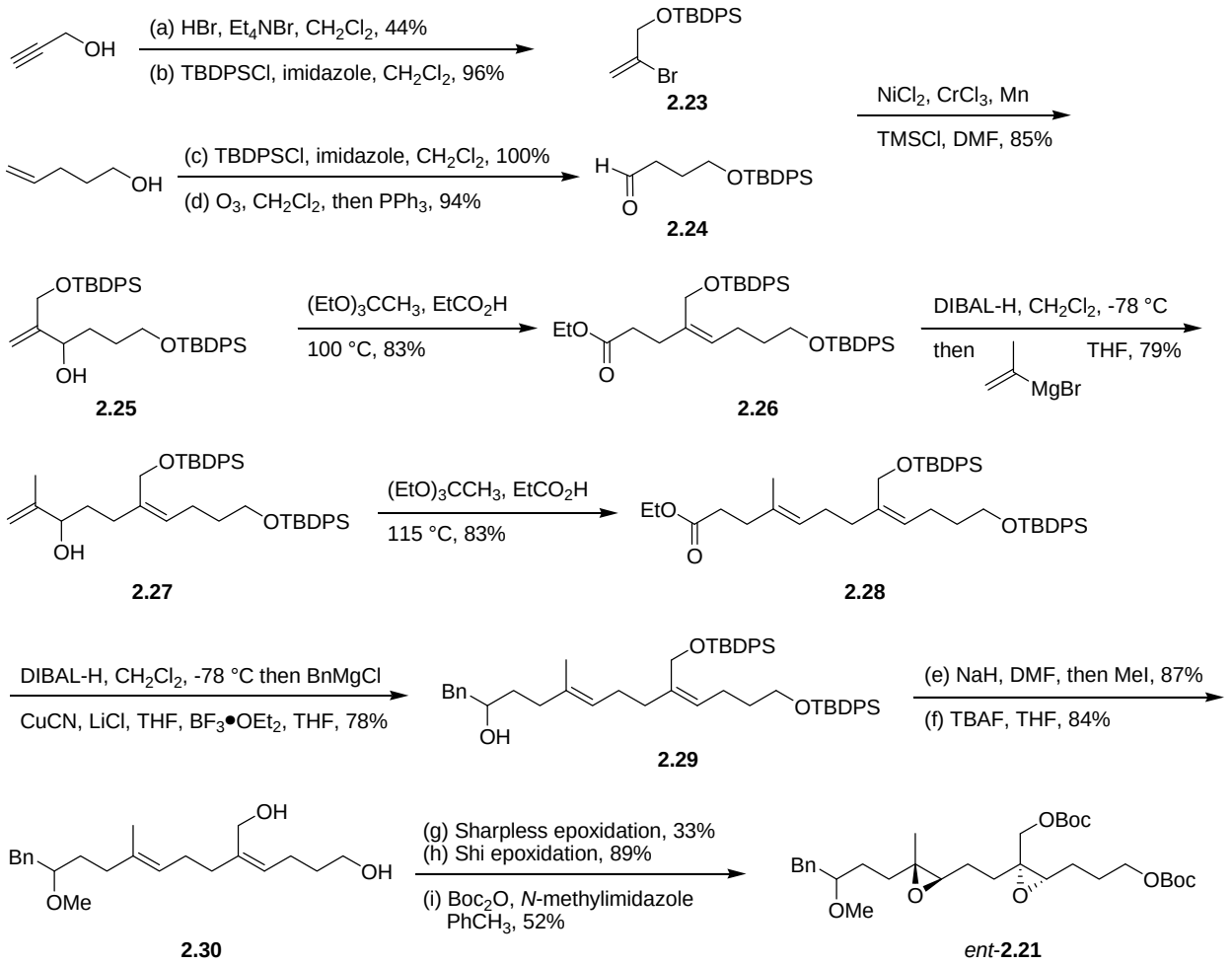


Figure 37. Synthesis of *ent*-**2.21**

Subjecting diepoxide *ent*-**2.21** to ETIC conditions produced desired tricycle **2.31** in 43% yield which contained small amounts of unknown materials (Figure 38). Also isolated from this reaction was tricycle **2.32**. Both **2.31** and **2.32** were oxidized by Jones reagent[25] to the corresponding lactones **2.33** and **2.34**, respectively. The relative stereochemical outcomes of the central *cis*-tetrahydropyran and the orientation of the 5-membered carbonate ring in lactone **2.33** were fully confirmed through 2D NMR NOESY studies. Subsequently, the Boc group was removed with TMSOTf in the presence of 2,6-lutidine[55] to give primary alcohol **2.35** in nearly quantitative yield. Oxidation of the hydroxyl group with Dess-Martin periodinane[56,57] provided aldehyde *ent*-**2.19** in 61% yield.

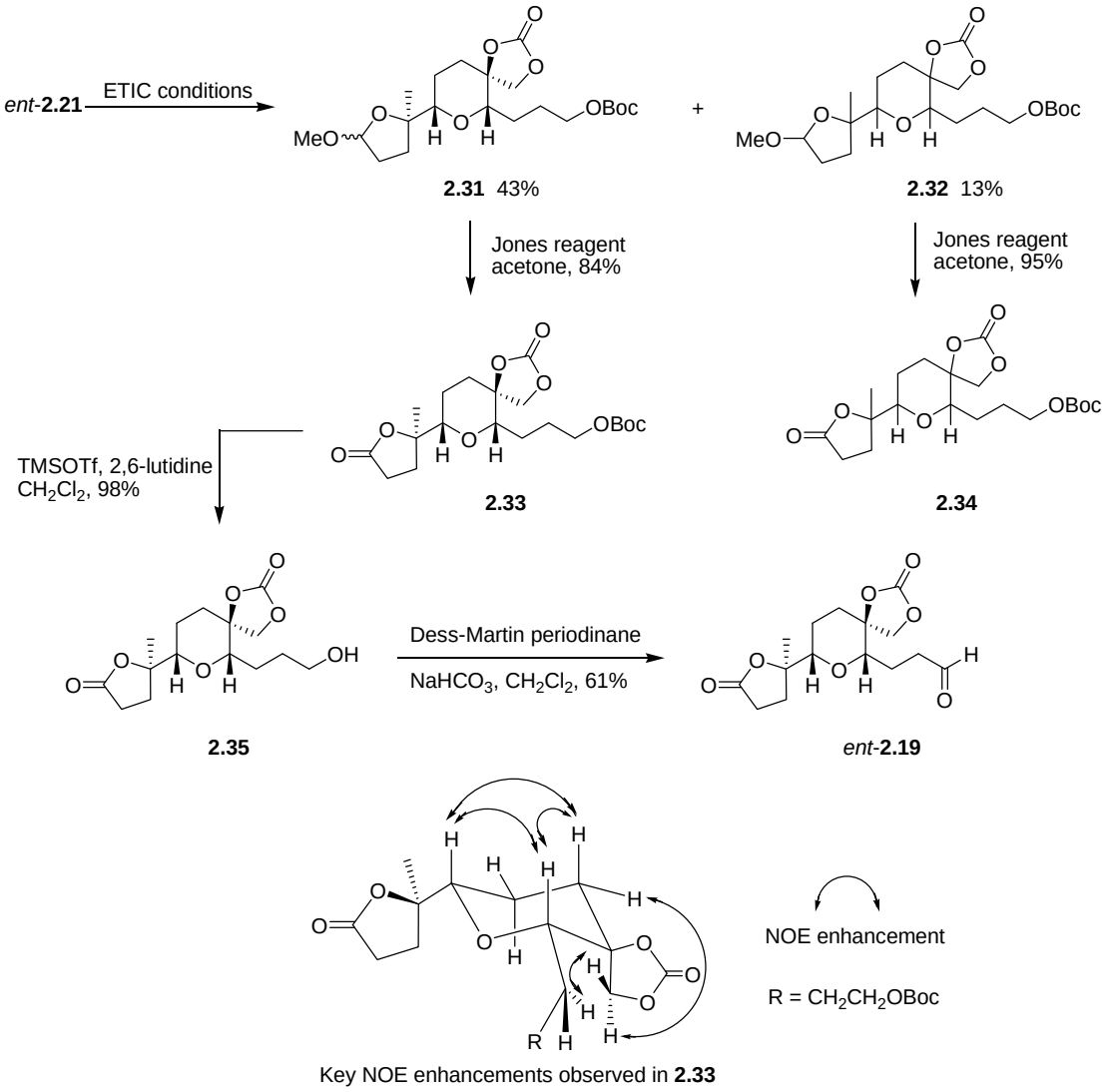
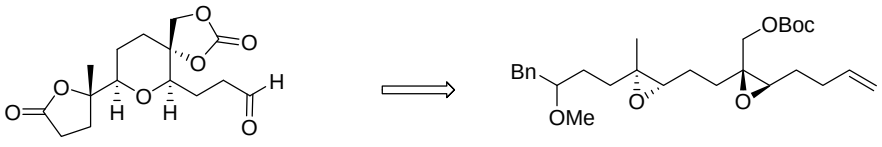


Figure 38. Synthesis of advanced intermediate *ent*-**2.19**

The above results clearly revealed that aldehyde **2.19** can be prepared from diepoxide **2.21**. As previously mentioned, there are two problems in this sequence. One is the low yield in Sharpless epoxidation and the other is low diastereoselectivity in the epoxidations of **2.30** presumably because of the interference of the hydroxyl group in Sharpless and/or Shi epoxidations. In order to circumvent these two problems, I proposed an alternative route to **2.19**

with replacement of one of the *tert*-butyl carbonates with a terminal alkene (Figure 39). I envisioned that oxidative cleavage of the terminal alkene would yield the desired aldehyde.



2.19 **2.36**

Figure 39. An alternative approach to **2.19**

The synthesis of **2.36** began with known dienol **2.37**, which was prepared from methyl acrylate and 4-pentenal through a Morita-Baylis-Hillman reaction (Figure 40).[58,59] Reduction of the methyl ester followed by selective protection of the primary hydroxyl group with TBDPSCl provided silyl ether **2.38**. Conversion of **2.38** into trienol **2.40** was achieved through a sequence similar to the synthesis of **2.30**. After Sharpless epoxidation, Shi epoxidation and protection of the hydroxyl group with Boc_2O, diepoxide **2.36** was obtained in higher efficiency compared to *ent*-**2.21**. Additionally, in this case, the diastereoselectivity in the epoxidations is about 4.6:1 with regard to the stereochemical orientations of the two epoxide functionalities.

Under ETIC conditions, diepoxide **2.36** underwent a cascade cyclization to afforded tricyclic product **2.37** (Figure 40). After removal of the anomeric center with Jones reagent, the corresponding lactone was obtained in 17% yield over two steps as a single diastereomer. The lower efficiency in the cascade cyclization is attributed to the intervention of the nucleophilic terminal alkene in the final cyclization process, suggesting that the terminal alkene must be replaced by non-nucleophilic groups. The ensuing cleavage of the terminal olefin under ozonolytic conditions smoothly afforded aldehyde **2.19** in 83% yield.

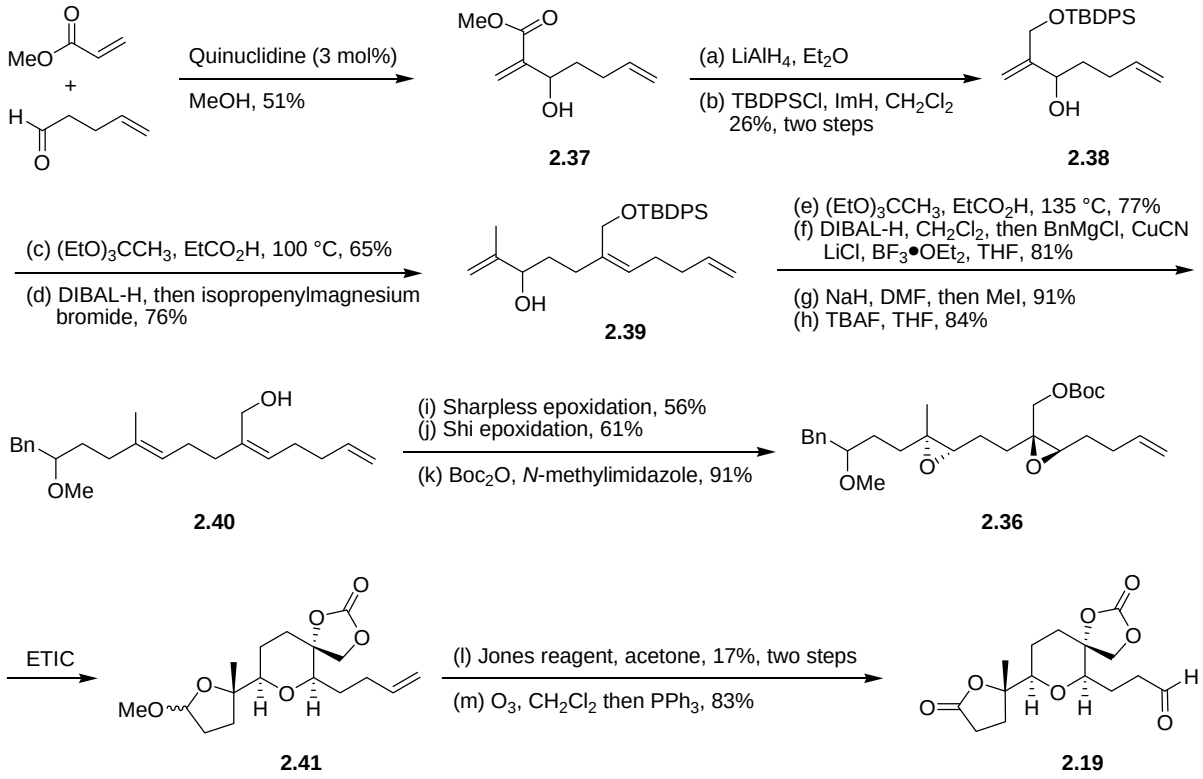


Figure 40. New approach to aldehyde **2.19**

With aldehyde **2.19** in hand, I next addressed to the preparation of vinyl iodide **2.45** (Figure 41). Sharpless asymmetric epoxidation of geraniol followed by Sharpless asymmetric dihydroxylation[60] gave a mixture of triol **2.22** and tetrahydrofuran **2.42**, which was converted into **2.42** completely with the promotion by pyridinium 10-camphorsulfonate complex.[61] The stereochemical outcome in **2.42** was established through mechanistic analysis. Activation of the primary hydroxyl group with TsCl followed by elimination under basic conditions provided the epoxide[62] whose tertiary hydroxyl group was protected as silyl ether **2.43** in excellent yield. The epoxide was opened by 1,3-dilithiopropyne[63] and the nascent secondary hydroxyl group was protected with TESCl to give bis-silyl ether **2.44**. The terminal alkyne was transformed into the

vinylstannane in the presence of the Bu_3Sn-$AlEt_2$ complex and CuCN in 29% (59% brsm) yield, which was further converted into vinyl iodide **2.45** in good yield.[64,65]

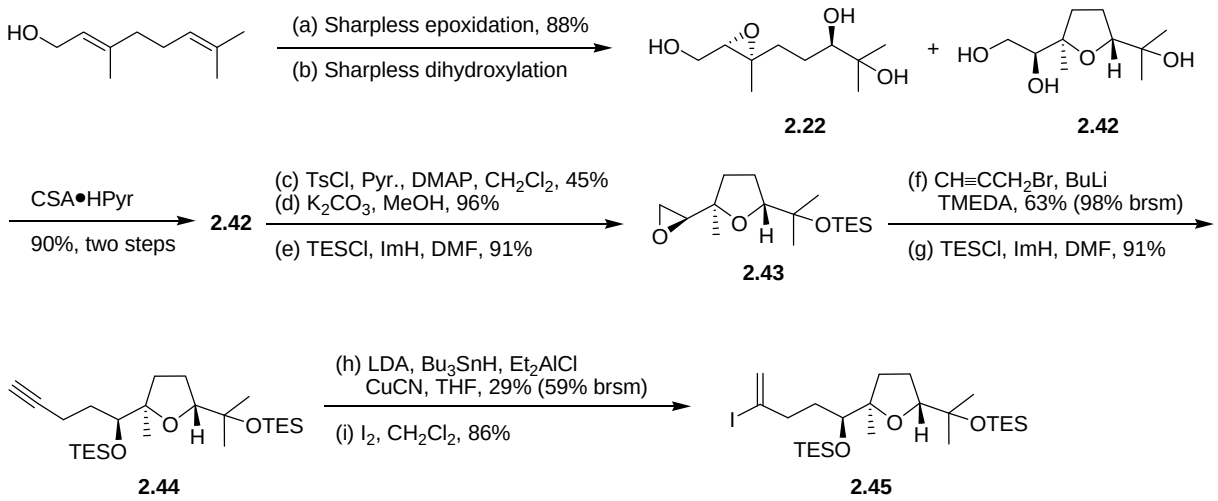


Figure 41. Synthesis of vinyl iodide **2.45**

2.3 FUTURE WORK

Though aldehyde **2.19** could be produced from diepoxides **2.21** and **2.36**, the efficiency for the substrate preparation or cascade cyclization was still low. Therefore, a better substrate is necessary for the total synthesis. I am intended to prepare a new diepoxide **2.49** from known vinyl bromide **2.46**[66,67] to differentiate the protecting groups for the two primary hydroxyl groups (Figure 42). Coupling of **2.46** with aldehyde **2.24** will afford the allylic alcohol, which will be converted into ethyl ester **2.47** through a Johnson-Claisen rearrangement. Similarly, **2.48** can be obtained through a repeated ester reduction/nucleophilic addition protocol followed by methylation of the secondary alcohol. Removal of the PMB group with DDQ followed by

epoxidations and carbonate formation will deliver diepoxide **2.49**. Since no extra hydroxyl group in the two epoxidations, a better yield from Sharpless epoxidation can be expected and the diastereoselectivity can be retained at a level of 4~5:1. Cyclization of **2.49** under ETIC conditions will give a comparable yield to that of *ent*-**2.21** due to the bulky and non-nucleophilic *tert*-butyldiphenylsilyloxy group.

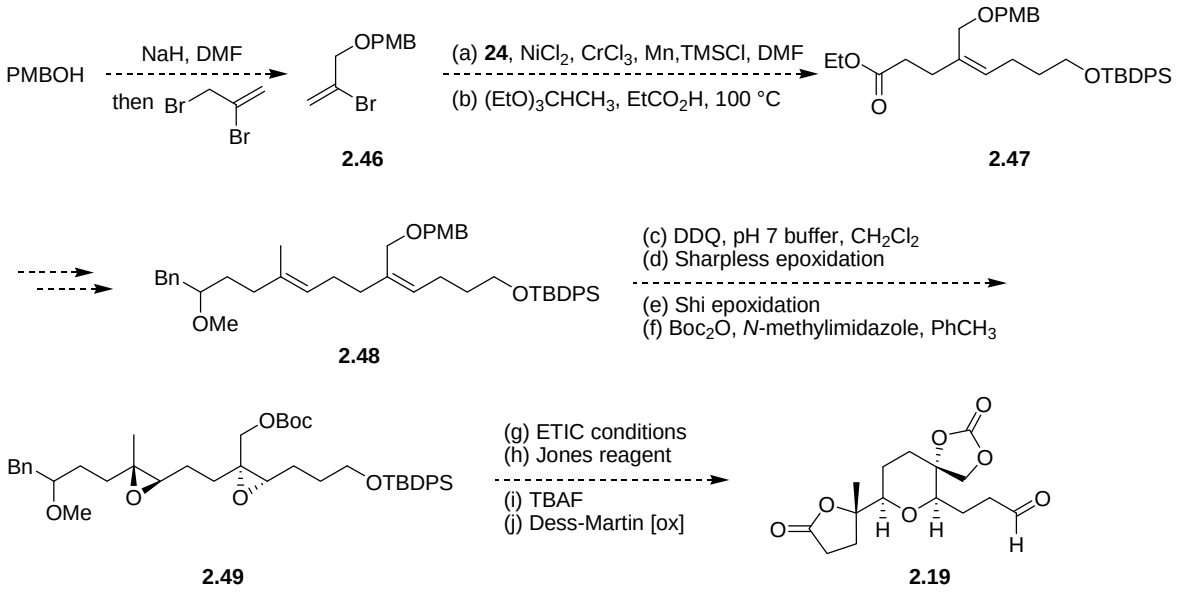


Figure 42. New approach to aldehyde **2.19**

With sufficient amounts of aldehyde **2.19** and vinyl iodide **2.42** in hand, I will next investigate the coupling of these two fragments under Fürstner-modified Nozaki-Hiyama-Kishi conditions (Figure 43).[53] Once **2.50** is formed, the allylic alcohol can be selectively oxidized with MnO_2 and the rest two hydroxyl group will be appropriately protected to give **2.51**. Opening of the 5-member carbonate under basic conditions[68] followed by $BiBr_3$-promoted ketal formation[69] will afford pentacycle **2.18**.

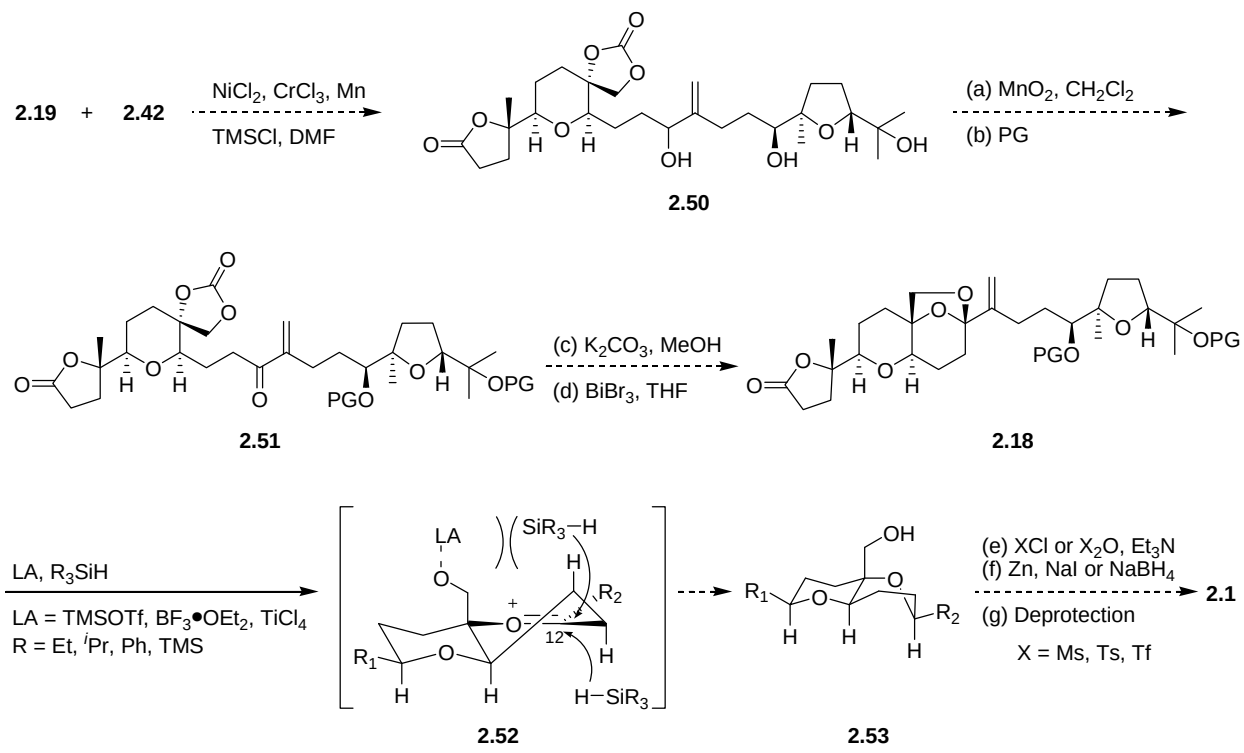


Figure 43. Future plan for completion of the total synthesis

From the retrosynthetic analysis, a challenging stereoselective reduction is required to complete the total synthesis. In the presence of suitable Lewis acids, ketal **2.18** will be opened to form oxocarbenium ion **2.52**, and various hydride sources will be examined in hope that bulkier hydrides will provide a better diastereoselectivity by favoring approach from the bottom face in order to avoid the severe steric repulsion from the axial substitution groups when approaching from the top face.[70] Subsequently, the hydroxyl group can be removed through sulfonate formation and reduction[71,72] to give desired angular methyl group. Removal of the two hydroxyl groups will furnish the natural product **2.1**. Modification of C-12 stereochemical orientation or at other positions will generate a number of analogs. Biological activity of **2.1** and these analogs

will be investigated toward a series of protein phosphatases and the structure-activity relationship pattern can be established accordingly.

2.4 SUMMARY

I am currently pursuing a convergent approach to the total synthesis of (+)-lactodehydrothyrsiferol and its analogs. This route includes the coupling of two functionalized intermediates aldehyde **2.19** and vinyl iodide **2.42**, both of which result from cyclizations of chiral epoxides with the former being obtained through oxocarbenium ion-initiated cascade cyclizations under ETIC conditions and the latter being obtained through a Brønsted acid-mediated cyclization. All the stereocenters in **2.1** will be ultimately derived from chiral reagents except the stereochemical outcome at the C-12 center which will be formed through a stereoselective reduction controlled by both substrate and the reducing agent. This remains a challenge to be explored.

3.0 MULTICOMPONENT APPROACH TO THE SYNTHESIS OF OXIDIZED AMIDES THROUGH NITRILE HYDROZIRCONATION

3.1 BACKGROUND

Oxidized amides, in which the carbon atom connected to the nitrogen has a higher oxidation state than the normal (+1) valence, have been discovered in a number of natural products. These compounds usually possess acyl aminal, acyl hemiaminal or enamide functionalities, as exemplified by protein synthesis inhibitors pederin[73,74] and psymberin,[75,76] cytotoxin zampanolide,[77] and cytotoxins apicularen A[78] and salicylihalamide A,[79] respectively (Figure 44).

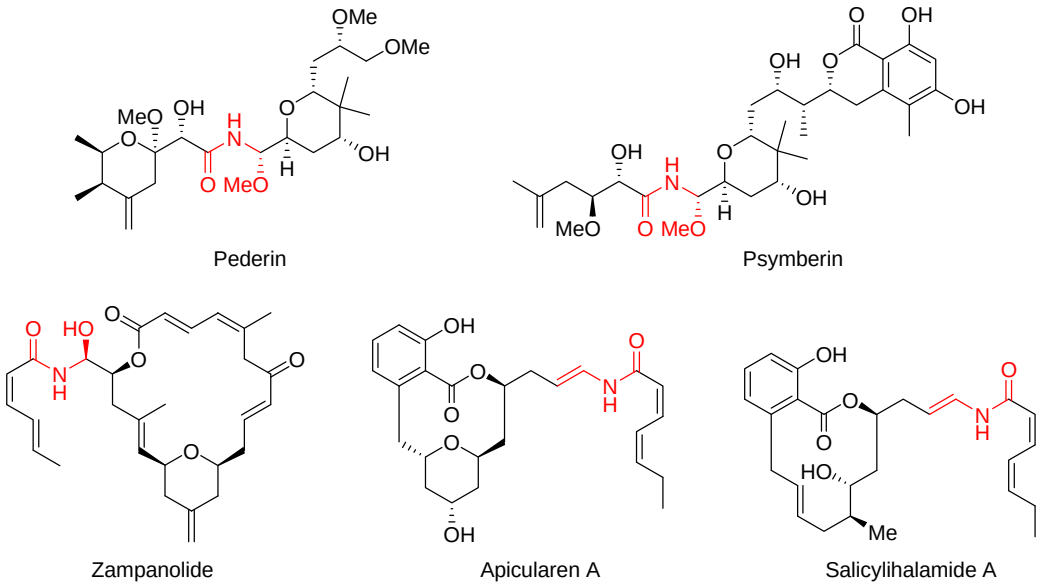


Figure 44. Representative natural products containing oxidized amides

Structure-activity relationship studies have shown that the oxidized amide moieties are closely related to the biological acitivities of these complex compounds (Figure 45).[80-84] For example, apicularen A shows strong growth inhibitory effect against the human melanoma cell line SK-MEL-5 with GI_{50} value of 6 nM. However, its synthetic analogs, with the enamide side chain being replace by simple alkenes or other enamides, have significantly reduced activity.[82] Due to the structural complexity and interesting biological activities, these natural products have attracted considerable attention from synthetic organic community.

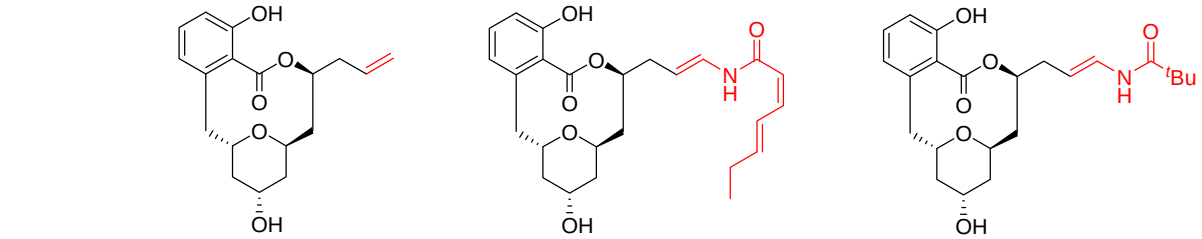


Figure 45. Apicularen A analogs

As for the synthesis of acyl aminals, a common method is through a Curtius rearrangement of acyl azide followed by nucleophilic addition to the isocyanate intermediate, as evidenced in the synthetic efforts towards mycalamides A and B (Figure 46, A).[85] A direct coupling of the activated carboxylic acid with α-alkoxy amine provides acyl aminal and this strategy has been successfully applied to the total synthesis of mycalamides A and B by Kishi (Figure 46, B).[86] Alternatively, coupling of carboxylic acid chlorides with alkyl imidates followed by reduction of the newly-formed acyl imines could also deliver acyl aminals (Figure 46, C), whereas the diastereoselectivity in the reduction varies with the substrates.[87] Our group also developed an

efficient approach to the acyl aminals through addition of oxygen-containing nucleophiles to oxidatively generated acyl iminium ions under very mild conditions (Figure 46, D).[88]

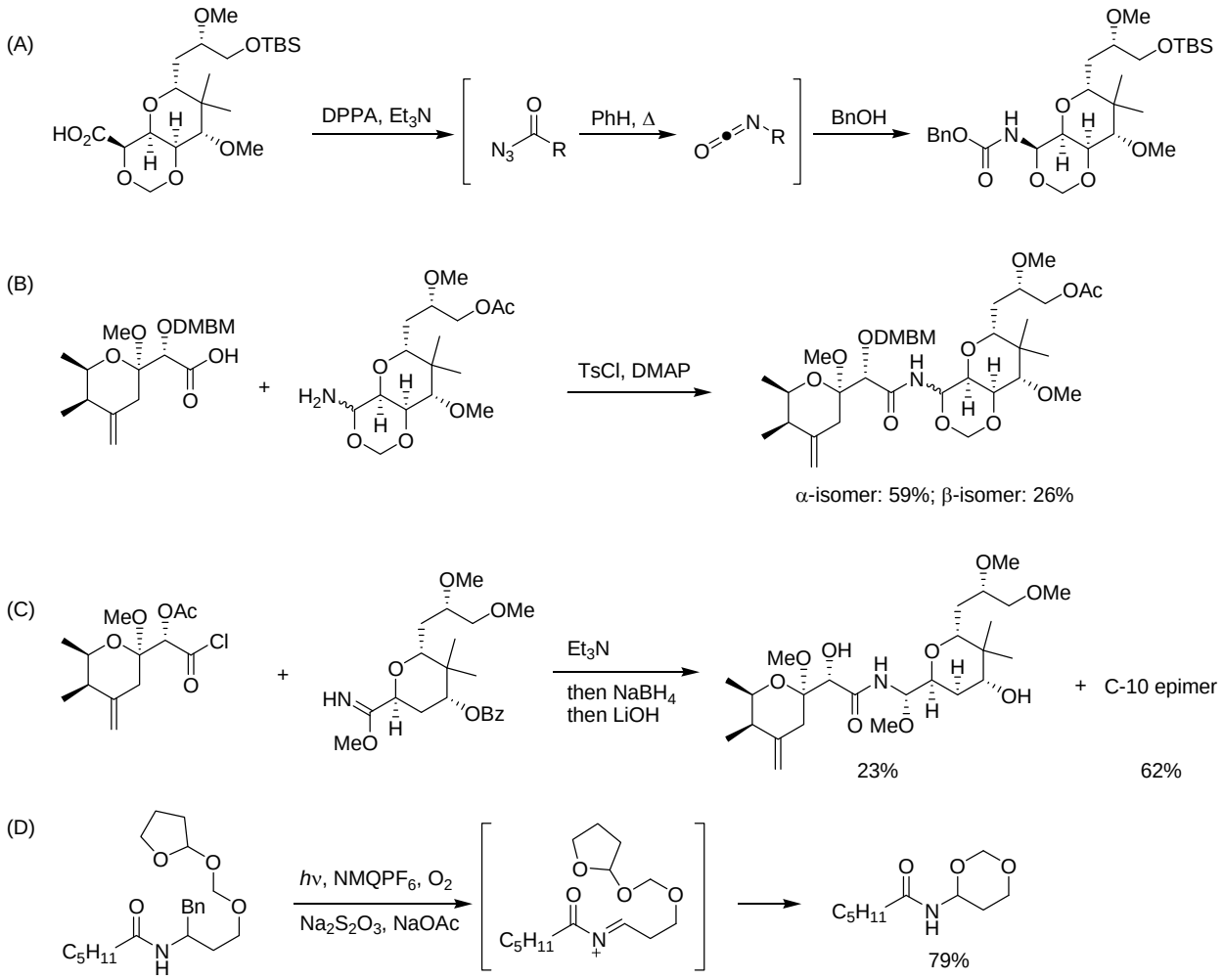


Figure 46. Preparation of acyl aminals

Acyl hemiaminals are relatively more difficult to prepare than acyl aminals. In the total synthesis of (+)-zampanolide, Smith employed a Curtius rearrangement of the acyl azide to set up the acyl aminal functionality (Figure 47, A).[89] After installation of the side chain, the PMB group was removed with DDQ and the desired acyl hemiaminal was obtained as a 1.3:1 mixture

of the two epimers, with the desired antipode of the natural product being slightly favored. Subsequently, Hoye developed a unique approach to the total synthesis of naturally occurring (-)-zampanolide through an aluminum-mediated aza-aldol reaction of the aluminum imidate with (-)-dactylolide and a mixture of 1:1 diastereomers was obtained (Figure 47, B).[90] In an effort toward the model synthesis of the zampanolide side chain, Porco[91] studied the oxidative decarboxylation of the amino acid derivative and obtained α-acyloxy amide (Figure 47, C). Hydrolysis of the acetate yielded the desired acyl hemiaminal in good yield.

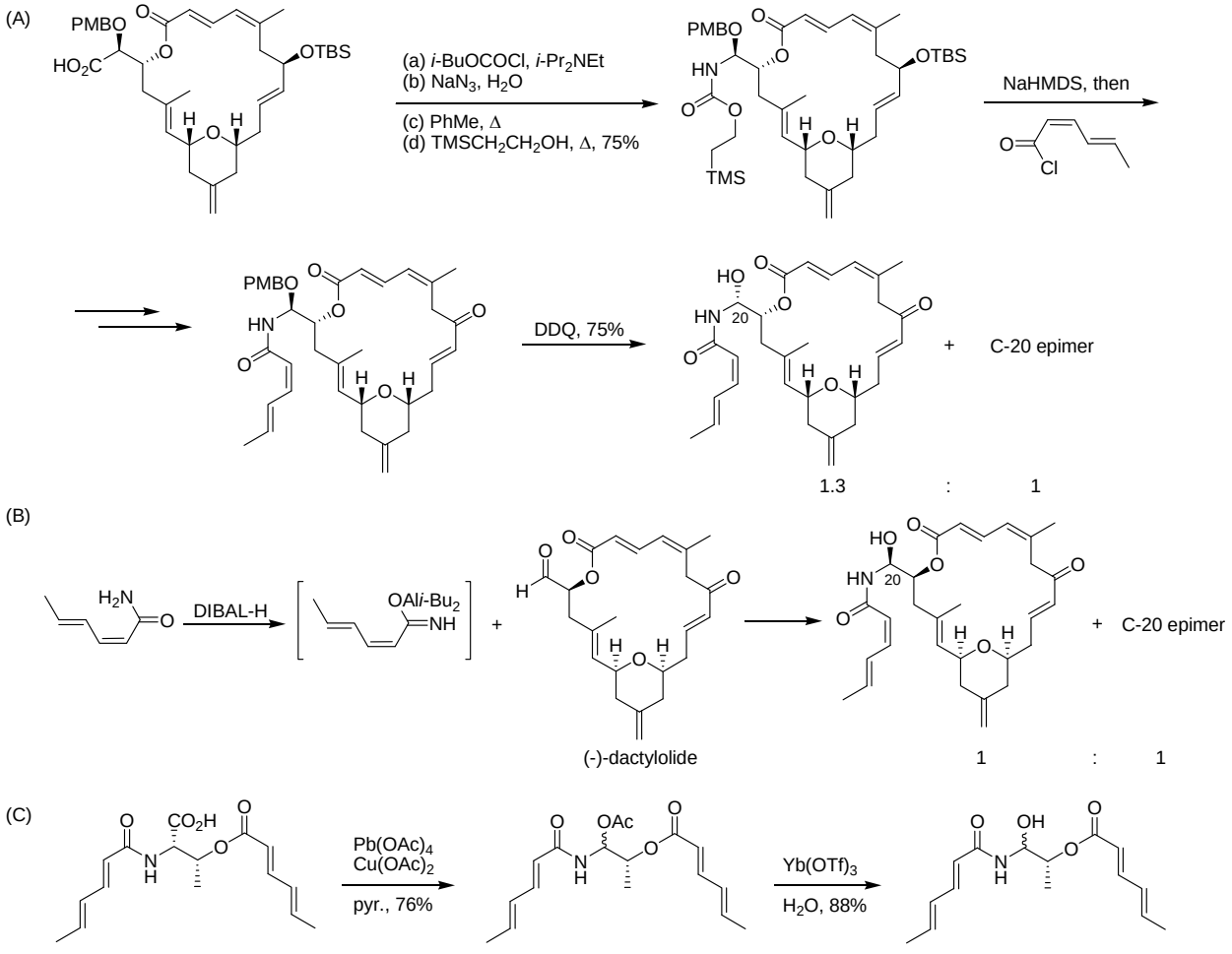


Figure 47. Preparation of acyl hemiaminals

Enamide synthesis has been extensively investigated. A Curtius rearrangement has also been employed to generate isocyanate intermediate from α,β-unsaturated acyl azides, which can be added by alkyllithium or Grignard reagents to afford enamides (Figure 48, A).[92] This strategy has been utilized in the total synthesis of salicylihalamide A[93,94] and palmeralide.[95] Fürstner developed an approach to either *E*-enamides or *Z*-enamides from *E*- or *Z*-alkenylsilanes stereospecifically (Figure 48, B).[96] Starting from alkenylsilanes, a sequence of epoxidation, epoxide opening with NaN_3 and reduction gives α-silyl amines which are further converted into the corresponding enamides through acylation and Peterson olefination. Coupling of amides with vinyl iodides, cyclic enol triflates or tosylates under Cu (I)- or Pd (0)-catalyzed conditions delivers enamides (Figure 48, C and D).[97,98] Recently, Goossen reported a stereoselective enamide formation via a Ru(II)-catalyzed hydroamination of terminal alkynes, with *E*-enamides being favored in the presence of tributylphosphine and *Z*-enamides being preferred when bis(dicyclohexylphosphino)methane was used as the ligand (Figure 48, E).[99] A traditional Wittig olefination of *N*-acyl formamides with phosphonium ylides have also been utilized to generate *E*-enamides (Figure 48, F).[100]

While most of the aforementioned methods provide entries into oxidized amides specifically, a general and mild route to all these three types of oxidized amides from a common intermediate needed to be developed. Details will be followed in the subsequent section.

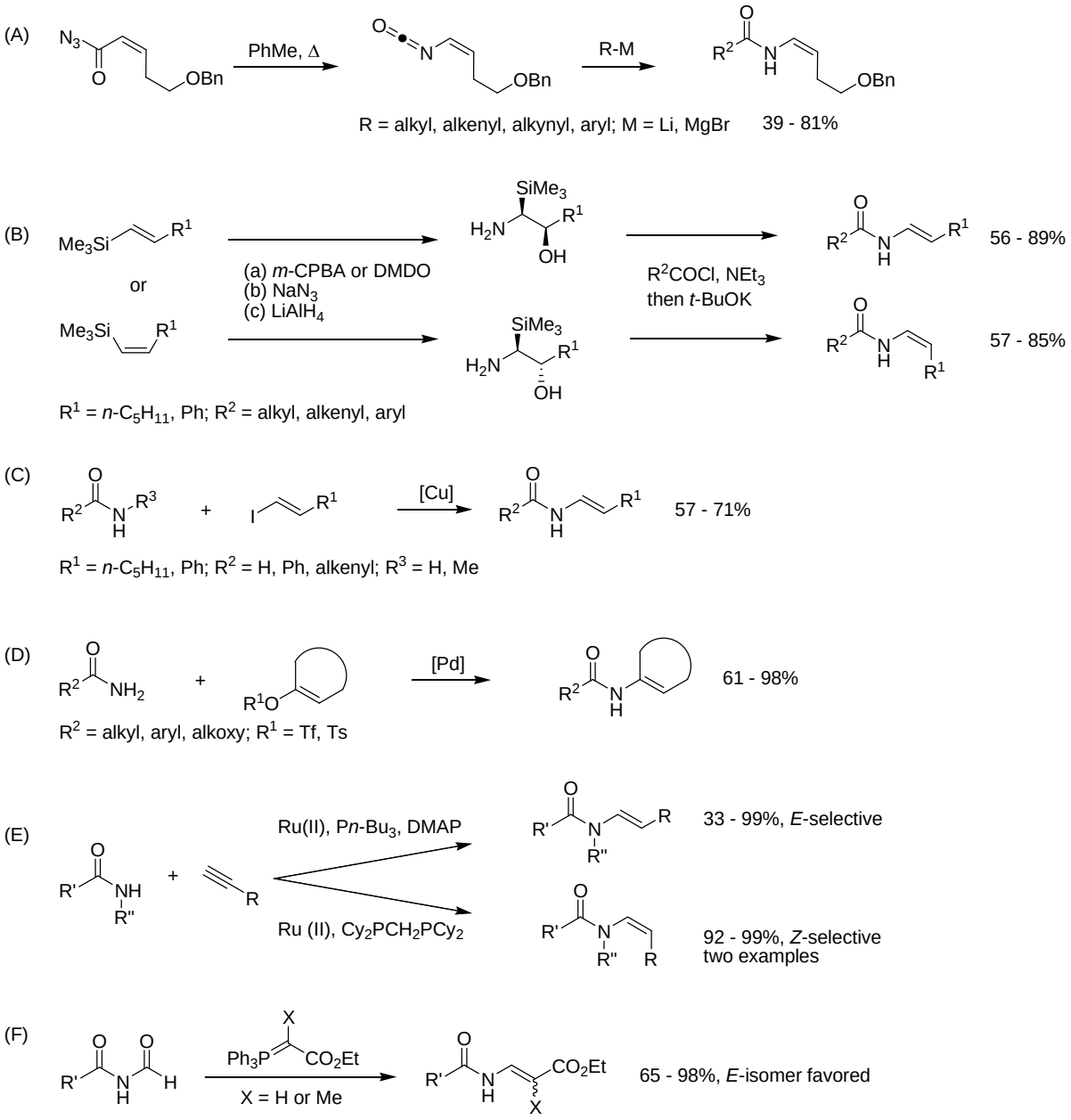


Figure 48. Preparation of enamides

3.2 RESEARCH DESIGN AND RESULTS

Based on the structural features, I proposed that oxidized amides can be accessed from common acylimine intermediates. As depicted in Figure 49, acyl aminals can be prepared from acylimines through alcohol addition,[101] acyl hemiaminals can be prepared from acylimines through water addition and enamides can be prepared from acylimines through a tautomerization.

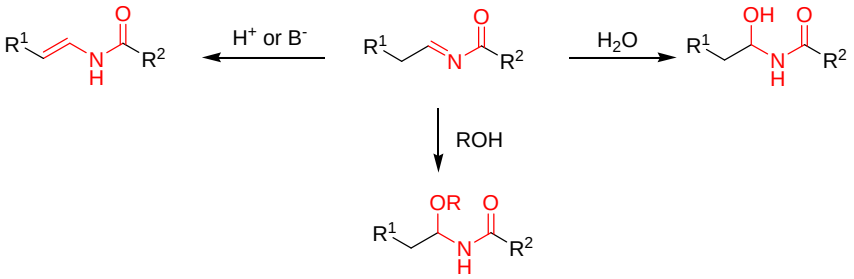


Figure 49. Oxidized amides from acylimines

For the preparation of the key intermediates acylimines, the common known method is condensation of aldehyde with amide (Figure 50).[102-104] However, when enolizable aldehydes are used, tautomerization of the forming acylimines could be a problem. Though this problem can be tackled by addition of sulfinic acids or sulfinate salts to the reaction system to form α-amido sulfones,[105,106] reforming and isolating the acylimine is still inefficient, although it is possible.[107]

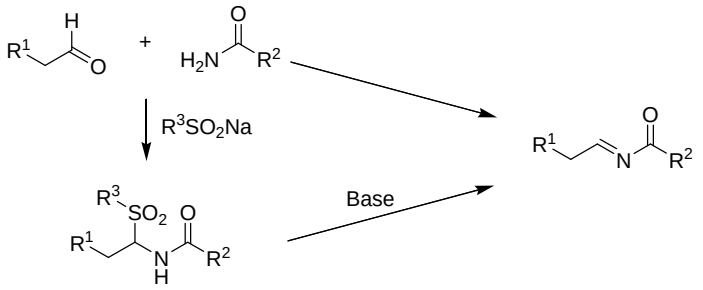


Figure 50. Generation of acylimines

Metalloimines could be acylated with acid chlorides or carboxylic acid anhydrides to give acylimines.[108,109] Majoral[110] reported that when sterically hindered nitriles were treated with Schwartz' reagent ($Cp_2Zr(H)Cl$)[111,112] followed by acylation with sterically hindered acid chlorides, acylimines were obtained in excellent yields (Figure 51).[113-115] My approach to acylimines begins with simple nitriles as well. Hydrometallation of nitriles will be expected to give metalloimines which will react with acid chlorides to afford desired acylimines (Figure 52). Once acylimines are successfully prepared, investigations of the formation of acyl aminals, acyl hemiaminals and enamides under different conditions can be performed.

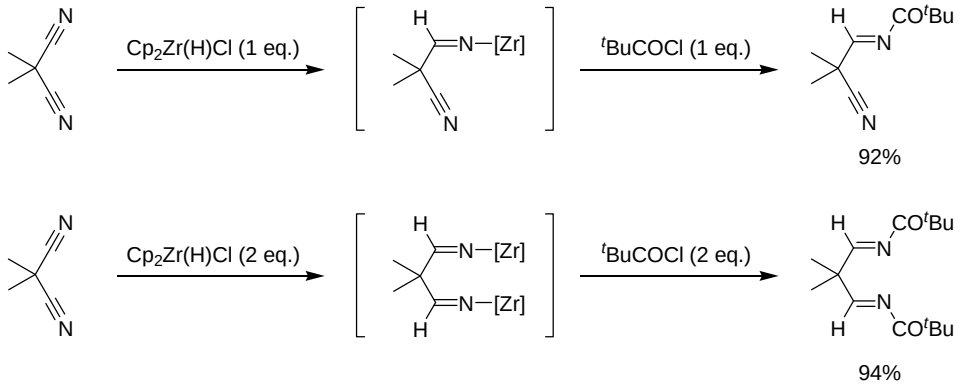


Figure 51. Hydrozirconation of nitriles

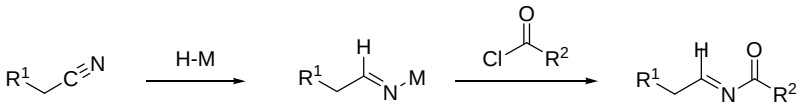


Figure 52. Proposed acylimine formation from nitriles through hydrometallation and acylation

I initiated my study by using the known α-methoxy nitrile **1**[116] as the substrate, which was prepared from addition of TMSCN to the corresponding dimethyl acetal mediated by $BiBr_3$ (Figure 53).[117] Subjecting **3.1** to Schwartz' reagent in CH_2Cl_2 followed by sequential addition of PhOC(O)Cl and MeOH provided acyl aminals **3.2** and **3.3** in combined 55% yield and with a 2.4:1 diastereomeric ratio (see below for stereochemical assignment). The observation confirmed the formation of acylimine intermediate **3.4** from acylation of *N*-zircono-imine that arose from the nitrile reduction. From a mechanistic point of view, the major product **3.2** resulted from chelation-controlled MeOH addition while the minor product **3.3** was from addition of MeOH through a Felkin pathway.

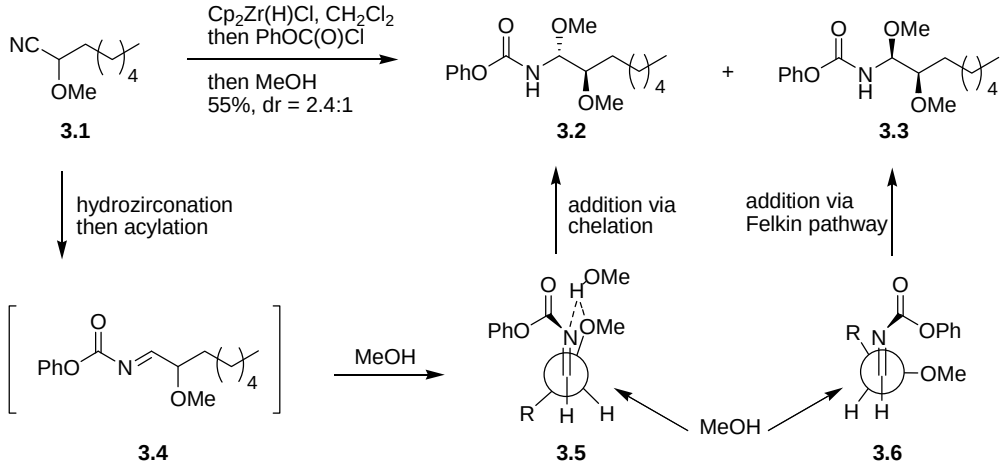


Figure 53. Acyl aminal formation in initial studies

To assign the relative stereochemical outcomes of the two products, I prepared the α,β-dimethoxy carboxylic acid **3.8** from α,β-unsaturated ester **3.7** through Sharpless asymmetric dihydroxylation,[60] double methylation[118] and hydrolysis of the ethyl ester (Figure 54). Subsequently, **3.8** was converted into acyl azide **3.9** which underwent a spontaneous Curtius rearrangement to form isocyanate **3.10**.[119] The phenoxide anion, which arose from hydrolysis of diphenylphosphoryl azide with adventitious moisture, added to the isocyanate to form (-)-**3.3** as a single enantiomer which showed identical spectroscopic features to racemate **3.3**.

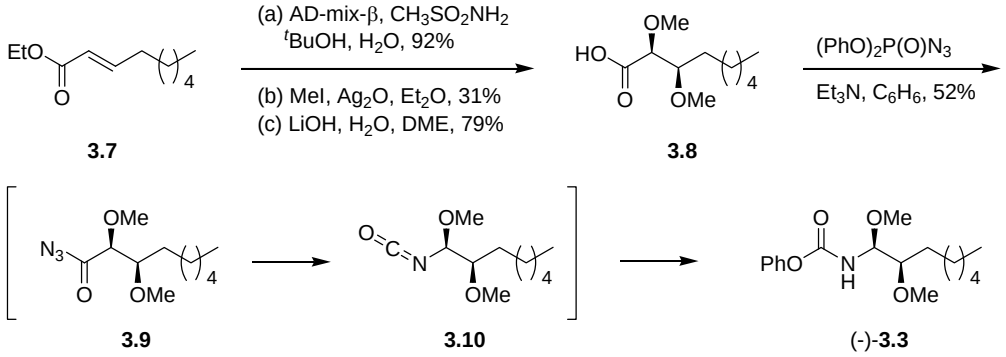
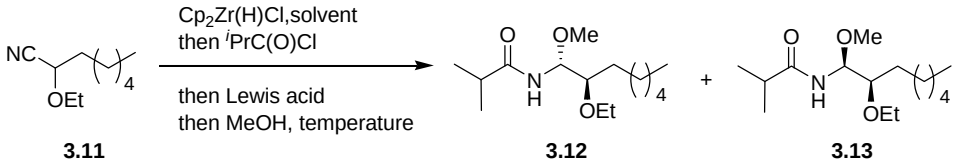


Figure 54. Confirmation of stereochemical outcomes

Having established the reactivity pattern, I next addressed the formation of acyl aminals and acyl hemiaminals extensively. Ethoxy nitrile **3.11** (prepared in a similar manner to **3.1**) was used as the substrate for exploring the diastereocontrol in the alcohol addition and the acyl aminal formation with different acylating reagents and nucleophiles.

When **3.11** was subjected to hydrozirconation, acylation with isobutyryl chloride and MeOH addition at 0 °C, both CH_2Cl_2 and THF were suitable solvents, with the products **3.12** and **3.13** being isolated in combined 75% and 64% yields, respectively (entries 1 and 2, Figure 55). It is worth noting that chelation control was preferred in CH_2Cl_2 while Felkin-pathway was slightly

favored in THF. The reversed stereoselectivity may be explained by the formation of hydrogen bonds between THF and MeOH, which results in the weakening of chelation control. Since CH_2Cl_2 is a good solvent for chelation control, several conditions were tested to improve it. Simply lowering down the temperature for MeOH addition to -78 °C gave a slightly better result (entry 3). When proper chelating Lewis acids were employed, chelation control could be enhanced to a synthetically useful level. As shown in entries 4 and 5, when MeOH addition was carried out in the presence of a stoichiometric amount of $Zn(OTf)_2$ or $Mg(ClO_4)_2$, a decent diastereocontrol (dr = 5.0:1 or 5.7:1) was accomplished with the reaction efficiency being retained.



3.11 **3.12** **3.13**

entry	solvent	Lewis acid	temperature	yield (**3.12**:**3.13**)
1	CH_2Cl_2	N/A	0 °C	75% (2.3:1)
2	THF	N/A	0 °C	64% (1:1.4)
3	CH_2Cl_2	N/A	0 °C	N/A (3.5:1)
4	CH_2Cl_2	$Zn(OTf)_2$	-78 °C	70% (5.0:1)
5	CH_2Cl_2	$Mg(ClO_4)_2$	-78 °C	71% (5.7:1)

Figure 55. Optimization of chelation control

Electrophiles other than isobutyryl chloride were also investigated (Figure 56). Acylation of the metalloimine with α-methoxyacetyl chloride give a mixture of **3.14** and **3.15** in a combined 69% yield and 1.7:1 diastereomeric ratio. The products are electronically similar to the acyl aminals in pederin and psymberin. CbzCl is also a suitable acylating reagent, with *N*,*O*-

acetals **3.16** and **3.17** being isolated in 64% overall yield. In this case, the Cbz group can serve as a protecting group and can be removed readily. Unfortunately, when the metalloimine was acylated with methanesulfonic anhydride, only modest yield of sulfonyl aminals **3.18** and **3.19** were obtained. From this reaction, considerable amounts of the aldehyde from hydrolysis of the metalloimine were also isolated.

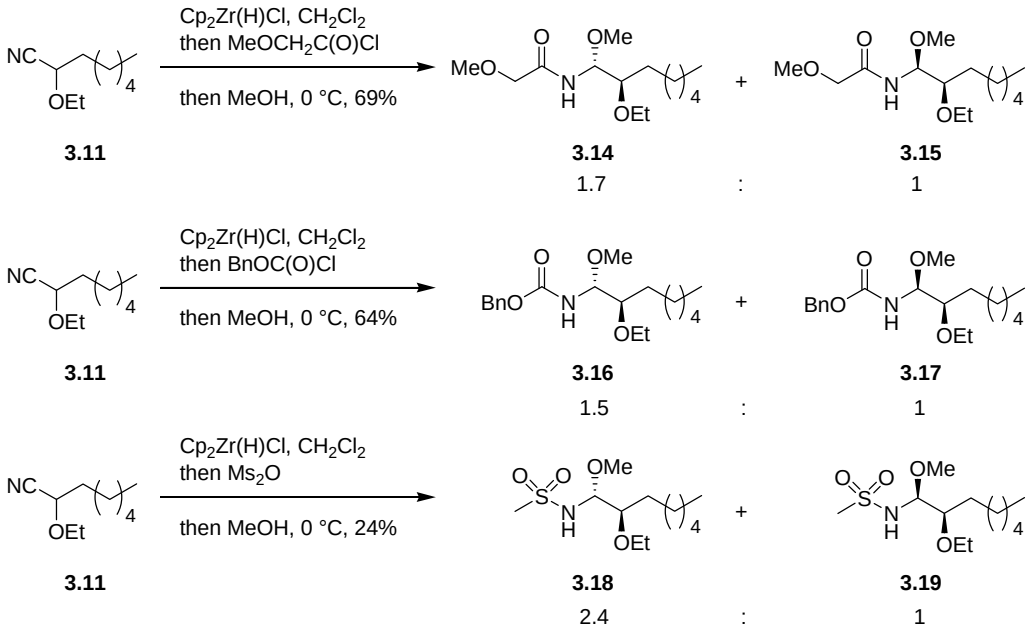


Figure 56. Acyl aminal formation from **3.11** with various electrophiles

Besides MeOH, other heteronucleophiles also afforded satisfactory results when acylimine **3.20** was utilized as the common intermediate (Figure 57). Sterically hindered ^{t}BuOH had no influence on the reactivity, with the desired acyl aminals being isolated in 71% yield and the Felkin-pathway being favored. PhOH and PhSH are also suitable for this reaction, providing 69% and 72% yields, respectively. It is noteworthy that the chelation-controlled product **3.23** was dominant in the case of PhOH while the product **3.26** from Felkin-type pathway was

predominantly formed in the case of PhSH as the nucleophile. This observation is consistent with the hydrogen-bond-forming abilities of these two nucleophiles.

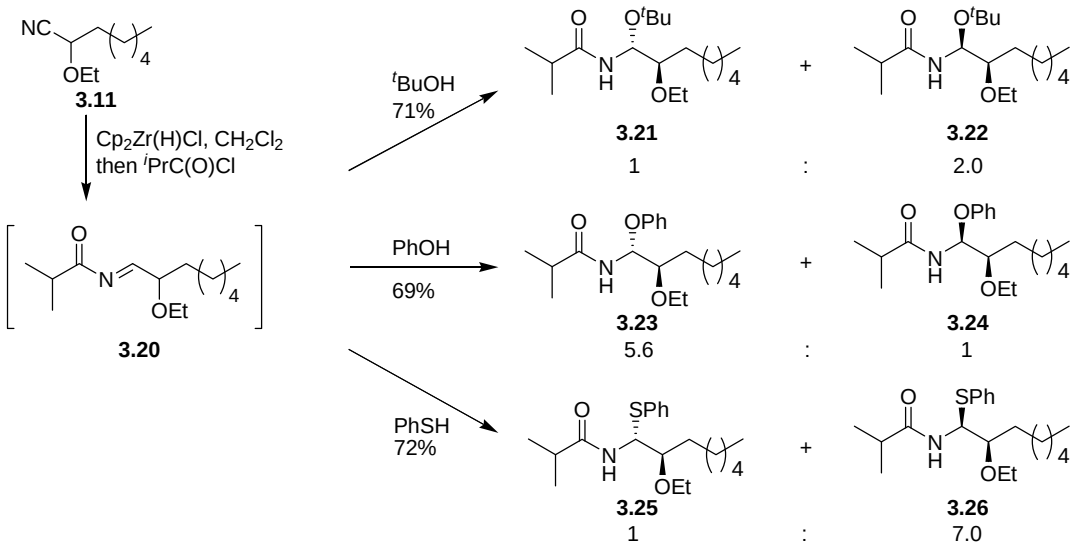


Figure 57. Acyl aminal formation from **3.11** with various nucleophiles

Nitriles with different substitutions are good substrates for the synthesis of acyl aminals and acyl hemiaminals (Figure 58). Subjecting α-benzoyloxy nitrile **3.27**[120] to hydrozirconation, acylation with isobutyryl chloride and MeOH addition, acyl aminal **3.28** was isolated in 64% yield (contaminated with 4% BnOH), indicating that ester groups can be tolerated in hydrozirconation.[121] Instead of MeOH addition, a simple aqueous workup after the acylimine formation provided acyl hemiaminal **3.29** in 52% yield, which is structurally relevant to the zampanolide side chain. Also isolated from this reaction was **3.29A** in 13% yield which resulted from addition of BnOH to the acylimine intermediate. It is worth noting that from the reactions of **3.27**, the side product from migration of the benzoyl group to the metalloimine nitrogen was not observed. Octyl cyanide **3.30**, with no branching at the α-carbon, afforded the desired acyl

aminal **3.31** and acyl hemiaminal **3.32** in good yields as well. It was found that THF is a better solvent than CH_2Cl_2 to suppress the acylimine tautomerization to the corresponding enamide. Aromatic nitriles also proved to be excellent substrates, with acyl aminal **3.34** being obtained in 73% isolated yield from phenyl cyanide **3.33** though it underwent a much slower hydrozirconation than aliphatic nitriles.

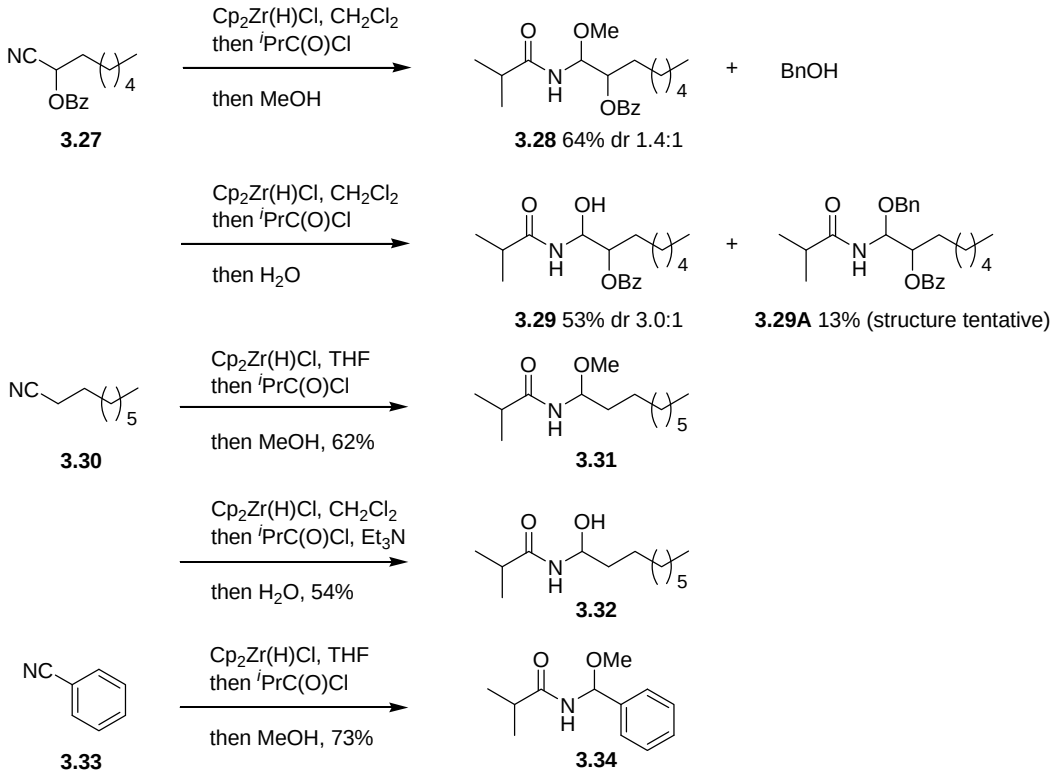


Figure 58. Acyl aminal and acyl hemiaminal synthesis from various nitriles

Having achieved smooth transformations from nitriles to acyl aminals and acyl hemiaminals, I next examined the enamide synthesis. Octyl cyanide **3.30** and isobutyryl chloride were used to explore the optimum reaction conditions (Figure 59). In CH_2Cl_2, 22% of the desired *E*-enamide **3.36** was obtained when the metalloimine was acylated in the presence of Et_3N

followed by addition of Lewis acid BF_3•OEt_2 (entry 1, Table 1). In the absence of BF_3•OEt_2, a mixture of **3.36** and **3.37** in ~1:1 ratio resulted from acylimine **3.35** (entry 2); without Et_3N base, no product (**3.36** or **3.37**) was observed (entry 3). When the reaction was conducted in THF, acylimine **3.35** was successfully generated in the presence of Et_3N and was smoothly tautomerized to afford *E*-enamide **3.36** in 57% yield in the presence of BF_3•OEt_2 (entry 4). From this reaction, only minimum amount of *Z*-enamide **3.37** was observed. When the tautomerization was performed in the absence of BF_3•OEt_2, only trace amount of **3.36** was observed (entry 5); and when the metalloimine was acylated in the absence of Et_3N, less than 10% yield of **3.36** was isolated (entry 6). These results convincingly demonstrated that both Et_3N and BF_3•OEt_2 are crucially important in this reaction, presumably due to their synergistic effect in converting **3.35** to **3.36.** Also of note is that use of more than 1 equiv. of isobutyryl chloride would result in the formation of significant amount of diacylation product **3.38**. Following the established conditions, allylic nitrile **3.40**, prepared in four steps from methacrolein and 1-dodecene, gave rise to *E*,*E*-dienamide **3.41** in 62% yield (Figure 60).

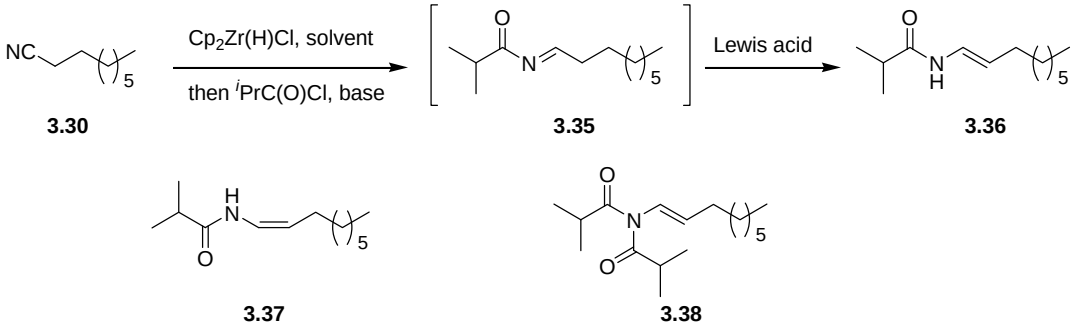


Figure 59. Synthesis of enamide **3.36** from octyl cyanide **3.30**

Table 1. Optimization of reaction conditions for enamide formation

entry	solvent	base (3.0 eq.)	Lewis acid (1.3-1.5 eq.)	yield (**3.36**)
1	CH_2Cl_2	Et_3N	$BF_3•OEt_2$	22%
2	CH_2Cl_2	Et_3N	N/A	*E*:*Z* ~ 1:1
3	CH_2Cl_2	N/A	$BF_3•OEt_2$	no product
4	THF	Et_3N	$BF_3•OEt_2$	57%
5	THF	Et_3N	N/A	trace
6	THF	N/A	$BF_3•OEt_2$	<10%

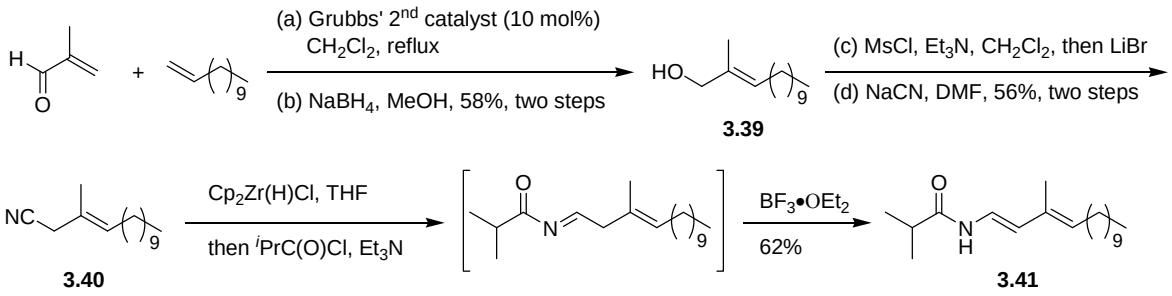


Figure 60. Synthesis of *E*,*E*-dienamide **3.41** from allylic nitrile **3.40**

With successful synthesis of oxidized amides from simple nitrile substrates, I next applied this methodology to the synthesis of a more complex model compound that is related to pederin and psymberin. For this purpose, tetrahydropyranyl nitrile **3.43** was prepared (by Michael Green in the Floreancig group at the University of Pittsburgh) in its racemic form from known ketone **3.42**[88] through methylation, aluminum-mediated reduction of ketone,[122] cleavage of the terminal alkene, acylation and displacement of the anomeric acetate group with cyanide (Figure 61).

Reaction of **3.43** through a sequence of hydrozirconation, acylation with isobutyryl chloride and MeOH addition at 0 °C provided desired acyl aminal **3.44** and its diastereomer **3.45** in a combined 75% yield and with a 1.9:1 ratio favoring the chelation control (entry 1, Table 2). Also isolated for this reaction was amide **3.46** in 8% yield, which resulted from direct reduction of the acylimine intermediate by the slightly excess amount of $Cp_2Zr(H)Cl$. Conducting the MeOH addition at lower temperature (-78 °C) was found to slightly improve the diastereoselectivity (entry 2). Employment of $Mg(ClO_4)_2$, which promoted chelation control to a considerable extent (*cf*. Figure 55), did not provide a better diastereocontrol, with acyl aminals being obtained in 77% yield and 2.3:1 ratio (entry 3). Although only moderate diastereocontrol was obtained under the conditions studied here, the high yield of the acyl aminal together with the desired stereochemical orientation still makes this method attractive for the synthesis of acyl aminals with similar structures in natural products and their analogues.

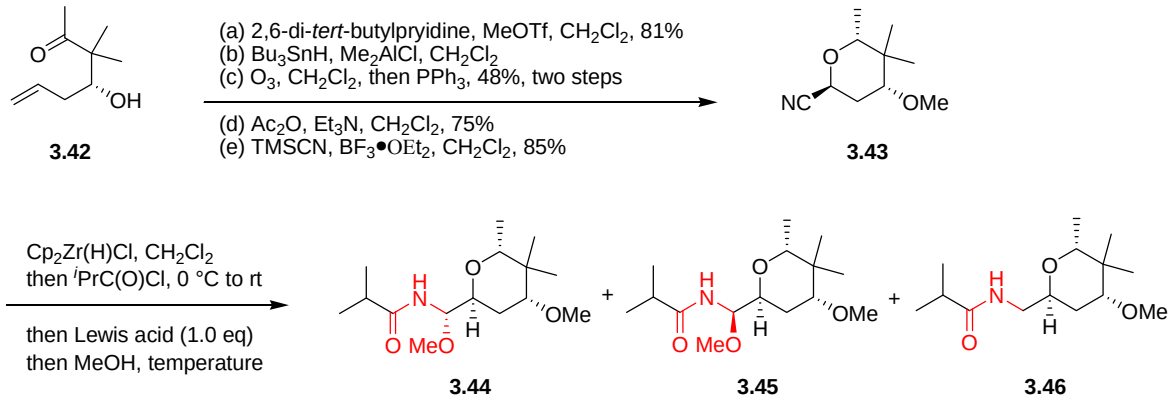


Figure 61. Synthesis of tetrahydropyranyl acyl aminals

Table 2. Reaction of **3.43** under various conditions

entry	temperature	Lewis acid (1 eq.)	yield (**3.44**+**3.45**)	dr (**3.44**/**3.45**)	yield (**3.46**)
1	0 °C	N/A	75%	1.9:1	8%
2	-78 °C	N/A	71%	2.3:1	10%
3	-78 °C	$Mg(ClO_4)_2$	77%	2.3:1	10%

3.3 CONCLUSIONS

An efficient one-pot approach to the synthesis of oxidized amides from nitriles was developed. In this process, the acylimines, which are generated from hydrozirconation of nitriles followed by acylation with suitable electrophiles, serve as the common intermediates to deliver acyl aminals, acyl hemiaminals or enamides through nucleophilic addition or tautomerization. In the acyl aminal formation, moderate to good diastereocontrol could be achieved with the assistance of Lewis acids through chelation-controlled nucleophilic addition. It was also found that the base and Lewis acid played a synergistic role in the *E*-enamide syntheses. In the absence of base or Lewis acid, low efficiency for *E*-enamide formation was observed. With the known methods for the synthesis of nitriles, along with various available electrophiles and nucleophiles, this method will provide a convenient and effective access to oxidized amides with diverse structures.

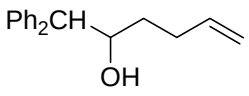
APPENDIX A

STUDIES ON THE STRUCTURE/REACTIVITY REALTIONSHIPS OF BICYCLIC EPOXONIUM IONS AND TETHERED NUCLEOPHILES (SUPPORTING INFORMATION)

General Experimental Proton (^{1}H NMR) and carbon (^{13}C NMR) nuclear magnetic resonance spectra were recorded at ambient temperatures on Bruker Avance 300 spectrometer at 300 MHz and 75 MHz, respectively, Bruker Avance 500 spectrometer at 500 MHz and 125 MHz, or at Bruker Avance 600 spectrometer at 600 MHz and 151 MHz if specified. The chemical shifts are given in parts per million (ppm) on the delta (δ) scale. The solvent peak was used as a reference value, for ^{1}H NMR: $CDCl_3$ = 7.27 ppm, C_6D_6 = 7.15 ppm, for ^{13}C NMR: $CDCl_3$ = 77.23. Data are reported as follows: (s = singlet; d = doublet; t = triplet; q = quartet; dd = doublet of doublets; dt = doublet of triplets; br = broad; app = apparently). High resolution mass spectra were recorded on a MICROMASS AUTOSPEC (for EI) or WATERS Q-TOF API-US (for ESI) spectrometer. Infrared (IR) spectra were collected on a Mattson Cygnus 100 spectrometer. Samples for IR were prepared as a thin film on a NaCl plate by dissolving the compound in CH_2Cl_2 and then evaporating the CH_2Cl_2. Optical rotations were measured on a Perkin-Elmer 241 polarimeter. Activated 4 Å molecular sieves were obtained through drying in oven at 150 °C

overnight. Tetrahydrofuran and diethyl ether were dried by passage through an activated alumina column under positive N_2 pressure. Methylene chloride and benzene were distilled under N_2 from CaH_2. Diphenylmethane was purchased from Aldrich and used without further purification. Anhydrous DMF and MeI were purchased from Acros. *m*CPBA was purchased from Acros and purified according to the standard procedure (*cf.* Purification of Laboratory Chemicals, 4th Ed., by Armarego, W. L. F. and Perrin, D. D.). Boc_2O and *N*-methylimidole were purchased from Acros and used without further purification. Anhydrous $Na_2S_2O_3$ was purchased from Aldrich and used as received. Toluene and 1,2-dichloroethane were purchased from Fisher Scientific and dried with 4 Å molecular sieves overnight prior to use. Analytical TLC was performed on E. Merck pre-coated (0.25 mm) silica gel 60F-254 plates. Visualization was done under UV (254 nm). Flash chromatography was done using ICN SiliTech 32-63 60 Å silica gel. Reagent grade ethyl acetate, diethyl ether, and hexanes (commercial mixture) were purchased from EM Science and used as is for chromatography. All reactions were performed in oven or flame-dried glassware under a positive pressure of N_2 with magnetic stirring unless otherwise noted.

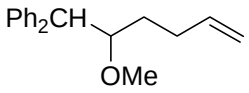
1,1-Diphenylhex-5-en-2-ol (A1)



A solution of diphenylmethane (1.262 g, 7.50 mmol) in THF (7.5 ml) in a two-necked round-bottom flask was treated dropwise *n*-BuLi (1.6 M in hexanes, 4.7 mL, 7.5 mmol). The resulting deep orange solution was refluxed for 1 h and then cooled to 0 °C. A solution of 4-pentenal (0.252g, 3.00 mmol) in THF (3.0 mL) was added dropwise and the flask formerly containing 4-pentenal was rinsed with THF (2 x 1.0 mL). The reaction mixture was stirred at 0 °C for 1 h, then warmed to room temperature and quenched by slow addition of saturated NH_4Cl solution (10 mL). The mixture was poured onto water (20 mL)

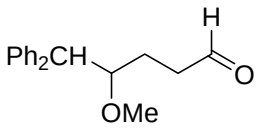
and extracted with Et_2O (3 x 30 mL). The organic extracts were dried over $MgSO_4$, filtered and concentrated. The residue was purified by flash chromatography (3% - 12% Et_2O in hexanes) to give the secondary alcohol **A1** (0.628 g, 83.0%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42-7.17 (m, 10H), 5.80 (ddt, *J* = 17.0, 13.4, 6.8 Hz, 1H), 5.06-4.94 (m, 2H), 4.42-4.35 (m, 1H), 3.90 (d, *J* = 8.4 Hz, 1H), 2.35-2.12 (m, 2H), 1.67-1.41 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.5, 141.6, 138.7, 129.0, 129.0, 128.9 128.4, 127.1, 126.8, 115.1, 73.4, 59.1, 34.4, 30.4; IR (neat) 3560, 3062, 2916, 1640, 1598, 1494, 1451, 1080, 913, 745, 703 cm^{-1}; HRMS (EI): *m/z* calcd for $C_{18}H_{20}O$ ($M^{+\bullet}$) 252.1514, found 252.1523.

5-Methoxy-6,6-diphenylhex-1-ene (A2)



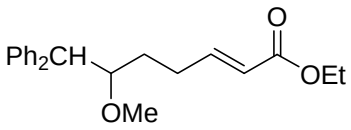
The secondary alcohol **A1** (0.585 g, 2.32 mmol) in anhydrous DMF (14.0 mL) at 0 °C was treated with NaH (60% dispersion in mineral oil, 0.232 g, 5.80 mmol) and the suspension was stirred at 0 °C for 30 min. MeI (0.58 mL, 9.28 mmol) was added dropwise and the cold bath was then removed. After stirred for 2 h at room temperature, the reaction was quenched with water (20 mL) cautiously and extracted with Et_2O (3 x 40 mL). The organic extracts were dried over $MgSO_4$, filtered and concentrated. The resulting residue was purified by flash chromatography (3% - 6% Et_2O in hexanes) to give the secondary alcohol **A2** (0.598 g, 96.8%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44-7.16 (m, 10H), 5.80 (ddt, *J* = 17.0, 13.3, 6.7 Hz, 1H), 5.06-4.95 (m, 2H), 4.05 (d, *J* = 8.2 Hz, 1H), 3.98 (m, 1H), 3.19 (s, 3H), 2.25-2.15 (m, 2H), 1.70-1.54 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.9, 142.5, 138.7, 129.1, 128.7, 128.4, 126.5, 126.4, 114.9, 83.2, 58.1, 56.4, 31.8, 29.6; IR (neat) 3027, 2928, 1640, 1599, 1495, 1451, 1101, 911, 745, 701 cm^{-1}; HRMS (EI): *m/z* calcd for $C_{15}H_{15}O$ ($M-C_4H_7$)$^{+\bullet}$ 211.1123, found 211.1125.

4-Methoxy-5,5-diphenylpentanal (1.56)



At -78 °C, the terminal olefin **A2** (193 mg, 0.724 mmol) in CH_2Cl_2 (7.5 mL) was bubbled gently with ozone until the solution retained a deep blue color and then PPh_3 (570 mg, 2.17 mmol) was added in one portion. The mixture was warmed to room temperature, stirred for 3 h and then concentrated. The residue was purified by column chromatography (20% - 30% Et_2O in hexanes) to give the aldehyde **1.56** (186 mg, 95.8%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.74 (t, *J* = 1.7 Hz, 1H), 7.44-7.21 (m, 10H), 4.04-3.96 (m, 2H), 3.12 (s, 3H), 2.60-2.45 (m, 2H), 2.05-1.95 (m, 1H), 1.80-1.68 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.3, 142.3, 142.2, 128.8, 128.6, 128.5, 126.8, 126.6, 83.0, 58.3, 56.6, 39.8, 25.3; IR (neat) 2928, 2827, 2726, 1722, 1495, 1451, 1113, 747, 704 cm^{-1}; HRMS (EI): *m*/*z* calcd for $C_{15}H_{15}O$ $(M-C_3H_5O)^{+\bullet}$ 211.1123, found 211.1124.

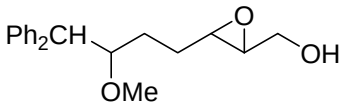
(*E*)-Ethyl 6-methoxy-7,7-diphenylhept-2-enoate (A3)



At 0 °C, triethyl phosphonoacetate (0.25 mL, 1.27 mmol) was added dropwise to a suspension of NaH (60% dispersion in mineral oil, 51.0 mg, 1.27 mmol) in THF (4.0 mL) and the resulting solution was stirred at 0 °C for 30 min. The aldehyde **1.56** (171 mg, 0.637 mmol, dissolved in 1.0 mL THF) was introduced dropwise and the flask formerly containing the aldehyde was rinsed with THF (2 x 0.5 mL). The reaction mixture was stirred at 0 °C for 1 h, then quenched with saturated NH_4Cl (5 mL) and poured onto water (10 mL). The mixture was extracted with CH_2Cl_2 (3 x 25 mL) and the organic extracts were dried ($MgSO_4$) and concentrated. The residue was purified by column chromatography (10% - 15% EtOAc in hexanes) to give the ethyl ester **A3** (202 mg, 93.8%) as a

colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50-7.17 (m, 10H), 6.96 (dt, *J* = 15.6, 6.9 Hz, 1H), 5.82 (br d, *J* = 15.6 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 4.04 (d, *J* = 8.5 Hz, 1H), 3.99-3.94 (m, 1H), 3.19 (s, 3H), 2.44-2.25 (m, 2H), 1.75-1.50 (m, 2H), 1.32 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.8, 149.0, 142.5, 142.2, 128.9, 128.8, 128.5, 128.5, 126.7, 126.5, 121.6, 83.0, 60.3, 58.2, 56.4, 30.8, 27.9, 14.4; IR (neat) 2980, 2931, 1717, 1653, 1495, 1451, 1267, 1202, 1109, 1043, 746, 704 cm^{-1}; HRMS (EI): *m/z* calcd for $C_{20}H_{21}O_2$ $(M\text{-}C_2H_5O)^{+\bullet}$ 293.1542, found 293.1538.

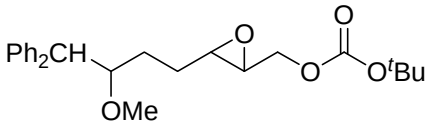
(3-(3-Methoxy-4,4-diphenylbutyl)oxiran-2-yl)methanol (A4)



At -78 °C, DIBAL-H (1 M in hexanes, 1.5 mL, 1.5 mmol) was added dropwise to a solution of the ethyl ester **A3** (202 mg, 0.598 mmol) in THF (6.0 mL). The mixture was stirred at -78 °C for 30 min, then quenched with saturated sodium tartrate (6.0 mL) and diluted with water (5 mL). The mixture was warmed to room temperature and stirred vigorously for 2 h. After that time, the mixture was extracted with CH_2Cl_2 (3 x 30 mL) and the extracts were dried ($MgSO_4$) and concentrated. The residue was dissolved in CH_2Cl_2 (6.0 mL) and cooled to 0 °C. $NaHCO_3$ (100 mg, 1.20 mmol) and *m*CPBA (pure, 134 mg, 0.777 mmol) were added sequentially. The suspension was stirred at 0 °C for 1.5 h, then quenched with saturated $Na_2S_2O_3$ (3 mL) and water (10 mL). The mixture was stirred at room temperature for 30 min, and extracted with CH_2Cl_2 (3 x 40 mL). The extracts were dried ($MgSO_4$), and concentrated and the residue was purified by column chromatography (40% - 70% EtOAc in hexanes containing 0.5% Et_3N) to give the epoxy alcohol **A4** (132 mg, 70.4%, dr ~ 1:1) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39-7.17 (m, 10H), 4.02-3.94 (m, 2H), 3.91-3.82 (m, 1H), 3.66-3.56 (m, 1H), 3.17/3.16 (s, 3H), 2.93-2.86 (m, 2H), 1.81-1.47 (m, 4H);

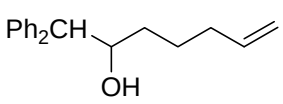
^{13}C NMR (75 MHz, $CDCl_3$) δ 142.6, 142.3, 142.2, 128.9, 128.8, 128.8, 128.6, 128.5, 126.7, 126.5, 83.2, 83.1, 61.9, 61.8, 58.6, 58.6, 58.2, 57.9, 56.5, 56.1, 56.0, 28.8, 28.0, 27.4, 27.1; IR (neat) 3428, 2928, 1495, 1451, 1095, 746, 704 cm^{-1}; HRMS (ESI): *m*/*z* calcd for $C_{20}H_{24}O_3Na$ $[M+Na]^+$ 335.1623, found 335.1636.

***tert*-Butyl (3-(3-methoxy-4,4-diphenylbutyl)oxiran-2-yl)methyl carbonate (1.47)**



The epoxy alcohol **A4** (124.0 mg, 0.397 mmol) in dry toluene (4.0 mL) at 0 °C was treated with 1-methylimidazole (32 μL, 0.397 mmol) followed by Boc_2O (173 mg, 0.794 mmol). The mixture was stirred at 0 °C for 2 h, then at room temperature for 1 h. After that time, the reaction was quenched with water (15 mL) and extracted with CH_2Cl_2 (3 x 20 mL). The organic extracts were dried over $MgSO_4$, filtered and concentrated. The residue was azeotroped with hexanes (3 x 10 mL) and then purified by flash chromatography (15% - 20% EtOAc in hexanes containing 0.5% Et_3N) to give the *t*-butyl carbonate **1.47** (146.8 mg, 89.7%, dr ~ 1:1) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38-7.16 (m, 10H), 4.23-4.18 (m, 1H), 3.99-3.92 (m, 3H), 3.14/3.13 (s, 3H), 2.94-2.91 (m, 1H), 2.81-2.77 (m, 1H), 1.79-1.42 (m, 4H), 1.48 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.4, 142.6, 142.3, 142.2, 128.9, 128.9, 128.8, 128.6, 128.5, 126.7, 126.5, 83.1, 83.0, 82.7, 67.2, 67.1, 58.3, 57.9, 56.8, 56.6, 56.5, 56.2, 55.2, 28.8, 28.0, 27.9, 27.4, 27.1; IR (neat) 2981, 2933, 1743, 1495, 1452, 1370, 1281, 1163, 1101, 912, 733, 704 cm^{-1}; HRMS (ESI): *m*/*z* calcd for $C_{25}H_{32}O_5Na$ $[M+Na]^+$ 435.2147, found 435.2140.

1,1-Diphenylhept-6-en-2-ol (A5)

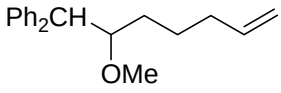


At -78 °C, a solution of DMSO (1.1 mL, 15.0 mmol) in CH_2Cl_2 (2 mL)

was added dropwise to a mixture of $(COCl)_2$ (0.65 mL, 7.5 mmol) in CH_2Cl_2 (20 mL). After 10 min, a solution of 5-hexen-1-ol (0.60 mL, 5.0 mmol) in CH_2Cl_2 (5 mL) was introduced. The white suspension was stirred at -78 °C for 30 min, then Et_3N (4.2 mL, 30.0 mmol) was added and the suspension was stirred for 30 min. After that time, the reaction was warmed to room temperature, diluted with CH_2Cl_2 (80 mL) and washed with saturated $NaHCO_3$ (80 mL). The organic layer was dried (Na_2SO_4), filtered and concentrated to give crude 5-hexenal.

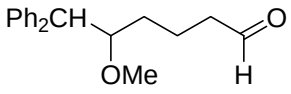
A solution of diphenylmethane (2.52 g, 15.0 mmol) in THF (15 ml) in a two-necked round-bottom flask was treated dropwise *n*-BuLi (1.6 M in hexanes, 9.4 mL, 15.0 mmol). The resulting deep orange solution was refluxed for 1 h and then cooled to 0 °C. A solution of as-prepared crude 5-hexenal in THF (3.0 mL) was added dropwise and the flask formerly containing 4-pentenal was rinsed with THF (2 x 1.0 mL). The reaction mixture was stirred at 0 °C for 1 h, then warmed to room temperature and quenched by slow addition of saturated NH_4Cl solution (15 mL). The mixture was poured onto water (40 mL) and extracted with Et_2O (3 x 50 mL). The organic extracts were dried over $MgSO_4$, filtered and concentrated. The residue was purified by flash chromatography (3% - 15% Et_2O in hexanes) to give the secondary alcohol **A5** (0.928 g, 70%, two steps) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43-7.19 (m, 10H), 5.80 (tdd, J = 16.9, 13.2, 6.6 Hz, 1H), 5.02-4.93 (m, 2H), 4.40-4.36 (m, 1H), 3.92 (d, J = 8.3 Hz, 1H), 2.12-1.96 (m, 2H), 1.76-1.37 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.6, 141.6, 138.9, 129.0, 128.8, 128.4, 127.0, 126.7, 114.7, 73.8, 59.0, 34.6, 33.8, 25.3; IR (neat) 3561, 3453, 3026, 2918, 1640, 1598, 1494, 1451, 1080, 911, 746, 703 cm^{-1}; HRMS (ESI): *m*/*z* calcd for $C_{19}H_{22}ONa$ $[M+Na]^+$ 289.1568, found 289.1600.

6-Methoxy-7,7-diphenylhept-1-ene (A6)



The secondary alcohol **A5** (0.918 g, 3.45 mmol) in anhydrous DMF (20 mL) at 0 °C was treated with NaH (60% dispersion in mineral oil, 0.345 g, 8.62 mmol) and the suspension was stirred at 0 °C for 30 min. MeI (0.86 mL, 13.8 mmol) was added dropwise and the cold bath was then removed. After stirred overnight, the reaction was quenched with water (40 mL) cautiously and extracted with Et_2O (3 x 60 mL). The organic extracts were dried over $MgSO_4$, filtered and concentrated. The resulting residue was purified by flash chromatography (1% - 5% Et_2O in hexanes) to give the secondary alcohol **A6** (0.921 g, 95.4%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45-7.20 (m, 10H), 5.81 (tdd, *J* = 16.9, 13.1, 6.7 Hz, 1H), 5.05-4.96 (m, 2H), 4.06 (d, *J* = 8.3 Hz, 1H), 3.98-3.94 (m, 1H), 3.22 (s, 3H), 2.15-1.95 (m, 2H), 1.70-1.43 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.1, 142.6, 129.0, 128.7, 128.4, 126.5, 126.4, 114.7, 83.6, 58.0, 56.3, 34.0, 31.7, 24.5; IR (neat) 2934, 1640, 1495, 1451, 1101, 910, 737, 701 cm^{-1}; HRMS (EI): *m*/*z* calcd for $C_{20}H_{24}O$ ($M^{+\bullet}$) 280.1827, found 280.1823.

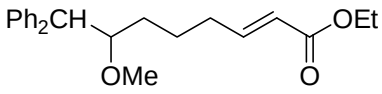
5-Methoxy-6,6-diphenylhexanal (1.58)



At -78 °C, the terminal olefin **A6** (400 mg, 1.43 mmol) in CH_2Cl_2 (145 mL) was bubbled gently with ozone until the solution retained a deep blue color and then PPh_3 (750 mg, 2.86 mmol) was added in one portion. The mixture was warmed to room temperature, stirred overnight and then concentrated. The residue was purified by column chromatography (20% - 30% Et_2O in hexanes) to give the aldehyde **1.58** (386 mg, 95.9%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ) δ 9.71 (t, *J* = 1.6 Hz, 1H), 7.39-7.16 (m, 10H), 4.02 (d, *J* = 8.4 Hz, 1H), 3.94-3.88 (m, 1H), 3.12 (s, 3H), 2.38 (dt, *J* = 7.2, 1.5 Hz, 2H), 1.79-1.70 (m, 2H), 1.58-1.53 (m, 1H), 1.48-1.42 (m, 1H),;^{13}C NMR (75 MHz, $CDCl_3$) δ

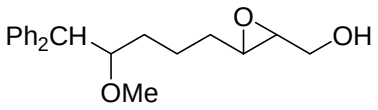
202.2, 142.7, 142.3, 128.9, 128.7, 128.6, 128.4, 126.6, 126.5, 83.5, 58.1, 56.2, 44.0, 31.7, 17.9; IR (neat) 2929, 2825, 2721, 1722, 1495, 1451, 1112, 747, 704 cm^{-1}; HRMS (ESI): *m*/*z* calcd for $C_{19}H_{22}ONa$ $[M+Na]^+$ 305.1517, found 305.1564.

(*E*)-Ethyl 7-methoxy-8,8-diphenyloct-2-enoate (A7)



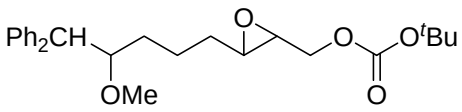
At 0 °C, triethyl phosphonoacetate (0.52 mL, 2.60 mmol) was added dropwise to a suspension of NaH (60% dispersion in mineral oil, 104 mg, 2.60 mmol) in THF (9.0 mL) and the resulting solution was stirred at 0 °C for 30 min. The aldehyde **1.58** (367 mg, 1.30 mmol, dissolved in 3.0 mL THF) was introduced dropwise and the flask formerly containing the aldehyde was rinsed with THF (2 x 0.5 mL). The reaction mixture was stirred at 0 °C for 1 h, then quenched with saturated NH_4Cl (10 mL) and poured onto water (20 mL). The mixture was extracted with CH_2Cl_2 (3 x 30 mL) and the organic extracts were dried ($MgSO_4$) and concentrated. The residue was purified by column chromatography (10% - 15% EtOAc in hexanes) to give the ethyl ester **A7** (426 mg, 93%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44-7.20 (m, 10H), 6.96 (td, *J* = 15.6, 6.8 Hz, 1H), 5.82 (d, *J* = 15.6 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 4.05 (d, *J* = 8.4 Hz, 1H), 3.98-3.92 (m, 1H), 3.21 (s, 3H), 2.25-2.10 (m, 2H), 1.71-1.44 (m, 4H), 1.34 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.8, 149.0, 142.8, 142.4, 128.9, 128.7, 128.5, 128.4, 126.6, 126.4, 121.6, 83.5, 60.3, 58.1, 56.3, 32.3, 31.8, 23.6, 14.4; IR (neat) 2979, 2934, 1718, 1654, 1495, 1451, 1368, 1269, 1186, 1098, 1043, 746, 703 cm^{-1}; HRMS (EI): *m*/*z* calcd for $C_{21}H_{23}O_3$ $(M-C_2H_5O)^{+\bullet}$ 307.1698, found 307.1684.

(3-(4-Methoxy-5,5-diphenylpentyl)oxiran-2-yl)methanol (A8)



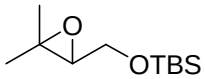
At -78 °C, DIBAL-H (1 M in hexanes, 2.9 mL, 2.9 mmol) was added dropwise to a solution of the ethyl ester **A7**(413 mg, 1.17 mmol) in THF (12 mL). The mixture was stirred at -78 °C for 30 min, then quenched with saturated sodium tartrate (12 mL) and diluted with water (10 mL). The mixture was warmed to room temperature and stirred vigorously for 2 h. After that time, the mixture was extracted with CH_2Cl_2 (3 x 40 mL) and the extracts were dried ($MgSO_4$) and concentrated. The residue was passed through a short silica gel column and eluted with 50% EtOAc in hexanes. The product was concentrated and dissolved in CH_2Cl_2 (12 mL) and cooled to 0 °C. $NaHCO_3$ (196 mg, 2.34 mmol) and *m*CPBA (pure, 262 mg, 1.52 mmol) were added sequentially. The suspension was stirred at 0 °C for 3.5 h, then quenched with saturated $Na_2S_2O_3$ (10 mL) and water (20 mL). The mixture was stirred at room temperature for 20 min, and extracted with CH_2Cl_2 (3 x 30 mL). The extracts were dried ($MgSO_4$), and concentrated and the residue was purified by column chromatography (50% - 70% EtOAc in hexanes containing 0.5% Et_3N) to give the epoxy alcohol **A8** (348 mg, 91%, dr ~ 1:1) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39-7.17 (m, 10H), 4.00 (d, *J* = 8.4 Hz, 1H), 3.93-3.81 (m, 2H), 3.61-3.53 (m, 1H), 3.17/3.16 (s, 3H), 2.89-2.84 (m, 2H), 1.66-1.40 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.8, 142.4, 128.9, 128.6, 128.5, 128.4, 126.5, 126.4, 83.5, 61.8, 58.6, 58.5, 58.1, 58.0, 56.2, 56.0, 55.9, 32.0, 31.7, 21.6; IR (neat) 3435, 2929, 1599, 1495, 1451, 1098, 910, 732, 703 cm^{-1}; HRMS (ESI): *m*/*z* calcd for $C_{21}H_{26}O_3Na$ $[M+Na]^+$ 349.1780, found 349.1792.

***tert*-Butyl (3-(4-methoxy-5,5-diphenylpentyl)oxiran-2-yl)methyl carbonate (1.48)**



The epoxy alcohol **A8** (336 mg, 1.03 mmol) in anhydrous toluene (10 mL) at 0 °C was treated with 1-methylimidazole (82 μL, 1.03 mmol) followed by Boc_2O (449 mg, 2.06 mmol). The mixture was stirred at 0 °C for 30 min, then at room temperature for 1.5 h. After that time, the reaction was quenched with water (15 mL) and extracted with CH_2Cl_2 (3 x 30 mL). The organic extracts were dried over $MgSO_4$, filtered and concentrated. The residue was azeotroped with hexanes (3 x 10 mL) and then purified by flash chromatography (15% - 20% EtOAc in hexanes containing 0.5% Et_3N) to give the *t*-butyl carbonate **1.48** (369 mg, 84%, dr ~ 1:1) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39-7.16 (m, 10H), 4.23-4.18 (m, 1H), 4.00 (d, *J* = 8.4 Hz, 1H), 3.97-3.88 (m, 2H), 3.16/3.16 (s, 3H), 2.96-2.91 (m, 1H), 2.81-2.79 (m, 1H), 1.59-1.43 (m, 6H), 1.50 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.4, 142.8, 142.4, 129.0, 128.7, 128.6, 128.4, 126.6, 126.4, 83.6, 82.7, 67.2, 58.2, 58.1, 56.6, 56.5, 56.3, 55.2, 55.2, 32.0, 32.0, 31.7, 27.9, 21.6, 21.6; IR (neat) 2980, 2936, 1742, 1495, 1452, 1370, 1280, 1163, 1099, 858, 733, 704 cm^{-1}; HRMS (ESI): *m*/*z* calcd for $C_{26}H_{34}O_5Na$ $[M+Na]^+$ 449.2304, found 449.2308.

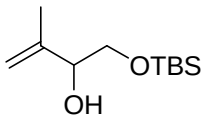
((3,3-Dimethyloxiran-2-yl)methoxy)(*tert*-butyl)dimethylsilane (1.59)



A solution of (3-methylbut-2-enyloxy)(*tert*-butyl)dimethylsilane (6.012 g, 30.0 mmol) in CH_2Cl_2 (300 mL) at 0 °C was treated with $NaHCO_3$ powder (5.04 g, 60.0 mmol) followed by *m*-chloroperbenzoic acid (70-75%, 7.25 g, 31.5 mmol). The reaction mixture was stirred at 0 °C for 1.5 h and then quenched with saturated $Na_2S_2O_3$ solution (100 mL). After warmed to room temperature, the biphasic mixture was poured into water (100 mL) and the two layers were separated. The aqueous layer was extracted with CH_2Cl_2 (2 x 150 mL) and the combined organic extracts were dried over $MgSO_4$, filtered and concentrated. The residue was purified by flash chromatography (15% Et_2O in hexanes) to give the epoxide **1.59**

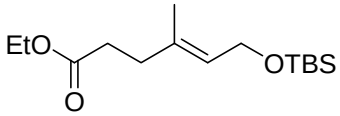
(6.312 g, 97.2%) as a colorless liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.75 (d, *J* = 5.3 Hz, 1H), 3.74 (d, *J* = 5.4 Hz, 1H), 2.91 (t, *J* = 5.4 Hz, 1H), 1.34 (s, 3H), 1.29 (s, 3H), 0.92 (s, 9H), 0.10 (s, 3H), 0.09 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 64.2, 62.5, 58.3, 26.1, 24.9, 19.0, 18.5, -5.0, -5.2; IR (neat) 2958, 2930, 2886, 2858, 1472, 1379, 1256, 1140, 1086, 838, 778 cm^{-1}.

1-(*tert*-Butyldimethylsilanyloxy)-3-methylbut-3-en-2-ol (A9)



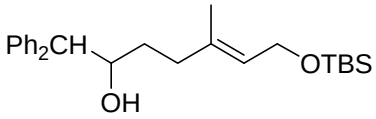
A solution of 2,2,6,6-tetramethylpiperidine (2.825 g, 20.0 mmol) in anhydrous benzene (12.0 mL) at 0 °C was treated dropwise with *n*-BuLi (1.6 M in hexanes, 12.5 mL, 20.0 mmol). After 10 min, diethylaluminum chloride (1.0 M in heptanes, 20.0 mL, 20.0 mmol) was added dropwise and the resulting white suspension was stirred at 0 °C for 30 min. The epoxide **1.59** (1.731 g, 8.00 mmol, dissolved in 8.0 mL of anhydrous benzene) was added dropwise and the flask formerly containing the epoxide was rinsed twice with benzene (2 x 4.0 mL). The reaction mixture was stirred further for 1.5 h at 0 °C and then quenched with saturated sodium tartrate solution (50 mL). The biphasic mixture was poured onto water (100 mL) and extracted with Et_2O (3 x 50 mL). The organic extracts were dried over $MgSO_4$, filtered and concentrated in vacuo. The resulting residue was purified by column chromatography (15% Et_2O in hexanes) to give allylic alcohol **A9** (1.5581 g, 90.0%) as a colorless liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.04 (m, 1H), 4.92 (m, 1H), 4.12 (m, 1H), 3.71 (dd, *J* = 9.9, 3.6 Hz, 1H), 3.48 (dd, *J* = 9.9, 8.0 Hz, 1H), 2.66 (d, *J* = 3.0 Hz, 1H), 1.75 (s, 3H), 0.92 (s, 9H), 0.09 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.0, 112.0, 75.4, 66.4, 26.0, 19.0, 18.4, -5.2; IR (neat) 3446, 2955, 2929, 2858, 1472, 1256, 1113, 899, 836, 777 cm^{-1}; HRMS (EI): *m*/*z* calcd for $C_7H_{15}O_2Si$ $(M\text{-}C_4H_9)^{+\bullet}$ 159.0841, found 159.0811.

Ethyl (*E*)-6-(*tert*-butyldimethylsilanyloxy)-4-methylhex-4-enoate (A10)



A mixture of allylic alcohol **A9** (2.7093 g, 12.52 mmol), triethyl orthoacetate (freshly distilled, 9.2 mL, 50.1 mmol) and propionic acid (46.4 mg, 0.626 mmol) in a round-bottom flask was equipped with a fractional distillation apparatus to allow for removal of ethanol. The mixture was heated to 145 °C for 4 h. (During this period of time, a lot of volatiles were distilled out.) The unreacted triethyl orthoacetate was removed by simple distillation and the residue was purified by column chromatography (5% EtOAc in hexanes) to give ethyl ester **A10** (3.433 g, 95.7%) as a colorless liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.32 (qt, *J* = 6.3, 1.2 Hz, 1H), 4.20 (d, *J* = 6.3 Hz, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 2.46-2.40 (m, 2H), 2.37-2.30 (m, 2H), 1.64 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H), 0.90 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.5, 135.3, 125.3, 60.5, 60.4, 34.6, 33.0, 26.2, 18.6, 16.6, 14.5, -4.9; IR (neat) 2956, 2930, 2857, 1739, 1472, 1255, 1158, 1110, 1068, 836, 776 cm^{-1}; HRMS (EI): *m*/*z* calcd for $C_{15}H_{29}O_3Si$ $(M-H)^{+\bullet}$ 285.1886, found 285.1840.

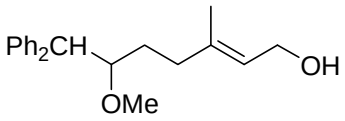
(*E*)-7-(*tert*-Butyldimethylsilanyloxy)-5-methyl-1,1-diphenylhept-5-en-2-ol (A11)



Ethyl ester **A10** (1.000 g, 3.49 mmol) in CH_2Cl_2 (10.0 mL) at -78 °C was treated dropwise with DIBAL-H (1.0 M in hexanes, 3.7 mL, 3.7 mmol). The reaction mixture was stirred at -78 °C for 1 h and then quenched with saturated sodium tartrate solution (15 mL). After warmed up to room temperature, the mixture was stirred vigorously for 30 min and extracted with CH_2Cl_2 (3 x 30 mL). The organic extracts were dried over $MgSO_4$, filtered and concentrated. The crude aldehyde **1.60** was used in the next step without further purification.

In a separate two-necked round-bottom flask, a solution of diphenylmethane (1.76 g, 10.5 mmol) in THF (10.0 ml) was treated dropwise with *n*-BuLi (1.6 M in hexanes, 6.5 mL, 10.5 mmol). The resulting deep orange solution was refluxed for 1 h, and then cooled to 0 °C. The as-prepared crude aldehyde (dissolved in 2.0 mL of THF) was added dropwise and the flask formerly containing the aldehyde was rinsed with THF (2 x 0.5 mL). The reaction mixture was stirred at 0 °C for 1 h, then warmed to room temperature and quenched by slow addition of saturated $NaHCO_3$ solution (10 mL). The mixture was poured onto water (20 mL) and extracted with Et_2O (3 x 40 mL). The organic extracts were dried over $MgSO_4$, filtered and concentrated. The residue was purified by flash chromatography (3% - 12% EtOAc in hexanes) to give the secondary alcohol **A11** (0.997 g, 69.6%, two steps) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42-7.17 (m, 10H), 5.32 (qt, *J* = 6.4, 1.2 Hz, 1H), 4.40-4.29 (m, 1H), 4.18 (d, *J* = 6.2 Hz, 2H), 3.92 (d, *J* = 8.4 Hz, 1H), 2.30-2.20 (m, 1H), 2.17-2.07 (m, 1H), 1.66 (d, *J* = 3.4 Hz, 1H), 1.70-1.44 (m, 2H), 1.56 (s, 3H), 0.92 (s, 9H), 0.08 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.6, 141.7, 136.9, 129.0, 128.8, 128.4, 127.0, 126.7, 125.0, 73.5, 60.4, 59.0, 35.9, 33.1, 26.2, 18.6, 16.4, -4.8; IR (neat) 3458, 2954, 2928, 2856, 1599, 1494, 1451, 1386, 1254, 1112, 1067, 835, 776, 702 cm^{-1}; HRMS (ESI): *m*/*z* calcd for $C_{26}H_{38}O_2SiK$ $[M+K]^+$ 449.2278, found 449.2287.

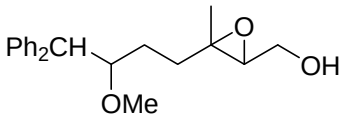
(*E*)-6-Methoxy-3-methyl-7,7-diphenylhept-2-en-1-ol (A12)



The secondary alcohol **A11** (0.908 g, 2.21 mmol) in anhydrous DMF (10.0 mL) at 0 °C was treated with NaH (60% dispersion in mineral oil, 0.221 g, 5.52 mmol) and the suspension was stirred at 0 °C for 30 min. MeI (0.55 mL, 8.84 mmol) was added dropwise and the reaction mixture was allowed to warm up to room temperature. After stirred for 3 h, the reaction was quenched with water (30 mL) cautiously and

extracted with Et_2O (3 x 50 mL). The organic extracts were dried over $MgSO_4$, filtered and concentrated. The resulting residue was dissolved in THF (11.0 mL) and TBAF monohydrate (0.693 g, 5.730 mmol) was added in one portion. The yellow solution was stirred for 1.5 h and then concentrated. The residue was purified by column chromatography (30% - 40% EtOAc in hexanes) to give allylic alcohol **A12** (0.684 g, 99.7%, two steps) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40-7.08 (m, 10H), 5.37 (qt, *J* = 6.9, 1.2 Hz, 1H), 4.12 (d, *J* = 6.8 Hz, 2H), 4.02 (d, *J* = 8.4 Hz, 1H), 3.92 (ddd, *J* = 8.2, 6.4, 4.1 Hz, 1H), 3.17 (s, 3H), 2.22-2.03 (m, 2H), 1.73-1.48 (m, 2H), 1.58 (s, 3H), 1.30 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.9, 142.5, 139.7, 129.0, 128.7, 128.4, 126.6, 126.4, 123.8, 83.4, 59.5, 58.1, 56.4, 35.1, 30.5, 16.4; IR (neat) 3396, 3026, 2929, 1599, 1494, 1451, 1374, 1241, 1102, 1002, 756, 703 cm^{-1}; HRMS (ESI): *m*/*z* calcd for $C_{21}H_{26}O_2Na$ $[M+Na]^+$ 333.1831, found 333.1817.

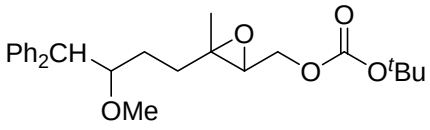
(3-(3-Methoxy-4,4-diphenylbutyl)-3-methyloxiran-2-yl)methanol (A13)



A solution of allylic alcohol **A12** (252 mg, 0.812 mmol) in CH_2Cl_2 (8.0 mL) at 0 °C was treated with $NaHCO_3$ powder (136 mg, 1.62 mmol) followed by *m*CPBA (pure, 147 mg, 0.852 mmol). The reaction mixture was stirred at 0 °C for 1 h and then quenched with saturated $Na_2S_2O_3$ solution (2.0 mL). After warmed to room temperature, the biphasic mixture was poured onto water (5 mL) and the two layers were separated. The aqueous layer was extracted with CH_2Cl_2 (2 x 20 mL) and the combined organic extracts were dried over $MgSO_4$, filtered and concentrated. The residue was purified by flash chromatography (40% - 50% EtOAc in hexanes) to give the epoxy alcohol **A13** (251 mg, 94.9%, dr ~ 1:1) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38-7.17 (m, 10H), 4.00-3.91 (m, 2H), 3.81-3.73 (m, 1H), 3.68-3.59 (m, 1H), 3.16/3.14 (s, 3H), 2.91-2.85 (m, 1H), 1.80-1.38 (m,

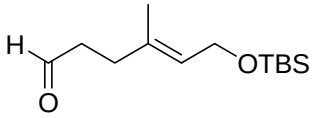
4H), 1.19/1.17 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.7, 142.4, 142.3, 128.9, 128.8, 128.6, 128.4, 126.7, 126.5, 83.4, 83.3, 63.0, 62.7, 61.5, 61.5, 61.4, 61.4, 58.1, 57.9, 56.4, 56.2, 33.9, 33.7, 27.5, 27.2, 17.0, 16.7; IR (neat) 3418, 2931, 1599, 1495, 1452, 1385, 1099, 1032, 747, 704 cm^{-1}; HRMS (ESI): *m*/*z* calcd for $C_{21}H_{26}O_3Na$ $[M+Na]^+$ 349.1780, found 349.1766.

***tert*-Butyl (3-(3-methoxy-4,4-diphenylbutyl)-3-methyloxiran-2-yl)methyl carbonate (1.49)**



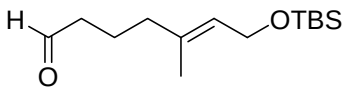
Epoxy alcohol **A13** (192 mg, 0.588 mmol) in anhydrous toluene (5.8 mL) at 0 °C was treated with 1-methylimidazole (46.9 μL, 0.588 mmol) followed by Boc_2O (321 mg, 1.47 mmol). The reaction mixture was stirred at 0 °C for 4 h, then diluted with CH_2Cl_2 (20 mL) and poured onto water (10 mL). The biphasic mixture was separated and the aqueous layer was washed with CH_2Cl_2 (3 x 15 mL). The combined organic extracts were dried over $MgSO_4$, filtered and concentrated. The residue was purified by flash chromatography (10% - 12.5% EtOAc in hexanes containing 0.5% Et_3N) to give the *t*-butyl carbonate **1.49** (216 mg, 86.3%, dr ~ 1:1) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39-7.17 (m, 10H), 4.20-4.14 (m, 1H), 4.09 (dd, *J* = 11.8, 6.1 Hz, 1H), 3.99-3.91 (m, 2H), 3.15/3.14 (s, 3H), 2.97-2.91 (m, 1H), 1.83-1.42 (m, 4H), 1.50 (s, 9H), 1.20/1.18 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.5, 142.6, 142.4, 142.3, 128.9, 128.9, 128.7, 128.6, 128.4, 126.7, 126.5, 83.2, 83.0, 82.7, 65.7, 65.6, 60.8, 60.6, 59.6, 59.2, 58.1, 57.8, 56.4, 56.2, 33.5, 33.3, 27.9, 27.4, 27.1, 17.1, 16.7; IR (neat) 2980, 2933, 1743, 1495, 1453, 1370, 1327, 1279, 1163, 1098, 859, 738, 704 cm^{-1}; HRMS (ESI): *m*/*z* calcd for $C_{26}H_{34}O_5Na$ $[M+Na]^+$ 449.2304, found 449.2278.

(*E*)-6-(*tert*-Butyldimethylsilanyloxy)-4-methylhex-4-enal (1.60)



Ethyl ester **A10** (5.84 g, 20.4 mmol) in CH_2Cl_2 (58.0 mL) at -78 °C was treated dropwise with DIBAL-H (1.0 M in hexanes, 21.4 mL, 21.4 mmol). The reaction mixture was stirred at -78 °C for 2 h and then quenched with saturated sodium tartrate solution (120 mL). After warmed up to room temperature, the mixture was extracted with CH_2Cl_2 (3 x 70 mL) and the organic extracts were dried over $MgSO_4$, filtered and concentrated. The residue was purified by flash chromatography (6% - 8% EtOAc in hexanes) to give the aldehyde **1.60** (4.31 g, 87.4%) as a colorless liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.79 (t, *J* = 1.7 Hz, 1H), 5.33 (qt, *J* = 6.2, 1.3 Hz, 1H), 4.19 (d, *J* = 6.2 Hz, 2H), 2.59-2.54 (m, 2H), 2.35 (app t, *J* = 7.7 Hz, 2H), 1.65 (s, 3H), 0.91 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.4, 135.0, 125.6, 60.3, 42.1, 31.7, 26.2, 18.6, 16.7, -4.9; IR (neat) 2955, 2929, 2857, 2714, 1728, 1472, 1255, 1114, 1074, 836, 776 cm^{-1}; HRMS (EI): *m*/*z* calcd for $C_{13}H_{25}O_2Si$ $(M-H)^{+\bullet}$ 241.1624, found 241.1606.

(*E*)-7-(*tert*-Butyldimethylsilanyloxy)-5-methylhept-5-enal (A14)

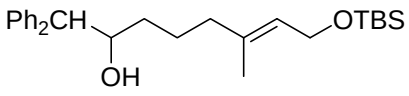


(Methoxymethyl)triphenylphosphonium chloride (2.587 g, 7.55 mmol) in a dry flask under high vacuum was heated with heat gun for 3 min to remove the moisture. The flask was cooled to 0 °C and THF (8.0 mL) was added in. NaHMDS (7.55 mL, 7.55 mmol) was added dropwise and the resulting deep orange suspension was stirred at 0 °C for 1 h. Aldehyde **1.60** (0.610 g, 2.52 mmol, dissolved in 1.0 mL of THF) was added dropwise and the flask formerly containing the aldehyde was rinsed twice with THF (2 x 0.5 mL). The reaction mixture was stirred at 0 °C for 1 h, then quenched with saturated $NaHCO_3$ (10 mL) and extracted with Et_2O (3 x 30 mL). The organic extracts were dried over $MgSO_4$,

filtered and concentrated. The residue was purified by flash chromatography (3.5% EtOAc in hexanes) to give the crude methyl vinyl ether.

The methyl vinyl ether in THF-H_2O (10:1, 40 mL) was treated with $Hg(OAc)_2$ (1.277 g, 4.01 mmol). The reaction mixture was stirred for 20 min and saturated KI (20 mL) was added. The resulting yellowish green mixture was stirred for 1 h and then diluted with Et_2O (50 mL). The two layers were separated and the organic layer was washed with saturated KI (40 mL), dried over $MgSO_4$, filtered and concentrated. The residue was purified by flash chromatography (4% - 6% EtOAc in hexanes) to give the title aldehyde **A14** (0.526 g, 81.6%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.78 (t, *J* = 1.5 Hz, 1H), 5.32 (qt, *J* = 6.2, 1.0 Hz, 1H), 4.19 (d, *J* = 6.3 Hz, 2H), 2.42 (dt, *J* = 7.3, 1.5 Hz, 2H), 2.04 (t, *J* = 7.3 Hz, 2H), 1.76 (pent, *J* = 7.6 Hz, 2H), 1.62 (s, 3H), 0.91 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.6, 136.0, 125.9, 60.5, 43.5, 39.0, 26.3, 20.3, 18.7, 16.4, -4.8; IR (neat) 2930, 2856, 2713, 1728, 1472, 1387, 1255, 1115, 1080, 836, 776 cm^{-1}; HRMS (ESI): *m*/*z* calcd for $C_{14}H_{28}O_2SiNa$ $[M+Na]^+$ 279.1756, found 279.1745.

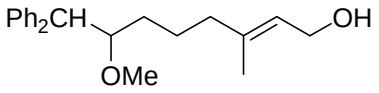
(*E*)-8-(*tert*-Butyldimethylsilanyloxy)-6-methyl-1,1-diphenyl-oct-6-en-2-ol (A15)



A solution of diphenylmethane (0.80 mL, 4.77 mmol) in THF (4.5 mL) was treated with *n*-BuLi (1.6 M in hexanes, 2.74 mL, 4.39 mmol) and the resulting deep-orange solution was refluxed for 2 h. After cooling to room temperature, the solution was cooled further to 0 °C and the aldehyde **A14** (0.489 g, 1.91 mmol, dissolved in 1.0 mL of THF) was added dropwise. The flask formerly containing the aldehyde was rinsed with THF (2 x 0.5 mL). The deep-orange solution was stirred at 0 °C for 1 h, then quenched by slow addition of saturated $NaHCO_3$ (10 mL). The biphasic mixture was diluted with

Et_2O (10 mL) and poured onto water (10 mL). The two layers were separated and the aqueous layer was extracted with Et_2O (3 x 20 mL). The combined organic extracts were dried over $MgSO_4$, filtered and concentrated. The residue was purified by flash chromatography (7% - 13% EtOAc in hexanes) to give the alcohol **A15** (0.638 g, 78.7%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41-7.16 (m, 10H), 5.26 (qt, *J* = 6.4, 1.2 Hz, 1H), 4.36 (dt, *J* = 8.3, 3.0 Hz, 1H), 4.16 (d, *J* = 6.3 Hz, 2H), 3.88 (d, *J* = 8.3 Hz, 1H), 1.99-1.92 (m, 2H), 1.70-1.35 (m, 4H), 1.57 (s, 3H), 0.91 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.6, 141.6, 137.1, 129.0, 128.8, 128.4, 127.1, 126.7, 124.7, 73.8, 60.5, 59.0, 39.6, 34.8, 26.2, 24.0, 18.6, 16.4, -4.8; IR (neat) 3458, 2928, 2856, 1599, 1494, 1386, 1254, 1082, 835, 702 cm^{-1}; HRMS (ESI): *m*/*z* calcd for $C_{27}H_{40}O_2SiNa$ $[M+Na]^+$ 447.2695, found 447.2741.

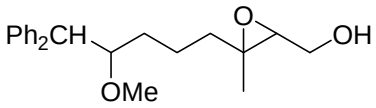
(*E*)-7-Methoxy-3-methyl-8,8-diphenyloct-2-en-1-ol (A16)



The secondary alcohol **A15** (0.638g, 1.50 mmol) in anhydrous DMF (10 mL) at 0 °C was treated with NaH (60% dispersion in mineral oil, 150 mg, 3.75 mmol) and the yellow suspension was stirred at 0 °C for 30 min. MeI (0.37 mL, 6.00 mmol) was added dropwise and the reaction mixture was stirred overnight at room temperature. The flask was cooled to 0 °C and the reaction was quenched with ice chips. The mixture was poured into water (20 mL) and extracted with Et_2O (3 x 30 mL). The organic extracts were dried over $MgSO_4$, filtered and concentrated. The residue was dissolved in THF (7.5 mL) and TBAF monohydrate (0.471 g, 1.80 mmol) was added in. The yellow solution was stirred for 1.5 h and then concentrated in vacuo. The residue was purified by flash chromatography (25% - 35% EtOAc in hexanes) to give the allylic alcohol **A16** (0.475 g, 97.4%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42-7.19 (m, 10H), 5.36 (qt, *J* = 6.9, 1.0 Hz,

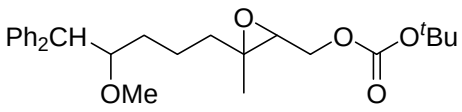
1H), 4.11 (d, J = 6.9 Hz, 2H), 4.04 (d, J = 8.4 Hz, 1H), 3.97-3.92 (m, 1H), 3.19 (s, 3H), 1.98-1.96 (m, 2H), 1.62 (s, 3H), 1.58-1.41 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.9, 142.5, 139.4, 128.9, 128.6, 128.4, 126.5, 126.4, 123.7, 83.6, 59.3, 58.0, 56.2, 39.5, 31.6, 22.9, 16.2; IR (neat) 3386, 2934, 1667, 1599, 1495, 1451, 1380, 1186, 1100, 1002, 746, 703 cm^{-1}; HRMS (ESI): m/z calcd for $C_{22}H_{28}O_2Na$ $[M+Na]^+$ 347.1987, found 347.1966.

(3-(4-Methoxy-5,5-diphenylpentyl)-3-methyloxiran-2-yl)methanol (A17)



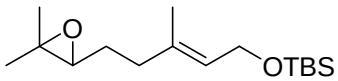
A solution of allylic alcohol **A16** (85.0 mg, 0.262 mmol) in CH_2Cl_2 (2.6 mL) at 0 °C was treated with $NaHCO_3$ powder (55.0 mg, 0.655 mmol) followed by *m*-chloroperbenzoic acid (pure, 47.5 mg, 0.275 mmol). The reaction mixture was stirred at 0 °C for 50 min and then quenched with saturated $Na_2S_2O_3$ solution (2.0 mL). After warmed to room temperature, the biphasic mixture was poured into water (5 mL) and the two layers were separated. The aqueous layer was extracted with CH_2Cl_2 (5 x 10 mL) and the combined organic extracts were dried over $MgSO_4$, filtered and concentrated. The residue was purified by flash chromatography (40% - 45% EtOAc in hexanes containing 0.5% Et_3N) to give the epoxy alcohol **A17** (88.7 mg, 99.4%, dr ~ 1:1) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38-7.17 (m, 10H), 4.00 (d, J = 8.4 Hz, 1H), 3.91-3.89 (m, 1H), 3.80-3.74 (m, 1H), 3.65 (dd, J = 12.1, 6.6 Hz, 1H), 3.17/3.16 (s, 3H), 2.92-2.87 (m, 1H), 1.64-1.34 (m, 6H), 1.23 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.8, 142.4, 128.9, 128.9, 128.7, 128.6, 128.4, 126.6, 126.4, 83.6, 83.5, 63.1, 63.0, 61.5, 61.4, 58.1, 58.0, 56.3, 38.6, 32.1, 32.0, 20.7, 20.6, 16.8, 16.7; IR (neat) 3420, 2935, 1599, 1495, 1452, 1385, 1249, 1100, 1031, 862, 747, 704 cm^{-1}; HRMS (ESI): m/z calcd for $C_{22}H_{28}O_3Na$ $[M+Na]^+$ 363.1936, found 363.1947.

***tert*-Butyl (3-(4-methoxy-5,5-diphenylpentyl)-3-methyloxiran-2-yl)methyl carbonate (1.50)**



Epoxy alcohol **A17** (72.9 mg, 0.214 mmol) in anhydrous toluene (2.0 mL) at 0 °C was treated with 1-methylimidazole (22 μL, 0.278 mmol) followed by Boc_2O (187 mg, 0.856 mmol, dissolved in 0.5 mL of toluene). The reaction mixture was stirred at 0 °C for 4 h, then diluted with CH_2Cl_2 (5.0 mL) and poured into water (6 mL). The biphasic mixture was separated and the aqueous layer was washed with CH_2Cl_2 (3 x 5 mL). The combined organic extracts were dried over $MgSO_4$, filtered and concentrated. The residue was purified by flash chromatography (10% - 15% EtOAc in hexanes containing 0.5% Et_3N) to give the *t*-butyl carbonate **1.50** (83.9 mg, 89.0%, dr ~ 1:1) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39-7.17 (m, 10H), 4.18 (dd, *J* = 11.9, 4.8 Hz, 1H), 4.09 (dd, *J* = 11.9, 6.3 Hz, 1H), 4.00 (d, *J* = 8.4 Hz, 1H), 3.93-3.87 (m, 1H), 3.17 (br s, 3H), 2.98-2.94 (m, 1H), 1.64-1.41 (m, 6H), 1.52 (s, 9H), 1.24 (br s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.4, 142.8, 142.4, 128.9, 128.6, 128.5, 128.4, 126.5, 126.4, 83.5, 82.6, 65.7, 60.6, 59.5, 59.4, 58.1, 58.0, 56.2, 38.3, 32.0, 27.9, 20.5, 20.5, 16.8, 16.8; IR (neat) 2934, 1742, 1495, 1452, 1369, 1279, 1255, 1163, 1098, 859, 704 cm^{-1}; HRMS (ESI): *m*/*z* calcd for $C_{27}H_{36}O_5Na$ $[M+Na]^+$ 463.2460, found 463.2462.

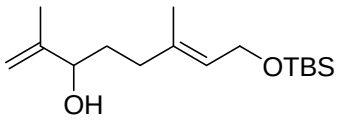
((*E*)-3-Methyl-5-(3,3-dimethyloxiran-2-yl)pent-2-enyloxy)(*tert*-butyl)dimethylsilane (1.61)



((*E*)-3,7-dimethylocta-2,6-dienyloxy)(tert-butyl)dimethylsilane (5.370 g, 20.0 mmol) in $CHCl_3$ (180 mL) at 0 °C was treated with *m*CPBA (70-75%, 5.621 g, 22.8 mmol) in small portions. The white suspension was stirred at 0 °C for 30 min, and then quenched with saturated $Na_2S_2O_3$ solution (20 mL) and saturated $NaHCO_3$ solution (100 mL). The mixture was warmed up to room temperature and the two

layers were separated. The aqueous was washed with CH_2Cl_2 (2 x 100 mL) and the combination of the organic extracts were dried over $MgSO_4$ and evaporated. The residue was purified by column chromatography (8%-12% Et_2O in hexanes) to give the desired monoepoxide **1.61** (4.375 g, 76.9%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.36 (qt, *J* = 6.3, 1.2 Hz, 1H), 4.20 (d, *J* = 6.3, Hz, 1H), 4.20 (d, *J* = 6.3, Hz, 1H), 2.72 (t, *J* = 6.2 Hz, 1H), 2.25-2.06 (m, 2H), 1.65 (s, 3H), 1.71-1.61 (m, 2H), 1.31 (s, 3H), 1.27 (s, 3H), 0.91 (s, 9H), 0.08 (s, 6H).

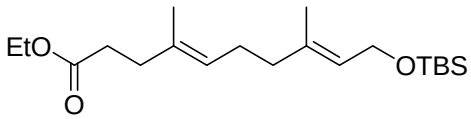
(*E*)-8-(*tert*-Butyldimethylsilanyloxy)-2,6-dimethylocta-1,6-dien-3-ol (A18)



A solution of 2,2,6,6-tetramethylpiperidine (5.297 g, 37.5 mmol) in anhydrous benzene (25.0 mL) at 0 °C was treated dropwise with *n*-BuLi (1.6 M in hexanes, 23.4 mL, 37.5 mmol). After 10 min, diethylaluminum chloride (1.0 M in heptanes, 37.5 mL, 37.5 mmol) and the resulting white suspension was stirred at 0 °C for 30 min. Monoepoxide **1.61** (4.268 g, 15.0 mmol, dissolved in 5.0 mL of anhydrous benzene) was added dropwise and the flask formerly containing the epoxide was rinsed twice with benzene (2 x 2.5 mL). The reaction mixture was stirred further at 0 °C for 1.5 h and then quenched with saturated sodium tartrate solution (100 mL). The biphasic mixture was poured into water (100 mL) and extracted with Et_2O (3 x 150 mL). The organic extracts were dried over $MgSO_4$, filtered and concentrated in vacuo. The resulting residue was purified by column chromatography (12%-21% Et_2O in hexanes) to give the allylic alcohol **A18** (3.924 g, 91.9%) as a colorless liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.34 (qt, *J* = 6.3, 1.2 Hz, 1H), 4.94 (t, *J* = 0.8 Hz, 1H), 4.84 (t, *J* = 1.5 Hz, 1H), 4.19 (d, *J* = 6.3 Hz, 2H), 4.05 (t, *J* = 6.2 Hz, 1H), 2.17-1.95 (m, 2H), 1.73 (s, 3H), 1.64 (s, 3H), 1.70-1.60 (m, 2H), 0.90 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.6, 136.8, 124.9, 111.3, 75.8, 60.4, 35.6, 33.0, 26.2, 18.6, 17.8, 16.6, -4.8; IR (neat) 3382, 2929,

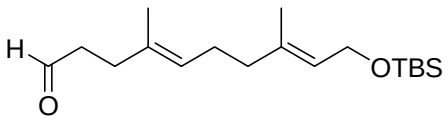
2857, 1472, 1382, 1255, 1112, 1070, 836, 776 cm^{-1}; HRMS (EI): *m*/*z* calcd for $C_{12}H_{23}O_2Si$ (M-C_4H_9)$^{+\bullet}$ 227.1467, found 227.1450.

(4*E*,8*E*)-Ethyl 10-(*tert*-butyldimethylsilanyloxy)-4,8-dimethyl-deca-4,8-dienoate (A19)



A mixture of allylic alcohol **A18** (3.671 g, 12.90 mmol), triethyl orthoacetate (freshly distilled, 10.46 g, 64.50 mmol) and propionic acid (47.8 mg, 0.645 mmol) in a round-bottom flask was equipped with a fractional distillation apparatus to allow for removal of ethanol. The mixture was heated to 145 °C for 1.5 h. (During this period of time, a lot of volatiles were distilled out.) The unreacted triethyl orthoacetate was removed by simple distillation and the residue was purified by column chromatography (3% EtOAc in hexanes) to give the ethyl ester **A19** (4.281 g, 93.6%) as a colorless liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.30 (qt, *J* = 6.3, 1.2 Hz, 1H), 5.14 (qt, *J* = 6.9, 1.2 Hz, 1H), 4.19 (d, *J* = 6.3 Hz, 1H), 4.19 (d, *J* = 6.3 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.42-2.35 (m, 2H), 2.31-2.26 (m, 2H), 2.14-2.06 (m, 2H), 2.02-1.97 (m, 2H), 1.62 (s, 3H), 1.61 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H), 0.90 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.7, 136.9, 133.7, 125.0, 124.7, 60.5, 60.4, 39.6, 34.9, 33.5, 26.4, 26.2, 18.6, 16.5, 16.1, 14.5, -4.8; IR (neat) 2929, 2856, 1738, 1463, 1254, 1158, 1063, 836, 776 cm^{-1}; HRMS (ESI): *m*/*z* calcd for $C_{20}H_{38}O_3SiNa$ $[M+Na]^+$ 377.2488, found 377.2513.

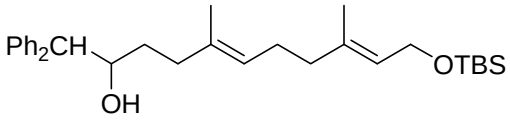
(4*E*,8*E*)-10-(*tert*-Butyldimethylsilanyloxy)-4,8-dimethyldeca-4,8-dienal (1.62)



Ethyl ester **A19** (2.3345g, 6.58 mmol) in CH_2Cl_2 (20.0 mL) at -78 °C was treated dropwise with DIBAL-H (1.0 M in hexanes, 6.91 mL, 6.91 mmol). The reaction mixture was stirred at -78 °C for 40 min and

DIBAL-H (1.0 M in hexanes, 0.66 mL, 0.66 mmol) were added. The mixture was stirred for 30 min more and then quenched with saturated sodium tartrate solution (30 mL). After warmed up to room temperature, the mixture was extracted with CH_2Cl_2 (3 x 40 mL) and the organic extracts were dried over $MgSO_4$, filtered and concentrated. The residue was purified by flash chromatography (4% - 20% EtOAc in hexanes) to give the aldehyde **1.62** (1.884 g, 92.1%) as a colorless liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.75 (t, *J* = 1.9 Hz, 1H), 5.30 (qt, *J* = 6.3, 1.1 Hz, 1H), 5.15 (qt, *J* = 6.8, 1.0 Hz, 1H), 4.19 (d, *J* = 6.3 Hz, 2H), 2.52 (dt, *J* = 7.9, 1.7 Hz, 2H), 2.32 (t, *J* = 7.5 Hz, 2H), 2.15-2.08 (m, 2H), 2.03-1.98 (m, 2H), 1.62 (s, 6H), 0.91 (s, 9H), 0.08 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.8, 136.8, 133.4, 125.3, 124.8, 60.5, 42.4, 39.5, 32.0, 26.4, 26.2, 18.6, 16.5, 16.3, -4.8; IR (neat) 2928, 2856, 1728, 1472, 1386, 1254, 1110, 1066, 836, 776 cm^{-1}; HRMS (ESI): *m*/*z* calcd for $C_{18}H_{35}O_2Si$ $[M+H]^+$ 311.2406, found 311.2386.

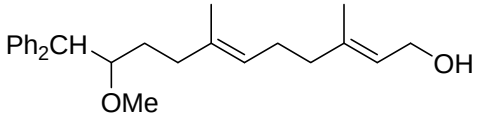
(5*E*,9*E*)-11-(*tert*-Butyldimethylsilanyloxy)-5,9-dimethyl-1,1-diphenylundeca-5,9-dien-2-ol (A20)



A solution of diphenylmethane (1.625 g, 9.66 mmol) in THF (9.0 ml) was treated dropwise with *n*-BuLi (1.6 M in hexanes, 6.04 mL, 9.66 mmol). The resulting deep orange solution was stirred at 75 °C for 1 h and cooled to 0 °C. Dienal **1.62** (1.000 g, 3.22 mmol, dissolved in 2.0 mL of THF) was added dropwise and the flask formerly containing the aldehyde was rinsed with THF (2 x 0.5 mL). The reaction mixture was stirred at 0 °C for 1 h and quenched by slow addition of saturated $NaHCO_3$ solution (10 mL). The mixture was poured onto water (15 mL) and extracted with Et_2O (3 x 30 mL). The organic extracts were dried over $MgSO_4$, filtered and concentrated. The residue was purified by flash chromatography (4% - 10% EtOAc in hexanes) to give the secondary alcohol

A20 (1.243 g, 80.6%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41-7.16 (m, 10H), 5.30 (qt, *J* = 6.3, 1.1 Hz, 1H), 5.14 (app t, *J* = 6.2 Hz, 1H), 4.38-4.30 (m, 1H), 4.18 (d, *J* = 6.3 Hz, 2H), 3.91 (d, *J* = 8.4 Hz, 1H), 2.20-2.00 (m, 6H), 1.62 (s, 3H), 1.52 (s, 3H), 1.67-1.42 (m, 2H), 0.92 (s, 9H), 0.08 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.7, 141.8, 137.1, 135.2, 129.0, 129.0, 128.8, 128.5, 127.0, 126.7, 124. 8, 124.6, 73.6, 60.5, 58.9, 39.7, 36.1, 33.3, 26.5, 26.2, 18.6, 16.6, 16.1, -4.8; IR (neat) 3466, 2928, 2855, 1598, 1494, 1450, 1384, 1254, 1067, 835, 776, 702 cm^{-1}; HRMS (ESI): *m*/*z* calcd for $C_{31}H_{46}O_2SiNa$ $[M+Na]^+$ 501.3165, found 501.3150.

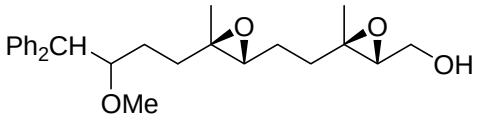
(2*E*,6*E*)-10-Methoxy-3,7-dimethyl-11,11-diphenylundeca-2,6-dien-1-ol (1.63)



The secondary alcohol **A20** (1.200 g, 2.507 mmol) in anhydrous DMF (14.0 mL) at 0 °C was treated with NaH (60% dispersion in mineral oil, 0.251 g, 6.268 mmol) and the suspension was stirred at 0 °C for 30 min. MeI (0.62 mL, 10.0 mmol) was added dropwise and the reaction mixture was allowed to warm up to room temperature. After stirred for 3 h, the reaction was quenched with water (25 mL) cautiously and extracted with Et_2O (3 x 35 mL). The organic extracts were dried over $MgSO_4$, filtered and concentrated. The resulting residue was dissolved in THF (12.5 mL) and TBAF monohydrate (0.787 g, 3.01 mmol) was added in one portion. The yellow solution was stirred for 1.3 h and then concentrated. The residue was purified by flash chromatography (20% - 30% EtOAc in hexanes) to give the allylic alcohol **1.63** (0.923 g, 97.2%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40-7.16 (m, 10H), 5.40 (qt, *J* = 6.9, 1.1 Hz, 1H), 5.10 (t, *J* = 5.5 Hz, 1H), 4.14 (d, *J* = 6.7 Hz, 2H), 4.02 (d, *J* = 8.3 Hz, 1H), 3.92-3.87 (m, 1H), 3.16 (s, 3H), 2.11-2.01 (m, 6H), 1.68 (s, 3H), 1.51 (s, 3H), 1.62-1.46 (m, 2H), 0.92 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.0, 142.5, 139.8, 135.3, 129.1, 128.7, 128.6, 128.4, 126.5, 126.4, 124.3, 123.6, 83.3,

59.6, 58.0, 56.2, 39.7, 35.3, 30.8, 26.4, 16.5, 16.1; IR (neat) 3388, 3026, 2925, 1599, 1494, 1451, 1382, 1189, 1102, 1002, 755, 703 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{26}H_{34}O_2Na$ $[M+Na]^+$ 401.2457, found 401.2477.

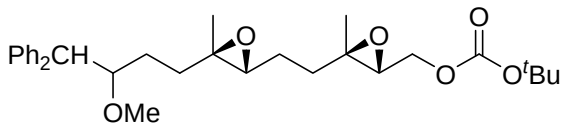
((2*R*,3*R*)-3-(2-((2*R*,3*R*)-3-(3-Methoxy-4,4-diphenylbutyl)-3-methyloxiran-2-yl)ethyl)-3-methyloxiran-2-yl)methanol (A21)



To a solution of dienol **1.63** (100 mg, 0.264 mmol) in CH_3CN/DMM (8.0 mL, 1:2, v/v) were added a 0.05 M solution of $Na_2B_4O_7$ in $4x10^{-4}$ M Na_2(EDTA) (5.2 mL), Bu_4NHSO_4 (7.2 mg, 21.1 μmol) and Shi ketone (68.2 mg, 0.264 mmol) sequentially. The mixture was cooled to 0 °C, and the Oxone (448 mg, 0.729 mmol), dissolved in $4x10^{-4}$ M Na_2(EDTA) (3.4 mL), and K_2CO_3 (424 mg, 3.06 mmol), dissolved in water (3.4 mL), were added simultaneously via a syringe pump over 2.0 h. After the addition was completed, the slightly blue reaction mixture was stirred further for 15 min at 0 °C, then diluted with water (10 mL) and extracted with CH_2Cl_2 (3 x 30 mL). The organic extracts were dried over $MgSO_4$, filtered and concentrated. The residue was purified by flash chromatography (40% - 80% EtOAc in hexanes) to give the diepoxy alcohol **A21** (95.8 mg, 88.4%, dr ~ 1:1 regarding the stereochemical outcomes of the homobenzylic center and the two epoxide groups) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42-7.17 (m, 10H), 4.00-3.85 (m, 2H), 3.81-3.61 (m, 2H), 3.16/3.14 (s, 3H), 2.96 (t, *J* = 6.0 Hz, 1H), 2.64-2.60 (m, 1H), 2.01 (br s, 1H), 1.86-1.73 (m, 2H), 1.66-1.42 (m, 6H), 1.31/1.30 (s, 3H), 1.15/1.13 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.7, 142.4, 142.2, 129.0, 128.9, 128.7, 128.7, 128.6, 128.4, 126.7, 126.5, 83.3, 63.1, 62.6, 62.5, 61.4, 61.2, 61.1, 61.0, 60.7, 58.2, 57.9, 56.4, 56.1, 35.2, 33.9, 33.8, 27.6, 27.3, 24.4, 17.1, 16.8, 16.4; IR (neat) 3435, 3026, 2929, 1495, 1452, 1386, 1100, 1032, 747, 704

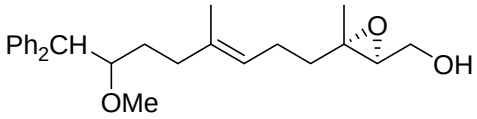
cm^{-1}; HRMS (ESI): *m*/*z* calcd for $C_{26}H_{34}O_4Na$ $[M+Na]^+$ 433.2355, found 433.2348; $[\alpha]_D$ = +13.3 ($CHCl_3$, *c* 1.34).

***tert*-Butyl ((2*R*,3*R*)-3-(2-((2*R*,3*R*)-3-(3-methoxy-4,4-diphenylbutyl)-3-methyloxiran-2-yl)ethyl)-3-methyloxiran-2-yl)methyl carbonate (1.51)**



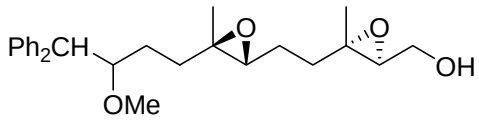
To a solution of diepoxy alcohol **A21** (112 mg, 0.273 mmol) in anhydrous toluene (2.7 mL) at 0 °C were added *N*-methylimidazole (22 μL, 0.273 mmol) and Boc_2O (119 mg, 0.546 mmol) and the reaction mixture was stirred overnight, allowing the temperature to warm to room temperature slowly. After that time, the reaction was quenched with water (10 mL) and extracted with CH_2Cl_2 (3 x 25 mL). The organic extracts were dried over $MgSO_4$, filtered and concentrated. The residue was azeotroped with hexanes (3 x 10 mL) and then purified by column chromatography (20% - 25% EtOAc in hexanes containing 0.5% Et_3N) to give the *tert*-butyl carbonate **1.51** (129 mg, 92.7%, dr ~ 1:1 regarding the stereochemical outcomes of the homobenzylic center and the two epoxide groups) as a colorless oil: ^1H NMR (300 MHz, $CDCl_3$) δ 7.39-7.17 (m, 10H), 4.27-4.10 (m, 2H), 4.00-3.88 (m, 2H), 3.17/3.16 (s, 3H), 3.02 (t, *J* = 5.8 Hz, 1H), 2.63-2.59 (m, 1H), 1.84-1.38 (m, 8H), 1.52 (s, 9H), 1.32 (s, 3H), 1.14/1.13 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.5, 142.7, 142.4, 142.3, 129.0, 128.9, 128.8, 128.7, 128.6, 128.4, 126.7, 126.5, 83.3, 82.8, 65.6, 61.1, 61.0, 60.3, 59.2, 58.2, 57.9, 56.4, 34.8, 33.9, 33.8, 27.9, 27.4, 24.3, 17.2, 16.9, 16.8, 16.4; IR (neat) 2978, 2932, 1743, 1495, 1453, 1370, 1279, 1256, 1163, 1098, 858, 756, 704 cm^{-1}; HRMS (ESI): *m*/*z* calcd for $C_{31}H_{42}O_6Na$ $[M+Na]^+$ 533.2879, found 533.2859; $[\alpha]_D$ = +17.3 ($CHCl_3$, *c* 1.49).

((2*S*,3*S*)-3-((*E*)-7-Methoxy-4-methyl-8,8-diphenyloct-3-enyl)-3-methyloxiran-2-yl)methanol (A22)



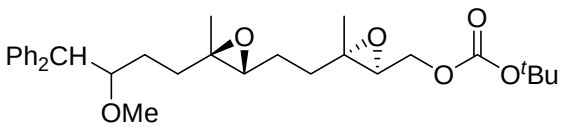
A suspension of the activated 4Å molecular sieves powder (95 mg) in CH_2Cl_2 (2.4 mL) was treated with (+)-diisopropyl tartrate (8.0 μL, 38.0 μmol) and the mixture was cooled to -35 to -30 °C. The mixture was stirred for 10 min and Ti(O-*i*-Pr)$_4$ (9.5 μL, 31.7 μmol) was added and the mixture was stirred for 15 min more. After that time, *t*-butyl hydroperoxide (5.0-6.0 M in decane, 0.19 mL, ~0.951 mmol) was added dropwise and the mixture was stirred for 30 min. Dienol **1.63** (120.0 mg, dissolved in 0.5 mL of CH_2Cl_2) was added dropwise and the flask formerly containing the dienol was rinsed with CH_2Cl_2 (2 x 0.1 mL). The reaction mixture was stirred at -35 to -30 °C for 40 min and then water (0.5 mL) was added. The mixture was allowed to warm up to 0 °C and stirred for 1 h. A solution of 30% of NaOH saturated with NaCl (0.3 mL) was added and the mixture was warmed up to room temperature and stirred for 1.5 h. The suspension was filtered through a pad of Celite and the filtrate was dried over $MgSO_4$, filtered and concentrated. The residue was purified by flash chromatography (30% - 40% EtOAc in hexanes) to give the monoepoxy alcohol **A22** (120.0 mg, 95.9%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39-7.17 (m, 10H), 5.07 (app t, *J* = 6.7 Hz, 1H), 4.01 (d, *J* = 8.3 Hz, 1H), 3.92-3.86 (m, 1H), 3.81-3.75 (m, 1H), 3.71-3.63 (m, 1H), 3.15 (s, 3H), 2.94 (dd, *J* = 6.5, 4.5 Hz, 1H), 2.11-2.04 (m, 4H), 1.74-1.43 (m, 4H), 1.51 (s, 3H), 1.29 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.9, 142.5, 135.8, 135.7, 129.0, 128.6, 128.4, 126.5, 126.4, 123.7, 123.6, 83.3, 83.2, 63.1, 61.6, 61.2, 58.0, 57.8, 56.2, 38.6, 35.2, 30.7, 30.6, 23.8, 16.9, 16.0; IR (neat) 3424, 3026, 2930, 1598, 1494, 1451, 1384, 1103, 1032, 862, 746, 704 cm^{-1}; HRMS (ESI): *m*/*z* calcd for $C_{26}H_{34}O_3Na$ $[M+Na]^+$ 417.2406, found 417.2436; $[\alpha]_D$ = -3.8 ($CHCl_3$, *c* 1.08).

((2*S*,3*S*)-3-(2-((2*R*,3*R*)-3-(3-Methoxy-4,4-diphenylbutyl)-3-methyloxiran-2-yl)ethyl)-3-methyloxiran-2-yl)methanol (A23)



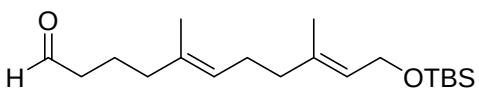
To a solution of monoepoxy alcohol **A22** (170.0 mg, 0.431 mmol) in CH_3CN/DMM (6.5 mL, 1:2, v/v) were added a 0.05 M solution of $Na_2B_4O_7$ in $4x10^{-4}$ M Na_2(EDTA) (4.3 mL), Bu_4NHSO_4 (5.8 mg, 17.2 μmol) and Shi ketone (55.6 mg, 0.216 mmol) sequentially. The mixture was cooled to 0 °C, and the Oxone (366 mg, 0.595 mmol), dissolved in $4x10^{-4}$ M Na_2(EDTA) (2.8 mL), and K_2CO_3 (346 mg, 2.50 mmol), dissolved in water (2.8 mL), were added simultaneously via a syringe pump over 2.0 h. After the addition was completed, the blue reaction mixture was stirred further for 15 min at 0 °C, then diluted with water (15 mL) and extracted with CH_2Cl_2 (3 x 30 mL). The organic extracts were dried over $MgSO_4$, filtered and concentrated. The residue was purified by flash chromatography (50% - 80% EtOAc in hexanes) to give the diepoxy alcohol **A23** (160.6 mg, 90.8%, dr ~ 1:1 regarding the stereochemical outcomes of the homobenzylic center and the two epoxide groups): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38-7.17 (m, 10H), 3.99-3.95 (m, 1H), 3.93-3.87 (m, 1H), 3.83-3.73 (m, 1H), 3.71-3.60 (m, 1H), 3.15/3.14 (s, 3H), 2.98-2.90 (m, 1H), 2.67-2.60 (m, 1H), 2.35-2.28 (m, 1H), 1.91-1.86 (m, 1H), 1.78-1.71 (m, 2H), 1.69-1.55 (m, 3H), 1.52-1.44 (m, 3H), 1.30 (s, 3H), 1.16/1.14 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.6, 142.6, 142.3, 142.2, 128.9, 128.8, 128.7, 128.6, 128.4, 126.6, 126.5, 83.3, 83.1, 63.6, 63.0, 63.0, 61.4, 61.2, 61.0, 60.8, 58.2, 57.8, 56.2, 56.0, 36.1, 34.0, 33.7, 27.6, 27.1, 24.7, 16.9, 16.5, 16.4; IR (neat) 3438, 3026, 2929, 1495, 1452, 1385, 1100, 1032, 746, 704 cm^{-1}; HRMS (ESI): *m*/*z* calcd for $C_{26}H_{34}O_4Na$ $[M+Na]^+$ 433.2355, found 433.2346; $[\alpha]_D$ = +19.3 ($CHCl_3$, *c* 1.55).

***tert*-Butyl ((2*S*,3*S*)-3-(2-((2*R*,3*R*)-3-(3-methoxy-4,4-diphenylbutyl)-3-methyloxiran-2-yl)ethyl)-3-methyloxiran-2-yl)methyl carbonate (1.52)**



To a solution of diepoxy alcohol **A23** (145.1 mg, 0.353 mmol) in anhydrous toluene (3.5 mL) at 0 °C were added 1-methylimidazole (28 μL, 0.353 mmol) and Boc_2O (154 mg, 0.706 mmol). The reaction mixture was stirred overnight, allowing the temperature to warm to room temperature slowly. The reaction was quenched with water (15 mL) and extracted with CH_2Cl_2 (3 x 25 mL). The organic extracts were dried over $MgSO_4$, filtered and concentrated. The residue was purified by flash chromatography (20% - 25% EtOAc in hexanes containing 0.5% Et_3N) to give the *tert*-butyl carbonate **1.52** (154.8 mg, 85.8%, dr ~ 1:1 regarding the stereochemical outcomes of the homobenzylic center and the two epoxide groups) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41-7.18 (m, 10H), 4.29-4.21 (m, 1H), 4.19-4.11 (m, 1H), 4.02-3.92 (m, 2H), 3.18/3.17 (s, 3H), 3.04 (dd, *J* = 6.2, 4.8 Hz, 1H), 2.63-2.59 (m, 1H), 1.82-1.40 (m, 8H), 1.53 (s, 9H), 1.32 (s, 3H), 1.17/1.15 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.5, 142.7, 142.4, 142.2, 129.0, 128.7, 128.6, 128.4, 126.6, 126.4, 83.3, 82.7, 65.6, 63.1, 62.7, 60.9, 60.3, 59.8, 58.1, 57.8, 56.3, 56.1, 35.2, 33.9, 33.8, 27.9, 27.6, 27.3, 24.5, 16.9, 16.8, 16.4; IR (neat) 2977, 2932, 1742, 1495, 1453, 1370, 1279, 1256, 1163, 1097, 858, 704 cm^{-1}; HRMS (ESI): *m*/*z* calcd for $C_{31}H_{42}O_6Na$ $[M+Na]^+$ 533.2879, found 533.2857; $[\alpha]_D$ = +1.3 ($CHCl_3$, *c* 2.15).

(5*E*,9*E*)-11-(*tert*-Butyldimethylsilanyloxy)-5,9-dimethylundeca-5,9-dienal (1.64)

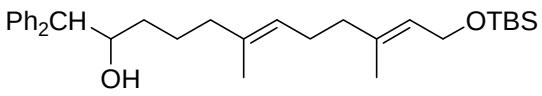


(Methoxymethyl)triphenylphosphonium chloride (1.656 g, 4.830 mmol) in a dry flask under high vacuum was heated with heat gun for 3 min to remove the moisture. After the flask was cooled to room

temperature, THF (8.0 mL) was added in and the suspension was cooled to 0 °C. NaHMDS (1 M in THF, 4.83 mL, 4.83 mmol) was added dropwise and the resulting deep orange suspension was stirred at 0 °C for 1 h. Dienal **1.62** (0.500 g, 1.61 mmol, dissolved in 2.0 mL of THF) was added dropwise and the flask formerly containing the aldehyde was rinsed with THF (2 x 1.0 mL). The reaction mixture was stirred at 0 °C for 1 h, then quenched with saturated $NaHCO_3$ (10 mL) and poured into water (20 mL). The mixture was extracted with Et_2O (3 x 30 mL). The organic extracts were dried over $MgSO_4$, filtered and concentrated. The residue was purified by flash chromatography (3.5% EtOAc in hexanes) to give the methyl vinyl ether.

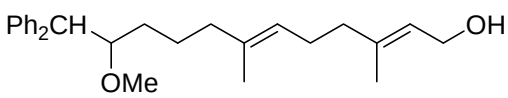
The methyl vinyl ether in THF–H_2O (10:1, 16.5 mL) was treated with $Hg(OAc)_2$ (0.558 g, 1.65 mmol). The reaction mixture was stirred for 30 min and saturated KI (30 mL) was added. The resulting yellowish green mixture was stirred for 1 h, then diluted with Et_2O (30 mL). The two layers were separated and the aqueous layer was extracted with Et_2O (2 x 40 mL). The combination of the organic extracts were dried over $MgSO_4$, filtered and concentrated. The residue was purified by flash chromatography (3% - 5% EtOAc in hexanes) to give the titled aldehyde (0.474 g, 90.7%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.77 (t, *J* = 1.7 Hz, 1H), 5.30 (qt, *J* = 6.3, 1.1 Hz, 1H), 5.12 (qt, *J* = 6.9, 1.1 Hz, 1H), 4.20 (d, *J* = 6.3 Hz, 2H), 2.39 (dt, *J* = 7.3, 1.7 Hz, 2H), 2.17-2.08 (m, 2H), 2.01 (app t, *J* = 7.9 Hz, 4H), 1.74 (pent, *J* = 7.3 Hz, 2H), 1.62 (s, 3H), 1.59 (s, 3H), 0.91 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.8, 136.9, 134.2, 125.5, 124.8, 60.5, 43.4, 39.6, 39.0, 26.4, 26.2, 20.4, 18.6, 16.5, 15.9, -4.8; IR (neat) 2929, 2856, 2712, 1728, 1472, 1386, 1254, 1110, 1068, 836, 776 cm^{-1}; HRMS (ESI): *m*/*z* calcd for $C_{19}H_{36}O_2SiNa$ $[M+Na]^+$ 347.2382, found 347.2402.

(6*E*,10*E*)-12-(*tert*-Butyldimethylsilanyloxy)-6,10-dimethyl-1,1-diphenyldodeca-6,10-dien-2-ol (A24)



A solution of diphenylmethane (0.66 mL, 3.93 mmol) in THF (3.9 mL) was treated with *n*-BuLi (1.6 M in hexanes, 2.46 mL, 3.93 mmol) and the resulting deep-orange solution was refluxed for 1 h. After cooling to room temperature, the solution was cooled further to 0 °C and the above aldehyde **1.64** (0.426 g, 1.31 mmol, dissolved in 1.0 mL of THF) was added dropwise. The flask formerly containing the aldehyde was rinsed with THF (2 x 0.5 mL). The deep-orange solution was stirred at 0 °C for 2 h, then quenched with saturated $NaHCO_3$ (5 mL). The biphasic mixture was poured into water (25 mL) and extracted with Et_2O (3 x 25 mL). The combined organic extracts were dried over $MgSO_4$, filtered and concentrated. The residue was purified by flash chromatography (3% - 9% EtOAc in hexanes) to give the secondary alcohol **A24** (0.519 g, 80.3%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38-7.13 (m, 10H), 5.28 (qt, *J* = 6.3, 1.1 Hz, 1H), 5.03 (qt, *J* = 6.9, 1.0 Hz, 1H), 4.37-4.29 (m, 1H), 4.18 (d, *J* = 6.3 Hz, 2H), 3.86 (d, *J* = 8.3 Hz, 1H), 2.08-2.00 (m, 2H), 1.96-1.85 (m, 4H), 1.60 (s, 3H), 1.52 (s, 3H), 1.69-1.30 (m, 4H), 0.89 (s, 9H), 0.06 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.8, 141.7, 137.1, 135.2, 129.0, 129.0, 128.8, 128.5, 127.0, 126.7, 124.6, 124.3, 73.9, 60.6, 59.0, 39.7, 39.6, 34.8, 26.5, 26.2, 24.2, 18.6, 16.6, 16.0, -4.8; IR (neat) 3467, 2928, 2856, 1599, 1494, 1451, 1384, 1253, 1107, 1065, 1005, 835, 775, 702 cm^{-1}; HRMS (ESI): *m*/*z* calcd for $C_{32}H_{48}O_2SiNa$ $[M+Na]^+$ 515.3321, found 515.3317.

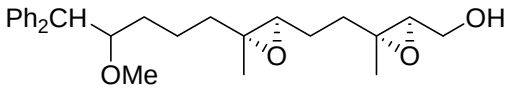
(2*E*,6*E*)-11-Methoxy-3,7-dimethyl-12,12-diphenyldodeca-2,6-dien-1-ol (1.65)



The secondary alcohol **A24** (0.473 g, 0.960 mmol) in

anhydrous DMF (5.0 mL) at 0 °C was treated with NaH (60% dispersion in mineral oil, 96.0 mg, 2.40 mmol) and the yellow suspension was stirred at 0 °C for 30 min. MeI (0.24 mL, 3.84 mmol) was added dropwise and the reaction mixture was stirred for 2.5 h at room temperature. The reaction was quenched with water (10 mL) and extracted with Et_2O (3 x 30 mL). The organic extracts were dried over $MgSO_4$, filtered and concentrated. The residue was dissolved in THF (5.0 mL) and TBAF monohydrate (0.301 g, 1.15 mmol) was added in. The yellow solution was stirred for 2 h and then concentrated in vacuo. The residue was purified by flash chromatography (20% - 30% EtOAc in hexanes) to give the dienol **1.65** (0.368 g, 97.5%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40-7.16 (m, 10H), 5.40 (qt, *J* = 6.9, 1.2 Hz, 1H), 5.05 (qt, *J* = 6.8, 1.0 Hz, 1H), 4.16 (d, *J* = 6.8 Hz, 2H), 4.02 (d, *J* = 8.3 Hz, 1H), 3.94-3.88 (m, 1H), 3.18 (s, 3H), 2.13-1.98 (m, 4H), 1.93-1.90 (m, 2H), 1.68 (s, 3H), 1.54 (s, 3H), 1.58-1.30 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.1, 142.6, 139.7, 135.4, 129.1, 128.7, 128.6, 128.4, 126.5, 126.4, 124.2, 123.7, 83.8, 59.6, 58.0, 56.3, 39.8, 39.7, 31.7, 26.4, 23.4, 16.4, 16.0; IR (neat) 3388, 3026, 2931, 1667, 1599, 1495, 1451, 1382, 1186, 1102, 1003, 745, 703 cm^{-1}; HRMS (ESI): *m*/*z* calcd for $C_{27}H_{36}O_2Na$ $[M+Na]^+$ 415.2613, found 415.2607.

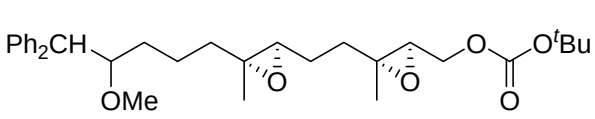
((2*R*,3*R*)-3-(2-((2*R*,3*R*)-3-(4-methoxy-5,5-diphenylpentyl)-3-methyloxiran-2-yl)ethyl)-3-methyloxiran-2-yl)methanol (A25)



To a solution of monoepoxy alcohol **A24** (112 mg, 0.287 mmol) in CH_3CN/DMM (4.3 mL, 1:2, v/v) were added a 0.05 M solution of $Na_2B_4O_7$ in 4x10^{-4} M Na_2(EDTA) (2.9 mL), Bu_4NHSO_4 (7.8 mg, 22.9 μmol) and Shi ketone (74 mg, 0.287 mmol) sequentially. The mixture was cooled to 0 °C, and the Oxone (486 mg, 0.791 mmol), dissolved in 4x10^{-4} M Na_2(EDTA) (3.7 mL), and K_2CO_3

(460 mg, 3.32 mmol), dissolved in water (3.7 mL), were added simultaneously via a syringe pump over 1.5 h. After the addition was completed, the blue reaction mixture was stirred further for 15 min at 0 °C, then diluted with water (20 mL) and extracted with CH_2Cl_2 (3 x 30 mL). The organic extracts were dried over $MgSO_4$, filtered and concentrated. The residue was purified by flash chromatography (35% - 85% EtOAc in hexanes containing 0.5% Et_3N) to give diepoxy alcohol **A25** (78 mg, 64%, dr ~ 1:1 regarding the stereochemical outcomes of the homobenzylic center and the two epoxide groups) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62-7.16 (m, 10H), 4.00 (*J* = 8.4 Hz, 1H), 3.92-3.83 (m, 1H), 3.82-3.79 (m, 1H), 3.75-3.64 (m, 1H), 3.17/3.16 (s, 3H), 3.01-2.96 (m, 1H), 2.68-2.63 (m, 1H), 1.96-1.70 (m, 2H), 1.64-1.40 (m, 8H), 1.33 (s, 3H), 1.20/1.19 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.8, 142.4, 128.9, 128.9, 128.7, 128.6, 128.4, 126.6, 126.4, 83.6, 63.0, 62.9, 62.6, 61.4, 61.2, 61.1, 60.7, 58.1, 58.0, 56.2, 38.8, 38.7, 35.2, 32.1, 24.4, 20.8, 20.7, 17.0, 16.5, 16.5; IR (neat) 3433, 2930, 1599, 1495, 1452, 1386, 1102, 1032, 734, 704 cm^{-1}.

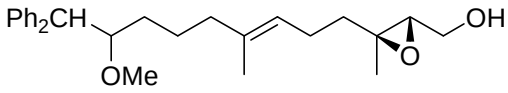
***tert*-Butyl ((2*R*,3*R*)-3-(2-((2*R*,3*R*)-3-(4-methoxy-5,5-diphenylpentyl)-3-methyloxiran-2-yl)ethyl)-3-methyloxiran-2-yl)methyl carbonate (1.53)**



The diepoxy alcohol **A25** (74 mg, 0.174 mmol) was dissolved in dry toluene (1.7 mL) and cooled to 0 °C. *N*-Methylimidazole (18 μL, 0.226 mmol) and Boc_2O (152 mg, 0.696 mmol) were added sequentially. The reaction mixture was stirred overnight, allowing the temperature to warm to room temperature slowly. The reaction was quenched with water (10 mL) and extracted with CH_2Cl_2 (3 x 20 mL). The extracts were dried over $MgSO_4$, filtered and concentrated. The residue was purified by column chromatography (20% - 25% EtOAc in hexanes containing 0.5%

Et_3N) to give the desired product **1.53** (72 mg, 78%, dr ~ 1:1 regarding the stereochemical outcomes of the homobenzylic center and the two epoxide groups) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41-7.18 (m, 10H), 4.30-4.14 (m, 2H), 4.02 (d, *J* = 8.4 Hz, 1H), 3.98-3.85 (m, 1H), 3.19/3.18 (s, 3H), 3.05 (t, *J* = 5.7 Hz, 1H), 2.66-2.63 (m, 1H), 1.81-1.39 (m, 8H), 1.52 (s, 9H), 1.35 (s, 3H), 1.20/1.19 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.5, 142.9, 142.5, 142.4, 129.0, 128.9, 128.7, 128.6, 128.4, 126.6, 126.4, 83.7, 83.6, 82.7, 65.6, 62.9, 62.8, 61.0, 60.3, 59.3, 58.1, 58.0, 56.3, 38.8, 38.8, 34.8, 32.2, 27.9, 24.4, 20.9, 20.8, 17.1, 16.5, 16.5; IR (neat) 3026, 2934, 1743, 1495, 1453, 1370, 1279, 1256, 1163, 1098, 859, 747, 705 cm^{-1}; HRMS (ESI): *m*/*z* calcd for $C_{32}H_{44}O_6Na$ $[M+Na]^+$ 547.3036, found 547.3002; $[\alpha]_D$ = +11.0 ($CHCl_3$, *c* 2.01).

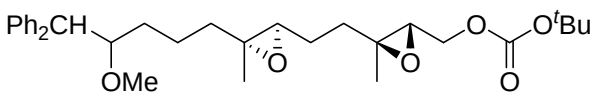
((2*S*,3*S*)-3-((*E*)-8-Methoxy-4-methyl-9,9-diphenylnon-3-enyl)-3-methyloxiran-2-yl)methanol (A26)



A suspension of the activated 4Å molecular sieves powder (115.0 mg) in CH_2Cl_2 (3.3 mL) was treated with (+)-diisopropyl tartrate (9.6 μL, 45.8 μmol) and the mixture was cooled to -35 to -30 °C. The mixture was stirred for 10 min and Ti(O-*i*-Pr)$_4$ (11.4 μL, 38.2 μmol) was added and the mixture was stirred for 15 min more. After that time, *t*-butyl hydroperoxide (5.0-6.0 M in decane, 0.23 mL, ~1.15 mmol) was added dropwise and the mixture was stirred for 30 min. Dienol **1.65** (150.0 mg, 0.382 mmol, dissolved in 1.0 mL of CH_2Cl_2) was added dropwise and the flask formerly containing the allylic alcohol was rinsed with CH_2Cl_2 (2 x 0.5 mL). The reaction mixture was stirred at -35 to -30 °C for 1.5 h and then water (0.6 mL) was added. The mixture was allowed to warm up to 0 °C and stirred for 1 h. A solution of 30% of NaOH saturated with NaCl (0.2 mL) was added and the mixture was warmed up to room temperature and stirred for

1.5 h. The suspension was filtered through a pad of Celite and the filtrate was dried over $MgSO_4$, filtered and concentrated. The residue was purified by flash chromatography (30% - 40% EtOAc in hexanes) to give the monoepoxy alcohol **A26** (156.0 mg, 97.3%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44-7.23 (m, 10H), 5.09 (t, *J* = 6.6 Hz, 1H), 4.06 (d, *J* = 8.3 Hz, 1H), 3.99-3.93 (m, 1H), 3.86-3.83 (m, 1H), 3.70 (dd, *J* = 12.0, 6.6 Hz, 1H), 3.22 (s, 3H), 3.02-2.99 (m, 1H), 2.46 (br s, 1H), 2.10 (q, *J* = 7.7 Hz, 2H), 1.96-1.91 (m, 2H), 1.72-1.43 (m, 6H), 1.59 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.0, 142.5, 135.7, 128.9, 128.6, 128.3, 126.4, 126.3, 123.5, 83.6, 63.2, 61.5, 61.2, 57.9, 56.2, 39.6, 38.6, 31.6, 23.6, 23.2, 16.9, 15.9; IR (neat) 3425, 3027, 2934, 1599, 1495, 1452, 1385, 1103, 1032, 910, 733, 703 cm^{-1}; HRMS (ESI): *m*/*z* calcd for $C_{27}H_{36}O_3Na$ $[M+Na]^+$ 431.2562, found 431.2556; $[\alpha]_D$ = -3.8 ($CHCl_3$, *c* 1.17).

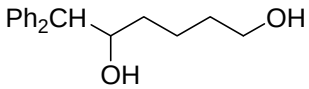
***tert*-Butyl ((2*S*,3*S*)-3-(2-((2*R*,3*R*)-3-(4-methoxy-5,5-diphenylpentyl)-3-methyloxiran-2-yl)ethyl)-3-methyloxiran-2-yl)methyl carbonate (1.54)**



A solution of monoepoxy alcohol **A26** (145.0 mg, 0.3549 mmol) in CH_3CN/DMM (5.3 mL, 1:2, v/v) was treated a 0.05 M solution of $Na_2B_4O_7$ in 4x10^{-4} M Na_2(EDTA) (3.5 mL), Bu_4NHSO_4 (4.8 mg, 14.2 μmol) and Shi ketone (45.8 mg, 0.177 mmol) sequentially. The mixture was cooled to 0 °C, and the Oxone (301 mg, 0.490 mmol), dissolved in 4x10^{-4} M Na_2(EDTA) (2.3 mL), and K_2CO_3 (284 mg, 2.06 mmol), dissolved in water (2.3 mL), were added simultaneously via a syringe pump over 2.0 h. After the addition was completed, the blue reaction mixture was stirred further for 15 min at 0 °C, then diluted with water (5 mL) and extracted with CH_2Cl_2 (3 x 25 mL). The organic extracts were dried over $MgSO_4$, filtered and concentrated. The residue was dissolved in dry toluene (3.5 mL) and cooled to 0 °C. *N*-

Methylimidazole (36.8 μL, 0.4614 mmol) and Boc_2O (232 mg, 1.06 mmol) were added sequentially. The reaction mixture was stirred overnight, allowing the temperature to warm to room temperature slowly. The reaction was quenched with water (5 mL) and extracted with CH_2Cl_2 (3 x 20 mL). The extracts were dried over $MgSO_4$, filtered and concentrated. The residue was azeotroped with hexanes (3 x 20 mL) to removed *t*-BuOH and the residue was purified by column chromatography (12% - 24% EtOAc in hexanes containing 0.5% Et_3N) to give the desired product **1.54** (153.5 mg, 82.4%, dr ~ 1:1 regarding the stereochemical outcomes of the homobenzylic center and the two epoxide groups) as a colorless oil: ^1H NMR (300 MHz, $CDCl_3$) δ 7.43-7.20 (m, 10H), 4.29 (dd, *J* = 11.9, 4.8 Hz, 1H), 4.17 (dd, *J* = 11.9, 6.3 Hz, 1H), 4.04 (d, *J* = 8.4 Hz, 1H), 3.99-3.90 (m, 1H), 3.20/3.19 (s, 3H), 3.07 (t, *J* = 5.3 Hz, 1H), 2.67-2.62 (m, 1H), 1.77-1.42 (m, 10H), 1.54 (s, 9H), 1.35 (s, 3H), 1.22 (br s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.4, 142.8, 142.4, 142.4, 128.9, 128.8, 128.6, 128.5, 128.3, 126.5, 126.4, 83.5, 83.5, 82.6, 65.6, 63.0, 62.9, 60.8, 60.8, 60.3, 59.7, 58.0, 57.9, 56.2, 38.7, 38.7, 35.1, 32.1, 27.8, 24.4, 20.8, 20.6, 16.8, 16.5, 16.4; IR (neat) 2979, 2935, 1743, 1495, 1453, 1370, 1279, 1163, 1098, 912, 859, 733, 704 cm^{-1}; HRMS (ESI): *m*/*z* calcd for $C_{32}H_{44}O_6Na$ $[M+Na]^+$ 547.3036, found 547.3031; $[\alpha]_D$ = +0.5 ($CHCl_3$, *c* 1.21).

6,6-Diphenylhexane-1,5-diol (A27)

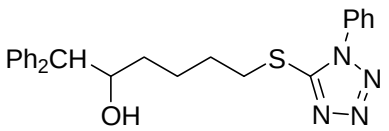


In a round-bottomed flask, the *δ*−valerolactone (1.82 mL, 20.0 mmol) in CH_2Cl_2 (20.0 mL) at -78 °C was treated dropwise with DIBAL-H (1 M in hexanes, 22.0 mL, 22.0 mmol). The mixture was stirred at -78 °C for 1h, then quenched with saturated sodium tartrate (80 mL) and extracted with Et_2O (3 x 100 mL). The extracts were

dried over $MgSO_4$, filtered and concentrated. The crude lactol was used in the next step without further purification.

In another two-necked round-bottomed flask, diphenylmethane (13.4 mL, 80.0 mmol) in THF (50.0 mL) was treated dropwise with *n*-BuLi (1.6 M in hexanes, 50.0 mL, 80.0 mmol). The resulting deep orange solution was refluxed for 1 h and then cooled to 0 °C. The as-prepared crude lactol (dissolved in 5 mL THF) was added dropwise and the flask formerly containing the lactol was rinsed with THF (2 x 1.5 mL). The deep-orange mixture was stirred at 0 °C for 0.5 h, then quenched with saturated NH_4Cl (80 mL) and extracted with Et_2O (3 x 100 mL). The combined extracts were dried over $MgSO_4$ and evaporated. The resulting residue was purified by column chromatography (40% - 80% EtOAc in hexanes) to give the diol **A27** (4.42 g, 81.8%) as a white solid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57-7.18 (m, 10H), 4.38 (app t, *J* = 8.0 Hz, 1H), 3.90 (d, *J* = 8.5 Hz, 1H), 3.59 (t, *J* = 5.7 Hz, 2H), 1.88 (br s, 1H), 1.81 (br s, 1H), 1.67-1.42 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.6, 141.7, 129.0, 129.0, 128.8, 128.4, 127.0, 126.7, 73.9, 62.7, 59.0, 34.6, 32.6, 22.0; IR (neat) 3358, 3023, 2948, 1596, 1493, 1450, 1345, 1039, 696 cm^{-1}; HRMS (ESI): *m*/*z* calcd for $C_{18}H_{22}O_2Na$ $[M+Na]^+$ 293.1517, found 293.1537.

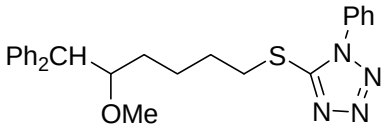
6-(1-Phenyl-1*H*-tetrazol-5-ylthio)-1,1-diphenylhexan-2-ol (A28)



At 0 °C, to a mixture of diol **A27** (1.000 g, 3.699 mmol), 1-phenyl-1*H*-tetrazole-5-thiol (0.791 g, 4.44 mmol) and Ph_3P (1.164 g, 4.44 mmol) in THF (30.0 mL) was added dropwise diisopropyl azodicarboxylate (0.82 mL, 4.07 mmol). The mixture was warmed to room temperature and stirred for 20 min. The reaction was quenched with water (60 mL) and extracted with Et_2O (3 x 70 mL). The organic extracts were dried over $MgSO_4$ and evaporated. The resulting residue was purified by column

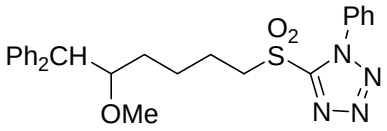
chromatography (25% - 40% EtOAc in hexanes) to give the crude product which was further purified by column chromatography (3.5% Et_2O in CH_2Cl_2) to give **A28** (1.542 g, 96.8%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60-7.50 (m, 5H), 7.40-7.15 (m, 10H), 4.39-4.33 (m, 1H), 3.86 (d, *J* = 8.5 Hz, 1H), 3.35 (t, *J* = 7.1 Hz, 2H), 1.86-1.38 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.6, 142.4, 141.5, 133.8, 130.2, 129.9, 129.0, 128.9, 128.8, 128.3, 127.0, 126.8, 124.0, 73.6, 59.1, 34.4, 33.4, 29.1, 25.0; IR (neat) 3439, 3026, 2942, 1597, 1499, 1451, 1387, 1243, 1088, 1015, 910, 760, 733, 704 cm^{-1}; HRMS (ESI): *m*/*z* calcd for $C_{25}H_{26}N_4OSNa$ $[M+Na]^+$ 453.1725, found 453.1705.

5-(5-Methoxy-6,6-diphenylhexylthio)-1-phenyl-1*H*-tetrazole (A29)



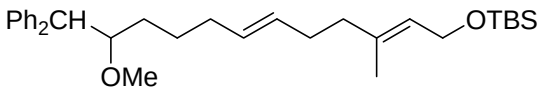
The secondary alcohol **A28** (1.444 g, 3.354 mmol) in anhydrous DMF (17.0 mL) at 0 °C was treated with NaH (60% dispersion in mineral oil, 0.335 g, 8.38 mmol) and the yellow suspension was stirred at 0 °C for 30 min. MeI (0.84 mL, 13.42 mmol) was added dropwise and the reaction mixture was stirred for 4 h at room temperature. The reaction was quenched with water (60 mL) and extracted with Et_2O (3 x 50 mL). The organic extracts were dried over $MgSO_4$, filtered and concentrated. The residue was purified by flash chromatography (13% - 20% EtOAc in hexanes) to give the desired product **A29** (1.268 g, 85.0%) as a pale yellow oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59-7.56 (m, 5H), 7.38-7.17 (m, 10H), 3.98 (d, *J* = 8.4 Hz, 1H), 3.93-3.88 (m, 1H), 3.34 (t, *J* = 7.2 Hz, 2H), 3.15 (s, 3H), 1.86-1.70 (m, 2H), 1.65-1.40 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.6, 142.8, 142.4, 133.9, 130.2, 129.9, 128.9, 128.7, 128.6, 128.4, 126.6, 126.4, 124.0, 83.5, 58.1, 56.3, 33.4, 31.7, 29.3, 24.2; IR (neat) 3026, 2938, 1597, 1498, 1451, 1386, 1242, 1102, 759, 697 cm^{-1}; HRMS (ESI): *m*/*z* calcd for $C_{26}H_{28}N_4OSNa$ $[M+Na]^+$ 467.1882, found 467.1876.

5-(5-Methoxy-6,6-diphenylhexylsulfonyl)-1-phenyl-1*H*-tetrazole (1.66)



At 0 °C, $NaHCO_3$ (312 mg, 3.71 mmol) was added to a solution of the thioether **A29** (330 mg, 0.742 mmol) in CH_2Cl_2 (10.0 mL) and then *m*CPBA (pure, 435 mg, 2.52 mmol) was added in small portions. The mixture was stirred at 0 °C for 15 min, then at room temperature overnight. The reaction was quenched with saturated $Na_2S_2O_3$ solution (20 mL), stirred for 30 min and extracted with CH_2Cl_2 (3 x 25 mL). The extracts were dried over $MgSO_4$, filtered and concentrated. The residue was purified by flash chromatography (16% - 24% EtOAc in hexanes) to give the desired sulfone **1.66** (336 mg, 95.0%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70-7.60 (m, 5H), 7.38-7.17 (m, 10H), 3.99 (d, *J* = 8.5 Hz, 1H), 3.94-3.88 (m, 1H), 3.72-3.64 (m, 2H), 3.15 (s, 3H), 1.96-1.84 (m, 2H), 1.68-1.53 (m, 3H), 1.49-1.43 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.7, 142.6, 142.3, 133.2, 131.6, 129.9, 128.9, 128.8, 128.6, 128.5, 126.7, 126.6, 125.3, 83.4, 58.2, 56.4, 56.1, 31.7, 23.9, 22.3; IR (neat) 3027, 2934, 2828, 1597, 1496, 1452, 1342, 1153, 1103, 762, 705 cm^{-1}; HRMS (ESI): *m*/*z* calcd for $C_{26}H_{28}N_4O_3SNa$ $[M+Na]^+$ 499.1780, found 499.1787.

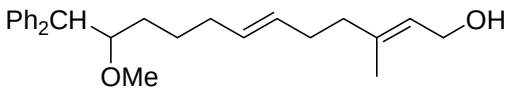
((2*E*,6*E*)-11-Methoxy-3-methyl-12,12-diphenyldodeca-2,6-dienyloxy)(*tert*-butyl)dimethyl-silane (A30)



A solution of sulfone **1.66** (300 mg, 0.630 mmol, azeotropically dried with benzene) in anhydrous 1,2-dimethoxyethane (3.8 mL) at -78 °C was treated dropwise with KHMDS (0.5 M in 1,2-dimethoxyethane, 1.51 mL, 0.755 mmol) and the resulting yellow mixture was stirred at this temperature for 1 h. After that time, aldehyde **1.60** (183 mg, 0.755 mmol, dissolved in 0.5 mL of

1,2-dimethoxyethane) was added dropwise. The reaction mixture was stirred at -78 °C for 1.5 h, then at room temperature overnight. The reaction was quenched with saturated NH_4Cl solution (5 mL), poured onto water (10 mL) and extracted with Et_2O (3 x 30 mL). The extracts were dried over $MgSO_4$, filtered and concentrated. The residue was purified by flash chromatography (2% - 3% EtOAc in hexanes) to give the desired diene **A30** (196.4 mg, 63.3%) as a pale yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38-7.17 (m, 10H), 5.35-5.33 (m, 2H), 5.30 (qt, *J* = 6.3, 1.0 Hz, 1H), 4.20 (d, *J* = 6.3 Hz, 1H), 4.00 (d, *J* = 8.2 Hz, 1H), 3.91-3.88 (m, 1H), 3.17 (s, 3H), 2.09-2.05 (m, 2H), 2.20-1.99 (m, 2H), 1.92-1.91 (m, 2H), 1.61 (s, 3H), 1.52-1.48 (m, 2H), 1.45-1.40 (m, 2H), 0.92 (s, 9H), 0.08 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.2, 142.6, 136.9, 130.4, 130.3, 129.1, 128.7, 128.6, 128.4, 126.5, 126.4, 124.7, 83.8, 60.5, 58.0, 56.3, 39.8, 32.7, 31.7, 31.1, 26.2, 25.2, 18.6, 16.6, -4.8; IR (neat) 3027, 2928, 2855, 1599, 1495, 1451, 1381, 1254, 1105, 1062, 836, 775, 701 cm^{-1}; HRMS (EI): *m*/*z* calcd for $C_{28}H_{39}OSi$ $(M-C_4H_9)^{+\bullet}$ 435.2719, found 435.2706.

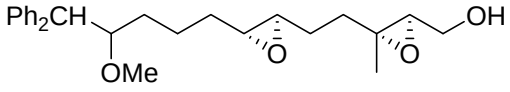
(2*E*,6*E*)-11-Methoxy-3-methyl-12,12-diphenyldodeca-2,6-dien-1-ol (A31)



To a solution of silyl ether **A30** (196.4 mg, 0.398 mmol) in THF (4.0 mL) was added TBAF monohydrate (125 mg, 0.478 mmol). The yellow solution was stirred for 1.5 h and the concentrated. The resulting residue was purified by flash chromatography (20% - 30% EtOAc in hexanes) to give the allylic alcohol **A31** (143.1 mg, 94.8%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49-7.18 (m, 10H), 5.44-5.36 (m, 3H), 4.15 (d, *J* = 6.8 Hz, 2H), 4.04 (d, *J* = 8.3 Hz, 1H), 3.96-3.91 (m, 1H), 3.19 (s, 3H), 2.14-2.02 (m, 4H), 2.00-1.90 (m, 2H), 1.75 (br s, 1H), 1.68 (s, 3H), 1.60-1.39 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.0, 142.5, 139.1, 130.4, 130.0,

129.0, 128.6, 128.3, 126.4, 126.3, 123.8, 83.7, 59.3, 57.9, 56.2, 39.6, 32.6, 31.6, 30.9, 25.0, 16.4; IR (neat) 3390, 3026, 2930, 1599, 1495, 1451, 1101, 1003, 969, 745, 703 cm^{-1}; HRMS (ESI): *m*/*z* calcd for $C_{26}H_{34}O_2Na$ $[M+Na]^+$ 401.2457, found 401.2464.

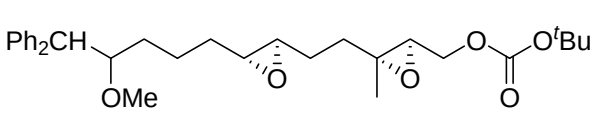
((2*R*,3*R*)-3-(2-((2*R*,3*R*)-3-(4-Methoxy-5,5-diphenylpentyl)oxiran-2-yl)ethyl)-3-methyloxiran-2-yl)methanol (A32)



To a solution of dienol **A31**(100.0 mg, 0.264 mmol) in CH_3CN/DMM (7.9 mL, 1:2, v/v) were added a 0.05 M solution of $Na_2B_4O_7$ in $4x10^{-4}$ M Na_2(EDTA) (5.3 mL), Bu_4NHSO_4 (7.2 mg, 21.1 μmol) and Shi ketone (102 mg, 0.396 mmol) sequentially. The mixture was cooled to -5 °C, and the Oxone (672 mg, 1.09 mmol), dissolved in $4x10^{-4}$ M Na_2(EDTA) (3.4 mL), and K_2CO_3 (635 mg, 4.59 mmol), dissolved in water (3.4 mL), were added simultaneously via a syringe pump over 2.0 h. After the addition was completed, the slightly blue reaction mixture was stirred further for 15 min at 0 °C, then diluted with water (10 mL) and extracted with CH_2Cl_2 (4 x 20 mL). The organic extracts were dried over $MgSO_4$, filtered and concentrated. The residue was purified by flash chromatography (50% - 70% EtOAc in hexanes) to give the diepoxy alcohol **A32** (101.9 mg, 94.0%, dr ~ 1:1 regarding the stereochemical outcomes of the homobenzylic center and the two epoxide groups) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39-7.15 (m, 10H), 4.01 (d, *J* = 8.4 Hz, 1H), 3.94-3.89 (m, 1H), 3.79 (dd, *J* = 12.1, 4.7 Hz, 1H), 3.69 (dd, *J* = 12.0, 6.3 Hz, 1H), 3.17/3.16 (s, 3H), 2.98-2.95 (m, 1H), 2.66-2.60 (m, 2H), 1.86-1.46 (m, 10H), 1.3 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.8, 142.4, 128.9, 128.7, 128.6, 128.4, 126.5, 126.4, 83.6, 62.6, 61.4, 60.7, 58.9, 58.8, 58.3, 58.2, 58.1, 58.0, 56.2, 34.5, 32.1, 32.0, 27.6, 21.6, 17.1; IR (neat)

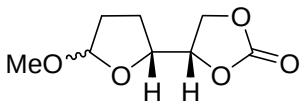
3426, 2934, 1495, 1452, 1097, 1032, 732, 704 cm^{-1}; HRMS (EI): *m/z* calcd for $C_{26}H_{34}O_4$ ($M^{+\bullet}$) 410.2457, found 410.2447; $[\alpha]_D$ = +14.3 ($CHCl_3$, *c* 1.20).

tert-Butyl ((2*R*,3*R*)-3-(2-((2*R*,3*R*)-3-(4-methoxy-5,5-diphenylpentyl)oxiran-2-yl)ethyl)-3-methyloxiran-2-yl)methyl carbonate (1.55)



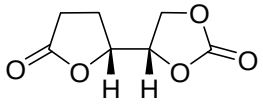
A solution of diepoxy alcohol **A32** (99.2 mg, 0.242 mmol) in toluene (2.4 mL) at 0 °C was added 1-Methylimidazole (19 μL, 0.24 mmol) and Boc_2O (106 mg, 0.484 mmol) sequentially. The reaction mixture was stirred overnight, allowing the temperature to warm to room temperature slowly. After that time, the reaction was quenched with water (10 mL) and extracted with CH_2Cl_2 (3 x 25 mL). The extracts were dried over $MgSO_4$, filtered and concentrated. The residue was azeotroped with hexanes (2 x 20 mL) to remove *t*-BuOH and the residue was purified by column chromatography (16% - 20% EtOAc in hexanes containing 0.5% Et_3N) to give the desired product **1.55** (102.0 mg, 82.6%, dr ~ 1:1 regarding the stereochemical outcomes of the homobenzylic center and the two epoxide groups) as a colorless oil: ^1H NMR (300 MHz, $CDCl_3$) δ 7.39-7.17 (m, 10H), 4.22 (dd, *J* = 11.8, 4.7 Hz, 1H), 4.14 (dd, *J* = 11.9, 6.0 Hz, 1H), 4.00 (d, *J* = 8.3 Hz, 1H), 3.93-3.88 (m, 1H), 3.17/3.16 (s, 3H), 3.02 (t, *J* = 5.4 Hz, 1H), 2.64-2.60 (m, 2H), 1.75-1.44 (m, 10H), 1.50 (s, 9H), 1.32 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.5, 142.9, 142.4, 129.0, 128.7, 128.6, 128.4, 126.6, 126.4, 83.7, 82.8, 65.6, 60.2, 59.3, 58.8, 58.8, 58.2, 58.1, 56.3, 34.2, 32.2, 27.9, 27.6, 21.7, 17.1; IR (neat) 2978, 2934, 1743, 1495, 1453, 1370, 1279, 1256, 1163, 1097, 859, 746, 704 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{31}H_{42}O_6Na$ $[M+Na]^+$ 533.2879, found 533.2866; $[\alpha]_D$ = +19.1 ($CHCl_3$, *c* 1.08).

(*S*)-4-((*R*)-Tetrahydro-5-methoxyfuran-2-yl)-1,3-dioxolan-2-one (1.68)



To *tert*-butyl carbonate **1.47** (92.0 mg, 0.223 mmol) in dichloroethane/toluene (8.6 mL, 5:1, v/v) in borosilicate flask at room temperature were added the activated 4Å molecular sieves (184 mg), anhydrous $Na_2S_2O_3$ (184 mg), NaOAc (184 mg) and *N*-methylquinolinium hexafluorophosphate (6.4 mg, 22.3 μmol). The mixture was photoirradiated with gentle air bubbling for 3 h while stirring at room temperature. The reaction mixture was filtered through a small plug of silica gel and the residue was washed with Et_2O (40 mL). The filtrate was concentrated and the resulting residue was purified by flash chromatography (45% - 55% EtOAc in hexanes) to give the product **1.68** (24.8 mg, 59.0%) in a 1.9:1 ratio as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.04 (dd, J = 4.5, 1.8 Hz, 66% of 1H), 5.01-4.99 (m, 34% of 1H), 4.67-4.46 (m, 2.4H), 4.39-4.20 (m, 1.6H), 3.33/3.32 (s, 3H), 2.26-1.93 (m, 3H), 1.74-1.66 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.1 (minor), 154.9 (major), 105.7 (minor), 105.6 (major), 79.4 (minor), 77.8 (minor), 77.1 (major), 66.8 (major), 66.4 (minor), 55.1 (major), 32.7 (minor), 31.7 (major), 25.9 (minor), 25.5 (major); IR (neat) 2920, 1807, 1464, 1376, 1170, 1088, 1031, 955 cm^{-1}; HRMS (EI): *m*/*z* calcd for $C_7H_9O_4$ (M-CH_3O)$^{+\bullet}$ 157.0501, found 157.0499.

(*S*)-4-((*R*)-Tetrahydro-5-oxofuran-2-yl)-1,3-dioxolan-2-one (1.69)

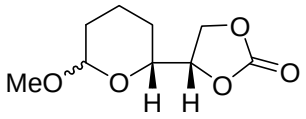


At 0 °C, the acetal **1.68** (6.4 mg, 34.0 μmol) in acetone (1.0 mL) was treated with Jones reagent (2.67M, 60 μL, 0.160 mmol). The mixture was stirred at 0 °C for 1 h, and Jones reagent (2.67M, 60 μL, 0.160 mmol) was added. The mixture was stirred at 0 °C fro 30 min, then at room temperature for 2 h. After that time, the mixture was purified by column chromatography (10% - 20% EtOAc in CH_2Cl_2) to give the lactone **1.69** (4.3

mg, 74.1%) as a pale yellow solid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.74 (ddd, *J* = 8.0, 6.7, 5.8 Hz, 1H), 4.64 (t, *J* = 8.9 Hz, 1H), 4.65-4.58 (m, 1H), 4.40 (dd, *J* = 8.9, 5.6 Hz, 1H), 2.68-2.62 (m, 2H), 2.60-2.50 (m, 1H), 2.20-2.10 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.2, 154.0, 78.1, 76.2, 66.7, 27.5, 24.0; IR (neat) 2919, 1778, 1462, 1401, 1328, 1173, 1087, 1048 cm^{-1}; HRMS (EI): *m*/*z* calcd for $C_7H_8O_5$ $[M+H]^+$ 173.0450, found 173.0455.

To monoepoxide **1.48** (102.0 mg, 0.239 mmol) in dichloroethane/toluene (9.2 mL, 5:1, v/v) in borosilicate flask at room temperature were added the activated 4Å molecular sieves (204 mg), anhydrous $Na_2S_2O_3$ (204 mg), NaOAc (204 mg) and *N*-methylquinolinium hexafluorophosphate (6.9 mg, 23.9 μmol). The mixture was photoirradiated with gentle air bubbling for 3 h while stirring at room temperature. The reaction mixture was filtered through a small plug of silica gel and the residue was washed with Et_2O (50 mL). The filtrate was concentrated and the resulting yellowish-green residue was dissolved in CH_2Cl_2 (2.0 mL). To this solution were added Et_3N (0.22 mL, 1.6 mmol), Ac_2O (57 μL, 0.6 mmol) and DMAP (2.4 mg, 20 μmol) sequentially. The mixture was stirred at room temperature for 3 h, then concentrated and purified by column chromatography (20% - 50% EtOAc in hexanes) to provide the cyclization products, which were further purified by column chromatography (4% - 10% EtOAc in CH_2Cl_2) to give *exo*-product **1.71** (14.6 mg, 30%, dr = 2:1) and *endo*-product **1.72** (10.6 mg, 22%, dr = 3.4:1) as colorless oils.

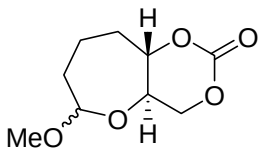
(*S*)-4-((*R*)-Tetrahydro-6-methoxy-2H-pyran-2-yl)-1,3-dioxolan-2-one (1.71)



^{1}H NMR (300 MHz, $CDCl_3$) δ 4.74 (app d, *J* = 2.5 Hz, 67% of 1H), 4.62-4.45 (m, 3H), 4.37 (dd, *J* = 9.3, 2.2 Hz, 33% of 1H), 3.96 (ddd, *J* = 11.8, 4.4, 1.9 Hz, 67% of 1H), 3.66 (ddd, *J* = 11.2, 5.6, 2.2 Hz, 33% of 1H), 3.46 (s, 33% of

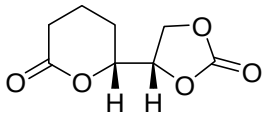
3H), 3.36 (s, 67% of 3H), 1.98-1.16 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.1 (major), 155.0 (minor), 103.4 (minor), 98.4 (major), 78.0 (major), 77.4 (minor), 75.3 (minor), 68.2 (major), 66.4 (minor), 66.1 (major), 56.4 (minor), 55.0 (major), 30.9 (minor), 29.5 (major), 26.6 (minor), 26.5 (major), 21.2 (minor), 17.2 (major); IR (neat) 2952, 2851, 1799, 1389, 1174, 1078, 1031 cm^{-1}; HRMS (EI): *m*/*z* calcd for $C_8H_{11}O_4$ ($M^{+\bullet}$) 171.0657, found 171.0650.

(4a*R*,9a*S*)-Hexahydro-6-methoxy-4*H*-[1,3]dioxino[5,4-*b*]oxepin-2-one (1.72)



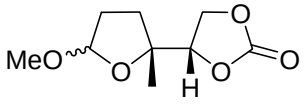
^{1}H NMR (300 MHz, $CDCl_3$) δ 4.74 (t, *J* = 4.2 Hz, 23% of 1H), 4.66 (dd, *J* = 8.6, 5.7 Hz, 77% of 1H), 4.42 (dd, *J* = 10.6, 5.8 Hz, 23% of 1H), 4.36-4.29 (m, 77% of 1H), 4.22-4.06 (m, 2.8H), 3.79 (dt, *J* = 9.7, 5.8 Hz, 23% of 1H), 3.42 (s, 23% of 3H), 3.36 (s, 77% of 3H), 2.37-2.14 (m, 3H), 1.96-1.93 (m, 23% of 1H), 1.77-1.42 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.5 (minor), 148.1 (major), 104.9 (minor), 102.8 (major), 81.2 (minor), 80.8 (major), 69.3 (major), 69.2 (minor), 68.2 (minor), 61.5 (major), 56.4 (minor), 55.8 (major), 35.5 (major), 34.2 (major), 33.5 (minor), 27.9 (minor), 17.7 (major), 16.6 (minor); IR (neat) 2943, 1760, 1403, 1382, 1224, 1140, 1057 cm^{-1}; HRMS (EI): *m*/*z* calcd for $C_8H_{11}O_4$ ($M^{+\bullet}$) 171.0657, found 171.0651; an analytical sample of the major diastereomer was obtained through purifying the above mixture by column chromatography (35% - 45% EtOAc in hexanes): ^{1}H NMR (300 MHz, C_6D_6) δ 4.02 (dd, *J* = 8.9, 5.8 Hz, 1H), 3.60 (dd, *J* = 10.1, 5.5 Hz, 1H), 3.42 (t, *J* = 10.2 Hz, 1H), 3.34-3.27 (m, 2H), 2.85 (s, 3H), 1.76-1.67 (m, 1H), 1.57-1.47 (m, 1H), 1.10 (dddd, *J* = 15.3, 11.6, 8.9, 1.0 Hz, 1H), 0.95-0.85 (m, 2H), 0.82-0.71 (m, 1H).

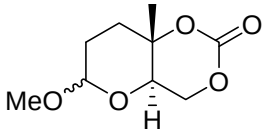
(*R*)-Tetrahydro-6-((*S*)-2-oxo-1,3-dioxolan-4-yl)pyran-2-one (1.73)

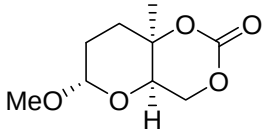


A solution of acetal **1.71** (6.0 mg, 29.7 μmol) in CH_2Cl_2 (0.6 mL) at 0 °C was treated with *m*CPBA (pure, 6.7 mg, 38.6 μmol) and BF_3•OEt_2 (4.5 μL, 35.6 μmol) sequentially. After stirred at 0 °C for 10 min and then at room temperature for 1.5 h, the mixture was cooled to 0 °C and Et_3N (20.7 μL, 148 μmol) was added dropwise. The mixture was stirred at 0 °C for 1 h, then concentrated, and the resulting residue was purified by column chromatography (15% - 25% EtOAc in CH_2Cl_2) to give the desired lactone **1.73** (4.6 mg, 83.6%) as a colorless liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.69-4.59 (m, 2H), 4.56-4.41 (m, 2H), 2.69 (dddd, *J* = 18.0, 6.8, 4.8, 1.1 Hz, 1H), 2.54 (ddd, *J* = 17.9, 9.3, 7.0 Hz, 1H), 2.24-2.16 (m, 1H), 2.08-1.90 (m, 2H), 1.64 (dtd, *J* = 13.8, 11.0, 5.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.3, 154.2, 79.0, 76.3, 66.9, 29.8, 24.6, 18.2; IR (neat) 2919, 1790, 1732, 1376, 1239, 1166, 1056 cm^{-1}; HRMS (EI): *m*/*z* calcd for $C_8H_{10}O_5$ ($M^{+\bullet}$) 186.0528, found 186.0536.

4-(Tetrahydro-5-methoxy-2-methylfuran-2-yl)-1,3-dioxolan-2-one (1.76), **Hexahydro-6-methoxy-8a-methylpyrano[3,2-d][1,3]dioxin-2-one (1.77)** and **(4a*R*,6*S*,8a*R*)-Hexahydro-6-methoxy-8a-methylpyrano[3,2-d][1,3]dioxin-2-one (1.78)**



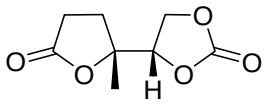




To *tert*-butyl carbonate **1.49** (125.2 mg, 0.294 mmol) in dichloroethane/toluene (11.3 mL, 5:1, v/v) in borosilicate flask at room temperature were added the activated 4Å molecular sieves (250 mg), anhydrous $Na_2S_2O_3$ (250 mg), NaOAc (250 mg) and *N*-methylquinolinium hexafluorophosphate (8.5 mg, 29.4 μmol). The mixture was photoirradiated with gentle air bubbling for 2.5 h while stirring at room temperature. The reaction mixture was filtered through a small plug of silica gel

and the residue was washed with EtOAc (30 mL). The filtrate was concentrated and the resulting residue was purified by flash chromatography (30% - 45% EtOAc in hexanes) to provide a mixture of **1.76** and **1.77** (19.7 mg, 33.2%, a pale yellow oil) with a molar ratio of 4.8:1 and *cis*-fused *endo*-product **1.78** (3.8 mg, 8.0%) as a white solid. For the mixture of **1.76** and **1.77**: IR (neat) 2928, 2835, 1791, 1755, 1463, 1375, 1170, 1084, 1034, 951 cm^{-1}. For *cis*-fused *endo*-product **1.78**: ^1H NMR (300 MHz, $CDCl_3$) δ 4.78 (app d, J = 2.0 Hz, 1H), 4.66 (dd, J = 12.1, 2.7 Hz, 1H), 4.34 (dd, J =12.1, 0.4 Hz, 1H), 3.86 (app d, J = 2.0 Hz, 1H), 3.41 (s, 3H), 2.12-2.00 (m, 1H), 1.94 (dd, J = 12.8, 4.0 Hz, 1H), 1.87-1.81 (m, 1H), 1.67-1.61 (m, 1H), 1.45 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.5, 98.3, 78.6, 69.3, 63.2, 55.4, 29.4, 25.3, 25.1; IR (neat) 2932, 1748, 1212, 1178, 1130, 1060, 1024 cm^{-1}; HRMS (EI): *m*/*z* calcd for $C_9H_{15}O_5$ $[M+H]^+$ 203.0919, found 203.0929.

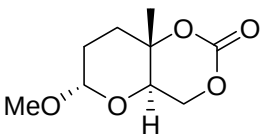
(*S*)-4-((*R*)-Tetrahydro-2-methyl-5-oxofuran-2-yl)-1,3-dioxolan-2-one (1.79)



To a solution of the mixture of **1.76** and **1.77** (18.9 mg, 93.5 μmol) in acetone (3.0 mL) at 0 °C was added Jones reagent (0.3 mL). The mixture was stirred at 0 °C for 15 min and then at room temperature for 3 h. After that time, the reaction was quenched with isopropyl alcohol (1 drop), concentrated and purified by column chromatography (2% - 20% EtOAc in CH_2Cl_2) to give the unreacted acetal **1.77** (2.9 mg, 15.3%) as a white solid and the title lactone **1.79** (11.0 mg, ~74.8% based on unreacted acetal): ^1H NMR (300 MHz, $CDCl_3$) δ 4.72 (dd, J = 8.4, 6.2 Hz, 1H), 4.57 (t, J = 9.0 Hz, 1H), 4.36 (dd, J = 9.2, 6.1 Hz, 1H), 2.70 (t. J = 8.8 Hz, 2H), 2.34-2.24 (m, 1H), 2.19-2.09 (m, 1H), 1.47 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.0, 154.1, 83.9, 78.7, 65.4, 30.0, 28.2, 20.8; IR (neat) 2920, 1789,

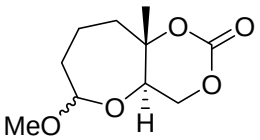
1463, 1267, 1167, 1082 cm^{-1}; HRMS (EI): *m*/*z* calcd for $C_8H_{11}O_5$ $[M+H]^+$ 187.0606, found 187.0612.

(4a*R*,6*S*,8a*S*)-Hexahydro-6-methoxy-8a-methylpyrano[3,2-d][1,3]dioxin-2-one (1.77)



^1H NMR (300 MHz, $CDCl_3$) δ 4.75-4.71 (app d, *J* = 2.4 Hz, 1H), 4.37 (dd, *J* = 8.0, 4.4 Hz, 1H), 4.18 (d, *J* = 8.2 Hz, 1H), 4.16 (d, *J* = 4.7 Hz, 1H), 3.38 (s, 3H), 2.13-2.04 (m, 1H), 1.95-1.76 (m, 3H), 1.50 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.1, 98.3, 77.5, 67.0, 62.7, 55.3, 31.1, 27.8, 17.5; IR (neat) 2917, 1757, 1464, 1196, 1111, 1068 cm^{-1}; HRMS (EI): *m*/*z* calcd for $C_9H_{15}O_5$ $[M+H]^+$ 203.0919, found 203.0930.

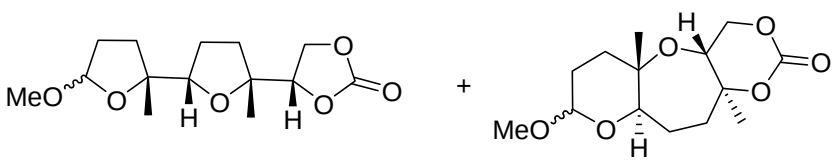
(4a*R*,9a*S*)-Hexahydro-6-methoxy-9a-methyl-4*H*-[1,3]dioxino[5,4-b]oxepin-2-one (1.81)



To *tert*-butyl carbonate **1.50** (65.8 mg, 149 μmol) in dichloroethane/toluene (5.7 mL, 5:1, v/v) in borosilicate flask at room temperature were added the activated 4Å molecular sieves (132 mg), anhydrous $Na_2S_2O_3$ (132 mg), NaOAc (132 mg) and *N*-methylquinolinium hexafluorophosphate (4.3 mg, 14.9 μmol). The mixture was photoirradiated with gentle air bubbling for 2 h while stirring at room temperature. The reaction mixture was filtered through a small plug of silica gel and the residue was washed with EtOAc (20 mL). The filtrate was concentrated and the resulting residue was purified by flash chromatography (5% - 15% EtOAc in CH_2Cl_2) to provide the desired compound **1.81** (23.7 mg, 73.4%) as a mixture of two diastereomers in a 1.2:1 ratio: ^1H NMR (300 MHz, $CDCl_3$) δ 4.76 (t, *J* = 3.8 Hz, 46% of 1H), 4.66 (dd, *J* = 8.8, 5.8 Hz, 54% of 1H), 4.34 (dd, *J* = 10.8, 6.4 Hz, 46% of 1H), 4.29-4.18 (m, 54% of 2H), 4.19 (t, *J* = 10.8 Hz, 46% of 1H), 3.88 (dd, *J* = 10.6, 6.4 Hz, 46% of 1H), 3.42 (s, 46% of 3H), 3.35 (s, 54% of 3H),

2.23-2.01 (m, ~1.5H), 1.96-1.92 (m, 46% of 1H), 1.75-1.58 (m, ~3.5H), 1.51 (s, 46% of 3H), 1.48 (s, 54% of 3H), 1.45-1.35 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.2, 148.0, 104.3, 102.8, 84.2, 83.0, 68.1, 66. 7, 66.3, 62.7, 56.3, 55.7, 43.2, 41.6, 34.5, 34.4, 19.5, 19.3, 18.3, 16.7; IR (neat) 2941, 1755, 1464, 1384, 1252, 1199, 1128, 1091, 1050, 969 cm^{-1}; HRMS (EI): *m*/*z* calcd for $C_9H_{13}O_4Na$ $(M\text{-}CH_3O)^{+\bullet}$ 185.0814, found 185.0811. An analytical sample of the slightly major diastereomer was obtained through purifying the above mixture by column chromatography (35% - 40% EtOAc in hexanes): ^{1}H NMR (300 MHz, C_6D_6) δ 4.00 (dd, *J* = 8.8, 5.9 Hz, 1H), 3.60 (d, *J* = 10.4 Hz, 1H), 3.58 (d, *J* = 6.8 Hz, 1H), 3.44 (dd, *J* = 10.4, 6.8 Hz, 1H), 2.85 (s, 3H), 1.56-1.48 (m, 2H), 1.19-1.10 (m, 2H), 0.98-0.88 (m, 1H), 0.94 (s, 3H), 0.75-0.66 (m, 1H).

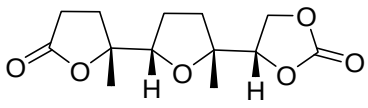
(*S*)-4-((2*R*,5*S*)-Tetrahydro-5-((*R*)-tetrahydro-5-methoxy-2-methylfuran-2-yl)-2-methylfuran-2-yl)-1,3-dioxolan-2-one (1.85) and **(4a*R*,5a*S*,9a*R*,11a*S*)-8-Methoxy-5a,11a-dimethyldecahydro-1,3,5,9-tetraoxadibenzo[a,d]cyclohepten-2-one (1.86)**



To diepoxide **1.51** (129.1 mg, 0.253 mmol) in dichloroethane/toluene (9.7 mL, 5:1, v/v) in borosilicate flask at room temperature were added the activated 4Å molecular sieves (258 mg), anhydrous $Na_2S_2O_3$ (258 mg), NaOAc (258 mg) and *N*-methylquinolinium hexafluorophosphate (7.3 mg, 25.3 μmol). The mixture was photoirradiated with gentle air bubbling for 4.5 h while stirring at room temperature. The reaction mixture was filtered through a small plug of silica gel and the residue was washed with EtOAc (40 mL). The filtrate was concentrated and the resulting residue was purified by flash chromatography (35% - 50% EtOAc

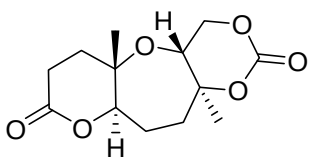
in hexanes) to provide a mixture of the above two products (28.7 mg, 39.6%) as a colorless oil: IR (neat) 2926, 1796, 1754, 1460, 1374, 1166, 1085, 1036, 1006, 952 cm^{-1}.

(*S*)-4-((2*R*,5*S*)-Tetrahydro-5-((*R*)-tetrahydro-2-methyl-5-oxofuran-2-yl)-2-methylfuran-2-yl)-1,3-dioxolan-2-one (A33)



A mixture of acetals **1.85** and **1.86** (20.8 mg, 72.6 μmol) in acetone (2.1 mL) at 0 °C was treated dropwise with Jones reagent (0.2 mL). The mixture was stirred at 0 °C for 10 min, then at room temperature for 1.5 h and purified without workup by column chromatography (50% - 90% EtOAc in hexanes) to give the unreacted acetal **1.86** (3.2 mg, 15.4%, nearly pure) and lactone **A33** (13.8 mg, ~80%). For lactone **A33**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.60 (dd, *J* = 8.4, 6.2 Hz, 1H), 4.50 (t, *J* = 8.6 Hz, 1H), 4.38 (dd, *J* = 8.7, 6.2 Hz, 1H), 4.08 (dd, *J* = 8.6, 6.3 Hz, 1H), 2.64-2.58 (m, 2H), 2.31-2.19 (m, 1H), 2.10-2.04 (m, 2H), 1.94-1.73 (m, 3H), 1.39 (s, 3H), 1.27 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.7, 155.1, 86.9, 83.5, 83.2, 79.5, 66.0, 34.1, 29.3, 29.2, 26.7, 23.8, 21.0; IR (neat) 2958, 2924, 2853, 1790, 1770, 1456, 1382, 1248, 1166, 1085, 1020, 944, 770, 728 cm^{-1}; HRMS (EI): *m*/*z* calcd for $C_{13}H_{18}O_6$ ($M^{+\bullet}$) 270.1103, found 270.1094; $[\alpha]_D$ = +4.5 ($CHCl_3$, *c* 0.24).

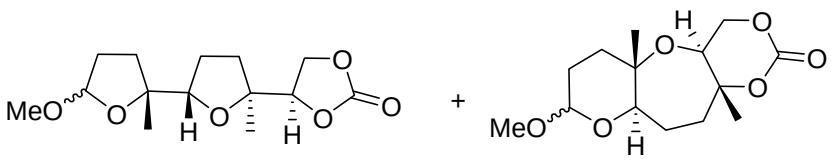
(4a*R*,5a*S*,9a*R*,11a*S*)-5a,11a-Dimethyloctahydro-1,3,5,9-tetraoxadibenzo[a,d]cycloheptene-2,8-dione (A34)



A solution of acetal **1.86** (2.9 mg, 11.2 μmol) in CH_2Cl_2 (0.5 mL) at 0 °C was treated with *m*CPBA (pure, 2.5 mg, 14.6 μmol) and BF_3•OEt_2 (1.9 μL, 13.4 μmol) sequentially. After stirred at 0 °C for 10 min and then at room temperature for 30 min, the mixture was cooled to 0 °C and Et_3N (7.8 μL, 56.0

μmol) was added dropwise. The mixture was stirred at 0 °C for 30 min, and purified by column chromatography (10% - 20% EtOAc in CH_2Cl_2) to give the desired lactone **A34** (1.8 mg, 66.7%) as colorless needles: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.28 (dd, *J* = 8.6, 5.1 Hz, 1H), 4.21-4.14 (m, 1H), 4.09 (dd, *J* = 10.1, 8.6 Hz, 1H), 4.06 (dd, *J* = 11.0, 2.9 Hz, 1H), 2.80 (ddd, *J* = 18.3, 9.4, 5.5 Hz, 1H), 2.64 (ddd, *J* = 18.3, 8.7, 7.4 Hz, 1H), 2.35-2.28 (m, 1H), 2.17-1.88 (m, 5H), 1.50 (s, 3H), 1.38 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.4, 148.2, 83.1, 82.7, 77.4, 75.7, 66.5, 65.2, 37.2, 34.3, 27.5, 24.8, 22.4, 16.0; IR (neat) 2923, 1747, 1463, 1408, 1229, 1124, 1068 cm^{-1}; ^{1}H NMR (300 MHz, C_6D_6) δ 3.44 (d, *J* = 7.7 Hz, 1H), 3.43 (d, *J* = 9.6 Hz, 1H), 3.18 (dd, *J* = 9.6, 7.7 Hz, 1H), 2.93 (dd, *J* = 10.9, 3.0 Hz, 1H), 2.02-1.97 (m, 2H), 1.65 (td, *J* = 15.3, 4.8 Hz, 1H), 1.43-1.26 (m, 3H), 1.17-1.04 (m, 2H), 0.81 (s, 3H), 0.48 (s, 3H); HRMS (ESI): *m*/*z* calcd for $C_{13}H_{18}O_6Na$ $[M+Na]^+$ 293.1001, found 293.1020; $[\alpha]_D$ = +101 ($CHCl_3$, *c* 0.15).

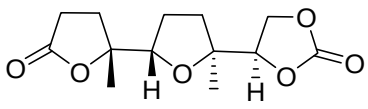
(*R*)-4-((2*S*,5*S*)-tetrahydro-5-((*R*)-tetrahydro-5-methoxy-2-methylfuran-2-yl)-2-methylfuran-2-yl)-1,3-dioxolan-2-one (1.87) and **(4a*S*,5a*S*,9a*R*,11a*R*)-8-Methoxy-5a,11a-dimethyldecahydro-1,3,5,9-tetraoxadibenzo[a,d]cyclohepten-2-one (1.88)**



To diepoxide **1.52** (150 mg, 0.294 mmol) in dichloroethane/toluene (11.3 mL, 5:1, v/v) in borosilicate flask at room temperature were added the activated 4Å molecular sieves (300 mg), anhydrous $Na_2S_2O_3$ (300 mg), NaOAc (300 mg) and *N*-methylquinolinium hexafluorophosphate (8.5 mg, 29.4 μmol). The mixture was photoirradiated with gentle air bubbling for 4.5 h while stirring at room temperature. The reaction mixture was filtered through a small plug of silica gel and the residue was washed with EtOAc (40 mL). The filtrate was

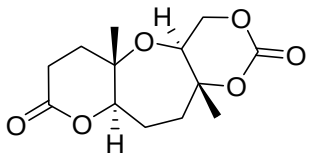
concentrated and the resulting residue was purified by flash chromatography (35% - 50% EtOAc in hexanes) to provide a mixture of the above two products (51.2 mg, 60.9%): IR (neat) 2925, 1797, 1750, 1462, 1384, 1259, 1167, 1120 cm^{-1}.

(*R*)-4-((2*S*,5*S*)-tetrahydro-5-((*R*)-tetrahydro-2-methyl-5-oxofuran-2-yl)-2-methylfuran-2-yl)-1,3-dioxolan-2-one (A35)



A mixture of acetals **1.87** and **1.88** (34.9 mg, 122 μmol) in acetone (1.8 mL) at 0 °C was treated dropwise with Jones reagent (0.3 mL). The mixture was stirred at 0 °C for10 min, then at room temperature for 1.5 h and purified without workup by column chromatography (50% - 90% EtOAc in hexanes) to give the unreacted acetal **1.88** (4.9 mg, nearly pure) and lactone **A35** (22.1 mg, ~81%). For lactone **A35**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.58 (dd, *J* = 8.3, 6.1 Hz, 1H), 4.48 (t, *J* = 8.4 Hz, 1H), 4.32 (dd, *J* = 8.8, 6.1 Hz, 1H), 4.08 (dd, *J* = 8.8, 5.6 Hz, 1H), 2.65-2.59 (m, 2H), 2.24 (ddd, *J* = 12.9, 9.6, 6.9 Hz, 1H), 2.07-1.81 (m, 5H), 1.38 (s, 3H), 1.27 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.7, 155.0, 86.9, 85.1, 83.1, 80.3, 66.2, 34.5, 29.4, 29.1, 27.0, 23.4, 21.3; IR (neat) 2979, 2880, 1790, 1767, 1454, 1382, 1170, 1111, 1085, 944 cm^{-1}; HRMS (EI): *m*/*z* calcd for $C_{13}H_{18}O_6$ ($M^{+\bullet}$) 270.1103, found 270.1095; $[\alpha]_D$ = -11.3 ($CHCl_3$, *c* 1.03).

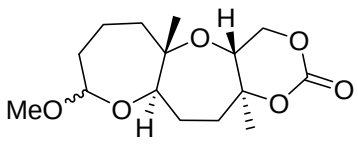
(4a*S*,5a*S*,9a*R*,11a*R*)-5a,11a-Dimethyloctahydro-1,3,5,9-tetraoxadibenzo[a,d]cycloheptene-2,8-dione (A36)



A solution of acetal **1.88** (4.5 mg, 15.7 μmol) in CH_2Cl_2 (0.5 mL) at 0 °C was treated with *m*CPBA (pure, 3.5 mg, 20.4 μmol) and BF_3•OEt_2 (2.7 μL, 18.8 μmol) sequentially. After stirred at 0 °C for 10 min and

at room temperature for 20 min, the mixture was cooled to 0 °C and Et_3N (10.9 μL, 78.5 μmol) was added dropwise. The mixture was stirred at 0 °C for 30 min and purified by column chromatography (15% - 25% EtOAc in CH_2Cl_2) to give the desired lactone **A36** (3.0 mg, 71.4%) as colorless needles: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.40 (app dd, *J* = 10.0, 2.2 Hz, 1H), 4.23 (dd, *J* = 10.5, 6.1 Hz, 1H), 4.09 (t, *J* = 10.2, Hz, 1H), 4.00 (dd, *J* = 10.1, 6.1 Hz, 1H), 2.88 (ddd, *J* = 18.3, 11.2, 4.7 Hz, 1H), 2.72 (ddd, *J* = 18.3, 9.6, 5.5 Hz, 1H); 2.21-1.76 (m, 6H), 1.49 (s, 3H), 1.24 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.7, 147.4, 83.8, 81.4, 77.4, 66.6, 64.9, 39.1, 30.8, 28.1, 24.4, 20.5, 19.5; IR (neat) 2924, 1748, 1463, 1408, 1229, 1124, 1068 cm^{-1}; HRMS (ESI): *m*/*z* calcd for $C_{13}H_{18}O_6Na$ $[M+Na]^+$ 293.1001, found 293.0988; $[\alpha]_D$ = +48.7 ($CHCl_3$, *c* 0.23).

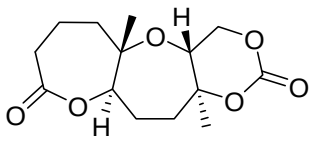
(4a*R*,5a*S*,10a*R*,12a*S*)-9-Methoxy-5a,12a-dimethyldecahydro-1,3,5,10-tetraoxabenzo[b]-heptalen-2-one (1.91)



To diepoxide **1.53** (145 mg, 276 μmol) in dichloroethane/toluene (10.6 mL, 5:1, v/v) in borosilicate flask at room temperature were added the activated 4Å molecular sieves (290 mg), anhydrous $Na_2S_2O_3$ (290 mg), NaOAc (290 mg) and *N*-methylquinolinium hexafluorophosphate (8.0 mg, 27.6 μmol). The mixture was photoirradiated with gentle air bubbling for 2 h while stirring at room temperature. The reaction mixture was filtered through a small plug of silica gel and the residue was washed with EtOAc (40 mL). The filtrate was concentrated and the resulting residue was purified by flash chromatography (25% - 35% EtOAc in hexanes) to provide the product **1.91** (44.8 mg, 54.0%, pale yellow liquid) as two diastereomers in about 1:1 ratio: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.54-4.48 (m, 1H), 4.25-3.98 (m, 3H), 3.92-3.85 (m, 0.5H), 3.56 (dd, *J* = 11.2, 2.4 Hz, 0.5H), 3.40/3.37 (s, 3H), 3.24 (dd, *J* = 10.8, 3.8 Hz, 0.5H), 2.26-1.94 (m, 2.5H), 1.91-

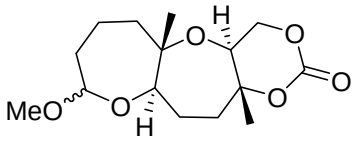
1.72 (m, 3.5H), 1.65-1.52 (m, 3.5H), 1.47/1.44 (s, 3H), 1.33/1.29 (s, 3H), 1.21-1.18 (m, 0.5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.0, 148.6, 105.2, 102.6, 83.3, 83.2, 81.4, 80.3, 79.7, 75.6, 67.0, 67.0, 65.2, 63.8, 56.1, 55.9, 44.6, 43.3, 37.5, 37.0, 35.3, 33.6, 27.6, 26.2, 22.3, 21.6, 19.2, 17.7, 17.0, 16.7; IR (neat) 2940, 1759, 1454, 1384, 1209, 1111, 1053, 1008, 921 cm^{-1}; HRMS (ESI): *m*/*z* calcd for $C_{15}H_{24}O_6Na$ $[M+Na]^+$ 323.1471, found 323.1500; $[\alpha]_D$ = +31.5 ($CHCl_3$, *c* 1.45).

(4a*R*,5a*S*,10a*R*,12a*S*)-5a,12a-Dimethyldecahydro-1,3,5,10-tetraoxabenzo[b]heptalene-2,9-dione (1.92)



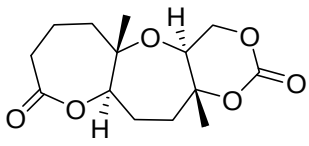
A solution of acetal **1.91** (15.6 mg, 51.9 μmol) in CH_2Cl_2 (0.5 mL) at 0 °C was treated with *m*CPBA (pure, 11.6 mg, 67.5 μmol) and BF_3•OEt_2 (7.2 μL, 57.1 μmol) sequentially. After stirred at 0 °C for 10 min, then at room temperature for 1 h, the mixture was cooled to 0 °C and Et_3N (36.2 μL, 256 μmol) was added dropwise. The mixture was stirred at 0 °C for 1.5 h, the quenched with a mixture of saturated $NaHCO_3$/saturated $Na_2S_2O_3$ (4 mL, 1:1, v/v). The mixture was poured onto water (5 mL) and extracted with Et_2O (3 x 25 mL). The extracts were dried over $MgSO_4$, filtered and concentrated, and the resulting residue was purified by column chromatography (10% - 20% EtOAc in CH_2Cl_2) to give the desired lactone **1.92** (9.9 mg, 66.9%) as a white crystalline solid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.26-4.20 (m, 2H), 4.14-4.06 (m, 2H), 2.70-2.55 (m, 2H), 2.35-2.23 (m, 2H), 1.99-1.81 (m, 4H), 1.77-1.68 (m, 2H), 1.46 (s, 3H), 1.31 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.3, 148.6, 84.3, 82.2, 78.9, 66.8, 64.3, 43.2, 36.2, 33.6, 26.6, 22.0, 20.0, 15.8; IR (neat) 2989, 2941, 2871, 1748, 1727, 1501, 1454, 1365, 1328, 1272, 1212, 1098, 1040 cm^{-1}; HRMS (ESI): *m*/*z* calcd for $C_{14}H_{20}O_6Na$ $[M+Na]^+$ 307.1158, found 307.1158. $[\alpha]_D$ = +50.4 ($CHCl_3$, *c* 0.42).

(4a*S*,5a*S*,10a*R*,12a*R*)-9-Methoxy-5a,12a-dimethyldecahydro-1,3,5,10-tetraoxabenzo[b]-heptalen-2-one (1.93)



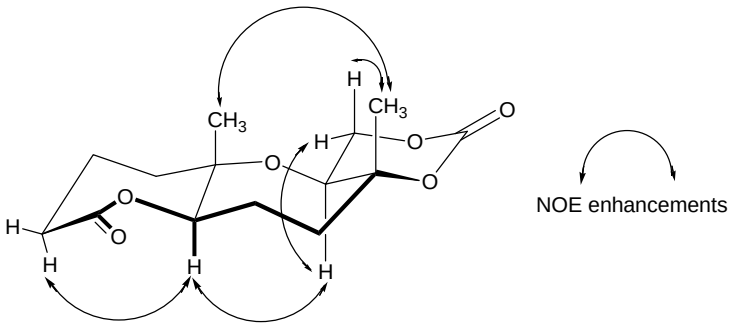
To diepoxide **1.54** (48.2 mg, 91.9 μmol) in dichloroethane/toluene (3.5 mL, 5:1, v/v) in borosilicate flask at room temperature were added the activated 4Å molecular sieves (96 mg), anhydrous $Na_2S_2O_3$ (96 mg), NaOAc (96 mg) and *N*-methylquinolinium hexafluorophosphate (2.6 mg, 9.2 μmol). The mixture was photoirradiated with gentle air bubbling for 3 h while stirring at room temperature. The reaction mixture was filtered through a small plug of silica gel and the residue was washed with EtOAc (30 mL). The filtrate was concentrated and the resulting residue was purified by flash chromatography (25% - 35% EtOAc in hexanes) to provide the product **1.93** (21.7 mg, 78.6%, pale yellow solid) as two diastereomers in about 1:1 ratio: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.69 (dd, *J* = 3.8, 2.2 Hz, 0.5H), 4.54 (dd, *J* = 8.9, 5.7 Hz, 0.5H), 4.17 (dd, *J* = 10.7, 6.6 Hz, 1H), 4.02 (t, *J* = 10.7 Hz, 1H), 3.90 (dd, *J* = 10.7, 6.6 Hz, 1H), 3.90-3.85 (m, 0.5H), 3.52 (dd, *J* = 10.1, 0.8 Hz, 0.5H), 3.40/3.37 (s, 3H), 2.08-2.00 (m, 2H), 1.89-1.53 (m, 8H), 1.44 (s, 3H), 1.21/1.17 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.6, 148.0, 102.7, 102.4, 83.6, 83.6, 81.3, 80.6, 78.8, 74.1, 67.0 (2C), 64.0, 63.9, 56.0, 55.8, 40.5, 40.2, 39.8, 39.5, 33.7, 33.4, 27.3 (2C), 20.8, 20.3, 19.4, 19.3, 19.3, 17.5; IR (neat) 2940, 1755, 1461, 1382, 1246, 1223, 1116, 1051, 913 cm^{-1}; HRMS (ESI): *m*/*z* calcd for $C_{15}H_{24}O_6Na$ $[M+Na]^+$ 323.1471, found 323.1462; $[\alpha]_D$ = +26.6 ($CHCl_3$, *c* 0.55).

(4a*S*,5a*S*,10a*R*,12a*R*)-5a,12a-Dimethyldecahydro-1,3,5,10-tetraoxabenzo[b]heptalene-2,9-dione (1.94)

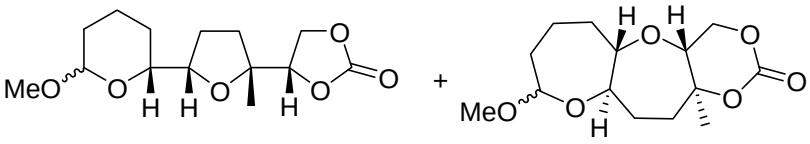


A solution of acetal **1.93** (19.0 mg, 63.2 μmol) in CH_2Cl_2 (2.0 mL) at 0 °C was treated with *m*CPBA (pure, 14.2 mg, 82.2 μmol) and BF_3•OEt_2 (9.5 μL, 75.8 μmol) sequentially. The mixture was stirred at 0 °C for 10 min, and then at room temperature for 1 h. After that time, the mixture was cooled to 0 °C and Et_3N (44.0 μL, 316 μmol) was added dropwise. The mixture was stirred at 0 °C for 30 min, then concentrated, and the resulting residue was purified by column chromatography (15% - 25% EtOAc in CH_2Cl_2) to give the desired lactone **1.94** (14.4 mg, 80.0%) as a white solid: ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.47 (dd, *J* = 10.4 Hz, 1H), 4.20 (dd, *J* = 10.7, 6.4 Hz, 1H), 4.05 (t, *J* = 10.7 Hz, 1H), 3.98 (dd, *J* = 10.5, 6.4 Hz, 1H), 2.70 (dt, *J* = 14.1, 2.2 Hz, 1H), 2.64 (ddd, *J* = 14.1, 5.8, 1.3 Hz, 1H), 2.12 (ddd, *J* = 13.6, 5.9, 2.0 Hz, 1H), 2.07-1.98 (m, 3H), 1.90 (dddd, *J* = 14.7, 5.8, 2.6, 1.0 Hz, 1H), 1.84 (app dt, *J* = 13.6, 1.7 Hz, 1H), 1.78-1.70 (m, 2H), 1.48 (s, 3H), 1.14 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.4, 147.8, 83.6, 82.7, 79.0, 66.8, 64.6, 39.3, 38.3, 33.4, 26.4, 20.4, 19.14, 19.10; IR (neat) 2984, 2941, 1747, 1732, 1444, 1388, 1274, 1252, 1200, 1116, 1100, 1070, 1049 cm^{-1}; HRMS (EI): *m*/*z* calcd for $C_{14}H_{20}O_6$ ($M^{+\bullet}$) 284.1260, found 284.1254; $[\alpha]_D$ = +17.2 ($CHCl_3$, *c* 0.52).

Key NOESY enhancements observed in lactone **1.94**:



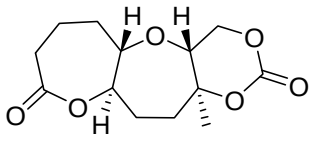
(*S*)-4-((2*R*,5*S*)-tetrahydro-5-((*R*)-tetrahydro-6-methoxy-2*H*-pyran-2-yl)-2-methylfuran-2-yl)-1,3-dioxolan-2-one (1.97) and **(4a*R*,5a*S*,10a*R*,12a*S*)-9-Methoxy-12a-methyldecahydro-1,3,5,10-tetraoxabenzo[b]heptalen-2-one (1.98)**



To diepoxide **1.55** (52.8 mg, 103 μmol) in dichloroethane/toluene (4.0 mL, 5:1, v/v) in borosilicate flask at room temperature were added the activated 4Å molecular sieves (106 mg), anhydrous $Na_2S_2O_3$ (106 mg,), NaOAc (106 mg) and *N*-methylquinolinium hexafluorophosphate (3.0 mg, 10.3 μmol). The mixture was photoirradiated with gentle air bubbling for 4 h while stirring at room temperature. The reaction mixture was filtered through a small plug of silica gel and the residue was washed with EtOAc (20 mL). The filtrate was concentrated and the resulting residue was purified by flash chromatography (5% - 20% EtOAc in CH_2Cl_2) to provide the *exo*, *exo*-product **1.97** (7.3 mg, 24.7%) as a white solid and *endo*, *endo*-product **1.98** (8.8 mg, 29.7%) as a colorless oil. For *exo*, *exo*-product **1.97** (dr = 2:1): ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.71 (br s, 67% of 1H), 4.61-4.56 (m, 1H), 4.54-4.50 (m, 1H), 4.44-4.41 (m, 1H), 4.32 (dd, *J* = 9.5, 2.0 Hz, 33% of 1H), 4.02 (dd, *J* = 7.1, 4.9 Hz, 33% of 1H), 3.98 (dd, *J* = 7.4, 4.4 Hz, 67% of 1H), 3.72 (ddd, *J* = 11.6, 4.2, 2.0 Hz, 67% of 1H), 3.48 (s, 33% of 3H), 3.40 (ddd, *J* = 11.3, 4.7, 1.9 Hz, 33% of 1H), 3.33 (s, 67% of 3H), 2.05-1.95 (m, 4H), 1.90-1.78 (m, 3H), 1.73-1.65 (m, 1H), 1.60 (s, 3H), 1.55-1.48 (m, 1H), 1.31-1.22 (m, 1H), 1.28 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.3 (major), 151.1 (minor), 103.7 (minor), 98.7 (major), 82.2 (major, 2C), 81.9 (minor), 79.6 (minor), 79.2 (major), 69.7 (major), 66.0 (major), 56.3 (minor), 54.7 (major), 35.1 (major), 34.7 (minor), 31.3 (minor), 29.9 (major), 27.6 (minor), 27.3 (major), 26.7

(minor), 26.3 (major), 22.0 (minor), 20.9 (minor), 20.5 (major), 17.8 (major); IR (neat) 2943, 1798, 1455, 1374, 1166, 1033, 949 cm^{-1}; HRMS (EI): *m*/*z* calcd for $C_{14}H_{22}O_6$ ($M^{+\bullet}$) 286.1416, found 286.1419; $[\alpha]_D$ = -24.1 ($CHCl_3$, *c* 0.71). For *endo*, *endo*-product **1.98** (dr = 2.3:1): ^1H NMR (600 MHz, $CDCl_3$) δ 4.56 (dd, *J* = 8.8, 5.8 Hz, 70% of 1H), 4.49-4.46 (m, 30% of 1H), 4.39-4.34 (m, 1H), 4.11 (t, *J* = 10.6 Hz, 70% of 1H), 4.10 (t, *J* = 10.6 Hz, 30% of 1H), 3.94 (dd, *J* = 11.3, 6.5 Hz, 70% of 1H), 3.84 (dd, *J* = 11.0, 6.3 Hz, 30% of 1H), 3.68 (dt, *J* = 8.5, 4.5 Hz, 70% of 1H), 3.62-3.59 (m, 30% of 1H), 3.49-3.47 (m, 30% of 1H), 3.42 (s, 30% of 3H), 3.38 (s, 70% of 3H), 3.37-3.33 (70% of 1H), 2.22-1.97 (m, 4H), 1.92-1.78 (m, 2H), 1.65-1.59 (m, 2H), 1.46 (s, 30% of 3H), 1.43 (s, 70% of 3H), 1.38-1.33 (m, 1H), 1.28-1.25 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.0 (minor), 148.9 (major), 106.9 (minor), 102.6 (major), 86.4 (major), 83.3 (minor), 82.6 (minor), 82.4 (major), 79.5 (minor), 75.2 (minor), 74.0 (major), 73.2 (minor), 73.1 (major), 66.5 (major), 56.1 (minor), 55.9 (major), 39.5 (minor), 36.7 (major), 35.9 (minor), 35.6 (major), 34.9 (minor), 33.5 (major), 29.7 (major), 28.6 (minor), 28.0 (minor), 21.0 (major), 18.9 (major),17.9 (minor); IR (neat) 2939, 1755, 1455, 1384, 1255, 1205, 1109, 1042, 999 cm^{-1}; HRMS (EI): *m*/*z* calcd for $C_{14}H_{22}O_6$ ($M^{+\bullet}$) 286.1416, found 286.1414; $[\alpha]_D$ = +11.8 ($CHCl_3$, *c* 0.85).

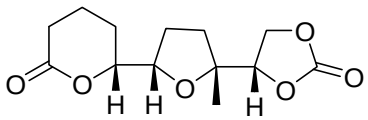
(4a*R*,5a*S*,10a*R*,12a*S*)-12a-Methyldecahydro-1,3,5,10-tetraoxa-benzo[b]heptalene-2,9-dione (1.99)



To a solution of acetal **1.98** (8.0 mg, 27.9 μmol) in CH_2Cl_2 (0.5 mL) at 0 °C were added *m*CPBA (pure, 6.2 mg, 36.3 μmol) and BF_3•OEt_2 (4.2 μL, 33.5 μmol) sequentially. After stirred at room temperature for 30 min, the mixture was cooled to 0 °C and Et_3N (19.4 μL, 140 μmol) was added dropwise. The

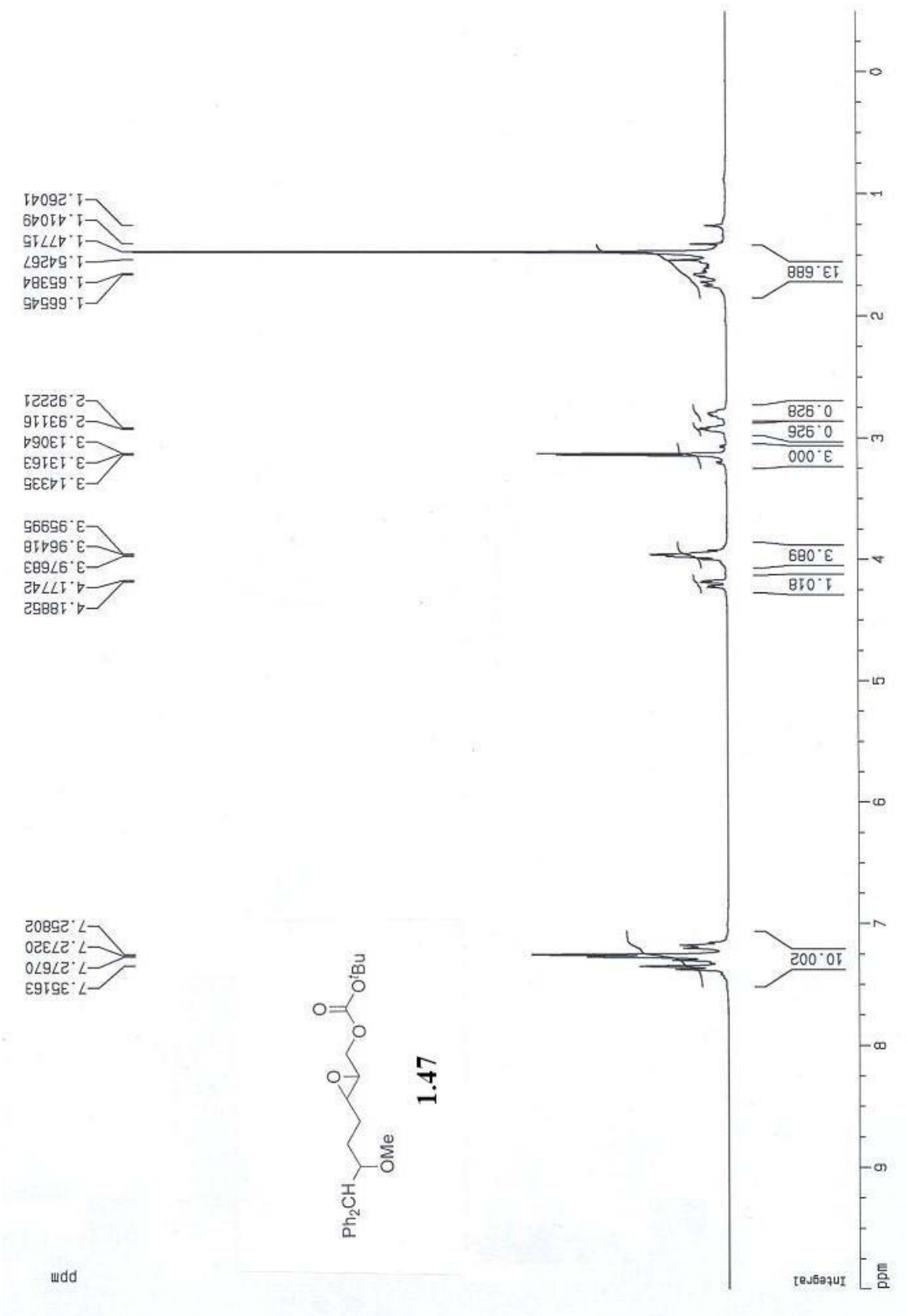
mixture was stirred at 0 °C for 30 min, then concentrated, and the resulting residue was purified by column chromatography (10% - 20% EtOAc in CH_2Cl_2) to give lactone **1.99** (5.3 mg, 70.2%) as a white crystalline solid: ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.43-4.39 (m, 1H), 4.40 (dd, *J* = 10.4, 6.5 Hz, 1H), 4.13 (dd, *J* = 11.2, 10.5 Hz, 1H), 3.86 (dd, *J* = 11.3, 6.5 Hz, 1H), 3.53 (ddd, *J* = 10.6, 8.0, 3.4 Hz, 1H), 2.70-2.61 (m, 2H), 2.22-2.17 (m, 3H), 2.07-2.01 (m, 2H), 1.92 (ddd, *J* = 15.4, 9.6, 2.2 Hz, 1H),1.77-1.73 (m, 2H), 1.48 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.9, 148.2, 85.5, 81.9, 81.2, 78.4, 66.5, 35.7, 34.5, 33.6, 27.5, 21.0, 19.2; ^{1}H NMR (500 MHz, C_6D_6) δ 3.58 (dd, *J* = 10.0, 6.6 Hz, 1H), 3.46 (dd, *J* = 11.2, 10.2 Hz, 1H), 3.38-3.34 (m, 1H), 2.66 (dd, *J* = 11.2, 6.6 Hz, 1H), 2.58 (ddd, *J* = 11.2, 7.8, 3.3 Hz, 1H), 2.22-2.18 (m, 1H), 1.73-1.65 (m, 2H), 1.52 (dddd, *J* = 15.8, 8.8, 3.8, 1.4 Hz, 1H), 1.42-1.38 (m, 1H), 1.30 (ddd, *J* = 14.4, 8.8, 1.4 Hz, 1H), 1.22 (dddd, *J* = 17.1, 11.6, 5.2, 1.5 Hz, 1H), 1.16-1.11 (m, 2H), 0.92-0.84 (m, 1H), 0.80 (s, 3H); IR (neat) 2922, 2850, 1747, 1453, 1387, 1273, 1204, 1106, 1058, 1015 cm^{-1}; HRMS (EI): *m*/*z* calcd for $C_{13}H_{18}O_6$ ($M^{+\bullet}$) 270.1103, found 270.1111; $[\alpha]_D$ = +12.7 ($CHCl_3$, *c* 0.26).

(*R*)-Tetrahydro-6-((2*S*,5*R*)-tetrahydro-5-methyl-5-((*S*)-2-oxo-1,3-dioxolan-4-yl)furan-2-yl)-pyran-2-one (A37)



To a solution of acetal **1.97** (6.8 mg, 23.7 μmol) in CH_2Cl_2 (0.5 mL) at 0 °C were added *m*CPBA acid (pure, 5.3 mg, 30.8 μmol) and BF_3•OEt_2 (4.0 μL, 28.4 μmol) sequentially. After stirred at room temperature for 30 min, the mixture was cooled to 0 °C and Et_3N (16.5 μL, 118 μmol) was added dropwise. The mixture was stirred at 0 °C for 30 min, then concentrated, and the resulting residue was purified by column chromatography (15% - 25% EtOAc in CH_2Cl_2) to give the desired lactone **A37** (5.2 mg, 81.2%) as a white solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.64 (dd, *J* = 8.4, 6.0 Hz, 1H), 4.52 (t, *J* = 8.8

Hz, 1H), 4.45 (dd, *J* = 8.8, 6.0 Hz, 1H), 4.30 (dd, *J* = 11.4, 4.6, 3.0 Hz, 1H), 4.10 (dt, *J* = 7.2, 4.6 Hz, 1H), 2.62 (dddd, *J* = 17.8, 6.6, 4.8, 1.4 Hz, 1H), 2.46 (ddd, *J* = 17.8, 9.3, 7.0 Hz, 1H), 2.19-2.12 (m, 1H), 2.07-2.02 (m, 1H), 2.01-1.93 (m, 3H), 1.90-1.85 (m, 1H), 1.84-1.79 (m, 1H), 1.50-1.44 (m, 1H), 1.28 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ171.1, 155.2, 83.0, 81.1, 80.7, 79.0, 66.1, 34.5, 29.9, 26.4, 24.8, 20.7, 18.5; IR (neat) 2957, 2929, 1789, 1731, 1242, 1173, 1084, 1049, 1018, 771 cm^{-1}; HRMS (EI): *m*/*z* calcd for $C_{13}H_{18}O_6$ ($M^{+\bullet}$) 270.1103, found 270.1104; $[\alpha]_D$ = -42.8 ($CHCl_3$, *c* 0.50).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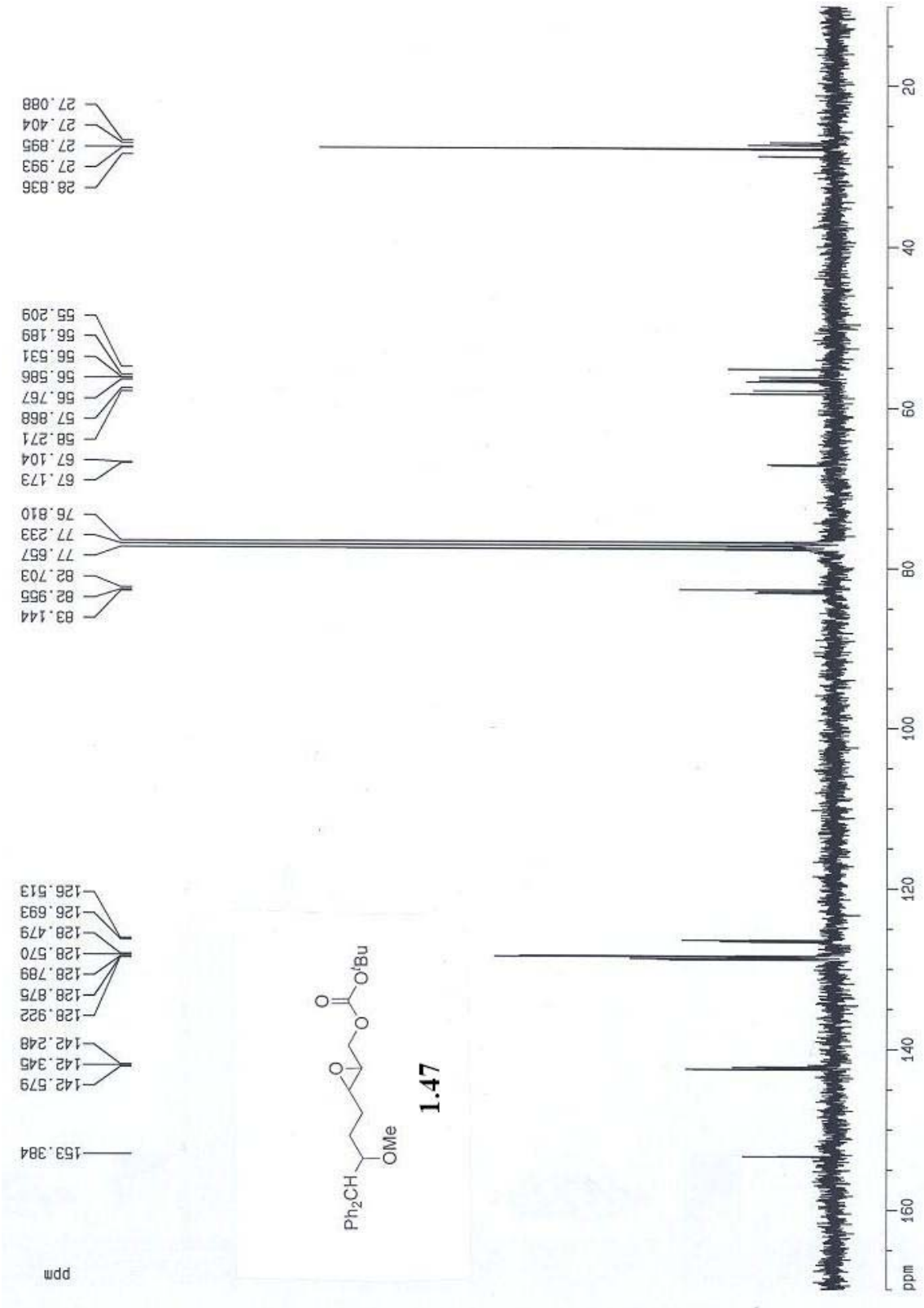
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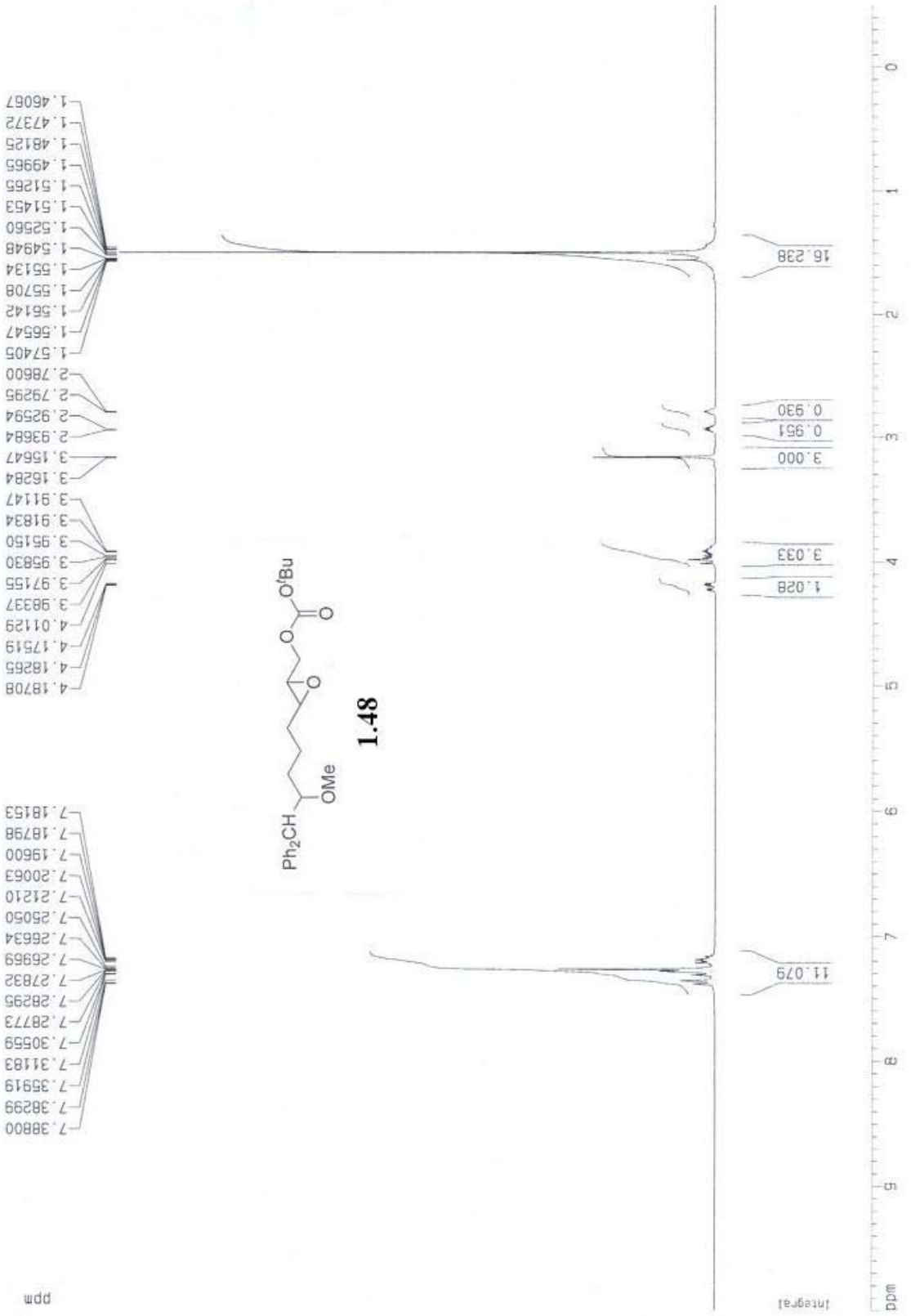
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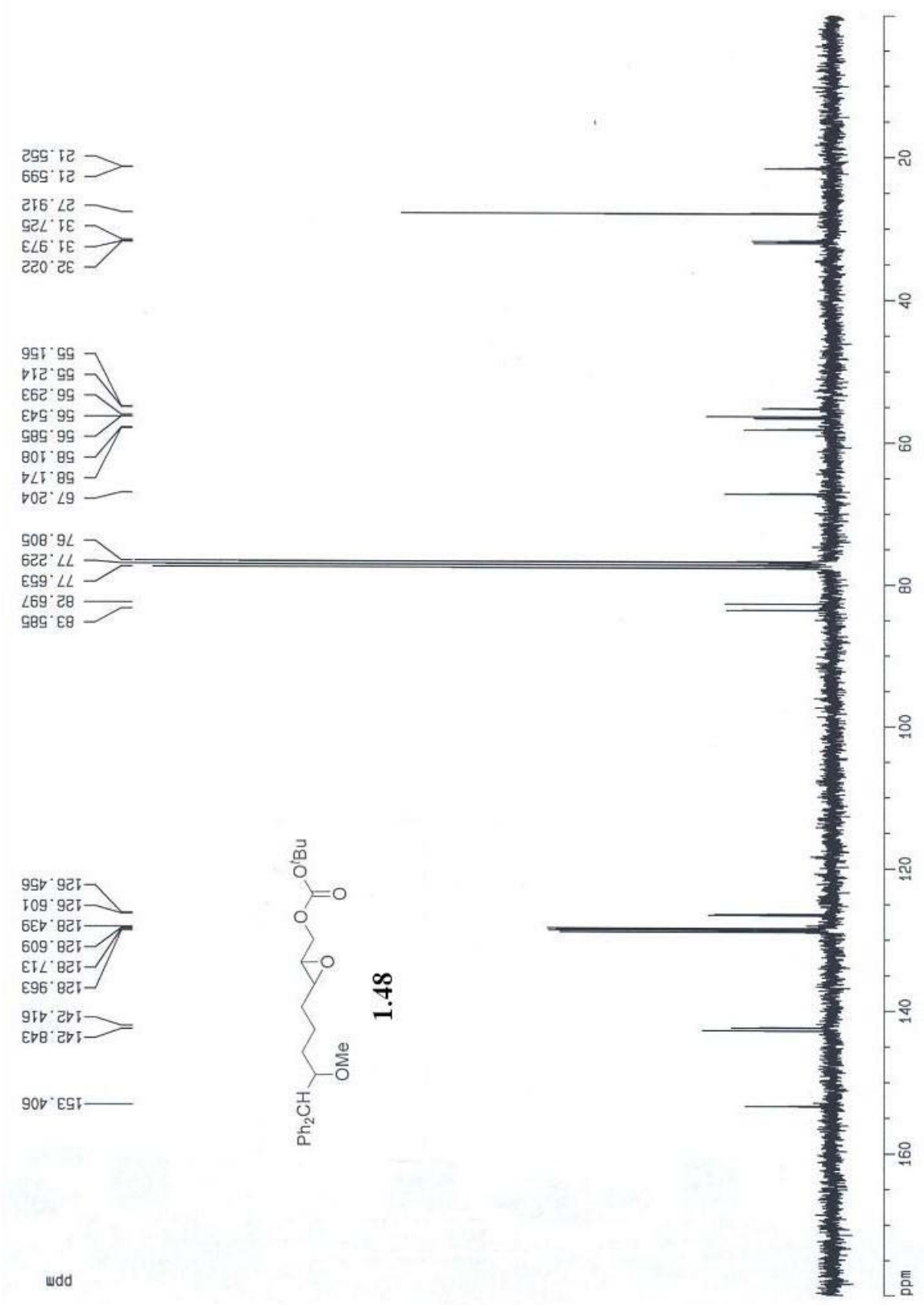
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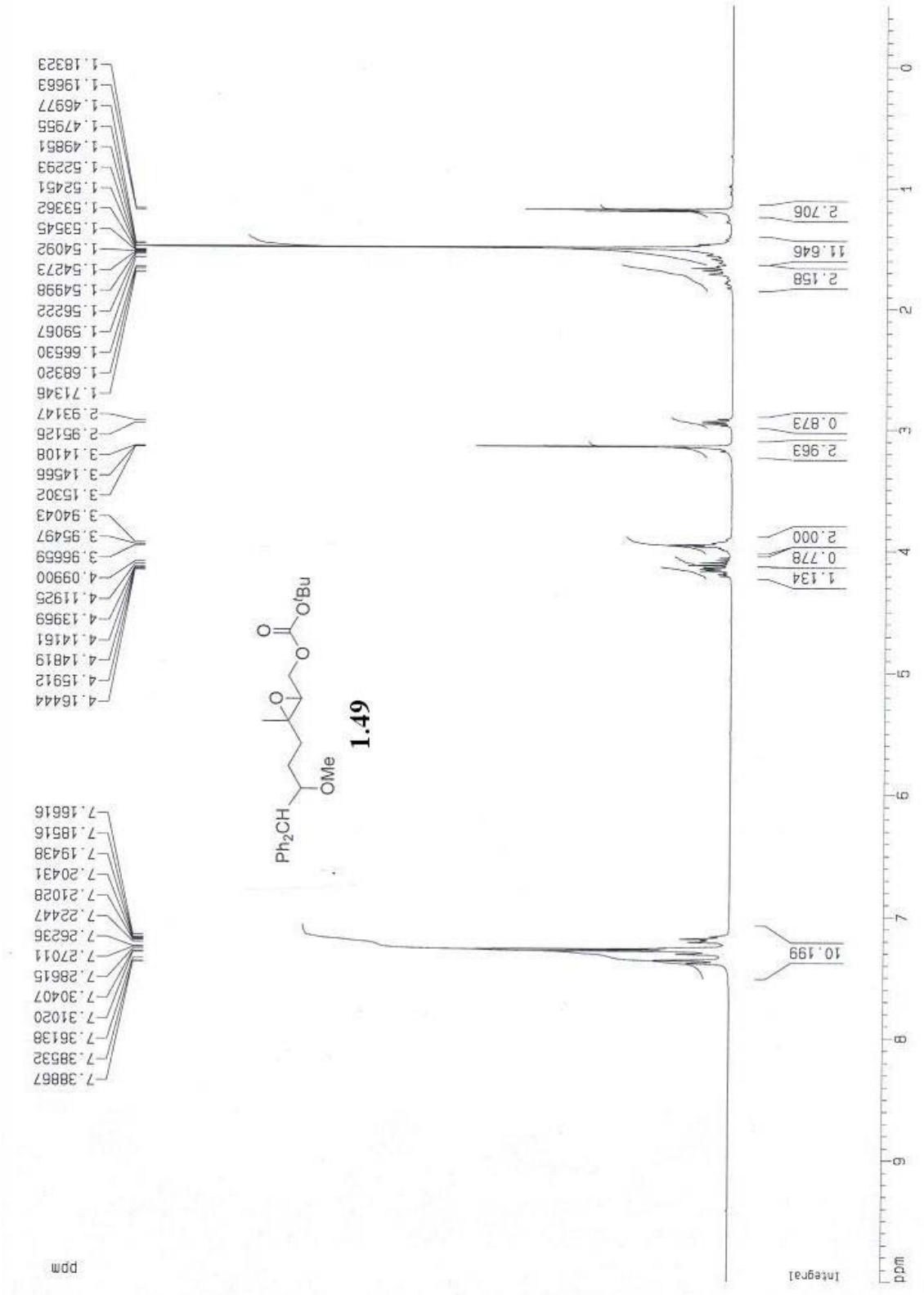
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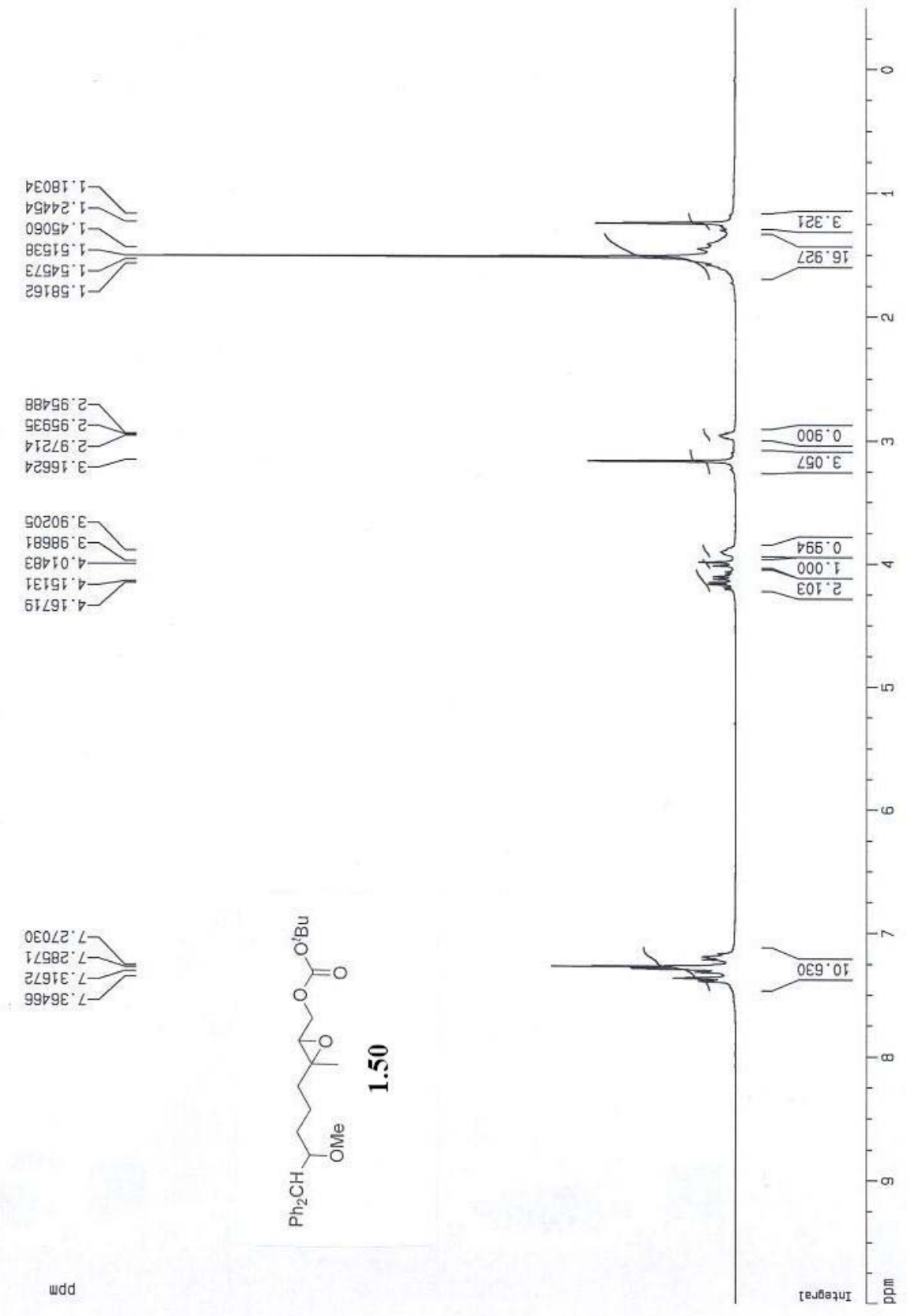
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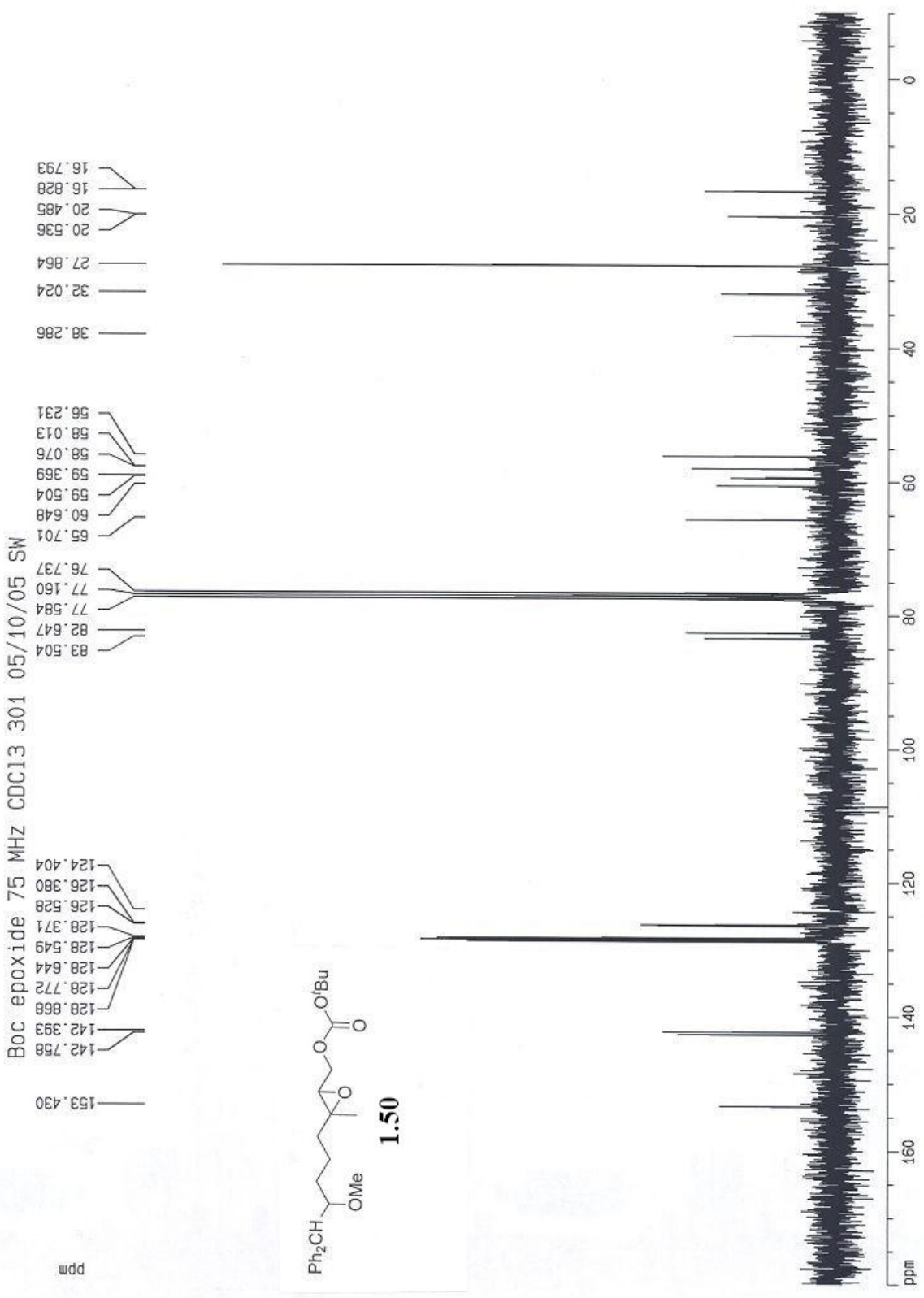
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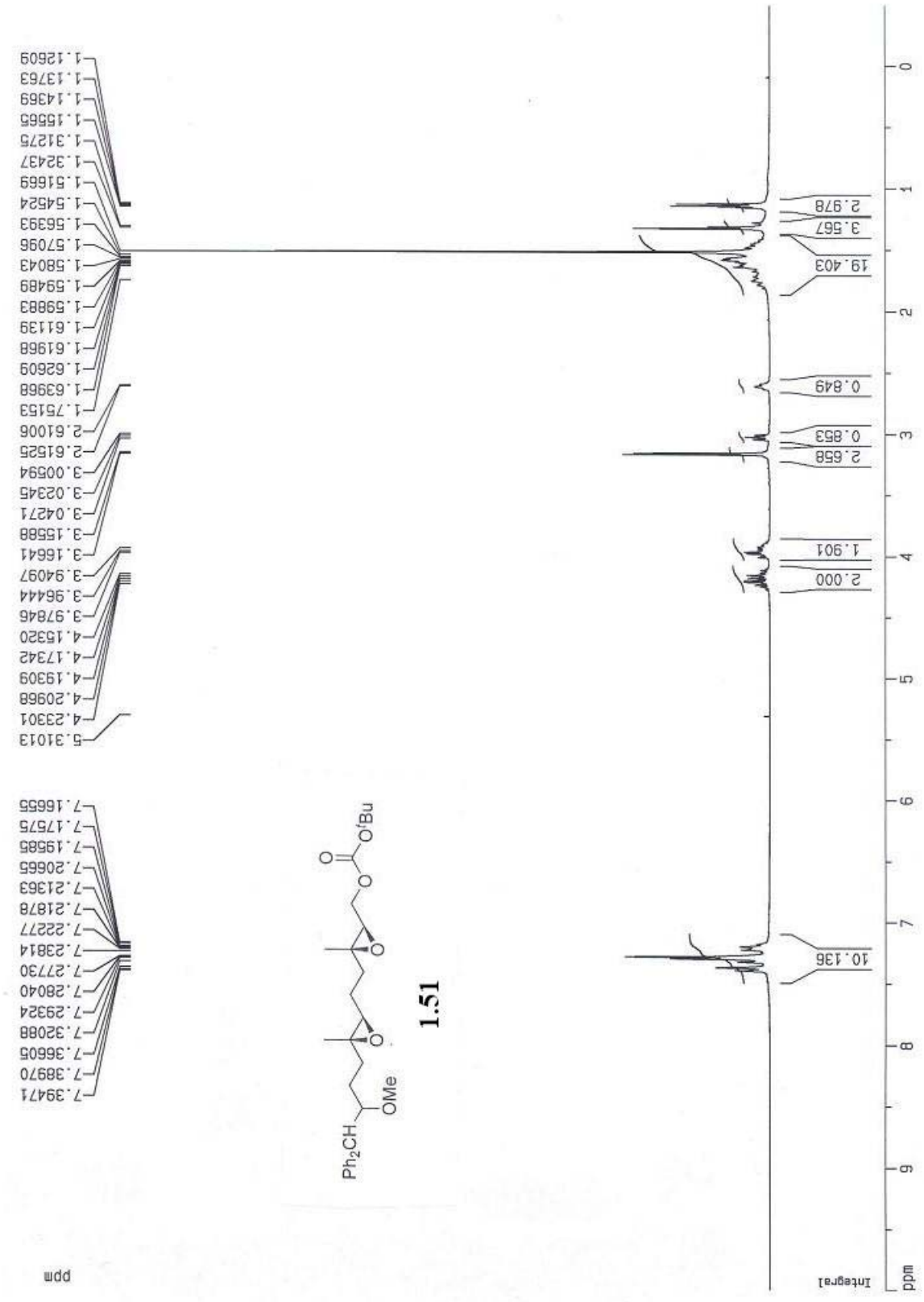
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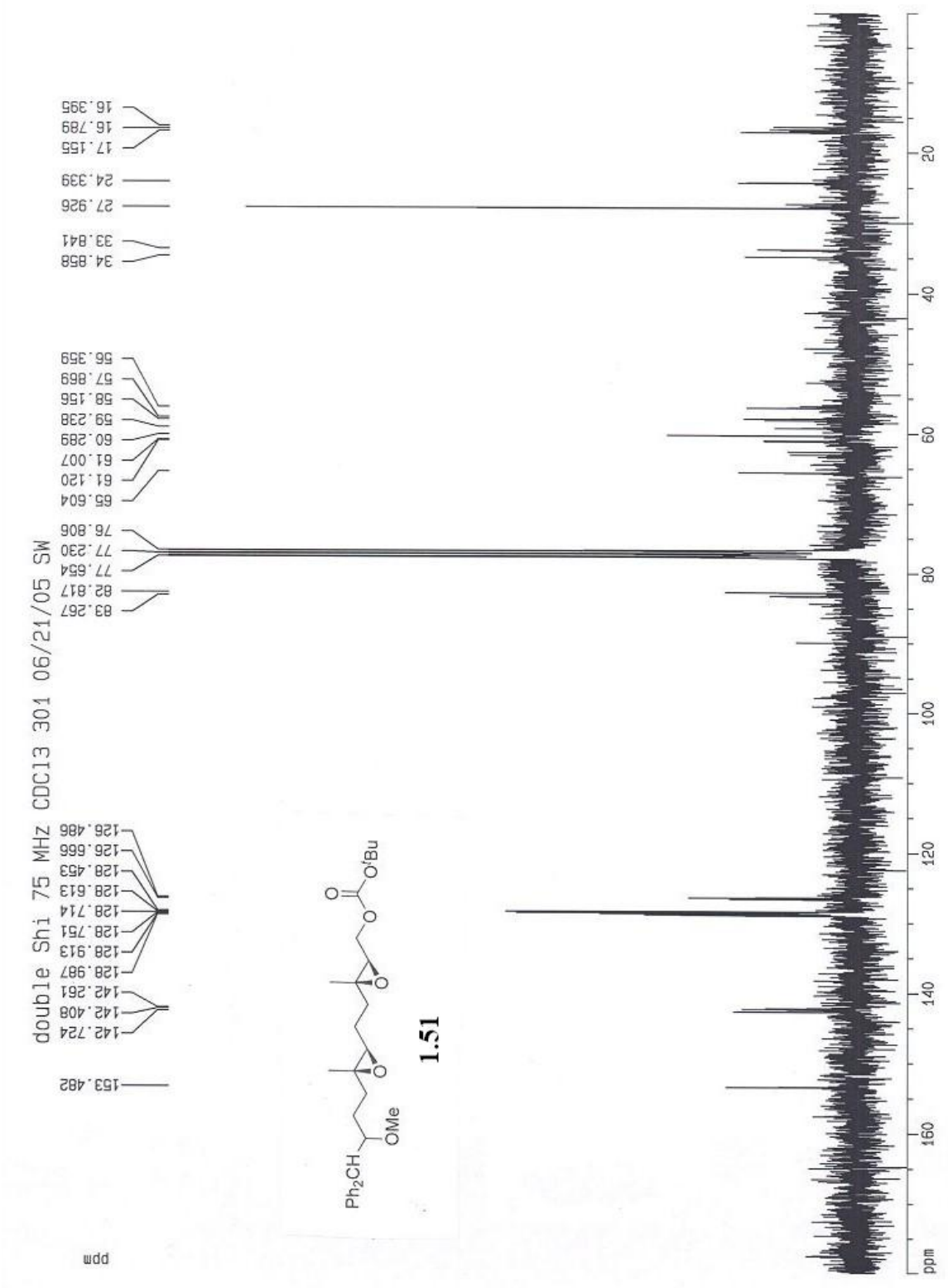
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O
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O
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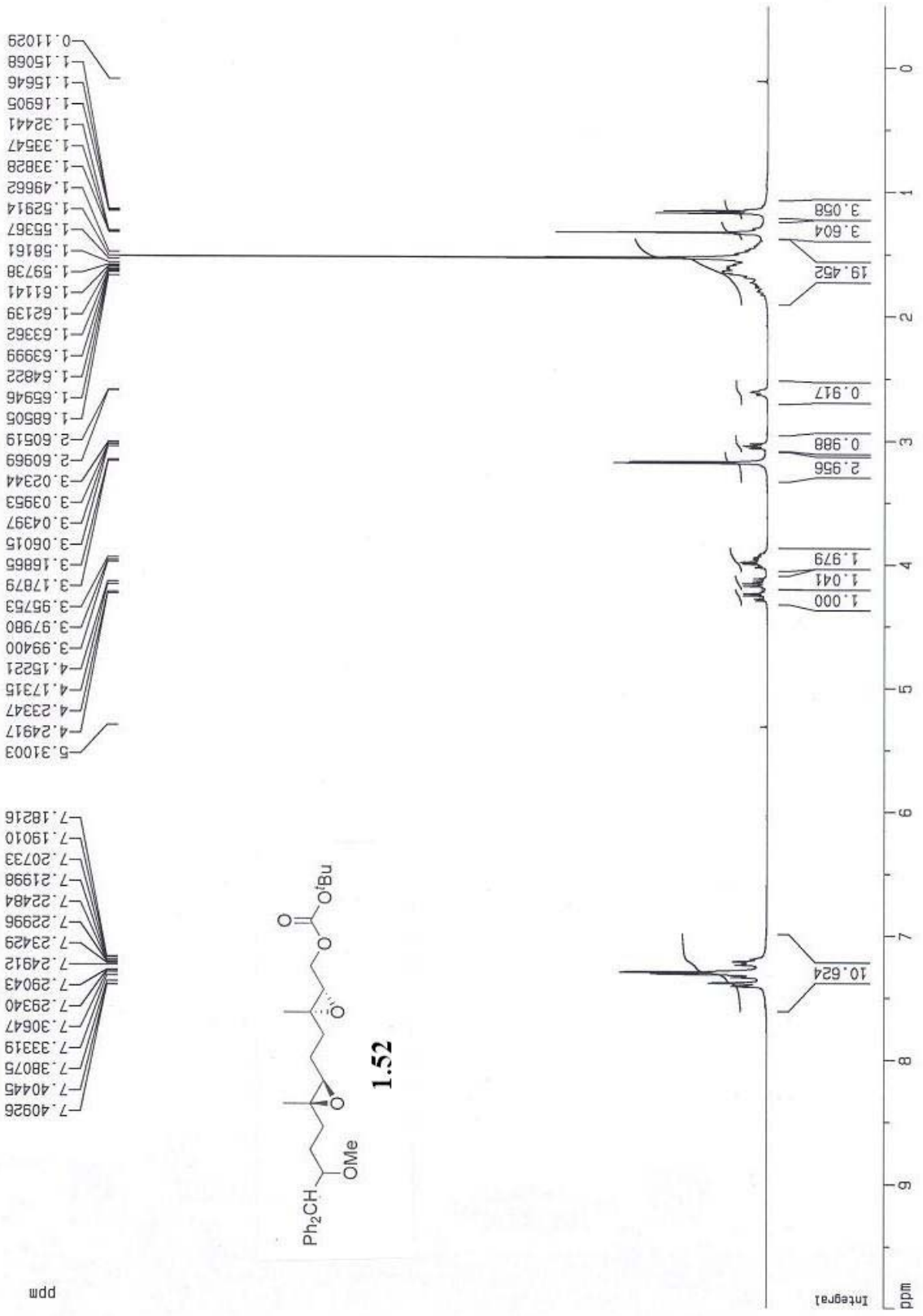
Ph2CH
OMe

1.51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3.06015
3.16865
3.17879
3.95753
3.97980
3.99400
4.15221
4.17315
4.23347
4.24917
5.31003
7.18216
7.19010
7.20733
7.21998
7.22484
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7.23429
7.24912
7.29043
7.29340
7.30647
7.33319
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7.40445
7.40926
ppm
Integral
10.624
19.452
3.058
3.604
0.917
0.988
2.956
1.000
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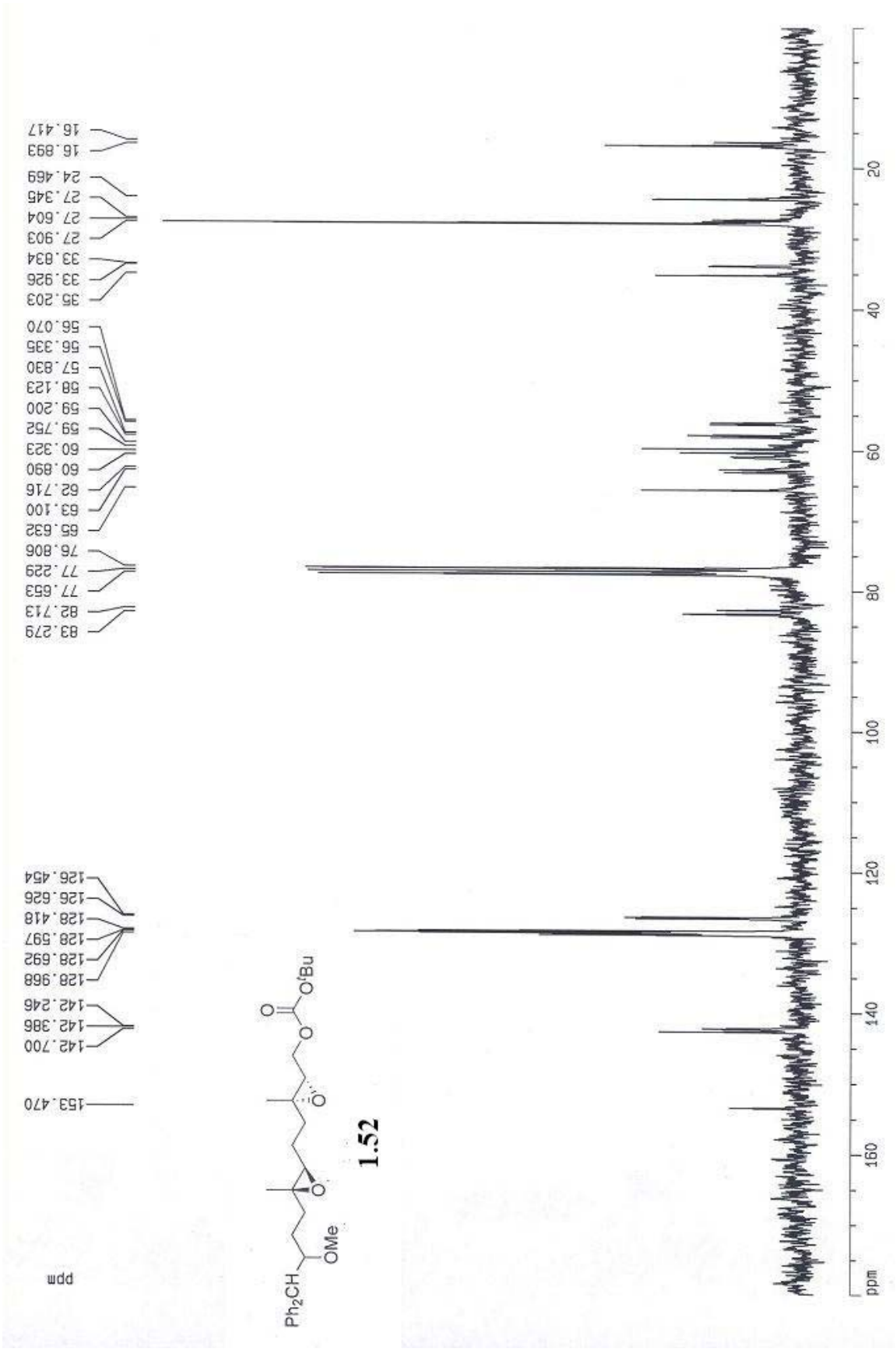
0 1 2 3 4 5 6 7 8 9
ppm
O
O
O
O
O
O
tBu
Ph2CH
OMe

1.52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77.653
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76.806
65.632
63.100
62.716
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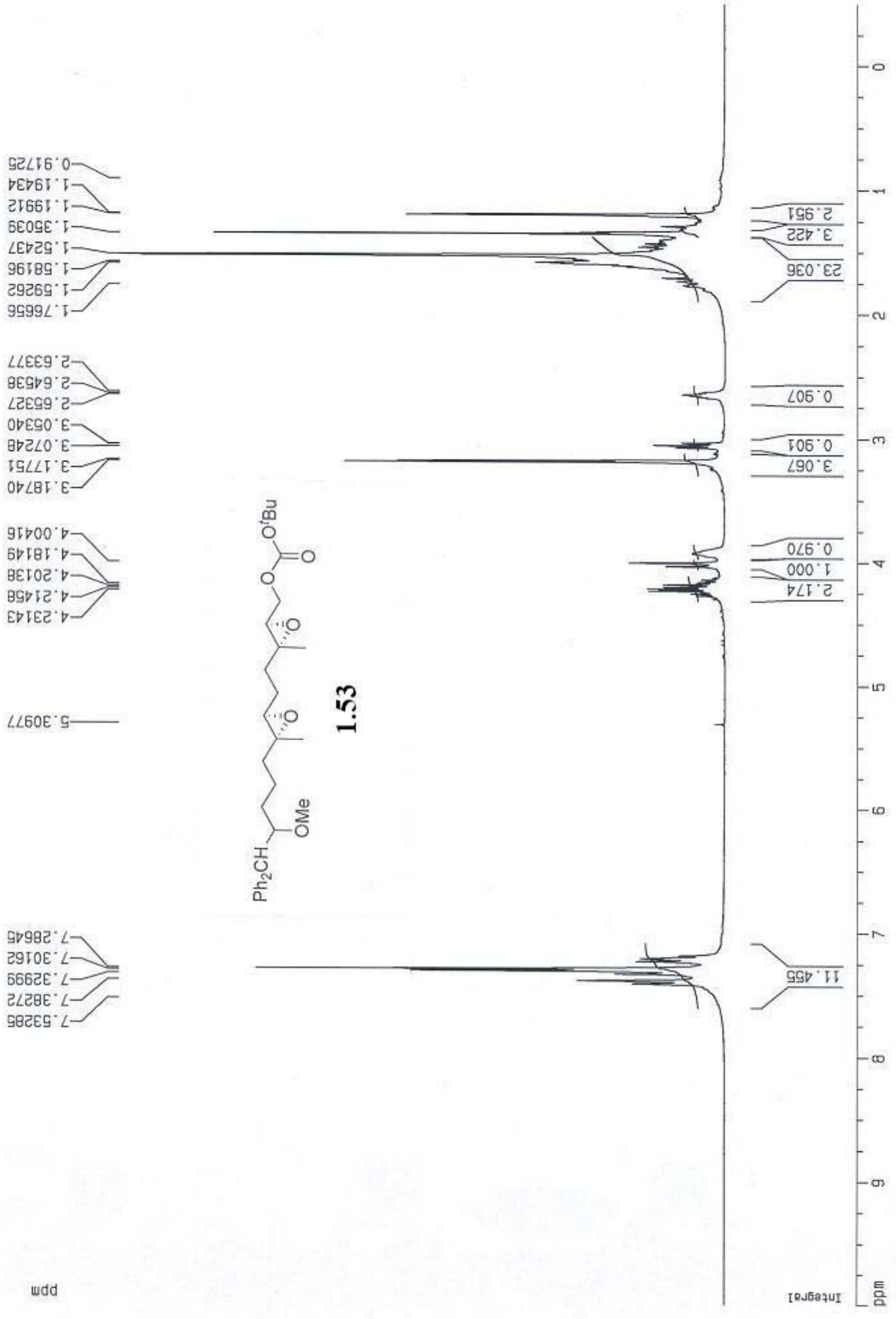
60.323
59.752
59.200
58.123
57.830
56.335
56.070
35.203
33.926
33.834
27.903
27.604
27.345
24.469
16.893
16.417
ppm
20
40
60
80
100
120
140
160
Ph2CH
OMe
O
O
O
O
O
O'Bu
1.52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Ph2CH
OMe
O
O
O
O
O
O'Bu
ppm
Integral
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1.52437
1.58196
1.59262
1.76656
2.63377
2.64538
2.65327
3.05340
3.07248
3.17751
3.18740
4.00416
4.18149
4.20138
4.21458
4.23143
5.30977
7.28645
7.30162
7.32999
7.38272
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11.455
2.951
3.422
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0.970
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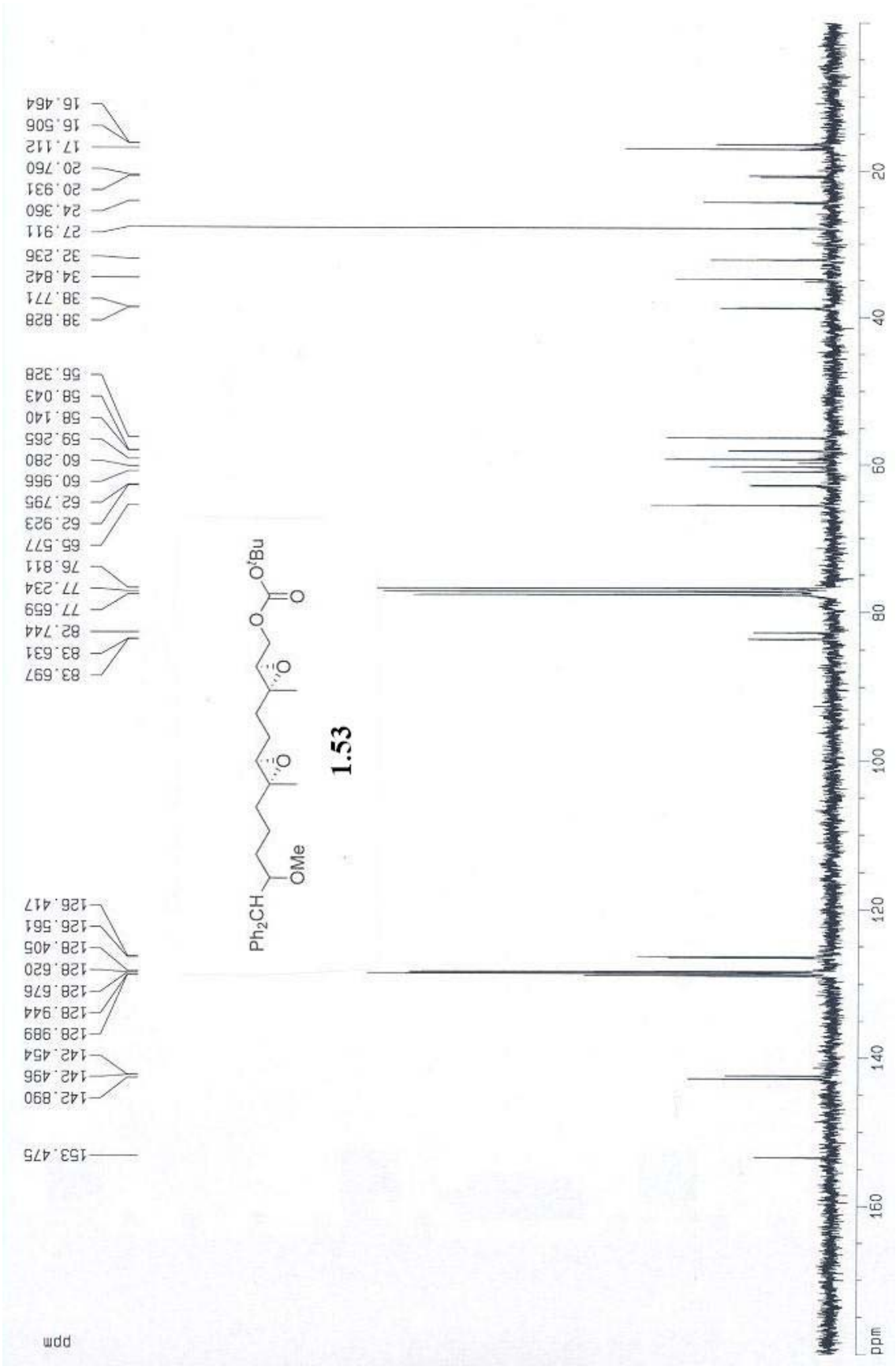
2.174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20.931
24.360
27.911
32.236
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38.771
38.828
56.328
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58.140
59.265
60.280
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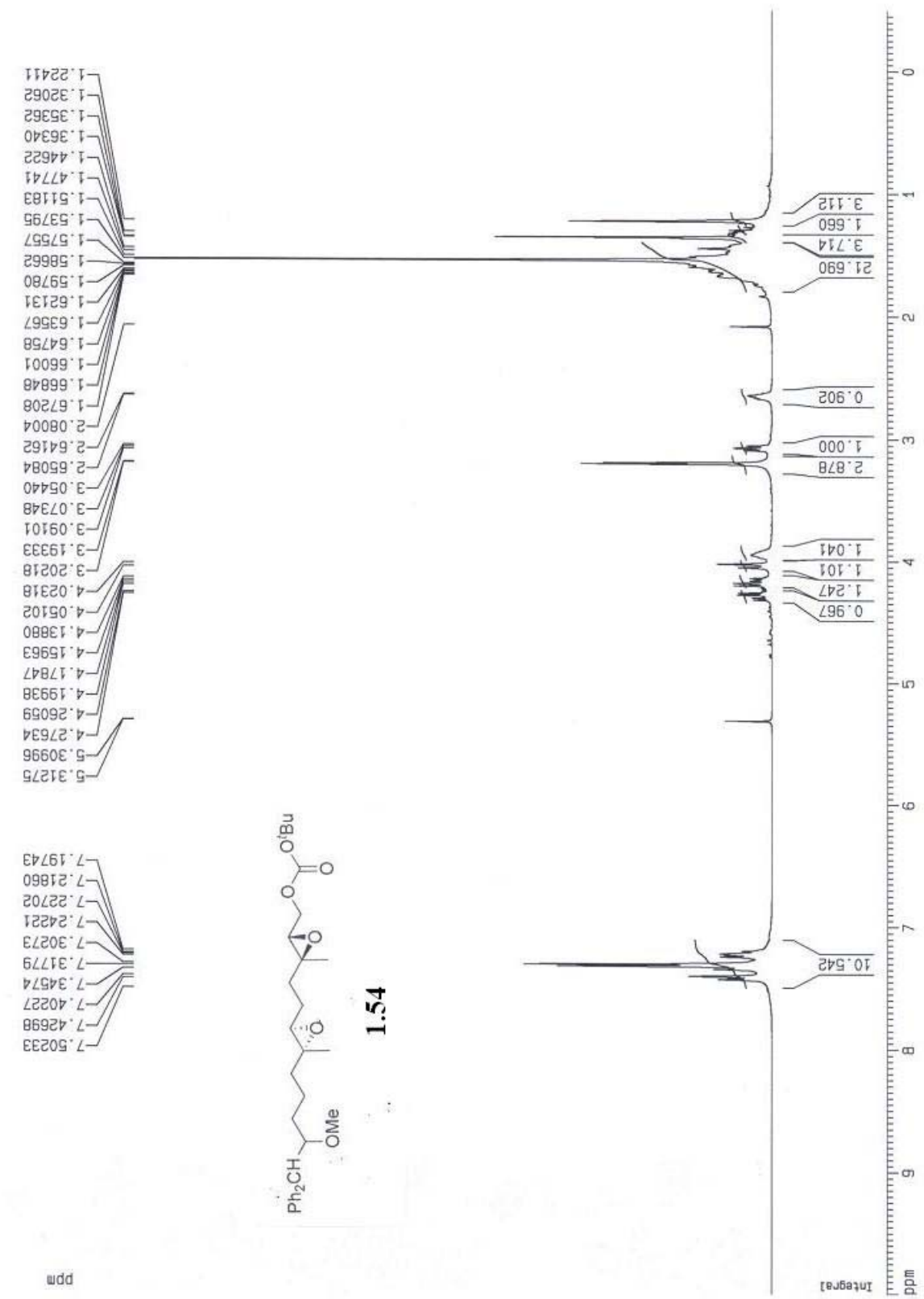
77.234
77.659
82.744
83.631
83.697
126.417
126.561
128.405
128.620
128.676
128.944
128.989
142.454
142.496
142.890
153.475
Ph2CH
OMe
O
O
O
O
O'Bu
1.53
ppm
20
40
60
80
100
120
140
160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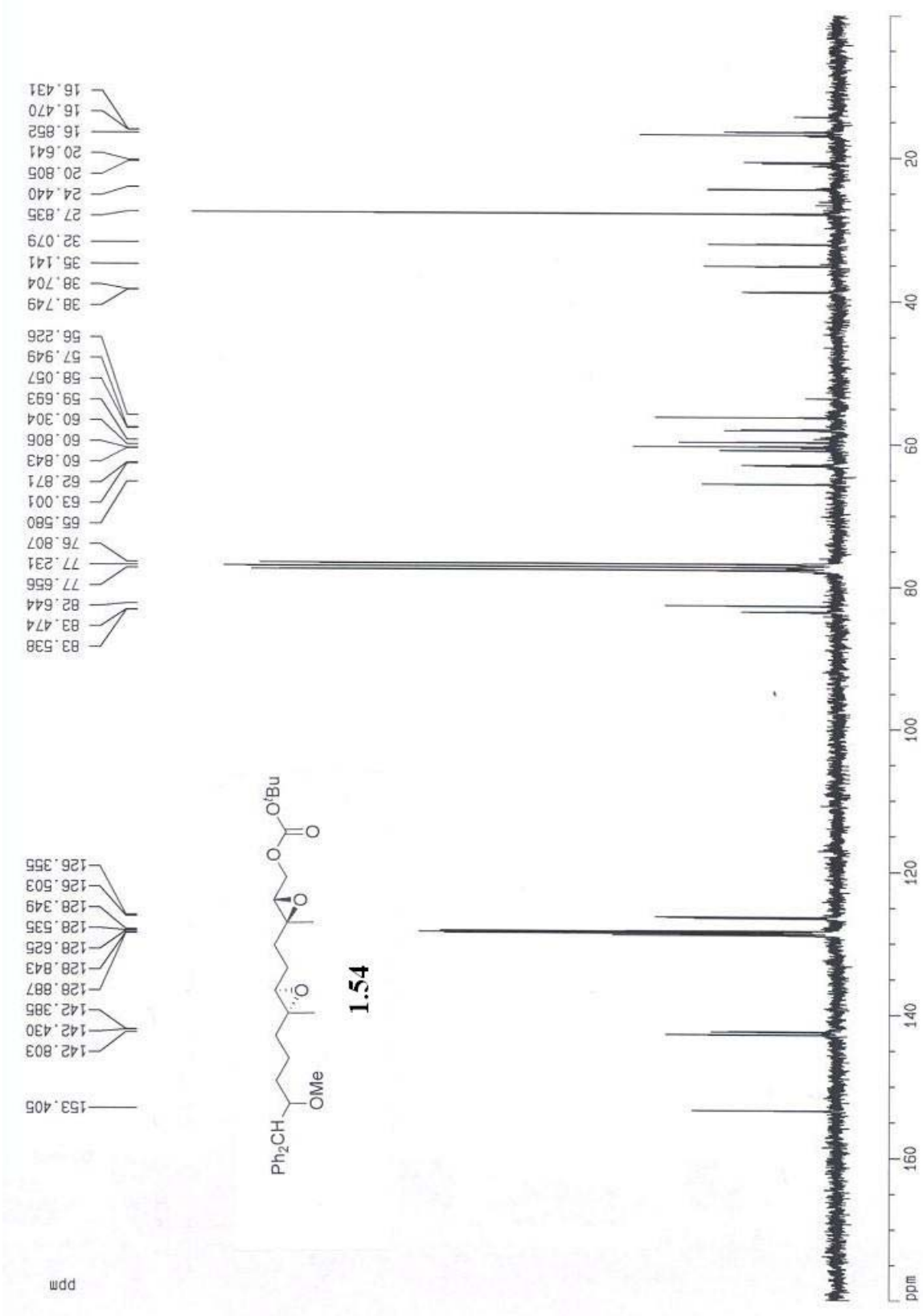
1.59780
1.62131
1.63567
1.64758
1.66001
1.66848
1.67208
2.08004
2.64162
2.65084
3.05440
3.07348
3.09101
3.19333
3.20218
4.02318
4.05102
4.13880
4.15963
4.17847
4.19938
4.26059
4.27634
5.30996
5.31275
7.19743
7.21860
7.22702
7.24221
7.30273
7.31779
7.34574
7.40227
7.42698
7.50233
3.412
1.660
3.714
21.690
0.902
1.000
2.878
1.041
1.101
1.247
0.967
10.542
Integral
ppm
O'Bu
O
O
O
O
Ph2CH
OMe
1.54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142.803
142.430
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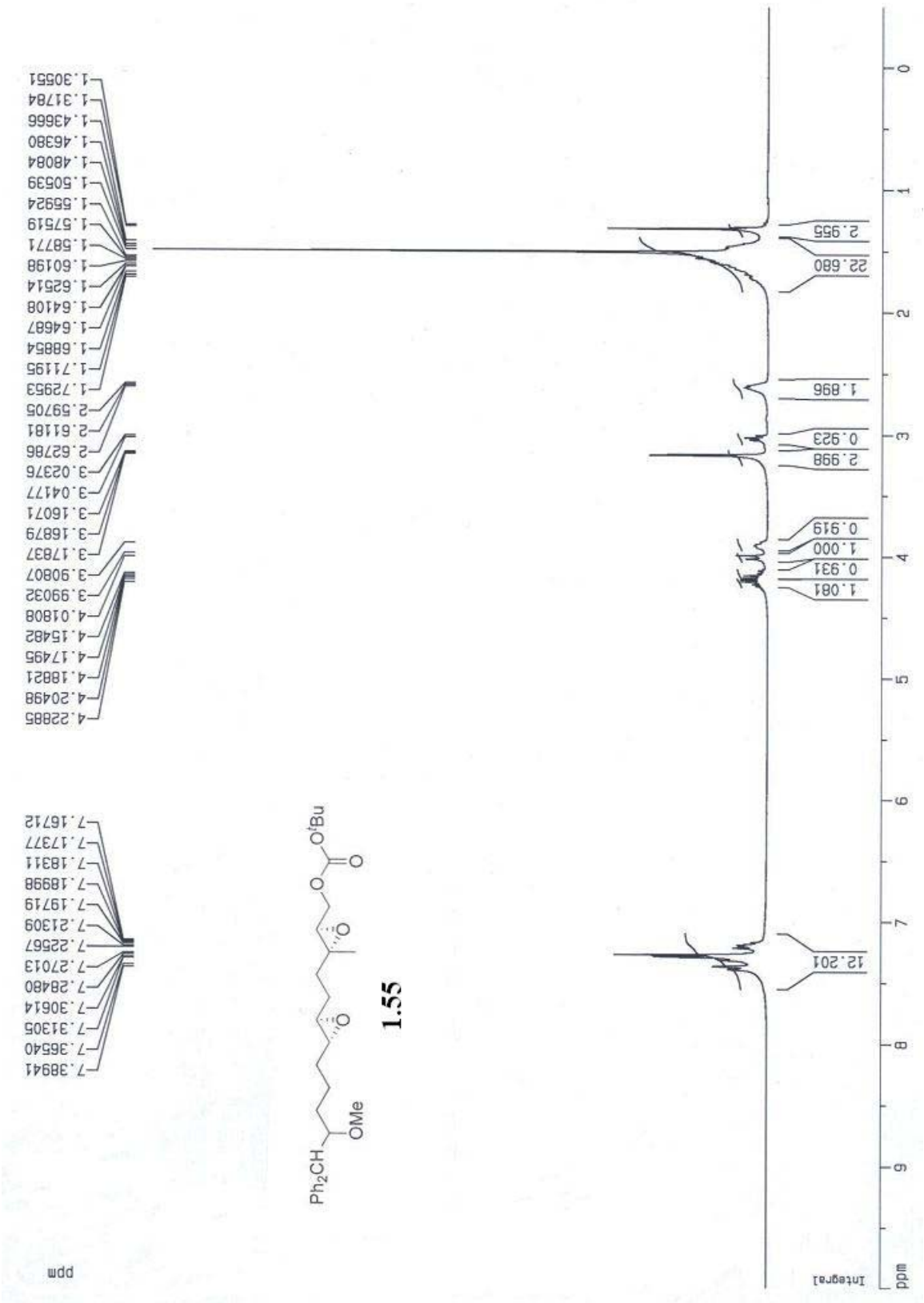
128.843
128.625
128.535
128.349
126.503
126.355
83.538
83.474
82.644
77.656
77.231
76.807
65.580
63.001
62.871
60.843
60.806
60.304
59.693
58.057
57.949
56.226
38.749
38.704
35.141
32.079
27.835
24.440
20.805
20.641
16.852
16.470
16.431
Ph2CH
OMe
O
O
O
O
O
O'Bu
1.54
ppm
20
40
60
80
100
120
140
160
ppm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1.31784
1.43666
1.46380
1.48084
1.50539
1.55924
1.57519
1.58771
1.60198
1.62514
1.64108
1.64687
1.68854
1.71195
1.72953
2.59705
2.61181
2.62786
3.02376
3.04177
3.16071
3.16879
3.17837
3.90807
3.99032
4.01808
4.15482
4.17495
4.18821
4.20498
4.22885
7.16712
7.17377
7.18311
7.18998
7.19719
7.21309
7.22567
7.27013
7.28480
7.30614
7.31305
7.36540
7.38941
ppm
Ph2CH
OMe
O
O
O
O
OtBu
1.55
Integral
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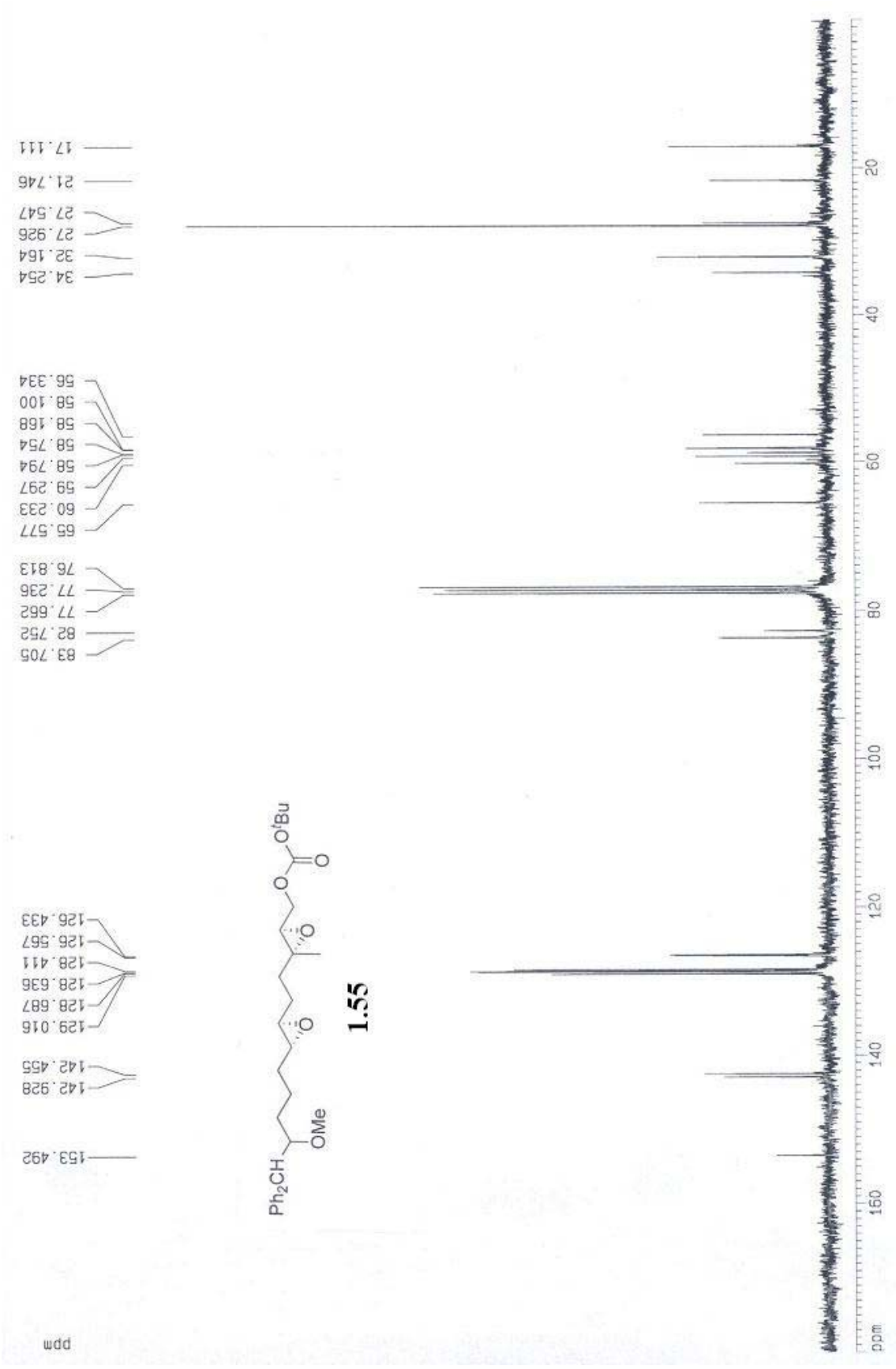
2.955
22.680
1.896
0.923
2.998
0.919
1.000
0.931
1.081
ppm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27.926
32.164
34.254
56.334
58.100
58.168
58.754
58.794
59.297
60.233
65.577
76.813
77.236
77.662
82.752
83.705
126.433
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128.411
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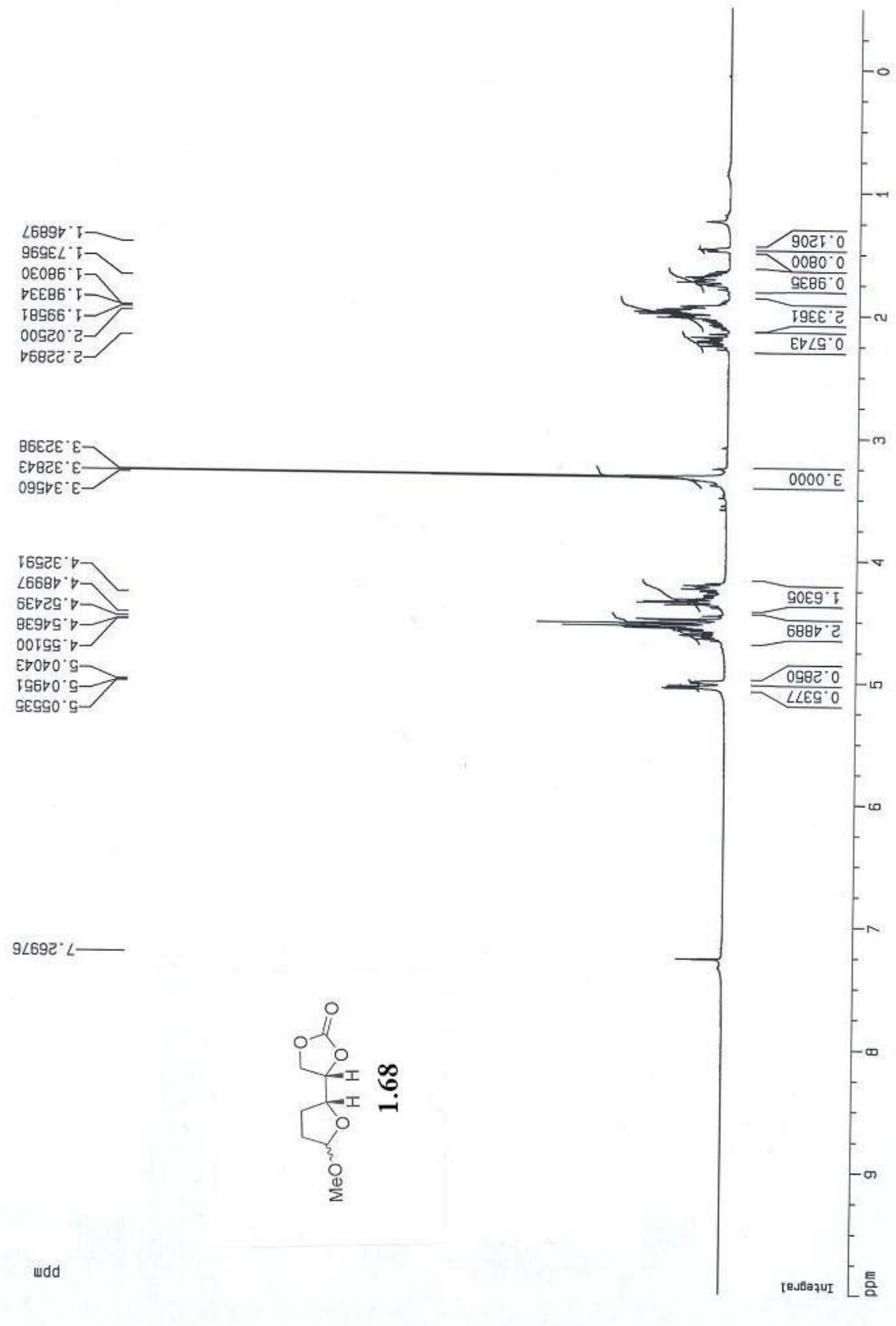
128.687
129.016
142.455
142.928
153.492
Ph2CH
OMe
O'Bu
1.55
ppm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5.04951
5.04043
4.55100
4.54638
4.52439
4.48997
4.32591
3.34560
3.32843
3.32398
2.28894
2.02500
1.99581
1.98334
1.98030
1.75596
1.46897
0.5377
0.2850
2.4889
1.6305
3.0000
0.5743
2.3361
0.9835
0.0800
0.1206
Integral
ppm
MeO
H
H
O
O
O
O

1.68

155.115
154.948
105.744
105.634
79.441
77.854
77.654
77.231
77.142
76.806
66.849
66.393
55.116
32.706
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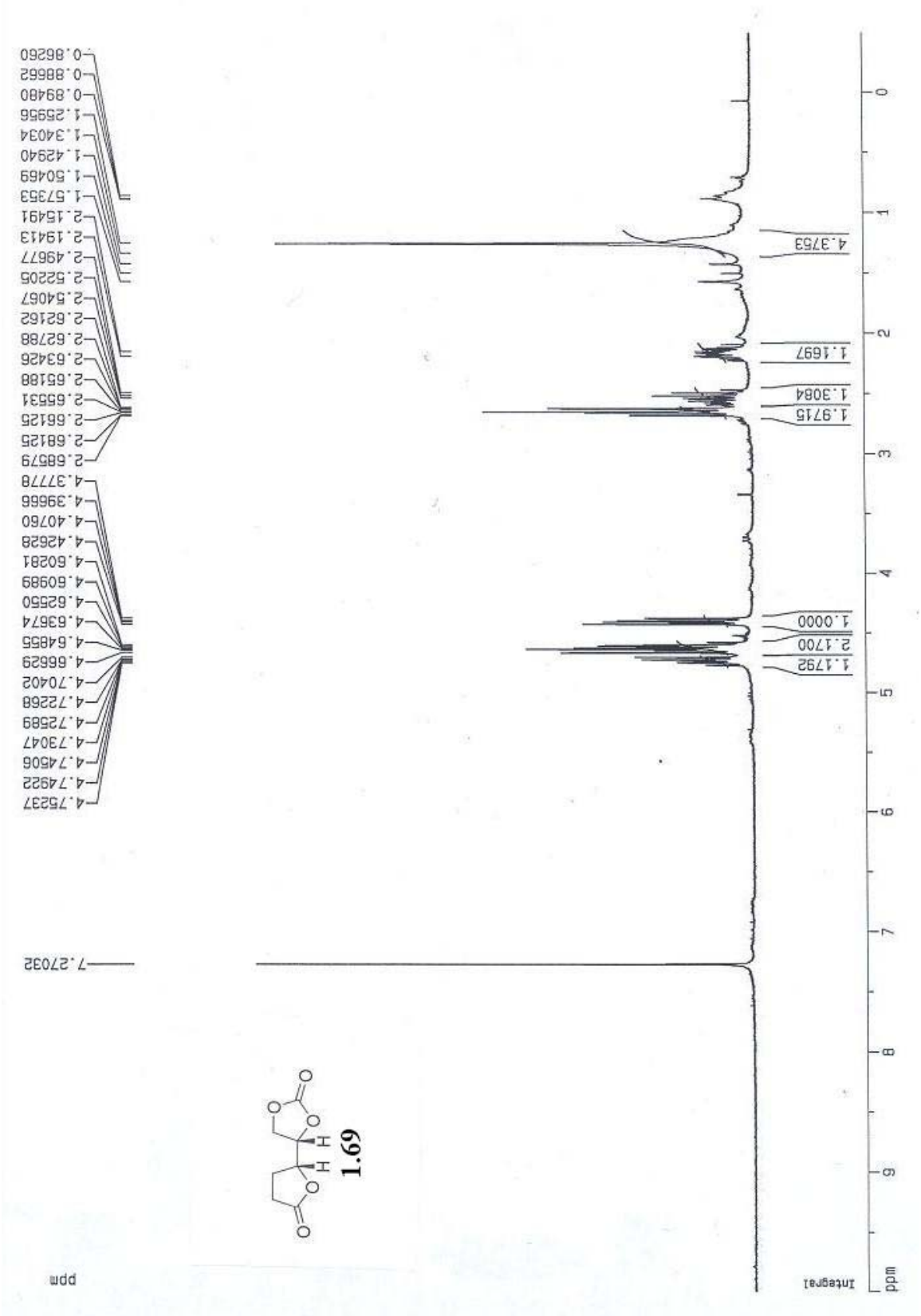
25.879
25.519
MeO
1.68
ppm
20
40
60
80
100
120
140
160
ppm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4.75237
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4.73047
4.72589
4.72268
4.70402
4.66629
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4.63674
4.62550
4.60989
4.60281
4.42628
4.40760
4.39666
4.37778
2.68579
2.68125
2.66125
2.65531
2.65188
2.63426
2.62788
2.62162
2.54067
2.52205
2.49677
2.19413
2.15491
1.57353
1.50469
1.42940
1.34034
1.25956
0.89480
0.88662
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1.1697
1.3084
1.9715
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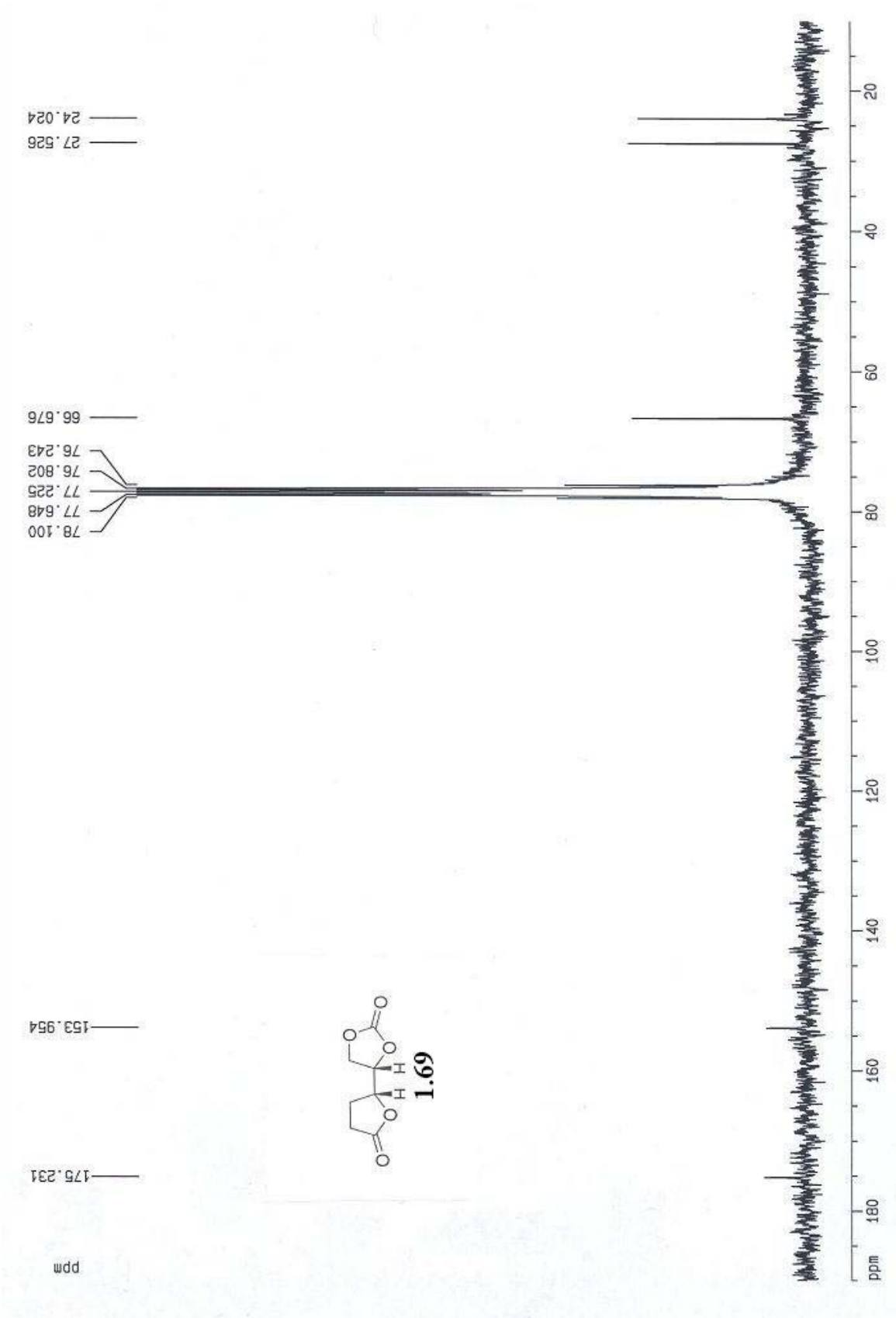
integral
ppm
1.69
ppm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77.648
78.100
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175.231
ppm
20
40
60
80
100
120
140
160
180
1.69

ppm
7.27036
4.74381
4.52821
4.52467
4.47996
4.47529
3.98917
3.95634
3.94892
3.46275
3.39022
3.35685
1.85500
1.70413
1.69164
1.68095
1.63522
1.27553
1.24645
MeO
H
H
Integral
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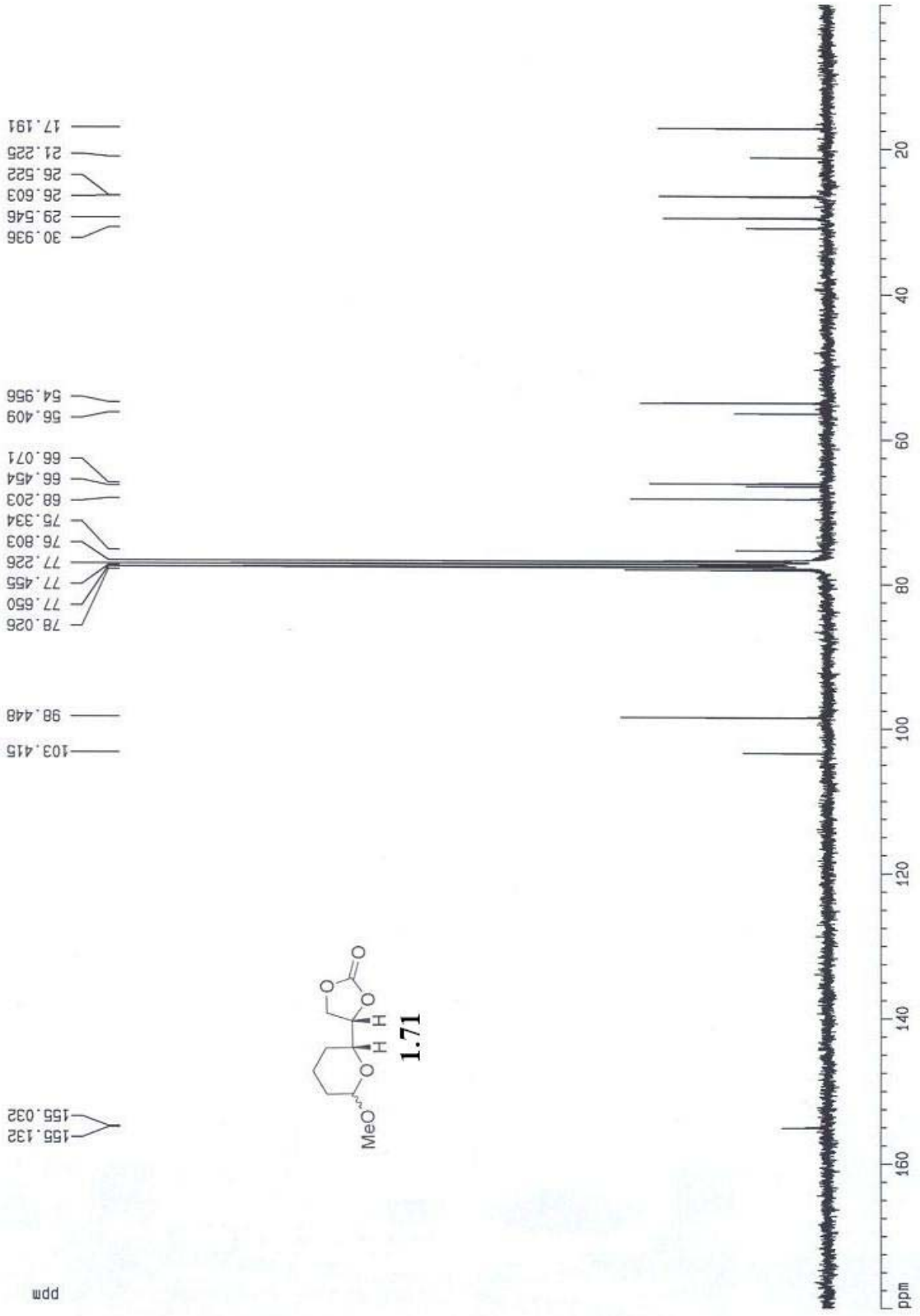
1.71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26.603
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30.936
54.956
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68.203
75.334
76.803
77.226
77.455
77.650
78.026
98.448
103.415
155.032
155.132
MeO
H
H
1.71
ppm
20
40
60
80
100
120
140
160

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1.50714
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3.46779
3.80526
4.12633
4.14471
4.17745
4.32519
4.34145
4.66092
4.67998
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0.2971
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0.3274
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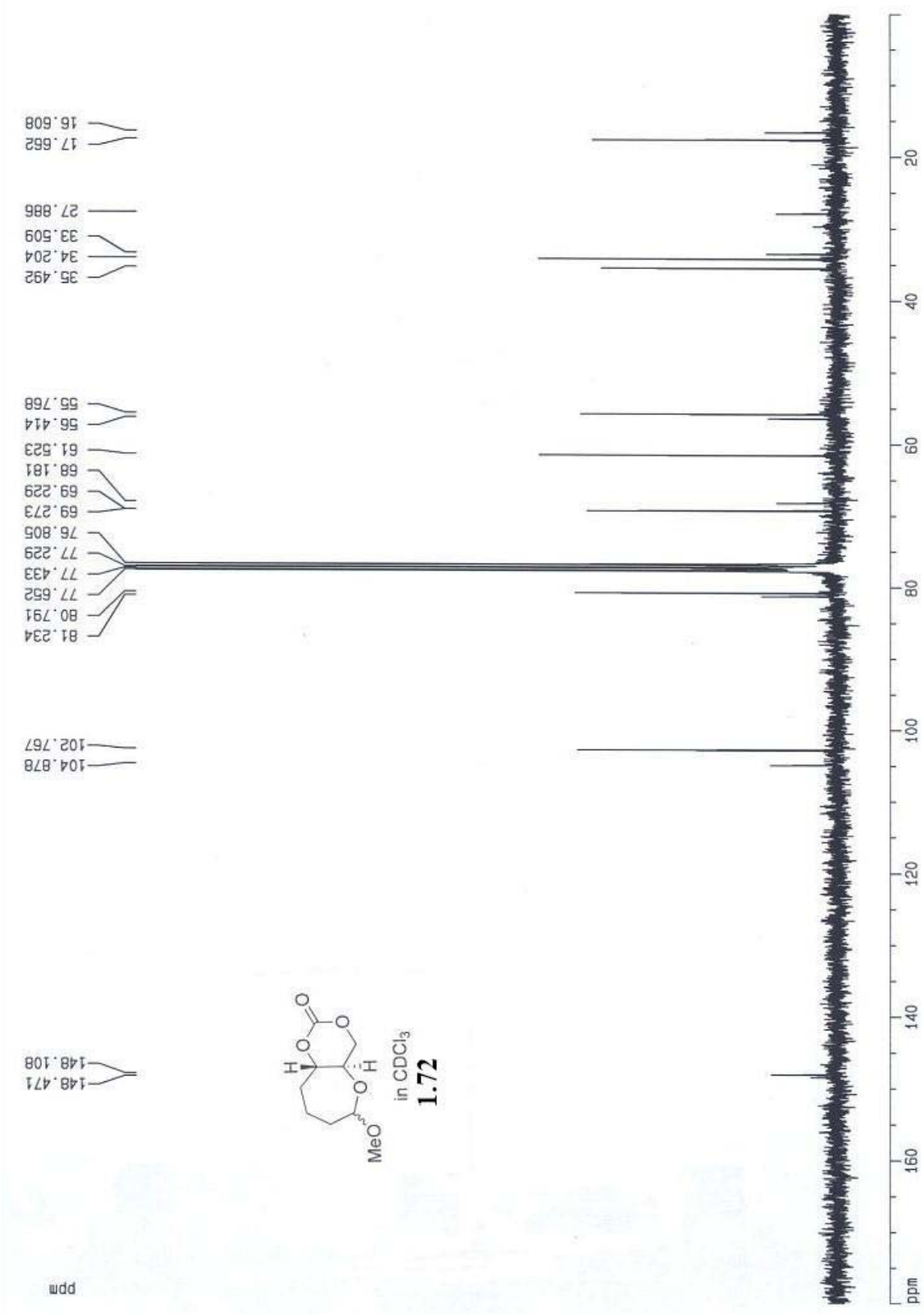
Integral
ppm
MeO
H
H
in CDCl3
1.72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56.414
61.523
68.181
69.229
69.273
76.805
77.229
77.433
77.652
80.791
81.234
102.767
104.878
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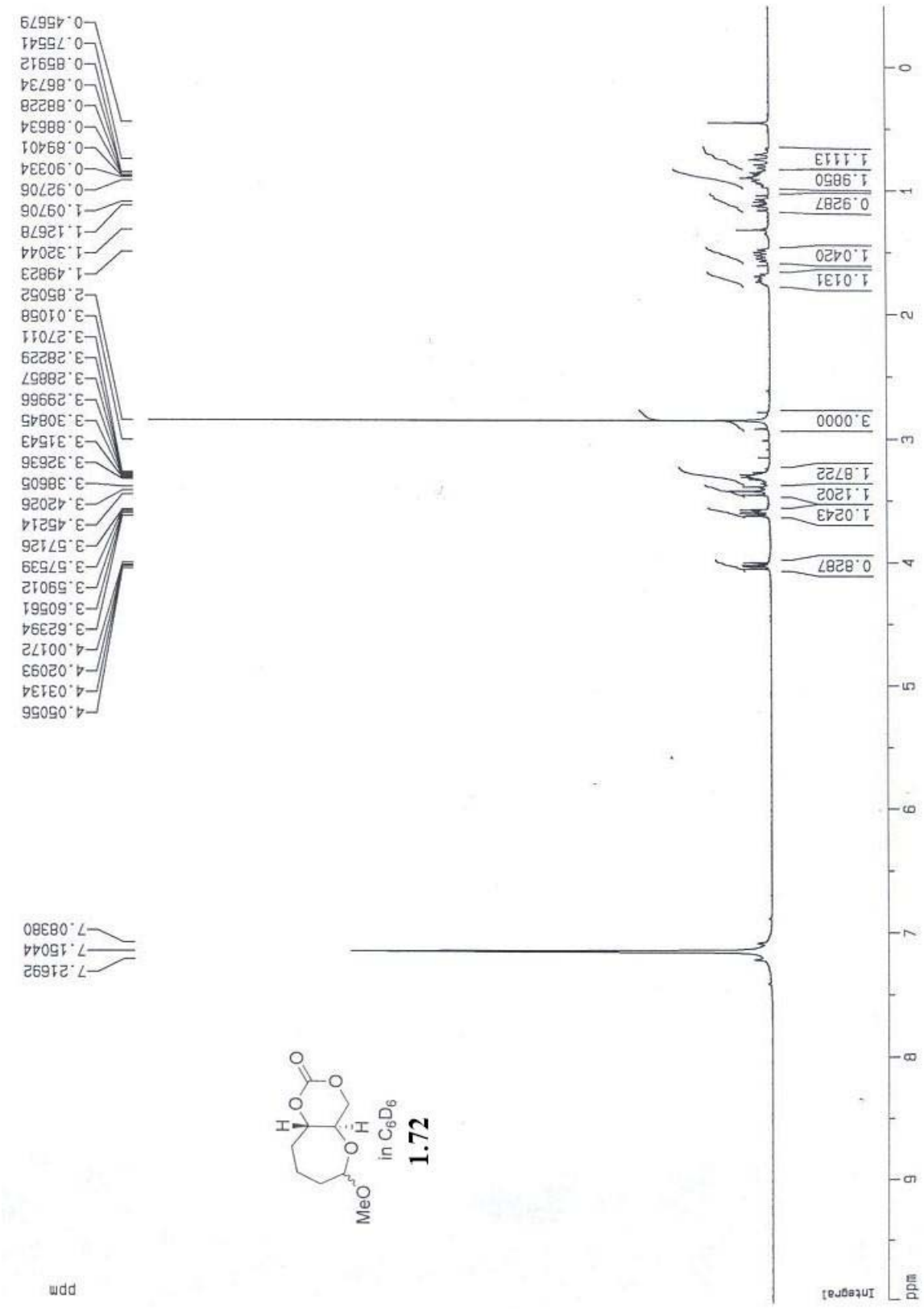
148.471
ppm
20
40
60
80
100
120
140
160
MeO
in CDCl3
1.72


MeO
in C_6D_6
1.72

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4.64921
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4.45407
4.44219
4.43018
2.66751
2.66360
2.66100
2.65714
2.59781
2.57445
2.56689
2.54338
2.19130
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2.05526
2.03946
2.03196
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1.59107
1.28736
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0.86079
0.72215
1.1343
0.9392
0.9852
0.9757
0.8762
0.9011
1.9578
2.0000
Integral
ppm
ppm
1.73

18.186
24.597
29.854
66.901
76.295
76.804
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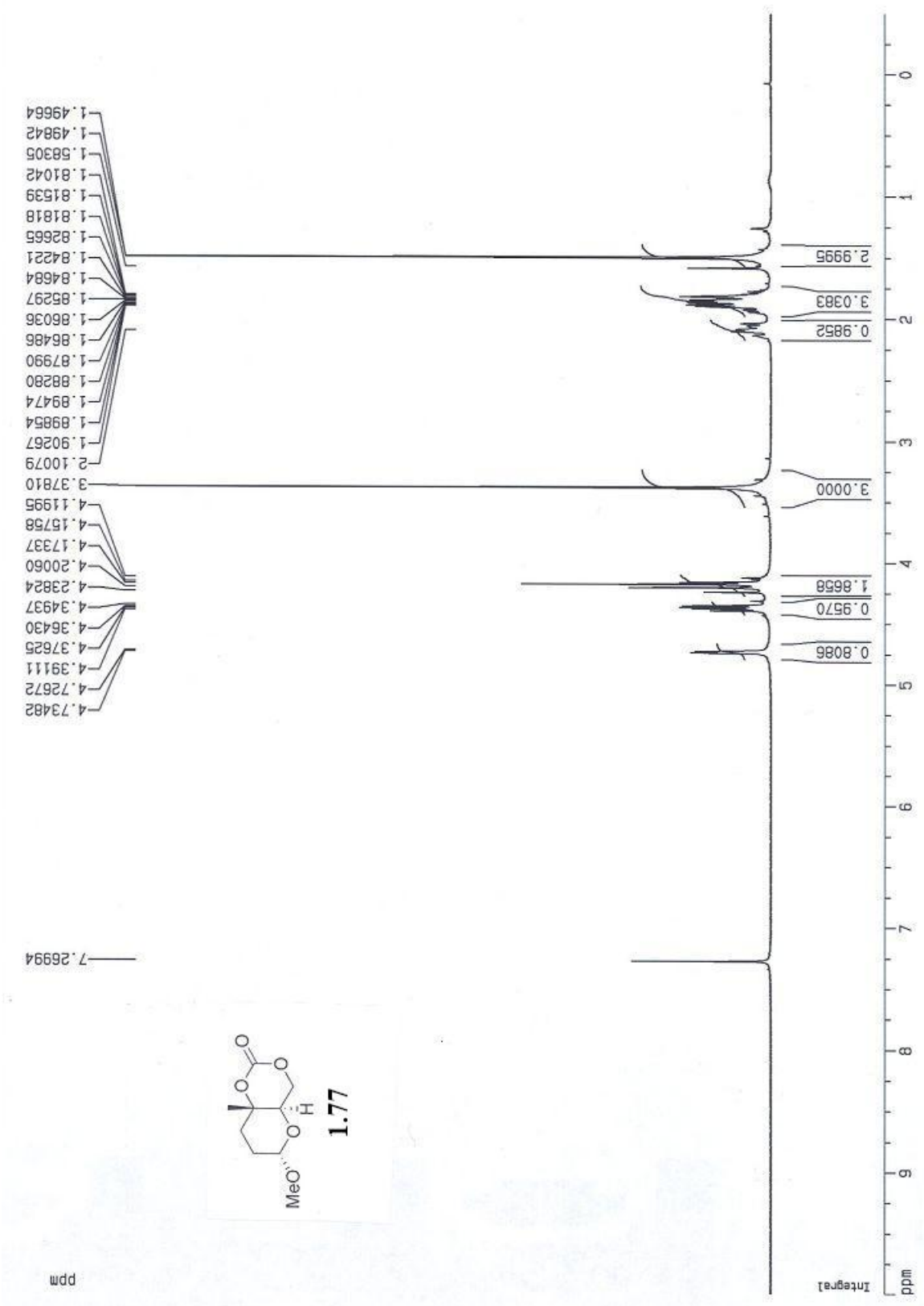
140
160
180
ppm

1.73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4.11995
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2.10079
1.90267
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1.89474
1.88280
1.87990
1.86486
1.86036
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1.81042
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1.49842
1.49664
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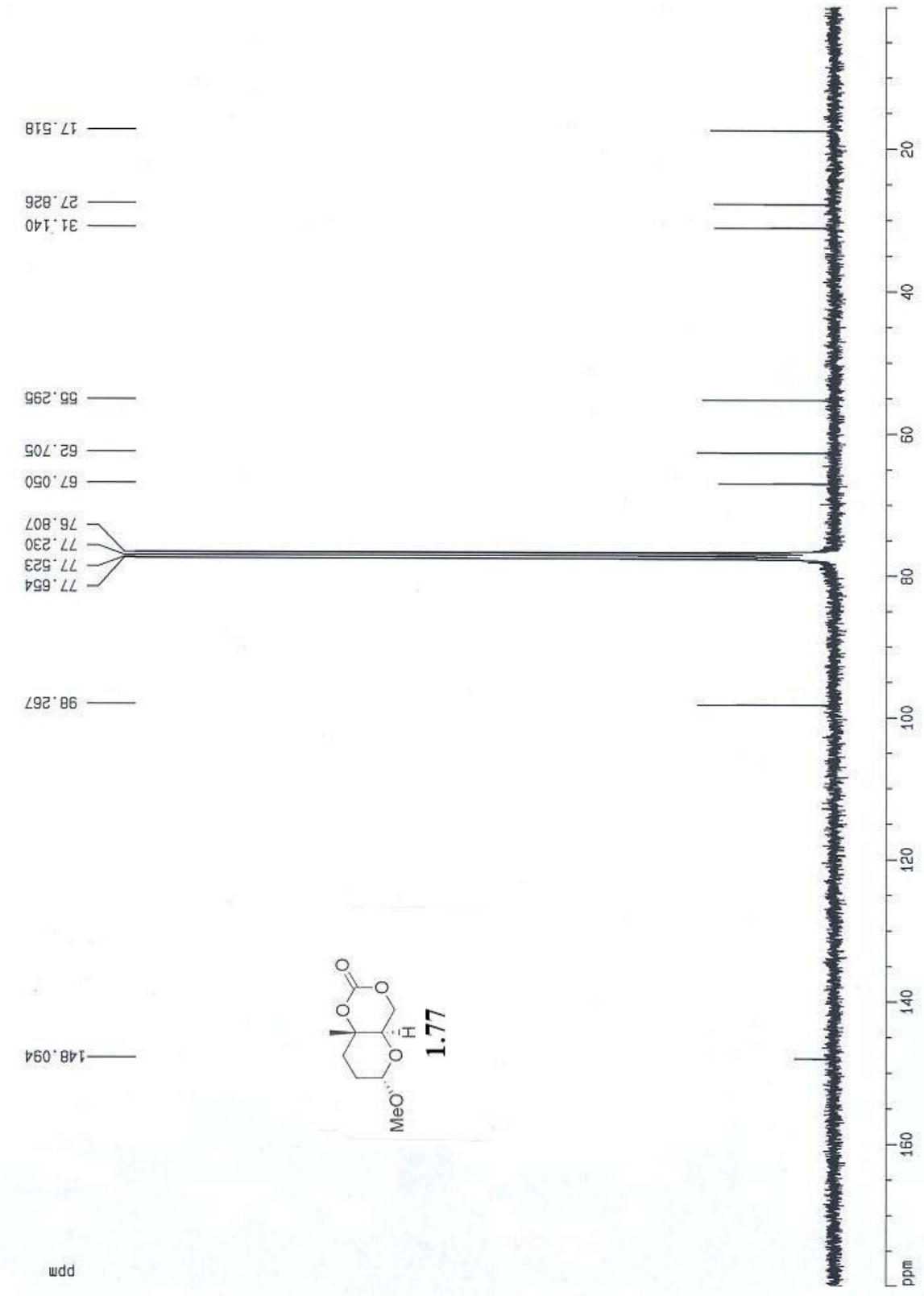
0.8086
Integral
ppm
MeO
H
1.77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27.826
31.140
55.295
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67.050
76.807
77.230
77.523
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98.267
148.094
MeO
H
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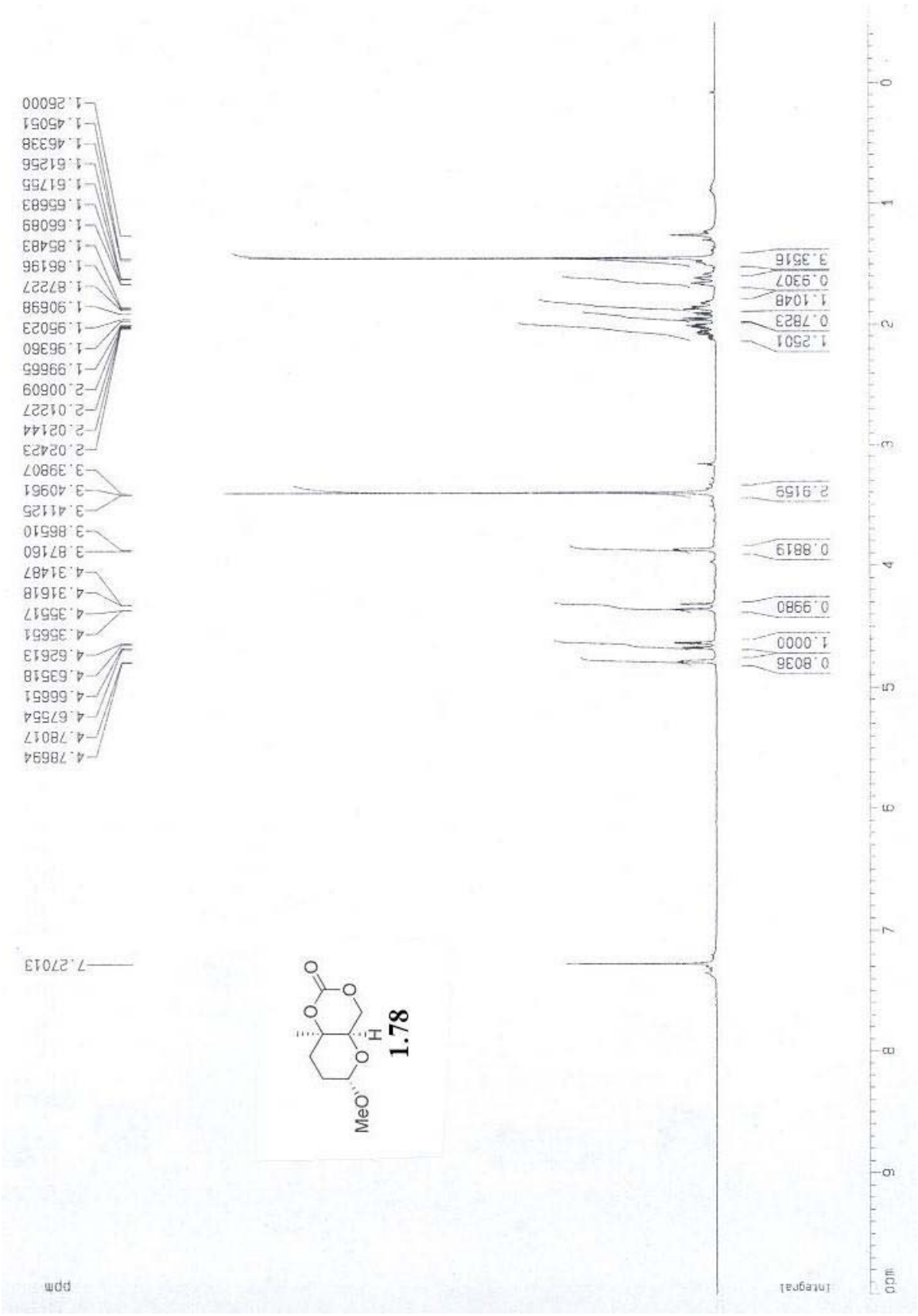
ppm
20
40
60
80
100
120
140
160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1.46338
1.61256
1.61755
1.65683
1.66089
1.85483
1.86196
1.87227
1.90698
1.95023
1.96360
1.99665
2.00809
2.01227
2.02144
2.02423
3.39807
3.40951
3.41125
3.86510
3.87160
4.31487
4.31618
4.35517
4.35651
4.62613
4.63518
4.66651
4.67554
4.78017
4.78694
7.27013
3.3516
0.9307
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MeO
H
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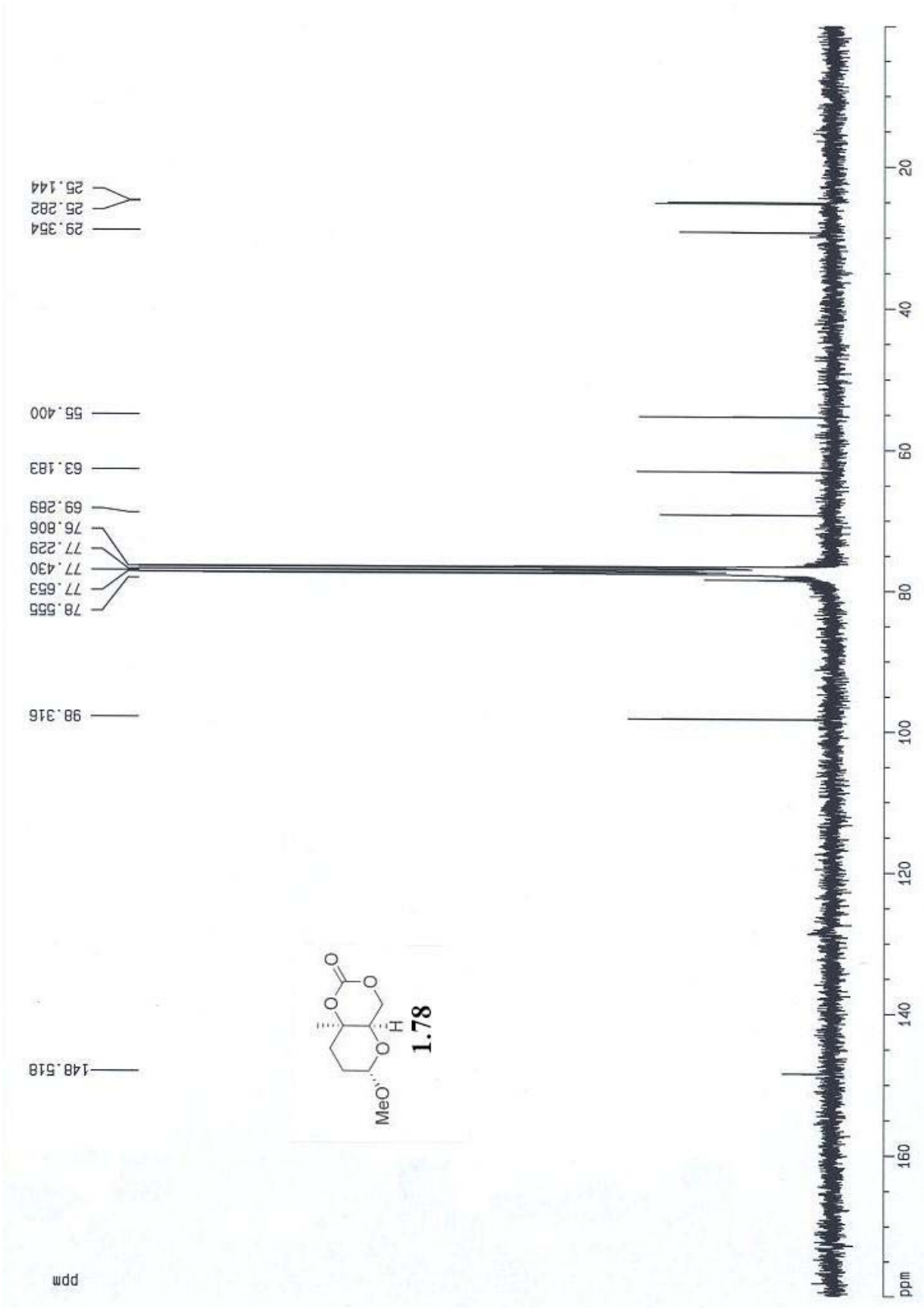
ppm
Integral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77.229
76.806
69.289
63.183
55.400
29.354
25.282
25.144
MeO
H
1.78
ppm
20
40
60
80
100
120
140
160

1.77
7.27046
4.74463
4.72379
4.71655
4.69618
4.59931
4.56926
4.54051
4.38488
4.36448
4.35915
4.35434
4.33396
2.73298
2.70370
2.67568
2.34597
2.31812
2.30105
2.29010
2.27322
2.24523
2.18864
2.16232
2.14380
2.13173
2.11607
1.47476
1.27954
1.25720
0.8352
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1.0000
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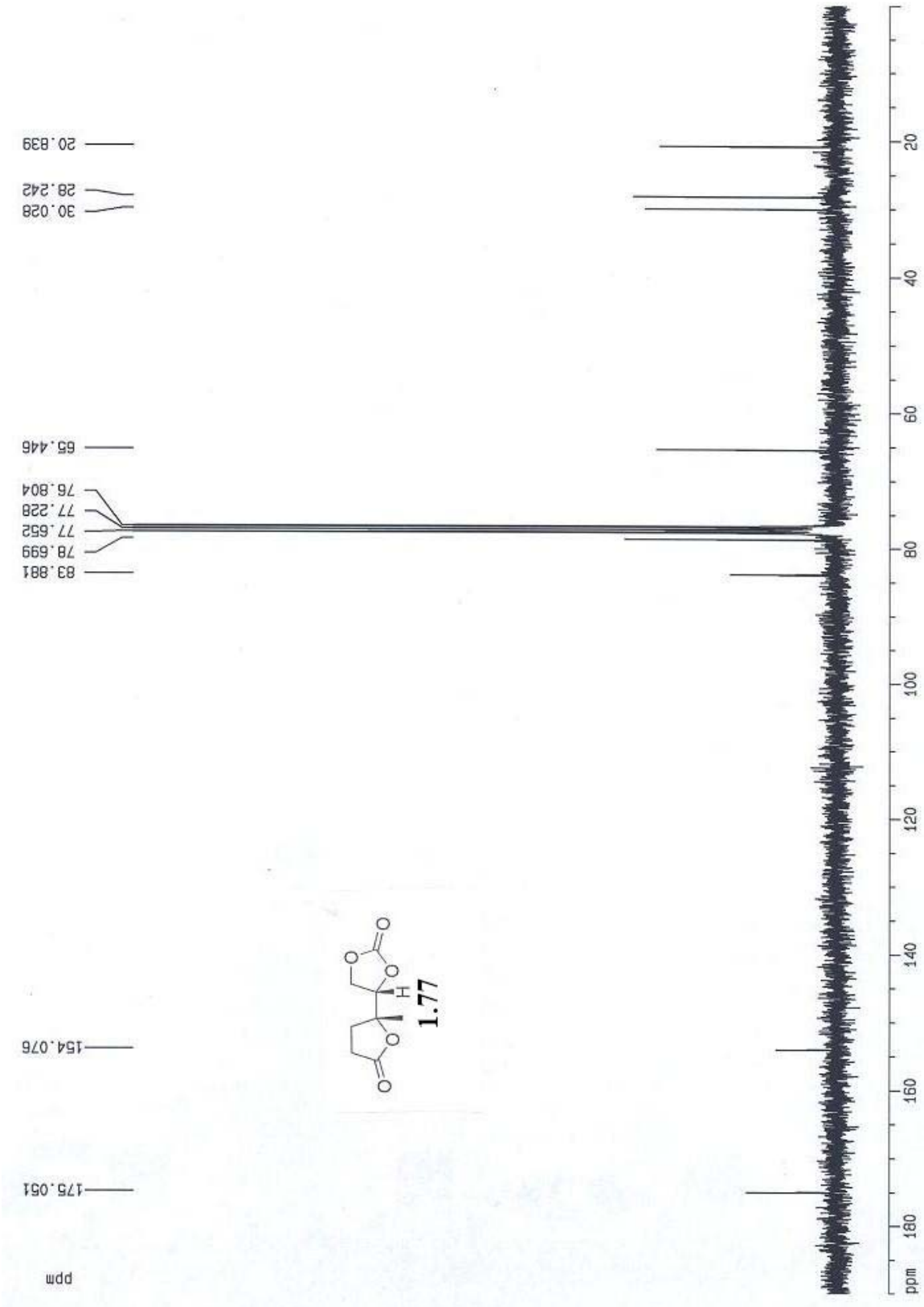
1.1679
1.1227
3.9929
Integral
ppm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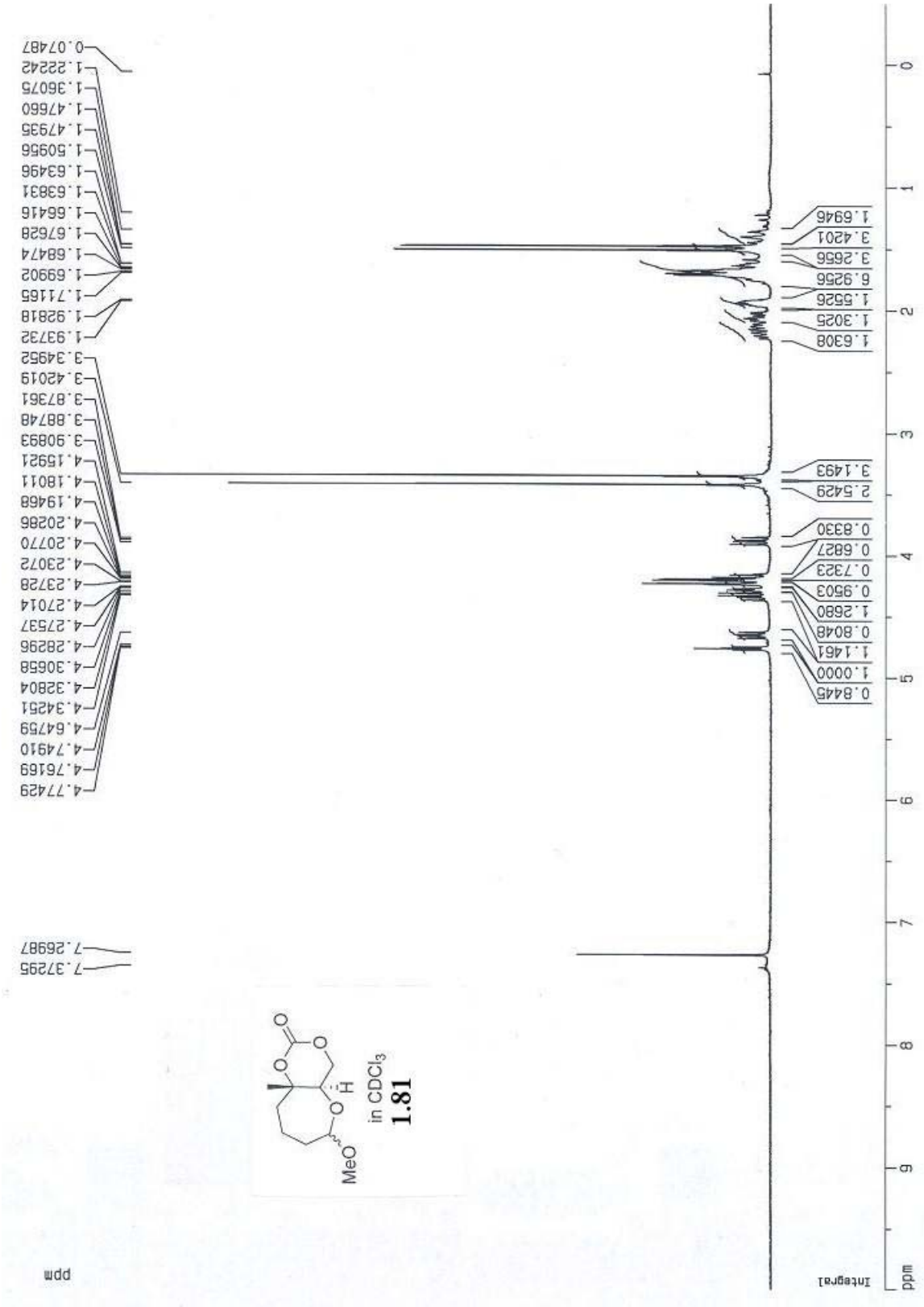
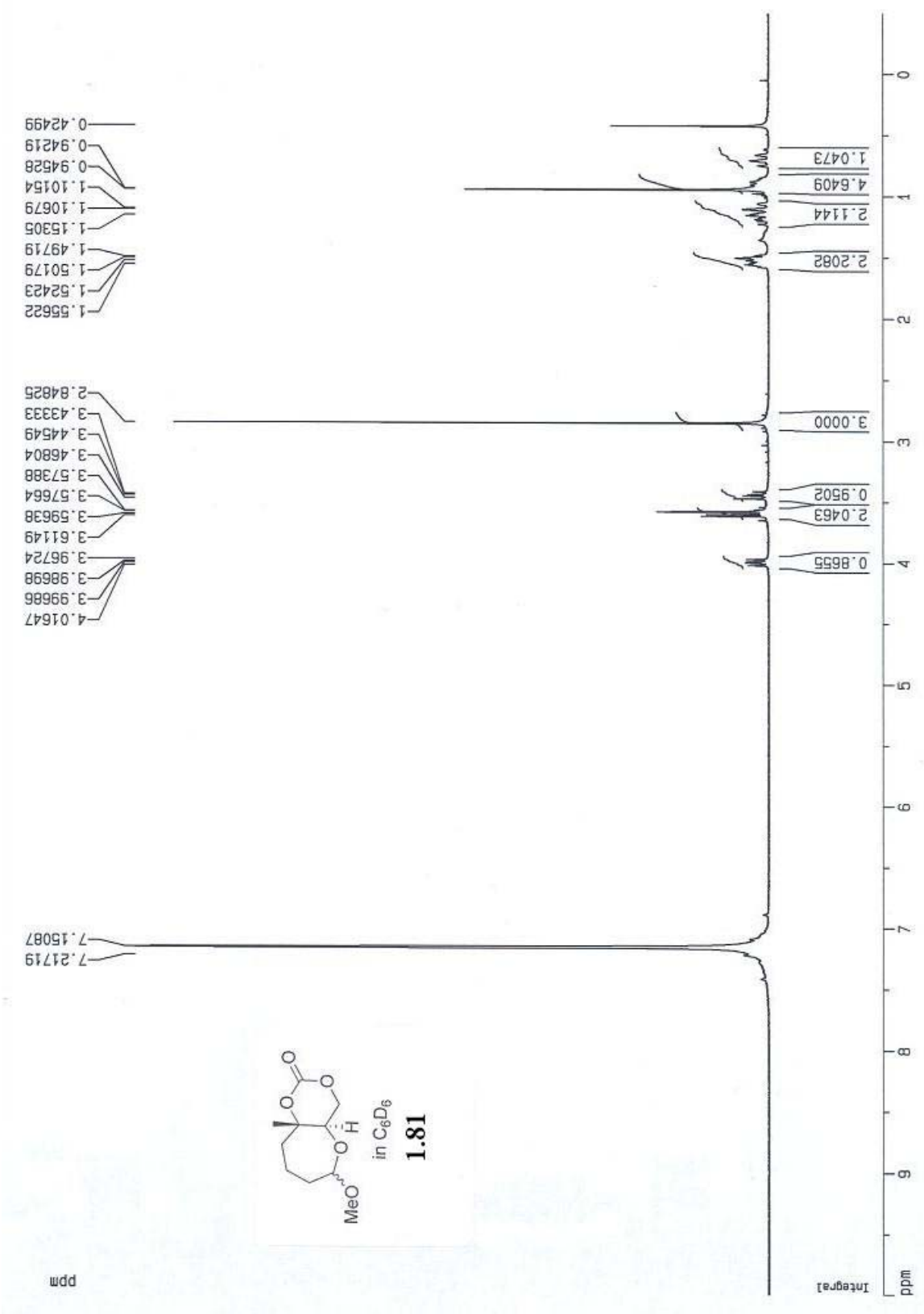
65.446
76.804
77.228
77.652
78.699
83.881
154.076
175.051
ppm
20
40
60
80
100
120
140
160
180
ppm

1.77

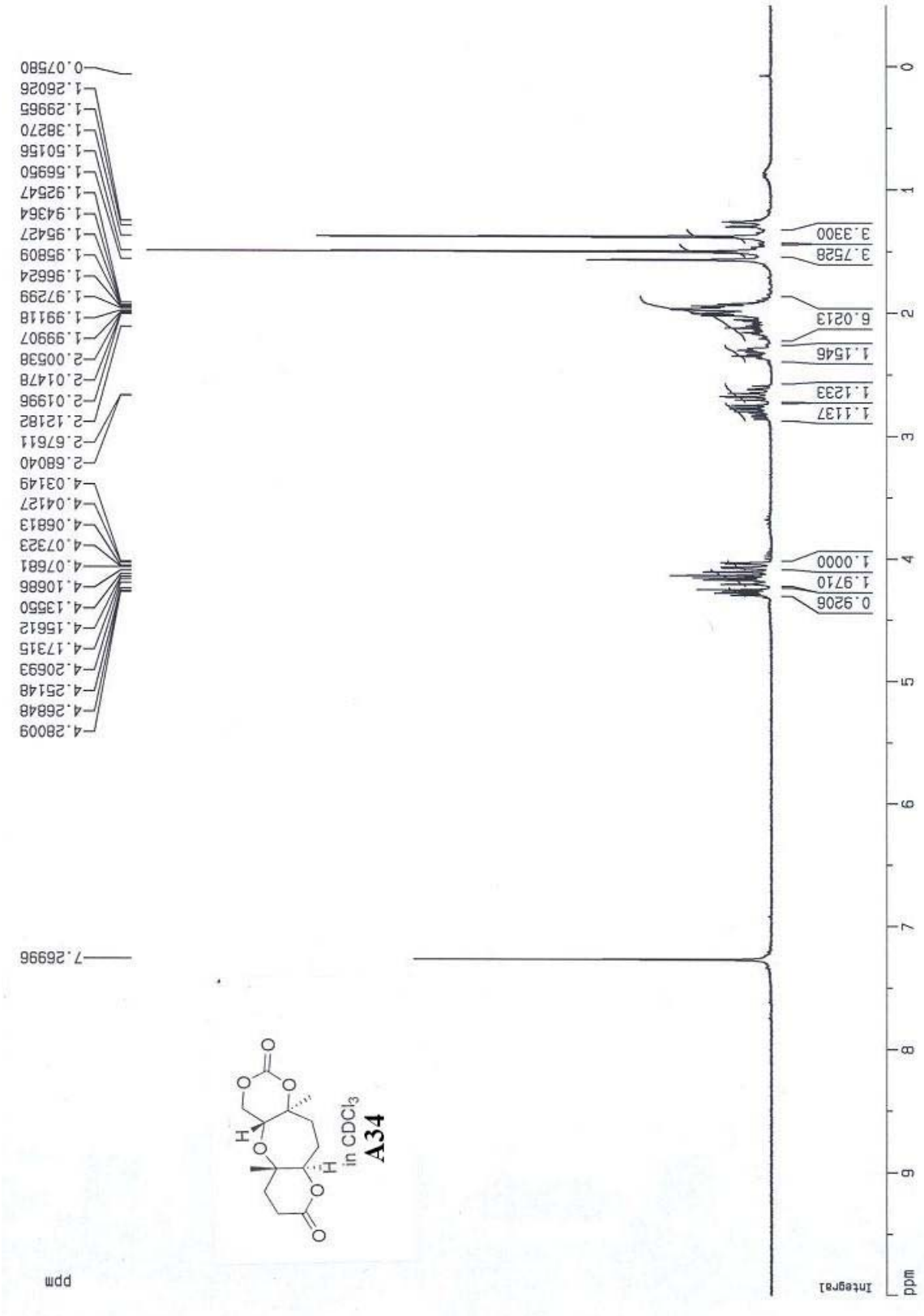

in $CDCl_3$
1.81
MeO
H
Integral
ppm

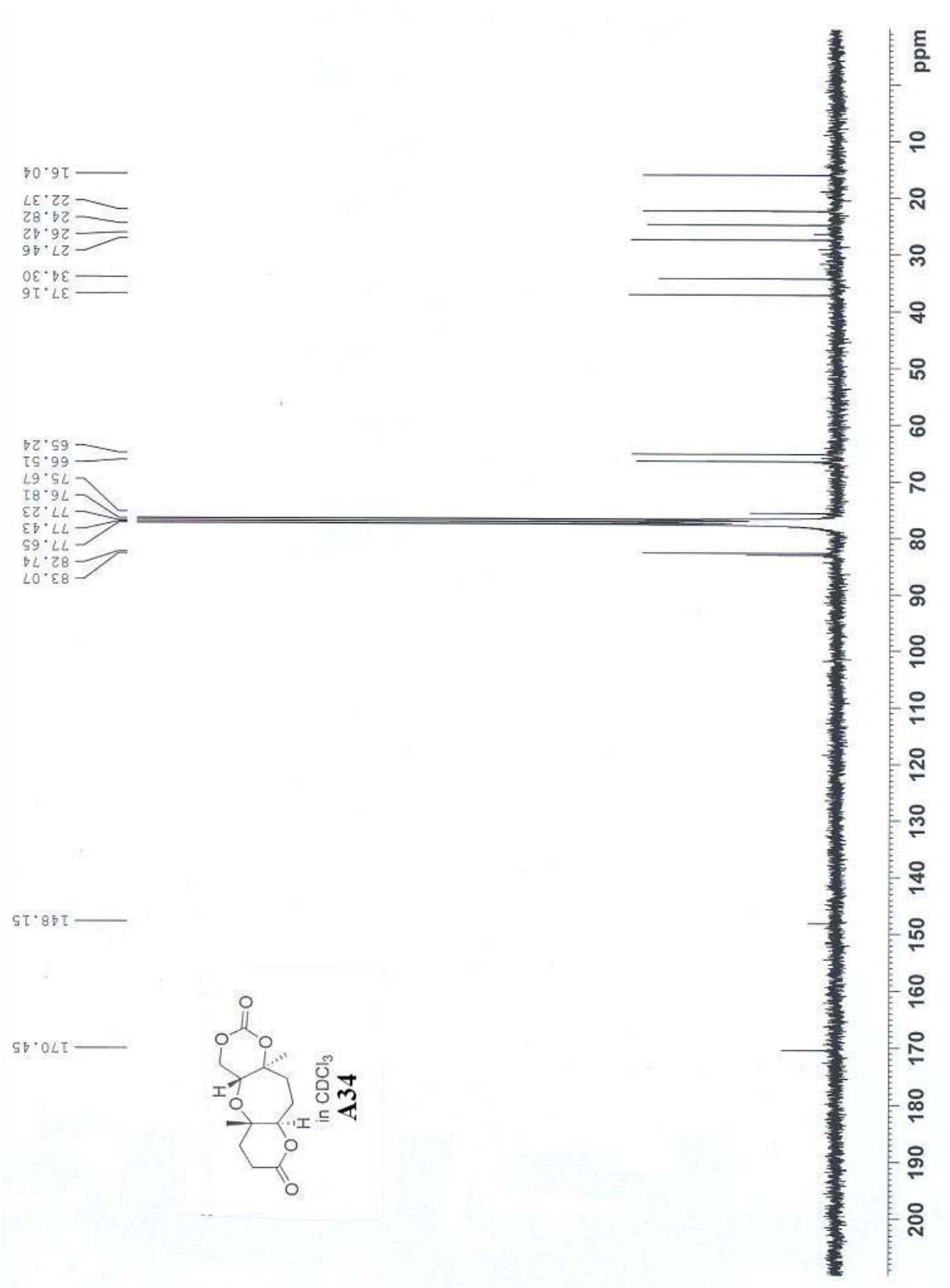
16.724
18.332
19.323
19.547
34.356
34.464
41.655
43.225
55.711
56.322
62.700
66.339
66.666
68.069
76.806
77.230
77.654
83.028
84.219
102.818
104.337
148.202
147.959
MeO
H
O
in CDCl3
1.81
ppm
20
40
60
80
100
120
140
160
ppm

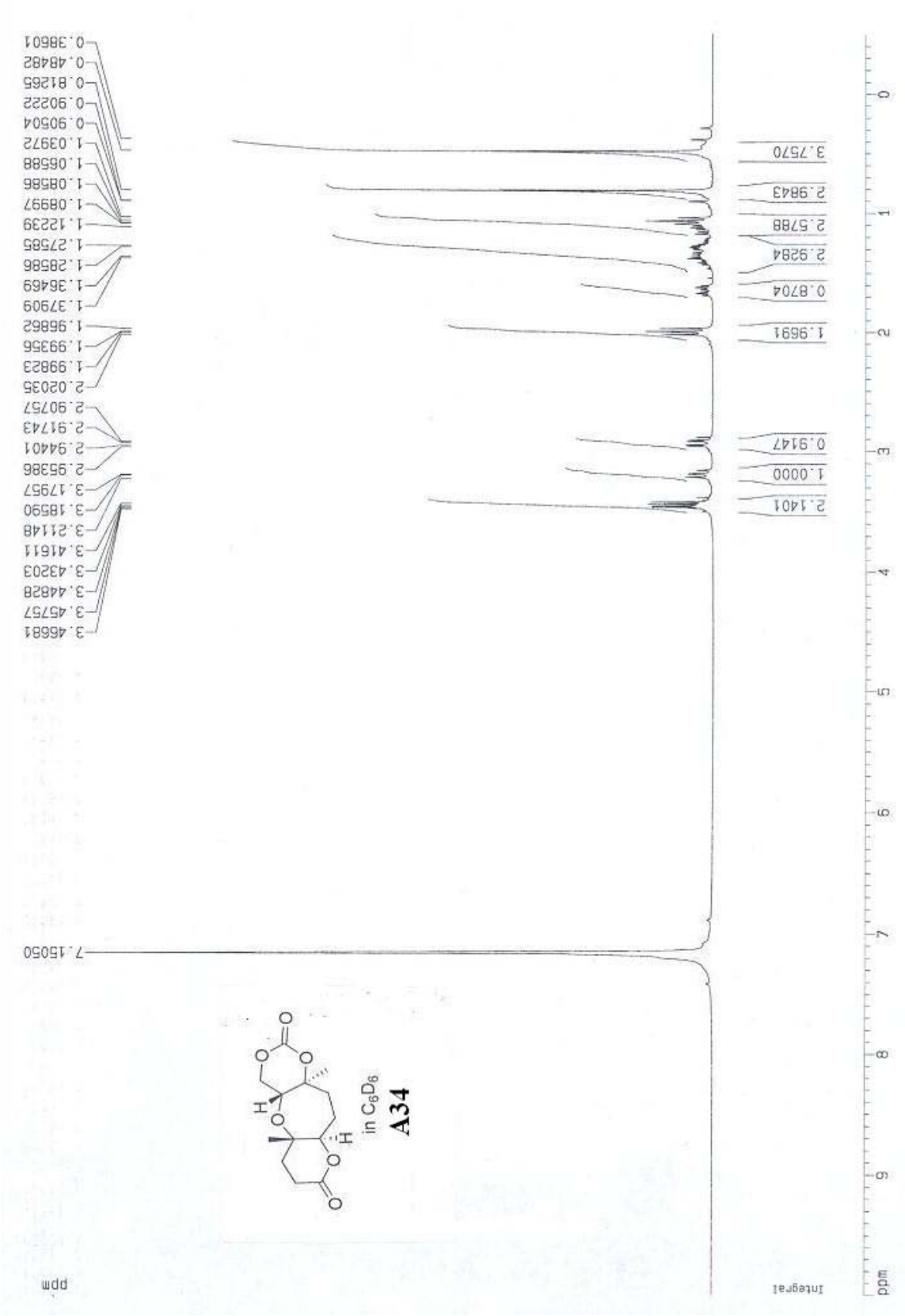

MeO
H
in C_6D_6
1.81
ppm
Integral

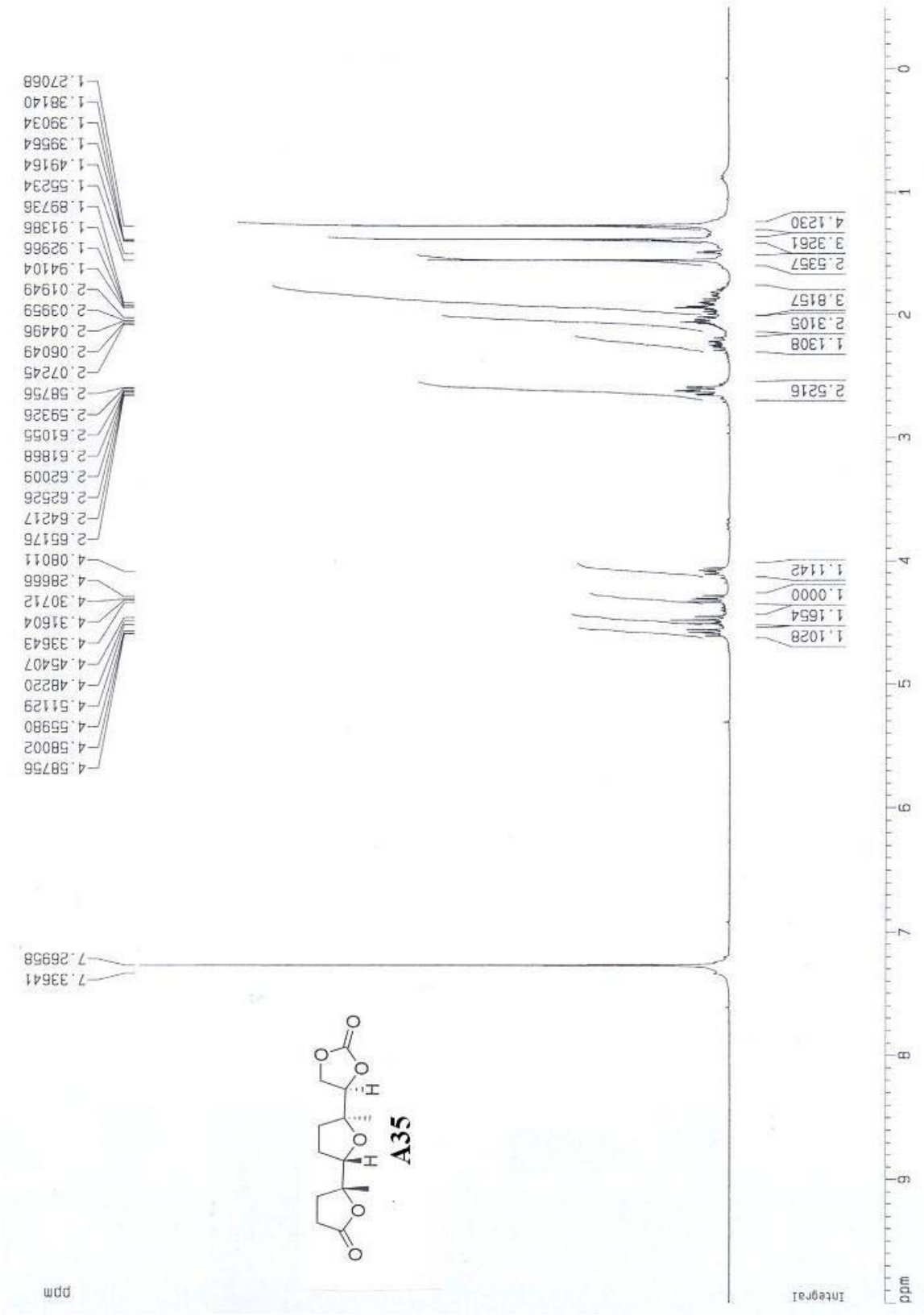
7.26997
4.59965
4.57914
4.49815
4.40627
4.38559
4.08263
2.64166
2.61465
2.61092
2.58296
2.06890
2.05464
2.04141
1.57770
1.39305
1.37848
1.26885
1.22607
0.8408
1.0000
0.8707
0.8771
1.9825
1.2538
2.3549
3.5553
3.1409
3.1814
A33
ppm
Integral

ppm
176.743
155.065
86.903
83.549
83.152
79.495
77.657
77.233
76.809
66.058
34.121
29.264
29.185
26.704
23.830
21.026
A33


0.07580
1.26026
1.29965
1.38270
1.50156
1.56950
1.92547
1.94364
1.95427
1.95809
1.96624
1.97299
1.99118
1.99907
2.00538
2.01478
2.01996
2.12182
2.67611
2.68040
4.03149
4.04127
4.06813
4.07323
4.07681
4.10686
4.13550
4.15612
4.17315
4.20693
4.25148
4.26848
4.28009
7.26996
3.3300
3.7528
6.0213
1.1546
1.1233
1.1137
1.0000
1.9710
0.9206
Integral
ppm
0
1
2
3
4
5
6
7
8
9
ppm
H
H
in CDCl3
A34


170.45
148.15
83.07
82.74
77.65
77.43
77.23
76.81
75.67
66.51
65.24
37.16
34.30
27.46
26.42
24.82
22.37
16.04
ppm
in CDCl3
A34


in C_6D_6
A34


A35
ppm
Integral

21.296
23.383
26.987
29.120
29.444
34.524
66.201
76.810
77.233
77.657
80.346
83.128
85.121
86.947
154.974
176.721
ppm
20
40
60
80
100
120
140
160
180
A35

A36
ppm
Integral
7.27004
4.42314
4.38493
4.26078
4.24030
4.22566
4.20520
4.12408
4.09020
4.05512
4.02809
4.00761
2.73514
2.71683
2.11211
2.05369
1.99248
1.98406
1.97506
1.95822
1.94585
1.90610
1.89023
1.85815
1.84257
1.81486
1.58042
1.49343
1.49131
1.47231
1.46833
1.25834
1.24092
1.23810
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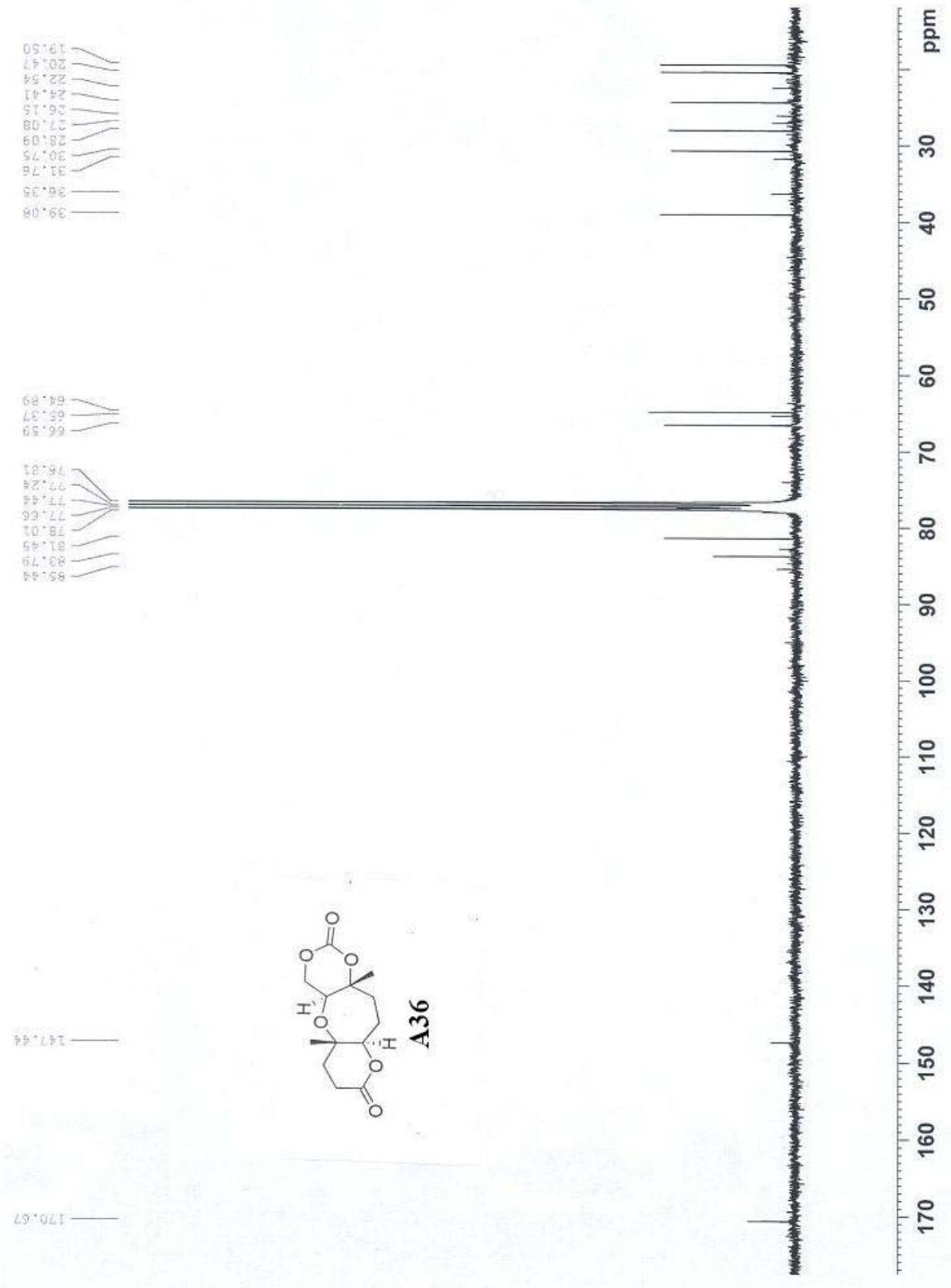
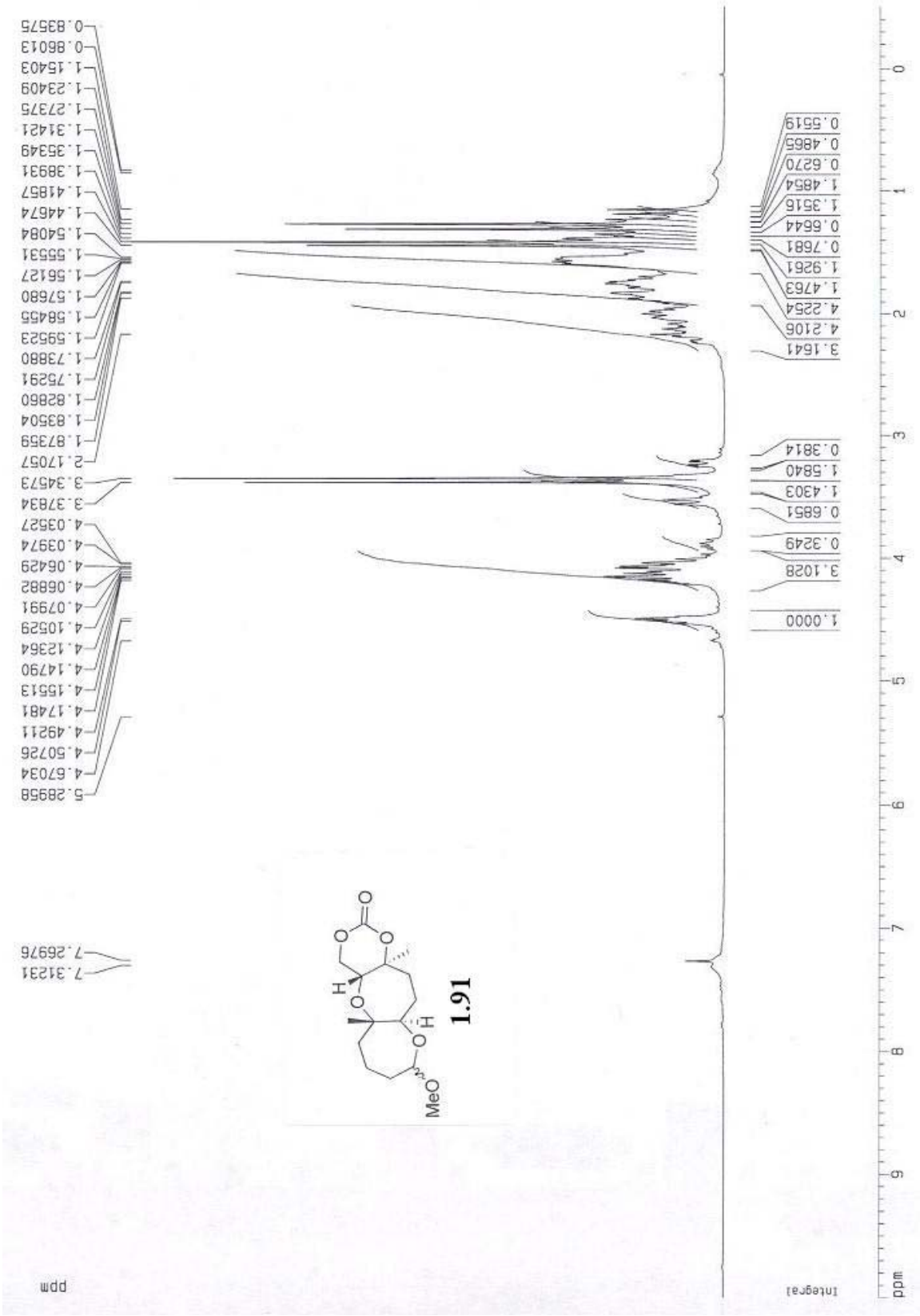
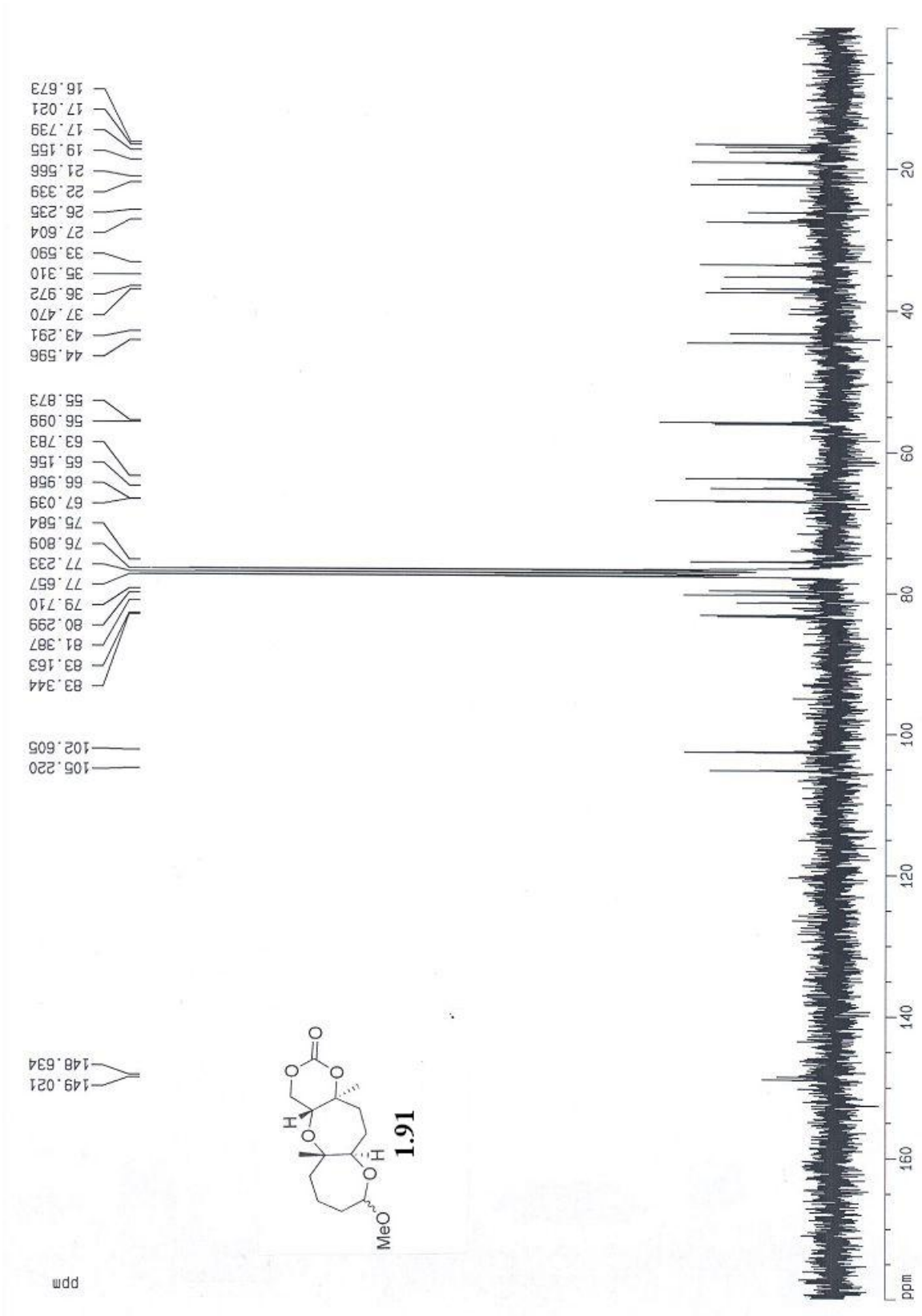
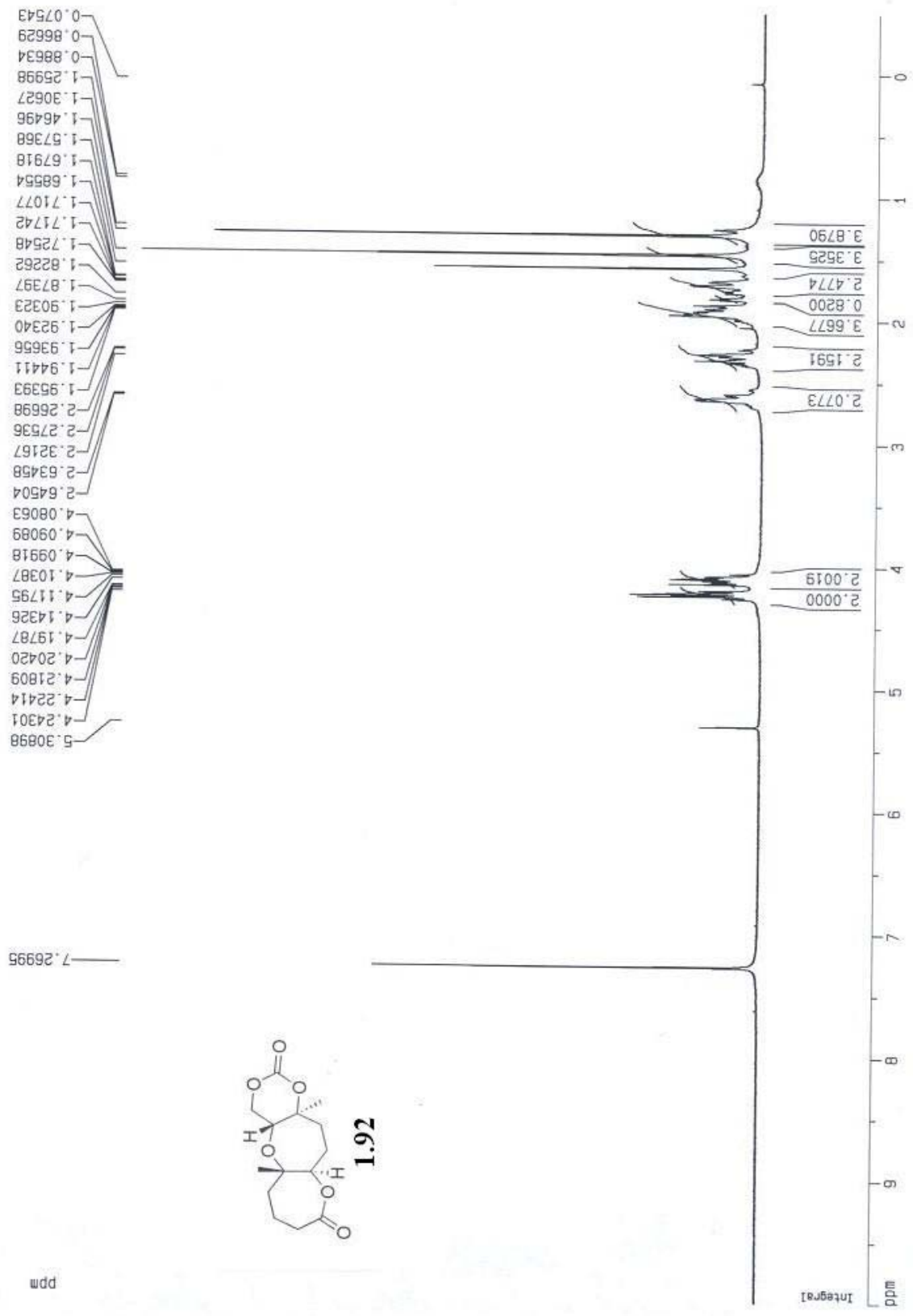
2.9240
3.0819
5.8799
0.9745
0.8810
2.0225
1.0000
0.9048

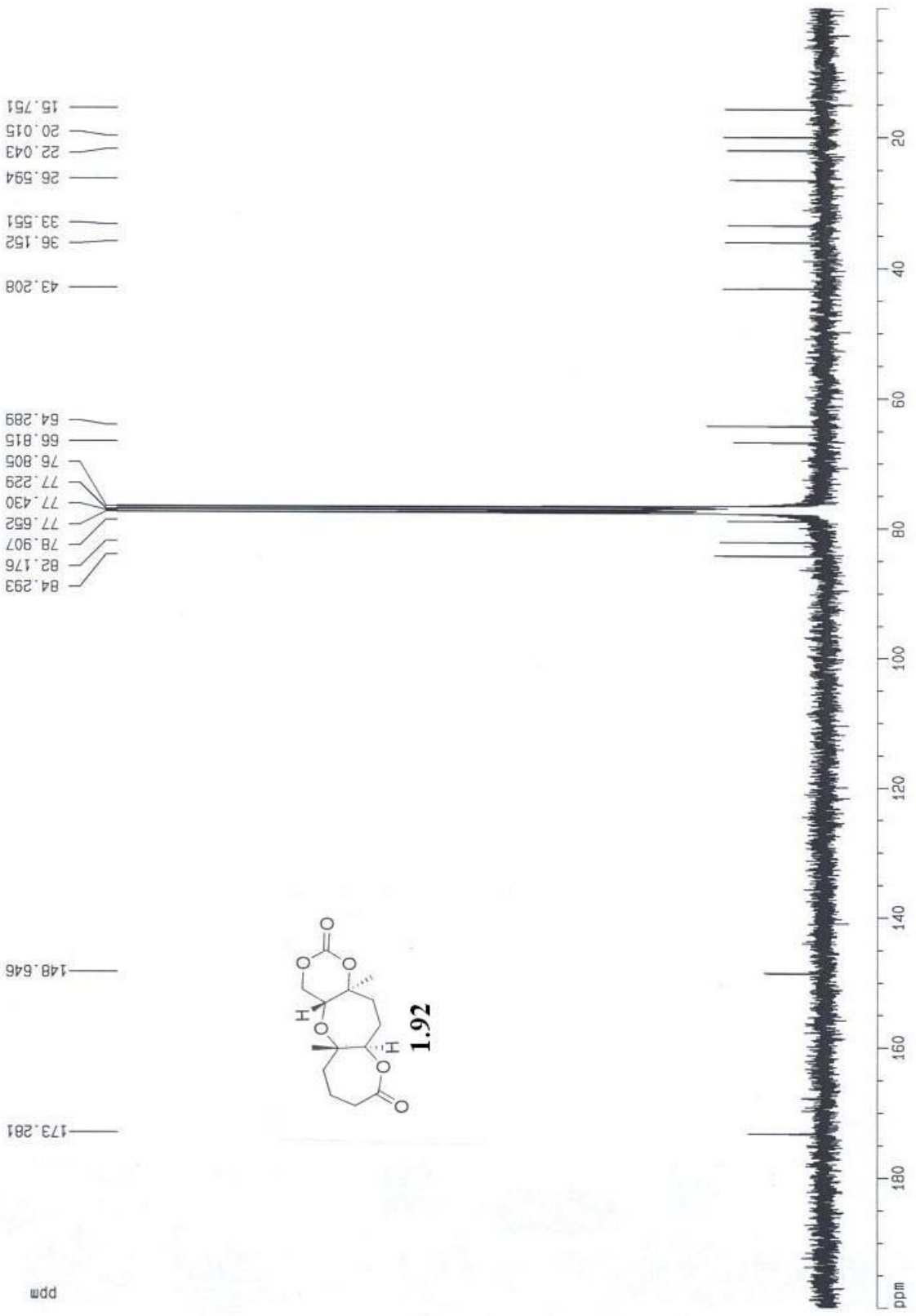

19.50
20.47
22.54
24.41
26.15
27.08
28.09
30.75
31.74
36.35
39.08
64.89
65.37
66.59
76.81
77.24
77.44
77.66
78.01
81.45
83.79
85.44
147.44
170.67
ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170

A36

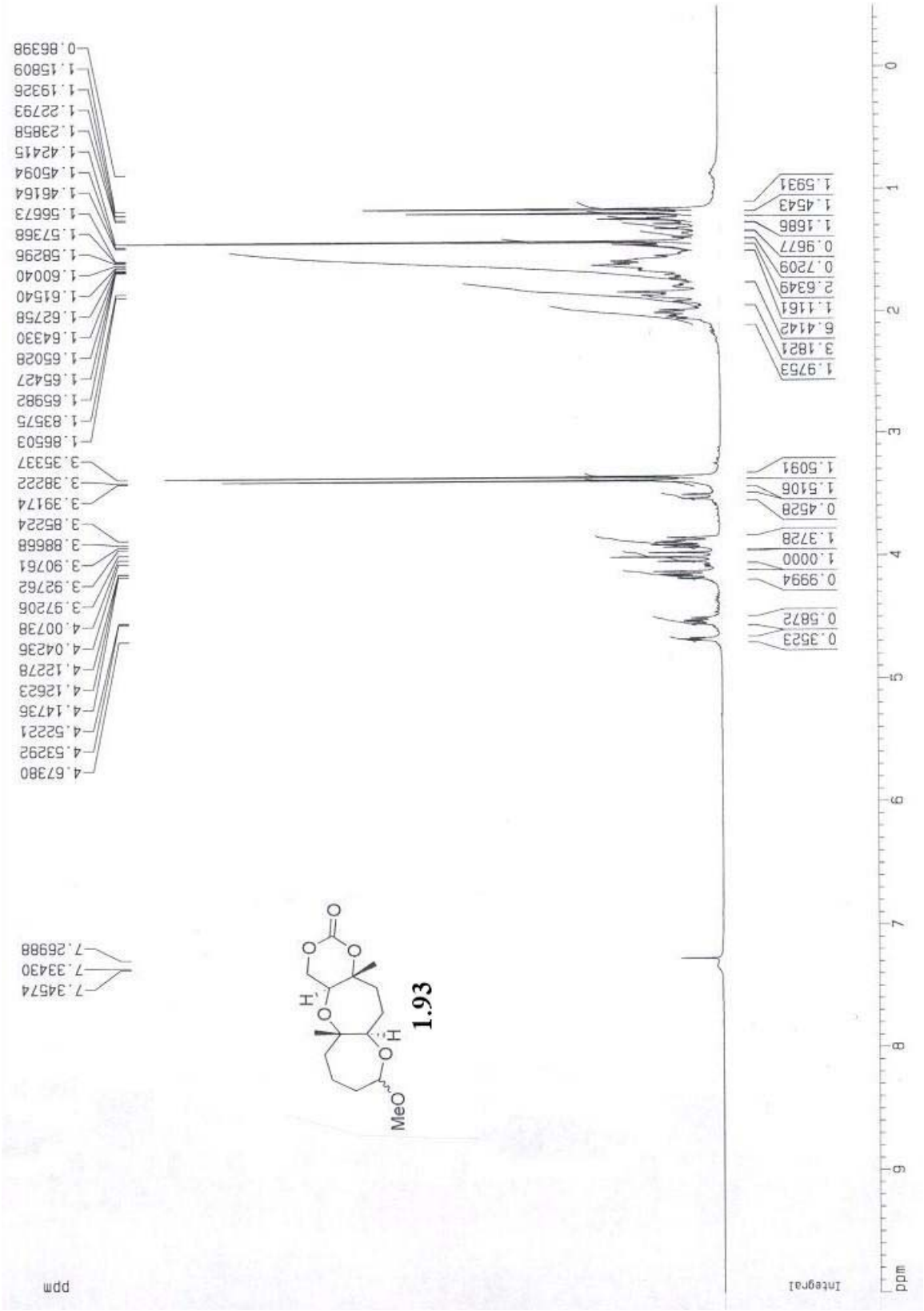

1.91
MeO
ppm
Integral

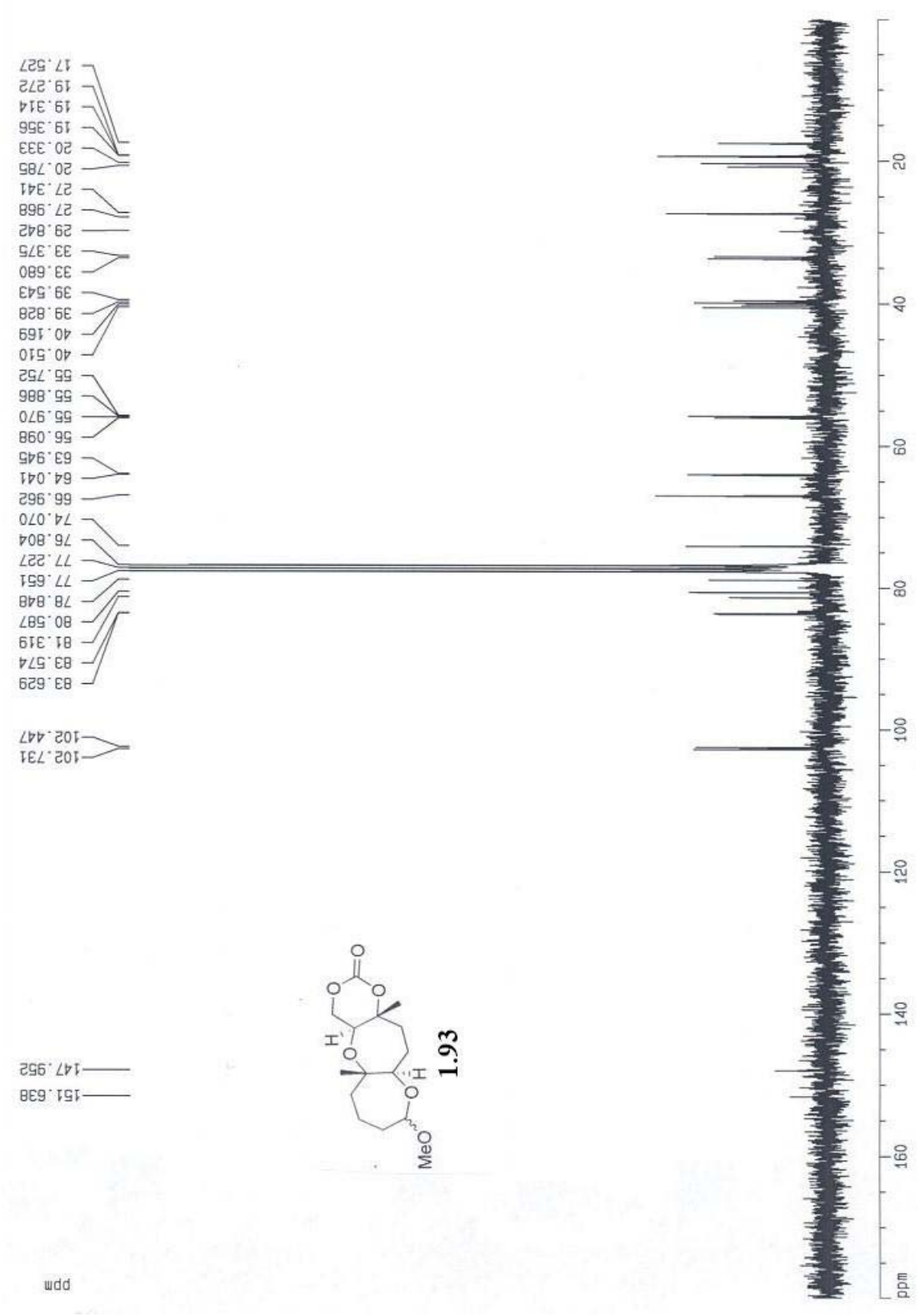

16.673
17.021
17.739
19.155
21.566
22.339
26.235
27.604
33.590
35.310
36.972
37.470
43.291
44.596
55.873
56.099
63.783
65.156
66.958
67.039
75.584
76.809
77.233
77.657
79.710
80.299
81.387
83.163
83.344
102.605
105.220
148.634
149.021
MeO
H
H
1.91
ppm
20
40
60
80
100
120
140
160


1.92
ppm
Integral

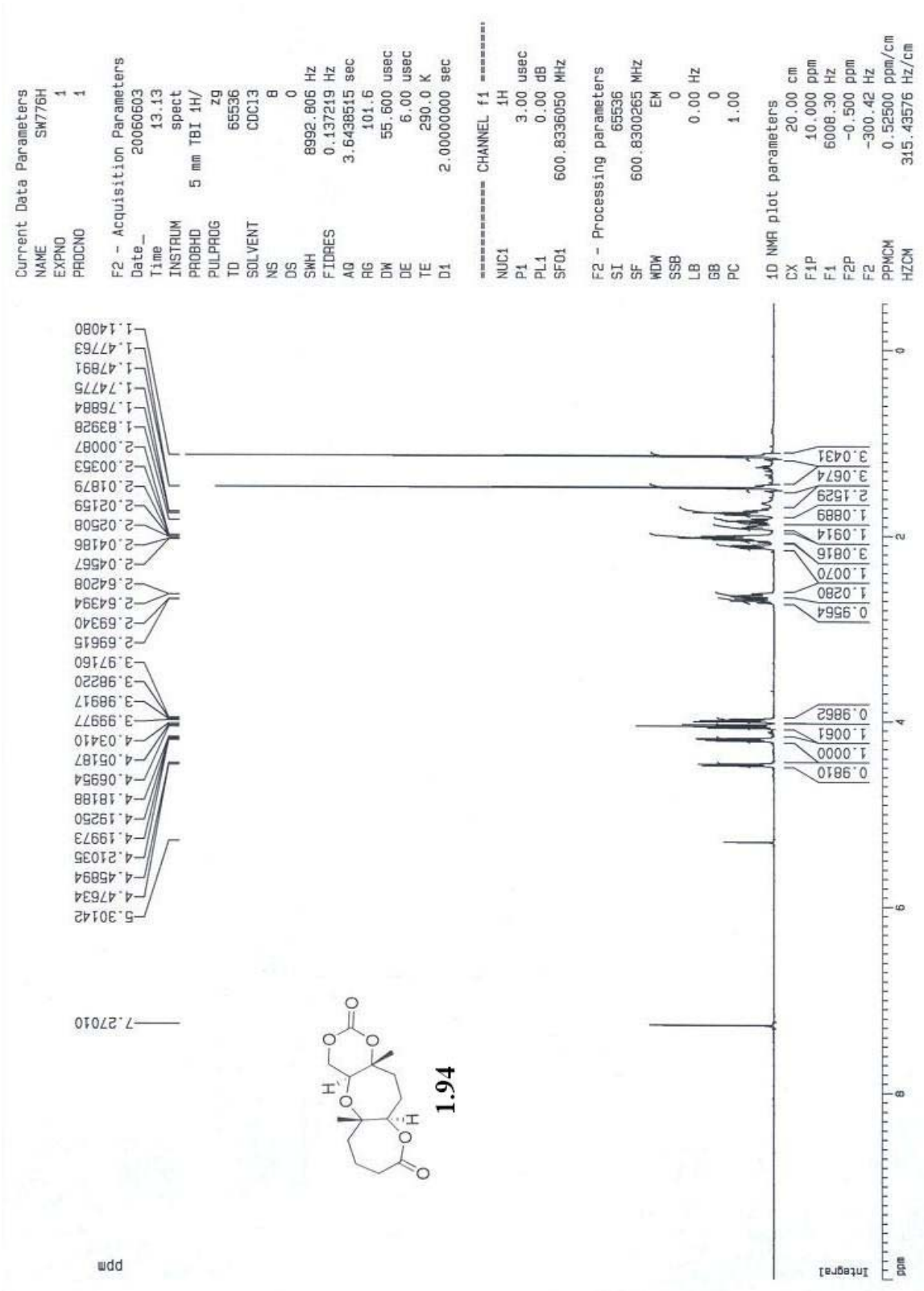

15.751
20.015
22.043
26.594
33.551
36.152
43.208
64.289
66.815
76.805
77.229
77.430
77.652
78.907
82.176
84.293
148.646
173.281
ppm
20
40
60
80
100
120
140
160
180
ppm

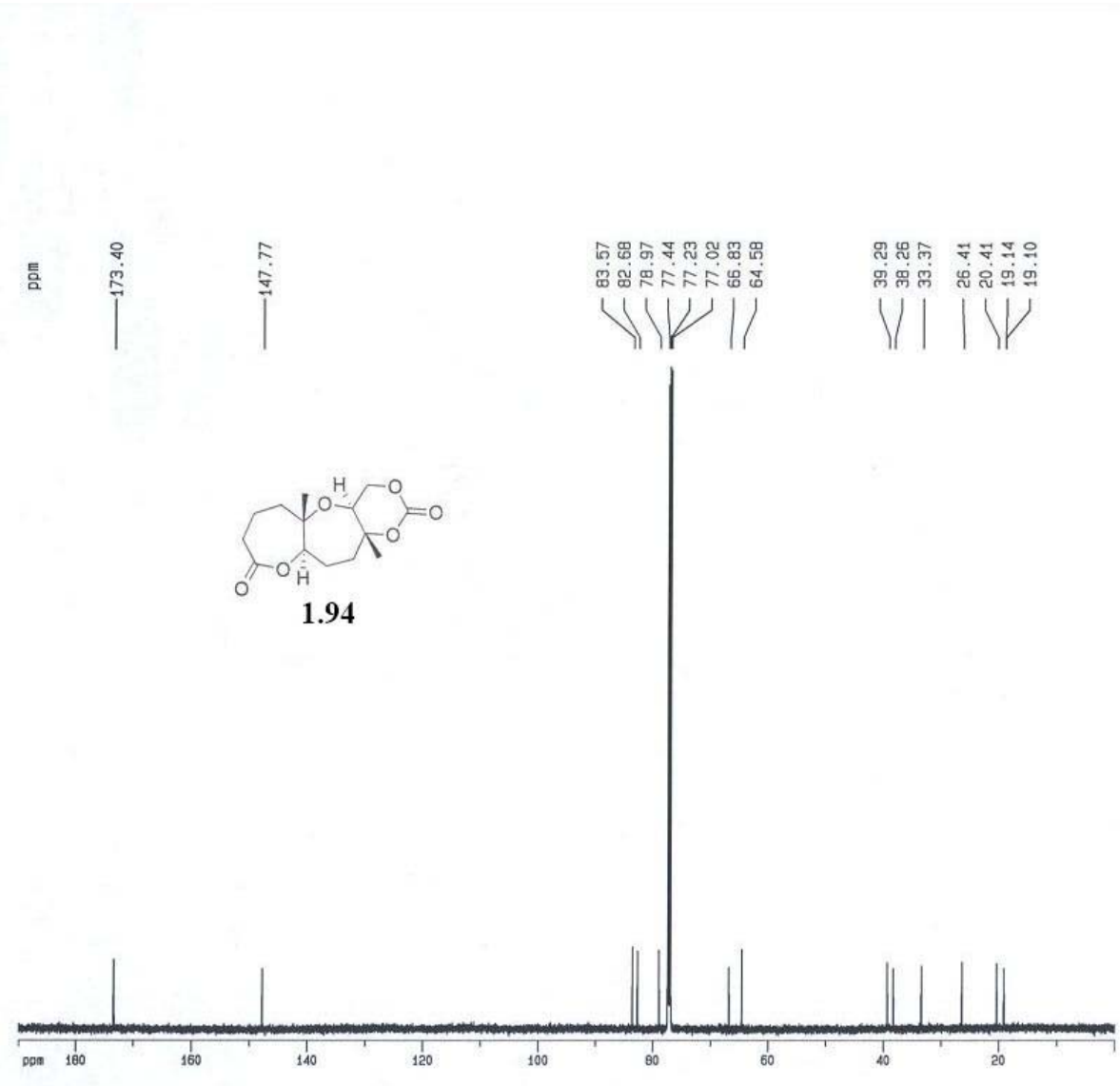
1.92


1.93
MeO
ppm
Integral


17.527
19.272
19.314
19.356
20.333
20.785
27.341
27.968
29.842
33.375
33.680
39.543
39.828
40.169
40.510
55.752
55.886
55.970
56.098
63.945
64.041
66.962
74.070
76.804
77.227
77.651
78.848
80.587
81.319
83.574
83.629
102.447
102.731
147.952
151.638
ppm
20
40
60
80
100
120
140
160
ppm
O
O
O
O
H
O
H
O
MeO

1.93


Current Data Parameters
NAME SW776H
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060603
Time 13.13
INSTRUM spect
PROBHD 5 mm TBI 1H/
PULPROG zg
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 8992.806 Hz
FIDRES 0.137219 Hz
AQ 3.6438515 sec
RG 101.6
DW 55.600 usec
DE 6.00 usec
TE 290.0 K
D1 2.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 3.00 usec
PL1 0.00 dB
SFO1 600.8336050 MHz
F2 - Processing parameters
SI 65536
SF 600.8300265 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
F1P 10.000 ppm
F1 6008.30 Hz
F2P -0.500 ppm
F2 -300.42 Hz
PPMCM 0.52500 ppm/cm
HZCM 315.43576 Hz/cm
1.14080
1.47763
1.47891
1.74775
1.76884
1.83928
2.00087
2.00353
2.01879
2.02159
2.02508
2.04186
2.04567
2.64208
2.64394
2.69340
2.69615
3.97160
3.98220
3.98917
3.99977
4.03410
4.05187
4.06954
4.18188
4.19250
4.19973
4.21035
4.45894
4.47634
5.30142
7.27010
0.9564
1.0280
1.0070
3.0816
1.0914
1.0889
2.1529
3.0674
3.0431
0.9862
1.0061
1.0000
0.9810
1.94
Integral
ppm
ppm



1.94

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Current Data Parameters
NAME              SW776C13
EXPNO                    1
PROCNO                   1

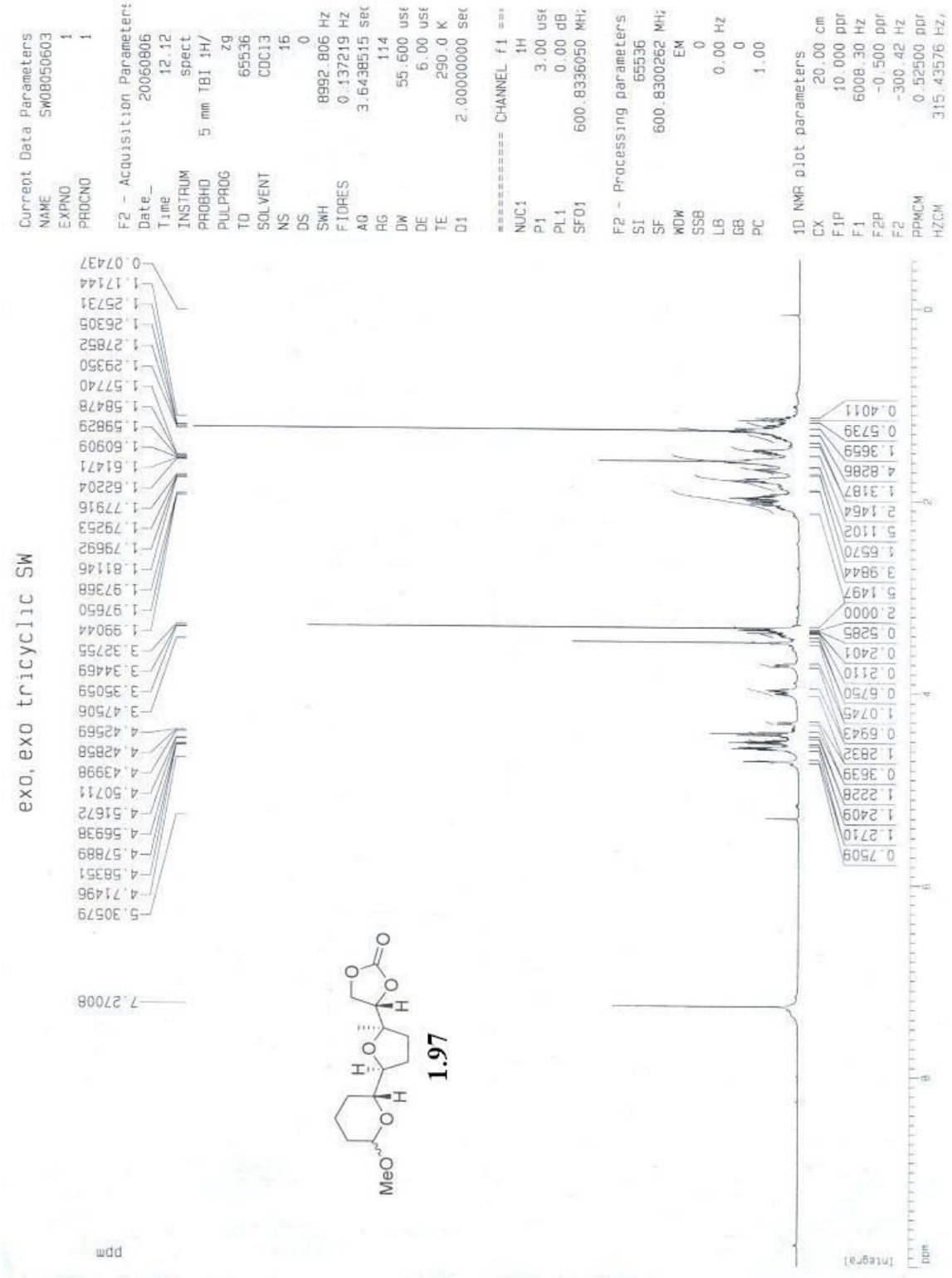
F2 - Acquisition Parameters
Date_             20060603
Time                 13.40
INSTRUM              spect
PROBHD     5 mm TBI 1H/
PULPROG               zgpg
TD                   65536
SOLVENT              CDCl3
NS                     779
DS                       0
SWH              37878.789 Hz
FIDRES           0.577984 Hz
AQ               0.8651252 sec
RG                   32768
DW                  13.200 usec
DE                   6.00 usec
TE                  290.0 K
D1               8.00000000 sec
d11              0.03000000 sec
d12              0.00002000 sec

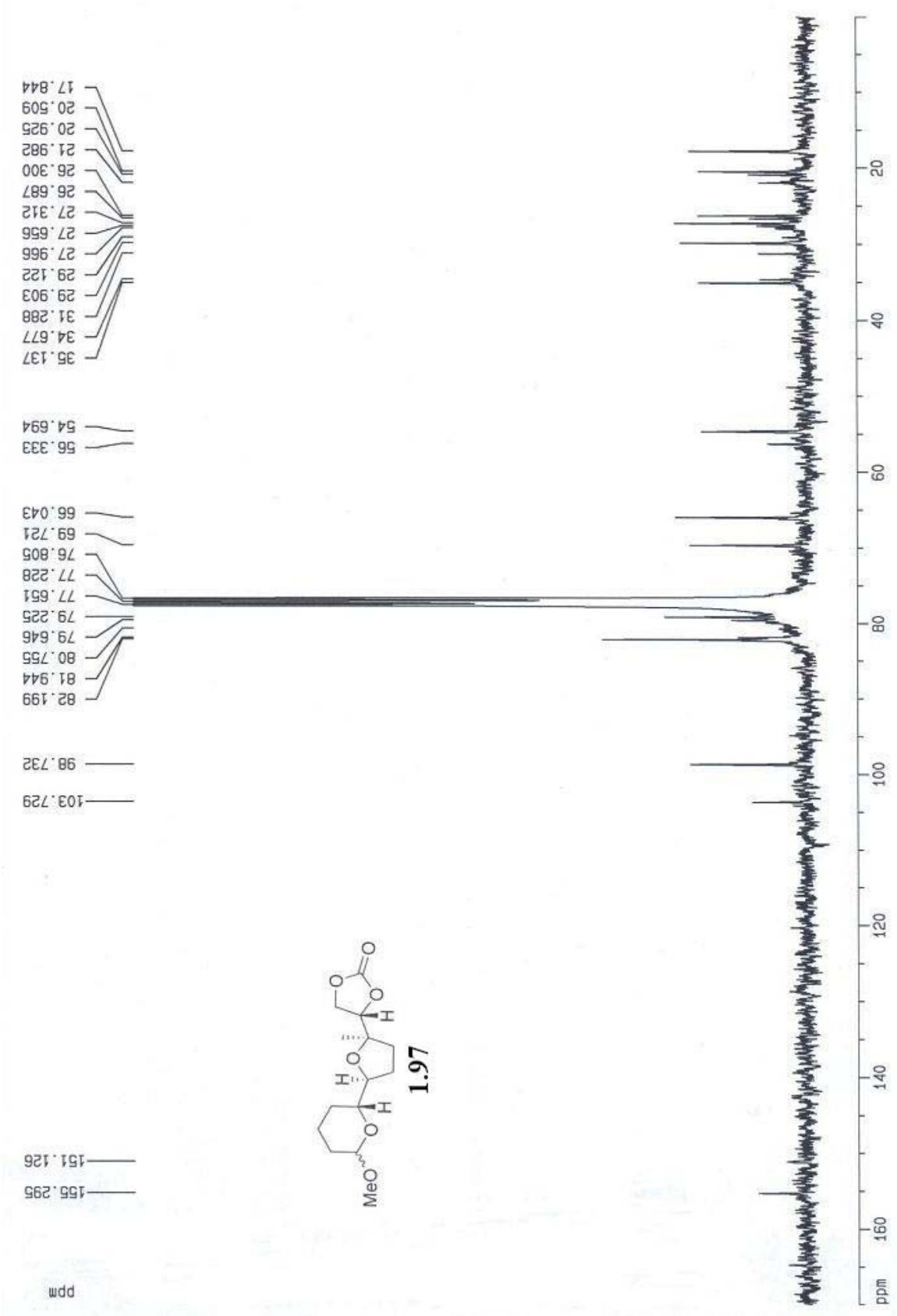
========== CHANNEL f1 ==========
NUC1                    13C
P1                   10.00 usec
PL1                   0.00 dB
SFO1           151.0953827 MHz

========== CHANNEL f2 ==========
CPDPRG2              waltz16
NUC2                    1H
PCPD2               100.00 usec
PL2                   0.00 dB
PL12                 12.00 dB
PL13                 120.00 dB
SFO2           600.8336050 MHz

F2 - Processing parameters
SI                   65536
SF             151.0788008 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.00

1D NMR plot parameters
CX                   20.00 cm
F1P                190.000 ppm
F1                28704.97 Hz
F2P                  0.000 ppm
F2                    0.00 Hz
PPMCM              9.50000 ppm/cm
HZCM            1435.24854 Hz/cm
```


exo,exo tricyclic SW
1.97
MeO


17.844
20.509
20.925
21.982
26.300
26.687
27.312
27.656
27.966
29.122
29.903
31.288
34.677
35.137
54.694
56.333
66.043
69.721
76.805
77.228
77.651
79.225
79.646
80.755
81.944
82.199
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MeO
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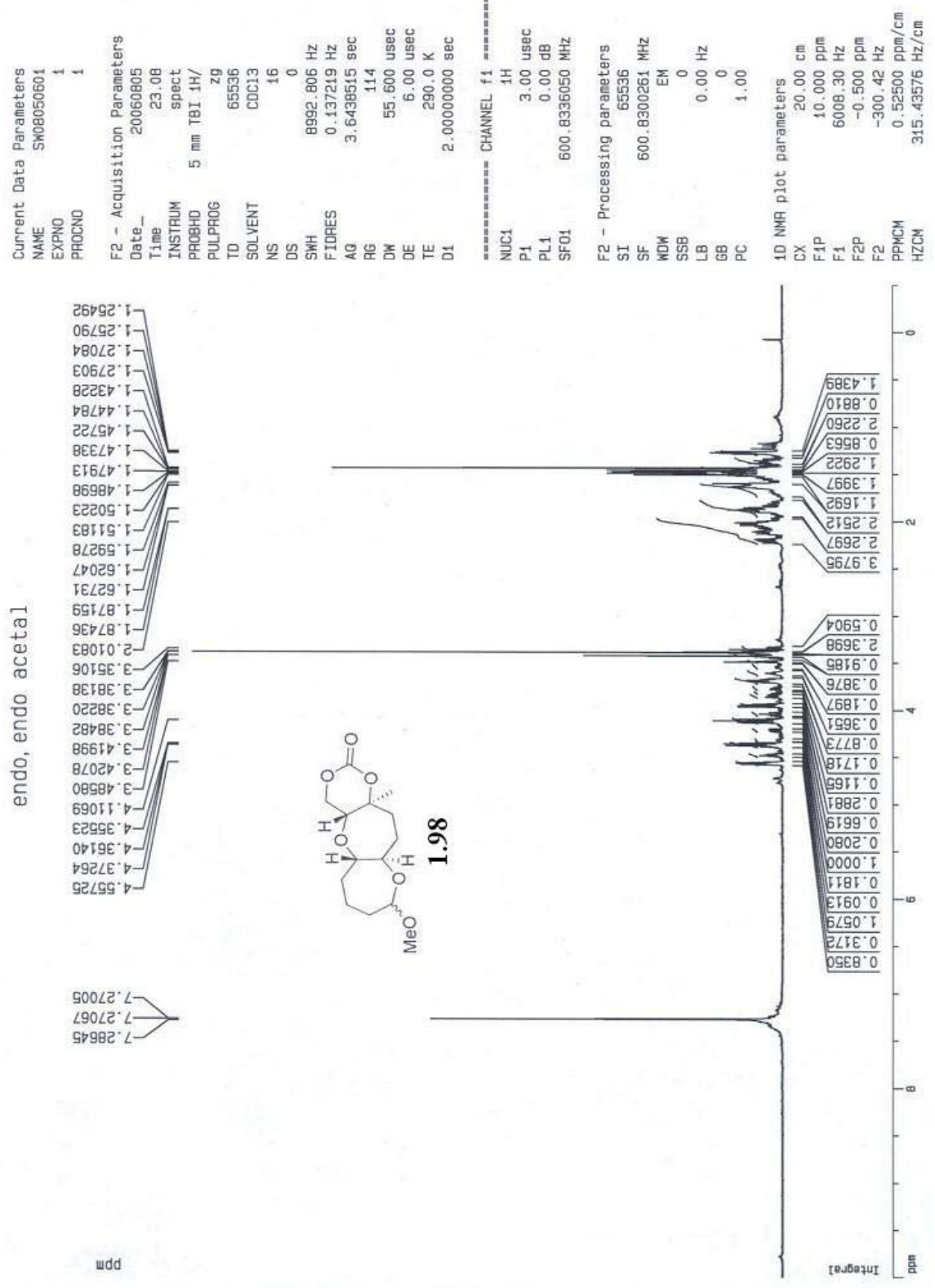
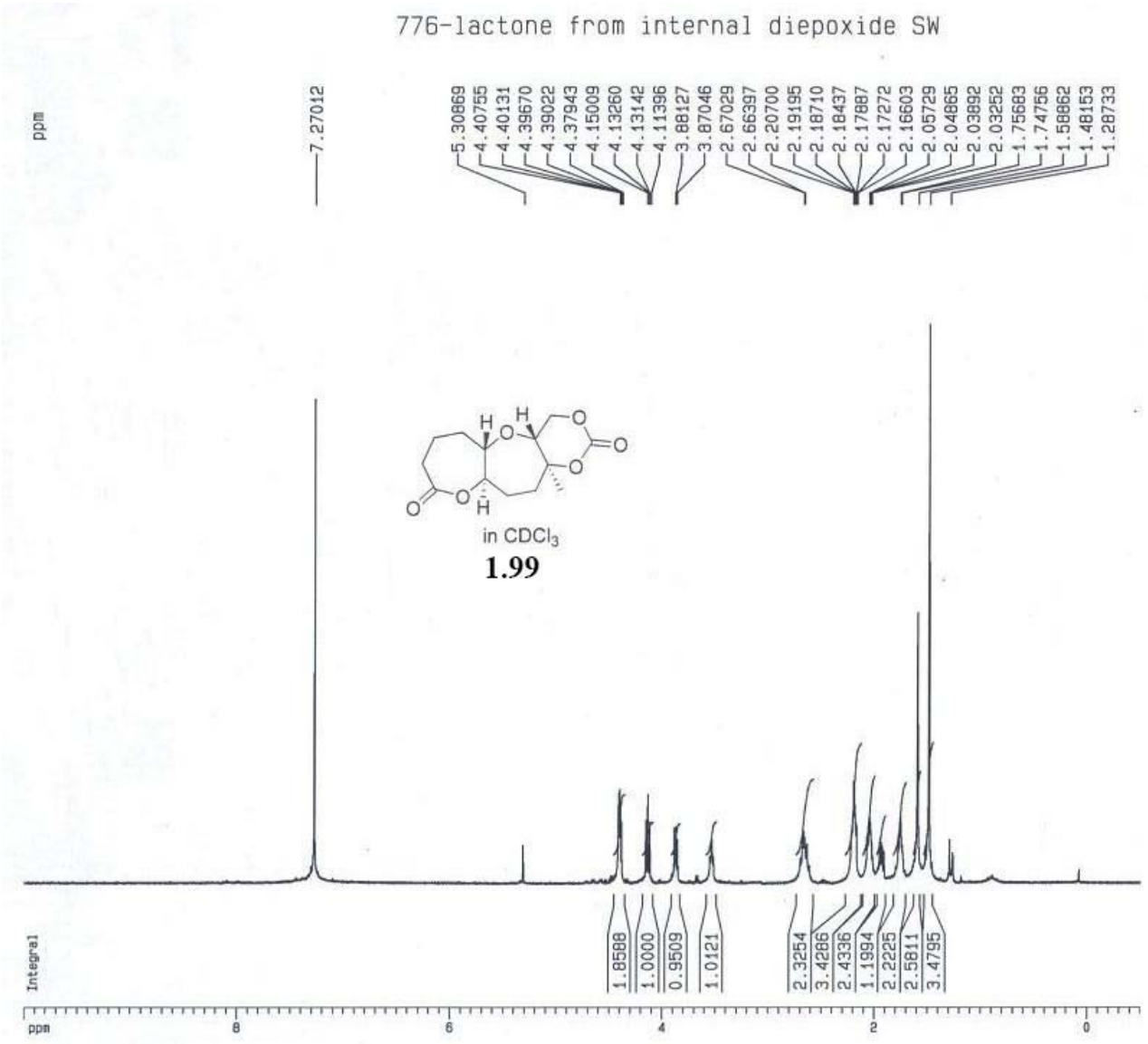
ppm
20
40
60
80
100
120
140
160


endo, endo acetal
Current Data Parameters
NAME SM08050601
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060805
Time 23.08
INSTRUM spect
PROBHD 5 mm TBI 1H/
PULPROG zg
TD 65536
SOLVENT CDCl3
NS 16
DS 0
SWH 8992.806 Hz
FIDRES 0.137219 Hz
AQ 3.6438515 sec
RG 114
DW 55.600 usec
DE 6.00 usec
TE 290.0 K
D1 2.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 3.00 usec
PL1 0.00 dB
SFO1 600.8336050 MHz
F2 - Processing parameters
SI 65536
SF 600.8300261 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
F1P 10.000 ppm
F1 6008.30 Hz
F2P -0.500 ppm
F2 -300.42 Hz
PPMCM 0.52500 ppm/cm
HZCM 315.43576 Hz/cm
7.28645
7.27067
7.27005
4.55725
4.37264
4.36140
4.35523
4.11069
3.48580
3.42078
3.41998
3.38482
3.38220
3.38138
3.35106
2.01083
1.87436
1.87159
1.62731
1.62047
1.59278
1.51183
1.50223
1.48698
1.47913
1.47338
1.45722
1.44784
1.43228
1.27903
1.27084
1.25790
1.25492
0.8350
0.3172
1.0579
0.0913
0.1811
1.0000
0.2080
0.6619
0.2881
0.1165
0.1718
0.8773
0.3651
0.1897
0.3876
0.9185
2.3698
0.5904
3.9795
2.2697
2.2512
1.1692
1.3997
1.2922
0.8563
2.2260
0.8810
1.4389
MeO
1.98
ppm
Integral

F2 - Acquisition Parameters
Date_ 20060805
Time 23.19
INSTRUM spect
PROBHD 5 mm TBI 1H/
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 5186
DS 0
SWH 37878.789 Hz
FIDRES 0.577984 Hz
AQ 0.8651252 sec
RG 32768
DW 13.200 usec
DE 6.00 usec
TE 290.0 K
D1 8.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec
======== CHANNEL f1 ======
NUC1 13C
P1 10.00 usec
PL1 0.00 dB
SFO1 151.0953827 MHz
======== CHANNEL f2 ======
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 0.00 dB
PL12 12.00 dB
PL13 120.00 dB
SFO2 600.0336050 MHz
F2 - Processing parameters
SI 65536
SF 151.0787974 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 0.85
1D NMR plot parameters
CX 20.00 cm
F1P 160.000 ppm
F1 24172.61 Hz
F2P 10.000 ppm
F2 1510.79 Hz
PPMCM 7.50000 ppm/cm
HZCM 1133.09062 Hz/cm
17.86
17.91
18.92
20.95
27.92
27.97
28.59
29.72
33.40
33.54
34.14
34.40
34.91
35.64
35.94
36.70
55.79
55.86
56.06
66.50
73.15
73.25
73.99
75.15
77.02
77.23
77.44
79.50
82.36
82.59
83.29
86.44
102.55
106.94
148.87
ppm
MeO
1.98



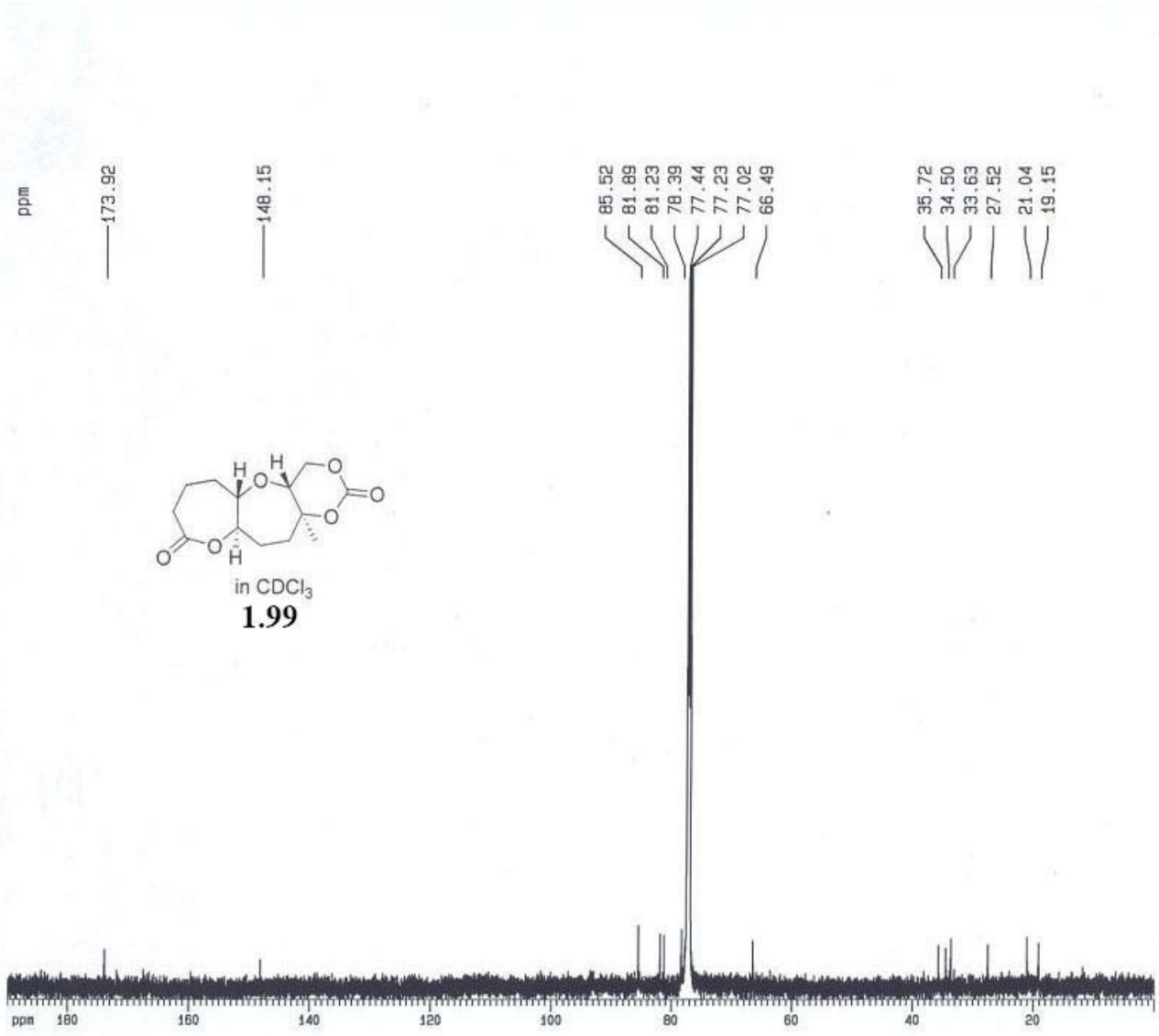
Current Data Parameters
NAME SW08070602
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060807
Time 15.51
INSTRUM spect
PROBHD 5 mm TBI 1H/
PULPROG zg
TD 65536
SOLVENT CDCl3
NS 32
DS 0
SWH 8992.806 Hz
FIDRES 0.137219 Hz
AQ 3.6438515 sec
RG 322.5
DW 55.600 usec
DE 6.00 usec
TE 290.0 K
D1 2.00000000 sec

========== CHANNEL f1 ========
NUC1 1H
P1 3.00 usec
PL1 0.00 dB
SFO1 600.8336050 MHz

F2 - Processing parameters
SI 65536
SF 600.8300262 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
F1P 10.000 ppm
F1 6008.30 Hz
F2P -0.500 ppm
F2 -300.42 Hz
PPMCM 0.52500 ppm/cm
HZCM 315.43576 Hz/cm



in $CDCl_3$

1.99

F2 - Acquisition Parameters

Date_	20060807
Time	16.09
INSTRUM	spect
PROBHD	5 mm TBI 1H/
PULPROG	zgpg
TD	65536
SOLVENT	CDCl3
NS	6000
DS	0
SWH	37878.789 Hz
FIDRES	0.577984 Hz
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TE	290.0 K
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d12	0.00002000 sec

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========== CHANNEL f2 ==========

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F2 - Processing parameters

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1D NMR plot parameters

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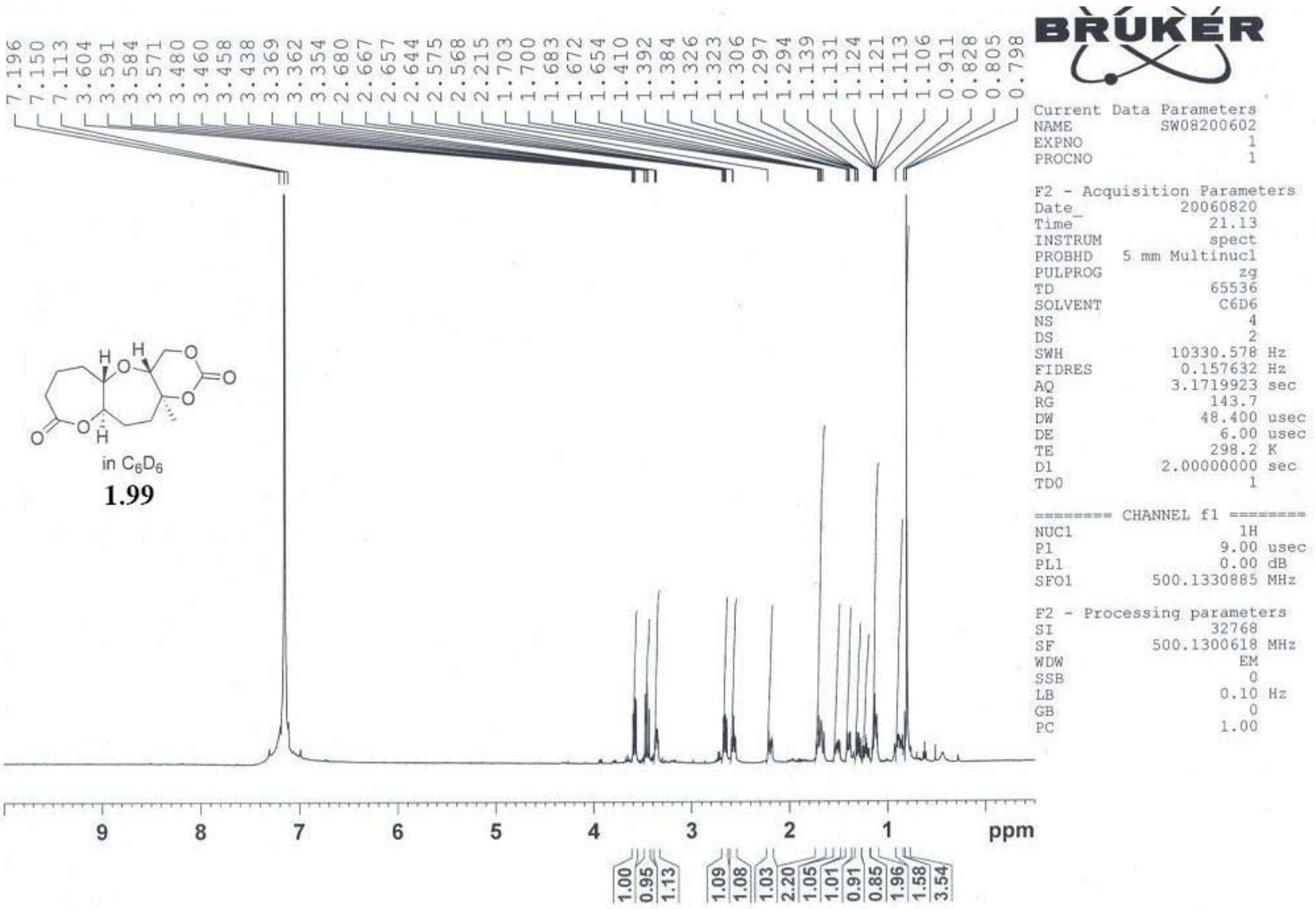
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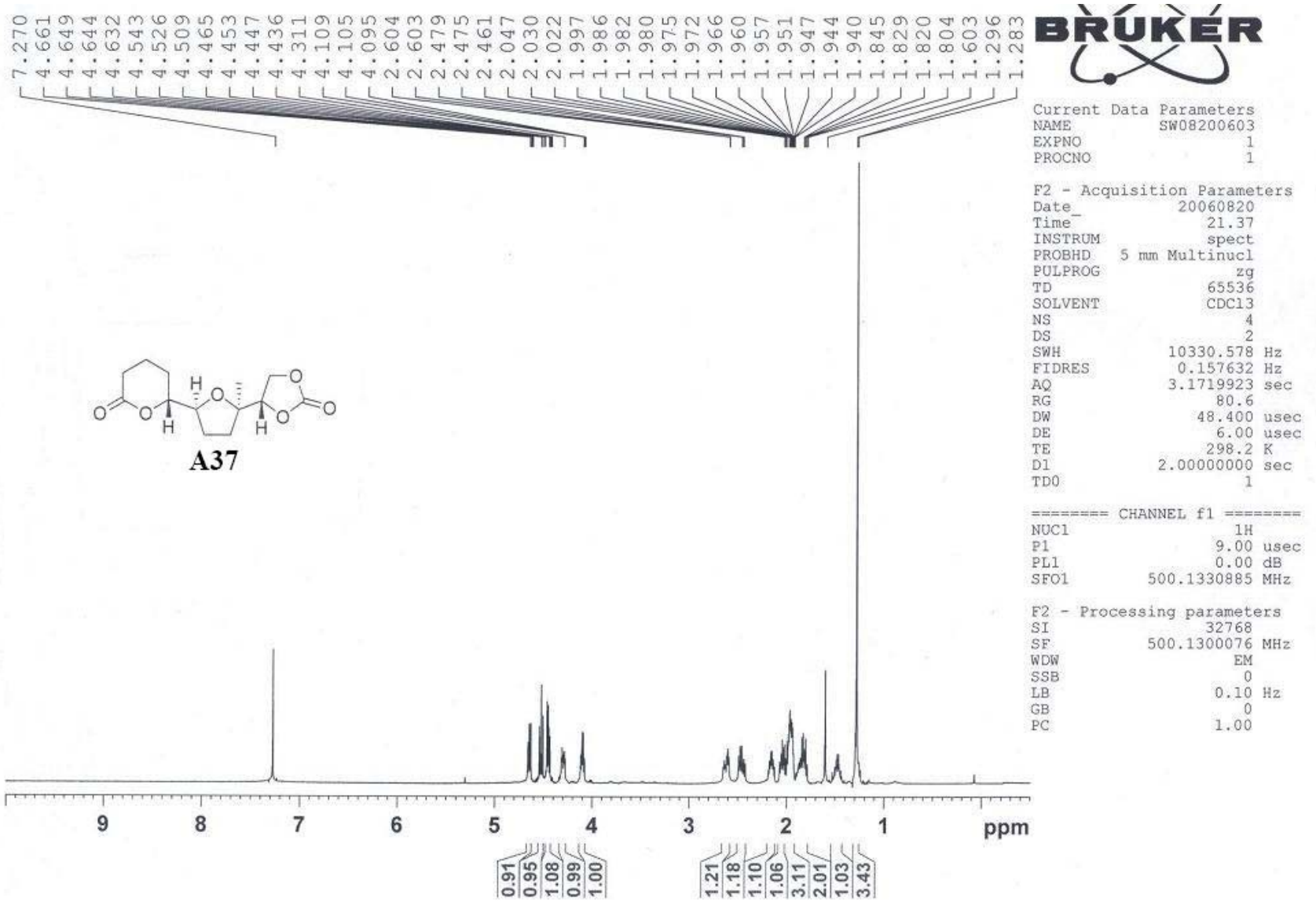

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PROCNO 1

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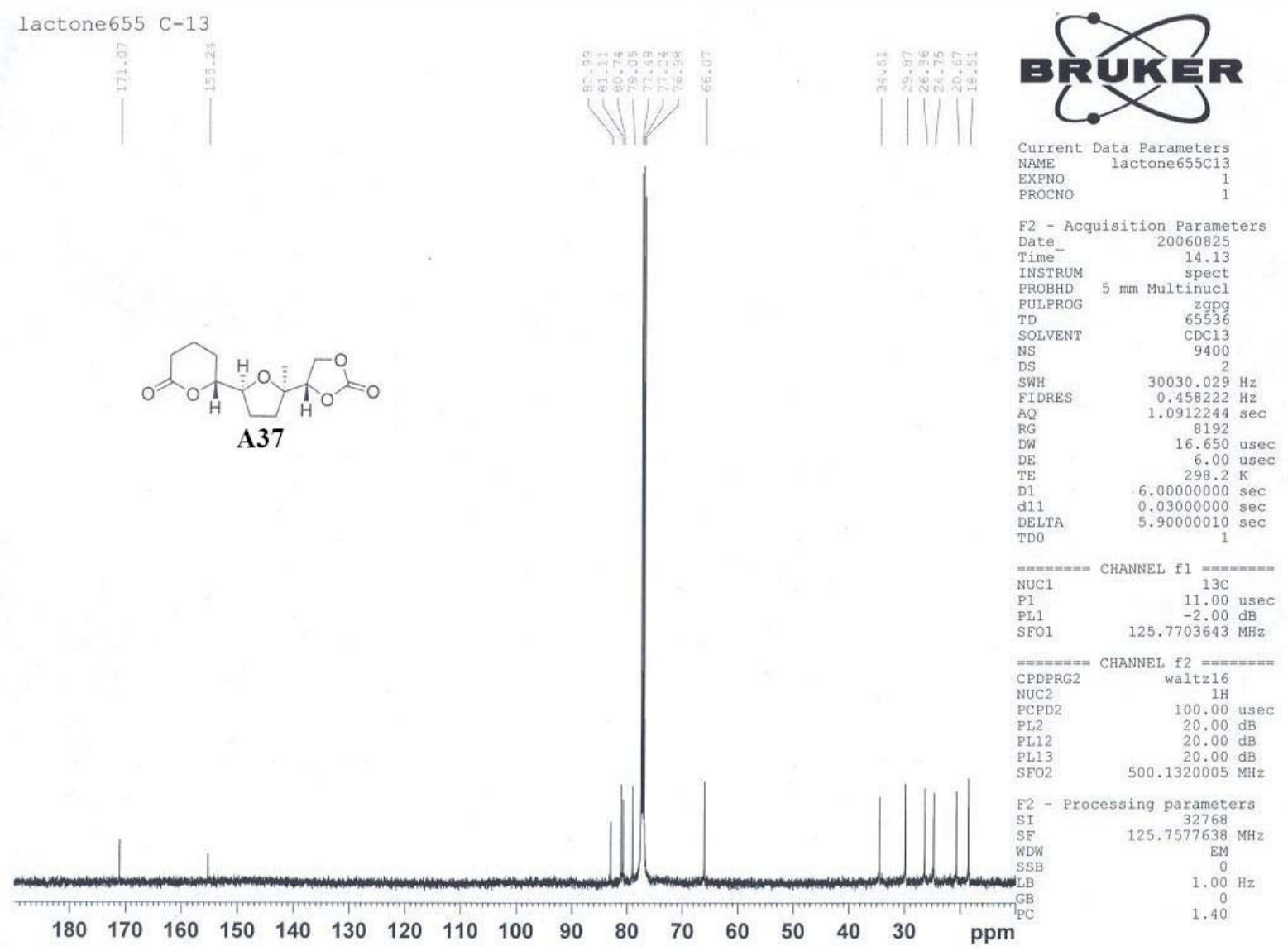
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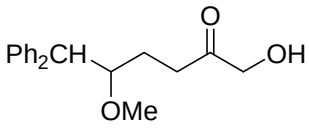
APPENDIX B

EFFORTS TOWARDS THE TOTAL SYNTHESIS OF (+)-LACTODEHYDROTHYRSIFEROL AND ITS ANALOGS (SUPPORTING INFORMATION)

General Experimental Proton (^{1}H NMR) and carbon (^{13}C NMR) nuclear magnetic resonance spectra were recorded at ambient temperature on Bruker Avance 300 spectrometer at 300 MHz and 75 MHz or Bruker Avance 500 spectrometer at 500 MHz and 125 MHz if specified. The chemical shifts are given in parts per million (ppm) on the delta (δ) scale. The solvent peak was used as a reference value, for ^{1}H NMR: $CDCl_3$ = 7.27 ppm, for ^{13}C NMR: $CDCl_3$ = 77.23. Data are reported as follows: (s = singlet; d = doublet; t = triplet; q = quartet; dd = doublet of doublets; ddd = doublet of doublet of doublets; dt = doublet of triplets; td = triplet of doublets; br = broad). High resolution mass spectra were recorded on a MICROMASS AUTOSPEC (for EI) or WATERS Q-TOF API-US (for ESI) spectrometer. Infrared (IR) spectra were collected on a Mattson Cygnus 100 spectrometer. Samples for IR were prepared as a thin film on a NaCl plate by dissolving the compound in CH_2Cl_2 and then evaporating the CH_2Cl_2. Tetrahydrofuran was distilled from sodium and benzophenone. Activated 4 Å molecular sieves were obtained through drying in oven at 150 °C overnight. Boc_2O and *N*-methylimidole were purchased from Acros and

used without further purification. Anhydrous $Na_2S_2O_3$ was purchased from Aldrich and used as received. Toluene and 1,2-dichloroethane were purchased from Fisher Scientific and dried with 4 Å molecular sieves overnight prior to use. Anhydrous DMF and MeI were purchased from Acros. $NiCl_2$, $CrCl_3$, Mn, and anhydrous LiCl were purchased from Aldrich and used without further purification. TMSCl (purchased from Aldrich) was distilled from anhydrous K_2CO_3 before use. Analytical TLC was performed on E. Merck pre-coated (25 mm) silica gel 60F-254 plates. Visualization was done under UV (254 nm). Flash chromatography was done using ICN SiliTech 32-63 60 Å silica gel. Reagent grade ethyl acetate, diethyl ether and hexanes (commercial mixture) were purchased from EM Science and used as is for chromatography. All reactions were performed in flame-dried glassware under nitrogen with magnetic stirring unless otherwise noted.

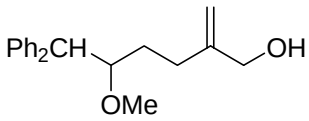
1-Hydroxy-5-methoxy-6,6-diphenylhexan-2-one (2.11)



To a solution of terminal olefin **2.10** (407 mg, 1.53 mmol) in acetone/H_2O (15 mL, 4.5:1, v/v) and AcOH (0.58 mL) was added dropwise a solution of $KMnO_4$ (435 mg, 2.75 mmol) in acetone/H_2O (6.9 mL). The mixture was stirred for 5 min and EtOH (0.8 mL) was added. After 20 min, the mixture was filtered through Celite and the residue was washed with acetone (50 mL). The filtrate was concentrated and the residue was azeotroped with acetone (3 x) and purified by column chromatography (35% - 40% EtOAc in hexanes) to give hydroxyl ketone **2.11** (258 mg, 57%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38-7.18 (m, 10H), 4.29-4.14 (m, 2H), 4.02-3.95 (m, 2H), 3.10 (s, 3H), 3.08-3.06 (m, 1H), 2.58-2.38 (m, 2H), 2.07-1.95 (m, 1H), 1.73-1.64 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.7, 142.2, 128.9, 128.8, 128.6, 126.9, 126.7, 82.6,

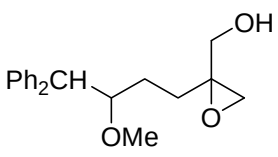
68.2, 58.1, 56.4, 33.9, 26.3; IR (neat) 3435, 2931, 1718, 1494, 1451, 1102, 748; HRMS (ESI): *m*/*z* calcd for $C_{19}H_{22}O_3K$ $[M+K]^+$ 337.1206, found 337.1176.

5-Methoxy-2-methylene-6,6-diphenylhexan-1-ol (2.12)



To a solution of hydroxyl ketone **2.11** (235 mg, 0.788 mmol) in THF (7 mL) were added PPh_3 (227 mg, 0.867 mmol), $(Ph_3P)_3RhCl$ (18.2 mg, 19.7 μmol) and ^{i}PrOH (0.6 mL, 7.88 mmol) sequentially. After 5 min, $TMSCHN_2$ (0.63 mL, 1.26 mmol) was added. The yellow mixture was stirred for 18 h, PPh_3 (200 mg, 0.788 mmol) was added followed by $TMSCHN_2$ (0.63 mL, 1.26 mmol). The reaction was stirred for another 18 h and TBAF (1 M in THF, 3.0 mL, 3.0 mmol) was added. The mixture was stirred for 30 min, then treated with saturated NH_4Cl (15 mL) and extracted with Et_2O (4 x 20 mL). The extract was dried ($MgSO_4$), filtered and concentrated. The residue was purified column chromatography (20% - 45% EtOAc in hexanes) to give allylic alcohol **2.12** (168 mg, 72%) and unreacted starting material **2.11** (23 mg, 10%). For allylic alcohol **2.12**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40-7.18 (m, 10H), 5.00 (br s, 1H), 4.82 (d, *J* = 0.9 Hz, 1H), 4.04 (d, *J* = 8.4 Hz, 1H), 4.00 (br s, 2H), 3.97-3.90 (m, 1H), 3.16 (s, 3H), 2.27-2.09 (m, 2H), 1.78-1.52 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.0, 142.8, 142.4, 129.0, 128.8, 128.7, 128.5, 126.7, 126.5, 109.8, 83.4, 66.1, 58.1, 56.4, 30.6, 28.7; IR (neat) 3397, 2928, 1599, 1494, 1451, 1103, 1030, 898, 745; HRMS (ESI): *m*/*z* calcd for $C_{20}H_{24}O_2K$ $[M+K]^+$ 335.1413, found 335.1404.

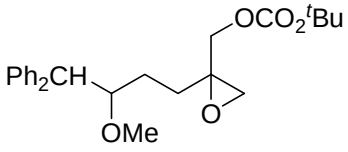
(2-(3-Methoxy-4,4-diphenylbutyl)oxiran-2-yl)methanol (2.13)



To a solution of allylic alcohol **2.12** (157 mg, 0.530 mmol) in benzene (3.0 mL) was added $VO(acac)_2$ (2.8 mg, 10.6 μmol) followed by

dropwise addition of ^{t}BuOOH (5-6 M in decane, 0.12 mL, ~0.65 mmol). The mixture was heated to 80 °C for 20 min, then cooled to room temperature and saturated Na_2SO_3 (2 mL) was added. The mixture was stirred for 10 min, the treated with saturated $NaHCO_3$ (10 mL) and extracted with Et_2O (4 x 20 mL). The extract was dried ($MgSO_4$), filtered and concentrated. The residue was purified column chromatography (30% - 60% EtOAc in hexanes containing 0.5% Et_3N) to give epoxy alcohol **2.13** (148 mg, 90%, dr ~ 1:1) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39-7.19 (m, 10H), 3.98 (d, *J* = 8.5 Hz, 1H), 3.96-3.90 (m, 1H), 3.65 (ddd, *J* = 12.3, 6.6, 4.4 Hz, 1H), 3.53 (dd, *J* = 12.2, 8.4 Hz, 1H), 3.16/3.15 (s, 3H), 2.81 (dd, *J* = 4.6, 2.2 Hz, 1H), 2.56 (dd, *J* = 4.6, 1.4 Hz, 1H), 1.98-1.56 (m, 4H), 1.56-1.38 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.6, 142.3, 128.9, 128.8, 128.6, 128.5, 126.8, 126.6, 83.4, 83.3, 63.2, 62.9, 59.8, 59.7, 58.2, 58.1, 56.3, 56.3, 50.2, 49.7, 27.5, 27.2, 27.0, 26.8; IR (neat) 3432, 2929, 1642, 1600, 1494, 1452, 1101, 747; HRMS (ESI): *m*/*z* calcd for $C_{20}H_{24}O_3Na$ $[M+Na]^+$ 335.1623, found 335.1607.

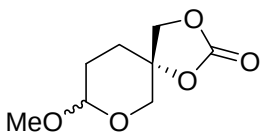
tert-Butyl 2-(3-methoxy-4,4-diphenylbutyl)oxiranylmethyl carbonate (2.14)



To a solution of epoxy alcohol **2.13** (135 mg, 0.432 mmol) in dry toluene (4.3 mL) at 0 °C were added 1-methylimidazole (34 μL, 0.432 mmol) and di-*tert*-butyl dicarbonate (188 mg, 0.864 mmol). The reaction mixture was stirred overnight, allowing the temperature to warm to room temperature slowly. After that time, water (2 drops) was added. After 10 min, the mixture was concentrated and the residue was azeotroped with acetone (5 mL), then hexanes (2 x 5 mL) and purified by flash chromatography (10% - 20% EtOAc in hexanes containing 0.5% Et_3N) to give the *tert*-butyl carbonate **2.14** (162 mg, 91%, dr ~ 1:1) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41-7.19 (m, 10H), 4.12-3.94 (m, 4H), 3.18/3.17 (s, 3H), 2.72 (t, *J* = 4.2 Hz, 1H), 2.58

(dd, J = 4.5, 2.0 Hz, 1H), 1.97-1.58 (m, 4H), 1.51 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.4, 153.4, 142.6, 142.3, 142.3, 129.0, 128.9, 128.8, 128.8, 128.6, 128.5, 126.7, 126.7, 126.5, 83.2, 82.6, 68.5, 68.1, 58.0, 58.0, 57.3, 57.2, 56.2, 56.2, 50.8, 50.3, 27.9, 27.4, 26.9, 26.8, 26.6; IR (neat) 2979, 2933, 1742, 1494, 1453, 1279, 1161, 1102, 743; HRMS (ESI): m/z calcd for $C_{25}H_{32}O_5Na$ $[M+Na]^+$ 435.2147, found 435.2150.

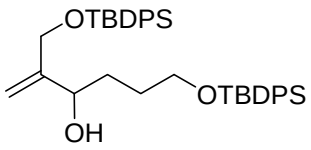
(5*S*)-8-Methoxy-1,3,7-trioxaspiro[4.5]decan-2-one (2.17)



To epoxide **2.14** (70 mg, 0.17 mmol) in dichloroethane/toluene (5.6 mL, 5:1, v/v) in borosilicate flask at room temperature were added the activated 4Å molecular sieves (140 mg), anhydrous $Na_2S_2O_3$ (140 mg), NaOAc (140 mg) and *N*-methylquinolinium hexafluorophosphate (24.6 mg, 85 μmol). The mixture was photoirradiated with gentle air bubbling for 8 h while stirring at room temperature. The reaction mixture was filtered through a small plug of silica gel and the residue was washed with Et_2O (30 mL). The filtrate was concentrated and the resulting residue was purified by flash chromatography (30% - 60% EtOAc in hexanes) to produce the bicycle **2.17** (25.2 mg, 79%, dr 1.1:1) as a pale yellow oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.70 (t, J = 2.3 Hz, 0.5H), 4.60 (app dd, J = 3.0, 2.3 Hz, 0.5H), 4.50 (d, J = 8.6 Hz, 0.5H), 4.20 (dd, J = 8.6, 1.4 Hz, 0.5H), 4.10 (d, J = 8.8 Hz, 0.5H), 4.06 (d, J = 8.8 Hz, 0.5H), 3.88 (dd, J = 11.0, 1.0 Hz, 0.5H), 3.72 (d, J = 12.4 Hz, 0.5H), 3.66 (dd, J = 12.4, 2.2 Hz, 0.5H), 3.52 (dd, J = 11.1, 2.4 Hz, 0.5H), 3.39 (s, 1.5H), 3.38 (s, 1.5H), 2.33 (dt, J = 12.8, 4.5 Hz, 0.5H), 2.15-2.00 (m, 1H), 1.99-1.90 (m, 1H), 1.84 (dtd, J = 12.4, 4.1, 2.4 Hz, 0.5H), 1.76-1.57 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.2, 154.2, 97.6, 96.9, 79.4, 78.6, 72.8, 71.7, 64.5, 63.3, 55.5, 55.3, 28.2, 28.1, 27.4, 26.1; IR (neat) 2921, 1804,

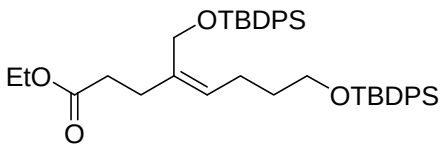
1389, 1183, 1125, 1050, 772; HRMS (EI): *m*/*z* calcd for $C_8H_{11}O_5$ ($M^{+\bullet}$) 187.0606, found 187.0606.

6-(*tert*-Butyldiphenylsilanyloxy)-2-(*tert*-butyldiphenylsilanyloxymethyl)hex-1-en-3-ol (2.25)



To a mixture of (2-bromoallyloxy)(*tert*-butyl)diphenylsilane **2.23** (2.764 g, 7.36 mmol), aldehyde **2.24** (1.200 g, 3.68 mmol), $CrCl_3$ (116 mg, 0.736 mmol), $NiCl_2$ (95 mg, 0.736 mmol) and Mn (1.011 g, 18.4 mmol) in anhydrous DMF (6 mL, degassed with argon prior to use) was added TMSCl (1.12 mL, 8.83 mmol). After stirring overnight, the reaction was quenched with water (15 mL) and transferred to a beaker. HCl (1 N) was added until all the manganese metal was completely consumed. The mixture was extracted with Et_2O (4 x 40 mL), and the extract was dried (MgSO4) and concentrated. The residue was purified by column chromatography (2% - 10% EtOAc in hexanes) to give allylic alcohol **2.25** (1.948 g, 85%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71-7.64 (m, 8H), 7.46-7.34 (m, 12H), 5.20 (q, *J* = 1.5 Hz, 1H), 5.12 (s, 1H), 4.30 (d, *J* = 13.6 Hz, 1H), 4.23-4.19 (m, 2H), 3.65 (app t, *J* = 6.0 Hz, 2H), 2.63 (d, *J* = 4.9 Hz, 1H), 1.70-1.51 (m, 4H), 1.07 (s, 9H), 1.04 (s, 9H).

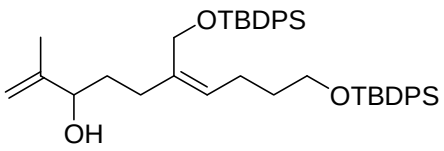
Ethyl (*Z*)-8-(*tert*-butyldiphenylsilanyloxy)-4-(*tert*-butyldiphenylsilanyloxymethyl)oct-4-eno-ate (2.26)



A mixture of allylic alcohol **2.25** (1.868 g, 3.00), triethyl orthoacetate (2.2 mL, 12.0 mmol) and propionic acid (11 μL, 0.15 mmol) was heated to 100 °C for 4 h and the unreacted triethyl orthoacetate was distilled out under reduced pressure. The residue was purified

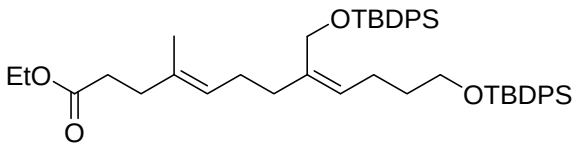
by column chromatography (1% - 3% EtOAc in hexanes) to give the ethyl ester **2.26** (1.724 g, 83%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69-7.60 (m, 8H), 7.43-7.32 (m, 12H), 5.19 (t, *J* =7.3 Hz, 1H), 4.20 (s, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.53 (t, *J* = 6.4 Hz, 2H), 2.51-2.41 (m, 4H), 1.86 (q, *J* = 7.3 Hz, 2H), 1.52-1.43 (m, 2H), 1.23 (t, *J* = 7.4 Hz, 3H), 1.04 (s, 9H), 1.00 (s, 9H).

(*Z*)-10-(*tert*-Butyldiphenylsilanyloxy)-6-(*tert*-butyldiphenylsilanyloxymethyl)-2-methyldeca-1,6-dien-3-ol (2.27)



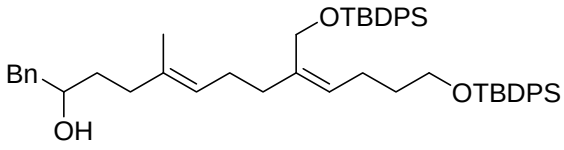
A solution of ethyl ester **2.26** (1.700 g, 2.45 mmol) in CH_2Cl_2 (3 mL) at -78 °C was treated with DIBAL-H (1 M in hexanes, 2.6 mL, 2.6 mmol) over 15 min. After 30 min, DIBAL-H (0.36 mL, 0.36 mmol) was added over 2 min. The mixture was stirred for 15 min and isopropenylmagnesium bromide (0.5 M in THF, 9.8 mL, 4.9 mmol) was added dropwise. The reaction was stirred at -78 °C for 1 h, then warmed to room temperature and quenched with saturated NH_4Cl solution (10 mL) and saturated sodium tartrate solution (25 mL). The mixture was stirred vigorously for 1 h and extracted with Et_2O (3 x 30 mL). The organic extract was dried ($MgSO_4$) and concentrated. The residue was purified by column chromatography (3% - 12% EtOAc in hexanes) to give secondary alcohol **2.27** (1.333 g, 79%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70-7.63 (m, 8H), 7.45-7.34 (m, 12H), 5.23 (t, *J* = 7.3 Hz, 1H), 4.97-4.96 (m, 1H), 4.87-4.86 (m, 1H), 4.22 (d, *J* = 2.5 Hz, 2H), 4.08-4.05 (m, 1H), 3.56 (t, *J* = 6.5 Hz, 2H), 2.28-2.21 (m, 2H), 1.91 (q, *J* = 7.2 Hz, 2H), 1.78-1.67 (m, 5H), 1.56-1.49 (m, 2H), 1.06 (s, 9H), 1.02 (s, 9H).

Ethyl (4*E*,8*Z*)-12-(*tert*-butyldiphenylsilanyloxy)-8-(*tert*-butyldiphenylsilanyloxymethyl)-4-methyldodeca-4,8-dienoate (2.28)



A mixture of allylic alcohol **2.27** (1.333 g, 1.93 mmol), triethyl orthoacetate (1.4 mL, 7.72 mmol) and propionic acid (7 μL, 96 μmol) was heated to 115 °C for 2 h and the unreacted triethyl orthoacetate was distilled out under reduced pressure. The residue was purified by column chromatography (2% - 4% EtOAc in hexanes) to give the ethyl ester **2.28** (1.216 g, 83%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69-7.60 (m, 8H), 7.41-7.32 (m, 12H), 5.16 (t, *J* = 6.8 Hz, 2H), 4.18 (s, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.55 (t, *J* = 6.4 Hz, 2H), 2.42-2.37 (m, 2H), 2.32-2.28 (m, 2H), 2.19-2.06 (m, 4H), 1.89 (q, *J* = 7.4 Hz, 2H), 1.60 (br s, 3H), 1.54-1.47 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.04 (s, 9H), 1.00 (s, 9H).

(5*E*,9*Z*)-13-(*tert*-Butyldiphenylsilanyloxy)-9-(*tert*-butyldiphenylsilanyloxymethyl)-5-methyl-1-phenyltrideca-5,9-dien-2-ol (2.29)

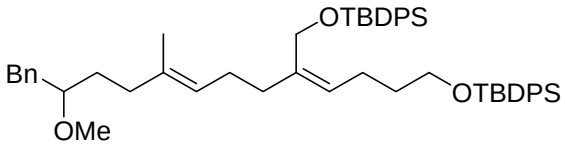


A solution of ethyl ester **2.28** (600 mg, 0.788 mmol) in CH_2Cl_2 (4 mL) at -78 °C was treated with DIBAL-H (1 M in hexanes, 0.83 mL, 0.83 mmol) over 10 min. After 30 min, DIBAL-H (0.12 mL, 0.12 mmol) was added and the mixture was stirred for 30 min.

In a separate round-bottom flask, a mixture of CuCN (282 mg, 3.15 mmol) and LiCl (294 mg, 6.93 mmol) in THF (10 mL) at -78 °C was treated with BnMgCl (2 M in THF, 1.6 mmol, 3.2 mmol) dropwise. After 1 h, BF_3•OEt_2 (0.28 mL, 2.26 mmol) was added and the mixture was stirred for 5 min. The reaction mixture from the first reaction was cannulated into the second

flask followed by rinse (2 x 0.5 mL THF). The mixture was stirred at -78 °C for 1 h and then at room temperature for 1 h. After that time, the reaction was quenched with saturated NH_4Cl solution (10 mL) /saturated sodium tartrate solution (5 mL) and stirred vigorously for 1 h. The mixture was extracted with Et_2O (4 x 20 mL) and the organic extract was dried ($MgSO_4$) and concentrated. The residue was purified by column chromatography (3% - 12% EtOAc in hexanes) to give secondary alcohol **2.29** (496 mg, 78%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70-7.62 (m, 8H), 7.44-7.30 (m, 12H), 7.30-7.20 (m, 5H), 5.21-5.15 (m, 2H), 4.19 (s, 2H), 3.86-3.76 (m, 1H), 3.55 (t, *J* = 6.5 Hz, 2H), 2.84 (dd, *J* = 13.6, 4.4 Hz, 1H), 2.67 (dd, *J* = 13.5, 8.3 Hz, 1H), 2.23-1.98 (m, 2H), 1.60 (s, 3H), 1.66-1.47 (m, 6H), 1.05 (s, 9H), 1.01 (s, 9H).

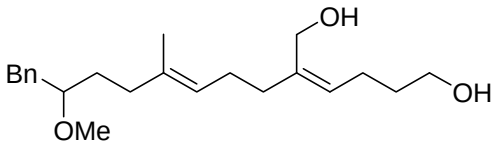
(*Z*)-6-((*E*)-7-Methoxy-4-methyl-8-phenyloct-3-enyl)-2,2-13,13-tetramethyl-3,3,12,12-tetraphenyl-4,11-dioxa-3,12-disilatetradec-6-ene (B1)



A solution of alcohol **2.29** (486 mg, 0.600 mmol) in DMF (5 mL) at 0 °C was treated with NaH (60% weight in mineral oil, 60 mg, 1.50 mmol). After 20 min, MeI (0.15 mL, 2.4 mmol) was added and the mixture was stirred overnight at room temperature. After that time, the reaction was quenched with water (20 mL) cautiously and extracted with Et_2O (3 x 20 mL). The organic extract was dried ($MgSO_4$) and concentrated. The residue was purified by column chromatography (2% - 5% EtOAc in hexanes) to give methyl ether **B1** (431 mg, 87%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69-7.61 (m, 8H), 7.43-7.30 (m, 12H), 7.29-7.26 (m, 2H), 7.22-7.18 (m, 3H), 5.20-5.10 (m, 2H), 4.19 (s, 2H), 3.55 (t, *J* = 6.5 Hz, 2H), 3.36-3.30 (m, 1H), 3.31 (s, 3H), 2.84 (dd, *J* = 13.7, 6.2 Hz, 1H), 2.72 (dd, *J* =

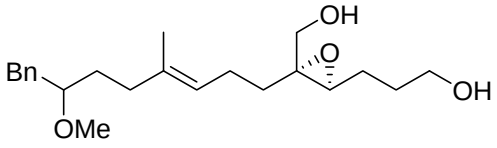
13.8, 6.2 Hz, 1H), 2.22-1.96 (m, 6H), 1.89 (q, *J* = 7.3 Hz, 2H), 1.58-1.48 (m, 7H), 1.04 (s, 9H), 1.00 (s, 9H).

(2*Z*)-2-((*E*)-7-Methoxy-4-methyl-8-phenyloct-3-enyl)hex-2-ene-1,6-diol (2.30)



To a solution of silyl ether **B1** (409 mg, 0.497 mmol) in THF (5 mL) was added TBAF·H_2O (312 mg, 1.19 mmol). The reaction was stirred for 4 h, then concentrated and the residue was purified by column chromatography (50% - 60% EtOAc in hexanes) to give the diol **2.30** (144 mg, 84%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32-7.19 (m, 5H), 5.28 (t, *J* = 7.8 Hz, 1H), 5.16-4.99 (m, 1H), 4.17 (s, 2H), 3.63 (t, *J* = 5.9 Hz, 2H), 3.39-3.35 (m, 1H), 3.32 (s, 3H), 2.86 (dd, *J* = 13.7, 6.2 Hz, 1H), 2.71 (dd, *J* = 13.7, 6.3 Hz, 1H), 2.24 (q, *J* = 7.1 Hz, 2H), 2.15-1.97 (m, 8H), 1.68-1.60 (m, 2H), 1.58-1.49 (m, 5H).

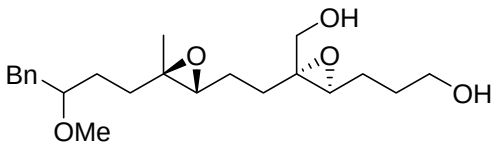
3-((2*S*,3*R*)-3-(Hydroxymethyl)-3-((*E*)-7-methoxy-4-methyl-8-phenyloct-3-enyl)oxiran-2-yl)propan-1-ol (B2)



To a mixture of diol **2.30** (138 mg, 0.398 mmol) and activated 4 Å molecular sieves (120 mg) in CH_2Cl_2 (4 mL) at -20 °C was added D--diisopropyl tartrate (8 μL, 48 μmol). After 10 min, Ti(O^iPr)$_4$ (12 μL, 40μmol) was introduced. The mixture was stirred for 30 min, and ^{t}BuOOH (5-6 M in decane, 0.22 mL, ~1.2 mmol) was added dropwise. The reaction was stirred for 5 h at -20 °C, and then stored in at -20 °C overnight. Water (0.5 mL) was added the mixture was stirred at 0 °C for 1 h. After that time, 30% NaOH saturated with NaCl (0.5 mL) was added and the mixture was stirred at room temperature for 2.5 h. The mixture was filtered

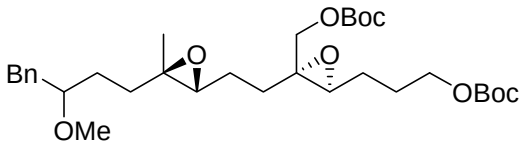
through a 1:1 mixture of $MgSO_4$/Celite and the residue was washed with CH_2Cl_2 (20 mL). The combined filtrates were concentrated and the residue was purified by column chromatography (60% - 80% EtOAc in hexanes containing 1% Et_3N) to give monoepoxy diol **B2** (47 mg, 33%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32-7.19 (m, 5H), 5.11 (t, *J* = 6.8 Hz, 1H), 3.78-3.65 (m, 4H), 3.39-3.34 (m, 1H), 3.32 (s, 3H), 2.90-2.83 (m, 2H), 2.70 (ddd, *J* =13.8, 6.3, 2.5 Hz, 1H), 2.38 (br s, 1H), 2.16-1.95 (m, 6H), 1.86-1.49 (m, 10H).

3-((2*S*,3*R*)-3-(Hydroxymethyl)-3-(2-((2*R*,3*R*)-3-(3-methoxy-4-phenylbutyl)-3-methyloxiran-2-yl)ethyl)oxiran-2-yl)propan-1-ol (B3)



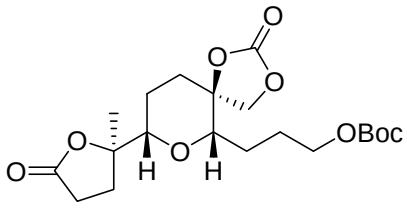
A solution of monoepoxide **B2** (45 mg, 0.124 mmol) in CH_3CN/DMM (1.8 mL, 1:2, v/v) was treated with 0.05 M solution of $Na_2B_4O_7$ in $4x10^{-4}$ M Na_2(EDTA) (1.2 mL), Bu_4NHSO_4 (1.7 mg, 4.5 μmol) and Shi ketone (16.0 mg, 62 μmol) sequentially. The mixture was cooled to -5 °C. Oxone (122 mg, 0.198 mmol), dissolved in $4x10^{-4}$ M Na_2(EDTA) (0.8 mL), and K_2CO_3 (115 mg, 0.831 mmol), dissolved in water (0.8 mL), were added simultaneously via a syringe pump over 2.0 h. After the addition was completed, the blue mixture was stirred further for 10 min, and anhydrous Na_2SO_4 was added in portions until all the water disappeared. The mixture was filtered and the residues was washed with CH_2Cl_2 (30 mL). The combined filtrates were concentrated and the residue was purified by flash chromatography (80% - 100% EtOAc in hexanes containing 1% Et_3N) to give diepoxide **B3** (42 mg, 89%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30-7.18 (m, 5H), 3.90-3.49 (m, 4H), 3.38-3.34 (m, 1H), 3.32 (s, 3H), 2.91-2.82 (m, 2H), 2.76-2.64 (m, 2H), 2.20-1.41 (m, 14H), 1.22/1.22/1.21 (s, 3H).

***tert*-Butyl 3-((2*S*,3*R*)-3-*tert*-butoxycarbonyloxymethyl-3-(2-[3-(3-methoxy-4-phenylbutyl)-(2*R*,3*R*)-3-methyloxiranyl]ethyl)oxiranyl)propyl carbonate (*ent*-2.21)**



A solution of the diepoxide **B3** (39 mg, 0.103 mmol) in dry toluene (1.0 mL) at 0 °C was treated with *N*-methylimidazole (16 μL, 0.206 mmol) followed by di-*tert*-butyl dicarbonate (90 mg, 0.412 mmol). The reaction mixture was stirred overnight, allowing the temperature to warm to room temperature slowly. After that time, the reaction was quenched with water (5 mL) and extracted with CH_2Cl_2 (3 x 15 mL). The organic extracts were dried ($MgSO_4$), filtered and concentrated. The residue was purified by flash chromatography (15% - 25% EtOAc in hexanes containing 1% Et_3N) to give the *tert*-butyl carbonate *ent*-**2.21** (31 mg, 52%, dr ~ 2:1 regarding the stereochemical outcomes of the two epoxide groups) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32-7.18 (m, 5H), 4.20-4.05 (m, 4H), 3.36-3.34 (m, 1H), 3.31 (s, 3H), 2.90-2.81 (m, 2H), 2.72-2.63 (m,, 2H), 1.90-1.70 (m, 6H), 1.66-1.56 (m, 5H), 1.54-1.43 (m, 1H), 1.49 (s, 9H), 1.20/1.20/1.19 (s, 3H).

***tert*-Butyl 3-[8-((*R*)-2-methyl-5-oxotetrahydrofuran-2-yl)-(5*S*,6*S*,8*S*)-2-oxo-1,3,7-trioxaspiro[4.5]dec-6-yl]propyl carbonate (2.32)**

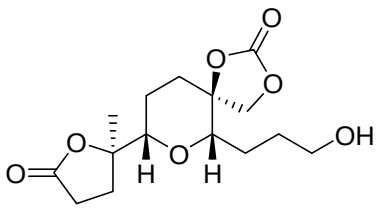


Diepoxide *ent*-**2.21** (30 mg, 51.8 μmol) in dichloroethane/toluene (1.7 mL, 5:1, v/v) in borosilicate flask at room temperature was treated with the activated 4Å molecular sieves (60 mg), anhydrous $Na_2S_2O_3$ (60 mg), NaOAc (60 mg) and *N*-methylquinolinium hexafluorophosphate (7.5 mg, 26 μmol). The mixture was photoirradiated

with gentle air bubbling for 3.5 h while stirring at room temperature. The reaction mixture was filtered through a small plug of silica gel and the residue was washed with Et_2O (25 mL). The filtrate was concentrated and the resulting residue was purified by column chromatography (25% - 40% EtOAc in hexanes) to provide a pale yellow oil **2.31** (9.5 mg, 43%, containing small amounts of unknown materials) and another pale yellow oil (3.0 mg, 13%). For the major product **2.31**: IR (neat) 2976, 1809, 1739, 1280, 1163, 1067.

The acetal **2.31** (3.2 mg) was dissolved in acetone (0.3 mL) at 0 °C and Jones reagent (16 μL) was added. The mixture was stirred for 1 h, then purified by column chromatography (50% - 80% EtOAc in hexanes) to give title lactone **2.33** (2.6 mg, 84%) as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.54 (d, *J* = 8.9 Hz, 1H), 3.41 (d, *J* = 9.0 Hz, 1H), 4.08 (t, *J* = 5.8 Hz, 2H), 3.50 (dd, *J* = 10.6, 1.4 Hz, 1H), 3.46 (dd, *J* = 11.6, 2.0 Hz, 1H), 2.62-2.58 (m, 2H), 2.24 (ddd, *J* = 13.1, 9.6, 6.9Hz, 1H), 2.18 (td, *J* = 12.8, 3.8 Hz, 1H), 2.10 (dt, *J* = 13.4, 4.4 Hz, 1H), 1,96-1.91 (m, 2H), 1.90-1.86 (m, 1H), 1.74-1.70 (m, 2H), 1.53-1.46 (m, 1H), 1.49 (s, 9H), 1.39-1.33 (m, 1H), 1.35 (s, 3H).

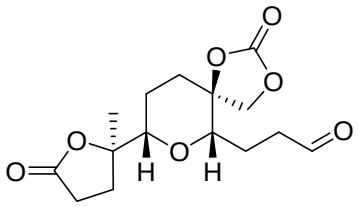
(5*S*,6*S*,8*S*)-6-(3-Hydroxypropyl)-8-((*R*)-2-methyl-5-oxotetrahydrofuran-2-yl)-1,3,7-trioxaspiro[4.5]decan-2-one (2.35)



A solution of lactone **2.33** (7.2 mg, 17.4 μmol) in CH_2Cl_2 (0.8 mL) at 0 °C was treated with 2,6-lutidine (7.1 μL, 61 μmol) followed by TMSOTf (10 μL, 52 μmol). The reaction was stirred at 0 °C for 1 h, and then quenched with saturated $NaHCO_3$ (0.5 mL). Anhydrous Na_2SO_4 was added and the mixture was filtered. The residue was washed with EtOAc (40 mL) and the filtrate was concentrated. The resulting residue was purified by column chromatography (70% - 100%

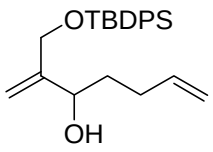
EtOAc in hexanes) to give the alcohol **2.35** (5.4 mg, 98%) as a white solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.54 (d, *J* = 8.8 Hz, 1H), 4.11 (d, *J* = 8.8Hz, 1H), 3.67 (br s, 2H), 3.54 (dd, *J* = 11.9, 1.8 Hz, 1H), 3.50 (dd, *J* = 11.8, 2.2 Hz, 1H), 2.68-2.54 (m, 2H), 2.24 (ddd, *J* = 13.1, 10.2, 5.5 Hz, 1H), 2.19 (ddd, *J* = 3.0, 4.2, 3.0 Hz, 1H), 2.11 (dt, *J* = 13.4, 4.6 Hz, 1H), 1.94-1.88 (m, 2H), 1.78-1.69 (m, 2H), 1.66-1.60 (m, 2H), 1.66-1.60 (m, 1H), 1.53-1.48 (m, 1H), 1.40-1.32 (m, 1H), 1.37 (s, 3H).

3-(5*S*,6*S*,8*S*)-[8-((*R*)-2-Methyl-5-oxotetrahydrofuran-2-yl)-2-oxo-1,3,7-trioxaspiro[4.5]dec-6-yl]propionaldehyde (*ent*-2.19)



A solution of alcohol **2.35** (5.2 mg, 16 μmol) in CH_2Cl_2 (0.5 mL) was treated with $NaHCO_3$ (5.5 mg, 66 μmol) and Dess-Martin periodinane (10.5 mg, 25 μmol) sequentially. The mixture was stirred for 30 min, then loaded onto column and purified (60% - 80% EtOAc in hexanes) to give the aldehyde *ent*-**2.19** (3.2 mg, 61%) as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.77 (s, 1H), 4.57 (d, *J* = 8.9 Hz, 1H), 4.13 (d, *J* = 9.0 Hz, 1H), 3.52 (dd, *J* = 11.1, 2.4 Hz, 1H), 3.47 (dd, *J* = 11.8, 2.2 Hz, 1H), 2.67-2.54 (m, 4H), 2.23-2.17 (m, 2H), 2.10 (dt, *J* = 8.6, 4.6 Hz, 1H), 1.99-1.86 (m, 3H), 1.84-1.76 (m, 1H), 1.39-1.32 (m, 2H), 1.34 (s, 3H).

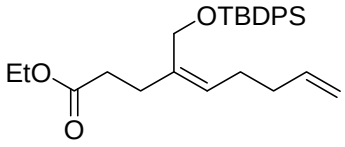
2-(*tert*-Butyldiphenylsilanyloxymethyl)hepta-1,6-dien-3-ol (2.38)



A solution of methyl ester **2.37** (2.050 g, 12.0 mmol) in Et_2O (24 mL) at 0 °C was treated with $LiAlH_4$ (1 M in Et_2O, 12.0 mL) dropwise over 20 min. The reaction was stirred at 0 °C for 1 h and then quenched with saturated NH_4Cl (20 mL) cautiously. Saturated sodium tartrate solution (40 mL) was added and the mixture was

stirred vigorously for 2 h. The mixture was extracted with EtOAc (3 x 60 mL) and the organic extract was dried ($MgSO_4$), filtered and concentrated. The crude product was purified by column chromatography (40% - 60% EtOAc in hexanes) to give a colorless oil (1.033 g). This oil was separated into two parts (325 mg and 708 mg). The first part (325 mg) was dissolved in CH_2Cl_2 (10 mL) and treated with TBDPSCl (0.47 mL, 1.83 mmol) and imidazole (155 mg, 2.28 mmol) at 0 °C. The mixture was stirred at 0 °C for 15 min, then quenched with water (20 mL) and extracted with CH_2Cl_2 (3 x 25 mL). The organic extract was dried ($MgSO_4$) and concentrated. The crude product was purified by column chromatography (5% - 10% EtOAc in hexanes) to give desired silyl ether. The second part (708 mg) was treated in a similar manner with TBDPSCl (1.15 mL, 4.48 mmol) and imidazole (373 mg, 5.48 mmol) in CH_2Cl_2 (10 mL). The combined silyl ether **2.38** (1.180g, 26%, two steps) was obtained as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71-7.69 (m, 4H), 7.48-7.38 (m, 6H), 5.89-5.75 (m, 1H), 5.18 (q, *J* = 1.4 Hz, 1H), 5.12 (s, 1H), 5.06-4.96 (m, 2H), 4.32 (d, *J* = 13.5 Hz, 1H), 4.24-4.18 (m, 2H), 2.25 (d, *J* = 4.9 Hz, 1H), 2.20-2.01 (m, 2H), 1.71-1.63 (m, 2H), 1.08 (s, 9H).

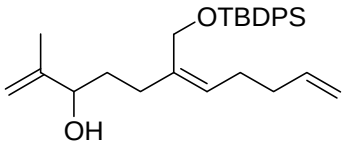
Ethyl (*Z*)-4-(*tert*-butyldiphenylsilanyloxymethyl)nona-4,8-dienoate (B4)



A mixture of allylic alcohol **2.38** (1.180 g, 3.10 mmol), triethyl orthoacetate (2.3 mL, 12.4 mmol) and propionic acid (11 μL, 0.16 mmol) was heated to 100 °C for 6 h and the unreacted triethyl orthoacetate was removed by distillation under reduced pressure. The residue was purified by column chromatography (1% - 4% EtOAc in hexanes) to give ethyl ester **B4** (0.903 g, 65%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71-7.68 (m, 4H), 7.47-7.36 (m, 6H), 5.76-5.63 (m,

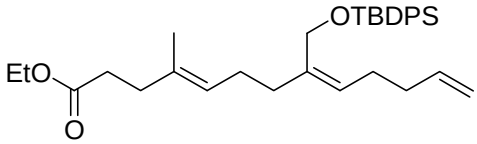
1H), 5.24 (t, *J* = 7.1 Hz, 1H), 4.97-4.89 (m, 2H), 4.21 (s, 2H), 4.14 (q, *J* = 7.1 Hz, 2H), 2.56-2.45 (m, 4H), 2.01-1.85 (m, 4H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.05 (s, 9H).

(*Z*)-6-(*tert*-Butyldiphenylsilanyloxymethyl)-2-methylundeca-1,6,10-trien-3-ol (2.39)



A solution of the ethyl ester **B4** (897 mg, 1.99 mmol) in CH_2Cl_2 (6 mL) at -78 °C was treated with DIBAL-H (1 M in hexanes, 2.10 mL, 2.1 mmol) over 30 min. After 40 min, DIBAL-H (0.30 mL, 0.30 mmol) was added over 5 min. The mixture was stirred for 15 min and isopropenylmagnesium bromide (0.5 M in THF, 6.0 mL, 3.0 mmol) was added dropwise. The reaction was stirred at -78 °C for 15 min, then warmed to room temperature and quenched with saturated NH_4Cl solution (10 mL) and saturated sodium tartrate solution (8 mL). The mixture was stirred vigorously for 1 h and extracted with Et_2O (3 x 30 mL). The organic extract was dried ($MgSO_4$) and concentrated. The residue was purified by column chromatography (3% - 10% EtOAc in hexanes) to give secondary alcohol **2.39** (678 mg, 76%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71-7.68 (m, 4H), 7.47-7.36 (m, 6H), 5.76-5.65 (m, 1H), 5.26 (t, *J* = 7.0 Hz, 1H), 4.99-4.90 (m, 3H), 4.87-4.85 (m, 1H), 4.24-4.16 (m, 2H), 4.11-4.06 (m, 1H), 2.29-2.22 (m, 2H), 2.04-1.89 (m, 4H), 1.79-1.66 (m, 2H), 1.74 (s, 3H), 1.62 (d, *J* = 3.9 Hz, 1H), 1.06 (s, 9H).

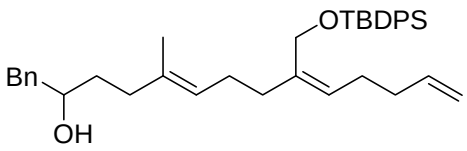
Ethyl (4*E*,8*Z*)-8-(*tert*-butyldiphenylsilanyloxymethyl)-4-methyltrideca-4,8,12-trienoate (B5)



A mixture of allylic alcohol **2.39** (670 mg, 1.49 mmol), triethyl orthoacetate (1.1 mL, 6.0 mmol) and propionic acid (5.5 μL, 74 μmol) was heated to 135 °C for 2 h and

then purified by column chromatography (1% - 3% EtOAc in hexanes) to give ethyl ester **B5** (594 mg, 77%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71-7.68 (m, 4H), 7.46-7.36 (m, 6H), 5.76-5.65 (m, 1H), 5.23-5.15 (m, 2H), 5.01-4.91 (m, 2H), 4.19 (s, 2H), 4.13 (q, *J* = 7.2 Hz, 2H), 2.43-2.37 (m, 2H), 2.35-2.28 (m, 2H), 2.22-2.10 (m, 4H), 2.03-1.88 (m, 4H), 1.61 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.05 (s, 9H).

(5*E*,9*Z*)-9-(*tert*-Butyldiphenylsilanyloxymethyl)-5-methyl-1-phenyltetradeca-5,9,13-trien-2-ol (B6)

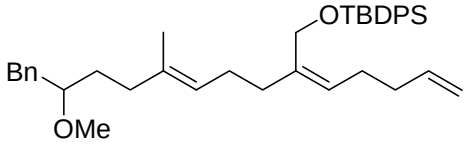


A solution of the ethyl ester **B5** (588 mg, 1.13 mmol) in CH_2Cl_2 (5.6 mL) at - 78 °C was added DIBAL-H (1 M in hexanes, 1.2 mL, 1.2 mmol) over 15 min. After 30 min, DIBAL-H (0.20 mL, 0.20 mmol) was added over 5 min. The mixture was stirred for 20 min.

In a separate round-bottom flask, to a mixture of CuCN (405 mg, 4.52 mmol) and LiCl (422 mg, 9.94 mmol) in THF (14 mL) at -78 °C was added BnMgCl (2 M in THF, 2.3 mmol, 4.6 mmol) dropwise over 15 min. After 1 h, BF_3•OEt_2 (0.28 mL, 2.26 mmol) was added and the mixture was stirred for 5 min. The reaction mixture from the first reaction was cannulated to the second flask followed by rinse (2 x 1 mL THF). The mixture was stirred at -78 °C for 1 h and then at room temperature for 2 h. After that time, the reaction was quenched with saturated NH_4Cl solution (10 mL)/saturated sodium tartrate solution (8 mL) and stirred vigorously for 1 h. The mixture was extracted with Et_2O (3 x 30 mL) and the organic extract was dried ($MgSO_4$) and concentrated. The residue was purified by column chromatography (3% - 12% EtOAc in hexanes) to give secondary alcohol **B6** (520 mg, 81%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73-7.70 (m, 4H), 7.48-7.37 (m, 6H), 7.35-7.22 (m, 5H), 5.77-5.66 (m, 1H), 5.24-5.19

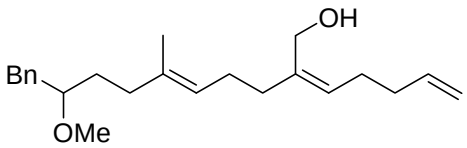
(m, 2H), 4.99-4.91 (m, 2H), 4.20 (s, 2H), 3.87-3.78 (m, 1H), 2.84 (dd, *J* = 13.5, 4.4 Hz, 1H), 2.68 (dd, *J* = 13.5, 8.3 Hz, 1H), 2.24-2.08 (m, 6H), 2.06-1.88 (m, 4H), 1.62 (s, 3H), 1.66-1.58 (m, 2H), 1.07 (s, 9H).

((2*Z*,5*E*)-9-Methoxy-6-methyl-2-(pent-4-enylidene)-10-phenyldec-5-enyloxy)(*tert*-butyl)diphenylsilane (B7)



A solution of the secondary alcohol **B6** (510 mg, 0.900 mmol) in DMF (8 mL) at 0 °C was treated with NaH (60% weight in mineral oil, 90 mg, 2.25 mmol). After 30 min, MeI (0.22 mL, 3.60 mmol) was added and the mixture was stirred overnight at room temperature. After that time, the reaction was quenched with water (20 mL) cautiously and extracted with Et_2O (3 x 30 mL) and the organic extract was dried ($MgSO_4$) and concentrated. The residue was purified by column chromatography (1% - 4% EtOAc in hexanes) to give the methyl ether **B7** (474 mg, 91%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72-7.66 (m, 4H), 7.47-7.36 (m, 6H), 7.32-7.25 (m, 2H), 7.23-7.18 (m, 3H), 5.79-5.66 (m, 1H), 5.21 (app t, *J* = 7.0 Hz, 1H), 5.14 (app qt, *J* = 6.8, 1.0 Hz, 1H), 4.99-4.91 (m, 2H), 4.20 (s, 2H), 3.39-3.32 (m, 1H), 3.32 (s, 3H), 2.86 (dd, *J* = 13.7, 6.1 Hz, 1H), 2.72 (dd, *J* = 13.7, 6.2 Hz, 1H), 2.25-2.07 (m, 5H), 2.04-1.88 (m, 5H), 1.59-1.51 (m, 2H), 1.54 (br s, 3H), 1.06 (s, 9H).

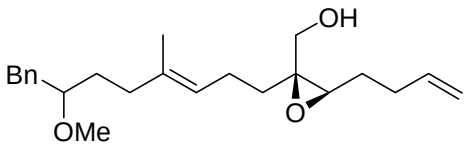
(2*Z*,5*E*)-9-Methoxy-6-methyl-2-(pent-4-enylidene)-10-phenyldec-5-en-1-ol (2.40)



A solution of the silyl ether **B7** (464 mg, 0.799 mmol) in THF (5 mL) was treated with TBAF (1 M in THF, 1.9 mL, 1.9 mmol). The reaction was stirred for 4 h, then

concentrated and the residue was purified by column chromatography (10% - 22% EtOAc in hexanes) to give the trienol **2.40** (230 mg, 84%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32-7.28 (m, 2H), 7.23-7.18 (m, 3H), 5.82 (tdd, *J* = 16.8, 10.2, 6.5 Hz, 1H), 5.31 (t, *J* = 6.8 Hz, 1H), 5.14-5.10 (m, 1H), 5.06-4.98 (m, 2H), 4.12 (d, *J* = 5.6 Hz, 2H), 3.38-3.30 (m, 1H), 3.32 (s, 3H), 2.86 (dd, *J* = 13.7, 6.1 Hz, 1H), 2.72 (dd, *J* =13.7, 6.2 Hz, 1H), 2.23-1.96 (m, 10H), 1.57-1.50 (m, 2H), 1.55 (s, 3H), 1.15 (t, *J* = 5.7 Hz, 1H).

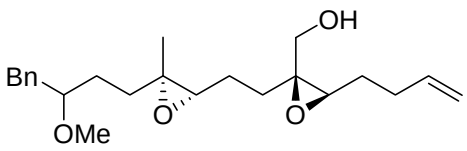
((2*S*,3*R*)-3-(But-3-enyl)-2-((*E*)-7-methoxy-4-methyl-8-phenyloct-3-enyl)oxiran-2-yl)methanol (B8)



A mixture of trienol **2.40** (223 mg, 0.651 mmol) and activated 4 Å molecular sieves (195 mg) in CH_2Cl_2 (6 mL) at -20 °C was treated with L-diisopropyl tartrate (16 μL, 78 μmol). After 15 min, Ti(O^iPr)$_4$ (20 μL, 65μmol) was introduced. The mixture was stirred for 30 min, and ^{t}BuOOH (5-6 M in decane, 0.36 mL, ~1.9 mmol) was added dropwise. The reaction was stirred for 40 min at -20 °C, and then water (0.3 mL) was added. The mixture was stirred at 0 °C for 1 h. After that time, 30% NaOH saturated with NaCl (0.3 mL) was added and the mixture was stirred at room temperature for 4 h. The mixture was filtered through a 1:1 mixture of $MgSO_4$/Celite and the residue was washed with CH_2Cl_2 (30 mL). The combined filtrates were concentrated and the residue was purified by column chromatography (20% - 25% EtOAc in hexanes containing 0.5% Et_3N) to give a colorless oil (150 mg, containing 7 mol% (+)-DIPT) which was treated with a mixture of 30% NaOH saturated with NaCl (0.3 mL) and CH_2Cl_2 (3 mL) for 5 h. The mixture was concentrated and the residue was purified by column chromatography (20% - 25% EtOAc in hexanes containing 0.5% Et_3N) to give the monoepoxide

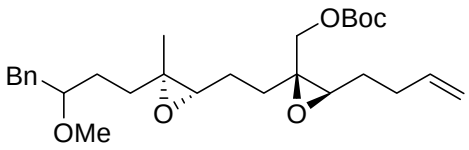
B8 (134 mg, 58%) as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31-7.20 (m, 5H), 5.84 (tdd, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.10-5.02 (m, 3H), 3.76 (dd, *J* = 11.8, 6.8 Hz, 1H), 3.67 (dd, *J* = 11.8, 5.3 Hz, 1H), 3.36-3.34 (m, 1H), 3.32 (s, 3H), 2.90-2.84 (m, 2H), 2.71 (dd, *J* = 13.7, 6.2 Hz, 1H), 2.28-1.99 (m, 6H), 1.94-1.90 (m, 1H), 1.78-1.45 (m, 6H), 1.55 (s, 3H).

((2*S*,3*R*)-3-(But-3-enyl)-2-(2-((2*S*,3*S*)-3-(3-methoxy-4-phenylbutyl)-3-methyloxiran-2-yl)ethyl)oxiran-2-yl)methanol (B9)



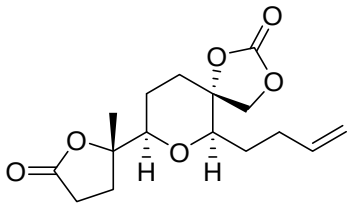
A solution of **B8** (125 mg, 0.349 mmol) in CH_3CN/DMM (5.2 mL, 1:2, v/v) was treated with a 0.05 M solution of $Na_2B_4O_7$ in $4x10^{-4}$ M Na_2(EDTA) (3.5 mL), Bu_4NHSO_4 (4.7 mg, 14.0 μmol) and *ent*-Shi ketone (27.0 mg, 0.105 mmol) sequentially. The mixture was cooled to - 5 °C. Oxone (268 mg, 0.436 mmol), dissolved in $4x10^{-4}$ M Na_2(EDTA) (2.0 mL), and K_2CO_3 (253 mg, 1.83 mmol), dissolved in water (2.0 mL), were added simultaneously via a syringe pump over 2.0 h. After the addition was completed, the slightly blue reaction mixture was stirred further for 15 min, then diluted with water (10 mL) and extracted with CH_2Cl_2 (4 x 15 mL). The organic extracts were dried ($MgSO_4$), filtered and concentrated. The residue was purified by flash chromatography (25% - 38% EtOAc in hexanes) to give unreacted starting material **B8** (37.4 mg, 30%) and the diepoxide **B9** (79.7 mg, 61%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32-7.19 (m, 5H), 5.91-5.78 (m, 1H), 5.11-5.01 (m, 2H), 3.73-3.71 (m, 2H), 3.38-3.34 (m, 1H), 3.32 (s, 3H), 2.92-2.83 (m, 2H), 2.71-2.65 (m, 1H), 2.32-2.18 (m, 2H), 2.03-1.91 (m, 1H), 1.87 (dt, *J* = 5.9, 2.2 Hz, 1H), 1.81-1.41 (m, 8H), 1.22 (s, 3H).

***tert*-Butyl ((2*S*,3*R*)-3-(but-3-enyl)-2-(2-((2*S*,3*S*)-3-(3-methoxy-4-phenylbutyl)-3-methyloxiran-2-yl)ethyl)oxiran-2-yl)methyl carbonate (2.36)**



A solution of the diepoxy alcohol **B9** (78 mg, 0.208 mmol) in dry toluene (2.0 mL) at 0 °C was treated with di-*tert*-butyl dicarbonate (91 mg, 0.416 mmol) and 1-methylimidazole (16 μL, 0.208 mmol). The reaction mixture was stirred overnight, allowing the temperature to warm to room temperature slowly. After that time, the reaction was quenched with water (10 mL) and extracted with CH_2Cl_2 (3 x 15 mL). The organic extracts were dried ($MgSO_4$), filtered and concentrated. The residue was purified by flash chromatography (15% - 20% EtOAc in hexanes containing 0.5% Et_3N) to give the *tert*-butyl carbonate **2.36** (90 mg, 91%, dr ~ 4.6:1 regarding the stereochemical outcomes of the two epoxide groups) as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31-7.28 (m, 2H), 7.23-7.19 (m, 3H), 5.85-5.80 (m, 1H), 5.08 (td, *J* = 17.1, 1.6 Hz, 1H), 5.02 (dd, *J* = 10.4, 1.2 Hz, 1H), 4.21-4.12 (m, 2H), 3.38-3.33 (m, 1H), 3.31 (s, 3H), 2.89-2.83 (m, 2H), 2.70-2.65 (m, 2H), 2.29-2.21 (m, 2H), 1.85-1.81 (m, 1H), 1.78-1.60 (m, 7H), 1.54-1.42 (m, 2H), 1.45 (s, 9H), 1.21/1.20 (s, 3H).

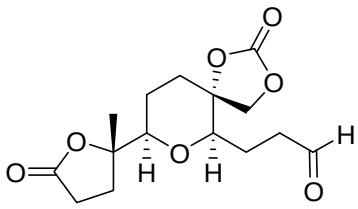
(5*R*,6*R*,8*R*)-6-But-3-enyl-8-((*S*)-2-methyl-5-oxo-tetrahydrofuran-2-yl)-1,3,7-trioxaspiro[4.5]decan-2-one (B10)



Diepoxide **2.36** (44 mg, 92.7 μmol) in dichloroethane/toluene (3.1 mL, 5:1, v/v) in borosilicate flask at room temperature was treated with activated 4Å molecular sieves (88 mg), anhydrous $Na_2S_2O_3$ (88 mg), NaOAc (88 mg) and *N*-methylquinolinium hexafluorophosphate (13.4 mg, 46.4 μmol). The mixture was photoirradiated with gentle air bubbling for 6.5 h while stirring at room

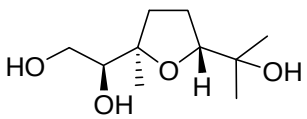
temperature. The reaction mixture was filtered through a small plug of silica gel and the residue was washed with EtOAc (20 mL). The filtrate was concentrated and the resulting residue was purified by flash chromatography (25% - 35% EtOAc in hexanes) to provide a pale yellow oil (10.5 mg), which was dissolved in acetone (1.0 mL) at 0 °C. Jones reagent (2.67 M, 6 drops) was added dropwise (1 drop/5 min). After completion of addition, the mixture was stirred for 1 h and then concentrated. The residues was purified by column chromatography (50% - 70% EtOAc in hexanes) to give the lactone **B10** (4.6 mg, 17%, two steps) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.83-5.69 (m, 1H), 5.11-5.01 (m, 2H), 4.54 (d, *J* = 8.8 Hz, 1H), 4.12 (d, *J* = 9.0 Hz, 1H), 3.50 (dd, *J* = 10.8, 2.0 Hz, 1H), 3.46 (dd, *J* = 11.7, 2.3 Hz, 1H), 2.64-2.57 (m, 2H), 2.32-2.05 (m, 5H), 1.97-1.87 (m, 2H), 1.69 (dtd, *J* = 13.6, 8.1, 2.2 Hz, 1H), 1.49 (dtd, *J* = 13.6, 5.7, 2.9 Hz, 1H), 1.40-1.32 (m, 1H), 1.36 (s, 3H).

3-((5*R*,6*R*,8*R*)-[8-((*S*)-2-Methyl-5-oxotetrahydrofuran-2-yl)-2-oxo-1,3,7-trioxaspiro[4.5]dec-6-yl])propionaldehyde (2.19)



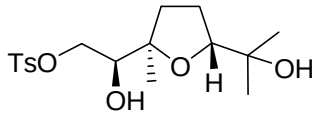
A solution of the lactone **B10** (3.3 mg, 10.6 μmol) in CH_2Cl_2 (0.8 mL) at - 78 °C was treated dropwise with a saturated solution of O_3 in CH_2Cl_2 at -78 °C until all the starting material disappeared. PPh_3 (a crystal) was added and the cold bath was removed. The reaction was stirred for 10 h, then concentrated and the residues was purified by column chromatography (60% - 80% EtOAc in hexanes) to give the aldehyde **2.19** (3.6 mg (containing ~17% Ph_3P=O, 83%) as a colorless oil, which has identical spectral data to *ent*-**2.19**.

(*S*)-1-((2*R*,5*R*)-Tetrahydro-5-(2-hydroxypropan-2-yl)-2-methylfuran-2-yl)ethane-1,2-diol (2.42)



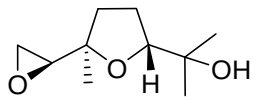
A mixture of AD-mix-β (12.35 g) in ^{t}BuOH/H_2O (88 mL, 1:1, v/v) at 0 °C was treated with $CH_3SO_2NH_2$ (0.839 g, 8.82 mmol). After 15 min, the epoxy alcohol (1.50 g, 8.82 mmol, prepared from geraniol through Sharpless asymmetric epoxidation) was added dropwise and the flask formerly containing the epoxy alcohol was rinsed with ^{t}BuOH/H_2O (2 x 2 mL, 1:1, v/v). The mixture was stirred at 0 °C for 2 days, then concentrated to ~50 mL and extracted with EtOAc (25 x 30 mL). The combined organic extracts were dried (Na_2SO_4), filtered and concentrated. The residue was purified by column chromatography (90% - 100% EtOAc in hexanes followed by 5% - 15% MeOH in EtOAc) to give a mixture of **2.22** and **2.42** (1.720 g). This mixture was dissolved in PhMe (200 mL) at 0 °C and CSA·pyridine (262 mg, 0.842 mmol) was added. The reaction was stirred for 1.5 h, and Et_3N (1 mL) was added. The solvent was removed under reduced pressure and the residue was purified by column chromatography (90% - 100% EtOAc in hexanes followed by 5% - 15% MeOH in EtOAc) to give triol **2.42** (1.627 g, 90%, two steps) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.79 (t, *J* = 8.2 Hz, 1H), 3.75-3.70 (m, 2H), 3.58-3.52 (m, 1H), 2.88 (br s, 1H), 2.53-2.51 (m, 1H), 2.18 (s, 1H), 2.10 (td, *J* = 11.3, 10.2 Hz, 1H), 1.90-1.81 (m, 2H), 1.65-1.57 (m, 1H), 1.22 (s, 3H), 1.18 (s, 3H), 1.14 (s, 3H); HRMS (ESI): *m*/*z* calcd for $C_{10}H_{20}O_4Na$ (M + Na^+) 227.1259, found 227.1246.

(*R*)-2-Hydroxy-2-[(5*R*)-5-(1-hydroxy-1-methylethyl)-(2*R*)-2-methyltetrahydrofuran-2-yl]ethyl toluene-4-sulfonate (B11)



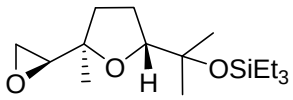
A solution of triol **2.42** (1.627 g, 7.96 mmol) in CH_2Cl_2 (20 mL) was treated with pyridine (1.3 mL, 15.9 mmol), TsCl (1.670 g, 8.76 mmol) and DMAP (49 mg, 0.40 mmol) sequentially. The reaction was stirred overnight, then concentrated and the residue was purified by column chromatography (30% - 60% EtOAc in hexanes) to give the tosylate **B11** (1.284 g, 45%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (td, *J* = 8.4, 1.9 Hz, 2H), 7.38-7.35 (m, 2H), 4.26 (dd, *J* = 10.4, 2.6 Hz, 1H), 4.02 (dd, *J* = 10.5, 7.8 Hz, 1H), 3.78 (td, *J* = 7.6, 2.9 Hz, 1H), 3.72 (dd, *J* = 8.9, 6.8 Hz, 1H), 2.52 (d, *J* = 3.2 Hz, 1H), 2.46 (s, 3H), 2.06 (td, *J* = 11.9, 9.2 Hz, 1H), 1.96 (s, 1H), 1.89-1.81 (m, 2H), 1.66 (ddd, *J* = 11.9, 6.2, 3.5 Hz, 1H), 1.18 (s, 3H), 1.13 (s, 3H), 1.11 (s, 3H); HRMS (ESI): *m*/*z* calcd for $C_{17}H_{26}O_6NaS$ $[M+Na]^+$ 381.1348, found 381.1340.

2-((2*R*,5*R*)-Tetrahydro-5-methyl-5-((*S*)-oxiran-2-yl)furan-2-yl)propan-2-ol (B12)



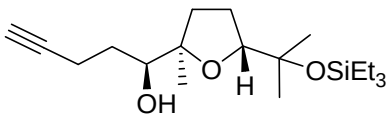
A solution of the tosylate **B11** (270 mg, 0.753 mmol) in dry MeOH (21 mL) was treated with anhydrous K_2CO_3 (104 mg, 0.753 mmol). The mixture was stirred for 1.5 h, then concentrated and the residue was purified by column chromatography (50% EtOAc in hexanes containing 0.5% Et_3N) to give the epoxide **B12** (134 mg, 96%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.81-3.76 (m, 1H), 3.04 (dd, *J* = 4.1, 2.8 Hz, 1H), 2.74 (dd, *J* = 5.0, 4.2 Hz, 1H), 2.58 (dd, *J* = 5.0, 2.8 Hz, 1H), 2.11 (s, 1H), 1.90-1.78 (m, 2H), 1.68-1.58 (m, 1H), 1.28 (s, 3H), 1.23 (s, 3H), 1.13 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 86.8, 81.4, 70.7, 57.2, 43.9, 32.8, 27.5, 26.3, 24.3, 24.3.

(2-((2*R*,5*R*)-Tetrahydro-5-methyl-5-((*S*)-oxiran-2-yl)furan-2-yl)propan-2-yloxy)triethyl-silane (2.43)



A solution of the tertiary alcohol **B12** (178 mg, 0.956 mmol) in DMF (5.8 mL) at 0 °C were treated with imidazole (130 mg, 1.91 mmol), TESCl (0.24 mL, 1.43 mmol) and DMAP sequentially. The mixture was stirred at 0 °C for 2 h and then at room temperature overnight. After that time, the reaction was quenched with water (15 mL) at 0 °C and extracted with Et_2O (3 x 20 mL). The organic extract was dried ($MgSO_4$), filtered and concentrated. The residue was purified by column chromatography (2% - 8% Et_2O in hexanes containing 0.5% Et_3N) to give the silyl ether **2.43** (261 mg, 91%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.72 (t, *J* = 7.0 Hz, 1H), 2.99 (dd, *J* = 4.1, 2.8 Hz, 1H), 2.73 (dd, *J* = 4.9, 4.2 Hz, 1H), 2.58 (dd, *J* = 5.1, 2.8 Hz, 1H), 1.98-1.73 (m, 3H), 1.58 (ddd, *J* = 13.7, 8.2, 5.2 Hz, 1H), 1.24 (s, 3H), 1.20 (s, 3H), 1.19 (s, 3H), 0.95 (t, *J* = 8.1 Hz, 9H), 0.58 (q, *J* = 7.8 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 87.7, 81.6, 74.3, 57.4, 44.2, 33.1, 28.1, 26.6, 25.5, 24.0, 7.3, 6.9; IR (neat) 2958, 2876, 1240, 1174, 1044, 726. HRMS (ESI): *m*/*z* calcd for $C_{16}H_{32}O_3NaSi$ $[M+Na]^+$ 323.2018, found 323.1993.

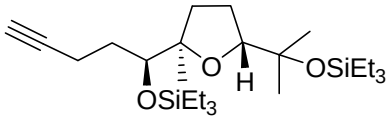
(*R*)-2-Methyl-(5*R*)-5-(1-methyl-1-triethylsilanyloxyethyl)-2-((*S*)-1-triethylsilanyloxypent-4-ynyl)tetrahydrofuran (B13)



A mixture of *n*-BuLi (1.6 M in hexanes, 23.2 mL, 37.2 mmol) in Et_2O (8 mL) at -78 °C was treated with tetramethylethylenediamine (1.4 mL, 9.3 mmol) followed by dropwise addition of propargyl bromide (80% weight in PhMe, 2.1 mL, 18.6 mmol). The resulting yellow suspension was stirred at -78 °C for 20 min, then transferred to a solution of epoxide **2.43** (180 mg, 0.6 mmol) in

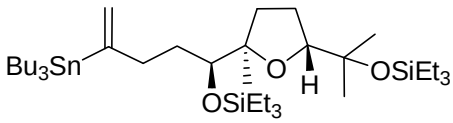
anhydrous Et_2O (1.0 mL) at -78 °C quickly via syringe. The mixture was stirred at -78 °C for 1 h, then quenched with saturated NH_4Cl (20 mL)/water (10 mL) and extracted with Et_2O (3 x 20 mL). The ether solution was dried ($MgSO_4$), filtered and concentrated. The residue was purified by column chromatography (4% - 12% Et_2O in hexanes) to give starting material **2.43** (65 mg, 36%) and the terminal alkyne **B13** (128 mg, 63%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.71-3.61 (m, 2H), 2.49-2.40 (m, 2H), 2.33 (ddd, *J* = 16.8, 8.0, 2.6 Hz, 1H), 2.04 (td, *J* = 11.2, 8.2 Hz, 1H), 1.97 (t, *J* = 2.7 Hz, 1H), 1.96-1.83 (m, 2H), 1.74-1.65 (m, 1H), 1.56-1.44 (m, 2H), 1.22 (s, 3H), 1.18 (s, 3H), 1.13 (s, 3H), 0.96 (t, *J* = 7.7 Hz, 9H), 0.59 (q, *J* = 8.0 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 88.9, 85.9, 84.7, 75.6, 74.1, 68.6, 31.1, 30.9, 27.7, 26.9, 26.1, 24.0, 16.1, 7.3, 7.0.

(*S*)-1-[(2*R*)-2-Methyl-(5*R*)-5-(1-methyl-1-triethylsilanyloxy-ethyl)-tetrahydro-furan-2-yl]-pent-4-yn-1-ol (2.44)



A solution of the secondary alcohol **B13** (120 mg, 0.352 mmol) in CH_2Cl_2 (3.5 mL) at 0 °C was treated with imidazole (27 mg, 0.396 mmol), TESCl (65 μL, 0.387 mmol) and DMAP (2.1 mg, 17 μmol) sequentially, and the cold bath was removed. After 1 h, the reaction mixture was concentrated and the residue was purified by column chromatography (1% - 3% Et_2O in hexanes) to give the bis-silyl ether **2.44** (145 mg, 91%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.67-3.63 (m, 2H), 2.38-2.29 (m, 1H), 2.23 (ddd, *J* = 16.9, 7.9, 2.6 Hz, 1H), 1.99-1.74 (m, 5H), 1.59-1.47 (m, 2H), 1.19 (s, 3H), 1.17 (s, 3H), 1.09 (s, 3H), 1.00-0.93 (m, 18H), 0.68-0.55 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 87.4, 85.8, 85.2, 76.3, 74.3, 68.4, 34.6, 32.8, 28.1, 26.5, 25.7, 22.7, 15.9, 7.3, 7.3, 7.0, 5.7.

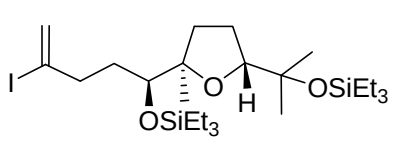
(2*R*)-2-Methyl-(5*R*)-5-(1-methyl-1-triethylsilanyloxyethyl)-2-((1*S*)-4-tributylstannanyl-1-triethylsilanyloxypent-4-enyl)tetrahydrofuran (B14)



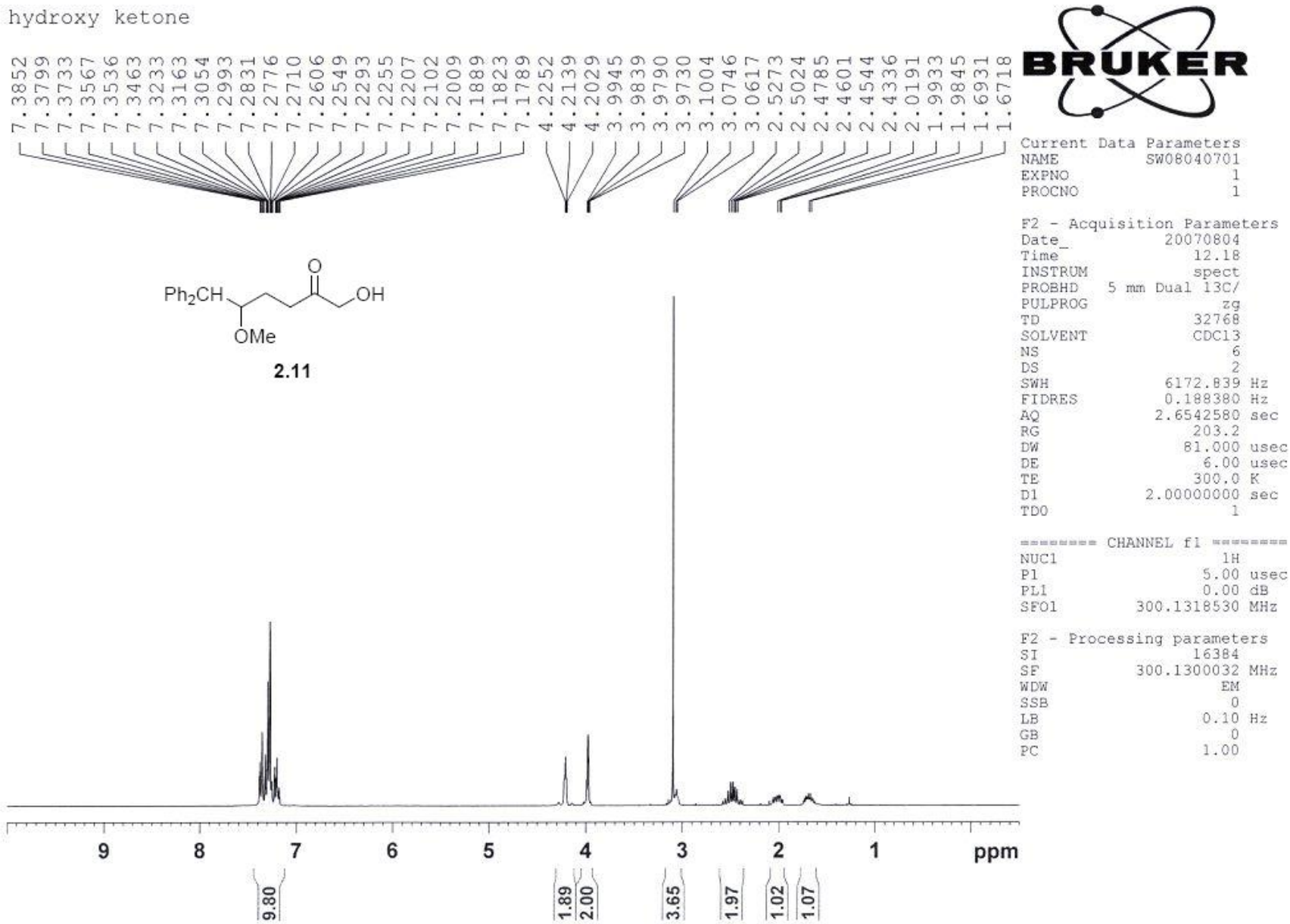
A solution of $^{i}Pr_2NH$ (0.57 mL, 4.05 mmol) in THF (3.5 mL) at 0 °C was treated with *n*-BuLi (1.6 M in hexanes, 2.3 mL, 3.6 mmol). After 30 min, the flask was cooled to -30 °C and a solution of *n*-Bu_3SnH (0.97 mL, 3.6 mmol) in THF (2.1 mL) was added dropwise. The pale yellow solution was stirred for 1 h and Et_2AlCl (1 M in heptane, 3.0 mL, 3.0 mmol) was added. The mixture was stirred at -30 °C for 5 h to form an *n*-$Bu_3SnAlEt_2$ solution (~0.244 M).

A solution of terminal alkyne **2.44** (140 mg, 0.308 mmol) in THF (11 mL) at -30 °C was treated with *n*-$Bu_3SnAlEt_2$ solution (6.2 mL, ~1.5 mmol) followed by CuCN (8.3 mg, 92.4 μmol). After 1 h, the *n*-$Bu_3SnAlEt_2$ solution (2.0 mL, ~0.5 mmol) and CuCN (8.0 mg, 89 μmol) were added. The mixture was stirred at -30 °C for 5 h, and then stored at -20 °C overnight. The reaction was quenched with saturated NH_4Cl (20 mL) and extracted with Et_2O (3 x 20 mL). The ether solution was dried ($MgSO_4$), filtered and concentrated. The residue was purified by column chromatography (2% - 2.5% Et_2O in hexanes) to give the desired vinyl stannane **B14** (67.8 mg, 29%) and unreacted starting material **2.44** (71.9 mg, 51%). For vinyl stannane: ^1H NMR (500 MHz, $CDCl_3$) δ 5.70 (*J* = 84.6, 0.8 Hz, 1H), 5.10 (*J* = 38.7, 1.5 Hz, 1H), 3.64 (dd, *J* = 5.5, 3.7 Hz, 1H), 3.52 (dd, *J* = 5.0, 1.9 Hz, 1H), 2.42 (dt, *J* = 8.2, 2.8 Hz, 1H), 2.22 (dt, *J* = 7.5, 2.8 Hz, 1H), 1.97 (dt, *J* = 6.5, 4.8 Hz, 1H), 1.92-1.84 (m, 1H), 1.82-1.76 (m, 1H), 1.66 (tt, *J* = 8.0, 2.0 Hz, 1H), 1.57-1.29 (m, 14H), 1.19 (s, 3H), 1.17 (s, 3H), 1.08 (s, 3H), 0.99-0.88 (m, 33H), 0.66-0.56 (m, 12H).

2-((1*S*)-4-Iodo-1-triethylsilanyloxypent-4-enyl)-(2*R*)-2-methyl-(5*R*)-5-(1-methyl-1-triethylsilanyloxy-ethyl)tetrahydrofuran (2.45)



A solution of the vinyl stannane **B14** (62 mg, 83 μmol) in CH_2Cl_2 (1.6 mL) was treated with I_2 (23 mg, 91μmol). The slightly purple solution was stirred for 10 min, then quenched with saturated $Na_2S_2O_3$ solution (5 mL) and extracted with CH_2Cl_2 (3 x 15 mL). The organic extract was dried (Na_2SO_4), filtered and concentrated. The residue was purified by column chromatography (2% Et_2O in hexanes containing 0.5% Et_3N) to give the vinyl iodide **2.45** (41.7 mg, 86%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.04 (q, *J* = 1.4 Hz, 1H), 5.69 (d, *J* = 0.8 Hz, 1H), 3.66-3.61 (m, 1H), 3.54 (dd, *J* = 7.5, 4.1 Hz, 1H), 2.60-2.41 (m, 2H), 1.99-1.73 (m, 4H), 1.60-1.50 (m, 2H), 1.19 (s, 3H), 1.17 (s, 3H), 1.10 (s, 3H), 1.00-0.93 (m, 18H), 0.67-0.54 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 125.2, 113.1, 87.4, 85.9, 76.8, 74.2, 42.9, 34.9, 33.9, 28.0, 26.5, 25.8, 22.6, 7.4, 7.0, 5.7; IR (neat) 2956, 2876, 1459, 1238, 1173, 1099, 1068. HRMS (ESI): *m*/*z* calcd for $C_{25}H_{51}IO_3NaSi$ $[M+Na]^+$ 605.2319, found 605.2341.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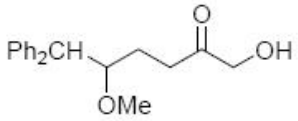

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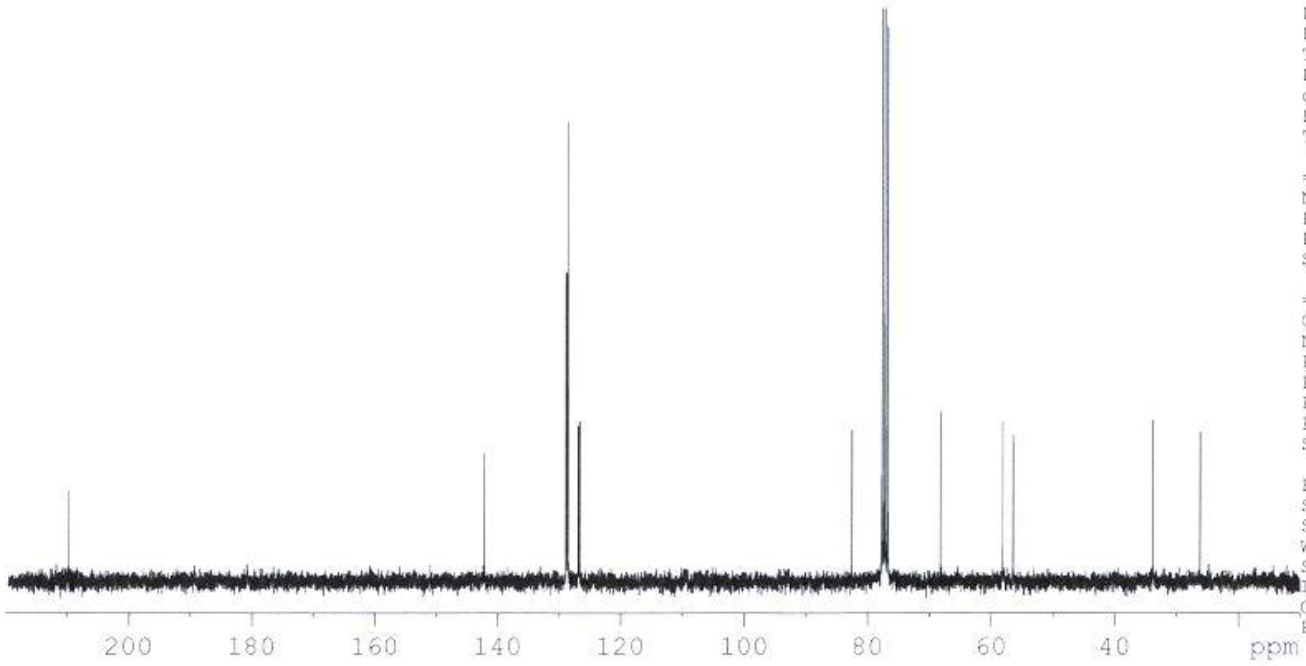

BRUKER

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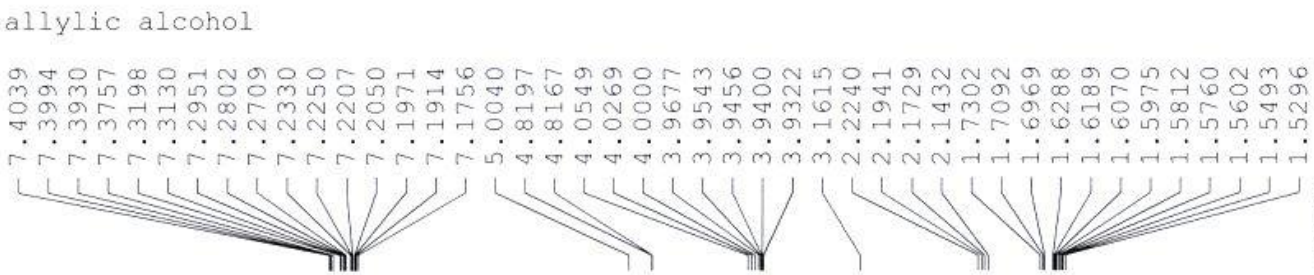

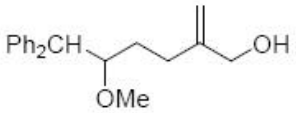

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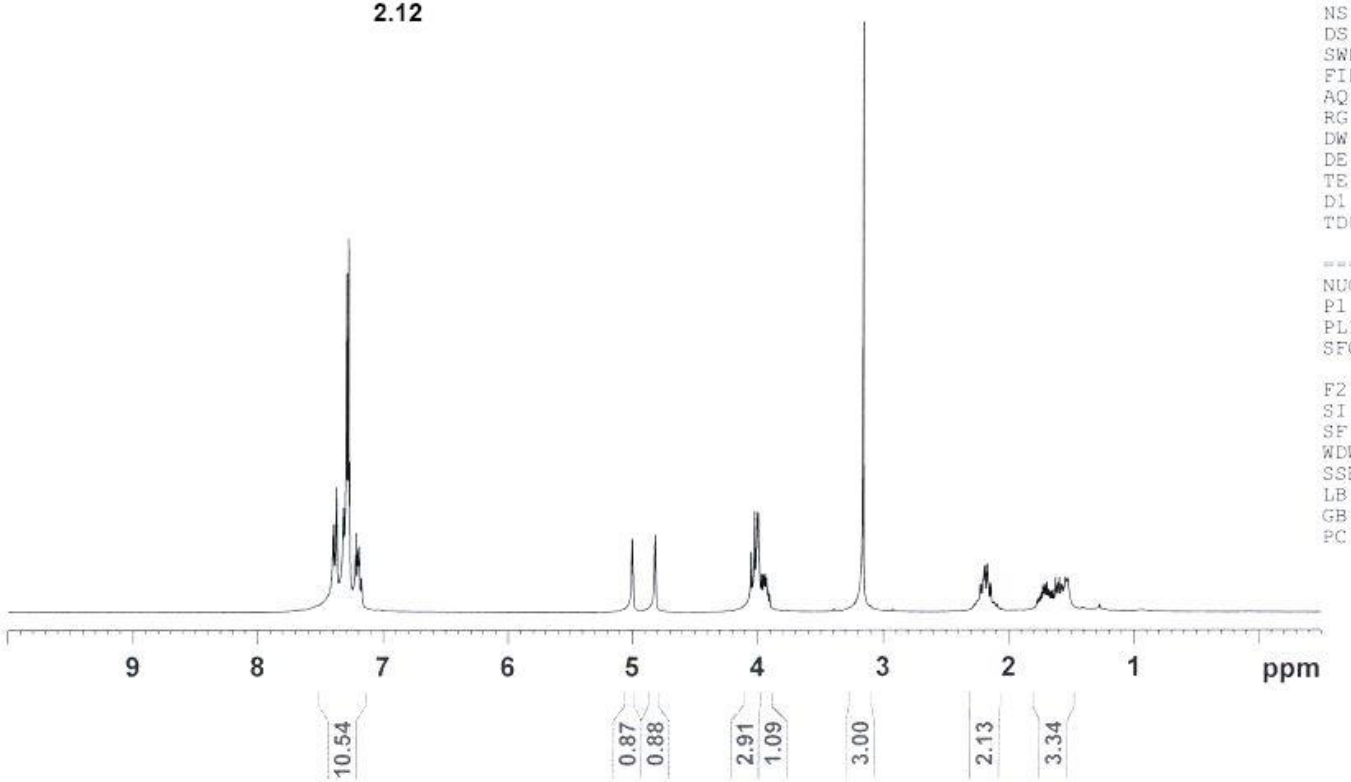

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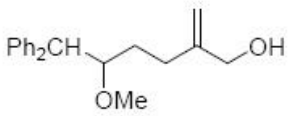
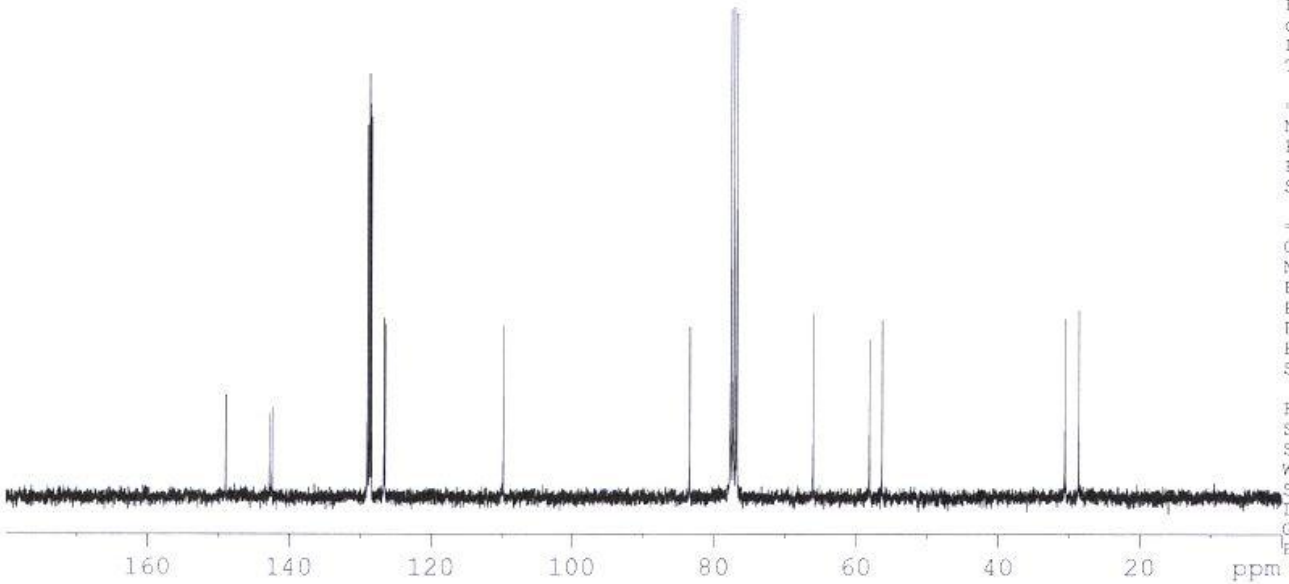
30.63
28.70



2.12



BRUKER

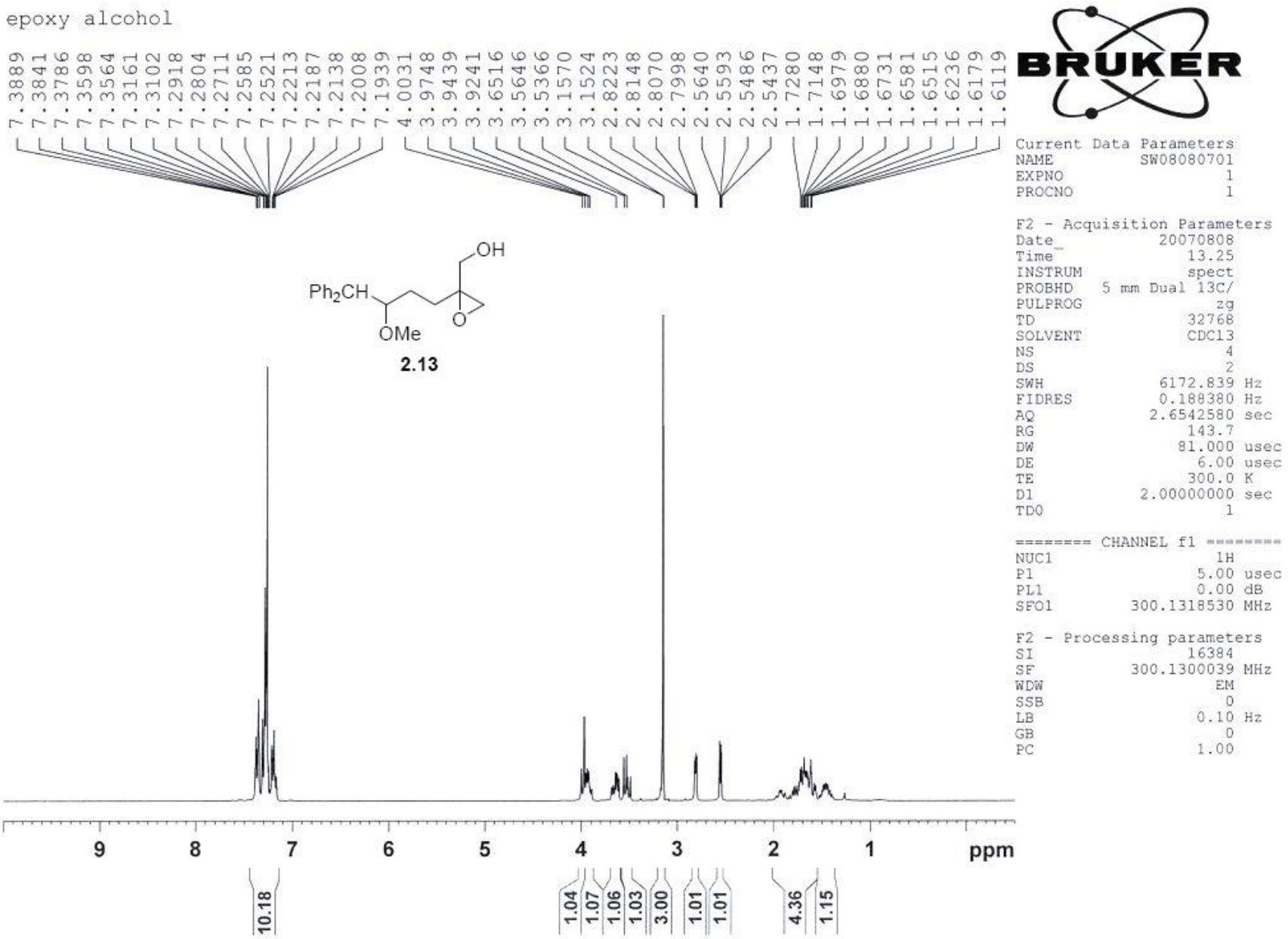
```
Current Data Parameters
NAME          SW08070702
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20070807
Time              16.09
INSTRUM           spect
PROBHD   5 mm QNP  1H/1
PULPROG           zgpg
TD               65536
SOLVENT          CDCl3
NS                 199
DS                   2
SWH          17985.611 Hz
FIDRES         0.274439 Hz
AQ             1.8219508 sec
RG                13004
DW               27.800 usec
DE                6.00 usec
TE               300.1 K
D1          10.00000000 sec
d11          0.03000000 sec
DELTA        9.89999962 sec
TD0                  1

======== CHANNEL f1 ========
NUC1                13C
P1                7.00 usec
PL1               0.00 dB
SFO1         75.4639789 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                1H
PCPD2           100.00 usec
PL2               0.00 dB
PL12             18.24 dB
PL13             18.24 dB
SFO2        300.0862003 MHz

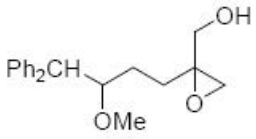
F2 - Processing parameters
SI                32768
SF          75.4564173 MHz
WDW                EM
SSB                 0
LB               1.00 Hz
GB                  0
PC               1.40
```


epoxy alcohol
7.3889
7.3841
7.3786
7.3598
7.3564
7.3161
7.3102
7.2918
7.2804
7.2711
7.2585
7.2521
7.2213
7.2187
7.2138
7.2008
7.1939
4.0031
3.9748
3.9439
3.9241
3.6516
3.5646
3.5366
3.1570
3.1524
2.8223
2.8148
2.8070
2.7998
2.5640
2.5593
2.5486
2.5437
1.7280
1.7148
1.6979
1.6880
1.6731
1.6581
1.6515
1.6236
1.6179
1.6119
OH
Ph2CH
OMe
O
2.13
9
8
7
6
5
4
3
2
1
ppm
10.18
1.04
1.07
1.06
1.03
3.00
1.01
1.01
4.36
1.15
BRUKER
Current Data Parameters
NAME SW08080701
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070808
Time 13.25
INSTRUM spect
PROBHD 5 mm Dual 13C/
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 4
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 143.7
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 5.00 usec
PL1 0.00 dB
SFO1 300.1318530 MHz
F2 - Processing parameters
SI 16384
SF 300.1300039 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

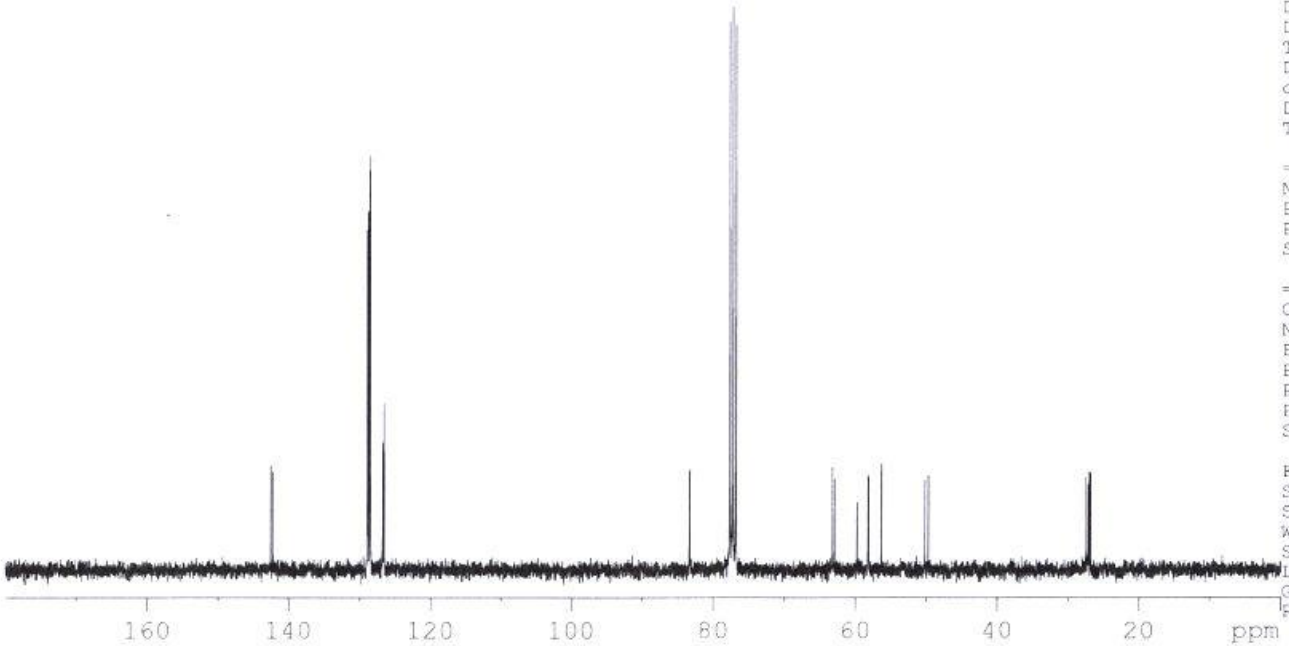
epoxy alcohol

142.58
142.27
128.93
128.81
128.61
128.52
126.77
126.58

83.41
83.29
77.66
77.23
76.81
63.21
62.90
59.78
59.72
58.23
58.10
56.33
56.28
50.17
49.68
27.51
27.17
27.03
26.83



2.13



BRUKER

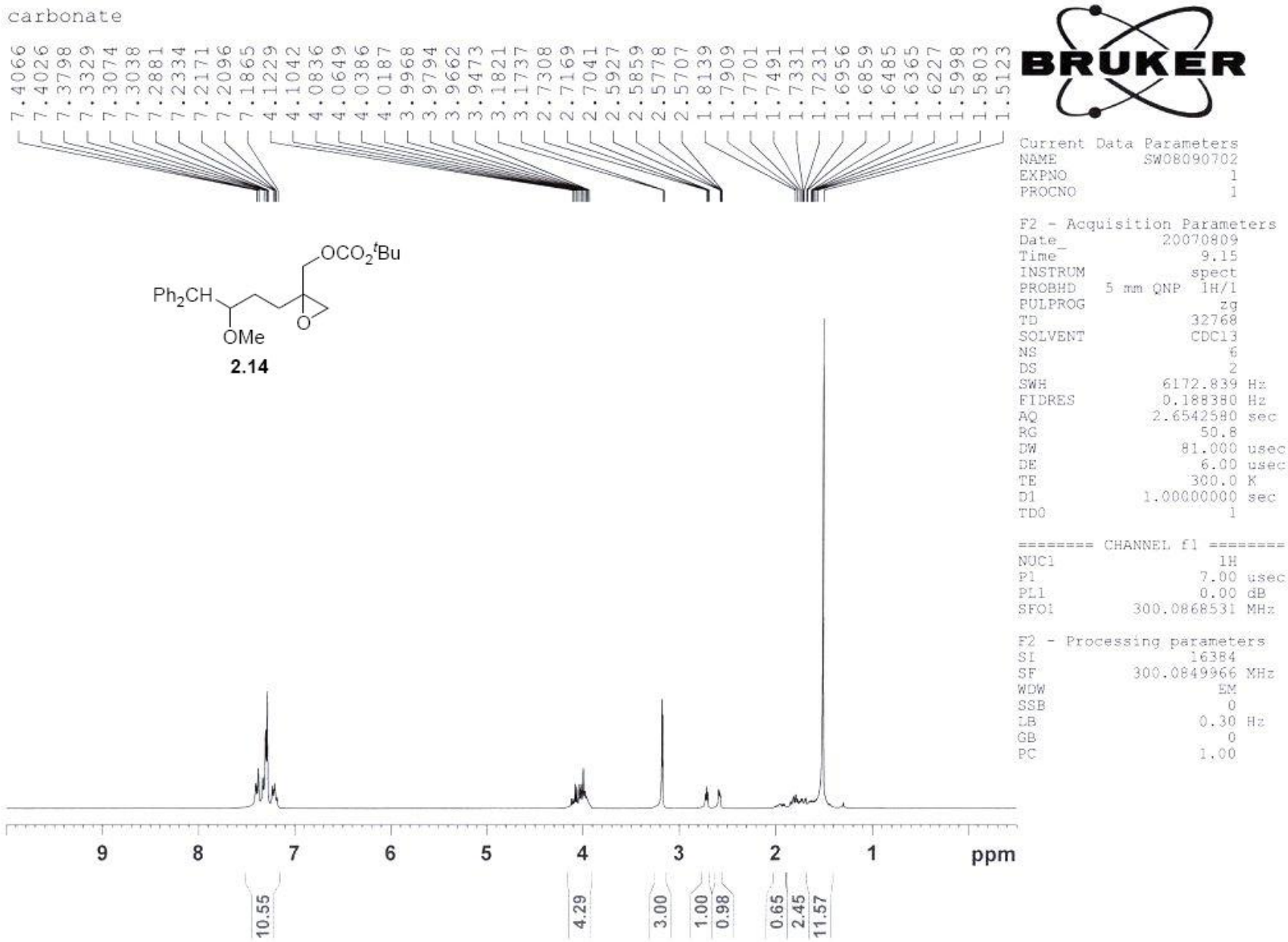
```
Current Data Parameters
NAME                 SW08080704
EXPNO                         1
PROCNO                        1

F2 - Acquisition Parameters
Date_                  20070808
Time                      17.07
INSTRUM                   spect
PROBHD    5 mm QNP  1H/1
PULPROG                    zgpg
TD                        65536
SOLVENT                   CDCl3
NS                          159
DS                            2
SWH                   17985.611 Hz
FIDRES                0.274439 Hz
AQ                    1.8219508 sec
RG                        13004
DW                       27.800 usec
DE                        6.00 usec
TE                       300.1 K
D1                   10.00000000 sec
d11                   0.03000000 sec
DELTA                 9.89999962 sec
TD0                           1

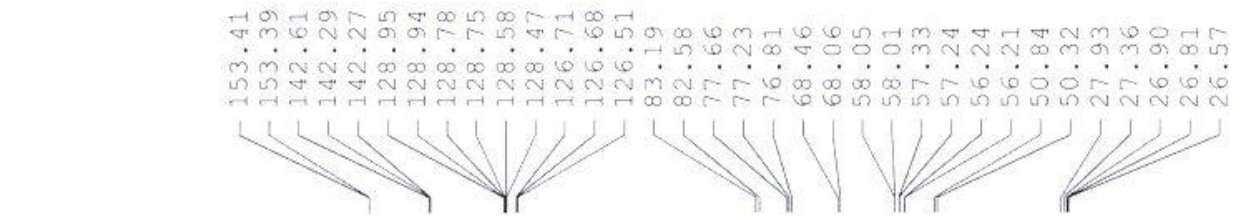
======== CHANNEL f1 ========
NUC1                        13C
P1                        7.00 usec
PL1                       0.00 dB
SFO1                75.4639789 MHz

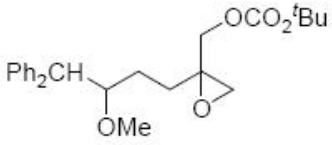
======== CHANNEL f2 ========
CPDPRG2                 waltz16
NUC2                        1H
PCPD2                   100.00 usec
PL2                       0.00 dB
PL12                     18.24 dB
PL13                     18.24 dB
SFO2                300.0862003 MHz

F2 - Processing parameters
SI                        32768
SF                  75.4564178 MHz
WDW                          EM
SSB                           0
LB                        1.00 Hz
GB                            0
PC                         1.40
```

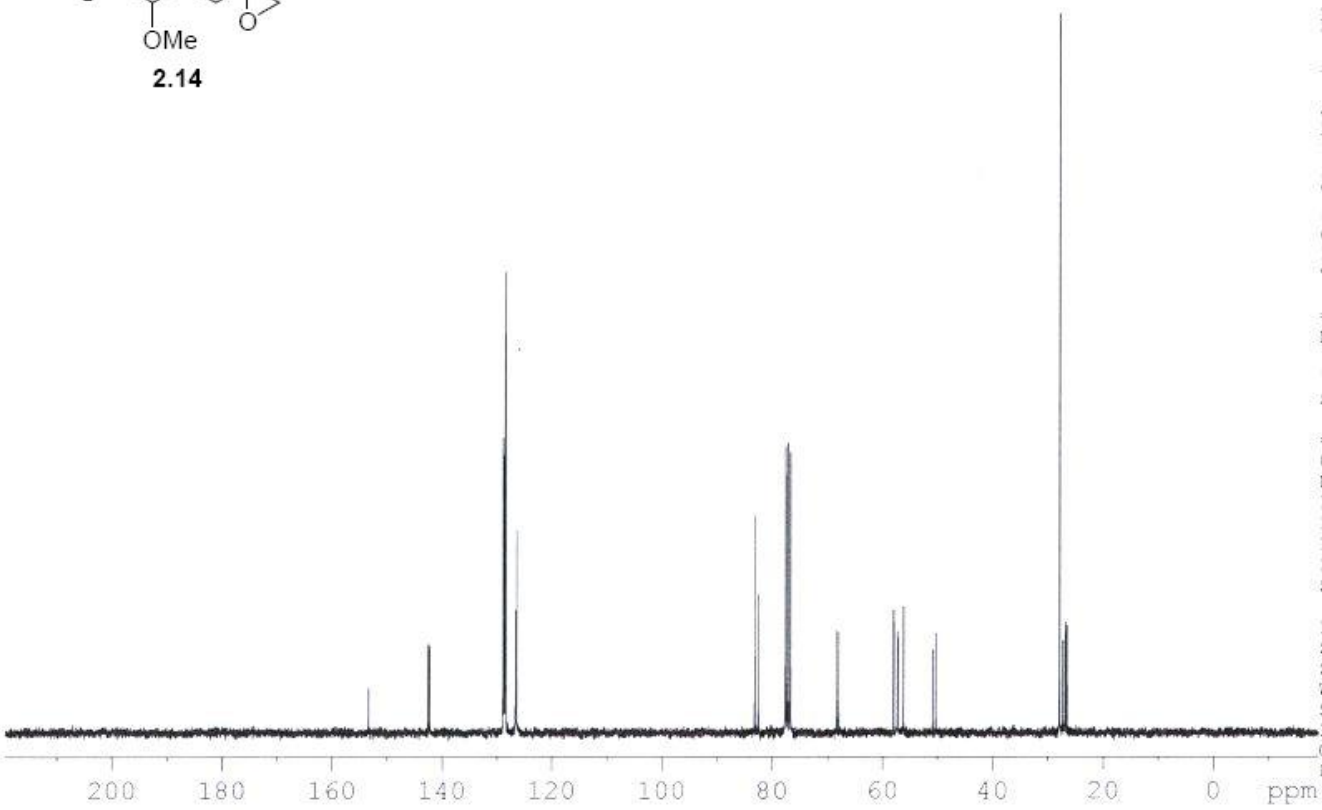

carbonate
7.4066
7.4026
7.3798
7.3329
7.3074
7.3038
7.2881
7.2334
7.2171
7.2096
7.1865
4.1229
4.1042
4.0836
4.0649
4.0386
4.0187
3.9968
3.9794
3.9662
3.9473
3.1821
3.1737
2.7308
2.7169
2.7041
2.5927
2.5859
2.5778
2.5707
1.8139
1.7909
1.7701
1.7491
1.7331
1.7231
1.6956
1.6859
1.6485
1.6365
1.6227
1.5998
1.5803
1.5123
OCO2tBu
Ph2CH
OMe
O
2.14
9
8
7
6
5
4
3
2
1
ppm
10.55
4.29
3.00
1.00
0.98
0.65
2.45
11.57
BRUKER
Current Data Parameters
NAME SW08090702
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070809
Time 9.15
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 6
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 50.8
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 7.00 usec
PL1 0.00 dB
SFO1 300.0868531 MHz
F2 - Processing parameters
SI 16384
SF 300.0849966 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

carbonate





2.14



BRUKER

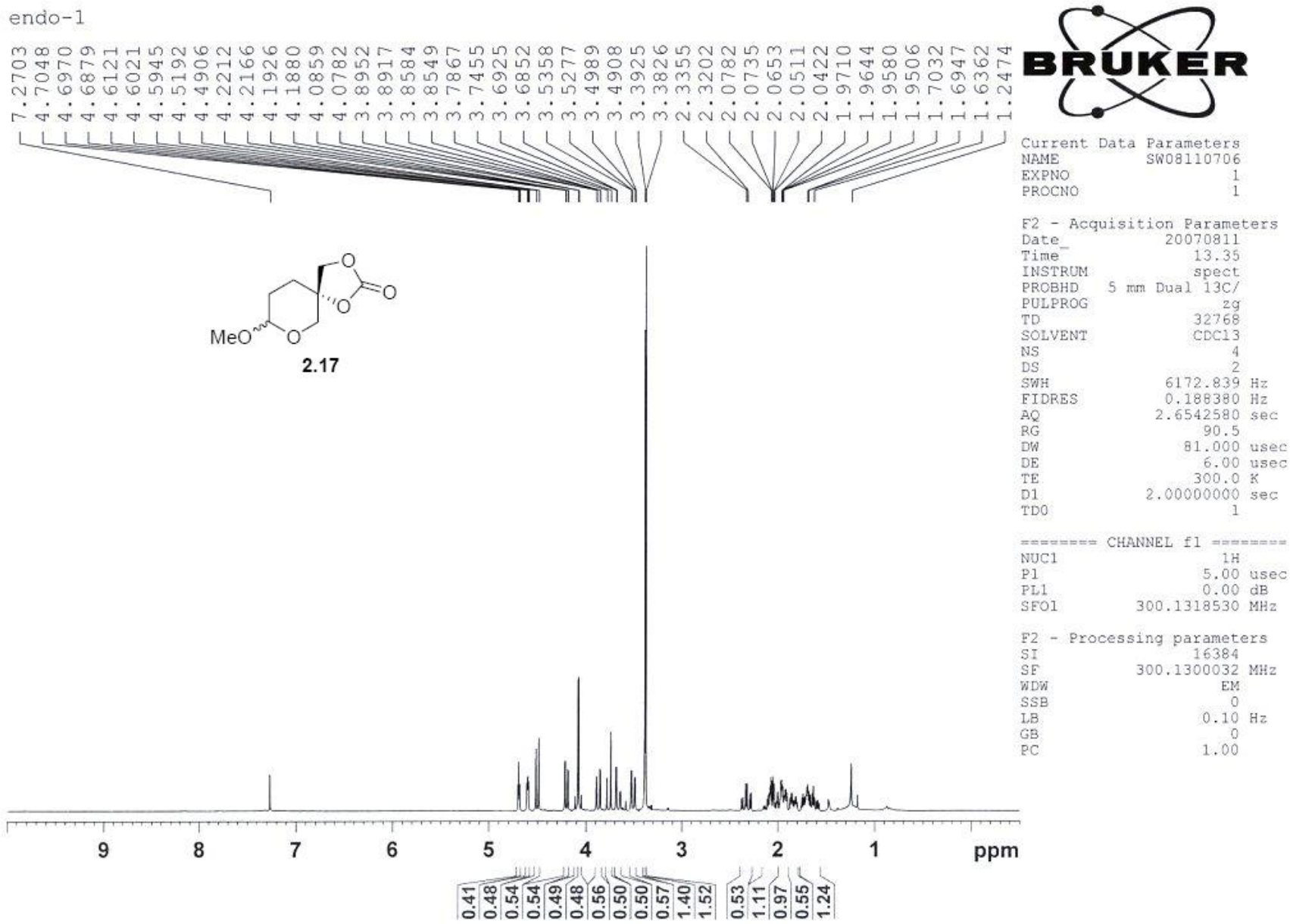
```
Current Data Parameters
NAME                 SW08090701
EXPNO                         1
PROCNO                        1

F2 - Acquisition Parameters
Date_                  20070809
Time                       8.46
INSTRUM                   spect
PROBHD    5 mm QNP  1H/1
PULPROG                   zgpg
TD                       65536
SOLVENT                  CDCl3
NS                         135
DS                           2
SWH                  17985.611 Hz
FIDRES                0.274439 Hz
AQ                    1.8219508 sec
RG                       13004
DW                      27.800 usec
DE                       6.00 usec
TE                      300.0 K
D1                   10.00000000 sec
d11                   0.03000000 sec
DELTA                 9.89999962 sec
TD0                          1

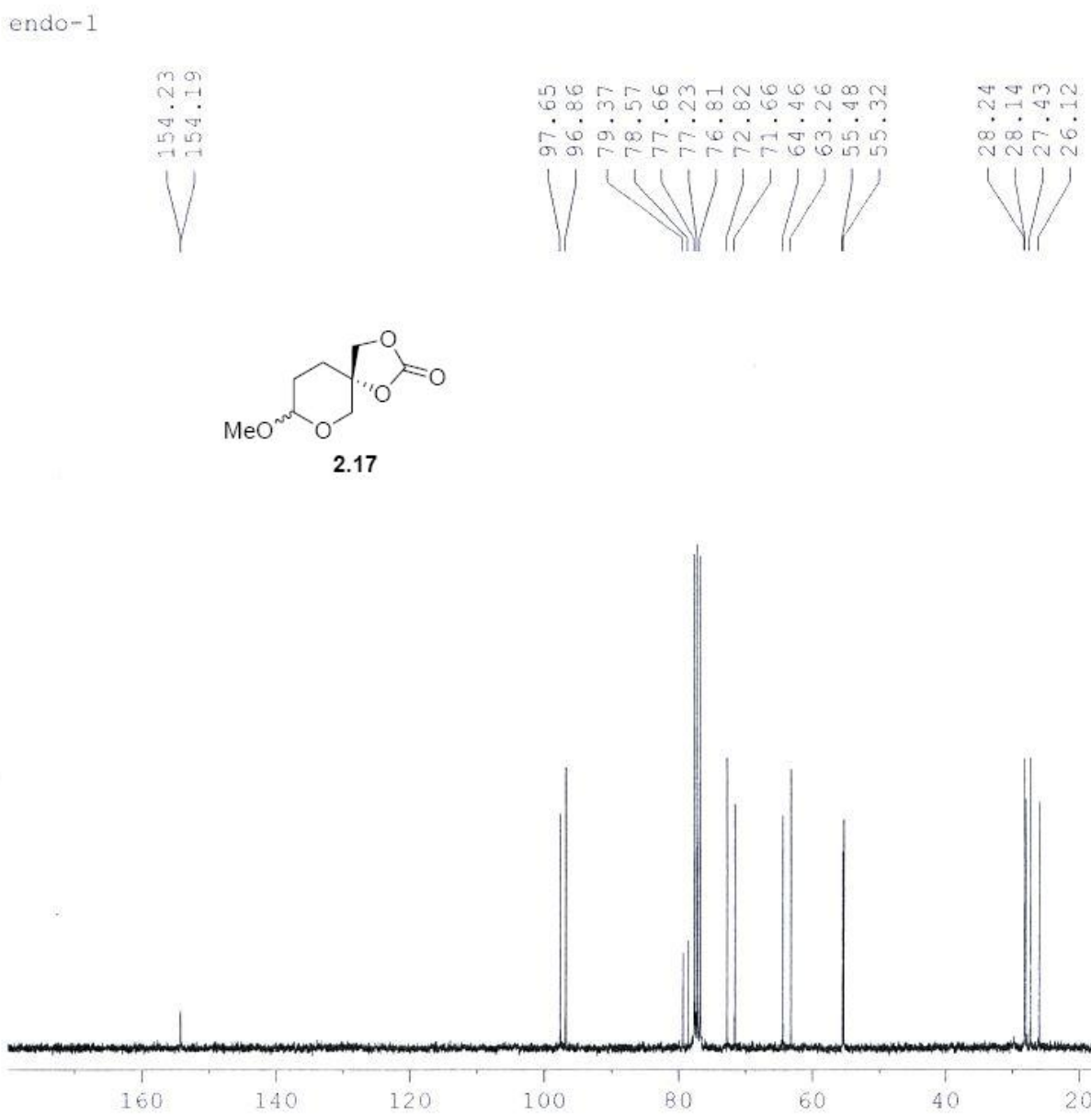
======== CHANNEL f1 ========
NUC1                       13C
P1                       7.00 usec
PL1                      0.00 dB
SFO1                75.4639789 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                  100.00 usec
PL2                      0.00 dB
PL12                    18.24 dB
PL13                    18.24 dB
SFO2               300.0862003 MHz

F2 - Processing parameters
SI                         32768
SF                  75.4564198 MHz
WDW                           EM
SSB                            0
LB                        1.00 Hz
GB                             0
PC                          1.40
```


endo-1
7.2703
4.7048
4.6970
4.6879
4.6121
4.6021
4.5945
4.5192
4.4906
4.2212
4.2166
4.1926
4.1880
4.0859
4.0782
3.8952
3.8917
3.8584
3.8549
3.7867
3.7455
3.6925
3.6852
3.5358
3.5277
3.4989
3.4908
3.3925
3.3826
2.3355
2.3202
2.0782
2.0735
2.0653
2.0511
2.0422
1.9710
1.9644
1.9580
1.9506
1.7032
1.6947
1.6362
1.2474
MeO
2.17
9
8
7
6
5
4
3
2
1
ppm
0.41
0.48
0.54
0.54
0.49
0.48
0.56
0.50
0.50
0.57
1.40
1.52
0.53
1.11
0.97
0.55
1.24
BRUKER
Current Data Parameters
NAME SW08110706
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070811
Time 13.35
INSTRUM spect
PROBHD 5 mm Dual 13C/
PULPROG zg
TD 32768
SOLVENT CDC13
NS 4
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 90.5
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 5.00 usec
PL1 0.00 dB
SFO1 300.1318530 MHz
F2 - Processing parameters
SI 16384
SF 300.1300032 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

endo-1



2.17

BRUKER

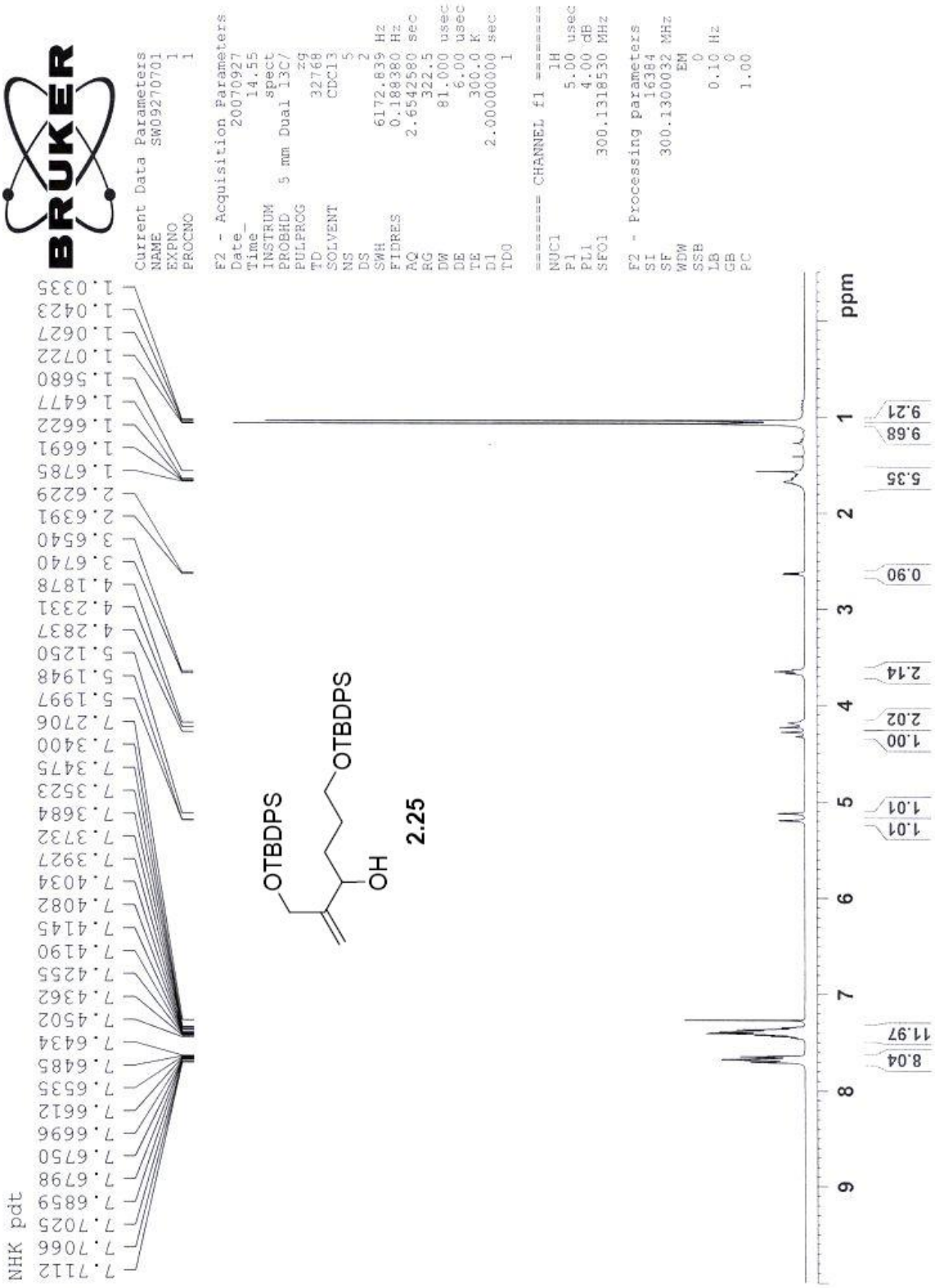
Current Data Parameters
NAME SW08110701
EXPNO 1
PROCNO 1

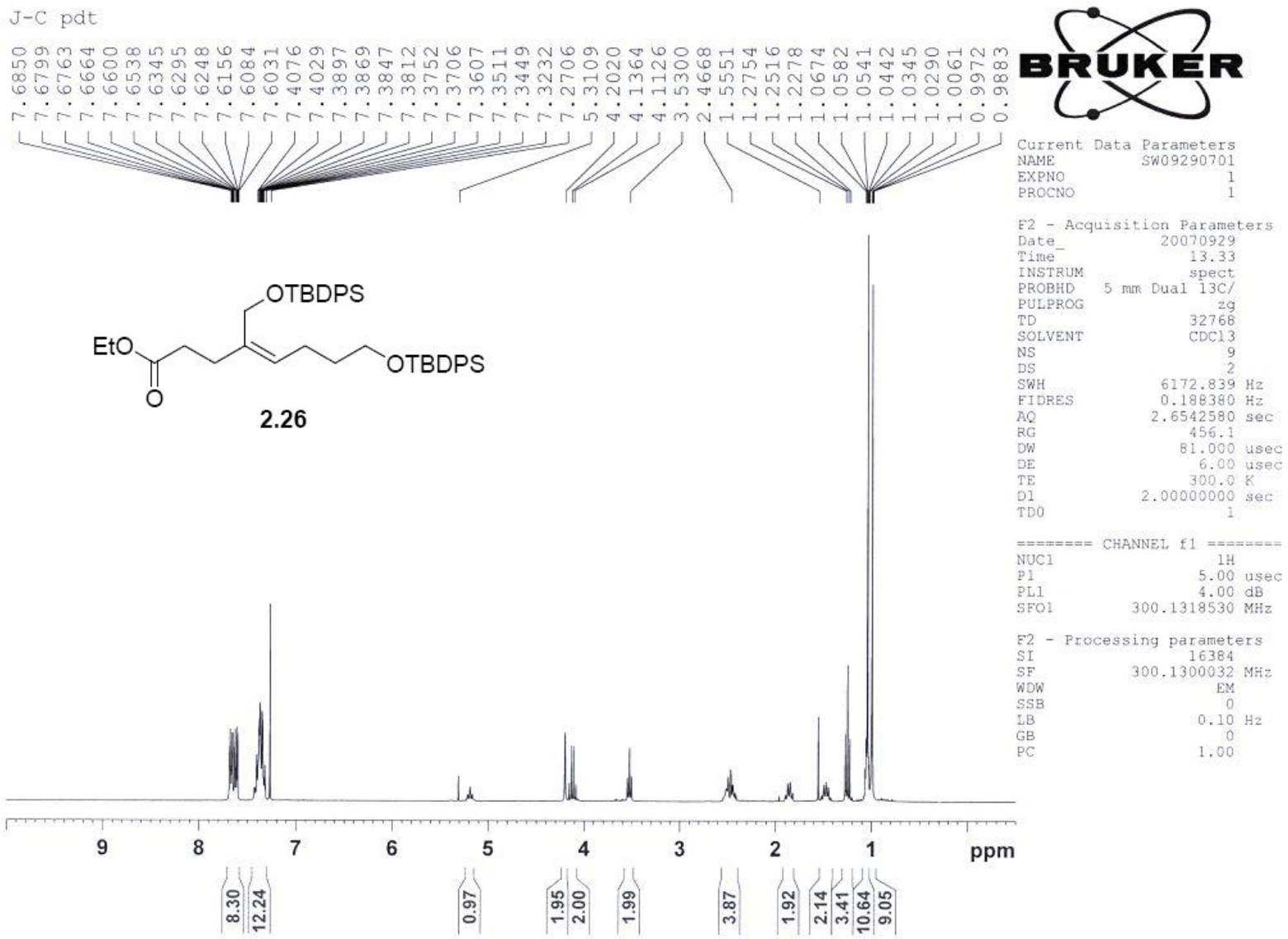
F2 - Acquisition Parameters
Date_ 20070811
Time 11.47
INSTRUM spect
PROBHD 5 mm DUL 1H-13
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 244
DS 4
SWH 18115.941 Hz
FIDRES 0.276427 Hz
AQ 1.8088436 sec
RG 4597.6
DW 27.600 usec
DE 6.00 usec
TE 300.0 K
D1 10.00000000 sec
d11 0.03000000 sec
DELTA 9.89999962 sec
TD0 1

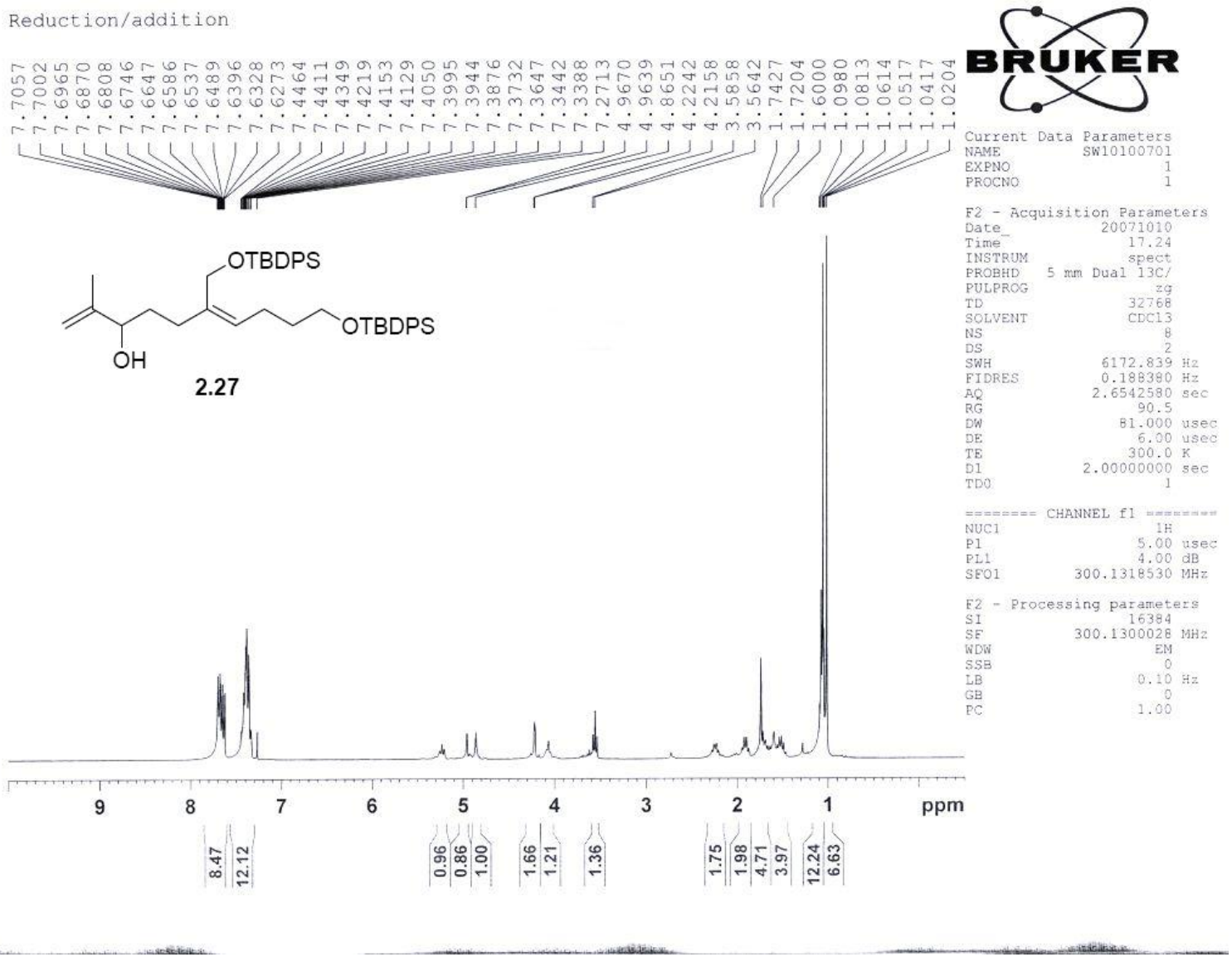
======== CHANNEL f1 ========
NUC1 13C
P1 9.00 usec
PL1 1.80 dB
SFO1 75.5381641 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 92.00 usec
PL2 0.00 dB
PL12 20.00 dB
PL13 20.00 dB
SFO2 300.3812015 MHz

F2 - Processing parameters
SI 65536
SF 75.5305967 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40


BRUKER
Current Data Parameters
NAME SW09270701
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070927
Time 14.55
INSTRUM spect
PROBHD 5 mm Dual 13C/
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 5
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 322.5
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 5.00 usec
PL1 4.00 dB
SFO1 300.1318530 MHz
F2 - Processing parameters
SI 16384
SF 300.1300032 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00
NHK pdt
7.7112
7.7066
7.7025
7.6859
7.6798
7.6750
7.6696
7.6612
7.6535
7.6485
7.6434
7.4502
7.4362
7.4255
7.4190
7.4145
7.4082
7.4034
7.3927
7.3732
7.3684
7.3523
7.3475
7.3400
7.2706
5.1997
5.1948
5.1250
4.2837
4.2331
4.1878
3.6740
3.6540
2.6391
2.6229
1.6785
1.6691
1.6622
1.6477
1.5680
1.0722
1.0627
1.0423
1.0335
OTBDPS
OTBDPS
OH
2.25
ppm
9.21
9.68
5.35
0.90
2.14
1.00
2.02
1.01
1.01
11.97
8.04


J-C pdt
7.6850
7.6799
7.6763
7.6664
7.6600
7.6538
7.6345
7.6295
7.6248
7.6156
7.6084
7.6031
7.4076
7.4029
7.3897
7.3869
7.3847
7.3812
7.3752
7.3706
7.3607
7.3511
7.3449
7.3232
7.2706
5.3109
4.2020
4.1364
4.1126
3.5300
2.4668
1.5551
1.2754
1.2516
1.2278
1.0674
1.0582
1.0541
1.0442
1.0345
1.0290
1.0061
0.9972
0.9883
OTBDPS
EtO
OTBDPS
O
2.26
9
8
7
6
5
4
3
2
1
ppm
8.30
12.24
0.97
1.95
2.00
1.99
3.87
1.92
2.14
3.41
10.64
9.05
BRUKER
Current Data Parameters
NAME SW09290701
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070929
Time 13.33
INSTRUM spect
PROBHD 5 mm Dual 13C/
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 9
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 456.1
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 5.00 usec
PL1 4.00 dB
SFO1 300.1318530 MHz
F2 - Processing parameters
SI 16384
SF 300.1300032 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00


Reduction/addition
7.7057
7.7002
7.6965
7.6870
7.6808
7.6746
7.6647
7.6586
7.6537
7.6489
7.6396
7.6328
7.6273
7.4464
7.4411
7.4349
7.4219
7.4153
7.4129
7.4050
7.3995
7.3944
7.3876
7.3732
7.3647
7.3442
7.3388
7.2713
4.9670
4.9639
4.8651
4.2242
4.2158
3.5858
3.5642
1.7427
1.7204
1.6000
1.0980
1.0813
1.0614
1.0517
1.0417
1.0204
OTBDPS
OTBDPS
OH
2.27
BRUKER
Current Data Parameters
NAME SW10100701
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071010
Time 17.24
INSTRUM spect
PROBHD 5 mm Dual 13C/
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 8
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 90.5
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 5.00 usec
PL1 4.00 dB
SFO1 300.1318530 MHz
F2 - Processing parameters
SI 16384
SF 300.1300028 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00
9
8
7
6
5
4
3
2
1
ppm
8.47
12.12
0.96
0.86
1.00
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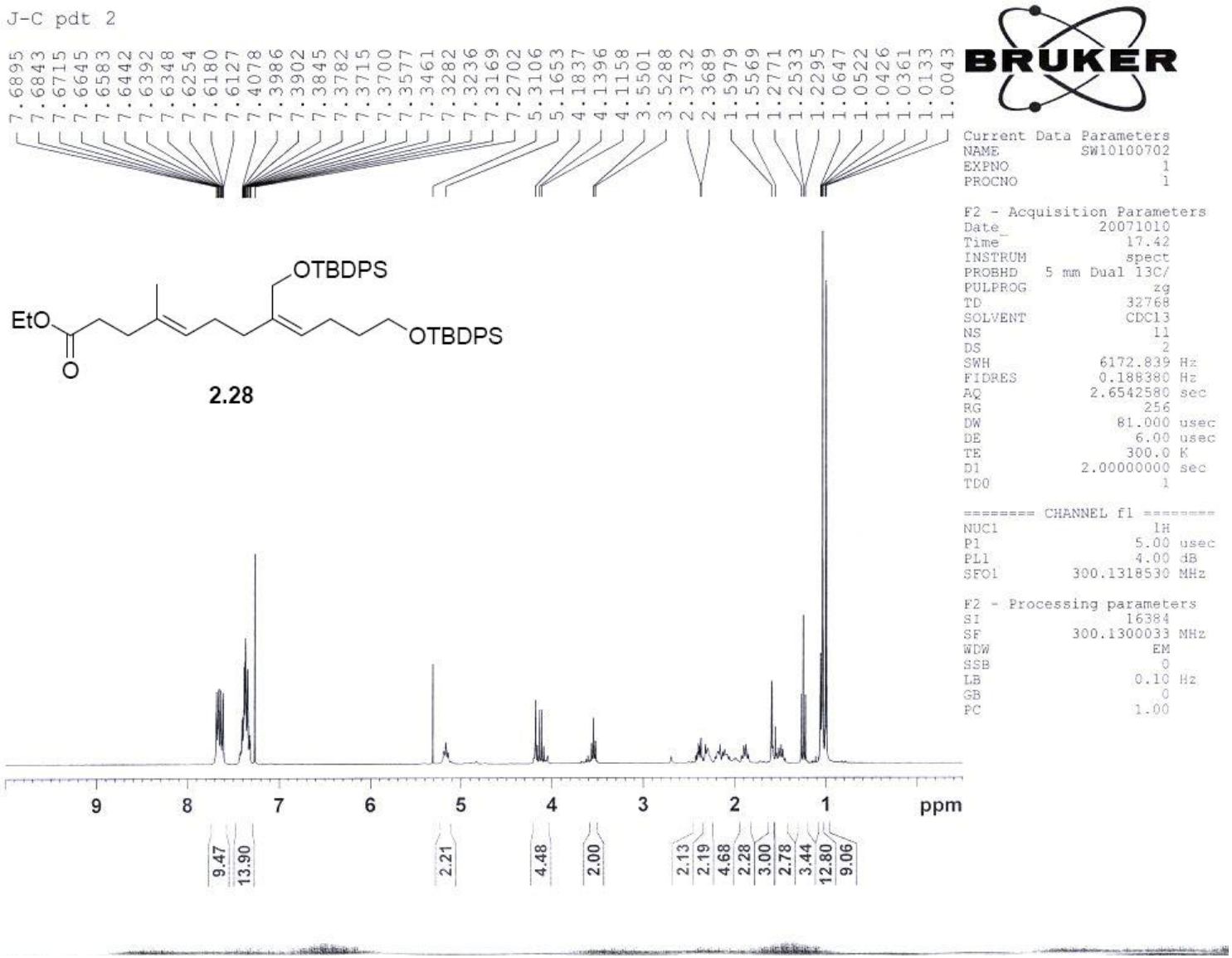
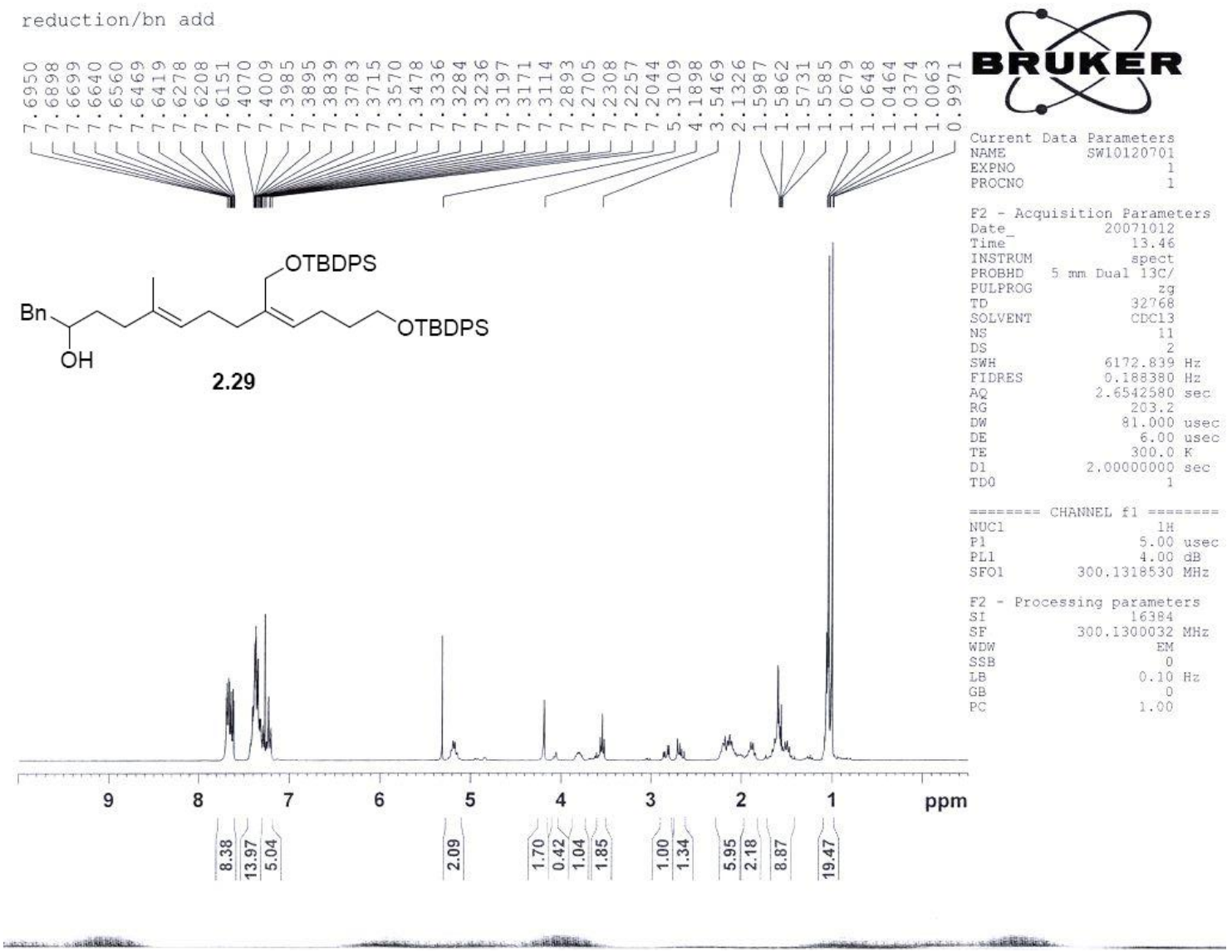
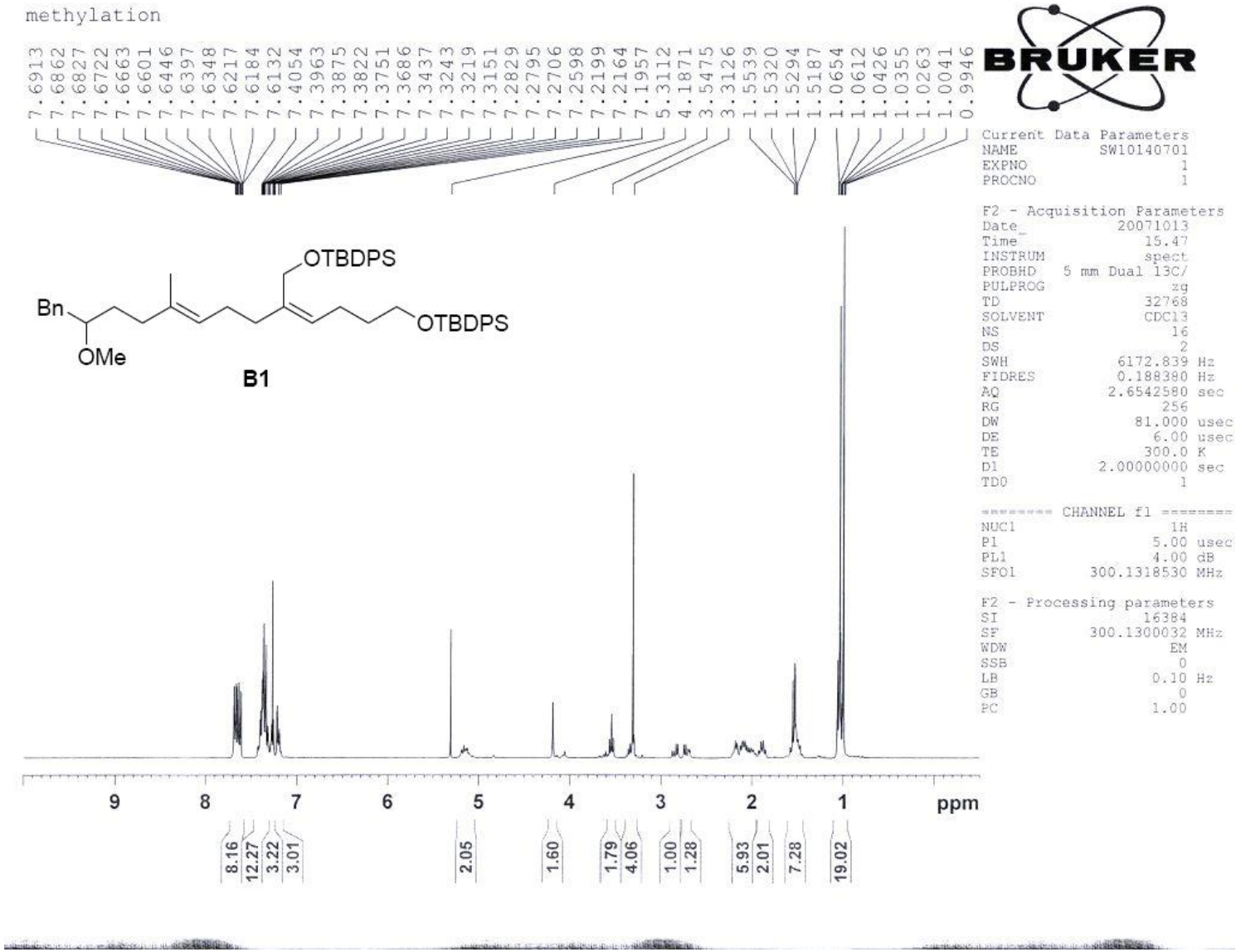
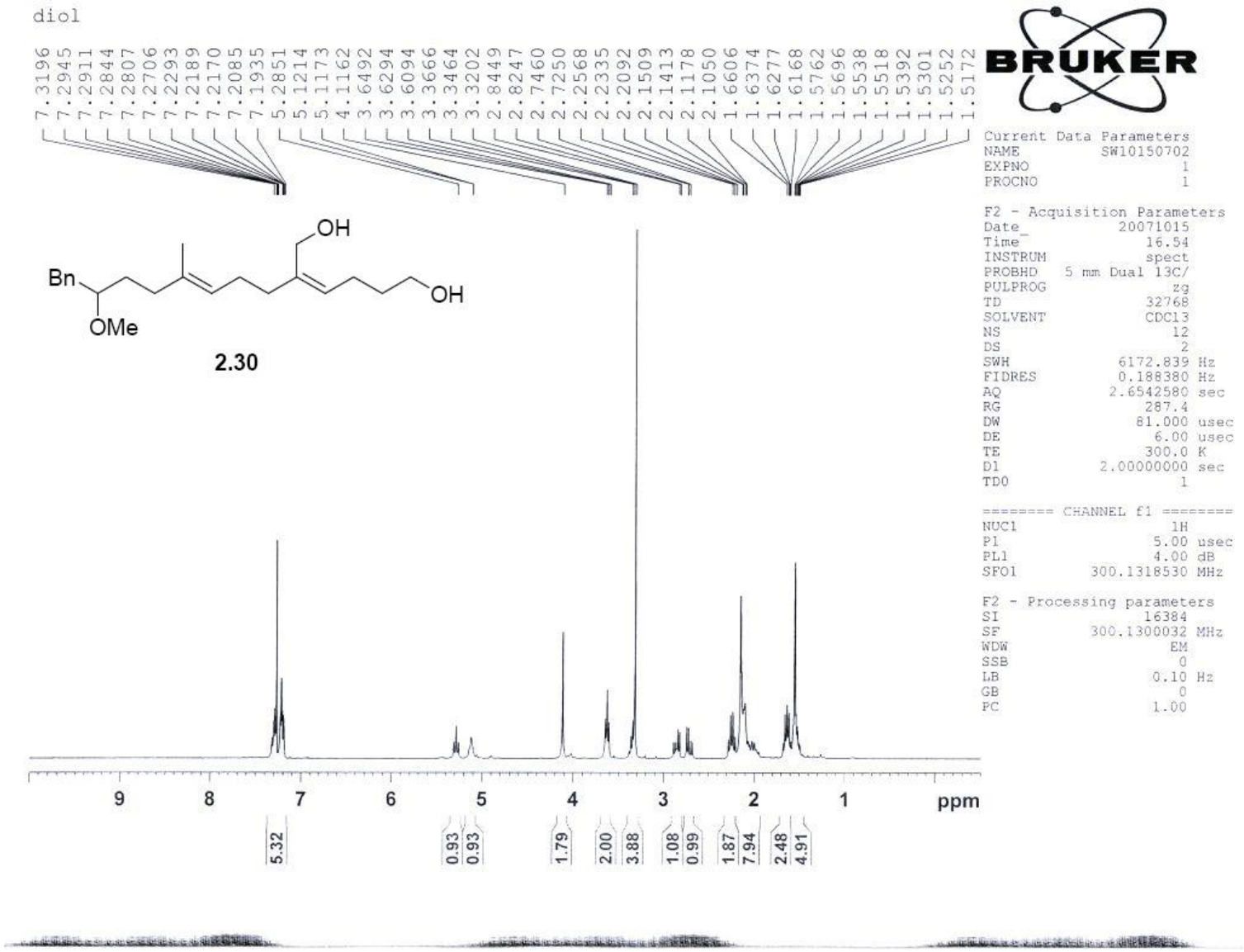
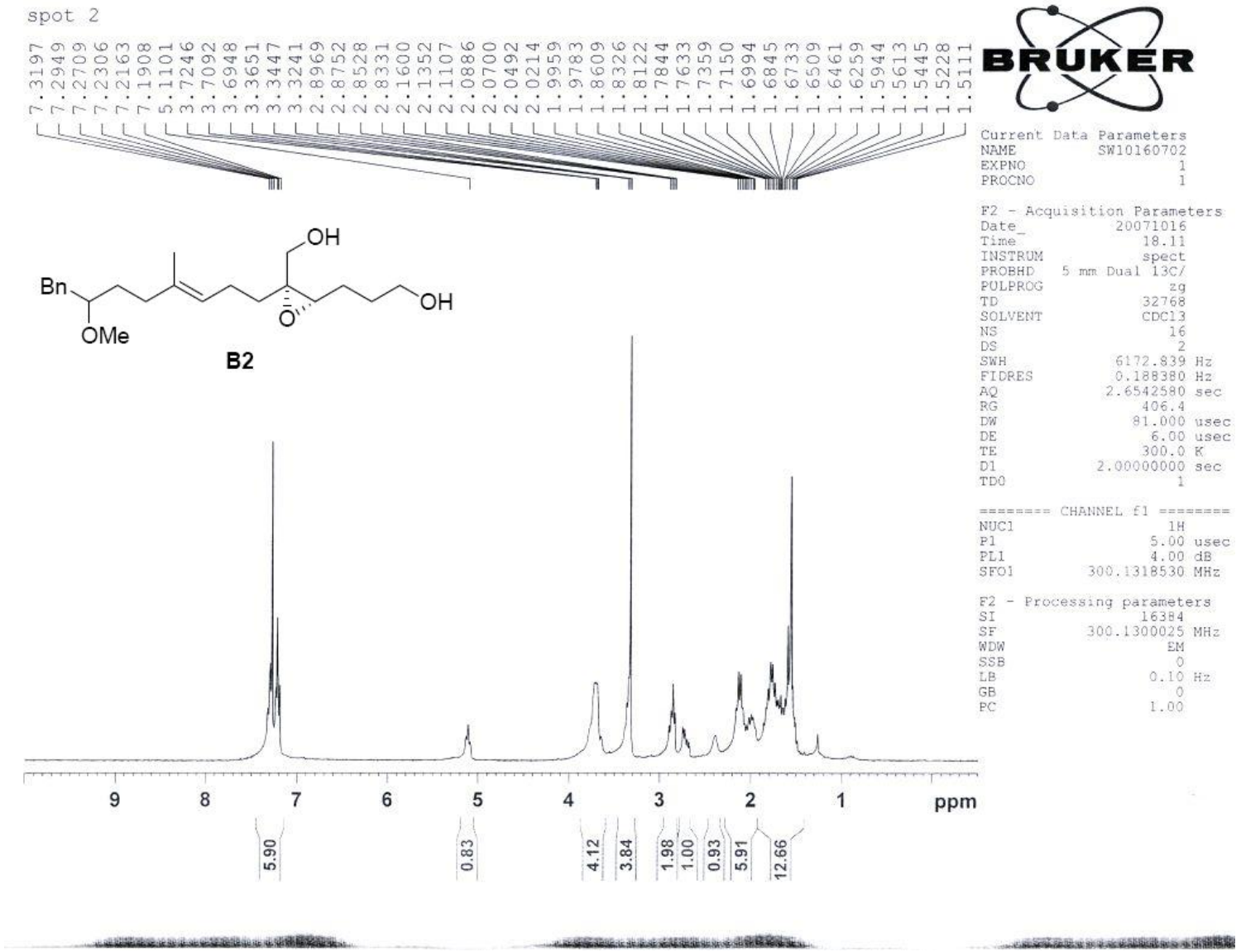
1.21
1.36
1.75
1.98
4.71
3.97
12.24
6.63

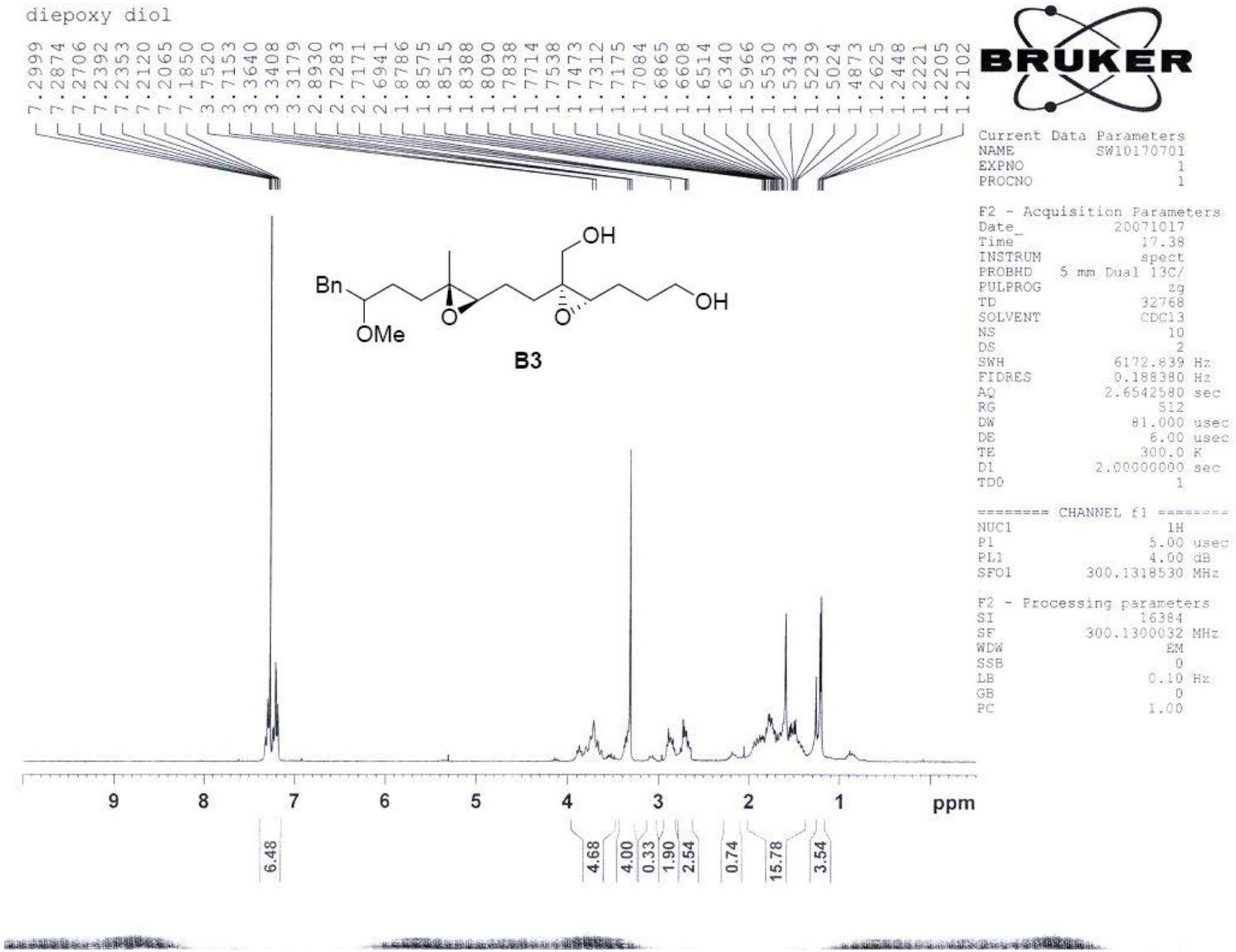

J-C pdt 2
7.6895 7.6843 7.6715 7.6645 7.6583 7.6442 7.6392 7.6348 7.6254 7.6180 7.6127 7.4078 7.3986 7.3902 7.3845 7.3782 7.3715 7.3700 7.3577 7.3461 7.3282 7.3236 7.3169 7.2702 5.3106 5.1653 4.1837 4.1396 4.1158 3.5501 3.5288 2.3732 2.3689 1.5979 1.5569 1.2771 1.2533 1.2295 1.0647 1.0522 1.0426 1.0361 1.0133 1.0043
OTBDPS
EtO
O
OTBDPS
2.28
9 8 7 6 5 4 3 2 1 ppm
9.47 13.90 2.21 4.48 2.00 2.13 2.19 4.68 2.28 3.00 2.78 3.44 12.80 9.06
BRUKER
Current Data Parameters
NAME SW10100702
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071010
Time 17.42
INSTRUM spect
PROBHD 5 mm Dual 13C/
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 11
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 256
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 5.00 usec
PL1 4.00 dB
SFO1 300.1318530 MHz
F2 - Processing parameters
SI 16384
SF 300.1300033 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

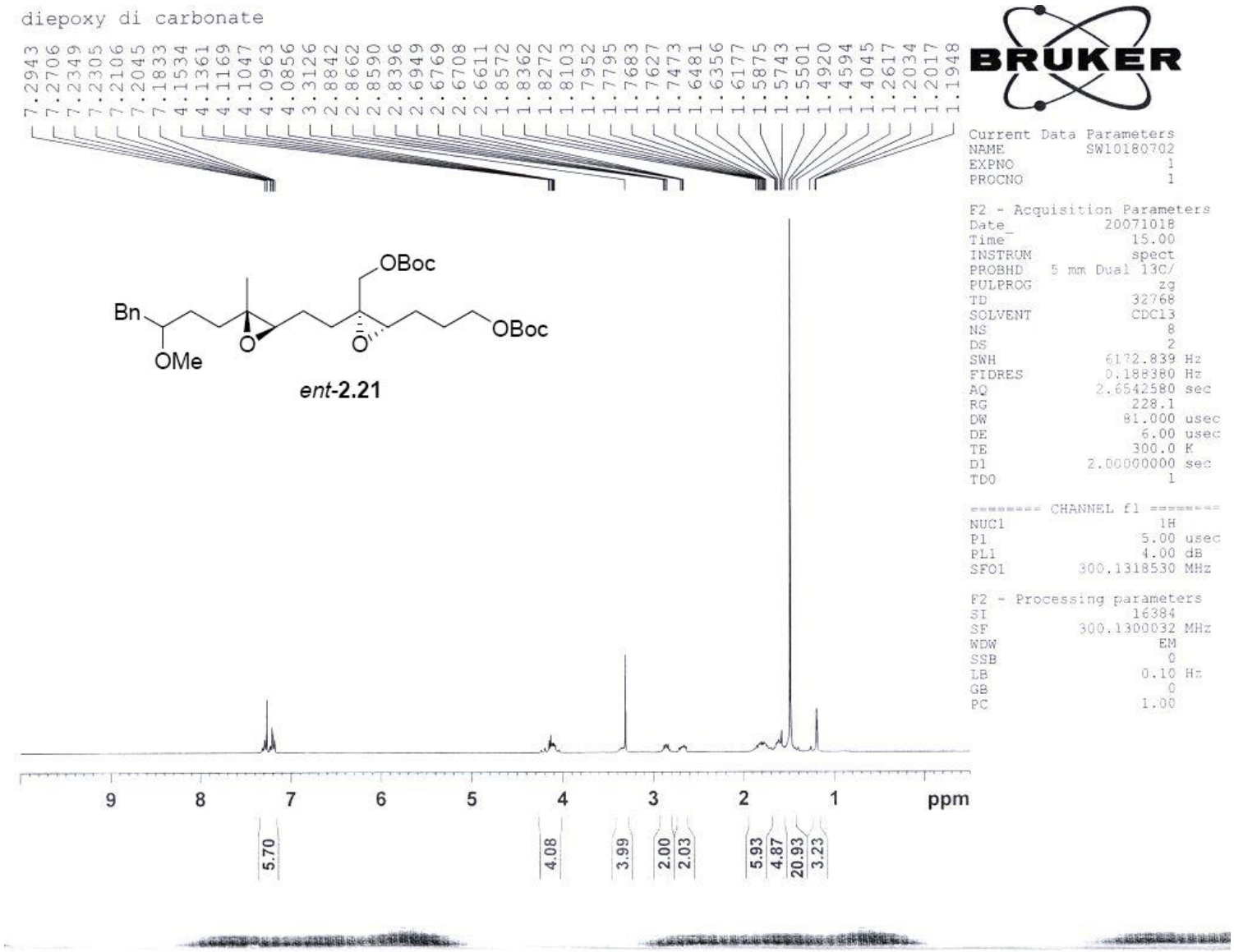

reduction/bn add
7.6950 7.6898 7.6699 7.6640 7.6560 7.6469 7.6419 7.6278 7.6208 7.6151 7.4070 7.4009 7.3985 7.3895 7.3839 7.3783 7.3715 7.3570 7.3478 7.3336 7.3284 7.3236 7.3197 7.3171 7.3114 7.2893 7.2705 7.2308 7.2257 7.2044 5.3109 4.1898 3.5469 2.1326 1.5987 1.5862 1.5731 1.5585 1.0679 1.0648 1.0464 1.0374 1.0063 0.9971
OTBDPS
Bn
OH
OTBDPS
2.29
9 8 7 6 5 4 3 2 1 ppm
8.38 13.97 5.04 2.09 1.70 0.42 1.04 1.85 1.00 1.34 5.95 2.18 8.87 19.47
BRUKER
Current Data Parameters
NAME SW10120701
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071012
Time 13.46
INSTRUM spect
PROBHD 5 mm Dual 13C/
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 11
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 203.2
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 5.00 usec
PL1 4.00 dB
SFO1 300.1318530 MHz
F2 - Processing parameters
SI 16384
SF 300.1300032 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

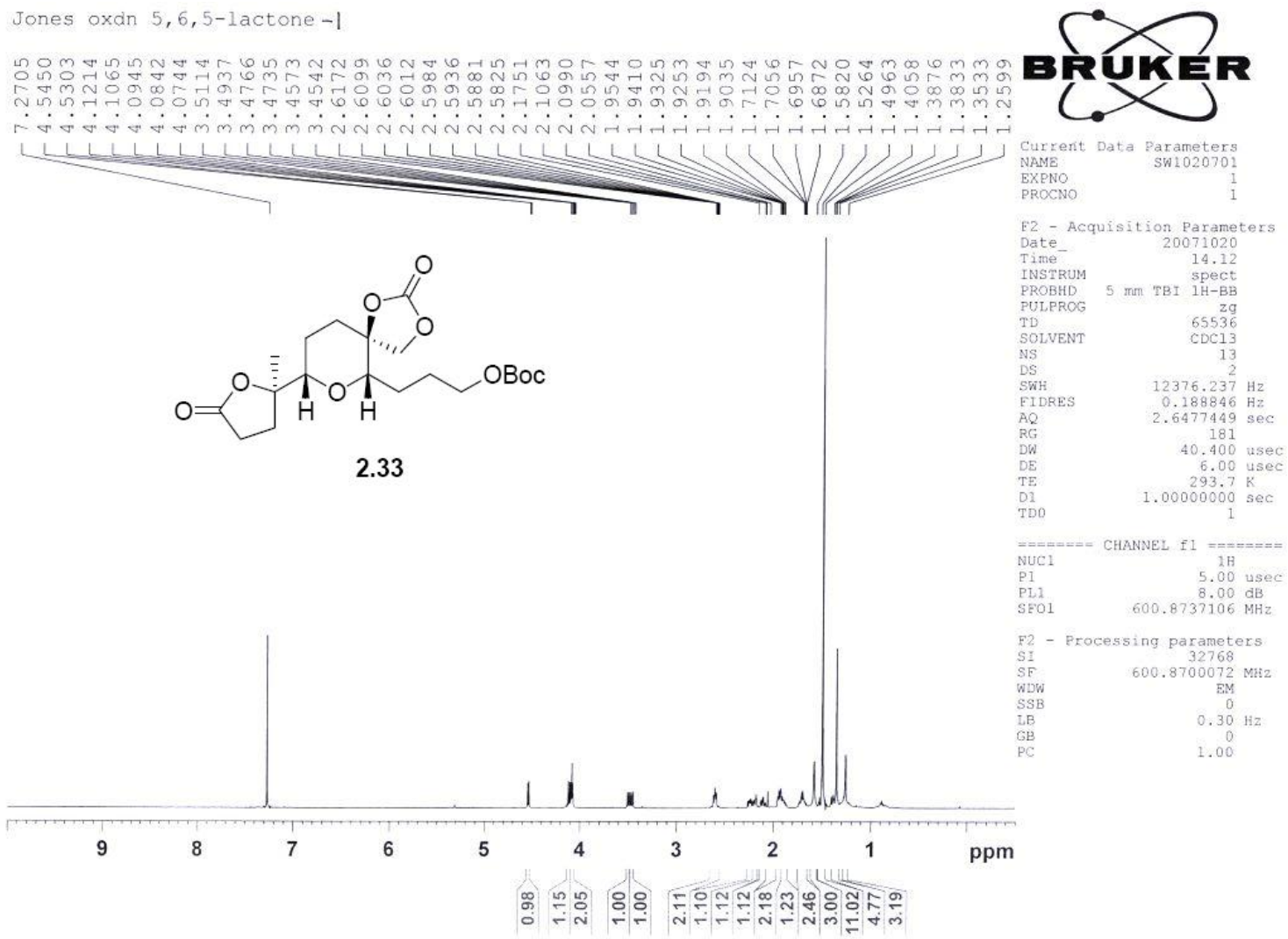

methylation
7.6913 7.6862 7.6827 7.6722 7.6663 7.6601 7.6446 7.6397 7.6348 7.6217 7.6184 7.6132 7.4054 7.3963 7.3875 7.3822 7.3751 7.3686 7.3437 7.3243 7.3219 7.3151 7.2829 7.2795 7.2706 7.2598 7.2199 7.2164 7.1957 5.3112 4.1871 3.5475 3.3126 1.5539 1.5320 1.5294 1.5187 1.0654 1.0612 1.0426 1.0355 1.0263 1.0041 0.9946
BRUKER
OTBDPS
Bn
OTBDPS
OMe
B1
Current Data Parameters
NAME SW10140701
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071013
Time 15.47
INSTRUM spect
PROBHD 5 mm Dual 13C/
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 256
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 5.00 usec
PL1 4.00 dB
SFO1 300.1318530 MHz
F2 - Processing parameters
SI 16384
SF 300.1300032 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00
9 8 7 6 5 4 3 2 1 ppm
8.16 12.27 3.22 3.01 2.05 1.60 1.79 4.06 1.00 1.28 5.93 2.01 7.28 19.02

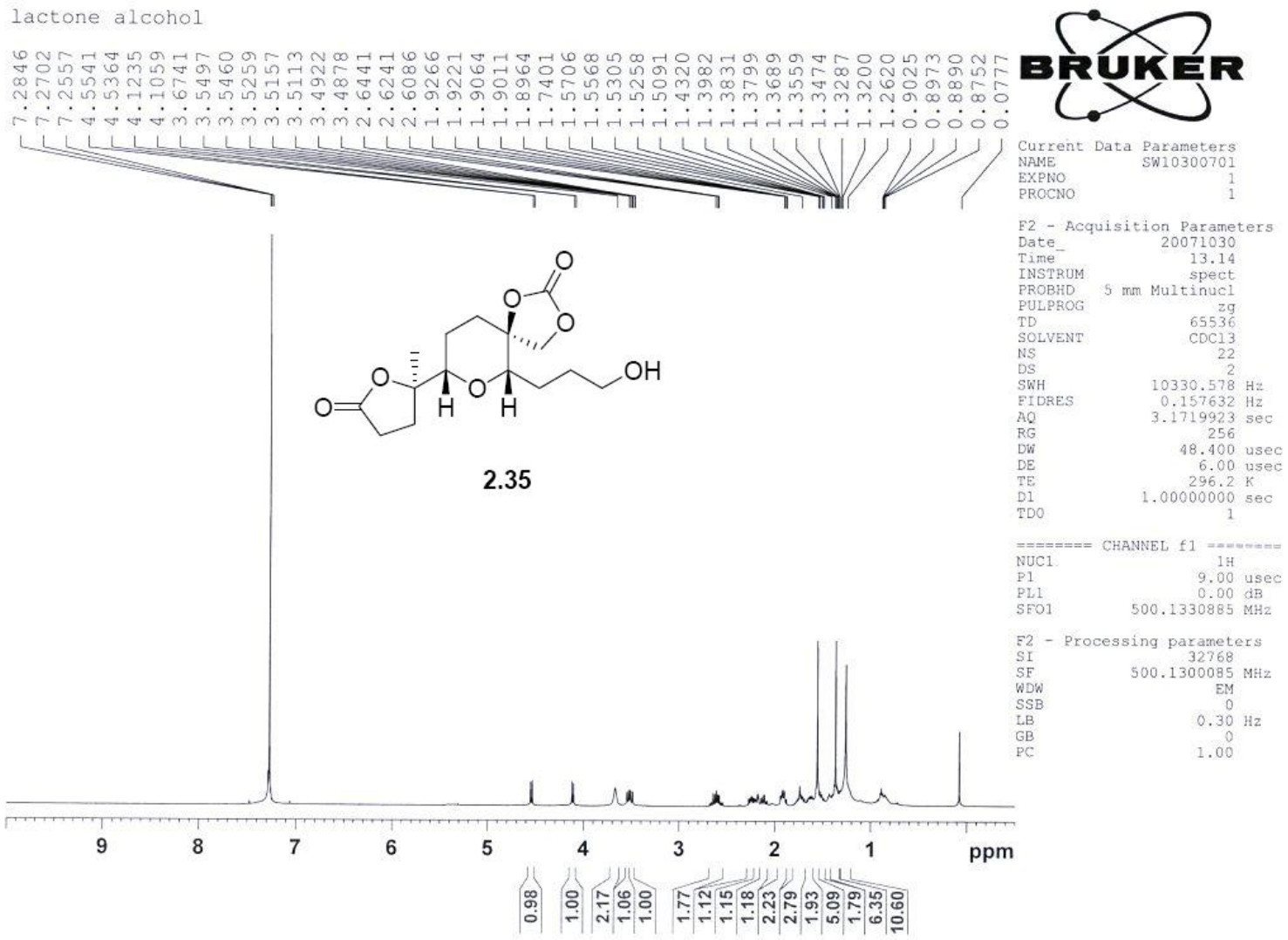

diol
7.3196
7.2945
7.2911
7.2844
7.2807
7.2706
7.2293
7.2189
7.2170
7.2085
7.1935
5.2851
5.1214
5.1173
4.1162
3.6492
3.6294
3.6094
3.3666
3.3464
3.3202
2.8449
2.8247
2.7460
2.7250
2.2568
2.2335
2.2092
2.1509
2.1413
2.1178
2.1050
1.6606
1.6374
1.6277
1.6168
1.5762
1.5696
1.5538
1.5518
1.5392
1.5301
1.5252
1.5172
OH
Bn
OMe
OH
2.30
BRUKER
Current Data Parameters
NAME SW10150702
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071015
Time 16.54
INSTRUM spect
PROBHD 5 mm Dual 13C/
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 12
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 287.4
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 5.00 usec
PL1 4.00 dB
SFO1 300.1318530 MHz
F2 - Processing parameters
SI 16384
SF 300.1300032 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00
9
8
7
6
5
4
3
2
1
ppm
5.32
0.93
0.93
1.79
2.00
3.88
1.08
0.99
1.87
7.94
2.48
4.91

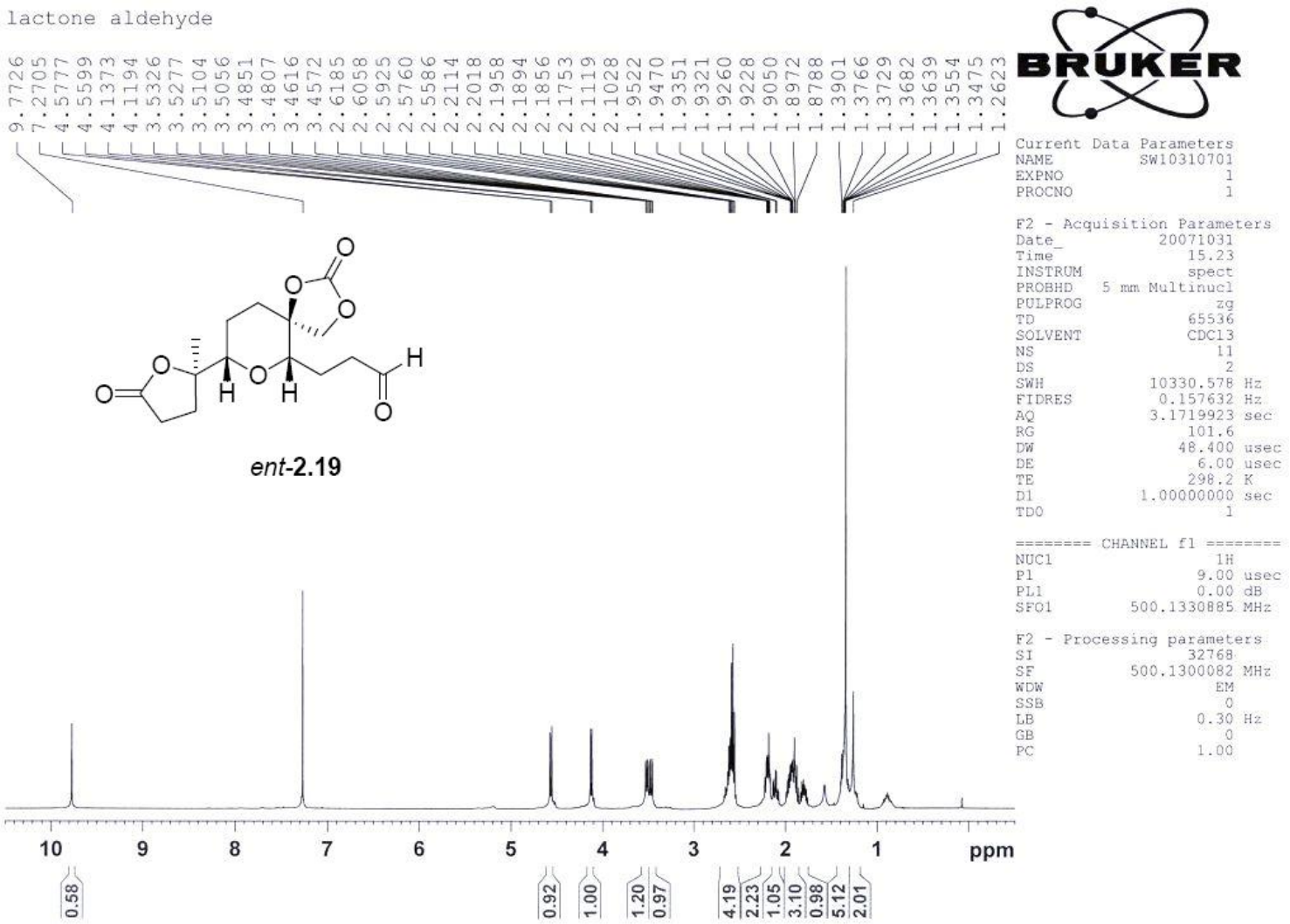

spot 2
7.3197
7.2949
7.2709
7.2306
7.2163
7.1908
5.1101
3.7246
3.7092
3.6948
3.3651
3.3447
3.3241
2.8969
2.8752
2.8528
2.8331
2.1600
2.1352
2.1107
2.0886
2.0700
2.0492
2.0214
1.9959
1.9783
1.8609
1.8326
1.8122
1.7844
1.7633
1.7359
1.7150
1.6994
1.6845
1.6733
1.6509
1.6461
1.6259
1.5944
1.5613
1.5445
1.5228
1.5111
BRUKER
Bn
OMe
OH
OH
O
B2
Current Data Parameters
NAME SW10160702
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071016
Time 18.11
INSTRUM spect
PROBHD 5 mm Dual 13C/
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 406.4
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 5.00 usec
PL1 4.00 dB
SFO1 300.1318530 MHz
F2 - Processing parameters
SI 16384
SF 300.1300025 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00
9
8
7
6
5
4
3
2
1
ppm
5.90
0.83
4.12
3.84
1.98
1.00
0.93
5.91
12.66

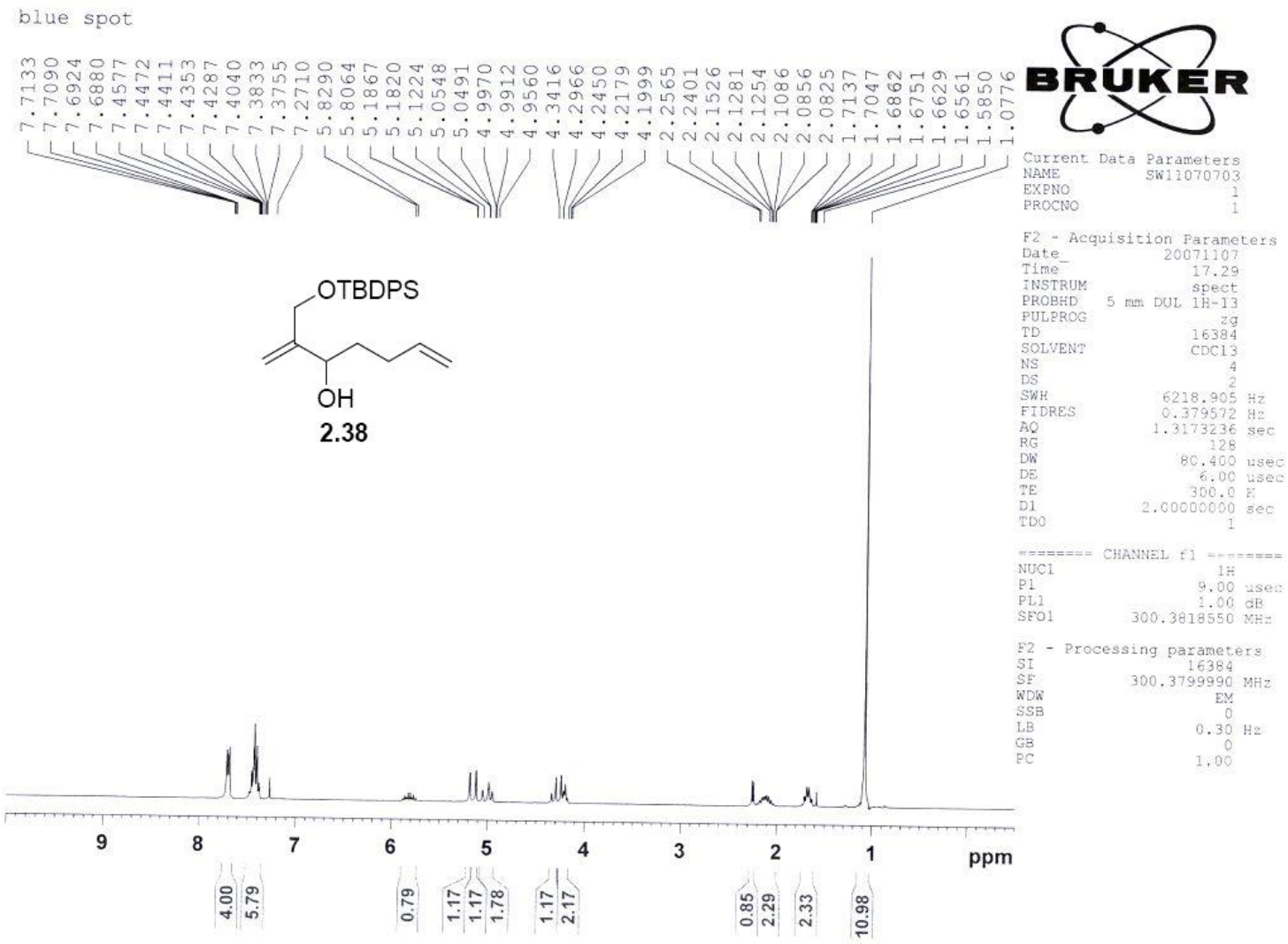

diepoxy diol
7.2999
7.2874
7.2706
7.2392
7.2353
7.2120
7.2065
7.1850
3.7520
3.7153
3.3640
3.3408
3.3179
2.8930
2.7283
2.7171
2.6941
1.8786
1.8575
1.8515
1.8388
1.8090
1.7838
1.7714
1.7538
1.7473
1.7312
1.7175
1.7084
1.6865
1.6608
1.6514
1.6340
1.5966
1.5530
1.5343
1.5239
1.5024
1.4873
1.2625
1.2448
1.2221
1.2205
1.2102
BRUKER
Bn
OMe
OH
OH
B3
Current Data Parameters
NAME SW10170701
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071017
Time 17.38
INSTRUM spect
PROBHD 5 mm Dual 13C/
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 10
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 512
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 5.00 usec
PL1 4.00 dB
SFO1 300.1318530 MHz
F2 - Processing parameters
SI 16384
SF 300.1300032 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00
9
8
7
6
5
4
3
2
1
ppm
6.48
4.68
4.00
0.33
1.90
2.54
0.74
15.78
3.54

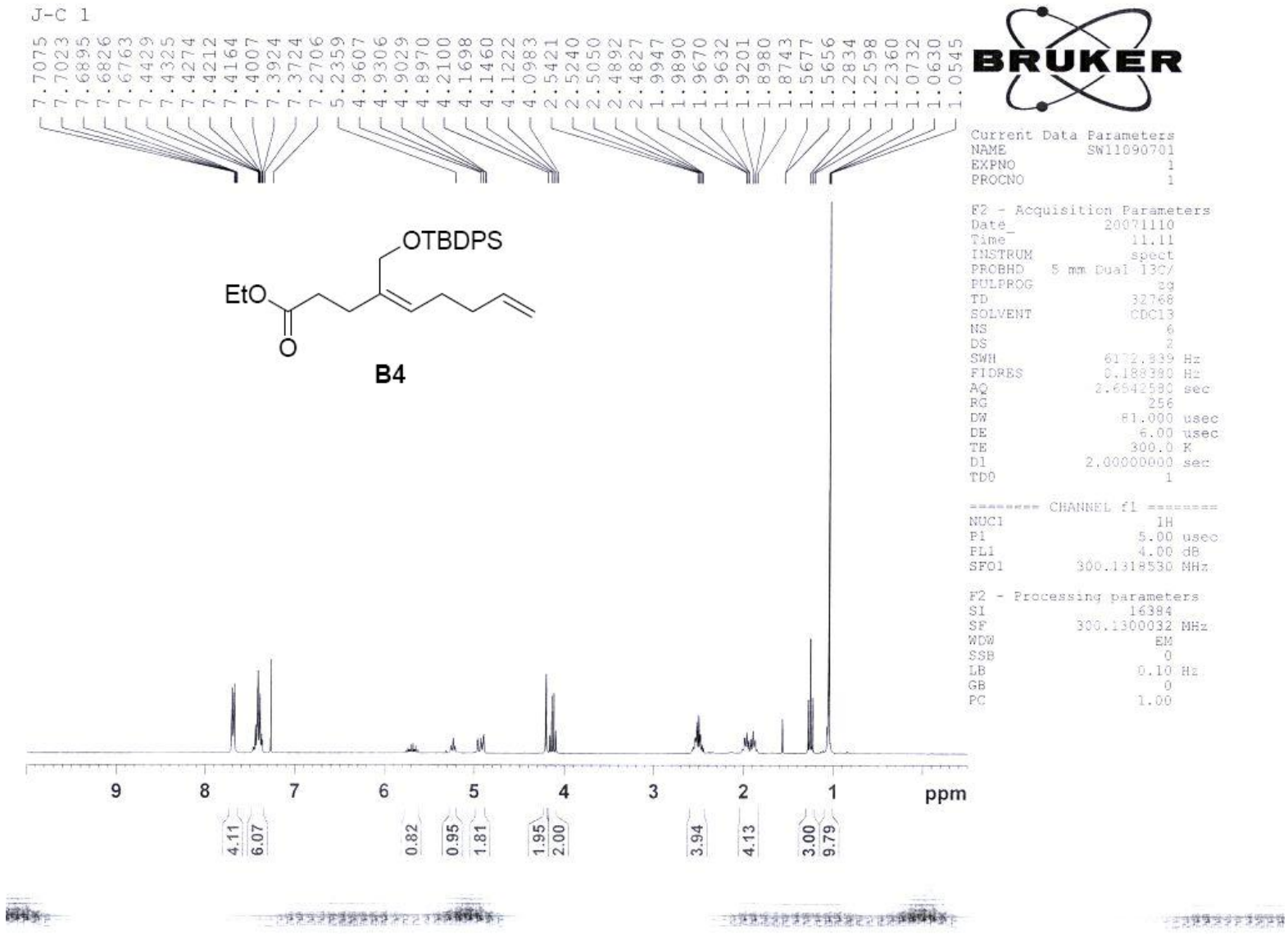

diepoxy di carbonate
7.2943
7.2706
7.2349
7.2305
7.2106
7.2045
7.1833
4.1534
4.1361
4.1169
4.1047
4.0963
4.0856
3.3126
2.8842
2.8662
2.8590
2.8396
2.6949
2.6769
2.6708
2.6611
1.8572
1.8362
1.8272
1.8103
1.7952
1.7795
1.7683
1.7627
1.7473
1.6481
1.6356
1.6177
1.5875
1.5743
1.5501
1.4920
1.4594
1.4045
1.2617
1.2034
1.2017
1.1948
BRUKER
Current Data Parameters
NAME SW10180702
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071018
Time 15.00
INSTRUM spect
PROBHD 5 mm Dual 13C/
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 8
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 228.1
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 5.00 usec
PL1 4.00 dB
SFO1 300.1318530 MHz
F2 - Processing parameters
SI 16384
SF 300.1300032 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00
OBoc
Bn
OMe
O
O
OBoc
ent-2.21
9
8
7
6
5
4
3
2
1
ppm
5.70
4.08
3.99
2.00
2.03
5.93
4.87
20.93
3.23

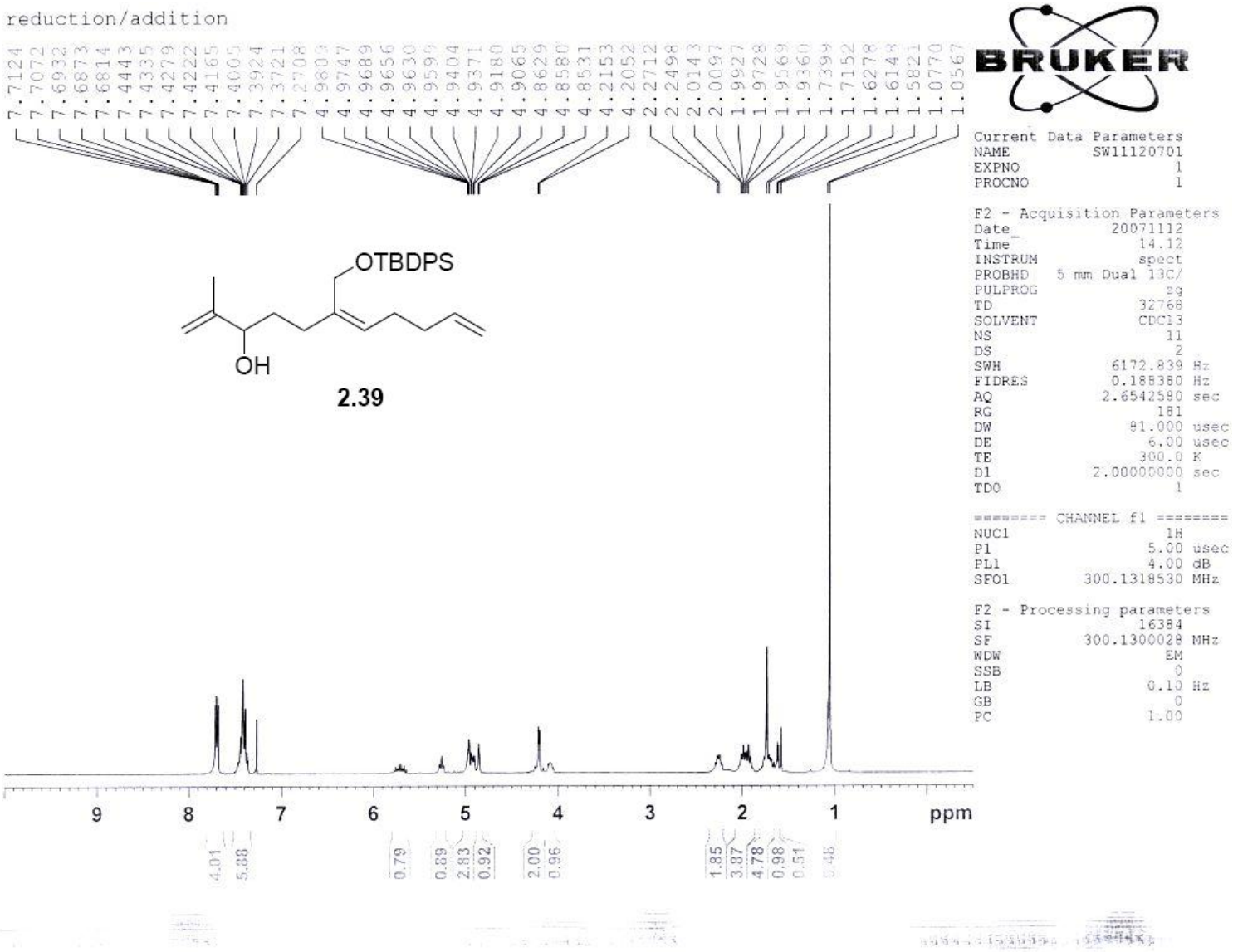

Jones oxdn 5,6,5-lactone -|
7.2705
4.5450
4.5303
4.1214
4.1065
4.0945
4.0842
4.0744
3.5114
3.4937
3.4766
3.4735
3.4573
3.4542
2.6172
2.6099
2.6036
2.6012
2.5984
2.5936
2.5881
2.5825
2.1751
2.1063
2.0990
2.0557
1.9544
1.9410
1.9325
1.9253
1.9194
1.9035
1.7124
1.7056
1.6957
1.6872
1.5820
1.5264
1.4963
1.4058
1.3876
1.3833
1.3533
1.2599
OBoc
H
H
2.33
9
8
7
6
5
4
3
2
1
ppm
0.98
1.15
2.05
1.00
1.00
2.11
1.10
1.12
1.12
2.18
1.23
2.46
3.00
11.02
4.77
3.19
BRUKER
Current Data Parameters
NAME SW1020701
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071020
Time 14.12
INSTRUM spect
PROBHD 5 mm TBI 1H-BB
PULPROG zg
TD 65536
SOLVENT CDCl3
NS 13
DS 2
SWH 12376.237 Hz
FIDRES 0.188846 Hz
AQ 2.6477449 sec
RG 181
DW 40.400 usec
DE 6.00 usec
TE 293.7 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 5.00 usec
PL1 8.00 dB
SFO1 600.8737106 MHz
F2 - Processing parameters
SI 32768
SF 600.8700072 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

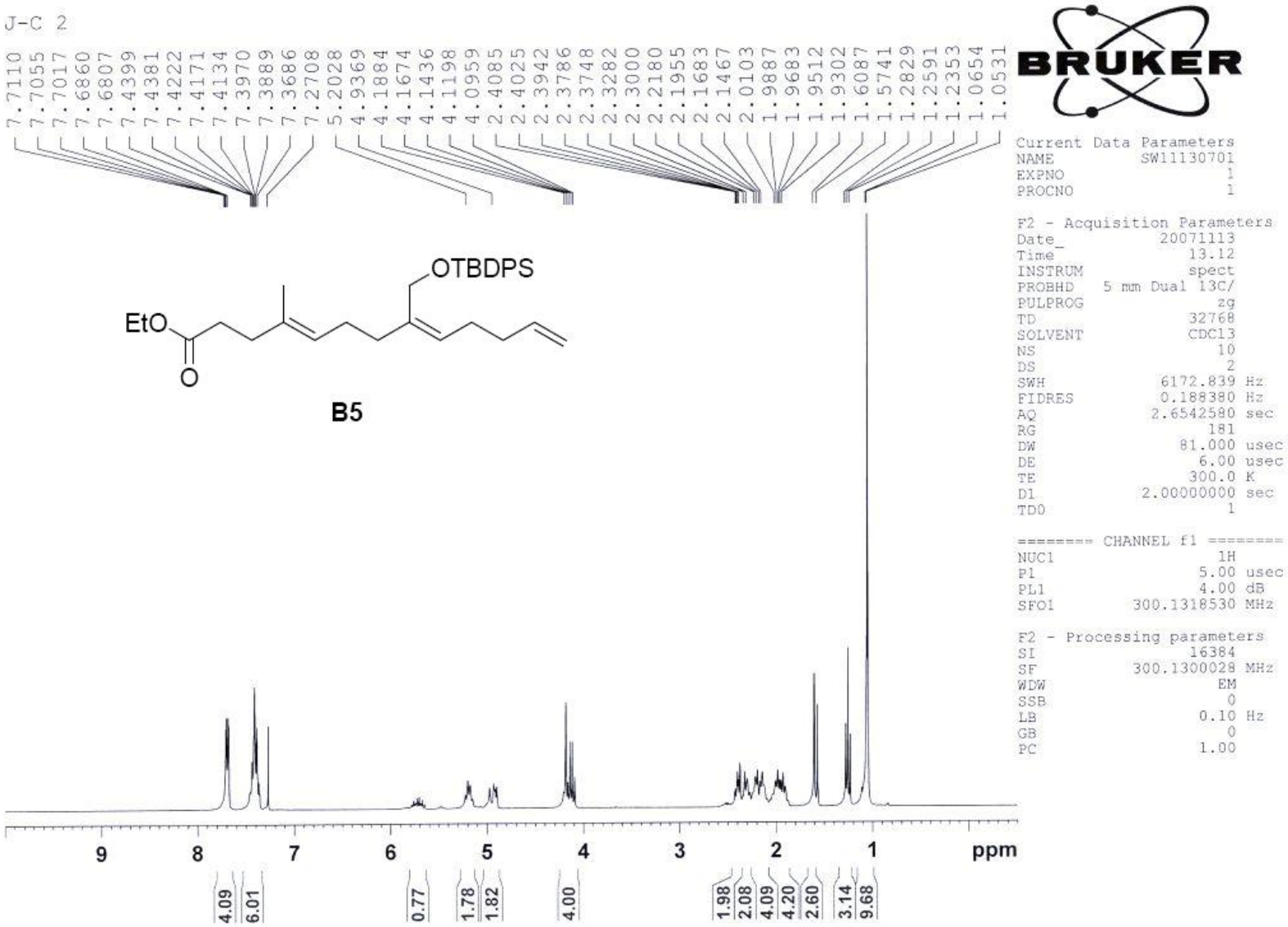

lactone alcohol
7.2846
7.2702
7.2557
4.5541
4.5364
4.1235
4.1059
3.6741
3.5497
3.5460
3.5259
3.5157
3.5113
3.4922
3.4878
2.6441
2.6241
2.6086
1.9266
1.9221
1.9064
1.9011
1.8964
1.7401
1.5706
1.5568
1.5305
1.5258
1.5091
1.4320
1.3982
1.3831
1.3799
1.3689
1.3559
1.3474
1.3287
1.3200
1.2620
0.9025
0.8973
0.8890
0.8752
0.0777
OH
H
H
2.35
9
8
7
6
5
4
3
2
1
ppm
0.98
1.00
2.17
1.06
1.00
1.77
1.12
1.15
1.18
2.23
2.79
1.93
5.09
1.79
6.35
10.60
BRUKER
Current Data Parameters
NAME SW10300701
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071030
Time 13.14
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zg
TD 65536
SOLVENT CDCl3
NS 22
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 256
DW 48.400 usec
DE 6.00 usec
TE 296.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.00 usec
PL1 0.00 dB
SFO1 500.1330885 MHz
F2 - Processing parameters
SI 32768
SF 500.1300085 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

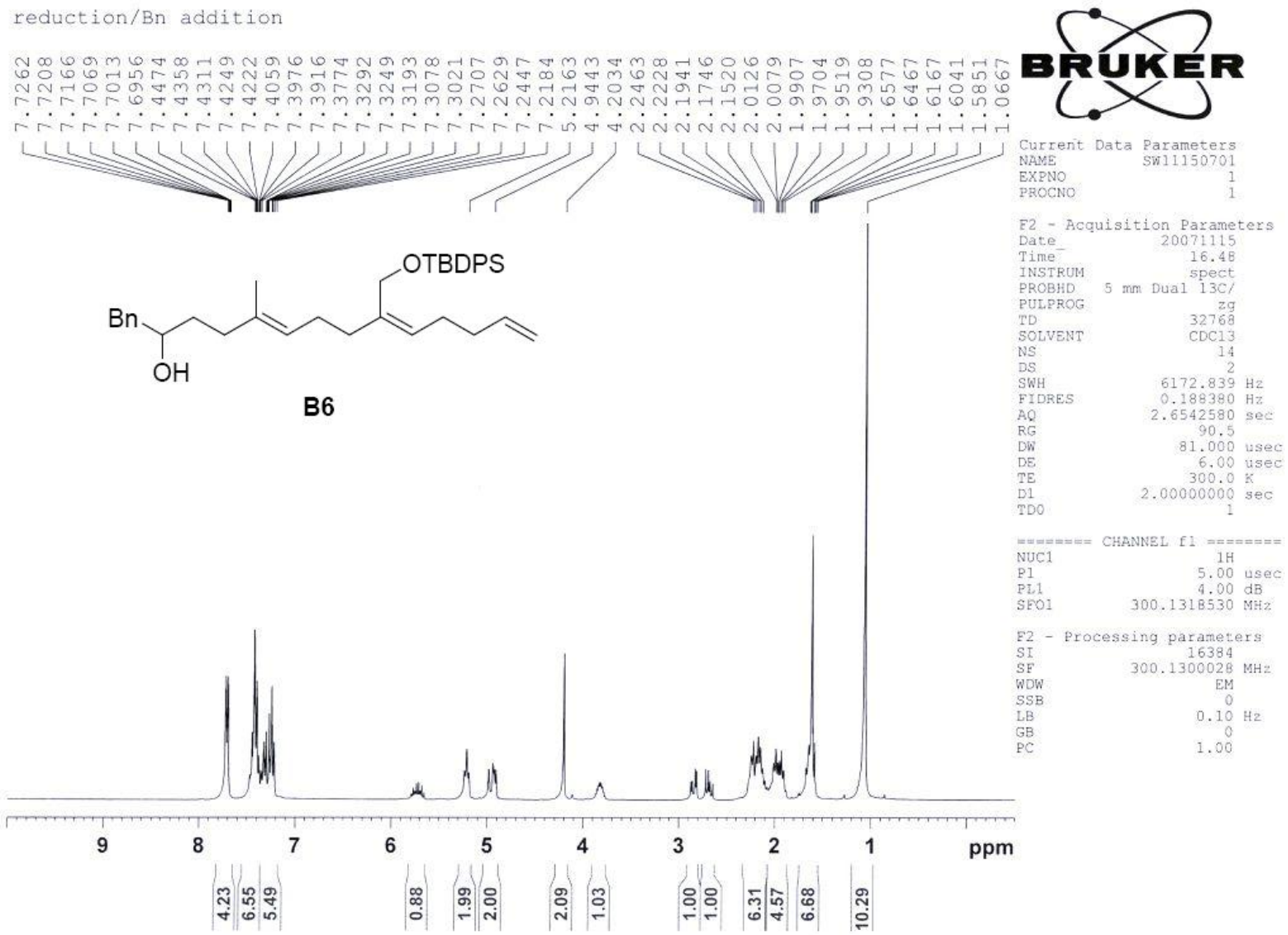

lactone aldehyde
9.7726 7.2705 4.5777 4.5599 4.1373 4.1194 3.5326 3.5277 3.5104 3.5056 3.4851 3.4807 3.4616 3.4572 2.6185 2.6058 2.5925 2.5760 2.5586 2.2114 2.2018 2.1958 2.1894 2.1856 2.1753 2.1119 2.1028 1.9522 1.9470 1.9351 1.9321 1.9260 1.9228 1.9050 1.8972 1.8788 1.3901 1.3766 1.3729 1.3682 1.3639 1.3554 1.3475 1.2623
BRUKER
Current Data Parameters
NAME SW10310701
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071031
Time 15.23
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zg
TD 65536
SOLVENT CDCl3
NS 11
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 101.6
DW 48.400 usec
DE 6.00 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.00 usec
PL1 0.00 dB
SFO1 500.1330885 MHz
F2 - Processing parameters
SI 32768
SF 500.1300082 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
ent-2.19
10 9 8 7 6 5 4 3 2 1 ppm
0.58 0.92 1.00 1.20 0.97 4.19 2.23 1.05 3.10 0.98 5.12 2.01

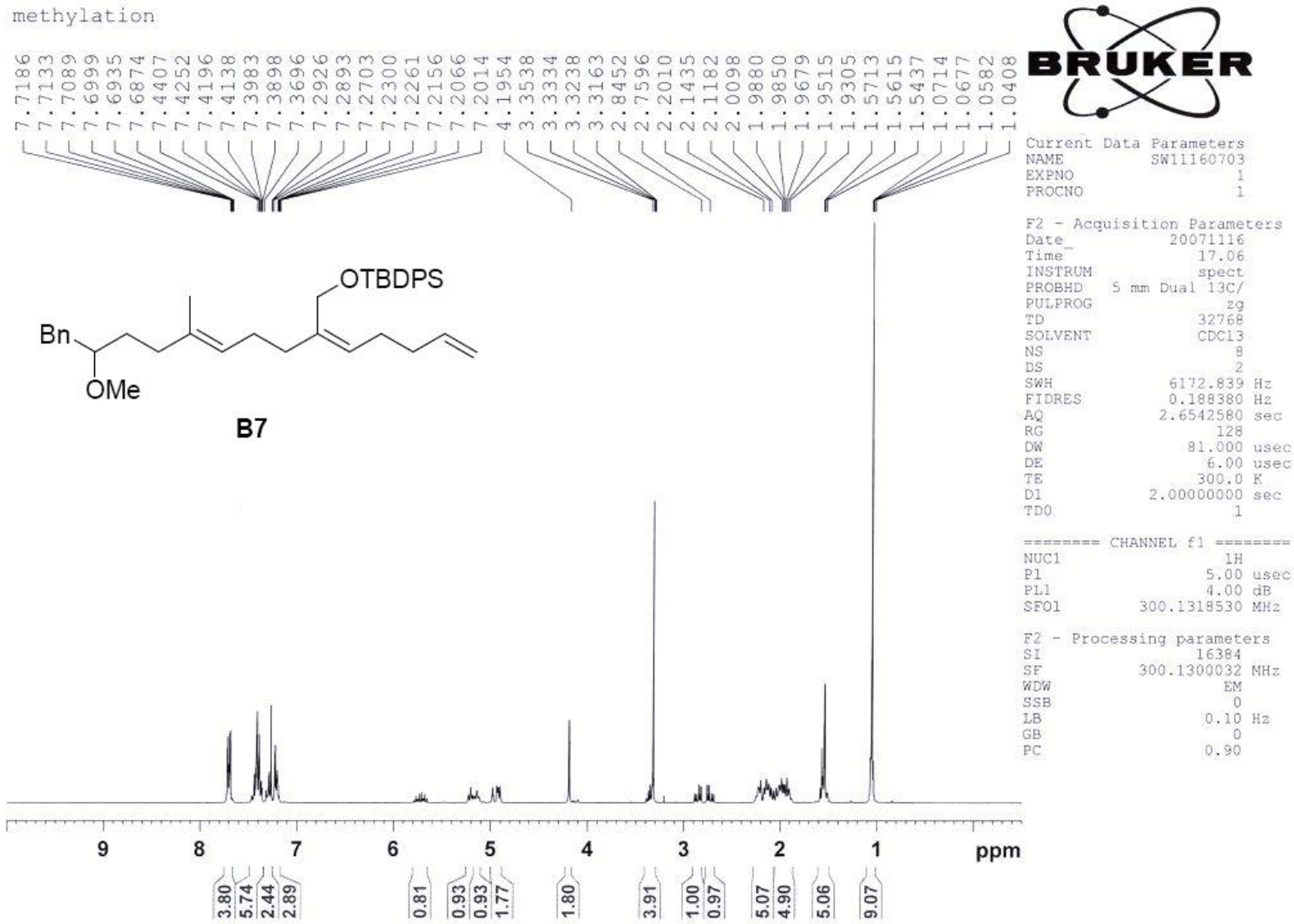

blue spot
7.7133
7.7090
7.6924
7.6880
7.4577
7.4472
7.4411
7.4353
7.4287
7.4040
7.3833
7.3755
7.2710
5.8290
5.8064
5.1867
5.1820
5.1224
5.0548
5.0491
4.9970
4.9912
4.9560
4.3416
4.2966
4.2450
4.2179
4.1999
2.2565
2.2401
2.1526
2.1281
2.1254
2.1086
2.0856
2.0825
1.7137
1.7047
1.6862
1.6751
1.6629
1.6561
1.5850
1.0776
OTBDPS
OH
2.38
BRUKER
Current Data Parameters
NAME SW11070703
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071107
Time 17.29
INSTRUM spect
PROBHD 5 mm DUL 1H-13
PULPROG zg
TD 16384
SOLVENT CDCl3
NS 4
DS 2
SWH 6218.905 Hz
FIDRES 0.379572 Hz
AQ 1.3173236 sec
RG 128
DW 80.400 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.00 usec
PL1 1.00 dB
SFO1 300.3818550 MHz
F2 - Processing parameters
SI 16384
SF 300.3799990 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
5.79
0.79
1.17
1.17
1.78
1.17
2.17
0.85
2.29
2.33
10.98

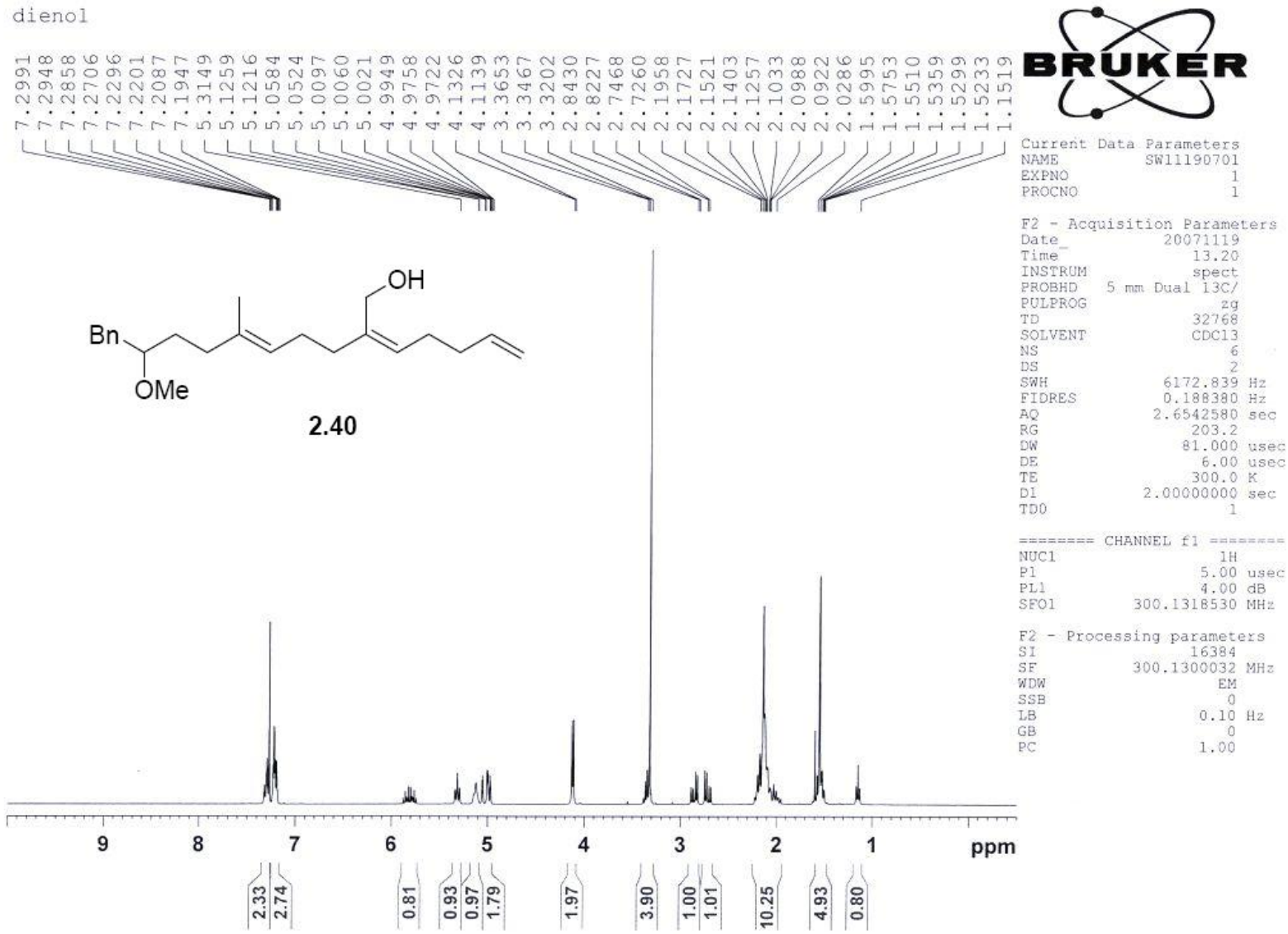

J-C 1
7.7075 7.7023 7.6895 7.6826 7.6763 7.4429 7.4325 7.4274 7.4212 7.4164 7.4007 7.3924 7.3724 7.2706 5.2359 4.9607 4.9306 4.9029 4.8970 4.2100 4.1698 4.1460 4.1222 4.0983 2.5421 2.5240 2.5050 2.4892 2.4827 1.9947 1.9890 1.9670 1.9632 1.9201 1.8980 1.8743 1.5677 1.5656 1.2834 1.2598 1.2360 1.0732 1.0630 1.0545
OTBDPS
EtO
O
B4
BRUKER
Current Data Parameters
NAME SW11090701
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071110
Time 11.11
INSTRUM spect
PROBHD 5 mm Dual 13C/
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 6
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 256
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 5.00 usec
PL1 4.00 dB
SFO1 300.1318530 MHz
F2 - Processing parameters
SI 16384
SF 300.1300032 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00
9 8 7 6 5 4 3 2 1 ppm
4.11 6.07 0.82 0.95 1.81 1.95 2.00 3.94 4.13 3.00 9.79

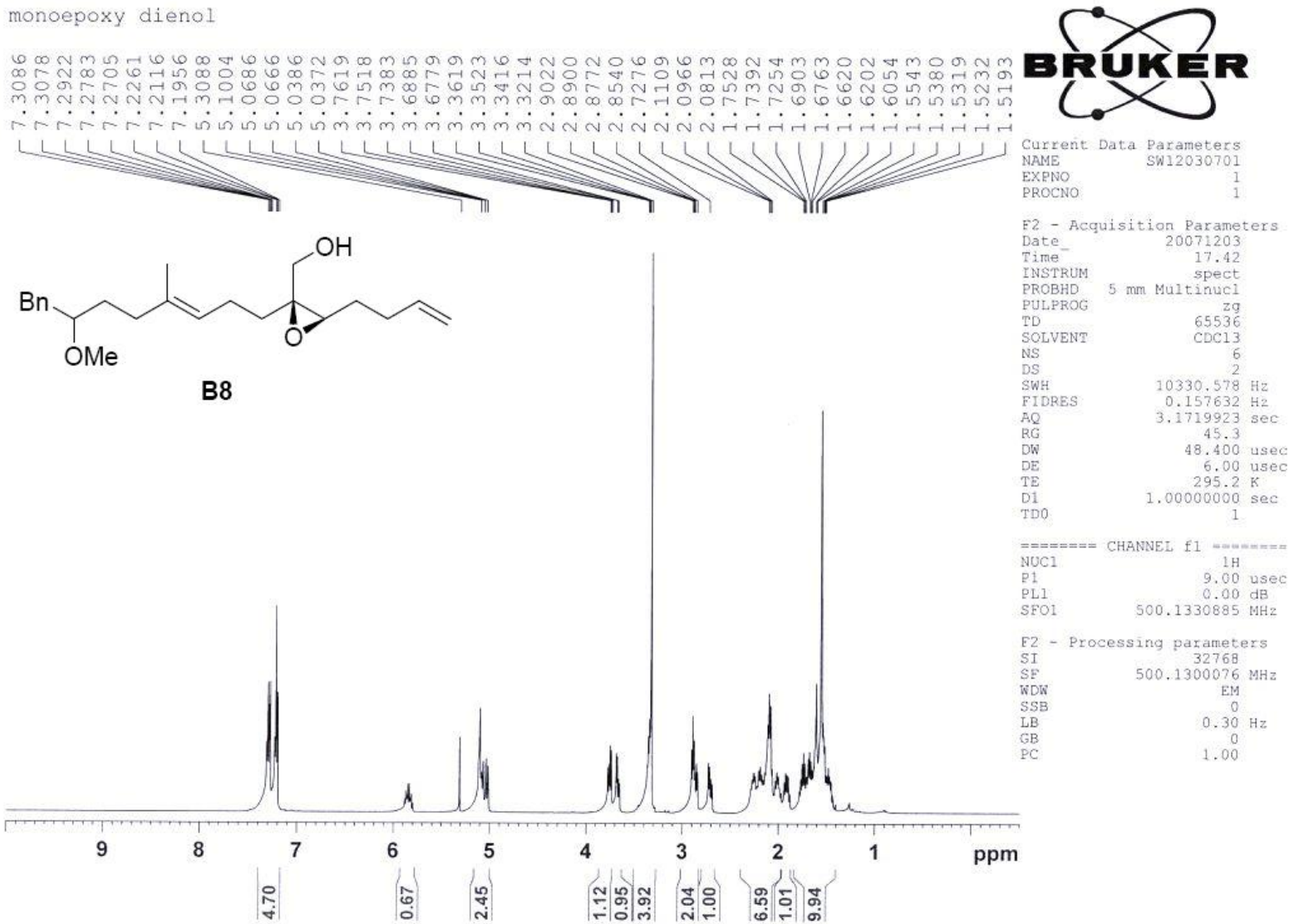

reduction/addition
7.7124
7.7072
7.6932
7.6873
7.6814
7.4443
7.4335
7.4279
7.4222
7.4165
7.4005
7.3924
7.3721
7.2708
4.9803
4.9747
4.9689
4.9656
4.9630
4.9599
4.9404
4.9371
4.9180
4.9065
4.8629
4.8580
4.8531
4.2153
4.2052
2.2712
2.2498
2.0143
2.0097
1.9927
1.9728
1.9569
1.9360
1.7399
1.7152
1.6278
1.6148
1.5821
1.0770
1.0567
OTBDPS
OH
2.39
BRUKER
Current Data Parameters
NAME SW11120701
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071112
Time 14.12
INSTRUM spect
PROBHD 5 mm Dual 13C/
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 11
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 181
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 5.00 usec
PL1 4.00 dB
SFO1 300.1318530 MHz
F2 - Processing parameters
SI 16384
SF 300.1300028 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00
9
8
7
6
5
4
3
2
1
ppm
4.01
5.88
0.79
0.89
2.83
0.92
2.00
0.96
1.85
3.87
4.78
0.98
0.51
0.48

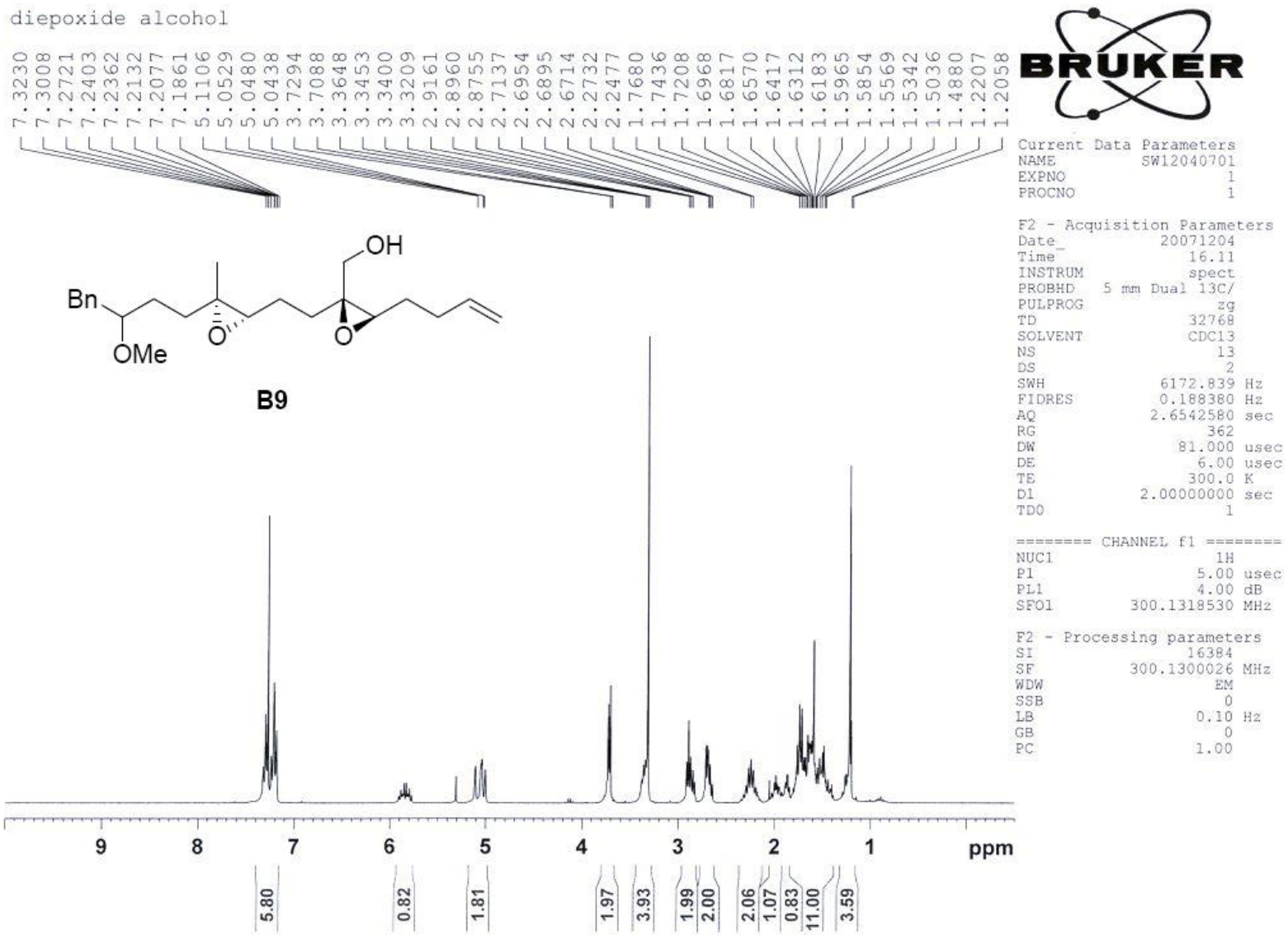

J-C 2
7.7110
7.7055
7.7017
7.6860
7.6807
7.4399
7.4381
7.4222
7.4171
7.4134
7.3970
7.3889
7.3686
7.2708
5.2028
4.9369
4.1884
4.1674
4.1436
4.1198
4.0959
2.4085
2.4025
2.3942
2.3786
2.3748
2.3282
2.3000
2.2180
2.1955
2.1683
2.1467
2.0103
1.9887
1.9683
1.9512
1.9302
1.6087
1.5741
1.2829
1.2591
1.2353
1.0654
1.0531
OTBDPS
EtO
O
B5
9
8
7
6
5
4
3
2
1
ppm
4.09
6.01
0.77
1.78
1.82
4.00
1.98
2.08
4.09
4.20
2.60
3.14
9.68
BRUKER
Current Data Parameters
NAME SW11130701
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071113
Time 13.12
INSTRUM spect
PROBHD 5 mm Dual 13C/
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 10
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 181
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 5.00 usec
PL1 4.00 dB
SFO1 300.1318530 MHz
F2 - Processing parameters
SI 16384
SF 300.1300028 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

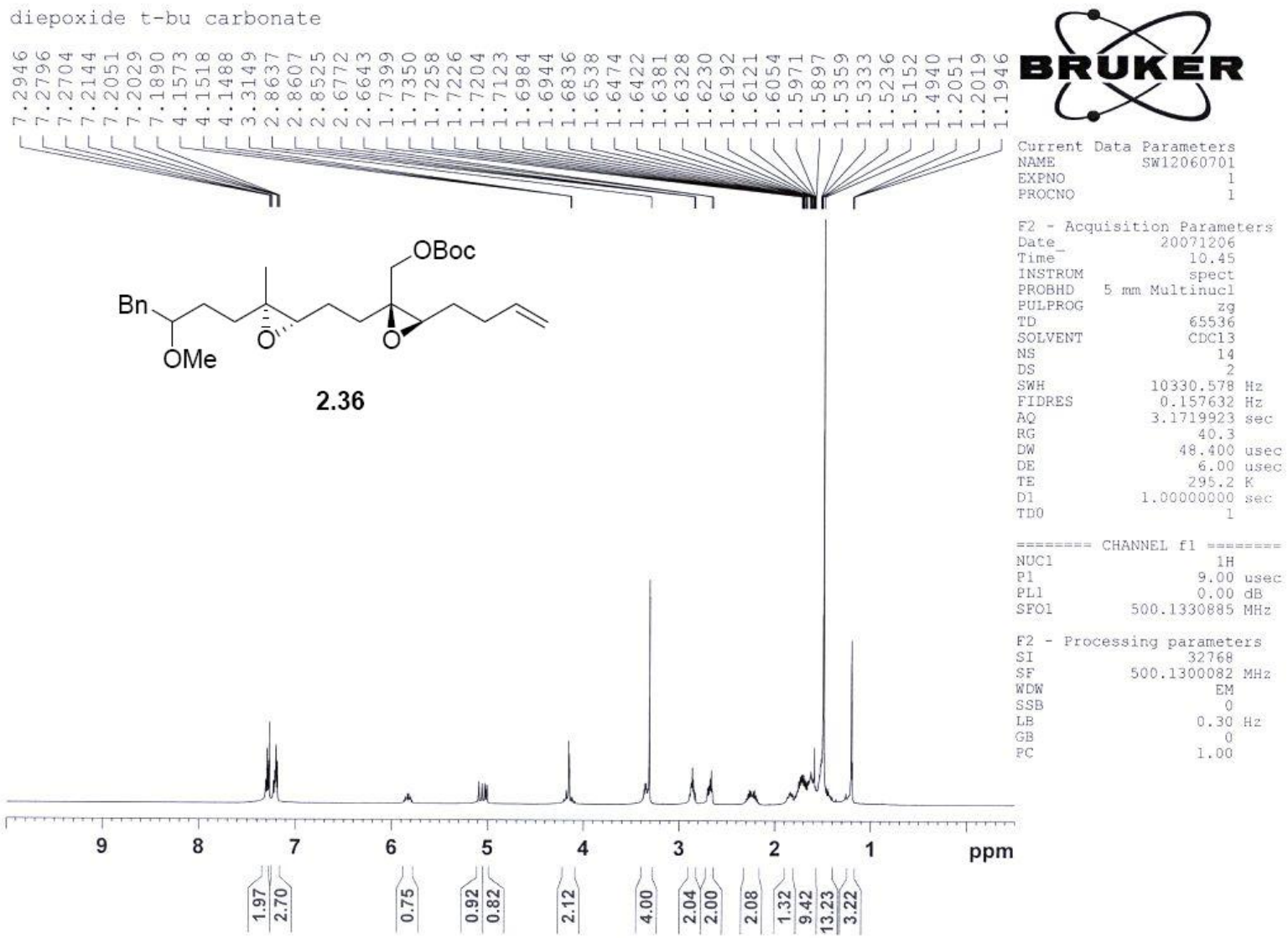

reduction/Bn addition
7.7262
7.7208
7.7166
7.7069
7.7013
7.6956
7.4474
7.4358
7.4311
7.4249
7.4222
7.4059
7.3976
7.3916
7.3774
7.3292
7.3249
7.3193
7.3078
7.3021
7.2707
7.2629
7.2447
7.2184
5.2163
4.9443
4.2034
2.2463
2.2228
2.1941
2.1746
2.1520
2.0126
2.0079
1.9907
1.9704
1.9519
1.9308
1.6577
1.6467
1.6167
1.6041
1.5851
1.0667
OTBDPS
Bn
OH
B6
9
8
7
6
5
4
3
2
1
ppm
4.23
6.55
5.49
0.88
1.99
2.00
2.09
1.03
1.00
1.00
6.31
4.57
6.68
10.29
BRUKER
Current Data Parameters
NAME SW11150701
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071115
Time_ 16.48
INSTRUM spect
PROBHD 5 mm Dual 13C/
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 14
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 90.5
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 5.00 usec
PL1 4.00 dB
SFO1 300.1318530 MHz
F2 - Processing parameters
SI 16384
SF 300.1300028 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

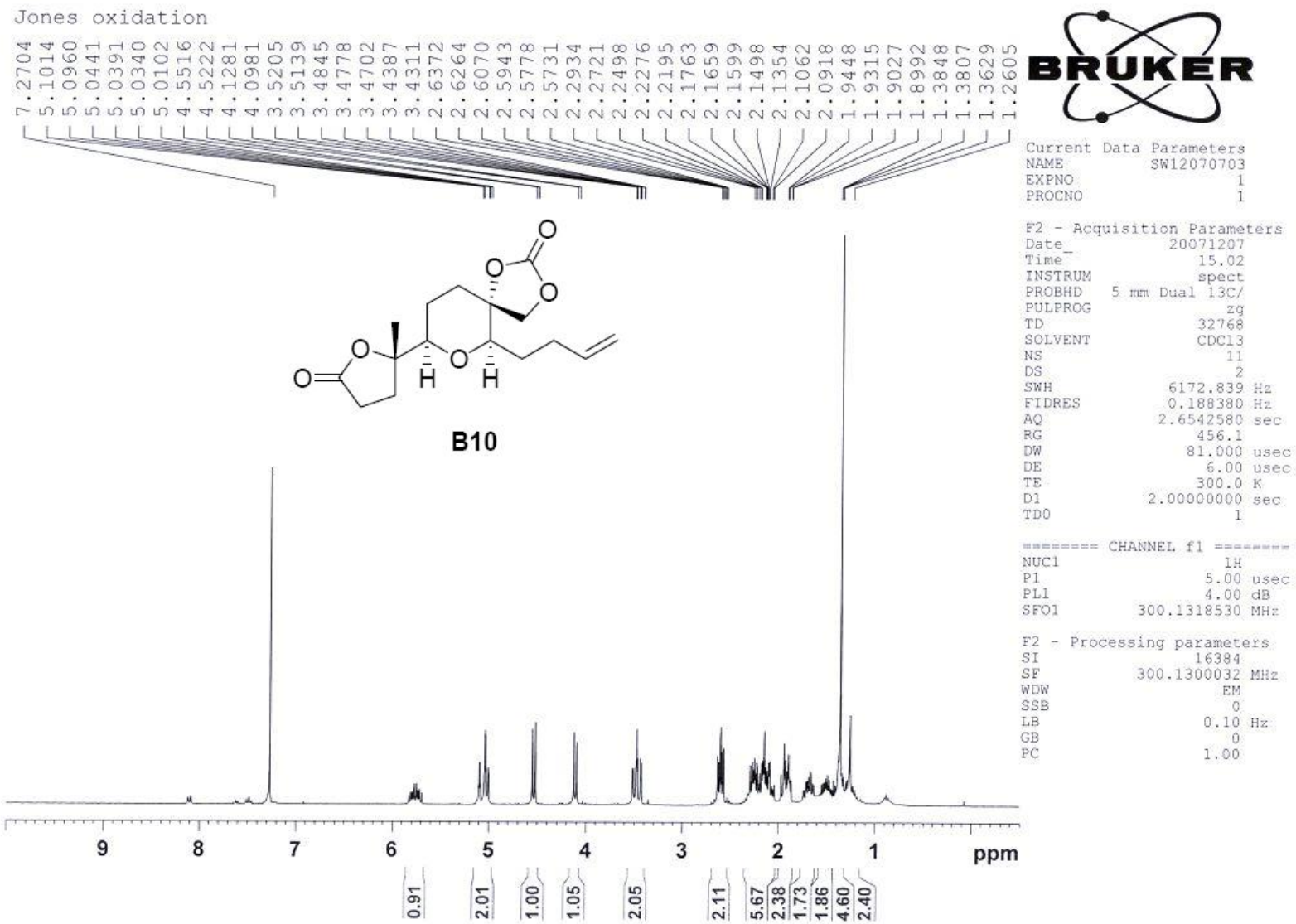

methylation
7.7186
7.7133
7.7089
7.6999
7.6935
7.6874
7.4407
7.4252
7.4196
7.4138
7.3983
7.3898
7.3696
7.2926
7.2893
7.2703
7.2300
7.2261
7.2156
7.2066
7.2014
4.1954
3.3538
3.3334
3.3238
3.3163
2.8452
2.7596
2.2010
2.1435
2.1182
2.0098
1.9880
1.9850
1.9679
1.9515
1.9305
1.5713
1.5615
1.5437
1.0714
1.0677
1.0582
1.0408
OTBDPS
Bn
OMe
B7
BRUKER
Current Data Parameters
NAME SW11160703
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071116
Time 17.06
INSTRUM spect
PROBHD 5 mm Dual 13C/
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 8
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 128
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 5.00 usec
PL1 4.00 dB
SFO1 300.1318530 MHz
F2 - Processing parameters
SI 16384
SF 300.1300032 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 0.90
9
8
7
6
5
4
3
2
1
ppm
3.80
5.74
2.44
2.89
0.81
0.93
0.93
1.77
1.80
3.91
1.00
0.97
5.07
4.90
5.06
9.07

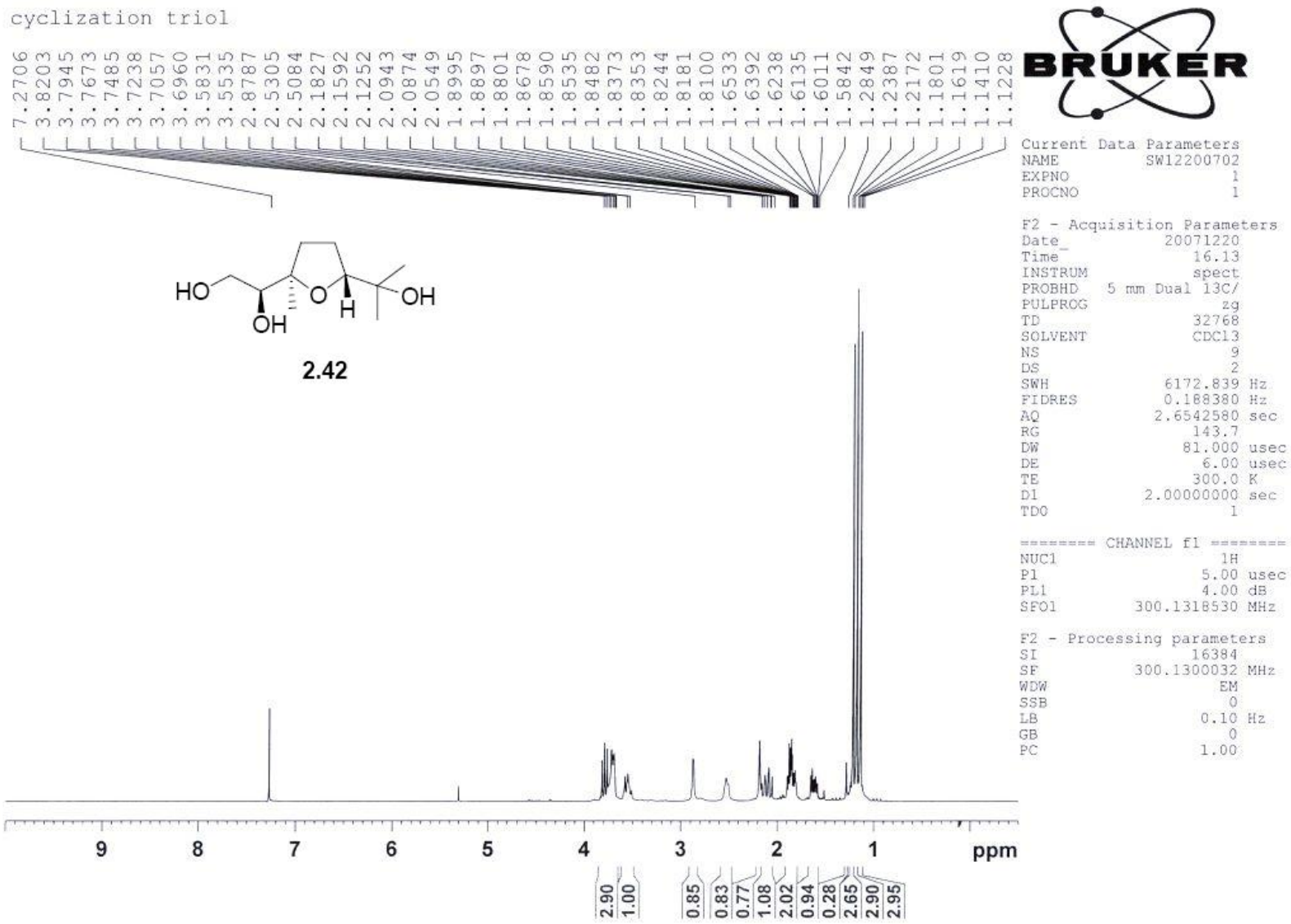

dienol
7.2991
7.2948
7.2858
7.2706
7.2296
7.2201
7.2087
7.1947
5.3149
5.1259
5.1216
5.0584
5.0524
5.0097
5.0060
5.0021
4.9949
4.9758
4.9722
4.1326
4.1139
3.3653
3.3467
3.3202
2.8430
2.8227
2.7468
2.7260
2.1958
2.1727
2.1521
2.1403
2.1257
2.1033
2.0988
2.0922
2.0286
1.5995
1.5753
1.5510
1.5359
1.5299
1.5233
1.1519
OH
Bn
OMe
2.40
BRUKER
Current Data Parameters
NAME SW11190701
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071119
Time 13.20
INSTRUM spect
PROBHD 5 mm Dual 13C/
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 6
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 203.2
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 5.00 usec
PL1 4.00 dB
SFO1 300.1318530 MHz
F2 - Processing parameters
SI 16384
SF 300.1300032 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00
9
8
7
6
5
4
3
2
1
ppm
2.33
2.74
0.81
0.93
0.97
1.79
1.97
3.90
1.00
1.01
10.25
4.93
0.80

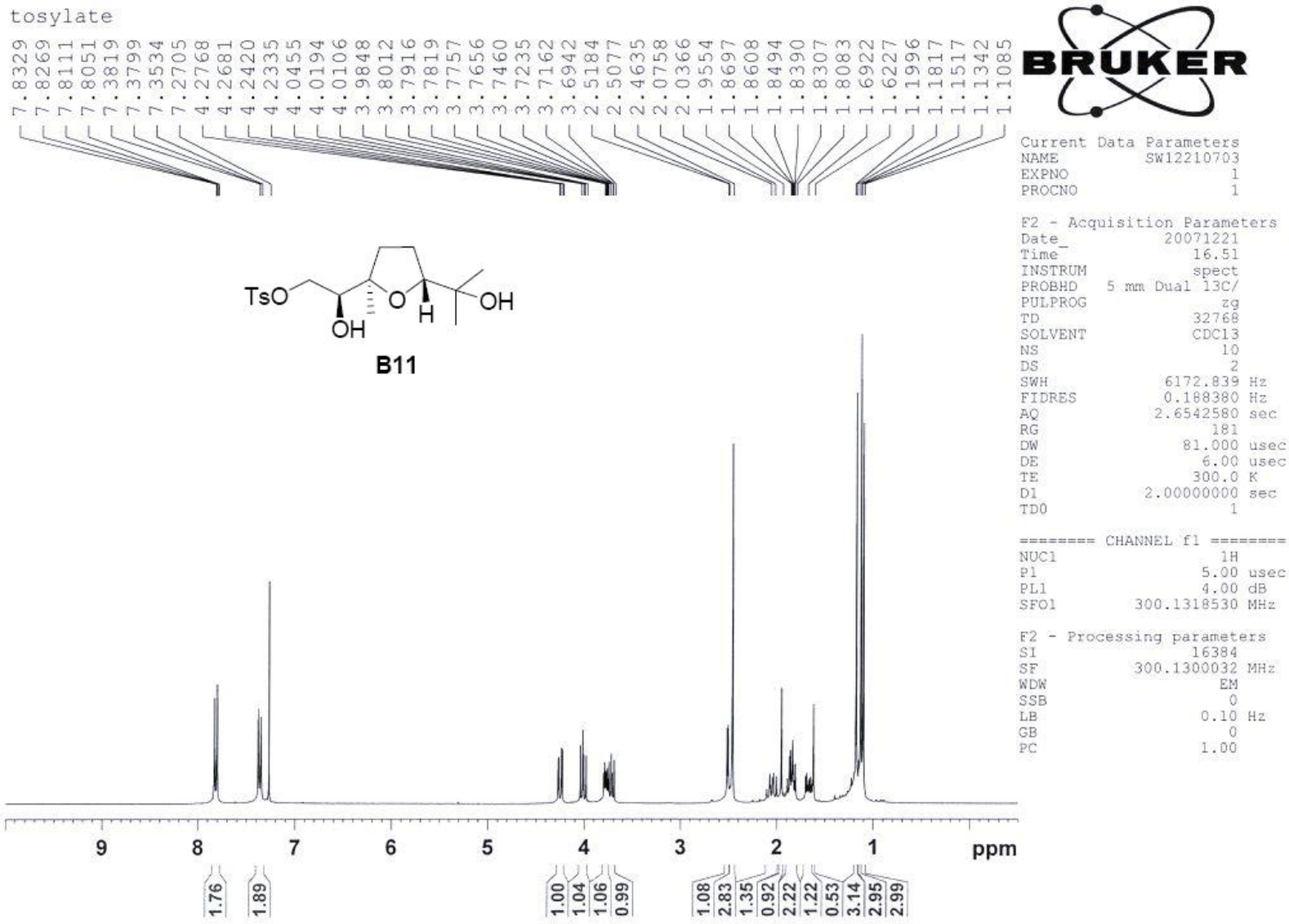

monoepoxy dienol
7.3086
7.3078
7.2922
7.2783
7.2705
7.2261
7.2116
7.1956
5.3088
5.1004
5.0686
5.0666
5.0386
5.0372
3.7619
3.7518
3.7383
3.6885
3.6779
3.3619
3.3523
3.3416
3.3214
2.9022
2.8900
2.8772
2.8540
2.7276
2.1109
2.0966
2.0813
1.7528
1.7392
1.7254
1.6903
1.6763
1.6620
1.6202
1.6054
1.5543
1.5380
1.5319
1.5232
1.5193
OH
Bn
OMe
O
B8
9
8
7
6
5
4
3
2
1
ppm
4.70
0.67
2.45
1.12
0.95
3.92
2.04
1.00
6.59
1.01
9.94
BRUKER
Current Data Parameters
NAME SW12030701
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071203
Time 17.42
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zg
TD 65536
SOLVENT CDCl3
NS 6
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 45.3
DW 48.400 usec
DE 6.00 usec
TE 295.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.00 usec
PL1 0.00 dB
SFO1 500.1330885 MHz
F2 - Processing parameters
SI 32768
SF 500.1300076 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

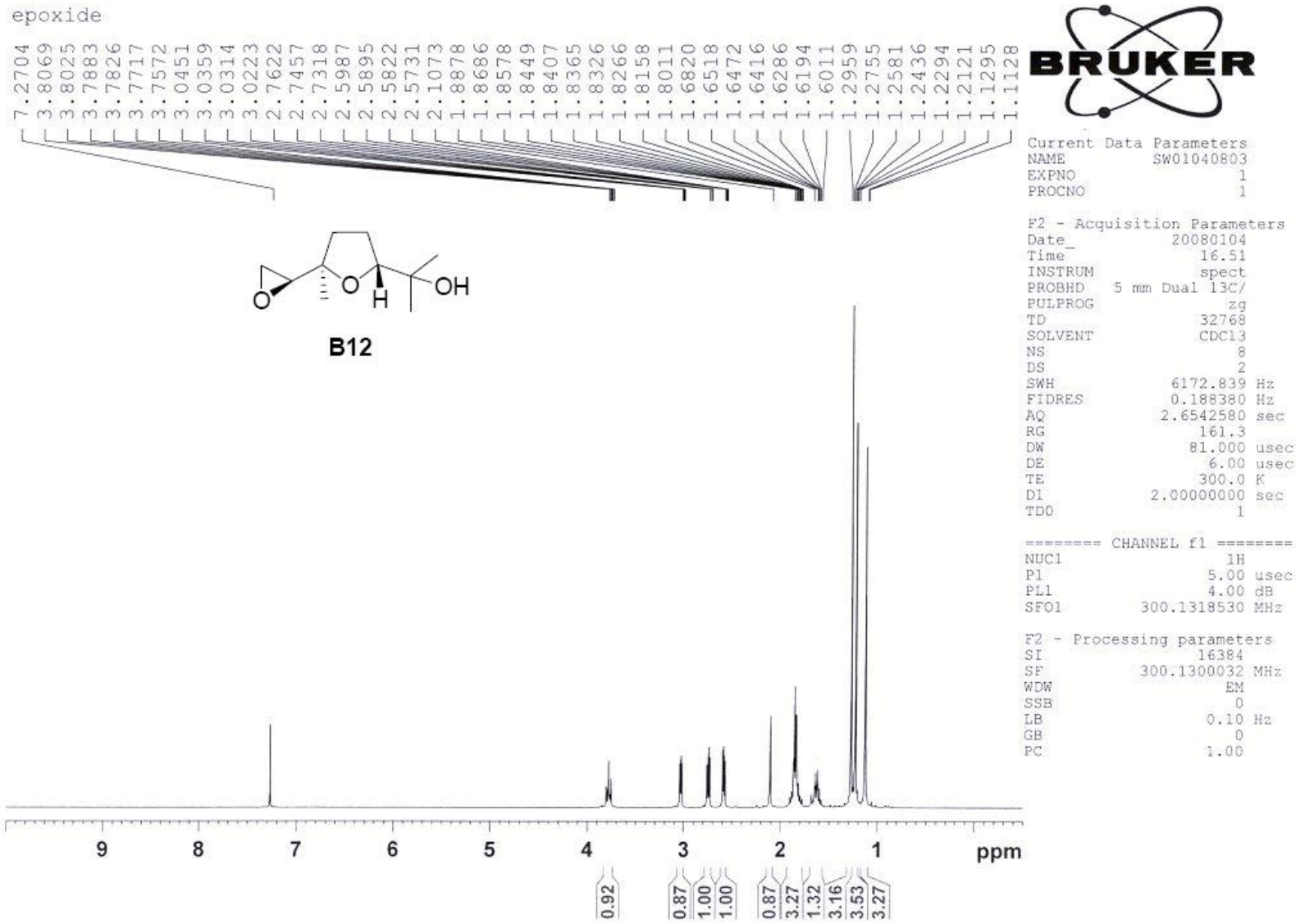

diepoxide alcohol
7.3230
7.3008
7.2721
7.2403
7.2362
7.2132
7.2077
7.1861
5.1106
5.0529
5.0480
5.0438
3.7294
3.7088
3.3648
3.3453
3.3400
3.3209
2.9161
2.8960
2.8755
2.7137
2.6954
2.6895
2.6714
2.2732
2.2477
1.7680
1.7436
1.7208
1.6968
1.6817
1.6570
1.6417
1.6312
1.6183
1.5965
1.5854
1.5569
1.5342
1.5036
1.4880
1.2207
1.2058
OH
Bn
OMe
B9
9
8
7
6
5
4
3
2
1
ppm
5.80
0.82
1.81
1.97
3.93
1.99
2.00
2.06
1.07
0.83
11.00
3.59
BRUKER
Current Data Parameters
NAME SW12040701
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071204
Time 16.11
INSTRUM spect
PROBHD 5 mm Dual 13C/
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 13
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 362
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 5.00 usec
PL1 4.00 dB
SFO1 300.1318530 MHz
F2 - Processing parameters
SI 16384
SF 300.1300026 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00


diepoxide t-bu carbonate
7.2946
7.2796
7.2704
7.2144
7.2051
7.2029
7.1890
4.1573
4.1518
4.1488
3.3149
2.8637
2.8607
2.8525
2.6772
2.6643
1.7399
1.7350
1.7258
1.7226
1.7204
1.7123
1.6984
1.6944
1.6836
1.6538
1.6474
1.6422
1.6381
1.6328
1.6230
1.6192
1.6121
1.6054
1.5971
1.5897
1.5359
1.5333
1.5236
1.5152
1.4940
1.2051
1.2019
1.1946
OBoc
Bn
OMe
O
O
2.36
9
8
7
6
5
4
3
2
1
ppm
1.97
2.70
0.75
0.92
0.82
2.12
4.00
2.04
2.00
2.08
1.32
9.42
13.23
3.22
BRUKER
Current Data Parameters
NAME SW12060701
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071206
Time 10.45
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zg
TD 65536
SOLVENT CDCl3
NS 14
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 40.3
DW 48.400 usec
DE 6.00 usec
TE 295.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.00 usec
PL1 0.00 dB
SFO1 500.1330885 MHz
F2 - Processing parameters
SI 32768
SF 500.1300082 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

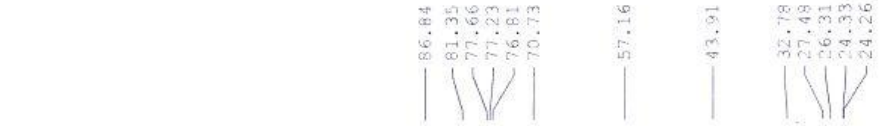

Jones oxidation
7.2704
5.1014
5.0960
5.0441
5.0391
5.0340
5.0102
4.5516
4.5222
4.1281
4.0981
3.5205
3.5139
3.4845
3.4778
3.4702
3.4387
3.4311
3.6372
2.6264
2.6070
2.5943
2.5778
2.5731
2.2934
2.2721
2.2498
2.2276
2.2195
2.1763
2.1659
2.1599
2.1498
2.1354
2.1062
2.0918
1.9448
1.9315
1.9027
1.8992
1.3848
1.3807
1.3629
1.2605
B10
9
8
7
6
5
4
3
2
1
ppm
0.91
2.01
1.00
1.05
2.05
2.11
5.67
2.38
1.73
1.86
4.60
2.40
BRUKER
Current Data Parameters
NAME SW12070703
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071207
Time 15.02
INSTRUM spect
PROBHD 5 mm Dual 13C/
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 11
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 456.1
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 5.00 usec
PL1 4.00 dB
SFO1 300.1318530 MHz
F2 - Processing parameters
SI 16384
SF 300.1300032 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

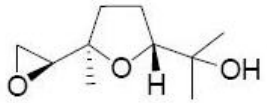

cyclization triol
7.2706
3.8203
3.7945
3.7673
3.7485
3.7238
3.7057
3.6960
3.5831
3.5535
2.8787
2.5305
2.5084
2.1827
2.1592
2.1252
2.0943
2.0874
2.0549
1.8995
1.8897
1.8801
1.8678
1.8590
1.8535
1.8482
1.8373
1.8353
1.8244
1.8181
1.8100
1.6533
1.6392
1.6238
1.6135
1.6011
1.5842
1.2849
1.2387
1.2172
1.1801
1.1619
1.1410
1.1228
HO
OH
O
H
OH
2.42
9
8
7
6
5
4
3
2
1
ppm
2.90
1.00
0.85
0.83
0.77
1.08
2.02
0.94
0.28
2.65
2.90
2.95
BRUKER
Current Data Parameters
NAME SW12200702
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071220
Time 16.13
INSTRUM spect
PROBHD 5 mm Dual 13C/
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 9
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 143.7
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 5.00 usec
PL1 4.00 dB
SFO1 300.1318530 MHz
F2 - Processing parameters
SI 16384
SF 300.1300032 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00


tosylate
7.8329
7.8269
7.8111
7.8051
7.3819
7.3799
7.3534
7.2705
4.2768
4.2681
4.2420
4.2335
4.0455
4.0194
4.0106
3.9848
3.8012
3.7916
3.7819
3.7757
3.7656
3.7460
3.7235
3.7162
3.6942
2.5184
2.5077
2.4635
2.0758
2.0366
1.9554
1.8697
1.8608
1.8494
1.8390
1.8307
1.8083
1.6922
1.6227
1.1996
1.1817
1.1517
1.1342
1.1085
TsO
OH
O
H
OH
B11
BRUKER
Current Data Parameters
NAME SW12210703
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071221
Time 16.51
INSTRUM spect
PROBHD 5 mm Dual 13C/
PULPROG zg
TD 32768
SOLVENT CDC13
NS 10
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 181
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 5.00 usec
PL1 4.00 dB
SFO1 300.1318530 MHz
F2 - Processing parameters
SI 16384
SF 300.1300032 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00
9
8
7
6
5
4
3
2
1
ppm
1.76
1.89
1.00
1.04
1.06
0.99
1.08
2.83
1.35
0.92
2.22
1.22
0.53
3.14
2.95
2.99

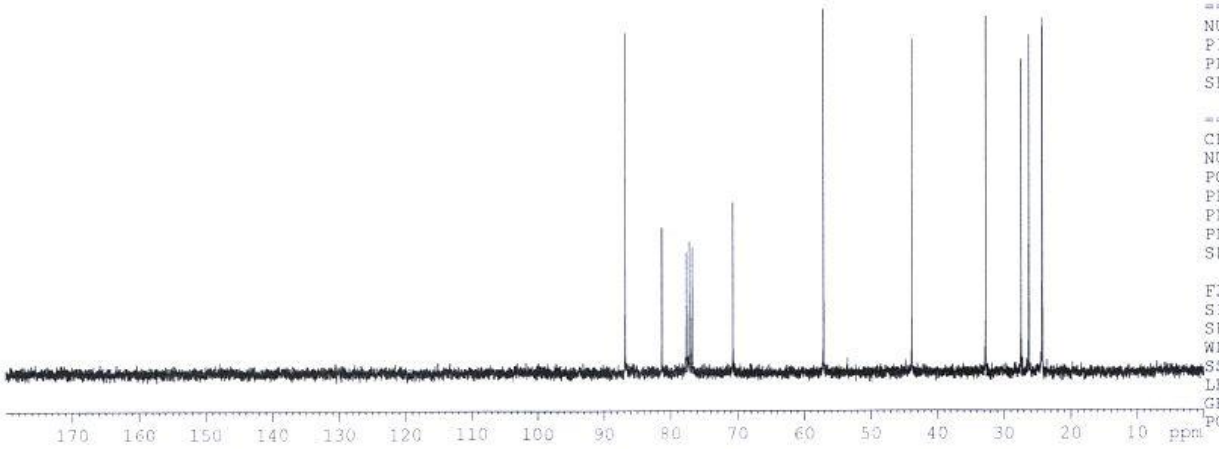

epoxide
7.2704
3.8069
3.8025
3.7883
3.7826
3.7717
3.7572
3.0451
3.0359
3.0314
3.0223
2.7622
2.7457
2.7318
2.5987
2.5895
2.5822
2.5731
2.1073
1.8878
1.8686
1.8578
1.8449
1.8407
1.8365
1.8326
1.8266
1.8158
1.8011
1.6820
1.6518
1.6472
1.6416
1.6286
1.6194
1.6011
1.2959
1.2755
1.2581
1.2436
1.2294
1.2121
1.1295
1.1128
O
O
H
OH
B12
9
8
7
6
5
4
3
2
1
ppm
0.92
0.87
1.00
1.00
0.87
3.27
1.32
3.16
3.53
3.27
BRUKER
Current Data Parameters
NAME SW01040803
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080104
Time 16.51
INSTRUM spect
PROBHD 5 mm Dual 13C/
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 8
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 161.3
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 5.00 usec
PL1 4.00 dB
SFO1 300.1318530 MHz
F2 - Processing parameters
SI 16384
SF 300.1300032 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

epoxide





B12



BRUKER

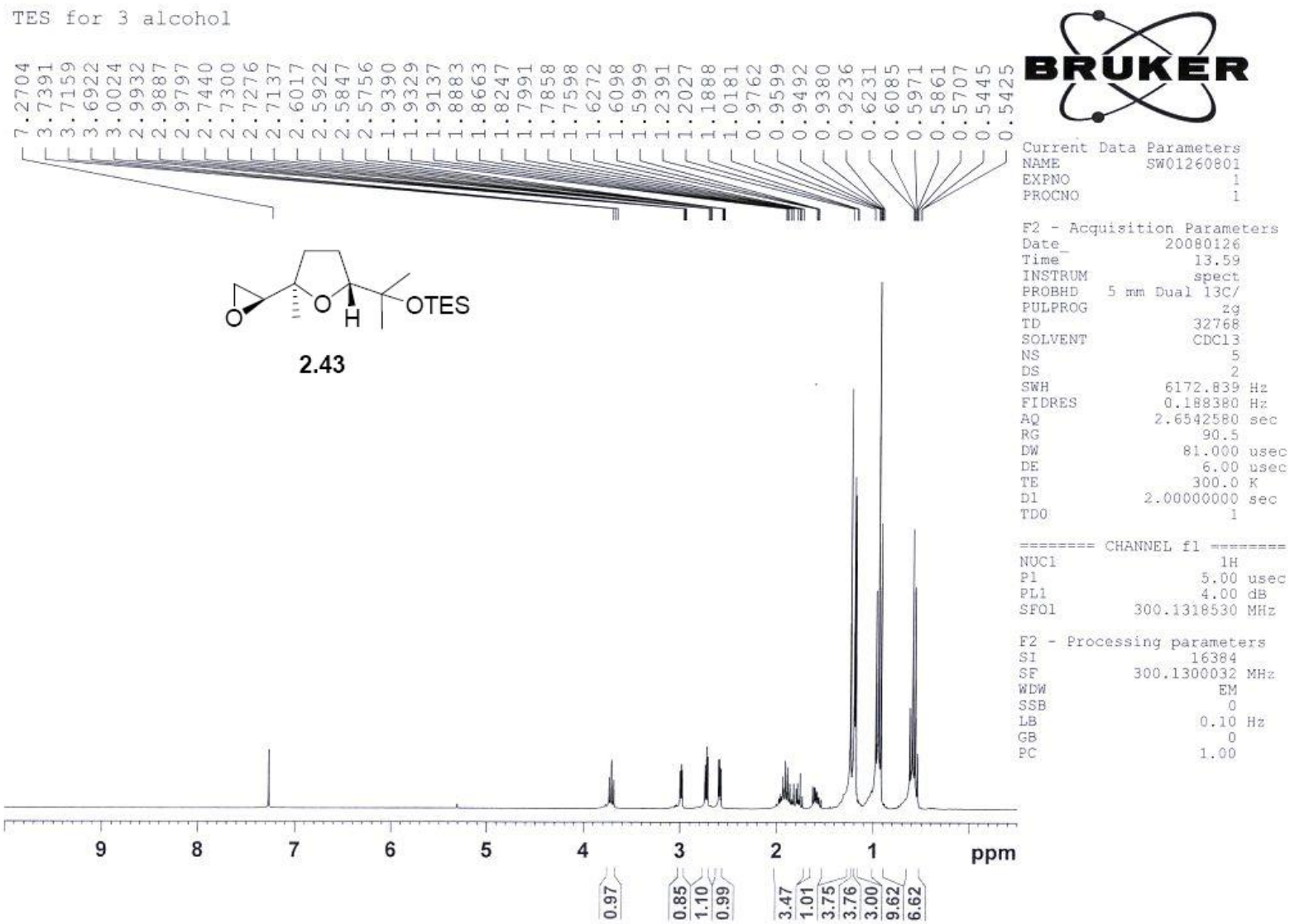
```
Current Data Parameters
NAME          SW02130804
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20080213
Time              16.55
INSTRUM           spect
PROBHD   5 mm QNP  1H/1
PULPROG           zgpg
TD               65536
SOLVENT          CDCl3
NS                  14
DS                   2
SWH          17985.611 Hz
FIDRES        0.274439 Hz
AQ            1.8219508 sec
RG               13004
DW              27.800 usec
DE               6.00 usec
TE              292.8 K
D1          10.00000000 sec
d11          0.03000000 sec
DELTA        9.89999962 sec
TD0                  1

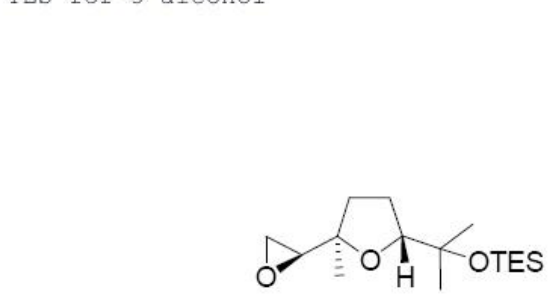
======== CHANNEL f1 ========
NUC1                13C
P1                7.00 usec
PL1               0.00 dB
SFO1        75.4639789 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                1H
PCPD2           100.00 usec
PL2               0.00 dB
PL12             18.24 dB
PL13             18.24 dB
SFO2       300.0862003 MHz

F2 - Processing parameters
SI                32768
SF          75.4564244 MHz
WDW                EM
SSB                 0
LB               1.00 Hz
GB                  0
PC                1.40
```


TES for 3 alcohol
7.2704
3.7391
3.7159
3.6922
3.0024
2.9932
2.9887
2.9797
2.7440
2.7300
2.7276
2.7137
2.6017
2.5922
2.5847
2.5756
1.9390
1.9329
1.9137
1.8883
1.8663
1.8247
1.7991
1.7858
1.7598
1.6272
1.6098
1.5999
1.2391
1.2027
1.1888
1.0181
0.9762
0.9599
0.9492
0.9380
0.9236
0.6231
0.6085
0.5971
0.5861
0.5707
0.5445
0.5425
OTES
2.43
BRUKER
Current Data Parameters
NAME SW01260801
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080126
Time 13.59
INSTRUM spect
PROBHD 5 mm Dual 13C/
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 5
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 90.5
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 5.00 usec
PL1 4.00 dB
SFO1 300.1318530 MHz
F2 - Processing parameters
SI 16384
SF 300.1300032 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00
9
8
7
6
5
4
3
2
1
ppm
0.97
0.85
1.10
0.99
3.47
1.01
3.75
3.76
3.00
9.62
6.62

TES for 3 alcohol



2.43

BRUKER

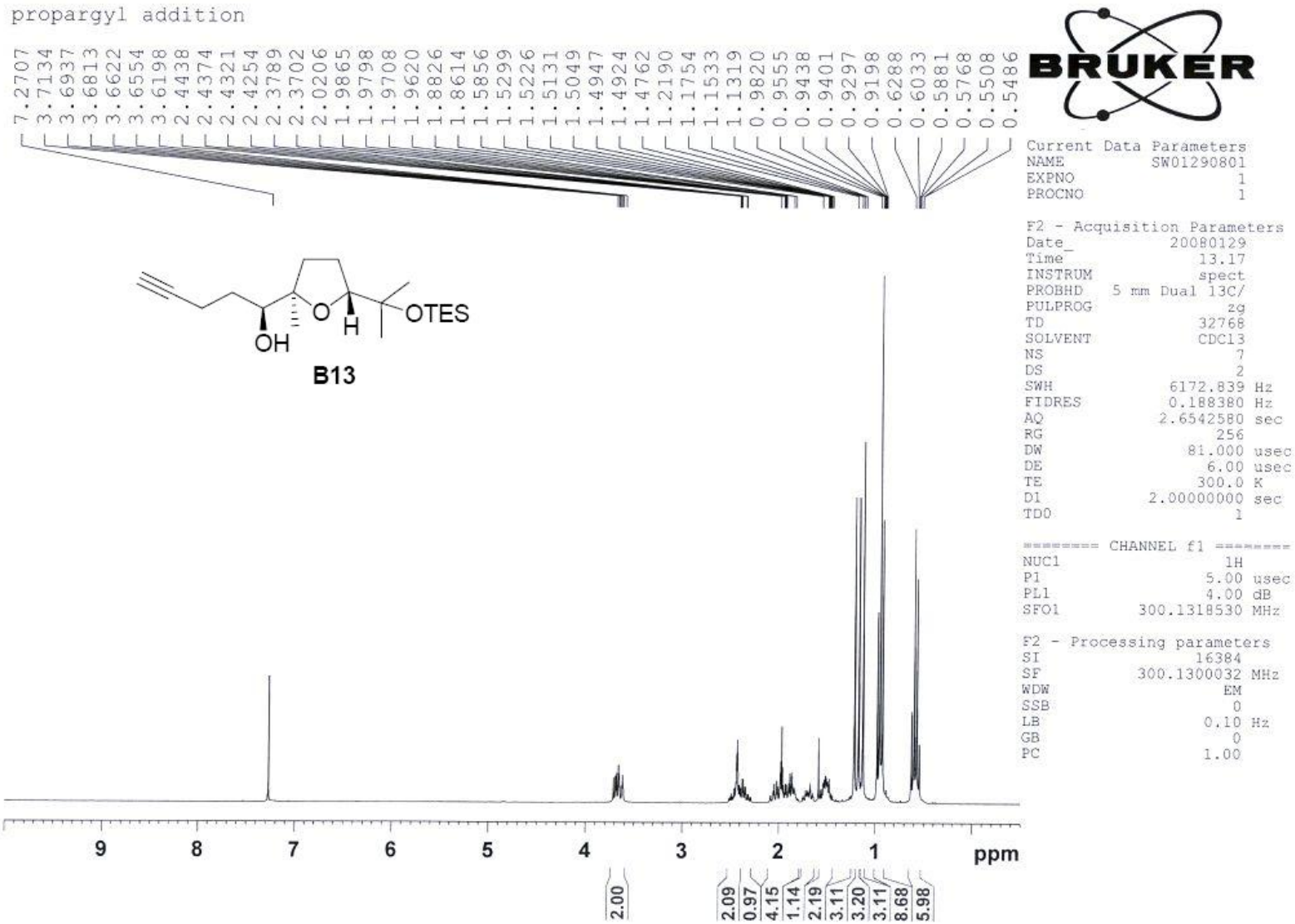
```
Current Data Parameters
NAME          SW02130802
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20080213
Time              13.26
INSTRUM           spect
PROBHD   5 mm QNP  1H/1
PULPROG           zgpg
TD               65536
SOLVENT          CDCl3
NS                  13
DS                   2
SWH          17985.611 Hz
FIDRES        0.274439 Hz
AQ            1.8219508 sec
RG                13004
DW               27.800 usec
DE                6.00 usec
TE               292.5 K
D1          10.00000000 sec
d11          0.03000000 sec
DELTA        9.89999962 sec
TD0                  1

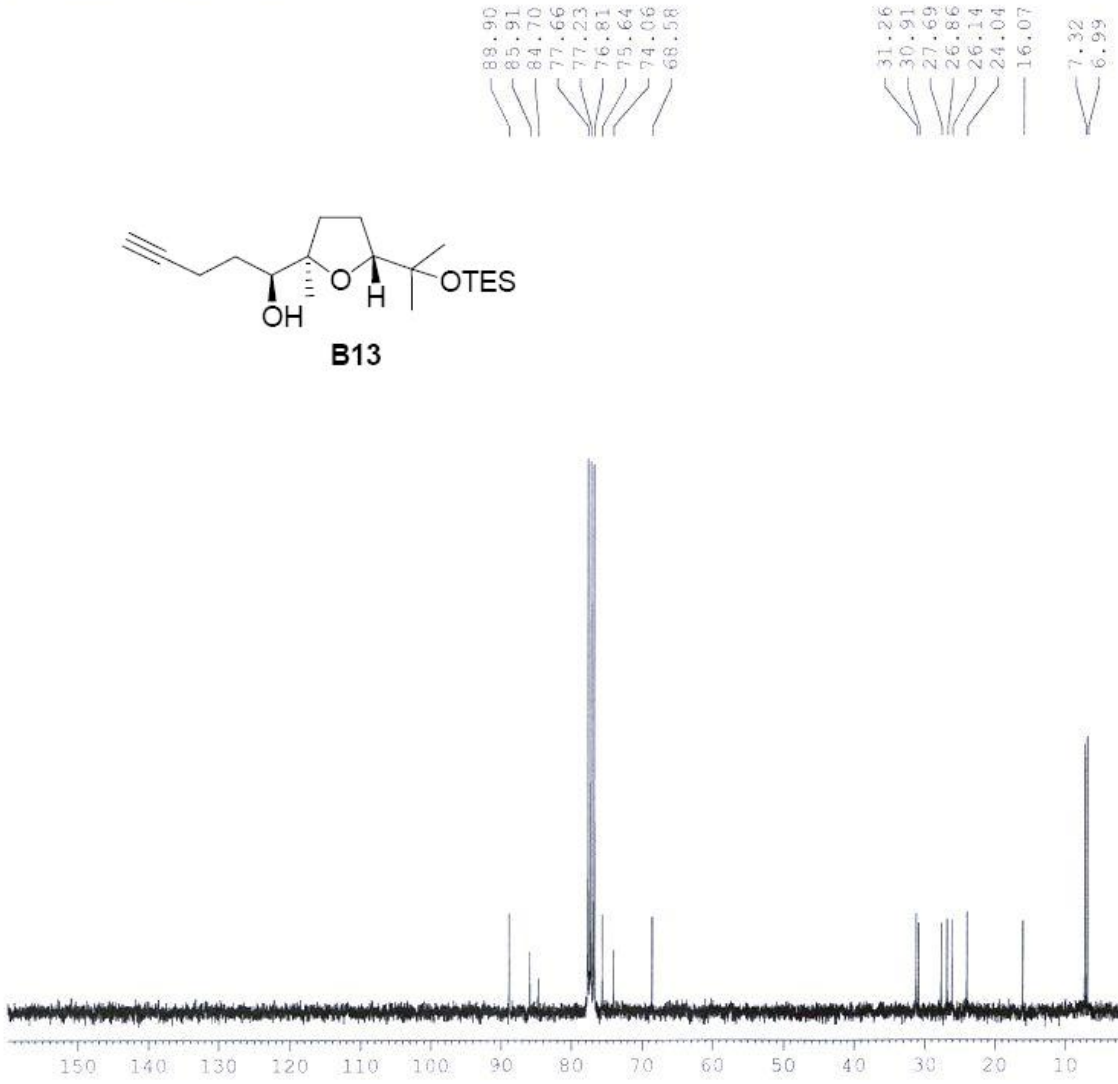
======== CHANNEL f1 ========
NUC1                13C
P1                 7.00 usec
PL1                0.00 dB
SFO1         75.4639789 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                1H
PCPD2            100.00 usec
PL2                0.00 dB
PL12              18.24 dB
PL13              18.24 dB
SFO2        300.0862003 MHz

F2 - Processing parameters
SI                 32768
SF          75.4564200 MHz
WDW                EM
SSB                 0
LB                1.00 Hz
GB                  0
PC                1.40
```


propargyl addition
7.2707
3.7134
3.6937
3.6813
3.6622
3.6554
3.6198
2.4438
2.4374
2.4321
2.4254
2.3789
2.3702
2.0206
1.9865
1.9798
1.9708
1.9620
1.8826
1.8614
1.5856
1.5299
1.5226
1.5131
1.5049
1.4947
1.4924
1.4762
1.2190
1.1754
1.1533
1.1319
0.9820
0.9555
0.9438
0.9401
0.9297
0.9198
0.6288
0.6033
0.5881
0.5768
0.5508
0.5486
OH
O
H
OTES
B13
BRUKER
Current Data Parameters
NAME SW01290801
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080129
Time 13.17
INSTRUM spect
PROBHD 5 mm Dual 13C/
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 7
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 256
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 5.00 usec
PL1 4.00 dB
SFO1 300.1318530 MHz
F2 - Processing parameters
SI 16384
SF 300.1300032 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
2.09
0.97
4.15
1.14
2.19
3.11
3.20
3.11
8.68
5.98

propargyl addition



BRUKER

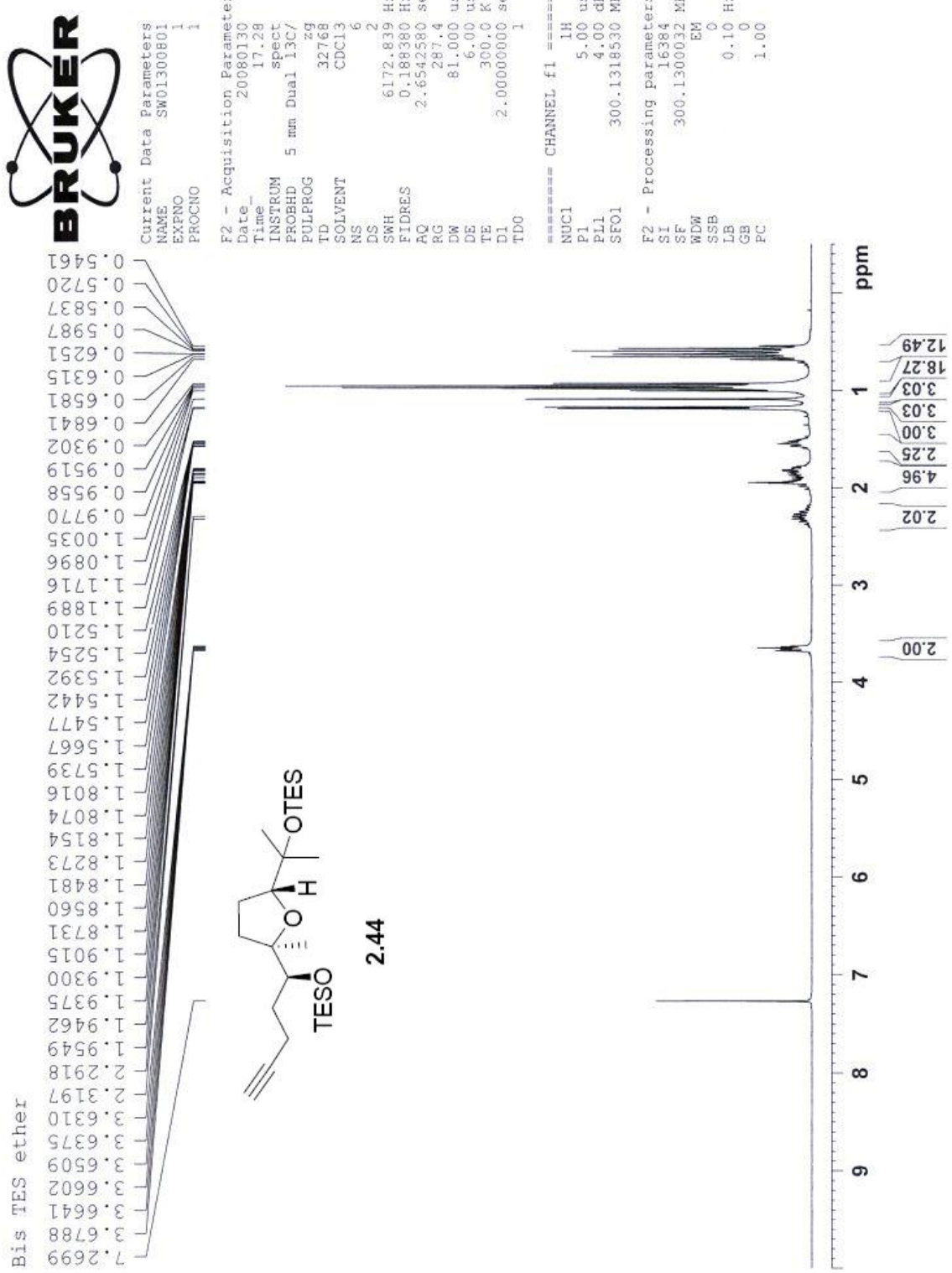
Current Data Parameters
NAME Sw01290803
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20080129
Time 13.50
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 168
DS 2
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 3251
DW 27.800 usec
DE 6.00 usec
TE 300.0 K
D1 10.00000000 sec
d11 0.03000000 sec
DELTA 9.89999962 sec
TD0 1

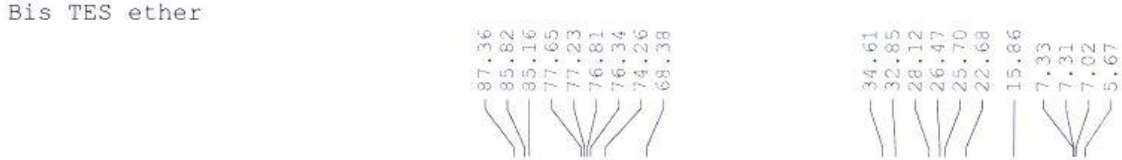
======== CHANNEL f1 ========
NUC1 13C
P1 7.00 usec
PL1 0.00 dB
SFO1 75.4639789 MHz

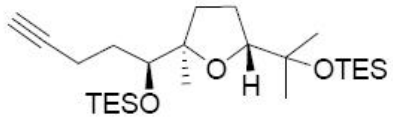
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 0.00 dB
PL12 18.24 dB
PL13 18.24 dB
SFO2 300.0862003 MHz

F2 - Processing parameters
SI 32768
SF 75.4564159 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

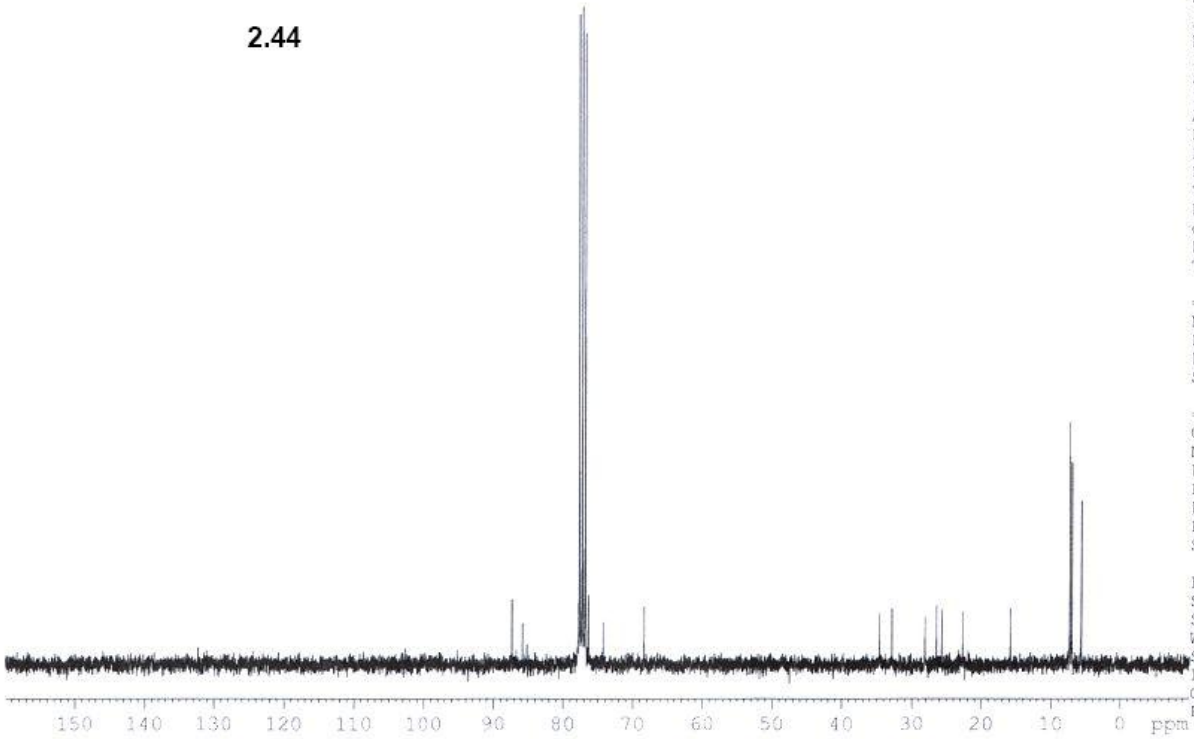

Bis TES ether
BRUKER
Current Data Parameters
NAME SW01300801
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080130
Time_ 17.28
INSTRUM spect
PROBHD 5 mm Dual 13C/
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 6
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 287.4
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 5.00 usec
PL1 4.00 dB
SFO1 300.1318530 MHz
F2 - Processing parameters
SI 16384
SF 300.1300032 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00
OTES
O
H
TESO
2.44
ppm
2.00
2.02
4.96
2.25
3.00
3.03
3.03
18.27
12.49

Bis TES ether





2.44



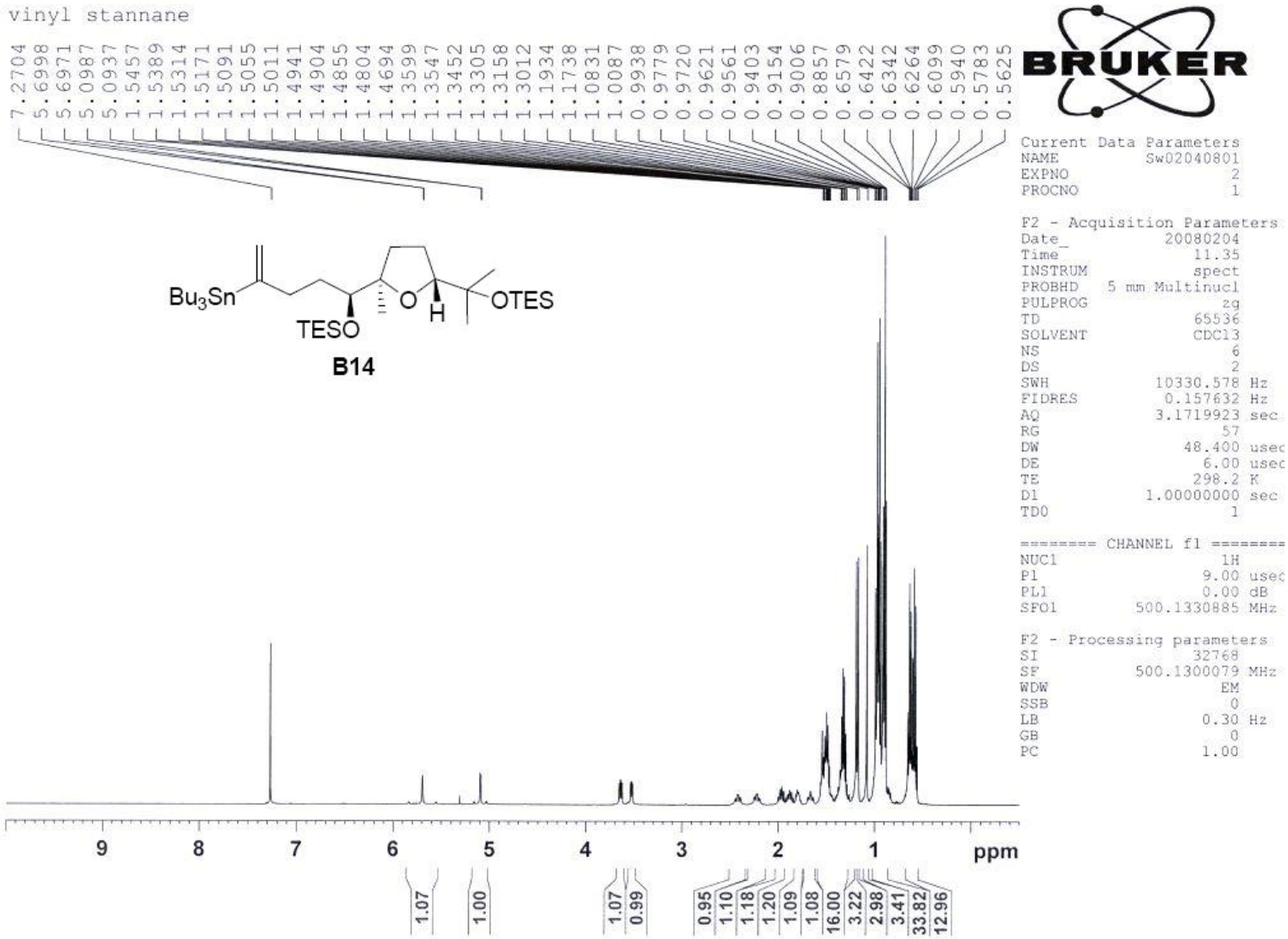

```
Current Data Parameters
NAME          Sw01310801
EXPNO                  1
PROCNO                 1

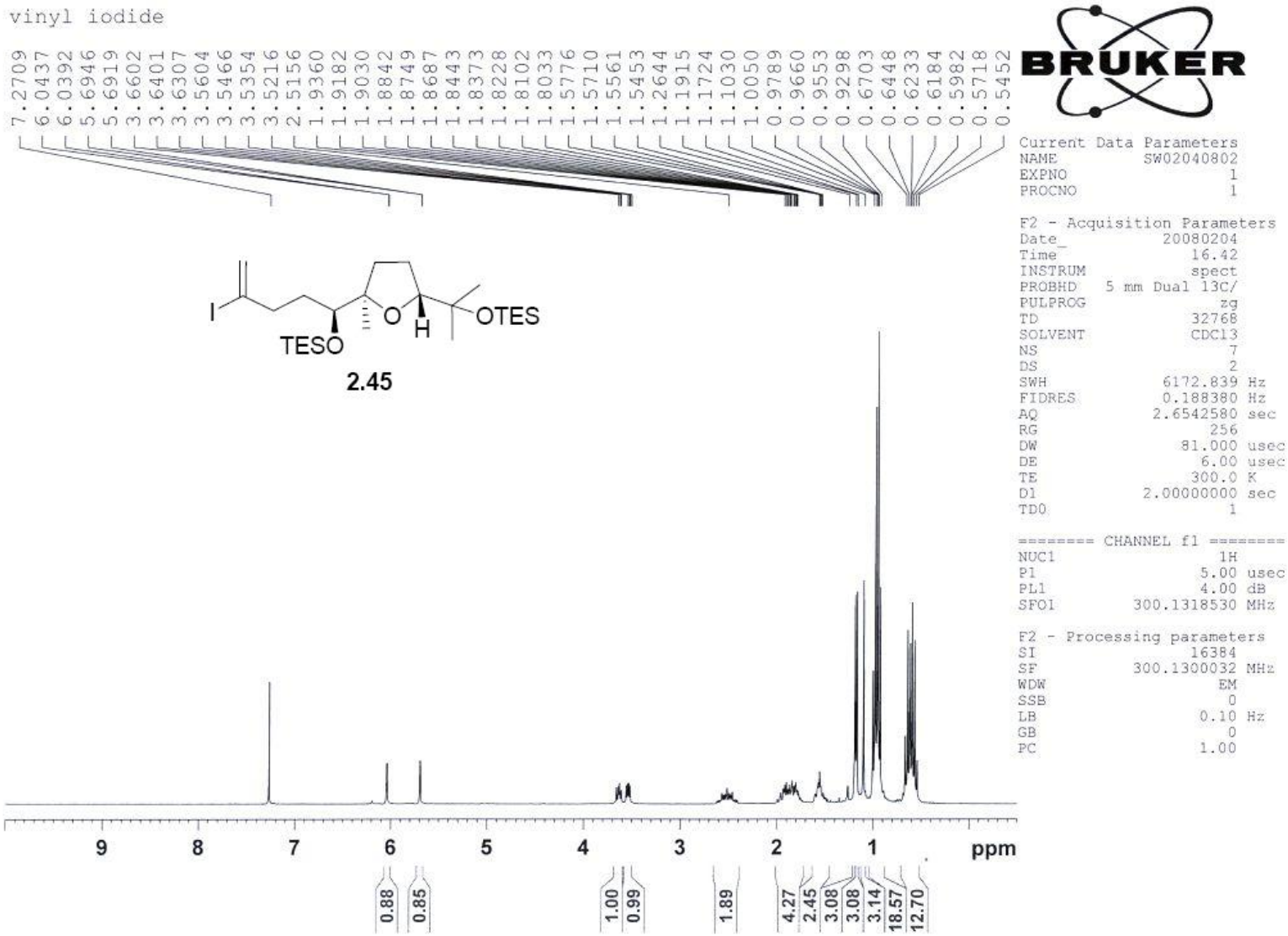
F2 - Acquisition Parameters
Date_           20080131
Time              11.05
INSTRUM           spect
PROBHD   5 mm QNP  1H/1
PULPROG           zgpg
TD               65536
SOLVENT          CDCl3
NS                 208
DS                   2
SWH           17985.611 Hz
FIDRES         0.274439 Hz
AQ             1.8219508 sec
RG                 13004
DW              27.800 usec
DE               6.00 usec
TE               300.0 K
D1          10.00000000 sec
d11          0.03000000 sec
DELTA        9.89999962 sec
TD0                  1

======== CHANNEL f1 ========
NUC1                13C
P1               7.00 usec
PL1              0.00 dB
SFO1        75.4639789 MHz

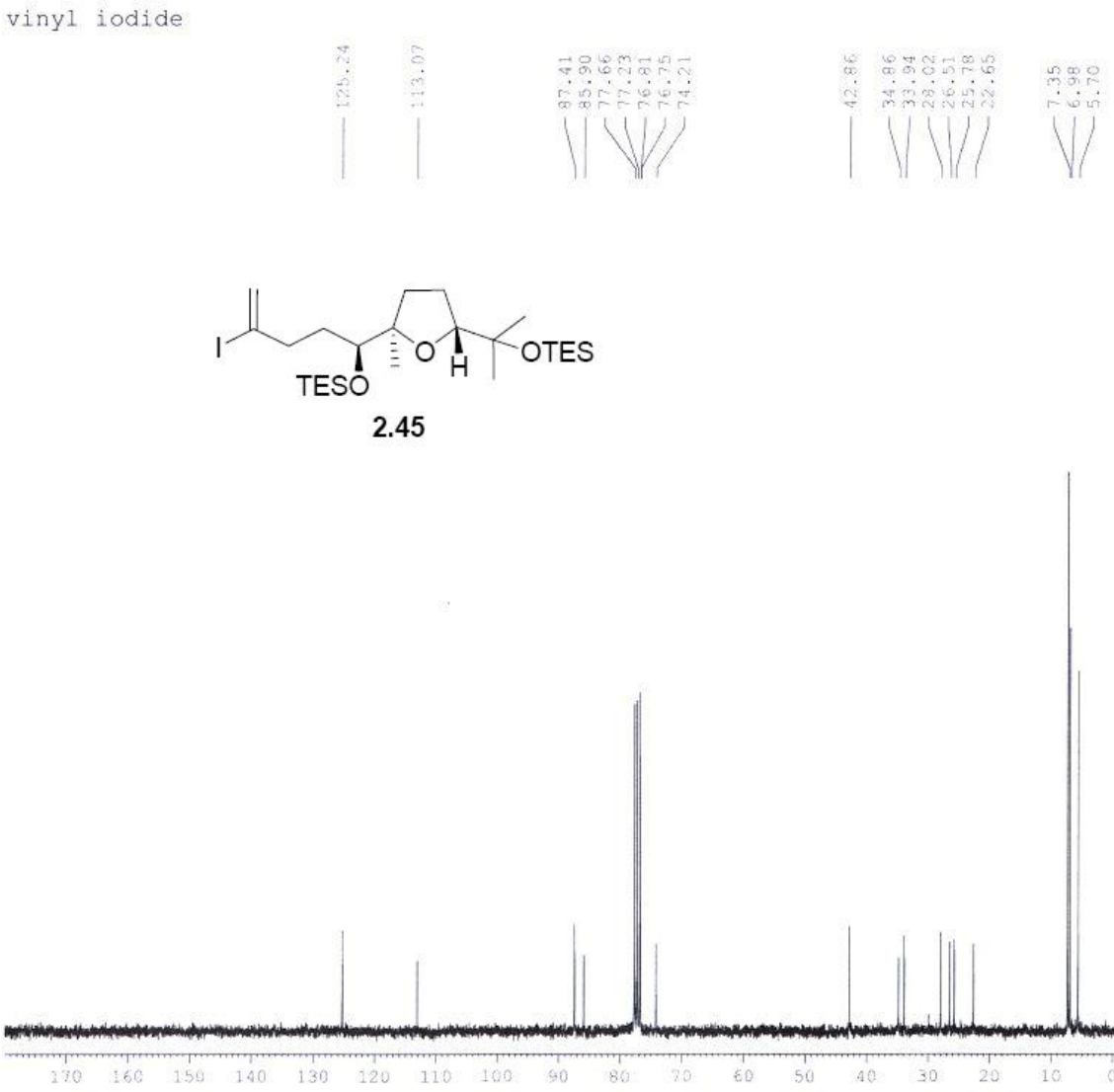
======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                1H
PCPD2          100.00 usec
PL2              0.00 dB
PL12            18.24 dB
PL13            18.24 dB
SFO2       300.0862003 MHz

F2 - Processing parameters
SI                32768
SF         75.4564161 MHz
WDW                EM
SSB                 0
LB               1.00 Hz
GB                  0
PC                1.40
```


vinyl stannane
7.2704
5.6998
5.6971
5.0987
5.0937
1.5457
1.5389
1.5314
1.5171
1.5091
1.5055
1.5011
1.4941
1.4904
1.4855
1.4804
1.4694
1.3599
1.3547
1.3452
1.3305
1.3158
1.3012
1.1934
1.1738
1.0831
1.0087
0.9938
0.9779
0.9720
0.9621
0.9561
0.9403
0.9154
0.9006
0.8857
0.6579
0.6422
0.6342
0.6264
0.6099
0.5940
0.5783
0.5625
Bu3Sn
TESO
O
H
OTES
B14
9
8
7
6
5
4
3
2
1
ppm
1.07
1.00
1.07
0.99
0.95
1.10
1.18
1.20
1.09
1.08
16.00
3.22
2.98
3.41
33.82
12.96
BRUKER
Current Data Parameters
NAME Sw02040801
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080204
Time 11.35
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zg
TD 65536
SOLVENT CDCl3
NS 6
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 57
DW 48.400 usec
DE 6.00 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.00 usec
PL1 0.00 dB
SFO1 500.1330885 MHz
F2 - Processing parameters
SI 32768
SF 500.1300079 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


vinyl iodide
7.2709
6.0437
6.0392
5.6946
5.6919
3.6602
3.6401
3.6307
3.5604
3.5466
3.5354
3.5216
2.5156
1.9360
1.9182
1.9030
1.8842
1.8749
1.8687
1.8443
1.8373
1.8228
1.8102
1.8033
1.5776
1.5710
1.5561
1.5453
1.2644
1.1915
1.1724
1.1030
1.0050
0.9789
0.9660
0.9553
0.9298
0.6703
0.6448
0.6233
0.6184
0.5982
0.5718
0.5452
I
TESO
O
H
OTES
2.45
9
8
7
6
5
4
3
2
1
ppm
0.88
0.85
1.00
0.99
1.89
4.27
2.45
3.08
3.08
3.14
18.57
12.70
BRUKER
Current Data Parameters
NAME SW02040802
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080204
Time 16.42
INSTRUM spect
PROBHD 5 mm Dual 13C/
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 7
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 256
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 5.00 usec
PL1 4.00 dB
SFO1 300.1318530 MHz
F2 - Processing parameters
SI 16384
SF 300.1300032 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

vinyl iodide



BRUKER

Current Data Parameters
NAME SW02130801
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20080213
Time 13.04
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 91
DS 2
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 13004
DW 27.800 usec
DE 6.00 usec
TE 292.7 K
D1 10.00000000 sec
d11 0.03000000 sec
DELTA 9.89999962 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 7.00 usec
PL1 0.00 dB
SFO1 75.4639789 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 0.00 dB
PL12 18.24 dB
PL13 18.24 dB
SFO2 300.0862003 MHz

F2 - Processing parameters
SI 32768
SF 75.4564179 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

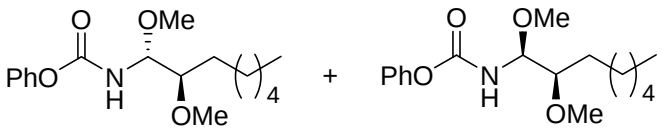
APPENDIX C

MULTICOMPONENT APPROACH TO THE SYNTHESIS OF OXIDIZED AMIDES THROUGH NITRILE HYDROZIRCONATION (SUPPORTING INFORMATION)

General Experimental Proton (^{1}H NMR) and carbon (^{13}C NMR) nuclear magnetic resonance spectra were recorded at ambient temperature on Bruker Avance 300 spectrometer at 300 MHz and 75 MHz or Bruker Avance 500 spectrometer at 500 MHz and 125 MHz if specified. The chemical shifts are given in parts per million (ppm) on the delta (δ) scale. The solvent peak was used as a reference value, for ^{1}H NMR: $CDCl_3$ = 7.27 ppm, CD_3OD = 3.31, for ^{13}C NMR: $CDCl_3$ = 77.23, CD_3OD = 49.00. Data are reported as follows: (s = singlet; d = doublet; t = triplet; q = quartet; sept = septet; sext = sextet; dd = doublet of doublets; ddd = doublet of doublet of doublets; dt = doublet of triplets; td = triplet of doublets; dtd = doublet of triplet of doublets; br = broad; app = apparently). High resolution mass spectra were recorded on a MICROMASS AUTOSPEC (for EI) or WATERS Q-TOF API-US (for ESI) spectrometer. Infrared (IR) spectra were collected on a Mattson Cygnus 100 spectrometer. Samples for IR were prepared as a thin film on a NaCl plate by dissolving the compound in CH_2Cl_2 and then evaporating the CH_2Cl_2. Optical rotations were measured on a Perkin-Elmer 241 polarimeter at ambient temperature. Tetrahydrofuran and diethyl ether were distilled from sodium and benzophenone. Methylene

chloride and benzene was distilled under N_2 from CaH_2. Anhydrous CH_2Cl_2 was obtained through distillation from CaH_2. PhOCOCl, ^{i}PrCOCl, $MeOCH_2COCl$, CbzCl, PhSH, Et_3N, and BF_3•OEt_2 were distilled prior to use. MeOH and ^{t}BuOH were distilled from Mg and stored over 4 Å molecular sieves prior to use. PhOH was azeotroped with toluene and dried under high vacuum before use. Methanesulfonic anhydride was purchased from Aldrich and used without further purification. Anhydrous $Mg(ClO_4)_2$ and $Zn(OTf)_2$ were purchased from Aldrich and Fluka, respectively, stored in dessicator, and used as received. Analytical TLC was performed on E. Merck pre-coated (25 mm) silica gel 60F-254 plates. Visualization was done under UV (254 nm). Flash chromatography was done using ICN SiliTech 32-63 60 Å silica gel. Reagent grade ethyl acetate, diethyl ether and hexanes (commercial mixture) were purchased from EM Science and used as is for chromatography. All reactions were performed in oven or flame-dried glassware under Ar with magnetic stirring unless otherwise noted. Schwartz' reagent, though commercially available, was prepared according to the literature.[112] All the compounds in this work were prepared in their racemic form unless otherwise noted.

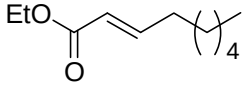
Phenyl (1*R*,2*R*)-1,2-dimethoxyoctylcarbamate (3.2) and **phenyl (1*S*,2*R*)-1,2-dimethoxy-octylcarbamate (3.3)**



A solution of 2-methoxyoctanenitrile **3.1** (70.0 mg, 0.451 mmol) in CH_2Cl_2 (43.5 mL) was treated with $Cp_2Zr(H)Cl$ (140 mg, 0.541 mmol). The reaction was stirred for 15 min, then cooled to 0 °C and phenyl chloroformate (79 μL, 0.631 mmol) was added dropwise. The cold bath was removed and the mixture was stirred for 10 min. After that time, the flask was cooled to 0 °C and phenyl chloroformate (56 μL, 0.451 mmol) was added. The mixture was

stirred at room temperature for 15 min and then cooled to 0 °C. A solution of MeOH (0.36 ml, 9.02 mmol) in CH_2Cl_2 (0.6 mL) was added dropwise. The reaction was stirred for 15 min at 0 °C and then quenched with saturated $NaHCO_3$ (25 mL). The mixture was extracted with CH_2Cl_2 (4 x 20 mL) and the combined organic extracts were dried (Na_2SO_4) and concentrated. The residue was purified by column chromatography (6% - 120% EtOAc in hexanes containing 0.5% Et_3N) to give the desired product (77.2 mg, 55.3%) as a colorless oil in a 2.4:1.0 diastereomeric ratio. Further purification by column chromatography (8% - 14% EtOAc in hexanes containing 0.5% Et_3N) yielded analytically pure samples. For faster eluting *anti*-product **3.2**: ^{1}H NMR (300 MHz, $CDCl_3$) 7.38 (app t, *J* = 7.7 Hz, 2H), 7.24-7.12 (m, 3H), 5.90 (d, *J* = 9.8 Hz, 1H), 4.88 (d, *J* = 10.0 Hz, 1H), 3.59-3.49 (m, 1H), 3.52 (s, 3H), 3.44 (s, 3H), 1.55-1.27 (m, 10H), 0.90 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 155.2, 151.0, 129.5, 125.6, 121.7, 85.6, 82.4, 59.7, 56.0, 31.9, 31.4, 29.5, 25.6, 22.8, 14.3; IR (neat) 3322, 2930, 2857, 1747, 1515, 1487, 1334, 1206, 1103, 1025, 952, 738; HRMS (ESI): *m*/*z* calcd for $C_{17}H_{27}NO_4Na$ $[M+Na]^+$ 332.1838, found 332.1830. For slower eluting *syn*-product **3.3**: ^{1}H NMR (300 MHz, $CDCl_3$) 7.40-7.34 (m, 2H), 7.29-7.22 (m, 3H), 5.82 (d, *J* = 9.7 Hz, 1H), 5.00 (dd, *J* = 10.0, 2.9 Hz, 1H), 3.41 (s, 3H), 3.40 (s, 3H), 3.18 (dt, *J* = 6.8, 2.9 Hz, 1H), 1.62-1.55 (m, 2H), 1.40-1.24 (m, 8H), 0.90 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 154.9, 151.0, 129.5, 125.7, 121.7, 82.9, 82.6, 58.4, 56.5, 31.9, 29.7, 29.0, 25.6, 22.8, 14.3; IR (neat) 3324, 2928, 2857, 1747, 1523, 1488, 1356, 1209, 1086, 954; HRMS (ESI): *m*/*z* calcd for $C_{17}H_{27}NO_4Na$ $[M+Na]^+$ 332.1838, found 332.1841.

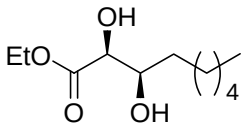
(*E*)-Ethyl non-2-enoate (3.7)



^{1}H NMR (300 MHz, $CDCl_3$) 6.97 (td, *J* = 15.6, 7.0 Hz, 1H), 5.81 (td, *J* = 15.7, 1.5 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 2.20 (qd, *J* = 7.0, 1.5 Hz, 2H),

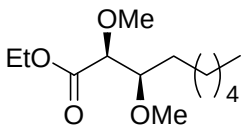
1.50-1.41 (m, 2H), 1.36-1.27 (m, 9H), 0.89 (t, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 167.0, 149.7, 121.4, 60.3, 32.4, 31.8, 29.0, 28.2, 22.8, 14.5, 14.3.

(2*S*,3*R*)-Ethyl 2,3-dihydroxynonanoate (C1)



A mixture of AD-mix-β in ^{t}BuOH/H_2O (20 mL, 1:1, v/v) at 0 °C was treated with $CH_3SO_2NH_2$ (0.190 g, 2.00 mmol) followed by a solution of enoate **3.7** (0.368 g, 2.00 mmol) in ^{t}BuOH (0.5 mL). The mixture was stirred at 0 °C for 6 h and then at room temperature for 10 h. The reaction was cooled to 0 °C and quenched with Na_2SO_3 solution (10%, 30 mL). After stirred at 0 °C for 1 h, the mixture was extracted with CH_2Cl_2 (3 x 30 mL). The organic extracts were dried ($MgSO_4$) and concentrated. The residue was purified by column chromatography (30% - 40% EtOAc in hexanes) to give the diol **C1** (0.402 g, 92.0%) as a white solid: ^{1}H NMR (300 MHz, $CDCl_3$) 4.29 (q, J = 7.1 Hz, 2H), 4.08 (dd, J = 5.3, 2.0 Hz, 1H), 3.88 (dtd, J = 8.9, 6.9, 2.1 Hz, 1H), 3.12 (d, J = 5.3 Hz, 1H), 1.98 (d, J = 9.2 Hz, 1H), 1.64-1.58 (m, 2H), 1.52-1.44 (m, 1H), 1.39-1.25 (m, 10H), 0.89 (t, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 173.9, 73.2, 72.7, 62.3, 34.0, 32.0, 29.4, 25.9, 22.8, 14.4, 14.3; IR (neat) 3377, 2925, 2854, 1737, 1462, 1294, 1136, 1099, 1072; HRMS (ESI): m/z calcd for $C_{11}H_{22}O_4Na$ $[M+Na]^+$ 241.1416, found 241.1420; $[\alpha]_D$ = +12.6 ($CHCl_3$, c 0.98).

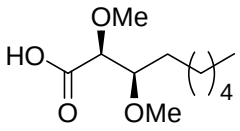
(2*S*,3*R*)-Ethyl 2,3-dimethoxynonanoate (C2)



A solution of the diol **C1** (170.0 mg, 0.779 mmol) in CH_2Cl_2 (4.0 mL) were treated with Ag_2O (271 mg, 1.17 mmol) and MeI (0.22 mL, 3.50 mmol). The reaction was refluxed for 10 h, and Ag_2O (271 mg, 1.17 mmol) and MeI (0.22 mL, 3.50 mmol) were added sequentially. After 12 h, Ag_2O (271 mg, 1.17 mmol) and MeI (0.22 mL, 3.50

mmol) were added. The mixture was refluxed for another 6 h, then filter through Celite and the residue was washed with CH_2Cl_2 (30 mL). The combined filtrate was concentrated and the resulting residue was purified by column chromatography (5% - 15% EtOAc in hexanes) to give the desired product **C2** (59.4 mg, 31.0%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) 4.32-4.21 (m, 2H), 3.78 (d, *J* = 4.1 Hz, 1H), 3.51 (dt, *J* = 6.5, 4.1 Hz, 1H), 3.44 (s, 3H), 3.39 (s, 3H), 1.61-1.54 (m, 2H), 1.34-1.26 (m, 11H), 0.89 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 171.4, 82.7, 82.0, 61.1, 59.2, 58.6, 32.0, 30.1, 29.6, 25.8, 22.8, 14.5, 14.3; IR (neat) 2927, 1747, 1464, 1261, 1190, 1143, 1105, 1031; HRMS (ESI): *m*/*z* calcd for $C_{13}H_{26}O_4Na$ $[M+Na]^+$ 269.1729, found 269.1713; $[\alpha]_D$ = -29.7 ($CHCl_3$, *c* 0.63).

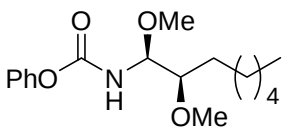
(2*S*,3*R*)-2,3-Dimethoxynonanoic acid (3.8)



A solution of the ethyl ester **C2** (40.0 mg, 0.162 mmol) in 1,2-dimethoxyethane/H_2O (2.8 mL, 4:1, v/v) was treated with LiOH·H_2O (13.6 mg, 0.324 mmol). After 3 and 4 h, LiOH·H_2O (6.8 mg, 0.162 mmol) was added, respectively. The reaction was stirred for another 3 h, then quenched with HCl (0.5 N, ~1.0 mL) to pH~1.5 and extracted with Et_2O (5 x 10 mL). The combined organic extracts were dried (Na_2SO_4) and concentrated. The residue was purified by column chromatography (30% EtOAc in hexanes followed by 50% MeOH in EtOAc) to give the unreacted ester (7.6 mg, 19.0%) and carboxylic acid **3.8** (28.1 mg, 79.4%) as a white sticky solid: ^{1}H NMR (300 MHz, CD_3OD) 3.66 (d, *J* = 3.0 Hz, 1H), 3.54 (dt, *J* = 6.7, 3.1 Hz, 1H), 3.42 (s, 3H), 3.41 (s, 3H), 1.69-1.57 (m, 2H), 1.46-1.29 (m, 8H), 0.91 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, CD_3OD) 178.2, 84.9, 83.9, 59.4, 58.9, 32.9, 31.2, 30.5, 26.8, 23.7, 14.4; IR (neat) 3401, 2926, 2856, 1618, 1418,

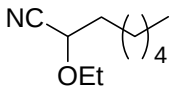
1194, 1091; HRMS (ESI): *m/z* calcd for $C_{11}H_{22}O_4Na$ $[M+Na]^+$ 241.1416, found 241.1407; $[\alpha]_D$ = -26.0 (CH_3OH, *c* 0.77).

Phenyl (1*S*,2*R*)-1,2-dimethoxyoctylcarbamate ((-)-3.3)



A stirred solution of the carboxylic acid **3.8** (15.4 mg, 70.5 μmol) in benzene (2.0 mL) was treated with Et_3N (0.12 ml, 0.846 mmol) and diphenyl phosphoryl azide (61 μL, 0.282 mmol). After 2 h, diphenylphosphoryl azide (30 μL, 0.140 mmol) was added. The reaction was stirred for 2 h, then quenched with water (10 mL) and extracted with Et_2O (3 x 20 mL). The organic extracts were dried (Na_2SO_4) and concentrated. The residue was purified by column chromatography (5% - 15% EtOAc in hexanes) to give the carbamate **(-)-3.3** (11.4 mg, 52.3%) as a colorless oil: $[\alpha]_D$ = -3.8 ($CHCl_3$, *c* 0.52). No other diastereomer was observed.

2-Ethoxyoctanenitrile (3.11)



A mixture of heptanal (4.00 g, 35.0 mmol), absolute EtOH (80 ml), $(EtO)_3CH$ (5.8 mL, 35.0 mmol) and the activated 4Å molecular sieves (4.00 g) at 0 °C was treated dropwise with concentrated H_2SO_4 (2.0 ml) and the mixture was stirred at room temperature overnight. After that time, the reaction mixture was concentrated to ~30 mL and slowly poured onto a cold saturated $NaHCO_3$ solution (80 mL) at 0 °C. The resulting mixture was filtered through Celite. The filtrate was extracted with CH_2Cl_2 (3 x 80mL) and the extracts were dried (Na_2SO_4) and concentrated. The resulting residue was dissolved in CH_2Cl_2 (70 mL), and $BiBr_3$ (1.57 g, 3.50 mmol) and TMSCN (5.60 ml, 42.0 mmol) were added sequentially. The reaction was stirred overnight, then quenched with saturated $NaHCO_3$ solution (50 mL)/water

(20 mL) and extracted with CH_2Cl_2 (3 x 100mL). The combined extracts were dried (Na_2SO_4) and concentrated. The residue was purified by column chromatography (2% - 5% EtOAc in hexanes) to give the ethoxy nitrile **3.11** (4.51 g, 76.0%) as a colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) 4.11 (t, *J* = 6.6 Hz, 1H), 3.82 (qd, *J* = 8.8, 6.9 Hz, 1H), 3.51 (qd, *J* = 8.9, 7.0 Hz, 1H), 1.87-1.80 (m, 2H), 1.52-1.44 (m, 2H), 1.38-1.30 (m, 6H), 1.26 (t, *J* = 7.0 Hz, 3H), 0.89 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 118.9, 69.0, 66.4, 33.8, 31.7, 28.9, 24.9, 22.7, 15.0, 14.2; IR (neat) 2957, 2930, 2860, 1468, 1335, 1126, 1108, 735; HRMS (EI): *m*/*z* calcd for $C_{10}H_{19}NO$ ($M^{+\bullet}$) 169.1467, found 169.1474.

Representative procedure for the preparation of acyl aminals:

***N*-((1*R*,2*R*)-2-Ethoxy-1-methoxyoctyl)isobutyramide (3.12)** and ***N*-((1*S*,2*R*)-2-ethoxy-1-methoxyoctyl)isobutyramide (3.13)**

A solution of ethoxynitrile **3.11** (100.0 mg, 0.591 mmol) in CH_2Cl_2 (4.5 mL) was treated with $Cp_2Zr(H)Cl$ (229 mg, 0.886 mmol). The reaction was stirred for 15 min, then cooled to 0 °C and isobutyryl chloride (94 μL, 0.886 mmol) was added dropwise. The mixture was stirred for 15 min at 0 °C and MeOH (1.0 mL, 23.6 mmol) was added dropwise. The reaction was stirred for 15 min at 0 °C and quenched with AcOH (2.0 mL)/water (20 mL). The mixture was extracted with CH_2Cl_2 (3 x 25 mL) and the combined organic extracts were washed with saturated $NaHCO_3$ (15 mL), dried (Na_2SO_4) and concentrated. The residue was purified by column chromatography (15% - 30% EtOAc in hexanes) to give the desired product (121.3 mg, 75.1%) as a white solid in a 2.3:1.0 diastereomeric ratio. Further purification (15% - 30% EtOAc in hexanes) yielded analytically

pure samples. For faster eluting *anti*-product **3.12**: ^{1}H NMR (300 MHz, $CDCl_3$) 6.20 (d, J = 9.5 Hz, 1H), 5.01 (dd, J = 9.7, 1.4 Hz, 1H), 3.74 (qd, J = 9.4, 7.0 Hz, 1H), 3.54 (qd, 9.4, 7.1 Hz, 1H), 3.47-3.43 (m, 1H), 3.29 (s, 3H), 2.40 (sept, J = 6.9 Hz, 1H), 1.37-1.23 (m, 10H), 1.18-1.14 (m, 9H), 0.84 (app t, J = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 177.9, 82.6, 80.6, 67.3, 55.8, 36.1, 31.9, 31.8, 29.4, 25.6, 22.7, 19.8, 19.7, 15.8, 14.2; IR (neat) 3271, 2965, 2920, 1653, 1540, 1467, 1233, 1113, 1101; HRMS (EI): *m*/*z* calcd for $C_{14}H_{28}NO_2$ $(M\text{-}CH_3O)^{+\bullet}$ 242.2120, found 242.2123. For slower eluting *syn*-product **3.13**: ^{1}H NMR (300 MHz, $CDCl_3$) 6.20 (d, J = 9.7 Hz, 1H), 5.17 (dd, J = 9.8, 2.9 Hz, 1H), 3.66 (qd, J = 9.4, 7.0 Hz, 1H), 3.46 (qd, J = 9.3, 7.0 Hz, 1H), 3.36 (s, 3H), 3.24 (dt, J = 6.8, 2.9 Hz, 1H), 2.42 (sept, J = 6.9 Hz, 1H), 1.63-1.55 (m, 2H), 1.40-1.25 (m, 10H), 1.23-1.17 (m, 9H), 0.88 (t, J = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 177.5, 81.0, 80.0, 66.1, 56.4, 36.2, 31.9, 29.8, 29.7, 25.6, 22.8, 19.9, 19.7, 15.8, 14.2; IR (neat) 3273, 2971, 2921, 1651, 1538, 1467, 1154, 1103, 1072; HRMS (EI): *m*/*z* calcd for $C_{14}H_{28}NO_2$ $(M\text{-}CH_3O)^{+\bullet}$ 242.2120, found 242.2119.

***N*-((1*R*,2*R*)-2-Ethoxy-1-methoxyoctyl)-2-methoxyacetamide (3.14)** and ***N*-((1*S*,2*R*)-2-ethoxy-1-methoxyoctyl)-2-methoxyacetamide (3.15)**

The title compounds were prepared by following the representative procedure with the following amounts of reagents: ethoxynitrile **3.11** (100.0 mg, 0.591 mmol), CH_2Cl_2 (4.5 mL), $Cp_2Zr(H)Cl$ (168 mg, 0.650 mmol), methoxyacetyl chloride (65 µL, 0.709 mmol) MeOH (1.0 ml, 23.6 mmol). The reaction was quenched with 1 N HCl (2.0 mL)/water (15 mL) and extracted with CH_2Cl_2 (3 x 25 mL). The combined organic extracts were washed with saturated $NaHCO_3$ (15 mL), dried (Na_2SO_4) and concentrated. The residue was

purified by column chromatography (20% - 40% EtOAc in hexanes) to give the desired product (111.8 mg, 68.7%) as a colorless oil in a 1.7:1.0 diastereomeric ratio. Further purification (20% - 40% EtOAc in hexanes) yielded analytically pure samples. For the faster eluting *anti*-product **3.14**: ^{1}H NMR (300 MHz, $CDCl_3$) 7.18 (d, J = 9.8 Hz, 1H), 5.06 (dd, J = 10.0, 1.5 Hz, 1H), 3.98 (d, J = 15.2 Hz, 1H), 3.90 (d, J = 15.2 Hz, 1H), 3.76 (qd, J = 9.4, 7.0 Hz, 1H), 3.56 (qd, J = 9.3, 7.0 Hz, 1H), 3.49-3.45 (m, 1H), 3.43 (s, 3H), 3.33 (s, 3H), 1.45-1.25 (m, 10H), 1.18 (t, J = 7.0 Hz, 3H), 0.86 (t, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 170.8, 82.4, 80.5, 72.0, 67.3, 59.4, 56.1, 31.9, 31.8, 29.4, 25.7, 22.8, 15.8, 14.2; IR (neat) 3413, 2930, 2858, 1695, 1506, 1113; HRMS (EI): *m*/*z* calcd for $C_{13}H_{26}NO_3$ $(M\text{-}CH_3O)^{+\bullet}$ 244.1913, found 244.1925. For the slower eluting *syn*-product **3.15**: ^{1}H NMR (300 MHz, $CDCl_3$) 7.22 (d, J = 10.0 Hz, 1H), 5.18 (dd, J = 10.1, 3.0 Hz, 1H), 3.98 (d, J = 15.3 Hz, 1H), 3.92 (d, J = 15.3 Hz, 1H), 3.66 (qd, J = 9.2, 7.0 Hz, 1H), 3.50 (qd, J = 9.2, 7.0 Hz, 1H), 3.43 (s, 3H), 3.36 (s, 3H), 3.26 (dt, J = 6.8, 3.0 Hz, 1H), 1.63-1.55 (m, 2H), 1.41-1.29 (m, 8H), 1.21 (t, J = 7.0 Hz, 3H), 0.88 (t, J = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 170.4, 81.0, 79.8, 72.0, 66.5, 59.4, 56.5, 31.9, 29.9, 29.6, 25.7, 22.8, 15.7, 14.3; IR (neat) 3417, 2928, 2858, 1686, 1510, 1112, 1078; HRMS (EI): *m*/*z* calcd for $C_{13}H_{26}NO_3$ $(M\text{-}CH_3O)^{+\bullet}$ 244.1913, found 244.1917.

Benzyl (1*R*,2*R*)-2-ethoxy-1-methoxyoctylcarbamate (3.16) and **benzyl (1*S*,2*R*)-2-ethoxy-1-methoxyoctylcarbamate (3.17)**

The title compounds were prepared by following the representative procedure with the following amounts of reagents: ethoxynitrile **3.11** (60.0 mg, 0.354 mmol), CH_2Cl_2 (3.5 mL), $Cp_2Zr(H)Cl$ (110.0 mg, 0.425 mmol). After completion of hydrozirconation,

the reaction mixture was cooled to 0 °C and benzyl chloroformate (71 μL, 0.500 mmol) was added dropwise. The cold bath was removed and the mixture was stirred for 10 min. After that time, the flask was cooled to 0 °C and benzyl chloroformate (50 μL, 0.354 mmol) was added. The mixture was stirred at room temperature for 30 min and then cooled to 0 °C. A solution of MeOH (0.28 ml, 7.08 mmol) in CH_2Cl_2 (0.5 mL) was added dropwise. The reaction was stirred for 10 min at 0 °C and then quenched with saturated $NaHCO_3$ (20 mL). The mixture was extracted with CH_2Cl_2 (3 x 20 mL) and the combined organic extracts were dried (Na_2SO_4) and concentrated. The residue was purified by column chromatography (5% - 20% EtOAc in hexanes containing 0.5% Et_3N) to give the desired product (76.3 mg, 63.8%) as a colorless oil in a 1.5:1.0 diastereomeric ratio. Further purification (10% - 13% EtOAc in hexanes containing 0.5% Et_3N) yielded analytically pure materials. For faster eluting *anti*-product **3.16**: ^{1}H NMR (300 MHz, $CDCl_3$) 7.39-7.30 (m, 5H), 5.66 (d, *J* = 9.8 Hz, 1H), 5.14 (s, 2H), 4.82 (dd, *J* = 9.9, 1.0 Hz, 1H), 3.74 (qd, *J* = 9.3, 7.0 Hz, 1H), 3.56 (qd, *J* = 9.2, 7.0 Hz, 1H), 3.48-3.44 (m, 1H), 3.37 (s, 3H), 1.46-1.28 (m, 10H), 1.17 (t, *J* = 7.0 Hz, 3H), 0.89 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 156.8, 136.6, 128.7, 128.4, 128.2, 85.6, 80.6, 67.4, 67.1, 55.7, 31.9, 29.5, 25.7, 22.8, 15.9, 14.3; IR (neat) 3337, 2929, 2858, 1731, 1497, 1456, 1326, 1216, 1107, 966, 735; HRMS (ESI): *m*/*z* calcd for $C_{19}H_{31}NO_4Na$ $[M+Na]^+$ 360.2151, found 360.2148. For slower eluting *syn*-product **3.17**: ^{1}H NMR (300 MHz, $CDCl_3$) 7.40-7.31 (m, 5H), 5.54 (d, *J* = 10.0 Hz, 1H), 5.15/5.14 (two s, 2H), 4.94 (dd, *J* = 10.1, 2.9 Hz, 1H), 3.64 (qd, *J* = 9.2, 7.0 Hz, 1H), 3.48 (qd, *J* = 9.2, 7.0 Hz, 1H), 3.38 (s, 3H), 3.28 (dt, *J* = 6.8, 2.9 Hz, 1H), 1.63-1.52 (m, 2H), 1.41-1.26 (m, 8H), 1.20 (t, *J* = 7.0 Hz, 3H), 0.89 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 156.6, 136.5, 128.8, 128.5, 128.4, 82.9, 81.1, 77.4, 67.2, 66.2, 56.3, 31.9, 29.7, 29.6, 25.7, 22.8, 15.8, 14.3; IR

(neat) 3334, 2928, 2858, 1729, 1501, 1455, 1232, 1097, 737; HRMS (ESI): *m*/*z* calcd for $C_{19}H_{31}NO_4Na$ $[M+Na]^+$ 360.2151, found 360.2149.

***N*-(2-Ethoxy-1-methoxyoctyl)methanesulfonamide (3.18** and **3.19)**

The title compounds were prepared by following the representative procedure with the following amounts of reagents: ethoxynitrile **3.11** (100.0 mg, 0.591 mmol), CH_2Cl_2 (4.5 mL), $Cp_2Zr(H)Cl$ (228 mg, 0.886 mmol). After addition of methanesulfonic anhydride (144 mg, 0.827 mmol), The mixture was stirred for 2 min at 0 °C and MeOH (1.0 mL, 23.6 mmol) was added dropwise. The reaction was stirred for 10 min at 0 °C and quenched with saturated $NaHCO_3$ (15 mL). The mixture was extracted with CH_2Cl_2 (3 x 20 mL) and the combined organic extracts were dried (Na_2SO_4) and concentrated. The residue was purified by column chromatography (20% - 30% EtOAc in hexanes) to give the desired product (40.8 mg, 24.5%) as a colorless oil in a 2.4:1.0 diastereomeric ratio: ^{1}H NMR (300 MHz, $CDCl_3$) 5.42 (d, *J* = 9.4 Hz, 71% of 1H), 5.22 (d, *J* = 9.5 Hz, 29% of 1H), 4.64 (dd, *J* = 9.5, 3.1 Hz, 29% of 1H), 4.48 (dd, *J* = 9.4, 2.4 Hz, 71% of 1H), 3.72-3.52 (m, 2H), 3.45 (s, 29% of 3H), 3.46-3.42 (m, 71% of 1H), 3.40 (s, 71% of 3H), 3.32 (ddd, *J* = 7.2, 5.6, 3.1 Hz, 29% of 1H), 3.06 (s, 29% of 3H), 3.05 (s, 71% of 3H), 1.56-1.25 (m, 10H), 1.21 (t, *J* = 6.9 Hz, 29% of 3H), 1.18 (t, *J* = 7.0 Hz, 71% of 3H), 0.88 (app t, *J* = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 88.1 (major), 86.0 (minor), 81.2 (minor), 79.5 (major), 67.2 (major), 66.4 (minor), 56.5, (minor), 55.7 (major), 43.3 (major), 43.2 (minor), 31.9, 31.6 (major), 29.6 (minor), 29.5 (major), 29.3 (minor), 25.8 (minor), 25.4 (major), 22.8, 15.8 (major), 15.7 (minor), 14.2; IR (neat) 3286, 2926, 2858, 1458, 1328, 1161, 1110, 978, 766; HRMS (EI): *m*/*z* calcd for $C_{11}H_{24}NO_3S$ $(M-CH_3O)^{+\bullet}$ 250.1477, found 250.1466.

***N*-((1*R*,2*R*)-2-Ethoxy-1-*tert*-butoxyoctyl)isobutyramide (3.21)** and ***N*-((1*S*,2*R*)-2-ethoxy-1-*tert*-butoxyoctyl)isobutyramide (3.22)**

The title compounds were prepared by following the representative procedure with the following amounts of reagents: ethoxynitrile **3.11** (60.0 mg, 0.354 mmol), CH_2Cl_2 (3.5 mL), $Cp_2Zr(H)Cl$ (110.0 mg, 0.425 mmol). After addition of isobutyryl chloride (52 μL, 0.500 mmol), the cold bath was removed and the mixture was stirred for 10 min. After that time, the flask was cooled to 0 °C and a solution of ^{t}BuOH (0.67 ml, 7.08 mmol) in CH_2Cl_2 (0.5 mL) was added dropwise to the reaction mixture over 3 min. The reaction was stirred for 10 min at 0 °C, then diluted with CH_2Cl_2 (10 mL) and quenched with saturated $NaHCO_3$ (20 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3 x 15 mL). The combined organic extracts were dried (Na_2SO_4) and concentrated. The residue was purified by column chromatography (10% - 20% EtOAc in hexanes containing 0.5% Et_3N) to give the desired product (79.2 mg, 70.8%) as a white solid in a 1.0:2.0 diastereomeric ratio. Further purification (12% - 18% EtOAc in hexanes containing 0.5% Et_3N) yielded analytically pure samples. For faster eluting *anti*-product **3.21**: ^{1}H NMR (300 MHz, $CDCl_3$) 6.10 (d, J = 9.2 Hz, 1H), 5.32 (dd, J = 9.4, 2.0 Hz, 1H), 3.84 (qd, J = 9.6, 7.1 Hz, 1H), 3.58 (qd, J = 9.6, 7.0 Hz, 1H), 3.30-3.26 (m, 1H), 2.33 (sept, J = 6.9 Hz, 1H), 1.38-1.27 (m, 10H), 1.22 (s, 9H), 1.19-1.12 (m, 9H), 0.87 (t, J = 6.8 Hz, 3H), ^{13}C NMR (75 MHz, $CDCl_3$) 175.8, 83.0, 75.5, 74.6, 67.6, 36.1, 32.0, 31.6, 29.5, 28.6, 25.9, 22.8, 19.7, 19.4, 15.9, 14.3; IR (neat) 3246, 2969, 2922, 2858, 1648, 1552, 1466, 1109, 1069; HRMS (ESI): *m*/*z* calcd for $C_{18}H_{37}NO_3Na$ $[M+Na]^+$ 338.2671, found 338.2663. For slower eluting *syn*-product **3.22**: ^{1}H NMR (300 MHz, $CDCl_3$) 6.00 (d, J = 9.2 Hz,

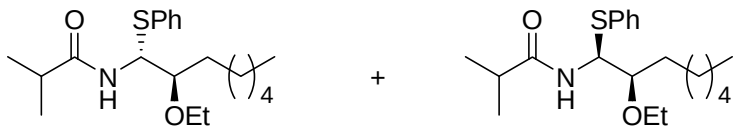
1H), 5.39 (dd, *J* = 9.4, 4.0 Hz, 1H), 3.64-3.54 (m, 2H), 3.14-3.09 (m, 1H), 2.30 (sept, *J* = 6.9 Hz, 1H), 1.51-1.38 (m, 2H), 1.35-1.24 (m, 8H), 1.20 (s, 9H), 1.19-1.11 (m, 9H), 0.87 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 175.3, 82.1, 74.9, 74.3, 66.8, 36.1, 32.0, 30.2, 29.6, 28.5, 26.0, 22.8, 19.5, 19.4, 15.8, 14.3; IR (neat) 3254, 2960, 2920, 2856, 1646, 1544, 1459, 1365, 1193, 1109, 1072, 731; HRMS (ESI): *m*/*z* calcd for $C_{18}H_{37}NO_3Na$ $[M+Na]^+$ 338.2671, found 338.2666.

_N_-((1_R_,2_R_)-2-Ethoxy-1-phenoxyoctyl)isobutyramide (3.23) and **_N_-((1_S_,2_R_)-2-ethoxy-1-phenoxyoctyl)isobutyramide (3.24)**

The title compounds were prepared by following the representative procedure with the following amounts of reagents: ethoxynitrile **3.11** (60.0 mg, 0.354 mmol), CH_2Cl_2 (3.5 mL), $Cp_2Zr(H)Cl$ (110.0 mg, 0.425 mmol). After addition of isobutyryl chloride (52 μL, 0.500 mmol), the cold bath was removed and the mixture was stirred for 10 min. The mixture was cooled to °C and a solution of PhOH (333 mg, 3.54 mmol) in CH_2Cl_2 (0.5 mL) was added dropwise. The reaction was stirred at °C for 40 min, then quenched with saturated $NaHCO_3$ solution (20 mL) and extracted with CH_2Cl_2 (4 x 15 mL). The organic extracts were washed with saturated Na_2CO_3 solution (20 mL), dried (Na_2SO_4) and concentrated. The residue was purified by column chromatography (7% - 10% EtOAc in hexanes containing 0.5% Et_3N) to give the desired product (81.7 mg, 68.7%) as a white solid in a 5.6:1.0 diastereomeric ratio. Further purification (7% - 10% EtOAc in hexanes containing 0.5% Et_3N) yielded analytically pure samples. For faster eluting *anti*-product **3.23**: ^{1}H NMR (300 MHz, $CDCl_3$) 7.30-7.23 (m, 2H), 7.03 (app td, *J* = 7.8, 1.0 Hz, 2H), 6.96 (app tt, *J* = 7.3, 0.9 Hz, 1H), 6.36 (d, *J* = 9.9 Hz, 1H), 5.92 (dd, *J* = 9.9, 1.4 Hz,

1H), 3.96 (qd, *J* = 9.4, 7.0 Hz, 1H), 3.72 (qd, *J* = 9.5, 7.0 Hz, 1H), 3.68-3.64 (m, 1H), 2.37 (sept, *J* = 6.9 Hz, 1H), 1.47-1.37 (m, 4H), 1.33-1.24 (m, 9H), 1.15 (d, *J* = 6.9 Hz, 3H), 1.08 (d, *J* = 6.9 Hz, 3H), 0.88 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 177.1, 156.4, 129.7, 121.8, 116.5, 80.7, 80.0, 68.1, 36.0, 31.9, 29.4, 25.7, 22.8, 19.6, 19.5, 16.0, 14.2; IR (neat) 3290, 2964, 2929, 2859, 1657, 1595, 1534, 1495, 1222, 1107, 753; HRMS (ESI): *m*/*z* calcd for $C_{20}H_{33}NO_3Na$ $[M+Na]^+$ 358.2358, found 358.2359. For slower eluting *syn*-product **3.24** (containing trace amount of unknown impurity): ^{1}H NMR (300 MHz, $CDCl_3$) 7.30-7.24 (m, 2H), 7.07-7.04 (m, 2H), 6.97 (app tt, *J* = 7.3, 0.9 Hz, 1H), 6.24 (d, *J* = 9.8 Hz, 1H), 6.02 (dd, *J* = 9.8, 3.4 Hz, 1H), 3.72 (qd, *J* = 9.4, 7.0 Hz, 1H), 3.62 (qd, *J* = 9.4, 7.0 Hz, 1H), 3.44 (dt, *J* = 7.0, 3.3 Hz, 1H), 2.36 (sept, *J* = 6.9 Hz, 1H), 1.71-1.62 (m, 2H), 1.47-1.21 (m, 11H), 1.15 (d, *J* = 6.9 Hz, 3H), 1.10 (d, *J* = 6.9 Hz, 3H), 0.87 (app t, *J* = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 176.5, 156.8, 129.7, 121.9, 116.2, 81.2, 77.8, 66.8, 36.0, 31.9, 30.1, 29.6, 25.7, 22.8, 19.6, 19.5, 15.9, 14.3; IR (neat) 3288, 2963, 2926, 2857, 1653, 1535, 1495, 1220, 1109, 1042, 752; HRMS (ESI): *m*/*z* calcd for $C_{20}H_{33}NO_3Na$ $[M+Na]^+$ 358.2358, found 358.2328.

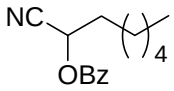
_N_-((1_R_,2_R_)-2-Ethoxy-1-(phenylthio)octyl)isobutyramide (3.25) and **_N_-((1_S_,2_R_)-2-ethoxy-1-(phenylthio)octyl)isobutyramide (3.26)**



The title compounds were prepared by following the representative procedure with the following amounts of reagents: ethoxynitrile **3.11** (60.0 mg, 0.354 mmol), CH_2Cl_2 (3.5 mL), $Cp_2Zr(H)Cl$ (110.0 mg, 0.425 mmol). After addition of isobutyryl chloride (52 μL, 0.500 mmol), the cold bath was removed and the mixture was stirred for 10 min. The mixture was cooled to °C and a solution of PhSH (117 mg, 1.06 mmol) in CH_2Cl_2 (0.3 mL) was

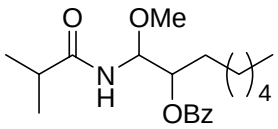
added dropwise. The reaction was stirred at °C for 10 min, then quenched with saturated $NaHCO_3$ solution (20 mL) and extracted with CH_2Cl_2 (4 x 15 mL). The organic extracts were dried (Na_2SO_4) and concentrated. The residue was purified by column chromatography (7% - 13% EtOAc in hexanes containing 0.5% Et_3N) to give the desired product (89.4 mg, 71.7%) as a white solid in a 1.0:7.1 diastereomeric ratio. Further purification (10% - 16% EtOAc in hexanes containing 0.5% Et_3N) yielded analytically pure samples. For faster eluting *anti*-product **3.25**: ^{1}H NMR (300 MHz, $CDCl_3$) 7.49-7.45 (m, 2H), 7.31-7.20 (m, 3H), 6.00 (d, *J* = 9.9 Hz, 1H), 5.58 (dd, *J* = 10.0, 1.8 Hz, 1H), 3.76-3.63 (m, 2H), 3.56 (dt, *J* = 6.5, 1.7 Hz, 1H), 2.29 (sept, *J* = 6.9 Hz, 1H), 1.60-1.48 (m, 1H), 1.40-1.14 (m, 12H), 1.08 (d, *J* = 6.9 Hz, 3H), 1.00 (d, *J* = 6.9 Hz, 3H), 0.87 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 176.3, 133.9, 132.3, 129.1, 127.5, 81.7, 67.3, 60.0, 35.9, 32.5, 31.9, 29.4, 25.7, 22.8, 19.7, 19.6, 15.9, 14.3; IR (neat) 3302, 2962, 2928, 2859, 1652, 1497, 1440, 1379, 1223, 1098, 739; HRMS (ESI): *m*/*z* calcd for $C_{20}H_{33}NO_2SNa$ $[M+Na]^+$ 374.2130, found 374.2130. For slower eluting *syn*-product **3.26**: ^{1}H NMR (300 MHz, $CDCl_3$) 7.47-7.44 (m, 2H), 7.30-7.18 (m, 3H), 6.00 (d, *J* = 9.5 Hz, 1H), 5.63 (dd, *J* = 9.7, 3.2 Hz, 1H), 3.69-3.49 (m, 3H), 2.25 (sept, *J* = 6.9 Hz, 1H), 1.73-1.66 (m, 2H), 1.42-1.28 (m, 8H), 1.21 (t, *J* = 7.0 Hz, 3H), 1.06 (d, *J* = 6.9 Hz, 3H), 0.98 (d, *J* = 6.9 Hz, 3H), 0.88 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 176.0, 133.6, 132.0, 129.1, 127.3, 82.0, 66.0, 59.8, 35.8, 31.9, 31.6, 29.5, 25.8, 22.7, 19.6, 19.5, 15.7, 14.2; IR (neat) 3293, 2962, 2927, 2858, 1650, 1526, 1223,, 1100, 736; HRMS (ESI): *m*/*z* calcd for $C_{20}H_{33}NO_2SNa$ $[M+Na]^+$ 374.2130, found 374.2115.

1-Cyanoheptyl benzoate (3.27)



A solution of 2-hydroxyoctanenitrile (0.600 g, 4.25 mmol) in CH_2Cl_2 (14 mL) was treated with Et_3N (1.2 mL, 8.50 mmol), DMAP (5.2 mg, 42.5 μmol) and benzoyl chloride (0.60 mL, 5.10 mmol). The reaction was stirred for 1 h, then quenched with water (30 mL) and extracted with CH_2Cl_2 (3 x 30 mL). The organic extracts were dried (Na_2SO_4) and concentrated. The residue was purified by column chromatography (5%- 10% Et_2O in hexanes) to give the benzoate **3.27** (1.042 g, 94.1%) as a colorless oil. For spectral data, see ref. 119.

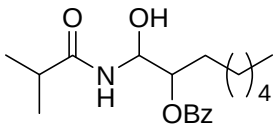
1-(Isobutyramido)-1-methoxyoctan-2-yl benzoate (3.28)



The title compound was prepared by following the representative procedure with the following amounts of reagents: benzoate **3.27** (100.0 mg, 0.408 mmol), CH_2Cl_2 (4.0 mL), $Cp_2Zr(H)Cl$ (158 mg, 0.612 mmol), isobutyryl chloride (52 μL, 0.490 mmol), MeOH (0.7 mL, 17.3 mmol). After the reaction was complete, it was quenched with 1 N HCl (1.5 mL) and water (15 mL) and extracted with CH_2Cl_2 (3 x 25 mL). The organic extracts were washed with saturated $NaHCO_3$ (15 mL), dried (Na_2SO_4) and concentrated. The residue was purified by column chromatography (15% - 30% EtOAc in hexanes) to give the product **3.28** (90.4 mg, 63.5%, containing 4% BnOH) as a white solid in a 1.4:1.0 diastereomeric ratio. Further purification (15% - 30% EtOAc in hexanes) yielded analytically pure materials. For faster eluting product: ^1H NMR (500 MHz, $CDCl_3$) 8.03-8.01 (m, 2H), 7.60-7.56 (m, 1H), 7.48-7.44 (m, 2H), 5.97 (d, J = 9.5 Hz, 1H), 5.24 (dd, J = 9.6, 6.6 Hz, 1H), 5.19 (ddd, J = 8.6, 6.6, 3.8 Hz, 1H), 3.38 (s, 3H), 2.32 (sept, J = 7.0 Hz, 1H), 1.86-1.80 (m, 1H), 1.78-1.70 (m, 1H), 1.44-1.23 (m, 7H), 1.21-1.15 (m, 1H), 1.10 (d, J = 7.0 Hz, 3H), 1.00 (d, J = 7.0 Hz, 3H), 0.86 (t,

J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 178.0, 167.0, 133.5, 130.0, 129.9, 128.7, 81.9, 74.5, 56.3, 36.1, 31.8, 31.3, 29.3, 25.3, 22.8, 19.6, 19.5, 14.2; IR (neat) 3295, 2959, 2929, 2858, 1721, 1663, 1529, 1452, 1273, 1113, 712; HRMS (ESI): m/z calcd for $C_{20}H_{31}NO_4Na$ $[M+Na]^+$ 372.2151, found 372.2123. For slower eluting product: ^{1}H NMR (500 MHz, $CDCl_3$) 8.08 (app d, J = 7.3 Hz, 2H), 7.59 (app t, J = 7.4 Hz, 1H), 7.47 (app t, J = 7.8 Hz, 2H), 6.01 (d, J = 9.6 Hz, 1H), 5.33 (dd, J = 9.8, 4.0 Hz, 1H), 5.12 (td, J = 8.6, 4.4 Hz, 1H), 3.38 (s, 3H), 2.40 (sept, J = 6.9 Hz, 1H), 1.82-1.73 (m, 2H), 1.44-1.26 (m, 8H), 1.18 (d, J = 7.0 Hz, 3H), 1.17 (d, J = 7.0 Hz, 3H), 0.87 (t, J = 6.7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 177.6, 166.7, 133.4, 130.1, 130.0, 128.7, 81.0, 75.8, 56.7, 36.1, 31.8, 30.6, 29.3, 25.4, 22.7, 19.8, 19.7, 14.2; IR (neat) 3299, 2929, 2858, 1722, 1661, 1527, 1453, 1273, 1113, 712; HRMS (ESI): m/z calcd for $C_{20}H_{31}NO_4Na$ $[M+Na]^+$ 372.2151, found 372.2133.

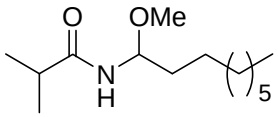
1-(Isobutyramido)-1-hydroxyoctan-2-yl benzoate (3.29)



The title compound was prepared by following the representative procedure with the following amounts of reagents: benzoate **3.27** (100.0 mg, 0.408 mmol), CH_2Cl_2 (4.0 mL), $Cp_2Zr(H)Cl$ (158 mg, 0.612 mmol), isobutyryl chloride (52 μL, 0.490 mmol). The reaction was quenched with water (15 mL) and extraction of the mixture with EtOAc (3 x 25 mL). After evaporation of the solvent, the crude product was purified by column chromatography (20% - 60% EtOAc in hexanes containing 0.5% Et_3N) gave the product **3.29** (71.6 mg, 52.4%, containing trace amount of impurity) as a colorless oil in a 3.0:1.0 diastereomeric ratio. ^{1}H NMR (300 MHz, $CDCl_3$) 8.10-8.07 (m, 1.5H), 8.03-7.99 (m, 0.5H), 7.61-7.56 (m, 1H), 7.48-7.42 (m, 2H), 7.11 (d, J = 7.5 Hz, 0.75H), 6.74 (d, J = 8.3 Hz, 0.25H), 5.53-5.36 (m, 1H), 5.22-5.17 (m, 0.25H), 5.15-5.10 (m, 0.75H), 4.74 (br s, 0.25H), 4.52

(br s, 0.75H), 2.47-2.22 (m, 1H), 1.92-1.78 (m, 2H), 1.44-1.20 (m, 8H), 1.13 (d, J = 6.8 Hz, 2.25H), 1.11 (d, J = 6.8 Hz, 2.25H), 1.04 (d, J = 6.9 Hz, 0.75H), 0.99 (d, J = 6.9 Hz, 0.75H), 0.85 (t, J = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) (for major diastereomer) 178.4, 167.7, 133.6, 130.1, 128.6, 76.2, 75.0, 35.6, 31.8, 30.7, 29.2, 25.5, 22.7, 19.5, 19.3, 14.2; IR (neat) 3338, 2959, 2928, 2858, 1720, 1657, 1530, 1451, 1274, 1119, 1070, 711; HRMS (EI): *m*/*z* calcd for $C_{19}H_{28}NO_3$ $(M\text{-}OH)^{+\bullet}$ 318.2069, found 318.2064.

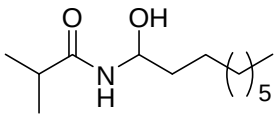
_N_-(1-Methoxynonyl)isobutyramide (3.31)



The title compound was prepared by following the representative procedure with the following amounts of reagents: octyl cyanide **3.30** (84.0 mg, 0.603 mmol), THF (6.0 mL), $Cp_2Zr(H)Cl$ (194 mg, 0.754 mmol). The hydrozirconation reaction was stirred for 30 min, then cooled to 0 °C and isobutyryl chloride (95 μL, 0.904 mmol) was added dropwise. The reaction was stirred for 10 min at 0 °C and MeOH (0.73 mL, 18.1 mmol) was added dropwise. The reaction was stirred at 0 °C for 15 min, then quenched with a solution of Et_3N (0.25 mL) in water (15 mL) and extracted with CH_2Cl_2 (4 x 20 mL). The combined organic extracts were dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by column chromatography (15% - 25% EtOAc in hexanes containing 0.5% Et_3N) to gave the title product (91.7 mg, 62.3%) as a white solid: ^{1}H NMR (300 MHz, $CDCl_3$) 5.66 (d, J = 9.5 Hz, 1H), 5.10 (td, J = 9.8, 6.1 Hz, 1H), 3.31 (s, 3H), 2.37 (sept, J = 6.9 Hz, 1H), 1.66-1.59 (m, 1H), 1.52-1.43 (m, 1H), 1.38-1.24 (m, 12H), 1.18 (app d, J = 6.4 Hz, 3H), 1.16 (app d, J = 6.4 Hz, 3H), 0.86 (t, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 177.4, 81.1, 55.9, 36.1, 35.8, 32.0, 29.6, 29.5, 29.4, 25.0, 22.8, 19.9, 19.7, 14.2; IR (neat) 3281, 2920, 2853, 1651,

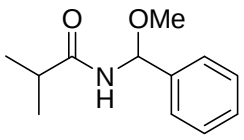
1538, 1466, 1377, 1236, 1081, 929, 720; HRMS (EI): *m*/*z* calcd for $C_{13}H_{26}NO$ (M- $CH_3O)^{+\bullet}$ 212.2014 found 212.2010.

_N_-(1-Hydroxynonyl)isobutyramide (3.32)



The title compound was prepared by following the representative procedure with the following amounts of reagents: octyl cyanide **3.30** (84.0 mg, 0.603 mmol), CH_2Cl_2 (4.5 mL), $Cp_2Zr(H)Cl$ (171 mg, 0.663 mmol). After hydrozirconation was complete, a solution of isobutyryl chloride (76 μL, 0.724 mmol) and Et_3N (0.25 mL, 1.81 mmol) in CH_2Cl_2 (0.5 mL) was added dropwise at 0 °C. The reaction was stirred for 15 min at 0 °C and quenched with water (20 mL). The mixture was acidified by adding 1 N HCl to pH~1.0 and extracted with CH_2Cl_2 (3 x 25 mL). The combined organic extracts were washed with saturated $NaHCO_3$ (20 mL), dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by column chromatography (10% - 70% EtOAc in hexanes) to give acyl hemiaminal **3.32** (74.7 mg, 54.0%) as white solids: ^{1}H NMR (300 MHz, $CDCl_3$) 6.17 (br s, 1H), 5.30 (q, *J* = 6.6 Hz, 1H), 4.27 (br s, 1H), 2.35 (sept, *J* = 6.9 Hz, 1H), 1.73-1.61 (m, 1H), 1.59-1.48 (m, 1H), 1.40-1.26 (m, 12H), 1.15 (d, *J* = 6.9 Hz, 3H), 1.14 (d, *J* = 6.9 Hz, 3H), 0.87 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 178.4, 74.5, 35.7, 35.3, 32.0, 29.6, 29.5, 29.4, 25.1, 22.8, 19.6, 19.4, 14.3; IR (neat) 3298, 2934, 2854, 1653, 1540, 1462, 1231, 1095; HRMS (EI): *m*/*z* calcd for $C_{13}H_{26}NO$ (M-OH)$^{+\bullet}$ 212.2014 found 212.2015.

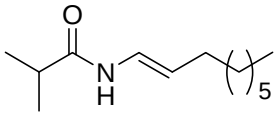
_N_-(Methoxy(phenyl)methyl)isobutyramide (3.34)



By following the representative procedure, reaction of benzonitrile **3.33** (60.0 mg, 0.582 mmol) with $Cp_2Zr(H)Cl$ (240 mg, 0.931 mmol) in THF (5.8

mL) for 2.5 h followed by acylation with isobutyryl chloride (92 μL, 0.873 mmol) and addition of MeOH (0.71 mL, 17.5 mmol) in CH_2Cl_2 (0.5 mL) gave the title product **3.34** (87.9 mg, 72.9%) as a white solid: ^{1}H NMR (300 MHz, $CDCl_3$) 7.42-7.30 (m, 5H), 6.14 (d, *J* = 9.4 Hz, 1H), 6.02 (d, *J* = 8.8 Hz, 1H), 3.45 (s, 3H), 2.40 (sept, *J* = 6.9 Hz, 1H), 1.21 (d, *J* = 6.9 Hz, 3H), 1.18 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 177.4, 139.6, 128.8, 128.6, 126.0, 81.3, 56.1, 36.0, 19.8, 19.6; IR (neat) 3286, 2967, 1653, 1535, 1451, 1230, 1099, 1046, 951, 746; HRMS (EI): *m*/*z* calcd for $C_{11}H_{14}NO_2$ $(M\text{-}CH_3O)^{+\bullet}$ 192.1024, found 192.1031.

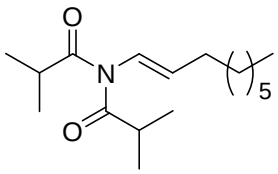
_N_-((_E_)-Non-1-enyl)isobutyramide (3.36)



A solution of octyl cyanide **3.30** (84.0 mg, 0.603 mmol) in THF (6.0 mL) was treated with $Cp_2Zr(H)Cl$ (171 mg, 0.663 mmol). The reaction was stirred for 20 min, then cooled to 0 °C and a solution of isobutyryl chloride (60 μL, 0.573 mmol) and Et_3N (0.25 mL, 1.81 mmol) in THF (4.0 mL) was added dropwise. The flask formerly containing the isobutyryl chloride and Et_3N was rinsed with THF (2 x 1 mL). The reaction was stirred for 10 min at 0 °C and BF_3•OEt_2 (98 μL, 0.784 mmol) was added dropwise. The cold bath was removed and the mixture was stirred overnight. After that time, the reaction was quenched with water (30 mL) and extracted with EtOAc (4 x 30 mL). The combined organic extracts were washed with water (30 mL), dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by column chromatography (10% - 20% EtOAc in hexanes) to gave the title product **3.36** (73.1 mg, 57.3%) as a white solid: ^{1}H NMR (300 MHz, $CDCl_3$) 7.24 (d, *J* = 9.6 Hz, 1H), 6.74 (app dd, *J* = 14.2, 10.5 Hz, 1H), 5.15 (td, *J* = 14.2, 7.1 Hz, 1H), 2.37 (sept, *J* = 6.9 Hz, 1H), 2.00 (q, *J* = 6.6 Hz, 2H), 1.36-1.22 (m, 10H), 1.17 (d, *J* = 6.9 Hz, 6H), 0.87 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 174.2, 122.7, 113.3, 35.7, 32.0, 30.1, 29.9, 29.3, 29.2, 22.8, 19.6, 14.3; IR (neat)

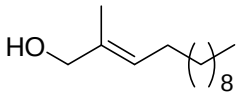
3283, 2967, 2921, 2851, 1680, 1647, 1526, 1467, 1238, 950, 723; HRMS (EI): *m*/*z* calcd for $C_{13}H_{25}NO$ ($M^{+\bullet}$) 211.1936, found 211.1938.

_N_-(Isobutyryl)-N-((_E_)-non-1-enyl)isobutyramide (3.38)



^{1}H NMR (500 MHz, $CDCl_3$) 6.22 (td, *J* = 13.9, 1.4 Hz, 1H), 5.47 (td, *J* = 14.2, 7.2 Hz, 1H), 3.21 (sept, *J* = 6.8 Hz, 1H), 2.16 (dq, *J* = 7.3, 1.4 Hz, 2H), 1.44 (pent, 2H), 1.34-1.26 (m, 8H), 1.17 (d, *J* = 6.8 Hz, 12H), 0.89 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 181.0, 132.6, 125.8, 35.0, 32.0, 30.1, 29.4, 29.3, 29.1, 22.8, 19.7, 14.3; IR (neat) 2962, 2928, 1706, 1466, 1383, 1187, 1162, 1092; HRMS (ESI): *m*/*z* calcd for $C_{17}H_{31}NO_2Na$ $[M+Na]^+$ 304.2252, found 304.2246.

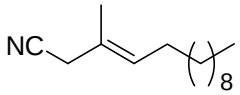
(_E_)-2-Methyltridec-2-en-1-ol (3.39)



A solution of 1-dodecene (freshly distilled, 0.842 g, 5.00 mmol) and methacrolein (90%, 3.89 g, 50.0 mmol) in CH_2Cl_2 (50 mL) was treated with Grubbs' 2nd generation catalyst (64.0 mg, 75 μmol). The reaction was refluxed for 1.5 h and then concentrated. The residue was purified by column chromatography (1% - 5% EtOAc in hexanes) to give the desired product (1.222 g, contaminated with unknown impurities). This product was dissolved in MeOH (29 mL) and cooled to 0 °C. $NaBH_4$ (219 mg, 5.80 mmol) was added. The reaction was stirred for 30 min and quenched with saturated NH_4Cl solution (1 mL). The mixture was stirred for 10 min while warming to room temperature and then concentrated. The residue was purified by column chromatography (10% - 20% EtOAc in hexanes) to give the allylic alcohol **3.39** (0.621 g, 58.5%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) 5.41 (app t, *J* = 7.1 Hz, 1H), 4.00 (s, 2H), 2.06-1.99 (m, 2H), 1.66 (s, 3H), 1.45 -1.27 (m, 16H), 0.88 (t, *J* = 7.0 Hz,

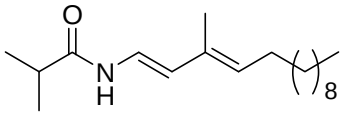
3H); ^{13}C NMR (75 MHz, $CDCl_3$) 134.7, 126.9, 69.3, 32.1, 29.9, 29.8, 29.7, 29.6, 27.8, 22.9, 14.3, 13.8; IR (neat) 3335, 2924, 2854, 1464, 1378, 1012; HRMS (EI): *m*/*z* calcd for $C_{14}H_{28}O$ ($M^{+\bullet}$) 212.2140, found 212.2150.

(*E*)-3-Methyltetradec-3-enenitrile (3.40)



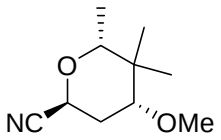
A solution of allylic alcohol **3.39** (505 mg, 2.38 mmol) and Et_3N (0.66 mL, 4.78 mmol) in CH_2Cl_2 (12 mL)/THF (6 mL) was cooled to -42 °C and methanesulfonyl chloride (0.24 mL, 3.09 mmol) was added dropwise. The mixture was stirred for 30 min and anhydrous LiBr (620 mg, 7.14 mmol) was added followed by THF (18 mL). The mixture was warmed to 0 °C and stirred for 1.5 h. After that time, the reaction was diluted with hexanes (150 mL), washed with water (80 mL) and brine (50 mL), dried (Na_2SO_4) and concentrated. The crude allylic bromide was dissolved in DMF (4.5 mL) and CuCN (213 mg, 2.38 mmol) was added in one portion. The reaction was stirred overnight, then quenched with water (30 mL) and extracted with EtOAc (3 x 25 mL). The organic extract was dried (Na_2SO_4) and concentrated. The resulting residue was purified by column chromatography (3% - 5% EtOAc in hexanes) to give allylic nitrile **3.40** (295 mg, 56.0%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) 5.49 (sext of t, J = 7.2, 1.4 Hz, 1H), 3.03 (s, 2H), 2.04 (q, J = 7.0 Hz, 2H), 1.73 (s, 3H), 1.38-1.27 (m, 16H), 0.89 (t, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 130.2, 124.0, 118.0, 32.0, 29.8, 29.6, 29.5, 29.4, 29.3, 28.2, 27.4, 22.8, 16.1, 14.2; IR (neat) 2925, 2854, 2249, 1464, 1412, 1114, 721; HRMS (EI): *m*/*z* calcd for $C_{15}H_{27}N$ ($M^{+\bullet}$) 221.2144, found 221.2152.

***N*-((1*E*,3*E*)-3-Methyltetradeca-1,3-dienyl)isobutyramide (3.41)**



A solution of allylic nitrile **3.40** (90.0 mg, 0.406 mmol) in THF (5.0 mL) was treated with $Cp_2Zr(H)Cl$ (157 mg, 0.609 mmol), The reaction was stirred for 30 min, then cooled to 0 °C and a solution of isobutyryl chloride (51 μL, 0.487 mmol) and Et_3N (0.18 mL, 1.26 mmol) in THF (2.0 mL) was added dropwise. The flask formerly containing the isobutyryl chloride and Et_3N was rinsed with THF (0.5 mL). The reaction was stirred for 2 min at 0 °C and BF_3•OEt_2 (76 μL, 0.609 mmol) was added dropwise. The cold bath was removed and the mixture was stirred for 2 h. After that time, the reaction was diluted with Et_2O (3 mL) and filtered through a small plug of silica gel. The residue was washed with Et_2O (30 mL) and the combined filtrate was dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by column chromatography (5% - 17% EtOAc in hexanes containing 0.5% Et_3N) to gave the title product **3.41** (74.1 mg, 62.1%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) 7.10 (d, *J* = 10.3 Hz, 1H), 6.91 (dd, *J* = 14.2, 10.7 Hz, 1H), 5.83 (d, *J* = 14.3Hz, 1H), 5.34 (t, *J* = 7.2 Hz, 1H), 2.40 (sept, *J* = 6.9 Hz, 1H), 2.10 (q, *J* = 7.0 Hz, 2H), 1.75 (s, 3H), 1.40-1.27 (m, 16H), 1.20 (d, *J* = 6.9 Hz, 6H), 0.88 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 174.3, 131.8, 130.8, 120.4, 118.5, 35.9, 32.1, 30.0, 29.9, 29.8, 29.6, 28.4, 22.9, 19.7, 14.3, 12.7; IR (neat) 3276, 2924, 2854, 1644, 1531, 1467, 1253, 950; HRMS (EI): *m*/*z* calcd for $C_{19}H_{35}NO$ ($M^{+\bullet}$) 293.2719, found 293.2717.

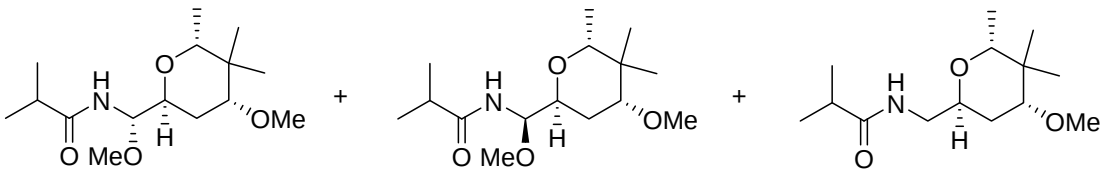
(2*S*,4*R*,6*R*)-Tetrahydro-4-methoxy-5,5,6-trimethyl-2*H*-pyran-2-carbonitrile (3.43)



^{1}H NMR (300 MHz, $CDCl_3$) 4.90 (dd, *J* = 6.0, 1.2 Hz, 1H), 3.63 (q, *J* = 6.3 Hz, 1H), 3.37 (s, 3H), 3.17 (dd, *J* = 11.7, 4.5 Hz, 1H), 2.06 (ddd, *J* = 13.5, 4.5, 1.4 Hz, 1H), 1.84 (ddd, *J* = 13.4, 11.8, 6.1 Hz, 1H), 1.12 (d, *J* = 6.3 Hz, 3H), 0.96 (s, 3H),

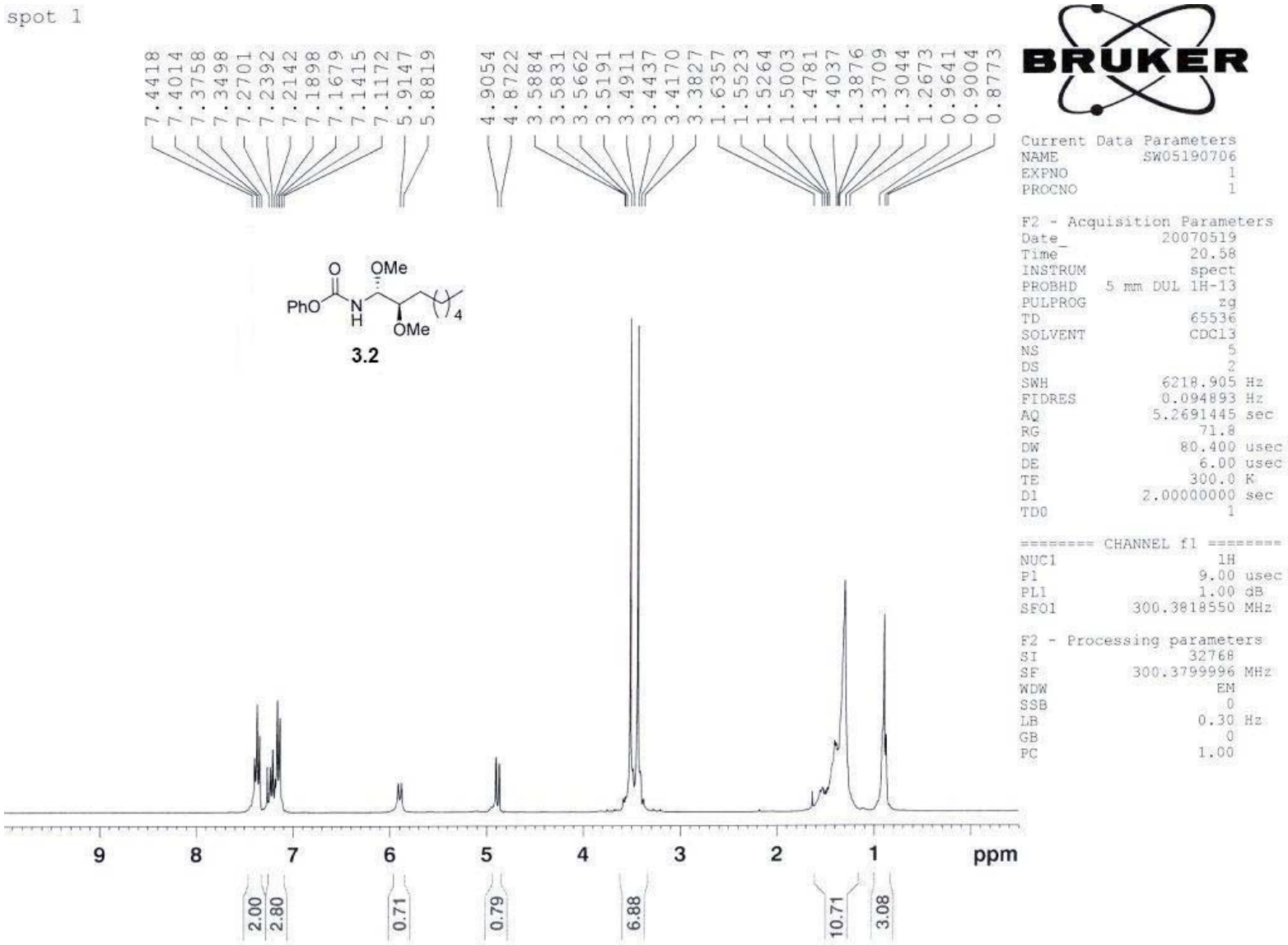
0.83 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 118.0, 81.4, 78.0, 64.2, 57.8, 39.4, 29.3, 22.6, 14.6, 12.2; IR (neat) 2980, 2941, 2874, 1470, 1450, 1391, 1164, 1104, 954, 867, 718; HRMS (EI): *m*/*z* calcd for $C_{10}H_{17}NO_2$ ($M^{+\bullet}$) 183.1259, found 183.1255.

_N_-((_S_)-((2_S_,4_R_,6_R_)-Tetrahydro-4-methoxy-5,5,6-trimethyl-2_H_-pyran-2-yl)(methoxy)methyl)isobutyramide (3.44), _N_-((_R_)-((2_S_,4_R_,6_R_)-Tetrahydro-4-methoxy-5,5,6-trimethyl-2_H_-pyran-2-yl)(methoxy)methyl)isobutyramide (3.45) and **_N_-(((2_S_,4_R_,6_R_)-Tetrahydro-4-methoxy-5,5,6-trimethyl-2_H_-pyran-2-yl)methyl)isobutyramide (3.46)**



A solution of tetrahydropyranyl cyanide **3.43** (50.0 mg, 0.273 mmol) in CH_2Cl_2 (2.7 mL) was treated with Schwartz reagent (84.5 mg, 0.328 mmol). The mixture was stirred for 15 min, then cooled to 0 °C and isobutyryl chloride (40 μL, 0.382 mmol) was added dropwise. The cold bath was removed and the mixture was stirred for 10 min. After that time, the flask was cooled to -78 °C and $Mg(ClO_4)_2$ (61 mg, 0.273 mmol) was added in one portion. After 30 min, a pre-cooled solution (-78 °C) of MeOH (0.22 ml, 5.46 mmol) in CH_2Cl_2 (0.5 mL) was cannulated dropwise to the reaction mixture over 5 min. After completion of addition, the reaction was stirred at -78 °C for 15 min, then quenched with saturated $NaHCO_3$ solution (15 mL) and warmed to room temperature. The biphasic mixture was extracted with CH_2Cl_2 (3 x 20 mL) and the combined organic extracts were dried (Na_2SO_4) and concentrated. The residue was purified by column chromatography (20% - 70% EtOAc in hexanes containing 0.5% Et_3N) to give the desired products **3.44** and **3.45** (60.2 mg, 76.8%) in a 2.3:1.0 diastereomeric ratio as a colorless oil and

the over-reduction product **3.46** (6.8 mg, 9.7%) as a colorless oil. For **3.46**: ^{1}H NMR (300 MHz, $CDCl_3$) 5.77 (br s, 1H), 4.05-3.97 (m, 1H), 3.48-3.39 (m, 3H), 3.32 (s, 3H), 3.03 (t, *J* = 6.4 Hz, 1H), 2.38 (sept, *J* = 6.9 Hz, 1H), 1.74-1.69 (m, 2H), 1.18-1.14 (m, 9H), 0.96 (s, 3H), 0.88 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 177.3, 82.0, 74.5, 69.0, 57.7, 41.0, 38.6, 35.9, 27.6, 24.5, 19.9, 19.8, 15.6, 15.5; IR (neat) 3305, 2970, 2933, 2874, 1651, 1548, 1468, 1386, 1243, 1103; HRMS (ESI): *m*/*z* calcd for $C_{14}H_{27}NO_3Na$ $[M+Na]^+$ 280.1889, found 280.1899. Further purification (20% - 40% EtOAc in hexanes containing 0.5% Et_3N) of the mixture of **3.44** and **3.45** yielded analytically pure diastereomers. For the faster eluting product **3.44** (major, white solid): ^{1}H NMR (500 MHz, $CDCl_3$) 6.01 (d, *J* = 9.0 Hz, 1H), 5.26 (dd, *J* = 9.5, 6.5 Hz, 1H), 3.84-3.80 (m, 1H), 3.39 (s, 3H), 3.36 (q, *J* = 6.5 Hz, 1H), 3.33 (s, 3H), 3.04 (dd, *J* = 8.6, 4.1 Hz, 1H), 2.44 (sept, *J* = 6.9 Hz, 1H), 1.92 (td, *J* = 13.7, 4.5 Hz, 1H), 1.66 (ddd, *J* = 13.8, 8.6, 5.2 Hz,1H), 1.20 (d, *J* = 6.9 Hz, 3H), 1.19 (d, *J* = 6.9 Hz, 3H), 1.10 (d, *J* = 6.6 Hz, 3H), 0.94 (s, 3H), 0.86 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 178.2, 82.0, 80.0, 76.2, 70.9, 57.7, 56.4, 38.2, 36.2, 26.0, 24.5, 19.9, 19.8, 16.1, 15.3; IR (neat) 3300, 2972, 2938, 1659, 1536, 1468, 1387, 1103; HRMS (ESI): *m*/*z* calcd for $C_{15}H_{29}NO_4Na$ $[M+Na]^+$ 310.1994, found 310.1985. For the slower eluting product **3.45** (minor, colorless oil): ^{1}H NMR (300 MHz, $CDCl_3$) 6.26 (d, *J* = 9.3 Hz, 1H), 5.16 (dd, *J* = 9.6, 3.9 Hz, 1H), 3.83-3.78 (m, 1H), 3.67 (q, *J* = 6.6 Hz, 1H), 3.38 (s, 3H), 3.31 (s, 3H), 3.18 (dd, *J* = 7.0, 3.8 Hz, 1H), 2.42 (sept, *J* = 6.9 Hz, 1H), 1.96 (ddd, *J* = 13.7, 6.6, 3.9 Hz, 1H), 1.71-1.63 (m, 1H), 1.22-1.17 (m, 9H), 1.00 (s, 3H), 0.88 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 177.5, 82.4, 81.7, 70.3, 57.8, 56.7, 38.0, 36.1, 26.3, 25.4, 19.9, 19.7, 17.6, 15.6; IR (neat) 3293, 2970, 2934, 1658, 1531, 1468, 1387, 1170, 1102; HRMS (ESI): *m*/*z* calcd for $C_{15}H_{29}NO_4Na$ $[M+Na]^+$ 310.1994, found 310.2002.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7.1172
5.9147
5.8819
4.9054
4.8722
3.5884
3.5831
3.5662
3.5191
3.4911
3.4437
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1.6357
1.5523
1.5264
1.5003
1.4781
1.4037
1.3876
1.3709
1.3044
1.2673
0.9641
0.9004
0.8773
PhO
O
N
H
OMe
OMe
4
3.2
9
8
7
6
5
4
3
2
1
ppm
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10.71
3.08
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PROCNO 1
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FIDRES 0.094893 Hz
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RG 71.8
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DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
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PL1 1.00 dB
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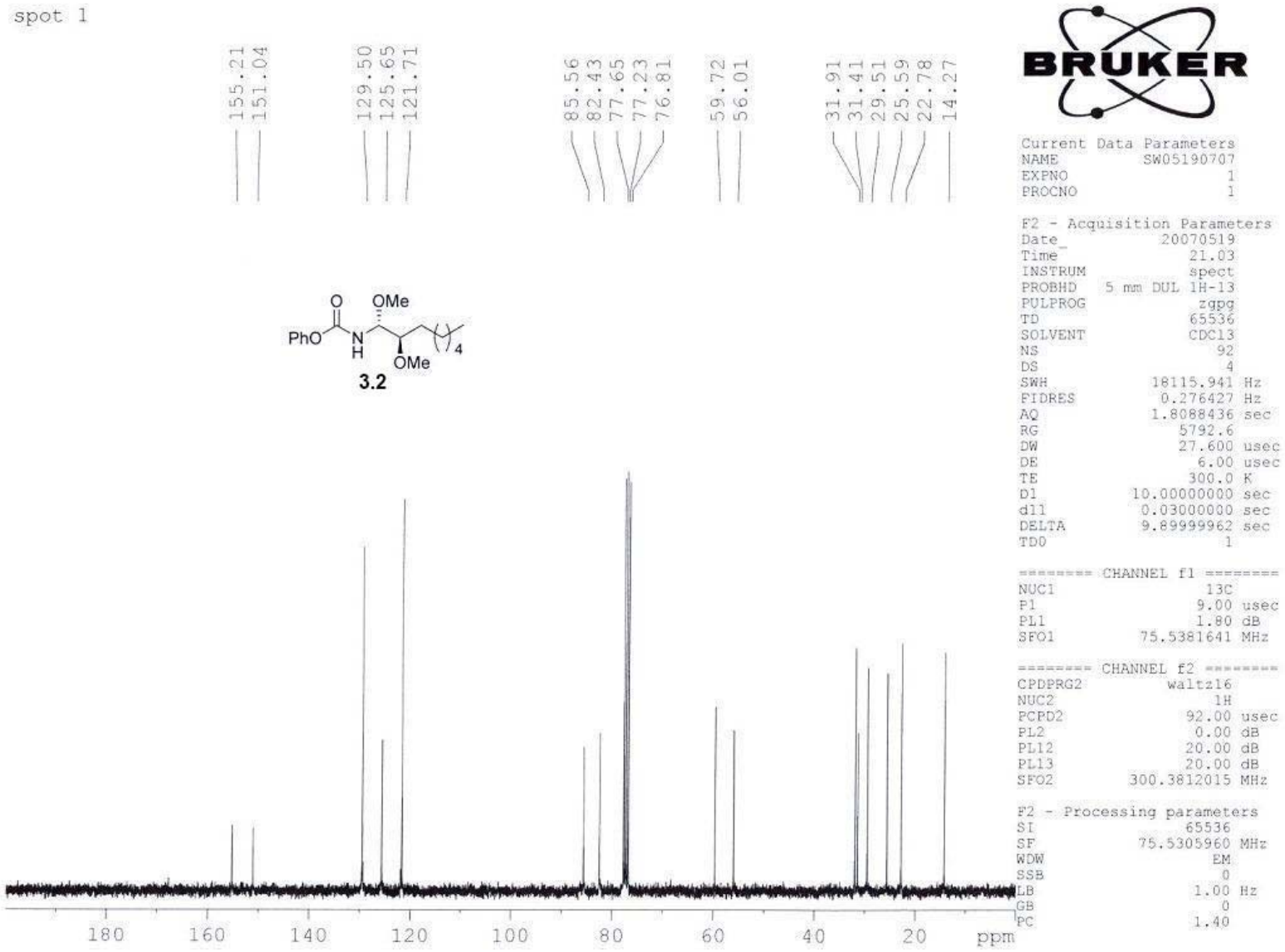
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56.01
31.91
31.41
29.51
25.59
22.78
14.27
PhO
O
OMe
N
H
OMe
4
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160
140
120
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80
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40
20
ppm
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PROCNO 1
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TE 300.0 K
D1 10.00000000 sec
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DELTA 9.89999962 sec
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SFO1 75.5381641 MHz
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NUC2 1H
PCPD2 92.00 usec
PL2 0.00 dB
PL12 20.00 dB
PL13 20.00 dB
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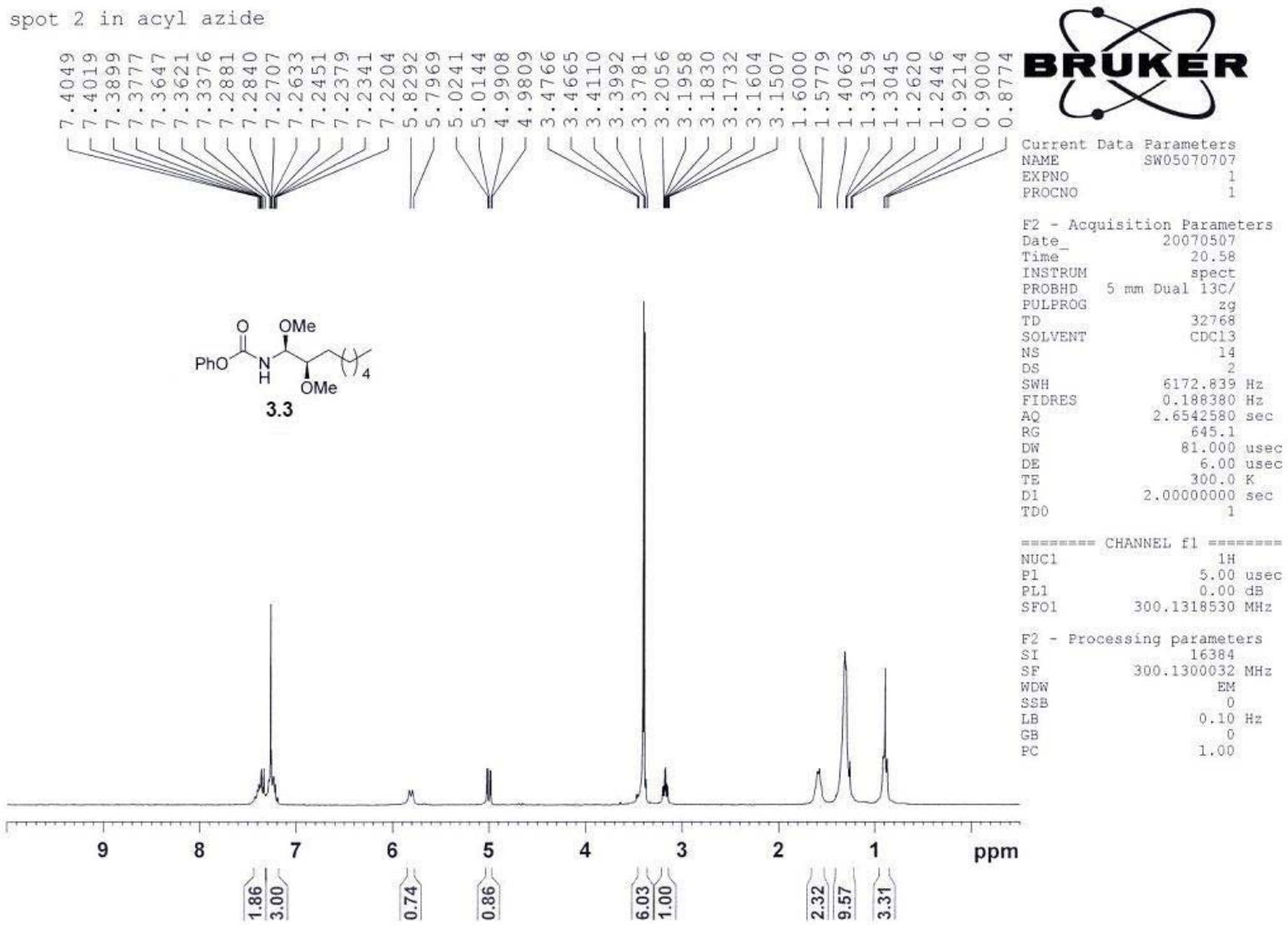
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7.3376
7.2881
7.2840
7.2707
7.2633
7.2451
7.2379
7.2341
7.2204
5.8292
5.7969
5.0241
5.0144
4.9908
4.9809
3.4766
3.4665
3.4110
3.3992
3.3781
3.2056
3.1958
3.1830
3.1732
3.1604
3.1507
1.6000
1.5779
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1.3159
1.3045
1.2620
1.2446
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PROCNO 1
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SOLVENT CDCl3
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DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
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DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1
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PL1 0.00 dB
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SSB 0
LB 0.10 Hz
GB 0
PC 1.00
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N
H
OMe
OMe
4
3.3
9
8
7
6
5
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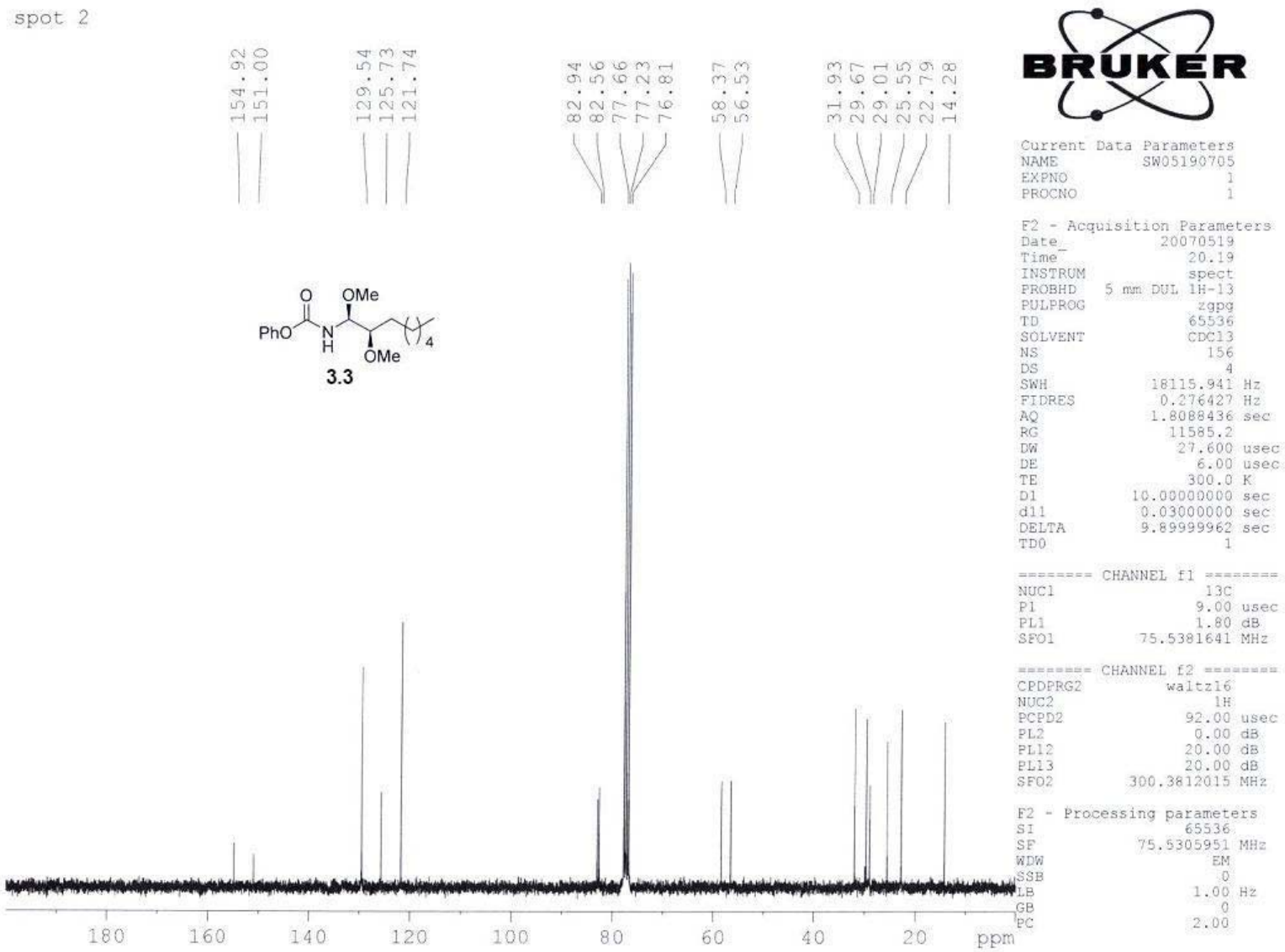
9.57
3.31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77.23
76.81
58.37
56.53
31.93
29.67
29.01
25.55
22.79
14.28
PhO
O
OMe
N
H
OMe
4
3.3
180
160
140
120
100
80
60
40
20
ppm
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Current Data Parameters
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PROCNO 1
F2 - Acquisition Parameters
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Time 20.19
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PULPROG zgpg
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SOLVENT CDCl3
NS 156
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SWH 18115.941 Hz
FIDRES 0.276427 Hz
AQ 1.8088436 sec
RG 11585.2
DW 27.600 usec
DE 6.00 usec
TE 300.0 K
D1 10.00000000 sec
d11 0.03000000 sec
DELTA 9.89999962 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.00 usec
PL1 1.80 dB
SFO1 75.5381641 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 92.00 usec
PL2 0.00 dB
PL12 20.00 dB
PL13 20.00 dB
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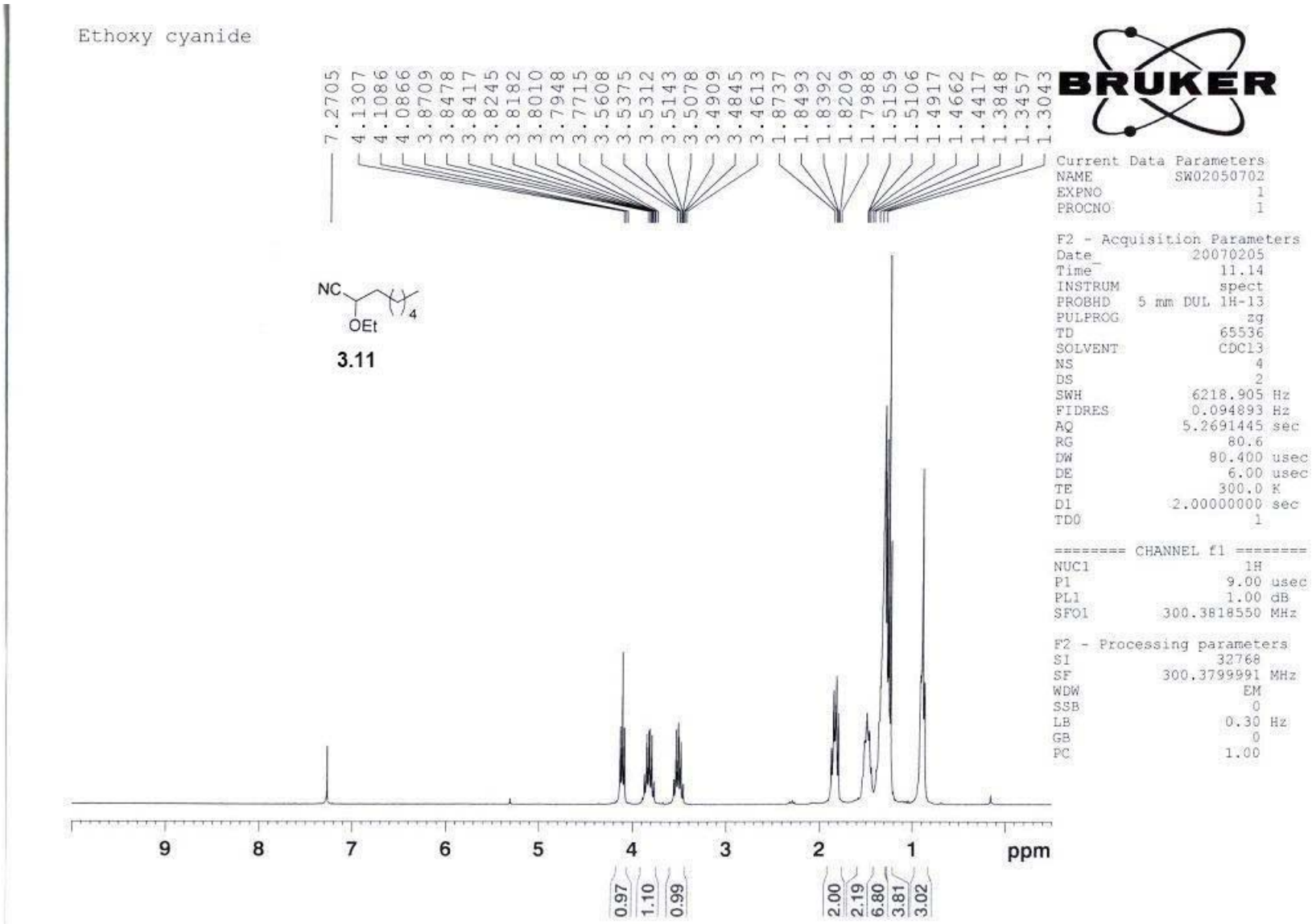
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3.7948
3.7715
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3.5312
3.5143
3.5078
3.4909
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3.4613
1.8737
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1.8392
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1.7988
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1.4417
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NC
OEt
4
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PROCNO 1
F2 - Acquisition Parameters
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Time 11.14
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PULPROG zg
TD 65536
SOLVENT CDCl3
NS 4
DS 2
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FIDRES 0.094893 Hz
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RG 80.6
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DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1
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PL1 1.00 dB
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F2 - Processing parameters
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SF 300.3799991 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9
8
7
6
5
4
3
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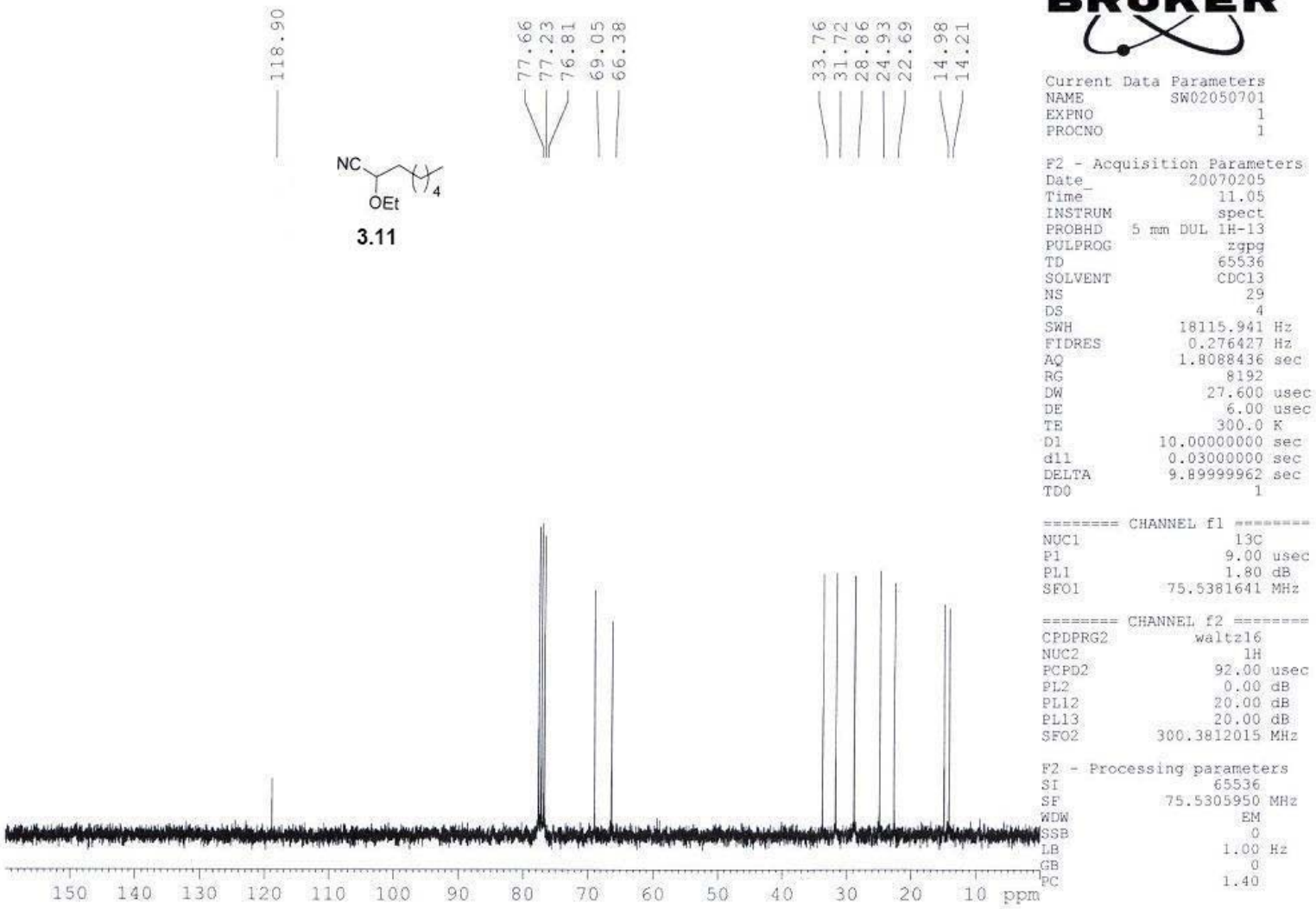
3.02

Ethoxy cyanide



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PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 29
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FIDRES 0.276427 Hz
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DE 6.00 usec
TE 300.0 K
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d11 0.03000000 sec
DELTA 9.89999962 sec
TD0 1

======== CHANNEL f1 ========
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P1 9.00 usec
PL1 1.80 dB
SFO1 75.5381641 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 92.00 usec
PL2 0.00 dB
PL12 20.00 dB
PL13 20.00 dB
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F2 - Processing parameters
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SSB 0
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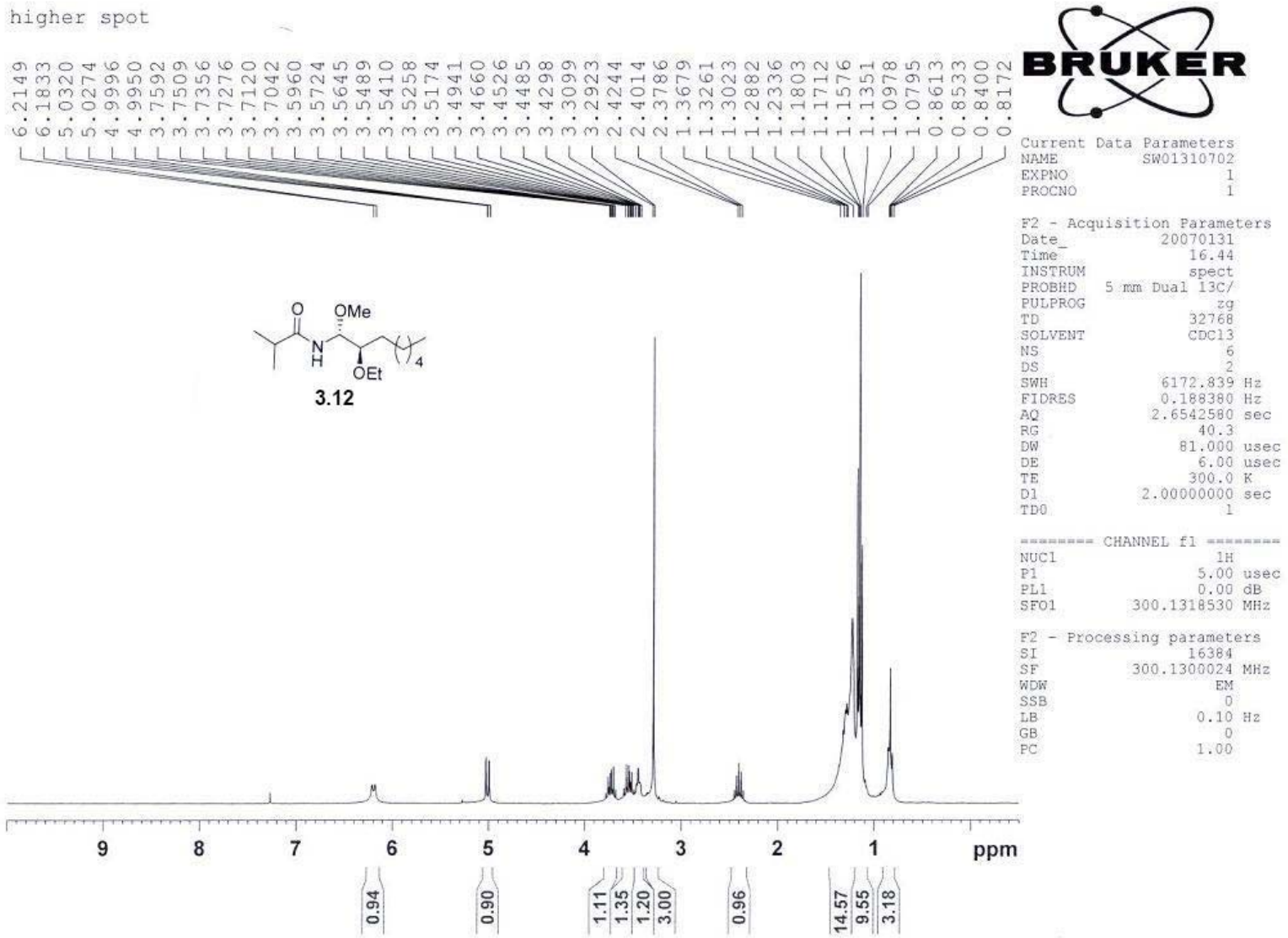
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3.7509
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3.5410
3.5258
3.5174
3.4941
3.4660
3.4526
3.4485
3.4298
3.3099
3.2923
2.4244
2.4014
2.3786
1.3679
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1.2336
1.1803
1.1712
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Current Data Parameters
NAME SW01310702
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
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Time 16.44
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PULPROG zg
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SOLVENT CDCl3
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SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 40.3
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1
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F2 - Processing parameters
SI 16384
SF 300.1300024 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00
O
OMe
N
H
OEt
4
3.12
9
8
7
6
5
4
3
2
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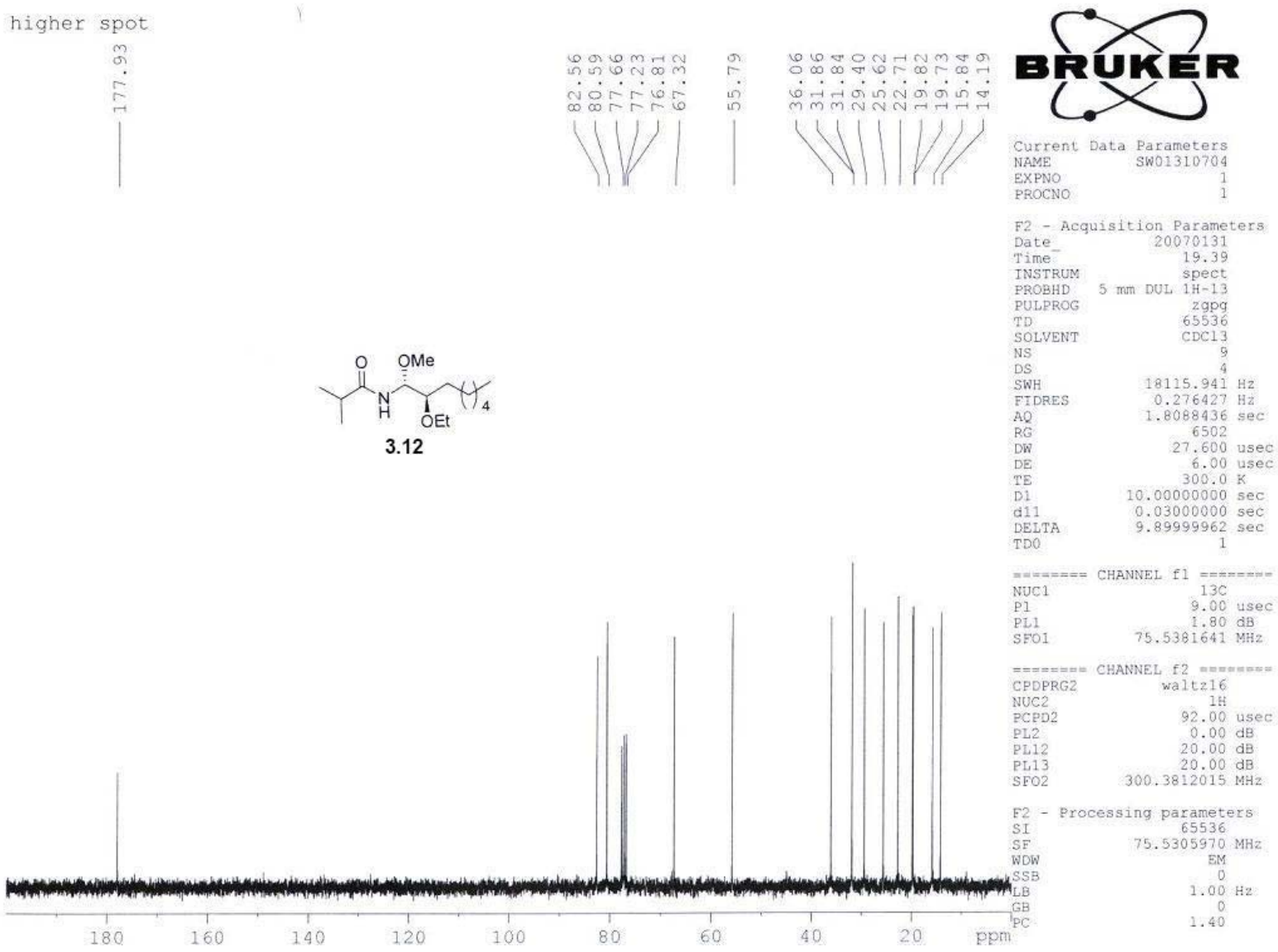
higher spot
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80.59
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77.23
76.81
67.32
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25.62
22.71
19.82
19.73
15.84
14.19
BRUKER
Current Data Parameters
NAME SW01310704
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
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Time 19.39
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PULPROG zgpg
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SOLVENT CDCl3
NS 9
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SWH 18115.941 Hz
FIDRES 0.276427 Hz
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TE 300.0 K
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SFO1 75.5381641 MHz
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NUC2 1H
PCPD2 92.00 usec
PL2 0.00 dB
PL12 20.00 dB
PL13 20.00 dB
SFO2 300.3812015 MHz
F2 - Processing parameters
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SF 75.5305970 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
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N
H
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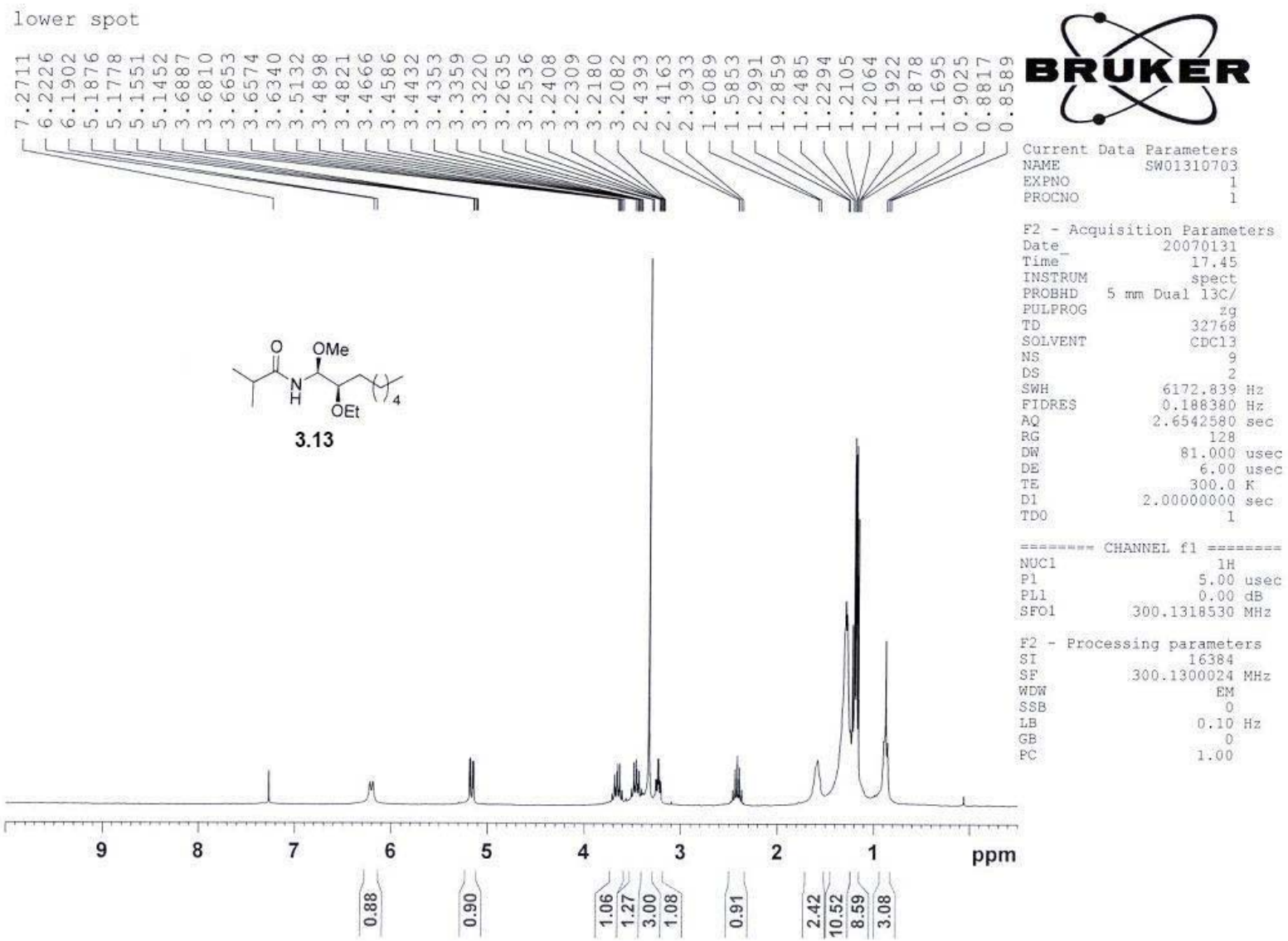
140
120
100
80
60
40
20
ppm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6.1902
5.1876
5.1778
5.1551
5.1452
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3.6810
3.6653
3.6574
3.6340
3.5132
3.4898
3.4821
3.4666
3.4586
3.4432
3.4353
3.3359
3.3220
3.2635
3.2536
3.2408
3.2309
3.2180
3.2082
2.4393
2.4163
2.3933
1.6089
1.5853
1.2991
1.2859
1.2485
1.2294
1.2105
1.2064
1.1922
1.1878
1.1695
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O
OMe
N
H
OEt
4
3.13
9
8
7
6
5
4
3
2
1
ppm
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BRUKER
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PULPROG zg
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AQ 2.6542580 sec
RG 128
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DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1
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P1 5.00 usec
PL1 0.00 dB
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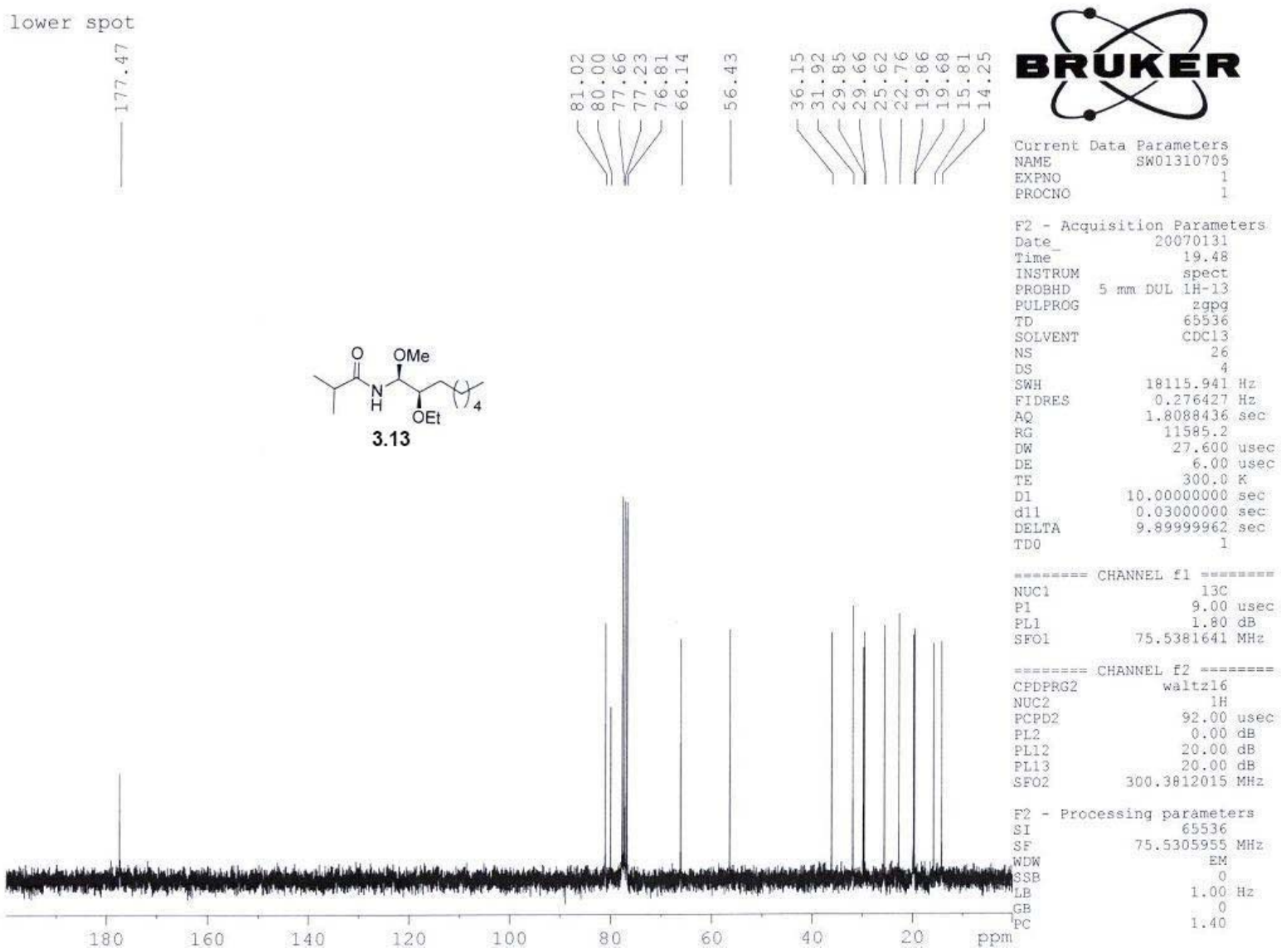
lower spot
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36.15
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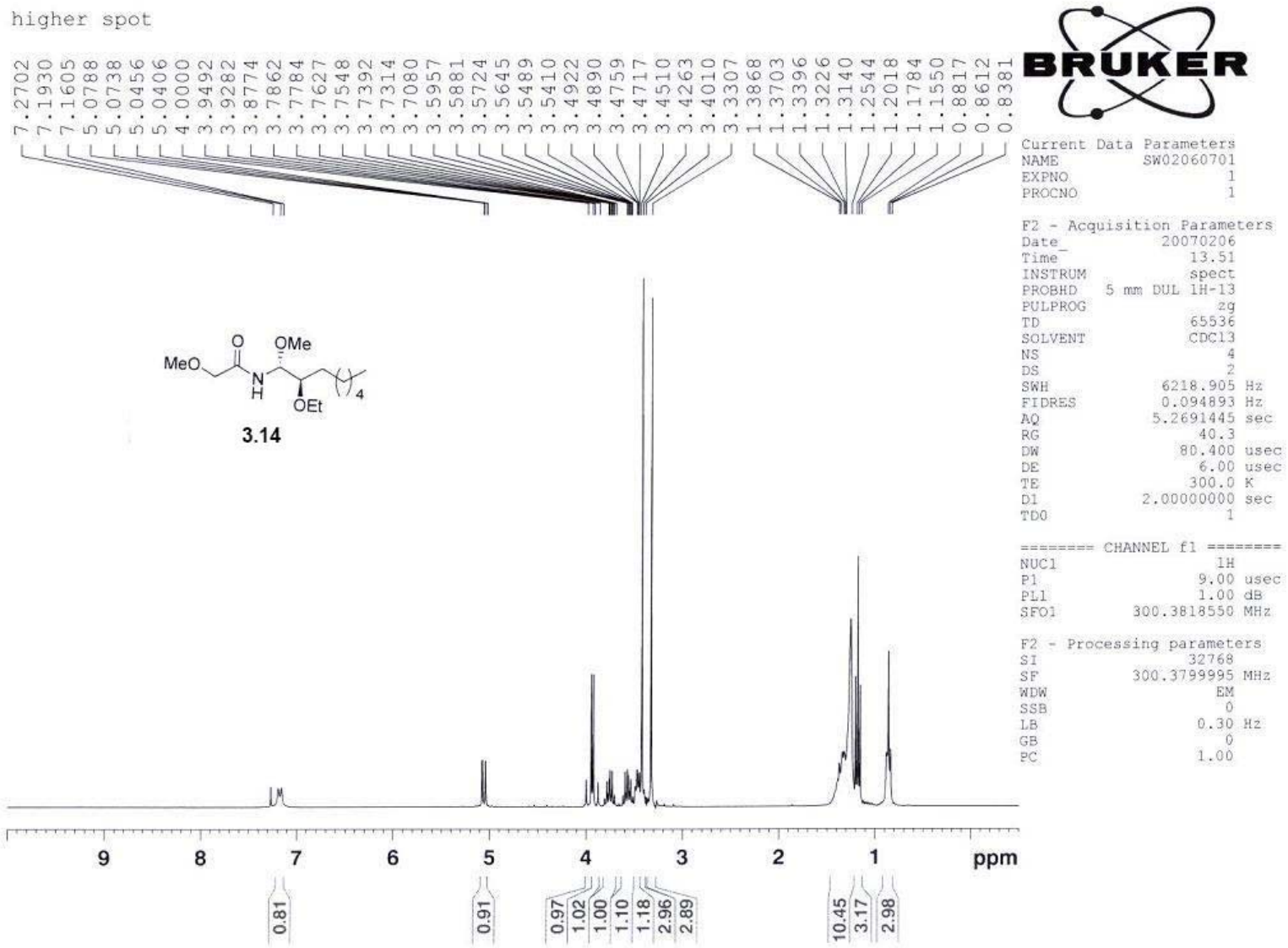
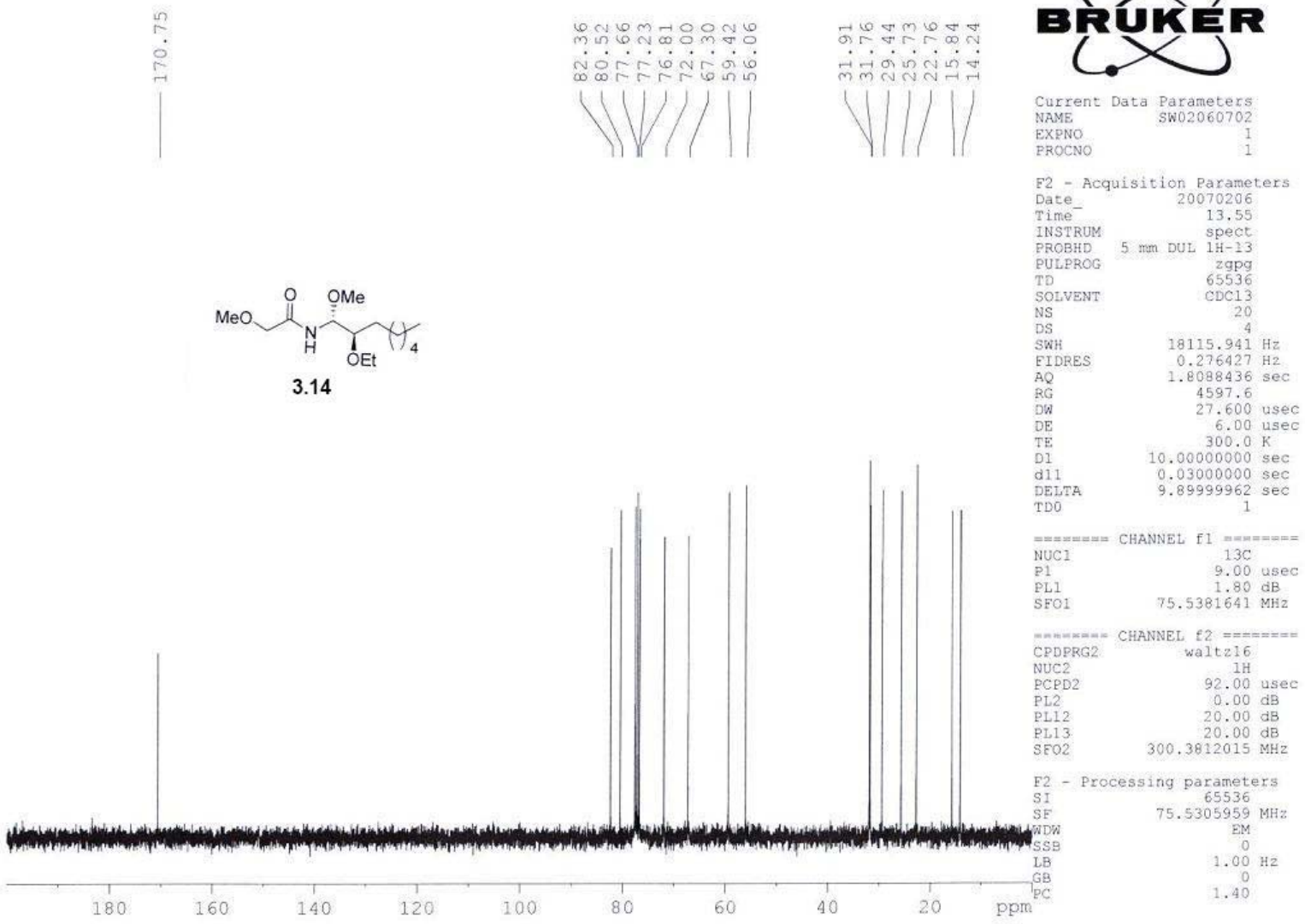
29.66
25.62
22.76
19.86
19.68
15.81
14.25
O
OMe
N
H
OEt
4
3.13
180
160
140
120
100
80
60
40
20
ppm
BRUKER
Current Data Parameters
NAME SW01310705
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070131
Time 19.48
INSTRUM spect
PROBHD 5 mm DUL 1H-13
PULPROG zgpg
TD 65536
SOLVENT CDC13
NS 26
DS 4
SWH 18115.941 Hz
FIDRES 0.276427 Hz
AQ 1.8088436 sec
RG 11585.2
DW 27.600 usec
DE 6.00 usec
TE 300.0 K
D1 10.00000000 sec
d11 0.03000000 sec
DELTA 9.89999962 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.00 usec
PL1 1.80 dB
SFO1 75.5381641 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 92.00 usec
PL2 0.00 dB
PL12 20.00 dB
PL13 20.00 dB
SFO2 300.3812015 MHz
F2 - Processing parameters
SI 65536
SF 75.5305955 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40


higher spot
7.2702
7.1930
7.1605
5.0788
5.0738
5.0456
5.0406
4.0000
3.9492
3.9282
3.8774
3.7862
3.7784
3.7627
3.7548
3.7392
3.7314
3.7080
3.5957
3.5881
3.5724
3.5645
3.5489
3.5410
3.4922
3.4890
3.4759
3.4717
3.4510
3.4263
3.4010
3.3307
1.3868
1.3703
1.3396
1.3226
1.3140
1.2544
1.2018
1.1784
1.1550
0.8817
0.8612
0.8381
MeO
O
N
H
OMe
OEt
4
3.14
9
8
7
6
5
4
3
2
1
ppm
0.81
0.91
0.97
1.02
1.00
1.10
1.18
2.96
2.89
10.45
3.17
2.98
BRUKER
Current Data Parameters
NAME SW02060701
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070206
Time 13.51
INSTRUM spect
PROBHD 5 mm DUL 1H-13
PULPROG zg
TD 65536
SOLVENT CDCl3
NS 4
DS 2
SWH 6218.905 Hz
FIDRES 0.094893 Hz
AQ 5.2691445 sec
RG 40.3
DW 80.400 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.00 usec
PL1 1.00 dB
SFO1 300.3818550 MHz
F2 - Processing parameters
SI 32768
SF 300.3799995 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

higher spot



BRUKER

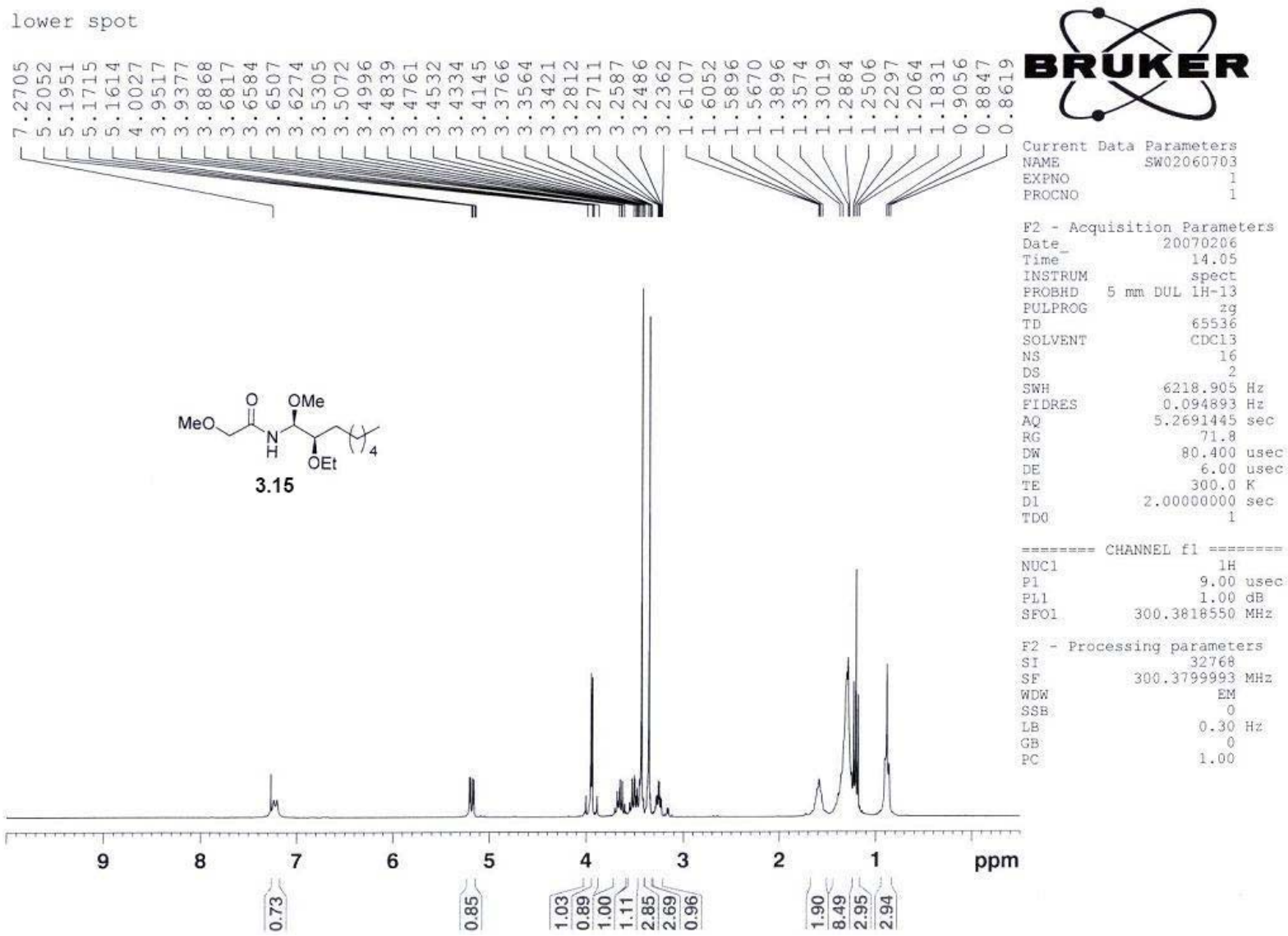
Current Data Parameters
NAME SW02060702
EXPNO 1
PROCNO 1

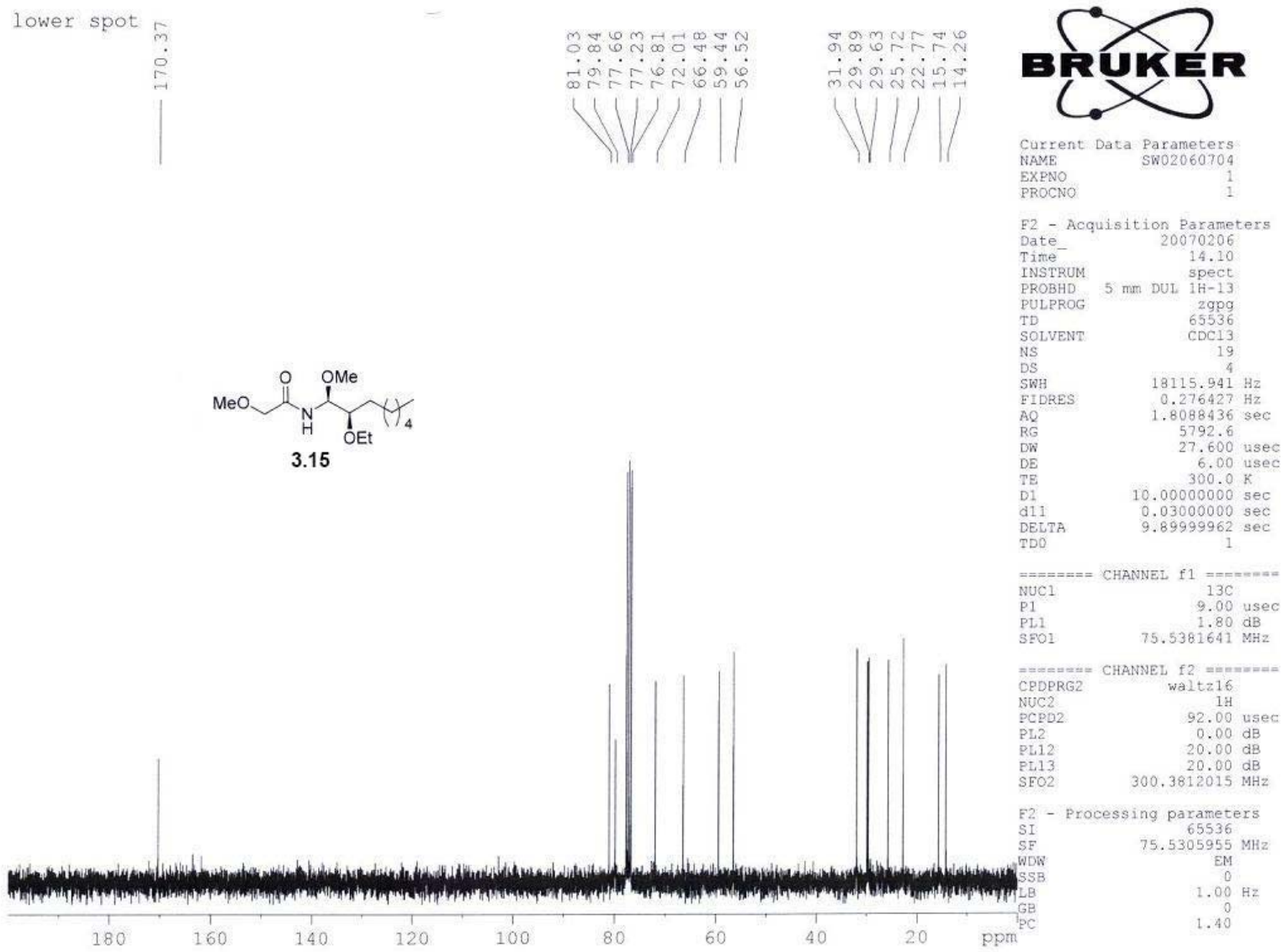
F2 - Acquisition Parameters
Date_ 20070206
Time 13.55
INSTRUM spect
PROBHD 5 mm DUL 1H-13
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 20
DS 4
SWH 18115.941 Hz
FIDRES 0.276427 Hz
AQ 1.8088436 sec
RG 4597.6
DW 27.600 usec
DE 6.00 usec
TE 300.0 K
D1 10.00000000 sec
d11 0.03000000 sec
DELTA 9.89999962 sec
TD0 1

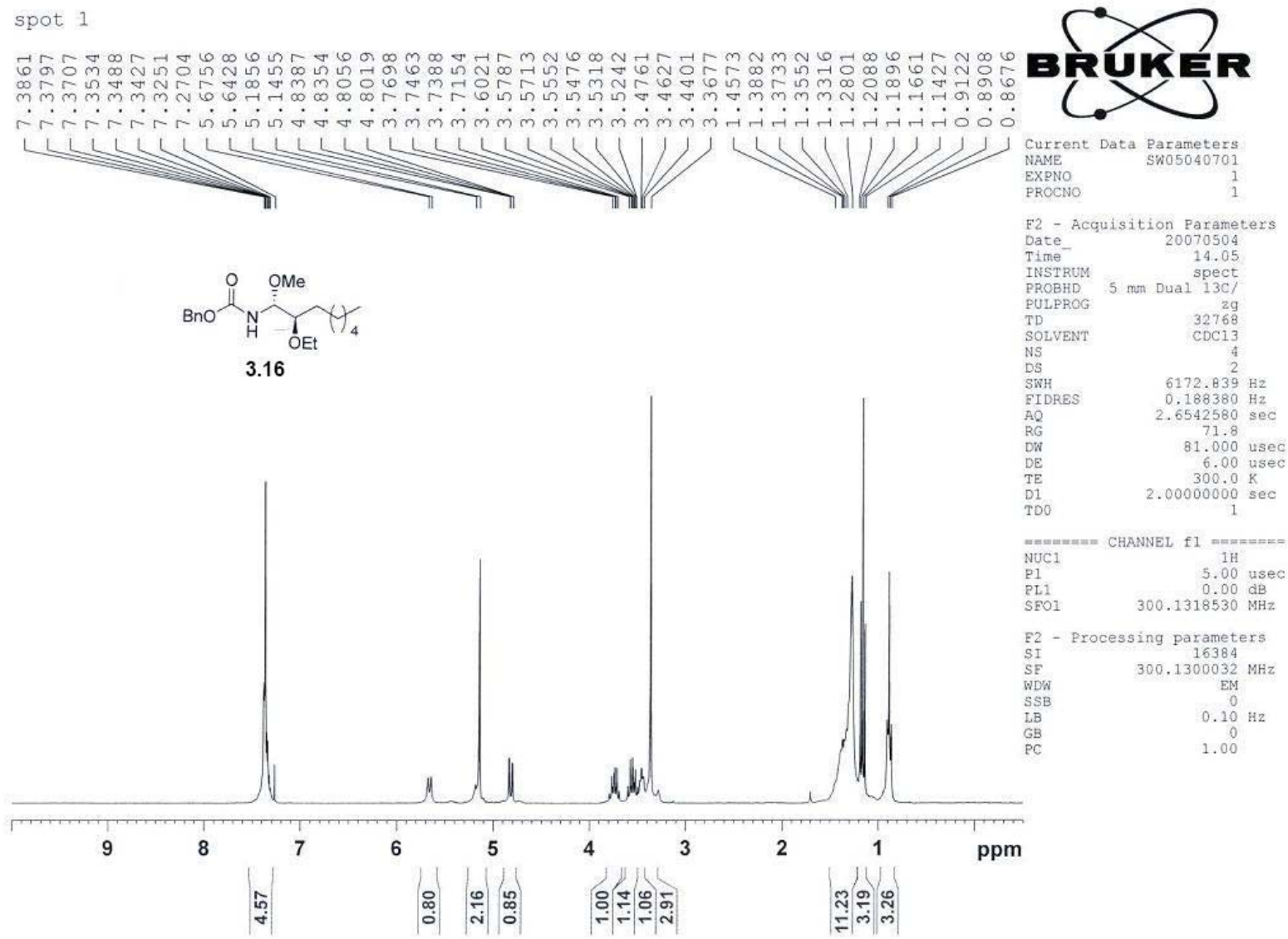
======== CHANNEL f1 ========
NUC1 13C
P1 9.00 usec
PL1 1.80 dB
SFO1 75.5381641 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 92.00 usec
PL2 0.00 dB
PL12 20.00 dB
PL13 20.00 dB
SFO2 300.3812015 MHz

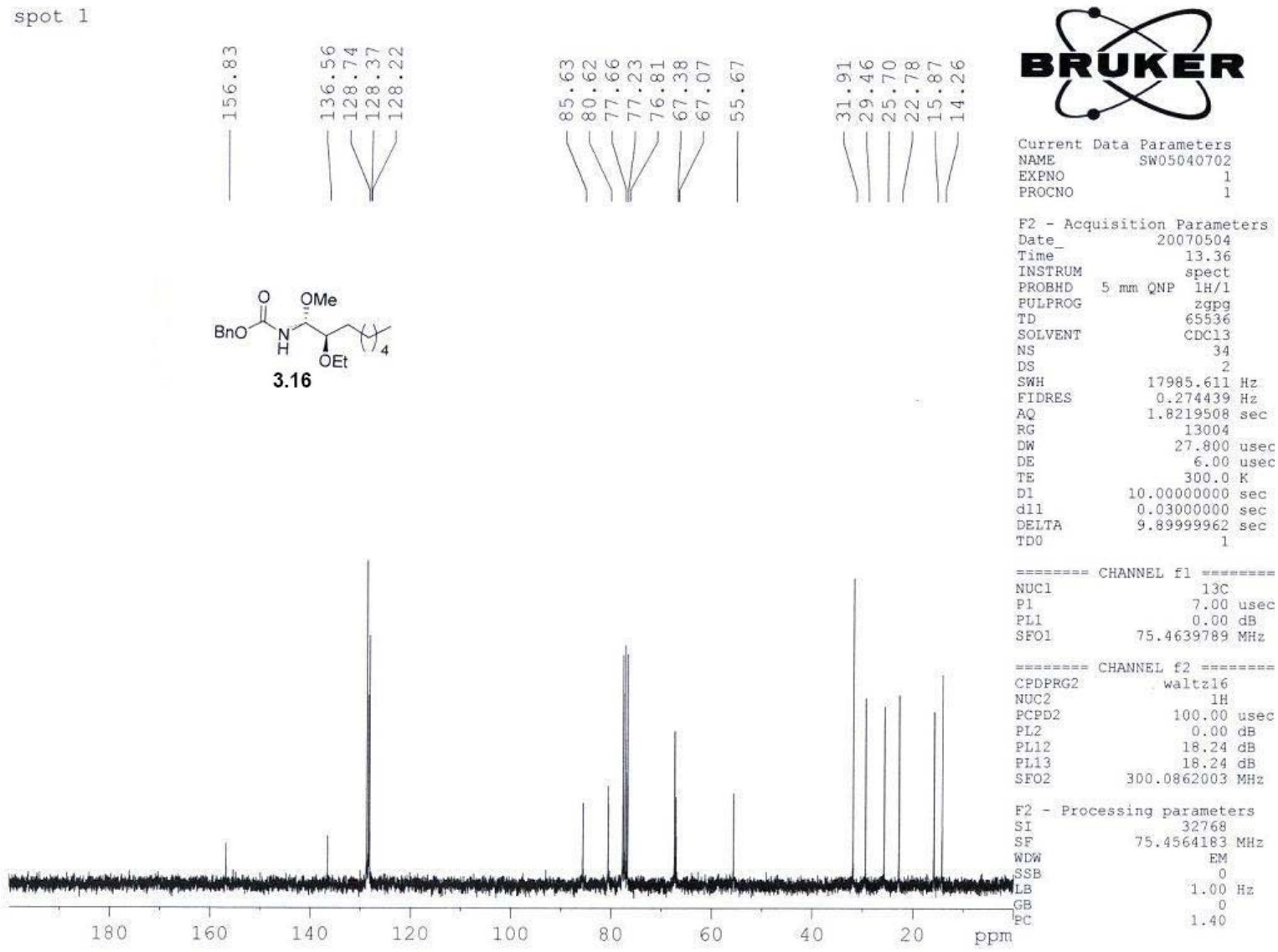
F2 - Processing parameters
SI 65536
SF 75.5305959 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40


lower spot
7.2705
5.2052
5.1951
5.1715
5.1614
4.0027
3.9517
3.9377
3.8868
3.6817
3.6584
3.6507
3.6274
3.5305
3.5072
3.4996
3.4839
3.4761
3.4532
3.4334
3.4145
3.3766
3.3564
3.3421
3.2812
3.2711
3.2587
3.2486
3.2362
1.6107
1.6052
1.5896
1.5670
1.3896
1.3574
1.3019
1.2884
1.2506
1.2297
1.2064
1.1831
0.9056
0.8847
0.8619
BRUKER
Current Data Parameters
NAME SW02060703
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070206
Time 14.05
INSTRUM spect
PROBHD 5 mm DUL 1H-13
PULPROG zg
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6218.905 Hz
FIDRES 0.094893 Hz
AQ 5.2691445 sec
RG 71.8
DW 80.400 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.00 usec
PL1 1.00 dB
SFO1 300.3818550 MHz
F2 - Processing parameters
SI 32768
SF 300.3799993 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
MeO
O
OMe
N
H
OEt
4
3.15
9
8
7
6
5
4
3
2
1
ppm
0.73
0.85
1.03
0.89
1.00
1.11
2.85
2.69
0.96
1.90
8.49
2.95
2.94


lower spot
170.37
81.03
79.84
77.66
77.23
76.81
72.01
66.48
59.44
56.52
31.94
29.89
29.63
25.72
22.77
15.74
14.26
BRUKER
Current Data Parameters
NAME SW02060704
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070206
Time 14.10
INSTRUM spect
PROBHD 5 mm DUL 1H-13
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 19
DS 4
SWH 18115.941 Hz
FIDRES 0.276427 Hz
AQ 1.8088436 sec
RG 5792.6
DW 27.600 usec
DE 6.00 usec
TE 300.0 K
D1 10.00000000 sec
d11 0.03000000 sec
DELTA 9.89999962 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.00 usec
PL1 1.80 dB
SFO1 75.5381641 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 92.00 usec
PL2 0.00 dB
PL12 20.00 dB
PL13 20.00 dB
SFO2 300.3812015 MHz
F2 - Processing parameters
SI 65536
SF 75.5305955 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
MeO
O
OMe
N
H
OEt
4
3.15
180
160
140
120
100
80
60
40
20
ppm


spot 1
7.3861
7.3797
7.3707
7.3534
7.3488
7.3427
7.3251
7.2704
5.6756
5.6428
5.1856
5.1455
4.8387
4.8354
4.8056
4.8019
3.7698
3.7463
3.7388
3.7154
3.6021
3.5787
3.5713
3.5552
3.5476
3.5318
3.5242
3.4761
3.4627
3.4401
3.3677
1.4573
1.3882
1.3733
1.3552
1.3316
1.2801
1.2088
1.1896
1.1661
1.1427
0.9122
0.8908
0.8676
BRUKER
Current Data Parameters
NAME SW05040701
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070504
Time 14.05
INSTRUM spect
PROBHD 5 mm Dual 13C/
PULPROG zg
TD 32768
SOLVENT CDC13
NS 4
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 71.8
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 5.00 usec
PL1 0.00 dB
SFO1 300.1318530 MHz
F2 - Processing parameters
SI 16384
SF 300.1300032 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00
BnO
OMe
OEt
4
3.16
9
8
7
6
5
4
3
2
1
ppm
4.57
0.80
2.16
0.85
1.00
1.14
1.06
2.91
11.23
3.19
3.26

spot 1



BRUKER

Current Data Parameters

NAME	SW05040702
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20070504	
Time	13.36	
INSTRUM	spect	
PROBHD	5 mm QNP 1H/1	
PULPROG	zgpg	
TD	65536	
SOLVENT	CDCl3	
NS	34	
DS	2	
SWH	17985.611	Hz
FIDRES	0.274439	Hz
AQ	1.8219508	sec
RG	13004	
DW	27.800	usec
DE	6.00	usec
TE	300.0	K
D1	10.00000000	sec
d11	0.03000000	sec
DELTA	9.89999962	sec
TD0	1	

======== CHANNEL f1 ========

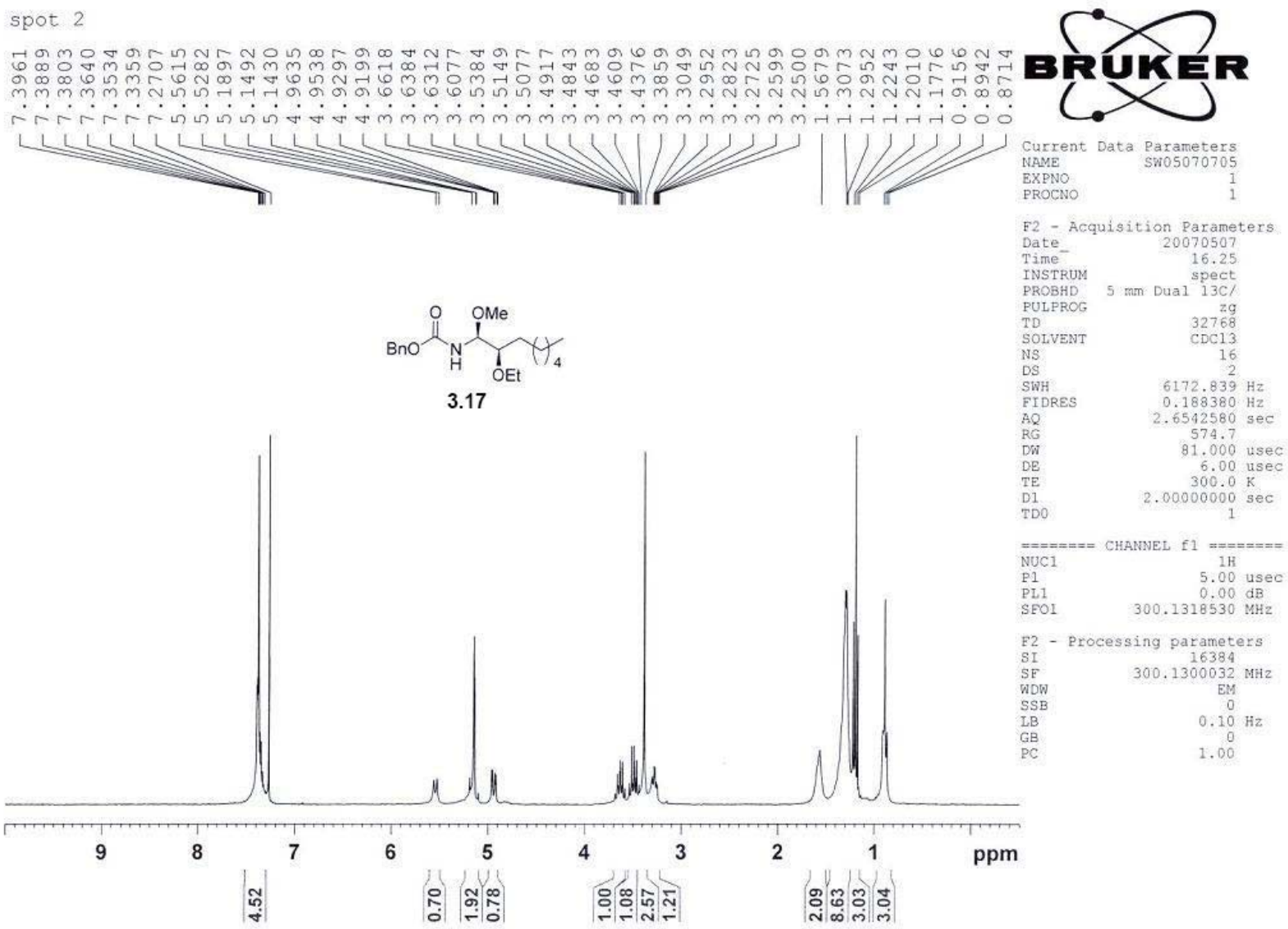
NUC1	13C	
P1	7.00	usec
PL1	0.00	dB
SFO1	75.4639789	MHz

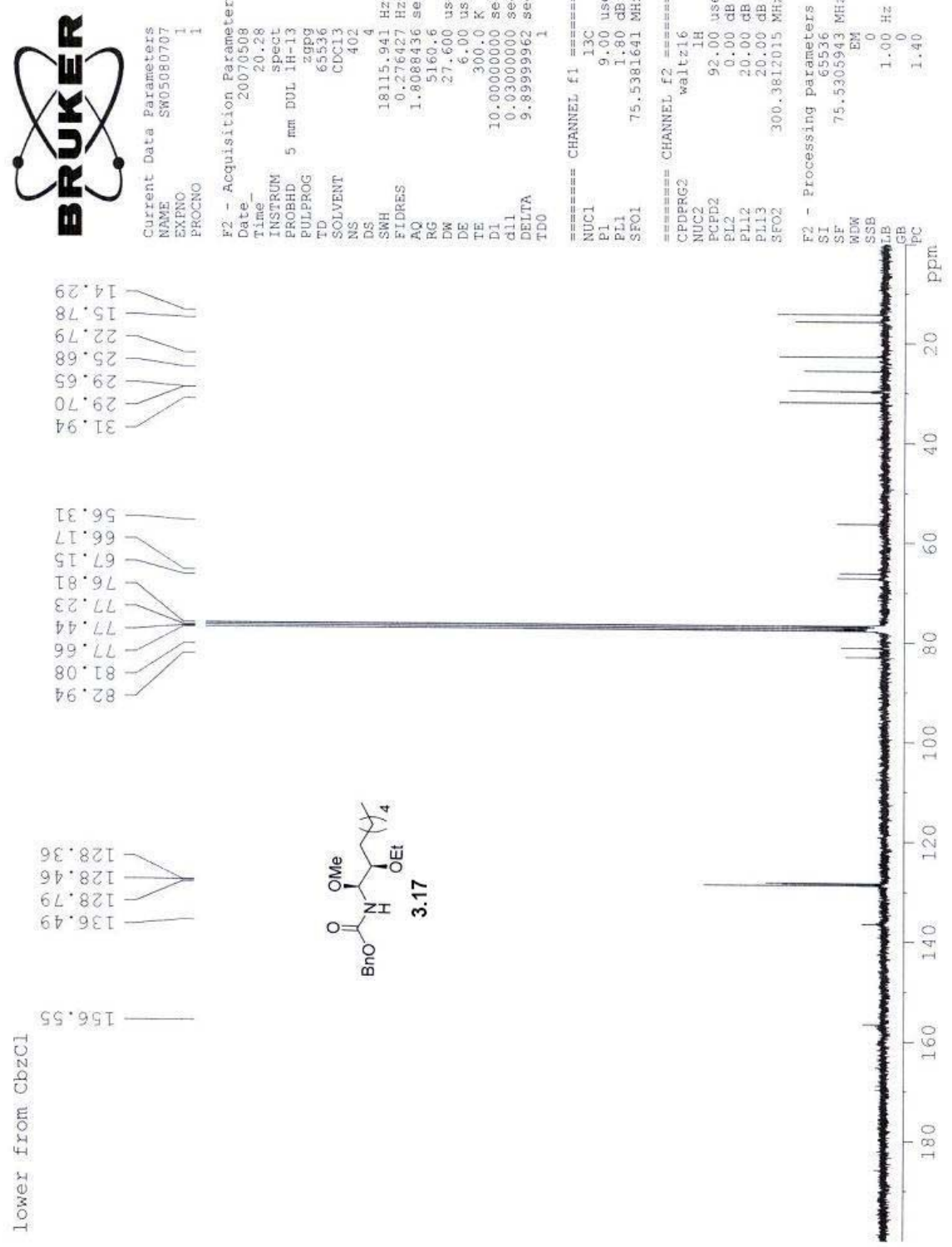
======== CHANNEL f2 ========

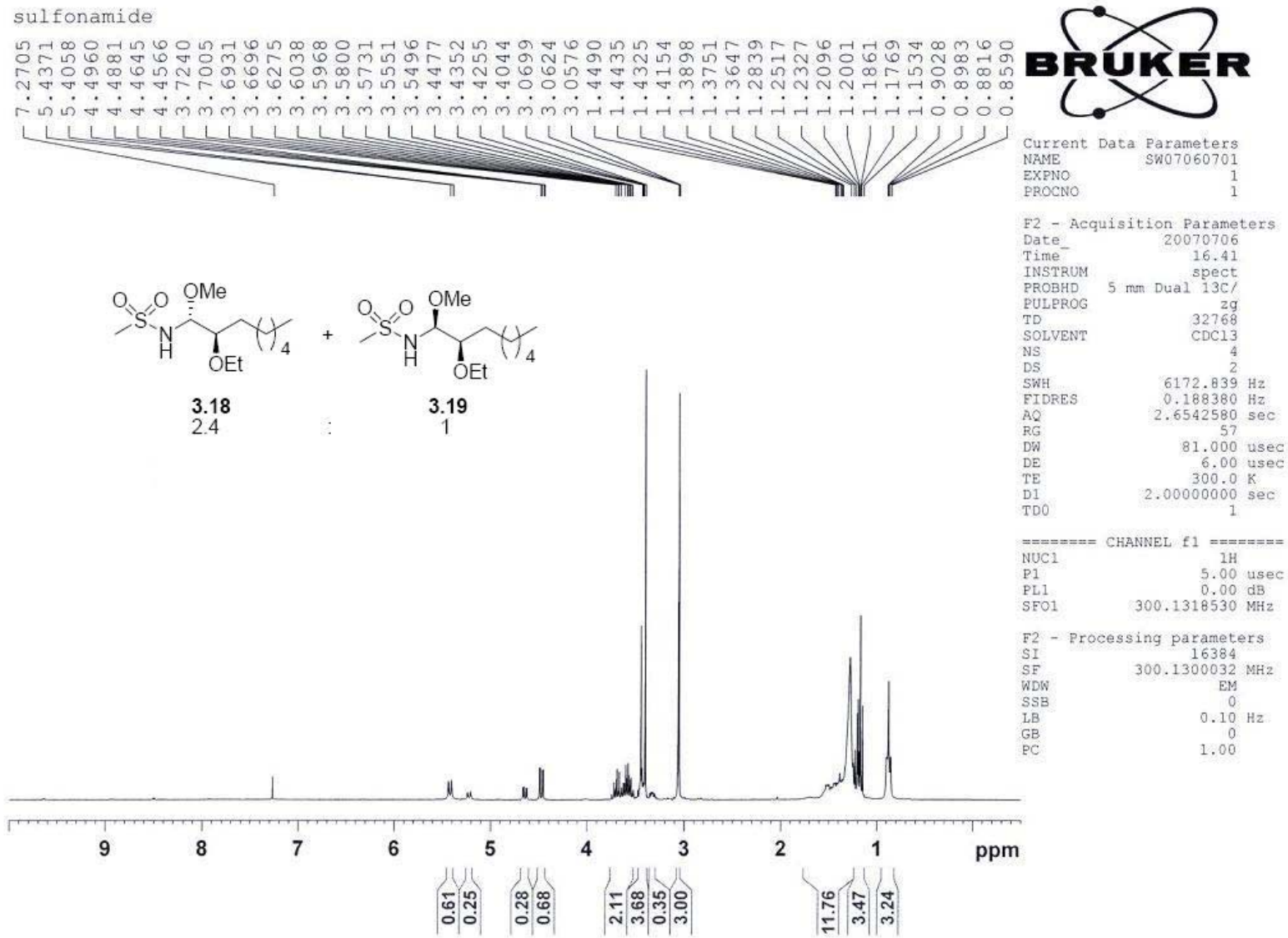
CPDPRG2	waltz16	
NUC2	1H	
PCPD2	100.00	usec
PL2	0.00	dB
PL12	18.24	dB
PL13	18.24	dB
SFO2	300.0862003	MHz

F2 - Processing parameters

SI	32768	
SF	75.4564183	MHz
WDW	EM	
SSB	0	
LB	1.00	Hz
GB	0	
PC	1.40	


spot 2
7.3961
7.3889
7.3803
7.3640
7.3534
7.3359
7.2707
5.5615
5.5282
5.1897
5.1492
5.1430
4.9635
4.9538
4.9297
4.9199
3.6618
3.6384
3.6312
3.6077
3.5384
3.5149
3.5077
3.4917
3.4843
3.4683
3.4609
3.4376
3.3859
3.3049
3.2952
3.2823
3.2725
3.2599
3.2500
1.5679
1.3073
1.2952
1.2243
1.2010
1.1776
0.9156
0.8942
0.8714
BRUKER
Current Data Parameters
NAME SW05070705
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070507
Time 16.25
INSTRUM spect
PROBHD 5 mm Dual 13C/
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 574.7
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 5.00 usec
PL1 0.00 dB
SFO1 300.1318530 MHz
F2 - Processing parameters
SI 16384
SF 300.1300032 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00
O
OMe
BnO
N
H
OEt
4
3.17
9
8
7
6
5
4
3
2
1
ppm
4.52
0.70
1.92
0.78
1.00
1.08
2.57
1.21
2.09
8.63
3.03
3.04


lower from CbzCl
156.55
136.49
128.79
128.46
128.36
82.94
81.08
77.66
77.44
77.23
76.81
67.15
66.17
56.31
31.94
29.70
29.65
25.68
22.79
15.78
14.29
BnO
O
N
H
OMe
OEt
4
3.17
Current Data Parameters
NAME SW05080707
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070508
Time 20.28
INSTRUM spect
PROBHD 5 mm DUL 1H-13
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 402
DS 4
SWH 18115.941 Hz
FIDRES 0.276427 Hz
AQ 1.80884436 sec
RG 5160.6
DW 27.600 usec
DE 6.00 usec
TE 300.0 K
D1 10.00000000 sec
d11 0.03000000 sec
DELTA 9.89999962 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.00 usec
PL1 1.80 dB
SFO1 75.5381641 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 92.00 usec
PL2 0.00 dB
PL12 20.00 dB
PL13 20.00 dB
SFO2 300.3812015 MHz
F2 - Processing parameters
SI 65536
SF 75.5305943 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
180 160 140 120 100 80 60 40 20 ppm



BRUKER

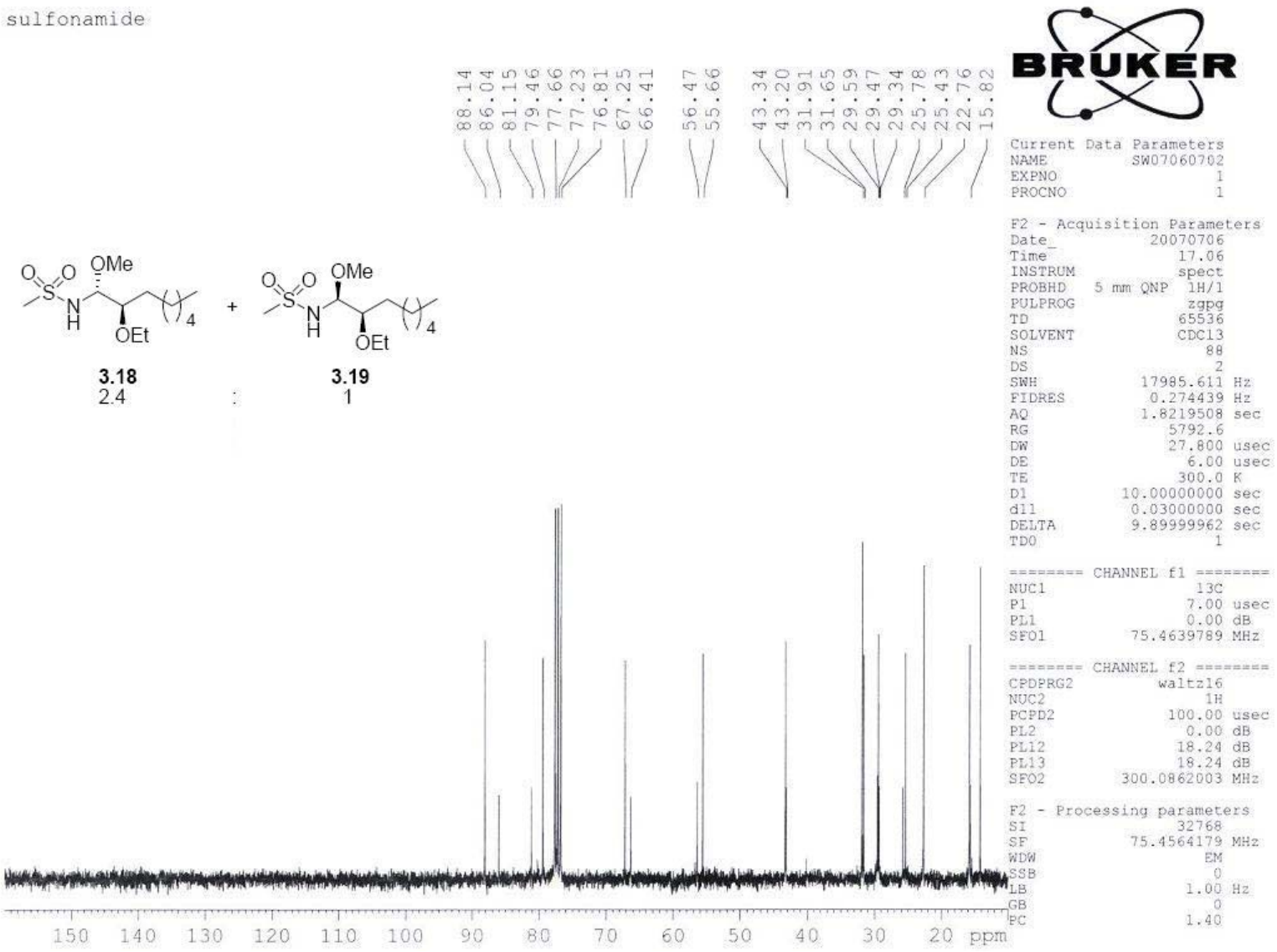
Current Data Parameters
NAME SW07060701
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20070706
Time 16.41
INSTRUM spect
PROBHD 5 mm Dual 13C/
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 4
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 57
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 5.00 usec
PL1 0.00 dB
SFO1 300.1318530 MHz

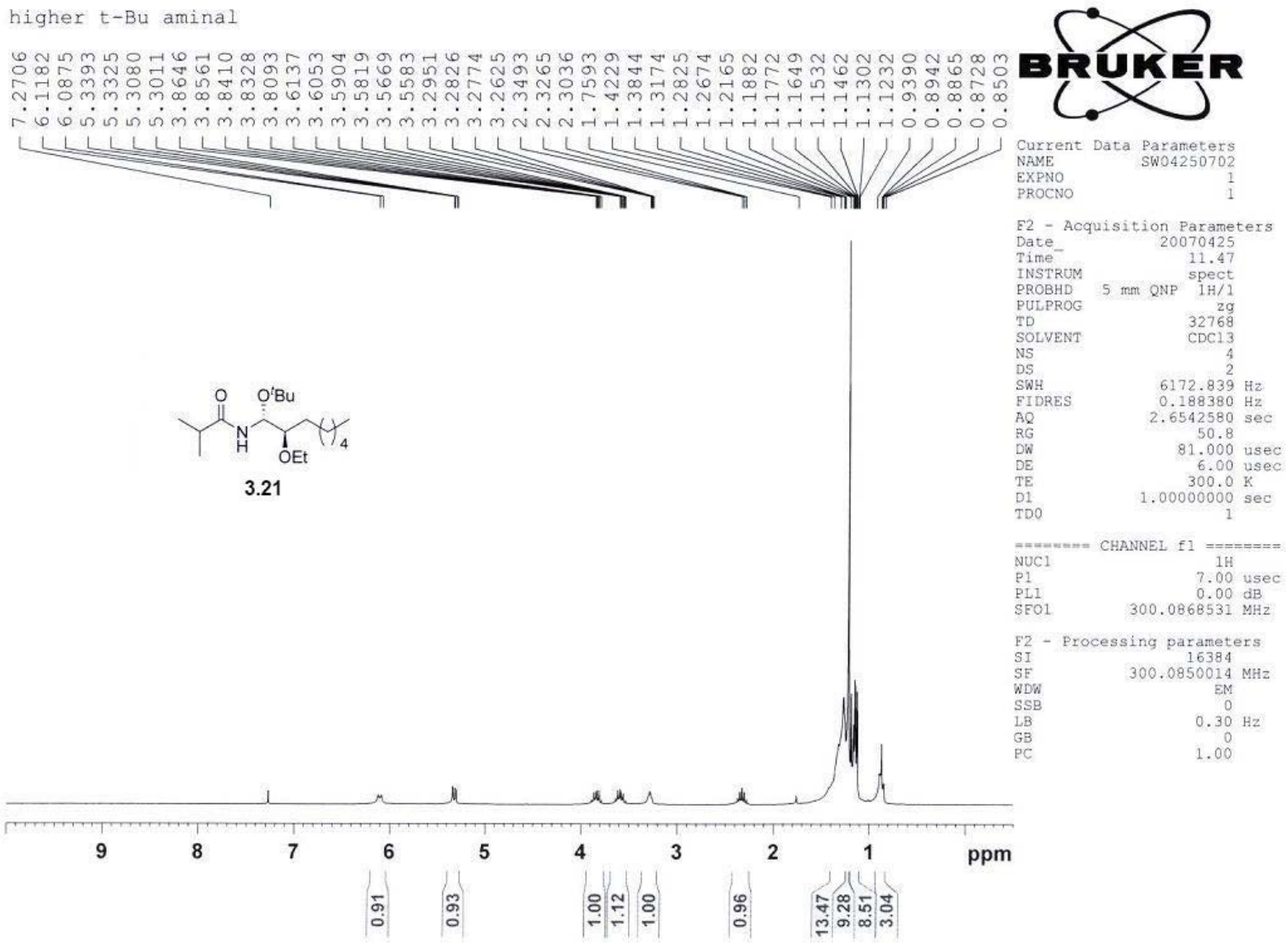
F2 - Processing parameters
SI 16384
SF 300.1300032 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

sulfonamide

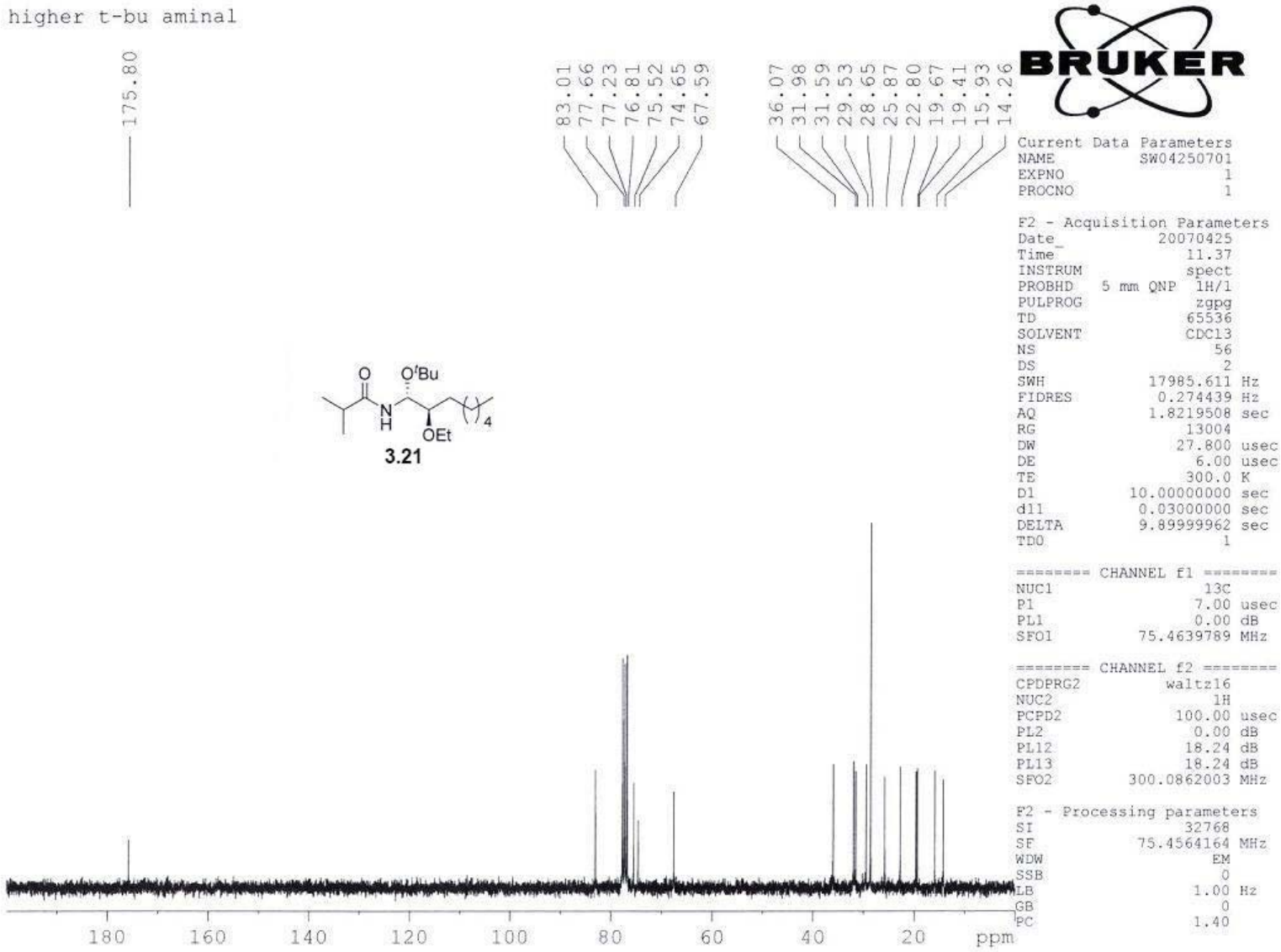


3.18 : **3.19**

2.4 : 1


higher t-Bu aminal
7.2706
6.1182
6.0875
5.3393
5.3325
5.3080
5.3011
3.8646
3.8561
3.8410
3.8328
3.8093
3.6137
3.6053
3.5904
3.5819
3.5669
3.5583
3.2951
3.2826
3.2774
3.2625
2.3493
2.3265
2.3036
1.7593
1.4229
1.3844
1.3174
1.2825
1.2674
1.2165
1.1882
1.1772
1.1649
1.1532
1.1462
1.1302
1.1232
0.9390
0.8942
0.8865
0.8728
0.8503
BRUKER
Current Data Parameters
NAME SW04250702
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070425
Time 11.47
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 4
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 50.8
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 7.00 usec
PL1 0.00 dB
SFO1 300.0868531 MHz
F2 - Processing parameters
SI 16384
SF 300.0850014 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
O
O^{t}Bu
N
H
OEt
4
3.21
9
8
7
6
5
4
3
2
1
ppm
0.91
0.93
1.00
1.12
1.00
0.96
13.47
9.28
8.51
3.04

higher t-bu aminal



BRUKER

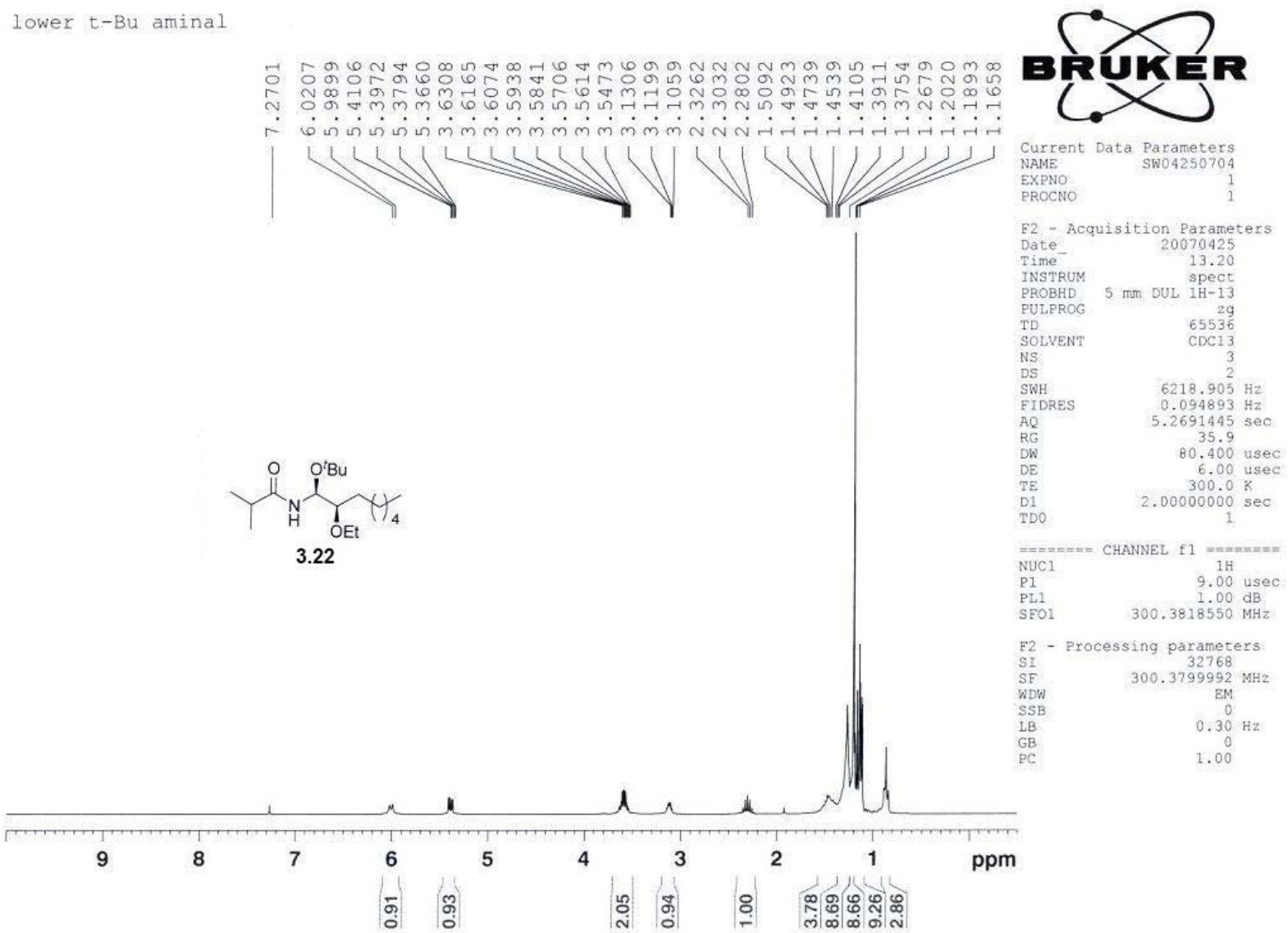
Current Data Parameters
NAME SW04250701
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20070425
Time 11.37
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 56
DS 2
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 13004
DW 27.800 usec
DE 6.00 usec
TE 300.0 K
D1 10.00000000 sec
d11 0.03000000 sec
DELTA 9.89999962 sec
TD0 1

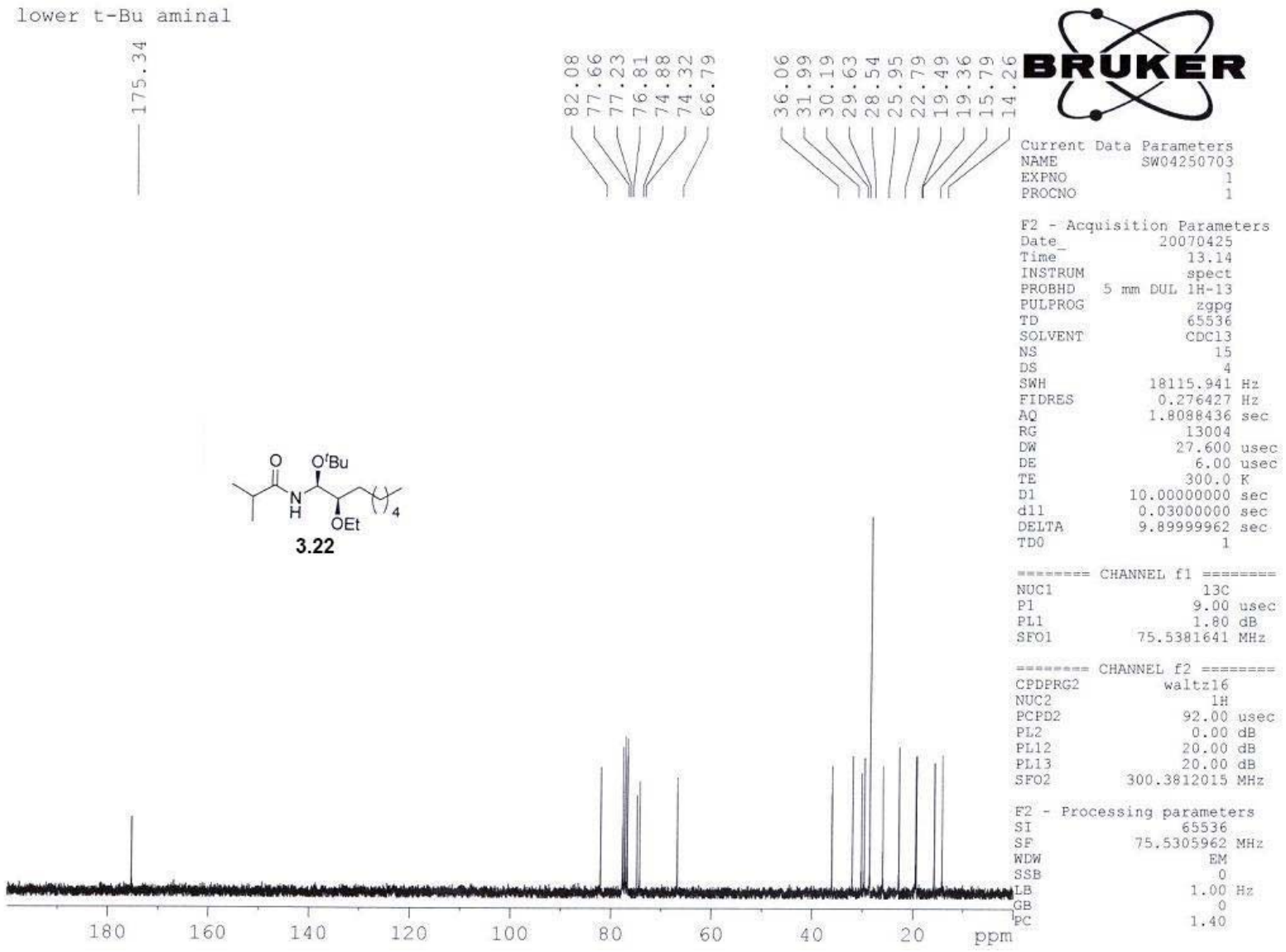
======== CHANNEL f1 ========
NUC1 13C
P1 7.00 usec
PL1 0.00 dB
SFO1 75.4639789 MHz

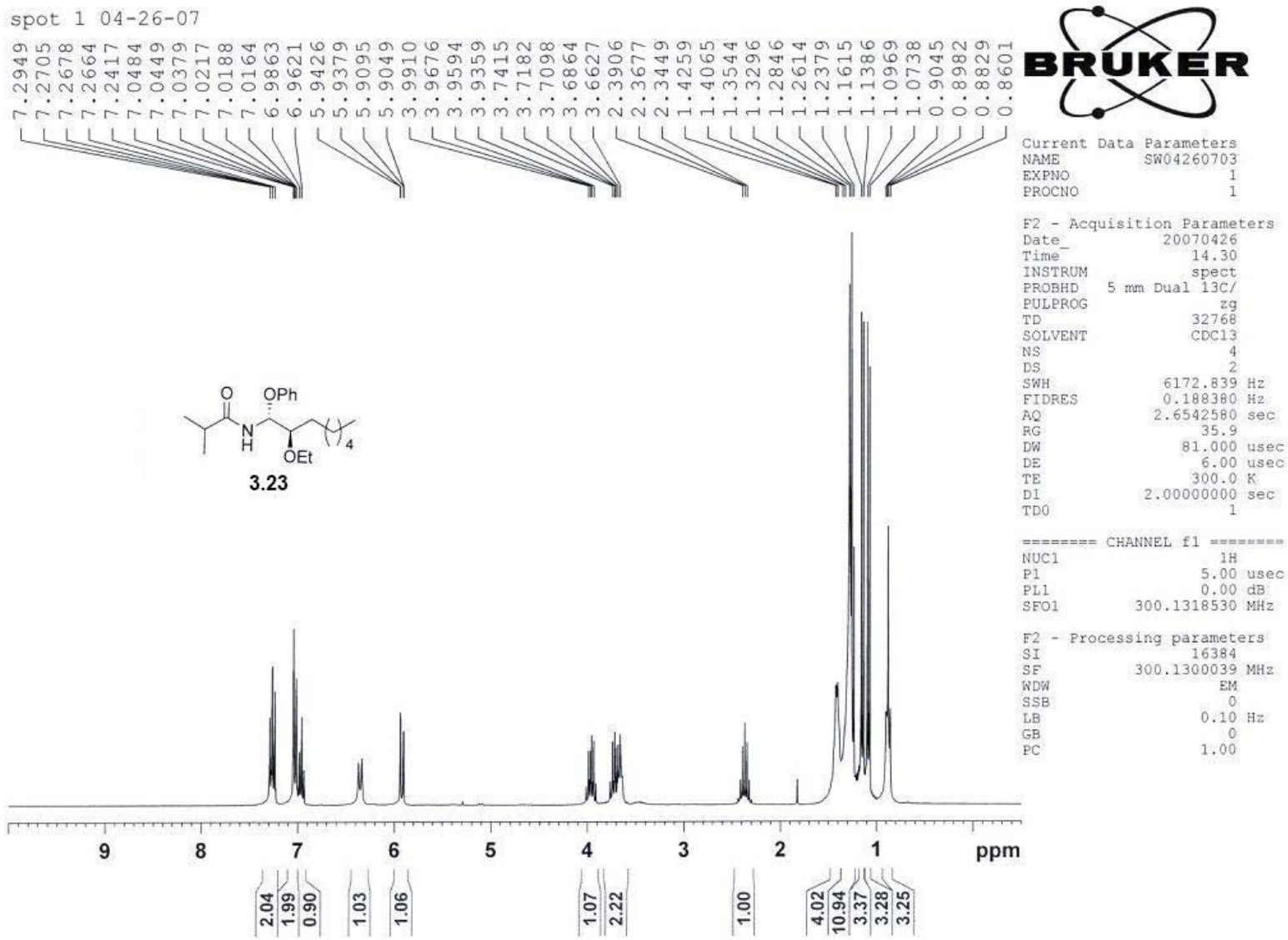
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 0.00 dB
PL12 18.24 dB
PL13 18.24 dB
SFO2 300.0862003 MHz

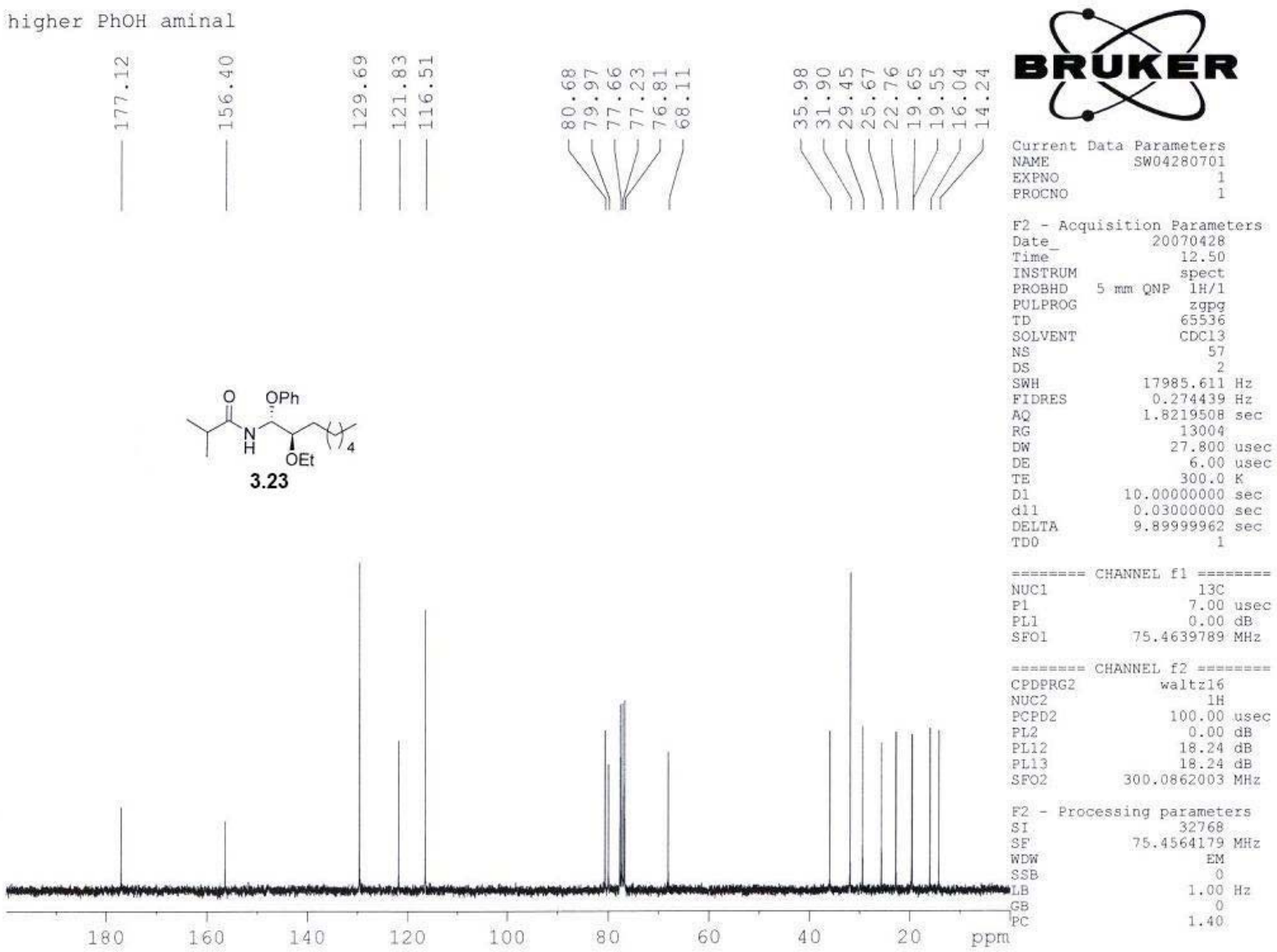
F2 - Processing parameters
SI 32768
SF 75.4564164 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

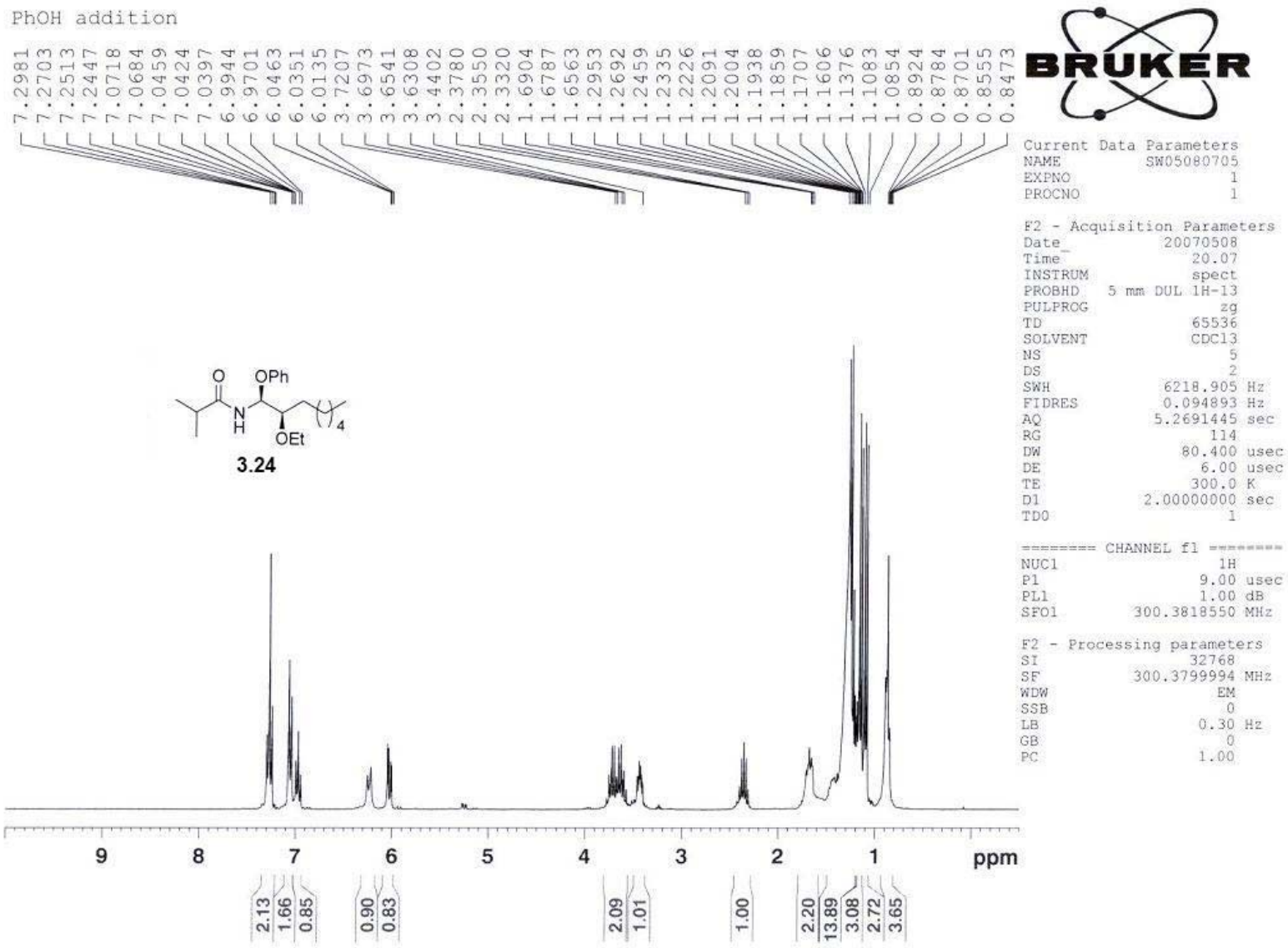

lower t-Bu aminal
7.2701
6.0207
5.9899
5.4106
5.3972
5.3794
5.3660
3.6308
3.6165
3.6074
3.5938
3.5841
3.5706
3.5614
3.5473
3.1306
3.1199
3.1059
2.3262
2.3032
2.2802
1.5092
1.4923
1.4739
1.4539
1.4105
1.3911
1.3754
1.2679
1.2020
1.1893
1.1658
O
O'Bu
N
H
OEt
4
3.22
9
8
7
6
5
4
3
2
1
ppm
0.91
0.93
2.05
0.94
1.00
3.78
8.69
8.66
9.26
2.86
BRUKER
Current Data Parameters
NAME SW04250704
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070425
Time 13.20
INSTRUM spect
PROBHD 5 mm DUL 1H-13
PULPROG zg
TD 65536
SOLVENT CDCl3
NS 3
DS 2
SWH 6218.905 Hz
FIDRES 0.094893 Hz
AQ 5.2691445 sec
RG 35.9
DW 80.400 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.00 usec
PL1 1.00 dB
SFO1 300.3818550 MHz
F2 - Processing parameters
SI 32768
SF 300.3799992 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

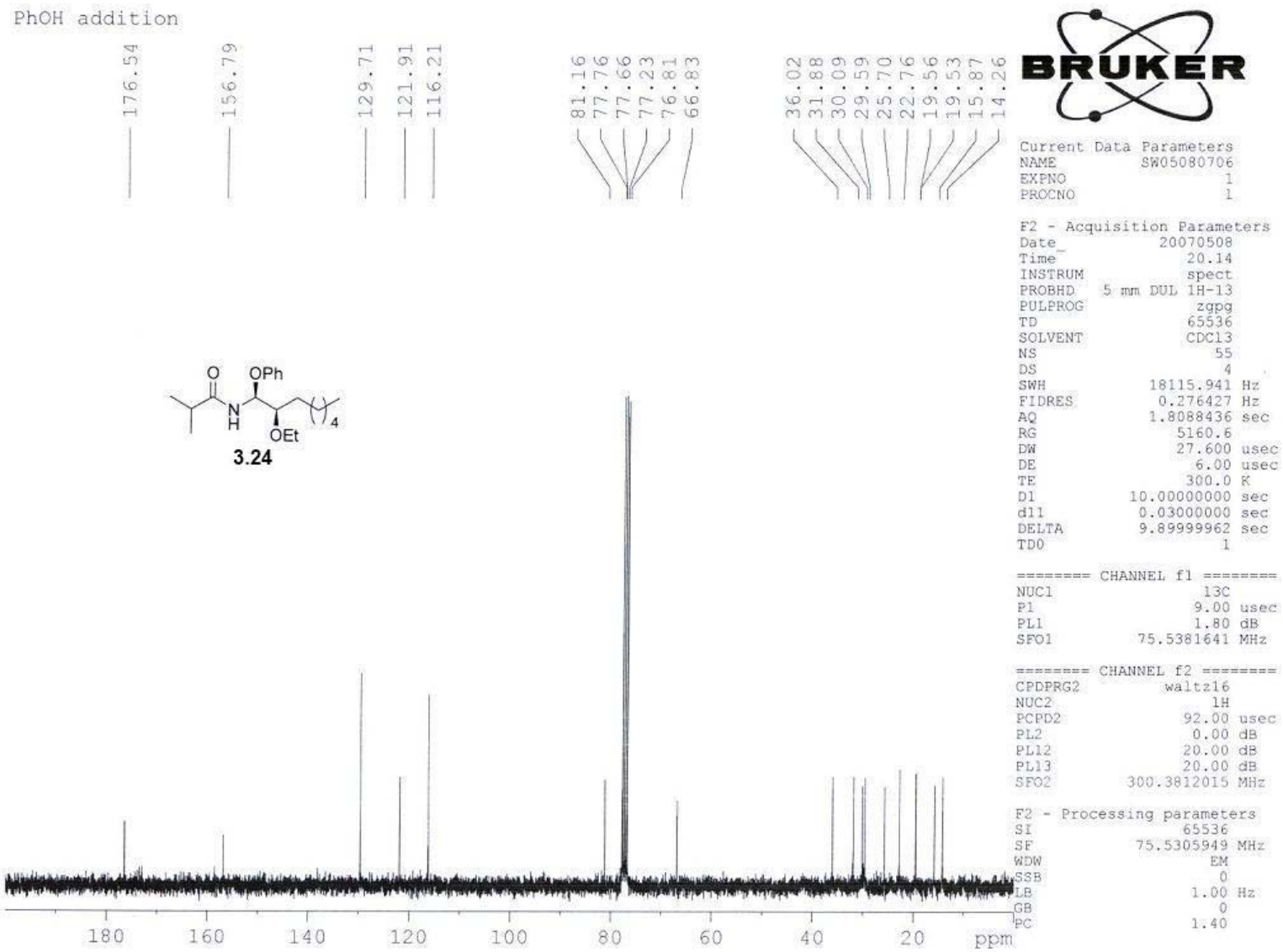
lower t-Bu aminal

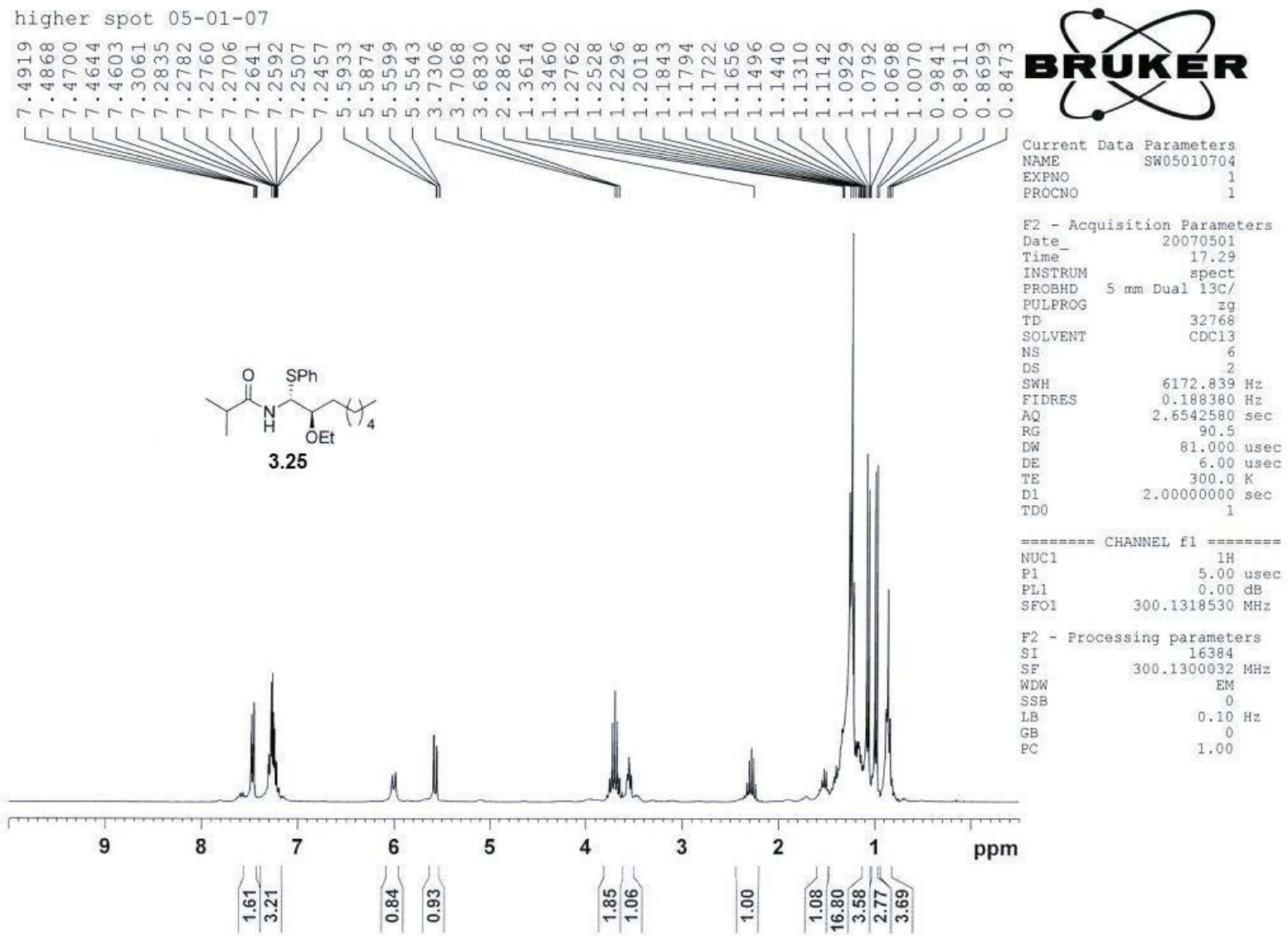



spot 1 04-26-07
7.2949
7.2705
7.2678
7.2664
7.2417
7.0484
7.0449
7.0379
7.0217
7.0188
7.0164
6.9863
6.9621
5.9426
5.9379
5.9095
5.9049
3.9910
3.9676
3.9594
3.9359
3.7415
3.7182
3.7098
3.6864
3.6627
3.3906
2.3677
2.3449
1.4259
1.4065
1.3544
1.3296
1.2846
1.2614
1.2379
1.1615
1.1386
1.0969
1.0738
0.9045
0.8982
0.8829
0.8601
BRUKER
Current Data Parameters
NAME SW04260703
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070426
Time 14.30
INSTRUM spect
PROBHD 5 mm Dual 13C/
PULPROG zg
TD 32768
SOLVENT CDC13
NS 4
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 35.9
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 5.00 usec
PL1 0.00 dB
SFO1 300.1318530 MHz
F2 - Processing parameters
SI 16384
SF 300.1300039 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00
O
OPh
N
H
OEt
4
3.23
9
8
7
6
5
4
3
2
1
ppm
2.04
1.99
0.90
1.03
1.06
1.07
2.22
1.00
4.02
10.94
3.37
3.28
3.25

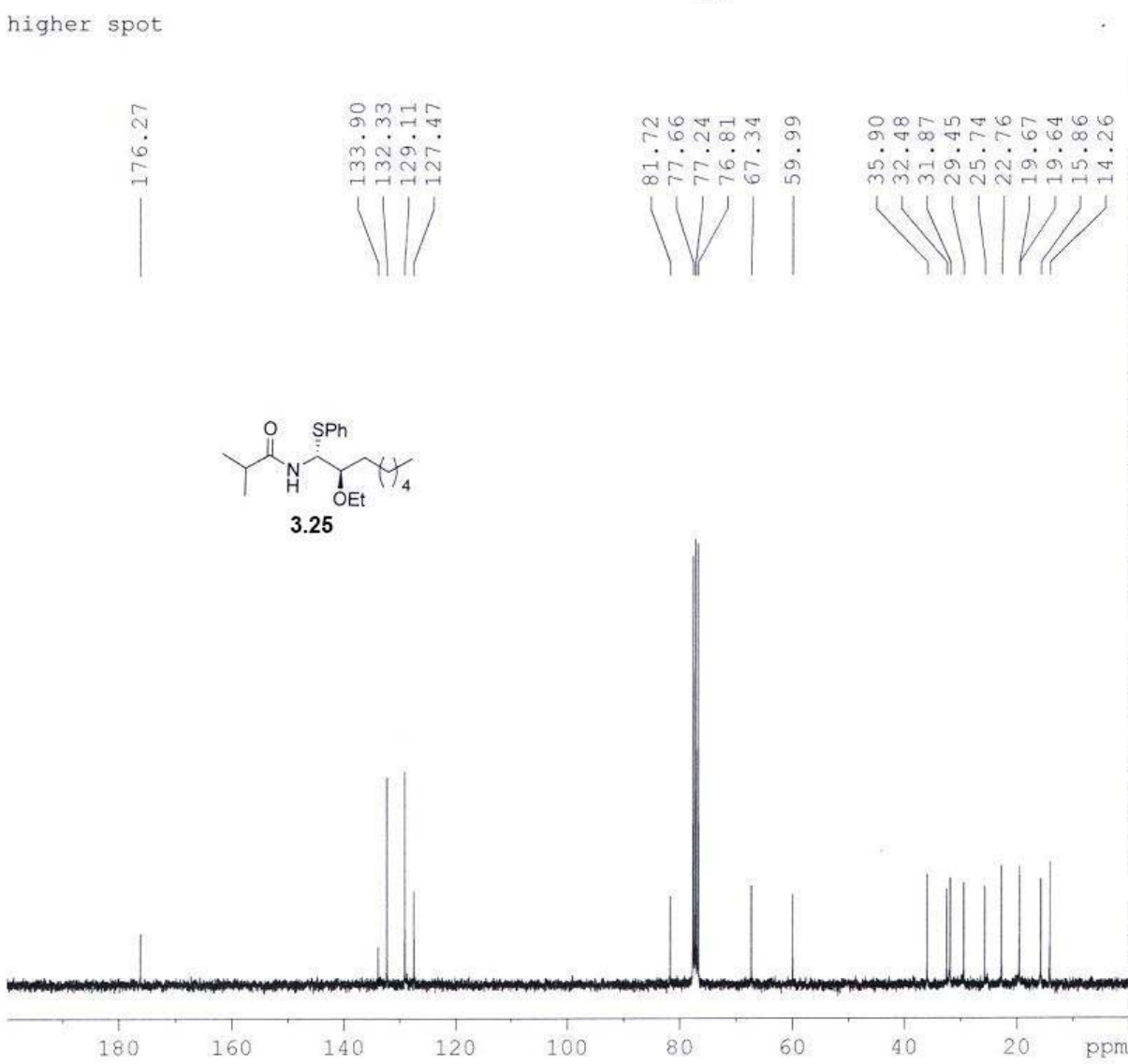

higher PhOH aminal
177.12
156.40
129.69
121.83
116.51
80.68
79.97
77.66
77.23
76.81
68.11
35.98
31.90
29.45
25.67
22.76
19.65
19.55
16.04
14.24
O
OPh
N
H
OEt
4
3.23
180
160
140
120
100
80
60
40
20
ppm
BRUKER
Current Data Parameters
NAME SW04280701
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070428
Time 12.50
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 57
DS 2
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 13004
DW 27.800 usec
DE 6.00 usec
TE 300.0 K
D1 10.00000000 sec
d11 0.03000000 sec
DELTA 9.89999962 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.00 usec
PL1 0.00 dB
SFO1 75.4639789 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 0.00 dB
PL12 18.24 dB
PL13 18.24 dB
SFO2 300.0862003 MHz
F2 - Processing parameters
SI 32768
SF 75.4564179 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40


PhOH addition
7.2981
7.2703
7.2513
7.2447
7.0718
7.0684
7.0459
7.0424
7.0397
6.9944
6.9701
6.0463
6.0351
6.0135
3.7207
3.6973
3.6541
3.6308
3.4402
2.3780
2.3550
2.3320
1.6904
1.6787
1.6563
1.2953
1.2692
1.2459
1.2335
1.2226
1.2091
1.2004
1.1938
1.1859
1.1707
1.1606
1.1376
1.1083
1.0854
0.8924
0.8784
0.8701
0.8555
0.8473
BRUKER
Current Data Parameters
NAME SW05080705
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070508
Time 20.07
INSTRUM spect
PROBHD 5 mm DUL 1H-13
PULPROG zg
TD 65536
SOLVENT CDCl3
NS 5
DS 2
SWH 6218.905 Hz
FIDRES 0.094893 Hz
AQ 5.2691445 sec
RG 114
DW 80.400 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.00 usec
PL1 1.00 dB
SFO1 300.3818550 MHz
F2 - Processing parameters
SI 32768
SF 300.3799994 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
O
OPh
N
H
OEt
4
3.24
9
8
7
6
5
4
3
2
1
ppm
2.13
1.66
0.85
0.90
0.83
2.09
1.01
1.00
2.20
13.89
3.08
2.72
3.65


PhOH addition
176.54
156.79
129.71
121.91
116.21
81.16
77.76
77.66
77.23
76.81
66.83
36.02
31.88
30.09
29.59
25.70
22.76
19.56
19.53
15.87
14.26
BRUKER
Current Data Parameters
NAME SW05080706
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070508
Time 20.14
INSTRUM spect
PROBHD 5 mm DUL 1H-13
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 55
DS 4
SWH 18115.941 Hz
FIDRES 0.276427 Hz
AQ 1.8088436 sec
RG 5160.6
DW 27.600 usec
DE 6.00 usec
TE 300.0 K
D1 10.00000000 sec
d11 0.03000000 sec
DELTA 9.89999962 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.00 usec
PL1 1.80 dB
SFO1 75.5381641 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 92.00 usec
PL2 0.00 dB
PL12 20.00 dB
PL13 20.00 dB
SFO2 300.3812015 MHz
F2 - Processing parameters
SI 65536
SF 75.5305949 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
O
OPh
N
H
OEt
4
3.24
180
160
140
120
100
80
60
40
20
ppm


higher spot 05-01-07
7.4919 7.4868 7.4700 7.4644 7.4603 7.3061 7.2835 7.2782 7.2760 7.2706 7.2641 7.2592 7.2507 7.2457 5.5933 5.5874 5.5599 5.5543 3.7306 3.7068 3.6830 2.2862 1.3614 1.3460 1.2762 1.2528 1.2296 1.2018 1.1843 1.1794 1.1722 1.1656 1.1496 1.1440 1.1310 1.1142 1.0929 1.0792 1.0698 1.0070 0.9841 0.8911 0.8699 0.8473
BRUKER
Current Data Parameters
NAME SW05010704
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070501
Time 17.29
INSTRUM spect
PROBHD 5 mm Dual 13C/
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 6
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 90.5
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 5.00 usec
PL1 0.00 dB
SFO1 300.1318530 MHz
F2 - Processing parameters
SI 16384
SF 300.1300032 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00
O
SPh
N
H
OEt
4
3.25
9 8 7 6 5 4 3 2 1 ppm
1.61 3.21 0.84 0.93 1.85 1.06 1.00 1.08 16.80 3.58 2.77 3.69

higher spot



BRUKER

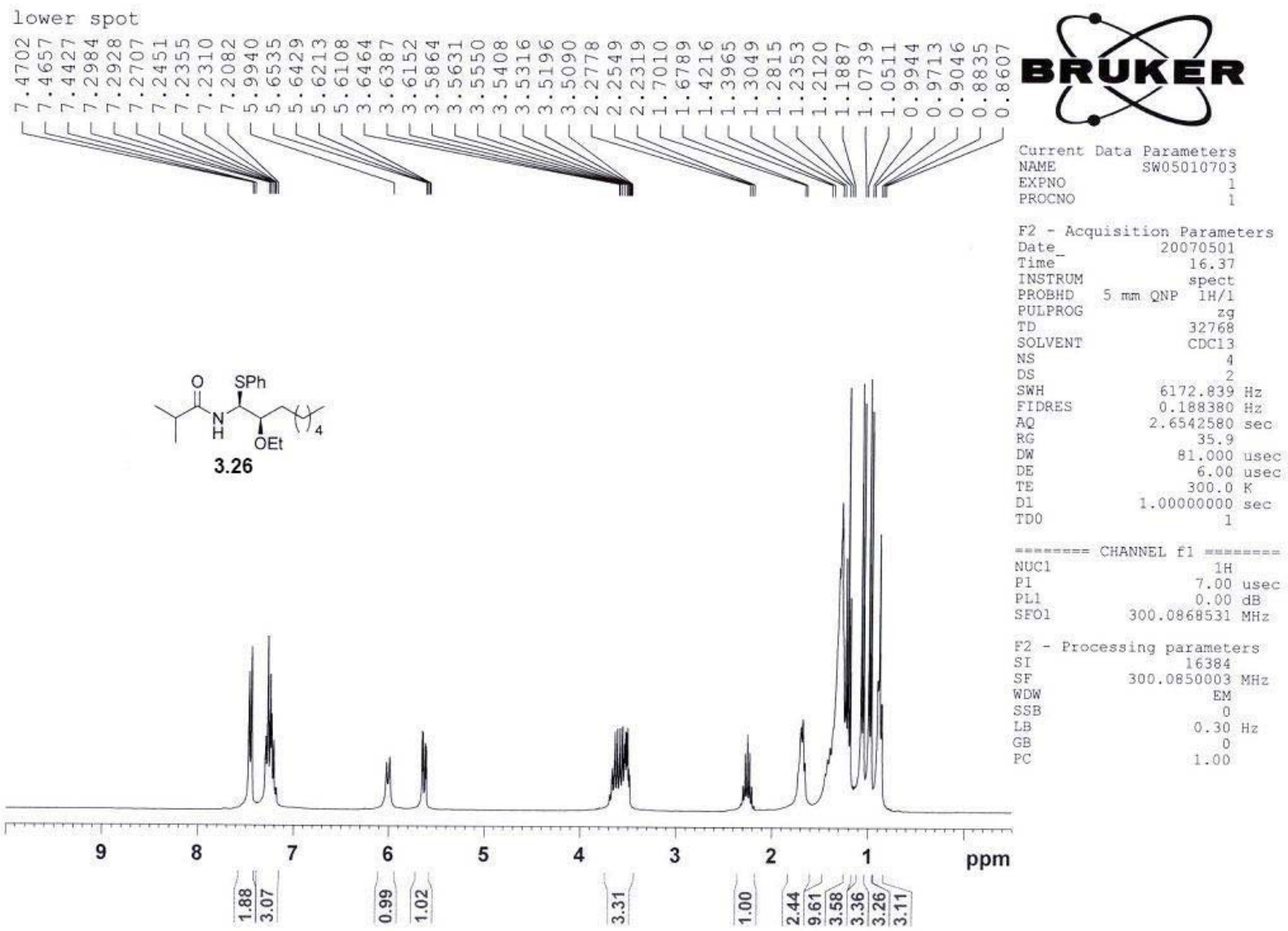
Current Data Parameters
NAME SW05020703
EXPNO 1
PROCNO 1

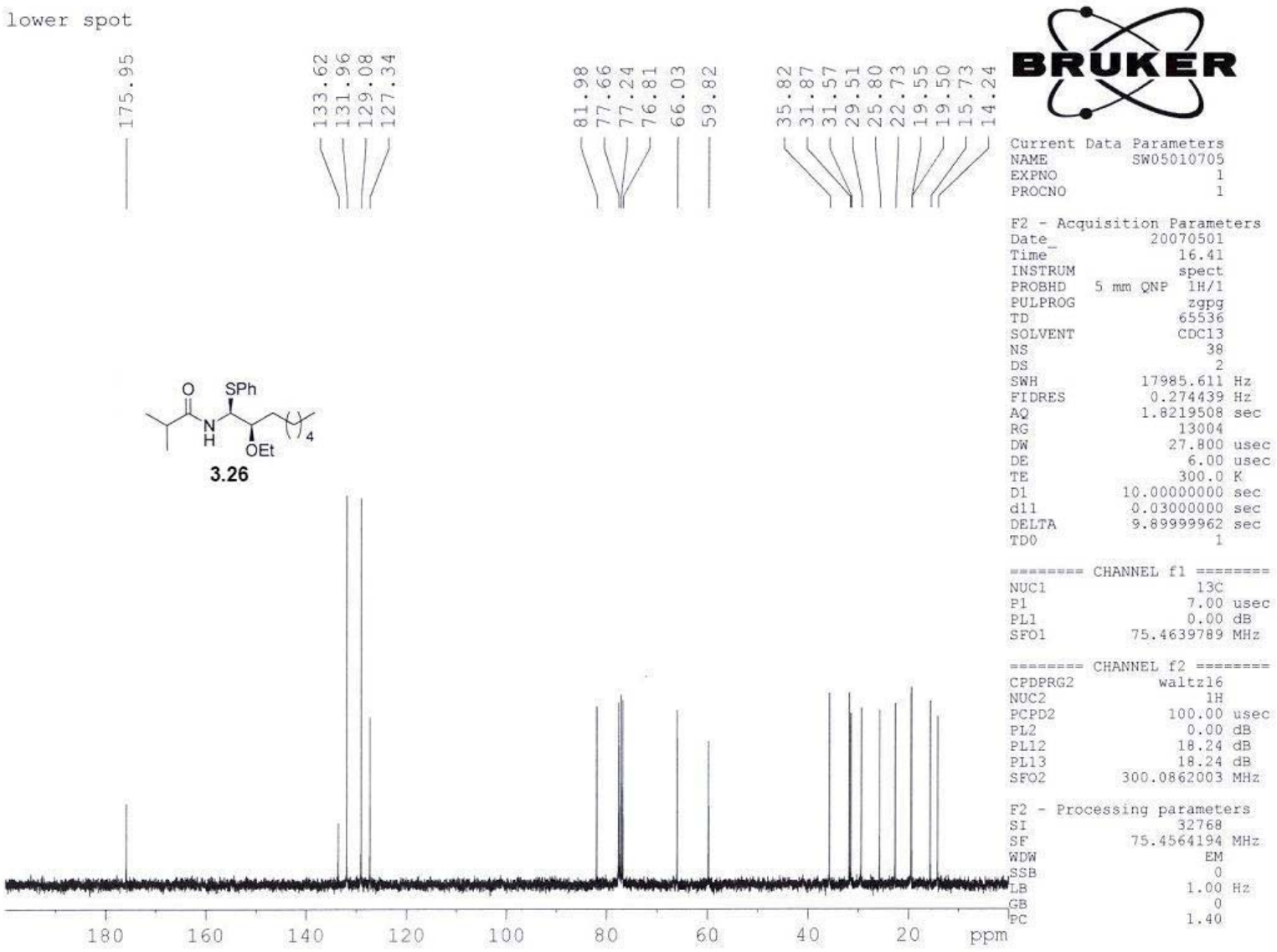
F2 - Acquisition Parameters
Date_ 20070502
Time 20.06
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 275
DS 2
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 13004
DW 27.800 usec
DE 6.00 usec
TE 300.0 K
D1 10.00000000 sec
d11 0.03000000 sec
DELTA 9.89999962 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 7.00 usec
PL1 0.00 dB
SFO1 75.4639789 MHz

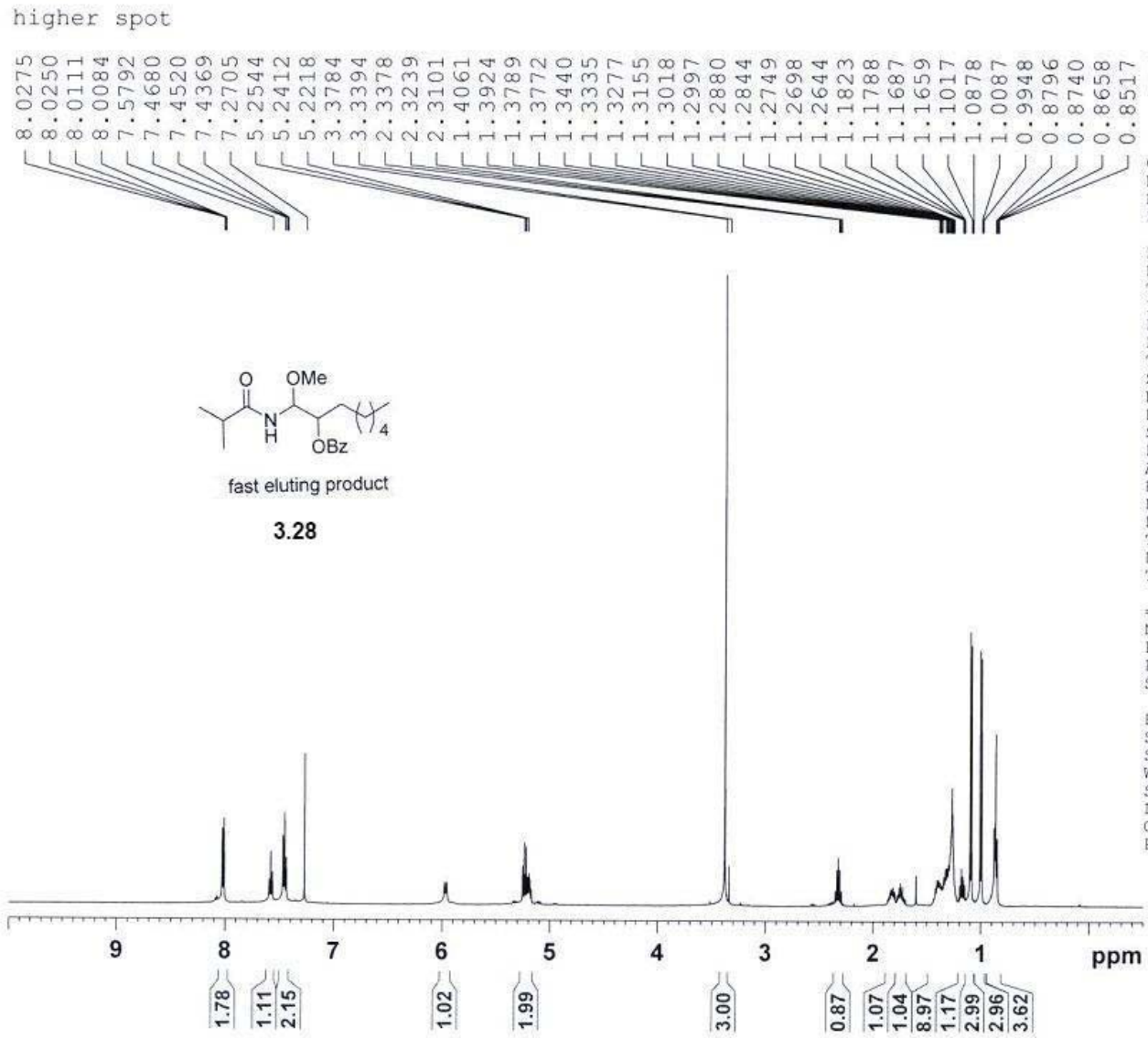
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 0.00 dB
PL12 18.24 dB
PL13 18.24 dB
SFO2 300.0862003 MHz

F2 - Processing parameters
SI 32768
SF 75.4564167 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40


lower spot
7.4702
7.4657
7.4427
7.2984
7.2928
7.2707
7.2451
7.2355
7.2310
7.2082
5.9940
5.6535
5.6429
5.6213
5.6108
3.6464
3.6387
3.6152
3.5864
3.5631
3.5550
3.5408
3.5316
3.5196
3.5090
2.2778
2.2549
2.2319
1.7010
1.6789
1.4216
1.3965
1.3049
1.2815
1.2353
1.2120
1.1887
1.0739
1.0511
0.9944
0.9713
0.9046
0.8835
0.8607
BRUKER
Current Data Parameters
NAME SW05010703
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070501
Time 16.37
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 4
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 35.9
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 7.00 usec
PL1 0.00 dB
SFO1 300.0868531 MHz
F2 - Processing parameters
SI 16384
SF 300.0850003 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
O
SPh
N
H
OEt
4
3.26
9
8
7
6
5
4
3
2
1
ppm
1.88
3.07
0.99
1.02
3.31
1.00
2.44
9.61
3.58
3.36
3.26
3.11


lower spot
175.95
133.62
131.96
129.08
127.34
81.98
77.66
77.24
76.81
66.03
59.82
35.82
31.87
31.57
29.51
25.80
22.73
19.55
19.50
15.73
14.24
BRUKER
Current Data Parameters
NAME SW05010705
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070501
Time 16.41
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 38
DS 2
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 13004
DW 27.800 usec
DE 6.00 usec
TE 300.0 K
D1 10.00000000 sec
d11 0.03000000 sec
DELTA 9.89999962 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.00 usec
PL1 0.00 dB
SFO1 75.4639789 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 0.00 dB
PL12 18.24 dB
PL13 18.24 dB
SFO2 300.0862003 MHz
F2 - Processing parameters
SI 32768
SF 75.4564194 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
O
SPh
N
H
OEt
4
3.26
180
160
140
120
100
80
60
40
20
ppm

higher spot



fast eluting product

3.28

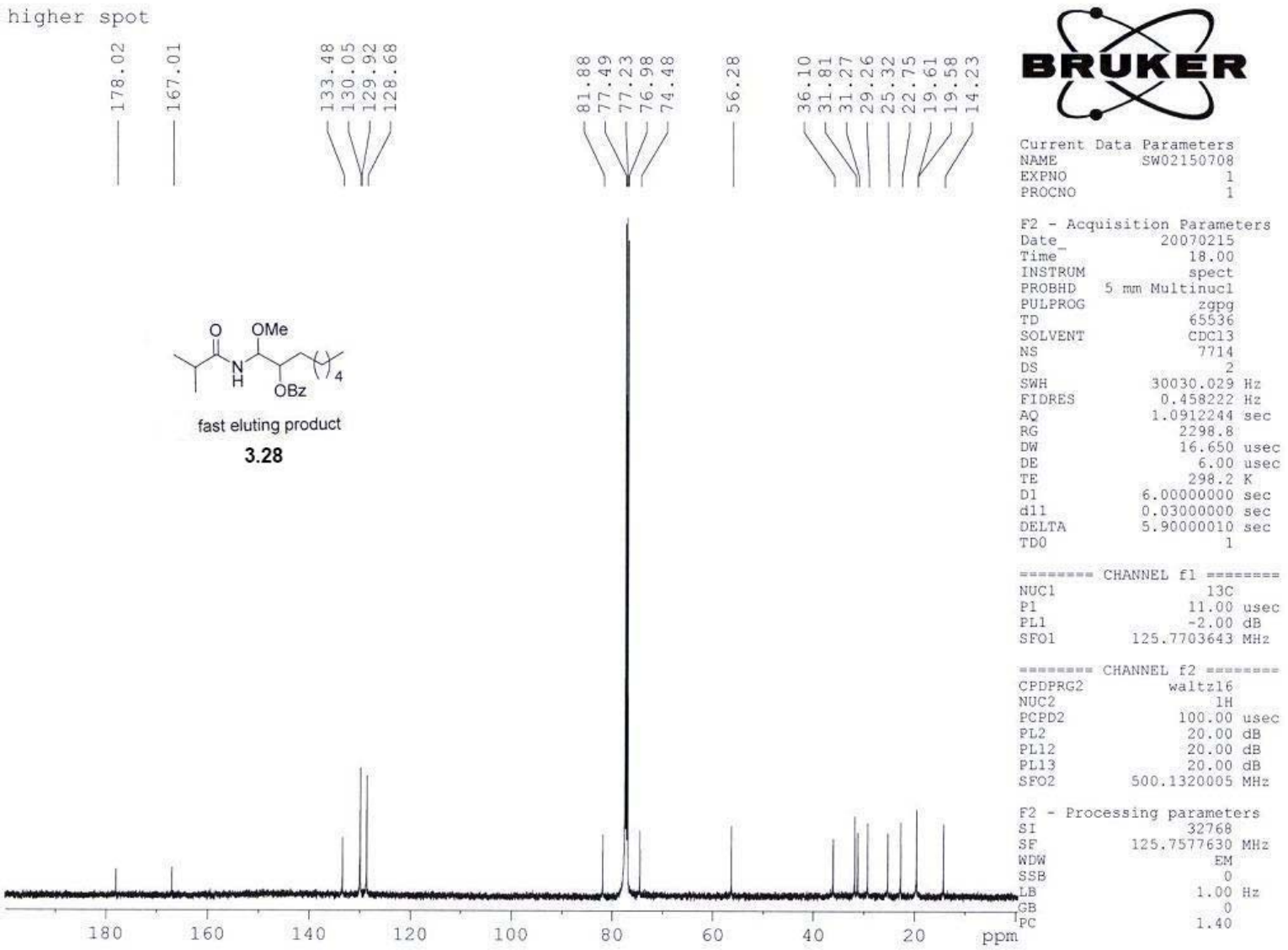
BRUKER

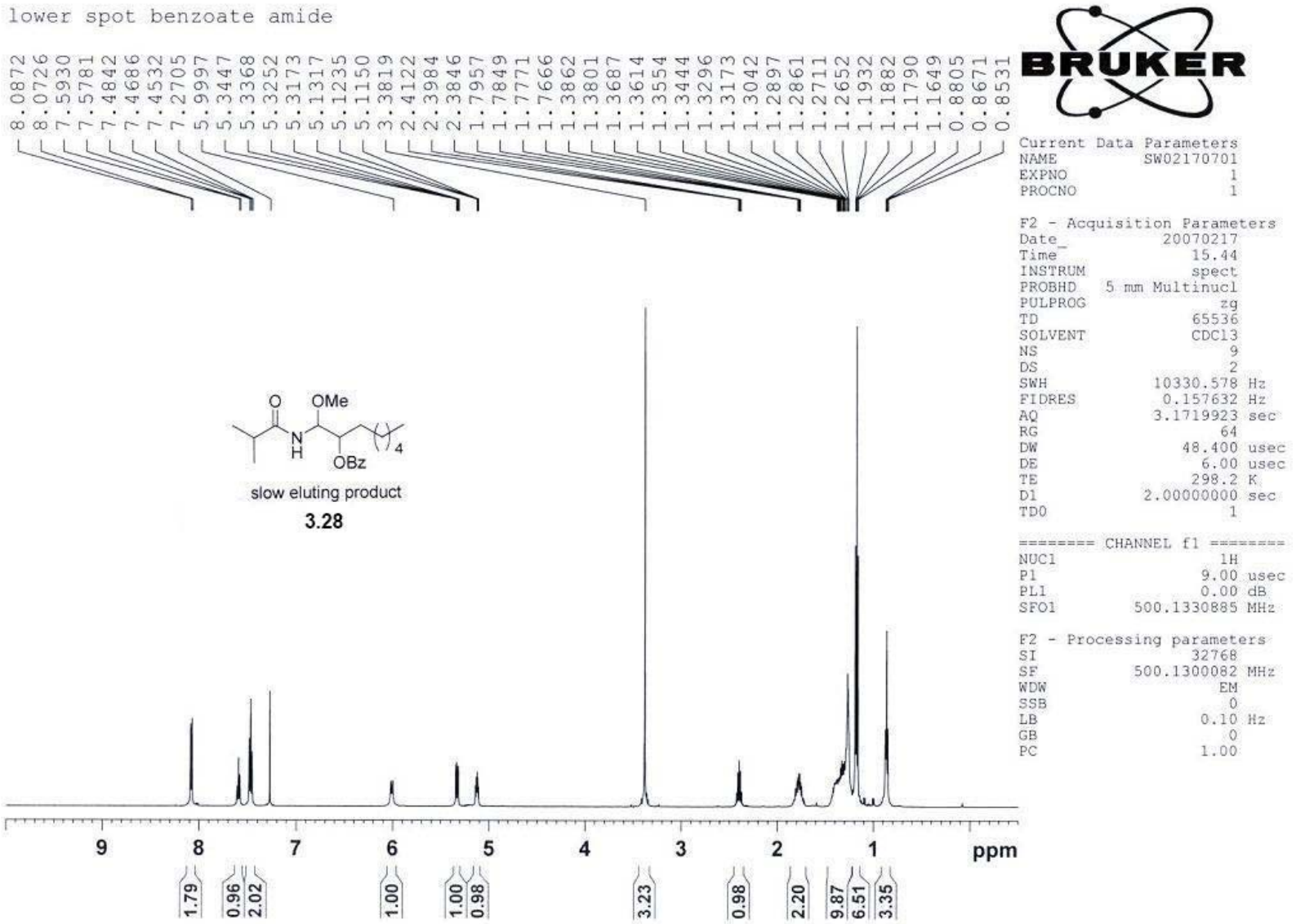
Current Data Parameters
NAME SW02160702
EXPNO 1
PROCNO 1

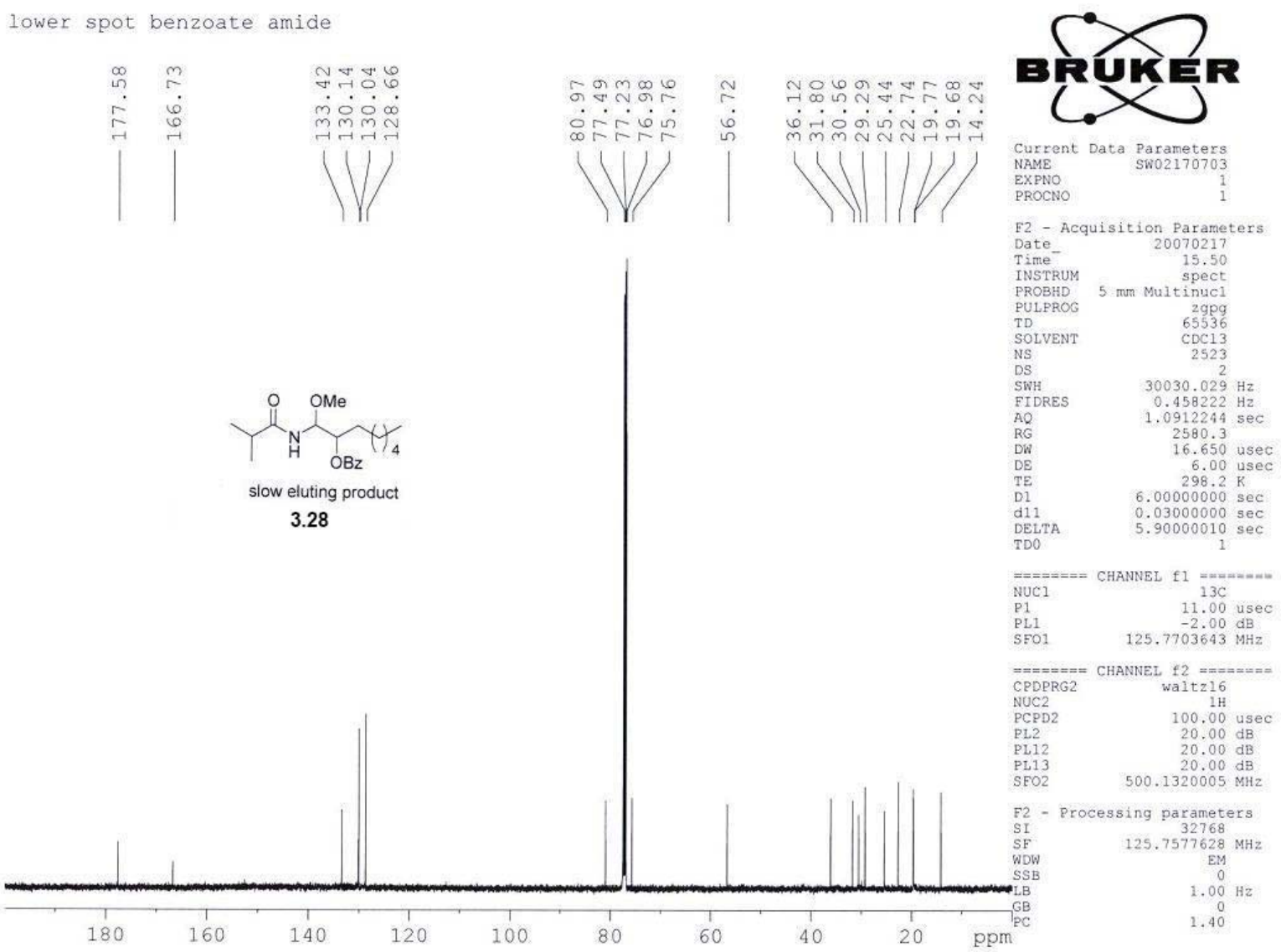
F2 - Acquisition Parameters
Date_ 20070216
Time 9.51
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zg
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 71.8
DW 48.400 usec
DE 6.00 usec
TE 298.2 K
D1 2.00000000 sec
TD0 1

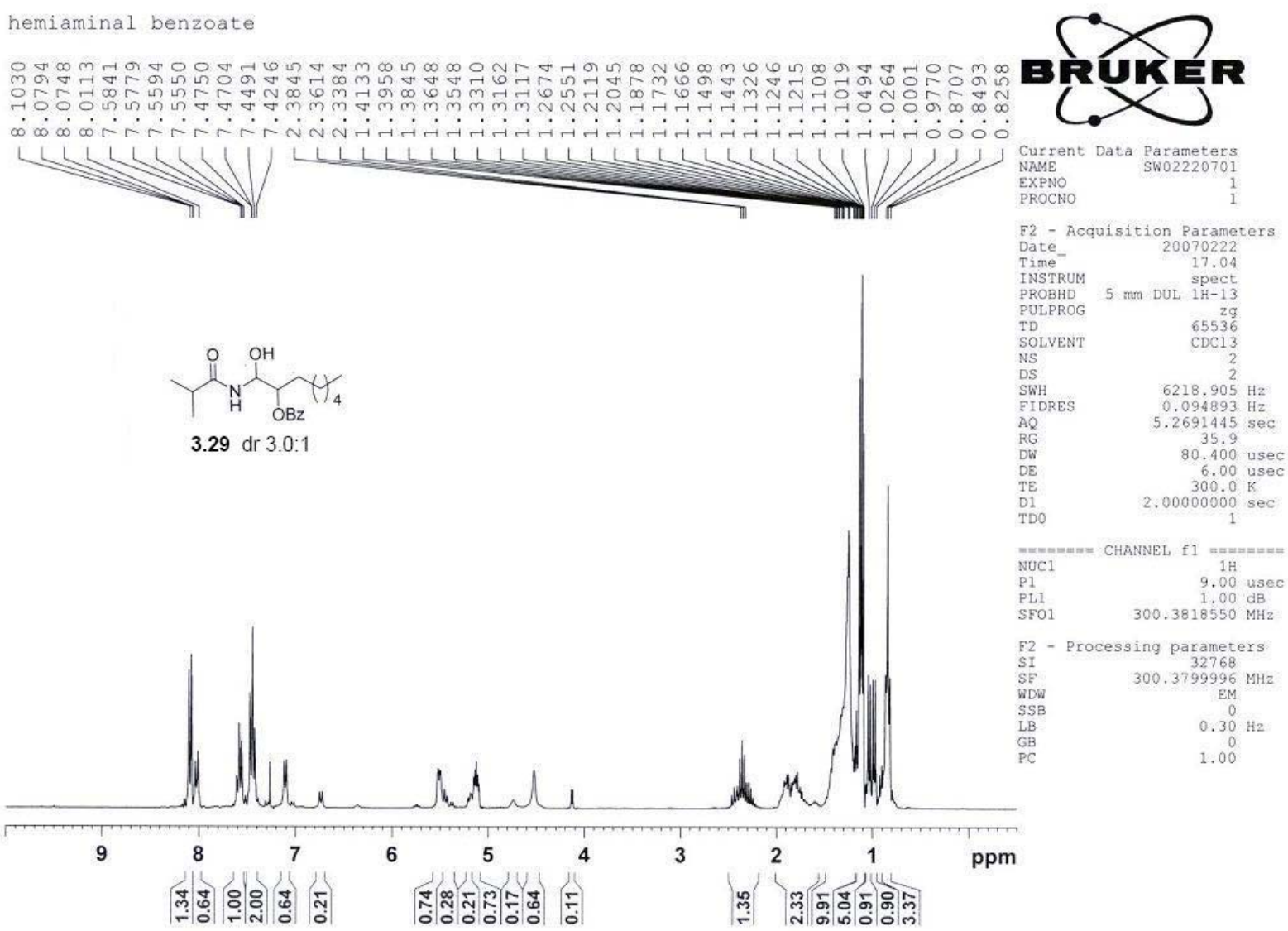
======== CHANNEL f1 ========
NUC1 1H
P1 9.00 usec
PL1 0.00 dB
SFO1 500.1330885 MHz

F2 - Processing parameters
SI 32768
SF 500.1300079 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

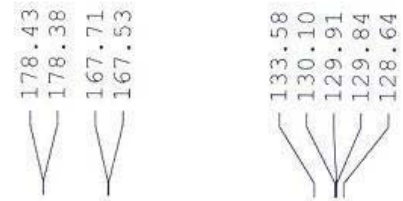

higher spot
178.02
167.01
133.48
130.05
129.92
128.68
81.88
77.49
77.23
76.98
74.48
56.28
36.10
31.81
31.27
29.26
25.32
22.75
19.61
19.58
14.23
O
OMe
N
H
OBz
4
fast eluting product
3.28
180
160
140
120
100
80
60
40
20
ppm
BRUKER
Current Data Parameters
NAME SW02150708
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070215
Time 18.00
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 7714
DS 2
SWH 30030.029 Hz
FIDRES 0.458222 Hz
AQ 1.0912244 sec
RG 2298.8
DW 16.650 usec
DE 6.00 usec
TE 298.2 K
D1 6.00000000 sec
d11 0.03000000 sec
DELTA 5.90000010 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 11.00 usec
PL1 -2.00 dB
SFO1 125.7703643 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 20.00 dB
PL12 20.00 dB
PL13 20.00 dB
SFO2 500.1320005 MHz
F2 - Processing parameters
SI 32768
SF 125.7577630 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

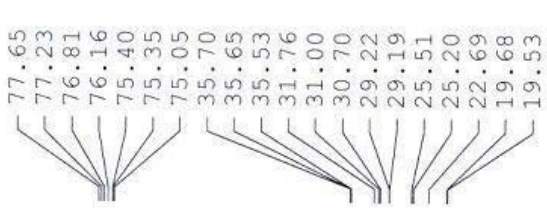

lower spot benzoate amide
8.0872
8.0726
7.5930
7.5781
7.4842
7.4686
7.4532
7.2705
5.9997
5.3447
5.3368
5.3252
5.3173
5.1317
5.1235
5.1150
3.3819
2.4122
2.3984
2.3846
1.7957
1.7849
1.7771
1.7666
1.3862
1.3801
1.3687
1.3614
1.3554
1.3444
1.3296
1.3173
1.3042
1.2897
1.2861
1.2711
1.2652
1.1932
1.1882
1.1790
1.1649
0.8805
0.8671
0.8531
BRUKER
Current Data Parameters
NAME SW02170701
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070217
Time 15.44
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zg
TD 65536
SOLVENT CDCl3
NS 9
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 64
DW 48.400 usec
DE 6.00 usec
TE 298.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.00 usec
PL1 0.00 dB
SFO1 500.1330885 MHz
F2 - Processing parameters
SI 32768
SF 500.1300082 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00
O
OMe
N
H
OBz
4
slow eluting product
3.28
9
8
7
6
5
4
3
2
1
ppm
1.79
0.96
2.02
1.00
1.00
0.98
3.23
0.98
2.20
9.87
6.51
3.35

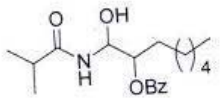

lower spot benzoate amide
177.58
166.73
133.42
130.14
130.04
128.66
80.97
77.49
77.23
76.98
75.76
56.72
36.12
31.80
30.56
29.29
25.44
22.74
19.77
19.68
14.24
O
OMe
N
H
OBz
4
slow eluting product
3.28
180
160
140
120
100
80
60
40
20
ppm
BRUKER
Current Data Parameters
NAME SW02170703
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070217
Time 15.50
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 2523
DS 2
SWH 30030.029 Hz
FIDRES 0.458222 Hz
AQ 1.0912244 sec
RG 2580.3
DW 16.650 usec
DE 6.00 usec
TE 298.2 K
D1 6.00000000 sec
d11 0.03000000 sec
DELTA 5.90000010 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 11.00 usec
PL1 -2.00 dB
SFO1 125.7703643 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 20.00 dB
PL12 20.00 dB
PL13 20.00 dB
SFO2 500.1320005 MHz
F2 - Processing parameters
SI 32768
SF 125.7577628 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40


hemiaminal benzoate
8.1030
8.0794
8.0748
8.0113
7.5841
7.5779
7.5594
7.5550
7.4750
7.4704
7.4491
7.4246
2.3845
2.3614
2.3384
1.4133
1.3958
1.3845
1.3648
1.3548
1.3310
1.3162
1.3117
1.2674
1.2551
1.2119
1.2045
1.1878
1.1732
1.1666
1.1498
1.1443
1.1326
1.1246
1.1215
1.1108
1.1019
1.0494
1.0264
1.0001
0.9770
0.8707
0.8493
0.8258
O
OH
N
H
OBz
4
3.29 dr 3.0:1
9
8
7
6
5
4
3
2
1
ppm
1.34
0.64
1.00
2.00
0.64
0.21
0.74
0.28
0.21
0.73
0.17
0.64
0.11
1.35
2.33
9.91
5.04
0.91
0.90
3.37
BRUKER
Current Data Parameters
NAME SW02220701
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070222
Time 17.04
INSTRUM spect
PROBHD 5 mm DUL 1H-13
PULPROG zg
TD 65536
SOLVENT CDCl3
NS 2
DS 2
SWH 6218.905 Hz
FIDRES 0.094893 Hz
AQ 5.2691445 sec
RG 35.9
DW 80.400 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.00 usec
PL1 1.00 dB
SFO1 300.3818550 MHz
F2 - Processing parameters
SI 32768
SF 300.3799996 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

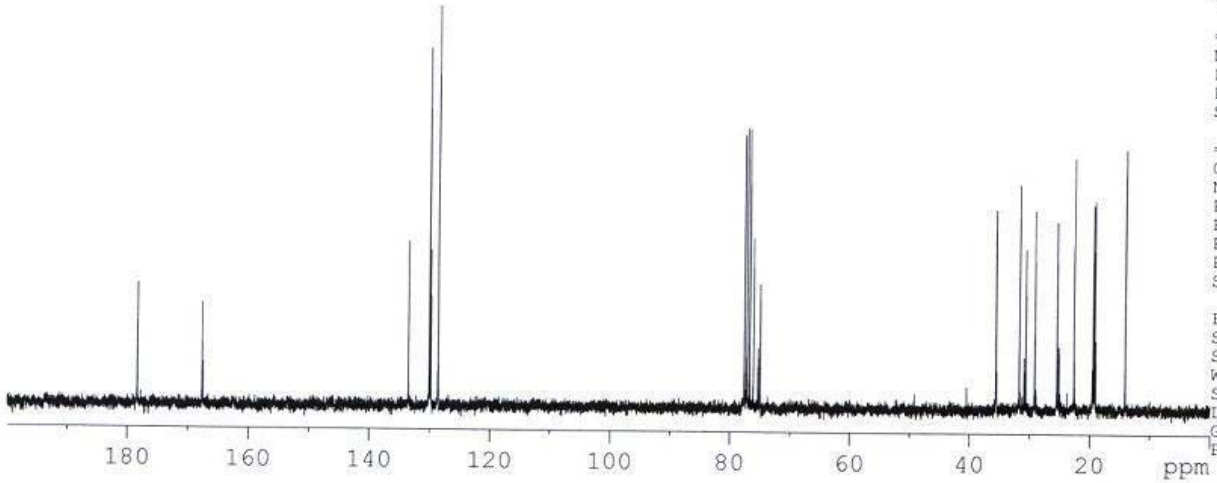
hemiaminal benzoate

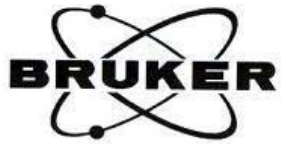






3.29 dr 3.0:1





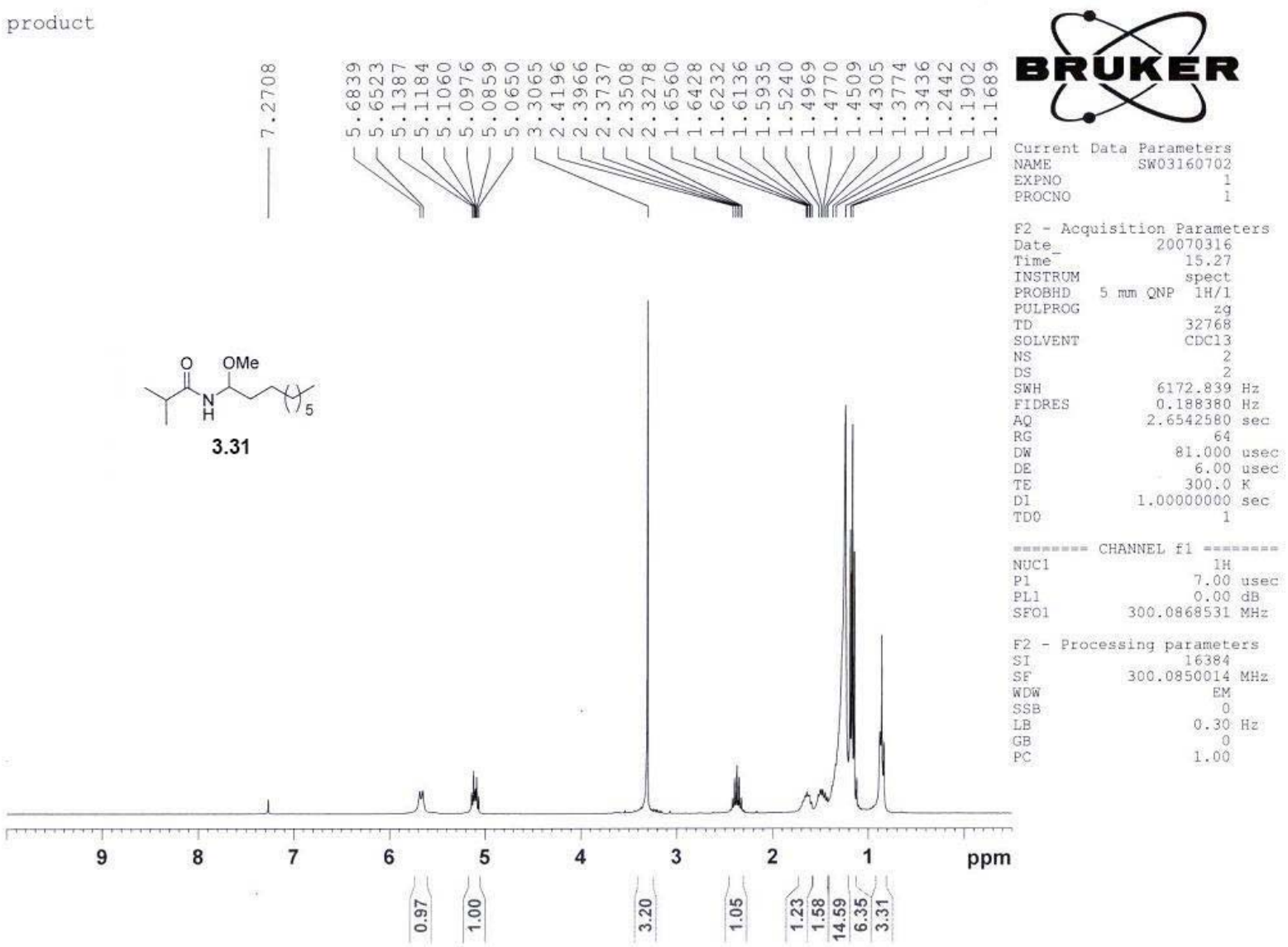

```
Current Data Parameters
NAME                SW02220702
EXPNO                        1
PROCNO                       1

F2 - Acquisition Parameters
Date_                 20070222
Time                     17.09
INSTRUM                  spect
PROBHD    5 mm DUL 1H-13
PULPROG                  zgpg
TD                      65536
SOLVENT                 CDCl3
NS                         37
DS                          4
SWH                18115.941 Hz
FIDRES             0.276427 Hz
AQ                 1.8088436 sec
RG                   10321.3
DW                    27.600 usec
DE                     6.00 usec
TE                    300.0 K
D1                10.00000000 sec
d11                0.03000000 sec
DELTA              9.89999962 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                      13C
P1                       9.00 usec
PL1                      1.80 dB
SFO1              75.5381641 MHz

======== CHANNEL f2 ========
CPDPRG2               waltz16
NUC2                      1H
PCPD2                   92.00 usec
PL2                      0.00 dB
PL12                    20.00 dB
PL13                    20.00 dB
SFO2             300.3812015 MHz

F2 - Processing parameters
SI                        65536
SF                75.5305975 MHz
WDW                         EM
SSB                          0
LB                        1.00 Hz
GB                           0
PC                        1.40
```


product
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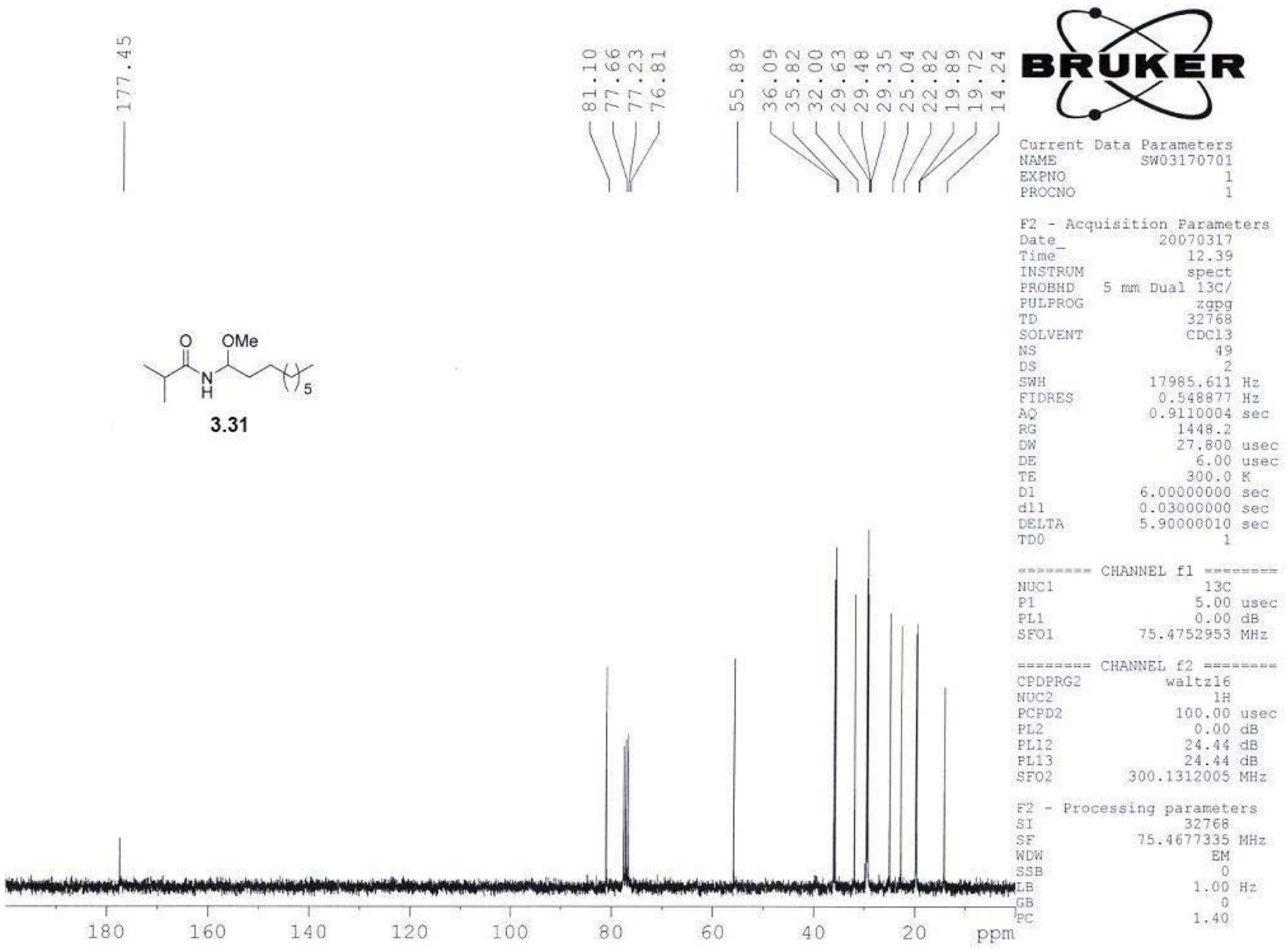
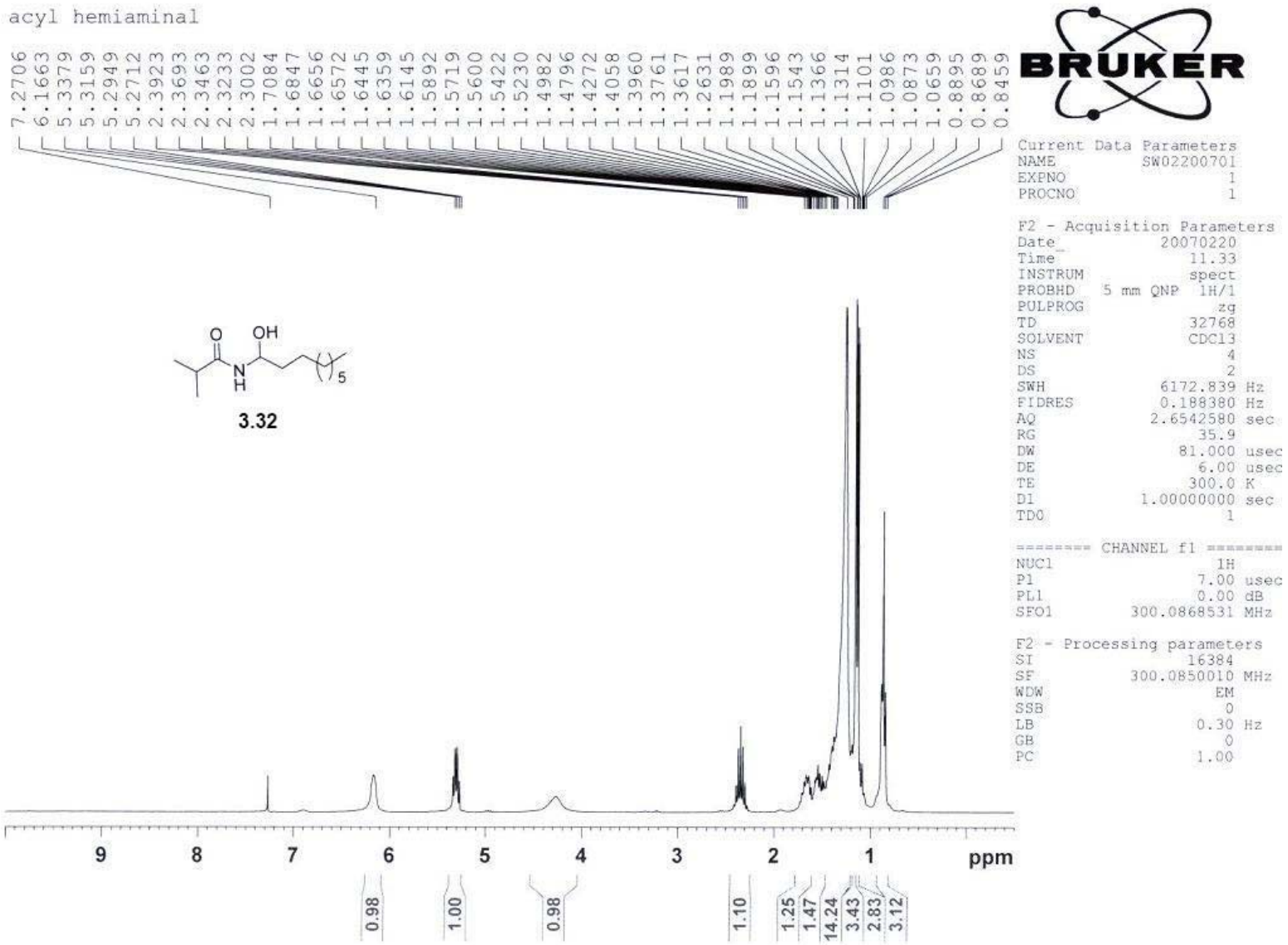
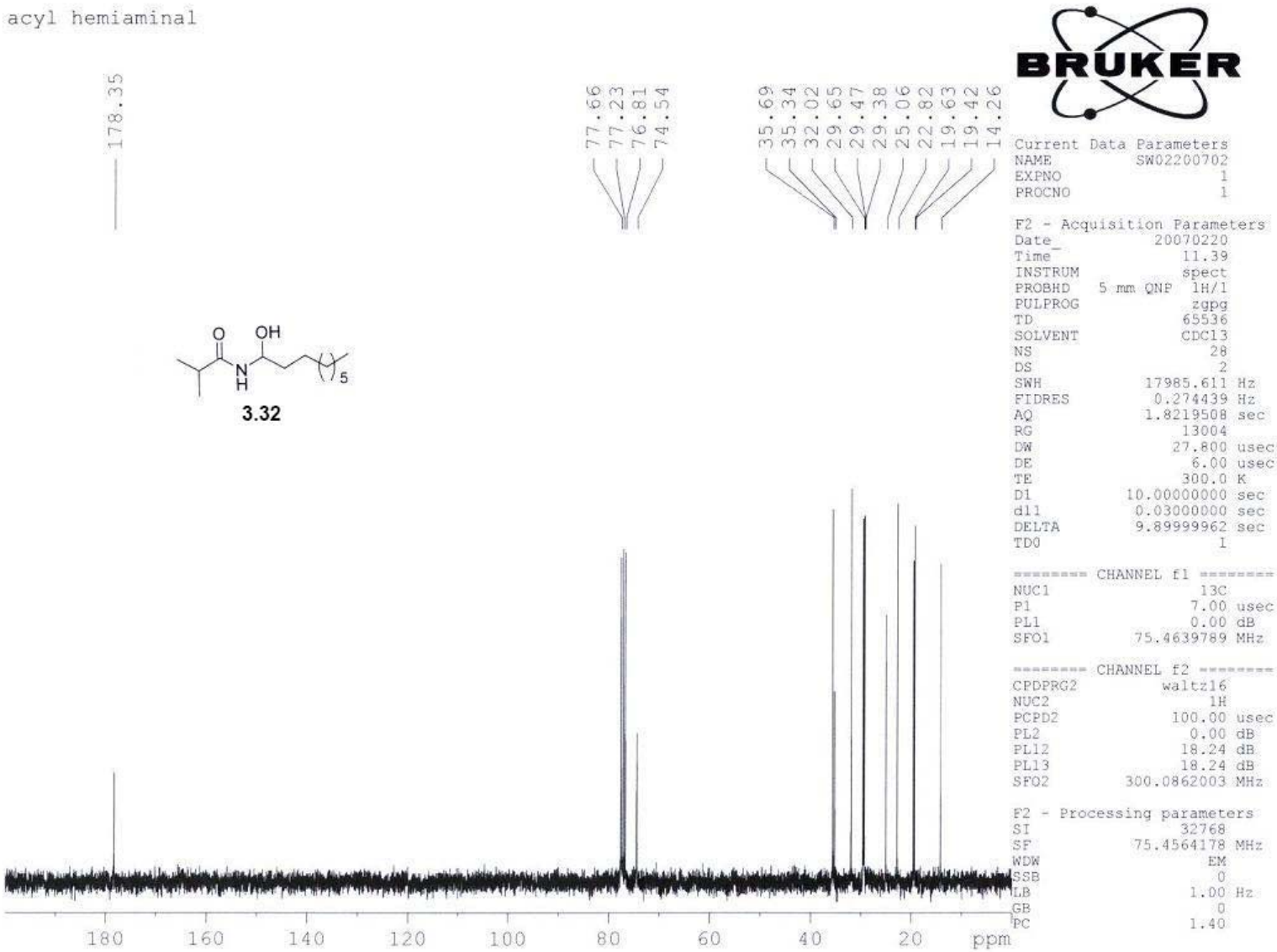
5.6839
5.6523
5.1387
5.1184
5.1060
5.0976
5.0859
5.0650
3.3065
2.4196
2.3966
2.3737
2.3508
2.3278
1.6560
1.6428
1.6232
1.6136
1.5935
1.5240
1.4969
1.4770
1.4509
1.4305
1.3774
1.3436
1.2442
1.1902
1.1689
O
OMe
N
H
5
3.31
9
8
7
6
5
4
3
2
1
ppm
0.97
1.00
3.20
1.05
1.23
1.58
14.59
6.35
3.31
BRUKER
Current Data Parameters
NAME SW03160702
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070316
Time 15.27
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 2
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 64
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 7.00 usec
PL1 0.00 dB
SFO1 300.0868531 MHz
F2 - Processing parameters
SI 16384
SF 300.0850014 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


177.45
81.10
77.66
77.23
76.81
55.89
36.09
35.82
32.00
29.63
29.48
29.35
25.04
22.82
19.89
19.72
14.24
BRUKER
Current Data Parameters
NAME SW03170701
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070317
Time 12.39
INSTRUM spect
PROBHD 5 mm Dual 13C/
PULPROG zgpg
TD 32768
SOLVENT CDCl3
NS 49
DS 2
SWH 17985.611 Hz
FIDRES 0.548877 Hz
AQ 0.9110004 sec
RG 1448.2
DW 27.800 usec
DE 6.00 usec
TE 300.0 K
D1 6.00000000 sec
d11 0.03000000 sec
DELTA 5.90000010 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 5.00 usec
PL1 0.00 dB
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 0.00 dB
PL12 24.44 dB
PL13 24.44 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677335 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
O
OMe
N
H
5
3.31
180
160
140
120
100
80
60
40
20
ppm


acyl hemiaminal
7.2706
6.1663
5.3379
5.3159
5.2949
5.2712
2.3923
2.3693
2.3463
2.3233
2.3002
1.7084
1.6847
1.6656
1.6572
1.6445
1.6359
1.6145
1.5892
1.5719
1.5600
1.5422
1.5230
1.4982
1.4796
1.4272
1.4058
1.3960
1.3761
1.3617
1.2631
1.1989
1.1899
1.1596
1.1543
1.1366
1.1314
1.1101
1.0986
1.0873
1.0659
0.8895
0.8689
0.8459
BRUKER
Current Data Parameters
NAME SW02200701
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070220
Time 11.33
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 4
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 35.9
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 7.00 usec
PL1 0.00 dB
SFO1 300.0868531 MHz
F2 - Processing parameters
SI 16384
SF 300.0850010 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
O
OH
N
H
5
3.32
9
8
7
6
5
4
3
2
1
ppm
0.98
1.00
0.98
1.10
1.25
1.47
14.24
3.43
2.83
3.12

acyl hemiaminal



BRUKER

Current Data Parameters
NAME SW02200702
EXPNO 1
PROCNO 1

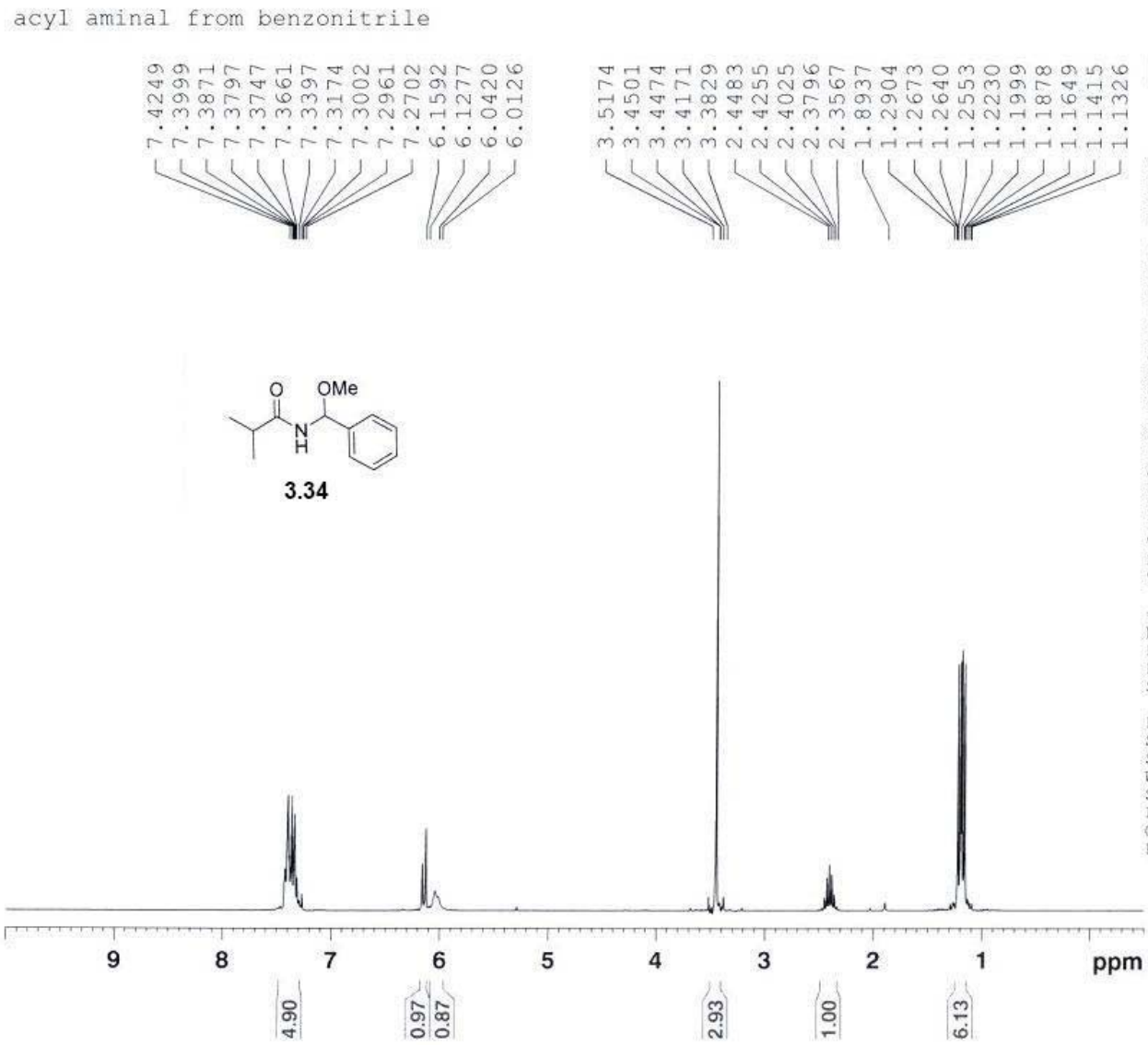
F2 - Acquisition Parameters
Date_ 20070220
Time 11.39
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 28
DS 2
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 13004
DW 27.800 usec
DE 6.00 usec
TE 300.0 K
D1 10.00000000 sec
d11 0.03000000 sec
DELTA 9.89999962 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 7.00 usec
PL1 0.00 dB
SFO1 75.4639789 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 0.00 dB
PL12 18.24 dB
PL13 18.24 dB
SFO2 300.0862003 MHz

F2 - Processing parameters
SI 32768
SF 75.4564178 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

acyl aminal from benzonitrile



BRUKER

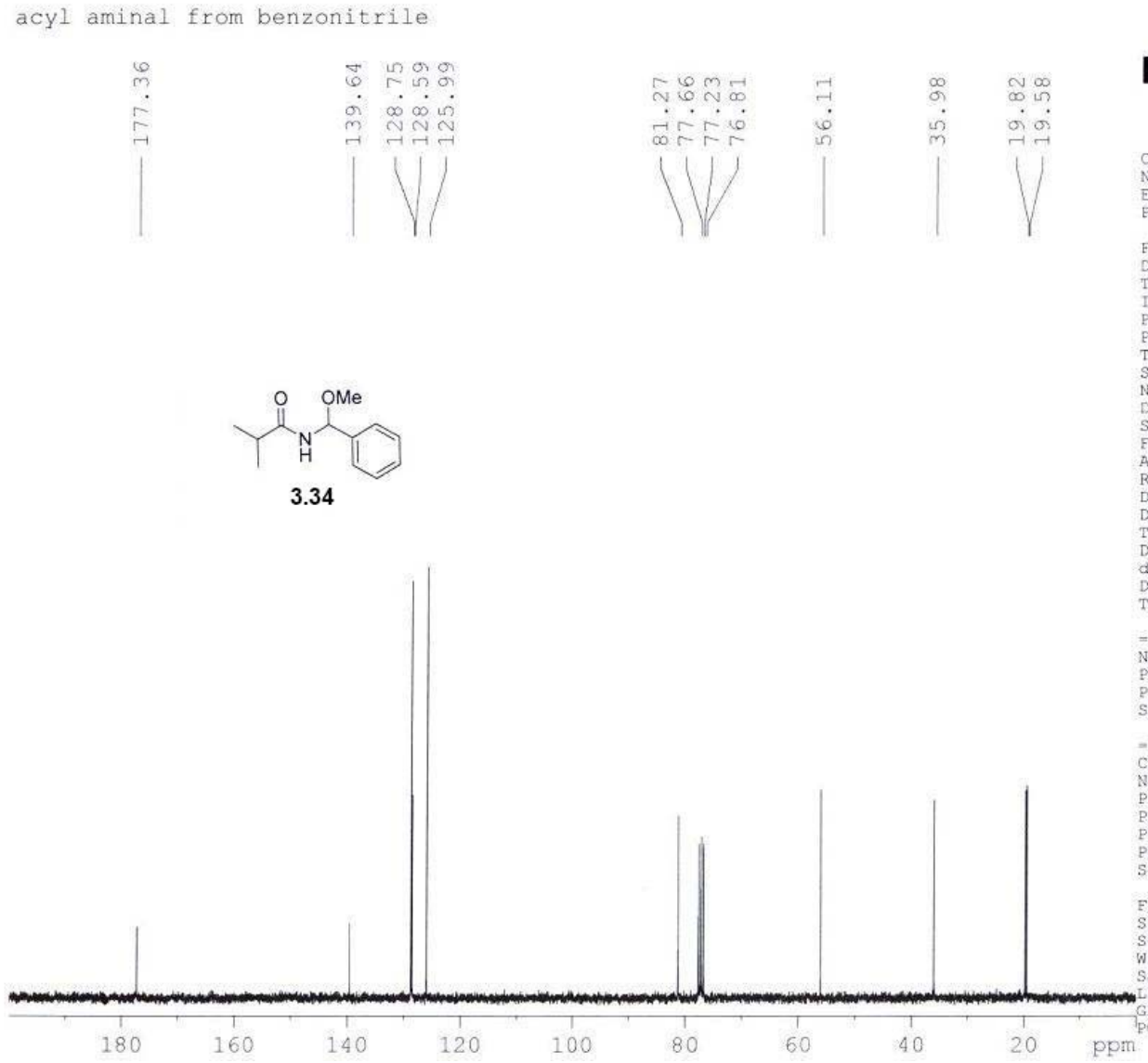
Current Data Parameters
NAME SW05250704
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20070525
Time 17.05
INSTRUM spect
PROBHD 5 mm DUL 1H-13
PULPROG zg
TD 65536
SOLVENT CDC13
NS 1
DS 2
SWH 6218.905 Hz
FIDRES 0.094893 Hz
AQ 5.2691445 sec
RG 57
DW 80.400 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 9.00 usec
PL1 1.00 dB
SFO1 300.3818550 MHz

F2 - Processing parameters
SI 32768
SF 300.3799996 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

acyl aminal from benzonitrile



BRUKER

Current Data Parameters
NAME SW05250705
EXPNO 1
PROCNO 1

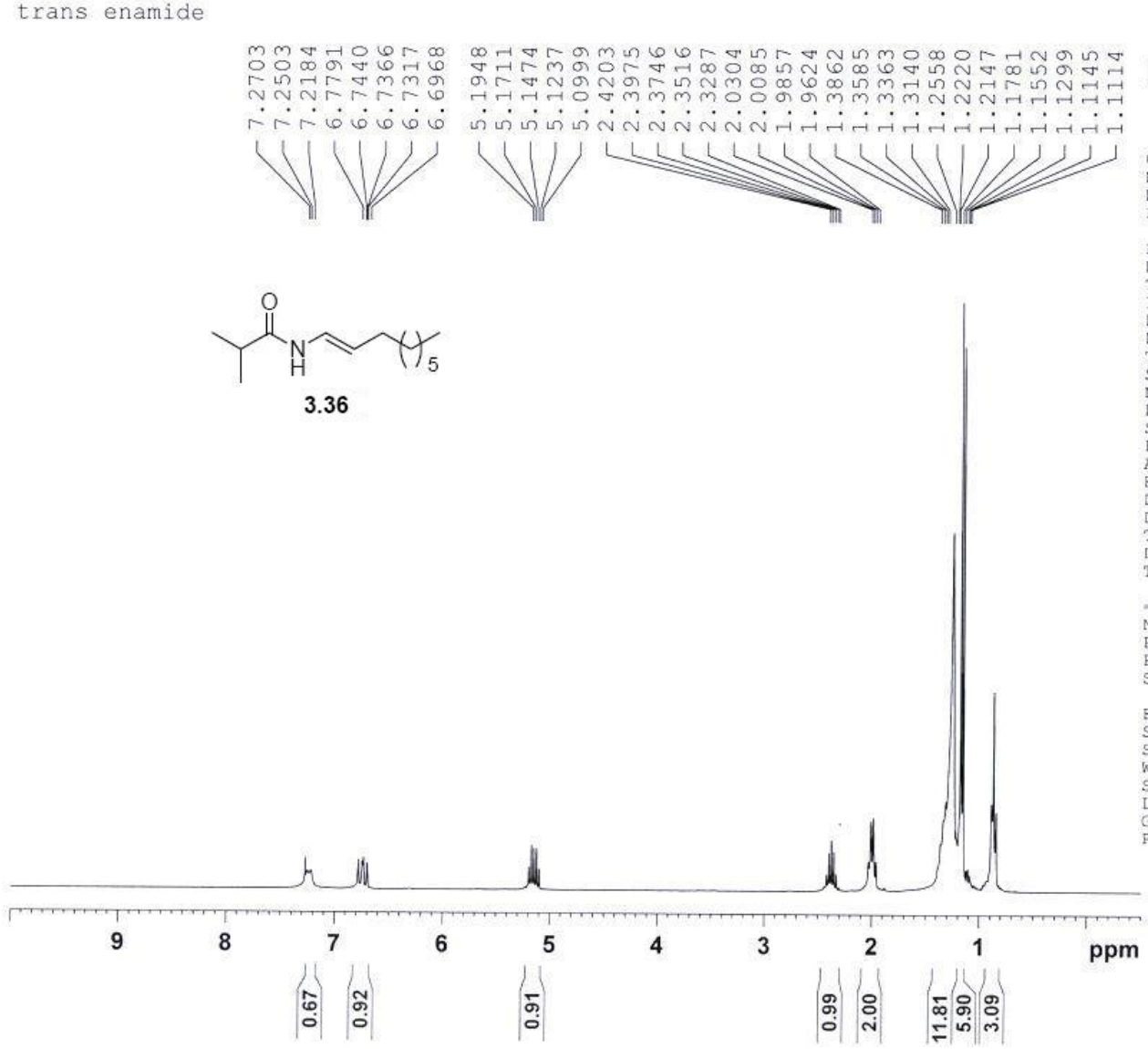
F2 - Acquisition Parameters
Date_ 20070525
Time 17.11
INSTRUM spect
PROBHD 5 mm DUL 1H-13
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 18
DS 4
SWH 18115.941 Hz
FIDRES 0.276427 Hz
AQ 1.8088436 sec
RG 9195.2
DW 27.600 usec
DE 6.00 usec
TE 300.0 K
D1 10.00000000 sec
d11 0.03000000 sec
DELTA 9.89999962 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 9.00 usec
PL1 1.80 dB
SFO1 75.5381641 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 92.00 usec
PL2 0.00 dB
PL12 20.00 dB
PL13 20.00 dB
SFO2 300.3812015 MHz

F2 - Processing parameters
SI 65536
SF 75.5305983 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

trans enamide



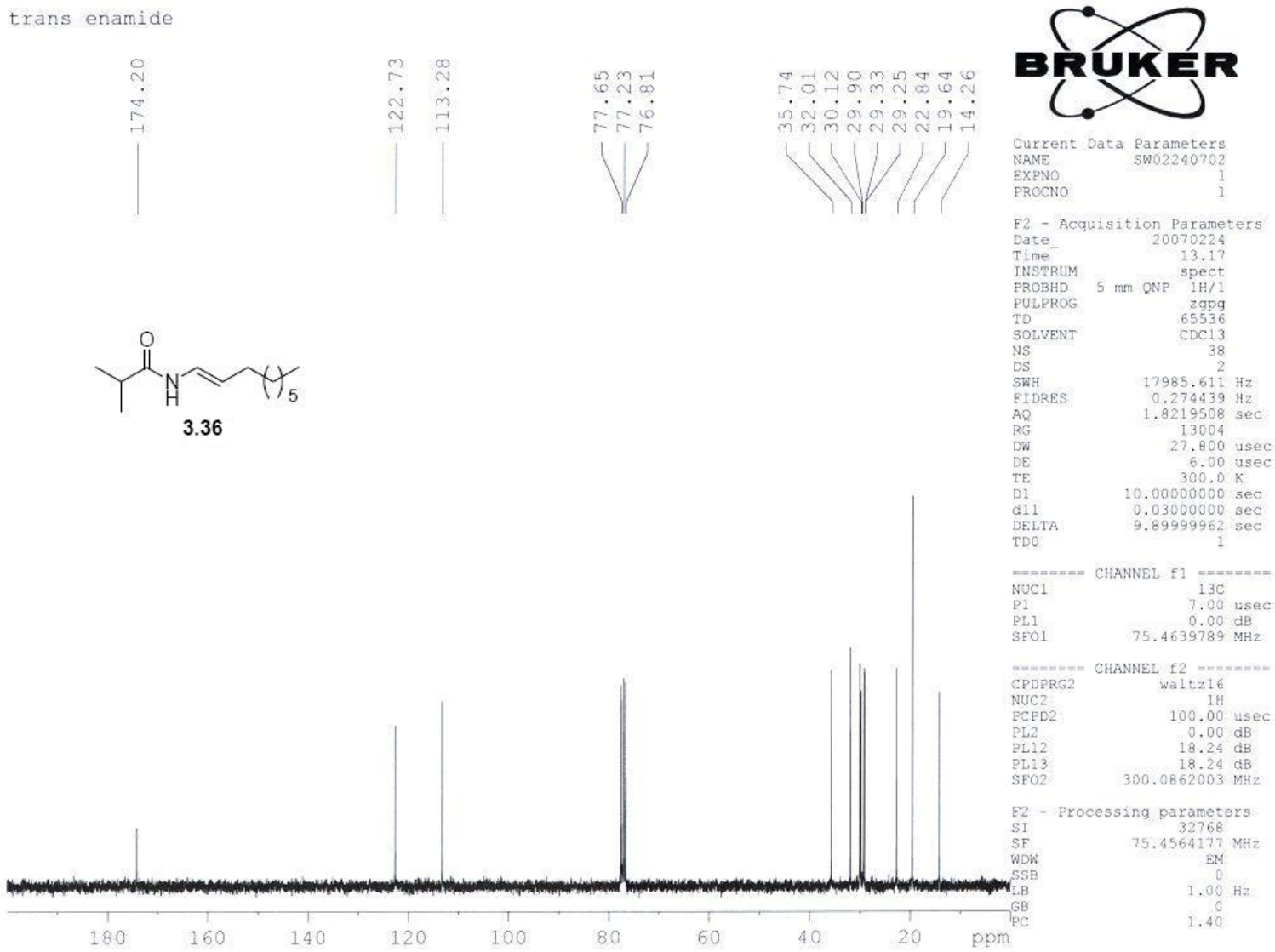
BRUKER

Current Data Parameters
NAME SW02240701
EXPNO 1
PROCNO 1

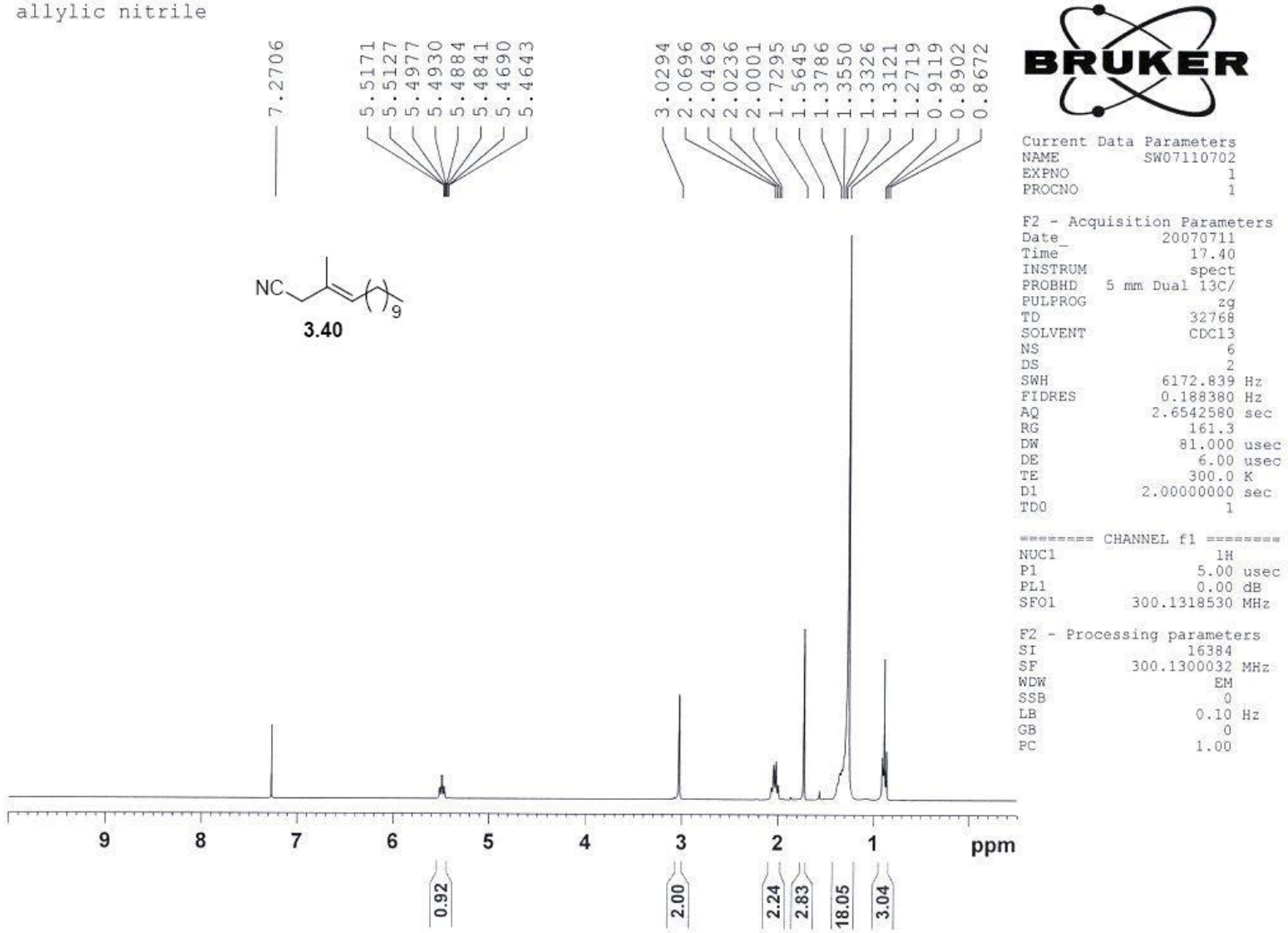
F2 - Acquisition Parameters
Date_ 20070224
Time 12.30
INSTRUM spect
PROBHD 5 mm DUL 1H-13
PULPROG zg
TD 65536
SOLVENT CDCl3
NS 3
DS 2
SWH 6218.905 Hz
FIDRES 0.094893 Hz
AQ 5.2691445 sec
RG 45.3
DW 80.400 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 9.00 usec
PL1 1.00 dB
SFO1 300.3818550 MHz

F2 - Processing parameters
SI 32768
SF 300.3799994 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


trans enamide
174.20
122.73
113.28
77.65
77.23
76.81
35.74
32.01
30.12
29.90
29.33
29.25
22.84
19.64
14.26
3.36
180
160
140
120
100
80
60
40
20
ppm
Current Data Parameters
NAME SW02240702
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070224
Time 13.17
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 38
DS 2
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 13004
DW 27.800 usec
DE 6.00 usec
TE 300.0 K
D1 10.00000000 sec
d11 0.03000000 sec
DELTA 9.89999962 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.00 usec
PL1 0.00 dB
SFO1 75.4639789 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 0.00 dB
PL12 18.24 dB
PL13 18.24 dB
SFO2 300.0862003 MHz
F2 - Processing parameters
SI 32768
SF 75.4564177 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

allylic nitrile



BRUKER

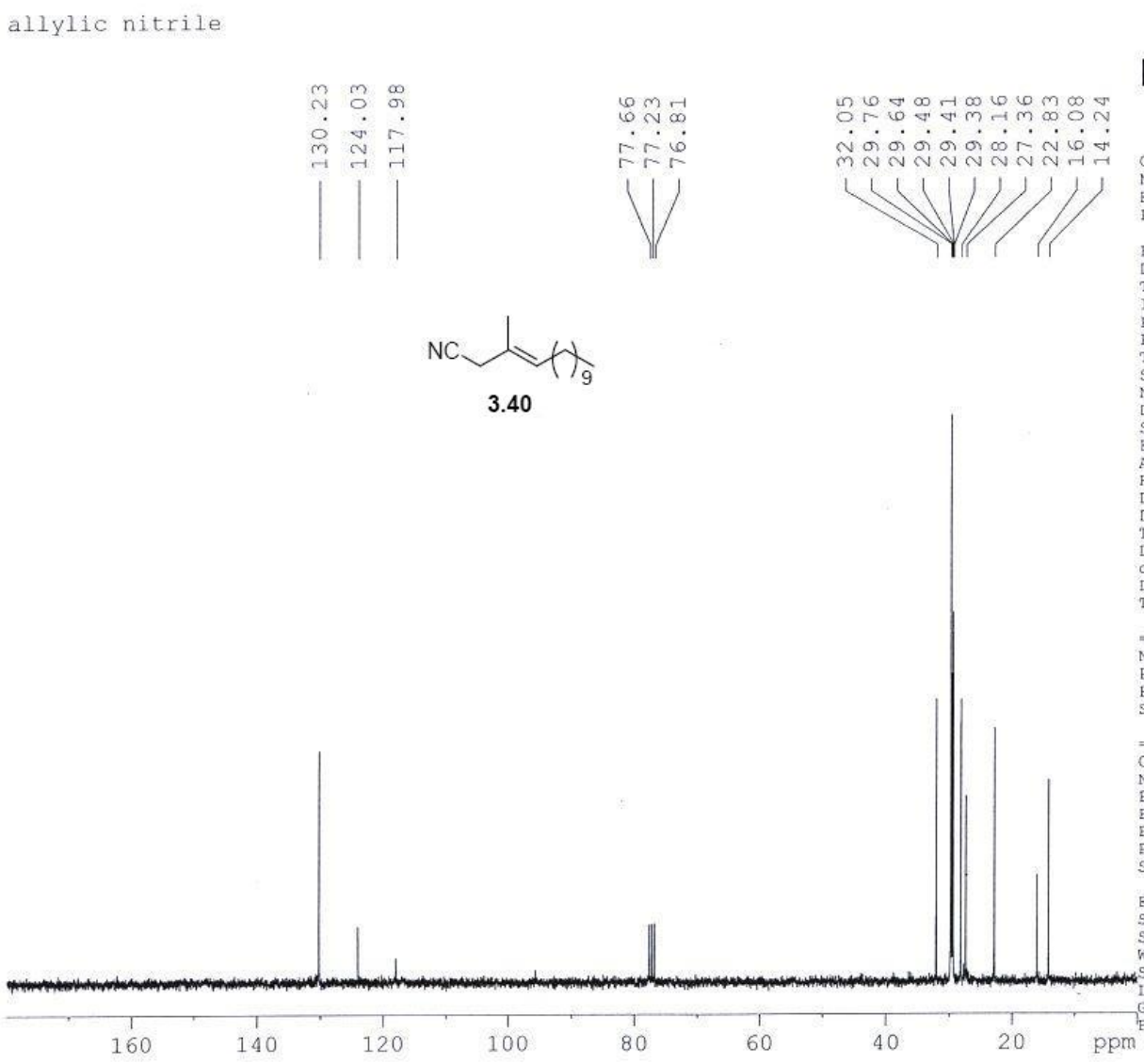
Current Data Parameters
NAME SW07110702
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20070711
Time 17.40
INSTRUM spect
PROBHD 5 mm Dual 13C/
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 6
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 161.3
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 5.00 usec
PL1 0.00 dB
SFO1 300.1318530 MHz

F2 - Processing parameters
SI 16384
SF 300.1300032 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

allylic nitrile



BRUKER

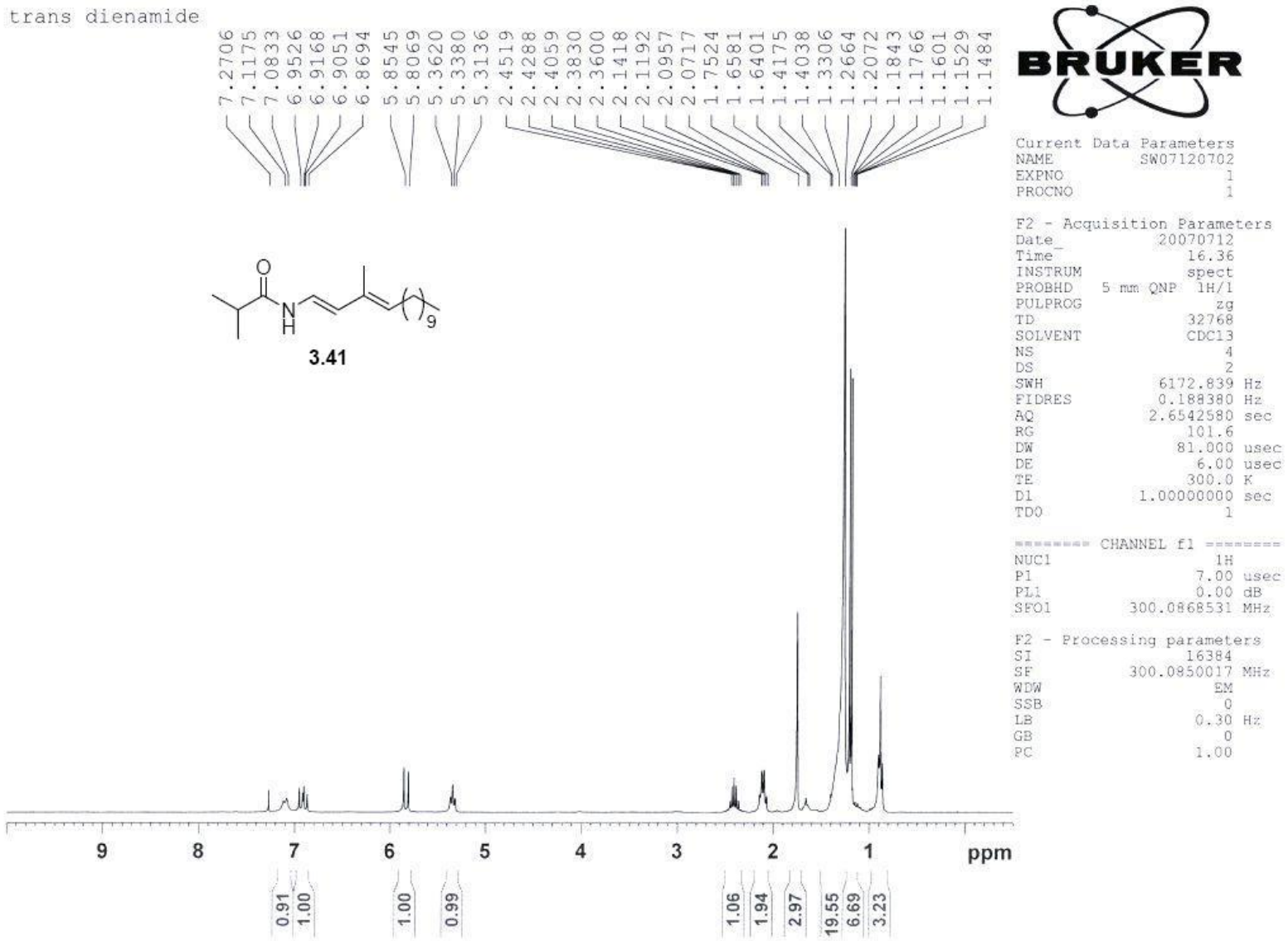
Current Data Parameters
NAME SW03230703
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20070323
Time 14.01
INSTRUM spect
PROBHD 5 mm Dual 13C/
PULPROG zgpg
TD 32768
SOLVENT CDCl3
NS 20
DS 2
SWH 17985.611 Hz
FIDRES 0.548877 Hz
AQ 0.9110004 sec
RG 1290.2
DW 27.800 usec
DE 6.00 usec
TE 300.0 K
D1 6.00000000 sec
d11 0.03000000 sec
DELTA 5.90000010 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 5.00 usec
PL1 0.00 dB
SFO1 75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 0.00 dB
PL12 24.44 dB
PL13 24.44 dB
SFO2 300.1312005 MHz

F2 - Processing parameters
SI 32768
SF 75.4677371 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40


trans dienamide
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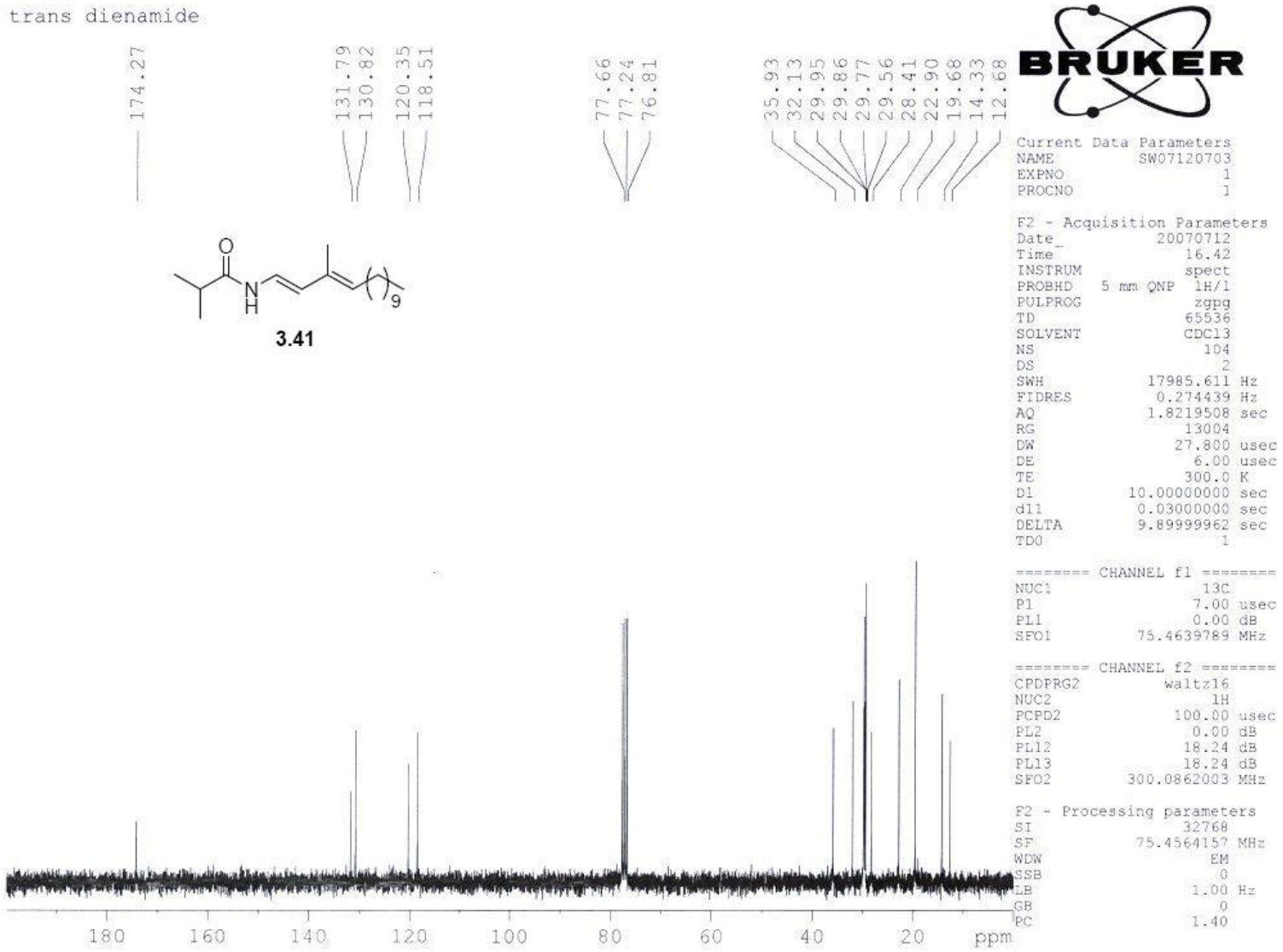
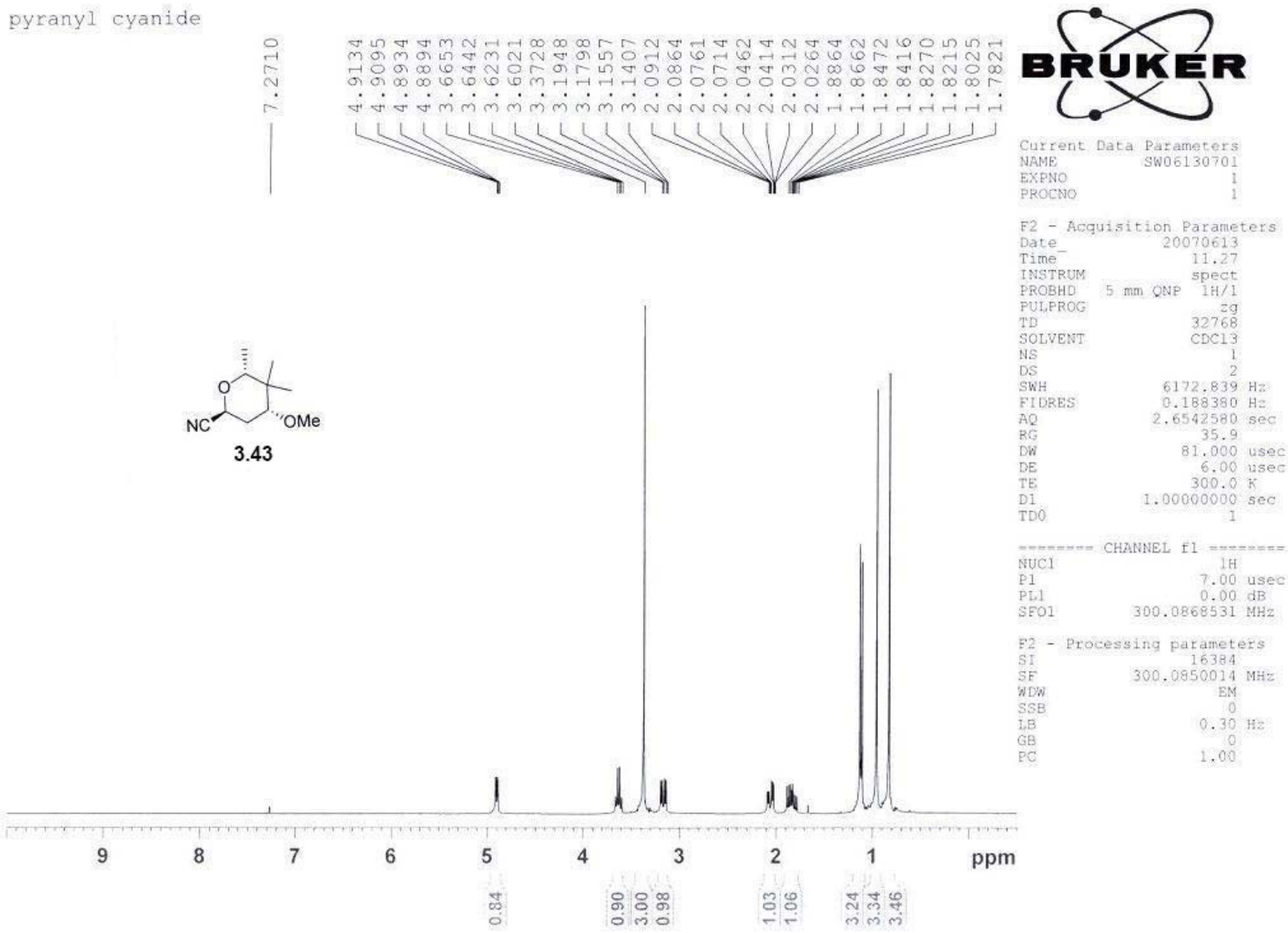
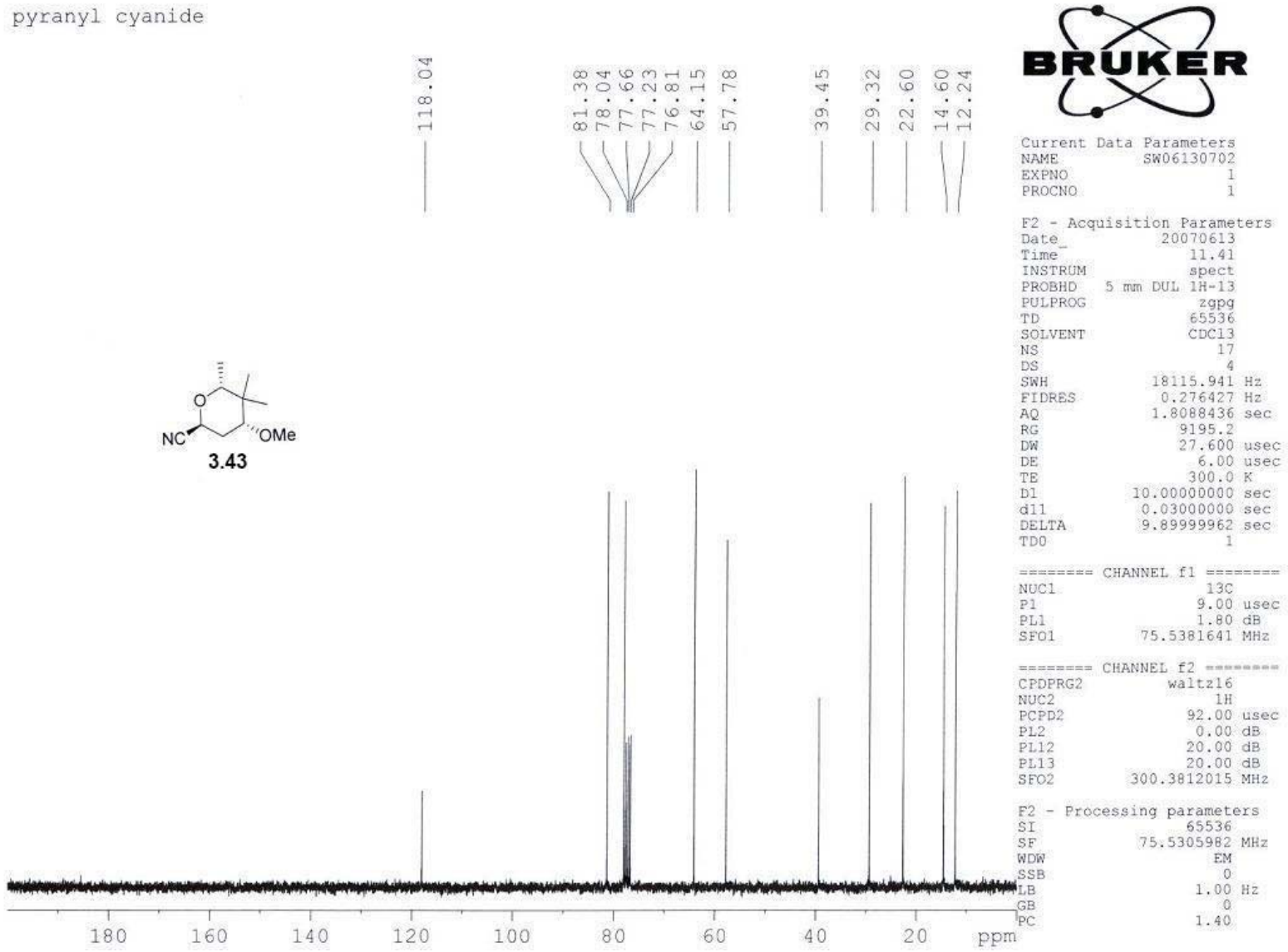
7.1175
7.0833
6.9526
6.9168
6.9051
6.8694
5.8545
5.8069
5.3620
5.3380
5.3136
2.4519
2.4288
2.4059
2.3830
2.3600
2.1418
2.1192
2.0957
2.0717
1.7524
1.6581
1.6401
1.4175
1.4038
1.3306
1.2664
1.2072
1.1843
1.1766
1.1601
1.1529
1.1484
3.41
9
BRUKER
Current Data Parameters
NAME SW07120702
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070712
Time 16.36
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zg
TD 32768
SOLVENT CDC13
NS 4
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 101.6
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 7.00 usec
PL1 0.00 dB
SFO1 300.0868531 MHz
F2 - Processing parameters
SI 16384
SF 300.0850017 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9
8
7
6
5
4
3
2
1
ppm
0.91
1.00
1.00
0.99
1.06
1.94
2.97
19.55
6.69
3.23


trans dienamide
174.27
131.79
130.82
120.35
118.51
77.66
77.24
76.81
35.93
32.13
29.95
29.86
29.77
29.56
28.41
22.90
19.68
14.33
12.68
3.41
BRUKER
Current Data Parameters
NAME SW07120703
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070712
Time 16.42
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 104
DS 2
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 13004
DW 27.800 usec
DE 6.00 usec
TE 300.0 K
D1 10.00000000 sec
d11 0.03000000 sec
DELTA 9.89999962 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.00 usec
PL1 0.00 dB
SFO1 75.4639789 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 0.00 dB
PL12 18.24 dB
PL13 18.24 dB
SFO2 300.0862003 MHz
F2 - Processing parameters
SI 32768
SF 75.4564157 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
180
160
140
120
100
80
60
40
20
ppm


pyranyl cyanide
7.2710
4.9134
4.9095
4.8934
4.8894
3.6653
3.6442
3.6231
3.6021
3.3728
3.1948
3.1798
3.1557
3.1407
2.0912
2.0864
2.0761
2.0714
2.0462
2.0414
2.0312
2.0264
1.8864
1.8662
1.8472
1.8416
1.8270
1.8215
1.8025
1.7821
NC
OMe
3.43
9
8
7
6
5
4
3
2
1
ppm
0.84
0.90
3.00
0.98
1.03
1.06
3.24
3.34
3.46
BRUKER
Current Data Parameters
NAME SW06130701
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070613
Time 11.27
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 1
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 35.9
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 7.00 usec
PL1 0.00 dB
SFO1 300.0868531 MHz
F2 - Processing parameters
SI 16384
SF 300.0850014 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

pyranyl cyanide



BRUKER

Current Data Parameters
NAME SW06130702
EXPNO 1
PROCNO 1

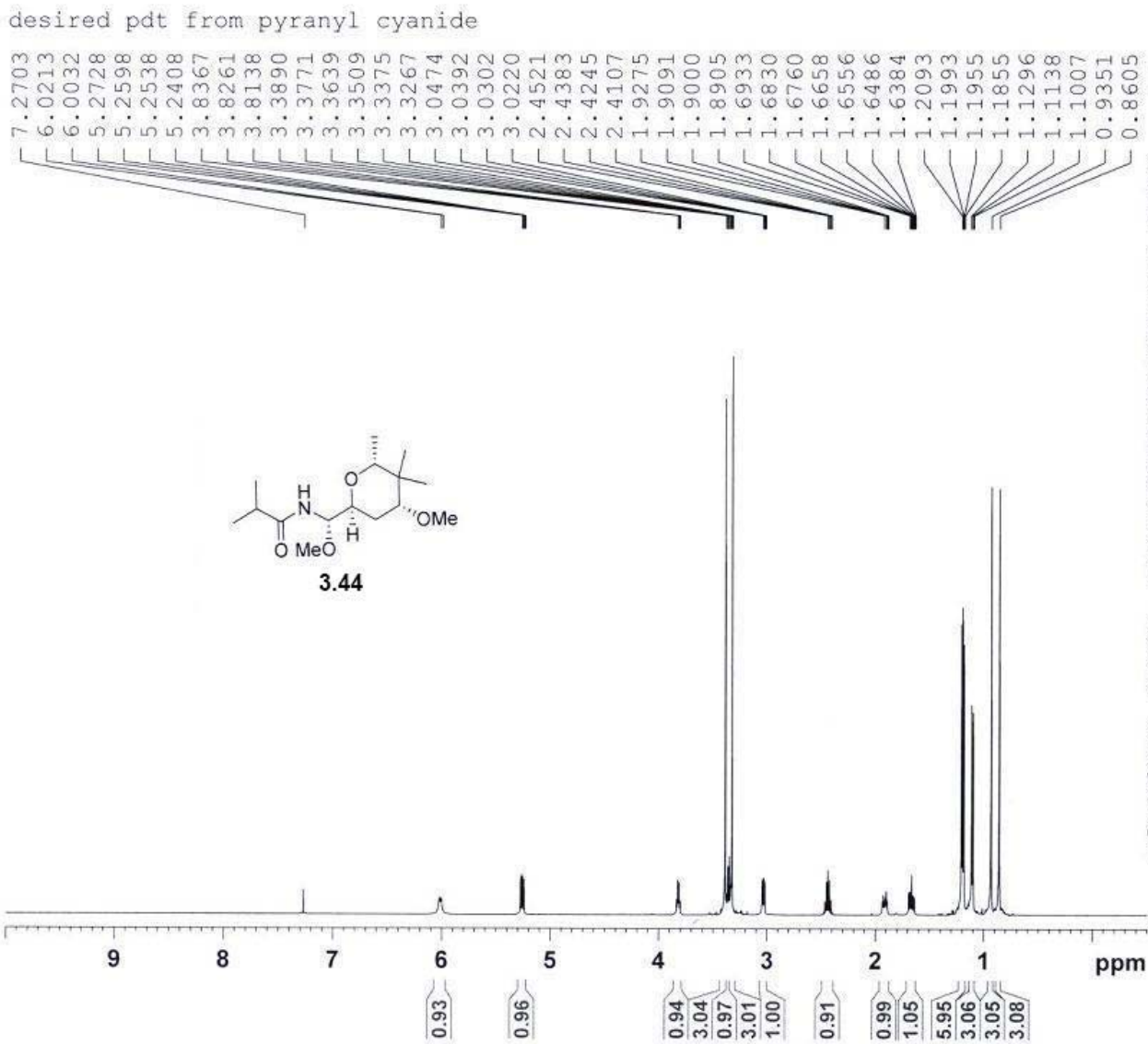
F2 - Acquisition Parameters
Date_ 20070613
Time 11.41
INSTRUM spect
PROBHD 5 mm DUL 1H-13
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 17
DS 4
SWH 18115.941 Hz
FIDRES 0.276427 Hz
AQ 1.8088436 sec
RG 9195.2
DW 27.600 usec
DE 6.00 usec
TE 300.0 K
D1 10.00000000 sec
d11 0.03000000 sec
DELTA 9.89999962 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 9.00 usec
PL1 1.80 dB
SFO1 75.5381641 MHz

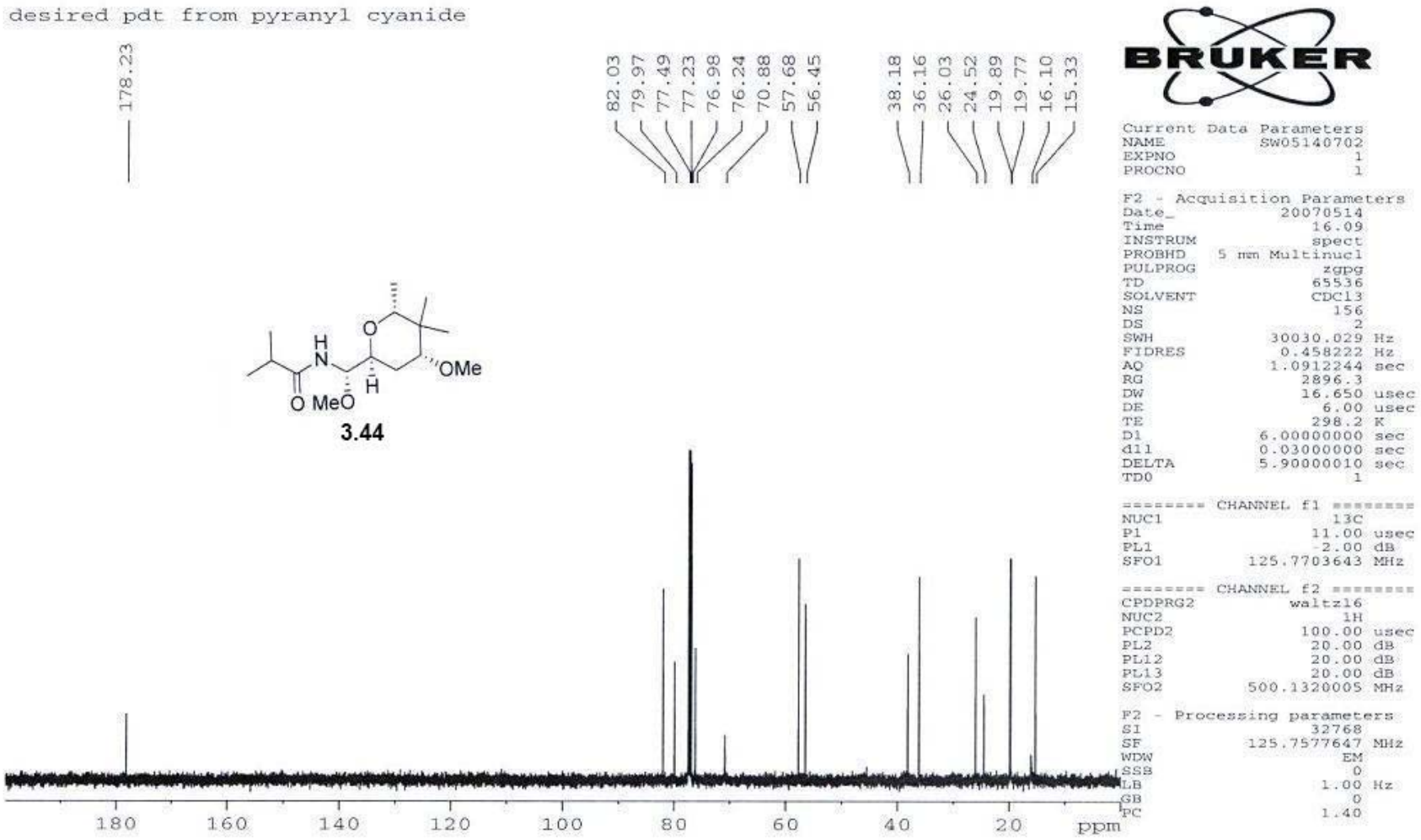
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 92.00 usec
PL2 0.00 dB
PL12 20.00 dB
PL13 20.00 dB
SFO2 300.3812015 MHz

F2 - Processing parameters
SI 65536
SF 75.5305982 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

desired pdt from pyranyl cyanide



desired pdt from pyranyl cyanide



BRUKER

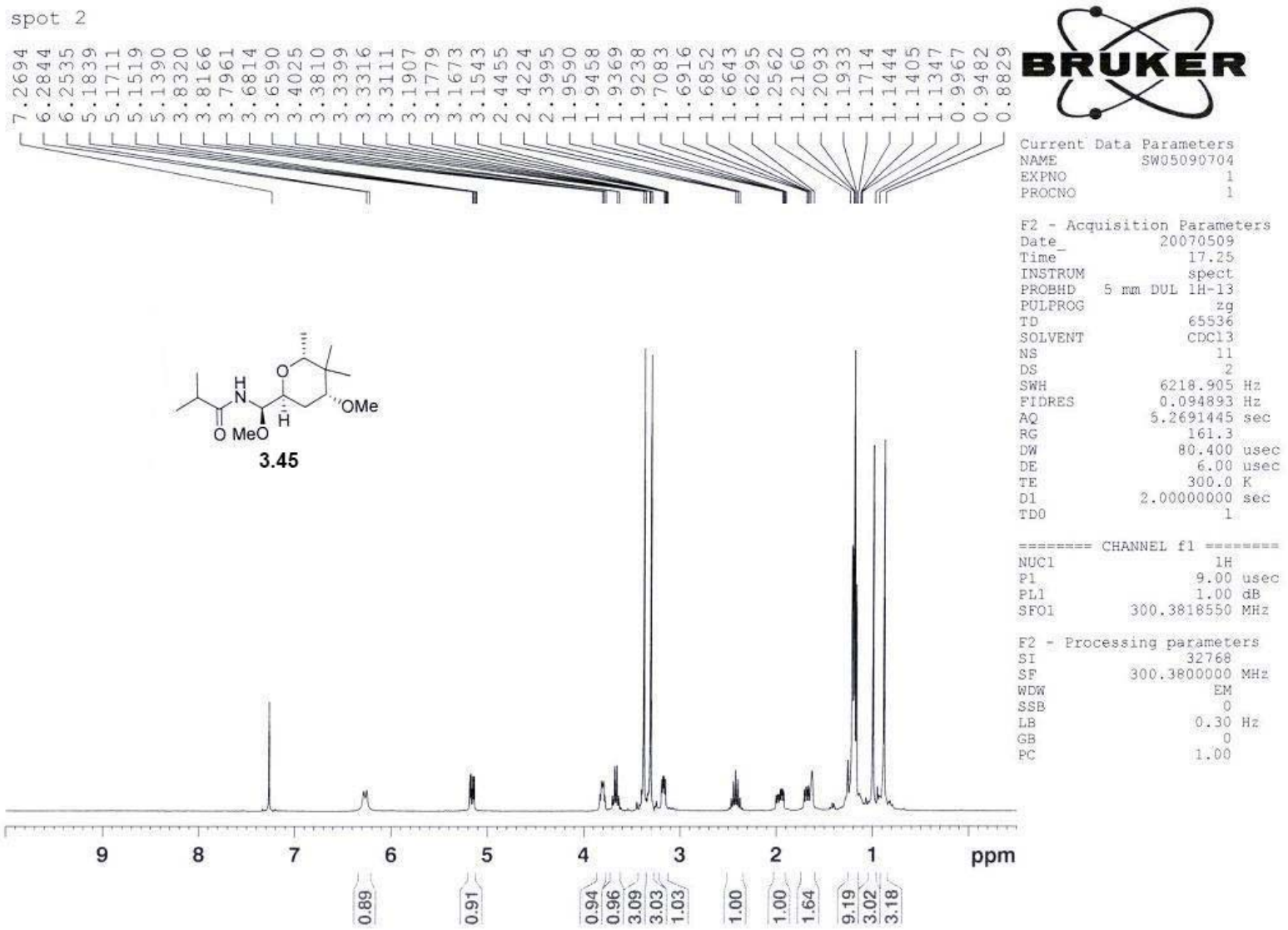
Current Data Parameters
NAME SW05140702
EXPNO 1
PROCNO 1

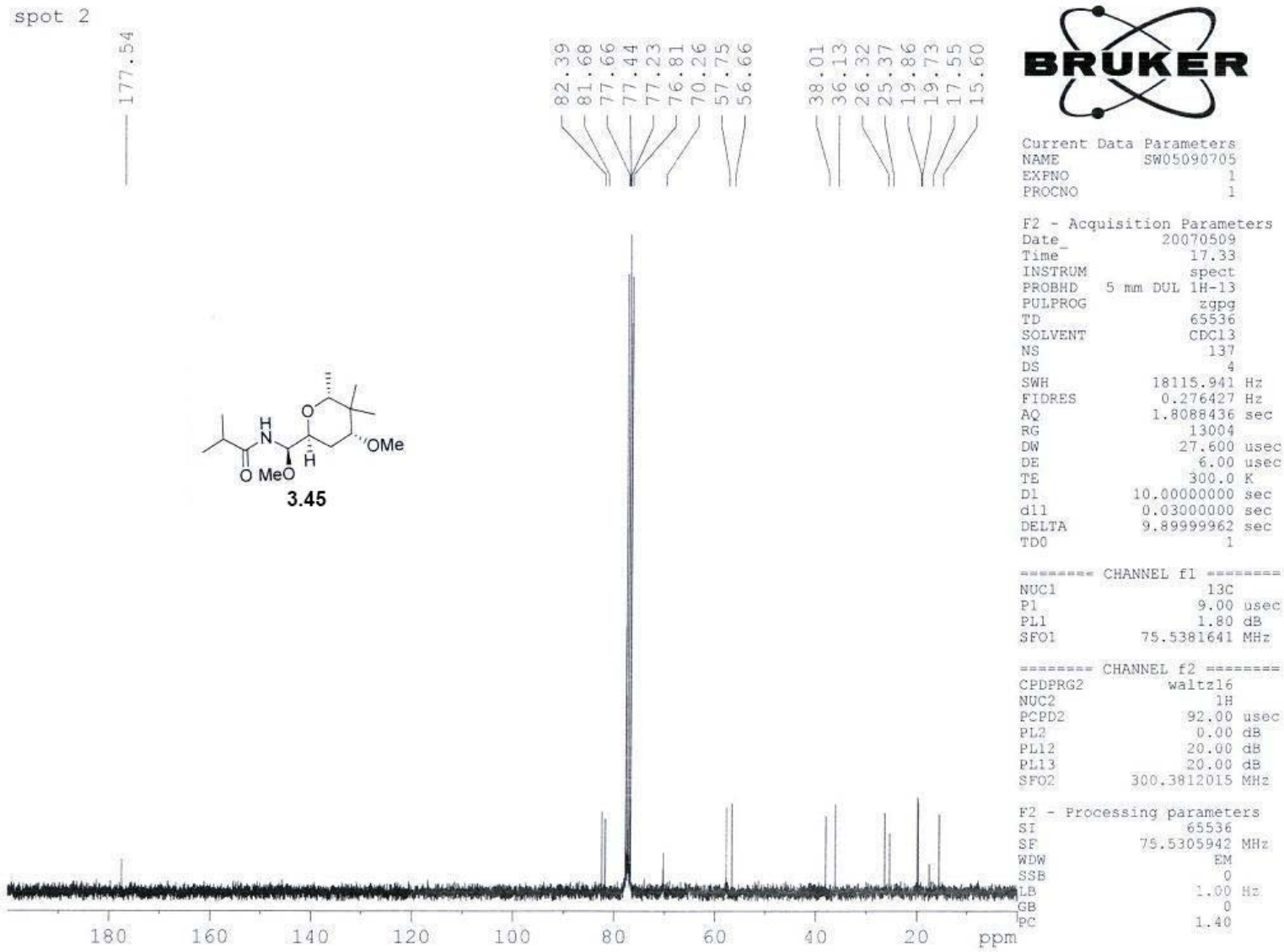
F2 - Acquisition Parameters
Date_ 20070514
Time 16.09
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 156
DS 2
SWH 30030.029 Hz
FIDRES 0.458222 Hz
AQ 1.0912244 sec
RG 2896.3
DW 16.650 usec
DE 6.00 usec
TE 298.2 K
D1 6.00000000 sec
d11 0.03000000 sec
DELTA 5.90000010 sec
TD0 1

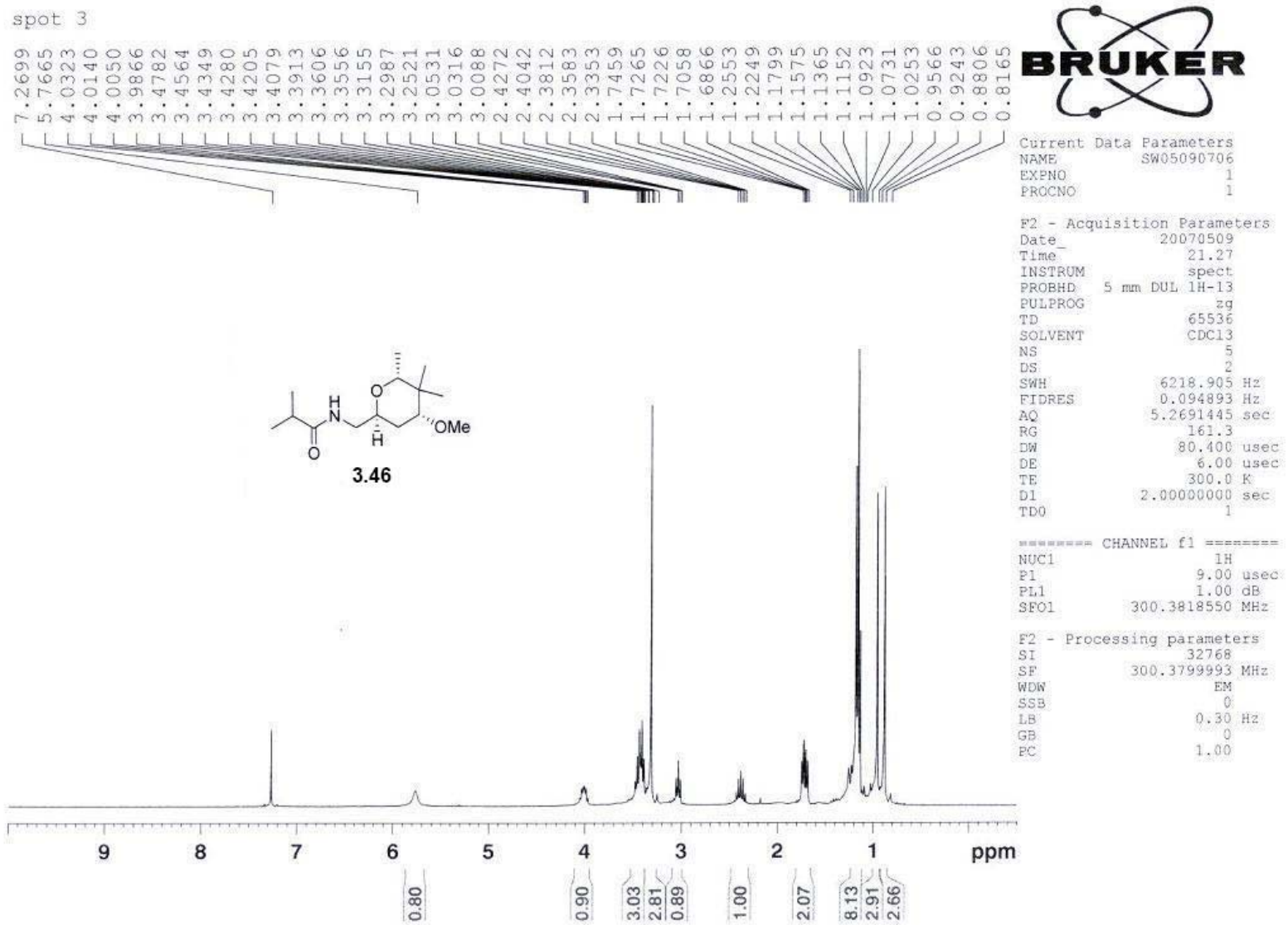
======== CHANNEL f1 ========
NUC1 13C
P1 11.00 usec
PL1 -2.00 dB
SFO1 125.7703643 MHz

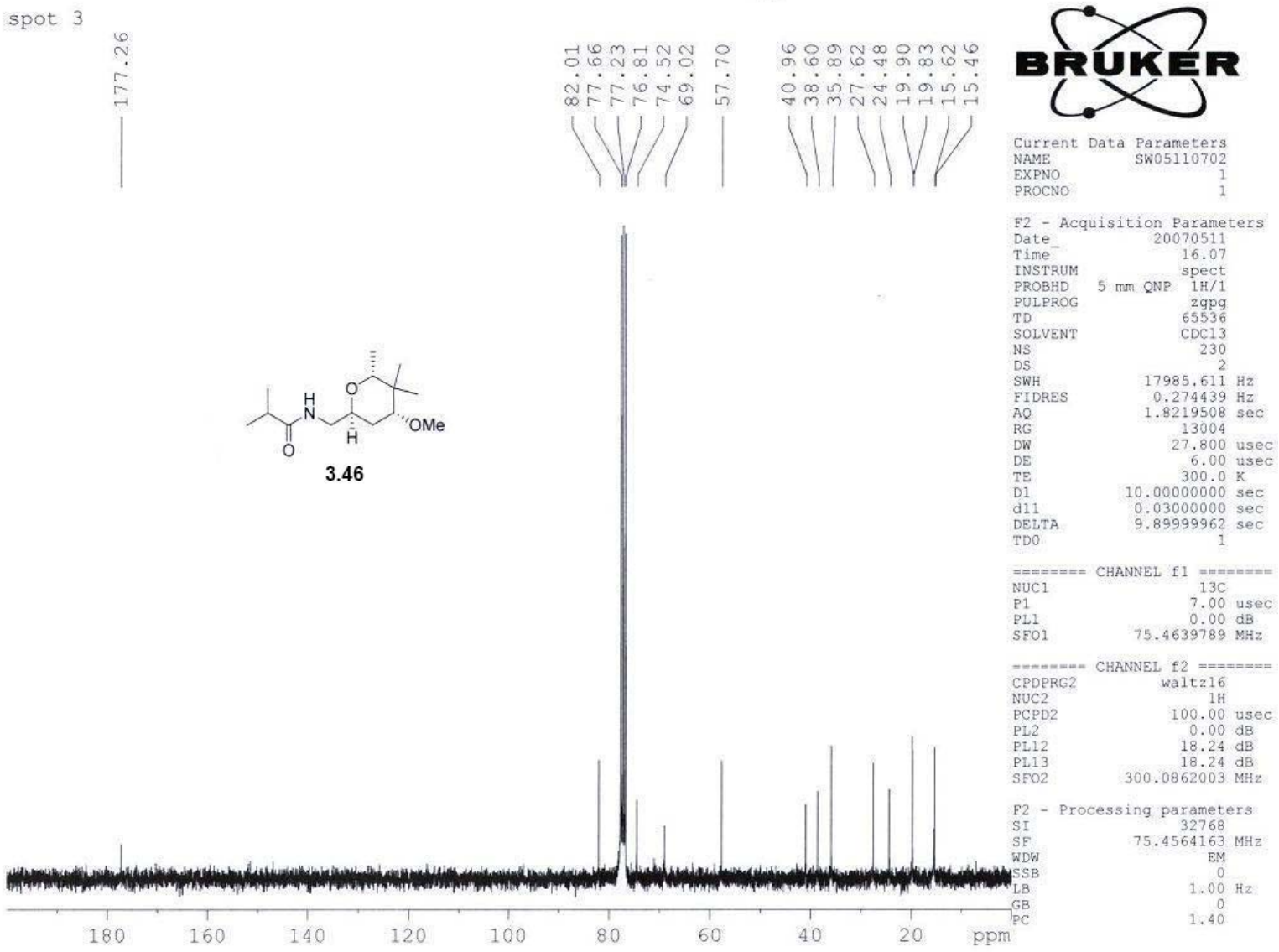
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 20.00 dB
PL12 20.00 dB
PL13 20.00 dB
SFO2 500.1320005 MHz

F2 - Processing parameters
SI 32768
SF 125.7577647 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40


spot 2
7.2694
6.2844
6.2535
5.1839
5.1711
5.1519
5.1390
3.8320
3.8166
3.7961
3.6814
3.6590
3.4025
3.3810
3.3399
3.3316
3.3111
3.1907
3.1779
3.1673
3.1543
2.4455
2.4224
2.3995
1.9590
1.9458
1.9369
1.9238
1.7083
1.6916
1.6852
1.6643
1.6295
1.2562
1.2160
1.2093
1.1933
1.1714
1.1444
1.1405
1.1347
0.9967
0.9482
0.8829
BRUKER
Current Data Parameters
NAME SW05090704
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070509
Time 17.25
INSTRUM spect
PROBHD 5 mm DUL 1H-13
PULPROG zg
TD 65536
SOLVENT CDCl3
NS 11
DS 2
SWH 6218.905 Hz
FIDRES 0.094893 Hz
AQ 5.2691445 sec
RG 161.3
DW 80.400 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.00 usec
PL1 1.00 dB
SFO1 300.3818550 MHz
F2 - Processing parameters
SI 32768
SF 300.3800000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
H
N
O
OMe
O MeO
H
3.45
9
8
7
6
5
4
3
2
1
ppm
0.89
0.91
0.94
0.96
3.09
3.03
1.03
1.00
1.00
1.64
9.19
3.02
3.18


spot 2
177.54
82.39
81.68
77.66
77.44
77.23
76.81
70.26
57.75
56.66
38.01
36.13
26.32
25.37
19.86
19.73
17.55
15.60
BRUKER
Current Data Parameters
NAME SW05090705
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070509
Time 17.33
INSTRUM spect
PROBHD 5 mm DUL 1H-13
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 137
DS 4
SWH 18115.941 Hz
FIDRES 0.276427 Hz
AQ 1.8088436 sec
RG 13004
DW 27.600 usec
DE 6.00 usec
TE 300.0 K
D1 10.00000000 sec
d11 0.03000000 sec
DELTA 9.89999962 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.00 usec
PL1 1.80 dB
SFO1 75.5381641 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 92.00 usec
PL2 0.00 dB
PL12 20.00 dB
PL13 20.00 dB
SFO2 300.3812015 MHz
F2 - Processing parameters
SI 65536
SF 75.5305942 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
H
N
O
O MeO
H
OMe
3.45
180
160
140
120
100
80
60
40
20
ppm


spot 3
7.2699
5.7665
4.0323
4.0140
4.0050
3.9866
3.4782
3.4564
3.4349
3.4280
3.4205
3.4079
3.3913
3.3606
3.3556
3.3155
3.2987
3.2521
3.0531
3.0316
3.0088
2.4272
2.4042
2.3812
2.3583
2.3353
1.7459
1.7265
1.7226
1.7058
1.6866
1.2553
1.2249
1.1799
1.1575
1.1365
1.1152
1.0923
1.0731
1.0253
0.9566
0.9243
0.8806
0.8165
BRUKER
Current Data Parameters
NAME SW05090706
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070509
Time 21.27
INSTRUM spect
PROBHD 5 mm DUL 1H-13
PULPROG zg
TD 65536
SOLVENT CDCl3
NS 5
DS 2
SWH 6218.905 Hz
FIDRES 0.094893 Hz
AQ 5.2691445 sec
RG 161.3
DW 80.400 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.00 usec
PL1 1.00 dB
SFO1 300.3818550 MHz
F2 - Processing parameters
SI 32768
SF 300.3799993 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
OMe
3.46
9
8
7
6
5
4
3
2
1
ppm
0.80
0.90
3.03
2.81
0.89
1.00
2.07
8.13
2.91
2.66


spot 3
177.26
82.01
77.66
77.23
76.81
74.52
69.02
57.70
40.96
38.60
35.89
27.62
24.48
19.90
19.83
15.62
15.46
OMe
3.46
180
160
140
120
100
80
60
40
20
ppm
Current Data Parameters
NAME SW05110702
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070511
Time 16.07
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 230
DS 2
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 13004
DW 27.800 usec
DE 6.00 usec
TE 300.0 K
D1 10.00000000 sec
d11 0.03000000 sec
DELTA 9.89999962 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.00 usec
PL1 0.00 dB
SFO1 75.4639789 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 0.00 dB
PL12 18.24 dB
PL13 18.24 dB
SFO2 300.0862003 MHz
F2 - Processing parameters
SI 32768
SF 75.4564163 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

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