CHEMISTRY AND APPLICATIONS OF N-HETEROCYCLIC CARBENE BORANES

by

Xiangcheng Pan

B.S., Magna Cum Laude, Eastern Washington University, Cheney, USA, 2009
B.S., Shanghai Normal University, Shanghai, China, 2009

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This dissertation was presented

by

Xiangcheng Pan

It was defended on

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and approved by

Paul E. Floreancig, Professor, Chemistry

Craig S. Wilcox, Professor, Chemistry

Wen Xie, Professor, Pharmaceutical Sciences and Pharmacology

Dissertation Advisor:

Dennis P. Curran, Distinguished Service Professor and Bayer Professor, Chemistry

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Xiangcheng Pan, PhD

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Chemistry and applications of N-heterocyclic carbene borane complex are demonstrated. Chapter 1 describes and introduces the background of NHC-boranes. Chapter 2 demonstrates the discovery and studies of thiol-catalyzed radical reduction reactions of alkyl and aryl halides with NHC-boranes. The radical reductive cyclization reactions with NHC-boranes were also investigated. These reactions occur by a polarity-reversal process, where thiol is the polarity-reversal catalysis. Chapter 3 describes the development and preparative experiments of first homolytic substitution reactions of NHC-boryl radicals at divalent atoms such as sulfur and selenium. The primary reaction products of heterocycle disulfides undergo a 1,3-boryl shift from S to N to give new class of stable NHC-boranes with B-N heterocycles bonds.

Chapter 4 describes the discovery that disulfides (RSSR), NHC-boryl mono- (NHC-BH_2SR) and bis-sulfides (NHC-$BH(SR)_2$) serve as both radical initiators and precatalysts in the radical reductions and reductive cyclizations with NHC-boranes. These reactions are also believed to occur by the polarity reversal catalysis mechanism. Chapter 5 describes the thiolation reactions with new synthesized NHC-boryl sulfides and –amido complexes. Chapter 6 introduces iodine-activated hydroboration and preliminary results of direct hydroboration.

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LIST OF ABBREVIATIONS

9-BBN   9-borabicyclo[3.3.1]nonane

Ad   1-adamantyl

AIBN   2,2'-azobis(2-methylpropionitrile) (azobisisobutyronitrile)

BDE   bond dissociation energy

BTF   (trifluoromethyl)benzene (benzotrifluoride)

Bn   benzyl

Bu   butyl

Cy   cyclohexyl

DCM   dichloromethane

diAd-Imd   1,3-bis(adamantyl)imidazol-2-ylidene

diCy-Imd   1,3-dicyclohexylimidazol-2-ylidene

diMe-BenzImd   1,3-dimethylbenzimidazol-2-ylidene

diMe-Imd   1,3-dimethylimidazol-2-ylidene

diMe-Tri   2,4-dimethyl-1,2,4-triazol-3-ylidene

diMes-Imd   1,3- dimesitylimidazol-2-ylidene

DFT   density functional theory

diiPr-Imd   1,3-diisopropylimidazol-2-ylidene

dipp   2,6-diisopropylphenyl

dipp-Imd	1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene
DMSO	dimethyl sulfoxide
DTBP	di-*tert*-butyl peroxide
El	electrophile
EPR	electron paramagnetic resonance
equiv	equivalent
Et	ethyl
FLP	frustrated Lewis pair
GP	general procedure
HMDS	bis(trimethylsilyl)amide (hexamethyldisilazide)
HPLC	high performance liquid chromatography
HRMS	high resolution mass spectrometry
Ipc	isopinocampheyl
Imd	imidazol-2-ylidene
IR	infrared
LB	Lewis base
LDBB	lithium 4,4'-di-*tert*-butyl biphenylide
mCPBA	*meta*-chloroperbenzoic acid
Me	methyl
Mes	2,4,6-trimethylphenyl (mesityl)
Ms	methylsulfonyl (mesyl)
MW	molecular weight
NMR	nuclear magnetic resonance

NHC	N-heterocyclic carbene
Nuc	nucleophile
Ph	phenyl
PT	1-phenyltetrazol-5-yl
PTOC	2-thiooxopyridin-1(2*H*)-yl (pyridine thiooxycarbonyl)
Py	pyridine
rt	room temperature
SOMO	singly occupied molecular orbital
TBHN	di-*tert*-butyl hyponitrite
*t*Bu	*tert*-butyl
TEMPO	(2,2,6,6-tetramethylpiperidin-1-yl)oxy
Tf	trifluoromethylsulfonyl (triflyl)
THF	tetrahydrofuran
TMS	trimethylsilyl
Tf	trifluoromethylsulfonyl (triflyl)
TLC	thin layer chromatography
Ts	4-methylphenylsulfonyl (tosyl)
χ_M	Mulliken electronegativity
UV	ultraviolet

PREFACE

I would never have been able to finish my dissertation without the guidance of my dissertation advisor and committee members, help from friends, and support from my family and wife. I would like to take this opportunity to thank a group of incredible people during my graduate studies.

I would like to express my deepest gratitude to my advisor, Professor Dennis Curran, for his excellent guidance and providing me with an excellent atmosphere for doing research. I am extremely grateful for his research philosophy and freedom that he has granted for me to conduct my research, as well as his help in improving my writing skills. I have certainly learned much from him over the years, not only from his chemistry knowledge but also from his brilliance, respectable personality, and relentless pursuit of innovation. I will always owe a great deal to him for helping me develop and mature as a scientist.

I am also grateful to my dissertation committee members Professors Paul Floreancig, Craig Wilcox, and Wen Xie, for their time and valuable suggestions on my comprehensive exam, research proposal, and dissertation writing. Special thanks to Professor Floreancig for his superb guiding me through the proposal writing. Professor Toby Chapman is greatly acknowledged for being my proposal reviewer.

This project was highly collaborative. The team of NHC-borane has always included brilliant students and postdocs who discussed their discoveries and failures, shared ideas and

1.0   INTRODUCTION

1.1   N-HETEROCYCLIC CARBENE BORANES

N-Heterocyclic carbenes (NHCs) are singlet carbenes, in which at least one nitrogen atom is directly bonded to the carbene in a heterocycle.[1-3] Compared to many other carbenes, NHCs are stable, and they behave like strong σ-donors and weak π-acceptors because of the stabilization by the lone pairs on the adjacent nitrogen atoms. These beneficial features make NHCs important ligands for transition metals such as ruthenium,[4] palladium,[5] silver[6] as well as some main group elements like phosphorus[7] and silicon.[8] The reactions and applications using NHCs as organocatalysis have also been broadly investigated.[9]

Complexes between NHCs as Lewis bases and boranes as Lewis acids are called *N*-heterocyclic carbene boranes (NHC-boranes).[10] The first NHC-borane 1,3,4,5-tetramethyl-imidazol-2-ylidene borane **1** was synthesized by complexation of the corresponding free carbene and BH_3•THF in 1993 (Figure 1).[11, 12] Ito's 1,3-diisopropyl- and 1,3-dimesitylimidazol-2-ylidene triethylborane complexes **2** and **3** were used as stable precursors of NHCs.[13] Dixneuf's stable 1-ethenyl-3-mesitylimidazol-2-ylidene borane **4** was used to investigate the hydroboration of NHC-boranes.[14] A unique dimer of NHC-boranes **5** was obtained by dimerization of *N*-monosubstituted imidazole complexes of boranes.[15]

1
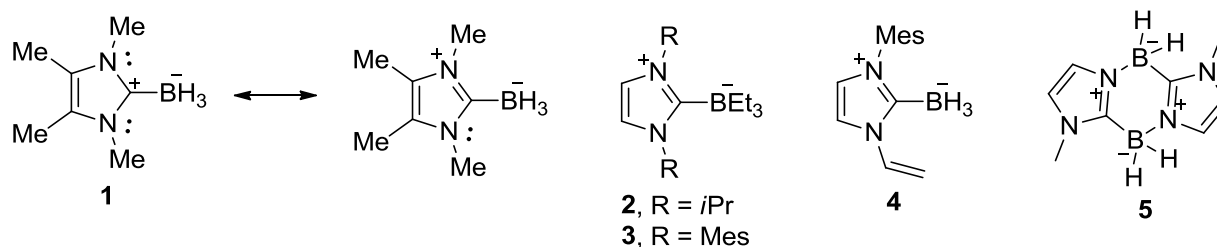
Figure 1. Resonance structures of **1** and selected NHC-boranes.

Since the publications on NHC-boranes from Curran in 2008[10] and from Robinson in 2007,[16] this field is beginning to flourish. NHC-boranes are precursors of new reactive intermediates including boryl radicals,[17] anions[18] and cations.[19] These reactive intermediates can generate new classes of NHC-boranes and are useful as reagents in organic synthesis.

Like amine- and phosphine-boranes, NHC-boranes react with strong acids and various electrophiles to give substitution products (Scheme 1).[20] For example, the reaction of 1,3-bis-(2,6-diisopropylphenyl)imidazol-2-ylidene borane (**6**, dipp-Imd-BH$_3$) and 1 equiv of HI or 0.5 equiv of I$_2$ gave the mono-substituted product dipp-Imd-BH$_2$I **7**.
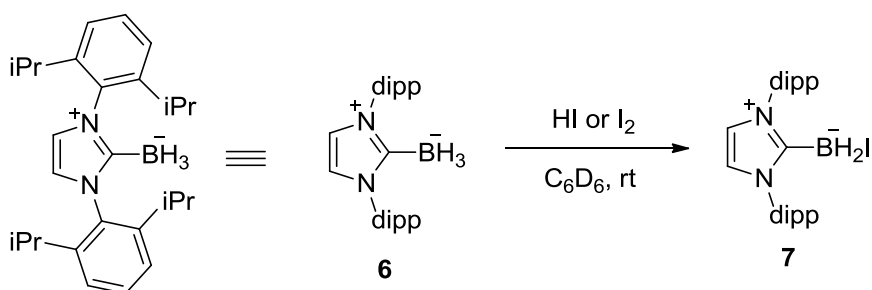
Scheme 1. Representative acid/base and electrophilic halogenation reactions of dipp-Imd-BH$_3$ **6**.

Although boron bears a formal negative charge in NHC-boranes, nucleophilic substitutions on boron center with a good leaving group can be achieved.[20] Substitution of NHC-

boryl iodide **7** with sodium azide or cyanide provided boron azides **8a** or isocyanates **8b**. Examples of such classes of boron compounds are rare.
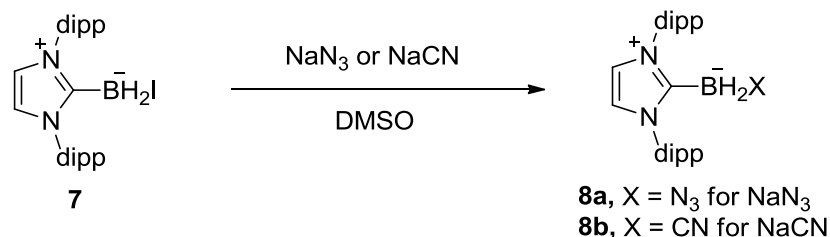
Scheme 2. Nucleophilic substitutions of dipp-Imd-BH$_2$I **7** with NaN$_3$ or NaCN.

Boryl anions are extremely rare,[21] and Curran group[18] reported that by treating **7** with lithium di-*tert*-butylbiphenyl (LDBB, Freeman's reagent[22]), NHC-boryl anion **9** could be generated in situ and trapped by diethyl carbonate to provide complex **10** in 61% yield (Scheme 3).
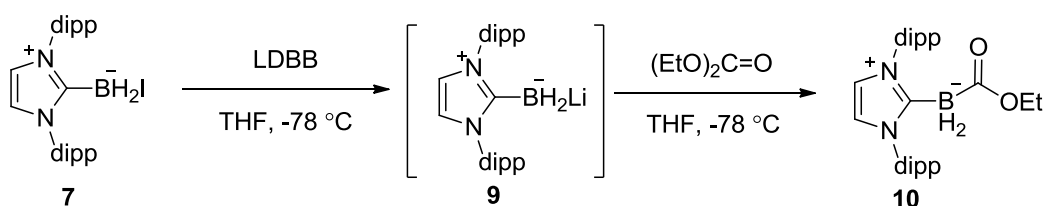
Scheme 3. Generation and trapping of an unsubstituted NHC-boryllithium reagent.

1.2   DEOXYGENATION OF XANTHATES AND EVIDENCE FOR NHC-BORYL

RADICAL INTERMEDIATES

Curran, Lacôte and coworkers were interested in NHC-boranes because they are promising radical H-atom donors. Free borane (BH_3) is not a good radical hydrogen atom donor because the B-H bond dissociation energy (BDE) is too high (106.6 kcal/mol).[10] Lower B-H BDEs could be achieved by complexion of borane with amines and phosphines. Calculations by Rablen show that B-H BDEs for NH_3-BH_3 and PH_3-BH_3 are 103.6 and 93.9 kcal/mol.[23] Compared to classic radical hydrogen donors like Bu_3Sn-H (74 kcal/mol) and $(Me_3Si)_3Si$-H (79 kcal/mol), amine- and phosphine boranes have limited applications in organic radical chemistry. A UB3LYP/LACVP* level calculation shows that NHC-boranes have significantly reduced B-H BDEs of 79-80 kcal/mol (Figure 2).[10] This is because spin density of boryl radicals can delocalize into the adjacent NHC rings.
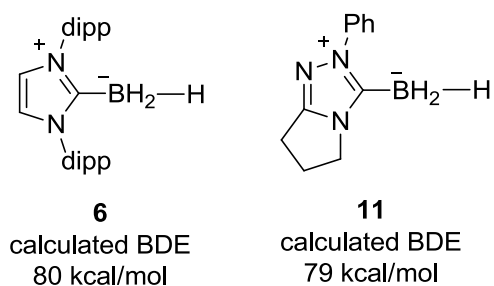
Figure 2. Calculated BDEs for NHC-boranes **6** and **11**.

Based on the promising calculated BDEs, Ueng and coworkers conducted Barton-McCombie's deoxygenation of secondary xanthates and related functional groups with NHC-borane **6** or **11** and radical initiator AIBN or Et_3B/O_2 to provide products in 57-84% isolated

yields.[10] Observations of radical rearrangement products suggested the radical intermediates were involved in these reactions. For example, deoxygenation of precursor **12** with **6** and Et₃B gave the cyclopropyl ring opening product **13** in 58% yield, and reduction of xanthate **14** with **11** and AIBN gave 5-*exo-trig* cyclization product **15** in 67% yield (Scheme 4). This was the first use of NHC-boranes as reagents in radical chemistry.
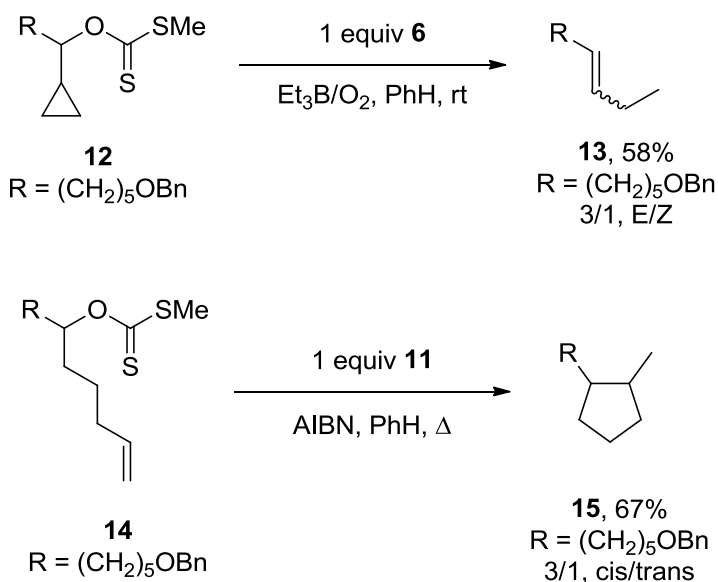
Scheme 4. Radical rearrangements observed when reduction of **12** and **14** with NHC-boranes.

Radical deoxygenations with second-generation NHC-boranes were reported by Ueng in 2009. [24] Low molecular weight NHC-boranes 1,3-dimethylimidazol-2-ylidene borane (diMe-Imd-BH₃, **16**) and 2,4-dimethyl-1,2,4-triazol-3-ylidene borane (diMe-Tri-BH₃, **17**) were superior to the first generation predecessors because they exhibited better performance even with lower amounts of initiator and reducing reagent. For example, reduction of sugar-derived xanthate **18** required 2 equiv of dipp-Imd-BH₃ **6** with 1 equiv AIBN initiator to provide an acceptable

isolated yield (75%) of **19** over 16 h. In contrast, reductions of **18** with 1 equiv of **16** or **17** and

0.1 equiv of initiator were completed in 2 h and gave **19** in 88–89% isolated yields (Scheme 5).

6, dipp-Imd-BH$_3$
MW 402 g/mol

16, diMe-Imd-BH$_3$
MW 110 g/mol

17, diMe-Tri-BH$_3$
MW 111 g/mol
soluble in water

NHC-borane	equiv	AIBN	time	isolated yield
6	2	1 equiv	16 h	75%
16	1	10 mol%	2 h	89%
17	1	10 mol%	2 h	88%
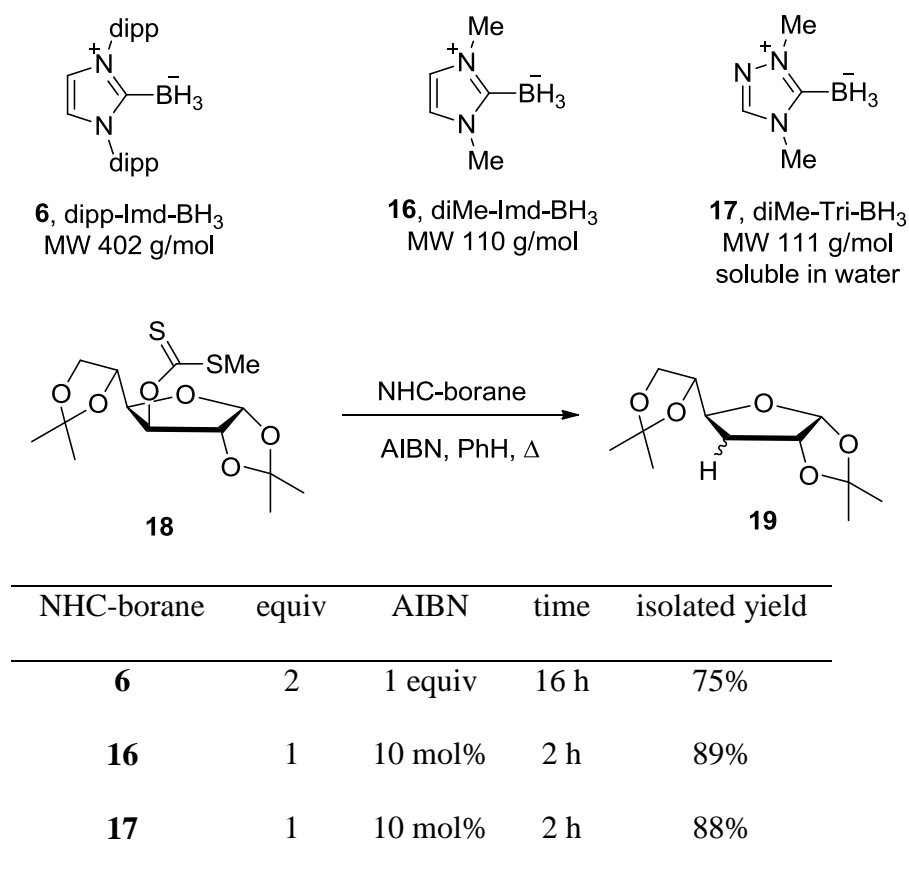
Scheme 5. Reductions of xanthate **18** with improved second-generation reagents **16** and **17**.

The mechanism of deoxygenations with NHC-borane is similar to the Barton-McCombie

mechanism (Scheme 6).[25] In the propagation steps, the NHC-boryl radical **21** adds to the

xanthate **22** to give the radical intermediate **23**. The intermediate **23** fragments to an alkyl radical

24 and a boron dithiocarbonate **25**. Finally radical H-atom transfer from NHC-BH$_3$ to the alkyl

radical **24** gives reduction product **26**. In this mechanism, NHC-BH$_3$ **20** is the radical H-atom source and NHC-boryl radical **21** is the radical chain transfer agent.[26]
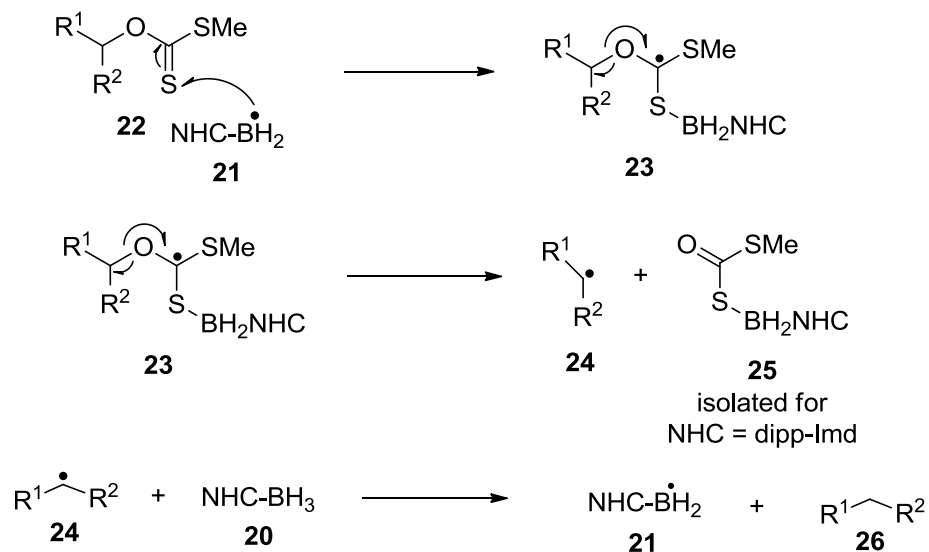
Scheme 6. Barton-McCombie mechanism with an NHC-boryl radical intermediate.

Because NHC-boryl radicals were unknown before 2008, the existence and reactions of these intermediates have been extensively investigated. The isolation of the boron by-product **25** of the xanthate reduction implied the existence of NHC-boryl radical intermediate **21** in Scheme 6. In addition, evidence has been obtained by observation of NHC-boryl radicals by EPR spectroscopy (either directly[26,27] or by spin trapping[28]) and by UV-visible spectroscopy during laser flash photolysis (LFP).[29]

For example, dipp-Imd-BH$_2$• **21** radical was directly detected by photolysis of a solution of dipp-Imd-BH$_3$ **6** and di-*tert*-butyl peroxide (*t*BuO-O*t*Bu, DTBP). The observed EPR spectrum of **21** matched very well to a simulated one with the g-factor 2.0028 and the hyperfine splitting values $a(^{11}B) = 7.3$ G, $a(2H\alpha) = 11.4$ G, $a(2N) = 4.03$ G, $a(2H_{4,5}) = 1.0$ G. These data suggest

that NHC-boryl radicals **21** are π-type radicals (Figure 3).[26] They are different from amine-boryl radicals **27** (σ-type radicals with pyramidal geometry at boron and much larger $a(^{11}\text{B}) = 51.3$ G and much smaller $a(1\text{N}) = 1.4$ G).[30]

21
$a(^{11}\text{B}) = 7.3$ G
$a(2\text{N}) = 4.03$ G

27
$a(^{11}\text{B}) = 51.3$ G
$a(1\text{N}) = 1.4$ G
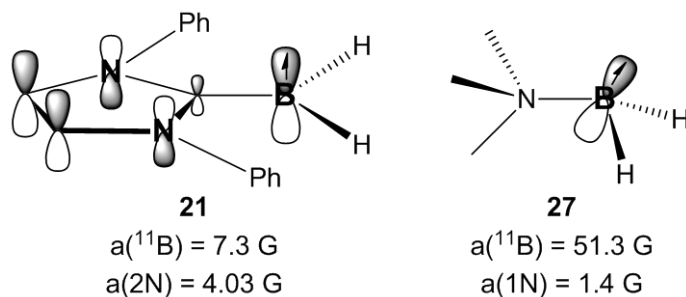
Figure 3. Sketches of the SOMOs of NHC-boryl radical **21** (left) and trimethyl amine-boryl radical (right).

Rate constants k_H for hydrogen transfer from boron to the primary nonyl radical **28** have been determined (Figure 4). The rate constant k_H of the dipp-Imd-BH$_3$ **6** is 2×10^4 M^{-1}s^{-1}. A similar k_H value is obtained for a comparable sterically hindered complex diAd-Imd-BH$_3$ **30**, and less sterically hindered complex **11** has the k_H value about 6×10^4 M^{-1} s^{-1}. Rate constants of 8×10^4 M^{-1}s^{-1} were measured for the least hindered complexes diMe-Imd-BH$_3$ **16** and diMe-Tri-BH$_3$ **17**.[31]

$$\overset{\bullet}{\text{C}_9\text{H}_{19}} + \text{NHC-BH}_3 \xrightarrow{k_\text{H}} \text{C}_9\text{H}_{20} + \text{NHC-}\overset{\bullet}{\text{BH}_2}$$

28 **20** **29** **21**

6
$k_\text{H} = 2 \times 10^4$

30
$k_\text{H} = 2 \times 10^4$

11
$k_\text{H} = 6 \times 10^4$

16
$k_\text{H} = 8 \times 10^4$

17
$k_\text{H} = 8 \times 10^4$
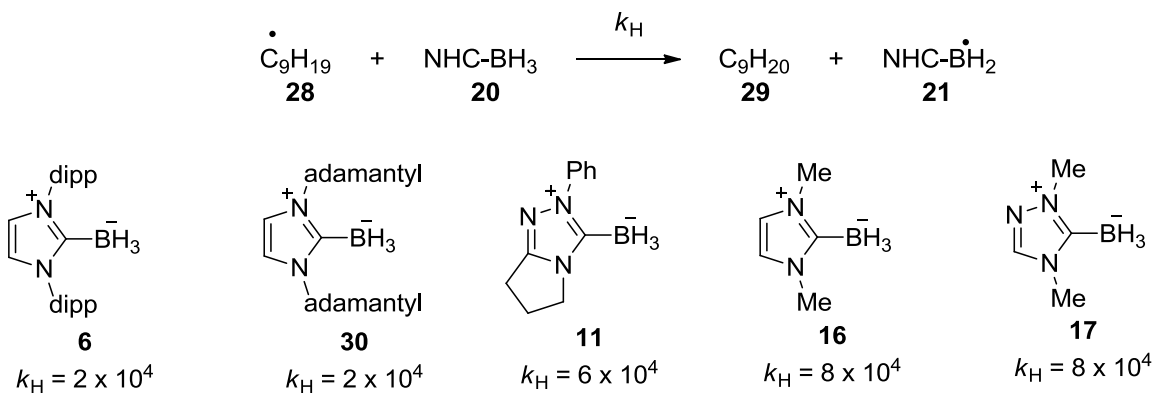
Figure 4. Rate constants k_H (M^{-1} s^{-1}) for selected NHC-boranes.

Figure 5 shows a scale of the rate constants of hydrogen transfer to alkyl radical for several popular radical hydrogen donor reagents. The rate constants for the NHC-boranes are lower than those of Bu_3Sn-H or $(Me_3Si)_3Si$-H. This is consistent with the calculated BDEs of NHC-boranes. In contrast, the *tert*-butoxy radical ($^tBuO\bullet$) abstracts hydrogen atoms from **16** up to 3 x 10^8 $M^{-1}s^{-1}$.[28] These results suggest that NHC-boranes and NHC-boryl radicals are nucleophilic, while alkoxy radicals are electrophilic and alkyl radicals are nucleophilic.
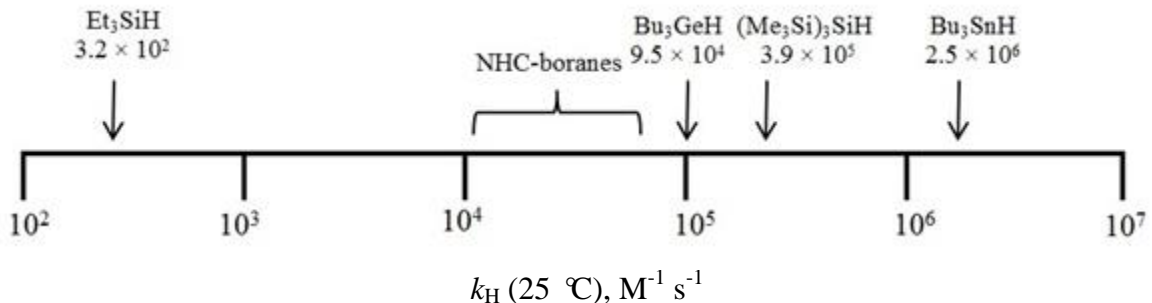
Figure 5. Scale of rate constants for donations of hydrogen atoms to alkyl radicals.[31]

After isolation of the xanthate-derivatived boron by-product **25**, direct observation of NHC-boryl radicals by EPR spectroscopy, and determination of the rate constants k_H for H-atom transfer from NHC-boranes, the existence of NHC-boryl radicals and the mechanism proposed in Scheme 6 are now all supported.

1.3   IONIC AND RADICAL REDUCTION WITH NHC-BORANES

1.3.1   Ionic Reduction with NHC-boranes

The hydride donor properties of NHC-boranes were discovered during the radical reductions of halides. Chu and coworkers reported reductions of dodecyl iodide to dodecane by dipp-Imd-BH$_3$ **6** with and without radical initiators. Comparable yields were obtained. Other clues further supported an ionic mechanism rather than a radical pathway for the halide reductions. For example, dodecyl iodide (a primary iodide) was selectively reduced in the presence of 1-iodoadamantane (a tertiary iodide), and radical probe experiments were negative. Reduction of 5-*exo-trig* cyclizable precursor **31** gave only directly reduced product **32** in 58% isolated yield without any cyclized product **33** (Scheme 7).[32]
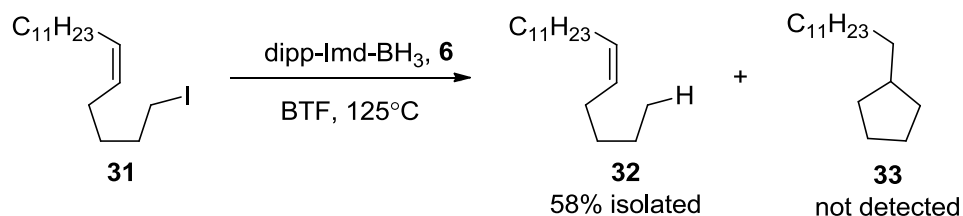
Scheme 7. Reductions of cyclizable probe **31** with dipp-Imd-BH$_3$ **6**.

Information about the scope of ionic reductions is shown in Scheme 8. Halides (**34a,b**), tosylates (**34c**) and mesylates (**34d**) usually require high temperature (110 or 140 ˚C) to give good yields (60–95%), but triflates (**34e**) can be reduced rapidly at or near room temperature in moderate yields (Scheme 8).
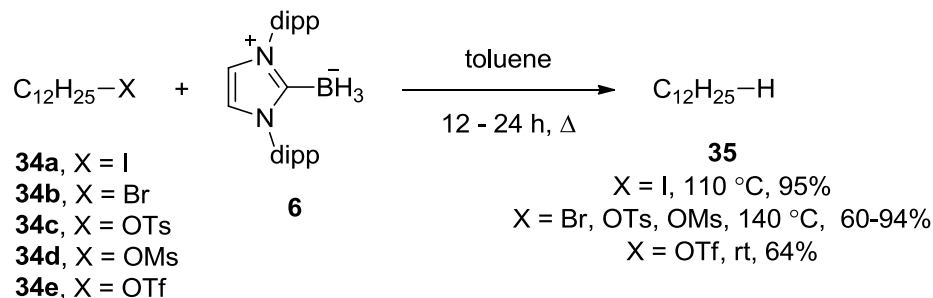
Scheme 8. Examples of ionic reductions of halides, tosylates, mesylates, triflates by NHC-borane **6**.

1.3.2 Problems with radical dehalogenation with NHC-boranes

Because of the success in the radical deoxygenation of xanthates, the radical reduction of halides with NHC-boranes was also investigated. In an initial LFP study, Lalevée found that diMe-Imd-$BH_2\bullet$ (**36**) could abstract chloride from $CHCl_3$ **37** (6×10^6 $M^{-1} s^{-1}$) and iodide from iodopropane **40** (1.8×10^8 $M^{-1} s^{-1}$) at quite high rate constants (Scheme 9).[28] Walton also showed that **36** readily abstracts primary and tertiary bromine atoms at room temperature based on EPR studies.[27]
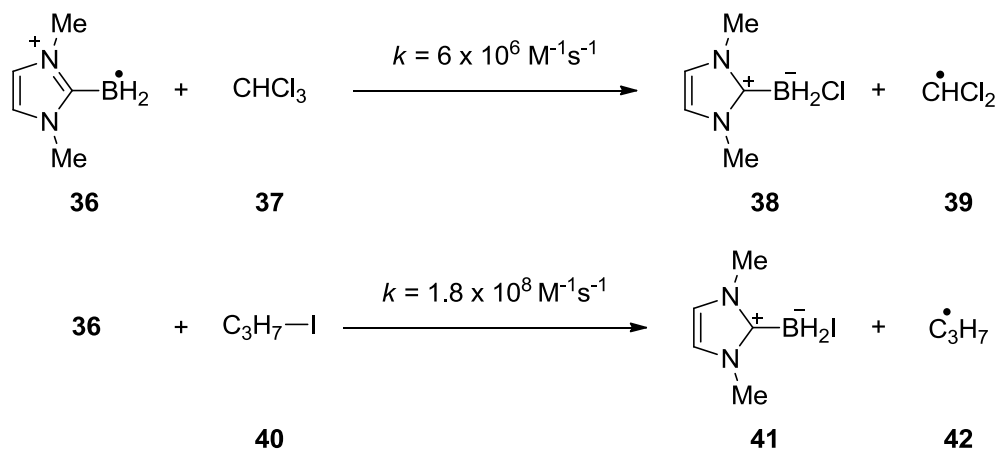
Scheme 9. Rate constants of halogen abstraction by diMe-Imd-$BH_2\bullet$ **36**.

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After the promising rate data for halogen abstraction with NHC-boranes was obtained, Ueng and coworkers tried the radical reductions of the secondary halides, 3-iodo- **43** and 3-bromo di-*O*-isopropylidene glucofuranoses **44**.[33] These halides should resist ionic reductions but not radical reductions. Halides **43** and **44** were reduced under standard conditions of initiation with AIBN (80 °C), Et₃B (ambient temperature) or di-*tert*-butyl peroxide (DTBP) by photolysis (60 °C) to generate the reduced product **19** in moderate isolated yields (57-77%, Scheme 10). When using diMe-Tri-BH$_3$ **17** as the reducing reagent, *tert*-butanol and other derived products from initiators are volatile, and all the boron-containing byproducts products (diMe-Tri-BH$_3$ and diMe-Tri-BH$_2$X) can be readily removed by aqueous extraction.
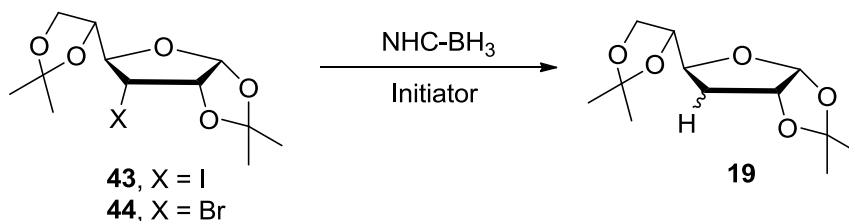
Substrate	NHC-BH$_3$	initiator	temp	isolated yield
43	**16**	Et₃B/O₂	rt	77%
43	**16**	AIBN	80 °C	63%
43	**17**	DTBP	60 °C	79%[a]
44	**16**	Et₃B/O₂	rt	77%
44	**16**	AIBN	80 °C	57%
44	**17**	DTBP	60 °C	63%[a]

a) aqueous extraction only

Scheme 10. Reductions of secondary halides **43** and **44** with NHC-boranes **16** and **17**.

Unfortunately, 1-iodoadamantane could only be reduced with NHC-boranes in 40% yield or less under radical conditions, while aryl halides and bromides were not reduced at all. In comparison, Bu_3Sn-H or even $(Me_3Si)_3Si$-H reduces such substrates rapidly and in high yields.

In summary, the best current conditions for radical dehalogenation using NHC-boranes only work for alkyl halides bearing nearby electron withdrawing groups. NHC-boryl radical abstracts halogen readily, and NHC-boranes are nucleophilic H-atom donors that react with the electrophilic radicals more readily than the nucleophilic radicals. Based on this, we hypothesized that the rate of the hydrogen atom transfer from NHC-boranes to alkyl or aryl radicals is too slow to propagate an efficient radical chain. This problem could potentially be solved by polarity-reversal catalysis.

1.4   THIOLS AS POLARITY-REVERSAL CATALYSTS

In 1952, Barrett and Waters reported the thiol-catalyzed decarbonylation of aldehydes.[34] For example, reaction of 2-ethyl-butanal **45** with 6% benzylthiol **47** and 12% dimethyl α,α'-azo-isobutyrate **48** gave the decarbonylated product pentane **46** in 81% yield. In the absence of the thiol, the decarbonylated product was obtained in less than 10% yield (Scheme 11).
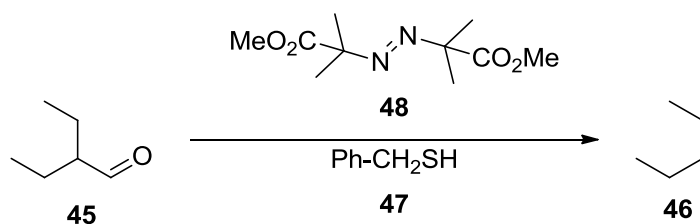
Scheme 11. Thiol-catalyzed decarbonylation of 2-ethyl-butanal **45**.

The thiol catalyzes this decarbonylation reaction due to favorable polar effects. Because both the alkyl radical and the acyl radical are nucleophilic, the alkyl radical cannot rapidly abstract hydrogen from an aldehyde (eq 2, Scheme 12). The hydrogen atom is efficiently abstracted from thiol by the alkyl radical to generate the reduced product and a thiyl radical (eq 3). The thiyl radical abstracts the hydrogen atom from the aldehyde to regenerate the thiol (eq 4).[35] In other words, one slow step (2) is replaced by two fast steps (3 and 4).

$$R\overset{\bullet}{C}{=}O \longrightarrow R^{\bullet} + CO \qquad\qquad (1)$$

$$R^{\bullet} + RCHO \xrightarrow{\text{slow}} R{-}H + R\overset{\bullet}{C}{=}O \qquad\qquad (2)$$

$$R^{\bullet} + XSH \xrightarrow{\text{fast}} R{-}H + XS^{\bullet} \qquad\qquad (3)$$

$$XS^{\bullet} + RCHO \xrightarrow{\text{fast}} XSH + R\overset{\bullet}{C}{=}O \qquad\qquad (4)$$
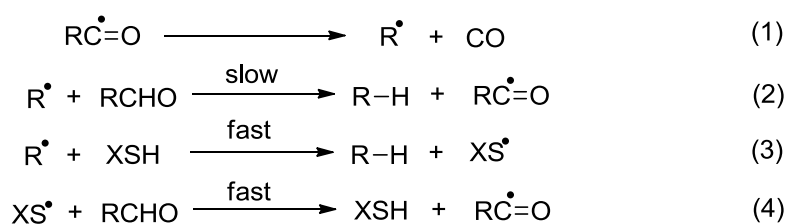
Scheme 12. Mechanism for the thiol-catalyzed decarbonylation of aldehydes.

The concept of polarity-reversal catalyst was generalized by Roberts to further expand this type of reaction.[35] The reactivity and selectivity of free radicals depend on polar effects that operate in transition states. Hence, an electrophilic radical abstracts hydrogen readily from a nucleophilic X-H bond, and *vice versa*. The reaction between an electrophilic radical and an electron-deficient X-H bond is not kinetically favored regardless of whether thermodynamically favored or not.

In general, the uncatalyzed reaction between electrophilic radical 1 ($El^1\bullet$) and electrophile 2 ($H{-}El^2$) is slow (eq 1, Scheme 13). A nucleophilic polarity-reversal catalyst (H-Nuc) reacts with $El^1\bullet$ readily to generate $H{-}El^1$ and the nucleophilic radical (Nuc•) in eq 2. The nucleophilic radical further reacts with the electrophilic hydrogen donor $H{-}El^2$ (eq 3, Scheme 13). Conversely,

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an electrophilic polarity-reversal catalyst can catalyze the reaction between a nucleophilic radical

and a nucleophilic hydrogen donor.

$$El^{1\bullet} \;+\; H\text{-}El^2 \xrightarrow{\text{slow}} H\text{-}El^1 \;+\; El^{2\bullet} \qquad \text{uncatalyzed reaction} \qquad (1)$$

$$El^{1\bullet} \;+\; \textbf{H-Nuc} \xrightarrow{\text{fast}} H\text{-}El^1 \;+\; \textbf{Nuc}^\bullet \left.\begin{array}{c}\\ \\ \\ \end{array}\right\}$$

$$\textbf{Nuc}^\bullet \;+\; H\text{-}El^2 \xrightarrow{\text{fast}} \textbf{H-Nuc} \;+\; El^{2\bullet} \qquad \text{catalytic cycle} \qquad \begin{array}{c}(2)\\ \\ (3)\end{array}$$

$$El^{1\bullet} \;+\; H\text{-}El^2 \xrightarrow[\textbf{H-Nuc}]{\text{fast}} H\text{-}El^1 \;+\; El^{2\bullet} \qquad \text{overall reaction} \qquad (4)$$
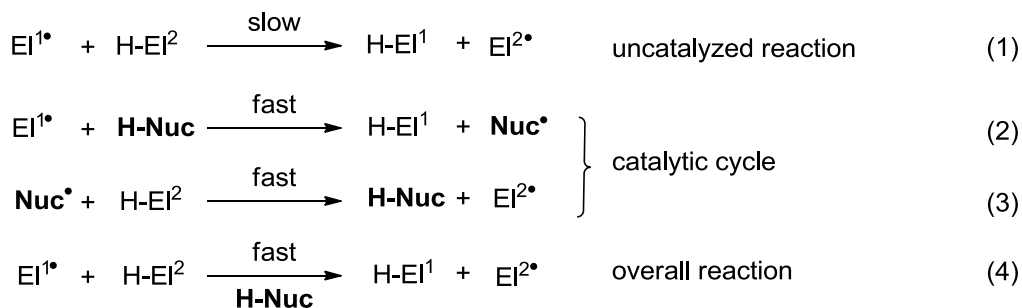
Scheme 13. Generalization of polarity reversal catalysts of hydrogen-atom transfer.

Although trialkylsilanes are not good radical H-atom donors, dehalogenation,

deoxygenation and desulfurization reactions can also be accomplished by polarity reversal

catalysts.[36] Reduction of ethyl 4-bromobutanoate **49** with 4 equiv of triethylsilane **50** in the

presence of *tert*-dodecanethiol **52** as the polarity-reversal catalyst and dilauroyl peroxide as the

initiator gave a quantitative yield of ethyl butanoate **51** (Scheme 14). In this reaction, both silyl

radicals and alkyl radicals are nucleophilic, and thiols are electrophilic polarity-reversal catalysts.
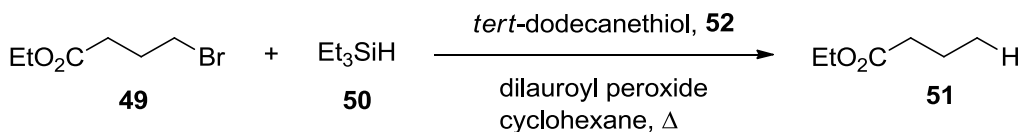
Scheme 14. A typical thiol-catalyzed radical reduction with triethylsilane **50**.

Similar to silanes, NHC-boranes are nucleophilic hydrogen donor sources, so transfer of a

hydrogen atom to alkyl radicals is not polarity-matched. We proposed to test the ability of thiols

to catalyze the radical dehalogenations with NHC-boranes via the polarity-reversal process.

2.0 THIOL-CATALYZED RADICAL REDUCTIONS OF HALIDES BY NHC-BORANES

This chapter describes the thiol-catalyzed radical reduction of halides by NHC-boranes. The reaction is believed to occur by a polarity-reversal process. Practical methods for radical reduction of alkyl and aryl halides as well as reductive cyclization were developed. Full studies of initial developments, control experiments, scope and mechanistic investigation are presented.

2.1 DISCOVERY OF THIOL-CATALYZED RADICAL REDUCTIONS OF HALIDES BY NHC-BORANES

As discussed in Chapter 1, NHC-boranes, especially diMe-Imd-BH$_3$ **16** and diMe-Tri-BH$_3$ **17**, are promising reagents in radical reductions. Dr. Ueng succeeded in reduction of secondary xanthates and a limited number of halides bearing electron withdrawing groups.[33] We set out to generalize the use of NHC-boranes as reducing reagents in radical dehalogenations.

2.1.1 Development of Reaction Conditions for Reduction of Adamantyl Halides

Tertiary halides 1-iodo- **53** and 1-bromo-adamantane **54** (Ad-I and Ad-Br, respectively) were selected to be reduced with NHC-boranes **16** and **17** because adamantyl halides **53** and **54** lack other functional groups and are not easily reduced under ionic conditions.

We selected common radical initiators such as triethylborane (Et$_3$B),[37] azo-bis-isobutyronitrile (AIBN)[38] and di-*tert*-butyl peroxide (*t*BuO-O*t*Bu, DTBP)[39] to initiate the radical chain. Di-*tert*-butyl hyponitrite (*t*BuO-N=N-O*t*Bu, TBHN)[40] was also selected because it provides two *tert*-butoxy radicals (*t*BuO•) under thermal conditions, while DTBP provides two *t*BuO• under photochemical conditions.

In an initial set of control experiments to assess the effectiveness of uncatalyzed reactions, Ad-I **53** (1 equiv) and diMe-Imd-BH$_3$ **16** (1 equiv) were reacted with 1 equiv of initiator in benzene-*d$_6$*. The triethylborane-initiated reaction was performed with ambient air in the flask at rt, while AIBN and TBHN-initiated reactions were heated in the sealed tube at 80 ℃. For the reaction initiated by DTBP, the mixture was charged to the NMR tube and irradiated with GE-275W sunlamp. After 1 h of irradiation, the temperature of the solution was measured at 50 ℃ by a thermometer. The progress of reactions with Ad-I **53** or Ad-Br **54** was monitored by ^{1}H spectroscopy with the addition of an internal standard **56** (1,3,5-trimethoxybenzene, 1 equiv).

The results of the initial control experiments without thiols are summarized in Table 1 (entries 1–4). The triethylborane-initiated reaction gave Ad-H in 16% yield with 62% conversion (entry 1, Table 1). The AIBN and TBHN-initiated radical reductions provided Ad-H **55** in 41% and 46% yields (entries 2 and 3, Table 1). For the reaction initiated by DTBP, Ad-H **55** was

obtained in 38% yield (entry 4, Table 1). These rather poor results are similar to those of Ueng

and confirm that direct radical reductions of halides are not efficient.

Table 1. Reduction of Ad-I **53** with **16** and 1 equiv of initiator with or without thiophenol.
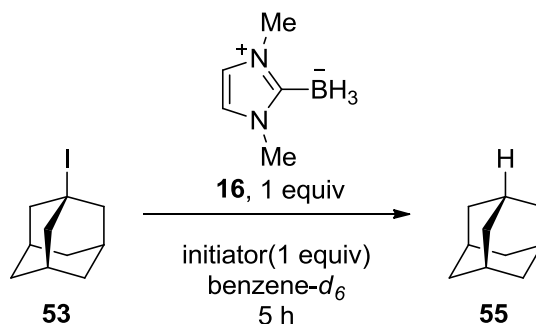
Entry	initiator	temperature	PhSH	conversion of 53	yield of 55[a]
1	Et$_3$B	rt	None	62%	16%
2	AIBN	80 ℃	None	65%	41%
3	TBHN	80 ℃	None	86%	46%
4	DTBP[b]	hʋ	None	39%	38%
5	Et$_3$B	rt	5 mol%	88%	76%
6	AIBN	80 ℃	5 mol%	82%	49%
7	TBHN	80 ℃	5 mol%	96%	80%
8	DTBP[b]	hʋ	5 mol%	99%	92%

[a] NMR yield determined with 1,3,5-trimethoxybenzene as the internal standard; [b] reaction time is 1 h.

Next, four similar reactions were conducted but now with 5 mol% of thiophenol (PhSH)

added to expedite the radical H-atom donor process. The yield of the Ad-H was significantly

improved from 16% to 76% (entry 5 compared to entry 1, Table 1) for triethylborane-initiated

conditions at rt, but little improvement was observed with the AIBN-initiated reaction (entry 6 compared to entry 2, Table 1). With TBHN under thermal conditions or DTBP under photochemical conditions, the yield was improved from 46% to 80% and from 38% to 92% (entries 7 and 8 compared to entries 3 and 4, Table 1).

To illustrate how these experiments were analyzed, Figure 6 shows ^{1}H NMR spectra of the DTBP-initiated reduction (entry 8, Table 1) at t = 0 (top) and 1 h (bottom). After 1 h, the resonances of Ad-I and diMe-Imd-BH$_3$ **16** disappeared and were replaced by signals of Ad-H and diMe-Imd-BH$_2$I **41**. The methyl resonance of *tert*-butanol was also detected.
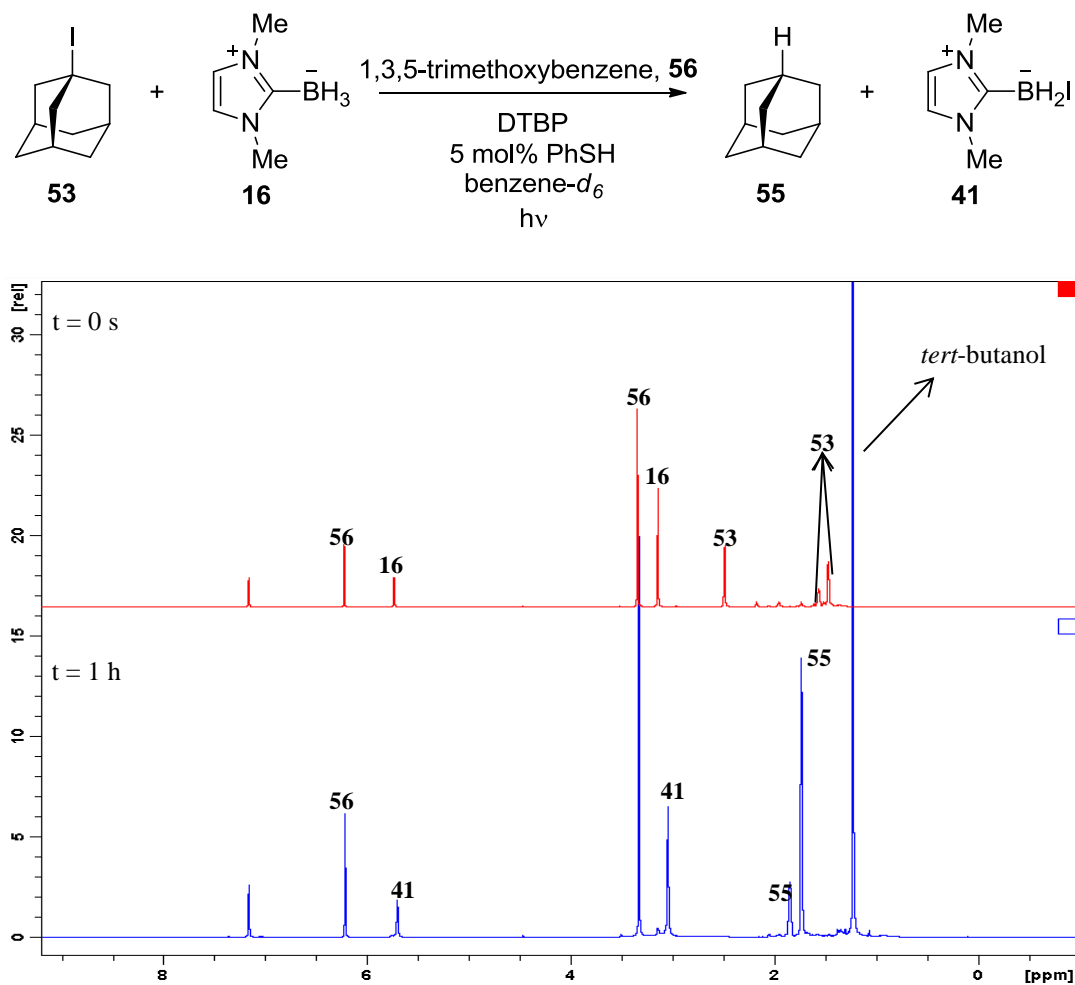
Figure 6. ^{1}H NMR spectra for reduction of Ad-I **53** under DTBP-initiated conditions with 5 mol% PhSH.

Furthermore, ^{11}B NMR spectroscopy was a handy tool to study the transformation occurring at boron. The starting reagent diMe-Imd-BH$_3$ **16** exhibits a quartet at –37 ppm.[24] The expected boron byproducts during radical reduction of Ad-Br and Ad-I are diMe-Imd-BH$_2$Br **57** (–23 ppm, t)[18] and diMe-Imd-BH$_2$I **41** (–32 ppm, t).[18] After reduction of Ad-I under DTBP-initiated photochemical conditions (entry 8, Table 1), the ^{11}B NMR spectrum of the product showed a large triplet from diMe-Imd-BH$_2$I **41** with a small quartet from remaining **16** (Figure 7).
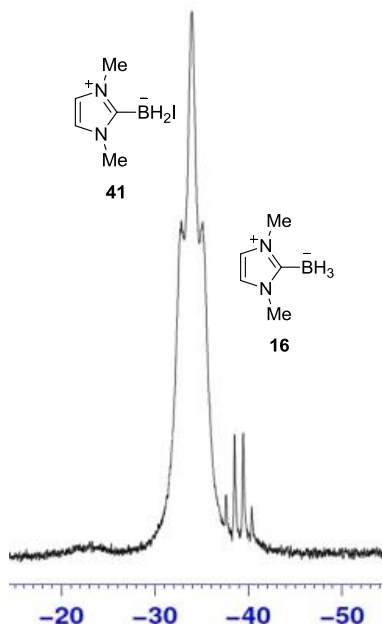
Figure 7. ^{11}B NMR spectrum in PhH-d_6 after the reduction of Ad-I **53** under DTBP-initiated conditions with 5 mol% PhSH.

Next we decreased the amount of initiator for the reduction of Ad-I by **16**, and the results of these experiments are depicted in Table 2. A reaction using 0.5 equiv of triethylborane gave similar yields and conversions compared to using 1 equiv of triethylborane (entry 1 compared to 2, Table 2). However, a lower conversion (12% or 30%) of **53** was obtained when 10% or 20% triethylborane was used (entries 3 and 4, Table 2). With 0.1 equiv of TBHN and 0.2 equiv of

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DTBP, similar yields were achieved compared to 1 equiv of TBHN and DTBP (entries 5 and 7 compared to 6 and 8, Table 2). These results suggest that the reactions with lower loading of initiator gave similar yields compared to the reactions with 1 equiv of initiator.

Table 2. Reduction of Ad-I **53** with diMe-Imd-BH$_3$ **16**, 5% thiophenol and less than 1 equiv of initiator.
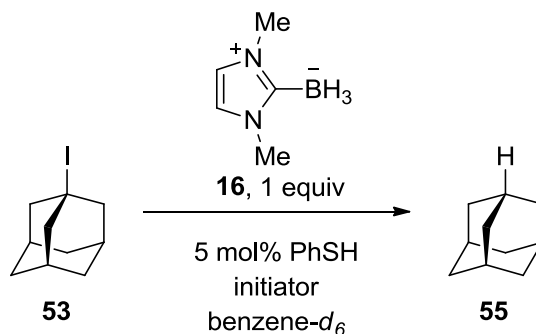
Entry	initiator	amount	temperature	time	conversion of **53**	yield of **55**[a]
1[b]	Et$_3$B	1 equiv	rt	5 h	88%	76%
2	Et$_3$B	0.5 equiv	rt	2 h	76%	76%
3	Et$_3$B	0.2 equiv	rt	5 h	30%	19%
4	Et$_3$B	0.1 equiv	rt	5 h	12%	10%
5[c]	TBHN	1 equiv	80 ℃	5 h	96%	80%
6	TBHN	0.1 equiv	80 ℃	2 h	82%	82%
7[d]	DTBP	1 equiv	hυ	1 h	99%	92%
8	DTBP	0.2 equiv	hυ	1 h	99%	99%
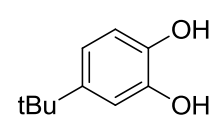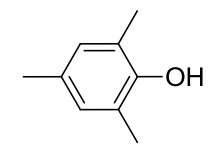
[a] NMR yield determined with 1,3,5-trimethoxybenzene as the internal standard; [b] data are from entry 5 in Table 1; [c] data are from entry 7 in Table 1; [d] data are from entry 8 in Table 1.

We next looked for other additives that might play a similar role to thiophenol (Table 3). The test reaction was reduction of Ad-I by diMe-Imd-BH₃ **16** in benzene-d_6 under DTBP-initiated photochemical conditions.

Table 3. Reduction of Ad-I **53** with diMe-Imd-BH₃ **16** with other additives.
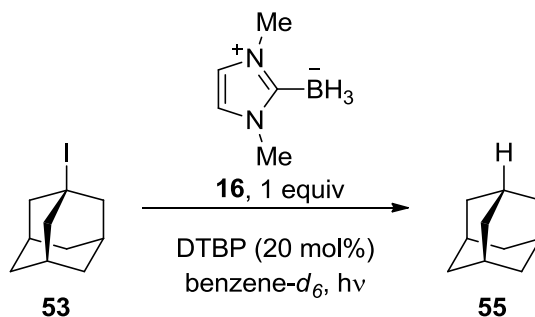
Entry	additive (5 mol%)	time	conversion of **53**	yield of **55**[a]
1[b]	PhSH	1 h	99%	99%
2	PhSeH	2 h	32%	-
3	**58**	3 h	47%	-
4	**59**	1 h	20%	-
5[c]	PhSH	3 h	88%	84%

[a] NMR yield determined with 1,3,5-trimethoxybenzene as the internal standard; [b] data are from entry 8 in Table 2; [c] initiator source: black light (15W and peak λ_{max} at 357 nm).

The control result with PhSH is shown in entry 1. Benzeneselenol (PhSeH) was evaluated because it is also a good radical hydrogen atom source.[41] After 2 h irradiation of the reaction mixture with 5 mol% of PhSeH, only 32% conversion was achieved, and the yield of Ad-H was hard to determine due to the low conversion (entry 2, Table 3).

DTBP-initiated dehalogenation of **53** with NHC-borane **16** and 4-*tert*-butylcatechol **58** or 2,4,6-trimethylphenol **59** as the additive only gave low conversions of 47% and 20% (entries 3 and 4, Table 3). Reaction of **53** with **16** and 5 mol% PhSH under DTBP-initiated conditions but with different light source 15W black light (λ_{max} at 357 nm) as recommended by Ryu[42] provided **55** in 84% yield with 88% conversion of **53** after 3 h of irradiation (entry 5, Table 3). The reactions with selenols and phenols gave similiar conversions compared to the reaction without catalysts. These results suggest that thiols are more promising catalysts.

Based on these aggregated results, we selected three conditions for further scope studies. All three gave good conversions and yields with 1 equiv of diMe-Imd-BH$_3$ **16** as the reducing reagent in benzene:

A) Conditions A (Et$_3$B): triethylborane, 5 mol% of thiophenol, ambient temperature;

B) Conditions B (TBHN): TBHN, 5 mol% of thiophenol, 80 °C;

C) Conditions C (DTBP): DTBP, 5 mol% of thiophenol, hυ with 275W sunlamp.

We next applied these conditions to reduce Ad-Br **54** with diMe-Imd-BH$_3$ **16**. These results are summarized in Table 4. Reduction of Ad-Br with Conditions A gave only 3% of conversion even though 1.5 equiv of triethylborane was used (entry 1, Table 4). With conditions B (TBHN-initiated) and C (DTBP-initiated), the product yields were 97% and 92% (entries 2 and 3, Table 4).

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Table 4. Reduction of Ad-Br **54** with diMe-Imd-BH$_3$ **16** under selected conditions.
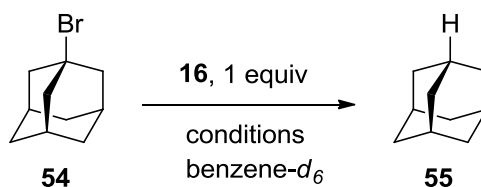
Entry	conditions[b]	time	conversion of **48**	yield of **49**[a]
1	A (Et$_3$B)	4 h	3%	-
2	B (TBHN)	4 h	99%	97%
3	C (DTBP)	1 h	99%	92%

[a] NMR yield determined with 1,3,5-trimethoxybenzene as the internal standard; [b] Conditions A: Et$_3$B (1.5 equiv), PhSH (5 mol%), rt; Conditions B: TBHN (20 mol%), PhSH (5 mol%), 80 °C; Conditions C: DTBP (20 mol%), PhSH (5 mol%), hυ.

Next the reactions between 1-chloroadamantane **60** (Ad-Cl) and **16** (1 equiv) with Conditions B (TBHN) and C (DTBP) gave only 5% conversion of **60** after 6 h (Scheme 15). The H-transfer step with AdCl is the same as with AdBr and AdI, so this step must be not a problem. Presumably the chloride abstraction by diMe-Imd-BH$_2$• **36** is too slow to efficiently propagate a radical chain.
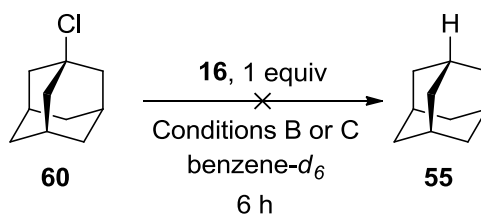
Scheme 15. Failed reduction of Ad-Cl **60** with NHC-borane **16** under Conditions B or C.

In summary, both Ad-I and Ad-Br were successfully reduced by thiol-catalyzed radical reduction with NHC-boranes under various conditions, while Ad-Cl was not reduced.

2.1.2 Development of Reaction Conditions for Reduction of Aryl Halides 61 and 62

After the successful reductions of Ad-I and Ad-Br, we next turned to the reduction of aryl iodides and bromides. 1-Iodo- **61** and 1-bromo-2-((octyloxy)methyl)benzene **62** were reduced with **16** under the three selected conditions (Conditions A-C). Yields and conversions were again determined by integration against 1,3,5-trimethoxybenzene as the internal standard.

To evaluate the role of thiol, aryl iodide **61** and diMe-Imd-BH$_3$ **16** (1 equiv) were reacted without PhSH in benzene-d_6 under Conditions A-C. Selected results are summarized in Table 5. In the control experiments, the control reaction without 5 mol% PhSH under Conditions A (Et$_3$B) gave no conversion of **61**, while the control reactions with Conditions B (TBHN) and C (DTBP) gave low yields (28% and 39%) of product **63** (entries 1, 2 and 3, Table 5).

With 5 mol% of thiophenol as catalyst, the yield of **63** was improved to 61% with Conditions A (Et$_3$B) (entry 4, Table 5). The reaction with Conditions B (TBHN) provided **63** in 86% isolated yield with full conversion after 3 h (entry 5, Table 5). The reaction with Conditions C (DTBP) required a longer reaction time (7 h) to obtain a good yield 86% of **63** (entry 6, Table 5). Apparently, TBHN-initiated reduction (Conditions B) under thermal conditions is faster than the photochemical conditions (Conditions C).

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Table 5. Reduction of aryl iodide **61** with diMe-Imd-BH₃ **16**.
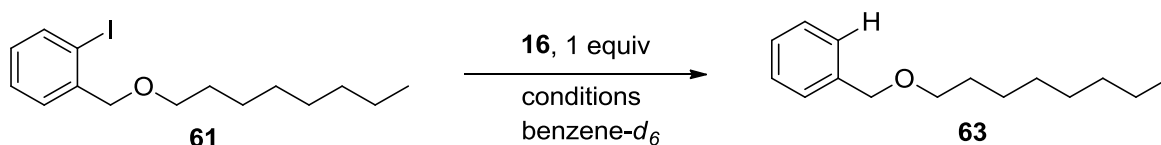
Entry	conditions[b]	PhSH	time	conversion of **61**	yield of **63**[a]
1	A (Et₃B)	none	7 h	0%	-
2	B (TBHN)	none	3 h	62%	28%
3	C (DTBP)	none	7 h	87%	39%
4	A (Et₃B)	5 mol%	3 h	61%	61%
5	B (TBHN)	5 mol%	3 h	99%	86%[c]
6	C (DTBP)	5 mol%	7 h	92%	86%

[a] NMR yield determined with 1,3,5-trimethoxybenzene as the internal standard; [b] Conditions A: Et₃B (0.5 equiv), rt; Conditions B: TBHN (10 mol%), 80 °C; Condition C: DTBP (10 mol%), hυ; [c] isolated yield after chromatography.

The three selected conditions were also applied to reduce the aryl bromide **62** with diMe-Imd-BH₃ **16**. These results are summarized in Table 6. Because low conversions were obtained in the control experiments with the iodide **61**, we did not conduct additional control experiments with bromide **62**. The reaction under Conditions A (Et₃B) gave only 6% conversion of **61** even though 1.5 equiv of triethylborane was used (entry 1, Table 6). TBHN-initiated reduction (Conditions B) of **62** provided the reduced product **63** in 81% yield after 3 h, while DTBP initiated reaction (Conditions C) gave product **63** in comparable yield of 82% after 7 h of irradiation (entries 2 and 3, Table 6).

Table 6. Reduction of aryl bromide **57** with diMe-Imd-BH$_3$ **16**.
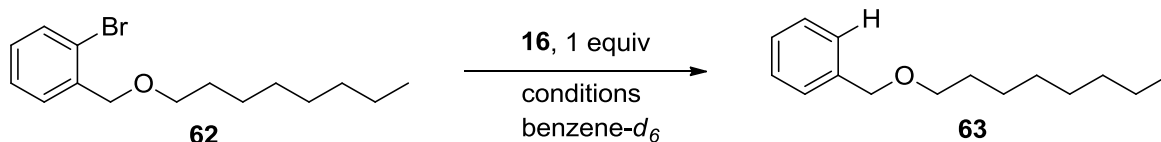
Entry	conditions[b]	time	conversion of **62**	yield of **63**[a]
1	A (Et$_3$B)	7 h	6%	-
2	B (TBHN)	3 h	95%	81%
3	C (DTBP)	7 h	87%	82%

[a] NMR yield determined with 1,3,5-trimethoxybenzene as the internal standard; [b] Conditions A: Et$_3$B (1.5 equiv), PhSH (5 mol%), rt; Conditions B: TBHN (10 mol%), PhSH (5 mol%), 80 °C; Conditions C: DTBP (10 mol%), PhSH (5 mol%), hυ.

Both TBHN- and DTBP-initiated conditions efficiently reduced the aryl iodide **61** and bromide **62** with NHC-borane **16** and thiophenol in good yields. The reaction under Et$_3$B conditions only reduced the iodide **61** in moderate yield, and bromide **62** could not be reduced at all.

2.1.3 Additional Control Experiments

The above results show that the thiol plays a crucial role in promising radical reductions with NHC-boranes. To further establish the reaction mechanism, we conducted a series of additional control experiments with aryl iodide **61**. The reaction time was fixed at 5 h. The results of these experiments are shown in Table 7. Different initiator and thiol combinations cannot reduce the iodide **61** in the absence of an NHC-borane (entries 1-3, Table 7). Clearly the presence of NHC-

boranes is crucial. In the absence of radical initiator, reduction of **61** with **16** (1 equiv) and 5 mol%

of thiophenol gave only 9% of **63** with 19% conversion (entry 4, Table 7). This suggests that the

reduction of **61** proceeds by a radical chain pathway rather than an ionic pathway.

Table 7. Additional control experiments.
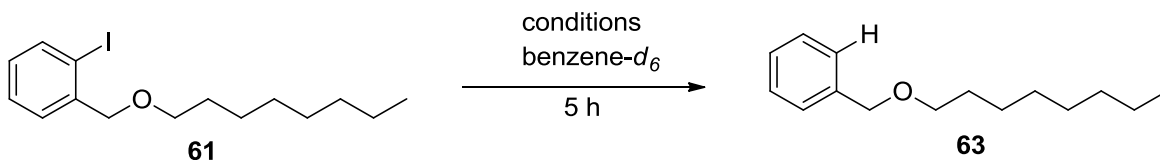
Entry	conditions	conversion of **61**	yield of **63**[a]
1	Et$_3$B (0.5 equiv), 5% PhSH, rt	0%	-
2	TBHN (0.1 equiv), 5% PhSH, 80 ℃	19%	-
3	DTBP (0.1 equiv), 5% PhSH, hυ	4%	-
4	diMe-Imd-BH$_3$ **16** (1 equiv), 5% PhSH, 80 ℃	19%	9%

[a] NMR yield determined with 1,3,5-trimethoxybenzene as the internal standard.

2.1.4 NHC-Boranes compared to other borane sources

The results of experiments targeted to learn more about the H-atom donor component are shown

in Table 8. The test reaction was reduction of Ad-I with 5 mol% PhSH as the catalyst and 20 mol%

DTBP as the initiator in benzene-d_6 under photochemical conditions (TBHN used for entries 4, 8

and 10 under thermal conditions). Again, the control result with PhSH and diMe-Imd-BH$_3$ **16** is

shown in entry 1. To evaluate the number of H-atoms used, Ad-I was reduced with 0.5 equiv of
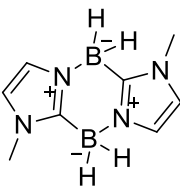
diMe-Imd-BH$_3$ **16**. The reaction only gave 50% conversion and 50% yield of reduced product (entry 2, Table 8). This suggests that **16** only donates one H-atom in the radical reduction of Ad-I. Reduction of Ad-I with 1 equiv of hindered dipp-Imd-BH$_3$ complex **6** gave full conversion with the comparable yield (86%) to the reaction with 1 equiv of **16** (entry 3 compared to entry 1, Table 8).

Reduction of Ad-I was also investigated with diMe-Tri-BH$_3$ **17** because it and its derived products (presumably the dehalogenation products are diMe-Tri-BH$_2$-I and -Br) can be removed by aqueous extraction.[33] Following the reaction with 1 equiv **17,** simple aqueous extraction and evaporation of the organic phase provided Ad-H in 77% isolated yield (entry 4, Table 8), and no boron byproducts were detected by either ^{1}H or ^{11}B NMR spectroscopy. The reactions with dimer of NHC-boranes **5**, Me$_3$N-BH$_3$ **64** and Ph$_3$P-BH$_3$ **65** complexes as the reducing reagents gave no desired product (entries 5, 6 and 7, Table 8). Unlike alkyl amine-borane complexes but similar to NHC-boranes, pyridine-borane **66** has a π-system adjacent to the boron atom. Reduction of Ad-I with 2 equiv of **66** and 5 mol% of thiophenol under DTBP and TBHN-initiated conditions gave Ad-H in 64% and 75% yields (entries 8 and 9, Table 8).

The reaction of **53** and 2 equiv tetrabutylammonium cyanoborohydride (**67**, Bu$_4$NBH$_3$CN) with 5 mol% PhSH provided around 20% yield of **55** with full conversion under TBHN conditions (entry 10, Table 8), while the reduction of **53** with 3 equiv Bu$_4$NBH$_3$CN and 5 mol% PhSH generated **55** in 93% yield with full conversion under DTBP-initiated conditions (entry 11, Table 8).

Table 8. Reduction of Ad-I **53** with 0.5 equiv of **16** and other borane sources with 5% PhSH.
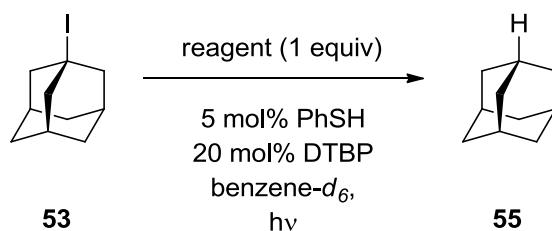
Entry	reagent	time	conversion of **53**	yield of **55**[a]
1[b]	diMe-Imd-BH$_3$ **16**	1 h	99%	99%
2	diMe-Imd-BH$_3$ **16**[c]	1 h	50%	50%
3	dipp-Imd-BH$_3$ **6**	1 h	99%	86%
4[d]	diMe-Tri-BH$_3$ **17**	1 h	99%	77%[e]
5	**5**	1 h	0%	-
6	Me$_3$N-BH$_3$ **64**	12 h	17%	-
7	Ph$_3$P-BH$_3$ **65**	4 h	0%	-
8[d]	pyridine-BH$_3$ **66**[f]	12 h	64%	64%
9	pyridine-BH$_3$ **66**[f]	12 h	89%	75%
10[d]	Bu$_4$NBH$_3$CN **67**[f]	2 h	99%	~20%
11	Bu$_4$NBH$_3$CN **67**[g]	3 h	99%	93%

[a] NMR yield determined with 1,3,5-trimethoxybenzene as the internal standard; [b] data are from entry 8 in Table 2; [c] 0.5 equiv used; [d] 20 mol% TBHN under thermal conditions; [e] isolated yield after aqueous extraction; [f] 2 equiv; [g] 5 equiv.

Since the radical reduction of **53** with excess pyridine-borane **66** and Bu$_4$NBH$_3$CN **67** provided good conversions and yields, dehalogenation reactions with other substrates such as **54**, aryl halides **61** and **62** were conducted with **66** and **67**. These results are summarized in Table 9.

Table 9. Additional reductions with Bu$_4$NBH$_3$CN and pyridine-BH$_3$.

Ad-Br or **54** / X = I, **61** ; X = Br, **62** → reagent / initiator (hv for DTBP or heat for TBHN) / 5 mol%PhSH / benzene → Ad-H **55** or **63**
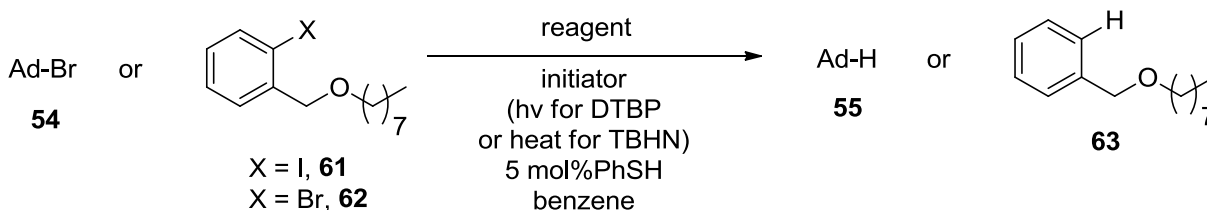
Entry	R-X	reagent	amount	initiator (20 mol%)	time	conv.	yield[a]
1	**54**	Bu$_4$NBH$_3$CN **67**	5 equiv	DTBP	2 h	~20%	-
2	**54**	Bu$_4$NBH$_3$CN **67**	2 equiv	TBHN	2 h	17%	-
3	**61**	Bu$_4$NBH$_3$CN **67**	5 equiv	DTBP	7 h	99%	56%
4	**61**	Bu$_4$NBH$_3$CN **67**	2 equiv	TBHN	2 h	99%	~25%
5	**54**	pyridine-BH$_3$ **66**	3 equiv	DTBP	8 h	0%	-
6	**61**	pyridine-BH$_3$ **66**	3 equiv	DTBP	8 h	72%	72%
7	**62**	pyridine-BH$_3$ **66**	3 equiv	DTBP	8 h	0%	-

[a] NMR yield determined with 1,3,5-trimethoxybenzene as the internal standard.

Radical reductions of AdBr **54** with Bu$_4$NBH$_3$CN under DTBP and TBHN conditions provided less than 20% conversion of **54**, and the yield of **55** was not determined (entries 1 and 2, Table 9). The reaction of **61** and Bu$_4$NBH$_3$CN under DTBP and TBHN conditions generated the product **54** in low yield (56% and 25%) but with full conversions (entries 3 and 4, Table 9). Reduction of iodide **61** with 3 equiv of pyridine-BH$_3$ gave the reduced product **63** in 72% yields

under DTBP-initiated conditions (entry 6, Table 9), while the reactions of **54** or **62** with pyridine-BH$_3$ under DTBP-initiated conditions gave no conversion (entries 5 and 7, Table 9). Both **66** and **67** can reduce alkyl and aryl iodide under thiol-catalyzed radical conditions, while they cannot reduce alkyl and aryl bromide under same conditions. This suggest both Bu$_4$N(CN)BH$_2\bullet$ and pyridine-BH$_2\bullet$ abstract iodide efficiently but not bromide. Ryu also reported the same reactivity of cyanoborohydrides in Giese reaction.[43] The alkyl radicals were feasibly generated from alkyl iodides but not form alkyl bromides and chlorides.

These experiments showed that NHC-boranes are different than other borane sources such as amine- and phosphine-boranes, and NHC-boranes can efficiently reduce alkyl and aryl bromides/iodides under thiol-catalyzed radical conditions.

2.1.5 Effect of the Thiol

Based on the successes with thiophenol, we examined two other thiols in different amounts. Tertiary alkanethiol *tert*-dodecanethiol **52** was selected because Roberts reported that it was most effective catalyst in the reduction of alkyl halides with silane-thiol couple.[44] The primary alkanethiol 1-pentadecanethiol **68** was selected because it does not have an unpleasant odor. The test reactions were conducted between iodide **61** and **16** under Conditions B (TBHN) and C (DTBP). To have a strict comparison, all the experiments were performed at the same time and under the same conditions. Only the thiol was varied. These results are shown in Table 10.

Table 10. Reduction of **61** with Conditions B and C under different thiols.
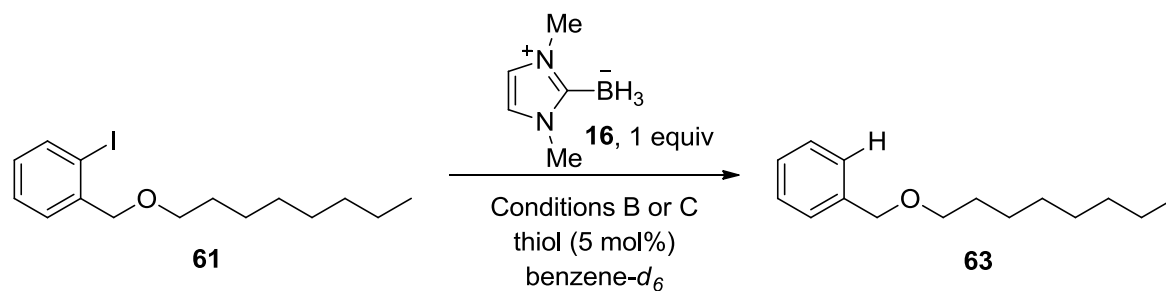
Entry	conditions[a]	thiol (5 mol%)	conversion of **61**	yield of **63**[b]
1	B (TBHN)	thiophenol	99%	92%
2	B (TBHN)	1-pentadecanethiol	72%	60%
3	B (TBHN)	*tert*-dodecanethiol	99%	96%
4	C (DTBP)	thiophenol	81%	76%
5	C (DTBP)	1-pentadecanethiol	88%	64%
6	C (DTBP)	*tert*-dodecanethiol	95%	89%

[a] Conditions B: TBHN (20 mol%), 80 °C, 3 h; Conditions C: DTBP (20 mol%), hυ, 6 h; [b] NMR yield determined with 1,3,5-trimethoxybenzene as the internal standard.

For reduction initiated by TBHN (Conditions B), the 1-pentadecanethiol-catalyzed reaction gave product **63** in 60% yield in 3 h, while the thiophenol- and *tert*-dodecanethiol-catalyzed reactions gave **63** in 92% and 96% yields (entries 1, 2 and 3, Table 10).

The 1-pentadecanethiol-catalyzed reduction with Conditions C (DTBP) gave 64% of **63** in 6 h (entry 4, Table 10). The DTBP-initiated reaction with thiophenol as catalyst gave product **63** in 76% yield, while DTBP-initiated reaction with *tert*-dodecanethiol gave **63** in 89% yield (entries 5 and 6, Table 10). Therefore, among these three thiols *tert*-dodecanethiol is the most effective catalyst for radical halides reduction with NHC-boranes.

At this point, we varied the amount of *tert*-dodecanethiol to investigate the reduction of

iodide **61** with diMe-Imd-BH$_3$ **16** under TBHN-initiated conditions (Conditions B). The results

of these experiments are shown in Table 11.

Table 11. Reduction of **61** with Conditions B with different amounts of *t*-dodecanethiol.
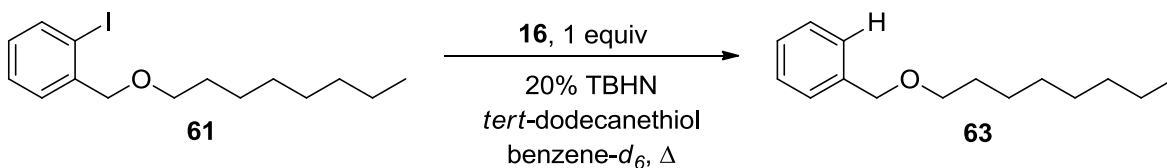
Entry	*tert*-dodecanethiol (%)	conversion of **61**	yield of **63**[a]
1	0.5%	58%	44%
2	1%	66%	53%
3	2%	83%	70%
4	5%	99%	87%
5	10%	99%	86%
6	20%	99%	82%

[a] NMR yield determined with 1,3,5-trimethoxybenzene as the internal standard.

The reactions with 0.5-2 mol% of *tert*-dodecanethiol gave **63** in 44-70% yield in 1 h

(entries 1, 2 and 3, Table 11). Reduction of **61** with 5, 10 or 20 mol% of *tert*-dodecanethiol gave

63 in 82-87% yield with full conversion (entries 4, 5 and 6, Table 11). These results suggest that

the radical chain is not propagated well at low concentration of thiols (0.5-2 mol%). At least 5

mol% of *tert*-dodecanethiol is required to obtain a good yield for the reduction of **61**.

2.2   SCOPE AND LIMITATIONS

After identifying the suitable conditions, we next explored the scope of the thiol-catalyzed radical dehalogenations with NHC-boranes. The reactions were conducted as usual; however, the yields are reported after purification by flash chromatography. NMR yields are only reported for volatile compounds.

Reduction of iodide **43** with **16** (1 equiv) and thiophenol (5 mol%) under Conditions A-C gave **19** in 79-82% isolated yields (entries 1-3, Table 12). Compared to Dr. Ueng's reduction of **43** with 1 equiv of initiator in absence of thiol catalyst (Scheme 10),[33] the thiol-catalyzed reductions gave the similar yields with 0.5 equiv of Et_3B, 20 mol% of TBHN and DTBP.

Since we have already shown that all three conditions can be used to successfully reduce alkyl/aryl iodides and bromides, only Conditions B (20 mol% of TBHN, and 1.1 equiv of **16**) were further investigated to reduce different halides at 80 °C. In addition, thiophenol was replaced by 5% *tert*-dodecanethiol because *tert*-dodecanethiol-catalyzed reductions gave better yields. The reaction time was fixed at 2 h. These results are summarized in Table 12.

Reductions of cholesterol-iodide **69** and bromide **70** with diMe-Imd-BH_3 **16** and *tert*-dodecanethiol gave **71** in 96% and 95% yield with TBHN-initiated conditions (entries 4 and 6, Table 12). Reduction of **69** with diMe-Tri-BH_3 **17** and thiophenol under Conditions B provided **71** in 81% isolated yield after simple aqueous/ether extraction (entry 5, Table 12). Residual thiophenol was successfully evaporated during removing of the solvents, and it was not detected in the isolated product **71** by ^{1}H NMR spectroscopy.

Table 12. Thiol catalyzed radical dehalogenations with diMe-Imd-BH$_3$ **16**.
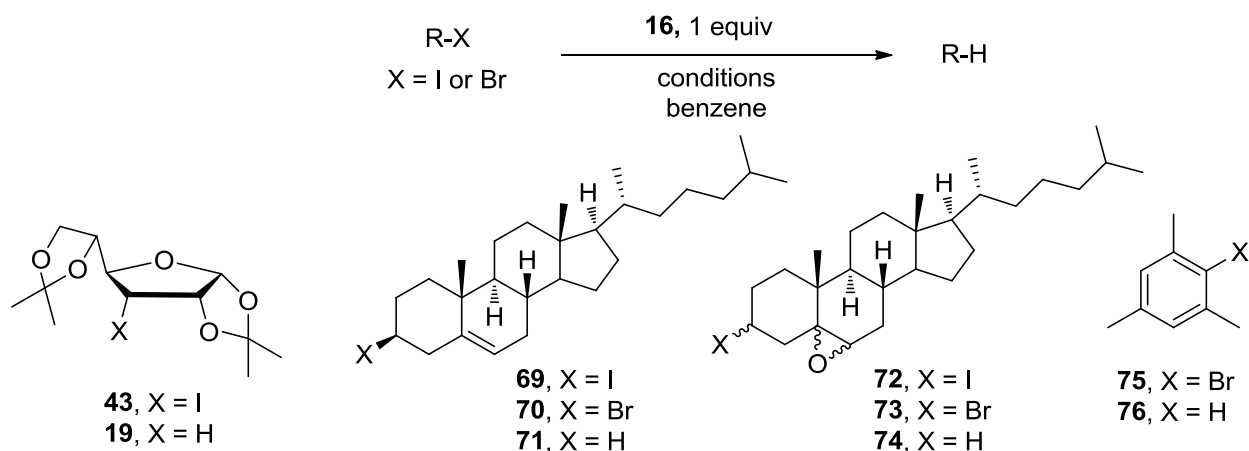
Entry	substrate	conditions[a]	thiol (5 mol%)	product	yield
1	**43**	A (Et$_3$B)	thiophenol	**19**	82%
2	**43**	B (TBHN)	thiophenol	**19**	79%
3	**43**	C (DTBP)	thiophenol	**19**	79%
4	**69**	B (TBHN)	*tert*-dodecanethiol	**71**	96%
5	**69**	B (TBHN)[c]	thiophenol	**71**	81%
6	**70**	B (TBHN)	*tert*-dodecanethiol	**71**	95%
7	**70**	B (TBHN)[d]	*tert*-dodecanethiol	**71**	95%
8	**70**	B (TBHN)[e]	*tert*-dodecanethiol	**71**	90%
9	**72**	B (TBHN)	*tert*-dodecanethiol	**74**	-
10	**73**	B (TBHN)	*tert*-dodecanethiol	**74**	91%
11	**75**	B (TBHN)	*tert*-dodecanethiol	**76**	95%[b]

[a] Conditions A: Et$_3$B (0.5 equiv), rt; Conditions B: TBHN (20 mol%), 80 °C; Conditions C: DTBP (20 mol%), hυ; Conditions D: PhSSPh (10 mol%), hυ; [b] NMR yield determined with 1,3,5-trimethoxybenzene as the internal standard; [c] diMe-Tri-BH$_3$ **17** used; [d] In PhCF$_3$; [e] In PhMe.
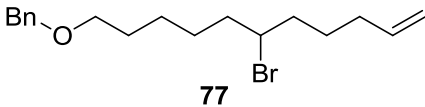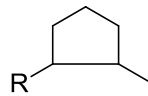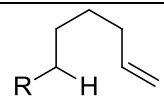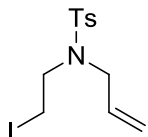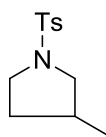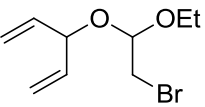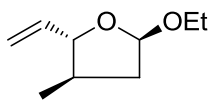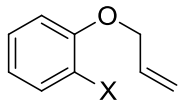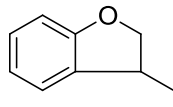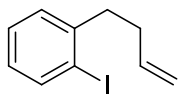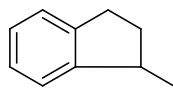
Reduction of epoxycholestane bromide **73** with **16** under Conditions B gave the reduced product **74** in 91% isolated yield, while reduction of iodide **72** gave a complex mixture (entries 9 and 10, Table 11). No starting iodide **72** was recovered, and no desired reduced product **74** was detected from the reduction of iodide **72**. This is probably because the borane byproduct diMe-Imd-BH$_2$I **41** is a Lewis acid and reacts with the epoxide **72**.

Reduction of 2-bromo-1,3,5-trimethylbenzene **75** under Conditions B (TBHN) gave a 77% NMR yield of 1,3,5-trimethylbenzene **76** with 23% of unreacted bromide **75**. To obtain full conversion of **75**, additional half-portions of initiator TBHN (0.1 equiv), *tert*-dodecanethiol (2.5 mol%), and **16** (0.5 equiv) were added. Finally, the reduced product **76** was formed in 95% yield (entry 5, Table 11). The reduction of **75** further suggests that aryl bromides are the most difficult to reduce among alkyl/aryl iodides and bromides. This is because NHC-boryl radicals abstract bromide much slower than iodide, and aryl radicals are more difficult to generate than alkyl radicals.

All these experiments used benzene as solvent for consistency; however, benzene is not an ideal green solvent. Accordingly, other alternatives such as benzotrifluoride (PhCF$_3$)[45] and toluene (PhMe) were investigated. Dehalogenation of **70** in these two solvents gave comparable yields to the reduction in benzene (entries 6-8, Table 12; PhH, 95%; PhCF$_3$, 95%; PhMe, 90%).

Then several substrates subject to 5-*exo-trig* cyclizations were investigated using thiol-catalyzed radical dehalogenations with NHC-boranes. The substrate (1 equiv) and diMe-Imd-BH$_3$ **16** (1 equiv) were reacted with 20 mol% of TBHN, 5 mol% of *tert*-dodecanethiol in benzene under thermal conditions for 2 h. Isolated yields for cyclized and reduced products were obtained after chromatographic purification. The results of these experiments are summarized in Table 13.

Table 13. Radical 5-*exo-trig* cyclization by thiol catalyzed radical dehalogenations with diMe-Imd-BH$_3$ **16**.

Entry	substrate	conc.	product	yield
	Bn–O–(CH$_2$)$_4$–CH(Br)–(CH$_2$)$_3$–CH=CH$_2$ **77**		**78**, R = (CH$_2$)$_5$-OBn + **79**	
1	**77**	0.16 M	**78** + **79**	90% (5:1)[b]
2	**77**	0.05 M	**78** + **79**	85% (5:1)[b]
3	**77**	0.01 M	**78** + **79**	80% (5:1)[b]
4	**80**	0.2 M	**81**	83%
5	**82**	0.2 M	**83**[c]	76%
6	**84**, X = I	0.2 M	**86**	80%
7	**85**, X = Br	0.2 M	**86**	83%
8	**87**	0.2 M	**88**	80%

[a] DTBP-initiated conditions (Conditions B): 20 mol% TBHN, 1.1 equiv of diMe-Imd-BH$_3$ **16**, 5 mol% of *tert*-dodecanethiol, 80 °C, 2 h; [b] the ratio of **78**:**79**; [c] 9/1 mixture of diastereomers at C2; the major product is shown.

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Treatment of bromide **77** (0.16 M in benzene) with diMe-Imd-BH$_3$ **16** under Conditions

B gave an inseparable mixture of 5-*exo-trig* cyclized product **78** (75%) and directly reduced

product **79** (15%) in 90% total isolated yield (entry 1, Table 13). Two more diluted solutions

(0.05 and 0.01M) of **77** were prepared in benzene. Treatment of both solutions with **16** under

Conditions B gave similar 5:1 ratio of cyclized/reduced product in 85% and 80% isolated yield

(entries 2 and 3, Table 13). We expected more diluted reaction solutions would give more

cyclized product, but we did not observe this. The significant amounts of directly reduced

product **79** suggest that the thiol is the real hydrogen donor source in the reaction. Based on its k_H

(Chapter 1.2), NHC-borane **16** is not capable of efficient transferring of a hydrogen to the radical

before cyclization.

In contrast, reduction of *N*-allyl-*N*-(2-iodoethyl)-4-methylbenzenesulfonamide **80**, a more

rapid radical cyclization precursor, provided exclusively 5-*exo-trig* cyclized product **81** in 83%

yield (entry 4, Table 13). No directly reduced product *N*-allyl-*N*-ethyl-4-methylbenzene-

sulfonamide was found.[46, 47] Stork-Ueno cyclization[48] of bromoacetal **82** with **16** under TBHN-

initiated conditions provided cyclic acetal **83** in 76% yield with a 9/1 mixture of diastereomers

(entry 5, Table 13). Next thiol-catalyzed radical reductions of aryl iodides **84**, **87** and bromide **85**

with **16** gave exclusively cyclized product **86** and **88** in 80–83% yield (Entry 5-7, Table 12). No

directly reduced products were detected due to the high rate constants (6.3×10^9 s^{-1} and $4.0 \times$

10^8 s^{-1} at 303 K) of 5-*exo-trig* cyclization of aryl radicals **89** and **90** (Scheme 16).[49]

$k = 6.3 \times 10^9$ s^{-1} for **89**

$k = 4.0 \times 10^8$ s^{-1} for **90**

89, X = O
90, X = C

91, X = O
92, X = C
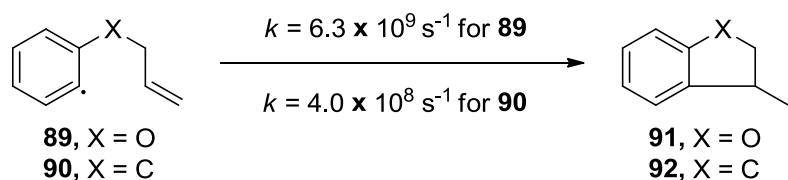
Scheme 16. Reaction rate for 5-*exo-trig* cyclization for aryl radicals at 303 K.

The thiol-catalyzed dehalogenations with NHC-boranes are practical for both direct reduction and 5-*exo-trig* cyclization of alkyl/aryl iodides and bromides. The observation of several 5-*exo-trig* cyclization products further supports a radical chain mechanism for these dehalogenations.

2.3   MECHANISTIC INVESTIGATION

Based on the observed results, we propose a radical chain mechanism for thiol-catalyzed dehalogenations with NHC-boranes. The key propagation steps are demonstrated in Scheme 17. Since the rate constants for aryl radicals and NHC-boranes are unknown, we focus the mechanistic investigation and analysis on alkyl radicals.

In the reaction without thiol, a NHC-BH$_2\bullet$ abstracts iodide or bromide to form an alkyl radical (R$\bullet$) (eq 1, Scheme 17). Then, R$\bullet$ abstracts a hydrogen atom directly from NHC-BH$_3$. The rate constant of transfer a hydrogen atom from NHC-BH$_3$ to a primary alkyl radicals (eq 2) is no more than 10^5 M^{-1} s^{-1} (Section 1.2).[31] This slow step is in part because of the electronic mismatch between a nucleophilic R$\bullet$ and a nucleophilic NHC-BH$_3$. So the radical reduction does not propagate efficiently.

In the reaction with thiophenol added, R$\bullet$ abstracts a hydrogen atom from thiophenol rather than NHC-BH$_3$. The rate constant[50] for hydrogen transfer from electrophilic thiophenol to a nucleophilic alkyl radical (eq 3) is up to 10^8 M^{-1} s^{-1} because of the low S-H BDE (79 kcal/mol) for thiophenol[51] and the electronic match of the radical (nucleophile) and the H-donor (electrophile) (eq 3). [35, 44]

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$$\text{NHC-BH}_2\bullet \quad + \quad \text{R--X} \quad \xrightarrow[\ k_1 > 10^5\ \text{M}^{-1}\text{s}^{-1}\ ]{\text{fast}} \quad \text{NHC-BH}_2\text{X} \quad + \quad \text{R}\bullet \qquad (1)$$

$$\text{NHC-BH}_3 \quad + \quad \text{R}\bullet \quad \xrightarrow[\ k_2 < 10^5\ \text{M}^{-1}\text{s}^{-1}\ ]{\text{slow}} \quad \text{NHC-BH}_2\bullet \quad + \quad \text{R--H} \qquad (2)$$

$$\text{PhS--H} \quad + \quad \text{R}\bullet \quad \xrightarrow[\ k_3 \approx 10^8\ \text{M}^{-1}\text{s}^{-1}\ ]{\text{fast}} \quad \text{PhS}\bullet \quad + \quad \text{R--H} \qquad (3)$$

$$\text{NHC-BH}_3 \quad + \quad \text{PhS}\bullet \quad \xrightarrow[\ k_4 = 1.2 \times 10^8\ \text{M}^{-1}\text{s}^{-1}\ ]{\text{fast}} \quad \text{NHC-BH}_2\bullet \quad + \quad \text{PhS--H} \qquad (4)$$
$$\text{for rxn of } \textbf{16} \text{ with PhS}\bullet$$
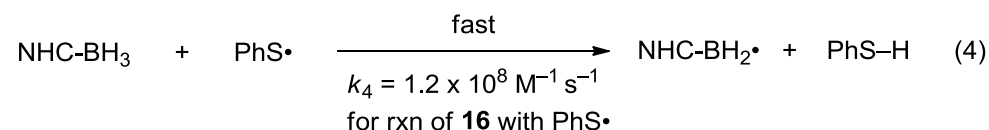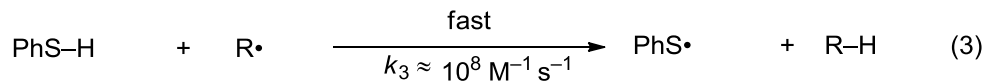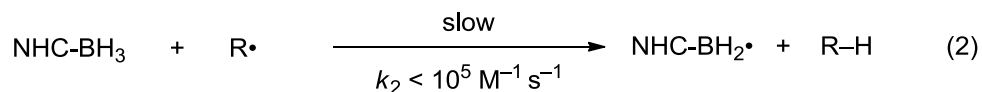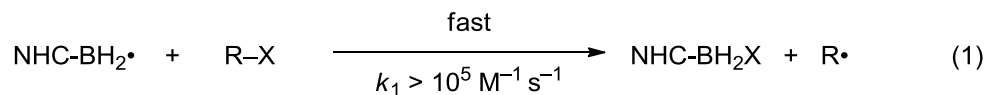
Scheme 17. Proposed propagation steps for radical dehalogenations with NHC-boranes.

The key step for this proposed radical mechanism is the reaction between a PhS• radical and NHC- BH$_3$ (eq 4). Based on the fact that a PhS• radical is an electrophile and NHC-BH$_3$ is a nucleophile, we suggest that hydrogen atom transfer from NHC-BH$_3$ to PhS• is a polarity matched process. Our collaborator Prof. J. Lalevée at the University of Haute Alsace in France directly measured of the rate constant (k_4) for transfer of a hydrogen atom from diMe-Imd-BH$_3$ **16** to a PhS• radical by laser flash photolysis (LFP) experiments. PhS• radical was generated by irradiation of diphenyl disulfide, and was quenched by increasing concentrations of **16** in ethylbenzene/acetonitrile (1:1). The lifetime of PhS• decreased with increasing concentration of **16** (Figure 8, left). The Stern-Volmer equation was used to determine the rate constant k_4:

$$\frac{1}{\tau} = \frac{1}{\tau_0} + k_4[\textbf{16}]$$

Where k_4 is the rate constant for transfer of a hydrogen atom from diMe-Imd-BH$_3$ **16** to a PhS•, [**16**] is the concentration of **16**, and τ_0 is the lifetime of PhS• without **16**. The rate constant (k_4)

was determined to be 1.2 x 10^8 M^{-1} s^{-1} by a plot of the concentration of **16** against the reciprocal of the lifetime of PhS• (Figure 8, right) .
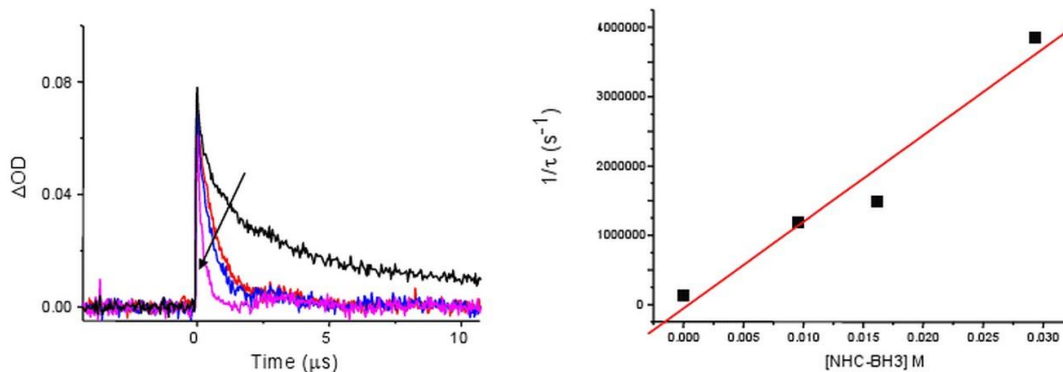
Figure 8. Left: decay of the PhS• signal at 480 nm with increasing concentration of 16; ΔOD is the change in optical density associated with the light excitation; right: the associated Stern-Volmer plot. Data is from Prof. J. Lalevée.

Prof. Lalevée also conducted DFT calculations to determine the electronegativity for both PhS• and NHC-BH$_2$•. The Mulliken electronegativity (χ_M) of a radical is defined by: χ_M = ½ (IP + EA), where IP is the ionization potential and EA is the electron affinity. Based on the UB3LYP/6-31+G* level calculation, PhS• and diMe-Imd-BH$_2$• were found to have χ_M = 5.33 and 2.72 eV, respectively. This suggested that PhS• is electrophilic and diMe-Imd-BH$_2$• is nucleophilic. For a comparison, the electrophilic hydroxyl radical (HO•) has χ_M value for 3.89 eV, and the nucleophilic methyl radical (CH$_3$•) has χ_M value for 2.63 eV.[52]

Therefore, the combination of eq 1, eq 3 and eq 4 results in an efficient radical chain reaction. The problematic step in the direct chain (eq 2) is solved by addition of the thiol which catalyzes the transfer of a hydrogen atom between NHC-BH$_3$ and an alkyl radical.

Newcomb and Solovyev[26, 31] used the PTOC ester method[53, 54] (pyridine thiooxycarbonyl, or Barton's ester[55]) to measure the approximate rate constant for abstraction of a hydrogen atom by an alkyl radical from NHC-borane. We used a similar method to investigate halide abstraction by an alkyl radical. A mixture of PTOC ester **93** and dipp-Imd-BH_2Br **94** was irradiated for 10 min (Scheme 18). Only self-trapped product **95** was formed, and no alkyl bromide **96** was detected by ^{1}H NMR spectroscopy. The absence of bromide **96** suggests that the rate constant ($k_{-1^{Br}}$) for abstraction of bromide by a primary alkyl radical is much smaller than the rate constant for self-trapping of PTOC ester (1.4×10^6 M s^{-1} at 25 °C)[56] and abstraction of bromide (k_{Br}) by a NHC-boryl radical. Hence, we can assume that the abstraction of bromide by a NHC-boryl radical is irreversible under the typical reaction conditions.
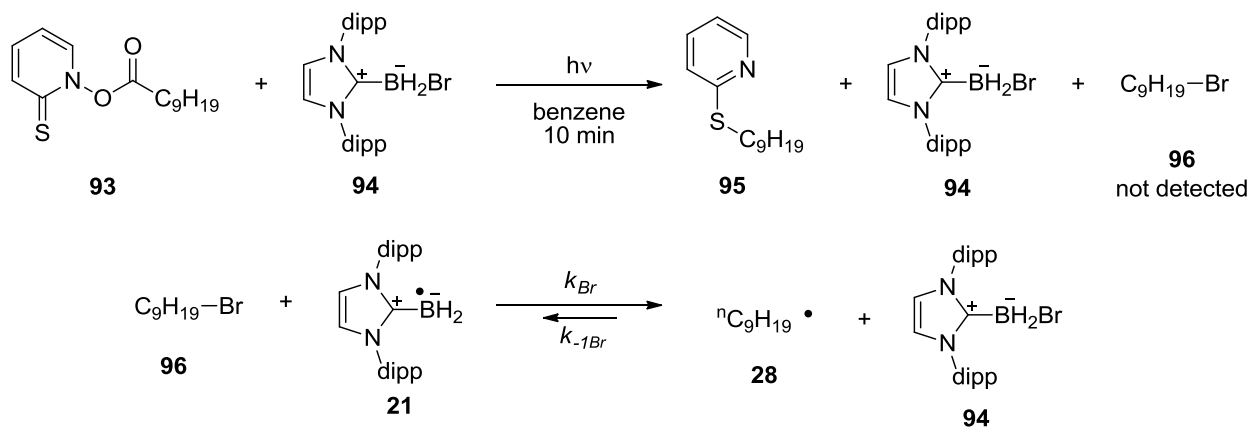
Scheme 18. PTOC ester **93** reacted with **94** to determine the reversibility of abstraction of halides.

While the chain propagation steps for the different conditions (A-C) are the same, the initiator steps differ. For initiation by triethylborane (Condition A), an ethyl radical is liberated from the reaction of triethylborane and oxygen (Scheme 19).[37] This can then abstract H-atom

from thiophenol. Because the ethyl radical competes between autoxidation and initiating the chain, the triethylborane-initiated reduction usually does not work very efficiently.

$$Et_3B \xrightarrow{\quad O_2 \quad} Et_2BOO^\bullet \quad + \quad Et^\bullet$$

$$Et^\bullet \xrightarrow{\quad O_2 \quad} EtOO^\bullet$$

$$EtOO^\bullet + Et_3B \xrightarrow{\quad\quad} (EtOO)BEt_2 + Et^\bullet$$
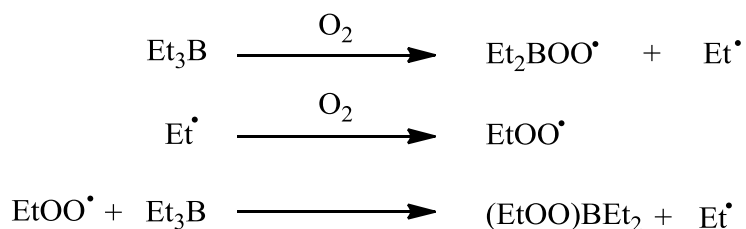
Scheme 19. The initiation mechanism of triethylborane.

Homolysis of TBHN or DTBP generates tBuO• by heating or irradiation. The rate constant for abstraction a hydrogen atom from NHC-BH$_3$ by a tBuO• radical is up to 3×10^8 M^{-1} s^{-1},[28] so TBHN and DTBP are efficient initiators.

In summary, thiol-catalyzed radical dehalogenation with NHC-boranes has been discovered, and this method is practical for reduction of alkyl and aryl bromides/iodides. Compared to traditional tin radical chemistry, there are several advantages of NHC-boranes radical chemistry. First, NHC-boranes (NHC-BH$_3$) only contain hydrogen and second-row elements. Second, they are more atom economic reagents than tributyltin hydride. The reagents **16** and **17** have low molecular weight (110 and 111 g/mol) while Bu$_3$SnH has 292 g/mol molecular weight. Third, NHC-boranes **16** and **17** could be easily removed after reaction. Fourth, they are white solids stable to air and moisture that are easy to handle and store. Fifth, they can be synthesized easily and cheaply.

3.0   RADICAL HOMOLYTIC SUBSTITUTION REACTIONS OF NHC-BORANES

AND DISULFIDES

Homolytic substitutions are major reactions in radical chemistry. Silicon, tin and carbon are known to react with divalent compounds such as disulfides via radical homolytic substitutions,[57, 58] but homolytic substitutions of boryl radicals have not been reported. This chapter describes the development and preparative experiments of first homolytic substitution reactions of NHC-boryl radicals at divalent atoms such as sulfur and selenium. The reactions of heterocycle disulfides undergo a 1,3-boryl shift from S to N to give new class of stable NHC-boranes with B-N heterocycles bonds.

3.1   DISCOVERY OF HOMOLYTIC SUBSTITUTION AT SULFUR

Based on successful thiol-catalyzed radical reduction of halides by NHC-boranes described in Chapter 2, we learned that the hydrogen transfer reaction between PhS• and **16** is very fast ($k = 1.2$ x 10^8 M^{-1} s^{-1}). Since PhS• can be derived from irradiation of diphenyl disulfide (PhSSPh),[59] we proposed that PhSSPh could behave as both the initiator and precatalyst in radical reductions of halides. The results of using disulfides as initiators and precatalysts are discussed in chapter 4.

During this study, we interestingly found that reaction of PhSSPh and **16** generated some new boron products that could be observed by ^{11}B NMR spectroscopy.

A series of reactions between PhSSPh and **16** were performed to identify the reaction conditions and products, and the results are summarized in Table 14. These reactions were conducted in NMR tubes with 1 equiv of **16** and 2 equiv of PhSSPh and were followed by ^{11}B NMR spectroscopy. Conversions were obtained by ^{11}B NMR spectroscopy without an internal standard.

Table 14. Homolytic substitution reactions of NHC-borane **16** and PhS–SPh.

		97	98	99
^{11}B NMR ppm		-25.7, t	-12.4, d	-2.0, s (tentative)
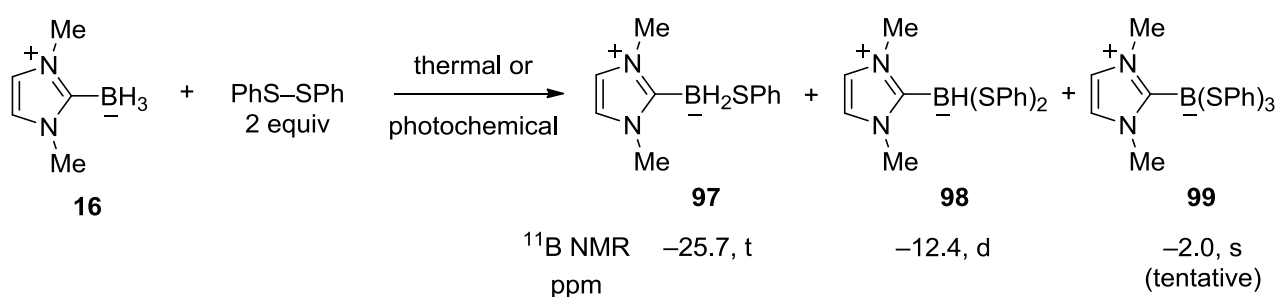
entry	conditions[a]	temperature	time	97[b]	98[b]
1	dark	25 °C	4 d	81%	19%
2	lab light	25 °C	2.5 h	83%[c]	16%
3	lab light	55 °C	1.3 h	67%	33%
4	sunlamp	30 °C	10 min	0%	100%

[a] 0.2M **16** and 2 equiv PhSSPh in C_6D_6; [b] determined by ^{11}B NMR spectroscopy without a standard; [c] with 1% remaining **16**.

NHC-boranes react with strong acids and electrophiles, so their reaction with disulfides could occur via an ionic pathway as well as a radical pathway. To prevent light-initiated radical

process, some reactions were conducted in NMR tubes shielded by aluminum foil in typical dark conditions. The reaction of 0.2 M concentration of **16** and 2 equiv PhSSPh in benzene provided 81% of **97** (triplet, -25.7 ppm, $J_{B-H} = 101$ Hz) and 19% of **98** (doublet, -12.4 ppm, $J_{B-H} = 121$ Hz) after 4 days (entry 1, Table 14). These dark experiments did not give consistent results. For example, similar reactions under dark conditions were stopped after 2 h, and provided 5–18% conversions to **97**. These inconsistencies may be caused by the initiation by stray light.

Acceleration of the reaction was observed when the mixture was exposed to ambient lab light. The lab light-initiated reaction gave 1% of unreacted **16**, 83% of **97** and 16% of **98** after only 2.5 h (entry 2, Table 14). An ever faster reaction at 55 °C provided 67% of **97** and 33% of **98** after 1.3 h (entry 3, Table 14). The results in entries 1–3 show that **97** and **98** are formed competitively. To induce the full conversion of **16** to **98**, a mixture of **16** and 2 equiv of PhSSPh was irradiated by a 275 W sunlamp. This provided **98** as the sole product without detection of **97** after only 10 min of irradiation.

In an attempt to obtain the trisubstituted complex diMe-Imd-B(SPh)$_3$ **99**, a mixture of large excess (10 equiv) of diphenyl disulfide and complex **16** (1 equiv) was irradiated for 10 h. Only a singlet (-2 ppm) without other resonances was detected by ^{11}B NMR spectroscopy. This implies the full conversion of **16** to **99**. However, chromatographic purification of this crude product gave the disubstituted complex **98** in 5% yield and **86** in 12% yield. Product **99** probably is unstable to flash chromatography (Scheme 20).

47
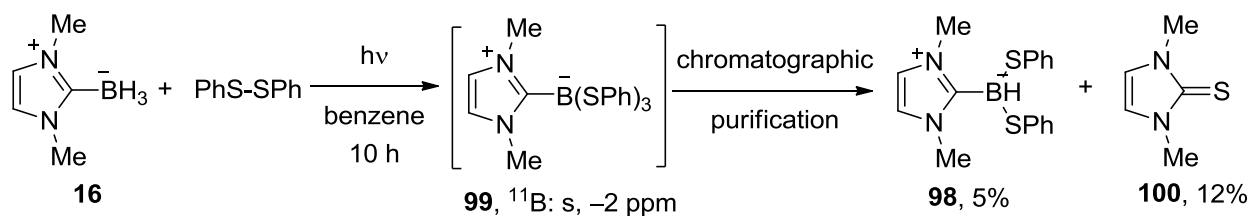
Scheme 20. The formation of diMe-Imd-B(SPh)$_3$ in situ.

Homolytic substitution reactions with other borane-Lewis base complexes were next conducted. Both Me$_3$N-BH$_3$ and Ph$_3$P-BH$_3$ did not react with PhSSPh under irradiation conditions to provide the corresponding amine-boryl sulfides **101** and phosphine-boryl sulfides **102** (Scheme 21, top). The photochemical reaction of pyridine-BH$_3$ **66** with 2 equiv PhSSPh provided the mixture of pyridine-BH$_2$SPh **103** (t, −4 ppm) and pyridine-BH(SPh)$_2$ **104** (d, +4 ppm), but the product pyridine-boryl sulfides did not survive flash chromatography (Scheme 21, bottom). Thus, among the ligated boranes investigated, only the NHC-boranes gave good yields of stable products.
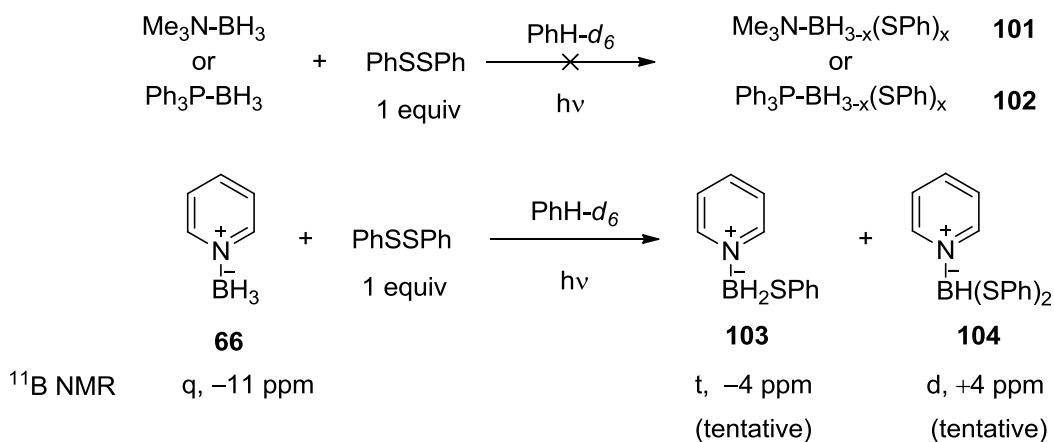
Scheme 21. Homolytic substitution reactions with amine-, phosphine-, and pyridine-borane sources and PhSSPh.

3.2 PREPARATIVE EXPERIMENTS

We next performed preparative experiments to synthesize NHC-boryl sulfides from different NHC-boranes and disulfides. NHC-boryl monosulfides were synthesized by thermal conditions, and NHC-boryl disulfides were generated by photochemical conditions. The thermal reactions and products are shown in Scheme 22. Among these products, **110**, **111**, **114**-**117**, **119** and **120** were synthesized by Ms. Anne-Laure Vallet in Prof. Lacôte's lab. All the products are stable, and they are characterized by usual ways such as ^{1}H, ^{13}C, and ^{11}B NMR spectroscopy, IR and HRMS.

In a typical thermal experiment, a solution of 1 equiv of NHC-borane **16** and 1 equiv of disulfide PhSSPh **108** was heated at 45 °C for 6 h in a flask shielded by aluminum foil. Purification by flash chromatography provided an inseparable mixture of **97** and **98** in 84% yield in a ratio of 83/17. The reaction between diMe-Imd-BH$_3$ **16** and PhSSPh **108** was successfully extended to other sulfides **107** and **109**. NHC-boryl mono-sulfides **110** and **111** were obtained in 86% and 76% isolated yields, and NHC-boryl bis-sulfides **121** and **122** were also isolated in 10% and 24% yield as minor products.

Larger imidazolylidene-derived NHC-boranes **105** and **6** were also investigated. The reaction between diiPr-Imd-BH$_3$ **105** and PhSSPh at room temperature provided **112** in 66% yield with good selectivity and boryl bis-sulfide **123** in 5% yield. The reaction of dipp-Imd-BH$_3$ **6** and PhSSPh was less efficient and less selective to provide an inseparable mixture (**113**, 36% and **124**, 14%) with 11% unreacted starting material. A low yield (28%) of **114** was obtained from **6** and **109** presumably due to steric hindrance of NHC-borane.

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$NHC\text{-}BH_3$ + ArSSAr $\xrightarrow[\text{PhH}]{45\,°C}$ $NHC\text{-}BH_2SAr$ + $NHC\text{-}BH(SAr)_2$

1 equiv

mono-SAr   bis-SAr
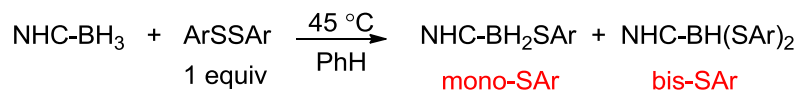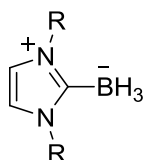
$NHC\text{-}BH_3$:

ArSSAr:

16, R = Me
105, R = iPr
6, R = dipp

106

17
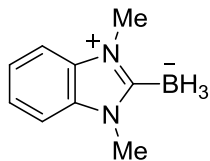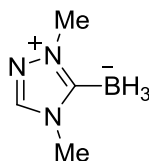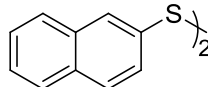
107
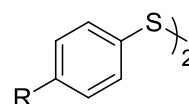
108, R = H
109, R = OMe

$NHC\text{-}BH_2SAr$:
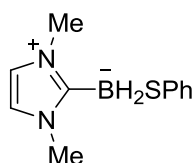
97, 70% (14% bis), 6 h[c]
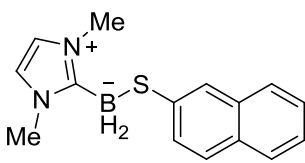
110, 86% (10% bis **121**), 1.5 h[a]
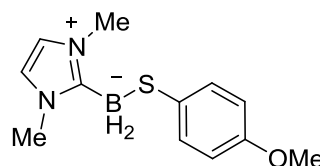
111, 76% (24% bis **122**), 1 h[a]
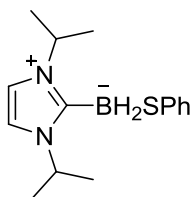
112, 66% (5% bis **123**), 48 h[b]
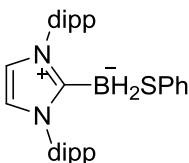
113, 36% (14% bis **124**), 48 h[b,c,d]
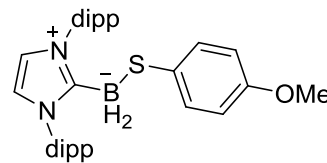
114, 28%, 2 h[a]
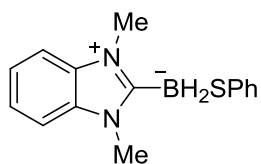
115, 52% (19% bis **126**), 1.5 h[a]
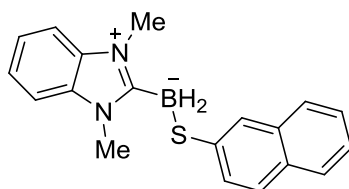
116, 48%, 2 h[a]
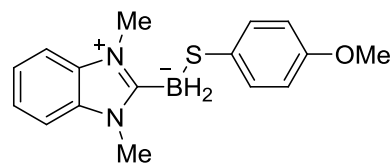
117, 40%, 2 h[a]
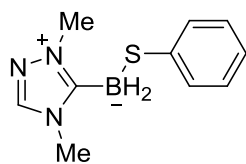
118, 43% (9% bis **129**), 6 h
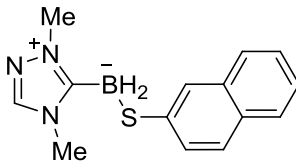
119, 40%, 2 h[a]
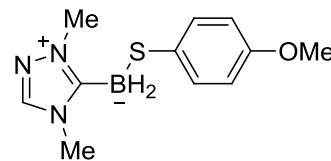
120, 64% (24% bis **131**), 2 h[a]

Scheme 22. Scope and limitations of homolytic substitutions leading to NHC-boryl monosulfides. [a] Performed by Ms. Vallet; [b] reaction was carried out at rt; [c] inseparable mixture; [d] isolated together with 11% of SM.

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Next we examined the benzo-fused NHC-borane diMe-BenzImd-BH$_3$ **106** with all three sulfides **107**-**109**. The reactions under thermal conditions gave the boryl monosulfides **115**, **116** and **117** in 40–52% isolated yields with good mono/di selectivities (19% yield of **126** and no boryl bis-sulfide formation of **127** and **128**). The reactions of triazolylidene borane **17** with all three sulfides **107**-**109** also provided corresponding boryl monosulfides **118**, **119** and **120** in good yields (40-64%) with good mono/bis selectivities.

These results show that the substitution reactions are general and tolerate changes in the both NHC-boranes and the disulfides. The thermal reactions with 1 equiv of disulfide usually give the mono-sulfide NHC-BH$_2$SAr predominantly but not exclusively. Usually but not always, the various NHC-boryl mono- and bis-sulfides can be separated by flash chromatography.

Then, similar experiments were conducted to generate NHC-boryl bis-sulfides under photochemical conditions, and the results are summarized in Scheme 23. Among these results, products **121**, **122**, **125**-**128**, **130** and **131** were synthesized by Ms. Vallet.

In a typical photochemical reaction, 1 equiv of the NHC-borane reacted with 2 equiv of disulfide in benzene under irradiation from a 275W sunlamp (conditions A), or an OmniCure lamp (conditions B), or ambient lab light (conditions C). The lamps (especially the sunlamp) generate some heat. The temperatures of these reaction mixtures are estimated to be 40–60 ˚C, while the lab-light irradiated reaction mixtures remain at room temperature.

Similar to the thermal reactions, the photochemical reactions targeting boryl bis-sulfides were successfully extended to different NHC-boranes such as diiPr-Imd-BH$_3$ **105**, dipp-Imd-BH$_3$ **6**, diMe-BenzImd-BH$_3$ **106** and diMe-Tri-BH$_3$ **17** as well as other sulfides such as **107** and **109**.

NHC-BH(SAr)₂:

98, 80%, 1 h, A

121, 86%, 72 h, Cᵇ

122, 91%, 0.5 h, Bᵇ

123, 72%, 4 h, A

124, 45%, 10 h, A

125, 35%, 2 h, Cᵇ

126, 68%, 0.5 h, Bᵇ

127, 70%, 16 h, Cᵇ

128, 95%, 0.5 h, Bᵇ

129, 85%, 1 h, A

130, 55%, 0.5 h, Bᵇ,ᶜ

131, 54%, 0.5 h, Bᵇ
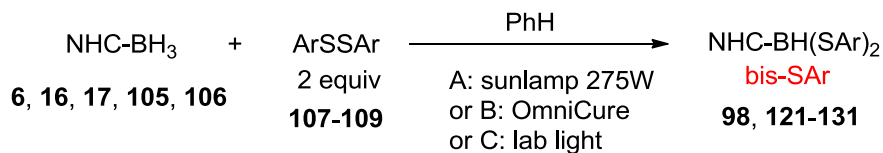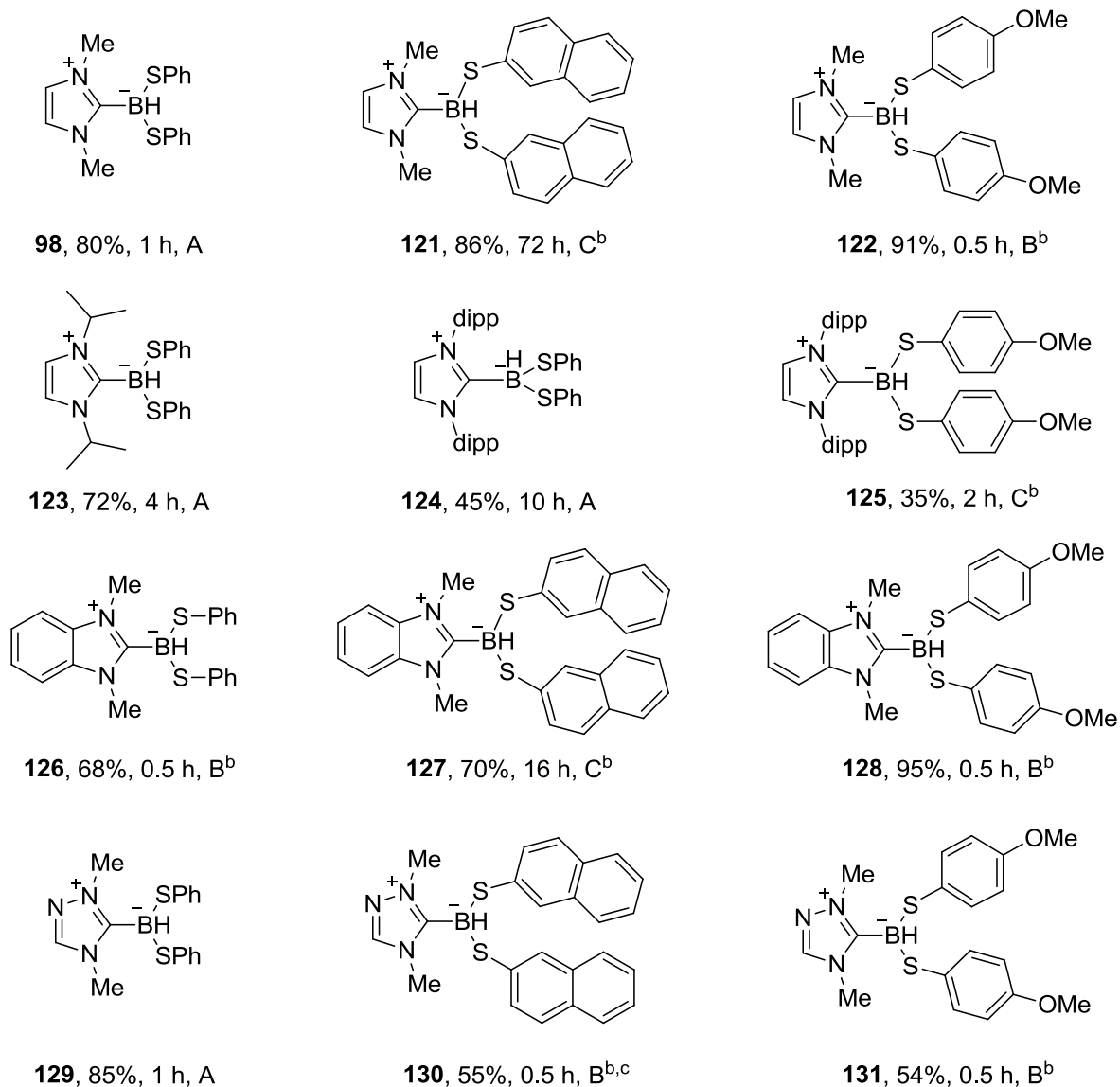
Scheme 23. Scope and limitations of homolytic substitutions leading to NHC-boryl bissulfides. [a] Conditions: NHC-boranes and disulfides (2 equiv), PhH, irradiation by A) 275W sunlamp, rt to 60 °C, or B) OmniCure, rt to 40 °C, or C) ambient lab light, rt; [b] performed by Ms. Vallet; [c] 2% of **119** was also isolated .

The reaction of **16** with PhSSPh provided boryl bis-sulfides **98** in 80% isolated yield after 1 h irradiation by 275W sunlamp, while the reaction with disulfide **107** gave **121** in 86% yield after 72 h irradiation by lab light. The reaction with **109** generated **122** in 91% yield after 0.5 h irradiation by OmniCure light. These three different experiments suggested that strong irradiation (conditions A and B) make the product formation more efficient.

A larger NHC-borane diiPr-Imd-BH$_3$ **105** was reacted with 2 equiv PhSSPh to generate diiPr-Imd-BH(SPh)$_2$ **123** under 275W sunlamp irradiation. This required a longer reaction time (4 h) than diMe-Imd-BH$_3$ **16** (1 h). The reaction of a hindered NHC-borane **6** with PhSSPh even required 10 h of irradiation by sunlamp to provide the product **124** in 45% yield, while the reaction with **109** required 2 h of irradiation by OmniCure to generate **125** in 35% yield. The longer irradiation time and low yield of products **124** and **125** are probably due to the steric hindrance of **6**.

Both diMe-BenzImd-BH$_3$ **106** and diMe-Tri-BH$_3$ **17** were treated with three different disulfides **107**-**109** under various irradiation conditions to provide NHC-boryl bis-sulfides **126**-**131** in 54-95% isolated yields.

We also briefly investigated other solvents for these reactions because benzene is not a preferred solvent for larger scale reactions. DiMe-Imd-BH(SPh)$_2$ **98** was also synthesized from **16** and **108** under photochemical conditions A in both toluene (PhMe) and benzotrifluoride (PhCF$_3$), and the yields are comparable to the result in benzene (PhH, 80%; PhMe, 71%; PhCF$_3$, 69%).

In general, the photochemical conditions with 2 equiv disulfide ArSSAr give faster reactions and higher yields than thermal conditions. In addition, they mainly produce the disulfide NHC-BH(SAr)$_2$ products.

3.3   DISCOVERY OF A 1,3-BORYL SHIFT FROM S TO N

We next conducted the reactions of NHC-boranes with two common di(heteroaryl) disulfides. The reaction of mercaptobenzothiazolyl disulfide **132** with NHC-borane **16** under the photochemical conditions gave unexpected results that are shown in Scheme 24. The product distributions depended on how many equiv of disulfide **132** was used.

The sunlamp irradiation of a mixture of 1 equiv **16** and 1 equiv **132** provided a new triplet consistent with expected boryl sulfide **133** appeared at –24 ppm in ^{11}B NMR spectrum. During the reaction progress, this triplet started to disappear and was replaced by another triplet at −20 ppm rather than the usual doublet of the boryl bis-sulfide. After 1 h of irradiation, all of starting NHC-borane **16** was converted to the product with the triplet at −20 ppm.
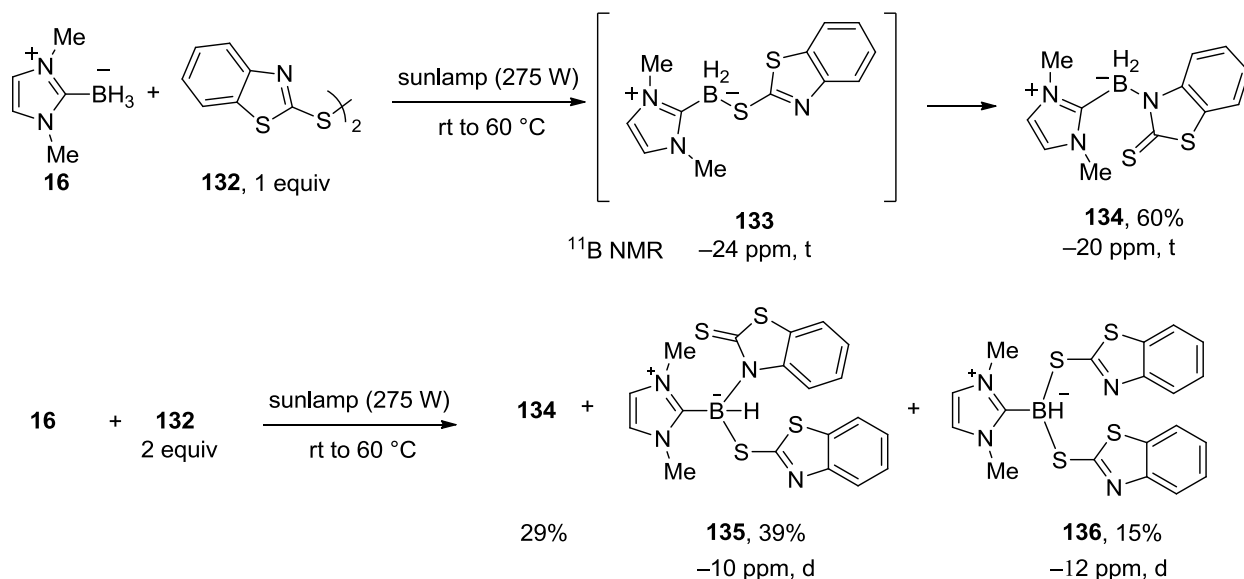
Scheme 24. top) A primary boryl sulfide product undergoes 1,3-shift of the boron from sulfur to nitrogen; bottom) symmetrical and unsymmetrical bis-adducts products.

The final product was isolated in 60% yield after flash chromatography. Based on ^{13}C NMR spectra data, we assigned the stable product as NHC-boryl benzo[*d*]thiazole-2(3*H*)-thione **134**. This features a B–N single bond and a C=S double bond. The resonance at 192 ppm in the ^{13}C NMR spectrum was assigned to the carbon atom of the C=S double bond of **134**. This assignment was further confirmed by X-ray structure (Figure 9). This result suggested that the initial product with the triplet of −24 ppm was indeed the boryl sulfide **133** with a B–S single bond and a C=N double bond, but it rearranged to provide **134** formally by 1,3-boryl shift from S to N.

A similar reaction of **16** with 2 equiv of disulfide **116** was conducted to give three separable products after 1 h. Besides the amidoborane-type NHC-complex **134** (29%), two B-disubstituted complexes **135** and **136** were isolated in 39% and 15% yields. The resonances of the heteroaryl carbons in the ^{13}C NMR spectrum of the major product **135** have two types of benzothiazole peaks and two resonances for C2s at 193 and 171 ppm, which implies **135** is an asymmetrical complex with one B–N bond (C2 at 193 ppm) and one B–S bond (C2' at 171 ppm). The only resonance for C2s in **136** (171 ppm) implies that this is a symmetrical bis-sulfide structure.
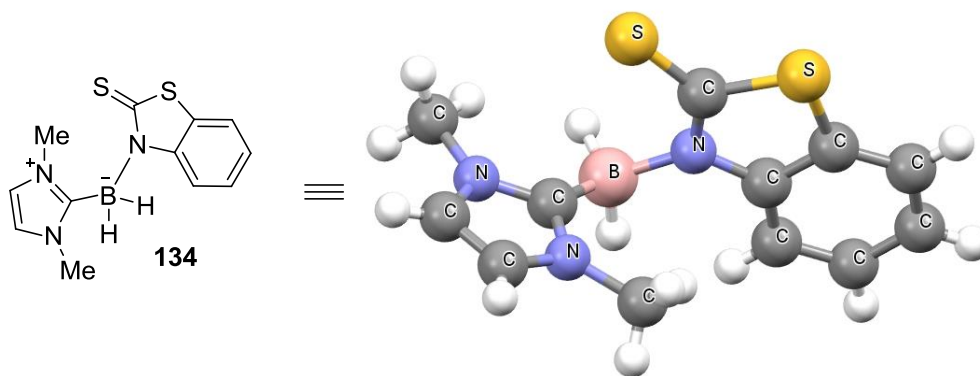
Figure 9. The X-ray crystallographic structures of NHC-boryl benzo[*d*]thiazole-2(3*H*)-thione **134**.

We next conducted several experiments to better understand the 1,3-boryl S-N shift. Prolonged irradiation or heating of symmetric boryl bis-sulfide **136** only gave gradual decomposition and did not generate **135**. In contrast, irradiation of a mixture of mono-adduct **134** with another 1 equiv disulfide **132** only provided the unsymmetrical product **135**. This suggests that the initial boryl sulfide **133** rearranges to **134** in competition with a second sulfanylation to give **135**, and asymmetric adduct **135** is obtained from the sulfanylation of already rearranged **134**.

To test the scope of the rearrangement of the boron from sulfur to nitrogen, we investigated the reactions with 5,5'-dithiobis(1-phenyl-1*H*-tetrazole) **137** (commonly called *bis*-1-phenyltetrazolyl disulfide, PTSSPT) using different NHC-boranes (**6**, **16** and **17**) under thermal and photochemical conditions. The results are summarized in Scheme 25. Among these results, products **139** and **141** were synthesized by Ms. Vallet.

Under thermal conditions with 1 equiv of PTSSPT, both diMe-Imd-BH$_3$ **16** and diMe-Tri-BH$_3$ **17** gave 1,3-boryl shifted NHC-amidoboranes **138** and **139** (C2 at 167 ppm in both products) in good yields (85% and 81%). Under photochemical conditions with 2 equiv **137**, the reaction provided asymmetrical disubstituted complexes **140** (C2 at 167 and C2' at 156 ppm) and **141** (similar values) in 75% and 60% isolated yields. No products with B-S bonds were isolated for this series, which suggests the first S-N shift is rapid.
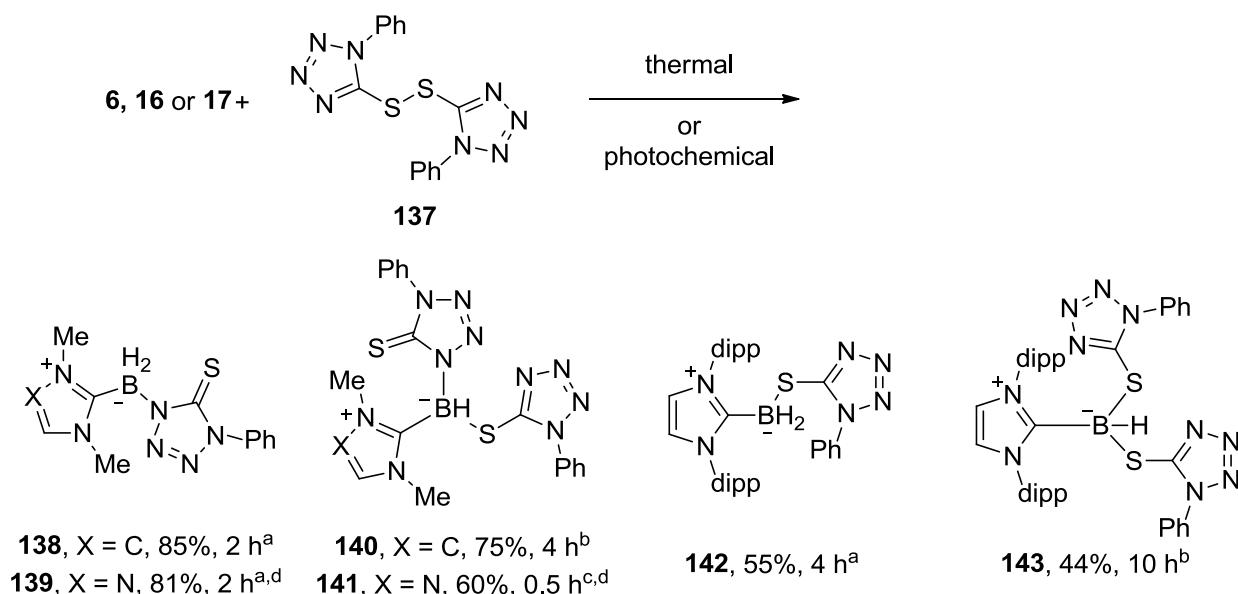
Scheme 25. Products and isolated yields in reaction with **6/16/17** and phenyltetrazolyl disulfide **137**; [a)] thermal conditions, [b)] photochemical conditions with 275W sunlamp, [c)] photochemical conditions with OmniCure, [d)] performed by Ms. Vallet.

Interestingly, the reactions of dipp-Imd-BH$_3$ **6** gave only normal boryl sulfide complexes **142** (C2 at 159 ppm) in 55% yield under thermal conditions and **143** (C2 at 156 ppm) in 44% yields under photochemical conditions. Prolonged irradiation or heating of **142** and **143** did not result in an arrangement to the NHC-boranes with B-N products. These results show the size of the N-substituent is important for the 1,3-boryl shift. 1,3-Boryl shift is feasible for small groups (Me), while it is not easy for large ones (dipp). Calculations by Prof. Lalevée showed that the B–N structure **138** is more favorable than boryl sulfide structure by 10 kcal/mol at B3LYP/6-31G* level. This in turn suggests that **142** does not rearrange due to a kinetic barrier.

Two more reactions were conducted to investigate the effects of steric hindrance on 1,3-boryl S-N shift, and the results are summarized in Scheme 26. A thermal reaction of diMe-Imd-BH$_2$thexyl **144** and PTSSPT **137** in benzene provided boryl sulfide product **145** (C2 at 159 ppm)

in 59% isolated yield after 3 d. The mixture of NHC-borane **144** and thiol **146** was heated at

80 °C for 16 h to give the full conversion, and boryl sulfide **147** (C2 at 175 ppm) was obtained in

58% isolated yield after flash chromatography. These NHC-alkyl-boryl sulfides suggest that both

steric hindrance from B-substituents and from N-substituents on NHC rings prevent the 1,3-boryl

shift from S to N.
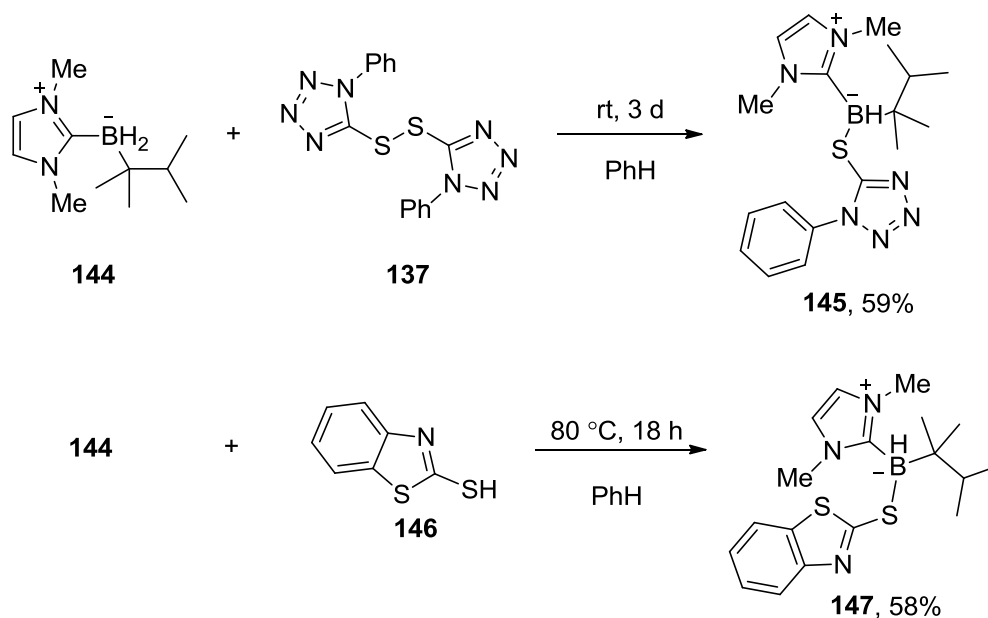
Scheme 26. Thiolation of **144** with disulfide **137** and thiol **146** to provide unarranged complexes **145** and **147**.

3.4   REACTION MECHANISM

The formation of NHC-boryl sulfides complexes promoted by irradiation suggests that the

reaction proceeds under a radical homolytic substitution mechanism (Scheme 27, diMe-Imd-BH$_3$

and PhSSPh were demonstrated in this case). The initiation step is photolytic cleavage of

diphenyl disulfide to form two PhS•. The propagation steps are 1) abstraction a hydrogen atom

from diMe-Imd-BH$_3$ **16** by a PhS• radical, and 2) the homolytic substitution between NHC-boryl

radicals **36**, **148** and **149** and diphenyl disulfide. The homolytic substitution steps (step 3-5) are

new for NHC-boryl radicals.

Initiation

$$PhS\text{-}SPh \xrightarrow{h\nu} 2\ PhS^{\bullet} \tag{1}$$

Propagation

(2)

(3)

(4)

(5)
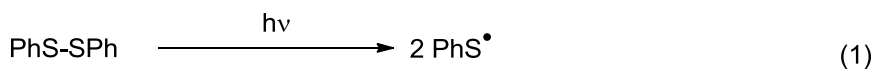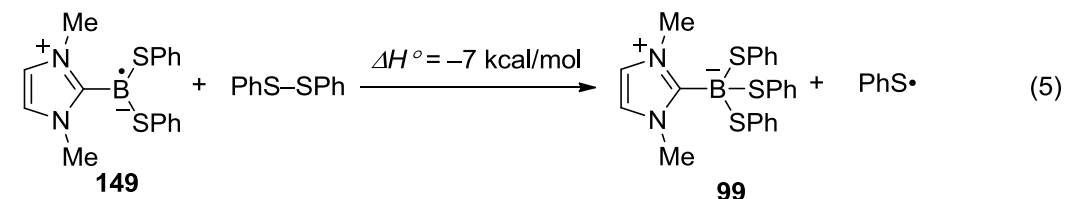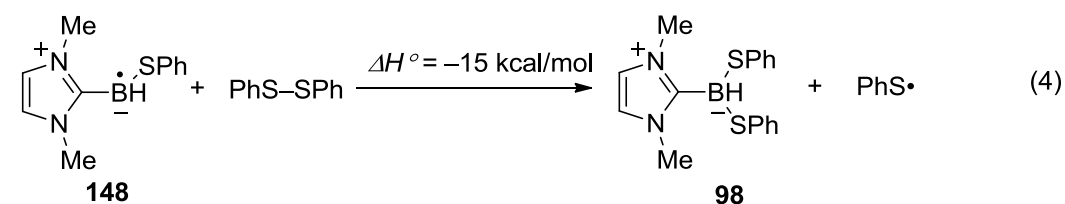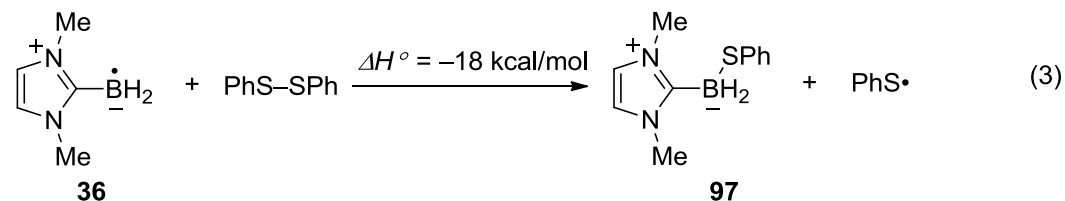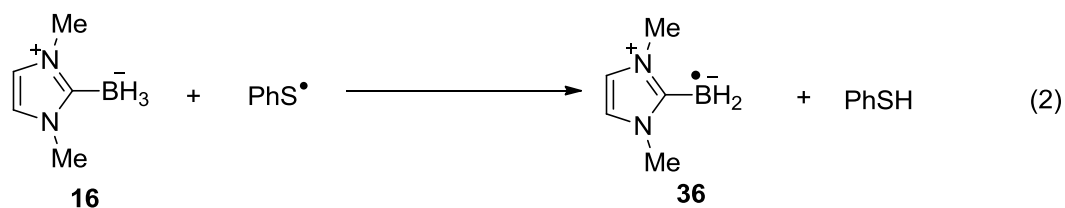
Scheme 27. Proposed mechanism for homolytic substitution reactions with NHC-boranes.

To support homolytic substitution steps, Prof. J. Lalevée calculated $\Delta H°$ of the three homolytic substitution reactions between NHC-boryl radicals and disulfide based on UB3LYP/6-31+G* level. He found that the first homolytic substitution reaction to give **97** is highly exothermic ($\Delta H° = -18$ kcal/mol), and the second homolytic substitution reaction to give **98** is less but still highly exothermic ($\Delta H° = -15$ kcal/mol). The third and final substitution of **149** to give diMe-Imd-B(SPh)$_3$ **99** is less so ($\Delta H° = -7$ kcal/mol). The calculation data is consistent with our experimental observations. Both **97** and **98** form rapidly, but a large excess of disulfide and longer irradiation time is required for full conversion to the third substituted product **99**.

The photochemical reactions are rapid and selective to provide boryl bis-sulfides, but the thermal reactions are much slower. This suggests that the dark reactions might occur either by the radical chain or by an ionic mechanism (Scheme 28). In an ionic mechanism, the NHC-boranes behave like hydride donors and reduce the electrophile like disulfides to thiols.[60]
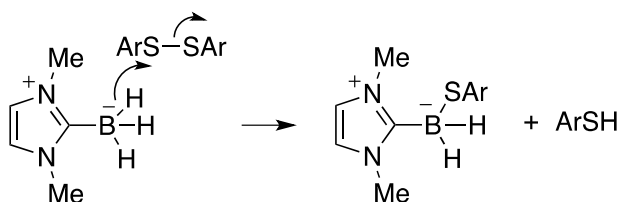
Scheme 28. Possible ionic mechanism. The NHC-borane behaves as a hydride donor.

To test the ionic mechanism, thermal reactions with **16** and PhSSPh or PTSSPT **137** in the presence of 1 equiv the radical trap (2,2,6,6-tetramethylpiperidin-1-yl)oxy (TEMPO). For the less electrophilic PhSSPh, no conversion was observed after 48 h. On the other hand, the reaction of **16** with more electrophilic disulfide **137** with TEMPO gave >90% conversion to rearranged **138** after 16 h. For the same reaction but without TEMPO, complete conversion was observed

after only 2 h (Scheme 26). These results suggest less electrophilic disulfides react primarily by radical chains even under dark conditions, while more electrophilic ones may react by either ionic or competing radical pathways.

We believe that 1,3-boryl shift from S to N rearrangement occurs by a non-radical mechanism because TEMPO did not inhibit the rearrangement to **138** in the reaction of diMe-Imd-BH$_3$ **16** and PTSSPT **137**.

Dr. Solovyev showed that NHC-borane **6** rapidly reacts with strong Brønsted acids of pKa's of 0 or below at rt to provide acid-base adducts.[20] For less acidic acids (pKa 1-2), the acid base reactions with **6** are slower, while **6** does not react with even less acidic acids (pKa >2). NHC-boryl sulfides and amido complexes could potentially be formed from acid/base reactions between NHC-boranes and thiols. To close this study, several acid-base reactions between diMe-Imd-BH$_3$ **16** and thiols were conducted, and the results are summarized in Scheme 29.

Again, reactions were conducted in flasks shielded by aluminum foil in typical dark conditions to prevent light-initiated radical process. NHC-borane **16** did not react with any of the three thiols **150**, **146** and **151** under rt for 18 h. After heating the mixture of diMe-Imd-BH$_3$ **16** and thiophenol **150** at 80 ℃ for 18 h, the reaction gave 22% conversion of **16** to the NHC-boryl sulfide **97** determined by ^{11}B NMR spectroscopy. The similar reaction with thiol **146** provided 30% conversion to the NHC-boryl amido complex **134**. Full conversion was detected from the reaction between **16** and 1-phenyltetrazole-5-thiol **151**, and the product **138** was isolated in 57% yield. Presumably, 1-phenyltetrazole-5-thiol **151** is more acidic than **150** and **146**. These results suggest that **16** could react slowly with more acidic thiols such as **151** to provide rearranged product **138** from 1,3-boryl shift from S to N.
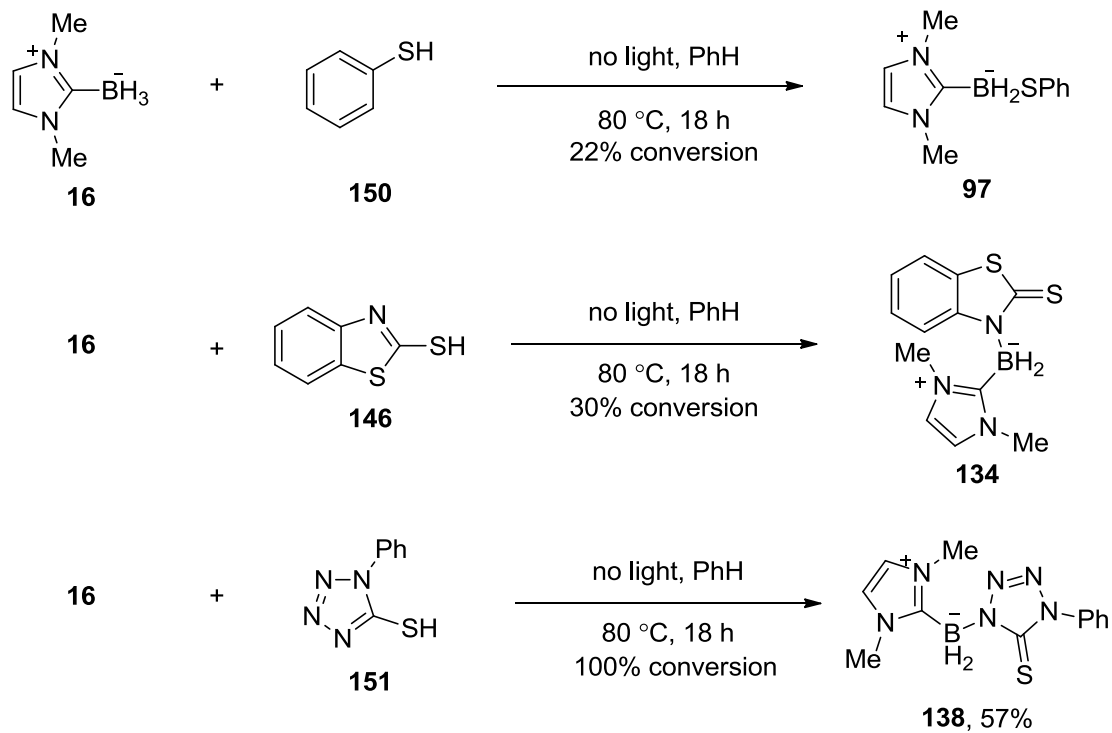
Scheme 29. Acid-base reactions between diMe-Imd-BH$_3$ **16** and thiols **150**, **146**, and **151**.

3.5   PRELIMINARY STUDIES OF HOMOLYTIC SUBSTITUTION REACTIONS OF NHC-BORANES WITH DISELENIDES

After radical homolytic substitution reaction of NHC-boranes at sulfur was discovered, we also briefly investigated the analogous reactions with diselenides. The preliminary results are summarized in Scheme 30.

In a typical experiment, a mixture of 1 equiv **16** and 1 equiv diphenyl diselenide (PhSeSePh, **152**) was irradiated by 275W sunlamp, and the reaction progress was followed by ^{11}B NMR spectroscopy. The reaction of **16** with **152** was complete after 4 h of irradiation, and provided **153** (triplet at −26 ppm) as the major products and **154** (doublet at −16 ppm) as the

minor products. Chromatographic purification of the mixture only gave a mixture of **153** and starting material **16** in 2:1 ratio. This suggests that both **153** and **154** are not stable to silica gel.
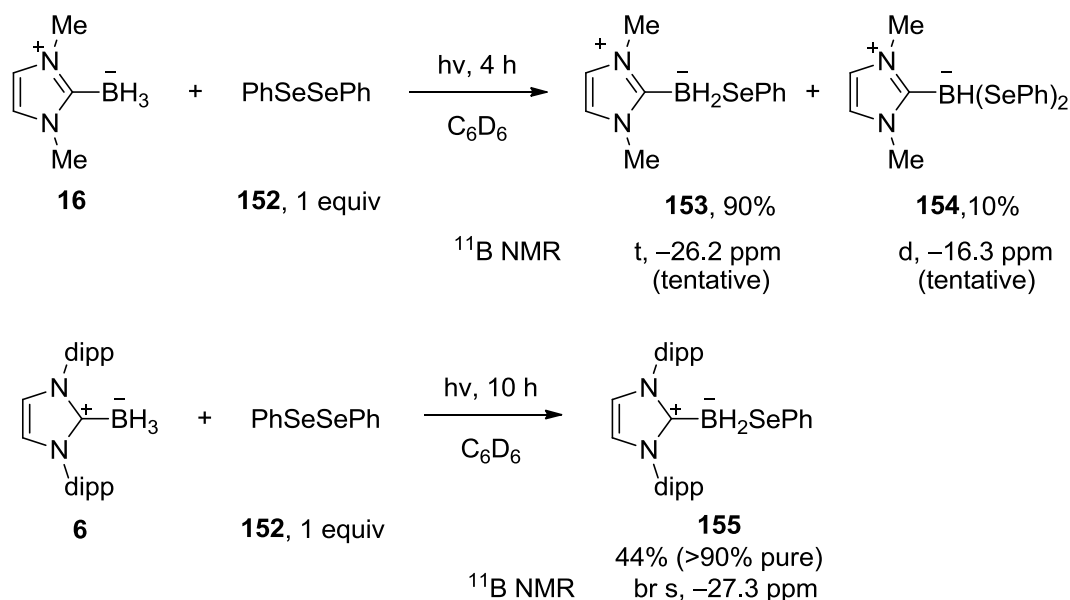
Scheme 30. Preliminary results of homolytic substitution reactions between NHC-boranes **6**, **16** and PhSeSePh.

The photochemical reaction of **6** with PhSeSePh provided NHC-boryl mono-selenide **155** in 44% isolated yield with >90% purity (the inseparable impurities are dipp-Imd-BH(SePh)$_2$ and a trace amount of **6**) after 10 h of irradiation by 275W sunlamp.

In summary, we discovered the first radical homolytic substitution reaction of NHC-boryl radicals at divalent compounds such as disulfides and diselenides. The thermal reactions were used to synthesize new class of NHC-boryl mono-sulfides complexes, and the photochemical reactions were targeted to synthesize NHC-boryl bis-sulfides complexes. Preliminary results about homolytic substitution reaction between NHC-boranes and diselenides were also described. Both boryl-sulfides and -selenides are rarely known, and now we have routes to

synthesize these compounds. Also, a new 1,3-boryl shift from S to N was discovered to provide first stable amidoborane-type NHC complexes when using diheteroaryl disulfides rather than diaryl disulfides. These new synthesized NHC-boryl sulfide, amido, and selenide complexes are stable to air, water and chromatography. The applications of these new compounds are described in next two chapters.

4.0 DISULFIDES AND BORYL SULFIDES SERVE AS BOTH INITIATORS AND PRECATALYSTS IN REDUCTIONS OF HALIDES WITH NHC-BORANES

This chapter describes the discovery that disulfides (RSSR), NHC-boryl mono-sulfide (NHC-BH$_2$SR) and NHC-boryl bis-sulfides (NHC-BH(SR)$_2$) serve as both radical initiators and precatalysts in the radical reductions of alkyl and aryl halides with NHC-boranes. These reactions are believed to involve by a polarity reversal catalysis mechanism as demonstrated in Chapter 2.

4.1 DISCOVERY OF THE REACTION

In Chapter 2, we have shown that various thiols such as thiophenol and *tert*-dodecanethiol catalyze the radical reductions of alkyl and aryl halides with NHC-boranes under suitable radical conditions. In Chapter 3, we have learned that disulfides react with NHC-boranes under radical conditions to provide NHC-boryl sulfides derivatives. Since thiophenol is generated in these reactions, we proposed that diphenyl disulfides could potentially serve as both radical initiators and precatalysts in thiol-catalyzed radical dehalogenation reactions.

In a collaborative study, Prof. Lalevée reported that B-S bond of NHC-boryl sulfides are cleaved under irradiation conditions.[61] This is because NHC-boryl sulfides have strong UV

absorption. The parent NHC-borane (NHC-BH$_3$) complexes with the *N,N*-disubstituted imidazol-2-ylidene ring are usually not UV active. Figure 10 shows the UV absorption spectra for the NHC-boryl sulfide diiPr-Imd-BH$_2$SPh **112** and parent NHC-borane **16**. Compared to **16**, **112** has strong absorption at 268 nm (ε = 12000 M^{-1} cm^{-1}). Based on UB3LYP/6-31G* level calculations, the BDE of B-S bonds in NHC-boryl sulfides are rather low (47.4–60 kcal/mol). Specifically, the calculated BDE of B-S for diiPr-Imd-BH$_2$SPh **112** is 60 kcal/mol, and the BDE for diMe-Imd-BH(SPh)$_2$ **98** is 53.3 kcal/mol.
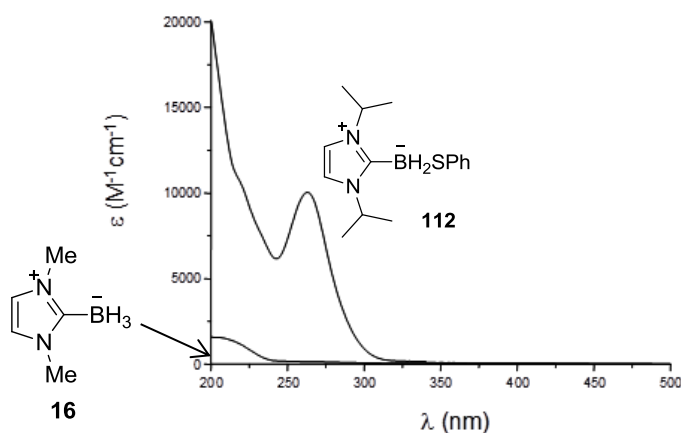
Figure 10. UV absorption spectra for diiPr-Imd-BH$_2$SPh **112** and diMe-Imd-BH$_3$ **16**.
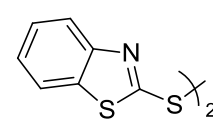
Due to these interesting properties of NHC-boryl sulfides, we hypothesized that the boryl sulfides complexes can also serve as precatalysts in radical reductions by either thermal or photolytic cleavage of their weak B-S bonds. This would result in thiols, the actual catalysts.
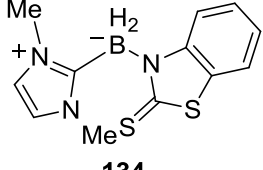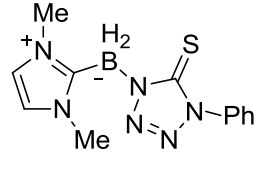
Table 15 summarizes the preliminary results of radical reductions of adamantyl iodide (Ad-I, **53**) with NHC-boranes and other additives such as disulfides or NHC-boryl sulfides. The reactions were performed as described in chapter 2. Ad-I **53** (1 equiv) and diMe-Imd-BH$_3$ **16** (1 equiv) were reacted with 10-15 mol% additives in benzene-d_6. The mixture was irradiated with

275W sunlamp, and the yields were determined by ^{1}H NMR spectroscopy with the addition of an internal standard (1,3,5-trimethoxybenzene, 1 equiv).

Table 15. Reductions of AdI using disulfides and NHC-boryl sulfides.
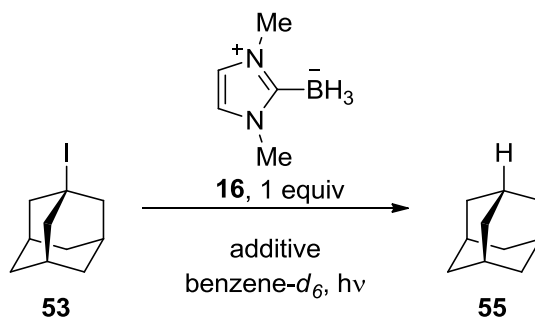
entry	additive	mol%	time	yield[a]
1	PhSSPh	10%	1 h	84%
2	PhSeSePh	10%	4 h	55%
3	132	10%	7 h	55%
4	PTSSPT	10%	7 h	73%
5	-	-	3 h	13%
6[b]	PhSSPh	20%	3 h	97%
7	diMe-Imd-BH(SPh)$_2$	15%	1 h	90%
8	diiPr-Imd-BH$_2$SPh	15%	1 h	92%

9	**134**	15%	7 h	48%
10	**138**	15%	7 h	73%
11[c]	diMe-Imd-BH(SPh)$_2$	15%	24 h	23%
12[c]	diiPr-Imd-BH$_2$SPh	15%	24 h	22%
13[b]	diMe-Imd-BH(SPh)$_2$	20%	1 h	98%
14[d]	diMe-Imd-BH(SPh)$_2$	110%	7 h	27%
15[d]	diiPr-Imd-BH$_2$SPh	110%	7 h	49%

[a] NMR yield determined with 1,3,5-trimethoxybenzene as the internal standard; [b] the sunlamp was replaced by a black light, 15 W, 357 nm max; [c] the sunlamp as not used, the mixture was heated at 80 ˚C in ambient light; [d] NHC-borane **16** was omitted and the additive **98** or **112** was also used as the reductant (1.1 equiv).

The radical reduction of AdI with 1 equiv of **16** and 10 mol% of PhSSPh produced 84% of Ad-H in 1 h, while the reaction with 10 mol% of PhSeSePh only gave the product in 55% after 4 h irradiation (entries 1 and 2, Table 15). Other sulfides such as **132** and **137** were also used as additives, and these reactions generated the product AdH in 55% and 73% yield after 7 h of irradiation (entries 3 and 4, Table 15). In a control experiment, the reaction without any additive provided the product in only 13% yield of AdH after 3 h of irradiation (entry 5, Table 15). A PhSSPh-mediated reduction with irradiation by 15W black light gave AdH in 97% yield

after 3 h (entry 6, Table 15). In presence of PhSSPh, NHC-borane **16** efficiently reduced AdI **53** in high yields. This suggests that PhSSPh behaves like both initiator and catalyst precursor.

Next, we examined NHC-boryl sulfides **98**, **112** and amido complexes **134**, **138** as the additives. Both boryl mono- **112** and bis-sulfide **98** initiated the reaction and provided the product in 90-92% yields in 1 h (entries 7 and 8, Table 15). The reaction with 15 mol% **134** only gave AdH in 48% yield in 7 h, while the reaction with 15 mol% **138** provided AdH in 73% yield after 7 h of irradiation by 275W sunlamp (entries 9 and 10, Table 15). The results of NHC-boryl amido complexes **134** and **138** are similar to the results of their corresponding disulfides **132** and **137**. We believe that irradiation of NHC-boryl amido complex such as **134** also provides the NHC-boryl radical **36** and corresponding thiyl radical **156'** which is the resonance structure of amido radical **156** (Scheme 29).
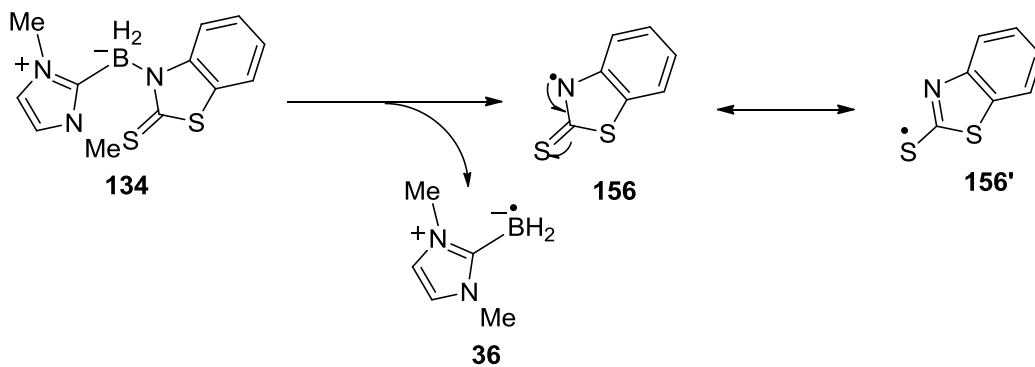
Scheme 31. Proposed radical initiator mechanism for NHC-boryl amido complex **134**.

Thermally initiated reactions with NHC-boryl sulfides **98**, **112** were also conducted. The reaction mixture was heated at 80 ˚C in the ambient lab light. However, these experiments gave much lower conversion, and only provided AdH in 22-23% yield after extended reaction times

24 h (entries 11 and 12, Table 15). Apparently the sunlamp irradiation is important. Again, black light successfully promoted the reduction of AdI with 1 equiv of **16** and 20 mol% of **98** at room temperature (98%, 1 h, entry 13, Table 15).

To test whether NHC-boryl sulfides **98** and **112** could replace **16** as the stoichiometric reductant, we conducted two reductions of AdI with 1.1 equiv of **98** or **112** rather than using 1 equiv of **16** as the reductants. Adamantane was formed, but in much lower yield (27% or 49%) after 7 h extended time (entries 14 and 15, Table 15). Thus, the NHC-boryl sulfides behave as efficient radical initiators and provide active thiols as catalysts, but they are not good at propagating the radical chains by H-transfer to intermediate radicals. Therefore, the less expensive parent complex NHC-BH$_3$ **16** was used as the stoichiometric reductant, and NHC-boryl sulfides were used as the radical initiator and precatalyst. Because diMe-Imd-BH(SPh)$_2$ **98** is readily available in pure form, it was used as additive in next scope and limitations study.
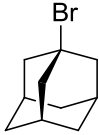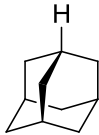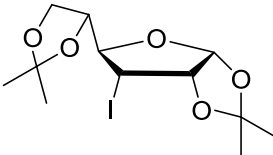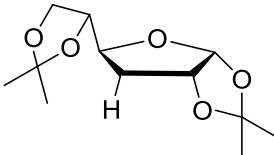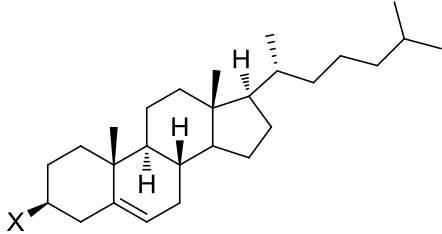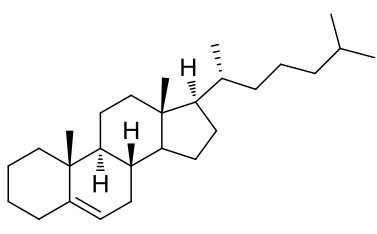
4.2   SCOPE AND LIMITATIONS

We conducted some preparative experiments to obtain isolated yields after flash chromatography, and the results are summarized in Table 16. The typical reactions were performed with 1 equiv of substrate, 1 equiv of **16**, either 10 mol% PhSSPh (conditions A) or 15 mol% **98** (conditions B) and irradiation with 275W sunlamp.

With 10 mol% PhSSPh, the reduction of AdBr **54** with 1 equiv **16** provided adamantane **55** in 81% yield (entry 1, Table 15). With 15 mol% boryl bis-sulfides **98**, the reaction with **54** and 1 equiv **16** gave **55** in 84% yield (entry 2, Table 15). A good yield (67%) was observed in

the reduction of glucosyl acetonide iodide **43** to 3-deoxylglucose diacetonide **19** (entry 3, Table 15). Under conditions B, reductions of both cholesterol iodide **69** and bromide **70** provided deoxycholesterol **71** in 98% and 82% yields, respectively (entries 4 and 5, Table 16).

Table 16. Disulfides and boryl sulfides are used as radical initiators and precatalysts in preparative reductions.

Entry	substrate	conditions[a]	time	product	yield[b]
1	**54**	A	3 h	**55**	81%[c]
2	**54**	B	5 h	**55**	84%[c]
3	**43**	A	2 h	**19**	67%
4	**69**, X = I	B	3 h	**71**	98%
5	**70**, X = Br	B	7 h	**71**	82%
6	**70**, X = Br	A (PhMe)	7 h	**71**	81%
7	**70**, X = Br	B (PhCF$_3$)	7 h	**71**	85%

8	**61**, X = I	A	3 h	**63**	88%[c]
9	**61**, X = I	B	7 h	**63**	91%[c]
10	**62**, X = Br	A	7 h	**63**	50%[c]
11	**62**, X = Br	B	10 h	**63**	40%[c]

12	**80**, X = I	A	1 h	**81**	98%
13	**158**, X = Br	B	4 h	**81**	94%

14	**82**	B	3 h	**83**	81%[d]

[a] 275W sunlamp irradiation of a mixture of the precursor either 10 mol% PhSSPh (conditions A) or 15 mol% diMe-Imd-BH(SPh)$_2$ 98 (conditions B) and 1 equiv of **16** in benzene unless otherwise indicated; [b] isolated yields after flash chromatography unless otherwise indicated; [c] NMR yield determined with 1,3,5-trimethoxybenzene as the internal standard; [d] 3/1 anomer ratio and the major is shown.

Aryl iodide **61** was efficiently reduced to provide **63** with both PhSSPh and boryl bis-sulfide **98** (88% and 91%, entries 8 and 9, Table 16), while the aryl bromide **62** only gave partial conversions. Under both conditions, the reductions of **62** were stopped after extended irradiation time 7 h and 10 h, and the yield of **63** was 50% and 40%, respectively (entries 10 and 11, Table 16).

Radical 5-*exo-trig* cyclizations were also investigated, and the results are summarized in entries 12-14 in Table 16. Reductive cyclization of precursor iodide **80** under conditions A and related bromide **158** under conditions B gave **81** in 98% and 94% yields, respectively (entries 12 and 13, Table 16). Stork-Ueno cyclization[48] of bromoacetal **82** with **16** under conditions B provided cyclic acetal **83** in 81% yield with a 3/1 mixture of anomers at C2 (entry 14, Table 16).

As usual, benzene was used as solvent in most of the reactions in Table 16. However, we also conducted experiments with other two common solvents toluene (PhMe) and benzotrifluoride (PhCF$_3$). The reduction of cholesterol bromide **70** with conditions A in PhMe and with conditions B in PhCF$_3$ gave the product **71** in comparable yields after flash chromatography (PhMe, 81%; PhCF$_3$, 85%, PhH, 82%, entries 5-7, Table 16). These results show that using benzene as the solvent is not crucial, and it can be replaced by other more green aromatic solvents.

In summary, the thiol-catalyzed radical reduction used the combinations of catalysts (thiols) and radical initiators, and this method was simplified and modified with using either disulfides or NHC-boryl sulfides. Both disulfides and boryl sulfides serve a dual role as both initiators and precatalysts. Both procedures gave the reduced and cyclized products with comparable rates and yields to the original thiol-catalyzed methods (Chapter 2).

5.0 SYNTHESIS OF THIOETHERS AND THIOESTERS BY NHC-BORYL SULFIDES AND –AMIDO COMPLEXES

Thioethers and thioesters are important synthetic and biological compounds.[62-64] For many decades, these compounds have been synthesized by nucleophilic substitution by thiolate salts.[65, 66] Recently, a great deal of attention was paid to new strategies for carbon-sulfur bond formation,[67] especially focused on using thiols instead of thiolates under transition-metal catalyzed conditions.[68-72] These C-S coupling reactions have to directly use volatile thiols, thus the application is limited to the small scale preparation.

Chapter 4 describes that NHC-boryl sulfide (NHC-BSAr) is a new type of radical initiator which generates NHC-boryl and thiyl radicals under irradiation conditions. Application of NHC-BSAr as radical initiators includes radical dehalogenation[73] and polymerization.[61] On the ionic side, by replacing a hydride on boron by an SAr group, we hypothesize that NHC-BSAr could be behaved as neutral source of a thiol nucleophile. This chapter describes a general method for thiolation with NHC-BSAr and NHC-BN complexes (Figure 11).
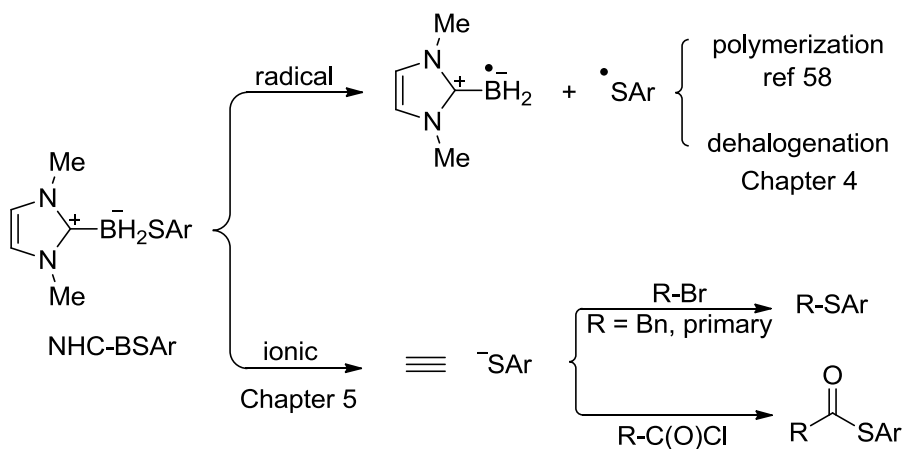
Figure 11. Elementary reactions of NHC-boryl sulfides.

5.1 DISCOVERY AND OPTIMIZATION OF THE REACTION

To test our initial hypothesis, we examined the reaction between benzyl bromide **159** and NHC-boryl bis-sulfide **98**, and the results are selected in Table 17. The first reaction was conducted in non-polar solvent benzene at 80 °C for 1 d, and the desired product benzyl phenyl sulfide **47** was isolated in 96% yield after chromatography (entry 1, Table 17). The reaction at room temperature was not complete after 3 d, and gave the product **47** in 89% NMR yield (entry 2, Table 17). By changing to the more polar solvent chloroform, the reaction went smoothly at rt, and quantitative yield was achieved after 6 h (entry 3, Table 17).

To test whether the second SPh group participated in the substitution reaction or not, 0.6 equiv of **98** and benzyl bromide **159** gave 86% NMR yield of **47** after 1 d (entry 4, Table 17). A similar reaction was conducted without any light to provide the product **47** in 87% yield (entry 5, Table 17). This suggests that the reaction does not occur by a light-initiated radical chain mechanism. Since the reactivity of primary bromide in chloroform is lower than in acetonitrile,

we optimized the reaction conditions as using 1.1 equiv of NHC-BSAr complex and heating in MeCN at 80 °C for 3 h. Under the optimized conditions, benzyl phenyl sulfide **47** was isolated in quantitative yield (entry 6). Among all these reaction mixtures, the resonance of toluene was not detected by ^{1}H NMR spectroscopy. If benzyl radicals were involved, some toluene would be expected. Again the observation supports the ionic mechanism.

Table 17. Optimization of thiolation between benzyl bromide **159** and **98**.
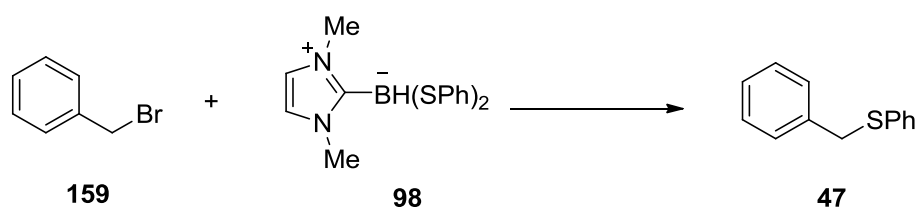
Entry	equiv of **98**	solvent	temp.	time	yield of **47**[a]	yield of toluene[a]
1	1.0	PhH	80 °C	1 d	96%[b]	<1%
2	1.0	PhH	rt	3 d	89%	<1%
3	1.0	CDCl$_3$	rt	6 h	99%	<1%
4	0.6	CDCl$_3$	rt	1 d	86%	<1%
5	0.6	CDCl$_3$	rt, black[c]	1 d	87%	<1%
6	1.1	MeCN	80 °C	3 h	99%[b]	<1%

[a] NMR yield determined with 1,3,5-trimethoxybenzene as the internal standard; [b] isolated yield; [c] performed in a flask shielded by aluminum foil.

For a typical thioetherification reaction, complex diMe-Imd-BH(SPh)$_2$ (**98**, 35.9 mg, 0.11 mmol, 1.1 equiv) was added to a solution of benzyl bromide (**159**, 0.10 mmol, 1.0 equiv) in MeCN (0.5 ml). The colorless solution was charged to a sealed tube and heated in oil bath at 80

76

°C for 3 h. The mixture was cooled to room temperature, then the solvent was evaporated and the crude product was purified by flash column chromatography to give **47** in 99% isolated yield.

5.2   SCOPE AND LIMITATIONS

The scope of the thioetherification was studied with other benzyl bromide derivatives, and the products and isolated yields are reported in Scheme 32. With optimized conditions, the reaction between the benzyl bromide derivatives **160** and **98** gave all corresponding sulfides **161-166** in excellent yields (94% for 4-CO₂Me-, 98% for 2-I-, 92% for 4-F-, 89% for 4-CF₃-, 97% for 2-Br-, and 96% for 4-tBu-).
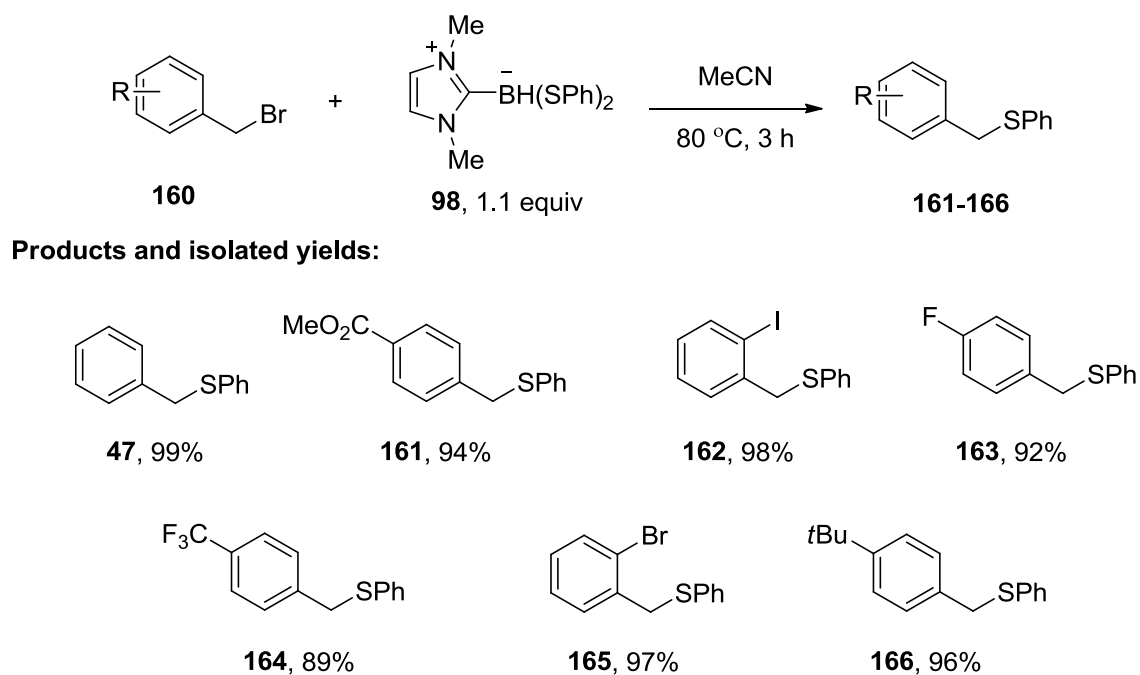
Scheme 32. Scope and limitations of thioetherification of benzyl bromide derivatives with **98**.

Next, we evaluated the reaction between NHC-boryl amido complex **138** and benzyl bromide derivatives **160** under same conditions, and the structures and isolated yields are showed in Scheme 33. All these reactions completed in 3 h of heating in acetonitrile, and the products were clean and easily purified. All the corresponding 1-phenyl-1*H*-tetrazole sulfides **167**-**173** were obtained in good yields (96% for BnBr, 93% for 4-CO$_2$Me-, 98% for 2-I-, 92% for 4-F-, 89% for 4-CF$_3$-, 88% for 2-Br-, and 96% for 4-*t*Bu-).

160   **138**, 1.1 equiv   **167-173**

Products and isolated yields:

167, 96%   **168**, 93%   **169**, 98%

170, 92%   **171**, 89%   **172**, 88%   **173**, 96%
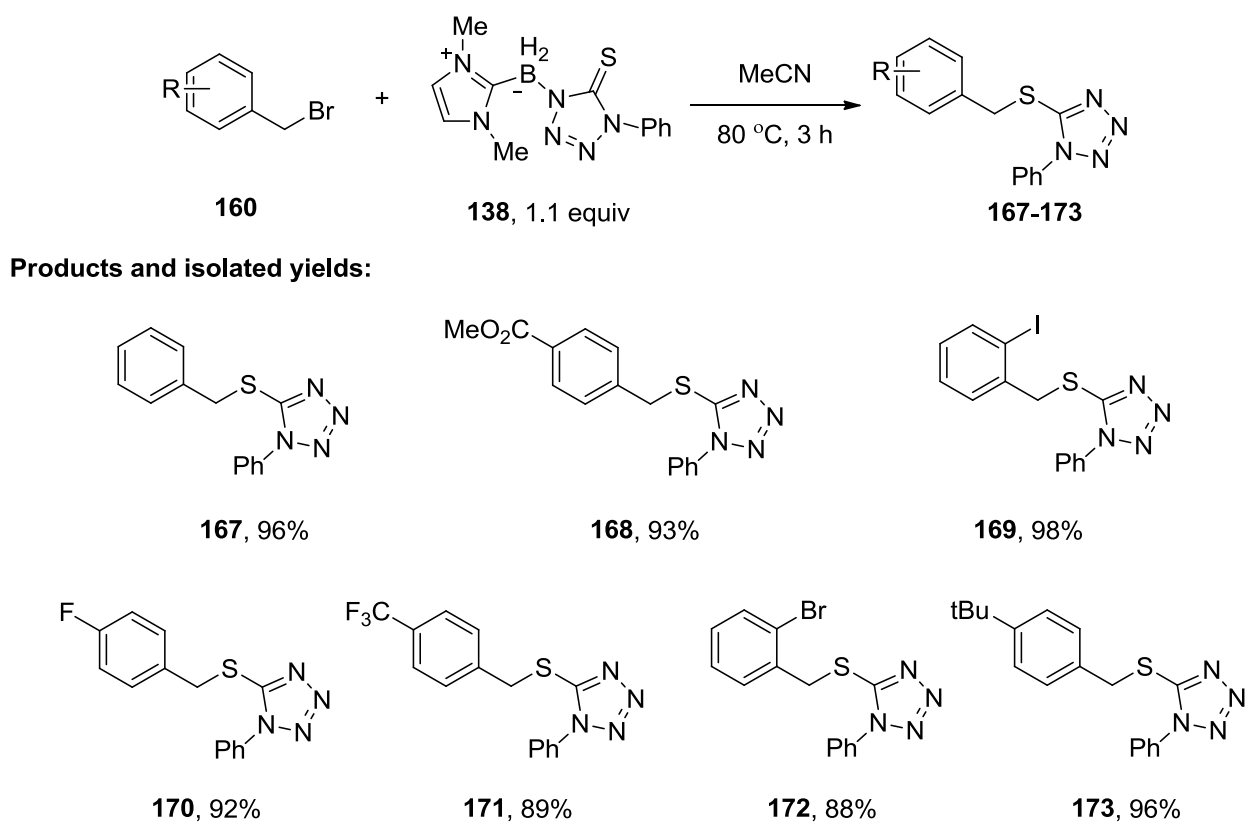
Scheme 33. Scope and limitations of thioetherification of benzyl bromide derivatives with **138**.

Figure 12 summarizes the results of thioetherification reaction between primary and propargyl bromides and **98**. The reaction time of bromides and NHC-BS complex **98** extends to

12 h to achieve full conversions. Treatment of 6-bromo-1-hexene with **98** gave corresponding

thioether **174** in 98% isolated yield. No *5-exo-trig* cyclized product was detected further

suggesting that the reaction by NHC-boryl sulfides has an ionic mechanism rather than the

radical chain mechanism. Reaction with other primary bromides gave sulfides **175**-**177** in 92-

97% isolated yields. Thioetherification of bromo-1-(trimethylsilyl)-1-propyne with **98** provided

corresponding sulfide **178** in 97% yield. Similar reactions between primary bromides and **138**

were conducted in acetonitrile, no conversions to desired 1-phenyl-1*H*-tetrazole sulfides were

detected even heated at 80 ℃ for 1 d.

174, 98%   **175**, 93%   **176**, 92%

177, 97%   **178**, 97%
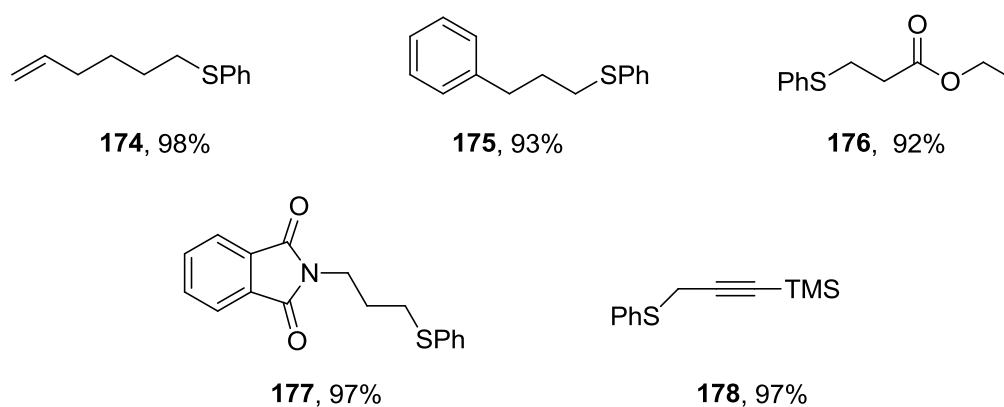
Figure 12. Scope and limitation of thioetherification of primary and propargyl bromides with **98**. Conditions: 1.0 equiv substrate, 1.1 equiv **98**, MeCN, 80 ℃, and 12 h.

Next, we investigated the thioesterification with NHC-BSAr and NHC-BN complexes by

using acid chlorides as electrophiles, and the results are summarized in Scheme 34. Benzoyl

chloride was studied first with **98** in chloroform at rt. After 2 h the reaction was complete and

provided *S*-phenyl thioester **180** in 96% isolated yield. The reaction of 2-furoyl- and 2-

thiophenecarbonyl chloride gave thioester derivatives **181** and **182** in 94% and 97% yields

respectively after flash chromatography. Thioesterification of 4-methoxyphenylacetyl- and cinnamoyl chloride provided **183** and **184** in 97% and 91% isolated yields, respectively. The modified conditions were used to conduct the similar transformation with **138** due to its low reactivity. The reaction mixtures were heated at 80 ℃ in acetonitrile for 16 h and finally provided *S*-phenyltetrazole thioesters **185** and **186** in 89% and 84% yields, respectively. Both NHC-boryl sulfide **98** and -amido complex **138** successfully converted benzyl bromides and acid chlorides to thioethers and thioesters, while only **98** could react with primary bromides to provide thioether products.
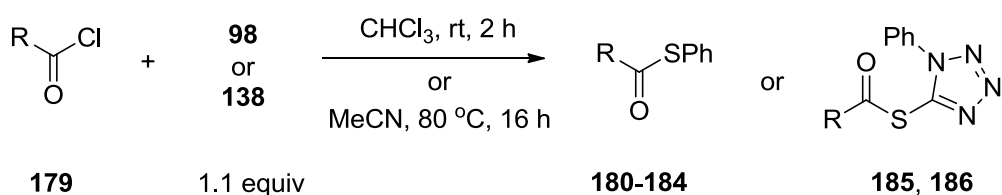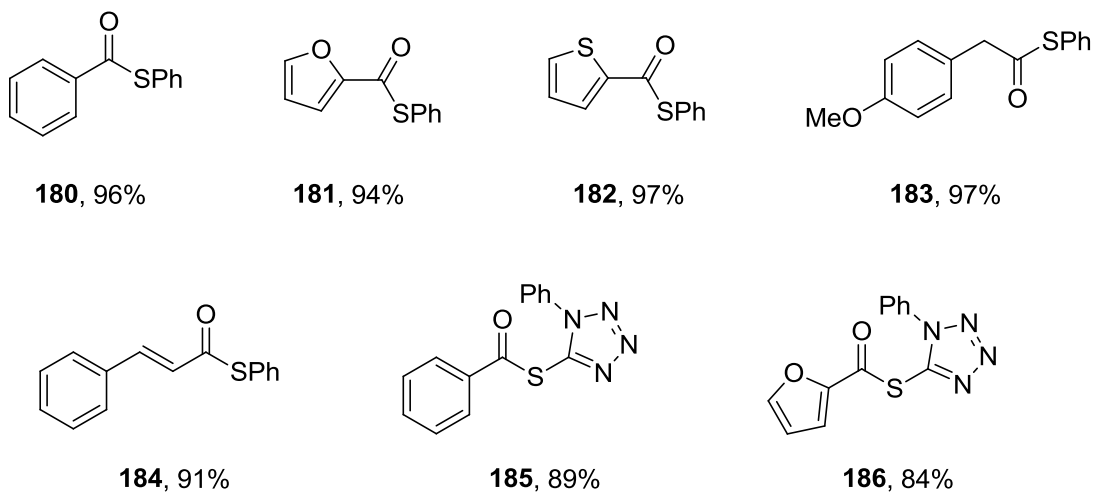
Scheme 34. Scope and limitations of thioesterification of acid chlorides with **98** or **138**.

5.3   ONE-POT THIOLATION

To make this protocol more useful and general, we investigated several one-pot reactions which are summarized in Scheme 35. These reactions combine the synthesis of the boryl sulfides with the subsequent reactions. For a typical procedure for substitution, diphenyl disulfide (1.2 equiv), diMe-Imd-BH$_3$ (**16**, 1.2 equiv) and 1-bromo-3-phenylpropane (**187**, 1 mmol) were mixed in acetonitrile (5 ml) in a sealed tube, and the sealed tube was heated at 80 ℃ for 1 d. The phenyl ester **175** was obtained in 93% isolated yield after purification. Similar one-pot reactions using phenyltetrazole disulfide **137** were conducted to substitute benzyl bromide derivatives to provide **167** and **173** in 88% and 91% yields, respectively.
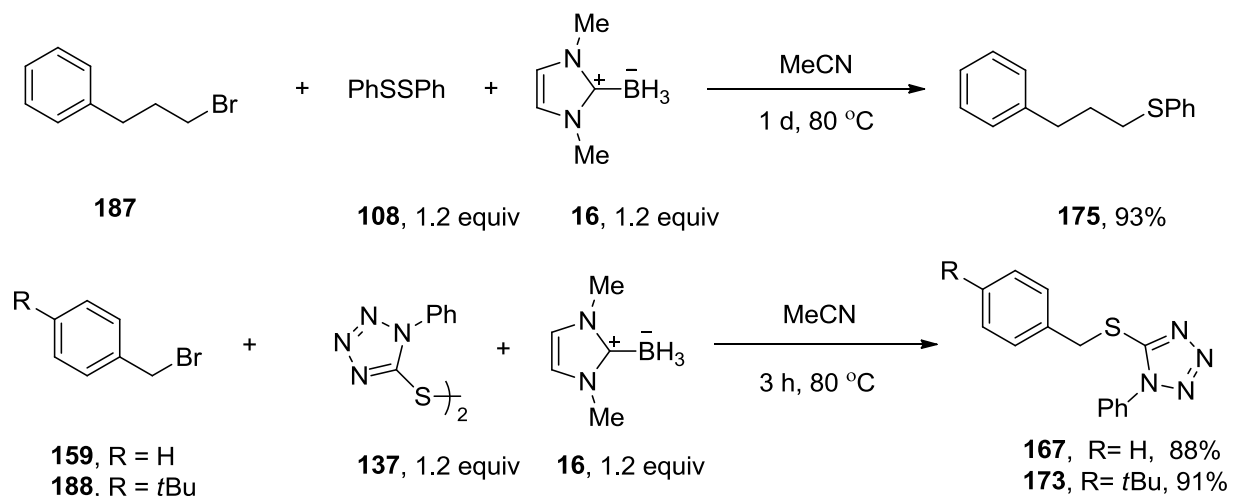
Scheme 35. One-pot thioetherifcation of benzyl and primary bromide with disulfides and **16**.

A limitation was observed for this one-pot procedure when using benzyl bromide **159** and benzoyl chloride **189** as substrates with **16** and PhSSPh. We interestingly found that diMe-Imd-BH$_3$ **16** efficiently reduced **159** and **189**. This is related to the work in Chapter 5.5.

To prevent the competition reaction between **16** and substrates, PhSSPh and **16** were mixed first and reacted to form NHC-boryl sulfides in situ. Benzyl bromide **159** or benzoyl chloride **189** was then added to the mixture. The reaction of benzyl bromide at 80 ℃ for 1 h provided quantitative yield of **47**, and the thioesterification of **189** at rt for 1 h produced **180** in 95% isolated yields.

5.4   REACTION MECHANISM

Based on the previous results, we propose that the substitution reactions undergo an ionic mechanism. Figure 13 shows plausible mechanisms for the substitution reaction with NHC-boryl sulfides. In the "borenium" pathway (Figure 13a), dissociation of NHC-BH$_2$SAr provides the borenium ion NHC-BH$_2^+$ and thiolate ArS$^-$, and followed by substitution by the thiolate to give the product. The first dissociation step must be the rate-determining step. Based on our experiment data, hindered NHC-borane such as **138** gave lower reactivity than **98**. This suggests that "borenium" pathway is unlikely because hindered sulfide part would facilitate the first dissociation process. If this borenium ion intermediate is involved in the reaction, it should react with alkenes to provide hydroboration products (Chapter 6). The boryl sulfide **98** was mixed with 1-hexene in dichloromethane to capture the borenium ion, but no hydroboration products were detected. This further excludes this pathway.

In the "four-center" pathway (Figure 13b), the substitution reaction could occur by a four-center cyclic transition state, which would rapidly deliver the substituted product. The mechanism involved four-center cyclic transition state is common for hydroboration. This

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pathway is reasonable for the substitution reaction with the NHC-boryl sulfide **98**. For the reaction with NHC-BN **138**, a similar six-center cyclic transition state with **138** would give *S*-substituted product.

(a) borenium

$$NHC\text{-}BH_2SAr \xrightarrow{\text{dissociation}} NHC\text{-}BH_2{}^+ + ArS^- \xrightarrow{RX} NHC\text{-}BH_2X + RSAr$$

(b) four-center

$$NHC\text{-}BH_2SAr + RX \longrightarrow \left[\begin{array}{c} NHC\text{-}BH_2 - SAr \\ \vdots \quad\quad \vdots \\ X - R \end{array} \right]^{\ddagger} \longrightarrow NHC\text{-}BH_2X + RSAr$$

(c) sulfanium

$$NHC\text{-}BH_2SAr + R\text{-}X \longrightarrow NHC\text{-}BH_2\overset{+}{\underset{R}{S}}Ar + X^- \longrightarrow NHC\text{-}BH_2X + RSAr$$
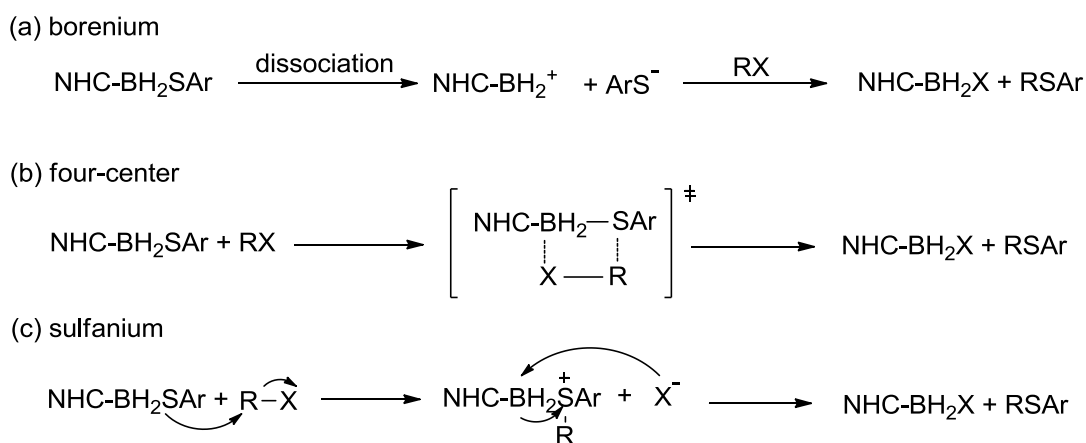
Figure 13. Plausible mechanisms for the substitution reaction with NHC-boryl sulfides.

In the "sulfanium" mechanism (Figure 13c), the nucleophilic sulfur could attack the substrate (R-X) to form NHC-boryl sulfanium ion intermediate and a leaving group (X^-). This sulfanium intermediate was followed by another attack at boron center from X^- to provide the substituted product and NHC-BH_2X. In this pathway, the first step would be a rate determining step, and the second step is fast. Based on the results that both hindered NHC-BN and secondary halides give low reactivities, we suggest that "sulfanium" pathway is more reasonable.

5.5   IONIC REDUCTIONS BY NHC-BORYL CHLORIDE

By monitoring the reaction progress by ^{1}H NMR spectroscopy, the reaction between **159** and **16** provided toluene as the major byproduct. For the reaction between benzoyl chloride **189** and **16**, benzyl alcohol **192** was isolated in 80% yield as the major product (Scheme 36). DiMe-Imd-BH$_3$ **16** is one of the most nucleophilic classes of neutral hydride donor,[60] so it is not surprising that **16** can directly reduce benzyl bromide to toluene.[32] Also, **16** and related NHC-BH$_3$ reduce carbonyl groups in presences of silica gel,[74] acetic acid[75] and Lewis acid.[76] The alcohol formation suggested that diMe-Imd-BH$_2$Cl **191**, which came from reduction of **189**, was a competent reductant.
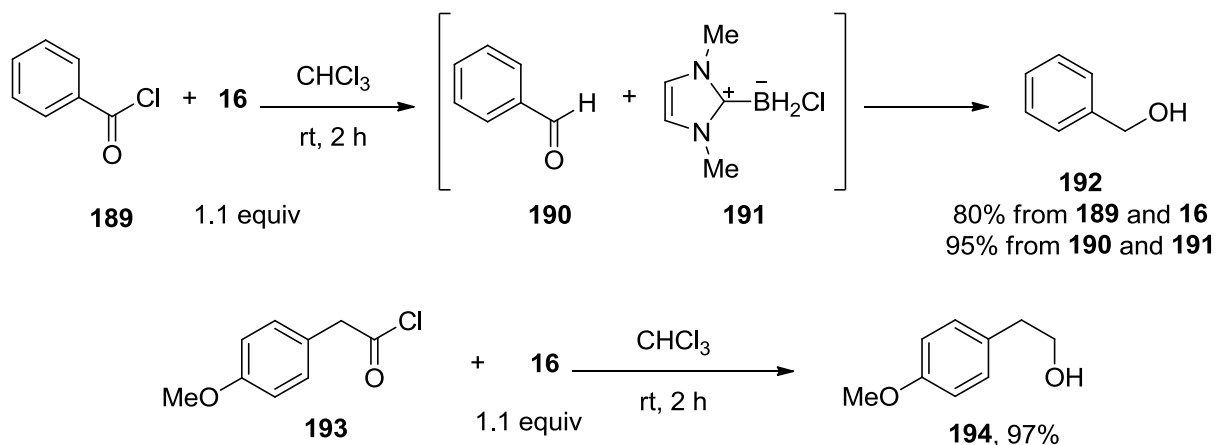
Scheme 36. Reduction of acid chloride **189** and **193** with NHC-borane **16**.

To test this idea, the reaction between benzaldehyde **190** and diMe-Imd-BH$_2$Cl **191** was investigated. First, the acid-base reaction between **16** and acid chloride (HCl, 1.8M in dioxane)

provided diMe-Imd-BH$_2$Cl **191** after evaporating the solvent. The NHC-boryl chloride **191** reacted benzyl aldehyde **190** at rt providing the corresponding alcohol **192** in 95% isolated yield.

To exclude the reduction catalyzed by **191**, the reaction was conducted with catalytic amount (10 mol%) of **191** and 1.1 equiv of **16** as reductant, but no significant conversion was observed. Again, the reduction of 4-methoxyphenylacetyl **193** with **16** provided **194** in 97% yield after flash chromatography. These results suggest that **16** can reduce the acid chlorides to alcohols and the NHC-boryl chloride **191** is active reductants for reduction of aldehydes.

In conclusion, we have developed a new synthetic procedure for thioetherification and thioesterification using our readily available NHC-boryl sulfides and NHC-boryl amido complexes. Both **98** and **138** are stable white solids which are easy to handle. The good solubility of these compounds in non-polar solvent makes this protocol more attractive. These thiolation reactions suggest that NHC-boryl sulfides and NHC-boryl amido complexes are good neutral thiolate nucleophile equivalents and encourage further study of these complexes.

6.0   HYDROBORATION OF ALKENES AND ALKYNES WITH NHC-BORANES

Hydroboration is one of the most fundamental and important reactions in organic boron chemistry.[77] Hydroboration produces various organoborane compounds that are useful synthetic intermediates.[78, 79] In this chapter, two different approaches of hydroboration with NHC-boranes will be presented. The molecular iodine-initiated hydroboration with NHC-boranes will be first introduced. This reaction is believed to occur by a borenium-catalysis mechanism, and it provides various NHC-alkylboranes complexes. After that, the preliminary results of direct, uncatalyzed hydroboration, with electron poor substrates will be shown.

6.1   BORENIUM-CATALYZED HYDROBORATION OF ALKENES AND ALKYNES WITH NHC-BORANES

Most Lewis base complexes (LB-BH$_3$) of boranes such as ether-boranes and sulfides-boranes undergo rapid hydroboration reactions. On the other hand, stable borane complexes of Lewis base such as amine-boranes, phosphine-boranes, and NHC-boranes are inert to hydroboration unless they dissociate. Vedejs and his coworkers reported that the hydroboration of alkenes with amine- and phosphine-boranes can be achieved by activation methods.[80-85] The activation of amine- and phosphine-boranes generates a borenium ion (LB-BH$_2^+$) or a borenium ion

equivalent.[86] Stable borenium ions often do not exist in solution, and they usually exist as borenium ion equivalents. These equivalents include charged complexes of borenium ions with solvent, or another Lewis base, or neutral, covalent LB−borane complexes with a good leaving group (LB−BH$_2$X where X is the leaving group).[86] The borenium ions and borenium ion equivalents are reactive in hydroboration.

6.1.1 Development of iodine-initiated hydroboration of alkenes and alkynes with NHC-boranes

Recently, Curran and Vedejs reported that, hydroboration of 1-hexene **195** was achieved with diMe-Imd-BH$_3$ **16** in presence of 5 mol% trifluoromethanesulfonimide ((CF$_3$SO$_2$)$_2$NH, Tf$_2$NH or triflimide).[87] The key hydroborated intermediates diMe-Imd-BHR$_2$ (**196**, R = 1-hexyl, [11]B: doublet at −19.0 ppm) and diMe-Imd-BHRR' (**197**, R = 1-hexyl, R' = 2-hexyl, [11]B: doublet at −15.8 ppm) were detected in 83:17 ratio by ^{11}B NMR spectroscopy (Scheme 37), but attempts to isolate them were unsuccessful presumably due to their instability on chromatography. By oxidizing **196** and **197** with H$_2$O$_2$/NaOH, traditional hydroboration/oxidation products 1- and 2-hexnaol were obtained in 91/9 ratio in high yield.
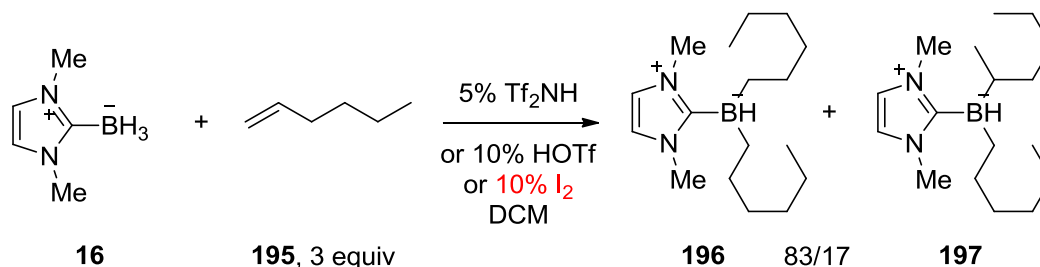
Scheme 37. Hydroboration of 1-hexene with Tf$_2$NH, HOTf or iodine and diMe-Imd-BH$_3$.

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Most organoborane hydroboration products are themselves highly reactive. The isolation of hydroboration adducts that are stable to air and water is rare and therefore interesting. We have already learned that NHC-monoalkyl- and aryl-borane complexes can be purified by chromatography.[8,11] We hypothesized that hydroboration of hindered alkenes would generate mono-hydroborated products NHC-alkylborane (NHC-BH₂alkyl). Herein we report synthesis and isolation of NHC-alkylborane and -allylborane complexes from the hydroboration of alkenes and alkynes with NHC-boranes.

At beginning of the work, we searched for a substitute for triflimide in the hydroboration of 1-hexene because triflimide is very sensitive to air and moisture. We found that either 10 mol% iodine (I_2) or 10 mol% triflic acid (HOTf) are hydroboration activators for NHC-boranes (Scheme 33). We chose iodine for further studies due to its availability and cheapness. In a typical iodine-initiated hydroboration procedure, diMe-Imd-BH₃ (**16**, 1 equiv) was dissolved in CH_2Cl_2, followed by slow addition of 10 mol% iodine crystals. Hydrogen gas formed immediately. After the bubbling stopped, 1-hexene (3 equiv) was added in one portion. The hydroboration reaction was easily monitored by ^{11}B NMR spectroscopy. One hour later, ^{11}B NMR spectroscopy showed that the peak of diMe-Imd-BH₃ **16** ([11]B: quartet, −37 ppm) disappeared and was replaced by the peaks of **196** and **197** detected in around 5:1 ratio. This shows that iodine-activated hydroboration gives similar results from triflimide methods.

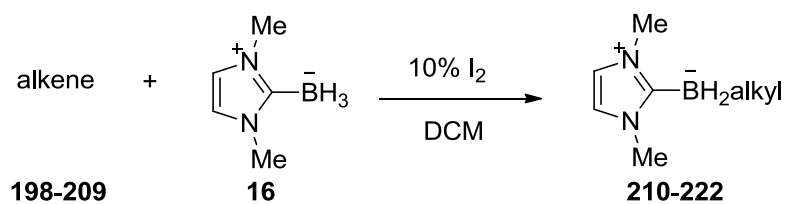### 6.1.2 Scope and limitations

The scope and limitations studies of the iodine-activated hydroboration method are summarized in Table 18. The goals were to both form and isolate the hydroboration products. First, the

iodine-initiated hydroboration was applied to four substituted hindered alkene 2,3-dimethyl-2-butene **198**. The goal was to obtain a mono hydroboration product, so 1.1 equiv of alkene was used rather than 3 equiv. Initially, diMe-Imd-BH$_2$I **41** was detected as a triplet peak at -32 ppm by ^{11}B NMR spectroscopy. Later on, this peak was replaced by the peak of product diMe-Imd-BH$_2$thexyl (**210**, ^{11}B: triplet, -24 ppm). No di-hydroborated complex, which usually gives a doublet at -20 ppm range, was detected. Once full conversion of starting borane **16** was achieved, the crude product was directly purified by flash chromatography to yield the product **210** in 75% yield (entry 1, Table 18).

This NHC-BH$_2$thexyl has some interesting radical properties. For example, under DTBP-initiated conditions, *t*BuO• abstracted the tertiary H atom from the branched thexyl group rather than from the boron center, followed by *β* scission of C-centered radical (NHC-BH$_2$thexyl•) to release the NHC-BH$_2$• and 2,3-dimethyl-2-butene **198**.[27, 88] NHC-BH$_2$thexyl **210** has previously been synthesized by direct complexion of NHC and BH$_2$thexyl,[27] and now it can be made by this iodine-initiated hydroboration way.

Next, we tried trisubstituted alkenes to see if selective mono-hydroboration occured. With 10 mol% iodine, hydroboration between diMe-Imd-BH$_3$ **16** and 2-methyl-2-butene **199** or 1-methylcyclohexne **200** gave complexes **211** or **212** in 59% or 68% yield (entry 2 or 3, Table 18). The hydroborated complex **212** was assigned as *cis*-addition product because oxidation of **212** with hydrogen peroxide and sodium hydroxide provided the *trans*-2-methylcyclohexanol as the sole product. To test a lower loading of iodine, a larger scale (2 mmol) reaction of **199** was tried with 2 mol% of iodine, but no reaction occurred. However, by increasing the iodine loading to 5 mol%, the hydroboration of **199** with **16** gave desired product **211** in 75% isolated yield.

Table 18. Synthesis of NHC-alkylborane complexes using iodine-initiated hydroboration.
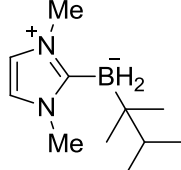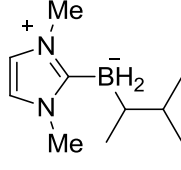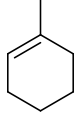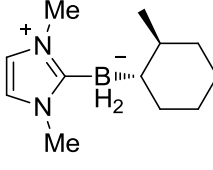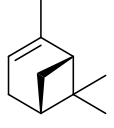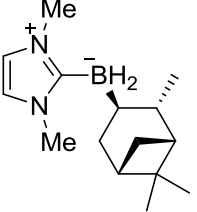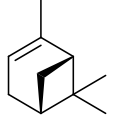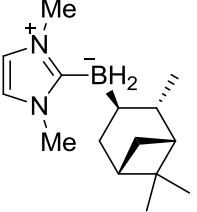
Entry	alkene	product	isolated yield
1	**198**	**210**	75%
2	**199**	**211**	59% (75%)[a]
3	**200**	**212**[b]	68%
4	(+)-**201**	**213**	61%
5	(−)-**201**	**ent-213**	61%
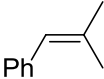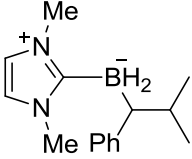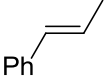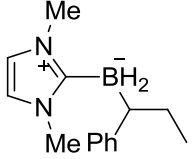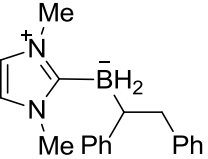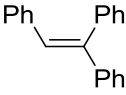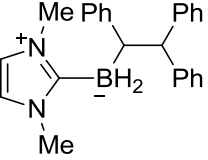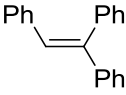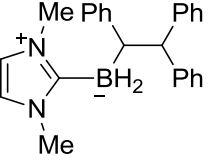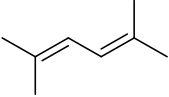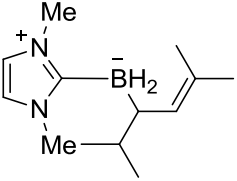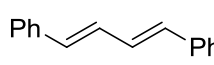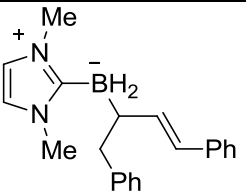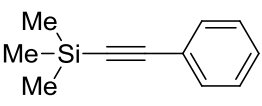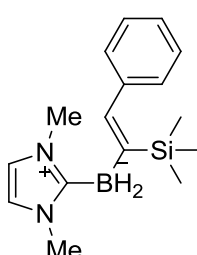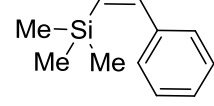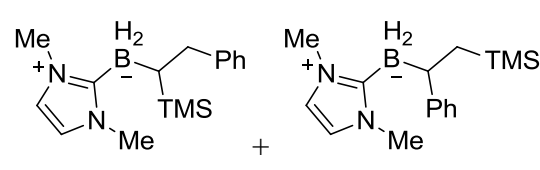
Table 18 (continued)

6	**202**	**214**	50%
7	**203**	**215**[c]	59% (80%)[d]
8	**Z-204**	**216**	66% (73%)[d]
9	**E-204**	**216**	64%
10	**205**	**217**	-
11	**206**	**218**	37%

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Table 18 (continued)

	Ph∼∼Ph	[structure 219]	-
12	**207**	**219**	-
13	**208**	**220**	34%
14	**209**	**221**+**222** (1:1)	72%

[a] 5 mol% Iodine was used for 2 mmol scale reaction; [b] the product is racemic; [c] trace amount of another regioisomer was only detected by crude ^{11}B NMR spectroscopy; [d] 1 equiv of alkene and 1.4 equiv of **16** were used.

Hydroboration of the two enantiomers (+)-**201** and (−)-**201** gave enantiomeric pinenyl boranes diMe-Imd-BH$_2$-Ipc **213** and ent-**213** as single regio- and stereoisomers in 61% yield (entries 4 and 5, Table 18).

With catalytic amount (5 mol%) of Tf$_2$NH, diMe-Imd-BH$_3$ **16** fails to hydroborate some alkenes containing a phenyl substituent close to the double bond such as β-methylstyrene **203** and 1-phenyl-1-butene.[87] By increasing the amount of Tf$_2$NH to 1 equiv, full conversion of

hydroboration of **203** with diMe-Imd-BH$_3$ **16** was finally obtained. Next we tried the hydroboration with phenyl-substituted substrates such as 2-methyl-1-phenyl-1-propene **202**, trans-*β*-methylstyrene **203**, *cis-* and *trans*-stibene **204** using iodine-activation conditions. All these substrates gave corresponding NHC-alkylboranes **214**-**216** in 50-66% isolated yields (entries 6-9, Table 18).

Hydroboration of a less reactive triphenylethylene **205** with diMe-Imd-BH$_3$ **16** activating by 10 mol% iodine gave no conversion at all (entry 10, Table 18). In the hydroboration of **203**, two resonances from the crude product were detected in a ratio of about 90/10 by ^{11}B NMR spectroscopy. The major resonance at –23.5 ppm is assigned to **215**, and the overlapping small resonance at –23.8 ppm probably belongs to the regioisomer of **215** (which could not be isolated from the crude products). The hydroboration of **203** with **16** appears to have higher regioselectivity than corresponding hydroborations with free borane and pyridine-iodoborane.[84]

A symmetrical diene 2,5-dimethyl-2,4-hexediene **206** was subjected to iodine-activated hydroboration conditions with diMe-Imd-BH$_3$ **16**, and the allyl borane **218** was isolated in 37% yield after flash chromatography. This is the first example of hydroboration of diene using NHC-boranes (entry 11, Table 18). However, hydroboration of (1*E*,3*E*)-1,4-diphenylbuta-1,3-diene **207**, a diene containing phenyl substituents on the double bond, gave no desired product under typical iodine conditions (entry 12, Table 18).

Two silyl-substituted alkenes **208** and alkynes **209** were also tested with iodine-activated hydroboration conditions, and the results are summarized in entries 13-14 in Table 18. Hydroboration of **208** with **16** provided the major monohydroboration product **220** in 34% yield after flash chromatography. The product **220** was about 90% pure by ^{11}B NMR spectroscopy, and it was further purified by crystallization. The structure of **220** was assigned by solving the X-

ray crystal structure of this sample by Dr. S. Geib (Figure 13). The product is the *Z*-isomer resulting from *cis* addition in the hydroboration reactions. The minor product was believed as the regioisomer of **220** since it showed a triplet in the ^{11}B NMR spectrum. Iodine-initiated hydroboration of **209** with **16** unselectively provided the two regioisomers **221** and **222** in about a 50/50 ratio in 72% isolated yield.
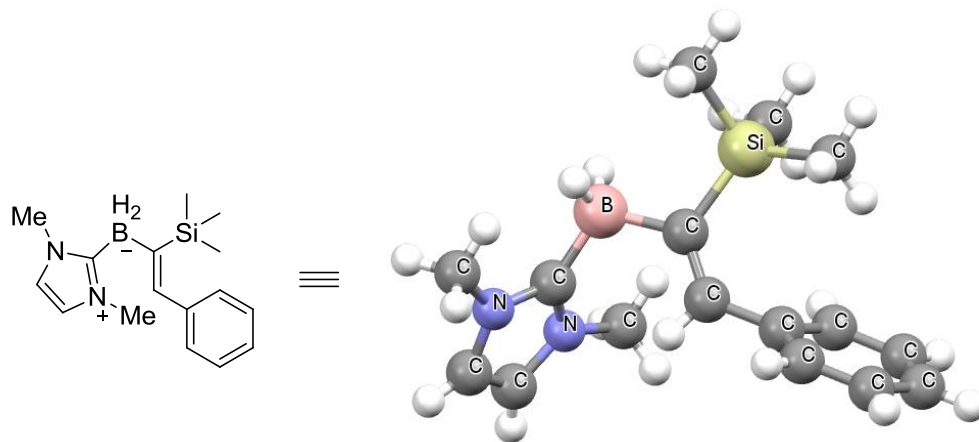
Figure 14. The X-ray crystallographic structure of monohydroboration product **220**.

We also briefly investigated a modification of the standard procedure. Since the formation of the intermediate NHC-BH$_2$I would cause a deficiency of NHC-BH$_3$ for the product formation with a 1/1 stoichiometry of **16** and alkene, we increased the amount of **16** to 1.4 equiv and used alkene as the limiting reagent (1.0 equiv) in two experiments. In entries 7 and 8, the yield of **215** and **216** significantly increased to 80% and 73% from 59% and 66%, respectively.

We next studied the scope of hydroboration on different NHC-boranes. The standard procedure was used (10 mol% iodine, DCM, rt), and the results are summarized in Scheme 38. The hydroboration of 2-methyl-2-butene with triazole borane (diMe-Tri-BH$_3$, **17**) and benzimidazole borane (diMe-BenzImd-BH$_3$, **106**) gave corresponding NHC-alkylborane

complexes **223** and **224** in good yields (70% and 71%). Larger imidazolylidene-derived NHC-boranes such as diiPr-Imd-BH$_3$ **105** and diCy-Imd-BH$_3$ under same hydroboration conditions gave lower isolated yields (57% for **225**, 50% for **226**). Treatment of more bulky imidazolylidene-derived NHC-boranes diMes-Imd-BH$_3$ and dipp-Imd-BH$_3$ **6** with hydroboration conditions did not provide any desired products. For dipp analog, by increasing iodine to 50 mol% the hydroboration still did not happen, and only dipp-Imd-BH$_2$I intermediate was detected by ^{11}B NMR spectroscopy. Even hindered NHC-boranes react with iodine rapidly. Presumably, the steric hindrances of mesityl and dipp groups prevent the hydroboration reaction.
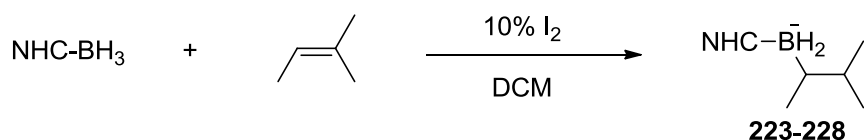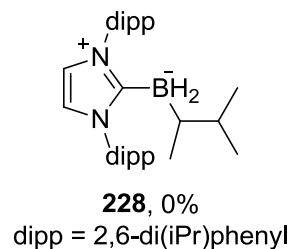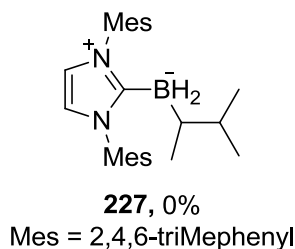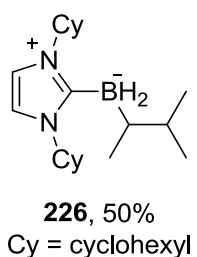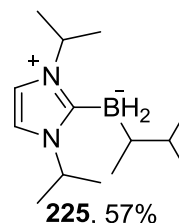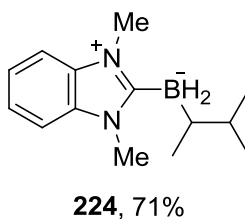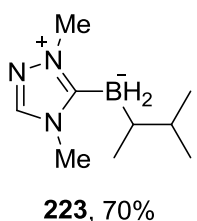
Scheme 38. Scope study of hydroboration of different NHC-boranes with 2-methyl-2-butene.

Recently, NHC-9-BBN (9-BBN is 9-borabicyclo[3.3.1]nonane) complexes received attention in several aspects. Lindsay described a stable dialkylborenium ion from the reaction of diMes-Imd-9-BBN with the Brønsted acid TfOH.[19] On the other hand, Stephan used dipp-Imd-9-BBN as a borenium cation precursor to activate dihydrogen by FLPs and to further catalyze the hydrogenation of imines and enamines at room temperature.[89] In both synthetic routes, NHC-9-BBN complexes were prepared from the complexion between the NHC part and 9-BBN. Here, we tried direct formation of the NHC-9-BBN complex from unsubstituted NHC-borane **16**. 1,5-Cyclooctadiene **229** was subject to diMe-Imd-BH$_3$ **16** with 10 mol% iodine in dichloromethane. After 2 d, an ^{11}B NMR spectrum of the mixture showed a doublet at −16.2 ppm (J_{BH} =85 Hz) which matches the literature data.[76] A white solid diMe-Imd-9-BBN **230** was obtained in 34% yield after chromatography (Scheme 39). Hence, it is now possible to make NHC-9-BBN complexes by hydroboration of cyclooctadiene with readily available and stable NHC-boranes.
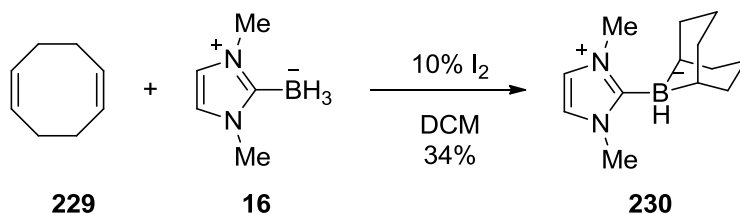
Scheme 39. Synthesis of diMe-Imd-9BBN **230** complex from dMe-Imd-BH$_3$ **16** and **229**.

Next, we turned our sights to intramolecular hydroboration. These experiments were conducted by Dr. A. Boussonnière, and the results are summarized in Scheme 40. NHC-boranes **233** and **234** were obtained in 88% yield from the reaction of corresponding NHC bromide salt precursor **231** and **232** with base and BH$_3$•THF. The iodine-activated hydroboration reaction of

N-allyl analog **233** did not provide a clean product **235**; however, the hydroboration of **234** with 10 mol% iodine gave the novel fused bicyclic NHC-borane **236** in 25% isolated yield after flash chromatography. We suspect that the complex **236** is not very stable to silica gel because more than 25% of **236** was detected during the reaction by ^{11}B NMR spectroscopy. Chuzel and Parrain reported the intramolecular hydroborations to make boracyclopentanes such as **235** under asymmetric Rhodium-catalyzed conditions. However, their method failed to generate the boracyclohexannulation products such as **236**.[90] This boracyclohexannulation is first discovered and is complementary to Chuzel and Parrain's results.
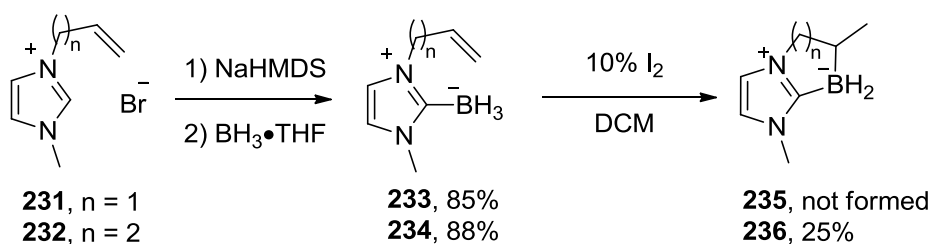
Scheme 40. Synthesis of complex and intramolecular hydroboration of **234**, performed by Dr. A. Boussonnière.

6.1.3 Mechanism investigation

Scheme 41 shows the proposed mechanism of iodine-activated hydroboration. First, iodine reaction with NHC-BH$_3$ gives dihydrogen gas and the key intermediate NHC-BH$_2$I. This boryl iodide is stable in solution for long periods, but it is sensitive to nucleophiles like water, methanol, and presumably alkenes. Because iodide on boron is a good leaving group, diMe-Imd-BH$_2$I can be considered as borenium ion (NHC-BH$_2^+$) equivalent. Although the reaction mechanism is similar to that with Tf$_2$NH-activation, the key intermediates are different. For

Tf$_2$NH-activation case, reaction of **16** with a substoichiometric amount of Tf$_2$NH provides a borenium ion complexed to the starting borane ([NHC−BH$_2$−H−BH$_2$−NHC]$^+$ Tf$_2$N$^-$).[87, 91] Both intermediates, one covalent (from I$_2$) and one ionic (from Tf$_2$NH), are reactive in hydroboration reactions.

The catalytic cycle includes two steps: hydroboration and hydride transfer. In the hydroboration step, the reaction with NHC-BH$_2$I **41** and alkene to form NHC-alkyl boryl iodide **237**. To detect the intermediate **237**, a stoichiometric reaction between NHC-BH$_2$I **41** and 2-methyl-2-butene **199** provided a single major product with a broad resonance at −12 ppm assigned as **237**. This assignment was further confirmed by direct formation of **237** from the reaction with **211** and iodine (0.5 equiv), but attempts to purify the intermediate failed due to the instability of boryl iodide. In the Tf$_2$NH catalyzed hydroboration case, the hydroboration key intermediates such as NHC-BHRNTf$_2$ and -BR$_2$NTf$_2$ (R = alkyl) were not clearly detected.
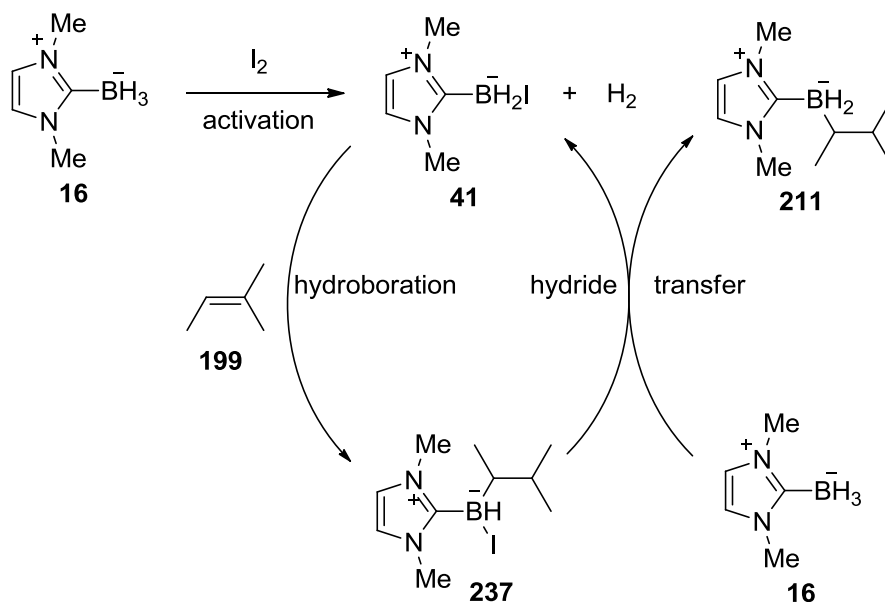
Scheme 41. Proposed mechanism for iodine-activated hydroboration of alkene.

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In the hydride transfer step, the intermediate **237** reacts with **16** to provide the NHC-alkyl borane **211** and regenerate the catalyst **41**. This hydride transfer step is unique to NHC-boranes, and it closes the catalytic cycle. In the activated hydroboration reactions with amine- and phosphine-boranes, stoichiometric amounts of activator have to be used because hydride transfer step fails. To simulate the catalytic conditions for the hydride transfer step, boryl iodide **237** was first generated in situ and then quenched by 10 equiv of starting NHC-borane **16**. The ^{11}B NMR spectrum of the reaction mixture showed the two new resonances formed which belonged to the product **211** and catalyst **41**.

In principle, the activated NHC-boryl iodide complex **237** could further undergo a second hydroboration to give NHC-dihydroborated complex, but in most cases described here the reaction stopped at mono-hydroboration step. Presumably the hydride transfer step is more rapid than second hydroboration reaction. The slow second hydroboration reaction is probably due to the sterically hindered alkenes or phenyl substituted alkenes.

In summary, we developed a hydroboration synthetic route to NHC-alkylborane complexes with iodine activated NHC-boranes. Applying these iodine-catalyzed hydroboration conditions, stable NHC-alkylborane complexes can be synthesized, purified and stored. Furthermore, a very useful complex NHC-9-BBN was synthesized from hydroboration with NHC-boranes, and intramolecular hydroboration was investigated.

6.2   PRELIMINARY RESULTS OF DIRECT HYDROBORATION WITH NHC-BORANES

During the research of borenium-catalyzed hydroboration, we unexpectedly found the direct hydroboration of dimethyl- **238** and diethyl-acetylene dicarboxylate **239** with NHC-borane **16**, and the results are summarized in Scheme 42. In a direct hydroboration reaction without any activation, dimethyl acetylene dicarboxylate **238** (1 equiv) was added to the solution of **16** in benzene at room temperature. ^{11}B NMR spectroscopy showed that the resonance of **16** at –37 ppm was replaced by the peak of the product (**240**, [11]B: triplet, –28 ppm). After full conversion was achieved, flash chromatography of the mixture provided the product **240** in 51% yield. Similar direct hydroboration reaction of **239** with **16** gave the NHC-allyl borane **241** in 47% isolated yield. These products are assigned as Z-isomers due to the *cis* addition in the hydroboration reactions.
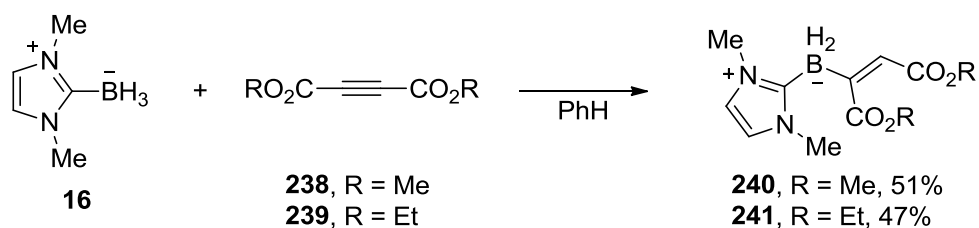
Scheme 42. Direct hydroboration of acetylene dicarboxylate **238** and **239** with NHC-borane **16**.

Direct hydroboration of ethyl propiolate with **16** failed at room temperature, but the same reaction at 80 °C for 1 d gave 17% conversion of **16** to NHC-allylborane product by ^{11}B NMR spectroscopy. This suggests the reactivity of propiolate is much lower than those of acetylene dicarboxylates.

These direct hydroboration reactions are believed to occur by a nucleophile-electrophile addition, where NHC-boranes are nucleophilic hydride donors and acetylene dicarboxylates are highly electrophilic. The reactions between NHC-boranes and other electrophiles were reported previously by Mr. E. Merling (Scheme 43).[60] For instance, NHC-borane **16** reacted with malononitriles **242** and **243** in CH_2Cl_2 to provide reduced borylated malononitrile **244** in 57% and **245** in 42% yield.
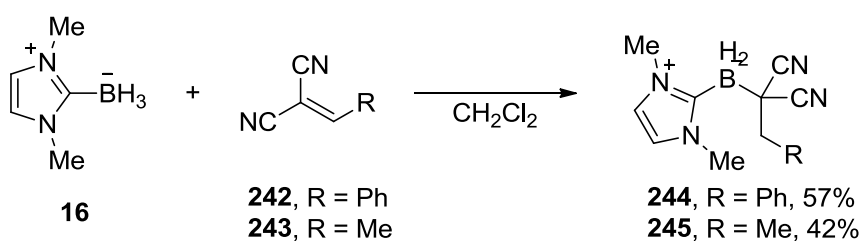
Scheme 43. Direct hydroboration of malononitriles **242** and **243** with NHC-borane **16**.

In this chapter, we present two different hydroboration approaches with NHC-boranes to synthesize various NHC-alkyl and -allyl borane complexes. This iodine-activation method has several advantages over triflimide-activation method: 1) easier performance while triflimide procedure usually requires glove box conditions, 2) much cheaper and easier accessible than triflimide, and 3) broader scope (working for phenyl contained alkenes). The mechanism of iodine-initiated hydroboration was investigated. Two step catalytic cycle of hydroboration and hydride transfer was supported. In the second method, the direct hydroboration between NHC-boranes as nucleophiles and acetylenedicarboxylates as electrophiles was briefly investigated. This opens the way for hydroboration with other electrophiles. In short, now we have several hydroboration ways to synthesize various NHC-boranes derivatives which are fully interesting in different chemistry areas.

7.0   CONCLUSIONS

The complexes between N-heterocyclic carbene and boranes are called NHC-boranes. NHC-boranes are useful reagents in organic chemistry. The researches on various aspects of their chemistry and application have been demonstrated. By using thiols as polarity reversal catalysis, radical reductions of alkyl and aryl halides with NHC-boranes were discovered. First radical homolytic substitution reaction at disulfides and diselenides are demonstrated. Various NHC-boryl sulfides, selenides and amido complexes are synthesized. These new synthesized NHC-boryl derivatives not only have unique structural motifs, but also they are potentially useful reagents in organic reactions and polymerizations. By using iodine as the activation, new borenium-catalyzed hydroboration procedure was developed to synthesize various stable NHC-alkylborane complexes. Intramolecular and direct hydroboration are also presented. Application of these chemistries provides the transformation from B-H to B-S, B-N, B-Se, B-alkyl and B-allyl bonds in NHC-boranes. All of these reactions expand the chemistry and application of NHC-boranes, and they provide the strong foundation for the future development in this area.

8.0   EXPERIMENTAL

General Information:

Reaction solvents were freshly dried either by distillation or by passing through an activated alumina column. All other reagents were purchased commercially and used without further purification unless stated otherwise. Reaction mixtures were stirred with a magnetic stirrer and reaction progress was monitored by TLC with 0.25 mm E. Merck precoated silica gel plates. Visualization of TLC plates was accomplished with a 254 nm UV lamp or by staining with vanillin, *p*-anisaldehyde, or phosphomolybdic acid solutions. Flash chromatography was performed with silica gel 60 (particle size 0.040–0.063 mm) supplied by Sorbent Technologies or by combiflash.

Reaction progress was monitored or products were analyzed by ^{1}H NMR, ^{11}B NMR, ^{13}C NMR, FT-IR, high and low resolution mass spectroscopy. NMR spectra were taken on a Bruker WH-300, IBM AF-300, a Bruker Avance^{TM} 400 NMR, and a Bruker Avance^{TM} 500 NMR spectrometer. Spectra were recorded at room temperature in the indicated deuteriated solvents, and chemical shifts were reported in parts per million (ppm) downfield relative to TMS using the residual solvent proton resonance of $CDCl_3$ (^{1}H = 7.27 ppm, ^{13}C =77.0 ppm) or C_6D_6 (^{1}H = 7.16 ppm, ^{13}C =128.0 ppm) as the internal standard. In reporting spectral data, the following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd =

doublet of doublets, dt = doublet of triplets, td = triplet of doublets. The resonances of hydrogen atoms connected to the boron atom are not usually observed in ^{1}H NMR spectra because of quadrupole broadening.[92] For the same reason, the resonances of carbon atoms connected to the boron atom could not be observed in ^{13}C NMR spectra of any NHC-borane. Copies of key NMR spectra could be found in the supporting information of the published papers. The published papers are listed in Appendix A.

Infrared spectra were taken on a Mattson Genesis Series FTIR using thin film on NaCl plate. Peaks are reported in wave numbers (cm^{-1}). Melting points (mp) were determined with a Mel-Temp II apparatus. High resolution mass spectra (HRMS) were obtained by electrospray ionization (ESI) on the Q-Tof Ultima API, Micromass UK Limited instrument or by electron impact ionization (EI) on the VG Autospec FISIONS instrument. X-ray diffraction was recorded and crystal structures were solved by Dr. Steve Geib (University of Pittsburgh).

8.1   EXPERIMENTAL DATA FOR CHAPTER 2

General procedure for tirethylborane-initiated free radical reactions:

Triethylborane (1 M solution in hexane, 0.05 mmol) was added to a solution of diMe-Imd-BH$_3$ **16** (12 mg, 0.11 mmol) and the substrate (0.1 mmol) in benzene (0.45 mL). Thiophenol or *tert*-dodecanethiol (11.0 mg, 0.1 mmol or 20.2 mg, 0.1 mmol) was dissolved in benzene (1 mL). The diluted thiol solution (0.1 M in benzene, 50 μL, 0.005 mmol) was added to the solution of the substrate and triethylborane. The septum was pierced with a needle to admit ambient air.

The colorless solution was stirred for 2-10 h. Then the solvent was evaporated and the crude product was purified by flash column chromatography.

General procedure for TBHN-initiated free radical reactions:

TBHN (3.5 mg, 0.02 mmol) was added to a solution of diMe-Imd-BH$_3$ **16** (12 mg, 0.11 mmol) and the substrate (0.1 mmol) in benzene (0.45 mL). Thiophenol or *tert*-dodecanethiol (11.0 mg, 0.1 mmol or 20.2 mg, 0.1 mmol) was dissolved in benzene (1 mL). The diluted thiol solution (0.1 M in benzene, 50 μL, 0.005 mmol) was added to the solution of the substrate and TBHN. The colorless solution was charged to a sealed tube and heated in oil bath at 80 ℃ for 2 h. The mixture was cooled to room temperature, then the solvent was evaporated and the crude product was purified by flash column chromatography.

General procedure for DTBP-initiated free radical reactions:

DTBP (2.9 mg, 0.02 mmol) was added to a solution of diMe-Imd-BH$_3$ **16** (12 mg, 0.11 mmol) and the substrate (0.1 mmol) in benzene (0.45 mL). Thiophenol or *tert*-dodecanethiol (11.0 mg, 0.1 mmol or 20.2 mg, 0.1 mmol) was dissolved in benzene (1 mL). The diluted thiol solution (0.1 M in benzene, 50 μL, 0.005 mmol) was added to the solution of the substrate and DTBP. The colorless solution was charged to a NMR tube and irradiated with GE-275W sunlamp at 60 ℃ for 1-10 h. The mixture was cooled to room temperature, then the solvent was evaporated and the crude product was purified by flash column chromatography.

General procedure for free radical reactions with diMe-Tri-BH₃:

TBHN (3.5 mg, 0.02 mmol) was added to a solution of diMe-Tri-BH₃ **17** (12 mg, 0.11 mmol) and the substrate (0.1 mmol) in benzene (0.45 mL). Thiophenol or *tert*-dodecanethiol (11.0 mg, 0.1 mmol or 20.2 mg, 0.1 mmol) was dissolved in benzene (1 mL). The diluted thiol solution (0.1 M in benzene, 50 μL, 0.005 mmol) was added to the solution of the substrate and TBHN. The colorless solution was charged to a sealed tube and heated in oil bath at 80 ℃ for 2 h. The mixture was cooled to room temperature, then ether and water (20 mL, respectively) were added to the mixture, and the organic layer was extracted with water (2 × 20 mL). The organic layer was washed with brine, dried over Na₂SO₄, and concentrated in *vacuo* to get the product.
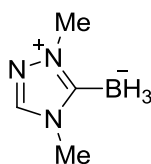
2,4-Dimethyl-1,2,4-triazol-3-ylideneborane (diMe-Tri-BH₃, 17):

The preparation this compound followed literature procedures[24] with some revisions and improvements: A mixture of 1,2,4-triazole (10.0 g, 0.145 mol), iodomethane (61.8 g, 0.435 mol), and potassium carbonate (30.0 g, 0.217 mol) in acetonitrile (80 mL) and methanol (20 mL) was heated at 40 ℃ for 3 days. The white mixture was filtered with a Buckner funnel, and the white solid was washed with CH₂Cl₂. The filtrate was concentrated to give 2,4-dimethyl-1,2,4-triazolium iodide (white solid, 32.8 g, 100%) . A solution of NaHMDS (1 M in THF, 110 mL, 0.11 mol) was added to a suspension of an imidazolium salt (22.5 g, 0.1 mol) in THF (100 mL) and CH₂Cl₂ (50 mL) at −78 ℃ under argon. After stirring of the reaction mixture for 1 h at −78 ℃, a solution of BH₃-THF (1 M in THF, 110 mL, 0.11 mol) was added. The resulting

mixture was warmed from −78 ℃ to rt and stirred for 2 days. The residue was dried in *vacuo* and purified by flash column chromatography (silica gel) to give the title compound (4.4 g, 40%) as a white solid, mp 60–62 ℃; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 7.88 (s, 1 H), 3.97 (s, 3 H), 3.77 (s, 3 H), 1.03 (q, J_{B-H} = 88 Hz, 3 H); ^{11}B NMR (CDCl$_3$, 96.3 MHz) δ −37.8 (q, J_{B-H} = 88 Hz). These data are consistent with the previously reported characterization.[24] Crystals of pure diMe-Tri-BH$_3$ were obtained by vaporizing the solvent (CH$_2$Cl$_2$) of the solution of the complex.

1-Iodo-2-((octyloxy)methyl)benzene (61):

Sodium hydride (60%, 0.34 g, 8.6 mmol) was added to a solution of 1-bromooctane (1.66 g, 8.6 mmol) and 2-iodobenzyl alcohol (1.00 g, 4.3 mmol) in DMF (10 mL). The mixture was heated at 70 ℃ for 2 h. The mixture was cooled to room temperature, and then quenched by water (30 mL) and diethyl ether (70 mL). The organic layer was extracted with water, and washed with brine, dried over MgSO$_4$ and concentrated in *vacuo*. The crude product was purified by flash column chromatography to give the title compound (1.41 g, 95%) as a colorless oil: ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.82 (d, J = 7.5 Hz, 1H), 7.45 (d, J = 7.5 Hz, 1H), 7.35 (t, J = 7.5 Hz,

1H), 6.98 (t, $J = 7.5$ Hz, 1H), 4.47 (s, 2H), 3.55 (t, $J = 6.4$ Hz, 2H), 1.66 (m, 2H), 1.49–1.20 (m, 10H), 0.90 (t, $J = 6.8$ Hz, 3H). These data are consistent with the previously reported characterization.[32]
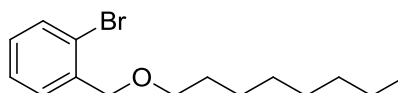
1-Bromo-2-((octyloxy)methyl)benzene (62):

Sodium hydride (60%, 0.43 g, 10.7 mmol) was added to a solution of 1-bromooctane (2.1 g, 10.7 mmol) and 2-bromobenzyl alcohol (1.0 g, 5.3 mmol) in DMF (10 mL). The mixture was heated at 70 °C for 2 h. The mixture was cooled to room temperature, then and quenched by water (30 mL) and diethyl ether (70 mL). The organic layer was extracted with water, and washed with brine, dried over MgSO$_4$ and concentrated in *vacuo*. The crude product was purified by flash column chromatography to give the title compound (1.5 g, 94%) as a colorless oil: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.55–7.49 (m, 2H), 7.33 (t, $J = 7.2$ Hz, 1H), 7.15 (t, $J = 7.2$ Hz, 1H), 4.58 (s, 2H), 3.56 (t, $J = 6.8$ Hz, 2H), 1.71–1.60 (m, 2H), 1.43–1.31 (m, 10H), 0.90 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 138.0, 132.4, 128.9, 128.7, 127.3, 122.6, 72.0, 71.0, 31.8, 29.7, 29.4, 29.2, 26.2, 22.6, 14.1; FTIR (thin film, CH$_2$Cl$_2$, cm^{-1}) 3065, 2926, 2855, 1570, 1466, 1357, 1104, 749; HRMS (ESI) *m/z* (M$^+$ + H) calculated for C$_{15}$H$_{23}$BrO 299.1011, found 299.1023.
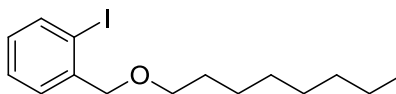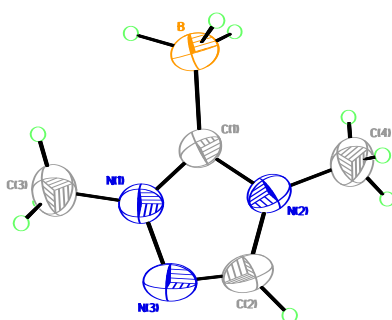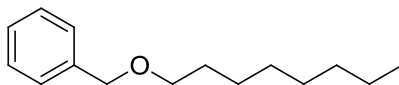
((Octyloxy)methyl)benzene (63):

TBHN (3.5 mg, 0.02 mmol) was added to a solution of diMe-Imd-BH$_3$ **16** (12 mg, 0.11 mmol) and the iodide **61** (0.1 mmol) in benzene (0.45 mL). Thiophenol or *tert*-dodecanethiol (11.0 mg, 0.1 mmol or 20.2 mg, 0.1 mmol) was dissolved in benzene (1 mL). The diluted thiol solution (0.1 M in benzene, 50 μL, 0.005 mmol) was added to the solution of the substrate and TBHN. The colorless solution was charged to a sealed tube and heated in oil bath at 80 °C for 2 h. The mixture was cooled to room temperature, then the solvent was evaporated and the crude product was purified by flash column chromatography to yield the title compound (18.9 mg, 86%) as a colorless oil: ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.35–7.26 (m, 5H), 4.50 (s, 2H), 3.46 (t, *J* = 6.7 Hz, 2H), 1.70–1.59 (m, 2H), 1.43–1.30 (m, 2H), 1.30–1.15 (m, 8H), 0.88 (t, *J* = 6.9 Hz, 3H). These data are consistent with the previously reported characterization.[32]
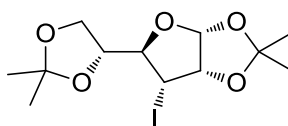
3-Iodo di-*O*-isopropylidene glucofuranoses (43):

Iodine (0.58 g, 2.28 mmol) was added to a solution of diacetone-D-glucose (0.50 g, 1.9 mmol), triphenylphosphine (0.60 g, 2.28 mmol), and imidazole (0.26 g, 3.8 mmol) in 12 mL of toluene. The brown mixture was stirred at rt for 3 h, and followed by the addition of 10 mL of saturated NaHCO$_3$ (aq). The reaction solution was diluted with 70 mL of ethyl ether and washed with 30 mL of saturated NaHCO$_3$ (aq), 30 mL of saturated Na$_2$S$_2$O$_3$ (aq), 30 mL of water, 30 mL of brine. The organic layer was dried with MgSO$_4$, and concentrated to give a yellow oil. The

crude product was purified by flash column chromatography to give the title compound (0. 38 g, 54%) as a white solid: ^{1}H NMR (CDCl$_3$, 400 MHz): δ 5.83 (d, J = 3.6 Hz, 1H), 4.62 (t, J = 4.0 Hz, 1H), 4.36–4.32 (m, 1H), 4.29–4.26 (m, 1H), 4.17–4.06 (m, 2H), 3.78 (dd, J = 3.6, 10.0 Hz, 1H), 1.58(s, 3H), 1.51 (s, 3H), 1.39 (s, 6H). These data are consistent with the previously reported characterization.[93]

Di-*O*-isopropylidene glucofuranose (19):

TBHN (3.5 mg, 0.02 mmol) was added to a solution of diMe-Imd-BH$_3$ **16** (12 mg, 0.11 mmol) and the iodide (**43**, 0.1 mmol) in benzene (0.45 mL). Thiophenol (11.0 mg, 0.1) was dissolved in benzene (1 mL). The diluted thiol solution (0.1 M in benzene, 50 μL, 0.005 mmol) was added to the solution of the substrate and TBHN. The colorless solution was charged to a sealed tube and heated in oil bath at 80 ℃ for 2 h. The mixture was cooled to room temperature, then the solvent was evaporated and the crude product was purified by flash column chromatography to yield the title compound (19.3 mg, 79%) as a colorless oil: ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ 5.58 (d, J = 3.6 Hz, 1H), 4.31–4.26 (m, 1H), 4.20–4.18 (m, 1H), 3.91–3.89 (m, 2H), 3.82–3.81 (m, 1H), 2.18 (dd, J = 4.4, 9.2 Hz, 1H), 1.45 (s, 3H), 1.37 (s, 3H), 1.26 (s, 3H), 1.13 (s, 3H). These data are consistent with the previously reported characterization.[10]
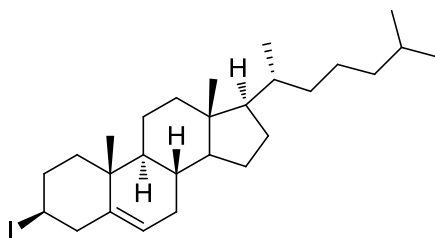
3β-Iodo-5-cholestene (69):

TMSI (2.62 g, 13.1 mmol) was added to a solution of methanesulfonate (5.55 g, 10.9 mmol) in anhydrous CH_2Cl_2 (80 mL), followed by adding boron trifluoride diethyl etherate (3.39 g, 23.9 mmol) at − 20 ℃. The reaction was stirred at − 20 to 0 ℃ for 1 h. The mixture was quenched by adding saturated aqueous $NaHCO_3$ solution. The organic phase was separated and the aqueous phase was extracted with CH_2Cl_2. The organic layers were combined, dried over anhydrous Na_2SO_4, and concentrated in *vacuo*. The crude product was purified by flash column chromatography to give the title compound (4.55 g, 77%) as a white solid: ^{1}H NMR (CDCl$_3$, 400 MHz) δ 5.35–5.33 (m, 1H), 4.05 (m, 1H), 2.97–2.90 (m, 1H), 2.71–2.67 (m, 1H), 2.30–0.93 (m, 29H), 0.92 (d, *J* = 6.8 Hz, 3H), 0.87 (dd, *J* = 6.8, 4.8 Hz, 6H), 0.68 (s, 3H). These data are consistent with the previously reported characterization.[94]
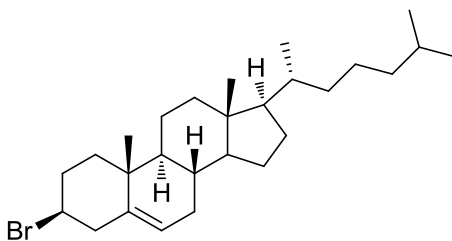
3β-Bromo-5-cholestene (70):

Triethylamine (4.5 g, 45 mmol) was added to a solution of cholesterol (11.6 g, 30 mmol) in anhydrous CH_2Cl_2 at 0 ℃, followed by dropwise addition of methanesulfonyl chloride (3.6 g,

31.5 mmol). The mixture was maintained 0 ℃ for 1 h, warmed to room temperature, and stirred

for overnight. When the reaction finished, the mixture was concentrated in *vacuo* to yield a white

solid methanesulfonate (13.9 g, 100%). TMSBr (1.68 g, 11.0 mmol) was added to a solution of

methanesulfonate (4.65 g, 10.0 mmol) in anhydrous CH_2Cl_2 (80 mL), followed by addition of

boron trifluoride diethyl etherate (2.84 g, 20.0 mmol). The reaction was stirred at ambient

temperature for 1 h. The mixture was quenched by adding saturated aqueous $NaHCO_3$ solution.

The organic phase was separated and the aqueous phase was extracted with CH_2Cl_2. The organic

layers were combined, dried over anhydrous Na_2SO_4, and concentrated in *vacuo*. The crude

product was purified by flash column chromatography to give the title compound (3.1 g, 69%) as

a white solid: ^{1}H NMR (CDCl$_3$, 400 MHz) δ 5.38–5.36 (m, 1H), 3.97–3.90 (m, 1H), 2.76–2.70

(m, 1H), 2.62–2.55 (m, 1H), 2.16 (m, 1H), 2.01–1.90 (m, 3H), 1.89–1.85 (m, 2H), 1.58–0.93 (m,

23H), 0.92 (d, *J* = 6.8 Hz, 3H), 0.87 (dd, *J* = 6.8, 4.8 Hz, 6H), 0.68 (s, 3H). These data are

consistent with the previously reported characterization.[94]
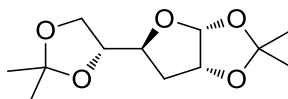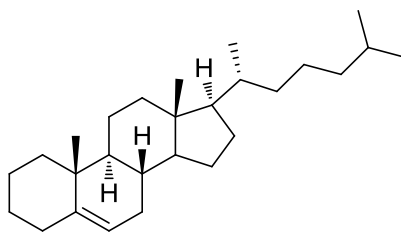

Cholest-5-ene (71):

TBHN (3.5 mg, 0.02 mmol) was added to a solution of diMe-Imd-BH$_3$ **16** (12 mg, 0.11

mmol) and the substrate (0.1 mmol) in benzene (0.45 mL). Thiophenol or *tert*-dodecanethiol

(11.0 mg, 0.1 mmol or 20.2 mg, 0.1 mmol) was dissolved in benzene (1 mL). The diluted thiol

solution (0.1 M in benzene, 50 μL, 0.005 mmol) was added to the solution of the substrate and

TBHN. The colorless solution was charged to a sealed tube and heated in oil bath at 80 ℃ for 2 h. The mixture was cooled to room temperature, then the solvent was evaporated and the crude product was purified by flash column chromatography to yield the title compound (35.5 mg, 96%) as a white solid: ^{1}H NMR (CDCl$_3$, 400 MHz) δ 5.29–5.27 (m, 1H), 2.28–2.20 (m, 1H), 2.00–1.99 (m, 3H), 1.85–1.82 (m, 2H), 1.75–1.72 (m, 1H), 1.62–0.93 (m, 26H), 0.92, (d, J = 6.4 Hz, 3H), 0.87 (dd, J = 6.8, 4.8 Hz, 6H), 0.68 (s, 3H). These data are consistent with the previously reported characterization.[95]
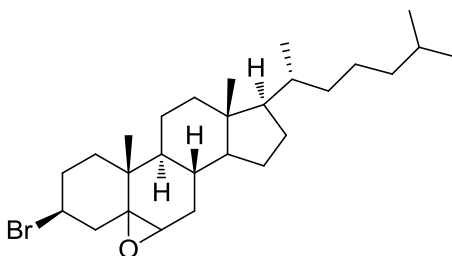
3β-Bromo-5,6-epoxycholestane (73):

meta-Chloroperoxybenzoic acid (mCPBA, max 77%, 0.45 g, 2 mmol) was added to the solution of 3β-bromo-5-cholestene (0.45 g, 1 mmol) in CH$_2$Cl$_2$ (30 mL). The mixture was stirred at rt for 2 h. The mixture was quenched by adding saturated aqueous NaHCO$_3$ solution. The organic phase was separated and extracted with saturated aqueous NaHCO$_3$ solution. The organic layers were dried over anhydrous Na$_2$SO$_4$, and concentrated in *vacuo*. The crude product was purified by flash column chromatography to give the title compound (0.41 g, 88%) as a white solid (two isomers 5:1): ^{1}H NMR (CDCl$_3$, 400 MHz) 3β-bromo-5α,6α-epoxycholestane δ 4.29–4.20 (m, 1H), 2.93 (d, J = 4.4 Hz, 1H), 0.61 (s, 3H); 3β-bromo-5β,6β-epoxycholestane δ 3.98 (m, 1H), 3.07 (m, 1H), 0.64 (s, 3H); overlapping signals: δ 2.57 (t, J = 12.8 Hz, 1H), 2.25–0.86 (m, 39H). These data are consistent with the previously reported characterization.[96]

5, 6-Epoxycholestan-3β-ol (246):

meta-Chloroperoxybenzoic acid (mCPBA, max 77%, 4.5 g, 20.0 mmol) was added to the solution of cholesterol (94%, 4.1 g, 10.0 mmol) in 300 mL of CH_2Cl_2. The mixture was stirred at rt for 1 h. The mixture was quenched by adding saturated aqueous $NaHCO_3$ solution. The organic phase was separated and extracted with saturated aqueous $NaHCO_3$ solution. The organic layers were dried over anhydrous Na_2SO_4, and concentrated in *vacuo*. The crude product was purified by flash column chromatography to give the title compound (3.6 g, 90%) as a white solid (two isomers 1:1): ^{1}H NMR (CDCl$_3$, 400 MHz) 5α,6α**-**epoxycholestan-3β-ol δ 3.94 (m, 1H), 2.89 (d, *J* = 4.4 Hz, 1H), 0.63 (s, 3H); 5β,6β**-**epoxycholestan-3β-ol δ 3.72 (m, 1H), 3.08 (m, 1H), 0.66 (s, 3H); overlapping signals: δ 2.25–0.86 (m, 40H). These data are consistent with the previously reported characterization.[97]
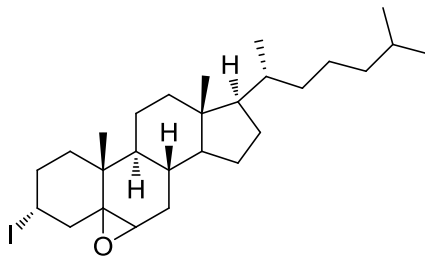
3β-Iodo-5,6-epoxycholestane (72):

Triphenylphosphine (1.04 g, 4.0 mmol), imidazole (0.27 g, 4.0 mmol), and iodine (1.01 g, 4.0 mmol) were added to a solution of 5, 6-epoxycholestan-3β-ol **246** (0.81 g, 2.0 mmol) in toluene (50 mL). The reaction was heated at 80 ℃ for 40 min. After cooling to room temperature, the mixture was quenched by adding saturated aqueous $NaHCO_3$ solution. The organic phase was separated and extracted with saturated aqueous $NaHCO_3$ solution, saturated aqueous $Na_2S_2O_3$ solution. The organic layers were dried over anhydrous Na_2SO_4, and concentrated in *vacuo*. The crude product was purified by flash column chromatography to give the title compound (0.38 g, 37%) as a white solid (two isomers 8:1): ^{1}H NMR (CDCl₃, 400 MHz) 3β-iodo-5α,6α-epoxycholestane δ 2.80 (d, *J* =4.0 Hz, 1H), 2.58 (dd, *J* = 15.6, 4.4 Hz, 1H), 0.62 (s, 3H); 3β-iodo-5β,6β-epoxycholestane δ 3.11 (m, 1H), 2.51 (dd, *J* = 15.2, 3.6 Hz, 1H), 0.66 (s, 3H); overlapping signals: δ 4.79 (brs, 1H), 2.15–0.86 (m, 39H). These data are consistent with the previously reported characterization.[98]
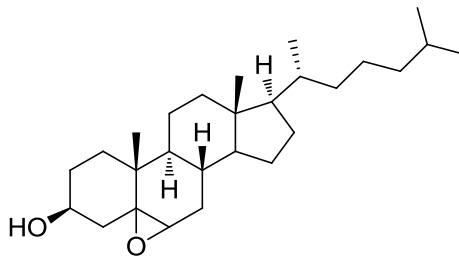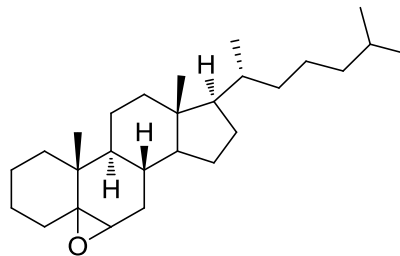
5,6-Epoxycholestane (74):

TBHN (3.5 mg, 0.02 mmol) was added to a solution of diMe-Imd-BH$_3$ **16** (12 mg, 0.11 mmol) and the substrate (0.1 mmol) in benzene (0.45 mL). Thiophenol or *tert*-dodecanethiol (11.0 mg, 0.1 mmol or 20.2 mg, 0.1 mmol) was dissolved in benzene (1 mL). The diluted thiol solution (0.1 M in benzene, 50 μL, 0.005 mmol) was added to the solution of the substrate and TBHN. The colorless solution was charged to a sealed tube and heated in oil bath at 80 °C for 2 h. The mixture was cooled to room temperature, then the solvent was evaporated and the crude product was purified by flash column chromatography to yield the title compound (two isomers 6:1) as a white solid (35.1 mg, 91%): ^{1}H NMR (CDCl$_3$, 300 MHz) 5α,6α-epoxycholestane δ 2.88 (d, *J* =4.5 Hz, 1H), 0.61 (s, 3H); 5β,6β-epoxycholestane δ 3.01 (m, 1H), 0.63 (s, 3H); overlapping signals: δ 2.15–0.85 (m, 42H). These data are consistent with the previously reported characterization.[99]
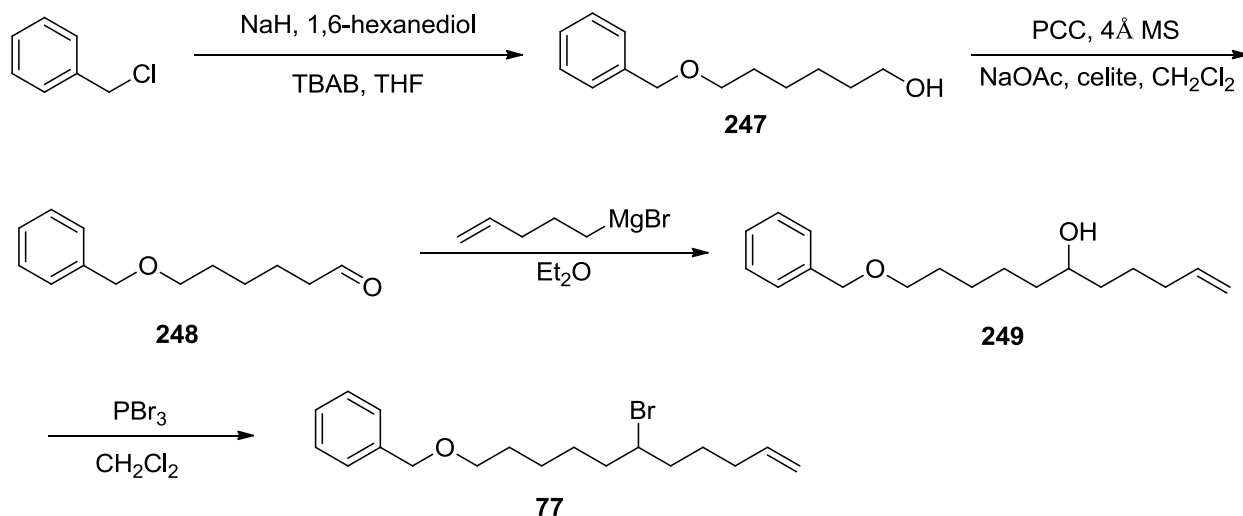
6-(Benzyloxy)hexan-1-ol (247):

Sodium hydride (60%, 0.96 g, 24.0 mmol) was added to the gray mixture of 1,6-hexanediol (2.36 g, 20.0 mmol), benzyl chloride (3.04 g, 24.0 mmol), and tetrabutylammonium bromide (1.60 g, 5.0 mmol) in THF (30 mL). The white mixture was refluxed for 2 h. The mixture was cooled to room temperature, and then quenched by water (30 mL) and diethyl ether (50 mL). The organic layer was extracted with water, and washed with brine, dried over $MgSO_4$ and concentrated in *vacuo*. The crude product was purified by flash column chromatography to give the title compound (2.40 g, 57%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.29 (m, 5H), 4.51 (s, 2H), 3.65 (t, J = 6.4 Hz, 2H), 3.48 (t, J = 6.8 Hz, 2H), 1.68 – 1.58 (m, 4H), 1.55 – 1.39 (m, 4H). These ^{1}H NMR data are consistent with the previously reported characterization.[100]

6-(Benzyloxy)hexanal (248):

CH$_2$Cl$_2$ solution (20 mL) of 6-(benzyloxy)hexan-1-ol **247** (2.37 g, 11.4 mmol) was added

to the organge mixture of PCC (pyridinium chlorochromate, 4.90 g, 22.8 mmol), 4 Å MS (2.40

g), sodium acetate (0.56 g, 6.84 mmol), and celite (2.40 g) in 70 mL of CH$_2$Cl$_2$. The browm

mixture was stirred at rt for 2 h, and celite (30 g) and diethyl ether (100 mL) were added. The

brown mixture was filtered through a plug of silica gel, and concentrate in *vacuo*. The crude

product was purified by flash column chromatography to give the title compound (1.55 g, 66%)

as a colorless oil: ^{1}H NMR (300 MHz, CDCl$_3$) δ 9.76 (t, J = 1.5 Hz, 1H), 7.35–7.27 (m, 5H),

4.50 (s, 2H), 3.47 (t, J = 6.3 Hz, 2H), 2.43 (td, J = 7.5, 1.8 Hz, 2H), 1.68–1.61 (m, 4H), 1.45–

.39 (m, 2H). These ^{1}H NMR data are consistent with the previously reported characterization.[101]

11-(Benzyloxy)undec-1-en-6-ol (249):

1,2-Dibromoethane (0.36 g, 1.9 mmol) was added to the mixture of Mg turnings (0.27 g,

10.9 mmol) in ethyl ether (0.8 mL) to activate the Mg turnings. After the generation of bubbles

was ceased, the solution of 5-bromo-1-pentene (1.27 g, 8.4 mmol) in ethyl ether (13 mL) was

added slowly over 30 min. The Grignard reagent was stirred at rt for 2 h, and then the Grignard

reagent was added to a solution of 6-(benzyloxy)hexanal (**248**, 1.46 g, 7.0 mmol) in THF (5 mL)

at −78 ℃ slowly. The white mixture was stirred at −78 ℃ to 0 ℃ for 3 h, and then saturated

NH$_4$Cl (aq) (10 mL) was added to the white mixture to quench the excess Grignard reagent. The

biphase system was partitioned between ethyl ether (70 mL) and saturated NH$_4$Cl (aq) (30 mL).

The organic layer was washed with water (30 mL), brine (30 mL), dried with MgSO$_4$, and

concentrated to give title compound (0.82 g, 56%) as a colorless oil: ^{1}H NMR (300 MHz,

CDCl$_3$) δ 7.37–7.28 (m, 5H), 5.82 (ddt, J = 17.2, 10.3, 6.6 Hz, 1H), 5.06–4.94 (m, 2H), 4.51 (s,

2H), 3.60 (m, 1H), 3.48 (t, J = 6.6 Hz, 2H), 2.10–2.05 (m, 2H), 1.67–1.30 (m, 12H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 138.7, 138.6, 128.3, 127.6, 127.5, 114.6, 72.8, 71.7, 70.3, 37.4, 36.8, 33.7, 29.7, 26.2, 25.4, 24.9; FTIR (thin film, CH$_2$Cl$_2$, cm^{-1}) 3405, 2933, 2858, 1640, 1454, 1363, 1101, 910, 736; HRMS (ESI) m/z (M$^+$ + Na) calculated for C$_{18}$H$_{28}$O$_2$Na 299.1987, found 299.2008.

((((6-Bromoundec-10-en-1-yl)oxy)methyl)benzene (77):

Phosphorus tribromide (0.73 g, 2.72 mmol) was added to a CH$_2$Cl$_2$ solution of 11-(benzyloxy)undec-1-en-6-ol (**249**, 0.50 g, 1.81 mmol) at 0 ℃. The colorless solution was stirred at 0 ℃ for 1 h, and then diluted with ethyl ether (70mL) and washed saturated NaHCO$_3$ (aq)(x4). The organic layer was dried with MgSO$_4$, and concentrated to give a colorless oil. The crude product was purified by flash column chromatography to give the title compound (0.13 g, 21%) as a colorless oil: ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.35–7.28 (m, 5H), 5.82 (ddt, J = 17.2, 10.3, 6.6 Hz, 1H), 5.05–4.96 (m, 2H), 4.50 (s, 2H), 4.05–4.00 (m, 1H), 3.47 (t, J = 6.6 Hz, 2H), 2.12–2.03 (m, 2H), 1.85–1.25 (m, 12H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 138.5, 138.2, 128.3, 127.5, 127.4, 114.9, 72.8, 70.2, 58.3, 39.0, 38.4, 33.0, 29.5, 27.3, 26.7, 25.6; FTIR (thin film, CH$_2$Cl$_2$, cm^{-1}) 3053, 2937, 2860, 2305, 1640, 1454, 1363, 1265, 1100, 739, 704; HRMS (ESI) m/z (M$^+$ − H) calculated for C$_{18}$H$_{26}$BrO 337.1167, found 337.1199.
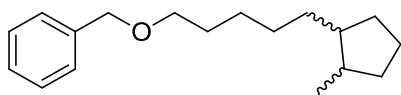
and
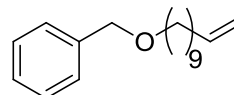
((((5-(2-methylcyclopentyl)pentyl)oxy)methyl)benzene **(78)** **and** **((undec-10-en-1-yloxy)methyl)benzene (79)**

General conditions were used to yield the title compounds (23.4 mg, 90%) of a 5:1 mixture of (((5-(2-methylcyclopentyl)pentyl)oxy)methyl)benzene (two stereoisomers) and ((undec-10-en-1-yloxy)methyl)benzene as a colorless oil: ^{1}H NMR (C$_6$D$_6$, 400 MHz) : major isomer of (((5-(2-methylcyclopentyl)pentyl)oxy)methyl)benzene: δ 0.79 (d, J = 6.8 Hz, 3H); minor isomer: δ 0.98 (d, J = 6.8 Hz, 3H); ((undec-10-en-1-yloxy)methyl)benzene: δ 5.84–5.73 (m, 1H), 5.07–4.94 (m, 2H); overlapping signals: δ 7.34–7.32 (m, 2H), 7.21–7.17 (m, 2H), 7.12–7.08 (m, 1H), 4.37 (s, 2H), 3.35 (t, J = 6.4 Hz, 2H), 1.97–1.05 (m, 16H). These data are consistent with the previously reported characterization.[24, 102]
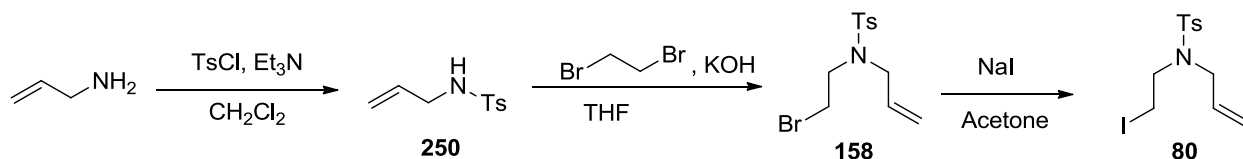
***N*-Allyl-4-methyl-benzensulfonamide (250):**

p-Toluenesulfonic chloride (12.0 g, 63 mmol) was added to the solution of allylamine (3.0 g, 52.5 mmol) and triethylamine (6.9 g, 68 mmol) in 60 mL of CH$_2$Cl$_2$ at 0 ℃. The yellow mixture was stirred at from 0 ℃ to rt for 16 h. The mixture was partitioned between ether (100 mL) and water (40 mL). The organic layer was extracted with water, and washed with brine, dried over MgSO$_4$ and concentrated in *vacuo* to give a yellow oil. The yellow oil was diluted with CH$_2$Cl$_2$ (50 mL) and filtered through a pad of silica gel and washed by ether and hexane.

The colorless solution was concentrated to give the title compound (8.9 g, 80%) as a yellow solid: ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.80–7.73 (m, 2H), 7.36–7.29 (m, 2H), 5.73 (ddt, J = 16.2, 10.3, 5.9 Hz, 1H), 5.22–5.06 (m, 2H), 4.65 (t, J = 5.9 Hz, 1H), 3.59 (m, 2H), 2.44 (s, 3H). These data are consistent with the previously reported characterization.[103]

N-Allyl-N-(2-bromoethyl)-4-methylbenzenesulfonamide (158):

Tetrabutylammonium bromide (0.15 g, 0.47 mmol) was added to the mixture of N-allyl-4-methyl-benzensulfonamide (**250**, 0.48 g, 2.3 mmol), 1,2-dibromoethane (0.65 g, 3.5 mmol), and potassium hydroxide (0.19 g, 3.5 mmol) in THF (12 mL). The mixture was stirred at rt for 3 days. The reaction was quenched by water (30 mL) and diethyl ether (70 mL). The organic layer was extracted with water, and washed with brine, dried over MgSO$_4$ and concentrated in *vacuo*. The crude product was purified by flash column chromatography to give the title compound (0.35 g, 48%) as a colorless oil: ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.71 (d, J = 8.0 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 5.74–5.65 (m, 1H), 5.23–5.19 (m, 2H), 3.82 (d, J = 6.4 Hz, 2H), 3.48–3.37 (m, 4H), 2.45 (s, 3H). These data are consistent with the previously reported characterization.[104]

N-Allyl-N-(2-iodoethyl)-4-methylbenzenesulfonamide (67):

Sodium iodide (1.98 g, 13.2 mmol) was added to the solution of bromide (**158**, 0.84 g, 2.6 mmol) in acetone (26 mL). The mixture was refluxed for 20 h. The mixture was partitioned between ether (80 mL) and water (30 mL). The organic layer was extracted with water, and washed with brine, dried over MgSO$_4$ and concentrated in *vacuo*. The crude product was purified by flash column chromatography to give the title compound (0.88 g, 92%) as a yellow oil: ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.71 (d, J = 8.0 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 5.74–5.64 (m, 1H),

5.23–5.18 (m, 2H), 3.80 (d, J = 6.8 Hz, 2H), 3.45–3.41 (m, 2H), 3.27–3.22 (m, 2H), 2.45 (s, 3H).

These data are consistent with the previously reported characterization.[105]
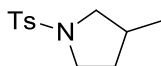
3-Methyl-1-tosylpyrrolidine (81):

TBHN (3.5 mg, 0.02 mmol) was added to a solution of diMe-Imd-BH$_3$ **16** (12 mg, 0.11 mmol) and the substrate (0.1 mmol) in benzene (0.45 mL). Thiophenol or *tert*-dodecanethiol (11.0 mg, 0.1 mmol or 20.2 mg, 0.1 mmol) was dissolved in benzene (1 mL). The diluted thiol solution (0.1 M in benzene, 50 μL, 0.005 mmol) was added to the solution of the substrate and TBHN. The colorless solution was charged to a sealed tube and heated in oil bath at 80 °C for 2 h. The mixture was cooled to room temperature, then the solvent was evaporated and the crude product was purified by flash column chromatography to yield the title compound (19.8 mg, 83%) as a white solid: ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.72 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 3.45–3.41 (m, 1H), 3.38–3.32 (m, 1H), 3.26–3.19 (m, 1H), 2.76 (t, J = 8.0 Hz, 1H), 2.44 (s, 3H), 2.12 (dq, J = 9.7, 7.3 Hz, 1H), 1.95–1.86 (m, 1H), 1.35 (dq, J = 9.7, 6.5 Hz, 1H), 0.92 (d, J = 6.5 Hz, 3H). These data are consistent with the previously reported characterization.[106]
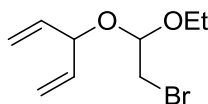
3-(2-Bromo-1-ethoxyethoxy)penta-1,4-diene (82):

Ethyl vinyl ether (1.44 g, 20 mmol) was added to the solution of 1,4-pentadien-3-ol (1.68 g, 20 mmol) and NBS (3.56 g, 20 mmol) in CH$_2$Cl$_2$ (20 mL) cooled at −20 °C. The resulting

mixture was stirred for 3 h at −20 ℃. Hexane was added and the precipitate was filtered off. The filtrate was washed successively with 5% aq. KOH, water and brine. After drying and evaporation of the solvents, the crude product was purified by flash column chromatography to give the title compound (2.4 g, 52%) as a colorless oil: ^{1}H NMR (CDCl₃, 300 MHz) δ 5.90–5.71 (m, 2H), 5.33–5.18 (m, 4H), 4.78 (t, J = 5.4 Hz, 1H), 4.58–4.53 (m, 1H), 3.72–2.53 (m, 2H), 3.40 (dd, J = 2.1, 5.1 Hz, 2H), 1.23 (t, J = 6.9 Hz, 3H). These data are consistent with the previously reported characterization.[48]
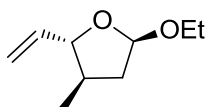
5-Ethoxy-3-methyl-2-vinyltetrahydrofuran (83):

TBHN (3.5 mg, 0.02 mmol) was added to a solution of diMe-Imd-BH₃ **16** (12 mg, 0.11 mmol) and the substrate (0.1 mmol) in benzene (0.45 mL). Thiophenol or *tert*-dodecanethiol (11.0 mg, 0.1 mmol or 20.2 mg, 0.1 mmol) was dissolved in benzene (1 mL). The diluted thiol solution (0.1 M in benzene, 50 μL, 0.005 mmol) was added to the solution of the substrate and TBHN. The colorless solution was charged to a sealed tube and heated in oil bath at 80 ℃ for 2 h. The mixture was cooled to room temperature, then the solvent was evaporated and the crude product was purified by flash column chromatography to yield the title compound (as two diastereoisomers, 9:1) as a colorless oil (11.9 mg, 76%): 1H NMR (CDCl3, 300 MHz) (2S,3R,5R)-5-ethoxy-3-methyl-2-vinyltetra-hydrofuran: δ 5.77 (ddd, J = 7.5, 10.2, 17.4 Hz, 1H), 5.32–5.15 (m, 3H), 3.95 (t, J = 8.4 Hz, 2H), 3.80 (dq, J = 7.2, 10.2 Hz, 1H), 3.45 (dq, J = 7.2, 10.2 Hz, 1H), 2.41 (ddd, J = 5.7, 8.7, 13.8 Hz, 1H), 1.91–1.77 (m, 1H), 1.57–1.49 (m, 1H), 1.22

(t, J = 7.2 Hz, 3H), 1.04 (d, J = 6.6 Hz, 3H). These data are consistent with the previously reported characterization.[48]
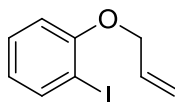
1-(Allyloxy)-2-iodobenzene (84):

Allylbromide (0.31 g, 2.5 mmol) was added to the mixture of 2-iodophenol (0.50 g, 2.3 mmol) and sodium hydride (60%, 0.10 g, 2.5 mmol) in DMF (6 mL). The mixture was stirred at rt for 18 h. The reaction was quenched by water (30 mL) and diethyl ether (70 mL). The organic layer was extracted with water, and washed with brine, dried over MgSO$_4$ and concentrated in *vacuo*. The crude product was purified by flash column chromatography to give the title compound (0.48 g, 81%) as a colorless oil: ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.80–7.77 (m, 1H), 7.32–7.29 (m, 1H), 6.83–6.81 (m, 1H), 6.75–6.70 (m, 1H), 6.12–6.03 (m, 1H), 5.57–5.51 (m, 1H), 5.35–5.30 (m, 1H), 4.62–4.59 (m, 2H). These data are consistent with the previously reported characterization.[107]
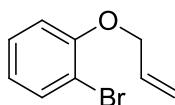
1-(Allyloxy)-2-bromobenzene (85):

Allylbromide (0.39 g, 3.2 mmol) was added to the mixture of 2-bromophenol (0.50 g, 2.9 mmol) and sodium hydride (60%, 0.13 g, 3.2 mmol) in DMF (8 mL). The mixture was stirred at rt for 18 h. The reaction was quenched by water (30 mL) and diethyl ether (70 mL). The organic layer was extracted with water, and washed with brine, dried over MgSO$_4$ and concentrated in

vacuo. The crude product was purified by flash column chromatography to give the title compound (0.51 g, 83%) as a colorless oil: ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.57–7.54 (m, 1H), 7.26–7.23 (m, 1H), 6.92–6.83 (m, 2H), 6.12–6.05 (m, 1H), 5.53–5.47 (m, 1H), 5.34–5.31 (m, 1H), 4.64–4.62 (m, 2H). These data are consistent with the previously reported characterization.[108]
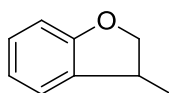
3-Methyl-2,3-dihydrobenzofuran (86):

TBHN (3.5 mg, 0.02 mmol) was added to a solution of diMe-Imd-BH$_3$ **16** (12 mg, 0.11 mmol) and the substrate (0.1 mmol) in benzene (0.45 mL). Thiophenol or *tert*-dodecanethiol (11.0 mg, 0.1 mmol or 20.2 mg, 0.1 mmol) was dissolved in benzene (1 mL). The diluted thiol solution (0.1 M in benzene, 50 μL, 0.005 mmol) was added to the solution of the substrate and TBHN. The colorless solution was charged to a sealed tube and heated in oil bath at 80 °C for 2 h. The mixture was cooled to room temperature, then the solvent was evaporated and the crude product was purified by flash column chromatography to yield the title compound (10.7 mg, 80%) as a colorless oil: ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ 7.02–6.97 (m, 1H), 6.94–6.86 (m, 1H), 6.81–6.80 (m, 1H), 6.79–6.77 (m, 1H), 4.24 (t, *J* = 8.8 Hz, 1H), 3.70 (t, *J* = 7.8 Hz, 1H), 3.06–2.96 (m, 1H), 0.89 (d, *J* = 6.8 Hz, 3H). These data are consistent with the previously reported characterization.[107]
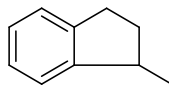
1-Methylindan (88):

TBHN (3.5 mg, 0.02 mmol) was added to a solution of diMe-Imd-BH$_3$ **16** (12 mg, 0.11 mmol) and the substrate (0.1 mmol) in benzene (0.45 mL). Thiophenol or *tert*-dodecanethiol (11.0 mg, 0.1 mmol or 20.2 mg, 0.1 mmol) was dissolved in benzene (1 mL). The diluted thiol solution (0.1 M in benzene, 50 μL, 0.005 mmol) was added to the solution of the substrate and TBHN. The colorless solution was charged to a sealed tube and heated in oil bath at 80 ℃ for 2 h. The mixture was cooled to room temperature, then the solvent was evaporated and the crude product was purified by flash column chromatography to yield the title compound (10.6 mg, 80%) as a colorless oil: ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.23 (m. 4H), 3.19 (qdd, *J* = 7.3, 7.3, 7.3 Hz, 1H), 2.88 (m, 2H), 2.31 (dddd, *J* = 12.3, 7.7, 7.5, 3.8 Hz, 1H), 1.61 (dddd, *J* = 12.4, 8.6, 8.6, 8.6 Hz, 1H), 1.29 (d, *J* = 6.8 Hz, 3H). These data are consistent with the previously reported characterization.[109]

8.2   EXPERIMENTAL DATA FOR CHAPTER 3

METHOD A – Preparation of monothiolated compounds (NHC-BH₂SAr)

Diaryl disulfide (1 mmol, 1 equiv) was added to a solution of NHC-borane (1 mmol, 1 equiv) in benzene (5 mL). The colorless solution was charged to a sealed tube. The sealed tube was stirred at 45 ℃ for 2 h under an aluminum foil. After all the NHC-borane was consumed, the mixture was cooled to room temperature, then the solvent was evaporated and the crude product was purified.

METHOD B – Preparation of bisthiolated compounds (NHC-BH(SAr)₂)

Diaryl disulfide (2 mmol, 2 equiv) was added to a solution of NHC-borane (1 mmol, 1 equiv) in benzene (5 mL). The colorless solution was charged to a small vial. The mixture was irradiated with GE-275W sunlamp at 60 ℃ or lab light at rt. After all the NHC-borane was consumed, the mixture was cooled to room temperature, then the solvent was evaporated and the crude product was purified.
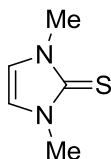
1,3-Dimethyl-1*H*-imidazole-2(3*H*)-thione (100):

Diphenyl disulfide (0.87 g, 4.0 mmol) was added to a solution of diMe-Imd-BH₃ **16** (44 mg, 0.4 mmol) in benzene (3 mL). The colorless solution was charged to a small vial. The vial was irradiated with GE-275W sunlamp for 10 h. The mixture was cooled to room temperature,

then the solvent was evaporated and the crude product was purified by flash column chromatography to give the title compound (6.2 mg, 12%) as a viscous colorless oil: ^{1}H NMR (300 MHz, CDCl$_3$) δ 6.68 (s, 2H), 3.62 (s, 6H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 117.53, 35.26; HRMS (ESI) *m/z* (M[+]) calculated for C$_5$H$_8$N$_2$S 128.0408, found 128.0392. These data are consistent with the previously reported characterization.[110]
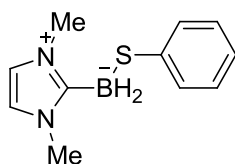
(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(phenylthio)dihydroborate, diMe-Imd-BH$_2$SPh (97):

Following **method A** from *N,N'*-1,3-dimethylimidazolylidene borane (diMe-Imd-BH$_3$, 56 mg, 0.51 mmol) and phenyl disulfide (114 mg, 0.52 mmol), a mixture of title compound and diMe-Imd-BH(SPh)$_2$ was obtained and mostly separated by preparative HPLC (Eurospher 100-5 Si column, Knauer, 250 x 20 mm, eluent: 60:40 → 30:70 heptane:AcOEt over 30 min, then 30:70 heptane:AcOEt during 30 min, 10 mL/min, UV detection at 254 nm). Minor impurities were diMe-Imd-BH(SPh)$_2$ and starting material. ^{1}H NMR (CDCl$_3$, 500 MHz): 7.35–7.38 (m, 2H), 7.09–7.12 (m, 2H), 6.99–7.01 (m, 1H), 6.81 (s, 2H), 3.71 (s, 6H), 2.62 (q, J_{B-H} = 96 Hz, 2H, BH$_2$),; ^{13}C NMR (CDCl$_3$, 75 MHz): 142.8, 131.2, 128.0, 123.4, 120.9, 36.1; ^{11}B NMR (CDCl$_3$, 160 MHz): –24.4 (t, *J* = 102 Hz); IR (neat): ν = 3127, 3052, 2950, 2375, 2343, 1576 cm^{-1}; HRMS calculated for C$_{16}$H$_{25}$B$_2$N$_4$S ([2M − SPh]$^+$): 327.1986, found 327.1935.
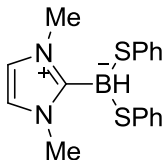
(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)bis(phenylthio)hydroborate, diMe-Imd-BH(SPh)$_2$ (98):

Following **method B** form diphenyl disulfide (0.44 g, 2.0 mmol) and diMe-Imd-BH$_3$ **1** (0.11 g, 1.0 mmol) in benzene (5 mL), the title compound (0.26 g, 80%) was obtained as a white solid after flash chromatgraphy. The similiar reaction can be conducted in PhMe (71% isolated yield) or PhCF$_3$ (69%) instead of PhH. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.37–7.41 (m, 4H), 7.11–7.16 (m, 4H), 7.01–7.06 (m, 2H), 6.78 (s, 2H), 3.80 (s, 6H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 140.4, 131.2, 128.1, 124.1, 121.6, 36.7; ^{11}B NMR (96.3 MHz, CDCl$_3$) δ −12.4 (d, J_{B-H} = 121 Hz); FTIR (thin film, CH$_2$Cl$_2$) ν = 3166, 3130, 3052, 3012, 2996, 2951, 2427, 1578, 1477, 1435, 1234, 1105 cm^{-1}; HRMS (ESI) *m/z* (M$^+$ − H) calculated for C$_{17}$H$_{18}$BN$_2$S$_2$ 325.1004, found 325.1010; mp 72–74 °C.
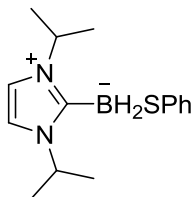
(1,3-Diisopropyl-1*H*-imidazol-3-ium-2-yl)(phenylthio)dihydroborate, diiPr-Imd-BH$_2$SPh (112):

Following **method A** from diiPr-Imd-BH$_3$ (16.6 mg, 0.1 mmol) and diphenyl disulfide (22 mg, 0.1 mmol), diiPr-Imd-BH$_2$SPh obtained as a white solid (18.2 mg, 66%) after flash chromatographic purification. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.42 (d, *J* = 7.8 Hz, 2H), 7.11 (t, *J*

= 7.6 Hz, 2H), 6.96–6.98 (m, 3H) , 5.17 (sep, J = 6.7 Hz, 2H), 2.67 (q, $J_{B\text{-}H}$ = 93 Hz, 2H, BH), 1.36 (d, J = 6.8 Hz, 12H); ^{11}B NMR (128.4 MHz, CDCl$_3$) δ –24.5 (t, $J_{B\text{-}H}$ = 99 Hz). These data are consistent with the previously reported characterization.[111]
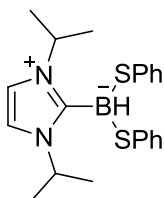
(1,3-Diisopropyl-1H-imidazol-3-ium-2-yl)bis(phenylthio)hydroborate, diiPr-Imd-BH(SPh)$_2$ (123):

Following **method B** from diiPr-Imd-BH$_3$ (16.6 mg, 0.1 mmol) and diphenyl disulfide (43.6 mg, 0.2 mmol), diiPr-Imd-BH$_2$SPh obtained as a white solid (27.6 mg, 72%) after flash chromatographic purification. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.45 (d, J = 7.5 Hz, 4H), 7.13 (t, J = 7.5 Hz, 4H), 7.00–7.03 (m, 4H), 5.44 (sep, J = 6.5 Hz, 2H), 1.39 (d, J = 6.5 Hz, 12H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 141.0, 131.0, 128.0, 123.8, 116.9, 50.4, 23.4; ^{11}B NMR (160.5 MHz, CDCl$_3$) δ –12.3 (d, $J_{B\text{-}H}$ = 124 Hz); FTIR (thin film, CH$_2$Cl$_2$) ν = 3162, 3131, 3064, 2966, 2921, 2431, 1578, 1460, 1403, 1210, 1178, 1080, 1046, 1024, 994, 744 cm^{-1}; HRMS (ESI) m/z (M$^+$ – H) calculated for C$_{21}$H$_{26}$BN$_2$S$_2$ 381.1630, found 381.1620; mp 163–165 ℃.
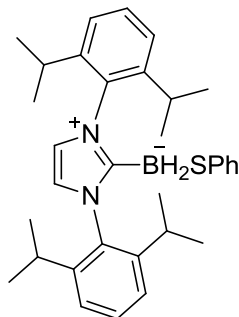
(1,3-Bis(2,6-diisopropylphenyl)-1*H*-imidazol-3-ium-2-yl)(phenylthio)dihydroborate, dipp-Imd-BH$_2$SPh (113):

Following **method A** from dipp-Imd-BH$_3$ (40.2 mg, 0.1 mmol) and diphenyl disulfide (21.8 mg, 0.1 mmol), a mixture of dipp-Imd-BH$_2$SPh (36%), dipp-Imd-BH(SPh)$_2$ (14%) and dipp-Imd-BH$_3$ (11%) were obtained after flash chromatographic purification. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.46 (t, *J* = 7.5 Hz, 2H); 7.27 (d, *J* = 7.5 Hz, 4H), 7.09 (s, 2H), 6.89 (d, *J* = 7.5 Hz, 2H), 6.83 (t, *J* = 7.5 Hz, 2H), 6.75 (t, *J* = 7.0 Hz, 1H), 2.64 (septet, *J* = 6.5 Hz, 4H), 1.32 (d, *J* = 6.5 Hz, 12H), 1.18 (d, *J* = 7.0 Hz, 12H), ^{11}B NMR (128.4 MHz, CDCl$_3$) δ −25.0 (br s). These data are consistent with the previously reported characterization.[20]
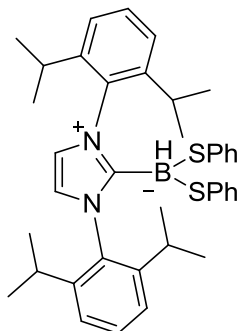
(1,3-Bis(2,6-diisopropylphenyl)-1*H*-imidazol-3-ium-2-yl)bis(phenylthio)hydroborate, dipp-Imd-BH(SPh)₂ (124):

Following **method B** from dipp-Imd-BH$_3$ (40.2 mg, 0.1 mmol) and diphenyl disulfide (44 mg, 0.2 mmol), the title product (28 mg, 45%) was obtained in colorless oil after flash chromatographic purification. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.50–7.52 (m, 2H); 7.28–7.30 (m, 4H), 7.10 (s, 2H), 6.75–6.85 (m, 10H), 2.77 (m, 4H), 1.29 (d, *J* = 6.4 Hz, 12H), 1.13 (d, *J* = 6.8 Hz, 12H); ^{13}C NMR (CDCl$_3$, 125 MHz) 145.9, 142.0, 133.5, 130.7, 130.5, 127.3, 124.1, 123.4, 122.6, 29.2, 26.1, 22.3; ^{11}B NMR (128.4 MHz, CDCl$_3$) δ –11.9 (br s); FTIR (thin film, CH$_2$Cl$_2$) ν = 3059, 2962, 2928, 2868, 1581, 1558, 1474, 1385, 1364, 761 cm^{-1}; HRMS (ESI) *m/z* (M$^+$ + H) calculated for C$_{39}$H$_{47}$BN$_2$S$_2$Na 641.3171, found 641.3184.
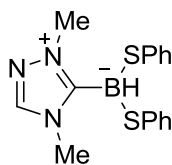
(1,4-Dimethyl-1*H*-1,2,4-triazol-4-ium-5-yl)bis(phenylthio)hydroborate, diMe-Tri-BH(SPh)₂ (129):

Following **method B** from diMe-Tri-BH$_3$ (11.1 mg, 0.1 mmol) and diphenyl disulifde (44 mg, 0.2 mmol), the title compound was obtained as colorless oil (26.9 mg, 85%) after flash

chromatographic purification. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.80 (s, 1H), 7.27–7.37 (m, 4H),

7.03–7.16 (m, 6H), 3.90 (s, 3H), 3.79 (s, 3H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 142.2, 139.4, 131.5,

128.3, 124.6, 38.9, 34.4; ^{11}B NMR (160.5 MHz, CDCl$_3$) δ −12.6 (d, J = 116 Hz); FTIR (thin

film, CH$_2$Cl$_2$) ν = 3066, 2952, 2427, 1579, 1503, 1475, 1436, 1087, 1025, 742 cm^{-1}; HRMS

(ESI) m/z (M$^+$ − H) calculated for C$_{16}$H$_{17}$BN$_3$S$_2$ 326.0957, found 326.0942.
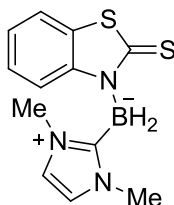
(1,3-Dimethyl-1H-imidazol-3-ium-2-yl)(2-thioxobenzo[d]thiazol-3(2H)-yl)dihydroborate

(134):

2,2'-Dithiobis(benzothiazole) (0.39 g, 1.1 mmol) was added to the benzene solution (5

mL) of diMe-Imd-BH$_3$ **1** (0.11 g, 1.0 mmol) in a small vial, and the vial was irradiated by 275W

sunlamp for 1 h. The mixture was purified via flash chromatgraphy to give the title compound

(0.18 g, 63%) as a white solid. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.84 (d, J = 8.4 Hz, 1H), 7.43 (dd,

J = 7.5, 1.0 Hz, 1H), 7.35 (td, J = 7.5, 1.5 Hz, 1H), 7.20 (td, J = 7.5, 0.9 Hz, 1H), 6.83 (s, 2H),

3.64 (s, 6H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 191.7, 147.5, 131.7, 125.9, 123.2, 120.6, 120.1,

116.7, 36.0; ^{11}B NMR (96.3 MHz, CDCl$_3$) δ −20.7 (t, $J_{B\text{-}H}$ = 100 Hz); FTIR (thin film, CH$_2$Cl$_2$)

ν = 2405, 1574, 1486, 1451, 1337, 1264, 1234, 1120, 1091, 1044, 752, 725 cm^{-1}; HRMS

calculated for C$_{12}$H$_{13}$BN$_3$S$_2$ (M$^+$ − H): 274.0644, found 274.0635; mp 154–157 ℃. Crystals of

pure **19** were obtained by vaporizing the solvent (CH$_2$Cl$_2$) of the solution of the complex.
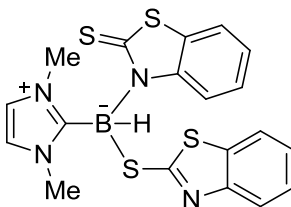
(Benzo[d]thiazol-2-ylthio)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)(2-thioxobenzo[d]thiazol-3(2*H*)-yl)hydroborate (135):

Following **method B** from *N,N'*-1,3-dimethyltriazolylidene borane (11 mg, 0.1 mmol) and 2,2'-dithiobis(benzothiazole) (66.5 mg, 0.2 mmol), the title compound was obtained as a yellowish oil (17.2 mg, 39%) after purification by flash chromatography (SiO$_2$, hexane:AcOEt = 60:40). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.90 (d, *J* = 8.4 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.42 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.30–7.38 (m, 1H), 7.22 (q, *J* = 6.8 Hz, 2H), 6.85 (s, 2H), 4.72–5.08 (br q, 1H), 3.78 (s, 6H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 193.5, 171.1, 154.0, 145.8, 135.8, 131.3, 126.5, 125.5, 124.0, 123.4, 121.9, 121.0, 120.5, 120.3, 116.7, 37.1; ^{11}B NMR (128.4 MHz, CDCl$_3$) δ −10.6 (br s); FTIR (thin film, CH$_2$Cl$_2$) ν = 2359, 1453, 1419, 1319, 1265, 1236, 1120, 1048, 1001, 757 cm^{-1}; HRMS calculated for C$_{19}$H$_{17}$BNaN$_4$S$_4$ (M$^+$ + Na): 463.0327, found 463.0332.
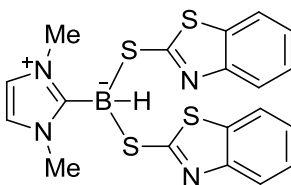
Bis(benzo[d]thiazol-2-ylthio)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)hydroborate (136):

Following **method B** from *N,N'*-1,3-dimethyltriazolylidene borane (11 mg, 0.1 mmol) and 2,2'-dithiobis(benzothiazole) (66.5 mg, 0.2 mmol), the title compound was obtained as a

yellowish oil (6.8 mg, 15%) after purification by flash chromatography (SiO$_2$, hexane:AcOEt = 40:60). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.69 (td, J = 7.5, 0.8 Hz, 4H), 7.32 (td, J = 7.0, 1.0 Hz, 2H), 7.21 (td, J = 8.0, 1.0 Hz, 2H), 6.92 (s, 2H), 4.14 (s, 6H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 170.6, 153.8, 136.0, 125.4, 123.4, 122.7, 122.0, 120.8, 120.6, 37.3; ^{11}B NMR (128.4 MHz, CDCl$_3$) δ −13.0 (br s); FTIR (thin film, CH$_2$Cl$_2$) ν = 3058, 2953, 2462, 1486, 1453, 1420, 1320, 1265, 1236, 1123, 1078, 1003, 947, 756, 727 cm^{-1}; HRMS calculated for C$_{19}$H$_{17}$BNaN$_4$S$_4$ (M$^+$ + Na): 463.0327, found 463.0340.
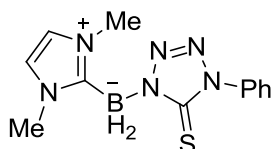
(1,3-Dimethyl-1H-imidazol-3-ium-2-yl)(4-phenyl-5-thioxo-4,5-dihydro-1H-tetrazol-1-yl)dihydroborate (138):

Following **method A** from N,N'-1,3-dimethylimidazolylidene borane (220 mg, 2.0 mmol) and 1-phenyltetrazoldisulfide (780 mg, 2.2 mmol), the title product was obtained as a white solid (488 mg, 85%) after purification by flash chromatography (SiO$_2$, heptane:AcOEt = 60:40). ^{1}H NMR (CDCl$_3$, 500 MHz): 7.94–7.96 (m, 2H), 7.48–7.51 (m, 2H), 7.40–7.44 (m, 1H), 6.92 (s, 2H), 3.92 (s, 6H), 3.18 (q, 2H, J_{B-H} = 110 Hz); ^{13}C NMR (CDCl$_3$, 75 MHz): 166.6, 135.5, 129.0, 128.9, 124.2, 121.3, 36.7; ^{11}B NMR (CDCl$_3$, 160 MHz): −20.3 (br s); FTIR (thin film, CH$_2$Cl$_2$) ν = 3132, 2952, 2413, 1595, 1496, 1380, 1330, 1269, 1235, 1202, 1175, 1106, 1058, 1007, 762 cm^{-1}; HRMS calculated for C$_{12}$H$_{16}$BN$_6$S ([M + H]$^+$): 287.1250, found 287.1260, mp = 119–121 °C. Crystals of pure **23** were obtained by vaporizing the solvent (CH$_2$Cl$_2$) of the solution of the complex.
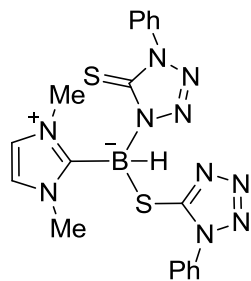
(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)((1-phenyl-1*H*-tetrazol-5-yl)thio)(4-phenyl-5-thioxo-4,5-dihydro-1*H*-tetrazol-1-yl)hydroborate (139):

Following **method B** from *N,N'*-1,3-dimethylimidazolylidene borane (53 mg, 0.5 mmol) and 1-phenyltetrazoldisulfide (354 mg, 1.0 mmol), the title product was obtained as a waxy white solid (75% for method B or 35% for method C) after purification by flash chromatography (SiO$_2$, heptane:AcOEt = 60:40). ^{1}H NMR (CDCl$_3$, 500 MHz): 7.92–7.97 (m, 2H), 7.69–7.75 (m, 2H), 7.43–7.56 (m, 6H), 6.94 (s, 2H), 4.00 (s, 6H); ^{13}C NMR (CDCl$_3$, 75 MHz): 166.7, 156.2, 135.2, 134.6, 129.7, 129.5, 129.3, 129.1, 124.5, 124.0, 122.3, 37.2; ^{11}B NMR (CDCl$_3$, 160 MHz): −11.4 (br s); IR (neat): ν = 3121, 2996, 2316, 1597, 1498 cm^{-1}; HRMS calculated for C$_{19}$H$_{20}$BN$_{10}$S$_2$ ([M + H]$^+$): 463.1407, found 463.1405; mp = 125–126 °C.
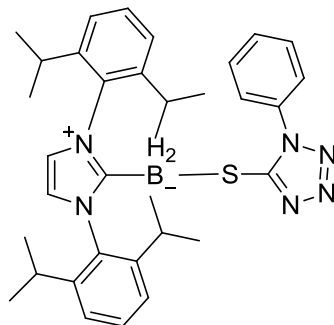
(1,3-Bis(2,6-diisopropylphenyl)-1*H*-imidazol-3-ium-2-yl)((1-phenyl-1*H*-tetrazol-5-yl)thio)dihydroborate, dipp-Imd-BH₂SPT (142):

Following **method A** from dipp-Imd-BH₃ (80.4 mg, 0.20 mmol) and 1-phenyltetrazoldisulfide (78.5 mg, 0.22 mmol), the title product (63.8 mg, 55%) was obtained as a white solid after flash chromatographic purification. ^{1}H NMR (400 MHz, CDCl₃) δ 7.44–7.47 (m, 4H); 7.33–7.41 (m, 3H), 7.23–7.25 (m, 4H), 7.11 (s, 2H), 2.68 (septet, J = 6.8 Hz, 4H), 1.18 (d, J = 6.8 Hz, 12H), 1.13 (d, J = 6.8 Hz, 12H); ^{11}B NMR (128.4 MHz, CDCl₃) δ –23.9 (br s). These data are consistent with the previously reported characterization.[20]
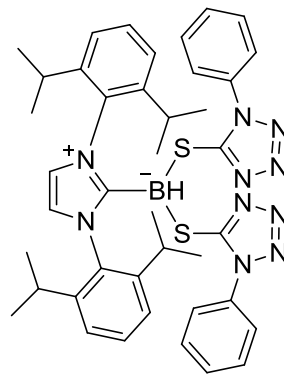
(1,3-Bis(2,6-diisopropylphenyl)-1*H*-imidazol-3-ium-2-yl)bis((1-phenyl-1*H*-tetrazol-5-yl)thio)hydroborated, dipp-Imd-BH(SPT)₂ (143):

Following **method B** from dipp-Imd-BH₃ (40.2 mg, 0.1 mmol) and 1-phenyltetrazoldisulfide (70.8 mg, 0.2 mmol), the title product (44.4 mg, 44%) was obtained as as a waxy yellow solid after flash chromatographic purification. ^{1}H NMR (700 MHz, CDCl₃) δ 7.43 (t, *J* = 7.7 Hz, 2H); 7.35–7.32 (m, 10H), 7.22 (d, *J* = 7.7 Hz, 4H), 7.17 (s, 2H), 2.84 (sep, *J* = 7.0 Hz, 4H), 1.12–1.10 (m, 24H); ^{13}C NMR (175 MHz, CDCl₃) δ 155.8, 146.0, 134.7, 133.3, 131.0, 128.91, 128.87, 124.6, 124.4, 124.2, 28.8, 26.2, 22.2; ^{11}B NMR (128.4 MHz, CDCl₃) δ −12.6 (br s); FTIR (thin film, CH₂Cl₂) ν = 3068, 2966, 2928, 2869, 1596, 1498, 1462, 1385, 1270, 761, 736 cm^{-1}; HRMS (ESI) *m/z* (M$^+$ + H) calculated for C₄₁H₄₈BN₁₀S₂ 755.3598, found 755.3602.
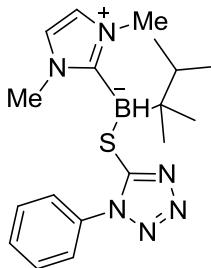
(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(2,3-dimethylbutan-2-yl)((1-phenyl-1*H*-tetrazol-5-yl)thio)hydroborate (145):

Following **method A** from diMe-Imd-BH$_2$thexyl (19.4 mg, 0.10 mmol) and 1-phenyltetrazoldisulfide (35.4 mg, 0.10 mmol), the title product (22.2 mg, 59%) was obtained as an oil after flash chromatographic purification. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.75 (d, *J* = 7.8 Hz, 2H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.47 (d, *J* = 7.2 Hz, 1H), 6.92 (d, *J* = 1.6 Hz, 1H), 6.78 (d, *J* = 1.6 Hz, 1H), 3.97 (s, 3H), 3.95 (s, 3H), 1.65 (br s, 1H), 1.55 (sep, *J* = 6.8 Hz, 1H), 0.93–0.91 (m, 6H), 0.85 (d, *J* = 6.8 Hz, 3H), 0.70 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 159.0, 135.2, 129.1, 128.9, 124.2, 121.9, 121.3, 37.9, 37.7, 36.9, 27.0, 24.1, 19.1, 17.9; ^{11}B NMR (128.4 MHz, CDCl$_3$) δ −10.9 (br s); FTIR (thin film, CH$_2$Cl$_2$) ν = 2954, 1597, 1499, 1477, 1375, 1232, 1090, 1005, 760, 694 cm^{-1}; HRMS (ESI) *m/z* (M$^+$ + H) calculated for C$_{18}$H$_{28}$BN$_6$S 371.2189, found 371.2192.
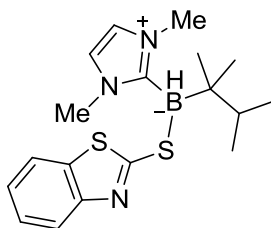
(Benzo[d]thiazol-2-ylthio)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)(2,3-dimethylbutan-2-yl)hydroborate (147):

Benzothiazole-2-thiol (17.6 mg, 0.10 mmol) was added to a benzene (0.5 mL) solution of diMe-Imd-BH$_2$thexyl (19.4 mg, 0.10 mmol). The colorless solution was charged to a sealed tube and heated in oil bath at 80 ℃ for 12 h. The mixture was cooled to room temperature, then the solvent was evaporated and the title product (21.0 mg, 58%) was obtained as an oil after flash chromatographic purification. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.64 (dd, J = 8.0, 0.4 Hz, 1H), 7.57 (dd, J = 7.2, 0.4 Hz, 1H), 7.30–7.23 (m, 1H), 7.12 (td, J = 7.2, 0.8 Hz, 1H), 6.91 (d, J = 2.0 Hz, 1H), 6.78 (d, J = 2.0 Hz, 1H), 4.05 (s, 3H), 4.04 (s, 3H), 3.70–3.30 (m, 1H), 1.71 (sep, J = 6.8 Hz, 1H), 0.98 (d, J = 6.8 Hz, 3H), 0.95 (s, 3H), 0.88 (d, J = 6.8 Hz, 3H), 0.69 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 175.2, 154.2, 135.7, 125.2, 122.4, 122.0, 121.5, 120.4, 120.1, 38.0, 37.5, 36.4, 27.0, 23.6, 19.2, 17.7; ^{11}B NMR (128.4 MHz, C$_6$D$_6$) δ −11.0 (d, J = 84.7 Hz); FTIR (thin film, CH$_2$Cl$_2$) ν = 2952, 1578, 1454, 1416, 1234, 1115, 998, 756, 727 cm^{-1}; HRMS (ESI) *m/z* (M$^+$ + H) calculated for C$_{18}$H$_{27}$BN$_3$S$_2$ 360.1739, found 360.1743.
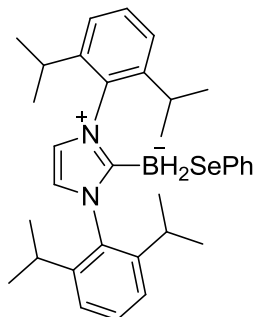
(1,3-bis(2,6-diisopropylphenyl)-1*H*-imidazol-3-ium-2-yl)(phenylselanyl)dihydroborate,

dipp-Imd-BH$_2$SePh (155):

Following **method B** from dipp-Imd-BH$_3$ (402 mg, 1.0 mmol) and diphenyl diselenide (312 mg, 1.0 mmol), the title product (246.8 mg, 44%) was obtained as as a white powder after flash chromatographic purification. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.43–7.30 (m, 2H), 7.30–7.25 (m, 2H), 7.08 (s, 2H), 6.93–6.81 (m, 3H), 6.79–6.68 (m, 4H), 2.62 (sep, *J* = 6.8 Hz, 4H), 1.30 (d, *J* = 6.8 Hz, 12H), 1.15 (d, *J* = 6.8 Hz, 12H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 145.4, 133.7, 132.6, 131.4, 130.4, 127.3, 124.0, 122.8, 122.3, 28.9, 25.5, 22.6; ^{11}B NMR (160.3 MHz, C$_6$D$_6$) δ −27.3 (br s); FTIR (thin film, CH$_2$Cl$_2$) ν = 3068, 2964, 2929, 2869, 2404, 1577, 1473, 1385, 1364, 1330, 1212, 1180, 1061, 1020, 984, 732 cm^{-1}; HRMS (ESI) *m/z* (M$^+$ − H) calculated for C$_{33}$H$_{42}$N$_2$BSe 557.2606, found 557.2568.

8.3   EXPERIMENTAL DATA FOR CHAPTER 4

Procedure A: PhSSPh-initiated conditions.

Diphenyl disulfide (PhSSPh, 0.01 mmol, 10 mol%, 2.2 mg) was added to a solution of diMe-Imd-BH$_3$ (12 mg, 0.11 mmol) and the substrate (0.1 mmol) in benzene (0.5 mL). The colorless solution was charged to a NMR tube and irradiated with a 275 W sunlamp at 60 ℃ for 1−7 h. The mixture was cooled to room temperature, then the solventwas evaporated and the crude product was purified by flash chromatography.

Procedure B: diMe-Imd-BH(SPh)$_2$-initiated conditions.

DiMe-Imd-BH(SPh)$_2$ (0.015 mmol, 15 mol%, 4.9 mg) was added to a solution of diMe-Imd-BH$_3$ (12 mg, 0.11 mmol) and the substrate (0.1 mmol) in benzene (0.5 mL). The colorless solution was charged to a NMR tube and irradiated with a 275 W sunlamp at 60 ℃ for 1−7 h. The mixture was cooled to room temperature, then the solventwas evaporated and the crude product was purified by flash chromatography.

8.4   EXPERIMENTAL DATA FOR CHAPTER 5

Procedure A: Thioetherification of benzyl bromide derivatives by diMe-Imd-BH(SPh)$_2$.

Complex diMe-Imd-BH(SPh)$_2$ (35.9 mg, 0.11 mmol, 1.1 equiv) was added to a solution of benzyl bromide derivative (0.10 mmol, 1.0 equiv) in MeCN (0.5 ml). The colorless solution was charged to a sealed tube and heated in oil bath at 80 ℃ for 3 h. The mixture was cooled to room temperature, then the solvent was evaporated and the crude product was purified by flash column chromatography.

Procedure B: Thioetherification of benzyl bromide derivatives by diMe-Imd-BH$_2$SPT.

Complex diMe-Imd-BH$_2$SPT (31.5 mg, 0.11 mmol, 1.1 equiv) was added to a solution of benzyl bromide derivative (0.10 mmol, 1.0 equiv) in MeCN (0.5 ml). The colorless solution was charged to a sealed tube and heated in oil bath at 80 ℃ for 3 h. The mixture was cooled to room temperature, then the solvent was evaporated and the crude product was purified by flash column chromatography.

Procedure C: Thioetherification of primary or propargyl bromide derivatives by diMe-Imd-BH(SPh)$_2$.

Complex diMe-Imd-BH(SPh)$_2$ (35.9 mg, 0.11 mmol, 1.1 equiv) was added to a solution of primary or propargyl bromide derivative (0.10 mmol, 1.0 equiv) in MeCN (0.5 ml). The colorless solution was charged to a sealed tube and heated in oil bath at 80 ℃ for 12 h. The mixture was cooled to room temperature, then the solvent was evaporated and the crude product was purified by flash column chromatography.

Procedure D: Thioesterification of acid chloride by diMe-Imd-BH(SPh)₂.

Complex diMe-Imd-BH(SPh)₂ (35.9 mg, 0.11 mmol, 1.1 equiv) was added to a solution of acid chloride derivative (0.10 mmol, 1.0 equiv) in chloroform (0.5 ml). The colorless solution was charged to a small vial and stirred at rt for 2 h. Then the solvent was evaporated and the crude product was purified by flash column chromatography.

Procedure E: Thioesterification of acid chloride by diMe-Imd-BH₂SPT.

Complex diMe-Imd-BH₂SPT (31.5 mg, 0.11 mmol, 1.1 equiv) was added to a solution of acid chloride derivative (0.10 mmol, 1.0 equiv) in MeCN (0.5 ml). The colorless solution was charged to a sealed tube and heated in oil bath at 80 ℃ for 16 h. The mixture was cooled to room temperature, then the solvent was evaporated and the crude product was purified by flash column chromatography.

Procedure F: One-pot thioetherification of benzyl bromide derivatives by diMe-Imd-BH₃ and PTS-SPT.

Benzyl bromide derivative (0.10 mmol, 1.0 equiv) was added to a solution of diMe-Imd-BH₃ (13.2 mg, 0.12 mmol, 1.2 equiv) and 5,5'-dithiobis(1-phenyl-1*H*-tetrazole) (PTS-SPT, 42.5 mg, 0.12 mmol, 1.2 equiv) in MeCN (0.5 ml). The colorless solution was charged to a sealed tube and heated in oil bath at 80 ℃ for 3 h. The mixture was cooled to room temperature, then the solvent was evaporated and the crude product was purified by flash column chromatography.

Procedure G: One-pot thioetherification of of benzyl bromide derivatives by diMe-Imd-BH$_3$ and PhS-SPh.

Complex diMe-Imd-BH$_3$ (13.2 mg, 0.12 mmol, 1.2 equiv) was added to a solution of diphenyl disulfide (PhS-SPh, 26.2 mg, 0.12 mmol, 1.2 equiv) in MeCN (0.5 ml). The colorless solution was charged to a sealed tube and heated in oil bath at 80 ℃ for 1 h. The mixture was cooled to room temperature, and then benzyl bromide derivative (0.10 mmol, 1.0 equiv) was added to the mixture. The mixture was heated at 80 ℃ for 2 h. The mixture was cooled to room temperature, then the solvent was evaporated and the crude product was purified by flash column chromatography.

Procedure H: One-pot thioetherification of primary bromide by diMe-Imd-BH$_3$ and PhS-SPh.

Primary bromide (0.10 mmol, 1.0 equiv) was added to a solution of diMe-Imd-BH$_3$ (13.2 mg, 0.12 mmol, 1.2 equiv) and diphenyl disulfide (PhS-SPh, 26.2 mg, 0.12 mmol, 1.2 equiv) in MeCN (0.5 ml). The colorless solution was charged to a sealed tube and heated in oil bath at 80 ℃ for 1 d. The mixture was cooled to room temperature, then the solvent was evaporated and the crude product was purified by flash column chromatography.

Procedure I: One-pot thioesterification by diMe-Imd-BH$_3$ and PhS-SPh.

Complex diMe-Imd-BH$_3$ (13.2 mg, 0.12 mmol, 1.2 equiv) was added to a solution of diphenyl disulfide (PhS-SPh, 26.2 mg, 0.12 mmol, 1.2 equiv) in MeCN (0.5 ml). The colorless solution was charged to a sealed tube and heated in oil bath at 80 ℃ for 2 h. The mixture was cooled to room temperature, and then acid chloride (0.10 mmol, 1.0 equiv) was added to the

mixture. The mixture was stirred at rt for 1 h. The solvent was evaporated and the crude product was purified by flash column chromatography.
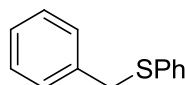
Benzyl phenyl sulfide (47):

Following Procedure A or G from diMe-Imd-BH(SPh)$_2$ (35.9 mg, 0.11 mmol, 1.1 equiv) and benzyl bromide (0.10 mmol, 1.0 equiv) to yield the title compound (19.8 mg, 99%) as colorless oil: ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.29–7.14 (m, 10H), 4.09 (s, 2H). These data are consistent with the previously reported characterization.[112]
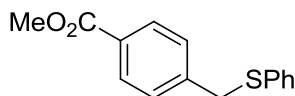
Methyl 4-((phenylthio)methyl)benzoate (161):

Following Procedure A from diMe-Imd-BH(SPh)$_2$ (35.9 mg, 0.11 mmol, 1.1 equiv) and benzyl bromide (0.10 mmol, 1.0 equiv) to yield the title compound (24.3 mg, 94%) as a white solid: ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.90–7.87 (m, 2H), 7.28–7.13 (m, 7H), 4.06 (s, 2H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 166.8, 143.0, 135.3, 130.4, 129.7, 128.9, 128.9, 128.8, 126.8, 52.0, 39.0; FTIR (thin film, CH$_2$Cl$_2$, cm^{-1}) 2947, 1717, 1481, 1439, 1409, 1280, 1110, 740; HRMS (ESI) *m/z* (M$^+$ + H) calculated for C$_{15}$H$_{15}$O$_2$S 259.0793, found 259.0784; mp 80–81 °C.

2-[(Phenylthio)methyl]-1-iodobenzene (162):

Following Procedure A from diMe-Imd-BH(SPh)$_2$ (35.9 mg, 0.11 mmol, 1.1 equiv) and benzyl bromide (0.10 mmol, 1.0 equiv) to yield the title compound (31.9 mg, 98%) as colorless oil: ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.88–7.85 (m, 1H), 7.37–7.24 (m, 7H), 6.97–6.91 (m, 1H), 4.22 (s, 2H); ^{13}C NMR ((CD$_3$)$_2$CO, 75 MHz) δ 141.1, 140.7, 136.9, 131.2, 131.2, 130.0, 130.0, 129.4, 127.6, 101.1, 44.8. These data are consistent with the previously reported characterization.[113]

1-[(Phenylthio)methyl]-4-fluoro-benzene (163):

Following Procedure A from diMe-Imd-BH(SPh)$_2$ (35.9 mg, 0.11 mmol, 1.1 equiv) and benzyl bromide (0.10 mmol, 1.0 equiv) to yield the title compound (20.0 mg, 92%) as colorless oil: ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.29–7.17 (m, 7H), 6.97–6.93 (m, 2H), 4.07 (s, 2H). These data are consistent with the previously reported characterization.[114]
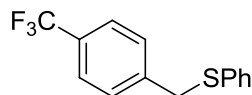
Phenyl(4-(trifluoromethyl)benzyl)sulfane (164):

Following Procedure A from diMe-Imd-BH(SPh)$_2$ (35.9 mg, 0.11 mmol, 1.1 equiv) and benzyl bromide (0.10 mmol, 1.0 equiv) to yield the title compound (23.9 mg, 89%) as colorless oil: ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.55–7.53 (m, 2H), 7.40–7.37 (m, 2H), 7.33–7.21 (m, 5H), 4.14 (s, 2H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 141.8, 135.3, 130.4, 129.4 (q, $J_{C\text{-}F}$ = 32 Hz), 129.0, 128.9, 126.9, 125.4 (q, $J_{C\text{-}F}$ = 4 Hz), 124.1 (q, $J_{C\text{-}F}$ = 271 Hz), 38.8; ^{19}F NMR (CDCl3, 471 MHz) δ −62.5; FTIR (thin film, CH$_2$Cl$_2$, cm^{-1}) 1481, 1439, 1415, 1327, 1167, 1154, 1098, 1069, 1019, 852, 737; HRMS (ESI) m/z (M$^+$) calculated for C$_{14}$H$_{11}$F$_3$S 268.0534, found 268.0517; mp 63–65 ℃.
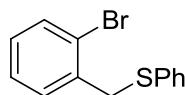
1-Bromo-2-(phenylthiomethyl)benzene (165):

Following Procedure A from diMe-Imd-BH(SPh)$_2$ (35.9 mg, 0.11 mmol, 1.1 equiv) and benzyl bromide (0.10 mmol, 1.0 equiv) to yield the title compound (27.0 mg, 97%) as colorless oil: ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.58–7.55 (m, 1H), 7.35–7.33 (m, 2H), 7.29–7.19 (m, 5H), 7.12–7.08 (m, 1H), 4.23 (s, 2H). These data are consistent with the previously reported characterization.[115]
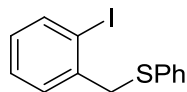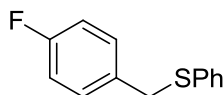
1-(1,1-Dimethylethyl)-4-[(phenylthio)methyl]benzene (166):

Following Procedure A from diMe-Imd-BH(SPh)$_2$ (35.9 mg, 0.11 mmol, 1.1 equiv) and benzyl bromide (0.10 mmol, 1.0 equiv) to yield the title compound (24.6 mg, 96%) as colorless oil: ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.35–7.33 (m, 4H), 7.29–7.26 (m, 4H), 7.21–7.17 (m, 1H), 4.13 (s, 2H), 1.32 (s, 9H). These data are consistent with the previously reported characterization.[116]
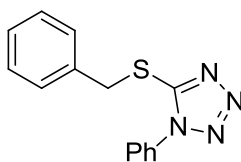
5-(Benzylthio)-1-phenyl-1*H*-tetrazole (167):

Following Procedure B or F from benzyl bromide (0.10 mmol, 1.0 equiv) to yield the title compound (25.7 mg, 96%) as colorless oil: ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.53 (brs, 5H), 7.45–7.42 (m, 2H), 7.34–7.31 (m, 3H), 4.64 (s, 2H). These data are consistent with the previously reported characterization.[68]
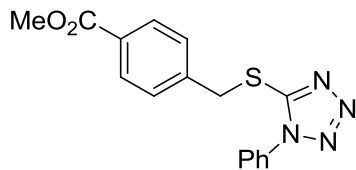
Methyl 4-(((1-phenyl-1*H*-tetrazol-5-yl)thio)methyl)benzoate (168):

Following Procedure B from benzyl bromide (0.10 mmol, 1.0 equiv) to yield the title compound (30.3 mg, 93%) as colorless oil: ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.98 (d, *J* = 8 Hz, 2H), 7.52–7.50 (m, 7H), 4.65 (s, 2H), 3.90 (s, 3H). These data are consistent with the previously reported characterization.[68]
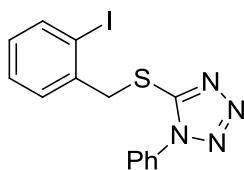
5-((2-Iodobenzyl)thio)-1-phenyl-1*H*-tetrazole (169):

Following Procedure B from benzyl bromide (0.10 mmol, 1.0 equiv) to yield the title compound (38.6 mg, 98%) as colorless liquid: ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.71 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.54 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.40 (brs, 5H), 7.18 (td, *J* = 7.5, 0.9 Hz, 1H), 6.85 (td, *J* = 7.8, 1.5 Hz, 1H), 4.62 (s, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 153.6, 139.7, 138.3, 133.6, 131.0, 130.0, 129.8, 129.7, 128.7, 123.8, 100.6, 42.8; FTIR (thin film, CH$_2$Cl$_2$, cm^{-1}) 1595, 1499, 1464, 1435, 1411, 1385, 1278, 1238, 1089, 1075, 1014, 760, 727; HRMS (ESI) *m/z* (M$^+$ + H) calculated for C$_{14}$H$_{12}$N$_4$SI 394.9827, found 394.9836.
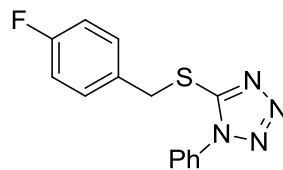
5-((4-Fluorobenzyl)thio)-1-phenyl-1*H*-tetrazole (170):

Following Procedure B from benzyl bromide (0.10 mmol, 1.0 equiv) to yield the title compound (26.3 mg, 92%) as a white solid: ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.55–7.51 (m, 5H), 7.44–7.39 (m, 2H), 7.04–6.97 (m, 2H), 4.60 (s, 2H). These data are consistent with the previously reported characterization.[68]
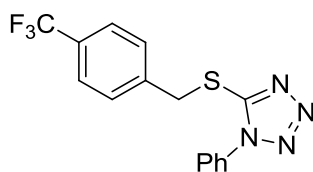
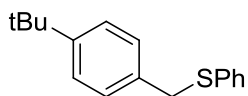**1-Phenyl-5-((4-(trifluoromethyl)benzyl)thio)-1*H*-tetrazole (171):**

Following Procedure B from benzyl bromide (0.10 mmol, 1.0 equiv) to yield the title compound (29.9 mg, 89%) as a white solid: ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.58–7.51 (m, 9H), 4.66 (s, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 153.3, 139.6, 133.4, 130.3 (q, $J_{C\text{-}F}$ = 32 Hz), 130.2, 129.8, 129.6, 125.7 (q, $J_{C\text{-}F}$ = 4 Hz), 123.8 (q, $J_{C\text{-}F}$ = 270 Hz), 123.7, 36.7; ^{19}F NMR (CDCl3, 471 MHz) δ –62.7; FTIR (thin film, CH$_2$Cl$_2$, cm^{-1}) 1615, 1500, 1418, 1389, 1324, 1167, 1108, 1068; HRMS (ESI) *m/z* (M$^+$ + H) calculated for C$_{15}$H$_{12}$N$_4$F$_3$S 337.0735, found 337.0745; mp 90–91 ℃.
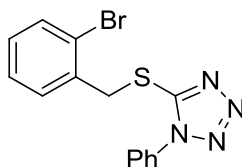
5-((2-Bromobenzyl)thio)-1-phenyl-1*H*-tetrazole (172):

Following Procedure B from benzyl bromide (0.10 mmol, 1.0 equiv) to yield the title compound (30.5 mg, 88%) as colorless oil: ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.59 (dd, J = 7.5, 1.8 Hz, 1H), 7.50–7.44 (m, 6H), 7.22–7.17 (m, 1H), 7.11–7.06 (m, 1H), 4.68 (s, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 153.8, 135.2, 133.5, 133.0, 131.8, 130.1, 129.9, 129.8, 127.8, 124.8, 123.8, 38.0; FTIR (thin film, CH$_2$Cl$_2$, cm^{-1}) 1642, 1596, 1499, 1469, 1440, 1412, 1386, 1279, 1239, 1089, 1046, 760, 730; HRMS (ESI) *m/z* (M$^+$ + H) calculated for C$_{14}$H$_{12}$N$_4$SBr 346.9966, found 346.9965.
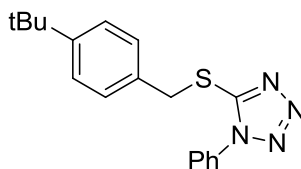
5-((4-(tert-Butyl)benzyl)thio)-1-phenyl-1*H*-tetrazole (173):

Following Procedure B from benzyl bromide (0.10 mmol, 1.0 equiv) to yield the title compound (31.1 mg, 96%) as a white solid: ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.53 (app s, 5H), 7.36 (app s, 4H), 4.62 (s, 2H), 1.31 (s, 9H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 154.0, 151.3, 133.6, 132.0, 130.0, 129.7, 128.9, 125.8, 123.8, 37.4, 34.6, 31.2; FTIR (thin film, CH$_2$Cl$_2$, cm^{-1}) 2962, 2868, 1596, 1500, 1462, 1411, 1386, 1237, 760; HRMS (ESI) *m/z* (M$^+$ + H) calculated for C$_{18}$H$_{21}$N$_4$S 325.1487, found 325.1487; mp 109–110 °C.
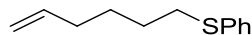
6-Phenylthio-1-hexene (174):

Following Procedure C from bromide (0.10 mmol, 1.0 equiv) to yield the title compound (18.8 mg, 98%) as colorless oil: ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.37–7.27 (m, 4H), 7.22–7.19 (m, 1H), 5.89–5.75 (m, 1H), 5.06–4.96 (m, 2H), 2.96 (t, J = 7.2 Hz, 2H), 2.10 (q, J = 7.2 Hz, 2H), 1.75–1.66 (m, 2H), 1.61–1.51 (m, 2H). These data are consistent with the previously reported characterization.[67]
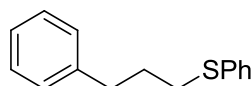

Phenyl 3-phenylpropyl sulfide (175):

Following Procedure C or H from bromide (0.10 mmol, 1.0 equiv) to yield the title compound (21.2 mg, 93%) as colorless oil: ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.33–7.25 (m, 6H), 7.22–7.17 (m, 4H), 2.96 (t, J = 7.5 Hz, 2H), 2.80 (t, J = 7.5 Hz, 2H), 2.01 (quint, J = 7.5 Hz, 2H). These data are consistent with the previously reported characterization.[67]
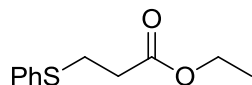
Ethyl 3-(phenylthio)propanoate (176):

Following Procedure C from bromide (0.10 mmol, 1.0 equiv) to yield the title compound (19.3 mg, 92%) as colorless oil: ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.33–7.31 (m, 2H), 7.26–7.20 (m, 2H), 7.18–7.14 (m, 1H), 4.08 (q, J = 7.2 Hz, 2H), 3.12 (t, , J = 7.2 Hz, 2H), 2.57 (t, J = 7.2

Hz, 2H), 1.20 (t, *J* = 7.2 Hz, 2H). These data are consistent with the previously reported characterization.[117]
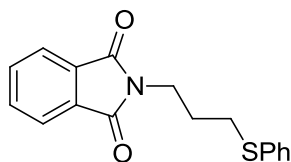
2-(3-(Phenylthio)propyl)isoindoline-1,3-dione (177):

Following Procedure C from bromide (0.10 mmol, 1.0 equiv) to yield the title compound (28.8 mg, 97%) as colorless oil: ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.87–7.83 (m, 2H), 7.74–7.71 (m, 2H), 7.38–7.35 (m, 2H), 7.31–7.26 (m, 2H), 7.21–7.17 (m, 1H), 3.84 (t, *J* = 6.9 Hz, 2H), 2.96 (t, *J* = 7.2 Hz, 2H), 2.06–2.00 (m, 2H). These data are consistent with the previously reported characterization.[124]

Phenyl 3-trimethylsilylprop-2-ynyl sulfide (178):

Following Procedure C from bromide (0.10 mmol, 1.0 equiv) to yield the title compound (21.3 mg, 97%) as colorless oil: ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.49–7.46 (m, 2H), 7.35–7.25 (m, 3H), 3.62 (s, 2H), 0.13 (s, 9H). These data are consistent with the previously reported characterization.[118]
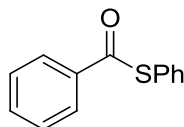
_S_-Phenyl benzothioate (180):

Following Procedure D or I from acid chloride (0.10 mmol, 1.0 equiv) to yield the title compound (20.5 mg mg, 96%) as colorless oil: ^{1}H NMR (CDCl$_3$, 300 MHz): δ 8.07–8.04 (m, 2H), 7.65–7.62 (m, 1H), 7.60–7.46 (m, 7H). These data are consistent with the previously reported characterization.[119]
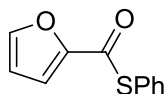
_S_-Phenyl furan-2-carbothioate (181):

Following Procedure D from acid chloride (0.10 mmol, 1.0 equiv) to yield the title compound (19.2 mg, 94%) as colorless oil: ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.59 (app s, 1H), 7.50–7.40 (m, 5H), 7.23–7.22 (m, 1H), 6.55–6.53 (m, 1H). These data are consistent with the previously reported characterization.[120]
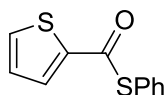
_S_-Phenyl thiophene-2-carbothioate (182):

Following Procedure D from acid chloride (0.10 mmol, 1.0 equiv) to yield the title compound (21.3 mg, 97%) as colorless oil: ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.94–7.91 (m, 1H), 7.69–7.66 (m, 1H), 7.56–7.45 (m, 5H), 7.19–7.15 (m, 1H). These data are consistent with the previously reported characterization.[119]
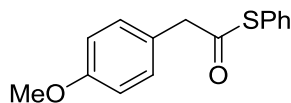
S-Phenyl 2-(4-methoxyphenyl)ethanethioate (183):

Following Procedure D from acid chloride (0.10 mmol, 1.0 equiv) to yield the title compound (25.0 mg, 97%) as colorless oil: ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.38 (app s, 5H), 7.26–7.23 (m, 2H), 6.91–6.87 (m, 2H), 3.85 (s, 2H), 3.80 (s, 3H). These data are consistent with the previously reported characterization.[121]
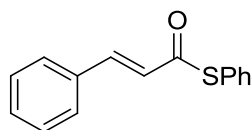
(*E*)-*S*-Phenyl 3-phenylprop-2-enethioate (184):

Following Procedure D from acid chloride (0.10 mmol, 1.0 equiv) to yield the title compound (21.8 mg, 91%) as a white solid: ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.70 (d, J = 15.6 Hz, 1H), 7.60–7.57 (m, 2H), 7.54–7.41 (m, 8H), 6.81 (d, J = 15.6 Hz, 1H). These data are consistent with the previously reported characterization.[122]
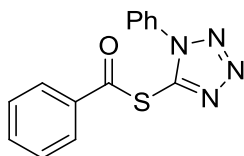
S-(1-Phenyl-1*H*-tetrazol-5-yl) benzothioate (185):

Following Procedure E from acid chloride (0.10 mmol, 1.0 equiv) to yield the title compound (25.0 mg, 89%) as a white solid: ^{1}H NMR (CDCl$_3$, 500 MHz): δ 7.89–7.87 (m, 2H), 7.69–7.49 (m, 8H). These data are consistent with the previously reported characterization.[123]

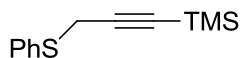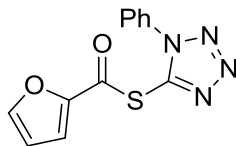**S-(1-Phenyl-1*H*-tetrazol-5-yl) furan-2-carbothioate (186):**

Following Procedure E from acid chloride (0.10 mmol, 1.0 equiv) to yield the title compound (22.8 mg, 84%) as colorless oid: ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.67 (d, *J* = 0.8 Hz, 1H), 7.56 (app s, 5H), 7.28 (d, *J* = 4 Hz, 1H), 7.63 (dd, *J* = 4, 0.8 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 171.8, 148.2, 145.4, 133.7, 130.7, 129.6, 125.0, 118.7, 113.4; FTIR (thin film, CH$_2$Cl$_2$, cm^{-1}) 3134, 2923, 2852, 1786, 1700, 1595, 1563, 1498, 1460, 1389, 1258, 1224, 1155, 1120, 1077, 1017, 951, 826, 763; HRMS (ESI) *m/z* (M$^+$ + H) calculated for C$_{12}$H$_9$N$_4$O$_2$S 273.0446, found 273.0418.

8.5   EXPERIMENTAL DATA FOR CHAPTER 6

General procedures for hydroboration:

Iodine (I$_2$, 25.4 mg, 0.1 mmol) was added to a solution of diMe-Imd-BH$_3$ (110 mg, 1.0 mmol) and alkene (1.1 mmol) in CH$_2$Cl$_2$ (1 mL). The solution was charged to a small vial and stirred until all starting material diMe-Imd-BH$_3$ consumed. The reaction progress was checked by TLC and ^{11}B NMR spectroscopy. Then, the solvent was evaporated and the crude product was purified by flash column chromatography.

Procedure for reaction between diMe-Imd-BH₂I and 2-methyl-2-butene (199):

Iodine (I₂, 50 mg, 0.2 mmol, 0.5 equiv) was added to a solution of diMe-Imd-BH₃ (44 mg, 0.4 mmol) and 2-methyl-2-butene (30.8 mg, 4.4 mmol, 1.1 equiv) in CH_2Cl_2 (0.5 mL). The solution was charged to a NMR tube. The reaction progress was monitored by ^{11}B NMR spectroscopy. The key intermediate NHC-alkylboryl iodide **237** was detected as a broad resonance at –12 ppm by ^{11}B NMR spectroscopy.

Procedure for reaction between NHC-alkylborane 211 and iodine:

Iodine (I₂, 12.7 mg, 0.05 mmol, 0.5 equiv) was added to a solution of NHC-alkylborane **211** (18 mg, 0.1 mmol) in CH_2Cl_2 (0.5 mL). The solution was charged to a NMR tube. The reaction progress was monitored by ^{11}B NMR spectroscopy. The key intermediate NHC-alkylboryl iodide **237** was detected as a broad resonance at –12 ppm by ^{11}B NMR spectroscopy.

Procedure for regeneration NHC-alkylborane 211 via reduction of 237 by diMe-Imd-BH₃:

Iodine (I₂, 12.7 mg, 0.05 mmol, 0.5 equiv) was added to a solution of NHC-alkylborane **211** (18 mg, 0.1 mmol) in CH_2Cl_2 (0.5 mL). The solution was charged to a NMR tube. The reaction progress was monitored by ^{11}B NMR spectroscopy. The key intermediate NHC-alkylboryl iodide **237** was detected as a broad resonance at –12 ppm by ^{11}B NMR spectroscopy, and no starting material **6b** was left. DiMe-Imd-BH₃ (**16**, 110 mg, 1 mmol, 10 equiv) was added to the mixture. NHC-alkylborane **6b** was reformed.

Me

^{+}N —$\bar{B}H_2$

N

Me
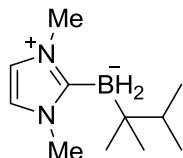
(1,3-Dimethyl-1_H_-imidazol-3-ium-2-yl)(2,3-dimethylbutan-2-yl)dihydroborate (210), diMe-Imd-BH$_2$(thexyl):

Iodine (25.4 mg, 0.1 mmol) was added to a solution of diMe-Imd-BH$_3$ (110 mg, 1.0 mmol) and 2,3-dimethylbutene (93 mg, 1.1 mmol) in CH$_2$Cl$_2$ (1 mL). The solution was charged to a small vial and stirred for 7 h. The solvent was evaporated and the crude product was purified by flash column chromatography to give the title compound (145.5 mg, 75%) as viscous colorless oil: ^{1}H NMR (300 MHz, CDCl$_3$) δ 6.83 (s, 2H), 3.81 (s, 6H), 1.40 (sept, J = 6.6 Hz, 1H), 0.92 (d, J = 6.6 Hz, 6H), 0.68 (s, 6H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 120.3, 39.8, 36.7, 28.3, 18.9; ^{11}B NMR (96.3 MHz, CDCl$_3$) δ −23.9 (t, J_{B-H} = 85 Hz); FTIR (thin film, CH$_2$Cl$_2$, cm^{-1}) 3441, 2952, 2272, 1643, 1466, 1364; HRMS (ESI) m/z (M^{+} − H) calculated for C$_{11}$H$_{22}$BN$_2$ 193.1876, found 193.1870.

Me

^{+}N —$\bar{B}H_2$

N

Me
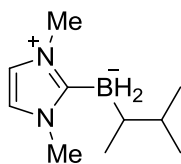
(1,3-Dimethyl-1_H_-imidazol-3-ium-2-yl)(3-methylbutan-2-yl)dihydroborate (211):

Iodine (25.4 mg, 0.1 mmol) was added to a solution of diMe-Imd-BH$_3$ (110.0 mg, 1 mmol) and 2-methyl-2-butene (77.0 mg, 1.1 mmol) in CH$_2$Cl$_2$ (1 mL). The solution was charged to a small vial and stirred for 3 h. The solvent was evaporated and the crude product was purified by flash column chromatography to give the title compound (106.9 mg, 59%) as viscous

colorless oil: [^1]H NMR (500 MHz, C_6D_6) δ 5.62 (s, 2H), 3.12 (s, 6H), 2.11 (br s, 1H), 2.02 (q, J = 85 Hz, 2H), 1.47 (d, J = 6.5 Hz, 3H), 1.45 (d, J = 7.0 Hz, 3H), 1.18 (br s, 3H), 0.94 (br s, 1H); [^13]C NMR (125 MHz, C_6D_6) δ 118.8, 35.5, 35.0, 31.0 (br), 22.2, 21.4, 19.5; [^11]B NMR (160.5 MHz, C_6D_6) δ −26.2 (t, J_{B-H} = 85 Hz); FTIR (thin film, CH_2Cl_2, cm^{-1}) 3139, 3047, 2948, 2860, 2272, 1575, 1476, 1399, 1360, 1266, 1231, 1052; HRMS (ESI) m/z (M$^+$ − H) calculated for $C_{11}H_{20}BN_2$ 179.1720, found 179.1717.
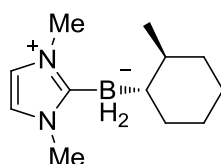
(1,3-Dimethyl-1H-imidazol-3-ium-2-yl)(-2-methylcyclohexyl)dihydroborate (212):

Iodine (25.4 mg, 0.1 mmol) was added to a solution of diMe-Imd-BH₃ (110.0 mg, 1.0 mmol) and 1-methylcyclohexene (105.8 mg, 1.1 mmol) in CH_2Cl_2 (1 mL). The solution was charged to a small vial and stirred for 1 d. The solvent was evaporated and the crude product was purified by flash column chromatography to give the title compound (139.9 mg, 68%) as viscous colorless oil: [^1]H NMR (400 MHz, C_6D_6) δ 5.67 (s, 2H), 3.14 (s, 6H), 2.60–2.00 (m, 2H), 2.08–1.94 (m, 2H), 1.84–1.74 (m, 3H), 1.73 (d, J = 9.6 Hz, 3H), 1.71–1.68 (m, 2H), 1.50–1.31 (m, 2H), 0.56 (br s, 1H); [^13]C NMR (125 MHz, CDCl3) δ 118.8, 40.6, 38.8, 36.2, 35.1, 29.5, 28.4, 23.5; [^11]B NMR (128.4 MHz, C_6D_6) δ −24.8 (t, J_{B-H} = 86 Hz); FTIR (thin film, CH_2Cl_2, cm^{-1}) 2910, 2841, 2276, 1477, 1445; HRMS (ESI) m/z (M$^+$ − H) calculated for $C_{12}H_{22}BN_2$ 205.1876, found 205.1886.
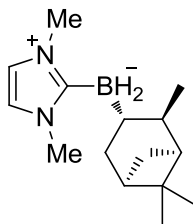
(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)((1*S*,2*R*,3*S*,5*S*)-2,6,6-trimethylbicyclo[3.1.1]heptan-3-yl)dihydroborate (213), diMe-Imd-BH$_2$-(+)-Ipc and its enantiomer ent-213:

Iodine (50.8 mg, 0.2 mmol) was added to a solution of diMe-Imd-BH$_3$ (220.0 mg, 2.0 mmol) and α-(+)-pinene (299.7 mg, 2.2 mmol) or its enantiomer in CH$_2$Cl$_2$ (3 mL). The solution was charged to a small vial and stirred for 2 d. The solvent was evaporated and the crude product was purified by flash column chromatography to give the title compound (297.9 mg, 61%) as a white solid: ^{1}H NMR (500 MHz, C$_6$D$_6$) δ 5.69 (s, 2H), 3.19 (s, 6H), 2.62–2.57 (m, 1H), 2.40–2.35 (m, 2H), 2.25–2.10 (m, 5H), 1.59 (d, *J* = 8.5 Hz, 1H), 1.43 (s, 3H), 1.41 (s, 3H), 1.15 (br s, 1H), 1.12 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, C$_6$D$_6$) δ 118.9, 50.2, 45.7, 43.6, 39.4, 37.3, 35.1, 34.5, 28.7, 28.1 (br), 23.1, 23.0; ^{11}B NMR (128.4 MHz, C$_6$D$_6$) δ –22.0 (t, $J_{B\text{-}H}$ = 86 Hz); FTIR (thin film, CH$_2$Cl$_2$, cm^{-1}) 3167, 3115, 2947, 2884, 2844, 2288, 2224, 1575, 1477, 1235, 1074; HRMS (ESI) *m/z* (M$^+$ – H) calculated for C$_{15}$H$_{26}$BN$_2$ 245.2189, found 245.2186; $[\alpha]_D^{20}$ for diMe-Imd-BH$_2$-(+)-Ipc **6d** is –19.7 ° while $[\alpha]_D^{20}$ for **ent-6d** is +19.7 °; mp 142–145 °C.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(2-methyl-1-phenylpropyl)dihydroborate (214):

Iodine (25.4 mg, 0.1 mmol) was added to a solution of diMe-Imd-BH$_3$ (110 mg, 1 mmol) and 2-methyl-1-phenyl-1-propene (145 mg, 1.1 mmol) in CH$_2$Cl$_2$ (1 mL). The solution was charged to a small vial and stirred for 24 h. The solvent was evaporated and the crude product was purified by flash column chromatography to give the title compound (120 mg, 50%) as viscous colorless oil: ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.02–6.99 (m, 2H), 6.88–6.84 (m, 1H), 6.81–6.79 (m, 2H), 6.63 (s, 2H), 3.38 (s, 6H), 2.07 (brs, 1H), 1.50 (brs, 1H), 1.20 (d, *J* = 6.5 Hz, 3H), 0.78 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 154.5, 127.4, 127.2, 122.1, 119.7, 35.3, 33.1, 23.8, 23.6; ^{11}B NMR (96.3 MHz, CDCl$_3$) δ –24.2 (t, $J_{B\text{-}H}$ = 87 Hz); FTIR (thin film, CH$_2$Cl$_2$, cm^{-1}) 3411, 3071, 3015, 2944, 2862, 2288, 1483; HRMS (ESI) *m/z* (M$^+$ – H) calculated for C$_{15}$H$_{22}$BN$_2$ 241.1876, found 241.1877.
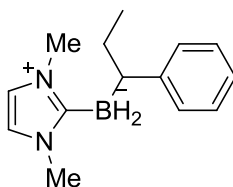
(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(1-phenylpropyl)dihydroborate (215):

Iodine (25.4 mg, 0.1 mmol) was added to a solution of diMe-Imd-BH$_3$ (110.0 mg, 1 mmol) and trans-β-nethylstyrene (130.0 mg, 1.1 mmol) in CH$_2$Cl$_2$ (1 mL). The solution was charged to a small vial and stirred for 2 d. The solvent was evaporated and the crude product was purified by flash column chromatography to give the title compound (135.3 mg, 59%) as a white

solid: ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.06–7.02 (m, 2H), 6.91–6.88 (m, 1H), 6.80–6.78 (m, 2H), 6.68 (s, 2H), 3.37 (s, 6H), 1.83–1.81 (m, 3H), 0.92 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, CDCl3) δ 154.6, 127.4, 126.6, 122.2, 119.8, 42.0 (q, J_{B-C} = 39 Hz), 35.4, 29.3, 14.7; ^{11}B NMR (160.5 MHz, CDCl$_3$) δ −23.5 (t, J_{B-H} = 87 Hz); FTIR (thin film, CH$_2$Cl$_2$, cm^{-1}) 3165, 3114, 3070, 3014, 2950, 2860, 2839, 2283, 1594, 1483. 1232. 1103; HRMS (ESI) m/z (M$^+$ + H) calculated for C$_{14}$H$_{22}$BN$_2$ 229.1876, found 229.1893; mp 68–69 ℃.
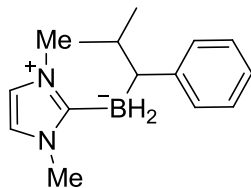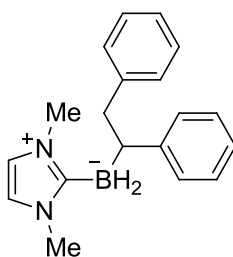

(1,3-Dimethyl-1H-imidazol-3-ium-2-yl)(1,2-diphenylethyl)dihydroborate (216):

Iodine (25.4 mg, 0.1 mmol) was added to a solution of diMe-Imd-BH$_3$ (110.0 mg, 1.0 mmol) and (Z)-stibene or (E)-stibene (198.3 mg, 1.1 mmol) in CH$_2$Cl$_2$ (0.5 mL). The solution was charged to a small vial and stirred for 2 d. The solvent was evaporated and the crude product was purified by flash column chromatography to give the title compound (191 mg, 66% for (Z)-stibene or 185.5 mg, 64% for (E)-stibene) as a white solid: ^{1}H NMR (500 MHz, C$_6$D$_6$) δ 7.45–7.43 (m, 2H), 7.17–7.14 (m, 2H), 7.07–6.92 (m, 5H), 6.91–6.89 (m, 1H), 5.54 (s, 2H), 3.67–3.58 (m, 2H), 2.79 (s, 6H), 2.56 (br s, 1H), 2.17 (q, J = 88 Hz, 2H); ^{13}C NMR (100 MHz, CDCl3) δ 153.5, 145.4, 128.8, 127.5, 127.4, 126.7, 124.5, 122.4, 119.9, 42.6, 35.4; ^{11}B NMR (160.5 MHz, C$_6$D$_6$) δ −22.1 (t, J_{B-H} = 88 Hz); FTIR (thin film, CH$_2$Cl$_2$, cm^{-1}) 3134, 3055, 3019, 2851, 2287, 1596, 1483, 1449, 1231, 1063; HRMS (ESI) m/z (M$^+$ + Na) calculated for C$_{19}$H$_{23}$BN$_2$Na 313.1852, found 313.1865; mp 119–121 ℃.
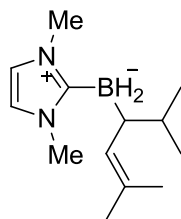
(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(2,5-dimethylhex-4-en-3-yl)dihydroborate (218):

Iodine (25.4 mg, 0.1 mmol) was added to a solution of diMe-Imd-BH$_3$ (110.0 mg, 1.0 mmol) and 2,5-dimethyl-2,4-hexediene (121.0 mg, 1.1 mmol) in CH$_2$Cl$_2$ (1 mL). The solution was charged to a small vial and stirred for 1 d. The solvent was evaporated and the crude product was purified by flash column chromatography to give the title compound (81.4 mg, 37%) as viscous colorless oil: ^{1}H NMR (400 MHz, C$_6$D$_6$) δ 5.67 (s, 2H), 5.54 (d, *J* = 10.4 Hz, 1H), 3.15 (s, 6H), 2.50–1.75 (m, 2H), 2.25–2.20 (m, 1H), 1.67 (s, 3H), 1.59 (br s, 1H), 1.55 (d, *J* = 6.8 Hz, 3H), 1.45 (d, *J* = 6.4 Hz, 3H), 1.09 (s, 3H); ^{13}C NMR (100 MHz, C$_6$D$_6$) δ 137.0, 119.6, 119.0, 40.0 (br), 35.2, 34.9, 26.5, 23.9, 23.1, 16.8; ^{11}B NMR (128.4 MHz, C$_6$D$_6$) δ –26.5 (t, J_{B-H} = 87 Hz); FTIR (thin film, CH$_2$Cl$_2$, cm^{-1}) 3168, 3118, 2947, 2859, 2281, 1574, 1478, 1404, 1374, 1231, 1195, 1169, 1098, 1052; HRMS (ESI) *m/z* (M$^+$ – H) calculated for C$_{13}$H$_{24}$BN$_2$ 219.2033, found 219.2024.
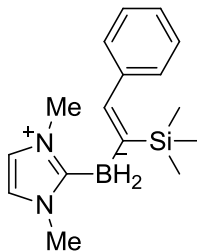
(Z)-(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(2-phenyl-1-(trimethylsilyl)vinyl)dihydroborate (220):

Iodine (25.4 mg, 0.1 mmol) was added to a solution of diMe-Imd-BH$_3$ (110.0 mg, 1.0 mmol) and 1-phenyl-2-trimethylsilylacetylene (191.7 mg, 1.1 mmol) in CH$_2$Cl$_2$ (1 mL). The solution was charged to a small vial and stirred for 4 h. The solvent was evaporated and the crude product was purified by flash column chromatography to give the title compound (97.8 mg, 34%) as a white crystal. ^{1}H NMR (400 MHz, C$_6$D$_6$) δ 7.38–7.36 (m, 2H), 7.22–7.16 (m, 2H), 7.09–7.06 (m, 1H), 6.72 (brs, 1H), 5.67 (s, 2H), 3.15 (s, 6H), 3.01–2.36 (q, J_{B-H} = 87 Hz, 2H), 0.45 (s, 9H); ^{13}C NMR (125 MHz, CDCl3) δ 144.6, 141.3, 128.2, 127.3, 125.3, 120.2, 36.0, 1.0; ^{11}B NMR (160.5 MHz, C$_6$D$_6$) δ –24.5 (t, J_{B-H} = 87 Hz); FTIR (thin film, CH$_2$Cl$_2$, cm^{-1}) 3172, 3143, 3067, 3016, 2953, 2893, 2320, 2282, 2239, 1573, 1477, 1439, 1401, 1233, 1102, 1082, 831, 788, 751, 727; HRMS (ESI) *m/z* (M$^+$ + Na) calculated for C$_{16}$H$_{25}$BN$_2$NaSi 307.1778, found 307.1764; mp 110–114 ℃; Crystals of pure product were obtained by vaporizing the solvent (CH2Cl2) of the solution of the complex.

Me—N⁺—B(H₂)—CH(CH₂Ph)(TMS) ... and ... Me—N⁺—B(H₂)—CH(CH₂TMS)(Ph)
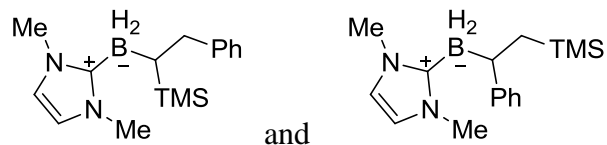
(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(2-phenyl-1-(trimethylsilyl)ethyl)dihydroborate and (1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)(1-phenyl-2-(trimethylsilyl)ethyl)dihydroborate (221 and 222):

Iodine (25.4 mg, 0.1 mmol) was added to a solution of diMe-Imd-BH$_3$ (110.0 mg, 1.0 mmol) and (*Z*)-trimethyl(styryl)silane (211.2 mg, 1.2 mmol) in CH$_2$Cl$_2$ (1 mL). The solution was charged to a small vial and stirred for 2 d. The solvent was evaporated and the crude product was purified by flash column chromatography to ~1:1 mixture of two regioisomers (205.5 mg, 72%) as colorless liquid: ^{1}H NMR (400 MHz, C$_6$D$_6$) one regioisomer: δ 5.44 (s, 2H), 2.93 (s, 6H), 0.49 (s, 9H); another regioisomer: δ 5.53 (s, 2H), 2.82 (s, 6H), 0.27 (s, 9H); overlapping peaks: 7.09–6.95 (m, 5H), 3.25 (brs, 1H), 2.55 (t, J = 11.2 Hz, 1H), 2.34 (brs, 2H), 2.30–1.55 (m, 4H); ^{13}C NMR (75 MHz, CDCl3) δ 156.7, 147.2, 127.7, 127.3, 127.2, 126.4, 124.1, 122.1, 119.8, 119.6, 38.3, 35.7, 35.4, 24.5, –0.4, –1.5; ^{11}B NMR (128.4 MHz, C$_6$D$_6$) δ –21.0 (t, $J_{B\text{-}H}$ = 90 Hz) and –27.0 (t, $J_{B\text{-}H}$ = 86 Hz); FTIR (thin film, CH$_2$Cl$_2$, cm^{-1}) 3169, 3136, 3057, 3019, 2949, 2890, 2286, 1596, 1574, 1480, 1450, 1237, 1110, 862, 833; HRMS (ESI) *m/z* (M$^+$ – H) calculated for C$_{16}$H$_{26}$BN$_2$Si 285.1958, found 285.1965.
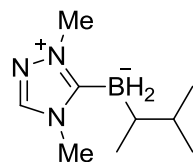
(1,4-Dimethyl-1*H*-1,2,4-triazol-4-ium-5-yl)(3-methylbutan-2-yl)dihydroborate (223):

Iodine (10.0 mg, 0.04 mmol) was added to a solution of diMe-Tri-BH$_3$ (44.4 mg, 0.4 mmol) and 2-methyl-2-butene (30.8 mg, 0.44 mmol) in CH$_2$Cl$_2$ (0.5 mL). The solution was charged to a small vial and stirred for 1 d. The solvent was evaporated and the crude product was purified by flash column chromatography to give the title compound (50.7 mg, 70%) as viscous colorless oil: ^{1}H NMR (500 MHz, C$_6$D$_6$) δ 6.48 (s, 1H), 3.53 (s, 3H), 2.84 (s, 3H), 1.97 (m, 1H), 1.36 (d, *J* = 6.5 Hz, 3H), 1.34 (d, *J* = 6.5 Hz, 3H), 1.06 (d, *J* = 7.0 Hz, 3H), 0.82 (br s, 1H); ^{13}C NMR (125 MHz, C$_6$D$_6$) δ 171.8 (br), 140.6, 37.4, 35.3, 32.5, 30.4 (q, $J_{B\text{-}C}$ = 36 Hz), 22.0, 21.2, 19.4; ^{11}B NMR (160.5 MHz, C$_6$D$_6$) δ −25.9 (t, $J_{B\text{-}H}$ = 88 Hz); FTIR (thin film, CH$_2$Cl$_2$, cm^{-1}) v = 2944, 2856, 2277, 1546, 1497, 1458, 1375, 1218, 1048; HRMS (ESI) *m/z* (M$^+$ + H) calculated for C$_9$H$_{21}$BN$_3$ 182.1829, found 182.1836.
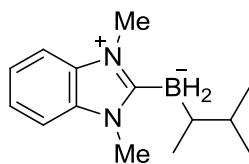
(1,3-Dimethyl-1*H*-benzo[*d*]imidazol-3-ium-2-yl)(3-methylbutan-2-yl)dihydroborate (224):

Iodine (10.0 mg, 0.04 mmol) was added to a solution of diMe-BenzImd-BH$_3$ (64.0 mg, 0.4 mmol) and 2-methyl-2-butene (30.8 mg, 0.44 mmol) in CH$_2$Cl$_2$ (0.5 mL). The solution was charged to a small vial and stirred for 1 d. The solvent was evaporated and the crude product was purified by flash column chromatography to give the title compound (65.3 mg, 71%) as viscous

colorless oil: ^{1}H NMR (300 MHz, C$_6$D$_6$) δ 6.93 (m, 2H), 6.62 (m, 2H), 3.41 (s, 6H), 2.12 (m, 1H), 1.46 (d, J = 6.6 Hz, 3H), 1.44 (d, J = 6.6 Hz, 3H), 1.17 (d, J = 6.6 Hz, 3H), 1.01 (br s, 1H); ^{13}C NMR (125 MHz, C$_6$D$_6$) δ 184.3 (br), 132.8, 122.9, 110.0, 35.6, 31.4, 22.0, 21.3, 19.5; ^{11}B NMR (160.5 MHz, C$_6$D$_6$) δ −25.3 (t, $J_{B\text{-}H}$ = 85 Hz); FTIR (thin film, CH$_2$Cl$_2$, cm^{-1}) v = 2944, 2858, 2293, 1464, 1198, 741; HRMS (ESI) m/z (M$^+$ + H) calculated for C$_{14}$H$_{24}$BN$_2$ 231.2033, found 231.2035.

(1,3-Diisopropyl-1H-imidazol-3-ium-2-yl)(3-methylbutan-2-yl)dihydroborate (225):

Iodine (10.0 mg, 0.04 mmol) was added to a solution of diiPr-Imd-BH$_3$ (66.4 mg, 0.4 mmol) and 2-methyl-2-butene (30.8 mg, 0.44 mmol) in CH$_2$Cl$_2$ (0.5 mL). The solution was charged to a small vial and stirred for 1 d. The solvent was evaporated and the crude product was purified by flash column chromatography to give the title compound (53.8 mg, 57%) as viscous colorless oil: ^{1}H NMR (400 MHz, C$_6$D$_6$) δ 6.23 (s, 2H), 5.33 (sep, J = 6.8 Hz, 2H), 2.55–1.55 (m, 2H), 2.10 (m, 1H), 1.46 (d, J = 6.8 Hz, 3H), 1.45 (d, J = 6.8 Hz, 3H), 1.20 (d, J = 7.2 Hz, 3H), 0.99–0.96 (m, 13H); ^{13}C NMR (100 MHz, C$_6$D$_6$) δ 173.5 (br), 114.6, 48.5, 35.4, 31.4 (br), 22.7, 22.5, 22.3, 21.2, 19.2; ^{11}B NMR (160.5 MHz, C$_6$D$_6$) δ −25.1 (t, $J_{B\text{-}H}$ = 85 Hz); FTIR (thin film, CH$_2$Cl$_2$, cm^{-1}) v = 2941, 2857, 2289, 1437, 1372, 1211, 1043; HRMS (ESI) m/z (M$^+$ − H) calculated for C$_{14}$H$_{28}$BN$_2$ 235.2346, found 235.2341.

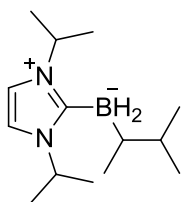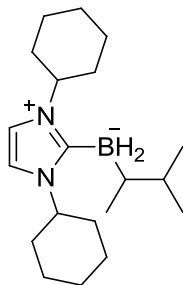**(1,3-Dicyclohexyl-1*H*-imidazol-3-ium-2-yl)(3-methylbutan-2-yl)dihydroborate (226):**

Iodine (10.0 mg, 0.04 mmol) was added to a solution of diCy-Imd-BH$_3$ (98.4 mg, 0.4 mmol) and 2-methyl-2-butene (30.8 mg, 0.44 mmol) in CH$_2$Cl$_2$ (0.5 mL). The solution was charged to a small vial and stirred for 1 d. The solvent was evaporated and the crude product was purified by flash column chromatography to give the title compound (63.2 mg, 50%) as a white solid: ^{1}H NMR (400 MHz, C$_6$D$_6$) δ 6.33 (s, 2H), 5.07 (tt, *J* = 12, 3.6 Hz, 2H), 2.16–2.08 (m, 1H), 1.89 (br t, 4H), 1.53–1.50 (m, 10H), 1.48–1.42 (m, 2H), 1.30–1.00 (m, 11H), 0.99–0.80 (m, 3H); ^{13}C NMR (75 MHz, C$_6$D$_6$) δ 115.1, 56.1, 35.6, 33.8, 33.4, 25.4, 25.2, 22.1, 21.7, 19.9; ^{11}B NMR (128.4 MHz, C$_6$D$_6$) δ –25.2 (t, $J_{B\text{-}H}$ = 85 Hz); FTIR (thin film, CH$_2$Cl$_2$, cm^{-1}) *v* = 2934, 2857, 2284, 1437, 1196; HRMS (ESI) *m/z* (M$^+$ – H) calculated for C$_{20}$H$_{37}$BN$_2$ 315.2972, found 315.2983; mp 94–95 ℃.
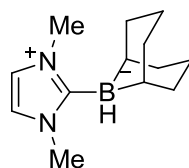
(1*R*,5*S*)-9-(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)-9-borabicyclo[3.3.1]nonan-9-uide (230):

Iodine (50.8 mg, 0.2 mmol) was added to a solution of diMe-Imd-BH$_3$ (220 mg, 2.0 mmol) and 1,5-cyclooctdiene (238 mg, 2.2 mmol) in CH$_2$Cl$_2$ (3 mL). The solution was charged to a small vial and stirred for 2 d. The solvent was evaporated and the crude product was purified

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by flash column chromatography to give the title compound (149 mg, 34%) as a white solid: ^{1}H NMR (400 MHz, C_6D_6) δ 5.50 (s, 2H), 3.05 (s, 6H), 2.40–2.29 (m, 4H), 2.20–2.06 (m, 6H), 1.95–1.93 (m, 3H), 1.64 (br s, 2H); ^{13}C NMR (100 MHz, C_6D_6) δ 119.2, 53.0, 38.9, 37.1, 35.0, 28.0; ^{11}B NMR (128.4 MHz, C_6D_6) δ –15.9 (d, J_{B-H} = 89 Hz); FTIR (thin film, CH_2Cl_2, cm^{-1}) 2898, 2849, 2256, 1469, 1265, 1230, 1134; HRMS (ESI) m/z (M$^+$ – H) calculated for $C_{13}H_{22}BN_2$ 217.1876, found 217.1869; mp 73–75 °C.
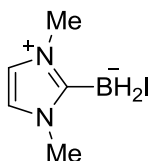
(1,3-Dimethyl-1H-imidazol-3-ium-2-yl)iododihydroborate, diMe-Imd-BH$_2$I (41):

Iodine (12.7 mg, 0.05 mmol) was slowly added to a solution of diMe-Imd-BH$_3$ (11.0 mg, 0.1 mmol) in C_6D_6 (0.5 mL) in a NMR tube. After bubbling ceased, the mixture spectra was recorded: ^{1}H NMR (300 MHz, C_6D_6) δ 5.52 (s, 2H), 2.98 (s, 6H); ^{13}C NMR (125 MHz, C_6D_6) δ 120.4, 35.2; ^{11}B NMR (96.3 MHz, C_6D_6) δ –31.5 (t, J_{B-H} = 116 Hz). This compound is not stable to workup or flash chromatography.
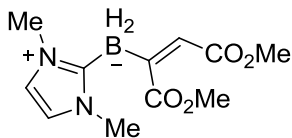
(Z)-(1,4-Dimethoxy-1,4-dioxobut-2-en-2-yl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)dihydroborate (240):

Dimethyl acetylenedicarboxylate (70 mg, 0.5 mmol, 1 equiv) was added to the solution of diMe-Imd-BH$_3$ (60 mg, 0.55 mmol, 1.1 equiv) in benzene (5 mL) at room temperature. The

solution was charged to a small vial and stirred for 1 h. The solvent was evaporated and the crude product was purified by flash column chromatography to give the title compound (62.3 mg, 51%) as oil: ^{1}H NMR (500 MHz, CDCl$_3$) δ 6.80 (s, 2H), 6.50 (s, 1H), 3.74 (s, 6H), 3.67 (s, 3H), 3.62 (s, 3H), 2.47–1.79 (m , 2H); ^{13}C NMR (125 MHz, C$_6$D$_6$) δ 175.1, 168.7, 127.5, 120.1, 51.6, 51.0, 36.1; ^{11}B NMR (96.3 MHz, C$_6$D$_6$) δ −28.7 (t, $J_{B\text{-}H}$ = 86.9 Hz); FTIR (thin film, CH$_2$Cl$_2$, cm^{-1}) 3133, 2951, 2343, 1712, 1600, 1485, 1433, 1235, 1019, 734; HRMS (ESI) m/z (M$^+$ + H) calculated for C$_{11}$H$_{18}$O$_4$N$_2$B 253.1360, found 253.1339.
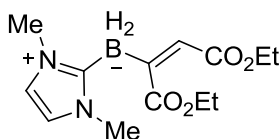
(Z)-(1,4-diethoxy-1,4-dioxobut-2-en-2-yl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)dihydroborate (241):

Diethyl acetylenedicarboxylate (74.5 mg, 0.44 mmol, 1.1 equiv) was added to the solution of diMe-Imd-BH$_3$ (44 mg, 0.40 mmol, 1.0 equiv) in benzene (2 mL) at room temperature. The solution was charged to a small vial and stirred for 1 h. The solvent was evaporated and the crude product was purified by flash column chromatography to give the title compound (52.3 mg, 47%) as oil: ^{1}H NMR (400 MHz, C$_6$D$_6$) δ 6.80 (s, 2H), 6.50 (s, 1H), 4.11 (q, J = 7.2 Hz, 2H), 4.10 (q, J = 7.2 Hz, 2H), 2.07 (q, $J_{B\text{-}H}$ = 88.0 Hz, 2H), 1.24 (t, J = 7.2 Hz, 3H), 1.22 (t, J = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 174.6, 168.3, 127.7, 120.1, 60.0, 59.6, 36.1, 14.3; ^{11}B NMR (128.4 MHz, C$_6$D$_6$) δ −28.7 (t, $J_{B\text{-}H}$ = 88.6 Hz); FTIR (thin film, CH$_2$Cl$_2$, cm^{-1}) 3169, 3133, 2981, 2903, 2343, 1710, 1599, 1576, 1484, 1233, 1181, 1037, 734; HRMS (ESI) m/z (M$^+$) calculated for C$_{13}$H$_{21}$BN$_2$O$_4$ 280.1594, found 280.1526.

APPENDIX A

Six papers with the Supporting Information where results of this dissertation work were

published:

1. Pan, X.; Lacôte, E.; Lalevée, J.; Curran, D. P., Polarity reversal catalysis in radical reductions of halides by N-heterocyclic carbene boranes *J. Am. Chem. Soc.* **2012,** *134*, 5669-5674.

2. Lamm, V.; Pan, X.; Taniguchi, T.; Curran, D. P., Reductions of aldehydes and ketones with a readily available N-heterocyclic carbene borane and acetic acid. *Beilstein J. Org. Chem.* **2013**, *9*, 675-680.

3. Pan, X.; Vallet, A.-L.; Schweizer, S.; Dahbi, K.; Delpech, B.; Blanchard, N.; Graff, B.; Geib, S. J.; Curran, D. P.; Lalevée, J.; Lacôte, E., Mechanistic and preparative studies of radical chain homolytic substitution reactions of N-heterocyclic carbene boranes and disulfides. *J. Am. Chem. Soc.* **2013,** *135*, 10484-10491.

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5. Pan, X.; Boussonnière, A.; Curran, D. P., Molecular iodine initiates hydroborations of alkenes with N-heterocyclic carbene boranes. *J. Am. Chem. Soc.* **2013,** *135*, 14433-14437.

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