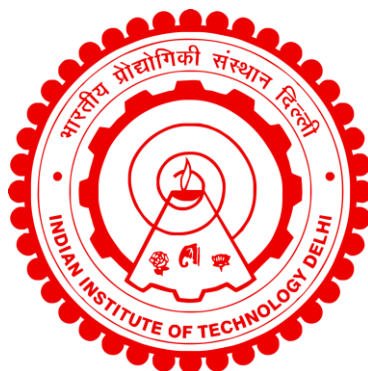


**EXPLORING NEW SYNTHETIC METHODS FOR  $\mu$ -  
AMINODIBORANE: AN *IN SITU*-GENERATED  
REDUCING AGENT FOR ORGANIC SUBSTRATES**

**ABHISHEK NAIR**



**DEPARTMENT OF CHEMISTRY  
INDIAN INSTITUTE OF TECHNOLOGY DELHI  
JULY 2025**

© Indian Institute of Technology Delhi (IITD), New Delhi, 2025

**EXPLORING NEW SYNTHETIC METHODS FOR  $\mu$ -  
AMINODIBORANE: AN *IN SITU*-GENERATED REDUCING  
AGENT FOR ORGANIC SUBSTRATES**

*by*

**ABHISHEK NAIR**

*Department of Chemistry*

*Submitted*

*in fulfillment of the requirements of the degree of*

**Doctor of Philosophy**

*to the*



**Indian Institute of Technology Delhi, India**

**July, 2025**

*Dedicated*

*to*

*My Parents and Teachers*

## CERTIFICATE

This is to certify that the thesis entitled “*Exploring new synthetic methods for  $\mu$ -aminodiborane: An in situ-generated reducing agent for organic substrates*” being submitted by Mr. **Abhishek Nair** to *Indian Institute of Technology Delhi*, for the award of the degree of **Doctor of Philosophy**, is a record of bonafide research work carried out by him. Mr. **Abhishek Nair** has worked under my supervision and guidance and has fulfilled all the requirements for the submission of a Ph.D. thesis, which to my knowledge has reached the requisite standard and is worthy of consideration for the award of Ph.D. degree.

The work embodied in this thesis has not been submitted, in part or full, to other university or institute for the award of any degree or diploma.

**Prof. Anil J. Elias**

Research Supervisor,

Professor (HAG),

Department of Chemistry

Indian Institute of Technology Delhi

Hauz Khas, New Delhi-110016, India.

## Acknowledgements

First and foremost, I would like to take this opportunity to thank my research supervisor, **Prof. Anil J. Elias** for his constant encouragement, patience and guidance which has enriched me as a student, a chemist and as a human being. His vast research experience and skills of the organometallics and main group chemistry has helped me a lot to complete this work. I wish to express my gratitude to him for mentoring me not only in academics but also personally. I would also like to thank him for keeping faith in me, with the responsibilities of the lab. He has set a standard as a perfect teacher, whom I see as a teaching-idol in my life.

I would like to extend my gratitude to Mrs. Latha Elias who treated us like children with her delicious dishes at home on various occasions, especially on Christmas every year, thereby making us feel like home at IIT Delhi.

I would like to thank Prof. S. Nagendran, Head, Dept. of Chemistry and former head of department Prof. Anil J. Elias, Prof. A. K Ganguli, Prof. Narayanan D. Kurur and Prof. Siddharth Pandey for providing me necessary research facilities. I would like to thank my student research committee (SRC) members, Prof. Selvarajan Nagendran, Prof. Sayantan Paria and Prof. Josemon Jacob for their time, interest, suggestions and helpful comments. I would like to extend my sincere thanks to all the teachers of this department for their support whenever it was required.

I would like to acknowledge all the teachers I have learnt from since my childhood, I would not have reached my present position without their guidance, blessings and prayers.

I also thank Mr. Narugopal Kully, Ms. Shubhra Gupta, Mr. Binit Kar, Mr. Sandeep and Ms. Poornima, for recording NMR, HRMS and IR spectra. I also thank Mr. Kannan, in-charge of central glass blowing facility for his timely help. Special thanks to Mr. Bhoopendra Singh and Mr. Chetan Kumar Gaur for assistance during M.Sc. Practicals and analysis of student records for Journal of Chemical Education work. I am thankful to all the members of this department who helped me in one way or the other to carry out my work successfully.

I don't find words to express my gratitude to my seniors, Dr. Mayukh Deb, Dr. Susanta Hazra, Dr. Pritam Dolui, Dr. Parul Saini, and Dr. Ashutosh Verma for help and support whenever I required their advice. I thank my current lab colleagues, Dr. Neha, Yogita, Vaibhav, and Aaqiba for creating an atmosphere of brotherhood in the lab. I want to thank all the project students, Vikas, Ankita, Ekta, Anandhu, Harshita, Anmol, Rishi, Sambhav, Pushpa, Somesh, Navneet, Priyanshu, and Ajay for their love, affection, and help shown towards me on and off the lab. I am very much grateful to all of them.

Thanks to all the group members of Prof. Nagendran's lab for being the ultimate lab neighbors, providing a great work environment, and for help and chats.

I thank all my Ph.D. friends with whom I shared memorable moments at IIT Delhi. I would like to acknowledge my dear friends, Shyamli, Kavita, Sagar, Harneet, Astha, Arjun, and Atul, for their unwavering moral support and motivation, which drives me to give my best.

I wish to convey my utmost respect to my parents, who sacrificed the best period of their lives and invested in them in nurturing my education and well-being. Their love, affection, support, blessings, and prayers for me are priceless. I would like to thank my

cousins Suvarna, Manish, and Akshay, my grandfather, grandmother, and my uncles Anil, Prem, and their families, who have been silent admirers, and their love; moral support has always helped me.

I acknowledge the Council of Scientific and Industrial Research (CSIR), Govt. of India, for providing me with a junior and senior research fellowship. I also thank DST and IIT Delhi for financial assistance in my research.

Abhishek Nair

## ABSTRACT

The thesis entitled " *Exploring new synthetic methods for  $\mu$ -aminodiborane: An in situ generated reducing agent for organic substrates* " presents the results obtained from the research work carried out on the development, characterization, and application of  $\mu$ -aminodiborane (ADB) as a reducing agent for organic substrates along with the reduction of ferrocene-based carbonyl compounds using ammonia borane (AB). The results obtained have been broadly divided into four parts. The accompanied research work has been divided into seven chapters.

**Chapter 1** provides a brief discussion of the chemistry and applications of boron-based reducing agents. This chapter also contains a brief discussion of the literature around ammonia borane and its dehydrogenated products. This is followed by a detailed discussion on the reduction of various functional groups using ammonia borane and  $\mu$ -aminodiborane.

The chapter ends with the scope of the work carried out in this thesis.

**Chapter 2** describes the general experimental procedures adopted in the synthesis of metallocene compounds and the characterization techniques utilized. Specific synthetic details of the starting materials described in the thesis are also presented.

**Chapter 3** describes a new method for the synthesis of aminodiborane ( $\mu$ - $\text{NH}_2\text{B}_2\text{H}_5$ ), by the reaction of  $\text{H}_3\text{N}\cdot\text{BH}_3$  and elemental iodine ( $\text{I}_2$ ). The *in situ*-generated aminodiborane is used as a reagent for the reduction of carboxamides to amines. This method is applicable to various secondary amides, tertiary amides, and trifluoroamides with yields obtained in the range of 67-94%. This protocol is also useful for preparing galipinine,

cinacalcet, and tetracaine hydrochloride, which are pharmaceutically important compounds. Control experiments and DFT studies have been carried out to explore the mechanistic pathway. These studies indicate that the active reagent in the reduction of secondary amides is aminodiborane and in the case of tertiary amides, aminodiborane and polyaminoborane.

**Chapter 4** describes an efficient methodology for the reduction of esters, carbonates, and anhydrides to alcohols using *in situ*-generated aminodiborane from iodine and ammonia borane. This methodology also finds use for the transformation of esters to iodides by varying the stoichiometry of reagents. The protocol has a broad substrate scope for the transformation of esters to alcohols and iodides with excellent yields. The method is also useful for synthesizing pharmaceutically and industrially important compounds such as the cinacalcet precursor, a streptoidole analogue, and 1,4-pentanediol. Control studies and DFT calculations carried out to study the reduction mechanism of esters using aminodiborane indicate that a dioxaborinamine intermediate is formed during the reaction.

**Chapter 5** describes the dehydrogenation of ammonia borane in the presence of a variety of Lewis acids, such as ICl, IBr, Br<sub>2</sub>, CuCl<sub>2</sub>, AlCl<sub>3</sub>, GaCl<sub>3</sub>, InCl<sub>3</sub>, and [Ph<sub>3</sub>C]BF<sub>4</sub> at a concentration of 7.5 mol% was effective in selectively producing aminodiborane ( $\mu$ -NH<sub>2</sub>B<sub>2</sub>H<sub>5</sub>, ADB) at 80 °C. Compounds such as ICl, IBr, Br<sub>2</sub>, AlCl<sub>3</sub>, and GaCl<sub>3</sub> at the same concentration could also generate ADB at lower temperatures of 35 °C and 50 °C. In contrast, BX<sub>3</sub> (X = Cl, Br) at the same concentration of 7.5 mol% was found to give exclusively B<sub>2</sub>H<sub>6</sub>. Further, the selective synthesis of diborane or ADB was achieved by adjusting the stoichiometry of the boron trihalides. A concentration of 7.5 mol% (up to 1

equivalent) of  $\text{BBr}_3$  favored the formation of  $\text{B}_2\text{H}_6$ , while 1 mol%  $\text{BBr}_3$  predominantly yielded ADB. Interestingly, both ADB and  $\text{B}_2\text{H}_6$  facilitated the reduction of acetanilides. A mechanism has been proposed for both diborane and ADB formation using these Lewis acids.

**Chapter 6** presents a methodology for the reduction of ferrocene-derived aldehydes and ketones to their respective alcohols, employing ammonia borane as the reducing agent and water as the solvent. I, also report the deoxygenation of the same precursors to the corresponding alkyl ferrocenes when reactions are performed under solvent-free conditions. Both methods are applicable to various carbonyl derivatives of ferrocene, and give product yields in the range of 40-95%, and, in most cases, a product purification that does not require column chromatography for product purification. The investigation for the deoxygenation of alkyl derivatives was extended to the cobalt sandwich compound –  $[(\text{CH}_3\text{CO})\text{C}_5\text{H}_4]\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)$  and ketone derivatives of ruthenocene as well. Ammonia borane has also been found to be a convenient reducing reagent for the selective reduction of ferrocenium compounds to their respective ferrocene derivatives at room temperature in water. Control experiments have been carried out to explore the mechanistic details of these reactions.

**Chapter 7** gives the overall conclusions of the entire work carried out in the present study and future prospects with aminodiborane.

## सार

" $\mu$ -अमीनोडिबोरेन के लिए नई सिंथेटिक विधियों की खोज: कार्बनिक सब्सट्रेट के लिए एक इन-सीटू जनरेटेड रिड्यूसिंग एजेंट" शीर्षक वाली थीसिस कार्बनिक सब्सट्रेट के लिए रिड्यूसिंग एजेंट के रूप में  $\mu$ -अमीनोडिबोरेन के विकास, लक्षण वर्णन और अनुप्रयोग पर किए गए शोध कार्य से प्राप्त परिणामों को प्रस्तुत करती है, साथ ही अमोनिया बोरेन का उपयोग करके फेरोसिन-आधारित कार्बोनिल यौगिकों की कमी भी करती है। प्राप्त परिणामों को मोटे तौर पर चार भागों में विभाजित किया गया है। साथ में किए गए शोध कार्य को सात अध्यायों में विभाजित किया गया है।

**अध्याय 1** थीसिस का पहला अध्याय बोरॉन-आधारित अपचायक एजेंटों के रसायन विज्ञान और अनुप्रयोगों की संक्षिप्त चर्चा से संबंधित है। इस अध्याय में अमोनिया बोरेन और इसके डीहाइड्रोजनेटेड उपोत्पादों के बारे में साहित्य की संक्षिप्त चर्चा भी शामिल है। इसके बाद अमोनिया बोरेन और एडीबी का उपयोग करके विभिन्न कार्यात्मक समूहों की कमी पर विस्तृत चर्चा की गई है। अध्याय वर्तमान में किए गए कार्य के दायरे के साथ समाप्त होता है, जिसे थीसिस में प्रस्तुत किया गया है।

**अध्याय 2** में मेटालोसिन यौगिकों के संश्लेषण में अपनाई गई सामान्य प्रयोगात्मक प्रक्रियाओं और उपयोग की गई अभिलक्षणिकरण तकनीकों का विवरण दिया गया है। थीसिस में वर्णित आरंभिक सामग्रियों के विशिष्ट संश्लेषण विवरण भी प्रस्तुत किए गए हैं।

**अध्याय 3** में  $H_3N \cdot BH_3$  और मौलिक आयोडीन ( $I_2$ ) की प्रतिक्रिया द्वारा एमिनोडिबोरेन ( $\mu$ - $NH_2B_2H_5$ ) के संश्लेषण के लिए एक नई विधि का वर्णन किया गया है। इन सीटू जनरेटेड एमिनोडिबोरेन का उपयोग कार्बोक्सामाइड्स को एमाइन में कम करने के लिए अभिकर्मक के रूप

में किया जाता है। यह विधि विभिन्न द्वितीयक एमाइड, तृतीयक एमाइड और ट्राइफ्लुओरोमाइड पर लागू होती है, जिसकी उपज 67-94% की सीमा में प्राप्त होती है। यह प्रोटोकॉल गैलीपिनिन, सिनाकैल्सेट और टेट्राकेन हाइड्रोक्लोराइड तैयार करने के लिए भी उपयोगी है, जो औषधीय रूप से महत्वपूर्ण यौगिक हैं। यांत्रिक मार्ग का पता लगाने के लिए नियंत्रण प्रयोग और DFT अध्ययन किए गए हैं। ये अध्ययन संकेत देते हैं कि द्वितीयक एमाइड के अपचयन में सक्रिय अभिकर्मक एमिनोडिबोरेन है और तृतीयक एमाइड के मामले में, एमिनोडिबोरेन और पॉलीएमिनोबोरेन है।

**अध्याय 4** में आयोडीन और अमोनिया बोरेन से इन-सीटू जनरेटेड एमिनोडिबोरेन का उपयोग करके एस्टर, कार्बोनेट और एनहाइड्राइड को अल्कोहल में कम करने के लिए एक कुशल पद्धति का वर्णन किया गया है। यह पद्धति अभिकर्मकों की स्टोइकोमेट्री को बदलकर एस्टर को आयोडाइड में बदलने के लिए भी उपयोगी है। प्रोटोकॉल में उत्कृष्ट पैदावार के साथ एस्टर को अल्कोहल और आयोडाइड में बदलने के लिए व्यापक सबस्ट्रेट स्कोप है। यह विधि फार्मास्यूटिकल और औद्योगिक रूप से महत्वपूर्ण यौगिकों जैसे कि सिनाकैल्सेट प्रीकर्सर, स्ट्रेप्टोइंडोल एनालॉग और 1,4-पेंटेनडिओल को संश्लेषित करने के लिए भी उपयोगी है। एमिनोडिबोरेन का उपयोग करके एस्टर के अपचयन तंत्र का अध्ययन करने के लिए किए गए नियंत्रण अध्ययन और DFT गणना से संकेत मिलता है कि प्रतिक्रिया के दौरान एक डाइऑक्साबोरिनामाइन मध्यवर्ती बनता है।

**अध्याय 5** में विभिन्न लुईस अम्लों जैसे ICl, IBr, Br<sub>2</sub>, CuCl<sub>2</sub>, AlCl<sub>3</sub>, GaCl<sub>3</sub>, InCl<sub>3</sub>, और [Ph<sub>3</sub>C]BF<sub>4</sub> की उपस्थिति में 7.5 mol% की सांद्रता पर अमोनिया बोरेन के विहाइड्रोजनीकरण का वर्णन किया गया है, जो 80°C पर चुनिंदा रूप से एमिनोडिबोरेन ( $\mu$ -NH<sub>2</sub>B<sub>2</sub>H<sub>5</sub>, ADB) का उत्पादन करने में प्रभावी था। समान सांद्रता पर ICl, IBr, Br<sub>2</sub>, AlCl<sub>3</sub>, और GaCl<sub>3</sub> जैसे यौगिक 35°C और 50°C के निम्न तापमान पर भी ADB उत्पन्न कर सकते हैं। इसके विपरीत, 7.5 mol%

की समान सांद्रता पर  $BX_3$  ( $X=Cl, Br$ ) केवल  $B_2H_6$  देता पाया गया। इसके अलावा, बोरॉन ट्राइहाइड्राइड की स्टोइकोमेट्री को समायोजित करके डिबोरेन या ADB का चयनात्मक संश्लेषण प्राप्त किया गया।  $BBr_3$  की 7.5 mol% (1 समतुल्य तक) सांद्रता  $B_2H_6$  के निर्माण को बढ़ावा देती है, जबकि 1 mol%  $BBr_3$  मुख्य रूप से ADB उत्पन्न करता है। दिलचस्प बात यह है कि ADB और  $B_2H_6$  दोनों ने एसिटानिलाइड्स के अपचयन को सुगम बनाया। इन लुईस एसिड का उपयोग करके डिबोरेन और ADB दोनों के निर्माण के लिए एक तंत्र प्रस्तावित किया गया है।

**अध्याय 6** फेरोसिन-व्युत्पन्न एल्डिहाइड और कीटोन को उनके संबंधित अल्कोहल में कम करने के लिए एक हरित पद्धति प्रस्तुत करता है, जिसमें अमोनिया बोरेन को कम करने वाले एजेंट और विलायक के रूप में शुद्ध पानी का उपयोग किया जाता है। जब प्रतिक्रिया विलायक-मुक्त परिस्थितियों में की जाती है, तो हम संबंधित एल्काइल फेरोसिन के लिए समान अग्रदूतों के डीऑक्सीजनेशन की भी रिपोर्ट करते हैं। फेरोसिन के विभिन्न कार्बोनिल व्युत्पन्नों पर लागू दोनों विधियाँ 40-95% की सीमा में उत्पाद की पैदावार देती हैं और, अधिकांश मामलों में, एक उत्पाद शुद्धिकरण जिसके लिए कॉलम क्रोमैटोग्राफी की आवश्यकता नहीं होती है। एल्काइल व्युत्पन्नों के डीऑक्सीजनेशन की जांच कोबाल्ट सैंडविच यौगिक -  $[(COCH_3)C_5H_4]Co(\eta^4-C_4Ph_4)$  और रूथेनोसिन के कीटोन व्युत्पन्नों तक भी विस्तारित की गई थी। अमोनिया बोरेन को जलीय माध्यम में कमरे के तापमान पर फेरोसेनियम यौगिकों को उनके संबंधित फेरोसिन व्युत्पन्नों में चयनात्मक रूप से कम करने के लिए एक सुविधाजनक अपचायक अभिकर्मक के रूप में भी उपयोगी पाया गया है। इन प्रतिक्रियाओं के यांत्रिक विवरणों का पता लगाने के लिए नियंत्रण प्रयोग किए गए हैं।

**अध्याय 7** वर्तमान अध्ययन में किए गए संपूर्ण कार्य के समग्र निष्कर्ष देता है।

## TABLE OF CONTENTS

	Page	
CERTIFICATE	I	
ACKNOWLEDGEMENTS	II	
ABSTRACT	V	
TABLE OF CONTENTS	XI	
LIST OF FIGURES	XVII	
LIST OF TABLES	XXII	
ABBREVIATIONS	XXIV	
CHAPTER		
1	Introduction	1
1.1	Boron-based reagents	1
1.1.1.	Boron-based Lewis acids	3
1.1.2.	Boron-based reagent for cross-coupling reactions	6
1.1.3.	Boron-based reducing agents	9
1.1.3.1.	Hydroboranes	9
1.1.3.1.1.	Anionic boron-hydride reducing agents	10
1.1.3.1.1.1.	Sodium borohydride	10
1.1.3.1.1.2.	Potassium borohydride	12
1.1.3.1.1.3.	Sodium cyanoborohydride	13
1.1.3.1.1.4.	Acyloxyborohydrides	15
1.1.3.1.1.5.	Lithium borohydride	17
1.1.3.1.1.6.	Lithium triethylborohydride	18
1.1.3.1.1.7.	Selectride	18

1.1.3.1.2.	Neutral boron hydride reducing agents	20
1.1.3.1.2.1.	Pinacolborane	20
1.1.3.1.2.2.	Catecholborane	22
1.1.3.1.2.3.	9-Borabicyclo[3.3.1]nonane	23
1.1.3.1.2.4.	Diborane and higher analogues of borane	24
1.1.3.1.3.	Adducts of borane	26
1.1.3.1.3.1.	H <sub>3</sub> B·THF	27
1.1.3.1.3.2.	H <sub>3</sub> B·SMe <sub>2</sub>	28
1.1.3.1.3.3.	Amine boranes	29
1.1.3.1.3.3.1	Ammonia borane	32
1.2.	Cyclic and acyclic B-N compounds	34
1.2.1.	Aminoboranes	35
1.2.2.	Iminoboranes	36
1.2.3.	Borazine	37
1.2.4.	Boron Nitrides	40
1.2.5.	Cyclotriborazane	41
1.2.6.	μ-Aminodiborane	42
1.3.	Reduction reaction using boron-nitrogen compounds	44
1.3.1.	Reduction using ammonia borane	44
1.3.1.1.	Reduction of aldehyde and ketones	45
1.3.1.2.	Reduction of imines and reductive amination	46
1.3.1.3.	Reduction of carboxylic acids to alcohols	47

	1.3.1.4.	Reduction of esters with AB	48
	1.3.1.5.	Reduction of amides with AB	48
	1.3.1.6.	Reduction of nitriles to amines with AB	49
	1.3.2.	Using $\mu$ -aminodiborane for reduction reactions	51
	1.3.2.1.	Reduction of carboxylic acids with ADB	51
	1.3.2.2.	Reduction of nitriles with ADB	51
	1.4.	Scope of the present work	51
CHAPTER	2	Experimental (Starting Materials and Techniques)	54
	2.1	Preparation, purification and characterization of starting materials	55
	2.2	Purification and drying of solvents and reagents used in the Study	59
	2.3	Experimental techniques	60
	2.4	Characterization techniques	61
CHAPTER	3	<i>In situ</i> generated aminodiborane as a reagent for deoxygenative reduction of carboxamides to amines	62
	3.1	Introduction	62
	3.2	Results and discussion	65

	3.2.1	Synthesis of $\mu$ -aminodiborane (ADB) by the reaction of $\text{H}_3\text{N}\cdot\text{BH}_3$ and iodine	65
	3.2.2	Mechanism for the formation of $\mu$ -aminodiborane	66
	3.2.3	Reduction of amides to amines using <i>in situ</i> generated $\mu$ -aminodiborane	68
	3.2.4	Mechanistic Insights into amide reduction	75
	3.3	Conclusions	78
	3.4	NMR spectra studies	79
	3.5	Experimental section	91
	3.6	Identification of products	93
CHAPTER	4	Reduction of esters to alcohols and iodides using aminodiborane ( $\mu$ - $\text{NH}_2\text{B}_2\text{H}_5$ ): Scope and mechanistic investigations	109
	4.1	Introduction	109
	4.2	Results and discussion	111
	4.2.1	Transformation of esters into alcohols and iodides	111
	4.2.2	Mechanistic insights for transformation of esters into alcohols and iodides	118
	4.3	Conclusions	126
	4.4	NMR spectral studies	127
	4.5	Experimental Section	136

	4.6	Identification of products	137
CHAPTER	5	Synthesis of Aminodiborane from Ammonia Borane Using Different Lewis Acids: A Competing Reaction for Diborane Formation with Boron Trihalides (BX <sub>3</sub> , X=Cl, Br)	152
	5.1	Introduction	152
	5.2	Results and discussion	154
	5.2.1	Synthesis of $\mu$ -aminodiborane (ADB) by the reaction of H <sub>3</sub> N·BH <sub>3</sub> and Lewis acids	154
	5.2.2	Unusual formation of diborane by the reaction of H <sub>3</sub> N·BH <sub>3</sub> and BX <sub>3</sub> (X = F, Cl and Br)	155
	5.2.3	Reduction of amides to amines and esters to alcohols using <i>in situ</i> generated ADB and diborane	158
	5.2.4	Mechanistic Insights for ADB and diborane formation using Lewis acids	160
	5.3	Conclusions	162
	5.4	NMR spectral studies	163
	5.5	Experimental Section	172
CHAPTER	6	Ammonia borane (H <sub>3</sub> N·BH <sub>3</sub> ) as a Convenient Metal- free Reagent for the Reduction of Ferrocenyl and	173

		Ferrocenium Carbonyl Derivatives in Water	
	6.1	Introduction	173
	6.2	Results and discussion	177
	6.2.1	Reduction of ferrocene-derived ketones and aldehydes	177
	6.2.2	One-pot conversion of acetyl ferrocenium into 1-(ferrocenyl)ethanol	184
	6.2.3	Mechanistic insights for reduction of ferrocene-derived ketones and aldehydes	184
	6.3	Conclusions	187
	6.4	NMR spectral studies	188
	6.5	Experimental Section	197
	6.6	Identification of products	200
CHAPTER	7	Conclusion	216-220
REFERENCES			221-234
RESUME			235

## LIST OF FIGURES

			Page
CHAPTER	1		
Figure	1.1	Some common boron-based reagents and compounds	2
Figure	1.2	Representation of the relative acidity of few boron-based Lewis acids	3
Figure	1.3	Examples of some of the popular types of boron reagents used directly or indirectly in the Suzuki-Miyaura coupling reaction.	7
Figure	1.4	Selectivity of borohydrides for different functional groups.	10
Figure	1.5	Various reduction reactions possible using acyloxyborohydride.	16
Figure	1.6	Structure of Selectride	19
Figure	1.7	Structure of bis(pinacolato)diboron ( $B_2Pin_2$ ) and pinacolborane (HBpin)	20
Figure	1.8	Structure of carborane-based superacids	26
Figure	1.9	Representative examples of amine-boranes	31
Figure	1.10	Orientation of the B-N bond of AB along the c axis of the (a) low-temperature/orthorhombic and (b) high-temperature/tetragonal phases.	32
Figure	1.11	Isolable iminoborane derivatives. LB=Lewis Base, TM=Transition Metal.	37
Figure	1.12	Structural comparison of ADB and diborane	43
CHAPTER	2		
Figure	2.1.	$^{11}B$ NMR spectra of $H_3N \cdot BH_3$ (in $CDCl_3$ )	59
CHAPTER	3		

Figure	3.1	Comparison of $^{11}\text{B}$ NMR spectra of reaction of ammonia borane with different amounts of iodine.	65
Figure	3.2	Free energy profiles for the dehydrogenation of $\text{H}_3\text{N}\cdot\text{BH}_3$ catalyzed by iodine.	67
Figure	3.3	$^1\text{H}$ NMR spectrum of compound <b>2a</b>	80
Figure	3.4	$^{13}\text{C}$ NMR spectrum of compound <b>2a</b>	80
Figure	3.5	$^1\text{H}$ NMR spectrum of compound <b>3a</b>	81
Figure	3.6	$^{13}\text{C}$ NMR spectrum of compound <b>3a</b>	81
Figure	3.7	$^1\text{H}$ NMR spectrum of compound <b>3i</b>	82
Figure	3.8	$^{13}\text{C}$ NMR spectrum of compound <b>3i</b>	82
Figure	3.9	$^1\text{H}$ NMR spectrum of compound <b>4c</b>	83
Figure	3.10	$^{13}\text{C}$ NMR spectrum of compound <b>4c</b>	83
Figure	3.11	$^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of compound <b>4c</b>	84
Figure	3.12	$^1\text{H}$ NMR spectrum of compound <b>4d</b>	84
Figure	3.13	$^{13}\text{C}$ NMR spectrum of compound <b>4d</b>	85
Figure	3.14	$^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of compound <b>4d</b>	85
Figure	3.15	$^1\text{H}$ NMR spectrum of compound <b>5a</b>	86
Figure	3.16	$^{13}\text{C}$ NMR spectrum of compound <b>5a</b>	86
Figure	3.17	$^1\text{H}$ NMR spectrum of compound <b>6a</b>	87
Figure	3.18	$^{13}\text{C}$ NMR spectrum of compound <b>6a</b>	87
Figure	3.19	$^{19}\text{F}$ NMR spectrum of compound <b>6a</b>	88
Figure	3.20	$^1\text{H}$ NMR spectrum of compound <b>7a</b>	88
Figure	3.21	$^{13}\text{C}$ NMR spectrum of compound <b>7a</b>	89
Figure	3.22	$^{11}\text{B}$ NMR spectrum of $\text{H}_3\text{N}\cdot\text{BH}_3$	89
Figure	3.23	$^{11}\text{B}$ NMR spectrum of $\text{NH}_2\text{B}_2\text{H}_5$	90
Figure	3.24	$^{11}\text{B}$ NMR spectrum of final reaction mixture	90
CHAPTER	4		
Figure	4.1	$^1\text{H}$ NMR study comparison of reaction mixture without any hydrolysis using $\text{H}_3\text{N}\cdot\text{BH}_3$	121

Figure	4.2	$^{11}\text{B}$ NMR of reaction mixture without any hydrolysis using $\text{H}_3\text{N}\cdot\text{BH}_3$ .	121
Figure	4.3	$^1\text{H}$ NMR study comparison of reaction mixture without any hydrolysis using $\text{HMe}_2\text{N}\cdot\text{BH}_3$	122
Figure	4.4	$^{11}\text{B}$ NMR of reaction mixture without any hydrolysis using $\text{HMe}_2\text{N}\cdot\text{BH}_3$	122
Figure	4.5	(i) $^{11}\text{B}$ NMR spectra of pure dimethylamine borane. (ii) Reaction of 1 eq. dimethylamine borane with 40 mol% of iodine at $80^\circ\text{C}$ in $\text{CDCl}_3$ .	124
Figure	4.6	A) Reaction of ester with ADB and $\text{NH}_2\text{BH}_2$ to form Int_2. B) Various pathways for the reduction of esters in the presence of $\text{I}_2/\text{H}_3\text{N}\cdot\text{BH}_3$ using DFT calculations.	125
Figure	4.7	$^1\text{H}$ NMR spectrum of compound <b>9k</b>	128
Figure	4.8	$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound <b>9k</b>	128
Figure	4.9	$^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of compound <b>9k</b>	129
Figure	4.10	$^1\text{H}$ NMR spectrum of compound <b>9u</b>	129
Figure	4.11	$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound <b>9u</b>	130
Figure	4.12	$^1\text{H}$ NMR spectrum of compound <b>11a</b>	130
Figure	4.13	$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound <b>11a</b>	131
Figure	4.14	$^1\text{H}$ NMR spectrum of compound <b>11e</b>	131
Figure	4.15	$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound <b>11e</b>	132
Figure	4.16	$^1\text{H}$ NMR spectrum of compound <b>11f</b>	132
Figure	4.17	$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound <b>11f</b>	133
Figure	4.18	$^1\text{H}$ NMR spectrum of compound <b>11h</b>	133
Figure	4.19	$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound <b>11h</b>	134
Figure	4.20	$^1\text{H}$ NMR spectrum of compound <b>17</b>	134
Figure	4.21	$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound <b>17</b>	135
Figure	4.22	$^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of compound <b>17</b>	135

CHAPTER	5		
Figure	5.1.	$^{11}\text{B}$ NMR spectra indicating the formation of ADB and diborane with changes in the stoichiometry of $\text{BBr}_3$	156
Figure	5.2.	$^{11}\text{B}$ NMR spectra of reaction mixture with $\text{ICl}$ as Lewis acid at $80\text{ }^\circ\text{C}$	164
Figure	5.3.	$^{11}\text{B}$ NMR spectra of reaction mixture with $\text{ICl}$ as Lewis acid at $50\text{ }^\circ\text{C}$	164
Figure	5.4.	$^{11}\text{B}$ NMR spectra of reaction mixture with $\text{ICl}$ as Lewis acid at rt	165
Figure	5.5.	$^{11}\text{B}$ NMR spectra of reaction mixture with $\text{IBr}$ as Lewis acid at $80\text{ }^\circ\text{C}$	165
Figure	5.6.	$^{11}\text{B}$ NMR spectra of reaction mixture with $\text{IBr}$ as Lewis acid at $50\text{ }^\circ\text{C}$	166
Figure	5.7.	$^{11}\text{B}$ NMR spectra of reaction mixture with $\text{Br}_2$ as Lewis acid at $80\text{ }^\circ\text{C}$	166
Figure	5.8.	$^{11}\text{B}$ NMR spectra of reaction mixture with $\text{Br}_2$ as Lewis acid at $50\text{ }^\circ\text{C}$	167
Figure	5.9.	$^{11}\text{B}$ NMR spectra of reaction mixture with $\text{Br}_2$ as Lewis acid at rt	167
Figure	5.10.	$^{11}\text{B}$ NMR spectra of the reaction mixture with $\text{GaCl}_3$ as Lewis acid at $80\text{ }^\circ\text{C}$	168
Figure	5.11.	$^{11}\text{B}$ NMR spectra of the reaction mixture with $\text{GaCl}_3$ as Lewis acid at $50\text{ }^\circ\text{C}$	168
Figure	5.12.	$^{11}\text{B}$ NMR spectra of the reaction mixture with $\text{GaCl}_3$ as Lewis acid at rt	169
Figure	5.13.	$^{11}\text{B}$ NMR spectra of the reaction mixture with $\text{InCl}_3$ as Lewis acid at $80\text{ }^\circ\text{C}$	169
Figure	5.14.	$^{11}\text{B}$ NMR spectra of the 2,4,6-tribromoborazine by the	170

		reaction of $\text{NH}_4\text{Br}$ and $\text{BBr}_3$ at rt	
Figure	5.15.	$^{11}\text{B}$ NMR spectra of the reaction mixture of $\text{H}_3\text{N}\cdot\text{BH}_3$ (1 eq.) and $\text{BBr}_3$ (25 mol%) at rt	170
Figure	5.16.	$^{11}\text{B}$ NMR spectra of ADB and $\text{B}_2\text{H}_6$ with change in stoichiometry of $\text{AlCl}_3$	171
Figure	5.17.	$^{11}\text{B}$ NMR spectra of ADB and $\text{B}_2\text{H}_6$ with change in stoichiometry of $\text{BCl}_3$	171
CHAPTER	6		
Figure	6.1	$^1\text{H}$ NMR spectrum of compound <b>27a</b>	189
Figure	6.2	$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound <b>27a</b>	189
Figure	6.3	$^1\text{H}$ NMR spectrum of compound <b>27j</b>	190
Figure	6.4	$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound <b>27j</b>	190
Figure	6.5	$^1\text{H}$ NMR spectrum of compound <b>28a</b>	191
Figure	6.6	$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound <b>28a</b>	191
Figure	6.7	$^1\text{H}$ NMR spectrum of compound <b>28l</b>	192
Figure	6.8	$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound <b>28l</b>	192
Figure	6.9	$^1\text{H}$ NMR spectrum of compound <b>28m</b>	193
Figure	6.10	$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound <b>28m</b>	193
Figure	6.11	$^1\text{H}$ NMR spectrum of compound <b>28p</b>	194
Figure	6.12	$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound <b>28p</b>	194
Figure	6.13	$^1\text{H}$ NMR spectrum of compound <b>26a</b>	195
Figure	6.14	$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound <b>26a</b>	195
Figure	6.15	$^{11}\text{B}$ NMR spectra of reaction mixture of acetyl ferrocene with $\text{H}_3\text{N}\cdot\text{BH}_3$ in $\text{D}_2\text{O}$ medium (in $\text{D}_2\text{O}$ )	196
Figure	6.16	$^{11}\text{B}$ NMR spectra of reaction mixture of acetyl ferrocene with $\text{H}_3\text{N}\cdot\text{BH}_3$ in the presence of dimethylamine in $\text{D}_2\text{O}$ (in $\text{D}_2\text{O}$ )	196

## LIST OF TABLES

CHAPTER			Page
3			
Table	3.1	Optimization of promoter and temperature for reduction of acetanilide	70
Table	3.2	Effect of solvent for reduction of secondary amides	70
Table	3.3	Effect of amount of ammonia-borane and time for reduction of secondary amides	71
Table	3.4	Effect of amount of iodine for reduction of tertiary amides	71
CHAPTER	4		
Table	4.1	Optimization of promoter and temperature for reduction of ethyl benzoate	112
Table	4.2	Effect of amount of ammonia-borane and time for reduction of esters	113
Table	4.3	Effect of solvent for reduction of ethyl benzoate	113
Table	4.4	Effect of temperature, amount of iodine and ammonia borane for the reduction of methyl 4-bromobenzoate	114
CHAPTER	5		
Table	5.1	Effect of reaction temperature on the formation of ADB from AB and Lewis acids	154

Table	5.2	Products formed with boron halides based Lewis acids	157
Table	5.3	Effect of temperation on formation of ADB and B <sub>2</sub> H <sub>6</sub>	158
Table	5.4	Reduction of acetanilide using different Lewis acids	158
Table	5.5	Reduction of esters using different Lewis acids	159

## CHAPTER 6

Table	6.1.	Optimization for reduction for acetylferrocene to alcohol	177
Table	6.2	Optimization for reduction for acetylferrocene to ethylferrocene	178
Table	6.3	Optimization for conversion of ferrocenium to ferrocene	179

## List of Abbreviations Used

AB	Ammonia borane
<sup>i</sup> Pr	Isopropyl
Calcd.	Calculated
Cp	Cyclopentadiene
ADB	$\mu$ -Aminodiborane
Me	Methyl
Et	Ethyl
Ph	Phenyl
Fc	Ferrocene
Mp	Melting point
rt	Room temperature
h	Hour(s)
min	Minutes
THF	Tetrahydrofuran
UV	Ultraviolet spectroscopy
TLC	Thin layer chromatography
NMR	Nuclear magnetic resonance spectroscopy
HRMS	High resolution mass spectroscopy
DMSO	Dimethyl sulfoxide
DCM	Dichloromethane
DMF	<i>N, N</i> -Dimethyl formamide

Aq.	Aqueous
DCE	1, 2-dichloroethane
GC-MS	Gas chromatography mass spectrometry
BCF	Tris(pentafluorophenyl)borane
<sup>t</sup> Bu	tert-butyl
MIDA	<i>N</i> -Methyliminodiacetic acid
SM	Suzuki-Miyaura
OAc	Acetoxy group
<sup>i</sup> Pr	isopropyl
X	Halide
OTf	Trifluoromethanesulfonate
Ar	Aryl
DCE	1,2-Dichloroethane
<sup>n</sup> Bu	n-butyl
Pin	Pinacol
Cat	Catalyst
BBN	9-Borabicyclo[3.3.1]nonane
BTHF	Borane–tetrahydrofuran
BMS	Borane dimethylsulfide
TMEDA	Tetramethylethylenediamine
TM	Transition metals
CTB	Cyclotriborazane
BCDB	B-(cyclodiborazanyl)amine borane

ADB	$\mu$ -Aminodiborane
DB	Diborane
TMS	Tetramethylsilane
Bn	Benzyl group
Cp	Cyclopentadiene
MTBE	Methyl tert-butyl ether
HFIP	Hexafluoroisopropanol
DFT	Density functional theory
RBF	Round bottom flask
Wt%	Weight %
NBS	<i>N</i> -Bromosuccinimide
NIS	<i>N</i> -Iodosuccinimide
1,4-PDO	1,4-Pentanediol
RDS	Rate-determining step