Boranes as an Effective Starting Point in Boron Mediated Reactions

M.Sc. Thesis

By

PARMOD

DEPARTMENT OF CHEMISTRY

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Boranes as an Effective Starting Point in Boron Mediated Reactions

A THESIS

Submitted in partial fulfilment of the

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by

PARMOD

DEPARTMENT OF CHEMISTRY

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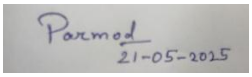
INDORE

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **Boranes as an Effective Starting Point in Boron Mediated Reactions** in the partial fulfillment of the requirements for the award of the degree of **MASTER OF SCIENCE** and submitted in the **DEPARTMENT OF CHEMISTRY, Indian Institute of Technology Indore**, is an authentic record of my own work carried out during the time period from July 2024 to May 2025 under the supervision of **Dr. Dipak K. Roy**. The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.



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Signature of M.Sc. Thesis Supervisor **Dr. Dipak K. Roy**

Parmod has successfully given his M.Sc. Oral Examination held on **14-05-2025**

Signature M.Sc. thesis Supervisor
Date: 21.05.2025

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Parmod

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ABSTRACT

Boranes as an Effective Starting Point in Boron Mediated Reactions

by

Parmod

Main Group and Organometallics (MGO) Laboratory

Department of Chemistry,

Indian Institute of Technology Indore, India.

Thesis supervisor: **Dr. Dipak K. Roy**

Boranes made up of boron and hydrogen atoms, are fascinating compounds known for their diverse structures and high reactivity. Because of these properties, they play important roles in various chemical transformations—ranging from reduction reactions and hydride transfers to catalysis in polymerization and cross-coupling processes. N-heterocyclic carbenes (NHCs), which are strong electron donors, are often used as ligands to stabilize reactive species, not only in transition metal chemistry but also in main group systems like boron. When NHCs form adducts with boranes, the resulting compounds are electrophilic and can undergo interesting acid-base reactions.

Building on this, introducing an extra carbon at the 2-position of the NHC ring leads to N-heterocyclic olefins (NHOs), which are even more nucleophilic and tunable than NHCs. In NHO–boranes, the alkene group donates electron density to the boron center, making it more reactive and opening the door to new types of reactivity.

In this thesis, I explore the synthesis of NHO–borane adducts and examine how they behave in acid–base reactions. Through this work, I aim to contribute to a better understanding of how these systems function and how we might harness them to design new, more versatile compounds in main-group chemistry.

LIST OF PUBLICATIONS

Co-author publications.

- Rahul Kumar Yadav, Darakshan Parveen, **Parmod Jangra**, Bijan Mondal* and Dipak Kumar Roy* (2025). Synthesis, Characterization, and Reactivity of Aminotroponiminate Based Difluoroboranes: A Pathway Towards Bore(boro)nium Cations. *Inorg. Chem.* DOI: 10.1021/acs.inorgchem.5c00451
- Rahul Kumar Yadav, Darakshan Parveen, **Parmod Jangra**, and Dipak Kumar Roy* (2025). Exploring New Frontiers in the Synthesis and Reactivity of N-Heterocyclic Olefin Borane Adducts **(*Manuscript under preparation*)**

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ABBREVIATIONS

°C	Temperature in degrees Celsius
br	Broad
d	Doublet
DCM	Dichloromethane
Dipp	2,6-Diisopenylphenyl
e^-	An electron
e.g.	Exempli gratia/for example
ESI	Electronspray ionisation
g	Gram
mg	Miligram
HOMO	Highest occupied molecular orbital
Hz	Hertz, s^{-1}
i.e.	id est/it is, in other words
in vacuo	In a vacuum/under vacuum
LUMO	Lowest unoccupied molecular orbital
m	Multiplet
MHz	Megahertz
mL	Millilitre/$1x10^{-3}$L
mol	Moles
NHC	N-heterocylic carbene
J	Coupling constant between nuclei
NMR	Nuclear Magnetic Resonance
ppm	Parts per million
s	Singlet
t	Triplet
THF	Tetrahydrofuran

“Dedicated to my Family”

Chapter 1

1.1 Importance of Boron in the Periodic table:

Group 13 elements of the periodic table, including boron (B), aluminum (Al), gallium (Ga), indium (In), thallium (Tl), and nihonium (Nh), exhibit a diverse range of chemical and physical properties. The variation within the group is primarily due to the transition from boron's nonmetallic behavior to the heavier elements' increasing metallic characteristics. *[1]* Boron stands out due to its unique electronic structure, bonding properties, and extensive chemistry, materials science, and industry applications. The electronic properties are discussed following:

1.1.1 Electronic Configuration and Oxidation States in Group 13

All the elements of group 13 have electronic configuration ns^2np^1, which commonly shows the +3-oxidation state. When we move down the group, the stability of this oxidation state decreases due to the inert pair effect, which arises from the poor shielding of the nuclear charge by *d*— and *f*-electrons. This makes the +1-oxidation state more stable in heavier elements like thallium and indium. *[1]*

1.1.2 Boron's Unique Bonding and Structural Features

Boron's chemistry is distinct from the other Group 13 elements due to its electron deficiency, which prevents it from forming covalent bonds like carbon or silicon. Boron can form electron-deficient bonds, like the three-center two-electron (3c–2e) bonds seen in boron hydrides (boranes). A well-known example is diborane (B_2H_6), where two hydrogen atoms bridge two boron atoms, creating delocalized bonds. *[2]*

Another important characteristic of boron is its tendency to form polyhedral boranes (B_nH_n) and carboranes, which are clusters with

delocalized bonding. These clusters are of particular interest in materials science and medicinal chemistry due to their thermal stability, electron delocalization, and chemical versatility. *[3]* Unlike the metallic elements of the group, boron exhibits extensive catenation (bonding to itself), forming complex structures such as boron nitride (BN) and boron-rich ceramics, which have industrial significance. *[4]*

1.1.3 Lewis Acidity of Boron Compounds

Boron compounds are known for their strong Lewis acidity, which arises from boron's electron deficiency. Compounds such as boron trifluoride (BF_3) and boron trichloride (BCl_3) readily accept electron pairs from Lewis bases, forming adducts. *[5]* This property is widely exploited in organic synthesis and catalysis, where boron-based Lewis acids facilitate important chemical reactions, such as hydroboration and Suzuki coupling. *[6]*

Boric acid (H_3BO_3), another significant boron compound, functions as a weak Lewis acid rather than a traditional Brønsted acid. This property is crucial in biological and industrial applications, particularly in antiseptics, pharmaceuticals, and buffer solutions. *[7]*

1.2 EXPLORATION OF LIGANDS IN MAIN GROUP CHEMISTRY: AN OUTLOOK

1.2.1 Historical Development and Comparative Analysis of N-Heterocyclic Olefins and N-Heterocyclic Carbenes

1.2.1.1 Introduction and background of N-Heterocyclic carbene:

N-heterocyclic carbenes (NHCs) have a rich history in chemistry, particularly in the field of catalysis. The discovery of the nucleophilic role of NHCs in coenzyme vitamin B12 by Mizuhara in 1951 sparked interest in these compounds.*[8]* Bertrand's discovery of the first stable carbene, an acyclic phosphino silyl, in 1988 *[9]* and Arduengo's synthesis of the first isolable and bottleable imidazoline-2-ylidene NHC, 1,3-di(adamantyl)imidazol-2-ylidene (**Figure 1.1**), in 1991 *[10]* paved

the way for further exploration of NHCs. Wanzlick and Ofele first applied NHCs as ligands in 1968, forming complexes with metals. *[11-12]* Arduengo's isolation of the first free, stable, and crystalline NHC solidified his position as the "godfather" of NHCs and marked the beginning of carbene chemistry. *[10]*

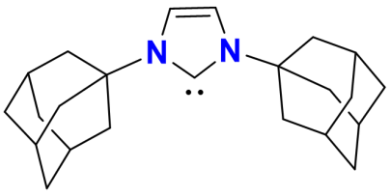


Figure 1.1. First crystalline NHC

NHCs are a class of ligands that have gained widespread attention in various fields of chemistry due to their unique electronic properties. Unlike traditional ligands such as phosphines, NHCs are neutral, divalent carbon-based ligands with a lone pair that makes them strong σ-donors. Their stability arises from electronic delocalization and the support of adjacent nitrogen atoms, though they remain highly reactive as ligands. *[13]* They are bivalent and possess six electrons in their valence shell, with at least one hetero atom present in the ring skeleton. NHCs are excellent two-electron donors and have found numerous applications in inorganic and organometallic chemistry, as well as in organocatalysis and transition-metal catalysis. *[13-14]* Due to their ease of synthesis and low cost, NHCs have become an attractive alternative to traditional ligands in many catalytic applications. *[14]*

NHCs' electronic and steric effects are characterized by the two bulky Adamantyl groups, which kinetically stabilize the carbene center by preventing dimerization to olefins. *[15]* The cyclic structure of NHCs favors the bent singlet ground state, and the backbone substituents affect the carbene electronics and are stabilized by aromaticity. *[13]* Furthermore, the nitrogen atoms in NHCs exhibit σ-electron donating and π-electron withdrawing effects (**Figure 1.2**), which lower the energy of the HOMO and raise the energy of the LUMO, enhancing the σ-donor strength of NHCs *[16]*. The lone pair on the carbene carbon lies in the

plane of the heterocyclic ring, making NHCs strong nucleophiles. Rotation around the metal–carbene bond can alter the steric and electronic environment of the NHC, leading to anisotropic behavior *[17]*.

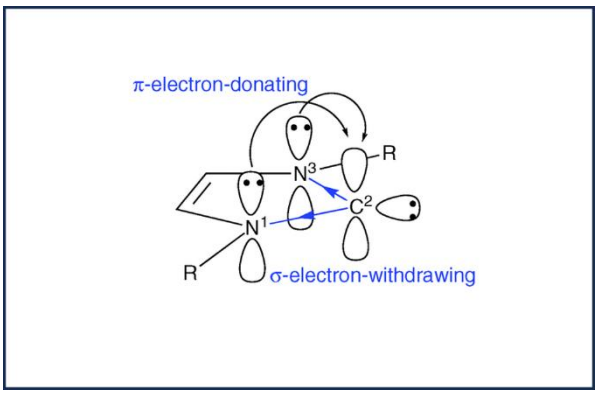


Figure 1.2. Electronic Nature in NHCs

NHCs possess a unique sp^2-hybridized lone pair, which allows them to form stronger bonds with various metal complexes than phosphines. *[16]* Singlet NHCs have their lone pair located in a hybridized orbital that resides in the plane of the ring (HOMO) and parallel to it (LUMO), contributing to their robust bonding characteristics *[16,18]*. These steric and electronic features make NHCs highly applicable as ligands in transition-metal catalysis, contributing to enhanced complex stability [20-21]. Additionally, NHCs can act as both electron donors and acceptors, making them versatile organocatalysts for a range of coupling reactions *[14]*.

N-heterocyclic carbenes have emerged as an effective method for stabilizing low-coordinated compounds in different oxidation states of main group elements *[14,19]*. NHCs form stable adducts with non-metals and semi-metallic species, and their complexes with metals exhibit σ-donation from the carbene to the vacant p-orbital of p-block elements, resulting in highly stable, non-labile complexes with unique properties and reactivities *[19-20] e.g.* the adducts **(a)** [(IMes)AlH_3] *[21]* and **(b)** [(IMes)-GeI_2] *[22]* demonstrate distinctive imidazolium character, with tetrahedral and trigonal-pyramidal geometries around the aluminum and germanium centers, respectively.

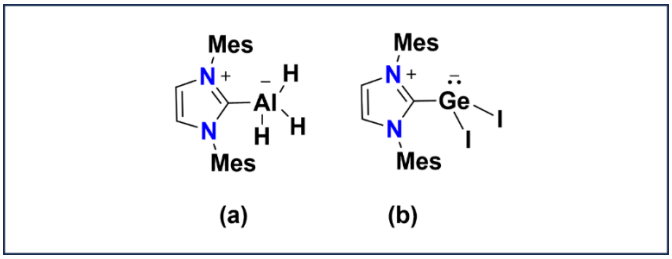


Figure 1.3 Examples of N-Heterocyclic Carbene Main Group Element Adducts

In main group chemistry, N-heterocyclic carbenes have two major applications in chemistry. First, they are widely used for stabilizing compounds in low oxidation states. Their strong electron-donating properties provide sufficient electron density to stabilize reactive species in their lower oxidation states, preventing excessive reactivity. Second, NHCs are utilized in the formation of multiple bonds in heavier p-block congeners. Their ability to form stable complexes with these elements allows for the creation of compounds with unusual bonding, enabling the study of new chemical species and reactions in main group chemistry *[20]*. The success of these applications depends on quantifying the steric and electronic properties of NHCs *[15,17]*. In particular, the sustainability of low-valent main group species relies on both strong electron donation and steric protection provided by bulky NHC ligands *[20,23]*. For multiple bonding in heavier congeners of carbon, such steric bulk prevents nucleophilic or electrophilic attack at the reactive centers *[23]*. Overall, the use of NHCs in main-group chemistry has proved to be a valuable tool in stabilizing and modifying the properties of low-coordinated compounds across various oxidation states.

1.2.2 Introduction to N-Heterocyclic Olefins (NHOs)

After the success of NHCs in main group chemistry, N-heterocyclic olefins (NHOs) were developed as a new type of ligand that offers similar stability but with different bonding and greater reactivity. N-heterocyclic olefins (NHOs) represent a relatively recent addition to the family of heterocycle-stabilized electron-rich organic species. Structurally, NHOs are composed of an electron-rich exocyclic double

bond (C=C) adjacent to a nitrogen-containing heterocycle, often derived from an imidazole or imidazoline backbone. Their conceptual design was inspired by the rich chemistry of N-heterocyclic carbenes (NHCs), but with key differences in electronic structure and reactivity.

The first significant recognition of NHOs as a unique class of compounds occurred in the late 2000s. Bertrand and co-workers were among the first to synthesize and characterize stable NHO derivatives, demonstrating that such compounds could exhibit remarkable donor properties and nucleophilicity due to conjugation between the exocyclic alkene and the electron-donating nitrogen atoms embedded in the ring system *[24]*. These findings paralleled the earlier revolution in stable carbenes initiated by Arduengo's work on NHCs in 1991 *[25]*, but offered new possibilities in both organocatalysis and coordination chemistry.

The development of NHOs has grown significantly, with contributions from both theoretical and synthetic chemists. Quantum chemical studies have highlighted their exceptionally high HOMO energies and strong π-donor abilities, making them some of the most nucleophilic neutral organic molecules. *[26]* In the last decade, their use as ligands to make NHO complexes with In (**Figure 1.4**) **(c)** low-valent metals *[26]*, **(d-e)** rare earth metals *[27]*, and **(f)** transition metal chemistry *[28]* has grown significantly.

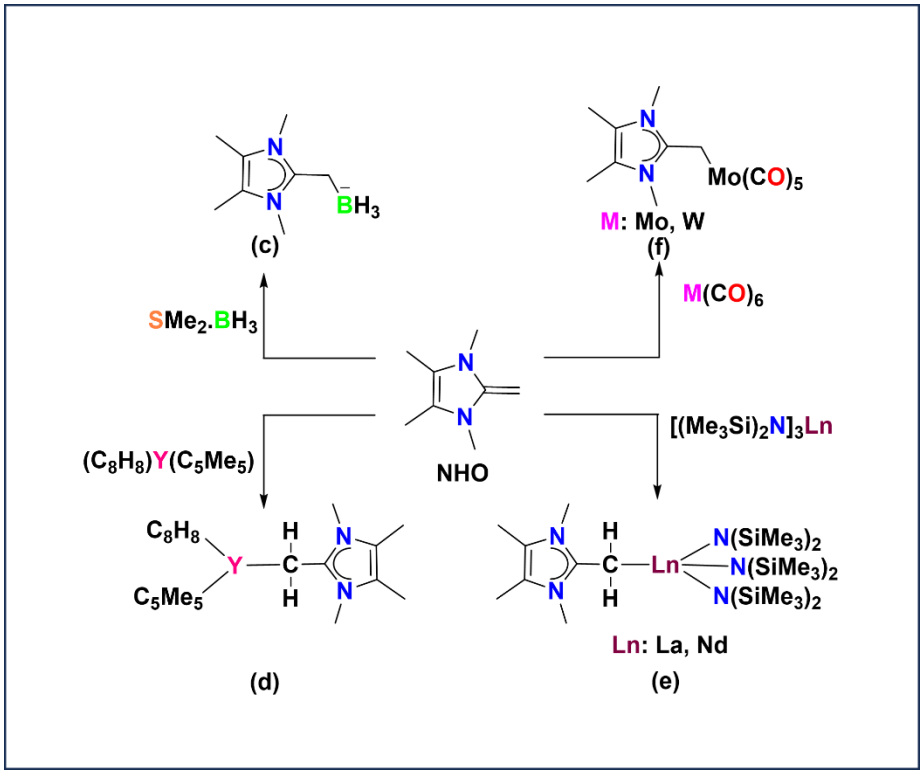


Figure 1.4 Examples of NHO Complexes

1.2.3 Comparison with N-Heterocyclic Carbenes (NHCs)

NHCs have long been recognized as versatile ligands in organometallic chemistry, particularly for their strong σ-donating and weak π-accepting character. This electronic profile allows NHCs to stabilize reactive metal centers, making them indispensable in homogeneous catalysis, organocatalysis, and coordination chemistry. The prototypical NHC features a divalent carbon atom flanked by two nitrogen atoms within a heterocyclic ring, which delocalizes electron density and imparts stability to the otherwise highly reactive carbene center *[25]*.

By contrast, NHOs replace the divalent carbene carbon with an exocyclic alkene moiety, resulting in a markedly different electronic distribution. The alkene in NHOs is conjugated to the nitrogen atoms of the heterocycle, leading to an electron-rich π-system. This configuration results in stronger overall donor character compared to NHCs, particularly in terms of π-donation *[26,30]*. As ligands, NHOs have demonstrated an ability to stabilize electron-deficient main-group

compounds, facilitate unusual bonding motifs, and modulate the reactivity of metal centers in novel ways.

Table 1. 1 Comparison between NHCs and NHOs

Feature	**N-heterocyclic carbenes (NHCs)**	**N-heterocyclic Olefins (NHOs)**
Central motif	Divalent carbene carbon	Exocyclic C=C alkene adjacent to heterocycle
First stable form isolated	1991 (Arduengo)	~2007 (Bertrand et al.)
Electronic properties	Strong σ-donor, weak π-acceptor	Very strong π-donor due to electron-rich alkene
Reactivity focus	Metal coordination, small molecule activation	Zwitterionic structures, nucleophilic catalysis
Donor strength	High (σ-donor)	Very high (π-donor dominant)
HOMO energy	High	Very high
Ligand applications	Organometallic catalysis, ligand design	Stabilization of low-valent species, donor ligands
Stability	Thermodynamically and kinetically stable	Stable, less reactive than typical olefins

Despite their structural resemblance, NHOs are not simply alkene analogues of NHCs. Their unique donor characteristics make them especially suited for roles where extreme electron donation is required, such as in stabilizing electron-deficient main group species or developing zwitterionic intermediates in organocatalytic processes *[30]*. Additionally, the relative kinetic and thermodynamic stability of NHOs allows for their incorporation into complex ligand scaffolds, paving the way for their use in advanced catalytic systems and supramolecular architectures.

1.3 Comparison of N-Heterocyclic Boranes and N-Heterocyclic Olefin–Boranes: Structural and Reactivity Aspects

The development of borane adducts with nitrogen-based heterocycles has significantly impacted main-group and organoboron chemistry. Two major classes in this field are N-Heterocyclic carbene Boranes (NHC·BH_3) and N-Heterocyclic Olefin–Boranes (NHO·BH_3). While both involve coordination to boron, they exhibit fundamentally different bonding and electronic properties, leading to divergent reactivity profiles. This section compares these two systems and elaborates on why NHO·BH_3 complexes demonstrate enhanced reactivity compared to NHC·BH_3 adducts. NHC·BH_3 c[7]lexes feature a direct σ-donation from a carbene lone pair (sp^2-hyb :ed carbon) to the empty p-orbital of BH_3, forming a localized and strong dative bond *[24]*. In contrast, NHO·BH_3 adducts involve π-donation from an exocyclic C=C bond of the NHO into the vacant orbital of boron, creating a delocalized π-complex *[25]*. The C=C double bond in NHOs has a higher HOMO energy than the lone pair in NHCs, contributing to stronger π-donation and increased polarization within the complex *[26]*.

Table 1.2 Electronic Effects and Bonding

Feature	**NHC·BH_3**	**NHO·BH_3**
Donor type	σ-donor (sp^2 lone pair on carbene)	π-donor (C=C double bond)
HOMO energy	High	Very high
Bonding interaction	Localized C→B σ-bond	Delocalized π→B donation
Bond strength	Strong, relatively inert	Strong but more labile/reactive
Reactivity	Low to moderate	High (due to polarized C=C–B bond)

1.4 NHO·BH_3 More Reactive than NHC·BH_3

Higher HOMO Energy: The exocyclic C=C bond in NHOs features a higher-energy HOMO, making it more nucleophilic and reactive toward BH_3 *[25-26,30]*. This results in enhanced π-donation and a more polarized B–C=C bond.

Polarized Bonding: The π-type B–C=C interaction is more polarized compared to the σ-donation in NHC·BH_3, which increases the electrophilic/nucleophilic duality of the complex *[31]*.

Dynamic Bonding: The fluxional nature of the B–C=C interaction allows NHO·BH_3 to engage in reversible bonding and makes the borane more accessible for further transformations *[32]*.

Facile Activation: NHO·BH_3 complexes can undergo deprotonation or participate in frustrated Lewis's pair (FLP) chemistry more readily than NHC·BH_3, enabling unique reactivity patterns in small molecule activation and catalysis *[33-34]*.

1.5 Application of N-heterocyclic carbene Boranes:

N-heterocyclic carbene (NHC) boranes are versatile compounds with a wide range of applications in organic synthesis, materials science, and catalysis, due to their stability, un[8]reactivity, and ability to serve as boron-based reagents.

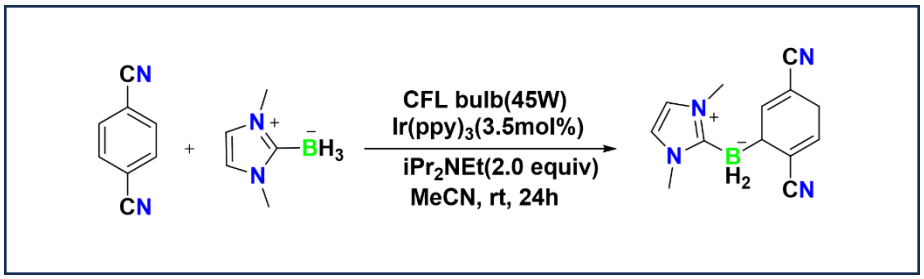
1.5.1 Hydroboration Reactions

NHC-boranes have been used as hydroborating agents to reduce alkenes, alkynes, and carbonyl compounds, providing an alternative to classical boranes like 9-BBN or catecholborane.

1.5.1.1 Selective 1,4-Hydroboration of Electron-Deficient Aromatic Systems via NHC–Borane Complexes:

A notable advancement in the functionalization of electron-deficient aromatic compounds was reported by Curran et al., who demonstrated that N-heterocyclic carbene boranes (NHC–boranes) can undergo

efficient 1,4-hydroboration under radical conditions. This transformation enables regioselective para-hydroboration of arenes bearing strong electron-withdrawing substituents such as nitro or cyano groups. The reaction proceeds via a radical chain mechanism, initiated through either thermal or photoredox activation, wherein the homolytic cleavage of the B–H bond in the NHC–borane generates a boryl radical.

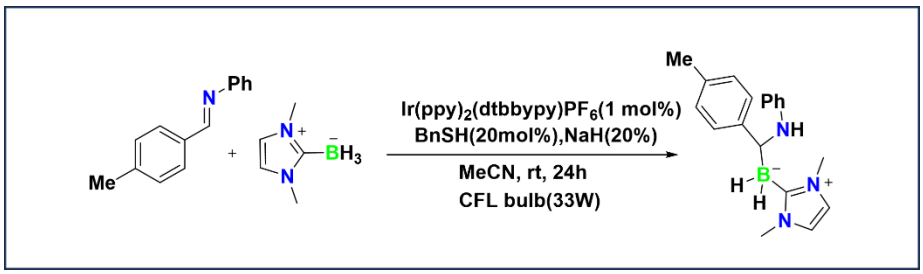


Scheme 1.1 1,4-Hydroboration of electron-poor aromatic rings

This species then undergoes selective addition to the para position of the aromatic ring, followed by hydrogen atom transfer to furnish the hydroborated product. This work significantly expands the synthetic utility of NHC–boranes, showcasing their potential in radical-mediated transformations and providing access to valuable boron-containing intermediates that are otherwise difficult to obtain via classical methods.*[35]*

1.5.1.2 Synergistic Photoredox Catalysis and Organocatalysis for the Inverse Hydroboration of Imines

Zhang and co-workers developed a novel method for the hydroboration of imines using a combination of photoredox catalysis and organocatalysis. In this process, instead of the usual reaction where boron acts as the nucleophile, the polarity is reversed—referred to as *inverse hydroboration*. The method uses visible light to activate a photocatalyst, which reduces the imine to form a carbon-centered radical

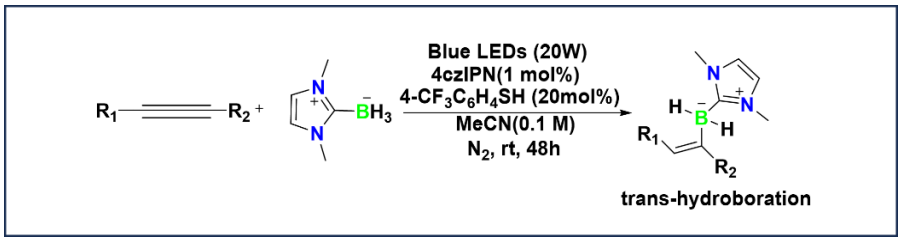


Scheme 1.2 Inverse hydroboration of imines with NHC·BH_3

This radical then reacts with an NHC–borane to form a new C–B bond. The reaction proceeds under mild conditions and shows good selectivity, providing a useful approach to synthesizing aminoborane compounds. This work highlights a new way to use NHC–boranes in radical chemistry and expands their role in C–B bond formation.*[36]*

1.5.1.3 Transition metal-free radical *trans*-hydroboration of alkynes with NHC-boranes *via* visible-light photoredox catalysis

The development of radical hydroboration for alkynes remains a significant challenge. In this work, they introduce a transition metal-free method for trans-hydroboration of alkynes using NHC-boranes. This is achieved through the synergistic combination of 4CzIPN as a photoredox organocatalyst and 4-CF_3-PhSH as a hydrogen atom transfer (HAT) catalyst.

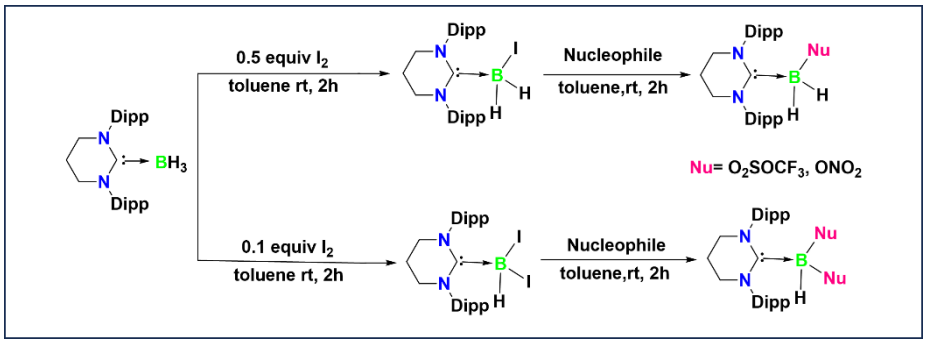


Scheme 1.3 Hydroboration of alkynes

They offer a practical, efficient, and sustainable strategy to synthesize a wide variety of (E)-alkenyl-boranes with excellent regio- and stereoselectivity, all under mild conditions. Importantly, the unique photoredox catalytic system plays a crucial role in optimizing both the reaction efficiency and selectivity.*[37]*

1.5.2 Nucleophilic Substitution Reactions:

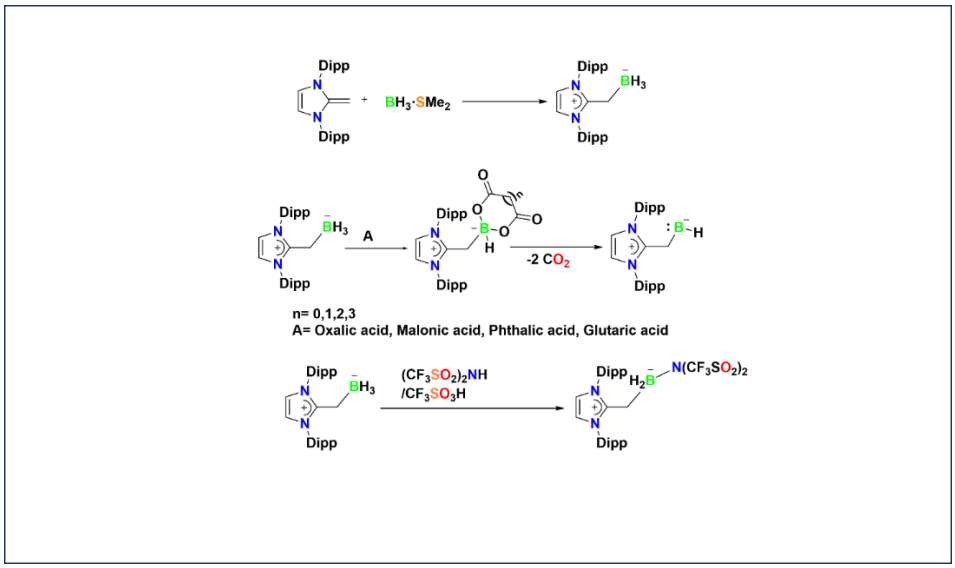
The NHC·BH_3 adduct is a highly versatile starting material that opens up many possibilities for further functionalization. When treated with a stoichiometric amount of iodine, it forms boryl iodides, which are useful intermediates for building more complex boron-containing molecules. By reacting these iodides with different nucleophiles, we can easily introduce functional groups like OTf and ONO_2 onto the borane framework.*[38]*



Scheme 1.4 Nucleophilic substitution reaction of boryl iodides.

1.6 Objective:

Many studies have focused on NHC·BH_3 and its wide applications. However, in my thesis, I am investigating the NHO·BH_3 borane adduct, which has received considerably less attention in recent years. Although there is one report that briefly discusses NHO·BH_3, comprehensive studies remain scarce *[39]*. In this work, I aim to synthesize NHO·BH_3 and explore its reactivity with diacids such as Oxalic acid, Phthalic acid, Malonic acid, and Glutaric acid in detail. I also tested the reactivity of NHO·BH_3 with strong acids like trifluoro acetic acid trifluoromethanesulfonamide, trifluoromethanesulfonimide, and was able to isolate monosubstituted products selectively.



CHAPTER 2

2. Experimental Section:

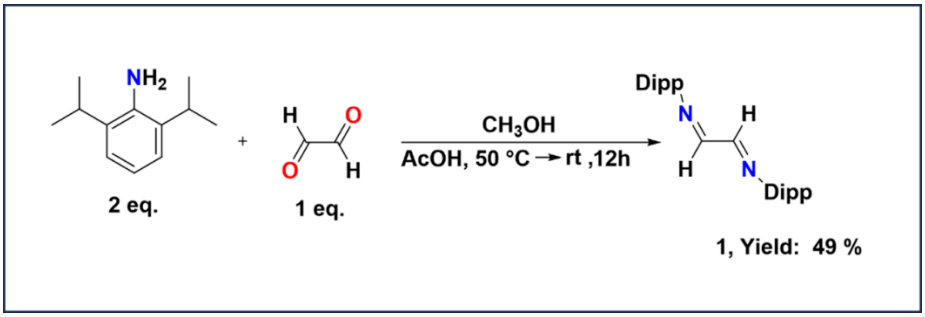
2.1 Material and Instrumentation

Reagents and chemicals were used as received if not mentioned somewhere. Solvents were purified as the standard method and stored under an inert atmosphere on 4Å molecular sieves. Several reactions were performed under the inert environment wherever mentioned and ligands or precursors were prepared in the open air. All the ^{1}H & ^{13}C NMR spectra were obtained on Bruker 500 spectrometer in $CDCl_3$ or in Benzene-d_6 operating at 500 MHz for ^{1}H NMR. Data for NMR Chemical shifts are mentioned in delta (**δ**) units, showed in ppm downfield from tetramethyl silane (TMS). $CDCl_3$ and C_6D_6 are internal standards with a residual peak at 7.26 and 7.16 ppm respectively. The ^{1}H NMR signals have been mentioned as singlet (s), doublet (d), triplet (t) & multiplet (m). Compounds were named by using Chem draw Ultra 16.0 and NMR data processed by Mestre Nova.

2.2 Synthesis of N-Heterocyclic olefin Borane adduct

Scheme 2.2.1 Synthesis of Bis(2,6-diisopropylphenyl)ethane-1,2-diimine [1]

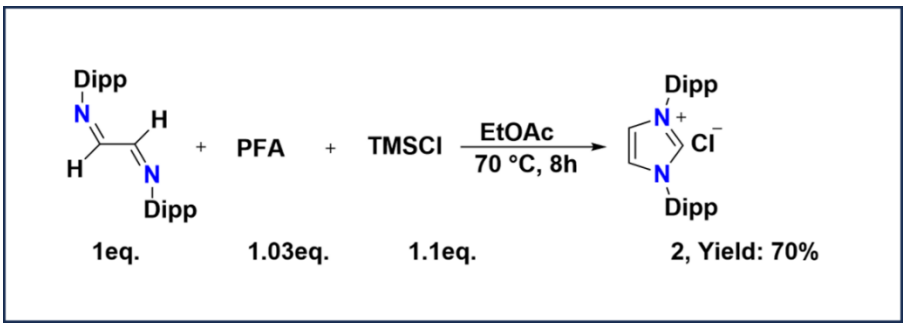
To an amine solution, 2,6-diisopropylaniline (30 ml, 180.38 mmol, 2 eq.) was added to methanol and a small amount of acetic acid. After the addition of glyoxal (5 ml, 90 mmol, 1 eq.), the mixture was heated to a temperature of 50°C. The reaction mixture was permitted to cool to room temperature and stirred for 12 hours. Once reaction was complete, a yellow solid was separated by filtration and washed with cold methanol to yield the final yellow product **[1].** Yield = **49%**.



^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (s, 2H), 7.19 (d, *J* = 6.1 Hz, 4H), 7.16 (d, *J* = 5.7 Hz, 2H), 2.94 (hept, *J* = 6.9 Hz, 4H), 1.21 (d, *J* = 6.9 Hz, 24H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.25, 148.15, 136.86, 125.26, 123.32, 31.08, 28.18, 23.53. **HRMS** (ESI) c: 13 ted for [$C_{26}H_{36}N_2$+H^+] 377.2951, found 377.2951.

Scheme 2.2.2 Synthesis of 1,3-bis(2,6-diisopropylphenyl)-1H-imidazol-3-iumchloride [2]

In a double-neck round-bottom flask, Bis(2,6-diisopropylphenyl) ethane-1,2-diimine (21.26 mmol, 8g, 1 eq.) and paraformaldehyde (21.90 mmol, 0.657g, 1.03 eq.) were added to an ethyl acetate solution. The mixture was heated under reflux for 8 hours at 70 °C in an argon atmosphere. After 3 hours of refluxing, Trimethylsilyl chloride (23.38 mmol, 2.17 ml, 1.1 eq.) was added slowly to the reaction mixture. Once the reaction was finished, the dark brown solid formed was filtered and rinsed with ethyl acetate to isolate the final dark brown product **[2].** Yield = **67%**.

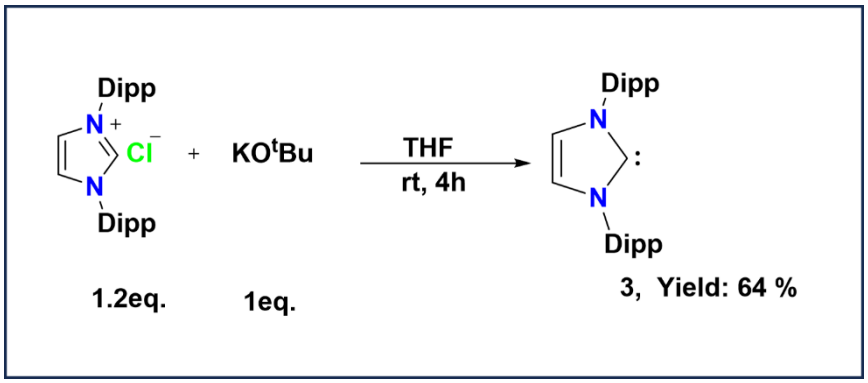


^{1}H NMR (500 MHz, $CDCl_3$) δ 10.04 (s, 1H), 8.12 (s, 2H), 7.55 (t, *J* = 7.8 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 4H), 2.42 (hept, *J* = 7.0 Hz, 4H), 1.27 (d, *J* = 6.8 Hz, 12H), 1.22 (d, *J* = 6.6 Hz, 12H). **^{13}C NMR** (126 MHz,

$CDCl_3$) δ 145.14, 132.33, 129.98, 126.86, 124.88, 29.26, 24.82, 23.87. **HRMS** (ESI) calculated for [$C_{27}H_{37}N_2$] 389.2957, found 389.2951.

Scheme 2.2.3 Synthesis of 1,3-bis(2,6-diisopropylphenyl)-1H-imidazol-3-ium-2-ide [3]

1,3-bis(2,6-diisopropylphenyl)-1H-imidazol-3-iumchloride(3g, 7mmol, 1eq.) and potassium t-butoxide (0.942g, 8.4 mmol, 1.2 eq.) were placed under vacuum in a Schlenk tube for 30 minutes. The reaction was performed in dry THF as the solvent and stirred at room temperature for four hours. After the reaction was complete, the solvent was evaporated under vacuum, and toluene was added to the mixture. The resulting brown liquid was then filtered through Celite. The solvent was once again evaporated under vacuum, and the resulting white solid was washed with hexane 2-3 times to obtain the product **[3].** Yield = **64%.**

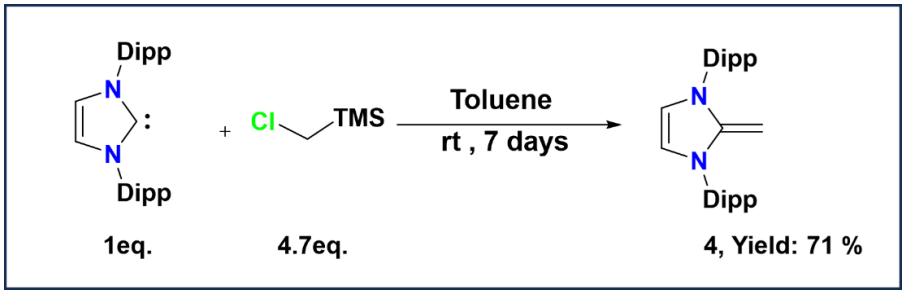


^{1}H NMR (500 MHz, C_6D_6) δ 7.32 – 7.27 (m, 2H), 7.19 (d, *J* = 7.7 Hz, 4H), 6.62 (s, 2H), 2.96 (hept, *J* = 6.9 Hz, 4H), 1.29 (d, *J* = 6.9 Hz, 12H), 1.19 (d, *J* = 7.0 Hz, 12H). **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6) δ 146.31, 138.99, 123.71, 121.57, 28.80, 24.82, 23.63.

Scheme 2.2.4 Synthesis of 2-methylene-2,3-dihydro-1H-imidazole [4]

In a Schlenk tube, 1,3-bis(2,6-diisopropylphenyl)-1H-imidazol-3-ium-2-ide (2 g, 3.86 mmol, 1 eq.) dissolved in toluene was reacted with trimethylsilyl methyl chloride (2.58 ml, 18.50 mmol, 4.79 eq.). After stirring for seven days, a minor residue formed, and the mixture was

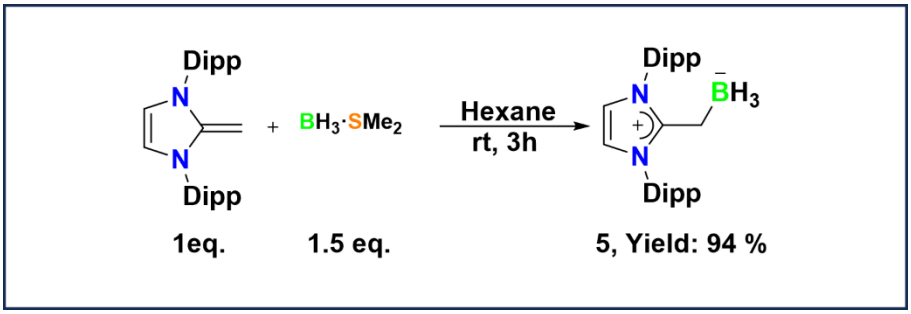
filtered through a Celite pad. The filtrate was then concentrated under a vacuum to afford the product **[4].** Yield = **71%.**



^{1}H NMR (500 MHz, C_6D_6) δ 7.24 (dd, *J* = 8.5, 6.9 Hz, 2H), 7.17 (s, 4H), 5.86 (s, 2H), 3.37 (hept, *J* = 6.9 Hz, 4H), 2.44 (s, 2H), 1.38 (d, *J* = 6.9 Hz, 12H), 1.23 (d, *J* = 6.9 Hz, 12H). **^{13}C NMR** (126 MHz, C_6D_6) δ 149.01, 134.99, 129.34, 124.60, 114.71, 28.78, 24.36, 23.91. **HRMS** (ESI) calculated for [$C_{28}H_{38}N_2$+H^+] 403.3108 ($C_{28}H_{38}N_2$+H^+), found 403.3128.

Scheme 2.2.5 Synthesis of ((1,3-bis(2,6-diisopropylphenyl)-1H-imidazol-3-ium-2-yl)methyl)trihydroboratect [5]

In a Schlenk tube, Borane dimethylsulfide (0.35ml, 3.6 mmol, 1.5 eq.) was added to a hexane solution of compound 2-methylene-2,3-dihydro-1H-imidazole (1 g, 2.4 mmol, 1 eq.). The mixture was allowed to stir at room temperature for three hours. Upon completion of the reaction, the mixture was filtered through a filter cannula, resulting in a white solid **[5]. Yield:** 94%.

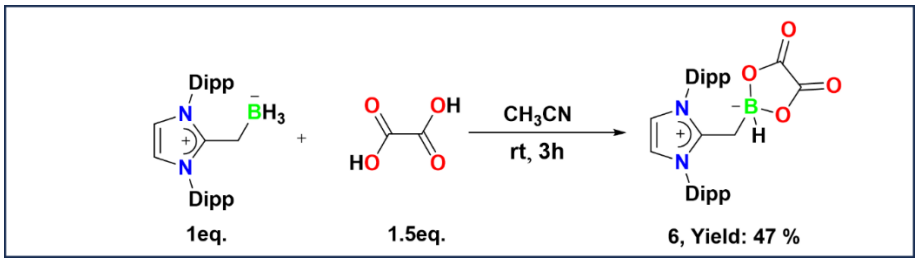


^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (t, *J* = 7.8 Hz, 2H), 7.18 (d, *J* = 7.8 Hz, 4H), 6.43 (s, 2H), 3.00 (hept, *J* = 6.8 Hz, 4H), 2.18 (q, *J* = 5.8 Hz, 2H), 1.42 (d, *J* = 6.8 Hz, 12H), 1.09 (d, *J* = 6.9 Hz, 12H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.04, 146.05, 131.09, 124.69, 120.92, 29.03, 25.89,

22.82. **^{11}B NMR** (160 MHz, $CDCl_3$) -30.50 (dd, *J* = 80.0, 54.6 Hz). **HRMS** (ESI) calculated for [$C_{28}H_{41}BN_2$-H^+] 415.3289 ($C_{28}H_{41}BN_2$-H^+) found 415.3285.

Scheme 2.2.6 Chemical reactivity of NHO·BH_3 adduct with oxalic acid [6]

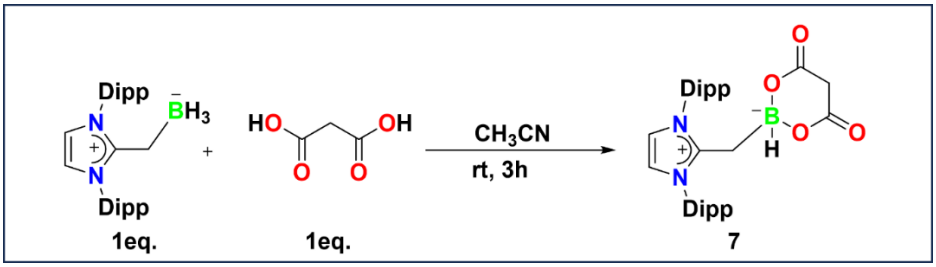
The NHO·BH_3 adduct (0.070 g, 0.16 mmol, 1 eq.) was dissolved in acetonitrile in a Schlenk tube, and oxalic acid (0.015 g, 0.16 mmol, 1.5eq.) was introduced. The mixture was stirred at room temperature for three hours under an argon atmosphere. After the reaction time, the mixture was allowed to cool to room temperature. The solvent was removed under reduced pressure, and the residue was washed with hexane, yielding the white solid product **[6].**



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (s, 2H), 7.52 (t, *J* = 7.8 Hz, 2H), 7.29 (d, *J* = 7.8 Hz, 4H), 2.20 (hept, *J* = 7.7, 6.9 Hz, 4H), 2.01 (s, 3H), 1.16 (d, *J* = 6.8 Hz, 12H), 1.09 (d, *J* = 6.9 Hz, 12H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 162.08, 159.02, 145.39, 145.13, 132.75, 129.12, 125.76, 125.56, 29.30, 24.64, 23.50, 10.88. **^{11}B NMR** (160 MHz, CDCl3) δ 7.16 – 3.16 (m). **LCMS** (ESI) calculated for [$C_{30}H_{39}N_2BO_4$+H^+] 503.3081 [$C_{30}H_{39}N_2BO_4$+H^+] found 503.3113.

Scheme 2.2.7 Chemical reactivity of NHO·BH_3 adduct with malonic acid [7]

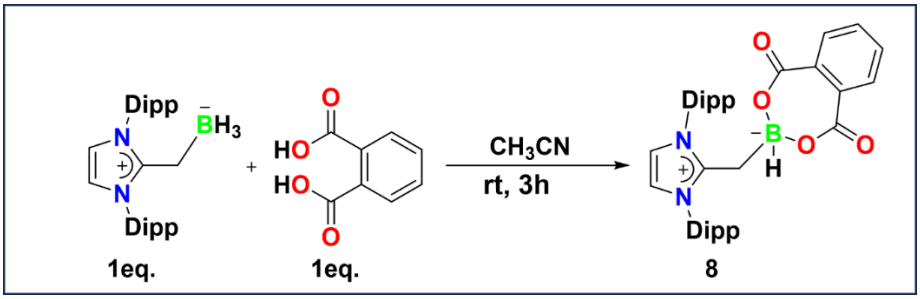
The NHO·BH_3 adduct (0.100g, 0.24 mmol, 1 eq.) and malonic acid (0.025g, 0.24 mmol, 1 eq.) were dissolved in acetonitrile in a Schlenk tube. The mixture was stirred at room temperature for three hours under an argon atmosphere. After the reaction time, solvent was removed under reduced pressure, and the residue was washed with hexane, yielding the white solid product **[7].**



^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 – 8.04 (m, 2H), 7.68 – 7.58 (m, 2H), 7.54 (q, *J* = 7.4, 6.9 Hz, 1H), 7.40 (d, *J* = 7.7 Hz, 4H), 2.30 (hept, *J* = 7.2 Hz, 4H), 2.10 (d, *J* = 2.3 Hz, 3H), 1.27 (d, *J* = 6.7 Hz, 13H), 1.19 (d, *J* = 6.9 Hz, 12H). **^{13}C{^{1}H} NMR** (126 MHz, CDCl3) δ 173.52, 144.82, 132.47, 128.90, 125.74, 125.28, 125.26, 124.71, 38.29, 29.05, 24.36, 23.21, 10.60. **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$) δ 3.34 (d, *J* = 97.1 Hz).

Scheme 2.2.8 Chemical reactivity of NHO·BH_3 adduct with phthalic acid [8]

The NHO·BH_3 adduct (0.180 g, 0.43 mmol, 1 eq.) and phthalic acid (0.070 g, 0.43 mmol, 1eq.) was dissolved in acetonitrile in a Schlenk tube. The reaction was stirred at room temperature for three hours under an argon atmosphere. After the reaction time, solvent was removed under reduced pressure, and the residue was washed with hexane, yielding the white solid product **[8].**

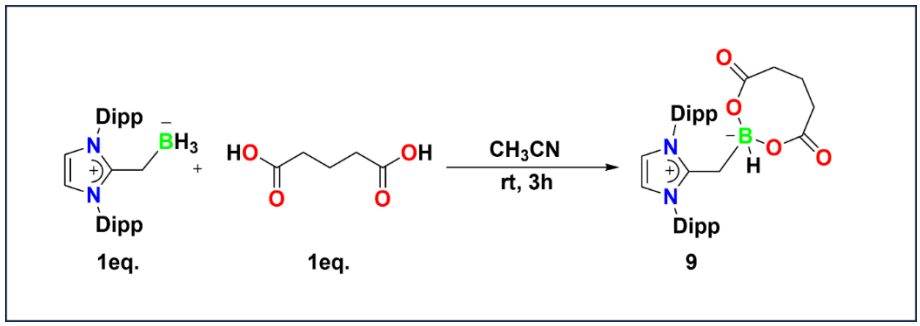


^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (dt, *J* = 7.8, 3.9 Hz, 1H), 8.06 (s, 1H), 7.78 (dd, *J* = 5.8, 3.4 Hz, 1H), 7.58 (t, *J* = 7.8 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 1H), 7.45 (dd, *J* = 6.0, 3.4 Hz, 1H), 7.42 – 7.38 (m, 1H), 7.36 (d, *J* = 7.8 Hz, 2H), 7.29 (d, *J* = 7.9 Hz, 2H), 7.12 (s, 1H), 2.64 (hept, *J* = 6.8 Hz, 2H), 2.28 (hept, *J* = 6.9 Hz, 2H), 1.98 (s, 2H), 1.23 (dd, *J* = 6.8, 3.5 Hz, 12H), 1.15 (dd, *J* = 10.1, 6.9 Hz, 12H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 170.67, 170.61, 157.78, 145.83, 145.03, 133.84, 133.53,

133.10, 132.71, 131.73, 131.06, 131.00, 130.86, 130.82, 130.77, 129.10, 125.94, 125.49, 124.95, 122.45, 29.27, 28.92, 25.99, 24.56, 23.44, 22.77, 10.84. **$^{11}B\{^{1}H\}$ NMR** (160 MHz, $CDCl_3$) δ 2.12 (d, J = 31.8 Hz).

Scheme 2.2.9. Chemical reactivity of NHO·BH_3 adduct with glutaric acid [9]

The NHO·BH_3 adduct (0.100 g, 0.24 mmol, 1 eq.) and glutaric acid (0.032 g, 0.24 mmol, 1eq.) was dissolved in acetonitrile in a Schlenk tube. The mixture was stirred at room temperature for three hours under an argon atmosphere. After the reaction completion. The solvent was removed under reduced vacco, and the residue was washed with hexane, yielding the dark yellow solid product **[9].**

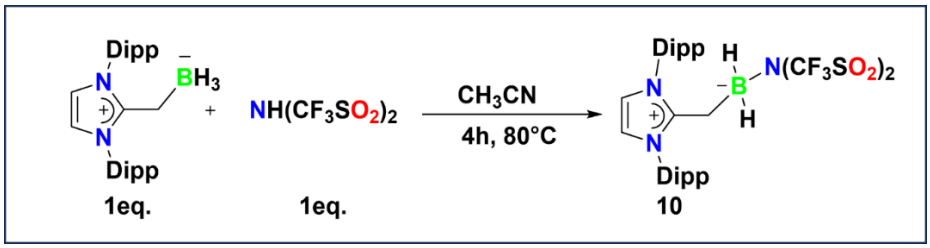


^{1}H NMR (500 MHz, CDCl3) δ 7.97 (s, 2H), 7.60 (t, J = 7.8 Hz, 2H), 7.42 – 7.33 (m, 4H), 4.64 – 3.99 (m, 3H), 2.34 – 2.21 (m, 4H), 1.99 (s, 2H), 1.25 (d, J = 6.7 Hz, 12H), 1.16 (d, J = 6.9 Hz, 13H). **$^{13}C\{^{1}H\}$ NMR** (126 MHz, $CDCl_3$) δ 177.99, 145.64, 145.10, 132.72, 129.22, 126.22, 125.53, 124.79, 35.57, 29.32, 25.82, 25.79, 25.69, 24.62, 23.51, 21.62. **^{11}B NMR** (160 MHz, $CDCl_3$) δ 1

Scheme 2.2.10. Chemical reactivity of NHO·BH_3 adduct with trifluoromethanesulfonimide [10]

The NHO·BH3 adduct (0.030 g, 0.72 mmol, 1 eq.) and trifluoromethanesulfonimide (0.030 g, 0.119 mmol, 1eq.) was dissolved in acetonitrile within a Schlenk tube. The mixture was heated at 80 °C for three hours under an argon atmosphere. After the reaction time, the mixture was allowed to cool to room temperature. The solvent was

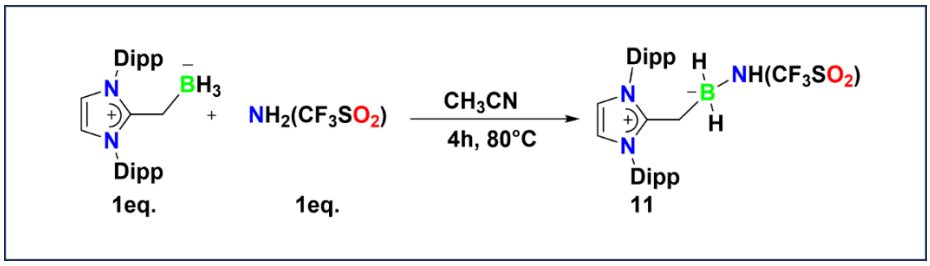
removed under reduced pressure, and the residue was washed with hexane, yielding a white solid product [10].



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (t, *J* = 7.8 Hz, 2H), 7.38 (d, *J* = 7.9 Hz, 4H), 7.23 (s, 2H), 2.50 – 2.39 (m, 4H), 2.15 (s, 2H), 1.27 (d, *J* = 6.7 Hz, 12H), 1.16 (d, *J* = 6.8 Hz, 12H). **^{11}B NMR** (160 MHz, $CDCl_3$) δ 29.16. **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 152.28, 145.69, 145.14, 132.69, 129.40, 125.65, 123.27, 29.10, 25.98, 22.80. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -78.81.

Scheme 2.2.11. Chemical reactivity of NHO·BH_3 adduct with trifluoromethanesulfonamide [11]

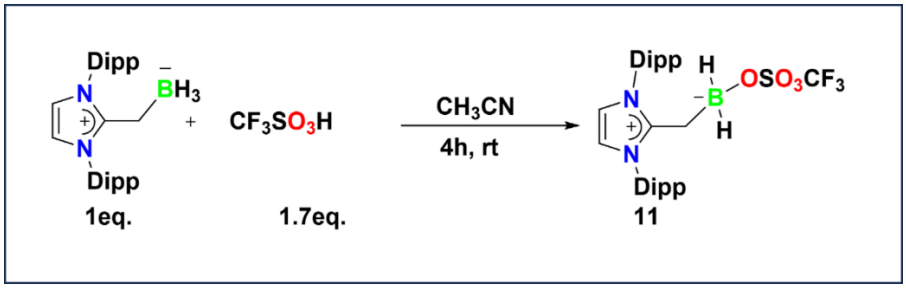
The NHO·BH_3 adduct (0.040 g, 0.096 mmol, 1 eq.) and trifluoromethanesulfonamide (0.035 g, 0.124 mmol, 1eq.) were dissolved in acetonitrile in a Schlenk tube. The mixture was heated at 80 °C for three hours under an argon atmosphere. After the reaction time, the mixture was allowed to cool to room temperature. The solvent was removed under reduced pressure, and the residue was washed with hexane, yielding the white solid product **[11].**



^{1}H NMR (500 MHz, C_6D_6) δ 7.57 – 7.50 (m, 2H), 7.40 (d, *J* = 7.8 Hz, 1H), 7.35 (d, *J* = 7.7 Hz, 4H), 7.10 (s, 1H), 6.11 (s, 2H), 2.56 – 2.43 (m, 4H), 1.63 (s, 2H), 1.32 (d, *J* = 6.9 Hz, 12H), 1.16 (d, *J* = 6.9 Hz, 12H). **^{11}B NMR** (160 MHz, C_6D_6) δ -17.99.

Scheme 2.2.12. Chemical reactivity of NHO·BH_3 adduct with triflic acid [12]

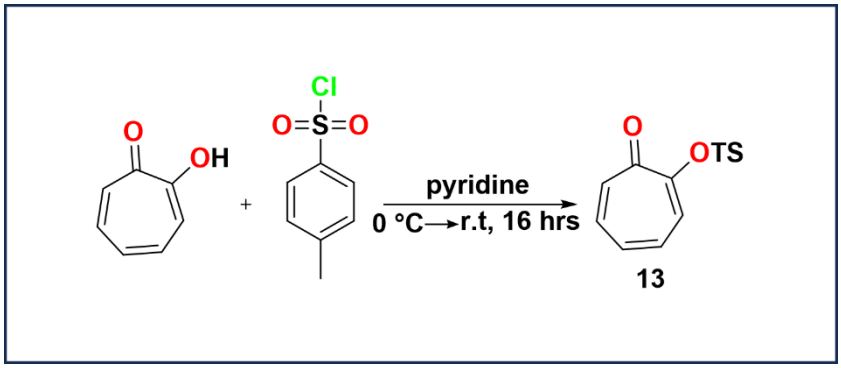
The NHO·BH_3 adduct (0.080 g, 0.192 mmol, 1 eq.) and triflic acid (0.033 ml, 0.384 mmol, 1.7 eq.) were introduced and dissolved in acetonitrile in a Schlenk tube. The reaction was performed at room temperature for four hours under an argon atmosphere. After the reaction time, solvent was removed under reduced pressure, and the residue was washed with hexane, yielding the white solid product **[12].**



^{1}H NMR (500 MHz, CDCl3) δ 8.89 (s, 1H), 7.56 (dt, *J* = 26.8, 7.7 Hz, 2H), 7.34 (dd, *J* = 20.7, 7.9 Hz, 4H), 7.20 (s, 1H), 2.41 (p, *J* = 6.8 Hz, 3H), 2.21 (p, *J* = 6.8 Hz, 1H), 2.06 (s, 2H), 1.21 (t, *J* = 6.9 Hz, 12H), 1.13 (dd, *J* = 21.1, 6.9 Hz, 12H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 152.20, 145.73, 145.03, 132.95, 132.51, 129.49, 125.65, 125.54, 125.25, 123.37, 29.36, 29.03, 25.88, 24.50, 23.44, 22.80, 19.44. **^{11}B NMR** (160 MHz, $CDCl_3$) δ 29.54. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -78.67.

Scheme 2.2.13. Synthesis of 2-(tosy1oxy) tropolone [13]

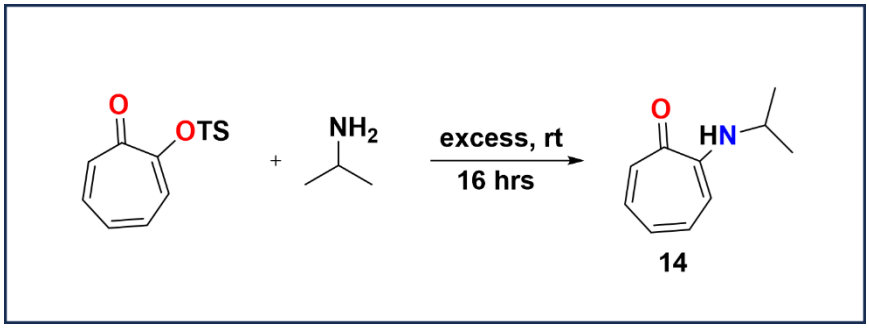
Weighed 2-hydroxycyclohepta-2,4,6-trien-1-one (32.75 mmol, 4g, 1 eq.) and 4-methylbenzenesulfonyl chloride (32.75 mmol, 6.172g, 1 eq.) in two neck round bottom flask. The pyridine solvent was used. The reaction mixture was stirred at 0 °C to room temperature under the inert atmosphere. After the completion of the reaction, add deionized water to the reaction mixture as a result, a white precipitate formed, and filtration was done to get the white solid product**.[13]**



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.3 Hz, 2H), 7.45 (d, *J* = 9.5 Hz, 1H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.23 – 7.18 (m, 1H), 7.14 (d, *J* = 12.1 Hz, 1H), 7.11 – 7.05 (m, 1H), 6.98 (t, *J* = 10.1 Hz, 1H), 2.45 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 179.56, 155.30, 145.64, 141.38, 136.46, 134.74, 133.56, 130.96, 130.13, 129.75, 128.75, 21.91. **HRMS** (ESI) calculated for [$C_{14}H_{12}O_4S$ + Na] 299.0349, found 299.0349.

Scheme 2.2.14. Synthesis of 2(isopropy1amino)-tropolone [14]

In a Schlenk tube, 2-(tosy1oxy) tropolone is kept under vacuum for 30 minutes. after that isopropylamine was added to the excess amount. The reaction mixture was performed in an inert atmosphere. After the completion of the reaction, the solvent was dried under a vacuum, 2N NaOH quenched the mixture, and the product was extracted in DCM.



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (dd, *J* = 18.8, 8.3 Hz, 3H), 7.14 (d, *J* = 11.5 Hz, 1H), 6.66 (t, *J* = 9.5 Hz, 1H), 6.56 (d, *J* = 10.5 Hz, 1H), 3.96 – 3.67 (m, 1H), 1.33 (d, *J* = 6.4 Hz, 6H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 176.73, 154.82, 137.34, 136.43, 128.40, 121.98, 109.03,

43.95, 22.15. **HRMS** (ESI) calculated for [$C_{14}H_{12}O_4S$ + Na] 299.0349, found 299.0349.

Chapter 3

3.1 Results and Discussion:

In my work, the NHO·BH_3 complex is successfully synthesized and characterized by ^{11}B NMR spectroscopy. The spectrum displays a quartet centered around –30 ppm, consistent with the expected borane–hydride coupling pattern and closely aligning with the quartet typically observed for NHC·BH_3, which appears between –32 and –40 ppm (all in the negative region) with a 1:3:3:1 intensity ratio. This result confirms the successful formation of the NHO·BH_3 adduct. The reactivity of NHO·BH_3 is evaluated with a series of diacids, including oxalic acid, malonic acid, phthalic acid, and glutaric acid. All reactions are carried out under an inert atmosphere at room temperature. Notably, while literature reports indicate that NHC·BH_3 requires heating to 80 °C in acetonitrile for similar transformations, NHO·BH_3 reacts smoothly at room temperature. The ^{11}B NMR spectra of the reaction mixtures show distinct signals for each diacid: oxalic acid (~5.3 ppm), malonic acid (~3.2 ppm), phthalic acid (~2.24 ppm), and glutaric acid (~1.31 ppm). These downfield shifts are characteristic of boroxolate-type species, indicating successful diacid activation and complex formation. Further reactivity studies are conducted with strong acids, including trifluoroacetic acid, trifluoromethanesulfonamide, and trifluoromethanesulfonimide. These reactions take place at 80 °C in acetonitrile and selectively produce monosubstituted products, as confirmed by ^{11}B NMR, which shows a broad resonance around 29 ppm. In addition to ^{11}B NMR, the formation of these products is also confirmed by ^{19}F NMR and ^{1}H NMR spectroscopy, providing further evidence for the success. Despite these promising results and extensive spectroscopic evidence confirming product formation, attempts to grow

single crystals suitable for X-ray diffraction analysis remain unsuccessful. Consequently, while NMR data strongly support the proposed structures.

3.2 Characterization of ligands:

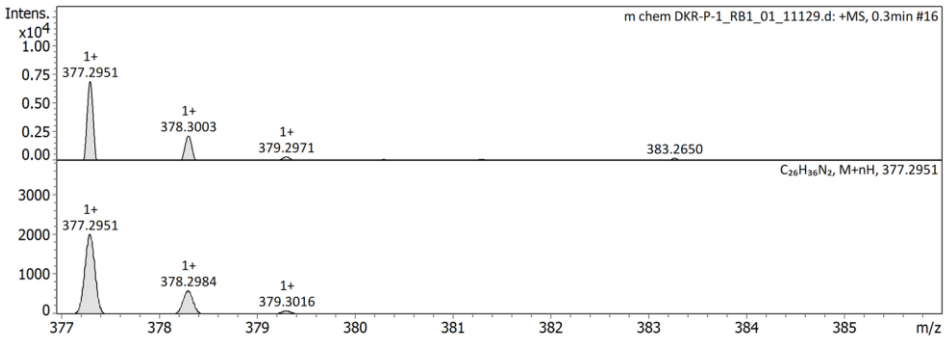


Figure 3.1 Mass Spectrum of 1

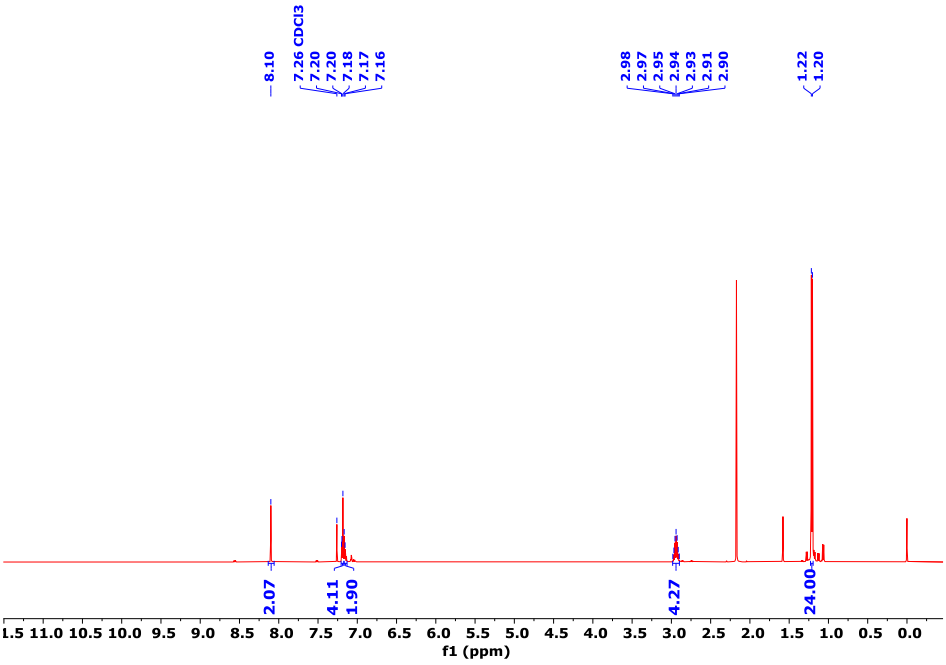


Figure 3.2 ^{1}H NMR Spectrum of 1

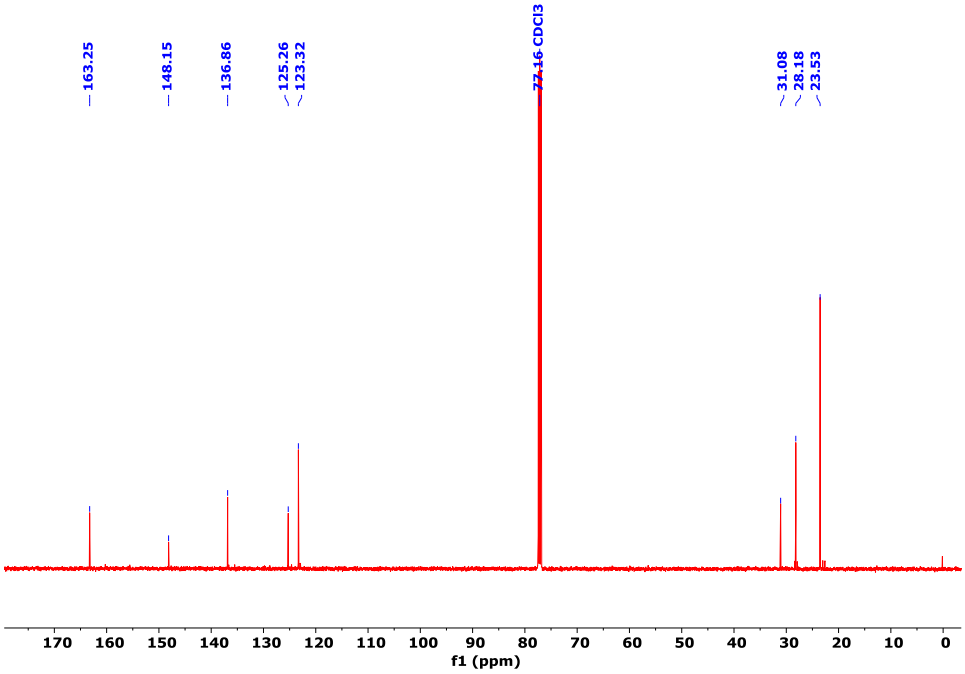


Figure 3.3 $^{13}C\{^{1}H\}$ NMR Spectrum of 1

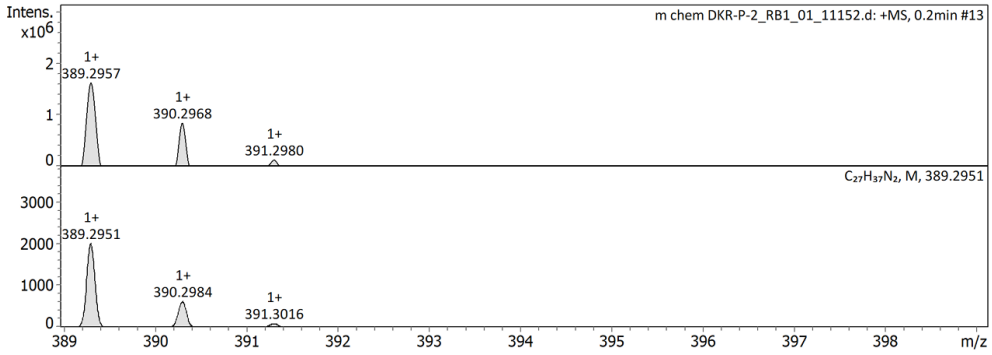


Figure 3.4 Mass Spectrum of 2

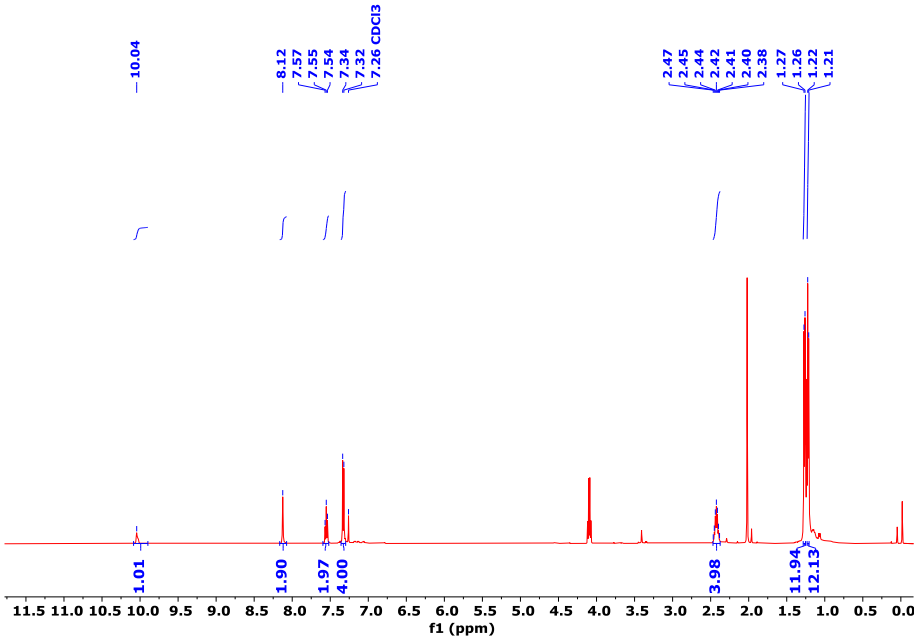


Figure 3.5 ^{1}H NMR Spectrum of 2

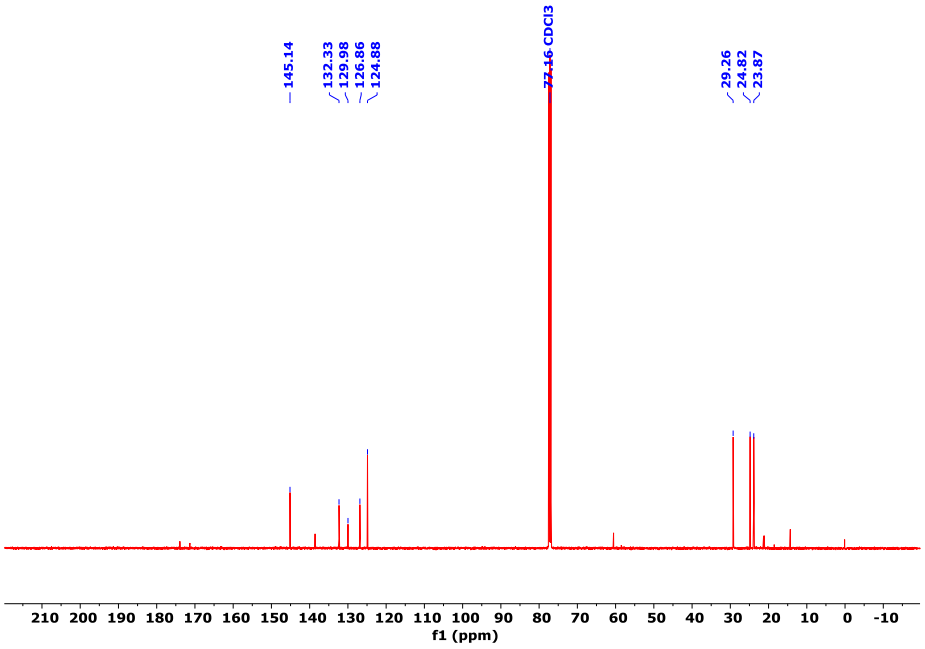


Figure 3.6 ^{13}C{^{1}H} NMR Spectrum of 2

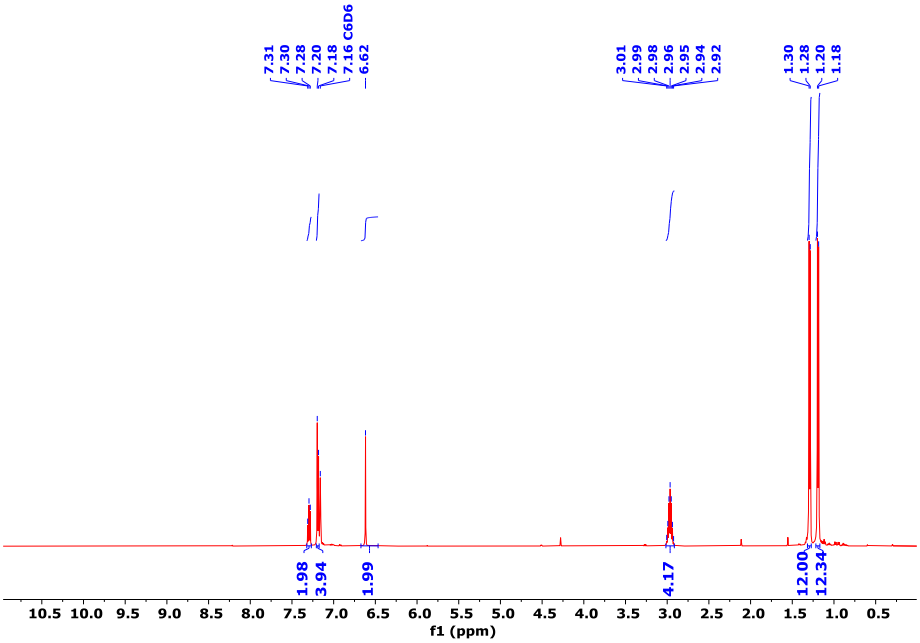


Figure 3.7 ^{1}H NMR Spectrum of 3

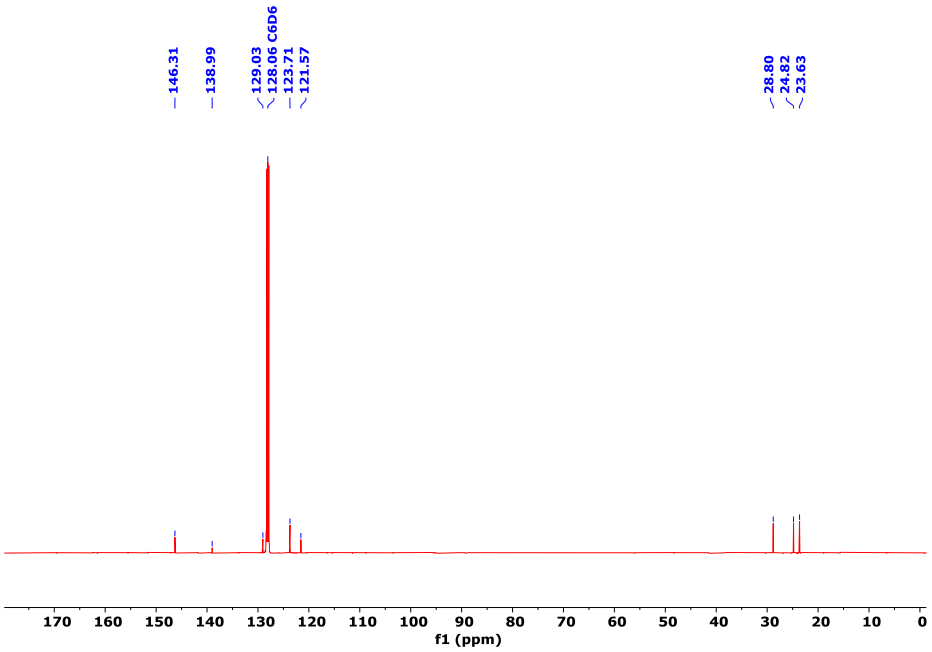


Figure 3.8 ^{13}C{^{1}H} NMR Spectrum of 3

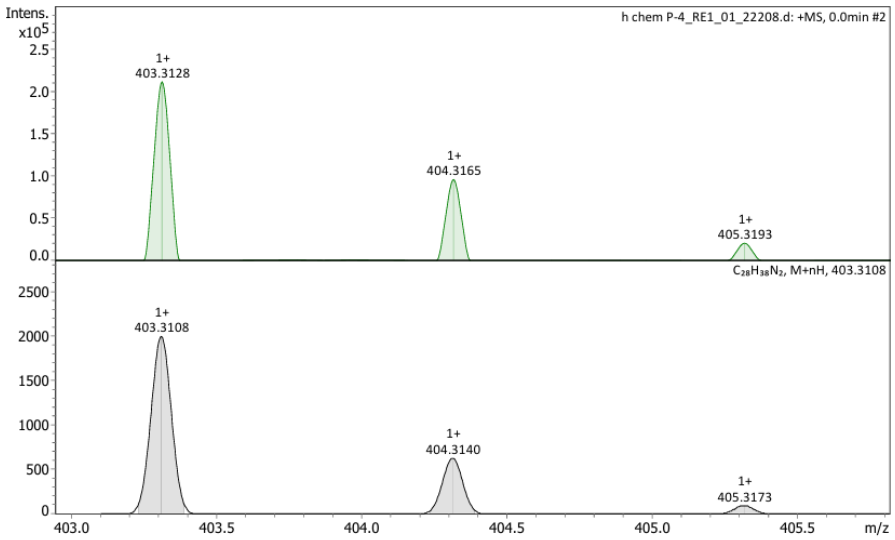


Figure 3.9 Mass Spectrum of 4

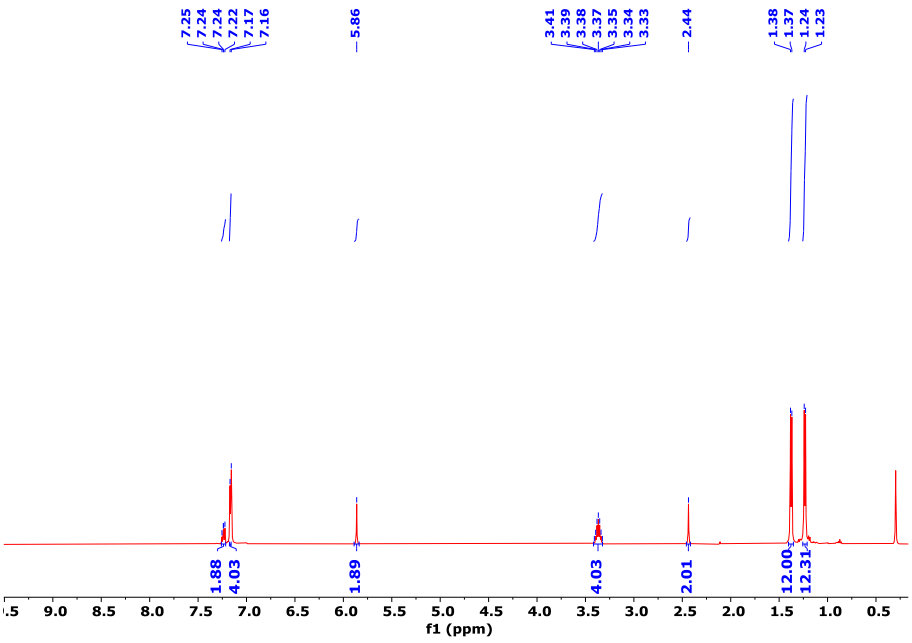


Figure 3.10 ^{1}H NMR Spectrum of 4

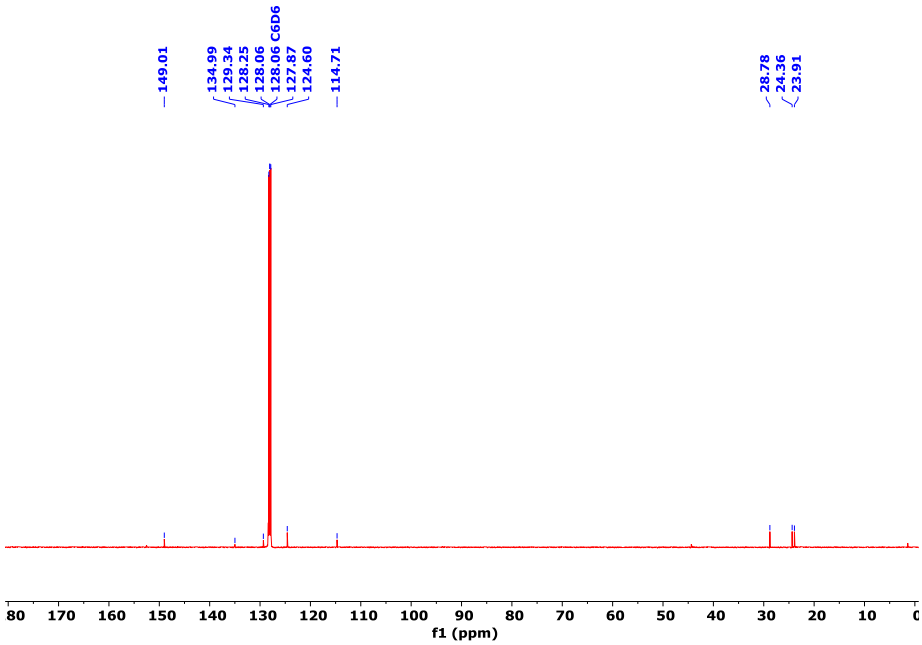


Figure 3.11 $^{13}C\{^{1}H\}$ NMR Spectrum of 4

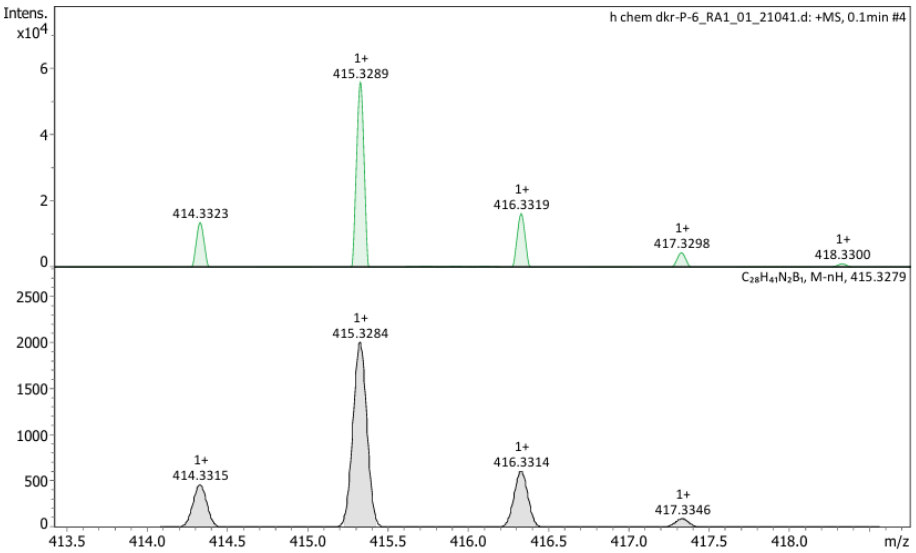


Figure 3.12 Mass Spectrum of 5

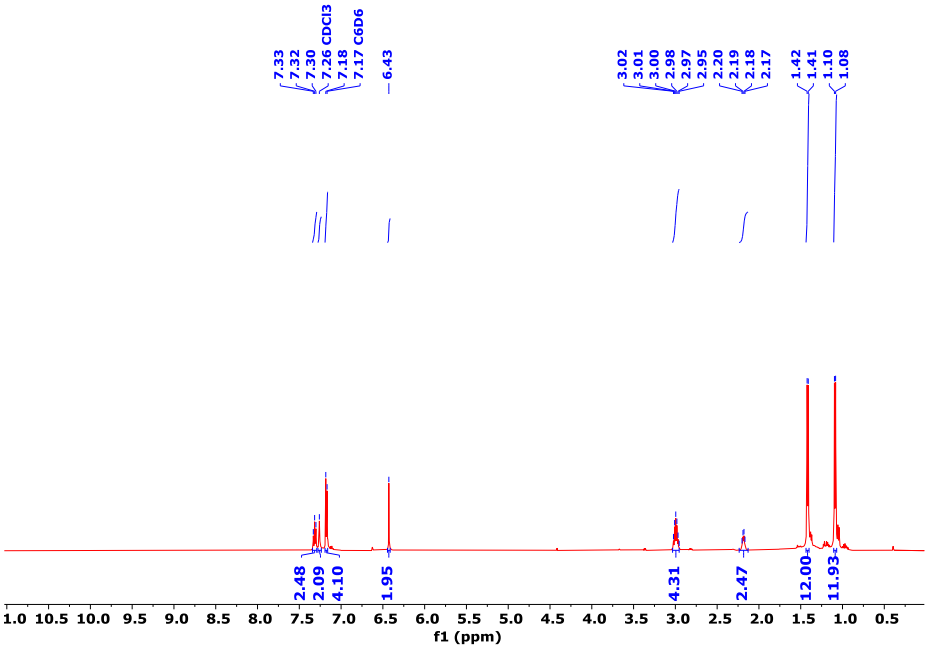


Figure 3.13 ^{1}H NMR Spectrum of 5

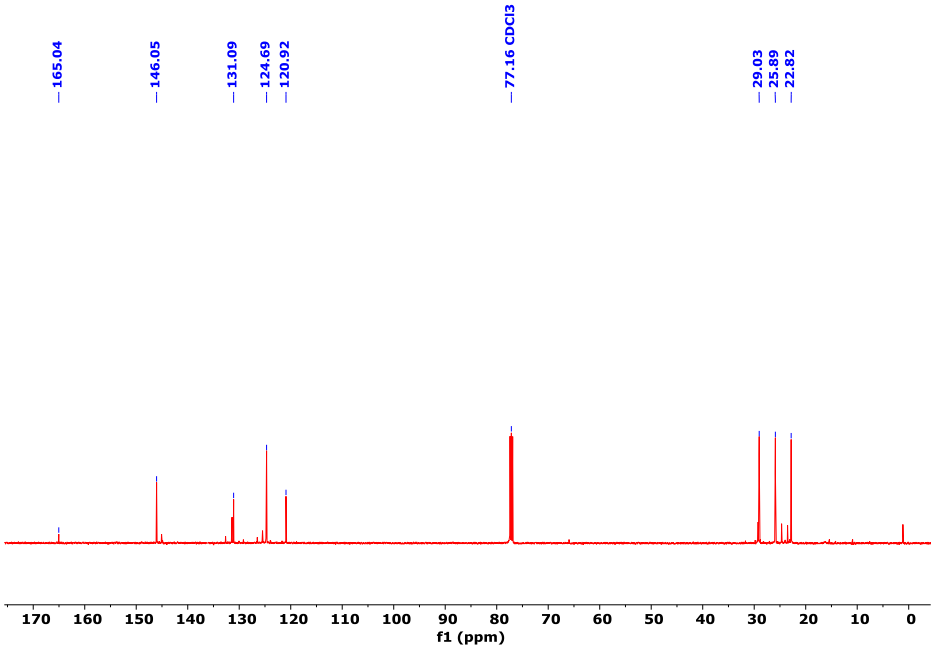


Figure 3.14 ^{13}C NMR Spectrum of 5

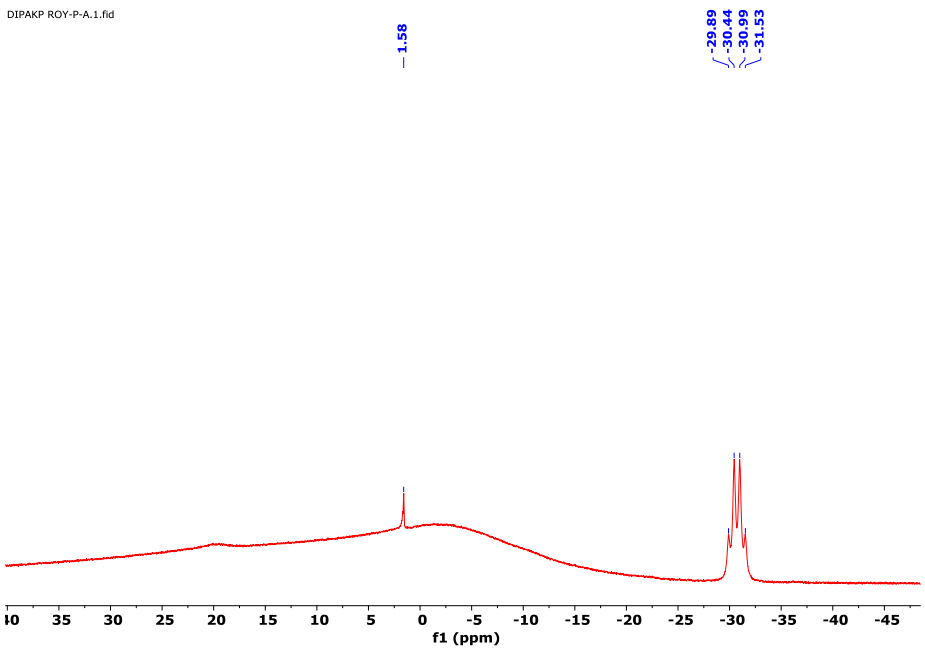


Figure 3.15 ^{11}B NMR spectrum of 5

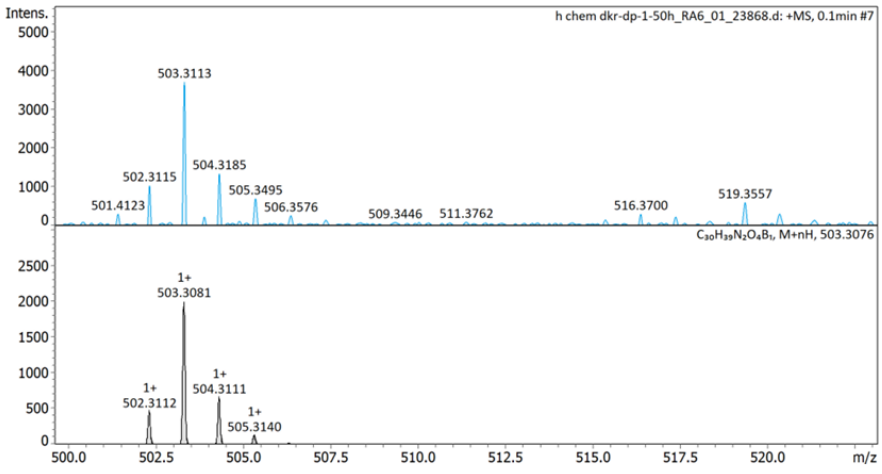


Figure 3.16 Mass Spectrum of 6

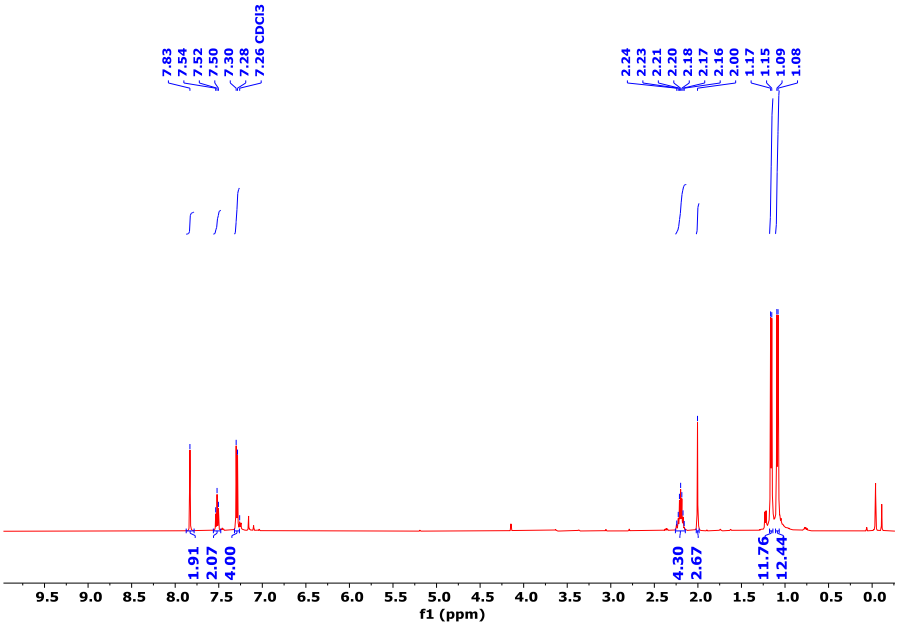


Figure 3.17 ^{1}H NMR spectrum of 6

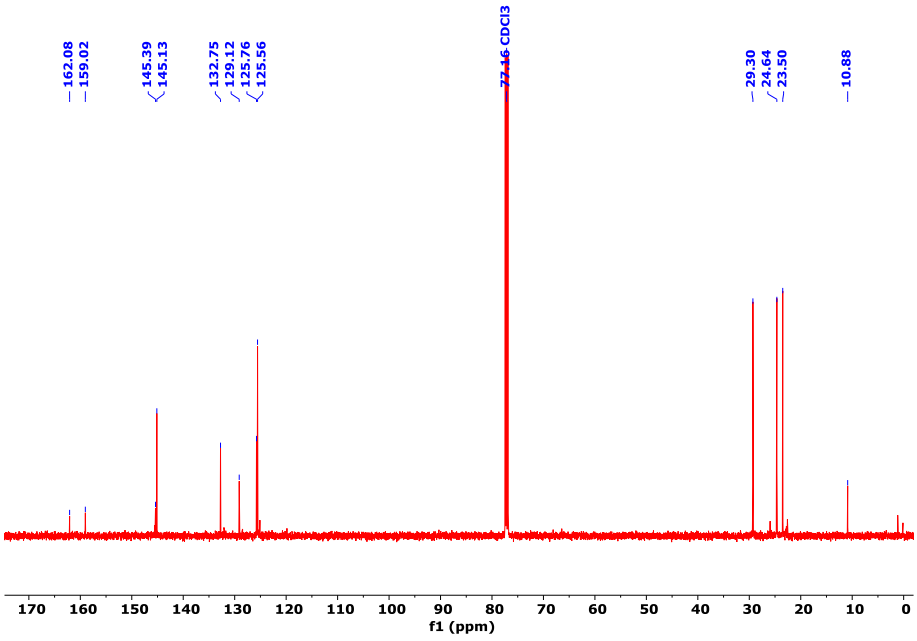


Figure 3.18 ^{13}C{^{1}H} MR Spectrum of 6

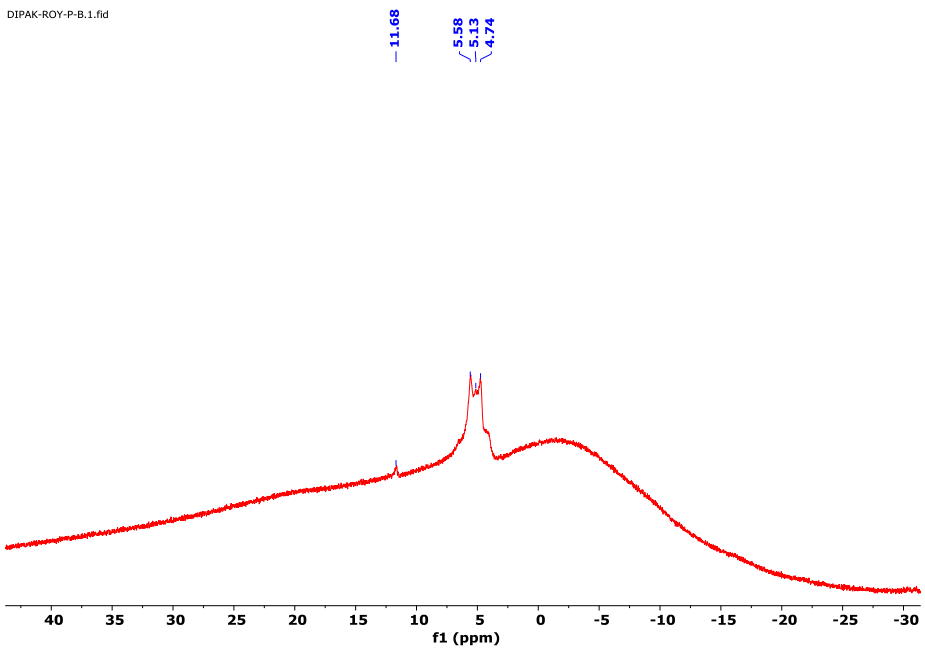


Figure 3.19 ^{11}B NMR Spectrum of 6

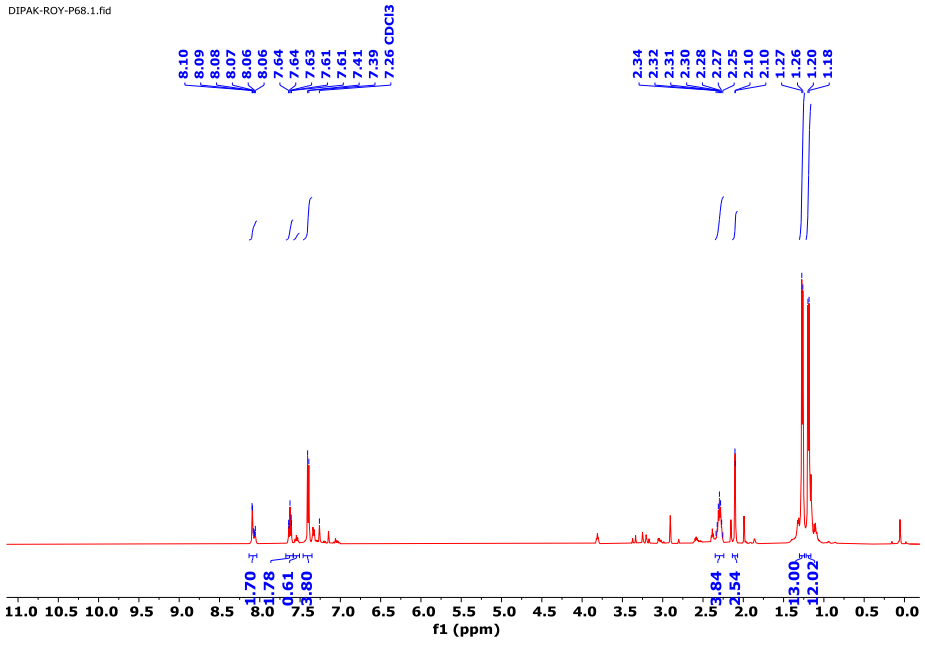


Figure 3.20 ^{1}H NMR spectrum of 7

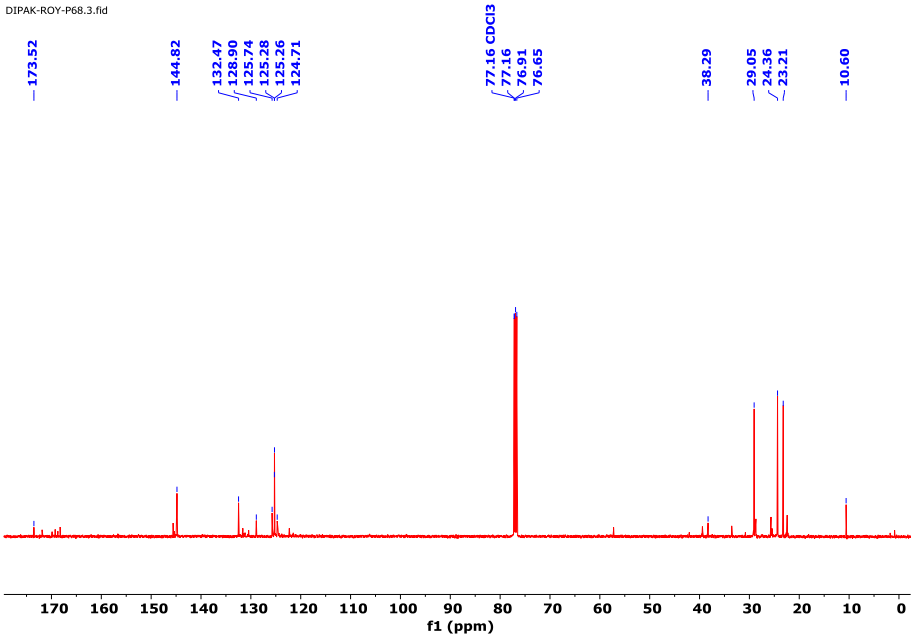


Figure 3.21 $^{13}C\{^{1}H\}$ NMR Spectrum of 7

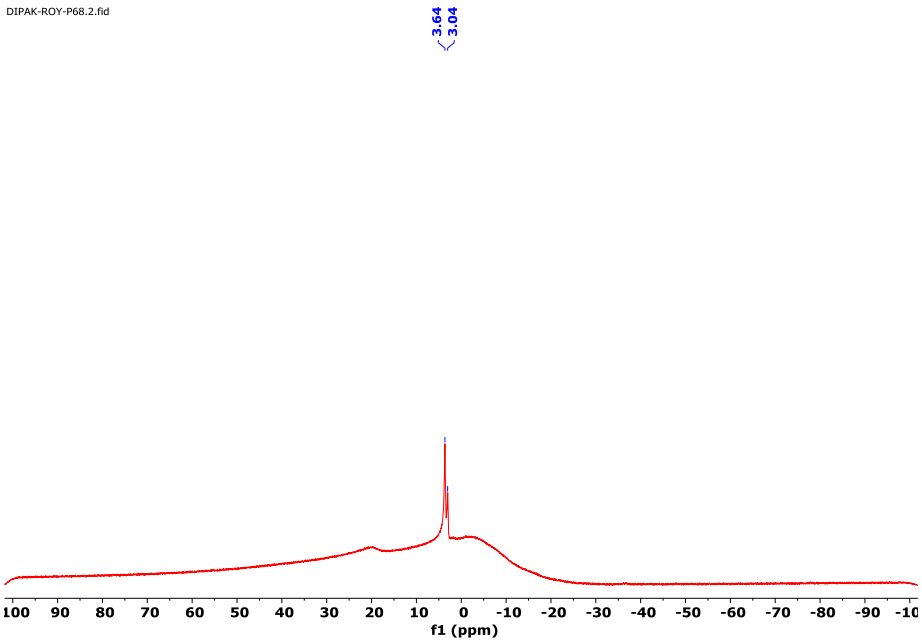


Figure 3.22 ^{11}B NMR Spectrum of 7

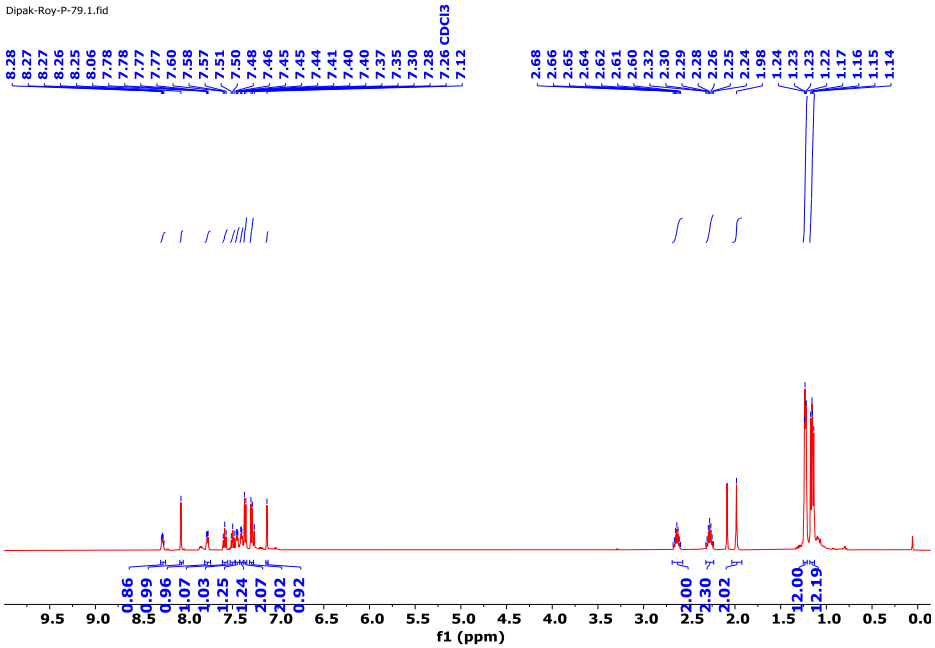


Figure 3.23 ^{1}H NMR spectrum of 8

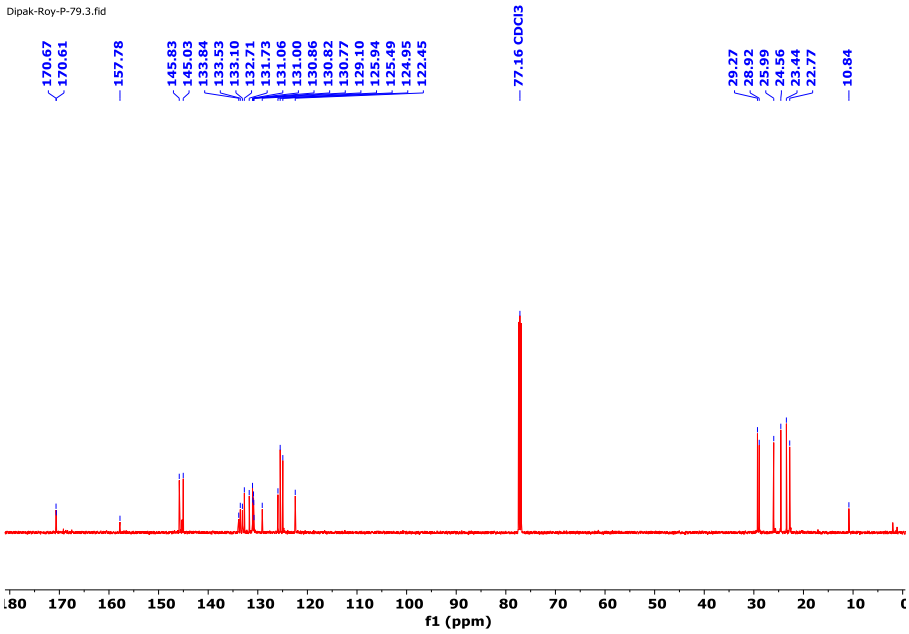


Figure 3.24 ^{13}C{^{1}H} NMR Spectrum of 8

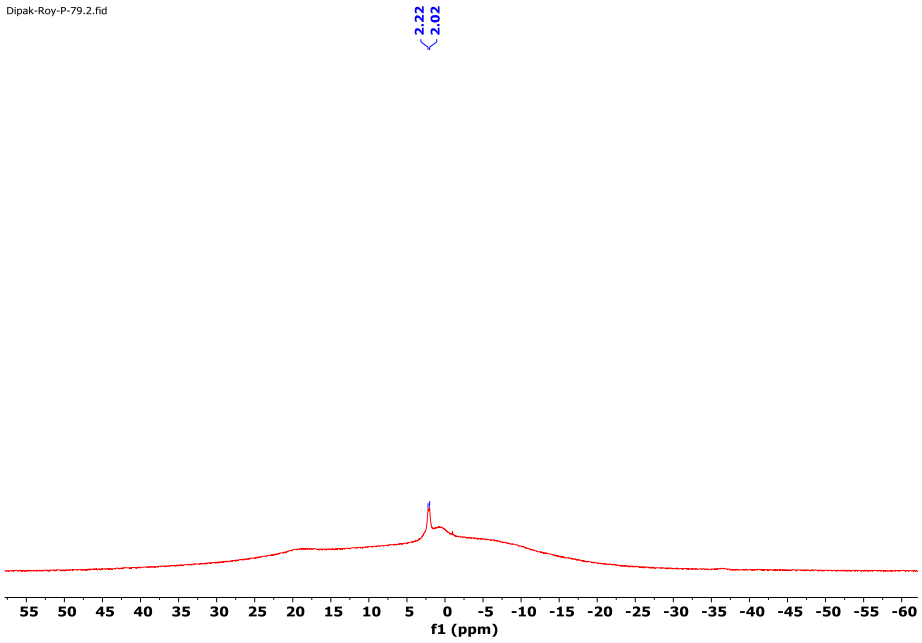


Figure 3.25 ^{11}B NMR Spectrum of 8

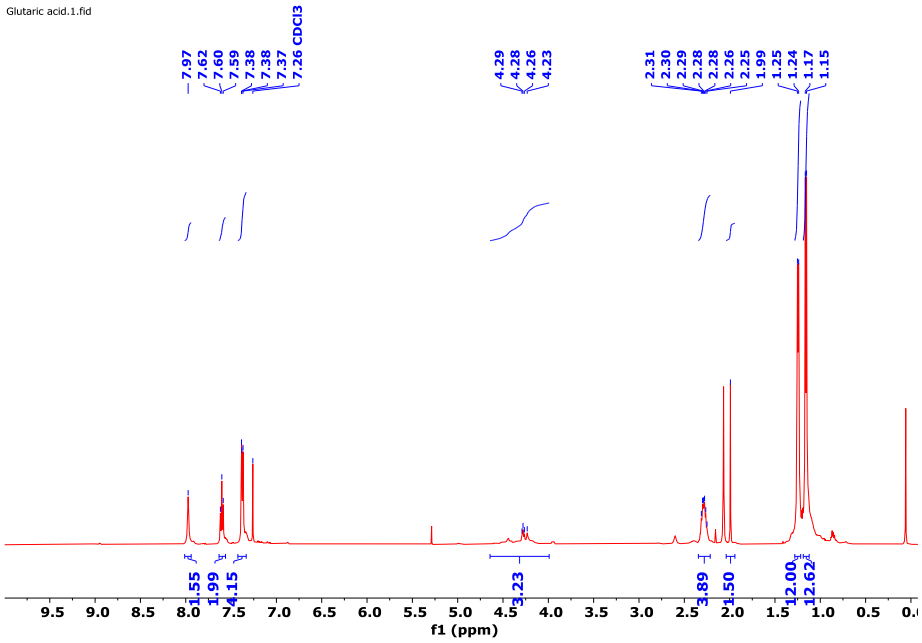


Figure 3.26 ^{1}H NMR spectrum of 9

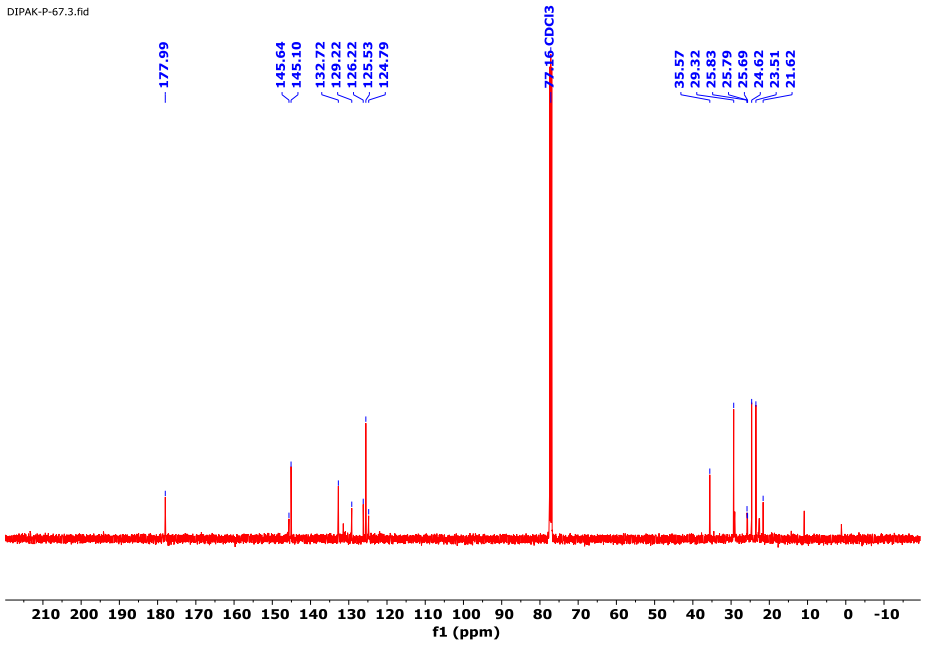


Figure 3.27 $^{13}C\{^{1}H\}$ NMR spectrum of 9

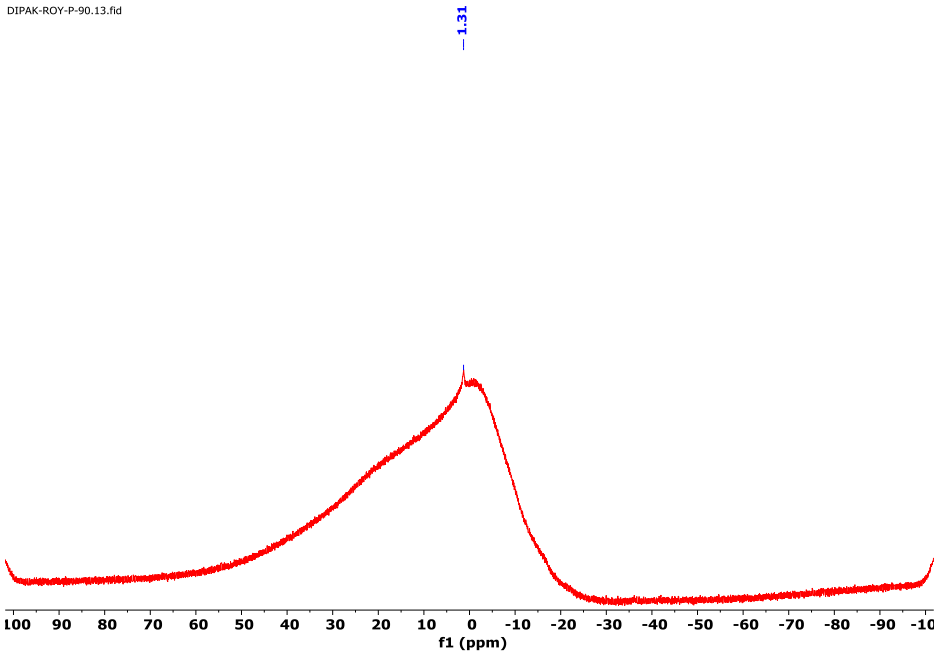


Figure 3.28 ^{11}B NMR Spectrum of 9

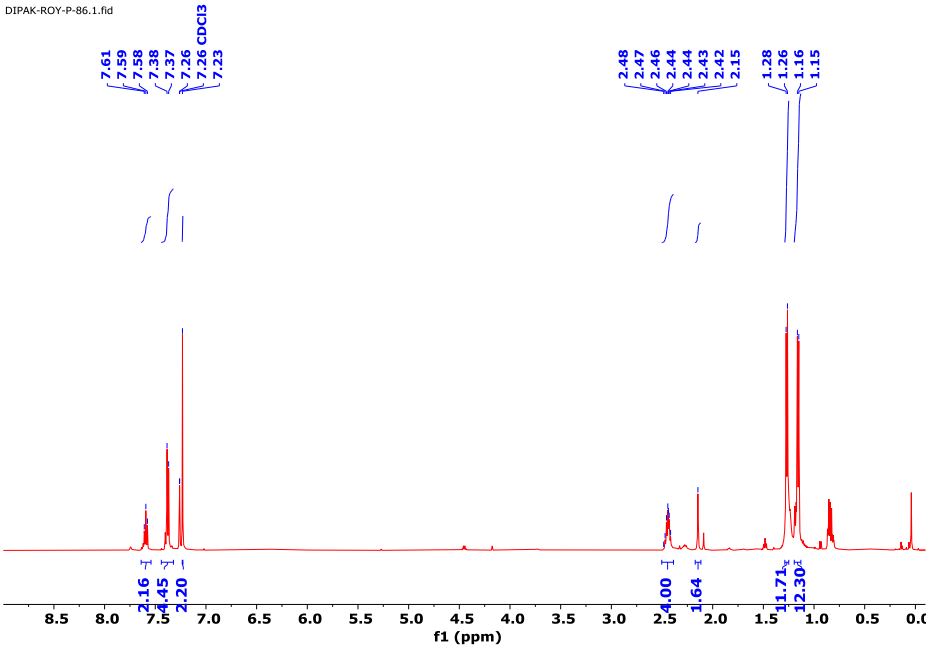


Figure 3.29 ^{1}H NMR spectrum of 10

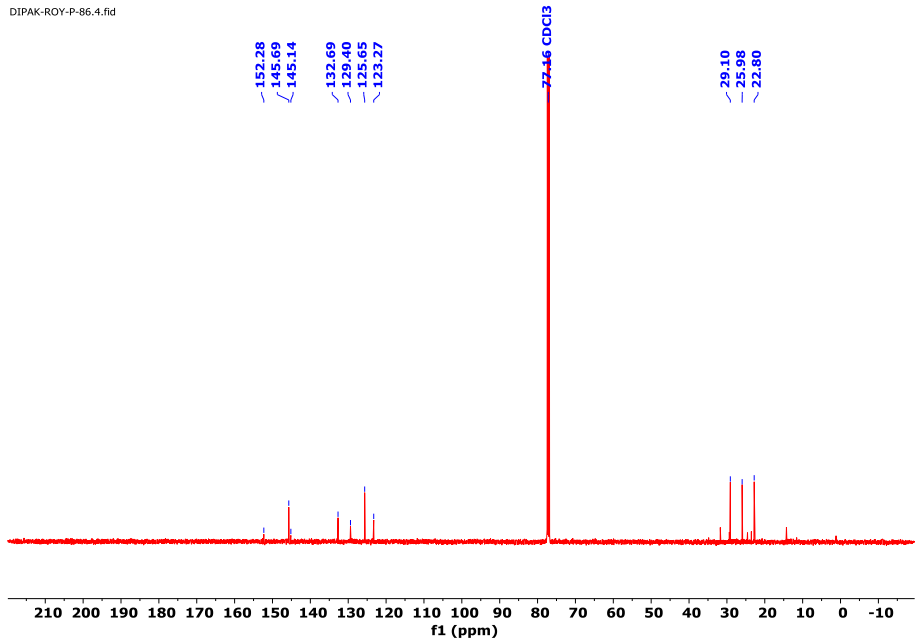


Figure 3.30 ^{13}C{^{1}H} NMR spectrum of 10

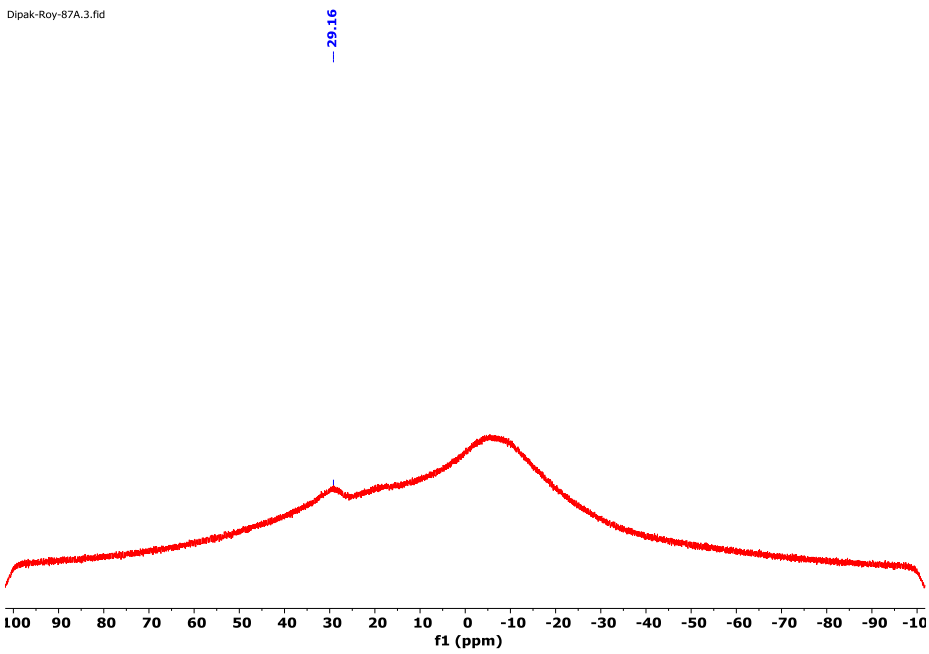


Figure 3.31 ^{11}B NMR Spectrum of 10

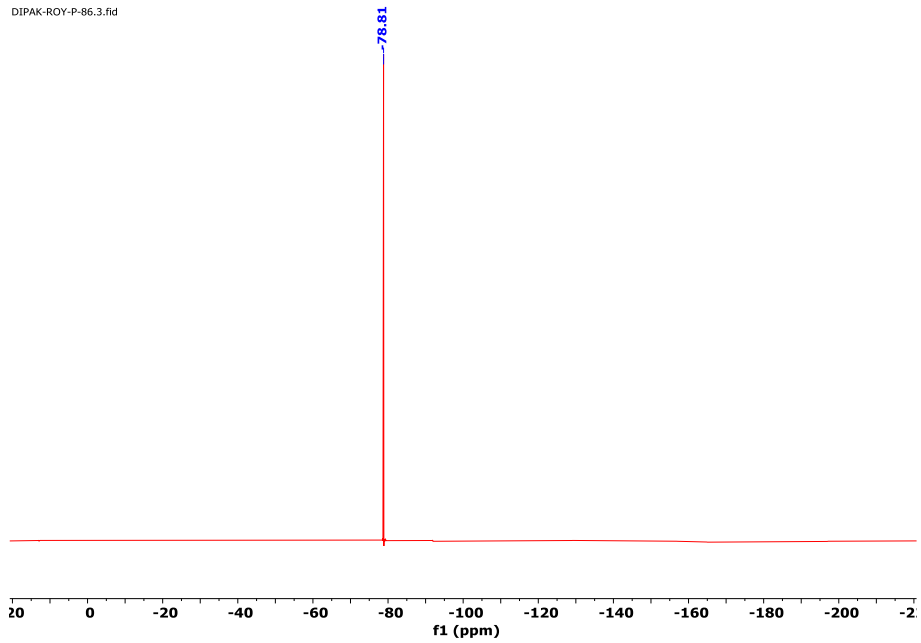


Figure 3.32 ^{19}F NMR Spectrum of 10

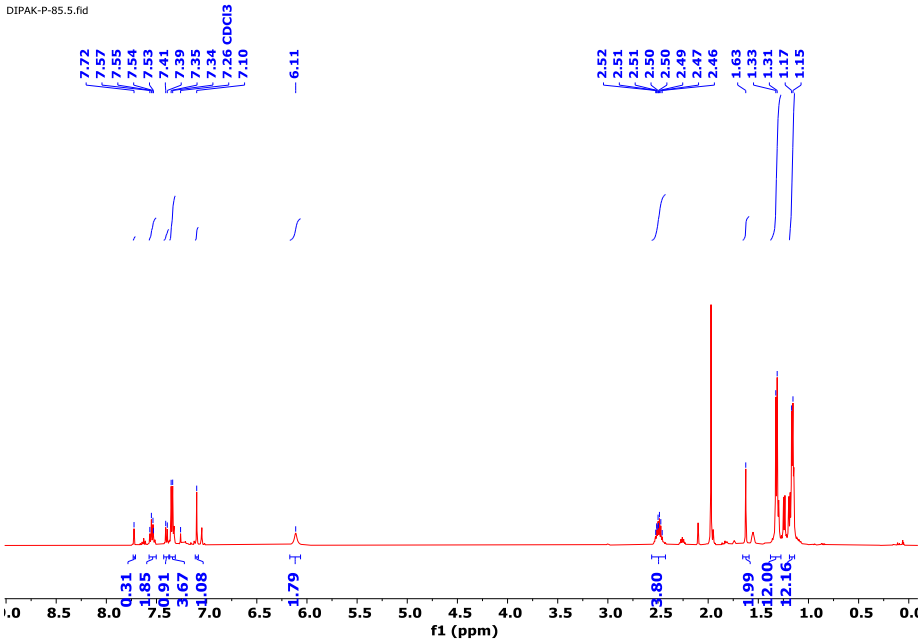


Figure 3.33 ^{1}H NMR spectrum of 11

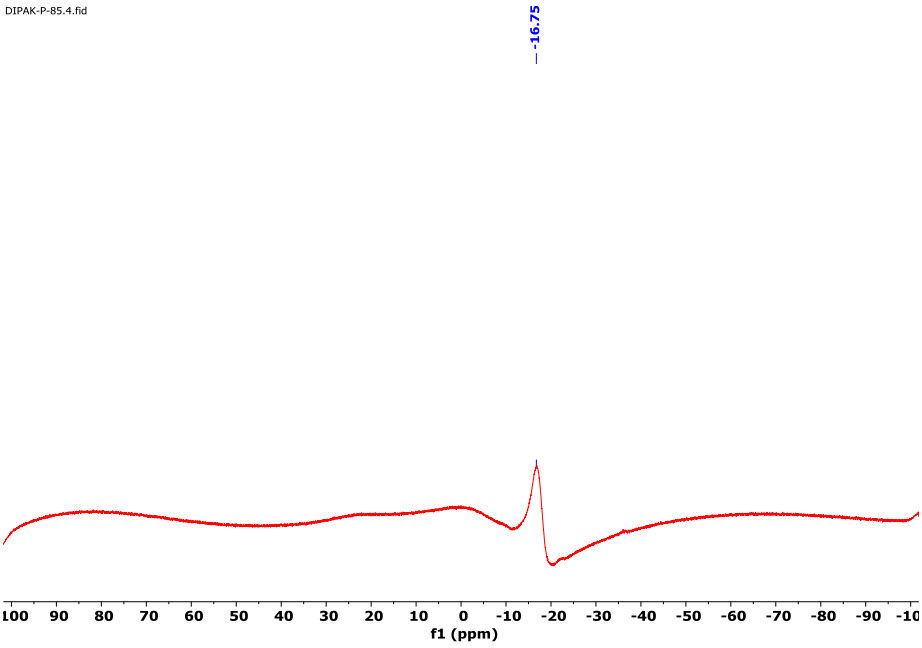


Figure 3.34 ^{11}B NMR spectrum of 11

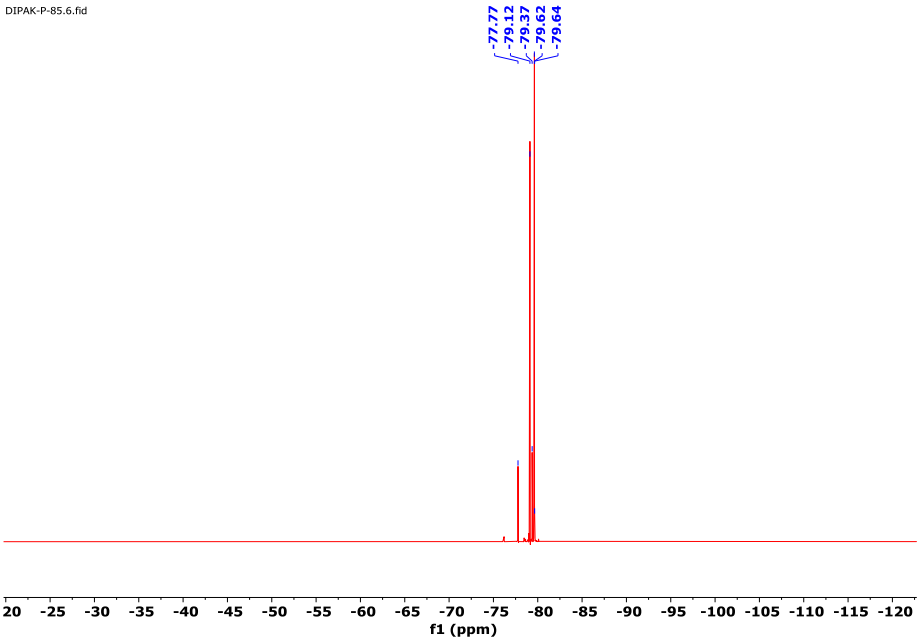


Figure 3.35 ^{19}F NMR Spectrum of 11

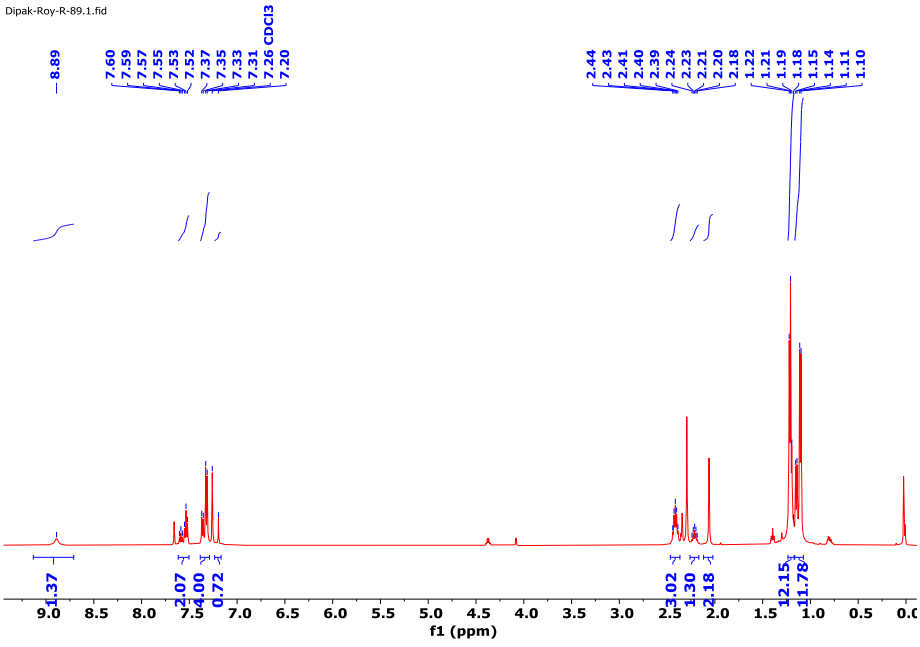


Figure 3.36 ^{1}H NMR Spectrum of 12

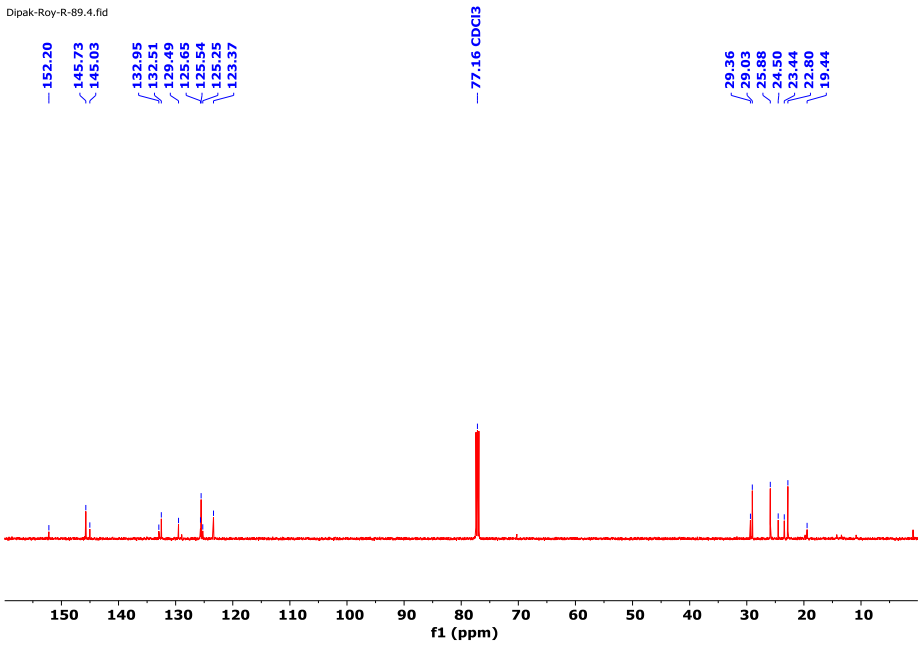


Figure 3.37 $^{13}C\{^{1}H\}$ NMR Spectrum of 12

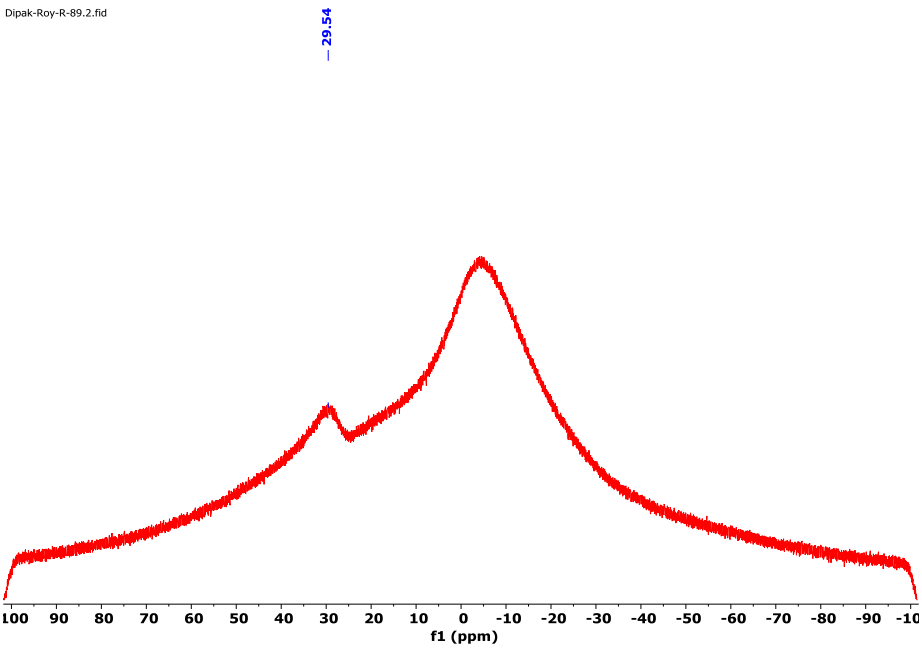


Figure 3.38 ^{11}B NMR Spectrum of 12

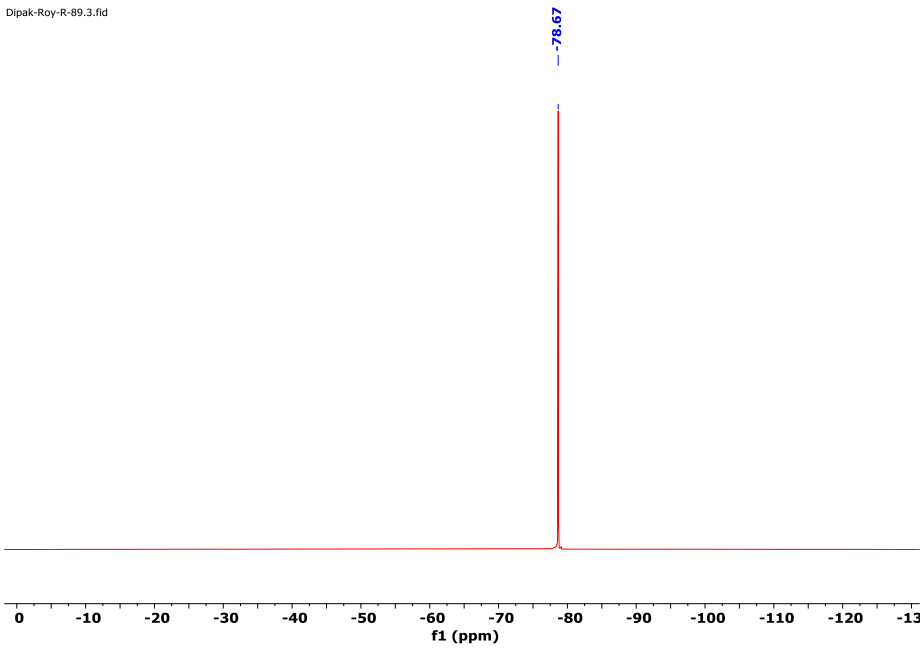


Figure 3.39 ^{19}F NMR Spectrum of 12

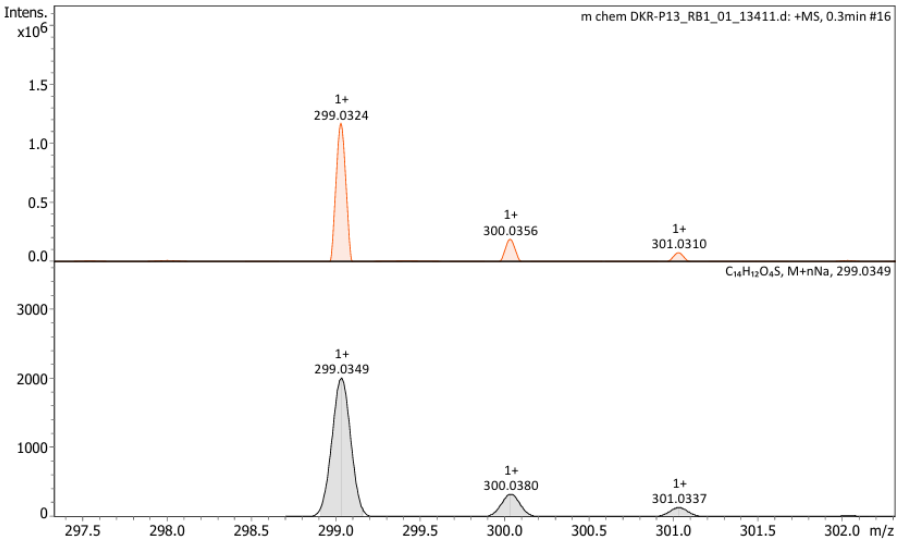


Figure 3.40 Mass Spectrum of 13

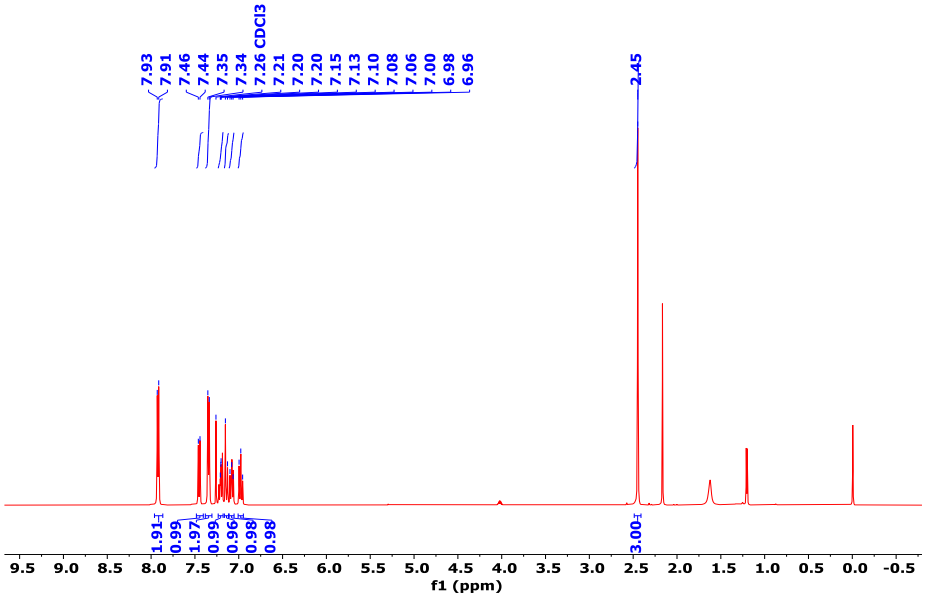


Figure 3.41 ^{1}H NMR Spectrum of 13

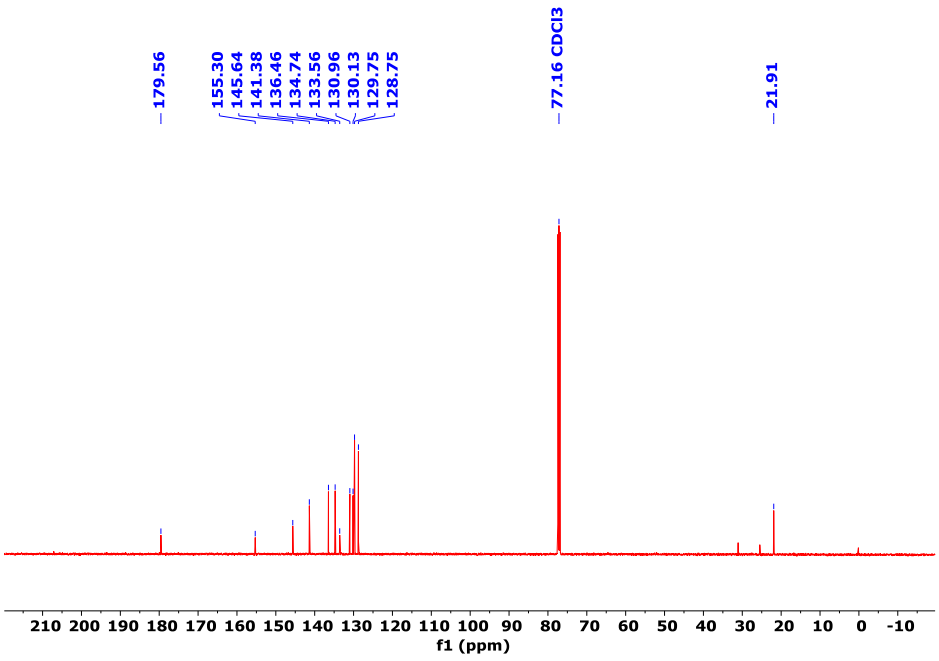


Figure 3.42 ^{13}C{^{1}H} NMR Spectrum of 13

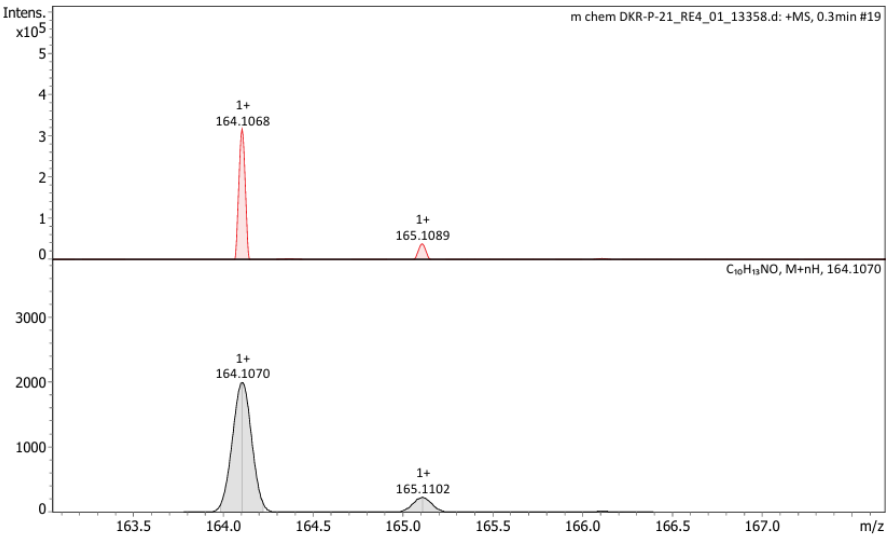


Figure 3.43 Mass Spectrum of 14

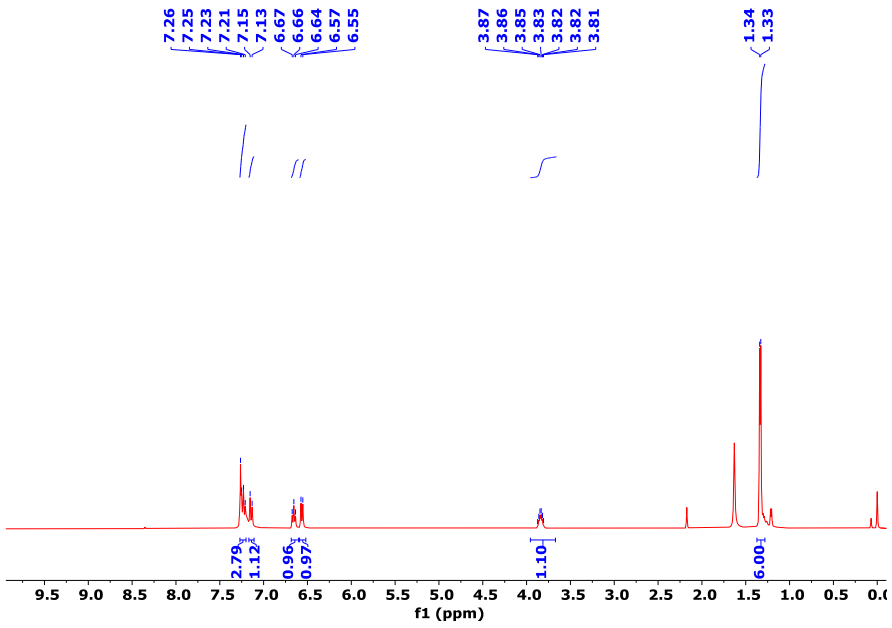


Figure 3.44 ^{1}H NMR Spectrum of 14

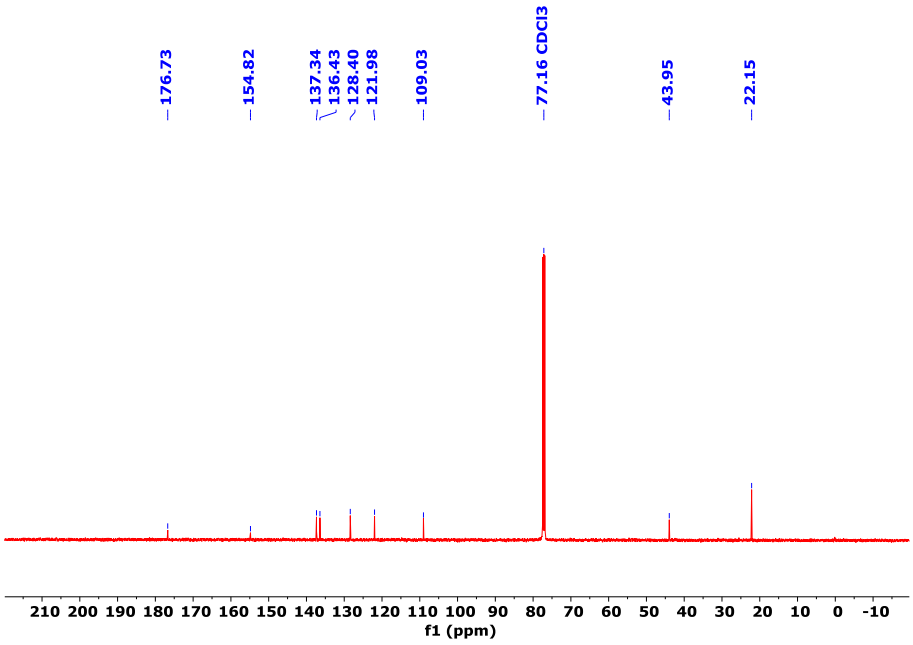


Figure 3.45 $^{13}C\{^{1}H\}$ NMR Spectrum of 14

Chapter 4:

4.1 Conclusion

During this project, I successfully synthesized a series of NHO–boryl complexes starting from NHO–borane. These new borane-containing heterocycles were carefully analyzed using various spectroscopic techniques to fully understand their structures.We also looked into how NHO–boranes react with strong acids like triflic acid, trifluoromethanesulfonamide, and trifluoromethanesulfonimide, and were able to isolate monosubstituted products selectively. We also tested their reactivity with diacids such as oxalic acid, malonic acid, phthalic acid, and glutaric acid, which led to the formation of disubstituted NHO–boranes. Altogether, these results give us a better understanding of how NHO–boranes behave and what they're capable of, opening up exciting possibilities for further research and applications in this developing area of chemistry.

4.2 Future Scope:

In this thesis, I've explored the fascinating and still-growing field of NHO–borane chemistry. Although these compounds are relatively new, they're already showing a lot of promise in areas ranging from academic research to industrial and pharmaceutical applications.

4.2.1 Radical Chemistry and Reactivity

NHO–boranes are likely to be useful for making boryl radicals easily, especially under mild conditions using photoredox catalysis. Their ability to break B–H bonds will help in carrying out metal-free borylation and forming carbon–boron bonds.

4.2.2 Application in Hydroboration

In the future, NHO–boranes will likely be used for hydroboration of compounds like alkenes, alkynes, and imines. Their strong reactivity is

expected to make these reactions faster, more selective, and possible under milder conditions than with traditional boranes.

Chapter 5

5.1 Reference:

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