SYNTHETIC ROUTES AND METHODS TOWARDS ACHIEVING

A TERMINAL BORYLENE

by

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SYNTHETIC ROUTES AND METHODS TOWARDS ACHIEVING

A TERMINAL BORYLENE

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DEDICATION

"It has been a long time comin", as grandmother would say, and I am pleased to say that I have finally made it. Mother I am graduating and it could not feel better. I have enjoyed my experience here at Texas State University, but it is now time for me to continue to pursue education in the next chapter of my life. I remember, growing up, when you would work through the hours of the night and day, just to be sure that my siblings and I had a place to sleep, and food on the table. You have made this chapter in my life possible. You are the driving force behind everything I do, and there is not a thing I would want to do without you backing me. You made the sacrifice to be sure that I did not astray down the wrong path, even though it was in my backyard. You motivated me, and inspired me to go pursue further education after High School, as you were a single mother with 3 children in the process of receiving your M.S in Health Education after your B.S in Nursing. I owe it all to you mother, you are the real MVP. This is me, doing what I love and having fun with it, always remembering to be the best garbage man that I can be. I love you.

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ABSTRACT

Carbenes were studied as early as the 19th century where the initial goal primarily focused on the possible avenues that could utilize the species. Initial attempts in obtaining and isolating the carbene moiety was through trapping methods, under extreme conditions. Upon further characterizations, the "trapped" carbene had a triplet ground state configuration precluding its ability to be stable and isolated. Bertrand and Arduego, in the 1990's were able to isolate the first stable carbene species. The divalent species, with a delocalized lone pair at the carbene carbon could undergo catalysis and be used as an ancillary ligand to electron deficient elements. James Hedrick and Robert Grubbs provided the first examples of carbenes to be used in catalysis through Ring Open Polymerization (ROP) and Ring Open Metathesis Polymerization (ROMP). As carbenes grew in prominence, the ability of carbenes to stabilize main group elements had become evident. Robinson, Bertrand, and Braunschweig with co-workers pioneered the field of carbene stabilized boron species that studied the reactivity of starting with a carbene stabilized B(III) and reducing it to B(I). this illuminated the reactive nature of the reduction of B(III) to B(I), as it afford boracycles, when not properly stabilized, or dimerization, when B(I) compensates for its vacant orbitals. We sought out to explore the chemistry of carbene-stabilized boron main group species by observing the reaction $CAAC\text{-}B(N(i\text{Pr})_2Cl_2)$ when treated with KC_8 as a reducing agent. With our best efforts to obtain full characterization of the CAAC-aminoborylene, we were unsuccessful in achieving a crystal structure of **29**. The treatment of $CAAC\text{-}Cp^*BCl_2$ with KC_8 led to a boracycle **32**, as seen in **11** which was attributed to the reactive nature of generating B(I) *in situ*, leading to further reaction to fulfill its coordination environment. Treatment of **30**

with AlCl$_3$ adopts its η^5-Cp*B orientation **33**, where it could be reduced subsequently to obtain the CAAC-CP*B(I) terminal. Unfortunately, the reaction affords **32**. Going from **33** to **34**, we report isolating the first example of a CAAC stabilized boryl radical cation that is 2-coordinate and B(II). DAC is a more π-acidic carbene (reference Figure 1.5) than CAAC. The formation of DAC-B(N(iPr)$_2$Cl$_2$) was unobserved due to the withdrawing properties of the carbene's carbonyl backbone. However, with the abstraction agent TMSOTf, the coordination of the aminoborane could be facilitated, generating a borenium cation with a triflate anion **35**. This adduct could be reduced once to form the **36**. Contrary to what literature suggest, this radical spends most of its time on the carbene carbon, accentuating the withdrawing character of the carbene (DAC). The radical could be further reduced to generate the borylene **37**, which is confirmed by NMR. In spite of our best efforts, X-Ray data was left to be obtained.

I. Introduction to Carbenes and Their Applications

1.a Generation of Carbenes
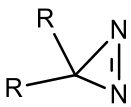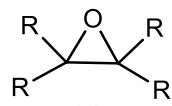
Carbenes have played an important role in the field of organic synthesis since the first evidence of their existence. Defined as a divalent carbon intermediate linked by adjacent covalent bonds, the carbene carbon possesses two nonbonding electrons. Early attempts to prepare carbenes date back to 1839, where Dumas and Regnault tried to synthesize the first carbene by dehydration of methanol using concentrated acid such as phosphorus pentoxide (P_2O_5), according to Scheme 1.[1]

$$CH_3OH \xrightarrow[\triangle]{P_2O_5} \begin{array}{c} H_3C \\ H_3C \end{array}\!\!\!> :$$
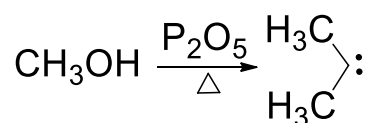
Scheme 1. Attempted synthesis of a carbene by Dumas and Regnault by dehydration of methanol.

Decades later, other pioneers in the field proposed that ethylene carbenes could be generated by reacting methyl iodide with copper, to afford the dimer of the simplest carbene, methylene ($:CH_2$).[2] Following the general methylene theory of carbenes, modern work in the field of carbene chemistry continued until the 1950's where the investigation of Staudinger focused on the generation of carbenes from diazo compounds and ketenes.[3] From this important discovery, many carbenes, such as those shown in Table 1 have been prepared.

Table 1. Shows the list of carbenes, generated from following reactions that were not stable and isolatable.

Precursor	Condition	Products
$CR_2={\overset{+}{N}}={N}^{-}$ Diazoalkanes	Photolysis, thermolysis, or metal-ion catalysis	$R_2C: + N_2$
$CR_2=N-\overset{-}{N}SO_2Ar$ Salts of Sulfonylhydrazones	Photolysis or thermolysis, diazoalkanes are intermediates	$R_2C: + N_2 + ArSO_2^-$
Diazirines	Photolysis	$R_2C: + N_2$
Epoxides	Photolysis	$R_2C: + R_2C=O$
$R_2CH\text{-}X$ Halides	Strong base or organometallic compound	$R_2C: + BH + X^-$
R_2CHgR' $\mid$ X X = Halomercury Compounds	Thermolysis	$R_2C: + R'HgX$

Unfortunately, these carbenes are incredibly reactive, and as such cannot be isolated; carbenes synthesized using the above reactions were generated *in situ* as reaction intermediates and were trapped, or studied in low-temperature. As the electronic ground states of organic molecules advanced with the advent of quantum mechanics, scientists realized that two carbenes could exist in two possible electronic ground states. Depending on the nature of the substituents flanking the carbene carbon, the two electrons could be localized in a single molecular orbital, and the carbene would exist in a singlet ground state (structure **A**, Figure, 1.1). Alternatively, the two electrons could be housed in two different orthogonal orbitals, and the carbene carbon could be considered a biradical, or a triplet ground state (structure **B**, Figure 1.1). The nature of the electronic ground state of the carbene directly influences the ability of these compounds to be readily isolated, and therefore, chemically stable. The carbenes in Table 1 are all triplet ground state carbenes, precluding the ability to isolate these compounds. Since the electronics of the triplet state carbene can be regarded as a biradical species, these carbene were too unstable when not subjected to extreme temperatures. Over time, by the 1960's, the analysis of these triplet ground state species were fully explored and explicated by Fischer and Massbol.[4]

A   **B**

Figure 1.1 Electronic composition of around the carbene's nucleus: singlet ground state, or triplet ground state

1.b The Generation of Stable Persistent Carbenes

However, the evolution of the stable carbene was not achieved until 1988 by Bertrand's phosphino-silyl carbene (structure **C**, Figure 1.2)[5] and later in 1991 by Arduengo (structure **D**, Figure 1.2)[6] through the discovery of the stable N-heterocyclic carbene (NHC) the imidazolyl-2-ylidenes.

$$R_2\overset{..}{P}\text{-}\overset{..}{C}\text{-}SiMe_3 \qquad Ad\overset{N}{\diagdown}\underset{..}{\diagup}\overset{N}{\diagup}Ad$$

C: R = N(iPr)$_2$ **D:** Ad = adamantyl
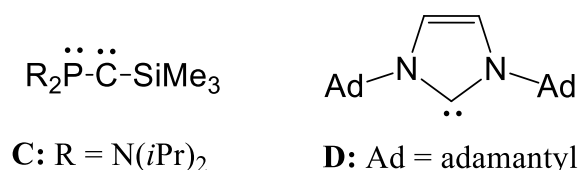
Figure 1.2 Structures of the first carbene species and the first N-heterocyclic carbene by

Bertrand and Arduengo

It was well established that aminonitrenes, phosphinonitrene could be regarded as a diazene, phosphinonitrile respectively, by virtue of its delocalization of the lone pair. Respectfully, Table 1 shows that diazo- compounds could be seen as a classical precursor of carbenes; experiments were performed, and the example of the first phosphino carbene bearing a strong multiple-bond character that is stable, and reacts as a carbene species was generated.[5]

$$PR_2\equiv C\text{—}SiMe_3 \rightleftharpoons \overset{..}{P}R_2\text{—}\overset{..}{C}\text{—}SiMe_3 \rightleftharpoons \overset{+}{P}R_2\text{—}\overset{-}{C}\text{—}SiMe_3$$
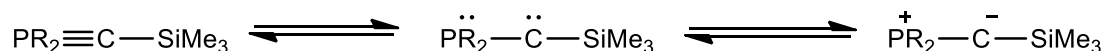
Figure 1.3 Resonance structures of the Bertrand's carbene

This finding was noted as one of the first example of a singlet ground state carbene with a lone pair of electrons at the carbene carbon, as opposed to a biradical electronic configuration. Along with this discovery, Arduengo was able to isolate the first

4

stable crystalline carbene that carries the methylene center group. The 1,3-diadamantylimidazol-2-ylidene exemplifies great stability as it enjoys both the steric protection from the adamantly substituents, and receives additional electronic stabilization by electron pair donation from the flanking amine nitrogen atoms into the carbene's empty p-orbital.[6] This amazing discovery by Arduengo was denoted as the first unambiguously stable N-hetrocyclic carbene.[6]

Carbenes have been studied more effectively with the focus on preparing derivatives with unique electronic properties. Ultimately these unique properties result in unusual bonding situations in the complexes that contain these carbenes. Recent advancements have shown that the reactivity of carbenes relies on the nature of its electronic properties such as the σ-donating and π-accepting characteristics. Electronic properties play a great deal of influence on the configuration of a persistent singlet ground state carbene. The immediate effects of the properties of the carbene can be seen in the way these compounds form complexes with transition metals, and more recently, main group elements. Attendant effects of the electronic properties of the carbene can be seen when examining the electrochemical, photophysical, and structural properties that accompany the complexes formed from a carbene. With respect to these properties, Bertrand[7], Ganter[8], and Hudnall[9] evaluated the π-accepting properties of several carbenes by using ^{31}P and ^{77}Se NMR shown in Figure 1.4. A carbene-phosphinidene (**C**), or seleno urea derived from carbenes (**D**) exhibit varying degrees of multiple bonding interaction with the main group center and the carbene nucleus depending on the electronic properties of the carbene. The ^{31}P and ^{77}Se NMR illuminate which carbenes are

strongly π-accepting (downfield NMR signals) or weakly accepting carbene centers (upfield NMR signals) as described in Figure 1.4.

downfield ^{31}P upfield ^{31}P downfield ^{77}Se upfield ^{77}Se

NMR signal   NMR signal   NMR signal   NMR signal

C   **C'**   **D**   **D'**

Figure 1.4 Resonance structures with the corresponding ^{31}P and ^{77}Se chemical shifts of complexes **C** and **D**

As carbenes became more ubiquitous, the methodology mentioned above became more apparent as the π-accepting properties of the carbenes were examined. As depicted in Figure 1.5, the π-accepting properties of the carbenes increases in order starting from unsaturated NHC ~ cyclopropenylidenes < saturated NHC < MAAC ~ antiBredt NHC < CAAC ~ thiazolylidene < ADC < DAC < AAAC.[6-8] π-accepting carbenes afford main group stabilized complex that exhibit more of a delocalized electronic structure, with a more electron-deficient carbene center. Contrarily, weak π-accepting carbenes result in an electon-rich center and are less delocalized at the carbene carbon.
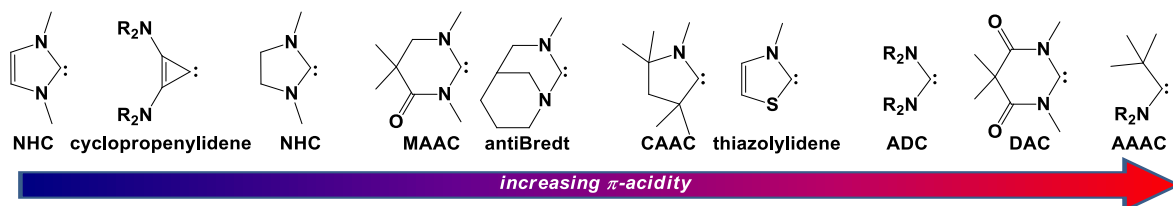
Figure 1.5 Major carbene structures ranked by their π-accepting characteristics

1.c The Utilities of Stable Carbenes in Catalysis

The persistence of the carbenes mentioned previously aid in their ability to be used in a variety of fields of chemistry. An important example from the group of James Hedrick, has shown that NHCs can be used as organocatalysts, and Robert Grubbs (2005

Nobel Prize) utilized carbenes as a ligand for ruthenium-based olefin metathesis catalysts.[10,11] In 2002, Hedrick was the first to carryout novel metal-free, organocatalytic polymerization of lactides. One of his first carbenes of choice was an NHC which was believed to initiate ring-opening polymerization (ROP) through a nucleophilic attack on the desired monomer (Figure 1.6).[10]
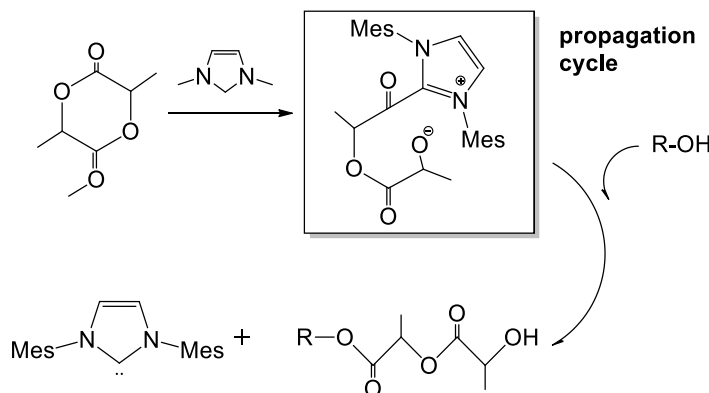
Figure 1.6 Shows the cycle taken by the NHC and its prey species for ROP

There are two ways that was seen which the N-heterocyclic carbene (NHC) can catalyze polymerization: a) the monomer activated mechanism, b) anionic mechanism.[10] The ability for the carbene to as a "catalytic anion" is the most promising since the propagating route as seen in Fig. 1.6 above would propose NHC activating the substrate to attack the propagating alcohol. This propagation was widely studied and was also postulated by Breslow and Stetter in thiazol-based NHC's.[10] Moreover, initiation occurs due the nucleophilicity of the alcohol which reacts with the lactide carbene complex to form the ring-opened adduct, then eventually a polylactide chain.[10]

In contrast to organocatalysis, Grubbs sought out to use the NHC as a ligand attached to a metal center that possessed higher catalytic activity that his initial catalysis, the Grubbs generation I olefin metathesis catalyst. Grubbs II [Fig1.7(GII)] was found to be a more active, and more robust homogenous catalyst for olefin metathesis. Unlike the

catalysis that was done by Hedrick using only the carbene framework, these complexes could undergo Ring Opening Metathesis Polymerization (ROMP) across an olefin.[11]

G(O)   G(I)   G(II)
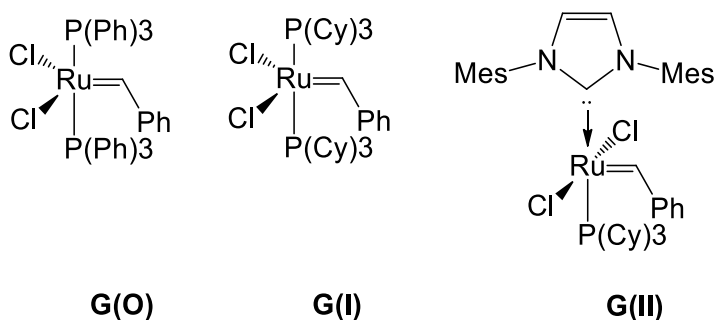
Figure 1.7 Grubb's catalyst

Metathesis is a general sense of exchanging bonds between products and starting materials, which can be through single and double displacement.[11] However, metathesis across an olefin involves the use of displacement to form a variety of alkenes. The way metathesis works is through the thermodynamic imperative that the final products could be determined by the energetics. In the olefin metathesis, using Generation I or II the energy of the products and the reactants should remain the same since they both contain an olefin. The metathesis reactions occur in a ring opening method (ROMP), transforming cyclized products into polymerized alkyl chains, seen in Fig1.8:
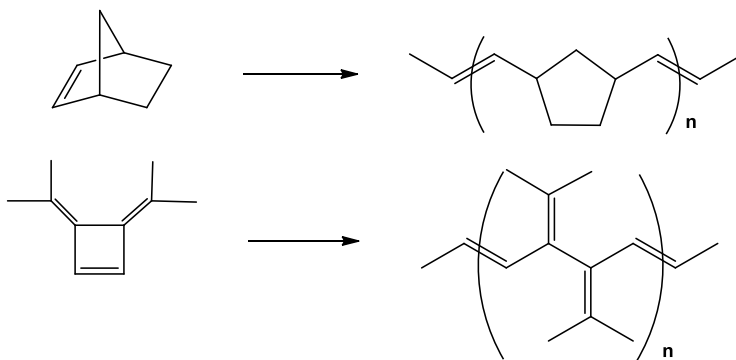
Figure 1.8 Shows ROMP pre- and post- treatment of Grubbs II catalyst

1.d The Utilities of Carbenes as Ligands

      More recent work, relevant to the work in this thesis, involves the use of carbenes as ancillary ligands, similar to what has been done in the field of organometallic chemistry by Wanzlick[12] and Öfele[13], later followed by Lappert[14] among many others. However, it was not until the discovery by groups such as Robinson, Bertrand, and Braunshweig that laid the foundation for the use of carbenes to stabilize main group species. Although some of the first main group element carbene complexes were simple Lewis adducts where the carbene was a Lewis base coordinated to a main group Lewis acid, much more contemporary carbene-main group complexes are characterized by main group elements in atypical oxidation states that are stabilized by a carbene ligand. In most of these examples, the main group element is low valent, and simultaneously electron-rich. To stabilize these main group species, carbenes can impart both σ-donating and π-back bonding effects. The upcoming chapter will introduce all of the recent discoveries in the field of organoboron chemistry that utilize carbenes as stabilizing ligands. In recent years, there has been some debate regarding depictions of the unique bonding situations that arise when using carbene ligands. This is most exemplified by an excellent paper from Krössing.[15] With this contention in mind, this thesis will only use of the dative arrow bond notation to denote bonding situations C: → E where nominal back bonding is observed.

II. Introduction of Main group Boron species stabilized by Carbene

2.a Main group boron species stabilized by carbenes with multiple bonding

Low valent main group species stabilized by carbenes were first studied by the group of Robinson.[16,17] The major issue with stabilizing these reactive compounds is that as you decrease in oxidation states from boron III to I, you increase the reactivity, and thus the rarity of the stable compounds. These species are highly reactive, and if to be studied, the molecules must be treated with an electron rich entity that can impart stability to the boron center to allow for analysis and characterization. The reactive species that was first stabilized by Robinson's group was parent borylene (:BH).[17] To access this molecule, a Lewis adduct of a carbene and BBr_3, was first prepared by mixing the two components together in a 1:1 stoichiometric ratio(**1**, Figure 2.1). Compound **1** was then treated with excess of the reducing agent KC_8 in diethyl ether to presumably afford a NHC-B(0) species. However, due to their highly reactive boron center, hydrogen abstraction from the surrounding solvent gave a complex with boron(I), **2**, in lieu of elemental boron. Respectfully so, the B=B double bond, seen in **2**, is presumed to occur from dimerization of the parent carbene-stabilized parent borylene (:BH), which was confirmed by X-ray crystallography (B=B=1.560 Å and DFT analysis).[17]

1   **2**
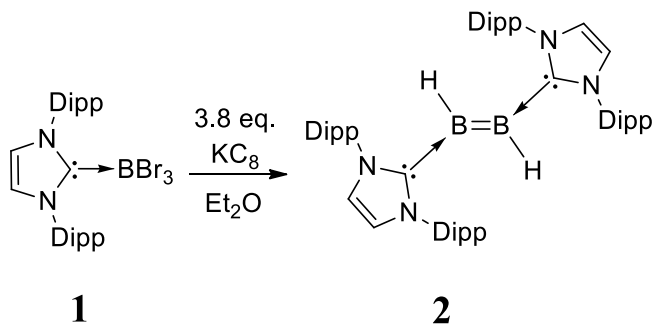
Figure 2.1 Synthesis of the first carbene complex that contains multiple bond-boron

character

As the concept of using carbenes to stabilize reactive boron species grew in prominence, more complexes featuring boron in several oxidation states became accessible. Additionally, several examples of compounds with never-before-seen boron-boron multiple bonding were realized, as seen in examples from Wang[18], and Braunschweig.[19,20,21]

2: R = Mes, Dur, thienyl,
2-(TMS)-thienyl, 2-(CH$_3$)-
furyl, ^{i}Pr

3: L = IPr, R = Br
4: L = IPr
5: L = ^{Me2}CAAC
6
7
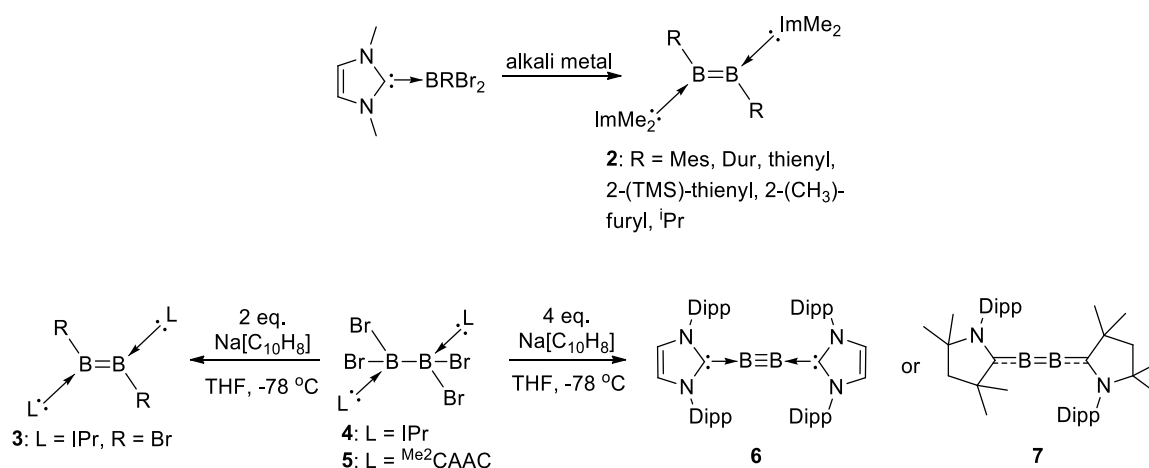
Figure 2.2 Syntheses of analogs **1** that afford boron-boron multiple bonds

Isostructural to Robinson's **2**, Braunshweig made analogs (**3** , **4** , **5**, Figure 2.2) using NHCs and a cyclic alkyl amino carbene (CAAC) via the reaction schemes shown in Figure 2.2.[21,22,23] Staying consistent with the double bond length of Robinson's **2** B=B length of 1.55–1.59 Å, the reduction using sodium napthalide makes for an NHC or CAAC supported diboron (**6** and **7**, Figure 2.2).[24] Molecules **6** and **7** are unique in that the boron atoms in each complex are formally in the zero oxidation state, making these

compounds the first examples of a complex that feature a novel allotrope of boron, namely B_2. Interestingly, these boron(0) complexes can be taken up in a solvent and treated with metal-chlorides to illuminate the utility of using the boron-boron π-electrons as donating ligands to give complexes **8** and **9**, Figure 2.3.[25]

8: M = Cu, Ag, or Au

9: M = Li or Na
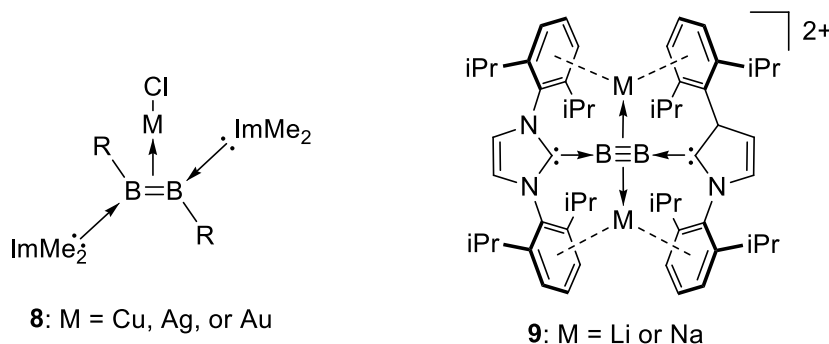
Figure 2.3 Examples of compounds that are produced from complexes in Figure 2.2

Nonetheless, the reduction of the carbene-boron species to achieve the dimer, with the addition of M-Cl best describes the Dewar-Chatt-Duncanson model that connects the synergetic concept of ligand→ metal σ-donation, metal→ ligand π-back donation.[25]

2.b The reactivity of carbene-stabilized borylene species

Electronically unsaturated 4-electron species have been known to be too unstable and reactive to isolate. Earlier works from Braunshweig have shown borylenes can be stabilized as ligands within the coordination sphere of transition metals[26], but more recently, several groups have focused on preparing organoborylenes. Interestingly, some of the first carbene-stabilized borylenes have shown to be formed, and trapped through cycloaddition/C-H insertion reaction to afford cyclic structure such as **10** and **11**, Figure 2.4.

Figure 2.4 Illuminates cycloaddition/C-H insertion products **10** and **11**

10 represents of an example where an acyclic diamino carbene (ADC) which is very π-acidic, was used in an attempt to stabilize borylene. Following the reduction of the boron(III) center in the ADC-BRCl$_2$ complex, another boron(III)-containing compound (**10**) was isola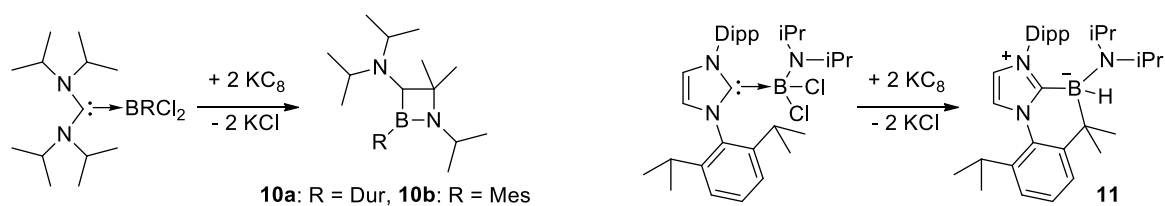ted. It is believed that **10** was generated through a C-H activation event that takes place when the purported transient ADC-supported borylene is formed.[26] This formation of the air-stable heterocycle was serendipitous in that the color change in hexane went from yellow to red, indicative of a carbene-borylene adduct.[26] Similarly, Robinson showed a similar C-H activation take place in the synthesis boracycle **11**.[27] With respect to the transformation seen in **10** and **11**, DFT calculations show that upon reduction, the borylene is in fact generated, however due to the high reactivity of the B(I) containing species, the adducts immediately convert into the heterocycle by a sequence of the precursor complex shift and C-H activation, affording a ring closure.[27,28]

Bertrand was the first to isolate a legitimate organoborylene, however, these molecules are three-coordinate dicarbene-stabilized borylenes[29] The first compound was isolated by reducing a ^{cy}CAAC-BBr$_3$ adduct with KC$_8$ to give the desired organoborylene **12** (Figure 2.5).One of the most impressive things of this discovery was that the boron atom in **12** is formally a 3-coordinate boron(I) center, in which the boron atom has a sterochemically-active lone pair of electrons. In this regard, it is appropriate to describe the boron atom in **12** as isoelectronic with a nitrogen atom in an amine, and, remarkably,

represents that first example of a boron atom that behaves as a Lewis base, not a Lewis acid.[29] Moreover, **12** can readily undergo 1-electron oxidation to afford a boron centered radical cation. Three years later in 2014, Bertrand extended this synthetic methodology to prepared derivatives with mixed carbenes (**13**, Figure 2.5), through the reduction of a boronium salt that can undergo 2-electron reduction .[30]
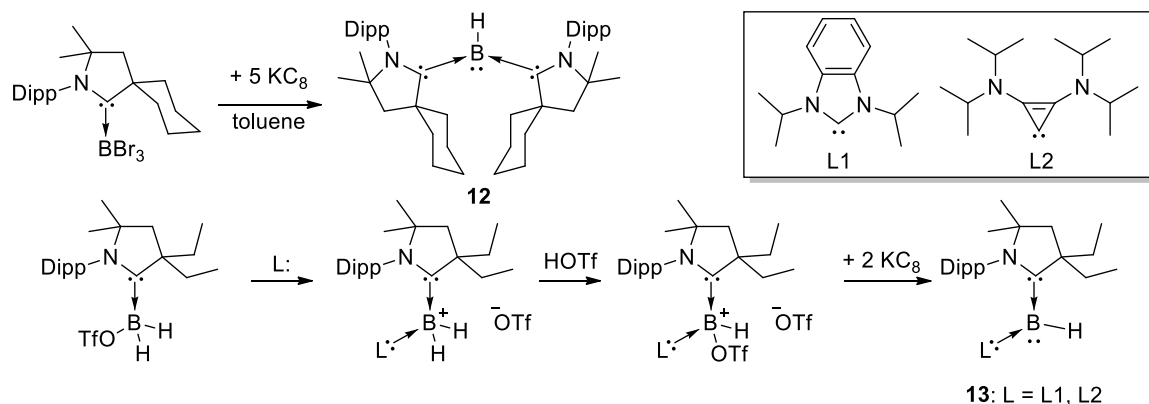

Figure 2.5 Synthesis of biscarbene-borylene complexes **12** and **13** that has been reported

by Bertrand

In 2015, impressively, Bertrand and Stephan successfully isolated the first monocarbene-stabilized 2-coordinate aminoborylene (**14**) by reduction of the Lewis adduct $^{cy}CAAC-B(N(SiMe_3)_2)Cl_2$.[31] What is most interesting about this discovery is, in comparison to **11**, (**14**, Figure 2.6) does not participate in cycloaddition/C-H insertion by virtue of its strong π-accepting character of the CAAC ligand, coupled with the donating ability of the nitrogen lone pair attached to the boron atom. Collectively, these electronic effects enforce the molecule to adopt a heterocumulene structure in the solid state as evidence by X-ray crystallographic data.[31] Despite observed solid state structure, organoborylene **14** was also shown to exhibit reactivity consistent with resonance structure **14'**(Figure 2.6) as the compound splits H_2 and coordinate CO in solution.[31]
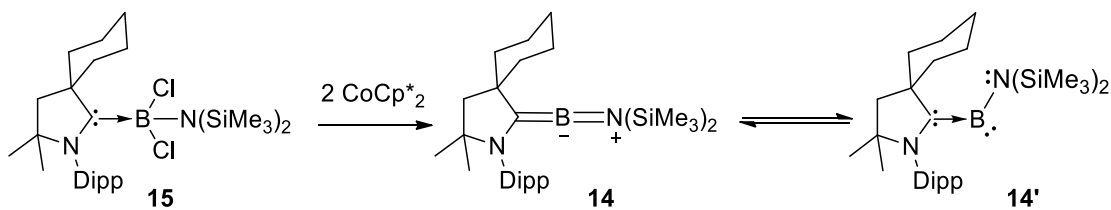
Figure 2.6 Synthesis of ^{cy}CAAC-supported aminoborylene **14** with resonance structure **14'**.

2.c Carbene stabilized boron radicals

Boron centered radicals predates to the 1920's where reports describe the synthesis and characterization of anionic boryl radicals. Phil Power and coworkers, in the 80's, reduced triaryl boranes[32] with alkali metals in diethyl ether to give the boron-centered radical anions as salts of the formula $[M]^+[BAr_3]^-$ similar to the compounds studied in 1924 by Krause.[33] It became apparent that to afford stable anionic radicals, large sterically demanding ligands to support kinetic stabilization would be essential. In the late 2000s, work on boron-centered radicals shifted from radical anions to neutral boron(II) radicals supported by carbenes. To date, there are several examples of such radicals that have been spectroscopically characterized from the group so of Gabbaï[34], Lacête[35] and Curran[36, 37] (See **16**-**20**, Figure 2.7). Of this series, only **16** has been structurally-characterized owing to the bulky aryl substituents at the boron and the π-accepting acridiniyl carbene.[34] (**16** and **17**, Figure 2.7) were prepared by 1-electron reduction of the borenium cation.[34,35] Contrarily, (**18-20**, Figure 2.7) were prepared by hydrogen abstraction from NHC-BH$_2$R adducts.[36,37] Of the molecules, **16** gives an EPR signal that's indicative of the spin density localized through the acridine species whereas

the EPR of compounds **17-20** reveal a spin density substantially throughout the molecule. This is attributed to the result of the π-accepting properties of the acridinyl carbene in the radical **16** in comparison to the use of the NHC in the B(II) radicals.[34]
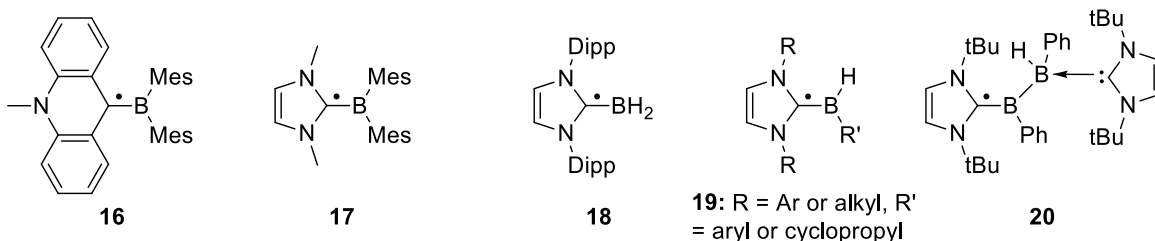

Figure 2.7 Examples of boron centered radicals from groups Gabbai, Locote and Curran.

More recently, examples of neutral B(II) radicals prepared by 1-electron reduction of a B(III) precursor have been explicated by Bertrand[38], and Braunshweig[39]. These radicals, (**21** and **22**, Figure 2.8) obtained from the parent species CAAC-BRCl$_2$ were treated with CrCp*$_2$ or CoCp*$_2$ as a reductant and then isolated to give rise to a similar EPR spectra. Furthermore, DFT analysis obtained by these compounds reveal that the singly occupied molecular orbital (SOMO) of the radicals are dominated by a π-bonding orbital between the boron and former carbene carbon centers. This data suggests that the unpaired radical electron resides in a formal 1-electron B-C π-system.[38,39]
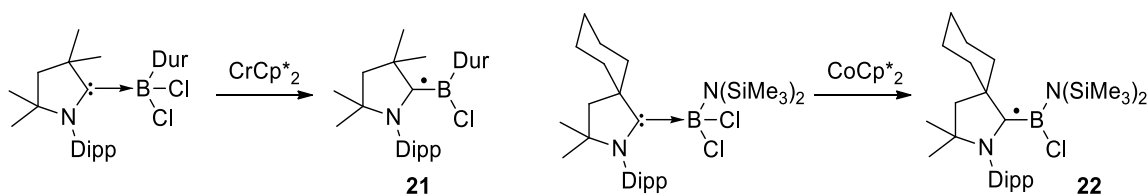

Figure 2.8 Synthesis of a stable B(II) CAAC-supported radical by Braunshweig **21**, and

Bertrand **22**

These boron(II) radicals can also be prepared by a 1-electron oxidation of a parent B(I) carbene stabilized species or diborene precursor.[29] The first example of the boron

(II) contained by 1-electron oxidation was reported by Bertrand in 2011 by treating **12** with GaCl$_3$ in DME to yield a stable boron(II) radical cation (**23**, Figure 2.9). [29] In a similar fashion, Braunshweig oxidized a B(I) borolyl (**24**, Figure 2.9) anion with Ph$_3$ECl (E=Sn or Pb), affording the neutral B(II) borolyl radical (**25**, Figure 2.9). [40]
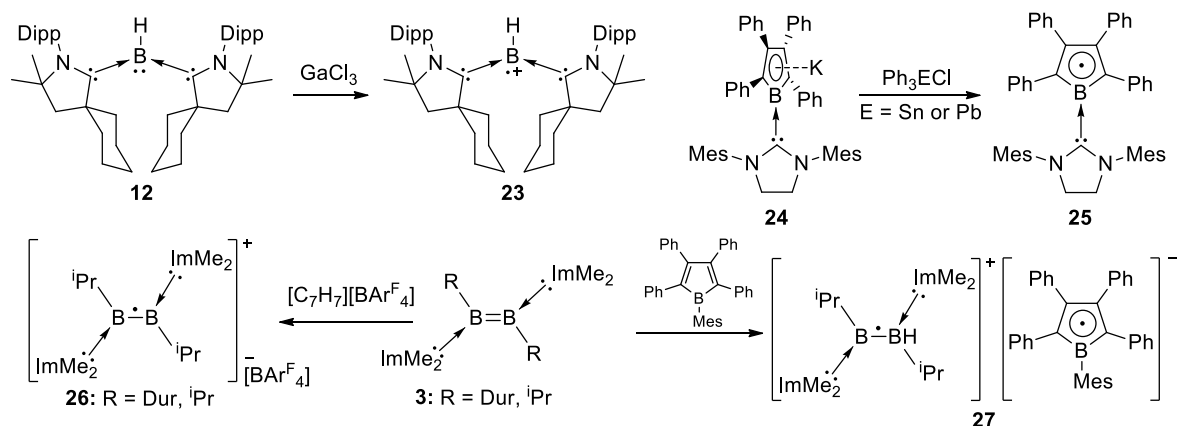
Figure 2.9 Shows examples of B(II) radicals by oxidation of B(I)(**12** or **24**) or diborene (**3**) precursors.

In addition to the oxidation of these carbene-stabilized boryl radicals, B=B double bond diborenes **3** could also be readily oxidized to afford the diboron radical cation (**26**, Figure 2.9) by using troplylium salts with non-coordinating borate anions, providing the first example of a stable boron-centered radical-anion/radical-cation pair (**27**, Figure 2.9). [41]

3.a Efforts Towards a CAAC stabilized Aminoborylene

During the course of the Bertrand and Stephan's work on the synthesis of organoborylene **14**, I was independently working toward a similar organoborylene during my research in Dr. Hudnall's group. To synthesize the desired organoborylene, a CAAC was first dissolved in hexanes, and then treated with $B(N(iPr)_2)Cl_2$. This resulted in the immediate precipitation of a yellow compound which has been identified as compound **28** (Figure 3.1). This Lewis adduct was characterized by multinuclear NMR spectroscopy, and X-Ray diffraction (see Figure 3.2 for X-ray structure, Appendix i for NMR). This adduct could then be treated with KC_8 as a reductant to afford the CAAC-aminoborylene (**29**, Figure 3.1). The optical properties of the complex changed as the system was perturbed with electrons from a yellow to red color. The identity of the desired CAAC-aminoborylene product was confirmed by multinuclear NMR spectroscopy (Appendix ii), but unfortunately, single crystals suitable for an X-ray diffraction analysis were elusive, and ultimately, Bertrand and Stephan published their organoborylene analogue (**14**) prior to completion of our project.
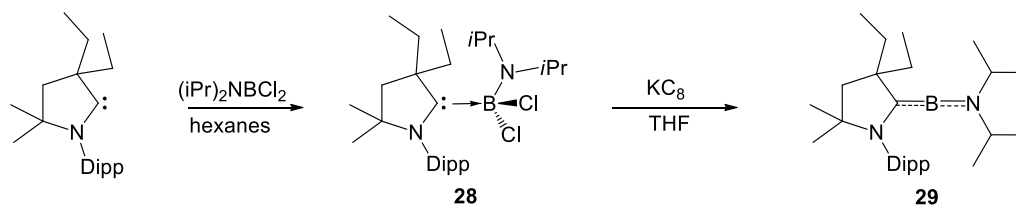

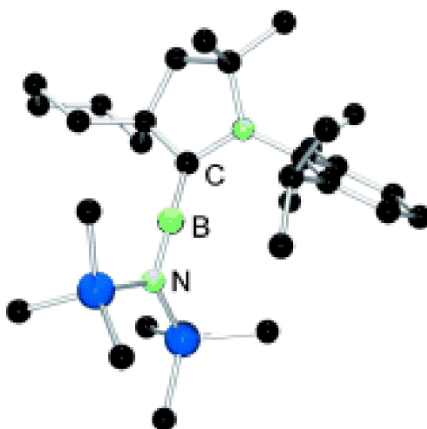**Figure 3.1** Synthesis of CAAC-supported aminoborylene

Figure 3.2 Shows the X-ray confirmation of the Lewis adduct CAAC-$(B(N(iPr)_2)Cl_2$

3.b Efforts Towards a CAAC stabilized η^5-Cp*borylene

During this time, I was also working toward synthesizing a carbene-stabilized borylene that featured a large, bulky η^5-pentamethyl cyclopentadienide (η^5-Cp*) as a stabilizing boron-substituent. The use of η^5-Cp* was inspired by work from the group of Alan Cowley at UT Austin, which synthesized the first example of a transition metal borylene $[(CO)_5Fe-B-(\eta^5-Cp^*)]$.[42] Since it is now established that carbenes can serve as transition metal mimics, my research was focused on replacing the $[(CO)_5Fe]$ fragment with a carbene. To test this hypotethsis, CAAC was treated with Cp*BCl$_2$ in hexanes affording **30** as confirmed by multinuclear NMR spectroscopy and X-ray analysis in Figure 3.3 (Appendix iii, iv, v for NMR)**.**
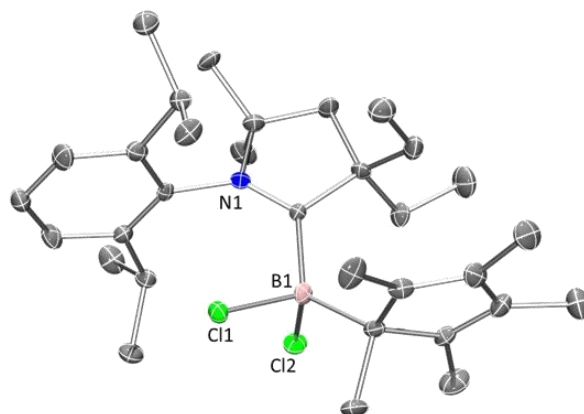
Figure 3.3 X-ray analysis conforming the coordination completion of CAAC-Cp*BCl$_2$

Direct reduction of **30** with 2 equivalents of reducing agent KC$_8$ to afford the terminal borylene species CAAC-B-η^5-Cp* unfortunately resulted in C-H activation similar to **10** and **11**, and gave boracyle (**32**), which presumably formed from a transient borylene (**31**, Figure 3.4). This boracycle was characterized via spectroscopy and X-ray crystallography and multinuclear NMR spectroscopy (see Figure 3.5 for X-ray structure, Appendix vi, vii, viii for NMR). This inserted product, as well with **10** and **11** are air stable molecules since they are now coordinately saturated.
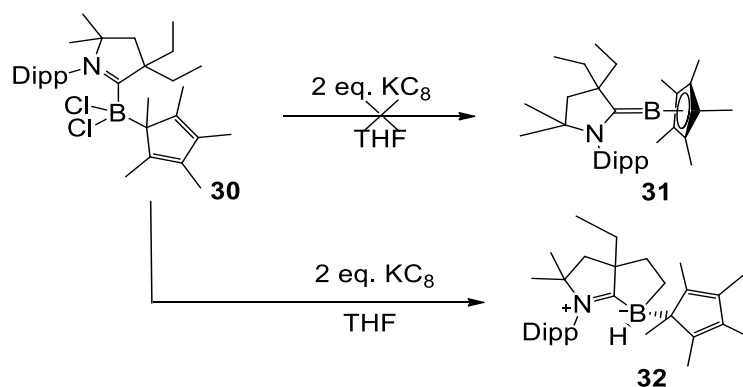

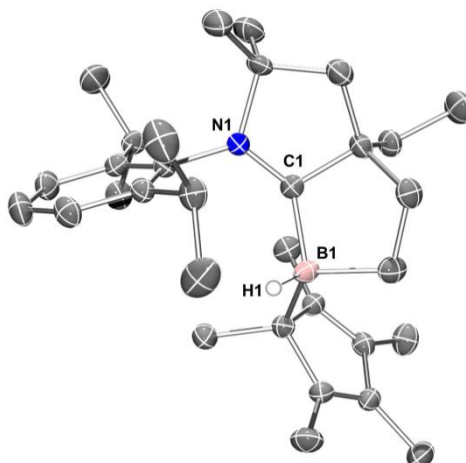**Figure 3.4** Synthesis of CAAC C-H inserted boracycle and the expected η^5-borylene

Figure 3.5 X-ray analysis confirmed the C-H insertion of the parent CAAC-Cp*BCl$_2$

A paper from Chiu and co-workers[43] published in 2015, demonstrated that NHC-supported B(III) dications with η^5-Cp* substituents could be readily prepared by halide abstraction from the Cp*BCl$_2$ moiety coordinated by the carbene. For this reason, **30** was taken up in chlorobenzene and treated with 2 molar equivalents of AlCl$_3$ as a halide abstracting agent to give the CAAC-supported boron(III) dication **33**(Figure 3.6) with an η^5-Cp* ligand. The η^5-orientation of the Cp* was confirmed by ^{11}B NMR spectroscopy (δ = -49 ppm), and by ^{1}H NMR which revealed a singlet that integrated to 15, consisted with 5 equivalent CH$_3$ groups (Appendix vii).
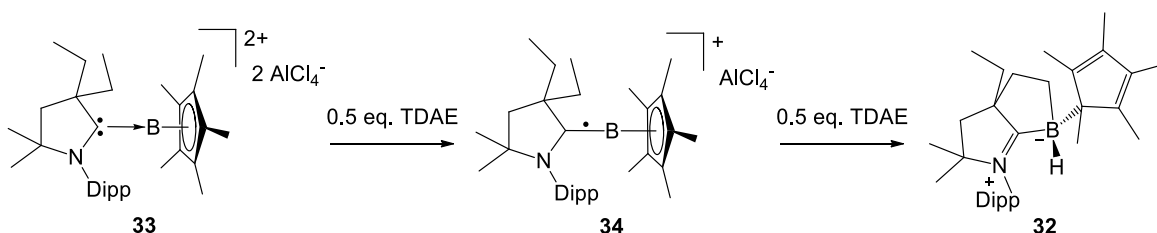

Figure 3.6 Synthesis of B(III) dication by the halide abstracting agent, followed by subsequent reduction.

Subsequent 1-electron reduction gave the boron(II) radical cation (**34**, Figure 3.6). Unfortunately, the addition of second reducing equivalent did not give the desired η^5-borylene, but instead gave boracycle **32**. Despite the difficulty in isolating the borylene **31**, the fact that radical cation **34** could be isolated proved to be far more exciting. To date, there are no known examples of 2-coordinate boron(II) radicals, and even rarer are boron(II) radical cations. The radical has been characterized by an EPR signal consistent with coupling to boron and nitrogen centers. Altogether, we believe that this pattern indicates that the unpaired radical electron populates a 1-electron B-C π-bond. Interestingly, DFT analysis on the parent CAAC-Cp*B-dication indicates that as we reduce **33** to **34**, we get a ring slip from η^5 to a η^3. Figure 3.7 illuminates the change in hapticity by the orientation change of the Cp* ring. In an η^5 complex, the methyl groups along the carbon Cp* ring should be planar, thus seen equivalently by the boron center. What we see now is only 3 methyl groups in than plane, thus confirmation of the slip in the ring.
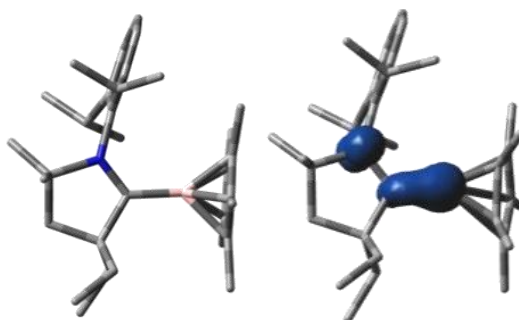

Figure 3.7 DFT of the ring slip from the η^5-dication to the η^3-radical cation

The radical cation of the parent function would then serve as a snapshot of the "ring-slip" taking place, providing further explanation of the insertion of the borylene into the carbene substituent after the addition of an electron to **34**.

IV. Synthesis and Characterization of Carbene Stabilized Boron Species using DAC

4.a Efforts towards Stabilizing DAC-aminoborylene

Despite the isolation of the first 2-coordinate organoborylene by Bertrand and Stephan[30], we were interested in isolating a similar molecule with a carbene that is a stronger π-acceptor than the CAAC ligand that they used. For this reason, we also began to look at using a diamidocarbene (DAC), which the strongest π-accepting carbene known to support a 2-coordinate borylene. $B(N(iPr)_2)Cl_2$ would be used to coordinate the DAC, and then subsequent 2-electron reduction should give a 2-coordinate organoborylene that is stabilized according to Scheme 2. According to Scheme 2, the DAC can stabilize the borylene by donating a lone pair of electrons into an empty orbital on boron while simultaneously accepting the boron lone pair, by virtue of the high π-accepting nature of the carbene. Additionally, the boron center is further stabilized by donation of the amine lone pair in the second vacant orbital, yielding a heterocumlene, similar to what was observed by Bertrand in **14**. However, due to the increase in π-acidity on going from CAAC to DAC, no reaction was observed when treating a DAC with $B(N(iPr)_2)Cl_2$.
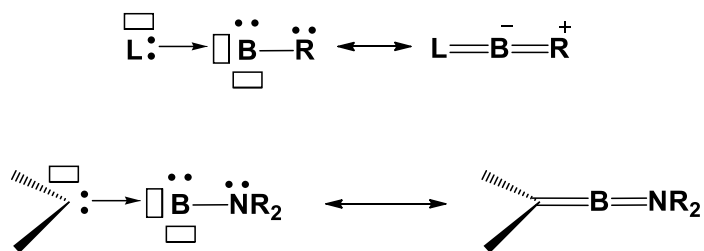
Scheme 2. Shows the ideal convention of stability of a carbene stabilized aminoborylene post reduction affording allene.

Cleverly, B(N(iPr)$_2$)Cl$_2$ could be treated with a halide abstracting agent TMSOTf to facilitate the reactivity of the boron species, resulting in the formation of the borenium salt **35** (Figure 4.1).
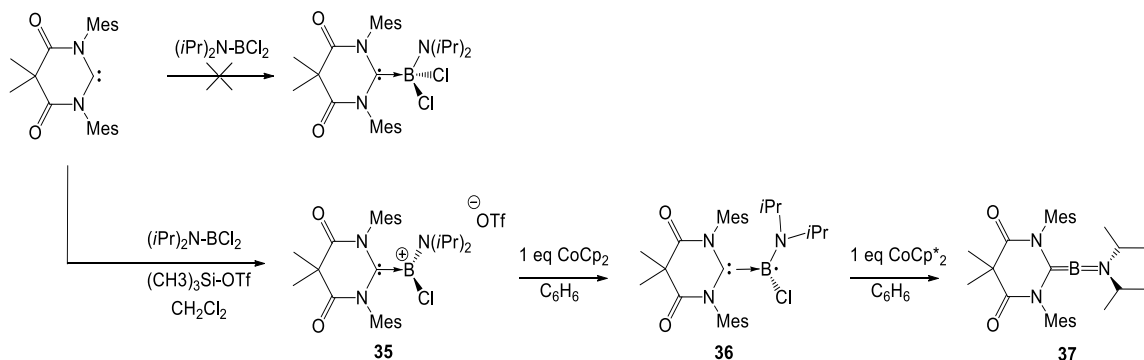

Figure 4.1 Synthesis of the borenium cation, radical, and borylene

This structure has a B1-C1 bond distance that is a bit elongated when compared to recent literature which is rightfully due to: 1) the weak donating ability of the DAC ligand when compared to the NHC 2) the steric interference when opting a 6 ring structure in lieu of 5.
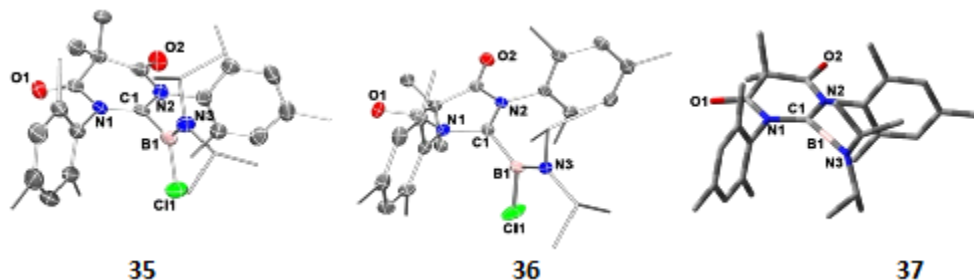

Figure 4.2 Shows the X-ray confirmation and analysis of the DAC-bornium cation from the parent species to the borylene.

The identity of this Lewis adduct confirmed by a combination of multinuclear NMR spectroscopy where we have two inequivalent isopropyl groups, that integrate to 6, and single crystal X-ray diffraction (see Figure 4.2(**35**) for crystal structure, Appendix xi

for NMR). From the cyclic voltammogram (CV), we observed that this cation undergoes one reversible and one irreversible 1-electron reductions **35** could be reduced by one electron to generate neutral radical **36**, followed by a second 1-electron reduction to give the desired borylene **37**. Being redox active, the borenium cation participated in subsequential reductions by the treatment of $CoCp_2$ to generate the radical **36**. The radical was characterized by X-Ray [Figure 4.1 (**36**)], and EPR with a signal showing the pattern in Figure 4.3 confirming a paramagnetic species. Being B(II), **36** can get reduced again using $CoCp*_2$ to generate the borylene **37.**

Uniquely, **36** had a disparity when compared to other neutral boryl radicals, as NBO analyses revealed 93% of the spin density was occupied on the carbene carbon, seen as such in figure Figure 4.3.
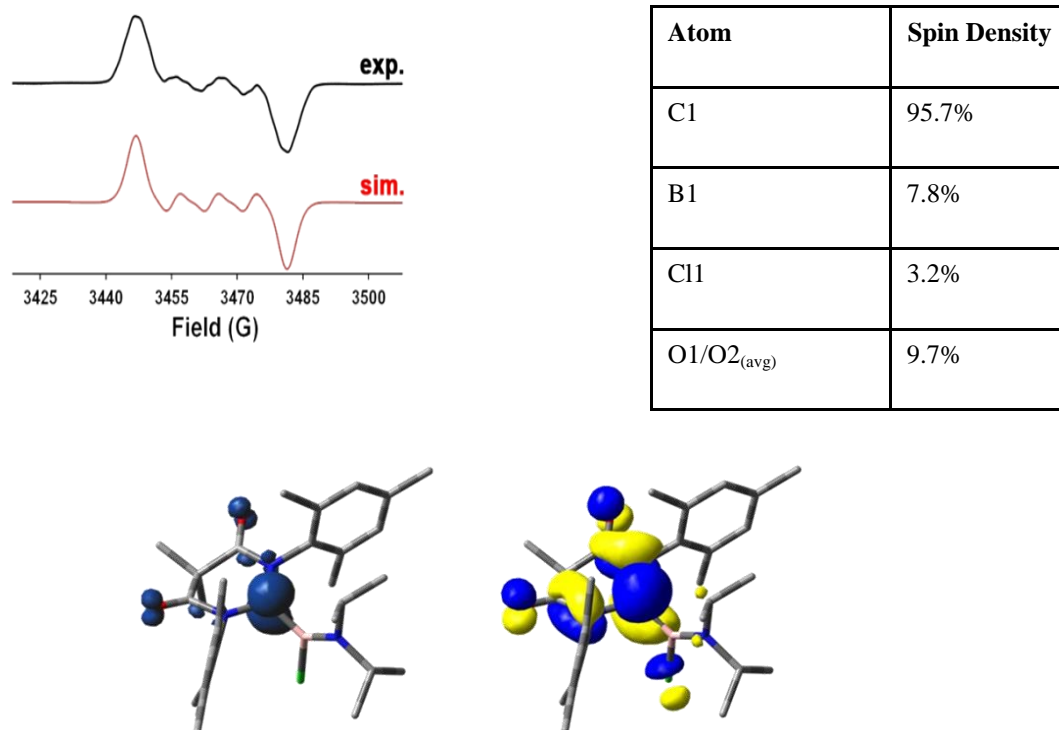

Atom	Spin Density
C1	95.7%
B1	7.8%
Cl1	3.2%
O1/O2$_{(avg)}$	9.7%

Figure 4.3 Shows the calculations made for the DAC-stabilized radical: EPR singal (top left), spin density (top left), NBO analyses (middle).

This disparity attributes the π-acidic character of the DAC ligand versus CAAC and NHC. Therefore, we conclude that due to the π-accepting nature of the DAC, **36** can be best described as a boryl-substituted DAC-centered radical instead of a boryl radical. Despite our best efforts, we were unable to conclusively identify the structure of **37** as a heterocumulene borylene as we were unable to obtain single crystals of sufficient quality to perform an X-ray anaylsis. However, DFT calculations and, ^{1}H NMR and ^{11}B NMR spectroscopy is consistent with **37** adopting a heterocumulene structure, even in solution where the isopropyl groups are now in the same place, a doublet integrating to 12 (Appendix xi).

V. Conclusion/ Summary

Carbenes have been studied since the early 19th century. Carbenes during the time were not isolatable, as they were intermediates from reactions that were trapped and characterized *in situ*. Studies have shown that these carbene species possess a triple state ground state character and are not stable when not subjected to extreme temperatures. Nonetheless, as more studies were devoted to the isolation and characterization of a persistent carbenes, scientists were able to tune the reactivity of these novel compounds. Through this finding, groups from Bertrand, and later Arduengo, were able to synthesize and isolate the first stable carbene species.

These ubiquitous ligands are now structurally diverse with unique steric and electronic properties that has significant influences in the resultant main group complexes photophysical, structural properties, along with the chemical reactivity. The nature of the carbenes electronic properties rely on its π-accepting properties, which influence the coordination to the Lewis acid main group fragment. The Lewis adduct focused primarily in this thesis is the main group Lewis acid: Borylene and Lewis Base: carbene. The coordination of the carbene with the borylene allows the study and reactivity of the reactive by providing stability the low valent species.

Bertrand uses the CAAC carbene as his Lewis base when coordinating low valent centers due to its nucleophilic nature. Successfully, we were able to coordinate CAAC with BN(iPr)$_2$Cl. **28** was treated with 2 equivalents of reducing agent to afford a carbene stabilized borylene that were unsuccessful in fully characterizing with our best attempts. CAAC was further exploited by using a boron species with a bulky aryl substituent that could assist in stability of the carbene-stabilized B(I) species. **30** was formed, and treated

with 2 equivalents of reducing agent to afford the suspected η^5-Cp*borylene. By going from B(III) to B(I) this would force the orientation of the boron to be seen by every carbon of the Cp*=pentamethycyclopentadiene ligand. Unfortunately, X-ray analysis revealed a C-H insertion of the borylene into the carbene substituent, in a B(II) state. The borylene was formed, but was unobserved due to the high reactive nature at boron. To further hone for **31**, **30** was forced into its η^5-orientation by applying an halide abstracting agent affording a B(III) dication **32**. From then, **33** was treated with TDAE stepwise to afford the equivalent of the product that was generated via direct reduction pathway. Most interesting finding of the stepwise reduction was the generation of the B(II) cation, which is the first example of a 2-coordinate B(II) containing species.

DAC was another in house carbene ligand. As referenced in Figure 1.2, DAC is a π-acidic carbene in comparison to CAAC. This was observed as attempts were unsuccessful in coordinating DAC to $B(N(iPr)_2)Cl_2$. However, DAC could be treated with a solution of TMSOTF & $B(N(iPr)_2)Cl_2$ to abstract a chloride from the boron center, accentuating reactivity and forming a clean adduct **35** DAC-BN($iPr)_2$Cl-OTf. This adduct could undergo subsequent reduction to achieve a stable radical that was fully characterized, then to the borylene which has yet to be fully characterized.

VI. Future Goals

A paper from Braunshweig in 2011, shown that metal borylene complexes can undergo liberation of the metal fragment, under UV conditions and in the presence of diphenylacetylene, can cyclize to form a borirene.[44] Borirenes represent the simplest boron-containing cyclic system that is a 2-π aromatic. **37** could be irradiated in benzene, with the addition of diphenylacetylene to form a borirene.
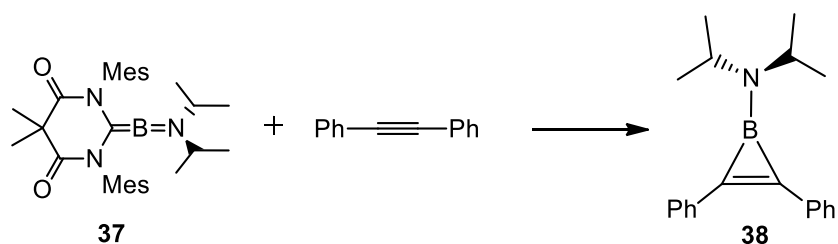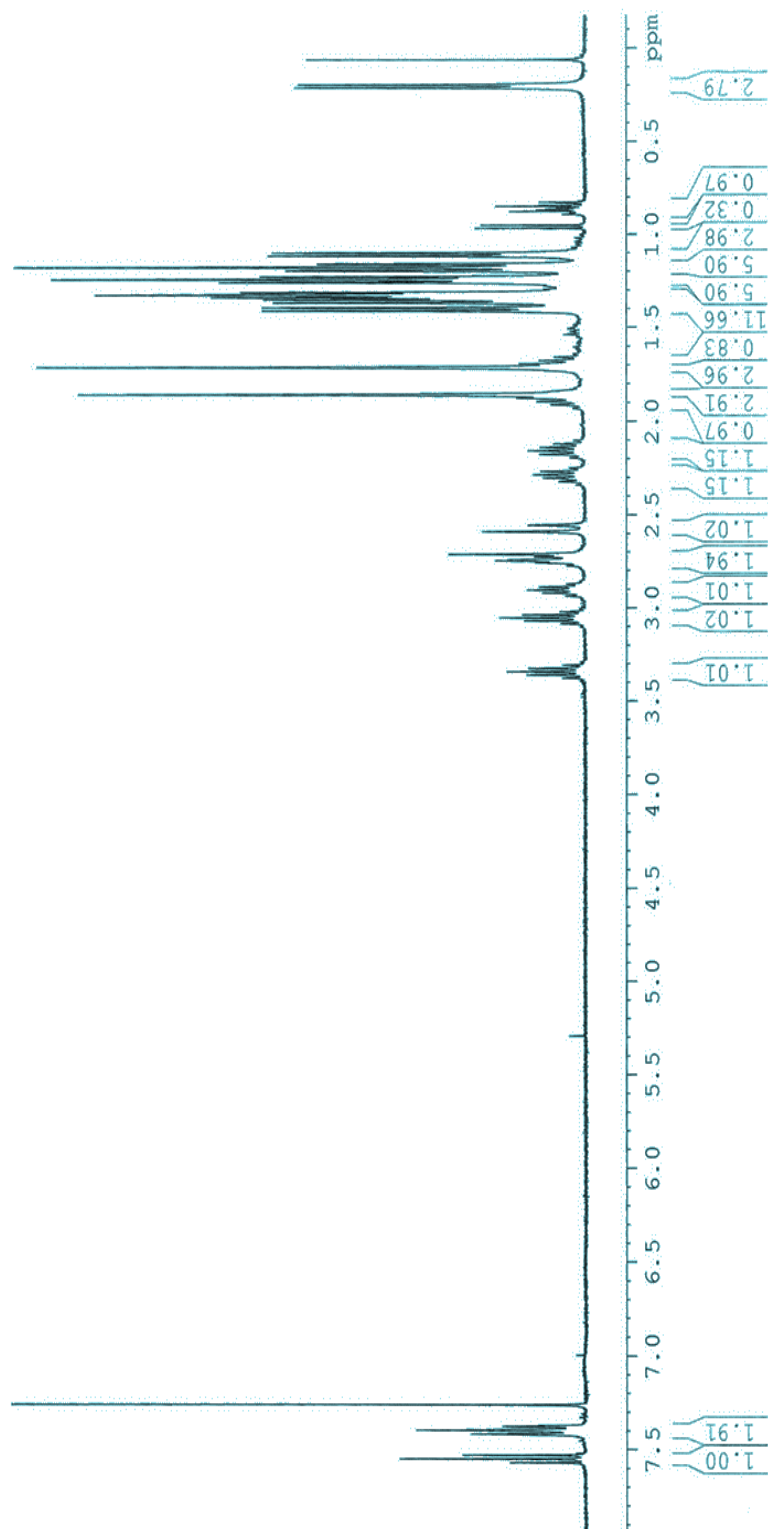

Figure 4.4 Formation of a 2-π aromatic system from a borylene

Though the photochemical transfer of borylenes, to alkynes are straightforward, **38** would be the first example of the formation of a 2-π aromatic boron-containing system utilizing the transfer from carbene in leiu of a metal. This is thought to work with any examples of alkyne containing species.
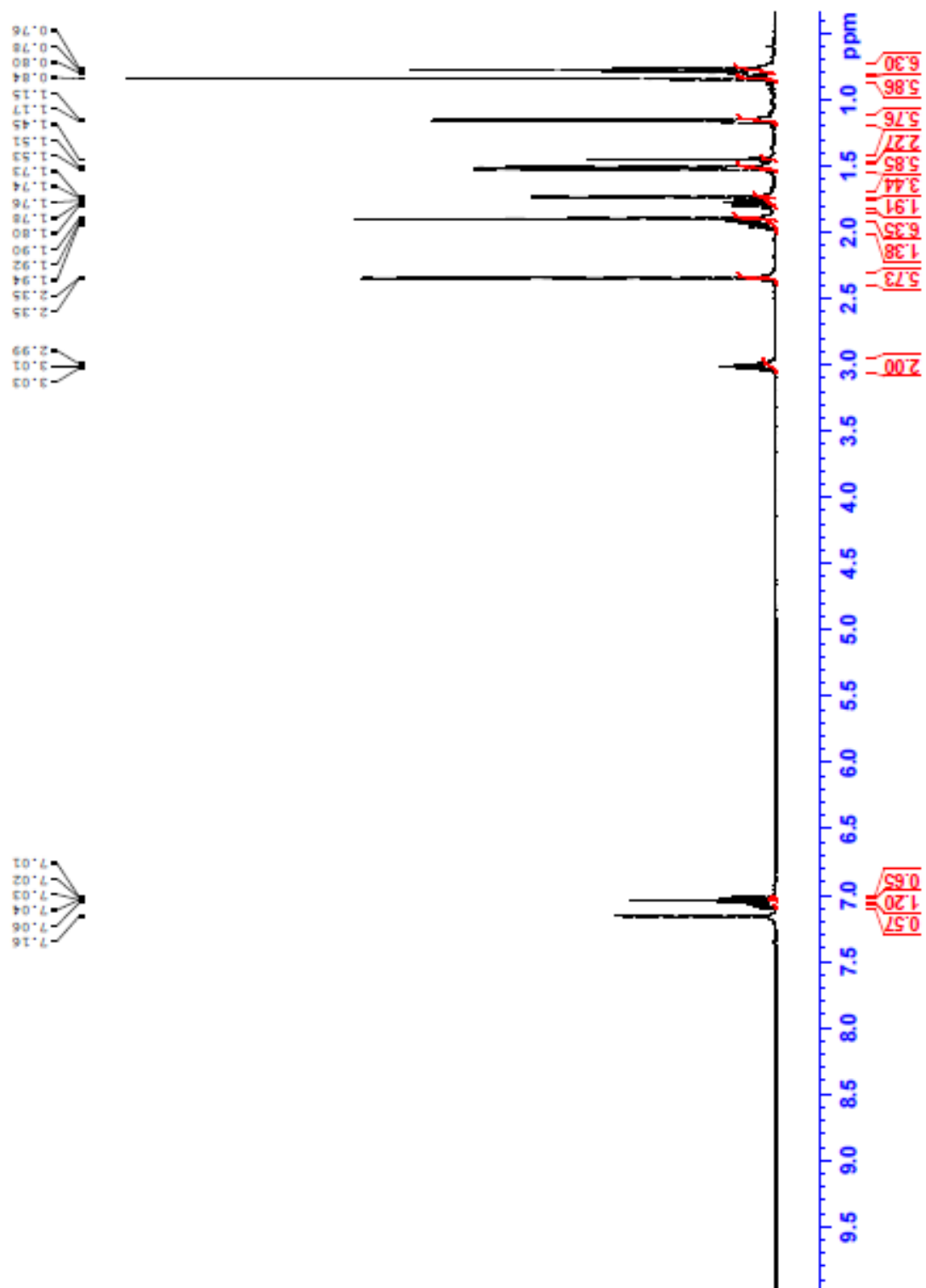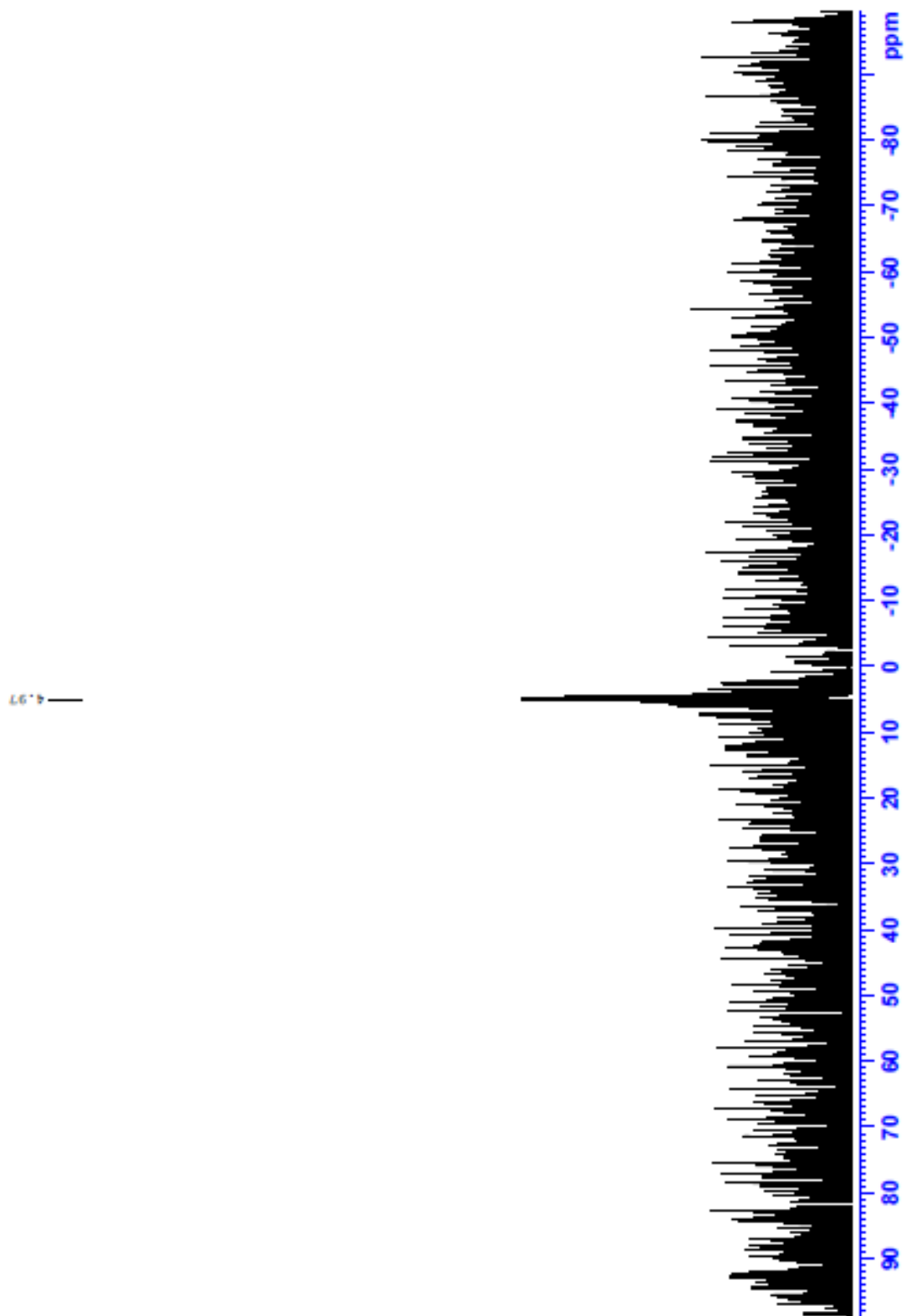
Appendix i. ^{1}H NMR of CAAC-B(N(iPr)$_2$)Cl$_2$
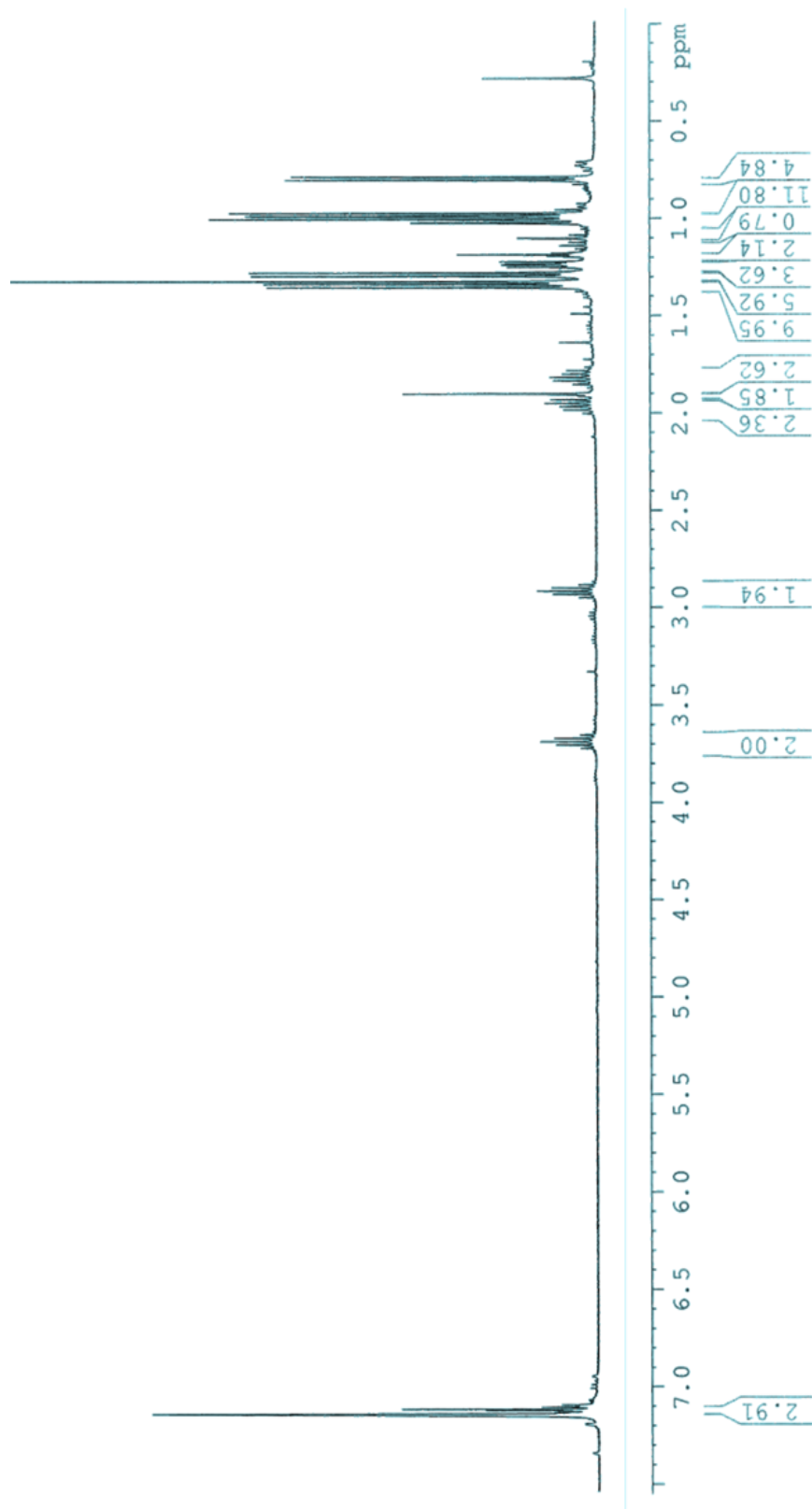
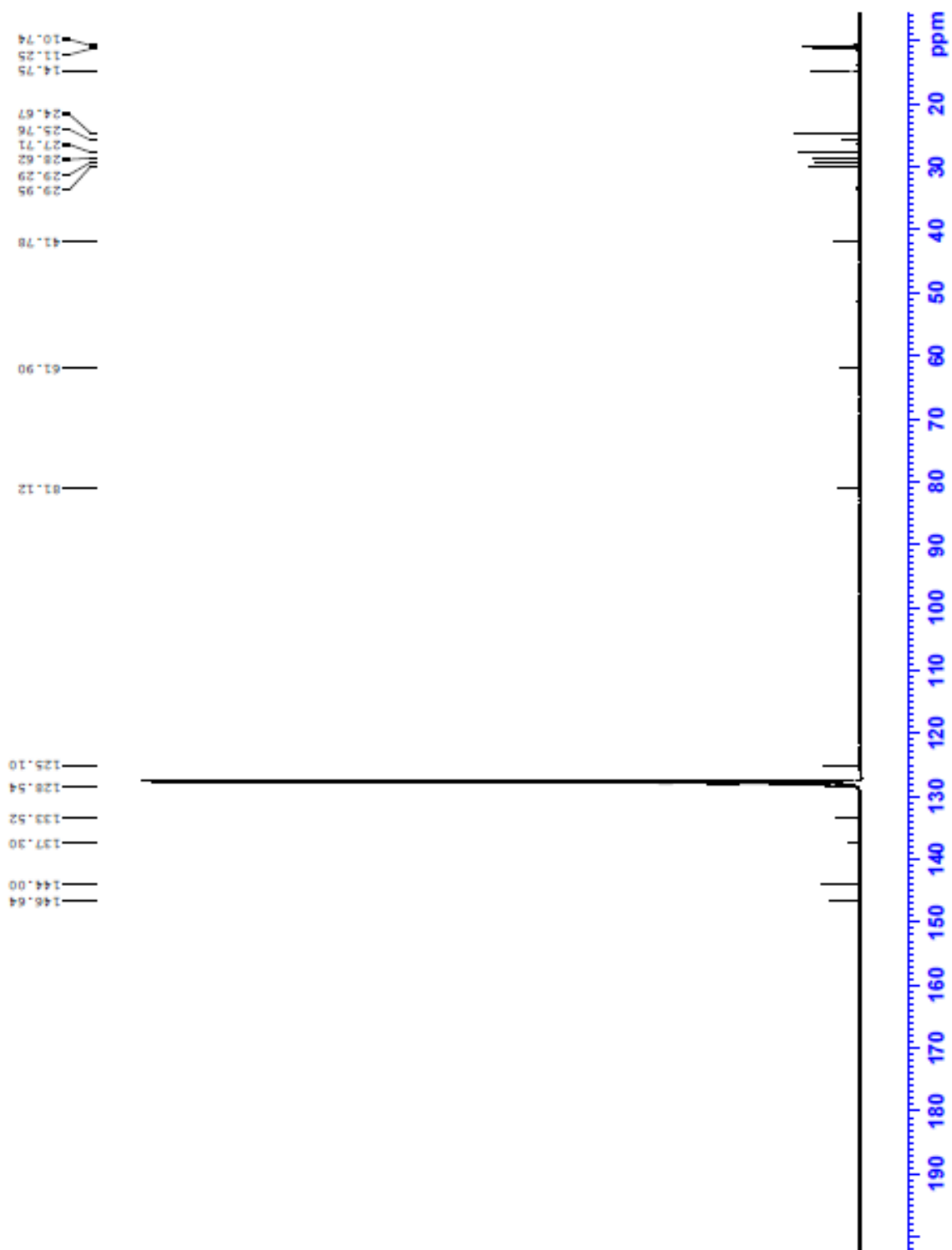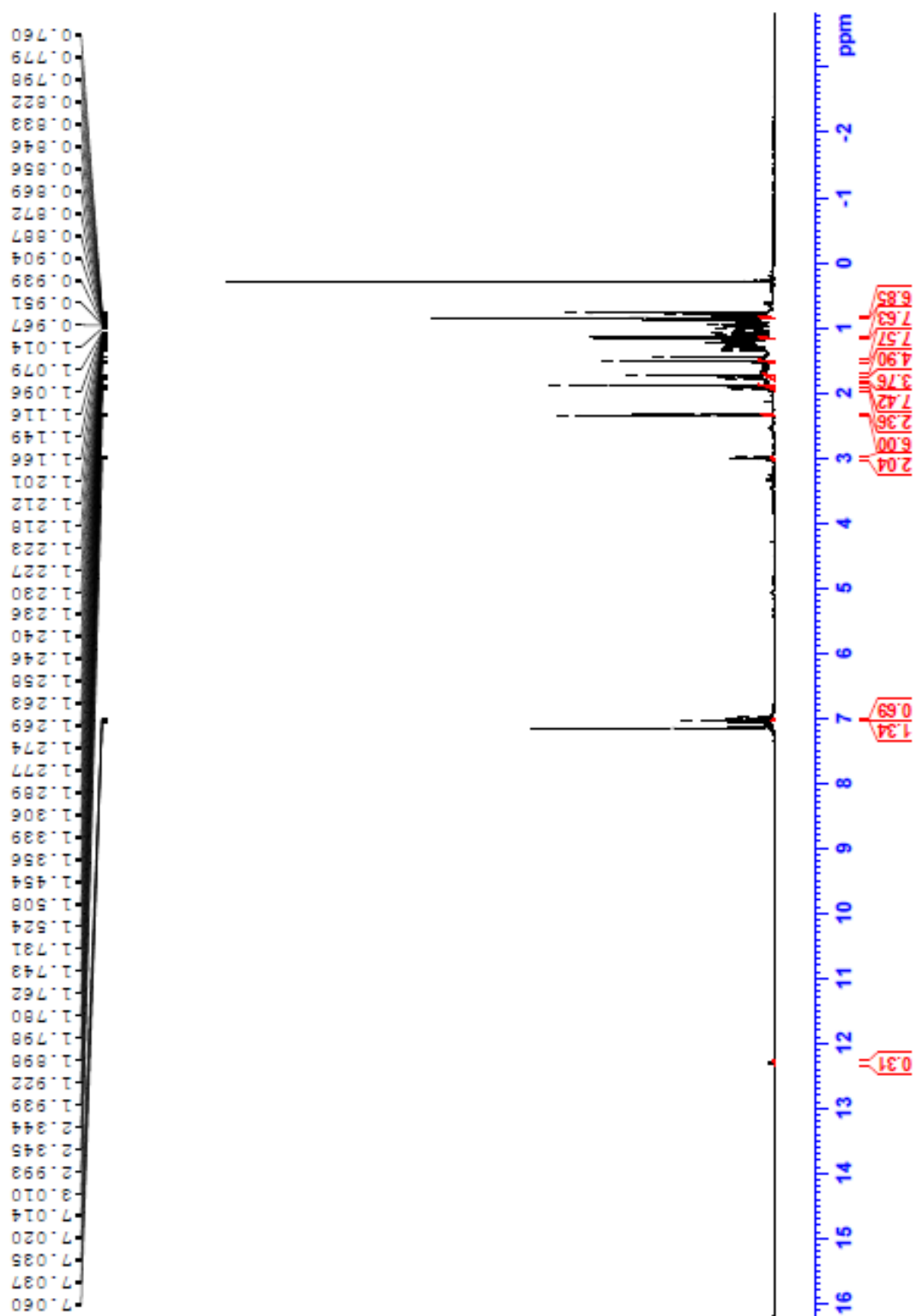Appendix ii. ^{1}H NMR of CAAC-B(N(iPr)$_2$)
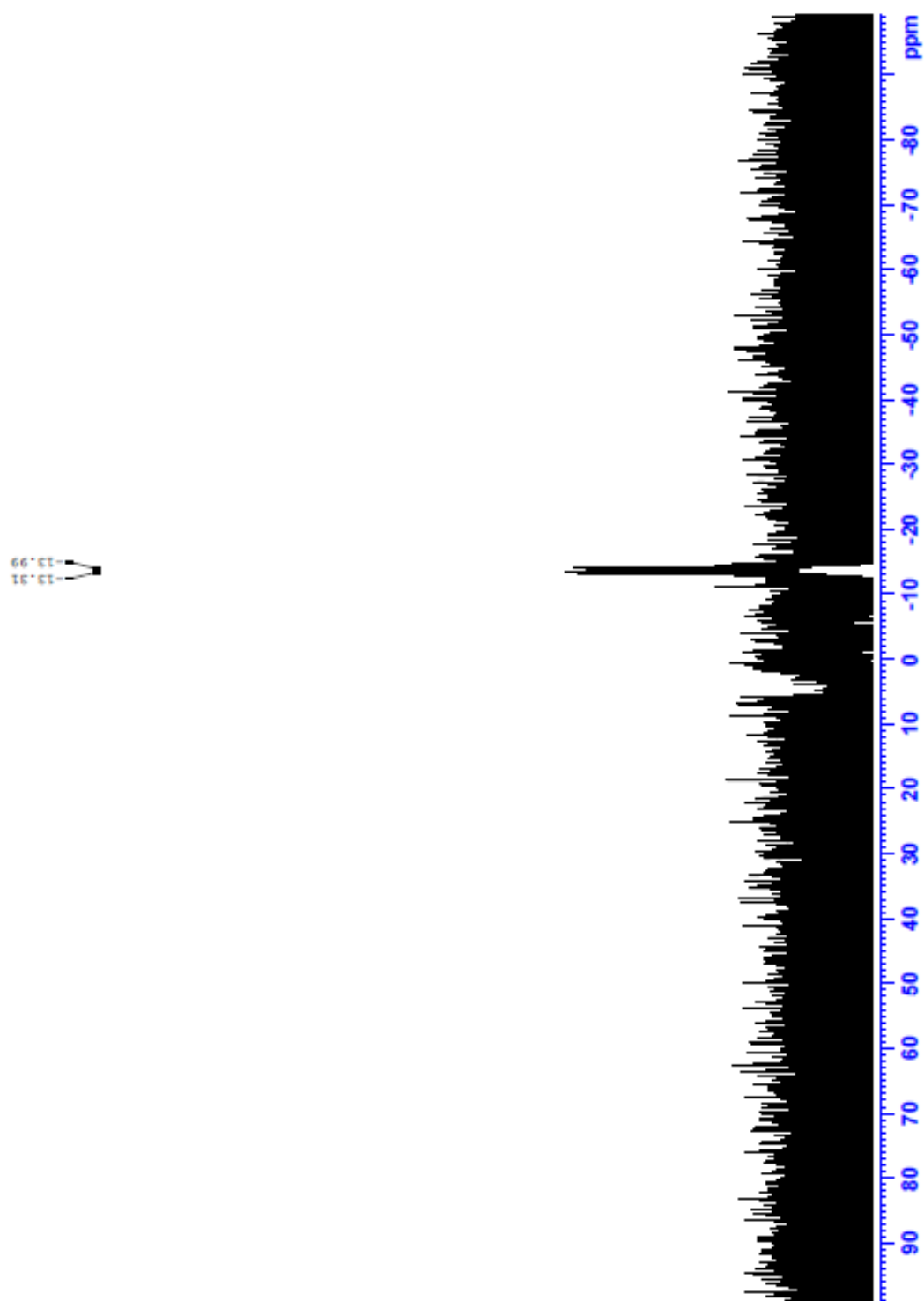
Appendix iii. ^{1}H NMR of CAAC-Cp*BCl$_2$

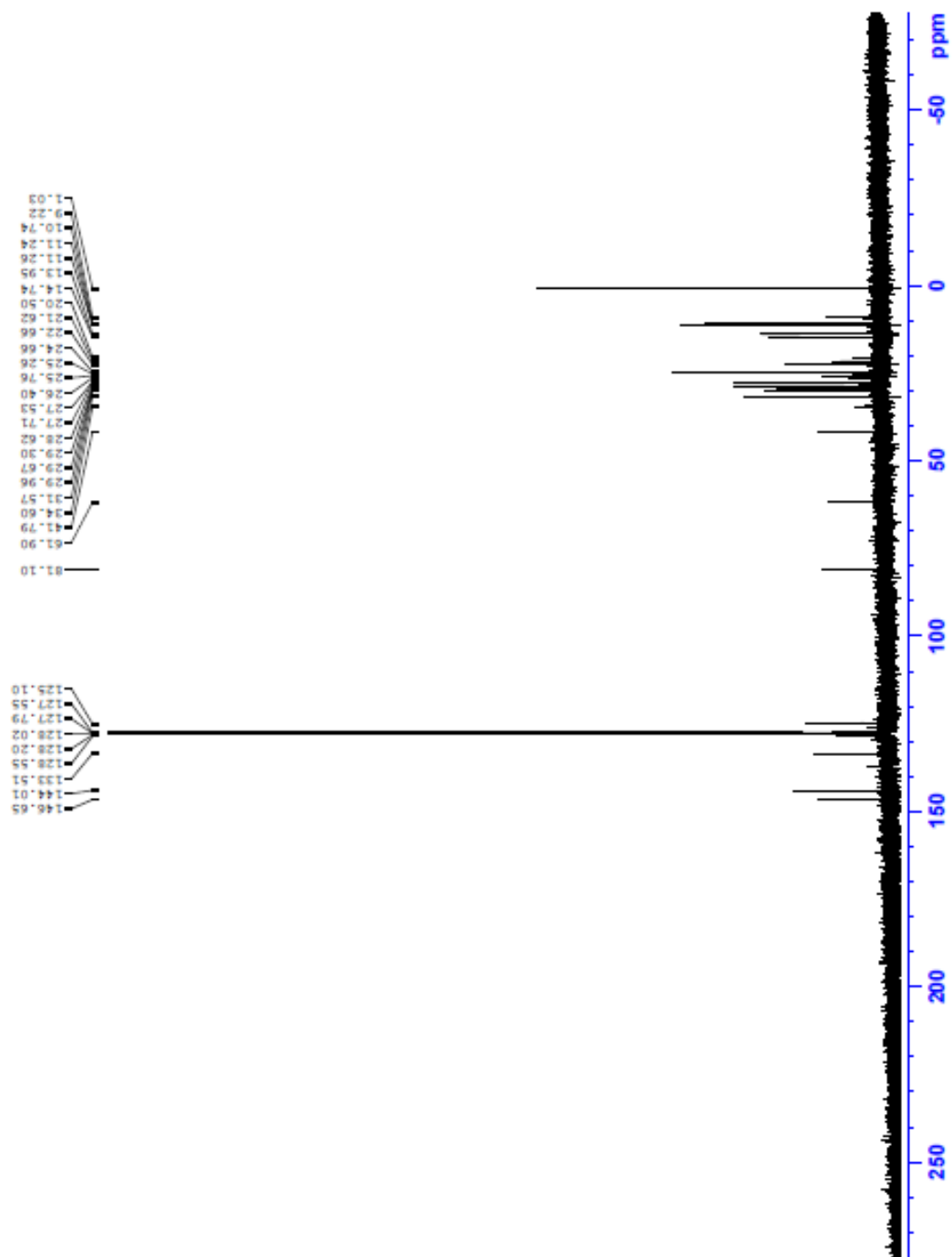Appendix iv. ^{11}B NMR of CAAC-Cp*BCl$_2$
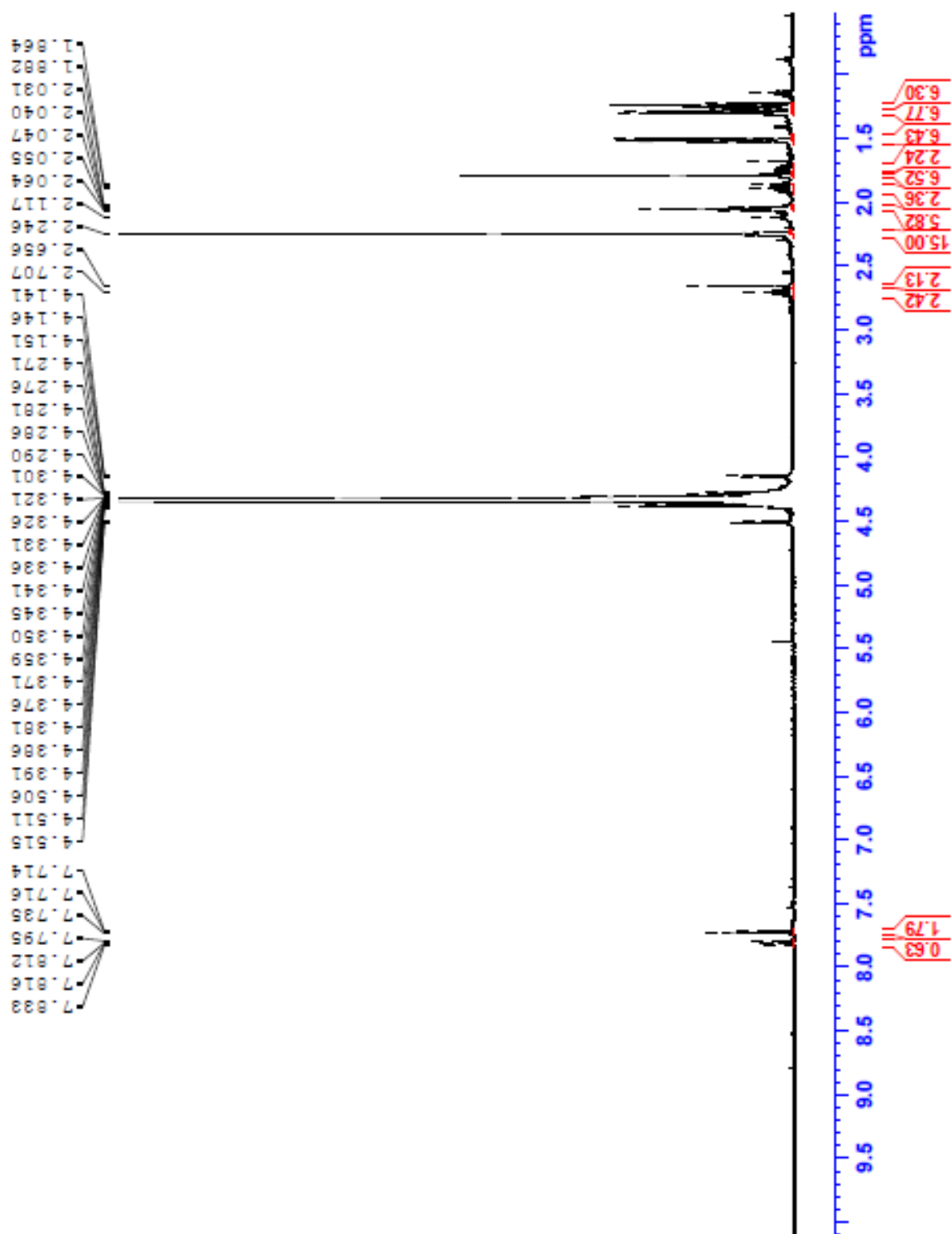
Appendix v. ^{13}C NMR of CAAC-Cp*BCl$_2$

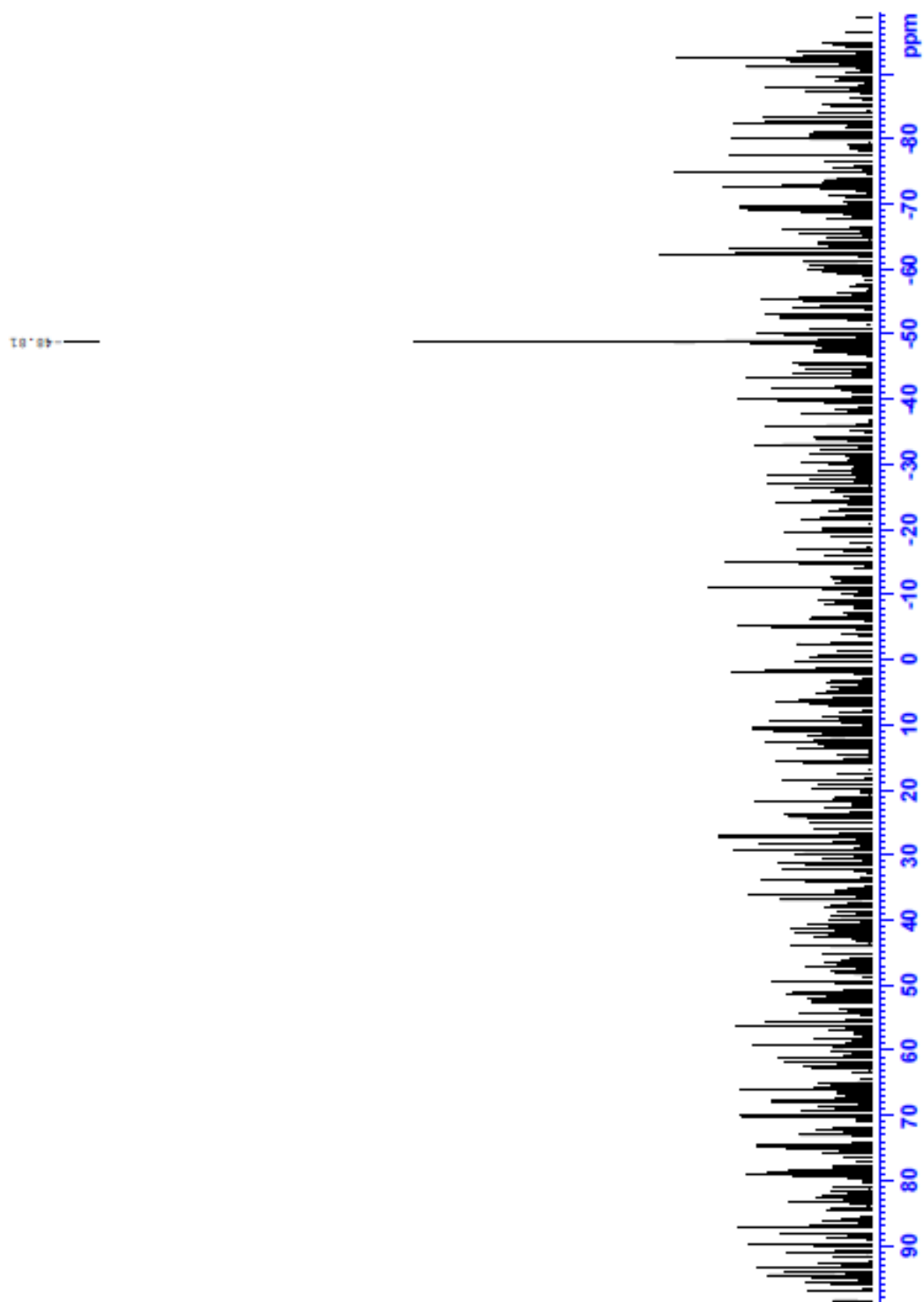Appendix vi. ^{1}H NMR of CAAC-Cp*BCl$_2$ C-H insertion

Appendix vii. ^{11}B NMR of CAAC-Cp*BCl$_2$ C-H insertion

Appendix viii. ^{13}C NMR of CAAC-Cp*BCl$_2$ C-H insertion

Appendix ix. ^{1}H NMR of η^5-CAAC-Cp*B dication
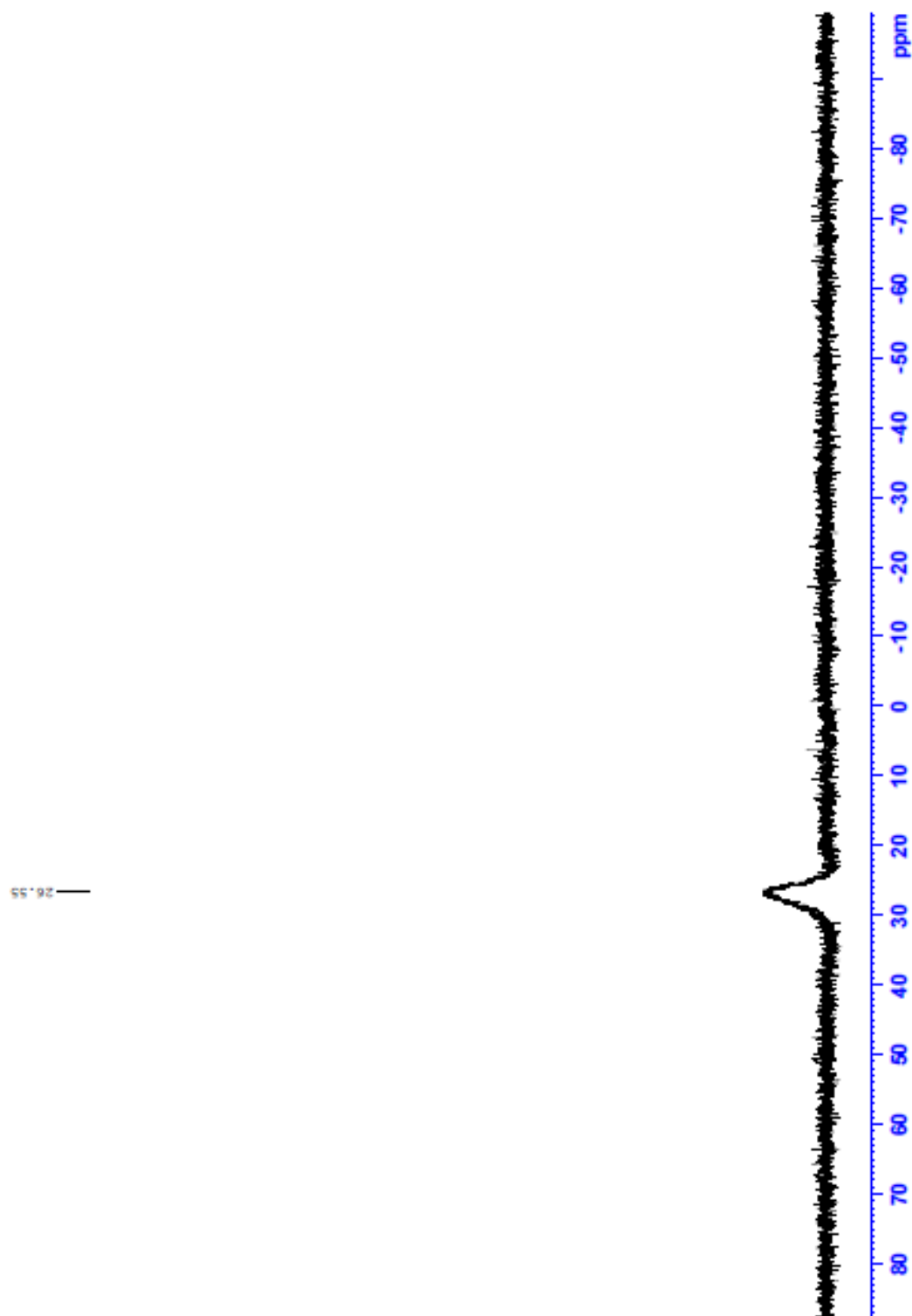
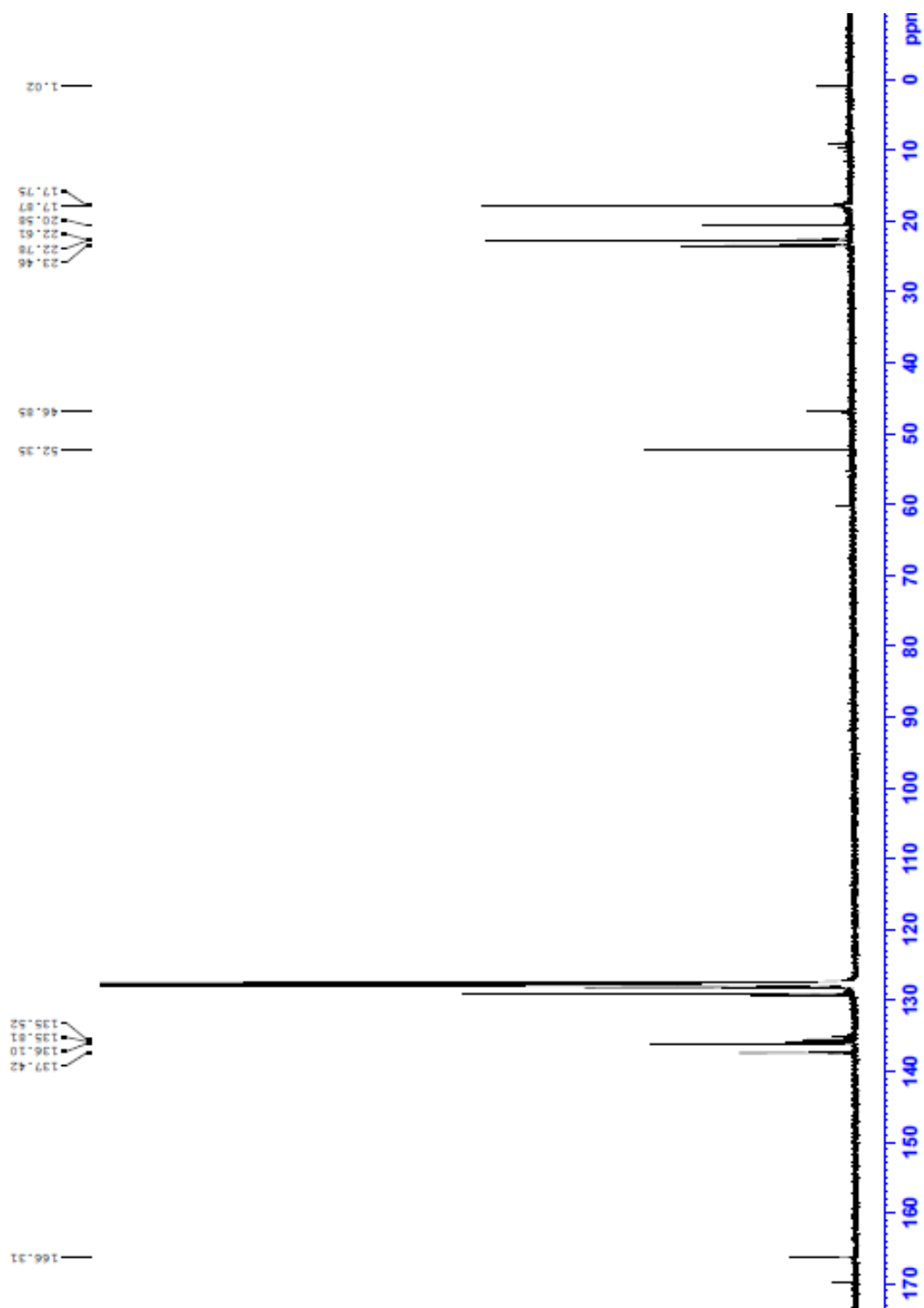Appendix x. ^{11}B NMR of η^5-CAAC-Cp*B dication
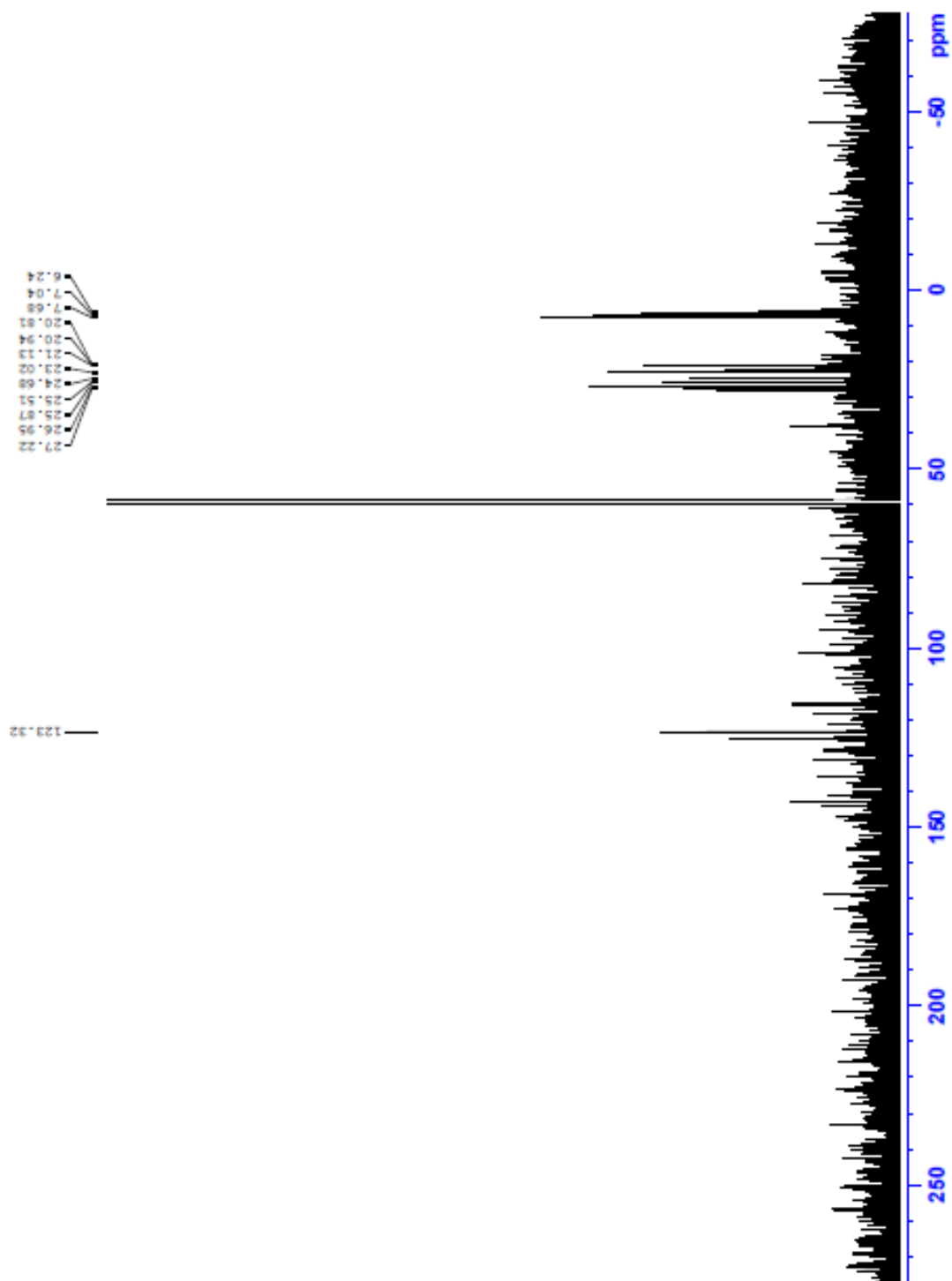
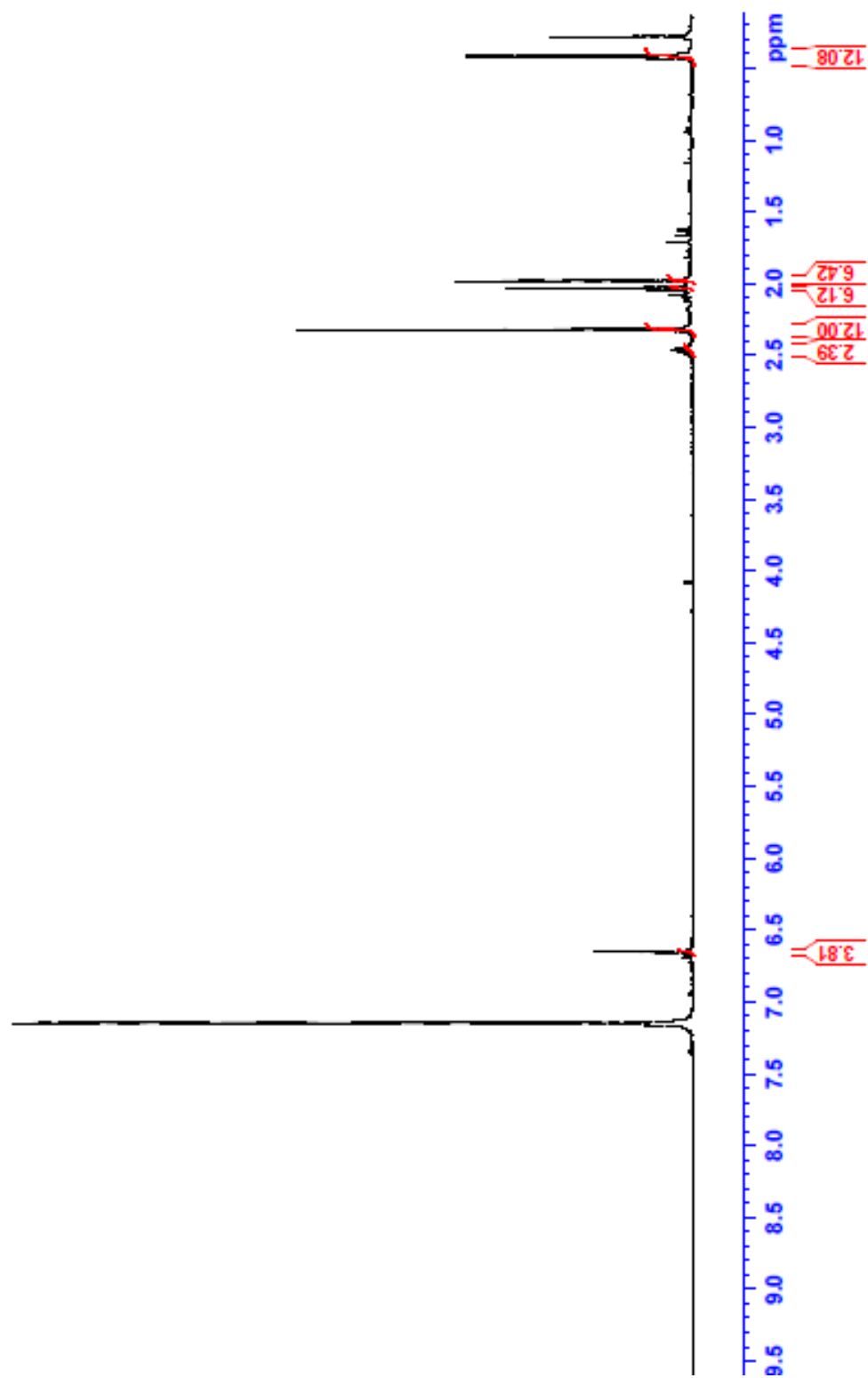Appendix xi. ^{13}C NMR of η^5-CAAC-Cp*B dication
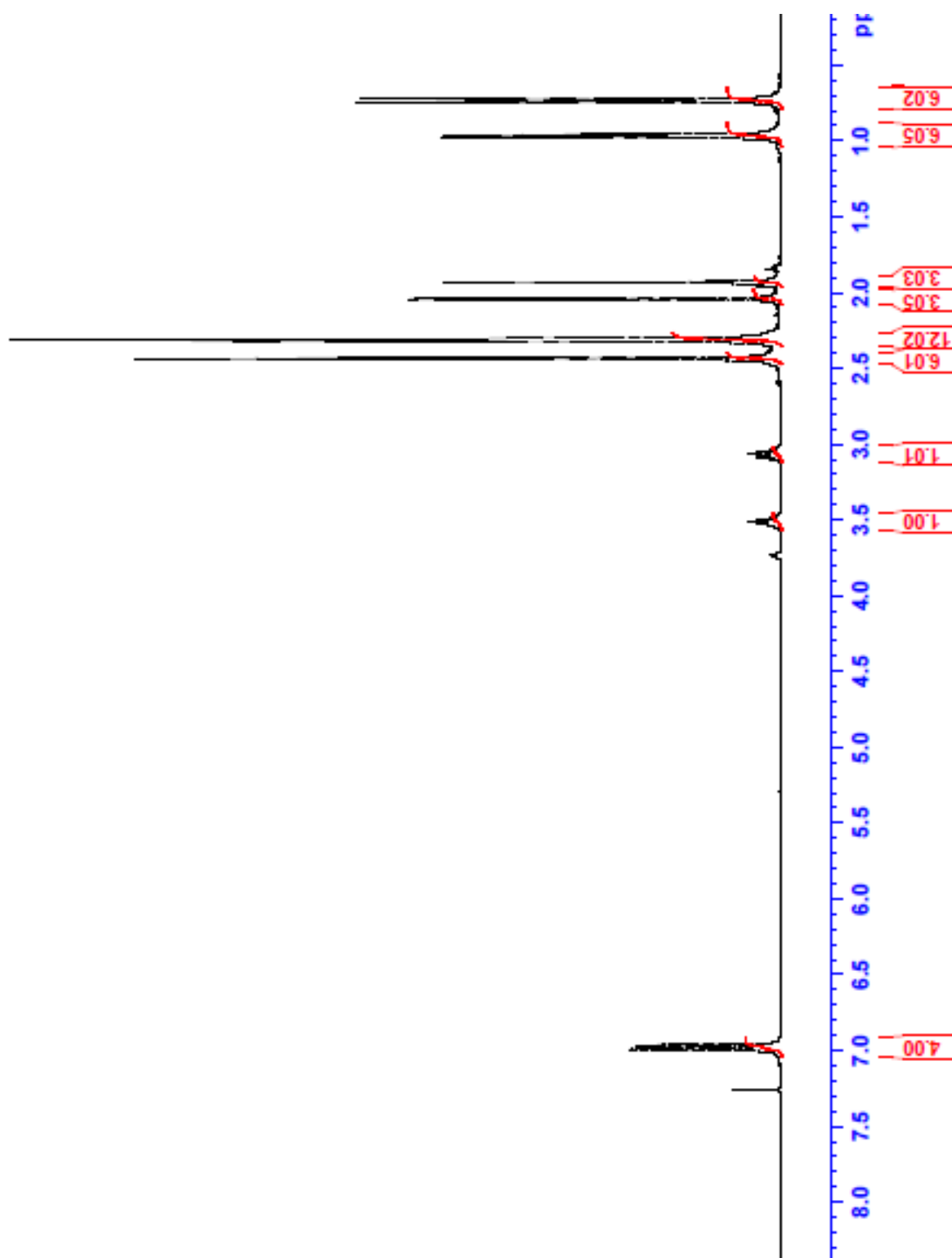
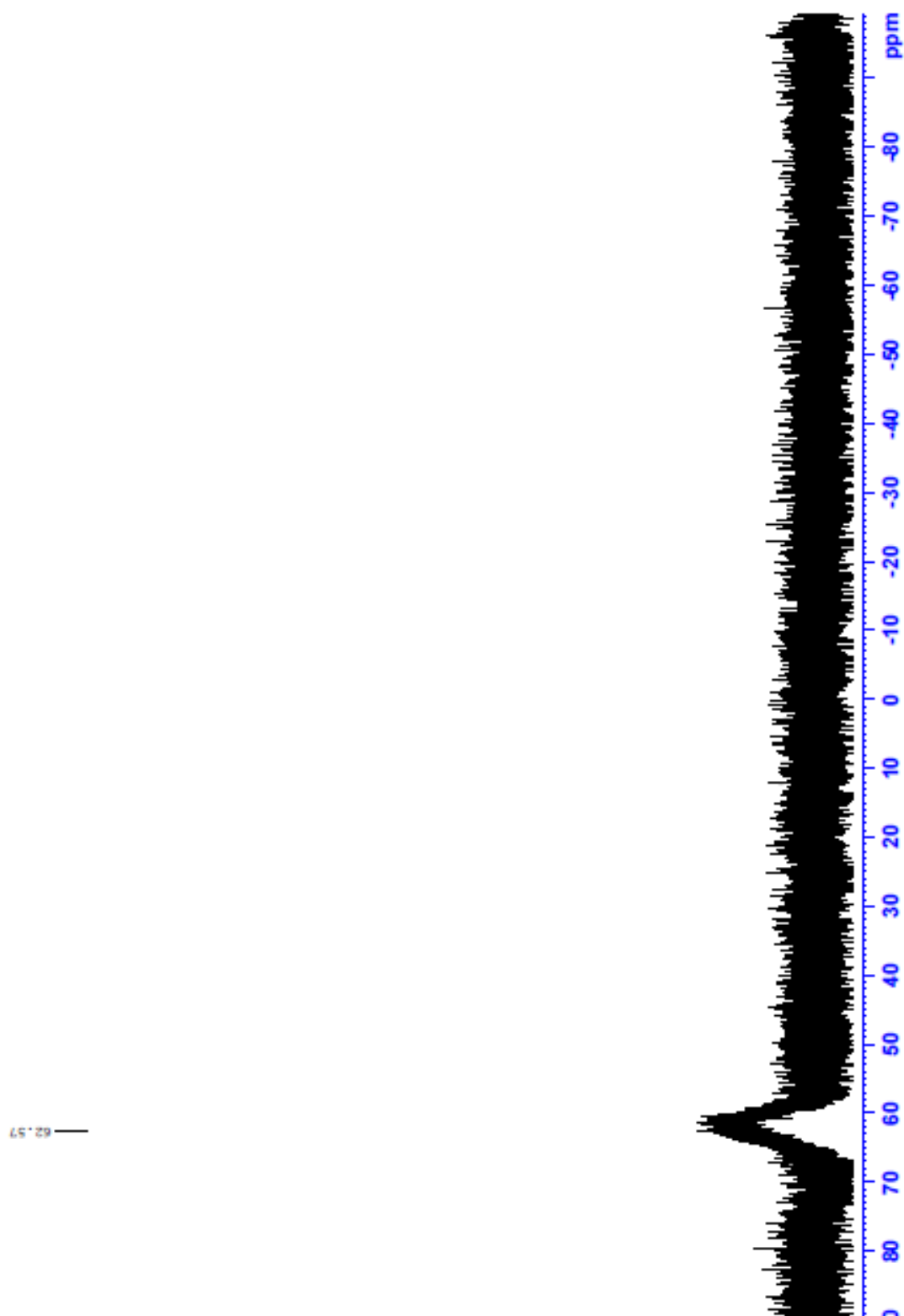Appendix xii. ^{1}H NMR of DAC-B(N(iPr)$_2$)Cl OTf

Appendix xiii. ^{11}B NMR of DAC-B(N(iPr)$_2$)Cl OTf

Appendix xiv. ^{13}C NMR of DAC-B(N(iPr)$_2$)Cl OTf

Appendix xv. ^{1}H NMR of DAC-B(N(iPr)$_2$)

Appendix xvi. ^{13}B NMR of DAC-B(N(iPr)$_2$)Cl OT

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