DIRECTED IRIDIUM C(sp^3)–H BORYLATION CATALYSIS WITH HIGH *N*-ADJACENT SELECTIVITY

By

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ABSTRACT

DIRECTED IRIDIUM C(sp^3)–H BORYLATION CATALYSIS WITH HIGH *N*-ADJACENT SELECTIVITY

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Modern approaches for the conversion of C–H bonds to C–B bonds involve transition metal catalysts that have various advantages over traditional methods by using cheap and abundant hydrocarbon starting materials, reducing toxic by-products and streamlining the synthesis of biologically important molecules. Metal-catalyzed C–H borylation reactions that produce organoboronic esters are mostly focused on the functionalization of sp^2 C–H bonds of heteroarenes and aromatic hydrocarbons. However, in this work the functionalization of sp^3 C–H bonds is being explored. Borylation involving sp^3 C–H bonds have been shown by Sawamura and co-workers with solid silica supported phosphine ligands offering a directing strategy where a metal center can accept donor directing groups. While this ligand generates highly active borylation catalysts, it requires a lot of steps in the synthesis of the ligand. In this work, easily synthesized homogeneous bidentate monoanionic ligands were tested for the borylation of sp^3 C–H bonds.

Herein is reported borylation of sp^3 C–H bonds of *N*-methyl amide groups using $[Ir(OMe)(cod)]_2$ as a precatalyst and B_2pin_2 as a commercially available boron source. Following the borylation of amide as a directing group, amidine molecules are being investigated.

To my friends and family

ACKNOWLEDGEMENTS

I would like to thank Professor Milton R. Smith III for giving me this opportunity to work in his lab. His guidance, advice and encouragement throughout my studies at Michigan state university are priceless to me. I would also like to thank Dr. Robert Maleczka Jr., Dr. Kin Sing Lee and Dr. James Geiger for serving on my guidance committee.

I would also like to thank my parents and my family for their support and encouragement throughout this journey. My studies would not have been possible without their support. I thank all my group members of the Smith lab and Maleczka lab for their friendship and help. I always enjoyed working with them in the lab.

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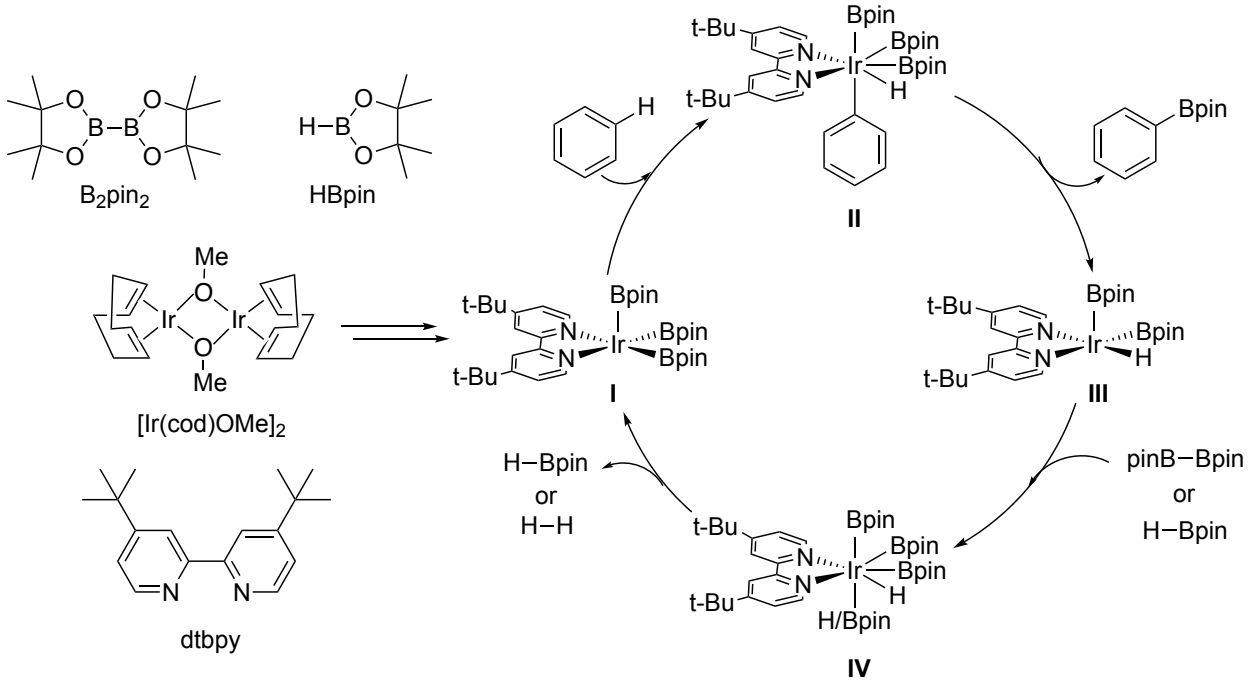
KEY TO ABBREVIATIONS

B_2pin_2	bis(pinacolato)diboron
BG	butane-1,2-diol
C–H	carbon–hydrogen
CHB	C–H Borylation
COD	1,5-cyclooctadiene
COE	1-cyclooctene
DTBPY	4,4’-di-tert-butyl-2,2’-dipyridyl
EG	ethane-1,2-diol
HBpin	pinacolborane
KIE	kinetic isotope study
MBG	3-methylbutane-1,3-diol
PG	propane-1,2-diol
TMPHEN	3,4,7,8-tetramethyl-1,10-phenanthroline

CHAPTER 1: INTRODUCTION

C–H borylation (CHB) is the direct functionalization of a C–H bond into a C-B bond eliminating the need of pre-installed halogens for the formation of boronic esters. Since the first thermal iridium catalyzed C–H borylation of arenes,[3] use of transition metals for borylation has become a method of choice for the formation of aryl boronic esters.[2] The standard procedure for iridium catalyzed C–H borylation involves use of $[Ir(OMe)(cod)]_2$ (cod = 1,5-cyclooctadiene) as the precatalyst, 4,4'-di-tert-butyl-2,2'-dipyridyl (dtbpy) as the ligand and pinacolborane(HBpin) or bis(pinacolato)diboron (B_2pin_2) as the boron source.[2] Borylation of arenes has been predominated by steric factors resulting in formation of meta and para substituted aryl boronic esters.

Scheme 1: Mechanism of iridium catalyzed C–H borylation

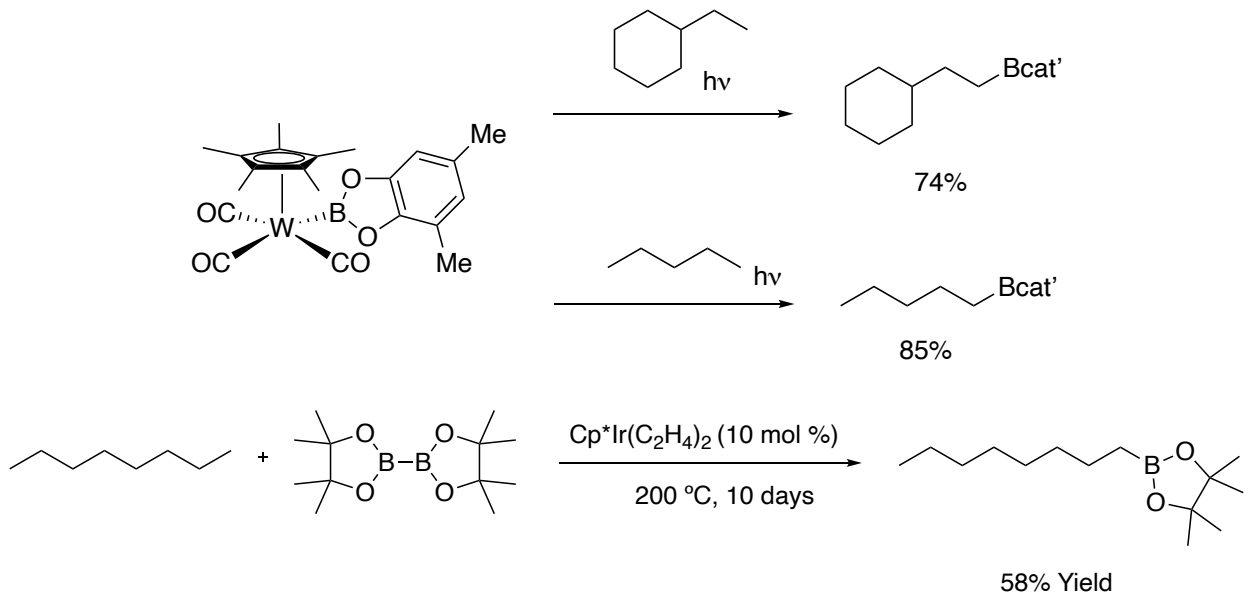


Adding the precatalyst, ligand and boron source results in the formation of trisboryl Ir(III) complex **I** as the active form of the catalyst. After the formation of trisboryl Ir(III) complex **I**, the oxidative addition of the arene C–H bond to the metal center by C–H activation has been determined to be the rate determining step to form Ir(V) complex **II**. Reductive elimination of the boronic ester

results in formation of intermediate complex **III**. To regenerated complex **I** B_2pin_2/HBpin adds to the metal center to form complex **IV** followed by reductive elimination of HBpin/H_2 respectively to close the catalytic cycle (Scheme 1).[4,5]

Borylation of sp^2 C–H bonds using transition metal catalysts has been researched extensively while sp^3 C–H bond has not been, which can be implied due to the large number of publications of C–H borylation of arenes following initial discovery as compared to the small prevalence of sp^3 C–H borylation in the literature.[2] Early interest in sp^3 C–H borylation used an electrophilic, covalently bound ligand with tungsten metal as center. Irradiation of the transition metal complex with a 450-W, medium-pressure hanovia mercury arc lamp resulted in the formation of alkyl boronic esters with regioselectivity for the terminal positions.[6]

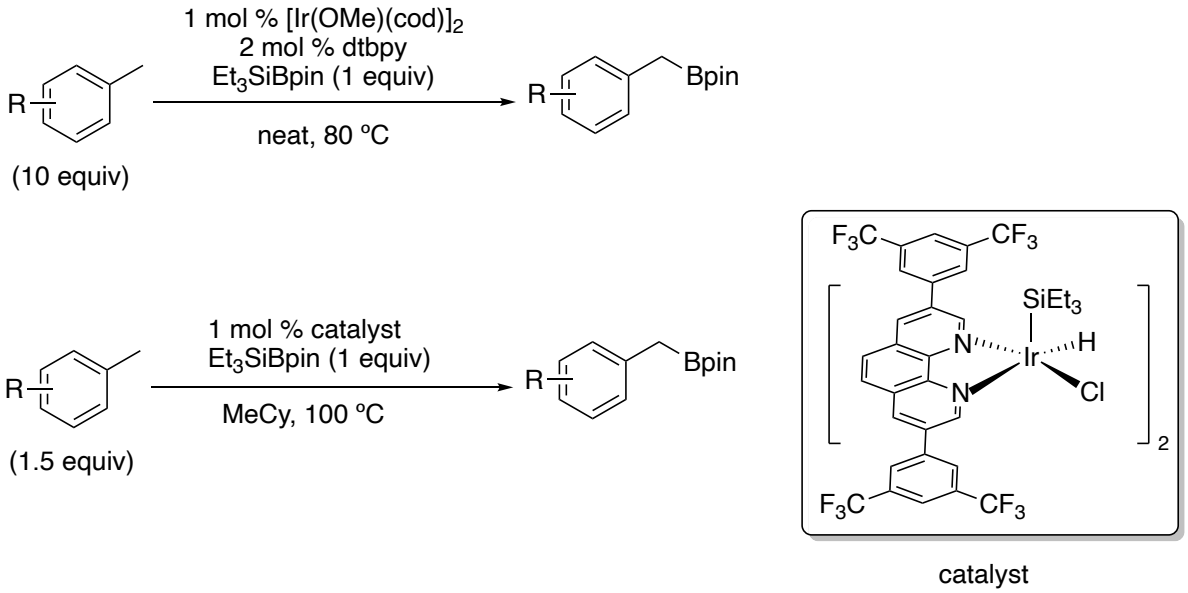
Scheme 2: Early examples of using transition metals in sp^3 C–H borylation



As Hartwig and co-workers demonstrated a photo induced sp^3 CHB of alkanes, the interest of many others to further study this type of reactions sparked. An iridium metal catalyst was used for formation of a single product at the terminal position of linear alkanes from commercially available

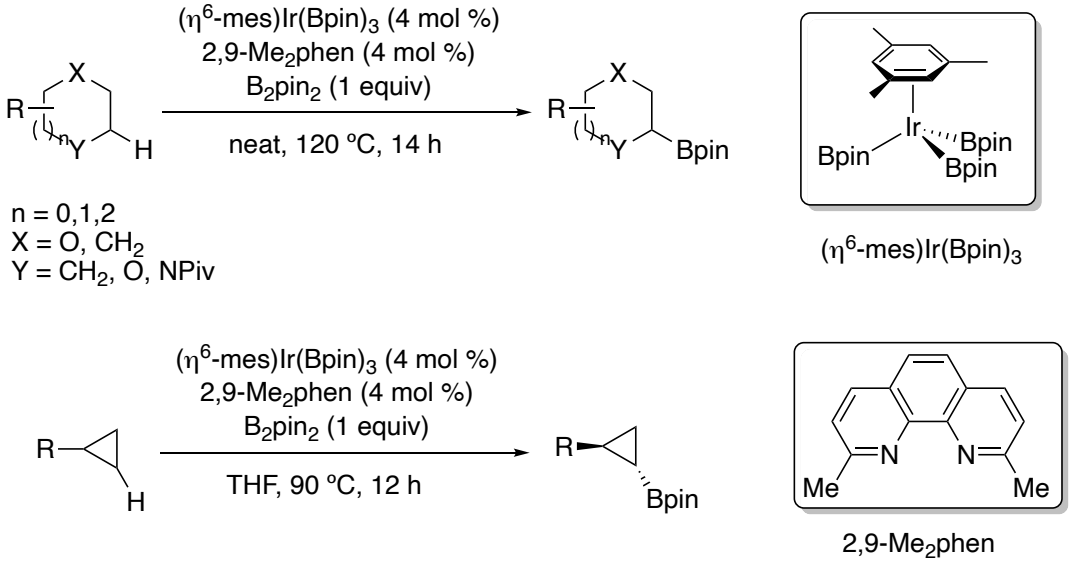
boron reagents under thermal conditions. It allowed catalytic, regiospecific borylation of alkanes (Scheme 2).[7]

Scheme 3: Primary benzylic sp^3 C–H borylation



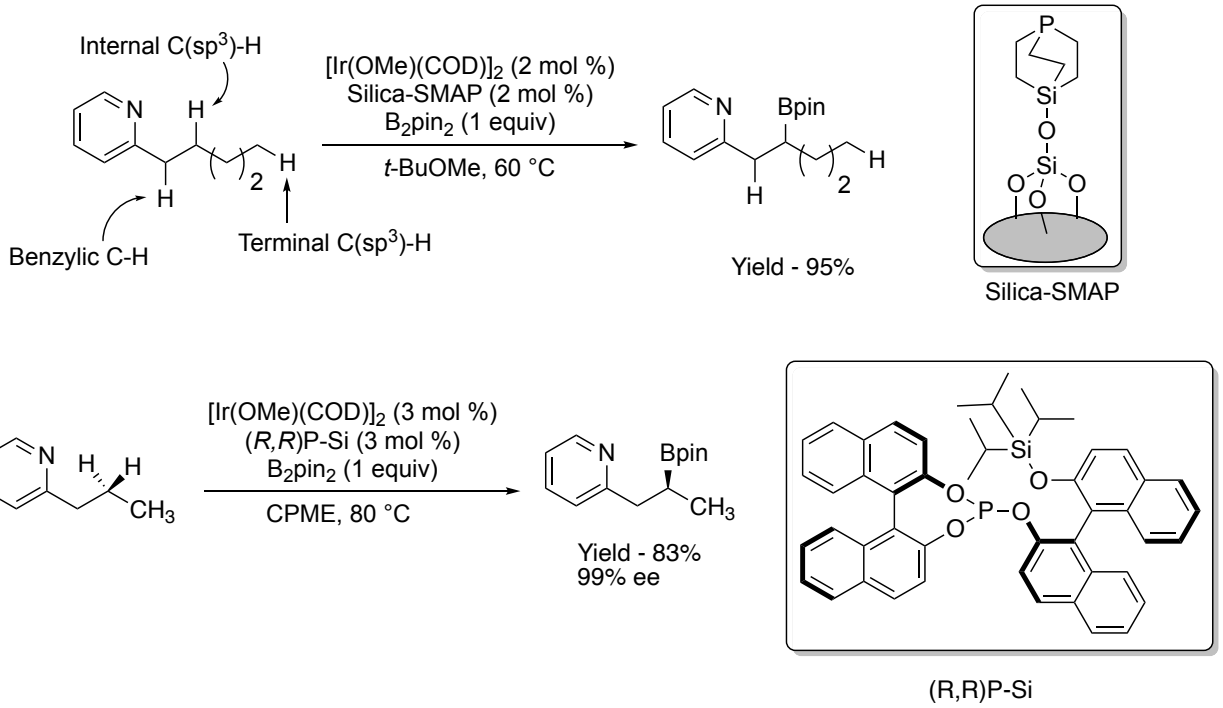
Substrates other than alkane containing terminal methyl groups have been used for sp^3 C–H borylation.[8] Hartwig and co-workers showed that by installing a silane in a diboron reagent, sp^3 C–H borylation could be done on derivatives of toluene, although borylation was observed both at aryl and methyl C–H bonds. Also, in absence of a terminal methyl position in case of ethylbenzene, borylation was observed exclusively on aryl C–H bonds.[9] Another example of benzylic C–H borylation involves the use of a preassembled catalyst. The preassembled catalyst was generated by combining a 1:1 mixture of iridium precatalyst $[Ir(COE)_2(Cl)]_2$ and an electron deficient phenanthroline ligand in THF with triethyl silane to form a purple/brown solid. The preassembled catalyst along with $Et_3SiBpin$ as the boron reagent of choice was used for the benzylic C–H borylation tolerating halogens, methoxy, carboalkoxy, carbamoyl and dialkylamino functional groups (Scheme 3).[10]

Scheme 4: Secondary sp^3 C–H borylation



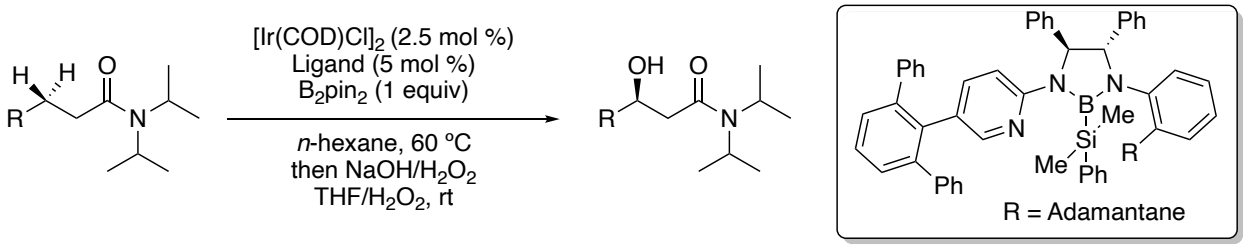
Hartwig and co-workers later found that in absence of terminal methyl groups, successful borylation of secondary sp^3 C–H bond could be done on cyclic ethers. The borylation happen with selectivity for C–H bonds at 3-position over the weaker C–H bonds located at 2-position.[11] Moreover, the borylation on cyclopropane derivatives were shown to occur selectively at the methylene C–H bonds of the cyclopropane ring over methine C–H bonds catalyzed by the combination of [(η^6-mes)Ir(Bpin)$_3$] pre-catalyst and 2,9-Me$_4$phen ligand to yield predominantly the trans-substituted boronic esters . The high diastereoselectivity was proposed to be due to the greater steric demand of ligand near the metal center (Scheme 4).[12]

Scheme 5: Pyridine as directing group



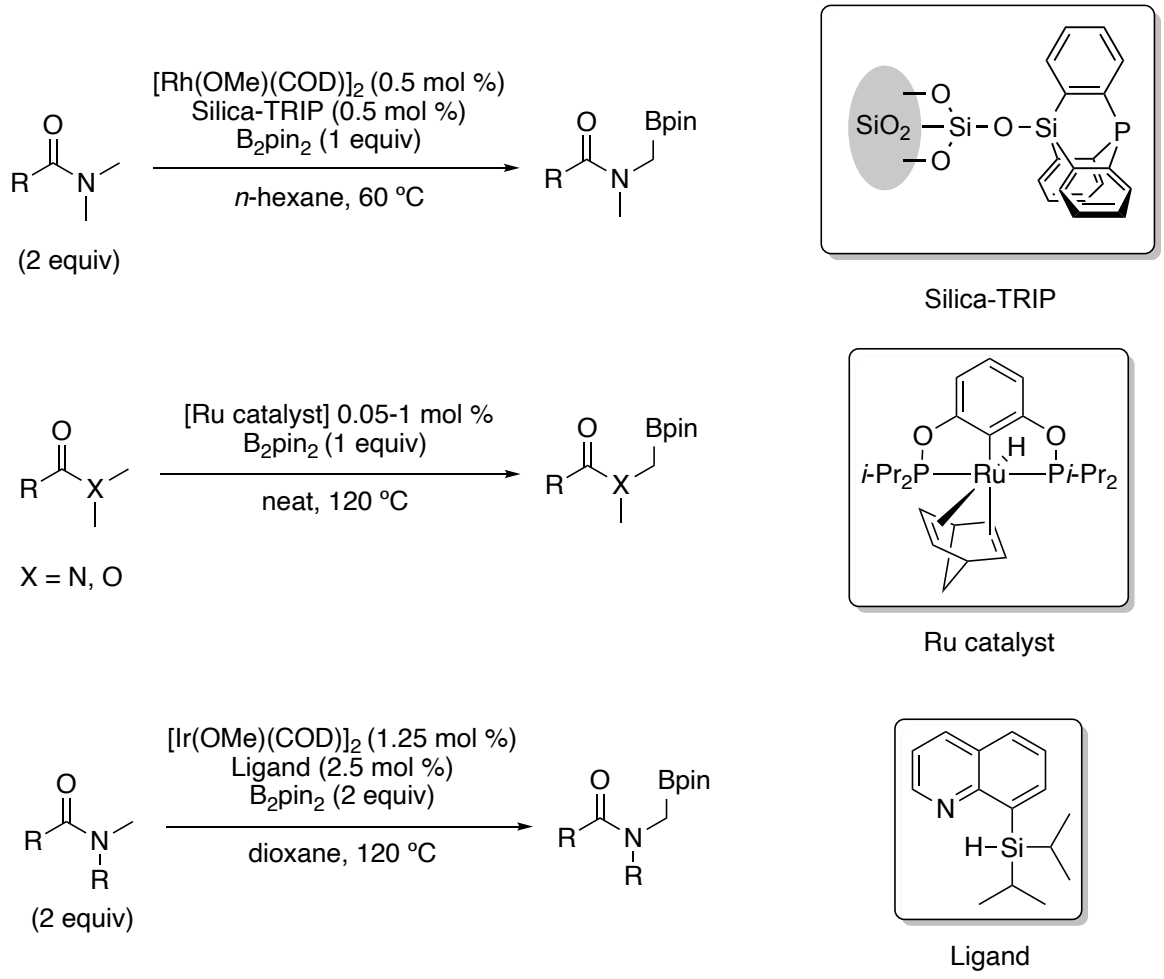
Directing groups have been used to facilitate borylation on secondary sp^3 C–H bonds in presence of primary sp^3 C–H bonds. Sawamura et. al. showed that they could direct sp^3 CHB using an iridium pre-catalyst bound by a silica tethered monodentate heterogeneous ligand. This system was capable of activating gamma(γ) C–H bonds from nitrogen atom in the presence of benzylic and primary C–H bonds.[13] Furthermore, asymmetric borylation of secondary C–H bonds was shown to be possible by the same group using pyridine again as the directing group and a chiral homogenous ligand with high enantioselectivity. This reaction was successful with both electron donating and electron withdrawing groups on pyridyl moiety (Scheme 5).[14]

Scheme 6: Amide as directing group



Enantioselective borylation of methylene C–H bonds β to the carbonyl group was later achieved by Xu and co-workers where amides were used as a directing group using commercially available iridium precatalyst and chiral bidentate ligand (Scheme 6).[15]

Scheme 7: C–H Borylation at N-methyl position using amide as directing group



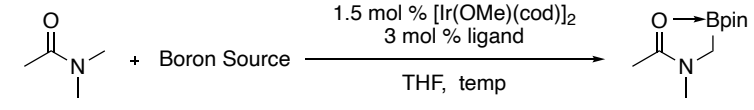
Various transition metals have been used for the borylation at the N-methyl position of amide group. A monodentate heterogeneous ligand with $[Rh(OMe)(cod)]_2$ as precatalyst was employed for the borylation in hexane by Sawamura and co-workers[16] while a ruthenium pincer catalyst was used by Hao group in a neat solution of amide and ester derivatives involving high temperature.[17] The Clark group has shown borylation of amide by $[Ir(OMe)(cod)]_2$ precatalyst and quinoline silyl ligand at high temperature with a limited substrate scope (Scheme 7).[18] Building on previous observations, amides were further studied by our group targeting N-methyl position for borylation using silylated pyridine ligands.

CHAPTER 2: AMIDE DIRECTED IRIDIUM (sp3) C–H BORYLATION CATALYSIS WITH HIGH N-METHYL SELECTIVITY

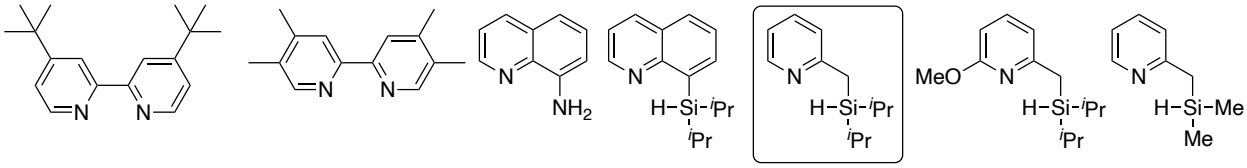
This project was in collaboration with Dr. Jonathan Dannat of the Maleczka Lab, who performed the optimization of reaction conditions and competitive kinetic isotope study. The study was initiated with the borylation of *N*,*N*-dimethylacetamide (**1a**) under various conditions (**Table 1**). As it has been shown that sp^3 CHB can occur without addition of a ligand,[19] and both dtbpy and tmphen (dtbpy = 4,4'-*tert*-butyl-2,2'-bipyridine, tmphen = 3,4,7,8-tetramethyl-1,10-phenanthroline) are common CHB ligands, we started by screening these conditions. No reaction occurred without ligand addition and both dtbpy and tmphen provided a complex mixture of products in the ^{1}H NMR spectrum (Table 1, entries 1-3). Ligand (**L1**), which has been used for ortho-selective borylations of arylimines,[20] provided low conversion of (**1a**). Unfortunately, increased reaction temperature provided no additional conversion (entry 5). Given the low reactivity of (**L1**) and that Sawamura demonstrated immobilization of the phosphine ligand was necessary for the sp^3 C–H activation to occur,[21] we expected that a covalent bond between the ligand and the precatalyst would be crucial for generating a catalyst with the proper geometry for directed CHB. In 2014, we published silyl phosphorus and nitrogen based bidentate, monoanionic ligand frameworks for iridium catalyzed ortho selective borylations.[22] The anionic silyl ligand replaces a spectating boryl and due to the bidentate nature, the metal to neutral donor ligand ratio is well controlled. Satisfyingly, previously reported silyl-nitrogen ligand (**L2**) provided 60% conversion of (**1a**) (entry 6).

With this result, we sought to optimize the structure of this ligand framework. The pK_a of 2-methylpyridinium is 1.36 units higher than the pK_a of quinolinium in acetonitrile.[23] Since more electron rich ligands accelerate borylation rates, we prepared pyridine-based ligand (**L3**), which

Table 1: Optimization of reaction conditions



1a **2a**



entry	ligand	temp °C	boron source	2a[a]
1	no ligand	60	B_2pin_2	0%
2	dtbpy	60	B_2pin_2	complex mixture
3	tmphen	60	B_2pin_2	complex mixture
4	**L1**	60	B_2pin_2	10%
5	**L1**	80	B_2pin_2	10%
6	**L2**	60	B_2pin_2	60%
7	**L3**	60	B_2pin_2	91%
8	**L4**	60	B_2pin_2	complex mixture
9	**L5**	60	B_2pin_2	11%
10[b]	**L3**	80	B_2pin_2	100%
11[c]	**L3**	80	HBpin	complex mixture
12	**L3**	80	B_2eg_2	0%
13[d]	**L3**	80	B_2pin_2	85%

Conditions: **1** (1 equiv, 0.5 mmol), Boron source (1.2 equiv, 0.6 mmol), $[Ir(OMe)(cod)]_2$ (1.5 mol %, 0.0075 mmol), ligand (3 mol %, 0.015 mmol) in 2 mL THF. [a]Based on ^1H NMR. [b]Reaction time: 7.5 h. [c]2 equiv HBpin. [d]0.75 mol % $[Ir(OMe)(cod)]_2$, 1.5 mol % L3. pin = pinacolate, eg = ethylene glycolate

gave nearly full conversion to the desired product. Additional donation (**L4**) and decreasing the steric hindrance around the silyl site (**L5**) both provided inferior results (entries 8 and 9); however, by simply increasing the reaction temperature to 80 °C, full conversion to the product was achieved in 7.5 hours (entry 10). Adjusting the boron source and lowering the catalyst loading all had negative impacts on the reaction. Solvent optimization revealed ethereal solvents provided superior conversion. Non-polar solvents such as hexane, cyclohexane and toluene provided 75%-

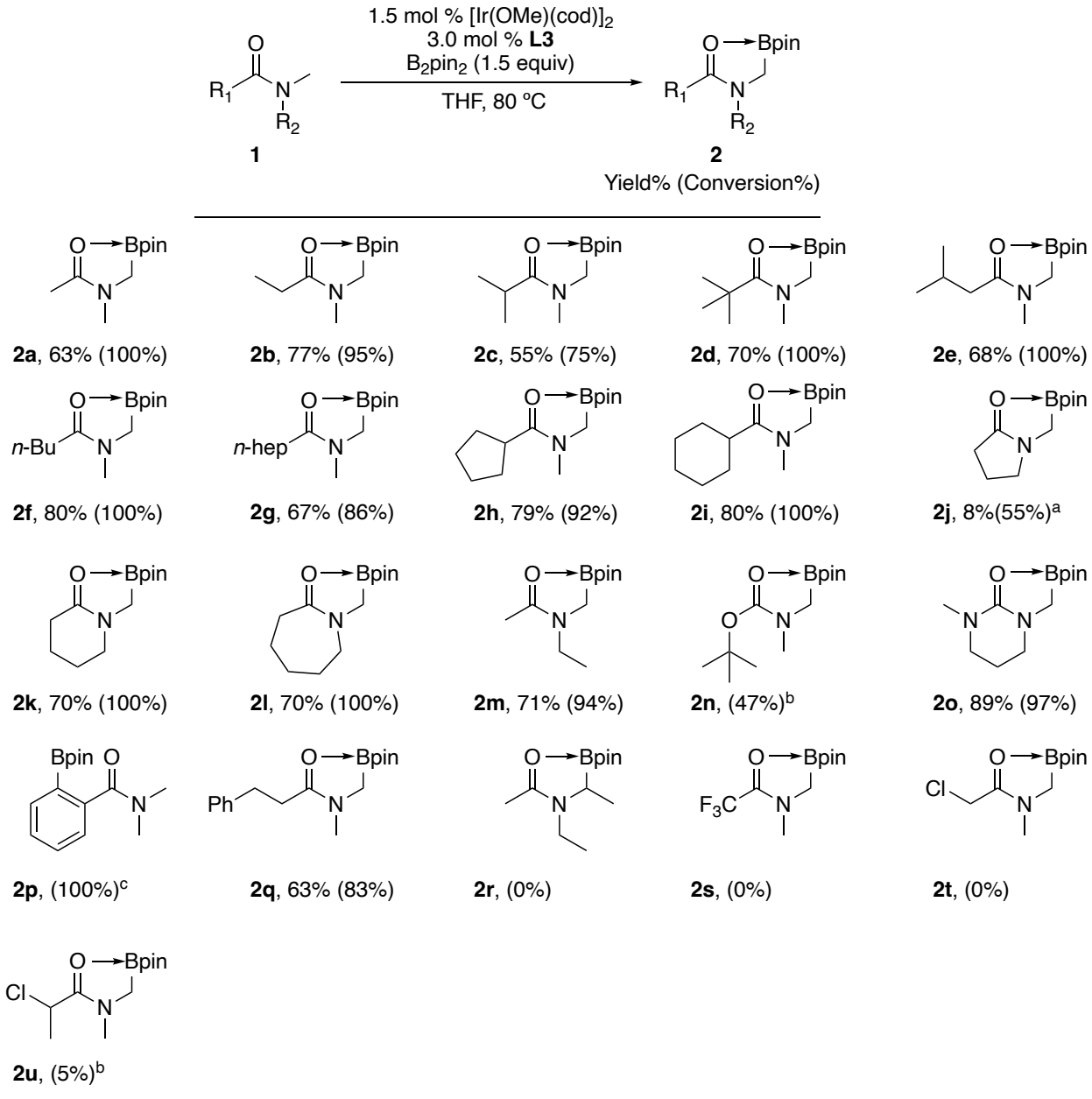
86% conversion while dioxane provided full conversion (see CH 5 for details). With optimum reaction conditions in hand, we sought to explore substrate scope.

We first selected a number of acyclic and cyclic alkyl dimethyl amides (**1a-l**). Notably, perfect *N*-methyl regioselectivity was observed for compounds (**1b**) and (**1c**) where two primary C(sp^3)–H bonds are equidistant from the directing carbonyl and could potentially be activated. The increased sterics of the isopropyl group (**1c**) had no adverse effect on the reaction. Moreover, increased chain length and acyclic alkyls (**1d-i**) were tolerated. Cyclic amides (**1j-l**) proceeded smoothly; however, the reactivity of (**1j**) was significantly attenuated. We attribute the low reactivity to the increased distance of the *N*-methyl C–H bond from the directing carbonyl in the 5-membered ring (2.414 Å, calculated at ωB97x-D 6-31G*) compared to the 6- and 7-membered rings (2.243 Å and 2.241 Å respectively). Where both primary and secondary C–H bonds are available, the catalyst displays high regioselectivity for the sterically least hindered C–H bond (**1m**)**.** While compound (**1m**) showed high selectivity for primary methyl C–H bonds, in cases with only secondary C–H bonds no reaction occurs (**1r**).

Other amide-like moieties such as a carbamate and urea directed the C(sp^3)–H borylation (**1n-o**). Product (**1n**) is a promising result as carbamates can be readily generated from the corresponding amines using standard protecting group protocols.[24] Since iridium based borylation catalysts are notably active toward C(sp^2)–H bonds, we wondered about the regioselectivity of *N*,*N*-dimethylbenzamide (**1p**). Interestingly, the C(sp^2)–H borylation was significantly favored and no C(sp^3)–H activation was observed. Interestingly, increasing the distance between the directing amide and the C(sp^2)–H bonds by two methylene linkers yielded perfect selectivity for the C(sp^3)–H bond (**2q**). This important result demonstrates the tolerance of aromatic C–H bonds.

There were also a number of instructive substrates with no observed reactivity. Trifluoromethyl and chloro-substituted compounds (**1s-1u**) showed little to no evidence of borylation. We hypothesized that this could be due to 1) a weaker interaction between the carbonyl oxygen and

Scheme 8: Substrate Scope of amide borylation



Conditions: **1** (1 equiv, 1.0 mmol), Boron Source (1.5 equiv, 1.5 mmol), $[Ir(OMe)(cod)]_2$ (1.5 mol %, 0.015 mmol), **L3** (3 mol %, 0.03 mmol) in 4 mL THF. [a]At 100 °C. [b]Low conversion inhibited isolation. [c]mono:diborylated 1.2:1 all $C(sp^2)$–H activation

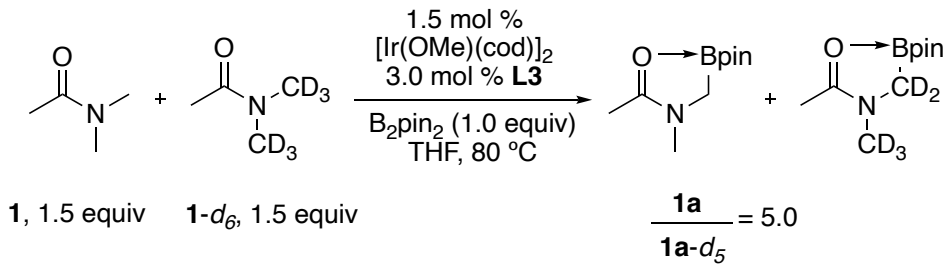
iridium vacant site prohibiting the directing effect or 2) substrates (**1s**-**1u**) poison the catalyst. To test these ideas, we performed two borylations of (**1a**) in the presence of (**1s**) and (**1t**), respectively. For the experiment with (**1s**), a 60% conversion of (**1a**) to (**2a**) was observed. This shows that the fluorinated substrate (**1s**) is not borylated when an active borylation catalyst is present, but (**1s**) does impede borylation. Substrate (**1a**) was not borylated in the presence of (**1t**), which indicates (**1t**) completely inhibits CHB. The cause of this inhibition is unclear, but it is noteworthy that B_2pin_2 is present at the conclusion of both reactions. Yao and co-workers recently reported Ru-catalyzed CHBs with B_2pin_2 in neat amide (1 equiv) at 120 °C.[17] Using these conditions, we attempted CHBs of substrates (**1a**), (**1c**), (**1f**) and (**1o**), but no borylation occurred (see CH 5 for details).

We were curious if increasing the reaction temperature would increase the reaction conversion in substrates with low conversion. For substrates (**1j**) and (**1s**), borylation at 100 °C was conducted. No change in conversion was observed for substrate (**1s**). In the case of (**1j**), conversion increased from 23% to 55%. Interestingly, this higher conversion also revealed small percentages of diborylation.

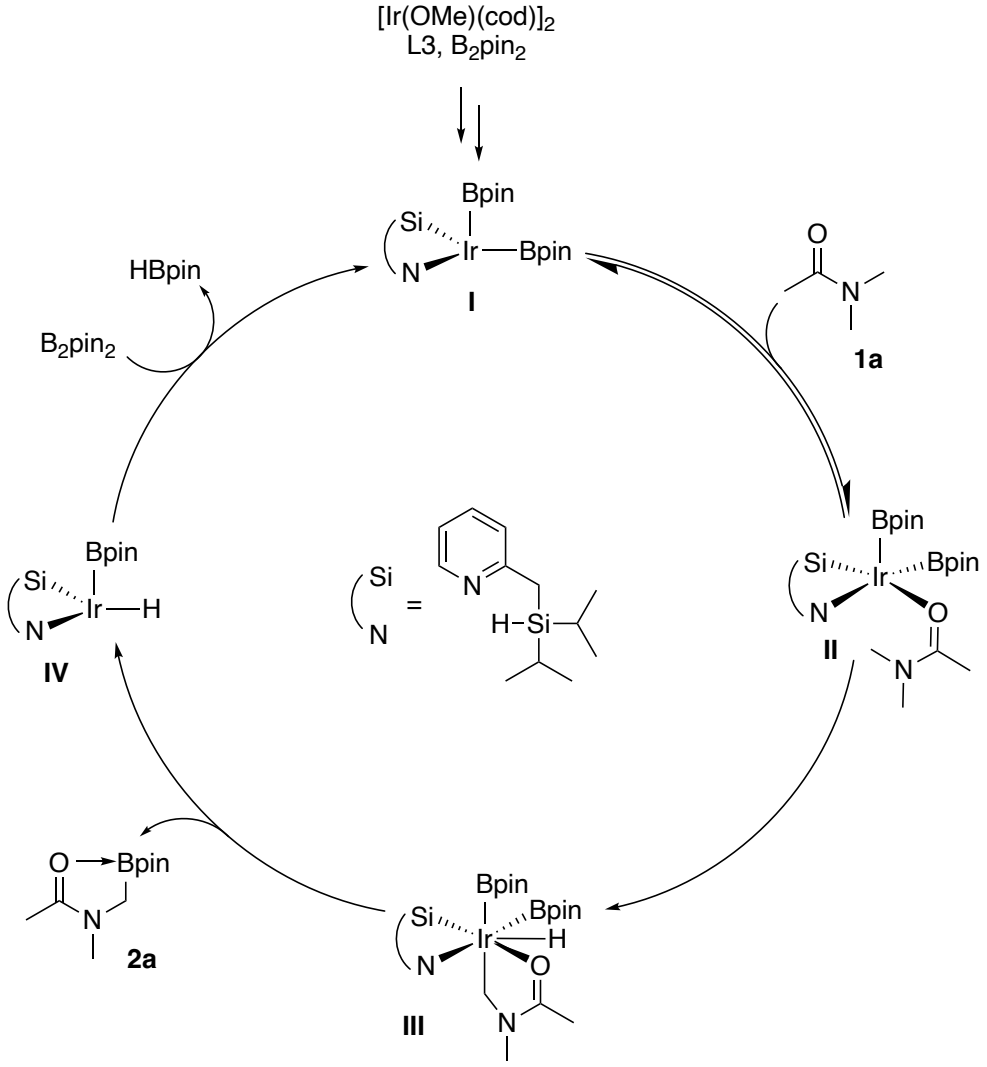
One noteworthy feature of these borylations is the difference between conversion and isolated yield. We found that the borylated products decomposed significantly when exposed to standard silica flash purification techniques. Initially, we attempted neutral alumina to isolate (**2a**) however, in our hands, only 39% isolated yield was observed. One method to mitigate the decomposition on silica was to deactivate the silica by adding deionized water to the gel (35% w/w) prior to packing the silica column. Deactivation of the silica with water presumably decreases the adsorption capacity of the silica and has been shown to increase isolated yields of borylated products previously.[18,25,26] We would note that silica isolation may not be necessary depending on a user's

desired follow-up chemistry as the only byproducts observed from these reactions are borates from the excess boron source.

Scheme 9: Competitive KIE study



Scheme 10: Plausible catalytic cycle

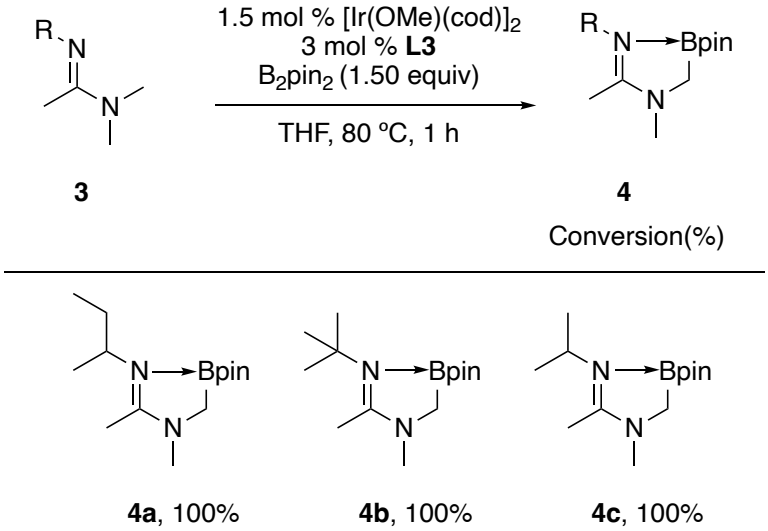


Typically, C–H activation is the turnover-limiting step for Ir-catalyzed aromatic C–H borylations, substantiated by primary kinetic isotope effects (KIEs) where k_H/k_D values range from 3-5.[4] Reported primary KIEs for Ir-catalyzed C(sp^3)–H borylations are typically lower, with k_H/k_D values ranging from 2-3.[27,10,12] In our system, a competitive kinetic isotope study between *N,N*-dimethylacetamide (**1**) and *N,N*-dimethylacetamide-d_6 (**1-**d_6) with limiting B_2pin_2 was conducted (**Scheme 9**). The k_H/k_D value of 5.0 is the largest primary KIE value reported for a C(sp^3)–H borylation. Thus, C–H cleavage is the turnover limiting step.

A proposed mechanism for amide borylation is presented in Scheme 10. Upon mixing the iridium precatalyst, ligand (L3) and B_2pin_2 complex I is generated. This 14-electron complex can readily coordinate amide substrate 1 generating 16-electron complex II. This initial coordination event explains the lack of reactivity observed in electron deficient substrates as they will only weakly coordinate. Complex II then proceeds through the turnover limiting step activating the amide N-methyl C(sp^3)–H bond generating complex III. This intermediate must then reductively eliminate the C-B bond and lose the product from the coordination sphere. The loss of product from the coordination sphere is likely assisted by a strong interaction between the carbonyl oxygen and boron in the boronic ester. This interaction is supported by a sharp boron peak in the 11B NMR observed for all C(sp^3) borylated products. Finally, regeneration of complex I from complex IV can occur through oxidative addition of B_2pin_2 followed by reductive elimination of HBpin.

CHAPTER 3: AMIDINE DIRECTED IRIDIUM (sp3) C–H BORYLATION CATALYSIS WITH HIGH N-ADJACENT SELECTIVITY

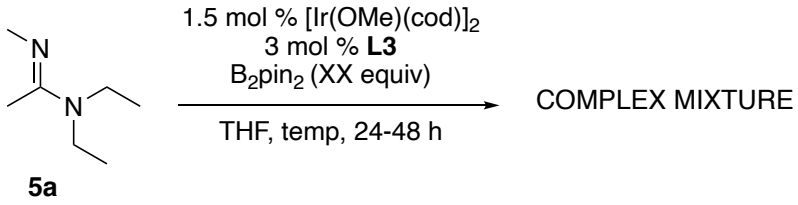
Scheme 11: Substrate scope of amidine borylation



Conditions: **3** (1 equiv, 0.5 mmol), boron source (1.5 equiv, 0.75 mmol), $[Ir(OMe)(cod)]_2$ (1.5 mol %, 0.0075 mmol), **L3** (3 mol %, 0.015 mmol) in 2 mL THF.

Successful CHB of amides[28] inspired me to try CHB on amidines as the oxygen atom in amides is replaced by a nitrogen atom that is a better donor and could act as a directing group. The study was initiated using the same reaction conditions as used for amide substrates. *N'*-(sec-Butyl)-*N,N*-dimethylacetimidamide (**3a**) was tested for the C–H borylation at the N-methyl position and 100% conversion of *N'*-(sec-butyl)-*N,N*-dimethylacetimidamide was observed in 1 hour as compared to 24 hours required for most amides. Two other amidine substrates (**3b-3c**), not having any chiral centers, gave complete conversion of starting material. Further, 0.5, 0.75, 1.0 and 1.5 equivalents of bis(pinacolato)diboron were tested with (**3c**) and C–H borylation was observed in all cases with 100% conversion.

Scheme 12: Attempted borylation of secondary amidine using bis(pinacolato)diboron



		Equivalents of B_2pin_2 (Boron Source)			
S.No.	Temp (ºC)	0.5	0.75	1.0	1.5
1	40	Complex mixture	Complex mixture	Complex mixture	Complex mixture
2	60	Complex mixture	Complex mixture	Complex mixture	Complex mixture
3	80	Complex mixture	Complex mixture	Complex mixture	Complex mixture

Conditions: **5** (1 equiv, 0.5 mmol), boron source (XX equiv, xx mmol), $[Ir(OMe)(cod)]_2$ (1.5 mol %, 0.0075 mmol), **L3** (3 mol %, 0.015 mmol) in 2 mL THF.

Excited with results for C–H borylation at the N-methyl position of amidines, the same reaction conditions were tested for C–H borylation of amidines at secondary C–H bonds. This resulted in formation of complex mixture. Upon looking at ^{11}B NMR spectrum of reaction, a peak at 8.57 ppm increases in intensity over time indicating formation of a bond between nitrogen and boron, which is an indication of formation of product. However, in the ^{1}H NMR spectrum no product peaks are observed and hence a complex mixture is observed. As C–H borylation was observed for different equivalents (0.5, 0.75, 1.0 and 1.5) of bis(pinacolato)diboron with (**3b**), we started our screening conditions with using those equivalents. Unfortunately, a complex mixture was

observed in all cases. Decreasing the reaction temperature from 80 ºC to 60 ºC and 40 ºC resulted in low reactivity.

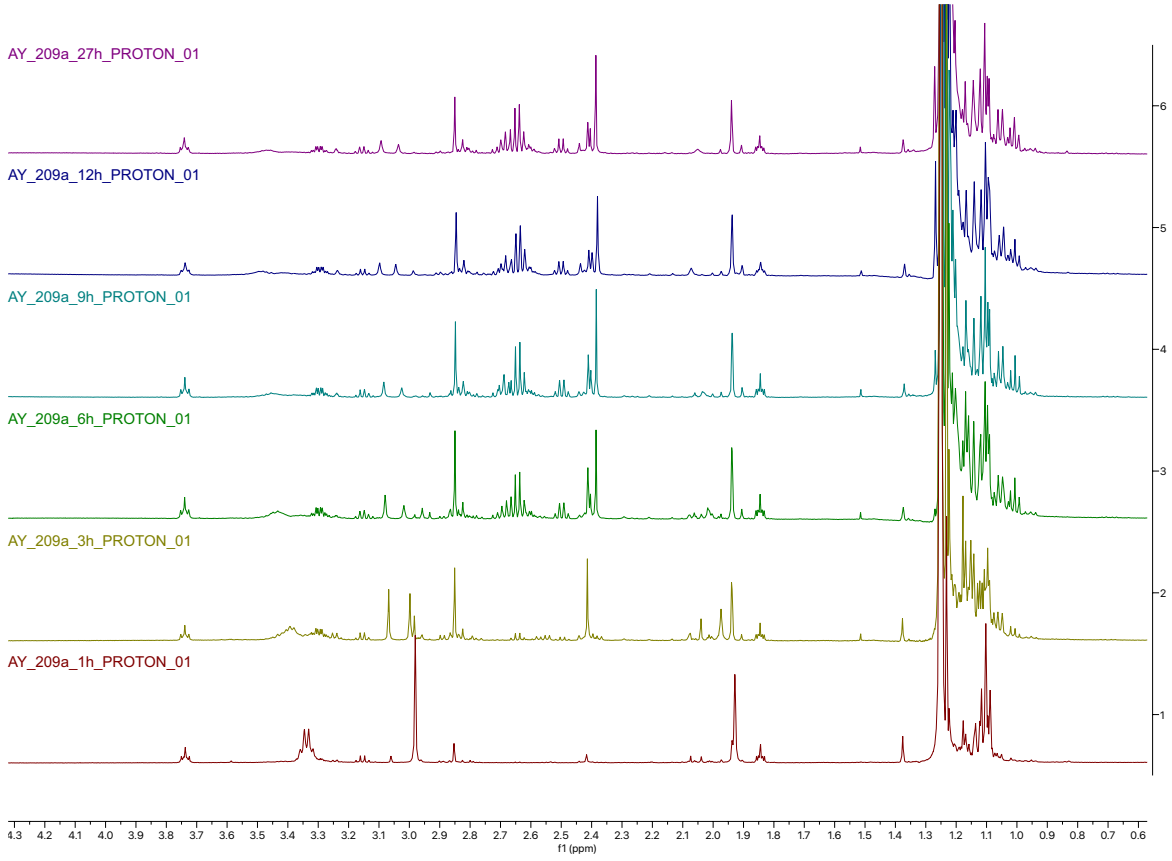


Figure 1: ^{1}H NMR spectrum of crude material at different interval of time of reaction of **5** with $[Ir(OMe)(cod)]_2$ (1.5 mol %, 0.0075 mmol), **L3** (3 mol %, 0.015 mmol), 1.5 equiv of B_2pin_2 at 80 ºC in 2 mL THF

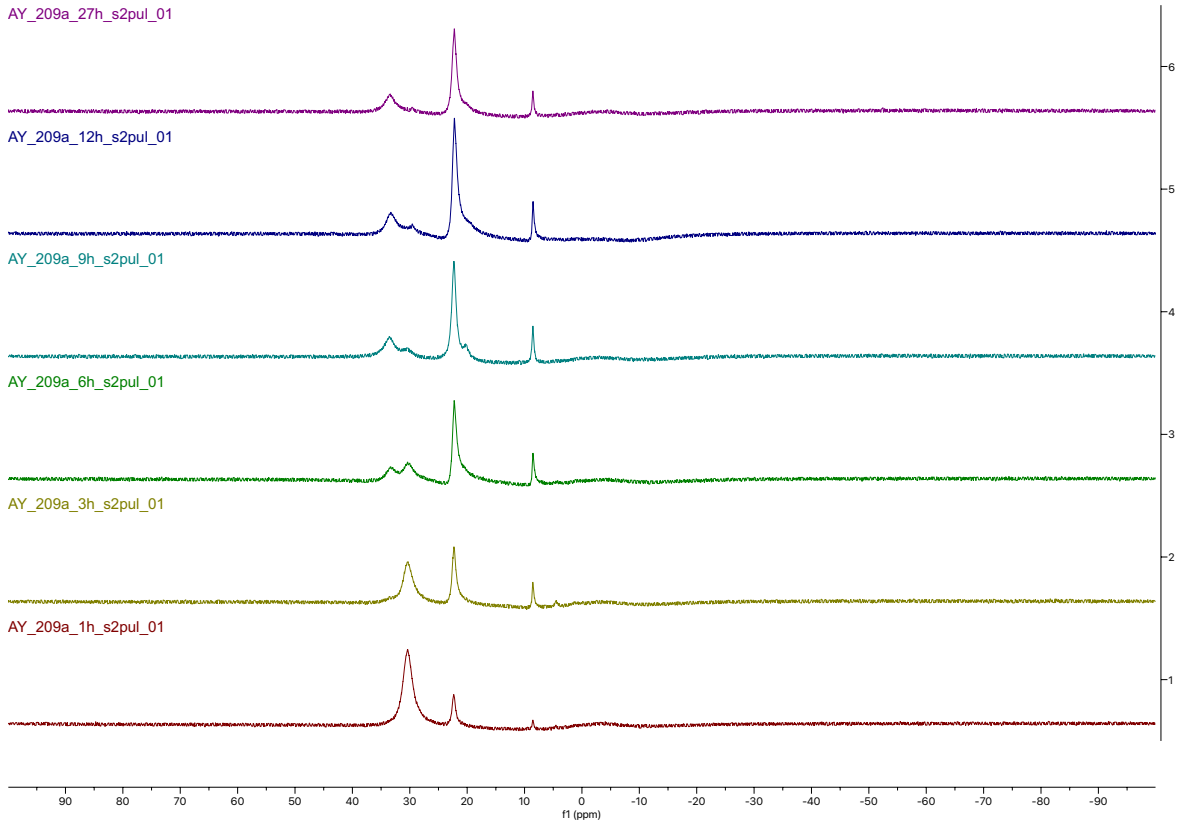
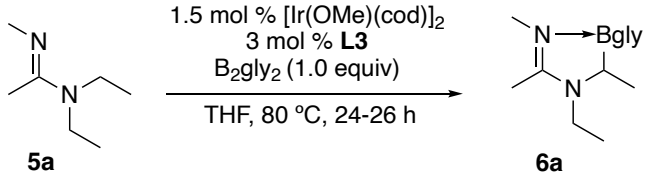


Figure 2: ^{11}B NMR spectrum of crude material at different interval of time of reaction of **5** with $[Ir(OMe)(cod)]_2$ (1.5 mol %, 0.0075 mmol), **L3** (3 mol %, 0.015 mmol), 1.5 equiv of B_2pin_2 at 80 ºC in 2 mL THF

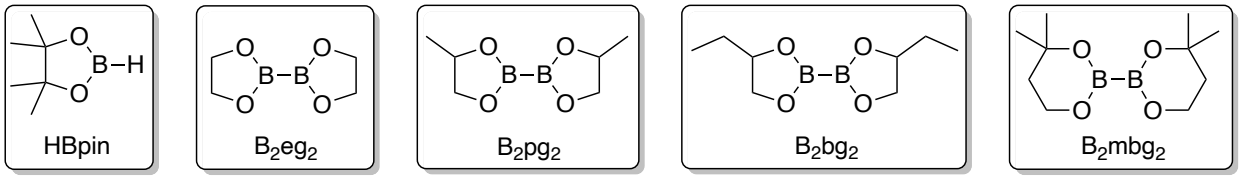
Pinacolborane and different diboron partners were also tested. Diboron partners were synthesized from the corresponding glycol and $B_2(OH)_4$ via a procedure developed in our lab by Ryan Fornwald.[29] B_2eg_2, B_2pg_2, B_2bg_2, B_2mbg_2 (eg = ethane-1,2-diol, pg = propane-1,2-diol, bg = butane-1,2-diol, mbg = 3-methylbutane-1,3-diol) were used as boron partners. Results are shown in Table **2.** Reactions with diboron reagents B_2eg_2 and B_2pg_2 gave 100% conversion of starting material in 1 h. A racemic mixture was observed with B_2pg_2 as the diboron partner. CHB on

substrate (**5b**) was performed successfully with 71% conversion of starting material (based on GC) with prior work showing its amide analog poisoning the catalyst.

Table 2: Optimization of reaction conditions: Screening of boron partner



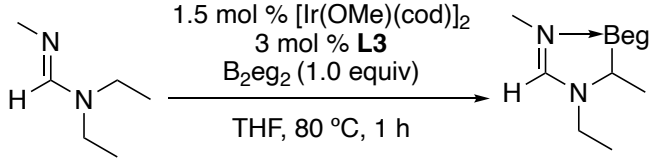
5a 6a



S.No.	B_2gly_2	Conversion (%)
1	**HBpin**	0
2	[a]**B_2eg_2**	100
3	[b]**B_2pg_2**	100
4	[b]**B_2bg_2**	15
5	**B_2mbg_2**	0

Conditions: **5** (1 equiv, 0.5 mmol), boron source (1.0 equiv, 0.5 mmol), $[Ir(OMe)(cod)]_2$ (1.5 mol %, 0.0075 mmol), **L3** (3 mol %, 0.015 mmol) in 2 mL THF. [a]NMR Yield = 33% with 1,3,5-trimethoxybenzene as internal standard. [b]Based on GC/MS.

Scheme 13: CHB of N,N-diethyl-N'-methylformimidamide

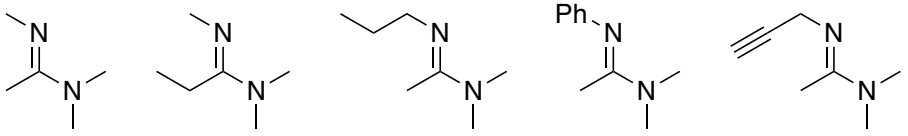


5b 6b

CHAPTER 4: SUMMARY AND FUTURE WORK

CHB on the N-methyl position of a variety of substrates was made possible with ligand (**L3**). Following successful CHB on amides, ligand (**L3**) was used to attempt CHB on the N-methyl position of amidines with 100% conversion of starting material in 1 h as compared to 24 h for amides. CHB from primary C–H bonds to secondary C–H bonds on amidines required change in the diboron partner, with racemic mixture being observed with B_2pg_2. With optimized conditions in hand, substrates for primary and secondary CHB would be attempted.

Scheme 14: Substrate scope for CHB on primary amidines

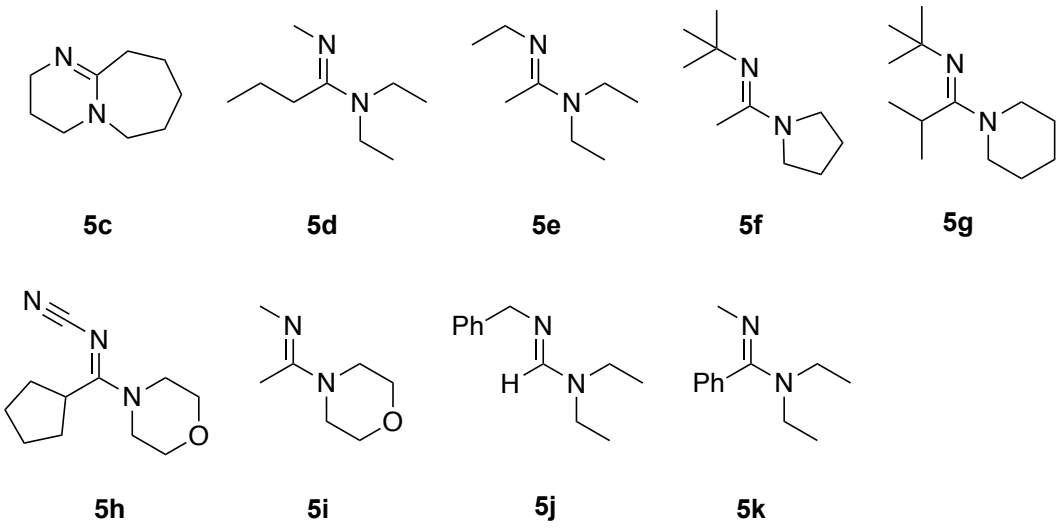


3d **3e** **3f** **3g** **3h**

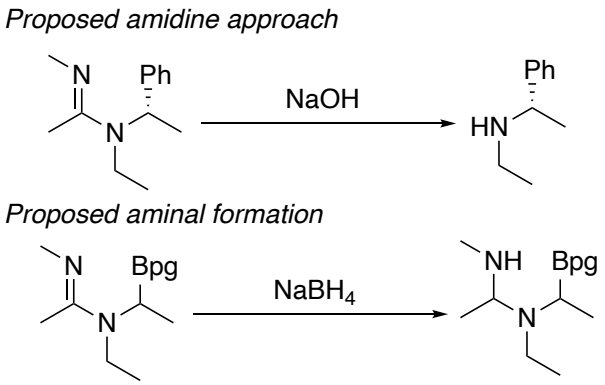
Scheme 14 shows such informative substrates. Substrate (**3d**) has two competing primary positions for CHB while substrate (**3e**) has three primary positions for CHB and substrate (**3f**) has primary vs secondary positions competing for CHB. It would be interesting to see CHB on primary sp^3 C–H bonds in presence of sp^2 C–H bonds (**3g**) and sp C–H bonds (**3h**).

With the CHB on an amidine secondary sp^3 C–H bonds demonstrated, extension of the substrate scope is needed. Scheme 15 shows several instructive substrates. Substrates (**5d**) and (**5e**) has two secondary position available competing for CHB, whereas (**5f**) and (**5g**) have different ring sizes. Morpholine derived amidine (**5h**) with nitrile group and (**5i**) would also be interesting, especially if the functionalized morpholine can be extruded from amidine. Reaction in presence of sp^2 C–H bonds would be tested with (**5j**) and (**5k**). Lastly, borylation of DBU (**5c**) could be a first step towards making this base chiral.

Scheme 15: Substrate scope for CHB on secondary amidines

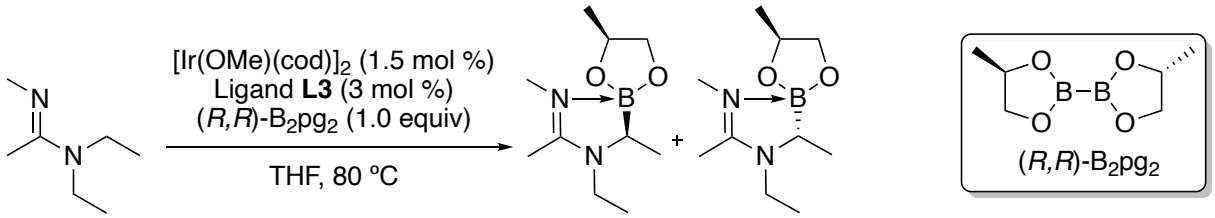


Scheme 16: Functionalization of borylated amidine



Further functionalization of CHB products would be attempted. The borylation of amidine could be followed by cross-couplings to install various aryl groups. Borylated amidines would be an attractive route to synthesize primary borylated amines, as after cross-coupling, simple saponification would free the amine. Likewise, reduction would result in formation of borylated aminals (Scheme 16).

Scheme 17: Introducing chirality in amidine CHB



With regards to chirality, using (*R,R*)-B_2pg_2 in the CHB of (*E*)-*N,N*-diethyl-*N'*-methylacetimidamide would result in formation of two diastereomers, the separation of which would provide the two enantiomers. Chiral variants of ligand (**L3**) would also be explored.

CHAPTER 5: EXPERIMENTAL DETAILS AND CHARACTERIZATION DATA

General Methods - All commercially available chemicals were used as received unless otherwise indicated. Bis(pinacolato)diboron (B_2pin_2) was generously supplied by BoroPharm, Inc. Bis(η^4-1,5-cyclooctadiene)-di-μ-methoxy-diiridium(I) $[Ir(OMe)(cod)]_2$ was made by a literature procedure[30] or purchased from Sigma-Aldrich. Tetrahydrofuran (THF) was refluxed over sodium/benzophenone ketyl, distilled and degassed before use.

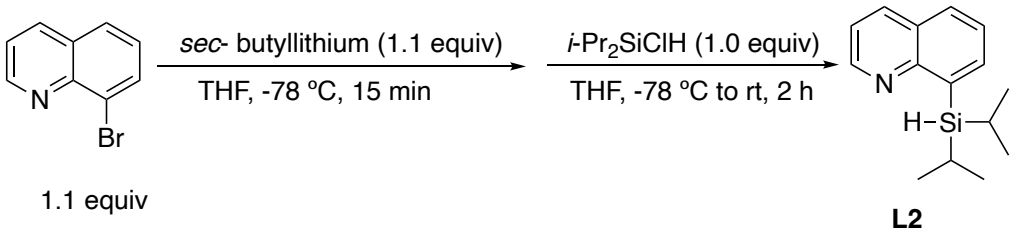
Column chromatography was performed on 240–400 mesh Silica P-Flash silica gel. In cases where deactivated silica gel was used, this was accomplished by adding deionized water (35% w/w) to silica gel and shaking for 60 seconds, afterwards any small chunks were crushed with spatula resulting a uniform powder in a round bottom flask, which was added into column. Thin layer chromatography was performed on 0.25 mm thick aluminum–backed silica gel plates and visualized with ultraviolet light (λ = 254 nm) and alizarin stain to visualize boronic esters according to a literature procedure.[31] Sublimations were conducted with a water-cooled cold finger.

^1H, ^{13}C, ^{11}B, ^{19}F and ^{29}Si NMR spectra were recorded on a Varian 500 MHz DD2 Spectrometer equipped with a ^1H-^{19}F/^{15}N-^{31}P 5 mm Pulsed Field Gradient (PFG) Probe, or an Innova 300 MHz spectrometer equipped with a QUAD (^1H/^{19}F and ^{11}B) PFG probe. Spectra were taken in $CDCl_3$ referenced to 7.26 ppm in ^1H NMR and 77.0 ppm in ^{13}C NMR. Resonances for the boron-bearing carbon atom were not observed due to quadrupolar relaxation. All coupling constants are apparent *J* values measured at the indicated field strengths in Hertz (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, ddd = doublet of doublet of doublets, bs = broad singlet). NMR spectra were processed for display using the MNova software program with only phasing and

baseline corrections applied. Reaction conversions were calculated by comparing the integration of the starting amide *N*-methyl peak with the borylated product methylene peak.

High-resolution mass spectra (HRMS) were obtained at the Mass spectrometry analysis was performed at the Molecular Metabolism and Disease Mass Spectrometry Core facility at Michigan State University using electrospray ionization (ESI+ or ESI-) on quadrupole time-of-flight (Q-TOF) instruments. Melting points were measured in a capillary melting point apparatus and are uncorrected.

Preparation of Ligand L2

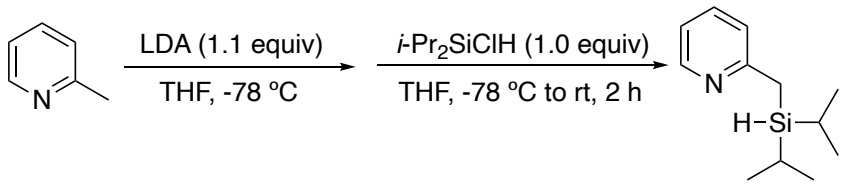


1.1 equiv

L2

Ligand **L2** was prepared in similar yield following the previously reported procedure.[22]

Preparation of Ligand L3



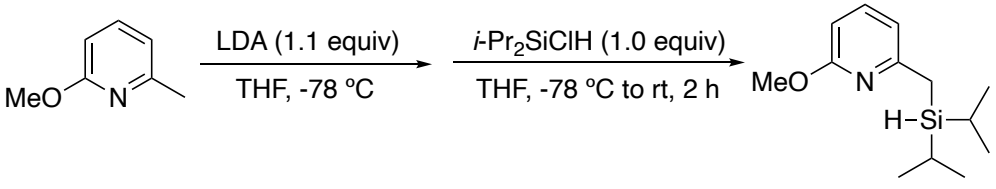
L3

To an oven dried 250 mL round bottom flask equipped with a stir bar, under nitrogen was added THF (40 mL) and diisopropylamine (1.1 equiv, 15.9 mmol, 2.25 mL) which was freshly distilled over calcium hydride. This solution was cooled to –78 °C in an acetone dry ice bath. Then n-butyllithium (2.5 M in hexanes, 1.1 equiv, 15.9 mmol, 6.36 mL) was added dropwise. This solution was allowed to stir for 5 min after which 2-methylpyridine (1.0 equiv, 14.5 mmol, 1.43 mL) which was freshly distilled over calcium hydride was slowly added dropwise. This addition took

approximately 5 min after which a reddish-orange solution was observed. In a separate oven dried 250 mL round bottom flask equipped with a stir bar, under nitrogen was added THF (20 mL) and diisopropylchlorosilane (1.0 equiv, 14.5 mmol, 2.47 mL) which was freshly distilled over calcium hydride. This solution was cooled to –78 °C in an acetone dry ice bath. The contents of the flask containing the lithiated 2-methylpyridine were then slowly cannula transferred into the second flask containing the chlorosilane. This cannula transfer took approximately 20 min. Upon completion the resulting solution was allowed to stir at –78 °C for 30 min after which an aliquot was removed, quenched with methanol, and GCMS was collected. The GCMS revealed two products in a 9:1 ratio with masses corresponding to the desired monosilylated product and undesired disilylated product. The entire reaction mixture was then quenched by the addition of methanol (5 mL), solvents were removed under reduced pressure and a DCM/H_2O extraction was performed. The resulting material was further purified by distillation (oil bath temperature: 60–80 °C; vacuum: 0.01 torr). This provided **L3** as a clear colorless liquid in 58% yield (1.743 g).

^{1}H NMR (500 MHz, $CDCl_3$): δ_H 8.42 (d, J = 4.9 Hz, 1H), 7.48 (td, J = 7.7, 1.9 Hz, 1H), 7.05 (d, J = 7.9 Hz, 1H), 6.96 (dd, J = 7.4, 5.0 Hz, 1H), 3.71–3.58 (s, 1H), 2.43 (d, J = 3.7 Hz, 2H), 0.99 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 161.45, 149.10, 135.91, 122.61, 119.39, 22.08, 18.70, 18.56, 10.60. ^{29}Si NMR (99 MHz, $CDCl_3$): δ_{Si} 7.32.

Preparation of Ligand L4



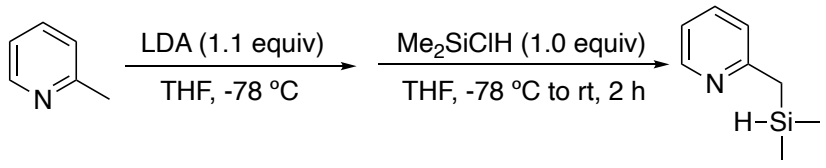
L4

To an oven dried 250 mL round bottom flask equipped with a stir bar, under nitrogen was added THF (50 mL) and diisopropylamine (1.1 equiv, 9.2 mmol, 1.3 mL) which was freshly distilled

over calcium hydride. This solution was cooled to –78 °C in an acetone dry ice bath. Then n-butyllithium (2.5 M in hexanes, 1.1 equiv, 9.2 mmol, 3.7 mL) was added dropwise. This solution was allowed to stir for 10 min after which 2-methoxy-6-methylpyridine (1.0 equiv, 8.4 mmol, 1.02 mL) which was placed over 4 Å molecular sieves 24 h before use was slowly added dropwise. This addition took approximately 5 min after which an orange-yellow solution was observed. The solution was allowed to stir for 30 min after which diisopropylchlorosilane (1.0 equiv, 8.4 mmol, 1.4 mL) freshly distilled over calcium hydride was added. This mixture stirred for 1 h then quenched by the addition of methanol (5 mL). Solvents were removed under reduced pressure and a DCM/H_2O extraction was performed. The resulting material was further purified by a silica column with a DCM/hexanes (1:9) solvent system. This provided **L4** as a clear colorless liquid in 38% yield (0.754 g).

^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.38 (t, J = 7.4 Hz, 1H), 6.63 (d, J = 7.2 Hz, 1H), 6.43 (d, J = 8.1 Hz, 1H), 3.88 (s, 3H), 3.59 (bs, 1H), 2.34 (d, J = 3.2 Hz, 2H), 1.02 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 163.31, 159.32, 138.52, 114.93, 105.64, 53.12, 21.47, 18.75, 18.58, 10.67. ^{29}Si NMR (99 MHz, $CDCl_3$): δ_{Si} 7.04.

Preparation of Ligand L5

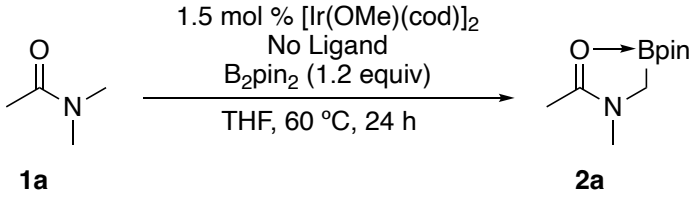


L5

To an oven dried 250 mL round bottom flask equipped with a stir bar, under nitrogen was added THF (50 mL) and diisopropylamine (1.1 equiv, 14.5 mmol, 2.05 mL) which was freshly distilled from calcium hydride. This solution was cooled to –78 °C in an acetone dry ice bath. Then n-butyllithium (2.5 M in hexanes, 1.1 equiv, 14.5 mmol, 5.8 mL) was added dropwise. This solution

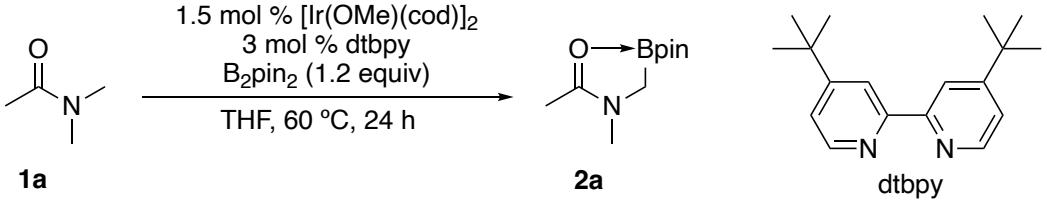
was allowed to stir for 10 min after which 2-methylpyridine (1.0 equiv, 13.1 mmol, 1.3 mL) which was freshly distilled over calcium hydride was slowly added dropwise. This addition took approximately 5 min after which a bright red-orange solution was observed. In a separate oven dried 250 mL round bottom flask equipped with a stir bar, under nitrogen was added THF (20 mL) and dimethylchlorosilane (1.0 equiv, 13.1 mmol, 1.46 mL) which was freshly distilled over calcium hydride. This solution was cooled to –78 °C in an acetone dry ice bath. The contents of the flask containing the lithiated 2-methylpyridine were then slowly cannula transferred into the second flask containing the chlorosilane. This cannula transfer took approximately 20 min. Upon completion the resulting solution was allowed to stir at –78 °C for 30 min after which the reaction was quenched by addition of silica. The silica was then rinsed with THF (250 mL) then volatiles were removed under reduced pressure. The oil was dissolved in DCM, and the solution was washed with H_2O. The organic phase was dried over $MgSO_4$, filtered, and the solvent was removed in vacuo. The ^{1}H NMR at this point showed 95% conversion of the starting material. Unusually, at ambient temperature over a week the product slowly converted back into the starting pyridine. To remove the starting materials and silicon byproducts, the compound was distilled twice with a short-path distillation head (oil bath temperature: 60–80 °C; vacuum: 0.01 torr). This provided **L5** as a clear colorless liquid in 22% yield (0.436 g), which matched previously reported spectra.[32] Unfortunately, this purified compound also slowly decomposed in a nitrogen filled glove box at ambient temperature.

^{1}H NMR (500 MHz, $CDCl_3$)[4]: δ_H 8.44 (d, J = 5.0 Hz, 1H), 7.51 (td, J = 7.7, 1.9 Hz, 1H), 7.04–6.93 (m, 2H), 4.02 (m, J = 3.6 Hz, 1H), 2.42 (d, J = 3.6 Hz, 2H), 0.10 (d, J = 3.6 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$)[4]: δ_C 160.88, 149.17, 136.03, 122.28, 119.42, 27.56, –4.50.



1a **2a**

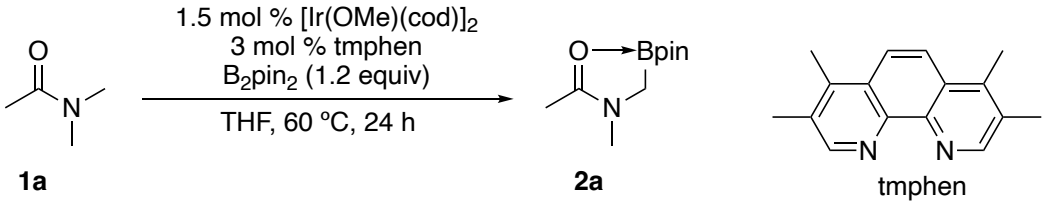
In a nitrogen filled glove box, $[Ir(OMe)(cod)]_2$ (4.97 mg, 0.0075 mmol, 1.5 mol %) and B_2pin_2 (152.4 mg, 0.6 mmol, 1.2 equiv) were weighed into separate test tubes and *N,N*-dimethylacetamide (43.5 mg, 0.5 mmol, 1.0 equiv) was weighed into a 5 mL conical vial equipped with a stir bar. To the test tube containing $[Ir(OMe)(cod)]_2$ was added ~0.3 mL THF. The resulting solution was then transferred into the test tube containing B_2pin_2. The contents of the first test tube were rinsed three times (~0.2 mL/rinse) and added to the test tube containing B_2pin_2. The solution of $[Ir(OMe)(cod)]_2$ and B_2pin_2 was then transferred into the 5 mL conical vial followed by a similar rinsing procedure described above. The conical vial was then sealed and placed in an aluminum block pre-heated to 60 °C and allowed to stir for 24 h. The vial was then opened, solvent was removed via rotary evaporation, and ^{1}H NMR of crude material was collected. Only starting material was observed.



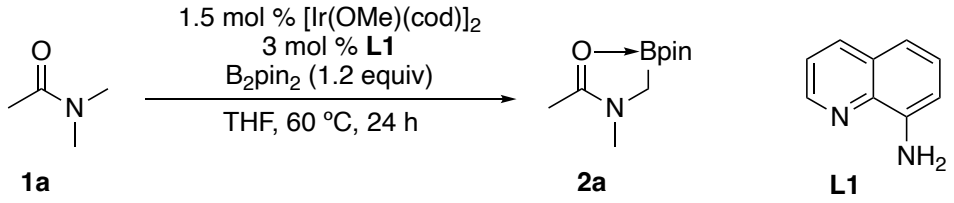
1a **2a**

In a nitrogen filled glove box, $[Ir(OMe)(cod)]_2$ (4.97 mg, 0.0075 mmol, 1.5 mol %), dtbpy (4.0 mg, 0.015 mmol, 3 mol %), and B_2pin_2 (152.4 mg, 0.6 mmol, 1.2 equiv) were weighed into separate test tubes and *N,N*-dimethylacetamide (43.5 mg, 0.5 mmol, 1.0 equiv) was weighed into a 5 mL conical vial equipped with a stir bar. To the test tube containing $[Ir(OMe)(cod)]_2$ was added ~0.2 mL THF. The resulting solution was then transferred into the test tube containing B_2pin_2. The contents of the first test tube were rinsed three times (~0.2 mL/rinse) and added to the test tube containing B_2pin_2. The solution of $[Ir(OMe)(cod)]_2$ and B_2pin_2 was then transferred into the test

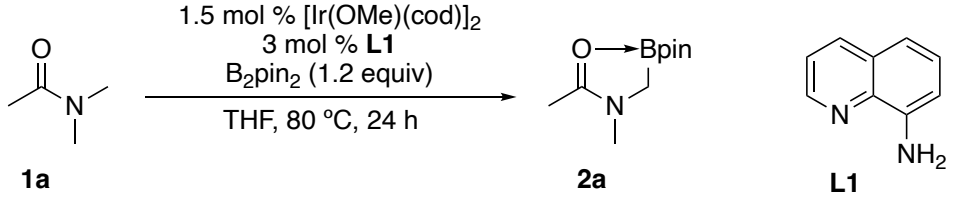
tube containing dtbpy and the rinsing procedure was repeated. Finally, the resulting solution was added to the 5 mL conical vial followed by the rinsing procedure. The conical vial was then sealed and placed in an aluminum block pre-heated to 60 °C and allowed to stir for 24 h. The vial was then opened, solvent was removed via rotary evaporation, and ^{1}H NMR of crude material was collected. A complex mixture of products was observed.



In a nitrogen filled glove box, $[Ir(OMe)(cod)]_2$ (4.97 mg, 0.0075 mmol, 1.5 mol %), tmphen (3.5 mg, 0.015 mmol, 3 mol %), and B_2pin_2 (152.4 mg, 0.6 mmol, 1.2 equiv) were weighed into separate test tubes and *N,N*-dimethylacetamide (43.5 mg, 0.5 mmol, 1.0 equiv) was weighed into a 5 mL conical vial equipped with a stir bar. To the test tube containing $[Ir(OMe)(cod)]_2$ was added ~0.2 mL THF. The resulting solution was then transferred into the test tube containing B_2pin_2. The contents of the first test tube were rinsed three times (~0.2 mL/rinse) and added to the test tube containing B_2pin_2. The solution of $[Ir(OMe)(cod)]_2$ and B_2pin_2 was then transferred into the test tube containing tmphen and the rinsing procedure was repeated. Finally, the resulting solution was added to the 5 mL conical vial followed by the rinsing procedure. The conical vial was then sealed and placed in an aluminum block pre-heated to 60 °C and allowed to stir for 24 h. The vial was then opened, solvent was removed via rotary evaporation, and ^{1}H NMR of crude material was collected. A complex mixture of products was observed.

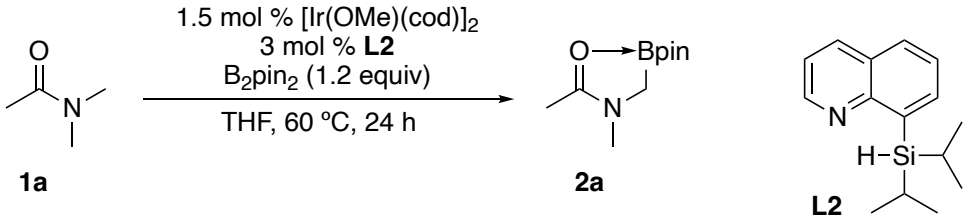


In a nitrogen filled glove box, $[Ir(OMe)(cod)]_2$ (4.97 mg, 0.0075 mmol, 1.5 mol %), **L1** (2.2 mg, 0.015 mmol, 3 mol %), and B_2pin_2 (152.4 mg, 0.6 mmol, 1.2 equiv) were weighed into separate test tubes and *N,N*-dimethylacetamide (43.5 mg, 0.5 mmol, 1.0 equiv) was weighed into a 5 mL conical vial equipped with a stir bar. To the test tube containing $[Ir(OMe)(cod)]_2$ was added ~0.2 mL THF. The resulting solution was then transferred into the test tube containing B_2pin_2. The contents of the first test tube were rinsed three times (~0.2 mL/rinse) and added to the test tube containing B_2pin_2. The solution of $[Ir(OMe)(cod)]_2$ and B_2pin_2 was then transferred into the test tube containing **L1** and the rinsing procedure was repeated. Finally, the resulting solution was added to the 5 mL conical vial followed by the rinsing procedure. The conical vial was then sealed and placed in an aluminum block pre-heated to 60 °C and allowed to stir for 24 h. The vial was then opened, solvent was removed via rotary evaporation, and ^{1}H NMR of crude material was collected. A 10% conversion of starting material was observed.

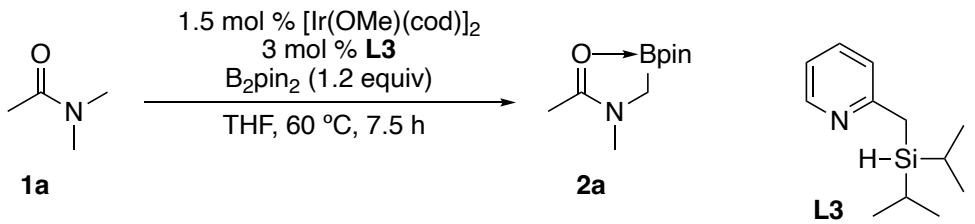


In a nitrogen filled glove box, $[Ir(OMe)(cod)]_2$ (4.97 mg, 0.0075 mmol, 1.5 mol %), **L1** (2.2 mg, 0.015 mmol, 3 mol %), and B_2pin_2 (152.4 mg, 0.6 mmol, 1.2 equiv) were weighed into separate test tubes and *N,N*-dimethylacetamide (43.5 mg, 0.5 mmol, 1.0 equiv) was weighed into a 5 mL conical vial equipped with a stir bar. To the test tube containing $[Ir(OMe)(cod)]_2$ was added ~0.2 mL THF. The resulting solution was then transferred into the test tube containing B_2pin_2. The contents of the first test tube were rinsed three times (~0.2 mL/rinse) and added to the test tube containing B_2pin_2. The solution of $[Ir(OMe)(cod)]_2$ and B_2pin_2 was then transferred into the test tube containing **L1** and the rinsing procedure was repeated. Finally, the resulting solution was

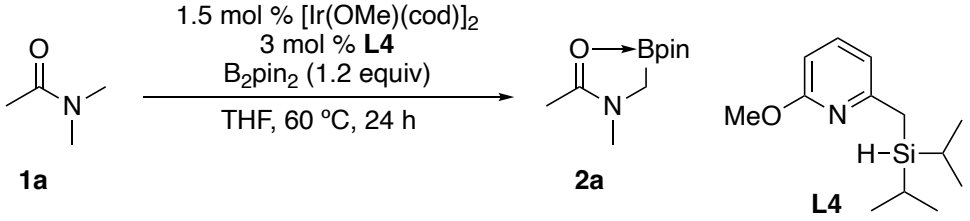
added to the 5 mL conical vial followed by the rinsing procedure. The conical vial was then sealed and placed in an aluminum block pre-heated to 80 °C and allowed to stir for 24 h. The vial was then opened, solvent was removed via rotary evaporation, and ^{1}H NMR of crude material was collected. A 10% conversion of starting material was observed.



In a nitrogen filled glove box, $[Ir(OMe)(cod)]_2$ (4.97 mg, 0.0075 mmol, 1.5 mol %), **L2** (3.7 mg, 0.015 mmol, 3 mol %), and B_2pin_2 (152.4 mg, 0.6 mmol, 1.2 equiv) were weighed into separate test tubes and *N,N*-dimethylacetamide (43.5 mg, 0.5 mmol, 1.0 equiv) was weighed into a 5 mL conical vial equipped with a stir bar. To the test tube containing $[Ir(OMe)(cod)]_2$ was added ~0.2 mL THF. The resulting solution was then transferred into the test tube containing B_2pin_2. The contents of the first test tube were rinsed three times (~0.2 mL/rinse) and added to the test tube containing B_2pin_2. The solution of $[Ir(OMe)(cod)]_2$ and B_2pin_2 was then transferred into the test tube containing **L2** and the rinsing procedure was repeated. Finally, the resulting solution was added to the 5 mL conical vial followed by the rinsing procedure. The conical vial was then sealed and placed in an aluminum block pre-heated to 60 °C and allowed to stir for 24 h. The vial was then opened, solvent was removed via rotary evaporation, and ^{1}H NMR of crude material was collected. A 60% conversion of starting material was observed.

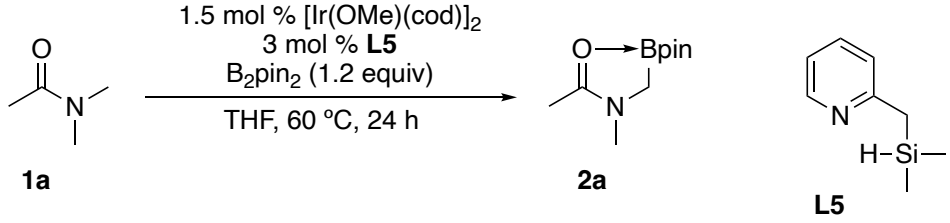


In a nitrogen filled glove box, $[Ir(OMe)(cod)]_2$ (4.97 mg, 0.0075 mmol, 1.5 mol %), **L3** (3.1 mg, 0.015 mmol, 3 mol %), and B_2pin_2 (152.4 mg, 0.6 mmol, 1.2 equiv) were weighed into separate test tubes and *N,N*-dimethylacetamide (43.5 mg, 0.5 mmol, 1.0 equiv) was weighed into a 5 mL conical vial equipped with a stir bar. To the test tube containing $[Ir(OMe)(cod)]_2$ was added ~0.2 mL THF. The resulting solution was then transferred into the test tube containing B_2pin_2. The contents of the first test tube were rinsed three times (~0.2 mL/rinse) and added to the test tube containing B_2pin_2. The solution of $[Ir(OMe)(cod)]_2$ and B_2pin_2 was then transferred into the test tube containing **L3** and the rinsing procedure was repeated. Finally, the resulting solution was added to the 5 mL conical vial followed by the rinsing procedure. The conical vial was then sealed and placed in an aluminum block pre-heated to 60 °C and allowed to stir for 24 h. The vial was then opened, solvent was removed via rotary evaporation, and ^{1}H NMR of crude material was collected. A 91% conversion of starting material was observed.

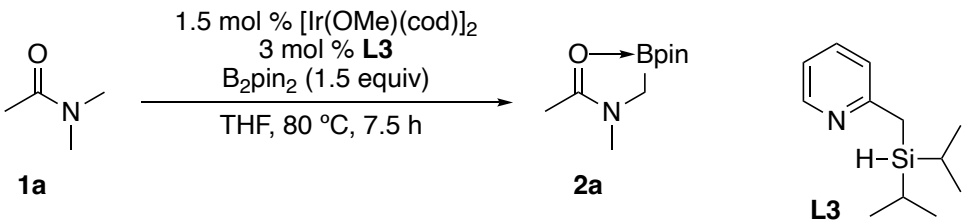


In a nitrogen filled glove box, $[Ir(OMe)(cod)]_2$ (4.97 mg, 0.0075 mmol, 1.5 mol %), **L4** (3.6 mg, 0.015 mmol, 3 mol %), and B_2pin_2 (152.4 mg, 0.6 mmol, 1.2 equiv)were weighed into separate test tubes and *N,N*-dimethylacetamide (43.5 mg, 0.5 mmol, 1.0 equiv) was weighed into a 5 mL conical vial equipped with a stir bar. To the test tube containing $[Ir(OMe)(cod)]_2$ was added ~0.2 mL THF. The resulting solution was then transferred into the test tube containing B_2pin_2. The contents of the first test tube were rinsed three times (~0.2 mL/rinse) and added to the B_2pin_2 containing test tube. The solution of $[Ir(OMe)(cod)]_2$ and B_2pin_2 was then transferred into the test tube containing **L4** and the rinsing procedure was repeated. Finally, the resulting solution was

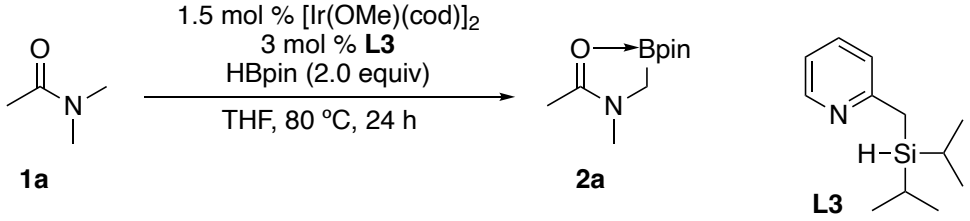
added to the 5 mL conical vial followed by the rinsing procedure. The conical vial was then sealed and placed in an aluminum block pre-heated to 60 °C and allowed to stir for 24 h. The vial was then opened, solvent was removed via rotary evaporation, and ^{1}H NMR of crude material was collected. A complex mixture of products was observed.



In a nitrogen filled glove box, $[Ir(OMe)(cod)]_2$ (4.97 mg, 0.0075 mmol, 1.5 mol %), **L5** (2.3 mg, 0.015 mmol, 3 mol %), and B_2pin_2 (152.4 mg, 0.6 mmol, 1.2 equiv)were weighed into separate test tubes and *N,N*-dimethylacetamide (43.5 mg, 0.5 mmol, 1.0 equiv) was weighed into a 5 mL conical vial equipped with a stir bar. To the test tube containing $[Ir(OMe)(cod)]_2$ was added ~0.2 mL THF. The resulting solution was then transferred into the test tube containing B_2pin_2. The contents of the first test tube were rinsed three times (~0.2 mL/rinse) and added to the test tube containing B_2pin_2. The solution of $[Ir(OMe)(cod)]_2$ and B_2pin_2 was then transferred into the test tube containing **L5** and the rinsing procedure was repeated. Finally, the resulting solution was added to the 5 mL conical vial followed by the rinsing procedure. The conical vial was then sealed and placed in an aluminum block pre-heated to 60 °C and allowed to stir for 24 h. The vial was then opened, solvent was removed via rotary evaporation, and ^{1}H NMR of crude material was collected. An 11% conversion of starting material was observed.

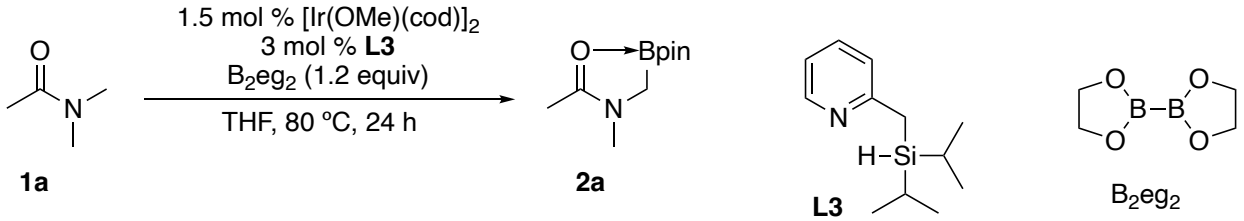


In a nitrogen filled glove box, $[Ir(OMe)(cod)]_2$ (4.97 mg, 0.0075 mmol, 1.5 mol %), **L3** (3.1 mg, 0.015 mmol, 3 mol %), and B_2pin_2 (152.4 mg, 0.6 mmol, 1.2 equiv) were weighed into separate test tubes and *N,N*-dimethylacetamide (43.5 mg, 0.5 mmol, 1.0 equiv) was weighed into a 5 mL conical vial equipped with a stir bar. To the test tube containing $[Ir(OMe)(cod)]_2$ was added ~0.2 mL THF. The resulting solution was then transferred into the test tube containing B_2pin_2. The contents of the first test tube were rinsed three times (~0.2 mL/rinse) and added to the test tube containing B_2pin_2. The solution of $[Ir(OMe)(cod)]_2$ and B_2pin_2 was then transferred into the test tube containing **L3** and the rinsing procedure was repeated. Finally, the resulting solution was added to the 5 mL conical vial followed by the rinsing procedure. The conical vial was then sealed and placed in an aluminum block pre-heated to 80 °C and allowed to stir for 7.5 h. The vial was then opened, solvent was removed via rotary evaporation, and ^{1}H NMR of crude material was collected. A 100% conversion of starting material was observed.

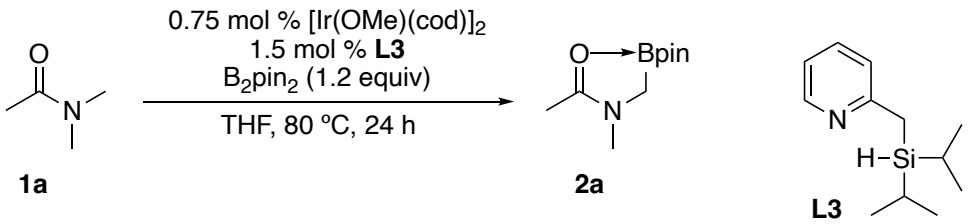


In a nitrogen filled glove box, $[Ir(OMe)(cod)]_2$ (4.97 mg, 0.0075 mmol, 1.5 mol %), **L3** (3.1 mg, 0.015 mmol, 3 mol %), and HBpin (128.0 mg, 1.0 mmol, 2.0 equiv) were weighed into separate test tubes and *N,N*-dimethylacetamide (43.5 mg, 0.5 mmol, 1.0 equiv) was weighed into a 5 mL conical vial equipped with a stir bar. To the test tube containing $[Ir(OMe)(cod)]_2$ was added ~0.2 mL THF. The resulting solution was then transferred into the test tube containing HBpin. The contents of the first test tube were rinsed three times (~0.2 mL/rinse) and added to the test tube containing HBpin. The solution of $[Ir(OMe)(cod)]_2$ and HBpin was then transferred into the test tube containing **L3** and the rinsing procedure was repeated. Finally, the resulting solution was

added to the 5 mL conical vial followed by the rinsing procedure. The conical vial was then sealed and placed in an aluminum block pre-heated to 80 °C and allowed to stir for 24 h. The vial was then opened, solvent was removed via rotary evaporation, and ^{1}H NMR of crude material was collected. A complex mixture of products was observed.



In a nitrogen filled glove box, $[Ir(OMe)(cod)]_2$ (4.97 mg, 0.0075 mmol, 1.5 mol %), **L3** (3.1 mg, 0.015 mmol, 3 mol %), and B_2eg_2 (85.0 mg, 0.6 mmol, 1.2 equiv) were weighed into separate test tubes and *N,N*-dimethylacetamide (43.5 mg, 0.5 mmol, 1.0 equiv) was weighed into a 5 mL conical vial equipped with a stir bar. To the test tube containing $[Ir(OMe)(cod)]_2$ was added ~0.2 mL THF. The resulting solution was then transferred into the test tube containing B_2eg_2. The contents of the first test tube were rinsed three times (~0.2 mL/rinse) and added to the test tube containing B_2eg_2. The solution of $[Ir(OMe)(cod)]_2$ and B_2eg_2 was then transferred into the test tube containing **L3** and the rinsing procedure was repeated. Finally, the resulting solution was added to the 5 mL conical vial followed by the rinsing procedure. The conical vial was then sealed and placed in an aluminum block pre-heated to 80 °C and allowed to stir for 24 h. The vial was then opened, solvent was removed via rotary evaporation, and ^{1}H NMR of crude material was collected. Only starting material was observed.



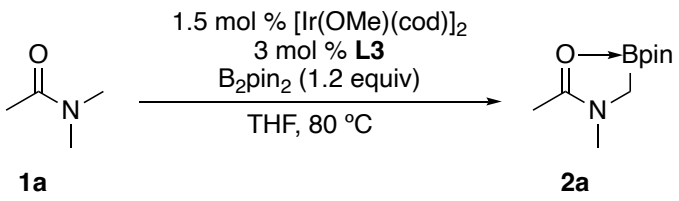
For the procedure see below. A 85% conversion of starting material was observed after 24 h.

Effect of Catalyst Loading, stock solutions of $[Ir(OMe)cod]_2$ and ligand **L3** were prepared to ensure accuracy in the amount of catalyst added. The procedure for the preparation of each stock solution is provided below.

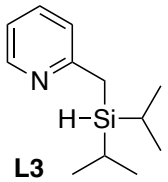
Preparation of $[Ir(OMe)cod]_2$ stock solution: In a test tube, 66.3 mg of $[Ir(OMe)cod]_2$ was weighed. Then THF was used to transfer this compound from the test tube to a 4 mL volumetric flask. The flask was shaken until no solids were observed. Then the flask was filled with THF to exactly 4 mL.

*Preparation of ligand **L3** stock solution:* To a 2 mL volumetric flask, 62.2 mg of ligand **L3** was added. Then 1.5 mL THF was added and the flask was shaken to ensure the solution was well mixed. The flask was then filled with THF to exactly 2 mL.

Catalyst Loading 1.5 mol % $[Ir(OMe)cod]_2$



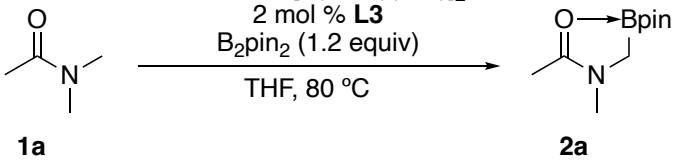
time(h)	% **2a**
1	70
4	84
7.5	100
10	100
24	100



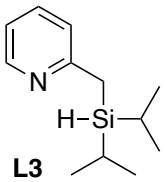
In a nitrogen filled glove box, B_2pin_2 (152.3 mg, 0.6 mmol, 1.2 equiv) was weighed into a test tube and *N,N*-dimethylacetamide (43.5 mg, 0.5 mmol, 1.0 equiv) was weighed into a 5 mL conical reaction vial equipped with a stir bar. $[Ir(OMe)cod]_2$ (0.3 mL from the stock solution, 1.5 mol %) and ligand **L3** (0.1 mL from the stock solution, 3 mol %) were added to the test tube with a microsyringe. The resulting solution was then transferred to the 5 mL reaction vial followed by rinsing the test tube with approximately 0.4 mL of THF three times. The reaction vials were then sealed and placed in an aluminum block pre-heated to 80 ˚C and allowed to stir. Aliquots were

removed at 1 h, 4 h, 7.5 h, 10 h, and 24 h. Proton NMR of each aliquot was obtained and the conversion of starting material to product was calculated. These data are displayed in the Scheme above.

Catalyst Loading 1.0 mol % $[Ir(OMe)cod]_2$

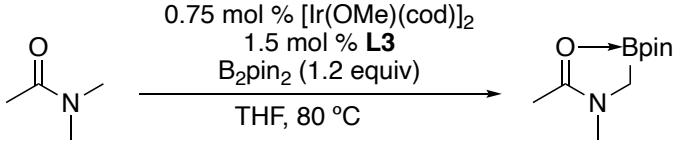


time(h)	% **2a**
1	61
4	70
7.5	78
10	83
24	92

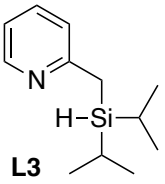


In a nitrogen filled glove box, B_2pin_2 (152.3 mg, 0.6 mmol, 1.2 equiv) was weighed into a test tube and *N,N*-dimethylacetamide (43.5 mg, 0.5 mmol, 1.0 equiv) was weighed into a 5 mL conical reaction vial equipped with a stir bar. $[Ir(OMe)cod]_2$ (0.2 mL from the stock solution, 1.0 mol %) and ligand **L3** (0.066 mL from the stock solution, 2 mol %) were added to the test tube with a microsyringe. The resulting solution was then transferred to the 5 mL reaction vial followed by rinsing the test tube with approximately 0.4 mL of THF three times. The reaction vials were then sealed and placed in an aluminum block pre-heated to 80 °C and allowed to stir. Aliquots were removed at 1 h, 4 h, 7.5 h, 10 h, and 24 h. Proton NMR of each aliquot was obtained and the conversion of starting material to product was calculated. These data are displayed in the Scheme above.

Catalyst Loading 0.75 mol % $[Ir(OMe)cod]_2$

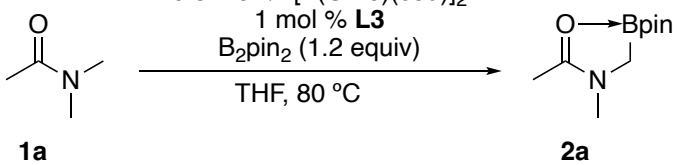


time(h)	% **2a**
1	55
4	68
7.5	73
10	75
24	85



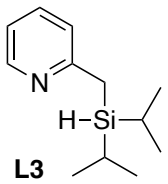
In a nitrogen filled glove box, B_2pin_2 (152.3 mg, 0.6 mmol, 1.2 equiv) was weighed into a test tube and *N,N*-dimethylacetamide (43.5 mg, 0.5 mmol, 1.0 equiv) was weighed into a 5 mL conical reaction vial equipped with a stir bar. $[Ir(OMe)cod]_2$ (0.15 mL from the stock solution, 0.75 mol %) and ligand **L3** (0.05 mL from the stock solution, 1.5 mol %) were added to the test tube with a microsyringe. The resulting solution was then transferred to the 5 mL reaction vial followed by rinsing the test tube with approximately 0.4 mL of THF three times. The reaction vials were then sealed and placed in an aluminum block pre-heated to 80 °C and allowed to stir. Aliquots were removed at 1 h, 4 h, 7.5 h, 10 h, and 24 h. Proton NMR of each aliquot was obtained and the conversion of starting material to product was calculated. These data are displayed in the Scheme above.

Catalyst Loading 0.5 mol % $[Ir(OMe)cod]_2$



1a **2a**

time(h)	% **2a**
1	49
4	58
7.5	61
10	63
24	70

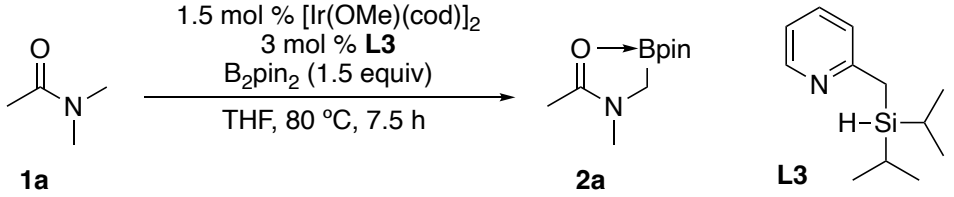


L3

In a nitrogen filled glove box, B_2pin_2 (152.3 mg, 0.6 mmol, 1.2 equiv) was weighed into a test tube and *N,N*-dimethylacetamide (43.5 mg, 0.5 mmol, 1.0 equiv) was weighed into a 5 mL conical reaction vial equipped with a stir bar. $[Ir(OMe)cod]_2$ (0.10 mL from the stock solution, 0.5 mol %) and ligand **L3** (0.033 mL from the stock solution, 1 mol %) were added to the test tube with a microsyringe. The resulting solution was then transferred to the 5 mL reaction vial followed by rinsing the test tube with approximately 0.4 mL of THF three times. The reaction vials were then sealed and placed in an aluminum block pre-heated to 80 °C and allowed to stir. Aliquots were removed at 1 h, 4 h, 7.5 h, 10 h, and 24 h. Proton NMR of each aliquot was obtained and the

conversion of starting material to product was calculated. These data are displayed in the Scheme above.

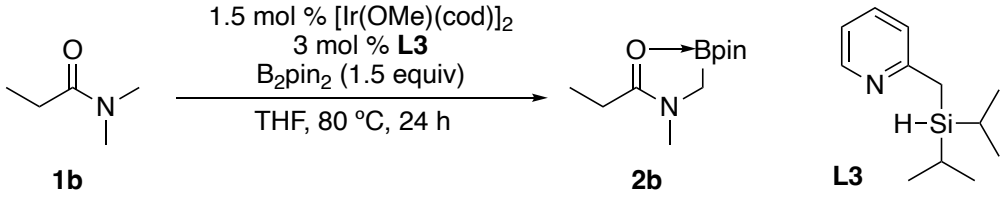
Borylation of *N,N*-dimethylacetamide (2a)



In a nitrogen filled glove box, $[Ir(OMe)(cod)]_2$ (0.015 mmol, 1.5 mol %, 9.9 mg), **L3** (0.03 mmol, 3 mol %, 6.2 mg), and B_2pin_2 (1.5 mmol, 1.5 equiv, 380.9 mg) were weighed into separate test tubes and *N,N*-dimethylacetamide (1 mmol, 1.0 equiv, 87.1 mg) was weighed into a 5 mL conical vial equipped with a stir bar. To the test tube containing $[Ir(OMe)(cod)]_2$ was added ~0.2 mL THF. The resulting solution was then transferred into the test tube containing B_2pin_2. The contents of the first test tube were rinsed three times (~0.2 mL/rinse) and added to the B_2pin_2 containing test tube. The solution of $[Ir(OMe)(cod)]_2$ and B_2pin_2 was then transferred into the test tube containing **L3** and the rinsing procedure was repeated. Finally, the resulting solution was added to the 5 mL conical vial followed by the rinsing procedure. The conical vial was then sealed and placed in an aluminum block pre-heated to 80 °C and allowed to stir for 24 h. The vial was then opened, solvent was removed via rotary evaporation, and ^1H NMR of crude material was collected. There was 100% conversion of starting material. The crude reaction mixture was passed through deactivated silica (35% H_2O w/w) with a gradient solvent system of 10% to 15% MeOH in EtOAc. After overnight drying under high vacuum, (**2a**) was obtained as a white solid (132.7 mg, 62% yield, mp = 116–121 °C, lit mp = 145.2-147.5 °C[21], 157.4–162.8 °C[18]) which matched previously reported spectra.[21]

^{1}H NMR (500 MHz, $CDCl_3$)[21]: δ_H 3.07 (s, 3H), 2.40 (s, 2H), 2.14 (s, 3H), 1.19 (s, 4H). ^{13}C NMR (125 MHz, $CDCl_3$)[21]: δ_C 174.21, 79.76, 35.98, 24.99, 15.40. ^{11}B NMR (160 MHz, $CDCl_3$): δ_B 12.61 (s). HRMS (ESI) *m/z* calc for $C_{10}H_{20}BNO_3Na$ [$(M+Na)^+$] 236.1433, found 236.1463.

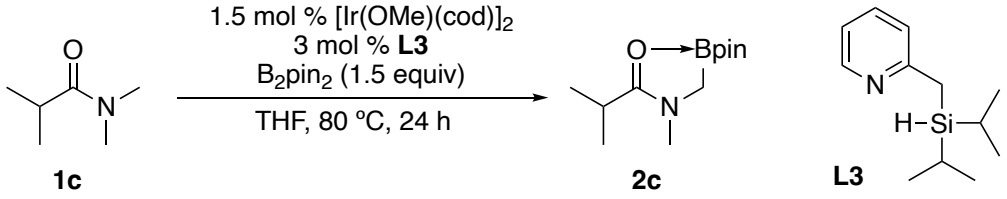
Borylation of *N,N*-dimethylpropionamide (2b)



In a nitrogen filled glove box, $[Ir(OMe)(cod)]_2$ (0.015 mmol, 1.5 mol %, 9.9 mg), **L3** (0.03 mmol, 3 mol %, 6.2 mg), and B_2pin_2 (1.2 mmol, 1.5 equiv, 380.9 mg) were weighed into separate test tubes and *N,N*-dimethylpropionamide (1 mmol, 1.0 equiv, 101.2 mg) was weighed into a 5 mL conical vial equipped with a stir bar. To the test tube containing $[Ir(OMe)(cod)]_2$ was added ~0.2 mL THF. The resulting solution was then transferred into the test tube containing B_2pin_2. The contents of the first test tube were rinsed three times (~0.2 mL/rinse) and added to the B_2pin_2 containing test tube. The solution of $[Ir(OMe)(cod)]_2$ and B_2pin_2 was then transferred into the test tube containing **L3** and the rinsing procedure was repeated. Finally, the resulting solution was added to the 5 mL conical vial followed by the rinsing procedure. The conical vial was then sealed and placed in an aluminum block pre-heated to 80 °C and allowed to stir for 24 h. The vial was then opened, solvent was removed via rotary evaporation, and ^{1}H NMR of crude material was collected. There was 95% conversion of starting material. The crude reaction mixture was passed through deactivated silica (35% H_2O w/w) with a gradient solvent system of 10% to 15% MeOH in EtOAc. After overnight drying under high vacuum (**2b**) was obtained as a white solid (174.9 mg, 77% yield, mp = 118–120 °C, lit mp = 151.1–152.7 °C1[7]) which matched previously reported spectra.[17]

^{1}H NMR (500 MHz, $CDCl_3$)[17]: δ_H 3.05 (s, 3H), 2.43–2.36 (m, 4H), 1.21 (t, J = 7.6 Hz, 3H), 1.19 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$)[17]: δ_C. 177.48, 79.88, 35.51, 25.13, 22.07, 8.70. ^{11}B NMR (160 MHz, $CDCl_3$)[17]: δ_B 12.2 (s) (12.5 ppm lit). HRMS (ESI) *m/z* calc for $C_{11}H_{22}BNO_3Na$ [$(M+Na)^+$] 250.1590, found 250.1953.

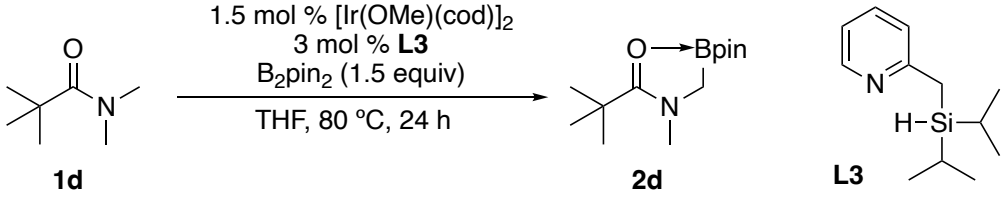
Borylation of *N,N*-dimethylisobutyramide (2c)



In a nitrogen filled glove box, $[Ir(OMe)(cod)]_2$ (0.015 mmol, 1.5 mol %, 9.9 mg), **L3** (0.03 mmol, 3 mol %, 6.2 mg), and B_2pin_2 (1.2 mmol, 1.5 equiv, 380.9 mg) were weighed into separate test tubes and *N,N*-dimethylisobutyramide (1 mmol, 1.0 equiv, 115.2 mg) was weighed into a 5 mL conical vial equipped with a stir bar. To the test tube containing $[Ir(OMe)(cod)]_2$ was added ~0.2 mL THF. The resulting solution was then transferred into the test tube containing B_2pin_2. The contents of the first test tube were rinsed three times (~0.2 mL/rinse) and added to the B_2pin_2 containing test tube. The solution of $[Ir(OMe)(cod)]_2$ and B_2pin_2 was then transferred into the test tube containing **L3** and the rinsing procedure was repeated. Finally, the resulting solution was added to the 5 mL conical vial followed by the rinsing procedure. The conical vial was then sealed and placed in an aluminum block pre-heated to 80 °C and allowed to stir for 24 h. The vial was then opened, solvent was removed via rotary evaporation, and ^{1}H NMR of crude material was collected. There was 75% conversion of starting material. The crude reaction mixture was passed through deactivated silica (35% H_2O w/w) with a gradient solvent system of 10% to 15% MeOH in EtOAc. After overnight drying under high vacuum (**2c**) was obtained as a white solid (132.6 mg, 55% yield, mp = 81–85 °C) which matched previously reported spectra.[17]

^{1}H NMR (500 MHz, $CDCl_3$)[17]: δ_H 3.09 (s, 3H), 2.75 (sept, J = 6.9 Hz, 1H), 2.40 (s, 2H), 1.18 (d, J = 6.0 Hz, 6H), 1.19 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$)[17]: δ_C 180.15, 79.75, 35.42, 27.36, 25.12, 18.47. ^{11}B NMR (160 MHz, $CDCl_3$)[17]: δ_B 12.37 (s) (12.1 ppm lit). HRMS (ESI) *m/z* calc for $C_{12}H_{24}BNO_3Na$ [$(M+Na)^+$] 264.1746, found 264.1778.

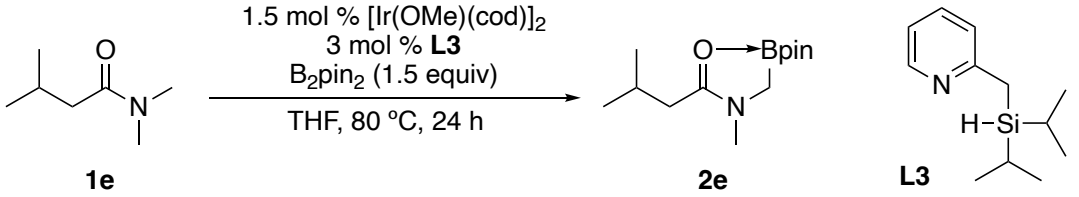
Borylation of *N,N*-dimethylpivalamide (2d)



In a nitrogen filled glove box, $[Ir(OMe)(cod)]_2$ (0.015 mmol, 1.5 mol %, 9.9 mg), **L3** (0.03 mmol, 3 mol %, 6.2 mg), and B_2pin_2 (1.2 mmol, 1.5 equiv, 380.9 mg) were weighed into separate test tubes and *N,N*-dimethylpivalamide (1 mmol, 1.0 equiv, 129.2 mg) was weighed into a 5 mL conical vial equipped with a stir bar. To the test tube containing $[Ir(OMe)(cod)]_2$ was added ~0.2 mL THF. The resulting solution was then transferred into the test tube containing B_2pin_2. The contents of the first test tube were rinsed three times (~0.2 mL/rinse) and added to the B_2pin_2 containing test tube. The solution of $[Ir(OMe)(cod)]_2$ and B_2pin_2 was then transferred into the test tube containing **L3** and the rinsing procedure was repeated. Finally, the resulting solution was added to the 5 mL conical vial followed by the rinsing procedure. The conical vial was then sealed and placed in an aluminum block pre-heated to 80 °C and allowed to stir for 24 h. The vial was then opened, solvent was removed via rotary evaporation, and ^{1}H NMR of crude material was collected. There was 100% conversion of starting material. The crude reaction mixture was passed through deactivated silica (35% H_2O w/w) with a gradient solvent system of 10% to 15% MeOH in EtOAc. After overnight drying under high vacuum (**2d**) was obtained as a white solid (178.6 mg, 70% yield, mp = 61–64 °C, lit mp = 60.8-63.9 °C[6]) which matched previously reported spectra.[18]

^{1}H NMR (500 MHz, $CDCl_3$)[18]: δ_H 3.20 (s, 3H), 2.45 (s, 2H), 1.31 (s, 9H), 1.17 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$)[18]: δ_C 181.12, 79.65, 37.57, 35.64, 27.24, 25.09. ^{11}B NMR (160 MHz, $CDCl_3$): δ_B 11.74 (s). HRMS (ESI) *m/z* calc for $C_{13}H_{26}BNO_3$ $[M]^+$ 255.2005, found 255.2099.

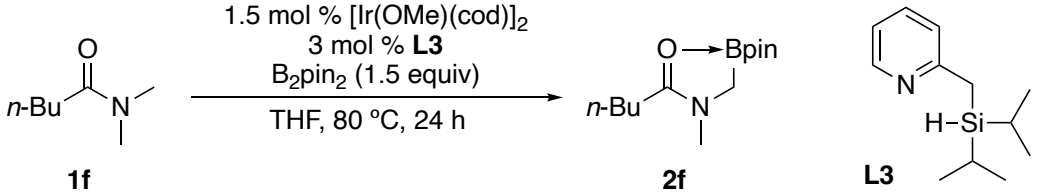
Borylation of *N,N*,3-trimethylbutanamide (2e)



In a nitrogen filled glove box, $[Ir(OMe)(cod)]_2$ (0.015 mmol, 1.5 mol %, 9.9 mg), **L3** (0.03 mmol, 3 mol %, 6.2 mg), and B_2pin_2 (1.2 mmol, 1.5 equiv, 380.9 mg) were weighed into separate test tubes and *N,N,*3-trimethylbutanamide (1 mmol, 1.0 equiv, 129.20 mg) was weighed into a 5 mL conical vial equipped with a stir bar. To the test tube containing $[Ir(OMe)(cod)]_2$ was added ~0.2 mL THF. The resulting solution was then transferred into the test tube containing B_2pin_2. The contents of the first test tube were rinsed three times (~0.2 mL/rinse) and added to the B_2pin_2 containing test tube. The solution of $[Ir(OMe)(cod)]_2$ and B_2pin_2 was then transferred into the test tube containing **L3** and the rinsing procedure was repeated. Finally, the resulting solution was added to the 5 mL conical vial followed by the rinsing procedure. The conical vial was then sealed and placed in an aluminum block pre-heated to 80 °C and allowed to stir for 24 h. The vial was then opened, solvent was removed via rotary evaporation, and ^{1}H NMR of crude material was collected. There was 100% conversion of starting material. The crude reaction mixture was passed through deactivated silica (35% H_2O w/w) with a gradient solvent system of 10% to 15% MeOH in EtOAc. After overnight drying under high vacuum (**2e**) was obtained as a white solid (173.5 mg, 68% yield, mp = 62–65 °C).

^{1}H NMR (500 MHz, $CDCl_3$): δ_H 3.06 (s, 3H), 2.25 (d, J = 7.6 Hz, 2H), 2.10 (s, 2H), 2.17 (m, 1H), 1.18 (s, 12H), 0.99 (d, J = 6.6 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 176.28, 79.70, 36.86, 35.85, 25.87, 25.08, 22.48. ^{11}B NMR (160 MHz, $CDCl_3$): δ_B 12.41 (s). HRMS (ESI) *m/z* calc for $C_{13}H_{26}BNO_3$ $[M]^+$ 255.2005, found 255.2138.

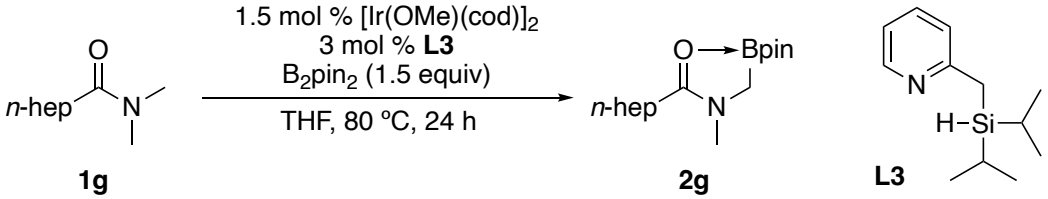
Borylation of *N,N*-dimethylpentanamide (2f)



In a nitrogen filled glove box, $[Ir(OMe)(cod)]_2$ (0.015 mmol, 1.5 mol %, 9.9 mg), **L3** (0.03 mmol, 3 mol %, 6.2 mg), and B_2pin_2 (1.2 mmol, 1.5 equiv, 380.9 mg) were weighed into separate test tubes and *N,N*-dimethylpentanamide (1 mmol, 1.0 equiv, 129.2 mg) was weighed into a 5 mL conical vial equipped with a stir bar. To the test tube containing $[Ir(OMe)(cod)]_2$ was added ~0.2 mL THF. The resulting solution was then transferred into the test tube containing B_2pin_2. The contents of the first test tube were rinsed three times (~0.2 mL/rinse) and added to the B_2pin_2 containing test tube. The solution of $[Ir(OMe)(cod)]_2$ and B_2pin_2 was then transferred into the test tube containing **L3** and the rinsing procedure was repeated. Finally, the resulting solution was added to the 5 mL conical vial followed by the rinsing procedure. The conical vial was then sealed and placed in an aluminum block pre-heated to 80 °C and allowed to stir for 24 h. The vial was then opened, solvent was removed via rotary evaporation, and ^{1}H NMR of crude material was collected. There was 100% conversion of starting material. The crude reaction mixture was passed through deactivated silica (35% H_2O w/w) with a gradient solvent system of 10% to 15% MeOH in EtOAc. After overnight drying under high vacuum (**2f**) was obtained as a white solid (202.8 mg, 80% yield, mp = 104–106 °C).

^{1}H NMR (500 MHz, $CDCl_3$): δ_H 3.05 (s, 3H), 2.38 (s, 2H), 2.36 (t, J = 7.8 Hz, 2H), 1.65 (m, 2H), 1.37 (h, J = 7.4 , 2H), 1.18 (s, 12H), 0.91 (t, J = 7.4 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 176.93, 79.78, 35.67, 28.15, 26.55, 25.13, 22.28, 13.57. ^{11}B NMR (160 MHz, $CDCl_3$): δ_B 12.44 (s). HRMS (ESI) *m/z* calc for $C_{13}H_{26}BNO_3Na$ [$(M+Na)^+$] 278.1903, found 278.1937.

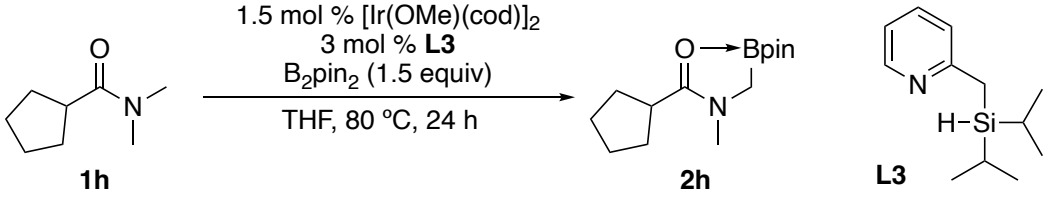
Borylation of *N,N*-dimethyloctanamide (2g)



In a nitrogen filled glove box, $[Ir(OMe)(cod)]_2$ (0.015 mmol, 1.5 mol %, 9.9 mg), **L3** (0.03 mmol, 3 mol %, 6.2 mg), and B_2pin_2 (1.2 mmol, 1.5 equiv, 380.9 mg) were weighed into separate test tubes and *N,N*-dimethyloctanamide (1 mmol, 1.0 equiv, 171.2 mg) was weighed into a 5 mL conical vial equipped with a stir bar. To the test tube containing $[Ir(OMe)(cod)]_2$ was added ~0.2 mL THF. The resulting solution was then transferred into the test tube containing B_2pin_2. The contents of the first test tube were rinsed three times (~0.2 mL/rinse) and added to the B_2pin_2 containing test tube. The solution of $[Ir(OMe)(cod)]_2$ and B_2pin_2 was then transferred into the test tube containing **L3** and the rinsing procedure was repeated. Finally, the resulting solution was added to the 5 mL conical vial followed by the rinsing procedure. The conical vial was then sealed and placed in an aluminum block pre-heated to 80 °C and allowed to stir for 24 h. The vial was then opened, solvent was removed via rotary evaporation, and ^{1}H NMR of crude material was collected. There was 86% conversion of starting material. The crude reaction mixture was passed through deactivated silica (35% H_2O w/w) with a gradient solvent system of 10% to 15% MeOH in EtOAc. After overnight drying under high vacuum (**2g**) was obtained as a white solid (199.1 mg, 67% yield, mp = 120–123 °C).

^{1}H NMR (500 MHz, $CDCl_3$): δ_H 3.05 (s, 3H), 2.38 (s, 2H), 2.35 (t, J = 7.6 Hz, 2H), 1.66 (q, J = 7.7 Hz, 2H), 1.35–1.26 (m, 8H), 1.18 (s, 12H), 0.88 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 176.97, 79.81, 35.68, 31.54, 29.11, 28.77, 28.46, 25.16, 24.54, 22.54, 14.04. ^{11}B NMR (160 MHz, $CDCl_3$): δ_B 12.49 (s). HRMS (ESI) *m/z* calc for $C_{16}H_{32}BNO_3$ $[M]^+$ 297.2475, found 297.2606.

Borylation of *N,N*-dimethylcyclopentanecarboxamide (2h)

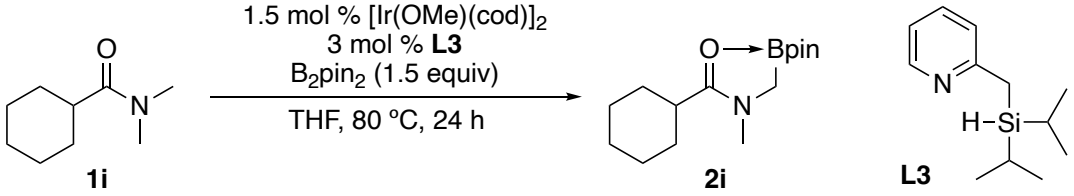


In a nitrogen filled glove box, $[Ir(OMe)(cod)]_2$ (0.015 mmol, 1.5 mol %, 9.9 mg), **L3** (0.03 mmol, 3 mol %, 6.2 mg), and B_2pin_2 (1.2 mmol, 1.5 equiv, 380.9 mg) were weighed into separate test tubes and *N,N*-dimethylcyclopentanecarboxamide (1 mmol, 1.0 equiv, 141.2 mg) was weighed into a 5 mL conical vial equipped with a stir bar. To the test tube containing $[Ir(OMe)(cod)]_2$ was added ~0.2 mL THF. The resulting solution was then transferred into the test tube containing B_2pin_2. The contents of the first test tube were rinsed three times (~0.2 mL/rinse) and added to the B_2pin_2 containing test tube. The solution of $[Ir(OMe)(cod)]_2$ and B_2pin_2 was then transferred into the test tube containing **L3** and the rinsing procedure was repeated. Finally, the resulting solution was added to the 5 mL conical vial followed by the rinsing procedure. The conical vial was then sealed and placed in an aluminum block pre-heated to 80 °C and allowed to stir for 24 h. The vial was then opened, solvent was removed via rotary evaporation, and ^{1}H NMR of crude material was collected. There was 92% conversion of starting material.. The crude reaction mixture was passed through deactivated silica (35% H_2O w/w) with a gradient solvent system of 10% to 15% MeOH

in EtOAc. After overnight drying under high vacuum (**2h**) was obtained as a white solid (210.2 mg, 79% yield, mp = 98–99 °C).

^{1}H NMR (500 MHz, $CDCl_3$): δ_H 3.06 (s, 3H), 2.83 (p, J = 8.0 Hz, 1H), 2.37 (s, 2H), 1.91–1.71 (m, 6H), 1.65–1.51 (m, 2H), 1.16 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 179.79, 79.72, 37.39, 35.59, 29.79, 25.87, 25.13. ^{11}B NMR (160 MHz, $CDCl_3$): δ_B 12.31 (s). HRMS (ESI) *m/z* calc for $C_{14}H_{26}BNO_3Na$ [$(M+Na)^+$] 290.1903, found 290.1940.

Borylation of *N,N*-dimethylcyclohexanecarboxamide (2i)

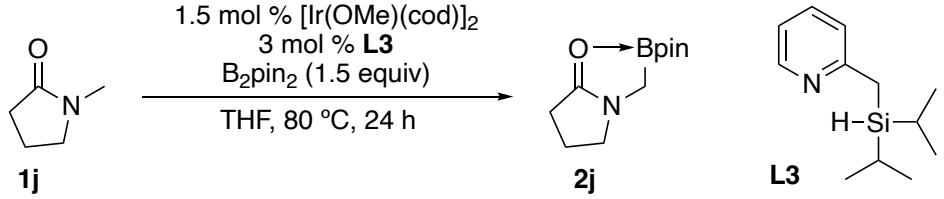


In a nitrogen filled glove box, $[Ir(OMe)(cod)]_2$ (0.015 mmol, 1.5 mol %, 9.9 mg), **L3** (0.03 mmol, 3 mol %, 6.2 mg), and B_2pin_2 (1.2 mmol, 1.5 equiv, 380.9 mg) were weighed into separate test tubes and *N,N*-dimethylcyclohexanecarboxamide (1 mmol, 1.0 equiv, 155.2 mg) was weighed into a 5 mL conical vial equipped with a stir bar. To the test tube containing $[Ir(OMe)(cod)]_2$ was added ~0.2 mL THF. The resulting solution was then transferred into the test tube containing B_2pin_2. The contents of the first test tube were rinsed three times (~0.2 mL/rinse) and added to the B_2pin_2 containing test tube. The solution of $[Ir(OMe)(cod)]_2$ and B_2pin_2 was then transferred into the test tube containing **L3** and the rinsing procedure was repeated. Finally, the resulting solution was added to the 5 mL conical vial followed by the rinsing procedure. The conical vial was then sealed and placed in an aluminum block pre-heated to 80 °C and allowed to stir for 24 h. The vial was then opened, solvent was removed via rotary evaporation, and ^{1}H NMR of crude material was collected. There was 100% conversion of starting material. The crude reaction mixture was passed through deactivated silica (35% H_2O w/w) with a gradient solvent system of 10% to 15% MeOH

in EtOAc. After overnight drying under high vacuum (**2i**) was obtained as a white solid (225.1 mg, 80% yield, mp = 139–140 °C).

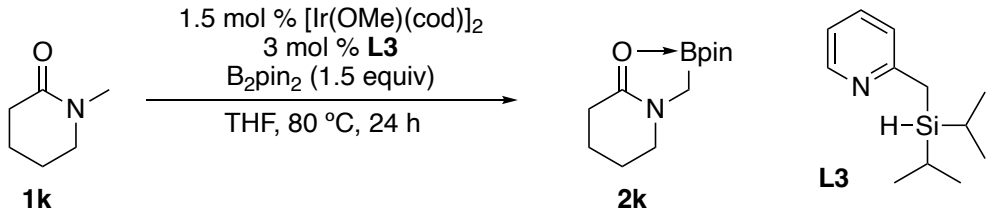
^{1}H NMR (500 MHz, $CDCl_3$): δ_H 3.07 (s, 3H), 2.44 (tt, J = 11.6, 3.5 Hz, 1H), 2.37 (s, 2H), 1.87–1.67 (m, 5H), 1.61–1.51 (m, 2H), 1.32–1.21 (m, 3H), 1.18 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 179.21, 79.68, 37.00, 35.43, 28.21, 25.34, 25.32, 25.14. ^{11}B NMR (160 MHz, $CDCl_3$): δ_B 12.38 (s). HRMS (ESI) *m/z* calc for $C_{15}H_{28}BNO_3Na$ [$(M+Na)^+$] 304.2059, found 304.2095.

Borylation of 1-methylpyrrolidin-2-one (2j)



In a nitrogen filled glove box, $[Ir(OMe)(cod)]_2$ (0.015 mmol, 1.5 mol %, 9.9 mg), **L3** (0.03 mmol, 3 mol %, 6.2 mg), and B_2pin_2 (1.2 mmol, 1.5 equiv, 380.9 mg) were weighed into separate test tubes and 1-methylpyrrolidin-2-one (1 mmol, 1.0 equiv, 99.1 mg) was weighed into a 5 mL conical vial equipped with a stir bar. To the test tube containing $[Ir(OMe)(cod)]_2$ was added ~0.2 mL THF. The resulting solution was then transferred into the test tube containing B_2pin_2. The contents of the first test tube were rinsed three times (~0.2 mL/rinse) and added to the B_2pin_2 containing test tube. The solution of $[Ir(OMe)(cod)]_2$ and B_2pin_2 was then transferred into the test tube containing **L3** and the rinsing procedure was repeated. Finally, the resulting solution was added to the 5 mL conical vial followed by the rinsing procedure. The conical vial was then sealed and placed in an aluminum block pre-heated to 80 °C and allowed to stir for 24 h. The vial was then opened, solvent was removed via rotary evaporation, and ^{1}H NMR of crude material was collected. There was 38% conversion of starting material to the product. No other byproducts were observed in the ^{1}H NMR or the GCMS of crude reaction mixture.

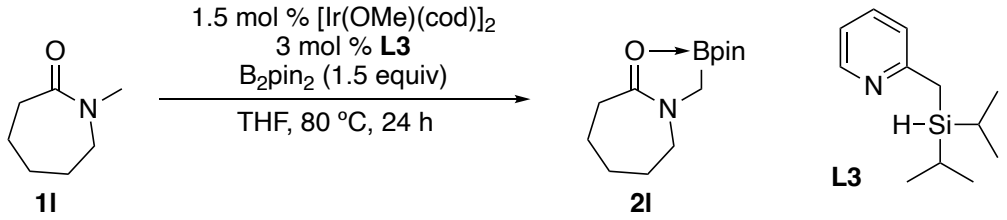
Borylation of 1-methylpiperidin-2-one (2k)



In a nitrogen filled glove box, $[Ir(OMe)(cod)]_2$ (0.015 mmol, 1.5 mol %, 9.9 mg), **L3** (0.03 mmol, 3 mol %, 6.2 mg), and B_2pin_2 (1.2 mmol, 1.5 equiv, 380.9 mg) were weighed into separate test tubes and 1-methylpiperidin-2-one (1 mmol, 1.0 equiv, 113.2 mg) was weighed into a 5 mL conical vial equipped with a stir bar. To the test tube containing $[Ir(OMe)(cod)]_2$ was added ~0.2 mL THF. The resulting solution was then transferred into the test tube containing B_2pin_2. The contents of the first test tube were rinsed three times (~0.2 mL/rinse) and added to the B_2pin_2 containing test tube. The solution of $[Ir(OMe)(cod)]_2$ and B_2pin_2 was then transferred into the test tube containing **L3** and the rinsing procedure was repeated. Finally, the resulting solution was added to the 5 mL conical vial followed by the rinsing procedure. The conical vial was then sealed and placed in an aluminum block pre-heated to 80 °C and allowed to stir for 24 h. The vial was then opened, solvent was removed via rotary evaporation, and ^{1}H NMR of crude material was collected. There was 100% conversion of starting material. The crude reaction mixture was passed through deactivated silica (35% H_2O w/w) with a gradient solvent system of 10% to 15% MeOH in EtOAc. After overnight drying under high vacuum (**2k**) was obtained as a white solid (107.1 mg, 70% yield, mp = 127–131 °C).

^{1}H NMR (500 MHz, $CDCl_3$): δ_H 3.31 (t, J = 5.7 Hz, 2H), 2.49 (t, J = 6.2 Hz, 2H), 2.34 (s, 2H), 1.90–1.75 (m, 4H), 1.19 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 173.93, 79.91, 47.82, 26.43, 25.15, 21.99, 19.45. ^{11}B NMR (160 MHz, $CDCl_3$): δ_B 12.68 (s). HRMS (ESI) *m/z* calc for $C_{12}H_{22}BNO_3Na$ [$(M+Na)^+$] 262.1590, found 262.1624.

Borylation of 1-methylazepan-2-one (2l)

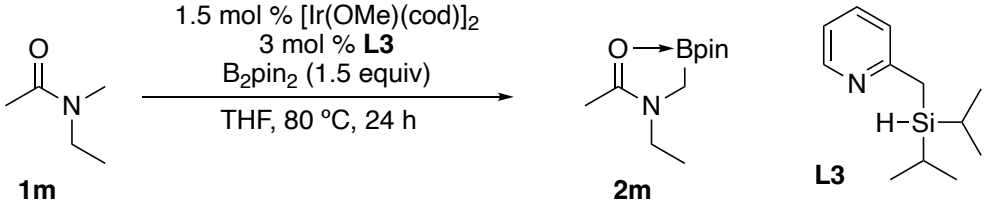


In a nitrogen filled glove box, $[Ir(OMe)(cod)]_2$ (0.015 mmol, 1.5 mol %, 9.9 mg), **L3** (0.03 mmol, 3 mol %, 6.2 mg), and B_2pin_2 (1.2 mmol, 1.5 equiv, 380.9 mg) were weighed into separate test tubes and 1-methylazepan-2-one (1 mmol, 1.0 equiv, 127.2 mg) was weighed into a 5 mL conical vial equipped with a stir bar. To the test tube containing $[Ir(OMe)(cod)]_2$ was added ~0.2 mL THF. The resulting solution was then transferred into the test tube containing B_2pin_2. The contents of the first test tube were rinsed three times (~0.2 mL/rinse) and added to the B_2pin_2 containing test tube. The solution of $[Ir(OMe)(cod)]_2$ and B_2pin_2 was then transferred into the test tube containing **L3** and the rinsing procedure was repeated. Finally, the resulting solution was added to the 5 mL conical vial followed by the rinsing procedure. The conical vial was then sealed and placed in an aluminum block pre-heated to 80 °C and allowed to stir for 24 h. The vial was then opened, solvent was removed via rotary evaporation, and ^{1}H NMR of crude material was collected. There was 100% conversion of starting material. The crude reaction mixture was passed through deactivated silica (35% H_2O w/w) with a gradient solvent system of 10% to 15% MeOH in EtOAc. After overnight drying under high vacuum (**2l**) was obtained as a white solid (176.6 mg, 70% yield, mp = 110–113 °C, lit mp =118.3–120.2 °C[17], 116.8–120.6 °C[18], 128.3-129.8 °C[21]), which matched previously reported spectra. [17]

^{1}H NMR (500 MHz, $CDCl_3$)[17]: δ_H 3.45–3.34 (m, 2H), 2.61–2.52 (m, 2H), 2.49 (s, 2H), 1.77–1.68 (m, 2H), 1.67–1.60 (m, 4H), 1.15 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$)[17]: δ_C 179.46, 79.83, 50.37,

31.19, 29.77, 26.32, 25.11, 22.11. ^{11}B NMR (160 MHz, $CDCl_3$): δ_B 12.52 (s). HRMS (ESI) *m/z* calc for $C_{13}H_{24}BNO_3Na$ [$(M+Na)^+$] 276.1746, found 276.1786.

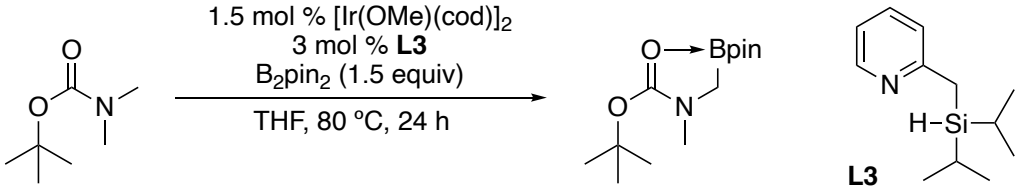
Borylation of *N*-ethyl-*N*-methylacetamide (2m)



In a nitrogen filled glove box, $[Ir(OMe)(cod)]_2$ (0.015 mmol, 1.5 mol %, 9.9 mg), **L3** (0.03 mmol, 3 mol %, 6.2 mg), and B_2pin_2 (1.2 mmol, 1.5 equiv, 380.9 mg) were weighed into separate test tubes and *N*-ethyl-*N*-methylacetamide (1 mmol, 1.0 equiv, 101.2 mg) was weighed into a 5 mL conical vial equipped with a stir bar. To the test tube containing $[Ir(OMe)(cod)]_2$ was added ~0.2 mL THF. The resulting solution was then transferred into the test tube containing B_2pin_2. The contents of the first test tube were rinsed three times (~0.2 mL/rinse) and added to the B_2pin_2 containing test tube. The solution of $[Ir(OMe)(cod)]_2$ and B_2pin_2 was then transferred into the test tube containing **L3** and the rinsing procedure was repeated. Finally, the resulting solution was added to the 5 mL conical vial followed by the rinsing procedure. The conical vial was then sealed and placed in an aluminum block pre-heated to 80 °C and allowed to stir for 24 h. The vial was then opened, solvent was removed via rotary evaporation, and ^{1}H NMR of crude material was collected. There was 94% conversion of starting material. The crude reaction mixture was passed through deactivated silica (35% H_2O w/w) with a gradient solvent system of 10% to 15% MeOH in EtOAc. After overnight drying under high vacuum (**2m**) was obtained as a white solid (161.2 mg, 71% yield, mp = 149–153 °C)

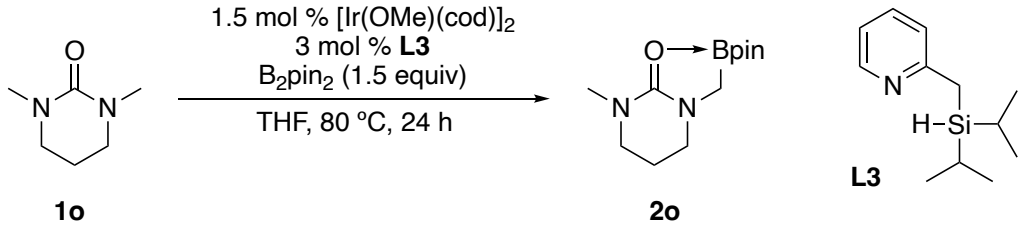
^{1}H NMR (500 MHz, $CDCl_3$): δ_H 3.37 (q, J = 7.3 Hz, 2H), 2.36 (s, 2H), 2.13 (s, 3H), 1.20 (t, J = 7.3 Hz, 3H), 1.17 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 173.70, 79.86, 43.65, 25.12, 15.40, 12.65. ^{11}B NMR (160 MHz, $CDCl_3$): δ_B 12.41 (s). HRMS (ESI) *m/z* calc for $C_{11}H_{22}BNO_3Na$ [$(M+Na)^+$] 250.1590, found 250.1620.

Borylation of *tert*-butyl dimethylcarbamate (2n)



In a nitrogen filled glove box, $[Ir(OMe)(cod)]_2$ (0.015 mmol, 1.5 mol %, 9.9 mg), **L3** (0.03 mmol, 3 mol %, 6.2 mg), and B_2pin_2 (1.2 mmol, 1.5 equiv, 380.9 mg) were weighed into separate test tubes and *tert*-butyl dimethylcarbamate (1 mmol, 1.0 equiv, 145.2 mg) was weighed into a 5 mL conical vial equipped with a stir bar. To the test tube containing $[Ir(OMe)(cod)]_2$ was added ~0.2 mL THF. The resulting solution was then transferred into the test tube containing B_2pin_2. The contents of the first test tube were rinsed three times (~0.2 mL/rinse) and added to the B_2pin_2 containing test tube. The solution of $[Ir(OMe)(cod)]_2$ and B_2pin_2 was then transferred into the test tube containing **L3** and the rinsing procedure was repeated. Finally, the resulting solution was added to the 5 mL conical vial followed by the rinsing procedure. The conical vial was then sealed and placed in an aluminum block pre-heated to 80 °C and allowed to stir for 24 h. The vial was then opened, solvent was removed via rotary evaporation, and ^{1}H NMR of crude material was collected. There was 47% conversion of starting material. ^{1}H NMR of crude material matched previous spectra.[33] No other byproducts were observed in the ^{1}H NMR or the GCMS of crude reaction mixture.

Borylation of 1,3-dimethyltetrahydropyrimidin-2(1*H*)-one (2o)

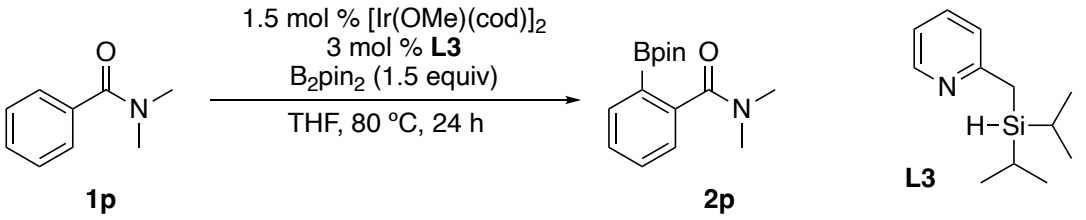


1o **2o**

In a nitrogen filled glove box, $[Ir(OMe)(cod)]_2$ (0.015 mmol, 1.5 mol %, 9.9 mg), **L3** (0.03 mmol, 3 mol %, 6.2 mg), and B_2pin_2 (1.2 mmol, 1.5 equiv, 380.9 mg) were weighed into separate test tubes and 1,3-dimethyltetrahydropyrimidin-2(1*H*)-one (1 mmol, 1.0 equiv, 128.2 mg) was weighed into a 5 mL conical vial equipped with a stir bar. To the test tube containing $[Ir(OMe)(cod)]_2$ was added ~0.2 mL THF. The resulting solution was then transferred into the test tube containing B_2pin_2. The contents of the first test tube were rinsed three times (~0.2 mL/rinse) and added to the B_2pin_2 containing test tube. The solution of $[Ir(OMe)(cod)]_2$ and B_2pin_2 was then transferred into the test tube containing **L3** and the rinsing procedure was repeated. Finally, the resulting solution was added to the 5 mL conical vial followed by the rinsing procedure. The conical vial was then sealed and placed in an aluminum block pre-heated to 80 °C and allowed to stir for 24 h.The vial was then opened, solvent was removed via rotary evaporation, and ^{1}H NMR of crude material was collected. There was 97% conversion of starting material. The crude reaction mixture was passed through deactivated silica (35% H_2O w/w) with a gradient solvent system of 10% to 15% MeOH in EtOAc. After overnight drying under high vacuum (**2o**) was obtained as a white solid (227.4 mg, 89% yield, mp = 165–167 °C, lit mp = 165.2–166.6 °C[21]) which matched previously reported spectra.[21]

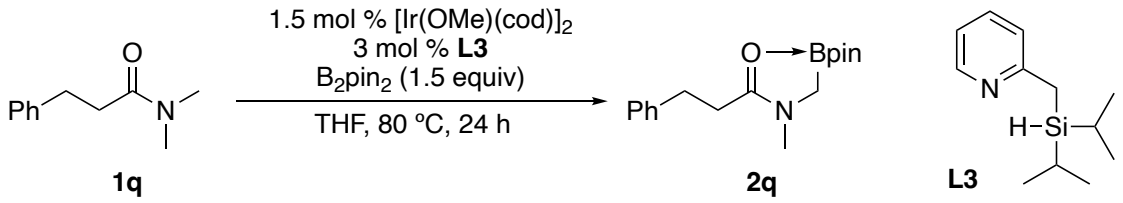
^{1}H NMR (500 MHz, $CDCl_3$)[21]: δ_H 3.34–3.14 (m, 4H), 2.98 (s, 3H), 2.34 (s, 2H), 1.96 (m, 2H), 1.18 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$)[21]: δ_C 159.52, 79.56, 46.55, 44.64, 36.01, 25.15, 20.93. ^{11}B NMR (160 MHz, $CDCl_3$): δ_B 11.53 (s). HRMS (ESI) *m/z* calc for $C_{12}H_{23}BN_2O_3Na$ [$(M+Na)^+$] 277.1699, found 277.1705.

Borylation of *N,N*-dimethylbenzamide (2p)



In a nitrogen filled glove box, $[Ir(OMe)(cod)]_2$ (0.015 mmol, 1.5 mol %, 9.9 mg), **L3** (0.03 mmol, 3 mol %, 6.2 mg), and B_2pin_2 (1.2 mmol, 1.5 equiv, 380.9 mg) were weighed into separate test tubes and *N,N*-dimethylbenzamide (1 mmol, 1.0 equiv, 149.2 mg) was weighed into a 5 mL conical vial equipped with a stir bar. To the test tube containing $[Ir(OMe)(cod)]_2$ was added ~0.2 mL THF. The resulting solution was then transferred into the test tube containing B_2pin_2. The contents of the first test tube were rinsed three times (~0.2 mL/rinse) and added to the B_2pin_2 containing test tube. The solution of $[Ir(OMe)(cod)]_2$ and B_2pin_2 was then transferred into the test tube containing **L3** and the rinsing procedure was repeated. Finally, the resulting solution was added to the 5 mL conical vial followed by the rinsing procedure. The conical vial was then sealed and placed in an aluminum block pre-heated to 80 °C and allowed to stir for 24 h. The vial was then opened, solvent was removed via rotary evaporation, and ^{1}H NMR of crude material was collected. The starting material was 100% consumed with the major product being the ortho borylated product. The spectra for **2p** was in accordance with a previous report.[34] The spectra also showed diborylated material in 1.2:1 ratio of mono:di-borylated.

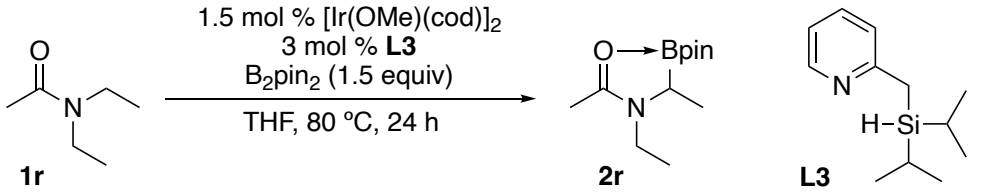
Borylation of *N,N*-dimethyl-3-phenylpropanamide (2q)



In a nitrogen filled glove box, $[Ir(OMe)(cod)]_2$ (0.015 mmol, 1.5 mol %, 9.9 mg), **L3** (0.03 mmol, 3 mol %, 6.2 mg), and B_2pin_2 (1.2 mmol, 1.5 equiv, 380.9 mg) were weighed into separate test tubes and *N,N*-dimethyl-3-phenylpropanamide (1 mmol, 1.0 equiv, 177.3 mg) was weighed into a 5 mL conical vial equipped with a stir bar. To the test tube containing $[Ir(OMe)(cod)]_2$ was added ~0.2 mL THF. The resulting solution was then transferred into the test tube containing B_2pin_2. The contents of the first test tube were rinsed three times (~0.2 mL/rinse) and added to the B_2pin_2 containing test tube. The solution of $[Ir(OMe)(cod)]_2$ and B_2pin_2 was then transferred into the test tube containing **L3** and the rinsing procedure was repeated. Finally, the resulting solution was added to the 5 mL conical vial followed by the rinsing procedure. The conical vial was then sealed and placed in an aluminum block pre-heated to 80 °C and allowed to stir for 24 h. The vial was then opened, solvent was removed via rotary evaporation, and ^{1}H NMR of crude material was collected. There was 83% conversion of starting material. The crude reaction mixture was passed through deactivated silica (35% H_2O w/w) with a gradient solvent system of 10% to 15% MeOH in EtOAc. After overnight drying under high vacuum (**2q**) was obtained as a white solid (191.0 mg, 63% yield, mp = 98–103 °C).

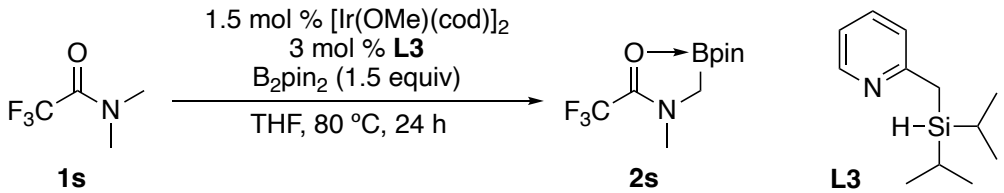
^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.34–7.27 (m, 2H), 7.24–7.22 (m, 1H), 7.21–7.15 (m, 2H), 3.05–2.97 (t, *J* = 8.2, 2H), 2.93 (s, 3H), 2.71–2.60 (t, J = 7.9, 2H), 2.39 (s, 2H), 1.21 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 175.84, 139.69, 128.72, 128.28, 126.64, 79.96, 35.54, 30.75, 30.59, 25.17. ^{11}B NMR (160 MHz, $CDCl_3$): δ_B 13.09 (s). HRMS (ESI) *m/z* calc for $C_{17}H_{26}BNO_3Na$ [$(M+Na)^+$] 326.1903, found 326.1956.

Borylation of *N,N*-diethylacetamide (2r)



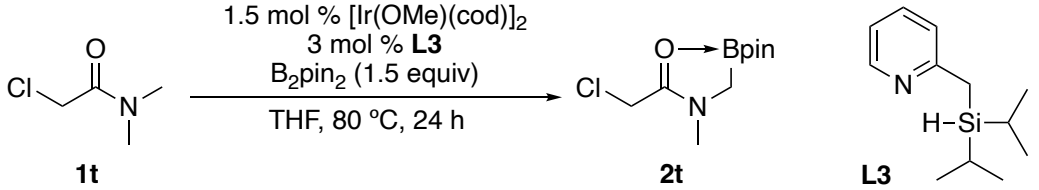
In a nitrogen filled glove box, $[Ir(OMe)(cod)]_2$ (0.0075 mmol, 1.5 mol %, 4.9 mg), **L3** (0.015 mmol, 3 mol %, 3.1 mg), and B_2pin_2 (0.75 mmol, 1.5 equiv, 190.5 mg) were weighed into separate test tubes and *N,N*-diethylacetamide (0.5 mmol, 1.0 equiv, 57.6 mg) was weighed into a 5 mL conical vial equipped with a stir bar. To the test tube containing $[Ir(OMe)(cod)]_2$ was added ~0.2 mL THF. The resulting solution was then transferred into the test tube containing B_2pin_2. The contents of the first test tube were rinsed three times (~0.2 mL/rinse) and added to the B_2pin_2 containing test tube. The solution of $[Ir(OMe)(cod)]_2$ and B_2pin_2 was then transferred into the test tube containing **L3** and the rinsing procedure was repeated. Finally, the resulting solution was added to the 5 mL conical vial followed by the rinsing procedure. The conical vial was then sealed and placed in an aluminum block pre-heated to 80 °C and allowed to stir for 21 h. The vial was then opened and ^{1}H and ^{11}B NMR of crude material were collected. In the ^{1}H NMR spectrum, starting material, B_2pin_2 and borates made up most of the material; however, some new peaks with complex multiplicity did appear. The ^{11}B NMR showed only two peaks corresponding to B_2pin_2 at 30 ppm and borates at 22 ppm. Based on these data, it was concluded that no product-like material was formed under these reaction conditions.

Borylation of 2,2,2-trifluoro-*N,N*-dimethylacetamide (2s)



In a nitrogen filled glove box, $[Ir(OMe)(cod)]_2$ (0.0075 mmol, 1.5 mol %, 4.9 mg), **L3** (0.015 mmol, 3 mol %, 3.1 mg), and B_2pin_2 (0.6 mmol, 1.2 equiv, 152.4 mg) were weighed into separate test tubes and 2,2,2-trifluoro-*N,N*-dimethylacetamide (0.5 mmol, 1.0 equiv, 70.5 mg) was weighed into a 5 mL conical vial equipped with a stir bar. To the test tube containing $[Ir(OMe)(cod)]_2$ was added ~0.2 mL THF. The resulting solution was then transferred into the test tube containing B_2pin_2. The contents of the first test tube were rinsed three times (~0.2 mL/rinse) and added to the B_2pin_2 containing test tube. The solution of $[Ir(OMe)(cod)]_2$ and B_2pin_2 was then transferred into the test tube containing **L3** and the rinsing procedure was repeated. Finally, the resulting solution was added to the 5 mL conical vial followed by the rinsing procedure. The conical vial was then sealed and placed in an aluminum block pre-heated to 80 °C and allowed to stir for 24 h. The vial was then opened, solvent was removed via rotary evaporation, and ^{1}H NMR of crude material was collected. Only starting material was observed.

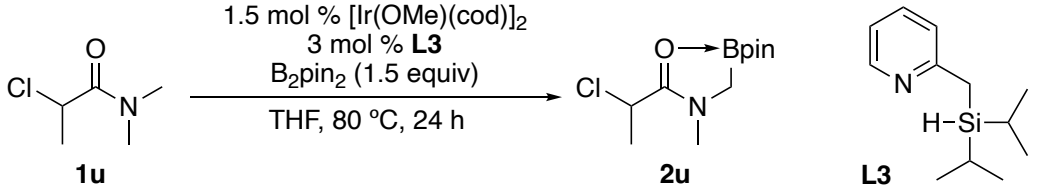
Borylation of 2-chloro-N,N-dimethylacetamide (2t)



In a nitrogen filled glove box, $[Ir(OMe)(cod)]_2$ (0.015 mmol, 1.5 mol %, 9.9 mg), **L3** (0.03 mmol, 3 mol %, 6.2 mg), and B_2pin_2 (0.75 mmol, 1.5 equiv, 380.8 mg) were weighed into separate test tubes and 2-chloro-*N,N*-dimethylacetamide (1.0 mmol, 1.0 equiv, 121.5 mg) was weighed into a 5 mL conical vial equipped with a stir bar. To the test tube containing $[Ir(OMe)(cod)]_2$ was added ~0.2 mL THF. The resulting solution was then transferred into the test tube containing B_2pin_2. The contents of the first test tube were rinsed three times (~0.2 mL/rinse) and added to the B_2pin_2 containing test tube. The solution of $[Ir(OMe)(cod)]_2$ and B_2pin_2 was then transferred into the test

tube containing **L3** and the rinsing procedure was repeated. Finally, the resulting solution was added to the 5 mL conical vial followed by the rinsing procedure. The conical vial was then sealed and placed in an aluminum block pre-heated to 80 °C and allowed to stir for 24 h. The vial was then opened, solvent was removed via rotary evaporation, and ^{1}H NMR of crude material was collected. Only starting material was observed.

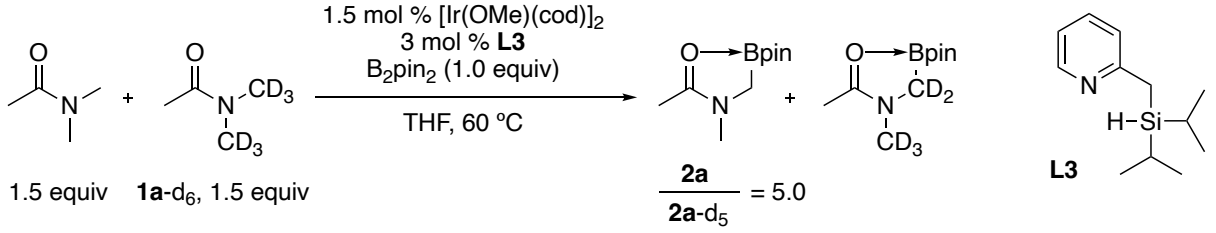
Borylation of 2-chloro-N,N-dimethylpropanamide (2u)



1u **2u** **L3**

In a nitrogen filled glove box, $[Ir(OMe)(cod)]_2$ (0.015 mmol, 1.5 mol %, 9.9 mg), **L3** (0.03 mmol, 3 mol %, 6.2 mg), and B_2pin_2 (0.75 mmol, 1.5 equiv, 380.8 mg) were weighed into separate test tubes and 2-chloro-*N,N*-dimethylpropanamide (1.0 mmol, 1.0 equiv, 135.5 mg) was weighed into a 5 mL conical vial equipped with a stir bar. To the test tube containing $[Ir(OMe)(cod)]_2$ was added ~0.2 mL THF. The resulting solution was then transferred into the test tube containing B_2pin_2. The contents of the first test tube were rinsed three times (~0.2 mL/rinse) and added to the B_2pin_2 containing test tube. The solution of $[Ir(OMe)(cod)]_2$ and B_2pin_2 was then transferred into the test tube containing **L3** and the rinsing procedure was repeated. Finally, the resulting solution was added to the 5 mL conical vial followed by the rinsing procedure. The conical vial was then sealed and placed in an aluminum block pre-heated to 80 °C and allowed to stir for 24 h. The vial was then opened, solvent was removed via rotary evaporation, and ^{1}H NMR of crude material was collected. 5% conversion of starting material was observed.

Competitive Kinetic Isotope Effect



time (h)	**Vial 1**	**Vial 2**	**Vial 3**
2	5.0	5.3	5.1
3	4.8	5.2	4.9
4	4.6	5.1	4.9

Stock solutions of each of the reagents were used for these reactions, and the reaction was carried out in triplicate to ensure accuracy. The procedure for the preparation of each stock solution is provided below.

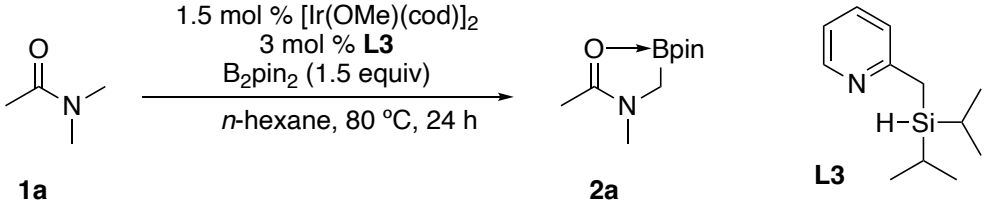
Preparation of [Ir(OMe)cod]$_2$ stock solution: In a test tube, 59.7 mg of [Ir(OMe)cod]$_2$ was weighed. Then THF was used to transfer this compound from the test tube to a 2 mL volumetric flask. The flask was shaken until no solids were observed then filled with THF to exactly 2 mL.

*Preparation of ligand **L3** stock solution:* To a 2 mL volumetric flask, 37.3 mg of ligand **L3** was added. Then 1.5 mL THF was added and the flask was shaken to ensure the solution was well mixed. The flask was then filled with THF to exactly 2 mL.

Preparation of B$_2$pin$_2$ stock solution: In a test tube, 634.9 mg of B$_2$pin$_2$ was weighed. Then THF was used to transfer this compound from the test tube to a 5 mL volumetric flask. The flask was shaken until no solids were observed then filled with THF to exactly 5 mL. *Preparation of N,N-dimethylacetamide **1a** stock solution*: To a 2 mL volumetric flask, 261.4 mg of *N,N*-dimethylacetamide **1a** was added. Then 1.5 mL THF was added and the flask was shaken to ensure the solution was well mixed. The flask was then filled with THF to exactly 2 mL.

*Preparation of N,N-dimethylacetamide-d_6 **1a**-d_6 stock solution:* To a 2 mL volumetric flask, 106.2 mg of *N,N*-dimethylacetamide-d_6 **1a**-d_6 was added. Then 1.5 mL THF was added and the flask was shaken to ensure the solution was well mixed. The flask was then filled with THF to exactly 2 mL. In a nitrogen filled glove box, $[Ir(OMe)cod]_2$ (0.1 mL from the stock solution, 1.5 mol %) and B_2pin_2 (0.2 mL from the stock solution, 0.1 mmol, 1.0 equiv) were added to three separate 3 mL conical reaction vials equipped with stir bars. To these solutions was then added ligand **L3** (0.1 mL from the stock solution, 3 mol %). Then to each of the three reaction vessels was added *N,N*-dimethylacetamide **1a** (0.1 mL from the stock solution, 0.15 mmol, 1.5 equiv) and *N,N*-dimethylacetamide-d_6 **1a**-d_6 (0.263 mL, 0.15 mmol, 1.5 equiv). The reaction vials were then sealed and placed in an aluminum block pre-heated to 60 °C and allowed to stir. Aliquots from each reaction vessel were removed at 2 h, 3 h, and 4 h and the ratio of **2a** to **2a**-d_5 was obtained by GC/MS analysis. The average of these data points is 5.0.

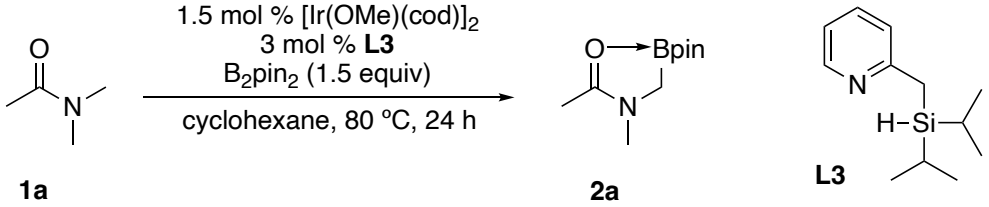
Borylation of N,N-dimethylacetamide in hexane



In a nitrogen filled glove box, $[Ir(OMe)(cod)]_2$ (0.0075 mmol, 1.5 mol %, 4.9 mg), **L3** (0.015 mmol, 3 mol %, 3.1 mg), and B_2pin_2 (0.75 mmol, 1.5 equiv, 190.4 mg) were weighed into separate test tubes and *N,N*-dimethylacetamide (0.5 mmol, 1.0 equiv, 43.5 mg) was weighed into a 5 mL conical vial equipped with a stir bar. To the test tube containing $[Ir(OMe)(cod)]_2$ was added ~0.2 mL hexane. The resulting solution was then transferred into the test tube containing B_2pin_2. The contents of the first test tube were rinsed three times (~0.2 mL/rinse) and added to the B_2pin_2 containing test tube. The solution of $[Ir(OMe)(cod)]_2$ and B_2pin_2 was then transferred into the test

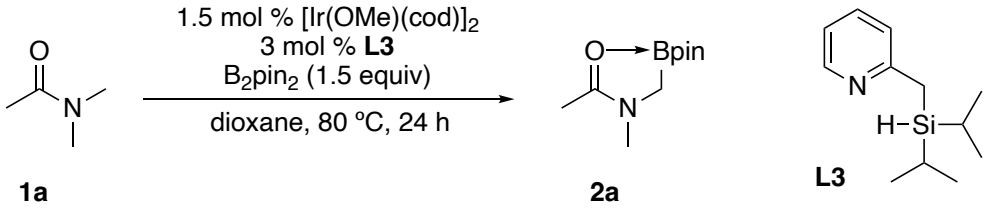
tube containing **L3** and the rinsing procedure was repeated. Finally, the resulting solution was added to the 5 mL conical vial followed by the rinsing procedure. The conical vial was then sealed and placed in an aluminum block pre-heated to 80 °C and allowed to stir for 24 h. The vial was then opened, solvent was removed via rotary evaporation, and ^{1}H NMR of crude material was collected. There was 75% conversion of starting material.

Borylation of N,N-dimethylacetamide in cyclohexane



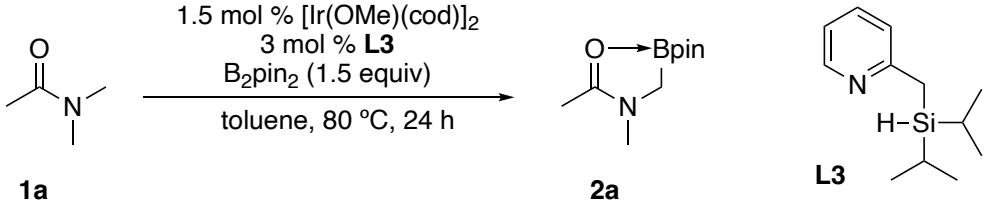
In a nitrogen filled glove box, $[Ir(OMe)(cod)]_2$ (0.0075 mmol, 1.5 mol %, 4.9 mg), **L3** (0.015 mmol, 3 mol %, 3.1 mg), and B_2pin_2 (0.75 mmol, 1.5 equiv, 190.4 mg) were weighed into separate test tubes and *N,N*-dimethylacetamide (0.5 mmol, 1.0 equiv, 43.5 mg) was weighed into a 5 mL conical vial equipped with a stir bar. To the test tube containing $[Ir(OMe)(cod)]_2$ was added ~0.2 mL cyclohexane. The resulting solution was then transferred into the test tube containing B_2pin_2. The contents of the first test tube were rinsed three times (~0.2 mL/rinse) and added to the B_2pin_2 containing test tube. The solution of $[Ir(OMe)(cod)]_2$ and B_2pin_2 was then transferred into the test tube containing **L3** and the rinsing procedure was repeated. Finally, the resulting solution was added to the 5 mL conical vial followed by the rinsing procedure. The conical vial was then sealed and placed in an aluminum block pre-heated to 80 °C and allowed to stir for 24 h. The vial was then opened, solvent was removed via rotary evaporation, and ^{1}H NMR of crude material was collected. There was 86% conversion of starting material.

Borylation of N,N-dimethylacetamide in dioxane



In a nitrogen filled glove box, $[Ir(OMe)(cod)]_2$ (0.0075 mmol, 1.5 mol %, 4.9 mg), **L3** (0.015 mmol, 3 mol %, 3.1 mg), and B_2pin_2 (0.75 mmol, 1.5 equiv, 190.4 mg) were weighed into separate test tubes and *N,N*-dimethylacetamide (0.5 mmol, 1.0 equiv, 43.5 mg) was weighed into a 5 mL conical vial equipped with a stir bar. To the test tube containing $[Ir(OMe)(cod)]_2$ was added ~0.2 mL dioxane. The resulting solution was then transferred into the test tube containing B_2pin_2. The contents of the first test tube were rinsed three times (~0.2 mL/rinse) and added to the B_2pin_2 containing test tube. The solution of $[Ir(OMe)(cod)]_2$ and B_2pin_2 was then transferred into the test tube containing **L3** and the rinsing procedure was repeated. Finally, the resulting solution was added to the 5 mL conical vial followed by the rinsing procedure. The conical vial was then sealed and placed in an aluminum block pre-heated to 80 °C and allowed to stir for 24 h. The vial was then opened, solvent was removed via rotary evaporation, and ^1H NMR of crude material was collected. There was 100% conversion of starting material.

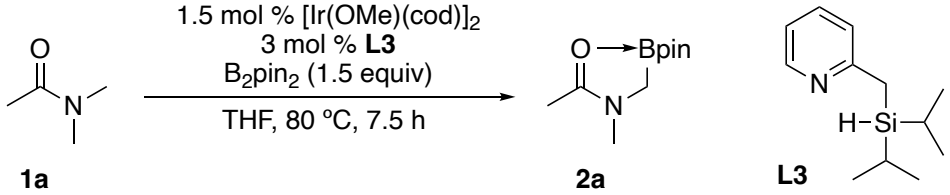
Borylation of N,N-dimethylacetamide in toluene



In a nitrogen filled glove box, $[Ir(OMe)(cod)]_2$ (0.0075 mmol, 1.5 mol %, 4.9 mg), **L3** (0.015 mmol, 3 mol %, 3.1 mg), and B_2pin_2 (0.75 mmol, 1.5 equiv, 190.4 mg) were weighed into separate test tubes and *N,N*-dimethylacetamide (0.5 mmol, 1.0 equiv, 43.5 mg) was weighed into a 5 mL conical vial equipped with a stir bar. To the test tube containing $[Ir(OMe)(cod)]_2$ was added ~0.2

mL toluene. The resulting solution was then transferred into the test tube containing B_2pin_2. The contents of the first test tube were rinsed three times (~0.2 mL/rinse) and added to the B_2pin_2 containing test tube. The solution of $[Ir(OMe)(cod)]_2$ and B_2pin_2 was then transferred into the test tube containing **L3** and the rinsing procedure was repeated. Finally, the resulting solution was added to the 5 mL conical vial followed by the rinsing procedure. The conical vial was then sealed and placed in an aluminum block pre-heated to 80 °C and allowed to stir for 24 h. The vial was then opened, solvent was removed via rotary evaporation, and ^{1}H NMR of crude material was collected. There was 81% conversion of starting material.

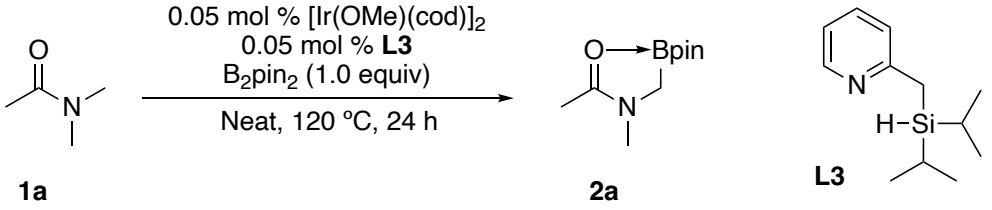
Isolation of borylated *N,N*-dimethylacetamide using neutral alumina



In a nitrogen filled glove box, $[Ir(OMe)(cod)]_2$ (0.015 mmol, 1.5 mol %, 9.9 mg), **L3** (0.03 mmol, 3 mol %, 6.2 mg), and B_2pin_2 (1.5 mmol, 1.5 equiv, 380.9 mg) were weighed into separate test tubes and *N,N*-dimethylacetamide (1 mmol, 1.0 equiv, 87.1 mg) was weighed into a 5 mL conical vial equipped with a stir bar. To the test tube containing $[Ir(OMe)(cod)]_2$ was added ~0.2 mL THF. The resulting solution was then transferred into the test tube containing B_2pin_2. The contents of the first test tube were rinsed three times (~0.2 mL/rinse) and added to the B_2pin_2 containing test tube. The solution of $[Ir(OMe)(cod)]_2$ and B_2pin_2 was then transferred into the test tube containing **L3** and the rinsing procedure was repeated. Finally, the resulting solution was added to the 5 mL conical vial followed by the rinsing procedure. The conical vial was then sealed and placed in an aluminum block pre-heated to 80 °C and allowed to stir for 24 h. The vial was then opened, solvent was removed via rotary evaporation, and ^{1}H NMR of crude material was collected. There was

100% conversion of starting material. The crude reaction mixture was passed through neutral alumina with a gradient solvent system of 10% MeOH in EtOAc. After overnight drying under high vacuum, (**2a**) was obtained as a white solid (83.1 mg, 39% yield) which matched previously reported spectra.[5]

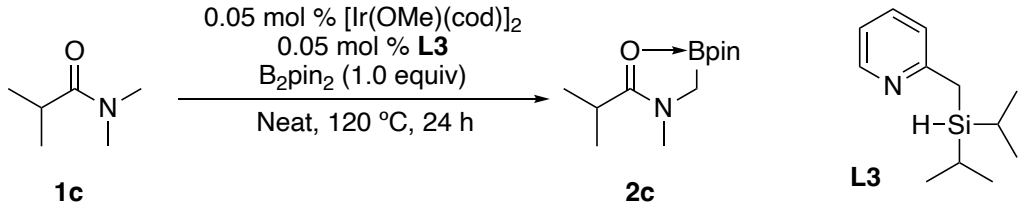
Repetition of reaction conditions shown by Yao for borylation of *N,N*-dimethylacetamide



In a nitrogen filled glove box, $[Ir(OMe)(cod)]_2$ (0.005 mmol, 0.05 mol %, 3.3 mg), **L3** (0.005 mmol, 0.05 mol %, 1.0 mg), and *N,N*-dimethylacetamide (10.0 mmol, 1.0 equiv, 0.87 g) were weighed into separate test tubes and B_2pin_2 (10.0 mmol, 1.0 equiv, 2.54 g) was weighed into a oven dried 25 mL round bottom flask equipped with a stir bar. To the test tube containing $[Ir(OMe)(cod)]_2$ was added ~0.2 mL *N,N*-dimethylacetamide. The resulting solution was then transferred into the round bottom flask containing B_2pin_2. The contents of the first test tube were rinsed two times (~0.2 mL/rinse) and added to the round bottom flask containing B_2pin_2. To the test tube containing **L3** was added ~0.2 mL *N,N*-dimethylacetamide. The contents of the second test tube were rinsed three times (~0.2 mL/rinse) and added to the round bottom flask containing B_2pin_2. Finally, the rest of *N,N*-dimethylacetamide was transferred into a round bottom flask which was sealed with a septa and placed in an oil bath pre-heated to 120 °C and allowed to stir for 24 h. The flask was then opened and ^1H and ^{11}B NMR of crude material were collected. In the ^1H NMR spectrum, starting material, B_2pin_2 and borates made up all the material. The ^{11}B NMR showed only three peaks corresponding to B_2pin_2 at 30 ppm and borates at 21 ppm and 22 ppm. Based on

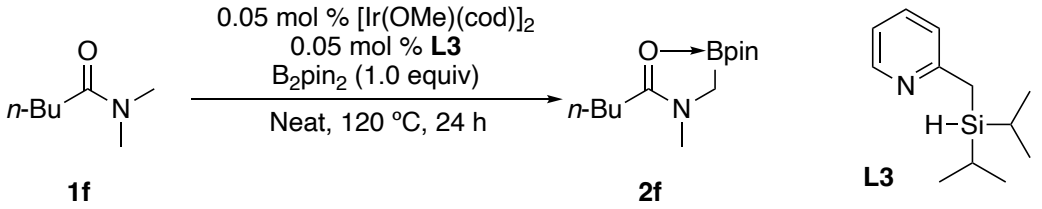
these data, it was concluded that no product-like material was formed under these reaction conditions.

Repetition of reaction conditions shown by Yao for borylation of *N,N*-dimethylisobutyramide

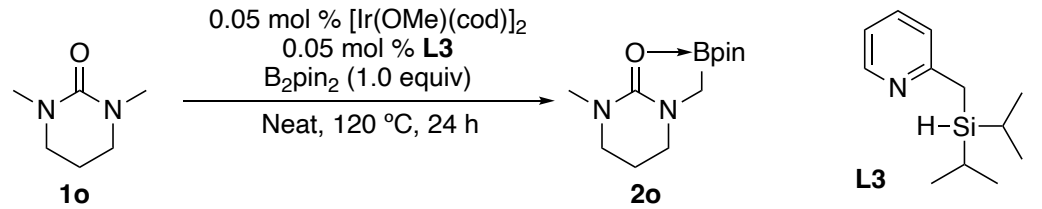


In a nitrogen filled glove box, $[Ir(OMe)(cod)]_2$ (0.005 mmol, 0.05 mol %, 3.3 mg), **L3** (0.005 mmol, 0.05 mol %, 1.0 mg), and *N,N*-dimethylisobutyramide (10.0 mmol, 1.0 equiv, 1.15 g) were weighed into separate test tubes and B_2pin_2 (10.0 mmol, 1.0 equiv, 2.54 g) was weighed into a oven dried 25 mL round bottom flask equipped with a stir bar. To the test tube containing $[Ir(OMe)(cod)]_2$ was added ~0.2 mL *N,N*-dimethylisobutyramide. The resulting solution was then transferred into the round bottom flask containing B_2pin_2. The contents of the first test tube were rinsed two times (~0.2 mL/rinse) and added to the round bottom flask containing B_2pin_2. To the test tube containing **L3** was added ~0.2 mL *N,N*-dimethylisobutyramide. The contents of the second test tube were rinsed three times (~0.2 mL/rinse) and added to the round bottom flask containing B_2pin_2. Finally, the rest of *N,N*-dimethylisobutyramide was transferred into a round bottom flask which was sealed with a septa and placed in an oil bath pre-heated to 120 °C and allowed to stir for 24 h. The flask was then opened and ^1H and ^{11}B NMR of crude material were collected. In the ^1H NMR spectrum, starting material, B_2pin_2 and borates made up all of the material. The ^{11}B NMR showed only three peaks corresponding to B_2pin_2 at 30 ppm and borates at 21 ppm and 22 ppm. Based on these data, it was concluded that no product-like material was formed under these reaction conditions.

Repetition of reaction conditions shown by Yao for borylation of *N,N*-dimethylpentanamide

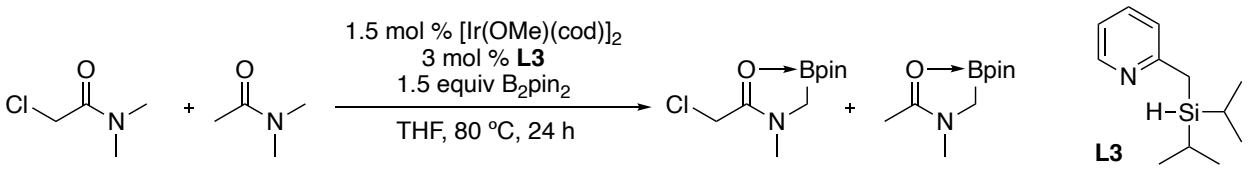


In a nitrogen filled glove box, $[Ir(OMe)(cod)]_2$ (0.005 mmol, 0.05 mol %, 3.3 mg), **L3** (0.005 mmol, 0.05 mol %, 1.0 mg), and *N,N*-dimethylpentanamide (10.0 mmol, 1.0 equiv, 1.29 g) were weighed into separate test tubes and B_2pin_2 (10.0 mmol, 1.0 equiv, 2.54 g) was weighed into a oven dried 25 mL round bottom flask equipped with a stir bar. To the test tube containing $[Ir(OMe)(cod)]_2$ was added ~0.2 mL *N,N*-dimethylpentanamide. The resulting solution was then transferred into the round bottom flask containing B_2pin_2. The contents of the first test tube were rinsed two times (~0.2 mL/rinse) and added to the round bottom flask containing B_2pin_2. To the test tube containing **L3** was added ~0.2 mL *N,N*-dimethylpentanamide. The contents of the second test tube were rinsed three times (~0.2 mL/rinse) and added to the round bottom flask containing B_2pin_2. Finally, the rest of *N,N*-dimethylpentanamide was transferred into a round bottom flask which was sealed with a septa and placed in an oil bath pre-heated to 120 °C and allowed to stir for 24 h. The flask was then opened and ^1H and ^{11}B NMR of crude material were collected. In the ^1H NMR spectrum, starting material, B_2pin_2 and borates made up all of the material. The ^{11}B NMR showed only two peaks corresponding to B_2pin_2 at 30 ppm and borates at 22 ppm. Based on these data, it was concluded that no product-like material was formed under these reaction conditions. Repetition of reaction conditions shown by Yao for borylation of 1,3-dimethyltetrahydropyrimidin-2(1*H*)-one



In a nitrogen filled glove box, $[Ir(OMe)(cod)]_2$ (0.005 mmol, 0.05 mol %, 3.3 mg), **L3** (0.005 mmol, 0.05 mol %, 1.0 mg), and 1,3-dimethyltetrahydropyrimidin-2(1*H*)-one (10.0 mmol, 1.0 equiv, 1.28 g) were weighed into separate test tubes and B_2pin_2 (10.0 mmol, 1.0 equiv, 2.54 g) was weighed into a oven dried 25 mL round bottom flask equipped with a stir bar. To the test tube containing $[Ir(OMe)(cod)]_2$ was added ~0.2 mL 1,3-dimethyltetrahydropyrimidin-2(1*H*)-one. The resulting solution was then transferred into the round bottom flask containing B_2pin_2. The contents of the first test tube were rinsed two times (~0.2 mL/rinse) and added to the round bottom flask containing B_2pin_2. To the test tube containing **L3** was added ~0.2 mL 1,3-dimethyltetrahydropyrimidin-2(1*H*)-one. The contents of the second test tube were rinsed three times (~0.2 mL/rinse) and added to the round bottom flask containing B_2pin_2. Finally, the rest of 1,3-dimethyltetrahydropyrimidin-2(1*H*)-one was transferred into a round bottom flask which was sealed with a septa and placed in an oil bath pre-heated to 120 °C and allowed to stir for 24 h. The flask was then opened and ^1H and ^{11}B NMR of crude material were collected. In the ^1H NMR spectrum, starting material, B_2pin_2 and borates made up all of the material. The ^{11}B NMR showed four peaks corresponding to B_2pin_2 at 30 ppm and borates at 21 ppm, 22 ppm, and 28 ppm. Based on these data, it was concluded that no product-like material was formed under these reaction conditions.

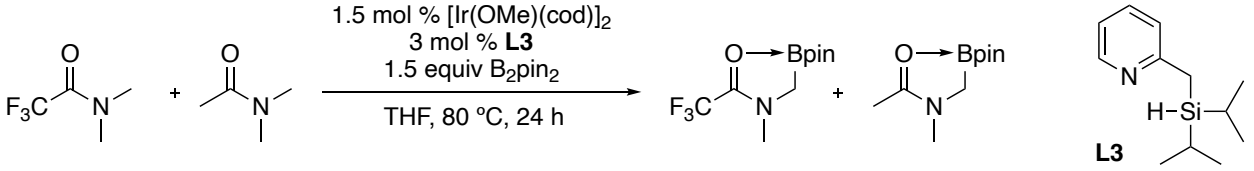
Competition reaction between 2-chloro-*N,N*-dimethylacetamide and *N,N*-dimethylacetamide



In a nitrogen filled glove box, $[Ir(OMe)(cod)]_2$ (0.015 mmol, 1.5 mol %, 9.9 mg), **L3** (0.03 mmol, 3 mol %, 6.2 mg), B_2pin_2 (0.75 mmol, 1.5 equiv, 380.8 mg), and *N,N*-dimethylacetamide (0.5 mmol, 0.5 equiv, 43.5 mg) were weighed into separate test tubes and 2-chloro-*N,N*-

dimethylacetamide (0.5 mmol, 0.5 equiv, 60.7 mg) was weighed into a 5 mL conical vial equipped with a stir bar. To the test tube containing $[Ir(OMe)(cod)]_2$ was added ~0.2 mL THF. The resulting solution was then transferred into the test tube containing B_2pin_2. The contents of the first test tube were rinsed three times (~0.2 mL/rinse) and added to the B_2pin_2 containing test tube. The solution of $[Ir(OMe)(cod)]_2$ and B_2pin_2 was then transferred into the test tube containing **L3** and the rinsing procedure was repeated. The solution of $[Ir(OMe)(cod)]_2$, B_2pin_2 and **L3** was then transferred into the test tube containing *N,N*-dimethylacetamide and the rinsing procedure was repeated Finally, the resulting solution was added to the 5 mL conical vial followed by the rinsing procedure. The conical vial was then sealed and placed in an aluminum block pre-heated to 80 °C and allowed to stir for 24 h. The vial was then opened, solvent was removed via rotary evaporation, and ^1H NMR of crude material was collected. Only starting material was observed.

Competition reaction between 2,2,2-trifluoro-*N*,*N*-dimethylacetamide and *N,N*-dimethylacetamide

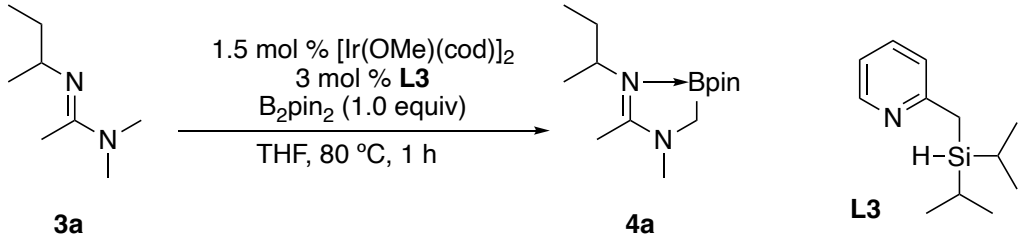


In a nitrogen filled glove box, $[Ir(OMe)(cod)]_2$ (0.015 mmol, 1.5 mol %, 9.9 mg), **L3** (0.03 mmol, 3 mol %, 6.2 mg), B_2pin_2 (0.75 mmol, 1.5 equiv, 380.8 mg), and *N,N*-dimethylacetamide (0.5 mmol, 0.5 equiv, 43.5 mg) were weighed into separate test tubes and 2,2,2-trifluoro-*N*,*N*-dimethylacetamide (0.5 mmol, 0.5 equiv, 70.5 mg) was weighed into a 5 mL conical vial equipped with a stir bar. To the test tube containing $[Ir(OMe)(cod)]_2$ was added ~0.2 mL THF. The resulting solution was then transferred into the test tube containing B_2pin_2. The contents of the first test tube were rinsed three times (~0.2 mL/rinse) and added to the B_2pin_2 containing test tube. The solution of $[Ir(OMe)(cod)]_2$ and B_2pin_2 was then transferred into the test tube containing **L3** and the rinsing procedure was repeated. The solution of $[Ir(OMe)(cod)]_2$, B_2pin_2 and **L3** was then transferred into

the test tube containing *N,N*-dimethylacetamide and the rinsing procedure was repeated Finally, the resulting solution was added to the 5 mL conical vial followed by the rinsing procedure. The conical vial was then sealed and placed in an aluminum block pre-heated to 80 °C and allowed to stir for 24 h. The vial was then opened, solvent was removed via rotary evaporation, and ^{1}H NMR of crude material was collected. Approximately 60% conversion of starting material was observed.

Experimental details Chapter 3

Borylation of *N'*-(sec-butyl)-*N,N*-dimethylacetimidamide

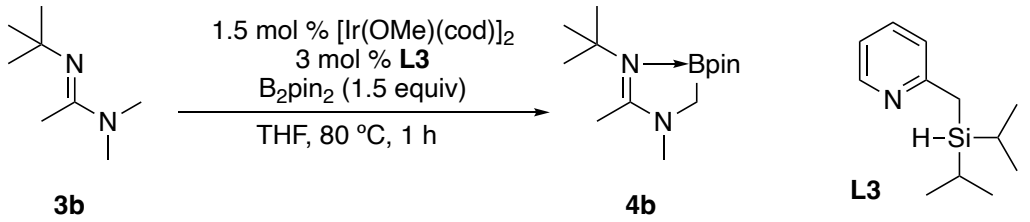


In a nitrogen filled glove box, $[Ir(OMe)(cod)]_2$ (0.0075 mmol, 1.5 mol %, 4.9 mg), **L3** (0.015 mmol, 3 mol %, 3.1 mg), and B_2pin_2 (0.75 mmol, 1.5 equiv, 190.9 mg) were weighed into separate test tubes and *N'*-(sec-butyl)-*N,N*-dimethylacetimidamide (0.5 mmol, 1.0 equiv, 71.1 mg) was weighed into a 5 mL conical vial equipped with a stir bar. To the test tube containing $[Ir(OMe)(cod)]_2$ was added ~0.2 mL THF. The resulting solution was then transferred into the test tube containing B_2pin_2. The contents of the first test tube were rinsed three times (~0.2 mL/rinse) and added to the B_2pin_2 containing test tube. The solution of $[Ir(OMe)(cod)]_2$ and B_2pin_2 was then transferred into the test tube containing **L3** and the rinsing procedure was repeated. Finally, the resulting solution was added to the 5 mL conical vial followed by the rinsing procedure. The conical vial was then sealed and placed in an aluminum block pre-heated to 80 °C and allowed to stir for 1 h. The vial was then opened, solvent was removed via rotary evaporation, and ^{1}H NMR

of crude material was collected. There was 100% conversion of starting material. The crude product was sublimed at 80 ºC to obtain **4a** as white solid (5mg, 4% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ_H 3.64 (m, 1H), 2.90 (s, 3H), 2.28 (s, 2H), 2.0 (s, 3H), 1.73 (m, 1H), 1.59 (m, 1H) 1.27 (d, J = 7.14 Hz, 3H), 1.15 (s, 6H), 1.08 (d, J = 2.11 Hz, 6H), 0.9 (t, J = 7.4 Hz, 3H). ^{11}B NMR (160 MHz, $CDCl_3$): δ_B 8.54 (s).

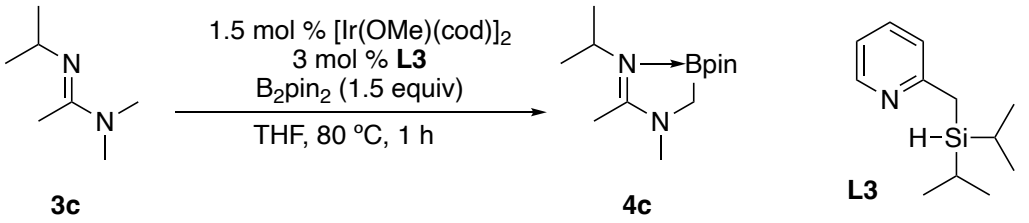
Borylation of *N'*-(*tert*-butyl)-*N,N*-dimethylacetimidamide



In a nitrogen filled glove box, $[Ir(OMe)(cod)]_2$ (0.0075 mmol, 1.5 mol %, 4.9 mg), **L3** (0.015 mmol, 3 mol %, 3.1 mg), and B_2pin_2 (0.75 mmol, 1.5 equiv, 190.9 mg) were weighed into separate test tubes and *N'*-(*tert*-butyl)-*N,N*-dimethylacetimidamide (0.5 mmol, 1.0 equiv, 71.1 mg) was weighed into a 5 mL conical vial equipped with a stir bar. To the test tube containing $[Ir(OMe)(cod)]_2$ was added ~0.2 mL THF. The resulting solution was then transferred into the test tube containing B_2pin_2. The contents of the first test tube were rinsed three times (~0.2 mL/rinse) and added to the B_2pin_2 containing test tube. The solution of $[Ir(OMe)(cod)]_2$ and B_2pin_2 was then transferred into the test tube containing **L3** and the rinsing procedure was repeated. Finally, the resulting solution was added to the 5 mL conical vial followed by the rinsing procedure. The conical vial was then sealed and placed in an aluminum block pre-heated to 80 °C and allowed to stir for 1 h. The vial was then opened, solvent was removed via rotary evaporation, and ^{1}H NMR of crude material was collected. There was 100% conversion of starting material. The crude ^{1}H and ^{11}B NMR contains product **4b** and B_2pin_2.

^{1}H NMR (500 MHz, $CDCl_3$): δ_H 2.93 (s, 3H), 2.29 (s, 2H), 1.93 (s, 3H), 1.24 (s, 12H), 1.16 (s, 6H), 1.09 (s, 6H). ^{11}B NMR (160 MHz, $CDCl_3$): δ_B 8.41 (s).

Borylation of *N'*-isopropyl-*N,N*-dimethylacetimidamide

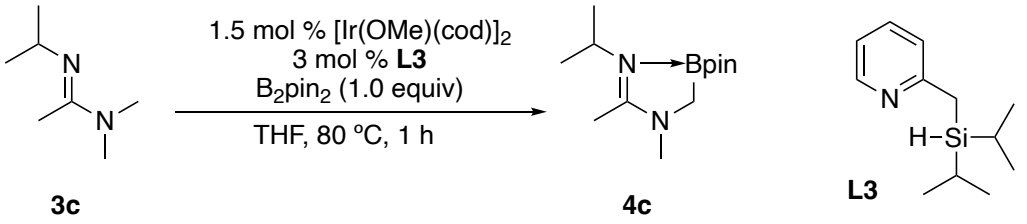


3c **4c** **L3**

In a nitrogen filled glove box, $[Ir(OMe)(cod)]_2$ (0.0075 mmol, 1.5 mol %, 4.9 mg), **L3** (0.015 mmol, 3 mol %, 3.1 mg), and B_2pin_2 (0.75 mmol, 1.5 equiv, 190.9 mg) were weighed into separate test tubes and *N'*-isopropyl-*N,N*-dimethylacetimidamide (0.5 mmol, 1.0 equiv, 64.1 mg) was weighed into a 5 mL conical vial equipped with a stir bar. To the test tube containing $[Ir(OMe)(cod)]_2$ was added ~0.2 mL THF. The resulting solution was then transferred into the test tube containing B_2pin_2. The contents of the first test tube were rinsed three times (~0.2 mL/rinse) and added to the B_2pin_2 containing test tube. The solution of $[Ir(OMe)(cod)]_2$ and B_2pin_2 was then transferred into the test tube containing **L3** and the rinsing procedure was repeated. Finally, the resulting solution was added to the 5 mL conical vial followed by the rinsing procedure. The conical vial was then sealed and placed in an aluminum block pre-heated to 80 °C and allowed to stir for 1 h. The vial was then opened, solvent was removed via rotary evaporation, and ^{1}H NMR of crude material was collected. There was 100% conversion of starting material. The crude ^{1}H and ^{11}B NMR contains product **4c** and B_2pin_2.

^{1}H NMR (500 MHz, $CDCl_3$): δ_H 3.99 (m, 1H), 2.92 (s, 3H), 2.29 (s, 2H), 2.05 (s, 3H), 1.32 (d, J = 7.13 Hz, 6H), 1.18 (s, 6H), 1.10 (s, 6H). ^{11}B NMR (160 MHz, $CDCl_3$): δ_B 8.52 (s).

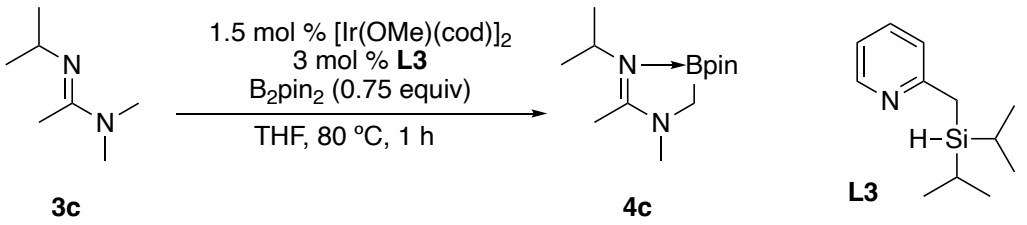
Borylation of *N'*-isopropyl-*N,N*-dimethylacetimidamide with 1.0 equiv B_2pin_2



3c **4c** **L3**

In a nitrogen filled glove box, $[Ir(OMe)(cod)]_2$ (0.0075 mmol, 1.5 mol %, 4.9 mg), **L3** (0.015 mmol, 3 mol %, 3.1 mg), and B_2pin_2 (0.5 mmol, 1.0 equiv, 126.5 mg) were weighed into separate test tubes and *N'*-isopropyl-*N,N*-dimethylacetimidamide (0.5 mmol, 1.0 equiv, 64.1 mg) was weighed into a 5 mL conical vial equipped with a stir bar. To the test tube containing $[Ir(OMe)(cod)]_2$ was added ~0.2 mL THF. The resulting solution was then transferred into the test tube containing B_2pin_2. The contents of the first test tube were rinsed three times (~0.2 mL/rinse) and added to the B_2pin_2 containing test tube. The solution of $[Ir(OMe)(cod)]_2$ and B_2pin_2 was then transferred into the test tube containing **L3** and the rinsing procedure was repeated. Finally, the resulting solution was added to the 5 mL conical vial followed by the rinsing procedure. The conical vial was then sealed and placed in an aluminum block pre-heated to 80 °C and allowed to stir for 1 h. The vial was then opened, solvent was removed via rotary evaporation, and ^1H NMR of crude material was collected. There was 100% conversion of starting material.

Borylation of *N'*-isopropyl-*N,N*-dimethylacetimidamide with 0.75 equiv B_2pin_2

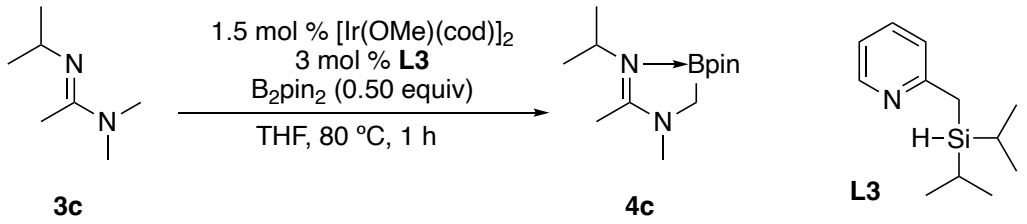


3c **4c** **L3**

In a nitrogen filled glove box, $[Ir(OMe)(cod)]_2$ (0.0075 mmol, 1.5 mol %, 4.9 mg), **L3** (0.015 mmol, 3 mol %, 3.1 mg), and B_2pin_2 (0.375 mmol, 0.75 equiv, 94.9 mg) were weighed into separate test tubes and *N'*-isopropyl-*N,N*-dimethylacetimidamide (0.5 mmol, 1.0 equiv, 64.1 mg) was

weighed into a 5 mL conical vial equipped with a stir bar. To the test tube containing $[Ir(OMe)(cod)]_2$ was added ~0.2 mL THF. The resulting solution was then transferred into the test tube containing B_2pin_2. The contents of the first test tube were rinsed three times (~0.2 mL/rinse) and added to the B_2pin_2 containing test tube. The solution of $[Ir(OMe)(cod)]_2$ and B_2pin_2 was then transferred into the test tube containing **L3** and the rinsing procedure was repeated. Finally, the resulting solution was added to the 5 mL conical vial followed by the rinsing procedure. The conical vial was then sealed and placed in an aluminum block pre-heated to 80 °C and allowed to stir for 1 h. The vial was then opened, solvent was removed via rotary evaporation, and ^{1}H NMR of crude material was collected. There was 100% conversion of starting material.

Borylation of *N'*-isopropyl-*N,N*-dimethylacetimidamide with 0.5 equiv B_2pin_2

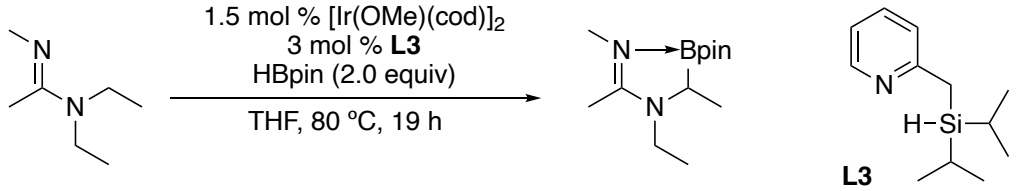


3c **4c** **L3**

In a nitrogen filled glove box, $[Ir(OMe)(cod)]_2$ (0.0075 mmol, 1.5 mol %, 4.9 mg), **L3** (0.015 mmol, 3 mol %, 3.1 mg), and B_2pin_2 (0.25 mmol, 0.5 equiv, 63.9 mg) were weighed into separate test tubes and *N'*-isopropyl-*N,N*-dimethylacetimidamide (0.5 mmol, 1.0 equiv, 64.1 mg) was weighed into a 5 mL conical vial equipped with a stir bar. To the test tube containing $[Ir(OMe)(cod)]_2$ was added ~0.2 mL THF. The resulting solution was then transferred into the test tube containing B_2pin_2. The contents of the first test tube were rinsed three times (~0.2 mL/rinse) and added to the B_2pin_2 containing test tube. The solution of $[Ir(OMe)(cod)]_2$ and B_2pin_2 was then transferred into the test tube containing **L3** and the rinsing procedure was repeated. Finally, the resulting solution was added to the 5 mL conical vial followed by the rinsing procedure. The conical vial was then sealed and placed in an aluminum block pre-heated to 80 °C and allowed to

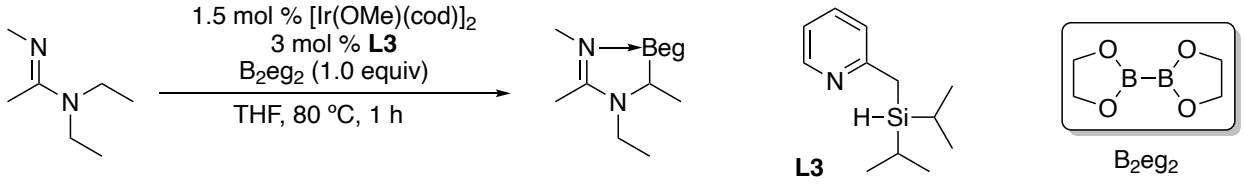
stir for 1 h. The vial was then opened, solvent was removed via rotary evaporation, and ^{1}H NMR of crude material was collected. There was 100% conversion of starting material.

Borylation of *N',N'*-diethyl-*N*-methylacetimidamide with HBpin



In a nitrogen filled glove box, $[Ir(OMe)(cod)]_2$ (0.0075 mmol, 1.5 mol %, 4.9 mg), **L3** (0.015 mmol, 3 mol %, 3.1 mg), and HBpin (0.5 mmol, 1.0 equiv, 127.9 mg) were weighed into separate test tubes and *N',N'*-diethyl-*N*-methylacetimidamide (1.0 mmol, 2.0 equiv, 64.1 mg) was weighed into a 5 mL conical vial equipped with a stir bar. To the test tube containing $[Ir(OMe)(cod)]_2$ was added ~0.2 mL THF. The resulting solution was then transferred into the test tube containing B_2pin_2. The contents of the first test tube were rinsed three times (~0.2 mL/rinse) and added to the B_2pin_2 containing test tube. The solution of $[Ir(OMe)(cod)]_2$ and B_2pin_2 was then transferred into the test tube containing **L3** and the rinsing procedure was repeated. Finally, the resulting solution was added to the 5 mL conical vial followed by the rinsing procedure. The conical vial was then sealed and placed in an aluminum block pre-heated to 80 °C and allowed to stir for 19 h. The vial was then opened, solvent was removed via rotary evaporation, and ^{1}H NMR of crude material was collected. There was 0% conversion of starting material. Also, 0% conversion of starting material was observed according to GC/MS.

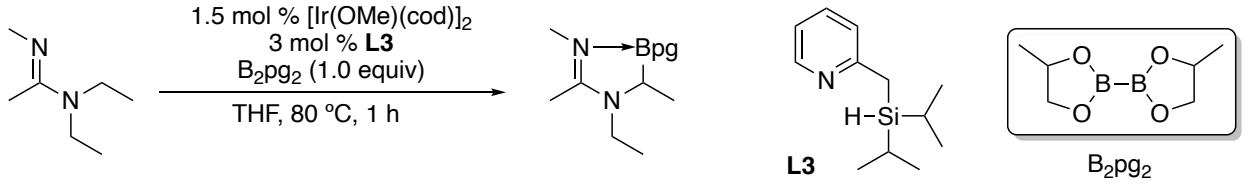
Borylation of *N',N'*-diethyl-*N*-methylacetimidamide with B_2eg_2



In a nitrogen filled glove box, $[Ir(OMe)(cod)]_2$ (0.0075 mmol, 1.5 mol %, 4.9 mg), **L3** (0.015 mmol, 3 mol %, 3.1 mg), and *N',N'*-diethyl-*N*-methylacetimidamide (0.5 mmol, 1.0 equiv, 64.1 mg) were weighed into separate test tubes and B_2eg_2 (0.5 mmol, 1.0 equiv, 70.5 mg) was weighed into a 5 mL conical vial equipped with a stir bar. To the test tube containing $[Ir(OMe)(cod)]_2$ was added ~0.2 mL THF. The resulting solution was then transferred into the conical vial containing B_2eg_2. The contents of the first test tube were rinsed three times (~0.2 mL/rinse) and added to the B_2eg_2 containing conical vial. To the test tube containing ligand **L3** was added ~0.2 mL THF. The resulting solution was then transferred into the conical vial containing B_2eg_2. The contents of the second test tube were rinsed three times (~0.2 mL/rinse) and added to the B_2eg_2 containing conical vial. Finally, To the test tube containing *N',N'*-diethyl-*N*-methylacetimidamide was added ~0.2 mL THF. The resulting solution was then transferred into the conical vial containing B_2eg_2. The contents of the third test tube were rinsed three times (~0.2 mL/rinse) and added to the B_2eg_2 containing conical vial. The conical vial was then sealed and placed in an aluminum block pre-heated to 80 °C and allowed to stir for 1 h. The vial was then opened, solvent was removed via rotary evaporation, and ^{1}H NMR of crude material was collected. There was 100% conversion of starting material.

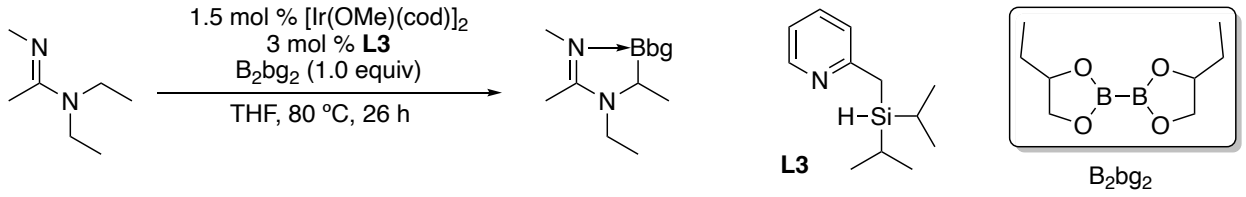
^{1}H NMR (500 MHz, C_6D_6): δ_H 4.20 (m, 1H), 4.13 (t, J = 7.12 Hz, 2H), 4.08 (m, 1H) 2.64 (s, 2H), 2.55 (s, 3H), 2.47 (m, 2H), 1.30 (d, J = 7.27 Hz, 3H), 0.98 (t, J = 7.11 Hz, 2H), 0.80 (s, 3H), 0.55 (t, J = 7.19 Hz 3H). ^{11}B NMR (160 MHz, C_6D_6): δ_B 10.05 (s).

Borylation of *N',N'*-diethyl-*N*-methylacetimidamide with B_2pg_2



In a nitrogen filled glove box, $[Ir(OMe)(cod)]_2$ (0.0075 mmol, 1.5 mol %, 4.9 mg), **L3** (0.015 mmol, 3 mol %, 3.1 mg), and B_2pg_2 (0.5 mmol, 1.0 equiv, 85.5 mg) were weighed into separate test tubes and *N',N'*-diethyl-*N*-methylacetimidamide (0.5 mmol, 1.0 equiv, 64.1 mg) was weighed into a 5 mL conical vial equipped with a stir bar. To the test tube containing $[Ir(OMe)(cod)]_2$ was added ~0.2 mL THF. The resulting solution was then transferred into the test tube containing B_2pg_2. The contents of the first test tube were rinsed three times (~0.2 mL/rinse) and added to the B_2pg_2 containing test tube. The solution of $[Ir(OMe)(cod)]_2$ and B_2pin_2 was then transferred into the test tube containing **L3** and the rinsing procedure was repeated. Finally, the resulting solution was added to the 5 mL conical vial followed by the rinsing procedure. The conical vial was then sealed and placed in an aluminum block pre-heated to 80 °C and allowed to stir for 1 h. The vial was then opened, solvent was removed via rotary evaporation, and ^{1}H NMR of crude material was collected. There was 100% conversion of starting material according to GC/MS.

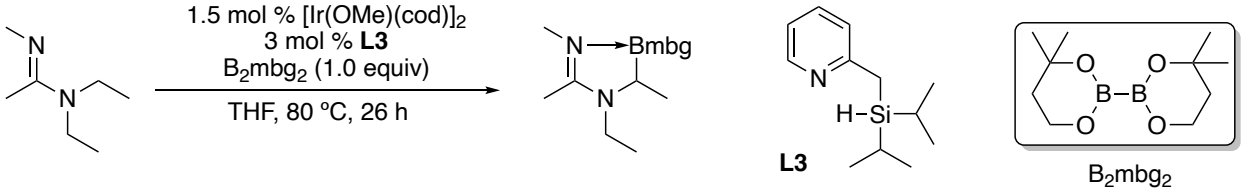
Borylation of *N',N'*-diethyl-*N*-methylacetimidamide with B_2bg_2



In a nitrogen filled glove box, $[Ir(OMe)(cod)]_2$ (0.0075 mmol, 1.5 mol %, 4.9 mg), **L3** (0.015 mmol, 3 mol %, 3.1 mg), and B_2bg_2 (0.5 mmol, 1.0 equiv, 98.9 mg) were weighed into separate test tubes and *N',N'*-diethyl-*N*-methylacetimidamide (0.5 mmol, 1.0 equiv, 64.1 mg) was weighed into a 5 mL conical vial equipped with a stir bar. To the test tube containing $[Ir(OMe)(cod)]_2$ was

added ~0.2 mL THF. The resulting solution was then transferred into the test tube containing B_2bg_2. The contents of the first test tube were rinsed three times (~0.2 mL/rinse) and added to the B_2bg_2 containing test tube. The solution of $[Ir(OMe)(cod)]_2$ and B_2pin_2 was then transferred into the test tube containing **L3** and the rinsing procedure was repeated. Finally, the resulting solution was added to the 5 mL conical vial followed by the rinsing procedure. The conical vial was then sealed and placed in an aluminum block pre-heated to 80 °C and allowed to stir for 26 h. The vial was then opened, solvent was removed via rotary evaporation, and ^{1}H NMR of crude material was collected. There was 15% conversion of starting material according to GC/MS.

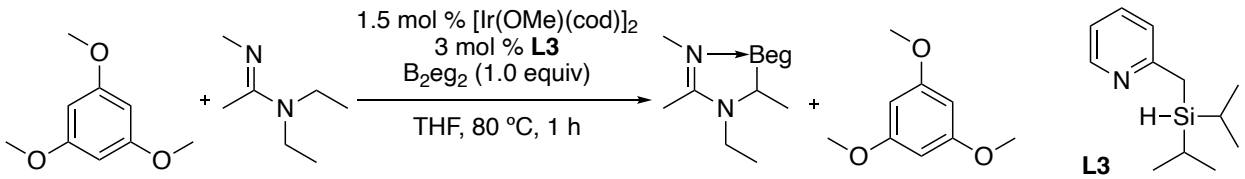
Borylation of *N',N'*-diethyl-*N*-methylacetimidamide with B_2mbg_2



In a nitrogen filled glove box, $[Ir(OMe)(cod)]_2$ (0.0075 mmol, 1.5 mol %, 4.9 mg), **L3** (0.015 mmol, 3 mol %, 3.1 mg), and B_2mbg_2 (0.5 mmol, 1.0 equiv, 112.9 mg) were weighed into separate test tubes and *N',N'*-diethyl-*N*-methylacetimidamide (0.5 mmol, 1.0 equiv, 64.1 mg) was weighed into a 5 mL conical vial equipped with a stir bar. To the test tube containing $[Ir(OMe)(cod)]_2$ was added ~0.2 mL THF. The resulting solution was then transferred into the test tube containing B_2mbg_2. The contents of the first test tube were rinsed three times (~0.2 mL/rinse) and added to the B_2mbg_2 containing test tube. The solution of $[Ir(OMe)(cod)]_2$ and B_2pin_2 was then transferred into the test tube containing **L3** and the rinsing procedure was repeated. Finally, the resulting solution was added to the 5 mL conical vial followed by the rinsing procedure. The conical vial was then sealed and placed in an aluminum block pre-heated to 80 °C and allowed to stir for 26 h.

The vial was then opened, solvent was removed via rotary evaporation, and ^{1}H NMR of crude material was collected. There was 0% conversion of starting material.

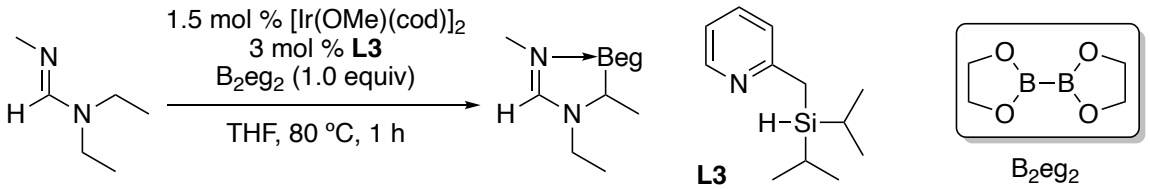
NMR Yield for borylated amidine with B_2eg_2 with 1,3,5-trimethoxybenzene as internal standard



In a nitrogen filled glove box, $[Ir(OMe)(cod)]_2$ (0.0075 mmol, 1.5 mol %, 4.9 mg), **L3** (0.015 mmol, 3 mol %, 3.1 mg), *N',N'*-diethyl-*N*-methylacetimidamide (0.5 mmol, 1.0 equiv, 64.8 mg) and 1,3,5-trimethoxybenzene (0.5 mmol, 1.0 equiv, 84 mg) were weighed into separate test tubes and B_2eg_2 (0.5 mmol, 1.0 equiv, 126.5 mg) was weighed into a 5 mL conical vial equipped with a stir bar. To the test tube containing $[Ir(OMe)(cod)]_2$ was added ~0.2 mL THF. The resulting solution was then transferred into the conical vial containing B_2eg_2. The contents of the first test tube were rinsed three times (~0.2 mL/rinse) and added to the B_2eg_2 containing conical vial. To the test tube containing ligand **L3** was added ~0.2 mL THF. The resulting solution was then transferred into the conical vial containing B_2eg_2. The contents of the second test tube were rinsed three times (~0.2 mL/rinse) and added to the B_2eg_2 containing conical vial. To the test tube containing *N',N'*-diethyl-*N*-methylacetimidamide was added ~0.2 mL THF. The resulting solution was then transferred into the conical vial containing B_2eg_2. The contents of the third test tube were rinsed three times (~0.2 mL/rinse) and added to the B_2eg_2 containing conical vial. Finally, to the test tube containing 1,3,5-trimethoxybenzene was added ~0.2 mL THF. The resulting solution was then transferred into the conical vial containing B_2eg_2. The contents of the fourth test tube were rinsed three times (~0.2 mL/rinse) and added to the B_2eg_2 containing conical vial. The conical vial was then sealed and placed in an aluminum block pre-heated to 80 °C and allowed to stir for 1 h. The vial was then opened, solvent was removed via rotary evaporation, and ^{1}H NMR of crude

material was collected. 33% NMR yield with respect to internal standard 1,3,5-trimethoxybenzene was observed.

Borylation of *N',N'*-diethyl-*N*-methylformimidamide with B_2eg_2



In a nitrogen filled glove box, $[Ir(OMe)(cod)]_2$ (0.0075 mmol, 1.5 mol %, 4.9 mg), **L3** (0.015 mmol, 3 mol %, 3.1 mg), and *N',N'*-diethyl-*N*-methylformimidamide (0.5 mmol, 1.0 equiv, 57.1 mg) were weighed into separate test tubes and B_2eg_2 (0.5 mmol, 1.0 equiv, 70.5 mg) was weighed into a 5 mL conical vial equipped with a stir bar. To the test tube containing $[Ir(OMe)(cod)]_2$ was added ~0.2 mL THF. The resulting solution was then transferred into the conical vial containing B_2eg_2. The contents of the first test tube were rinsed three times (~0.2 mL/rinse) and added to the B_2eg_2 containing conical vial. To the test tube containing ligand **L3** was added ~0.2 mL THF. The resulting solution was then transferred into the conical vial containing B_2eg_2. The contents of the second test tube were rinsed three times (~0.2 mL/rinse) and added to the B_2eg_2 containing conical vial. Finally, To the test tube containing *N',N'*-diethyl-*N*-methylacetimidamide was added ~0.2 mL THF. The resulting solution was then transferred into the conical vial containing B_2eg_2. The contents of the third test tube were rinsed three times (~0.2 mL/rinse) and added to the B_2eg_2 containing conical vial. The conical vial was then sealed and placed in an aluminum block pre-heated to 80 °C and allowed to stir for 1 h. The vial was then opened, solvent was removed via rotary evaporation, and ^1H NMR of crude material was collected. There was 71% conversion of starting material based on GC/MS.

APPENDIX

APPENDIX

Spectra

Figure 3: ^{1}H NMR (500 MHz, $CDCl_3$) L3

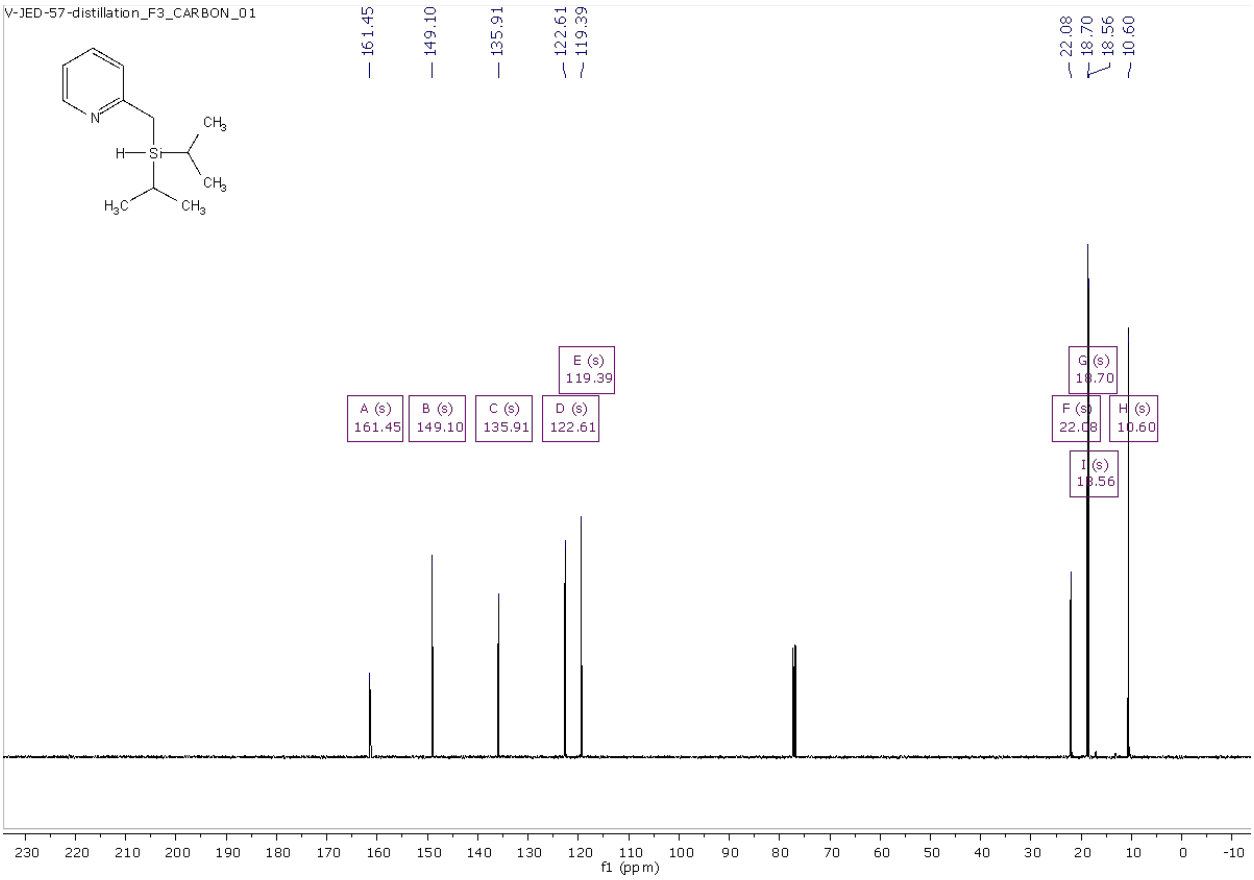


Figure 4: ^{13}C NMR (125 MHz, $CDCl_3$) L3

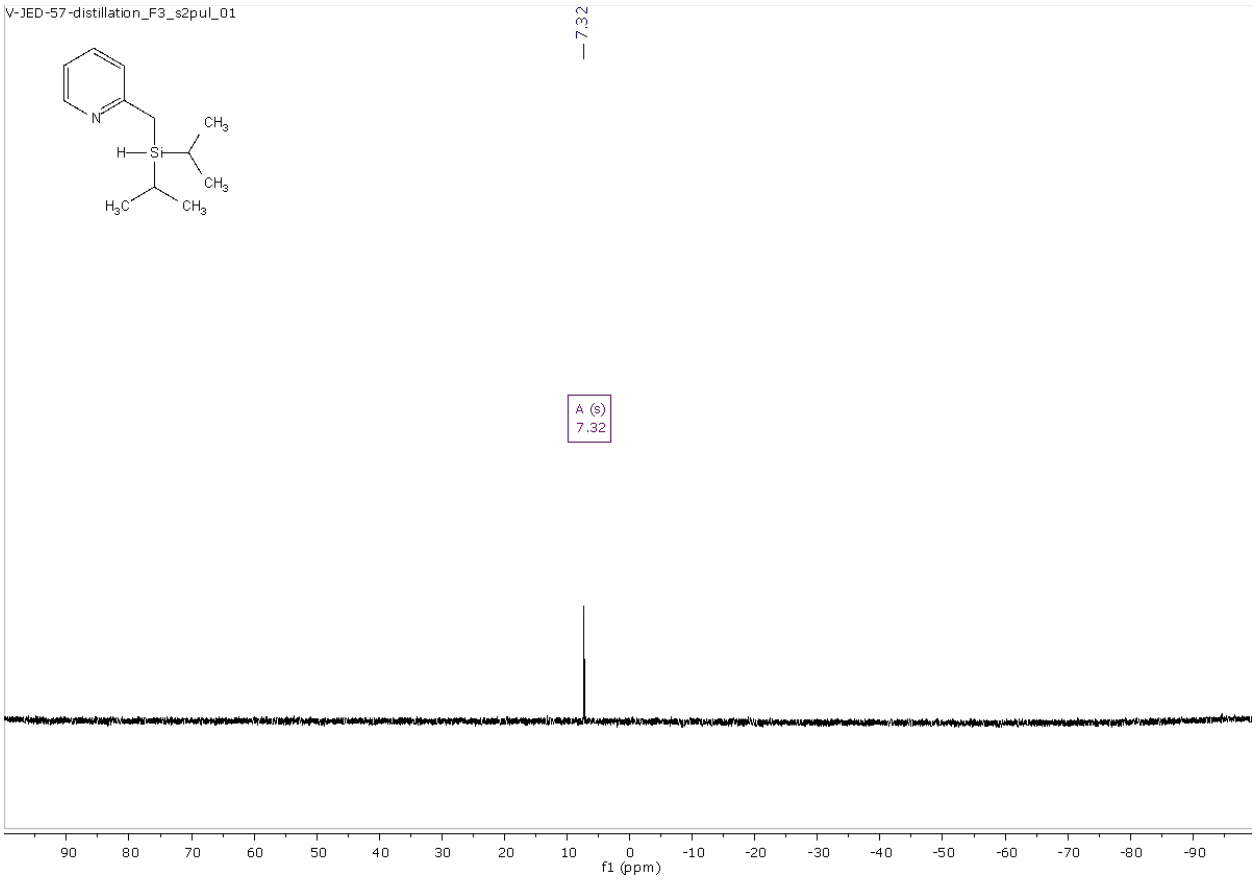


Figure 5: ^{29}Si NMR (99 MHz, $CDCl_3$) L3

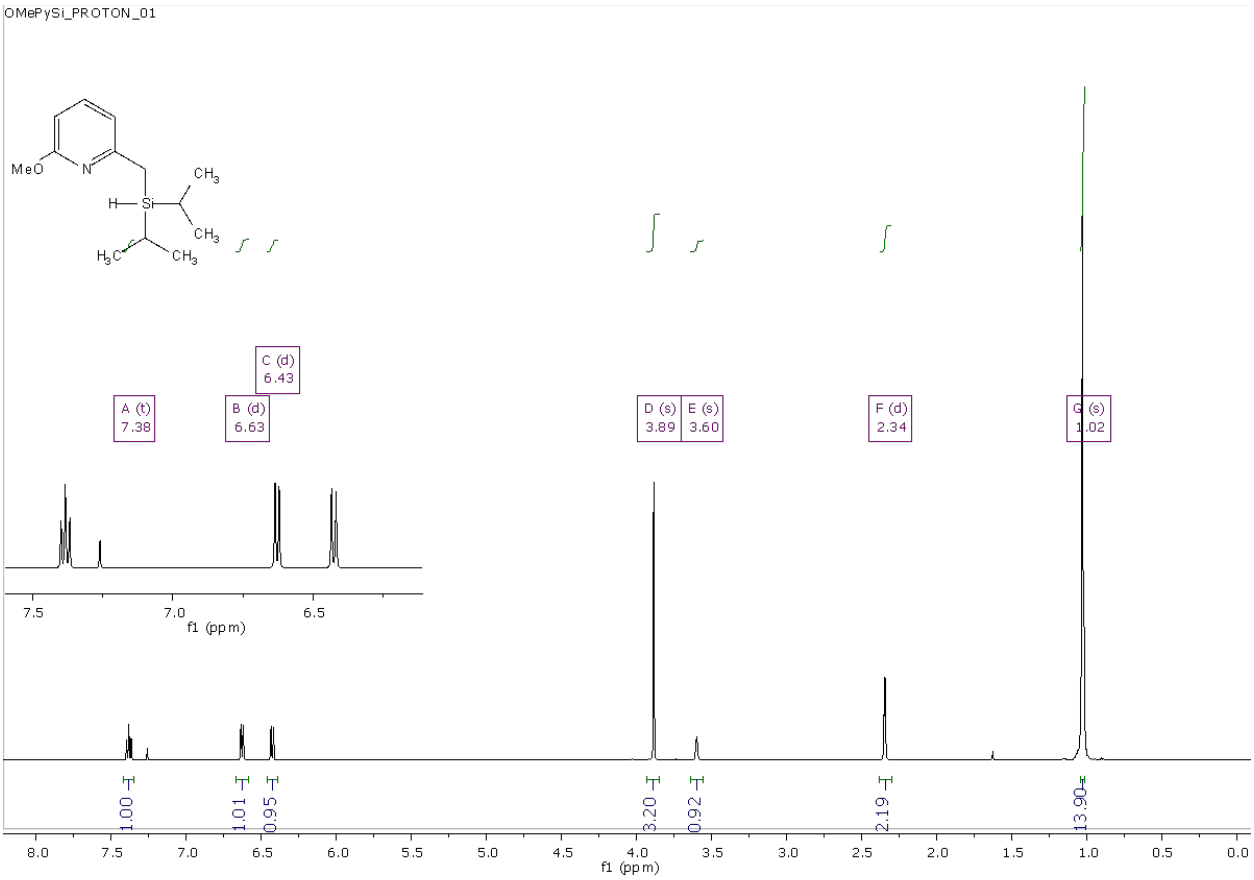


Figure 6: ^{1}H NMR (500 MHz, $CDCl_3$) L4

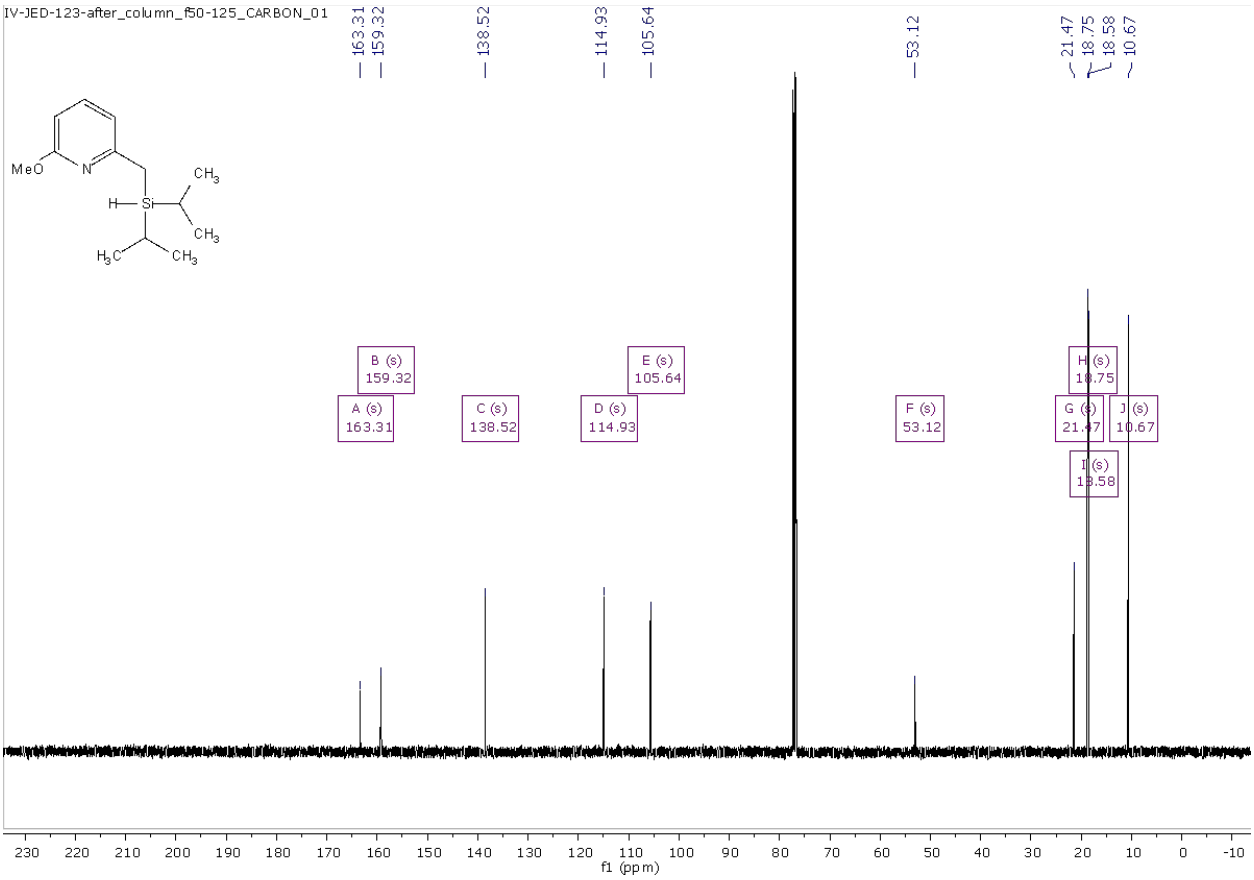


Figure 7: ^{13}C NMR (125 MHz, $CDCl_3$) L4

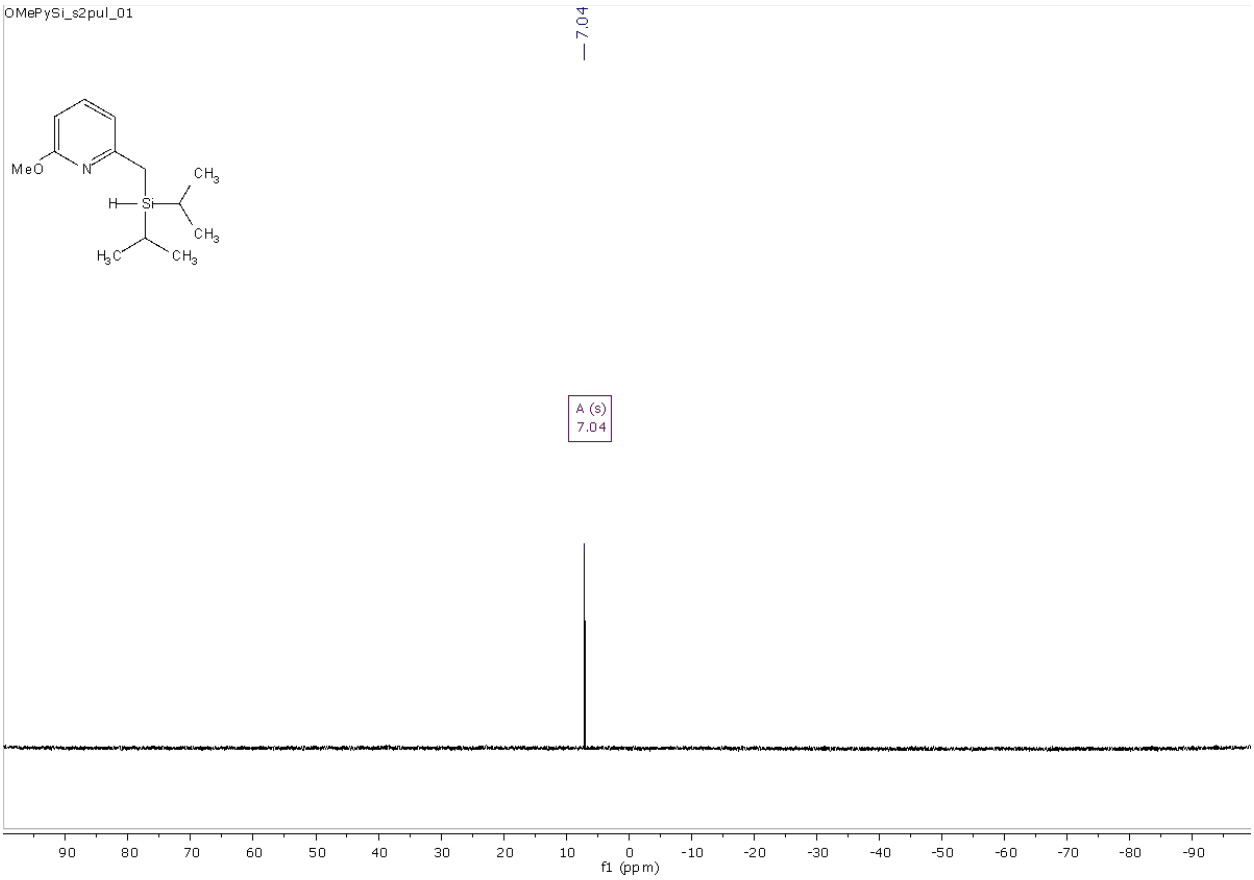


Figure 8: ^{29}Si NMR (99 MHz, $CDCl_3$) L4

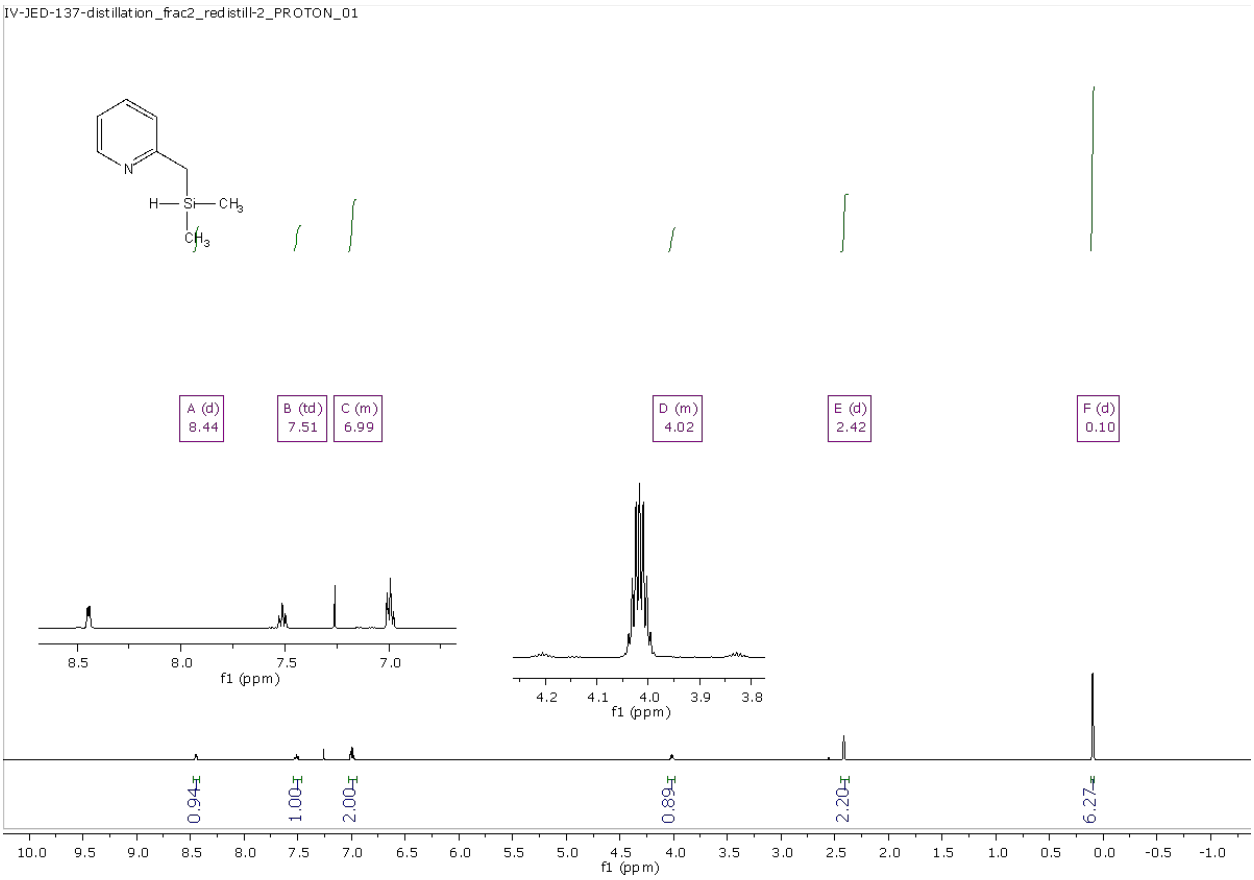


Figure 9: ^{1}H NMR (500 MHz, $CDCl_3$) L5

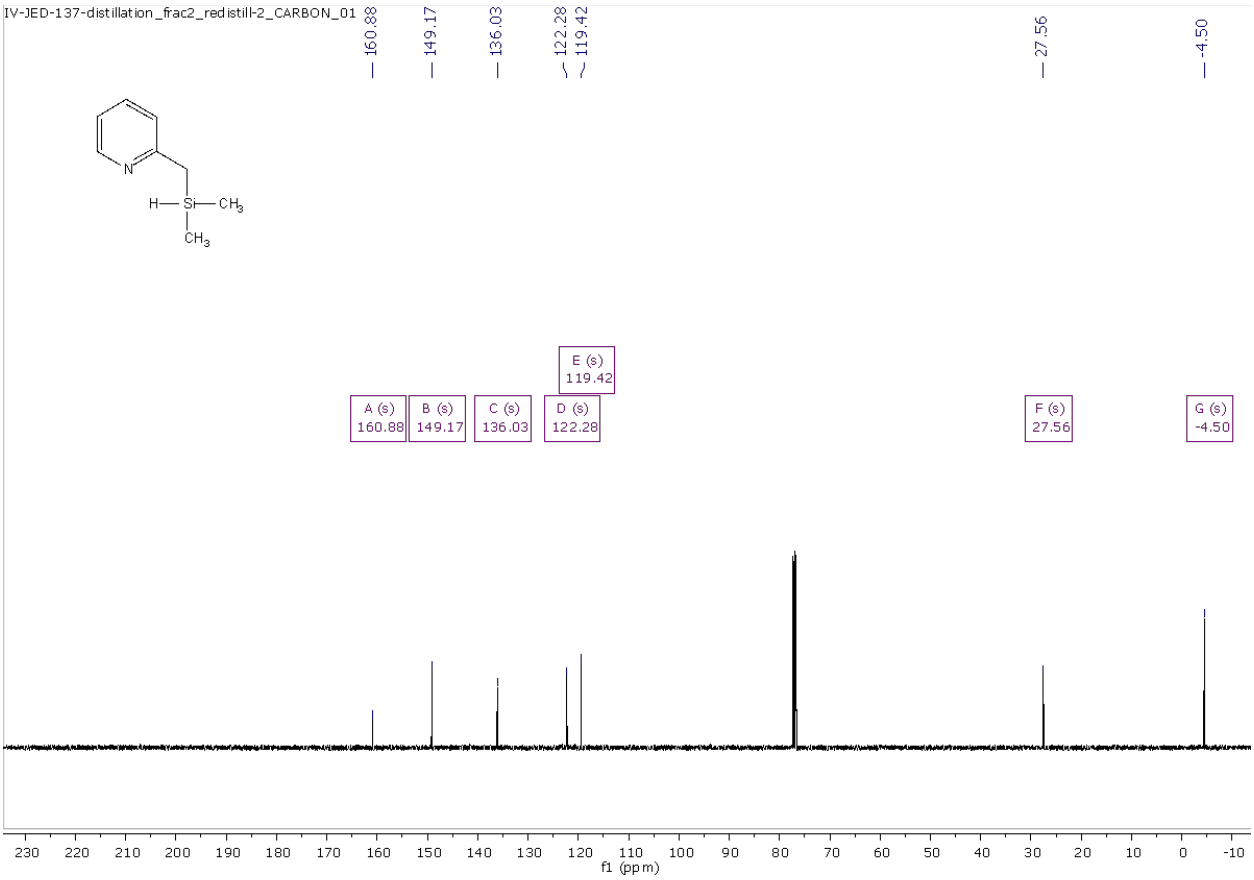


Figure 10: ^{13}C NMR (125 MHz, $CDCl_3$) L5

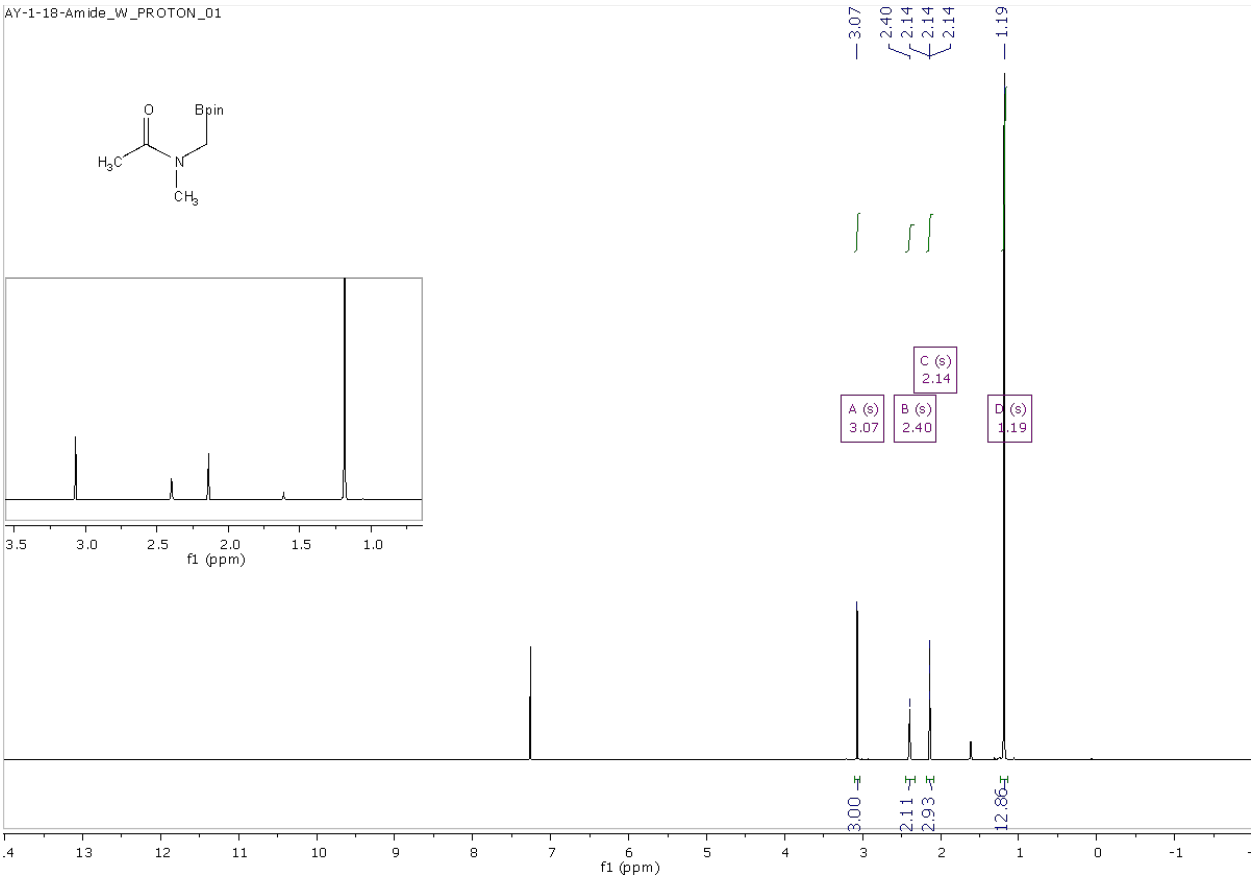


Figure 11: ^{1}H NMR ($CDCl_3$, 500 MHz) 3a

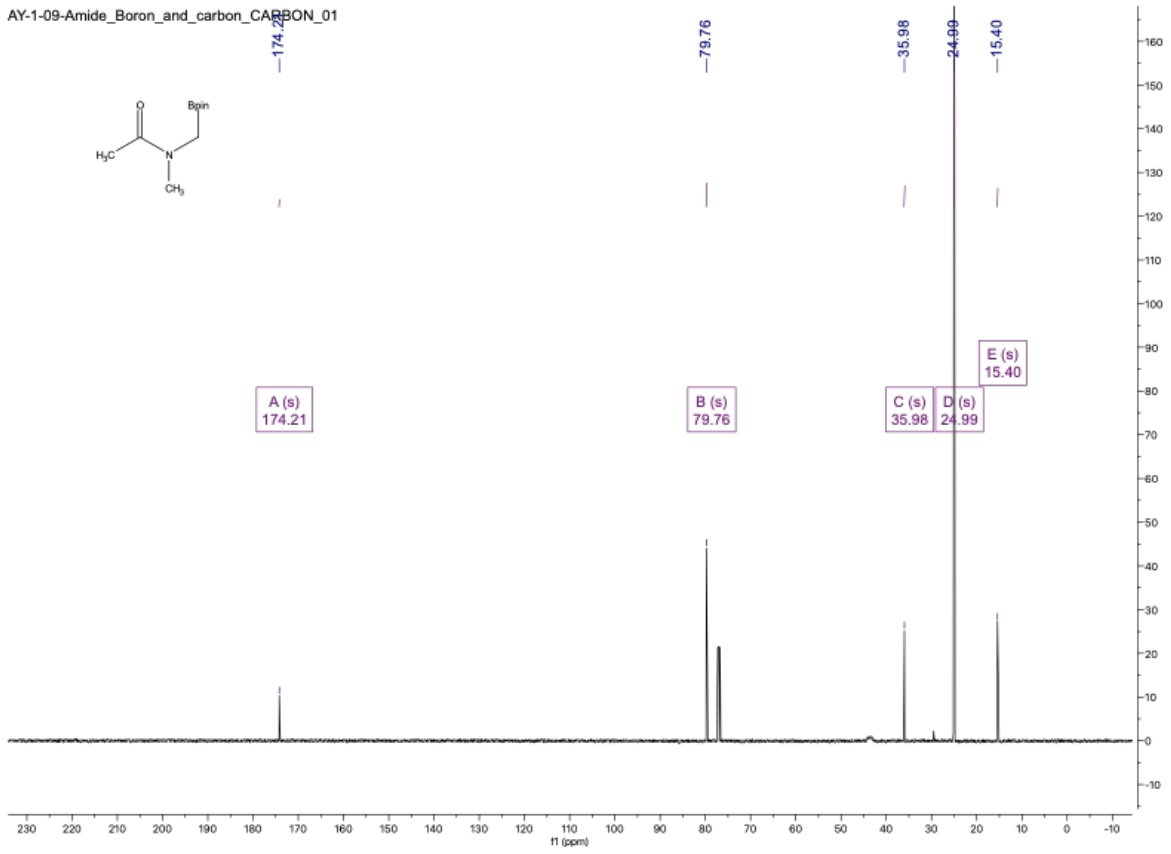


Figure 12: ^{13}C NMR (125 MHz, $CDCl_3$) 3a

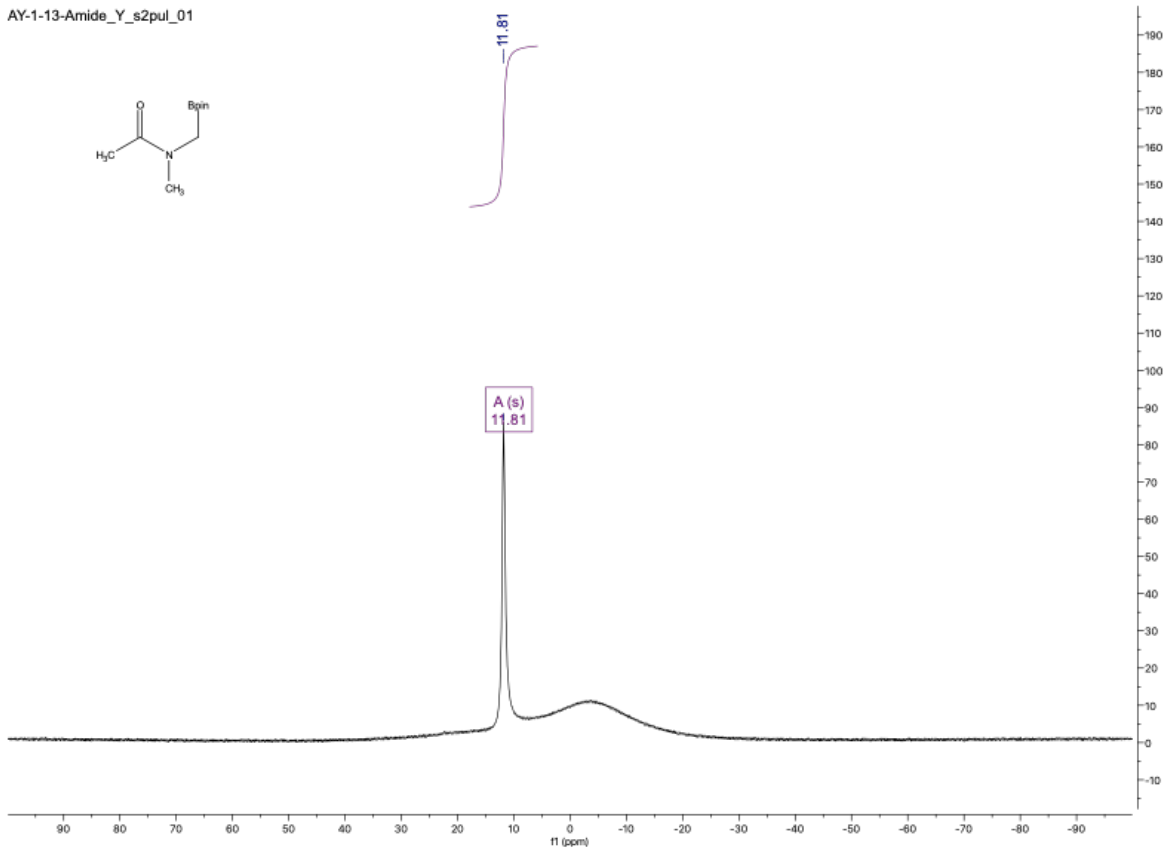


Figure 13: ^{11}B NMR ($CDCl_3$, 160 MHz) 3a

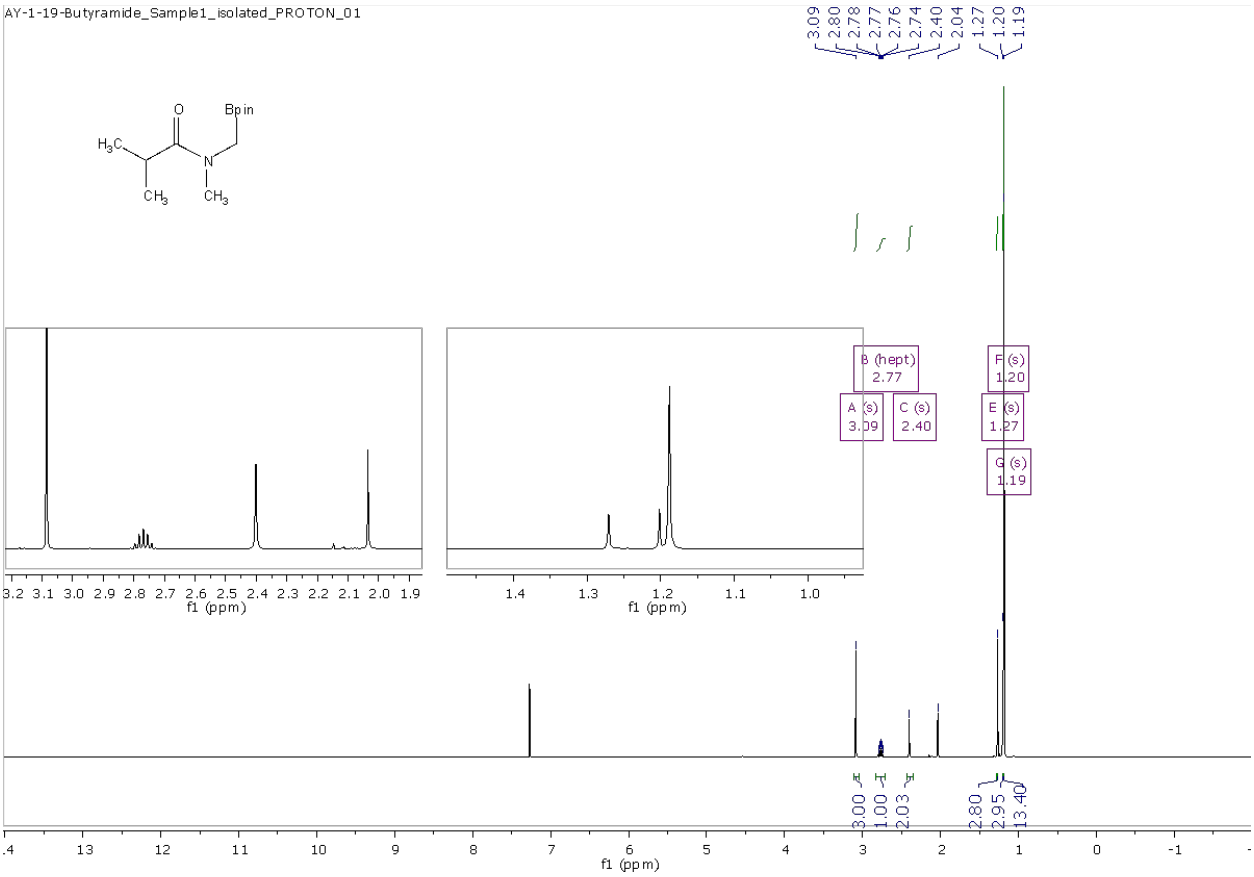


Figure 14: ^{1}H NMR ($CDCl_3$, 500 MHz) 3c

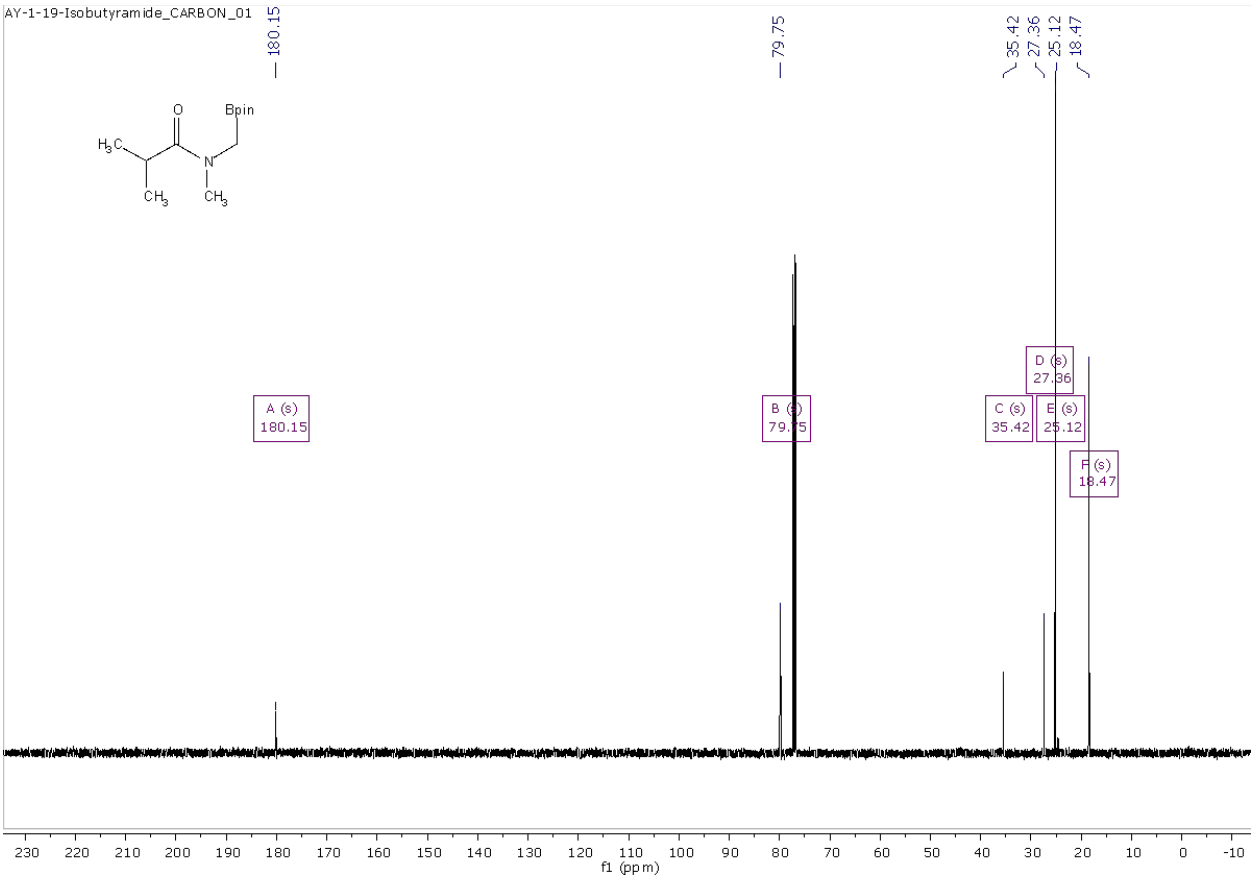


Figure 15: ^{13}C NMR (125 MHz, $CDCl_3$) 3c

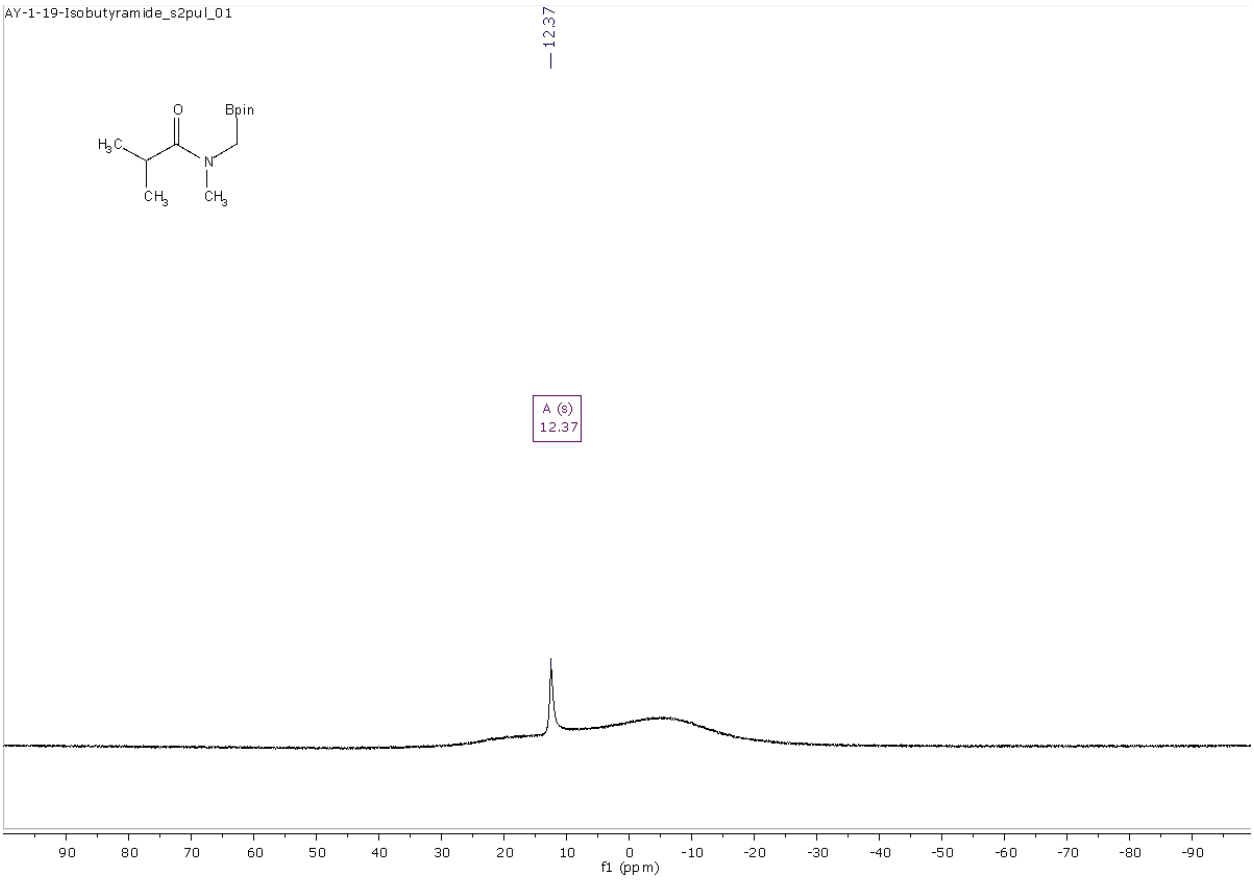


Figure 16: ^{11}B NMR ($CDCl_3$, 160 MHz) 3c

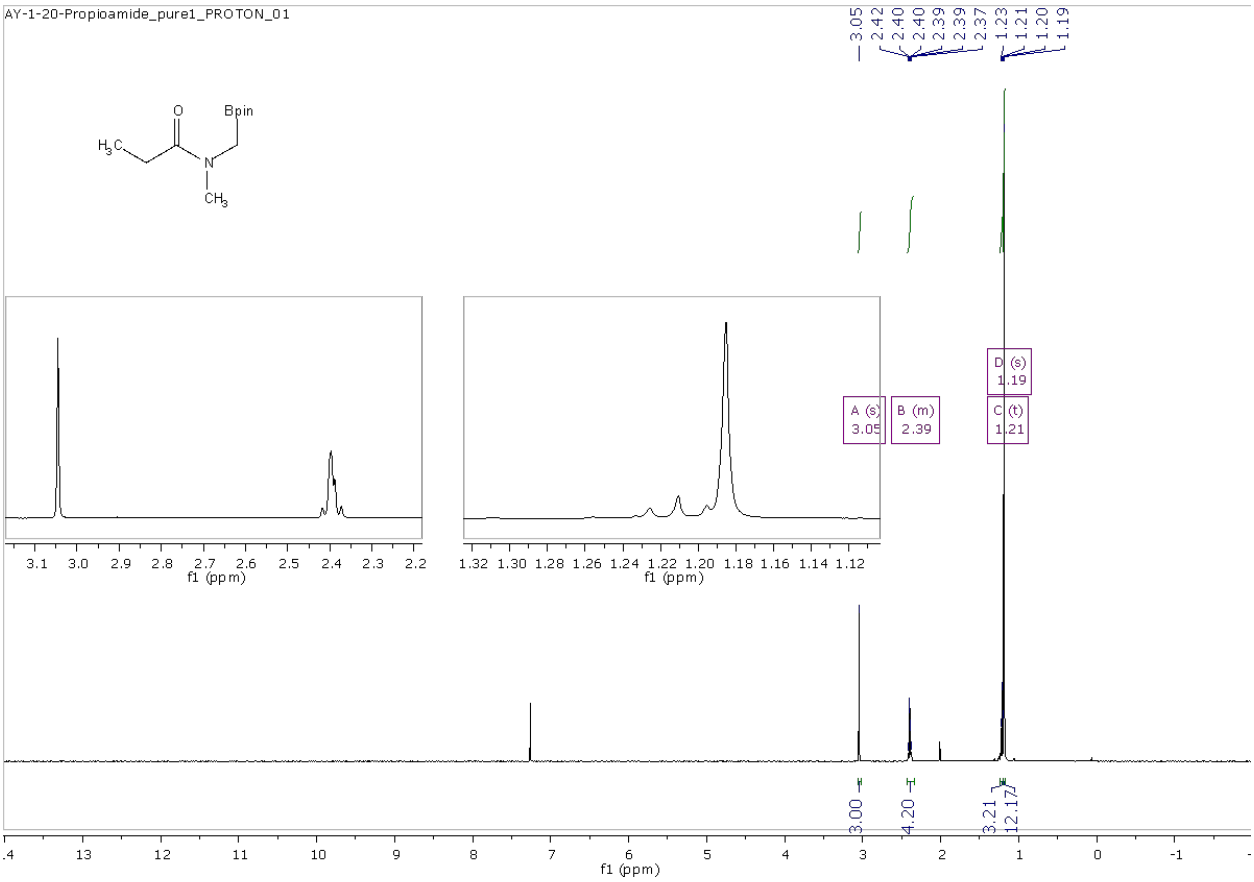


Figure 17: ^{1}H NMR ($CDCl_3$, 500 MHz) 3b

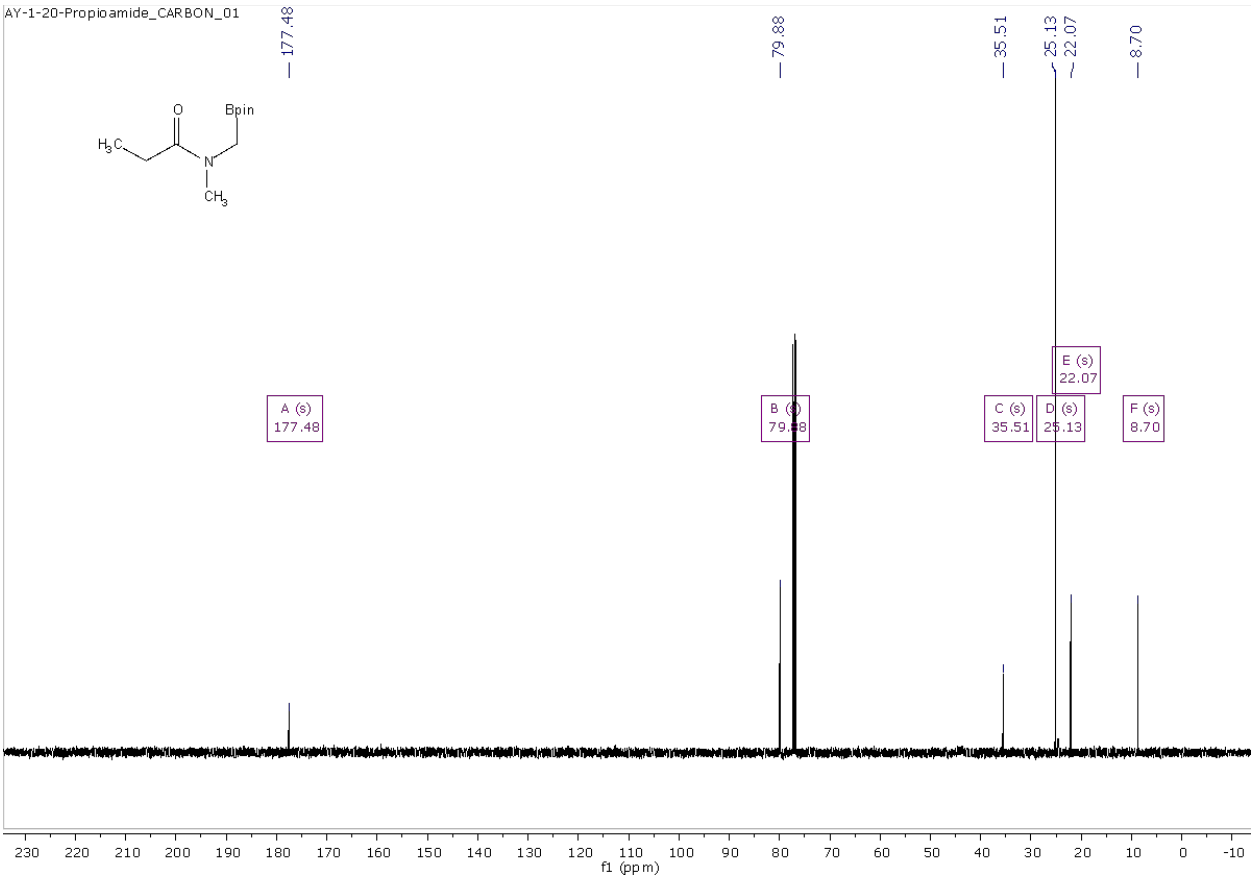


Figure 18: ^{13}C NMR (125 MHz, $CDCl_3$) 3b

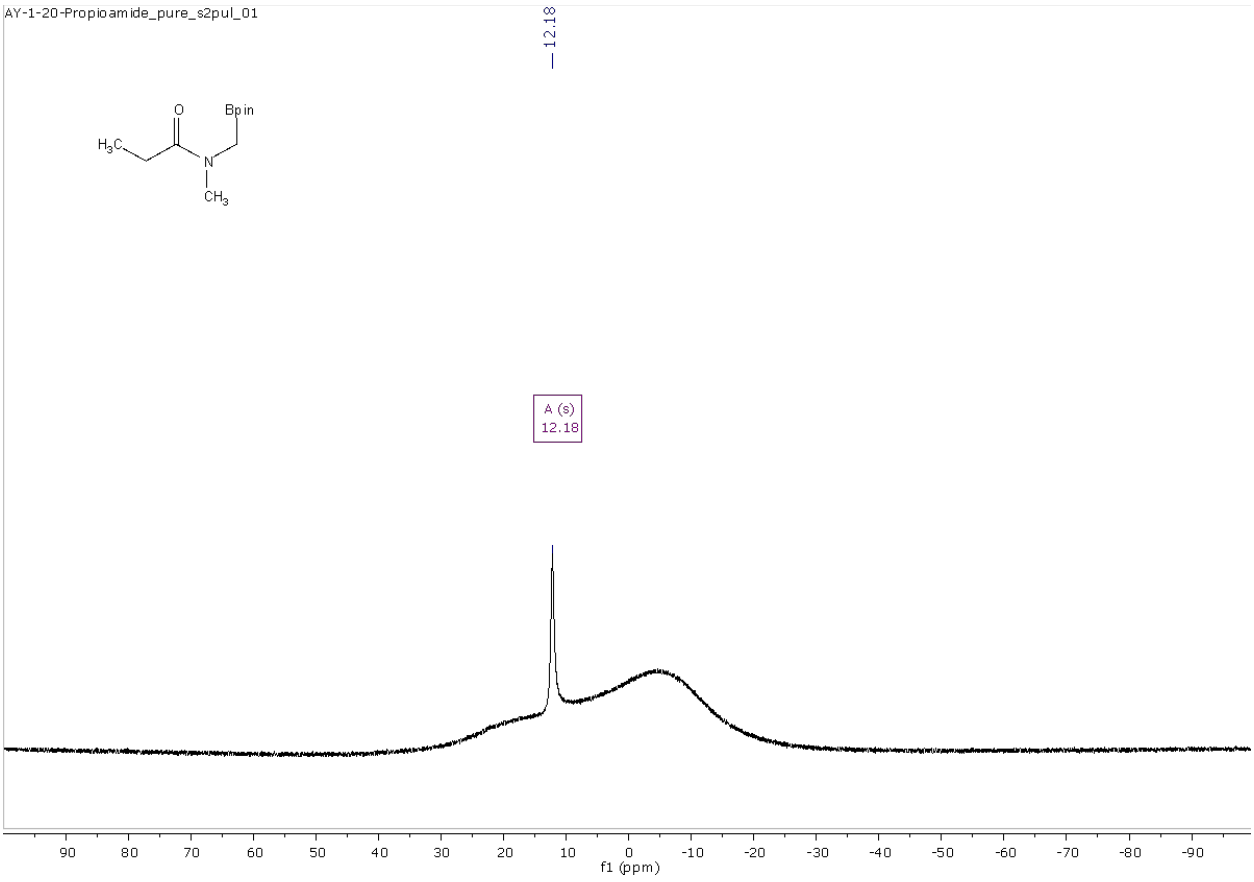


Figure 19: ^{11}B NMR ($CDCl_3$, 160 MHz) 3b

Figure 20: ^{1}H NMR ($CDCl_3$, 500 MHz) 3e

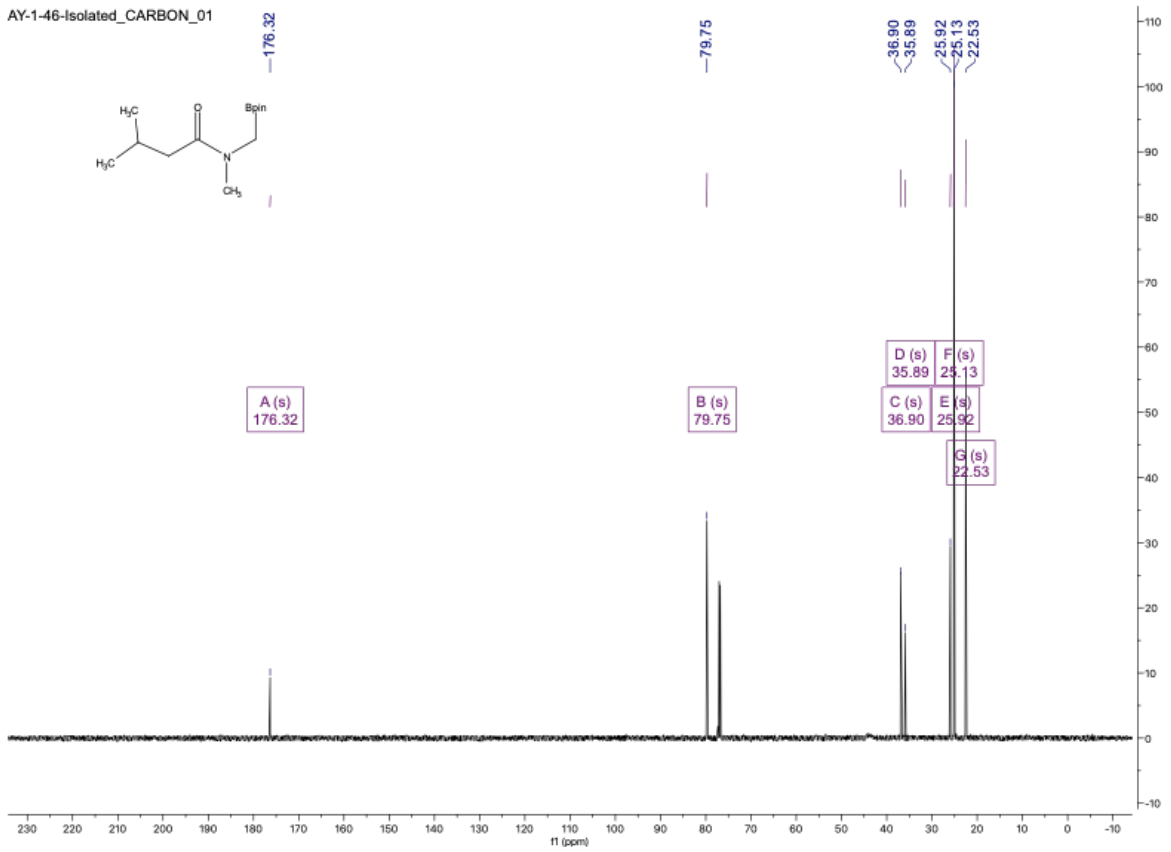


Figure 21: ^{13}C NMR (125 MHz, $CDCl_3$) 3e

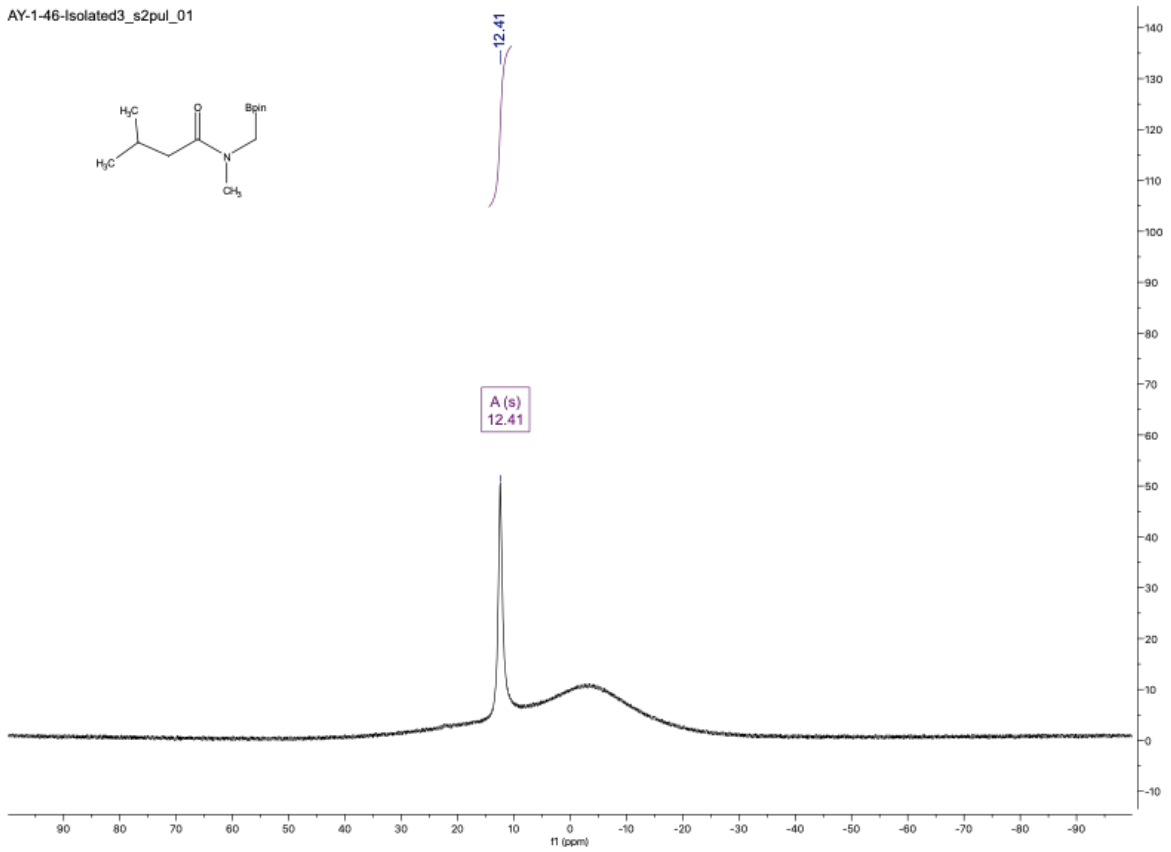


Figure 22: ^{11}B NMR ($CDCl_3$, 160 MHz) 3e

Figure 23: ^{1}H NMR ($CDCl_3$, 500 MHz) 3d

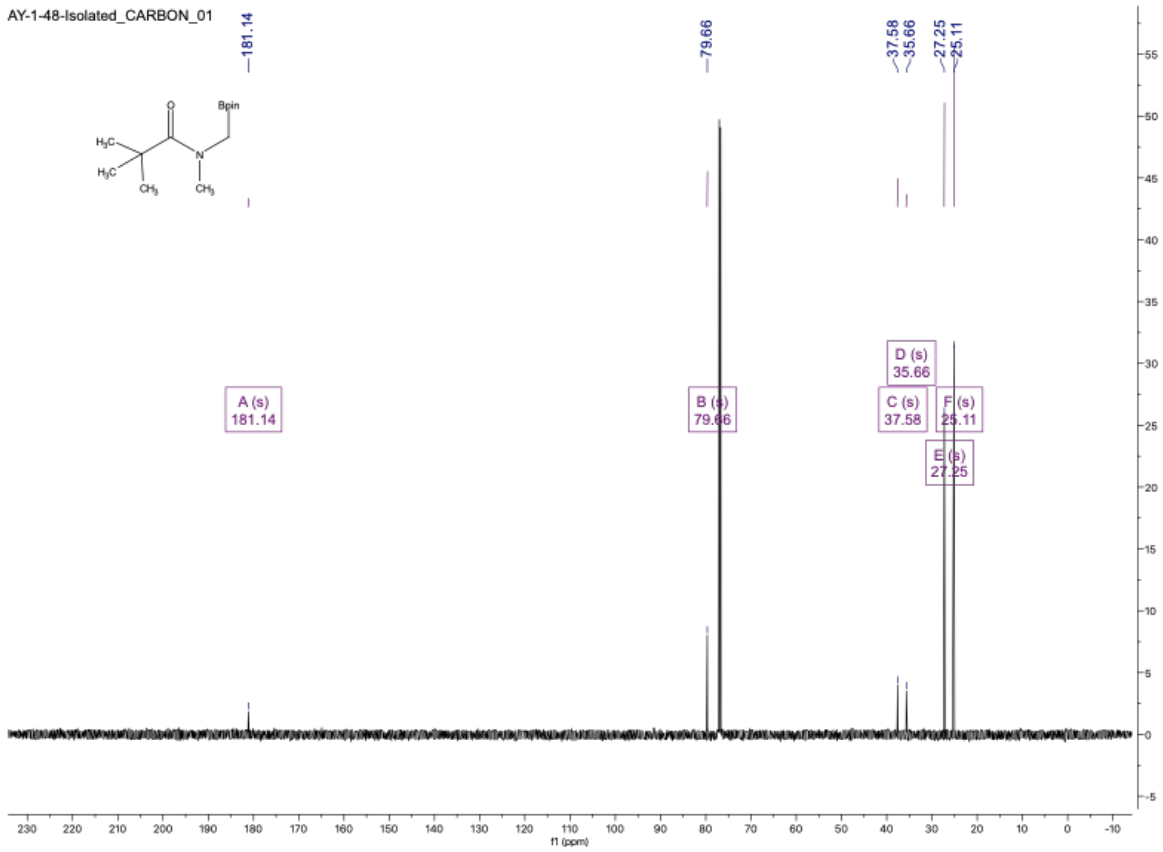


Figure 24: ^{13}C NMR (125 MHz, $CDCl_3$) 3d

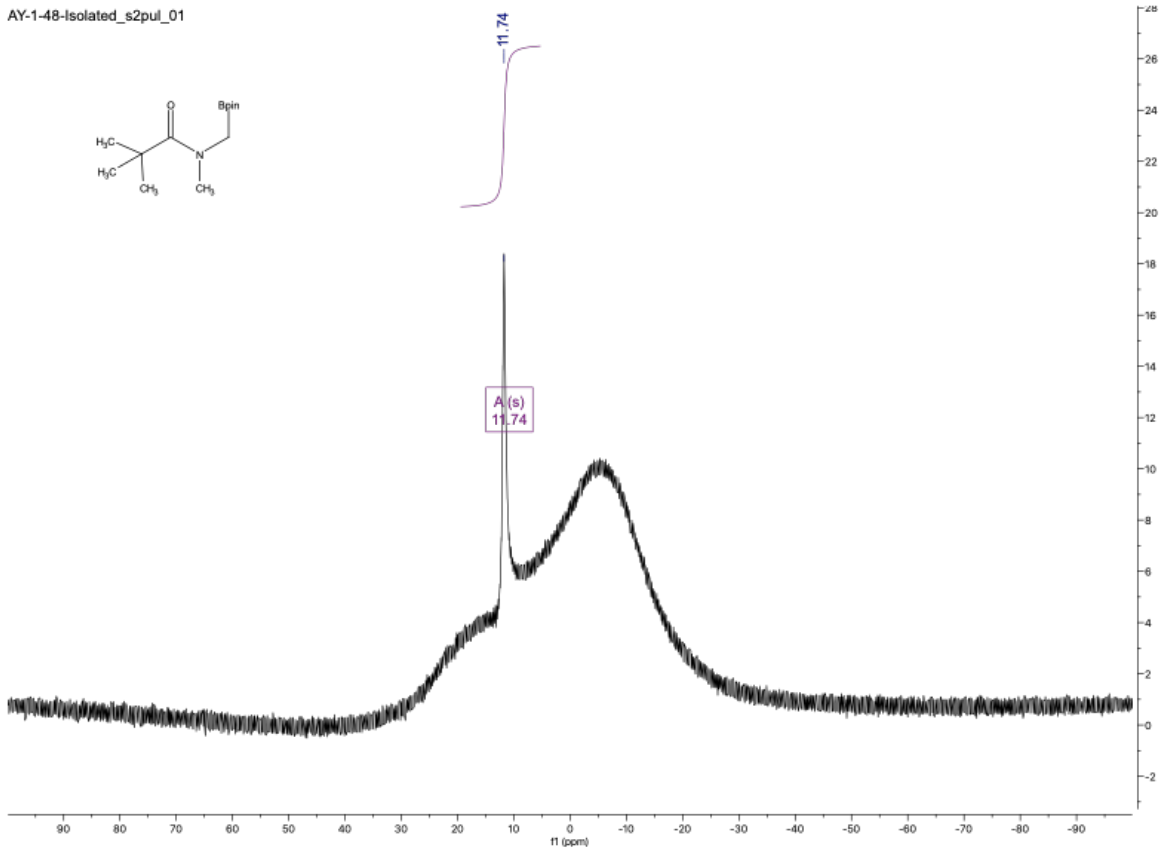


Figure 25: ^{11}B NMR ($CDCl_3$, 160 MHz) 3d

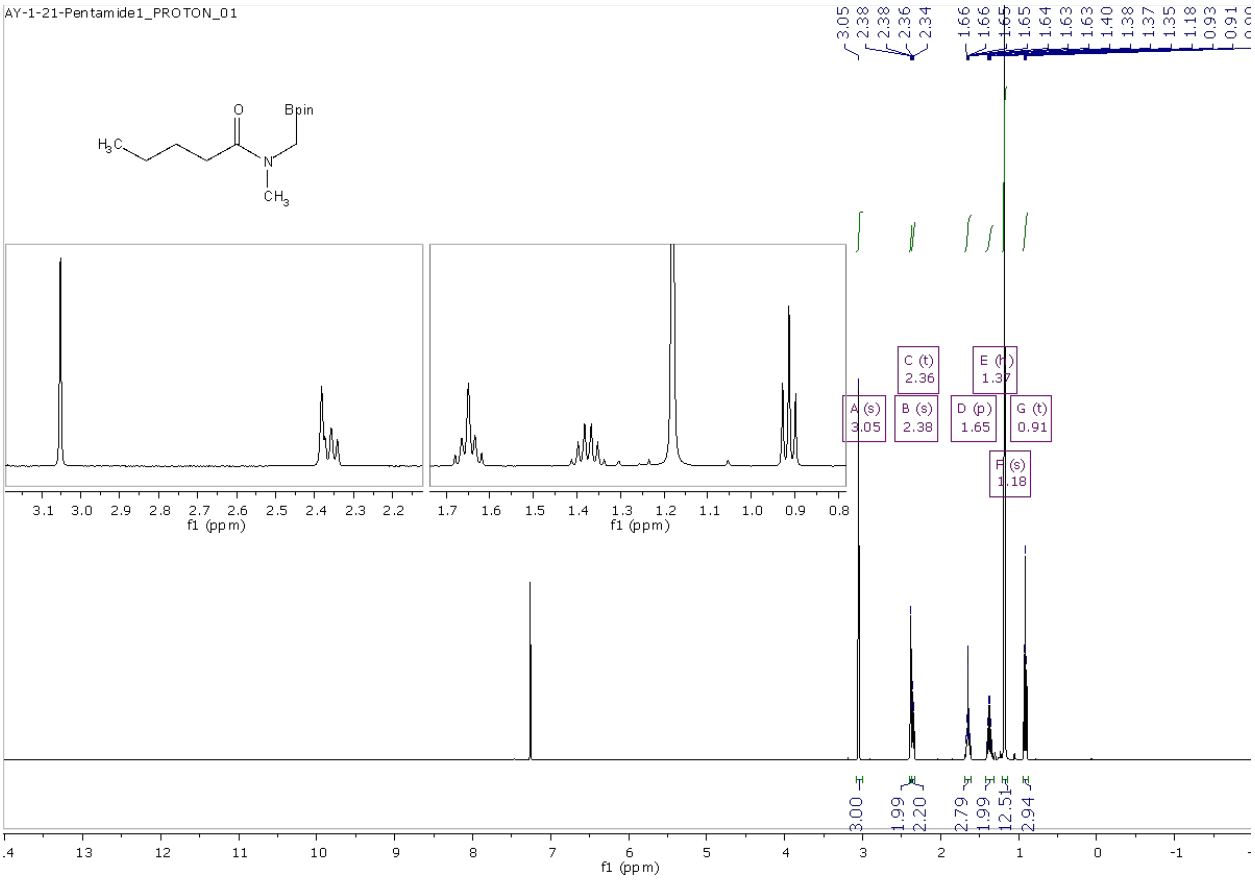


Figure 26: ^{1}H NMR ($CDCl_3$, 500 MHz) 3f

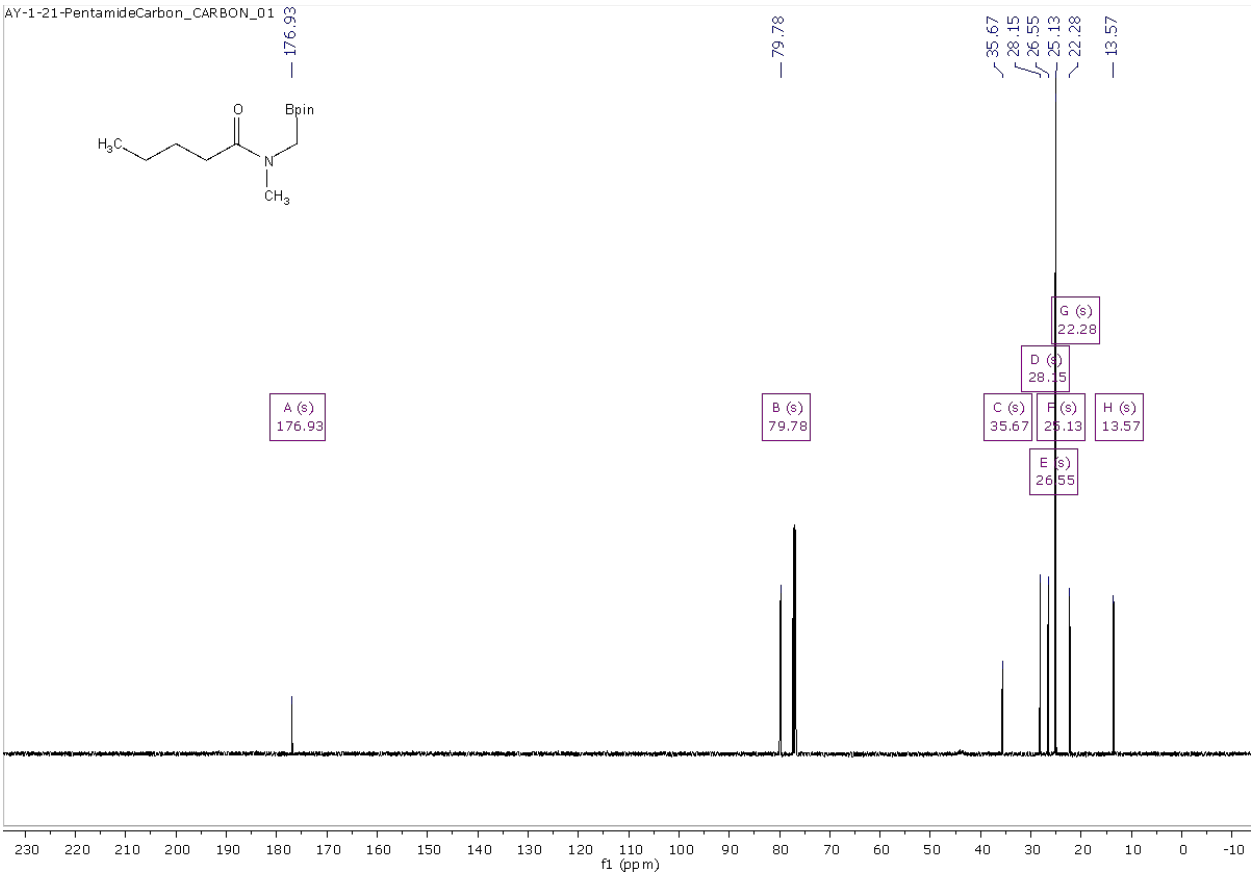


Figure 27: ^{13}C NMR (125 MHz, $CDCl_3$) 3f

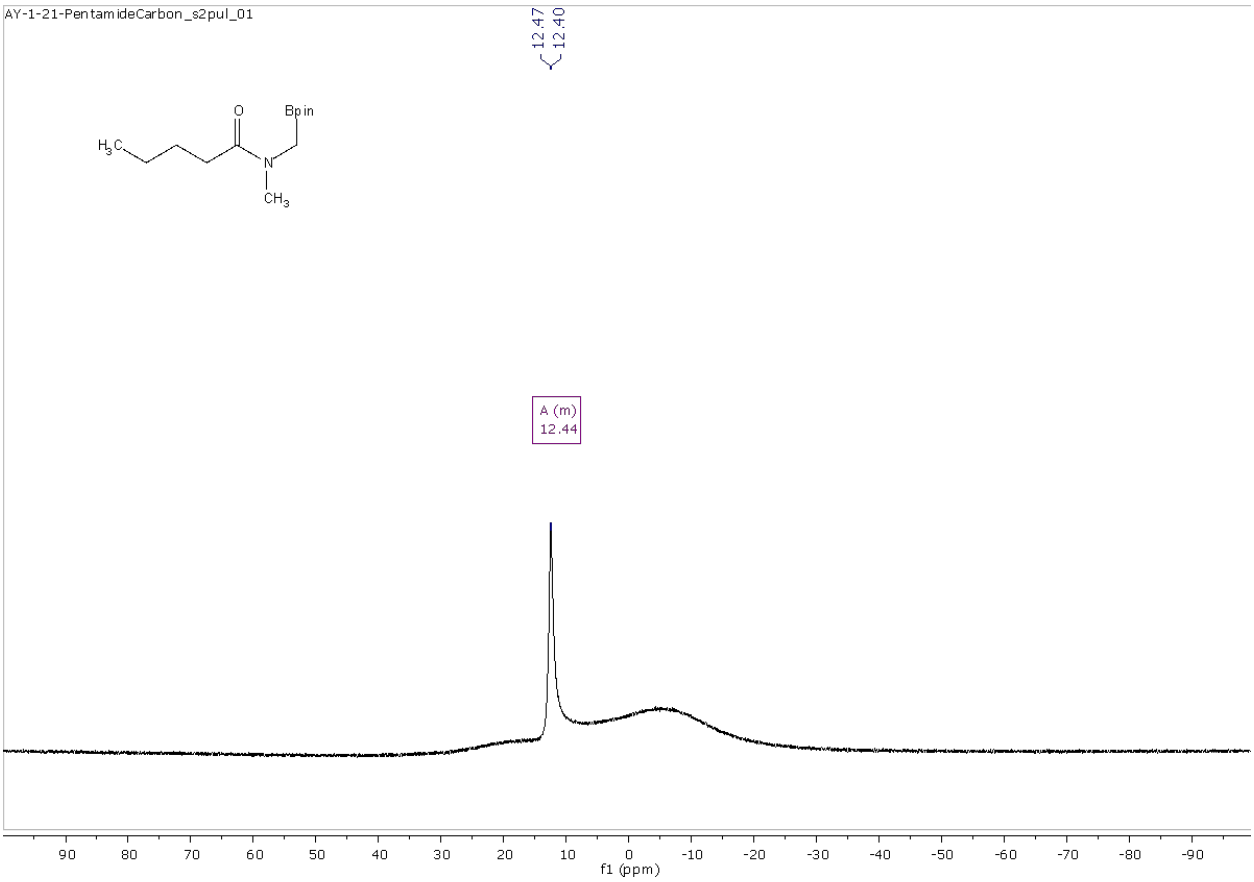


Figure 28: ^{11}B NMR ($CDCl_3$, 160 MHz) 3f

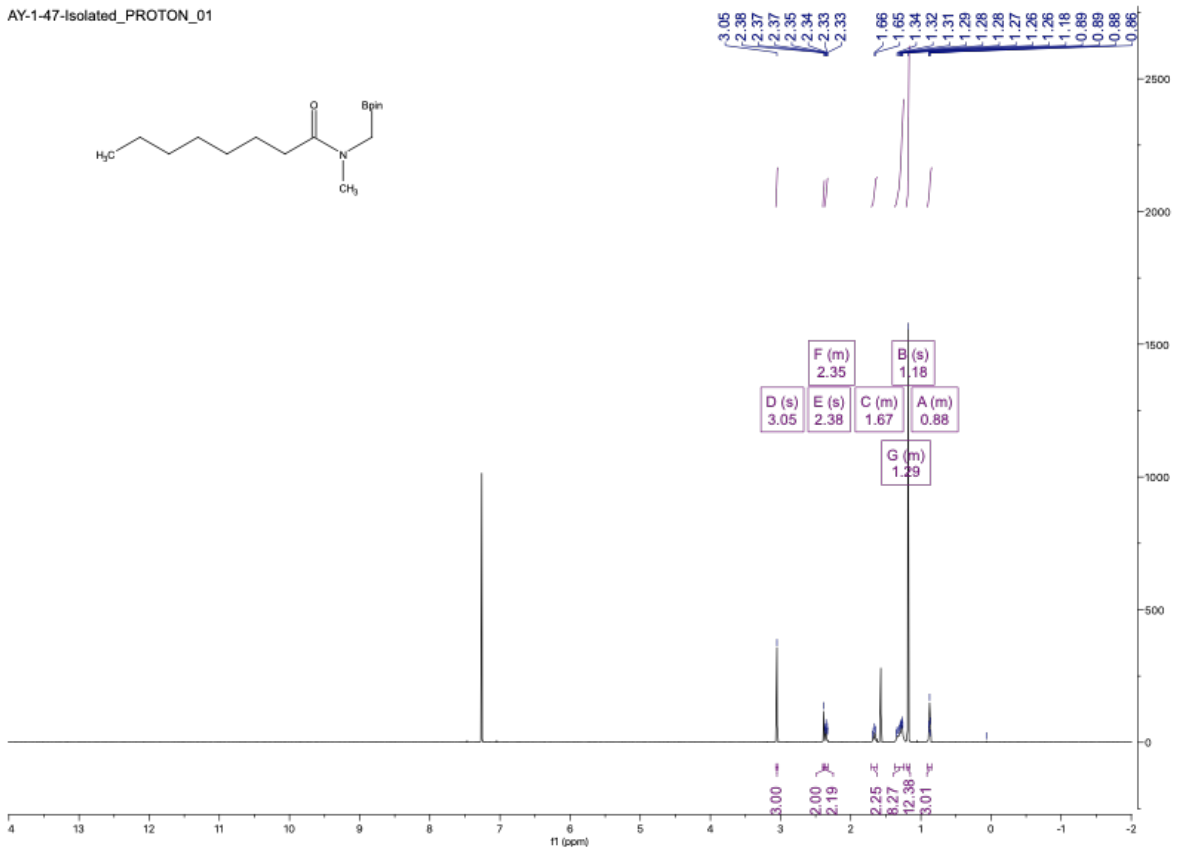


Figure 29: ^{1}H NMR ($CDCl_3$, 500 MHz) 3g

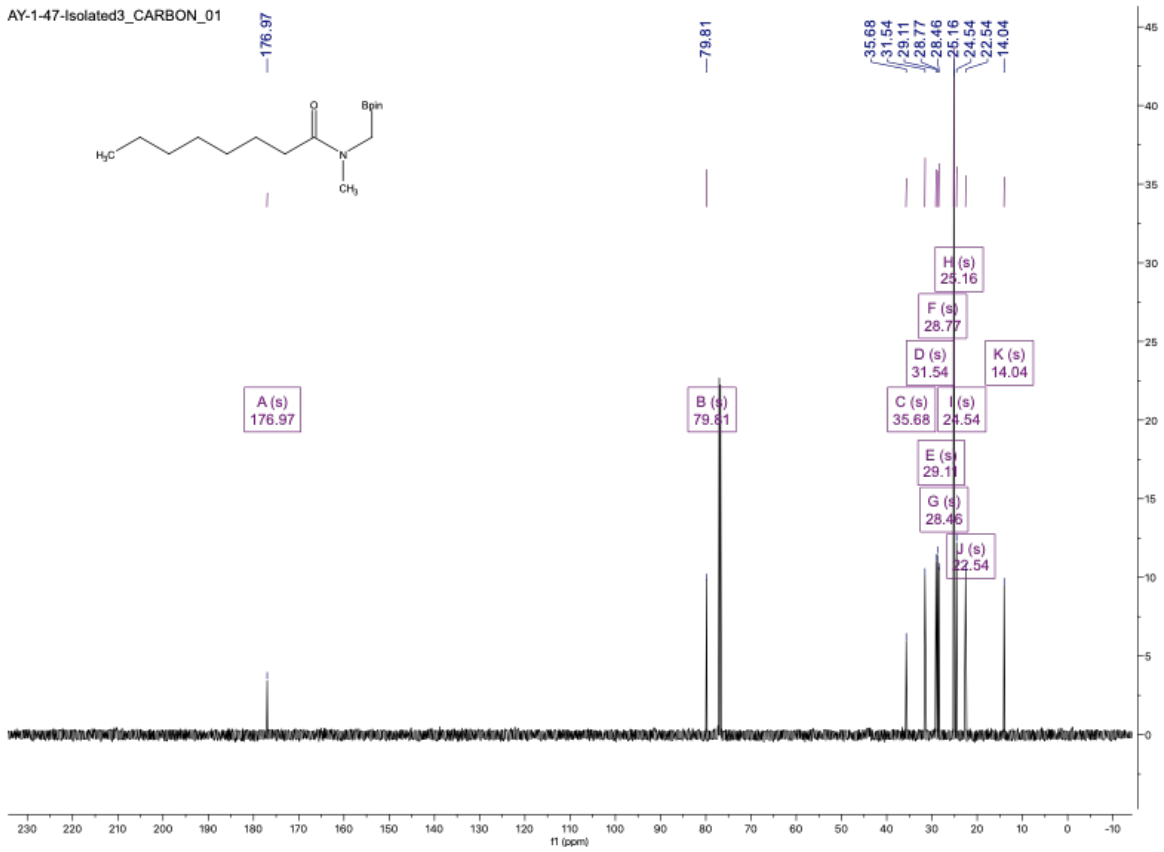


Figure 30: ^{13}C NMR (125 MHz, $CDCl_3$) 3g

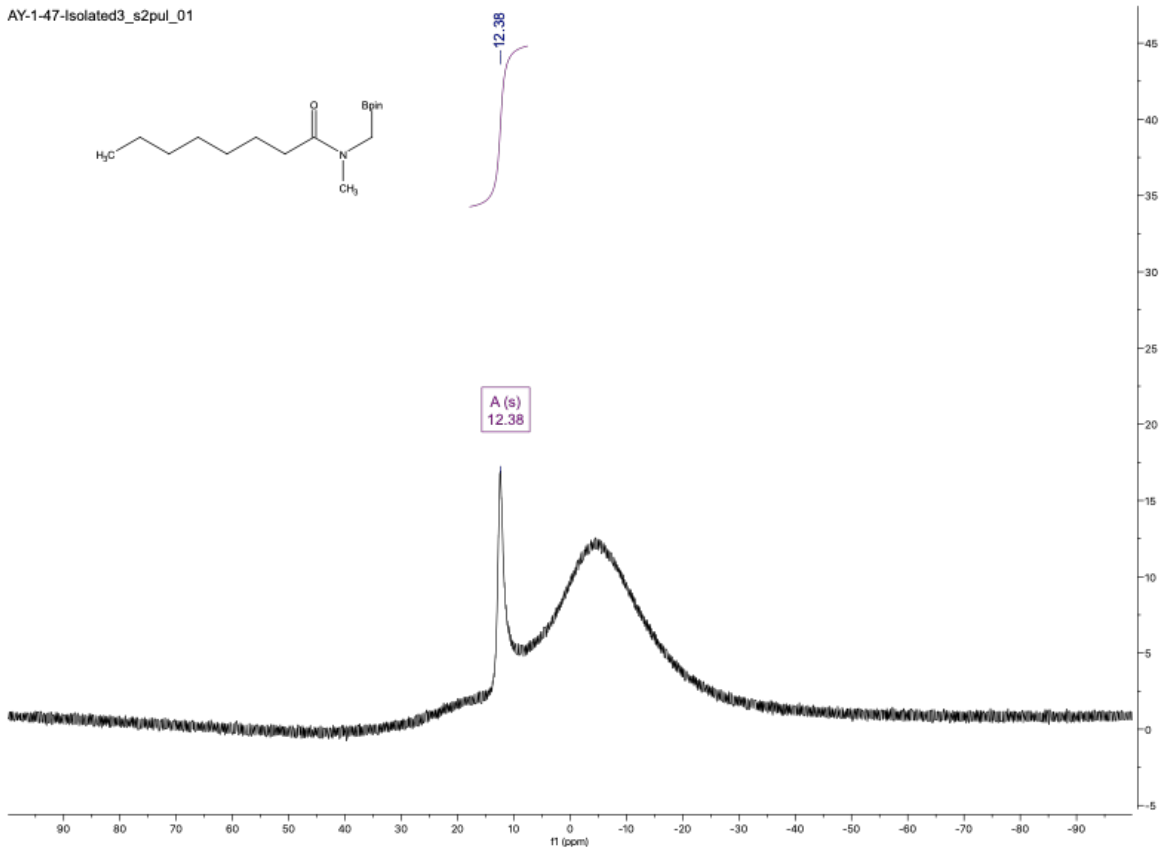


Figure 31: ^{11}B NMR ($CDCl_3$, 160 MHz) 3g

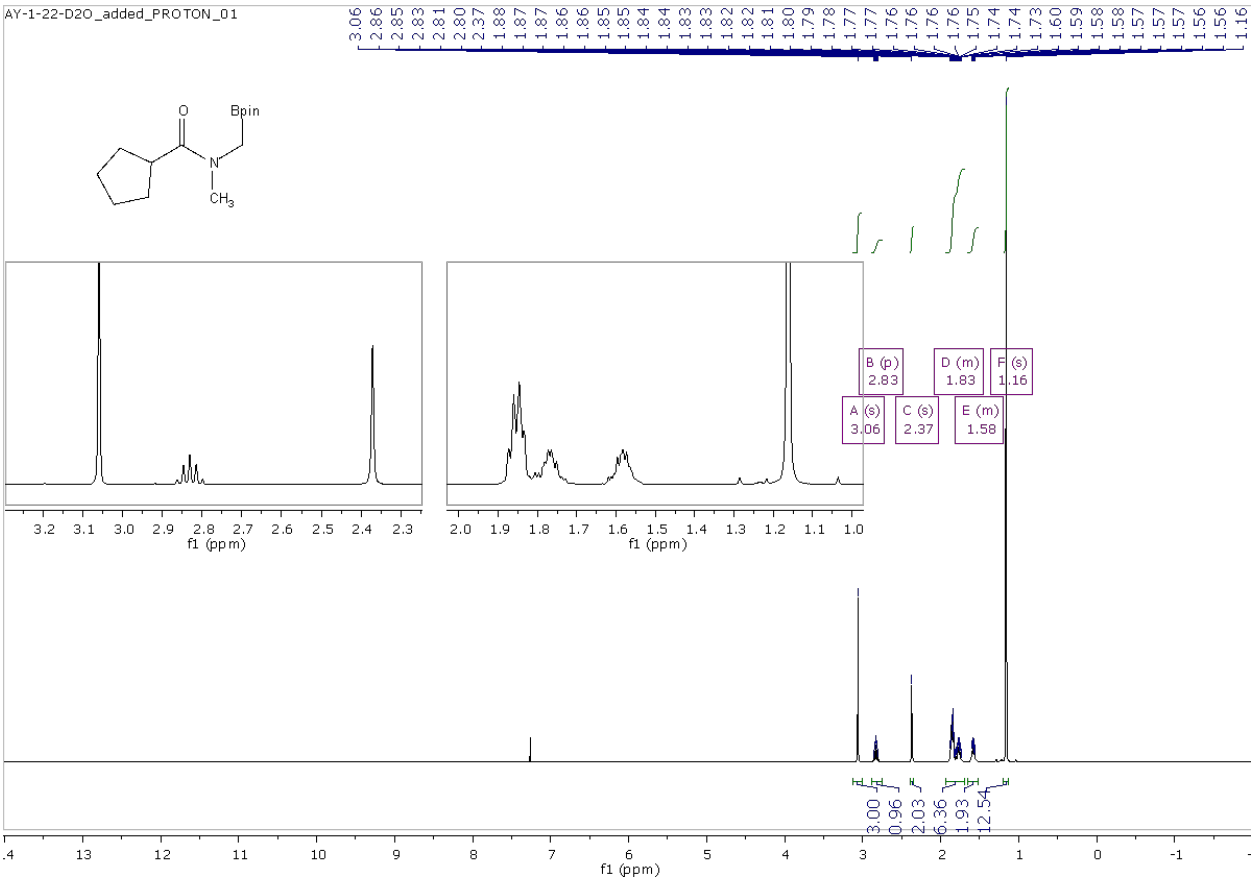


Figure 32: ^{1}H NMR ($CDCl_3$, 500 MHz) 3h

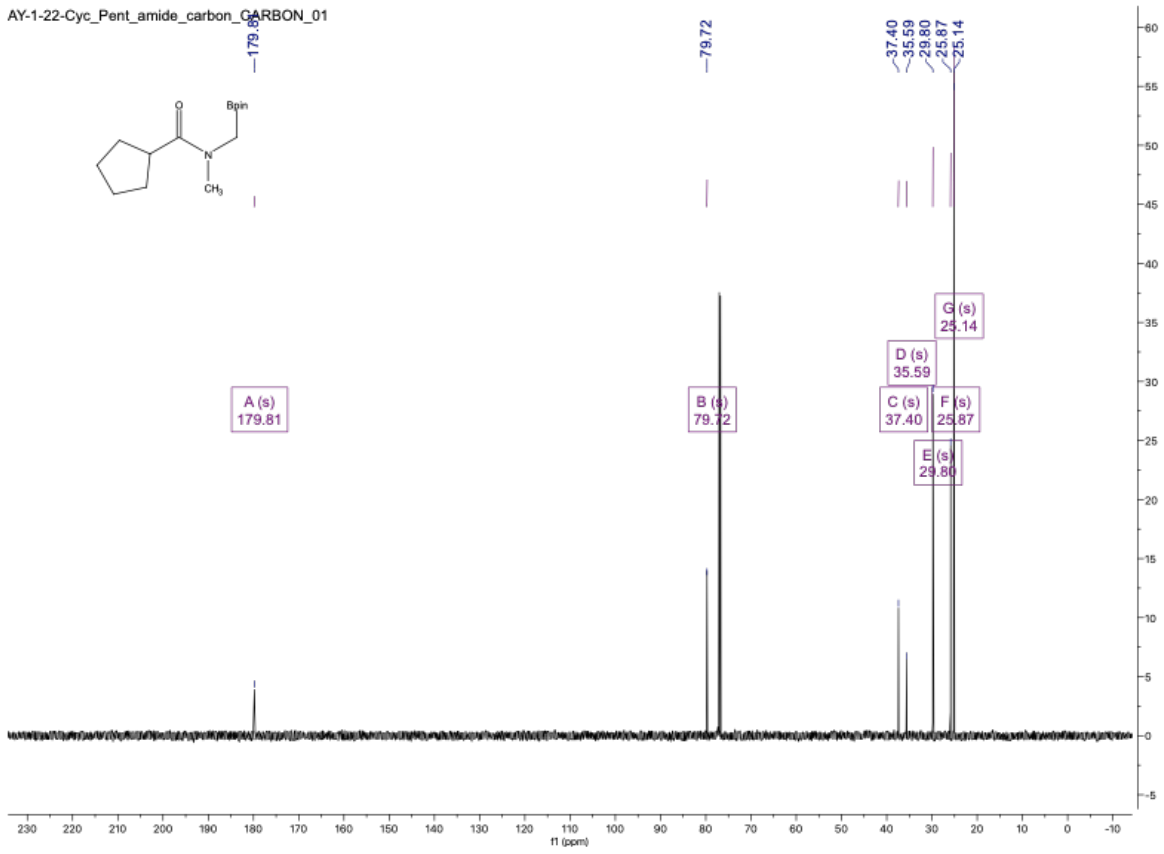


Figure 33: ^{13}C NMR (125 MHz, $CDCl_3$) 3h

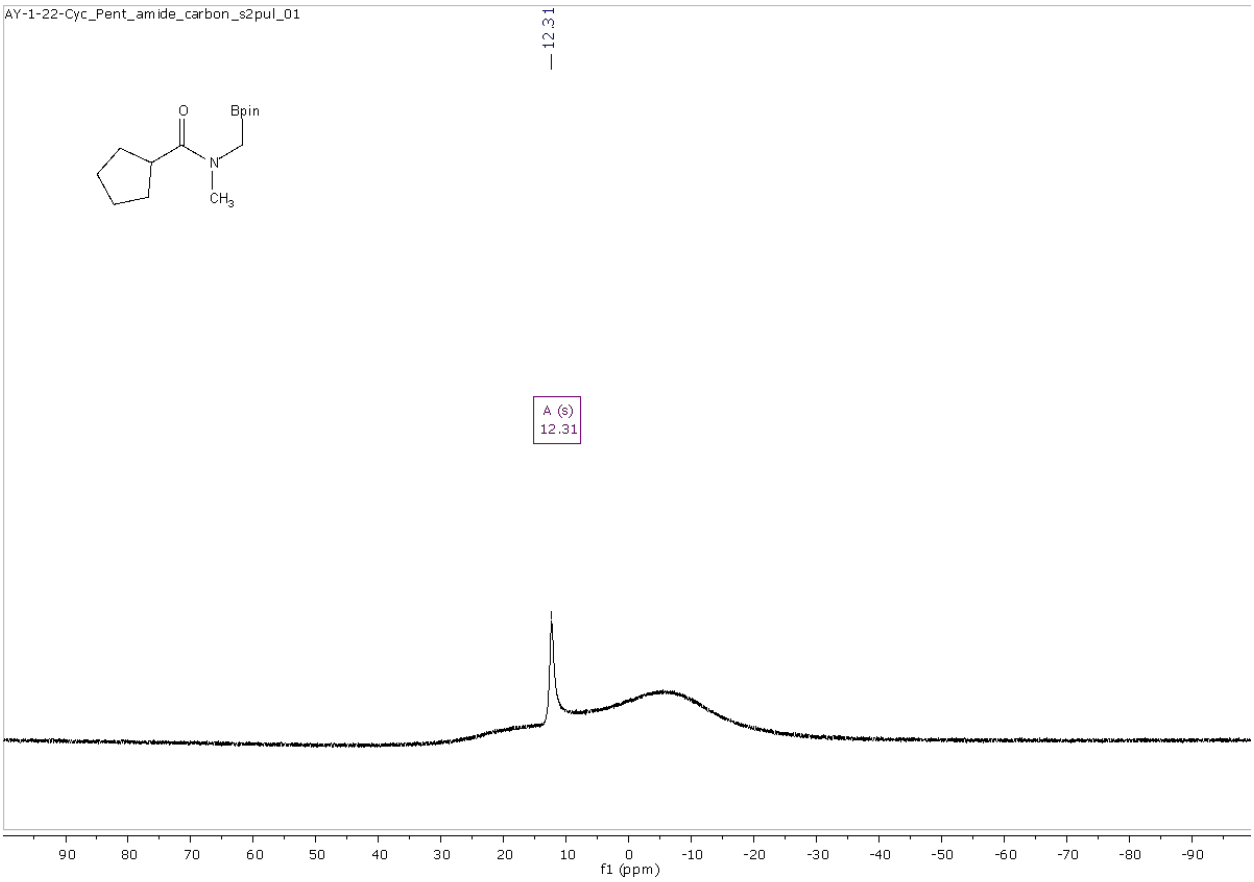


Figure 34: ^{11}B NMR ($CDCl_3$, 160 MHz) 3h

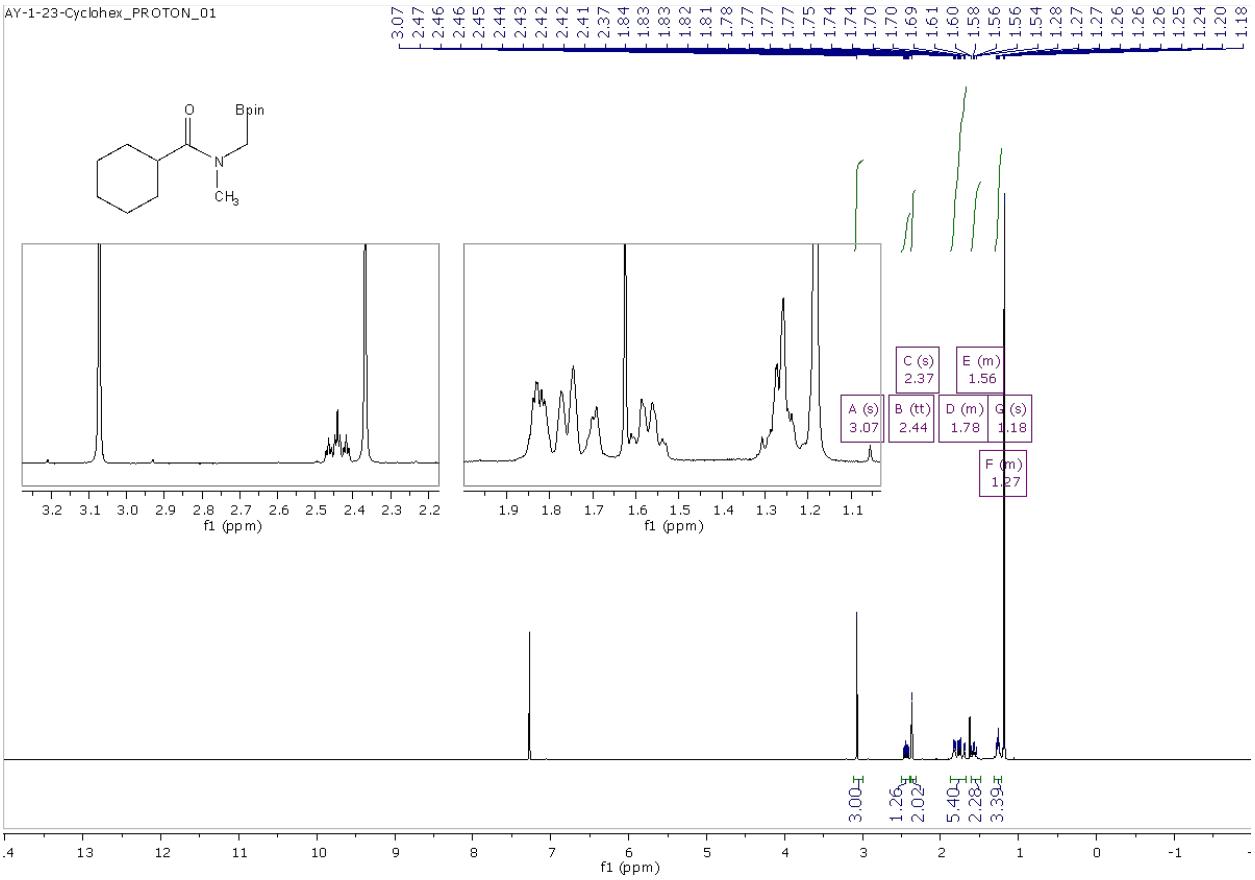


Figure 35: ^{1}H NMR ($CDCl_3$, 500 MHz) 3i

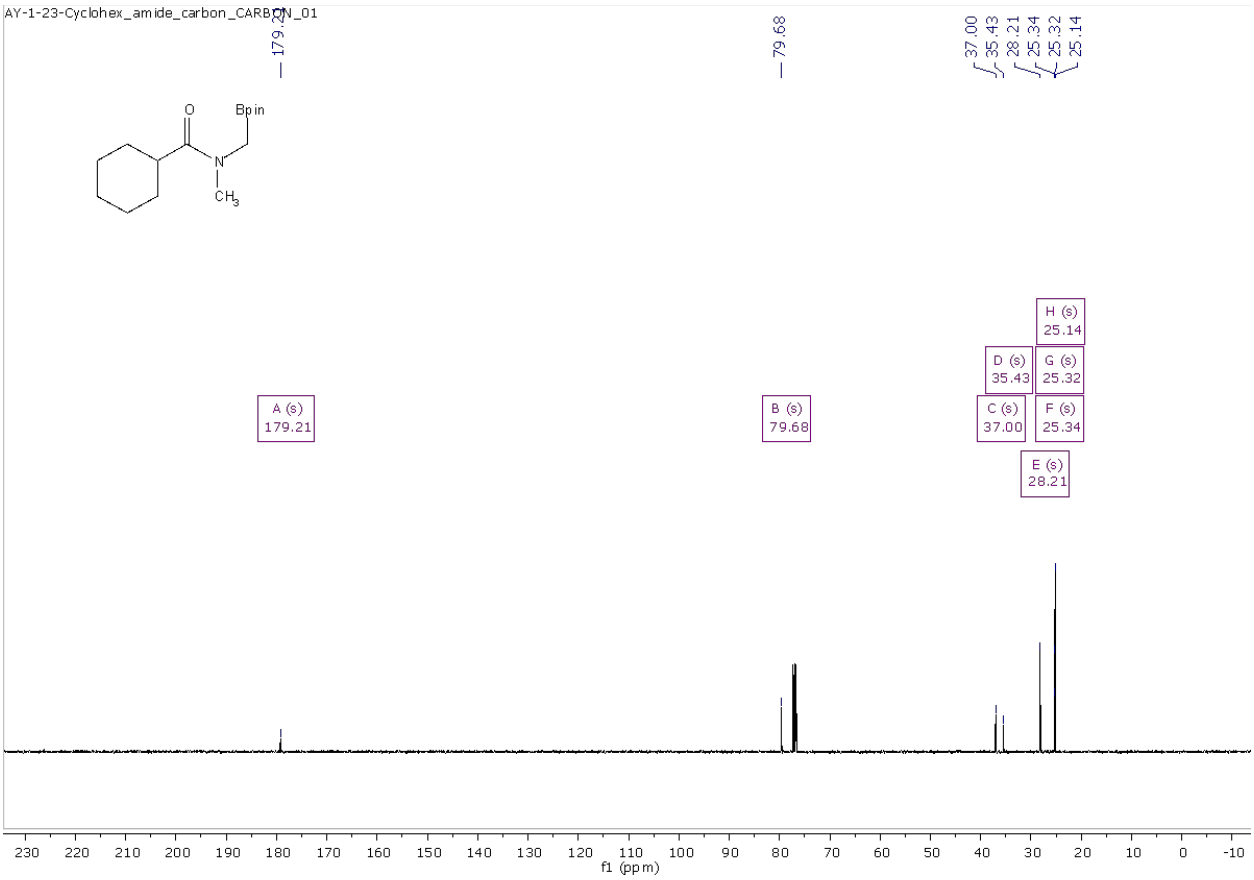


Figure 36: ^{13}C NMR (125 MHz, $CDCl_3$) 3i

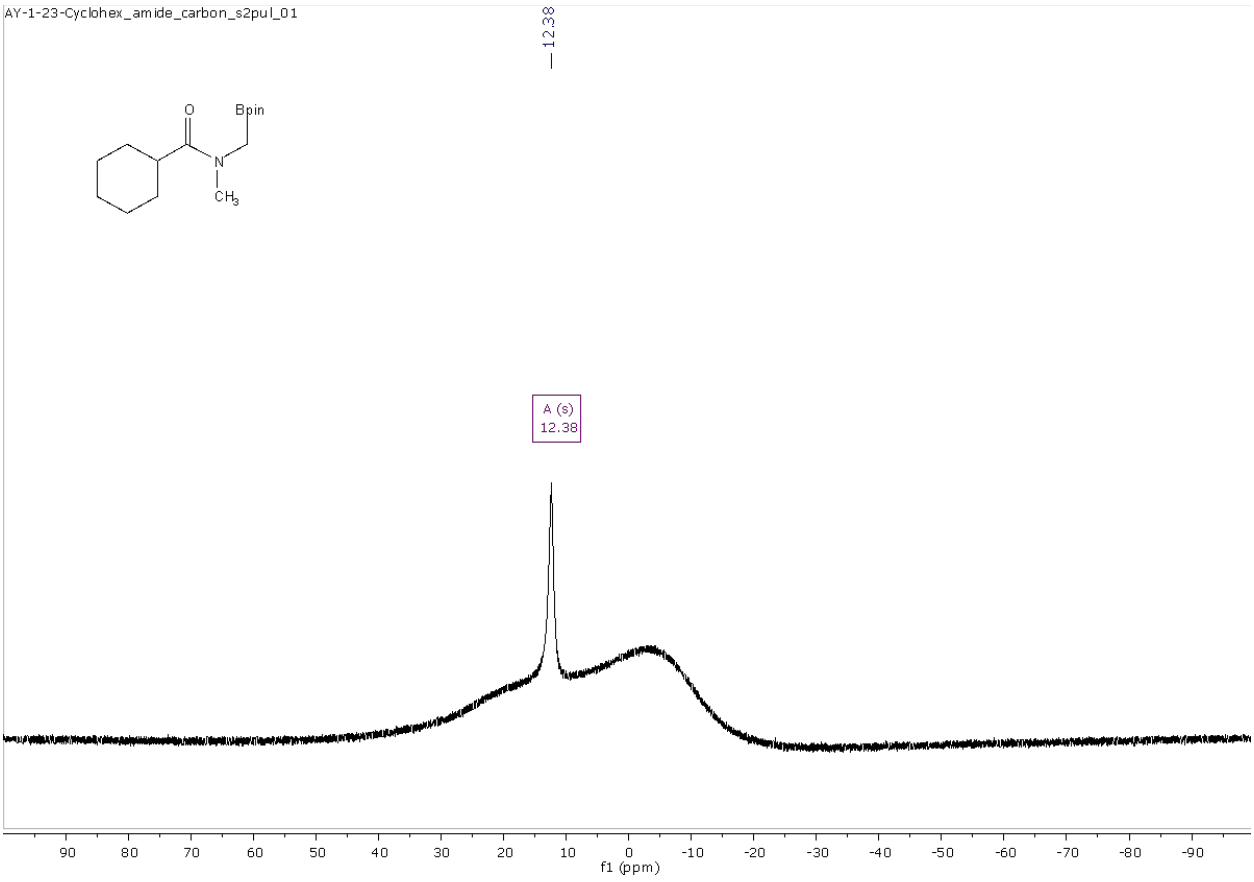


Figure 37: ^{11}B NMR ($CDCl_3$, 160 MHz) 3i

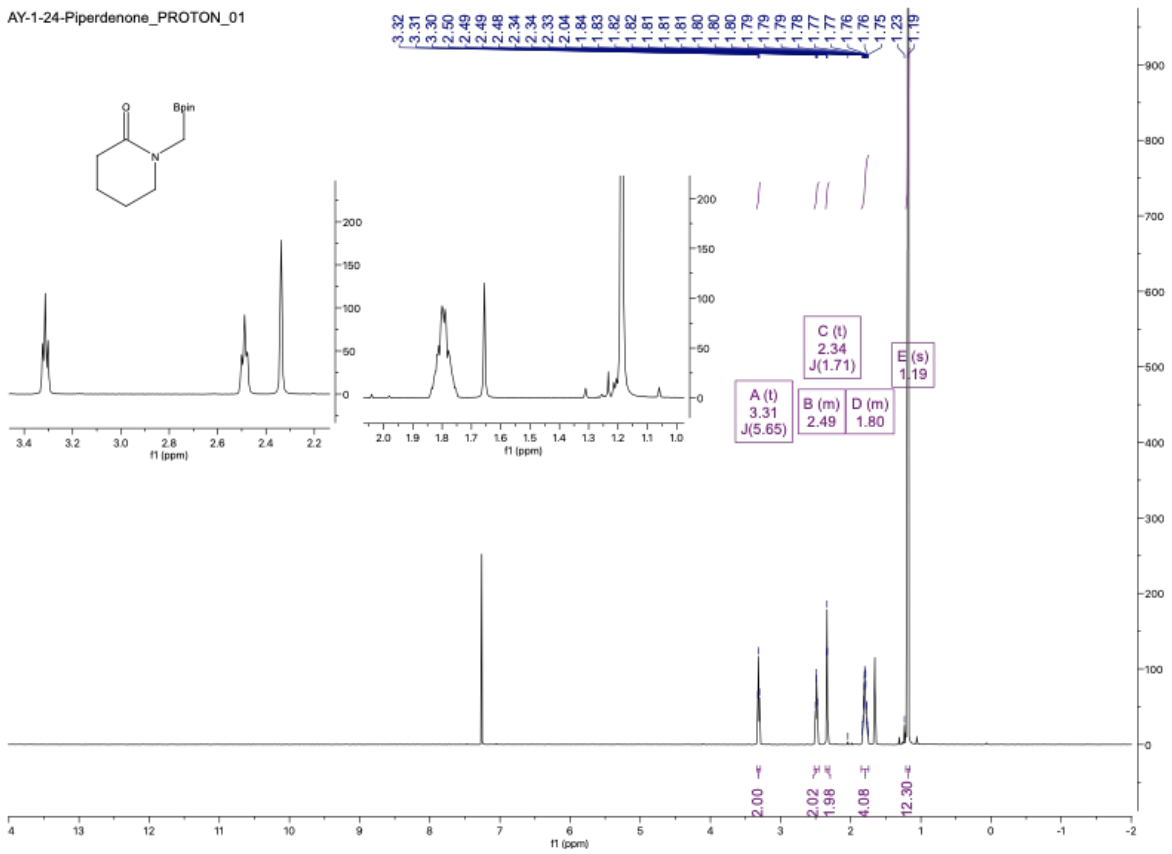


Figure 38: ^{1}H NMR ($CDCl_3$, 500 MHz) 3k

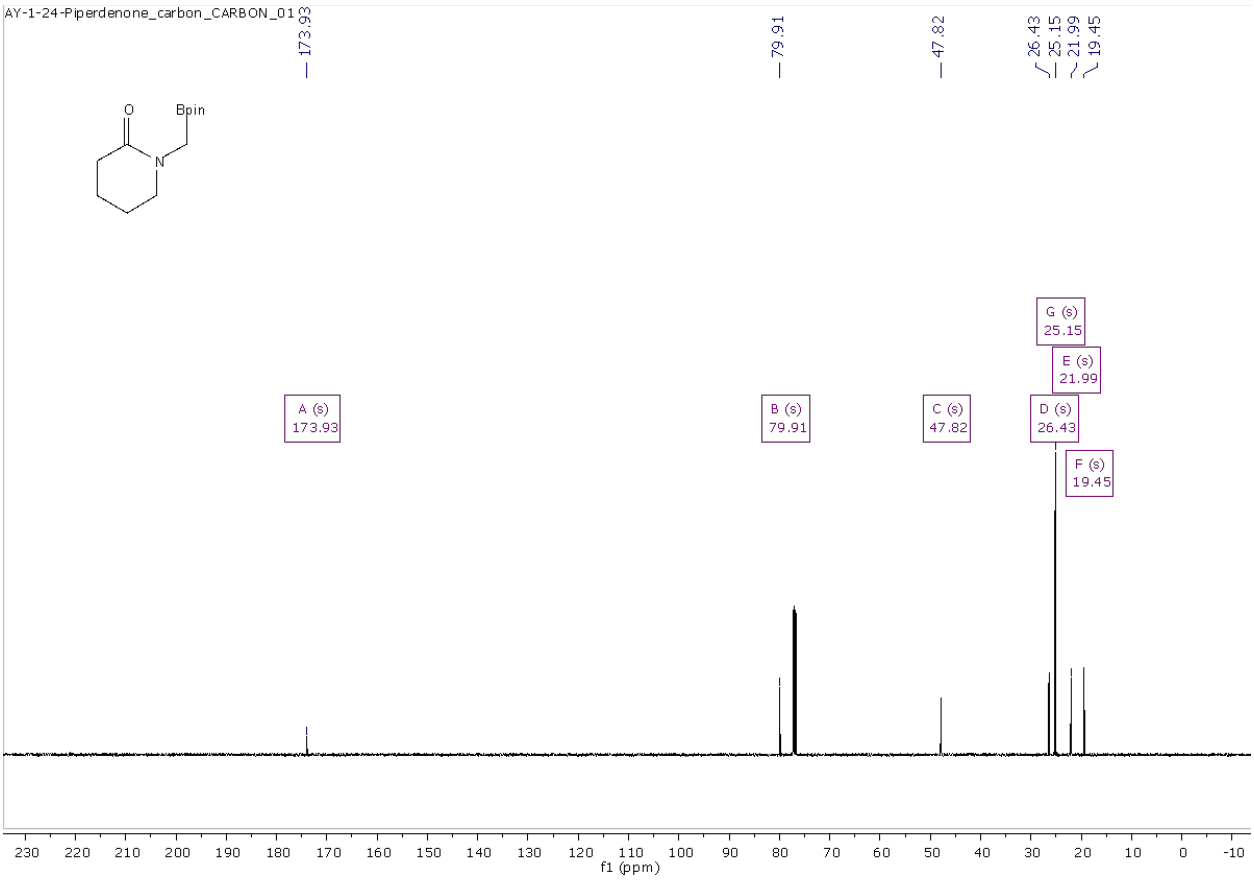


Figure 39: ^{13}C NMR (125 MHz, $CDCl_3$) 3k

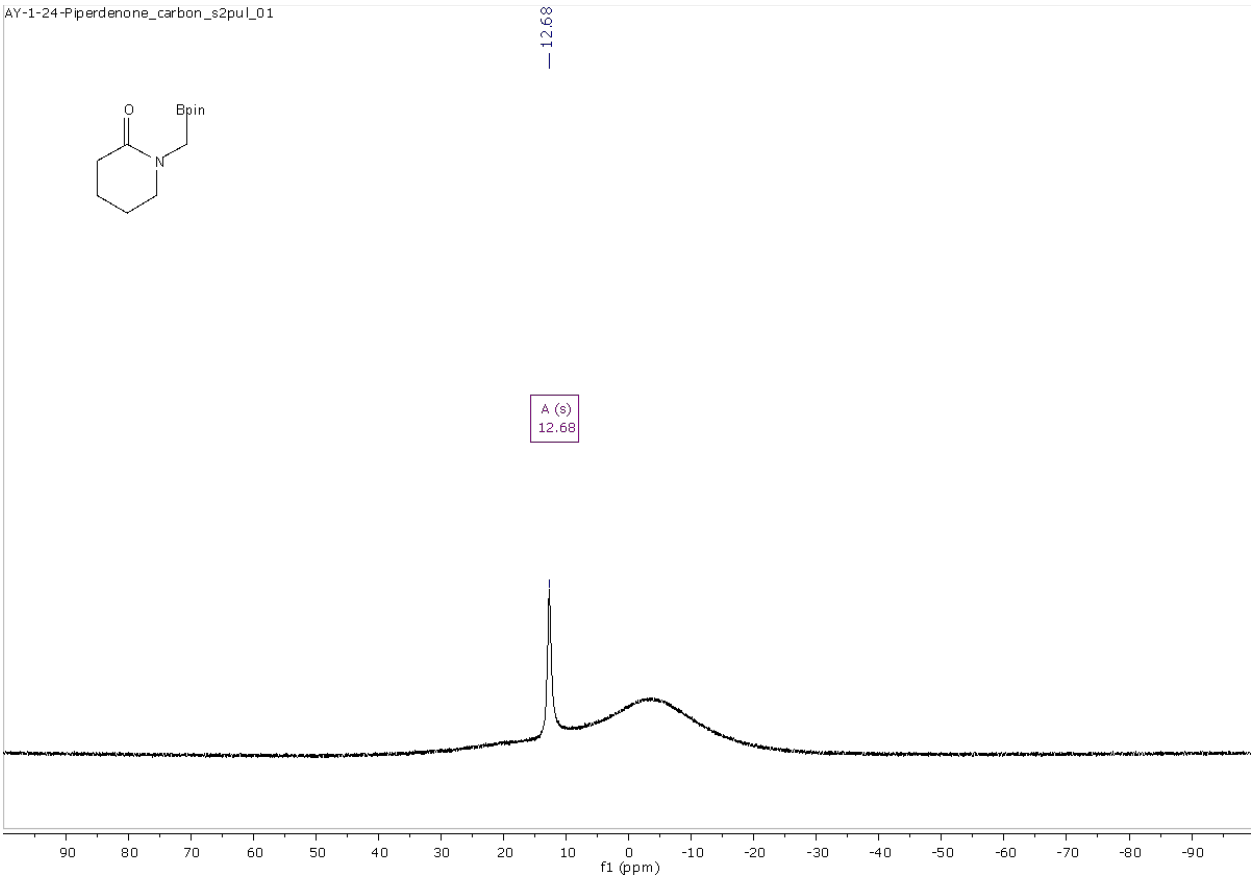


Figure 40: ^{11}B NMR ($CDCl_3$, 160 MHz) 3k

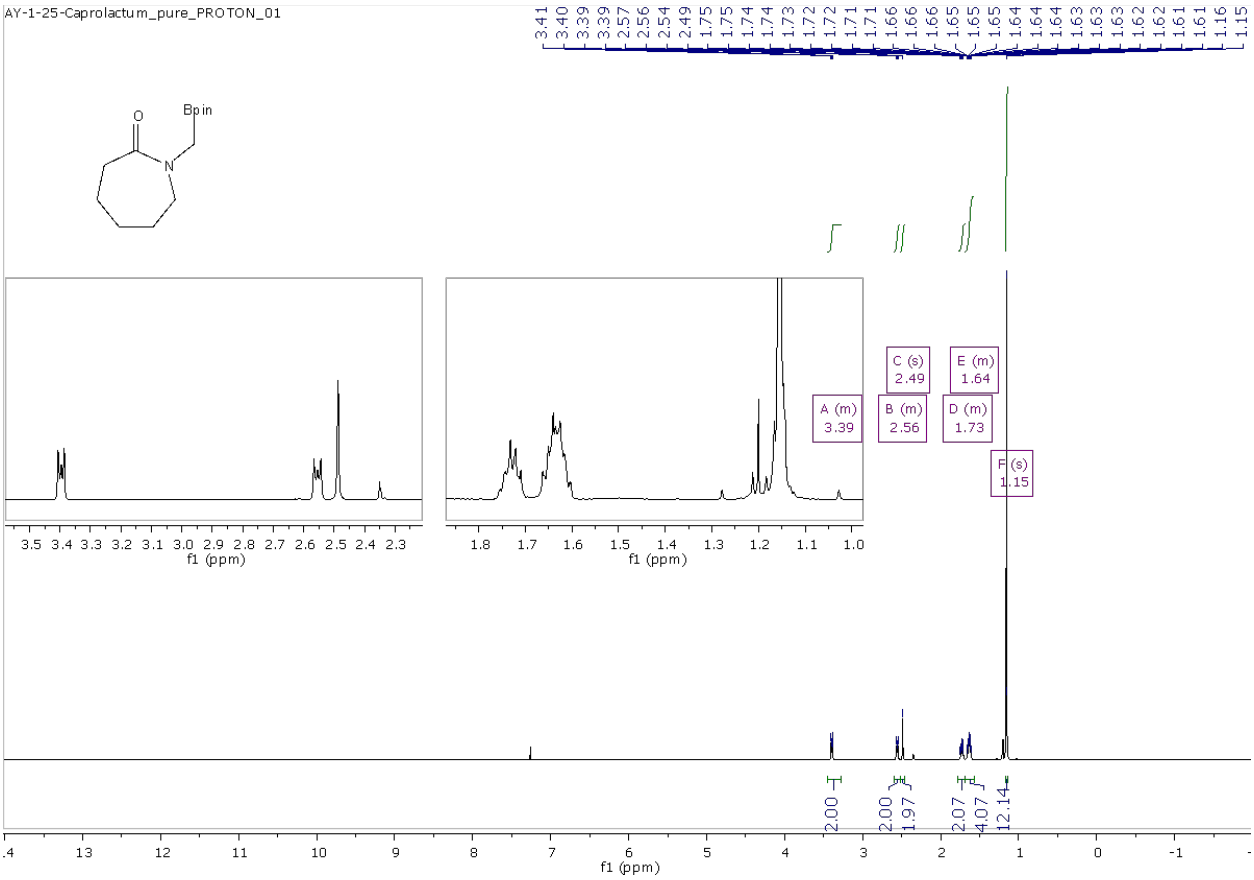


Figure 41: ^{1}H NMR ($CDCl_3$, 500 MHz) 3l

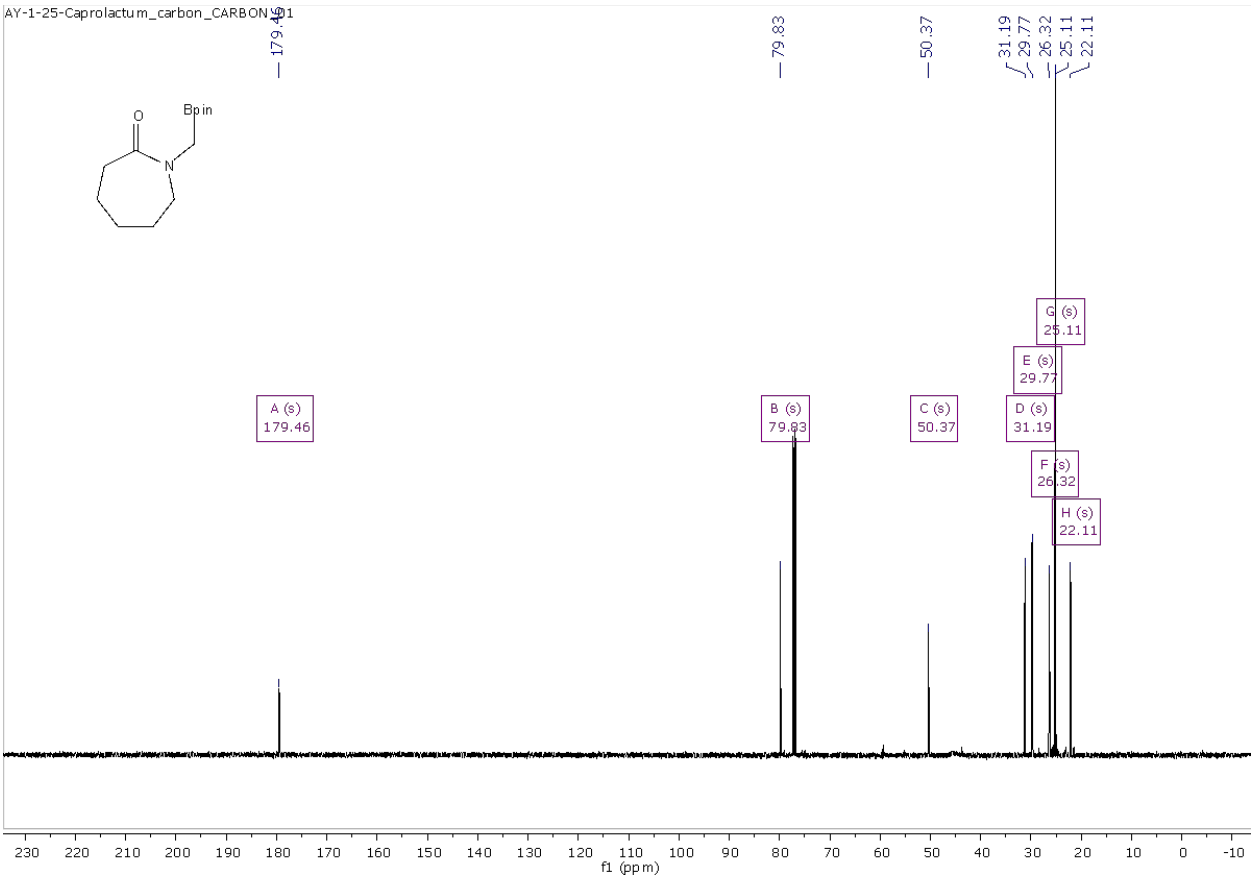


Figure 42: ^{13}C NMR (125 MHz, $CDCl_3$) 3l

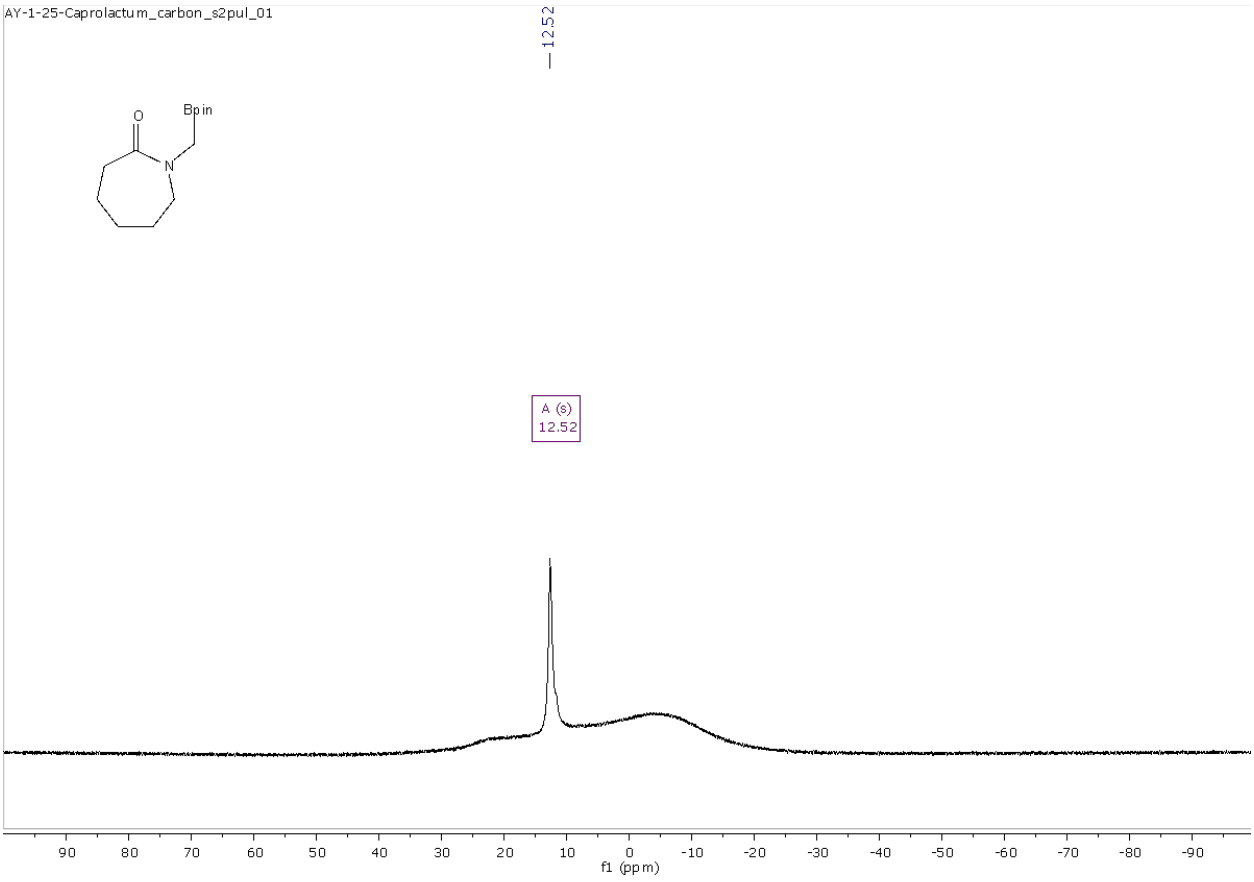


Figure 43: ^{11}B NMR ($CDCl_3$, 160 MHz) 3l

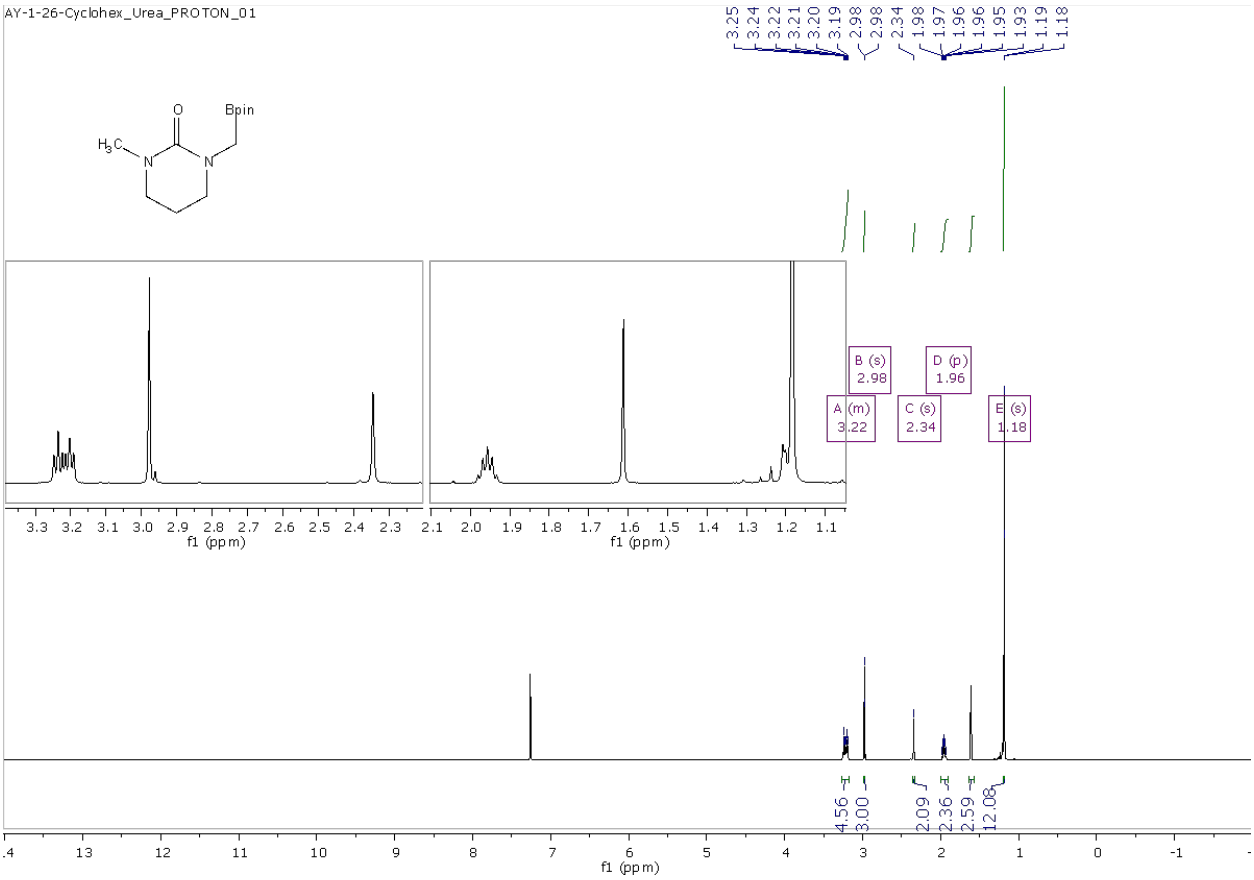


Figure 44: ^{1}H NMR ($CDCl_3$, 500 MHz) 3o

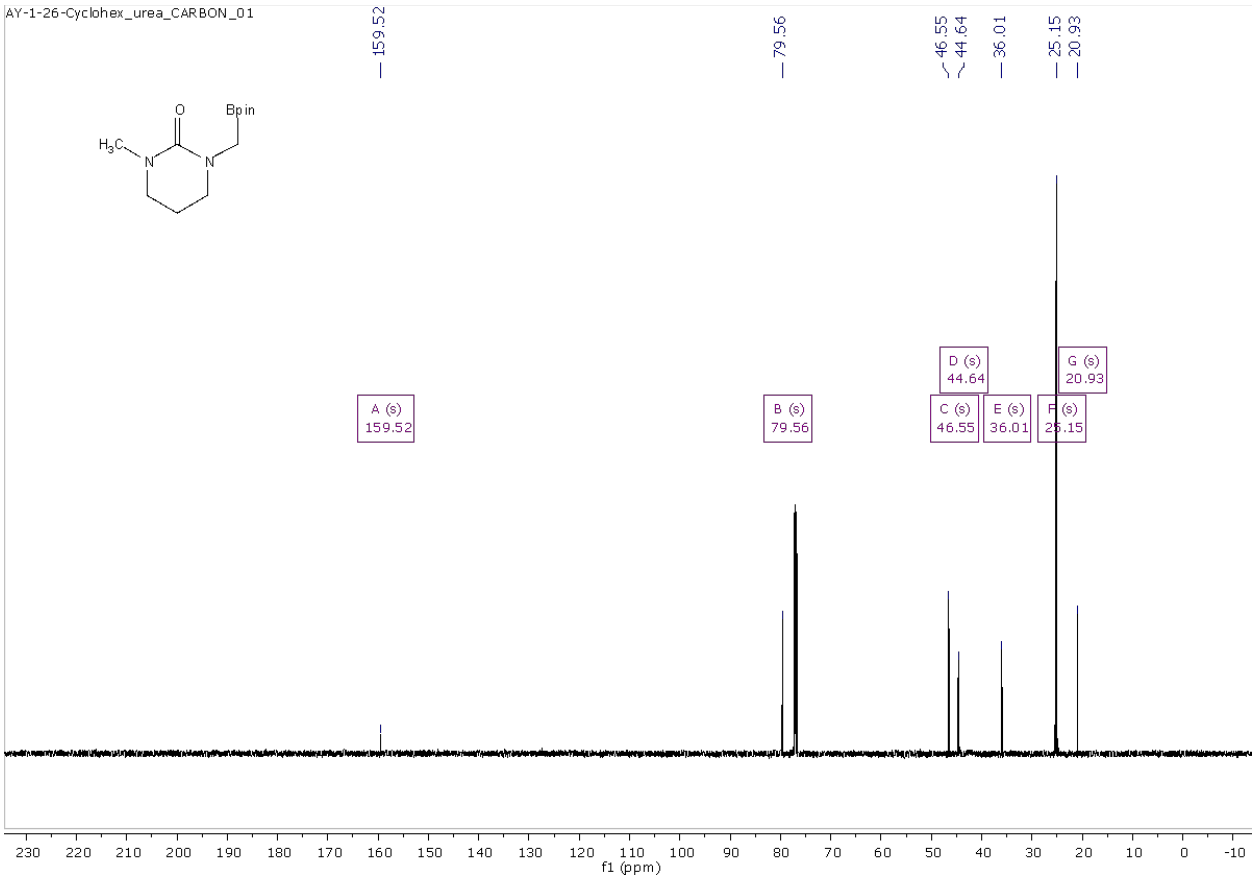


Figure 45: ^{13}C NMR (125 MHz, $CDCl_3$) 3o

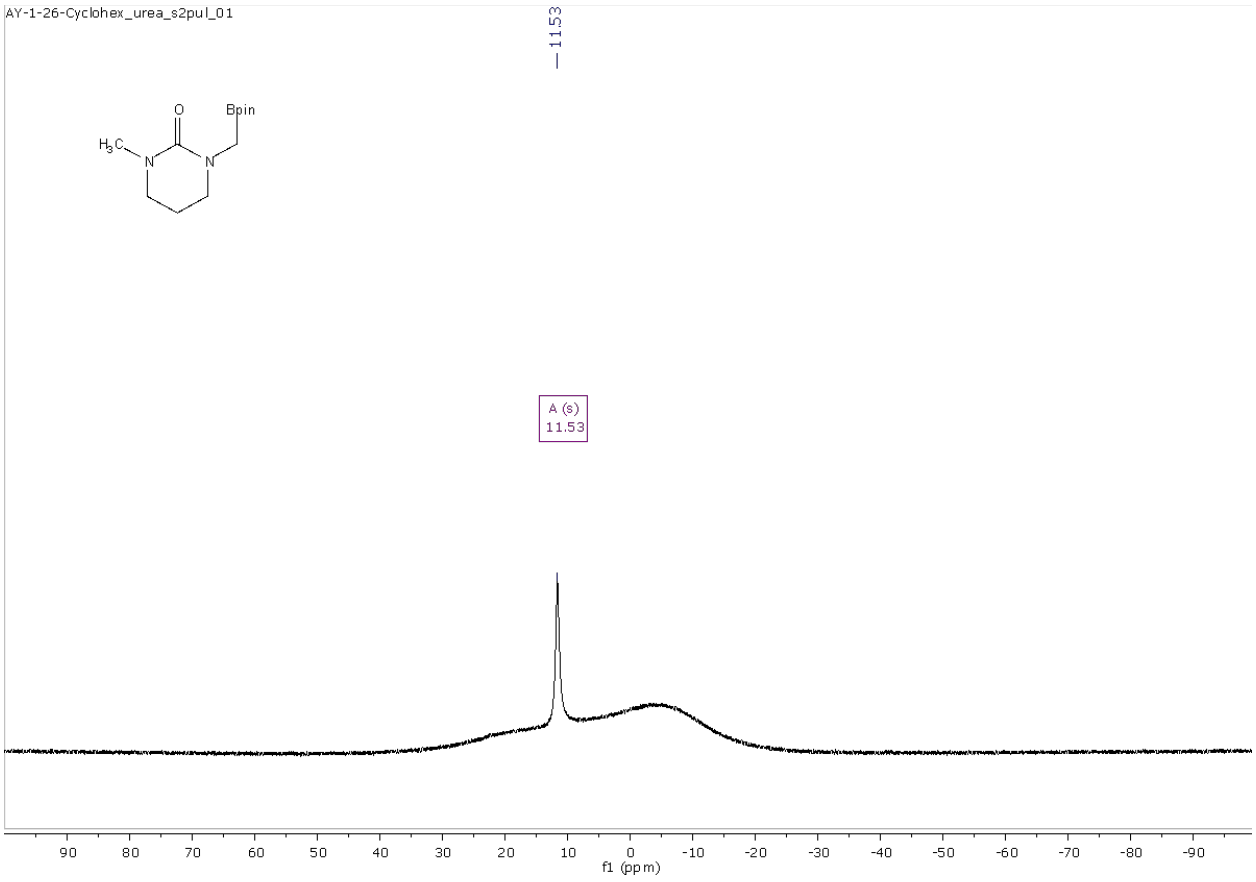


Figure 46: ^{11}B NMR ($CDCl_3$, 160 MHz) 3o

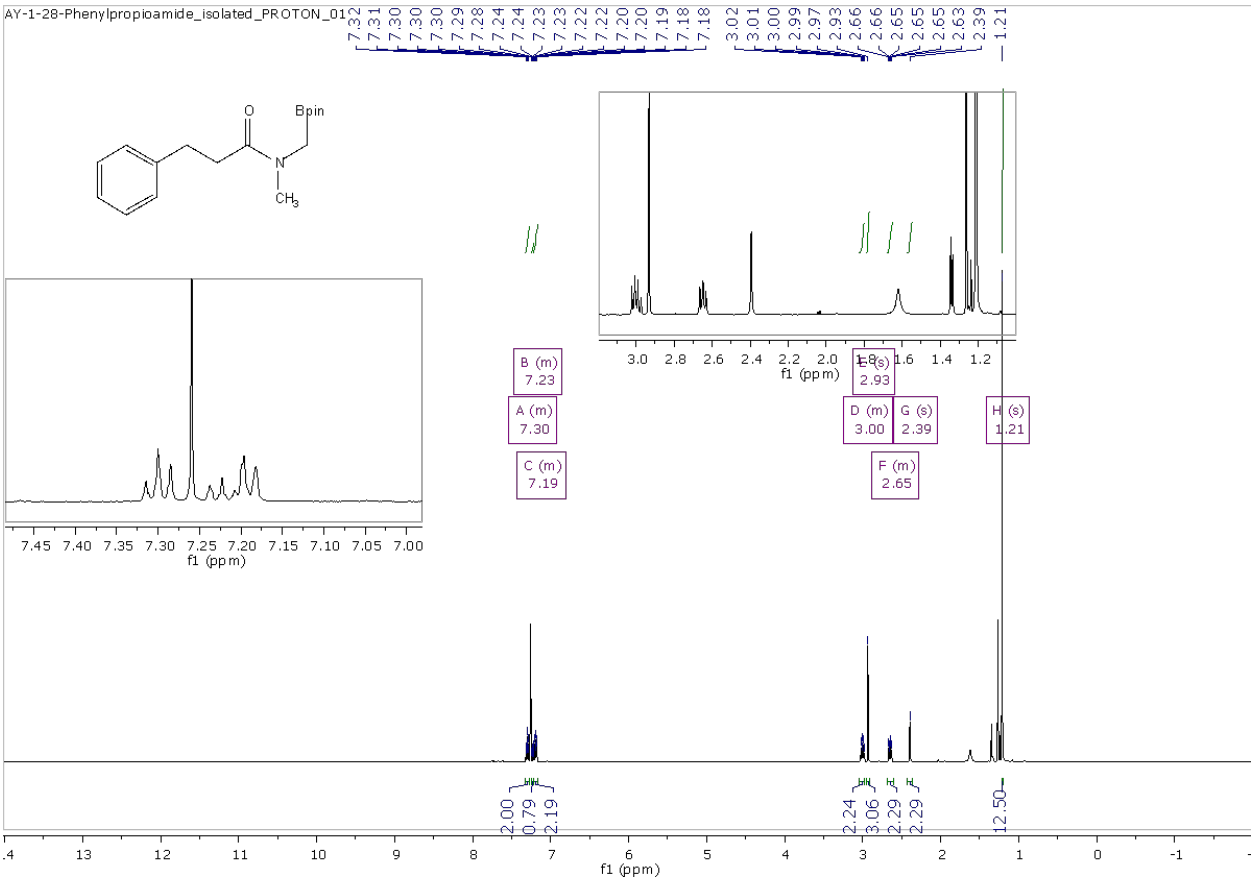


Figure 47: ^{1}H NMR ($CDCl_3$, 500 MHz) 3q

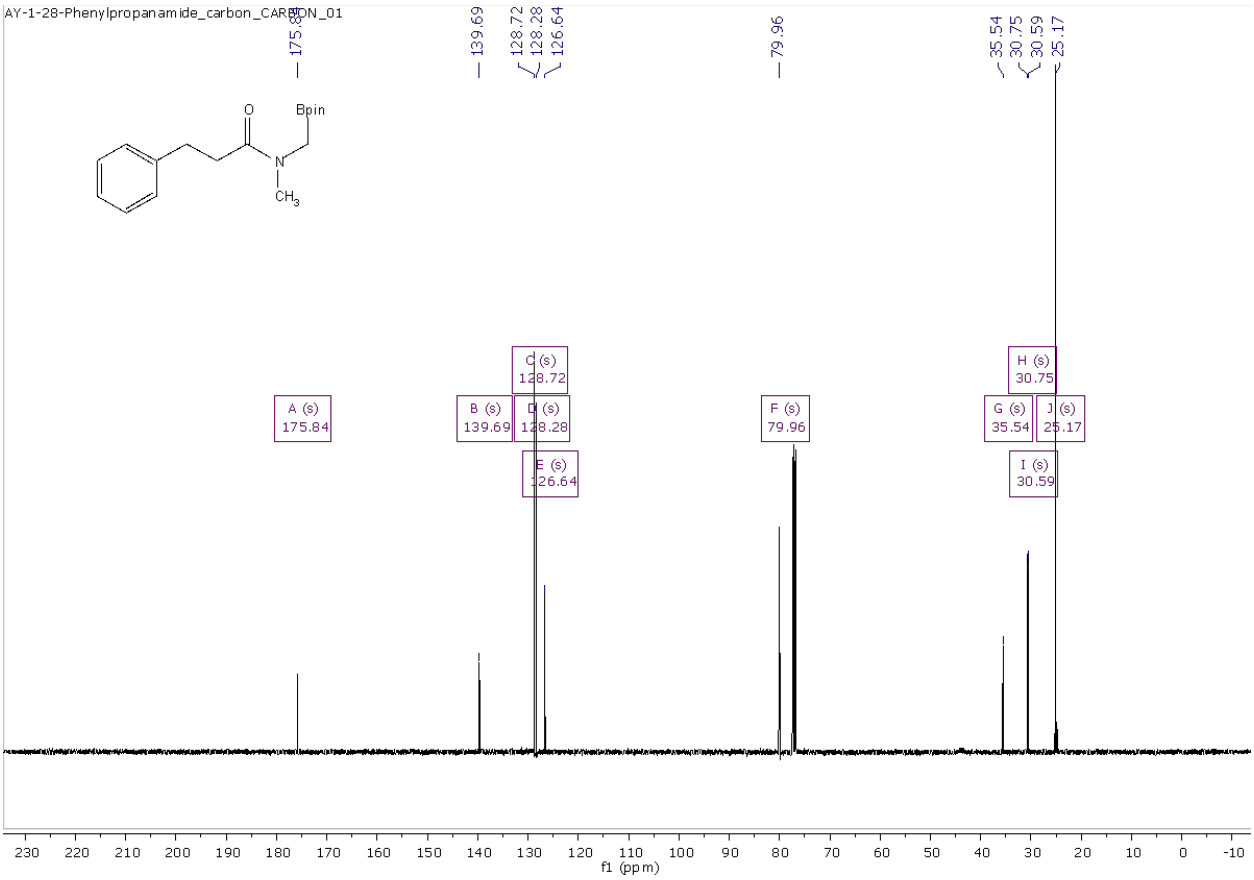


Figure 48: ^{13}C NMR (125 MHz, $CDCl_3$) 3q

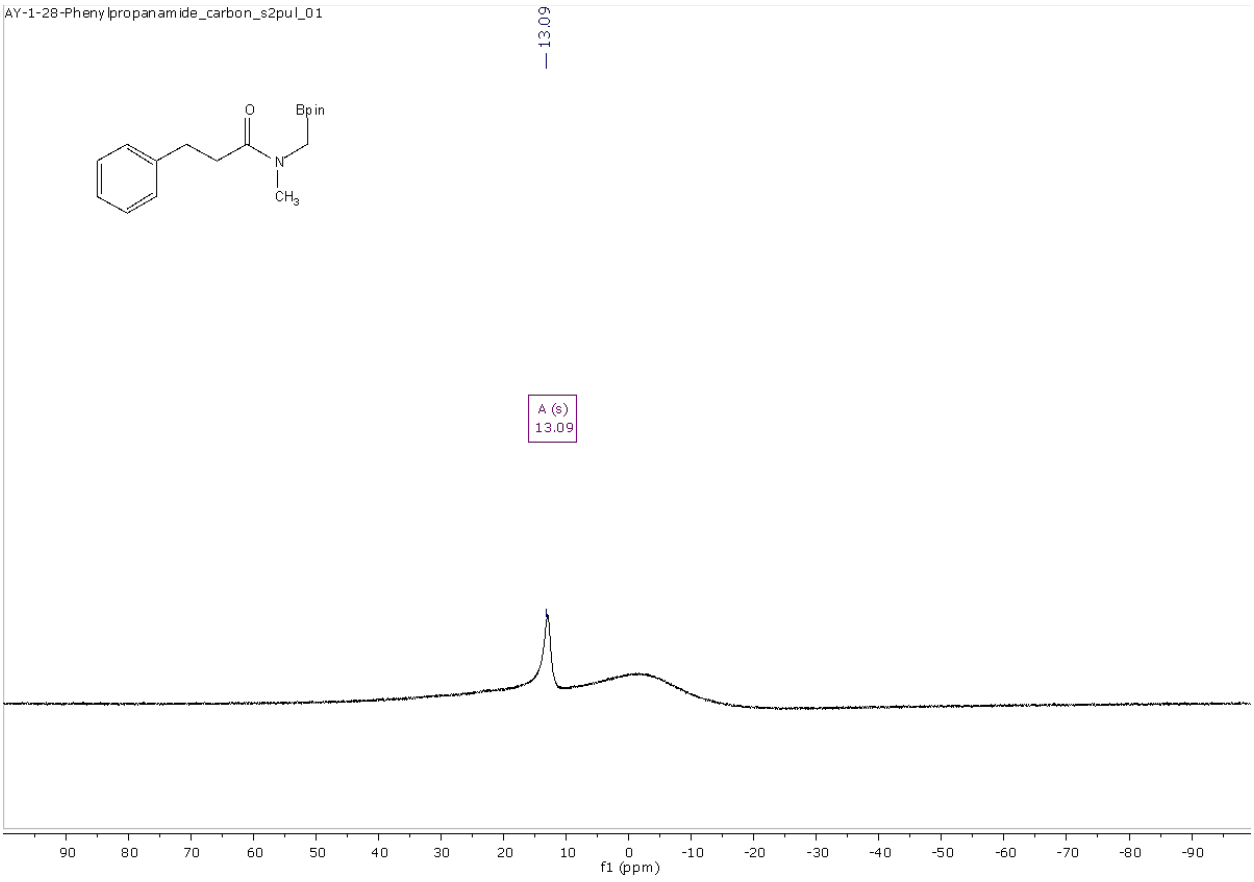


Figure 49: ^{11}B NMR ($CDCl_3$, 160 MHz) 3q

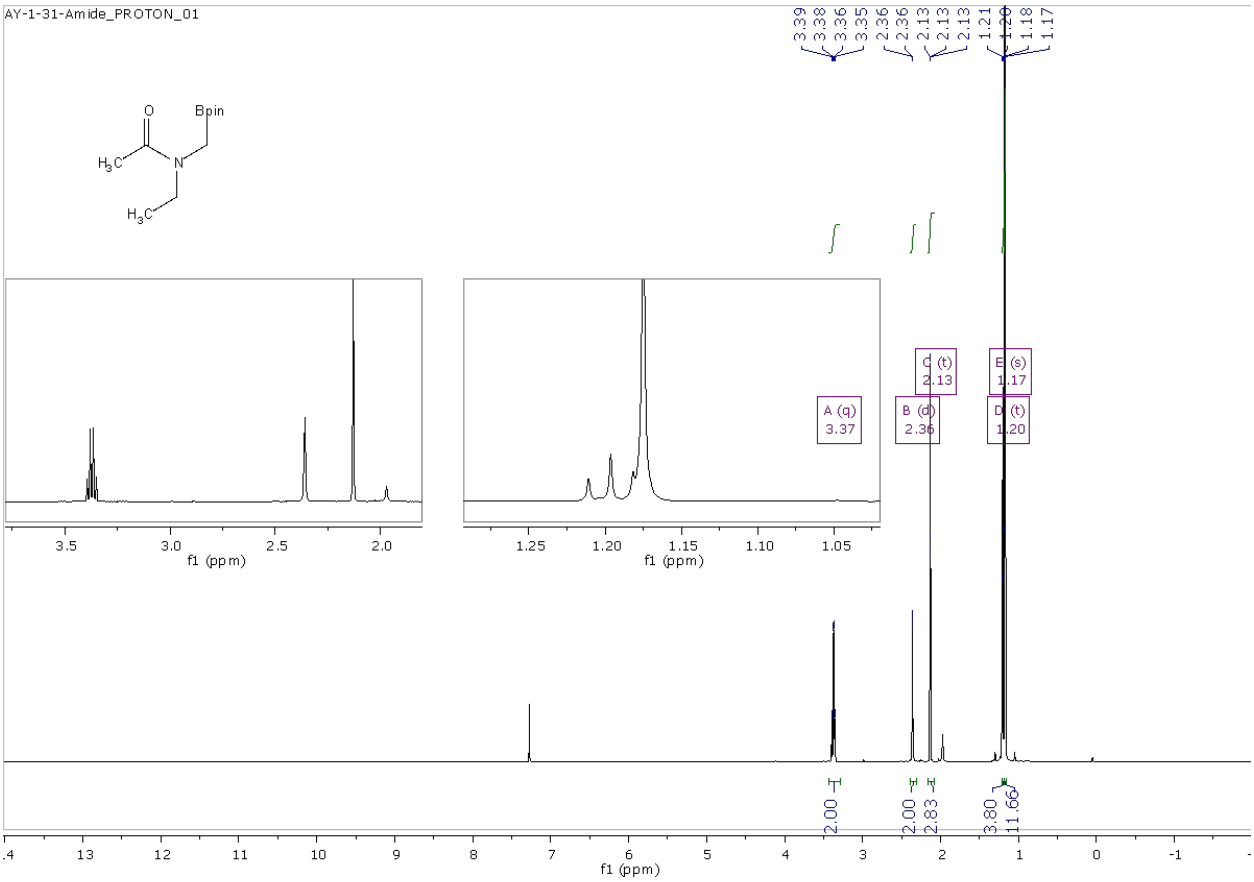


Figure 50: ^{1}H NMR ($CDCl_3$, 500 MHz) 3m

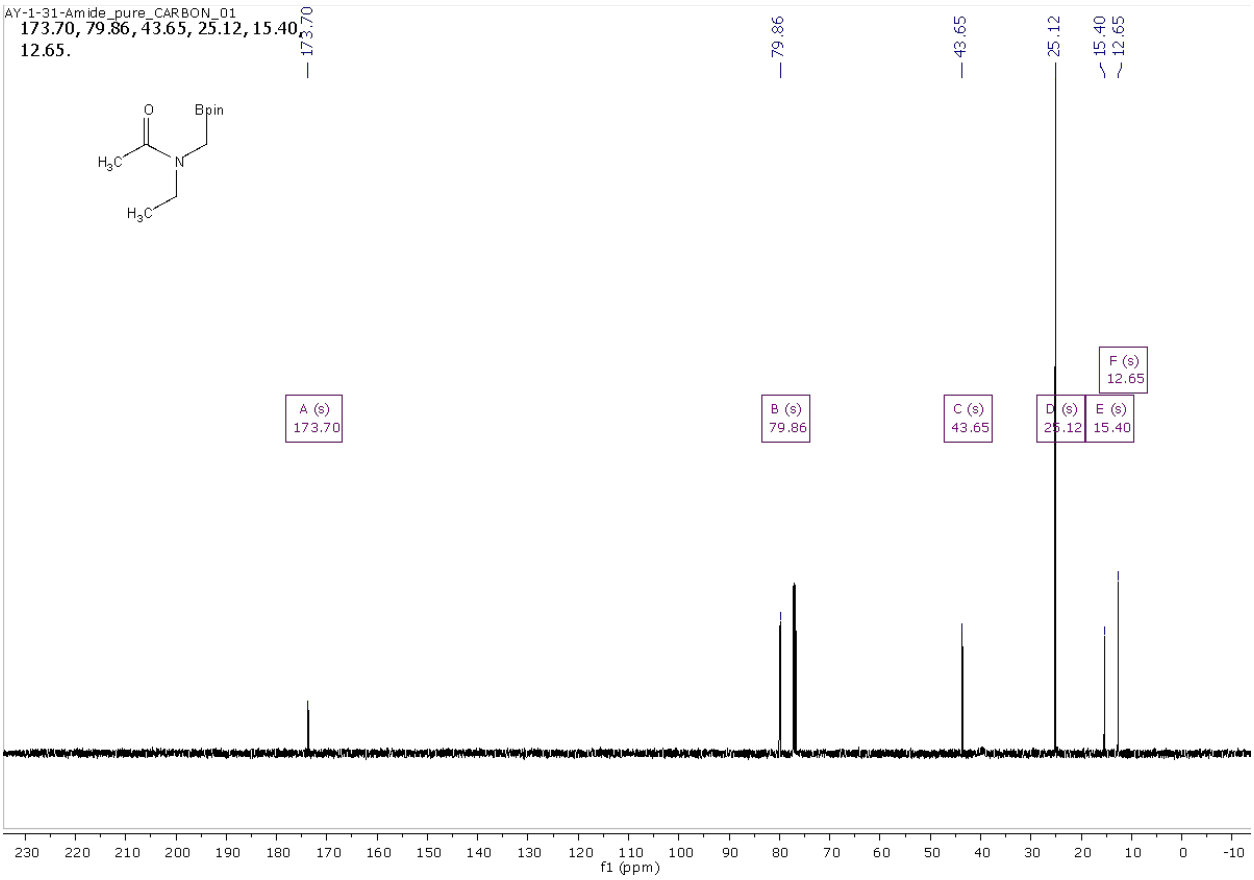


Figure 51: ^{13}C NMR (125 MHz, $CDCl_3$) 3m

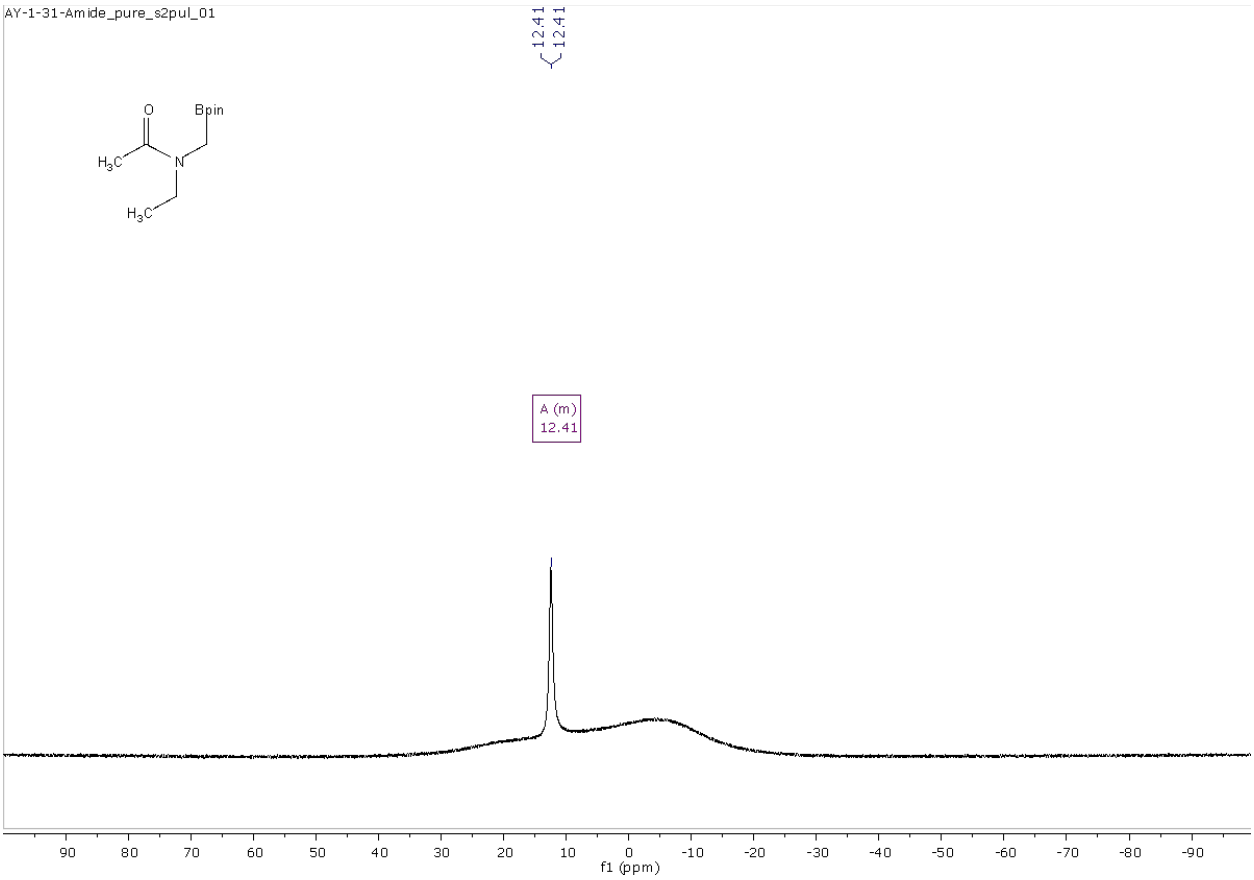


Figure 52: ^{11}B NMR ($CDCl_3$, 160 MHz) 3m

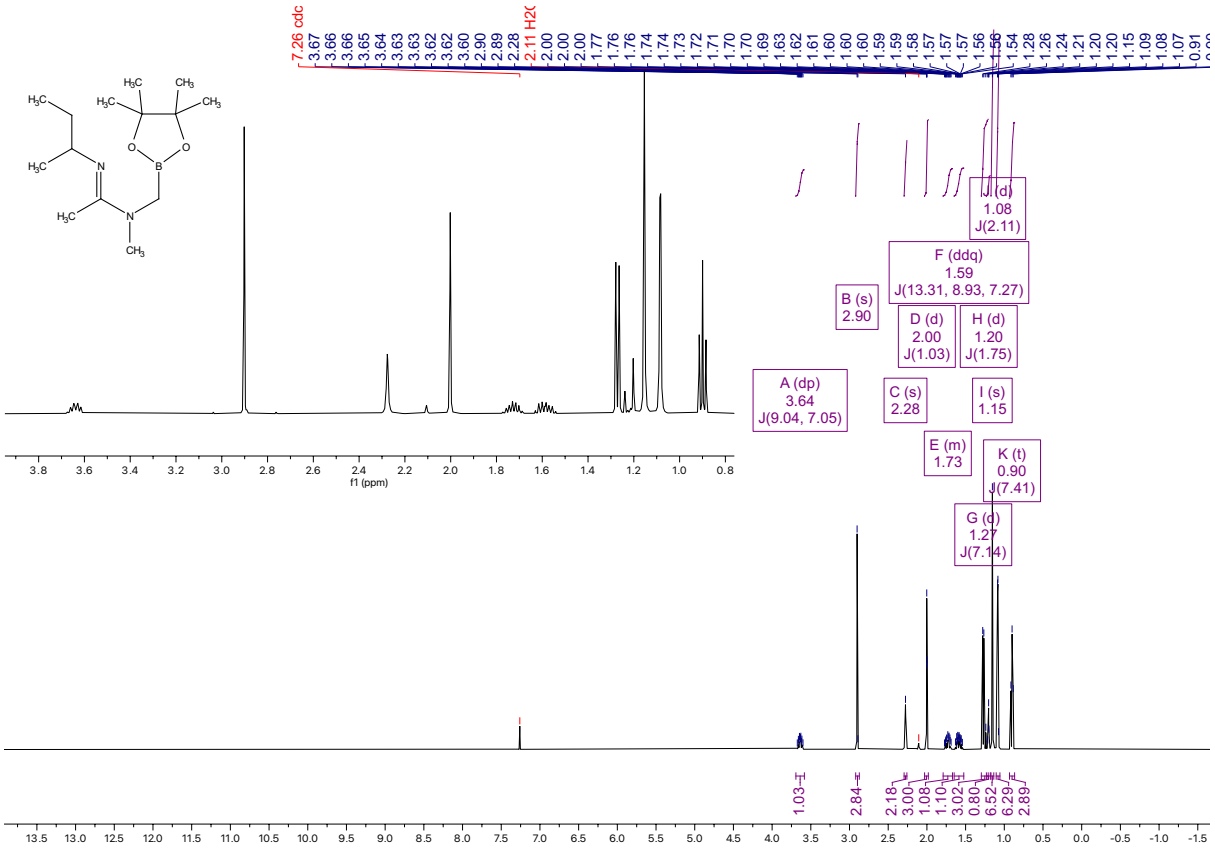


Figure 53: ^{1}H NMR ($CDCl_3$, 500 MHz) 4a

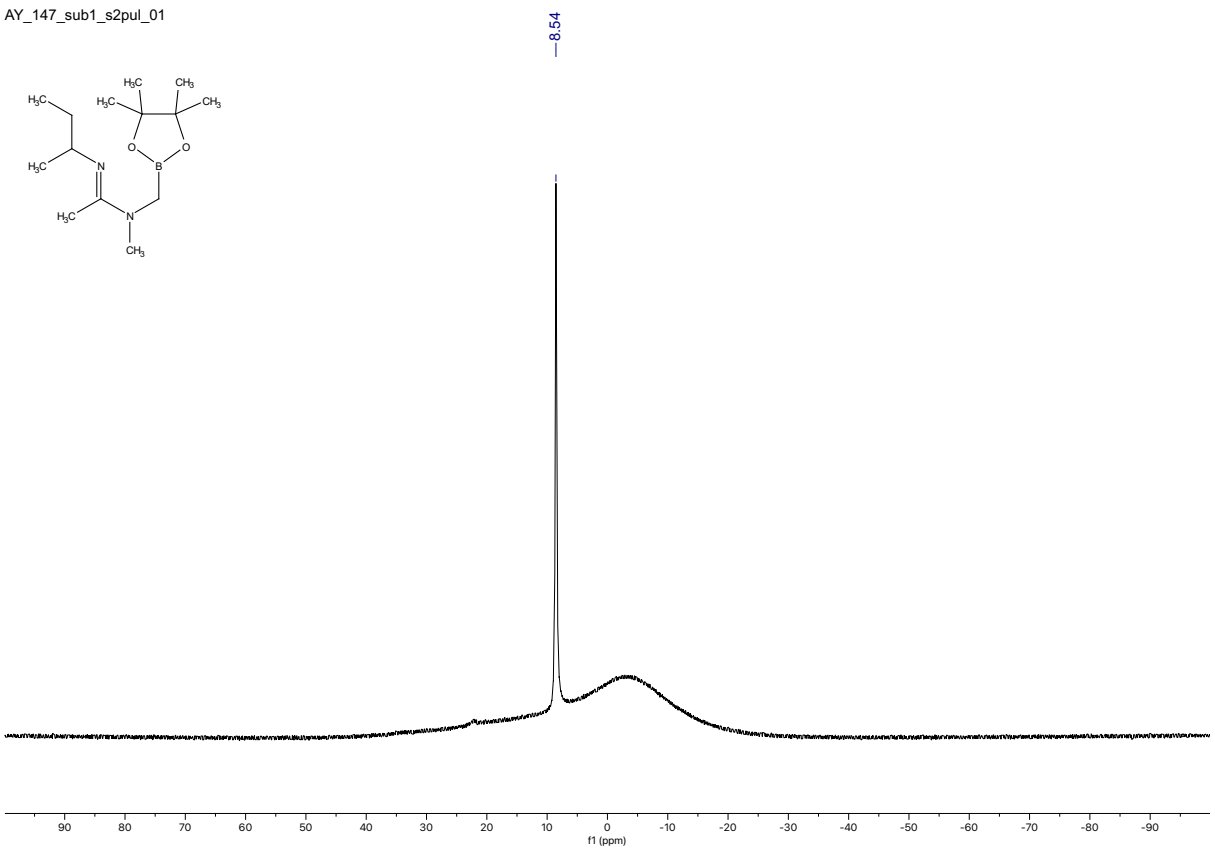


Figure 54: ^{11}B NMR ($CDCl_3$, 160 MHz) 4a

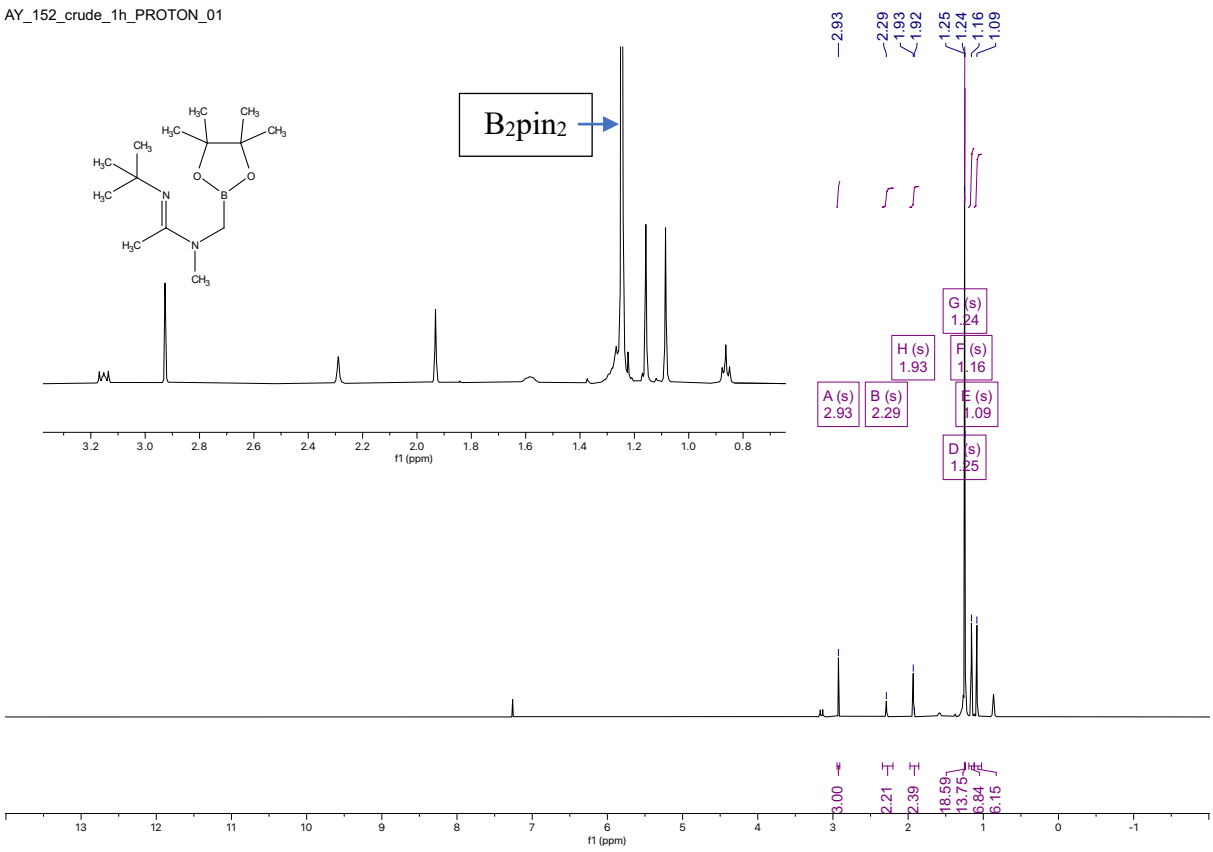


Figure 55: ^{1}H NMR ($CDCl_3$, 500 MHz) 4b

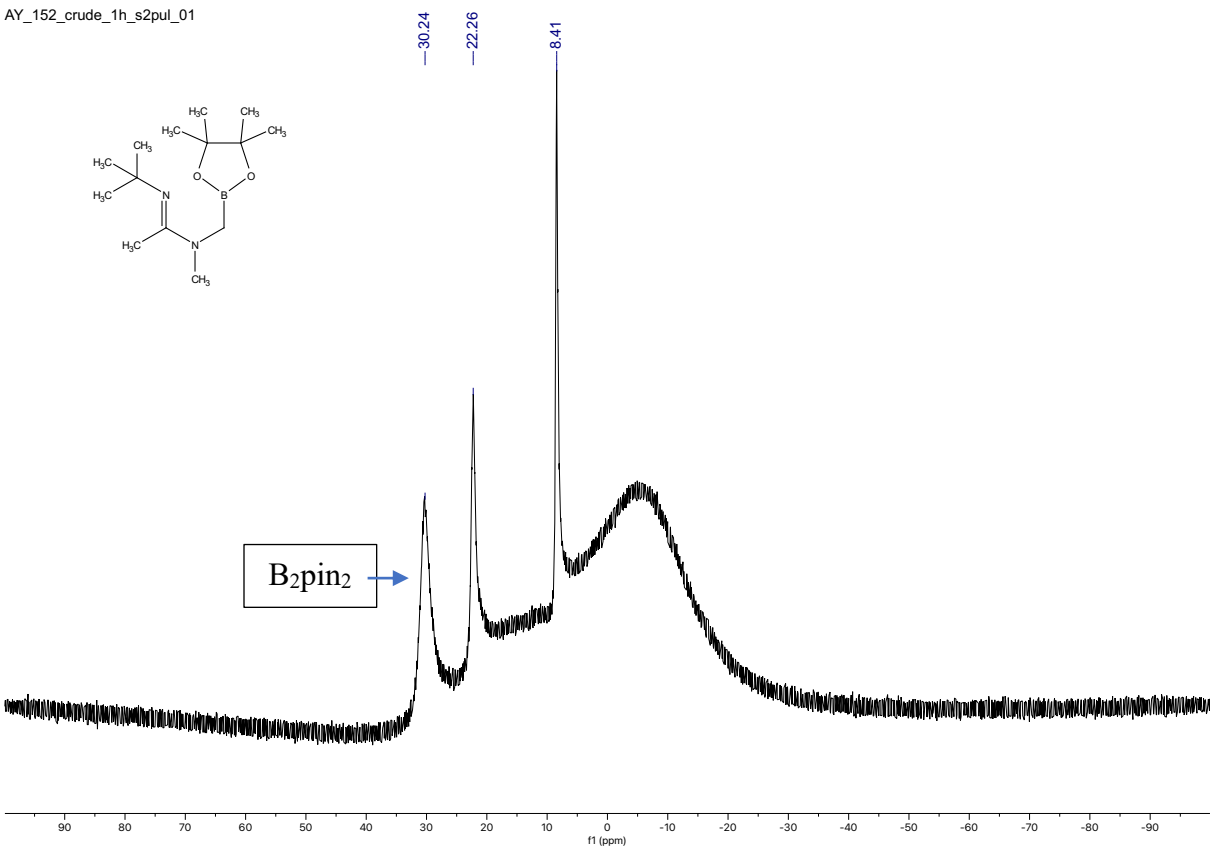


Figure 56: ^{11}B NMR ($CDCl_3$, 160 MHz) 4b

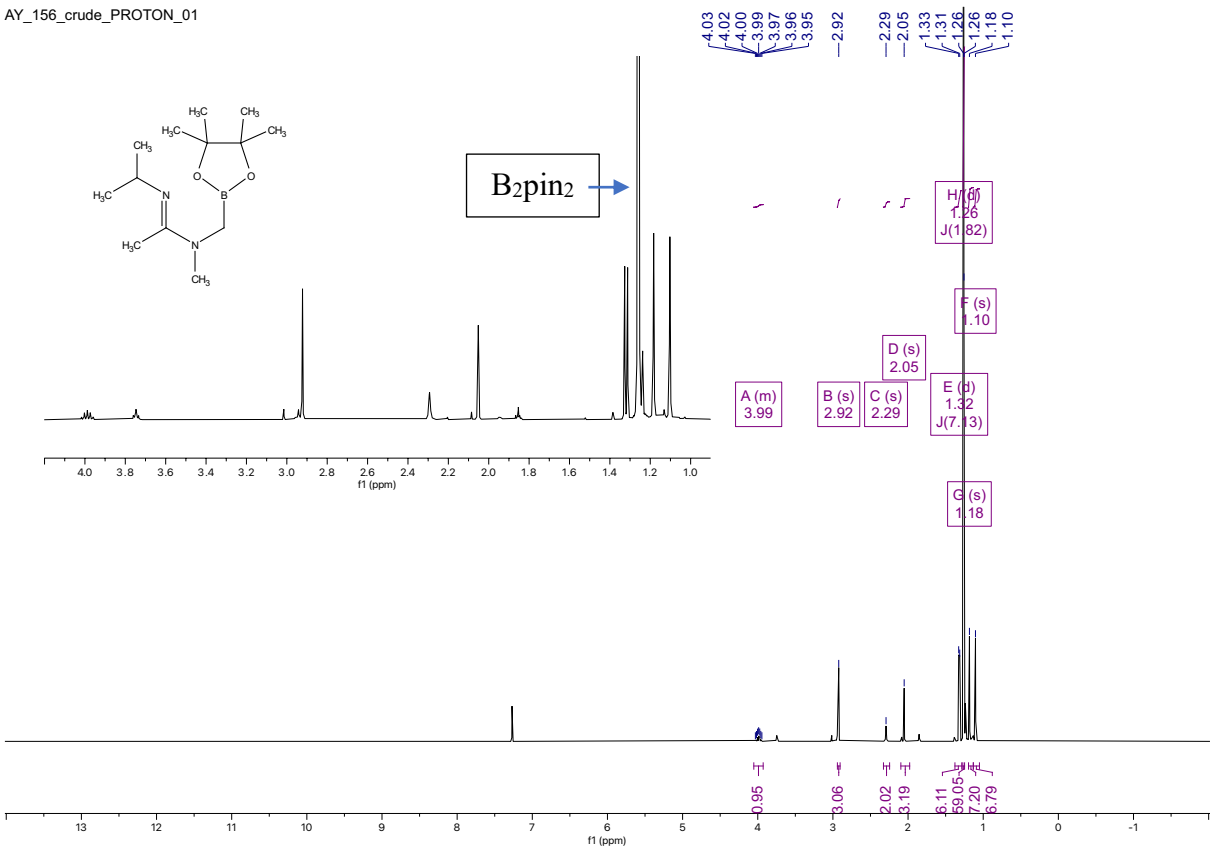


Figure 57: ^{1}H NMR ($CDCl_3$, 500 MHz) 4c

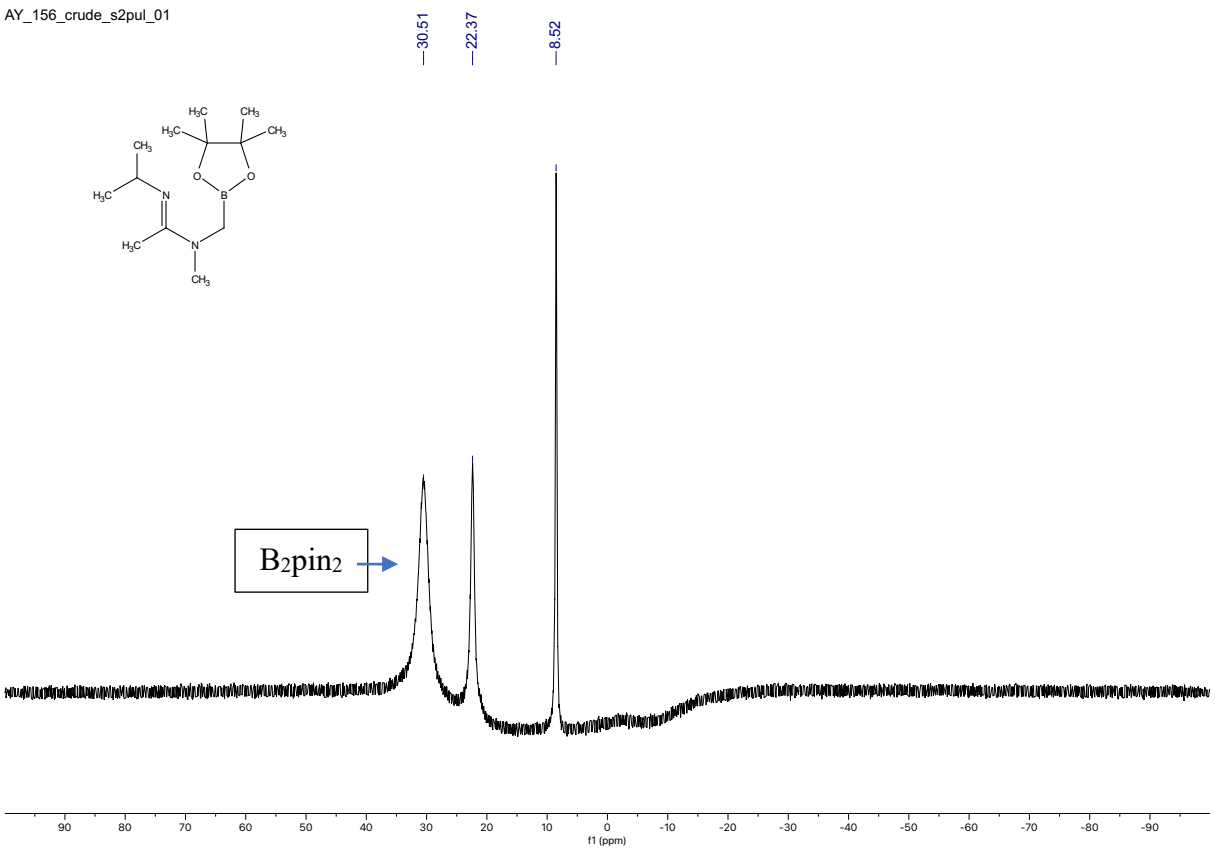


Figure 58: ^{11}B NMR ($CDCl_3$, 160 MHz) 4c

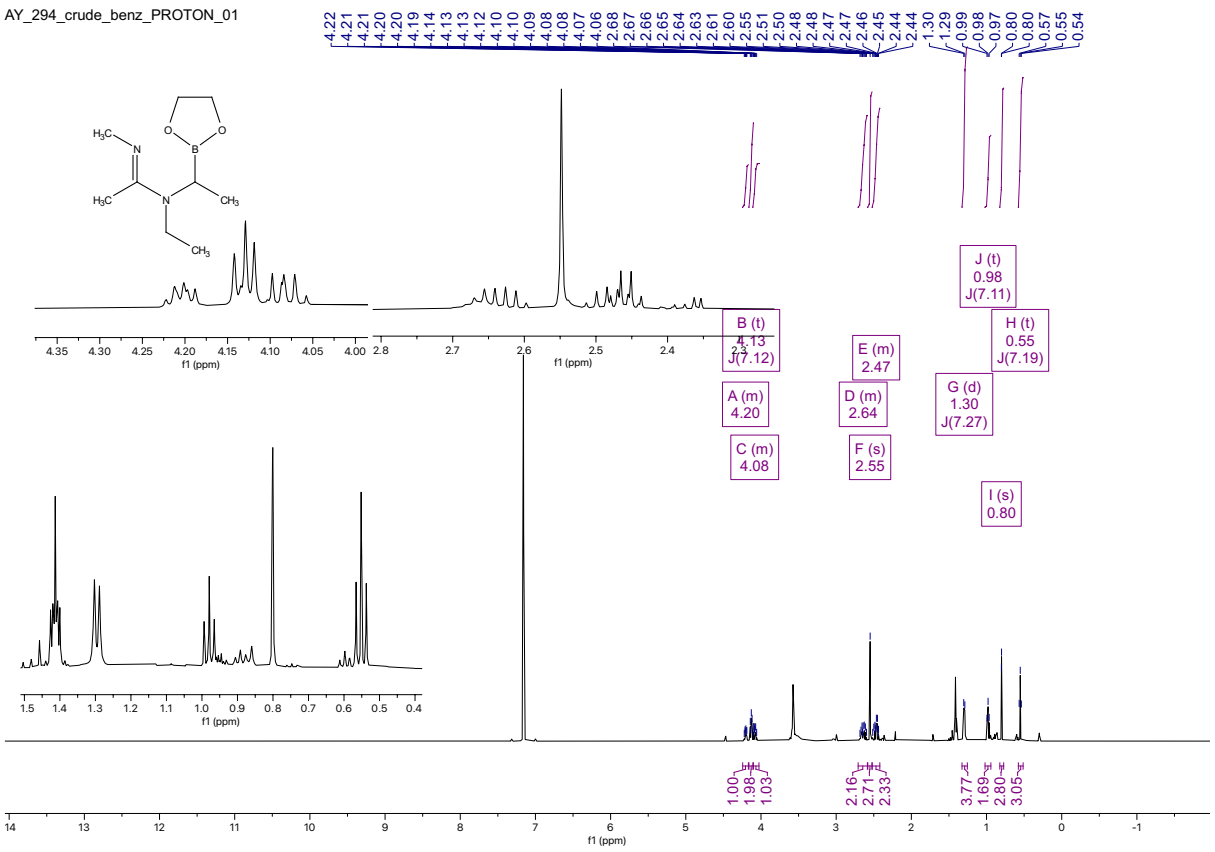


Figure 59: ^{1}H NMR (C_6D_6, 500 MHz) 6a

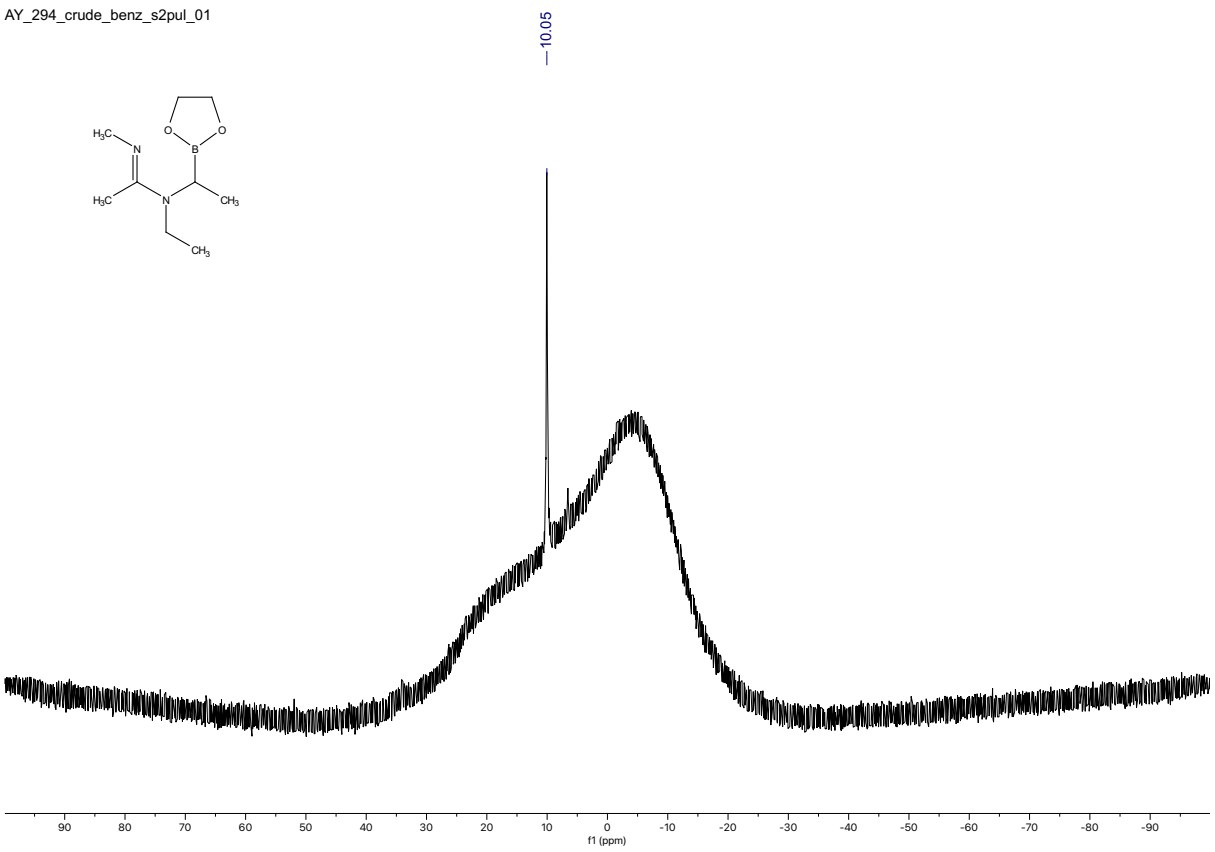


Figure 60: ^{11}B NMR (C_6D_6, 160 MHz) 6a

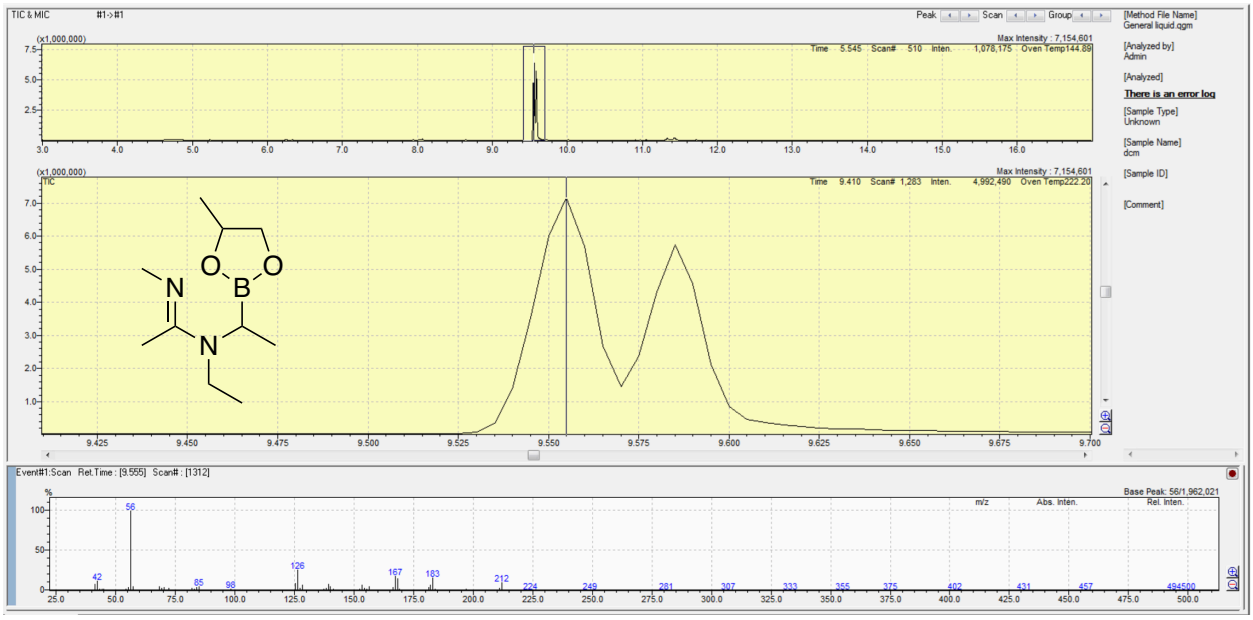


Figure 61: GC/MS Data 6a’

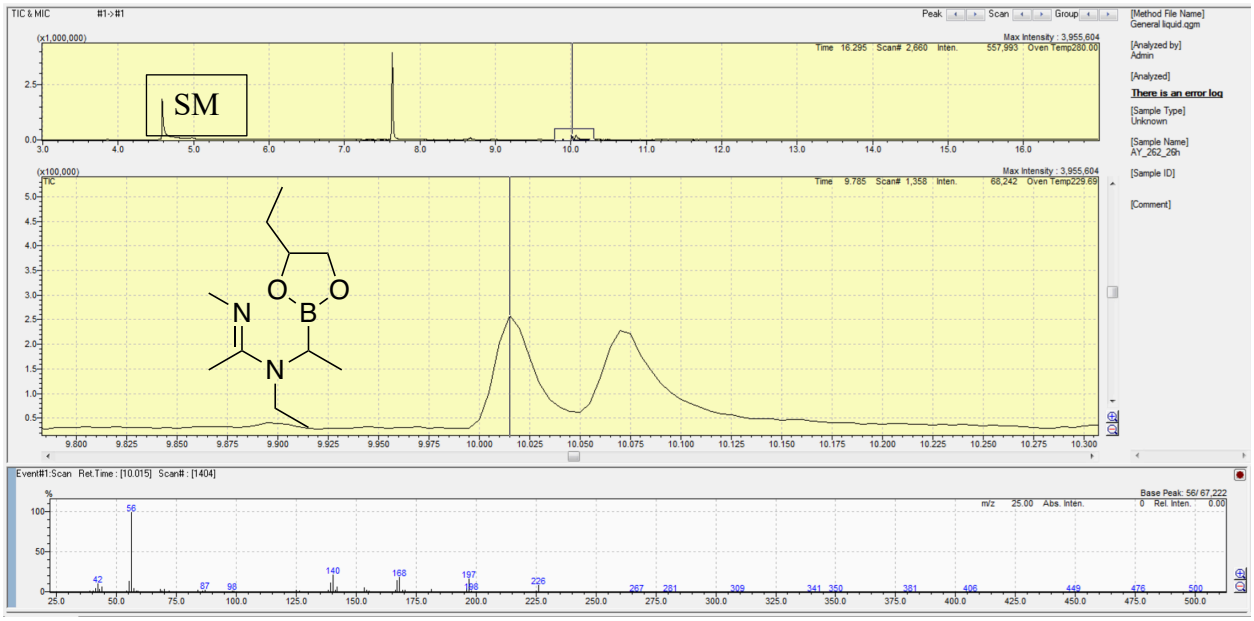


Figure 62: GC/MS Data 6a’’

REFERENCES

REFERENCES

1. Cho, J.-Y.; Tse, M. K.; Holmes, D.; Maleczka, R. E., Jr; Smith, M. R., 3rd. Remarkably Selective Iridium Catalysts for the Elaboration of Aromatic C–H Bonds. Science 2002, 295 (5553), 305–308.

2. Mkhalid, I. A. I.; Barnard, J. H.; Marder, T. B.; Murphy, J. M.; Hartwig, J. F. C–H Activation for the Construction of C-B Bonds. Chem. Rev. 2010, 110 (2), 890–931.

3. Iverson, C. N.; Smith, M. R. Stoichiometric and Catalytic B−C Bond Formation from Unactivated Hydrocarbons and Boranes. J. Am. Chem. Soc. 1999, 121 (33), 7696–7697.

4. Boller, T. M.; Murphy, J. M.; Hapke, M.; Ishiyama, T.; Miyaura, N.; Hartwig, J. F. Mechanism of the Mild Functionalization of Arenes by Diboron Reagents Catalyzed by Iridium Complexes. Intermediacy and Chemistry of Bipyridine-Ligated Iridium Trisboryl Complexes. J. Am. Chem. Soc. 2005, 127 (41), 14263–14278.

5. Tamura, H.; Yamazaki, H.; Sato, H.; Sakaki, S. Iridium-Catalyzed Borylation of Benzene with Diboron. Theoretical Elucidation of Catalytic Cycle Including Unusual Iridium(v) Intermediate. J. Am. Chem. Soc. 2003, 125 (51), 16114–16126.

6. Waltz, K. M.; Hartwig, J. F. Selective Functionalization of Alkanes by Transition-Metal Boryl Complexes. Science 1997, 277 (5323), 211–213.

7. Chen, H.; Schlecht, S.; Semple, T. C.; Hartwig, J. F. Thermal, Catalytic, Regiospecific Functionalization of Alkanes. Science 2000, 287 (5460), 1995–1997.

8. Jayasundara, C. R. K.; Sabasovs, D.; Staples, R. J.; Oppenheimer, J.; Smith, M. R.; Maleczka, R. E. Cobalt-Catalyzed C–H Borylation of Alkyl Arenes and Heteroarenes Including the First Selective Borylations of Secondary Benzylic C–H Bonds. Organometallics 2018, 37 (10), 1567–1574.

9. Boebel, T. A.; Hartwig, J. F. Iridium-Catalyzed Preparation of Silylboranes by Silane Borylation and Their Use in the Catalytic Borylation of Arenes. Organometallics 2008, 27 (22), 6013–6019.

10. Larsen, M. A.; Wilson, C. V.; Hartwig, J. F. Iridium-Catalyzed Borylation of Primary Benzylic C–H Bonds without a Directing Group: Scope, Mechanism, and Origins of Selectivity. J. Am. Chem. Soc. 2015, 137 (26), 8633–8643.

11. Liskey, C. W.; Hartwig, J. F. Iridium-Catalyzed Borylation of Secondary C–H Bonds in Cyclic Ethers. J. Am. Chem. Soc. 2012, 134 (30), 12422–12425.

12. Liskey, C. W.; Hartwig, J. F. Iridium-Catalyzed C–H Borylation of Cyclopropanes. J. Am. Chem. Soc. 2013, 135 (9), 3375–3378.

13. Kawamorita, S.; Murakami, R.; Iwai, T.; Sawamura, M. Synthesis of Primary and Secondary Alkylboronates through Site-Selective C(sp3)-H Activation with Silica-Supported Monophosphine-Ir Catalysts. J. Am. Chem. Soc. 2013, 135 (8), 2947–2950.

14. Reyes, R. L.; Iwai, T.; Maeda, S.; Sawamura, M. Iridium-Catalyzed Asymmetric Borylation of Unactivated Methylene C(sp3)-H Bonds. J. Am. Chem. Soc. 2019, 141 (17), 6817–6821.

15. Yang, Y.; Chen, L.; Xu, S. Iridium-Catalyzed Enantioselective Unbiased Methylene C(sp3)-H Borylation of Acyclic Amides. Angew. Chem. Int. Ed Engl. 2021, 60 (7), 3524–3528.

16. Iwai, T.; Murakami, R.; Harada, T.; Kawamorita, S.; Sawamura, M. Silica-Supported Tripod Triarylphosphane: Application to Transition Metal-Catalyzed C (sp3) H Borylations. Adv. Synth. Catal. 2014, 356 (7), 1563–1570.

17. Yao, W.; Yang, J.; Hao, F. Ru-Catalyzed Selective C(sp3)-H Monoborylation of Amides and Esters. ChemSusChem 2020, 13 (1), 121–125.

18. Hyland, S. N.; Meck, E. A.; Tortosa, M.; Clark, T. B. α-Amidoboronate Esters by Amide-Directed Alkane CH Borylation. Tetrahedron Lett. 2019, 60 (16), 1096–1098.

19. Mita, T.; Ikeda, Y.; Michigami, K.; Sato, Y. Iridium-Catalyzed Triple C(sp3)–H Borylations: Construction of Triborylated sp3-Carbon Centers. Chem. Commun. 2013, 49 (49), 5601.

20. Bisht, R.; Chattopadhyay, B. Formal Ir-Catalyzed Ligand-Enabled Ortho and Meta Borylation of Aromatic Aldehydes via in Situ-Generated Imines. J. Am. Chem. Soc. 2016, 138 (1), 84–87.

21. Kawamorita, S.; Miyazaki, T.; Iwai, T.; Ohmiya, H.; Sawamura, M. Rh-Catalyzed Borylation of N-Adjacent C(sp3)-H Bonds with a Silica-Supported Triarylphosphine Ligand. J. Am. Chem. Soc. 2012, 134 (31), 12924–12927.

22. Ghaffari, B.; Preshlock, S. M.; Plattner, D. L.; Staples, R. J.; Maligres, P. E.; Krska, S. W.; Maleczka, R. E., Jr; Smith, M. R., 3rd. Silyl Phosphorus and Nitrogen Donor Chelates for Homogeneous Ortho Borylation Catalysis. J. Am. Chem. Soc. 2014, 136 (41), 14345–14348.

23. Lõkov, M.; Tshepelevitsh, S.; Heering, A.; Plieger, P. G.; Vianello, R.; Leito, I. On the Basicity of Conjugated Nitrogen Heterocycles in Different Media. European J. Org. Chem. 2017, 2017 (30), 4475–4489.

24. Greene's Protective Groups in Organic Synthesis; Wiley-Interscience, 2006.

25. Li, C.; Wang, J.; Barton, L. M.; Yu, S.; Tian, M.; Peters, D. S.; Kumar, M.; Yu, A. W.; Johnson, K. A.; Chatterjee, A. K.; Yan, M.; Baran, P. S. Decarboxylative Borylation. Science 2017, 356 (6342).

26. Cahnmann, H. J. Partially Deactivated Silica Gel Columns in Chromatography. Chromatographic Behavior of Benzo [a]pyrene. Anal. Chem. 1957, 29 (9), 1307–1311.

27. Li, Q.; Liskey, C. W.; Hartwig, J. F. Regioselective Borylation of the C–H Bonds in Alkylamines and Alkyl Ethers. Observation and Origin of High Reactivity of Primary C–H Bonds Beta to Nitrogen and Oxygen. J. Am. Chem. Soc. 2014, 136 (24), 8755–8765.

28. Dannatt, J. E.; Yadav, A.; Smith, M. R.; Maleczka, R. E. Amide Directed Iridium C(sp3)–H Borylation Catalysis with High N-Methyl Selectivity. Tetrahedron 2022, 109, 132578.

29. Fornwald, R. M. 2021, Diboron-mediated reductive coupling of imines: Divergent diastereocontrol and activation of tetraalkoxydiborons, Michigan State University, East Lansing.

30. Uson, R.; Oro, L. A.; Cabeza, J. A.; Bryndza, H. E.; Stepro, M. P. Dinuclear Methoxy, Cyclooctadiene, and Barrelene Complexes of Rhodium(I) and Iridium(I). In Inorganic Syntheses; John Wiley & Sons, Inc.: Hoboken, NJ, USA, 2007; pp 126–130.

31. Duval, F.; van Beek, T. A.; Zuilhof, H. Sensitive Thin-Layer Chromatography Detection of Boronic Acids Using Alizarin. Synlett 2012, 23 (12), 1751–1754.

32. Schwieger, S.; Herzog, R.; Wagner, C.; Steinborn, D. Platina-β-Diketones as Catalysts for Hydrosilylation and Their Reactivity towards Hydrosilanes. J. Organomet. Chem. 2009, 694 (22), 3548–3558.

33. Lima, F.; Sharma, U. K.; Grunenberg, L.; Saha, D.; Johannsen, S.; Sedelmeier, J.; Van der Eycken, E. V.; Ley, S. V. A Lewis Base Catalysis Approach for the Photoredox Activation of Boronic Acids and Esters. Angew. Chem. Int. Ed Engl. 2017, 56 (47), 15136–15140.

34. Wang, G.; Liu, L.; Wang, H.; Ding, Y.-S.; Zhou, J.; Mao, S.; Li, P. N,B-Bidentate Boryl Ligand-Supported Iridium Catalyst for Efficient Functional-Group-Directed C–H Borylation. J. Am. Chem. Soc. 2017, 139 (1), 91–94.