SYNTHESIS OF HARD TO ACCESS BORYLATED COMPOUNDS AND A COMPUTATIONAL INVESTIGATION

By

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ABSTRACT

This thesis outlines methods for accessing both C(sp^2) and C(sp^3) C-H bonds.

C(Sp^2)-B bonds are highly versatile and can be easily converted into C-C, C-N, and C-O bonds. Achieving selective access to para C-H bonds has been challenging due to the similar reactivity of meta and para bonds. This work introduces a method that creates an in-situ hydrogen-bonded steric shield to protect the ortho and meta positions, allowing access to the para C-H site. Aryl Bpin compounds were demonstrated to undergo selective palladium-catalyzed Sarandeses-Sestelo coupling reactions with organoindium reagents. Additionally, a method for accessing sp^3 C-H bonds is discussed. Borylating sp^3 C-H bonds has traditionally been difficult and required large amounts of starting materials and reagents. This work presents an alternative strategy where sp^2 C-H bonds are initially borylated using iridium catalysis, followed by hydrogenation using a bench stable catalyst to obtain saturated borylated compounds. Furthermore, this thesis includes a study investigating the mechanism of C-H borylation using a hydrazone ligand. Theoretical investigations were conducted to understand the mechanism of C-H borylation employing a hydrazone ligand.

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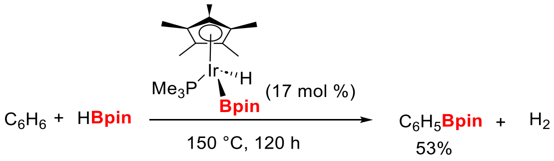
CHAPTER 1. LITERATURE SURVEY OF SYNTHESIS OF REGIOSELECTIVE BORYLATED COMPOUNDS

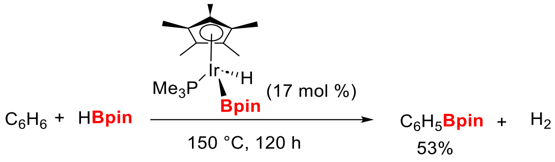
1.1. HISTORY AND DEVELOPMENT OF IRIDIUM CATALYZED BORYLATION REACTIONS

The first thermal catalytic C-H bond borylation was carried out in 1999 using benzene, an iridium catalyst (17 mol %) with HBpin as a boron source and phosphorus ligands to yield 53% of PhBpin (Scheme 1).[1] In 2002, our group reported conditions that involved 1,2-Bis(triphenylphosphine)ethane (dppe) as a ligand, HBpin as a boron source and [(Ind)Ir(cod)] (2 mol %) as the pre-catalyst for the borylation of arenes (Scheme 2).[2] Near the same time Hartwig reported the conditions for borylations on arenes using $[IrCl(coe)]_2$ or $[IrCl(cod)]_2$ (2.0 mol %) as the iridium precatalyst and 4,4-di-*tert*-butyl-2,2-dipyridyl (dtbpy) or 2,2'-bipyridine (bpy) as ligand and B_2pin_2 or HBpin as the boron source (Scheme 2).[3]

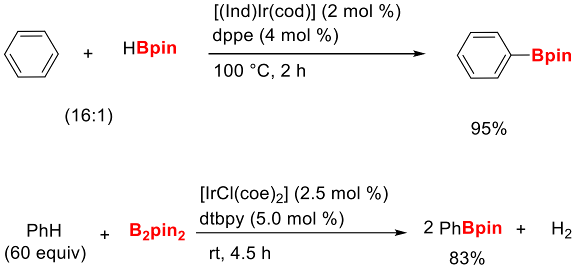
Scheme 1: The first thermal C-H bond functionalization using the Ir catalyst[1]



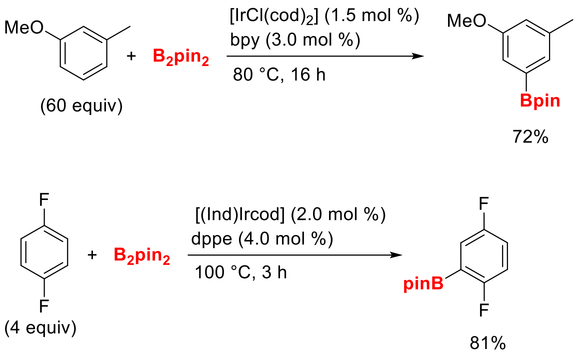
Scheme 2: Catalytic iridium catalyzed borylation developed by Maleczka and Smith groups[2] and below is the optimized conditions by the Hartwig group for iridium catalyzed borylation of benzene[3]



Scheme 3: C-H borylation at mono and disubstituted benzenes.[1,2]



Scheme 3 (cont'd)



The typical mechanism employed in iridium-catalyzed C-H borylation involves the generation of a trisboryl complex, the active catalyst in the reaction, utilizing $[Ir(cod)Cl]_2$ or $[Ir(cod)(OMe)]_2$ as a precatalyst. The commonly used ligand is dtbpy and B_2pin_2 serves as the boron source. In this catalytic cycle oxidation of iridium from Ir(III) to Ir(V) occurs and C-H insertion is usually the rate determining step of the cycle (Figure 1).[2]

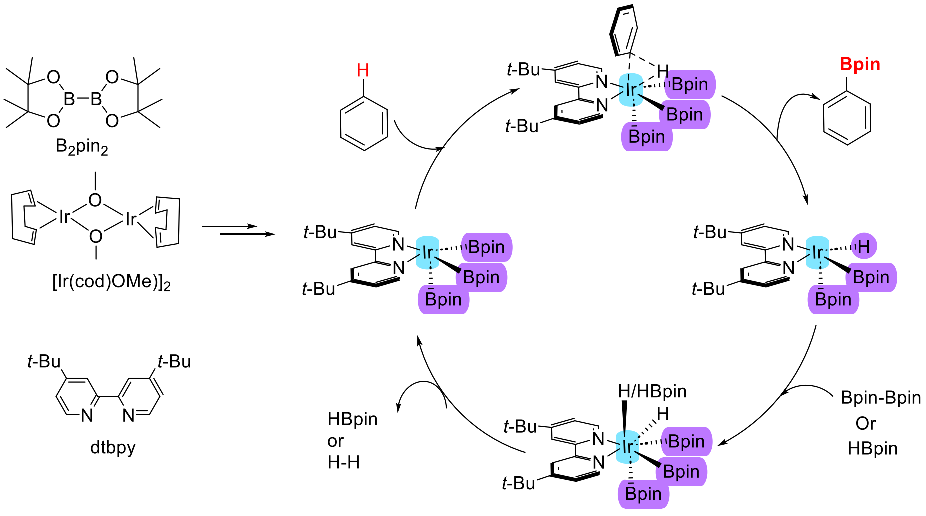
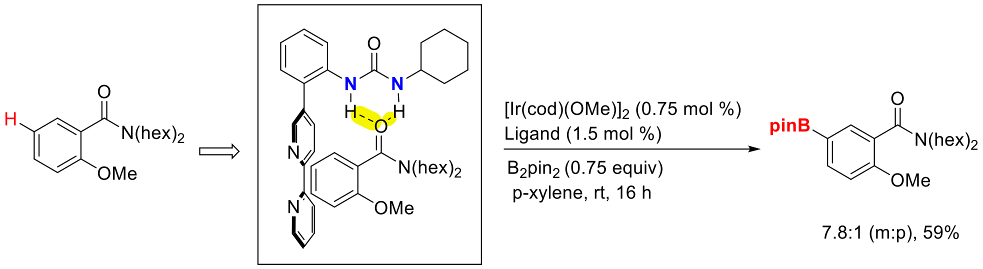


Figure 1: Mechanism of the iridium catalyzed C-H borylation[2]

Subsequent advances in catalytic C-H borylation chemistry included site selective borylation strategies focused on ortho, meta, and para C-H borylations. Traditionally, regiochemistry is guided by sterics. Thus, monosubstituted benzenes typically generate a mixture of meta and para borylated compounds because the ortho position is sterically blocked by the substituent (Scheme

3). A 1,2-disubstituted benzene ring generates a 4-borylated 1,2-disubstituted borylated benzene with a mixture occurring if the substituents differ. A typical 1,3-disubstituted benzene borylates at the meta-position and 1,4-substituted benzene borylates ortho to the less bulky substituent (Scheme 3). Differentially borylating the meta and para substituents on a monoborylated benzene has proven to be a challenge. However, researchers have successfully addressed this challenge, as detailed below.

Scheme 4: Meta selective C-H borylation controlled by hydrogen bonding interaction between ligand and substrate[4]



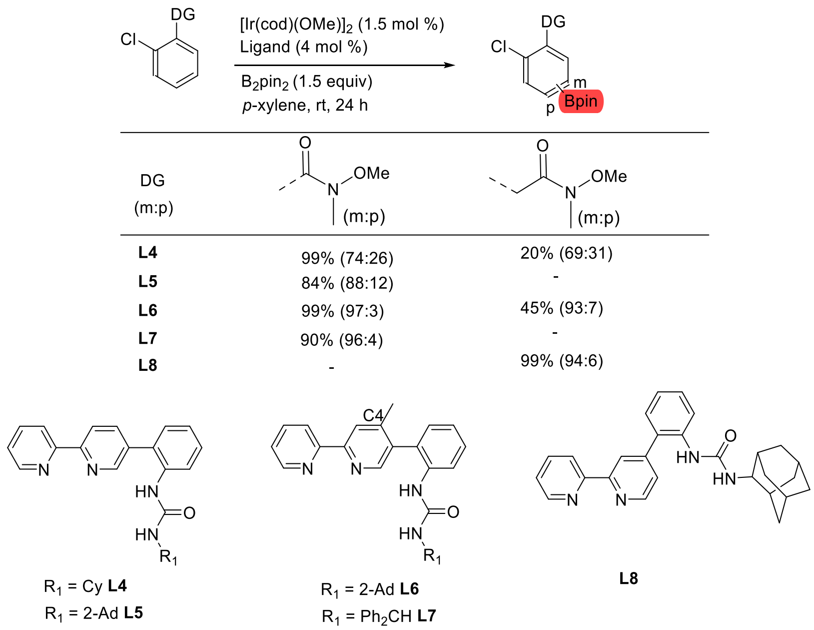
1.2. META SELECTIVE BORYLATION STRATEGIES

Various non-covalent interactions like hydrogen bonding, steric repulsion, Lewis's acid base interactions and electrostatic interactions have been utilized to guide the placement of the boryl to the meta position. These interactions have been organized into distinct categories, each illustrated with examples.

1.2.1. Hydrogen bonding interactions

One innovative strategy utilized by chemists to access meta-C-H bond borylation is by exploiting hydrogen bond interactions between the ligand and the substrate. For example, a ligand appended with a hydrogen bonding site (directing group) on a urea moiety can form hydrogen bonds with the substrate and places iridium in close proximity to the meta-C-H bond thereby controlling the regioselectivity (Scheme 4). This strategy was first developed by Kuninobu and Kanai in 2015. In that work, a bipyridine ligand linked to a urea moiety was employed as a hydrogen bond donor to carbonyl groups. An ortho phenylene group linked the urea and the bipyridine in this strategy. This strategy has been extended to other functional groups like amide, ester, phosphonate ester, phosphonamide, and phosphorus oxide.[4]

The ligand bearing the hydrogen bond donor, designed by Kuninobu and Kanai, was computationally evaluated by Liang (Scheme 4).[5] DFT studies revealed that a lower meta/para ratio for amides including Weinreb amide is obtained because of a plausible competitive non directing mechanism taking place in the reaction (where the amide group on substrate was not interacting with the ligand's hydrogen bond donors). The unwanted non directed pathway is proposed to be eliminated by switching the cyclohexane on the urea moiety to adamantane (**L5**, Figure 2). This allows the directed meta pathway to dominate and leads to increased meta selectivity.[5]



DG (m:p)	(m:p)	(m:p)
L4	99% (74:26)	20% (69:31)
L5	84% (88:12)	-
L6	99% (97:3)	45% (93:7)
L7	90% (96:4)	-
L8	-	99% (94:6)

R$_1$ = Cy **L4**
R$_1$ = 2-Ad **L5**

R$_1$ = 2-Ad **L6**
R$_1$ = Ph$_2$CH **L7**

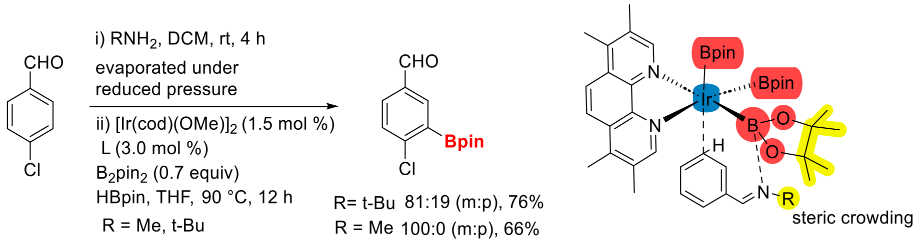
L8

Figure 2: Changes in meta selective borylation of Weinreb amide by changing the R1 group on the urea moiety of the ligand[5]

1.2.2. Steric repulsion

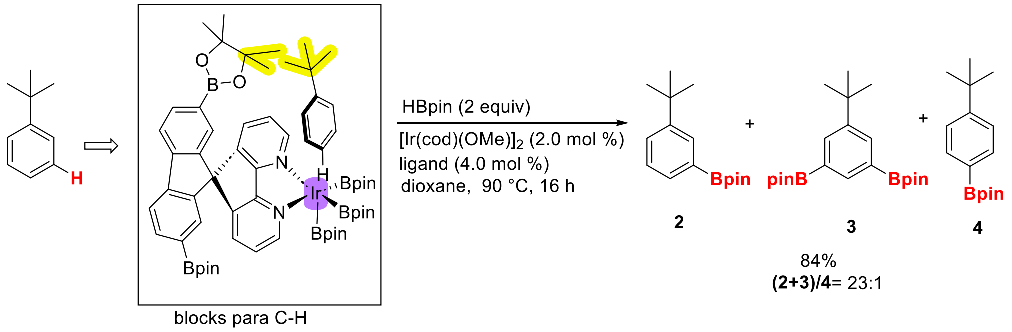
In 2016, the Chattopadhyay group reported the meta selective borylation of substituted benzaldehydes involving in-situ generated imines and tetramethyl phenanthroline as a ligand. Steric crowding/repulsion by the tert-butyl group on the imine and a methyl group on the pinacolate of boron in the active catalyst is proposed to be the driving force for meta borylation (Scheme 5). However, most of their substrates were benzaldehydes substituted with functional groups like chloro, methoxy, methyl, cyanide, fluoro, and ethoxy at the para position or the other meta position.[6] Essentially a competitive study for para vs meta was not carried out.

Scheme 5: Meta C-H functionalization using tetramethylphenanthroline ligand[6]



A specialized roof-like ligand recently reported in 2022 by Ilies utilizes steric repulsion between the ligand and substrate to meta borylate monosubstituted benzenes (Scheme 6). This strategy has been applied to a variety of substituted arenes, shows good meta selectivity and is not dependent on any directing functional group.[7]

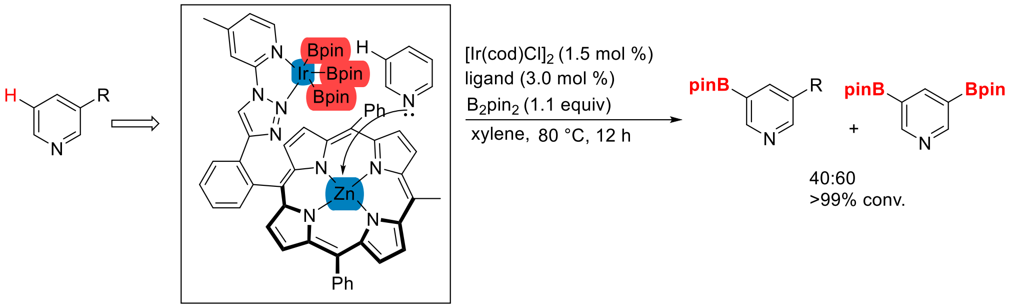
Scheme 6: Meta C-H functionalization using a roof like ligand[7]



1.2.3. Lewis acid-base interactions

The first demonstration of selective C-H borylation of benzamides and pyridines utilizing transition metal/Lewis acid catalysis was carried out by Nakao in 2019 (discussed under section 1.3).[8] In this report, a bifunctional ligand was designed to include: i) a bpy or phenanthroline ligand ii) a linker to control the site selectivity and iii) a Lewis acid to electronically activate the amide or pyridine. A modified application of this methodology was demonstrated by Gramage-Doria using a supramolecular iridium catalyst where a Zn atom encapsulated in a porphyrin ligand acts as a Lewis acid site and pyridine/imidazole's nitrogen acts as a Lewis base directing the borylation meta to the coordinating nitrogen (Scheme 7). This method uses a highly specialized ligand system and has only been shown to be applicable for pyridines and imidazoles.[9]

Scheme 7: Meta selective functionalization using a highly specialized ligand system[9]

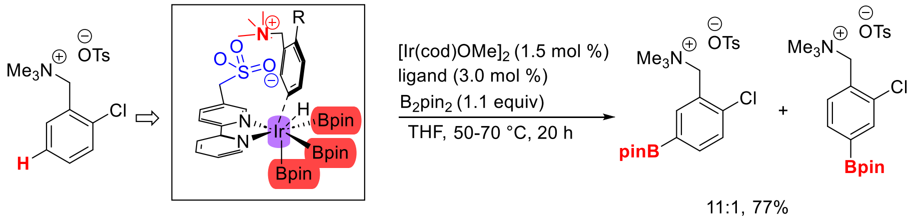


1.2.4. Electrostatic ion pair interactions (attractive)

The first ever ion pair directed borylations were demonstrated by Phipps and coworkers in 2016. Cationic arene substrates, namely tetra butyl-ammonium benzylamine and quarternized anilines, were borylated using a bipyridine ligand bearing an anionic sulphonate group (Scheme 8). The electrostatic ionic interactions held the substrate and ligand in close proximity and allowed easy access to the meta C-H bond.[10]

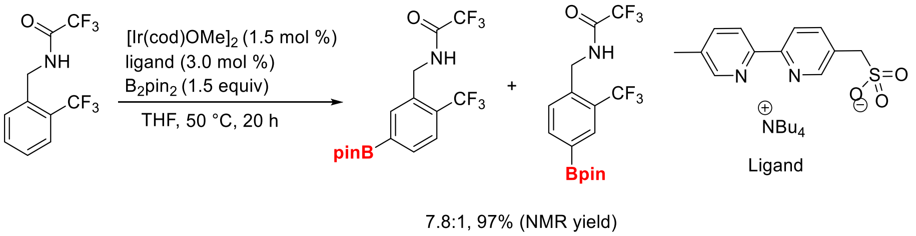
The same anionic ligand was further applied with neutral substrates as well. This chemistry is proposed to direct borylation to the meta position by the anionic ligand acting as a hydrogen bond acceptor and neutral amides as hydrogen bond donors (Scheme 9).[11]

Scheme 8: Meta C-H borylation directed by electrostatic interactions[10]

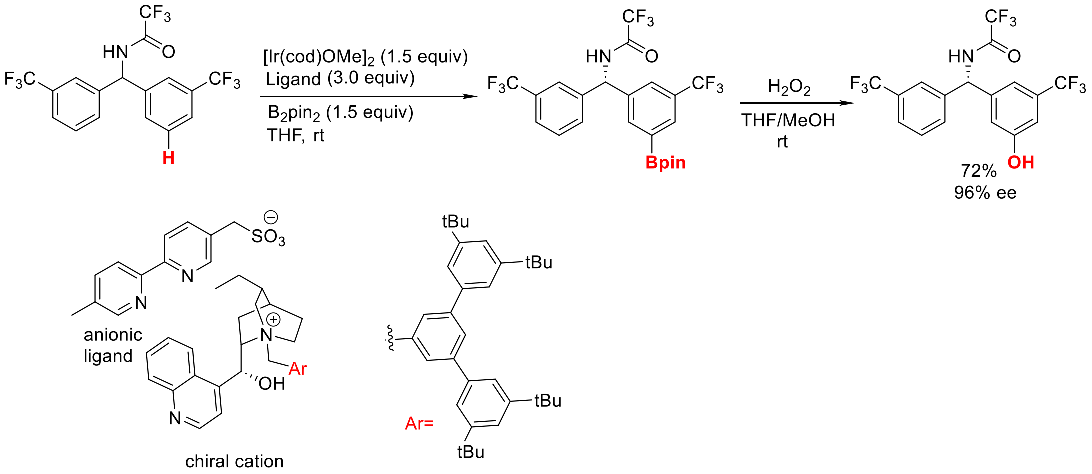


In 2020, Phipps and coworkers expanded the scope of his meta selective borylation with an anionic ligand to a desymmetrizing (enantioselective) meta borylation using the anionic ligand with a chiral cationic counter-ion (Scheme 10).[12] The substrate scope included the borylation of benzhydrylamides and diaryl phosphinamides.

Scheme 9: Meta C-H borylation utilizing the anionic ligand with a neutral substrate[11]



Scheme 10: Enantioselective desymmetrizing C-H borylation of benzhydrylamides[12]

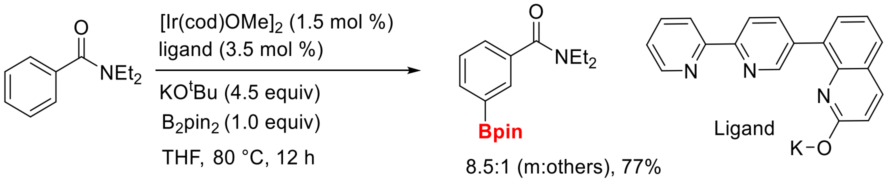


In 2018, similar to the Phipps anionic ligand,[11] the Chattopadhyay group developed a bifunctional anionic ligand system (L shaped) with a K$^+$ counter ion that is appended by a quinoline moiety on a bpy chelating ligand for borylation of substituted aromatic amides and heteroaromatic amides

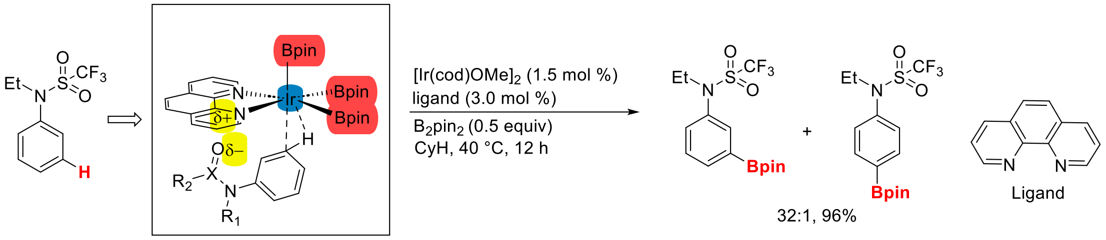
(Scheme 11). The K$^+$ counter ion interaction with the δ- oxygen of the substrate is proposed to direct the borylation meta to the amide.[13]

In 2021, the Chattopadhyay group also published meta borylation of a wide variety of substrates including substituted phenylamide, phenyl sulphonamides, and phenyl phosphonate esters using a phenanthroline ligand. It was proposed that the electrostatic interaction between the δ+ generated on the phenanthroline ligand and the δ- on the oxygen of the substrate directed the C-H borylation meta (Scheme 12). This strategy is practical in that a commercially available ligand is used to carry out the meta selective borylation.[14]

Scheme 11: Non-covalent interaction directed meta C-H borylation[13]



Scheme 12: Electrostatic interactions directed meta C-H borylation[14]

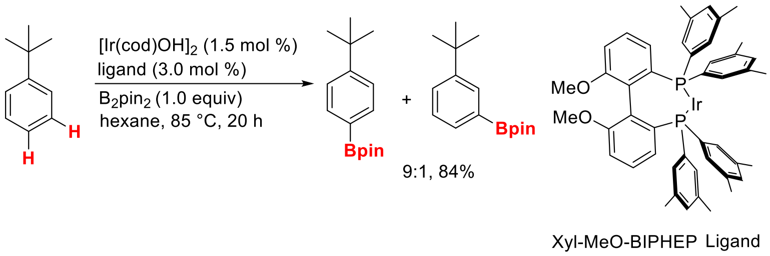


1.3. PARA SELECTIVE BORYLATION STRATEGIES

1.3.1. Steric Repulsion

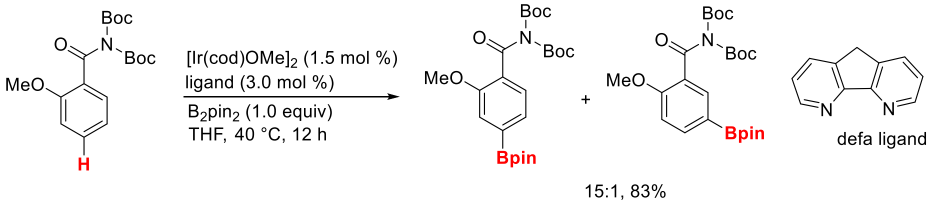
Itami, in 2015, developed the first para selective borylation strategy using a bulky diphosphine ligand, Xyl-MeO-BIPHEP (Scheme 13). The steric repulsion between the bulky catalyst and substrate is envisioned to control the regioselectivity. Notably they used [(Ir(cod)OH]$_2$ as a precatalyst in this reaction because they observed it to gave superior para borylation results compared to [[Ir(cod)(OMe)]$_2$. This work demonstrated high selectivities at the para position on mono substituted aryl substrates, however all the substrates used had bulky substituents. Example of some of the substrates are diethyl-2-ethyl-2-phenylmalonate, trimethyl((3-phenylpentan-3-yl)oxy)silane, trimethyl((1-phenylcyclohexyl)oxy)silane, 4-4’-(1-phenylethane-1,1-diyl)bis(methoxybenzene), 1-phenylcyclohexan-1-ol.[15] Regioselectivity ratios with this ligand and substrates bearing small substituent on the benzene ring, i.e. toluene, would be an interesting comparison.

Scheme 13: Sterically bulky ligand directed para C-H borylation[15]



Chattopadhyay’s group, in 2022, developed a methodology for diBoc protected aromatic and heteroaromatic amides using a 4,5-diazafluorene (defa) ligand (Scheme 14). The aromatic amides are twisted in nature, which shield the ortho and meta position and thereby enhance para selectivity. This reaction with dtbpy gives only moderate selectivity for the para isomer. Their research findings are supported by computational results, indicating that the activation energy for the para isomer was the lowest among the different isomers when employing the defa ligand.[16]

Scheme 14: Sterically bulky starting material directed para C-H borylation[16]



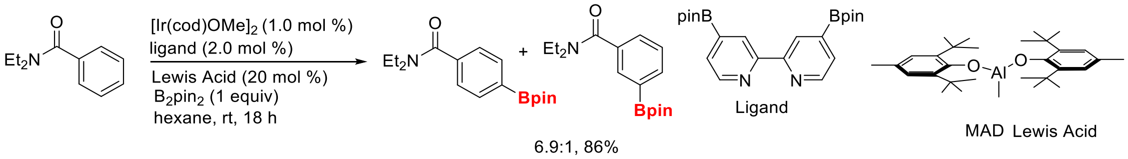
1.3.2. Lewis Acid Base

Nakao, in 2017, developed a para selective borylation strategy for substituted benzamides and pyridine substrates. Like in other cases,[17,18] an Al based Lewis acid, i.e. methylaluminumbis(2,6-di-*tert*-butyl-4-methylphenoxide) (MAD), was used to non-covalently interact with Lewis basic sites namely oxygen of benzamide and nitrogen of pyridine. MAD then sterically shields the ortho and meta sites and thus directs the borylation para (Scheme 15). Despite the use of a strong Lewis acid, good tolerance towards a range of functional groups like methoxy, bromo, chloro, and phosphonate was observed.[8]

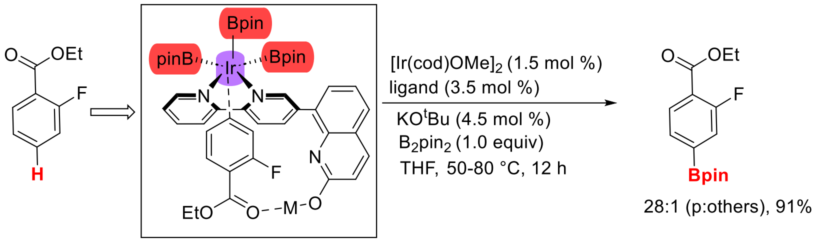
1.3.3. Electrostatic Interactions

In 2017, an L shaped ligand (similar to the one used for meta C-H borylation) was developed by Chattopadhyay and coworkers where they appended a dtbpy ligand with a quinoline oxide moiety with a K^+ counter ion that noncovalently interacts with the oxygen's δ- charge of an ester to direct the borylation para (Scheme 16). Amides and phosphonate esters showed moderate selectivity (e.g. 1.5:1 and 1.8:1 (p:other) and lower reactivities.[19]

Scheme 15: Para C-H borylation directed by bulky lewis acid[8]

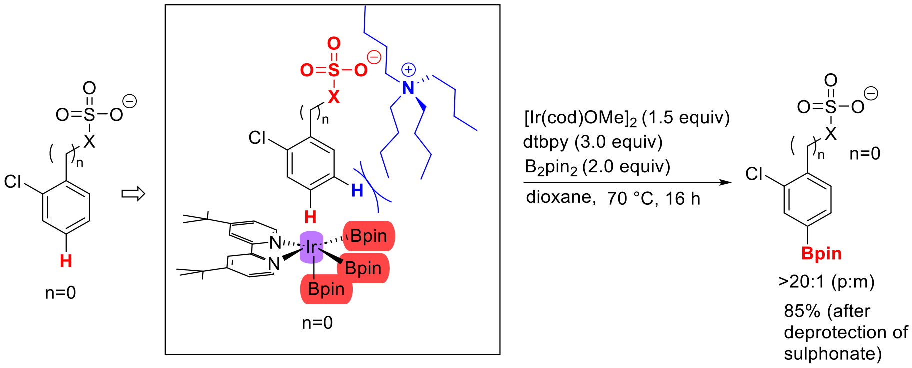


Scheme 16: Electrostatic interactions directed para C-H borylations[19]

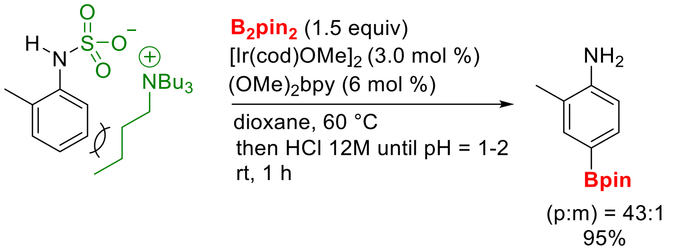


Phipps, in his previous work, used an anionic ligand or ligand appended with a sulphonate group.[10,11] He modified this strategy by appending the sulphonate group on substrates like anilines, phenols, aryls, and benzyls instead of the ligand. By using a cationic counter ion, he was able to shield ortho and meta positions owing to the long chain on the cationic counter ion (Scheme 17).[20] A similar strategy was independently developed in our lab and published at the same time (Scheme 18).[21]

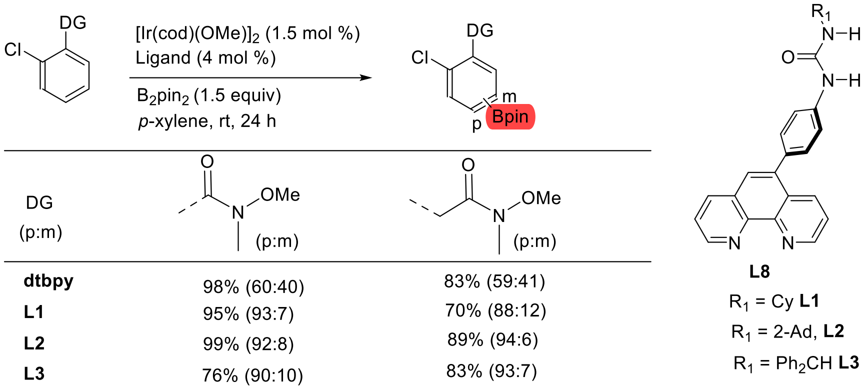
Scheme 17: Electrostatic ion pair strategy to access para C-H borylation[20]



Scheme 18: Electrostatic ion pair strategy developed in Maleczka and Smith lab[21]



1.3.4. Hydrogen bond and steric repulsion



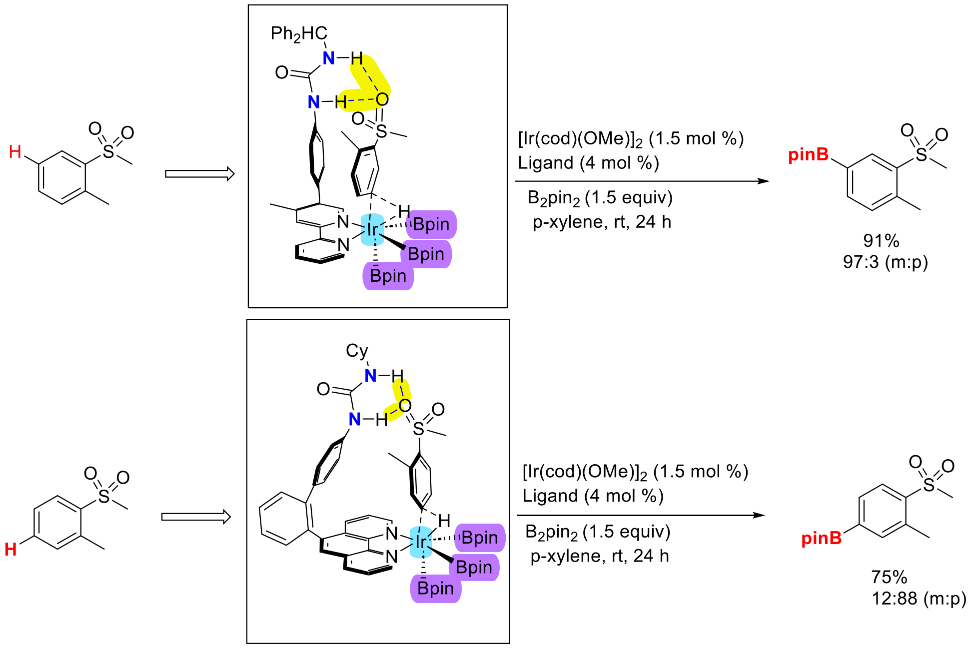
DG (p:m)	(p:m)	(p:m)
dtbpy	98% (60:40)	83% (59:41)
L1	95% (93:7)	70% (88:12)
L2	99% (92:8)	89% (94:6)
L3	76% (90:10)	83% (93:7)

Figure 3: Ligand design informed by computational studies[5]

The hydrogen bonding ligand system previously described[5] for meta borylation was computationally optimized to achieve para borylation. A modified ligand was proposed based on precise analysis of distances and angles between the linker and the recognition site of the substrate. This modification included adding an extra phenylene linker to the original ligand and substituting phenanthroline for bpy as the chelating ligand (**L8**). These adjustments led to enhanced para selectivity of amides (Figure 3).[5]

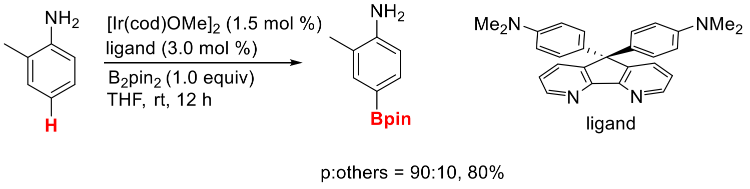
These ligand systems were also demonstrated to be successful on an aryl sulphone substrates (Scheme 19).[22]

Scheme 19: Computationally informed ligand design for site selective C-H functionalization of aryl sulfonyl compounds[22]



Another strategy developed in our lab is an in-situ generation of a steric shield, which blocks the ortho and meta position (discussed in detail in Chapter 2), thereby directing borylation at the para position. In 2022, the Chattopadhyay group developed a similar strategy with a more electronically rich ligand to increase the reactivity of the system so the reaction could be carried out at room temperature (Scheme 20).[23]

Scheme 20: Utilizing hydrogen bonding from an aniline and steric bulk of the ligand to direct para-C-H borylation



Keeping all non-covalent interactions in mind, it would be interesting to see how hydrophobic interactions would be utilized for C-H functionalization/borylation reaction.

1.4. DEVELOPMENT OF SP^3 BORYLATIONS

In the last two decades there have been many strategies to synthesize sp^2 C-B bonds. In contrast there are not many strategies to catalytically C-H borylate sp^3 compounds. Among the reasons for this non-reactiveness is the increased sterics inherent to the sp^3 geometry. In addition, the ΔH_r of reaction for a CH_4 molecule converting to CH_3-Bcat using HBcat (catecholate borane) is calculated to be 1.1 kCal/mol using the thermochemical data from literature[24,25] and those reported by Hartwig.[26]

Table 1: Bond dissociation energy table for the reaction of methane with pinacolborane[24,25,26]

Entry	Bond	BDE (kCal/mol)
1	H-Bcat	111.3[26]
2	catB-CH_3	113.0[26]
3	CH_4	104.8[24]
4	H_2	104.2[25]

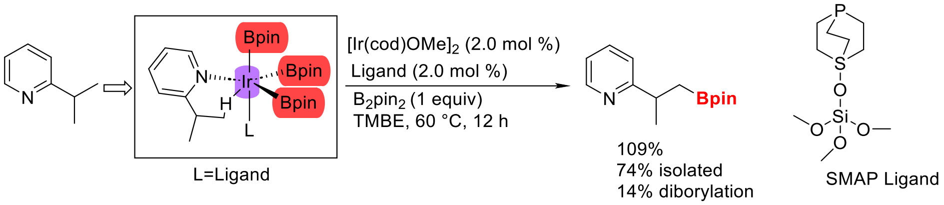
Iridium catalyzed C(sp^3)-H borylation strategies can be broadly classified into directed borylation and non-directed C-H borylations.

Directed Borylation: Directed borylation is the functionalization of sp^3 C-H bond because of coordination of a substrate atom (N) to the iridium center or ligands (dtbpy or boryl ligands)

Non-Directed borylation: Non directed borylation is the functionalization without any coordination of the substrate to the iridium center/ligand.

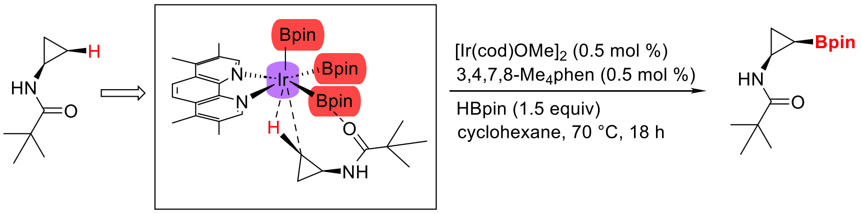
1.4.1. Directed sp^3 C-H Borylation

Scheme 21: sp^3 C-H borylation of isopropyl pyridine[27]



Sawamura and group, in 2013, demonstrated that 2-isopropyl pyridine could be borylated at the primary positions of the isopropyl group owing to the coordination of N to iridium (Scheme 21). However, in one of example in their optimization table they showed that for ethyl 2-pyridine they could borylate the primary C-H bond at 60 °C without using any ligand. Three equivalents of starting material were used to carry out this transformation.[27]

Scheme 22: sp^3 C-H borylation of cyclopropyl amide[28]



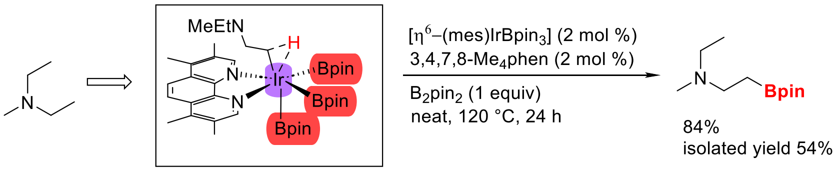
Similarly, in 2015, Miyamura, Araki, Suzuki, Yamaguchi, and Itami stereoselectively borylated a cyclopropyl amide (Scheme 22). For most directed ortho borylations to occur, the iridium center requires two accessible coordination sites for the substrate to chelate. However, this was not possible in this case because phenanthroline ligand is a bidentate ligand. Therefore, an interaction of oxygen or nitrogen from the amide to the electron deficient boron or hydrogen bonding from the hydrogen of N-H of the amide to the oxygen of boryl group generating a 7/6 membered ring was what led to C-H functionalization γ to the carbonyl. Large quantities (4.4 equivalents) of the starting material were used to yield 85% of the product by NMR and 62% isolated yield. Unprotected amines did not borylate.[28]

1.4.2. Non-directed borylations

Non directed borylations have been studied for benzylic C-H bonds and C-H bonds adjacent to heteroatoms. These are activated bonds compared to sp^3 C-H bonds of alkanes.

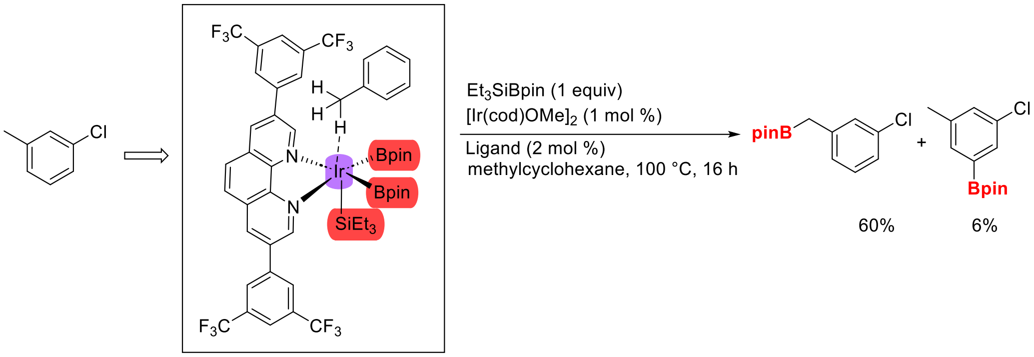
In 2014, Li, Linskey, and Hartwig studied the borylation of aliphatic C-H bonds in alkyl amines and alkyl ethers using tetramethylphenanthroline (tmphen) as a ligand. They observed high yields of 108% (yield is based on moles of product per moles of B_2pin_2) (Scheme 23). Their observation was that borylation preferentially occurred β to oxygen and nitrogen. Computational studies explained this observation as being a result of weak stabilizing Lewis acid-base interactions between the boron atom and the amine nitrogen or ether oxygen stabilizing the oxidative addition transition state for the primary C-H bond. This approach requires nine equivalents of the starting material and a high temperature of 120 °C.[29]

Scheme 23: sp^3 C-H borylation of diethylmethylamine[29]



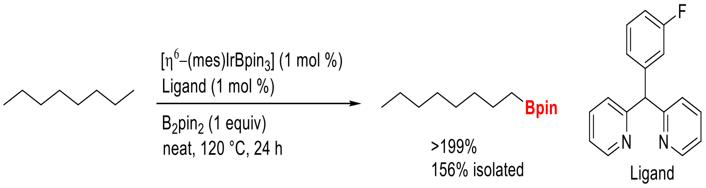
In 2015, Larsen, Wilson, and Hartwig investigated conditions for borylating benzylic C-H positions. It was found that using an electron deficient phenanthroline ligand and alkane solvents like cyclohexane instead of ethereal solvents like THF selectively borylated benzylic C-H bonds. Another tweak in the conditions was that they used a silyl boron reagent instead of a diboron reagent. The precatalyst with these conditions was a bisborylsilyl complex (Scheme 24) that was less electron donating as compared to a trisboryl complex. It was found that borylation of benzylic C-H bonds is unaffected by the reduced electron density metal center from a diborylmonosilyl complex and suppresses the borylation of aryl C-H bond. This is primarily because the rate limiting step for a benzylic C-H borylation is the isomerization step prior to reductive elimination unlike oxidative addition for the aryl C-H.[30]

Scheme 24: sp^3 C-H borylation of methylarene[30]



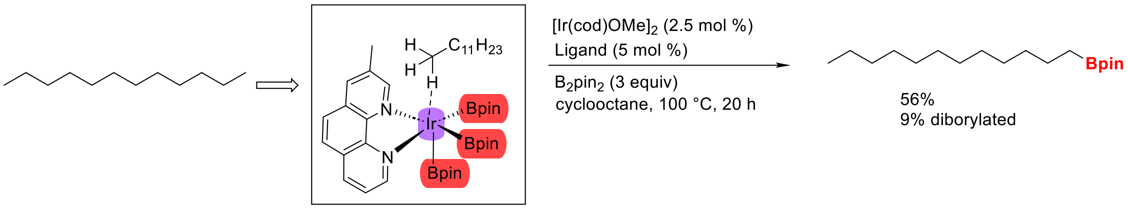
In 2020, reaction conditions were developed by Jones, Fast, and Schley that targeted the C-H bonds of alkanes (Scheme 25). Use of an electron deficient ligand showed highly improved conversions in neat conditions as well as in solvent. They tuned their catalyst to borylate various sp^3 C-H bonds including primary C-H bonds adjacent to heteroatoms, primary benzylic C-H bonds, and non-activated primary C-H bonds of alkanes. Any experiments to deduce the mechanism of this reaction and their observed selectivities have not yet been carried out. It was proposed that this ligand might be binding in a facial k^3 mode that would result in a 5-electron donor analogous to Cp* ligand, which might be responsible for modulation of steric and electronic parameters.[31] They did have to use a temperature of 120 °C and excess substrate (5 equivalents) to carry out the reaction.

Scheme 25: sp^3 C-H borylation of octane[31]



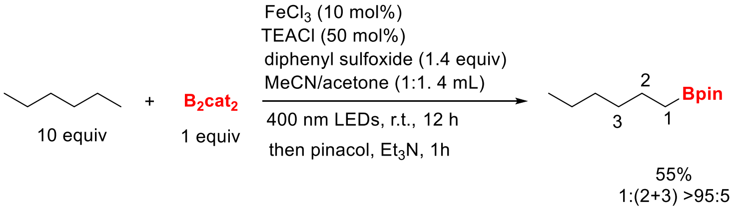
An attempt at sp^3 C-H borylation with limited concentration of the substrates was shown by Hartwig and group where they tweaked the tmphen ligand to 2-methylphenanthroline (2-mphen) (Scheme 26). They observed great selectivity and reactivity (accelerated rate by two orders of magnitude as compared to tmphen) for primary methyl groups. They also showed an expanded scope of the reaction successfully borylating various sp^3 C-H positions like primary C(sp^3)-H bond of alcohols, secondary C(sp^3)-H bonds of saturated heterocycles and carbocycles.[32]

Scheme 26: sp^3 C-H borylation of dodecane[32]



Another non directed borylation method was recently demonstrated by Wang and group. They describe a photochemical approach to achieve terminal C(sp^3)–H borylation of unbranched alkanes that tolerated functional groups like chloro, esters, ketone, cyanide, and silyl. This reaction is facilitated through photoinduced iron catalysis, involving a reversible hydrogen atom transfer (HAT) process assisted by chlorine radicals, followed by selective borylation of a primary radical intermediate at the terminal position (Scheme 27).[33] The reaction used 10 equivalents of starting alkane.

Scheme 27: Light induced C-H borylation mediated by irontrichloride[33]

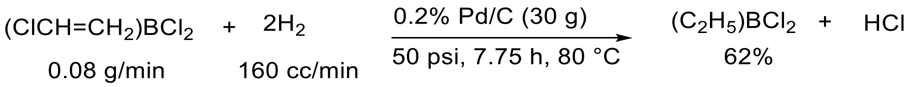


To summarize, sp^3 borylation is still limited to compounds with directing groups. In case of non-directed borylations, this chemistry requires large equivalents of starting material or diboron reagent. In reactions where large equivalents of starting materials were not used, reactive alkanes like benzylic or alkylsilanes were required. In the case of Hartwig's recent research, the catalyst only functionalizes the stronger C-H bond and the reason for this is unclear. Also, the Hartwig group used cyclooctane as a solvent, which is non-polar and cannot dissolve a lot of polar compounds.

1.4.3. Alternate strategy to access sp^3 boryl compounds

Hydrogenation has been a popular technique to transform aromatic compounds to hydrocarbons. An alternate approach to accessing three dimensional sp^3 boryl compounds is to hydrogenate the abundantly available sp^2 boryl compounds. The first hydrogenation of a borylated olefin was carried out by Clarke and Haller patented the hydrogenation of chlorovinyl groups of chlorovinylboranes of the class $(ClCH{=}CH)_a(R)_bBCl_{[3-(a+b)]}$ (R = alkyl radical with 1-5 C atoms, a= 1-3, b =0-2, and a + b < 3), using molecular hydrogen at temperatures of 20-160 °C and at pressures ranging from 0 psi to 50 psi while the reactants are in contact with the palladium catalyst (Scheme 28). This catalyst proved to be tolerable to B-Cl bonds and the reaction was carried out in a flow reactor using various catalysts and various temperatures to yield chloroalkylboranes.[34] It was noted that the C-Cl bond underwent hydrogenolysis during the reaction.

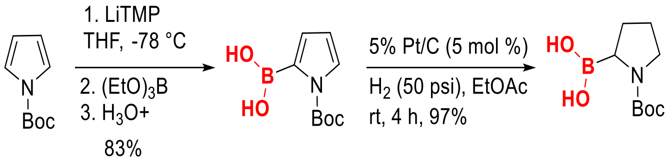
Scheme 28: Hydrogenation of chlorovinylborane[34]



$$\underset{0.08\text{ g/min}}{(ClCH{=}CH_2)BCl_2} + \underset{160\text{ cc/min}}{2H_2} \xrightarrow[\text{50 psi, 7.75 h, 80 °C}]{\text{0.2\% Pd/C (30 g)}} \underset{62\%}{(C_2H_5)BCl_2} + HCl$$

Following this report, many groups hydrogenated borylated olefins thereby expanding the scope. The first hydrogenation of borylated heteroarene was shown by Kelle and coworkers in 1993 where they hydrogenated Boc-pyrrole using platinum on carbon (Scheme 29).[35] The reaction was carried out at room temperature with a pressure of 50 psi using a high catalyst loading (5.0 mol %) to generate (1-(*tert*-butoxycarbonyl)pyrrolidin-2-yl)boronic acid.

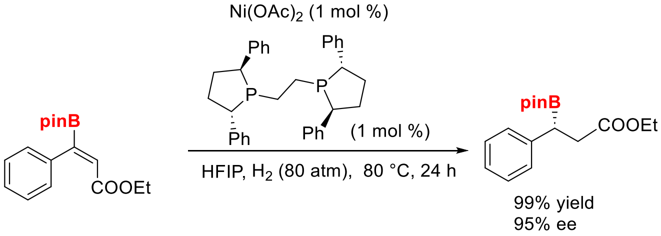
Scheme 29: Hydrogenation of borylated pyrrole



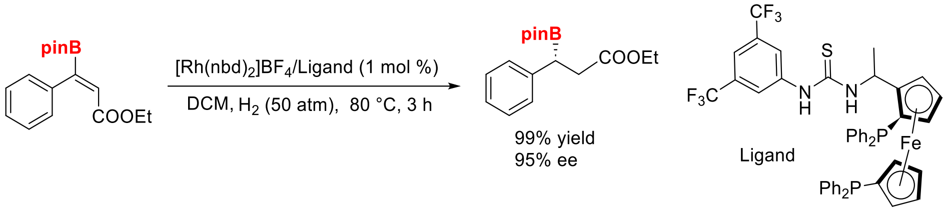
In 2019, Han, Liu, Zhang, Li, Dong, and Zhang hydrogenated a β-boronic ester substituted α,β unsaturated carboxylic ester in an asymmetric manner. They showed the hydrogenation of an alkene bearing a boronic ester using Ni as a catalyst (Scheme 30). Only the alkenes were hydrogenated under these conditions. Nickel did not break the aromaticity and hydrogenated the ring.[36]

Also in 2019, the same group hydrogenated similar compounds asymmetrically using Rh as a catalyst with a complex ligand system (Scheme 31). Under their reaction conditions Rh[(cod)Cl]$_2$ showed 57% conversion and [Ir(cod)$_2$Cl] showed trace conversion in the hydrogenation process.[37]

Scheme 30: Hydrogenation of borylated olefin using Nickel catalyst[36]

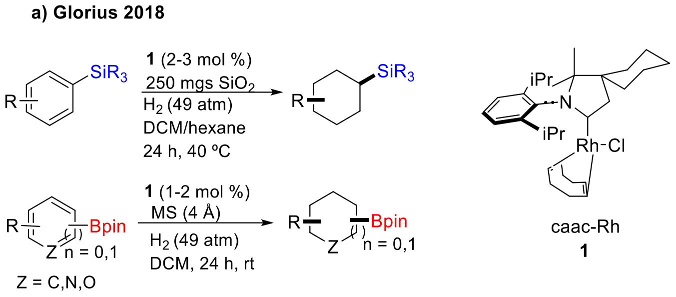


Scheme 31: Hydrogenation of borylated olefin using rhodium catalyst[37]

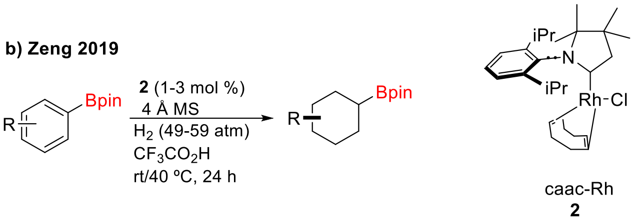


Glorius then expanded the scope of hydrogenation of borylated compounds by finding conditions amenable to a host of boryl heteroarenes and arenes.[38] He used a Rh catalyst with cyclic alkyl amino carbenes (caac) ligand at low catalytic loading (1-2 mol %), 50 bar pressure and room temperature. This catalytic system has also been used to hydrogenate fluoroarenes in 2017.[39]The same group also developed a method to hydrogenate various silylated arenes (Scheme 32).[40] The catalyst requires multistep synthesis. Using a slight variation in the catalyst, Ling, He, Zhang, Luo, and Zeng hydrogenated various boryalted arenes, heteroarenes and fused systems (Scheme 33).[41] The results of C(sp^3)-H borylation via hydrogenation of C(sp^2)-H borylation carried out using Rh/C as a catalyst are discussed in Chapter 4.

Scheme 32: Hydrogenation of borylated and silylated aromatic compounds[38,40]



Scheme 33: Hydrogenation of borylated and silylated aromatic compounds[41]



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CHAPTER 2. STERIC SHIELDING EFFECTS INDUCED BY INTRAMOLECULAR C–H•••O HYDROGEN BONDING: REMOTE BORYLATION DIRECTED BY BPIN GROUPS

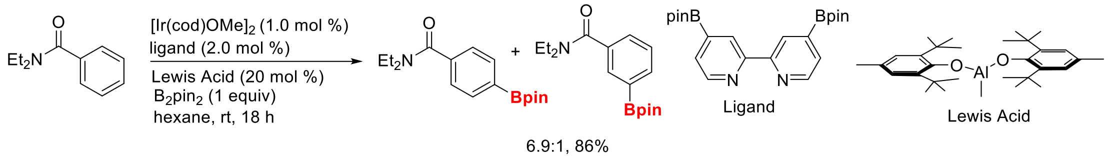
This chapter draws from the paper: Montero Bastidas, J. R.; Chhabra, A.; Feng, Y.; Oleskey, T. J.; Smith, M. R., III; Maleczka, R. E., Jr. Steric Shielding Effects Induced by Intramolecular C–H···O Hydrogen Bonding: Remote Borylation Directed by Bpin Groups. *ACS Catal.* **2022**, *12* (4), 2694–2705.

2.1. INTRODUCTION

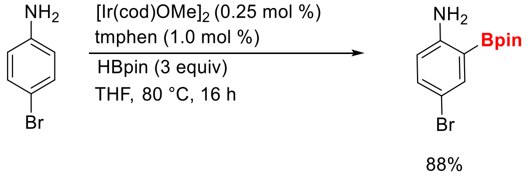
Nowadays, C–H bonds can be diversified via different C–H functionalization methods. Yet, targeting one C–H reactive site in the presence of similar C–H bonds remains challenging.[1,2] Although considered weak, noncovalent interactions can differentiate the energetics of otherwise similar reactive sites since an interaction where D*G*° ≤ -3.5 kcal/mol will be in force for ≥ 99% of the molecules at 100 °C. In the area of sp^2 C–H activation, pre-installed directing groups can interact with the catalyst via hydrogen bonding, Lewis acid-base, or electrostatic interactions to selectively functionalize ortho, meta or para positions of arenes.[3–9] However, selective reactions at distal C–H sites often require construction of complex directing groups/ligands.[4,5,9–11] A different strategy uses steric shields to block nearby C–H bonds, thus leaving the distal position as the only accessible reactive site. For example, Nakao's group used Lewis acidic additives that interact with aryl amides and shield the meta positions, enabling selective para functionalizations (Scheme 34).[12–15] In contrast, a complementary approach where intramolecular noncovalent interactions create steric shields leading to remote functionalization is far less common.

In the last decade, ortho regioselective sp^2 CHB has been achieved by means of chelating and relay directing groups as well as outer sphere interactions.[4,7,16] In 2013, our group reported that meta and para substituted anilines yield the corresponding ortho borylated product courtesy of an N–H hydrogen bonding with the catalyst (Scheme 35).[17]

Scheme 34: Iridium catalyzed para selective functionalization using a lewis acid additive[12]

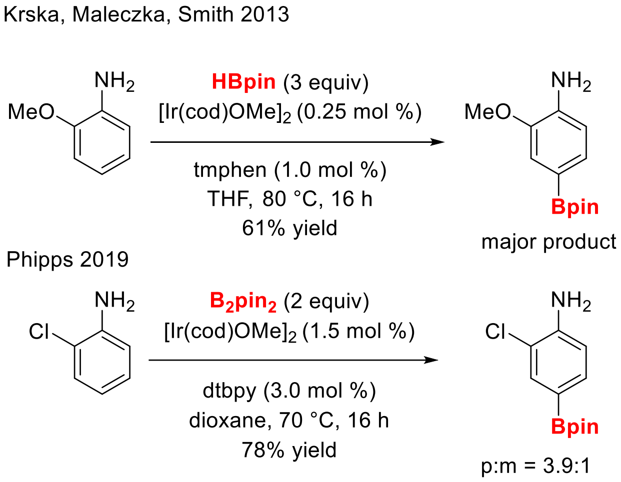


Scheme 35: Ortho borylation of 4-bromoaniline using iridium catalyzed C-H borylation[17]



Unexpectedly, 2-methoxyaniline was selectively borylated para to nitrogen. A similar result was reported by the Phipps group during their CHB of 2-chloroaniline (Scheme 36).[18] It was proposed that electronic effects might play a role in the change of selectivity for 2-chloro and 2-methoxyaniline, but there was no experimental corroboration of this hypothesis.

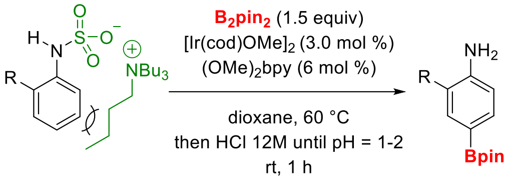
Scheme 36: Unexpected observation of para borylation using iridium catalyzed C-H borylation[17,18]



More recently, we and the Phipps group independently developed a protocol for para CHB of anilines directed by ion-pair electrostatic interactions of sulfamates with bulky tetraalkylammonium counterions (Scheme 37).[18,19] Steric shielding of C–H bonds ortho and meta to the sulfamate by alkyl chains of the tetraalkyl ammonium cation in the ion pair are proposed to account for the para selectivity. We wondered if a different sort of steric shielding might confer the para selectivity in CHBs of 2-methoxy and chloroaniline mentioned above.

It is well documented that *N*-borylation of *N*-unsubstituted anilines occurs rapidly under CHB conditions.[17] We hypothesized that in the presence of an ortho substituent like methoxy or chloro, the N–Bpin group could orientate towards the meta C–H where it would act as a steric shield, leading to para-selective CHB (Figure 4).

Scheme 37: Para C-H borylation of sulphamates driven by ion pair electrostatic interactions[17,18]



Bpin would be an attractive steric shield for anilines possessing an N–H bond since *in situ N*-borylation with B_2pin_2 or HBpin is rapid, and the aniline N–H is easily restored during workup by adding methanol, which rapidly cleaves the B–N bond. This contrasts with our previous approach to accessing para-borylated anilines, which required a step to install the sulfamate group and a step where highly acidic conditions were required to remove it from the product.

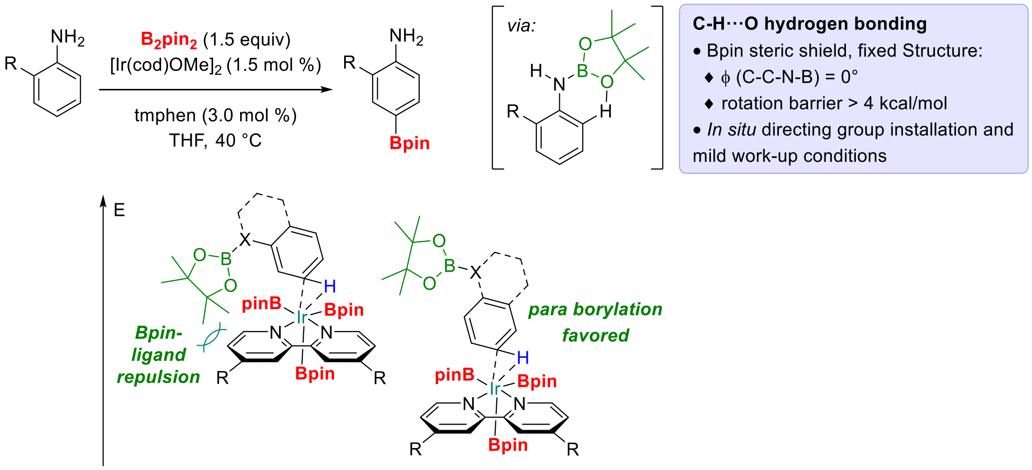


Figure 4: Remote CHB driven by intramolecular hydrogen bonding

2.2 RESULTS AND DISCUSSION

2.2.1. Para C–H borylation of anilines, *N*-alkylated anilines and indoles.

We set out to examine whether para selectivity after *N*-borylation of anilines and allied substrates was a general phenomenon. To do so, we first looked to optimize the reaction on 2-chloroaniline. Starting with our previously reported conditions, we compared the regioselectivity when B_2pin_2 was used in place of HBpin and found that the former yielded an improved para to meta ratio: 5.6 to 1 versus 4.5 to 1. With B_2pin_2 as the new boron partner we then explored temperature and solvent effects on selectivity (Figure 5). Cyclohexane gave higher para selectivity, especially at lower temperatures, but conversion dropped relative to THF. The best balance between reactivity and selectivity was found with THF at 40 °C. After 4 h, the conversion was 61% and >90% after 24 h.

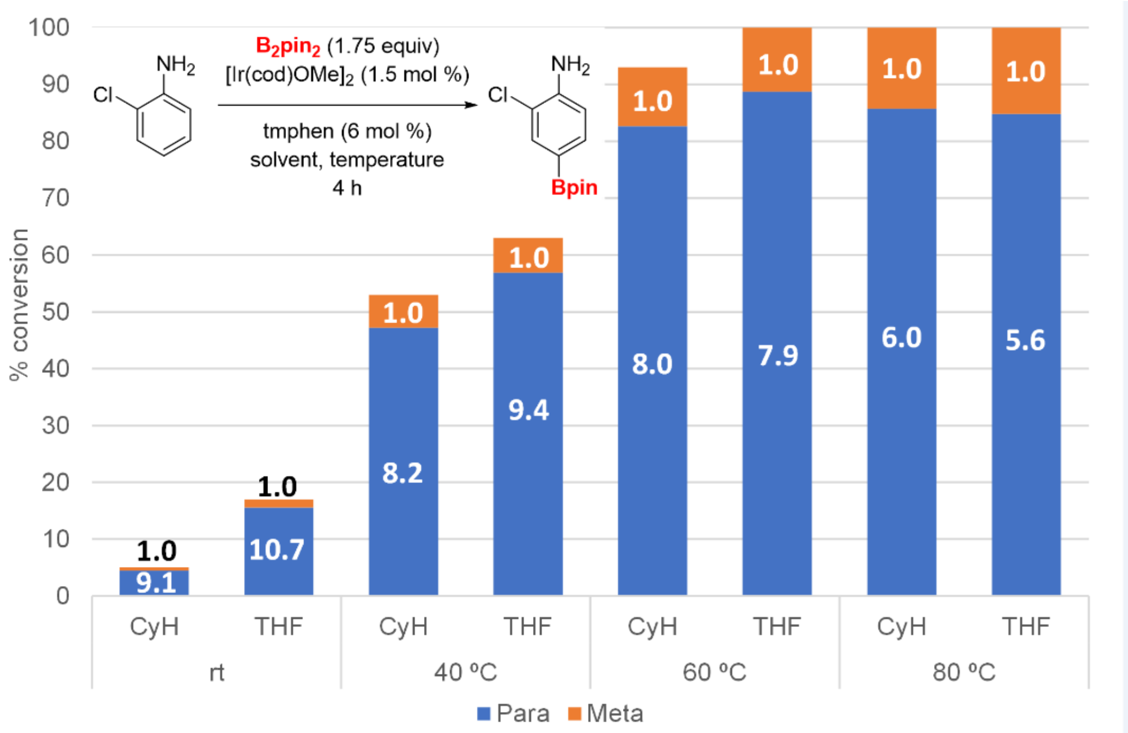
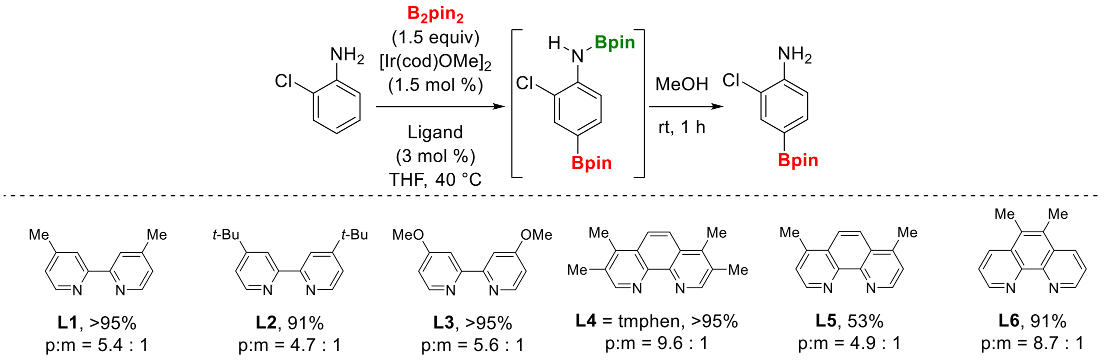


Figure 5: Temperature and solvent effect on para-C-H borylation of 2-chloroaniline.
Blue and orange bar represent conversion to the meta and para isomer, respectively. CyH=cyclohexane THF=tetrahydrofuran

With these conditions in hand, we evaluated the effect of the ligand and the diboron partner **(Scheme 37).** Bipyridine ligands (**L1**–**L3**) gave modest para/meta ratios (~5:1). Notably, 4,4'-dimethoxy-2,2'-bipyridine (**L3**), which was optimal in our previous para directed CHB of sulfamate salts, did not prove superior in this scenario. Selectivity with ligand **L5** was similar, but yield suffered. In contrast, the para:meta ratio doubled with phenanthrolines **L4** and **L6**, while yields remained high. We chose tmphen (**L4**) to continue our studies due to it being slightly better than **L6** in terms of regioselectivity and yield.

Scheme 38: Ligand effect on the selectivity of the para CHB of 2-chloroaniline[a]

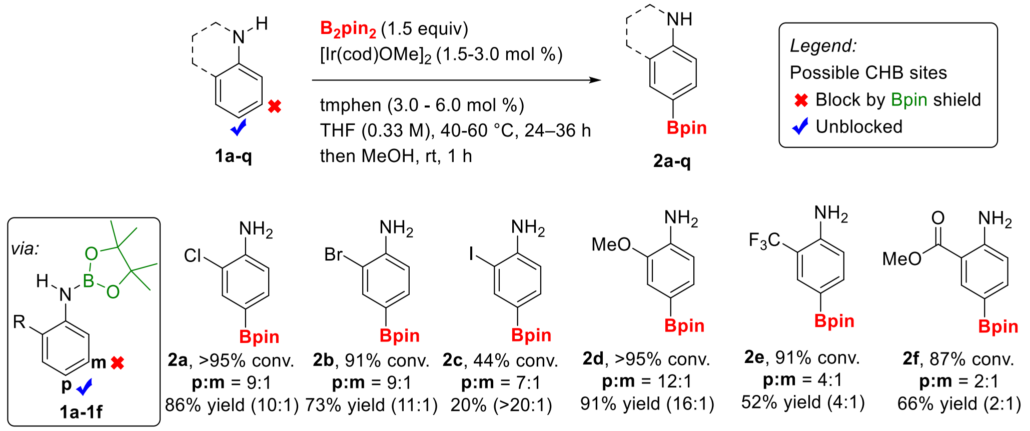


[a] The para to meta ratio (p:m) and conversions were calculated by ^{1}H NMR spectra of crude reaction mixtures.

Next, we evaluated the para borylation of different anilines, all of which are substituted at the 2-position (Scheme 39). The highest para selectivity (C4:C5 > 7:1) was observed in CHBs for substrates where the ortho substituents have electron lone pairs (**2a**–**2d**).

Given that CHBs is enhanced at the meta positions in monosubstituted benzenes C_6H_5X when X = Cl,[20] Br,[21] I,[22] or OMe[23], (Scheme 40) the 2-substiuent is enhancing selectivity para to N. In contrast, **2e** with a trifluoromethyl ortho substituent saw selectivity drop to 4:1. Benzoate **2f** with an electron withdrawing group by resonance gave an even lower ratio of 2 to 1 para to meta. This result bears some relationship to previous reports of ester groups favoring para CHB. In our case that position is meta respect to the aniline nitrogen.[20,23]

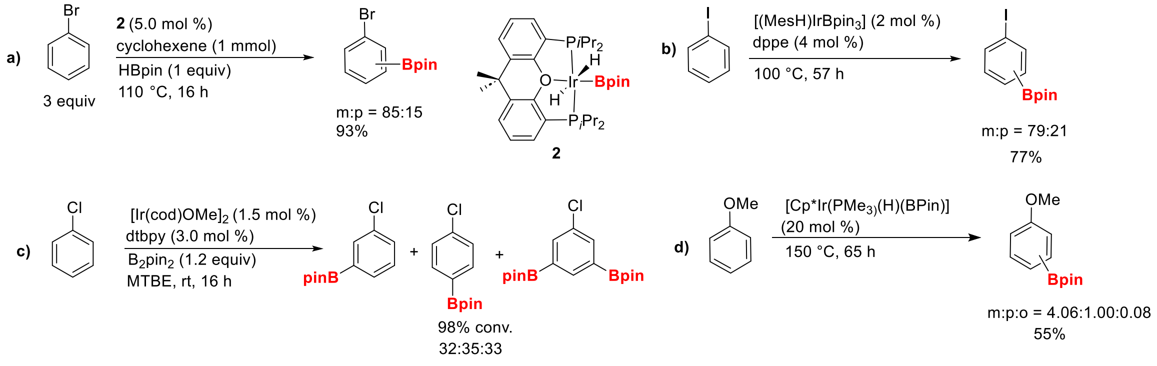
Scheme 39: Para borylation of N-anilines[a]



[a] Conversions and regioselective were measured by H NMR on crude reaction mixtures.. p and m refer to para and meta product respectively.

The size of alkyl ortho substituents (**2g**–**2i**) showed little effect, as para to meta ratios only ranged from 4:1 to 6:1 (Scheme 41). It should be noted that the 6:1 observed for 2-methylaniline (**2g**) was achieved by forming the N–Bpin bond prior to the CHB. In contrast, a selectivity of 4:1 is achieved with in situ N–Bpin bond formation of **2g** which suggests a slow formation of the N-borylated intermediate in this case. CHB at C4 was preferred for anilines when C3 was fluorine-substituted (substrate **1k**).

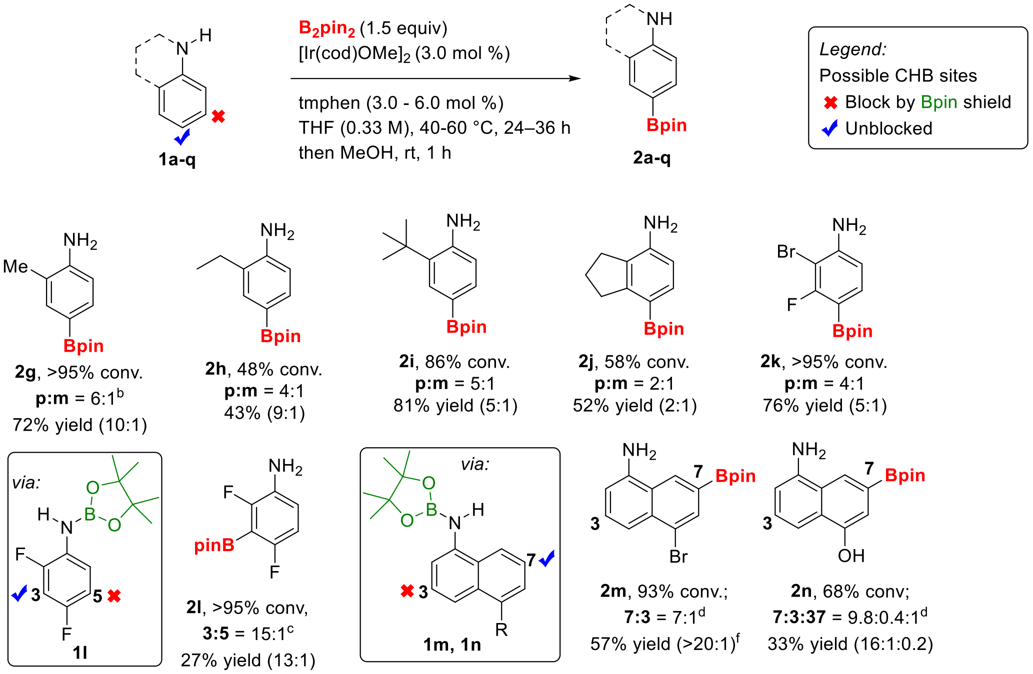
Scheme 40: Para borylation on anilines and naphthalene[20-23]



This is consistent with an electronic preference for CHBs ortho to F and attenuated steric interference from F since H, and its isotopes, are the only substituents that are less sterically demanding.[24,25] Para selectivity for substrate **1j**, albeit modest, is more significant since the only literature report where CHB at C3/C6 of an indane structure is preferred has a *tert*-butyl group at C4, obstructing C3/C5 positions.[26]

As stated above, fluorine atoms are relatively small and CHB next to them is observed. CHB of 2,4-difluoroaniline (**1l**) presented a more interesting scenario. In this case, were the N–Bpin orientated away from the ortho fluorine, the resultant steric shield would block the 5-position leaving the 3-borylation as the only option. This was the result as C3 borylation occurred with a 15:1 preference over C5 borylation.

Scheme 41: Para borylation on anilines and naphthalene[a]



[a] Conversions and regioselectivies were measured by H NMR on crude reaction mixtures. Yields refer to the isolated material with the ratios of major to minor products in the isolated material given in parentheses. [b] N-bpin bond formed prior to CHB with HBpin (1.2 equiv), [Ir(cod)Ome]2 (0.5 mol %), THF, 80 C, 2 h; under standard condition (A) the result are 61% conv.; p:m = 4:1 with 47% yield (>20:1) [c] C3 and C5 refer to 3- and 5- borylated product, respectively. [d] C3 and C7 refer to 3- and 7-borylated product respectively and C3 C7 refer to the 3,7-diboryalted product. Regioselectivity confirmed by x-ray crystallography.

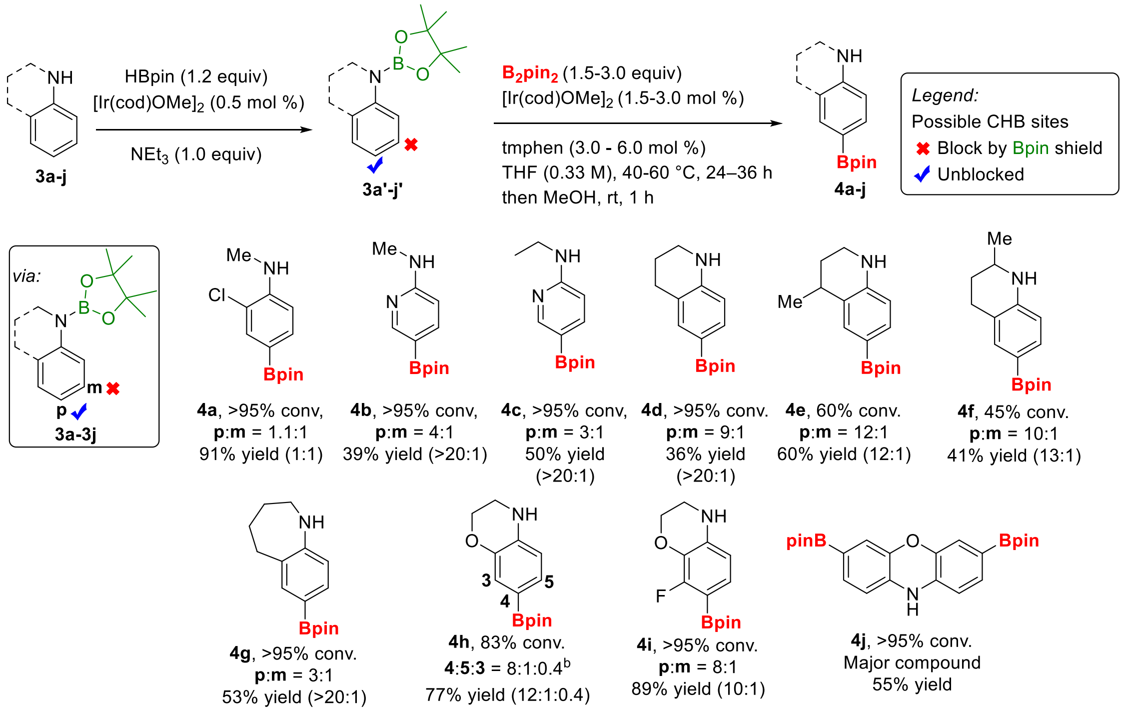
To probe other substrates with substituents at the ortho and meta C–H positions, we examined the CHB of N-borylated 5-substitued 1-naphthyl amines **1m** and **1n**. In these substrates, C4, C6, and C8 would be blocked from CHB by substituents, leaving only C3 and C7 sterically unencumbered. However, were our hypothesis correct, the N-Bpin would sterically shield C3, thus favoring C7 in a CHB. Indeed, borylation of **1m** and **1n** yield their 7-borylated product selectively (C7/C3 7:1 and 24:1 respectively). In the case of **1n**, a small amount of diborylation was observed. Although borenium C-H functionalization has not been applied to substrate **1m**, expected functionalization at C4 would complement the outcome from Bpin shielding.

We next turned our attention to other *in situ* borylated scaffolds, namely N-alkylated anilines (Scheme 42). Unfortunately, CHB of 2-chloro-N-methylaniline **3a** was not para selective under the optimized conditions. A slow rate of N–Bpin formation could explain the lack of selectivity. However, even after preformation of the N–Bpin bond no selectivity was observed. Thus, we considered other explanations. This led us to propose that a reluctance of N-borylated **3a** to orientate in the same plane as the aromatic ring, which per our hypothesis creates the N–Bpin steric shield, is responsible for the observed regiochemical result. Such a hypothesized planar conformation is supported by modeling the lowest energy conformation of N-borylated intermediates of N-unsubstituted anilines (see Section 2.3 and Figure 5 for further discussion).

In contrast, N-borylated 2-chloro-N-methyl aniline does not adopt a planar conformation (see Section 2.3 and Figure 5 for details) owing to an $A_{(1,3)}$ interaction between the N-methyl with the ortho chlorine. As N-borylated N-alkyl-2-aminopyridines should lack this steric clash, **3b** and **3c** should be para selective. This proved to be the case with **4b** and **4c** both being the major (4:1) CHB products.

1,2,3,4-Tetrahydroquinolines also drew our attention as in these N-alkylated anilines the covalent chain that links the aromatic ring with the nitrogen should allow the N-borylated intermediate to achieve a pseudo planar conformation. Para products **4d**–**4j** were obtained as the major regioisomer from their corresponding 1,2,3,4-tetrahydroquinolines. The size of the saturated ring does influence the level of selectivity, as illustrated in **4g** where the selectivity was only 2:1.

Scheme 42: Para borylation of N-cyclic amines[a]

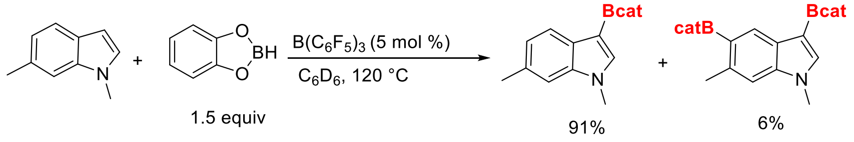


The conversions and regioselectivies were measured by 1-H NMR on crude reaction mixtures. Yields refer to the isolated material with the ratios of major to minor products in the isolated material given in parentheses. [b]C5 and C6 refer to 5- and 6- borylated product, respectively.

Adding a methyl group about the saturated ring did not significantly change the selectivity as show by products **4d–4f**. With **3h**, borylation next to the oxygen was also observed, but the para product still predominated (8:1). The fluorinate version of **3h**, namely **3i**, was equally selective. Diborylation of phenoxazine **3j** mainly yielded the bis para compound along with multiple minor products.

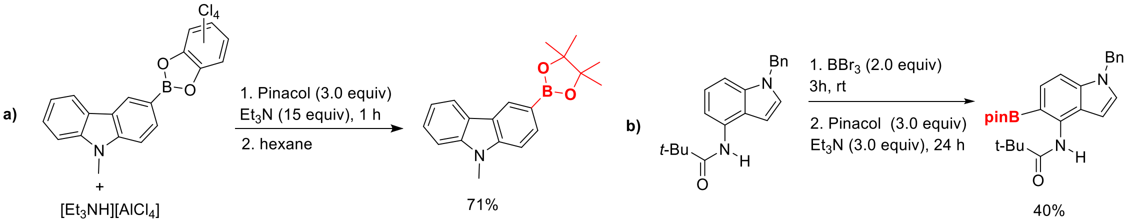
Indoles. N-Borylation of indoles is known to block the C2 CHB normally seen in the parent compounds, instead yielding the corresponding 3-borylated product (Scheme 43).[17]

Scheme 43: C3 borylation of indoles directed by N-borylation[17]



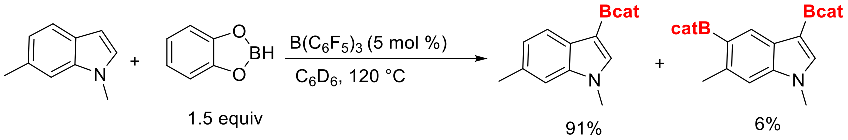
We asked if in an N-borylated 3-subsitued indole, the N–Bpin would shield the closer C6 position leading to the corresponding 5-borylated indoles. C5 borylation of indoles has been elusive besides some specific examples employing electrophilic borylation with borenium cations. The examples are limited to N-methyl carbazole or are trigger by the use of an amine pivaloate directing group at the 4 position (Scheme 44).[27,28]

Scheme 44: Rare C5 borylation of carbazole and indole[27,28]



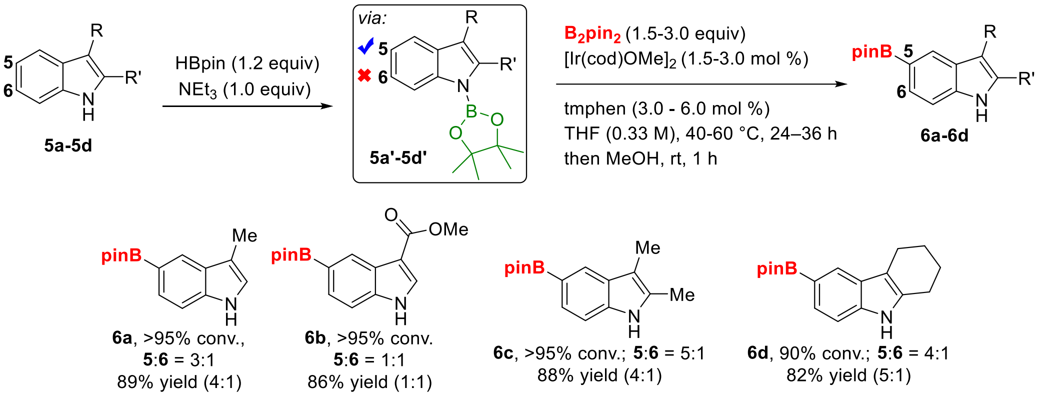
A protocol to access 3,5-diborylated indoles has been reported but suffers from low conversions (< 30%) (Scheme 45).[29]

Scheme 45: 3,5 diborylation of indoles[29]



Under our optimized conditions and after formation of the N–Bpin intermediate, 3-methylindole **5a** yielded the 5-borylated with a modest 3:1 selectivity over the minor 5-borylated isomer (Scheme 46). Replacement of the methyl group by a methyl ester as in **5b** resulted in the loss of selectivity. However, the presence of substituents at both C2 and C3 impacted selectivity little as shown in **6c** and **6d**. It should be stated that for **5c** and **5d**, formation of the N–Bpin intermediate is slow and additional HBpin and $[Ir(cod)OMe]_2$ as well as a 3-hour reaction time was needed to afford full N-borylation.

Scheme 46: Borylation of indoles



6a, >95% conv., **5**:**6** = 3:1
89% yield (4:1)

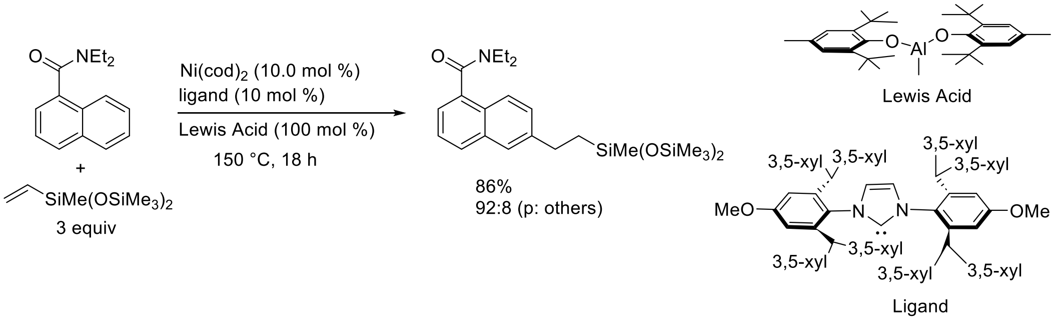
6b, >95% conv. **5**:**6** = 1:1
86% yield (1:1)

6c, >95% conv.; **5**:**6** = 5:1
88% yield (4:1)

6d, 90% conv.; **5**:**6** = 4:1
82% yield (5:1)

^{a}Conversions and regioselectivies were measured by 1H NMR on crude reaction mixtures. Yields refer to the isolated material with the ration of major to minor products in the isolated material given in parentheses. C5 and C6 refer to 5- and 6- borylated product, respectively.

Scheme 47: Para C-H alkylation of naphthylamide[30]

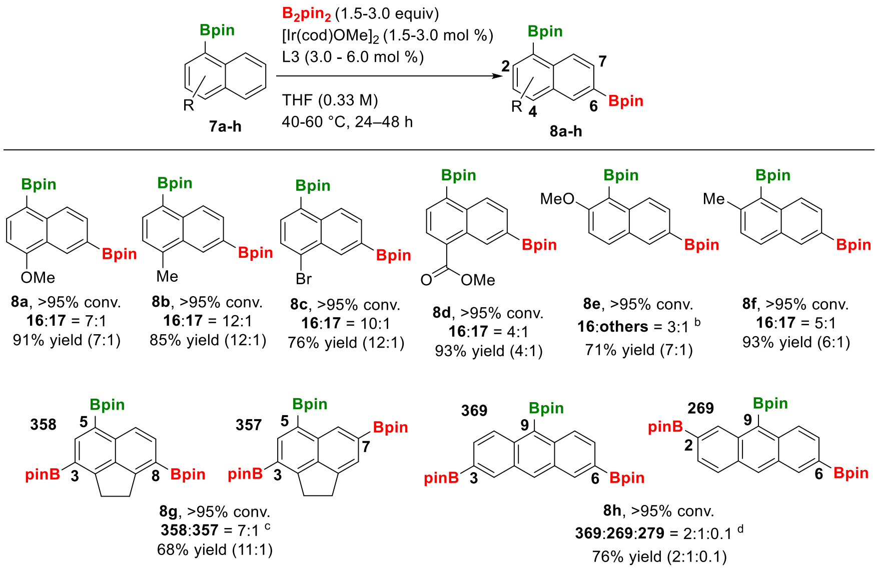


2.2.2. C6 borylation of 1-borylated naphthalenes.

We speculated that Bpin groups can create a steric shield even when not part of a N–Bpin moiety. We thus focused on 1-borylated naphthalenes, which could bear geometries similar to those of N-borylated 2-substitued anilines and N-borylated tetrahydroquinolines (Scheme 41). If so, the Bpin derived steric shield would block the C7-position leaving the C6-position available for CHB. Borylation of 1-borylated naphthalene **7a** supported our proposition and yielded the 1,6-diborylated product selectively. A ligand screening showed that 4,4’-dimethoxy-2,2’-bypiridine (**L3**) was the best choice for the C6-borylation of 1-borylated naphthalenes. This result is potentially valuable as C6 functionalization of naphthalenes remains rare.[30] A notable exception, comes from Nakao's group where a 1-naphtyl amide was made to undergo C6-alkylation by using an aluminum Lewis acid as a steric shield (Scheme 47).[13,14]

As shown in **Scheme 48**, a substituent on the C2- or C4-position is needed to avoid borylation at C3 (**7b**–**7f**). 5-Bpin acenaphthene **7g** borylated at both the expected C8 position and at C3. Under conditions that promote diborylation, 3,5,8-triborylated product **8g** was obtained as the major product along with the 3,5,7-triborylated product as a minor isomer. The Bpin shield in 9-borylated anthracene **7h** enabled remote borylation of both sides of the molecule leading to a 2:1 mixture of 3,6,9-triborylated and 2,6,9-triborylated products (**8h**).

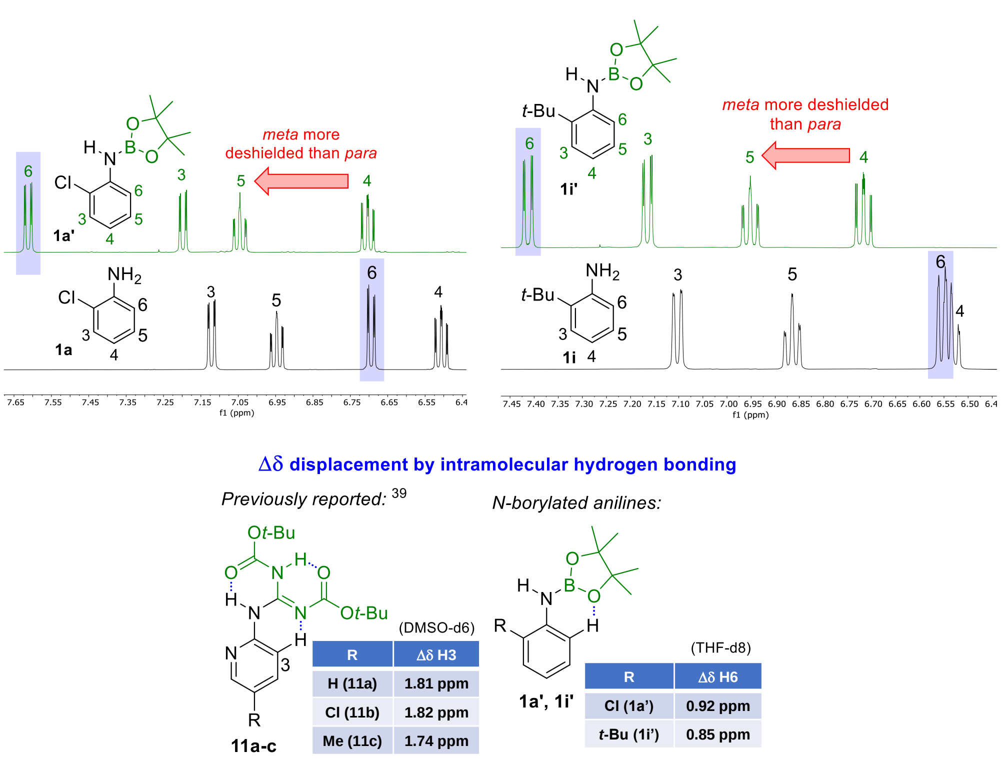
Scheme 48: Examples of chemoselective bond forming reactions[a]



[a]C1C6 and C1C7 refer to 1,6- and 1,7- diborylated naphthalene products, respectively. Conversions and C1C6/C1C7 ratios were measured by ^{1}H NMR on crude reaction mixtures. Yields refer to isolated material with the C1C6/C1C7 ratio of the isolated material given in parentheses. [b]For 8e there was an unknown minor isomer in the mixture besides the 7-borylated. [c]C3C5C8 and C3C5C7 refers to the 3,5,8- and 3,5,7- triborylated acenaphthelene, respectively. [d]C3C6C9, C2C6C9 and C2C7C9 refers to 3,6,9-, 2,6,9- and 2,7,9- triborylated anthracene, respectively.

2.2.3. Mechanistic Studies.

We began this study by suggesting the unusual para selective CHB of 2-methoxy and 2-chloroaniline came about by virtue of a N–Bpin steric shielding in contrast to the previously evoked electronic drivers. This steric shielding hypothesis could be understandably challenged as free rotation around the C–N and N–B bonds can avoid any steric perturbation caused by the N–Bpin group. Moreover, even in the orientation that maximizes the putative steric shield, one could question if the N–Bpin group is close enough to the meta C–H so as to block its borylation.


^{1}H NMR comparison of N-borylated anilines (solvent THF-d8)

Δδ displacement by intramolecular hydrogen bonding

(DMSO-d6)

R	Δδ H3
H (11a)	1.81 ppm
Cl (11b)	1.82 ppm
Me (11c)	1.74 ppm

(THF-d8)

R	Δδ H6
Cl (1a')	0.92 ppm
t-Bu (1i')	0.85 ppm

Figure 6: ^{1}H NMR comparison of N-borylated and unborylated 2-chloro and 2-methylaniline, and Δδ displacement due to C-H····N and C-H···O IMHB in 11**a-c** and **1a'**, **1i'** respectively

To address these questions and better understand the observed selectivities we performed the experiments described below. Steel and Marder have shown that ^{1}H NMR chemical shifts can be qualitative predictors of CHB selectivity when there is not a steric difference between two reactive sites.[20] More deshielded hydrogens are expected to be more acidic and more reactive towards

CHB. Based on 1D-NOE and 2D NMR experiments, we assigned the ^{1}H NMR chemical shifts of N-borylated 2-chloro (**1a’**) and 2-tertbutylaniline (**1i’**) (Figure 6). We acquired the spectra in THF-d_8 so as to best simulate solution structures present during the CHB. Spectra for both compounds had the meta proton appearing more downfield than the para proton. Per Steel and Marder, this would suggest the meta position should be electronically favored in a CHB. However, a preference for para borylation is the experimentally observed result. This points to factors besides electronic effects being responsible for the para preference.

A closer comparison of the ^{1}H NMR of the N-borylated intermediate versus the non-borylated version of 2-chloro and 2-tertbutyl aniline revealed a surprising deshielding effect on the chemical shift of the ortho proton after N-borylation (Figure 6). This displacement was also observed in other NMR solvents (C_6D_6, acetone-d_6, $CDCl_3$, pyridine-d_5). We attribute the downfield chemical shift movement to an intramolecular C–H•••O hydrogen bonding (IMHB) between the oxygen of the N–Bpin group and the ortho hydrogen in the aniline. Deshielding effects on chemical shifts caused by hydrogen bonds are well documented,[31–33] and one of the closest examples to our system is the IMHB present in N1,N’-diBoc protected pyridine-2-yl guanidine **11a–c**.[34] In this scenario, a C–H•••N IMHB is said to change the conformation, vs. analogous compound lacking a Boc group, to one where the pertinent protons are deshielded.

While the NMR studies argued against electronic effects being responsible for the para borylation of anilines, those studies did not shed light on the question of whether the N–Bpin group is actually close enough to the meta position to act as a steric shield. To begin addressing this question, we ran CHB reactions with larger diboron partners as B_2hg_2 and B_2pp_2 (Figure 7a). B_2hg_2 proved less reactive than B_2pin_2 in accordance with a previous report,[35] however the selectivity for the para position improved. We tested a novel diboron partner for CHB, B_2pp_2, and interestingly the conversion to the borylated product was greater than with B_2hg_2. The largest para to meta ratio was also found with B_2pp_2, which is consistent with our steric shield hypothesis.

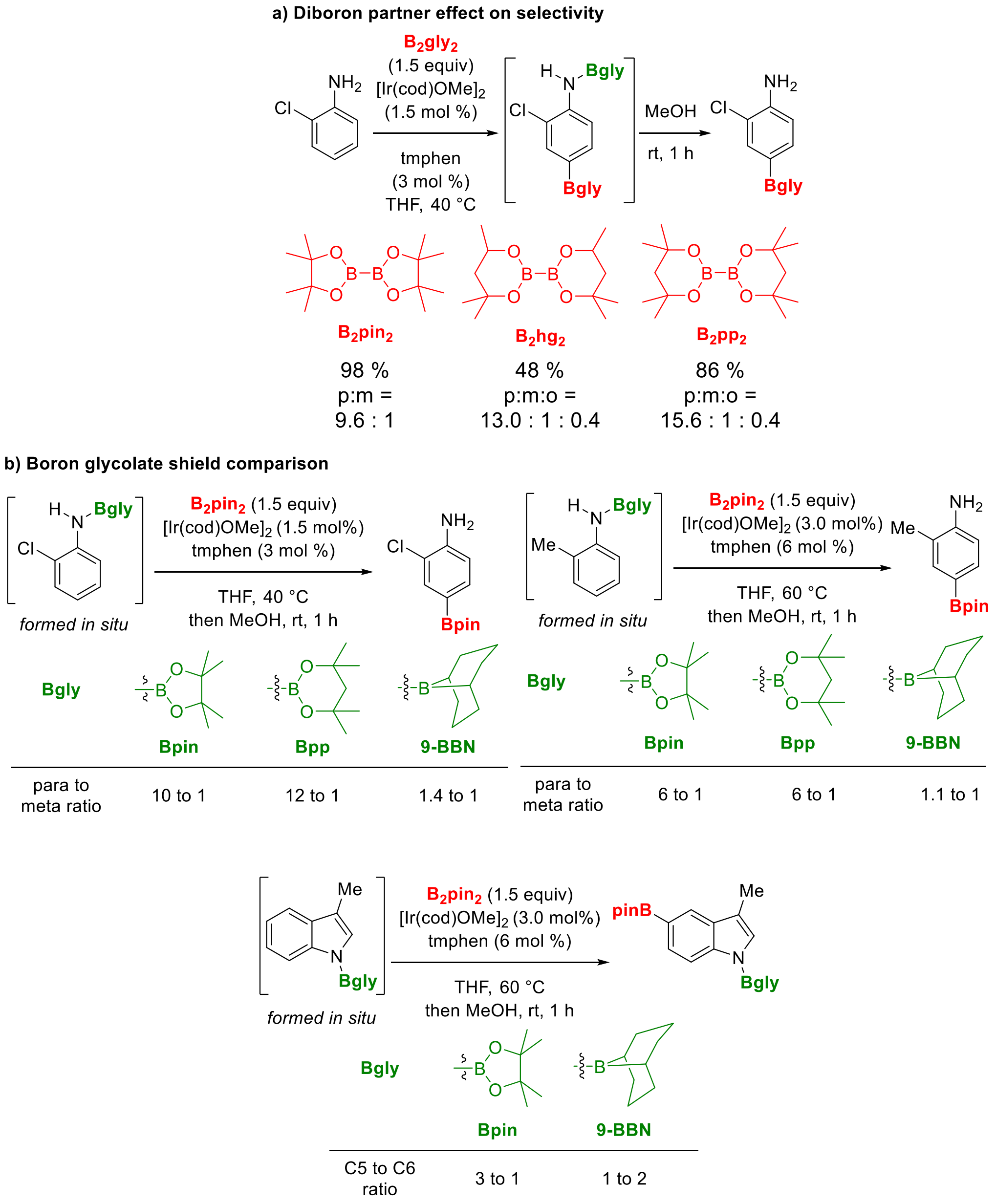


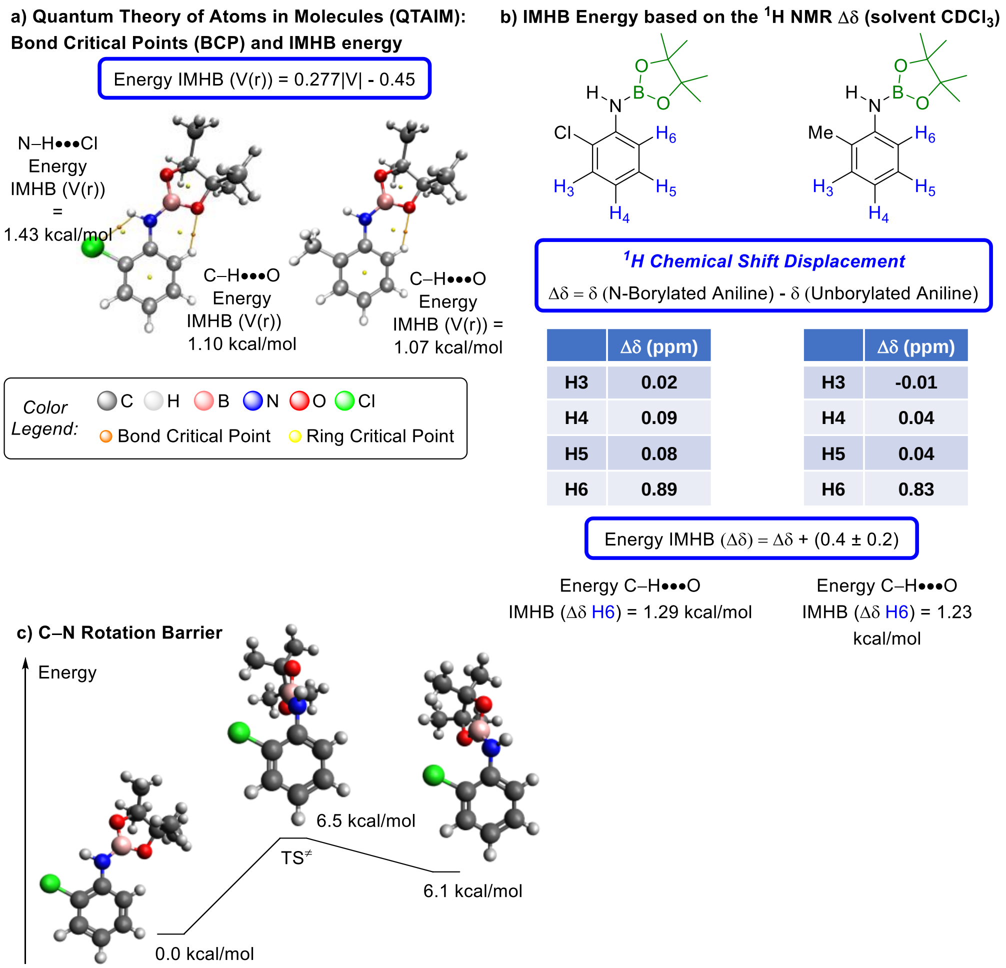
Figure 7: a) Diboron partner effect on CHB of 2-chloroaniline, b) Boron glycolate shield effect on the CHB of 2-chloroaniline, 2-methylaniline and 2-methylaniline

While this improved selectivity could be to the size of the installed N–Bpp group, a B_2pp_2 derived trisboryl active catalyst could also influence regiochemistry. Thus, we generated N–Bpin and N–Bpp compounds from 2-chloro and 2-methylaniline. These intermediates were then independently reacted under the same CHB conditions with B_2pin_2 as the diboron partner (Figure 7b). For 2-chloroaniline, the N–Bpp borylated derivative yielded a higher para/meta ratio as compared to the N–Bpin substrate. For 2-methylaniline, there was no observable change in selectivity; this may be a reflection of 2-methylaniline being inherently less para selective than 2-chloroaniline.

To probe the significance of the IMHB acceptor ability of N-Bpin toward selectivity, we decided to generate N–BBN, a boron group without oxygen, on the aniline. With an N–BBN in place, the para selectivity dramatically drops for both 2-chloro and 2-methylaniline. This further supports IMHB playing a direct role in selectivity. With N–BBN generated from 3-methylindole the CHB regiochemical preference flips and the C6-borylated isomer is major (2:1) as opposed to the C5 selectivity (3:1) seen with N–Bpin.

Seeking further evidence of IMHB involvement, we examined the N-borylated anilines with the Quantum Theory of Atoms in Molecules (QTAIM) developed by Bader using the multiwfn program.[36–38] QTAIM is used to identify IMHB based on a topological analysis of the electronic distribution. Bond critical points (BCP) are defined as the position between two atoms were the electron density reaches a minimum. QTAIM identifies BCP when two atoms are connected by any type of bond including interactions as IMHB. We used a B3LYP functional and 6-311++G(d,p) basis set to optimize the geometry of N-borylated 2-chloro and 2-methylaniline (Figure 8a). This basis set has been previously reported to work well when IMHB is present.[39] The QTAIM analysis of both N-borylated anilines shows a BCP between the oxygen of the N–Bpin group that is nearest to the ortho hydrogen of the aromatic ring supporting the existence of a C–H•••O IMHB. An additional BCP is found in N-borylated 2-chloroaniline between the chloride and the N–H. This additional N–H•••Cl IMHB may be one contributor to the greater para CHB selectivity of 2-chloroaniline vs. 2-methylaniline.

The energy of hydrogen bonds can be estimated by multiplying the potential energy density (V(r)) at the BCP found with QTAIM by a scaling factor determined from plotting V(r) vs. experimentally determined hydrogen bonding energies. The linear relationship initially found by Espinosa *et. al.* has been adapted by Afonin *et. al.* for the case of IMHB including cases with C–H•••O interactions.[39,40] Afonin's corrected equation to calculate the C–H•••O IMHB energy of N-borylated 2-chloro and 2-methylaniline gave comparable energies corresponding to 1.10 kcal/mol and 1.07 kcal/mol respectively (Figure 8a). IMHB energies can also be estimated using NMR spectroscopy. Typically, there is a linear relationship between the IMHB stabilization energy and the ^{1}H chemical shift difference, $\Delta\delta$, of the hydrogen involved in the IMHB in the target molecule versus a reference in which no IMHB occurs (Figure 8b).[39,41] We used $CDCl_3$ for these experiments since the relationship was established from ^{1}H NMR spectra of $CDCl_3$ solutions. We chose the non-borylated anilines as the references and found energies of 1.29 and 1.23 kcal/mol for the IMHB of 2-chloro and 2-methylaniline, respectively, in excellent agreement to the energy predictions from QTAIM.



	Δδ (ppm)
H3	0.02
H4	0.09
H5	0.08
H6	0.89

	Δδ (ppm)
H3	-0.01
H4	0.04
H5	0.04
H6	0.83

Figure 8: a) QTAIM analysis of N-borylated 2-chloro and 2-methylaniline. (left and right respectively). b) 1H NMR chemical shift of N-borylated 2-chloro and 2-methylaniline respect to unborylated anilines, c) C-N rotation barrier for N-borylated 2-chloroaniline

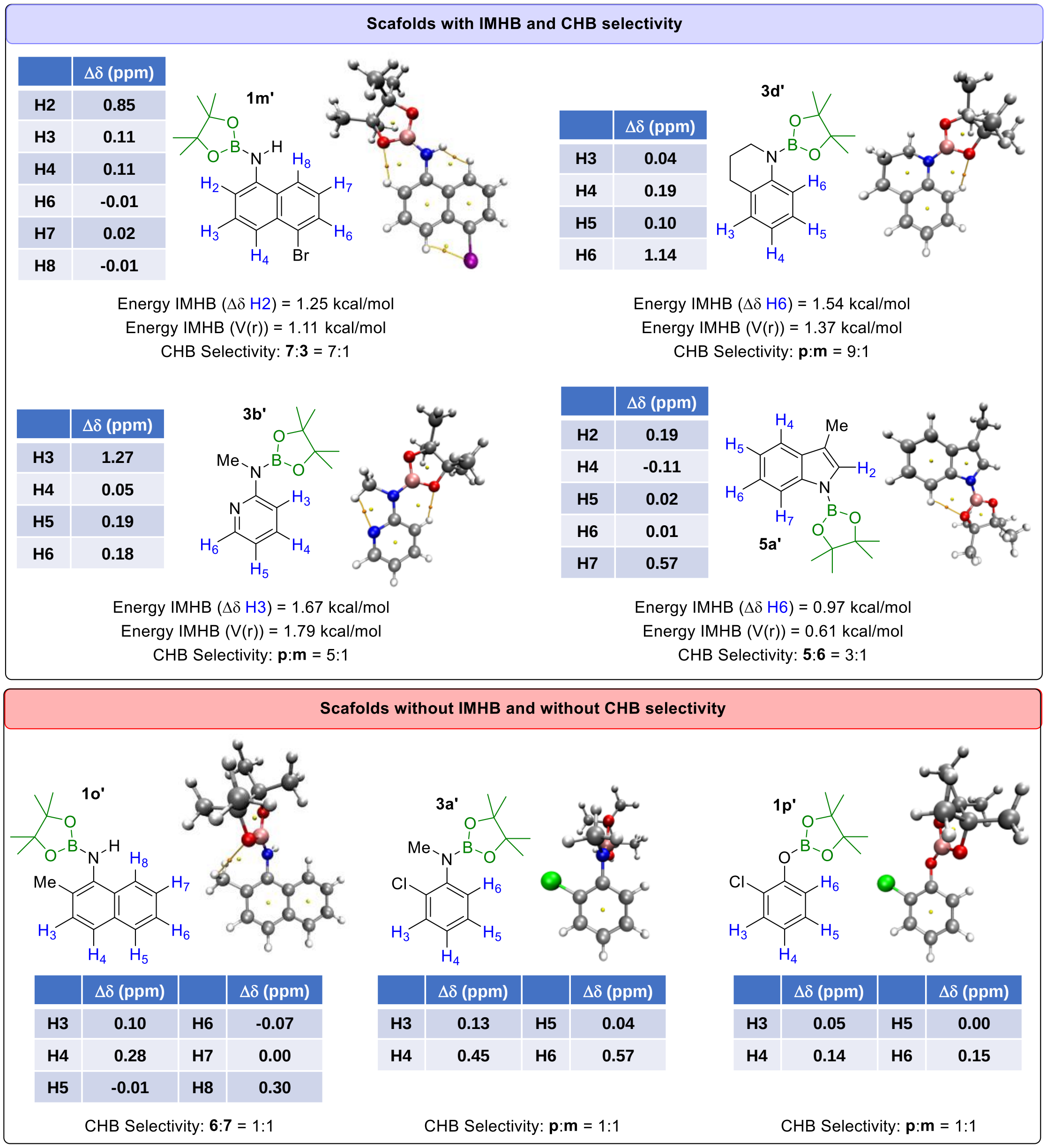
One potential pitfall in attributing para selectivity to IMHB Bpin shielding is the assumption that there is only one energy minimum on the conformational energy surface. For example, the presence of a second local minimum where the plane of the N–Bpin is orthogonal to the plane containing the aryl ring could erode selectivity if (i) the second local minimum has a comparable or lower Gibbs' energy than the IMHB local minimum, and (ii) the barrier connecting the local minima is small. Indeed, theory predicts that there are local minima similar to the aforementioned scenario for N-borylated 2-chloroaniline and 2-methylaniline at 5.4 and 3.1 kcal/mol relative to their respective IMHB local minima (Figure 8c) and the corresponding transition states that connect these local minima are 6.6 and 4.6 kcal/mol above the IMHB local minima. Based on the energies of the higher energy local minima, theory predicts that more than 99% on the N-borylated anilines adopt the IMHB structures. These findings support the hypothesis that IMHB between the Bpin O and the C6 proton creates a steric shield that accounts for the para selectivity.

We next asked if similar relationships could be found in other scaffolds with and without IMHB. Accordingly, good CHB selectivities are seen for substrates when protons proximal to Bpin substituents have the largest ^1H NMR chemical shift displacement, as well as a BCP between that proton and the Bpin O from QTAIM analysis. Specific examples are described below.

The H2 of N-borylated 5-bromo-1-aminonaphthalene **1m’** shows a 0.85 ppm difference from the reference 5-bromo-1-aminonaphthalene. By comparison, all the other protons deviate by <0.2 ppm. QTAIM shows a BCP that supports an IMHB with an energy of 1.25 kcal/mol, which is close to 1.11 kcal/mol calculated based on the spectroscopically observed ^1H NMR chemical shift displacement. As expected, 5-bromo-1-aminonaphthalene undergoes a C7-selective borylation by blocking the C3 position (Figure 9).

In contrast, N-borylated 2-methylnaphthalene **1o’** show no evidence of C–H•••O IMHB with the naphthalene as the hydrogen bond donor. H8 might be available for IMHB but $\Delta\delta$ is only 0.30 ppm, which is close to the $\Delta\delta$ of H4 (0.28 ppm), suggesting that chemical shift displacement results from electronic effects after N-borylation. No BCP is detected with the arene as the hydrogen bond donor, but a BCP corresponding to a C–H•••O IMHB between the N–Bpin and the methyl group is found. The lack of IMHB with the naphthalene ring might be due to steric effects that disrupts any 7-member ring IMHB from happening. Accordingly, no selectivity was found under CHB reaction conditions.

As shown in Figure 6, the CHB regioselectivity of N-alkylated aniline depends on the scaffold. CHB of N-borylated 2-chloro-N-methyl aniline **3a’** did not show any selectivity. The steric clash between the N– Me and Cl groups prevents IMHB formation with the BpinO. While chemical shift for H6 is 0.57 ppm, the significant displacement of 0.45 ppm for H4 again suggests that electronic effects are the actors.



Scafolds with IMHB and CHB selectivity

1m'

	Δδ (ppm)
H2	0.85
H3	0.11
H4	0.11
H6	-0.01
H7	0.02
H8	-0.01

Energy IMHB (Δδ H2) = 1.25 kcal/mol
Energy IMHB (V(r)) = 1.11 kcal/mol
CHB Selectivity: **7**:**3** = 7:1

3d'

	Δδ (ppm)
H3	0.04
H4	0.19
H5	0.10
H6	1.14

Energy IMHB (Δδ H6) = 1.54 kcal/mol
Energy IMHB (V(r)) = 1.37 kcal/mol
CHB Selectivity: **p**:**m** = 9:1

3b'

	Δδ (ppm)
H3	1.27
H4	0.05
H5	0.19
H6	0.18

Energy IMHB (Δδ H3) = 1.67 kcal/mol
Energy IMHB (V(r)) = 1.79 kcal/mol
CHB Selectivity: **p**:**m** = 5:1

5a'

	Δδ (ppm)
H2	0.19
H4	-0.11
H5	0.02
H6	0.01
H7	0.57

Energy IMHB (Δδ H6) = 0.97 kcal/mol
Energy IMHB (V(r)) = 0.61 kcal/mol
CHB Selectivity: **5**:**6** = 3:1

Scafolds without IMHB and without CHB selectivity

1o'

	Δδ (ppm)		Δδ (ppm)
H3	0.10	H6	-0.07
H4	0.28	H7	0.00
H5	-0.01	H8	0.30

CHB Selectivity: **6**:**7** = 1:1

3a'

	Δδ (ppm)		Δδ (ppm)
H3	0.13	H5	0.04
H4	0.45	H6	0.57

CHB Selectivity: **p**:**m** = 1:1

1p'

	Δδ (ppm)		Δδ (ppm)
H3	0.05	H5	0.00
H4	0.14	H6	0.15

CHB Selectivity: **p**:**m** = 1:1

Figure 9: Correlation between presence of IMHB and remote CHB selectivity

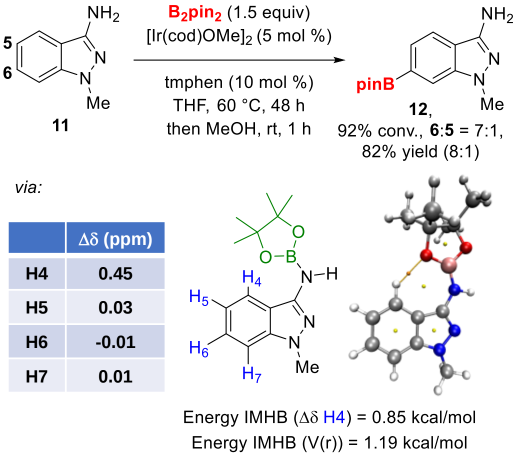
The ^{1}H NMR chemical shift displacements are shown by numbers in blue with respect to the corresponding non-compound as reference. The lowest energy conformations are shown which were calculated by B3LYP functional and 6-311++G(d,p) basis set. QTAIM was performed in each optimized structure and the critical points are shown by the dots in orange (BCP) and yellow (RCP). The energy of the C-H····O IMHB was calculated from V(r) at the corresponding BCP by using Afonin's equation and by the displacement of the ^{1}H NMR chemical shift of the proton involved in the IMHB CHB of N-borylated 2-amino-N-methylpyridine **3b'** gave the para borylated aniline selectively. This selectivity is astounding since meta selectivity would be expected by the strong electronic effects show by pyridines in CHB reactions.[42,43] Both QTAIM analysis (1.67 kcal/mol) and chemical shift displacement (1.79 kcal/mol) support Bpin shielding from C–H•••O IMHB as the directing element. Tetrahydroquinolines are also exhibit para selectivity in CHB reactions, but that could be explained by the fact that rotation about the C–N bond is impossible and p-bonding lock the N–Bpin group in place. Nonetheless, QTAIM and $\Delta\delta$ show evidence for IMHB in **3d'** with an energy comparable to N-borylated 2-amino-N-methylpyridine (Figure 9).

Indoles have similar conformational constraints to appropriately place the N–Bpin group. However, this group of compounds gave low to moderate selectivities. A BCP is found by QTAIM of **5a'** but only a 0.57 ppm of difference in chemical shifts is calculated. We speculate that the lower selectivity for indoles is due to (i) the angles of the 5-member bicyclic ring increasing the distance between the Bpin O and the H at C7 and (ii) a decrease in the negative charge on the Bpin O since the N lone pairs of indoles are weak p-donors. In our efforts to expand the Bpin steric effect to other directing groups without nitrogen, we found that CHB of 2-chlorophenol **1p** did not show selectivity. Neither QTAIM nor $\Delta\delta$ show any evidence of IMHB, which explains the experimental result.

2.2.4. Application of IMHB to remote borylation: 7-member ring IMHB and pyrimidines as directing groups.

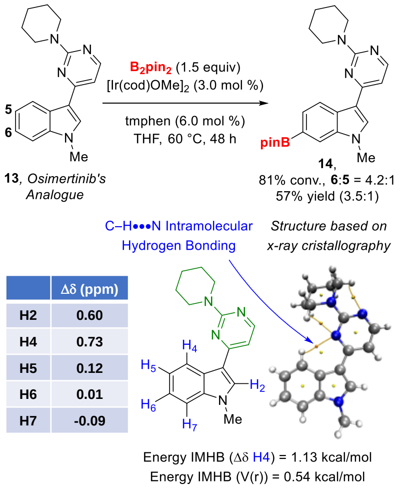
Inspired by literature precedent,[32,33,39] we sought to see if a 7-member ring can be created with IMHB to N–Bpin groups. As explained in the previous section, steric effects can disrupt IMHB. Hence, 7-member ring IMHB with arenes as hydrogen bond donors are uncommon. However, exceptions appear when hydrogen bond donor contain a bicyclic moiety with a 5- and 6-member fused rings.[32,33,39] We expected that 3-aminoindazoles would form a 7-member IMHB after N-borylation.

We were pleased to find that N-methyl-3-aminoindazol **11** undergoes a C6-selective CHB (Figure 10). ^{1}H NMR comparison of the N-borylated indazol versus the unborylated version shows a significant movement of the chemical shift of the C4 proton, as expected with an IMHB. QTAIM provides more support to this conclusion by recognizing a C–H•••O BCP between the C4 proton and the oxygen in the Bpin group. The calculate energy by QTAIM and Δδ are a comparable 1.19 and 0.85 kcal/mol respectively.



	Δδ (ppm)
H4	0.45
H5	0.03
H6	-0.01
H7	0.01

Figure 10: 7-member ring IMHB: C6 borylation of 3-aminoindazol



	Δδ (ppm)
H2	0.60
H4	0.73
H5	0.12
H6	0.01
H7	-0.09

Figure 11: Expanding IMHB to other scaffolds: C6 borylation of an Osimertinib analogue with a pyrimidine directing group directed by a C¬-H¨N IMHB

Certainly, Bpin is not the first IMHB acceptor found in molecules. Nitrogen heterocycles have appeared as part of IMHB networks including C–H•••N interactions within heteroarenes.[44–46] Pyridines, pyrimidines and triazines are key motifs of biologically active pharmaceuticals and therefore their potential use as steric shields via IMHB drew our attention.[47–53]. In particular, we became interested in osimertinib, an epidermal growth factor receptor tyrosine kinase inhibitor, which presents a pyrimidine group attached to an indole skeleton.[54] We subjected osimertinib analogue **13** to CHB conditions (Figure 11). The C6-borylated indole **14** was produced, although with moderate selectivity. We were fortunate to crystallize **13** and the crystal structure showed the C–H•••N that we had proposed with the pyrimidine groups as the hydrogen bond acceptor and the C4 hydrogen of the indole being the hydrogen bond donor. We used the x-ray coordinates to evaluate the QTAIM topology of **13** and found a BCP that supports the IMHB C–H•••N. Next, changes in ^{1}H NMR of **13** taking N-methylindole as the reference were calculated. Surprisingly, we found that both C2 and C4 hydrogens showed a significant chemical shift displacement. We propose that in solution the pyrimidine ring may equilibrate between two conformations involving IMHB with H2 and H4. The IMHB energy for H4 calculate from $\Delta\delta$ is 1.13 kcal/mol, which is higher than that calculated by QTAIM. This difference might be due to the different conformations found in solution in contrast to the solid state.

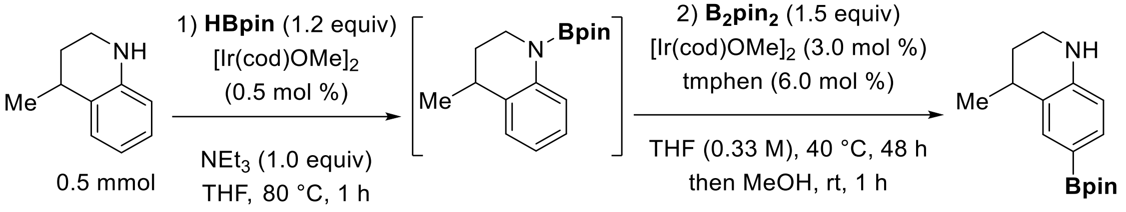
2.3. CONCLUSION

A diverse array of regioselective remote CHBs can be driven by intramolecular steric shields created via IMHB. The previously inexplicable para CHB found with 2-chloro and 2-methoxy aniline now is explained by a Bpin steric shield generated after *in situ* N-borylation. Furthermore, N–Bpin steric shields can lead to para CHB of other ortho substituted anilines, 7-borylation of 1-naphtylamines, para CHB of certain N-alkylated anilines, and to the elusive 5-borylation of indoles. Bpin steric shielding can be extended to motifs without nitrogen, such as 1-borylated naphthalenes, which undergo C6-selective CHB. The wide variety of scaffolds that can be selectively borylated at remote positions due to a Bpin group highlights the versatility of intramolecular steric shields.

We traced back the remote CHB selectivity to the presence of a C–H•••O IMHB in N-borylated intermediates with the Bpin as the hydrogen bond acceptor. A BCP found by QTAIM and a characteristic ^{1}H NMR chemical shift displacement of the hydrogen bond donor, the ortho aniline hydrogen after N-borylation here, is support for an IMHB. The energetic cost to disrupt the planarity of the N-borylated anilines and the necessity of an oxygen in the boryl group to achieve a para CHB also support the observed selectivity to involve IMHB. A 7-member ring IMHB can also produce the steric as shown in the C6-selective borylation of N-methyl-3-aminoindazole. Furthermore, a C5-borylation of the indole ring in an osimertinib analogue where a pyrimidine forms the steric shield via a C–H•••N IMHB further expands this means of remote regiocontrol. The most significant outcome of our study is that the IMHB Bpin steric shielding explains regioselectivities in catalytic C–H borylations where standard steric models and correlations with NMR chemical shifts fail. We anticipate that our efforts presented here will be used to design other methods for remote functionalization driven by intramolecular interactions.

2.4. EXPERIMENTALS

Para Borylation of 4-methyl-1,2,3,4-tetrahydroquinoline (4e)



60% conversion, *para* : *meta* = 12 : 1
60% isolated yield**,** *para* : *meta* = 12 : 1

In a glove box, a 5.0 mL Wheaton microreactor was charged with the 4-methyl-1,2,3,4-tetrahydroquinoline (74 mgs, 0.5 mmol), [Ir(cod)(OMe)]$_2$ (1.7 mg, 0.5 mol %), HBpin (77 mg, 0.6 mmol, 1.2 equiv), triethylamine (0.08 mL, 0.5 mmol, 1.0 equiv) and THF (0.5 mL). The microreactor was capped with a teflon pressure cap and placed into an aluminum block pre-heated to 80 ºC. After 1 h, the microreactor was brought back to the glove box. In a separate tube, [Ir(cod)(OMe)]$_2$ (10 mg, 3.0 mol %) and B$_2$pin$_2$ (190 mg, 0.75 mmol, 1.5 equiv) in THF (1.0 mL) were stirred for 5 min. The microreactor was charged with the [Ir(cod)(OMe)]$_2$/B$_2$pin$_2$ solution and with tmphen (7.1 mg, 6.0 mol %). The microreactor was capped with a teflon pressure cap and placed into an aluminum block pre-heated to 40 ºC. After 48 h, an aliquot of the reaction mixture was taken and analyzed directly by ^{1}H NMR to find the conversion and *para*:*meta* borylation ratio. MeOH (2.5 mL) was added and the mixture was stirred for 1 h. The mixture was concentrated and passed through a column of silica gel (chloroform as eluent). The fractions containing product were collected to give 72 mg of *para* borylated 4e with a minor byproduct corresponding to the *meta* borylated isomer (*para*:*meta* = 16:1) as a yellow sticky solid (53% yield). The *para* borylated product was characterized by ^{1}H-NOE. The correlation was observed between the methine proton (benzylic) and aromatic singlet.

Major Para Borylated Product.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (s, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 6.45 (d, *J* = 8.0 Hz, 1H), 4.12 (bs, 1H), 3.40 – 3.26 (m, 2H), 2.98 – 2.87 (m, 1H), 2.01 – 1.90 (m, 1H), 1.74 – 1.62 (m, 1H), 1.33 (s, 12 H), 1.31 (d, *J* = 6.9 Hz, 3H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 147.0, 135.4, 134.0, 125.4, 113.2, 83.2, 38.6, 30.2, 29.4, 25.0, 24.9 (two inequivalent types of methyl groups in the Bpin group), 22.6.

$^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$) 30.9

HRMS (ESI) m/z calcd for $C_{16}H_{25}BNO_2$ $[M+H]^+$ 274.1978, found 274.1982

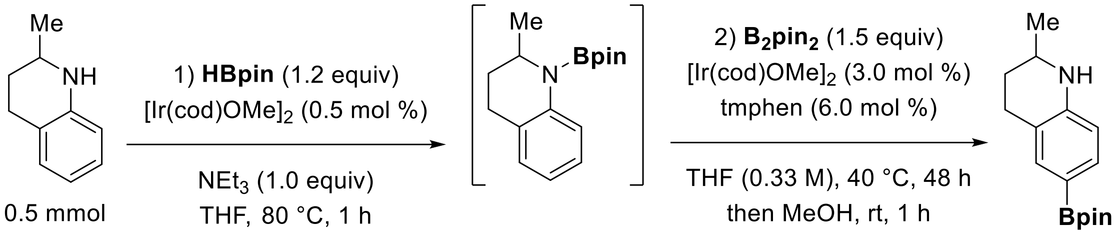
A second fraction was collected corresponding to 9.6 mg of *para* borylated **4e** with a minor byproduct corresponding to the *meta* borylated isomer (*para*:*meta* = 4:1) (7% yield). This fraction was taken as reference to make the assignment of the *meta* borylated isomer. The total isolated yield adds up to 60% (*para* : *meta* = 12 : 1).

Minor Meta Borylated Product.

^{1}H NMR (500 MHz, $CDCl_3$) 7.08 (s, 2H), 6.93 (s, 1H), 3.40 – 3.26 (m, 2H), 2.98 – 2.87 (m, 1H), 2.01 – 1.90 (m, 1H), 1.74 – 1.62 (m, 1H), 1.33 (s, 12 H), 1.31 (d, *J* = 7.0 Hz, 3H).

HRMS (ESI) m/z calcd for $C_{16}H_{25}BNO_2$ $[M+H]^+$ 274.1978, found 274.1982

Para Borylation of 2-methyl-1,2,3,4-tetrahydroquinoline (4f)



45% conversion, *para* : *meta*= 10 : 1

41% isolated yield**,** *para* : *meta*= 13 : 1

In a glove box, a 5.0 mL Wheaton microreactor was charged with the 2-methyl-1,2,3,4-tetrahydroquinoline (74 mg, 0.5 mmol), $[Ir(cod)(OMe)]_2$ (1.7 mg, 0.5 mol %), HBpin (77 mg, 0.6

mmol, 1.2 equiv), triethylamine (0.08 mL, 0.5 mmol, 1.0 equiv) and THF (0.5 mL). The microreactor was capped with a teflon pressure cap and placed into an aluminum block pre-heated to 80 ºC. After 1 h, the microreactor was brought back to the glove box. In a separate tube, $[Ir(cod)(OMe)]_2$ (10 mg, 3.0 mol %) and B_2pin_2 (190 mg, 0.75 mmol, 1.5 equiv) in THF (1.0 mL) were stirred for 5 min. The microreactor was charged with the $[Ir(cod)(OMe)]_2/B_2pin_2$ solution and with tmphen (7.1 mg, 6.0 mol %). The microreactor was capped with a teflon pressure cap and placed into an aluminum block pre-heated to 40 ºC. After 48 h, an aliquot of the reaction mixture was taken and analyzed directly by ^{1}H NMR to find the conversion and *para*:*meta* borylation ratio. MeOH (2.5 mL) was added and the mixture was stirred for 1 h. The mixture was concentrated and passed through a column of silica gel (chloroform as an eluent). The fractions containing product were collected and concentrated to give 48 mg of *para* borylated **4f** with only traces of the *meta* isomer (*para*:*meta* > 20:1) as a white solid (35% yield). The NMR data were consistent with previously reported values, designated as compound **3u** in the cited paper.[1]

Para isomer (C6)

^{1}H NMR (500 MHz, C_6D_6) δ 7.97 (d, *J* = 8.0 Hz, 1H), 7.90 (s, 1H), 6.28 (d, *J* = 8.0, 1H), 3.36 – 3.19 (bs, 1H), 3.00 – 2.83 (m, 1H), 2.61 – 2.45 (m, 2H), 1.49 – 1.40 (m, 1H), 1.34 – 1.23 (m, 1H), 1.18 (s, 12H), 0.74 (d, *J* = 5.7 Hz, 3H)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 – 7.38 (m, 2H), 6.43 (d, *J* = 7.9 Hz, 1H), 3.93 (bs, 1H), 3.43 (ddd, *J* = 9.5, 6.3, 3.1 Hz, 1H), 2.91 – 2.66 (m, 2H), 1.99 – 1.87 (m, 1H), 1.57 (dddd, *J* = 12.8, 11.1, 9.7, 5.4 Hz, 1H), 1.32 (s, 12H), 1.21 (d, *J* = 6.3 Hz, 3H).

^{13}C{^{1}H} NMR (126 MHz, C_6D_6) δ 147.9, 137.2, 134.6, 119.8, 113.5, 83.1, 47.0, 30.1, 26.7, 25.1, 22.4.

^{11}B{^{1}H} NMR (160 MHz, C_6D_6) δ 31.6

HRMS (ESI) m/z calcd for $C_{16}H_{25}BNO_2$ $[M+H]^+$ 274.1978, found 274.1982

A second fraction was collected corresponding to 8.2 mg of a mixture of the *meta* and *para* borylated isomer (*para*:*meta* = 1:1) (6% yield). This fraction was taken as reference to make the assignment of the

meta borylated isomer. The total isolated yield adds up to 41% (*para* : *meta* = 13 : 1).

Meta isomer (C7)

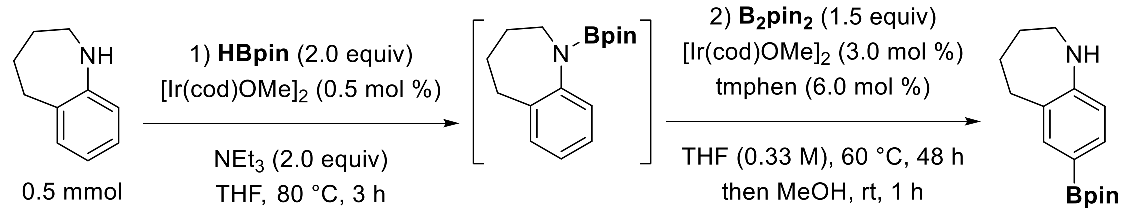
^{1}H NMR (500 MHz, C_6D_6) 7.63 (dd, *J* = 7.3, 1.1 Hz, 1H), 7.26 (d, *J* = 1.1 Hz, 1H), 6.98 (d, *J* = 7.3 Hz, 1H), 3.26 – 3.12 (bs, 1H), 2.97 – 2.86 (m, 1H), 2.62 – 2.44 (m, 2H), 1.59 – 1.40 (m, 1H), 1.38 – 1.22 (m, 1H), 1.16 (s, 12H), 0.78 (d, *J* = 6.2 Hz, 3H)

^{13}C{^{1}H} NMR (126 MHz, C_6D_6) δ 144.8, 129.2, 124.4, 124.2, 121.4, 83.4, 47.2, 30.3, 27.1, 25.0, 22.5

^{11}B{^{1}H} NMR (160 MHz, C_6D_6) δ 31.0

HRMS (ESI) m/z calcd for $C_{16}H_{25}BNO_2$ [M+H]$^+$ 274.1978, found 274.1982.

Para Borylation of 2,3,4,5-tetrahydro-1H-benzo[b]azepine (4g)



92% conversion, *para* : *meta* = 3 : 1
53% isolated yield, *para* : *meta* > 20 : 1

In a glove box, a 5.0 mL Wheaton microreactor was charged with 2,3,4,9-tetrahydro-1*H*-carbazole (86 mg, 0.5 mmol, 1 equiv), HBpin (154 mg, 1 mmol, 2 equiv), triethylamine (0.16 mL, 1 mmol, 2.0 equiv) and THF (0.5 mL). The microreactor was capped with a teflon pressure cap and placed into an aluminum block pre-heated to 80 ºC. After 3 h, the microreactor was brought back to the glove box. In a separate tube, [Ir(cod)(OMe)]$_2$ (10 mg, 3.0 mol %) and B$_2$pin$_2$ (190 mg, 1.5 mmol, 1.5 equiv) in THF (1.0 mL) were stirred for 5 min. The microreactor was charged with the [Ir(cod)(OMe)]$_2$/B$_2$pin$_2$ solution and with tmphen (7.1 mg, 6.0 mol %). The microreactor was capped with a teflon pressure cap and placed into an aluminum block pre-heated to 60 ºC. After 48 h, an aliquot of the reaction mixture was taken and analyzed directly by ^{1}H NMR to find the conversion and *para*:*meta* borylation ratio. MeOH (2.5 mL) was added and the mixture was stirred for 1 h. The mixture was concentrated and purified with a silica column (ethyl acetate:chloroform 1:25 as eluent). The fractions containing product were collected, concentrated to give 72 mg of *para* borylated **4g** with only traces of the *meta* borylated isomer (*para*:*meta* > 20:1) as yellowish solid (53% yield). *Para* isomer is assigned equivocally by gCOSY and NOE.

Major isomer, Para, (C7)

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.58 (s, 1H), 7.51 (d, *J* = 7.7 Hz, 1H), 6.71 (d, *J* = 7.7 Hz, 1H), 3.95 (bs, 1H), 3.12 – 3.00 (m, 2H), 2.91 – 2.75 (m, 2H), 1.84 – 1.74 (m, 2H), 1.70 – 1.61 (m, 2H), 1.33 (s, 12H).

^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 153.5, 137.8, 133.6, 132.0, 118.7, 83.4, 48.6, 35.8, 31.6, 26.8, 24.9.

^{11}B{^{1}H} NMR (160 MHz, CDCl$_3$) δ 30.5.

HRMS (ESI) m/z calcd for $C_{16}H_{25}BNO_2$ [M+H]$^+$ 274.1978, found 274.2035

A second fraction was collected corresponding to 29 mg of a mixture of *para* borylated **4g** with the *meta* isomer (*para*:*meta* = 1:1) (21% yield). This fraction was taken as reference to make the assignment of the *meta* borylated isomer.

Minor isomer, Meta, (C8)

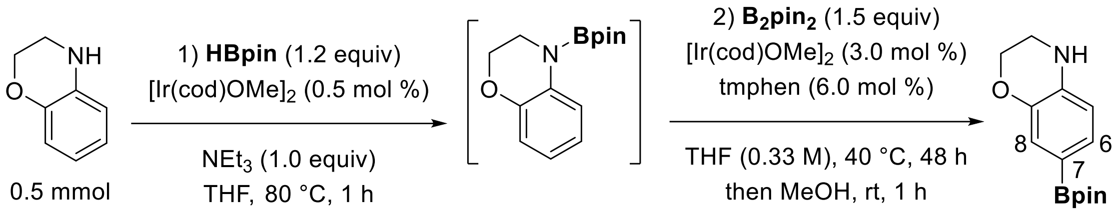
^{1}H NMR (500 MHz, CDCl$_3$) 7.29 (d, *J* = 7.4 Hz, 1H), 7.19 (s, 1H), 7.13 (d, *J* = 7.4 Hz, 1H), 3.89 (bs, 1H), 3.15 – 2.97 (m, 2H), 2.82 – 2.72 (m, 2H), 1.87 – 1.71 (m, 2H), 1.69 – 1.55 (m, 2H), 1.32 (s, 12H).

^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 149.9, 137.5, 130.4, 127.7, 125.8, 83.5, 48.6, 35.8, 31.6, 26.8, 24.9.

$^{11}B\{^{1}H\}$ NMR (160 MHz, $CDCl_3$) δ 31.2

HRMS (ESI) m/z calcd for $C_{16}H_{25}BNO_2$ $[M+H]^+$ 274.1978, found 274.2035

Para Borylation of 3,4-dihydro-2H-benzo[b][1,4]oxazine (4h)



83% conversion **C7 : C6 : C8 =** 29 : 1 : 3
77% isolated yield, **C7 : C6 : C8 =** 17 : 1 : 1

In a glove box, a 5.0 mL Wheaton microreactor was charged with the 3,4-dihydro-2*H*-benzo[1,4]oxazine (68 mgs, 0.5 mmol), $[Ir(cod)(OMe)]_2$ (1.7 mg, 0.5 mol %), HBpin (77 mg, 0.6 mmol, 1.2 equiv), triethylamine (0.08 mL, 0.5 mmol, 1.0 equiv) and THF (0.5 mL). The microreactor was capped with a teflon pressure cap and placed into an aluminum block pre-heated to 80 ºC. After 1 h, the microreactor was brought back to the glove box. In a separate tube, $[Ir(cod)(OMe)]_2$ (10 mg, 3.0 mol %) and B_2pin_2 (190 mg, 0.75 mmol, 1.5 equiv) in THF (1.0 mL) were stirred for 5 min. The microreactor was charged with the $[Ir(cod)(OMe)]_2/B_2pin_2$ solution and with tmphen (7.1 mg, 6.0 mol %). The microreactor was capped with a teflon pressure cap and placed into an aluminum block pre-heated to 40 ºC. After 48 h, an aliquot of the reaction mixture was taken and analyzed directly by ^1H NMR to find the conversion and **C7:C6:C8** borylation ratio. MeOH (2.5 mL) was added and the mixture was stirred for 1 h. The mixture was concentrated and passed through a plug of silica gel (chloroform/ethylacetate as eluent, 50:1). The fractions containing product were collected to give 83 mg of 7-borylated **4h** with minor byproducts corresponding to the 6-borylated and 8-borylated isomers (**C7:C6:C8 =** 17:1:1) as pale yellow solid (77% yield). The NMR data of the 7-borylated isomer were consistent with previously reported NMR values, designated as compound **13e** in the cited paper.[2]

C7:C6:C8 ratios = 29.2 (corresponding to 1H in C7, 6.56 ppm) : 1.0 (corresponding to 1H in C6, 6.65 ppm) : 3.0 (corresponding to 1H in C8, 6.73 ppm)

7-borylated isomer, major isomer:

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 – 7.19 (m, 2H), 6.56 (d, *J* = 8.1 Hz, 1H), 4.24 – 4.19 (m, 2H), 3.95 (bs, 1H), 3.44 (t, *J* = 4.5 Hz, 3H), 1.31 (s, 11H).

^{1}H NMR (500 MHz, C_6D_6) δ 7.94 (s, 1H), 7.78 (dd, *J* = 8.0, 0.9 Hz, 1H), 6.32 (d, *J* = 7.8 Hz, 1H), 3.70 – 3.65 (m, 2H), 2.80 (bs, 1H), 2.56 – 2.51 (m, 2H), 1.13 (s, 12H).

$^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6) δ 144.0, 137.5, 129.4, 124.0, 115.0, 83.5, 64.7, 41.0, 25.2

$^{11}B\{^1H\}$ NMR (160 MHz, C_6D_6) δ 31.4

HRMS (ESI) m/z calcd for $C_{14}H_{21}BNO_3$ $[M+H]^+$ 262.1614, found 262.1614

6-borylated isomer, minor isomer:

^{1}H NMR (500 MHz, C_6D_6) 7.65 (dd, *J* = 7.5, 1.1 Hz 1H), 7.3 (d, *J* = 8.0 Hz, 1H), 7.0 (s, 1H), 3.73 – 3.70 (m, 2H), 2.56 – 2.51 (m, 2H), 1.17 (s, 12H)

HRMS (ESI) m/z calcd for $C_{14}H_{21}BNO_3$ $[M+H]^+$ 262.1614, found 262.1614

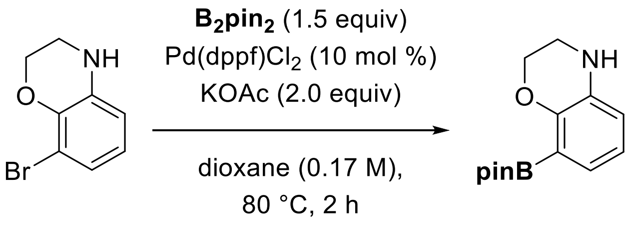
8-borylated isomer, minor isomer:

^{1}H NMR (500 MHz, C_6D_6) 7.67 (dd, *J* = 7.4, 1.7 Hz, 1H), 6.83 (t, *J* = 7.4 Hz, 1H), 6.34 (d, *J* =1.6 Hz, 1H), 3.88 – 3.85 (m, 2H), 2.59 – 2.56 (m, 2H), 1.15 (s, 12H)

HRMS (ESI) m/z calcd for $C_{14}H_{21}BNO_3$ $[M+H]^+$ 262.1614, found 262.1614

8-borylated isomer was assigned by preparing the title compound by Miyaura Borylation.

Miyaura Borylation of 8-bromo-3,4-dihydro-2H-benzo[b][1,4]oxazine



In a glove box, a 5.0 mL Wheaton microreactor was charged with the 8-bromo-3,4-dihydro-2H-1,4-benzoxazine (68 mg, 0.5 mmol) and dioxane (3 mL). KOAc (98 mg, 1.0 mmol, 2.0 equiv), bis(pinacolato)diboron (190 mg, 0.75 mmol, 1.5 equiv) and [1,1′-bis(diphenylphosphino) ferrocene]dicholoropalladium(II) (37 mg, 0.05 mol, 10 mol %) were added to the microreactor. The microreactor was capped with a teflon pressure cap and placed into an aluminum block pre-heated to 80 ºC. After 2 h, the mixture was concentrated and passed through a plug of silica gel (dichloromethane as eluent). The product was collected and concentrated to give 50 mg of the borylated product as an orange solid (38% yield, mp 121-123 °C).

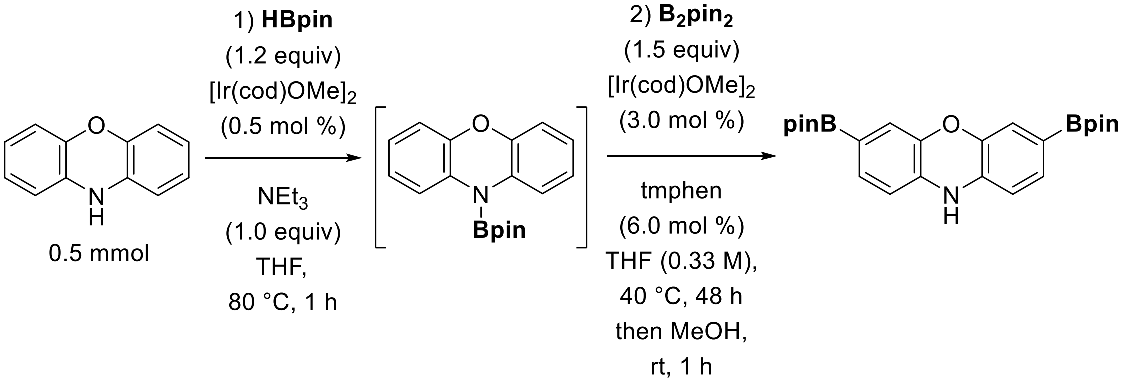
^{1}H NMR (500 MHz, C_6D_6) 7.66 (dd, *J* = 7.4, 1.6 Hz, 1H), 6.83 (t, *J* = 7.5 Hz, 1H), 6.43 (dd, *J* =7.7, 1.7, 1H), 3.88 (m, 2H), 2.60 (m, 2H), 1.16 (s, 12H)

^{13}C{^{1}H} NMR (126 MHz, C_6D_6 δ 149.8, 133.7, 126.8, 120.6,118.8 ,83.0, 65.0, 40.5, 24.8

^{11}B{^{1}H} NMR (160 MHz, C_6D_6) δ 31.5

GC-MS (EI) m/z calcd for $C_{14}H_{20}BNO_3$ [M] 261.2, found 261.1

Para Borylation of 10*H*-phenoxazine (4j)



>95% conversion to major diborylated product
55% isolated yield of major diborylated product

In a glove box, a 5.0 mL Wheaton microreactor was charged with HBpin (67 mg, 1 mmol, 1 equiv, 10*H*-phenoxazine (86 mg, 0.5 mmol, 1 equiv), triethylamine (0.08 mL, 1 mmol, 1.0 equiv) and THF (0.5 mL). The microreactor was capped with a teflon pressure cap and placed into an aluminum block pre-heated to 80 ºC. After 1 h, the microreactor was brought back to the glove box. In a separate tube, [Ir(cod)(OMe)]$_2$ (10 mg, 3.0 mol %) and B$_2$pin$_2$ (190 mg, 0.75 mmol, 1.5 equiv) in THF (1.0 mL) were stirred for 5 min. The microreactor was charged with the [Ir(cod)(OMe)]$_2$/B$_2$pin$_2$ solution and with tmphen (7.1 mg, 6.0 mol %). The microreactor was capped with a teflon pressure cap and placed into an aluminum block pre-heated to 40 ºC. After 48 h, an aliquot of the reaction mixture was taken, dissolve in DMSO-d6 and analyzed directly by ^{1}H NMR. Diborylated **4j** appeared as the major isomer (**4j**:other ≅ 2:1), the NMR data were consistent with previously reported NMR values designated as compound **PR1** in the cited paper.[55] MeOH (2.5 mL) was added and the mixture was stirred for 1 h. The mixture was concentrated and passed through silica gel gradient column chromatography (ethyl acetate/chloroform 1:50 → ethyl acetate/chloroform 1:25 as eluent). The mixture was passed one more time through silica gel gradient column chromatography with the same solvent system (ethyl acetate/chloroform 1:50 → ethyl acetate/chloroform 1:25 as eluent). The fractions containing product were collected, concentrated to give 15 mg of mostly **4j** (**4j**:other ≅ 4:1) as a bright yellow solid (7% yield).

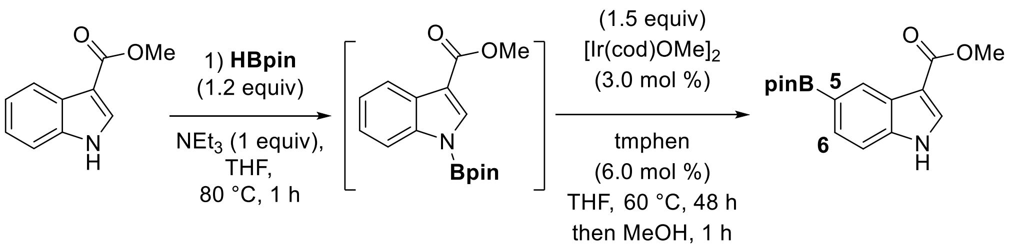
^{1}H NMR (500 MHz, CDCl$_3$) δ 7.17 (d, *J* = 7.6 Hz, 2H), 7.04 (s, 2H), 6.33 (d, *J* = 7.7 Hz, 2H), 5.50 (bs, 1H), 1.31 (s, 24H).

^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 143.4, 133.9, 131.0, 121.6, 112.9, 83.7, 24.9.

^{11}B{^{1}H} NMR (160 MHz, CDCl$_3$) δ 31.6.

GC-MS (EI) m/z calcd for $C_{24}H_{31}B_2NO_5$ [M] 435.2, found 435.1

C5 Borylation of methyl indole-3-carboxylate (6b)



>95% conversion, **C5** : **C6** = 1 : 1
86% isolated yield, **C5** : **C6** = 1 : 1

In a glove box, a 5.0 mL Wheaton microreactor was charged with methyl indole-3-carboxylate (88 mg, 0.5 mmol, 1 equiv), HBpin (77 mg, 0.6 mmol, 1.2 equiv), triethylamine (0.08 mL, 0.5 mmol, 1.0 equiv) and THF (0.5 mL). The microreactor was capped with a teflon pressure cap and placed into an aluminum block pre-heated to 80 ºC. After 1 h, the microreactor was brought back to the glove box. In a separate tube, $[Ir(cod)(OMe)]_2$ (10 mg, 3.0 mol %) and B_2pin_2 (190 mg, 1.5 mmol, 1.5 equiv) in THF (1.0 mL) were stirred for 5 min. The microreactor was charged with the $[Ir(cod)(OMe)]_2/B_2pin_2$ solution and with tmphen (7.1 mg, 6.0 mol %). The microreactor was capped with a teflon pressure cap and placed into an aluminum block pre-heated to 60 ºC. After 48 h, an aliquot of the reaction mixture was taken and analyzed directly by ^{1}H NMR to find the conversion and **5**:**6** borylation ratio. MeOH (2.5 mL) was added and the mixture was stirred for 1 h. The mixture was concentrated and passed through a plug of silica gel (chloroform/ethyl acetate 9:1). The fractions containing product were collected, concentrated and washed with water (3 mL). The water layer was decanted and the residue was dried to give 130 mg of 5-borylated and 6-borylated isomers **6b** (**C5**:**C6** = 1:1) as a beige solid (86% yield). The ^{1}H NMR data of the 5-borylated isomer in DMSO-d6 were consistent with previously reported values.[56]

C5 borylated product:

^{1}H NMR (500 MHz, DMSO-d6) δ 12.04 (bs, 1H), 8.41 (s, 1H), 8.11 (d, *J* = 2.9 Hz, 1H), 7.51 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.46 (dd, *J* = 8.2, 0.9 Hz, 1H), 3.81 (d, *J* = 2.9 Hz, 3H), 1.31 (s, 12H).

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.01 (bs, 1H), 8.67 (d, *J* = 1.1 Hz, 1H), 7.91 (d, *J* = 3.0 Hz, 1H), 7.70 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.39 (d, *J* = 8.2 Hz, 1H), 3.93 (s, 3H), 1.37 (s, 12H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 165.9, 138.3, 131.5, 129.3, 129.1, 125.4, 111.2, 109.2, 83.8, 51.4, 25.0.

$^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$) δ 31.6.

HRMS (ESI) m/z calcd for $C_{16}H_{21}BNO_4$ $[M+H]^+$ 302.1564, found 302.1563

C6 borylated product:

^{1}H NMR (500 MHz, DMSO-d6) δ 12.04 (bs, 1H), 8.19 (d, *J* = 3.1 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 1.0 Hz, 1H), 7.47 (dd, *J* = 8.0, 1.0 Hz, 1H), 3.81 (d, *J* = 3.1 Hz, 3H), 1.31 (s, 12H).

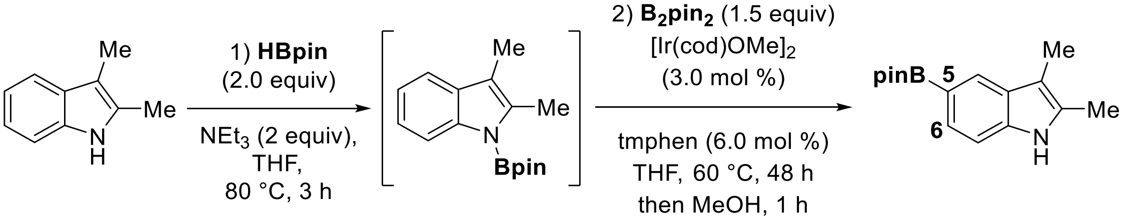
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.95 (bs, 1H), 8.17 (d, *J* = 8.0 Hz, 1H), 7.95 (d, *J* = 3.0 Hz, 1H), 7.91 (d, *J* = 0.9 Hz, 1H), 7.70 (dd, *J* = 8.0, 0.9 Hz, 1H), 3.93 (s, 3H), 1.37 (s, 12H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 165.8, 136.0, 132.4, 128.3, 128.0, 120.9, 118.6, 108.9, 83.9, 51.3, 25.0.

$^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$) δ 31.6.

HRMS (ESI) m/z calcd for $C_{16}H_{21}BNO_4$ $[M+H]^+$ 302.1564, found 302.1563

C5 Borylation of 2,3-dimethyl indole (6c)



>95% conversion, **C5** : **C6** = 5 : 1
88% isolated yield, **C5** : **C6** = 4 : 1

In a glove box, a 5.0 mL Wheaton microreactor was charged with 2,3-dimethyl-1*H*-indole (73 mg, 0.5 mmol, 1 equiv), HBpin (154 mg, 1 mmol, 2 equiv), triethylamine (0.16 mL, 1 mmol, 2.0 equiv) and THF (0.5 mL). The microreactor was capped with a teflon pressure cap and placed into an aluminum block pre-heated to 80 ºC. After 1 h, the microreactor was brought back to the glove box. In a separate tube, $[Ir(cod)(OMe)]_2$ (10 mg, 3.0 mol %) and B_2pin_2 (190 mg, 1.5 mmol, 1.5 equiv) in THF (1.0 mL) were stirred for 5 min. The microreactor was charged with the $[Ir(cod)(OMe)]_2/B_2pin_2$ solution and with tmphen (7.1 mg, 6.0 mol %). The microreactor was capped with a teflon pressure cap and placed into an aluminum block pre-heated to 60 ºC. After

48 h, an aliquot of the reaction mixture was taken and analyzed directly by ^{1}H NMR to find the conversion and C6:C5 borylation ratio. MeOH (2.5 mL) was added and the mixture was stirred for 1 h. The mixture was concentrated and passed through a plug of silica gel (chloroform as an eluent). The fractions containing product were collected and concentrated to yield 43 mg of the 5-borylated **6c** with a minor byproduct corresponding to the 6-borylated isomer (**C5**:**C6** = 8:1) as a yellowish solid (32% yield). The NMR data of the 5-borylated major isomer were consistent with previously reported values.[57]

C5 borylated product, major isomer

^{1}H NMR (500 MHz, C_6D_6) 8.59 (d, *J* = 1.0 Hz, 1H), 8.18 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.13 (d, *J* = 8.1, 1H), 6.61 (bs, 1H), 2.08 (s, 3H), 1.80 (s, 3H), 1.17 (s, 12H).

^{13}C{^{1}H} NMR (126 MHz, C_6D_6) δ 138.2, 130.4, 130.0, 128.4,127.0, 110.2, 107.8, 83.5, 25.3, 11.3, 8.7

^{11}B{^{1}H} NMR (160 MHz, C_6D_6) δ 32.4.

HRMS (ESI) m/z calcd for $C_{16}H_{23}BNO_2$ $[M+H]^+$ 272.1822, found 272.1826

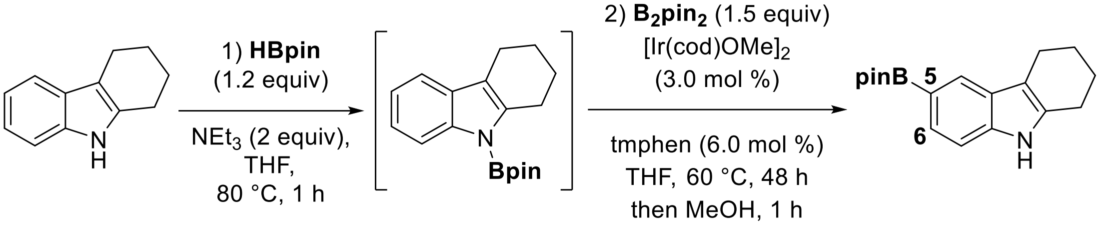
A second fraction was collected corresponding to 76 mg of the 5-borylated **6c** with a minor byproduct corresponding to the 6-borylated isomer (**C5:C6** = 3:1) (56% yield). This fraction was taken as reference to make the assignment of the 6-borylated isomer. The total yield adds up to 88% (**C5** : **C6** = 4 : 1).

C6 borylated isomer, minor product

^{1}H NMR (500 MHz, C_6D_6) 8.13 (dd, *J* = 7.9, 0.9 Hz, 1H), 8.05 (d, *J* = 0.9 Hz, 1H), 7.56 (d, *J* = 7.9 Hz, 1H) 6.61 (bs, 1H), 2.07 (s, 3H), 1.78 (s, 3H), 1.21 (s, 12H)

HRMS (ESI) m/z calcd for $C_{16}H_{23}BNO_2$ $[M+H]^+$ 272.1822, found 272.1826

C5 Borylation of 2,3,4,9-tetrahydro-1H-carbazole (6d)



>95% conversion, **C5**:**C6** = 4:1
82% isolated yield, **C5**:**C6** = 5:1

In a glove box, a 5.0 mL Wheaton microreactor was charged with 2,3,4,9-tetrahydro-1*H*-carbazole (86 mg, 0.5 mmol, 1 equiv), HBpin (154 mg, 1 mmol, 2 equiv), triethylamine (0.16 mL, 1 mmol, 2.0 equiv) and THF (0.5 mL). The microreactor was capped with a teflon pressure cap and placed into an aluminum block pre-heated to 80 ºC. After 3 h, the microreactor was brought back to the glove box. In a separate tube, $[Ir(cod)(OMe)]_2$ (10 mg, 3.0 mol %) and B_2pin_2 (190 mg, 1.5 mmol, 1.5 equiv) in THF (1.0 mL) were stirred for 5 min. The microreactor was charged with the $[Ir(cod)(OMe)]_2/B_2pin_2$ solution and with tmphen (7.1 mg, 6.0 mol %). The microreactor was capped with a teflon pressure cap and placed into an aluminum block pre-heated to 60 ºC. After 48 h, an aliquot of the reaction mixture was taken and analyzed directly by ^1H NMR to find the conversion and **5**:**6** borylation ratio. MeOH (2.5 mL) was added and the mixture was stirred for 1 h. The mixture was concentrated and purified with a silica column (chloroform as an eluent). The fractions containing product were collected and concentrated to yield 71 mg of the 5-borylated **6d** with a minor byproduct corresponding to the 6-borylated isomer (**C5**:**C6** = 5:1) as yellowish solid (82% yield, mp 135-137 °C).

5-borylated isomer, minor product

^1H NMR (500 MHz, C_6D_6) δ 8.58 (s, 1H), 8.19 (d, *J* = 8.1 Hz, 1H), 7.17 – 7.12 (m, 1H), 6.57 (bs, 1H), 2.61-2.54 (m, 2H), 2.23-2.17 (m, 2H), 1.61-1.55 (m, 4H), 1.21 (s, 12H).

$^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6) δ 138.5, 135.4, 133.6, 131.1, 126.5, 110.7, 110.3, 83.3, 25.2, 23.6, 23.4, 23.2, 21.1.

$^{11}B\{^{1}H\}$ NMR (160 MHz, C_6D_6) δ 31.6

HRMS (ESI) m/z calcd for $C_{18}H_{25}BNO_2$ $[M+H]^+$ 298.1978, found 298.1982

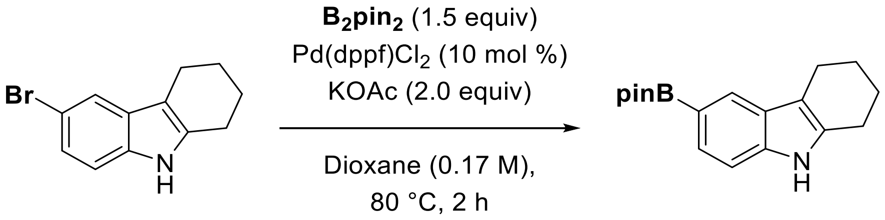
6-borylated isomer, minor product

^{1}H NMR (500 MHz, C_6D_6) 8.15 (d, *J* = 7.8 Hz, 1H), 8.10 (s, 1H), 7.60 (d, *J* = 7.9 Hz, 1H), 6.64 (bs, 1H), 2.61-2.54 (m, 2H), 2.23-2.17 (m, 2H), 1.61-1.55 (m, 4H), 1.22 (s, 12H).

HRMS (ESI) m/z calcd for $C_{18}H_{25}BNO_2$ $[M+H]^+$ 298.1978, found 298.1982

The major 6-borylated isomer was confirmed by synthesizing the compound independently via Miyaura borylation.

Miyaura Borylation of 6-bromo-2,3,4,9-tetrahydro-1H-carbazole



In a glove box, a 5.0 mL Wheaton microreactor was charged with 6-bromo-2,3,4,9-tetrahydro-1H-carbazole (125 mg, 0.5 mmol) and dioxane (3 mL). KOAc (98 mg, 1.0 mmol, 2.0 equiv), bis(pinacolato)diboron (190 mg, 0.75 mmol, 1.5 equiv) and [1,1'-bis(diphenylphosphino) ferrocene]dicholoropalladium(II) (37 mg, 0.05 mol, 10 mol %) were added to the microreactor. The microreactor was capped with a teflon pressure cap and placed into an aluminum block pre-heated to 80 ºC. After 2 h, the mixture was concentrated and passed through a plug of silica gel (dichloromethane as eluent). The product was collected and concentrated to give 72 mg of the borylated product as an orange solid (48% yield).

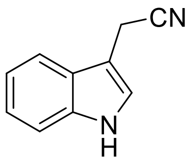
^{1}H NMR (500 MHz, C_6D_6) δ 8.62 (s, 1H), 8.24 (d, *J* = 8.1 Hz, 1H), 7.16 – 7.14 (m, 1H), 6.32 (bs, 1H), 2.61 (m, 2H), 2.18 (m, 2H), 1.58 (m, 4H), 1.21 (s, 12H).

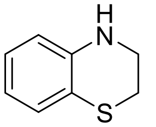
^{13}C{^{1}H} NMR (126 MHz, C_6D_6) δ 138.5, 135.4, 133.8, 131.6, 126.4, 110.6, 110.3, 83.4, 25.1, 23.6, 23.4, 23.2, 21.1

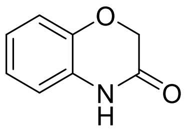
^{11}B{^{1}H} NMR (160 MHz, C_6D_6) δ 31.8

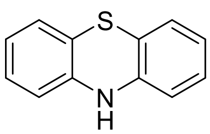
HRMS (ESI) m/z calcd for $C_{18}H_{25}BNO_2$ $[M+H]^+$ 298.1978, found 298.1958

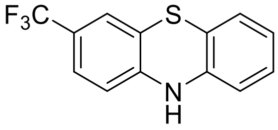
Compounds that gave very low conversion to product or no conversion to product at all:





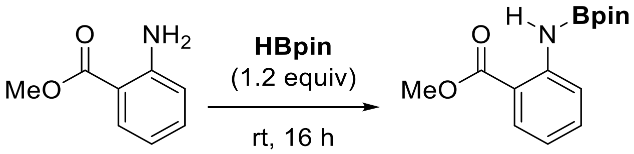






Experiments to probe mechanistic studies:

Synthesis of N-Bpin borylated methyl 2-aminobenzoate (1f')



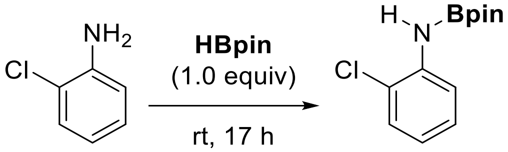
In a glovebox, under a N_2 atmosphere, methyl 2-aminobenzoate (75 mg, 0.5 mmol, 1 equiv) and HBpin (77 mg, 0.60 mmol, 1.2 equiv) were charged in a 5 mL vial and stirred at room temperature for 16 h. The final mixture was dissolved in 1.5 mL of dry $CDCl_3$ (0.33 M solution) and transfer to J-Young NMR tube. ^{1}H NMR showed 73% conversion to the N-borylated product.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.44 (bs, 1H), 7.90 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.73 (dd, *J* = 8.5, 1.2 Hz, 1H), 7.37 (ddd, *J* = 8.6, 7.1, 1.7 Hz, 1H), 6.80 (ddd, *J* = 8.2, 7.1, 1.2 Hz, 1H), 3.86 (s, 3H), 1.30 (s, 12H).

$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 168.6, 147.9, 134.0, 130.9, 119.3, 118.6, 113.8, 82.8, 51.7, 24.6.

$^{11}B\{^{1}H\}$ NMR (160 MHz, $CDCl_3$) δ 24.2.

Synthesis of N-Bpin borylated 2-chloroaniline (1a')



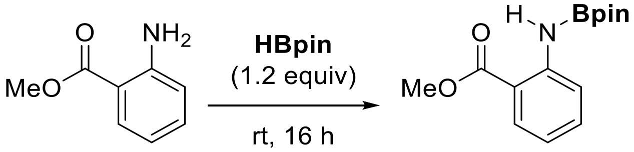
In a glovebox, under a N_2 atmosphere, a 5.0 mL Wheaton microreactor was charged with 2-chloroaniline (383 mg, 3 mmol, 1 equiv) and HBpin (384 mg, 3 mmol, 1 equiv). The reaction was stirred at room temperature for 17 h. From the final mixture, 51 mg was measured, dissolved in 0.6 mL of $CDCl_3$ (0.33 M solution) and transfer to J-Young NMR tube. TMS internal standard was added as reference. It is important to note that the reaction can be completed in one hour if $[Ir(cod)OMe]_2$ (0.5 mol %) is added and the reaction heated at 80 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.25 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.13 (ddd, *J* = 8.4, 7.3, 1.5 Hz, 1H), 6.77 (ddd, *J* = 7.9, 7.3, 1.5 Hz, 1H), 5.33 (bs, 1H), 1.31 (s, 12H).

$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 140.1, 128.9, 127.6, 121.5, 120.5, 118.5, 83.1, 24.6.

$^{11}B\{^{1}H\}$ NMR (160 MHz, $CDCl_3$) δ 24.1.

Synthesis of N-Bpin borylated methyl 2-aminobenzoate (1f')



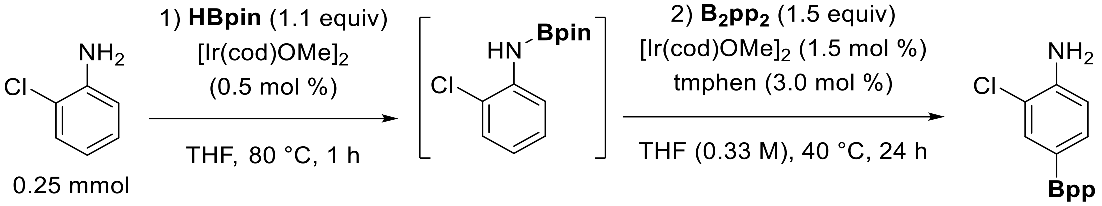
In a glovebox, under a N_2 atmosphere, methyl 2-aminobenzoate (75 mg, 0.5 mmol, 1 equiv) and HBpin (77 mg, 0.60 mmol, 1.2 equiv) were charged in a 5 mL vial and stirred at room temperature for 16 h. The final mixture was dissolved in 1.5 mL of dry $CDCl_3$ (0.33 M solution) and transferred to J-Young NMR tube. ^{1}H NMR showed 73% conversion to the N-borylated product.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.44 (bs, 1H), 7.90 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.73 (dd, *J* = 8.5, 1.2 Hz, 1H), 7.37 (ddd, *J* = 8.6, 7.1, 1.7 Hz, 1H), 6.80 (ddd, *J* = 8.2, 7.1, 1.2 Hz, 1H), 3.86 (s, 3H), 1.30 (s, 12H).

$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 168.6, 147.9, 134.0, 130.9, 119.3, 118.6, 113.8, 82.8, 51.7, 24.6.

$^{11}B\{^{1}H\}$ NMR (160 MHz, $CDCl_3$) δ 24.2.

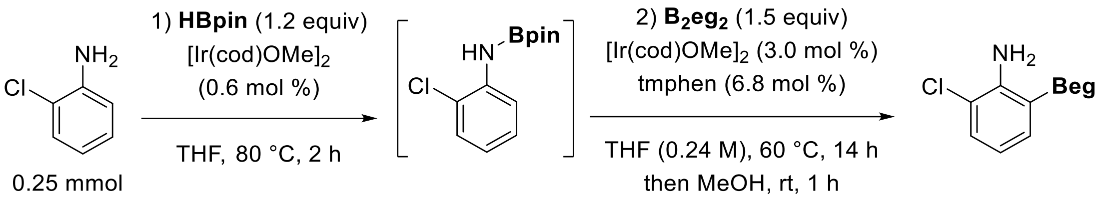
Diboron partner effect on the CHB of N-Bpin-2-chloroaniline



>95% conversion, *para*:*meta* = 11:1

Note: the order of addition of the reagents affects the CHB performance (conversions and selectivities) when B_2pp_2 and B_2hg_2 are the boron partners. Previously, this factor has been reported to influence CHB outcomes with HBpin as the boron partner.[58]

In a glove box, a 2.5 mL Wheaton microreactor was charged with 2-chloroaniline (32 mg, 0.25 mmol, 1 equiv), $[Ir(cod)(OMe)]_2$ (0.9 mg, 0.5 mol %) and HBpin (35 mg, 0.28 mmol, 1.10 equiv) in THF (0.25 mL). The microreactor was capped with a teflon pressure cap and placed into an aluminum block pre-heated to 80 ºC. After 1 h, the microreactor was brought back to the glove box. In a separate tube, a solution of $[Ir(cod)(OMe)]_2$ (2.5 mg, 1.5 mol %) and B_2pp_2 (106 mg, 0.37 mmol, 1.5 equiv) in THF (0.5 mL) was prepared. The microreactor was charged with tmphen (1.8 mg, 3.0 mol %) and with the stock solution containing $[Ir(cod)(OMe)]_2$ and B_2pin_2. The microreactor was capped with a teflon pressure cap and placed into an aluminum block pre-heated to 40 ºC. After 24 h, an aliquot of the reaction mixture was taken and analyzed directly by ^{1}H NMR to find the conversion and *para:meta* borylation ratio.

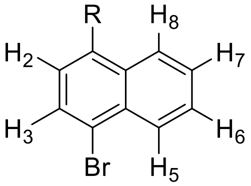


Mainly ortho borylated product

In a glove box, a 2.5 mL Wheaton microreactor was charged with 2-chloroaniline (32 mg, 0.25 mmol, 1 equiv), [Ir(cod)(OMe)]$_2$ (1.0 mg, 0.6 mol %), HBpin (38 mg, 0.3 mmol, 1.2 equiv) and THF (0.05 mL). The microreactor was capped with a teflon pressure cap and placed into an aluminum block pre-heated to 80 ºC. After 2 h, the microreactor was brought back to the glove box. In a separate tube, a suspension of [Ir(cod)(OMe)]$_2$ (5 mg, 3 mol %) and B$_2$eg$_2$ (53 mg, 0.375 mmol, 1.5 equiv) in THF (1.0 mL) was prepared. The microreactor was charged with tmphen (4.0 mg, 6.8 mol %) and with the suspension containing [Ir(cod)(OMe)]$_2$ and B$_2$eg$_2$. The microreactor was capped with a teflon pressure cap and placed into an aluminum block pre-heated to 60 ºC. After 48 h, the reaction mixture was evaporated and pinacol (100 mg, 0.85 mmol, 3.4 equiv) in dry CHCl$_3$ (2 mL) was added. After 12 h, MeOH (1 mL) was added and the mixture was stirred for 1 h. An aliquot of the reaction mixture was taken, evaporated and analyzed directly by ^{1}H NMR to find that the main product corresponds to the *ortho* borylated aniline besides some minor side products.

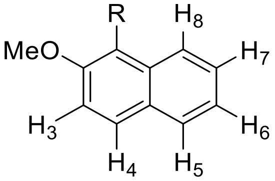
^{1}H NMR Assignments of N-Borylated and unborylated reagents

Chemical shifts are in ppm. The assignments were based on 1D-NOE and 2D NMR experiments unless otherwise noted. Samples were prepared in CDCl$_3$ with a concentration of 0.33 M to resemble the concentration in the reaction mixture. TMS was added as internal standard and referenced to 0.00 pm. The change in chemical shifts after dilution was tested to exclude any aggregation phenomena playing a role in the chemical shifts. Samples of all the compounds at 0.22 M, 0.17 M and 0.13 M showed a maximum deviation of 0.02 ppm respect to the 0.33 M initial concentration.



When R = H the chemical shifts of hydrogens were found to be 7.31, 7.77, 8.23, 7.59, 7.52 and 7.82 ppm for H2, H3, H5, H6, H7 and H8 respectively [59]

When R = Bpin, the chemical shifts of hydrogens were found to be 7.89, 7.78, 8.27, 7.57, 7.57 and 8.78 for H2, H3, H5, H6, H7 and H8 respectively.



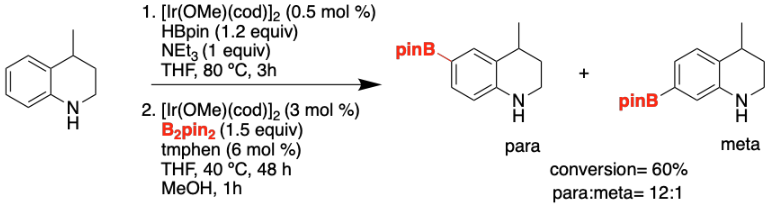
When R = H the chemical shifts of hydrogens were found to be 7.14, 7.72, 7.75, 7.32, 7.43 and 7.72 ppm for H3, H4, H5, H6, H7 and H8 respectively [59]

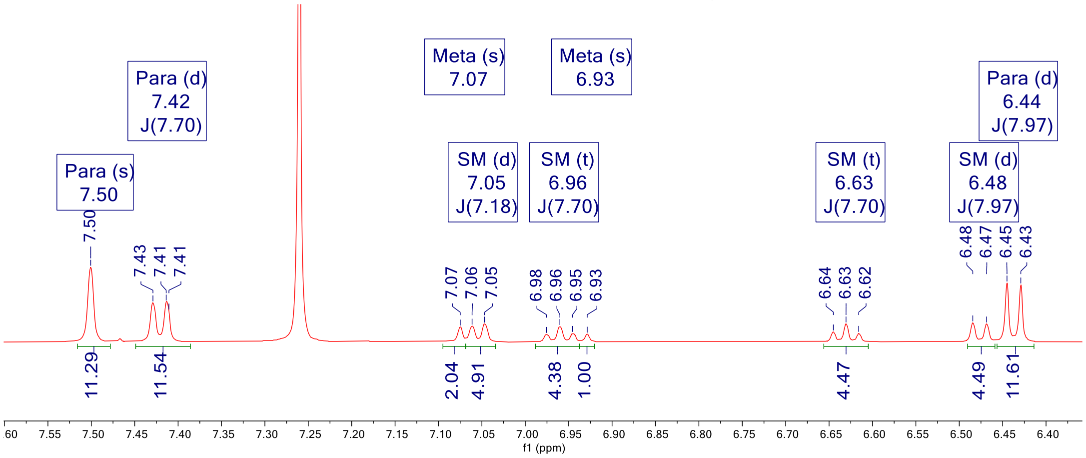
When R = Bpin, the chemical shifts of hydrogens were found to be 7.19, 7.83, 7.74, 7.29, 7.42 and 7.91 for H3, H4, H5, H6, H7 and H8 respectively.

2.5. SPECTRAL DATA

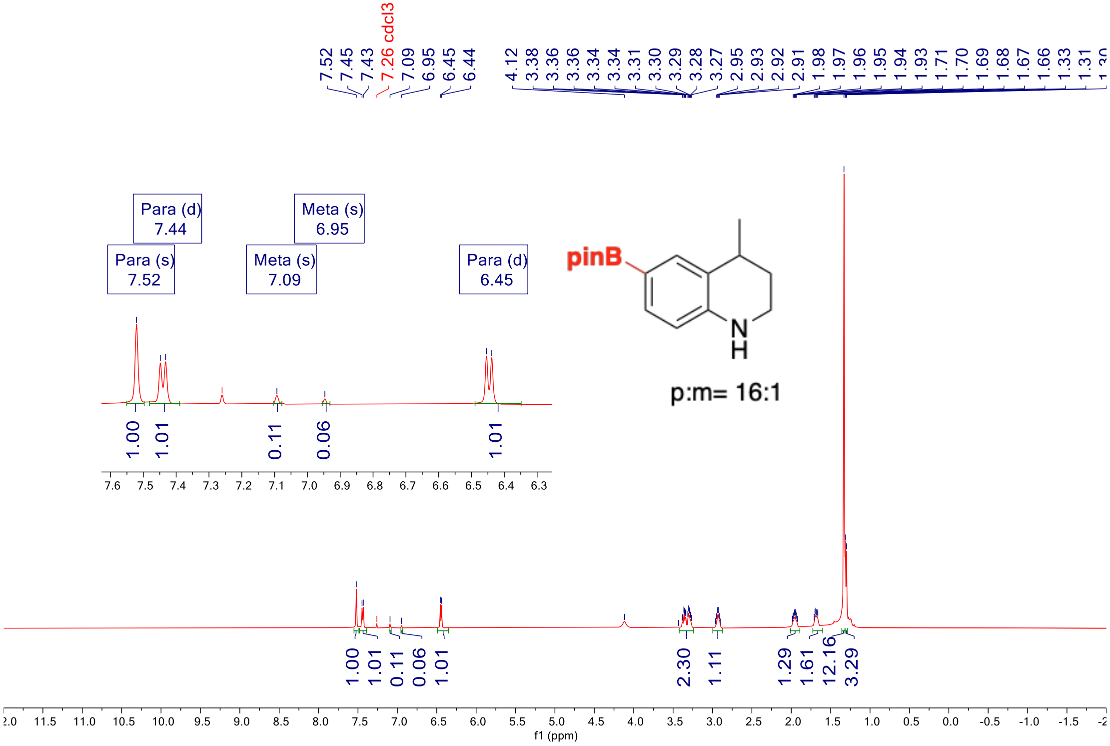
Para CHB of 4-methyl-1,2,3,4-tetrahydroquinoline (4e) ($CDCl_3$, 500 MHz)

500 MHz

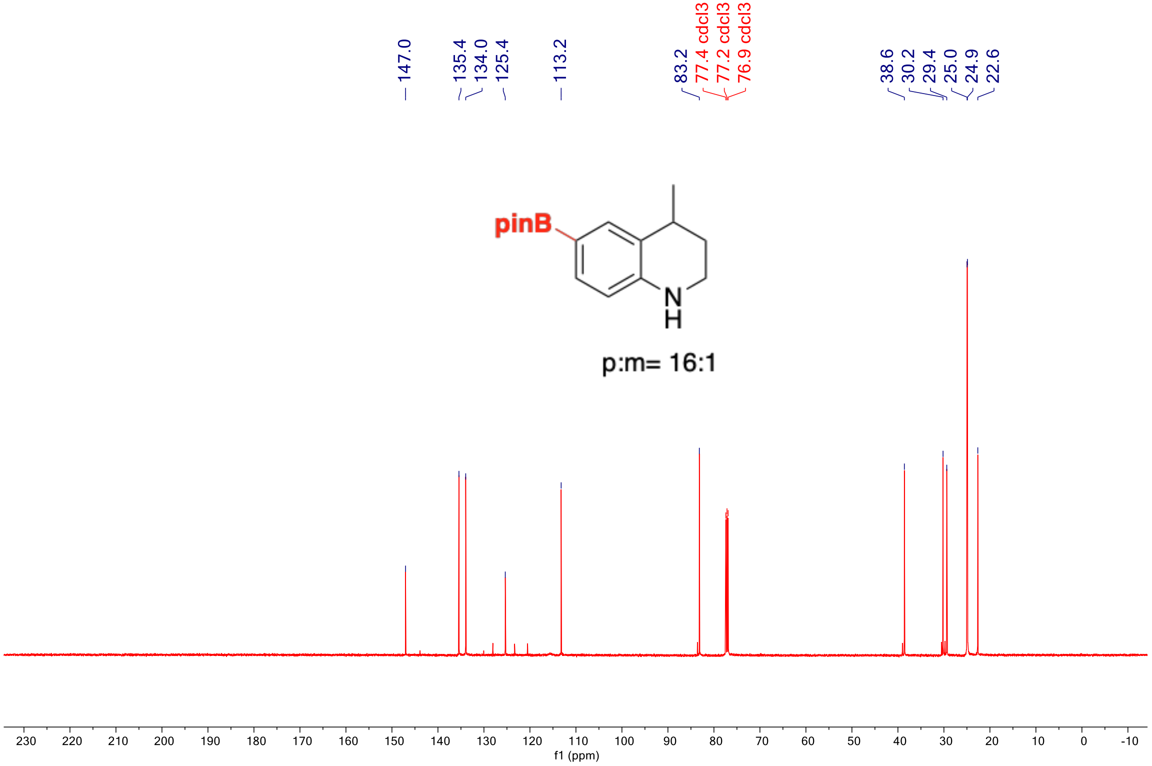




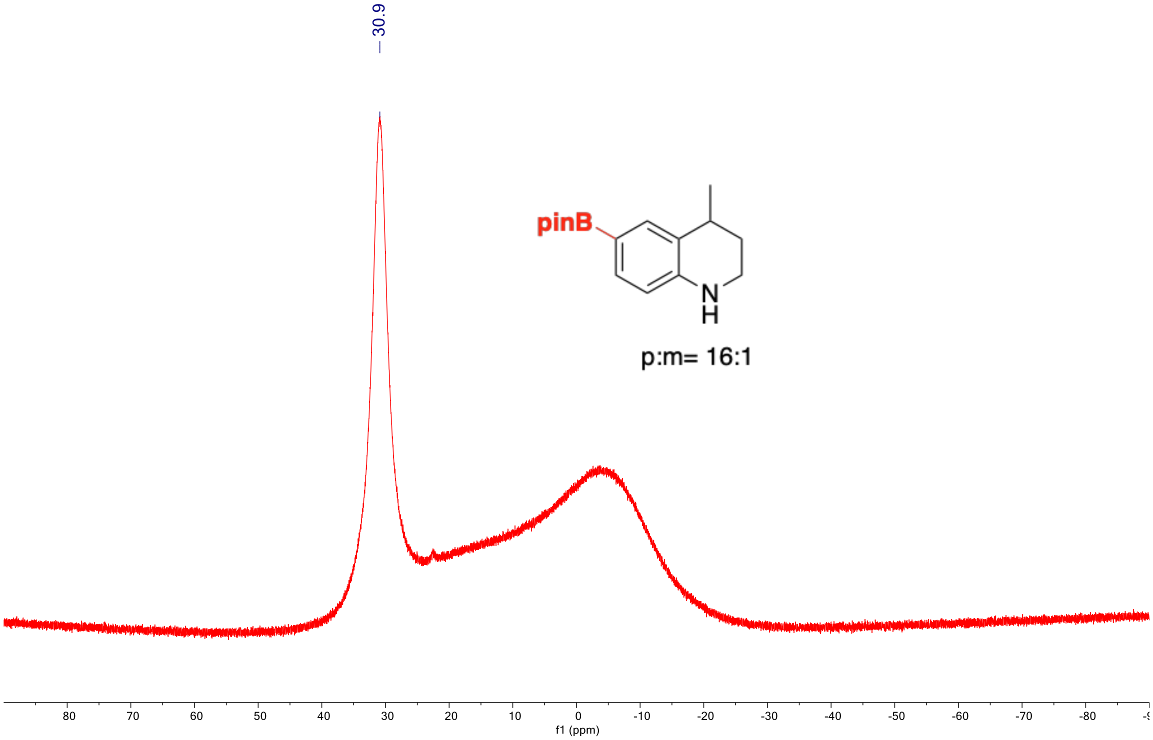
^1H NMR of para borylated 4-methyl-1,2,3,4-tetrahydroquinoline ($CDCl_3$, 500 MHz)



^{13}C{^{1}H} NMR of para borylated 4-methyl-1,2,3,4-tetrahydroquinoline (CDCl$_3$, 126 MHz)

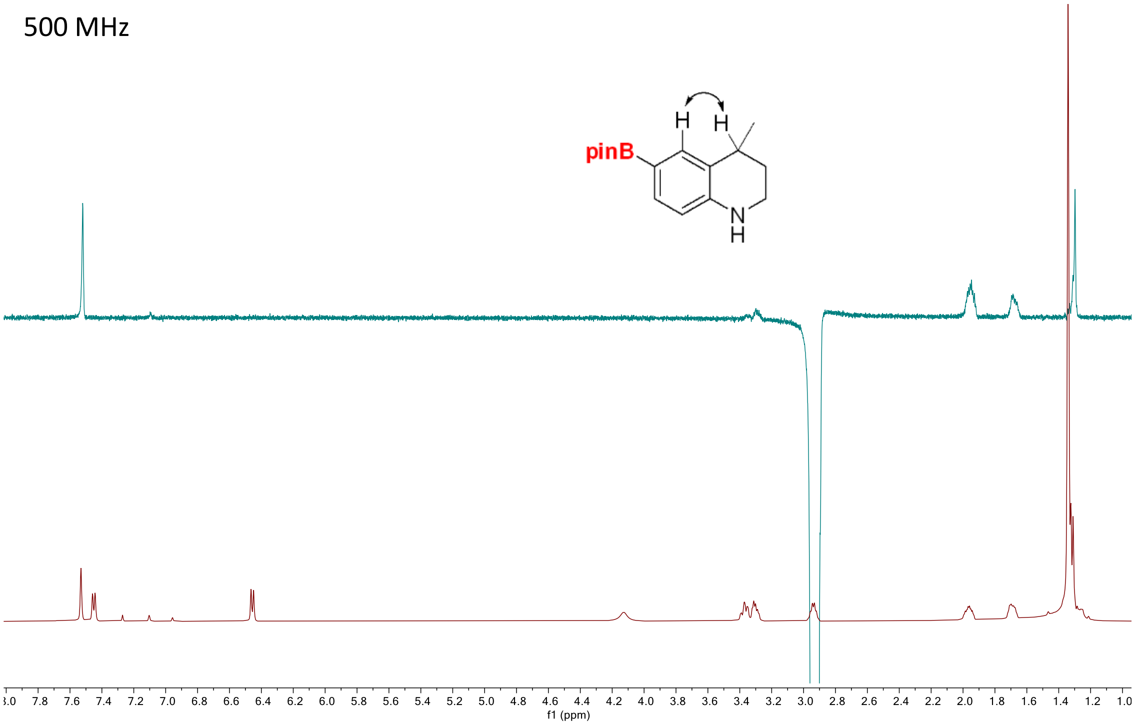


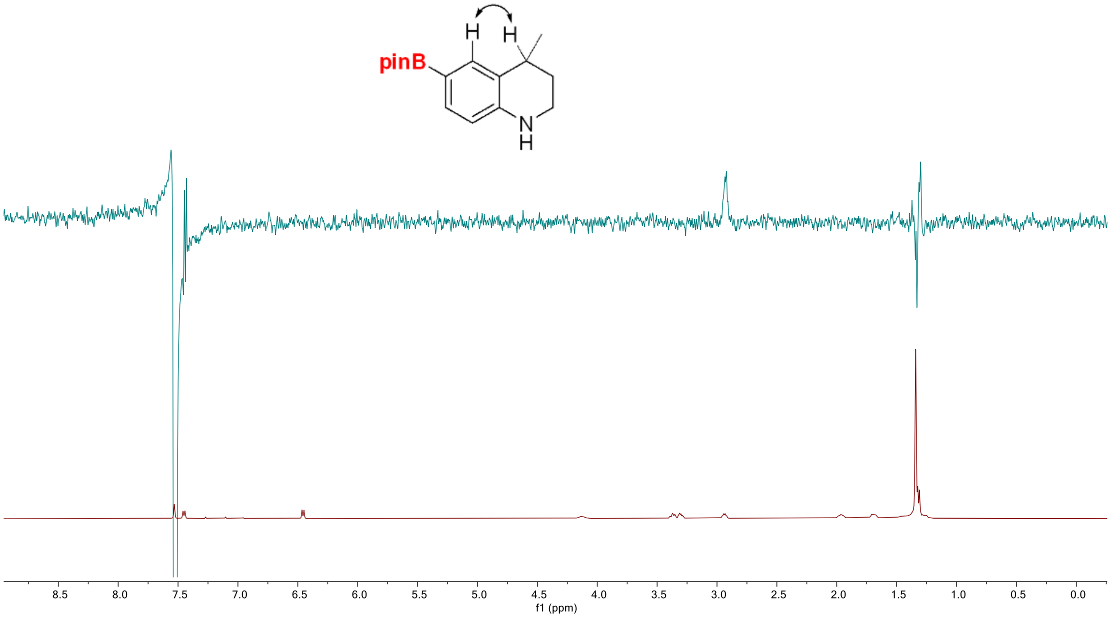
^{11}B{^{1}H} NMR of para borylated 4-methyl-1,2,3,4-tetrahydroquinoline (CDCl$_3$, 160 MHz)



1D-NOE of ^{1}H NMR of para borylated 4-methyl-1,2,3,4-tetrahydroquinoline ($CDCl_3$, 500 MHz)

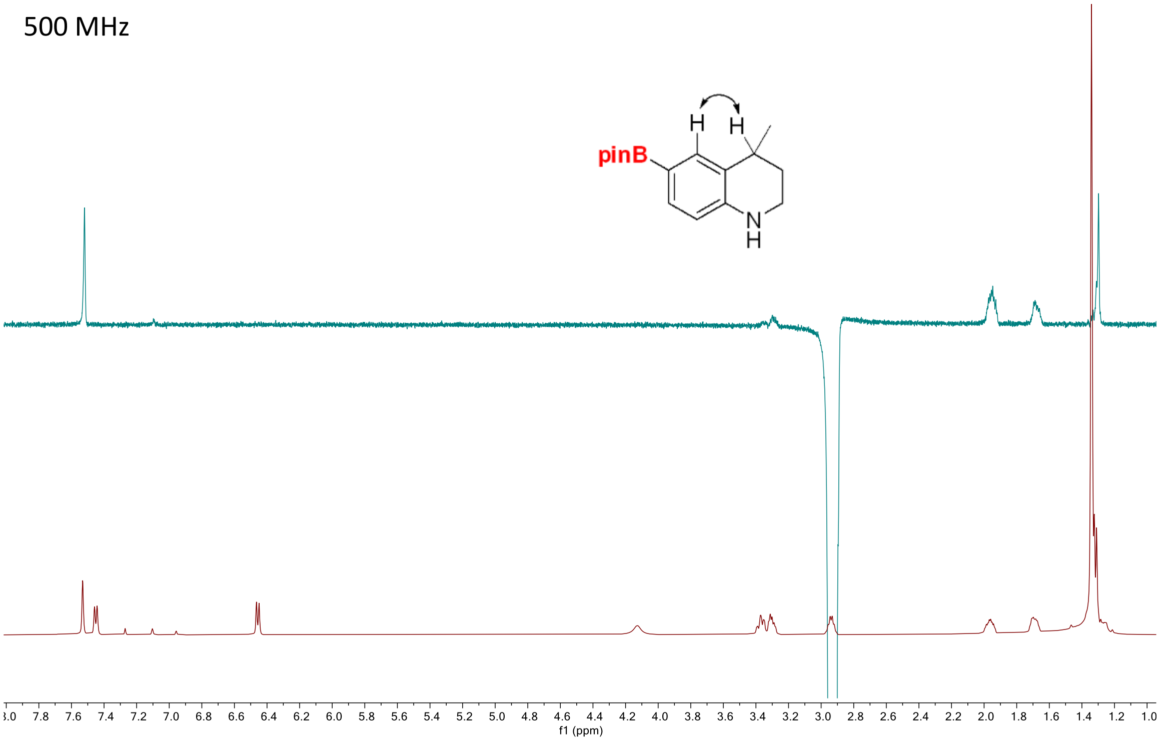
500 MHz

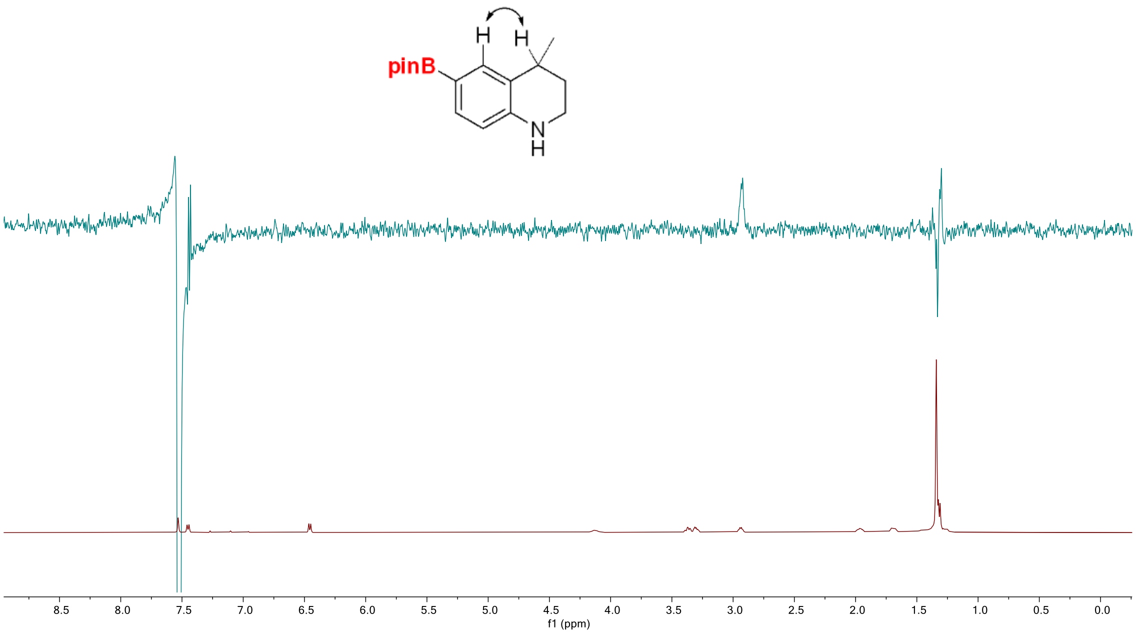




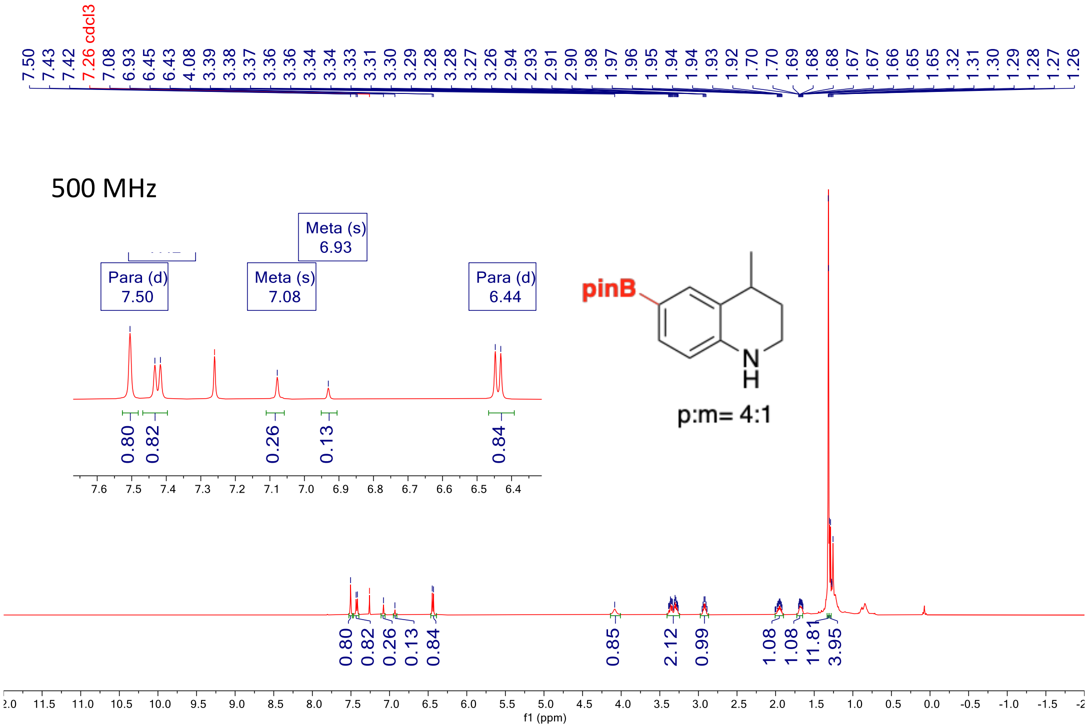
1D-NOE of ^{1}H NMR of para borylated 4-methyl-1,2,3,4-tetrahydroquinoline ($CDCl_3$, 500 MHz)

500 MHz

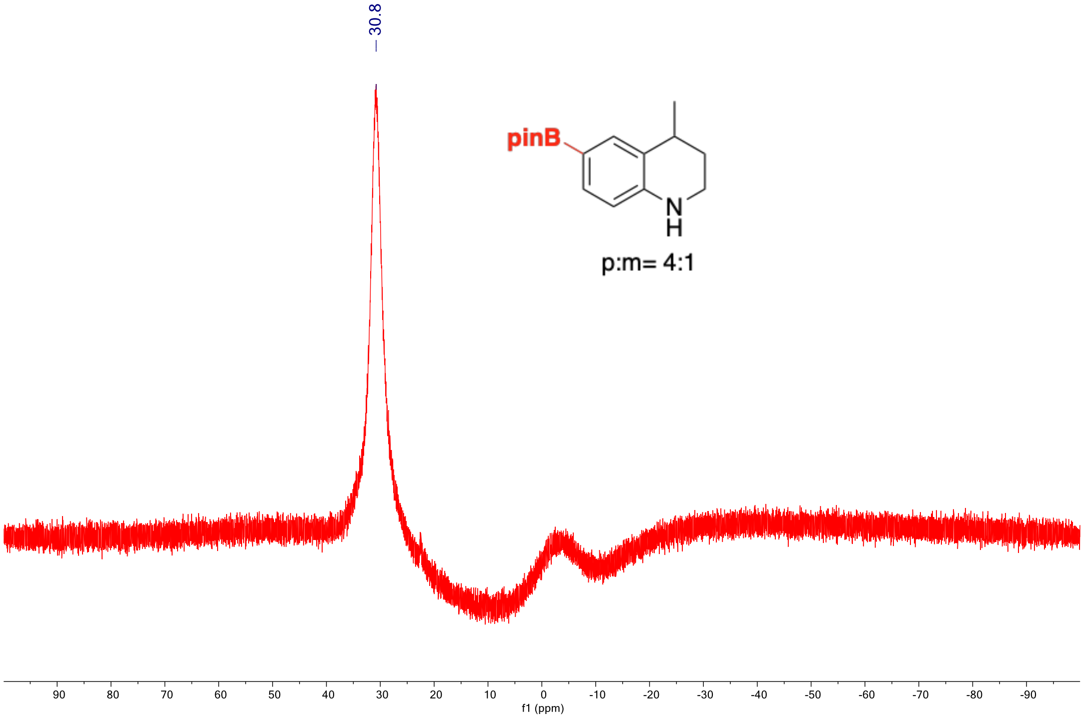




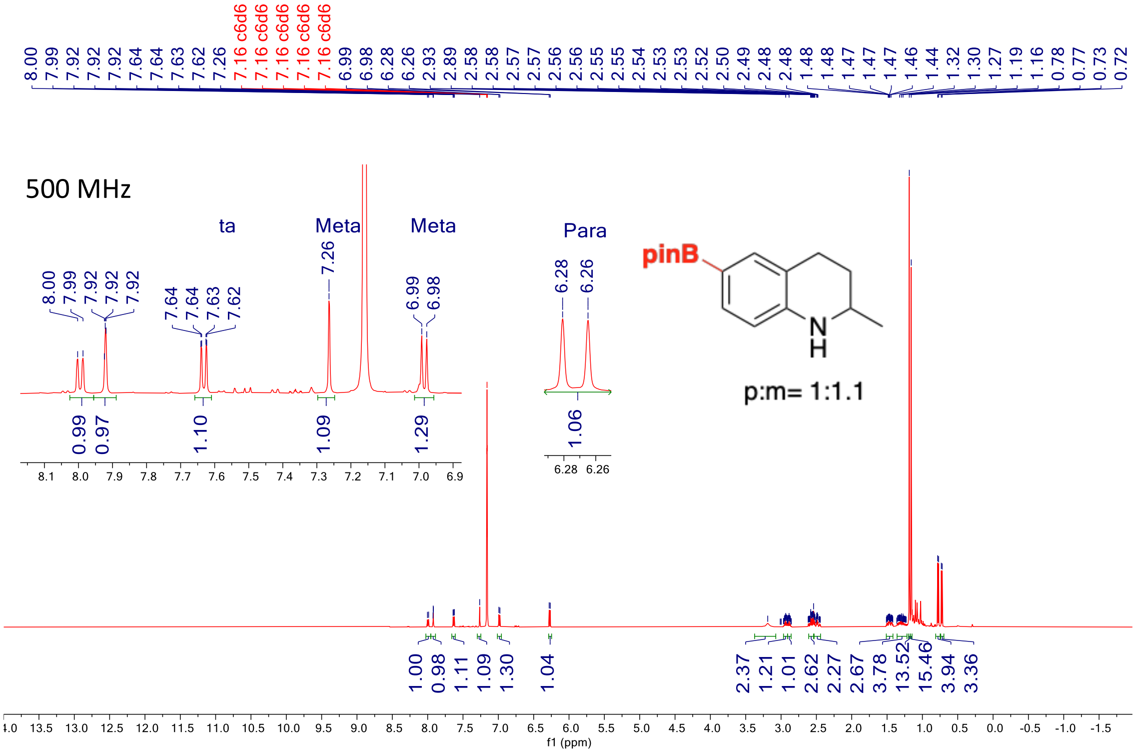
^{1}H NMR of para borylated 4-methyl-1,2,3,4-tetrahydroquinoline, second fraction ($CDCl_3$, 500 MHz)



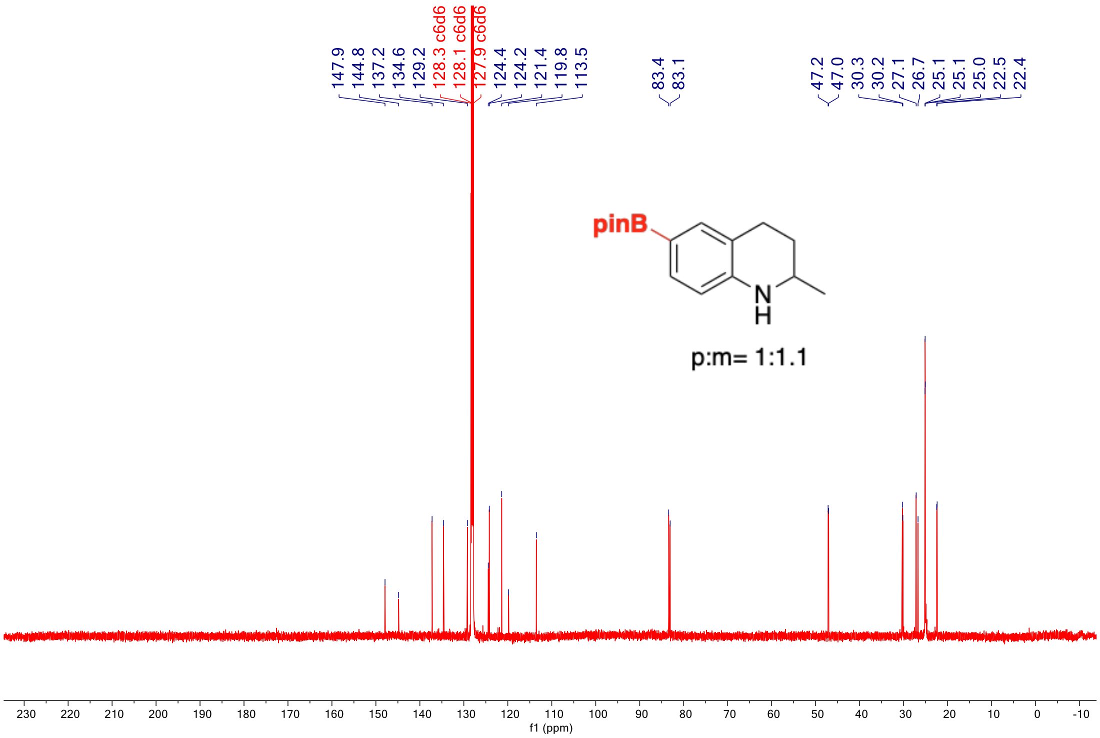
^{11}B{^{1}H} NMR of para borylated 4-methyl-1,2,3,4-tetrahydroquinoline, second fraction ($CDCl_3$, 160 MHz)



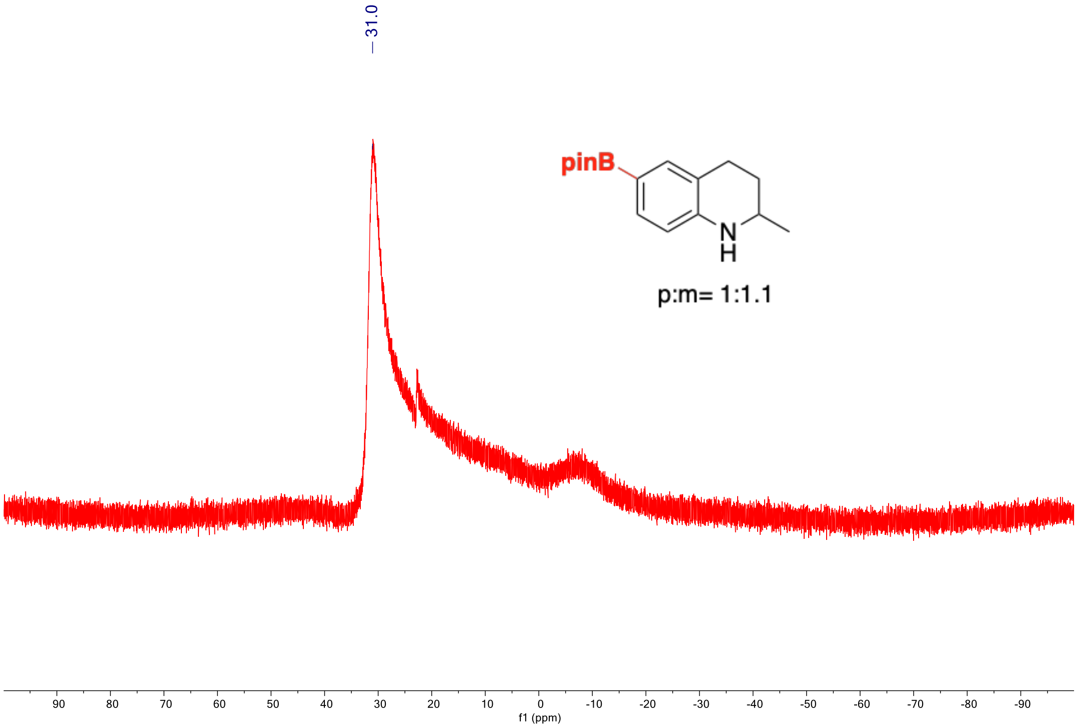
^{1}H NMR of para and meta borylated 2-methyl-1,2,3,4-tetrahydroquinoline, second fraction (C_6D_6, 500 MHz)



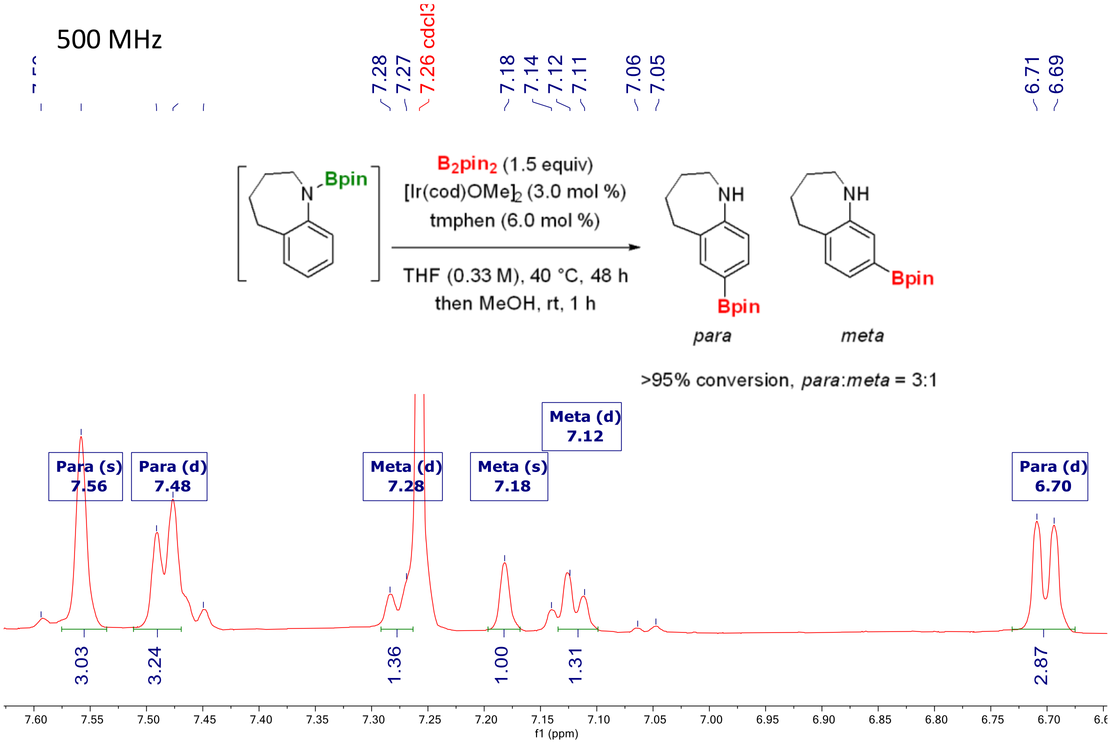
^{13}C{^{1}H} NMR of para and meta borylated 2-methyl-1,2,3,4-tetrahydroquinoline, second fraction (C_6D_6, 126 MHz)



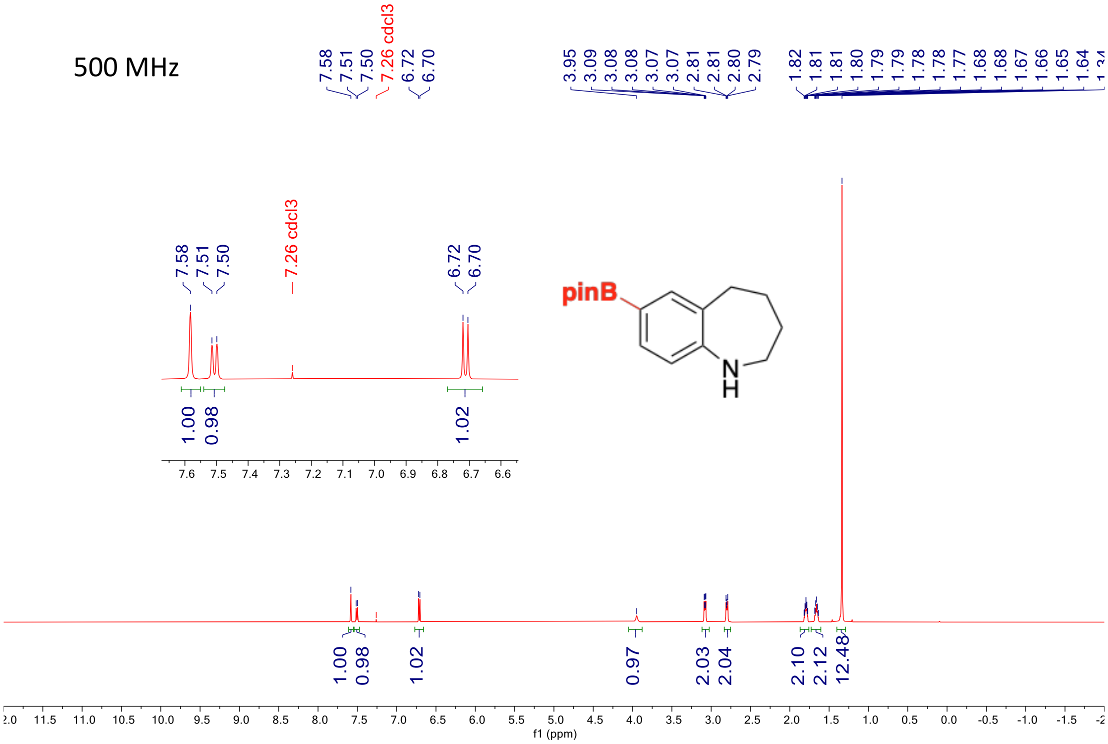
$^{11}B\{^1H\}$ NMR of para and meta borylated 2-methyl-1,2,3,4-tetrahydroquinoline, second fraction (C_6D_6, 160 MHz)



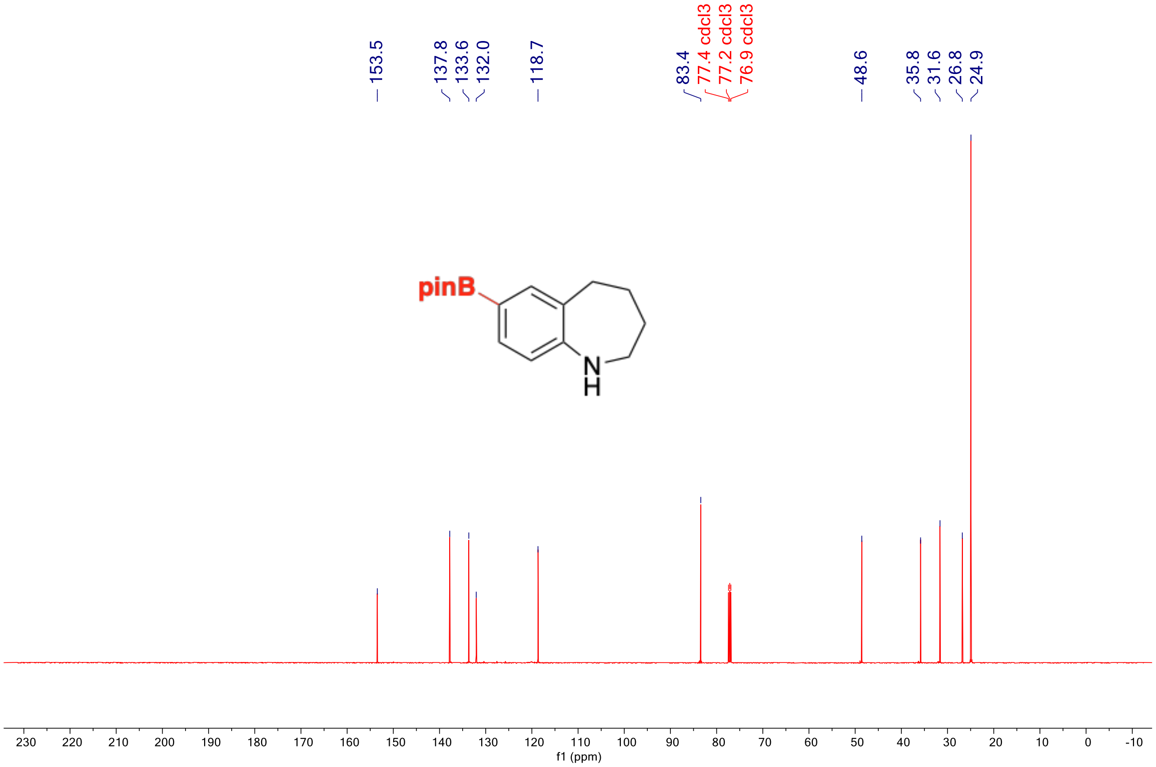
Para Borylation of 2,3,4,5-tetrahydro-1H-benzo[b]azepine (4g) ($CDCl_3$, 500 MHz)



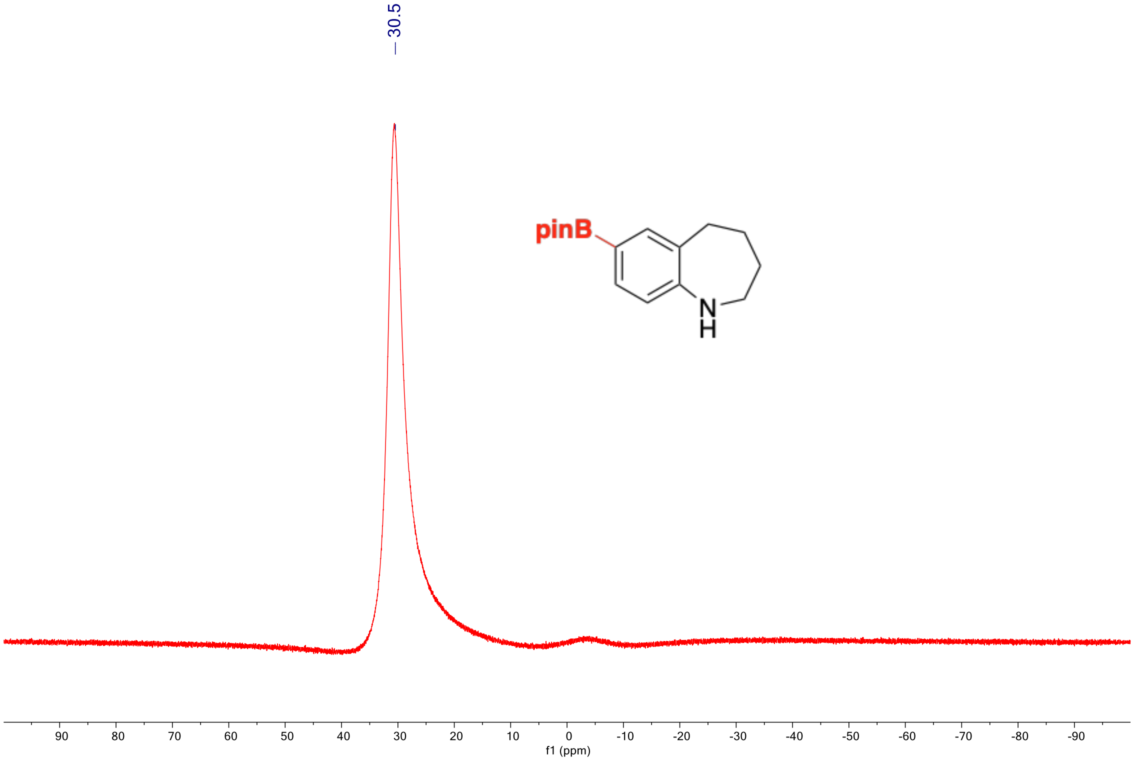
^{1}H NMR of para borylated 2,3,4,5-tetrahydro-1H-benzo[b]azepine ($CDCl_3$, 500 MHz)



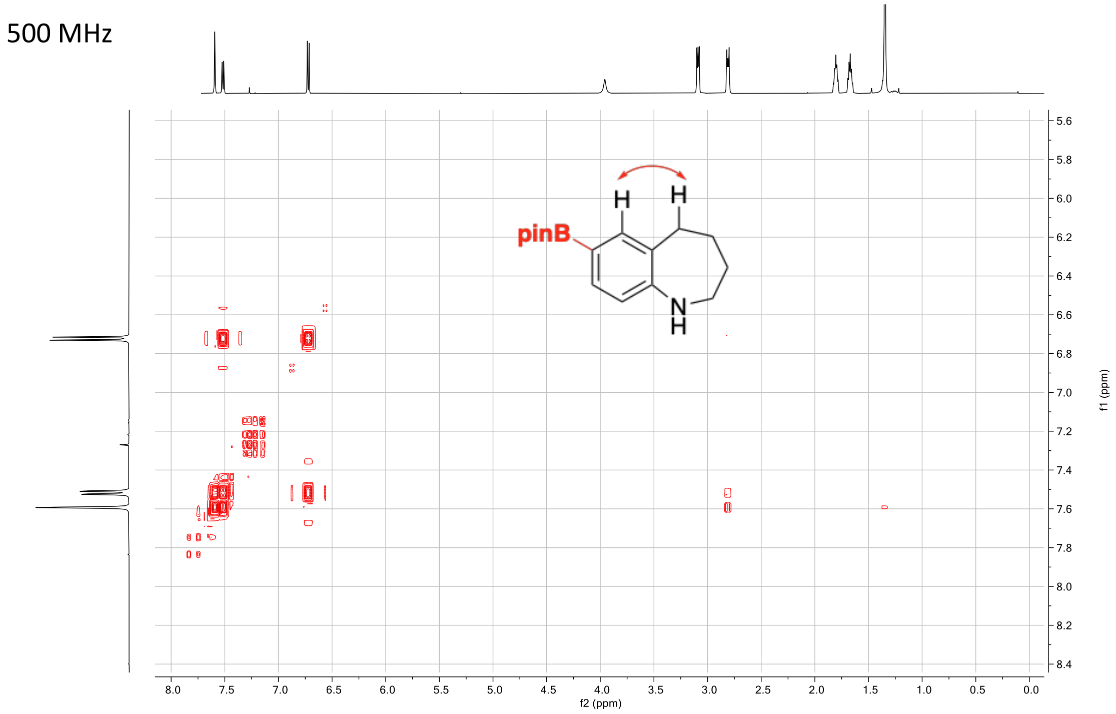
^{13}C{^{1}H} NMR of para borylated 2,3,4,5-tetrahydro-1H-benzo[b]azepine ($CDCl_3$, 126 MHz)



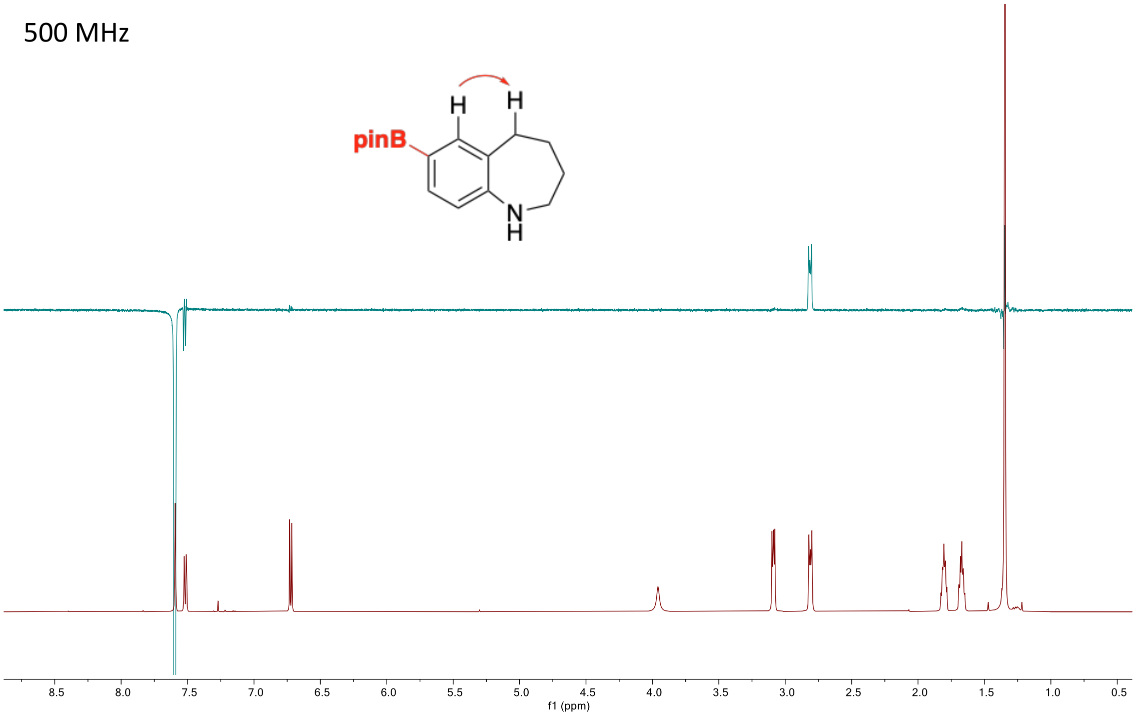
$^{11}B\{^1H\}$ NMR of para borylated 2,3,4,5-tetrahydro-1H-benzo[b]azepine ($CDCl_3$, 160 MHz)



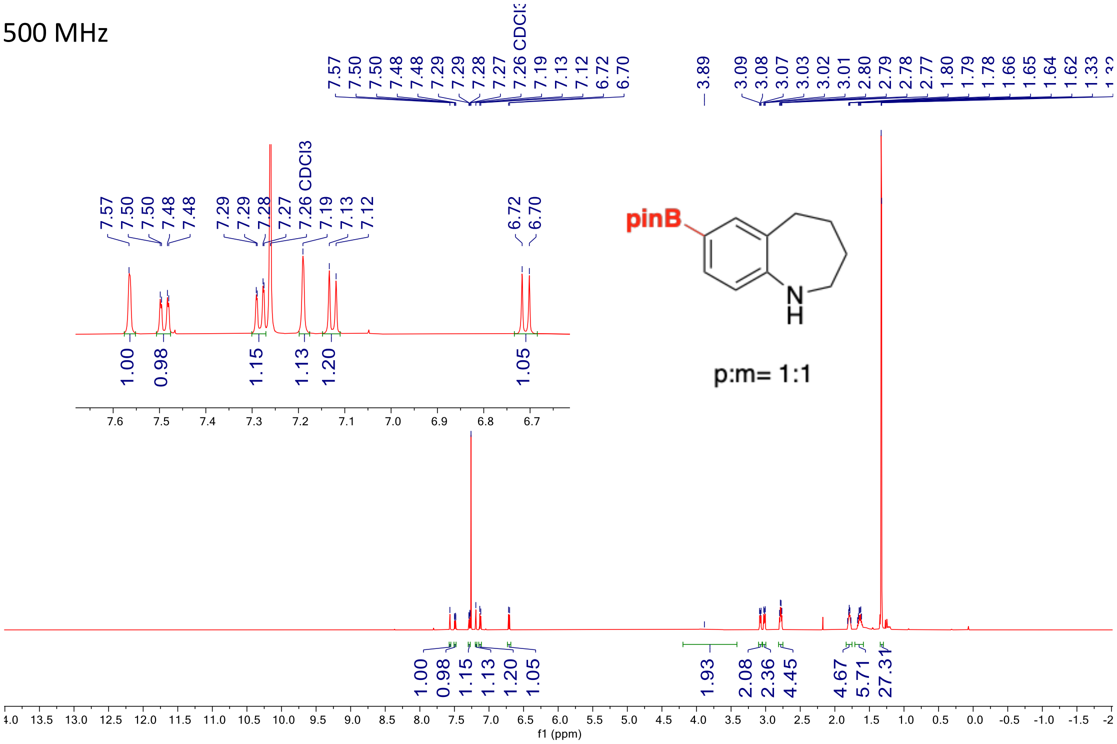
gCOSY of para borylated 2,3,4,5-tetrahydro-1H-benzo[b]azepine ($CDCl_3$, 500 MHz)



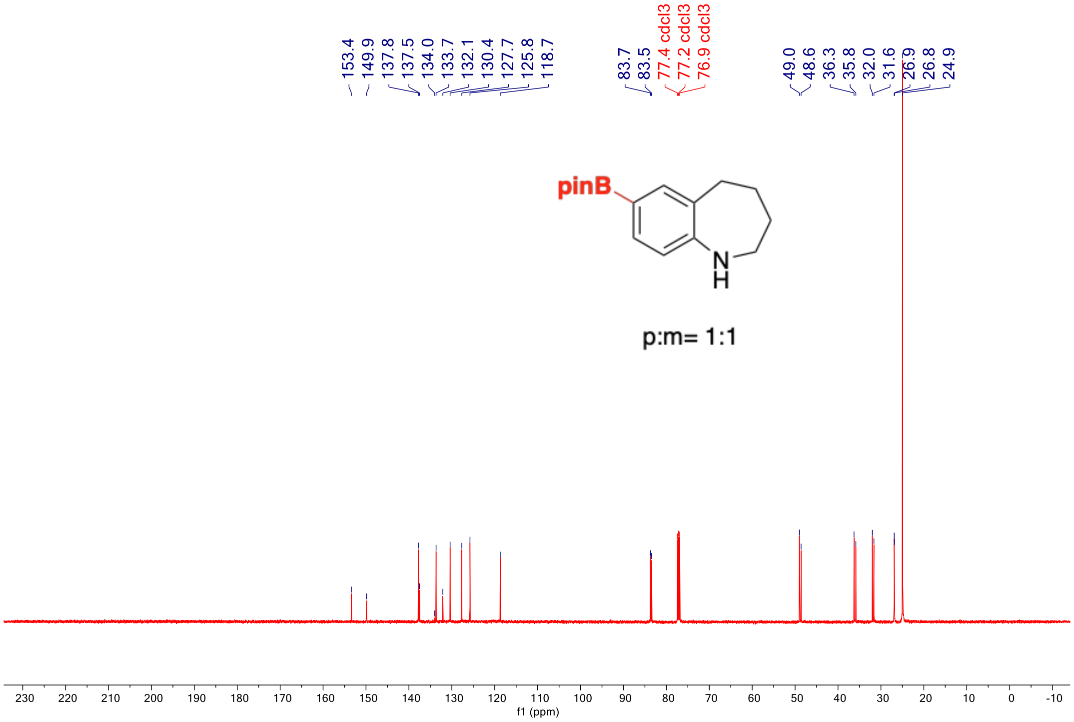
1D-NOE of para borylated 2,3,4,5-tetrahydro-1H-benzo[b]azepine ($CDCl_3$, 500 MHz)



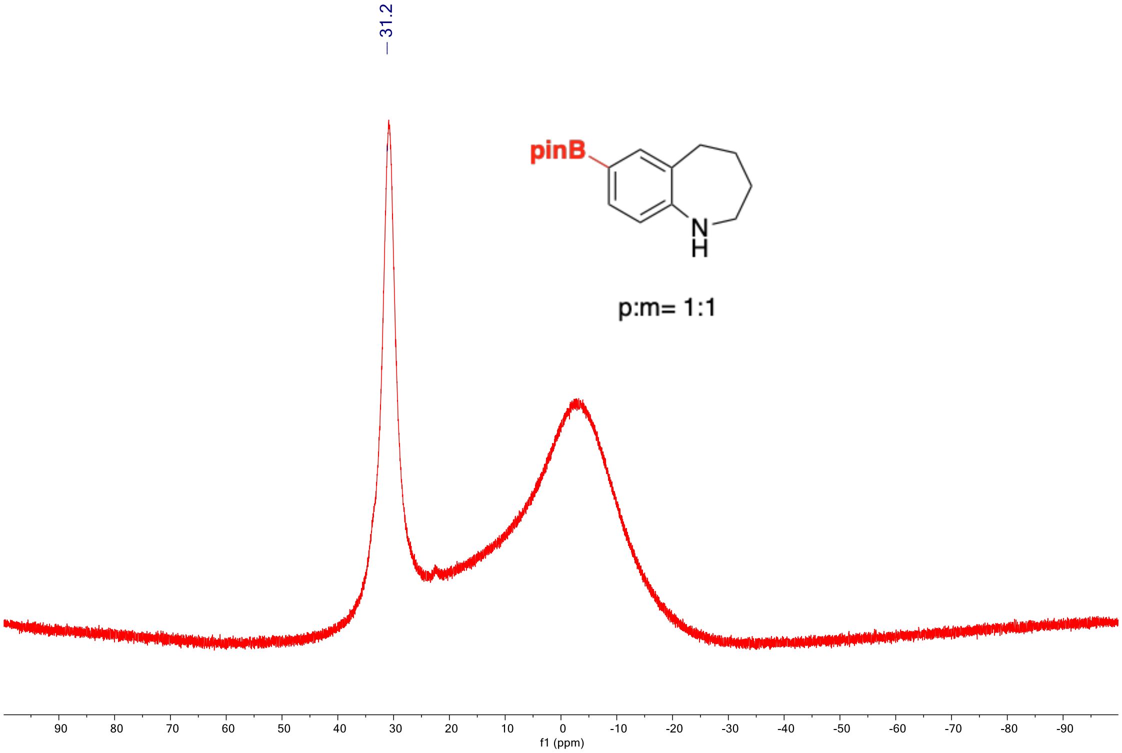
^{1}H NMR of para and meta borylated 2,3,4,5-tetrahydro-1H-benzo[b]azepine, second fraction ($CDCl_3$, 500 MHz)



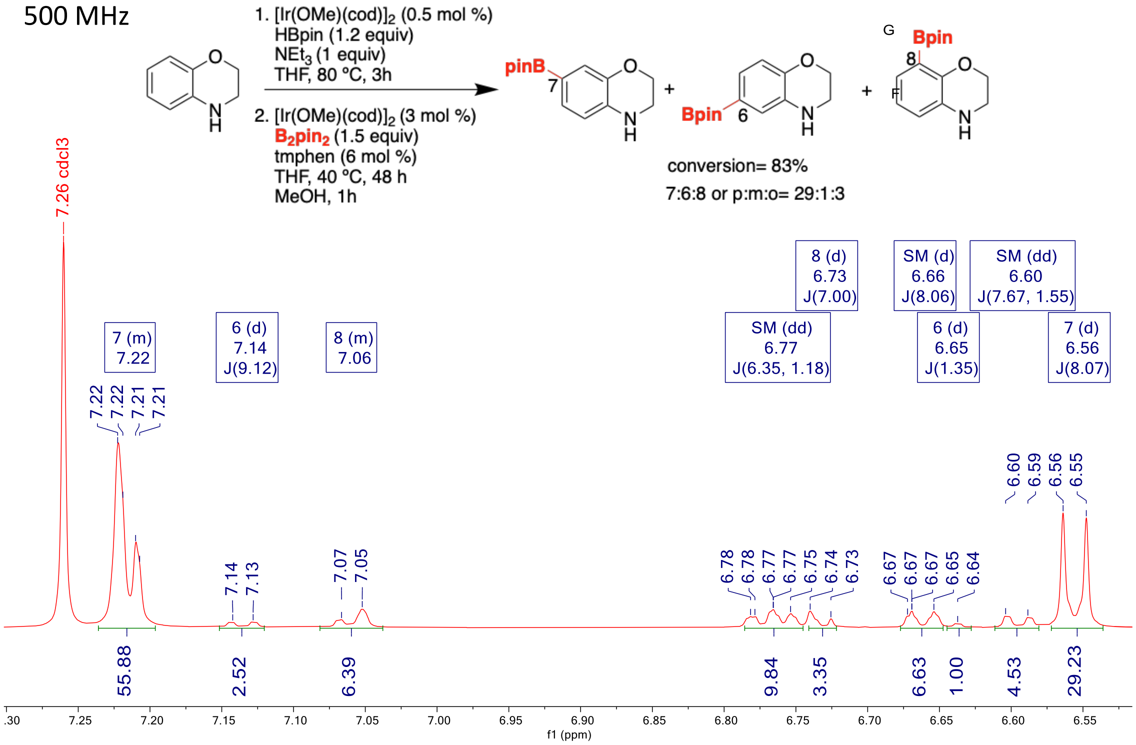
$^{13}C\{^1H\}$ NMR of para and meta borylated 2,3,4,5-tetrahydro-1H-benzo[b]azepine, second fraction ($CDCl_3$, 126 MHz)



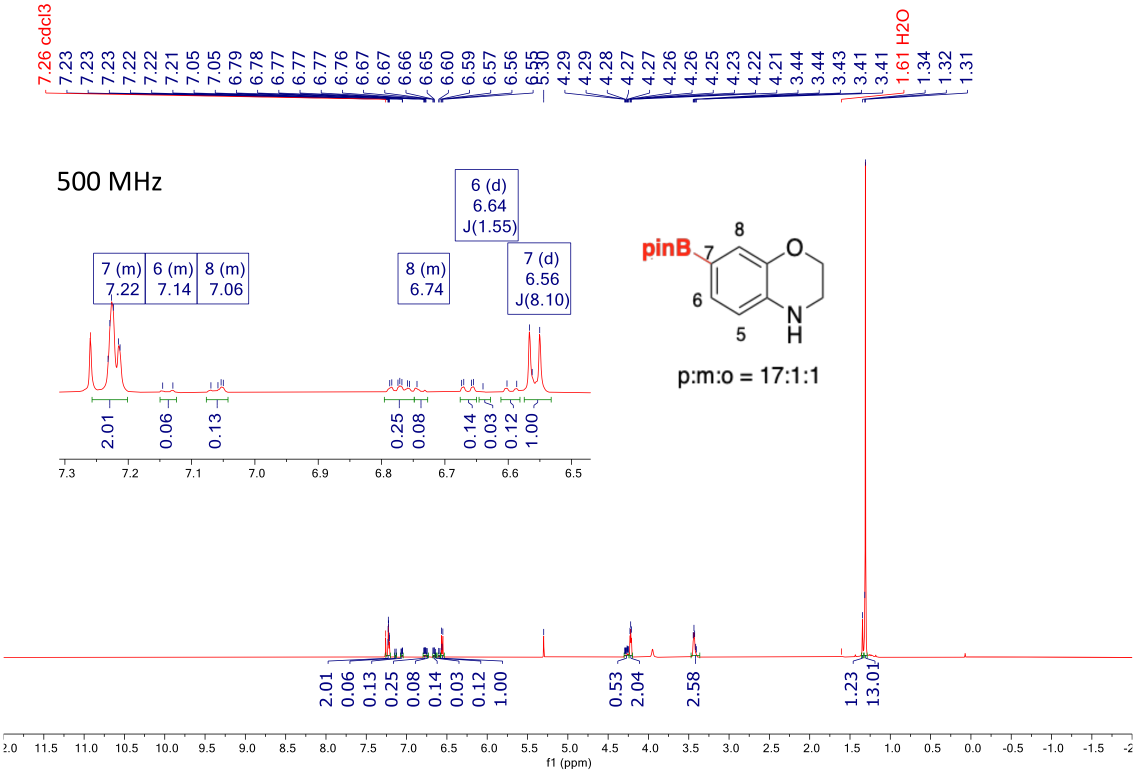
$^{11}B\{^1H\}$ NMR of para and meta borylated 2,3,4,5-tetrahydro-1H-benzo[b]azepine, second fraction ($CDCl_3$, 160 MHz)



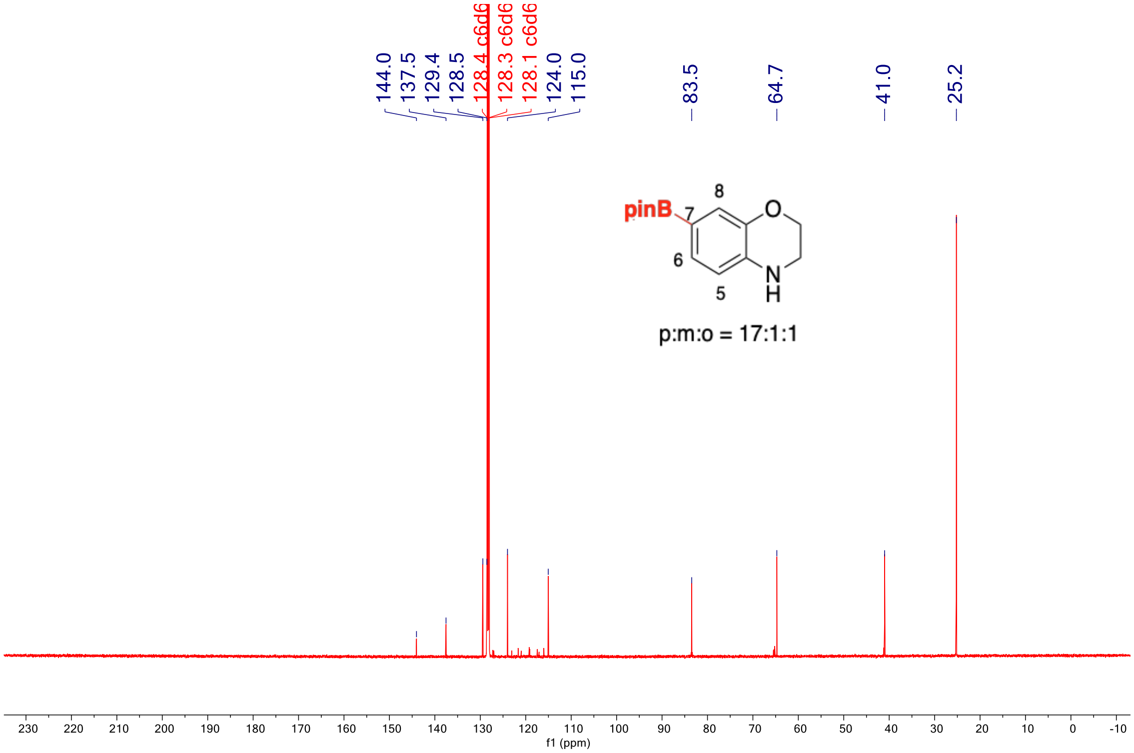
Para CHB of 3,4-dihydro-2H-benzo[b][1,4]oxazine (4h) (CDCl$_3$, 500 MHz)



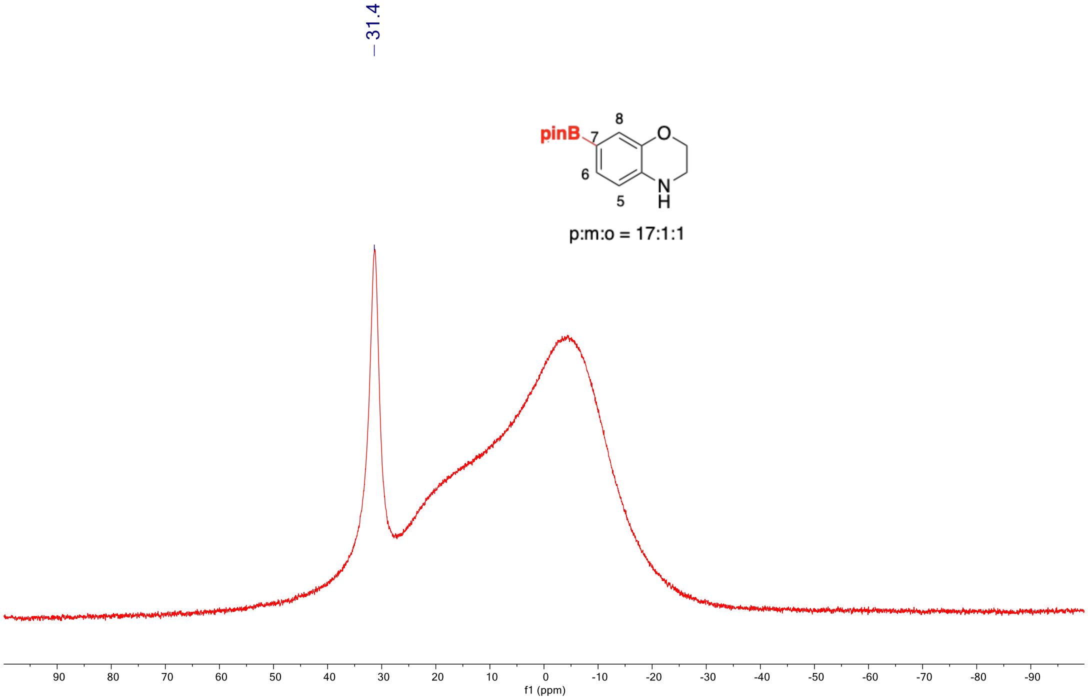
^{1}H NMR of para borylated 3,4-dihydro-2H-benzo[b][1,4]oxazine (CDCl$_3$, 500 MHz)



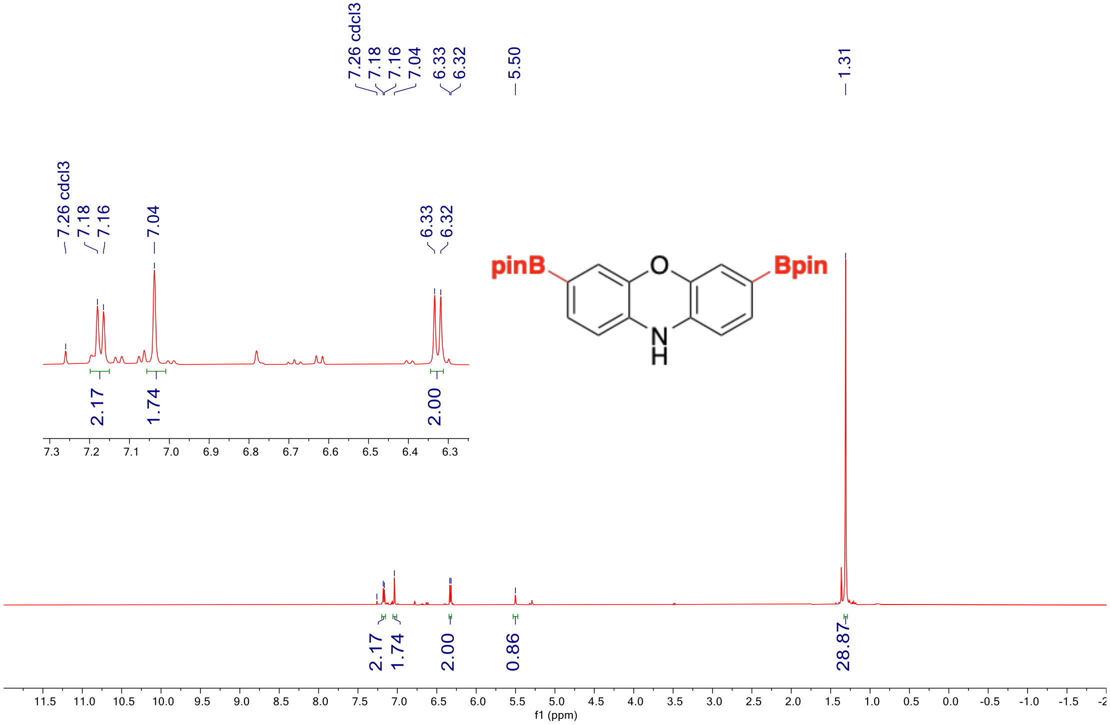
$^{13}C\{^1H\}$ NMR of para borylated 3,4-dihydro-2H-benzo[b][1,4]oxazine (C_6D_6, 126 MHz)



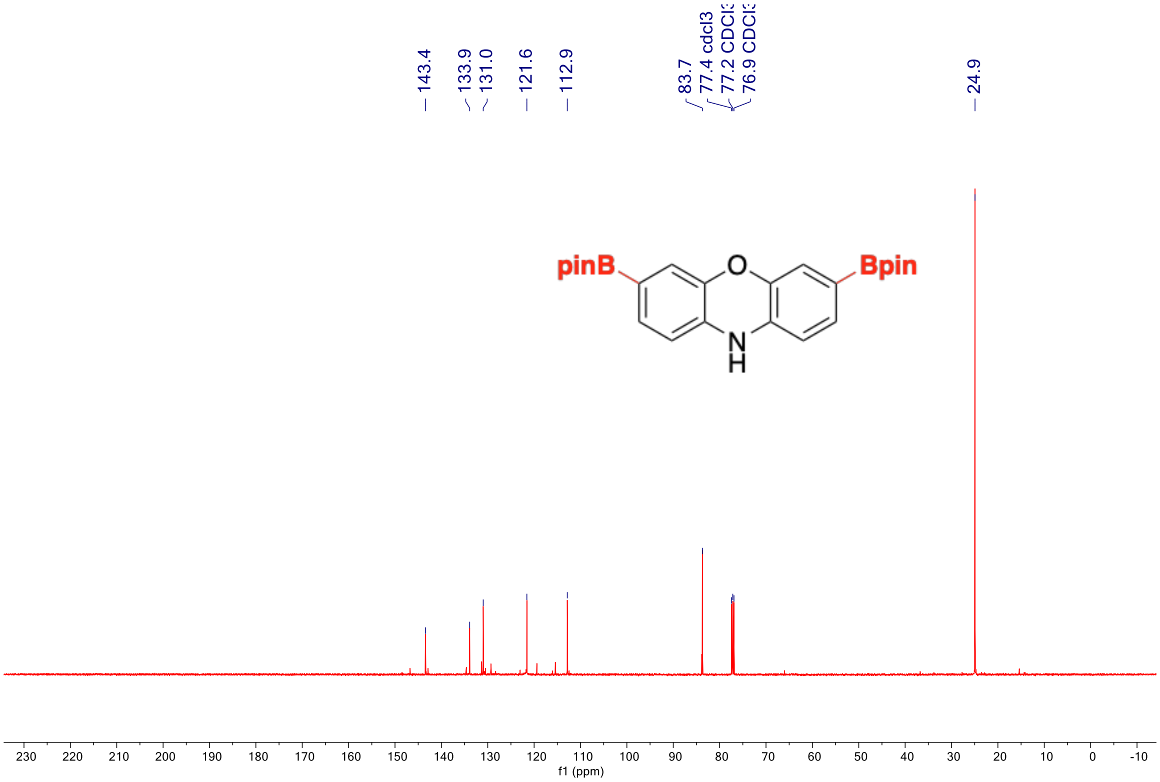
$^{11}B\{^1H\}$ NMR of para borylated 3,4-dihydro-2H-benzo[b][1,4]oxazine (C_6D_6, 126 MHz)



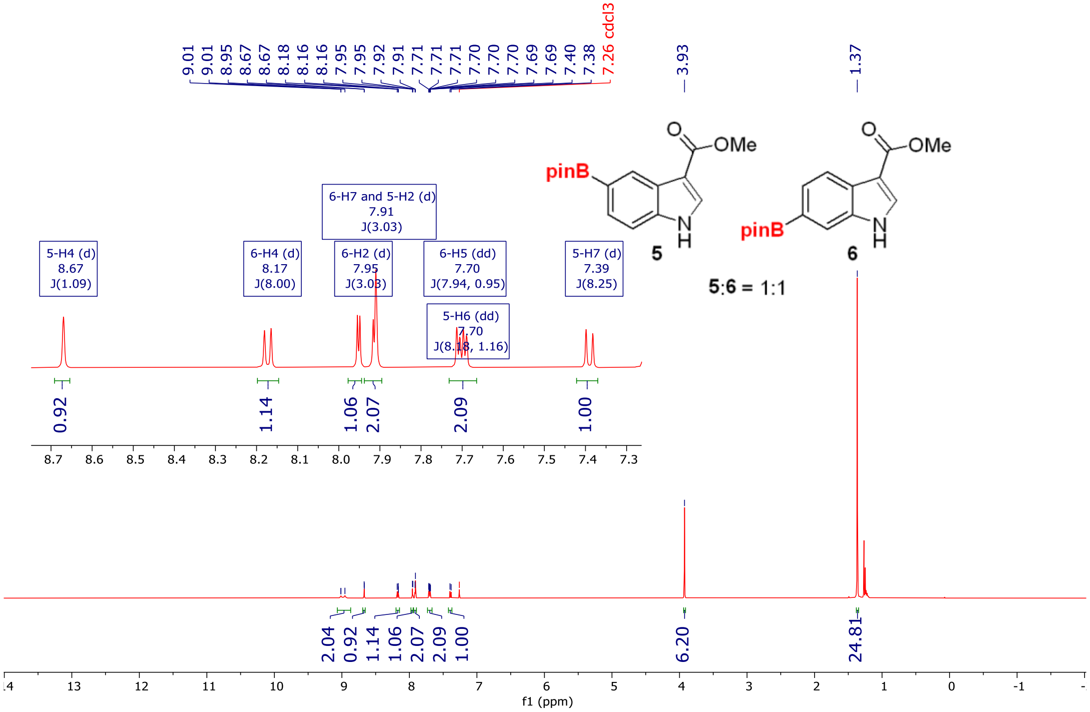
^{1}H NMR of para diborylated 10*H*-phenoxazine ($CDCl_3$, 500 MHz)



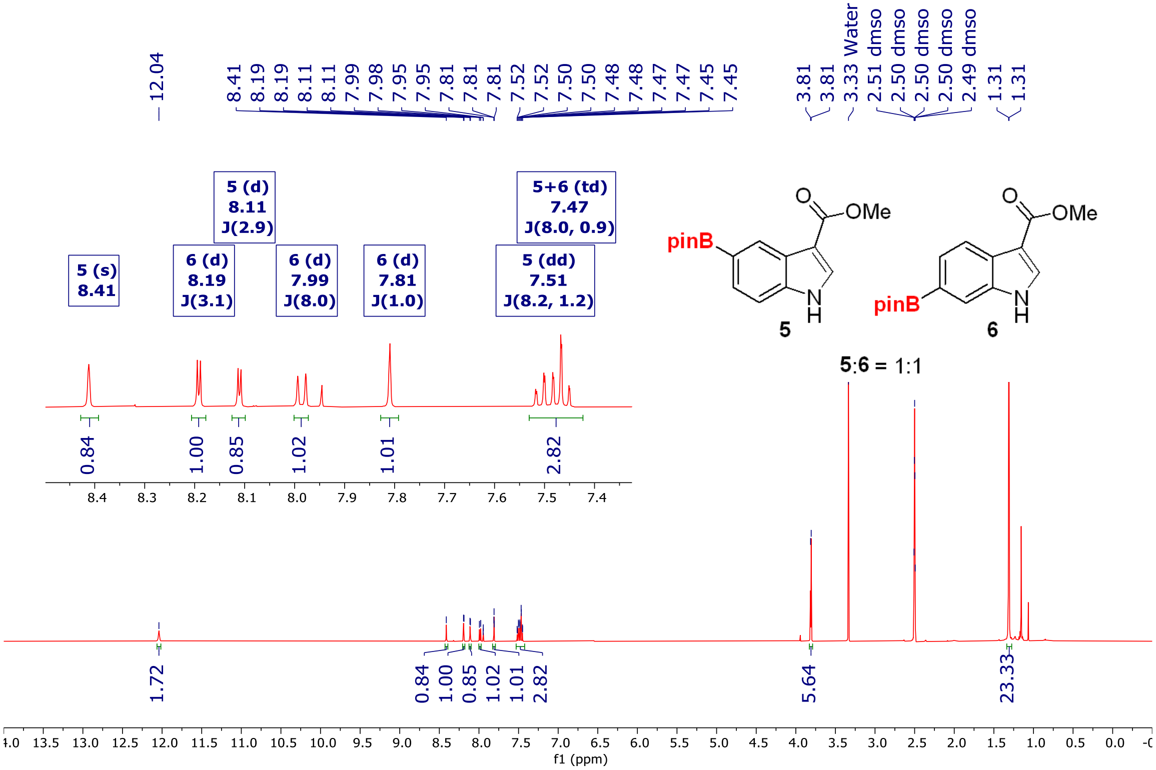
$^{13}C\{^{1}H\}$ NMR of para diborylated 10*H*-phenoxazine ($CDCl_3$, 126 MHz)



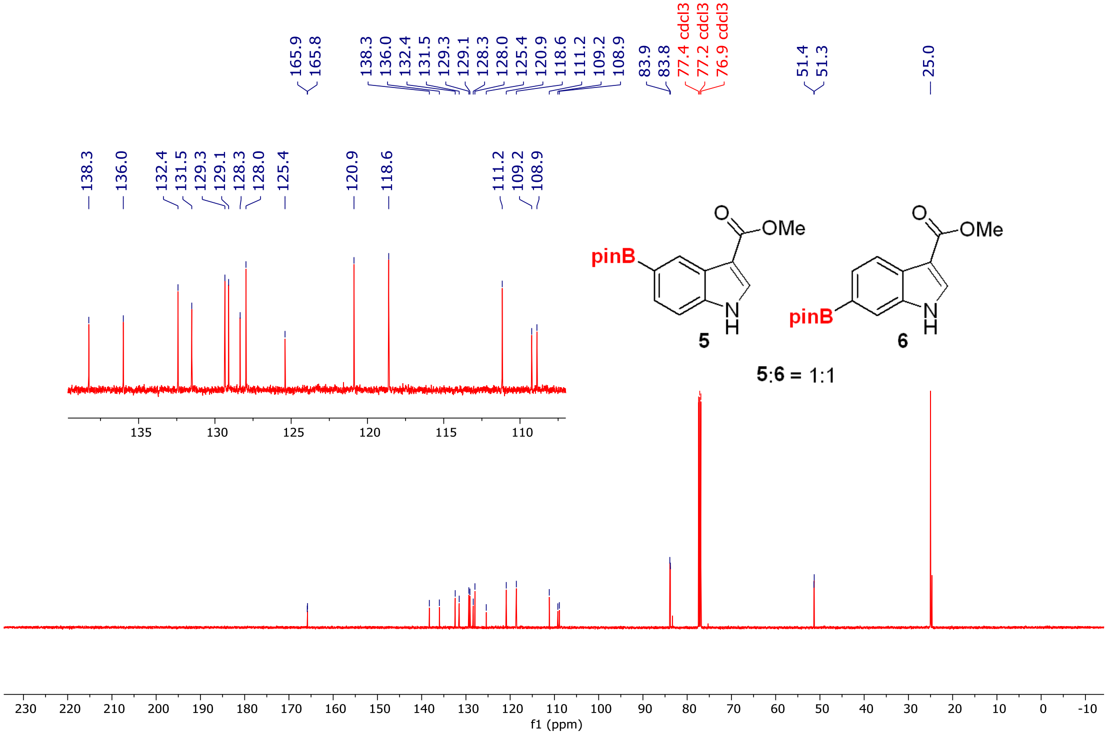
^{1}H NMR of 5- and 6-borylated methyl indole-3-carboxylate (CDCl$_3$, 500 MHz)



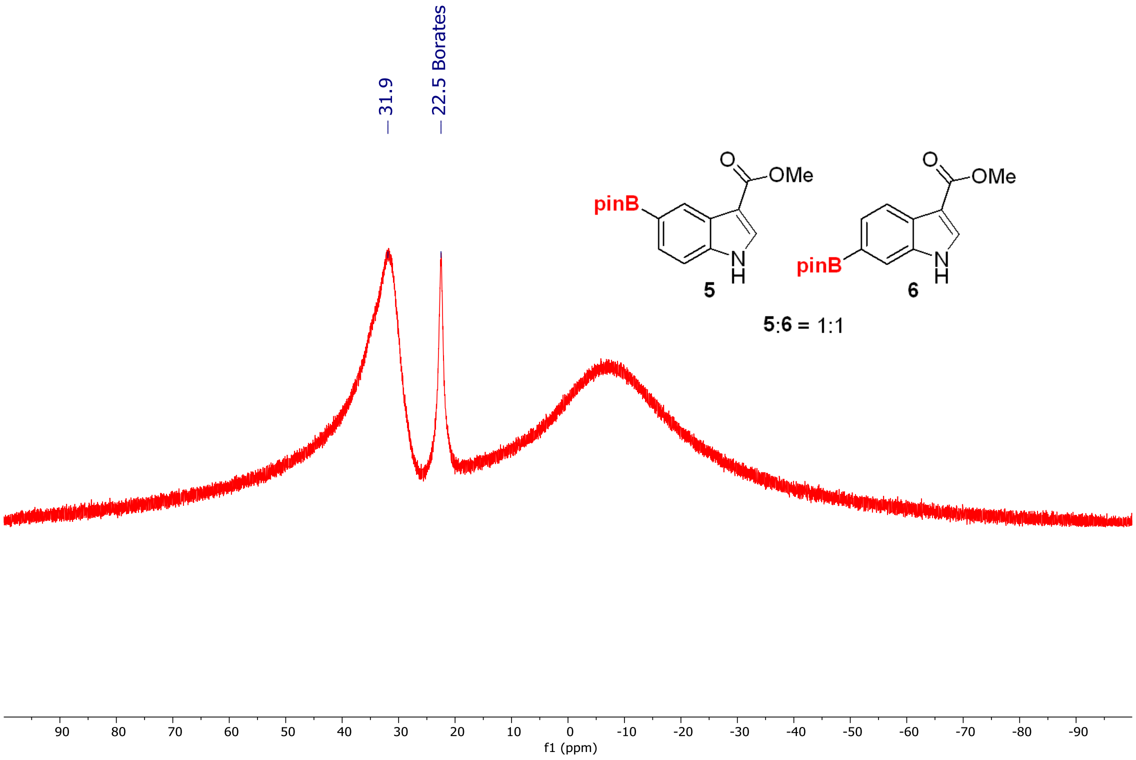
^{1}H NMR of 5- and 6-borylated methyl indole-3-carboxylate (CDCl$_3$, 500 MHz)



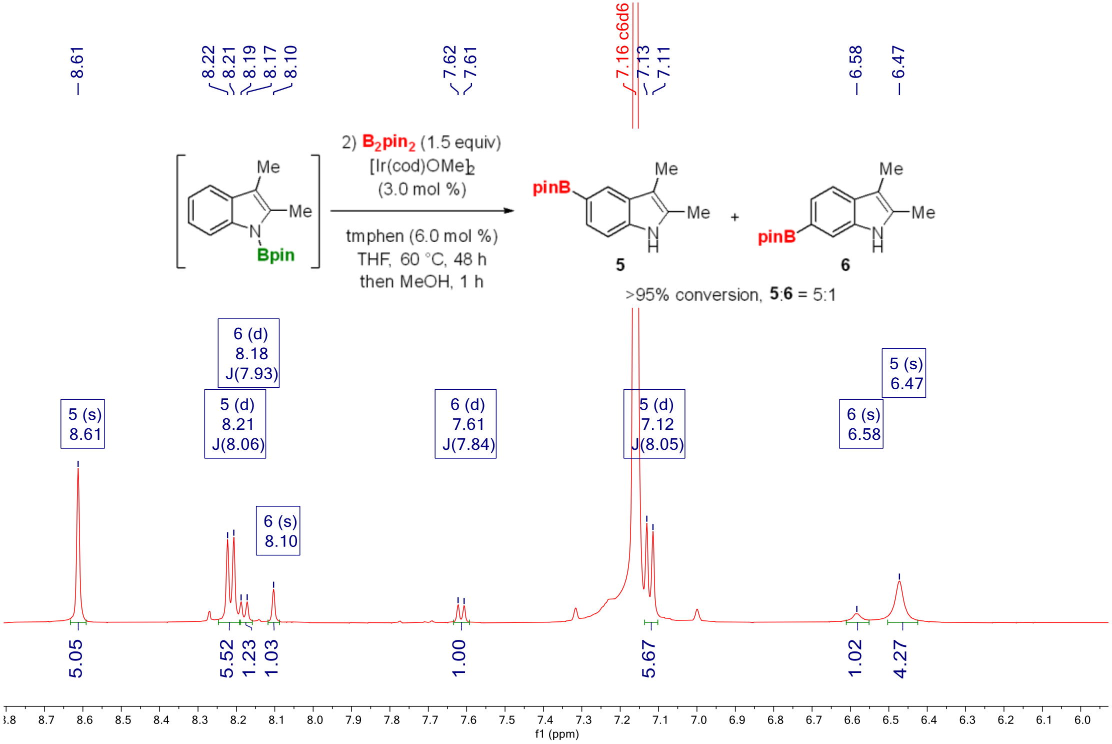
$^{13}C\{^1H\}$ NMR of 5- and 6-borylated methyl indole-3-carboxylate ($CDCl_3$, 126 MHz)



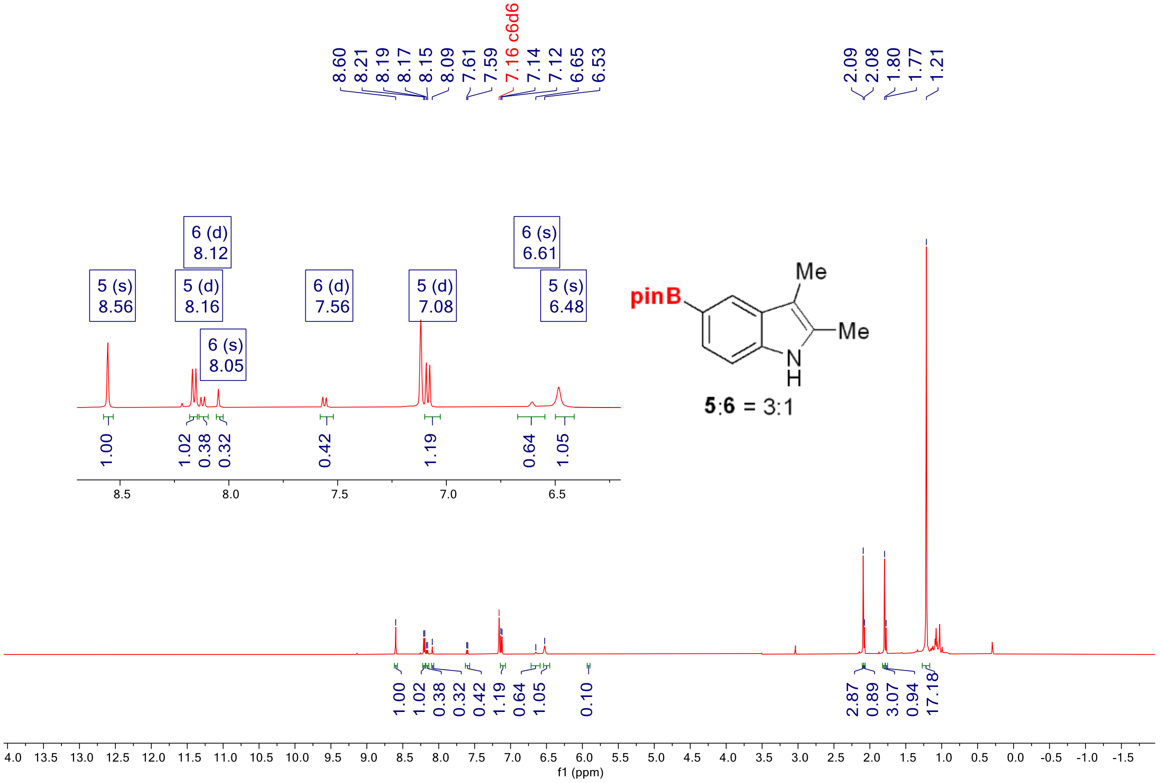
$^{11}B\{^1H\}$ NMR of 5- and 6-borylated methyl indole-3-carboxylate ($CDCl_3$, 160 MHz)



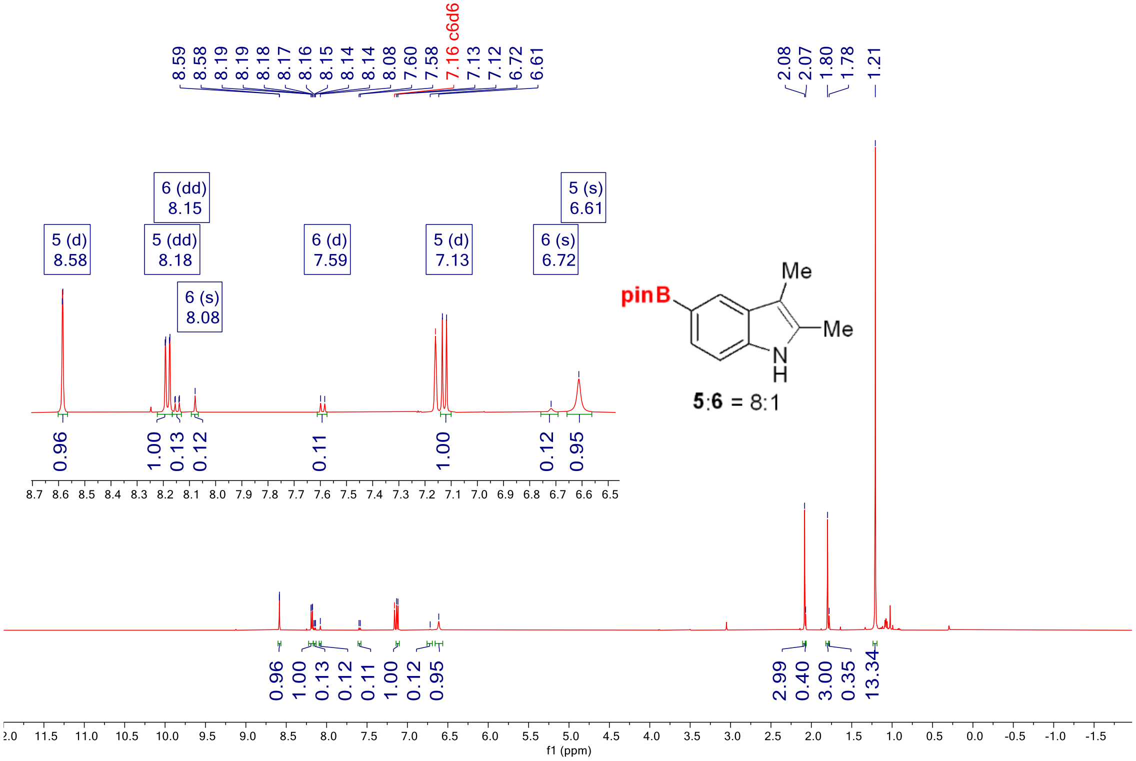
C5 CHB of 2,3-dimethyl indole (6c) (C_6D_6, 500 MHz)



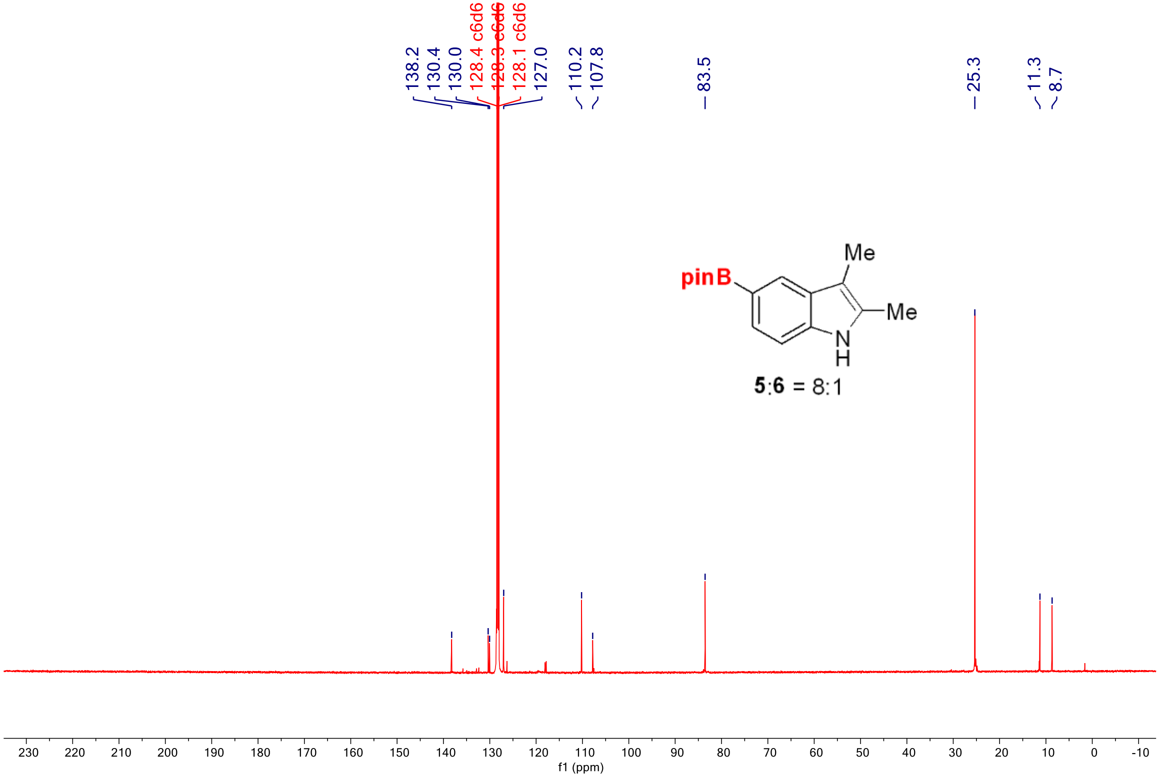
^{1}H NMR of C5 and C6 borylated 2,3-dimethyl indole, first fraction (C_6D_6, 500 MHz)



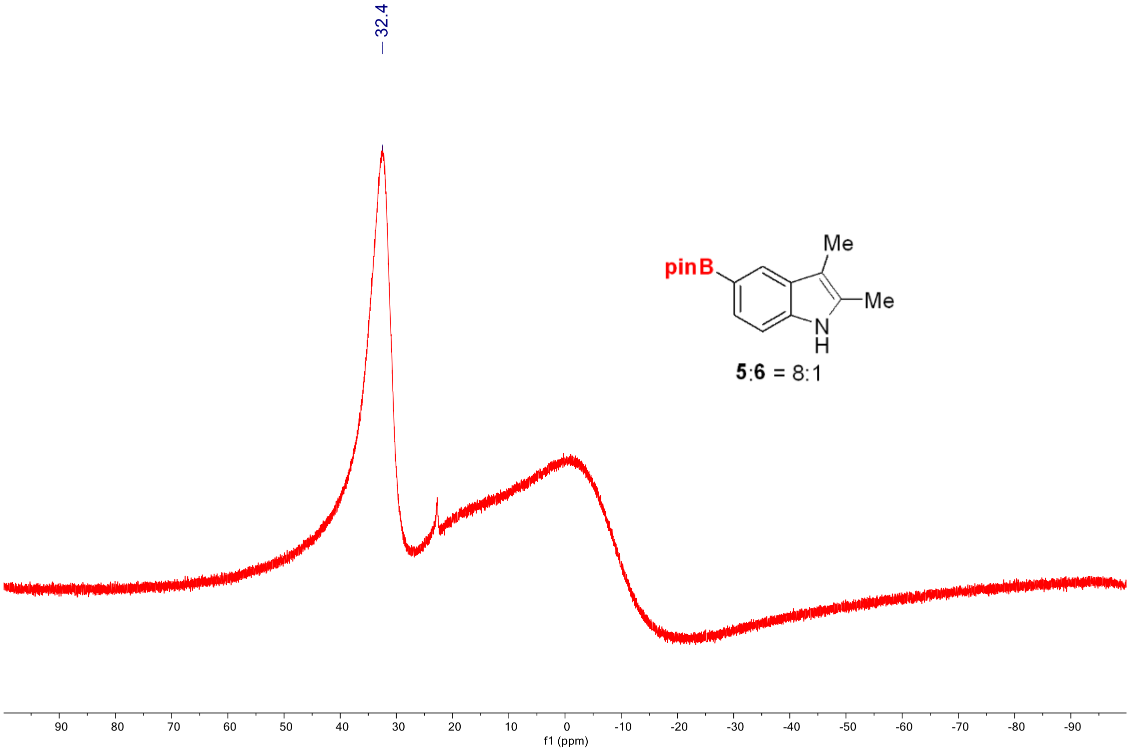
^{1}H NMR of C5 borylated 2,3-dimethyl indole (C_6D_6, 500 MHz)



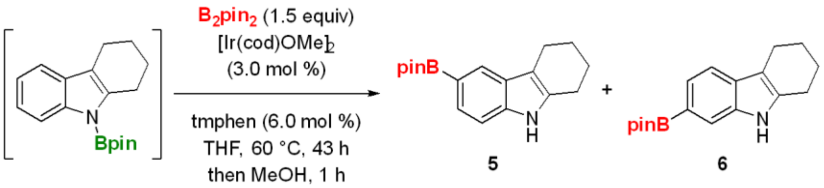
^{13}C{^{1}H} NMR of C5 borylated 2,3-dimethyl indole (C_6D_6, 126 MHz)



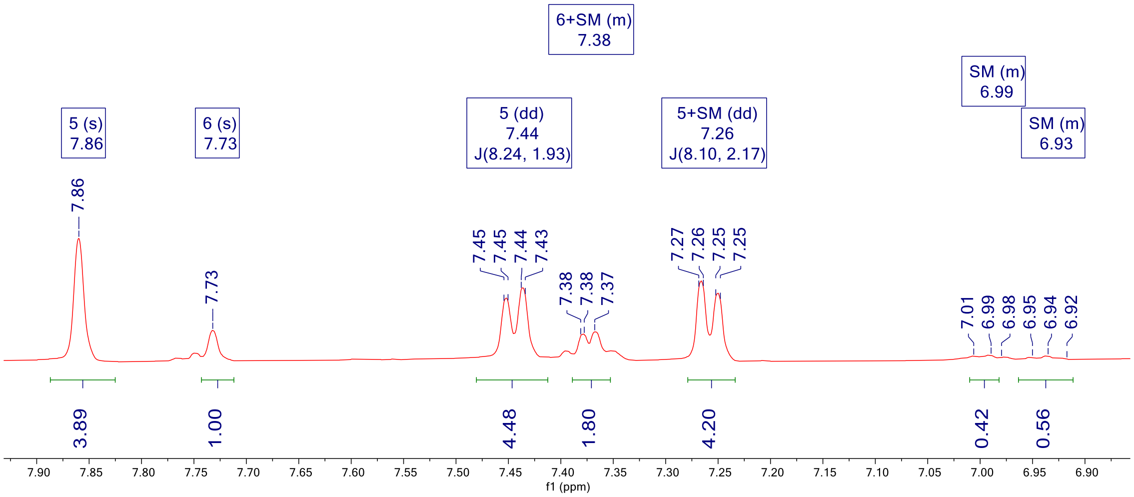
$^{11}B\{^1H\}$ NMR of C5 borylated 2,3-dimethyl indole (C_6D_6, 126 MHz)



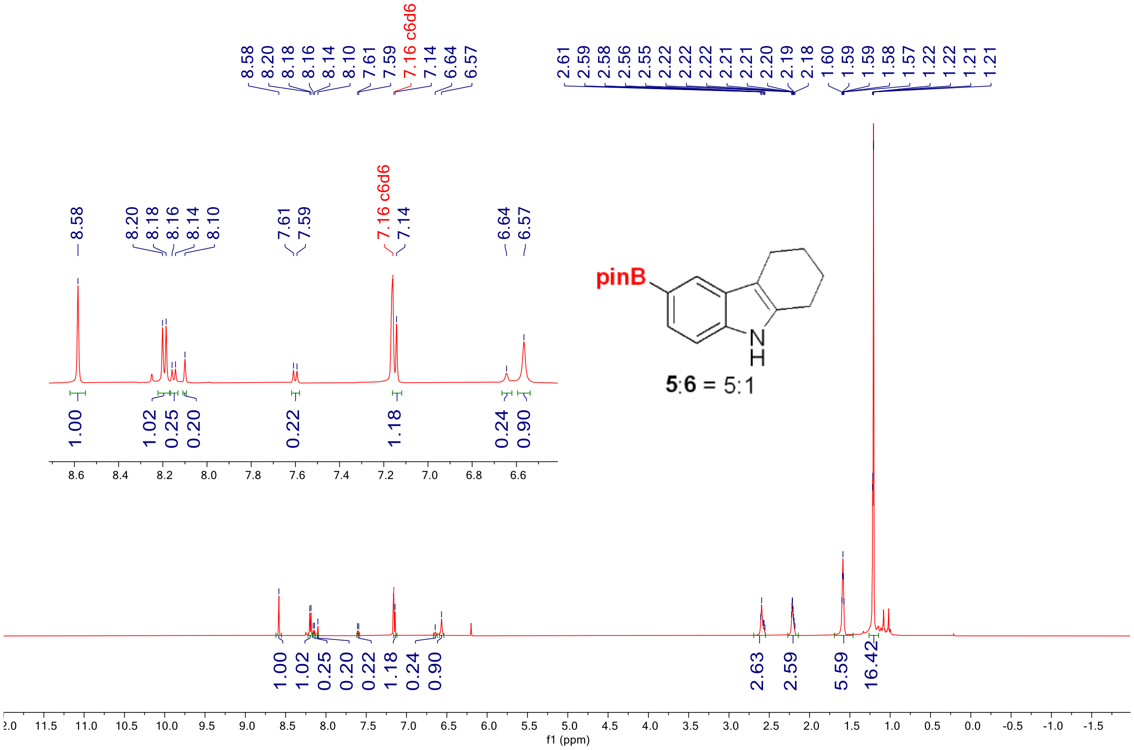
5 CHB of 2,3,4,9-tetrahydro-1H-carbazole (6d) (acetone-d6, 500 MHz)



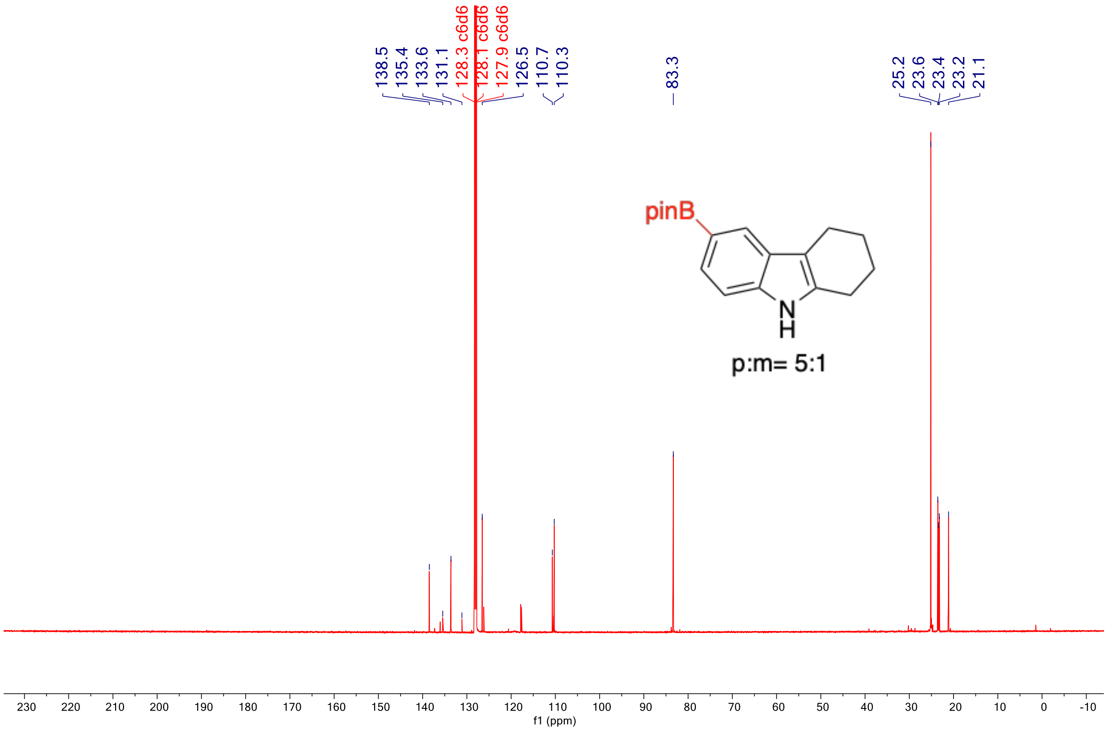
>95% conversion, **5**:**6** = 4:1



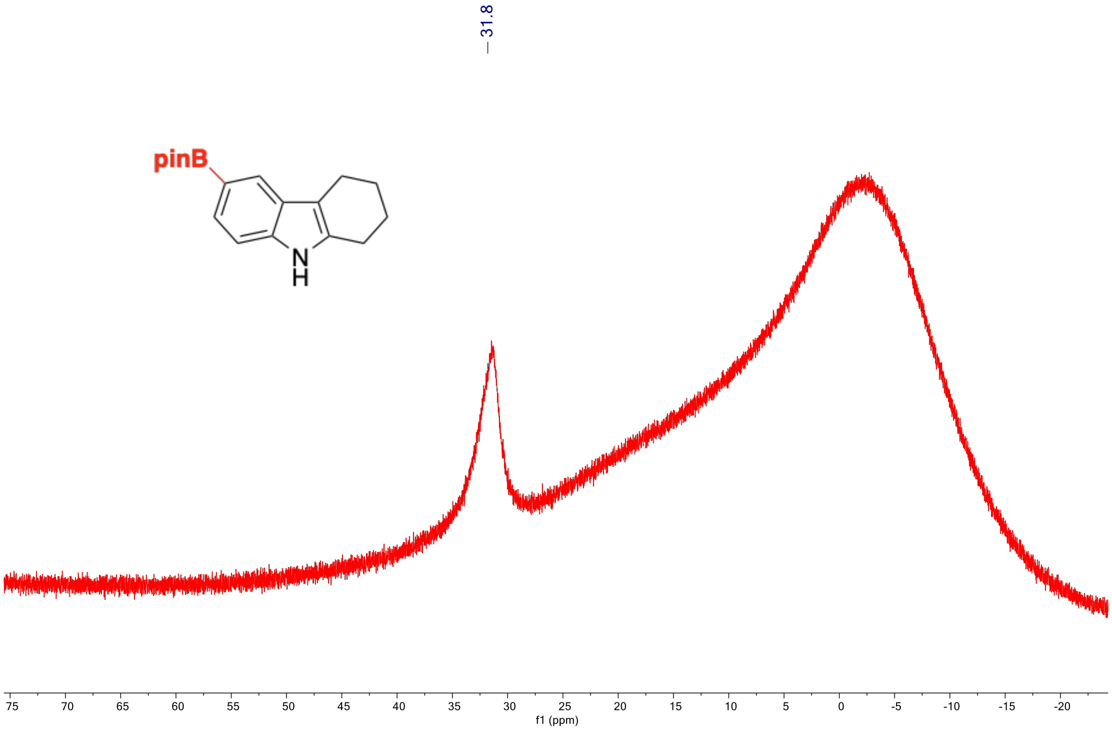
^{1}H NMR of 5-borylated 2,3,4,9-tetrahydro-1H-carbazole (C_6D_6, 500 MHz)



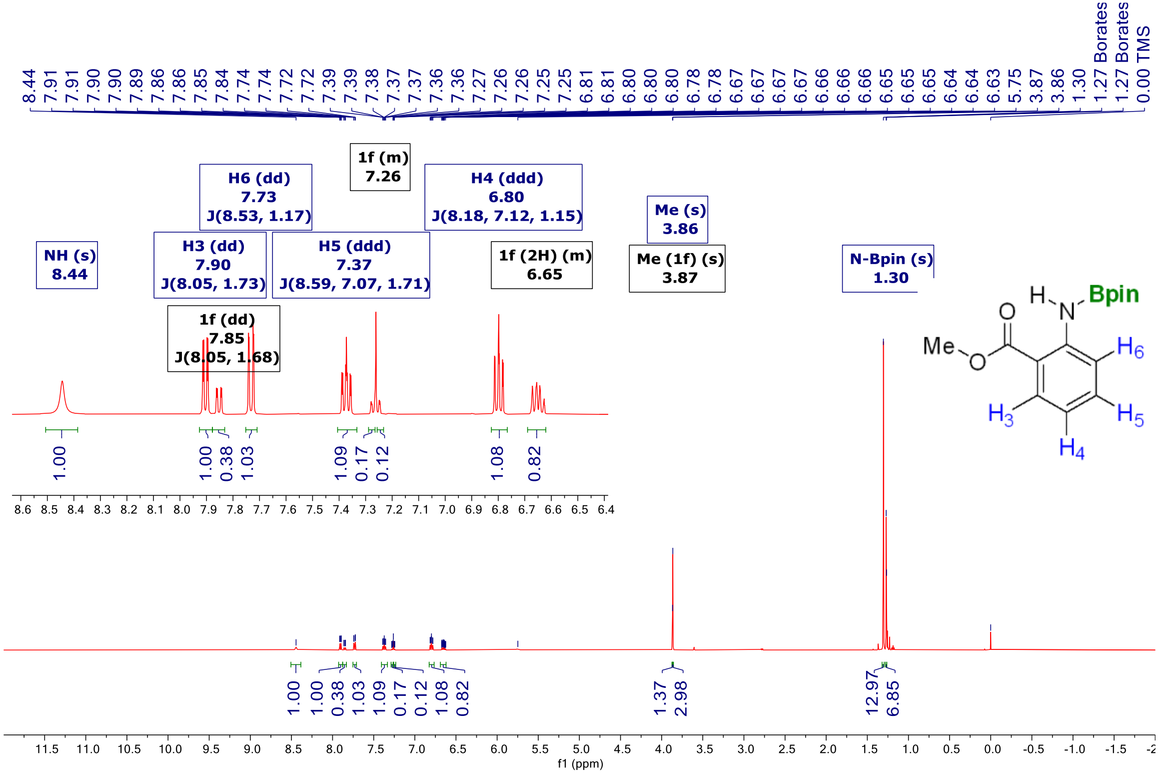
^{13}C{^{1}H} NMR of 5-borylated 2,3,4,9-tetrahydro-1H-carbazole (C_6D_6, 126 MHz)



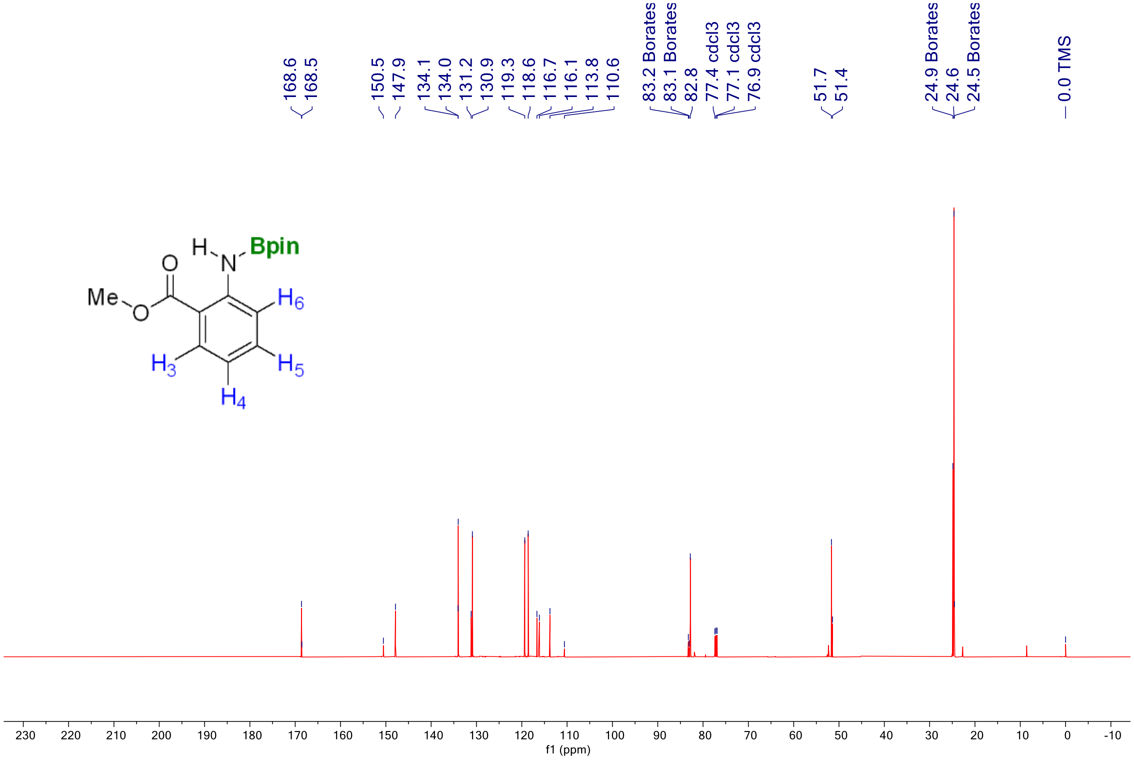
$^{11}B\{^1H\}$ NMR of 5-borylated 2,3,4,9-tetrahydro-1H-carbazole by Miyaura Borylation (C_6D_6, 126 MHz)



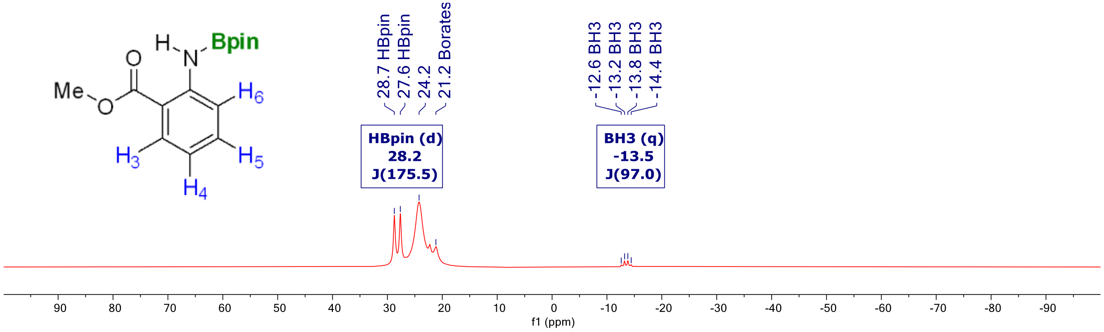
^1H NMR of N-Bpin borylated methyl 2-aminobenzoate (1f’) ($CDCl_3$, 500 MHz)



$^{13}C\{^{1}H\}$ NMR of N-Bpin borylated methyl 2-aminobenzoate (1f’) ($CDCl_3$, 126 MHz)



^{11}B NMR of N-Bpin borylated methyl 2-aminobenzoate (1f’) ($CDCl_3$, 160 MHz)



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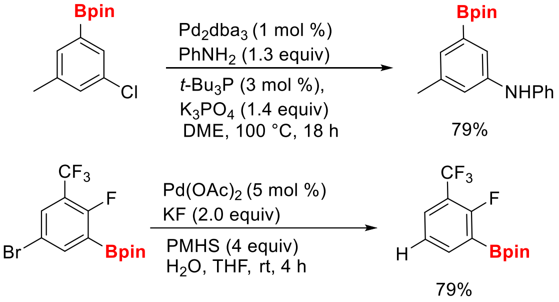
CHAPTER 3. MERGING IRIDIUM-CATALYZED C–H BORYLATIONS WITH PALLADIUM-CATALYZED CROSS-COUPLINGS USING TRIORGANOINDIUM REAGENTS

This chapter draws from: Jayasundara, C. R. K.; Gil-Negrete, J. M.; Montero Bastidas, J. R.; Chhabra, A.; Martínez, M. M.; Pérez Sestelo, J.; Smith, M. R., 3rd; Maleczka, R. E., Jr. Merging Iridium-Catalyzed C-H Borylations with Palladium-Catalyzed Cross-Couplings Using Triorganoindium Reagents. *J. Org. Chem.* 2022, *87* (1), 751–759.

3.1. INTRODUCTION

Ir-catalyzed C–H borylation (CHB) is a commonly practiced reaction for the generation of borylated arenes and heteroarenes. CHBs tolerate many functional groups including halogens like elucidated in chapter 1.[1] Halosubstituted aryl boronates so formed offer the potential for orthogonal reactivity in cross-coupling reactions (Scheme 3a). Despite the potential for competing self-polymerization,[2] halogen bearing arylboronates have been made to undergo chemoselective bond forming reactions with a C–X group where the boronic ester remains intact for subsequent chemistry (Scheme 49).[3,4]

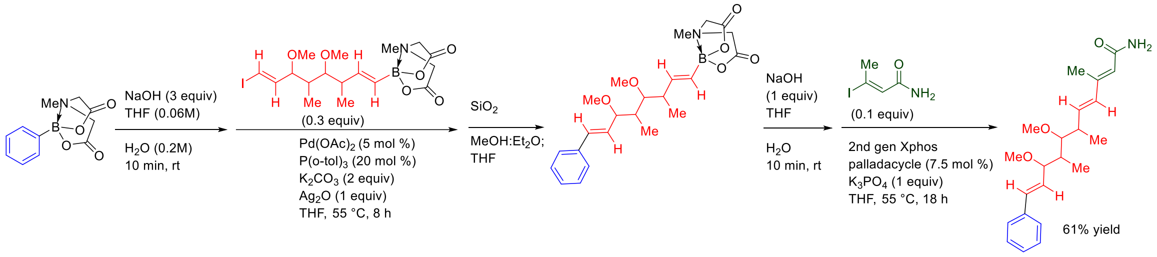
Scheme 49: Examples of chemoselective bond forming reactions[3,4]



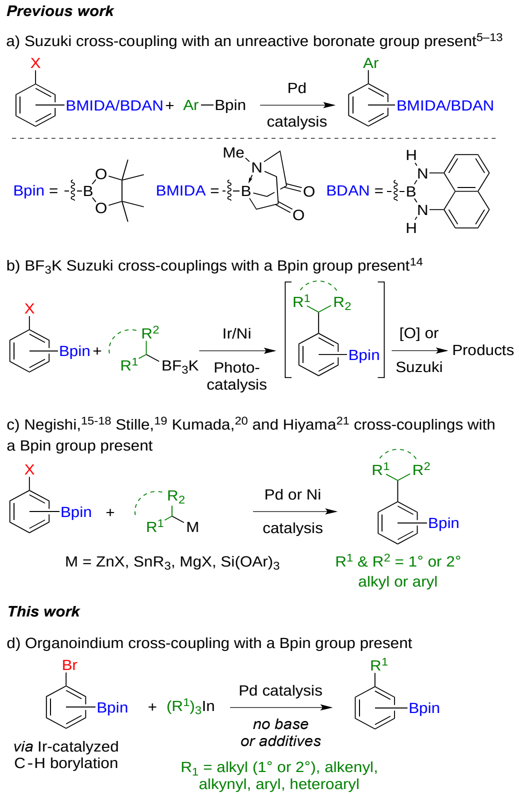
Reactions of haloarenes bearing *N*-methyliminodiacetic acid[5–10] and 1,8-diaminonaphthalene[11,12] boronic esters (BMIDA and BDAN respectively) avoid unwanted polyphenylene formation, as they are unreactive under certain Suzuki conditions. Such borylated biaryls have been employed in iterative Pd-catalyzed Suzuki-Miyaura cross-couplings popularized by Burke and others (Scheme 50).[13]

Molander and co-workers developed a complementary strategy whereby aryltrifluoroborate salts selectively couple with Bpin bearing haloarenes by way of photocatalysis (Scheme 51b).[14]

Scheme 50: An example iterative Pd-catalyzed Suzuki-Miyaura cross-coupling[13]



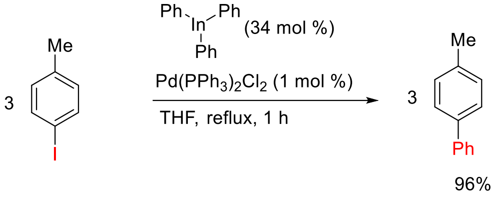
Scheme 51: Previous work and this work



Some successes have also been realized for the Negishi,[15–18] Stille,[19] Kumada,[20] and Hiyama[21] couplings of Bpin substituted haloarenes (Scheme 51c).

In contrast, no examples of Bpin substituted haloarenes undergoing selective metal-catalyzed cross-coupling with triorganoindium reagents (Sarandeses-Sestelo coupling)[22,23] have been reported. Triorganoindium compounds (R_3In), easily available from organolithium or Grignard reagents, are efficient reagents in palladium-catalyzed cross-coupling reactions, highly versatile in the transference of aryl-, alkynyl- or alkyl organic groups and are able to transfer all three groups attached to indium (Scheme 52).

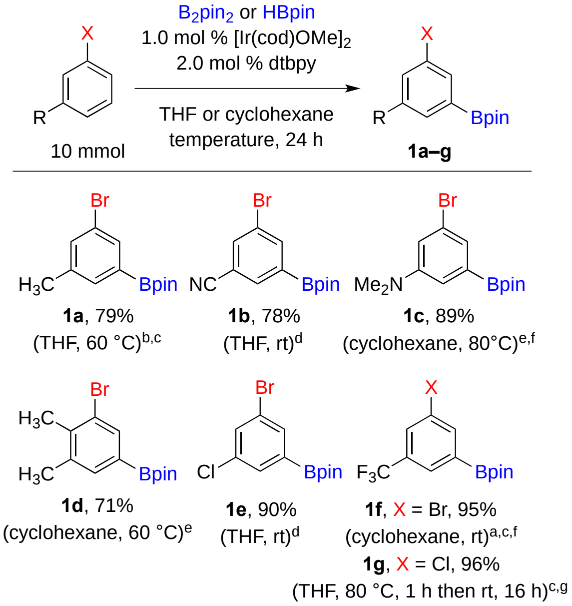
Scheme 52: An example of metal catalyzed cross coupling with triorganoindium compounds[22]



In addition, they present lower toxicity compared to tin derivatives and the palladium-catalyzed cross-coupling does not require the addition of base or additives.[24,25] Given these features, especially the ability to operate base-free and thereby minimize polyphenylene formation, we looked to merge Sarandeses-Sestelo cross-coupling reaction with CHB and establish a method for the cross-coupling of R_3In with CHB derived aryl halides bearing a Bpin substituent (Scheme 51d). To begin, a variety of haloarenes were reacted with 0.5 mol % $[Ir(cod)OMe]_2$, 1.0 mol % 4,4′-di-*tert*-butyl-2,2′-dipyridyl ligand (dtbpy) and 0.55 equiv of bis(pinacolato)diboron (B_2pin_2) in THF at room temperature to isolate borylated haloarenes **1a–g** (Scheme 53).

With our CHB produced borylated haloarenes in hand, the plan was to react them with *in situ* generated triorganoindium compounds by combining dry $InCl_3$ with a organolithium or Grignard reagents. We began the cross-coupling studies with Ph_3In prepared from commercial phenyllithium. Next, the capacity of haloarenes to undergo Pd-catalyzed cross-coupling reactions with R_3In was tested. After cannula transfer of a THF solution containing 0.40 molar equivalents of Ph_3In to a solution of $Pd(PPh_3)_2Cl_2$ (5 mol%) and **1a** in THF, the reaction was allowed to proceed at 65 °C (Scheme 54a). This reaction stalled after 16 h affording a 70:30 mixture of the desired cross-coupling product **2a**, unreacted **1a**, along with a substantial amount of biphenyl (~35% yield).[26,27] Despite additional experimentation and the potential of R_3In to transfer all three organic

Scheme 53: Ir-catalyzed borylation of haloarenes[a]

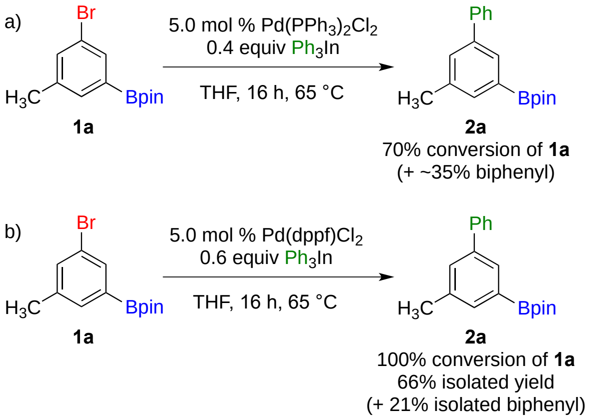


[a] Isolated yields. [b] 0.55 equiv of B_2pin_2 were used. [c] Run with 0.5 mol % of $[Ir(cod)OMe]_2$ and 1.0 mol % of dtbpy. [d] 2.1 equiv of HBpin were used. [e] 1.5 equiv of HBpin were used. [f] Run for 48 h. [g] 1.1equiv of HBpin were used.

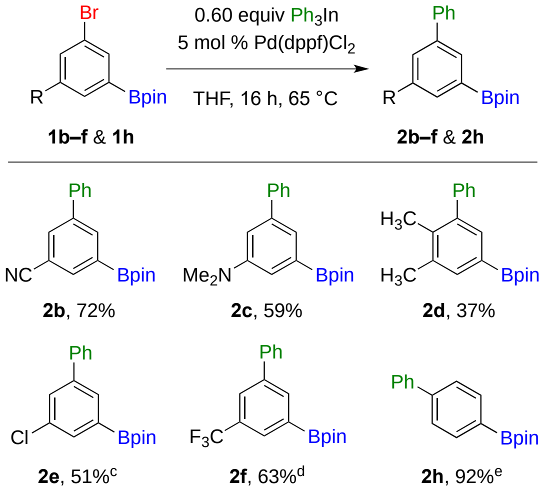
groups, elimination of biphenyl as a byproduct was never possible. Nonetheless, increasing the stoichiometry of the Ph_3In to 0.60 molar equivalents and changing the catalyst to $Pd(dppf)Cl_2$ resulted in the complete consumption of **1a** after 16 h in refluxing THF (Scheme 54b). Aside from byphenyl formation, NMR and GC analyses of the crude reaction mixture indicated that no other unwanted cross-coupling products had occurred, nor was there loss of the Bpin group. On the other hand, the complete coupling reaction using just 0.6 equiv of R_3In indicates that more than one organic group is efficiently transferred.

After these optimizations, we examined the reaction with Ph_3In with various borylated haloarenes (Scheme 55).

Scheme 54: Pd-catalyzed cross-couplings of Ph3In with borylated haloarene **1a**



Scheme 55: Pd-catalyzed cross-couplings of Ph3In with borylated haloarenes[a,b]



[a]Isolated yields. [b]Minor amounts of byproducts were also observed. [c]0.63 equiv of Ph3In were used. [d]No product was formed when the boronic ester form the aryl chloride (1g) was used as starting material. eRun at 80°C.

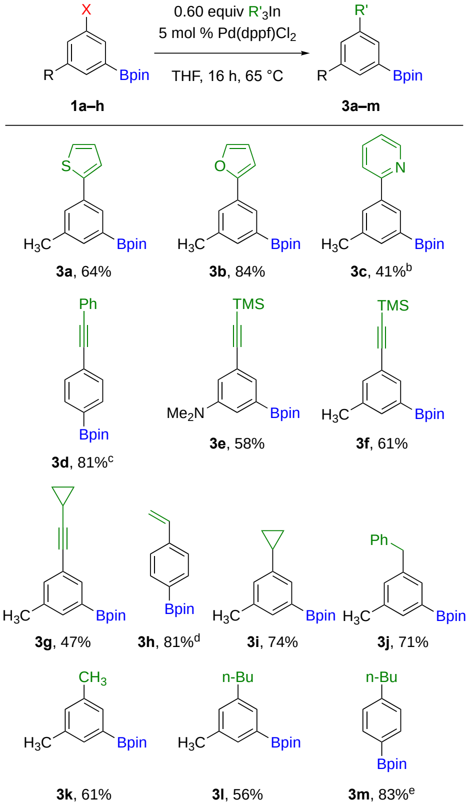
As with **1a**, borylated 3-bromobenzonitrile (**1b**) gave **2b** in 72% isolated yield without any evidence of unreacted starting material, other cross-coupling products (aside from biphenyl), or deborylated materials in the crude product mixture. Likewise, aniline derivative **1c** and 4-(Bpin)bromobenzene (**1h**) coupled without incident, affording **2c** and **2h** in 59% and 92% isolated yields, respectively. ^{1}H NMR spectra of the crude product mixture also indicated a clean reaction for **1d**, but **2d** was isolated in only 37% yield, presumably due to losses during chromatographic purification. In contrast, while the cross-coupling reaction of **1e** and **1f** gave desired products in 51% and 63% yields respectively, these reactions showed side products derived from the starting borylated haloarenes. Specifically, compounds stemming from the deboronation (~10–20%) of the cross-coupling products were observed for these substrates. In addition, small amounts (1–4%) of over coupled products could also be seen in the crude reaction mixtures (see Experimental Section for details). Lastly, under the previous developed reaction conditions, we were unable to affect the cross-coupling of chloroarene **1g**.

The scope of the reaction was then extended to triorganoindium species with various organic moieties (C-sp^3, C-sp^2 and C-sp) (Scheme 56). Under the previously optimized reaction conditions, triheteroarylindium reagents prepared from 2-lithio forms of thiophene, furan, and pyridine, afforded products **3a**, **3b**, and **3c** in good yields under mild reaction conditions. Using triorganoindium cross-couplings to introduce these heterocycles is notable as **3a**, **3b**, and **3c** would be difficult to access through the direct application of the CHB methodology. This is because CHB of heteroarenes tend to be very facile.[1] Hence, CHB on 2-tolyl derivatives of thiophene, furan, or pyridines would borylate the heterocycle instead of generating **3a–c**.[28–30]. Alkenes and alkynes are often problematic substituents in CHB owing to their ability to be hydroborated and/or otherwise compromise the effectiveness of the catalyst. This incompatibility creates the need for methods that can incorporate unsaturated groups post-CHB. With this purpose in mind, we were gratified to find that different trialkynylindium reagents successfully coupled with three different borylated haloarenes, affording compounds **3d–g** in good (81%) to modest (47%) isolated yields. Of similar utility, the cross-coupling reaction of trivinylindium with **1h** gave **3h** in 81% isolated yield, an example that could be extended to other alkenyl groups.

The substrate scope was also extended to alkyl (sp^3) organoindium reagents. The secondary alkyl cyclopropyl unit was efficiently transfer to bromoaryl boronic ester **1a** in 74% yield (**3i**). Analogously, Bn_3In and Me_3In coupled giving products **3j**, and **3k** in synthetically useful yields (71%

and 62%, respectively). Notably, even the *n*-butyl groups of *n*-Bu_3In were transferable, with **1a** and **1h** leading to products **3l** and **3m** in 56% and 83% isolated yields, respectively.

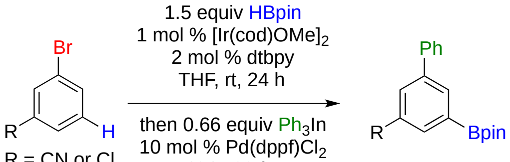
Scheme 56: Pd-catalyzed cross-couplings of R3In with borylated haloarenes[a]



[a]Isolated yields. [b]Run at 80 °C for 40 h. [c]Run at 80 °C for 24 h. [d]Run at 75 °C for 36 h. [e]Run at 80 °C for 16 h

Finally, we investigated performing the CHB and Sarandeses-Sestelo cross-coupling in a single vessel (Scheme 57). Following their respective generation, to crude solutions of **1b** and **1d** a THF solution of Ph_3In was added. For both substrates, the final products (**2b** and **2d**) corresponding to the Ir-catalyzed borylation and Pd-catalyzed coupling were formed in yields comparable to the two-pot protocol. However, to achieve full conversion, longer reaction times and higher palladium catalyst loadings were required. We have observed the same phenomena in past efforts to telescope CHB and subsequent Pd-catalyzed transformations.[4] We attribute this trend to residuals from the CHB step causing a loss of catalytic activity.

Scheme 57: One-pot CHB/Sarandeses-Sestelo cross-coupling



2b, 64% (R = CN)
2e, 50% (R = Cl)

In summary, we have established a new route to borylated aryl compounds that marries Ir-catalyzed C–H borylations with Pd-catalyzed cross-coupling with triorganoindium reagents. Good substrate scope for both the borylated bromoarenes and R_3In is demonstrated. This process appears to avoid the potential for polyphenylene formation that is inherent in palladium(0) reactions with borylated haloaromatics. Using triorganoindium cross-couplings to introduce unsaturated moieties also enables the synthesis of borylated arenes that would be difficult to access through the direct application of the CHB methodology. Finally, telescoping the borylation and Pd-cross-coupling into a single reaction flask is viable.

3.2. EXPERIMENTALS

Unless indicated otherwise all reactions were carried out in oven-dried glassware under an atmosphere of argon, with magnetic stirring, and monitored by GC-MS or ^{1}H-NMR/^{19}F-NMR. Tetrahydrofuran was freshly distilled from sodium/benzophenone under nitrogen. $InCl_3$ was dried under high vacuum at 80 °C prior use. Column chromatography was performed with silica gel (230–400 mesh). Spectra taken in $CDCl_3$ were referenced to 7.26 ppm in ^{1}H NMR and 77.2 ppm in ^{13}C NMR. Resonances for the boron-bearing carbon atom were not observed due to quadrupolar relaxation.

General Procedure A followed for synthesis of compounds in Scheme 2; C–H Borylation with B_2pin_2. In a nitrogen atmosphere glove box, bis(pinacolato)boron (B_2pin_2) (1.40 g, 5.5 mmol, 0.55 equiv) was weighed into a 20 mL vial containing a magnetic stir bar. [Ir(cod)OMe]$_2$ (33 mg, 0.05 mmol, 0.5 mol %) and 4,4'-di-*tert*-butyl-2,2'-dipyridyl ligand (27 mg, 0.10 mmol, 1.0 mol %) were weighed into two test tubes separately, each being diluted with THF or cyclohexane. The $[Ir(cod)OMe]_2$ solution was transferred into the 20 mL vial containing B_2pin_2. This mixture was stirred until a golden yellow clear solution was obtained (~ 1 min). Next the solution containing ligand was transferred into the vial and upon stirring the resulting solution turned a dark brown color. Finally, the substrate (10.0 mmol, 1.0 equiv) was added to the vial, which was then sealed and taken out of the glove box. The reaction mixture was stirred at the indicated temperature. Then, the reaction mixture was passed through a plug of silica (BD 60 mL Syringe/Luer-Lok Tip-silica up to 50 mL mark) eluting with a hexane/ethyl acetate solution as eluent. The volatiles were removed by rotary evaporation.

General Procedure B followed for synthesis of compounds in Scheme 2: C–H Borylation with HBpin. In a nitrogen atmosphere glove box, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (HBpin) (1.5 – 2.0 equiv) was weighed into a 5 mL vial containing a magnetic stir bar. $[Ir(cod)OMe]_2$ (6.6 mg, 0.01 mmol, 1.0 mol %) and 4,4'-di-tert-butyl-2,2'-dipyridyl ligand (5.4 mg, 0.02 mmol, 2.0 mol %) were weighed into two test tubes separately, each being diluted with 1 mL of THF or cyclohexane. The $[Ir(cod)OMe]_2$ solution was transferred into the 5 mL vial containing HBpin. This mixture was stirred until a golden yellow clear solution was obtained (~ 1 min). Next the solution containing ligand was transferred into the vial and upon stirring the resulting solution turned a dark brown. Finally, the substrate (1 mmol, 1.0 equiv) was added to the vial, which was then sealed and was taken out of the glove box. The reaction mixture was stirred for at the indicated temperature. Then, the reaction mixture was passed through a plug of silica (BD 60 mL Syringe/Luer-Lok Tip-silica up to 50 mL mark) eluting with a hexane/dichloromethane or hexane/ethyl acetate solution as eluent. The volatiles were removed by rotary evaporation.

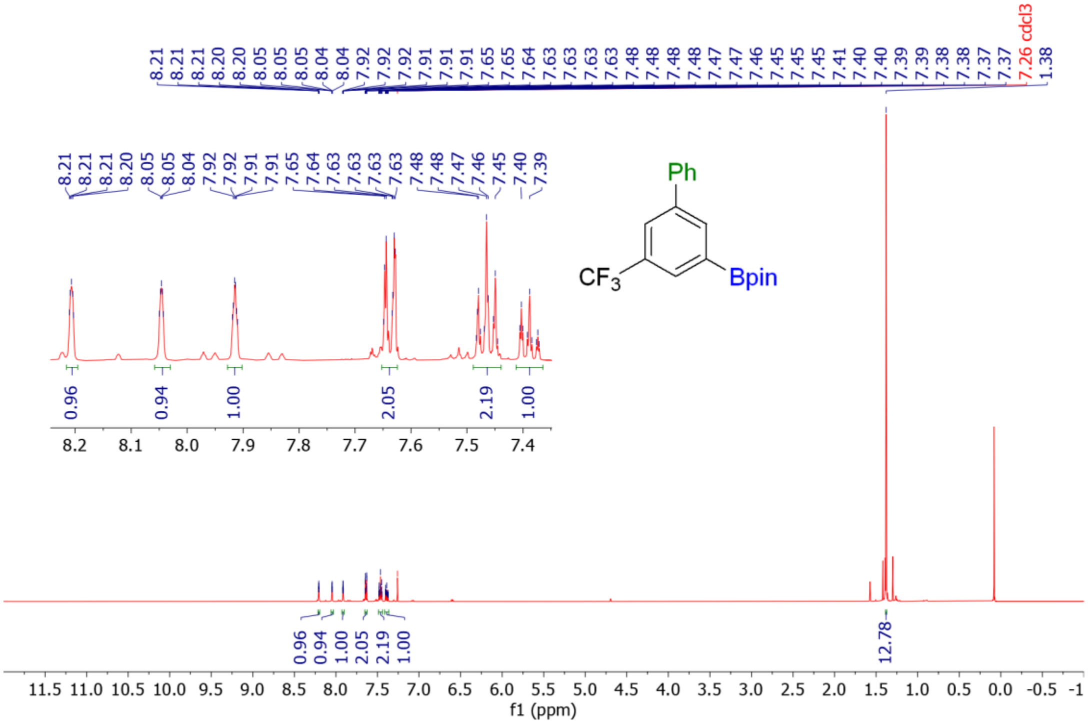
General Procedure C followed for synthesis of compounds in Scheme 4 and 5. Palladium-Catalyzed Cross-Coupling Reactions using Triorganoindium Reagents. A 25 mL round-bottomed flask with a stir bar was charged with dry $InCl_3$ (133 mg, 0.6 mmol, 0.6 equiv). A positive argon pressure was established and dry THF (3.0 mL) was added. The resulting solution was cooled to –78 °C, and a solution of RLi, or RMgBr (vinyl) (1.8–2.0 mmol, 1.8–2.0 equiv) was slowly added (30–60 min). After 60 min stirring, the reaction mixture was warmed to room temperature for 1–2 h. The freshly prepared solution of R_3In (0.6 mmol in dry THF) was added to mixture of the aryl boronic ester (1 mmol, 1 equiv) and Pd(dppf)Cl_2 (36.6 mg, 0.05 mmol, 5.0 mol %) or Pd(dppf)Cl_2.CH_2Cl_2 (40.8 mg, 0.05 mmol, 5.0 mol %) in dry THF (4.0 mL). The resulting mixture was refluxed under argon until the starting material was consumed (NMR or GC). The reaction was then quenched by the addition of few drops of MeOH, concentrated under reduce pressure. The crude mixture was passed through a plug of silica (BD 60 mL Syringe/Luer- Lok Tip-silica up to 50 mL mark) with dichloromethane as eluent to yield the product.

4,4,5,5-Tetramethyl-2-(5-(trifluoromethyl)-[1,1'-biphenyl]-3-yl)-1,3,2-dioxaborolane (2f).[7] The General Procedure was carried out with **1f** (351 mg, 1.0 mmol, 1.0 equiv) and a solution of Ph_3In (0.60 mmol, 0.60 equiv) in THF (4 mL) at 65 °C. After 16 h, an aliquot was taken and analyzed by NMR and GC-MS to find that a mixture of **2f**, 3-(trifluoromethyl)-1,1'-biphenyl and 3,5'-bis(trifluoromethyl)-1,1':3',1''-terphenyl in ratio of 72:20:8 was obtained. The reaction was then quenched by the addition of few drops of MeOH, concentrated under reduce pressure. The residue was passed through a plug of silica gel (DCM as eluent). The fractions containing product were collected and concentrated to yield 291 mg of compound **2f** with a minor byproduct corresponding to 3,5'-bis(trifluoromethyl)-1,1':3',1''-terphenyl (8 to 1 ratio) as a white sticky solid (83.1% yield). ^{1}H NMR (500 MHz, $CDCl_3$) 8.21 (m, 1H), 8.05 (m, 1H), 7.91 (m, 1H), 7.64 (m, 2H), 7.47 (m, 2H), 7.39 (tt, J= 7.3, 1.3 Hz, 1H), 1.38 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.4, 139.9, 136.8 (q, *J* = 1.5 Hz), 130.8 (q, *J* = 32.2 Hz), 130.2 (q, J= 3.7 Hz), 129.0, 128.4 (q, *J* = 217.9 Hz), 128.1, 127.4, 126.6 (q, *J* = 3.6 Hz), 84.5, 25.0. ^{19}F NMR (470 MHz, $CDCl_3$) δ –62.5. ^{11}B NMR (160 MHz, CDCl₃) δ 30.1 (brs). The spectral data were in accordance with those reported in the literature.[7]

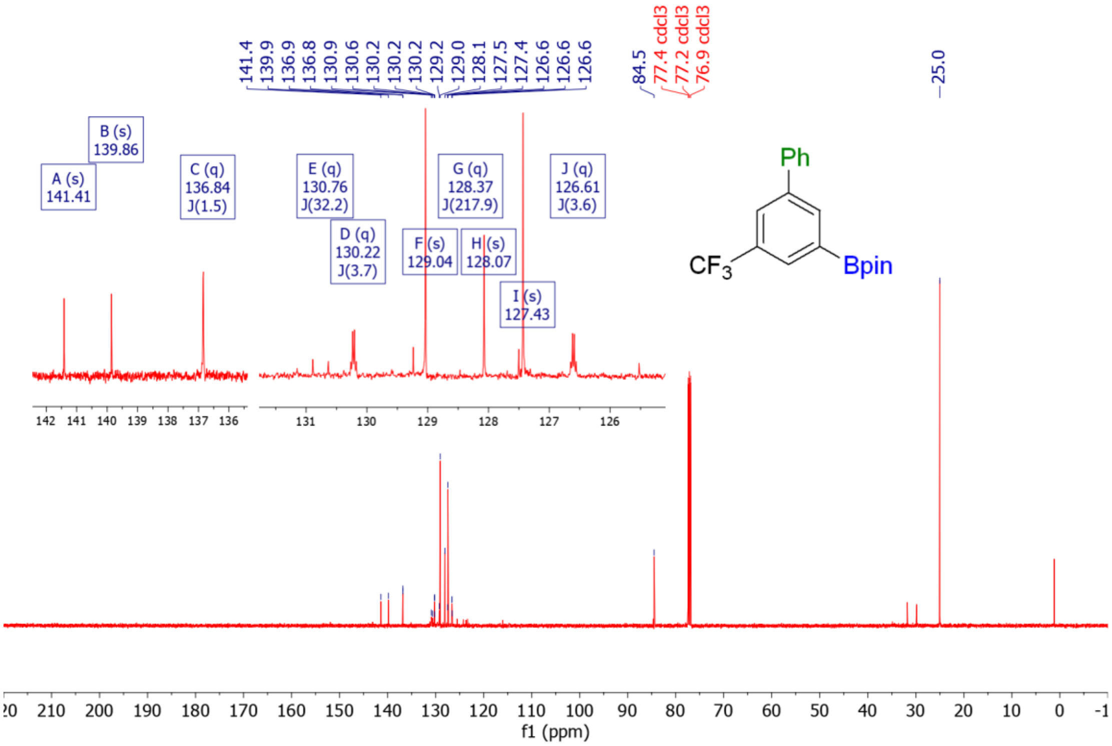
HRMS (ESI) m/z calcd for $C_{19}H_{21}BF_3O_2$ $[M+H]^+$ 349.1587, found 349.1561

3.3. SPECTRAL DATA

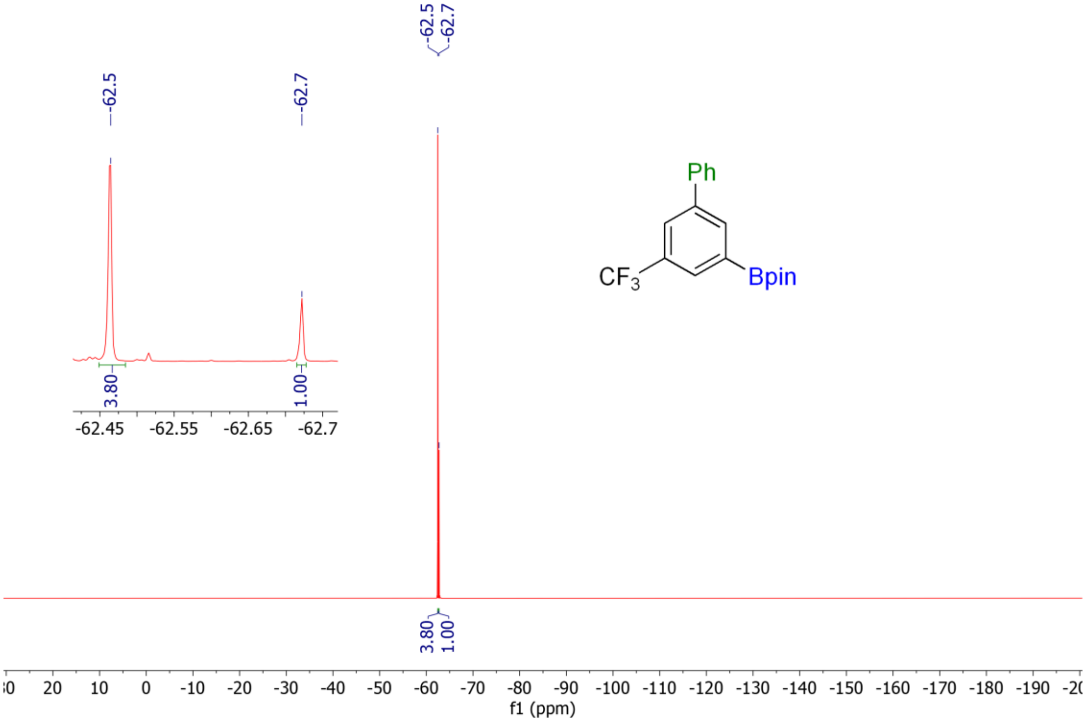
^{1}H NMR of 2f (CDCl$_3$)



^{13}C NMR of 2f (CDCl$_3$)



^{19}F NMR of 2f (CDCl$_3$)



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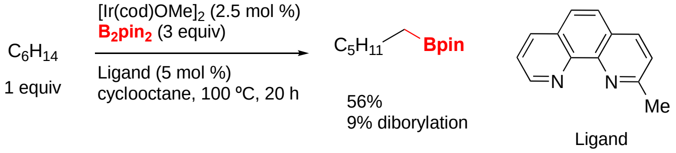
CHAPTER 4. ACCESS TO C(SP^3) BORYLATED AND SILYLATED CYCLIC MOLECULES: HYDROGENATION OF CORRESPONDING ARENES AND HETEROARENES

4.1. INTRODUCTION

Aromatic boronic compounds have been widely studied, differentially functionalized at ortho, meta and para positions as explained in chapter 1. Such boryls are often pivotal intermediates in the synthesis of natural products, biologically relevant molecules and compounds used in material science.[1] These broad applications are made possible by the ability of C–B bonds to be readily transformed to C–OH, C–NH_2, C–C bonds, etc. Additionally, boryl groups present on sp^3 carbons can undergo couplings with retention or inversion of stereochemistry, Matteson homologation reactions, etc.[2] Owing to their synthetic utility, the pursuit of new methods and strategies for making borylated compounds is an active area of research. Many sp^3 C–H borylation methods are highly substrate limited requiring the presence of a directing group (e.g. 2-alkyl pyridines, alkyl amines, benzylic compounds, cyclopropyl amides) and/or demand excess starting materials or reagents.[3–6]

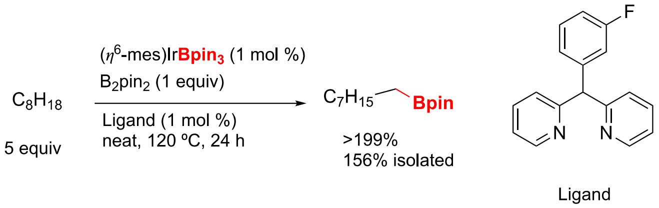
In recent years, some of these restraints have been eased. The Hartwig group has established directing group free sp^3 C–H borylation chemistry that encompasses a broader substrate scope, including alkanes, ethers, protected amines, alcohols, and carbocycles (Scheme 58). Their method affords good selectivity and when executed with an excess of boron reagent good reactivity. In addition, all reported examples were run in cyclooctane. As the authors note, this restricted functionalization of polar molecules due to poor solubility.[7]

Scheme 58: C-H borylation of hexane catalyzed by 2-mphen[7]



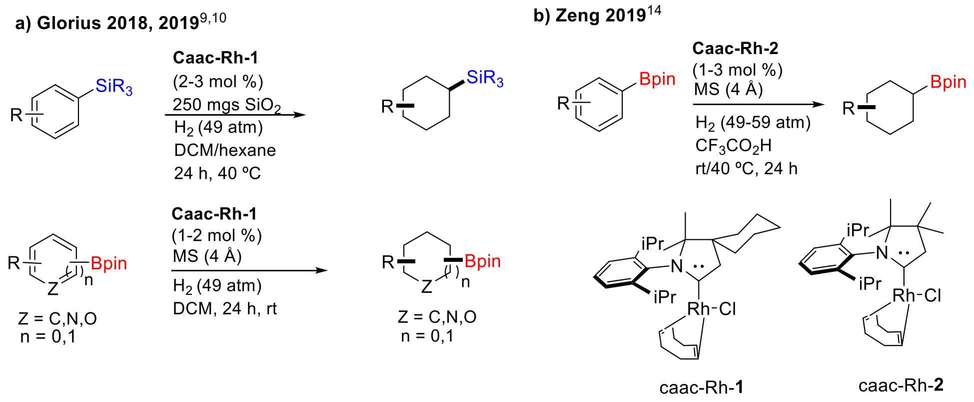
Schley and coworkers were able to overcome the limitation of excess of boron reagent through the thoughtful application of dipyridylarylmethane as ligand (Scheme 59)[8].

Scheme 59: C-H borylation of C(sp3)-H bond catalyzed by dipyridylarylmethane ligand[8]



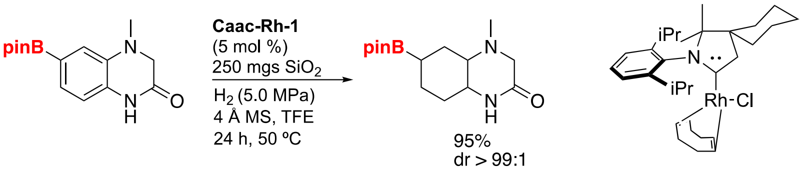
In an alternative strategy, sp^3 C–H borylated compounds can be accessed by hydrogenating corresponding borylated arenes, which themselves can be obtained via iridium catalyzed sp^2 C–H borylations. On this front, Glorius and coworkers pioneered the catalytic heterogeneous hydrogenation of boryl- and silyl- arenes/heteroarenes by a cyclic (alkyl)(amino)carbene rhodium complexes (Scheme 60).[9–13] In similar work, Zeng showed hydrogenation of borylated arenes and heteroarenes using a related Rh-catalyst (Scheme 60).[14]

Scheme 60: Strategy to access sp3 C-H borylated and silylated substrates via arene/heteroarene hydrogenation



Glorius' catalyst was utilized by Bach's group to hydrogenate one borylated 2-oxindole among other benzofused N-heterocycles, 2,5-diketopiperazine, and 3,4-dihydroquinolones (Scheme 61).[15–17]

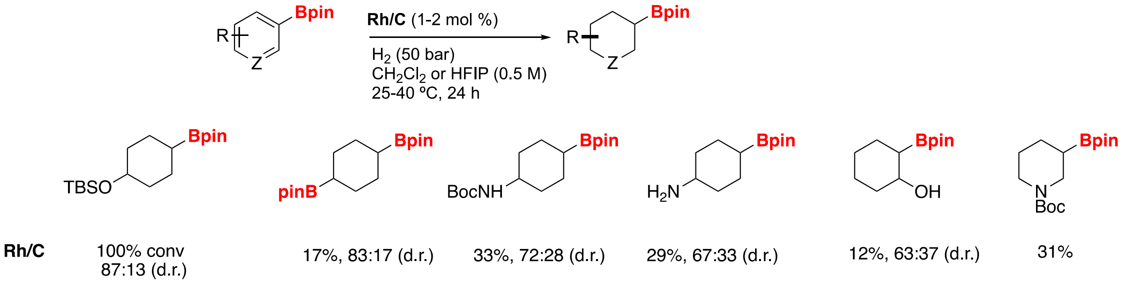
Scheme 61: Hydrogenation of benzofuzed N-heterocycle using caac-Rh-1 as a catalyst[15]



caac-Rh-**1**

Glorius also reported hydrogenations using Rh/C in their optimization studies on six borylated substrates (five benzenes and one pyridine) (Scheme 62).[9] Catalysis with Rh/C showed full conversion with TBS protected 4-Bpin phenol, but as the authors noted the other arenes tested and the pyridine gave diminished yields (17–33%).

Scheme 62: Glorius reported hydrogenation using Rh/C[9]

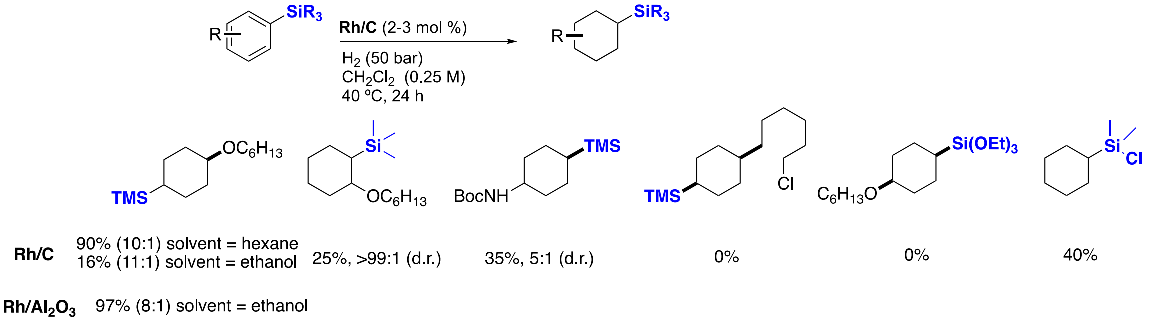


Separately,[10] Rh/C catalyzed hydrogenation of six silylated benzenes were examined (Scheme 63). It was reported that two of the six gave 0% of the corresponding cyclohexanes, but three substrates were saturated in 25, 35, and 40% yields respectively. In contrast, the hydrogenation of n-hexyl ether of 4-TMS-phenol was achieved in 90% yield with Rh/C in hexane (vs 16% in EtOH) and could be further optimized up to 97% using Rh/Al_2O_3.

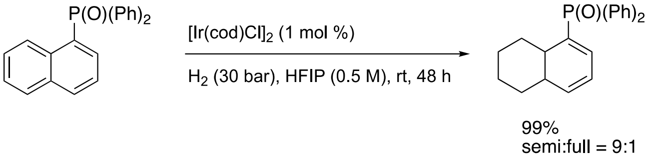
Other recent reports on saturating arenes and heteroarenes that do not bear boryl or silyl substituents include the work of Handa, who used $[Ir(cod)Cl]_2$ to hydrogenate phosphine oxide scaffolds with Ir nanoparticles being the active catalyst (Scheme 64).[18] A cooperative heterogenous and homogenous strategy for asymmetric hydrogenations of arenes and heteroarenes have also been developed, which has been applied to a single borylated substrate (benzofuran) (Scheme

65).[19–21] The hydrogenation of fluoropyridine using $Pd(OH)_{2,}$ in acidic media has also been reported (Scheme 66).[22]

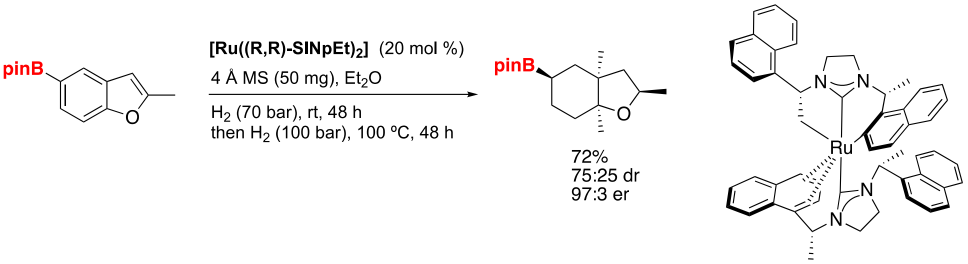
Scheme 63: Hydrogenation of silyated benzenes from Glorius' previous report[10]



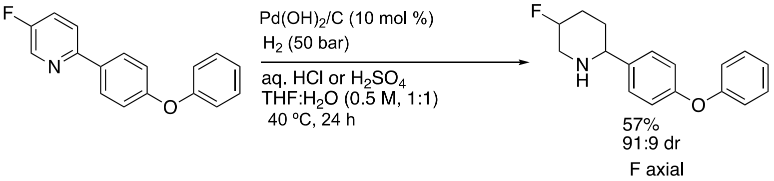
Scheme 64: Hydrogenation of phosphine oxide using [Ir(cod)Cl]2 as a catalyst[18]



Scheme 65: Cooperative asymmetric hydrogenation of borylated benzofuran[19]

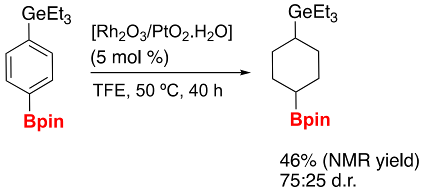


Scheme 66: Hydrogenation of fluoropyridines using Pd(OH)2[20]



While we considered all prior art cited above, Glorius' results motivated us to fully evaluate bench stable and commercially available Rh-catalysts, e.g. Rh/C or Rh/Al_2O_3, or other standard hydrogenation catalysts against a larger substrate set of arenes and heteroarenes with boryl or silyl substituents. We were further inspired by Glorius' recent report on hydrogenation of arenes that were bisfunctionalized with germyl and boryl, and germyl and silyl,[23] and sought to hydrogenate previously unexplored heteroarenes bearing both boryl and silyl substituents (Scheme 67).

Scheme 67: Hydrogenation of arene bearing germyl and boryl susbtitutent[23]

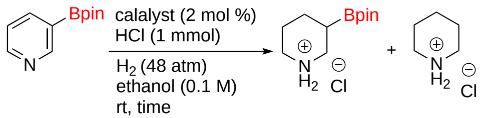


4.2. RESULTS AND DISCUSSION

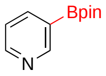
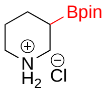
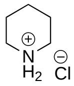
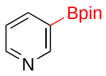
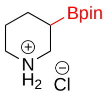
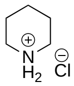
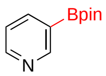
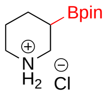
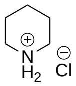
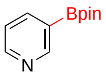
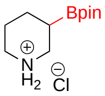
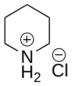
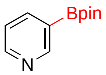
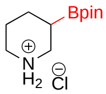
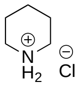
As the catalytic hydrogenations of pyridines using Rh/C is well established,[24] we began our study by subjecting an ethanolic mixture of 3-borylated pyridine **1a** to 5% Rh/C under a hydrogen atmosphere (Table 1; entry 1).

As piperidines are known to poison Rh-catalysis[25,24] and since pyridinium salts hydrogenate more readily than the free base,[26] HCl was added to the reaction mixture. After 1 h, the pyridine ring was fully saturated to afford the desired borylated piperidine (**2a**) along with the deborylated product (**3a**). Rhodium on alumina (entry 2) afforded a similar mix of **2a** and **3a**, but the reaction was incomplete after 2 hours. Though platinum oxide has long been used to hydrogenate pyridines, reactions catalyzed by Pt_2O and Pt/C met with an increased amount of deboronation (entries 3 and 4). Catalytic hydrogenations of pyridines with palladium typically demand higher temperatures (70–80 °C) and higher catalyst loads,[27] so it was not entirely surprising that 10% Pd/C failed to effect hydrogenation (entry 5). W2 Raney nickel[28] and Ru-catalysts[29] were not tested given the precedent for hydrogenations of pyridines with those catalysts requiring pressures > 1000 psi. With Rh/C proving fastest at hydrogenating **1a**, reactions with this catalyst were screened against different solvents (Table 2). In addition to ethanol, **1a** could be hydrogenated in methanol, dichloromethane, dioxane, and THF. Yields of **2a** were observed to be in order of ethanol/methanol > THF > dioxane>dichloromethane. This trend is consistent with previous reports on hydrogenations of non-polar.

Table 2: Hydrogenation catalysts screening



1a **2a** **3a**

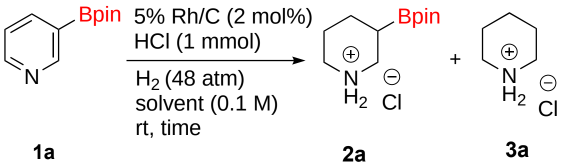
Entry	Starting Material	Product **2a**	Product **3a**	catalyst	Ratio[b] of **2a**:**3a**:**1a**	time
1.				5% Rh/C (2 mol %)	72:28:0	1 h
2.				5% Rh/Al_2O_3 (2 mol %)	50:15:35	2 h
3				PtO_2 (2 mol %)	32:32:36	2 h
4.				10% Pt/C (2 mol %)	24:38:38	2 h
5.				10% Pd/C (2 mol %)	0:0:100	2 h

[a](4,4,5,5-tetramethyl1,3,2-dioxaborolan-2-yl)pyridine (0.25 mmol), hydrochloric acid (1 mmol), hydrogen gas (48 atm), ethanol (2 mL), 5% Rh/C (10 mg). [b]Relative composition based on ^{1}H-NMR substrates in polar solvents, where it has been shown that higher yields correlate to higher activity coefficients.[30]

Unfortunately, with all solvents deboronation remained a problem, with **3a** being the only observed product when the reaction was run in dichloromethane for 36 hours. As metal mediated protiodeboronation by Brønsted acids and Lewis acids is well known,[31] the reaction was run without HCl (Table 2; entry 2). This led to no reaction. Reducing the amount of conc. HCl in the reaction or using dry HCl (Table 3) resulted in similar **2a**:**3a** ratios as those observed in entry 1, Table 1. Other Brønsted and Lewis acids were also tested (Table 3 and 4), but none solved the deboronation problem. Lastly, we explored the idea that by starting with a halogenated 3-

borylpyridine the reaction conditions would in situ generate 1 equiv of HX, which would immediately form the pyridinium and not promote deboronation. Thus 3-bromo-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (**2b**) was hydrogenated under the standard, albeit HCl free, conditions. Though debromination and hydrogenation occurred as predicted, deboronation was not eliminated.

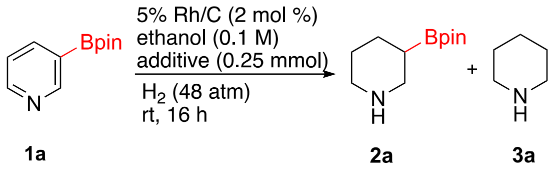
Table 3: Solvent screen for hydrogenation[a]



Entry	Solvent	Time (h)	2a[b](%)	3a[b](%)	1a[b]
1	EtOH	16	75	25	0
2	EtOH[c]	2	0	0	100
2	DCM	36	0	100	0
3	dioxane	7	47	53	0
4	THF	7	65	35	0
5	MeOH	2	75	25	0

[a](4,4,5,5-tetramethyl1,3,2-dioxaborolan-2-yl)pyridine (0.25 mmol), HCl (1 mmol), H_2 (48 atm), solvent (2 mL), 5% Rh/C (2 mol %), rt. [b]Relative composition determined by ^{1}H-NMR [c]without HCl

Table 4: Additives for the hydrogenation of 1a by Rh/C[a]

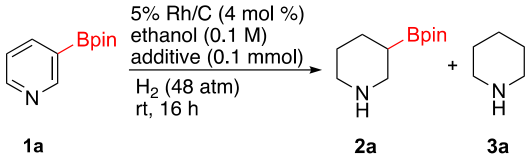


Entry	Additive (1 equiv)	Time (h)	1a (%)	2a (%)	1a’ (%)
1	HCl	16	75	25	0
2	HCl (dry)	1	72	28	0
3	HCl + 1 mL H_2O	1	71	28	1
4	$MeSO_3H$	2	63	37	0
5	NH_4Cl	24	0	70	30
6	H_3PO_4	2	58	42	0
7	2,6-Dichloropyridine	36	38	62	0
8	Sulfuric Acid	2	39	61	0
9	Triflic acid	2	52	48	0

[a]Conversion percentages determined by GCMS by comparing piperidine to starting material. 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (0.1 mmol), Additive (0.1 mmol), Hydrogen gas (700 psi), Ethanol (1 mL), 5% Rh/C (10 mg), rt.

Unable to eliminate deboronation, we reevaluated the early catalyst screening data. Catalysis using Rh/Al_2O_3 (entry 2, Table 5) was slower than Rh/C, but afforded a better ratio of **2a** to **3a**. Therefore, as we looked at the hydrogenation of additional borylated pyridines, Rh/Al_2O_3 was employed as catalyst and reactions were run for 16 h. As shown in Table 3 (entries 2–5) **2c**, **2d**, **2e**, and **2f** were all formed > 80% yield *with no deboronation*. Of note was the hydrogenation of **1f**, which was carried out without the addition or in situ generation of a Brønsted acid. Presumably, the methyl groups at C2 and C6 inhibit poisoning of the catalyst. Furthermore, **2f** was formed as single diastereomer, the stereochemistry of which as determined to be all cis by oxidizing the boronate ester to a hydroxy group and comparing that product to analogous literature compounds.[32,33]

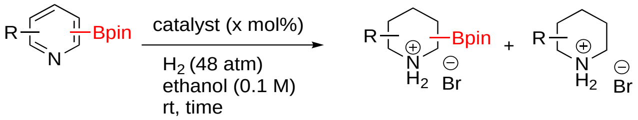
Table 5: Additives for the hydrogenation of 1a by Rh/C[a]

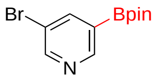
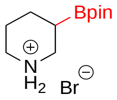
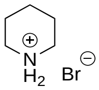
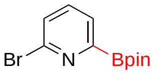
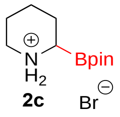
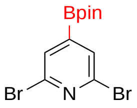
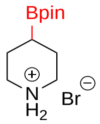
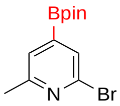
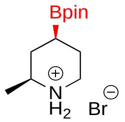
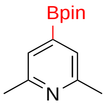
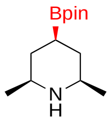


Entry	**Additive (1 equiv)**	**1a (%)**	**2a (%)**	**1a'**
1	Cerium (III) chloride	0	100	0
2	Magnesium chloride	0	30	70
3	Copper sulfate	20	18	62
4	Potassium Iodide	16	42	42
5	Zinc chloride	0	15	85
6	Iron powder (rusted)	0	15	85
7	Magnesium sulfate	0	17	83
8	Trimethyl borate	0	11	89
9	3Å molecular sieves	0	19	81

[a]Conversion percentages determined by GCMS by comparing piperidine to starting material. 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (0.1 mmol), Additive (0.1 mmol), Hydrogen gas (700 psi), Ethanol (1 mL), 5% Rh/C (10 mg), rt.

Table 6: Hydrogenation of Pyridines[a]

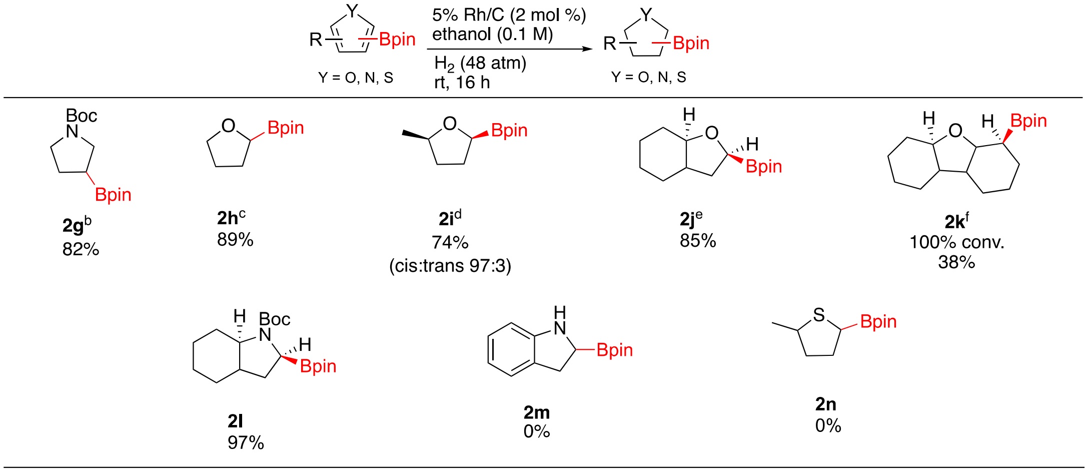


Entry	Starting Material	Products (Yield%)	catalyst	time
1	 **1b**	  **2b**[b] (73) **3b**[b] (27)	5% Rh/C (2 mol %)	16 h
2	 **1c**	 (99) **2c**	5% Rh/C (2 mol %)	16 h
3	 **1d**	 (82) **2d**	5% Rh/Al_2O_3 (8 mol %)	16 h
4	 **1e** 0.3 mmol	 (94) **2e**	5% Rh/Al_2O_3 (4 mol %)	16 h
5	 **1f**	 (86) **2f**	5% Rh/Al_2O_3 (4 mol %)	40 h

[a] isolated yields and relative stereochemistry shown, starting material (0.5 mmol), ethanol (5 mL)
[b] isolated as a mixture

Hydrogenation of different 5 membered borylated heterocycles were then investigated (Scheme 68). Under Rh/C catalysis, *N*-Boc-3-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-pyrrole (**1g**) was successfully hydrogenated (73% yield) on 1 gram scale without any observable loss of the Bpin. As Pd/C has been shown to selectively hydrogenate the pyrrole ring on nicotyrine,[34] the catalytic hydrogenation of **1g** was also run with 10% Pd/C and **2g** was afforded in 82% yield. We also attempted a one pot Ir-catalyzed borylation/hydrogenation sequence using Boc-pyrrole as the starting substrate. In practice, running the hydrogenation step on the crude borylation mixture was not successful as only **1g** was observed. Nonetheless, it should be noted that the CH borylation of Boc-pyrrole gives **1g** in 90% yield.

Scheme 68: Hydrogenation of borylated heteroarenes[a]

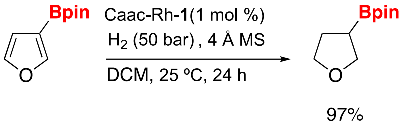


[a]Reaction conditions: 0.5 mmol substrate, relative stereochemistry shown, isolated yields shown.
[b]*N*-Boc-3-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-pyrrole (1.0 g, 3.4 mmol), Rh/C (170 mg, 2 mol %) EtOH (10 mL, 0.3 M). [c]13 h, 8% OBpin monomer, [d]1 mmol substrate, Rh/C (1 mol %), 6.3% HOBpin byproduct [e]solvent= hexane, P= 54 atm, ~20% OBpin monomer [f]8% deborylated product, solvent = hexane, P = 59 atm, T = 60 °C, t =21 h

Thus, the 74% two-step combined yield of **2g** from Boc-pyrrole compares favorably to 54% yield obtained in the Ir-catalyzed sp^3 C-H borylation of Boc-pyrrolidine.[7] Moving on to other heterocycles, hydrogenation of 2-borylated furan (**1h**) occurred with 100% conversion to **2h**. Isolation of **2h** (89%) was complicated by the presence of HOBpin or oligomers thereof (~8%). In this case, Rh/C is not as efficient as the Glorius catalyst, which affords **2h** from **1h** in 97% yield (Scheme 69).[9,14] It is worth nothing that when hydrogenating **1h** at 2.5 mmol scale the catalyst could be recycled five times with reproducible results after each cycle. Direct sp^3 Ir-catalyzed CH borylations of tetrahydrofuran gives the C-3 borylated product,[7] in contrast, the sp^2 Ir-catalyzed CH borylation of furan gives the C-2 borylated product, the hydrogenation of which produces the C-2 borylated tetrahydrofuran. This highlights the potential for direct borylation and borylation/hydrogenation approaches to be complementary.

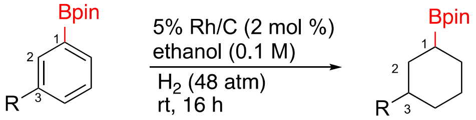
Hydrogenations of methyl substituted **1i**, benzofuran **1j** and dibenzofuran **1k** were then carried out. Compound **2i** was obtained in 74% yield as a 97:3 cis/trans mixture and as before a minor amount of boron byproduct (~6%) was present in the isolated material. The cis stereochemistry of the major product was ascertained by COSY and 1D NOE NMR. Interestingly, hydrogenation of **1j** generated the fully saturated borylated octahydrobenzofuran **2j** again contaminated by the boron byproduct (78:22 by NMR). Compound **1k** underwent full conversion affording **2k** with 8% of the deboronated product. Though a minor product, the presence of the deboronated material made purification of **2k** challenging and thus pristine **2k** was isolated in only 38% yield. We were also able to generate **2l** as an octahydroindole in 97% yield. The stereochemistry of hydrogen α to the nitrogen was found to be cis with the bridgehead hydrogen by 1D-NOE experiments. An unprotected borylated indole and a 2-borylated methylthiophene failed to produce saturated products **2m** and **2n** respectively, only starting material observed by ^{1}H-NMR in both cases.

Scheme 69: Hydrogenation of furan using Glorius's catalyst[9]



The hydrogenation of borylated arenes was also carried out (Scheme 70). All borylated arenes tested were easily hydrogenated with Rh/C and functional groups like esters, methoxy, alkyl, trifluoroalkane and alcohols were well tolerated.

Scheme 70: Hydrogenation of borylated benzenes[a]



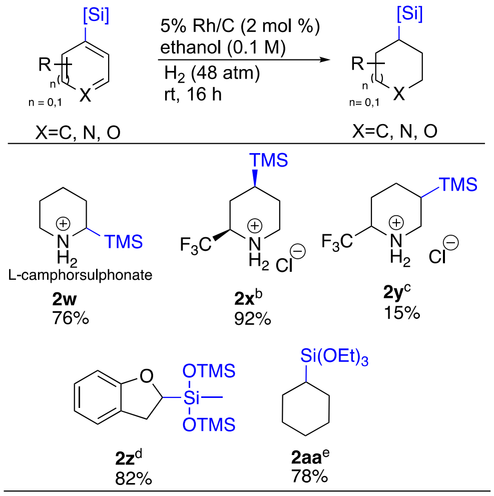
Scheme 70(cont'd)

Entry	Product	R	Yield (%)[b]	cis:trans[c]
1	**2p**[d]	H	99	-
2	**2q**	OH	71	5:4
3	**2r**	CF_3	80	3:1
4	**2s**	CO_2Et	81	3.3:1
5	**2t**	CH_3	77	2.2:1
6	**2u**[e]	OMe	68	5.6:1
7	**2v**	Bpin (at C2)	88	>99:1

[a]Run on 0.5 mmol substrate. [b]isolated yields. [c]cis/trans ratios determined by ^{1}H NMR on the crude reaction product. [d]1mmol substrate, Rh/C (1 mol %). [e]22% demethoxylated byproduct

For compounds **2q**, **2r**, **2s**, **2t**, and **2u** low ratios of cis and trans products were obtained with the cis diastereomers being major. The assignment for **2q** was made by comparisons to a known silylated derivative.[35] To do so for compounds **2r**, **2t**, and **2u**, each of these products were oxidized to their alcohols,[36] which were then compared to previously reported cis and trans alcohols. It is worth noting that when **2u** was generated using caac-Rh-2 as the catalyst, a yield of 55% yield was observed vs. the 68% with Rh/C. Diastereoselectivity was similar in both cases (~6:1).[14] The major stereoisomer of **2s** being cis was confirmed using 1D-NOE. The major stereochemistry of bisborylcyclohexane **2v** was made by direct comparison to literature data.[37]

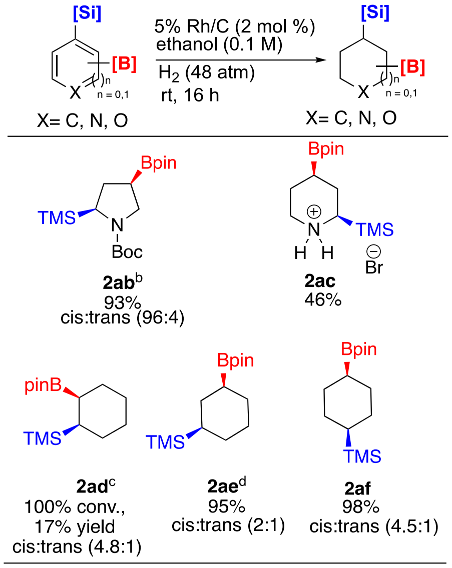
Scheme 71: Hydrogenation of silylated arenes[a]



[a]Reaction conditions: Heterocycle (0.5 mmol), relative stereochemistry shown, all yields are isolated. [b]Rh/Al$_2$O$_3$ (4.5 mol %), starting pyridine (0.2 mmol) [c]desilylated product observed. Ratio of desilylated: silylated = 5:1 [d]Pd/C (10 mol %) [e]Rh/Al$_2$O$_3$ (2 mol %)

Carbon-silicon bonds, similar to carbon-boron bonds, are also versatile as they can be transformed to various functional groups such as hydroxy, amine, halogen and aryl.[38] Thus, we sought to apply the same chemistry to organosilicon bearing heterocycles (Scheme 71). TMS-substituted pyridines 2-TMS **1w** and 4-TMS **1x** were easily hydrogenated with Rh/C and Rh/Al$_2$O$_3$ respectively, demonstrating the utility of both these catalysts for such substrates. Compound **1w** was hydrogenated as a salt of camphor sulphonate. This was to see whether adding an optically active acid could induce chirality in the hydrogenated product. This proved not to be the case as a 1:1 mixture of enantiomers was obtained. Surprisingly, **1y**, which only differs from **1x** by the position of the TMS group gave **2y** as a 1:5 mixture with the desilylated material being major as determined by LCMS and ^{19}F-NMR. Two siloxanes, **1z** and **1aa** were also tested. Compound **1z** presented the opportunity to probe complementary reactivity beyond just the ability to saturate siloxane containing hetero arenes. As Rh/C led to the saturation of both rings of **1j**, for **1z** we employed Pd/C to see if 2,3-dihydrobenzofuran **2z** could be formed selectively.[39] We were delighted to see this hypothesis realized. Catalytic hydrogenation of arene **1aa** showcased how catalyst choice matters. For this substrate, Pd/C only returned starting material. Rh/C saturated the ring, but of the siloxane was lost. In contrast, Rh/Al_2O_3 successfully provided **2aa** in 78% yield.[40]

Scheme 72: Hydrogenation of borylated and silylated arenes and heteroarenes[a]



[a]Reaction conditions: substrate (0.5 mmol) relative stereochemistry shown, all yields are isolated [b]t= 48 h, Rh/C (4 mol %) [c]12.5% desilylation observed [d]93:7 (product: desilylated product ratio) observed

Dual functionalized compounds that incorporate both silyl and boryl group have shown potential in facilitating diverse reaction pathways due to their orthogonal reactivity. An example of such reactivity was demonstrated by Hartwig where Bpin was converted to a Boc protected amine without compromising silyl groups. In another example, the silyl group was manipulated without compromising the Bpin group.[41] Given such demonstrations of Si/B dual functionality, we prepared and then hydrogenated **1ab–1af** under Rh/C catalysis (Scheme 72). To drive the hydrogenation of pyrrole **1ab** to full conversion, increasing the reaction time to 48 h and doubling the catalyst loading to 4 mol % was required. This enabled isolation of **2ab** in 93% yield with a high cis: trans ratio (96:4). The cis configuration was confirmed by NOE and 2D NMR experiments. Hydrogenation of 2-bromo-4-(Bpin)-6-(TMS)pyridine **1ac** was also carried out. As seen earlier, ring saturation was accompanied by debromination affording **2ac** as its HBr salt. Compound **2ac** was isolated in 46% yield by precipitating out the product using ethyl acetate. The 100% cis stereochemistry was determined by 1D-NOE.

Lastly, we examined the three substituted benzenes bearing boryl and silyl group in ortho, meta, and para arrangements. All three converted to the corresponding cyclohexanes, albeit with some differences. The reaction to produce ortho **2ad** showed 100% conversion to product (4.8:1 cis:trans) by ^{1}H-NMR, however ~12.5% of the material had desilylated. Difficulty in isolating **2ad** by flash column chromatography was experienced. In contrast, **2ae** (2:1 cis:trans) was isolated in higher yield, but some desilylation still occurred. As the amount of desilylation when forming **2ae** was lower than that experienced with **2ad**, we experimented to see if this side reaction could be eliminated. Unfortunately, we were unable to lessen desilylation by reducing the reaction time from 16 h to 8.5 h. Interestingly compound **2af** (4.5:1 cis:trans) was isolated in 98% yield with no desilylation. We note the observed diasteroselectivities of **2ae** and **2af** were lower (2:1 vs 4:1 for **2ae**) and (4.5:1 vs 7:1 for **2af**) than those observed with Glorius' catalyst,[10] whereas **2ad** was formed with a comparable cis:trans ratio (Fig 11). We also synthesized *tert*-butyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-(trimethylsilyl)-1*H*-pyrrole-1-carboxylate and trimethyl(6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dibenzo[*b*,*d*]furan-4-yl)silane compounds of dual functionality however their hydrogenation reactions under several different reaction conditions did not yield the desired hydrogenated products. They gave largely a mixture of deboronation and desilylation side products.

4.3. CONCLUSION

In summary, Rh/C, Rh/Al_2O_3, and other readily available catalysts can affect the hydrogenation of borylated and silylated arenes and heteroarenes. Demonstrations of these catalysts to substrates bearing both boryl and silyl group were also shown to be viable. Catalyst selection is often key to successful hydrogenations, especially for 5- and 6- membered heterocycles. In some cases, minimizing unwanted loss of the boron or silicon substituent can also be achieved through catalyst choice. The scope, including limitations disclosed, and comparisons made to the pioneering work of Glorius and Zheng can help guide practitioners as to whether to employ more complex Rh-catalysts or those tested herein. Spectroscopic data reported herein for new molecules as well as previously described compounds where full characterization data were lacking may also prove valuable for those who find those compounds of interest.

4.4. EXPERIMENTALS

General Remarks Unless indicated otherwise all reactions were carried out in oven-dried glassware with magnetic stirring and monitored by GC-MS or ^{1}HNMR/^{19}F-NMR. Tetrahydrofuran was freshly distilled from sodium/benzophenone under nitrogen. Diisopropylamine was freshly distilled from calcium hydride. n-BuLi was used as a 2.5 M solution in hexanes. Flash column chromatography was performed with silica gel (230–400 mesh). Spectra taken in $CDCl_3$ were referenced to 7.26 ppm in ^{1}H NMR and 77.2 ppm in $^{13}C\{^1H\}$ NMR, C_6D_6 was referenced to 7.16 ppm in ^{1}H NMR and 128.4 ppm in $^{13}C\{^1H\}$ NMR, C_7D_8 was referenced to 7.17 ppm in ^{1}H NMR and 128.9 ppm in $^{13}C\{^1H\}$ NMR, CD_2Cl_2 was referenced to 5.30 ppm in ^{1}H NMR and 53.5 ppm in $^{13}C\{^1H\}$ 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).

High-resolution mass spectra (HRMS) were obtained at the Michigan State University Mass Spectrometry Service Center using electrospray ionization (ESI+ or ESI-) on quadrupole time-of-flight (Q-TOF) instruments. Low resolution mass spectra were obtained on GCMS-QP2010 SE Shimadzu instrument. Melting points were measured in a capillary melting point apparatus and are uncorrected.

General Procedure A for synthesis of starting materials via Iridium catalysis (**1d-1g and 1z**). In a nitrogen filled glove box in a vial (5 mL)/round bottom (50 mL) loaded with a stir bar was added bis(1,5-cyclooctadiene)di-µ-methoxydiiridium(I), bis(pinacolato)diboron or bis(trimethylsiloxy)methylsilane, di-*tert*-butylbipyridine followed by addition of substrate in THF. The vial/round bottom was closed, removed from the glove box, connected to a Schlenk line, and placed in an oil bath. The solution was stirred under nitrogen at 70–80 °C for 16–48 h. The reaction mixture was concentrated by rotary evaporation and purified by passing through a silica plug or flash column chromatography.

*2,6-Dibromo-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (**1d**).* A modified general procedure A[42] was followed with $[IrOMe(cod)]_2$ (15.5 mg, 0.02 mmol, 0.25 mol %), dtbpy (12.5 mg, 0.04 mmol, 0.5 mol %), B_2pin_2 (2.13 g, 9.3 mmol) and THF (2 mL). To this solution was added 2,6-dibromopyridine (1.37 g, 9.3 mmol) and the resulting solution was stirred at 80 °C for 48 h. Upon completion, the reaction mixture was concentrated by rotary evaporation and the residue purified by silica gel chromatography (1% MeOH/DCM). Fractions containing the desired product were combined and the volatiles evaporated to afford a white solid. (1.19 g, 57% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (s, 2H), 1.33 (s, 12H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 140.9, 132.0, 85.4, 25.2. ^{11}B NMR (160 MHz, $CDCl_3$) δ 29.5. NMR data matched those reported in the literature.[42]

2-Bromo-6-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine[43] ***(1e)***. General procedure A was followed with bis(1,5-cyclooctadiene)di-µ-methoxydiiridium(I) (27 mg, 0.04 mmol, 0.4 mol %), dtbpy (24 mg, 0.09 mmol, 0.9 mol %), pinacol borane (1.4 g, 11 mmol, 1.1 equiv), THF (6 mL) and 2-bromo-6-methylpyridine (1.7 g, 10 mmol). The solution was stirred under nitrogen at 70 °C for 24 h. Upon completion, the reaction mixture was concentrated by rotary evaporation and the residue purified by silica gel chromatography (10:90 EtOAc/hexane). Fractions containing the desired product were combined and the volatiles evaporated to afford a white solid

(2.5 g, 86% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.62 (s, 1H), 7.43 (s, 1H), 2.52 (s, 3H), 1.33 (s, 12H). ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 159.6, 141.6, 130.1, 127.2, 84.9, 25.0, 24.1.^{11}B NMR (160 MHz, CDCl$_3$) δ 30.3 mp = 101–102 °C.

*2,6-Dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine **(1f)**.* General procedure A was followed with [IrOMe(cod)]$_2$ (17 mg, 0.02 mmol, 0.25 mol %), B$_2$pin$_2$ (2.52 g, 10 mmol, 1 equiv), dtbpy (13 mg, 0.05 mmol, 1.0 mol %) and THF (10 mL). To this solution was added 2,6-lutidine (2 mL, 10 mmol) and the resulting solution was stirred for 16 hours at 70 °C. After rotary evaporation, the residue was purified with Kugelrohr distillation at 60 °C (0.2 mm Hg) to yield a white solid (1.42 g, 61% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.31 (s, 2H), 2.52 (s, 6H), 1.35 (s, 12H). ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 157.2, 125.3, 84.4, 25.0, 24.4. ^{11}B NMR (160 MHz, CDCl$_3$) δ 30.7. NMR data matched those previously reported.[44]

*tert-Butyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-pyrrole-1-carboxylate (**1g**).* A modified general procedure A[32] was followed with [IrOMe(cod)]$_2$ (20 mg, 0.015 mmol, 0.25 mol %), B$_2$pin$_2$ (3.0 g, 12 mmol, 1 equiv), dtbpy (16 mg, 0.03 mmol, 0.5 mol %) and THF (10 mL). To this mixture was added n-Bocpyrrole (2 mL, 12 mmol). The solution was stirred for 16 hours at 60 °C. THF was removed via rotary evaporator, the residue was passed through a silica plug (DCM), and then concentrated on rotary evaporator and dried under high vacuum to yield a white solid (2.1 g, 70% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.65 (t, *J* = 1.7 Hz, 1H), 7.27 (m, 1H), 6.47 (dd, *J* = 3.1, 1.5 Hz, 1H), 1.58 (s, 9H), 1.32 (s, 12H). ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 148.8, 129.0, 120.9, 116.3, 84.0, 83.5, 28.1, 24.9. ^{11}B NMR (160 MHz, CDCl$_3$) δ 29.3. NMR data matched those previously reported.[32]

*3-(Benzofuran-2-yl)-1,1,1,3,5,5,5-heptamethyltrisiloxane (**1z**).* General procedure A was followed with 2,3 benzofuran (590 mg, 5 mmol), bis(trimethylsiloxy)methylsilane (1.2 g, 5.5 mmol, 1.1 equiv), norborene (475 mg, 5 mmol, 1 equiv), [Ir(OMe)cod]$_2$ (35.5 mg, 0.05 mmmol, 1.1 mol %), dtbpy (31 mg, 0.13 mmol, 2.4 mol %), THF (1 mL). The reaction was heated at 80 °C for 24 hours. The solution was concentrated by rotary evaporation and the residue purified by flash column chromatography (hexanes: ethyl acetate 95:5). Fractions containing the desired product were evaporated and dried under high vacuum to yield a clear colorless oil (1.3 g, 76% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.6 Hz, 1H), 7.51 (d, *J* = 8.3 Hz, 1H), 7.29 (t, *J* = 6.9 Hz, 1H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.01 (s, 1H), 0.35 (s, 3H), 0.13 (s, 18H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 160.8, 157.8, 127.8, 124.7, 122.5, 121.5, 116.5, 111.6, 1.9, 0.1. ^{29}Si NMR (99 MHz, $CDCl_3$) δ 10.0, –43.2. ^{1}H and ^{13}C{^{1}H} NMR values were consistent with those previously reported.[33]

General Procedure for synthesis of starting materials via pinacol coupling (*1j, 1l, 1q,1ae, 1af*). To an oven dried round bottom flask (50 mL)/ vial (5 mL) containing a stir bar was added pinacol (1 equiv) and the corresponding boronic acid (1 equiv) in hexane/DCM. The resulting solution was stirred for 2-48 hours at room temperature. The product was isolated by passing through a celite plug or washing with water.

2-(Benzofuran-7-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (***1j***). Benzofuran-7-ylboronic acid (1.5 g, 9.3 mmol) and pinacol (1.2 g, 10.1 mmol, 1.1 equiv) in DCM (30 mL) were consecutively added. The resulting solution was stirred overnight at room temperature. The solvent was concentrated by rotary evaporation to yield a white solid that was pure by NMR and used as is in the subsequent reaction (2.2 g, 99% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.8 Hz, 1H), 7.58 (d, *J* = 8.3 Hz, 1H), 7.41 (s, 1H), 7.39–7.31 (m, 1H), 7.29–7.20 (m, 1H), 1.40 (s, 12H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 157.6, 127.6, 126.1, 122.8, 122.0, 119.7, 112.1, 84.8, 24.9; ^{11}B NMR (160 MHz, $CDCl_3$) δ 27.7. NMR data matched those previously reported.[45]

tert-Butyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-indole-1-carboxylate (***1l***). (1-(*tert*-Butoxycarbonyl)-1*H*-indol-2-yl)boronic acid (1.0 g, 3.83 mmol) and pinacol (497 mg, 4.21 mmol, 1.1 equiv) in DCM (15 mL) were consecutively added and the mixture stirred for 5 h at room temperature. The solvent was removed by rotary evaporation and the solid residue was stirred with water (1 mL) to remove excess pinacol. After the water was decanted off, the remaining solid was dissolved in DCM and the solution dried over $MgSO_4$. After filtering off the $MgSO_4$, the volatiles were removed by rotary evaporation to yield a yellowish solid (1.06 g, 80.6% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.3 Hz, 1H), 7.54 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.31–7.24 (m, 1H), 7.19 (t, *J* = 7.5 Hz, 1H), 6.85 (s, 1H), 1.70 (s, 9H), 1.41 (s, 12H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 151.3, 136.7, 131.4, 124.5, 122.4, 121.2, 115.8, 115.0, 84.3, 84.2, 28.3, 24.9; ^{11}B NMR (160 MHz, $CDCl_3$) δ 29.1; mp 87–88 °C; GCMS for $C_{14}H_{18}BNO_2$ calcd $[M+H]^{+\cdot}$ 243.14 found 243.15.

*3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenol (**1q**).* (3-Hydroxyphenyl)boronic acid (551 mg, 4 mmol) and pinacol (473 mg, 4 mmol) in hexane were consecutively added. The resulting solution was stirred for two hours at room temperature. The product was isolated by filtration through a celite plug followed by removal of the volatiles by rotary evaporation to yield a white solid (790 mg, 89%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.0 Hz, 1H), 7.28–7.22 (m, 2H), 6.95 (ddd, *J* = 8.0, 2.8,1.0 Hz, 1H), 4.64 (s, 1H), 1.34 (s, 12H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 155.1, 129.4, 127.3, 121.2, 118.4, 84.1, 25.0; ^{11}B NMR (160 MHz, $CDCl_3$) δ 31.1; mp 85–87 °C; GCMS for $C_{12}H_{17}BO_3$ calcd $[M]^{+\cdot}$ 220.13 obtained 220.15. ^{1}H and ^{13}C{^{1}H} NMR data were consistent with those previously reported.[46]

*Trimethyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)silane (**1ae**).* A modified literature procedure was used for the synthesis.[10] (3-(Trimethylsilyl)phenyl)boronic acid (1.0 g, 5.1 mmol) and pinacol (733 mg, 6.2 mmol, 1.2 equiv) in hexane (20 mL) and DCM (7 mL) were consecutively added. (Note: DCM was added because the reagents were insoluble in hexane). The resulting solution was stirred for 27 h at room temperature. The volatiles were removed by rotary evaporation to yield a yellowish liquid. (1.4 g, 74% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.80 (d, *J* = 7.5 Hz, 1H), 7.62 (d, *J* = 7.4 Hz, 1H), 7.36 (t, *J* = 7.4 Hz, 1H), 1.35 (s, 12H), 0.28 (s, 9H);

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 139.8, 139.7, 136.4, 135.5, 127.2, 83.9, 25.0, –0.9; ^{11}B NMR (160 MHz, $CDCl_3$) δ 31.6; ^{29}Si NMR (99 MHz, $CDCl_3$) δ 4.0. ^1H and $^{13}C\{^1H\}$ NMR data were consistent with those previously reported[47] and ^{11}B NMR data were also consistent those previously reported.[48] (Note: reference 47 reports the Bpin at 1.54 in the tabulated data however in the spectrum provided the peak appears at 1.34 ppm. Our carbon NMR data are shifted by 0.9 ppm downfield from those reported owing to $CDCl_3$ being set to 78.1 ppm instead of 77.2 ppm).

*Trimethyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)silane (**1af**)*. A modified literature procedure was followed.[47] (4-(Trimethylsilyl)phenyl)boronic acid (500 mg, 2.6 mmol) and pinacol (303 mg, 2.6 mmol, 1.0 equiv) in hexane (20 mL) were consecutively added. The resulting solution was stirred for 2h at room temperature. The solvent was removed by rotary evaporation to yield a white solid (682 mg, 95% yield). This material was used as is in the subsequent reaction. ^1H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.2 Hz, 2H), 7.53 (d, *J* = 7.2 Hz, 2H), 1.34 (s, 12H), 0.27 (s, 9H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 144.4, 134.0, 132.7, 83.9, 25.0, –1.1; ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.9; ^{29}Si NMR (99 MHz, $CDCl_3$) δ –3.9. ^1H and $^{13}C\{^1H\}$ NMR data were consistent with those previously reported[47] as were ^{11}B NMR data.[48] (Note $CDCl_3$ reference reported in reference 47 was set at 78.1 instead of 77.2 thus their tabular data are shifted by 1.0 ppm relative to ours. Similarly, a 0.7 ppm shift is observed in the ^1H NMR spectrum).

Synthesis of starting material (1k) via Miyaura borylation.

*2-(Dibenzo[b,d]furan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1k**).* A modified literature procedure was followed**.**[49] In a nitrogen filled glove box in a 10 mL oven dried Wheaton vial with a stir bar was added 4-bromodibenzofuran (247 mg, 1 mmol), B_2pin_2 (279.4 mg, 1.1 mmol, 1.1 equiv), $Pd(dppf)Cl_2$ (37 mg, 5 mol %, 0.05 mmmol) and KOAc (294 mg, 3 mmol, 3 equiv) in dioxane (5 mL). The resulting solution was taken outside the box and stirred for 16 h at 80 °C in an oil bath. The solution was concentrated by rotary evaporation, purified using flash column chromatography with hexane/ethyl acetate (2-4% gradient) solvents and concentrated and dried by rotary evaporation to yield a white solid (193 mg, 66% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.06 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.94 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.90 (dd, *J* = 7.2, 1.4 Hz, 1H), 7.68 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.45 (dt, *J* =7.3, 1.3 Hz, 1H), 7.38–7.30 (m, 2H), 1.45 (s, 12H); ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 160.6, 156.4, 134.5, 127.0, 124.0, 123.8, 122.6, 122.3, 120.5, 112.5, 84.2, 25.1; ^{11}B NMR (160 MHz, CDCl$_3$) δ 30.3. NMR data matched those previously reported.[50]

Synthesis of starting materials via lithiation, silylation and borylation (***1y, 1x, 1ab, 1ac, 1ad***).

2-Chloro-6-(trifluoromethyl)-3-(trimethylsilyl)pyridine ***(1y)***. Synthesis of **1y** was carried out using the reported literature procedure.[51] Diisopropylamine (2 mL, 11.0 mmol) and 2-chloro-6-(trifluoromethyl))pyridine (2.0 g, 11.0 mmol) were consecutively added to a solution of n-BuLi (2.5 M in hexanes, 4.4 mL, 11.0 mmol) and THF (30 mL) at –85 °C. After 4 hours at –85 °C, chlorotrimethylsilane (3 mL, 2.7 g, 25 mmol) was added. The mixture was poured into water and extracted with DCM (3 x 20 mL). The combined organics were evaporated, and the residue purified by flash column chromatography on silica gel using hexane as the eluent. The product obtained after evaporation by rotary evaporation was a colorless liquid (2.25 g, 80% yield). 4-Chloro-6-trifluoromethyl-4-(trimethylsilyl)pyridine (**1x**) as a colorless liquid (128 mg, 5% yield) was obtained as a side product and was used as a starting material for **2x**. ^{1}H and ^{13}C{^{1}H} NMR data of **1y** matched those previously reported.[51] For **1x**, while the observed aromatic protons were both shifted by 0.15 and 0.16 ppm relative to the reported in reference, carbon data matched those previously reported. Thus, we are confident in our assignment.[51] For **1y**: ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.95 (d, 7.6 Hz, 1H), 7.58 (d, 7.5 Hz, 1H), 0.42 (s, 9H); ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 157.3, 148.7 (q, *J* = 35.7 Hz), 146.4, 140.1, 120.9 (q, *J* = 274.2 Hz), 118.5, –1.34; ^{19}F NMR (470 MHz, CDCl$_3$) δ 68.3; ^{29}Si NMR (99 MHz, CDCl$_3$) δ –1.3. For **1x**: ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.64 (s, 1H), 7.58 (s, 1H), 0.3 (s, 9H); $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 157.5, 151.7, 147.4 (d, *J* = 34.9 Hz), 131.9, 122.9 (q, *J* = 2.9 Hz), 121.1 (d, *J* = 274.6 Hz), –1.76.

*tert-Butyl-2-(trimethylsilyl)-1H-pyrrole-1-carboxylate (**1ab'**).* The compound was prepared according to a reported procedure.[52] Freshly distilled diisopropylamine (4 mL, 29.9 mmol) in THF was cooled to –78 °C under a nitrogen atmosphere. n-BuLi (2.5 M in hexanes, 12 mL, 30.0. mmol) was added slowly, and reaction mixture was allowed to warm to 0 °C for 10 mins before re-cooling to –78 °C. *tert*-Butyl-1*H*-pyrrole (5.0 g, 29.9 mmol) was added dropwise to the solution prepared above. The reaction mixture was allowed to stir at –78 °C for 1 h before trimethylsilyl chloride (4 mL, 31.0 mmol) was added at –78 °C. The mixture was allowed to warm to room temperature, quenched with methanol, and stirred overnight. The solvent was then removed by rotary evaporation and the crude mixture was purified by short neck distillation at 110 °C, 0.05 atm to give a colorless oil (5.76 g, 80% yield). NMR data matched those previously reported.[52]

*tert-Butyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(trimethylsilyl)-1H-pyrrole-1-carboxylate (**1ab**)*. A modified literature procedure was used to carry out the synthesis of **1ab**.[52] In a nitrogen filled glove box an oven dried round bottom flask (50 mL) was loaded with bis(1,5-cyclooctadiene)di-µ-methoxydiiridium(I) (14 mg, 0.02 mmol 0.5 mol %), bis(pinacolato)diboron (1.05 g, 4.2 mmol), di-*tert*-butyl bipyridine(11 mg, 0.04 mmol, 1 mol %), THF (10 mL) and a stir bar. To this solution was added *tert*-butyl-2-(trimethylsilyl)-1*H*-pyrrole-1-carboxylate (1g, 4.2 mmol) (**1ab'**). The flask was placed in an oil bath and the reaction mixture stirred for 16 hours at 70 °C. THF was removed via rotary evaporation, the residue was passed through a silica plug (DCM). Rotary evaporation yielded a white solid (1.5 g, 96% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (s, 1H), 6.73 (s, 1H), 1.58 (s, 9H), 1.32 (s, 12H), 0.26 (s, 9H); $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 149.5, 136.0, 133.4, 128.1, 83.7, 83.4, 28.1, 24.9, –0.2; ^{29}Si NMR (99 MHz, $CDCl_3$) δ 10.8; ^{11}B NMR (160

MHz, $CDCl_3$) δ 30.2; mp 93.8–94.2 °C; GCMS $C_{15}H_{25}BNO_4$ calcd mass $[M+H]^{+\cdot}$ 294.19 obtained 294.20. ^1H and $^{13}C\{^1H\}$ NMR data were consistent with those previously reported in C_6D_6.[52]

*2-Bromo-6-(trimethylsilyl)pyridine (**1ac'**).* n-BuLi (2.5 M in hexanes, 3.4 mL, 8.5 mmol) was added dropwise to a stirred solution of 2,6 dibromopyridine (2.0 g, 8.4 mmol) in THF (40 mL) at –78 °C under nitrogen and subsequently warmed to –40 °C for 30 mins before being cooled to –78 °C and dropwise addition of trimethylsilyl chloride (1 mL, 9.3 mmol) in THF (10 mL) via cannula. After 3 hours, the solution was allowed to warm to room temperature, filtered through celite, washed with water (20 mL), dried and concentrated in vacuo to give 2-bromo-6-(trimethylsilyl)pyridine as yellow/brown oil (3.0 g, 79% yield). NMR data matched those previously reported.[53]

*2-Bromo-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6-(trimethylsilyl)pyridine (**1ac**).* A nitrogen filled glove box an oven dried round bottom flask (50 mL) was loaded with bis(1,5-cyclooctadiene)di-µ-methoxydiiridium(I) (11 mg, 0.01 mmol, 0.25 mol %), bis(pinacolato)diboron (1.65 g, 6.5 mmol), di-*tert*-butyl bipyridine (9 mg, 0.03 mmol, 0.5 mol %), THF (10 mL) and a stir bar. To this solution was added 2-bromo-6-(trimethylsilyl)pyridine (**1ac'**) (2.0 g, 6.5 mmol). The resulting solution was heated to 70 °C via an oil bath and stirred for 16 hours. THF was removed by rotary evaporation, the residue passed through a silica plug (DCM) and evaporated to yield a white solid (2.0 g, 70 % yield). ^1H NMR (500 MHz, $CDCl_3$) δ 7.71 (s, 2H), 1.35 (s, 12H), 0.32 (s, 9H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 170.7, 143.8, 132.4, 132.3, 84.9, 25.0, 1.6, ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.6; ^{29}Si NMR (99 MHz, $CDCl_3$) δ 4.3; mp 101.5–102.5 °C; HRMS (ESI) m/z calcd. for $C_{14}H_{24}BNBrSiO_2$ $[M+H]^{+\cdot}$ 356.0852 found 356.0851.

*Trimethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)silane (**1ad**).* A modified literature procedure was used for this synthesis.[10] HBpin (0.36 mL, 0.32 g, 2.47 mmol) was added to a mixture of catalyst [Pd(dppf)Cl_2] (67.3 mgs, 1.65 mol %), 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (0.49 mL, 0.5 g, 1.65 mmol) and Hünig's base (0.66 mL, 489.7 mg, 3.78

mmol) in dioxane (4 mL) and the contents heated to 80 °C for 24 h. After cooling to room temperature sat. ammonium chloride ~10 mL was added to neutralize the solution. The mixture was extracted with DCM (3 x 20 mL) and the organics then washed with H_2O (50 mL). The organic layer was dried over Na_2SO_4. After filtration, the mixture was concentrated via rotary evaporation, and purified by flash column chromatography (10-20% Et_2O and hexane). Product containing fractions were combined and concentrated by rotary evaporation to obtain a white solid (442 mg, 98% yield). ^1H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.3 Hz, 1H), 7.62 (d, *J* = 7.3 Hz, 1H), 7.40 (td, *J* = 7.4, 1.5 Hz, 1H), 7.35 (td, *J* = 7.4, 1.4 Hz, 1H), 1.35 (s, 12H), 0.34 (s, 9H). NMR data were consistent with those previously reported.[54]

*1,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (**1v**).* In a 20 mL oven dried sealed tube under nitrogen blanket with a stir bar was added (2-chlorophenyl)trimethylsilane (600 mg, 4.3 mmol), B_2pin_2 (1.1 g, 4.2 mmol, 1.0 equiv), Pd_2dba_3 (80 mg, 2 mol %, 0.09 mmol), xphos (81 mg, 0.17 mmol, 4 mol %,) and NaOAc (424 mg, 5.7 mmol, 1.2 equiv) in dioxane (5 mL). The resulting solution was taken outside the box and stirred for 16 h at 120 °C in an oil bath. The solvent was removed by rotary evaporation and the residue purified by flash column chromatography eluting with DCM. Product containing fractions were combined and concentrated by rotary evaporation to yield a white solid (119 mg, 9% yield). ^1H NMR (500 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 5.5, 3.3 Hz, 2H), 7.37 (dd, *J* = 5.5, 3.3 Hz, 2H), 1.37 (s, 24H). NMR data were consistent with those previously reported.[55]

General Procedure B for hydrogenation. Arene/Heteroarene (0.5 mmol), 5% Rh/C (25 mg, 2 mol %) or Rh/Al_2O_3 (50 mg, 4 mol %), and a stir bar were loaded into a 300 mL Parr reactor pressure vessel. Each run was flushed with hydrogen at least twice. Ethanol (5 mL) was added and the reactor was sealed and pressurized with hydrogen gas (48 atm). After 16 hours the reactor was opened and the reaction mixture filtered through celite. The celite was washed with methanol (3 x 5 mL) and the solvent was removed by rotary evaporation to yield the corresponding product.

*3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)piperidin-1-ium bromide (**2b**).* General procedure B was followed with 3-bromo-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (142 mg, 0.5 mmol) and 5% Rh/C (25 mg, 2 mol %) for 16 h. After purification the solvent was removed under vacuum to yield 134 mg of a white solid consisting of 73:27 molar mixture of **2b**:**3b** (106 mg of **2b**). ^{1}H NMR (500 MHz, D_2O) δ 3.42–3.29 (m, 2H), 3.13 (t, *J* = 5.8 Hz, 1H, deboronated piperidine), 3.04–2.86 (m, 2H), 1.96–1.80 (m, 2H), 1.80–1.59 (m, 3H, deboronated piperidine), 1.55–1.42 (m, 1H), 1.42–1.32 (m, 1H), 1.19 (s, 12H); $^{13}C\{^1H\}$ NMR (126 MHz, D_2O) δ 75.6, 45.9, 44.4, 44.3, 23.6, 23.4, 22.8, 22.1, 21.4; ^{11}B NMR (160 MHz, D_2O) δ 30.2; HRMS (ESI) m/z calcd. for $C_{11}H_{23}BNO_2$ $[M\text{-}Br]^{+\cdot}$ 212.1821; Found. 212.1826.

*2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)piperidin-1-ium bromide (**2c**).* General procedure B was followed with bromo-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (142 mg, 0.5 mmol) and 5% Rh/C (25 mg, 2 mol %) for 16 h. After purification the solvent was removed under vacuum to yield a white solid (143 mg, 99% yield). ^{1}H NMR (500 MHz, D_2O) δ 3.37–3.28 (m, 1H), 3.13 (t, *J* = 6.0 Hz, 1H), 2.91 (td, *J* = 12.5, 3.1 Hz, 1H), 2.71 (dd, *J* = 12.6, 3.2 Hz, 1H), 1.93 (ddd, *J* = 14.3, 3.6, 1.6 Hz, 1H), 1.88–1.78 (m, 2H), 1.78–1.72 (m, 1H), 1.71–1.57 (m, 2H), 1.55–1.44 (m, 1H), 1.19 (s, 12H); $^{13}C\{^1H\}$ NMR (126 MHz, D_2O) δ 75.5, 44.5, 24.3, 23.6, 22.5, 22.0; ^{11}B NMR (160 MHz, D_2O) δ 28.42. mp 198–199 °C; HRMS (ESI) m/z calcd. for $C_{11}H_{23}BNO_2$ $[M\text{-}Br]^{+\cdot}$ 212.1821; Found. 212.1822.

*4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)piperidin-1-ium bromide (**2d**).* General procedure B was followed with 2,6-dichloro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (**1d**) (90 mg, 0.25 mmol) and 5% Rh/Al_2O_3 (50 mg, 8 mol %) for 16 h. MeOH was used for filtration through celite to avoid deboronation and the solvent was removed under vacuum. The reaction mixture showed 85% conversion to product. Diethyl ether was added to the reaction mixture, which dissolved the starting material and not **2d**. Decantation and drying by rotary evaporation yielded a white solid (60 mg, 82% yield). (Notes: Adding ethyl acetate or hexane to the crude reaction mixture resulted in deboronation. Dissolving **1d** in D_2O also resulted in deboronation). While the HBr salt has not been reported, the HCl salt has been.[56] ^{1}H NMR (500 MHz, DMSO) δ 3.08 (d, *J* = 12.4 Hz, 2H), 2.87 (t, *J* = 11.5 Hz, 2H), 1.77–1.67 (m, 2H), 1.60–1.48 (m, 2H), 1.28 (s, 1H), 1.19 (s, 12H).^{13}C{^{1}H} NMR (126 MHz, DMSO) δ 83.2, 43.7, 24.6, 23.4; ^{11}B NMR (160 MHz, DMSO) δ 33.1. mp 169–170 °C; GCMS for $C_{11}H_{22}BNO_2$ (free base) calcd $[M]^{+\cdot}$ 211.17 found 211.15.

*2-Methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)piperidin-1-ium bromide (**2e**).* General procedure B was followed with 2-bromo-6-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine **(1e)** (85 mg, 0.3 mmol), 5 % Rh/Al_2O_3 (50 mg, 4 mol %) for 16 h. After purification the solvent was removed under vacuum to yield a tan solid (86 mg, 94% yield). Stereochemistry was assumed to be cis based on analogy to **2f**. ^{1}H NMR (500 MHz, D_2O) δ 3.41–3.35 (m, 1H), 3.24–3.08 (m, 1H), 2.93 (td, *J* = 13.0, 3.3 Hz, 1H), 2.02–1.84 (m, 2H), 1.53 (dq, *J* = 13.2, 4.1 Hz, 1H), 1.43–1.30 (m, 1H), 1.29–1.24 (m, 4H), 1.18 (s, 12H); ^{13}C{^{1}H} NMR (126 MHz, D_2O) δ 75.5, 53.4, 45.1, 31.7, 23.6, 23.2, 18.7; ^{11}B NMR (160 MHz, D_2O) 30.2, mp 209211 °C, HRMS (ESI) m/z calcd. for $C_{12}H_{25}BNO_2$ $[M–Br]^{+\cdot}$ 226.1978 found 226.1986.

*2,6-Dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)piperidine (**2f**).* General procedure B was followed with 2,6-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (**1f**) (117 mg, 0.5 mmol), 5 % Rh/Al_2O_3 (50 mg, 4 mol %) for 40 h. After purification the solvent was removed under vacuum to yield a white solid (102 mg, 86% yield). This reaction gave 81% conversion to product in 19 h, 95% conversion to product in 28 h and 100% conversion to product in 10 h. Cis diastereoselectivity of the compound was ascertained by oxidation of the boronic ester to and comparing the NMR data of the hydroxy bearing methine in **2f** to analogous literature data reported for cis 2-methyl-6-propyl piperidin-4-ol[57] and cis 2-methyl-6-nonylpiperidin-4-ol.[58] Literature reports the chemical shift of the protons on the OH bearing carbon appearing at 3.65 (tt, *J*=11.8, 4.5 Hz) ppm for cis 2-methyl-6-propyl piperidin-4-ol[56] and at 3.66 (dddd, *J* = 11.0, 11.0, 4.6, 4.6) for cis 2-methyl-6-nonylpiperidin-4-ol.[56] The corresponding chemical shift for **2f** appears at 3.68 (tt, *J*= 11.1, 4.5 Hz) ppm. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.68–2.52 (m, 2H), 1.64 (d, *J* = 12.8 Hz, 2H), 1.20 (s, 12H), 1.03 (d, *J* = 6.2 Hz, 6H), 0.94 (q, *J* = 12.3 Hz, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 83.1, 53.5, 33.8, 24.9, 21.6; ^{11}B NMR (160 MHz, $CDCl_3$) δ 33.7; HRMS (ESI) m/z calcd. for $C_{13}H_{26}BNO_2$ $[M]^{+\cdot}$ 239.2057 found 239.2059.

*tert-Butyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrrolidine-1-carboxylate (**2g**).* General procedure B was followed with *tert*-butyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-pyrrole-1-carboxylate (**1g**) (142 mg, 0.5 mmol), 10 % Pd/C (15 mg, 3 mol %) for 16 h. After purification solvent was removed under vacuum to yield a clear oil (122 mg, 82% yield). A mixture of two rotational isomers was observed. Running this reaction on one gram scale using 5% Rh/C (138 mgs) and 13 mL ethanol afforded 1g in 73% yield. ^{1}H NMR (500 MHz, C_6D_6) δ 3.74 (dd, *J* = 10.7, 8.5 Hz, 1H), 3.59–3.47 (m, 3H), 3.40 (t, *J* = 10.3 Hz, 1H), 3.32 (ddd, *J* = 10.6, 7.5, 3.2 Hz, 1H), 3.17 (td, *J* = 10.1, 6.8 Hz, 1H), 3.01 (td, *J* = 9.8, 7.0 Hz, 1H), 1.74–1.54 (m, 4H), 1.47 (d, *J* = 7.9 Hz, 18H), 1.44–1.34 (m, 2H), 0.98 (s, 24H, mixture of 2 rotamers); ^{13}C{^{1}H} NMR (126 MHz, C_6D_6) δ 154.3, 83.3, 78.3 (2 rotamer peaks), 48.4 (2 rotamer peaks), 47.0, 28.7, 27.7, 24.8; ^{11}B NMR (160 MHz, C_6D_6) δ 33.4; NMR data were consistent with those previously reported.[59] HRMS (ESI) m/z calcd. for $C_{15}H_{28}BNO_4Na$ $[M+Na]^{+\cdot}$ 320.2009 found 320.2013. *4,4,5,5-Tetramethyl-2-(tetrahydrofuran-2-yl)-1,3,2-dioxaborolane (**2h**)*. General procedure B was followed with 2-(furan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (100 mg, 0.5 mmol), 5% Rh/C (25 mg, 2 mol %) for 13 h. After purification, the solvent was removed using rotary evaporator to yield a clear oil (100% conversion, 8.3% OBpin monomer) which amounted to 93 mgs of **2h** (89% yield). ^{1}H NMR (500

MHz, $CDCl_3$) δ 4.10–3.76 (m, 1H), 3.62 (q, *J* = 7.7 Hz, 1H), 3.42 (dd, *J* = 10.9, 7.2 Hz, 1H), 2.11–2.01 (m, 1H), 1.92–1.83 (m, 2H), 1.77–1.64 (m, 1H), 1.28 (s, 12H), 1.24 (s, 1H, B byproduct); $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 83.8, 74.9 (B byproduct), 68.9, 28.1, 26.2, 24.7 (B byproduct), 24.7 (Bpin C), 24.6 (Bpin C); ^{11}B NMR (160 MHz, $CDCl_3$) δ 32.3, 22.3 (B byproduct). NMR data were consistent with those previously reported.[9]

Recyclability Test Experiment:

Test 1: General procedure B was followed with 2-(furan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (500 mg, 2.5 mmol), 5% Rh/C (235 mg, 4 mol %) with 10 mL ethanol for 4 h. The catalyst was recycled by filtration using a sintered funnel and washed with EtOAc. After purification of the filtrate, the solvent was removed by rotary evaporation to yield a clear oil of **1h** (100% conversion, 66% yield).

Test 2: The recovered catalyst from test 1 was used again with (500 mg, 2.5 mmol) with 10 mL ethanol for 4 h. The catalyst was recycled by filtration using a sintered funnel and washed with EtOAc. After purification of the filtrate, the solvent was removed by rotary evaporation to yield a clear oil (80% conversion to product, 414 mg of mixture, 82% crude yield).

Test 3: The recovered catalyst from test 2 was used again with (500 mg, 2.5 mmol) with 10 mL ethanol for 6 h. The catalyst was recycled by filtration using a sintered funnel and washed with EtOAc. After purification of the filtrate, the solvent was removed by rotary evaporation to yield a clear oil. (100% conversion, 376 mg, 75% yield)

Test 4: The recovered catalyst from test 3 was used again with (500 mg, 2.5 mmol) with 10 mL ethanol for 5 h. The catalyst was recycled by filtration using a sintered funnel and washed with EtOAc. After purification of the filtrate, the solvent was removed by rotary evaporation to yield a clear oil. (100% conversion, 421 mg, 84% yield)

Test 5: The recovered catalyst from test 4 was used again with (500 mg, 2.5 mmol) with 10 mL ethanol for 5 h. After purification, the solvent was removed by rotary evaporation to yield a clear oil. (100% conversion, 427 mg, 84% yield)

*4,4,5,5-Tetramethyl-2-(5-methyltetrahydrofuran-2-yl)-1,3,2-dioxaborolane (**2i**).* General procedure B was followed with 4,4,5,5-tetramethyl-2-(5-methylfuran-2-yl)-1,3,2-dioxaborolane 208 mg, 1.0 mmol), 5% Rh/C (25 mg, 1 mol %) for 16 h. After purification solvent was removed by rotary evaporation to yield a clear oil (165 mg (with 6.3% HOBpin) amounting to 157 mg of **2i** (74% yield). A diastereomeric ratio of 97:3 was measured by ^{1}H NMR and GC. Cis stereochemistry was established by COSY and 1D NOE NMR experiments. In the NOE experiments, irradiating 3.63 ppm (H on C2) showed enhancement of the peak at 3.73 ppm (H on C5) and irradiating the peak 3.73 ppm (H on C5) showed enhancement of the peak at 3.63 ppm (H on C2). Byproduct HOBpin was confirmed by adding HOBpin to the NMR tube and observing the increase in intensity of the ^{11}B peak for HOBpin. When Pd/C was used as a catalyst, 18% HOBpin was observed. Attempts to remove HOBpin by sublimation were unsuccessful. Hydrogenation using Rh/C gave only 6.3% HOBpin and reducing the time of reaction to 12.5 h further lowered the amount of HOBpin to 4%. ^{1}H NMR (500 MHz, C_6D_6) δ 3.77 (dq, *J* = 12.8, 6.3 Hz, 1H), 3.67 (dd, *J* = 9.9, 7.9 Hz, 1H), 2.04–1.84 (m, 2H), 1.75–1.64 (m, 1H), 1.34–1.26 (m, 1H), 1.24 (d, *J* = 6.0 Hz, 3H), 1.028 (s, 6H, Bpin), 1.035 (s, 6H, Bpin); ^{13}C{^{1}H} NMR (126 MHz, C_6D_6) δ 83.4 (Bpin CH), 76.8 (Bpin CH), 34.0, 28.8, 24.9 (Bpin CH_3), 24.8 (Bpin CH_3), 21.2; ^{11}B NMR (160 MHz, C_6D_6) δ 32.7; HRMS (ESI) m/z calcd. for $C_{11}H_{21}BO_3Na$ $[M+Na]^{+\cdot}$ 235.1481 found 235.1493.

*4,4,5,5-Tetramethyl-2-(octahydrobenzofuran-2-yl)-1,3,2-dioxaborolane (**2j**).* General procedure B was followed with 2-(benzofuran-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1j**) (122 mg, 0.5 mmol), 5 % Rh/C (25 mg, 2 mol %) dissolved in hexane (5 mL) for 16 h at 55 atm pressure. This compound was purified by passing the reaction mixture in ethyl acetate through celite and evaporating the mother liquor by rotary evaporation to yield a clear oil (124 mg (with ~20 mol % OBpin monomer via ^{1}H-NMR)) amounting to ~107 mg of **2j** (~85% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.73 (q, *J* = 4.1 Hz, 1H), 3.69 (dd, *J* = 10.9, 7.1 Hz, 1H), 2.22–2.12 (m, 1H), 2.05–1.97 (m, 1H), 1.97–1.89 (m, 1H), 1.61–1.46 (m, 5H), 1.40–1.31 (m, 1H), 1.27 (s, 6H), 1.25 (s, 6H), 1.25 (s, 3H, B byproduct) 1.23–1.17 (m, 2H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 83.7, 83.1 (B byproduct), 78.3, 38.2, 34.5, 28.2, 28.21, 24.77 (Bpin CH_3), 24.55 (B byproduct), 24.53 (Bpin CH_3), 24.3, 21.0; ^{11}B NMR (160 MHz, $CDCl_3$) δ 32.7, 22.4 (B byproduct). The stereochemcal assignment and NMR data were consistent with those previously reported.[9]

*2-(Dodecahydrodibenzo[b,d]furan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2k**)*. General procedure B was followed with 4,4,5-trimethyl-2-(tetrahydrodibenzofuran-4-yl)-1,3,2-dioxaborolane (147 mg, 0.5 mmol) (**1k**), 5 % Rh/C (25 mg, 2 mol %), H_2 at 60 atm, using hexane (5 mL) as a solvent at 60 °C for 21 h. The catalyst was removed by passing through celite using diethyl ether as a solvent (3 x 5 mL). The solvent was removed by rotary evaporation to give a colorless oil that contained product (100% conversion by ^{1}H NMR) and 8% deboronated material (tetrahydrodibenzofuran) as determined by GCMS analysis. The desired compound was purified by flash column chromatography eluting with an ethyl acetate/hexane gradient (2%-10%) to give a colorless oil (58 mg, 38%). Only the major isomer was isolated. The stereochemistry was determined to be cis using 2-D NMRs and 1D NOE (see S49). All spectral data matched those previously reported[14] except for the ^{11}B chemical shift that was reported to be at 22.40, which is inconsistent with a C–boronic ester peak and is more likely boron byproducts. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.88 (t, *J* = 3.7 Hz, 1H), 3.82 (td, *J* = 10.5, 5.9 Hz, 1H), 2.29–2.16 (m, 1H), 1.87–1.75 (m, 2H), 1.68 (dt, *J* = 12.9, 3.5 Hz, 1H), 1.64–1.53 (m, 2H), 1.47 (tt, *J* = 12.8, 4.7 Hz, 5H), 1.42–1.35 (m, 1H), 1.33–1.25 (m, 2H), 1.22 (s, 6H), 1.23 (s, 7H) 1.19 (s, *J* = 4.6 Hz, 1H), 1.07 (qt, *J* = 12.7, 3.0 Hz, 1H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 82.9, 77.6, 76.4, 42.0, 41.4, 28.6, 25.7, 25.1, 24.8 (Bpin C), 24.5 (Bpin C), 22.1, 21.3, 21.2, 19.6; ^{11}B NMR (160 MHz, $CDCl_3$) δ 33.4; GCMS $C_{18}H_{31}BO_3$ calcd $[M]^{+\cdot}$ 306.24 found 306.25.

*tert-Butyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octahydro-1H-indole-1-carboxylate (**2l**).* General procedure B was followed with *tert*-butyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole-1-carboxylate (**1l**) (174 mg, 0.5 mmol), 5 % Rh/C (25 mg, 2 mol %) for 16 h. After purification solvent was removed by rotary evaporation to yield a colorless oil (170 mg, 97% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.78 (dt, *J* = 11.6, 6.3 Hz, 1H), 3.74–3.68 (m, 1H), 3.62–3.50 (m, 1H), 3.18–3.01 (m, 2H), 2.33–2.18 (m, 2H), 2.07–1.97 (m, 2H), 1.89–1.77 (m, 2H), 1.76–1.52 (m, 8H), 1.46–1.39 (m, 19H, Boc of 2 rotamers), 1.37–1.28 (m, 2H), 1.27–1.18 (m, 25H, 2 Bpin rotamers), 1.18–1.07 (m, 3H); ^{13}C{^{1}H} NMR (151 MHz, toluene-d_8, 80 °C) δ 154.4, 83.4, 78.2, 57.0, 28.9, 28.6, 26.8, 25.2, 24.8, 24.3, 21.4; ^{11}B NMR (160 MHz, $CDCl_3$) δ 32.5; GCMS $C_{15}H_{25}BNO_4$ calcd $[M\text{-}tBu]^{+\cdot}$ 294.19 found 294.20. ^{1}H and ^{13}C{^{1}H} NMR data are consistent with those previously reported,[9] however that report only tabulated data for one rotamer although both the rotamers are observed in the spectrum.[9]

*2-Cyclohexyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2p**).* General procedure B was followed with 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane (210 mg, 1 mmol), 5 % Rh/C (25 mg, 1 mol %) for 16 h. After purification solvent was removed by rotary evaporation to yield a clear oil (208 mg, 99% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.69–1.62 (m, 2H), 1.62–1.53 (m, 3H), 1.37–1.26 (m, 5H), 1.23 (s, 12H), 1.01–0.92 (m, 1H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 82.9, 28.1, 27.3, 26.9, 24.9; ^{11}B NMR (160 MHz, $CDCl_3$) δ 33.8. NMR data matched those previously reported.[9]

*3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexan-1-ol (**2q**).* General procedure B was followed with 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenol (**1q**) (110 mg, 0.5 mmol), 5 % Rh/C (25 mg, 2 mol %) for 16h. After purification solvent was removed by rotary evaporation to yield a clear oil (80 mg, 71% yield). A 1.2:1 mixture of diastereomers was obtained. The major product was assumed to be the cis isomer based on a comparison of its ^{1}H NMR to that of known[35] TMS protected **2q**. NMR data of the mixture are reported. ^{1}H NMR[67] (500 MHz, CDCl$_3$) δ 3.79 (s, 1H), 3.59 (s, 1H), 1.96 (d, *J* = 13.0 Hz, 1H), 1.93–1.82 (m, 2H), 1.82–1.70 (m, 2H), 1.70–1.60 (m, 2H), 1.55–1.44 (m, 3H), 1.44–1.32 (m, 6H), 1.23 (s, 24H), 1.20–1.11 (m, 1H), 1.00 (t, *J* = 11.3 Hz, 1H), 0.91–0.79 (m, 1H); ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 83.16, 83.13, 71.01, 68.29, 36.77, 35.99, 35.46, 34.50, 26.92, 26.78, 24.87, 24.83, 24.80; ^{11}B NMR (160 MHz, CDCl$_3$) δ 34.0. GCMS $C_{11}H_{20}BO_2$ calcd [M-OH-Me]$^{+\cdot}$ 195.16 found 195.05.

*4,4,5,5-Tetramethyl-2-(-3-(trifluoromethyl)cyclohexyl)-1,3,2-dioxaborolane (**2r**)*. General procedure B was followed with 4,4,5,5-tetramethyl-2-(3-(trifluoromethyl)phenyl)-1,3,2-dioxaborolane (136 mg, 0.5 mmol), 5 % Rh/C (25 mg, 2 mol %) for 16h. After purification solvent was removed by rotary evaporation to yield a clear oil (109 mg, 80% yield). Cis and trans diastereomers were observed via ^{19}F NMR in a 3:1 cis to trans ratio. ^{1}H NMR[66] (500 MHz, CDCl$_3$) δ 2.19–2.07 (m, 1H), 2.04–1.89 (m, 8H), 1.89–1.70 (m, 8H), 1.48–1.32 (m, 3H), 1.24 (s, 17H), 1.23 (s, 29H), 1.21–1.09 (m, 4H), 0.99–0.87 (m, 2H); ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 129.1 (q), 83.4, 83.3, 42.7 (q, *J* = 26.1 Hz), 40.2 (q, *J* = 25.8 Hz), 27.0, 26.9, 26.2 (q, *J* = 2.5 Hz), 26.0, 25.2 (q, *J* = 2.6 Hz), 25.0 (q, *J* = 2.9 Hz), 24.9 (d, *J* = 4.3 Hz), 24.9 (d, *J* = 3.3 Hz), 24.0; ^{19}F NMR (470 MHz, CDCl$_3$) δ –73.61 (d, *J* = 8.8 Hz, 1H), –74.03 (d, *J* = 8.3 Hz, 3H); ^{11}B NMR (160 MHz, CDCl$_3$) δ 33.7; GCMS calcd. for $C_{12}H_{19}BO_2F_3$ [M-Me]$^{+\cdot}$ 263.14, found 263.20

Cis and trans isomers were assigned by oxidation of the Bpin and then comparing spectra of the alcohols to those previously reported.[60] The proton peak on the OH bearing carbon appeared at 4.23 ppm (t, *J* = 3.29 Hz) (lit[60] 4.23 (brtt *J* = 3.5, 3.0 Hz) and for the cis isomer at 3.62 ppm (tt, *J* = 10.8, 4.2 Hz) (lit[60] 3.60 ppm (tt, *J* = 10.7, 4.2 Hz). The ratios of cis and trans isomers after oxidation (2.6:1) (cis:trans) was comparable to the ratio before oxidation.

*Ethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexane-1-carboxylate (**2s**)*. General procedure B was followed with ethyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (116 mg, 0.42 mmol), 5 % Rh/C (25 mg, 2 mol %) for 16 h. After purification solvent was removed by rotary evaporation to yield a clear oil (95 mg, 81% yield). ^{1}H-NMR showed both cis and trans diastereomers that were isolated as a mixture in a 3.3: 1 ratio. The major isomer was determined using 2D NMR and 1D NOE. The proton α to carboxyl group and the proton α to Bpin both showed NOEs with each other indicating a cis orientation. ^{1}H NMR[67] (500 MHz, $CDCl_3$) δ 4.15–4.02 (m, 7H), 2.44–2.34 (m, 1H), 2.26–2.12 (m, 4H), 1.99 (d, *J* = 13.3 Hz, 4H), 1.90 (d, *J* = 12.8 Hz, 5H), 1.83–1.75 (m, 5H), 1.73 (d, *J* = 13.0 Hz, 4H), 1.68–1.58 (m, 4H), 1.56–1.42 (m, 5H), 1.40–1.27 (m, 12H), 1.25–1.17 (m, 57H), 1.14 (dt, *J* = 12.8, 3.0 Hz, 3H), 1.13–1.06 (m, 1H), 0.92 (dt, *J* = 11.4, 3.2 Hz, 3H), 0.87–0.78 (m, 1H) $^{13}C\{^1H\}$ NMR(126 MHz, $CDCl_3$) δ 176.4, 176.3, 83.1, 60.1, 44.3, 41.4, 30.4, 29.5, 29.1, 29.0, 27.2, 27.1, 26.5, 24.9, 24.9, 24.8, 24.8, 24.5, 14.4, 14.3; ^{11}B NMR (160 MHz, $CDCl_3$) δ 33.2; GCMS calcd. for $C_{14}H_{24}BO_4$ $[M\text{-}Me]^{+\cdot}$ 267.18, found 267.20.

*4,4,5,5-Tetramethyl-2-(3-methylcyclohexyl)-1,3,2-dioxaborolane (**2t**).* General procedure B was followed with 4,4,5,5-tetramethyl-2-(*m*-tolyl)-1,3,2-dioxaborolane (109 mg, 0.5 mmol), 5 % Rh/C (25 mg, 2 mol %) for 16 h. After purification, solvent was removed under vacuum to yield a clear oil (86 mg, 77% yield). The cis and trans diastereomeric ratio was 2.2:1 via NMR and 2.6:1 via GC. ^{1}H NMR[67] (500 MHz, $CDCl_3$) δ 2.17 (s, 1H), 1.77 (d, *J* = 13.0 Hz, 1H), 1.71 (d, *J* = 10.5 Hz, 8H), 1.67–1.55 (m, 5H), 1.43 (ddp, *J* = 10.1, 6.8, 3.3 Hz, 1H), 1.36–1.28 (m, 6H), 1.23 (s, 12H, Bpin, minor isomer), 1.22 (s, 26H, Bpin, Major isomer), 1.19 (t, *J* = 2.8 Hz, 1H), 1.12–1.05 (m, 4H), 0.92 (tt, *J* = 12.8, 2.7 Hz, 4H), 0.87 (d, *J* = 6.6 Hz, 4H), 0.84 (d, *J* = 6.5 Hz, 9H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 82.93, 82.87, 36.59, 36.06, 35.47, 35.14, 33.64, 30.98, 27.64, 27.58, 25.00, 24.93, 24.87, 24.86, 23.22, 22.46; ^{11}B NMR (160 MHz, $CDCl_3$) 33.8. GCMS calcd. for $C_{12}H_{22}BO_2$ $[M\text{-}Me]^{+\cdot}$ 209.17 found 209.20. The NMR data of the mixture were consistent with those previously reported.[9] Cis and trans isomer assignments were confirmed by oxidation of the Bpin and comparing the spectra of the alcohols to those previously reported.[61] The proton on the OH bearing carbon appeared at 4.05 ppm (1H, m) (lit[61] 4.06 (m)) for the trans isomer and 3.57 ppm (lit[61] 3.57 (m)) for the cis isomer. The cis and trans ratio after oxidation (3.3:1) was comparable to that before oxidation ratio (2.6:1, via GC).

*2-(3-Methoxycyclohexyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2u**).* General procedure B was followed with 2-(3-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (117 mg, 0.5 mmol), 5 % Rh/C (25 mg, 2 mol %) for 16 h. After purification, solvent was removed by rotary evaporation to yield a clear oil (104 mg with 22% (by GCMS) demethoxylated cyclohexane-Bpin, which corresponded to 82 mg of **2u** as a 5.6:1 cis/trans mixture (68% yield). For the cis isomer: ^{1}H NMR (500 MHz, CDCl$_3$) δ 3.33 (s, 3H), 3.08 (tt, *J* = 10.2, 4.0 Hz, 1H), 2.08 (d, *J* = 10.5 Hz, 1H), 1.97 (d, *J* = 13.8 Hz, 1H), 1.83–1.75 (m, 1H), 1.70–1.53 (m, 2H), 1.23 (s, 12H), 1.20–1.07 (m, 3H), 1.00–0.85 (m, 1H). (Note: The integration values reported were adjusted for the presence of overlapping signals from cyclohexane-Bpin.) ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 83.0, 80.0, 55.6, 32.9, 32.4, 27.1, 25.7, 24.8; ^{11}B NMR (160 MHz, CDCl$_3$) δ 33.8; HRMS (ESI) m/z calcd. for $C_{13}H_{25}BO_3Na$ $[M+Na]^{+\cdot}$ 263.1794 found 263.1806. NMR data match those previously reported.[14] Cis and trans isomer assignments were confirmed by oxidation of the Bpin and comparing the spectra of the alcohols to those previously reported.[62] The proton on the OH bearing carbon appeared at 3.69 ppm (dp, *J* = 8.1, 3.6 Hz) (lit[62] 3.71 ppm (tt, *J* = 8.2, 3.9 Hz)) for the cis isomer and at 3.99 ppm (tt, *J* = 7.9, 3.7 Hz) (lit[62] 4.02 ppm (tt, *J* = 7.9, 3.8 Hz) for the trans isomer. The cis and trans ratios after oxidation was found to be 3.3:1.

*Cis-1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexane (**2v**).* General procedure B was followed with 1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (**1v**) (165 mg, 0.5 mmol), 5% Rh/C (25 mg, 2 mol %) for 6 h. After filtration solvent was removed under reduced pressure, mixture purified over flash column chromatography (hexane as eluent) and concentrated and dried over rotovap to give colorless oil (106 mg, 88% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.69–1.49 (m, 5H), 1.49–1.35 (m, 5H), 1.22 (s, 24H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 82.9, 28.2, 27.0, 25.0, 24.9; ^{11}B NMR (160 MHz, $CDCl_3$) δ 34.0. NMR data were consistent with those previously reported.[37]

*2-(Trimethylsilyl)piperidin-1-ium (+)-camphorsulfonate (**2w**)*. General procedure B was followed with 2-bromo-6-(trimethylsilyl)pyridine (115 mg, 0.5 mmol), 5 % Rh/C (25 mg, 0.2 mol %), (+)-camphor sulfonic acid (CS) (116 mg, 0.5 mmol). After purification, solvent was removed under reduced pressure to give a colorless oil (181 mg, 76% yield). ^{1}H NMR (500 MHz, D_2O) δ 3.32–3.22 (m, 1H,), 3.17 (d, *J* = 14.8 Hz, 1H, CS), 2.84 (td, *J* = 13.0, 2.4 Hz, 1H), 2.74 (d, *J* = 14.9 Hz, 1H, CS), 2.62–2.52 (m, 1H), 2.41–2.16 (m, 2H, CS), 2.06 (t, *J* = 4.5 Hz, 1H, CS), 1.99–1.90 (m, 1H, CS), 1.90–1.85 (m, 1H, CS), 1.85–1.73 (m, 3H), 1.66–1.28 (m, 5H, CS + compound), 0.94 (s, 3H, CS), 0.73 (s, 3H, CS), 0.04 (s, 9H); ^{13}C{^{1}H} NMR (126 MHz, D_2O) δ 221.6 (CS), 58.3 (CS), 48.2, 48.0 (CS), 47.0 (CS), 46.4, 42.4 (CS), 42.1 (CS), 26.1 (CS), 24.3 (CS), 24.1, 22.8, 22.2, 18.8 (CS), 18.6 (CS), –4.9; ^{29}Si NMR (99 MHz, D_2O) δ 2.7; mp 122–124 °C; GCMS calcd for $C_8H_{19}NSi$ $[M\text{-}CS\text{-}H]^{+\cdot}$ 157.13 found 157.15.

*2-(Trifluoromethyl)-4-(trimethylsilyl)piperidine (**2x**)*. General procedure B was followed with 2-chloro-6-(trifluoromethyl)-4-(trimethylsilyl)pyridine (**1x**) (44 mg, 0.17 mmol), 5% Rh/Al_2O_3 (20 mg, 4.5 mol %) After purification, the solvent was removed by rotary evaporation. Adding ethyl acetate formed a white solid precipitate whuch was dried under vacuum (44 mg, 92% yield). ^{1}H NMR (500 MHz, D_2O) δ 4.02–3.92 (m, 1H), 3.57 (dd, *J* = 12.5, 4.0 Hz, 1H), 3.07 (td, *J* = 13.0, 3.3 Hz, 1H), 2.19 (d, *J* = 14.0 Hz, 1H), 1.94 (d, *J* = 14.8 Hz, 1H), 1.67–1.45 (m, 2H), 1.00 (tt, *J* = 13.3, 3.4 Hz, 1H), 0.01 (s, 9H); ^{13}C{^{1}H} NMR (126 MHz, D_2O δ 123.1 (d, *J* = 280.4 Hz), 57.1 (q, *J* = 31.5 Hz), 46.1, 22.5, 22.1, 19.8, –5.1; ^{19}F NMR (470 MHz, D2O) δ -75.47 (d, *J* = 6.6 Hz); ^{29}Si NMR (99 MHz, D_2O) δ 3.6; mp: decomposes at 237 °C; HRMS (ESI) m/z calcd. for $C_9H_{19}F_3NSi$ $[M\text{-}Cl]^{+\cdot}$ 226.1238 found 226.1239.

Stereochemistry was ascertained by 2D NMR and the cis geometry determined by a 1D-NOE experiment. Irradiation of the proton at the carbon with a CF_3 substituent showed enhancement of the proton at the carbon bearing TMS confirming the cis assignment.

*2-(Trifluoromethyl)-5-(trimethylsilyl)piperidine (**2y**).* General procedure B was followed with 2-chloro-5-(trifluoromethyl)-4-(trimethylsilyl)pyridine (**1y**) (126 mg, 0.5 mmol) , 5% Rh/C (25 mg, 2 mol %). After purification, solvent was removed by rotary evaporation to yield a yellow oil (90 mg (mixture), 15% yield of **2y**). A 5:1 ratio of desilylated to silylated product was observed in the ^{1}H NMR, which was confirmed by LCMS (226.3 m/z for silylated material and 154.1 m/z for desilylated material) and ^{19}F NMR. Spectral data of the mixture (**2y+ desilylated 2y**): ^{1}H NMR (500 MHz, D_2O) δ 4.46–4.14 (m, 1H), 4.09–3.97 (m, 5H), 3.53 (d, *J* =12.96, 5H), 3.40 (dd, *J* = 13.0, 4.2 Hz, 1H), 3.21–3.01 (m, 6H), 2.22 (s, 1H), 2.21–2.12 (m, 5H), 2.03–1.85 (m, 12H), 1.82–1.50 (m, 18H), 1.27–1.09 (m, 1H), 0.01 (d, *J* = 1.2 Hz, 9H); ^{13}C{^{1}H} NMR (126 MHz, D_2O) δ 123.75, 51.4, 51.2, 45.1, 43.6, 30.1, 21.4, 21.4, 21.3, 21.0, 20.6, 20.1, 17.7, –4.9; ^{19}F NMR (470 MHz, D_2O) δ –68.51 (d, *J* = 8.9 Hz), –75.55 (d, *J* = 6.8 Hz). ^{1}H-NMR data for the desilylated compound matched those previously reported.[63] ^{1}H NMR (500 MHz, D_2O) 4.09–3.97 (m, 1H), 3.53 (d, *J* = 13.0, 1H), 3.21–3.01 (m, 1H), 2.21–2.12 (m, 1H), 2.03–1.85 (m, 2H), 1.82–1.50 (m, 3H);^{19}F NMR (470 MHz, D_2O) δ –75.6 (d, *J* = 6.7 Hz).

*3-(2,3-Dihydrobenzofuran-2-yl)-1,1,1,3,5,5,5-heptamethyltrisiloxane (**2z**)*. General procedure B was followed with 3-(benzofuran-2-yl)-1,1,1,3,5,5,5-heptamethyltrisiloxane (**1z**) (169 mg, 0.5 mmol), 10 % Pd/C (20 mg, 3 mol %), ethanol (5 mL) for 16h. After purification, the solvent was removed by rotary evaporation to yield a yellowish oil (139 mg, 82% yield); ^{1}H NMR (500 MHz, C_6D_6) δ 7.04 (d, *J* = 7.3 Hz, 1H), 7.01–6.94 (m, 1H), 6.87–6.81 (m, 1H), 6.77 (td, *J* = 7.4, 1.0 Hz, 1H), 4.14 (t, *J* = 11.1 Hz, 1H), 3.15 (dd, *J* = 15.0, 11.4 Hz, 1H), 3.03 (dd, *J* = 15.0, 10.8 Hz, 1H), 0.21 (s, 3H), 0.16 (s, 9H), 0.10 (s, 9H); ^{13}C{^{1}H} NMR (126 MHz, C_6D_6) δ 161.2, 124.7, 120.0, 109.6, 75.0, 31.1, 1.5, 1.4, –2.9; ^{29}Si NMR (99 MHz, $CDCl_3$) δ 9.1, 9.3, –31.62; HRMS (APCI) m/z calcd. for $C_{15}H_{29}O_3Si_3$ $[M]^{+\cdot}$ 341.1425 found 341.1428.

*Cyclohexyltriethoxysilane (**2aa**)*[40]. General procedure B was followed with triethoxy(phenyl)silane (120 mg, 0.5 mmol), 5% Rh/Al_2O_3 catalyst (25 mg, 2 mol %). After purification, the solvent was removed by rotary evaporation to yield a colorless oil (95.8 mg, 78% yield). Per Reaxys the only IR data were previously reported.[64] ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.82 (q, *J* = 7.0 Hz, 6H), 1.77 (d, *J* = 11.4 Hz, 2H), 1.70 (d, *J* = 12.1 Hz, 2H), 1.67 (s, 1H), 1.32–1.25 (m, 2H), 1.22 (t, *J* = 7.0 Hz, 12H), 0.81 (tt, *J* = 12.5, 3.1 Hz, 1H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 58.6, 27.9, 27.0, 26.9, 23.0, 18.5; ^{29}Si NMR (99 MHz, $CDCl_3$) δ 48.5; GCMS for $C_{12}H_{26}O_3Si$ calcd $[M]^{+\cdot}$ 246.17 found 246.10.

*tert-Butyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2(trimethylsilyl)pyrrolidine-1-carboxylate (**2ab**).* General procedure B was followed with *tert*-butyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(trimethylsilyl)-1*H*-pyrrole-1-carboxylate) (**1ab**) (182 mg, 0.5 mmol), 5% Rh/C (25 mg, 2 mol %). After 16 h, the reaction had run to 40% conversion of **1ab** and was worked up. After filtration, solvent was removed by rotary evaporation. The resulting mixture was purified by silica flash column chromatography. Fractions containing the desired product were combined and the volatiles evaporated to yield a white solid (66 mg, 36% yield, 96:4 dr). Increasing the stirring speed from 300 rpm to 1000 rpm did not affect conversion. Increasing the pressure to 72 atm from 48 atm gave a 66% conversion and 60% yield. The reaction showed full conversion after 48 h with 4 mol % catalyst and 93–100% yields were obtained. The cis configuration of the compound was confirmed by 2D NMRs, COSY and 2D NOESY NMR. By 2D NOESY NMR, the peak at 2.93 ppm (H at C α to N with TMS) showed a stronger correlation with the neighboring proton at 1.96 ppm and a weaker correlation with the neighbor at 1.72 ppm. The peak at 1.96 ppm showed a correlation with the proton at 1.44 ppm whereas no correlation was observed with the proton at 1.72 ppm. Characterization of the major cis diastereomer: ^{1}H NMR (500 MHz, C_6D_6) δ 3.85 (t, *J* = 9.6 Hz, 1H), 3.40 (t, *J* = 11.4 Hz, 1H), 2.97–2.87 (m, 1H), 2.00–1.89 (m, 1H), 1.72 (q, *J* = 12.6 Hz, 1H), 1.41 (s, 10H), 0.95 (s, 12H), 0.20 (s, 9H); $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6) δ 154.3, 82.8, 77.8, 50.1, 49.3, 32.3, 28.3, 24.4, –1.8; ^{11}B NMR (160 MHz, C_6D_6) δ 33.4; ^{29}Si NMR (99 MHz, C_6D_6) δ 1.7; mp 85–87 °C. HRMS (ESI) m/z calcd. for $C_{18}H_{36}BNO_4Si$ $[M]^{+\cdot}$ 369.2506 found 369.2510.

*4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(trimethylsilyl)piperidin-1-ium bromide (**2ac**).* General procedure B was followed with 2-bromo-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6-(trimethylsilyl)pyridine (**1ac**) (178 mg, 0.5 mmol), 5% Rh/C (25 mg, 2 mol %). After purification, solvent was concentrated by rotary evaporation and the product precipitated by adding ethyl acetate. After drying under vacuum a white solid was obtained (83 mg, 46% yield). Structure determination was made by 2D NMRs and the cis stereochemistry was ascertained by 1D NOE. ^1H NMR (500 MHz, D_2O) δ 3.22 (d, *J* = 12.4 Hz, 1H), 2.78 (dt, *J* = 12.79 Hz, 2.45 Hz, 1H), 2.52 (dd, *J* = 13.2 Hz, 2.45, 1H), 1.80 (d, *J* = 14.4 Hz, 2H), 1.56–1.33 (m, 2H), 1.12 (s, 12H), 1.09 (s,1H), –0.02 (s, 9H); $^{13}C\{^1H\}$ NMR (126 MHz, D_2O) δ 75.5, 48.6, 46.7, 25.7, 23.7, 23.6, –5.01; ^{11}B NMR (160 MHz, D_2O) δ 31.2; ^{29}Si NMR (99 MHz, D_2O) δ 2.7; mp: decomposes at 230 °C; HRMS (ESI) m/z calcd. for $C_{14}H_{31}BNSiO_2$ calcd $[M\text{-}Br]^{+\cdot}$ 284.2217 found 284.2220.

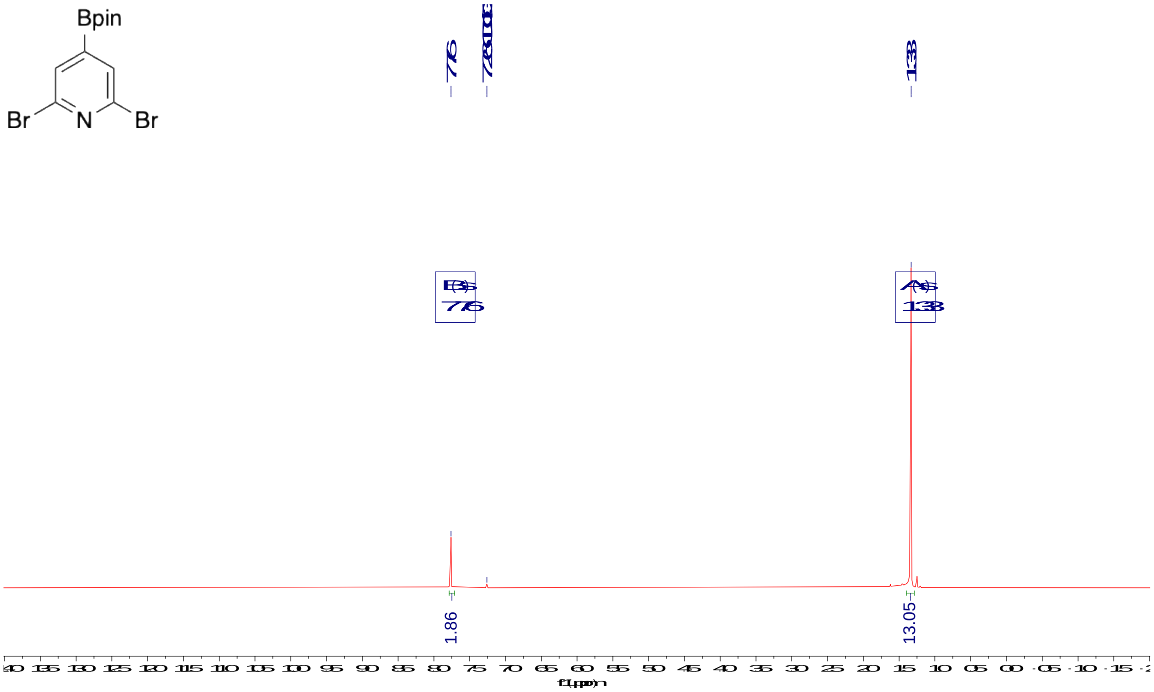
*Cis-trimethylsilyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexane (**2ad**).* General procedure B was followed with trimethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)silane (**1ad**) (138 mg, 0.5 mmol), 5% Rh/C (25 mg, 2 mol %) at 48 atm pressure for 6 h. After purification, solvent was removed under reduced pressure and the residue purified by flash column chromatography (diethyl ether/hexane 1-10% gradient). Fractions containing the desired product were combined and the volatiles evaporated to give a colorless oil (86% conversion, 17% yield). ^1H NMR (500 MHz, $CDCl_3$) δ 1.92–1.83 (m, 1H), 1.72 (dtt, *J* = 12.8, 3.6, 1.8 Hz, 1H), 1.65–1.58 (m, 1H), 1.58–1.50 (m, 1H), 1.48–1.25 (m, 4H), 1.24 (d, *J* = 3.6 Hz, 12H), 1.19 (dt, *J* = 12.3, 3.8 Hz, 1H), 0.71 (dt, *J* = 12.7, 3.3 Hz, 1H), –0.04 (s, 9H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 82.9, 31.1, 28.9, 26.3, 25.8, 25.1, 25.0, –1.8; ^{11}B NMR (160 MHz, $CDCl_3$) δ 34.1; ^{29}Si NMR (99 MHz, $CDCl_3$) δ 1.9. GCMS calcd. for $C_{14}H_{28}BO_2Si$ [M-Me]$^{+\cdot}$ 267.20 found 267.20. NMR data and the stereochemcal assignment were consistent with those previously reported.[10]

*Trimethyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexyl)silane (**2ae**).* General procedure B was followed with trimethyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)silane (**1ae**) (138 mg, 0.5 mmol), 5% Rh/C (25 mg, 2 mol %). After purification, the solvent was removed by rotary evaporation and compound obtained as a colorless liquid (141 mgs (with ~7% desilylated material observed via GC-MS)), which corresponded to 133.5 mg of **2ae** (95% yield). The major diastereomer was identified by oxidizing the boronic ester. The peak for the proton α to the OH in the cis isomer was observed at 3.55 ppm (sept) (lit[65] 3.42 ppm, sept) and the peak for proton α to OH was observed at 4.0 ppm (bs) (lit[65] 3.96 ppm (bs)) for the trans diastereomer. Cis/trans ratios were before (2.1:1) and after (2.5:1) oxidation were comparable. Data of the mixture: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.91–1.53 (m, 6H), 1.42–1.27 (m, 2H), 1.27–1.20 (m, 14H), 1.19 (d, *J*=10 Hz, 1H), 1.12–0.98 (m, 2H), 0.89 (t, *J* = 11.7 Hz, 1H), 0.53 (t, *J* = 12.6 Hz, 1H),–0.07 (s, 9H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 82.9, 82.8, 28.7, 28.7, 28.3, 28.3, 28.1, 28.0, 27.5, 27.3, 27.1, 26.9, 25.2, 25.2, 24.9, 24.9, 24.8, –3.3, –3.4; ^{11}B NMR (160 MHz, $CDCl_3$) δ 34.0; ^{29}Si NMR (99 MHz, $CDCl_3$) δ 2.1, 2.3; GCMS for $C_{14}H_{28}BO_2Si$ [M–Me]$^{+\cdot}$ calcd 267.20 found 267.20. The NMR data were consistent with those previously reported.[10]

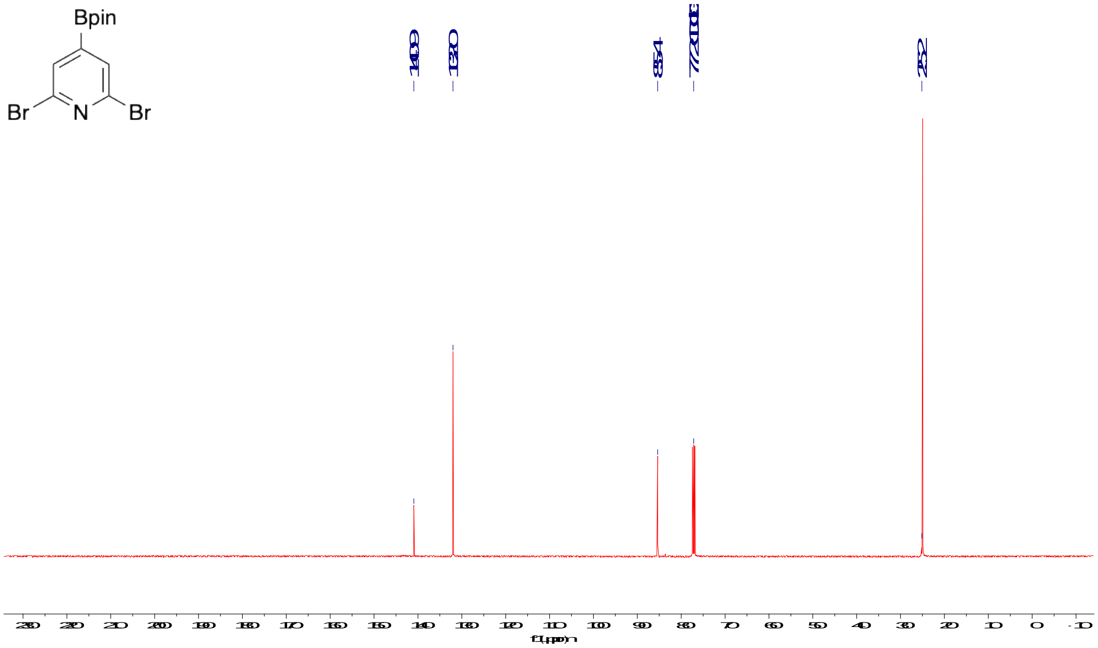
*Trimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexyl)silane (**2af**).* General procedure B was followed with trimethyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)silane (**1af**) (138 mg, 0.5 mmol), 5% Rh/C (25 mg, 2 mol %) at 48 atm pressure for 8.5 h. After purification, solvent was removed under reduced pressure to obtain a colorless oil (138 mg, 98% yield). A 4.5:1 cis to trans ratio was observed by ^{1}H NMR and 6:1 via GC. Data for the major cis diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.95–1.86 (m, 2H), 1.64–1.55 (m, 2H), 1.41–1.30 (m, 3H), 1.25 (s, 12H), 1.15 (qd, J = 12.8, 3.3 Hz, 2H), 0.56–0.47 (m, 1H), –0.09 (s, 9H).$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 83.0, 29.2, 26.2, 25.9, 25.0, –3.5. ^{11}B NMR (160 MHz, $CDCl_3$) δ 34.6; ^{29}Si NMR (99 MHz, $CDCl_3$) δ 2.4, 2.2. ^1H-NMR data were consistent with those previously reported.[10] (Note: The major diastereomer was identified by oxidizing the boronic ester. The differentiable peak for the proton α to the OH in the cis isomer was observed at 4.05 ppm (s, 1H) (lit[66] 4.07 ppm (s, 1H)). The proton α to the OH in the trans isomer was observed at 3.54–3.46 ppm (m, 1H) (lit[66] 3.58–3.52 ppm (m, 1H)). By ^1H NMR the cis:trans ratios were comparable before (4.5:1) and after (4.4:1) oxidation.

4.5. SPECTRAL DATA

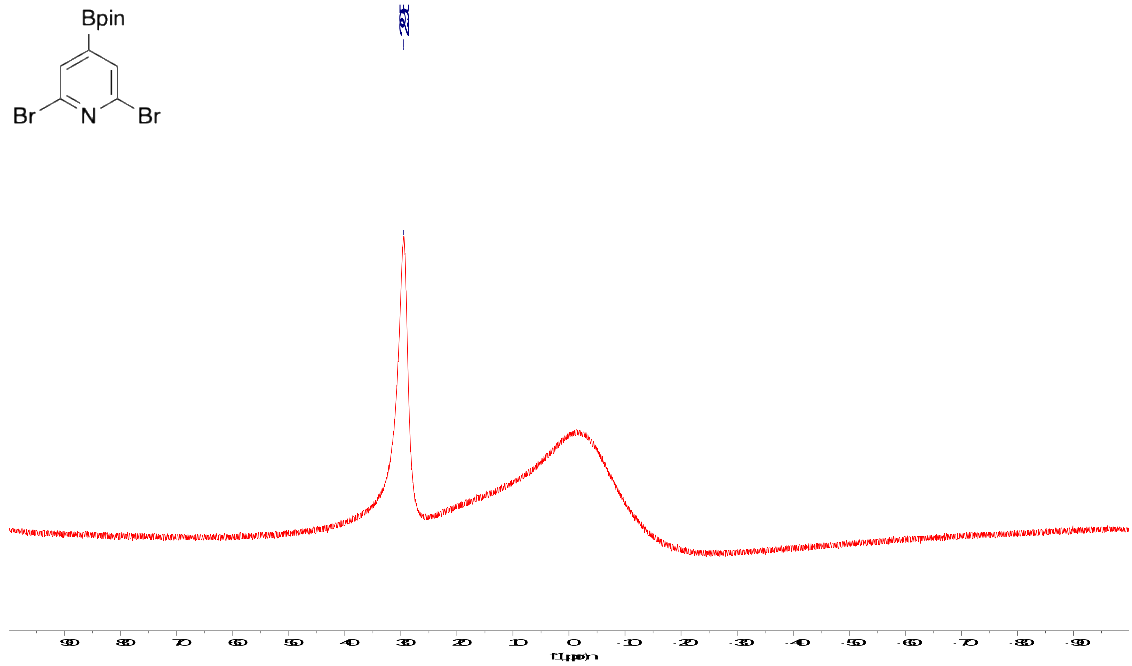
^{1}H NMR (500MHz, $CDCl_3$) of 2,6-dibromo-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (1d)



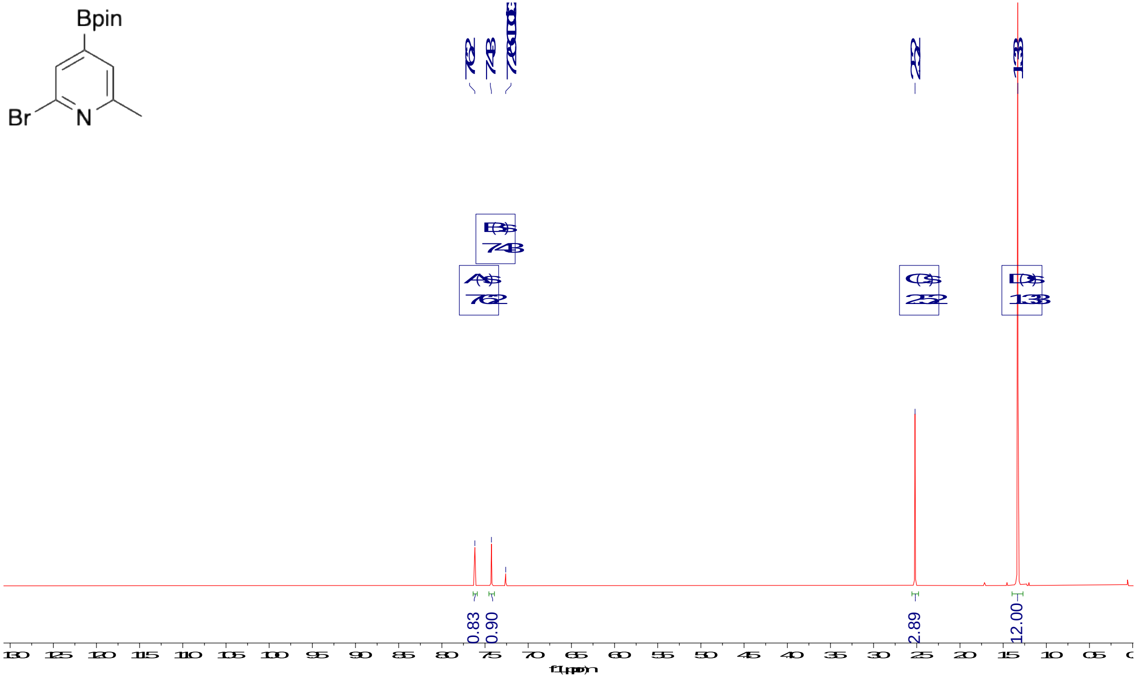
^{13}C{^{1}H} (126 MHz, $CDCl_3$) NMR of 2,6-dibromo-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (1d)



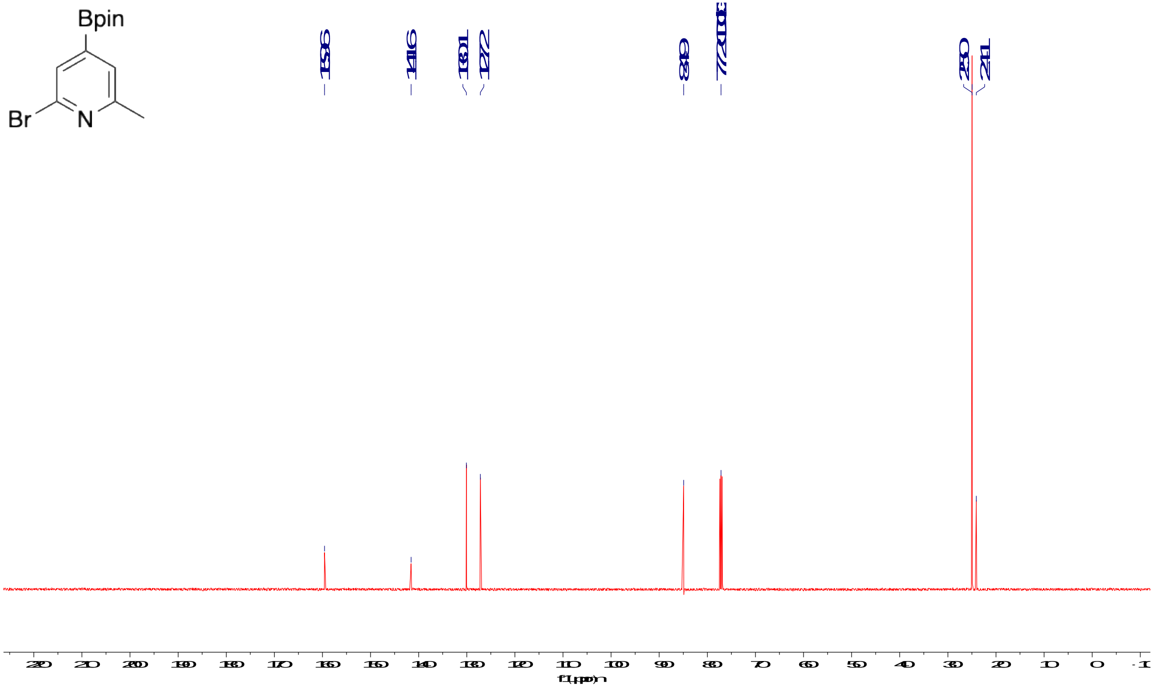
^{11}B NMR (160MHz, $CDCl_3$) of 2,6-dibromo-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (1d)



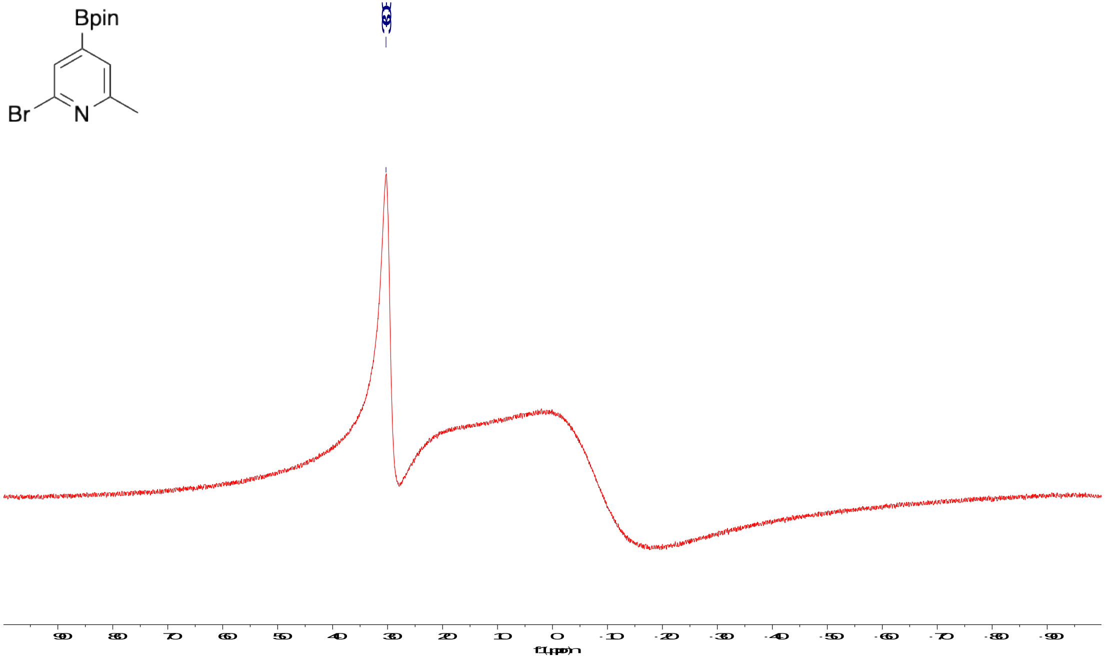
^{1}H NMR (500MHz, $CDCl_3$) of 2-bromo-6-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (1e)



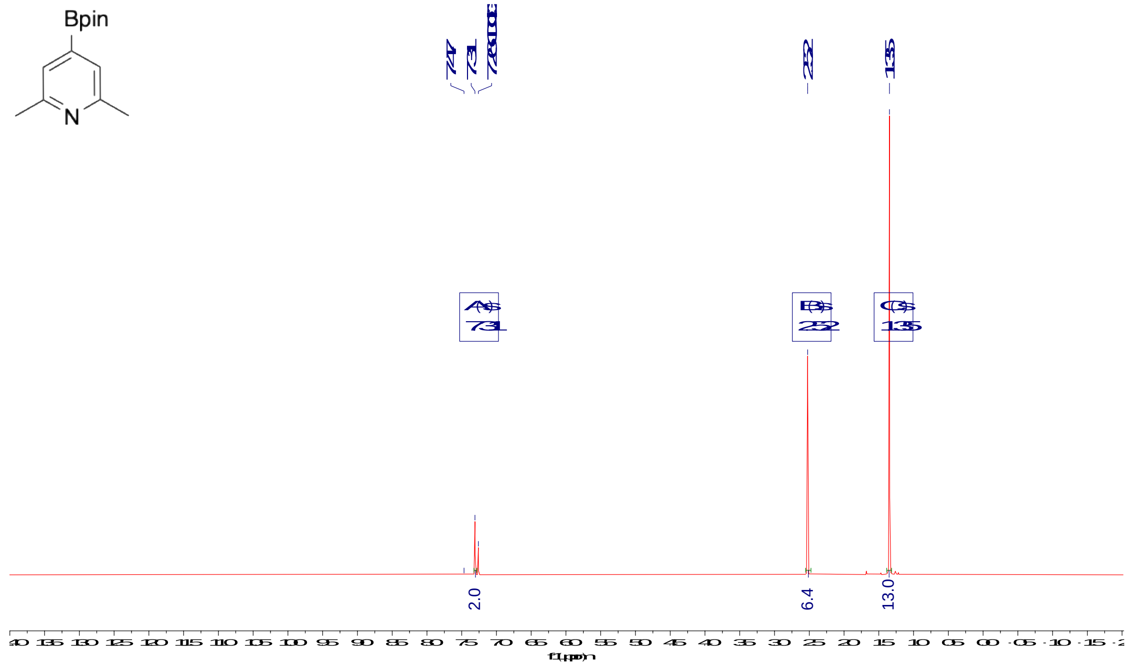
$^{13}C\{^{1}H\}$ (126 MHz, $CDCl_3$) NMR of 2-bromo-6-methyl-4-(4,4,5,5-tetramethyl-1,3,2 dioxaborolan-2-yl)pyridine (1e)



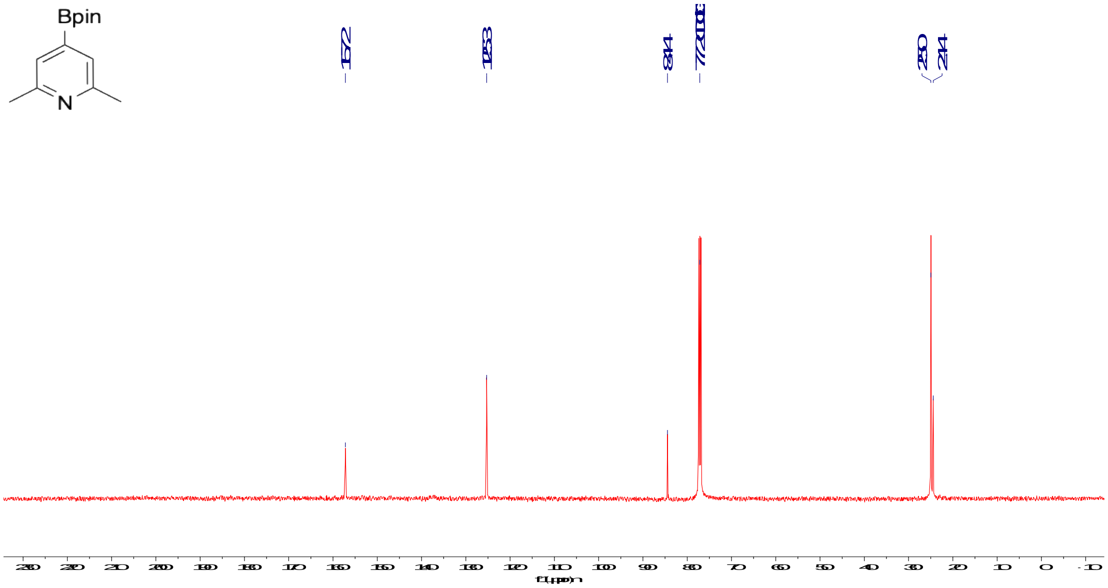
^{11}B NMR (160MHz, $CDCl_3$) of 2-bromo-6-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (1e)



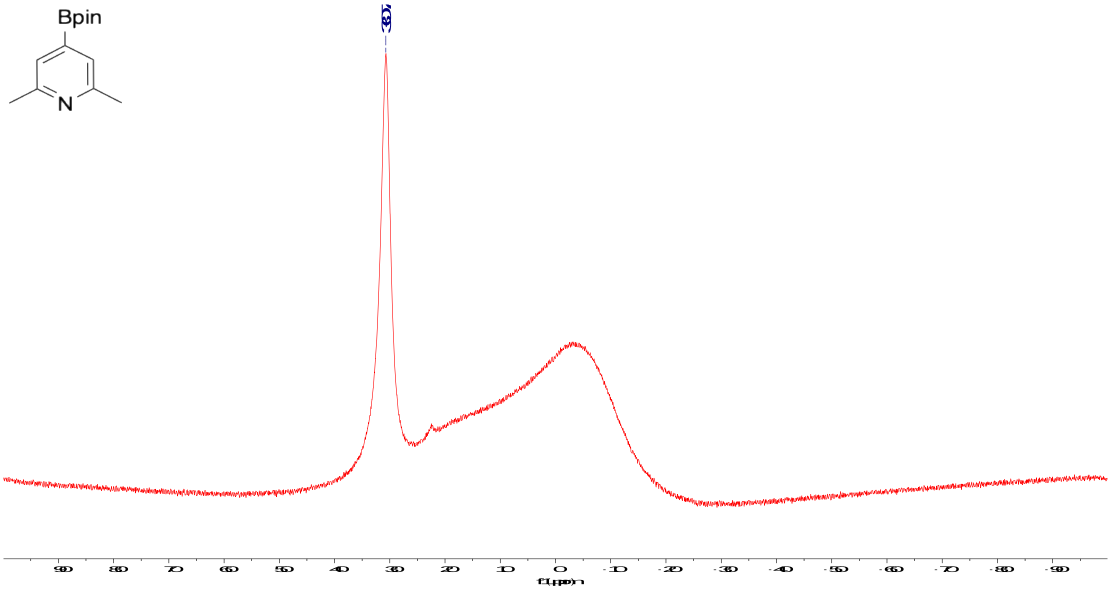
^{1}H NMR (500MHz, CDCl$_3$) of 2,6-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (1f)



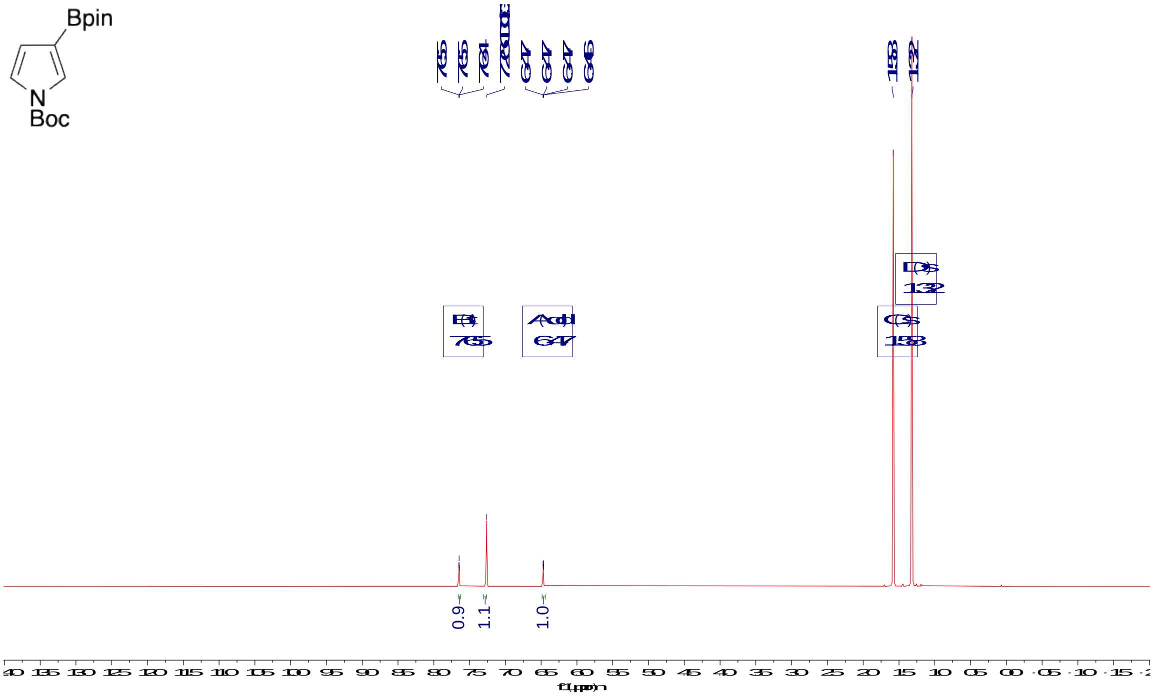
^{13}C{^{1}H} (126 MHz, CDCl$_3$) NMR of 2,6-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (1f)



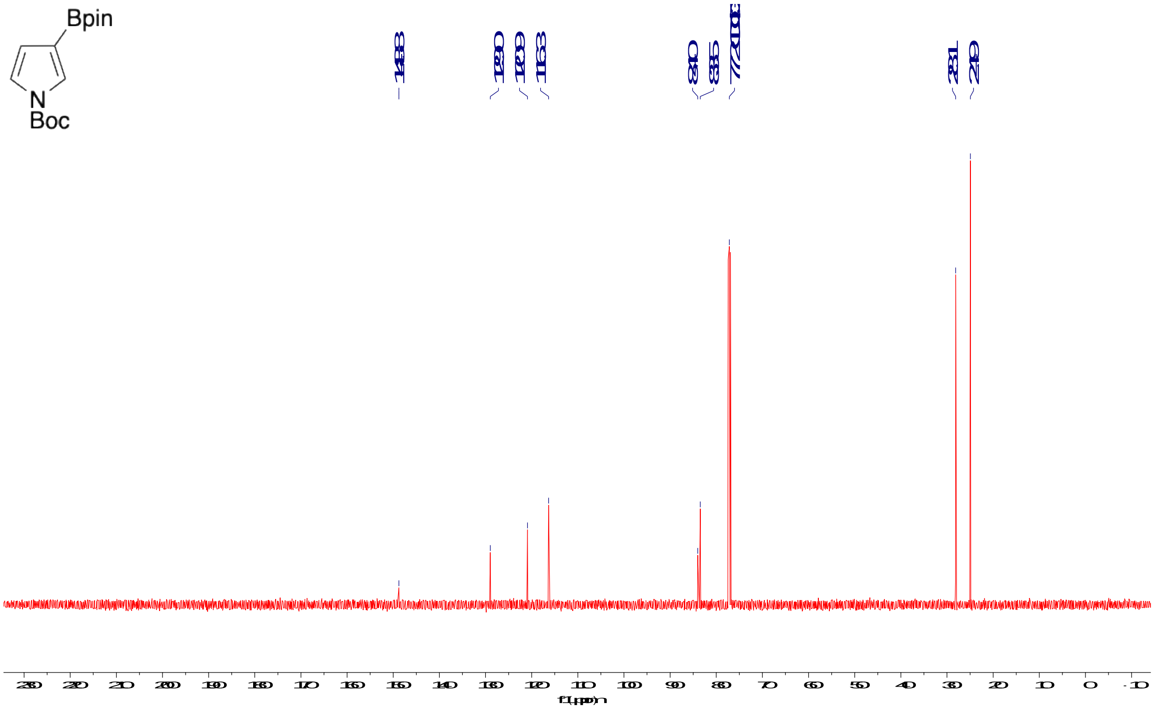
^{11}B NMR (160MHz, CDCl$_3$) of 2,6-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (1f)



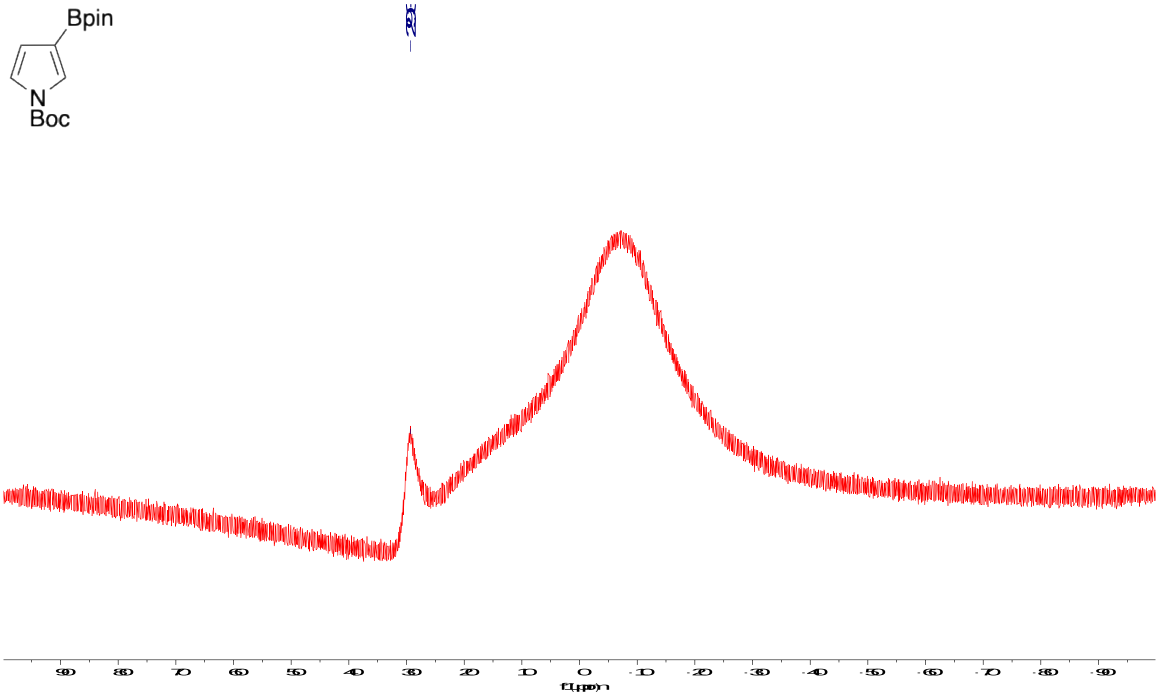
^{1}H NMR (500MHz, CDCl$_3$) of *Tert*-butyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-pyrrole-1-carboxylate (1g)



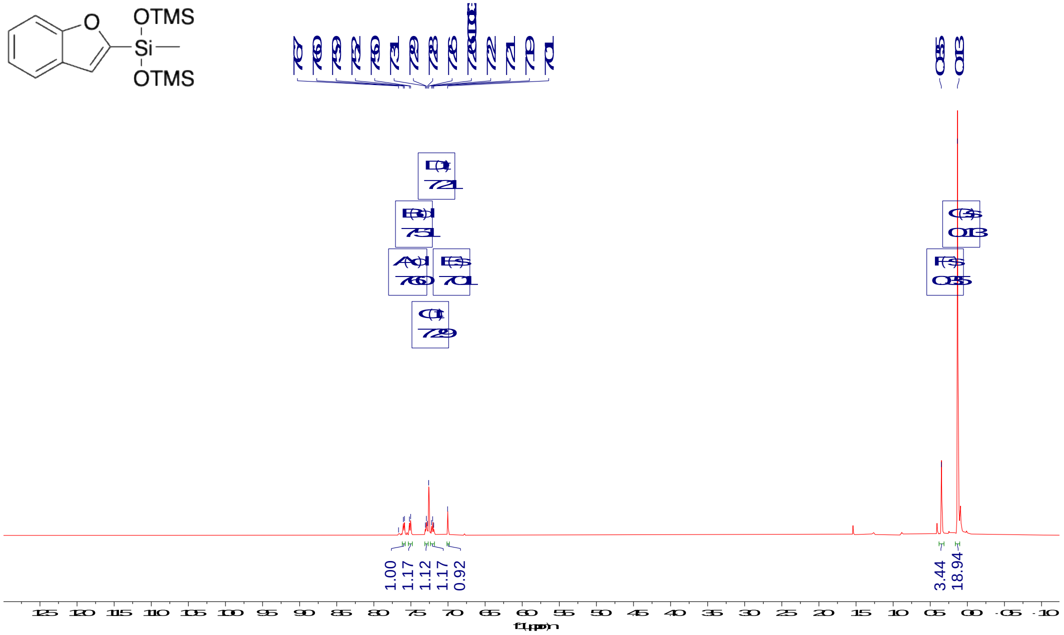
$^{13}C\{^{1}H\}$ (126 MHz, $CDCl_3$) NMR of *Tert*-butyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-pyrrole-1-carboxylate (1g)



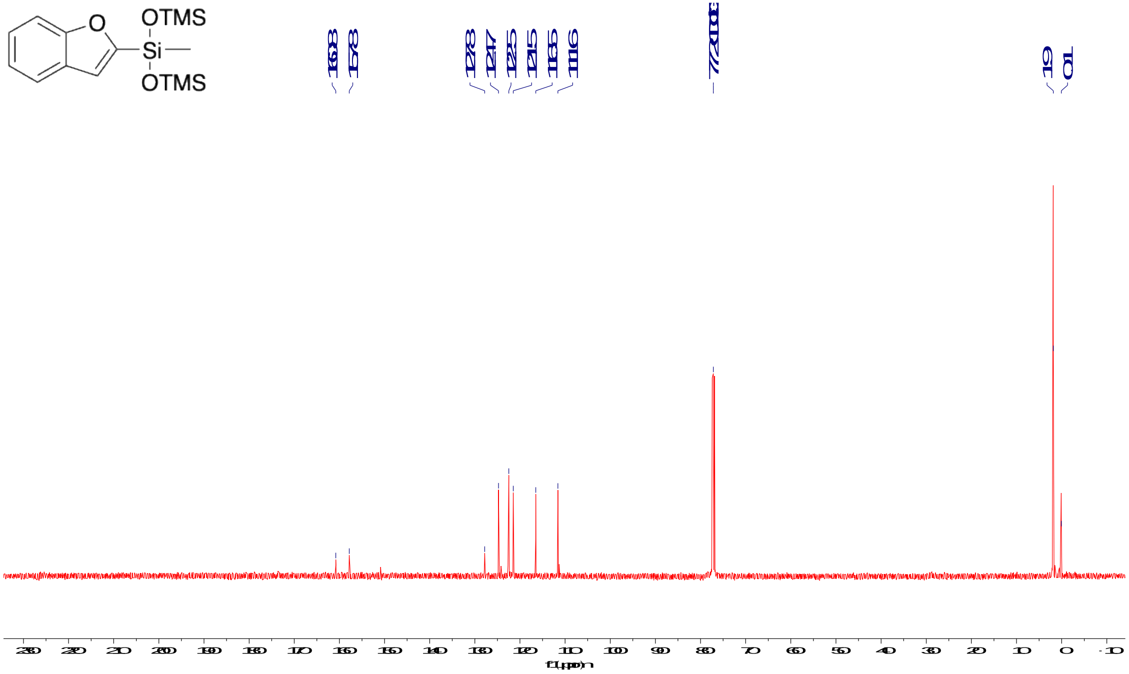
^{11}B NMR (160MHz, $CDCl_3$) of *Tert*-butyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-pyrrole-1-carboxylate (1g)



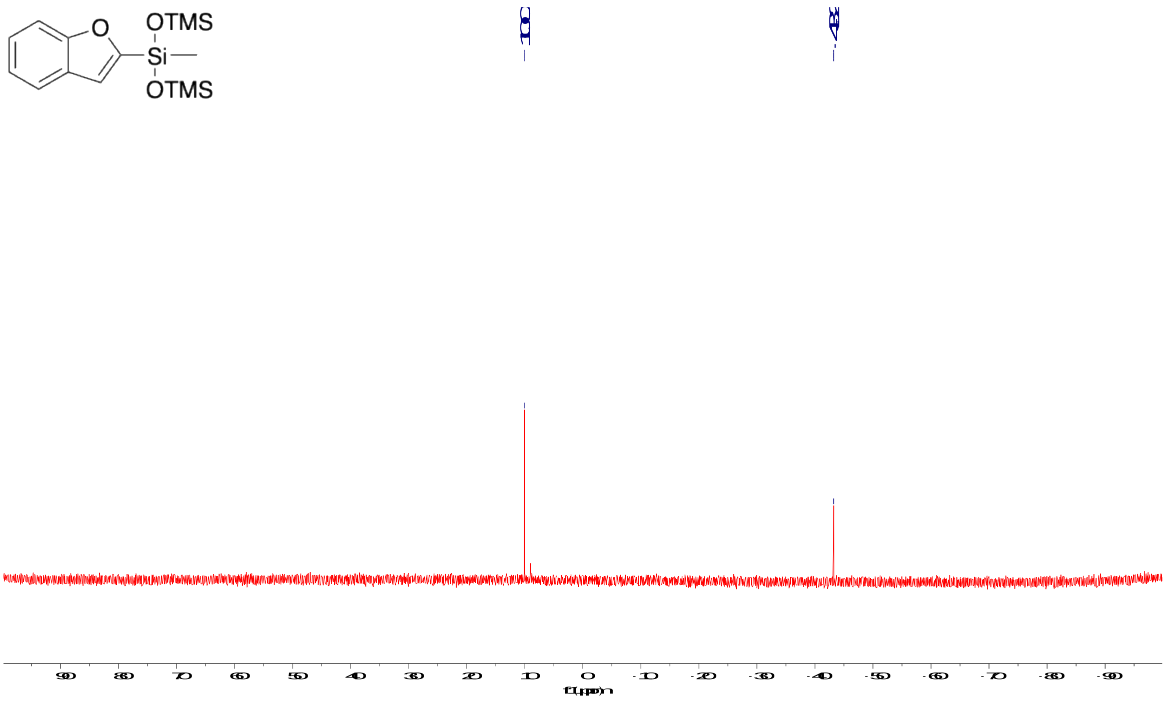
^1H NMR (500 MHz, $CDCl_3$) of 3-(benzofuran-2-yl)-1,1,1,3,5,5,5-heptamethyltrisiloxane (1z)



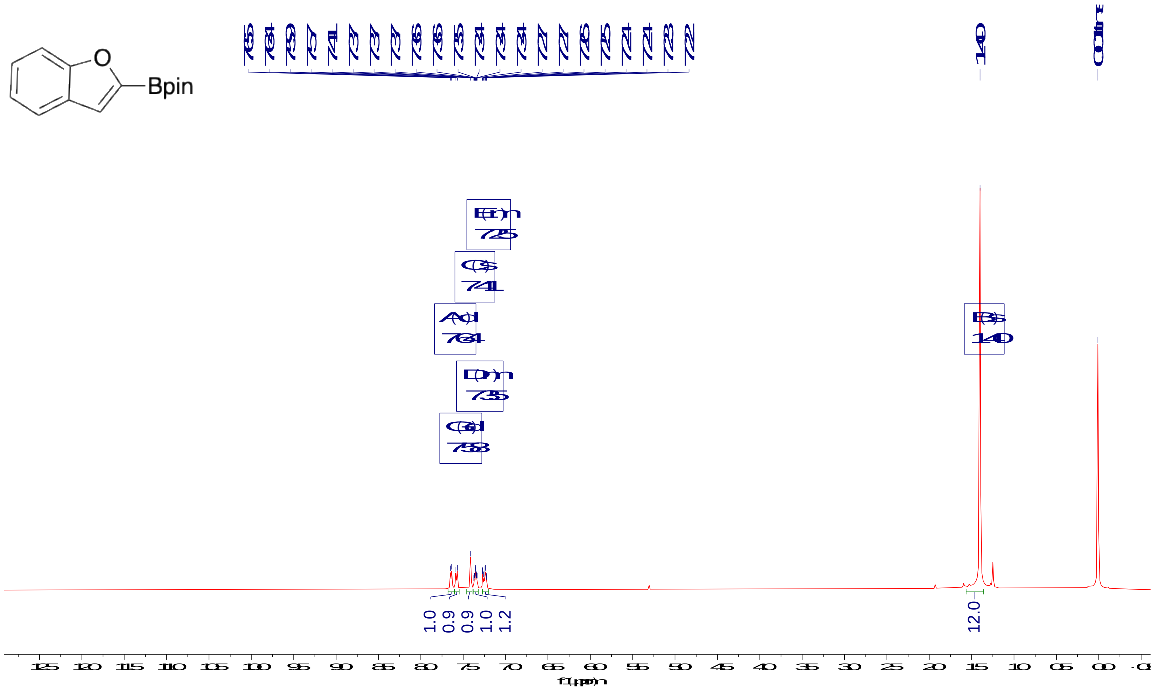
$^{13}C\{^1H\}$ (126 MHz, $CDCl_3$) NMR of 3-(benzofuran-2-yl)-1,1,1,3,5,5,5-heptamethyltrisiloxane (1z)



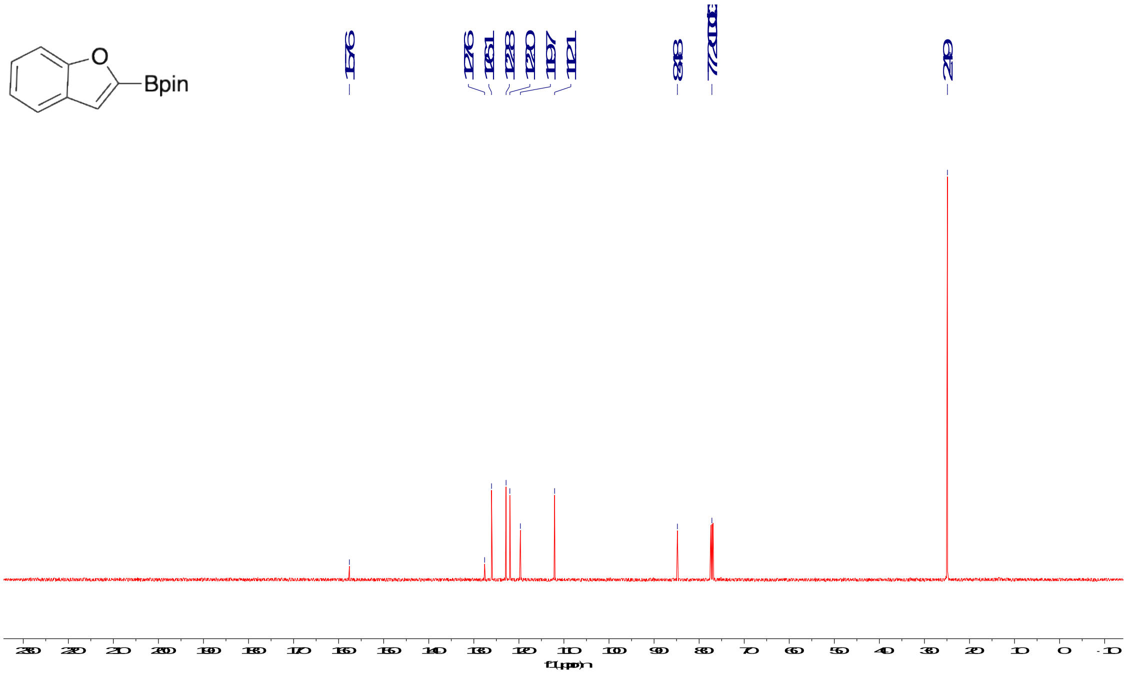
^{29}Si NMR (99MHz, CDCl$_3$) of 3-(benzofuran-2-yl)-1,1,1,3,5,5,5-heptamethyltrisiloxane (1z)



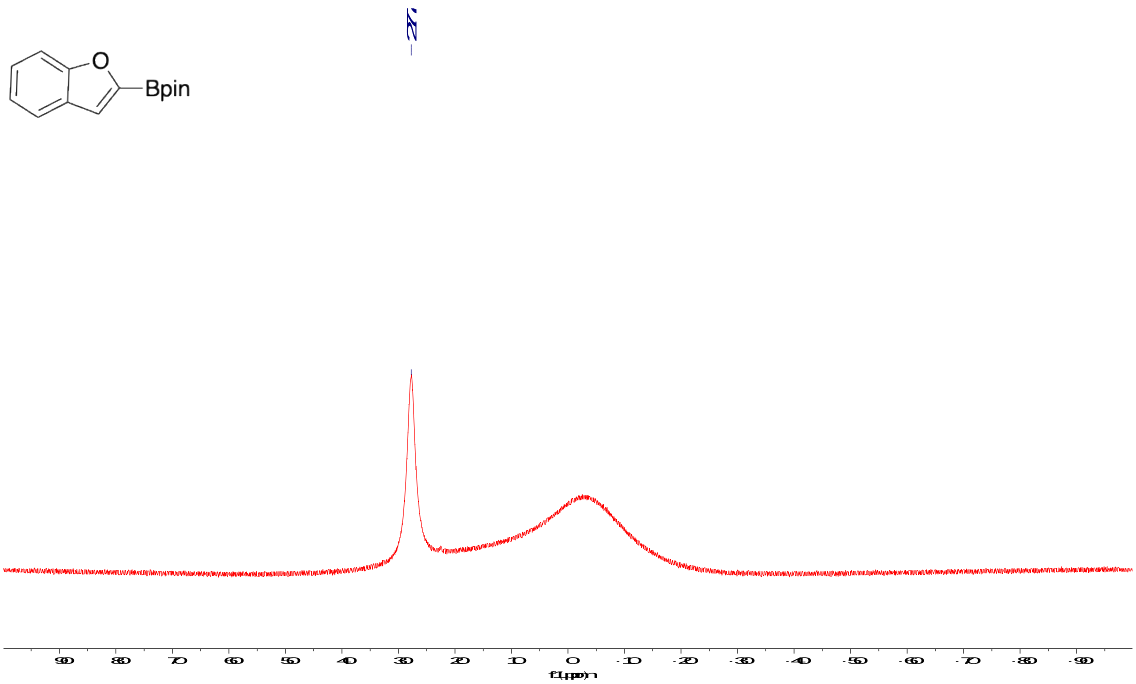
^{1}H NMR (500 MHz, CDCl$_3$) of 2-(benzofuran-7-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1j)



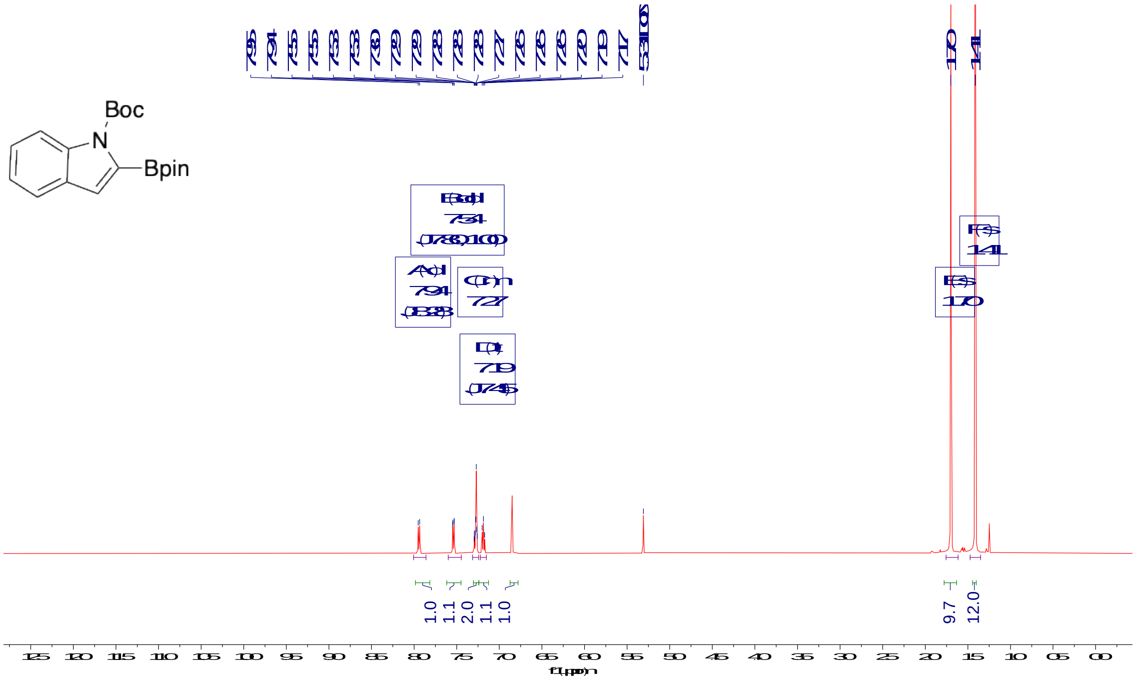
$^{13}C\{^1H\}$ (126 MHz, $CDCl_3$) NMR of 2-(benzofuran-7-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1j)



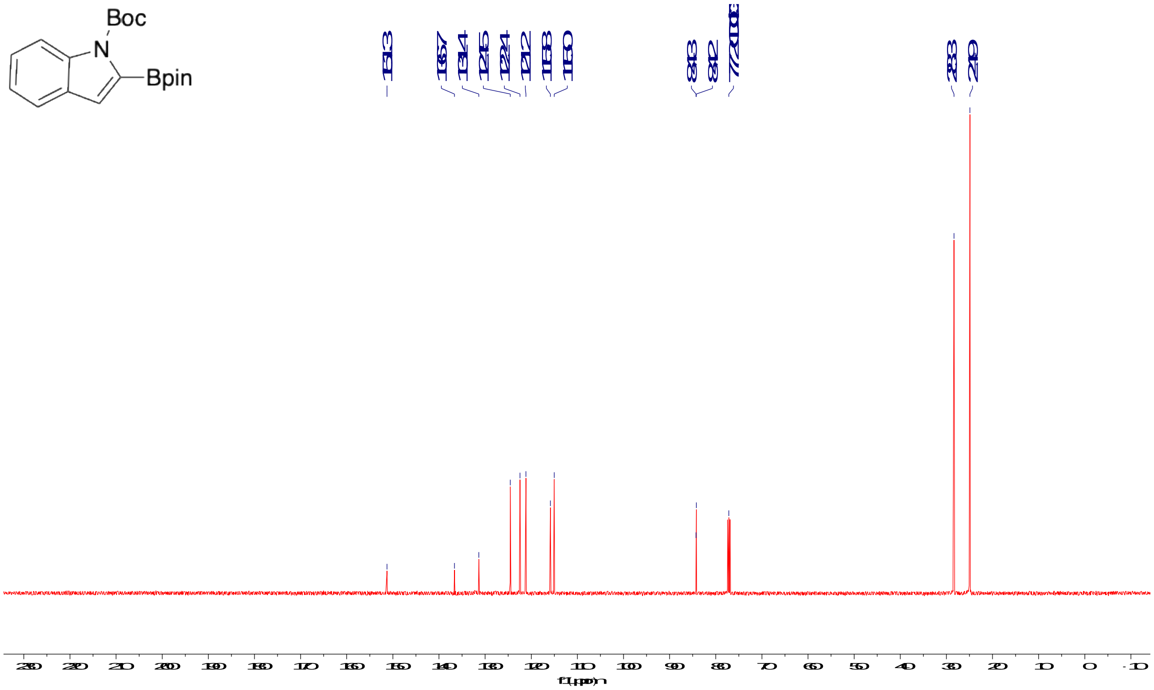
^{11}B NMR (160MHz, $CDCl_3$) of 2-(benzofuran-7-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1j)



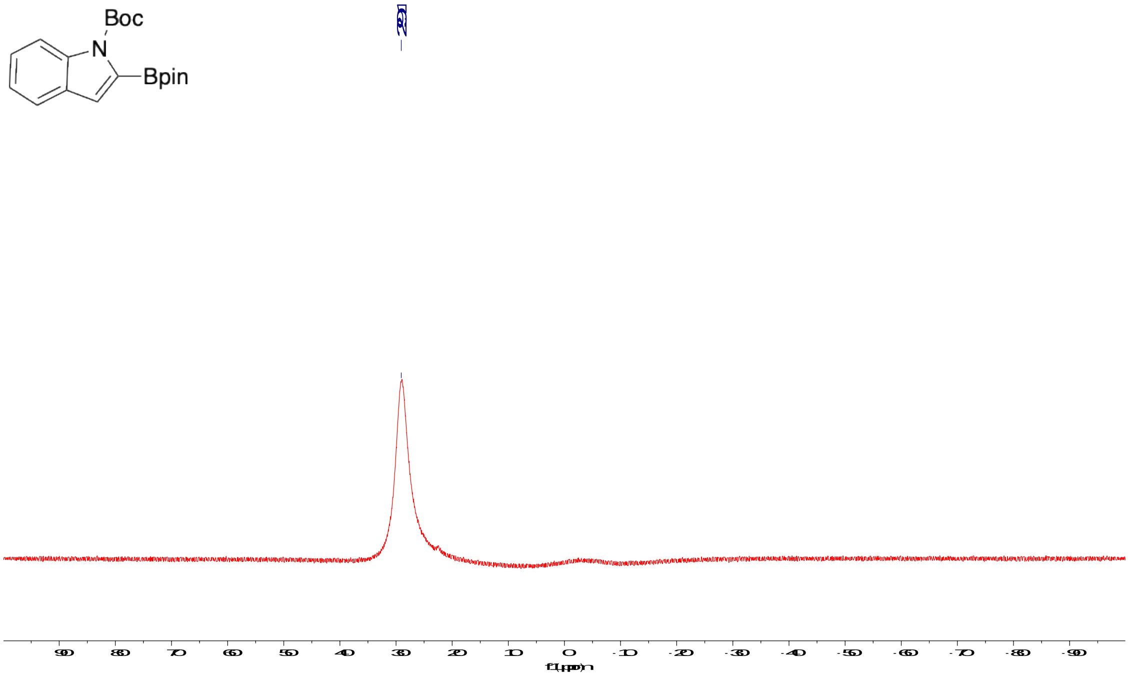
^{1}H NMR (500MHz, $CDCl_3$) of *tert*-Butyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole-1-carboxylate (1l)



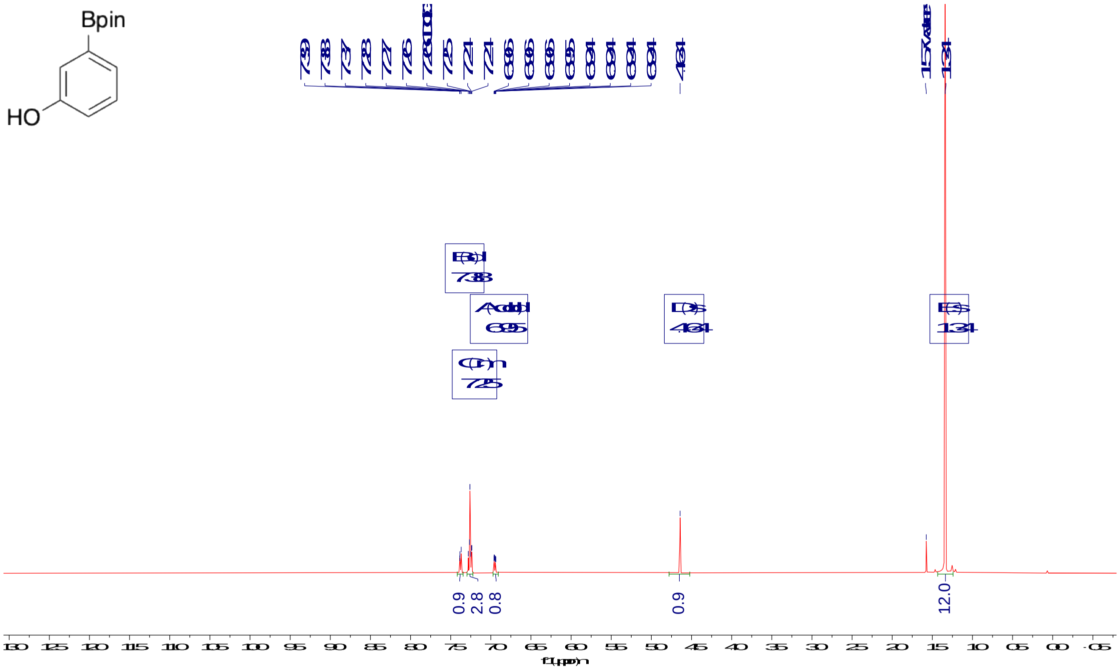
$^{13}C\{^1H\}$ (126 MHz, $CDCl_3$) NMR of *tert*-Butyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole-1-carboxylate (1l)



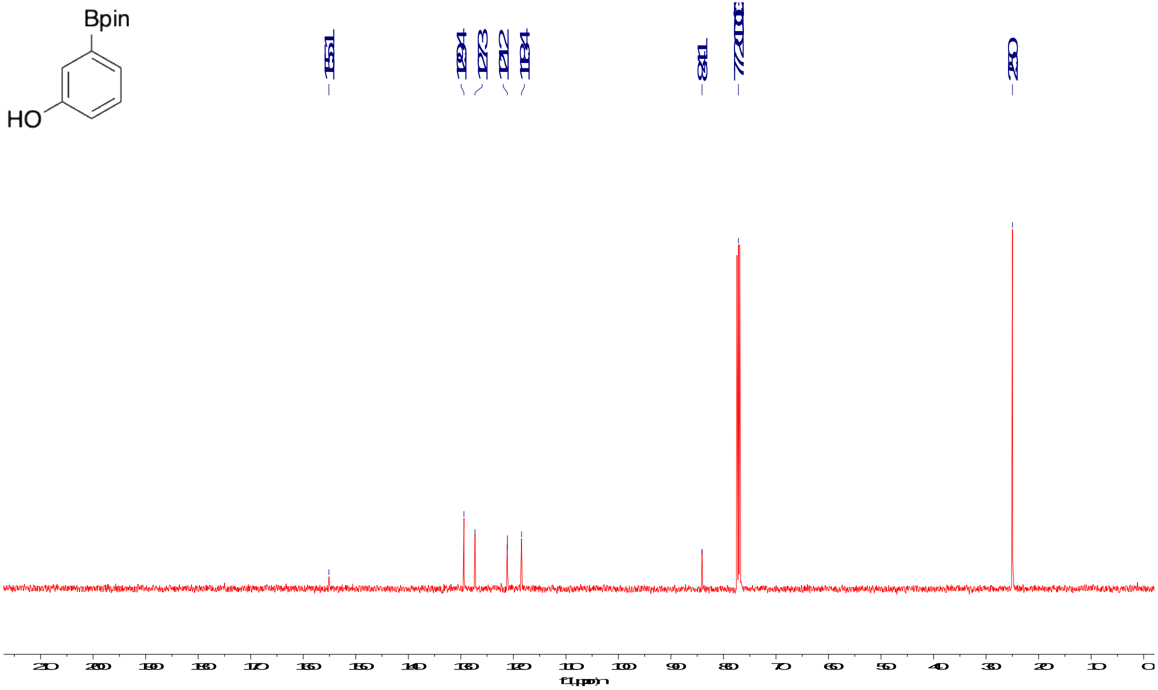
^{11}B NMR (160MHz, CDCl$_3$) of *tert*-Butyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole-1-carboxylate (1l)



^{1}H NMR (500MHz, CDCl$_3$) of 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenol (1q)

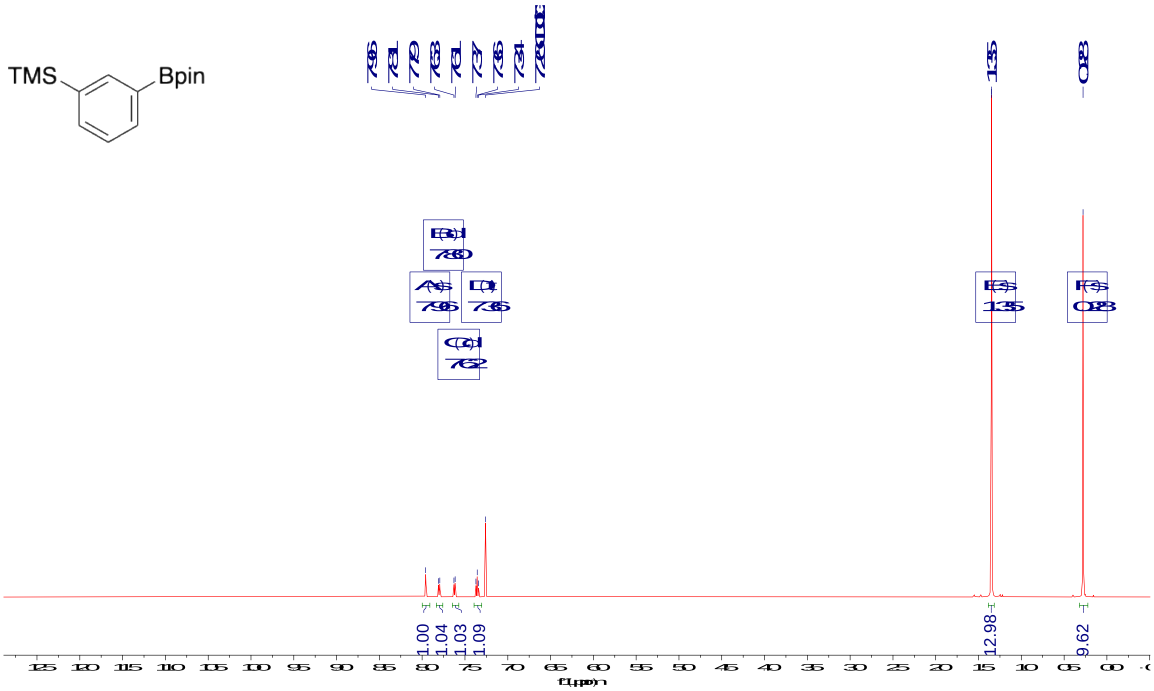


$^{13}C\{^{1}H\}$ (126 MHz, $CDCl_3$) NMR of 3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenol (1q)

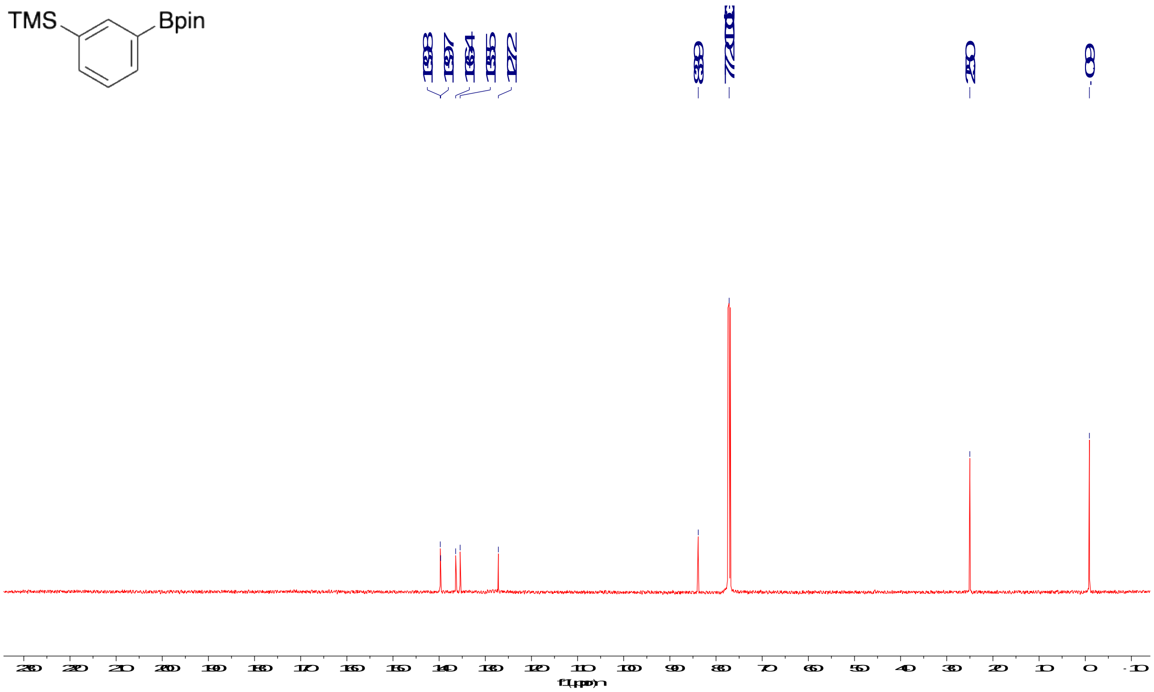


^{11}B NMR (160 MHz, $CDCl_3$) of 3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenol (1q)

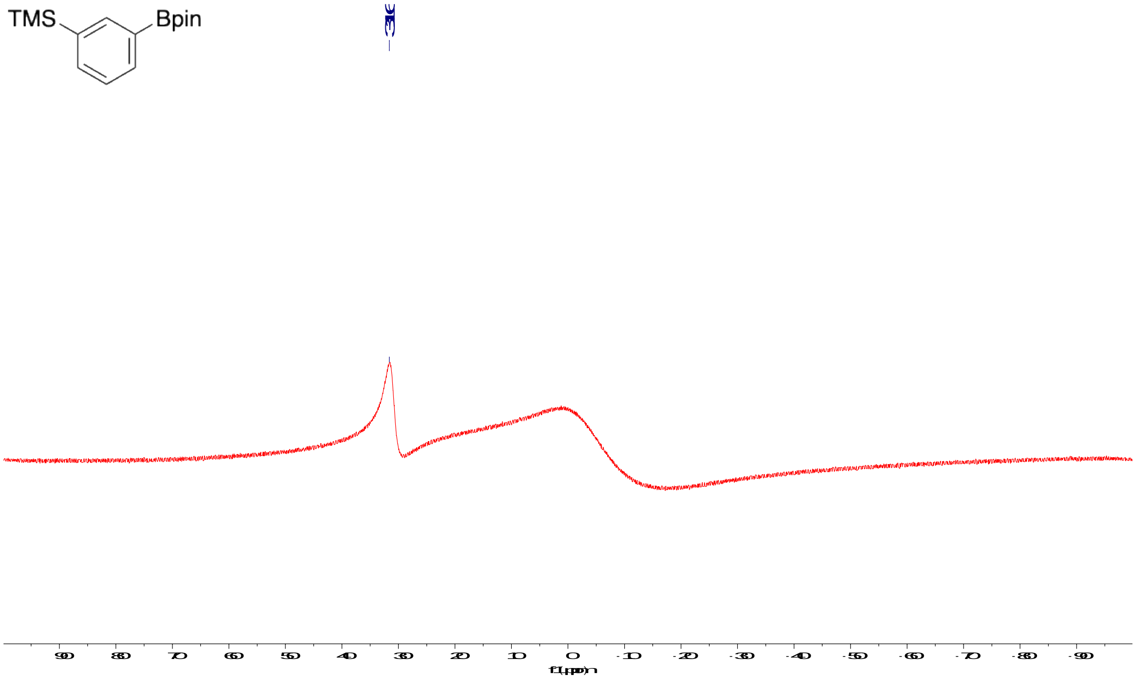
^{1}H NMR (500 MHz, CDCl$_3$) of trimethyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)silane (1ae)



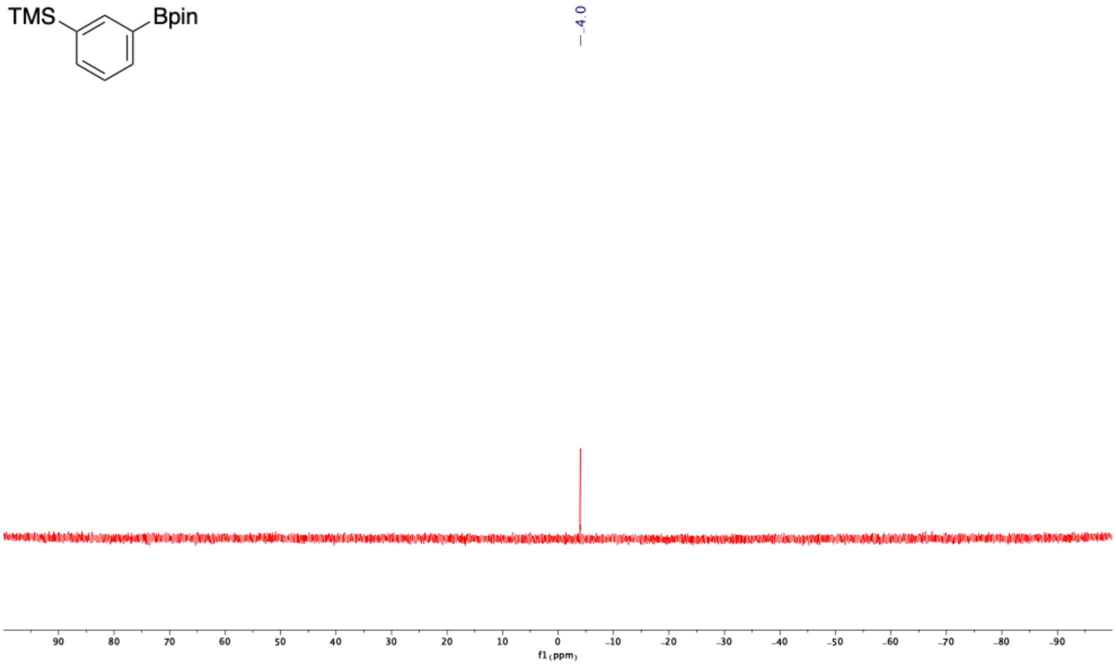
^{13}C{^{1}H} (126 MHz, CDCl$_3$) NMR of trimethyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)silane (1ae)



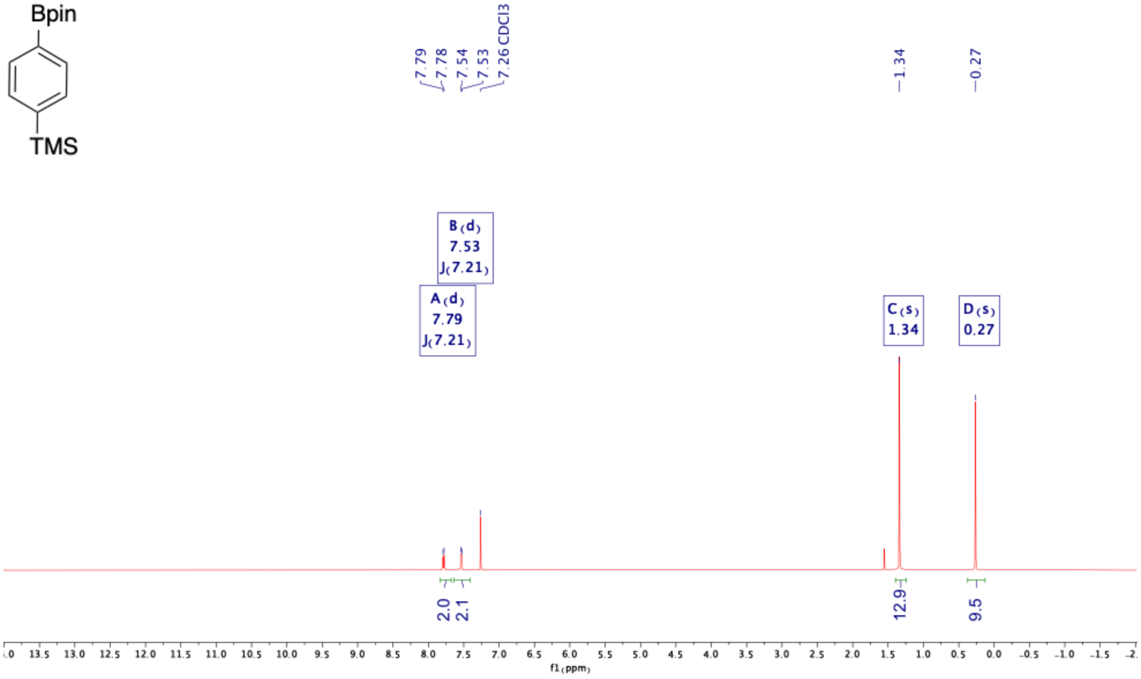
^{11}B NMR (160 MHz, CDCl$_3$) of trimethyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)silane (1ae)



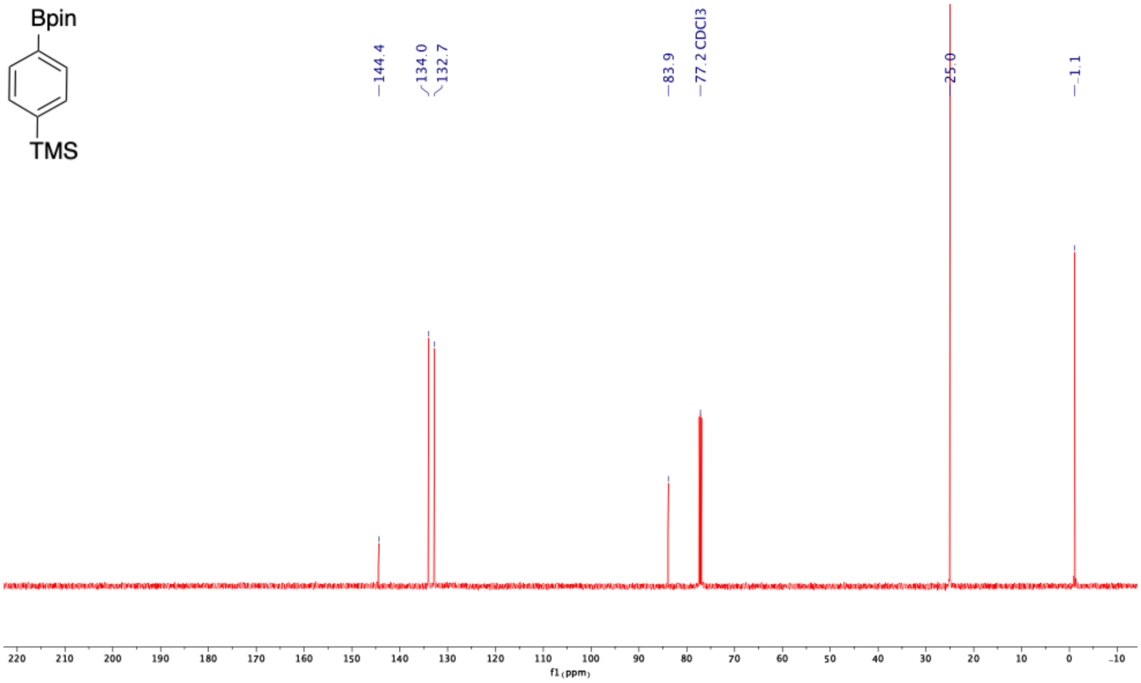
^{29}Si NMR (99 MHz, CDCl$_3$) of trimethyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)silane (1ae)



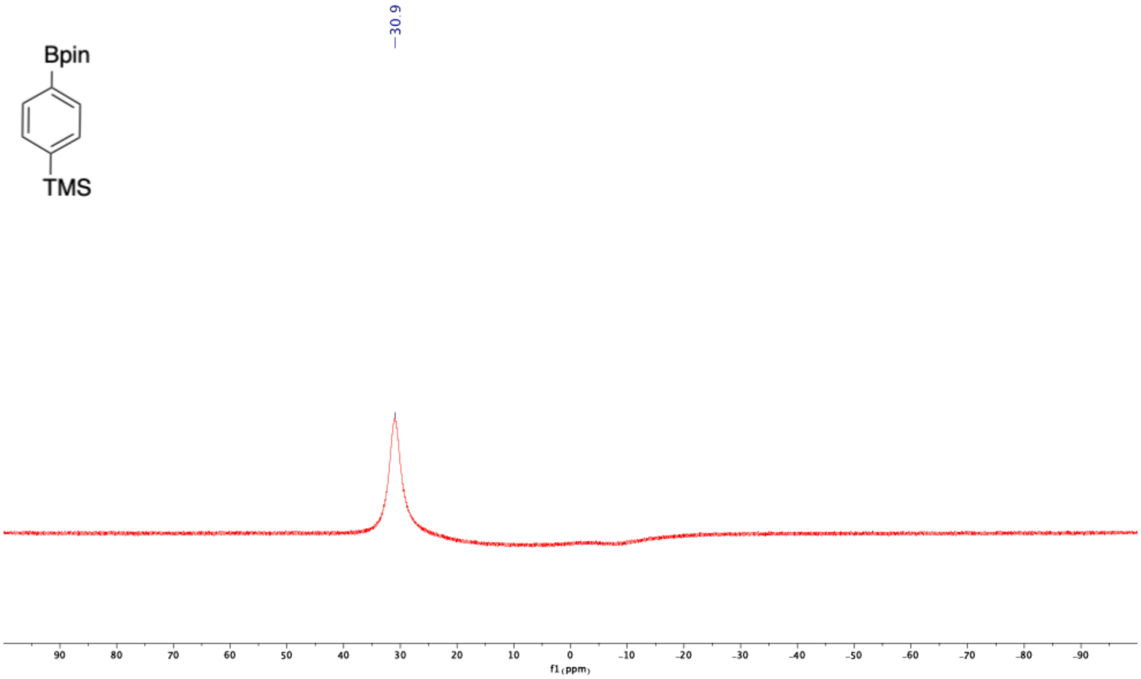
^{1}H NMR (500 MHz, $CDCl_3$) of trimethyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)silane (1af)



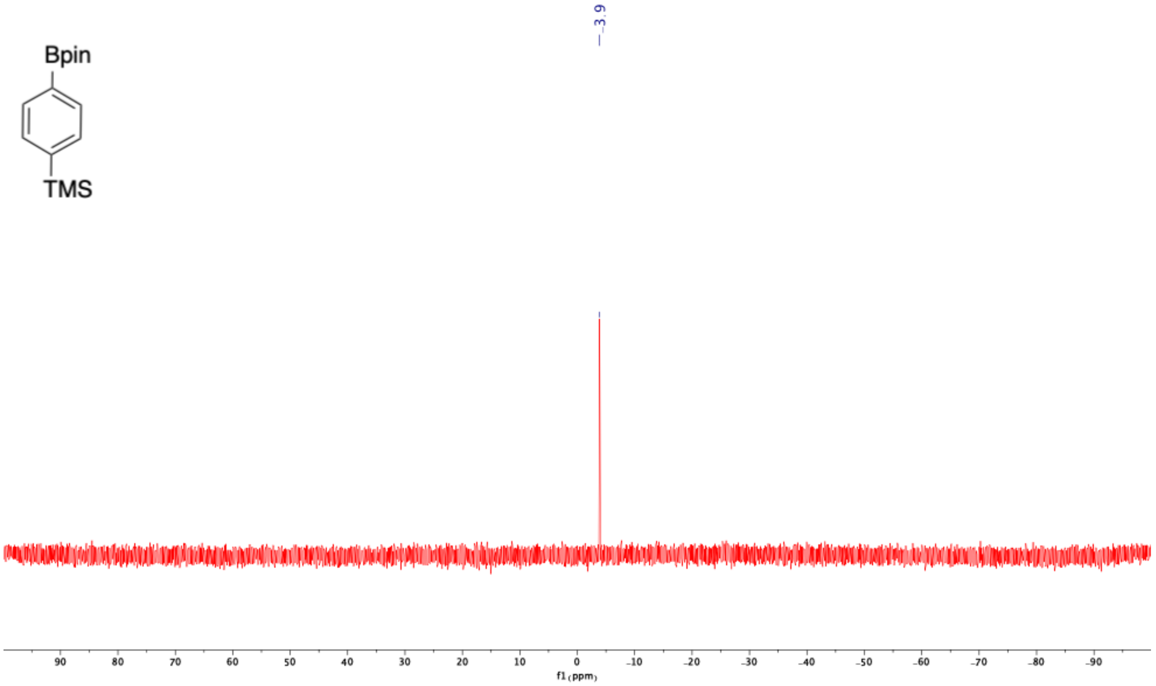
$^{13}C\{^1H\}$ (126 MHz, $CDCl_3$) NMR of trimethyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)silane (1af)



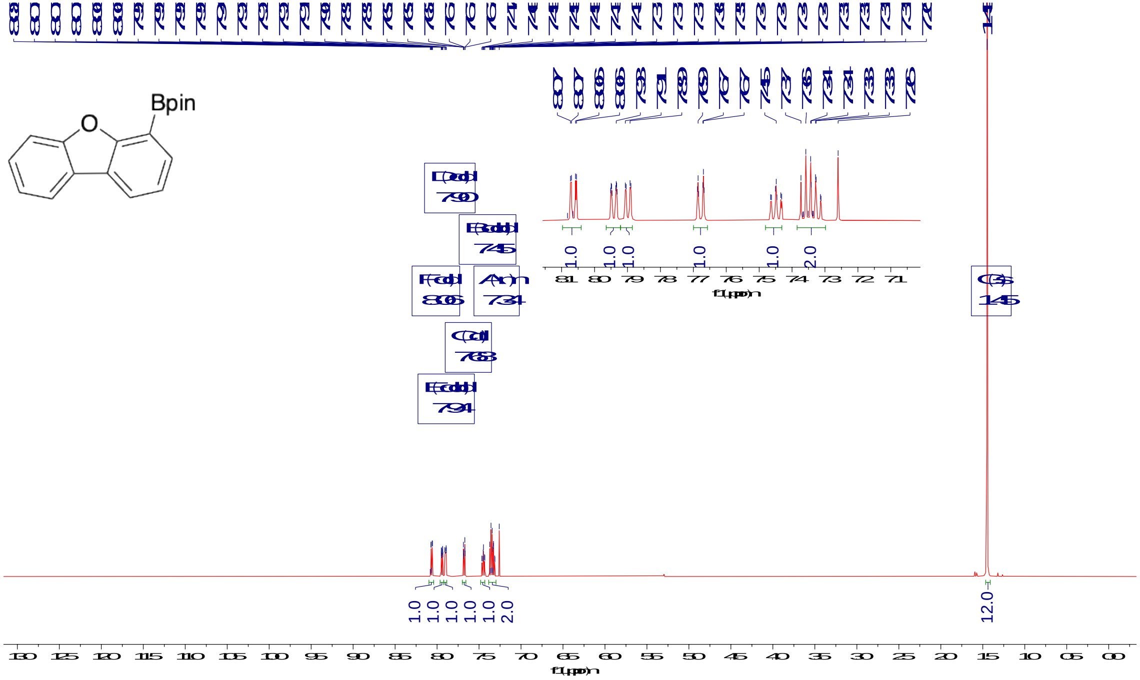
^{11}B NMR (160 MHz, CDCl$_3$) of trimethyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)silane (1af)



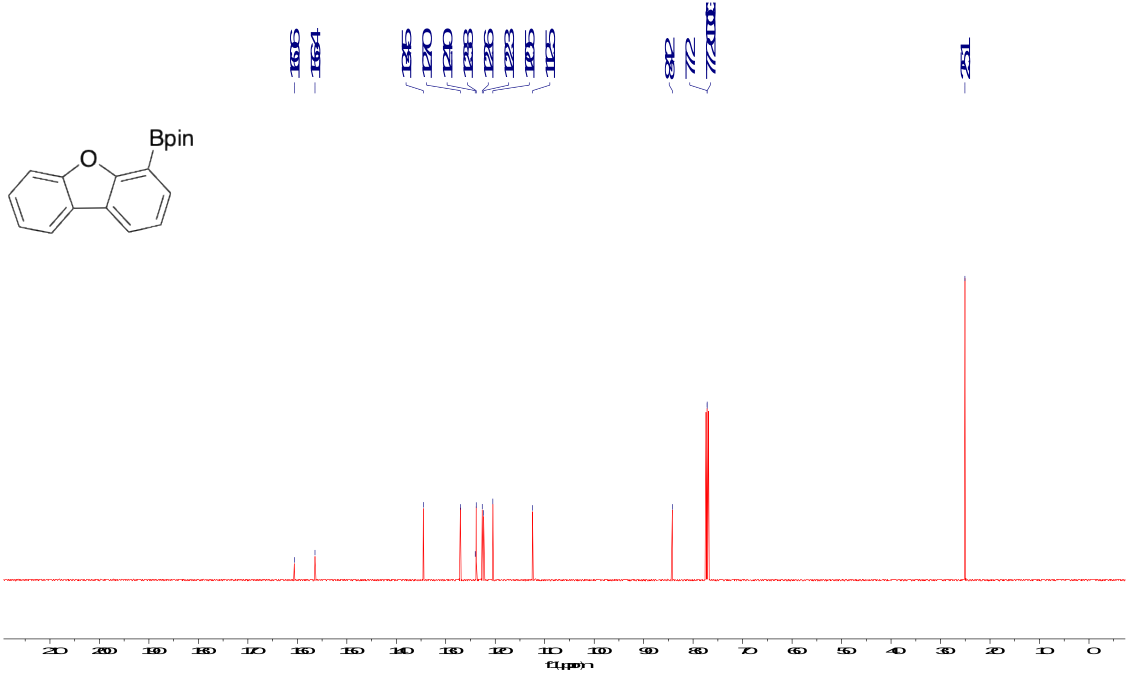
^{29}Si NMR (99 MHz, CDCl$_3$) of trimethyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)silane (1af)



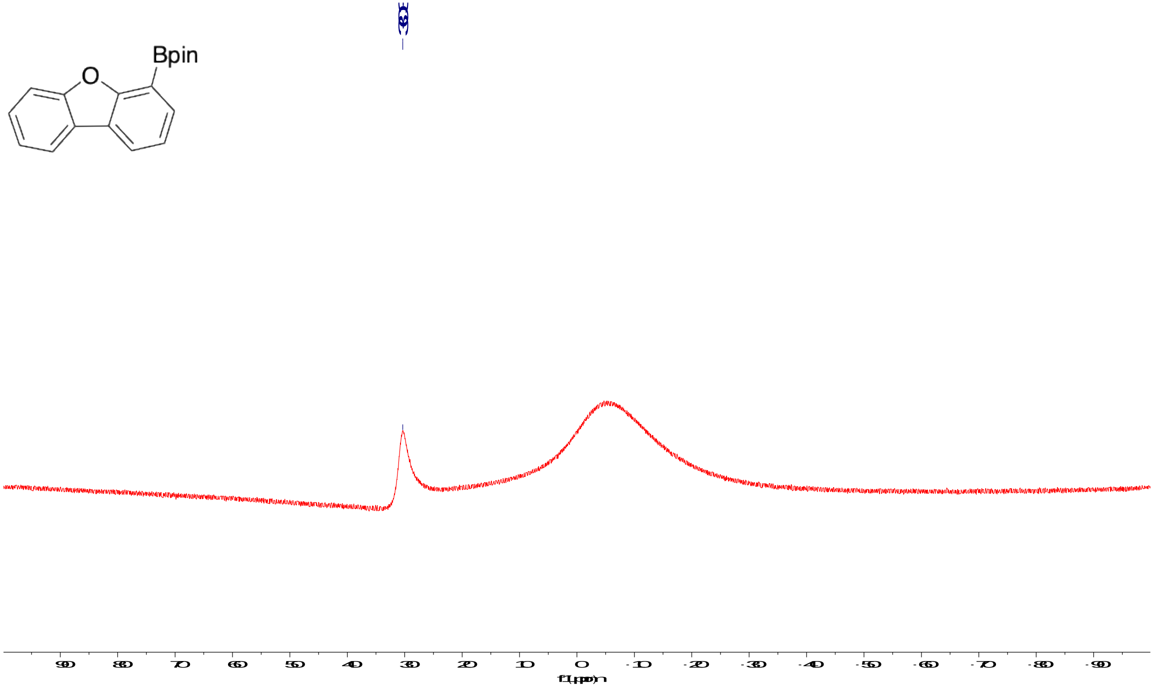
^{1}H NMR (500MHz, $CDCl_3$) of 2-(dibenzo[*b*,*d*]furan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1k)



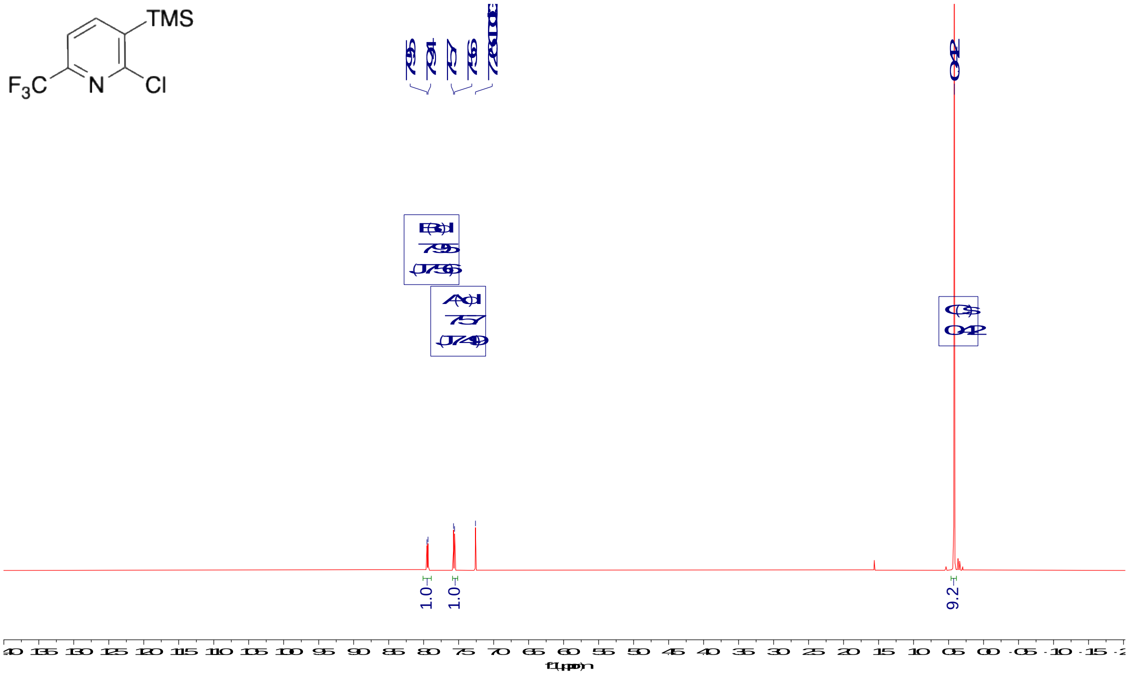
^{13}C{^{1}H} (126 MHz, $CDCl_3$) NMR of 2-(dibenzo[*b*,*d*]furan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1k)



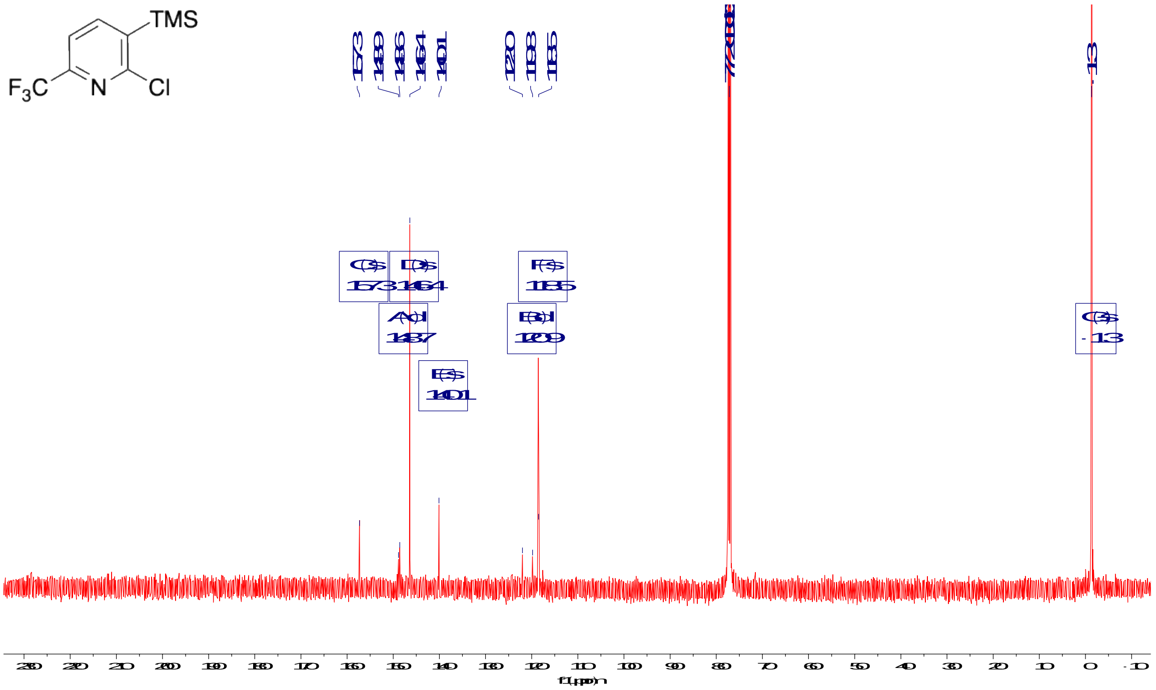
^{11}B NMR (160MHz, CDCl$_3$) of 2-(dibenzo[*b*,*d*]furan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1k)



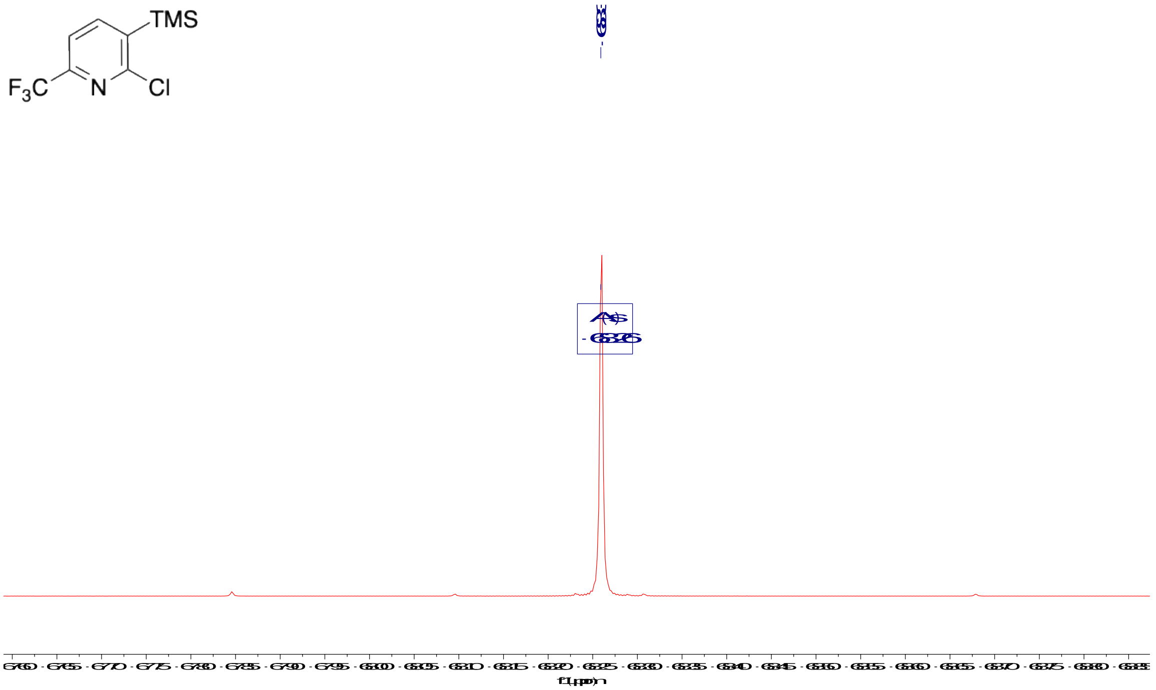
^{1}H NMR (500MHz, CDCl$_3$) 2-Chloro-6-(trifluoromethyl)-3-(trimethylsilyl)pyridine (1y)



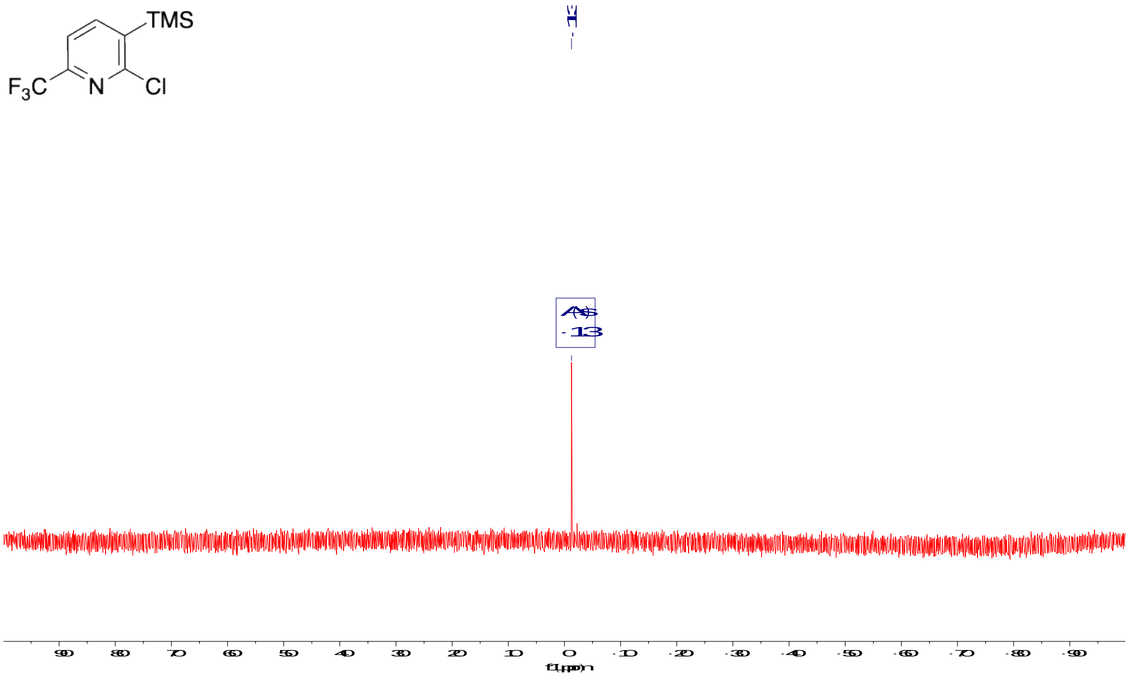
$^{13}C\{^{1}H\}$ (126 MHz, $CDCl_3$) NMR of 2-Chloro-6-(trifluoromethyl)-3-(trimethylsilyl)pyridine (1y)



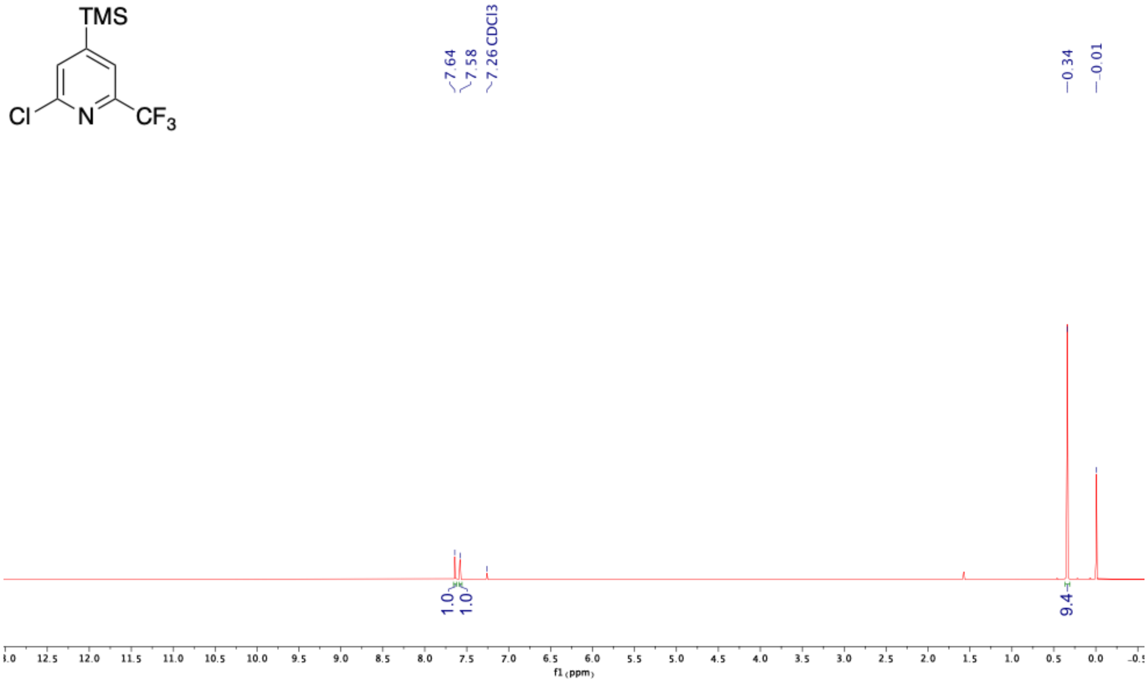
^{19}F NMR (470 MHz, $CDCl_3$) of 2-Chloro-6-(trifluoromethyl)-3-(trimethylsilyl)pyridine (1y)



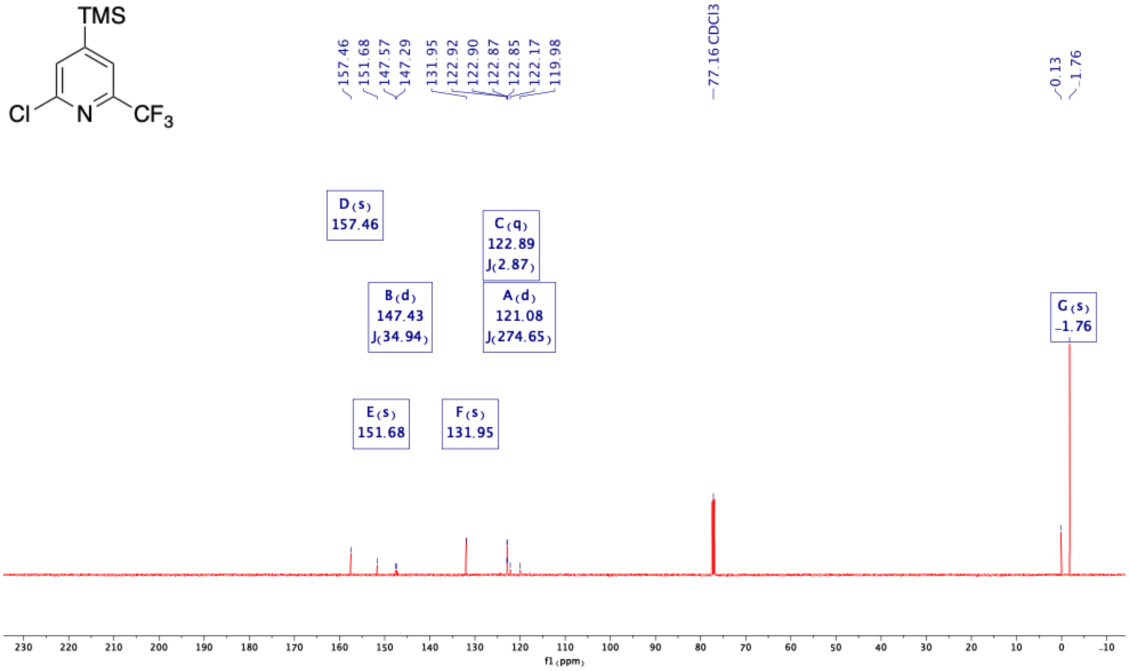
^{29}Si NMR (99MHz, $CDCl_3$) of 2-Chloro-6-(trifluoromethyl)-3-(trimethylsilyl)pyridine (1y)



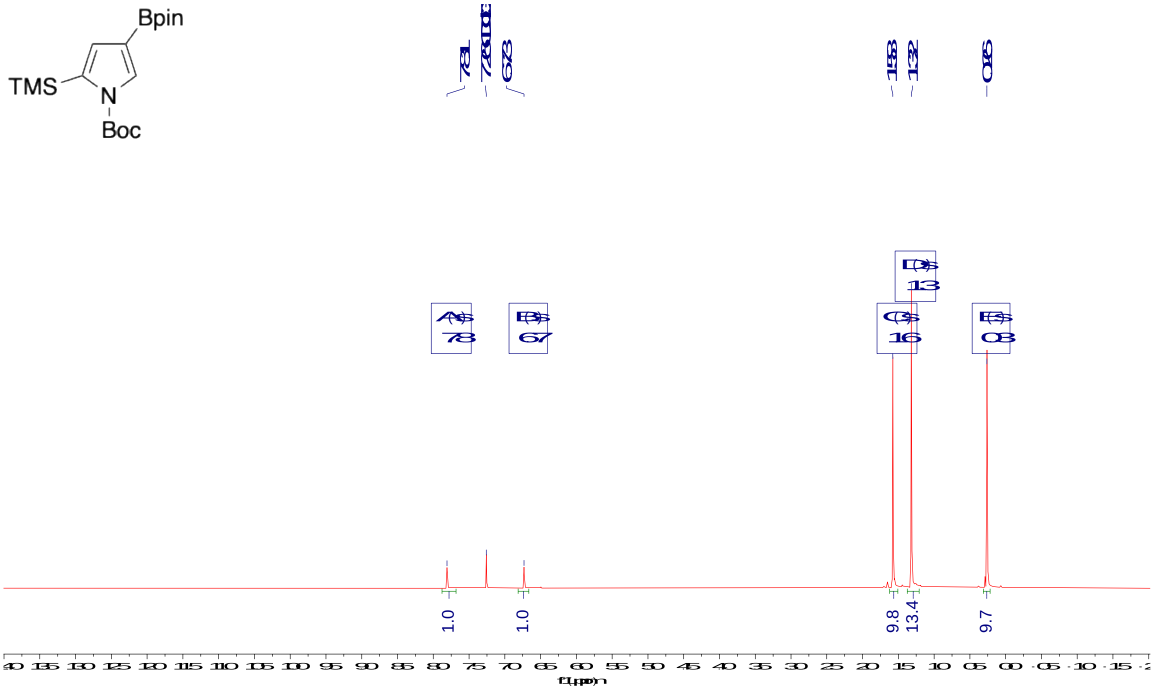
^{1}H NMR (500MHz, $CDCl_3$) 2-chloro-6-(trifluoromethyl)-4-(trimethylsilyl)pyridine (1x)



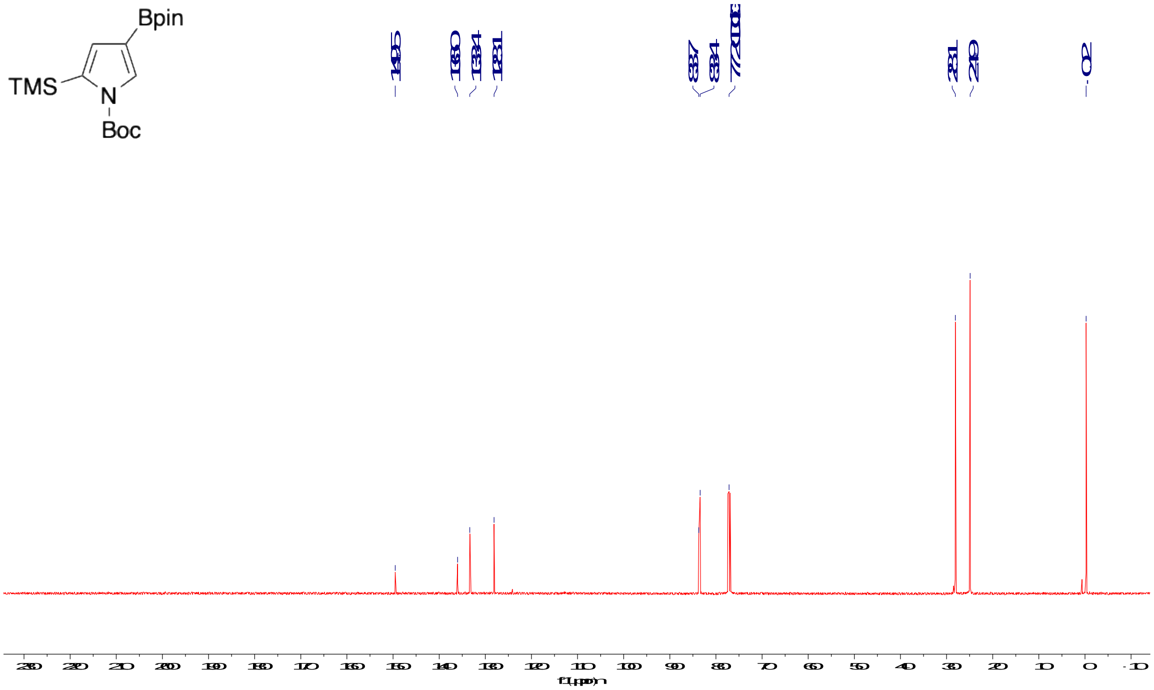
$^{13}C\{^1H\}$ (126 MHz, $CDCl_3$) NMR of 2-chloro-6-(trifluoromethyl)-4-(trimethylsilyl)pyridine (1x)



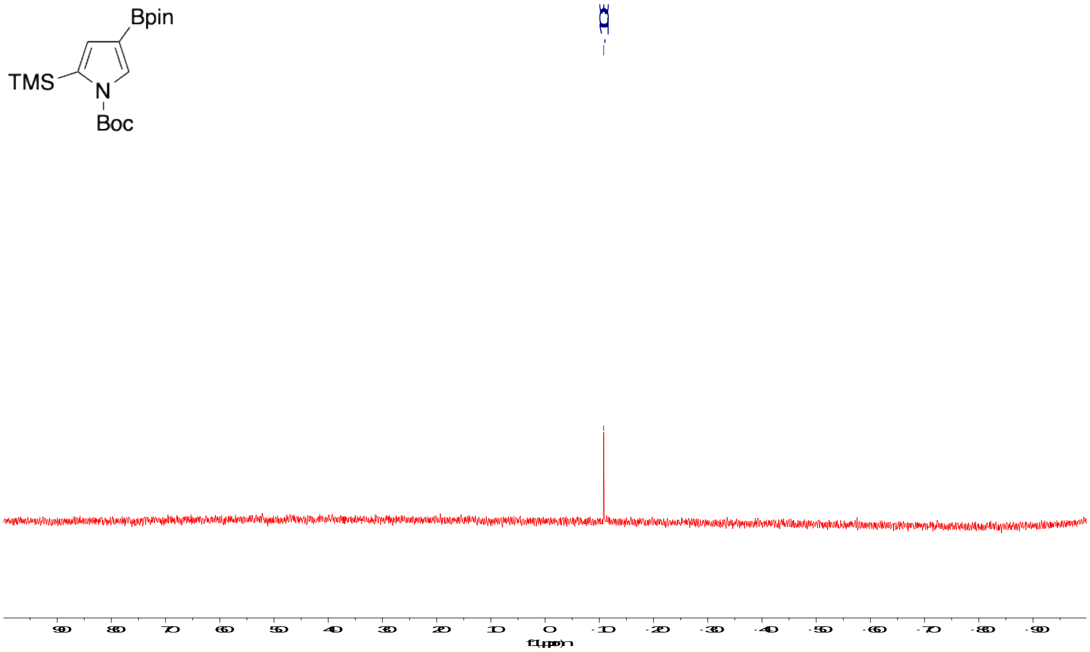
^1H NMR (500MHz, $CDCl_3$) *t*-butyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(trimethylsilyl)pyrrole-1-carboxylate (1ab)



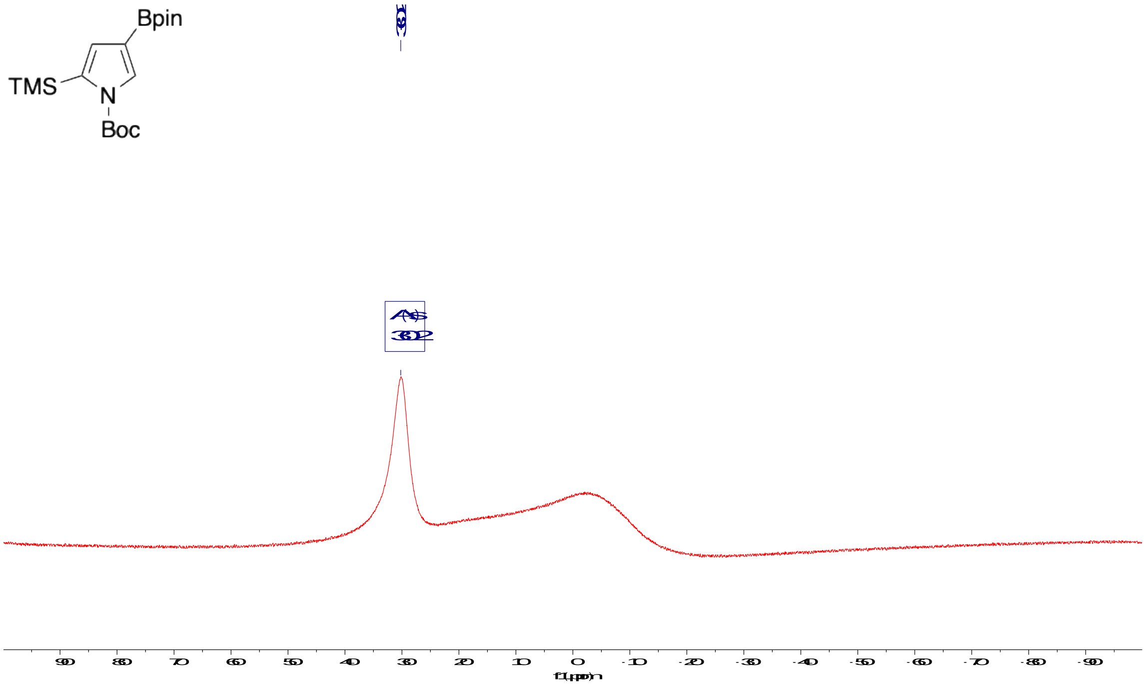
$^{13}C\{^1H\}$ (126 MHz, $CDCl_3$) of *t*-butyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(trimethylsilyl)pyrrole-1-carboxylate (1ab)



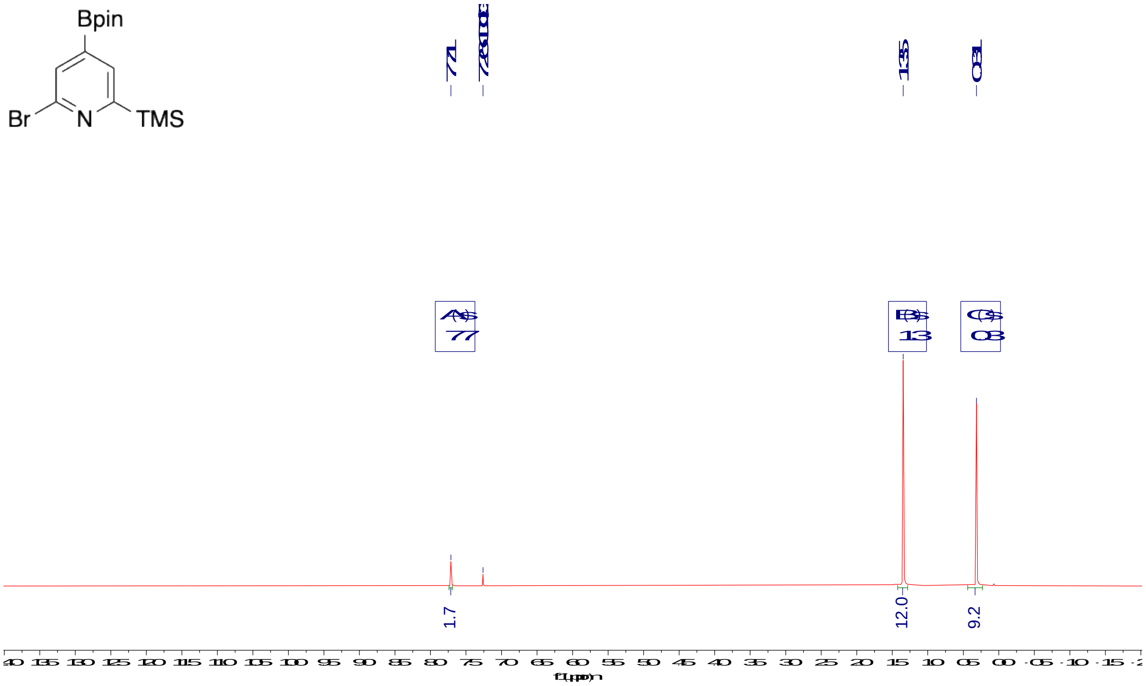
^{29}Si NMR (99 MHz, $CDCl_3$) of *t*-butyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(trimethylsilyl)pyrrole-1-carboxylate (1ab)



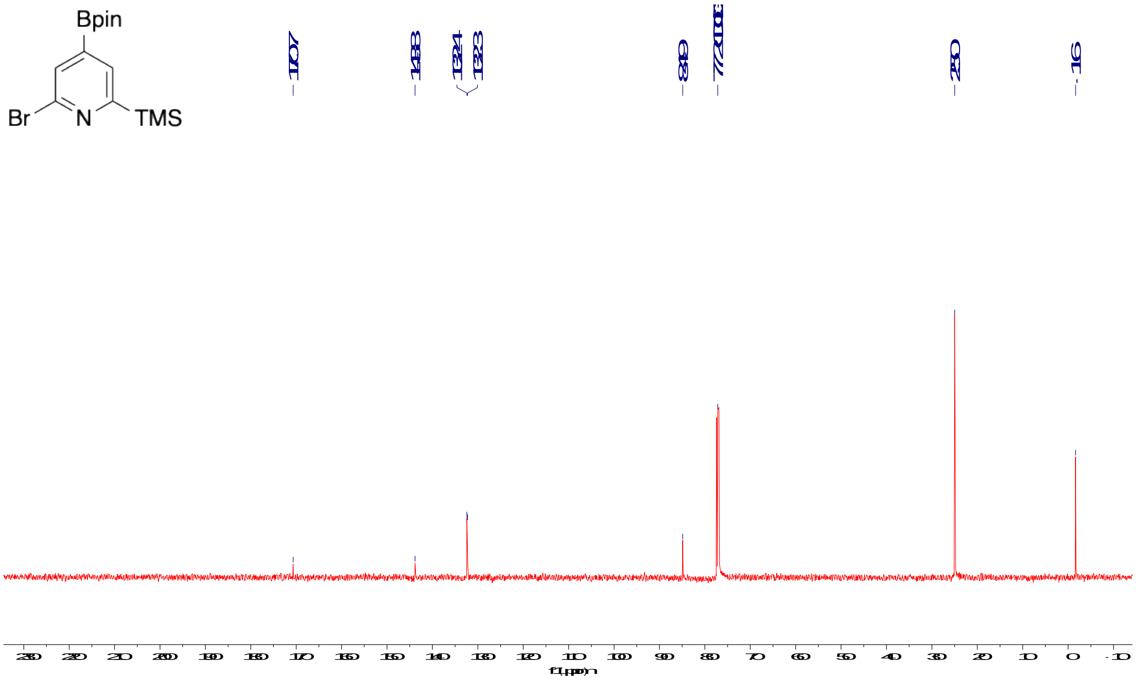
^{11}B NMR (160 MHz, CDCl$_3$) of *t*-butyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(trimethylsilyl)pyrrole-1-carboxylate (1ab)



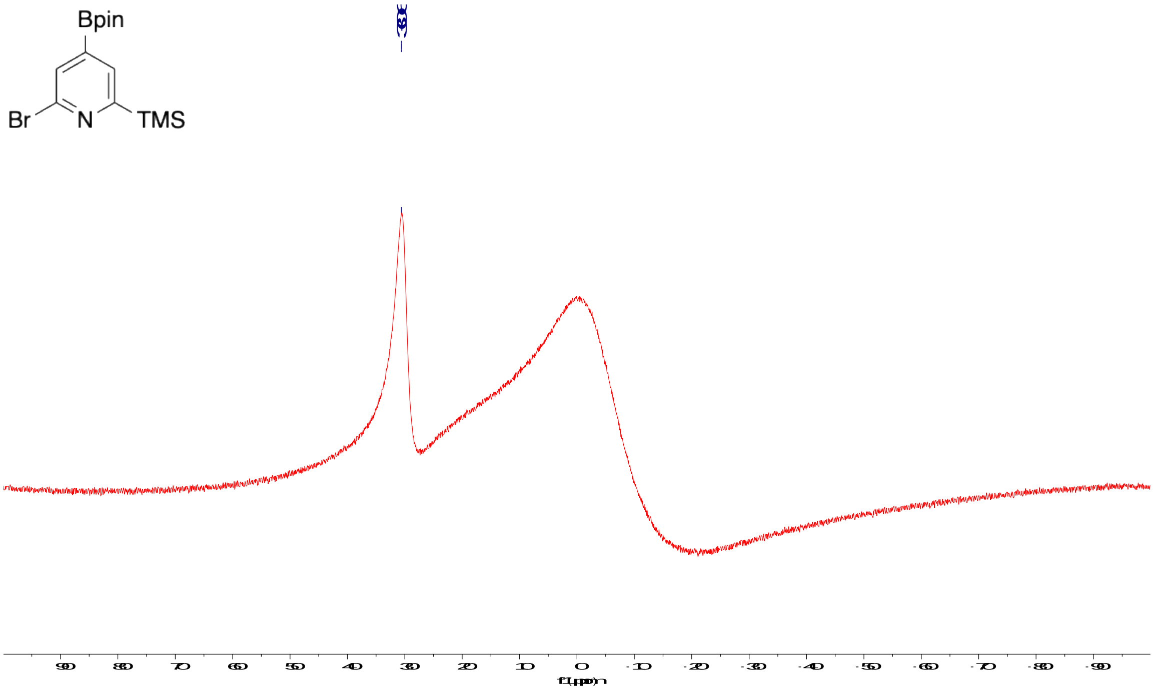
^{1}H NMR (500 MHz, CDCl$_3$) of 2-bromo-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6-(trimethylsilyl)pyridine (1ac)



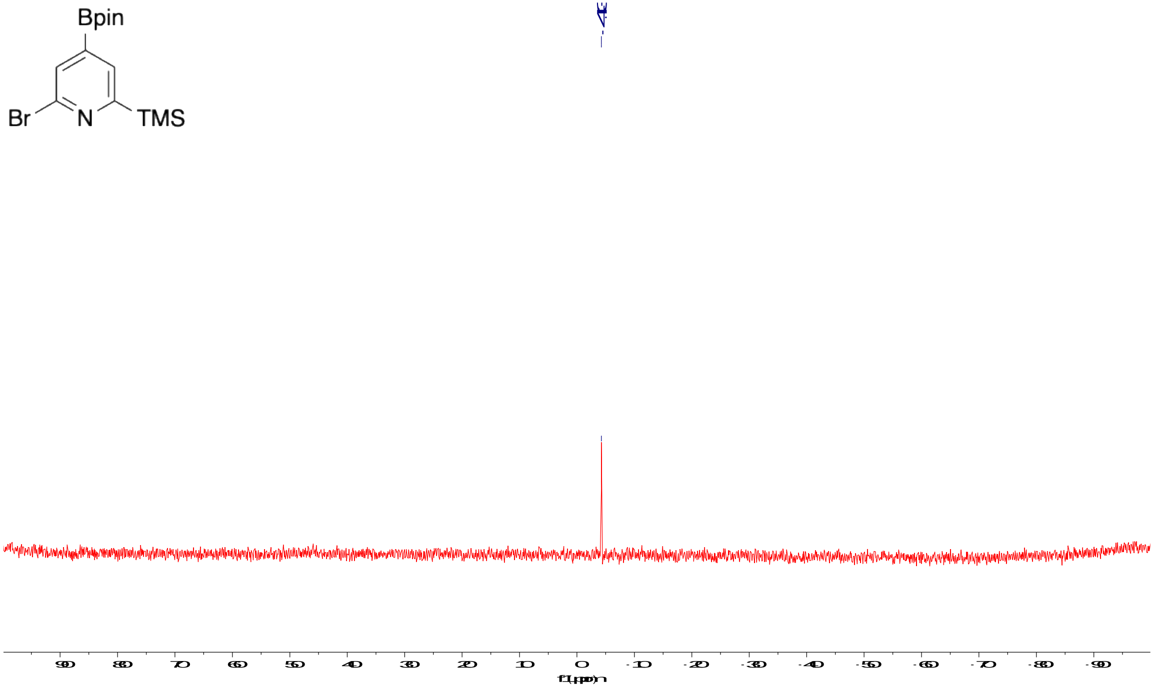
$^{13}C\{^{1}H\}$ (126 MHz, $CDCl_3$) NMR of 2-bromo-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6-(trimethylsilyl)pyridine (1ac)



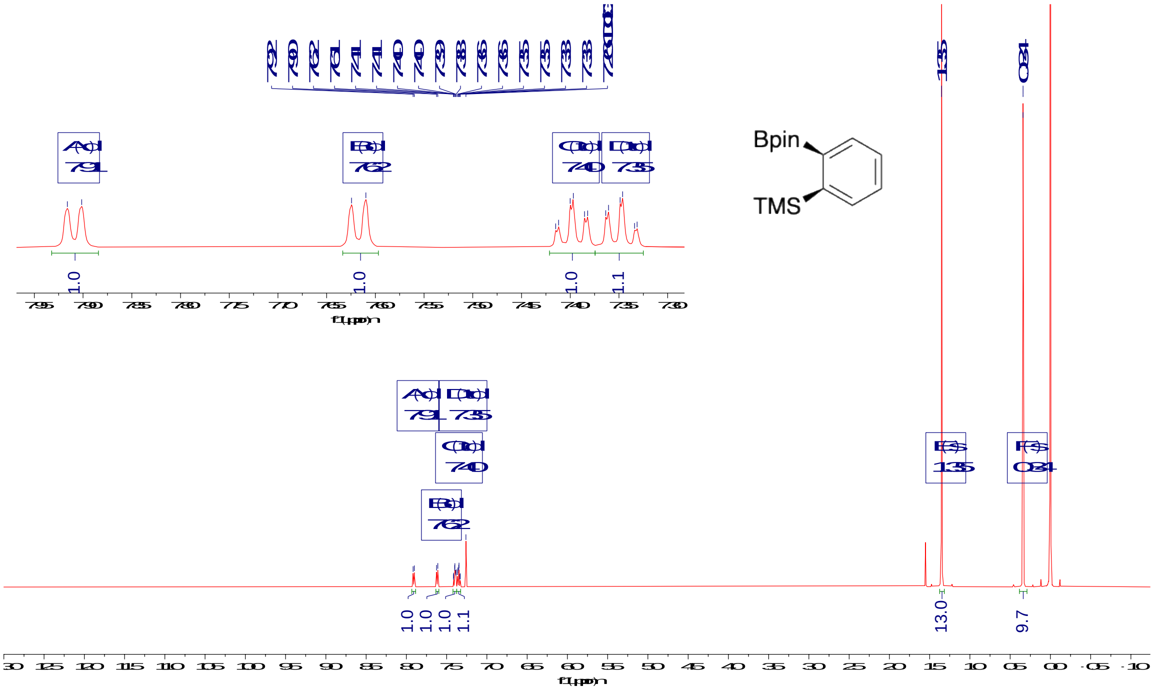
^{11}B NMR (160 MHz, $CDCl_3$) of 2-bromo-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6-(trimethylsilyl)pyridine (1ac)



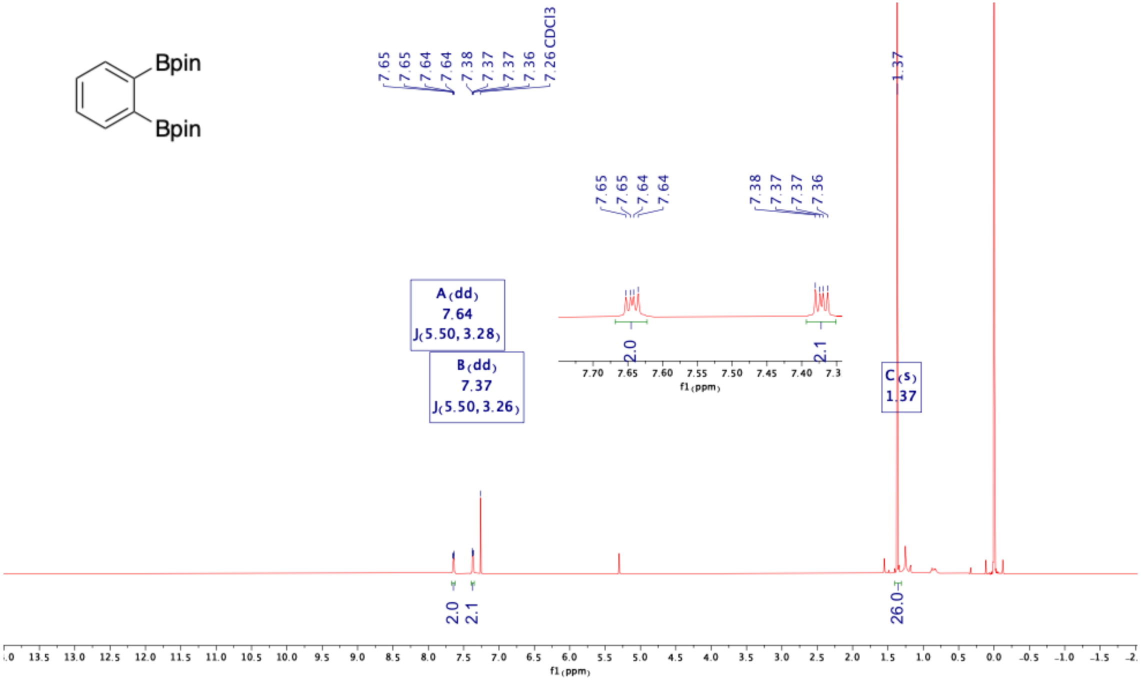
^{29}Si NMR (99 MHz, $CDCl_3$) of 2-bromo-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6-(trimethylsilyl)pyridine (1ac)



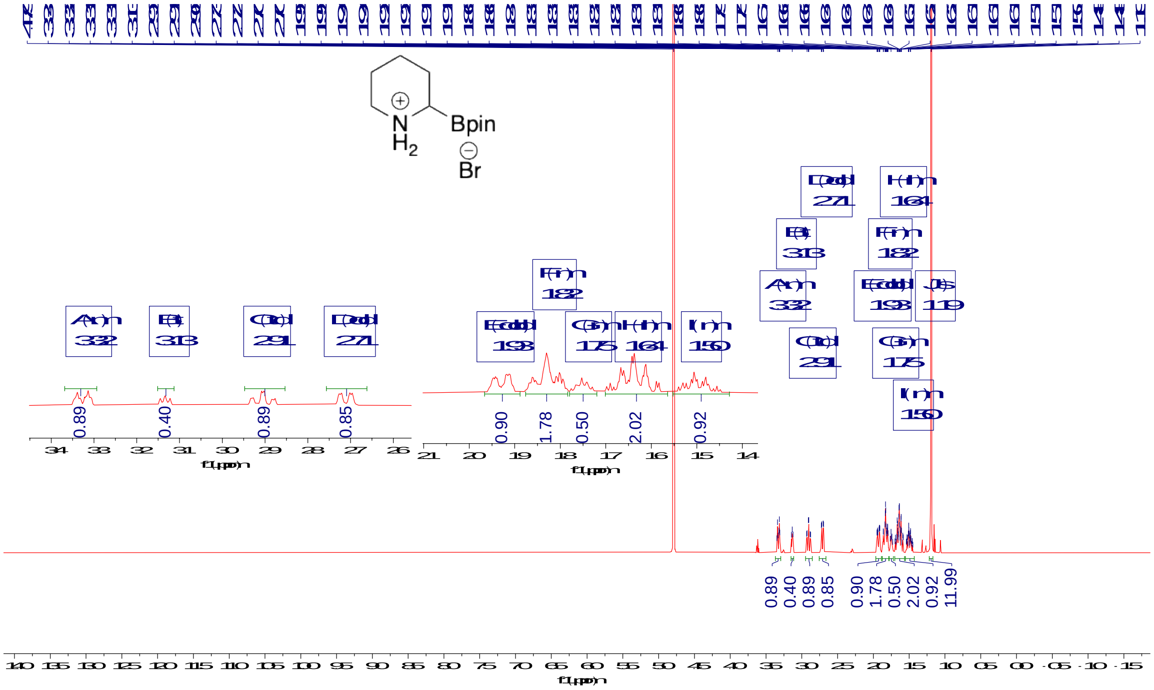
^{1}H NMR (500 MHz, $CDCl_3$) of trimethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)silane (1ad)



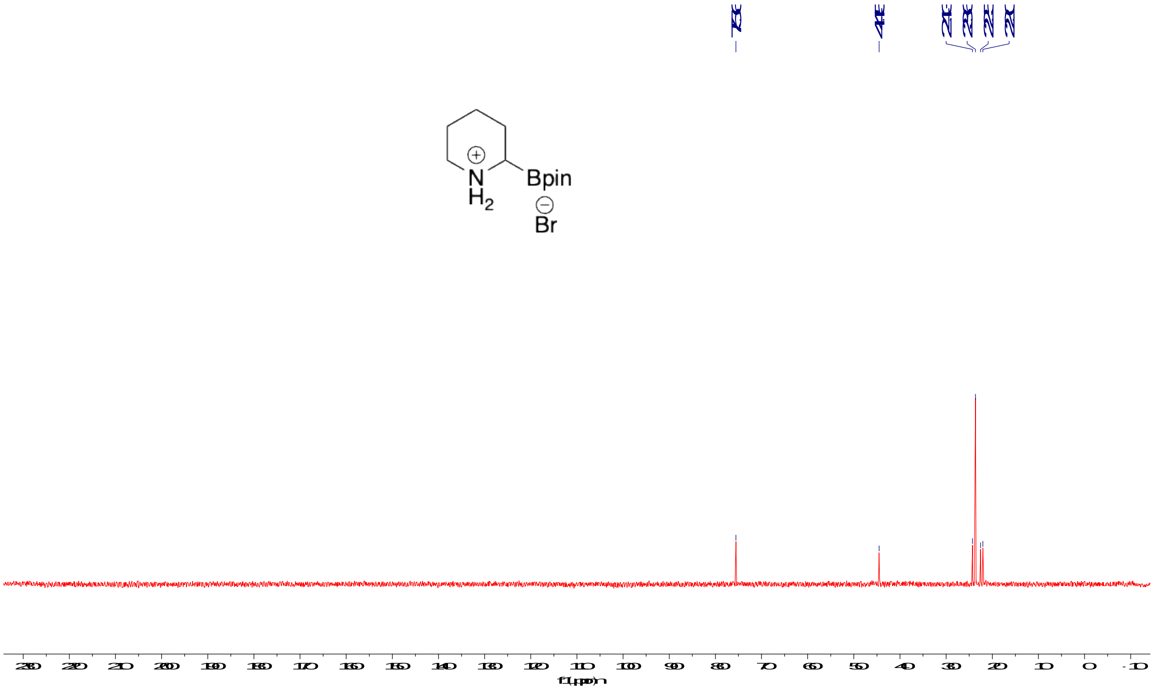
^{1}H NMR (500 MHz, CDCl$_3$) of trimethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)silane (1v)



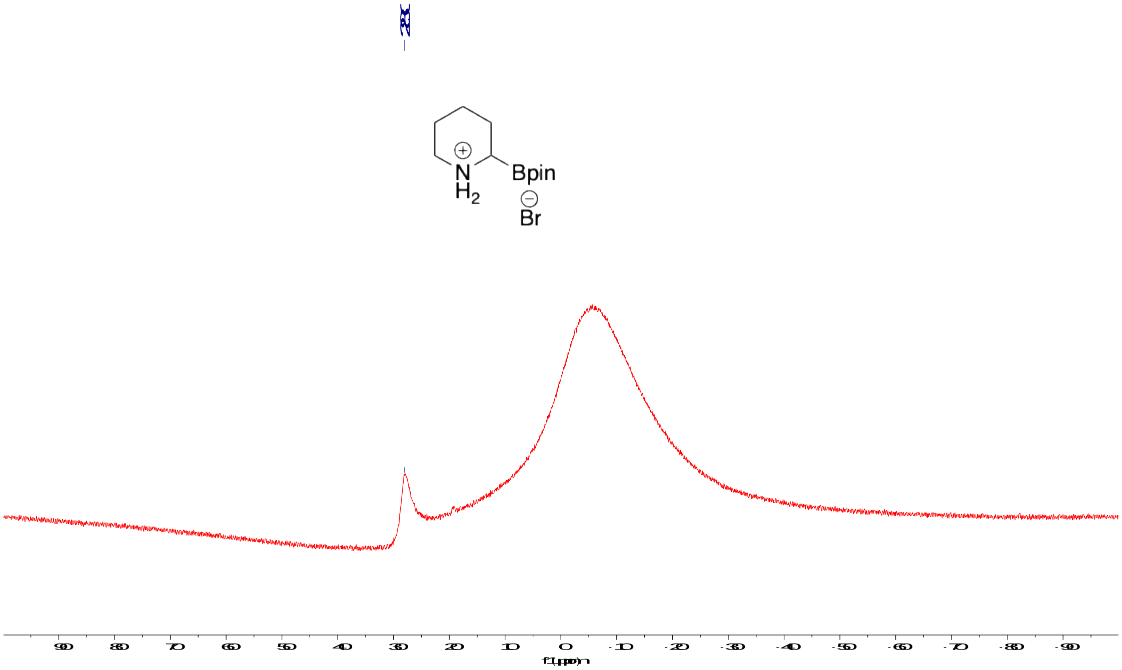
^{1}H NMR (500 MHz, D$_2$O) of 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)piperidin-1-ium bromide (2c)



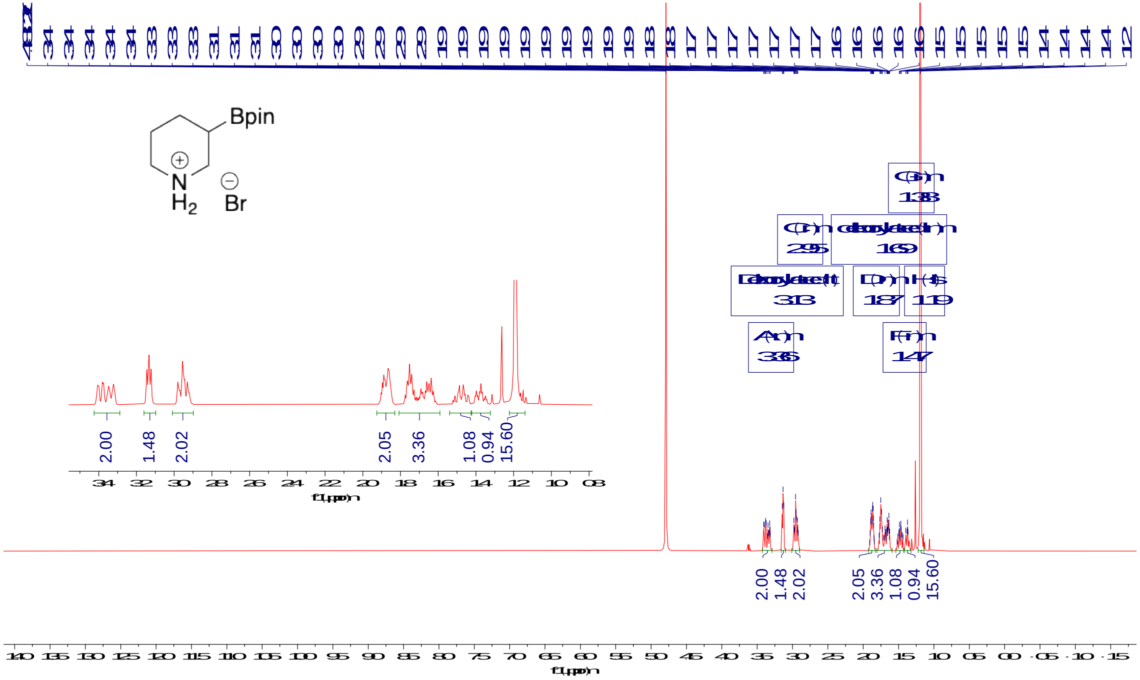
$^{13}C\{^1H\}$ (126 MHz, D_2O) NMR of 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)piperidin-1-ium bromide (2c)



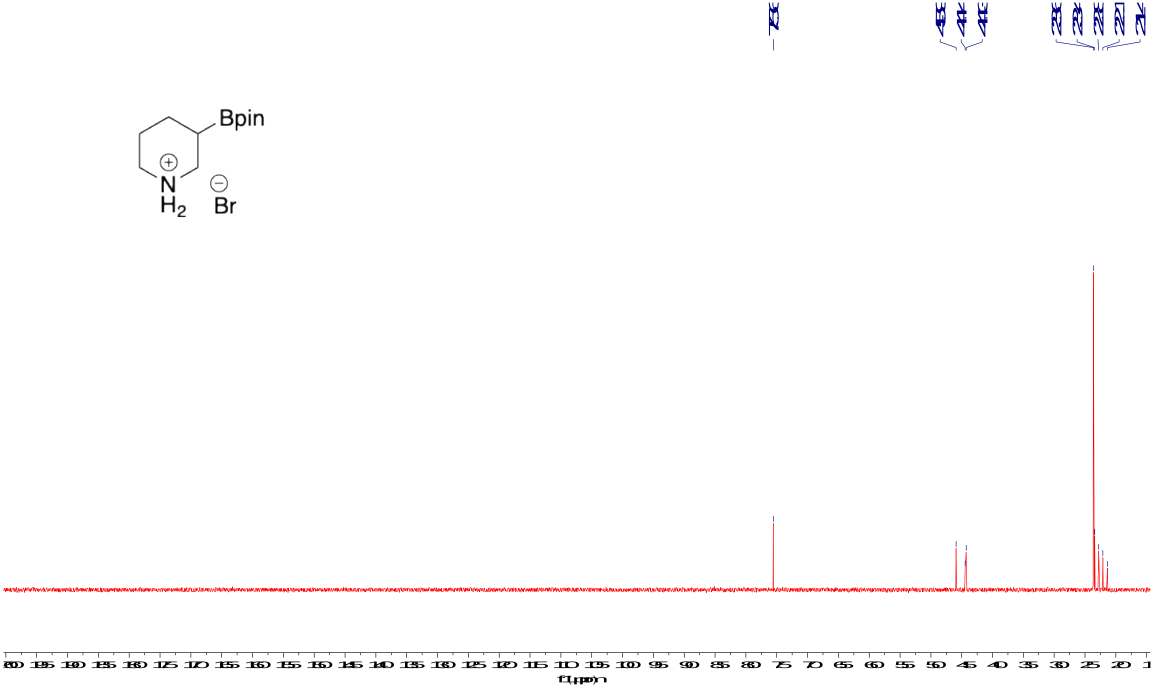
^{11}B NMR (160 MHz, D_2O) of 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)piperidin-1-ium bromide (2c)



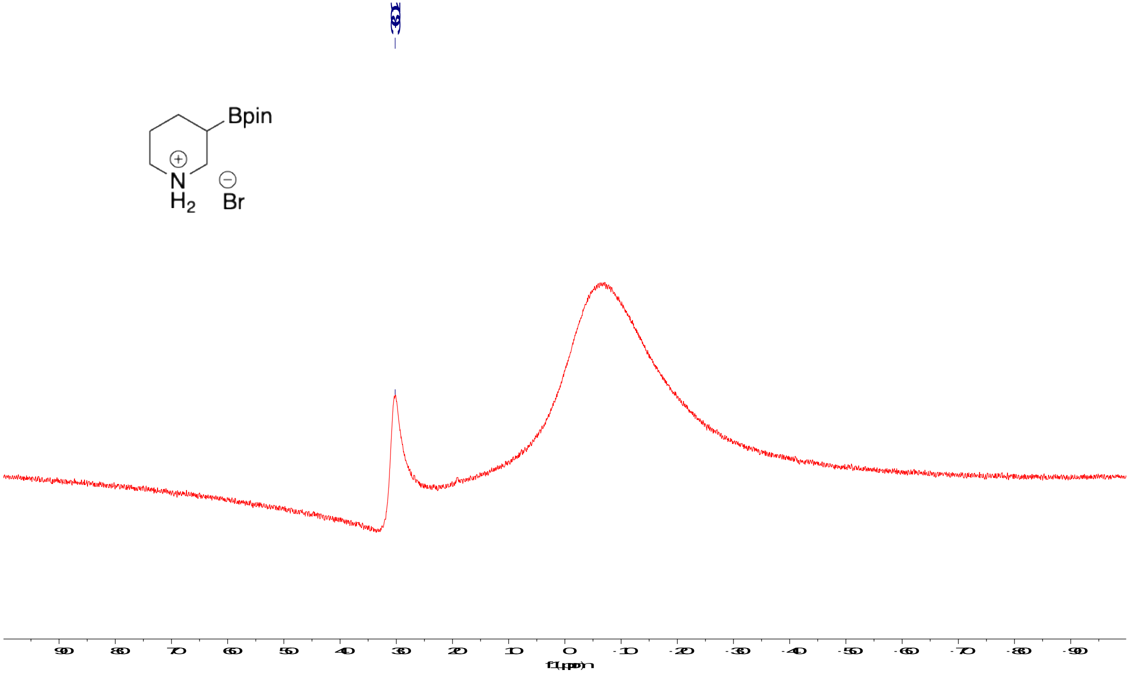
^{1}H NMR (500 MHz, D_2O) of 3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)piperidin-1-ium bromide (2b)



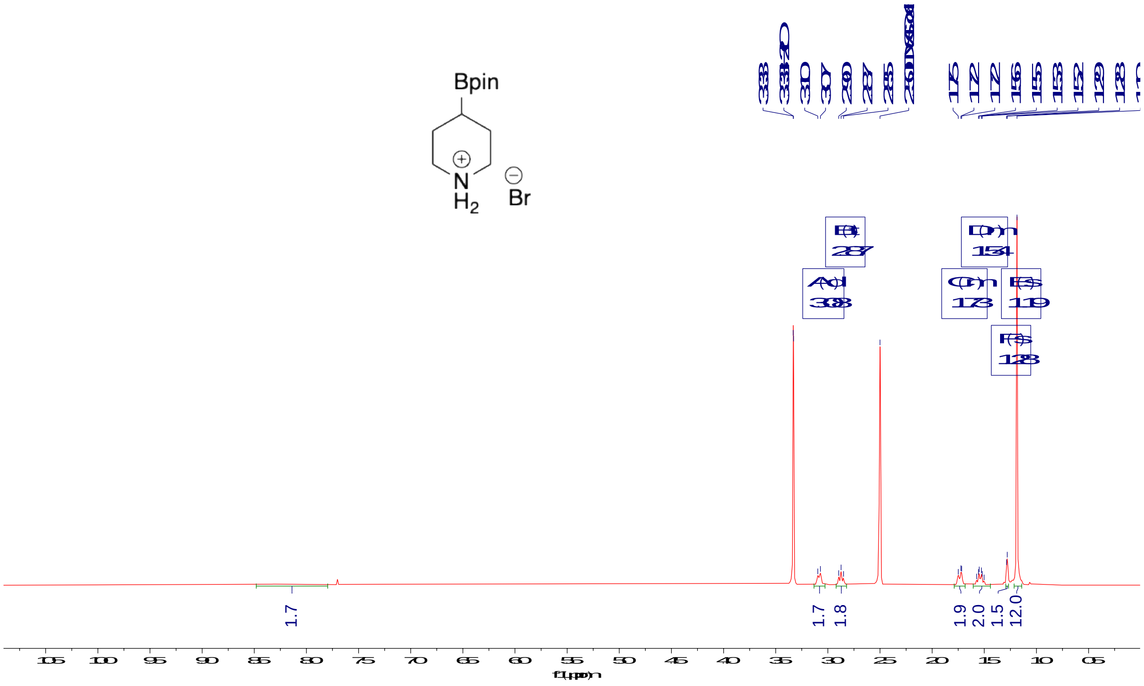
$^{13}C\{^1H\}$ (126 MHz, D_2O) NMR of 3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)piperidin-1-ium bromide (2b)



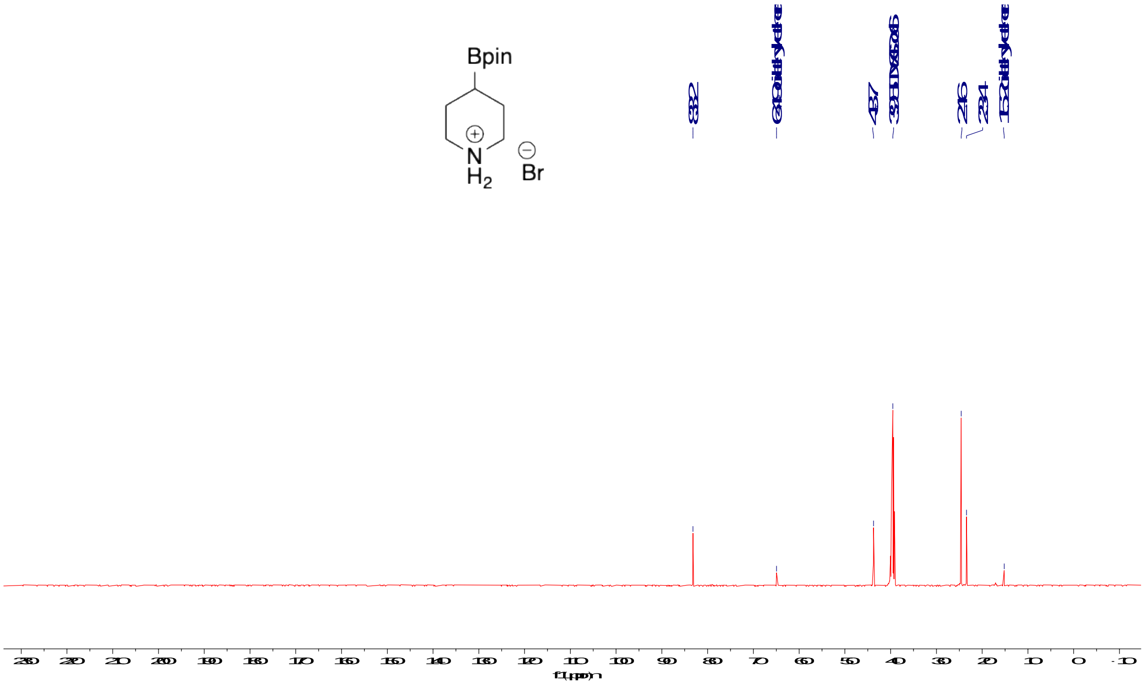
^{11}B NMR (160 MHz, D_2O) of 3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)piperidin-1-ium bromide (2b)



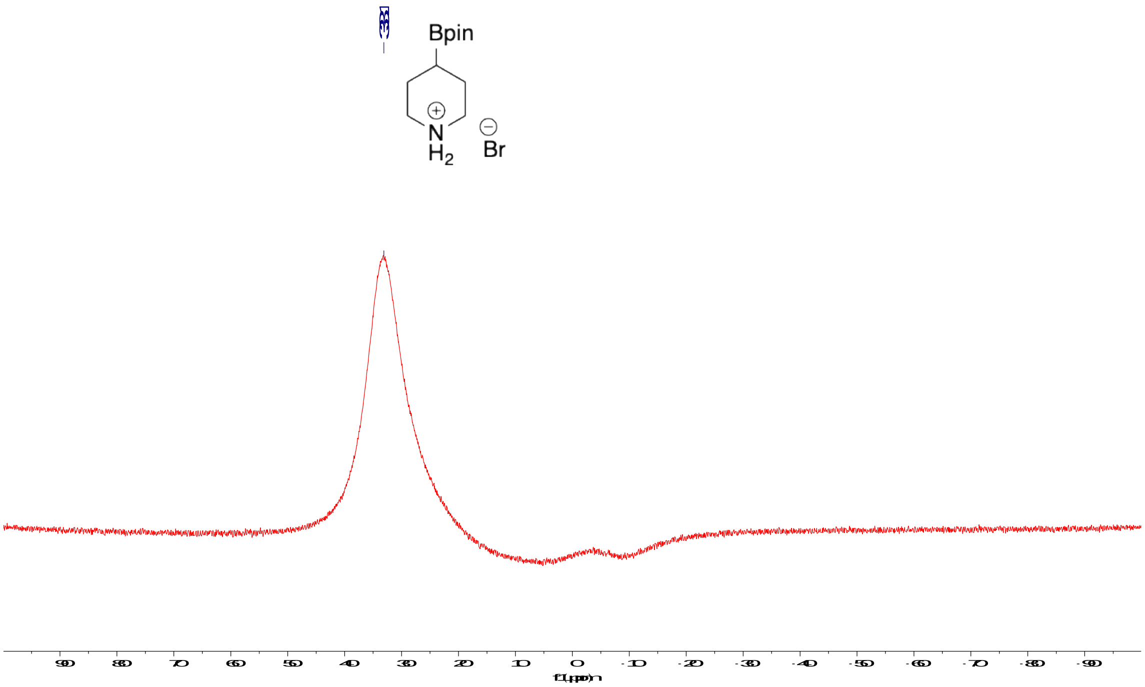
^{1}H NMR (500 MHz, DMSO) of 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)piperidin-1-ium bromide (2d)



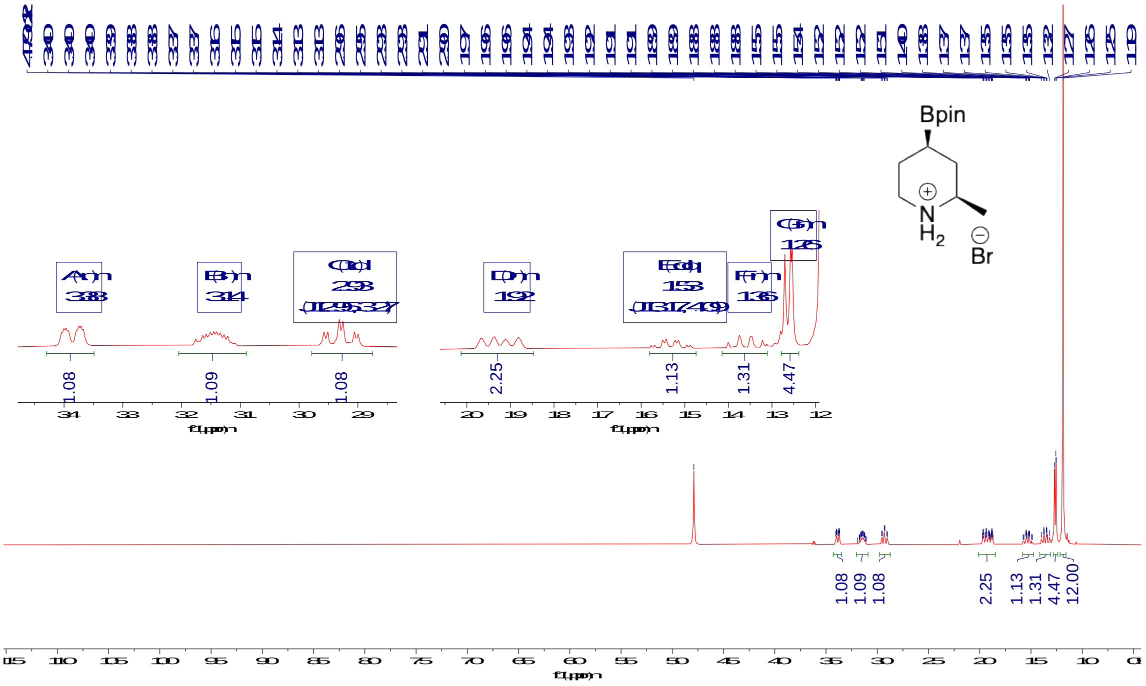
$^{13}C\{^1H\}$ (126 MHz, DMSO) NMR of 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)piperidin-1-ium bromide (2d)



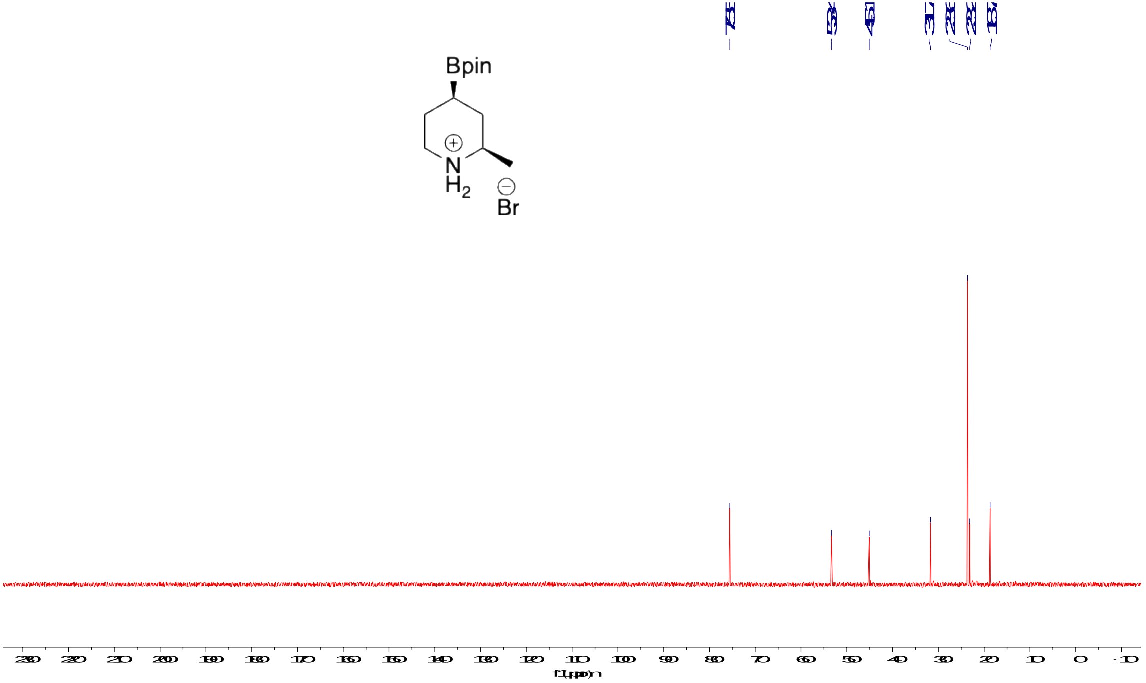
^{11}B NMR (160 MHz, DMSO) of 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)piperidin-1-ium bromide (2d)



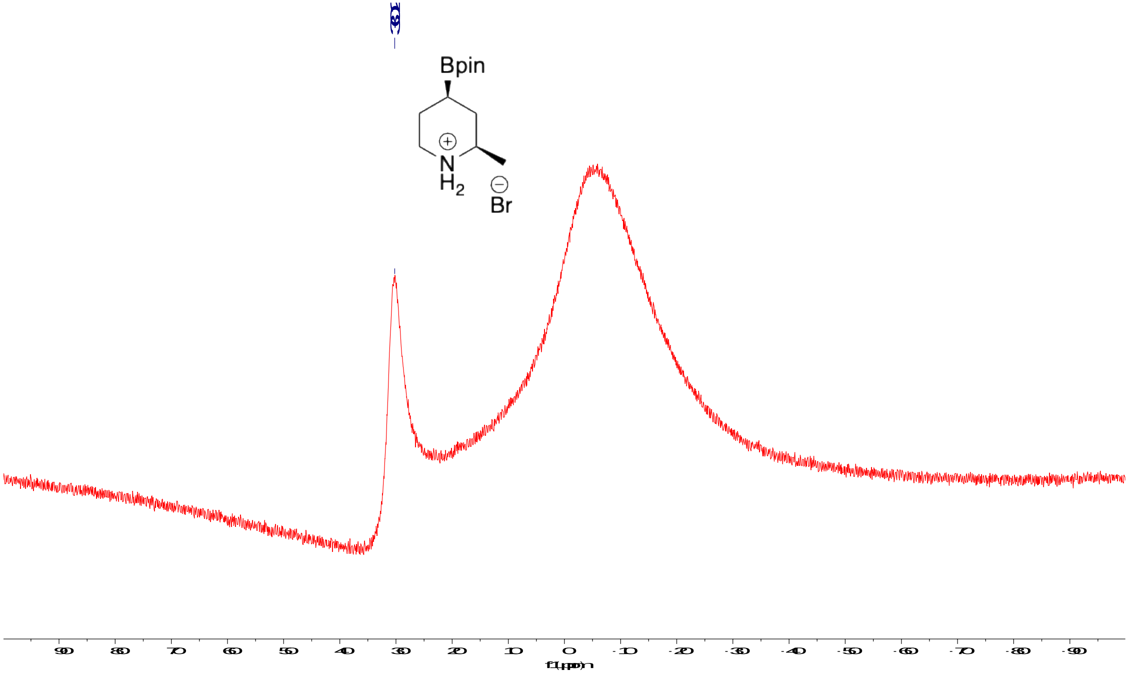
^1H NMR (500 MHz, D_2O) of 2-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)piperidin-1-ium bromide (2e)



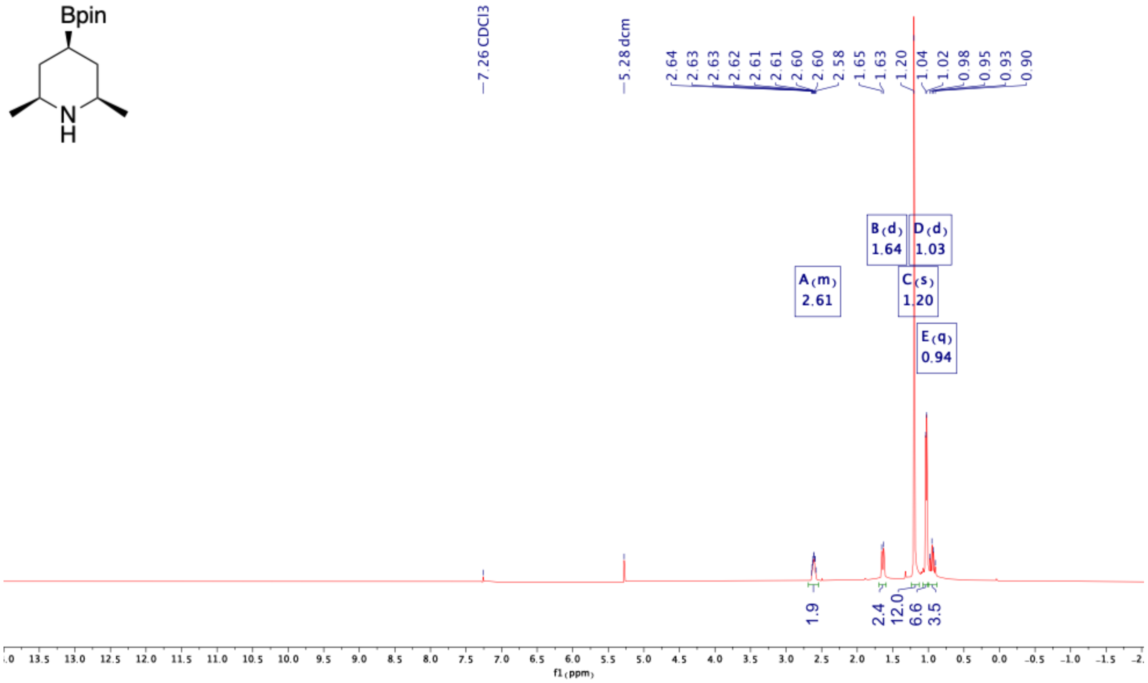
$^{13}C\{^1H\}$ (126 MHz, D_2O) NMR of 2-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)piperidin-1-ium bromide (2e)



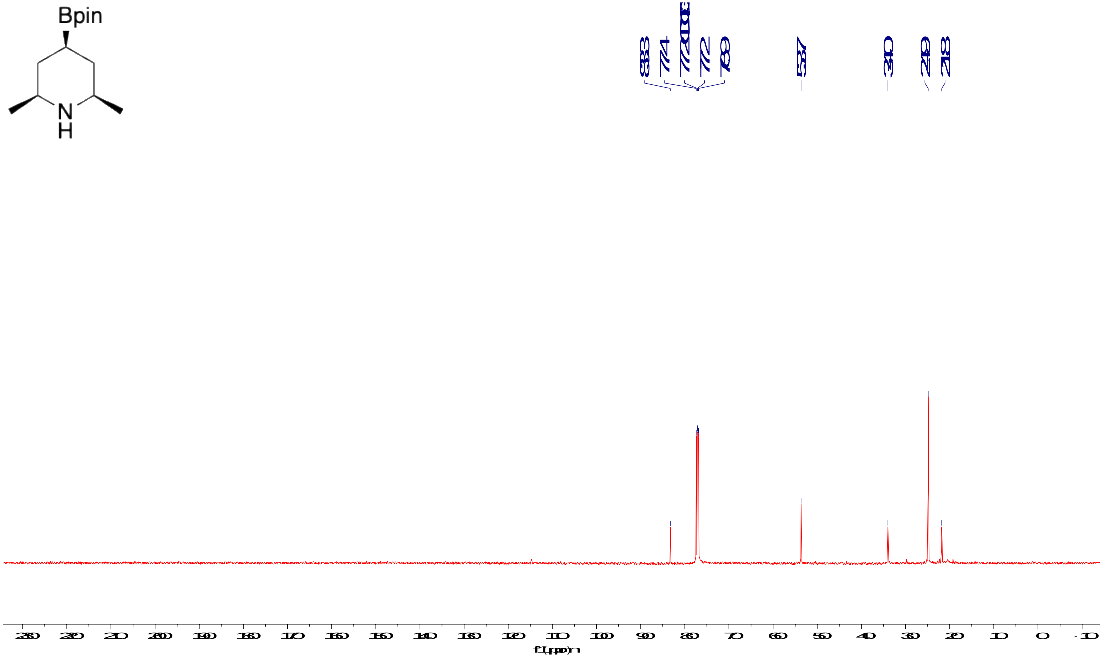
^{11}B NMR (160 MHz, D_2O) of 2-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)piperidin-1-ium bromide (2e)



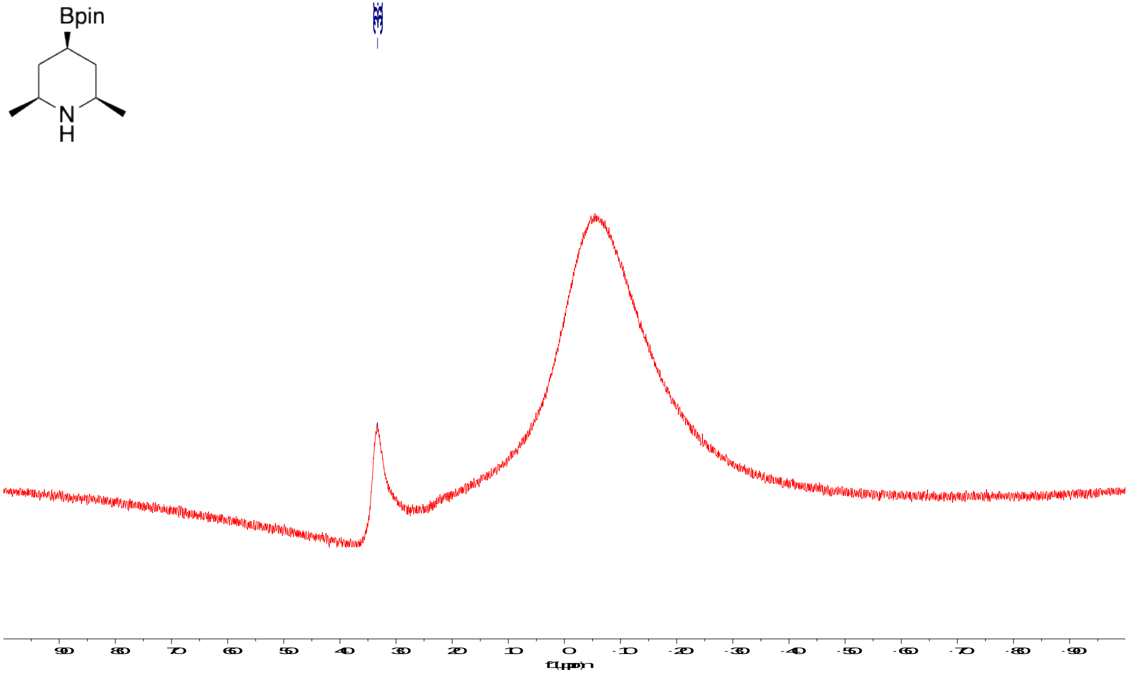
^{1}H NMR (500 MHz, $CDCl_3$) of 2,6-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)piperidine (2f)



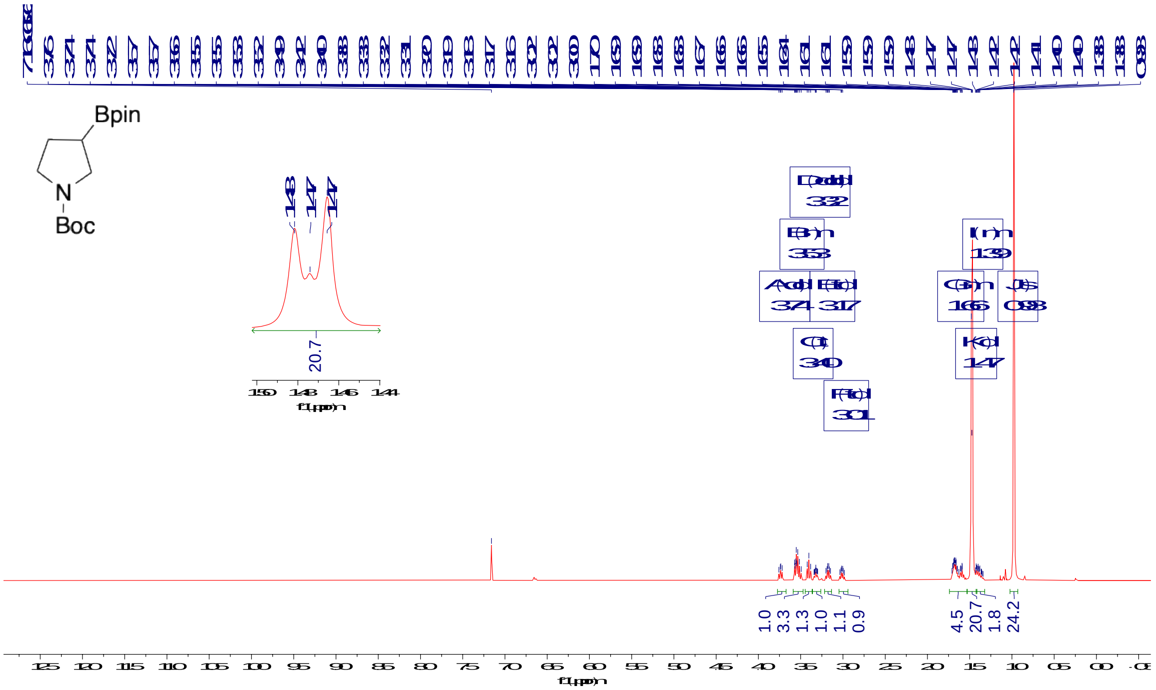
$^{13}C\{^{1}H\}$ (126 MHz, $CDCl_3$) NMR of 2,6-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)piperidine (2f)



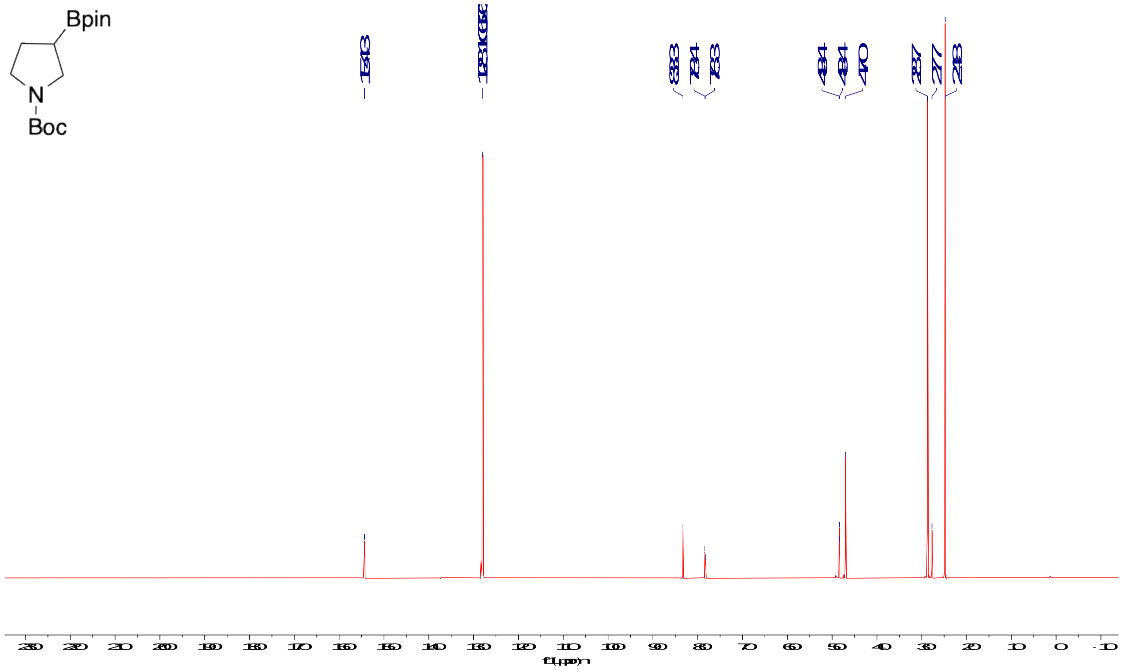
^{11}B NMR (160 MHz, $CDCl_3$) of 2,6-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)piperidine (2f)



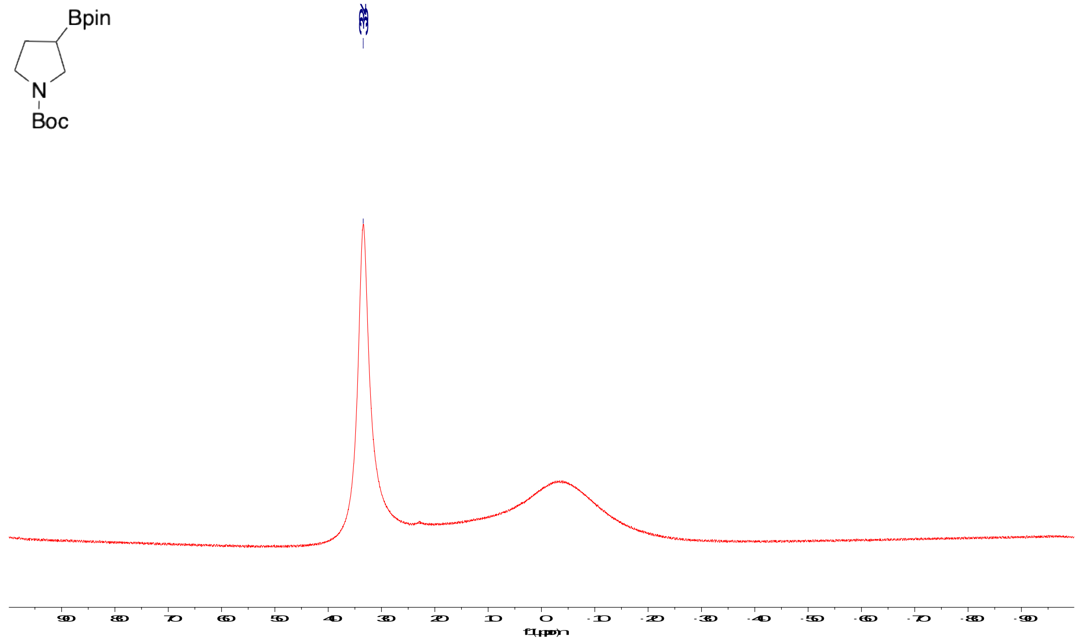
^{1}H NMR (500 MHz, C_6D_6) of *tert*-Butyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrrolidine-1-carboxylate (2g)



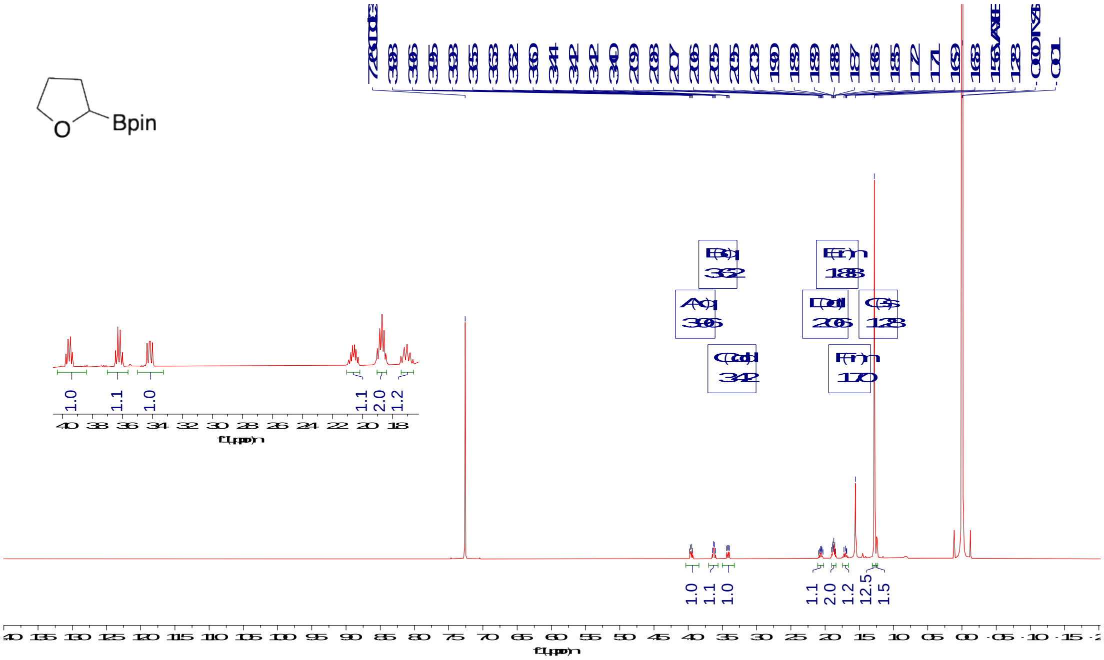
^{13}C{^{1}H} (126 MHz, C_6D_6) NMR of *tert*-Butyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrrolidine-1-carboxylate (2g)



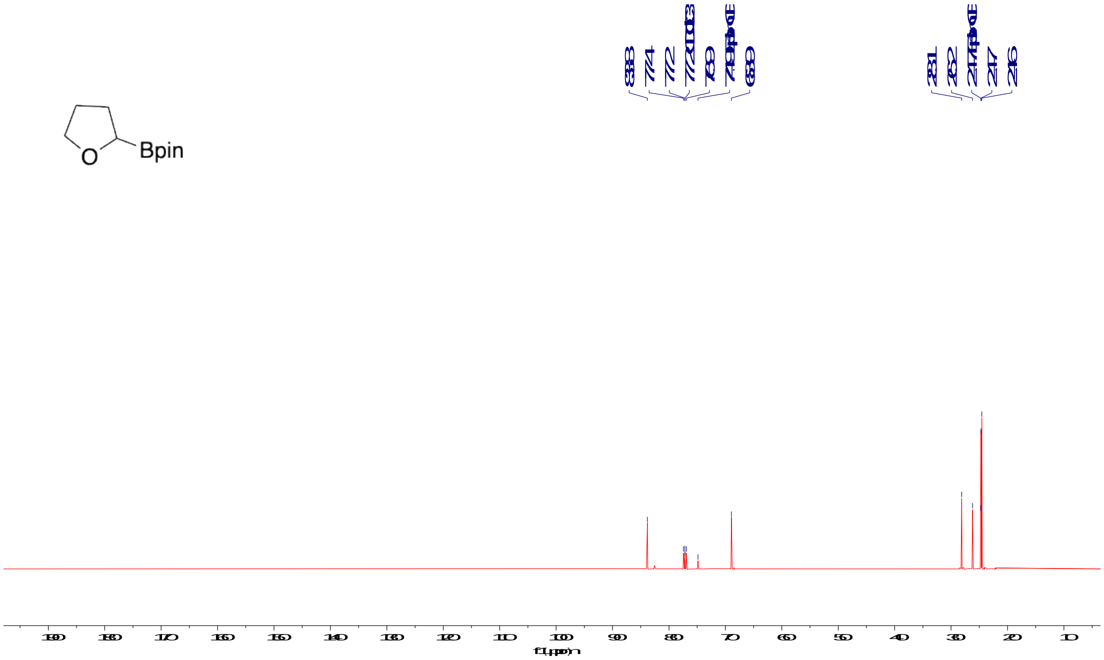
^{11}B NMR (160 MHz, C_6D_6) of *tert*-Butyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrrolidine-1-carboxylate (2g)



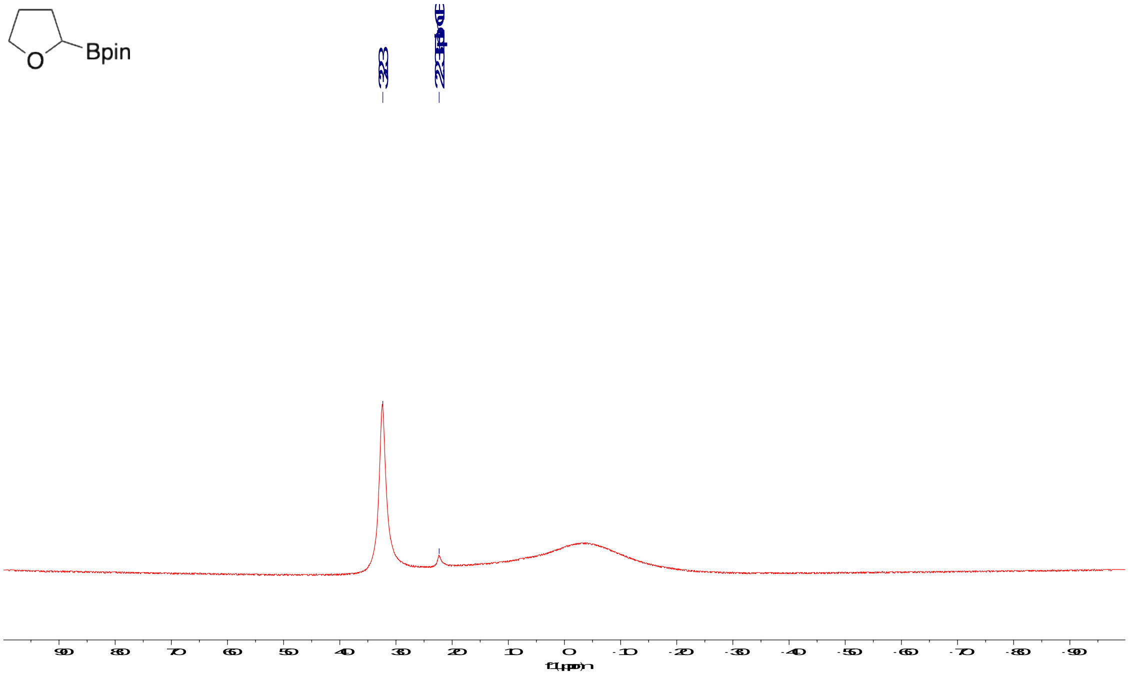
^{1}H NMR (500 MHz, $CDCl_3$) of 4,4,5,5-tetramethyl-2-(tetrahydrofuran-2-yl)-1,3,2-dioxaborolane (2h)



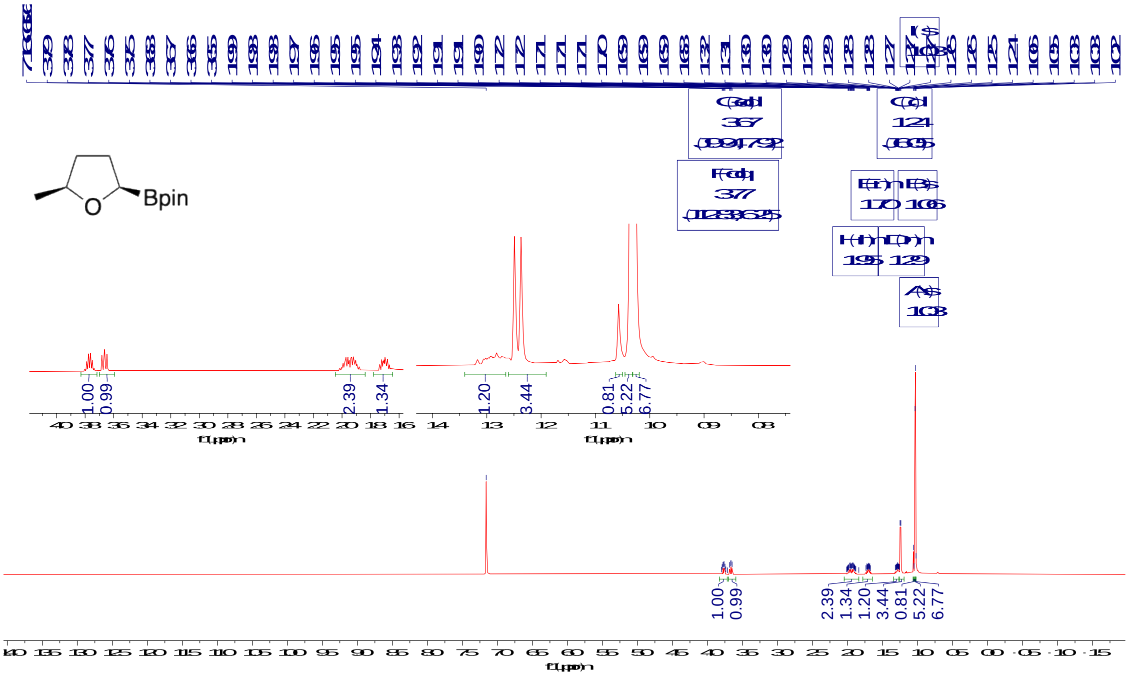
$^{13}C\{^{1}H\}$ (126 MHz, $CDCl_3$) NMR of 4,4,5,5-tetramethyl-2-(tetrahydrofuran-2-yl)-1,3,2-dioxaborolane (2h)



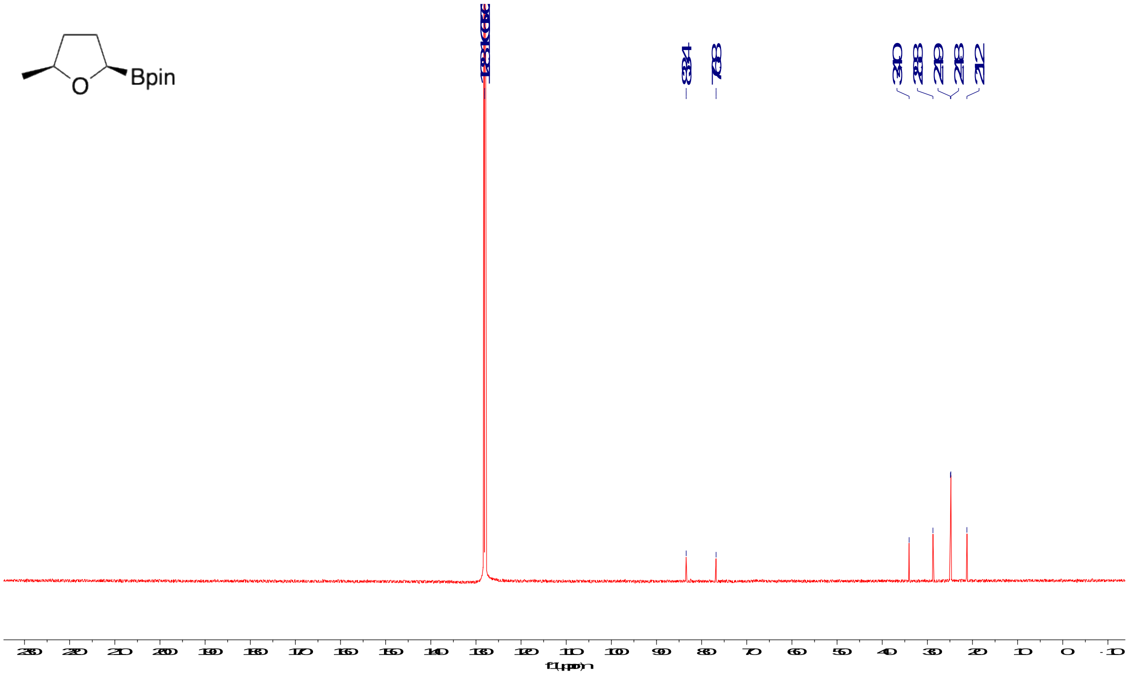
^{11}B NMR (160MHz, $CDCl_3$) of 4,4,5,5-tetramethyl-2-(tetrahydrofuran-2-yl)-1,3,2-dioxaborolane (2h)



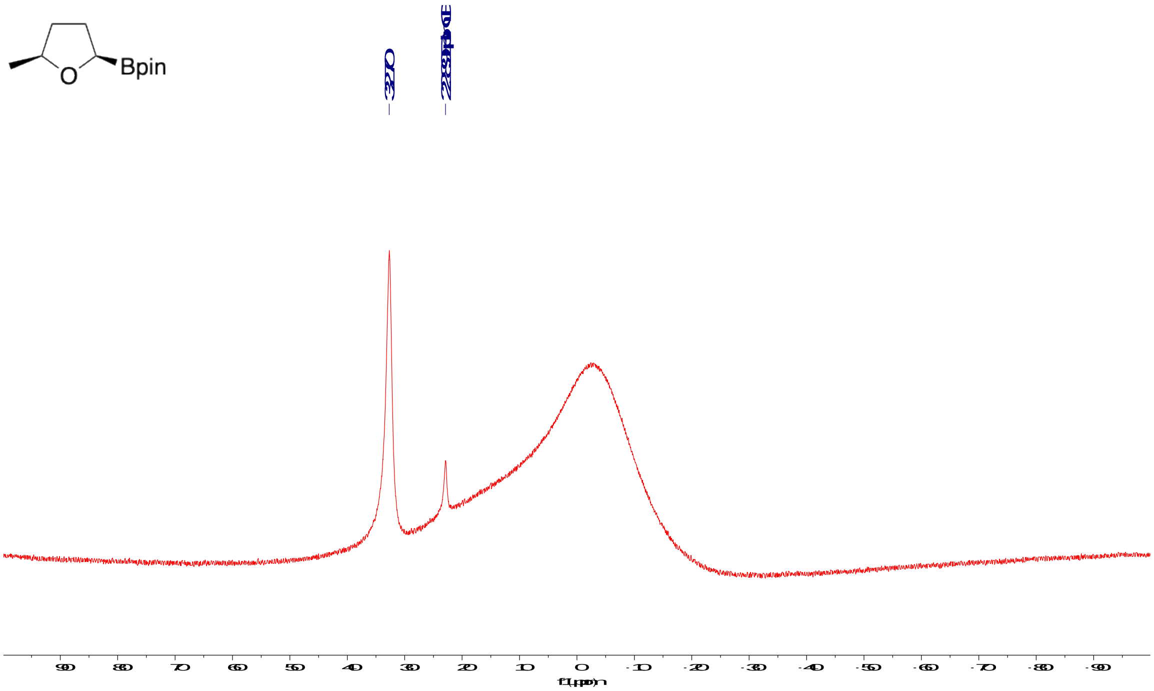
^{1}H NMR (500MHz, C_6D_6) of 4,4,5,5-Tetramethyl-2-(5-methyltetrahydrofuran-2-yl)-1,3,2-dioxaborolane (2i)



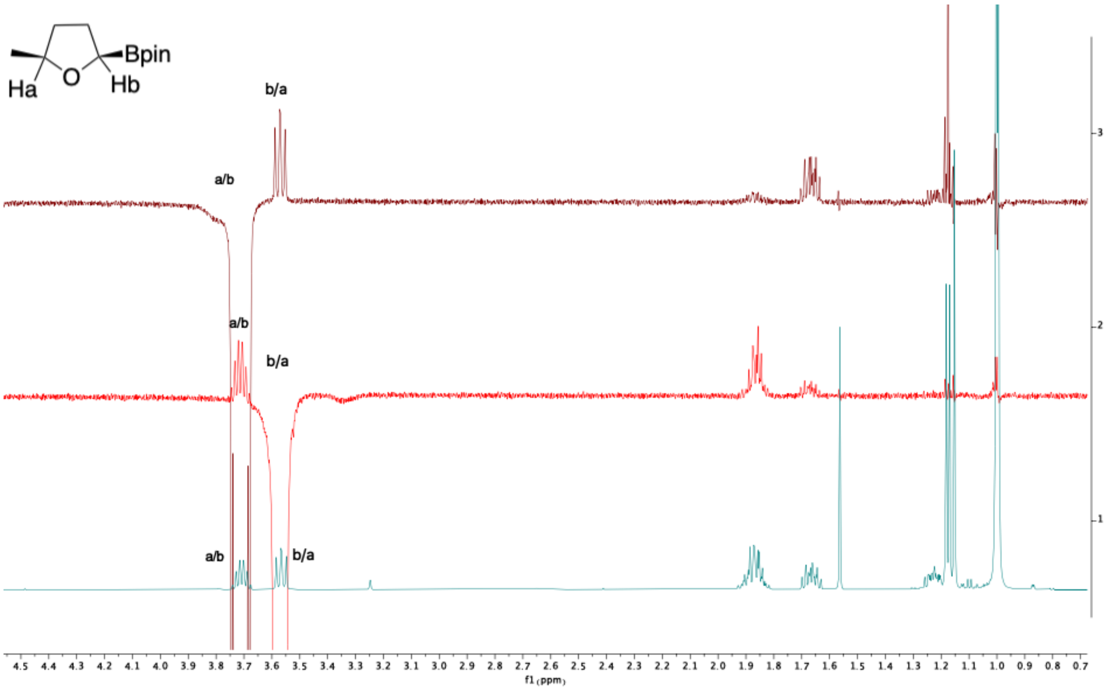
^{13}C{^{1}H} (126 MHz, C_6D_6) NMR of 4,4,5,5-Tetramethyl-2-(5-methyltetrahydrofuran-2-yl)-1,3,2-dioxaborolane (2i)



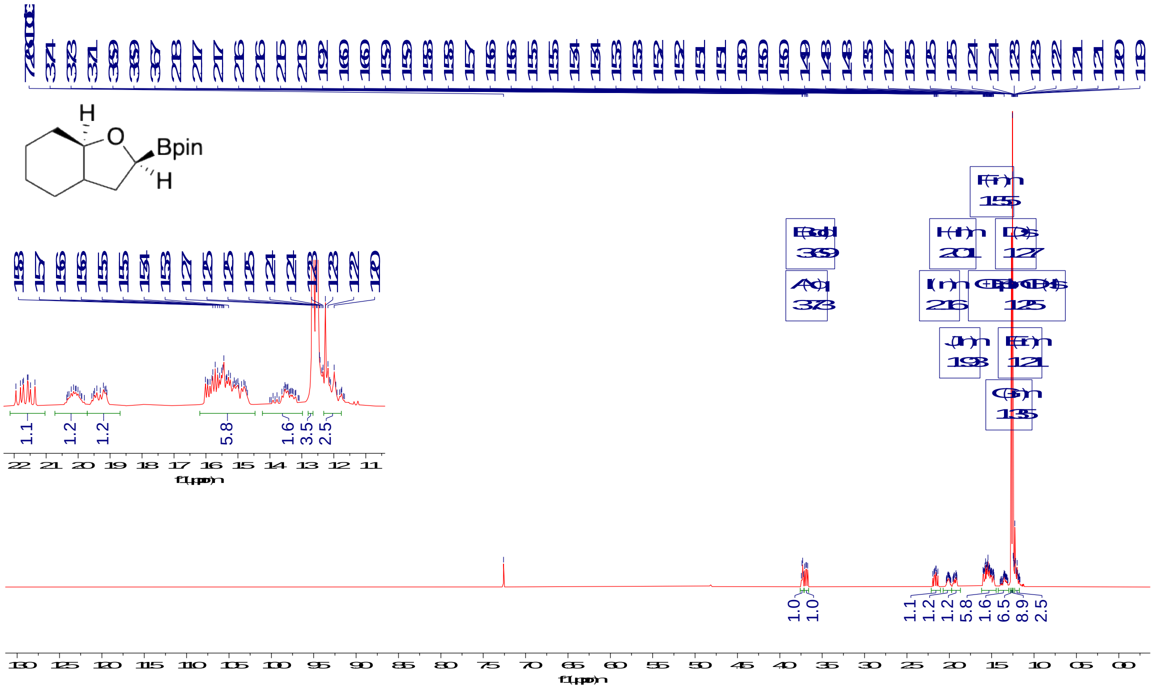
^{11}B NMR (160MHz, $CDCl_3$) of 4,4,5,5-Tetramethyl-2-(5-methyltetrahydrofuran-2-yl)-1,3,2-dioxaborolane (2i)



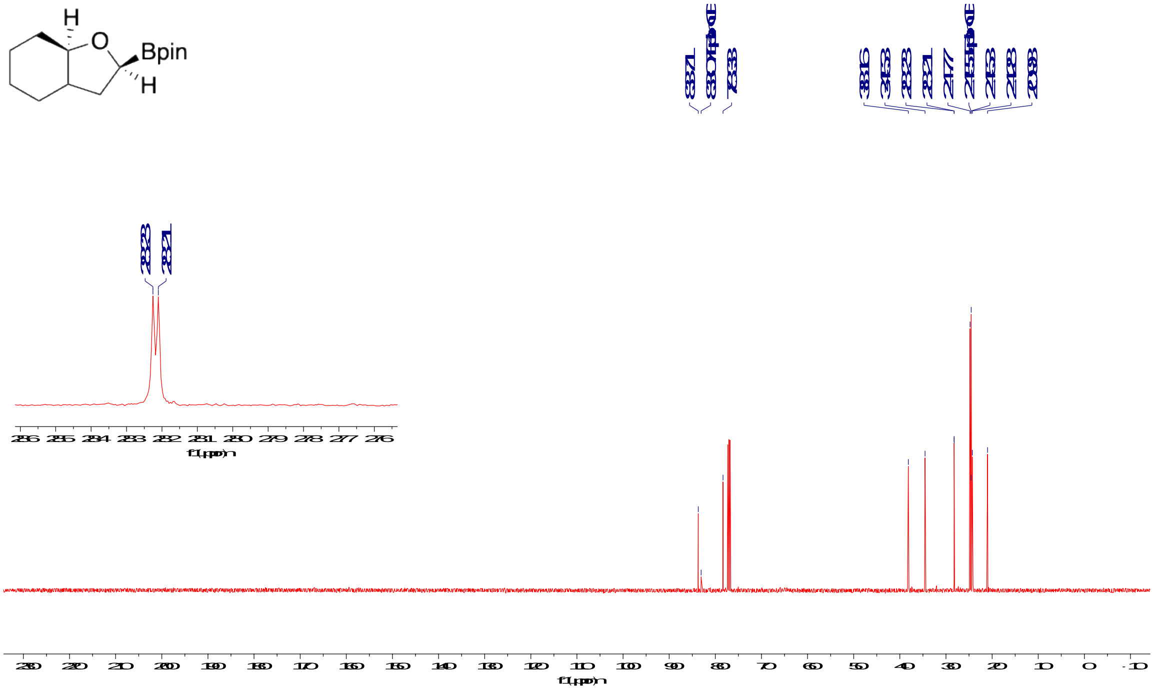
1D-NOE NMR of 4,4,5,5-Tetramethyl-2-(5-methyltetrahydrofuran-2-yl)-1,3,2-dioxaborolane (2i)



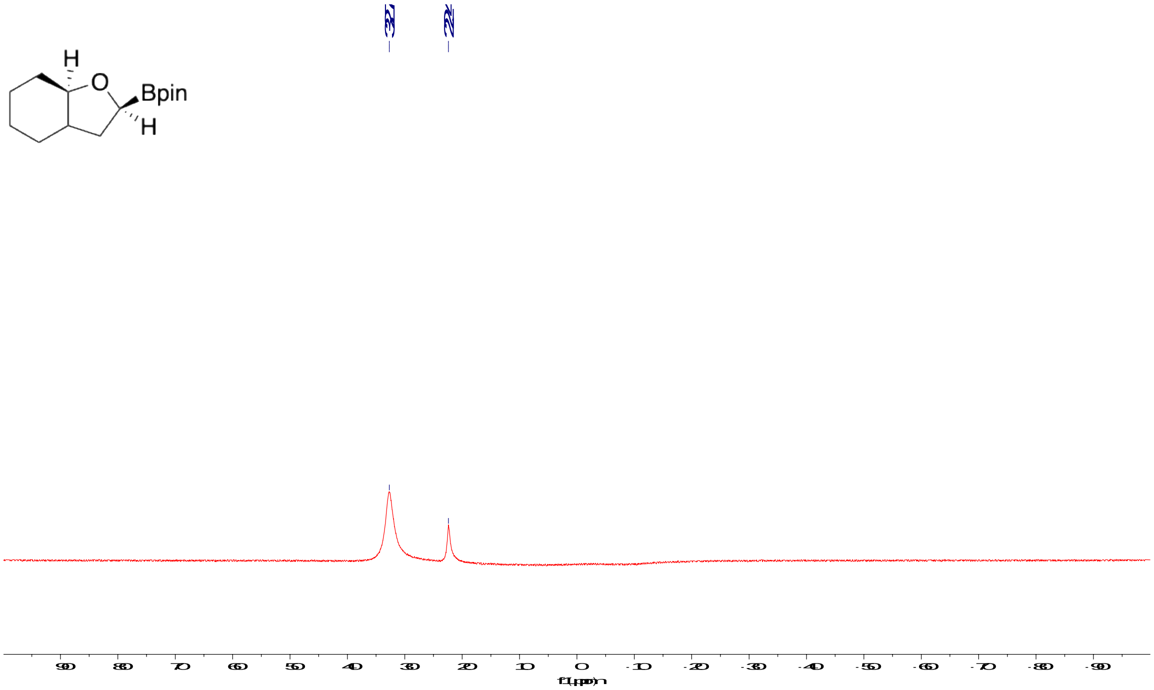
^{1}H NMR (500MHz, $CDCl_3$) of 4,4,5,5-tetramethyl-2-(octahydrobenzofuran-2-yl)-1,3,2-dioxaborolane (2j)



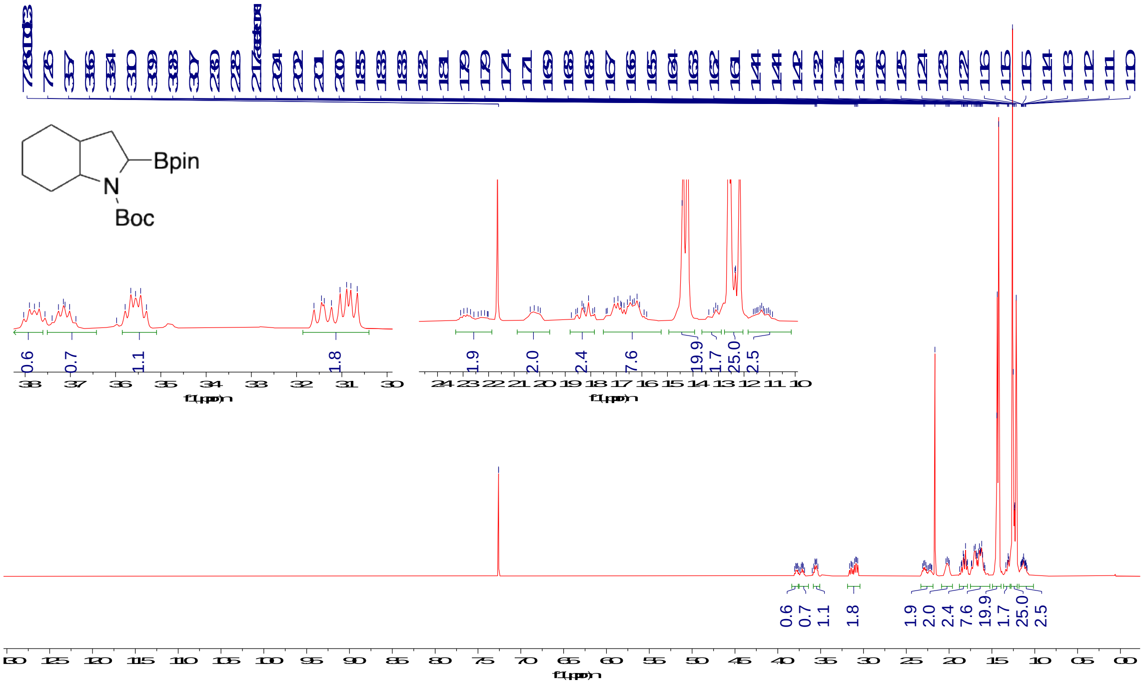
$^{13}C\{^{1}H\}$ (126 MHz, $CDCl_3$) NMR of 4,4,5,5-tetramethyl-2-(octahydrobenzofuran-2-yl)-1,3,2-dioxaborolane (2j)



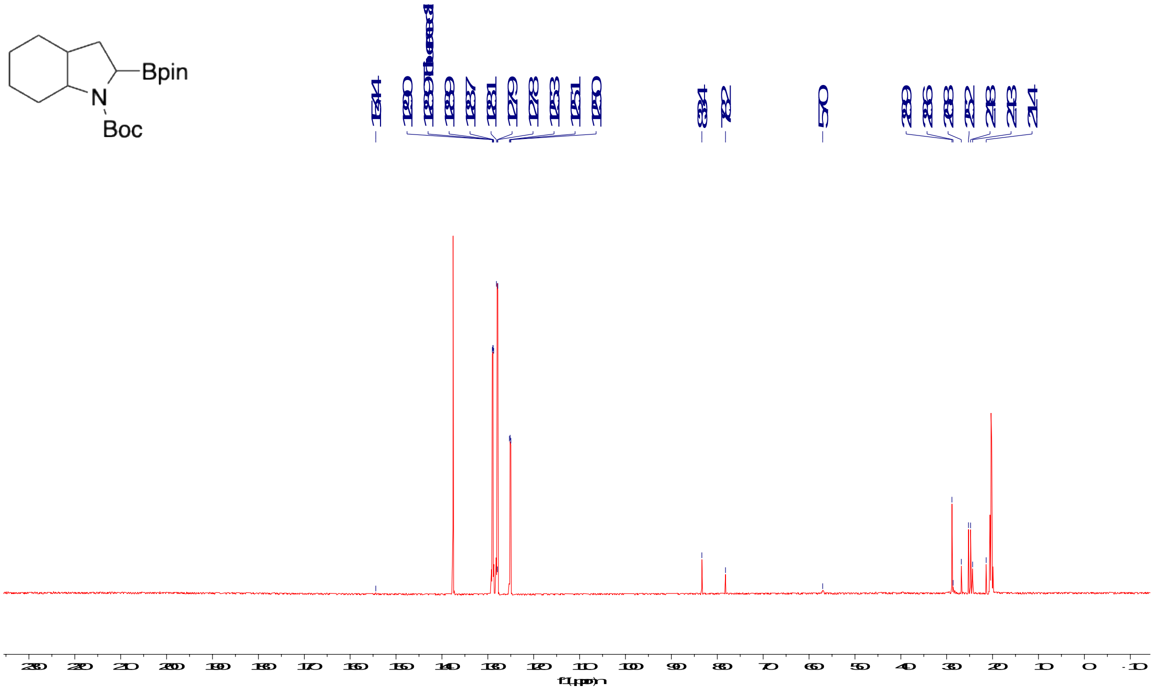
^{11}B NMR (160 MHz, $CDCl_3$) of 4,4,5,5-tetramethyl-2-(octahydrobenzofuran-2-yl)-1,3,2-dioxaborolane (2j)



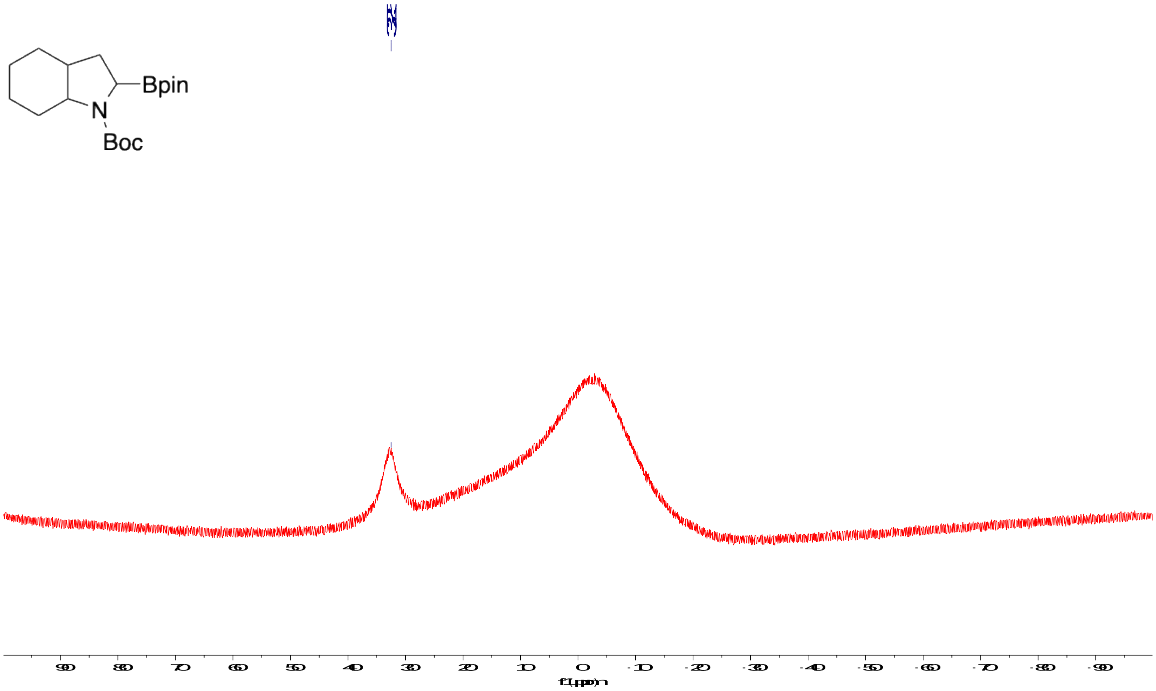
^{1}H NMR (500 MHz, $CDCl_3$) of *t*-butyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octahydroindole-1-carboxylate (2l)



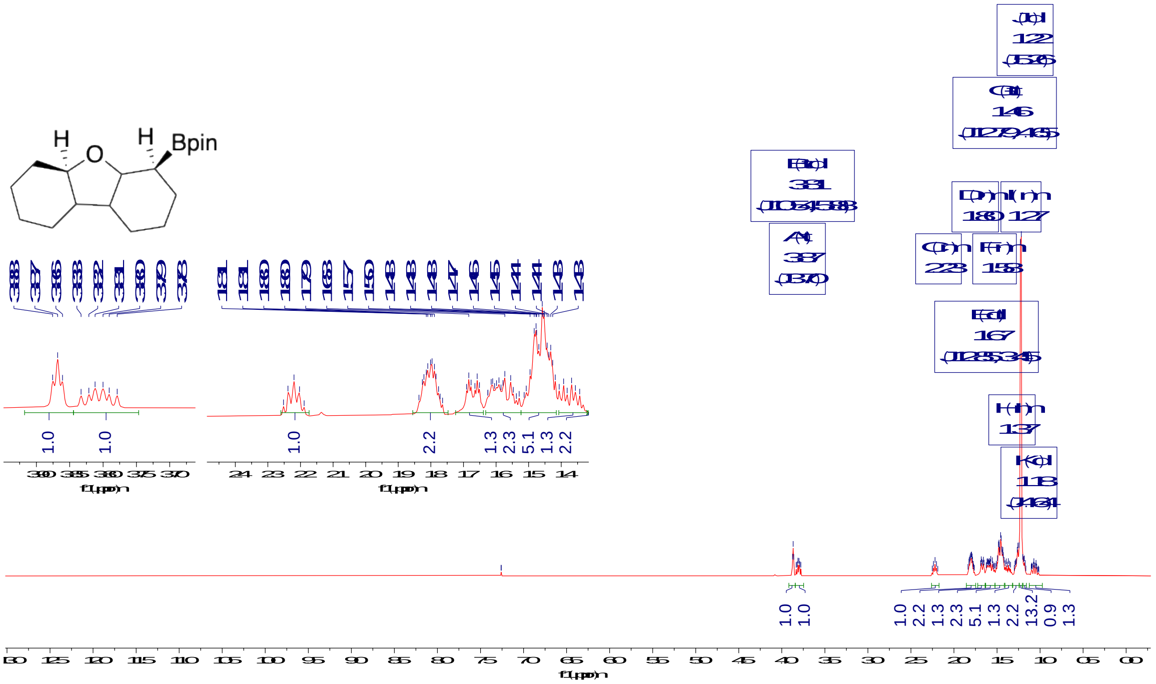
$^{13}C\{^1H\}$ (126 MHz, Toluene) NMR of *t*-butyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octahydroindole-1-carboxylate (2l)



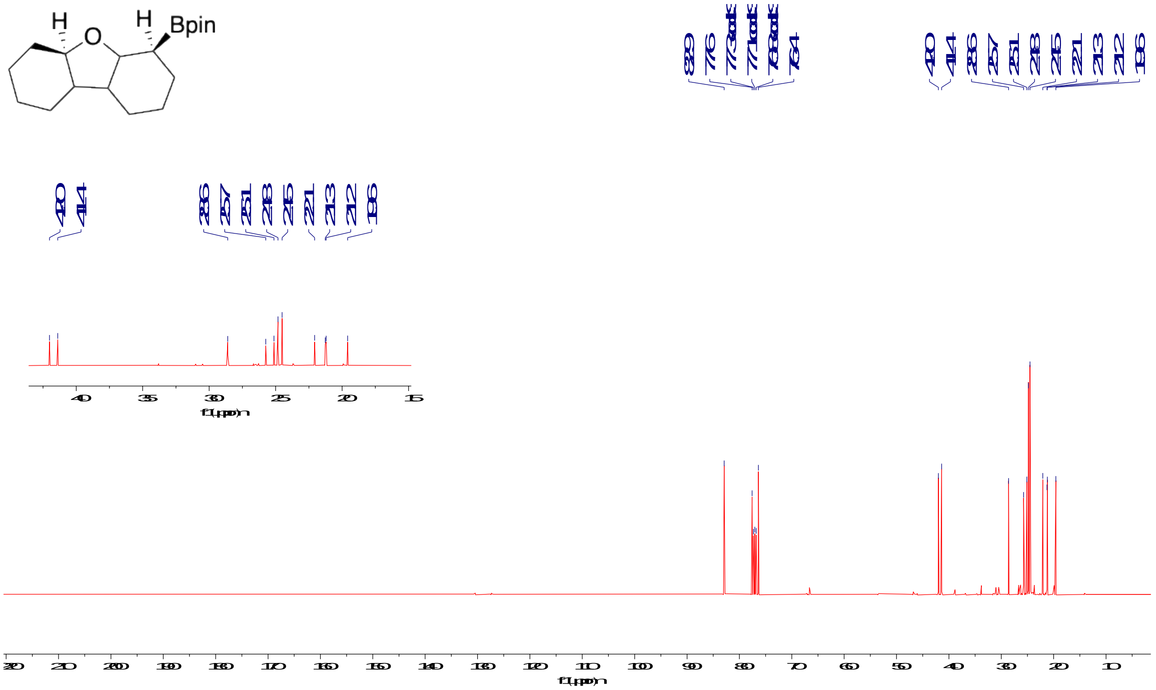
^{11}B NMR (160MHz, $CDCl_3$) of *t*-butyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octahydroindole-1-carboxylate (2l)



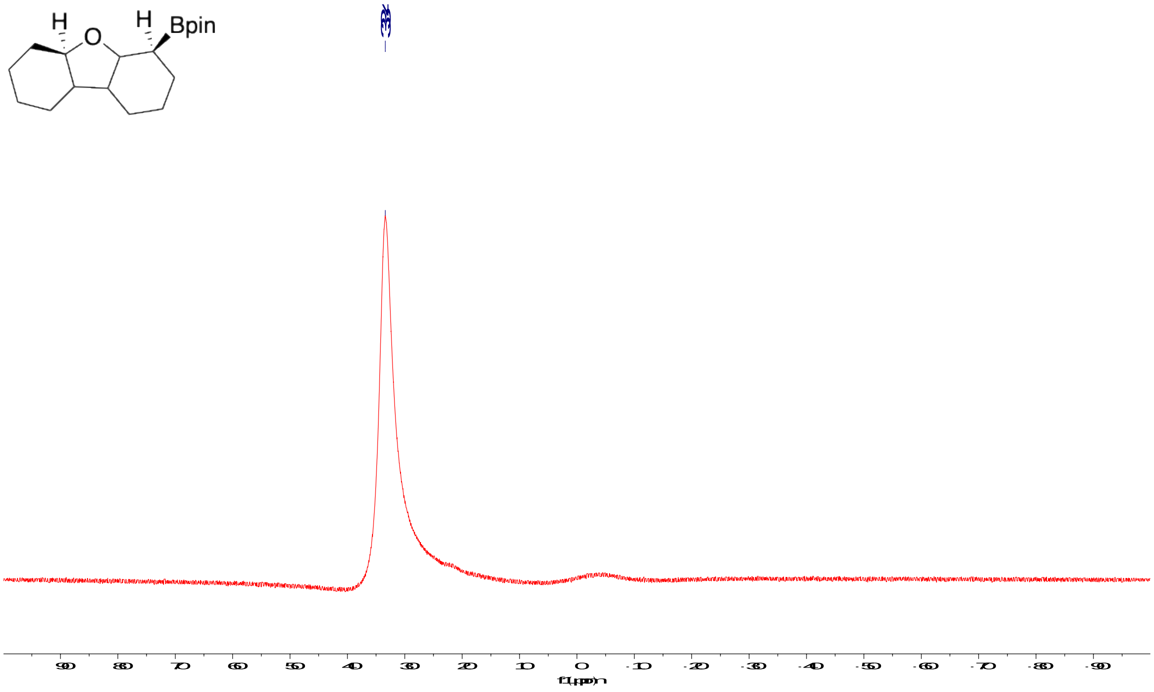
^1H NMR (500MHz, $CDCl_3$) of 2-(dodecahydrodibenzo[*b*,*d*]furan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2k)



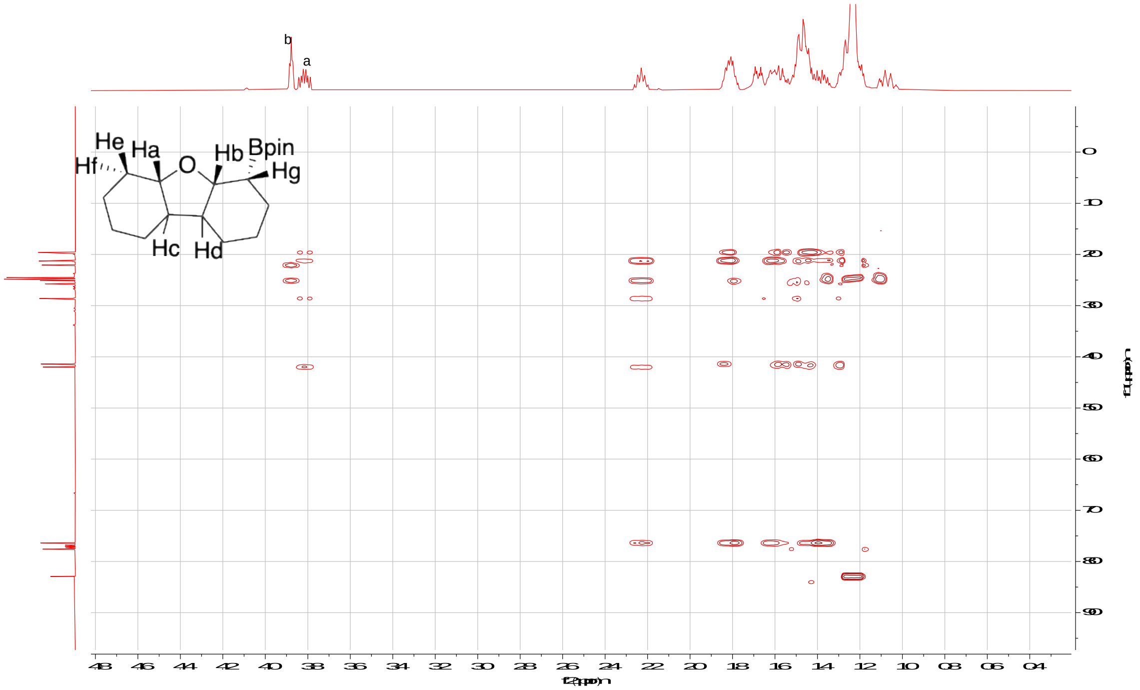
$^{13}C\{^1H\}$ (126 MHz, $CDCl_3$) NMR of 2-(dodecahydrodibenzo[*b*,*d*]furan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2k)



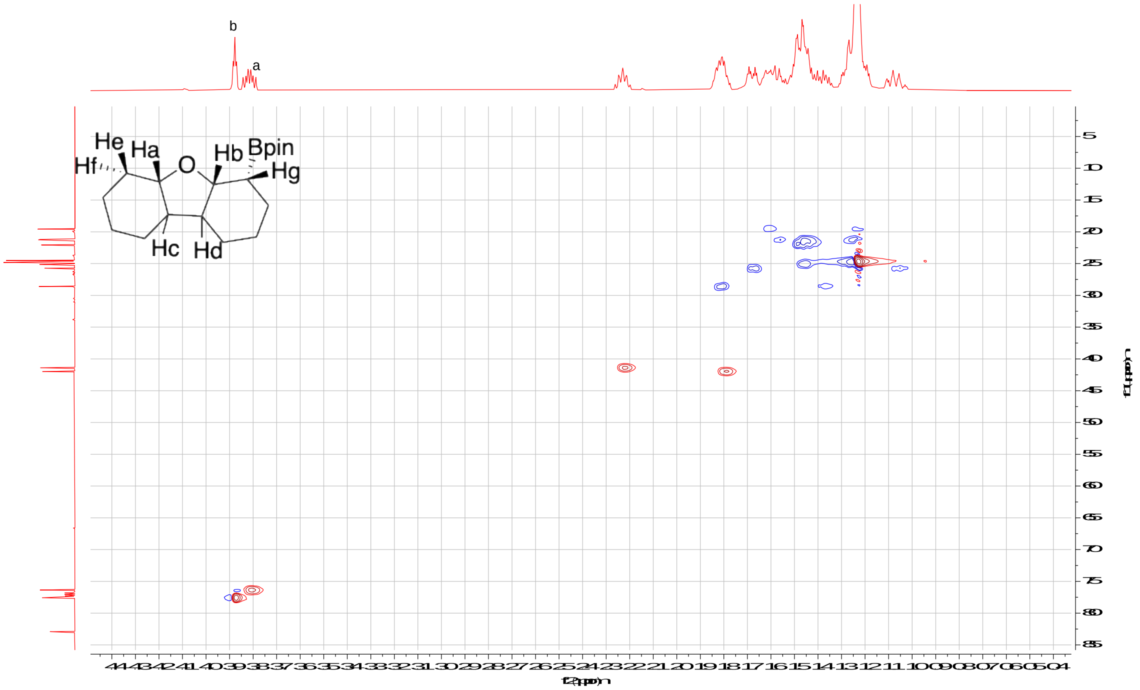
^{11}B NMR (160 MHz, CDCl$_3$) of 2-(dodecahydrodibenzo[*b*,*d*]furan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2k)



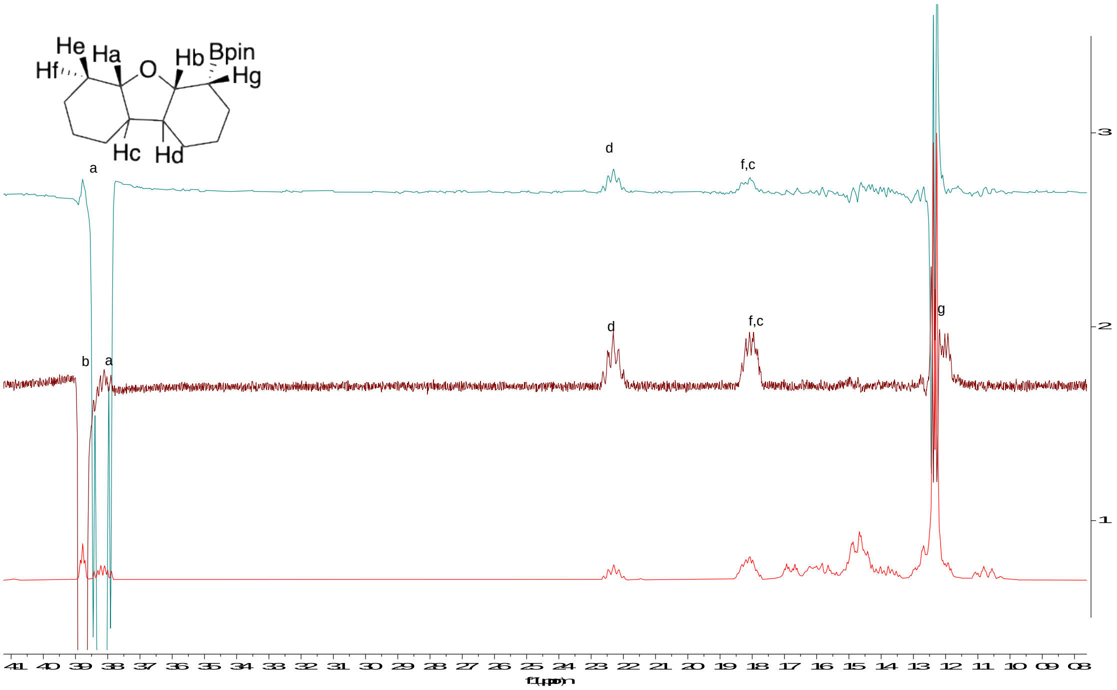
HMBC of 2-(dodecahydrodibenzo[*b*,*d*]furan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2k)



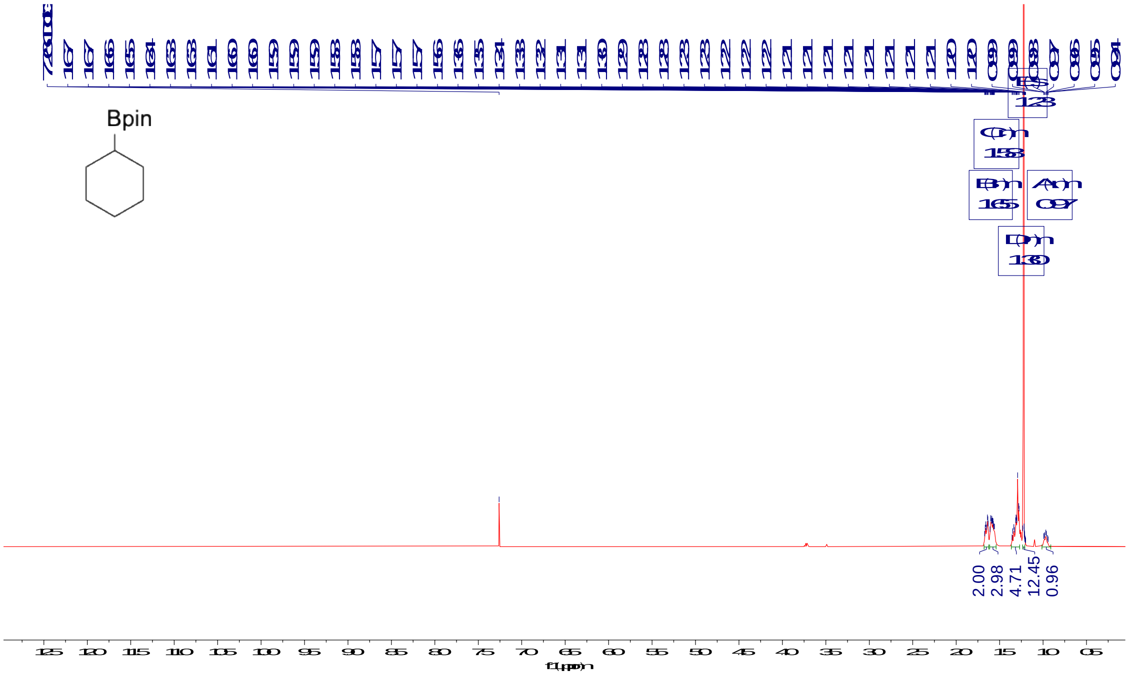
HSQC of 2-(dodecahydrodibenzo[*b*,*d*]furan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2k)



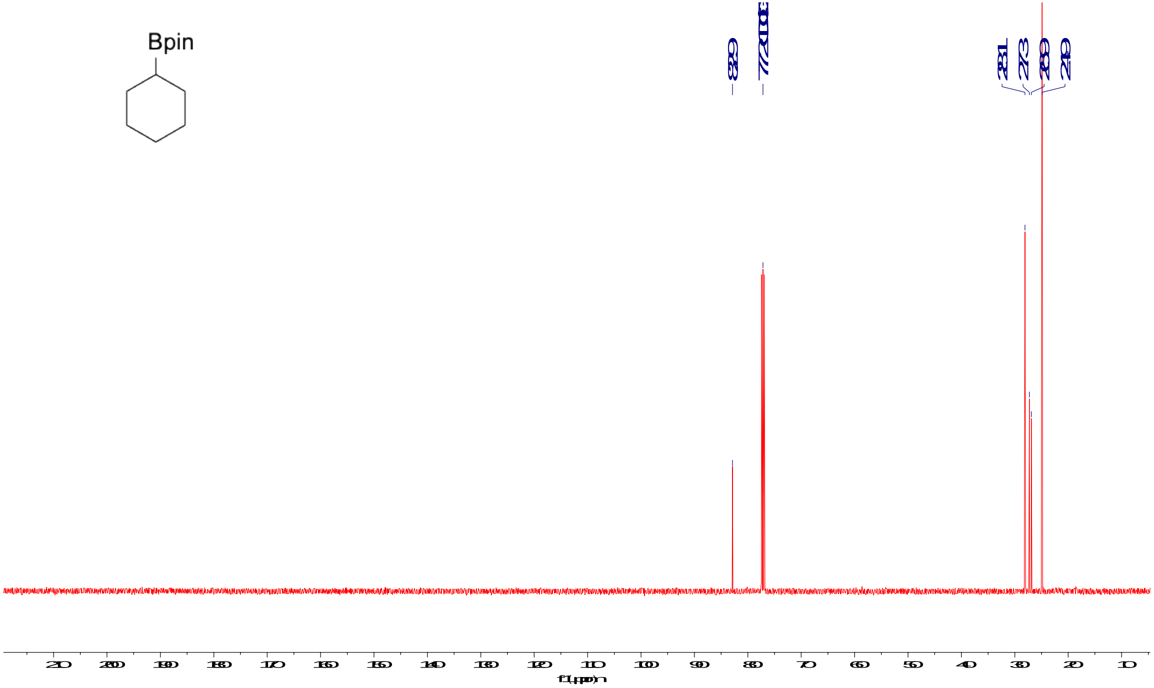
NOE of 2-(dodecahydrodibenzo[*b*,*d*]furan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2k)



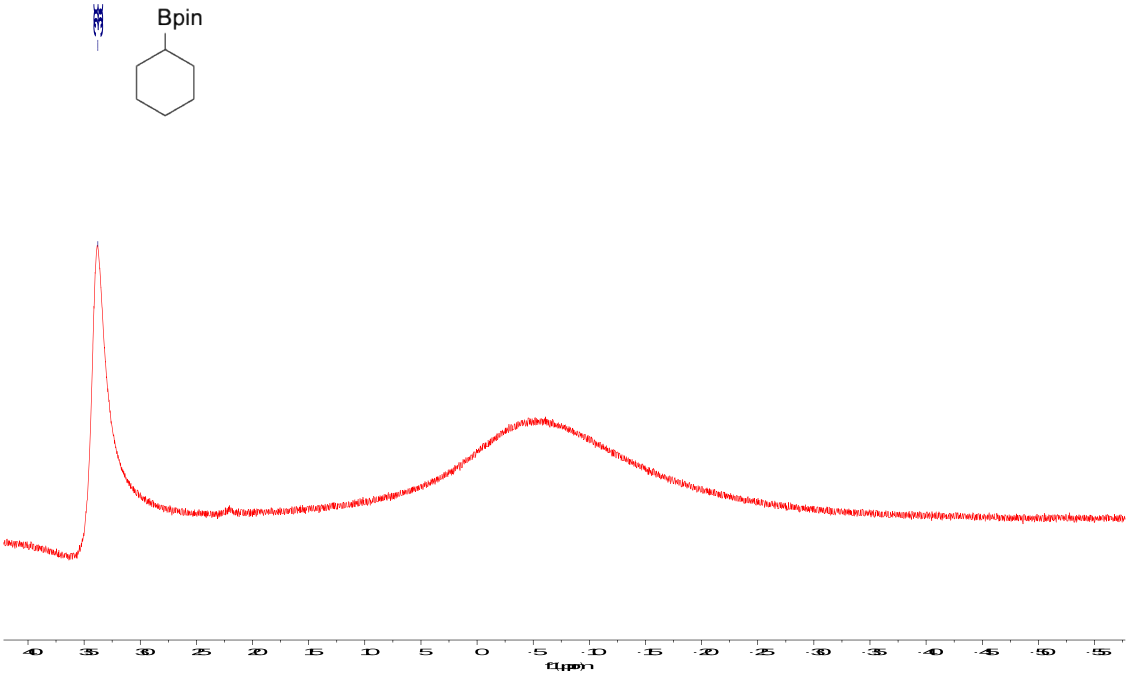
^{1}H NMR (500MHz, CDCl$_3$) of 2-cyclohexyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2p)



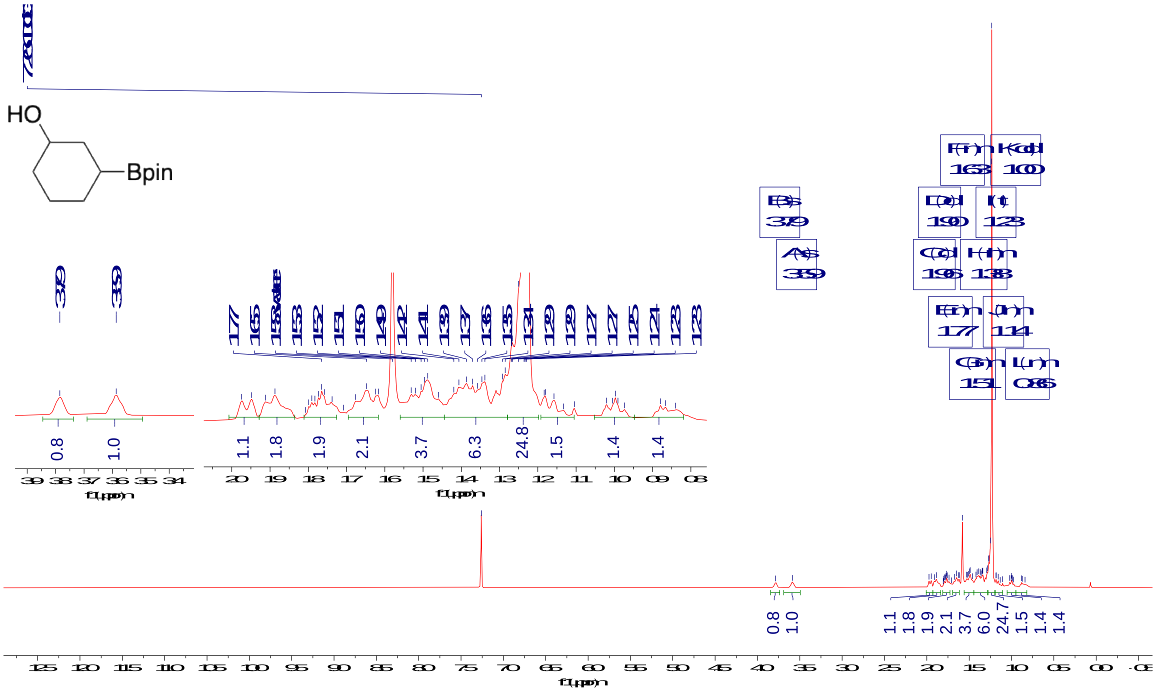
^{13}C{^{1}H} (126 MHz, CDCl$_3$) NMR of 2-cyclohexyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2p)



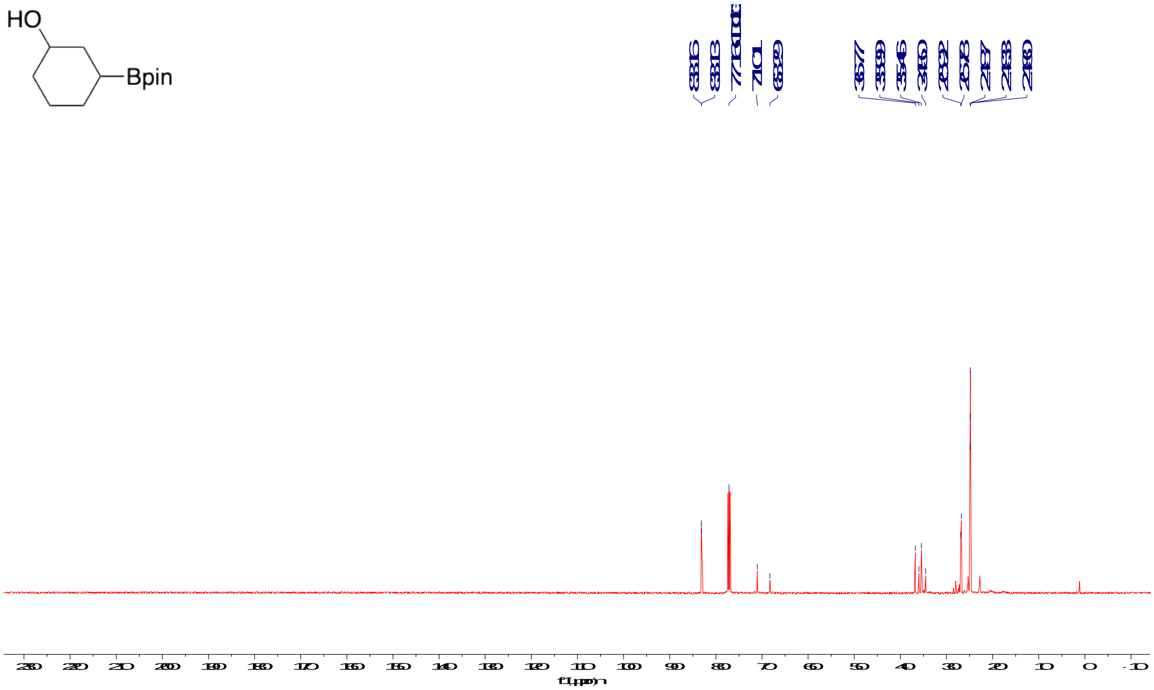
^{11}B NMR (160MHz, CDCl$_3$) of 2-cyclohexyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2p)



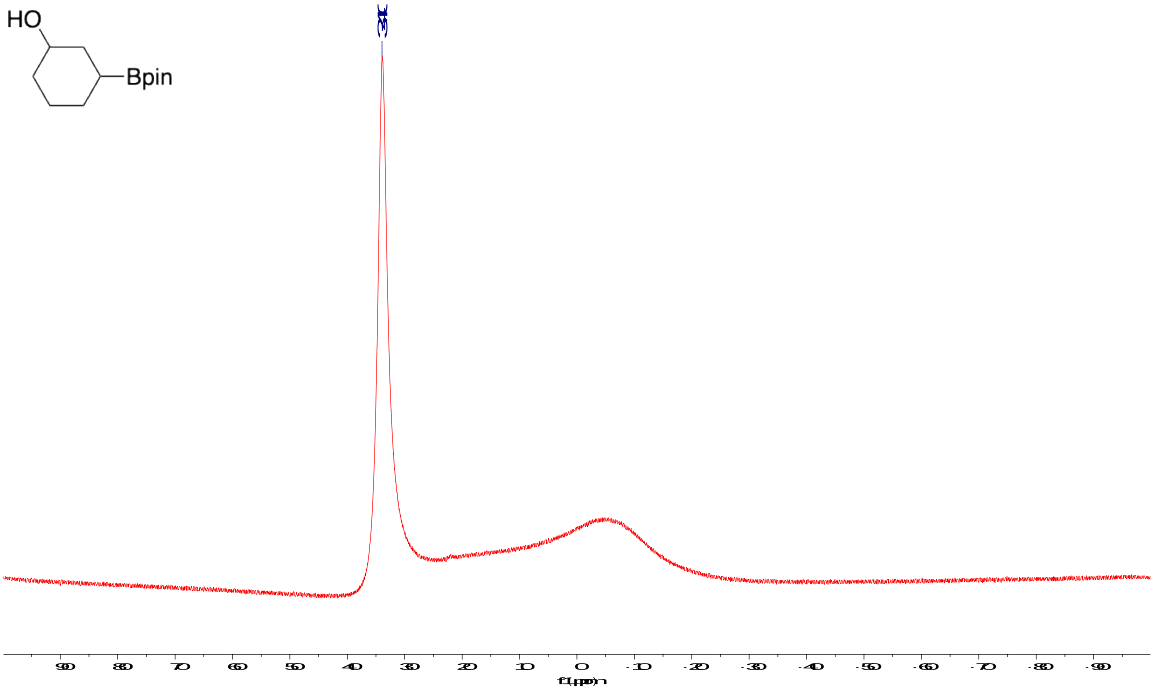
^{1}H NMR (500MHz, CDCl$_3$) of 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexan-1-ol (2q)



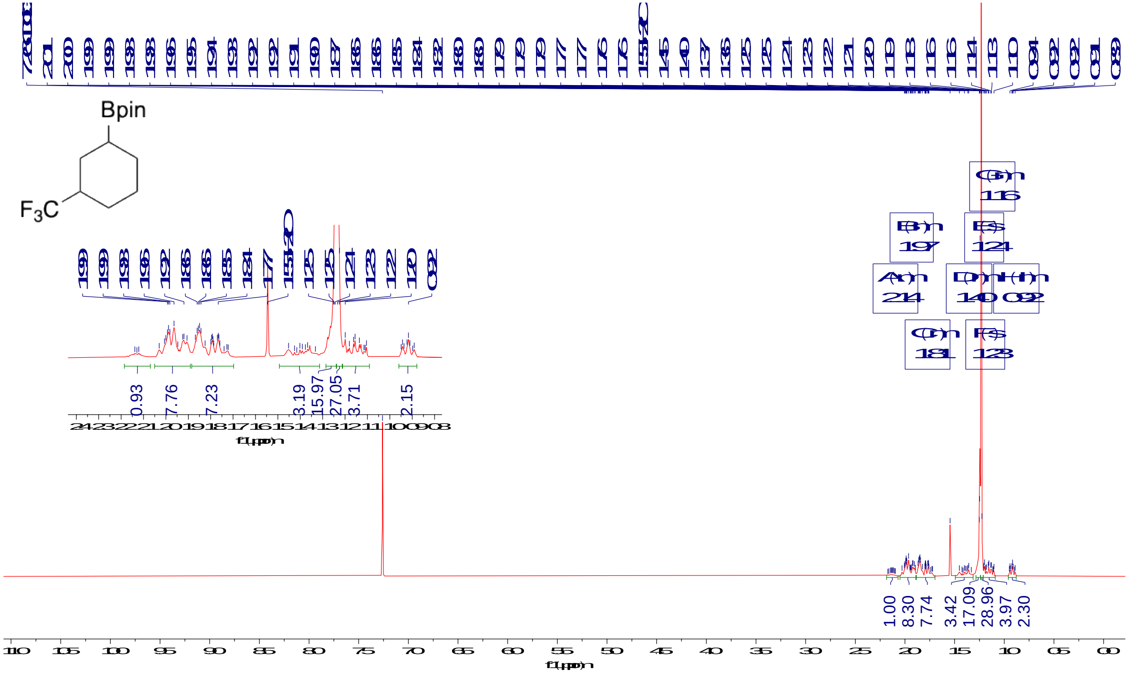
$^{13}C\{^{1}H\}$ (126 MHz, $CDCl_3$) NMR of 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexan-1-ol (2q)



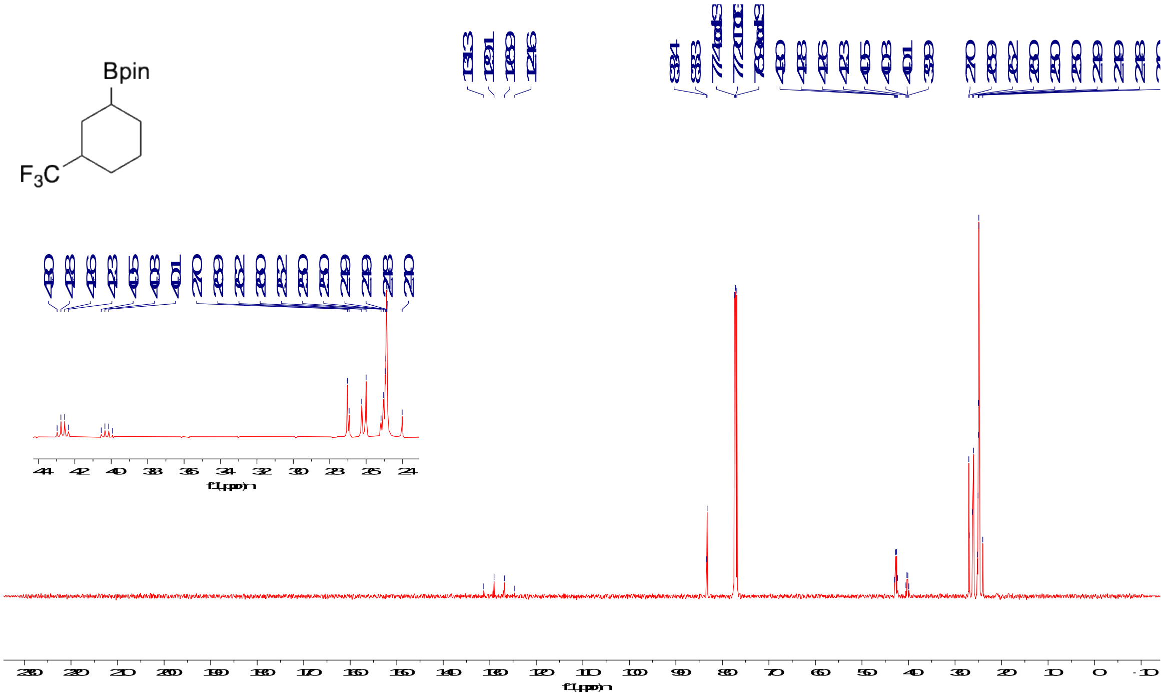
^{11}B NMR (160MHz, $CDCl_3$) of 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexan-1-ol (2q)



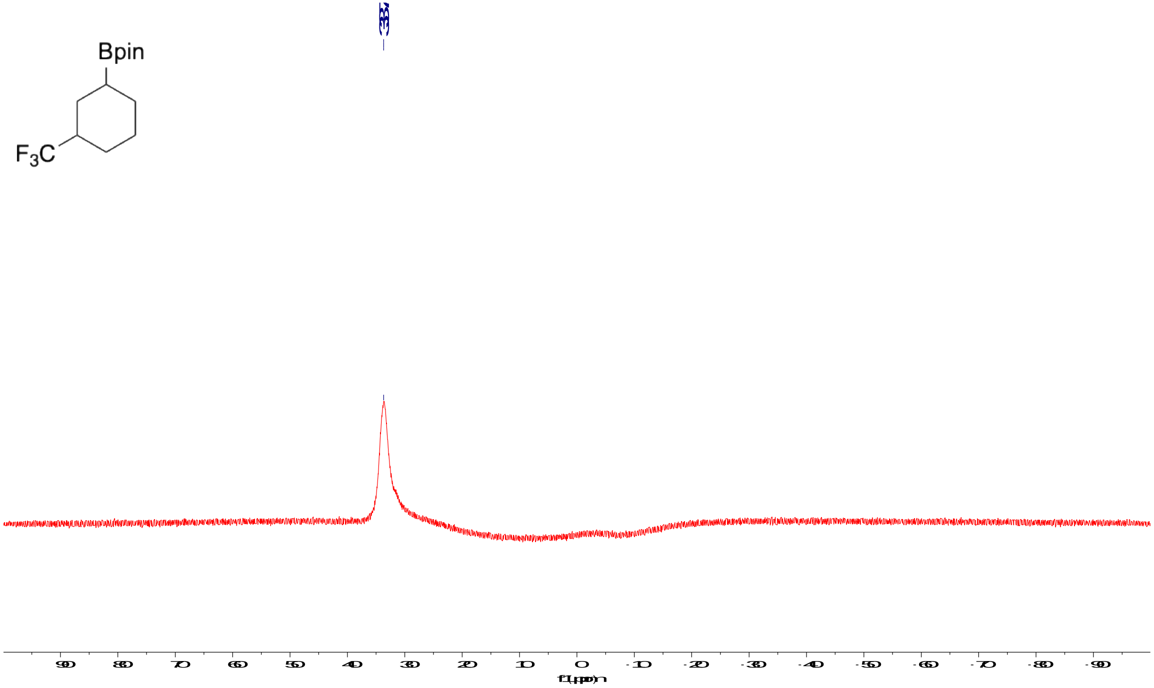
^{1}H NMR (500 MHz, CDCl$_3$) of 4,4,5,5-tetramethyl-2-(-3-(trifluoromethyl)cyclohexyl)-1,3,2-dioxaborolane (2r)



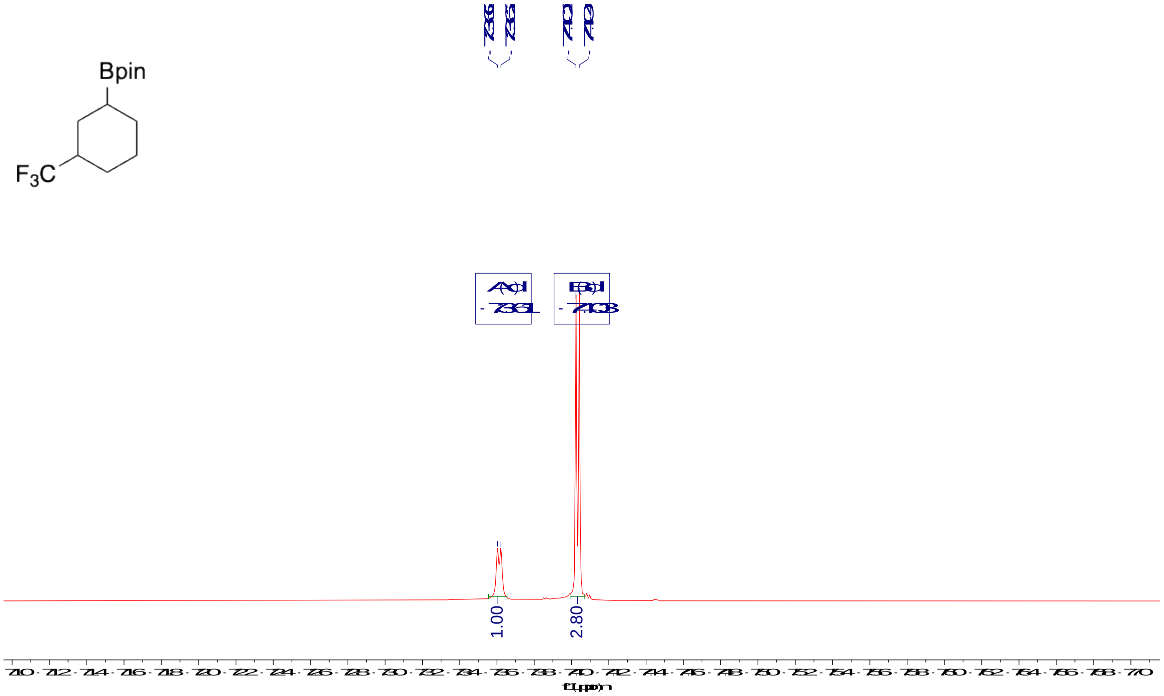
^{13}C{^{1}H} (126 MHz, CDCl$_3$) NMR of 4,4,5,5-tetramethyl-2-(-3-(trifluoromethyl)cyclohexyl)-1,3,2-dioxaborolane (2r)



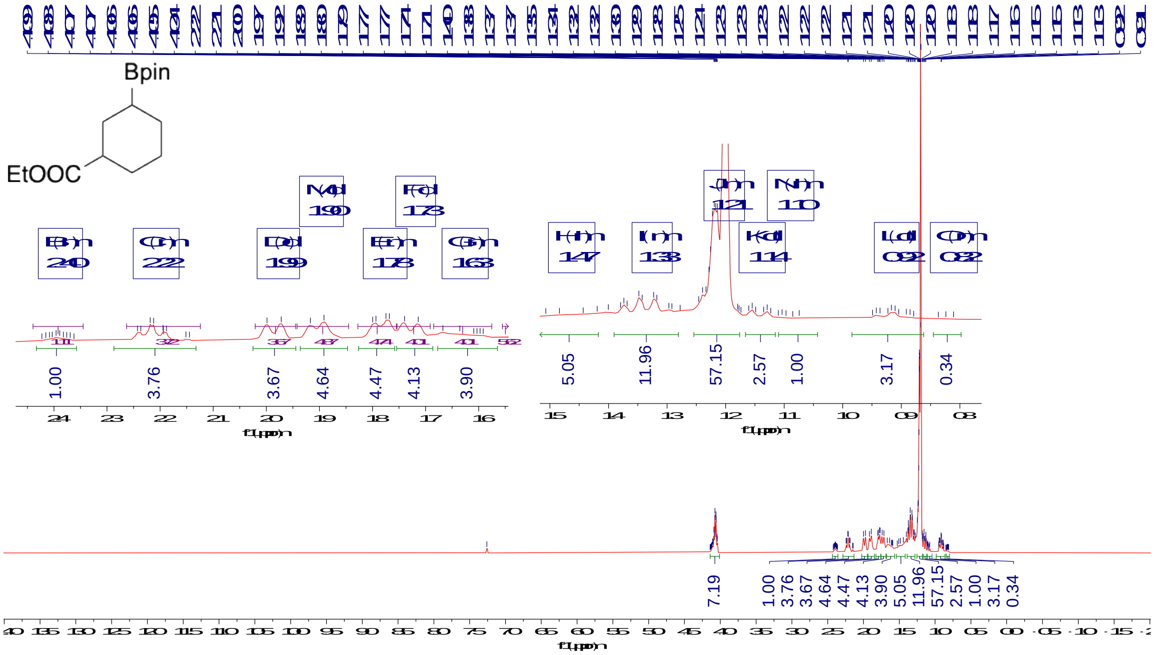
^{11}B NMR (160 MHz, CDCl$_3$) of 4,4,5,5-tetramethyl-2-(-3-(trifluoromethyl)cyclohexyl)-1,3,2-dioxaborolane (2r)



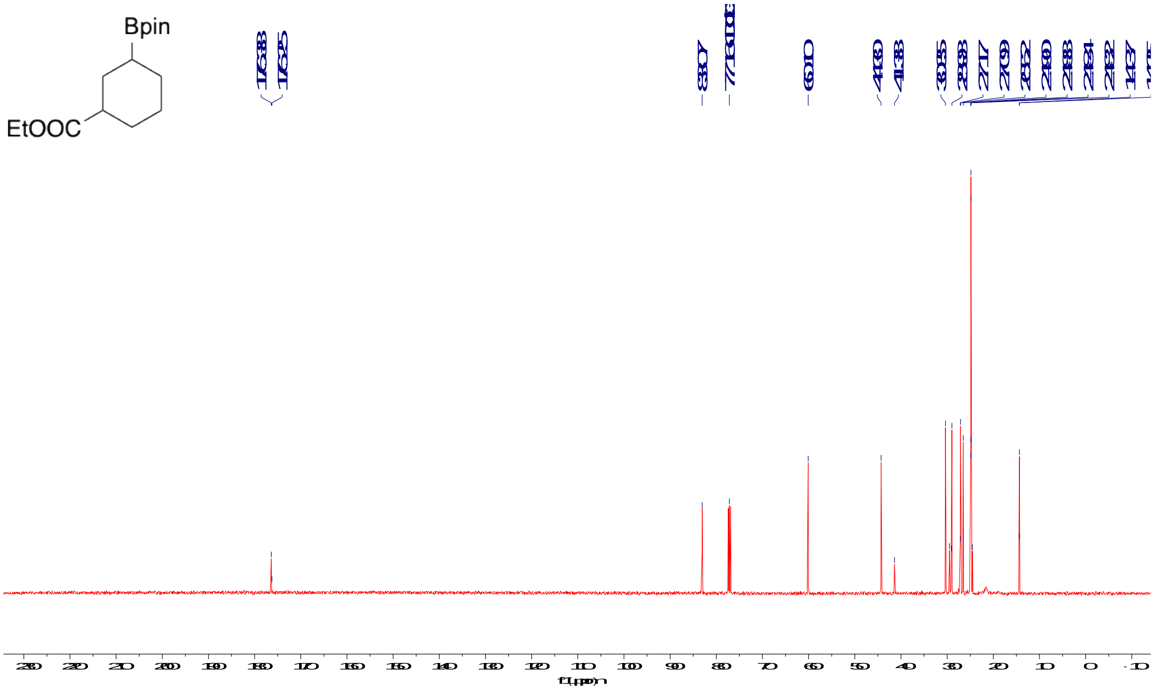
^{19}F NMR (470 MHz, CDCl$_3$) of 4,4,5,5-tetramethyl-2-(-3-(trifluoromethyl)cyclohexyl)-1,3,2-dioxaborolane (2r)



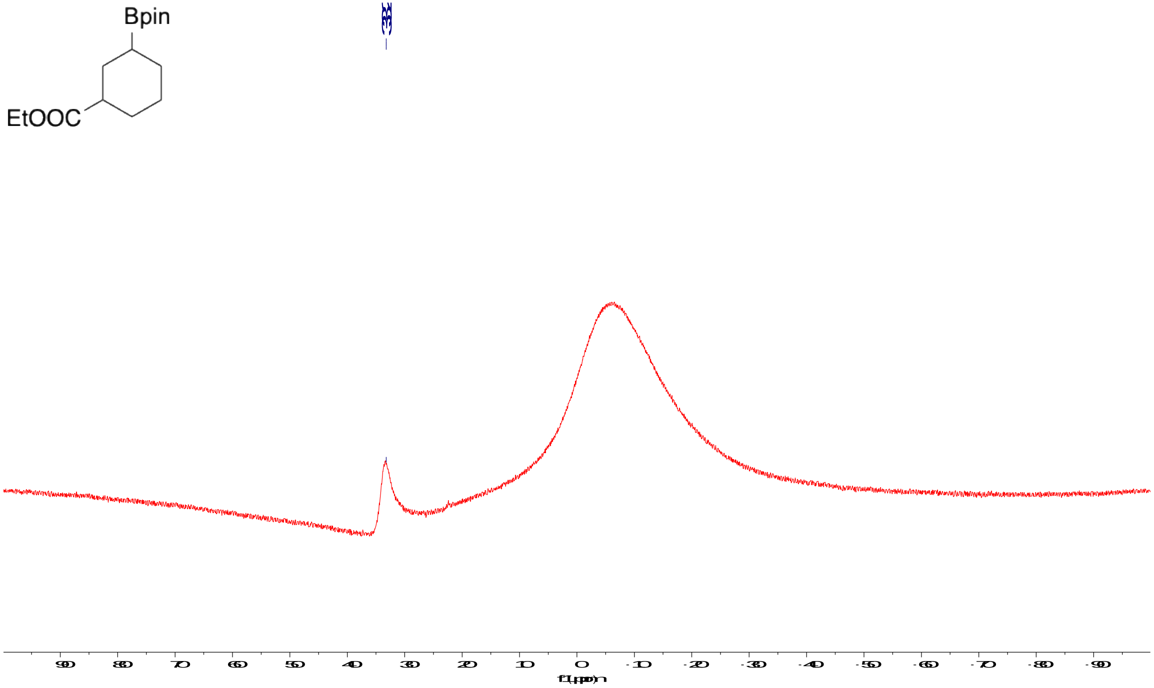
^{1}H NMR (500 MHz, CDCl$_3$) of ethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexane-1-carboxylate (2s)



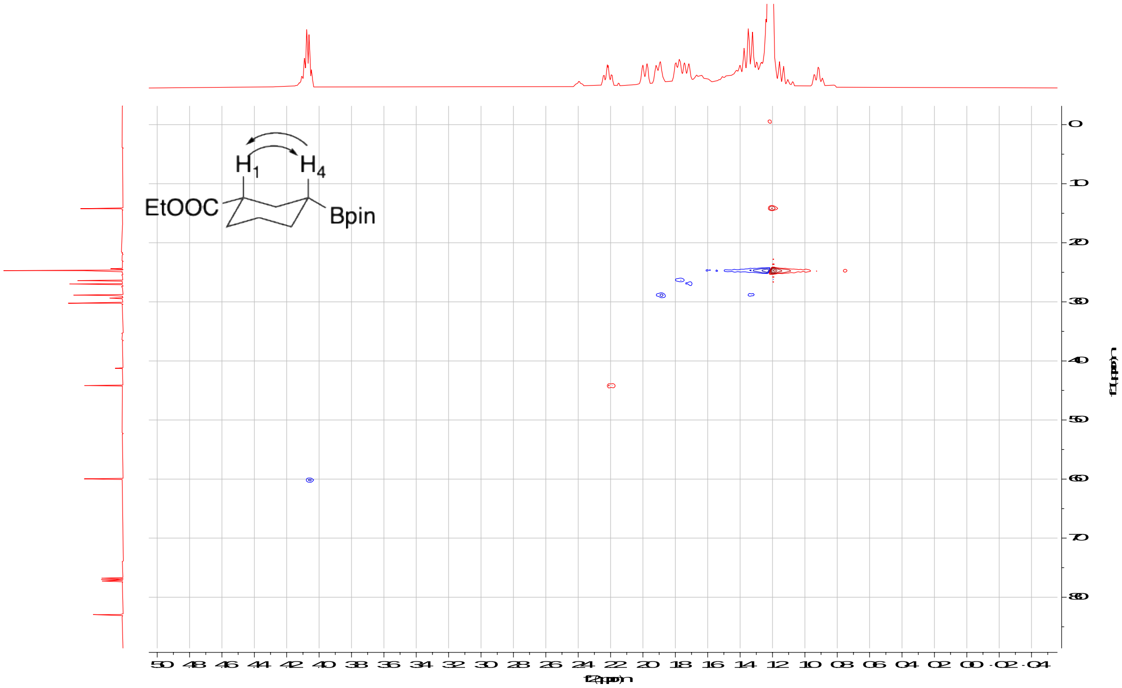
^{13}C{^{1}H} (126 MHz, CDCl$_3$) NMR of ethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexane-1-carboxylate (2s)



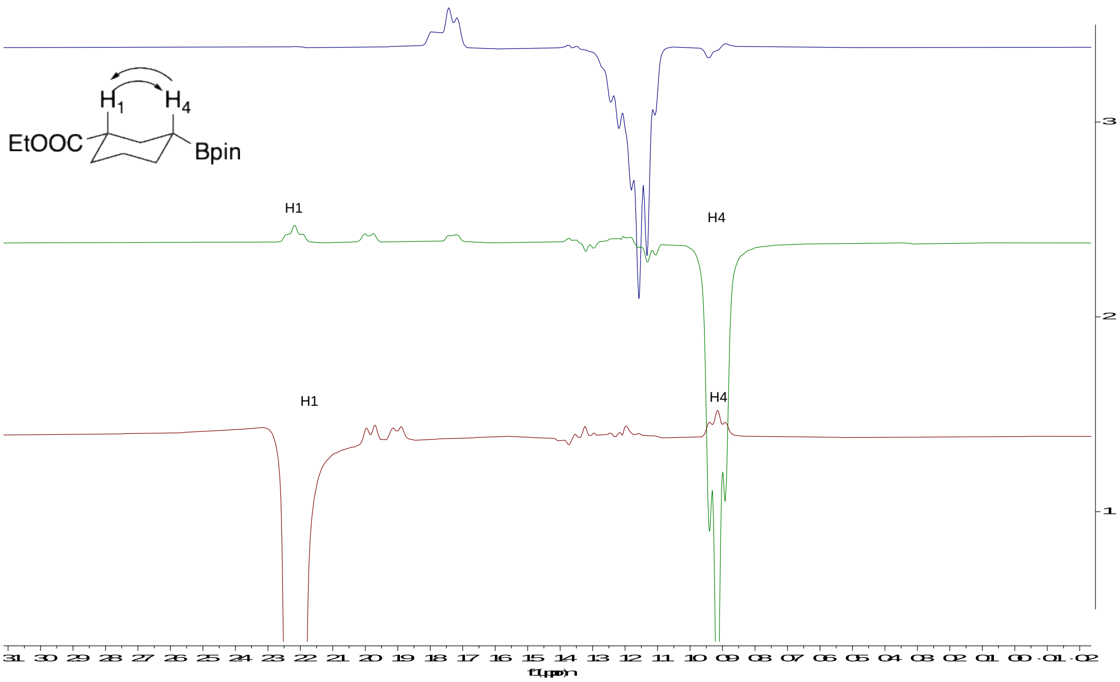
^{11}B NMR (160MHz, CDCl$_3$) of ethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexane-1-carboxylate (2s)



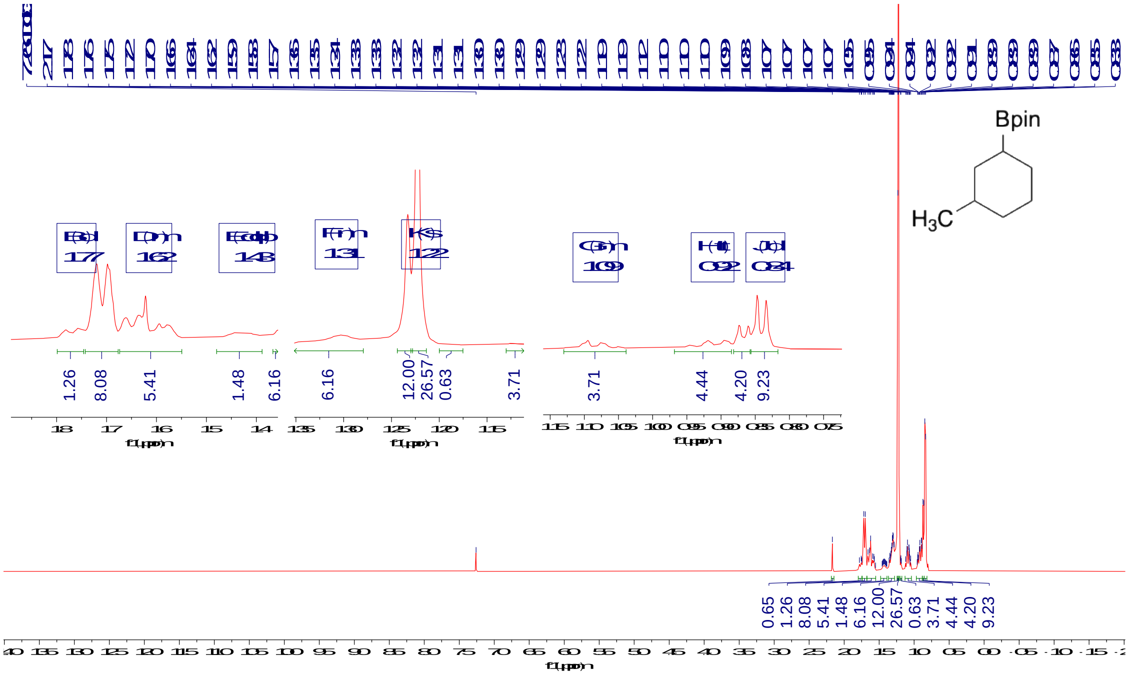
HSQC of ethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexane-1-carboxylate (2s)



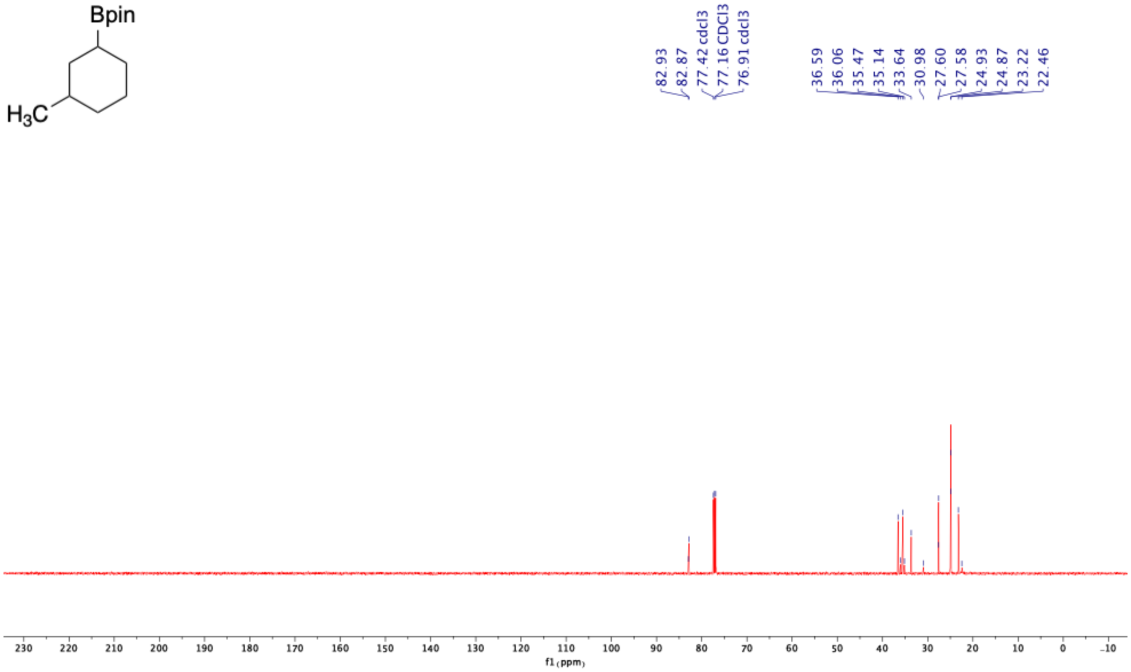
NOE of ethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexane-1-carboxylate (2s)



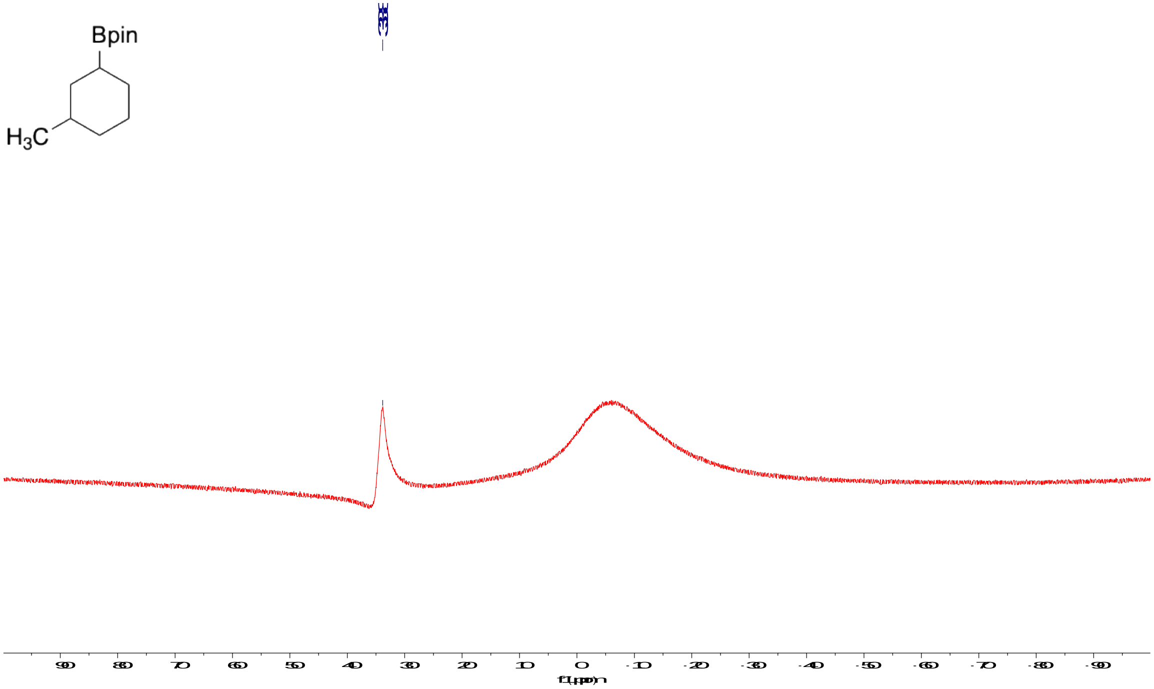
^{1}H NMR (500MHz, $CDCl_3$) of 4,4,5,5-tetramethyl-2-(3-methylcyclohexyl)-1,3,2-dioxaborolane (2t)



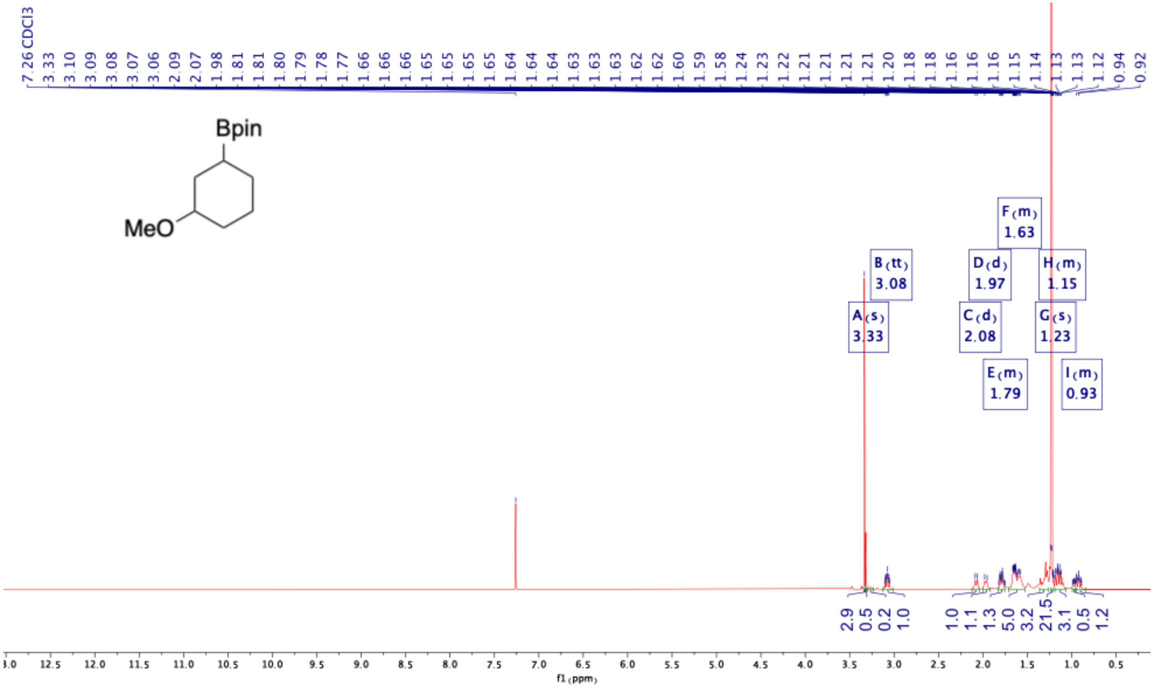
$^{13}C\{^{1}H\}$ (126 MHz, $CDCl_3$) NMR of 4,4,5,5-tetramethyl-2-(3-methylcyclohexyl)-1,3,2-dioxaborolane (2t)



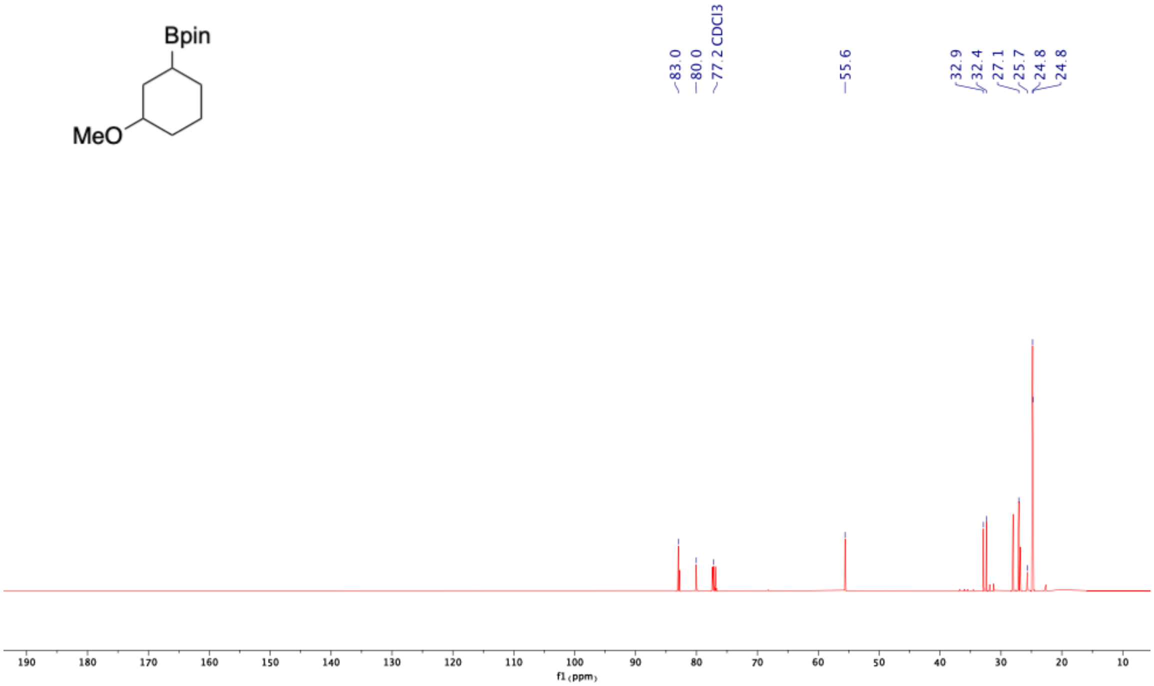
^{11}B NMR (160MHz, $CDCl_3$) of 4,4,5,5-tetramethyl-2-(3-methylcyclohexyl)-1,3,2-dioxaborolane (2t)



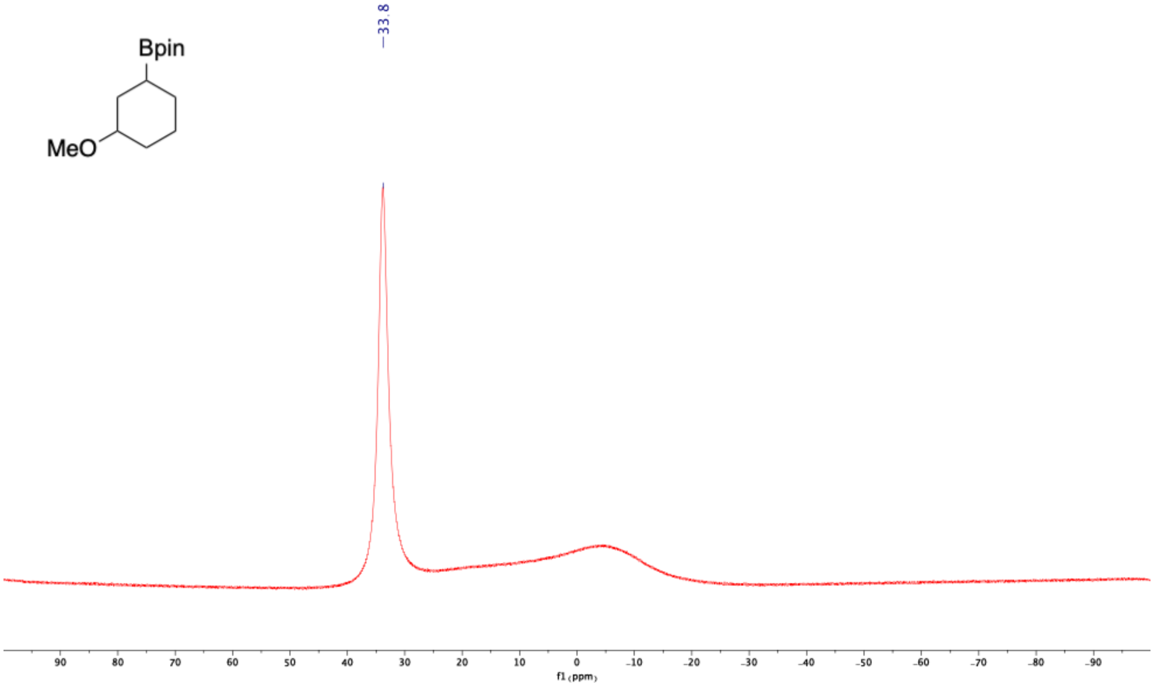
^{1}H NMR (500MHz, $CDCl_3$) of 2-(-3-methoxycyclohexyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2u)



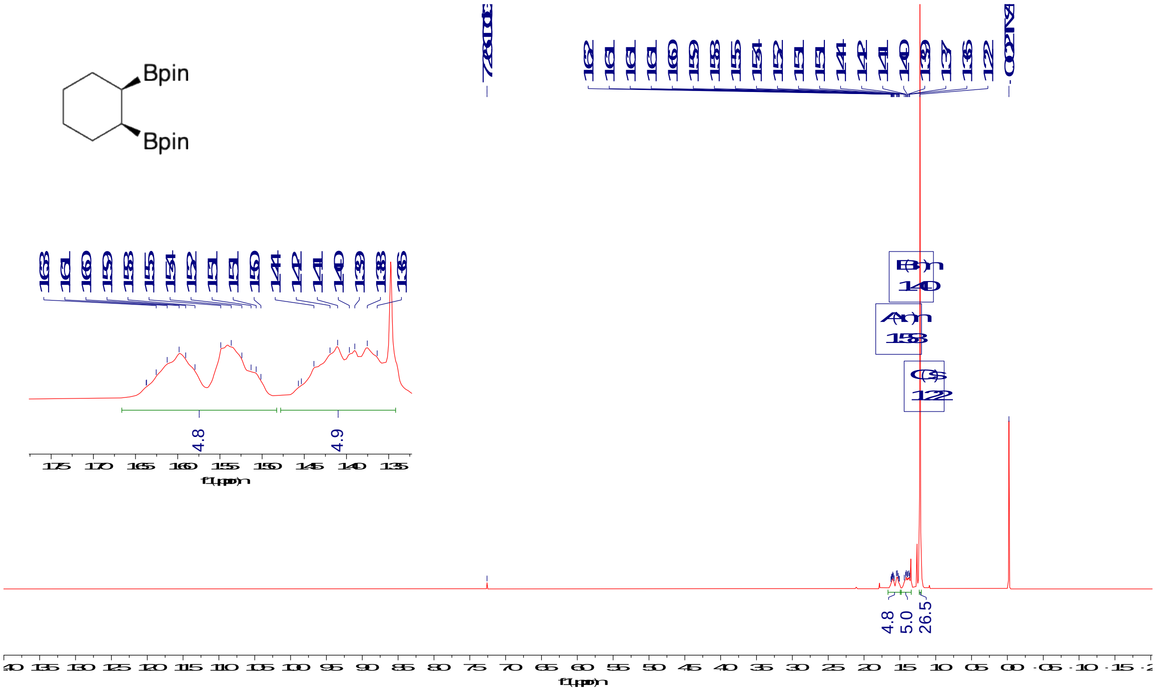
$^{13}C\{^1H\}$ (126 MHz, $CDCl_3$) NMR of 2-(-3-methoxycyclohexyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2u)



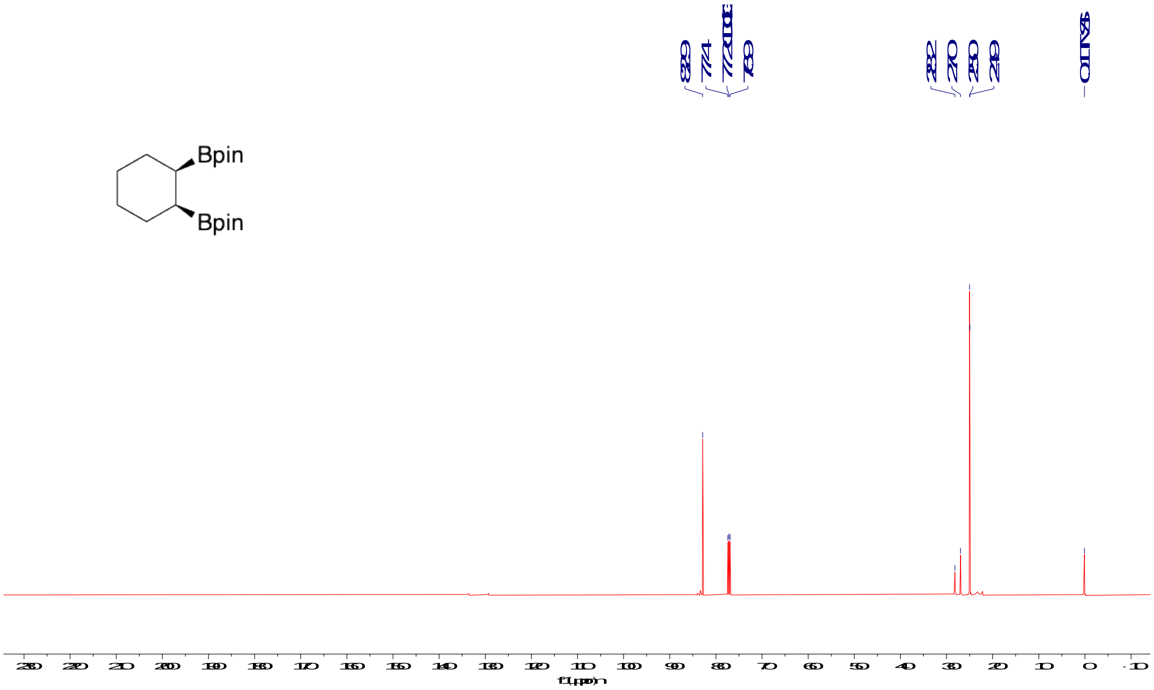
^{11}B NMR (160MHz, CDCl$_3$) of 2-(-3-methoxycyclohexyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2u)



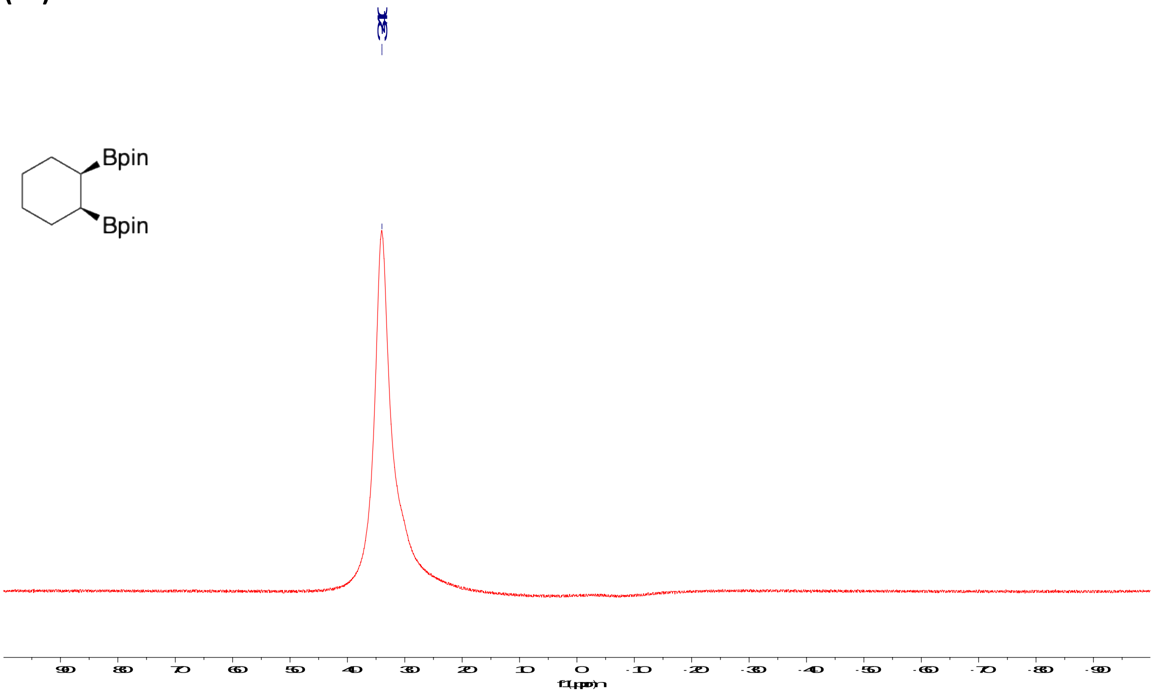
^{1}H NMR (500MHz, CDCl$_3$) of cis-1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexane (2v)



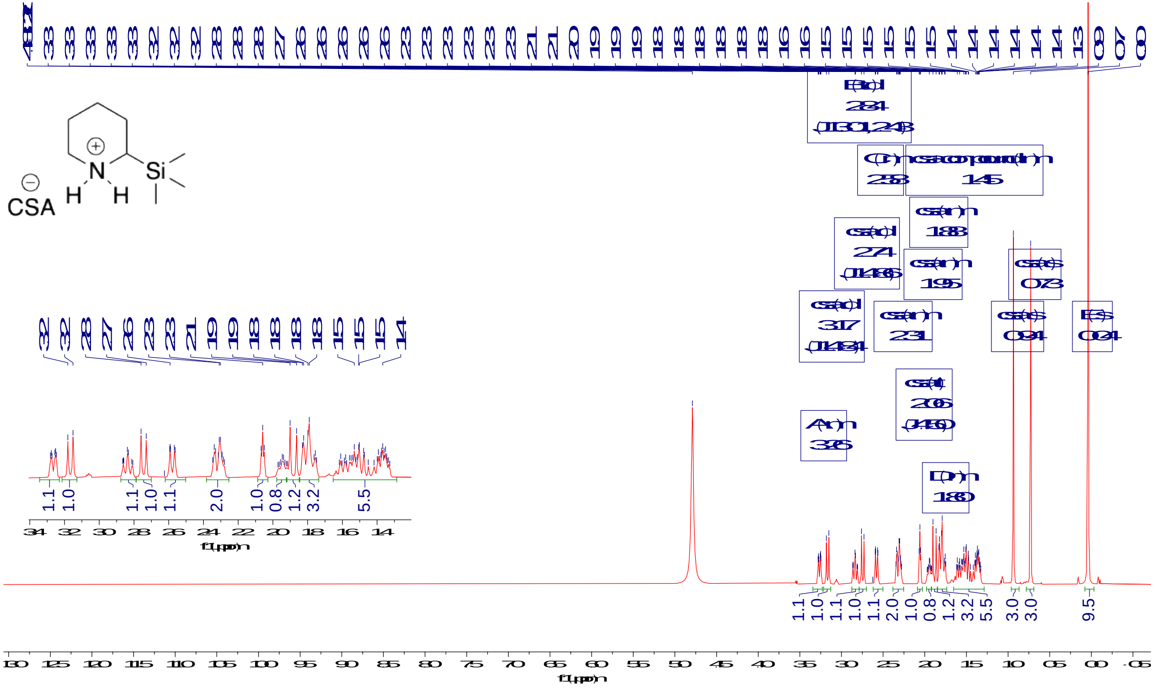
$^{13}C\{^{1}H\}$ (126 MHz, $CDCl_3$) of cis-1,2-bis(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)cyclohexane (2v)



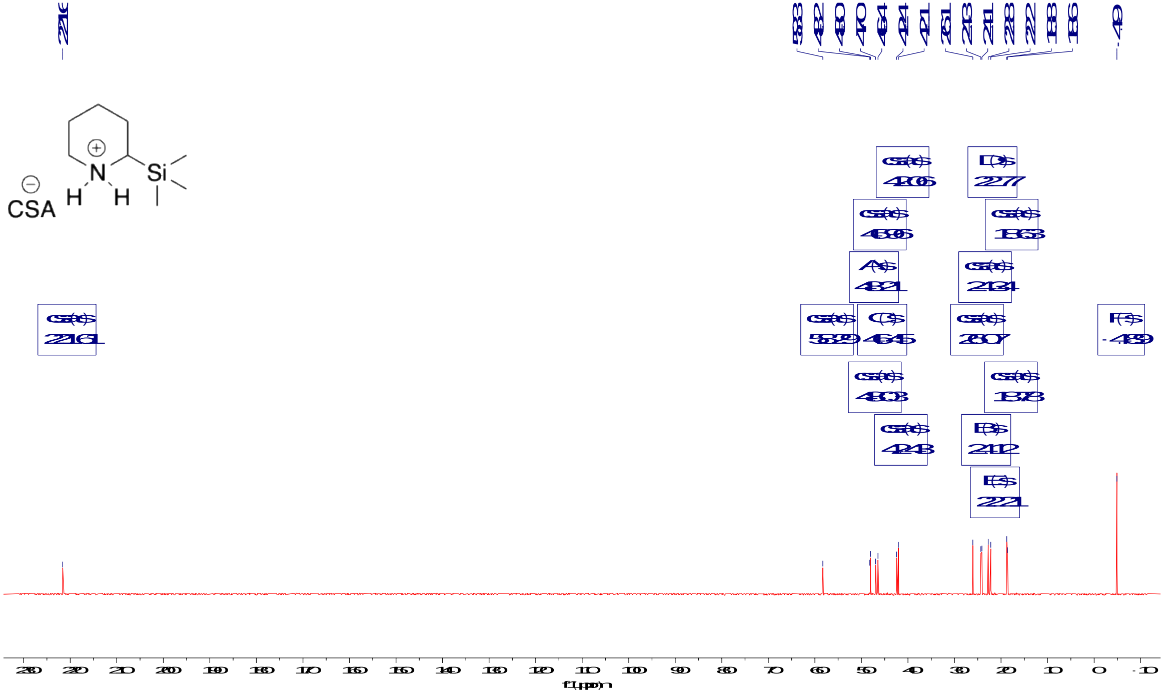
^{11}B NMR (160MHz, $CDCl_3$) of cis-1,2-bis(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)cyclohexane (2v)



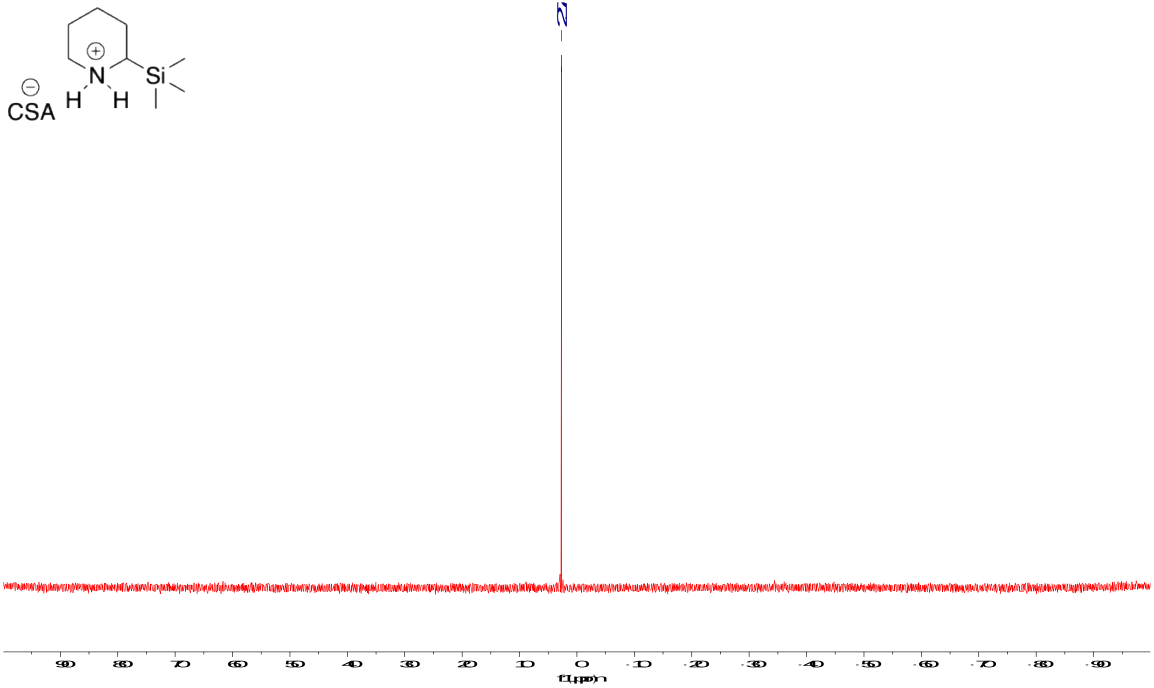
^{1}H NMR (500MHz, D_2O) of 2-(trimethylsilyl)piperidin-1-ium (+)-camphorsulfonate (2w)



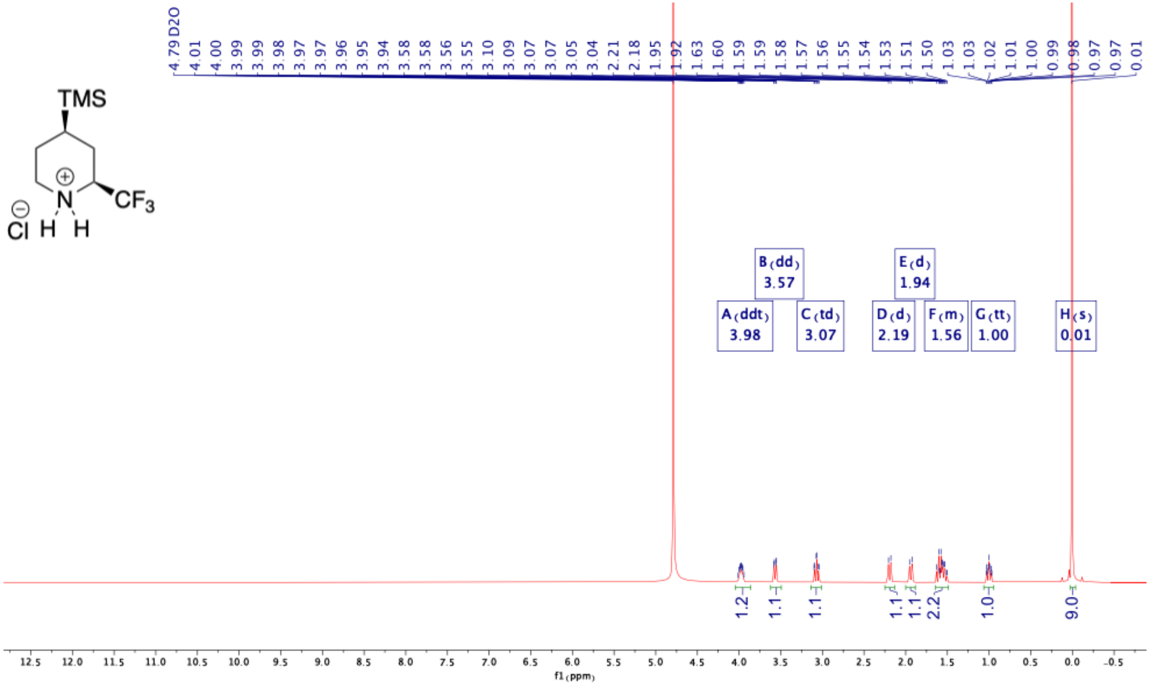
^{13}C{^{1}H} (126 MHz, D_2O) NMR of 2-(trimethylsilyl)piperidin-1-ium (+)-camphorsulfonate (2w)



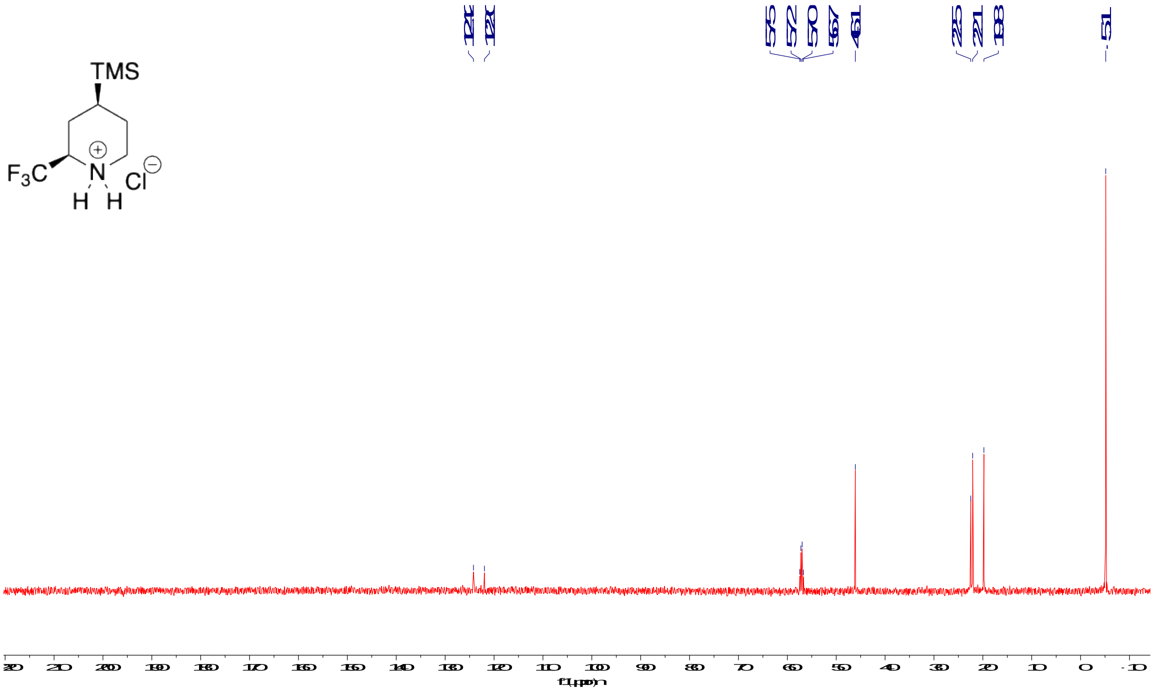
^{29}Si NMR (99 MHz, D$_2$O) of 2-(trimethylsilyl)piperidin-1-ium (+)-camphorsulfonate (2w)



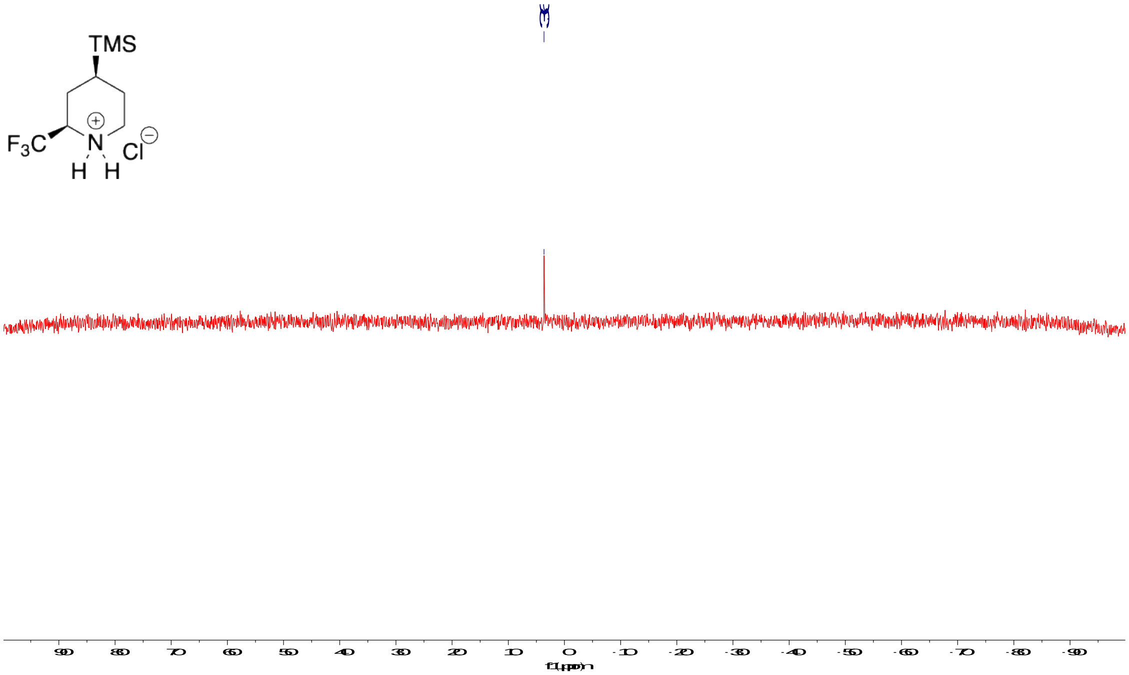
^{1}H NMR (500 MHz, D$_2$O) of 2-(Trifluoromethyl)-4-(trimethylsilyl)piperidine (2x)



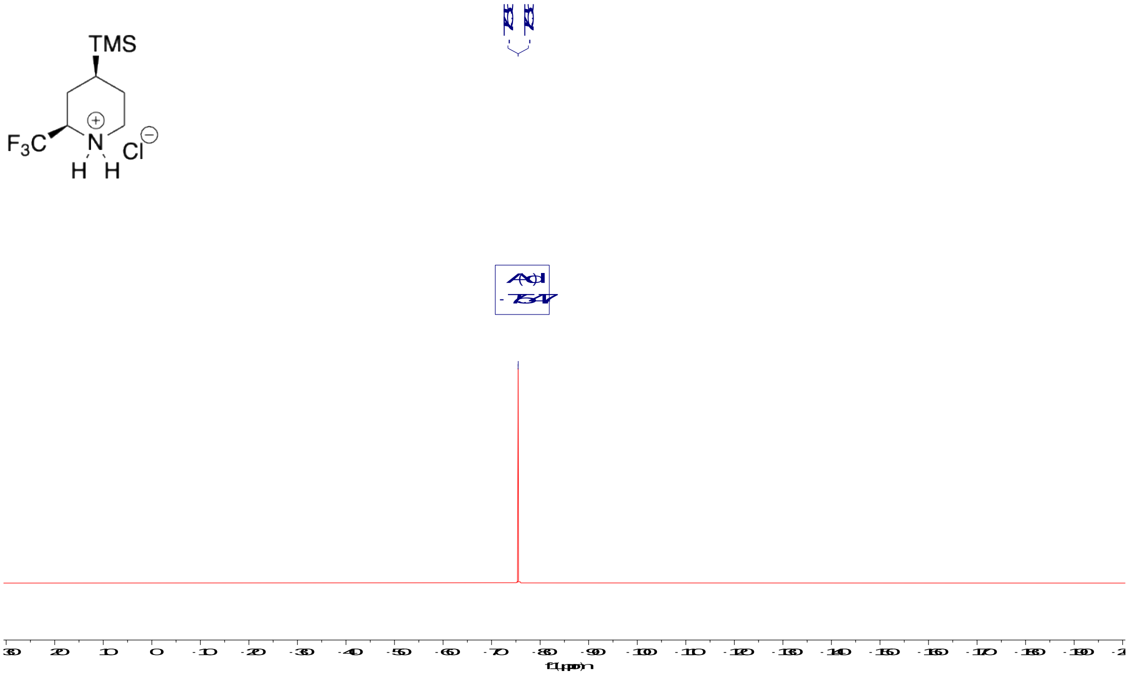
$^{13}C\{^{1}H\}$ (126 MHz, D_2O) NMR of 2-(Trifluoromethyl)-4-(trimethylsilyl)piperidine (2x)



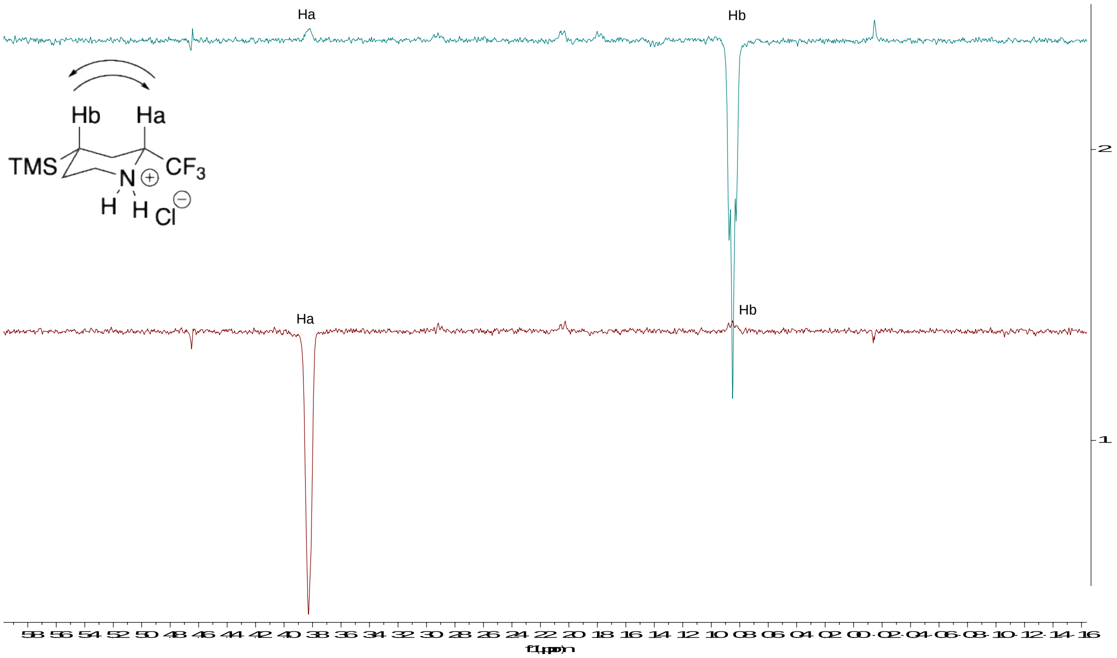
^{29}Si NMR (99MHz, D_2O) of 2-(Trifluoromethyl)-4-(trimethylsilyl)piperidine (2x)



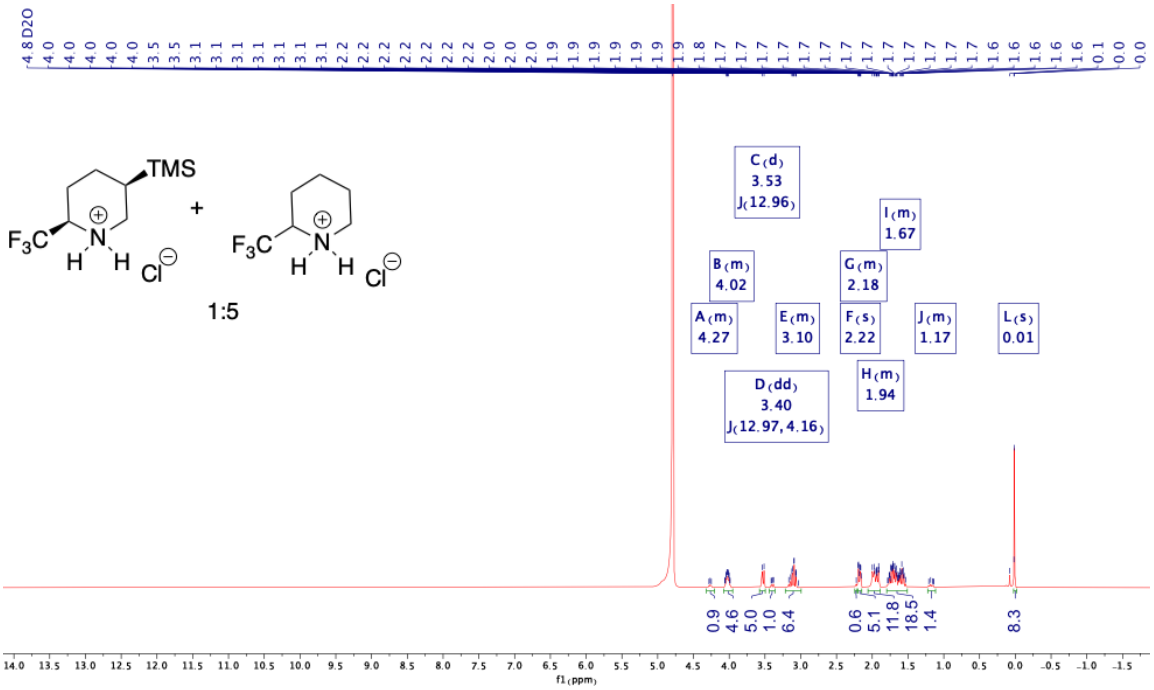
^{19}F NMR (470 MHz, D_2O) of 2-(Trifluoromethyl)-4-(trimethylsilyl)piperidine (2x)



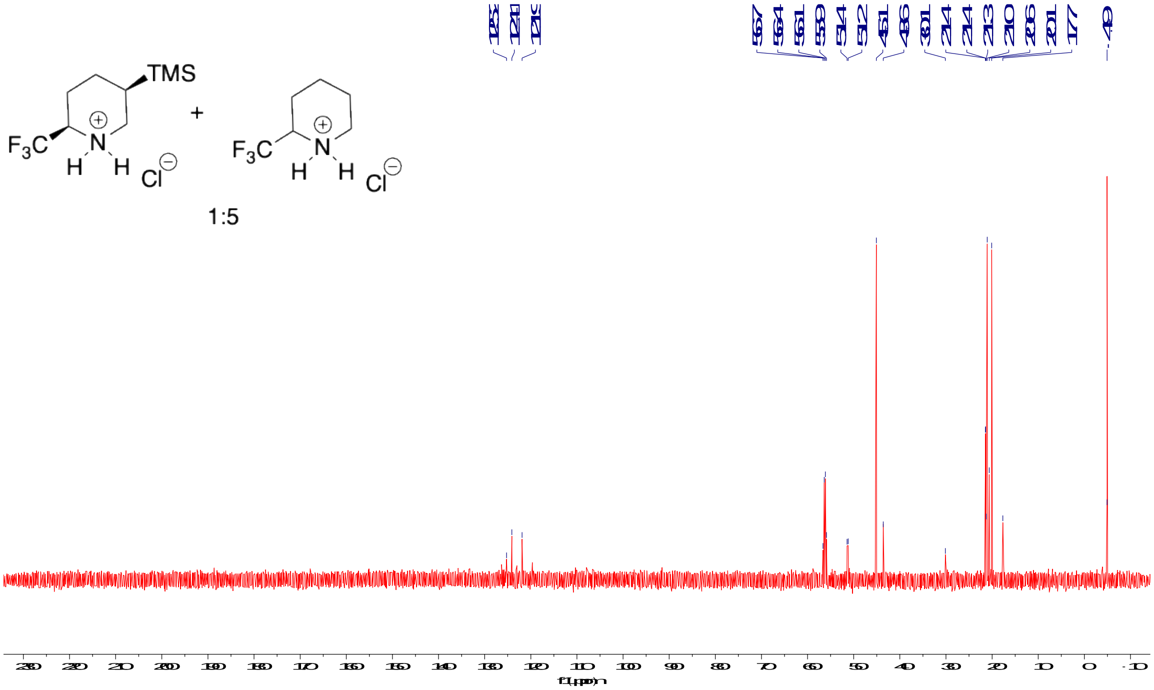
NOE of 2-(Trifluoromethyl)-4-(trimethylsilyl)piperidine (2x)



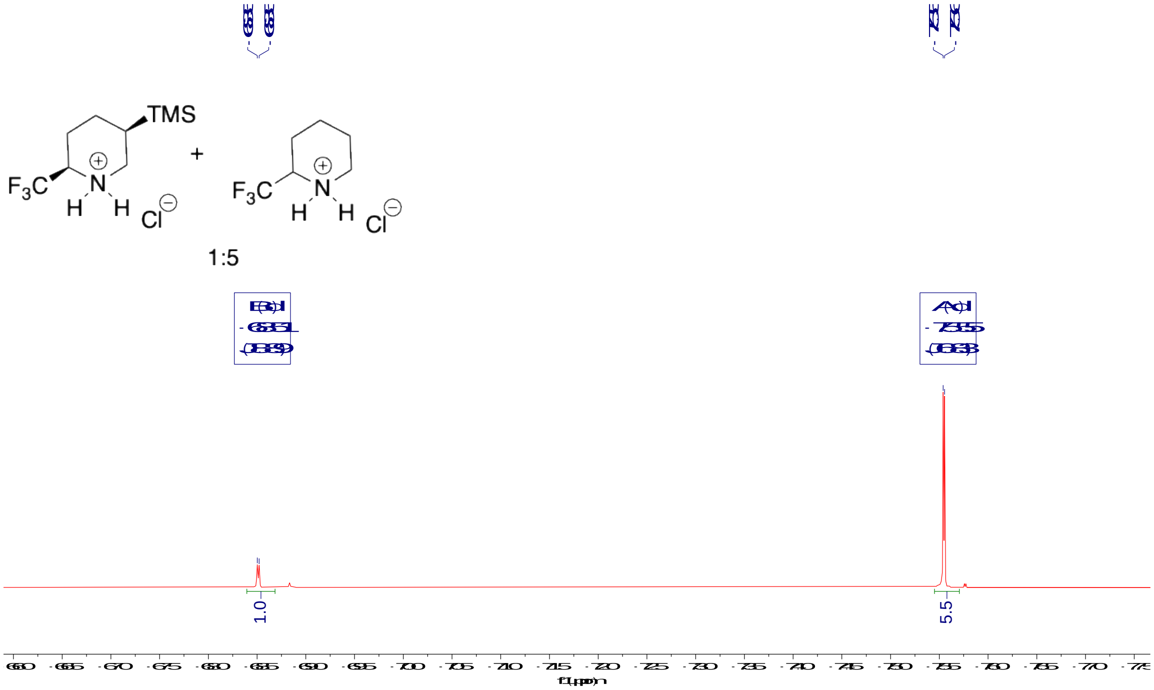
^{1}H NMR (500MHz, D_2O) of 2-(Trifluoromethyl)-5-(trimethylsilyl)piperidine (2y)



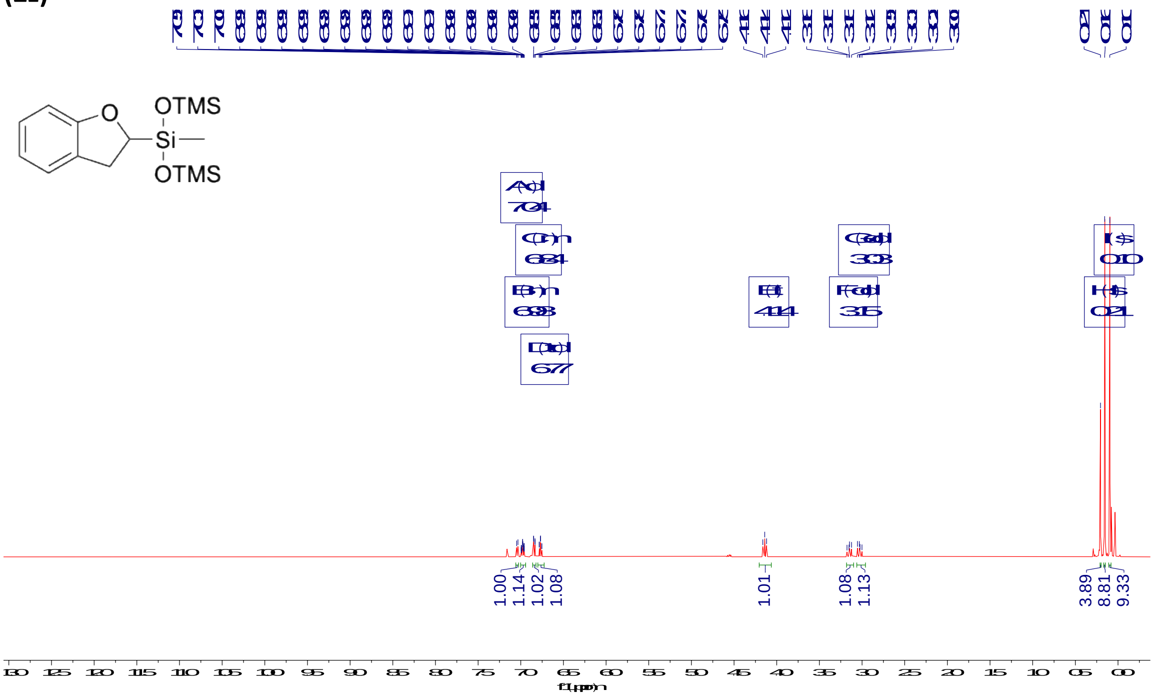
^{13}C{^{1}H} (126 MHz, D_2O) NMR of 2-(Trifluoromethyl)-5-(trimethylsilyl)piperidine (2y)



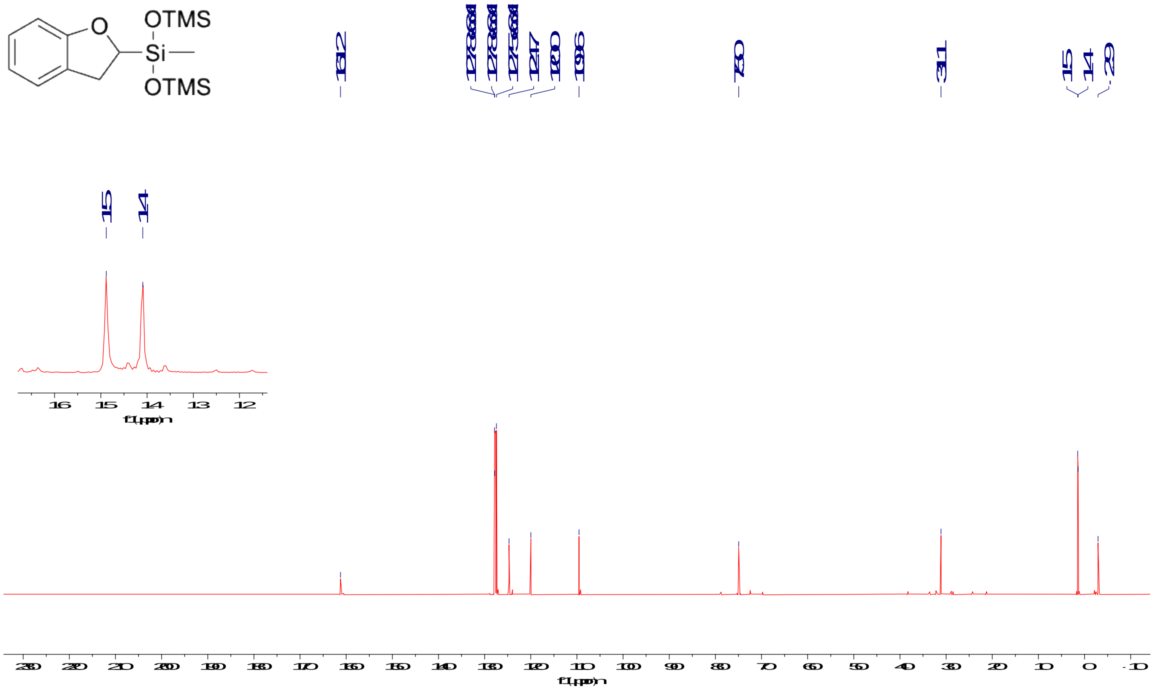
^{19}F NMR (470 MHz, D_2O) of 2-(Trifluoromethyl)-5-(trimethylsilyl)piperidine (2y)



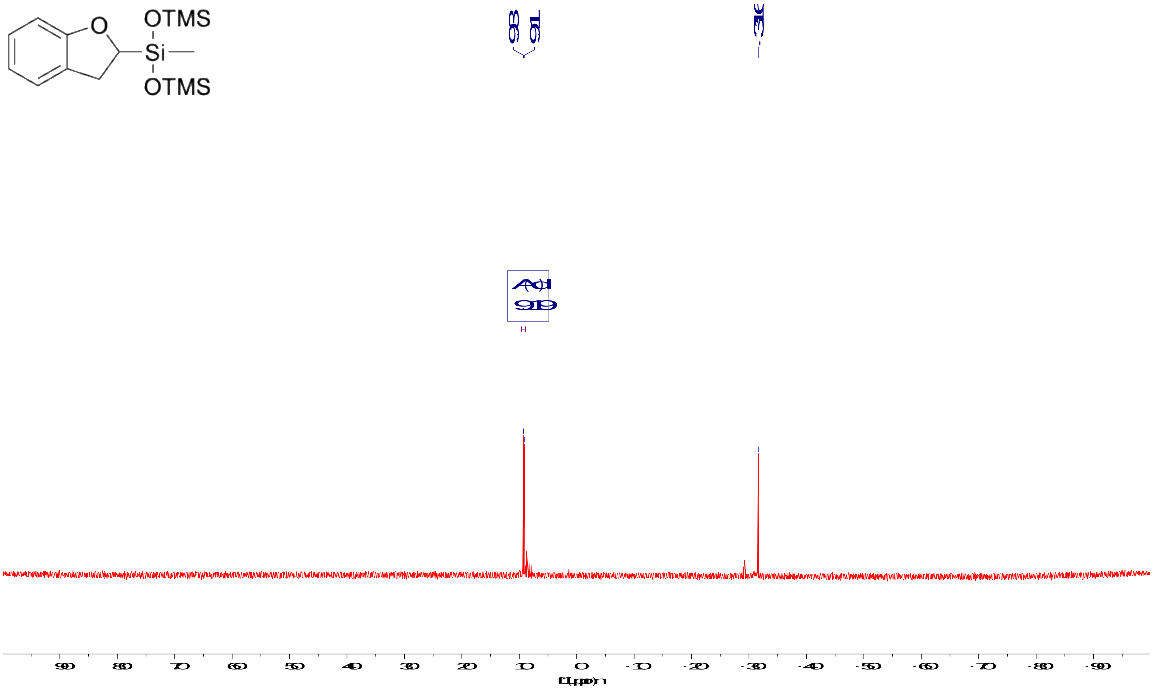
^1H NMR (500MHz, C_6D_6) of 3-(2,3-dihydrobenzofuran-2-yl)-1,1,1,3,5,5,5-heptamethyltrisiloxane (2z)



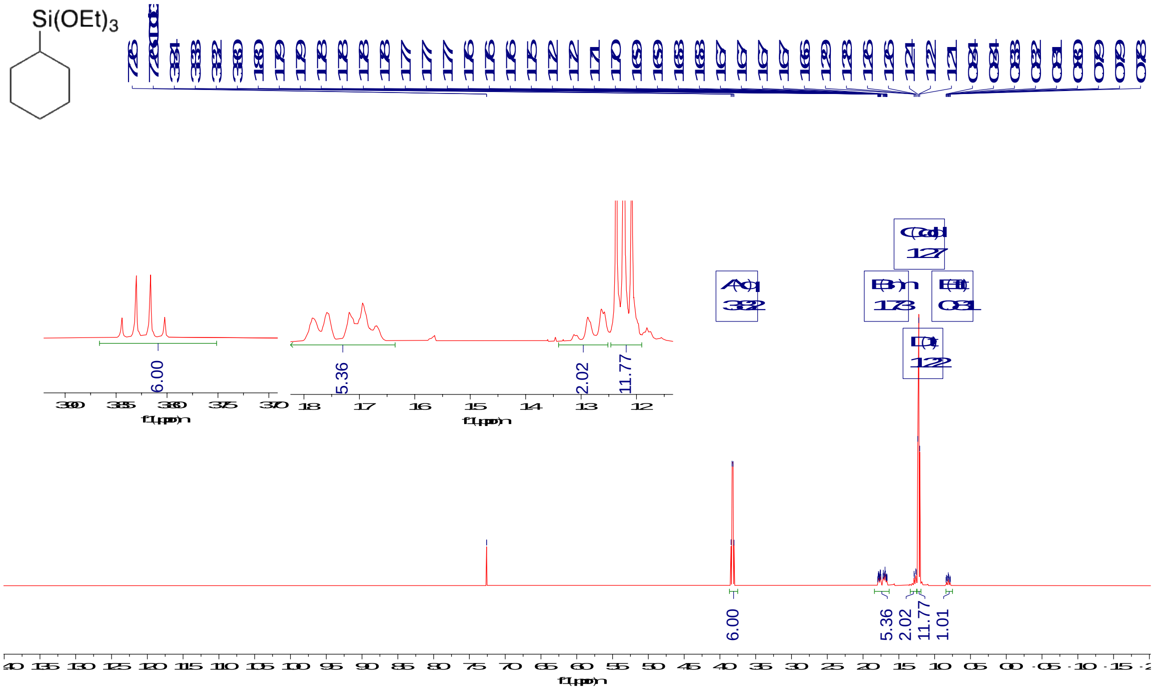
$^{13}C\{^{1}H\}$ (126 MHz C_6D_6) NMR of 3-(2,3-dihydrobenzofuran-2-yl)-1,1,1,3,5,5,5-heptamethyltrisiloxane (2z)



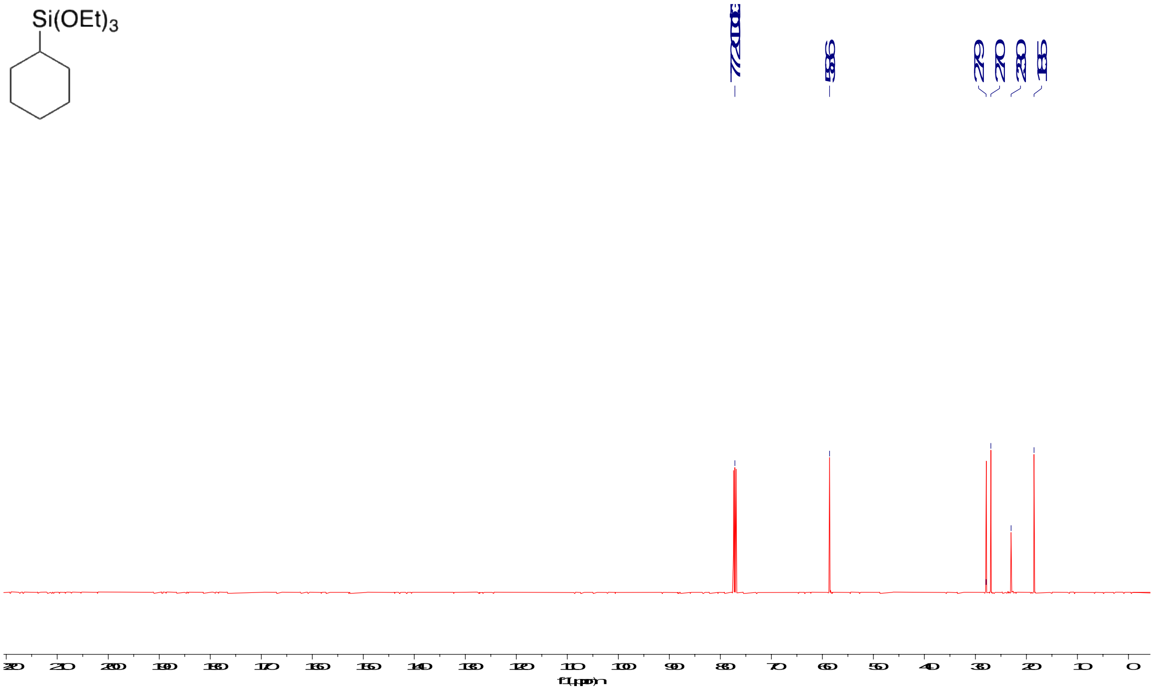
^{29}Si NMR (99MHz, $CDCl_3$) of 3-(2,3-dihydrobenzofuran-2-yl)-1,1,1,3,5,5,5-heptamethyltrisiloxane (2z)



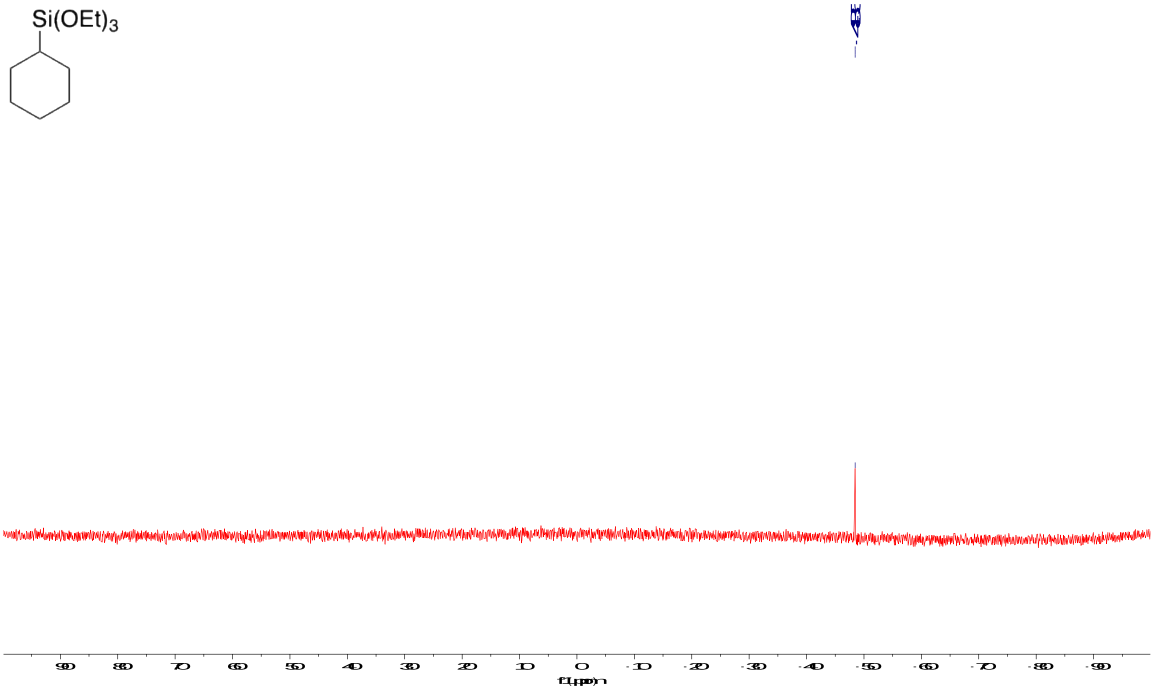
^{1}H NMR (500MHz, CDCl$_3$) of Cyclohexyltriethoxysilane (2aa)



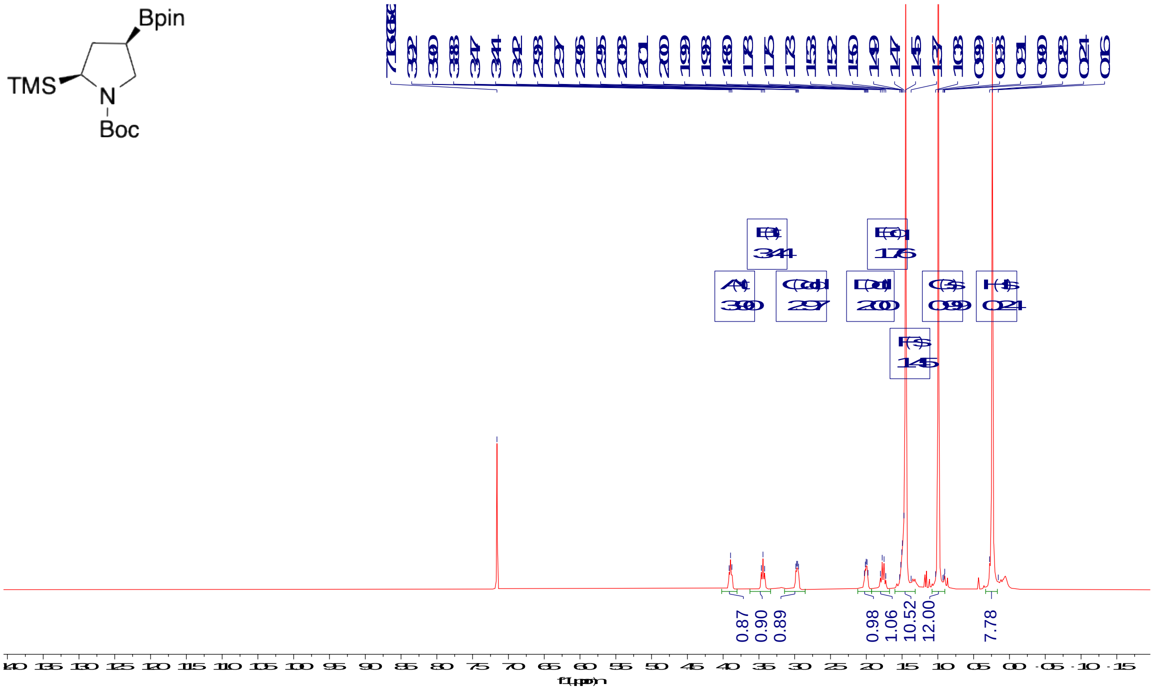
^{13}C{^{1}H} (126 MHz, CDCl$_3$) NMR of Cyclohexyltriethoxysilane (2aa)



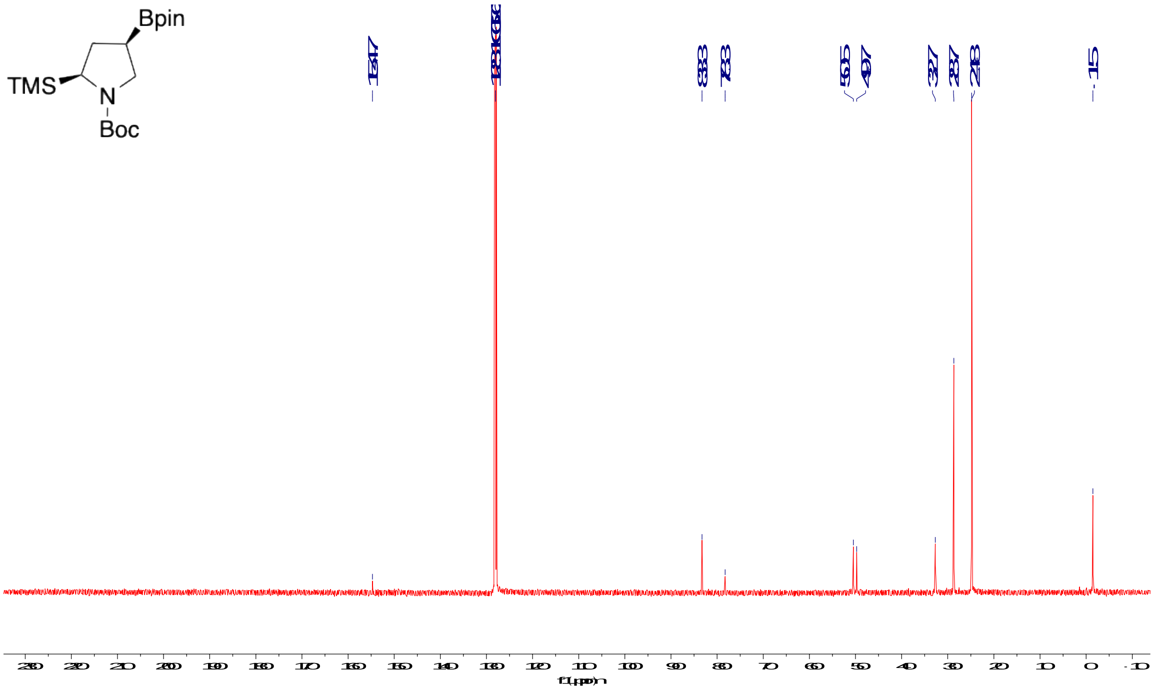
^{29}Si NMR (99MHz, $CDCl_3$) of Cyclohexyltriethoxysilane (2aa)



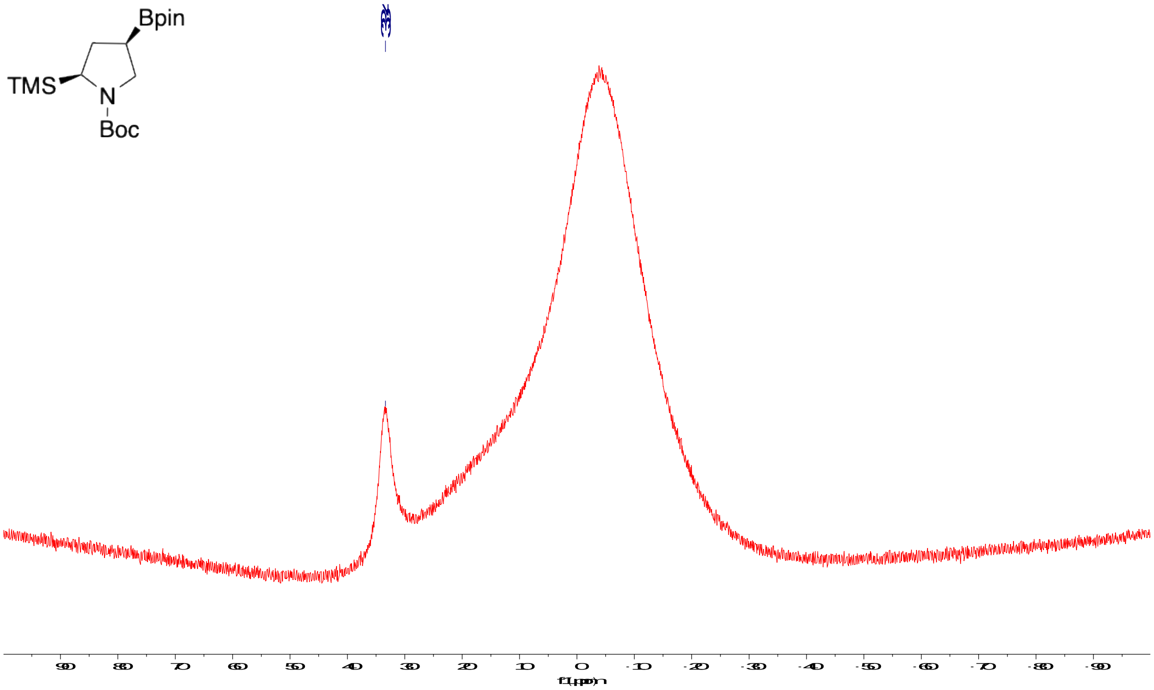
^{1}H NMR (500MHz, C_6D_6) of *t*-butyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2(trimethylsilyl)pyrrolidine-1-carboxylate (2ab)



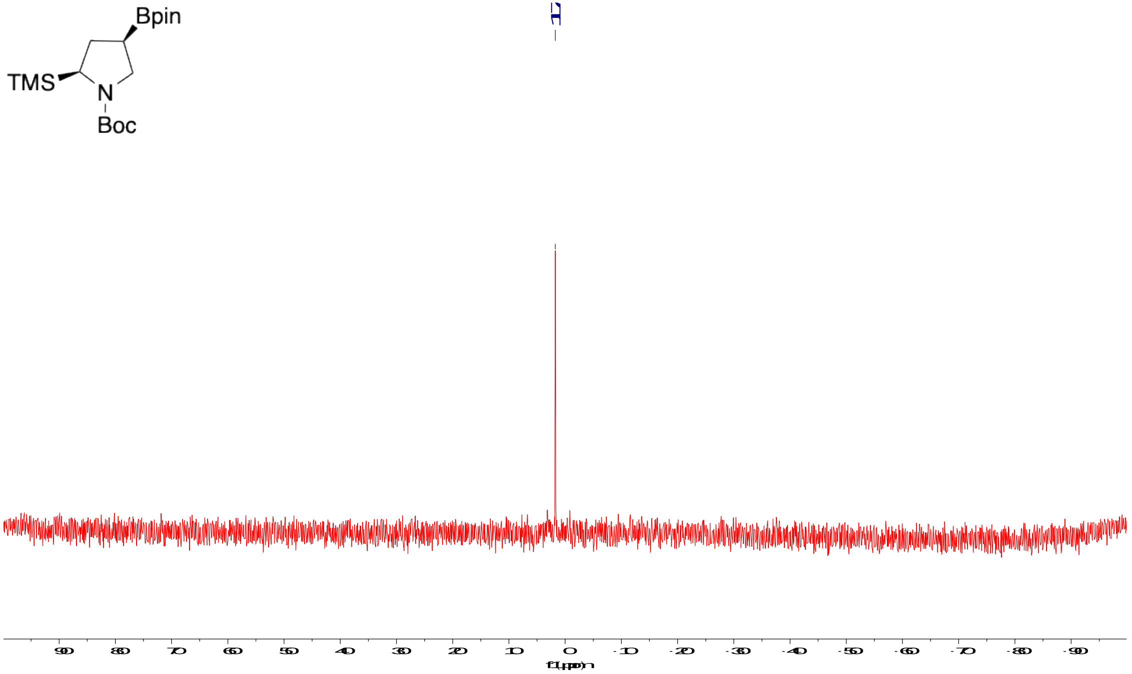
$^{13}C\{^{1}H\}$ **(126 MHz, C_6D_6) of *t*-butyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2(trimethylsilyl)pyrrolidine-1-carboxylate (2ab)**



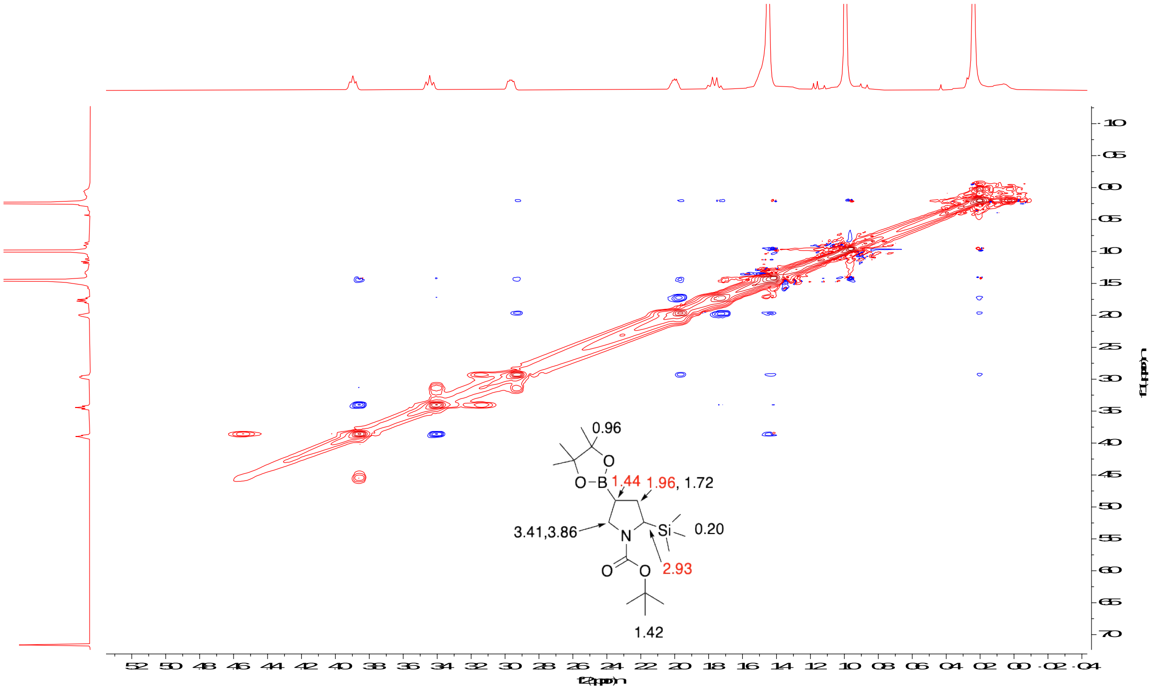
^{11}B **NMR (160 MHz, C_6D_6)of *t*-butyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2(trimethylsilyl)pyrrolidine-1-carboxylate (2ab)**



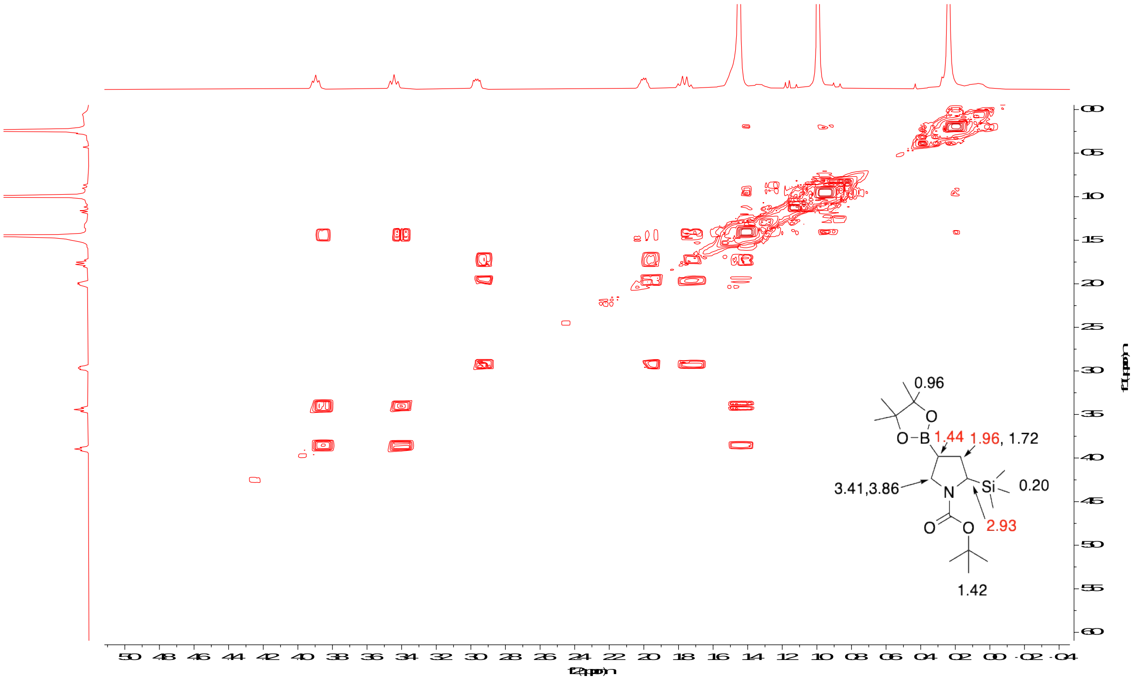
^{29}Si NMR (99 MHz, C_6D_6) *t*-butyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-trimethylsilyl)pyrrolidine-1-carboxylate (2ab)



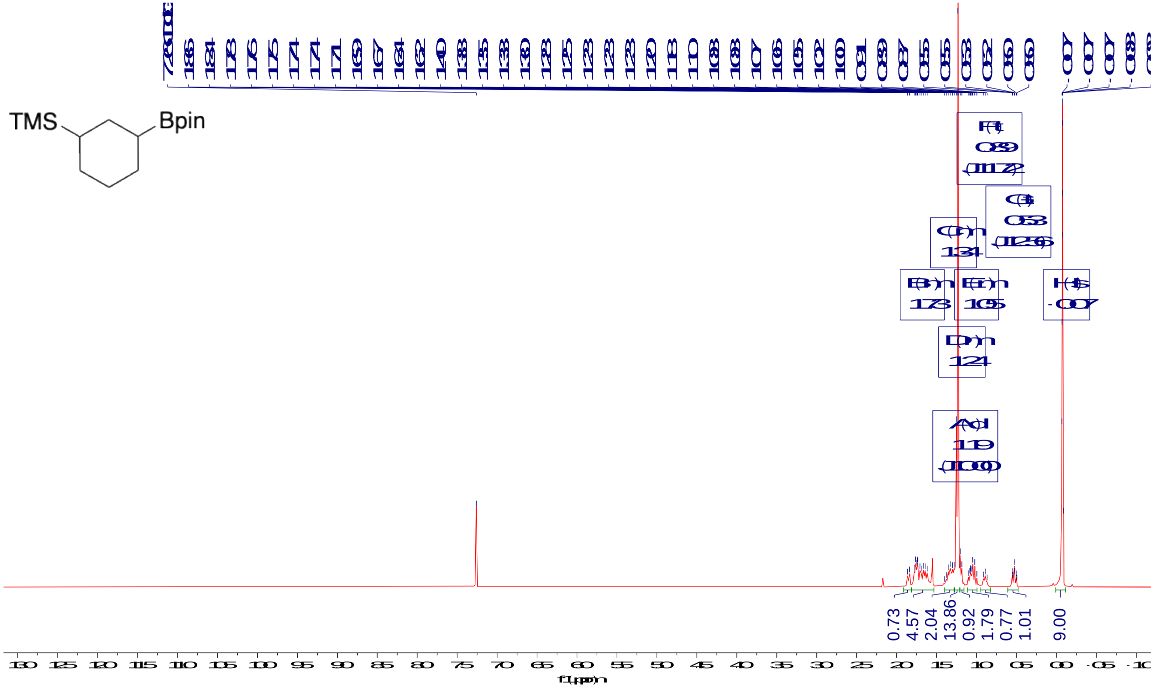
2D-NOE of *t*-butyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2(trimethylsilyl)pyrrolidine-1-carboxylate (2ab)



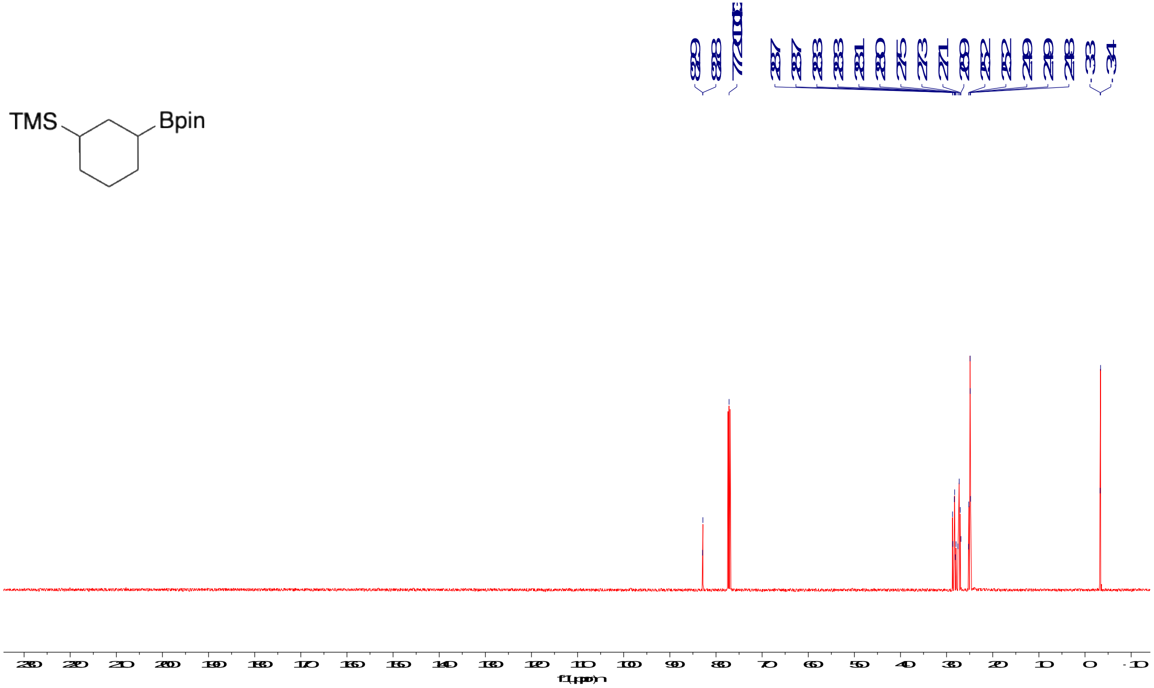
COSY of *t*-butyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2(trimethylsilyl)pyrrolidine-1-carboxylate (2ab)



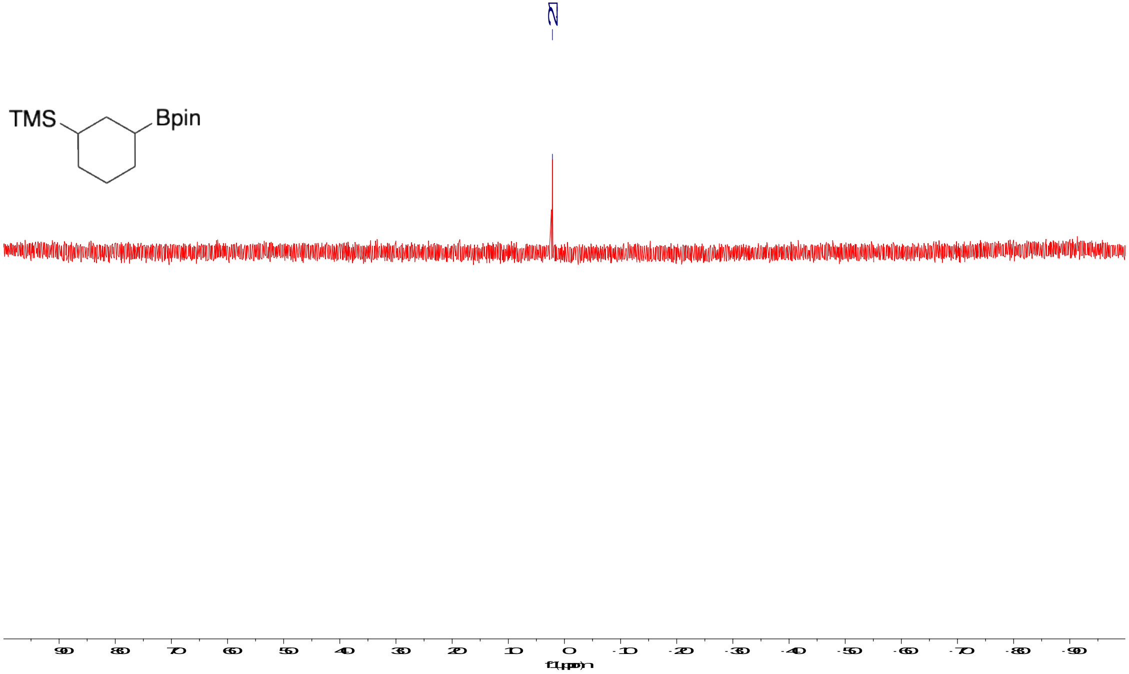
^{1}H NMR (500MHz, CDCl$_3$) of Trimethyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexyl)silane (2ae)



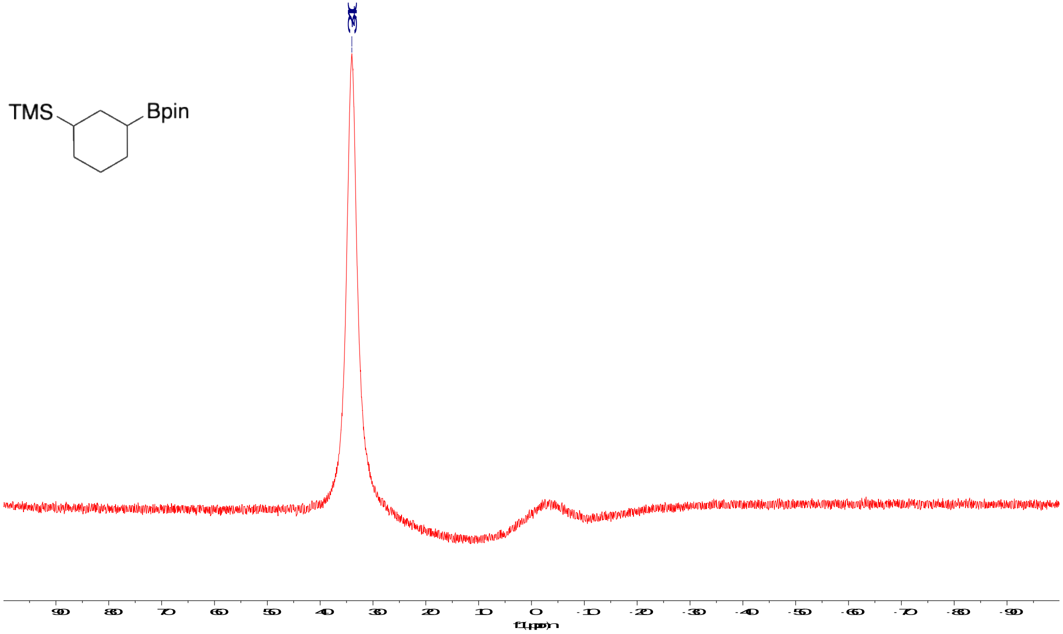
$^{13}C\{^1H\}$ (126 MHz, $CDCl_3$) NMR of Trimethyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexyl)silane (2ae)



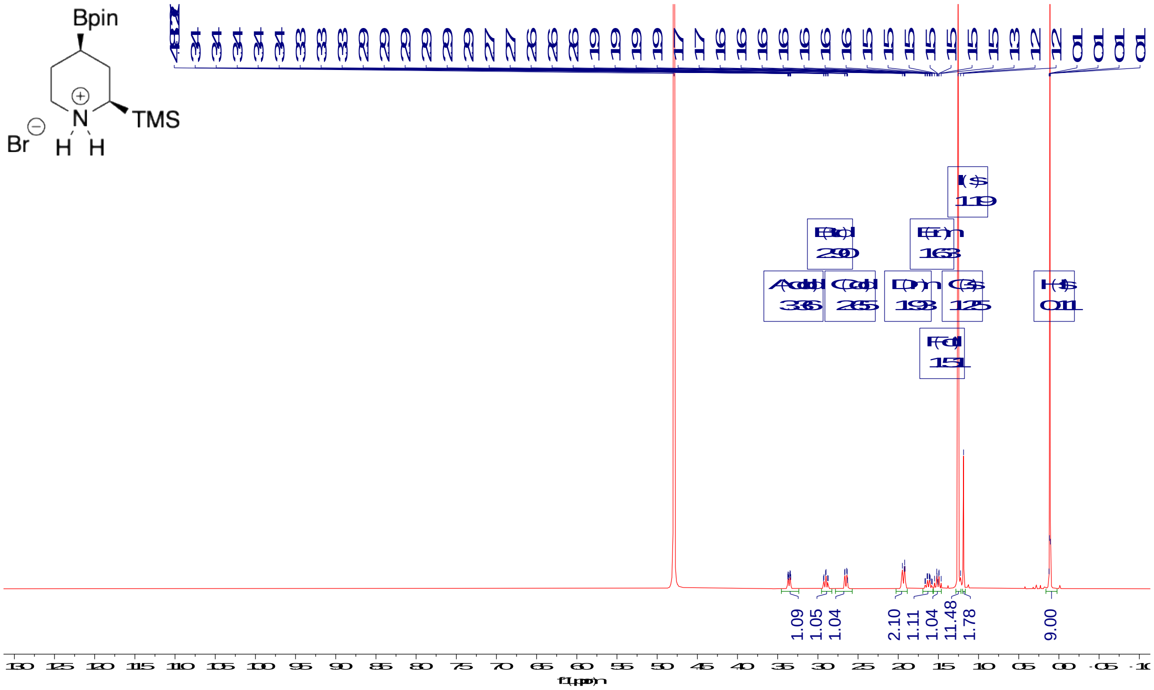
^{29}Si NMR (99MHz, $CDCl_3$) of Trimethyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexyl)silane (2ae)



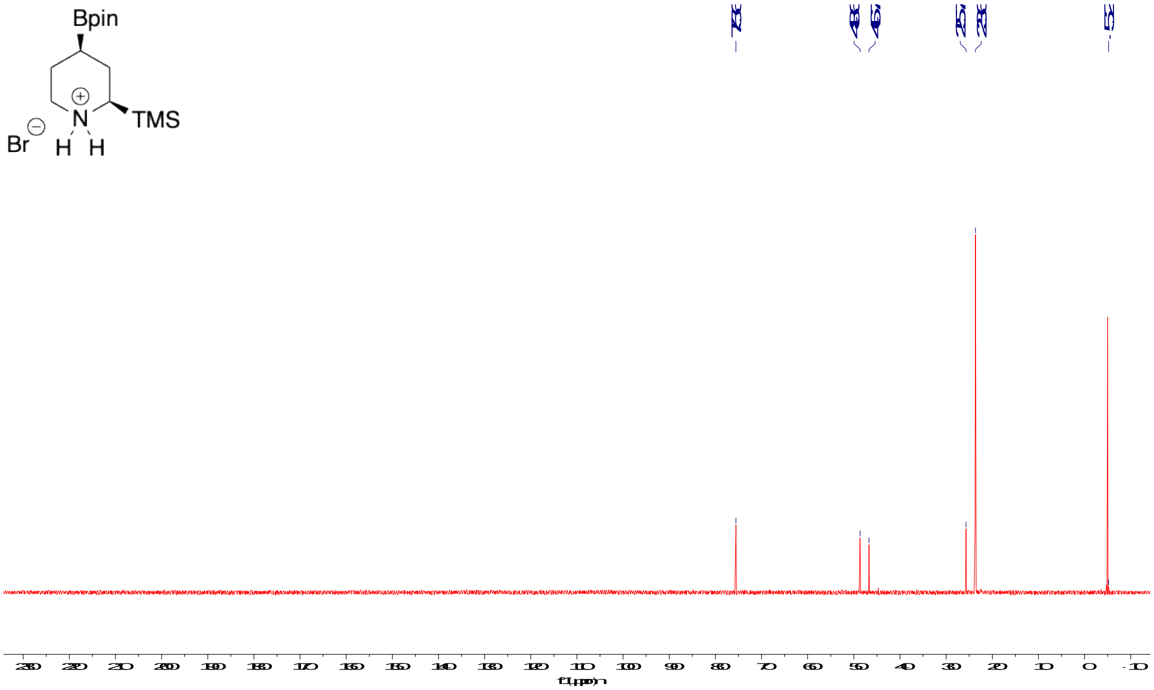
^{11}B NMR (160MHz, $CDCl_3$) of Trimethyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexyl)silane (2ae)



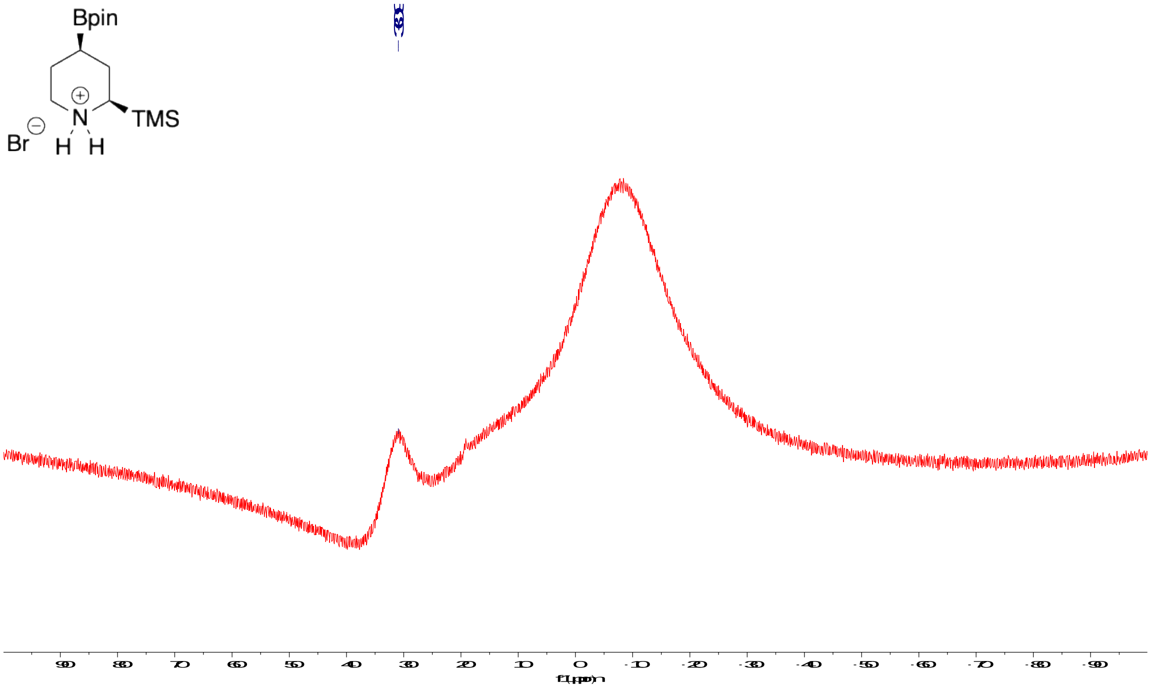
^{1}H NMR (500MHz, D_2O) of 4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(trimethylsilyl)piperidin-1-ium bromide (2ac)



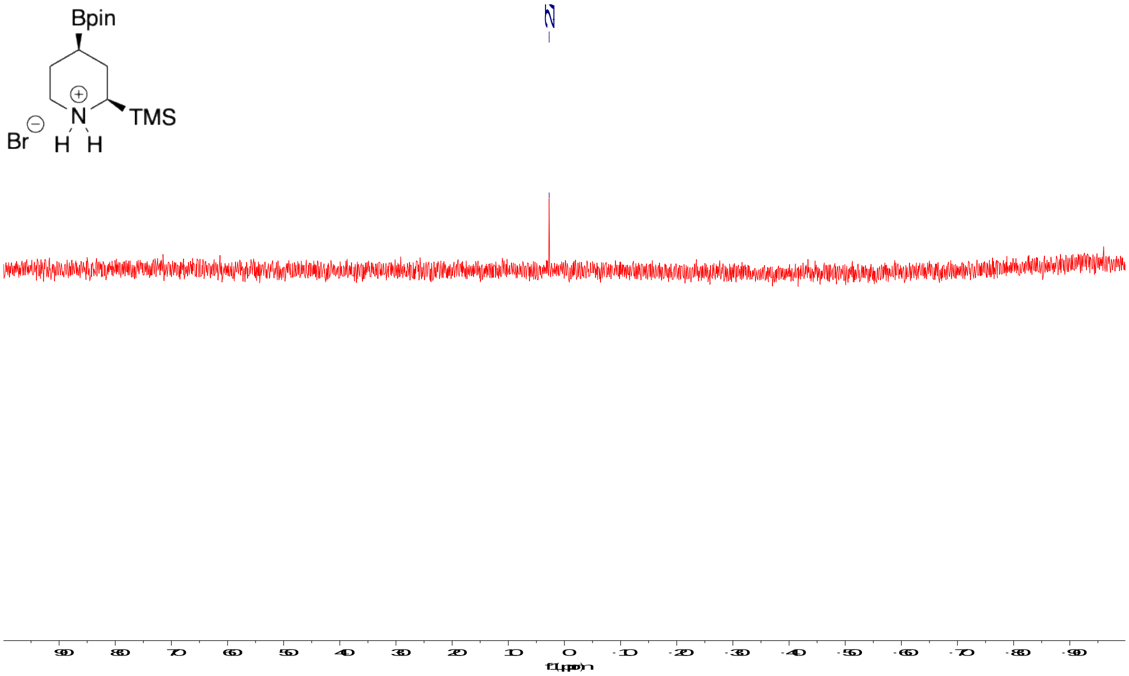
$^{13}C\{^1H\}$ (126 MHz, D_2O) of 4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(trimethylsilyl)piperidin-1-ium bromide (2ac)



^{11}B NMR (160MHz, D_2O) of 4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(trimethylsilyl)piperidin-1-ium bromide (2ac)



^{29}Si NMR (99MHz, CDCl$_3$) of 4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(trimethylsilyl)piperidin-1-ium bromide (2ac)



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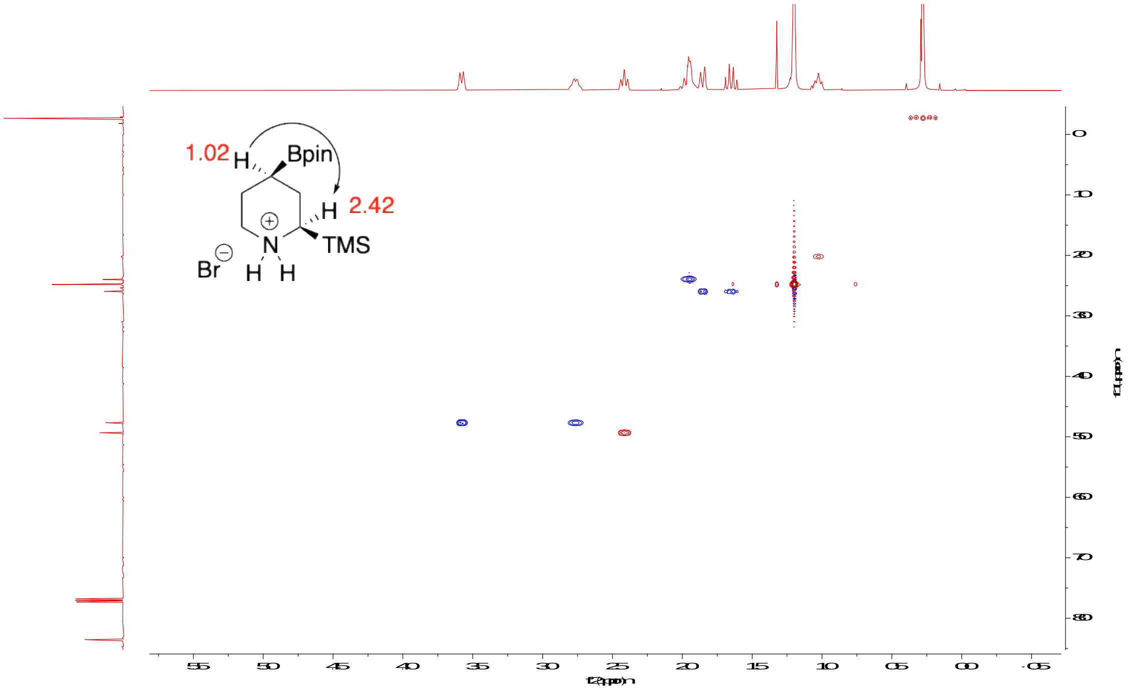
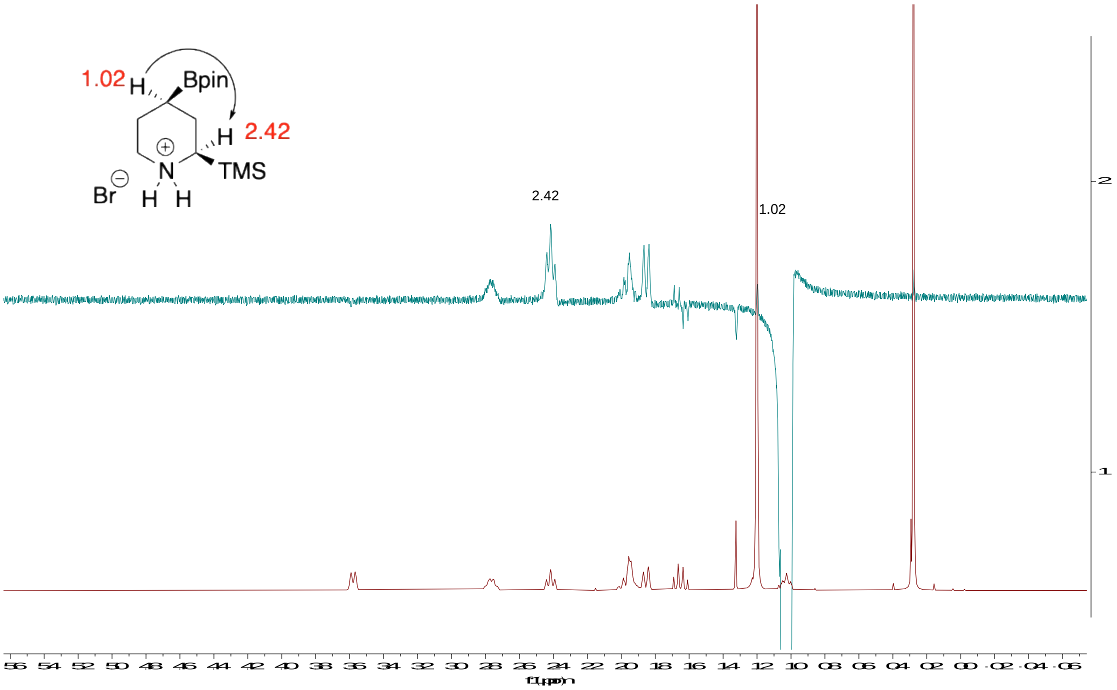
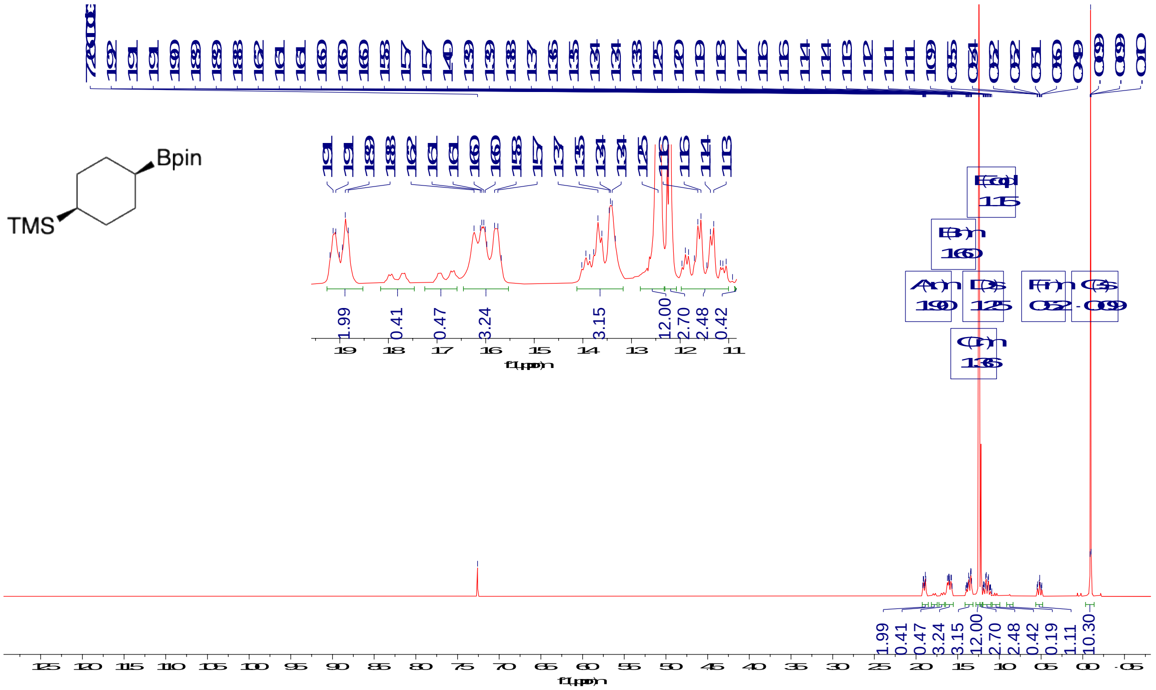


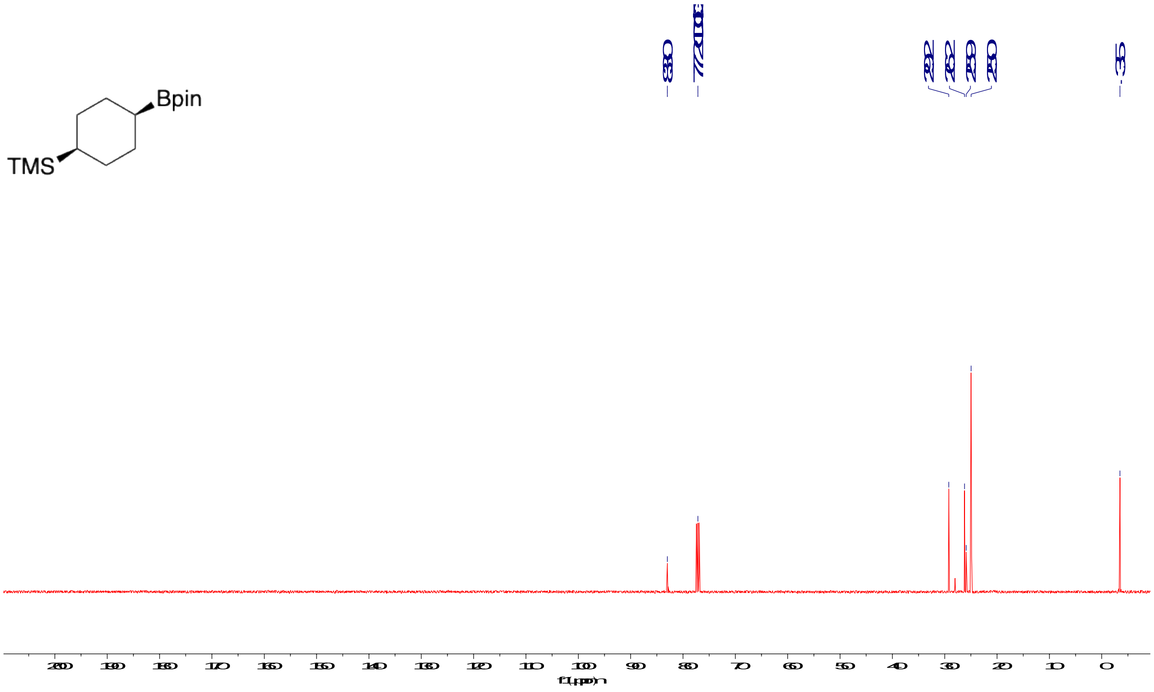
NOE of 4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(trimethylsilyl)piperidin-1-ium bromide (2ac)



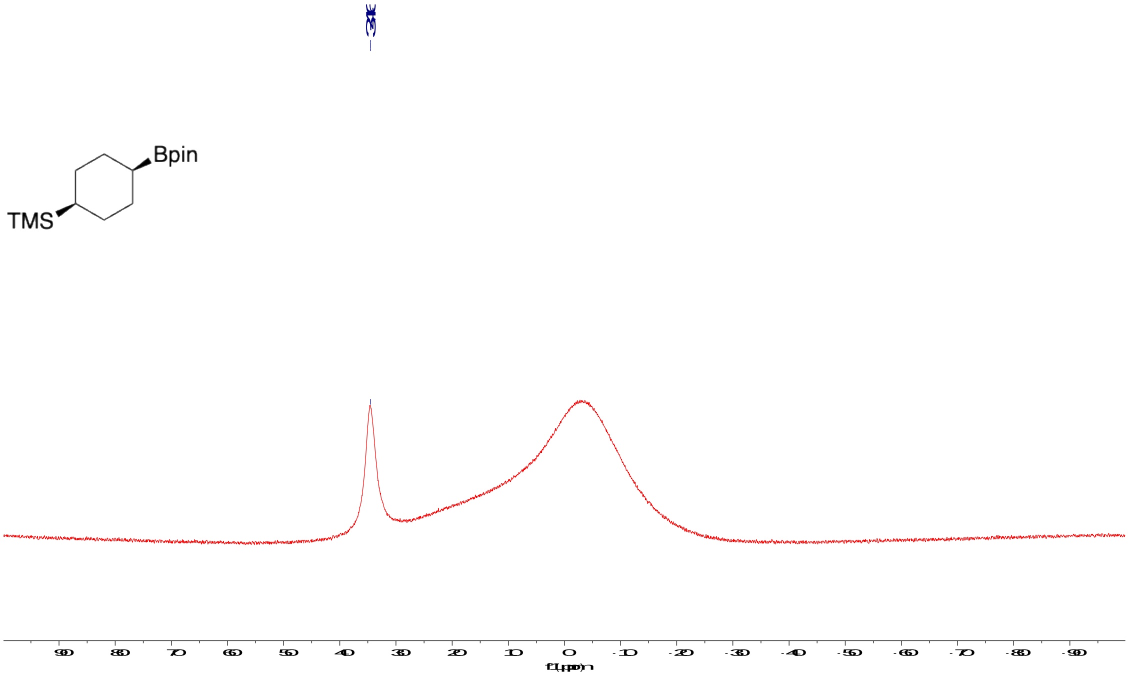
^{1}H NMR (500MHz, CDCl$_3$) of Trimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexyl)silane (2af)



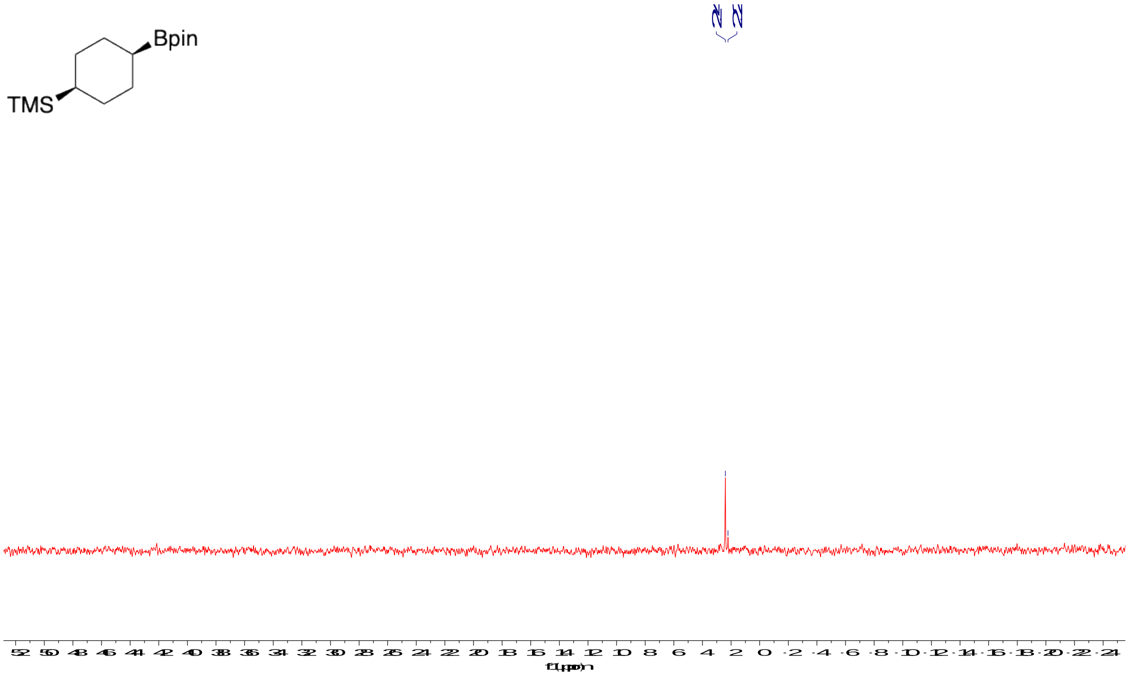
$^{13}C\{^1H\}$ (126 MHz, $CDCl_3$) of Trimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexyl)silane (2af)



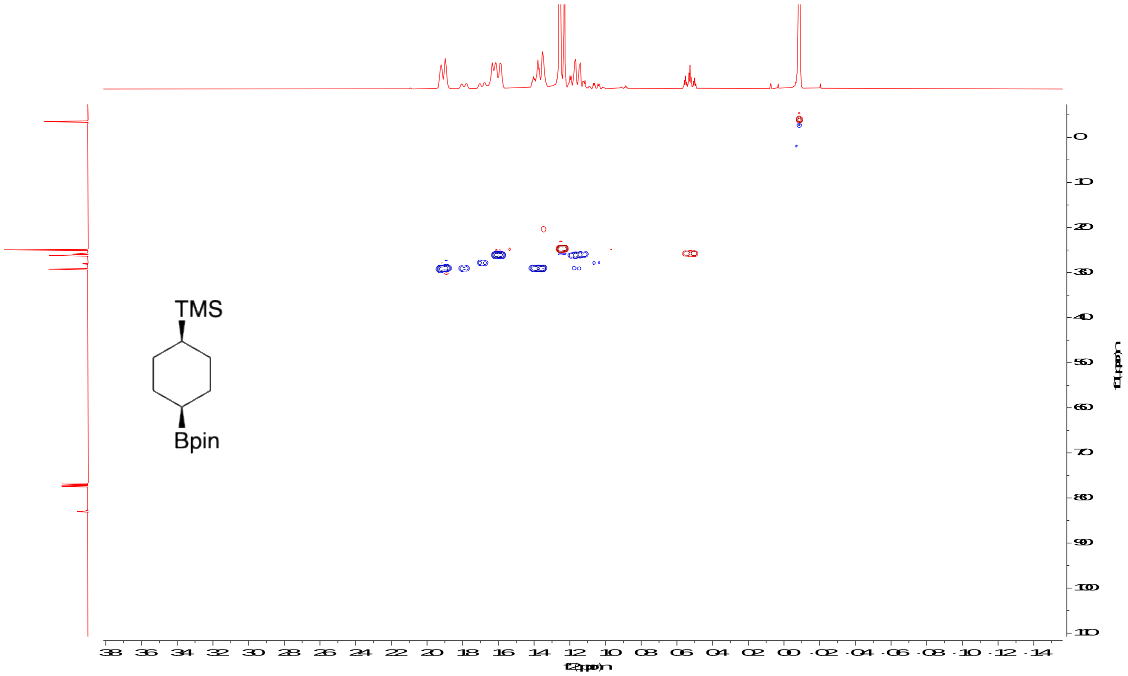
^{11}B NMR (160MHz, $CDCl_3$) of Trimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexyl)silane (2af)



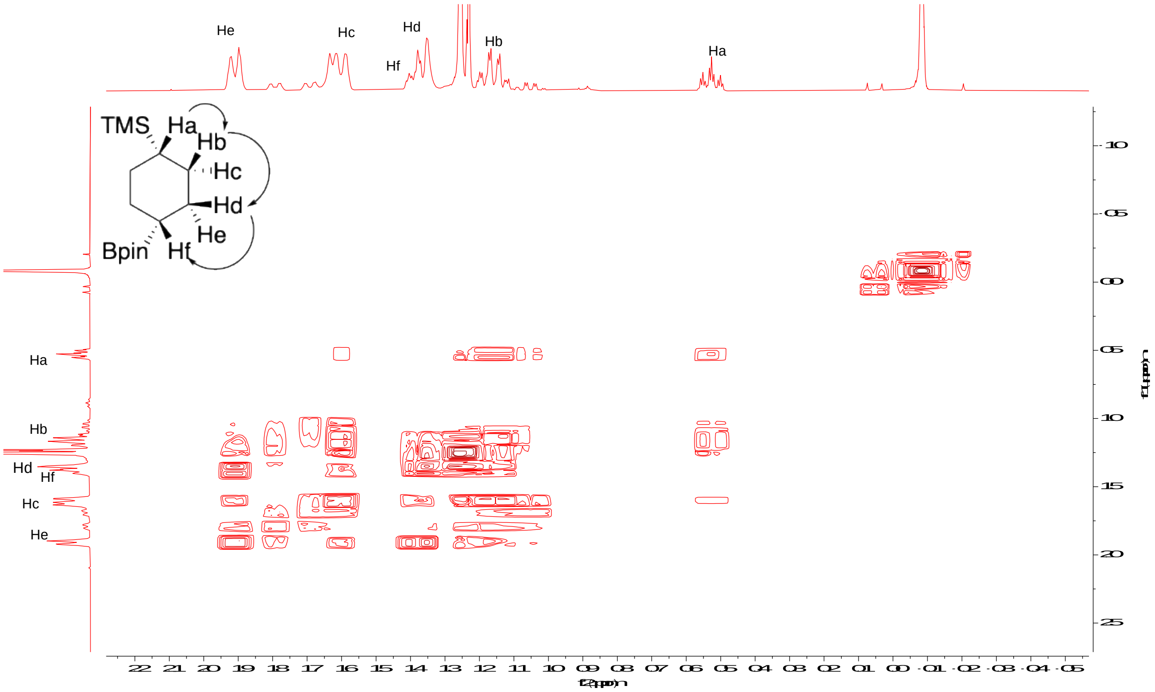
^{29}Si NMR (99MHz, $CDCl_3$) of Trimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexyl)silane (2af)



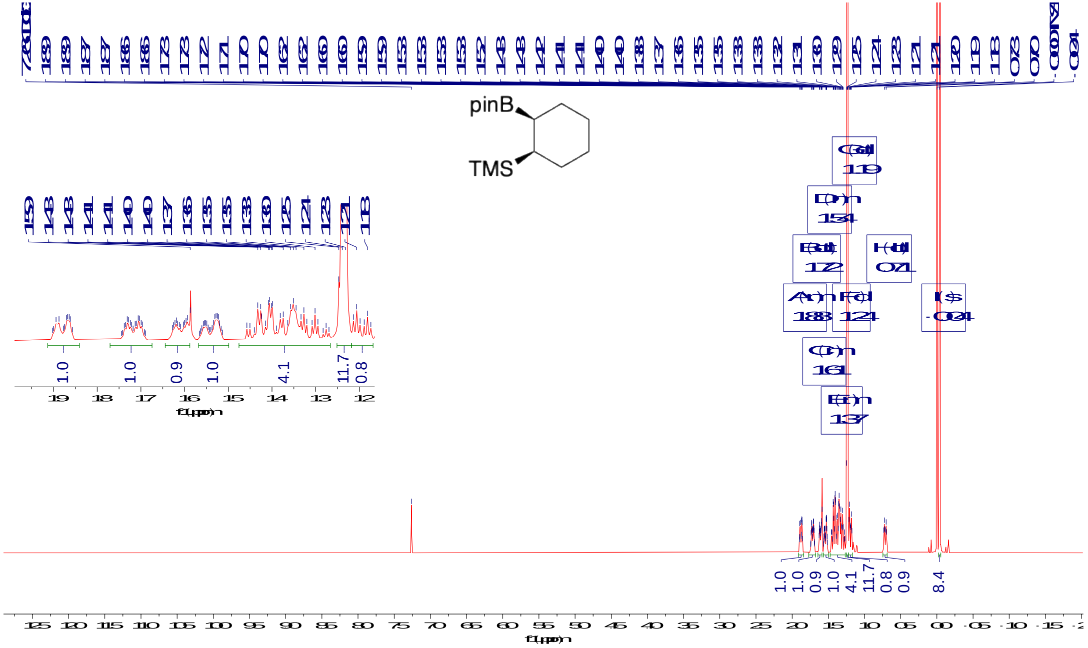
HSQC NMR Trimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexyl)silane (2af)



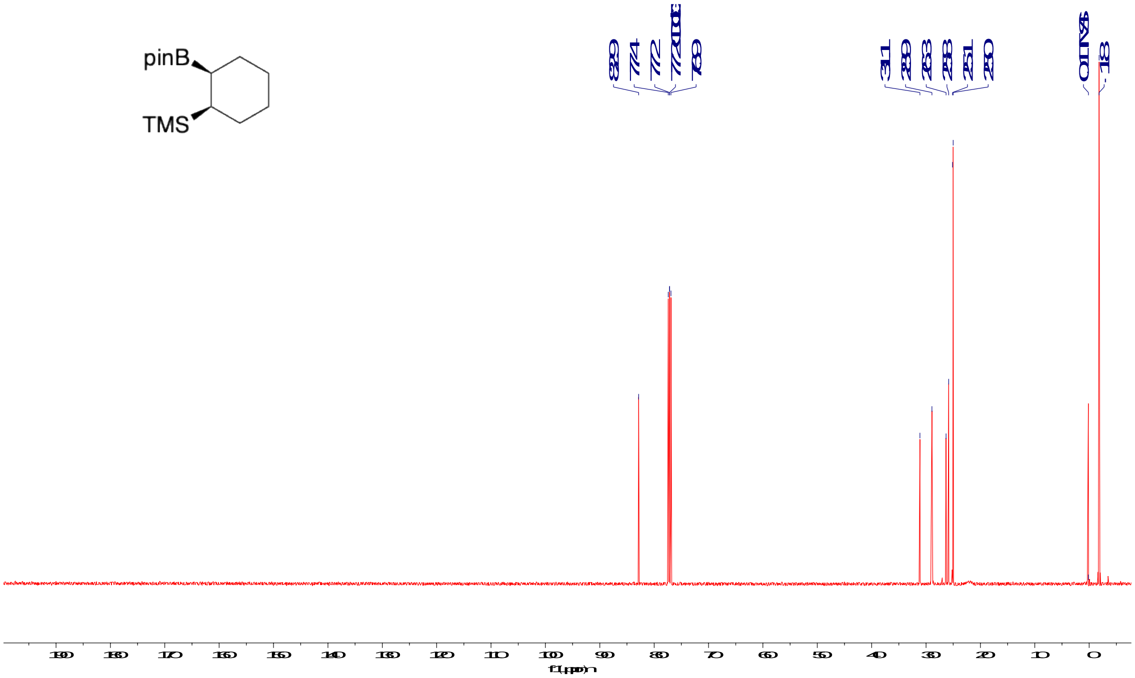
COSY NMR Trimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexyl)silane (2af)



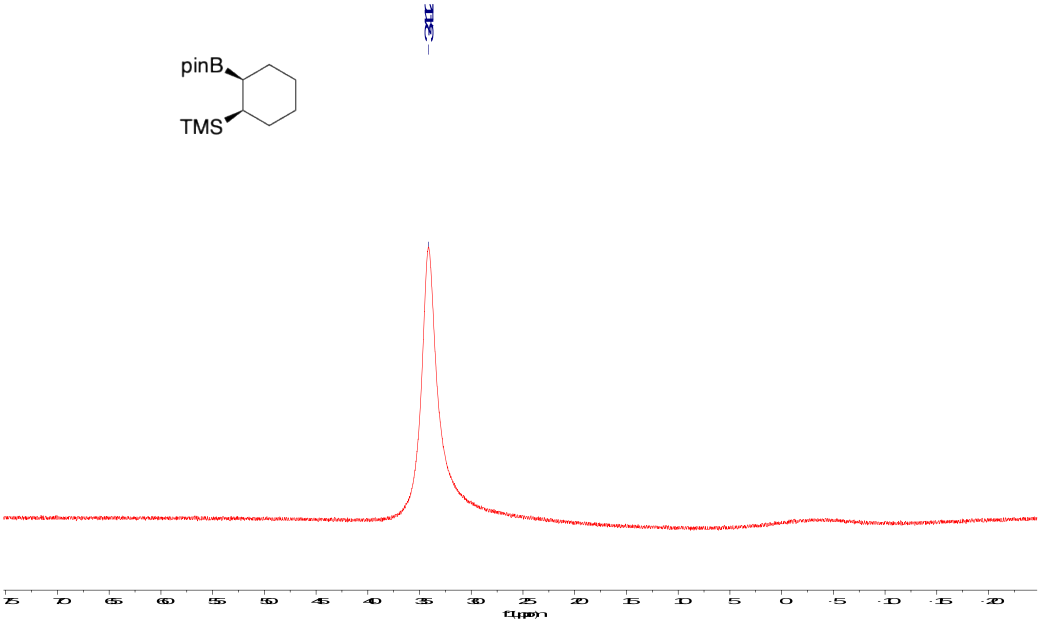
^{1}H NMR (500MHz, $CDCl_3$) of cis-trimethylsilyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexane (2ad)



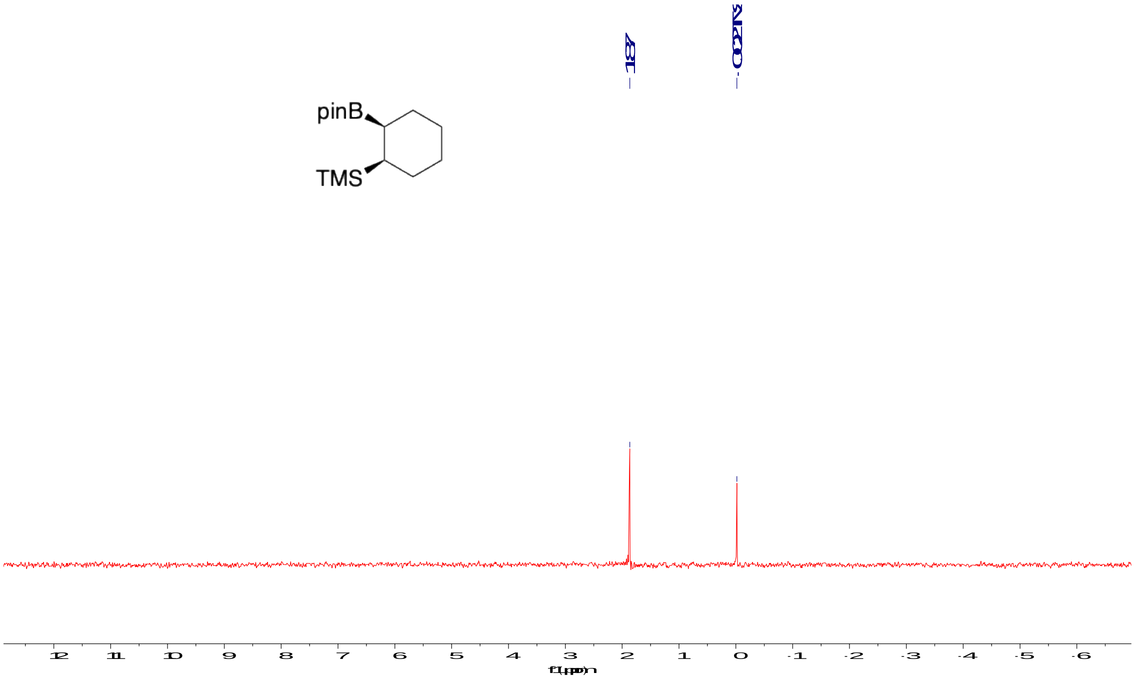
$^{13}C\{^{1}H\}$ (126 MHz, $CDCl_3$) of cis-trimethylsilyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexane (2ad)



^{11}B NMR (160MHz, $CDCl_3$) of cis-trimethylsilyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexane (2ad)



^{29}Si NMR (99MHz, CDCl$_3$) of cis-trimethylsilyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexane (2ad)



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CHAPTER 5. ENHANCED META-SELECTIVE IRIDIUM CATALYZED BORYLATION: A THEORETICAL EXPLORATION OF A HYDRAZONE LIGAND

5.1. INTRODUCTION

Ir(III)-Ir(V) mechanistic pathway

Iridium catalyzed borylation reactions have been experimentally studied for about 2 decades. The proposed Ir(III)-Ir(V) catalytic cycle with trisboryl as the active catalyst was first validated by the theoretical investigation of C-H borylation reaction in 2003 by Sakaki and coworkers.[1] DFT calculations were carried out on a model system where a boron ethylene glycol (Beg) was used as a boron partner and bipyridine (bpy) was used as a ligand. The oxidative addition of C-H activation bond was found to be 24.2 kCal/mol to afford an unusual seven coordinate iridium(V) complex, $Ir(H)(Ph)(Beg)_3(bpy)$. This complex was found to undergo reductive elimination to give phenylborane with an activation barrier of 4.9 kCal/mol. The complex $IrH(Beg)_2(bpy)$ formed after reductive elimination then reacted with diboron (B_2eg_2) to form $Ir(H)(Beg)_4(bpy)$ with an activation barrier of 8.0 kCal/mol. This complex reductively eliminated H-Beg (Ea= 2.6 kCal/mol) to regenerate $Ir(Beg)_3(bpy)$. It has been well established that oxidative addition is the rate limiting step of the reaction.[1–3] Calculations for Ir(I)-Ir(III) catalytic pathway were also carried out and were dismissed as less favorable compared Ir(III)-Ir(V) pathway because Ir(I) rapidly reacts with B_2pin_2 to form Ir(III). The authors noted that due to the seven-coordinate structure of Ir(V), the less bulky substrates are preferred, making planar compound like benzene favorable for C-H borylation due to reduced steric hinderance (Figure 12).[1] Iridium catalyzed C-H borylations have also been now studied using a hybrid computational model that combines density functional theory, semi-empirical quantum mechanics, cheminformatics, linear regression and machine learning to predict site selectivity.[4]

Implication of nature of boryls in the transition state

In 2010, Singleton, in collaboration with our group, investigated regioselective borylations. Computational and theoretical analyses were conducted on various substrates, such as anisole, veratrole, and benzodioxole. A computational model, [(dmpe)Ir(Beg)$_3$], employing (bis(dimethylphosphino)ethane) (dmpe) as a ligand, was utilized to probe the regioselectivity of substrates. Transition state structures for oxidative addition were calculated across different substrates because its known to be the rate-determining step.[1] The activation barrier (ΔG†) for C-H activation of anisole by [dmpeIr(Beg)$_3$] exhibited values of 32.3, 29.5, and 30.2 kcal/mol for the ortho, meta, and para isomers, respectively, as depicted in Figure 13. These computational findings mirrored the experimental meta:para:ortho ratio of 73:23:4. Veratrole calculations yielded the anticipated meta-borylated product regioisomer. Reaction of benzodioxole with the bpy iridium complex lead to a lower energy transition state compared to the one with dmpe. It was inferred from this result that boryl nucleophilicity facilitates the C-H borylation (Figure 14).[2]

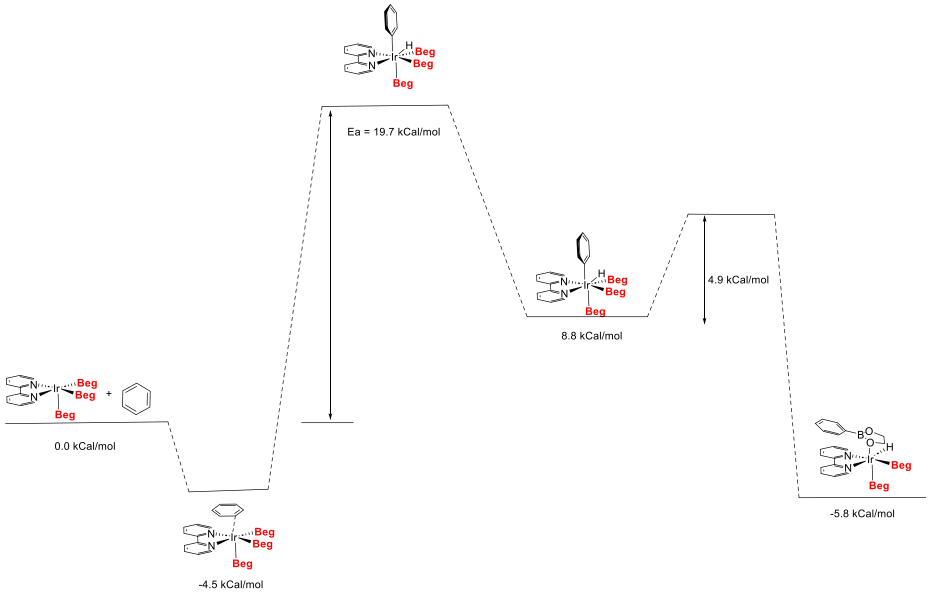


Figure 12: Energy changes in the oxidative addition step of Ir catalyzed borylation and the reductive elimination step[1]

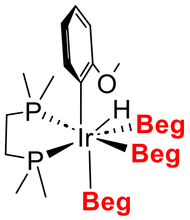
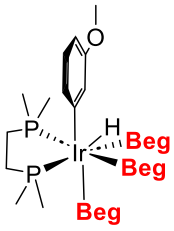
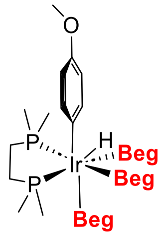
		
ΔG† = 32.3	ΔG† = 29.5	ΔG† = 30.2

Figure 13: (ΔG† are in kCal/mol). Transition structures for C-H activation of anisole at ortho, meta and para positions

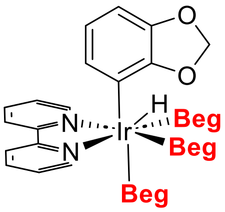
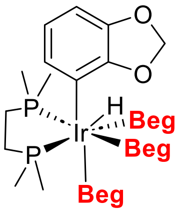
	
ΔG† = 22.9	ΔG† = 23.5

Figure 14: (ΔG† are in kCal/mol). Transition structures for borylation of benzodioxole[2]

Computation of regioisomers with 2 different ligand systems by Sunoj

The Sunoj group extensively investigated regioselective Ir-catalyzed borylation reactions of benzaldimine. They also determined the oxidative addition of the C-H bond as the rate-limiting step in the reaction. Their study aimed to elucidate the mechanism behind the exclusive ortho selectivity achieved with the aminoquinoline (8-AQ) ligand and the meta selectivity achieved with the tetramethylphenanthroline (TMP) ligand, both under identical reaction conditions.

They separately examined the pre-reacting complexes leading to oxidative addition for ortho, meta, and para positions using the 8-AQ and TMP ligands. The geometric accessibility of benzaldimine binding to the Ir via Ir-π coordination mode was studied which led to the C-H bond activation at ortho, meta, and para positions (referred to as the catalyst-substrate complex).

The activation barrier for the oxidative addition of the C-H bond with the 8-AQ ligand was determined to be 26.0 kcal/mol relative to the catalyst-substrate complex. The activation energies (δE) were found to be ortho (26.0) < para (27.0) < meta (30.1) (Figure 15).

Additionally, they conducted calculations for the 8-AQ ligand with a hemilabile mode of binding to the iridium center, resulting in a δE of 24 kcal/mol. This mode of binding not only exhibited lower δE but also exclusively predicted the ortho product of the reaction.

For the Ir-TMP system, the δE of the ortho transition state (TS) and para TS were found to be higher than the δE of the meta TS by 6.1 and 1.5 kcal/mol, respectively (Figure 15). Although the strength of non-covalent interactions was calculated for each isomer, they did not fully explain the observed trend in the activation energy of the isomers.[5]

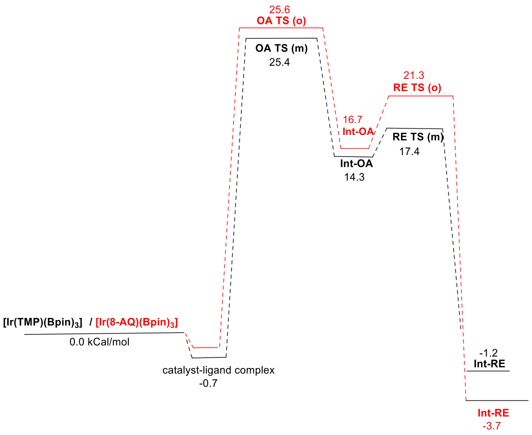


Figure 15: Activation energies of oxidative addition step and reductive elimination step using the 8-AQ and TMP ligand

The graph in red represents the energetics of the 8-AQ ligand system and the graph in black represent the energetics of the TMP ligand system. The energies compared for two ligand systems are the comparison between lowest energy isomer of the product formed in the reaction i.e. meta isomer with the TMP and ortho isomer for the 8-AQ ligand system. OA TS(m) represents oxidative addition transition state for meta isomer, Int OA refers to Intermediate formed following the oxidative addition. RE TS(m) refers to reductive elimination transition state for the meta isomer and Int-RE refers to the intermediate formed following the reductive elimination[3].

5.2. COMPUTATIONAL METHODS

The Gaussian 16 suite of the quantum chemical program was employed for all computations. The first set of calculations were carried out on a lower level of theory using the DFT method with B3LYP/3-21G basis set on C,N,O,H,B,F and LANL08 (f) pseudopotential on Iridium. For this preliminary study, this reaction was modelled in the gas phase.

Higher level of theory included the hybrid density functional B3LYP with Grimme's dispersion correction (D3) in combination with the 6-31G** basis set for all elements except iridium was used. The Stuttgart-Dresden double zeta basis set (SDD) was used for iridium that consists of an effective core potential for the 60 inner core electrons out of the total 77 electrons. The remaining 17 non-core electrons were explicitly treated using a double-ƒ basis set. In all my computations, the solvent effect was implicitly taken into account using the SMD solvation model using tetrahydrofuran (THF, $\varepsilon = 7.42$) for the catalytic cycle, as the continuum dielectric. The choice of B3LYP-D3 functional and the SDD basis set for iridium has been motivated by the earlier successful reports[5,6]. Intermediates and transition states were examined by performing frequency calculations. The transition states were characterized by one and only one imaginary frequency that corresponds to the expected reaction coordinate. Metal substrate complexes were first optimized using the geometry of transition state using Avogadro and then optimized using Gaussian to get the correct orientation.

5.3. RESULTS AND DISCUSSION

5.3.1. Reaction under investigation

Despite theoretical reports on activation barriers using commonly used ligands such as 4,4'-di*tert*-butylpyridine (dtbpy), this study aimed to explore the energetic pathway for iridium-catalyzed borylation using the hydrazone ligand, dimethylaminodipyridinehydrazone (dmadph) developed in our lab. This ligand experimentally resulted in heightened meta selectivity of substrates, which was both unusual and unexpected (Figure 16). The study aimed to investigate the activation energy of the oxidative addition step, rationalize the computed energetic differences among the key regio-controlling transition states, and compare the observed energetic differences with those obtained using the traditionally used ligand dtbpy. The subsequent discussion outlines the initial results of this investigation.

5.3.2. Calculation of ortho, meta and para isomer with fluorobenzene using a proposed bisboryl mechanistic route for an oxidative addition step

3 different conformers were utilized to elucidate the energy pathways for the ortho, meta and para isomer of F-Benzene using the dmapdph ligand. Given the ligand's anionic nature, it was proposed that, to maintain the +III oxidation state of iridium, a bisboryl pathway should be adopted. With one coordination site potentially vacant, it was suggested that a solvent molecule would occupy this site. Three potential conformers were identified based on the arrangement of Bpin and THF.

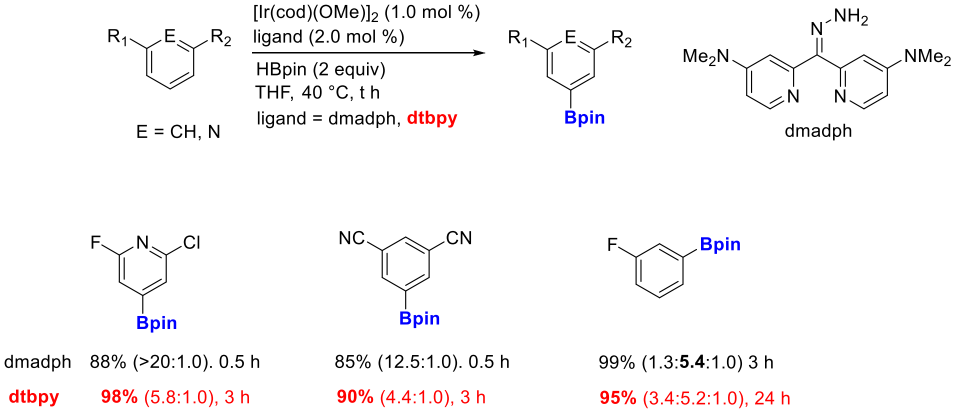
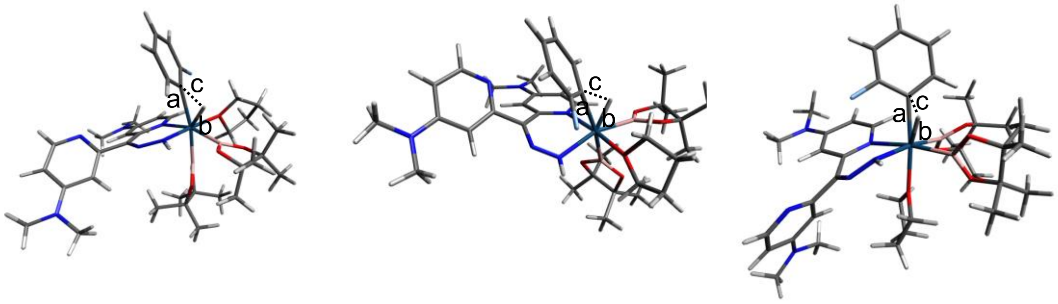


Figure 16: Experimental results of reaction of substrates with dmadph compared to dtbpy ligand

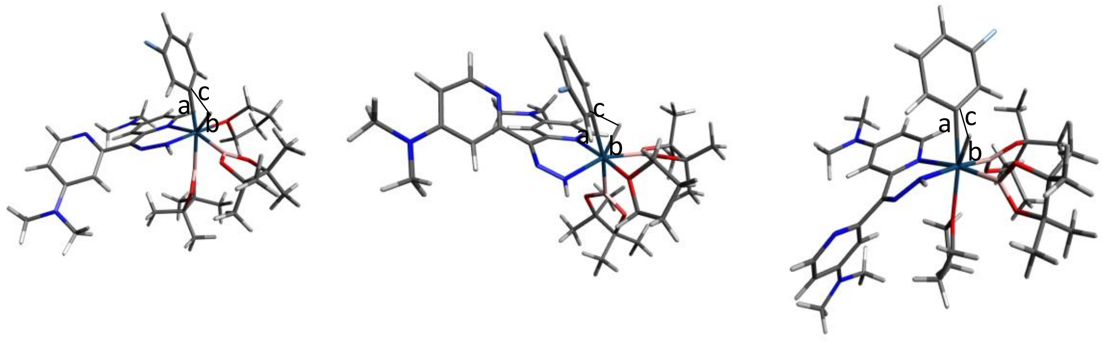
The first conformer, named **B-ax** geometry had one boryl in the square plane facing towards the observer, THF facing backwards and the other boryl on an axial bond. The second conformer, labelled **B-back** situated the boryl ligand in the square plane but facing backwards with THF facing towards the observer and a boryl on the axial bond. The third conformer **Beq** positioned both boryl ligands in the square plane with THF at the axial position. Theoretical comparison of energy levels of O.A. (oxidative addition) transition state of three o-F-Benzene conformers revealed that the energy of B-ax conformer had the lowest energy, with the energy of B-back conformer being 7.75 kcal/mol higher. Additionally, the energy of B-eq conformer was found to be 3.27 kcal/mol higher than that of B-ax (Figure 17).



0.0 kcal/mol (B-ax)	7.75 kcal/mol (B-back)	3.27 kcal/mol (B-eq)
Ir-C (a) = 2.26	Ir-C (a) = 2.29	Ir-C (a) = 2.14
Ir-H (b) = 1.62	Ir-H (b) = 1.63	Ir-H (b) = 1.62
C-H (c) =1.62	C-H (c) =1.60	C-H (c) =1.36

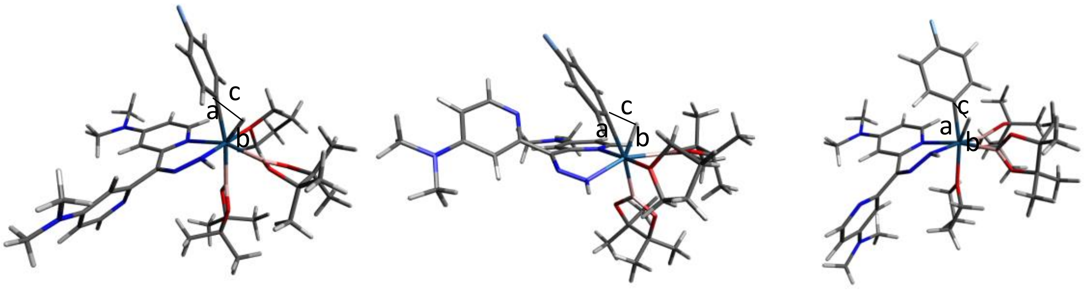
Figure 17: Comparative free energy of transition state of O.A. step for B-ax, B-back and B-eq with ortho-Fluorobenzene. Bond lengths are in Å

A similar energy trend emerged when the transition state Gibbs free energies were compared for meta-Fluorobenzene and para-Fluorobenzene (Figure 18 and 19).



0.67 kcal/mol (B-ax)	10.0 kcal/mol (B-back)	0.00 kcal/mol (B-eq)
Ir-C (a) = 2.24	Ir-C (a) = 2.27	Ir-C (a) = 2.15
Ir-H (b) = 1.62	Ir-H (b) = 1.63	Ir-H (b) = 1.61
C-H (c) = 1.65	C-H (c) =1.61	C-H (c) =1.39
Angle C-Ir-H = 47.2	Angle C-Ir-H = 45.2	Angle C-Ir-H = 40.2

Figure 18: Comparative free energy of transition state of O.A. step for B-ax, B-back and B-eq with meta-Fluorobenzene. Bond lengths are in Å



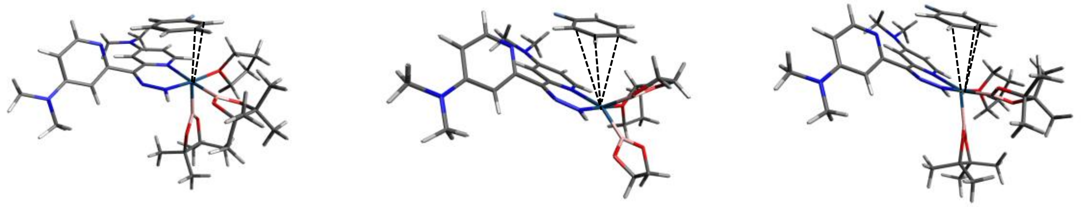
0.0 kcal/mol (B-ax)	9.7 kcal/mol (B-back)	0.49 kcal/mol (B-eq)
Ir-C (a) = 2.25	Ir-C (a) = 2.27	Ir-C (a) = 2.15
Ir-H (b) = 1.62	Ir-H (b) = 1.63	Ir-H (b) = 1.61
C-H (c) = 1.65	C-H (c) = 1.62	C-H (c) =1.41
Angle C-Ir-H = 46.9	Angle C-Ir-H = 45.5	Angle C-Ir-H = 41.1

Figure 19: Comparative free energy of transition state of O.A. step for B-ax, B-back and B-eq with para-Fluorobenzene. Bond lengths are in Å

Upon calculating the activation energy by subtracting the Gibbs free energy of the transition state from the energy of fluorobenzene and the iridium catalyst at their ground states, it was determined that the energy for the **B-ax** conformer for the ortho, meta, and para isomers were 37.06, 39.24, and 39.39 kcal/mol, respectively. Conversely, the energy for the **B-back** conformer was found to be 41.09, 43.45, and 44.32 kcal/mol for the para isomer. The corresponding energies for the **B-eq** conformer were calculated to be -0.5, -2.01, and -0.69 kcal/mol for ortho, meta, and para F-Benzene, respectively. The B-eq conformer was subsequently disregarded because of unreasonable transition state activation energy. Given that the energies of the transition states were higher (in 30s) than typically observed (in 20s) for C-H borylation of arenes, attention was turned towards a metal substrate complex, serving as an intermediate π complex preceding the oxidative addition reaction (Figure 20). This metal substrate complex was also included by Sakaki in 2003.[1] Incorporating this pre-reacting complex led to activation energies within the expected energy range.[6–8] Just like demonstrated in Sunoj's paper[5], the geometric requirements for the **2a** complexes were met for the ortho **2a**; specifically, the C-H bond at the ortho position of fluorobenzene is in the closest proximity to the iridium. This arrangement is replicated for the meta and para positions. As these complexes proceed to form the oxidative addition transition states, they serve as the pre-reacting complex for each regio isomeric pathway. This pre-reacting complex has been termed the turnover-determining Transition Intermediate (TDI) by Sunoj.[5]

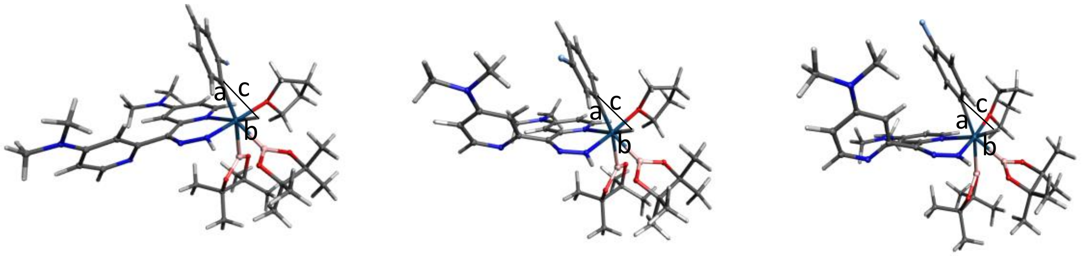
Details of B-ax conformer

2a complex for ortho isomer in the B-ax conformer had the bond distance of 3.7 Å from the C(o-F) to the iridium centre (Figure 21). This distance when previously calculated for a benzene system was found to be 2.4 Å.[1] My difference in the distance can be attribited to a THF molecule in the square plane instead of Bpin.



C(o-F)-Ir = 3.7 C(m-F)-Ir= 4.1	C(m-F)-Ir = 3.8 C(o-F)-Ir = 4.5 C(p-F)-Ir= 4.0	C(m1-F)-Ir = 3.8 C(p-F)-Ir = 3.7 C(m2-F)-Ir= 4.2

Figure 20: Metal substrate complexes in the ortho, meta and para fluorobenzene in the B-ax confomer. Bond lengths are in Å



Ir-C (a) = 2.16 Ir-H (b) = 1.61 C-H (c) = 2.54 Angle C-Ir-H = 83.2	Ir-C (a) = 2.15 Ir-H (b) = 1.61 C-H (c) = 2.57 Angle C-Ir-H = 85.2	Ir-C (a) = 2.15 Ir-H (b) = 1.61 C-H (c) = 2.55 Angle C-Ir-H = 84.6

Figure 21: Intermediates formed after oxidative addition of ortho, meta and para fluorobenzene in the B-ax confomer. Bond lengths are in Å

In this TS$_{2-3}$ for **B-ax** confomer, C-H bond considerably lengthens to 1.65 Å for ortho, meta and para fluorobenzene (Figure 21). On the other hand, Ir-H distance for ortho, meta and para shortens to 1.62 Å which very well complements the Ir-H bond distance of 1.607 Å (benzene substrate, dtbpy ligand) calculated by Sakaki[1]. Ir-C distance shortened to 2.24 Å for ortho, and 2.25 for meta and para. Ir-C and Ir-H bond lengths in the transition state are very similar to that in the product/intermediate formed after oxidative addition (Ir-C is 2.24 (TS) vs 2.16 (int) for ortho, 2.25

(TS) vs 2.15 (int) for meta and para isomer; Ir-H is 1.62 (TS) vs 1.61 (int) for ortho, meta and para isomer). Therefore, it can be concluded that the transition states represent late transition states, aligning with prior literature reports.[2]

The activation energy, calculated by subtracting the energy of transition state from the energy of metal substrate complex (TDI), was found to be 35.24 kcal/mol for meta, 35.9 kcal/mol for the ortho and 36.27 for para isomer (Figure 22). The calculated Boltzmann ratio of isomers was found to be 1.6:4.9:1.0 9 (o:m:p) which aligned with the experimental ratios of 1.5:5.7:1.0 for (o:m:p).

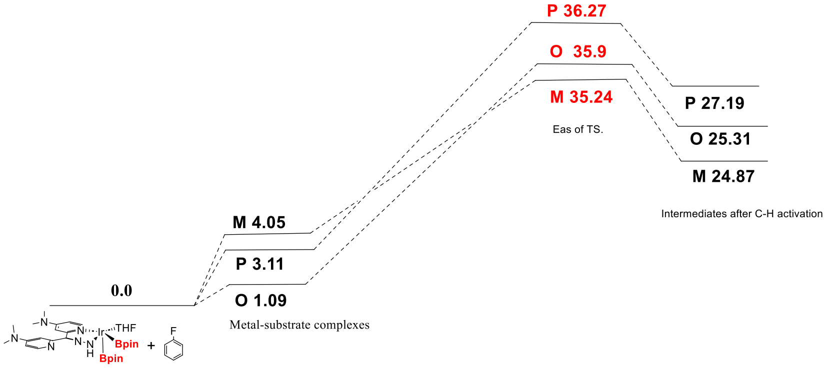
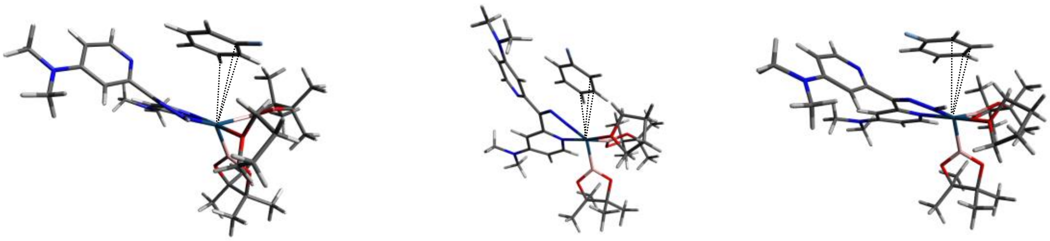


Figure 22: Potential energy graph of oxidative addition step for B-ax conformer

Details of B-back conformer

Just like previously described catalyst substrate complex (**2a**) for three distinct oxidative addition pathways is separately considered. In the case of ortho isomer however, the C2-C3 bond of fluorobenzene is in closest proximity to the iridium. Meta and para isomers still follow the criteria (Figure 23).

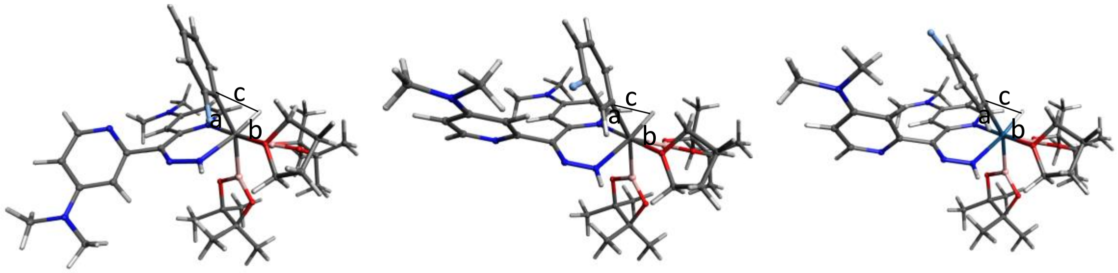
Analysis of **B-back** conformer's $TS_{2\text{-}3}$ was carried out similar to that of **B-ax** conformer and they revealed similar nature of the transition state that they were late. C-H bond considerably lengthens to 1.60 Å for ortho, 1.61 Å for meta and 1.62 Å para fluorobenzene (Figure 24). Ir-H distance for ortho, meta and para shortens to 1.62 Å for ortho, 1.63 Å for meta and para isomer. Ir-C distance shortened to 2.29 Å for ortho, and 2.27 for meta and para. Ir-C and Ir-H bond lengths



C(F)-Ir = 4.3	C(m-F)-Ir = 3.6	C(o-F)-Ir = 4.2
C(o-F)-Ir = 3.7	C(o-F)-Ir = 4.1	C(m-F)-Ir = 3.8
C(m-F)-Ir= 3.6	C(p-F)-Ir= 4.1	C(p-F)-Ir= 3.6

Figure 23: Metal substrate complexes in the ortho, meta and para fluorobenzene in the B-back confomer. Bond lengths are in Å

in the transition state are very similar to that in the product/intermediate formed after oxidative addition (Ir-C is 2.29 (TS) vs 2.15 (int) for ortho C-H, 2.27 (TS) vs 2.14 (int) for meta and para isomer; Ir-H is 1.63 (TS) vs 1.63 (int) for o, m and p isomer).



Ir-C (a) = 2.15	Ir-C (a) = 2.14	Ir-C (a) = 2.14
Ir-H (b) = 1.63	Ir-H (b) = 1.63	Ir-H (b) = 1.63
C-H (c) = 2.60	C-H (c) = 2.58	C-H (c) = 2.59
Angle C-Ir-H = 85.6	Angle C-Ir-H = 85.1	Angle C-Ir-H = 85.7

Figure 24: Intermediates formed after oxidative addition of ortho, meta and para fluorobenzene in the B-back conformer. Bond lengths are in Å

The activation energy, calculated by subtracting the energy of transition state from the energy of metal substrate complex (TDI), was found to be 35.8 kcal/mol for meta, 36.3 kcal/mol for the ortho and 37.0 for para complex (Figure 25). The calculated Boltzmann ratio of isomers was found to be 1.6:4.9:1.0 (o:m:p) which aligned with the experimental ratios of 5.0:12:1.0 for (o:m:p).

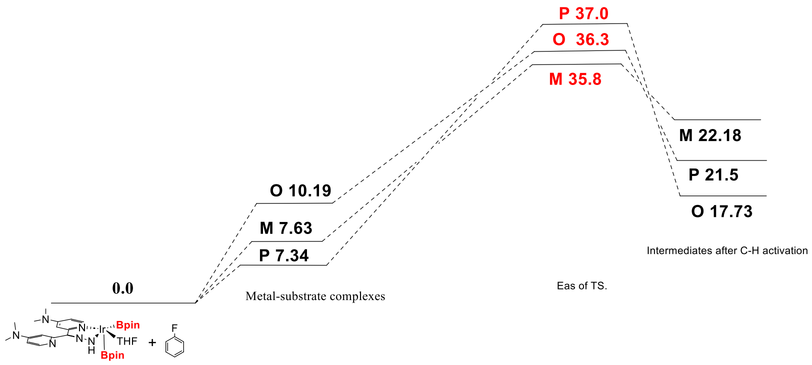
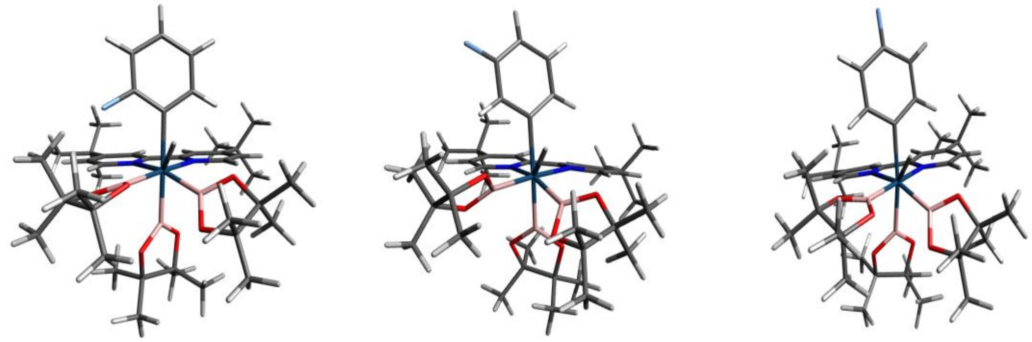


Figure 25: Potential energy graph of oxidative addition step for B-back conformer

5.3.3 Calculation of ortho, meta and para isomer with fluorobenzene using a traditional trisboryl Ir(III) route for an oxidative addition step.

The catalyst-substrate complexes are denoted as **2a-OD-HBS**, where '**2a**' represents the catalyst-substrate complex, '**OD**' signifies the ortho isomer with the dtbpy ligand, and '**HBS**' indicates high basis set calculations for the ortho pathway.



a) Ir-C= 2.21	a) Ir-C= 2.23	a) Ir-C = 2.23
b) Ir-H= 1.615	b) Ir-H= 1.62	b) Ir-H = 1.62
c) C-H= 1.584	c) C-H= 1.62	c) C-H= 1.60

Figure 26: Potential energy graph of oxidative additions of o, m and p fluorobenzenes

The structures shown above are the most stable configuration of oxidative addition reactions (Figure 26). The structures of additional confomers investigated are detailed in the compound's structure section.

Again the $TS_{2\text{-}3}$ of oxidative addition were compared to that of the intermediate formed after the oxidative addition. The forming Ir-C is somewhat similar for meta 2.23, para 2.23 and for ortho 2.21. However the breaking C-H bond for meta is 1.62 compared to 1.58 for ortho and 1.60 for para. The structure of intermediate formed upon oxidative addition showed that the forming Ir-H bond is longer in the meta 2.51 and 2.52 in para compared to Ir-H bond in ortho 2.47. The relatively short Ir-C bond 2.24 for ortho, 2.23 for meta and 2.23 for para indicates that the transition states are late which matches the previous literature.[2]

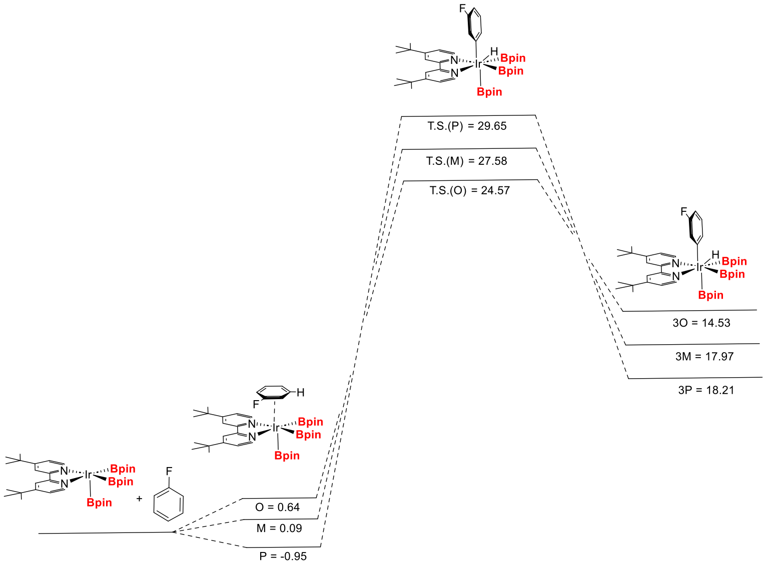


Figure 27: Relative oxidative addition energy of ortho, meta and para F-Benzene using dtbpy as a ligand

The OA to the ortho C-H bond is found to proceed with a barrier of 24.5 kCal/mol with respect to catalyst substrate complex. The same energy barrier for meta is found to be 27.58 and 29.65 for para fluorobenzene (Figure 27). Based on calculations, the calculated boltzmann ratio at room temperature indicates ortho as the major product with a ratio of o:m:p (270:1:0.02 or

1:0.003:7.4*10^{-5}). This trend of the ratio aligns with previous literature findings on borylation of fluroborylated product using B_2pin_2 as the boron source, where ortho borylated compound is the major product.[9,10] However our experimental results, with product ratio of 3.4:5.2:1.0 when HBpin is used, shows a deviation. This deviation is also reported in the literature example that observed the major product as the meta isomer when HBpin was used as a boron source.[11–13]

5.3.4. Explanation of results observed with dtbpy ligand and hydrazone ligand

DtbpyIr(III) Results:

It is observed that going from the ortho to the meta fluorine transition state in the dtbpyIr(III) trisboryl complex involves one of the Bpin in the meta isomer twisting upwards, indicating the formation of a new hydrogen bond between the aromatic ortho C-H and the oxygen of the boryl in the meta transition state (Figure 15). The bond distance between the aromatic C-H (ortho to F) and the boryl oxygen measures 2.42 Å, contrasting with the bond distance in the para transition state, where the aromatic C-H (meta to F) and the boryl oxygen are 2.60 Å apart. Notably, the distance between the aromatic C-H in the ortho transition state and the boryl oxygen is 3.07 Å. However, despite the extra stability in the meta transition state due to the additional hydrogen bond, it is not reflected in the activation energies of the meta isomer.

Further, analysis of ortho Ir-C and Ir-H bond dissociation energy was carried out using the intermediates formed after oxidative addition. Calculations showed that Ir-C bond is the strongest (BDE= 57.7 kCal/mol) when F is at the ortho followed by F situated in the para position followed by F situated in meta position. (BDE= 52.3 kCal/mol for para and 51.7 kCal/mol for meta). This suggests that under thermodynamic control, the system should predominantly yield the ortho product. Similarly, analysis of BDEs of ortho, meta and para C-H bonds were calculated to be 106.65, 104.1, 104.9 kCal/mol respectively. These relative energies indicate that the ortho C-H bond is substantially stronger than meta and para. Consequently, the system under kinetic control would functionalize the weakest C-H i.e. the meta, which is aligned with our experimental results. This elucidates that our system is in kinetic control.

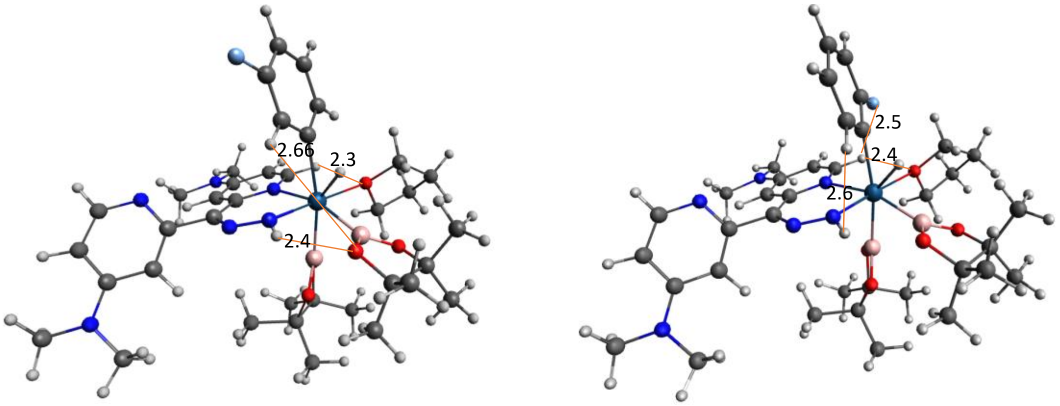
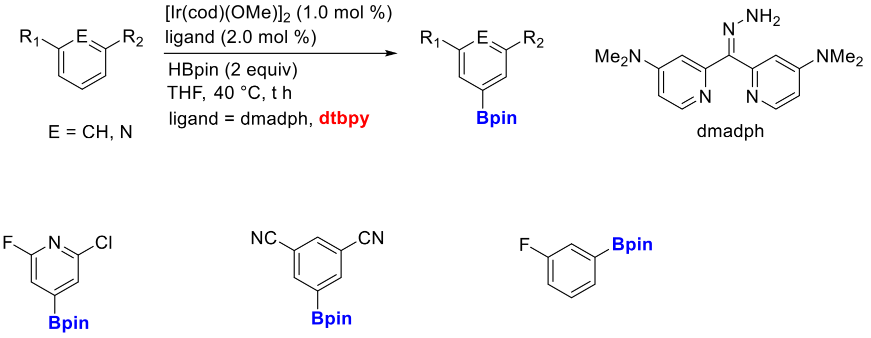


Figure 28: Comparison of hydrogen bonds in the meta and ortho C-H transition state for the B-ax conformer

dmadphIr(III) system (B-ax conformer): The hydrogen bonds were estimated for the meta and ortho isomeric transition states (Figure 28). The N-H of the ligand showed a hydrogen bond with the oxygen of the boryl. The aromatic C-H in the ortho isomer also formed a hydrogen bond with the nitrogen of the ligand with a bond length of 2.6. Such a hydrogen bond in the meta isomer was observed with the oxygen of the THF(solvent) molecule with a bond length of 2.6 which possibly is a very weak bond. The F present in the ortho isomer was also found to be hydrogen bonding with the C-H of the ligand with a bond length of 2.5 Å. This bonding was completely absent in the meta isomer. Conversely aromatic N-H of the ligand in the meta isomer was found to be hydrogen bonding with the oxygen of the THF molecule with a bond length of 2.3. These results indicate that the ortho transition state is more stable than the meta, however its not reflected in calculations or experiments. It can be concluded that the resulting trend in product formation has been the result of relative stability of metal substrate complexes.

dmadphIr(III) system (B-back conformer): No apparent hydrogen bonds were observed in the ortho or meta transition state structure.

5.3.5. Exploration of a trisboryl-Ir(III) route using a hydrazone ligand for an oxidative addition step

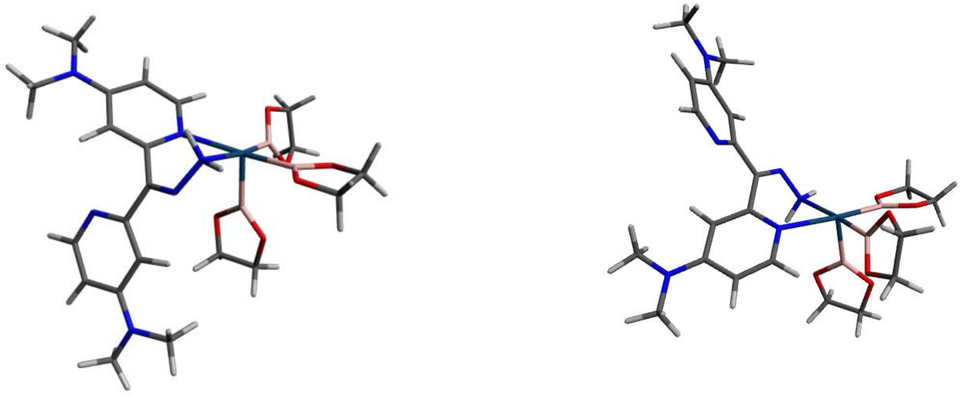


dmadph	88% (>20:1.0). 0.5 h	85% (12.5:1.0). 0.5 h	99% (1.3:**5.4**:1.0) 3 h
dtbpy	**98%** (5.8:1.0), 3 h	**90%** (4.4:1.0), 3 h	**95%** (3.4:5.2:1.0), 24 h

Figure 29: Meta selective C-H borylation using dmadph and dtbpy ligand

The reaction proceeds faster with the dmadph ligand. Accordingly, the energy barrier for oxidative addition, the rate limiting step, with the hydrazone ligand should have been lower than the dtbpy ligand (Figure 29). However, calculations were inconsistent with this experimental finding. As mentioned in Sec 5.3.3, the activation energy with the dtbpy ligand was calculated to be in 20s whereas the hydrazone ligand was calculated to be in 30s. This led me to explore alternate mechanistic route involving a trisboryl iridium(III) as the active catalyst, which has been theoretically explored in the literature.[1,5,7,8]

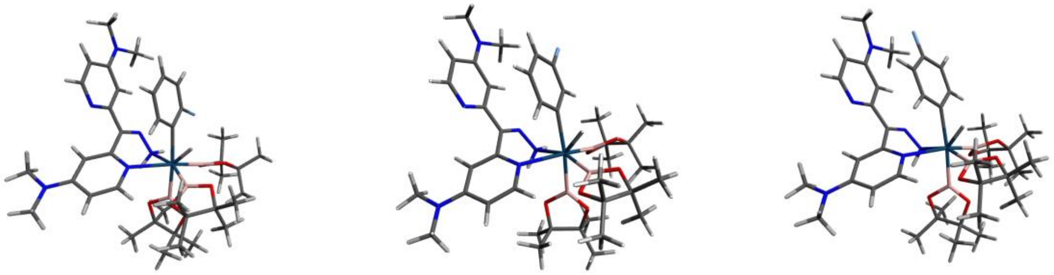
In the trisboryl iridium(III) complex pathway, ligand was assumed to be a neutral chelating ligand. In this route first two possibilities of position of ligand was taken into consideration. Two ligand orientations were evaluated: one with hydrazone's NH_2 group oriented towards the observer and the other where it was facing away. The ground state energy was 2.6 kCal/mol higher when the NH_2 faced towards the observer (**I**, Figure 30), leading to the dismissal of this configuration in favor of the latter for subsequent calculations.



I 2.6 kCal/mol **II** 0 kCal/mol

Figure 30: Two orientations of the ligand in the ground state of trisboryl; the active catalyst

In the trisboryl pathway, with hydrazone ligand facing away from the observer, the calculations for the metal substrate complex **2a** were performed similarly to previous methods to confirm that the ortho C-H bond was proximal to the iridium in the ortho pathway. From **2**, the oxidative addition of fluorobenzene to the Ir center takes place through the transition state TS_{2-3} to afford [Ir(Bpin)$_3$(dmaph)(H)(F-Benzene)], labelled as **TS2-3-OD-HBS**. In this $TS_{2-3,}$ C-H bond considerably lengthens to 1.61 Å for ortho, 1.64 Å for meta and para fluorobenzene (Figure 31). On the other hand, Ir-H distance for ortho, meta and para shortens to 1.60 Å which very well complements the Ir-H bond distance of 1.607 Å calculated by Sakaki[1]. Ir-C distance shortened to 2.26 Å for ortho, and 2.22 for meta and para. This unexpected elongated Ir-C(F-Ph) can be explained by the *ortho fluorine* effect. This effect explains the increased ionicity of the metal-carbon bond with increasing ortho fluorine substitution. The proposed reasoning for the effect being that when the metal cation is placed with an aryl anion, ortho fluorine stabilizes the anionic component. More specifically it is likely that C-F σ* antibonding orbital accepts the electron density stabilizing the bonding interaction. This effect has also been explain using Pople-Gordon effect.[14] The Ir-H bond distance for 1.64 for meta and para compared to 1.61 for ortho transition state. The meta and para transition state were later compared to ortho transition state. The ortho fluorine effect was observed to be negligible with dtbpy ligand.



Ir-C = 2.26	Ir-C = 2.22	Ir-C = 2.22
Ir-H = 1.60	Ir-H = 1.60	Ir-H = 1.60
C-H = 1.61	C-H = 1.64	C-H = 1.64
Angle Ir C H= 46.5	Angle Ir C H = 47.2	Angle Ir C H = 47.2

Figure 31: Transition state for the oxidative addition energy of ortho, meta and para F-Benzene using hydrazone as a ligand. Bond distances are in Å

The calculated Gibbs free energy of activation (ΔG†) for the oxidative addition via the ortho pathway was determined to be 22.5 kcal/mol, with the meta and para pathways yielding values of 26.1 kcal/mol and 27.03 kcal/mol, respectively (Figure 32). While these ΔG† magnitudes are similar to those of the dtbpy pathway, they do not account for the experimental preference observed for the meta product. To understand this chemistry better, calculations were also carried out on dicyanobenzene substrate.

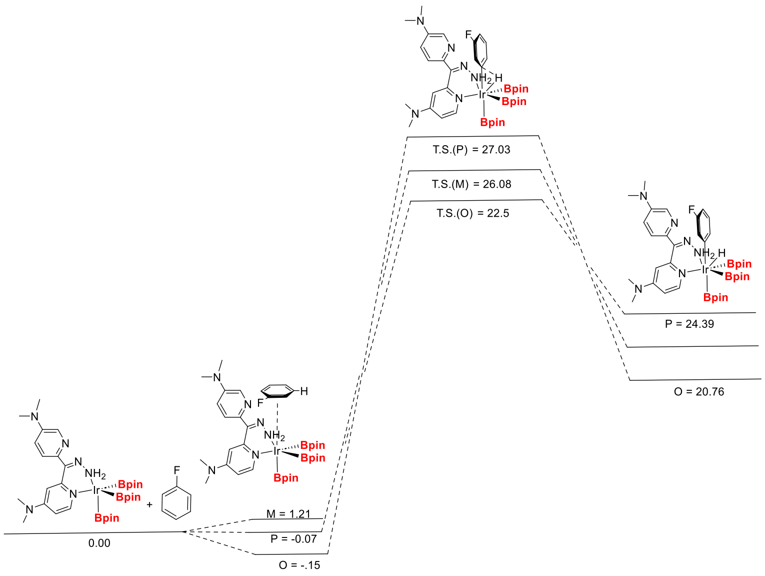


Figure 32: Relative oxidative addition pathway of ortho, meta and para F-Benzene using hydrazone ligand

5.3.6. Explanation of DmpadphIr(III)trisboryl results.

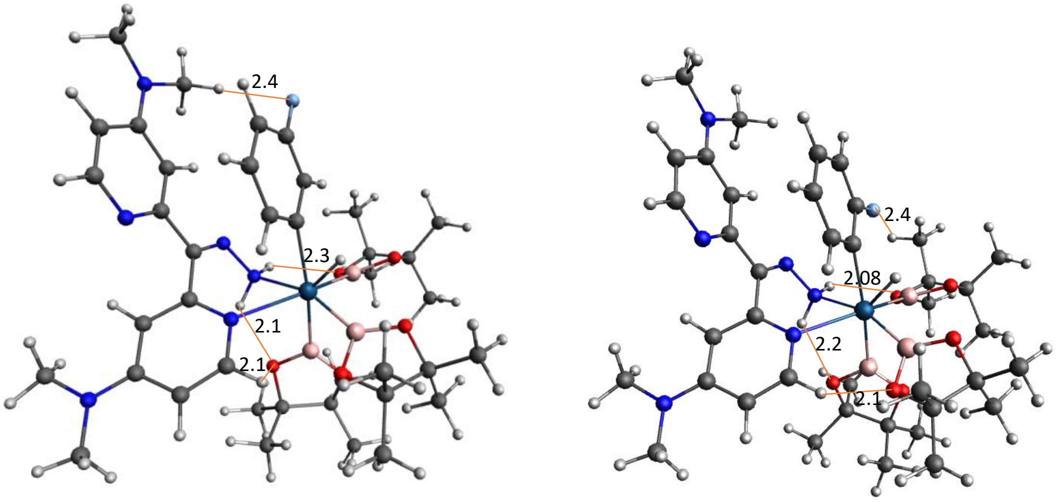


Figure 33: Comparison of H-bond distance in the transition state in the meta(left) and ortho (right) isomer

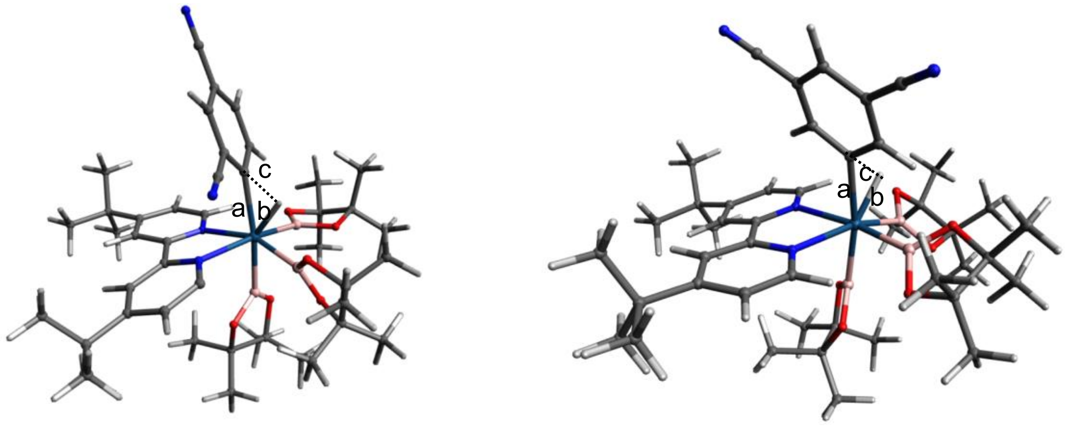
The analysis of hydrogen bonding in both the ortho and meta isomer revealed a similar number of hydrogen bonds for both the cases (Figure 33). In the ortho and the meta isomer, ligand formed 3 hydrogen bonds. The calculated bond distance between NH (NH_2 of the dmapdph) with the oxygen of the boryl (equitorial) was found to be 2.08 while the bond distance between the other

NH (NH_2 of the dmadph) with the oxygen of the boryl (apical) was found to be 2.2. The bond distance between the aromatic C-H (from pyridine) to the oxygen of boryl (equitorial) was found to be 2.1. These hydrogen bonds were also observed in the meta transition state isomer as well. However some distinction was noted in the ortho and the meta isomer. In the ortho isomer, the bond distance between F and one of the boryl was found to be 2.4 which was absent in the meta isomer. Conversely, in the meta isomer, the meta F was found to be forming a hydrogen bond with the H of (N-CH3) with a bond distance of 2.4. The comparison did not elucidate a reasoning for preference of meta transition state over the other in the experiments and for ortho's preference in the calculations.

5.3.7. Exploration of activation energy of 1,3-dicyanobenzene with dtbpy and hydrazone ligand

5.3.7.1. Reaction of 1,3-dicyanobenzene with dtbpy

Theoretical calculations were performed for two isomeric positions i.e. with ortho and meta. The oxidative addition of 1,3-dicyanobenzene to the Ir center takes place through the transition state $TS_{2\text{-}3}$ to afford [Ir(Bpin)$_3$(dtbpy)(H)(1,3dicyanobenzene)], denoted as **TS2-3-CN2-OD** for the ortho isomer signifying (TS= transition state, CN2 = dicyanobenzene as substrate and OD= ortho position using dtbpy as ligand). In this $TS_{2\text{-}3,}$ C-H bond considerably lengthens to 1.56 Å for ortho, 1.61 Å for meta (Figure 34). On the other hand, Ir-H distance for ortho shortened to 1.62 Å and 1.60 Å for meta isomer. Ir-C distance shortened to 2.20 Å for ortho, and 2.22 for meta. Ir-C and Ir-H bond

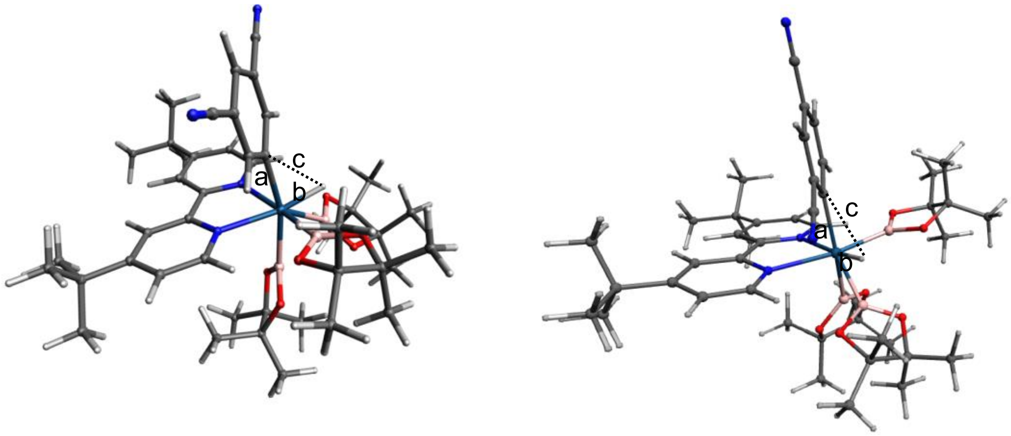


a = 2.22 b = 1.63 c = 1.58 Angle between C-Ir-H= 45.1	a = 2.24 b = 1.63 c = 1.57 Angle between C-Ir-H= 44.6

Figure 34: Transition state for oxidative addition of cyanobenzene for the ortho (left) and meta (right) isomer

lengths in the transition state are very similar to that in the product (i.e. 2.22 vs 2.16 for Ir-C and 1.63 vs 1.60 for Ir-H in the meta isomer). Again, it was discovered that the transition states represent late transition states.

The calculated Gibbs free energy of activation (ΔG†) for the oxidative addition via the ortho pathway was determined to be 28.0 kcal/mol and 26.64 kcal/mol for the meta pathway. The calculated boltzmann ratio at 40 °C indicates meta as the major product with a ratio of m:o (9.02:1.0) which is in striking agreement with the experimentally observed m:o ratio of (4.4:1.0). So indeed the meta borylation of 1,3 dicyanobenzene was associated with the oxidative addition as the rate limiting step and the trisboryliridium(III) as the active catalyst.

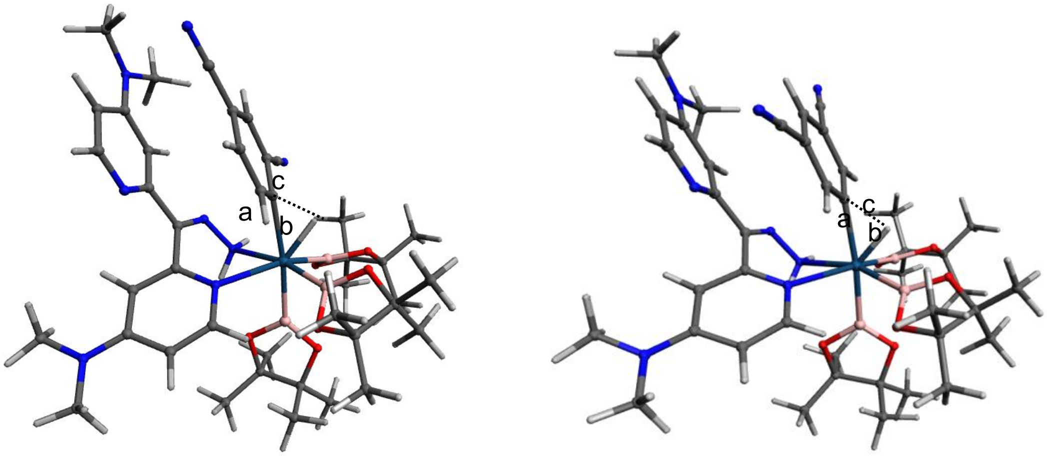


a = 2.16 b = 1.60 c = 2.53 Angle between C-Ir-H= 83.4	a = 2.14 b = 1.60 c = 2.56 Angle between C-Ir-H= 85.2

Figure 35: Intermediates formed after the oxidative addition of C-H bond in the meta 1,3 dicyanobenzene (left) and ortho 1,3 dicyanobenzene (right)

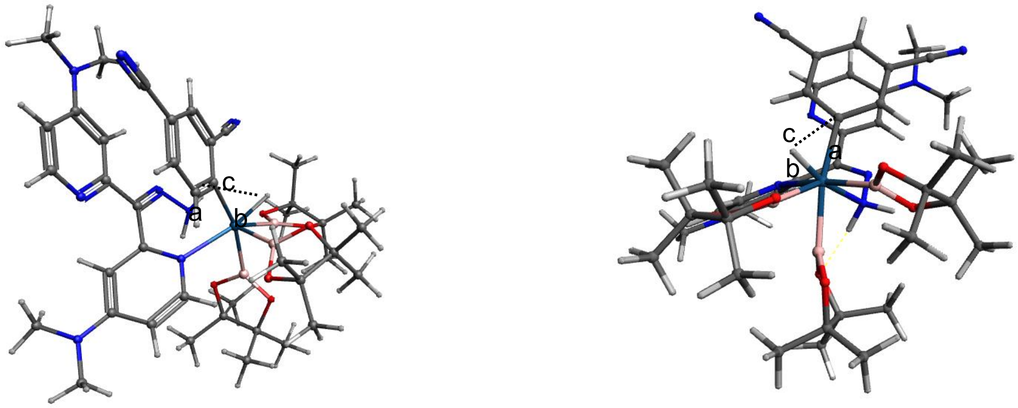
5.3.7.2 Reaction of 1,3-dicyanobenzene with the hydrazone (dmadph) ligand

Theoretical calculations were performed for two isomeric positions i.e ortho and meta. The oxidative addition of 1,3-dicyanobenzene to the Ir center takes place through the transition state TS_{2-3} to afford [Ir(Bpin)$_3$(dmadph)(H)(1,3dicyanobenzene)], labelled as **TS2-3-CN2-OT** for the ortho isomer referring to (TS= transition state, CN2 = dicyanobenzene as substrate and OT= ortho position for a trisboryl mechanism using dmadph). In this $TS_{2-3,}$ C-H bond considerably lengthens to 1.56 Å for ortho, 1.61 Å for meta. On the other hand, Ir-H distance for ortho shortened to 1.62 Å and 1.60 Å for meta isomer exactly the same observed with the dtbpy ligand (Figure 35). Ir-C distance shortened to 2.22 Å for ortho, and 2.21 for meta. Ir-C and Ir-H bond lengths in the transition state are very similar to that in the product (i.e. 2.21 vs 2.16 for Ir-C and 1.60 vs 1.60 for Ir-H in the meta isomer) (Figure 36). Again, it was discovered that the transition states represent late transition states because of similarity in the bond distances of the transition state to the intermediate formed after oxidative addition . The calculated Gibbs free energy of activation ($\Delta G^{\dagger}$) for the oxidative addition via the ortho pathway was determined to be 22.1 kcal/mol and 24.4 kcal/mol for the meta pathway. This activation energy, when compared to the dtbpy, elucidates a higher reactivity of the hydrazone ligand due to its lower activation energy in comparison. Despite this, the predicted ratios still suggest that ortho should be the major product and not meta. The cause of the inconsistency with the experimental results is not understood, prompting speculation regarding whether the hydrazone ligand alters the mechanistic pathway for the reaction.



a = 2.22 b = 1.62 c = 1.56 Angle between C-Ir-H= 44.6	a = 2.21 b = 1.60 c = 1.61 Angle between C-Ir-H= 46.3

Figure 36: Transition state for oxidative addition of cyanobenzene for the ortho (left) and meta (right) isomer with the dmadph ligand



a = 2.14 b = 1.60 c = 2.52 Angle between C-Ir-H= 83.8	a = 2.16 b = 1.60 c = 2.42 Angle between C-Ir-H= 78.8

Figure 37: Intermediates formed after oxidative addition of cyanobenzene for the ortho (left) and meta (right) isomer with the dmadph ligand

5.3.8. Higher reactivity of dmadph ligand

The experimental data suggests that the hydrazone ligand is more reactive because it was observed that the reaction carried out by the hydrazone ligand were completed in 3 h as compared to 24 h for fluorobenzene with dtbpy. When comparing the Highest Occupied Molecular Orbitals (HOMOs) of dtbpy and the dmpadph (hydrazone ligand), it is observed that the HOMO of hydrazone (anionic form) ligand exhibited higher energy (-0.11 eV) compared to dtbpy (-0.23 eV). This disparity in energy levels can be attributed to higher electron donation ability of hydrazone ligand towards the catalyst which also explains the higher reactivity of hydrazone ligand in the reaction.

5.4. MOLECULE SPECIFICATION

Starting Material

F-Benzene

C	0.00000	1.21937	0.26108
C	0.00000	1.20989	-1.13589
C	0.00000	0.00000	0.92760
C	0.00000	0.00000	-1.83574
C	0.00000	-1.21937	0.26108
F	0.00000	0.00000	2.28441
C	0.00000	-1.20989	-1.13589
H	0.00000	-2.14332	0.82962
H	0.00000	0.00000	-2.92145
H	0.00000	-2.15227	-1.67552
H	0.00000	2.14332	0.82962
H	0.00000	2.15227	-1.67552

Sum of electronic and zero-point Energies= -331.410301
Sum of electronic and thermal Energies= -331.405158
Sum of electronic and thermal Enthalpies= -331.404214
Sum of electronic and thermal Free Energies= -331.438474

Bisboryl, hydrazone(dmadph) ligand

Conformer B-ax (ortho)

2a-O-conformer-B-ax

Ir	0.86980	-0.34650	-0.13958
N	-0.95110	-1.48063	0.41029
C	-0.78903	-2.70368	0.96754
N	-0.30162	1.14358	-0.67738
C	-1.80496	-3.47895	1.47536
C	-2.21970	-0.97207	0.33342
C	-3.13487	-2.97283	1.43797
C	-3.30130	-1.69841	0.87326
H	0.23438	-3.06163	0.99435
H	-1.56656	-4.44654	1.89678
N	-4.19348	-3.69296	1.92518
H	-4.28261	-1.25697	0.82532
C	-2.46618	0.33432	-0.27763
N	-1.59921	1.25848	-0.67288
H	0.13339	2.01384	-0.96648
C	-3.87474	0.75055	-0.57069
C	-4.33303	2.00210	-0.15468
N	-4.63686	-0.10774	-1.29088
C	-5.63339	2.44209	-0.49623
C	-5.87686	0.30364	-1.59339
C	-3.96056	-4.94437	2.63442
C	-5.52491	-3.10199	1.94057
H	-5.57975	-2.22136	2.59648
H	-6.24153	-3.84151	2.29873
H	-5.83082	-2.79549	0.93368
H	-3.45737	-5.67832	1.99396
H	-4.91885	-5.36835	2.93564
H	-3.35050	-4.80097	3.53713
C	-6.42436	1.52887	-1.23852
N	-6.10335	3.67475	-0.12180
H	-6.48221	-0.39637	-2.16941
C	-5.29486	4.53108	0.73568
C	-7.49425	4.02724	-0.37024
H	-8.19204	3.35770	0.15269
H	-7.72807	3.99390	-1.44102
H	-7.67346	5.04506	-0.02268
H	-4.32573	4.75210	0.27375
H	-5.10818	4.07679	1.71920
H	-5.81505	5.47709	0.88917
H	-7.43970	1.76074	-1.53420
H	-3.66594	2.62331	0.42730
B	1.41121	0.64974	1.50229
O	1.72406	0.04991	2.72515
C	2.28486	1.07247	3.59111
O	1.46885	2.04182	1.62150
C	1.61100	2.36954	3.02724
C	0.71794	-1.67985	-3.59307
C	-0.36961	-2.22938	-2.92177
F	-0.20165	-3.41466	-2.26947
C	-1.61689	-1.61993	-2.88254
H	-2.43182	-2.07237	-2.32973
C	-1.77534	-0.40130	-3.54481
H	-2.73952	0.09451	-3.50276
C	-0.70166	0.18267	-4.22295
C	0.53966	-0.45886	-4.24926
H	1.37782	-0.00798	-4.77242
H	-0.83127	1.13579	-4.72650
C	0.19960	2.59923	3.58062
C	2.44414	3.63922	3.16105
C	3.80407	1.04796	3.37976
C	1.93959	0.73909	5.03704
O	2.15737	-2.13300	0.27733
C	2.76396	-2.75898	-0.89882
C	3.09041	-2.22959	1.39021
C	3.99513	-3.52162	-0.38716
C	3.79275	-3.55282	1.13762
H	4.90765	-2.96894	-0.63148

H 4.07152 -4.51843 -0.82888
H 3.14278 -4.38597 1.42749
H 4.73221 -3.63533 1.69102
H 2.50074 -2.17547 2.30229
H 3.77421 -1.37714 1.34667
B 2.52047 0.66840 -0.79338
O 2.48714 1.78892 -1.63186
O 3.85216 0.35206 -0.48433
C 3.81060 2.38022 -1.66944
C 4.72511 1.15332 -1.31861
C 5.08163 0.30074 -2.54293
C 5.98356 1.49115 -0.52631
C 3.84065 3.47415 -0.59623
C 4.04452 2.98338 -3.05026
H 1.66903 -2.19934 -3.60121
H 3.02839 -1.97222 -1.60718
H 1.99670 -3.40192 -1.33275
H 0.21921 2.91093 4.62952
H -0.40569 1.69199 3.49463
H -0.28564 3.38659 2.99605
H 2.62352 3.87188 4.21619
H 1.90867 4.48246 2.71339
H 3.40771 3.54712 2.65687
H 3.63699 3.04892 0.38863
H 3.05234 4.20224 -0.81092
H 4.79975 4.00111 -0.57579
H 5.06822 3.36247 -3.14072
H 3.35803 3.82126 -3.20865
H 3.87131 2.25273 -3.84334
H 5.73995 1.95963 0.42958
H 6.63231 2.16759 -1.09298
H 6.54727 0.57562 -0.31898
H 5.54079 -0.63310 -2.20384
H 5.78980 0.81024 -3.20372
H 4.18529 0.05024 -3.11824
H 2.26586 1.54168 5.70704
H 2.44943 -0.18177 5.33826
H 0.86599 0.58890 5.16807
H 4.31707 1.76240 4.03077
H 4.05421 1.27033 2.33826
H 4.17816 0.04559 3.60928
Sum of electronic and zero-point Energies=
-2401.810072
Sum of electronic and thermal Energies=
-2401.754193
Sum of electronic and thermal Enthalpies=
-2401.753249
Sum of electronic and thermal Free
Energies= -2401.904487

TS2-3O-B-ax-HBS-Bpin
Ir -1.09955 0.47183 -0.41514
N 0.65005 1.55965 0.33841
C 0.41526 2.52291 1.25315
N 0.14077 -0.60179 -1.56332
C 1.38911 3.16774 1.98130
C 1.94317 1.19723 0.08820
C 2.74458 2.79431 1.78211
C 2.98279 1.78917 0.82650
H -0.62598 2.78128 1.39323
H 1.09499 3.93377 2.68613
N 3.76499 3.38199 2.47792
H 3.99173 1.47706 0.61905
C 2.25881 0.15723 -0.90403
N 1.43478 -0.63701 -1.57215
H -0.25171 -1.40378 -2.04481
C 3.69157 -0.16783 -1.20128
C 4.11257 -1.49818 -1.12338
N 4.52019 0.84191 -1.55499
C 5.44422 -1.85296 -1.43686
C 5.78702 0.50360 -1.83750
C 3.46807 4.33296 3.54121
C 5.13408 2.91773 2.29451
H 5.25951 1.87152 2.60719
H 5.80506 3.53642 2.89089
H 5.44206 2.99877 1.24569
H 2.91605 5.19967 3.15872
H 4.40303 4.69552 3.96856
H 2.87631 3.87737 4.34713
C 6.30239 -0.78501 -1.80013
N 5.87895 -3.15390 -1.37660
H 6.44595 1.32522 -2.11844
C 4.99957 -4.18269 -0.83650
C 7.29547 -3.45068 -1.53999
H 7.91291 -2.98372 -0.75876
H 7.66128 -3.10715 -2.51430
H 7.44378 -4.53004 -1.49341
H 4.07553 -4.25920 -1.42068
H 4.72530 -3.98833 0.21075
H 5.50483 -5.14787 -0.88499
H 7.34548 -0.94515 -2.04182
H 3.39291 -2.24298 -0.81591
B -0.58932 -0.90908 1.10598
O -0.21927 -0.52740 2.38831
C 0.01970 -1.72551 3.17788

O	-0.41757	-2.27631	0.93769
C	0.34188	-2.78495	2.06832
C	-1.24331	1.95178	-2.12940
C	-1.30912	3.32670	-1.90868
F	-1.55952	3.79491	-0.64509
C	-1.09936	4.29186	-2.88806
H	-1.14604	5.34315	-2.61973
C	-0.82236	3.87525	-4.19139
H	-0.65795	4.61283	-4.97166
C	-0.75610	2.50896	-4.47517
C	-0.96621	1.57452	-3.45715
H	-0.89937	0.51450	-3.68865
H	-0.54082	2.17057	-5.48520
C	1.81438	-2.78384	1.63965
C	-0.11941	-4.20520	2.37428
C	-1.27943	-2.02317	3.93447
C	1.15697	-1.44503	4.15281
O	-2.53799	1.59555	0.88580
C	-3.80834	2.06281	0.31680
C	-2.76620	1.16887	2.26081
C	-4.81154	2.05780	1.47371
C	-3.91191	2.05244	2.72004
H	-5.41254	1.14351	1.44673
H	-5.48598	2.91684	1.43081
H	-3.54853	3.06159	2.94461
H	-4.41057	1.65411	3.60787
H	-1.82597	1.29639	2.79363
H	-3.04224	0.11102	2.25731
B	-2.54735	-1.00600	-0.61286
O	-2.53601	-1.95985	-1.62075
O	-3.65190	-1.16231	0.21322
C	-3.55025	-2.95864	-1.31125
C	-4.53597	-2.14586	-0.39466
C	-5.58938	-1.36129	-1.18453
C	-5.19752	-2.95372	0.71552
C	-2.84513	-4.10112	-0.57412
C	-4.15524	-3.46079	-2.61712
H	-2.17932	0.74001	-1.59663
H	-4.09631	1.38808	-0.49010
H	-3.61583	3.05787	-0.08251
H	2.46296	-3.20708	2.41285
H	2.15589	-1.77205	1.40629
H	1.91430	-3.38933	0.73429
H	0.38893	-4.59221	3.26377
H	0.12281	-4.86116	1.53232
H	-1.19727	-4.25452	2.54073
H	-2.37850	-3.74072	0.34432
H	-2.05125	-4.49737	-1.21461
H	-3.53723	-4.91579	-0.34000
H	-4.98340	-4.14920	-2.41831
H	-3.39612	-4.00120	-3.19130
H	-4.52397	-2.63928	-3.23475
H	-4.45646	-3.38997	1.38844
H	-5.80881	-3.75993	0.29691
H	-5.85111	-2.30386	1.30625
H	-6.10407	-0.67485	-0.50541
H	-6.33575	-2.02333	-1.63362
H	-5.12455	-0.76953	-1.97867
H	1.43393	-2.35353	4.69802
H	0.84163	-0.69354	4.88371
H	2.03921	-1.06245	3.63538
H	-1.16975	-2.88014	4.60596
H	-2.09877	-2.22579	3.23854
H	-1.55079	-1.14947	4.53463

Sum of electronic and zero-point Energies= -2401.754848

Sum of electronic and thermal Energies= -2401.699880

Sum of electronic and thermal Enthalpies= -2401.698936

Sum of electronic and thermal Free Energies= -2401.845715

Imaginary frequency= -907.12

3O-B-ax-HBS-Bpin

Ir	-0.97648	0.29695	-0.74377
N	0.59043	1.22135	0.43204
C	0.29002	2.38318	1.04968
N	0.28264	-1.20854	-1.13450
C	1.18525	3.15198	1.75538
C	1.87201	0.74776	0.51928
C	2.53713	2.72420	1.83070
C	2.84566	1.51626	1.17819
H	-0.73258	2.71207	0.94491
H	0.83780	4.06696	2.21567
N	3.48461	3.44030	2.50490
H	3.84961	1.13075	1.21355
C	2.24565	-0.55431	-0.04684
N	1.49931	-1.39513	-0.74447
H	-0.12419	-2.06334	-1.49790
C	3.61658	-1.11258	0.18902
C	4.34489	-1.59629	-0.90011
N	4.07572	-1.17288	1.46143
C	5.60623	-2.20770	-0.70953
C	5.28214	-1.73168	1.63578
C	3.15184	4.74550	3.06208

C	4.86477	2.97229	2.54175
H	4.92400	1.95186	2.93720
H	5.44626	3.62112	3.19709
H	5.32875	2.98068	1.54585
H	2.80386	5.44176	2.28771
H	4.03920	5.17385	3.52819
H	2.37150	4.66747	3.82920
C	6.07806	-2.25538	0.62636
N	6.33159	-2.71306	-1.75738
H	5.64274	-1.77052	2.66371
C	5.85635	-2.53327	-3.12279
C	7.67711	-3.22169	-1.53081
H	7.67359	-4.04728	-0.80904
H	8.35740	-2.44352	-1.15627
H	8.07995	-3.60305	-2.46962
H	5.78778	-1.47222	-3.40117
H	4.86743	-2.98555	-3.26156
H	6.54699	-3.02260	-3.81000
H	7.04000	-2.68373	0.87796
H	3.91574	-1.49529	-1.88755
B	-1.29235	-0.55405	1.23000
O	-1.74432	0.22892	2.27465
C	-1.62054	-0.52727	3.51242
O	-0.73169	-1.72839	1.68400
C	-0.55904	-1.62319	3.12824
C	-0.09247	1.32544	-2.43355
C	0.19301	2.68830	-2.50584
F	-0.16410	3.50623	-1.45700
C	0.81291	3.33112	-3.57410
H	0.99364	4.40100	-3.52196
C	1.18275	2.57346	-4.68609
H	1.66725	3.05056	-5.53355
C	0.91806	1.20171	-4.68891
C	0.29889	0.60608	-3.58405
H	0.12013	-0.46633	-3.60871
H	1.19497	0.59464	-5.54762
C	0.88612	-1.17646	3.36763
C	-0.79610	-2.99676	3.74514
C	-3.00889	-1.09461	3.82190
C	-1.18481	0.42985	4.61709
O	-2.44030	1.98151	-0.46526
C	-3.06282	2.55054	-1.66576
C	-3.35576	2.11786	0.67000
C	-4.46420	2.97758	-1.23844
C	-4.28658	3.24758	0.26163
H	-5.17660	2.15959	-1.39057
H	-4.81158	3.84790	-1.80130
H	-3.80802	4.22010	0.42449
H	-5.22623	3.22322	0.82029
H	-2.75078	2.31685	1.55233
H	-3.88076	1.17079	0.80216
B	-2.49694	-1.14456	-0.52126
O	-2.32014	-2.44504	-0.98663
O	-3.80528	-0.93688	-0.10478
C	-3.51287	-3.21005	-0.66730
C	-4.59931	-2.07960	-0.53615
C	-5.23414	-1.69264	-1.87589
C	-5.67609	-2.34005	0.50966
C	-3.23795	-3.94504	0.64740
C	-3.76423	-4.21099	-1.78965
H	-2.02414	-0.22074	-1.85243
H	-3.05789	1.79266	-2.45003
H	-2.44249	3.39406	-1.97236
H	1.11815	-1.13638	4.43640
H	1.07723	-0.19367	2.93266
H	1.56671	-1.88607	2.89195
H	-0.73677	-2.94368	4.83721
H	-0.02621	-3.69183	3.39637
H	-1.76978	-3.40473	3.46774
H	-3.02473	-3.23778	1.44980
H	-2.35387	-4.57647	0.52134
H	-4.08003	-4.57969	0.93894
H	-4.70656	-4.74408	-1.62612
H	-2.95639	-4.94895	-1.81214
H	-3.80286	-3.72243	-2.76532
H	-5.24596	-2.45568	1.50642
H	-6.24152	-3.24463	0.26355
H	-6.37578	-1.49882	0.53794
H	-5.82671	-0.78325	-1.73787
H	-5.89486	-2.47908	-2.25217
H	-4.46833	-1.48813	-2.63007
H	-0.99669	-0.11366	5.54876
H	-1.97806	1.16044	4.80528
H	-0.28101	0.97609	4.34079
H	-3.01775	-1.64839	4.76537
H	-3.35216	-1.75553	3.02260
H	-3.72088	-0.26741	3.90000

Sum of electronic and zero-point Energies= -2401.774223

Sum of electronic and thermal Energies= -2401.719069

Sum of electronic and thermal Enthalpies= -2401.718125

Sum of electronic and thermal Free Energies= -2401.864634

Conformer B-ax (meta)
2a-M-B-ax-conformer
Ir -0.83898 0.08555 0.39111
N 1.07695 0.88954 1.10814
C 1.03239 2.01482 1.86726
N 0.19472 -1.35156 -0.47068
C 2.12096 2.77098 2.22236
C 2.31282 0.42827 0.72194
C 3.41185 2.35021 1.79764
C 3.47163 1.13764 1.10025
H 0.04080 2.31440 2.18276
H 1.96416 3.67327 2.79781
N 4.53649 3.10073 2.04869
H 4.41672 0.77192 0.73969
C 2.43710 -0.78184 -0.08367
N 1.47426 -1.56390 -0.56475
H -0.31928 -2.09876 -0.92641
C 3.78865 -1.30103 -0.47980
C 4.10470 -2.63762 -0.22636
N 4.63710 -0.46165 -1.11925
C 5.33774 -3.18177 -0.65665
C 5.81508 -0.97293 -1.50639
C 4.37057 4.49802 2.43875
C 5.76816 2.76264 1.34068
H 6.09054 1.74526 1.58116
H 6.55956 3.44309 1.65806
H 5.64669 2.84112 0.25101
H 3.85524 5.08226 1.66247
H 5.35387 4.93845 2.60976
H 3.80734 4.58222 3.37243
C 6.21841 -2.28577 -1.31464
N 5.66564 -4.49451 -0.44067
H 6.48762 -0.28209 -2.01420
C 4.77346 -5.35126 0.32909
C 6.99082 -4.98079 -0.79870
H 7.78550 -4.46608 -0.24036
H 7.18745 -4.85018 -1.86970
H 7.05366 -6.04628 -0.57642
H 3.78330 -5.41521 -0.13734
H 4.64245 -4.99184 1.35936
H 5.19010 -6.35804 0.36969
H 7.19340 -2.59741 -1.66707
H 3.37943 -3.24362 0.29910
B -2.17188 -1.31816 0.96985
O -2.93508 -1.25907 2.13834
C -3.83213 -2.40006 2.15557
O -2.35091 -2.56176 0.34707
C -3.05872 -3.43321 1.26437
C 0.07716 3.45027 -2.14749
C 1.18368 4.07229 -1.56158
H 1.13625 5.08542 -1.17571
C 2.37078 3.35400 -1.47138
F 3.44276 3.94471 -0.87199
C 2.50594 2.05997 -1.95595
H 3.43943 1.51917 -1.83688
C 1.38329 1.44919 -2.51945
C 0.16857 2.13470 -2.61235
H 1.45608 0.42086 -2.85931
C -1.99957 -4.22263 2.04306
C -3.94219 -4.38488 0.46541
C -5.15244 -1.93586 1.52931
C -4.05212 -2.83280 3.60057
O -1.91042 1.81501 1.32031
C -2.05755 3.02126 0.50443
C -3.06740 1.68495 2.19481
C -3.28773 3.75144 1.05403
C -3.48034 3.12551 2.44523
H -4.15954 3.53871 0.42736
H -3.14145 4.83420 1.08392
H -2.81244 3.59139 3.17854
H -4.50790 3.20324 2.81069
H -2.73944 1.12930 3.07194
H -3.83620 1.11298 1.67115
B -2.33634 -0.00227 -0.97908
O -2.17572 -0.51096 -2.27037
O -3.61348 0.55783 -0.83999
C -3.46621 -0.50562 -2.93324
C -4.23918 0.61432 -2.14699
C -3.99706 2.02201 -2.70516
C -5.73574 0.37058 -1.98189
C -4.07163 -1.90005 -2.74058
C -3.25570 -0.21981 -4.41627
H -0.86041 3.99283 -2.22408
H -2.17210 2.72107 -0.53528
H -1.13035 3.58946 0.61621
H -2.45271 -4.95111 2.72244
H -1.35974 -3.55178 2.62390
H -1.36694 -4.76242 1.33189
H -4.54177 -5.00846 1.13706
H -3.31789 -5.04588 -0.14421
H -4.61600 -3.84753 -0.20412
H -4.19104 -2.12218 -1.67828
H -3.38741 -2.64397 -3.15963
H -5.03884 -1.99895 -3.24294
H -4.21636 -0.13240 -4.93496
H -2.69671 -1.04161 -4.87480

H	-2.68974	0.70080	-4.57393
H	-5.93500	-0.56195	-1.45075
H	-6.23295	0.33113	-2.95678
H	-6.18196	1.18827	-1.40655
H	-4.39626	2.75745	-2.00003
H	-4.49378	2.16694	-3.66929
H	-2.92895	2.21815	-2.83220
H	-4.65193	-3.74824	3.64289
H	-4.59028	-2.04984	4.14451
H	-3.10566	-3.01106	4.11514
H	-5.90729	-2.72804	1.53355
H	-4.99408	-1.59625	0.50279
H	-5.53947	-1.08976	2.10543
H	-0.69946	1.63065	-3.02311

Sum of electronic and zero-point Energies= -2401.808076
Sum of electronic and thermal Energies= -2401.752700
Sum of electronic and thermal Enthalpies= -2401.751756
Sum of electronic and thermal Free Energies= -2401.899779

TS2-3-3-B-ax-HBS-Bpin

Ir	1.11565	-0.54897	-0.30926
N	-0.64441	-1.50561	0.59139
C	-0.41528	-2.38477	1.58629
N	-0.12094	0.36332	-1.59145
C	-1.38787	-2.93143	2.39344
C	-1.93414	-1.14457	0.32200
C	-2.73668	-2.53892	2.18641
C	-2.97105	-1.63162	1.13575
H	0.62290	-2.65555	1.73678
H	-1.09778	-3.63449	3.16269
N	-3.75600	-3.02113	2.95926
H	-3.97741	-1.32455	0.90921
C	-2.24421	-0.22312	-0.78384
N	-1.41337	0.44061	-1.57416
H	0.28022	1.08086	-2.18607
C	-3.67290	0.10640	-1.09855
C	-4.04598	1.44841	-1.21355
N	-4.54382	-0.91219	-1.28607
C	-5.37031	1.80235	-1.55721
C	-5.80375	-0.57246	-1.59611
C	-3.46320	-3.88024	4.09898
C	-5.11996	-2.55655	2.74076
H	-5.22215	-1.47938	2.93266
H	-5.79225	-3.08972	3.41326
H	-5.44533	-2.75138	1.71218
H	-2.96971	-4.80835	3.78559
H	-4.39628	-4.14840	4.59451
H	-2.81787	-3.37948	4.83342
C	-6.27291	0.72568	-1.74365
N	-5.75747	3.11310	-1.68779
H	-6.49636	-1.40152	-1.74149
C	-4.83351	4.17735	-1.31768
C	-7.16573	3.43500	-1.87332
H	-7.78294	3.11892	-1.01958
H	-7.56376	2.95891	-2.77655
H	-7.27424	4.51345	-1.99304
H	-3.91604	4.12964	-1.91504
H	-4.55127	4.13302	-0.25555
H	-5.30415	5.14271	-1.50758
H	-7.31446	0.88766	-1.99049
H	-3.29446	2.20334	-1.03440
B	0.62237	1.03049	1.02449
O	0.26759	0.81371	2.34969
C	0.05000	2.10108	2.98992
O	0.45724	2.36795	0.69127
C	-0.27387	3.02350	1.76389
C	1.20298	-2.32776	-1.67017
C	1.44252	-3.60493	-1.13057
H	1.77833	-3.70166	-0.10338
C	1.20859	-4.76477	-1.87572
H	1.38090	-5.74096	-1.42876
C	0.74889	-4.68459	-3.19279
H	0.56177	-5.56598	-3.79708
C	0.53037	-3.41798	-3.72038
C	0.74968	-2.25231	-2.99741
H	0.54392	-1.29340	-3.46372
F	0.08562	-3.31663	-5.00227
C	-1.75307	2.99944	1.36111
C	0.21649	4.46162	1.88834
C	1.35971	2.47184	3.69434
C	-1.07933	1.95375	4.00279
O	2.56615	-1.54085	1.10540
C	3.87878	-1.97987	0.60317
C	2.74912	-0.96334	2.43509
C	4.86076	-1.77330	1.75846
C	3.94494	-1.71355	2.99086
H	5.38278	-0.81924	1.63832
H	5.60368	-2.57338	1.80751
H	3.65253	-2.71957	3.31243
H	4.39933	-1.19338	3.83843
H	1.81136	-1.09358	2.97199
H	2.95655	0.10318	2.32218

B 2.56400 0.89362 -0.68214
O 2.56659 1.70325 -1.80902
O 3.66056 1.15820 0.12800
C 3.58120 2.73240 -1.62770
C 4.55327 2.05225 -0.59523
C 5.61858 1.17113 -1.25674
C 5.19913 3.00375 0.40500
C 2.87222 3.96798 -1.06538
C 4.20416 3.04692 -2.98293
H 2.15483 -0.99858 -1.47243
H 4.12977 -1.38756 -0.27588
H 3.77416 -3.02893 0.32157
H -2.38113 3.52105 2.08988
H -2.11479 1.97394 1.25143
H -1.85883 3.49840 0.39370
H -0.27006 4.96306 2.73172
H -0.02903 5.01539 0.97682
H 1.29771 4.51066 2.03132
H 2.39075 3.73837 -0.11335
H 2.08962 4.27501 -1.76595
H 3.56541 4.80476 -0.93544
H 5.03201 3.75517 -2.87173
H 3.45383 3.50287 -3.63640
H 4.57786 2.14679 -3.47520
H 4.44897 3.52838 1.00016
H 5.81921 3.74509 -0.10963
H 5.84174 2.44013 1.08902
H 6.12653 0.58615 -0.48400
H 6.36897 1.76888 -1.78264
H 5.16613 0.47461 -1.96876
H -1.34126 2.92443 4.43692
H -0.76350 1.29243 4.81603
H -1.97094 1.52131 3.54402
H 1.26609 3.40417 4.25943
H 2.17496 2.57989 2.97312
H 1.62697 1.67280 4.39248
Sum of electronic and zero-point Energies= -2401.751385
Sum of electronic and thermal Energies= -2401.696309
Sum of electronic and thermal Enthalpies= -2401.695365
Sum of electronic and thermal Free Energies= -2401.843707
Imaginary Freq= -858.12

3-conformer-B-ax-HBS-Bpin

Ir 0.76474 -0.61016 0.39649
N -0.48696 1.13622 0.66791
C -0.12766 2.05397 1.59026
N -0.21755 -0.95422 -1.30800
C -0.85845 3.17446 1.91233
C -1.66791 1.31438 -0.00506
C -2.08178 3.40690 1.22696
C -2.45296 2.44751 0.26645
H 0.80863 1.86496 2.09311
H -0.47845 3.84456 2.67156
N -2.85217 4.50512 1.47822
H -3.34275 2.58359 -0.32684
C -2.11796 0.35938 -1.02124
N -1.41289 -0.58578 -1.63079
H 0.17335 -1.62059 -1.96391
C -3.55761 0.32228 -1.43933
C -4.23669 -0.87738 -1.21627
N -4.14321 1.40461 -1.99909
C -5.58937 -1.02593 -1.59872
C -5.43229 1.26656 -2.34842
C -2.40210 5.51265 2.43004
C -4.07528 4.72714 0.71636
H -3.87062 4.85252 -0.35503
H -4.56456 5.63040 1.08077
H -4.77409 3.88990 0.83271
H -2.27582 5.08885 3.43396
H -3.14758 6.30542 2.49164
H -1.44833 5.96355 2.12517
C -6.19101 0.11472 -2.18644
N -6.26902 -2.20083 -1.39431
H -5.89931 2.14430 -2.79468
C -5.66053 -3.24232 -0.57223
C -7.70446 -2.25270 -1.63508
H -8.26756 -1.58684 -0.96419
H -8.05675 -3.27339 -1.48084
H -7.93881 -1.97456 -2.66827
H -5.47355 -2.90265 0.45594
H -4.70765 -3.57596 -0.99245
H -6.32784 -4.10436 -0.53575
H -7.22784 0.11803 -2.49828
H -3.70171 -1.67900 -0.72668
B 1.93553 0.93265 -0.61797
O 2.55001 1.93123 0.11316
C 2.95480 2.99558 -0.79406
O 1.78118 1.29543 -1.93881
C 2.04884 2.72301 -2.05133
C -0.85048 -1.60584 1.39880
C -1.42973 -1.09945 2.58047
H -1.01028 -0.20618 3.03677

C	-2.54409	-1.69463	3.18018
H	-2.96496	-1.27089	4.08936
C	-3.13600	-2.82828	2.61447
H	-4.00574	-3.31056	3.04831
C	-2.56285	-3.32814	1.45288
C	-1.44913	-2.75586	0.84903
H	-1.07868	-3.19769	-0.07158
F	-3.13559	-4.42208	0.86488
C	0.68942	3.42723	-1.98208
C	2.71578	2.98662	-3.39611
C	4.45046	2.80201	-1.05765
C	2.70759	4.33296	-0.10351
O	1.76952	-0.39190	2.39627
C	1.79963	-1.58179	3.26235
C	2.99559	0.38338	2.61077
C	3.12565	-1.51410	4.01661
C	3.44535	-0.01361	4.00570
H	3.90137	-2.06569	3.47478
H	3.04079	-1.93574	5.02148
H	2.85808	0.51401	4.76600
H	4.50432	0.20377	4.16961
H	2.74128	1.43436	2.49215
H	3.71813	0.10234	1.84297
B	2.55095	-1.12735	-0.60865
O	2.50820	-1.78244	-1.83743
O	3.84474	-1.10853	-0.09909
C	3.87221	-2.02500	-2.27243
C	4.65911	-2.00307	-0.90998
C	4.66867	-3.35863	-0.19570
C	6.06882	-1.43081	-0.98953
C	4.25581	-0.87955	-3.21412
C	3.91752	-3.35610	-3.01459
H	1.45307	-2.06440	0.35088
H	1.70041	-2.46819	2.63550
H	0.93416	-1.51478	3.92433
H	0.04359	3.02798	-2.76921
H	0.78949	4.50682	-2.12927
H	0.19605	3.24830	-1.02416
H	2.01707	2.75119	-4.20474
H	3.60789	2.37213	-3.53195
H	2.99822	4.04061	-3.48674
H	3.54735	-0.85448	-4.04687
H	5.26361	-1.01037	-3.61922
H	4.19691	0.08249	-2.70233
H	6.69099	-2.02935	-1.66279
H	6.53078	-1.44541	0.00271
H	6.06167	-0.39809	-1.34388
H	5.30391	-4.08393	-0.71248
H	3.65791	-3.77030	-0.11899
H	5.05793	-3.22254	0.81785
H	3.33826	-3.28150	-3.94010
H	3.49511	-4.16592	-2.41635
H	4.94799	-3.61522	-3.27909
H	4.85194	3.58781	-1.70429
H	4.64675	1.83136	-1.51955
H	4.98569	2.83273	-0.10380
H	2.91105	5.16466	-0.78582
H	3.37478	4.43134	0.75886
H	1.67923	4.41402	0.25382

Sum of electronic and zero-point Energies=
-2401.768270

Sum of electronic and thermal Energies=
-2401.712943

Sum of electronic and thermal Enthalpies=
-2401.711999

Sum of electronic and thermal Free Energies= -2401.860244

Conformer B-ax (para)

2aP-B-ax

Ir	0.89646	-0.21873	0.31944
N	-0.97411	-1.07479	1.11827
C	-0.94051	-2.37165	1.52020
N	-0.16599	1.33644	-0.26271
C	-2.04473	-3.15625	1.74427
C	-2.20351	-0.47996	0.99135
C	-3.33635	-2.59343	1.54626
C	-3.37373	-1.23825	1.19757
H	0.05275	-2.78360	1.65122
H	-1.90156	-4.18607	2.04259
N	-4.48191	-3.34482	1.67609
H	-4.32001	-0.75175	1.03596
C	-2.32137	0.90912	0.55043
N	-1.40193	1.67155	-0.03247
H	0.33258	2.11031	-0.68993
C	-3.64238	1.60356	0.64624
C	-4.11821	2.33744	-0.44578
N	-4.32147	1.50970	1.81370
C	-5.33821	3.04630	-0.36050
C	-5.48956	2.16394	1.88177
C	-4.37549	-4.79979	1.61825
C	-5.74689	-2.76722	1.23402
H	-5.96215	-1.84259	1.77751
H	-6.55297	-3.47098	1.44658
H	-5.74383	-2.54849	0.15648
H	-3.97717	-5.14340	0.65239

H -5.36610 -5.23457 1.76030
H -3.73470 -5.18142 2.41783
C -6.04263 2.92934 0.86442
N -5.81742 3.79278 -1.40722
H -6.02796 2.07625 2.82558
C -5.11656 3.78724 -2.68384
C -7.14808 4.37921 -1.32963
H -7.22759 5.07472 -0.48566
H -7.93237 3.61672 -1.21877
H -7.34586 4.94086 -2.24301
H -5.09205 2.78726 -3.14083
H -4.08292 4.13380 -2.56964
H -5.62133 4.46555 -3.37258
H -6.99539 3.41726 1.02624
H -3.52350 2.35538 -1.34824
B 2.19723 1.03802 1.19387
O 2.95800 0.72923 2.32356
C 3.87672 1.82745 2.56345
O 2.38854 2.37972 0.83944
C 3.11379 3.03277 1.91253
C -0.46713 -1.35877 -2.82344
C -0.42566 -2.73164 -2.56297
H 0.49066 -3.29033 -2.72477
C -1.55612 -3.39547 -2.07773
H -1.54779 -4.45672 -1.85255
C -2.71680 -2.65866 -1.87778
F -3.81405 -3.29665 -1.38738
C -2.79831 -1.29848 -2.14973
C -1.65571 -0.64972 -2.62042
H -1.68602 0.41955 -2.80148
H -3.72249 -0.76387 -1.96142
C 2.07050 3.65657 2.84703
C 4.00740 4.11736 1.32138
C 5.18175 1.47902 1.83705
C 4.11789 1.95037 4.06328
O 2.00376 -2.08570 0.85398
C 2.12095 -3.09346 -0.20080
C 3.19346 -2.13322 1.69303
C 3.36526 -3.92021 0.14313
C 3.61127 -3.59219 1.62506
H 4.21537 -3.58390 -0.45870
H 3.21251 -4.98628 -0.04351
H 2.96999 -4.20214 2.27119
H 4.65155 -3.73858 1.92812
H 2.90057 -1.77220 2.67719
H 3.94409 -1.46220 1.26946
B 2.35232 0.17662 -1.04597
O 2.15719 0.95999 -2.18899
O 3.63635 -0.38378 -1.06666
C 3.43426 1.12426 -2.85824
C 4.22442 -0.14179 -2.37014
C 3.95248 -1.38539 -3.22534
C 5.72600 0.05964 -2.19801
C 4.03809 2.43840 -2.35202
C 3.19719 1.19419 -4.36287
H 0.42191 -0.83269 -3.15488
H 2.20705 -2.58276 -1.15914
H 1.19575 -3.67581 -0.18041
H 4.18123 2.40272 -1.27027
H 3.34145 3.25436 -2.56689
H 4.99296 2.66268 -2.83739
H 5.94409 0.84449 -1.47115
H 6.19512 0.32455 -3.15143
H 6.18470 -0.86802 -1.84046
H 4.36233 -2.26362 -2.71714
H 4.42021 -1.31050 -4.21174
H 2.87809 -1.54089 -3.36145
H 4.14855 1.23360 -4.90407
H 2.63195 2.09954 -4.60605
H 2.62700 0.33511 -4.72282
H 4.61662 4.58209 2.10400
H 3.38996 4.89714 0.86428
H 4.67283 3.72108 0.55248
H 2.53827 4.22237 3.65864
H 1.42433 2.88813 3.28123
H 1.44094 4.33976 2.26899
H 4.73767 2.82579 4.28482
H 4.64353 1.06217 4.42855
H 3.17971 2.03779 4.61499
H 5.95185 2.24075 1.99236
H 5.00657 1.35856 0.76470
H 5.55850 0.52685 2.22323
Sum of electronic and zero-point Energies= -2401.808341
Sum of electronic and thermal Energies= -2401.752816
Sum of electronic and thermal Enthalpies= -2401.751872
Sum of electronic and thermal Free Energies= -2401.901278

TS2-3P-B-ax-HBS-Bpin
Ir -1.02882 0.52664 -0.28854
N 0.71932 1.26715 0.81006
C 0.53559 2.30099 1.65443
N 0.23916 -0.45518 -1.50177

C	1.54666	2.95869	2.32007
C	1.98996	0.82215	0.59257
C	2.88787	2.55145	2.09381
C	3.07100	1.47923	1.19883
H	-0.49293	2.61333	1.79228
H	1.29255	3.77287	2.98541
N	3.94306	3.16578	2.70809
H	4.06520	1.13016	0.97493
C	2.25161	-0.31282	-0.31435
N	1.46307	-0.81910	-1.24573
H	-0.19393	-1.11728	-2.13760
C	3.57214	-1.01079	-0.24990
C	4.22900	-1.37959	-1.42773
N	4.05498	-1.30923	0.97993
C	5.43411	-2.11654	-1.37766
C	5.20948	-1.98870	1.02287
C	3.71976	4.34436	3.53561
C	5.30662	2.74725	2.40802
H	5.44526	1.67892	2.61063
H	5.99848	3.30278	3.04127
H	5.57333	2.93433	1.35865
H	3.26682	5.16592	2.96430
H	4.67512	4.69114	3.92975
H	3.06684	4.11789	4.38739
C	5.93280	-2.41204	-0.08322
N	6.08860	-2.51375	-2.51617
H	5.58727	-2.21916	2.01909
C	5.59324	-2.09881	-3.82150
C	7.40224	-3.13457	-2.41853
H	7.36214	-4.06393	-1.83772
H	8.14115	-2.47006	-1.94841
H	7.75678	-3.38320	-3.41923
H	5.62296	-1.00737	-3.95058
H	4.56034	-2.43123	-3.97631
H	6.20919	-2.55206	-4.59889
H	6.85759	-2.95519	0.06402
H	3.78624	-1.09392	-2.37167
B	-0.84868	-1.15905	0.99836
O	-0.70185	-1.06036	2.37632
C	-0.74392	-2.40088	2.93974
O	-0.74822	-2.48347	0.59462
C	-0.28780	-3.27766	1.72368
C	-0.82268	2.35981	-1.57529
C	-1.02028	3.63595	-1.01885
H	-1.46214	3.73424	-0.03292
C	-0.62280	4.80170	-1.68238
H	-0.75945	5.78515	-1.24247
C	-0.03412	4.68304	-2.93449
F	0.35202	5.80990	-3.59085
C	0.16785	3.44834	-3.53799
C	-0.23394	2.29909	-2.85154
H	-0.06874	1.32862	-3.31156
H	0.62800	3.39734	-4.52027
C	1.23488	-3.38796	1.59905
C	-0.92699	-4.65981	1.64737
C	-2.19735	-2.65736	3.35494
C	0.17597	-2.45104	4.15352
O	-2.49676	1.62543	1.02226
C	-3.72418	2.17761	0.42450
C	-2.83057	1.06736	2.33062
C	-4.80962	2.04016	1.49345
C	-4.00252	1.91168	2.79445
H	-5.38683	1.12609	1.32410
H	-5.49477	2.89168	1.48794
H	-3.65845	2.89236	3.14219
H	-4.56168	1.43032	3.60133
H	-1.93055	1.12190	2.94069
H	-3.11187	0.02094	2.19782
B	-2.56966	-0.74371	-0.86154
O	-2.56569	-1.47651	-2.04061
O	-3.74147	-0.95280	-0.14544
C	-3.68084	-2.41262	-1.99983
C	-4.65713	-1.71274	-0.98374
C	-5.59412	-0.69687	-1.64628
C	-5.44983	-2.66321	-0.09432
C	-3.12814	-3.74525	-1.48703
C	-4.23361	-2.57373	-3.41144
H	-1.89582	1.11329	-1.52780
H	-3.94951	1.62006	-0.48337
H	-3.51365	3.21851	0.17316
H	-2.69073	-3.62476	-0.49497
H	-2.33302	-4.08021	-2.16021
H	-3.90216	-4.51822	-1.45739
H	-4.79026	-3.29265	0.50649
H	-6.09708	-3.30901	-0.69678
H	-6.08417	-2.08804	0.58779
H	-6.09877	-0.11764	-0.86711
H	-6.35765	-1.18788	-2.25700
H	-5.03529	-0.00153	-2.27957
H	-5.12813	-3.20547	-3.40551
H	-3.48393	-3.05437	-4.04774
H	-4.48863	-1.61088	-3.85893
H	-0.65002	-5.25978	2.52078
H	-0.57299	-5.18054	0.75217
H	-2.01608	-4.60373	1.59636
H	1.65436	-4.04047	2.37148

H 1.71634 -2.41033 1.66827
H 1.48138 -3.81019 0.62031
H 0.23877 -3.47020 4.54961
H -0.21756 -1.80380 4.94405
H 1.18268 -2.10870 3.90577
H -2.31460 -3.62930 3.84379
H -2.86268 -2.61694 2.48752
H -2.50930 -1.87973 4.05887
Sum of electronic and zero-point Energies= -2401.751578
Sum of electronic and thermal Energies= -2401.696615
Sum of electronic and thermal Enthalpies= -2401.695671
Sum of electronic and thermal Free Energies= -2401.843465
Imaginary Freq = -858.07

3P-conformer-B-ax-HBS-Bpin
Ir 0.79119 -0.65530 0.34071
N -0.45461 1.08168 0.67214
C -0.11183 1.95172 1.64608
N -0.13872 -0.89027 -1.41546
C -0.84456 3.06022 2.00397
C -1.61738 1.29983 -0.01939
C -2.04922 3.33400 1.30093
C -2.40197 2.42427 0.28664
H 0.81116 1.73261 2.16143
H -0.47962 3.69096 2.80328
N -2.81980 4.42405 1.58576
H -3.27572 2.59623 -0.32045
C -2.05116 0.39360 -1.08643
N -1.33904 -0.52152 -1.72912
H 0.24902 -1.54811 -2.08141
C -3.48439 0.40033 -1.53086
C -4.21363 -0.77293 -1.32620
N -4.01478 1.50940 -2.09356
C -5.56734 -0.85976 -1.72941
C -5.30385 1.42991 -2.45993
C -2.38022 5.38988 2.58472
C -4.01810 4.69371 0.80003
H -3.78105 4.87488 -0.25672
H -4.51523 5.57838 1.19754
H -4.72305 3.85526 0.85091
H -2.26927 4.92388 3.57143
H -3.12457 6.18171 2.66980
H -1.42095 5.85007 2.31239
C -6.11261 0.31128 -2.31340
N -6.30458 -2.00268 -1.55478
H -5.72658 2.32908 -2.90774
C -5.74482 -3.12260 -0.80635
C -7.73646 -1.98436 -1.82132
H -8.27213 -1.27658 -1.17222
H -8.14512 -2.98075 -1.65030
H -7.94144 -1.71438 -2.86362
H -5.56965 -2.88127 0.25035
H -4.79436 -3.44788 -1.24177
H -6.43686 -3.96444 -0.85607
H -7.14365 0.36021 -2.64014
H -3.72017 -1.59970 -0.83285
B 2.01427 0.93359 -0.54172
O 2.60901 1.88545 0.26586
C 3.04997 2.99815 -0.56324
O 1.91199 1.37307 -1.84465
C 2.18946 2.80251 -1.86593
C -0.86992 -1.72798 1.17402
C -1.65400 -1.23638 2.23525
H -1.35998 -0.31862 2.73870
C -2.83572 -1.86039 2.65376
H -3.44433 -1.45642 3.45771
C -3.23750 -3.01604 1.99920
F -4.41203 -3.61204 2.36238
C -2.49169 -3.57374 0.97031
C -1.31749 -2.92241 0.57334
H -0.75662 -3.34701 -0.25572
H -2.83516 -4.48360 0.48687
C 0.83102 3.50985 -1.80678
C 2.90602 3.13739 -3.16885
C 4.55374 2.81409 -0.78393
C 2.78159 4.29441 0.19494
O 1.68932 -0.54051 2.38983
C 1.57014 -1.72965 3.24610
C 2.94785 0.14107 2.69826
C 2.78455 -1.69875 4.17643
C 3.20744 -0.22310 4.14878
H 3.58818 -2.32410 3.77311
H 2.53686 -2.06201 5.17709
H 2.57473 0.37619 4.81346
H 4.25293 -0.06960 4.42959
H 2.79697 1.20026 2.50369
H 3.72016 -0.23710 2.02470
B 2.60680 -1.13071 -0.62772
O 2.60218 -1.71745 -1.89225
O 3.88341 -1.15502 -0.07405
C 3.97880 -1.95001 -2.29078
C 4.71396 -2.01747 -0.90197

C	4.67472	-3.41040	-0.26427
C	6.13474	-1.46725	-0.89772
C	4.40830	-0.75475	-3.14697
C	4.04014	-3.23533	-3.10859
H	1.48280	-2.10530	0.24258
H	1.53729	-2.61453	2.60893
H	0.62145	-1.63981	3.77791
H	5.32184	-4.11639	-0.79299
H	3.65609	-3.80964	-0.25359
H	5.02104	-3.33555	0.77110
H	6.77148	-2.03762	-1.58179
H	6.55986	-1.54680	0.10783
H	6.15702	-0.41604	-1.19209
H	3.49702	-3.10015	-4.04904
H	3.58864	-4.07446	-2.57545
H	5.07765	-3.48957	-3.34937
H	3.73033	-0.67017	-4.00093
H	5.42861	-0.87329	-3.52354
H	4.34054	0.17483	-2.57919
H	2.23660	2.95027	-4.01402
H	3.80079	2.52710	-3.30607
H	3.19454	4.19341	-3.19067
H	4.97917	3.63594	-1.36743
H	4.76555	1.87267	-1.29674
H	5.05461	2.78568	0.18849
H	0.21424	3.16145	-2.64003
H	0.94019	4.59568	-1.88617
H	0.30073	3.27777	-0.88045
H	3.01469	5.16365	-0.42857
H	3.41547	4.33749	1.08651
H	1.74069	4.36085	0.51716

Sum of electronic and zero-point Energies= -2401.768270
Sum of electronic and thermal Energies= -2401.712943
Sum of electronic and thermal Enthalpies= -2401.711999
Sum of electronic and thermal Free Energies= -2401.860244

Conformer B-back (ortho)
2aO-B-back

Ir	-0.67157	-0.35059	0.48392
N	0.50220	1.17170	-0.26906
C	-0.09537	2.24666	-0.85732
N	1.04154	-1.18087	1.31865
C	0.54888	3.39057	-1.25948
C	1.87661	1.22825	-0.12564
C	1.94108	3.52461	-1.02918
C	2.56629	2.40746	-0.45348
H	-1.15807	2.15978	-1.00625
H	-0.03843	4.16833	-1.72982
N	2.63201	4.65790	-1.35500
H	3.62848	2.42537	-0.27508
C	2.69467	0.10135	0.35677
N	2.31098	-0.96221	1.02856
B	-2.10873	0.86911	1.20922
O	-1.93455	2.24462	1.40382
C	-3.19026	2.80815	1.85324
C	-3.88083	1.56791	2.52107
C	-3.92759	3.30479	0.60386
C	-2.90044	3.97099	2.79603
O	-3.34327	0.46845	1.74448
C	-5.40216	1.54490	2.41959
C	-3.44476	1.35138	3.97560
C	4.16033	0.07470	0.04100
C	5.07599	-0.27529	1.03514
N	4.52897	0.32911	-1.23737
C	6.45223	-0.40389	0.73172
C	5.83429	0.21540	-1.51905
C	1.94910	5.76432	-2.01238
C	4.08310	4.68707	-1.21882
H	4.38945	4.56758	-0.17214
H	4.45705	5.64820	-1.57198
H	4.56199	3.89309	-1.80712
H	1.57991	5.48870	-3.01010
H	2.64332	6.59749	-2.12346
H	1.09831	6.11459	-1.41658
C	6.82203	-0.14173	-0.61164
N	7.37334	-0.75068	1.68414
H	6.11575	0.41676	-2.55250
C	6.93902	-1.07357	3.03645
C	8.77270	-0.91617	1.31767
H	8.91104	-1.71348	0.57451
H	9.34770	-1.17755	2.20639
H	9.19257	0.01002	0.90536
H	6.24595	-1.92548	3.05065
H	6.43933	-0.22087	3.51317
H	7.80921	-1.33331	3.63959
H	7.84906	-0.21248	-0.94664
H	4.70333	-0.45791	2.03349
B	-2.23226	-0.23606	-0.86444
O	-2.66774	0.82451	-1.67288
O	-2.99473	-1.37541	-1.16503
C	-3.59928	0.32420	-2.66524
C	-4.12565	-0.98599	-1.98190

O -1.67622 -2.03125 1.39014
C -1.57492 -3.35938 0.80874
C -1.86810 -2.11505 2.83721
C -2.32893 -4.23337 1.79810
C -5.29723 -0.73638 -1.02531
C -4.45610 -2.12519 -2.94023
C -2.79744 0.06071 -3.94492
C -4.66045 1.38866 -2.92480
H -0.51802 -3.63912 0.73330
H -2.01423 -3.29495 -0.18362
H -3.40826 -4.13419 1.63794
H 0.97560 -2.06898 1.81130
C 2.59517 -2.80501 -1.97044
C 1.77652 -3.90558 -1.70537
C 0.40973 -3.77301 -1.92257
C -0.16784 -2.60150 -2.38891
C 2.04612 -1.60767 -2.43965
C 0.66802 -1.50949 -2.64582
H 3.66418 -2.87652 -1.79281
H 2.17515 -4.84422 -1.33421
F -0.40268 -4.82789 -1.63356
H 2.69214 -0.75075 -2.59753
C -1.92126 -3.61350 3.14546
H -2.05651 -5.28820 1.70957
H -2.62241 -3.83719 3.95359
H -0.93115 -3.97831 3.44012
H -2.79973 -1.58948 3.05141
H -1.04091 -1.59651 3.32861
H -1.24403 -2.53128 -2.48859
H 0.23191 -0.57518 -2.98438
H -3.82857 4.36378 3.22501
H -2.41270 4.78113 2.24438
H -2.23712 3.67266 3.61060
H -3.85163 2.11905 4.64094
H -2.35417 1.35588 4.06169
H -3.80886 0.37724 4.31612
H -5.83722 2.40462 2.94040
H -5.79091 0.63355 2.88527
H -5.73757 1.56107 1.38096
H -5.04503 0.04818 -0.30816
H -5.49018 -1.65267 -0.45882
H -6.21210 -0.46247 -1.55993
H -5.26533 -1.83859 -3.62028
H -4.78557 -3.00083 -2.37174
H -3.58899 -2.41816 -3.53596
H -4.88108 3.78105 0.85237
H -4.10382 2.47993 -0.09010
H -3.29904 4.04080 0.09282
H -5.16082 1.69533 -2.00462
H -5.41620 1.01691 -3.62486
H -4.19495 2.27507 -3.36764
H -2.28949 0.98359 -4.24130
H -3.44290 -0.25704 -4.76957
H -2.03630 -0.70667 -3.78344

Sum of electronic and zero-point Energies= -2401.799215

Sum of electronic and thermal Energies= -2401.743806

Sum of electronic and thermal Enthalpies= -2401.742862

Sum of electronic and thermal **Free Energies= -2401.890971**

TS2-3O-B-back-HBS

Ir -0.66547 -0.65878 0.00561
N 0.39451 1.03349 -0.56953
C -0.23919 2.07057 -1.16669
N 0.83375 -0.91696 1.49250
C 0.35749 3.26042 -1.51439
C 1.73091 1.17887 -0.28064
C 1.72504 3.46491 -1.20664
C 2.36859 2.39403 -0.55975
H -1.28953 1.92583 -1.36746
H -0.24709 4.01312 -2.00290
N 2.37598 4.62550 -1.51229
H 3.40412 2.48428 -0.27413
C 2.54253 0.13338 0.37747
N 2.11019 -0.74950 1.25898
B -1.67671 0.61156 1.35911
O -1.12741 1.82981 1.73855
C -2.16326 2.62291 2.37502
C -3.12722 1.51513 2.91898
C -2.79674 3.48097 1.27303
C -1.52491 3.50529 3.44081
O -2.92624 0.44709 1.95104
C -4.60379 1.89285 2.93665
C -2.70255 0.96067 4.28295
C 4.00298 0.06030 0.10542
C 4.89247 -0.34644 1.10859
N 4.41053 0.33865 -1.15697
C 6.26737 -0.50148 0.83016
C 5.71664 0.19222 -1.41398
C 1.63022 5.75639 -2.04972
C 3.77760 4.79550 -1.14969
H 3.92174 4.83106 -0.06086
H 4.14689 5.72864 -1.57583

H	4.38732	3.97758	-1.54935
H	1.17709	5.51374	-3.01877
H	2.30930	6.59613	-2.19735
H	0.83156	6.07858	-1.36816
C	6.67531	-0.22054	-0.49917
N	7.16319	-0.88683	1.79849
H	6.02511	0.41146	-2.43651
C	6.67799	-1.30515	3.10648
C	8.54604	-1.16284	1.43652
H	8.63356	-1.99534	0.72328
H	9.10633	-1.42345	2.33523
H	9.02291	-0.28199	0.99083
H	6.01138	-2.17706	3.04351
H	6.13111	-0.49584	3.60447
H	7.52850	-1.56868	3.73615
H	7.70593	-0.31770	-0.81597
H	4.49318	-0.55092	2.09164
B	-2.53725	-0.28190	-0.89920
O	-3.04585	0.92593	-1.36385
O	-3.49085	-1.28416	-1.03587
C	-4.32081	0.68304	-2.02279
C	-4.76666	-0.68026	-1.38193
O	-1.53695	-2.51539	0.73416
C	-1.86445	-3.62429	-0.17880
C	-2.46128	-2.52729	1.86483
C	-3.09067	-4.29578	0.42799
C	-5.54636	-0.51157	-0.07435
C	-5.50908	-1.62005	-2.32565
C	-4.02685	0.58225	-3.52294
C	-5.24347	1.86251	-1.73934
H	-0.99150	-4.27544	-0.19670
H	-2.04749	-3.20851	-1.16746
H	-4.00144	-3.84377	0.02415
H	0.71258	-1.70811	2.11925
C	2.90925	-2.71565	-3.00323
C	2.49638	-3.36942	-1.84147
C	1.40659	-2.86566	-1.13934
C	0.69541	-1.72446	-1.50580
C	2.22648	-1.57386	-3.42612
C	1.14132	-1.09879	-2.68514
H	3.76098	-3.09218	-3.56232
H	3.01261	-4.24689	-1.46364
F	1.08409	-3.52732	0.01507
H	2.54174	-1.04808	-4.32321
C	-2.95527	-3.96222	1.92146
H	-3.10752	-5.36955	0.22347
H	-3.89777	-4.04611	2.46946
H	-2.21276	-4.61137	2.39895
H	-3.26584	-1.82092	1.66230
H	-1.89822	-2.19517	2.73890
H	-0.83397	-1.26952	-1.49392
H	0.63569	-0.19306	-3.01239
H	-2.29137	4.05159	4.00086
H	-0.86403	4.23763	2.96643
H	-0.92874	2.91914	4.14321
H	-2.87410	1.68401	5.08583
H	-1.64382	0.68539	4.27972
H	-3.28809	0.06187	4.49933
H	-4.77482	2.74133	3.60757
H	-5.19917	1.04876	3.29895
H	-4.96499	2.15905	1.94152
H	-4.99150	0.11414	0.62675
H	-5.67912	-1.49551	0.38637
H	-6.53678	-0.07935	-0.24646
H	-6.43793	-1.15949	-2.67809
H	-5.76890	-2.54303	-1.79784
H	-4.90040	-1.88712	-3.19188
H	-3.56266	4.15383	1.67097
H	-3.24005	2.84950	0.49824
H	-2.01426	4.08631	0.80575
H	-5.34700	2.04328	-0.66767
H	-6.23778	1.68486	-2.16203
H	-4.83634	2.76884	-2.19850
H	-3.53785	1.50426	-3.85162
H	-4.94254	0.45115	-4.10710
H	-3.35279	-0.25286	-3.73519

Sum of electronic and zero-point Energies= -2401.743567

Sum of electronic and thermal Energies= -2401.688800

Sum of electronic and thermal Enthalpies= -2401.687856

Sum of electronic and thermal Free Energies= -2401.833002

Imaginary Freq = -942.83

3O-re-B-back-HBS-Bpin

C	-1.03920	-0.83517	-0.11304
N	0.33430	-0.06102	-1.44583
C	-0.13303	0.46094	-2.60557
N	0.47417	-1.08135	1.29406
C	0.63442	1.10270	-3.54703
C	1.68140	0.03197	-1.18857
C	2.02059	1.27008	-3.29921
C	2.49803	0.72991	-2.09308
H	-1.19602	0.36552	-2.76457

H	0.15130	1.47255	-4.44125
N	2.84316	1.91463	-4.17902
H	3.54120	0.82503	-1.84754
C	2.31853	-0.53944	0.00957
N	1.75648	-1.00930	1.11067
B	-0.89553	1.08136	0.90883
O	0.11100	1.94213	0.52205
C	0.17463	3.04175	1.46638
C	-0.54477	2.43935	2.72832
C	-0.58407	4.21135	0.83258
C	1.64056	3.40940	1.67340
O	-1.43268	1.44716	2.13009
C	-1.38799	3.42627	3.52638
C	0.40423	1.67368	3.65612
C	3.81279	-0.57654	0.09544
C	4.43942	-0.06883	1.23666
N	4.49847	-1.13449	-0.92948
C	5.84437	-0.13915	1.37876
C	5.83204	-1.18222	-0.79962
C	2.28141	2.56629	-5.35549
C	4.24815	2.11796	-3.84807
H	4.37438	2.76762	-2.97069
H	4.75251	2.58338	-4.69509
H	4.74610	1.16392	-3.64104
H	1.76844	1.84553	-6.00326
H	3.08709	3.01950	-5.93307
H	1.56680	3.35560	-5.08523
C	6.55036	-0.71637	0.29366
N	6.48370	0.33608	2.49584
H	6.37403	-1.63122	-1.63197
C	5.72262	1.02730	3.52750
C	7.93875	0.38398	2.53276
H	8.37233	-0.61606	2.41403
H	8.26060	0.77294	3.49929
H	8.35309	1.03135	1.74658
H	4.93589	0.38339	3.93739
H	5.24917	1.94555	3.15053
H	6.39108	1.29822	4.34530
H	7.62967	-0.80140	0.29363
H	3.82047	0.37354	2.00486
B	-2.56791	0.59842	-0.39347
O	-2.57721	1.71276	-1.22507
O	-3.82620	0.38612	0.16843
C	-3.96417	2.10003	-1.43361
C	-4.66207	1.53012	-0.14634
O	-2.39352	-1.78643	1.25973
C	-3.47507	-2.63199	0.75831
C	-2.70973	-1.28217	2.58864
C	-4.53832	-2.60395	1.85333
C	-4.59331	2.48125	1.05248
C	-6.09197	1.04349	-0.35515
C	-4.42457	1.41095	-2.72325
C	-4.02978	3.61422	-1.58618
H	-3.04832	-3.62542	0.59970
H	-3.81937	-2.21813	-0.18934
H	-5.25355	-1.79950	1.65656
H	0.26470	-1.58163	2.15056
C	0.24651	-5.38461	-1.81003
C	0.05929	-5.17184	-0.44326
C	-0.30336	-3.90017	-0.00816
C	-0.50080	-2.79181	-0.83390
C	0.06557	-4.31831	-2.69364
C	-0.29838	-3.05843	-2.20377
H	0.53143	-6.36811	-2.17338
H	0.19148	-5.96746	0.28442
F	-0.47275	-3.77238	1.35201
H	0.20877	-4.46415	-3.76162
C	-3.72322	-2.28449	3.11662
H	-5.08232	-3.54968	1.91778
H	-4.32932	-1.86421	3.92365
H	-3.21762	-3.18238	3.48841
H	-3.12012	-0.27721	2.48618
H	-1.77544	-1.24094	3.15013
H	-2.18986	-0.86388	-1.27130
H	-0.42277	-2.24677	-2.91658
H	1.74388	4.18519	2.43926
H	2.05569	3.79617	0.73752
H	2.23399	2.54142	1.96724
H	1.08820	2.34954	4.17791
H	0.98817	0.93815	3.09713
H	-0.18680	1.13906	4.40625
H	-0.75962	4.22219	3.93935
H	-1.87153	2.90847	4.36070
H	-2.16872	3.88113	2.91396
H	-3.56579	2.79911	1.23817
H	-4.94158	1.95111	1.94402
H	-5.22541	3.36225	0.90711
H	-6.73433	1.86408	-0.69147
H	-6.49494	0.66472	0.58944
H	-6.13961	0.23756	-1.09029
H	-0.55028	5.10579	1.46191
H	-1.62739	3.94540	0.64751
H	-0.12501	4.44822	-0.13174
H	-3.56395	4.12311	-0.74038
H	-5.06947	3.94802	-1.66739
H	-3.50251	3.91798	-2.49586

H	-3.76543	1.71414	-3.54225
H	-5.44926	1.68849	-2.98739
H	-4.37079	0.32224	-2.62810

Sum of electronic and zero-point Energies= -2401.769846

Sum of electronic and thermal Energies= -2401.714735

Sum of electronic and thermal Enthalpies= -2401.713790

Sum of electronic and thermal Free Energies= -2401.861280

Conformer B-back (meta)

2a-meta-B-back

Ir	0.75540	-0.40079	-0.64543
N	-0.21534	1.27653	0.06932
C	0.47900	2.21374	0.76865
N	-0.93950	-0.77933	-1.81640
C	0.04489	3.49403	1.01934
C	-1.50542	1.61322	-0.30712
C	-1.18791	3.92696	0.47386
C	-1.94393	2.93385	-0.17735
H	1.44172	1.89821	1.13538
H	0.68115	4.14565	1.60379
N	-1.63114	5.21336	0.59277
H	-2.93128	3.16190	-0.54131
C	-2.47534	0.61117	-0.80830
N	-2.18430	-0.46067	-1.51505
B	2.46076	0.61849	-1.02332
O	2.44757	1.99469	-1.28297
C	3.81704	2.46550	-1.31543
C	4.58757	1.17436	-1.75571
C	4.16743	2.91371	0.10959
C	3.91356	3.63926	-2.28275
O	3.76497	0.12826	-1.17944
C	6.00287	1.04639	-1.20311
C	4.58999	0.96422	-3.27429
C	-3.92709	0.71041	-0.45432
C	-4.84726	-0.14973	-1.07336
N	-4.30111	1.55812	0.53146
C	-6.19433	-0.18564	-0.66410
C	-5.58980	1.54527	0.89573
C	-0.84043	6.19153	1.32730
C	-2.96326	5.57220	0.12057
H	-3.05832	5.41977	-0.96159
H	-3.14553	6.62624	0.33048
H	-3.74243	4.98096	0.61900
H	-0.76494	5.94443	2.39541
H	-1.30884	7.17173	1.23598
H	0.17478	6.26522	0.92005
C	-6.56686	0.71602	0.36538
N	-7.09485	-1.06099	-1.23258
H	-5.86244	2.23999	1.69060
C	-6.58232	-2.17677	-2.02242
C	-8.41846	-1.20265	-0.64112
H	-8.38435	-1.60059	0.38491
H	-9.01260	-1.88232	-1.25384
H	-8.94033	-0.24072	-0.61724
H	-5.86792	-2.78687	-1.45210
H	-6.08181	-1.82209	-2.92998
H	-7.41612	-2.80904	-2.33028
H	-7.57652	0.76607	0.75236
H	-4.48148	-0.81834	-1.83662
B	2.03296	-0.70670	0.92858
O	2.47581	0.17136	1.92625
O	2.53714	-1.99123	1.19042
C	3.13722	-0.58233	2.97328
C	3.55293	-1.89653	2.22055
O	1.42241	-2.26120	-1.55913
C	0.93686	-3.51182	-0.96223
C	2.73664	-2.48297	-2.14964
C	1.98158	-4.57065	-1.32285
C	4.90227	-1.77852	1.50261
C	3.51295	-3.16343	3.06847
C	2.10369	-0.82069	4.07991
C	4.29810	0.24938	3.50904
H	-0.04366	-3.70707	-1.40462
H	0.84172	-3.36425	0.11121
H	2.68124	-4.70013	-0.49122
H	-0.95406	-1.63795	-2.36365
C	-3.82464	-1.47478	1.92620
C	-3.32903	-2.53902	1.18509
C	-1.98139	-2.87690	1.16313
C	-1.09126	-2.09801	1.90765
C	-2.92018	-0.70076	2.65656
C	-1.55664	-1.00489	2.64533
H	-4.88217	-1.23938	1.89267
F	-4.19727	-3.27797	0.44193
H	-1.64491	-3.71627	0.56468
H	-3.28470	0.15591	3.21436
H	-0.85565	-0.38961	3.19982
C	2.71036	-3.95362	-2.52739
H	1.52296	-5.53783	-1.54383
H	3.71579	-4.35816	-2.67178
H	2.13717	-4.10320	-3.44916
H	3.49738	-2.25165	-1.40279

H 2.82654 -1.78852 -2.98514
H -0.03252 -2.33379 1.89704
H 4.95381 3.96171 -2.39926
H 3.33728 4.48552 -1.89530
H 3.51424 3.38282 -3.26623
H 5.23946 1.68345 -3.78269
H 3.57952 1.05609 -3.68314
H 4.95718 -0.04313 -3.49329
H 6.63256 1.86744 -1.56208
H 6.44901 0.10481 -1.53906
H 6.01188 1.05319 -0.11157
H 5.17688 3.33229 0.16926
H 4.08372 2.07770 0.80966
H 3.45675 3.68581 0.41974
H 4.91603 -0.90002 0.85419
H 5.04368 -2.66148 0.87116
H 5.73709 -1.72620 2.20848
H 4.97133 0.56057 2.70787
H 4.87327 -0.31642 4.24956
H 3.91289 1.15106 3.99601
H 1.71076 0.14512 4.41194
H 2.54421 -1.32794 4.94381
H 1.26582 -1.41978 3.71425
H 4.21445 -3.09301 3.90657
H 3.80193 -4.02509 2.45790
H 2.51341 -3.35251 3.46564
Sum of electronic and zero-point Energies= -2401.795603
Sum of electronic and thermal Energies= -2401.740316
Sum of electronic and thermal Enthalpies= -2401.739372
Sum of electronic and thermal Free Energies= -2401.886326

TS2-3-2-re-B-back-HBS-Bpin

Ir -0.70000 -0.66300 -0.00700
N 0.34900 0.99100 -0.69200
C -0.28600 1.97000 -1.38000
N 0.81100 -0.86500 1.47800
C 0.30100 3.14000 -1.80300
C 1.67700 1.17600 -0.39100
C 1.65700 3.39100 -1.47700
C 2.30100 2.38000 -0.74100
H -1.33000 1.79500 -1.58800
H -0.30300 3.84400 -2.36000
N 2.29600 4.53800 -1.85000
H 3.32900 2.50800 -0.44100
C 2.50000 0.19100 0.34200
N 2.08400 -0.66100 1.26000
B -1.66700 0.69100 1.31200
O -1.11000 1.93400 1.58200
C -2.11000 2.75700 2.23700
C -3.02900 1.67700 2.90300
C -2.81600 3.55000 1.13100
C -1.41300 3.70000 3.21000
O -2.87600 0.55400 1.98900
C -4.50500 2.04700 2.98800
C -2.51800 1.20600 4.26800
C 3.96800 0.15200 0.10100
C 4.85400 -0.10100 1.15500
N 4.38600 0.31100 -1.17900
C 6.24000 -0.22500 0.91500
C 5.70200 0.19800 -1.39900
C 1.54600 5.61100 -2.49000
C 3.68000 4.76700 -1.45200
H 3.78400 4.87800 -0.36400
H 4.04400 5.67800 -1.92700
H 4.32200 3.93900 -1.77500
H 1.11400 5.28400 -3.44400
H 2.21600 6.44600 -2.69500
H 0.73000 5.97600 -1.85200
C 6.66000 -0.06900 -0.43000
N 7.13200 -0.46500 1.93200
H 6.02100 0.31900 -2.43500
C 6.63800 -0.76700 3.26900
C 8.53200 -0.71800 1.62200
H 8.66700 -1.61400 1.00000
H 9.08400 -0.86200 2.55200
H 8.98100 0.13200 1.09600
H 6.01000 -1.66900 3.28600
H 6.04800 0.06500 3.67200
H 7.48600 -0.92700 3.93600
H 7.70000 -0.15300 -0.72000
H 4.44500 -0.21400 2.14900
B -2.60500 -0.30100 -0.84400
O -3.12100 0.88400 -1.35900
O -3.57600 -1.29600 -0.88500
C -4.41800 0.61600 -1.96100
C -4.85700 -0.69800 -1.22100
O -1.52200 -2.50700 0.82600
C -1.98400 -3.62200 -0.02100
C -2.32400 -2.46500 2.05100
C -3.20100 -4.19100 0.69500
C -5.58400 -0.43600 0.10100
C -5.64500 -1.68400 -2.07600

C -4.17400 0.41600 -3.46000
C -5.32000 1.82200 -1.72500
H -1.16500 -4.34200 -0.07500
H -2.20400 -3.22800 -1.01000
H -4.10200 -3.66600 0.36600
H 0.70000 -1.61100 2.16100
C 2.84700 -3.15600 -2.63900
C 2.26200 -3.66900 -1.48800
C 1.18600 -3.06500 -0.85200
C 0.65900 -1.86800 -1.36400
C 2.31600 -1.97500 -3.16200
C 1.23400 -1.34800 -2.53700
H 3.68900 -3.66500 -3.09500
F 2.77300 -4.81400 -0.95400
H 0.81700 -3.49900 0.07000
H 2.75400 -1.54000 -4.05600
H 0.84900 -0.42000 -2.95100
C -2.90700 -3.86300 2.16700
H -3.32000 -5.26100 0.50400
H -3.79900 -3.87700 2.79900
H -2.17200 -4.56100 2.58200
H -3.09500 -1.70500 1.92900
H -1.65200 -2.17500 2.86200
H -0.86100 -1.35000 -1.47600
H -2.14600 4.27600 3.78400
H -0.78700 4.40600 2.65400
H -0.77000 3.15800 3.90600
H -2.64900 1.97400 5.03700
H -1.45800 0.93900 4.21700
H -3.08000 0.31700 4.57100
H -4.64300 2.93100 3.61900
H -5.07100 1.22200 3.43200
H -4.92800 2.25600 2.00300
H -3.56500 4.23700 1.53700
H -3.29500 2.87500 0.41700
H -2.06900 4.13600 0.58800
H -4.99500 0.22400 0.74000
H -5.71100 -1.38700 0.62800
H -6.57500 -0.00200 -0.06100
H -5.38900 2.07200 -0.66500
H -6.32900 1.62800 -2.10500
H -4.92000 2.69200 -2.25400
H -3.68500 1.30900 -3.86300
H -5.10900 0.26100 -4.00600
H -3.51700 -0.44000 -3.64000
H -6.58100 -1.23200 -2.42200
H -5.89600 -2.56800 -1.48200
H -5.07300 -2.01200 -2.94600

Sum of electronic and zero-point Energies= -2401.738882
Sum of electronic and thermal Energies= -2401.683934
Sum of electronic and thermal Enthalpies= -2401.682989
Sum of electronic and thermal Free Energies= -2401.829608
Imaginary Freq = -890.76

3-conformer-2-B-back-HBS-Bpin

C -0.66340 -0.65564 -0.27308
N 0.29254 1.09418 -0.79897
C -0.25750 1.88003 -1.75328
N 0.48693 -0.70411 1.47481
C 0.29962 3.04374 -2.22904
C 1.49010 1.48254 -0.24565
C 1.53241 3.48520 -1.68623
C 2.08773 2.67448 -0.67878
H -1.21146 1.55130 -2.13680
H -0.22961 3.59117 -2.99733
N 2.14598 4.62933 -2.10772
H 2.99640 2.96880 -0.17806
C 2.19169 0.69432 0.78769
N 1.70580 -0.24858 1.57368
B -1.78800 0.54726 1.15765
O -1.41945 1.86520 1.33399
C -2.14043 2.40033 2.47511
C -2.54792 1.09693 3.25520
C -3.33823 3.17387 1.91649
C -1.20724 3.33744 3.23443
O -2.60069 0.10427 2.18610
C -3.91005 1.14921 3.93614
C -1.47497 0.62094 4.23903
C 3.67658 0.83735 0.96662
C 4.43736 -0.31920 0.78050
N 4.22261 2.02645 1.30574
C 5.83707 -0.30435 0.97853
C 5.55539 2.04558 1.46620
C 1.49044 5.49049 -3.08401
C 3.37418 5.07665 -1.46128
H 3.21614 5.31367 -0.40058
H 3.73801 5.97305 -1.96372
H 4.15597 4.31076 -1.52509
H 1.29783 4.95490 -4.02131
H 2.13985 6.33625 -3.31003
H 0.53515 5.88204 -2.70904

C	6.39684	0.95013	1.32786
N	6.59820	-1.43642	0.82986
H	5.98729	3.01048	1.73085
C	5.99067	-2.64292	0.27829
C	8.05096	-1.33424	0.85133
H	8.43902	-0.71066	0.03247
H	8.48100	-2.33193	0.75526
H	8.40181	-0.91065	1.79891
H	5.64754	-2.49946	-0.75552
H	5.13138	-2.96387	0.87370
H	6.72457	-3.44986	0.29219
H	7.46108	1.07973	1.47941
H	3.92520	-1.21864	0.46920
B	-2.67551	-0.13807	-0.68412
O	-3.20824	1.04623	-1.18476
O	-3.64511	-1.14036	-0.65811
C	-4.51138	0.74464	-1.75926
C	-4.93163	-0.54045	-0.96017
O	-1.39603	-2.61294	0.28067
C	-1.77940	-3.55793	-0.77689
C	-2.19309	-2.85884	1.47932
C	-2.83199	-4.46674	-0.14352
C	-5.60680	-0.22890	0.37912
C	-5.76215	-1.54460	-1.75188
C	-4.28441	0.47814	-3.25144
C	-5.42047	1.95137	-1.56497
H	-0.86554	-4.08346	-1.06269
H	-2.16008	-2.98600	-1.62213
H	-3.83338	-4.09220	-0.37555
H	0.34014	-1.44925	2.14832
C	3.24818	-2.98183	-2.35332
C	2.74373	-3.34670	-1.11145
C	1.63888	-2.73539	-0.53251
C	0.98201	-1.67869	-1.19085
C	2.59727	-1.94435	-3.02661
C	1.49120	-1.30825	-2.45249
H	4.11239	-3.49281	-2.76459
F	3.38228	-4.33950	-0.41998
H	1.31253	-3.07257	0.44691
H	2.96254	-1.62894	-4.00138
H	1.02274	-0.49075	-2.99550
C	-2.55753	-4.32894	1.36278
H	-2.75103	-5.49553	-0.50339
H	-3.42248	-4.58468	1.98062
H	-1.71339	-4.95908	1.66398
H	-3.06347	-2.20332	1.45696
H	-1.56797	-2.60979	2.33724
H	-1.36199	-0.75196	-1.74164
H	-1.39122	1.29163	5.09913
H	-0.50155	0.54970	3.74729
H	-1.74582	-0.37421	4.60562
H	-3.92575	1.92951	4.70407
H	-4.11683	0.19069	4.42259
H	-4.71285	1.34630	3.22319
H	-1.68051	3.69774	4.15388
H	-0.97160	4.20508	2.61030
H	-0.26761	2.84345	3.49027
H	-3.92053	3.64929	2.71153
H	-3.99231	2.51601	1.33940
H	-2.97176	3.95351	1.24217
H	-5.47321	2.25015	-0.51646
H	-6.43303	1.72997	-1.91803
H	-5.03754	2.80023	-2.13991
H	-3.62306	-0.38046	-3.40118
H	-3.80979	1.35563	-3.70082
H	-5.22558	0.29112	-3.77670
H	-6.00454	-2.40421	-1.11913
H	-5.22309	-1.91064	-2.62799
H	-6.70322	-1.09251	-2.08216
H	-4.99538	0.45271	0.97336
H	-5.71173	-1.15884	0.94609
H	-6.60204	0.20355	0.24051

Sum of electronic and zero-point Energies= -2401.764056

Sum of electronic and thermal Energies= -2401.709744

Sum of electronic and thermal Enthalpies= -2401.708800

Sum of electronic and thermal Free Energies= -2401.850947

Conformer B-back (para)

2aP-conformer-B-back

Ir	-0.72456	-0.55862	0.30148
N	0.45676	0.98254	-0.39244
C	-0.14139	2.07876	-0.93821
N	0.99414	-1.46778	1.06802
C	0.49549	3.24919	-1.26889
C	1.82353	1.05164	-0.19749
C	1.87963	3.38811	-0.99694
C	2.50079	2.25969	-0.44105
H	-1.20243	1.99110	-1.10689
H	-0.09237	4.04443	-1.70861
N	2.56531	4.53955	-1.26764
H	3.55256	2.29193	-0.21216
C	2.64629	-0.08438	0.25279

N 2.26449 -1.20123 0.83828
B -1.93444 0.68924 1.30516
O -1.57616 2.00123 1.63146
C -2.72888 2.65986 2.20972
C -3.54171 1.44669 2.78705
C -3.45172 3.37794 1.06382
C -2.25027 3.66765 3.24918
O -3.17448 0.37524 1.88223
C -5.05711 1.61427 2.75601
C -3.08379 1.03167 4.19057
C 4.12438 -0.05368 0.00266
C 5.00513 -0.43852 1.01554
N 4.54476 0.30241 -1.23437
C 6.39743 -0.50181 0.77257
C 5.86479 0.25838 -1.45621
C 1.84893 5.72170 -1.72812
C 3.98386 4.63528 -0.94943
H 4.16906 4.58802 0.13290
H 4.37160 5.58368 -1.32228
H 4.54918 3.82708 -1.42789
H 1.35826 5.54429 -2.69326
H 2.55642 6.54078 -1.85786
H 1.08375 6.04207 -1.00839
C 6.82173 -0.12257 -0.52549
N 7.28470 -0.89602 1.74103
H 6.18815 0.54706 -2.45627
C 6.81348 -1.16762 3.09224
C 8.71637 -0.82571 1.48484
H 8.99765 -1.44456 0.62434
H 9.25582 -1.20147 2.35475
H 9.05300 0.20262 1.29016
H 6.06769 -1.97130 3.09898
H 6.36320 -0.28076 3.56014
H 7.65497 -1.48738 3.70750
H 7.86673 -0.11933 -0.80810
H 4.59364 -0.69434 1.98199
B -2.40531 -0.23792 -0.87122
O -2.93554 0.94075 -1.42195
O -3.22098 -1.31370 -1.25315
C -4.02413 0.61736 -2.32199
C -4.45564 -0.80193 -1.80992
O -1.76592 -2.24293 1.17204
C -1.88777 -3.52636 0.50645
C -1.86516 -2.40432 2.62232
C -2.68829 -4.35993 1.49459
C -5.46614 -0.74352 -0.65773
C -4.93991 -1.75716 -2.89536
C -3.44815 0.60779 -3.74239
C -5.09622 1.69677 -2.20489
H -0.88584 -3.93964 0.33781
H -2.37926 -3.33128 -0.44466
H -3.75113 -4.10270 1.42550
H 0.93257 -2.38652 1.50207
C 2.20521 -2.51048 -2.14097
C 1.25149 -3.50069 -1.94196
C -0.06041 -3.24642 -2.34907
C -0.39396 -2.03092 -2.94724
C 1.90551 -1.28588 -2.72677
C 0.58872 -1.05180 -3.12832
F 3.47707 -2.74671 -1.73473
H 1.53814 -4.43727 -1.47482
H -0.82074 -4.00653 -2.20297
H 2.68420 -0.53639 -2.81303
H 0.32773 -0.09328 -3.56693
C -2.10441 -3.90006 2.84112
H -2.57459 -5.43321 1.32079
H -2.77217 -4.08460 3.68653
H -1.15723 -4.41581 3.03336
H -2.69821 -1.77715 2.94149
H -0.94201 -2.03688 3.07732
H -1.42110 -1.83835 -3.23134
H -2.99402 1.58232 -3.94683
H -4.22199 0.42456 -4.49411
H -2.67104 -0.15323 -3.84856
H -5.83576 -1.36469 -3.38827
H -5.19545 -2.72370 -2.44909
H -4.17247 -1.92868 -3.65333
H -5.09823 -0.09402 0.14056
H -5.58201 -1.74945 -0.24159
H -6.44882 -0.39427 -0.98995
H -5.43191 1.82363 -1.17419
H -5.96373 1.44823 -2.82550
H -4.69599 2.65547 -2.55008
H -3.10001 4.12224 3.76981
H -1.68816 4.46721 2.75605
H -1.59464 3.20306 3.98862
H -4.32392 3.93729 1.41651
H -3.76208 2.66300 0.29895
H -2.75643 4.08360 0.59821
H -5.36570 2.46483 3.37319
H -5.53775 0.71439 3.15325
H -5.42305 1.77064 1.73941
H -3.36536 1.77195 4.94570
H -1.99907 0.89361 4.22305
H -3.55618 0.08019 4.45348

Sum of electronic and zero-point Energies= -2401.796182

Sum of electronic and thermal Energies= -2401.741371

Sum of electronic and thermal Enthalpies= -2401.740427

Sum of electronic and thermal Free Energies= -2401.886782

TS2-3P-B-back-HBS

Ir	-0.71872	-0.67925	0.05493
N	0.33775	0.92468	-0.72867
C	-0.28543	1.84190	-1.50593
N	0.75269	-0.73782	1.59929
C	0.30288	2.98391	-1.99806
C	1.65612	1.14519	-0.40794
C	1.64550	3.27491	-1.65295
C	2.27916	2.32677	-0.82931
H	-1.32249	1.64194	-1.72759
H	-0.29200	3.63866	-2.62086
N	2.28294	4.40219	-2.08720
H	3.29743	2.48616	-0.51361
C	2.46660	0.22426	0.41731
N	2.03049	-0.54872	1.39494
B	-1.72427	0.76042	1.24999
O	-1.19499	2.03337	1.41866
C	-2.20137	2.87736	2.03533
C	-3.08805	1.82631	2.78580
C	-2.94062	3.58264	0.89231
C	-1.50831	3.89574	2.93300
O	-2.92487	0.64748	1.94720
C	-4.57024	2.17104	2.87087
C	-2.54682	1.45860	4.17163
C	3.93663	0.15871	0.19843
C	4.80708	-0.05926	1.27416
N	4.37354	0.26095	-1.08070
C	6.19249	-0.21854	1.05621
C	5.69226	0.13416	-1.27784
C	1.53748	5.42135	-2.81520
C	3.64301	4.68764	-1.64653
H	3.69744	4.86660	-0.56360
H	4.00578	5.57836	-2.16021
H	4.31664	3.85888	-1.89135
H	1.12054	5.02079	-3.74671
H	2.20928	6.23949	-3.07458
H	0.71199	5.83091	-2.21701
C	6.63469	-0.10093	-0.28649
N	7.06599	-0.46369	2.08881
H	6.02690	0.22147	-2.31180
C	6.58557	-0.44219	3.46320
C	8.50113	-0.43034	1.84464
H	8.79415	-1.17756	1.09819
H	9.02751	-0.66406	2.77081
H	8.84291	0.55447	1.49388
H	5.78336	-1.17383	3.61133
H	6.20387	0.54625	3.75849
H	7.40492	-0.70689	4.13265
H	7.67943	-0.18831	-0.55611
H	4.38604	-0.11428	2.26791
B	-2.60971	-0.38327	-0.83622
O	-3.11707	0.76038	-1.44664
O	-3.58112	-1.37857	-0.81725
C	-4.40210	0.44458	-2.05214
C	-4.85501	-0.80731	-1.22014
O	-1.55501	-2.46831	0.99355
C	-2.00147	-3.63495	0.20943
C	-2.37880	-2.35043	2.19790
C	-3.22529	-4.16583	0.94345
C	-5.60386	-0.44379	0.06546
C	-5.63137	-1.85582	-2.00932
C	-4.12739	0.12721	-3.52575
C	-5.30902	1.66344	-1.93149
H	-1.17881	-4.35277	0.20950
H	-2.21052	-3.30311	-0.80450
H	-4.12475	-3.66980	0.56750
H	0.62813	-1.42263	2.34126
C	2.88674	-3.35816	-2.21052
C	2.29996	-3.82774	-1.04187
C	1.19916	-3.13960	-0.52499
C	0.68720	-1.98775	-1.14724
C	2.41096	-2.23574	-2.87272
C	1.31014	-1.56399	-2.33325
F	3.95943	-4.02105	-2.72052
H	2.71133	-4.70282	-0.54763
H	0.77252	-3.47959	0.41300
H	2.90174	-1.89410	-3.77862
H	0.94656	-0.67279	-2.83833
C	-2.95532	-3.74176	2.39482
H	-3.33539	-5.24632	0.81940
H	-3.85663	-3.72243	3.01347
H	-2.22222	-4.40730	2.86438
H	-3.15158	-1.60561	2.01209
H	-1.72344	-2.00223	2.99884
H	-0.83391	-1.47927	-1.35927
H	-3.63046	0.98590	-3.98726
H	-5.05164	-0.07194	-4.07625

H	-3.46701	-0.73947	-3.62375
H	-6.56090	-1.43219	-2.40390
H	-5.89325	-2.69227	-1.35367
H	-5.04578	-2.25064	-2.84201
H	-5.02532	0.26528	0.65987
H	-5.73809	-1.35046	0.66381
H	-6.59245	-0.02493	-0.14577
H	-5.40165	1.99562	-0.89582
H	-6.30882	1.43897	-2.31746
H	-4.89671	2.49096	-2.51733
H	-2.24427	4.49315	3.48168
H	-0.90601	4.57587	2.32244
H	-0.84389	3.41173	3.65175
H	-3.69878	4.27839	1.26490
H	-3.41404	2.85261	0.23073
H	-2.21433	4.14818	0.30083
H	-4.71752	3.09133	3.44591
H	-5.11089	1.36471	3.37668
H	-5.01254	2.30589	1.88219
H	-2.68270	2.27320	4.88942
H	-1.48279	1.20942	4.12153
H	-3.08542	0.58080	4.54175

Sum of electronic and zero-point Energies= -2401.737603
Sum of electronic and thermal Energies= -2401.682789
Sum of electronic and thermal Enthalpies= -2401.681845
Sum of electronic and thermal Free Energies= -2401.827840
Imaginary Frequency =-911.06

3P-B-back-HBS

Ir	-0.72903	-0.73676	-0.18516
N	0.33764	0.89465	-0.85228
C	-0.10093	1.57176	-1.93889
N	0.31607	-0.64202	1.63549
C	0.54689	2.64278	-2.50820
C	1.50726	1.30271	-0.26008
C	1.75460	3.10559	-1.92539
C	2.19759	2.40395	-0.78885
H	-1.03690	1.23114	-2.35498
H	0.10651	3.10633	-3.38062
N	2.44469	4.16821	-2.43137
H	3.08302	2.72782	-0.26635
C	2.09531	0.63159	0.91020
N	1.54204	-0.20372	1.76218
B	-1.82541	0.67992	1.06000
O	-1.37986	1.98528	1.11054
C	-2.10370	2.68142	2.15942
C	-2.61718	1.49552	3.05600
C	-3.23168	3.46101	1.47671
C	-1.14039	3.63884	2.85261
O	-2.69960	0.39953	2.09522
C	-3.99456	1.70159	3.67438
C	-1.60880	1.06541	4.12597
C	3.56467	0.82381	1.17240
C	4.41589	-0.21806	0.80727
N	3.99275	1.97191	1.74042
C	5.80929	-0.12110	1.04100
C	5.31637	2.06547	1.95177
C	1.91014	4.91197	-3.56519
C	3.65470	4.63599	-1.76587
H	3.44967	4.98598	-0.74550
H	4.07874	5.46399	-2.33401
H	4.40855	3.84149	-1.70812
H	1.79633	4.27016	-4.44734
H	2.59898	5.71647	-3.82214
H	0.93342	5.35810	-3.33584
C	6.25019	1.08801	1.63550
N	6.67032	-1.13323	0.70713
H	5.66091	2.99348	2.40756
C	6.17976	-2.27283	-0.06001
C	8.10666	-0.93680	0.84409
H	8.48251	-0.13543	0.19140
H	8.62127	-1.86164	0.58143
H	8.37437	-0.68876	1.87753
H	5.78977	-1.97439	-1.04137
H	5.37968	-2.79497	0.47431
H	6.99573	-2.97935	-0.21460
H	7.29676	1.27242	1.84328
H	3.98159	-1.09290	0.34112
B	-2.68968	-0.13220	-0.72241
O	-3.11423	1.01386	-1.38626
O	-3.72689	-1.05940	-0.62972
C	-4.40987	0.73184	-1.98681
C	-4.95374	-0.41824	-1.06607
O	-1.61982	-2.57603	0.52639
C	-2.04755	-3.58763	-0.44871
C	-2.45734	-2.64975	1.72065
C	-3.19460	-4.33755	0.22565
C	-5.66238	0.09533	0.19118
C	-5.81822	-1.45397	-1.77657
C	-4.14017	0.27487	-3.42475
C	-5.23782	2.01050	-1.97984
H	-1.17403	-4.21414	-0.64406

H	-2.34928	-3.07403	-1.36016
H	-4.15005	-3.89556	-0.07185
H	0.11456	-1.31946	2.36366
C	3.24804	-3.39227	-1.48572
C	2.52045	-3.75579	-0.36038
C	1.36641	-3.02602	-0.05288
C	0.92473	-1.93935	-0.83232
C	2.85205	-2.34936	-2.31074
C	1.69153	-1.64013	-1.97459
F	4.39766	-4.06971	-1.77749
H	2.86160	-4.58080	0.25849
H	0.80796	-3.29940	0.83880
H	3.44632	-2.09705	-3.18421
H	1.39971	-0.81107	-2.61478
C	-2.94580	-4.08841	1.72169
H	-3.20006	-5.39781	-0.03951
H	-3.84434	-4.21246	2.33200
H	-2.16790	-4.75864	2.10390
H	-3.26713	-1.92763	1.61985
H	-1.82955	-2.38278	2.57150
H	-1.32919	-0.97427	-1.67744
H	-1.62069	4.12073	3.71073
H	-0.83220	4.42075	2.15155
H	-0.24170	3.12179	3.19407
H	-1.51254	1.81868	4.91337
H	-0.62540	0.88340	3.68515
H	-1.95431	0.13336	4.58430
H	-3.98669	2.56192	4.35163
H	-4.27559	0.81646	4.25380
H	-4.76026	1.86403	2.91341
H	-3.80417	4.05640	2.19436
H	-3.91170	2.78653	0.95138
H	-2.79504	4.13717	0.73585
H	-5.03132	0.80443	0.73033
H	-5.85536	-0.74992	0.85862
H	-6.61836	0.57037	-0.04795
H	-5.30877	2.43709	-0.97763
H	-6.24934	1.81578	-2.35109
H	-4.77343	2.75619	-2.63261
H	-5.06977	0.08804	-3.97041
H	-3.53528	-0.63662	-3.44081
H	-3.58707	1.05977	-3.94937
H	-6.15052	-2.21240	-1.06072
H	-5.26835	-1.95868	-2.57349
H	-6.70836	-0.98381	-2.20752

Sum of electronic and zero-point Energies= -2401.764136

Sum of electronic and thermal Energies= -2401.709376

Sum of electronic and thermal Enthalpies= -2401.708432

Sum of electronic and thermal Free Energies= -2401.852635

Conformer B-eq

TS2-3-O-4-HBS-Bpin

C	5.57379	-2.15126	-2.32140
C	6.29966	-2.34587	-1.15387
C	5.76993	-1.84923	0.06339
C	4.51382	-1.21212	-0.02268
C	3.86423	-1.05792	-1.25728
N	4.39284	-1.52314	-2.41271
H	7.24681	-2.86834	-1.19705
N	6.43288	-1.98611	1.26094
H	4.02855	-0.83101	0.86480
H	5.98326	-2.52662	-3.25977
C	2.27518	0.80965	-0.53726
N	1.03328	1.16248	-0.08691
C	3.36826	1.66678	-0.32349
C	3.25024	2.86949	0.39912
C	1.94681	3.19482	0.85969
C	0.91088	2.33027	0.57973
H	4.32174	1.38102	-0.74032
N	4.32655	3.67668	0.64221
H	1.73912	4.09796	1.41810
Ir	-0.85080	0.03615	-0.61656
H	-0.08925	2.56602	0.92169
C	5.63831	3.32225	0.11525
C	4.13319	4.98156	1.26238
H	5.93649	2.31983	0.44412
H	6.37727	4.03134	0.48906
H	5.66330	3.34301	-0.98311
H	5.09801	5.48084	1.35286
H	3.70682	4.88740	2.26844
H	3.46995	5.62331	0.66705
C	7.61078	-2.84008	1.33773
C	5.76616	-1.60428	2.49758
H	7.38745	-3.88541	1.07895
H	8.00459	-2.81586	2.35453
H	8.40087	-2.48427	0.66700
H	4.86169	-2.20175	2.68942
H	5.47662	-0.54748	2.47887
H	6.45308	-1.74500	3.33291
O	0.12777	-1.53495	0.59249

C	0.23432	-2.92943	0.16745
C	0.92141	-1.30088	1.79504
C	1.24366	-2.69648	2.31013
C	1.37109	-3.49826	1.00666
B	-1.94844	0.59564	1.06100
B	-2.51222	-1.17739	-0.75904
O	-3.48755	-1.12143	-1.75144
O	-2.80115	-2.18713	0.15342
O	-1.37172	0.73587	2.32676
O	-3.32309	0.82035	1.15603
C	-2.43596	0.74220	3.31750
C	-3.63747	1.30396	2.48732
C	-2.00444	1.60048	4.49963
C	-5.00762	0.77291	2.89334
C	-3.65828	2.83487	2.41532
H	-2.67788	3.22661	2.12922
H	-3.95007	3.28160	3.37069
H	-4.38100	3.14553	1.65507
H	-5.06248	-0.31297	2.79399
H	-5.78041	1.21091	2.25384
H	-5.23400	1.04121	3.93070
H	-1.69779	2.59875	4.18033
H	-1.15539	1.13209	5.00774
H	-2.81997	1.69937	5.22384
C	-2.64116	-0.71474	3.75078
H	-2.93574	-1.33287	2.89758
H	-3.39924	-0.80264	4.53503
H	-1.69689	-1.10462	4.14341
C	-4.60959	-1.95286	-1.34144
C	-3.92273	-2.96056	-0.34987
C	-5.22694	-2.58939	-2.58143
C	-5.61906	-1.02459	-0.65754
C	-4.78444	-3.38343	0.83495
C	-3.33834	-4.19340	-1.04865
H	-5.16683	-0.53533	0.20749
H	-6.51757	-1.56481	-0.34366
H	-5.91848	-0.24682	-1.36722
H	-4.48299	-3.12589	-3.17388
H	-5.66676	-1.81253	-3.21476
H	-6.02230	-3.28816	-2.30137
H	-5.08680	-2.52331	1.43564
H	-4.21808	-4.06411	1.47859
H	-5.68376	-3.90729	0.49443
H	-2.69586	-3.90344	-1.88528
H	-4.12332	-4.85700	-1.42358
H	-2.73013	-4.75486	-0.33308
C	-3.21138	3.61420	-1.88447
C	-2.87508	2.34762	-1.40991
C	-2.28251	4.36205	-2.61214
C	-1.59535	1.78498	-1.61720
C	-1.02478	3.82073	-2.87731
C	-0.71428	2.55153	-2.40394
F	0.51166	2.07408	-2.72181
H	-4.20226	4.01329	-1.68717
H	-3.59759	1.77154	-0.84807
H	-2.53422	5.35111	-2.98324
H	-0.27730	4.35789	-3.45256
H	-1.77077	0.45983	-1.88216
C	2.50945	-0.43151	-1.30110
N	1.67185	-1.05335	-2.11655
N	0.39721	-0.76935	-2.20588
H	-0.00679	-1.36956	-2.92002
H	-0.72600	-3.40329	0.37852
H	0.42527	-2.93926	-0.90434
H	0.32249	-0.68446	2.46145
H	1.82595	-0.76075	1.50710
H	0.41868	-3.08281	2.91956
H	2.15597	-2.70391	2.91356
H	2.33611	-3.29382	0.53081
H	1.27107	-4.57782	1.14786

Sum of electronic and zero-point Energies= -2401.750715

Sum of electronic and thermal Energies= -2401.695664

Sum of electronic and thermal Enthalpies= -2401.694720

Sum of electronic and thermal Free Energies= -2401.842423

Imaginary frequency = -412.60

TS2-3-4-HBS-Bpin

C	5.68647	-1.95478	-2.38686
C	6.41608	-2.13264	-1.21899
C	5.87118	-1.65633	-0.00032
C	4.59678	-1.05598	-0.08554
C	3.94475	-0.91725	-1.32033
N	4.48767	-1.36123	-2.47731
H	7.37786	-2.62747	-1.26319
N	6.53685	-1.77754	1.19718
H	4.09881	-0.69341	0.80259
H	6.10797	-2.31429	-3.32604
C	2.29417	0.89180	-0.58037
N	1.04057	1.18575	-0.11960
C	3.35244	1.78802	-0.35971
C	3.18870	2.97471	0.38267
C	1.87551	3.23829	0.85527

C	0.87401	2.33696	0.56719
H	4.31578	1.54498	-0.78162
N	4.23064	3.82132	0.63075
H	1.63516	4.12266	1.43047
Ir	-0.79762	-0.03213	-0.61856
H	-0.13376	2.52692	0.91567
C	5.56222	3.51032	0.12597
C	3.99509	5.09042	1.30816
H	5.89334	2.52193	0.46680
H	6.26910	4.25015	0.50186
H	5.59997	3.52359	-0.97171
H	4.93486	5.63801	1.37879
H	3.61322	4.93942	2.32562
H	3.27700	5.71483	0.76109
C	7.73917	-2.59722	1.27187
C	5.85664	-1.42389	2.43506
H	7.54547	-3.64882	1.01463
H	8.13502	-2.56026	2.28745
H	8.51678	-2.21916	0.59889
H	4.97246	-2.05209	2.62313
H	5.53223	-0.37724	2.42108
H	6.54703	-1.54562	3.27053
O	0.30559	-1.54757	0.53351
C	0.50966	-2.92195	0.07962
C	1.03754	-1.29665	1.77070
C	1.41419	-2.68370	2.27126
C	1.63501	-3.45163	0.95969
B	-1.91742	0.45330	1.05981
B	-2.37650	-1.35515	-0.75291
O	-3.35601	-1.37401	-1.74154
O	-2.59006	-2.37549	0.16837
O	-1.37221	0.60331	2.33737
O	-3.30090	0.64801	1.12527
C	-2.45921	0.60201	3.30462
C	-3.64812	1.14468	2.44424
C	-2.06444	1.47200	4.49094
C	-5.02230	0.60716	2.82604
C	-3.67890	2.67524	2.35631
H	-2.69389	3.07317	2.09550
H	-4.00017	3.12718	3.29966
H	-4.38154	2.97693	1.57369
H	-5.06576	-0.48051	2.74190
H	-5.78274	1.02888	2.16133
H	-5.27570	0.88900	3.85351
H	-1.76265	2.47218	4.17301
H	-1.22178	1.01646	5.02087
H	-2.89745	1.56506	5.19571
C	-2.65687	-0.85463	3.74144
H	-2.92880	-1.48041	2.88641
H	-3.42864	-0.94644	4.51176
H	-1.71586	-1.23252	4.15332
C	-4.41732	-2.27653	-1.31900
C	-3.65843	-3.22857	-0.32506
C	-4.99768	-2.96107	-2.55116
C	-5.48137	-1.41302	-0.63375
C	-4.48373	-3.70202	0.86642
C	-2.99446	-4.42265	-1.01960
H	-5.05550	-0.88669	0.22303
H	-6.33878	-2.00982	-0.30778
H	-5.83759	-0.66215	-1.34604
H	-4.22304	-3.45144	-3.14431
H	-5.49118	-2.21918	-3.18678
H	-5.74350	-3.70892	-2.26176
H	-4.84199	-2.86141	1.46395
H	-3.86945	-4.33873	1.51106
H	-5.34656	-4.28806	0.53294
H	-2.37586	-4.09460	-1.86014
H	-3.73490	-5.13865	-1.38863
H	-2.34814	-4.93929	-0.30367
C	-2.93504	3.66127	-1.80797
C	-2.70992	2.39417	-1.28948
C	-2.06565	4.28302	-2.69401
C	-1.53490	1.70602	-1.64251
C	-0.92287	3.57608	-3.08100
C	-0.66218	2.30056	-2.58005
H	0.22422	1.76283	-2.89271
F	-4.06108	4.31829	-1.42239
H	-3.42550	1.95674	-0.60673
H	-2.28838	5.27518	-3.07186
H	-0.22793	4.02689	-3.78403
H	-1.84130	0.36170	-1.78403
C	2.57309	-0.33037	-1.36465
N	1.75490	-0.95454	-2.19349
N	0.47345	-0.67305	-2.28766
H	0.07920	-1.28505	-2.99773
H	-0.43201	-3.45229	0.23156
H	0.75579	-2.89165	-0.98076
H	0.38041	-0.72944	2.42596
H	1.92086	-0.70031	1.52811
H	0.58722	-3.12392	2.84001
H	2.30125	-2.65669	2.91067
H	2.60844	-3.19245	0.53002
H	1.58146	-4.53726	1.07727

Sum of electronic and zero-point Energies= -2401.752105

Sum of electronic and thermal Energies= -2401.696848
Sum of electronic and thermal Enthalpies= -2401.695904
Sum of electronic and thermal Free Energies= -2401.844778
Imaginary Frequency = -493.69

Dtbpy-trisboryl

C	-1.51649	2.81155	-0.29936
C	-2.68512	3.56032	-0.31584
C	-3.93011	2.91963	-0.42096
C	-3.90810	1.52323	-0.48546
C	-2.69773	0.82066	-0.44350
N	-1.51082	1.46811	-0.36765
H	-2.61316	4.64042	-0.25104
C	-5.22644	3.73775	-0.45493
H	-4.83264	0.97180	-0.57985
H	-0.53770	3.27204	-0.21293
C	-2.63284	-0.66503	-0.46551
N	-1.40614	-1.20340	-0.64477
C	-3.76041	-1.47126	-0.26543
C	-3.65212	-2.86458	-0.25799
C	-2.36521	-3.39340	-0.45071
C	-1.28618	-2.54154	-0.63089
H	-4.71831	-1.00167	-0.09274
C	-4.85022	-3.79611	-0.04021
H	-2.19205	-4.46387	-0.45142
Ir	0.37560	0.19340	-0.60189
H	-0.27782	-2.92285	-0.74732
C	-6.16668	-3.02211	0.14600
C	-4.59880	-4.65031	1.22391
C	-4.99321	-4.72268	-1.26957
H	-5.17375	-4.14140	-2.18037
H	-5.83895	-5.40444	-1.12755
H	-4.09722	-5.33041	-1.42849
H	-6.13537	-2.37014	1.02561
H	-6.98924	-3.73003	0.28912
H	-6.40634	-2.40931	-0.72974
H	-4.48446	-4.01530	2.10907
H	-3.69782	-5.26392	1.12959
H	-5.44585	-5.32399	1.39430
C	-5.33732	4.55058	0.85586
C	-6.47578	2.84965	-0.58770
C	-5.18026	4.70608	-1.65937
H	-5.36487	3.88773	1.72749
H	-6.25802	5.14435	0.84997
H	-4.49650	5.23942	0.98112
H	-4.33565	5.39882	-1.59497
H	-6.09882	5.30214	-1.69426
H	-5.09567	4.15556	-2.60261
H	-6.57709	2.15932	0.25669
H	-6.46331	2.26427	-1.51349
H	-7.37068	3.47972	-0.60763
B	0.79820	-0.32808	1.27098
O	1.90907	0.01885	2.04397
O	-0.06265	-1.14797	2.02186
C	0.65631	-1.59520	3.19628
C	1.69806	-0.43843	3.39814
C	1.31256	-2.93400	2.83423
C	-0.33332	-1.78016	4.34183
C	1.13212	0.74543	4.19250
C	3.03933	-0.87277	3.98093
H	0.16938	1.06395	3.78174
H	1.82654	1.58764	4.11646
H	0.99973	0.50277	5.25171
H	3.53601	-1.59860	3.33400
H	2.90917	-1.31670	4.97392
H	3.69899	-0.00473	4.08139
H	1.99480	-2.80782	1.98971
H	0.52928	-3.63717	2.53209
H	1.85282	-3.36748	3.68204
H	-0.92589	-0.87853	4.51145
H	0.18911	-2.03547	5.27023
H	-1.02307	-2.59744	4.10650
B	1.86826	-1.06903	-1.12169
B	1.84708	1.59133	-0.37414
O	1.62582	2.82807	0.27065
O	3.18877	1.54011	-0.78754
O	2.39130	-1.13012	-2.42774
O	2.47242	-2.07409	-0.34495
C	3.24067	-2.29540	-2.54260
C	3.63888	-2.55545	-1.04942
C	4.40663	-1.96845	-3.47094
C	3.87103	-4.01802	-0.68528
C	4.82242	-1.69232	-0.59026
H	4.64326	-0.64288	-0.83822
H	5.76701	-2.01837	-1.03778
H	4.91092	-1.76982	0.49790
H	2.97258	-4.61843	-0.84521
H	4.14534	-4.09831	0.37172
H	4.68712	-4.44405	-1.27904
H	4.92527	-1.06191	-3.15272
H	4.03812	-1.80623	-4.48935
H	5.12661	-2.79387	-3.49947

C	2.39134	-3.42547	-3.13918
H	1.55783	-3.67759	-2.47660
H	2.98042	-4.33043	-3.31968
H	1.97524	-3.09084	-4.09469
C	2.79253	3.66783	0.11641
C	3.92237	2.61360	-0.15617
C	2.97509	4.49554	1.38528
C	2.52962	4.59083	-1.08078
C	5.02649	3.08178	-1.09986
C	4.53254	2.04166	1.13061
H	2.39155	4.00962	-1.99737
H	3.34615	5.30283	-1.23764
H	1.61193	5.15915	-0.89803
H	3.00547	3.86089	2.27325
H	2.13797	5.19274	1.49771
H	3.89972	5.08149	1.34111
H	4.63158	3.34814	-2.08272
H	5.75823	2.27922	-1.23875
H	5.55180	3.94990	-0.68657
H	3.74731	1.65837	1.78576
H	5.13218	2.78559	1.66526
H	5.18266	1.20126	0.86806

Sum of electronic and zero-point Energies= -2147.522160

Sum of electronic and thermal Energies= -2147.469368

Sum of electronic and thermal Enthalpies= -2147.468424

Sum of electronic and thermal Free Energies= -2147.608554

Catalyst Substrate Complexes

2a-F-OD-1-HBS

C	-1.16674	2.55138	-0.04375
C	-2.27060	3.35810	0.18944
C	-3.52882	2.77860	0.42244
C	-3.58563	1.38203	0.40507
C	-2.43816	0.62400	0.14211
N	-1.24410	1.21164	-0.08272
H	-2.13854	4.43454	0.19578
C	-4.75376	3.66218	0.68658
H	-4.51709	0.87340	0.60929
H	-0.17571	2.96361	-0.19170
C	-2.44522	-0.86152	0.10818
N	-1.22944	-1.46450	0.09935
C	-3.62268	-1.60797	0.05669
C	-3.59054	-3.00873	0.01211
C	-2.32385	-3.60288	0.03758
C	-1.18310	-2.80444	0.07492
H	-4.57517	-1.09478	0.01971
C	-4.89859	-3.80159	-0.09623
H	-2.19800	-4.67801	0.01216
Ir	0.57950	-0.11486	-0.23709
H	-0.18496	-3.23028	0.06450
C	-5.60491	-3.40955	-1.41550
C	-5.81128	-3.45280	1.10144
C	-4.65634	-5.32065	-0.10226
H	-4.04479	-5.63166	-0.95584
H	-5.61503	-5.84411	-0.17455
H	-4.16258	-5.65647	0.81585
H	-5.84250	-2.34154	-1.44838
H	-6.54462	-3.96374	-1.51706
H	-4.97637	-3.64550	-2.28121
H	-6.06204	-2.38797	1.12929
H	-5.32902	-3.71186	2.05012
H	-6.74968	-4.01379	1.03200
C	-4.48839	4.53286	1.93632
C	-6.02978	2.83707	0.92716
C	-4.98286	4.57513	-0.54010
H	-4.30931	3.90784	2.81795
H	-5.35633	5.16962	2.14027
H	-3.62015	5.18498	1.80263
H	-4.11688	5.21296	-0.74115
H	-5.84598	5.22706	-0.36581
H	-5.18110	3.98100	-1.43908
H	-5.93603	2.18790	1.80441
H	-6.28083	2.21394	0.06189
H	-6.87335	3.51188	1.10397
B	0.95591	0.25966	1.68307
O	0.66533	1.47530	2.31432
O	1.37812	-0.67723	2.63905
C	1.60121	0.01753	3.88949
C	0.64963	1.25496	3.74205
C	3.08419	0.40706	3.93050
C	1.26744	-0.92051	5.04442
C	-0.80243	0.94418	4.13170
C	1.12382	2.52228	4.44561
H	-1.14929	0.02956	3.64124
H	-1.44057	1.76859	3.79814
H	-0.92303	0.82972	5.21359
H	2.08940	2.85546	4.05975
H	1.21381	2.35869	5.52504
H	0.40040	3.32835	4.28430
H	3.33066	1.08224	3.10624
H	3.69088	-0.49644	3.81822
H	3.35384	0.88888	4.87571

H	0.26423	-1.34013	4.94255
H	1.33159	-0.39460	6.00317
H	1.97964	-1.75184	5.06655
B	2.11591	-1.45117	-0.14561
B	1.98015	1.23539	-0.81057
O	2.29694	2.46056	-0.19961
O	2.68148	1.14909	-2.03378
O	1.96105	-2.84508	-0.35177
O	3.45134	-1.20647	0.20833
C	3.11100	-3.52392	0.20800
C	4.21890	-2.42216	0.09212
C	3.37427	-4.79678	-0.58967
C	5.27052	-2.44731	1.19804
C	4.90037	-2.40474	-1.28233
H	4.15594	-2.38581	-2.08384
H	5.55234	-3.27223	-1.42790
H	5.50814	-1.49926	-1.36453
H	4.81759	-2.30072	2.18081
H	5.99404	-1.64109	1.03826
H	5.81651	-3.39722	1.20060
H	3.45936	-4.58907	-1.65871
H	2.54743	-5.50104	-0.44882
H	4.29489	-5.28571	-0.25284
C	2.75982	-3.86585	1.66244
H	2.53602	-2.95492	2.22436
H	3.56620	-4.41321	2.16114
H	1.86468	-4.49683	1.67150
C	3.02337	3.28441	-1.14093
C	3.65263	2.21702	-2.09992
C	4.02809	4.13927	-0.37509
C	1.99300	4.17871	-1.84436
C	3.80058	2.66083	-3.55251
C	4.98220	1.65452	-1.58119
H	1.26830	3.57468	-2.39738
H	2.46637	4.88220	-2.53675
H	1.45064	4.75686	-1.08936
H	4.67247	3.52517	0.25762
H	3.49674	4.84579	0.27112
H	4.65726	4.71561	-1.06225
H	2.83417	2.91296	-3.99456
H	4.23970	1.85043	-4.14380
H	4.46020	3.53194	-3.63130
H	4.87828	1.30391	-0.55149
H	5.78627	2.39593	-1.63094
H	5.26654	0.79722	-2.19834
C	-1.58421	-1.90214	-3.41999
C	-0.25166	-1.48081	-3.47011
C	-2.60946	-0.95849	-3.30642
C	0.06729	-0.11902	-3.40794
C	-2.31234	0.40552	-3.23470
C	-0.97897	0.78972	-3.28433
F	-0.68387	2.11388	-3.18483
H	-1.82223	-2.96049	-3.45883
H	0.55134	-2.20811	-3.54407
H	-3.64489	-1.28208	-3.26049
H	-3.08488	1.15911	-3.12371
H	1.09161	0.23619	-3.41088

Sum of electronic and zero-point Energies= -2478.952685

Sum of electronic and thermal Energies= -2478.893528

Sum of electronic and thermal Enthalpies= -2478.892584

Sum of electronic and thermal Free Energies= -2479.046005

2a-F-MD-1-HBS-8-re-2

C	1.21087	-2.61949	0.40316
C	2.35214	-3.40922	0.50708
C	3.61381	-2.80374	0.53067
C	3.63362	-1.40343	0.48643
C	2.45153	-0.66723	0.39591
N	1.24676	-1.28332	0.32563
H	2.23264	-4.48423	0.55317
C	4.93036	-3.58796	0.58417
H	4.58463	-0.88804	0.49792
H	0.22390	-3.06683	0.37129
C	2.42731	0.81813	0.34076
N	1.21830	1.38729	0.13556
C	3.58594	1.59432	0.47345
C	3.53204	2.98609	0.37475
C	2.26112	3.54810	0.17264
C	1.14674	2.72850	0.06698
H	4.53195	1.10242	0.64696
C	4.77556	3.87932	0.45101
H	2.12760	4.62097	0.08750
Ir	-0.55190	-0.01184	-0.20466
H	0.15303	3.12683	-0.10562
C	6.06077	3.07388	0.70912
C	4.60044	4.90649	1.59227
C	4.92470	4.62427	-0.89605
H	5.04758	3.91638	-1.72335
H	5.80671	5.27383	-0.87047
H	4.05392	5.25031	-1.11332
H	6.01735	2.53120	1.65965
H	6.91590	3.75567	0.75598

H	6.25809	2.35307	-0.09174
H	4.48121	4.40337	2.55789
H	3.72873	5.54864	1.43490
H	5.48314	5.55270	1.65146
C	4.69587	-5.10687	0.65039
C	5.73063	-3.15817	1.83498
C	5.75101	-3.27029	-0.68782
H	4.12756	-5.39219	1.54215
H	5.65954	-5.62451	0.69192
H	4.16100	-5.47438	-0.23185
H	5.19890	-3.54638	-1.59119
H	6.69187	-3.83151	-0.67207
H	5.99521	-2.20645	-0.75987
H	5.16842	-3.36616	2.75179
H	5.97072	-2.09047	1.82019
H	6.67525	-3.71113	1.88184
B	-1.24693	0.06007	1.65907
O	-0.86549	-0.85986	2.64737
O	-2.08549	1.03313	2.21964
C	-2.51123	0.56603	3.52167
C	-1.32333	-0.37472	3.93006
C	-3.82943	-0.19053	3.31302
C	-2.72514	1.76886	4.43425
C	-0.15186	0.38321	4.56880
C	-1.71641	-1.56643	4.79721
H	0.13499	1.24291	3.95560
H	0.70995	-0.28841	4.63428
H	-0.39058	0.73549	5.57737
H	-2.43303	-2.21141	4.28435
H	-2.15793	-1.23300	5.74276
H	-0.82953	-2.16495	5.03055
H	-3.68325	-1.02919	2.62721
H	-4.55488	0.49007	2.85607
H	-4.24703	-0.55409	4.25749
H	-1.84379	2.41330	4.46391
H	-2.95761	1.44636	5.45509
H	-3.56699	2.36630	4.06940
B	-2.02572	1.30761	-0.70467
B	-1.97465	-1.42080	-0.55687
O	-2.93165	-1.91724	0.34290
O	-2.11709	-2.11660	-1.78376
O	-1.78538	2.67780	-0.96935
O	-3.40328	1.07327	-0.85021
C	-3.04831	3.38481	-0.96071
C	-4.04930	2.25207	-1.37305
C	-2.96519	4.56149	-1.92737
C	-5.44038	2.36450	-0.75568
C	-4.16053	2.07502	-2.89346
H	-3.16892	1.99111	-3.34816
H	-4.69356	2.90653	-3.36558
H	-4.70686	1.15130	-3.10533
H	-5.39490	2.32565	0.33463
H	-6.06509	1.53197	-1.09575
H	-5.92908	3.29838	-1.05466
H	-2.65145	4.24278	-2.92386
H	-2.23491	5.29098	-1.56143
H	-3.93355	5.06686	-2.01102
C	-3.27133	3.88490	0.47288
H	-3.28756	3.04433	1.17149
H	-4.19916	4.45833	0.56659
H	-2.43807	4.53794	0.75309
C	-3.58743	-3.06656	-0.22985
C	-3.37312	-2.83579	-1.76492
C	-5.04455	-3.07998	0.22381
C	-2.86139	-4.31261	0.29625
C	-3.23126	-4.10622	-2.59693
C	-4.43127	-1.90953	-2.37871
H	-1.82033	-4.32765	-0.04051
H	-3.34625	-5.23950	-0.02698
H	-2.86221	-4.28555	1.39038
H	-5.53363	-2.12640	0.01496
H	-5.09574	-3.25499	1.30356
H	-5.60361	-3.87956	-0.27472
H	-2.38022	-4.70869	-2.27146
H	-3.07599	-3.84520	-3.64906
H	-4.13764	-4.71819	-2.53135
H	-4.50813	-0.98838	-1.79653
H	-5.41271	-2.39117	-2.43823
H	-4.11888	-1.64233	-3.39363
C	2.99360	0.65973	-2.98246
C	1.78547	1.33458	-3.16060
C	2.96593	-0.72805	-2.88041
C	0.58223	0.62294	-3.22979
C	1.79174	-1.46268	-2.95428
H	3.94017	1.18445	-2.91043
H	1.78350	2.41845	-3.22634
F	4.13998	-1.38512	-2.68242
H	-0.35677	1.15372	-3.34635
H	1.82433	-2.54186	-2.84977
H	-0.34898	-1.32627	-3.15261
C	0.58557	-0.77469	-3.13105

Sum of electronic and zero-point Energies=
-2478.952595

Sum of electronic and thermal Energies=
-2478.893020

Sum of electronic and thermal Enthalpies= -2478.892076
Sum of electronic and thermal Free Energies= -2479.046890

2a-F-PD-3-HBS

C 1.48920 -2.53945 0.67857
C 2.71009 -3.19087 0.83564
C 3.90358 -2.46482 0.75569
C 3.77896 -1.08452 0.54426
C 2.52655 -0.48465 0.41274
N 1.38620 -1.22061 0.46181
H 2.70321 -4.26002 1.00643
C 5.29345 -3.10151 0.87785
H 4.66985 -0.47595 0.46165
H 0.54537 -3.07233 0.72650
C 2.35216 0.97694 0.21002
N 1.10269 1.38596 -0.09899
C 3.40350 1.89264 0.35115
C 3.18989 3.26122 0.17077
C 1.87584 3.65508 -0.13453
C 0.87628 2.70195 -0.25294
H 4.38581 1.52911 0.61718
C 4.30382 4.30710 0.29712
H 1.62208 4.69947 -0.27876
Ir -0.52375 -0.15837 -0.19619
H -0.15142 2.97645 -0.46568
C 5.66326 3.67537 0.64314
C 3.93008 5.31155 1.41136
C 4.43658 5.05621 -1.04901
H 4.69893 4.36580 -1.85819
H 5.22439 5.81446 -0.97983
H 3.50731 5.56378 -1.32551
H 5.63615 3.15183 1.60481
H 6.42294 4.46012 0.71583
H 5.99187 2.96805 -0.12602
H 3.81861 4.80377 2.37545
H 2.99298 5.83269 1.19324
H 4.71665 6.06744 1.51280
C 5.21433 -4.61993 1.11269
C 6.04245 -2.45813 2.06765
C 6.08291 -2.84720 -0.42735
H 4.68130 -4.86193 2.03837
H 6.22576 -5.03028 1.19615
H 4.71627 -5.13370 0.28346
H 5.56593 -3.27701 -1.29002
H 7.07597 -3.30434 -0.35448
H 6.21979 -1.77905 -0.62026
H 5.50007 -2.61776 3.00584
H 6.17520 -1.38014 1.93306
H 7.03731 -2.90572 2.16908
B -1.30837 0.49717 1.51363
O -2.57653 0.23203 2.04249
O -0.60693 1.35369 2.38008
C -1.55132 1.90111 3.33105
C -2.65059 0.78214 3.37619
C -2.06516 3.21970 2.73769
C -0.83438 2.15576 4.65273
C -2.31231 -0.35088 4.35338
C -4.07046 1.28343 3.62137
H -1.29615 -0.71937 4.18439
H -3.00454 -1.18161 4.18549
H -2.40296 -0.03318 5.39703
H -4.39073 1.96991 2.83491
H -4.14293 1.79601 4.58681
H -4.76581 0.43784 3.63359
H -2.54419 3.04133 1.77142
H -1.21160 3.88537 2.57176
H -2.76760 3.72498 3.40833
H -0.32481 1.25957 5.01331
H -1.54075 2.48980 5.42057
H -0.08252 2.94085 4.52078
B -1.96020 0.95201 -1.09470
B -1.88002 -1.67806 -0.03573
O -1.66515 -2.77495 0.83144
O -3.10680 -1.86521 -0.68963
O -2.41062 0.77055 -2.41854
O -2.52670 2.14415 -0.59409
C -3.08553 1.96996 -2.85690
C -3.56385 2.58609 -1.49930
C -4.20205 1.58461 -3.82242
C -3.63613 4.10903 -1.46704
C -4.88297 1.97912 -1.00454
H -4.83674 0.88690 -1.03027
H -5.73710 2.31356 -1.60205
H -5.04682 2.28533 0.03302
H -2.66001 4.56146 -1.65610
H -3.97713 4.44446 -0.48212
H -4.34454 4.48190 -2.21475
H -4.86591 0.83593 -3.38548
H -3.77255 1.16077 -4.73626
H -4.79670 2.46095 -4.10279
C -2.04498 2.84128 -3.57470
H -1.24186 3.13228 -2.89083
H -2.48947 3.74798 -3.99744
H -1.60308 2.26345 -4.39245

C -2.67108 -3.78257 0.58774
C -3.83064 -2.93795 -0.04543
C -3.01525 -4.46676 1.90752
C -2.06575 -4.79907 -0.39000
C -4.66613 -3.67208 -1.09013
C -4.74317 -2.29274 1.00629
H -1.81347 -4.32065 -1.34110
H -2.74506 -5.63428 -0.58799
H -1.14408 -5.20313 0.04116
H -3.29723 -3.73886 2.67103
H -2.14576 -5.02149 2.27601
H -3.83958 -5.17661 1.77796
H -4.05551 -4.01001 -1.93042
H -5.43680 -3.00141 -1.48394
H -5.16702 -4.54140 -0.64978
H -4.14959 -1.72480 1.72656
H -5.35288 -3.03495 1.53183
H -5.41616 -1.59034 0.50416
C 2.30434 -0.18031 -3.07053
C 0.93210 -0.00703 -3.27356
C 2.77221 -1.46054 -2.80395
C 0.05917 -1.10022 -3.21176
C 1.93572 -2.56949 -2.74146
C 0.56803 -2.37859 -2.94831
H -0.10524 -3.22859 -2.88912
H 2.99921 0.65226 -3.09915
H 0.53707 0.98575 -3.46213
F 4.10238 -1.63500 -2.58547
H 2.35385 -3.54608 -2.52314
H -1.00424 -0.93777 -3.34030

Transition States Structures used for calculations

TS2-3-F-OD-1-HBS

C 1.01905 -2.71768 0.02603
C 2.07563 -3.57193 0.32403
C 3.36823 -3.05947 0.47653
C 3.51113 -1.67648 0.30565
C 2.41600 -0.86464 0.00485
N 1.17396 -1.39393 -0.13080
H 1.86243 -4.62748 0.43630
C 4.58716 -3.92162 0.82562
H 4.49035 -1.22877 0.41102
H 0.00367 -3.08109 -0.07370
C 2.53279 0.60424 -0.17354
N 1.39234 1.26190 -0.46713
C 3.75212 1.28239 -0.04073
C 3.82553 2.66685 -0.20613
C 2.62177 3.32129 -0.51132
C 1.44735 2.59283 -0.63212
H 4.64445 0.72141 0.19493
C 5.13186 3.45753 -0.06685
H 2.58538 4.39553 -0.65599
Ir -0.52269 0.00221 -0.57606
H 0.50323 3.06959 -0.86690
C 6.33262 2.55065 0.25459
C 4.97338 4.48794 1.07486
C 5.41653 4.19745 -1.39420
H 5.52197 3.48929 -2.22323
H 6.34900 4.76670 -1.31193
H 4.61836 4.90104 -1.64952
H 6.19981 2.01909 1.20308
H 7.23747 3.16042 0.34209
H 6.50755 1.81152 -0.53471
H 4.76584 3.98859 2.02749
H 4.15938 5.19220 0.87784
H 5.89682 5.06677 1.18722
C 4.22731 -5.41338 0.93459
C 5.15756 -3.45082 2.18380
C 5.66284 -3.75360 -0.27187
H 3.49119 -5.59809 1.72406
H 5.12559 -5.98911 1.17947
H 3.82860 -5.80486 -0.00736
H 5.27866 -4.06472 -1.24925
H 6.53543 -4.37252 -0.03589
H 6.00440 -2.71738 -0.35624
H 4.41254 -3.55698 2.97975
H 5.47170 -2.40285 2.15260
H 6.03158 -4.05457 2.45196
B -0.70564 0.13266 1.52604
O -1.60813 -0.52761 2.35036
O 0.19409 0.87118 2.30113
C -0.28251 0.88119 3.67282
C -1.15378 -0.42024 3.72022
C -1.11396 2.15815 3.84087
C 0.91714 0.89457 4.61306
C -0.33329 -1.68238 4.01687
C -2.37078 -0.35433 4.63682
H 0.54313 -1.74062 3.36429
H -0.95610 -2.56062 3.82228
H 0.00071 -1.71805 5.05863
H -3.05588 0.44015 4.33413
H -2.06906 -0.18243 5.67571
H -2.91596 -1.30289 4.59471
H -1.96367 2.14830 3.15376
H -0.48858 3.02354 3.60035

H	-1.48227	2.27512	4.86492
H	1.60540	0.07448	4.39691
H	0.59423	0.81461	5.65669
H	1.46631	1.83507	4.49989
B	-1.82801	1.58830	-0.33767
B	-2.09686	-1.29763	-0.45982
O	-2.03418	-2.57196	0.11482
O	-3.38654	-1.07407	-0.95304
O	-1.66716	2.77785	-1.06678
O	-2.89783	1.72186	0.53917
C	-2.51376	3.80017	-0.47487
C	-3.62421	2.93188	0.20885
C	-3.00325	4.73107	-1.57805
C	-4.21089	3.52097	1.48704
C	-4.74915	2.53227	-0.75315
H	-4.34321	2.10660	-1.67474
H	-5.38570	3.38535	-1.00806
H	-5.36867	1.76819	-0.27526
H	-3.44396	3.69266	2.24439
H	-4.94935	2.82957	1.90524
H	-4.71465	4.47098	1.27883
H	-3.48314	4.17692	-2.38716
H	-2.15700	5.28191	-2.00134
H	-3.71728	5.46007	-1.18034
C	-1.65338	4.57274	0.53212
H	-1.28677	3.91104	1.32161
H	-2.21066	5.39408	0.99272
H	-0.78816	4.99861	0.01463
C	-3.27744	-3.26791	-0.13852
C	-4.26450	-2.07566	-0.38670
C	-3.60250	-4.13481	1.07414
C	-3.07043	-4.14566	-1.37849
C	-5.39176	-2.36300	-1.37202
C	-4.82484	-1.49076	0.91700
H	-2.82861	-3.53630	-2.25175
H	-3.95526	-4.75143	-1.59850
H	-2.22934	-4.82280	-1.19801
H	-3.58568	-3.55030	1.99614
H	-2.85965	-4.93406	1.16814
H	-4.58852	-4.60043	0.96914
H	-5.00495	-2.63246	-2.35731
H	-6.01705	-1.47164	-1.48751
H	-6.02780	-3.17827	-1.01023
H	-4.01168	-1.25711	1.60953
H	-5.53214	-2.17378	1.39888
H	-5.34859	-0.55822	0.68784
C	0.92907	0.67818	-4.82611
C	0.42210	0.87320	-3.53758
C	0.90430	-0.59525	-5.40085
C	-0.11041	-0.18098	-2.77074
C	0.36383	-1.66361	-4.68126
C	-0.13364	-1.42378	-3.40516
F	-0.65073	-2.50180	-2.73834
H	1.33728	1.51934	-5.38038
H	0.43505	1.87031	-3.10667
H	1.29476	-0.75978	-6.40105
H	0.32361	-2.66872	-5.09054
H	-1.33141	0.36925	-1.92523

Sum of electronic and zero-point Energies= -2412.028967

Sum of electronic and thermal Energies= -2411.975963

Sum of electronic and thermal Enthalpies= -2411.975019

Sum of electronic and thermal Free Energies= -2412.110052

TS2-3-F-MD-1-HBS

C	0.79434	-2.59842	0.76514
C	1.83241	-3.43992	1.15108
C	3.15942	-3.06902	0.90719
C	3.35417	-1.83179	0.27861
C	2.27441	-1.02242	-0.07632
N	0.99949	-1.42237	0.15748
H	1.57998	-4.37175	1.64094
C	4.36634	-3.92421	1.31078
H	4.36052	-1.49586	0.06602
H	-0.23966	-2.84597	0.96927
C	2.44189	0.32918	-0.66885
N	1.31045	0.94762	-1.06806
C	3.68740	0.96553	-0.75071
C	3.79544	2.26327	-1.25657
C	2.60173	2.87134	-1.67789
C	1.39741	2.19198	-1.56395
H	4.56754	0.44873	-0.39692
C	5.12570	3.02141	-1.33558
H	2.59623	3.87836	-2.08012
Ir	-0.65047	-0.09194	-0.49058
H	0.45412	2.64477	-1.84790
C	6.31278	2.17332	-0.84689
C	5.02694	4.28621	-0.45117
C	5.38710	3.43529	-2.80182
H	5.45418	2.55612	-3.45182
H	6.33299	3.98349	-2.87186
H	4.59652	4.08421	-3.19042
H	6.20101	1.88150	0.20295

H 7.23607 2.75535 -0.93003
H 6.43863 1.26527 -1.44654
H 4.83497 4.01940 0.59393
H 4.22480 4.95269 -0.78227
H 5.96743 4.84666 -0.49263
C 3.94212 -5.25206 1.96165
C 5.22144 -3.12915 2.32524
C 5.21197 -4.23920 0.05572
H 3.36902 -5.09001 2.88062
H 4.83318 -5.83042 2.22586
H 3.33904 -5.86329 1.28184
H 4.62434 -4.79314 -0.68419
H 6.07607 -4.85271 0.33324
H 5.59000 -3.33097 -0.42366
H 4.64045 -2.88585 3.22148
H 5.59402 -2.19216 1.89970
H 6.08814 -3.72502 2.63190
B -0.26261 0.83192 1.38220
O -0.03234 0.14959 2.57107
O 0.06208 2.18123 1.54031
C 0.35033 2.43792 2.93890
C 0.73168 1.00746 3.45610
C -0.93143 2.98652 3.57540
C 1.46647 3.47482 3.01988
C 2.21196 0.66527 3.23671
C 0.33125 0.70962 4.89675
H 2.51791 0.88392 2.20990
H 2.35816 -0.40498 3.41143
H 2.86287 1.21919 3.92039
H -0.74877 0.78822 5.03626
H 0.82613 1.39878 5.58946
H 0.63151 -0.30972 5.16013
H -1.74617 2.26157 3.50032
H -1.23412 3.89312 3.04363
H -0.78206 3.24216 4.62901
H 2.33388 3.17634 2.42691
H 1.78434 3.62614 4.05702
H 1.10926 4.43424 2.63210
B -1.90916 1.55397 -0.53024
B -2.24591 -1.10290 0.27688
O -2.26060 -1.78843 1.49658
O -3.45696 -1.32150 -0.39288
O -1.76574 2.58194 -1.46991
O -2.95516 1.84570 0.33720
C -2.55838 3.71815 -1.03181
C -3.65158 3.02305 -0.14430
C -3.09124 4.44625 -2.26100
C -4.11649 3.83752 1.05821
C -4.85928 2.53395 -0.95159
H -4.54047 1.92670 -1.80373
H -5.46619 3.36720 -1.31916
H -5.48529 1.90967 -0.30874
H -3.28843 4.05986 1.73367
H -4.86621 3.27068 1.61954
H -4.57329 4.77992 0.73757
H -3.63158 3.77112 -2.92767
H -2.25809 4.88046 -2.82317
H -3.76205 5.26100 -1.96809
C -1.62236 4.63259 -0.23313
H -1.19558 4.09416 0.61566
H -2.13757 5.53071 0.12143
H -0.79707 4.94719 -0.88039
C -3.42382 -2.64958 1.54360
C -4.38743 -1.96551 0.50950
C -3.94207 -2.69176 2.97797
C -2.96612 -4.04884 1.11134
C -5.26139 -2.92816 -0.28896
C -5.24998 -0.85980 1.12913
H -2.57538 -4.03907 0.08971
H -3.77905 -4.77938 1.16643
H -2.16361 -4.38140 1.77749
H -4.12592 -1.68763 3.36536
H -3.20075 -3.17180 3.62503
H -4.87136 -3.26822 3.04062
H -4.66043 -3.63608 -0.86374
H -5.88233 -2.36527 -0.99328
H -5.92701 -3.49189 0.37364
H -4.62790 -0.13386 1.65837
H -5.99977 -1.26426 1.81635
H -5.77018 -0.33008 0.32627
C 0.46747 -1.73083 -4.52903
C 0.23188 -0.88039 -3.44503
C -0.19874 -2.95507 -4.63383
C -0.66495 -1.22841 -2.41281
C -1.10670 -3.27339 -3.63229
C -1.36273 -2.44292 -2.54829
H -2.11342 -2.73932 -1.82568
H 1.17356 -1.43915 -5.30287
H 0.76097 0.06579 -3.39610
H -0.03818 -3.63619 -5.46293
F -1.78306 -4.45324 -3.71841
H -1.52386 0.03033 -1.84901

Sum of electronic and zero-point Energies=
-2478.909805

Sum of electronic and thermal Energies=
-2478.850756

Sum of electronic and thermal Enthalpies= -2478.849812
Sum of electronic and thermal Free Energies= -2479.002944

TS2-3-F-PD-2-HBS

C	-0.79334	-2.71345	0.07044
C	-1.77143	-3.60533	-0.35858
C	-3.05296	-3.14099	-0.67055
C	-3.27963	-1.77118	-0.48058
C	-2.26835	-0.92492	-0.02363
N	-1.02035	-1.40026	0.22425
H	-1.50023	-4.64825	-0.46296
C	-4.16762	-4.03361	-1.22779
H	-4.25220	-1.35729	-0.71159
H	0.22023	-3.03614	0.27561
C	-2.47742	0.52919	0.18432
N	-1.37441	1.25674	0.45703
C	-3.74379	1.12460	0.10543
C	-3.90230	2.49973	0.28897
C	-2.73330	3.23083	0.55438
C	-1.50983	2.58147	0.63221
H	-4.60620	0.50413	-0.08933
C	-5.26271	3.20324	0.21405
H	-2.76346	4.30409	0.70747
Ir	0.59919	0.11256	0.59951
H	-0.58939	3.11732	0.83252
C	-6.41220	2.22428	-0.08231
C	-5.21662	4.26291	-0.91077
C	-5.54426	3.89757	1.56651
H	-5.57488	3.16793	2.38298
H	-6.51257	4.40873	1.52985
H	-4.78191	4.64425	1.80861
H	-6.27813	1.71760	-1.04426
H	-7.35750	2.77434	-0.12757
H	-6.51022	1.46266	0.69882
H	-5.01427	3.79622	-1.88094
H	-4.44377	5.01627	-0.73041
H	-6.17970	4.78111	-0.97596
C	-3.73670	-5.50756	-1.31872
C	-4.52861	-3.53611	-2.64744
C	-5.41043	-3.93887	-0.31394
H	-2.88283	-5.64117	-1.99132
H	-4.56390	-6.10694	-1.71205
H	-3.46946	-5.91349	-0.33726
H	-5.17729	-4.27680	0.70152
H	-6.21231	-4.57255	-0.70820
H	-5.79623	-2.91683	-0.25007
H	-3.65759	-3.57948	-3.31059
H	-4.89391	-2.50441	-2.63686
H	-5.31613	-4.16584	-3.07593
B	0.65754	0.03358	-1.51655
O	1.20194	-1.00648	-2.26504
O	-0.03679	0.91072	-2.34922
C	0.23050	0.54804	-3.73071
C	0.62908	-0.96215	-3.59696
C	1.38693	1.43155	-4.20901
C	-1.02291	0.81481	-4.55688
C	-0.58316	-1.90425	-3.58836
C	1.67187	-1.45031	-4.59598
H	-1.33733	-1.56589	-2.87228
H	-0.25481	-2.90208	-3.28379
H	-1.04635	-1.97996	-4.57717
H	2.60507	-0.89090	-4.50496
H	1.30336	-1.35424	-5.62297
H	1.89243	-2.50686	-4.41227
H	2.27468	1.26636	-3.59461
H	1.09595	2.48136	-4.10735
H	1.63352	1.24509	-5.25892
H	-1.89725	0.31704	-4.13171
H	-0.89045	0.46995	-5.58803
H	-1.22651	1.89024	-4.58276
B	1.79680	1.71761	0.08380
B	2.25569	-1.08672	0.57810
O	2.19553	-2.48830	0.51048
O	3.59229	-0.69577	0.68250
O	1.58935	2.99342	0.63557
O	2.80954	1.78423	-0.86755
C	2.28955	3.96193	-0.19082
C	3.44099	3.08609	-0.78724
C	2.74156	5.12401	0.68470
C	3.91187	3.49865	-2.17734
C	4.64027	2.95002	0.15843
H	4.31608	2.66370	1.16263
H	5.21159	3.88140	0.22386
H	5.30100	2.16441	-0.21852
H	3.09918	3.47060	-2.90419
H	4.69541	2.81498	-2.51980
H	4.33003	4.51086	-2.15762
H	3.32119	4.77834	1.54314
H	1.86864	5.66644	1.06240
H	3.35330	5.82645	0.10858
C	1.29497	4.44203	-1.25521
H	0.95858	3.60445	-1.87285
H	1.73112	5.21015	-1.90124
H	0.41922	4.87201	-0.75910

C 3.52522 -3.03769 0.68655
C 4.42699 -1.81433 0.30323
C 3.67061 -4.25924 -0.21534
C 3.65888 -3.44641 2.15789
C 5.75051 -1.72548 1.05483
C 4.66299 -1.69994 -1.20941
H 3.56857 -2.57762 2.81567
H 4.61652 -3.93773 2.35672
H 2.85626 -4.14778 2.40705
H 3.41679 -4.02270 -1.25060
H 2.99802 -5.05382 0.12483
H 4.69453 -4.64708 -0.18429
H 5.59736 -1.65201 2.13366
H 6.29838 -0.83455 0.73137
H 6.37541 -2.60118 0.84841
H 3.71330 -1.73264 -1.75091
H 5.32028 -2.49248 -1.58142
H 5.13429 -0.73520 -1.41893
C -0.96765 0.51047 4.83207
C -0.50855 0.80988 3.54560
C -0.64131 -0.72290 5.38066
C 0.25619 -0.10358 2.79562
C 0.13205 -1.65102 4.69494
C 0.58560 -1.32678 3.41267
H 1.18541 -2.05295 2.87352
H -1.56231 1.21531 5.40546
H -0.75923 1.77687 3.11929
F -1.08305 -1.02659 6.63097
H 0.37199 -2.60200 5.16137
H 1.30990 0.72882 1.92006
Sum of electronic and zero-point Energies= -2478.907697
Sum of electronic and thermal Energies= -2478.848761
Sum of electronic and thermal Enthalpies= -2478.847817
Sum of electronic and thermal Free Energies= -2479.001431
Imaginary frequency = -768.94

Products formed after oxidative addition

3-F-OD-1-HBS
C 0.72185 -2.51788 0.45246
C 1.71654 -3.38925 0.87999
C 3.04706 -2.96395 0.93436
C 3.29542 -1.64797 0.52279
C 2.26468 -0.81727 0.08346
N 0.98015 -1.26215 0.05589
H 1.42204 -4.38594 1.18278
C 4.19739 -3.83769 1.44635
H 4.30547 -1.26304 0.56045
H -0.32008 -2.80747 0.43572
C 2.48788 0.58816 -0.33294
N 1.37848 1.30137 -0.61774
C 3.76472 1.15775 -0.42147
C 3.92716 2.49214 -0.80041
C 2.75246 3.21131 -1.07176
C 1.51636 2.58840 -0.97128
H 4.63096 0.55095 -0.20200
C 5.29892 3.16503 -0.92832
H 2.78777 4.25416 -1.36687
Ir -0.57046 0.09773 -0.61438
H 0.59161 3.12006 -1.15889
C 6.45353 2.21540 -0.56447
C 5.35063 4.38726 0.01681
C 5.48805 3.63371 -2.38958
H 5.45210 2.78497 -3.08108
H 6.46101 4.12461 -2.50236
H 4.71575 4.34797 -2.69071
H 6.38224 1.86557 0.47119
H 7.40693 2.74271 -0.67011
H 6.48564 1.34119 -1.22362
H 5.20896 4.08337 1.05967
H 4.58123 5.12561 -0.22804
H 6.32501 4.88133 -0.06486
C 3.72246 -5.24806 1.83547
C 4.81072 -3.16081 2.69459
C 5.27452 -3.96520 0.34507
H 2.98363 -5.21996 2.64342
H 4.57543 -5.83670 2.18788
H 3.28243 -5.77776 0.98396
H 4.86169 -4.43370 -0.55474
H 6.10247 -4.58647 0.70371
H 5.68770 -2.99240 0.06102
H 4.05916 -3.03627 3.48195
H 5.22260 -2.17412 2.46058
H 5.62443 -3.77688 3.09271
B -0.68742 0.33957 1.52719
O -1.02226 -0.72365 2.34920
O -0.14354 1.37917 2.27929
C -0.27169 1.05209 3.69409
C -0.43117 -0.50824 3.65666
C -1.52138 1.75981 4.22701
C 0.97051 1.56214 4.41672

C	0.91051	-1.25171	3.67786
C	-1.36549	-1.09505	4.70998
H	1.59287	-0.86287	2.91759
H	0.73538	-2.30847	3.46223
H	1.39586	-1.17452	4.65562
H	-2.37827	-0.69923	4.61311
H	-0.99918	-0.88297	5.72006
H	-1.41608	-2.18171	4.58871
H	-2.40798	1.45666	3.66462
H	-1.40206	2.84126	4.12470
H	-1.68140	1.54021	5.28665
H	1.88642	1.17574	3.96473
H	0.95193	1.27316	5.47290
H	1.00338	2.65503	4.36454
B	-1.80425	1.68565	-0.03328
B	-2.18251	-1.16965	-0.64861
O	-2.36226	-2.29890	0.14924
O	-3.26693	-1.03090	-1.51952
O	-1.48058	3.00252	-0.36952
O	-3.02518	1.63994	0.62982
C	-2.43286	3.89857	0.25575
C	-3.65724	2.94377	0.52121
C	-2.71637	5.04869	-0.70620
C	-4.41944	3.22356	1.81141
C	-4.62878	2.86396	-0.66157
H	-4.09926	2.62932	-1.58960
H	-5.18085	3.79878	-0.79756
H	-5.34809	2.06234	-0.47388
H	-3.76989	3.15254	2.68536
H	-5.22642	2.49326	1.92785
H	-4.86625	4.22306	1.78705
H	-3.03988	4.68788	-1.68456
H	-1.80698	5.64124	-0.84858
H	-3.49061	5.70926	-0.30194
C	-1.77201	4.42679	1.53088
H	-1.49314	3.59854	2.18136
H	-2.42236	5.11948	2.07349
H	-0.85498	4.95860	1.25783
C	-3.51087	-3.04242	-0.32698
C	-4.31455	-1.94080	-1.10682
C	-4.23369	-3.63493	0.87927
C	-2.98938	-4.16546	-1.23078
C	-5.05033	-2.44019	-2.34632
C	-5.26978	-1.14338	-0.21006
H	-2.45380	-3.76092	-2.09099
H	-3.80168	-4.80907	-1.58276
H	-2.28796	-4.78256	-0.66001
H	-4.47555	-2.86753	1.61735
H	-3.59294	-4.37856	1.36444
H	-5.15957	-4.13392	0.57340
H	-4.36121	-2.87547	-3.07302
H	-5.56741	-1.60534	-2.83038
H	-5.79968	-3.19293	-2.07839
H	-4.74031	-0.73689	0.65524
H	-6.11152	-1.75270	0.13394
H	-5.66755	-0.30073	-0.78288
C	0.78812	0.13930	-4.88105
C	0.36446	0.47390	-3.58878
C	0.85861	-1.20113	-5.26845
C	-0.00846	-0.48799	-2.62480
C	0.49490	-2.19137	-4.35337
C	0.07505	-1.80119	-3.08512
F	-0.28151	-2.82590	-2.23617
H	1.06152	0.92451	-5.58212
H	0.32516	1.52658	-3.31635
H	1.18749	-1.47697	-6.26660
H	0.52733	-3.24719	-4.60697
H	-1.62936	0.96276	-1.44672

Sum of electronic and zero-point Energies=
-2478.931261
Sum of electronic and thermal Energies=
-2478.872374
Sum of electronic and thermal Enthalpies=
-2478.871429
Sum of electronic and thermal Free
Energies= -2479.023862

3-F-MD-1-HBS

C	0.68509	-2.45699	0.66935
C	1.64809	-3.28217	1.23924
C	2.96145	-2.82888	1.38604
C	3.23071	-1.54551	0.89248
C	2.23744	-0.76909	0.29571
N	0.95704	-1.22370	0.21224
H	1.33838	-4.26140	1.58144
C	4.07160	-3.64116	2.06138
H	4.23169	-1.14560	0.98064
H	-0.34555	-2.77297	0.57681
C	2.50690	0.56947	-0.27959
N	1.43182	1.24129	-0.74248
C	3.79849	1.10628	-0.36732
C	4.01363	2.36306	-0.93606
C	2.87594	3.03651	-1.40758
C	1.62373	2.44970	-1.29544
H	4.63666	0.53156	-0.00184

C	5.40238	3.00109	-1.05816
H	2.95332	4.01663	-1.86508
Ir	-0.55401	0.10278	-0.63399
H	0.72772	2.95515	-1.63016
C	6.51364	2.09782	-0.49592
C	5.40911	4.33480	-0.27601
C	5.69835	3.27613	-2.55037
H	5.69442	2.34590	-3.12871
H	6.68525	3.73977	-2.65677
H	4.96164	3.95289	-2.99369
H	6.37029	1.89088	0.57015
H	7.48127	2.59721	-0.60782
H	6.57134	1.14295	-1.02940
H	5.19698	4.16802	0.78567
H	4.66536	5.03781	-0.66313
H	6.39279	4.81036	-0.35667
C	3.57932	-5.02736	2.51072
C	4.56495	-2.86413	3.30443
C	5.24332	-3.83068	1.07107
H	2.76761	-4.95327	3.24213
H	4.40239	-5.57189	2.98422
H	3.22756	-5.62691	1.66444
H	4.91596	-4.36780	0.17449
H	6.04092	-4.41286	1.54531
H	5.67266	-2.87485	0.75522
H	3.74877	-2.70711	4.01808
H	4.97368	-1.88467	3.03690
H	5.35561	-3.42992	3.80930
B	-0.79869	0.46740	1.47775
O	-1.43230	-0.47274	2.27659
O	-0.11750	1.39314	2.26085
C	-0.45911	1.16412	3.66057
C	-0.95756	-0.32481	3.64127
C	-1.56741	2.15236	4.03298
C	0.78396	1.42263	4.50540
C	0.17510	-1.33766	3.84203
C	-2.11239	-0.64027	4.58643
H	1.01428	-1.13288	3.17317
H	-0.19766	-2.34020	3.61587
H	0.54026	-1.32991	4.87368
H	-2.99444	-0.03959	4.35598
H	-1.82631	-0.46188	5.62830
H	-2.38786	-1.69498	4.48620
H	-2.43506	2.01899	3.38286
H	-1.19956	3.17461	3.91261
H	-1.87919	2.02785	5.07414
H	1.63375	0.82626	4.16682
H	0.59214	1.19317	5.55889
H	1.06283	2.47867	4.43390
B	-1.66456	1.81808	-0.15679
B	-2.19977	-1.11050	-0.59506
O	-2.18315	-2.45641	-0.21303
O	-3.47971	-0.76466	-1.02527
O	-1.23253	3.06920	-0.61099
O	-2.88538	1.94164	0.49602
C	-2.11301	4.09112	-0.08141
C	-3.41493	3.26642	0.22674
C	-2.27975	5.18267	-1.13388
C	-4.20294	3.73977	1.44222
C	-4.34231	3.13018	-0.98658
H	-3.79164	2.78026	-1.86458
H	-4.83124	4.07779	-1.23232
H	-5.11493	2.39026	-0.75930
H	-3.59638	3.72331	2.34900
H	-5.06675	3.08606	1.59936
H	-4.57201	4.75923	1.28786
H	-2.61064	4.77434	-2.09086
H	-1.32278	5.68939	-1.29512
H	-3.00686	5.93116	-0.80167
C	-1.43375	4.65691	1.16816
H	-1.25822	3.86356	1.89495
H	-2.02449	5.45268	1.63197
H	-0.46136	5.07097	0.88334
C	-3.45018	-3.06420	-0.57507
C	-4.39384	-1.81409	-0.62428
C	-3.80875	-4.10815	0.47666
C	-3.25927	-3.72873	-1.94307
C	-5.52644	-1.89933	-1.64090
C	-4.94086	-1.42739	0.75611
H	-2.99879	-2.98914	-2.70476
H	-4.16036	-4.26191	-2.26163
H	-2.43843	-4.44958	-1.88002
H	-3.78740	-3.68570	1.48336
H	-3.08935	-4.93293	0.44019
H	-4.80589	-4.52098	0.29012
H	-5.14534	-2.01837	-2.65734
H	-6.12084	-0.98051	-1.60897
H	-6.19027	-2.74065	-1.41426
H	-4.12908	-1.34977	1.48500
H	-5.68055	-2.14856	1.11798
H	-5.42120	-0.44740	0.68261
C	0.75466	-0.56237	-4.85234
C	0.35805	-0.00020	-3.63386
C	0.79065	-1.95036	-5.01893
C	-0.01862	-0.79078	-2.52532
C	0.41416	-2.72740	-3.93133

C	0.01660	-2.18623	-2.71459
H	-0.28664	-2.86573	-1.92432
H	1.03863	0.08136	-5.68223
H	0.34567	1.08387	-3.54417
H	1.09174	-2.41907	-5.95016
F	0.42811	-4.08649	-4.06621
H	-1.56831	0.93234	-1.55192

Sum of electronic and zero-point Energies= -2478.925863

Sum of electronic and thermal Energies= -2478.866927

Sum of electronic and thermal Enthalpies= -2478.865983

Sum of electronic and thermal Free Energies= -2479.018392

3-F-PD-2-HBS

C	-0.67325	-2.49615	-0.66934
C	-1.62970	-3.32258	-1.24851
C	-2.93465	-2.86015	-1.43632
C	-3.20322	-1.56529	-0.97369
C	-2.21767	-0.78756	-0.36578
N	-0.94445	-1.25248	-0.24102
H	-1.32104	-4.31058	-1.56558
C	-4.03539	-3.67464	-2.12442
H	-4.19730	-1.15659	-1.09413
H	0.35222	-2.81892	-0.54691
C	-2.48874	0.56442	0.17635
N	-1.42099	1.23108	0.66269
C	-3.77515	1.11988	0.20900
C	-3.99227	2.39084	0.74459
C	-2.86210	3.05874	1.24107
C	-1.61517	2.45304	1.18403
H	-4.60831	0.54917	-0.17386
C	-5.37506	3.05021	0.80535
H	-2.94107	4.04910	1.67564
Ir	0.55868	0.07291	0.62604
H	-0.72435	2.95354	1.53938
C	-6.47970	2.14965	0.22587
C	-5.33639	4.36583	-0.00597
C	-5.71692	3.36324	2.28018
H	-5.74551	2.44665	2.87922
H	-6.70014	3.84243	2.34263
H	-4.98603	4.04025	2.73267
H	-6.30442	1.91836	-0.83039
H	-7.44348	2.66395	0.29537
H	-6.56773	1.20705	0.77679
H	-5.08989	4.17227	-1.05561
H	-4.59698	5.06790	0.39115
H	-6.31564	4.85583	0.02949
C	-3.54704	-5.07526	-2.53151
C	-4.48605	-2.91852	-3.39621
C	-5.23547	-3.83108	-1.16259
H	-2.71596	-5.02554	-3.24288
H	-4.36363	-5.62099	-3.01476
H	-3.22417	-5.66027	-1.66381
H	-4.93879	-4.35467	-0.24750
H	-6.02727	-4.41282	-1.64693
H	-5.66126	-2.86447	-0.87629
H	-3.64915	-2.78554	-4.09046
H	-4.89022	-1.92916	-3.16000
H	-5.26947	-3.48585	-3.91055
B	0.84423	0.41466	-1.48513
O	1.47827	-0.54074	-2.26549
O	0.18637	1.34083	-2.28780
C	0.54513	1.09305	-3.67987
C	1.02368	-0.40193	-3.63778
C	1.67141	2.06297	-4.04654
C	-0.68232	1.35860	-4.54512
C	-0.11968	-1.40199	-3.84238
C	2.18676	-0.74314	-4.56366
H	-0.96435	-1.17882	-3.18639
H	0.23677	-2.40680	-3.60076
H	-0.47168	-1.40059	-4.87860
H	3.07349	-0.15136	-4.32827
H	1.91688	-0.57322	-5.61126
H	2.44712	-1.80009	-4.44763
H	2.52815	1.92519	-3.38300
H	1.31550	3.09114	-3.94182
H	1.99608	1.92357	-5.08186
H	-1.54475	0.77781	-4.21152
H	-0.47909	1.11424	-5.59310
H	-0.94773	2.41906	-4.48970
B	1.69478	1.77096	0.14964
B	2.19701	-1.14905	0.63003
O	2.18590	-2.49450	0.24402
O	3.46983	-0.80750	1.08559
O	1.26571	3.03173	0.58078
O	2.93019	1.87569	-0.47870
C	2.16766	4.03900	0.05932
C	3.46729	3.19797	-0.21353
C	2.32402	5.13957	1.10398
C	4.28419	3.64908	-1.41844
C	4.36894	3.06673	1.01960
H	3.79746	2.73158	1.88995

H	4.86145	4.01265	1.26474
H	5.13919	2.31751	0.81629
H	3.69589	3.62633	-2.33712
H	5.14484	2.98558	-1.54983
H	4.65960	4.66703	-1.26950
H	2.63066	4.73762	2.07167
H	1.36929	5.65769	1.24022
H	3.06566	5.87717	0.77959
C	1.52034	4.59894	-1.20965
H	1.35099	3.79981	-1.93140
H	2.12917	5.38332	-1.66945
H	0.54687	5.02640	-0.94932
C	3.44783	-3.10403	0.61885
C	4.39021	-1.85393	0.69304
C	3.82314	-4.13822	-0.43687
C	3.23746	-3.78163	1.97743
C	5.50541	-1.94672	1.72808
C	4.96049	-1.45795	-0.67535
H	2.95885	-3.05027	2.74070
H	4.13558	-4.31281	2.30746
H	2.42259	-4.50709	1.89187
H	3.81698	-3.70652	-1.43976
H	3.10378	-4.96369	-0.41937
H	4.81751	-4.55241	-0.23884
H	5.10684	-2.07275	2.73697
H	6.10030	-1.02779	1.71283
H	6.17300	-2.78654	1.50697
H	4.16105	-1.37410	-1.41699
H	5.70544	-2.17736	-1.02989
H	5.44027	-0.47907	-0.58703
C	-0.92421	-0.50982	4.80000
C	-0.46940	0.01727	3.58443
C	-0.94878	-1.88933	4.95405
C	-0.03852	-0.79491	2.51421
C	-0.52945	-2.74432	3.94423
C	-0.07682	-2.18574	2.74225
H	0.26982	-2.86098	1.96484
H	-1.25421	0.12897	5.61453
H	-0.45845	1.09965	3.47424
F	-1.39187	-2.41795	6.13112
H	-0.55179	-3.81878	4.10428
H	1.55565	0.90265	1.56177

Sum of electronic and zero-point Energies=
-2478.924211
Sum of electronic and thermal Energies=
-2478.865116
Sum of electronic and thermal Enthalpies=
-2478.864172
Sum of electronic and thermal Free
Energies= -2479.017999

Other configurations of transition states

TS2-3-F-OD-3-HBS

C	-1.28536	2.28852	-1.52981
C	-2.43314	3.07582	-1.56005
C	-3.63978	2.56624	-1.06784
C	-3.61269	1.24721	-0.59468
C	-2.43469	0.49922	-0.61655
N	-1.27589	1.03368	-1.06755
H	-2.35657	4.08211	-1.95220
C	-4.93854	3.37916	-1.00094
H	-4.51470	0.81056	-0.18601
H	-0.32762	2.67330	-1.86293
C	-2.35960	-0.89891	-0.12637
N	-1.12145	-1.43883	-0.01977
C	-3.49910	-1.63683	0.21612
C	-3.39578	-2.94711	0.68778
C	-2.09722	-3.46986	0.79567
C	-1.00271	-2.69750	0.43815
H	-4.47077	-1.18034	0.09692
C	-4.61197	-3.79411	1.07933
H	-1.92440	-4.47750	1.15698
Ir	0.59316	-0.14442	-0.59740
H	0.01170	-3.06398	0.53612
C	-5.93864	-3.04154	0.87770
C	-4.48798	-4.18388	2.57057
C	-4.63480	-5.07345	0.21158
H	-4.71305	-4.82444	-0.85224
H	-5.49787	-5.69204	0.48125
H	-3.73394	-5.67827	0.35208
H	-5.99088	-2.13595	1.49176
H	-6.77271	-3.68712	1.17043
H	-6.09133	-2.75861	-0.16942
H	-4.46388	-3.29326	3.20803
H	-3.58128	-4.76431	2.76593
H	-5.34725	-4.79413	2.86985
C	-4.77695	4.77957	-1.61700
C	-5.34617	3.53689	0.48268
C	-6.05416	2.63162	-1.76623
H	-4.02524	5.37370	-1.08670
H	-5.72771	5.31865	-1.55467
H	-4.49290	4.72766	-2.67352

H	-5.78282	2.49255	-2.81827
H	-6.98469	3.20853	-1.72791
H	-6.25723	1.64603	-1.33629
H	-4.57142	4.06714	1.04713
H	-5.51348	2.56845	0.96446
H	-6.27552	4.11265	0.55706
B	0.30911	0.61625	1.35961
O	-0.25590	1.86235	1.63260
O	0.46647	-0.10829	2.53189
C	0.20183	0.76833	3.65763
C	-0.71277	1.86493	3.00933
C	1.55869	1.30994	4.12079
C	-0.45357	-0.04524	4.76835
C	-2.19597	1.47191	2.98305
C	-0.55158	3.26806	3.58301
H	-2.32803	0.46702	2.57137
H	-2.73691	2.17206	2.33973
H	-2.64297	1.50357	3.98155
H	0.47145	3.63129	3.47430
H	-0.81987	3.28639	4.64481
H	-1.21383	3.96151	3.05424
H	2.05019	1.84808	3.30688
H	2.19875	0.46817	4.40086
H	1.46166	1.97218	4.98678
H	-1.34013	-0.57316	4.41044
H	-0.74334	0.60016	5.60464
H	0.25309	-0.79149	5.14535
B	2.17072	-1.25646	0.09469
B	1.91850	1.45141	-0.47768
O	1.99169	2.44113	-1.46784
O	2.79485	1.76243	0.55883
O	2.03529	-2.35187	0.95590
O	3.52111	-1.10129	-0.23872
C	3.34376	-2.71339	1.45853
C	4.28508	-2.20158	0.31179
C	3.37800	-4.21808	1.70494
C	5.63707	-1.66762	0.77658
C	4.48438	-3.23358	-0.80488
H	3.52585	-3.62438	-1.15643
H	5.10565	-4.07159	-0.47353
H	4.98452	-2.75268	-1.65134
H	5.51931	-0.82004	1.45466
H	6.21628	-1.32809	-0.08839
H	6.21323	-2.44850	1.28475
H	3.08276	-4.77796	0.81488
H	2.68364	-4.47522	2.51158
H	4.38030	-4.54157	2.00561
C	3.54101	-1.95626	2.77800
H	3.51103	-0.87688	2.61358
H	4.48967	-2.21848	3.25728
H	2.72395	-2.21325	3.45731
C	3.13288	3.29349	-1.19142
C	3.31885	3.09843	0.35415
C	2.80069	4.71453	-1.63295
C	4.30439	2.73948	-2.01122
C	4.76506	3.13098	0.83876
C	2.46019	4.05810	1.18600
H	4.54370	1.71738	-1.70430
H	5.20137	3.35796	-1.90807
H	4.01975	2.71906	-3.06765
H	1.87103	5.06654	-1.18066
H	2.68059	4.74459	-2.72073
H	3.60614	5.40528	-1.36197
H	5.36336	2.34788	0.36893
H	4.79327	2.97151	1.92144
H	5.22592	4.10178	0.62691
H	1.40874	3.98968	0.89799
H	2.79879	5.09364	1.08312
H	2.53600	3.78036	2.24040
C	2.02099	-2.66433	-4.13810
C	1.98167	-1.80896	-3.03390
C	0.85030	-2.94834	-4.84521
C	0.78923	-1.21116	-2.57034
C	-0.34796	-2.35830	-4.44033
C	-0.34018	-1.50521	-3.34105
F	-1.54853	-0.95544	-3.00808
H	2.96623	-3.10521	-4.44437
H	2.89845	-1.59254	-2.49719
H	0.86453	-3.61348	-5.70396
H	-1.28332	-2.54438	-4.96002
H	1.27315	0.21223	-2.00850

Sum of electronic and zero-point Energies= -2478.909962

Sum of electronic and thermal Energies= -2478.850944

Sum of electronic and thermal Enthalpies= -2478.850000

Sum of electronic and thermal Free Energies= -2479.003199

Imaginary frequency= -730.53

TS2-3-F-OD-4

C	-1.31144	2.46346	-1.17549
C	-2.46361	3.24532	-1.20448
C	-3.69134	2.69146	-0.82473

C	-3.67538	1.34335	-0.44075
C	-2.48768	0.60949	-0.44178
N	-1.31433	1.17774	-0.80529
H	-2.37604	4.27918	-1.51400
C	-5.00516	3.48242	-0.79601
H	-4.59483	0.87074	-0.12080
H	-0.34114	2.87049	-1.43846
C	-2.41651	-0.80584	0.00612
N	-1.17711	-1.33199	0.13287
C	-3.55519	-1.55845	0.31905
C	-3.44292	-2.86650	0.79556
C	-2.13928	-3.36483	0.95183
C	-1.04724	-2.58044	0.61419
H	-4.53037	-1.11485	0.18066
C	-4.65567	-3.73540	1.14830
H	-1.96161	-4.36440	1.33239
Ir	0.55360	-0.11319	-0.53248
H	-0.03025	-2.93161	0.73538
C	-5.98855	-3.00829	0.89950
C	-4.57631	-4.12162	2.64340
C	-4.62406	-5.01579	0.28213
H	-4.67032	-4.76937	-0.78416
H	-5.48390	-5.65054	0.52302
H	-3.71704	-5.60284	0.45477
H	-6.07957	-2.10360	1.51042
H	-6.82003	-3.66944	1.16342
H	-6.10952	-2.72869	-0.15262
H	-4.59020	-3.23029	3.28010
H	-3.66696	-4.68588	2.87106
H	-5.43446	-4.74684	2.91354
C	-4.81375	4.93830	-1.25481
C	-5.55456	3.49051	0.64956
C	-6.02815	2.80083	-1.73354
H	-4.11871	5.48125	-0.60557
H	-5.77469	5.46154	-1.22144
H	-4.44108	4.99494	-2.28308
H	-5.65944	2.77606	-2.76467
H	-6.97252	3.35607	-1.72277
H	-6.24287	1.77258	-1.42656
H	-4.84100	3.95672	1.33761
H	-5.76400	2.47985	1.01367
H	-6.48960	4.05999	0.69057
B	0.51502	0.58744	1.46244
O	0.30000	1.92595	1.80820
O	0.46548	-0.20804	2.59903
C	0.42233	0.64966	3.76850
C	-0.17085	1.97425	3.17863
C	1.86626	0.80551	4.25874
C	-0.43249	-0.02125	4.83821
C	-1.70457	1.97180	3.11570
C	0.32629	3.25717	3.83533
H	-2.07588	1.05309	2.65245
H	-2.03453	2.81509	2.50141
H	-2.15432	2.07018	4.10859
H	1.41089	3.35280	3.76425
H	0.04085	3.28584	4.89244
H	-0.12259	4.12441	3.33998
H	2.48571	1.27513	3.49013
H	2.27943	-0.18596	4.46569
H	1.92391	1.40164	5.17495
H	-1.41903	-0.28936	4.45383
H	-0.56067	0.63785	5.70365
H	0.05629	-0.93899	5.18065
B	2.10294	-1.37496	-0.11863
B	1.99589	1.37640	-0.51345
O	1.88705	2.54425	-1.27704
O	3.16965	1.41035	0.23530
O	2.16331	-2.28382	0.94286
O	3.27291	-1.47193	-0.88341
C	3.53498	-2.72672	1.07720
C	4.07878	-2.56354	-0.38529
C	3.54612	-4.15140	1.61913
C	5.55037	-2.16925	-0.48151
C	3.80359	-3.78458	-1.27130
H	2.75459	-4.08043	-1.21487
H	4.43205	-4.63723	-0.99421
H	4.02153	-3.52202	-2.31143
H	5.73866	-1.21008	0.00469
H	5.83997	-2.07587	-1.53345
H	6.19088	-2.92952	-0.02094
H	2.93811	-4.81844	1.00387
H	3.13897	-4.16427	2.63557
H	4.56722	-4.54601	1.65844
C	4.20624	-1.76756	2.07011
H	4.17942	-0.74321	1.68728
H	5.24429	-2.04880	2.27498
H	3.64940	-1.78989	3.01144
C	3.14274	3.26852	-1.20525
C	3.75775	2.73089	0.13602
C	2.84624	4.76412	-1.22895
C	3.95356	2.86695	-2.44302
C	5.27663	2.58778	0.13675
C	3.29858	3.52158	1.36626
H	4.16049	1.79285	-2.44098
H	4.90298	3.40822	-2.50122
H	3.37041	3.09790	-3.33982

H	2.13795	5.04355	-0.44617
H	2.40985	5.03908	-2.19477
H	3.76455	5.34556	-1.09485
H	5.61709	1.90342	-0.64290
H	5.60650	2.18918	1.10160
H	5.76049	3.55916	-0.01202
H	2.20922	3.58256	1.39924
H	3.72398	4.52994	1.38260
H	3.63135	2.99593	2.26633
C	-0.27517	-2.82571	-4.03027
C	0.21172	-2.24710	-2.86357
C	-0.79714	-1.99609	-5.02541
C	0.20083	-0.87515	-2.60031
C	-0.82249	-0.61404	-4.82297
C	-0.32631	-0.07385	-3.63279
H	-0.34791	1.00343	-3.49018
H	-0.24577	-3.90552	-4.14209
F	0.68010	-3.10972	-1.91003
H	-1.17825	-2.42934	-5.94565
H	-1.22300	0.04344	-5.59014
H	1.33718	-0.03188	-1.95154

Sum of electronic and zero-point Energies= -2478.913466

Sum of electronic and thermal Energies= -2478.854412

Sum of electronic and thermal Enthalpies= -2478.853468

Sum of electronic and thermal Free Energies= -2479.006763

Imaginary frequency= -829.40

TS2-3-F-MD-2-HBS

C	0.67379	-2.71748	-0.59783
C	1.60426	-3.71119	-0.30967
C	2.89207	-3.36281	0.10906
C	3.17853	-1.99204	0.16011
C	2.21504	-1.03765	-0.16869
N	0.95624	-1.40867	-0.51627
H	1.29022	-4.74401	-0.39187
C	3.95004	-4.38470	0.53962
H	4.15752	-1.66483	0.48424
H	-0.34666	-2.95528	-0.87290
C	2.48651	0.41976	-0.12038
N	1.41688	1.23077	-0.25825
C	3.77732	0.93493	0.05903
C	3.99594	2.31237	0.12790
C	2.86063	3.12886	0.00380
C	1.61090	2.55814	-0.19052
H	4.61010	0.25052	0.13228
C	5.38393	2.93073	0.33188
H	2.93666	4.20955	0.05210
Ir	-0.60297	0.21269	-0.61097
H	0.71593	3.16128	-0.28811
C	6.49129	1.86604	0.41798
C	5.37639	3.74317	1.64730
C	5.69815	3.87148	-0.85406
H	5.69665	3.32191	-1.80158
H	6.68882	4.32031	-0.72206
H	4.97192	4.68593	-0.93426
H	6.33732	1.18473	1.26173
H	7.45907	2.35664	0.56264
H	6.55595	1.27109	-0.49948
H	5.15373	3.09906	2.50495
H	4.63266	4.54542	1.62499
H	6.35842	4.20084	1.81026
C	3.45547	-5.83198	0.37582
C	4.28313	-4.14219	2.03074
C	5.22578	-4.19938	-0.31279
H	2.57245	-6.03225	0.99175
H	4.24215	-6.52506	0.69056
H	3.20834	-6.06084	-0.66635
H	5.01293	-4.35315	-1.37617
H	5.98592	-4.92730	-0.00894
H	5.65724	-3.20069	-0.19474
H	3.39026	-4.25772	2.65496
H	4.68567	-3.13836	2.19909
H	5.03300	-4.86550	2.36972
B	-0.68518	-0.26376	1.45101
O	-1.27641	-1.40604	1.98247
O	0.03159	0.40978	2.43950
C	-0.26139	-0.20331	3.72439
C	-0.71896	-1.64188	3.30074
C	-1.38549	0.61615	4.36559
C	0.99535	-0.15250	4.58622
C	0.45415	-2.61496	3.11719
C	-1.79350	-2.26881	4.18180
H	1.23019	-2.17766	2.48308
H	0.08959	-3.52142	2.62581
H	0.90124	-2.89722	4.07556
H	-2.70154	-1.66274	4.19757
H	-1.43418	-2.38993	5.20937
H	-2.05524	-3.25902	3.79495
H	-2.27414	0.61004	3.73063
H	-1.05242	1.65281	4.47209
H	-1.64822	0.23777	5.35836

H 1.85173 -0.59592 4.07342
H 0.84070 -0.68223 5.53236
H 1.24269 0.88862 4.81751
B -1.73337 1.74087 0.20314
B -2.30457 -0.90728 -0.80936
O -2.30158 -2.29866 -1.00089
O -3.62304 -0.44915 -0.83763
O -1.45358 3.08829 -0.07925
O -2.75777 1.66814 1.14156
C -2.11456 3.90583 0.92369
C -3.31993 2.99164 1.32272
C -2.49017 5.24510 0.30220
C -3.79291 3.14043 2.76427
C -4.50843 3.11416 0.36142
H -4.18182 3.02387 -0.67824
H -5.03264 4.06708 0.48503
H -5.21251 2.30230 0.56424
H -2.99536 2.92426 3.47599
H -4.61560 2.44416 2.95661
H -4.15924 4.15661 2.94589
H -3.07275 5.11456 -0.61208
H -1.58396 5.80482 0.04852
H -3.07375 5.84743 1.00663
C -1.11241 4.10243 2.06838
H -0.82934 3.13844 2.50049
H -1.51723 4.74427 2.85690
H -0.20798 4.57659 1.67455
C -3.65066 -2.74877 -1.28100
C -4.50558 -1.58328 -0.67544
C -3.85547 -4.11144 -0.62723
C -3.78546 -2.86547 -2.80348
C -5.81782 -1.30020 -1.39825
C -4.74940 -1.74416 0.83170
H -3.65111 -1.89248 -3.28395
H -4.76074 -3.26798 -3.09468
H -3.01040 -3.54105 -3.17904
H -3.60546 -4.08531 0.43526
H -3.21083 -4.85464 -1.10838
H -4.89355 -4.44373 -0.73583
H -5.65172 -1.02943 -2.44318
H -6.33337 -0.46556 -0.91224
H -6.47848 -2.17330 -1.36320
H -3.80704 -1.92412 1.35679
H -5.44701 -2.55974 1.04790
H -5.17550 -0.81369 1.21826
C 1.00302 1.31716 -4.66512
C 0.55842 1.41909 -3.35271
C 0.67681 0.25015 -5.49263
C -0.24684 0.40445 -2.80453
C -0.14312 -0.74948 -4.96110
C -0.60868 -0.66790 -3.64572
H -1.23947 -1.45970 -3.25533
F 1.79176 2.30943 -5.16290
H 0.85227 2.28571 -2.76952
H 1.04723 0.21765 -6.51182
H -0.42128 -1.59783 -5.58189
H -1.29240 1.06763 -1.80906
Sum of electronic and zero-point Energies= -2478.909070
Sum of electronic and thermal Energies= -2478.850154
Sum of electronic and thermal Enthalpies= -2478.849210
Sum of electronic and thermal Free Energies= -2479.001545
Imaginary Frequency = -831.94

TS2-3-F-MD-4

C -1.23145 2.34894 -1.33990
C -2.34017 3.19168 -1.30785
C -3.54868 2.73502 -0.77026
C -3.56616 1.40992 -0.31272
C -2.42582 0.60925 -0.38829
N -1.26190 1.08890 -0.88851
H -2.22992 4.19954 -1.68782
C -4.79951 3.61048 -0.62881
H -4.46705 1.01144 0.13569
H -0.27060 2.68679 -1.71192
C -2.38946 -0.77901 0.13584
N -1.16351 -1.32458 0.29771
C -3.54766 -1.48923 0.47384
C -3.46965 -2.77396 1.01627
C -2.17859 -3.29065 1.21300
C -1.06758 -2.54840 0.84400
H -4.51007 -1.03189 0.29432
C -4.70448 -3.60143 1.39107
H -2.02571 -4.27292 1.64558
Ir 0.58089 -0.22723 -0.49848
H -0.06097 -2.91798 0.99692
C -6.01831 -2.85986 1.08942
C -4.65387 -3.92067 2.90304
C -4.68711 -4.92012 0.58375
H -4.71234 -4.72105 -0.49305
H -5.56363 -5.52560 0.83933
H -3.79533 -5.51722 0.79679

H	-6.09877	-1.92595	1.65623
H	-6.86680	-3.49119	1.37158
H	-6.11904	-2.62743	0.02379
H	-4.65761	-3.00125	3.49852
H	-3.76030	-4.49303	3.16989
H	-5.52892	-4.51503	3.18816
C	-4.59029	5.01724	-1.21470
C	-5.13743	3.74745	0.87458
C	-5.98184	2.94038	-1.36508
H	-3.78776	5.55678	-0.70079
H	-5.50854	5.60175	-1.09862
H	-4.35243	4.98089	-2.28315
H	-5.76351	2.82213	-2.43189
H	-6.88070	3.55904	-1.26809
H	-6.21338	1.95226	-0.95552
H	-4.30731	4.20595	1.42294
H	-5.35073	2.77738	1.33428
H	-6.02257	4.38025	1.00290
B	0.53853	0.76204	1.37990
O	0.67352	2.13948	1.57304
O	0.14236	0.15852	2.56810
C	0.24064	1.13056	3.64046
C	0.10741	2.48348	2.86399
C	1.61917	0.94483	4.28599
C	-0.86382	0.85593	4.65487
C	-1.34995	2.89312	2.60981
C	0.88641	3.65171	3.45823
H	-1.92145	2.06370	2.18456
H	-1.36389	3.71582	1.88912
H	-1.84520	3.22795	3.52660
H	1.95598	3.44056	3.50752
H	0.52795	3.88089	4.46757
H	0.74650	4.54404	2.83949
H	2.41520	1.14207	3.56246
H	1.71622	-0.09225	4.62031
H	1.75601	1.60151	5.15094
H	-1.84608	0.82460	4.17822
H	-0.87712	1.62536	5.43430
H	-0.69166	-0.11178	5.13694
B	2.08518	-1.44336	0.14553
B	2.08054	1.19757	-0.70608
O	1.93449	2.33364	-1.50651
O	3.34191	1.18746	-0.12041
O	2.18588	-2.01130	1.42079
O	3.15727	-1.87612	-0.64321
C	3.53115	-2.52577	1.57888
C	3.93462	-2.84633	0.09754
C	3.49669	-3.72630	2.51788
C	5.41116	-2.63939	-0.22715
C	3.48499	-4.24015	-0.35754
H	2.43186	-4.41114	-0.11580
H	4.08125	-5.03175	0.10731
H	3.60146	-4.31528	-1.44297
H	5.71070	-1.60152	-0.06814
H	5.59755	-2.88675	-1.27745
H	6.04251	-3.28735	0.39063
H	2.78623	-4.48352	2.17880
H	3.19263	-3.40335	3.51886
H	4.48719	-4.18722	2.59707
C	4.36361	-1.39082	2.19102
H	4.36078	-0.51837	1.53159
H	5.39668	-1.69853	2.38206
H	3.91024	-1.09686	3.14255
C	3.22466	2.98719	-1.62957
C	3.98492	2.46480	-0.35738
C	3.00632	4.49561	-1.67723
C	3.84187	2.49687	-2.94473
C	5.47915	2.22687	-0.55349
C	3.74320	3.32709	0.88634
H	3.99023	1.41315	-2.92571
H	4.80246	2.97967	-3.14920
H	3.15772	2.72993	-3.76645
H	2.42485	4.84231	-0.82050
H	2.45989	4.76172	-2.58799
H	3.96365	5.02732	-1.68962
H	5.67015	1.48389	-1.33054
H	5.91841	1.85872	0.37927
H	5.99002	3.15743	-0.82326
H	2.67443	3.47023	1.05166
H	4.23852	4.29998	0.80686
H	4.14994	2.80540	1.75847
C	0.08430	-3.49813	-3.56246
C	0.58308	-2.70953	-2.52124
C	-0.77871	-2.95668	-4.51925
C	0.21469	-1.35703	-2.38126
C	-1.10749	-1.61277	-4.39465
C	-0.62994	-0.81010	-3.36613
H	-0.93010	0.23225	-3.33603
H	0.37307	-4.54403	-3.63571
H	1.27211	-3.14597	-1.80824
H	-1.17737	-3.54193	-5.34128
F	-1.93599	-1.05668	-5.32265
H	1.35289	-0.27569	-1.92018

Sum of electronic and zero-point Energies= -2478.908441

Sum of electronic and thermal Energies= -2478.849395
Sum of electronic and thermal Enthalpies= -2478.848451
Sum of electronic and thermal Free Energies= -2479.002085

Imaginary frequency = -814.72

TS2-3-F-MD-5-HBS
C 1.30519 -2.25776 -1.58137
C 2.44495 -3.05498 -1.65434
C 3.65868 -2.58555 -1.13992
C 3.64777 -1.29401 -0.59423
C 2.47513 -0.53742 -0.56505
N 1.30978 -1.03052 -1.04708
H 2.35594 -4.03958 -2.09572
C 4.94593 -3.41822 -1.11275
H 4.55315 -0.89058 -0.15934
H 0.34138 -2.60818 -1.93394
C 2.40694 0.80930 0.05641
N 1.16870 1.28899 0.31022
C 3.54997 1.54441 0.39267
C 3.44569 2.78297 1.02985
C 2.14562 3.22822 1.31973
C 1.04917 2.46657 0.94624
H 4.52075 1.14486 0.13648
C 4.66307 3.63299 1.41130
H 1.97415 4.17005 1.82868
Ir -0.56878 0.17859 -0.48894
H 0.03651 2.78093 1.16759
C 5.98906 2.97736 0.98792
C 4.67598 3.82717 2.94513
C 4.55201 5.01015 0.71718
H 4.52889 4.89955 -0.37232
H 5.41658 5.63016 0.97863
H 3.65047 5.55028 1.02159
H 6.13790 2.00711 1.47411
H 6.82421 3.62280 1.27782
H 6.04367 2.83282 -0.09649
H 4.75020 2.86423 3.46203
H 3.77271 4.33265 3.29992
H 5.53758 4.43784 3.23672
C 4.76194 -4.79010 -1.78392
C 5.35676 -3.64089 0.36191
C 6.06777 -2.65458 -1.85229
H 4.00344 -5.39395 -1.27467
H 5.70503 -5.34464 -1.74718
H 4.47510 -4.69207 -2.83641
H 5.79587 -2.47301 -2.89771
H 6.99181 -3.24280 -1.83811
H 6.28238 -1.68835 -1.38557
H 4.57186 -4.17177 0.91157
H 5.54927 -2.69539 0.87841
H 6.27242 -4.24068 0.40885
B -0.40303 -0.94299 1.30644
O -0.45608 -2.33697 1.39208
O -0.00105 -0.41301 2.52718
C -0.01378 -1.46977 3.52082
C 0.16611 -2.74910 2.63617
C -1.37971 -1.40992 4.21513
C 1.10581 -1.21452 4.52351
C 1.63418 -3.05945 2.31234
C -0.53325 -4.00031 3.15585
H 2.15001 -2.17051 1.93948
H 1.66799 -3.82147 1.52840
H 2.17316 -3.43787 3.18652
H -1.61018 -3.85120 3.24964
H -0.13297 -4.28815 4.13396
H -0.36651 -4.83265 2.46438
H -2.18617 -1.59245 3.49928
H -1.51945 -0.40870 4.63303
H -1.45634 -2.13821 5.02865
H 2.06955 -1.09242 4.02418
H 1.18397 -2.04025 5.23893
H 0.89821 -0.29791 5.08498
B -2.08574 1.28323 0.30448
B -2.02151 -1.28602 -0.73967
O -1.87404 -2.34014 -1.64555
O -3.24706 -1.38511 -0.09005
O -2.14026 1.76590 1.61707
O -3.21239 1.72182 -0.40033
C -3.49494 2.21056 1.87568
C -3.98631 2.61014 0.44107
C -3.45972 3.34713 2.89112
C -5.46856 2.36477 0.17494
C -3.61232 4.04764 0.05989
H -2.55600 4.24574 0.26410
H -4.21436 4.78212 0.60424
H -3.78404 4.18998 -1.01137
H -5.72032 1.30731 0.27775
H -5.71697 2.67258 -0.84613
H -6.09172 2.94468 0.86446
H -2.79711 4.15421 2.57068
H -3.09368 2.97226 3.85246
H -4.46210 3.75988 3.04815

C	-4.24959	1.00327	2.44926
H	-4.24612	0.17641	1.73342
H	-5.28303	1.25349	2.70968
H	-3.73775	0.66695	3.35614
C	-3.14230	-3.03683	-1.76029
C	-3.84916	-2.66508	-0.40726
C	-2.86785	-4.52358	-1.95858
C	-3.85194	-2.45784	-2.99004
C	-5.36073	-2.48022	-0.50034
C	-3.49983	-3.62153	0.73806
H	-4.04148	-1.38788	-2.86320
H	-4.80288	-2.96230	-3.18716
H	-3.20680	-2.58525	-3.86479
H	-2.22469	-4.91966	-1.17004
H	-2.36493	-4.68208	-2.91818
H	-3.80256	-5.09419	-1.96856
H	-5.62651	-1.68121	-1.19551
H	-5.76018	-2.21645	0.48422
H	-5.84753	-3.40593	-0.82561
H	-2.41813	-3.72790	0.83185
H	-3.95710	-4.60605	0.59740
H	-3.87710	-3.19898	1.67467
C	-0.36474	3.64560	-3.31955
C	-0.78958	2.78168	-2.31778
C	0.48199	3.25475	-4.34900
C	-0.33640	1.45041	-2.30123
C	0.90556	1.92274	-4.36103
C	0.49738	1.03581	-3.36063
H	0.83862	0.00579	-3.39738
F	-0.80317	4.93561	-3.29240
H	-1.47410	3.14965	-1.56398
H	0.78039	3.96699	-5.11108
H	1.55698	1.57669	-5.16003
H	-1.38964	0.27877	-1.87980

Sum of electronic and zero-point Energies= -2478.908739
Sum of electronic and thermal Energies= -2478.849637
Sum of electronic and thermal Enthalpies= -2478.848693
Sum of electronic and thermal Free Energies= -2479.002847
Imaginary frequency = -813.65

Structures for trisborylhydrazone mechanism were optimized with different configurations using Beg as the ligand and the most stable conformer was then optimized with Bpin to make comparisons.

Substrate Metal Complexes

Ortho

2a-OT-HBS-3

Ir	-1.47880	-0.38164	-0.22320
N	-0.11524	1.49609	0.30330
C	-0.74966	2.55045	0.86029
N	0.01809	-0.10541	-2.06525
C	-0.27819	3.85039	0.83118
C	1.08408	1.75357	-0.27879
C	0.94959	4.14031	0.18466
C	1.62938	3.02645	-0.36842
H	-1.69149	2.31750	1.34504
H	-0.86590	4.62326	1.30944
N	1.45768	5.40235	0.11332
H	2.59966	3.13649	-0.83100
C	1.84172	0.58698	-0.83903
N	1.34198	-0.27722	-1.65539
C	3.25120	0.35706	-0.39516
C	4.02720	-0.61505	-1.02541
N	3.68053	1.09099	0.65185
C	5.32383	-0.90600	-0.54509
C	4.92394	0.83846	1.08204
C	0.74622	6.51134	0.73779
C	2.74984	5.63703	-0.52107
H	3.55568	5.09510	-0.00978
H	2.97806	6.70207	-0.48373
H	2.74070	5.32833	-1.57364
H	-0.25822	6.63136	0.31358
H	1.29879	7.43434	0.56372
H	0.64746	6.37030	1.82185
C	5.77240	-0.12288	0.54927
N	6.08884	-1.89682	-1.10300
H	5.26590	1.43570	1.92629
C	5.46166	-2.84497	-2.01985
C	7.36639	-2.24967	-0.49696
H	8.03098	-1.38037	-0.45088
H	7.85588	-3.00694	-1.11018
H	7.25044	-2.64952	0.52117
H	5.14286	-2.35257	-2.94577
H	4.58440	-3.32540	-1.56618
H	6.18353	-3.61775	-2.28465

H	6.75184	-0.26294	0.98833
H	3.59819	-1.15927	-1.85301
B	-2.71415	-0.38899	1.38079
O	-3.33786	-1.50784	1.97266
O	-3.02460	0.75650	2.13973
C	-3.94005	-1.10831	3.21198
C	-4.02028	0.42022	3.11403
B	-2.52234	-1.99926	-0.84380
O	-1.99925	-3.31094	-0.73136
O	-3.76969	-2.06124	-1.48449
C	-3.02148	-4.24910	-1.09469
C	-4.02425	-3.40978	-1.89725
H	-5.00473	0.75447	2.75770
H	-3.80530	0.92268	4.06307
H	-3.30071	-1.42911	4.04709
H	-4.91985	-1.58361	3.32494
H	-3.47515	-4.66469	-0.18421
H	-2.58872	-5.07208	-1.67330
H	-3.85504	-3.49976	-2.98011
H	-5.06610	-3.67697	-1.69003
H	-0.23415	0.85004	-2.33125
H	-0.15545	-0.72891	-2.84676
C	2.68230	-1.92910	1.86942
C	1.78402	-2.55775	1.01717
C	0.42240	-2.64107	1.28567
F	2.25367	-3.11186	-0.13394
C	-0.05017	-2.06630	2.47184
C	0.82636	-1.41295	3.34398
C	2.18816	-1.34519	3.03895
H	3.73259	-1.88005	1.60871
H	0.44814	-0.95995	4.25567
H	2.87534	-0.83476	3.70750
B	-2.77693	0.78732	-1.16741
O	-4.10700	1.08694	-0.87385
O	-2.36013	1.52900	-2.30157
C	-3.50637	2.18985	-2.85913
C	-4.54323	2.15300	-1.72573
H	-4.55537	3.09307	-1.15622
H	-5.55842	1.95511	-2.08550
H	-3.84976	1.63725	-3.74422
H	-3.24150	3.20718	-3.16513
H	-0.24961	-3.13574	0.59140
H	-1.11007	-2.12717	2.69158

Sum of electronic and zero-point Energies=
-2109.615937

Sum of electronic and thermal Energies=
-2109.571022

Sum of electronic and thermal Enthalpies=
-2109.570078

Sum of electronic and thermal Free Energies= -2109.698827

2a-F-OT-HBS-1-Bpin-1

Ir	0.62184	-0.13367	-0.06096
N	-0.90838	1.60180	-0.34798
C	-0.40650	2.78906	-0.75005
N	-0.82743	-0.37884	1.75631
C	-1.02094	4.00812	-0.53044
C	-2.11489	1.62967	0.27268
C	-2.26257	4.05791	0.15328
C	-2.80187	2.80561	0.54095
H	0.55164	2.73610	-1.25715
H	-0.53359	4.90513	-0.88978
N	-2.90780	5.23038	0.40913
H	-3.76660	2.73692	1.02402
C	-2.73231	0.32016	0.66877
N	-2.14182	-0.61020	1.33982
C	-4.12384	0.03236	0.21075
C	-4.89475	-0.92212	0.87274
N	-4.53700	0.70645	-0.88192
C	-6.17909	-1.25589	0.38166
C	-5.75659	0.39233	-1.34095
C	-2.31834	6.49491	-0.01456
C	-4.19297	5.22418	1.09827
H	-4.94762	4.65861	0.53736
H	-4.54721	6.24911	1.20445
H	-4.10927	4.78632	2.10108
H	-1.33369	6.65162	0.44355
H	-2.96843	7.31413	0.29195
H	-2.20185	6.54068	-1.10479
C	-6.60039	-0.55674	-0.77948
N	-6.96417	-2.19287	0.99455
H	-6.08527	0.93252	-2.22771
C	-8.23749	-2.57787	0.39924
C	-6.44130	-2.95224	2.12365
H	-7.21073	-3.63509	2.48335
H	-6.16363	-2.29168	2.95345
H	-5.55753	-3.54357	1.84731
H	-8.91690	-1.72057	0.32282
H	-8.71587	-3.32822	1.02894
H	-8.10883	-3.00438	-0.60505
H	-7.56673	-0.73619	-1.23332
H	-4.48061	-1.40480	1.74619
B	1.78976	0.22437	-1.67233

O	2.38087	1.46772	-1.98426
O	2.02970	-0.66397	-2.73665
C	2.81418	1.44991	-3.36315
C	3.01601	-0.08274	-3.61805
B	1.84887	-1.62275	0.55272
O	2.71211	-2.44710	-0.17679
O	1.91728	-1.98471	1.91993
C	3.59752	-3.12226	0.74575
C	2.73859	-3.16792	2.05781
C	2.73985	-0.54493	-5.04537
C	4.38951	-0.58677	-3.15504
C	4.07303	2.30108	-3.49881
C	1.67790	2.04919	-4.20294
C	4.84581	-2.23887	0.87907
C	3.96923	-4.48430	0.16911
C	1.79571	-4.37580	2.11455
C	3.53759	-3.06360	3.35386
H	-0.67554	0.52261	2.21724
H	-0.53608	-1.13159	2.37262
C	-2.70116	-3.07676	-1.06854
C	-1.32060	-3.20789	-0.99228
C	-0.44798	-2.55318	-1.85461
F	-0.80312	-3.99739	-0.00982
C	-1.00157	-1.70539	-2.82273
C	-2.38725	-1.54809	-2.92283
C	-3.23349	-2.23931	-2.05131
H	-3.33213	-3.60375	-0.36124
H	-2.80682	-0.87957	-3.66853
H	-4.30916	-2.10641	-2.11233
H	-0.32508	-1.16205	-3.47299
H	0.62527	-2.66700	-1.75404
B	1.84271	0.91305	1.10000
O	3.23743	0.98882	1.10956
O	1.32204	1.67648	2.16927
C	2.41989	2.01103	3.05653
C	3.64187	1.98818	2.07302
C	3.81969	3.30702	1.31047
C	4.96397	1.55743	2.69995
C	2.48816	0.90265	4.11443
C	2.13905	3.35987	3.70855
H	1.71191	-0.33060	-5.34617
H	2.89342	-1.62652	-5.11975
H	3.41914	-0.05706	-5.75302
H	4.60298	-0.24776	-2.13771
H	5.19369	-0.24890	-3.81688
H	4.38003	-1.68056	-3.14986
H	3.83465	3.35082	-3.29756
H	4.48255	2.23543	-4.51286
H	4.84291	1.99036	-2.78947
H	0.76886	1.44707	-4.11206
H	1.94521	2.12406	-5.26184
H	1.45518	3.05565	-3.83476
H	5.60022	-2.68738	1.53375
H	4.57494	-1.24999	1.25896
H	5.28775	-2.10533	-0.11339
H	4.57653	-5.05729	0.87840
H	4.55445	-4.34992	-0.74646
H	3.08161	-5.06879	-0.08267
H	1.08819	-4.23413	2.93811
H	2.33960	-5.31009	2.28769
H	1.22248	-4.46647	1.18953
H	2.85743	-3.08487	4.21193
H	4.10749	-2.13332	3.39946
H	4.23318	-3.90418	3.45289
H	4.19895	4.10468	1.95721
H	2.87297	3.63164	0.86913
H	4.53439	3.15081	0.49705
H	5.25964	2.24598	3.49890
H	5.75195	1.56077	1.93994
H	4.90029	0.54887	3.11361
H	1.52800	0.85558	4.63897
H	3.27209	1.09028	4.85489
H	2.66177	-0.06728	3.64046
H	1.26874	3.27960	4.36826
H	1.92662	4.12918	2.96303
H	2.99284	3.68410	4.31333

Sum of electronic and zero-point Energies= -2581.188152

Sum of electronic and thermal Energies= -2581.127420

Sum of electronic and thermal Enthalpies= -2581.126476

Sum of electronic and thermal Free Energies= -2581.286229

Meta

2a-MT-HBS-13

Ir	-1.50750	-0.37137	-0.20662
N	-0.18780	1.52318	0.34340
C	-0.84933	2.57231	0.87824
N	0.02514	-0.08589	-2.01690
C	-0.39509	3.87817	0.84847
C	1.02091	1.79146	-0.21075
C	0.84337	4.17966	0.22715
C	1.55303	3.07036	-0.29710

H -1.79828 2.32939 1.34394
H -1.00441 4.64714 1.30548
N 1.33256 5.44871 0.15262
H 2.53279 3.18995 -0.73751
C 1.80555 0.62991 -0.74328
N 1.34049 -0.24495 -1.56853
C 3.20356 0.43004 -0.25674
C 4.05693 -0.44947 -0.92047
N 3.54597 1.10969 0.85745
C 5.35194 -0.69668 -0.40879
C 4.78043 0.88814 1.32836
C 0.58308 6.55503 0.73603
C 2.62618 5.70012 -0.47206
H 3.43677 5.18050 0.05446
H 2.83377 6.76971 -0.44589
H 2.63391 5.37756 -1.52061
H -0.40786 6.65449 0.27582
H 1.12827 7.48368 0.56923
H 0.44891 6.42650 1.81764
C 5.70450 0.01885 0.76448
N 6.20871 -1.57437 -1.01425
H 5.05164 1.43586 2.22998
C 5.72223 -2.42860 -2.09292
C 7.50619 -1.85372 -0.41363
H 8.08884 -0.93381 -0.28908
H 8.07004 -2.51654 -1.07049
H 7.41366 -2.33791 0.56909
H 5.43025 -1.83760 -2.96948
H 4.85814 -3.02411 -1.77452
H 6.51789 -3.10854 -2.39771
H 6.67207 -0.09947 1.23508
H 3.69526 -0.95218 -1.80526
B -2.71447 -0.42042 1.41530
O -3.22932 -1.57735 2.03559
O -3.08788 0.70660 2.17220
C -3.82602 -1.21439 3.28839
C -4.01550 0.30554 3.18839
B -2.54717 -1.99865 -0.81812
O -2.01834 -3.30476 -0.70512
O -3.81027 -2.06804 -1.42860
C -2.90303 -4.23065 -1.34924
C -4.20726 -3.44070 -1.53171
H -5.03511 0.56922 2.87430
H -3.79650 0.82693 4.12636
H -3.14718 -1.48804 4.10846
H -4.76847 -1.75452 3.42702
H -3.02876 -5.12464 -0.72879
H -2.47210 -4.53834 -2.31277
H -4.68538 -3.62386 -2.50022
H -4.93428 -3.66943 -0.73982
H -0.22344 0.86733 -2.29359
H -0.11937 -0.71162 -2.80252
C 2.20689 -2.83919 0.81918
C 0.84540 -3.08581 0.69645
C -0.01445 -2.54517 1.65800
H 0.45345 -3.66862 -0.12870
C 0.49284 -1.75201 2.69420
C 1.86765 -1.51942 2.78646
C 2.74174 -2.07297 1.84680
F 3.05212 -3.35875 -0.11283
H 2.26756 -0.89799 3.58234
H 3.80983 -1.89151 1.88307
H -0.18616 -1.31537 3.42051
H -1.07957 -2.72540 1.57609
B -2.81331 0.79131 -1.14551
O -4.14260 1.09140 -0.84820
O -2.40223 1.52793 -2.28617
C -3.55250 2.18080 -2.84416
C -4.58490 2.14944 -1.70657
H -4.59785 3.09394 -1.14431
H -5.60094 1.94611 -2.06114
H -3.89801 1.62052 -3.72372
H -3.29244 3.19669 -3.15927
Sum of electronic and zero-point Energies= -2109.616448
Sum of electronic and thermal Energies= -2109.571413
Sum of electronic and thermal Enthalpies= -2109.570469
Sum of electronic and thermal Free Energies= -2109.700318

2a-F-MT-HBS-Bpin-1

Ir 0.65909 -0.12502 -0.07662
N -0.76384 1.68433 -0.40405
C -0.18080 2.82393 -0.83525
N -0.75925 -0.20043 1.77851
C -0.68123 4.09133 -0.60120
C -1.94181 1.81712 0.25853
C -1.88605 4.24838 0.13025
C -2.51637 3.04742 0.54363
H 0.75375 2.69055 -1.37082
H -0.13085 4.94259 -0.98019
N -2.41521 5.47243 0.40919

H	-3.46518	3.06233	1.06161
C	-2.63891	0.56127	0.69621
N	-2.08928	-0.37776	1.39024
C	-4.04639	0.33755	0.25405
C	-4.82325	-0.64555	0.86482
N	-4.46884	1.09267	-0.78097
C	-6.11901	-0.92713	0.37428
C	-5.70557	0.83782	-1.23001
C	-1.72001	6.68135	-0.01694
C	-3.63048	5.57971	1.20833
H	-4.47970	5.09169	0.71454
H	-3.87711	6.63233	1.34526
H	-3.50186	5.12739	2.20015
H	-0.72737	6.76215	0.44525
H	-2.30493	7.55315	0.27530
H	-1.59534	6.70723	-1.10613
C	-6.55491	-0.13446	-0.71908
N	-6.89986	-1.90590	0.92554
H	-6.04290	1.44666	-2.06780
C	-6.32931	-2.80560	1.92328
C	-8.18216	-2.23828	0.31853
H	-8.84131	-1.36346	0.28423
H	-8.67612	-3.00186	0.91983
H	-8.06898	-2.62396	-0.70471
H	-6.03963	-2.26084	2.82988
H	-5.44593	-3.32810	1.53683
H	-7.07631	-3.54790	2.20476
H	-7.53144	-0.26851	-1.16651
H	-4.39823	-1.20185	1.68709
B	1.85643	0.11009	-1.68870
O	2.56613	1.28880	-2.00219
O	2.01437	-0.80244	-2.74742
C	3.01608	1.21943	-3.37394
C	3.06086	-0.32722	-3.62339
B	1.74438	-1.71114	0.55930
O	2.57744	-2.59016	-0.14028
O	1.67422	-2.12675	1.91273
C	3.29146	-3.41344	0.81115
C	2.31819	-3.41573	2.04052
C	2.74853	-0.76204	-5.05199
C	4.37216	-0.96890	-3.15076
C	4.35941	1.93365	-3.49142
C	1.96299	1.93230	-4.23299
C	4.61956	-2.70279	1.10342
C	3.54783	-4.78148	0.18746
C	2.99750	-3.49679	3.40394
C	1.22244	-4.48379	1.93124
H	-0.54829	0.70656	2.20311
H	-0.49069	-0.94888	2.41064
C	-2.91516	-2.91773	-1.05927
C	-1.56596	-3.21755	-0.92325
C	-0.64991	-2.54307	-1.73920
H	-1.24813	-3.95394	-0.19285
C	-1.09920	-1.58183	-2.65467
C	-2.46532	-1.30361	-2.76395
C	-3.39100	-1.97892	-1.96624
F	-3.81090	-3.56490	-0.26405
H	-2.81613	-0.55024	-3.46317
H	-4.45313	-1.76870	-2.01695
H	-0.37057	-1.05536	-3.25966
H	0.41194	-2.74715	-1.65502
B	1.96598	0.82307	1.07854
O	3.36163	0.77151	1.10034
O	1.51028	1.63571	2.14323
C	2.62648	1.86147	3.04143
C	3.84733	1.73218	2.06613
C	4.14326	3.03036	1.30482
C	5.12326	1.18885	2.70097
C	2.58345	0.74347	4.09112
C	2.46648	3.22527	3.70257
H	2.62372	-5.23796	-0.17392
H	4.01427	-5.45976	0.91027

Sum of electronic and zero-point Energies= -2581.187174

Sum of electronic and thermal Energies= -2581.127322

Sum of electronic and thermal Enthalpies= -2581.126378

Sum of electronic and thermal Free Energies= -2581.284053

Para

2a-PT-HBS-7

Ir	-1.58165	-0.37988	-0.21875
N	-0.24298	1.50108	0.32465
C	-0.88314	2.54062	0.90199
N	-0.06969	-0.09086	-2.04772
C	-0.41030	3.84011	0.91106
C	0.96245	1.76977	-0.23633
C	0.82405	4.14520	0.28369
C	1.50978	3.04454	-0.28816
H	-1.82768	2.29442	1.37532
H	-1.00035	4.60046	1.40598
N	1.33391	5.40885	0.25007
H	2.48681	3.16508	-0.73402

C 1.73509 0.61597 -0.80298
N 1.25591 -0.25220 -1.62744
C 3.14715 0.42171 -0.35397
C 4.00402 -0.41039 -1.07432
N 3.50322 1.06170 0.77801
C 5.32054 -0.63596 -0.61152
C 4.75964 0.86158 1.20179
C 0.63778 6.49376 0.93231
C 2.65325 5.64974 -0.32343
H 3.43848 5.10807 0.22016
H 2.87494 6.71572 -0.27358
H 2.69026 5.34566 -1.37615
H -0.37687 6.62412 0.53799
H 1.18243 7.42409 0.77242
H 0.56746 6.31696 2.01380
C 5.69111 0.05018 0.57283
N 6.18521 -1.46841 -1.26993
H 5.04152 1.38120 2.11662
C 5.71891 -2.23534 -2.41781
C 7.45529 -1.82467 -0.64919
H 8.09234 -0.94326 -0.51007
H 7.98797 -2.52132 -1.29694
H 7.31144 -2.30442 0.32877
H 5.33734 -1.57461 -3.20416
H 4.92199 -2.94280 -2.14779
H 6.55371 -2.79948 -2.83444
H 6.67739 -0.05366 1.00626
H 3.62988 -0.88810 -1.96812
B -2.76846 -0.42006 1.41952
O -3.20505 -1.58028 2.09071
O -3.18184 0.71155 2.14775
C -4.05195 -1.20229 3.18497
C -3.75790 0.29068 3.39123
B -2.63445 -2.01039 -0.79073
O -2.07937 -3.30898 -0.72008
O -3.93401 -2.09669 -1.31676
C -3.11443 -4.26614 -0.97959
C -4.19960 -3.45267 -1.69615
H -4.65741 0.87711 3.60680
H -3.03479 0.45532 4.20260
H -3.82066 -1.80902 4.06687
H -5.10087 -1.37742 2.90901
H -3.47645 -4.67843 -0.02719
H -2.72325 -5.08968 -1.58668
H -4.12385 -3.54960 -2.78909
H -5.21457 -3.73593 -1.39705
H -0.32300 0.86457 -2.31261
H -0.22862 -0.70975 -2.83595
C 2.23475 -3.16456 0.57740
C 0.83831 -3.14690 0.58500
C 0.14492 -2.43761 1.57240
H 0.27215 -3.67537 -0.17397
C 0.85239 -1.71457 2.53959
C 2.24924 -1.72385 2.54737
C 2.90734 -2.46215 1.56954
H 2.80054 -3.70713 -0.17258
H 2.82585 -1.17495 3.28384
F 4.26495 -2.49555 1.58041
H 0.31470 -1.14502 3.29243
H -0.93985 -2.44747 1.57451
B -2.89452 0.78457 -1.14722
O -4.22867 1.06828 -0.85890
O -2.47997 1.53882 -2.27548
C -3.63002 2.19268 -2.83288
C -4.67180 2.13569 -1.70473
H -4.69686 3.07150 -1.12850
H -5.68334 1.93013 -2.07074
H -3.96376 1.64457 -3.72457
H -3.37444 3.21538 -3.12900
Sum of electronic and zero-point Energies= -2109.614793
Sum of electronic and thermal Energies= -2109.570601
Sum of electronic and thermal Enthalpies= -2109.569656
Sum of electronic and thermal Free Energies= -2109.696473

2a-PT-HBS-Bpin-1

Ir -0.63570 -0.04419 0.03270
N 0.75732 1.74964 0.54509
C 0.18526 2.80847 1.15647
N 0.73356 0.20281 -1.89065
C 0.69188 4.09378 1.12830
C 1.92956 1.98164 -0.09693
C 1.89368 4.35949 0.42194
C 2.51079 3.23756 -0.18750
H -0.74145 2.59851 1.68025
H 0.15467 4.87358 1.65205
N 2.43342 5.60738 0.34702
H 3.45783 3.32840 -0.70115
C 2.61798 0.79989 -0.71464
N 2.06333 -0.02419 -1.53787
C 4.00741 0.48618 -0.27393
C 4.79144 -0.40811 -1.00044

N	4.39355	1.05186	0.88867
C	6.05041	-0.80945	-0.50017
C	5.59755	0.68413	1.35036
C	1.77884	6.72776	1.01273
C	3.68856	5.82074	-0.36466
H	4.50930	5.24727	0.08438
H	3.94891	6.87797	-0.32199
H	3.60404	5.53366	-1.42015
H	0.76139	6.88016	0.63190
H	2.34932	7.63759	0.82730
H	1.72168	6.57530	2.09796
C	6.44339	-0.22514	0.73093
N	6.84040	-1.71280	-1.16338
H	5.90555	1.13730	2.29160
C	6.29800	-2.42672	-2.31465
C	7.96643	-2.31757	-0.46033
H	8.46749	-3.01913	-1.12789
H	7.64499	-2.86232	0.43893
H	8.70061	-1.56111	-0.16405
H	5.97486	-1.72604	-3.09094
H	5.44645	-3.06206	-2.03817
H	7.08023	-3.05459	-2.74338
H	7.38614	-0.47034	1.20267
H	4.39023	-0.81882	-1.91531
B	-1.70159	-0.19790	1.73655
O	-2.92557	0.38671	2.07986
O	-1.22657	-0.94427	2.84212
C	-3.18703	0.16131	3.48155
C	-2.30898	-1.10143	3.78805
B	-1.83323	-1.49208	-0.72772
O	-2.60732	-2.45691	-0.06619
O	-1.99530	-1.65403	-2.12142
C	-3.53358	-3.03752	-1.01446
C	-2.77986	-2.84127	-2.37757
C	-1.73221	-1.16123	5.19915
C	-3.01437	-2.42108	3.44688
C	-4.68782	-0.03548	3.67599
C	-2.71721	1.41337	4.23484
C	-4.82642	-2.21562	-0.92514
C	-3.79543	-4.48864	-0.62527
C	-1.79694	-3.97529	-2.69251
C	-3.68373	-2.58271	-3.58007
H	0.49418	1.16764	-2.13593
H	0.47616	-0.42255	-2.64721
C	2.45179	-4.08808	-0.02978
C	1.09579	-3.95794	0.27934
C	0.66209	-2.96544	1.16509
H	0.37738	-4.63824	-0.16812
C	1.59368	-2.09264	1.74212
C	2.95539	-2.21016	1.44494
C	3.35052	-3.21163	0.56789
H	2.81709	-4.85172	-0.70887
H	3.69637	-1.54197	1.86921
F	4.67402	-3.34574	0.27681
H	1.24265	-1.32232	2.42123
H	-0.38935	-2.85126	1.39949
B	-1.96591	1.10484	-0.88784
O	-3.35859	1.10286	-0.86732
O	-1.51087	2.06736	-1.82283
C	-2.64148	2.45857	-2.64219
C	-3.83962	2.21077	-1.66201
C	-4.07914	3.38516	-0.70496
C	-5.14602	1.80013	-2.33363
C	-2.66066	1.51541	-3.85200
C	-2.45560	3.90378	-3.08907
H	-1.09484	-0.29993	5.41085
H	-1.12415	-2.06485	5.31195
H	-2.53230	-1.19660	5.94683
H	-3.38139	-2.40494	2.41770
H	-3.84394	-2.63134	4.12968
H	-2.29013	-3.23815	3.52841
H	-5.21771	0.89238	3.43612
H	-4.91835	-0.29895	4.71417
H	-5.07296	-0.82011	3.02128
H	-1.63968	1.55875	4.11213
H	-2.94331	1.36020	5.30471
H	-3.22757	2.28788	3.81897
H	-5.60779	-2.60541	-1.58558
H	-4.63044	-1.16800	-1.16956
H	-5.19655	-2.25342	0.10427
H	-4.42514	-4.98571	-1.37120
H	-4.31707	-4.52586	0.33651
H	-2.86438	-5.05083	-0.52372
H	-1.17550	-3.68000	-3.54400
H	-2.31198	-4.90620	-2.95010
H	-1.13500	-4.16210	-1.84271
H	-3.07419	-2.44418	-4.47921
H	-4.28620	-1.68283	-3.44029
H	-4.35591	-3.43004	-3.75425
H	-4.51367	4.24878	-1.21839
H	-3.14444	3.69390	-0.22745
H	-4.77069	3.06517	0.08000
H	-5.49549	2.58106	-3.01769
H	-5.91868	1.64257	-1.57432
H	-5.03118	0.86998	-2.89411
H	-1.70704	1.60314	-4.38330

H	-3.46461	1.76375	-4.55199
H	-2.77264	0.47748	-3.52585
H	-1.59506	3.97676	-3.76237
H	-2.27507	4.56603	-2.23960
H	-3.33900	4.25983	-3.62995

Sum of electronic and zero-point Energies= -2581.185985

Sum of electronic and thermal Energies= -2581.125295

Sum of electronic and thermal Enthalpies= -2581.124350

Sum of electronic and thermal Free Energies= -2581.286102

TS2-3-OT-HBS-5

Ir	-1.38689	-0.47389	0.09319
N	-0.21216	1.53143	0.13393
C	-0.83985	2.66896	0.50008
N	-0.04728	-0.45923	-1.83124
C	-0.31001	3.93744	0.35777
C	1.03615	1.66975	-0.39094
C	0.97458	4.10288	-0.21607
C	1.63549	2.90597	-0.58713
H	-1.82506	2.53542	0.92969
H	-0.89968	4.78196	0.69004
N	1.54791	5.32489	-0.39057
H	2.63354	2.92724	-0.99938
C	1.79845	0.44475	-0.80520
N	1.31019	-0.52006	-1.50411
C	3.20964	0.27171	-0.33902
C	4.01433	-0.71433	-0.91064
N	3.60402	1.05662	0.68311
C	5.31320	-0.94776	-0.40403
C	4.84014	0.83984	1.15421
C	0.83548	6.53029	0.01748
C	2.89269	5.43105	-0.94651
H	3.62469	4.89345	-0.33114
H	3.18322	6.48053	-0.98074
H	2.93883	5.03048	-1.96696
H	-0.12246	6.62540	-0.50840
H	1.44122	7.40358	-0.22372
H	0.63826	6.53688	1.09706
C	5.71910	-0.12002	0.67393
N	6.12606	-1.91813	-0.92565
H	5.15029	1.47331	1.98409
C	5.59865	-2.84399	-1.92084
C	7.40863	-2.20487	-0.29648
H	8.04967	-1.31600	-0.28191
H	7.92408	-2.97619	-0.86921
H	7.29289	-2.56168	0.73678
H	5.28648	-2.31594	-2.82961
H	4.73649	-3.40876	-1.54000
H	6.37807	-3.55375	-2.19840
H	6.69329	-0.22160	1.13491
H	3.61150	-1.30225	-1.72227
B	-2.69574	-0.07190	1.61372
O	-3.13930	-0.97384	2.58283
O	-3.21462	1.20329	1.87841
C	-3.86955	-0.25892	3.59155
C	-4.16214	1.10797	2.95401
B	-2.44657	-2.03170	-0.71924
O	-3.33595	-2.91729	-0.12607
O	-2.24941	-2.36668	-2.07161
C	-3.88452	-3.76614	-1.14824
C	-2.90988	-3.61934	-2.32445
H	-5.17798	1.15997	2.54103
H	-4.02413	1.94311	3.64811
H	-3.24599	-0.16639	4.49069
H	-4.77824	-0.80932	3.85522
H	-4.89197	-3.41365	-1.40640
H	-3.95785	-4.79344	-0.77868
H	-2.16289	-4.42402	-2.34067
H	-3.41115	-3.58631	-3.29657
H	-0.34137	0.41631	-2.27330
H	-0.28072	-1.24084	-2.43722
C	2.23054	-2.78947	1.50812
C	1.02699	-2.41797	0.92195
C	0.25160	-1.33459	1.32941
F	0.60116	-3.16099	-0.14774
C	0.72535	-0.64290	2.45908
C	1.92837	-0.98574	3.08563
C	2.68804	-2.05548	2.60580
H	2.78956	-3.62864	1.10552
H	2.27721	-0.41001	3.93882
H	3.63091	-2.31904	3.07611
H	0.15340	0.20170	2.83470
H	-1.31732	-1.71985	1.08866
B	-2.82093	0.48092	-1.12316
O	-4.20824	0.38189	-1.11304
O	-2.40459	1.33837	-2.15349
C	-3.55293	1.71043	-2.94055
C	-4.75032	1.31699	-2.06276
H	-5.16311	2.17837	-1.52176
H	-5.55761	0.84332	-2.62975

H -3.53459 1.15399 -3.88634
H -3.51854 2.78109 -3.16344
Sum of electronic and zero-point Energies= -2109.581237
Sum of electronic and thermal Energies= -2109.536745
Sum of electronic and thermal Enthalpies= -2109.535800
Sum of electronic and thermal Free Energies= -2109.662452
Imaginary frequency = -748.68

TS2-3-OT-HBS-6

Ir -1.38386 -0.53457 0.01565
N -0.17795 1.42968 0.04941
C -0.77956 2.57036 0.44789
N -0.03476 -0.55673 -1.93727
C -0.22414 3.82973 0.32972
C 1.07073 1.55196 -0.47425
C 1.05964 3.98167 -0.25061
C 1.69552 2.77988 -0.64656
H -1.76162 2.44633 0.88773
H -0.79239 4.67835 0.68776
N 1.65420 5.19651 -0.40636
H 2.69478 2.78848 -1.05712
C 1.81501 0.31994 -0.89956
N 1.31834 -0.63552 -1.60563
C 3.21454 0.12360 -0.41180
C 4.04616 -0.81279 -1.02607
N 3.56831 0.83820 0.67511
C 5.33197 -1.06942 -0.49668
C 4.79005 0.59693 1.17047
C 0.97407 6.40501 0.04518
C 3.00591 5.28628 -0.94788
H 3.72530 4.73593 -0.32843
H 3.31089 6.33186 -0.97600
H 3.05565 4.88948 -1.96944
H 0.00570 6.52715 -0.45491
H 1.58857 7.27268 -0.19431
H 0.80313 6.39333 1.12940
C 5.69352 -0.31888 0.65106
N 6.17422 -1.98920 -1.06262
H 5.06646 1.17035 2.05413
C 5.68428 -2.85613 -2.12759
C 7.44060 -2.30720 -0.41565
H 8.05964 -1.41080 -0.29833
H 7.99378 -3.01165 -1.03744
H 7.29879 -2.75874 0.57664
H 5.38814 -2.27516 -3.00897
H 4.82052 -3.45418 -1.80551
H 6.47938 -3.53820 -2.42916
H 6.65311 -0.44546 1.13564
H 3.67591 -1.34338 -1.89128
B -2.62024 -0.14013 1.58841
O -2.95506 -1.03804 2.60526
O -3.18030 1.11627 1.85491
C -3.58346 -0.31113 3.67034
C -4.00772 1.01631 3.02474
B -2.57491 -1.99578 -0.80291
O -3.63431 -2.70153 -0.25024
O -2.32709 -2.43164 -2.11771
C -4.24838 -3.48439 -1.28659
C -3.18165 -3.55766 -2.38787
H -5.06235 1.00597 2.71883
H -3.84147 1.88109 3.67518
H -2.85566 -0.15600 4.47830
H -4.42865 -0.88231 4.06786
H -5.15639 -2.97286 -1.63255
H -4.52843 -4.46722 -0.89537
H -2.59151 -4.48165 -2.32752
H -3.59871 -3.47451 -3.39616
H -0.32801 0.33072 -2.35569
H -0.27525 -1.32287 -2.55923
C 2.20899 -2.91748 1.42011
C 1.02170 -2.54969 0.78193
C 0.22543 -1.47854 1.23072
H 0.71181 -3.08407 -0.11238
C 0.67150 -0.85380 2.39536
C 1.84602 -1.18660 3.06206
C 2.62704 -2.23060 2.56342
H 2.80822 -3.73289 1.02375
H 2.13747 -0.62376 3.94362
H 3.55362 -2.49845 3.06279
F -0.05034 0.18573 2.91799
H -1.30395 -1.85874 0.91663
B -2.77428 0.48445 -1.20416
O -4.16354 0.44784 -1.21004
O -2.30937 1.32347 -2.23063
C -3.43120 1.75013 -3.02763
C -4.65390 1.40706 -2.16362
H -5.03535 2.28427 -1.62526
H -5.47462 0.96947 -2.74027
H -3.42781 1.19745 -3.97584
H -3.34668 2.81909 -3.24525

Sum of electronic and zero-point Energies= -2109.580638

Sum of electronic and thermal Energies= -2109.536122

Sum of electronic and thermal Enthalpies= -2109.535178

Sum of electronic and thermal Free Energies= -2109.662137

Imaginary frequency= -801.7858

TS2-3-OT-HBS-14

Ir	-1.34847	-0.51022	0.11865
N	-0.16498	1.60922	0.34538
C	-0.82873	2.70368	0.76989
N	-0.06837	-0.26418	-1.76466
C	-0.40738	4.00559	0.56537
C	1.00810	1.83141	-0.29908
C	0.79679	4.25233	-0.13941
C	1.50424	3.10053	-0.56399
H	-1.75152	2.50280	1.30089
H	-1.01671	4.81313	0.95052
N	1.25787	5.51111	-0.38233
H	2.45704	3.18337	-1.06652
C	1.79512	0.64165	-0.76819
N	1.30695	-0.31218	-1.48078
C	3.21661	0.49220	-0.32846
C	3.98495	-0.56818	-0.80771
N	3.65242	1.37345	0.59385
C	5.28804	-0.78009	-0.30339
C	4.89412	1.17891	1.05868
C	0.51400	6.66587	0.10616
C	2.52054	5.70523	-1.08582
H	3.36046	5.25900	-0.53832
H	2.71152	6.77299	-1.19164
H	2.49123	5.26471	-2.09014
H	-0.49599	6.70208	-0.32096
H	1.03676	7.57752	-0.18229
H	0.42462	6.65526	1.19996
C	5.73737	0.14764	0.67059
N	6.06289	-1.82717	-0.72744
H	5.23944	1.89139	1.80664
C	5.48121	-2.85051	-1.58851
C	7.32997	-2.10315	-0.06259
H	8.00829	-1.24546	-0.13306
H	7.81381	-2.94904	-0.55154
H	7.19604	-2.34903	1.00066
H	5.13632	-2.42113	-2.53579
H	4.62965	-3.35502	-1.11118
H	6.24070	-3.59790	-1.81882
H	6.71664	0.06764	1.12501
H	3.54729	-1.23360	-1.53683
B	-2.84818	-0.19521	1.50554
O	-3.83975	-1.08228	1.90216
O	-2.96552	1.01035	2.21103
C	-4.77868	-0.37868	2.72750
C	-4.01767	0.87431	3.18236
B	-2.19124	-2.17410	-0.67600
O	-2.77000	-3.27035	-0.04874
O	-2.12798	-2.38469	-2.06925
C	-3.21790	-4.19222	-1.05445
C	-2.48209	-3.75290	-2.32826
H	-4.63755	1.77625	3.18722
H	-3.57369	0.74862	4.17856
H	-5.09311	-1.01455	3.56099
H	-5.66340	-0.12310	2.12920
H	-4.30784	-4.10847	-1.16271
H	-2.97630	-5.21702	-0.75519
H	-1.56756	-4.33831	-2.49313
H	-3.10375	-3.81494	-3.22705
H	-0.38772	0.62676	-2.15762
H	-0.29177	-1.01215	-2.41721
C	2.21791	-3.07477	1.15901
C	0.99065	-2.60695	0.70575
C	0.35763	-1.46223	1.18923
F	0.41177	-3.30308	-0.32204
C	1.02911	-0.79764	2.23209
C	2.26492	-1.23533	2.72133
C	2.86354	-2.37587	2.18320
H	2.65477	-3.95958	0.70586
H	2.76151	-0.67960	3.51190
H	3.82757	-2.71962	2.54672
H	0.57880	0.09965	2.64814
H	-1.23008	-1.45121	1.41992
B	-2.80597	0.49114	-1.03159
O	-4.19493	0.43663	-0.97132
O	-2.40477	1.36218	-2.05784
C	-3.56765	1.76920	-2.80468
C	-4.74256	1.40305	-1.88709
H	-5.10507	2.26964	-1.31907
H	-5.58607	0.96352	-2.42778
H	-3.59703	1.21681	-3.75248
H	-3.51109	2.83958	-3.02363

Sum of electronic and zero-point Energies= -2109.581814

Sum of electronic and thermal Energies= -2109.537198
Sum of electronic and thermal Enthalpies= -2109.536254
Sum of electronic and thermal Free Energies= -2109.663918

Imaginary frequency= -778.84

TS2-3-OT-HBS-14-Bpin (Lowest Energy)

Ir	-0.48993	-0.31287	0.30415
N	0.79622	1.71458	0.22283
C	0.20407	2.89207	0.51087
N	0.74741	-0.40022	-1.65118
C	0.69649	4.12985	0.13842
C	1.96766	1.78352	-0.46047
C	1.89796	4.21429	-0.60738
C	2.52828	2.97762	-0.89183
H	-0.72588	2.81519	1.06141
H	0.14049	5.01351	0.42426
N	2.42492	5.40232	-1.01605
H	3.47312	2.93852	-1.41448
C	2.67761	0.50325	-0.79583
N	2.12160	-0.49432	-1.38993
C	4.09665	0.32540	-0.35980
C	4.80014	-0.82186	-0.72623
N	4.59724	1.28124	0.44928
C	6.10349	-1.04082	-0.22552
C	5.83812	1.07649	0.91159
C	1.75574	6.65200	-0.67517
C	3.68760	5.43077	-1.74534
H	4.50546	5.00186	-1.15258
H	3.94259	6.46399	-1.97939
H	3.61822	4.87529	-2.68890
H	0.73465	6.68029	-1.07508
H	2.31001	7.48549	-1.10637
H	1.70391	6.80047	0.41123
C	6.62124	-0.03300	0.62714
N	6.81699	-2.16637	-0.54244
H	6.23493	1.84975	1.56809
C	6.16736	-3.24861	-1.27279
C	8.08986	-2.42448	0.11834
H	8.80278	-1.61289	-0.06624
H	8.52166	-3.34172	-0.28274
H	7.97699	-2.54212	1.20565
H	5.82540	-2.91164	-2.25796
H	5.30120	-3.65025	-0.72881
H	6.88301	-4.05657	-1.42663
H	7.60646	-0.11105	1.06858
H	4.31420	-1.54337	-1.36606
B	-1.91185	0.28534	1.66834
O	-2.66635	-0.51878	2.51556
O	-2.22912	1.63100	1.89013
C	-3.71464	0.29105	3.10550
C	-3.08042	1.72362	3.06126
B	-1.53507	-1.94346	-0.31921
O	-2.28477	-2.86473	0.39629
O	-1.53381	-2.28056	-1.68601
C	-3.04661	-3.66179	-0.54583
C	-2.16480	-3.57729	-1.84164
C	-4.06963	2.86503	2.85482
C	-2.16787	2.01761	4.25747
C	-4.01919	-0.23494	4.50356
C	-4.94446	0.15195	2.19945
C	-4.40809	-2.97234	-0.70262
C	-3.22111	-5.06564	0.02205
C	-1.04777	-4.62592	-1.88071
C	-2.94395	-3.58617	-3.15282
H	0.45806	0.45791	-2.13098
H	0.45754	-1.20569	-2.20022
C	2.97776	-2.91572	1.56613
C	1.76828	-2.44000	1.07606
C	1.19086	-1.22566	1.44241
F	1.14288	-3.20919	0.12954
C	1.89815	-0.49242	2.41319
C	3.11992	-0.93253	2.93503
C	3.66441	-2.14581	2.50967
H	3.36952	-3.86125	1.20338
H	3.64811	-0.32357	3.66366
H	4.61695	-2.49264	2.89955
H	1.49041	0.45971	2.74297
H	-0.41456	-1.21160	1.62748
B	-1.93045	0.58696	-0.94089
O	-3.31447	0.45288	-0.96140
O	-1.51543	1.38944	-2.01242
C	-2.63645	1.55057	-2.92579
C	-3.86095	1.34587	-1.96773
C	-4.28322	2.63002	-1.24556
C	-5.07201	0.67447	-2.60620
C	-2.50452	0.44282	-3.97704
C	-2.54504	2.92525	-3.57665
H	-4.61410	2.75551	1.91532
H	-3.53410	3.81973	2.82563
H	-4.79123	2.90660	3.67758
H	-1.45219	1.20474	4.41185
H	-2.73940	2.16166	5.17953

H	-1.60282	2.93327	4.05720
H	-4.44482	-1.24107	4.43499
H	-4.74800	0.40795	5.00889
H	-3.11812	-0.29195	5.11785
H	-4.71338	0.48898	1.18572
H	-5.80107	0.71311	2.58618
H	-5.22252	-0.90499	2.14446
H	-5.07255	-3.52698	-1.37284
H	-4.28172	-1.95272	-1.07616
H	-4.88464	-2.90975	0.28042
H	-3.72197	-5.71759	-0.70178
H	-3.83826	-5.02464	0.92525
H	-2.26162	-5.51284	0.29022
H	-0.35467	-4.37439	-2.68999
H	-1.44193	-5.62992	-2.06668
H	-0.48551	-4.63312	-0.94471
H	-2.25112	-3.50050	-3.99642
H	-3.64720	-2.75285	-3.20784
H	-3.50160	-4.52197	-3.26653
H	-4.74644	3.34632	-1.93105
H	-3.42634	3.10568	-0.76145
H	-5.01202	2.37703	-0.47034
H	-5.46738	1.28449	-3.42535
H	-5.86336	0.55371	-1.85971
H	-4.82369	-0.31476	-2.99578
H	-1.53730	0.54597	-4.47977
H	-3.29093	0.50389	-4.73549
H	-2.53565	-0.54200	-3.50327
H	-1.65682	2.97420	-4.21481
H	-2.46734	3.71804	-2.82974
H	-3.42278	3.11726	-4.20281

Sum of electronic and zero-point Energies= -2581.154528

Sum of electronic and thermal Energies= -2581.094259

Sum of electronic and thermal Enthalpies= -2581.093314

Sum of electronic and thermal Free Energies= -2581.250315

Imaginary frequency= -710.33

Ir	-1.36093	-0.57190	0.08282
N	-0.34861	1.51913	0.22822
C	-1.05932	2.56724	0.69616
N	-0.10414	-0.31669	-1.89226
C	-0.67711	3.88961	0.57496
C	0.83653	1.81129	-0.37360
C	0.53029	4.21462	-0.09107
C	1.28453	3.11096	-0.56065
H	-1.98924	2.31067	1.18926
H	-1.32281	4.65233	0.99051
N	0.95177	5.49782	-0.25862
H	2.24229	3.25443	-1.03851
C	1.69394	0.68496	-0.87666
N	1.26504	-0.27643	-1.61774
C	3.12167	0.60055	-0.43606
C	3.94540	-0.40574	-0.94175
N	3.51521	1.48002	0.50687
C	5.26335	-0.55434	-0.45359
C	4.77002	1.34569	0.95764
C	0.14649	6.60180	0.25066
C	2.21566	5.77329	-0.93356
H	3.05996	5.30919	-0.40908
H	2.38065	6.85028	-0.95722
H	2.20762	5.40603	-1.96745
H	-0.85097	6.61435	-0.20611
H	0.64028	7.54372	0.01352
H	0.02606	6.54359	1.33977
C	5.66890	0.37653	0.53635
N	6.09145	-1.54630	-0.90913
H	5.07927	2.05721	1.72215
C	5.54156	-2.61298	-1.74089
C	7.38610	-1.75268	-0.27323
H	7.99725	-0.84490	-0.32234
H	7.92259	-2.54075	-0.80245
H	7.29082	-2.04713	0.78212
H	5.15877	-2.21786	-2.68871
H	4.72817	-3.14522	-1.23197
H	6.33253	-3.32631	-1.97422
H	6.65517	0.34298	0.98116
H	3.54115	-1.07869	-1.68308
B	-2.62214	-0.39232	1.68221
O	-2.93464	-1.39960	2.59736
O	-3.23472	0.80850	2.06951
C	-3.91096	-0.89981	3.52410
C	-3.83944	0.62489	3.36083
B	-2.38757	-2.10963	-0.80376
O	-3.32181	-2.98586	-0.27087
O	-2.13544	-2.41907	-2.15268
C	-3.86244	-3.77877	-1.34048
C	-2.83936	-3.63250	-2.47551
H	-4.82237	1.10559	3.38222
H	-3.20509	1.09093	4.12674
H	-3.66804	-1.23263	4.53806
H	-4.89981	-1.29401	3.25463

H	-4.84486	-3.37796	-1.62325
H	-3.98941	-4.81393	-1.00942
H	-2.12703	-4.46770	-2.49688
H	-3.30265	-3.54199	-3.46263
H	-0.49651	0.55861	-2.25182
H	-0.29242	-1.06670	-2.55153
C	2.43447	-2.74188	1.08896
C	1.18137	-2.45648	0.56598
C	0.40914	-1.42233	1.12485
H	0.83226	-3.01554	-0.29697
C	0.92881	-0.75696	2.25110
C	2.19579	-1.06319	2.75940
C	2.97474	-2.06414	2.17445
F	3.17952	-3.72480	0.50041
H	2.58783	-0.51033	3.60934
H	3.96613	-2.31550	2.53559
H	0.35201	0.03755	2.71603
H	-1.16891	-1.89738	0.94551
B	-2.89533	0.38225	-1.02213
O	-4.27187	0.19431	-0.99698
O	-2.55556	1.33459	-1.99673
C	-3.74163	1.69110	-2.73372
C	-4.89285	1.15669	-1.86860
H	-5.35078	1.94724	-1.26029
H	-5.67823	0.67109	-2.45581
H	-3.70864	1.21046	-3.71975
H	-3.77852	2.77557	-2.87385

TS2-3MT-HBS-8

Ir	-1.36093	-0.57190	0.08282
N	-0.34861	1.51913	0.22822
C	-1.05932	2.56724	0.69616
N	-0.10414	-0.31669	-1.89226
C	-0.67711	3.88961	0.57496
C	0.83653	1.81129	-0.37360
C	0.53029	4.21462	-0.09107
C	1.28453	3.11096	-0.56065
H	-1.98924	2.31067	1.18926
H	-1.32281	4.65233	0.99051
N	0.95177	5.49782	-0.25862
H	2.24229	3.25443	-1.03851
C	1.69394	0.68496	-0.87666
N	1.26504	-0.27643	-1.61774
C	3.12167	0.60055	-0.43606
C	3.94540	-0.40574	-0.94175
N	3.51521	1.48002	0.50687
C	5.26335	-0.55434	-0.45359
C	4.77002	1.34569	0.95764
C	0.14649	6.60180	0.25066
C	2.21566	5.77329	-0.93356
H	3.05996	5.30919	-0.40908
H	2.38065	6.85028	-0.95722
H	2.20762	5.40603	-1.96745
H	-0.85097	6.61435	-0.20611
H	0.64028	7.54372	0.01352
H	0.02606	6.54359	1.33977
C	5.66890	0.37653	0.53635
N	6.09145	-1.54630	-0.90913
H	5.07927	2.05721	1.72215
C	5.54156	-2.61298	-1.74089
C	7.38610	-1.75268	-0.27323
H	7.99725	-0.84490	-0.32234
H	7.92259	-2.54075	-0.80245
H	7.29082	-2.04713	0.78212
H	5.15877	-2.21786	-2.68871
H	4.72817	-3.14522	-1.23197
H	6.33253	-3.32631	-1.97422
H	6.65517	0.34298	0.98116
H	3.54115	-1.07869	-1.68308
B	-2.62214	-0.39232	1.68221
O	-2.93464	-1.39960	2.59736
O	-3.23472	0.80850	2.06951
C	-3.91096	-0.89981	3.52410
C	-3.83944	0.62489	3.36083
B	-2.38757	-2.10963	-0.80376
O	-3.32181	-2.98586	-0.27087
O	-2.13544	-2.41907	-2.15268
C	-3.86244	-3.77877	-1.34048
C	-2.83936	-3.63250	-2.47551
H	-4.82237	1.10559	3.38222
H	-3.20509	1.09093	4.12674
H	-3.66804	-1.23263	4.53806
H	-4.89981	-1.29401	3.25463
H	-4.84486	-3.37796	-1.62325
H	-3.98941	-4.81393	-1.00942
H	-2.12703	-4.46770	-2.49688
H	-3.30265	-3.54199	-3.46263
H	-0.49651	0.55861	-2.25182
H	-0.29242	-1.06670	-2.55153
C	2.43447	-2.74188	1.08896
C	1.18137	-2.45648	0.56598
C	0.40914	-1.42233	1.12485
H	0.83226	-3.01554	-0.29697
C	0.92881	-0.75696	2.25110
C	2.19579	-1.06319	2.75940
C	2.97474	-2.06414	2.17445

F 3.17952 -3.72480 0.50041
H 2.58783 -0.51033 3.60934
H 3.96613 -2.31550 2.53559
H 0.35201 0.03755 2.71603
H -1.16891 -1.89738 0.94551
B -2.89533 0.38225 -1.02213
O -4.27187 0.19431 -0.99698
O -2.55556 1.33459 -1.99673
C -3.74163 1.69110 -2.73372
C -4.89285 1.15669 -1.86860
H -5.35078 1.94724 -1.26029
H -5.67823 0.67109 -2.45581
H -3.70864 1.21046 -3.71975
H -3.77852 2.77557 -2.87385
Sum of electronic and zero-point Energies=
-2109.576054
Sum of electronic and thermal Energies=
-2109.531680
Sum of electronic and thermal Enthalpies=
-2109.530736
Sum of electronic and thermal Free
Energies= -2109.656907
Imaginary frequency: -734.33

TS2-3MT-HBS-9
Ir -1.41036 -0.56135 0.08166
N -0.22775 1.54983 0.29825
C -0.87750 2.63902 0.75560
N -0.17028 -0.30505 -1.81808
C -0.44684 3.94168 0.57782
C 0.94054 1.77615 -0.35508
C 0.75176 4.19467 -0.13439
C 1.44425 3.04721 -0.59451
H -1.79588 2.43253 1.29276
H -1.04348 4.74461 0.99123
N 1.22133 5.45490 -0.35191
H 2.39231 3.13442 -1.10524
C 1.71681 0.59270 -0.85916
N 1.21298 -0.35612 -1.56765
C 3.15066 0.43822 -0.45928
C 3.91935 -0.58693 -1.00931
N 3.59209 1.26933 0.50511
C 5.23116 -0.81578 -0.53635
C 4.83772 1.05257 0.94838
C 0.50242 6.60264 0.18817
C 2.48812 5.65461 -1.04669
H 3.32370 5.19249 -0.50553
H 2.68543 6.72307 -1.13161
H 2.45880 5.23407 -2.05931
H -0.51770 6.65910 -0.21123
H 1.02571 7.51702 -0.09057
H 0.44165 6.56354 1.28347
C 5.68356 0.05332 0.48908
N 6.01110 -1.82523 -1.03618
H 5.18398 1.71749 1.73814
C 5.42453 -2.80444 -1.94395
C 7.29294 -2.12425 -0.41064
H 7.95671 -1.25281 -0.43619
H 7.78109 -2.92860 -0.96162
H 7.18088 -2.44070 0.63635
H 5.06125 -2.32639 -2.86076
H 4.58519 -3.34273 -1.48187
H 6.18655 -3.53072 -2.22750
H 6.66709 -0.04834 0.92951
H 3.47547 -1.21430 -1.76780
B -2.92639 -0.25588 1.45726
O -3.95812 -1.12133 1.78783
O -3.00576 0.91686 2.21854
C -4.72516 -0.54781 2.85674
C -4.25821 0.91525 2.92518
B -2.23965 -2.24249 -0.67936
O -2.66758 -3.39040 -0.02058
O -2.28476 -2.43843 -2.07522
C -3.17887 -4.31682 -0.99301
C -2.61082 -3.81634 -2.32886
H -4.95642 1.59311 2.41734
H -4.10694 1.27102 3.94891
H -4.51070 -1.09145 3.78622
H -5.79396 -0.64147 2.63945
H -4.27645 -4.28644 -0.97823
H -2.85571 -5.33264 -0.74514
H -1.69837 -4.35714 -2.61409
H -3.32799 -3.88476 -3.15271
H -0.49711 0.58955 -2.19751
H -0.40551 -1.04276 -2.47807
C 2.00439 -3.31254 1.11155
C 0.75155 -2.83488 0.71704
C 0.30318 -1.55302 1.09289
H 0.12195 -3.45635 0.08735
C 1.12341 -0.80438 1.95588
C 2.36069 -1.30475 2.34279
C 2.83548 -2.54236 1.93095
H 2.34199 -4.29147 0.77928
F 3.15086 -0.54115 3.14639
H 3.81599 -2.88184 2.24748

H 0.83050 0.18430 2.29231
H -1.31187 -1.40349 1.44684
B -2.86683 0.47044 -1.06298
O -4.25538 0.45207 -0.98647
O -2.45793 1.33486 -2.09268
C -3.61875 1.77303 -2.82502
C -4.79073 1.43335 -1.89401
H -5.12555 2.30708 -1.32005
H -5.65105 1.01514 -2.42499
H -3.67300 1.22442 -3.77383
H -3.53773 2.84230 -3.04147
Sum of electronic and zero-point Energies= -2109.575407
Sum of electronic and thermal Energies= -2109.530871
Sum of electronic and thermal Enthalpies= -2109.529927
Sum of electronic and thermal Free Energies= -2109.656959
Imaginary frequency: -759.19

TS2-3MT-HBS-11

Ir -1.39652 -0.56695 0.05815
N -0.25183 1.45274 0.17101
C -0.88008 2.54661 0.65280
N -0.16468 -0.40958 -1.94982
C -0.41299 3.83979 0.51847
C 0.93497 1.66433 -0.45724
C 0.79717 4.08273 -0.17780
C 1.46636 2.92999 -0.65803
H -1.81345 2.35341 1.16793
H -0.99549 4.64474 0.94747
N 1.29642 5.33529 -0.36225
H 2.42344 3.00713 -1.15330
C 1.70848 0.48416 -0.97016
N 1.21019 -0.45374 -1.69746
C 3.13032 0.31900 -0.53757
C 3.93662 -0.65332 -1.12835
N 3.52472 1.08889 0.49666
C 5.23420 -0.89520 -0.62149
C 4.75607 0.86064 0.97158
C 0.59156 6.48869 0.18543
C 2.56239 5.52428 -1.06228
H 3.39107 5.03318 -0.53674
H 2.78140 6.58996 -1.12450
H 2.51730 5.12684 -2.08364
H -0.41756 6.57788 -0.23559
H 1.14290 7.39588 -0.06058
H 0.50522 6.42695 1.27759
C 5.63437 -0.09316 0.47744
N 6.05057 -1.85585 -1.15775
H 5.06160 1.47559 1.81672
C 5.52415 -2.76904 -2.16500
C 7.31749 -2.17098 -0.51025
H 7.96363 -1.28763 -0.45613
H 7.84038 -2.92810 -1.09518
H 7.17794 -2.55722 0.50962
H 5.20406 -2.22742 -3.06266
H 4.66800 -3.34665 -1.78982
H 6.30734 -3.46796 -2.45919
H 6.60355 -0.20978 0.94507
H 3.53304 -1.23204 -1.94625
B -2.58686 -0.29152 1.69655
O -2.88751 -1.25504 2.66227
O -3.15231 0.93898 2.06225
C -3.81580 -0.69554 3.60415
C -3.70915 0.81944 3.38225
B -2.58400 -2.01066 -0.79213
O -3.57333 -2.80197 -0.22595
O -2.41122 -2.33460 -2.15028
C -4.22375 -3.53570 -1.27656
C -3.23416 -3.47693 -2.44862
H -4.67691 1.32870 3.42431
H -3.03179 1.29384 4.10494
H -3.54551 -0.99890 4.62037
H -4.82404 -1.07089 3.38386
H -5.17481 -3.04463 -1.52146
H -4.43288 -4.55687 -0.94367
H -2.60245 -4.37367 -2.49838
H -3.72378 -3.33980 -3.41758
H -0.50802 0.48640 -2.30879
H -0.40937 -1.15006 -2.60108
C 2.23578 -3.11261 0.93933
C 0.97497 -2.70338 0.49937
C 0.34395 -1.56043 1.02839
H 0.48240 -3.26177 -0.29287
C 1.00131 -0.87625 2.06514
C 2.26193 -1.29411 2.47695
C 2.90550 -2.39962 1.93838
H 2.70837 -3.98790 0.50029
F 2.90483 -0.57453 3.43806
H 3.89336 -2.67826 2.28893
H 0.57317 0.01142 2.51968
H -1.27256 -1.90271 0.91785
B -2.88410 0.49294 -1.01460

O -4.26952 0.40170 -0.96259
O -2.49759 1.41090 -2.00473
C -3.66893 1.83720 -2.72765
C -4.83865 1.39305 -1.83692
H -5.23170 2.22037 -1.23220
H -5.66481 0.95447 -2.40490
H -3.68486 1.34234 -3.70711
H -3.63515 2.91972 -2.88290
Sum of electronic and zero-point Energies= -2109.574495
Sum of electronic and thermal Energies= -2109.529891
Sum of electronic and thermal Enthalpies= -2109.528947
Sum of electronic and thermal Free Energies= -2109.656703
Imaginary frequency: -741.48

TS2-3MT-HBS-13

Ir -1.32299 -0.57575 0.10570
N -0.33728 1.61717 0.37075
C -1.08171 2.63250 0.85291
N -0.13908 -0.15728 -1.80300
C -0.78000 3.97324 0.69098
C 0.79736 1.96416 -0.29203
C 0.37853 4.35016 -0.03184
C 1.17080 3.28122 -0.51960
H -1.97242 2.33302 1.39293
H -1.44558 4.70861 1.12428
N 0.72412 5.65214 -0.23599
H 2.09659 3.46646 -1.04344
C 1.67242 0.86449 -0.82654
N 1.24416 -0.09976 -1.56371
C 3.11564 0.80900 -0.43212
C 3.90224 -0.26399 -0.85213
N 3.55730 1.77843 0.39324
C 5.23194 -0.38969 -0.39177
C 4.82619 1.66895 0.81052
C -0.11131 6.72046 0.29888
C 1.95973 5.98147 -0.93816
H 2.83627 5.56363 -0.42732
H 2.07190 7.06490 -0.97428
H 1.94943 5.60468 -1.96863
H -1.13528 6.65886 -0.08962
H 0.30464 7.68279 0.00151
H -0.15688 6.68985 1.39529
C 5.69006 0.63720 0.47270
N 6.02231 -1.44977 -0.75192
H 5.17738 2.45576 1.47690
C 5.43123 -2.58318 -1.45790
C 7.31830 -1.63004 -0.10977
H 7.96387 -0.76046 -0.27466
H 7.81528 -2.49741 -0.54513
H 7.22755 -1.79141 0.97425
H 4.99100 -2.26635 -2.40950
H 4.65322 -3.08178 -0.86492
H 6.21413 -3.30848 -1.68210
H 6.68996 0.63047 0.88707
H 3.45712 -1.00979 -1.49279
B -2.88641 -0.44759 1.45817
O -3.75162 -1.46336 1.84227
O -3.19241 0.73660 2.14170
C -4.80178 -0.89065 2.63499
C -4.23494 0.45986 3.09349
B -1.98546 -2.31435 -0.69631
O -2.31390 -3.51050 -0.06836
O -1.99855 -2.48271 -2.09711
C -2.72684 -4.45851 -1.06615
C -2.19339 -3.87881 -2.38399
H -4.97545 1.26542 3.07719
H -3.79883 0.40419 4.09951
H -5.04632 -1.55726 3.46779
H -5.69659 -0.76594 2.01098
H -3.82264 -4.52964 -1.06441
H -2.31387 -5.44537 -0.83532
H -1.23188 -4.32691 -2.66869
H -2.89250 -3.99458 -3.21795
H -0.54368 0.71862 -2.14901
H -0.31958 -0.89211 -2.48333
C 2.36621 -2.91674 1.10994
C 1.09214 -2.59042 0.66508
C 0.48077 -1.40588 1.11492
H 0.60230 -3.24558 -0.04800
C 1.17622 -0.63614 2.06833
C 2.44835 -1.00103 2.51922
C 3.06989 -2.15258 2.03254
F 2.96880 -4.03296 0.60158
H 2.96908 -0.37624 3.24017
H 4.06419 -2.45374 2.34456
H 0.72336 0.27679 2.44278
H -1.12240 -1.44149 1.44593
B -2.89031 0.30553 -1.01268
O -4.26090 0.06947 -0.97148
O -2.60024 1.27332 -1.98770
C -3.80434 1.56999 -2.72242
C -4.92490 1.01026 -1.83537

H	-5.39199	1.79180	-1.22216
H	-5.70725	0.50060	-2.40557
H	-3.76195	1.06956	-3.69811
H	-3.88244	2.64908	-2.88402

Sum of electronic and zero-point Energies= -2109.577033

Sum of electronic and thermal Energies= -2109.532574

Sum of electronic and thermal Enthalpies= -2109.531630

Sum of electronic and thermal Free Energies= -2109.657992

Imaginary frequency= -777.58

TS2-3MT-HBS-13-Bpin

Ir	-0.50887	-0.36152	0.25426
N	0.63962	1.78996	0.33200
C	-0.04178	2.89117	0.70661
N	0.68622	-0.16525	-1.69939
C	0.31977	4.18676	0.38101
C	1.77117	2.00058	-0.38821
C	1.47493	4.41760	-0.40567
C	2.20367	3.26040	-0.77773
H	-0.93634	2.70064	1.28741
H	-0.30282	5.00035	0.73023
N	1.87141	5.66832	-0.77387
H	3.12503	3.33453	-1.33705
C	2.56978	0.80174	-0.81696
N	2.07031	-0.18892	-1.46953
C	4.00442	0.69013	-0.41117
C	4.73587	-0.44679	-0.75557
N	4.49183	1.68780	0.35367
C	6.05607	-0.60931	-0.27861
C	5.75002	1.53863	0.79024
C	1.09278	6.82936	-0.36078
C	3.06603	5.84787	-1.59084
H	3.96312	5.47705	-1.07942
H	3.20492	6.90951	-1.79421
H	2.97757	5.32622	-2.55222
H	0.07089	6.79226	-0.76004
H	1.57161	7.73416	-0.73453
H	1.03155	6.90365	0.73218
C	6.56096	0.44446	0.52534
N	6.79563	-1.72604	-0.56785
H	6.13759	2.34634	1.40983
C	6.15684	-2.86530	-1.22046
C	8.07718	-1.93086	0.09548
H	8.76738	-1.10674	-0.11626
H	8.53203	-2.84765	-0.28055
H	7.97168	-2.01969	1.18648
H	5.74702	-2.57944	-2.19531
H	5.34594	-3.28894	-0.61393
H	6.90371	-3.64143	-1.39110
H	7.55672	0.41206	0.94834
H	4.25530	-1.20916	-1.34989
B	-1.99826	0.00914	1.63787
O	-2.83038	-0.90830	2.26344
O	-2.26956	1.29750	2.10872
C	-3.86192	-0.18696	2.98374
C	-3.17524	1.20120	3.23876
B	-1.37150	-2.04233	-0.46949
O	-1.91675	-3.13417	0.19145
O	-1.38012	-2.27043	-1.86041
C	-2.57368	-3.97817	-0.78866
C	-1.77630	-3.64573	-2.09800
C	-4.11347	2.40290	3.21203
C	-2.31182	1.22718	4.50490
C	-4.21699	-0.96833	4.24442
C	-5.07756	-0.09534	2.05401
C	-4.03686	-3.52287	-0.84931
C	-2.48498	-5.42962	-0.33207
C	-0.49108	-4.46786	-2.24608
C	-2.59289	-3.70732	-3.38439
H	0.33849	0.71226	-2.09922
H	0.44050	-0.93417	-2.31872
C	3.06081	-2.84442	1.34264
C	1.80253	-2.47559	0.88702
C	1.24714	-1.24873	1.29307
H	1.28469	-3.12844	0.19193
C	1.98044	-0.47650	2.21595
C	3.23796	-0.88043	2.67495
C	3.80401	-2.07743	2.23104
F	3.60661	-4.00922	0.87946
H	3.79129	-0.25216	3.36815
H	4.78494	-2.41151	2.55176
H	1.57213	0.47096	2.55480
H	-0.36097	-1.23058	1.59431
B	-2.01664	0.55860	-0.90845
O	-3.39820	0.40546	-0.89470
O	-1.65205	1.46198	-1.91542
C	-2.85200	2.11637	-2.41174
C	-3.95692	1.05917	-2.06670
C	-5.31716	1.64305	-1.70127
C	-4.11304	-0.01999	-3.14395
C	-2.67299	2.40928	-3.89643
C	-3.00029	3.42149	-1.62141

H	-4.61894	2.49335	2.24844
H	-3.54381	3.32211	3.38375
H	-4.87082	2.32191	3.99888
H	-1.62863	0.37311	4.52979
H	-2.92162	1.21514	5.41347
H	-1.71066	2.14172	4.50598
H	-4.67710	-1.92251	3.96885
H	-4.93345	-0.41076	4.85727
H	-3.33296	-1.18344	4.84820
H	-4.81902	0.42917	1.13184
H	-5.92129	0.40609	2.53868
H	-5.38953	-1.10890	1.78343
H	-4.62751	-4.13395	-1.53898
H	-4.10104	-2.47438	-1.15301
H	-4.47386	-3.60974	0.14985
H	-2.89830	-6.10093	-1.09247
H	-3.06183	-5.56361	0.58849
H	-1.45344	-5.72480	-0.12874
H	0.11634	-4.03641	-3.04801
H	-0.70247	-5.51141	-2.49874
H	0.09786	-4.44513	-1.32488
H	-1.95935	-3.44668	-4.23869
H	-3.43111	-3.00904	-3.36107
H	-2.98198	-4.71799	-3.54783
H	-5.73481	2.20688	-2.54226
H	-5.25333	2.30513	-0.83552
H	-6.01219	0.83362	-1.45713
H	-4.55795	0.38216	-4.05928
H	-4.76862	-0.80810	-2.76254
H	-3.14730	-0.47214	-3.38272
H	-1.87654	3.14776	-4.03427
H	-3.59339	2.81991	-4.32479
H	-2.40016	1.50973	-4.45228
H	-2.08847	4.01417	-1.73860
H	-3.13406	3.21792	-0.55530
H	-3.84865	4.01478	-1.97623

Sum of electronic and zero-point Energies= -2581.148218

Sum of electronic and thermal Energies= -2581.088318

Sum of electronic and thermal Enthalpies= -2581.087373

Sum of electronic and thermal Free Energies= -2581.242481

Imaginary frequency: -724.69

TS2-3PT-HBS-7

Ir	-1.31030	-0.64211	0.08700
N	-0.36643	1.59529	0.38196
C	-1.11843	2.56707	0.93609
N	-0.23098	-0.11108	-1.85827
C	-0.88144	3.92220	0.78711
C	0.70731	2.00297	-0.34205
C	0.21184	4.36214	-0.00008
C	1.01483	3.33824	-0.56147
H	-1.95769	2.21770	1.52669
H	-1.54480	4.62080	1.28056
N	0.48898	5.68213	-0.19464
H	1.90179	3.57098	-1.13226
C	1.59153	0.94460	-0.94081
N	1.15922	-0.01779	-1.67774
C	3.04217	0.91127	-0.57281
C	3.83976	-0.14979	-1.00317
N	3.46727	1.86707	0.27593
C	5.14729	-0.30073	-0.49337
C	4.72166	1.74069	0.73114
C	-0.33128	6.70115	0.44871
C	1.66833	6.07923	-0.95562
H	2.59309	5.71712	-0.48816
H	1.71256	7.16728	-1.00286
H	1.62864	5.69639	-1.98263
H	-1.38136	6.61892	0.14295
H	0.02902	7.68695	0.15574
H	-0.28473	6.62959	1.54330
C	5.58128	0.69983	0.41299
N	5.94446	-1.36464	-0.83653
H	5.05984	2.51617	1.41715
C	5.38726	-2.44568	-1.64169
C	7.10483	-1.66990	-0.00541
H	7.83481	-0.85413	-0.02838
H	7.59640	-2.56200	-0.39475
H	6.81788	-1.85682	1.03818
H	4.99001	-2.06089	-2.58601
H	4.58286	-2.98248	-1.12062
H	6.18097	-3.15444	-1.88206
H	6.56295	0.66925	0.86786
H	3.40516	-0.88592	-1.66206
B	-2.79124	-0.61307	1.52907
O	-3.68635	-1.62650	1.84264
O	-2.99718	0.49630	2.35695
C	-4.66836	-1.09870	2.74592
C	-4.01357	0.16582	3.32014
B	-1.98812	-2.35274	-0.75058
O	-2.23145	-3.58818	-0.15900
O	-2.11290	-2.45309	-2.15178

C	-2.71060	-4.49453	-1.16596
C	-2.30054	-3.83816	-2.49184
H	-4.71183	1.00202	3.42435
H	-3.54030	-0.01953	4.29316
H	-4.90778	-1.84201	3.51267
H	-5.58338	-0.86492	2.18592
H	-3.80096	-4.58924	-1.07665
H	-2.26254	-5.48250	-1.02143
H	-1.35654	-4.24728	-2.87639
H	-3.06352	-3.93132	-3.27087
H	-0.68059	0.76288	-2.14994
H	-0.42013	-0.82516	-2.55795
C	2.41187	-3.09743	0.77519
C	1.09968	-2.71469	0.48068
C	0.55728	-1.50229	0.94739
H	0.49591	-3.36667	-0.14372
C	1.35781	-0.73316	1.81391
C	2.66727	-1.10331	2.13771
C	3.17678	-2.26928	1.58672
H	2.84056	-4.01579	0.38570
H	3.29635	-0.48572	2.77058
F	4.47268	-2.61283	1.84025
H	0.96772	0.19806	2.21363
H	-1.04520	-1.52191	1.40484
B	-2.94423	0.27743	-0.90526
O	-4.31306	0.07036	-0.76630
O	-2.70766	1.25886	-1.88209
C	-3.95488	1.59350	-2.52114
C	-5.01896	1.03831	-1.56454
H	-5.42554	1.81718	-0.90647
H	-5.85011	0.55314	-2.08488
H	-3.99420	1.11191	-3.50636
H	-4.02191	2.67695	-2.65669

Sum of electronic and zero-point Energies= -2109.576016

Sum of electronic and thermal Energies= -2109.531411

Sum of electronic and thermal Enthalpies= -2109.530467

Sum of electronic and thermal Free Energies= -2109.657685

Imaginary frequency= -795.70

TS2-3PT-HBS-7-Bpin

Ir	-0.48645	-0.36885	0.26216
N	0.68799	1.77216	0.34987
C	0.02799	2.86017	0.79777
N	0.61910	-0.12421	-1.74534
C	0.36369	4.16550	0.48510
C	1.76931	2.00907	-0.43558
C	1.46794	4.42385	-0.36438
C	2.17410	3.28098	-0.81483
H	-0.82901	2.65047	1.42720
H	-0.23706	4.96658	0.89635
N	1.84041	5.68616	-0.71759
H	3.05849	3.37405	-1.42853
C	2.54459	0.82421	-0.93832
N	2.01215	-0.15216	-1.58612
C	3.98924	0.69560	-0.57640
C	4.69414	-0.45609	-0.92822
N	4.49933	1.67661	0.19371
C	5.99153	-0.67179	-0.41560
C	5.74464	1.48475	0.65064
C	1.07940	6.83249	-0.23603
C	2.97822	5.89246	-1.60608
H	3.90468	5.49853	-1.17023
H	3.11031	6.96074	-1.77585
H	2.82283	5.40903	-2.57914
H	0.03879	6.80130	-0.58411
H	1.53629	7.74858	-0.60993
H	1.07367	6.87844	0.86008
C	6.51502	0.35720	0.40788
N	6.69745	-1.81946	-0.68144
H	6.15126	2.28015	1.27387
C	6.03795	-2.91526	-1.38286
C	7.84272	-2.15063	0.16036
H	8.62662	-1.39075	0.07871
H	8.26779	-3.09775	-0.17368
H	7.55585	-2.24912	1.21636
H	5.66065	-2.58241	-2.35474
H	5.19935	-3.33237	-0.80919
H	6.76435	-3.70850	-1.56455
H	7.49609	0.28205	0.85872
H	4.19411	-1.20387	-1.52487
B	-1.91817	-0.03200	1.71422
O	-2.68483	-0.97516	2.38576
O	-2.21201	1.24834	2.19092
C	-3.71579	-0.28523	3.13608
C	-3.07164	1.12935	3.35461
B	-1.44252	-1.98779	-0.48658
O	-2.06582	-3.05329	0.14490
O	-1.48365	-2.17011	-1.88522
C	-2.81665	-3.79457	-0.85099
C	-2.01231	-3.49140	-2.16313

C -4.05396 2.29538 3.35128
C -2.16432 1.19810 4.58784
C -3.99894 -1.06567 4.41520
C -4.96380 -0.24946 2.24599
C -4.23054 -3.19935 -0.86652
C -2.85978 -5.26379 -0.44784
C -0.81386 -4.42517 -2.36607
C -2.85190 -3.42609 -3.43454
H 0.24215 0.76113 -2.10006
H 0.33986 -0.87770 -2.36926
C 2.98526 -3.12672 1.03629
C 1.71062 -2.63316 0.74185
C 1.29416 -1.35294 1.15374
H 1.04015 -3.24965 0.14966
C 2.18207 -0.62303 1.96768
C 3.45821 -1.09957 2.28750
C 3.84303 -2.33568 1.79005
H 3.31655 -4.09980 0.68660
H 4.15732 -0.51319 2.87517
F 5.10698 -2.78746 2.03633
H 1.89116 0.36108 2.32356
H -0.31383 -1.23571 1.59602
B -2.02510 0.59902 -0.82242
O -3.40190 0.40788 -0.80231
O -1.69301 1.52120 -1.82591
C -2.85565 1.70911 -2.68015
C -4.02754 1.36610 -1.69774
C -4.46526 2.56131 -0.84379
C -5.23844 0.70409 -2.34555
C -2.72029 0.70257 -3.82850
C -2.84902 3.13747 -3.21042
H -4.59041 2.36097 2.40276
H -3.51382 3.23619 3.50007
H -4.78292 2.19143 4.16189
H -1.45093 0.36875 4.59494
H -2.73996 1.17359 5.51819
H -1.59652 2.13328 4.55930
H -4.43005 -2.03996 4.16422
H -4.71656 -0.52942 5.04547
H -3.08837 -1.23955 4.99226
H -4.74812 0.26256 1.30585
H -5.80701 0.23728 2.74621
H -5.25286 -1.27713 2.00513
H -4.88701 -3.72475 -1.56736
H -4.19976 -2.13723 -1.12536
H -4.65809 -3.28552 0.13683
H -3.34880 -5.86379 -1.22284
H -3.43109 -5.37624 0.47901
H -1.85813 -5.66377 -0.27646
H -0.18269 -4.02393 -3.16533
H -1.12737 -5.43454 -2.64976
H -0.20919 -4.49004 -1.45697
H -2.21133 -3.19118 -4.29093
H -3.62167 -2.65482 -3.36720
H -3.33738 -4.38847 -3.62852
H -4.98913 3.31402 -1.44084
H -3.60527 3.03147 -0.35916
H -5.14577 2.21064 -0.06269
H -5.69006 1.36641 -3.09176
H -5.99295 0.48684 -1.58304
H -4.96918 -0.23649 -2.83028
H -1.78014 0.89279 -4.35655
H -3.53940 0.79251 -4.54845
H -2.68980 -0.31994 -3.44249
H -1.99166 3.28112 -3.87585
H -2.77213 3.86557 -2.40026
H -3.75997 3.34282 -3.78256
Imaginary frequency= -690.90

Products formed after oxidative addition

3OT-conformer-1

Ir -1.33260 -0.60556 -0.28543
N -0.29301 1.19335 0.37301
C -0.92001 1.99244 1.28317
N 0.02332 -0.40310 -2.04096
C -0.53623 3.29091 1.55482
C 0.85447 1.69203 -0.20400
C 0.56364 3.86286 0.87965
C 1.27101 2.99599 0.01544
H -1.75087 1.53805 1.80811
H -1.10081 3.84749 2.28830
N 0.95657 5.15831 1.06741
H 2.20108 3.28742 -0.44895
C 1.75803 0.79000 -0.98238
N 1.45487 -0.17939 -1.77206
B 0.02702 -1.49420 1.08411
O 1.38238 -1.89659 0.88096
C 2.01224 -2.19516 2.19547
C 0.84070 -2.16892 3.21141
H 2.75802 -1.42265 2.40407
H 2.49639 -3.17309 2.13968
O -0.28035 -1.55311 2.46591
H 1.05792 -1.55926 4.09048
H 0.54361 -3.17584 3.51780
C 3.24580 0.87989 -0.73498

C	3.91250	-0.31403	-0.48157
N	3.86628	2.08102	-0.80698
C	5.31633	-0.31607	-0.31008
C	5.20611	2.08037	-0.63498
C	0.19662	6.03640	1.97153
C	2.12302	5.68741	0.33693
H	3.02900	5.11390	0.56640
H	2.27984	6.72473	0.63621
H	1.96110	5.65417	-0.74765
H	-0.85261	6.11385	1.65959
H	0.63976	7.03287	1.94555
H	0.22559	5.66993	3.00601
C	5.96120	0.94334	-0.39601
N	6.01118	-1.47682	-0.07511
H	5.69889	3.04506	-0.69849
C	5.30428	-2.76862	-0.07655
C	7.47041	-1.44268	0.09745
H	7.97797	-1.06890	-0.80241
H	7.82286	-2.45604	0.29595
H	7.75698	-0.80633	0.94479
H	4.78542	-2.93729	-1.02846
H	4.56191	-2.82089	0.72895
H	6.03465	-3.56601	0.07053
H	7.03108	1.03350	-0.27798
H	3.31746	-1.20965	-0.39668
B	-2.62371	-0.86284	1.27568
O	-3.43982	-1.99839	1.49681
O	-2.93445	0.12488	2.27531
C	-4.14285	-1.87469	2.79004
C	-3.99379	-0.37974	3.17891
B	-0.93744	-2.61505	-0.53187
O	-1.11618	-3.74063	0.30796
O	-0.40874	-3.04788	-1.79442
C	-0.81912	-4.97753	-0.44932
C	-0.09243	-4.48933	-1.73200
H	-4.91285	0.18518	2.99257
H	-3.67554	-0.24216	4.21429
H	-3.65786	-2.53053	3.51968
H	-5.18464	-2.17368	2.65806
H	-1.76230	-5.48015	-0.68249
H	-0.19555	-5.62729	0.16750
H	0.99242	-4.61151	-1.65670
H	-0.46108	-4.97335	-2.63823
H	-0.35556	0.28304	-2.70549
H	-0.01108	-1.34593	-2.46018
C	-4.60985	2.56380	-2.41086
C	-3.75565	1.78994	-3.19444
C	-2.86969	0.92362	-2.56602
H	-3.76857	1.84106	-4.27603
C	-2.74342	0.75933	-1.18732
C	-3.64768	1.54433	-0.43217
C	-4.55398	2.43087	-1.02238
H	-5.31070	3.24582	-2.87823
H	-3.65193	1.42806	0.64327
H	-5.22605	3.00778	-0.39514
H	-2.38990	-1.60268	-0.95745
F	-2.05452	0.16442	-3.43166

Sum of electronic and zero-point Energies= -2098.820513

Sum of electronic and thermal Energies= -2098.776606

Sum of electronic and thermal Enthalpies= -2098.775661

Sum of electronic and thermal Free Energies= -2098.900260

3PT-HBS-16-Bpin

Ir	-0.46632	-0.40612	0.36918
N	0.76903	1.70354	0.65452
C	0.11722	2.75238	1.19549
N	0.65623	-0.11678	-1.52697
C	0.39973	4.07980	0.92481
C	1.80058	2.00391	-0.17585
C	1.42987	4.40334	0.00902
C	2.13988	3.30186	-0.53136
H	-0.70073	2.49608	1.85787
H	-0.18870	4.84469	1.41519
N	1.73802	5.68808	-0.32453
H	2.98066	3.44878	-1.19097
C	2.58992	0.85847	-0.74901
N	2.06876	-0.11476	-1.40766
C	4.06925	0.77893	-0.50985
C	4.71616	-0.45132	-0.64102
N	4.69155	1.91440	-0.13794
C	6.11134	-0.54361	-0.42001
C	6.00771	1.82067	0.09212
C	0.99440	6.79284	0.26793
C	2.82419	5.96239	-1.25822
H	3.78332	5.58450	-0.88263
H	2.91326	7.03967	-1.39635
H	2.63567	5.50759	-2.23894
H	-0.07504	6.72987	0.03008
H	1.37484	7.73425	-0.12787
H	1.10272	6.81282	1.35990
C	6.75438	0.65813	-0.02551

N	6.80925	-1.71321	-0.57891
H	6.50457	2.73977	0.40003
C	6.11548	-2.98032	-0.78746
C	8.19332	-1.78624	-0.12453
H	8.82136	-1.05886	-0.65021
H	8.58564	-2.78047	-0.34065
H	8.28591	-1.60761	0.95618
H	5.31818	-2.87224	-1.52595
H	5.68752	-3.37221	0.14259
H	6.82622	-3.71045	-1.18046
H	7.81233	0.69085	0.19967
H	4.12373	-1.32089	-0.88238
B	-2.18897	0.02013	1.50320
O	-3.22113	-0.85806	1.79634
O	-2.37866	1.23449	2.16754
C	-4.23014	-0.16947	2.57078
C	-3.43104	1.05636	3.15340
B	-1.37759	-2.02619	-0.42709
O	-2.04243	-3.08399	0.16792
O	-1.36820	-2.18362	-1.82576
C	-2.81619	-3.75438	-0.86215
C	-1.96894	-3.46506	-2.15136
C	-4.22291	2.35525	3.25286
C	-2.73718	0.75145	4.48573
C	-4.77033	-1.13529	3.62244
C	-5.34928	0.23286	1.60722
C	-4.19264	-3.07648	-0.88867
C	-2.95299	-5.22811	-0.49975
C	-0.82739	-4.46485	-2.36130
C	-2.77848	-3.30831	-3.43410
H	0.28614	0.76913	-1.89519
H	0.40289	-0.86039	-2.17592
C	2.84192	-3.39574	0.93354
C	1.67916	-2.73565	0.51970
C	1.26584	-1.50249	1.06390
H	1.09824	-3.19360	-0.27656
C	2.08378	-0.97667	2.08528
C	3.25165	-1.61331	2.52659
C	3.60747	-2.81543	1.93509
H	3.15415	-4.33776	0.49211
H	3.88060	-1.18643	3.30253
F	4.75957	-3.43902	2.32969
H	1.82169	-0.02345	2.53853
H	-0.91400	-0.84525	1.84550
B	-1.93813	0.68991	-0.76963
O	-3.29060	0.50526	-1.00921
O	-1.43491	1.65055	-1.66190
C	-2.40030	1.82414	-2.73864
C	-3.73919	1.46247	-2.01276
C	-4.35274	2.65769	-1.27634
C	-4.78543	0.78007	-2.88592
C	-2.02067	0.82162	-3.83530
C	-2.29759	3.25262	-3.25745
H	-4.59367	2.67266	2.27613
H	-3.58208	3.15032	3.64764
H	-5.07474	2.23863	3.93085
H	-2.14560	-0.16654	4.41960
H	-3.45603	0.64607	5.30378
H	-2.05763	1.57414	4.72851
H	-5.29201	-1.96022	3.12720
H	-5.48330	-0.63104	4.28349
H	-3.96949	-1.56156	4.22989
H	-4.96095	0.88140	0.82395
H	-6.17185	0.73346	2.12735
H	-5.74102	-0.66828	1.12616
H	-4.86379	-3.55240	-1.61084
H	-4.09745	-2.01370	-1.12702
H	-4.63909	-3.15547	0.10606
H	-3.46271	-5.77695	-1.29891
H	-3.54741	-5.32949	0.41370
H	-1.98056	-5.69232	-0.32234
H	-0.14835	-4.07413	-3.12572
H	-1.19911	-5.43793	-2.69686
H	-0.25703	-4.60973	-1.43996
H	-2.10752	-3.09700	-4.27321
H	-3.49317	-2.48647	-3.35675
H	-3.32645	-4.22864	-3.66235
H	-4.71747	3.41223	-1.97944
H	-3.62242	3.12294	-0.60835
H	-5.20130	2.32098	-0.67596
H	-5.09417	1.43731	-3.70563
H	-5.66968	0.54542	-2.28546
H	-4.40767	-0.15304	-3.30853
H	-2.67564	0.91019	-4.70707
H	-2.06457	-0.20431	-3.45859
H	-0.99469	1.02239	-4.16130
H	-3.07254	3.44925	-4.00559
H	-1.32245	3.40246	-3.73172
H	-2.39498	3.98123	-2.45025

Sum of electronic and zero-point Energies= -2581.152258

Sum of electronic and thermal Energies= -2581.092473

Sum of electronic and thermal Enthalpies= -2581.091529

Sum of electronic and thermal Free Energies= -2581.247107

1,3 DICYANOBENZENE-DTBPY

SM

1,3 DICYANOBENZENE

C	0.00006	-0.76983	0.00013
C	1.20600	-0.05727	0.00004
C	-1.20589	-0.05742	0.00011
C	1.20852	1.34867	-0.00014
C	-1.20860	1.34858	0.00009
C	-0.00010	2.04114	0.00001
H	-0.00005	3.12575	-0.00009
H	0.00009	-1.85373	0.00019
C	2.44842	-0.77268	-0.00001
C	-2.44833	-0.77285	-0.00001
H	-2.15153	1.88435	0.00018
N	3.45802	-1.34940	-0.00002
N	-3.45808	-1.34932	-0.00016
H	2.15135	1.88464	-0.00033

ORTHO

Metal substrate complexes weren't calculated for this system

TS2-3-CN2-OD-18

C	0.98371	2.20940	1.69792
C	1.97040	3.18850	1.75662
C	3.19121	2.98775	1.10320
C	3.34351	1.76826	0.42953
C	2.31332	0.82734	0.41090
N	1.13813	1.05439	1.03960
H	1.75900	4.09729	2.30566
C	4.31990	4.02505	1.07736
H	4.25846	1.56617	-0.11228
H	0.02806	2.34556	2.18899
C	2.41098	-0.43956	-0.35326
N	1.24876	-1.08890	-0.59550
C	3.63088	-0.94030	-0.82251
C	3.68445	-2.11363	-1.57823
C	2.45706	-2.74498	-1.83598
C	1.27927	-2.21415	-1.33202
H	4.53939	-0.40904	-0.57774
C	4.99363	-2.70600	-2.11119
H	2.40543	-3.65500	-2.42317
Ir	-0.60255	-0.28469	0.38986
H	0.31646	-2.67469	-1.51928
C	6.21918	-1.86312	-1.71771
C	4.91867	-2.77785	-3.65400
C	5.16914	-4.13028	-1.53537
H	5.21769	-4.10779	-0.44132
H	6.09983	-4.57122	-1.90880
H	4.34662	-4.79147	-1.82442
H	6.16034	-0.84555	-2.11898
H	7.12490	-2.32572	-2.12222
H	6.33801	-1.79976	-0.63070
H	4.78356	-1.78087	-4.08732
H	4.09296	-3.41010	-3.99413
H	5.84789	-3.19946	-4.05257
C	3.96114	5.28972	1.87625
C	4.59183	4.43021	-0.39033
C	5.59667	3.40206	1.68696
H	3.07844	5.79213	1.46669
H	4.79479	5.99796	1.83350
H	3.77132	5.06386	2.93088
H	5.42739	3.09969	2.72602
H	6.41233	4.13335	1.67374
H	5.93009	2.52176	1.12860
H	3.69549	4.86105	-0.84985
H	4.90672	3.57661	-0.99874
H	5.38945	5.18028	-0.42999
B	-0.65820	0.93318	-1.34109
O	0.03341	2.13615	-1.44321
O	-1.20445	0.58222	-2.56746
C	-1.06800	1.70817	-3.47476
C	0.14228	2.48593	-2.84614
C	-2.38509	2.48859	-3.41244
C	-0.83088	1.17344	-4.88286
C	1.50639	1.96833	-3.32090
C	0.07752	4.00305	-2.97956
H	1.56674	0.88017	-3.22478
H	2.28793	2.40692	-2.69293
H	1.70674	2.23979	-4.36193
H	-0.81536	4.40785	-2.49912
H	0.07617	4.30251	-4.03303
H	0.95245	4.45348	-2.49932
H	-2.57887	2.82672	-2.39260
H	-3.20392	1.82310	-3.70298
H	-2.38232	3.34735	-4.09091
H	0.01528	0.48370	-4.91442
H	-0.64054	1.99399	-5.58297
H	-1.71839	0.63310	-5.22702
B	-2.06284	-1.37729	-0.54274

B	-2.06013	1.11464	0.86521
O	-2.28522	1.54994	2.17435
O	-2.85318	1.84336	-0.01653
O	-1.79234	-2.46542	-1.38506
O	-3.44080	-1.24167	-0.38945
C	-3.02830	-2.87646	-2.02785
C	-4.10237	-2.37741	-0.99856
C	-2.98958	-4.38534	-2.24265
C	-5.41476	-1.90569	-1.61565
C	-4.37511	-3.38725	0.12297
H	-3.44013	-3.72828	0.57779
H	-4.92915	-4.25949	-0.23752
H	-4.96957	-2.89913	0.90126
H	-5.25487	-1.07195	-2.30227
H	-6.09305	-1.56722	-0.82581
H	-5.90594	-2.72016	-2.15882
H	-2.78431	-4.92089	-1.31325
H	-2.20069	-4.63678	-2.95909
H	-3.94139	-4.74366	-2.64878
C	-3.09568	-2.14585	-3.37343
H	-3.07359	-1.06430	-3.22554
H	-3.99067	-2.42312	-3.93902
H	-2.21643	-2.41599	-3.96652
C	-3.43801	2.43536	2.17355
C	-3.43609	2.96232	0.69847
C	-3.24096	3.50124	3.24472
C	-4.66010	1.56813	2.49594
C	-4.81282	3.25425	0.11224
C	-2.50547	4.16408	0.49317
H	-4.80124	0.79891	1.73124
H	-5.57380	2.16595	2.56951
H	-4.49742	1.06866	3.45589
H	-2.28956	4.02331	3.12283
H	-3.24548	3.03619	4.23555
H	-4.05100	4.23757	3.21126
H	-5.43969	2.36055	0.09867
H	-4.70801	3.60821	-0.91832
H	-5.32277	4.03348	0.68864
H	-1.50953	3.96408	0.89767
H	-2.90383	5.06714	0.96567
H	-2.39934	4.35453	-0.57813
C	0.14177	-4.20921	2.32075
C	-0.36320	-3.15390	1.57293
C	0.78047	-3.95854	3.55028
C	-0.23536	-1.80433	1.97283
C	0.87933	-2.64494	4.01777
C	0.36696	-1.59222	3.24221
C	0.46007	-0.28324	3.82243
H	0.04698	-5.22954	1.96194
H	-0.85045	-3.37790	0.63052
C	1.31127	-5.03793	4.32406
H	1.34585	-2.43853	4.97531
H	-1.39856	-0.76642	1.72585
N	0.54564	0.74303	4.36355
N	1.74376	-5.92011	4.94802

Sum of electronic and zero-point Energies= -2564.162594

Sum of electronic and thermal Energies= -2564.100754

Sum of electronic and thermal Enthalpies= -2564.099810

Sum of electronic and thermal Free Energies= -2564.259322

Imaginary Frequency = -803.64

3-CN2-OD-6-HBS

C	-1.54007	-2.33060	1.43013
C	-2.78872	-2.89241	1.68584
C	-3.94527	-2.27366	1.20062
C	-3.75776	-1.10251	0.45316
C	-2.47844	-0.59392	0.22474
N	-1.37877	-1.20457	0.72570
H	-2.82946	-3.80473	2.26722
C	-5.36140	-2.80882	1.44521
H	-4.61965	-0.58505	0.05275
H	-0.62906	-2.79118	1.78588
C	-2.22965	0.61786	-0.59121
N	-0.94754	1.05244	-0.66279
C	-3.24822	1.26482	-1.30129
C	-2.97787	2.36733	-2.11347
C	-1.64000	2.78912	-2.16386
C	-0.66830	2.11738	-1.44085
H	-4.25530	0.88174	-1.22992
C	-4.04820	3.07415	-2.95028
H	-1.33696	3.63214	-2.77422
Ir	0.58174	-0.04988	0.45553
H	0.37306	2.40898	-1.47026
C	-5.44817	2.47337	-2.73789
C	-3.67028	2.93264	-4.44370
C	-4.08866	4.57061	-2.56560
H	-4.34517	4.69722	-1.50825
H	-4.84642	5.08776	-3.16400
H	-3.12926	5.06553	-2.74355
H	-5.48990	1.42013	-3.03584

H	-6.17487	3.01745	-3.34925
H	-5.76967	2.55092	-1.69367
H	-3.62007	1.87824	-4.73686
H	-2.70175	3.39187	-4.66388
H	-4.42426	3.42487	-5.06757
C	-5.35451	-4.10602	2.27207
C	-6.03495	-3.09532	0.08327
C	-6.17702	-1.74092	2.21022
H	-4.80571	-4.90766	1.76650
H	-6.38292	-4.45069	2.41989
H	-4.91028	-3.95491	3.26158
H	-5.71521	-1.51301	3.17689
H	-7.19215	-2.10879	2.39567
H	-6.25894	-0.80684	1.64577
H	-5.47177	-3.84514	-0.48281
H	-6.11201	-2.19379	-0.53250
H	-7.04891	-3.47869	0.24149
B	0.85635	-0.72360	-1.58325
O	0.14606	-1.72542	-2.22164
O	1.46486	0.11728	-2.49277
C	1.23345	-0.36964	-3.84181
C	0.06351	-1.41371	-3.64140
C	2.54594	-0.99223	-4.32161
C	0.87732	0.82823	-4.72009
C	-1.33175	-0.82345	-3.87398
C	0.21583	-2.71161	-4.42840
H	-1.47538	0.09381	-3.30111
H	-2.08284	-1.54757	-3.54443
H	-1.50473	-0.60380	-4.93183
H	1.14320	-3.23022	-4.17833
H	0.20433	-2.51551	-5.50548
H	-0.61864	-3.38061	-4.19599
H	2.84107	-1.82603	-3.68402
H	3.33485	-0.23571	-4.27326
H	2.47039	-1.34679	-5.35406
H	0.03156	1.38770	-4.31605
H	0.63343	0.50705	-5.73793
H	1.73447	1.50655	-4.77458
B	2.17915	1.22397	0.29811
B	1.74974	-1.77131	0.12323
O	1.24263	-3.02583	0.45820
O	3.08838	-1.86395	-0.23888
O	2.13876	2.44544	-0.37780
O	3.39980	1.08358	0.95017
C	3.47730	3.00616	-0.39511
C	4.11375	2.34367	0.87543
C	3.37237	4.52618	-0.35021
C	5.60820	2.05924	0.77281
C	3.80418	3.10878	2.16822
H	2.73365	3.31748	2.25262
H	4.35358	4.05370	2.22398
H	4.09524	2.49051	3.02284
H	5.83005	1.37785	-0.05099
H	5.96058	1.59445	1.69916
H	6.17091	2.98700	0.62347
H	2.76152	4.86137	0.49064
H	2.91003	4.89323	-1.27243
H	4.36487	4.98108	-0.26527
C	4.13396	2.55287	-1.70374
H	4.20298	1.46313	-1.74593
H	5.13478	2.97939	-1.82260
H	3.51540	2.88290	-2.54355
C	2.36868	-3.91978	0.65474
C	3.45996	-3.26967	-0.26718
C	1.94216	-5.32978	0.26270
C	2.73312	-3.86916	2.14314
C	4.89266	-3.40180	0.23746
C	3.36297	-3.73679	-1.72207
H	3.03758	-2.86201	2.44146
H	3.54238	-4.56558	2.38285
H	1.85549	-4.14109	2.73575
H	1.52148	-5.35619	-0.74450
H	1.17719	-5.68888	0.95855
H	2.79202	-6.01879	0.30812
H	5.01893	-2.93313	1.21527
H	5.57719	-2.91245	-0.46257
H	5.17959	-4.45605	0.31262
H	2.34431	-3.61347	-2.09874
H	3.65716	-4.78517	-1.82883
H	4.03571	-3.13079	-2.33498
C	-0.61625	3.37304	3.03862
C	-0.25469	2.54552	1.98348
C	-0.70521	2.85053	4.34407
C	0.03566	1.16812	2.13255
C	-0.41768	1.49973	4.55912
C	-0.05502	0.68922	3.47077
C	0.23221	-0.68378	3.77833
H	-0.82495	4.42499	2.86687
H	-0.17004	2.99416	0.99998
C	-1.07924	3.69023	5.43863
H	-0.47357	1.08185	5.55903
H	1.59078	-0.76306	1.47151
N	0.45469	-1.78894	4.06966
N	-1.38686	4.37894	6.32560

Sum of electronic and zero-point Energies= -2564.189766

Sum of electronic and thermal Energies= -2564.128980

Sum of electronic and thermal Enthalpies= -2564.128036

Sum of electronic and thermal Free Energies= -2564.283221

META, DTBPY

TS2-3-CN2-MD-4

C	0.61657	2.30742	-1.44826
C	1.59822	3.11354	-2.01604
C	2.94824	2.86914	-1.74071
C	3.22595	1.78523	-0.89675
C	2.20137	1.00113	-0.36663
N	0.90082	1.28293	-0.63314
H	1.28474	3.92099	-2.66547
C	4.09696	3.70226	-2.31995
H	4.25322	1.55349	-0.64736
H	-0.43462	2.45471	-1.66376
C	2.45860	-0.19780	0.47095
N	1.37643	-0.76141	1.04930
C	3.73449	-0.75695	0.61363
C	3.92761	-1.90974	1.37971
C	2.78567	-2.45518	1.98803
C	1.54512	-1.86553	1.79388
H	4.57022	-0.29902	0.10453
C	5.29561	-2.57955	1.55213
H	2.84783	-3.34858	2.59925
Ir	-0.64973	0.01963	0.33670
H	0.63865	-2.28547	2.21494
C	6.41275	-1.82781	0.80802
C	5.21750	-4.02131	0.99790
C	5.64797	-2.62288	3.05674
H	5.70480	-1.61243	3.47581
H	6.62119	-3.10548	3.19810
H	4.90862	-3.18738	3.63287
H	6.23029	-1.79052	-0.27142
H	7.36565	-2.34337	0.96362
H	6.52820	-0.80239	1.17534
H	4.95920	-4.01875	-0.06671
H	4.47012	-4.62154	1.52570
H	6.18713	-4.51819	1.11219
C	3.58842	4.84601	-3.21383
C	5.00430	2.77945	-3.16652
C	4.91702	4.31002	-1.15884
H	3.02338	4.47040	-4.07349
H	4.44078	5.41355	-3.60053
H	2.95078	5.54239	-2.65898
H	4.29418	4.96311	-0.53817
H	5.74359	4.90710	-1.55911
H	5.34611	3.53781	-0.51284
H	4.44156	2.32259	-3.98782
H	5.44194	1.97472	-2.56758
H	5.82733	3.35934	-3.59820
B	-0.26009	-1.23346	-1.32436
O	-0.20402	-0.80837	-2.64406
O	0.23424	-2.53344	-1.21592
C	0.46544	-3.05923	-2.54989
C	0.61395	-1.74492	-3.39273
C	-0.76721	-3.88454	-2.93366
C	1.70574	-3.94622	-2.51059
C	2.04351	-1.18610	-3.38696
C	0.08579	-1.82595	-4.82041
H	2.44110	-1.13273	-2.36969
H	2.02946	-0.17162	-3.79682
H	2.71962	-1.79515	-3.99492
H	-0.98035	-2.06094	-4.83977
H	0.62449	-2.58941	-5.39181
H	0.22808	-0.86328	-5.32187
H	-1.66810	-3.26561	-2.93120
H	-0.90317	-4.68445	-2.20042
H	-0.65448	-4.34270	-3.92105
H	2.56054	-3.41970	-2.08056
H	1.97272	-4.28792	-3.51630
H	1.50976	-4.82890	-1.89348
B	-1.80141	-1.65675	0.75075
B	-2.33798	0.75677	-0.54733
O	-2.40424	1.29742	-1.83478
O	-3.56904	0.93817	0.09694
O	-1.60061	-2.43721	1.89527
O	-2.80143	-2.21300	-0.03585
C	-2.29010	-3.70404	1.70920
C	-3.41668	-3.30766	0.69118
C	-2.78682	-4.19645	3.06361
C	-3.79819	-4.39868	-0.30329
C	-4.67108	-2.74795	1.37074
H	-4.41310	-1.95125	2.07423
H	-5.22330	-3.52651	1.90609
H	-5.32765	-2.32335	0.60676
H	-2.94389	-4.70311	-0.91004
H	-4.57557	-4.02629	-0.97817
H	-4.19265	-5.27805	0.21691
H	-3.39340	-3.44278	3.56976
H	-1.93324	-4.43173	3.70751
H	-3.38417	-5.10710	2.94800

C	-1.26533	-4.68381	1.12572
H	-0.86882	-4.30556	0.18072
H	-1.69665	-5.67760	0.97094
H	-0.42948	-4.78165	1.82615
C	-3.63037	2.05965	-1.96535
C	-4.54386	1.41103	-0.86567
C	-4.14238	1.91921	-3.39521
C	-3.28126	3.52504	-1.67418
C	-5.49467	2.37775	-0.16606
C	-5.31138	0.18271	-1.36674
H	-2.89448	3.64599	-0.65814
H	-4.14707	4.18264	-1.79710
H	-2.50410	3.85121	-2.37265
H	-4.24718	0.87052	-3.68029
H	-3.43630	2.38786	-4.08830
H	-5.11224	2.41437	-3.51239
H	-4.95634	3.18727	0.33203
H	-6.07272	1.84162	0.59342
H	-6.19934	2.81627	-0.88070
H	-4.63284	-0.53686	-1.83173
H	-6.09177	0.45607	-2.08373
H	-5.78592	-0.30841	-0.51277
C	0.54203	2.77787	3.67568
C	0.36480	1.64529	2.85852
C	-0.38161	3.83041	3.66319
C	-0.72576	1.53776	1.97870
C	-1.49690	3.70819	2.82599
C	-1.67249	2.57559	2.01052
H	-2.56330	2.50207	1.39838
C	1.69294	2.85406	4.52672
H	1.10381	0.85374	2.90639
H	-0.24216	4.70505	4.28786
C	-2.48174	4.74920	2.78637
H	-1.38140	0.12234	1.78755
N	-3.29163	5.58287	2.73350
N	2.63380	2.90300	5.20941

Sum of electronic and zero-point Energies= -2564.164017

Sum of electronic and thermal Energies= -2564.102164

Sum of electronic and thermal Enthalpies= -2564.101220

Sum of electronic and thermal Free Energies= -2564.261545

Imaginary Freq = -800.89

3-CN2-MD-2

C	0.56105	2.28934	-1.17824
C	1.47073	3.03131	-1.91297
C	2.77282	2.55395	-2.11617
C	3.08739	1.33875	-1.50392
C	2.14242	0.64154	-0.74194
N	0.87649	1.11209	-0.60485
H	1.13999	3.96878	-2.34505
C	3.76226	3.33686	-2.98461
H	4.07675	0.92182	-1.61949
H	-0.45922	2.62006	-1.03850
C	2.46000	-0.62783	-0.04532
N	1.43345	-1.22150	0.59985
C	3.74785	-1.17950	-0.03129
C	4.01046	-2.36779	0.65387
C	2.92311	-2.95838	1.31618
C	1.67063	-2.36335	1.26492
H	4.54743	-0.67107	-0.54871
C	5.39868	-3.01648	0.70258
H	3.03890	-3.88055	1.87464
Ir	-0.55605	-0.07958	0.53191
H	0.80982	-2.81023	1.74449
C	6.44666	-2.21699	-0.09099
C	5.30729	-4.43877	0.10298
C	5.85769	-3.10542	2.17632
H	5.92466	-2.10942	2.62721
H	6.84742	-3.57183	2.23160
H	5.17149	-3.70533	2.78171
H	6.18349	-2.14010	-1.15159
H	7.41548	-2.72231	-0.02705
H	6.57575	-1.20514	0.30804
H	4.97639	-4.40415	-0.94068
H	4.60896	-5.07197	0.65866
H	6.29094	-4.92002	0.13313
C	3.97272	4.73955	-2.37010
C	3.16336	3.47809	-4.40398
C	5.12722	2.63623	-3.09313
H	3.03650	5.30238	-2.30796
H	4.66922	5.31634	-2.98829
H	4.39230	4.66682	-1.36096
H	5.60680	2.52527	-2.11464
H	5.79461	3.23343	-3.72227
H	5.04095	1.64469	-3.55074
H	2.21805	4.02916	-4.39281
H	2.97795	2.49565	-4.85188
H	3.86009	4.02260	-5.05054
B	-0.96230	-0.70973	-1.48634
O	-1.61826	0.14557	-2.35727
O	-0.36651	-1.75592	-2.17902

C -0.79816 -1.69664 -3.57259
C -1.24037 -0.19728 -3.71902
C -1.96431 -2.67447 -3.73605
C 0.37292 -2.11763 -4.45348
C -0.08789 0.73051 -4.12003
C -2.44382 0.04417 -4.62391
H 0.78493 0.57991 -3.48024
H -0.40975 1.76925 -4.01052
H 0.20917 0.56973 -5.16088
H -3.32937 -0.48212 -4.26254
H -2.23418 -0.28011 -5.64856
H -2.67374 1.11413 -4.64713
H -2.78096 -2.41647 -3.05815
H -1.62689 -3.68691 -3.49995
H -2.34057 -2.67638 -4.76319
H 1.26538 -1.52233 -4.24970
H 0.11755 -2.01524 -5.51339
H 0.61643 -3.16759 -4.26309
B -1.71037 -1.83024 0.37676
B -2.21223 1.12293 0.45969
O -2.21452 2.42693 -0.04631
O -3.46710 0.82017 0.97882
O -1.25506 -3.01153 0.96744
O -2.96810 -2.02045 -0.17686
C -2.16613 -4.08681 0.62268
C -3.48320 -3.29684 0.28968
C -2.27006 -5.03534 1.81226
C -4.34246 -3.91367 -0.80722
C -4.33746 -2.99791 1.52691
H -3.73593 -2.54569 2.32072
H -4.81402 -3.90176 1.91830
H -5.11953 -2.28471 1.25182
H -3.79059 -4.02069 -1.74205
H -5.21216 -3.27662 -0.99662
H -4.70447 -4.90073 -0.50077
H -2.54463 -4.50753 2.72771
H -1.30503 -5.52418 1.98001
H -3.01503 -5.81447 1.61970
C -1.56093 -4.80868 -0.58370
H -1.42908 -4.11388 -1.41364
H -2.17740 -5.65256 -0.90770
H -0.57323 -5.19033 -0.30646
C -3.46850 3.06821 0.31018
C -4.40398 1.82887 0.52519
C -3.87701 4.00237 -0.82301
C -3.21745 3.86606 1.59448
C -5.48395 2.01230 1.58498
C -5.01818 1.31097 -0.78177
H -2.91484 3.20722 2.41310
H -4.10686 4.42387 1.90284
H -2.40916 4.58273 1.41992
H -3.90216 3.48112 -1.78210
H -3.15823 4.82453 -0.90236
H -4.86504 4.43442 -0.63214
H -5.05275 2.22797 2.56481
H -6.07585 1.09543 1.67082
H -6.16094 2.82896 1.31241
H -4.24463 1.16040 -1.54021
H -5.77670 1.99557 -1.17407
H -5.49211 0.34418 -0.58944
C 1.27956 1.15690 4.41704
C 0.73774 0.42885 3.33762
C 1.26578 2.55706 4.42082
C 0.16593 1.06051 2.21902
C 0.69248 3.20288 3.31887
C 0.15388 2.46605 2.24541
C 1.85931 0.45232 5.52202
C 0.64135 4.63450 3.27839
H -1.48522 -0.77606 1.63522
H 0.77783 -0.65553 3.38591
N 0.58700 5.79589 3.22398
N 2.33058 -0.13390 6.41019
H 1.68158 3.11978 5.24865
H -0.29671 3.01411 1.42473
Sum of electronic and zero-point Energies= -2564.183733
Sum of electronic and thermal Energies= -2564.121743
Sum of electronic and thermal Enthalpies= -2564.120799
Sum of electronic and thermal Free Energies= -2564.282722

1,3-dicyanobenzene, hydrazone ligand

Ortho

TS2-3-CN2-OT-7

Ir -0.57036 -0.39136 0.13185
N 0.51232 1.69196 0.16921
C -0.14339 2.76645 0.65942
N 0.51751 -0.22028 -1.94749
C 0.21016 4.07848 0.40967
C 1.61143 1.94987 -0.58650
C 1.32456 4.36311 -0.41900
C 2.03078 3.23319 -0.90205

H	-1.00494	2.53871	1.27539
H	-0.38621	4.86584	0.85220
N	1.70531	5.63358	-0.72116
H	2.92889	3.34494	-1.49274
C	2.40530	0.78877	-1.10801
N	1.90373	-0.19378	-1.77149
C	3.84957	0.68505	-0.73950
C	4.63747	-0.33368	-1.27675
N	4.28241	1.54725	0.20181
C	5.95291	-0.53281	-0.79943
C	5.54277	1.37606	0.62759
C	0.94973	6.76556	-0.19708
C	2.86611	5.86884	-1.57319
H	3.78210	5.46525	-1.12426
H	2.99767	6.94181	-1.70936
H	2.73632	5.41287	-2.56259
H	-0.09188	6.74613	-0.54163
H	1.40603	7.69211	-0.54465
H	0.95000	6.77566	0.89994
C	6.40266	0.38094	0.18839
N	6.73610	-1.56040	-1.25101
H	5.88688	2.07456	1.38885
C	6.17015	-2.55445	-2.15486
C	8.00775	-1.84128	-0.59338
H	8.68922	-0.98614	-0.66806
H	8.48433	-2.68927	-1.08559
H	7.87412	-2.08544	0.46942
H	5.82846	-2.09225	-3.08796
H	5.31857	-3.08536	-1.70606
H	6.93699	-3.28705	-2.40658
H	7.39123	0.30836	0.62248
H	4.20093	-0.98664	-2.01825
B	-1.70756	-0.14363	1.81689
O	-2.08721	-1.13461	2.71759
O	-2.17142	1.09930	2.26000
C	-3.08064	-0.57498	3.61538
C	-2.70830	0.94647	3.59879
B	-1.80637	-1.85412	-0.63322
O	-2.53249	-2.82403	0.03703
O	-1.99961	-1.96565	-2.01541
C	-3.48144	-3.41103	-0.89134
C	-2.79406	-3.15558	-2.28204
C	-3.88178	1.90517	3.76588
C	-1.58483	1.30190	4.57944
C	-2.96174	-1.25559	4.97365
C	-4.45261	-0.85691	2.98990
C	-4.79659	-2.64190	-0.71607
C	-3.67465	-4.87982	-0.53039
C	-1.82637	-4.26799	-2.69299
C	-3.75685	-2.85146	-3.42554
H	0.10669	0.64796	-2.30478
H	0.27475	-0.99264	-2.56197
C	3.37589	-2.51295	0.97626
C	2.07926	-2.26523	0.50709
C	1.23598	-1.28068	1.08424
C	1.64974	-3.00171	-0.64521
C	1.74172	-0.62165	2.22329
C	3.02921	-0.84021	2.69981
C	3.85965	-1.78620	2.06972
C	5.20268	-1.99300	2.51392
H	-0.26201	-1.71456	1.00720
B	-2.13519	0.66265	-0.80218
O	-3.50578	0.61663	-0.59636
O	-1.82730	1.58761	-1.80500
C	-3.06550	2.01314	-2.43996
C	-4.11928	1.72095	-1.31391
C	-4.26303	2.87216	-0.31202
C	-5.48931	1.27633	-1.81280
C	-3.24674	1.13254	-3.67963
C	-2.93045	3.47935	-2.83435
H	-4.62362	1.77063	2.97656
H	-3.52478	2.93928	3.72094
H	-4.36909	1.75653	4.73533
H	-0.74085	0.61420	4.47158
H	-1.92815	1.27366	5.61811
H	-1.22900	2.31388	4.36248
H	-3.23273	-2.31224	4.88264
H	-3.63891	-0.79299	5.69967
H	-1.94266	-1.20173	5.36260
H	-4.53762	-0.37305	2.01282
H	-5.27002	-0.51393	3.63204
H	-4.55694	-1.93562	2.84295
H	-5.58936	-3.04100	-1.35668
H	-4.65389	-1.58021	-0.93077
H	-5.11926	-2.73076	0.32570
H	-4.32840	-5.37479	-1.25640
H	-4.14320	-4.95765	0.45580
H	-2.72346	-5.41480	-0.49466
H	-1.24404	-3.93275	-3.55653
H	-2.36124	-5.18127	-2.97185
H	-1.12393	-4.49788	-1.88986
H	-3.19168	-2.64969	-4.34116
H	-4.37769	-1.97977	-3.21156
H	-4.41315	-3.70768	-3.61441
H	-4.77032	3.73412	-0.75613
H	-3.28544	3.18895	0.06104

H -4.85114 2.52628 0.54261
H -5.95437 2.06010 -2.42000
H -6.14407 1.07371 -0.95939
H -5.42334 0.36494 -2.41038
H -2.37917 1.26022 -4.33500
H -4.14434 1.40243 -4.24426
H -3.30203 0.07909 -3.39590
H -2.17315 3.58321 -3.61807
H -2.62318 4.09520 -1.98654
H -3.87778 3.86515 -3.22549
H 4.00467 -3.24925 0.48762
H 3.40398 -0.27740 3.54884
N 6.30370 -2.15885 2.85412
H 1.12179 0.11728 2.72043
N 1.33893 -3.61151 -1.58644
Sum of electronic and zero-point Energies= -2666.409047
Sum of electronic and thermal Energies= -2666.346311
Sum of electronic and thermal Enthalpies= -2666.345367
Sum of electronic and thermal Free Energies= -2666.507726
Imaginary Freq = -779.40

3-CN2-OT-1

Ir -0.54251 -0.48908 0.01695
N 0.36043 1.54554 0.20821
C -0.25012 2.49788 0.94654
N 0.33591 -0.03288 -2.17240
C 0.05055 3.84402 0.89076
C 1.39506 1.96107 -0.58058
C 1.05533 4.30550 0.00454
C 1.74052 3.29520 -0.71579
H -1.02075 2.13774 1.61457
H -0.50353 4.51942 1.52942
N 1.36337 5.62176 -0.13165
H 2.57955 3.53602 -1.35143
C 2.21789 0.93398 -1.30414
N 1.72267 0.02728 -2.07234
C 3.68421 0.85040 -1.01185
C 4.43419 -0.19518 -1.55267
N 4.18337 1.75015 -0.14115
C 5.77843 -0.37901 -1.15697
C 5.46844 1.59141 0.20747
C 0.62681 6.62460 0.62967
C 2.46324 6.03292 -0.99930
H 3.41066 5.57754 -0.68655
H 2.57342 7.11572 -0.94826
H 2.27408 5.75649 -2.04385
H -0.44995 6.55631 0.43397
H 0.96083 7.61813 0.33182
H 0.79008 6.51525 1.70951
C 6.29529 0.57247 -0.24020
N 6.52664 -1.42810 -1.61570
H 5.86378 2.32287 0.91094
C 5.91444 -2.43686 -2.47143
C 7.85424 -1.66894 -1.06190
H 8.52128 -0.81806 -1.24467
H 8.28951 -2.54335 -1.54594
H 7.81724 -1.85515 0.01961
H 5.52419 -1.99161 -3.39405
H 5.08812 -2.95833 -1.96902
H 6.66702 -3.17513 -2.74856
H 7.31001 0.51229 0.13125
H 3.94883 -0.88220 -2.22946
B -1.30736 -0.67033 1.89380
O -1.66525 -1.85984 2.51577
O -1.48592 0.40415 2.76540
C -2.37507 -1.53350 3.73938
C -1.79272 -0.11905 4.08602
B -2.12987 -1.49559 -0.92767
O -3.16753 -2.21021 -0.35228
O -2.12743 -1.64689 -2.31729
C -4.01011 -2.73775 -1.40721
C -3.04061 -2.73276 -2.64756
C -2.76549 0.83255 4.77284
C -0.47135 -0.18313 4.85983
C -2.09685 -2.61594 4.77566
C -3.86805 -1.49518 3.39214
C -5.19474 -1.78119 -1.56106
C -4.50182 -4.11845 -0.98408
C -2.19838 -4.00691 -2.75911
C -3.70361 -2.41746 -3.98331
H -0.13397 0.85557 -2.37048
H 0.06842 -0.72967 -2.86076
C 3.38067 -2.56358 0.68184
C 2.08516 -2.23436 0.25755
C 1.33811 -1.14923 0.79605
C 1.56251 -2.99438 -0.84117
C 1.98022 -0.45678 1.84820
C 3.26360 -0.75594 2.28943
C 3.98230 -1.81093 1.69569
C 5.33283 -2.08118 2.07439
H -0.86566 -2.05253 -0.05521

B -2.24288 0.70233 -0.61854
O -3.50287 0.88090 -0.08561
O -1.98399 1.65663 -1.59919
C -3.19170 2.42481 -1.85881
C -4.05627 2.13916 -0.57080
C -3.85744 3.16925 0.54594
C -5.54882 1.95304 -0.82774
C -3.79851 1.86443 -3.14785
C -2.79663 3.88557 -2.05457
H -3.64270 1.02480 4.15161
H -2.27198 1.79038 4.96752
H -3.09753 0.42184 5.73213
H 0.23455 -0.86341 4.37548
H -0.62317 -0.51062 5.89285
H -0.02230 0.81477 4.87849
H -2.53213 -3.56433 4.44514
H -2.54611 -2.35400 5.73957
H -1.02518 -2.76887 4.91924
H -4.07446 -0.72233 2.64667
H -4.48506 -1.31034 4.27710
H -4.15547 -2.45949 2.96395
H -5.91462 -2.14347 -2.30119
H -4.85082 -0.78902 -1.85175
H -5.70225 -1.68662 -0.59694
H -5.07498 -4.58999 -1.78924
H -5.15645 -4.02245 -0.11211
H -3.67279 -4.77462 -0.71220
H -1.42027 -3.85559 -3.51224
H -2.80761 -4.86515 -3.05839
H -1.70344 -4.23854 -1.81268
H -2.95181 -2.42207 -4.77894
H -4.18086 -1.43558 -3.97475
H -4.45881 -3.17221 -4.22601
H -4.31074 4.13097 0.28763
H -2.79961 3.32985 0.75764
H -4.33284 2.79692 1.45823
H -5.98709 2.87898 -1.21441
H -6.05283 1.70515 0.11144
H -5.75023 1.15189 -1.53904
H -3.06715 1.96341 -3.95583
H -4.70558 2.40331 -3.43678
H -4.03499 0.80335 -3.04190
H -2.18435 3.98215 -2.95671
H -2.21280 4.25901 -1.21117
H -3.68381 4.51517 -2.17751
H 3.92274 -3.37774 0.21265
H 3.72565 -0.16918 3.07752
N 6.44267 -2.28963 2.36000
H 1.46136 0.37262 2.31722
N 1.17335 -3.61558 -1.74608
Sum of electronic and zero-point Energies= -2666.428498
Sum of electronic and thermal Energies= -2666.365869
Sum of electronic and thermal Enthalpies= -2666.364925
Sum of electronic and thermal Free Energies= -2666.525122

Meta

TS2-3-CN2-MT-1
Ir -0.68232 -0.27685 0.24871
N 0.51319 1.79450 0.00019
C -0.11095 2.96004 0.26870
N 0.49717 -0.41250 -1.74270
C 0.33924 4.20232 -0.13978
C 1.67292 1.88095 -0.70237
C 1.53084 4.30559 -0.89969
C 2.19470 3.08141 -1.16309
H -1.02967 2.86976 0.83609
H -0.23910 5.07552 0.13326
N 2.01803 5.49795 -1.34056
H 3.13416 3.05924 -1.69664
C 2.41968 0.61804 -1.02224
N 1.88411 -0.43337 -1.53768
C 3.86569 0.52211 -0.65452
C 4.64519 -0.52798 -1.13908
N 4.31177 1.44501 0.22137
C 5.97825 -0.68198 -0.69057
C 5.57486 1.29658 0.64501
C 1.32290 6.73673 -1.00986
C 3.28250 5.54875 -2.06661
H 4.11242 5.16615 -1.45907
H 3.50181 6.58278 -2.33087
H 3.23496 4.96390 -2.99329
H 0.29278 6.72736 -1.38578
H 1.84289 7.57478 -1.47354
H 1.29302 6.90803 0.07400
C 6.43166 0.27903 0.25002
N 6.77808 -1.69927 -1.13471
H 5.92309 2.03243 1.36754
C 6.22476 -2.74062 -1.99359
C 8.07898 -1.91771 -0.51413
H 8.72520 -1.03992 -0.62863

H	8.57076	-2.75955	-1.00174
H	7.99216	-2.14390	0.55791
H	5.78128	-2.30870	-2.89719
H	5.45918	-3.33832	-1.48054
H	7.02857	-3.40790	-2.30577
H	7.43021	0.24130	0.66602
H	4.19965	-1.22785	-1.83105
B	-2.07349	0.33184	1.64228
O	-2.72214	-0.45043	2.59015
O	-2.47257	1.66561	1.77319
C	-3.80126	0.33217	3.16489
C	-3.27445	1.79607	2.97675
B	-1.66563	-1.99198	-0.23361
O	-2.37302	-2.88291	0.55655
O	-1.61186	-2.45874	-1.56028
C	-3.05318	-3.82468	-0.31520
C	-2.13811	-3.81190	-1.58882
C	-4.35162	2.84621	2.73167
C	-2.33167	2.24816	4.09742
C	-4.00755	-0.09688	4.61268
C	-5.05371	0.03472	2.33099
C	-4.45065	-3.25014	-0.57593
C	-3.15193	-5.17084	0.39266
C	-0.93981	-4.76167	-1.47884
C	-2.86659	-4.02700	-2.91037
H	0.15076	0.40682	-2.25214
H	0.22391	-1.25468	-2.24373
C	2.99866	-2.57112	1.38980
C	1.68700	-2.26319	0.98687
C	1.08217	-1.05002	1.34891
H	1.15878	-2.96056	0.34441
C	1.79838	-0.19948	2.20340
C	3.10380	-0.51528	2.62588
C	3.72553	-1.69709	2.21014
C	3.62264	-3.76872	0.91319
C	3.82520	0.40657	3.45190
H	4.74229	-1.92614	2.50606
H	1.36056	0.74229	2.51753
H	-0.50145	-1.09420	1.61701
B	-2.20821	0.46266	-1.00152
O	-3.58034	0.24789	-0.95849
O	-1.87601	1.20753	-2.13956
C	-3.03753	1.24071	-3.01750
C	-4.21217	1.04288	-1.99838
C	-4.67053	2.35098	-1.34487
C	-5.41126	0.27232	-2.53901
C	-2.88178	0.06606	-3.98989
C	-3.04722	2.56568	-3.76917
H	-4.92775	2.62381	1.83180
H	-3.88852	3.82988	2.60194
H	-5.03704	2.90399	3.58381
H	-1.55425	1.50040	4.27998
H	-2.86987	2.42941	5.03278
H	-1.84253	3.17990	3.79691
H	-4.36308	-1.13162	4.64454
H	-4.75804	0.53477	5.09996
H	-3.07944	-0.04184	5.18553
H	-4.89261	0.30804	1.28476
H	-5.93290	0.56170	2.71495
H	-5.25329	-1.04046	2.36913
H	-5.05430	-3.91459	-1.20201
H	-4.38092	-2.26752	-1.04945
H	-4.96227	-3.12146	0.38270
H	-3.58491	-5.92608	-0.27196
H	-3.79968	-5.07981	1.27026
H	-2.17469	-5.52205	0.73069
H	-0.23499	-4.53989	-2.28631
H	-1.24195	-5.80984	-1.56482
H	-0.41892	-4.62706	-0.52612
H	-2.15288	-3.98348	-3.73954
H	-3.62684	-3.26158	-3.07790
H	-3.34957	-5.00965	-2.93021
H	-5.19951	2.99394	-2.05493
H	-3.82080	2.90164	-0.93289
H	-5.35135	2.11559	-0.52192
H	-5.87195	0.80926	-3.37497
H	-6.16309	0.16027	-1.75147
H	-5.12901	-0.72594	-2.87886
H	-1.93901	0.18043	-4.53466
H	-3.69559	0.03130	-4.72045
H	-2.84509	-0.88233	-3.44671
H	-2.18744	2.61424	-4.44516
H	-2.98741	3.41486	-3.08531
H	-3.95707	2.66237	-4.37095
N	4.41048	1.16102	4.11655
N	4.13314	-4.72953	0.49959

Sum of electronic and zero-point Energies= -2666.404815

Sum of electronic and thermal Energies= -2666.341816

Sum of electronic and thermal Enthalpies= -2666.340872

Sum of electronic and thermal Free Energies= -2666.504002

Imaginary Freq = -725.74

3-CN2-MT-2

Ir	-0.66898	-0.19407	0.37333
N	0.51070	1.91252	0.16775
C	-0.08500	3.07815	0.49074
N	0.42658	-0.29733	-1.56633
C	0.37675	4.32660	0.11336
C	1.65579	2.00417	-0.55615
C	1.55073	4.43564	-0.67249
C	2.18826	3.21064	-0.99007
H	-0.99653	2.98551	1.06878
H	-0.17909	5.19954	0.43022
N	2.04692	5.63398	-1.08687
H	3.11575	3.19210	-1.54415
C	2.38301	0.74574	-0.93343
N	1.83570	-0.30154	-1.44058
C	3.84232	0.63196	-0.61610
C	4.59231	-0.41785	-1.14410
N	4.31839	1.51956	0.27933
C	5.92835	-0.61191	-0.72109
C	5.58341	1.33223	0.68101
C	1.38654	6.87234	-0.69029
C	3.29386	5.68824	-1.84217
H	4.13432	5.28169	-1.26526
H	3.51818	6.72588	-2.08767
H	3.21615	5.12668	-2.78109
H	0.34692	6.89790	-1.03840
H	1.91184	7.71717	-1.13519
H	1.38861	7.00206	0.39975
C	6.41329	0.30997	0.24232
N	6.69965	-1.63266	-1.20626
H	5.95662	2.03786	1.42106
C	6.10907	-2.64073	-2.08045
C	7.99793	-1.90442	-0.60106
H	8.66532	-1.03986	-0.69070
H	8.46583	-2.74145	-1.11955
H	7.91084	-2.16405	0.46333
H	5.65972	-2.17708	-2.96513
H	5.34026	-3.23537	-1.56858
H	6.89309	-3.31638	-2.42355
H	7.41533	0.23735	0.64515
H	4.11957	-1.09210	-1.84303
B	-2.42599	0.46733	1.33681
O	-3.38313	-0.32843	1.94393
O	-2.69320	1.81800	1.56865
C	-4.42897	0.51294	2.48798
C	-3.71234	1.91038	2.60258
B	-1.45673	-2.03650	0.04997
O	-2.10308	-2.91954	0.89516
O	-1.33059	-2.59404	-1.23451
C	-2.72838	-3.94645	0.07781
C	-1.80539	-3.96732	-1.19216
C	-4.59471	3.11618	2.30126
C	-2.97290	2.10815	3.93031
C	-4.88077	-0.08125	3.81911
C	-5.58628	0.49986	1.48727
C	-4.15171	-3.46176	-0.22561
C	-2.76656	-5.25002	0.86634
C	-0.57733	-4.86903	-1.03181
C	-2.51853	-4.27256	-2.50467
H	0.06377	0.50567	-2.09409
H	0.16058	-1.14964	-2.05766
C	3.01222	-2.56250	1.36498
C	1.73944	-2.18005	0.90118
C	1.13247	-0.97146	1.28586
H	1.25011	-2.82422	0.17838
C	1.84669	-0.19371	2.21293
C	3.11771	-0.57323	2.69319
C	3.72385	-1.75787	2.26486
C	3.61416	-3.76005	0.86169
C	3.82922	0.29745	3.58044
H	4.71489	-2.03577	2.60381
H	1.44298	0.75913	2.54121
H	-1.10510	-0.26647	1.90802
B	-2.21788	0.44655	-0.98670
O	-3.52580	0.03426	-1.17938
O	-1.79763	1.21049	-2.08457
C	-2.72447	0.96307	-3.18370
C	-4.04205	0.62890	-2.40793
C	-4.83776	1.88120	-2.02792
C	-4.95002	-0.39187	-3.08344
C	-2.17027	-0.23470	-3.96544
C	-2.77594	2.20245	-4.06688
H	-5.00558	3.06867	1.29078
H	-4.00669	4.03573	2.38573
H	-5.42310	3.17681	3.01456
H	-2.31582	1.26016	4.14522
H	-3.66746	2.23263	4.76628
H	-2.35290	3.00725	3.86186
H	-5.35108	-1.05396	3.64491
H	-5.61606	0.56972	4.30382
H	-4.04156	-0.23132	4.50117
H	-5.25471	0.87425	0.52024
H	-6.43528	1.09322	1.84021
H	-5.91990	-0.53254	1.34671
H	-4.71271	-4.19618	-0.81197

H	-4.13191	-2.50861	-0.76117
H	-4.67665	-3.30218	0.72059
H	-3.15995	-6.06395	0.24813
H	-3.42294	-5.13603	1.73475
H	-1.77587	-5.53344	1.22780
H	0.12804	-4.65825	-1.84171
H	-0.84612	-5.92875	-1.07764
H	-0.07106	-4.68154	-0.08118
H	-1.80068	-4.24650	-3.33101
H	-3.30213	-3.54143	-2.71320
H	-2.96895	-5.27032	-2.47849
H	-5.25277	2.36903	-2.91471
H	-4.20944	2.59939	-1.49385
H	-5.67135	1.60255	-1.37897
H	-5.29845	-0.01751	-4.05169
H	-5.82594	-0.57763	-2.45445
H	-4.43886	-1.34363	-3.23958
H	-1.15930	0.00219	-4.31282
H	-2.78414	-0.46075	-4.84218
H	-2.11624	-1.12539	-3.33231
H	-1.80590	2.34910	-4.55241
H	-3.00346	3.09987	-3.48835
H	-3.53252	2.08690	-4.84985
N	4.40890	1.01544	4.28979
N	4.10365	-4.72117	0.42289

Sum of electronic and zero-point Energies= -2666.413896

Sum of electronic and thermal Energies= -2666.351086

Sum of electronic and thermal Enthalpies= -2666.350142

Sum of electronic and thermal Free Energies= -2666.512893

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