Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Bis-aminocyclopropenylidene Carbene Borane Catalyzed Imine Hydrogenation

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General Considerations

Boron compounds, carbene complexes, imines, trityl salts and solvents were dispensed in a 2001 issue IT Glovebox (H_2O levels are approximately 30ppm on average). Carbene complexes and precursors were prepared in oven dried 4-dram scintillation vials equipped with magnetic stir bars and green Qorpak® PTFElined caps. Hydrogenations were carried out in 1-dram scintillation vials equipped with a magnetic stir bar and septa caps pierced with a needle were screwed on. All reactions were conducted at ambient temperature unless otherwise stated. ^{1}H, ^{11}B, ^{19}F and ^{13}C NMR data were collected at 300K on either a Bruker AV-300 or AV-500 spectrometer. ^{1}H NMR spectra are referenced to residual non-deuterated NMR solvent from the sample (C_6H_6 = 7.16 ppm, $CHCl_3$ = 7.26 ppm, CH_3CN = 1.94 ppm). ^{13}C NMR spectra are referenced to residual non-deuterated NMR solvent from the sample (C_6H_6 = 128.06 ppm, $CHCl_3$ = 77.16 ppm, CH_3CN = 1.32 ppm or 118.26 ppm).

Solvents

Ether was purchased as anhydrous >99% ACS grade from Sigma Aldrich and stored over 3Å molecular sieves under nitrogen.

Trifluorotoluene was purchased as anhydrous >99% ACS grade from Sigma Aldrich and dried over 3Å molecular sieves under nitrogen.

Pentane was purchased in a drum as ACS grade from Fisher, sparged with N_2 and stored over 3Å molecular sieves under nitrogen.

Dichloromethane was distilled from calcium hydride under nitrogen.

Tetrahydrofuran was distilled from a purple sodium benzophenone mixture under nitrogen. The solvent was stored over 3Å molecular sieves under nitrogen.

Reagents

Imines were prepared according to literature procedures.

Dimethylchorosilane was purchased from Sigma Aldrich and used as received

Chlorotrimethylsilane was purchased from Sigma Aldrich and distilled before use.

Pentachlorocyclopropane was prepared according to a literature procedure.[1]

$[Ph_3C][BAr^F{}_{24}]$ was prepared according to literature procedures.[2]

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[1] E. D. Nacsa, T. H. Lambert, *J. Am. Chem. Soc.* 2015, **137**, 10246.
[2] S. R. Bahr, P. Boudjouk, *J. Org. Chem.* 1992, **57**, 5545.

^{i}PrBAC-BCy$_2$H was prepared according to previously reported methods.[3]

^{i}PrBAC-LiBF$_4$ was prepared according to previously reported methods.[4]

Tricyclohexylphosphine was purchased from Oakwood Chemical and stored under nitrogen.

Boranes were prepared according to literature procedures.[5]

[3] B. S. N. Huchenski, M. R. Adams, R. McDonald, M. J. Ferguson, A. W. H. Speed, *Organometallics* 2016, **35**, 3101.
[4] V. Lavallo, Y. Ishida, B. Donnadieu, G. Bertrand, *Angew. Chem., Int. Ed.* 2006, **45**, 6652.
[5] 9BBN: J. A. Soderquist, A. Negron, *J. Org. Chem.* 1987, *52*, 3441. Cy2BH: A. Abiko, *Org. Synth.* 2002, **79**, 103. Thexylborane: J. C. Walton, M. M. Brahmi, J. Monot, L. Fensterbank, M. Malacria, D. P. Curran, E. Lacôte, *J. Am. Chem. Soc.* 2011, **133**, 10312.

X-Ray Crystallography

Each of the crystals chosen was attached to the tip of a MicroLoop with paratone-N oil. Measurements were made on a Bruker APEXII CCD equipped diffractometer (30 mA, 50 kV) using monochromated Mo Kα radiation (λ = 0.71073 Å) at 125 K.[6] The initial orientation and unit cell were indexed using a least-squares analysis of a random set of reflections collected from three series of 0.5° ω-scans, 10 seconds per frame and 12 frames per series, that were well distributed in reciprocal space. For data collection, four ω-scan frame series were collected with 0.5° wide scans, 30 (compounds **23** and **6**) or 45 (compound **24**) second frames and 366 frames per series at varying φ angles (φ = 0°, 90°, 180° and 270°). The crystal to detector distance was set to 6 cm and a complete sphere of data was collected. Cell refinement and data reduction were performed with the Bruker SAINT[7] software, which corrects for beam inhomogeneity, possible crystal decay, Lorentz and polarisation effects. A multi-scan absorption correction was applied (SADABS).[8] The structure was solved using SHELXT-2014 and was refined using a full-matrix least-squares method on F^2 with SHELXL-2018.[9] The initial refinements were unremarkable. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms bonded to carbon were included at geometrically idealized positions and were not refined. The isotropic thermal parameters of these hydrogen atoms were fixed at $1.2U_{eq}$ of the parent carbon atom or $1.5U_{eq}$ for methyl hydrogens. The hydrogen atom bonded to boron in compound **24** was located in a near final Fourier difference map. Its position was refined, while its isotropic thermal parameter was fixed at 1.5 times that of the boron atom to which it was bonded.

Compound **23**

There was some minor disorder in the structure, involving one of the N(*i*Pr)$_2$ groups. The heavy atoms involved were each split over two positions with the occupancies of the two parts refined (to a total of 100%). A SAME instruction was used in Shelxl to add restraints to keep the geometries of the two parts similar. The disordered heavy atoms were all restrained to have similar thermal parameters. The C-C bonds in the disordered group were restrained to 1.51 (0.015) Å, while the bond lengths N2A-C3 and N2B-C3 were restrained to be similar. In addition, RIGU was used on the disordered group to add enhanced rigid bond restraints to the atomic displacement parameters for 1,2- and 1,3- heavy atom pairs. The occupancies of the disordered group refined to 88.1(4)/11.9% for part 1 and part 2, respectively.

Using a disordered model for the structure resulted in a checkcif file with several more warnings (and of higher level) than had been obtained with the original unsplit results. Of primary concern is the level B warning that is obtained with the split model:
Short Intermolecular Interaction H27…H15E = 1.91 Ang.

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[6] APEX II (Bruker, 2008) Bruker AXS Inc., Madison, Wisconsin, USA.
[7] SAINT (Bruker, 2008) Bruker AXS Inc., Madison, Wisconsin, USA.
[8] SADABS (Bruker, 2009) Bruker AXS Inc., Madison, Wisconsin, USA.
[9] Sheldrick, G.M. (2008) *Acta Cryst*., A64, 112-122; Sheldrick, G.M. (2015) *Acta Cryst*., A71, 3-8; Sheldrick, G.M. (2015) *Acta Cryst*., C71, 3-8.

This interaction arises between a phenyl ring of the main molecule and one of the methyl protons in the second (minor) part of the disordered group on a second molecule. Since this methyl position is occupied only a small fraction of the time, it is unlikely to be of serious concern in the overall stability of the system. Overall, the split model is to be preferred as it results in better statistical parameters than the unsplit refinement.

The Flack parameter refined to a final value of 0.25(14). This result was supported by values calculated for the Hooft and Parson's parameters using the program Platon.[10] These values came out to 0.20(13) and 0.23(14), respectively. The result is likely slightly unreliable (owing to the lack of heavier atoms in the structure) and likely not an indication of racemic twinning being present in the crystal.

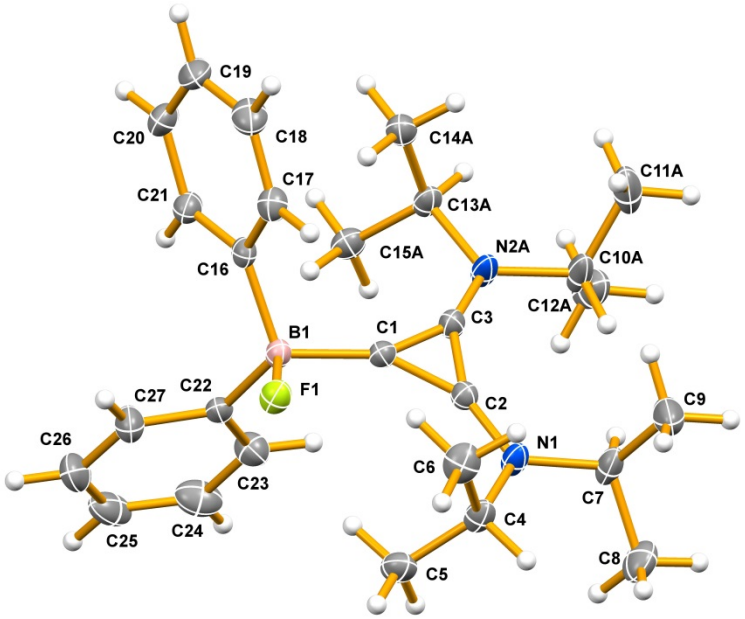


Figure S1. Structural diagram of compound **23.** Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have not been labelled. Only the major component (part A) of the disorder is shown. This, and all other structural diagrams presented in this work were generated using the program Mercury CSD 4.1.0.[11]

Compound **24**

There was some minor disorder in the structure, involving one of the N(*i*Pr)$_2$ groups. The disorder was modelled exactly as described for the preceding structure (see above). In this case, the occupancies of the disordered group refined to 87.4(6)/12.6% for part 1 and part 2, respectively.

[10] Spek, A. L. (2003). *J. Appl. Cryst.* 36, 7-13.

[11] Macrae, C.F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L.. Taylor, R., van de Streek, J., Wood, P. A. (2008) *J. Appl. Cryst.*, 41, 466-470.

Just as with compound **23**, using a disordered model for the structure resulted in a checkcif file with several more warnings (and of higher level) than had been obtained with the original unsplit results. Again, a level B warning was obtained with the split model:
Short Intermolecular Interaction H23...H15F = 1.95 Ang.
This interaction arises between a phenyl ring of the main molecule and one of the methyl protons in the second (minor) part of the disordered group on a second molecule. Since this methyl position is occupied only a small fraction of the time, it is unlikely to be of serious concern in the overall stability of the system. Overall, the split model is to be preferred as it results in better statistical parameters than the unsplit refinement.

The absolute structure could not be reliably determined, the Flack parameter having a final value of -2.0(10). This result was supported by values calculated for the Hooft and Parson's parameters using the program Platon. These values came out to -1.0(7) and -1.8(12), respectively. The lack of heavier atoms in the structure and the use of Mo radiation made calculations based on the anomalous scattering in the crystal ambiguous.

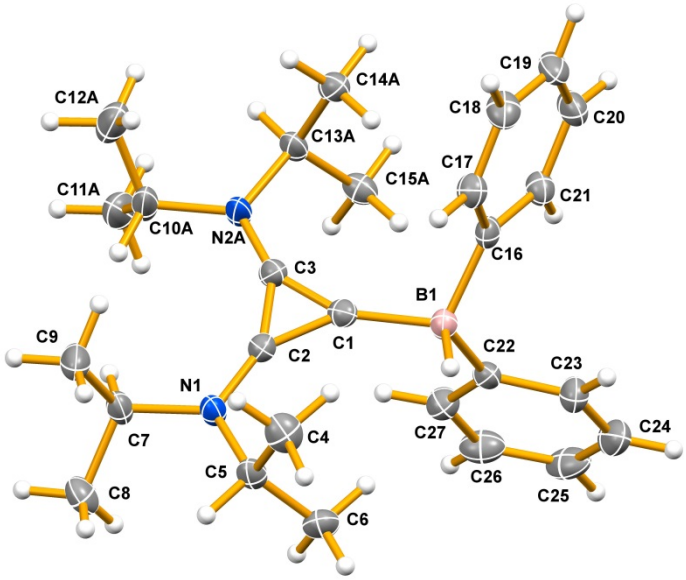


Figure S2. Structural diagram of compound **6.** Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have not been labelled. Only the major component (part A) of the disorder is shown.

Compound **24**
One reflection (0 0 -1) was found to have been partially obscured by the beam stop during the data collection and was removed from the refinement.

This compound crystallized in the space group *P*1 with two complete molecules in the asymmetric unit. Because of low coverage the absolute structure was not well determined, the Flack parameter having a final value of 0.04(4). This result was supported by values calculated for the Hooft and Parson's parameters using the program Platon [5]. These values came out to 0.03(4) and 0.04(4),

respectively. That all of the values lie close to zero does suggest that the absolute structure is correct as given in these results.

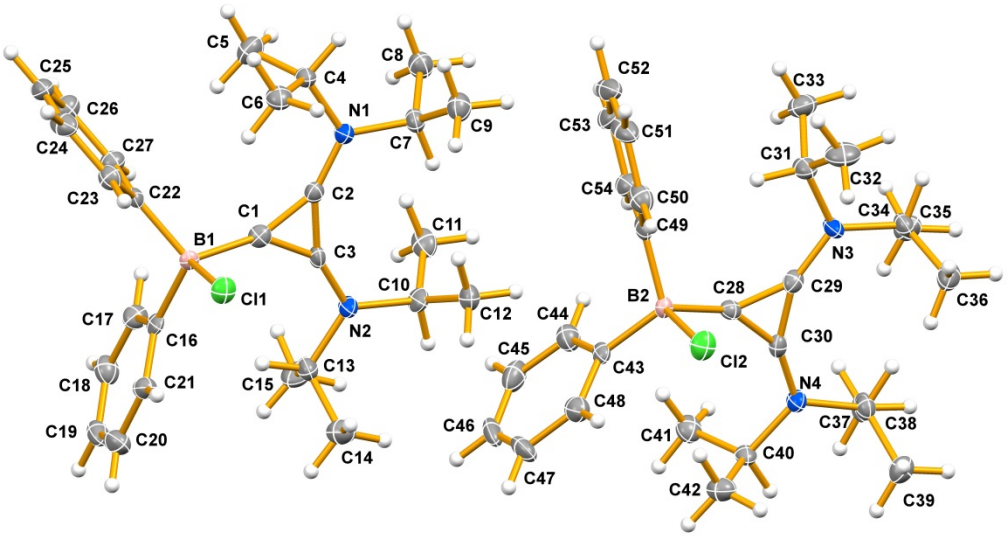


Figure S3. Structural diagram for compound **24.** Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have not been labelled. There are two complete molecules in the asymmetric unit.

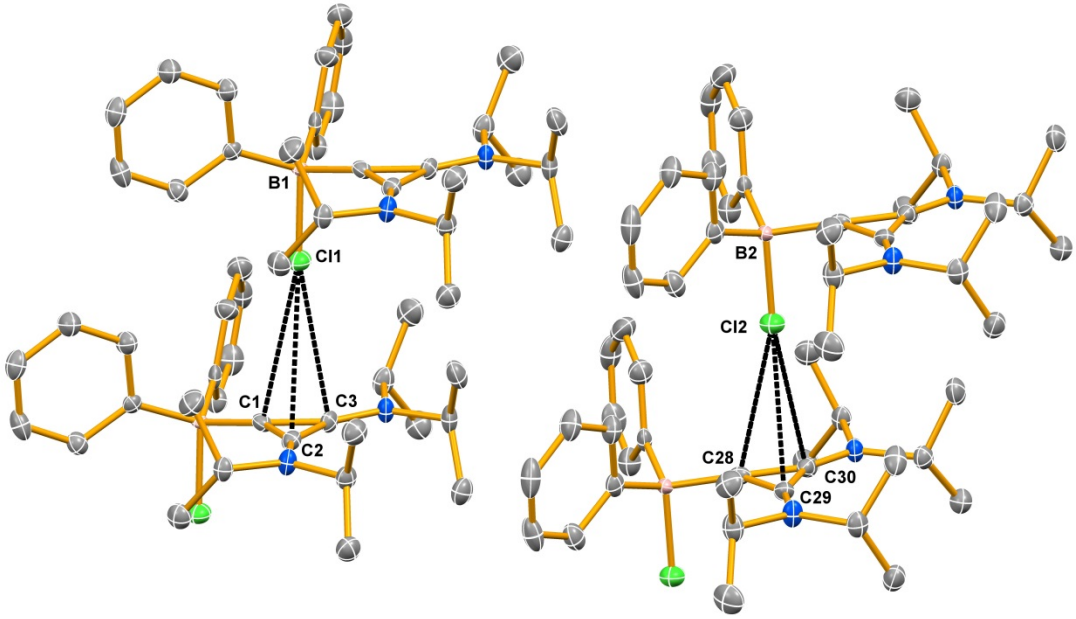
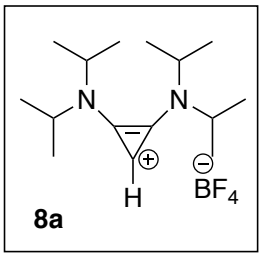


Figure S3. Compound **24** drawn to show the intermolecular contacts that occur between the chlorine atom on one molecule and the 3-membered ring on an adjacent molecule. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been removed for clarity.

Table S1. Crystal data and structural refinement details.

Identification code	**23**	**6**	**24**
Empirical formula	$C_{27}H_{38}BFN_2$	$C_{27}H_{39}BN_2$	$C_{27}H_{38}BClN_2$
Formula weight	420.40	402.41	436.85
Crystal system	Orthorhombic	Orthorhombic	Triclinic
Space group	*Pna*2$_1$	*Pna*2$_1$	*P*1
Unit cell dimensions (Å and °)	a = 17.3954(17)	17.467(4)	6.2971(15)
	b = 9.9115(10)	9.736(2) Å	10.739(3)
	c = 14.4462(14)	14.482(3) Å	18.714(5)
	α = 90	90	92.240(3)
	β = 90	90	91.774(3)
	γ = 90	90	94.792(3)
Volume (Å^3)	2490.7(4)	2462.9(10)	1259.4(5)
Z	4	4	2
Density (calculated, Mg/m^3)	1.121	1.085	1.152
Absorption coefficient (mm^{-1})	0.069	0.062	0.168
F(000)	912	880	472
Crystal size (mm^3)	0.520x0.450x0.350	0.350x0.250x0.200	0.450x0.200x0.150
Theta range for data collection (°)	2.342 - 28.960	2.332 - 28.951	1.905 - 29.028
Index ranges (h,k,l)	-23/22, -13/12, -19/19	-23/23, -12/13, -19/19	-8/8, -13/14, -25/25
Reflections collected	28896	28757	15446
Independent reflections [R(int)]	6214 [0.0192]	6169 [0.0532]	11562 [0.0351]
Completeness to theta = 25.242°	100.0 %	100.0 %	99.8 %
Max. and min. transmission	0.7458 and 0.7074	0.7458 and 0.6979	0.7458 and 0.6760
Data / restraints / parameters	6214 / 250 / 352	6169 / 202 / 350	11562 / 3 / 575
Goodness-of-fit on F^2	1.041	1.029	0.993
Final R indices [I>2sigma(I)]	R1 = 0.0324	0.0440	0.0643
	wR2 = 0.0835	0.0817	0.1190
R indices (all data)	R1 = 0.0354	0.0681	0.1083
	wR2 = 0.0857	0.0914	0.1392
Absolute structure parameter	0.25(14)	-2.0(10)	0.04(4)
Largest diff. peak and hole (e.Å^{-3})	0.245 and -0.156	0.174 and -0.152	0.460 and -0.294

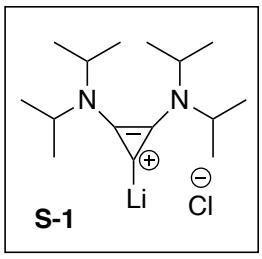
Synthesis of Borane Complexes and Precursors



8a

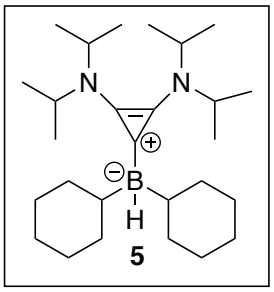
Caution: the following reaction is exothermic and undergoes a delayed exotherm. Use of oversized glassware and a condenser is recommended. This is the largest scale upon which we have conducted the reaction: In a 3-neck 2 L flask equipped with a reflux condenser, pentachlorocyclopropane (30 g, 0.14 mol) is dissolved in 400 mL dichloromethane, under ambient atmosphere. The mixture is cooled in an ice bath, and diisopropylamine (98 mL, 0.70 mol, 5 equiv.) is added over 5 minutes with stirring. A copious precipitate formed and the reaction turned a pale yellow colour. Heating of the reaction mixture to reflux was observed around the end of the addition of base, despite the use of an ice bath. The reflux subsided after several minutes. The cooling bath was allowed to decay naturally, and the reaction was stirred for 16 hours. After this time, the reaction was an amber colour. To the reaction was added 100 mL deionized water, then triphenylphosphine (36.7 g, 0.140 mmol, 1 equiv.). Solid sodium tetrafluoroborate (15.4 g, 0.14 mmol, 1 equiv) was added, and the biphasic reaction was stirred vigorously for 12 hours. The aqueous layer is colourless and cloudy in appearance. After the completion of 12 hours of stirring, the layers were separated. The organic layer was washed with 100 mL of deionized water containing 12 grams of sodium tetrafluoroborate. The amber organic layer was dried over Na2SO4, filtered, and concentrated to give a brown oil. To this residue was added 100 mL of diethyl ether, which caused it to solidify. The diethyl ether was removed in vacuo. The residue was slurried in 30 mL of a 2:1 mixture of diethyl ether and isopropanol, and filtered. The solid filter cake was washed with 2x 100 mL cold diethyl ether, then dried in vacuo to afford 33g (0.10 mol, 73% yield) of compound **x** as an off-white solid. Spectral data were in agreement with literature values.

^{1}H (500 MHz, $CDCl_3$): δ 7.42 (s, 1H), 4.02 (sept, 2H, J = 6.6 Hz), 3.85 (s, 2H, J = 6.6 Hz), 1.4 (d, 12H, J = 6.6 Hz), 1.37 (d, 12H, J = 6.6 Hz).



S-1

^{i}PrBAC-LiCl: **^{i}PrBAC-HCl** (412 mg, 1.509 mmol, 1 equiv.) was added to an oven dried 4-dram vial equipped with a magnetic stir bar. **^{i}PrBAC-HCl** was suspended in diethyl ether (8 mL) and the slurry was cooled to -35 °C. A solution of n-BuLi in pentane (2.5 M, 0.6 mL, 1.5 mmol) was added drop-wise with stirring. The reaction briefly clarified, and then became turbid again with a beige colour over a 10-minute period. After 20 minutes, volatiles were removed *in vacuo*. The resulting solid was then washed on a frit with pentane (3 x 5 mL) and dried *in vacuo* to obtain **^{i}PrBAC-LiCl** as a white powder, (363 mg, 1.3 mmol, 86%).

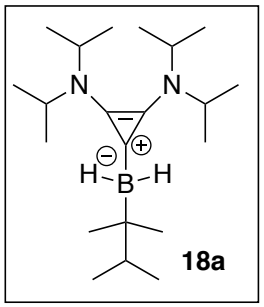


5

^{i}PrBAC-BCy$_2$H: **^{i}PrBAC-LiCl** (55 mg, 0.197mmol) was placed in an oven dried 4-dram vial equipped with a magnetic stir bar. **^{i}PrBAC-LiCl** was then suspended in ether (3 mL) and the solution was cooled to -35 °C. Then dicyclohexylborane (35 mg, 0.197 mmol) was added in one portion to the resulting suspension and stirred for 1 h. The solution was filtered with a 3-micron syringe filter and ether rinse (2 x 1 mL). Volatiles were removed in vacuo resulting in the title compound **^{i}PrBAC-BCy$_2$H** as a beige solid (70 mg, 0.169 mmol, 86%). Spectral data was in accordance with previously reported data.

^{1}H (500 MHz, $CDCl_3$): δ 4.01 (br s, 4H), 1.78 (d, 2H, J = 13 Hz), 1.60 (m, 6H), 1.31 (d, 24H, J = 6.5 Hz), 1.17 (m, 8H), 0.83 (m, 4H), 0.44 (t, 2H, J = 10 Hz).

^{11}B (160.4 MHz, $CDCl_3$): δ -12.11 (d, J = 74 Hz).



18a

^{i}PrBAC-BH$_2$Thex: **^{i}PrBAC-LiBF$_4$** (212 mg, 0.6 mmol) was weighed in an oven dried 4-dram vial equipped with a magnetic stir bar. Toluene (5 mL) was then added and the slurry was cooled to -35 °C. Thexylborane (0.6 mL, 0.6 mmol, 1 M toluene) was added slowly to the slurry and a white precipitate formed after 3 min. The slurry stirred for 1h and then volatiles were removed in vacuo. Dichloromethane (3 mL) was then added to the crude material and the mixture was filtered on a fine porous frit containing celite and the celite was washed further with dichloromethane (3 x 3 mL). Dichloromethane was then removed

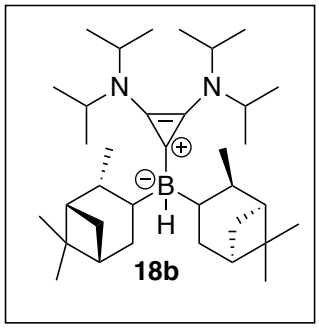
in vacuo resulting in the title compound **^{i}PrBAC-BH$_2$Thex** as a beige solid (166 mg, 0.496 mmol, 83%).

^{1}H (500 MHz, $CDCl_3$): δ 4.07 (br s, 4H), 1.42 (m, 1H), 1.32 (d, 24H, J = 6.7 Hz), 0.88 (d, 6H, J = 6.6 Hz), 0.74 (s, 6H).

^{13}C {^{1}H} (125.76 MHz, C_6D_6): δ 142, 50.2, 39.6, 28.9, 21.8, 19.1.

^{11}B (160.4 MHz, $CDCl_3$): δ -21.3 (t, J = 82 Hz).

HRMS (APCI): calc'd for $C_{21}H_{43}BN_2Na$ [M + Na+] 357.3412; Found: 357.3403



18b

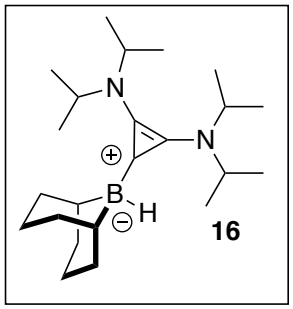
^{i}PrBAC-Bipc$_2$H: **^{i}PrBAC-LiBF$_4$** (327 mg, 0.925mmol) was placed in an oven dried 4-dram vial equipped with a magnetic stir bar. **^{i}PrBAC-LiBF$_4$** was dissolved in ether (5 mL) and the solution was cooled to -35 °C. Then diisocamphenylborane (264mg, 0.925 mmol) was added in one portion to the resulting suspension and stirred for 1 h. Ether was then removed *in vacuo* and the residue was taken up in benzene (4 mL) and filtered on a fine frit. The collected solids were washed with benzene (3 x 3mL) and volatiles removed in vacuo resulting in the title **^{i}PrBAC-Bipc$_2$H** as a beige solid (415 mg 0.794 mmol, 86%).

^{1}H (500 MHz, $CDCl_3$): δ 4.04 (br s, 4H), 2.09 (m, 4H), 2.01 (m, 2H), 1.87 (m, 4H), 1.76 (m, 4H), 1.58 (m, 4H), 1.33 (m, 24H), 1.13 (s, 3H), 1.1 (s, 3H), 1.10 (s, 3H), 1.09 (s, 3H), 1.0 (d, J = 7.1 Hz, 3H), 0.75 (d, J = 7.1 Hz, 3H).

^{13}C {^{1}H} (125.76 MHz, $CDCl_3$): δ 143, 50.7, 49.5, 44.3, 43.4, 43.0, 42.5, 39.6, 35.0, 34.2, 33.6, 33, 28.7, 24.5, 23.1, 22.8, 21.7.

^{11}B (160.4 MHz, $CDCl_3$): δ -9.7 (d, J = 73 Hz).

HRMS (APCI): calc'd for $C_{35}H_{64}BN_2$ [M + H+] 523.5157; Found: 523.5156



16

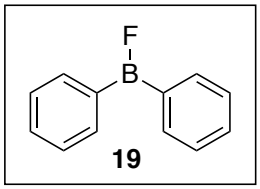
^{i}PrBAC-9BBNH: ^{i}PrBAC-LiBF$_4$ (200 mg, 0.566 mmol) was weighed in an oven dried 4-dram vial equipped with a magnetic stir bar followed by 9BBN (69 mg, 0.566 mmol. Toluene (3 mL) was added in one portion to the solids and the slurry stirred for 1 h. The slurry was the filtered on a fine porous fit and the solid was washed further with toluene (5 x 1 mL). Toluene was then removed *in vacuo* and the residue was triturated with pentane until a solid beige powder formed. The resulting solid was washed with pentane by decanting (2 x 1 mL) and then remaining volatiles were removed in vacuo resulting in the title compound **^{i}PrBAC-9BBNH** as a white solid (118 mg, 0.329 mmol, 58%).

^{1}H (500 MHz, $CDCl_3$): δ 4.06 (br s, 4H), 1.87 (m, 4H), 1.7 (m, 4H), 1.7 (m, 2H), 1.6 (m, 6H), 1.31 (d, 24H, J = 6.9 Hz), 1.15 (m, 2H).

^{13}C {^{1}H} (125.76 MHz, C_6D_6): δ 143, 50.4, 37.0, 33.7, 26.8, 26.2, 24.6 (br), 21.5.

^{11}B (160.4 MHz, $CDCl_3$): δ -16.3 (d, J = 75 Hz).

HRMS (APCI): calc'd for $C_{23}H_{44}BN_2$ [M + H+] 359.3592; Found: 359.3587

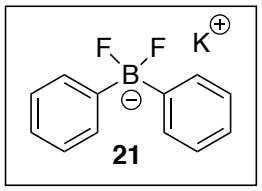


19

Boron diphenylfluoride (19). Under a nitrogen atmosphere, potassium diphenyldifluoroborate (0.967 g, 3.99 mmol) was dissolved in THF (10 mL). TMS-Cl (0.5 mL, 3.99 mmol) was added dropwise. The reaction was stirred at room temperature for 2 hours, and the solvent was removed under reduced pressure. In the glovebox, the product was extracted with ether, filtered, and the filtrate was concentrated to afford diphenylboron fluoride as an off-white solid (0.565 g, 3.07 mmol, 77% yield).

^{11}B (96 MHz, $CDCl_3$) δ 43.8 (s).

^{19}F (282 MHz, $CDCl_3$) δ -73.6 (s).



21

KF_2BPh_2:

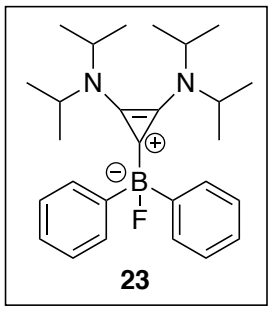
A 1.47 M solution of phenylmagnesium bromide in tetrahydrofuran (37.4 mL, 55 mmol, 1 equiv) was cooled to 0 C, and triisopropyl borate (6.34 mL, 27.5 mmol, 0.5 equiv.) was added over 30 minutes. A light-yellow precipitate formed. The solution was stirred at ambient temperature for 16 hours, after which time 55 mL of 1N aqueous HCl was added. The layers were separated, and the organic layer extracted with diethyl ether. The combined organic layers were dried over Na_2SO_4, concentrated, and the oily colourless residue was used directly in the next reaction. The residue was dissolved in 80 mL methanol, cooled to 0 C, and KHF_2 (8.6 g, 110 mmoL, 2 equiv) was added. The cloudy solution was stirred for 1 hour, then volatiles were removed. The residue was taken up in 100 mL of acetone, and filtered. The filtrate was concentrated, and the residue was slurried in 50 mL diethyl ether and collected by suction filtration affording the title compound as a white powder (10.2 g, 42 mmol, 76% yield over 2 steps).

^{1}H (300 MHz, CD_3CN): δ 7.42 (m, 4H), 7.12 (t, 4H), 7.02 (m, 2H).

^{13}C {^{1}H} (75.4 MHz, CD_3CN): δ 132 (t, J = 3.8 Hz), 127, 125.

^{19}F (282.23 MHz, CD_3CN): δ -159.

^{11}B (96.25 MHz, CD_3CN): δ 7.29 (t, J = 66 Hz).



23

***i*PrBAC-BPh_2F:** ***i*PrBAC-$LiBF_4$** (300 mg, 0.848 mmol) and potassium difluorodiphenylborate (205 mg, 0.848 mmol) were weighed into an oven dried 4-dram vial equipped with a magnetic stir bar. Ether was added to the solids and the slurry was stirred overnight. Solvent was removed *in vacuo* and the product was taken up in toluene (3 mL). The slurry was then filtered through a fine porous frit filled with celite. The celite was washed with toluene (4 x 3 mL) and the resulting toluene was removed *in vacuo* to obtain the title compound ***i*PrBAC-BPh_2F** as a beige solid (307 mg, 0.730 mmol, 86 %).

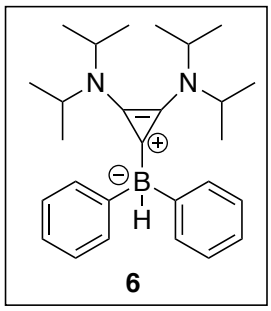
^{1}H (300 MHz, $CDCl_3$): δ 7.38 (m, 4H), 7.22 (m, 4H), 7.12 (m, 2H), 3.88 (br s, 4H), 1.24 (br s, 24H).

^{13}C {^{1}H} (75.4 MHz, $CDCl_3$): δ 139 (d, *J* = 5 Hz), 133 (d, *J* = 3Hz), 127, 125, 51.1, 21.0.

^{19}F (282.23 MHz, $CDCl_3$): δ -192.

^{11}B (96.25 MHz, $CDCl_3$): δ 2.6 (br s).

HRMS (ESI): calc'd for $C_{27}H_{38}BFN_2Na$ [M + Na+] 443.3004; Found: 443.3011



6

^{i}PrBAC-BPh$_2$H: ^{i}PrBAC-BPh$_2$F (464 mg, 1.10 mmol) was placed in an oven dried 4-dram vial equipped with a magnetic stir bar and then dissolved in dichloromethane (5 mL). Chlorodimethylsilane (0.12 mL, 1.10 mmol) was added to the suspension and stirred overnight. Volatiles were removed *in vacuo* and the product was taken up in dichloromethane (5 mL) and chlorodimethylsilane was added once more (0.24 mL, 2.20mmol, 2 eq) to stir overnight. Volatiles were removed *in vacuo* and the residue was triturated with pentane to obtain a beige solid as the title compound **^{i}PrBAC-BPh$_2$H** (409 mg, 1.01 mmol, 92%)

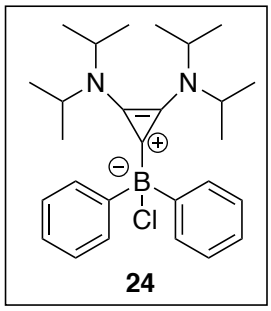
^{1}H (300 MHz, $CDCl_3$): δ 7.26 (m, 4H), 7.16 (m, 4H), 7.03 (m, 2H), 3.87 (br s, 4H), 3.67 (br q, BH) 1.24 (br s, 24H).

^{1}H (500 MHz, C_6D_6): δ 7.78 (d, 4H), 7.41 (t, 4H), 7.24 (t, 2H), 4.39 (br q, BH), 3.45 (br s, 4H), 0.88 (br s, 24H).

^{13}C {^{1}H} (75.4 MHz, $CDCl_3$): δ 140, 134, 127, 124, 50.7, 21.4.

^{11}B (96.25 MHz, $CDCl_3$): δ -14.7 (d, *J* = 81 Hz).

HRMS (ESI): calc'd for $C_{27}H_{39}BN_2Na$ [M + Na+] 425.3099; Found: 425.3109



24

^{i}PrBAC-BPh$_2$Cl: ^{i}PrBAC-BPh$_2$F (100 mg, 0.238 mmol) was placed in an oven dried 4-dram vial equipped with a magnetic stir bar and dissolved in dichloromethane (3 mL). Trimethylsilylchloride (0.06 mL, 0.476 mmol, 2 eq) was added to the solution and stirred overnight. Volatiles were removed *in vacuo* and the product was triturated with pentane to obtain a

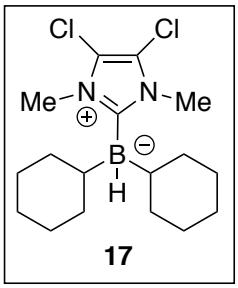
beige solid as the title compound **^{i}PrBAC-BPh$_2$Cl** (102 mg, 0.233 mmol, 98%)

^{1}H (300 MHz, $CDCl_3$): δ 7.40 (m, 4H), 7.18 (m, 4H), 7.08 (m, 2H), 3.92 (br s, 4H), 1.15 (br s, 24H).

^{13}C {^{1}H} (75.4 MHz, $CDCl_3$): δ 139, 134, 127, 125, 51.1, 21.4.

^{11}B (96.25 MHz, $CDCl_3$): δ -1.28 (br s).

HRMS (ESI): calc'd for $C_{27}H_{38}BN_2$ [M - Cl] 401.3123; Found: 401.3127



17

Cl-NHC-BCy$_2$H: Dimethylimidazolium iodide (151 mg, 0.515 mmol) was weighed into an oven dried 4-dram vial equipped with a magnetic stir bar. Potassium hexamethyldisilazide (108 mg, 0.541 mmol, 1.05 eq) and dicyclohexylborane (151 mg, 0.515 mmol) were then added to the vial and cooled to -35 °C and a separate vial containing tetrahydrofuran (5 mL) was also cooled to -35 °C. The tetrahydrofuran was added in one portion to the vial containing the solids and the reaction was left to stir overnight. Volatiles were removed *in vacuo* and the resulting solid was taken up in pentane (3 mL) and filtered over celite. The resulting celite was washed with pentane (4 x 3 mL) and the pentane was removed *in vacuo*. The resulting solid was triturated with pentane to afford the product **Cl-NHC-BCy$_2$H** (148 mg, 0.431 mmol, 84%)

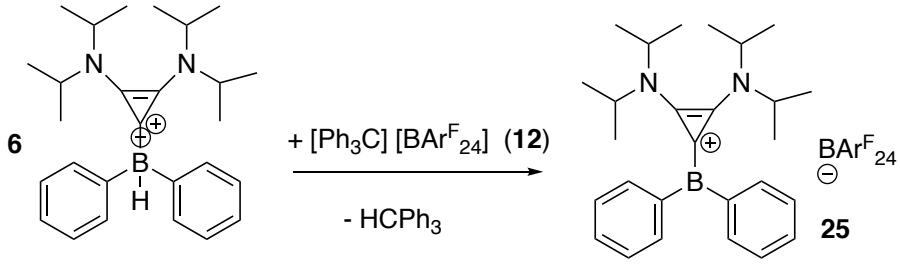
^{1}H (500 MHz, $CDCl_3$): δ 3.82 (s, 3H), 3.72 (s, 3H), 1.84 (d, 2H, J = 13 Hz), 1.63 (m, 6H), 1.17 (m, 8H), 0.77 (m, 4H), 0.64 (m, 2H).

^{13}C {^{1}H} (125.7 MHz, $CDCl_3$): δ 116, 115, 35.8, 36.8, 34.4, 31.5, 29.3, 29.2, 27.9.

^{11}B (160.4 MHz, $CDCl_3$): δ -12.6 (d, J = 79 Hz).

Procedure and Spectra for Borenium Formation

Formation of Borenium Cation [^{i}PrBAC-BPh$_2$][BArF^{24}] in situ from trityl BArF^{24} :



In a glovebox, **^{i}PrBAC-BPh$_2$H** (15 mg 0.037 mmol) and **trityl BArF^{24} (12)** (41 mg, 0.037 mmol) were placed in an oven dried 1-dram vial. The solids were dissolved in $CDCl_3$ (approx 1 mL) and the solution was transferred to a standard NMR tube and NMR spectra were acquired after 15 min.

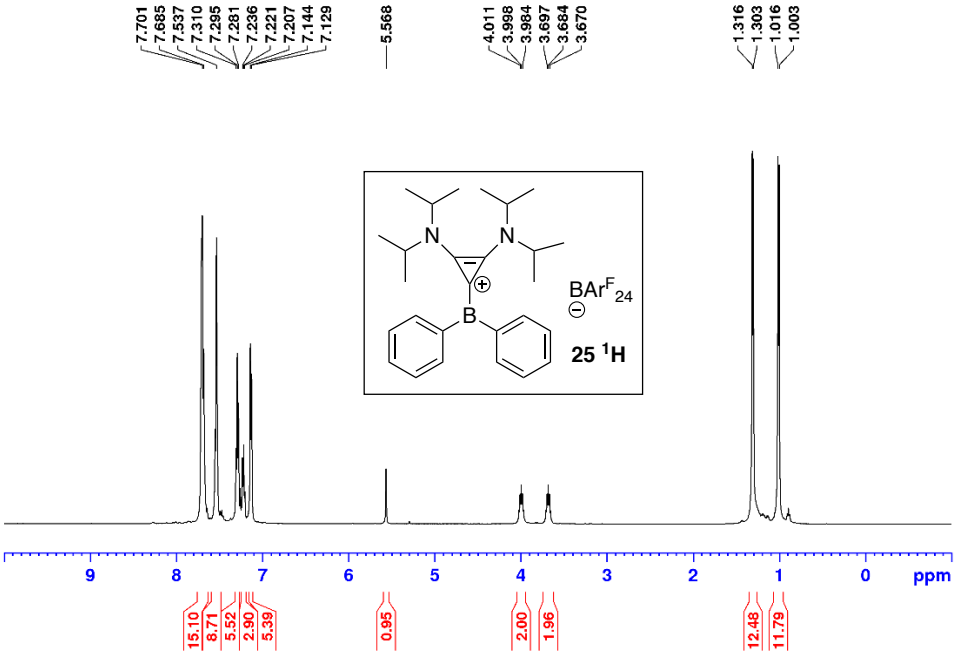
Diagnostic NMR Data:

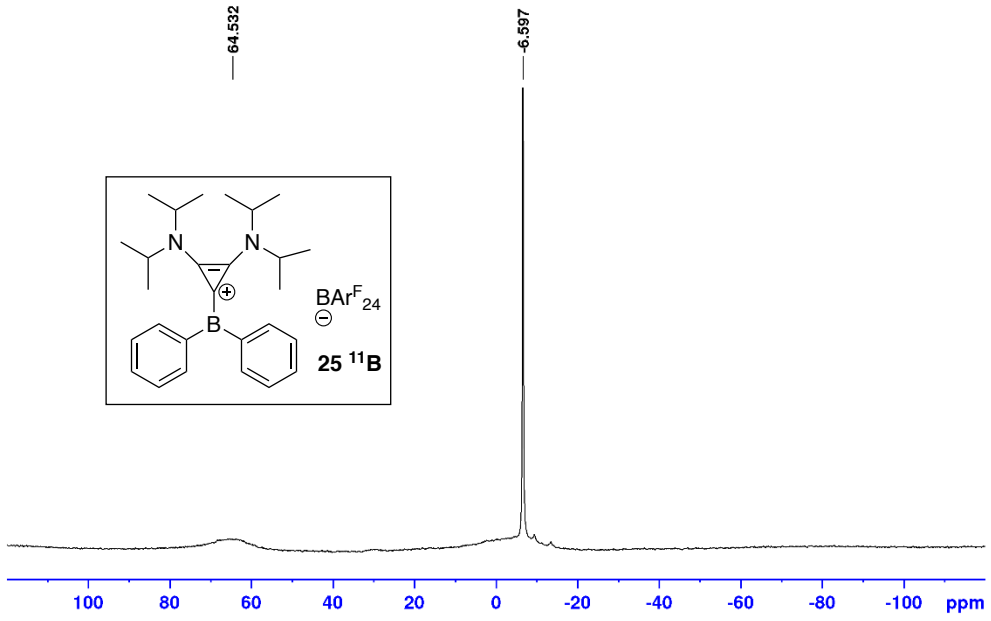
^{1}H (500 MHz, $CDCl_3$): δ 5.56 (s, 1H, Ph_3C**H**), 3.99 (sept, 2H, *J* = 6.7Hz), 3.68 (s, 2H, *J* = 6.7Hz), 1.30 (d, 12H, *J* = 6.7Hz), 1.00 (d, 12H, *J* = 6.7Hz).

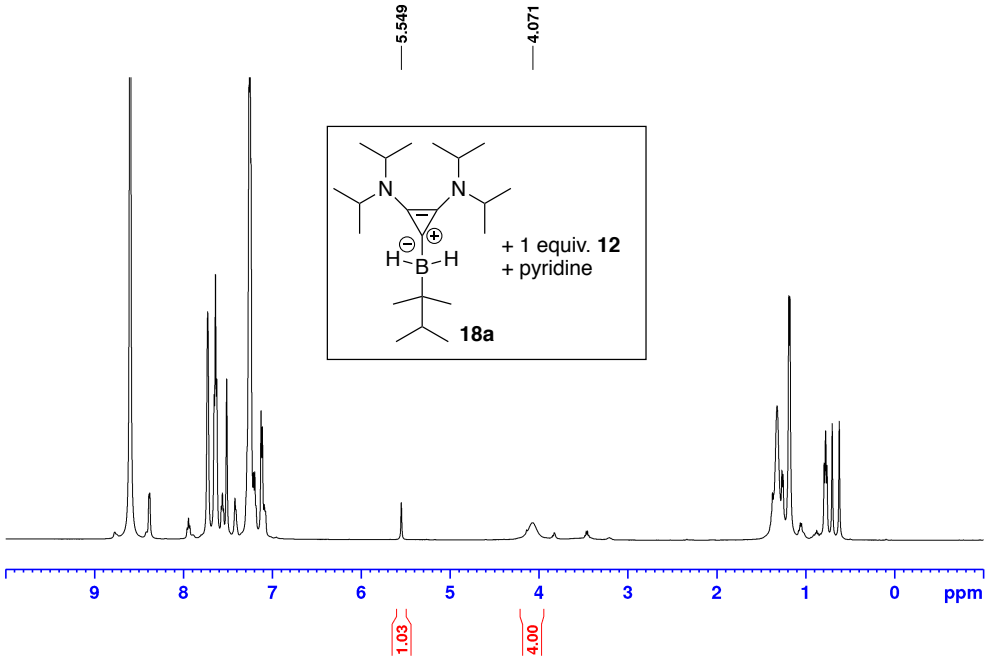
^{11}B (160.4 MHz, $CDCl_3$): δ 64.5 (B+), -6.6 (BArF^{24}).

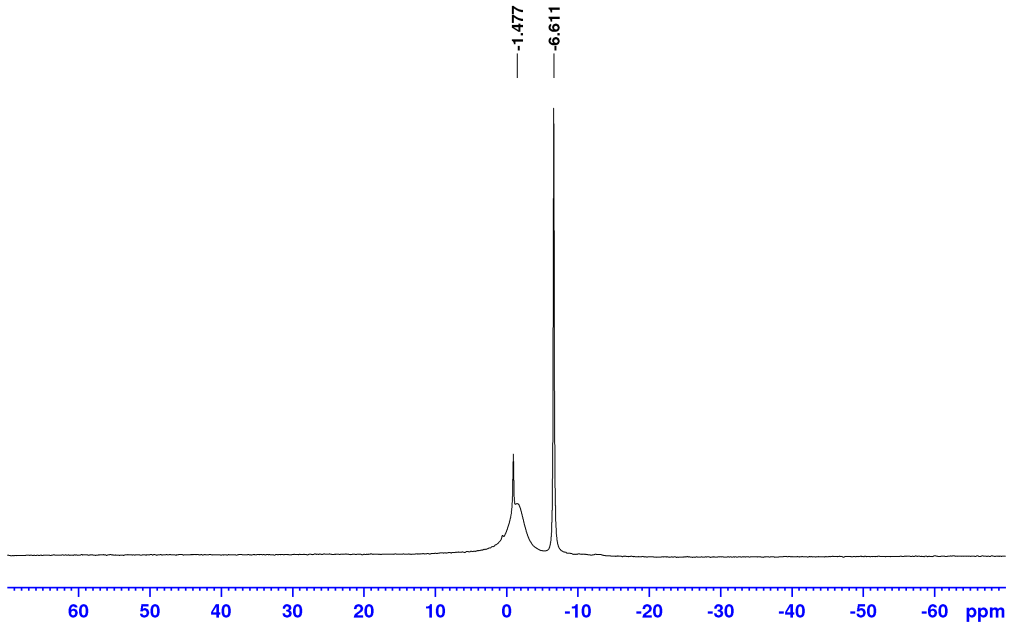
BACBH$_2$Thex pyridine trityl addition:

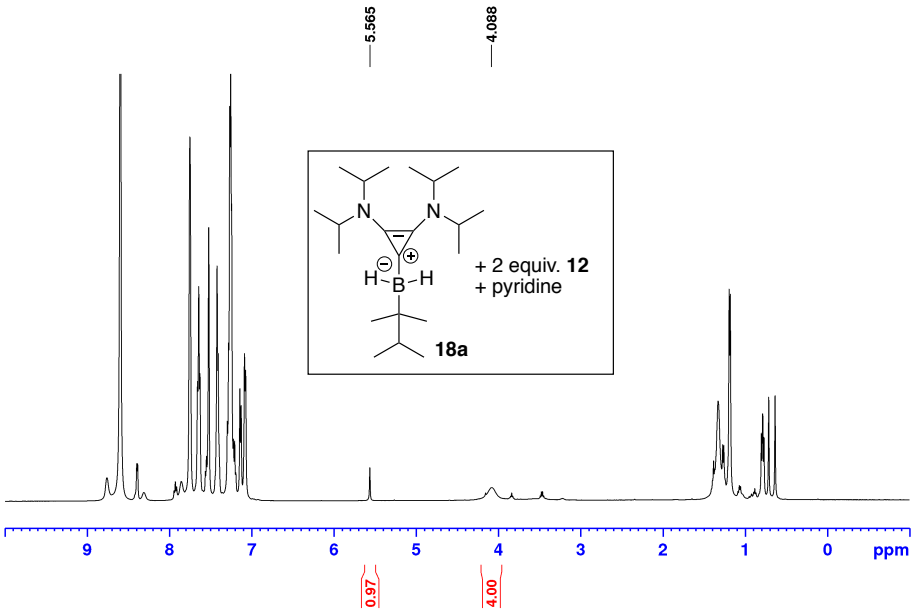
In the glove-box, BAC-BH$_2$Thex **18a** (12.5 mg, 0.0373 mmol) was weighed into a 1-dram vial and the solid dissolved in chloroform (1 mL). Pyridine was added (3 drops) followed by Trityl Barf (41 mg, 0.0373 mmol). The use of pyridine was necessary to maintain homogeneity in this solvent. The sample was then transferred to an NMR tube, which was sealed with a standard cap and Teflon tape. The mixture analyzed using ^{1}H and ^{11}B NMR spectroscopy. The solution was then transferred back into the 1-dram vial and another equivalent of Trityl barf (41mg, 0.0373 mmol) was added. The sample was then transferred to an NMR tube once more and analyzed using ^{1}H and ^{11}B NMR spectroscopy. No change in the key chemical shifts was observed, indicating a second hydride abstraction did not occur under these conditions. In addition, no increase in the amount of triphenylmethane was observed, as further evidence a second hydride abstraction did not occur.

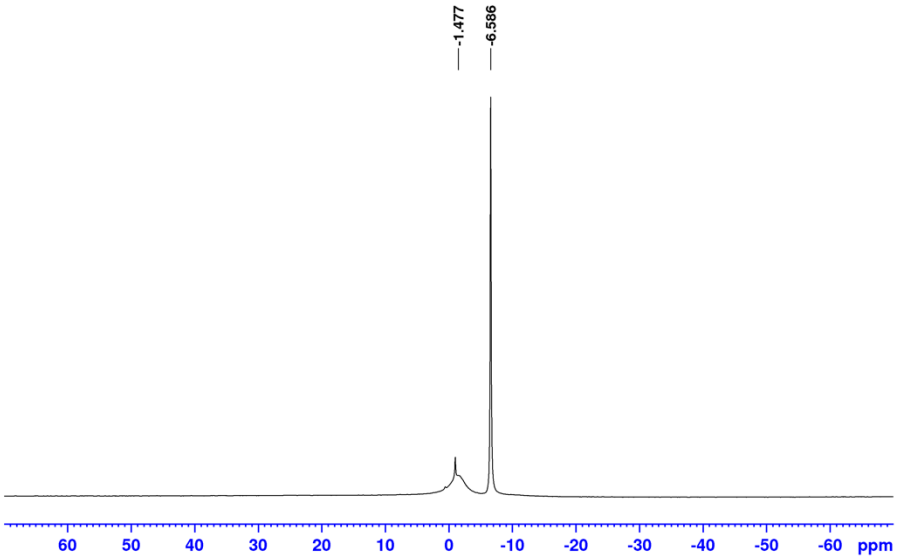

7.701
7.685
7.537
7.310
7.295
7.281
7.236
7.221
7.207
7.144
7.129
5.568
4.011
3.998
3.984
3.697
3.684
3.670
1.316
1.303
1.016
1.003
N
N
B
BAr$^{F}_{24}$
25 ^{1}H
9
8
7
6
5
4
3
2
1
0
ppm
15.10
8.71
5.52
2.90
5.39
0.95
2.00
1.96
12.48
11.79


64.532
-6.597
N
N
B
BAr$^{F}_{24}$
25 ^{11}B
100
80
60
40
20
0
-20
-40
-60
-80
-100
ppm


5.549
4.071
+ 1 equiv. 12
+ pyridine
18a
9
8
7
6
5
4
3
2
1
0
ppm
1.03
4.00

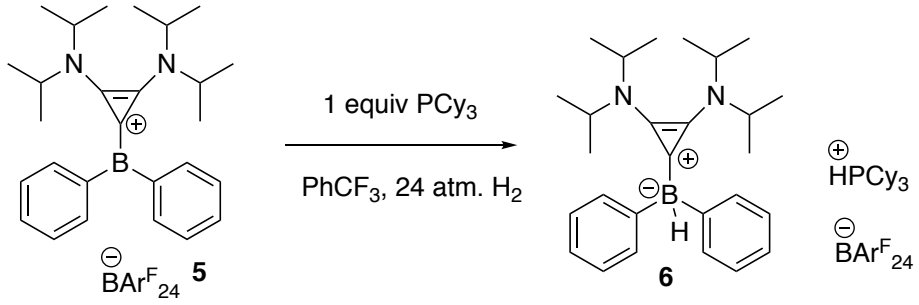

-1.477
-6.611
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
ppm


5.565
4.088
+ 2 equiv. 12
+ pyridine
18a
9
8
7
6
5
4
3
2
1
0
ppm
0.97
4.00


-1.477
-6.586
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
ppm

Procedure and Spectra for Hydrogen Activation

Hydrogen activation with [^{i}PrBAC-BPh$_2$][BArF^{24}] and PCy$_3$



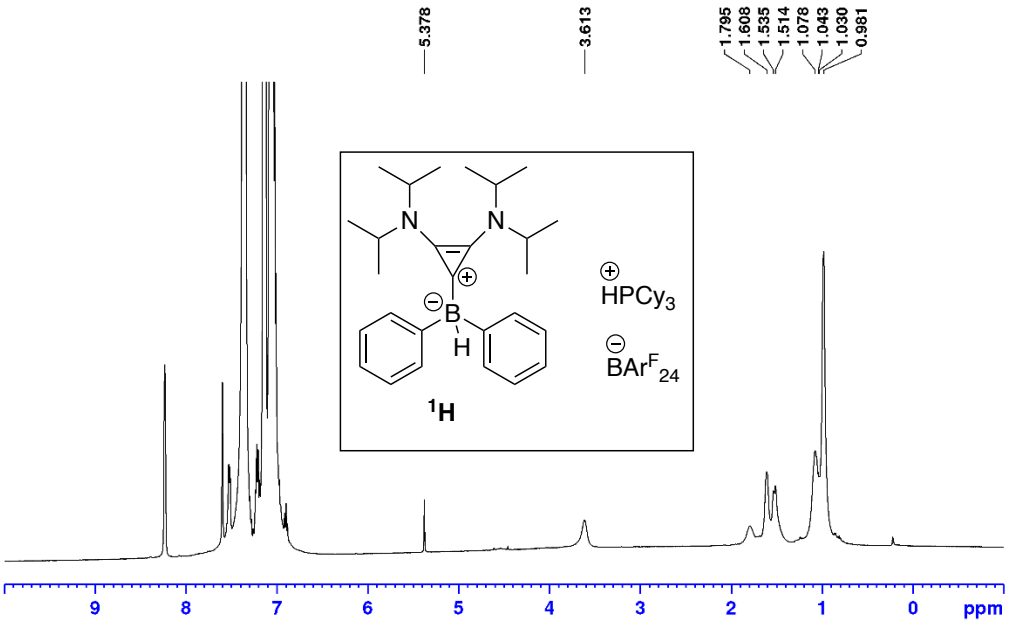
In a glovebox, **^{i}PrBAC-BPh$_2$H** (15 mg 0.037 mmol) and **trityl BArF^{24}** (41 mg, 0.037 mmol) were weighed into an oven dried 1-dram vial. In a separate vial, tricyclohexylphosphine (10.5 mg, 0.037 mmol was weighed and equipped with a magnetic stir bar. The solids in the vial containing **^{i}PrBAC-BPh$_2$H** and **trityl BArF^{24}** were dissolved trifluorotoluene (approx 0.3 mL). The solution was transferred to the vial containing PCy$_3$ and the previous vial was washed with trifluorotoluene (0.4 mL). The vial was closed with a septa cap pierced with a needle. The vial was then paced in a parr bomb and pressurized with 10 atm of H_2. The mixture was stirred for 18 h and was then brought back into the glove box and 11 drops of deuterated benzene were added. The solution was transferred to a standard NMR tube and NMR spectra were acquired.

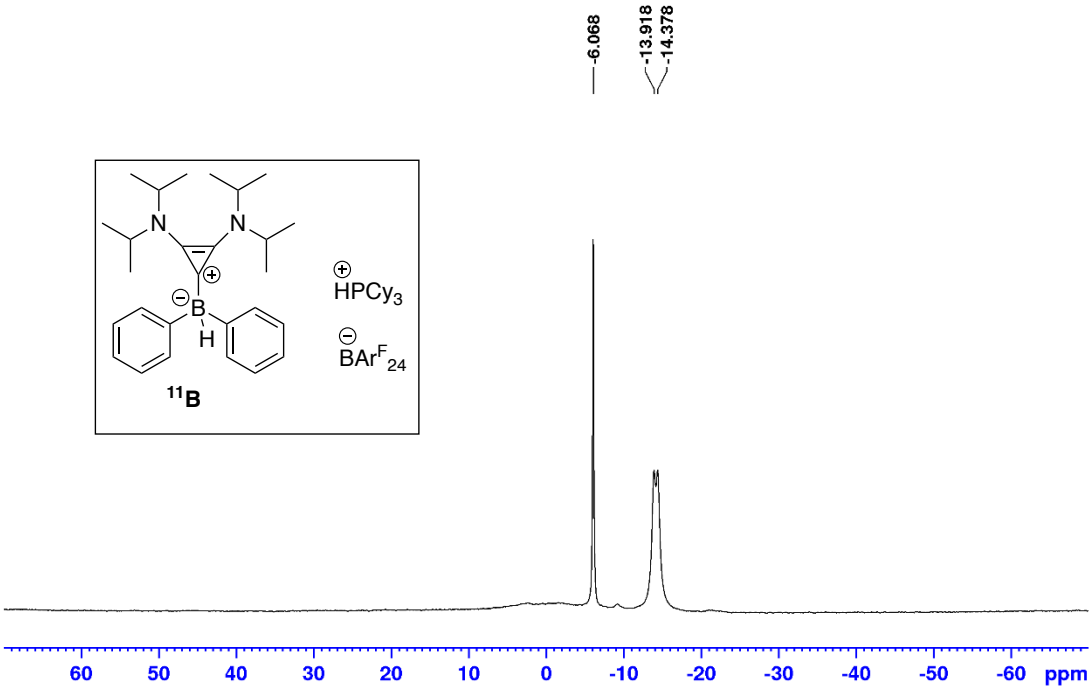
Diagnostic NMR Data:

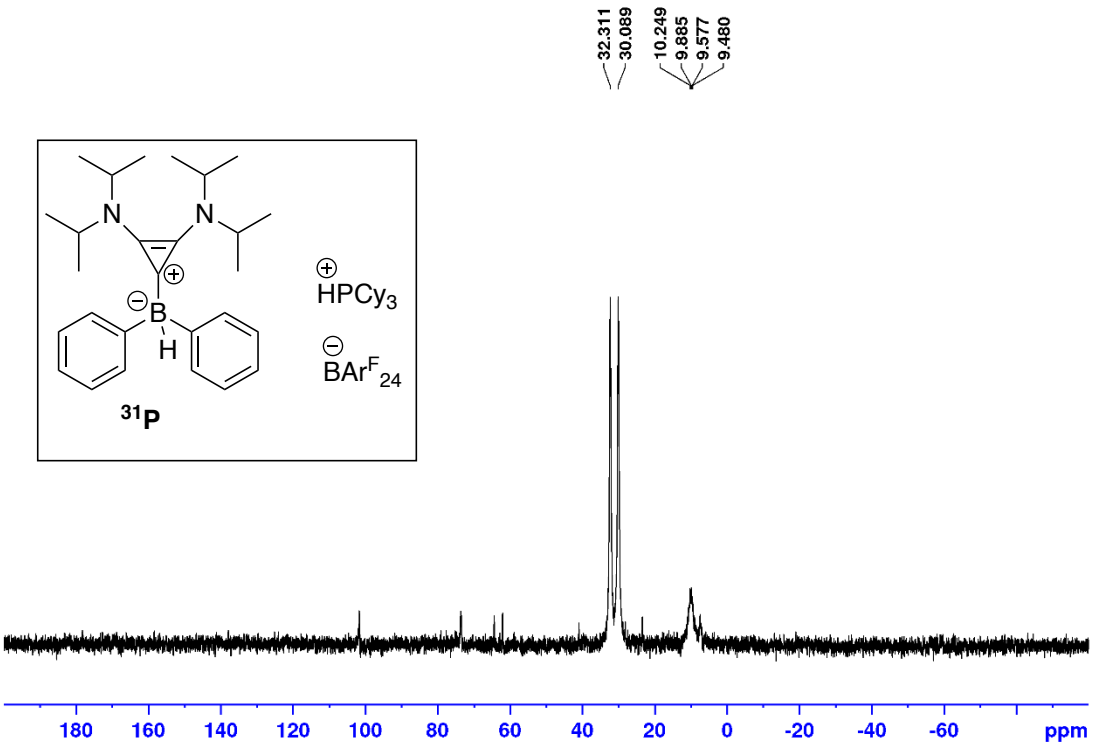
^{1}H (500 MHz, C_6D_6): δ 5.37 (s, 1H, Ph_3C**H**), 3.61 (br s, 4H), 0.98 (br s, 24H).

^{11}B (160.4 MHz, C_6D_6): δ -6.1 (BArF^{24}), -14.2 (d, J = 74Hz).

^{31}P (202.4 MHz, C_6D_6): δ 31 (d, J = 450Hz).


5.378
3.613
1.795
1.608
1.535
1.514
1.078
1.043
1.030
0.981
N
N
B
H
HPCy3
BArF24
1H
9
8
7
6
5
4
3
2
1
0
ppm


-6.068
-13.918
-14.378
N
N
B
H
HPCy3
BArF24
11B
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
ppm


32.311
30.089
10.249
9.885
9.577
9.480
N
N
B
H
HPCy3
BArF24
31P
180
160
140
120
100
80
60
40
20
0
-20
-40
-60
ppm

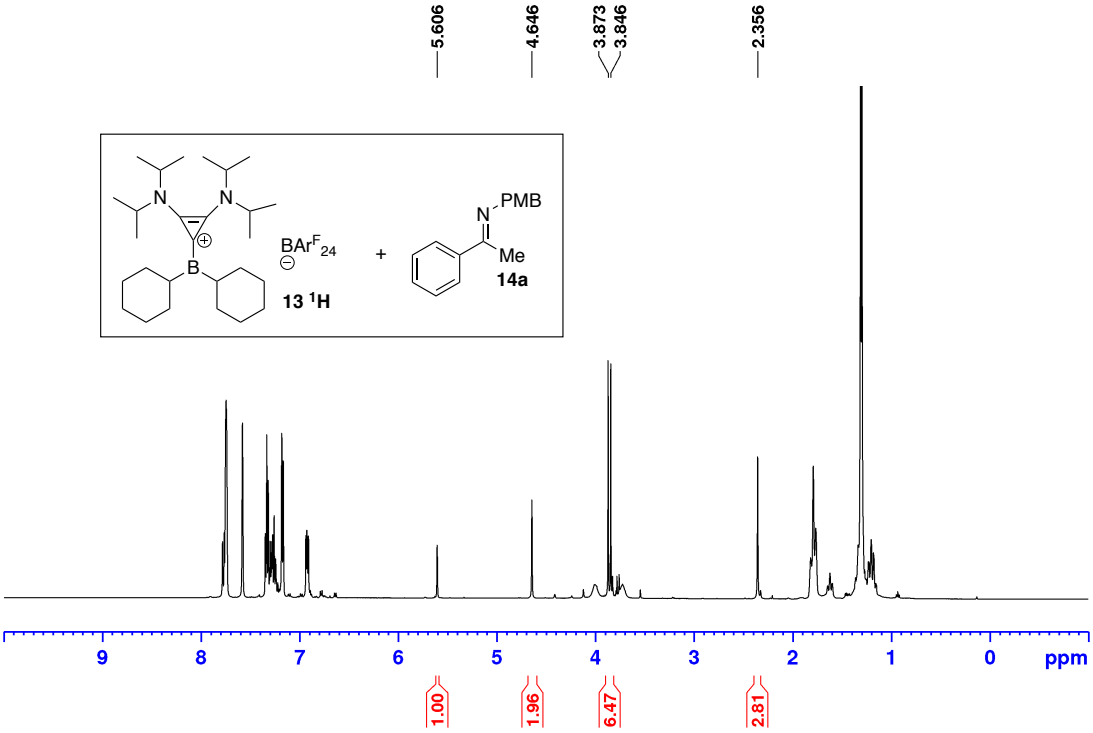
Procedure and Spectra for Imine Addition to Borenium Cations:

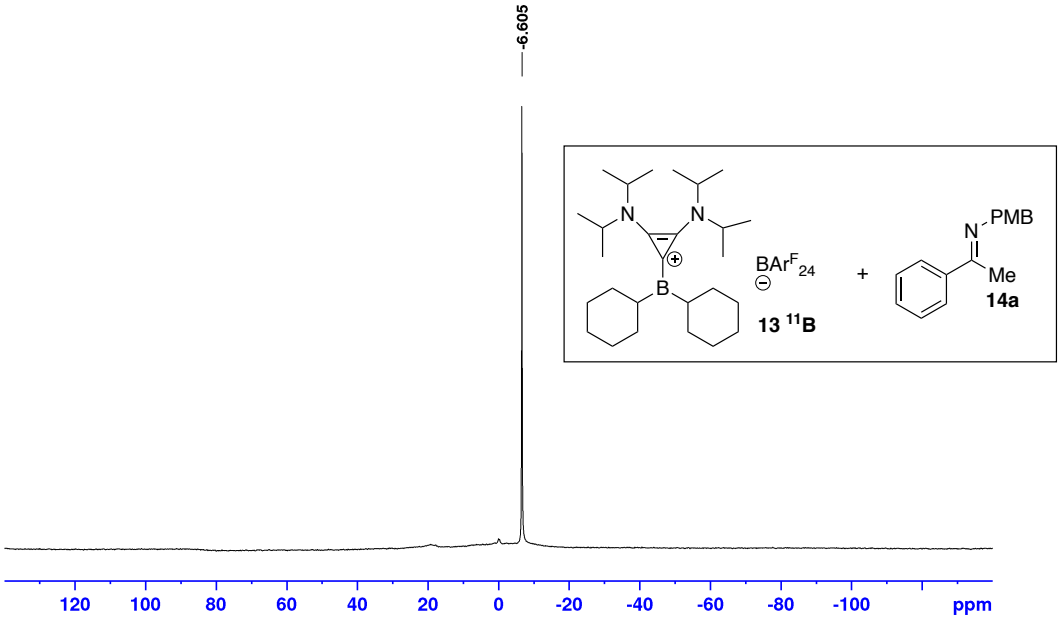
Imine complexation reaction:

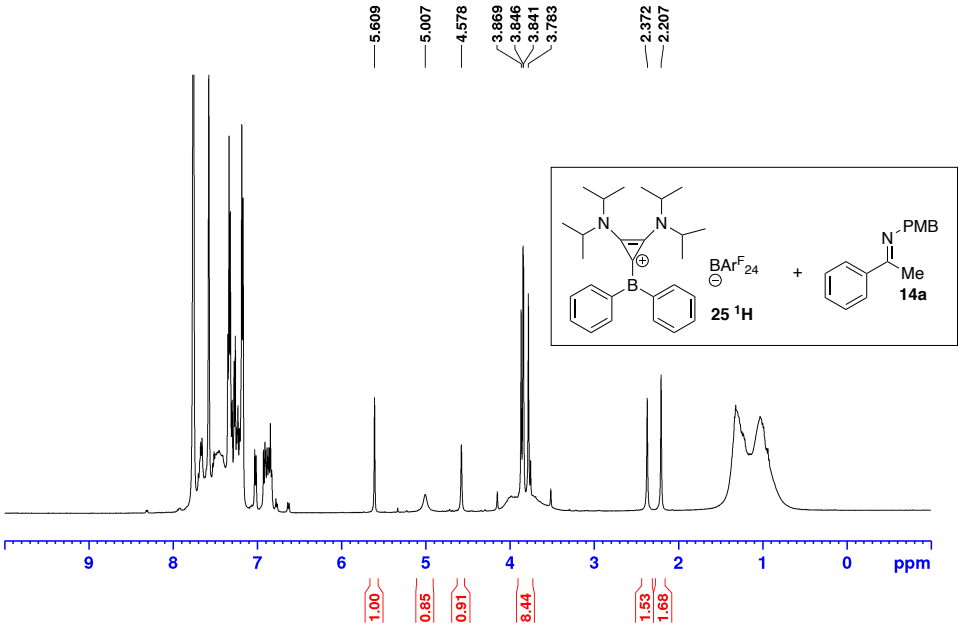
BAC-BCy_2H **5** (15.5 mg, 0.0373 mmol) or BAC-BPh_2H **6** (15 mg, 0.0373 mmol) was weighed into a 1-dram vial along with Trityl BArF **12** (41 mg, 0.0373 mmol). Approximately 1 mL of chloroform-*d* was used to dissolve the solids and the solutions were left for 2 min. Imine **14a** (10 mg, 0.0373 mmol) was then added in one portion and the resulting solution was transferred to an NMR tube and analyzed using ^{11}B and ^{1}H NMR spectroscopy.

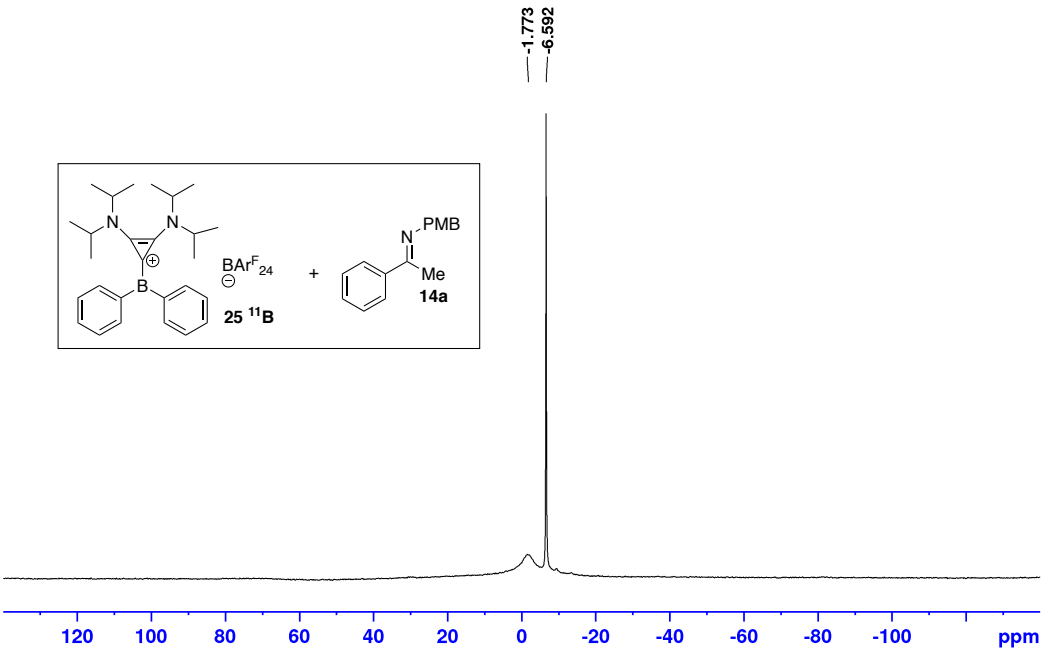
For dicyclohexylboron adduct **5**, minimal peturbations in the spectra were observed upon imine addition. While the borenium peak is not well defined in the ^{11}B NMR, the inequivalent signals of the methane signals of the isopropyl peaks on the BAC scaffold, which are consistent with borenium **13** persist. (See ref 3 for spectra of **13**).

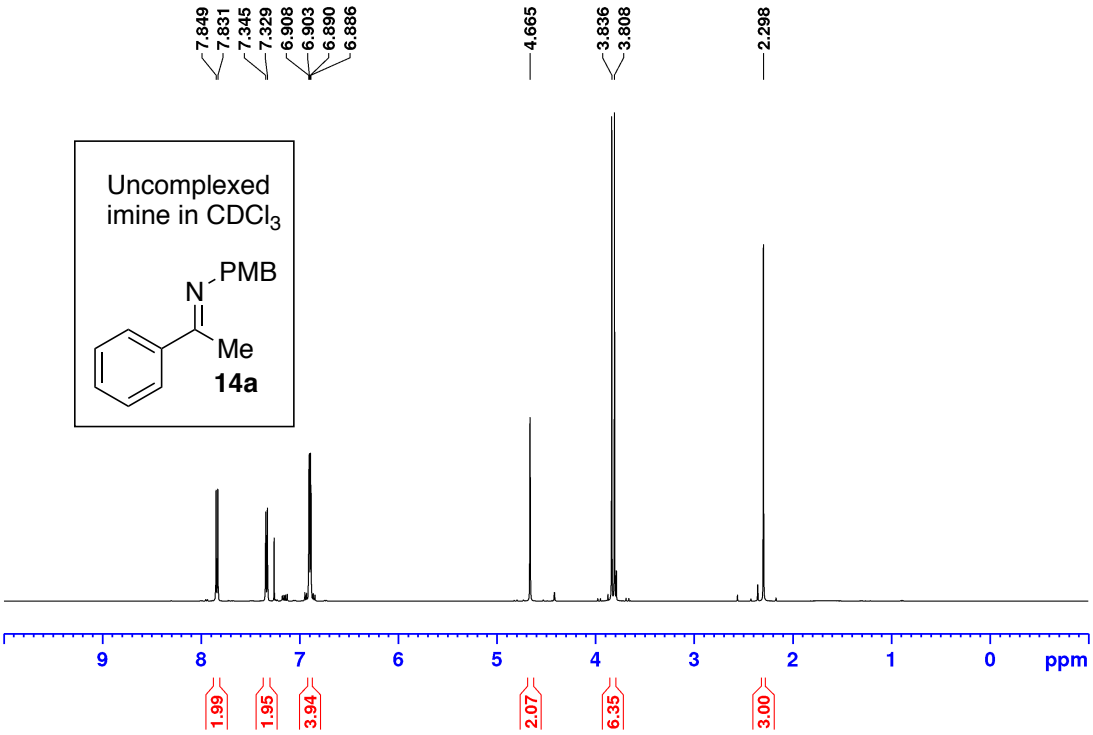
With **12**, significant peturbations in the ^{1}H and ^{11}B spectra are observed, which we take as evidence of formation of a Lewis adduct.


5.606
4.646
3.873
3.846
2.356
N
N
B
BAr$^{F}_{24}$
13 ^{1}H
+
N
PMB
Me
14a
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.96
6.47
2.81


-6.605
N
N
B
BAr$^{F}_{24}$
13 ^{11}B
+
N
PMB
Me
14a
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
ppm

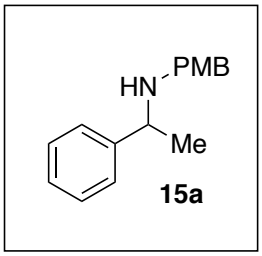

5.609
5.007
4.578
3.869
3.846
3.841
3.783
2.372
2.207
N
N
B
BAr$^{F}_{24}$
25 ^{1}H
+
N
PMB
Me
14a
9
8
7
6
5
4
3
2
1
0
ppm
1.00
0.85
0.91
8.44
1.53
1.68


-1.773
-6.592
N
N
B
BAr$^{F}_{24}$
25 ^{11}B
+
N
PMB
Me
14a
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
ppm


7.849
7.831
7.345
7.329
6.908
6.903
6.890
6.886
4.665
3.836
3.808
2.298
Uncomplexed imine in CDCl3
PMB
N
Me
14a
9
8
7
6
5
4
3
2
1
0
ppm
1.99
1.95
3.94
2.07
6.35
3.00

General Hydrogenation Procedure

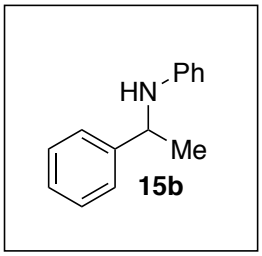
^{i}PrBAC-BR$_2$H (0.02 mmol, 10 mol %) and **trityl BArF^{24} 2-21** (22 mg, 0.02 mmol, 10 mol %) were placed in an oven dried 1-dram vial equipped with a magnetic stir bar. To this vial trifluorotoluene (0.2 mL) was added and the solution stirred for 2 minutes. Then substrate was added (0.2 mmol) as a solid and then the solution was diluted with trifluorotoluene (0.1 mL) or a solution of the substrate (0.1 mL, 2M) was added, and the vial equipped with a septum cap and 16-gauge needle. Vials were placed into a Parr-bomb which was then assembled and removed from the glove box. In a fume hood, the bomb was placed on a stir plate, and purged seven times by pressurizing to 20 atm of H_2 followed by careful release. The bomb was subsequently pressurized to 24 atm. The parr bomb was left on the stir plate over night and then was carefully depressurized, disassembled, and the vials were removed. $CDCl_3$ (approx. 0.5 mL) was added and conversion was ascertained by ^{1}H NMR (comparison of starting material and product, or triphenyl methane and product give values that agree). The solvents were then removed *in vacuo* and the crude material was then subjected to column chromatography with a gradient of 2.5% to 100% ether to hexanes as needed. ^{1}H NMR data was then acquired of the amine products.



15a

PMB amine: 48mg, 0.177mmol, 88%

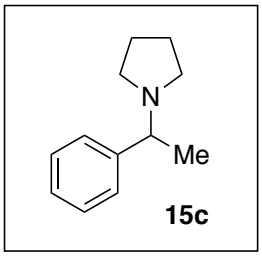
^{1}H (300 MHz, $CDCl_3$): δ 7.25 (m, 2H), 7.18 (m, 2H), 6.87 (m, 2H), 6.83 (m, 2H), 3.79 (s, 3H), 3.77 (s, 3H). 3.74 (q, 1H, *J* = 6.6Hz), 3.55 (ab q, 2H), 1.53 (s, 1H), 1.32 (d, 3H, *J* = 6.6Hz).



15b

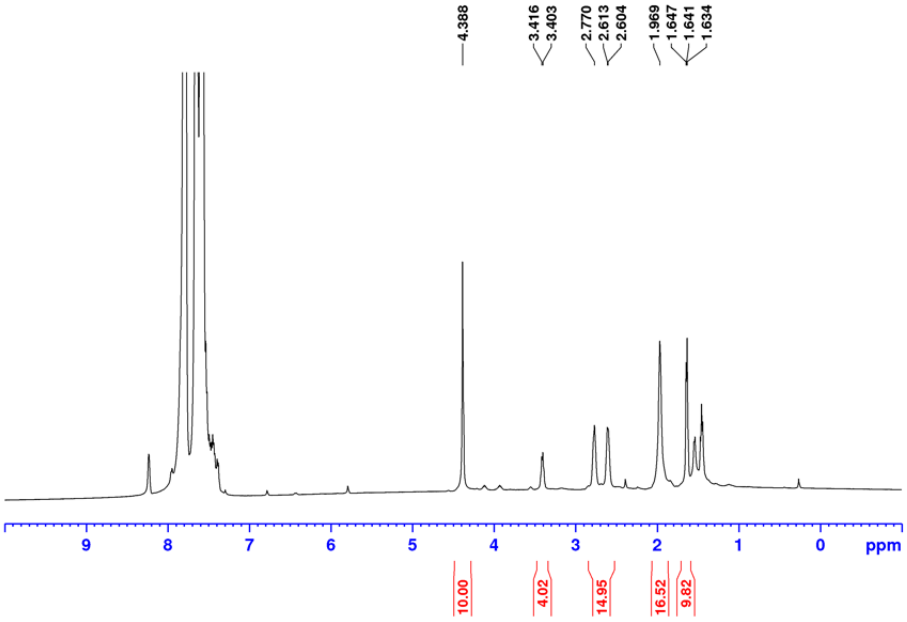
Aniline amine: 0.172 mmol as determined by ferrocene internal standard = 85% yield.

^{1}H (300 MHz, $CDCl_3$): δ 7.34 (m, 2H), 7.29 (m, 2H), 7.20 (m, 1H), 7.07 (m, 2H), 6.6 (t, 1H), 6.50 (d, 2H). 4.47 (q, 1H, *J* = 6.7Hz), 3.99 (s, 1H), 1.49 (d, 3H, *J* = 6.7Hz).

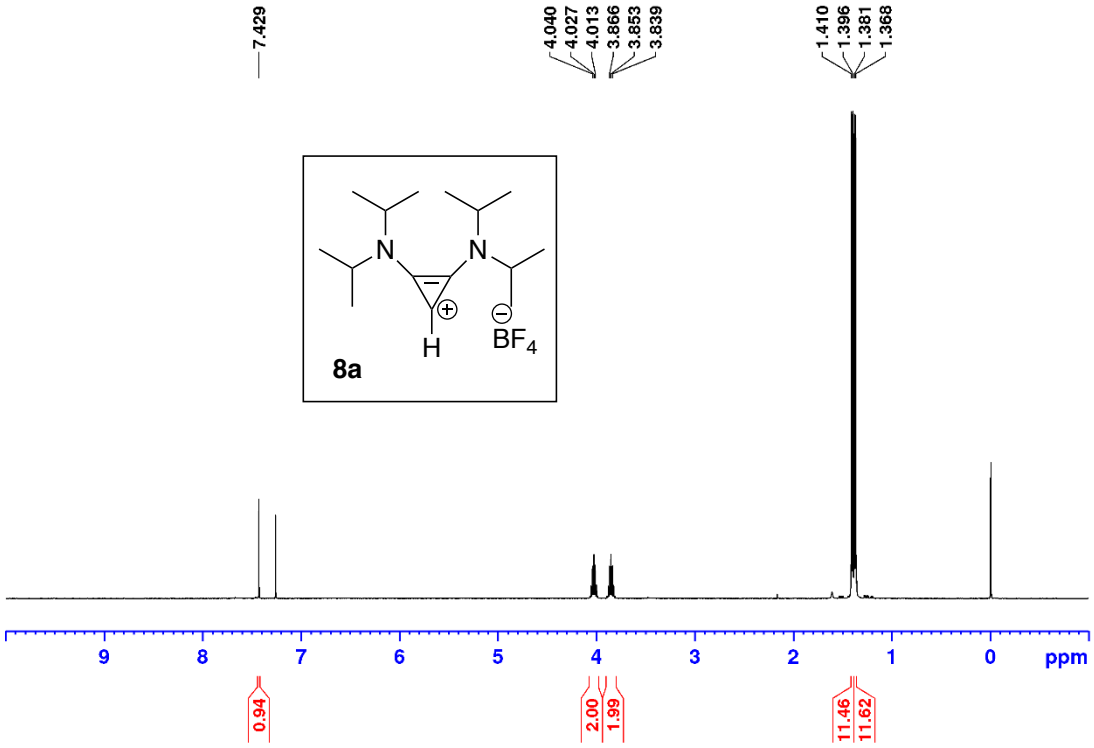


Pyrolidine amine: 22mg, 0.123 mmol, isolated yield 63%

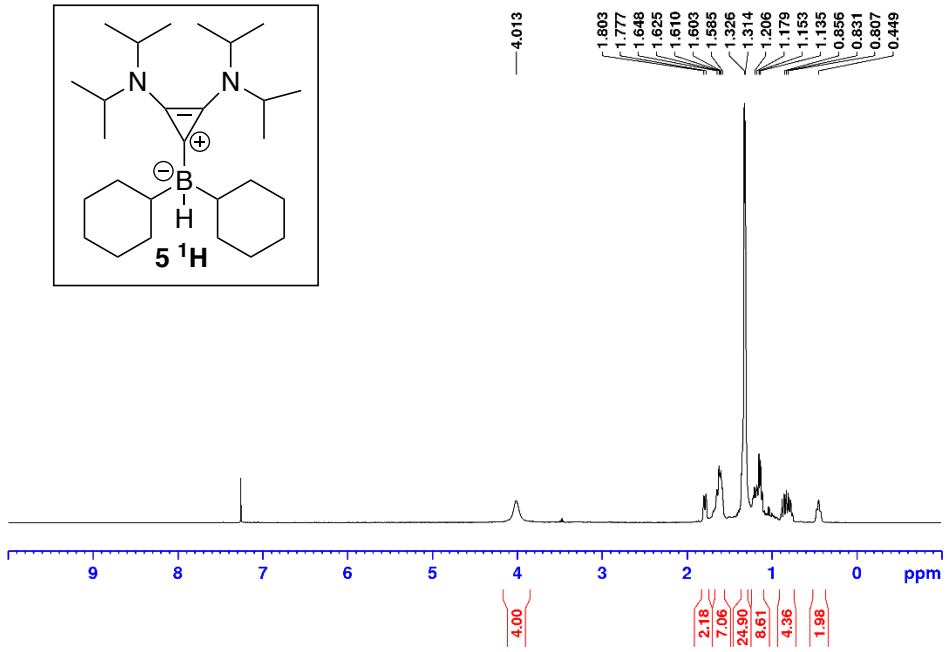
^{1}H (300 MHz, $CDCl_3$): δ 7.31 (m, 5H), 3.17 (q, 1H, *J* = 6.6Hz), 2.53 (m, 2H), , 2.37 (m, 2H), 1.75 (m, 4H), 1.39 (d, 3H, *J* = 6.6Hz). Several impurities were noted in this compound, which were not readily removed by column chromatography. This product was also somewhat volatile complicating isolation. In a separate procedure, 0.5 mL of a 0.1 molar solution of ferrocene was added directly to the reaction mixture without removal of the trifluorotoluene. Since there are 0.5 mmol of ferrocene, and the integral for the ferrocene is set to 10.00, the integral of 4.02 for the benzylic proton indicates 0.2 mmol of amine product are present, which essentially indicates quantitative conversion and NMR yield for this reaction.

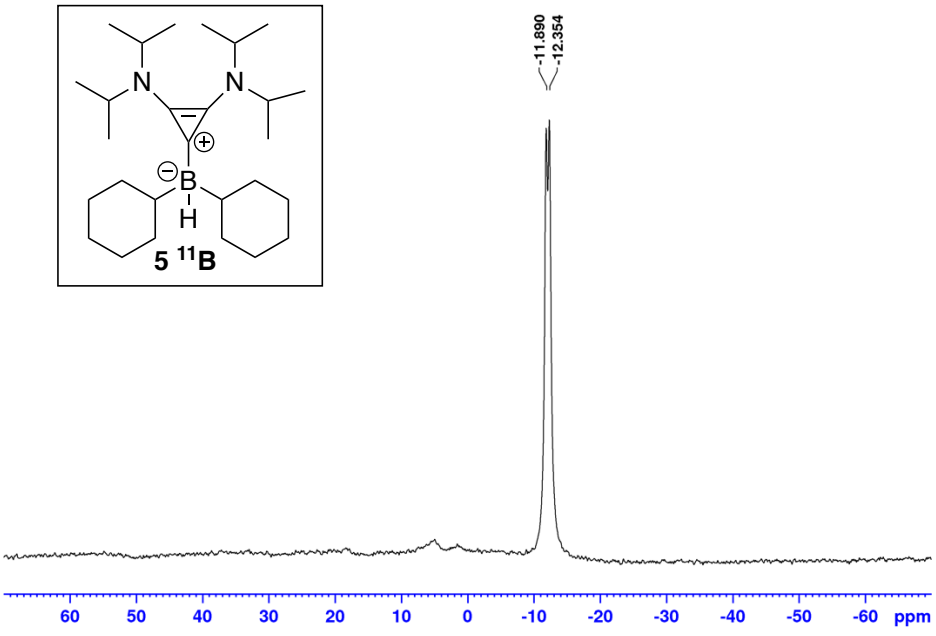


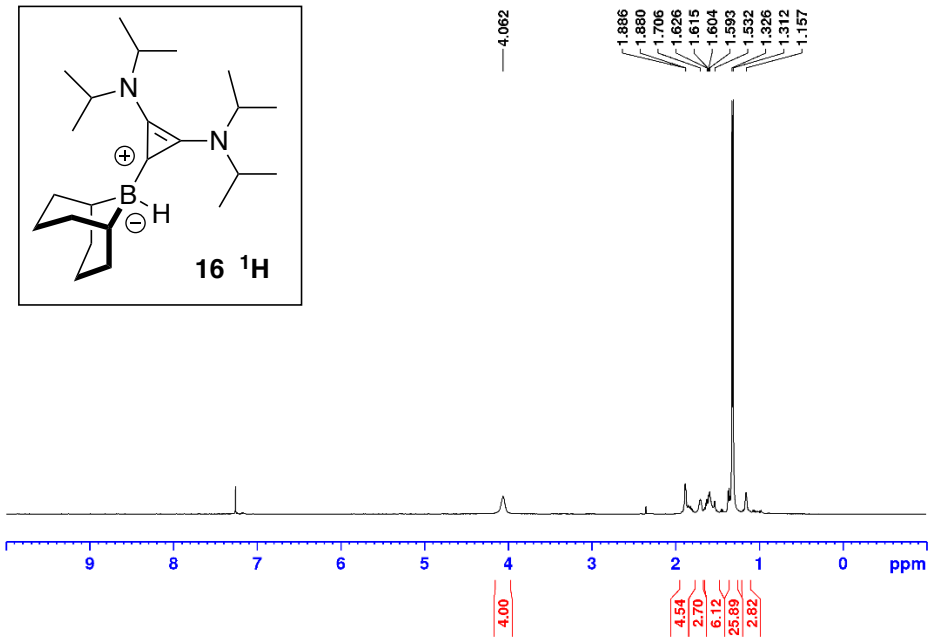
NMR Spectra of Borane Complexes and Precursors

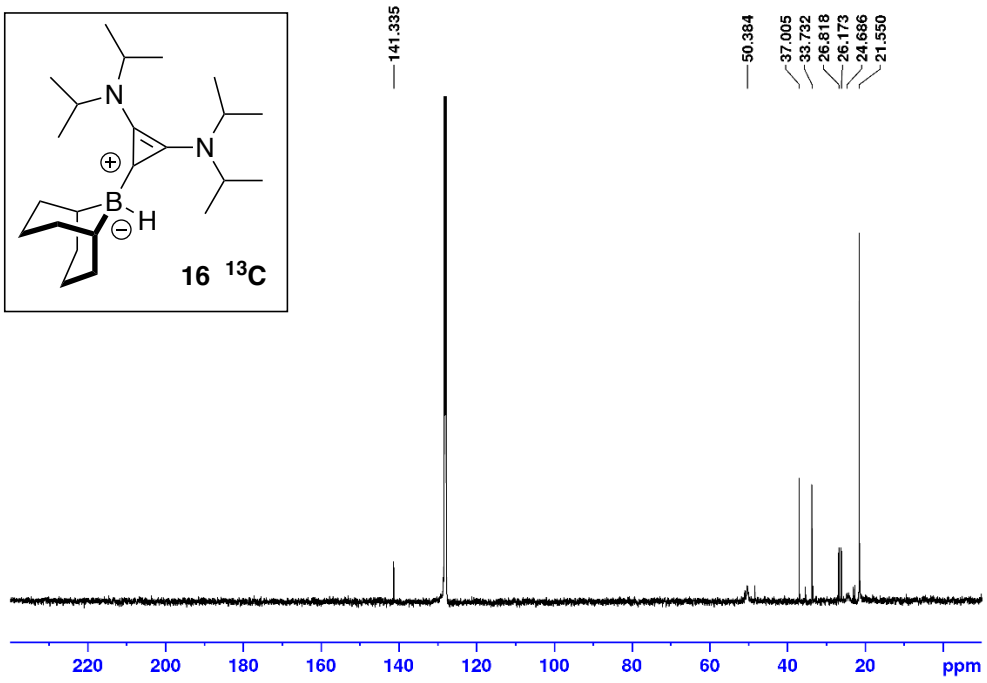


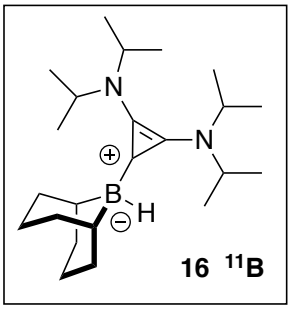
Compound **5** prepared via LiCl carbene adduct:





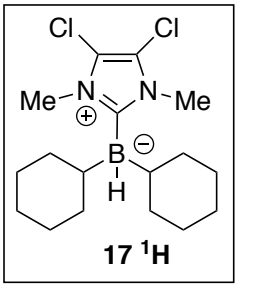

16 1H
4.062
1.886
1.880
1.706
1.626
1.615
1.604
1.593
1.532
1.326
1.312
1.157
9
8
7
6
5
4
3
2
1
0
ppm
4.00
4.54
2.70
6.12
25.89
2.82


16 13C
141.335
50.384
37.005
33.732
26.818
26.173
24.686
21.350
220
200
180
160
140
120
100
80
60
40
20
ppm


N
N
B
H

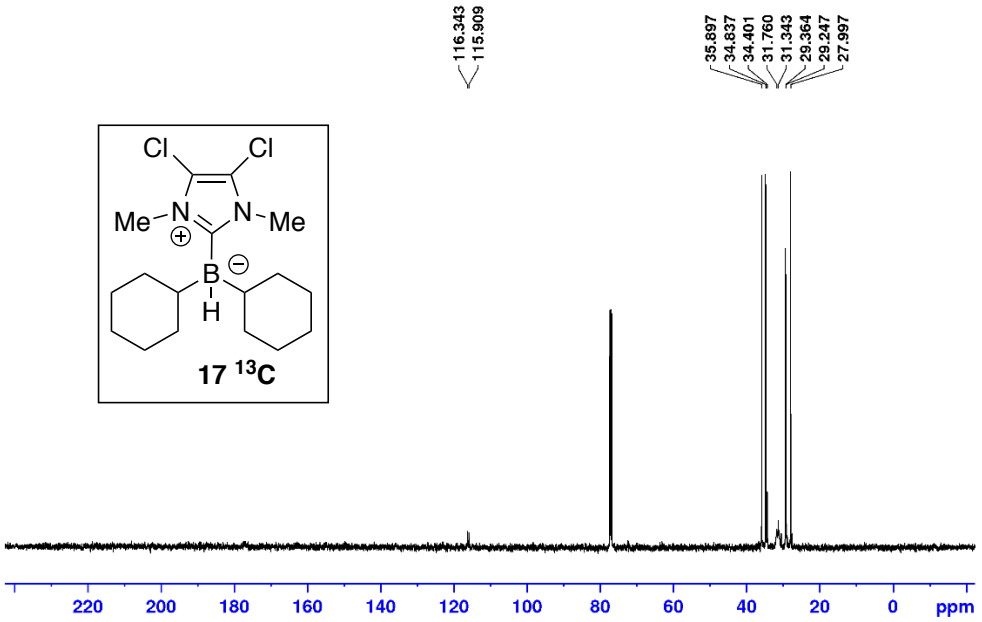
16 ^{11}**B**

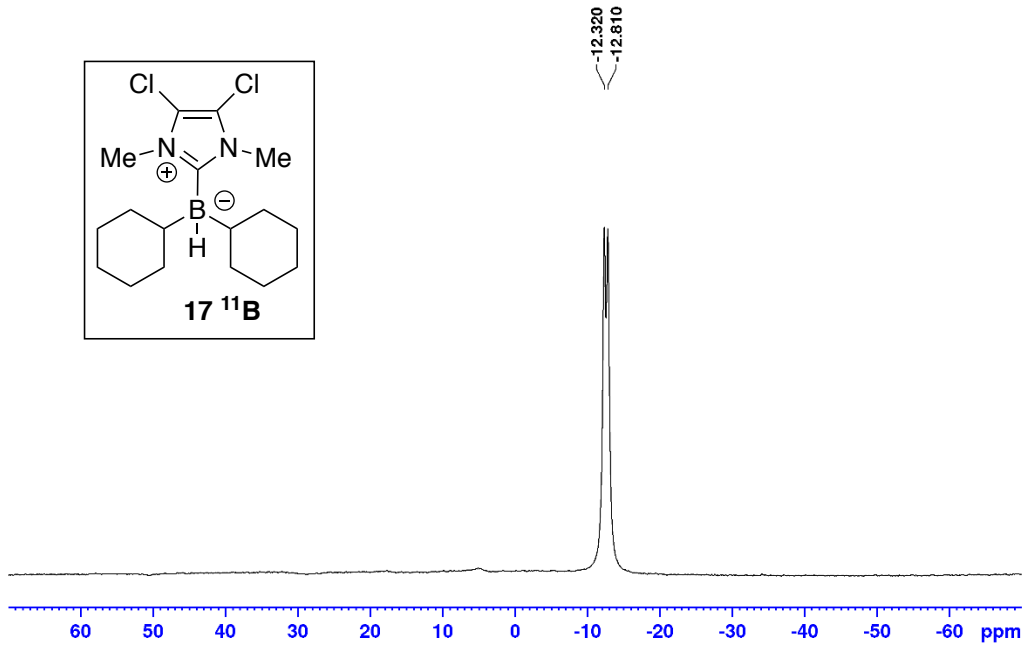
-16.116
-16.575
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
ppm

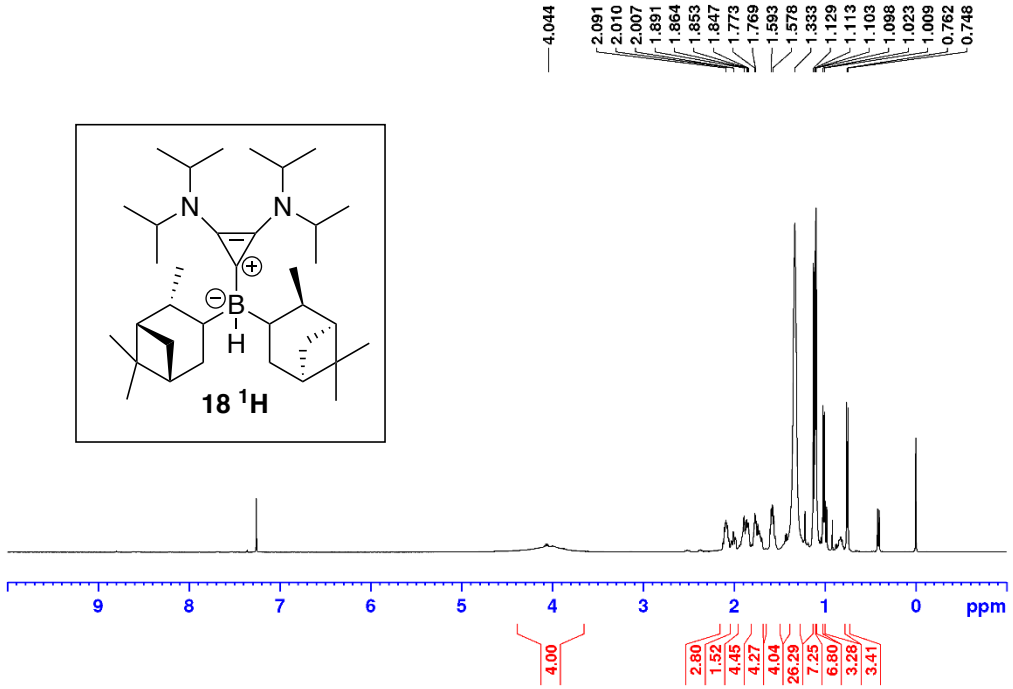

Cl
Cl
Me
N
N
Me
B
H

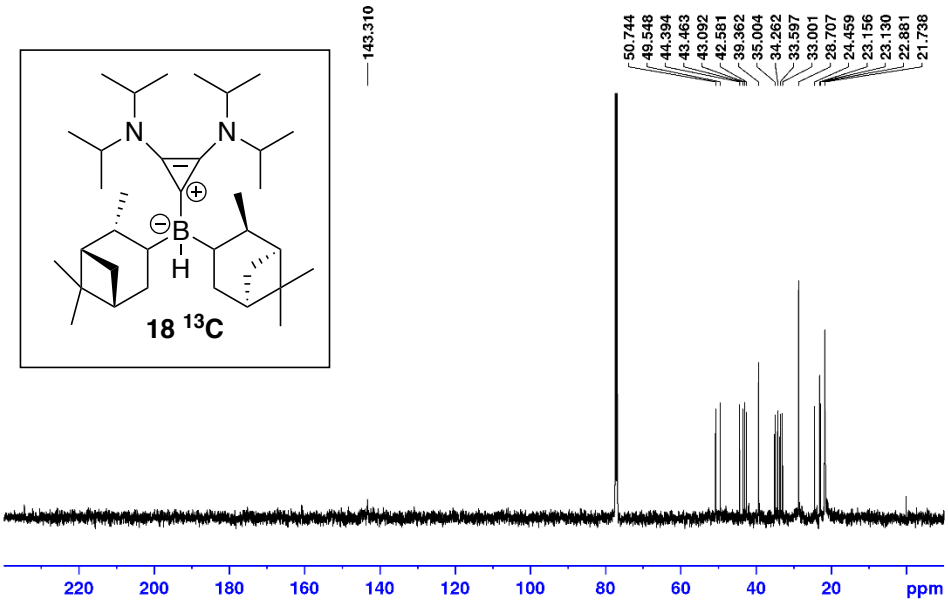
17 ^{1}**H**

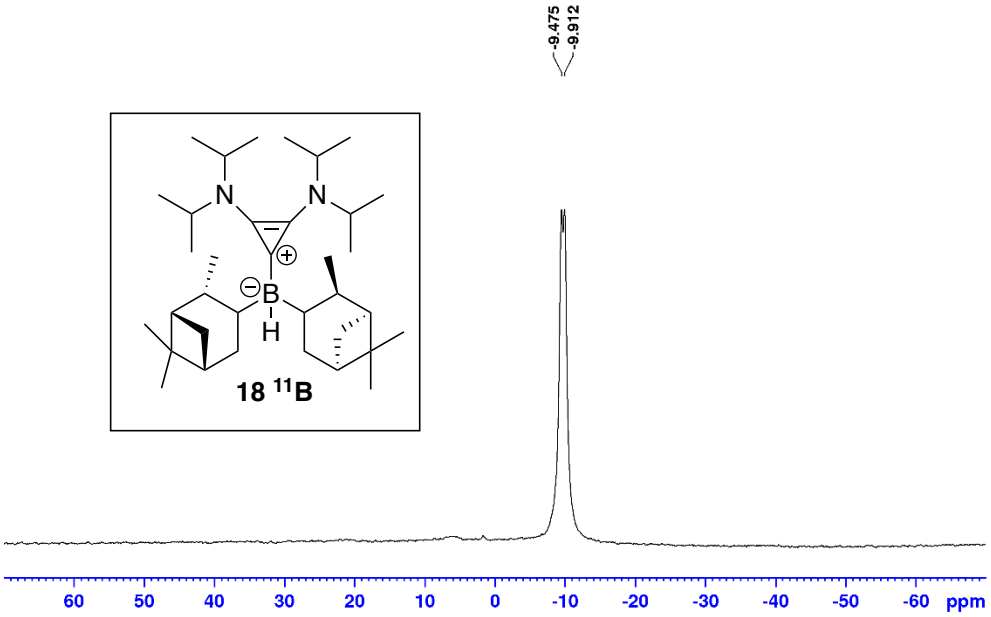
3.821
3.726
1.847
1.821
1.660
1.632
1.573
1.569
1.561
1.243
1.224
1.218
1.195
1.176
1.155
1.141
1.131
1.125
1.109
0.842
0.819
0.798
0.794
0.775
0.768
9
8
7
6
5
4
3
2
1
0
ppm
3.00
3.04
2.09
7.34
9.23
4.53
2.26

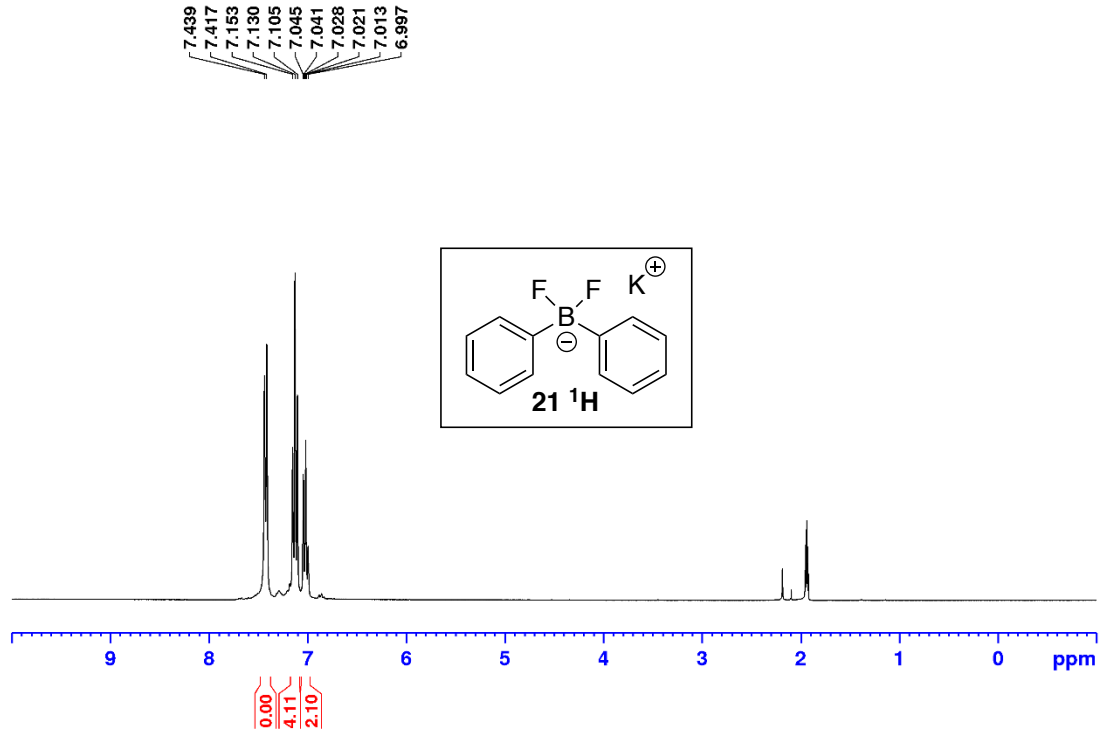

116.343
115.909
35.897
34.837
34.401
31.760
31.343
29.364
29.247
27.997
Cl
Cl
Me
N
N
Me
B
H
17 13C
220
200
180
160
140
120
100
80
60
40
20
0
ppm

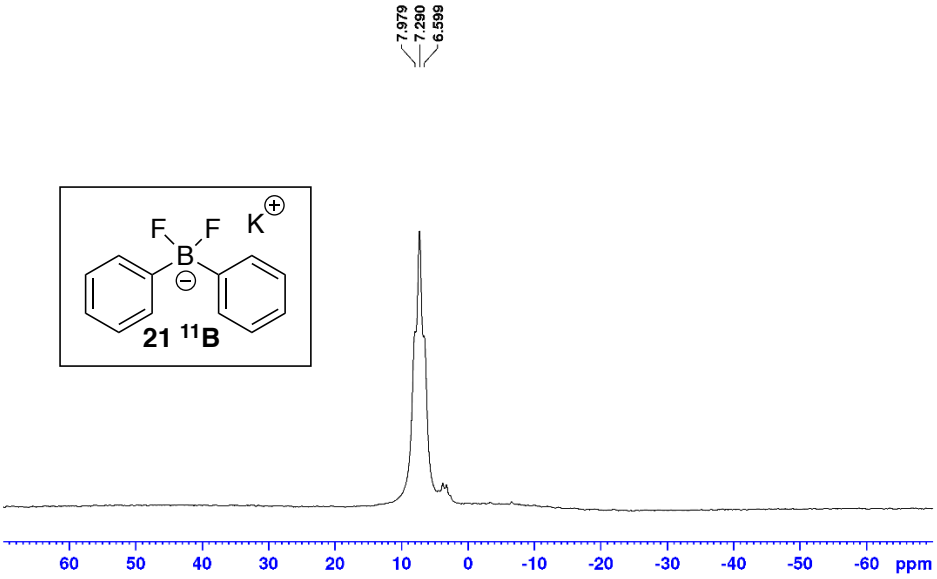

-12.320
-12.810
Cl
Cl
Me
N
N
Me
B
H
17 11B
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
ppm

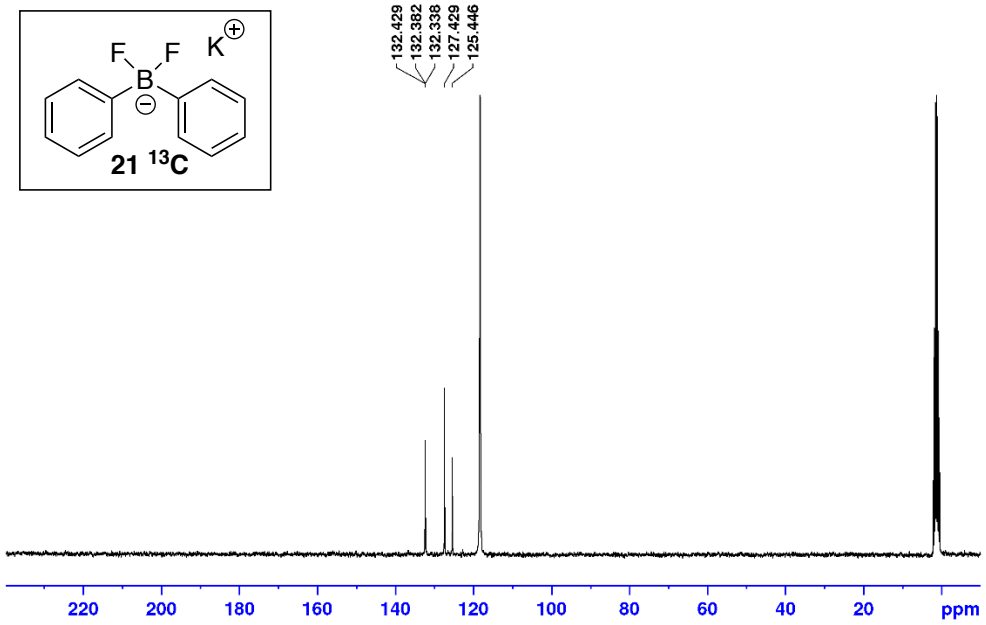

4.044
2.091
2.010
2.007
1.891
1.864
1.853
1.847
1.773
1.769
1.593
1.578
1.333
1.129
1.113
1.103
1.098
1.023
1.009
0.762
0.748
18 1H
9
8
7
6
5
4
3
2
1
0
ppm
4.00
2.80
1.52
4.45
4.27
4.04
26.29
7.25
6.80
3.28
3.41

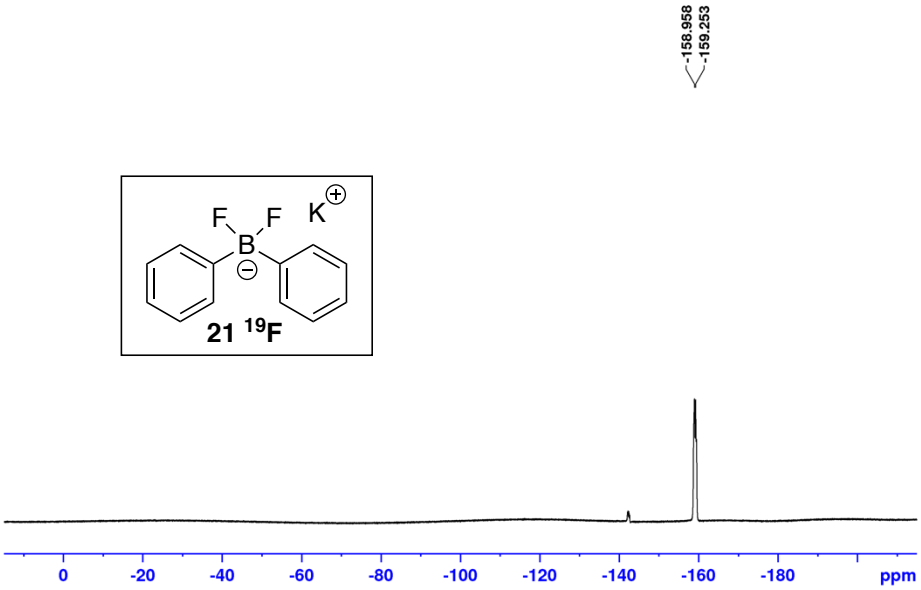

143.310
50.744
49.548
44.394
43.463
43.092
42.581
39.362
35.004
34.262
33.597
33.001
28.707
24.459
23.156
23.130
22.881
21.738
18 13C
220
200
180
160
140
120
100
80
60
40
20
ppm

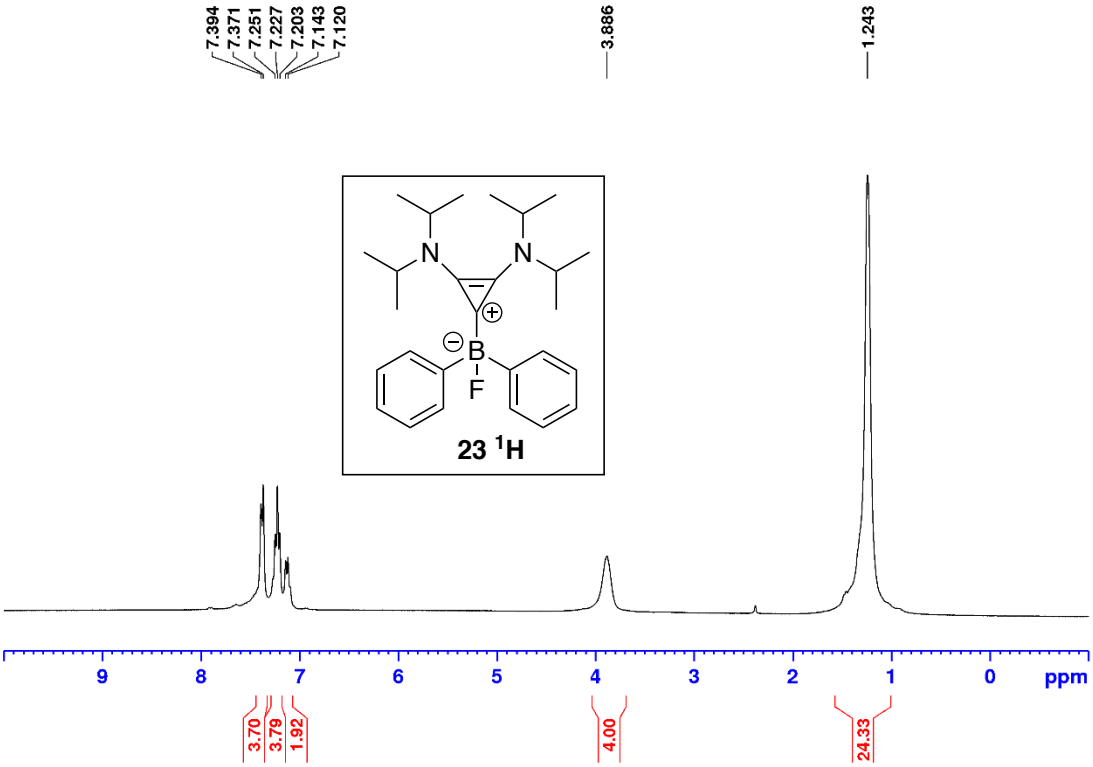

-9.475
-9.912
18 11B
60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 ppm

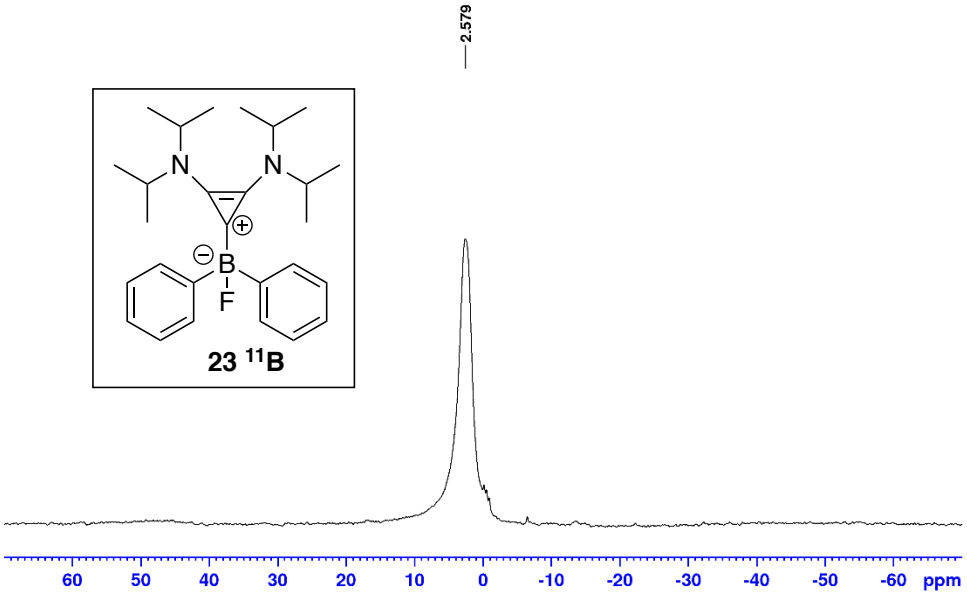

7.439
7.417
7.153
7.130
7.105
7.045
7.041
7.028
7.021
7.013
6.997
21 1H
9 8 7 6 5 4 3 2 1 0 ppm
0.00
4.11
2.10

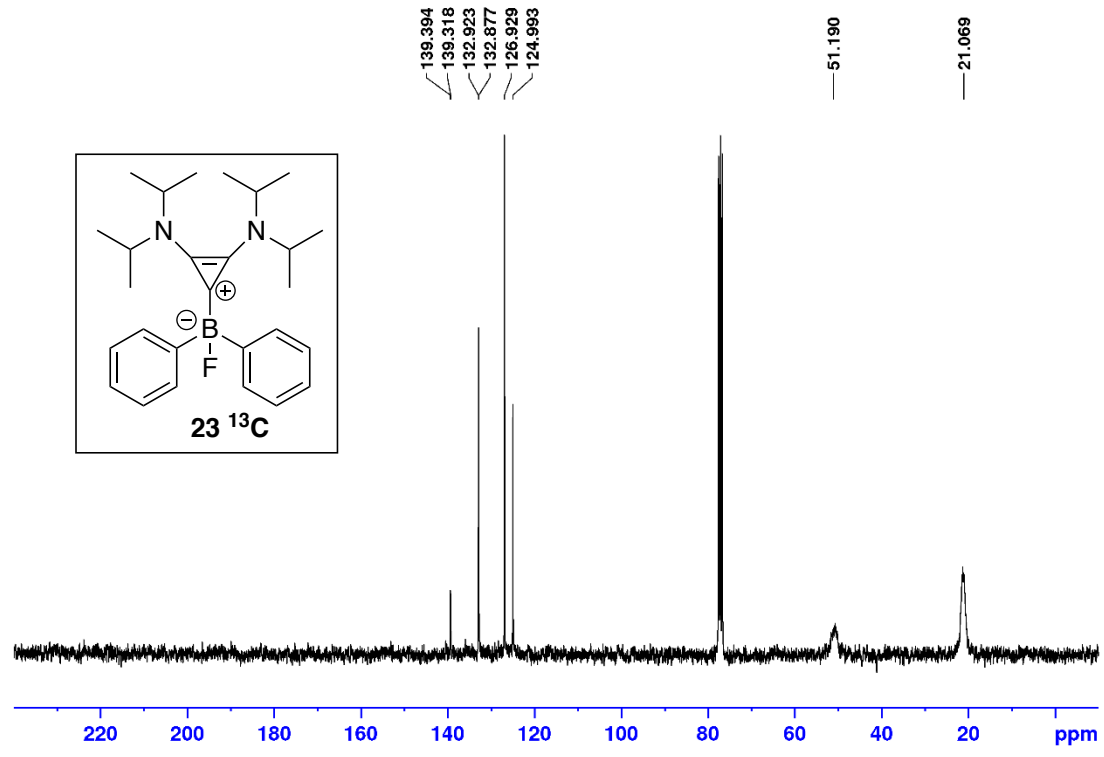

7.979
7.290
6.599
F
F
B
K
21 11B
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
ppm

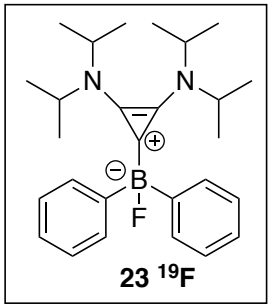

132.429
132.382
132.338
127.429
125.446
F
F
B
K
21 13C
220
200
180
160
140
120
100
80
60
40
20
ppm


-158.958
-159.253
F
F
B
K
21 19F
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

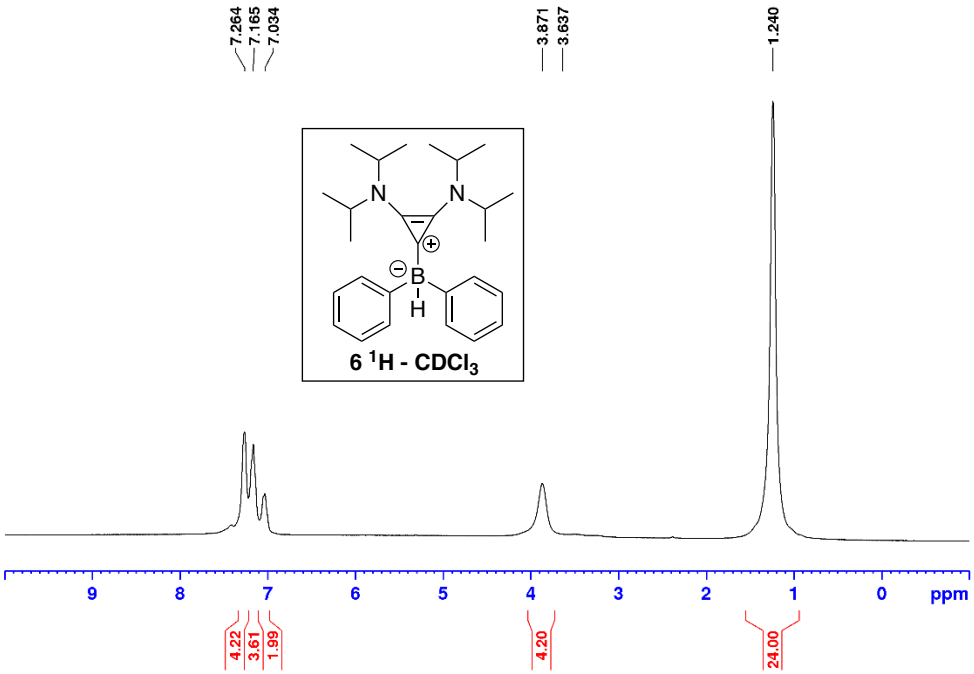

7.394
7.371
7.251
7.227
7.203
7.143
7.120
3.886
1.243
N
N
B
F
23 1H
9
8
7
6
5
4
3
2
1
0
ppm
3.70
3.79
1.92
4.00
24.33


2.579
N
N
B
F
23 11B
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
ppm

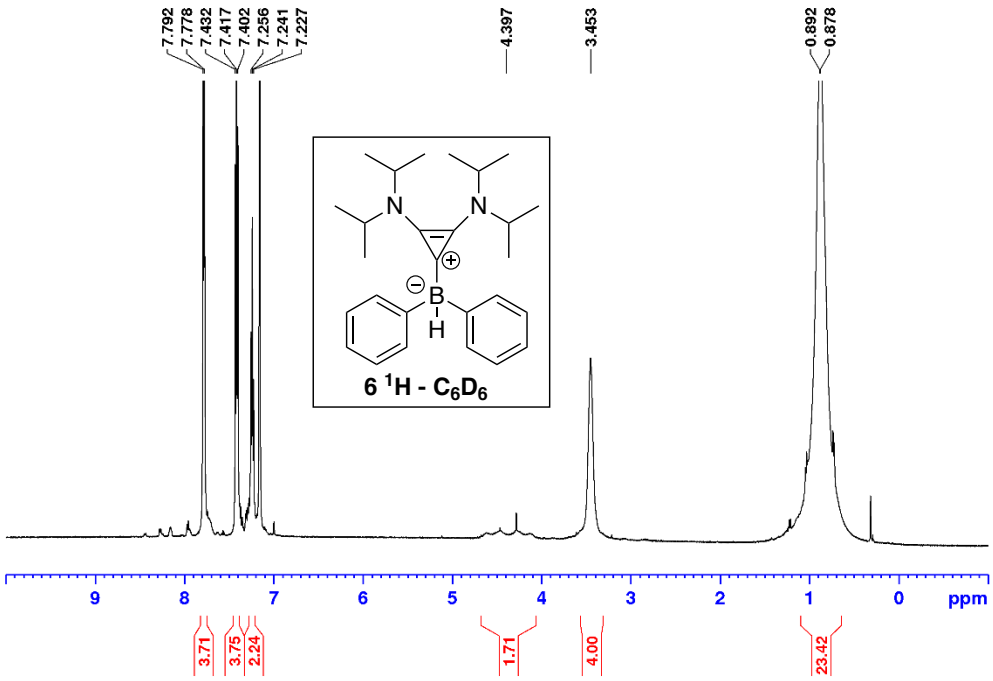

139.394
139.318
132.923
132.877
126.929
124.993
51.190
21.069
N
N
B
F
23 13C
220
200
180
160
140
120
100
80
60
40
20
ppm

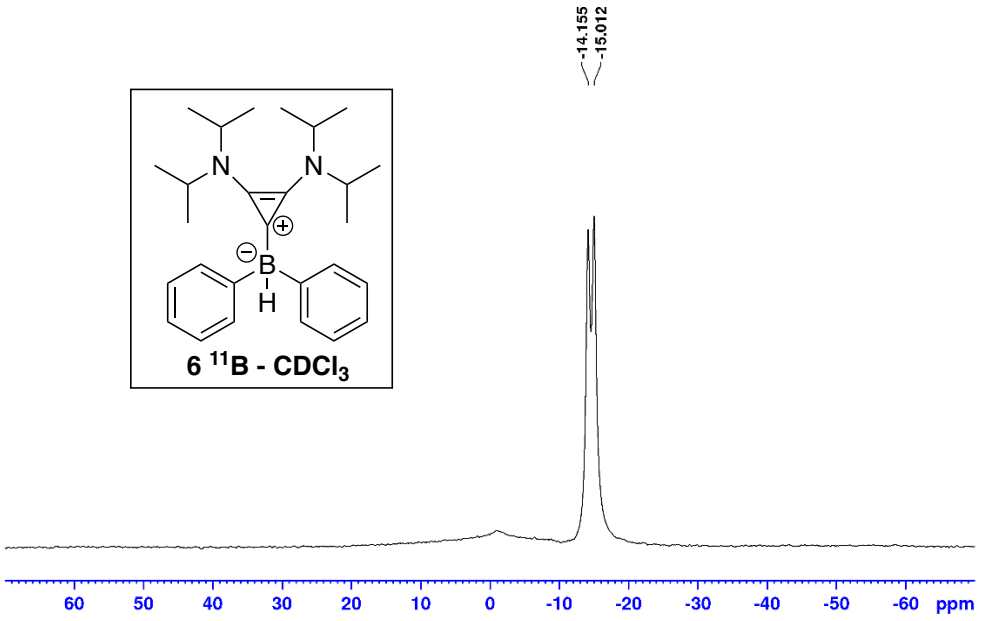


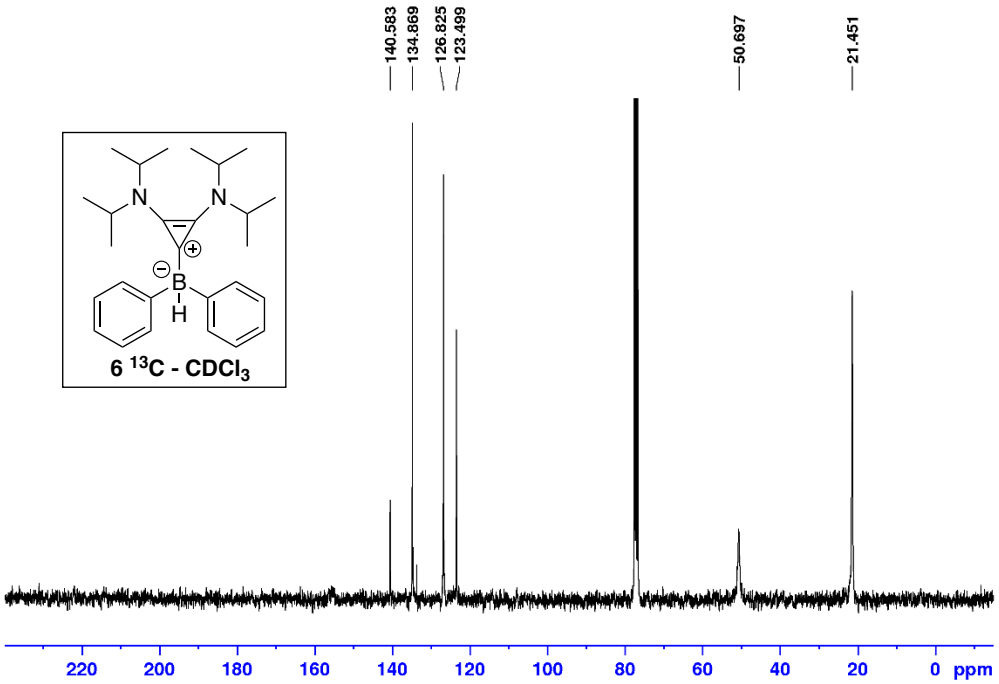
23 ^{19}F

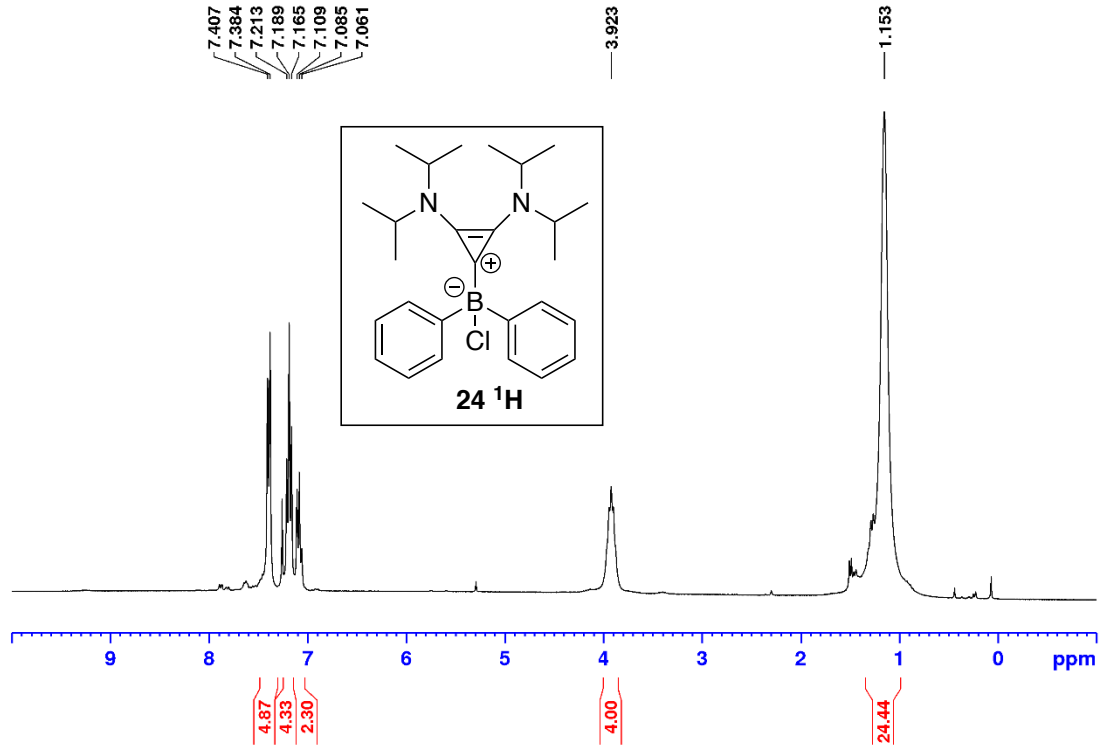


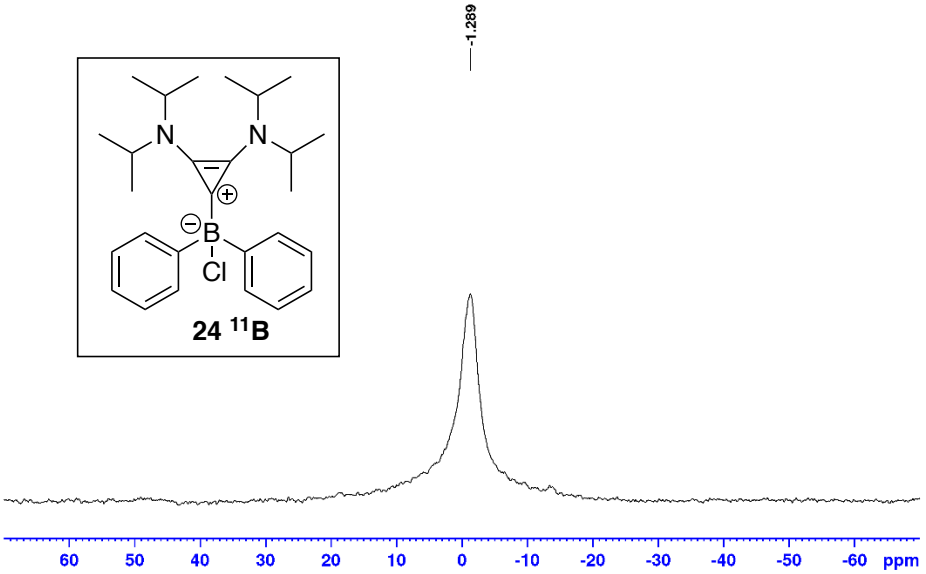
6 ^{1}H - $CDCl_3$

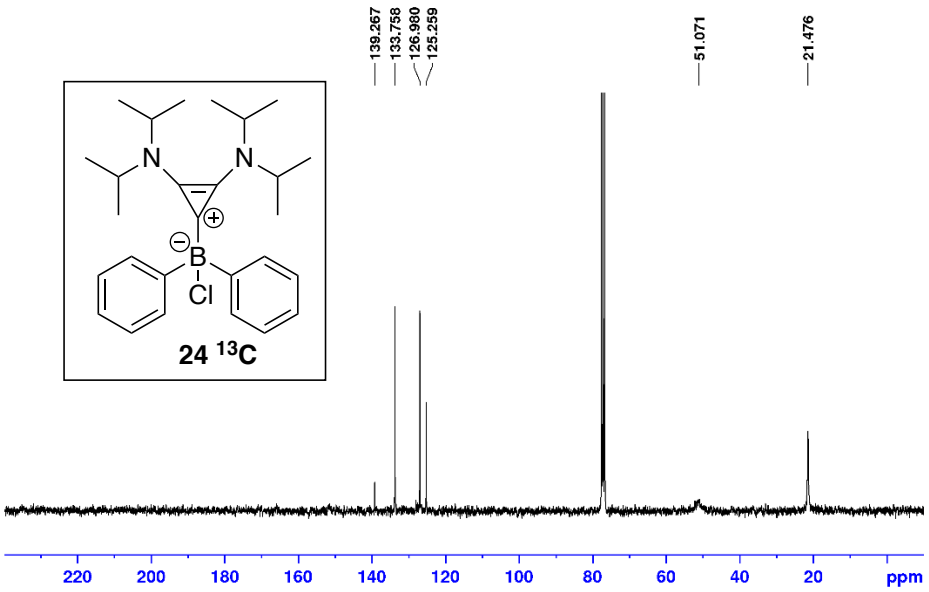

7.792
7.778
7.432
7.417
7.402
7.256
7.241
7.227
4.397
3.453
0.892
0.878
N
N
B
H
6 ^{1}H - C_6D_6
9
8
7
6
5
4
3
2
1
0
ppm
3.71
3.75
2.24
1.71
4.00
23.42

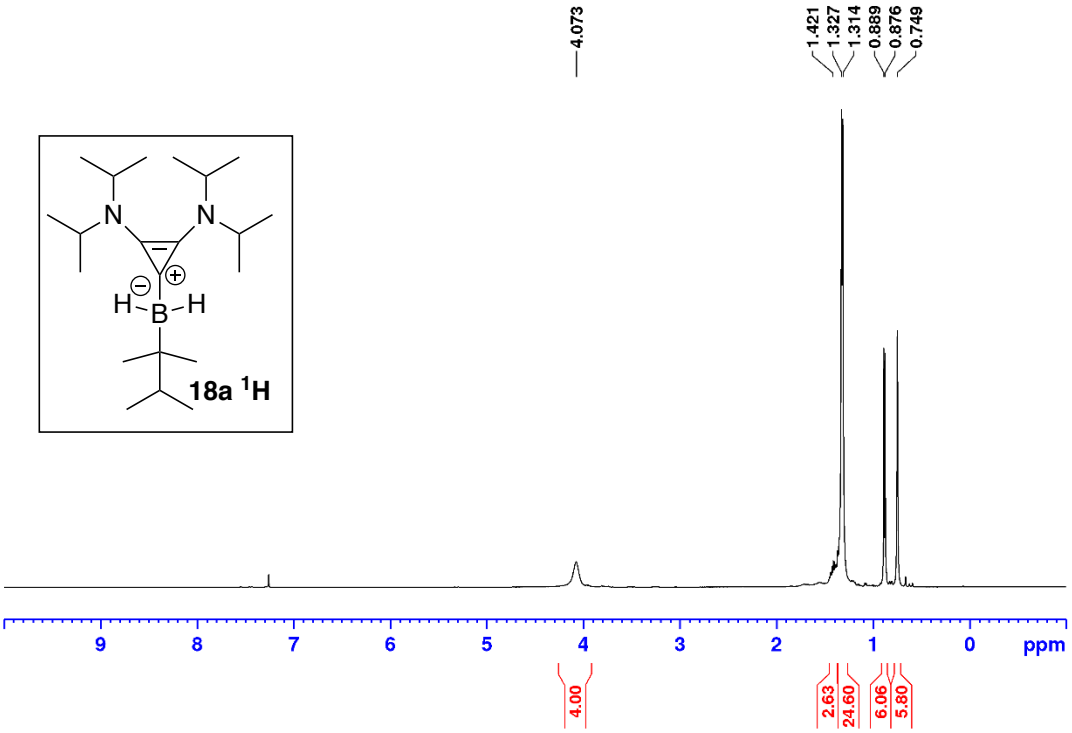

-14.155
-15.012
N
N
B
H
6 ^{11}B - $CDCl_3$
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
ppm

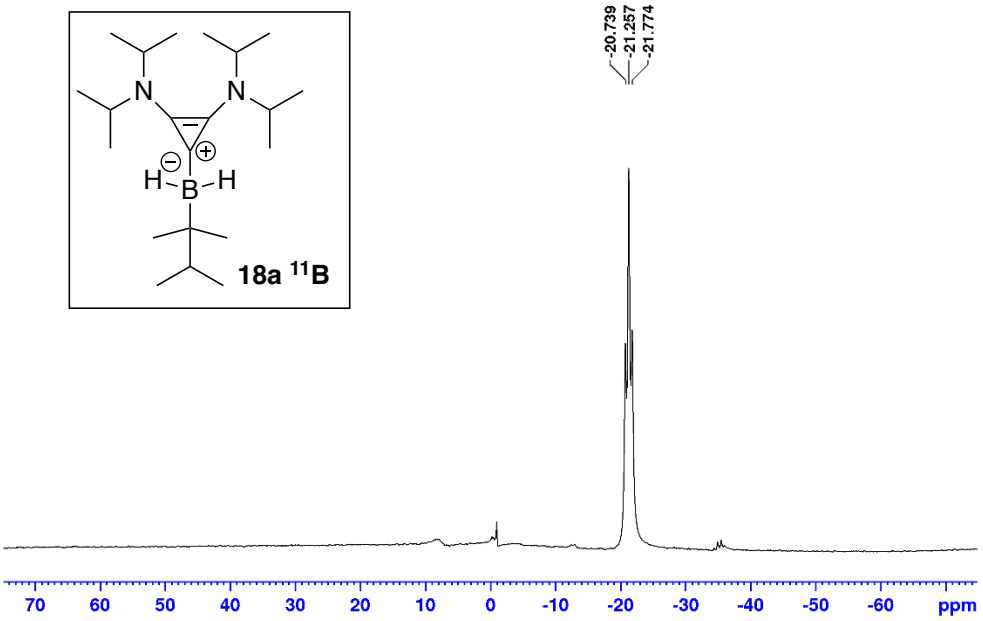

140.583
134.869
126.825
123.499
50.697
21.451
6 13C - CDCl3
220
200
180
160
140
120
100
80
60
40
20
0
ppm

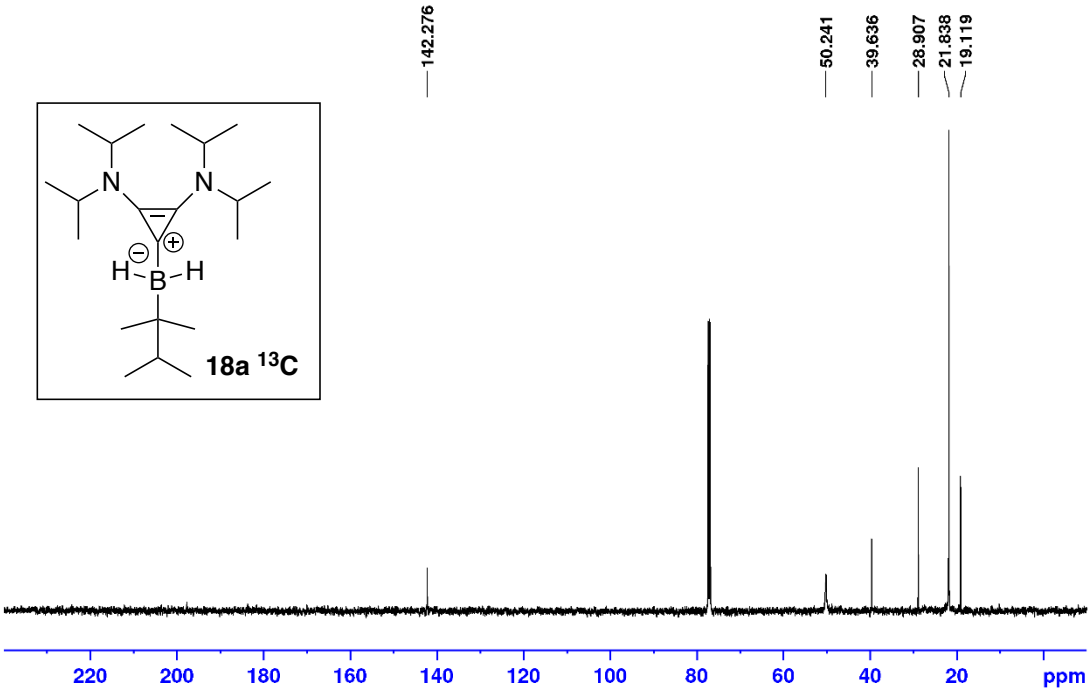

7.407
7.384
7.213
7.189
7.165
7.109
7.085
7.061
3.923
1.153
24 1H
9
8
7
6
5
4
3
2
1
0
ppm
4.87
4.33
2.30
4.00
24.44


-1.289
N
N
B
Cl
24 11B
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
ppm

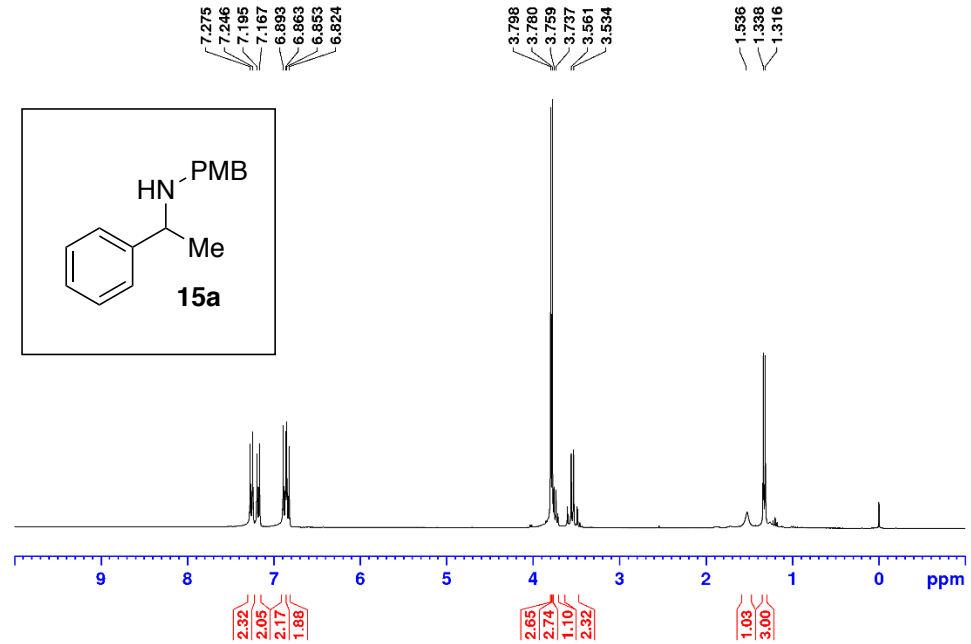

139.267
133.758
126.980
125.259
51.071
21.476
N
N
B
Cl
24 13C
220
200
180
160
140
120
100
80
60
40
20
ppm

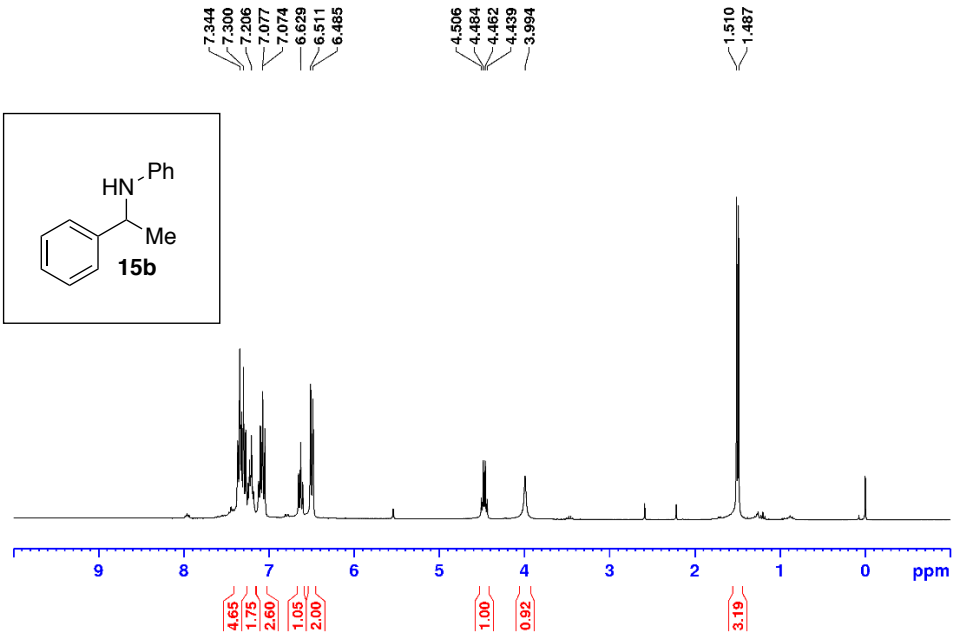

4.073
1.421
1.327
1.314
0.889
0.876
0.749
N
N
H
B
H
18a ^{1}H
9
8
7
6
5
4
3
2
1
0
ppm
4.00
2.63
24.60
6.06
5.80

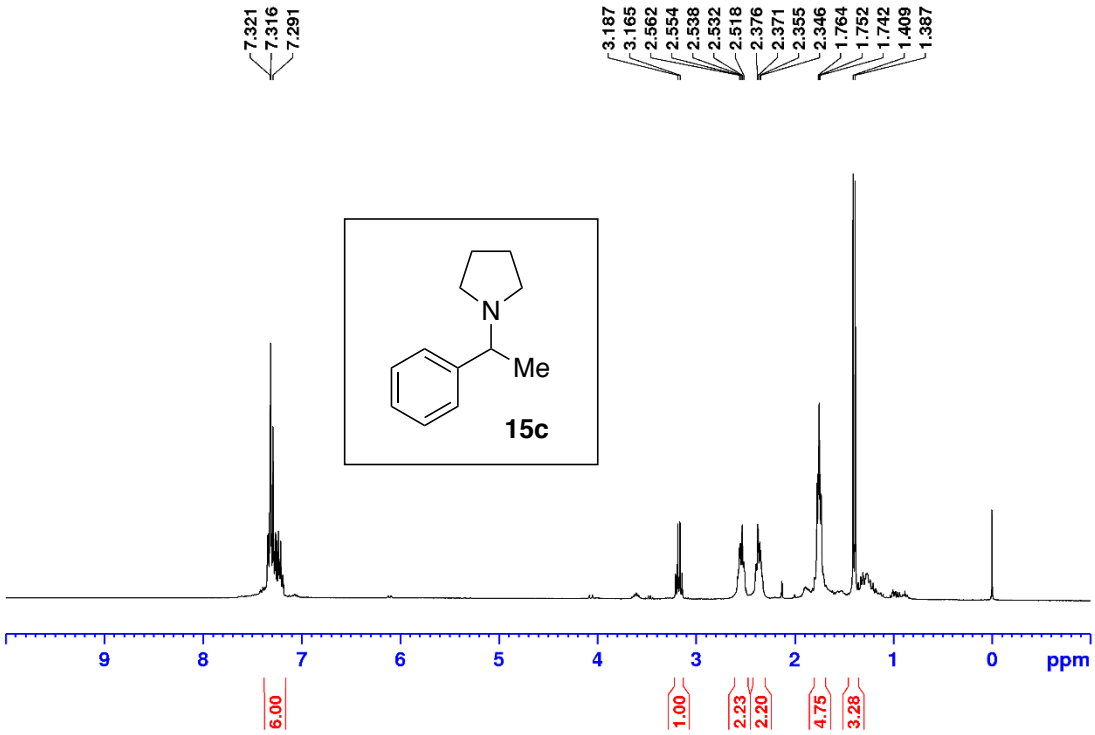

-20.739
-21.257
-21.774
N
N
H
B
H
18a ^{11}B
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
ppm


142.276
50.241
39.636
28.907
21.838
19.119
N
N
H
B
H
18a ^{13}C
220
200
180
160
140
120
100
80
60
40
20
ppm

NMR Spectra of Reduction Products






7.321
7.316
7.291
3.187
3.165
2.562
2.554
2.538
2.532
2.518
2.376
2.371
2.355
2.346
1.764
1.752
1.742
1.409
1.387
N
Me
15c
9
8
7
6
5
4
3
2
1
0
ppm
6.00
1.00
2.23
2.20
4.75
3.28