Supporting Information for:

Silicon–Carbon Bond Cleavage from a Hydroboration Sequence

Manjur O. Akram, Ayesha Begum, Caleb D. Martin*

Baylor University, Department of Chemistry and Biochemistry, One Bear Place #97348, Waco, TX 76798, USA

Author to address correspondence: Caleb D. Martin (caleb_d_martin@baylor.edu)

Table of Contents

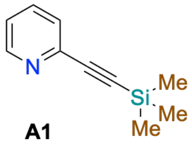
1. General Details

All manipulations were performed under an inert atmosphere in a nitrogen filled MBraun Unilab glove box or using standard Schlenk techniques. Chloroform-d for NMR spectroscopy was purchased from Cambridge Isotope Laboratories Inc., dried by stirring over CaH_2, distilled, and stored over 4 Å molecular sieves. All other solvents were purchased from commercial sources as anhydrous grade, dried further using a JC Meyer Solvent System with dual columns packed with solvent-appropriate drying agents, and stored over 3 or 4 Å molecular sieves. The reagents 2-bromo-6-(*tert*-butyl)pyridine and bis(1-methyl-*ortho*-carboranyl)borane ($HB^{Me}oCb_2$) were synthesized based on the literature procedures.[1],[2] Multinuclear NMR spectra (^{1}H, $^{1}H\{^{11}B\}$, $^{13}C\{^{1}H\}$, ^{11}B, $^{11}B\{^{1}H\}$, and $^{29}Si\{^{1}H\}$) were recorded on a Bruker Avance III HD 400 MHz or 600 MHz instrument. High Resolution mass spectra (HRMS) were obtained in the Baylor University Mass Spectrometry Center on a Thermo Scientific Q Exactive spectrometer. FT-IR spectra were recorded on a Bruker Alpha ATR FT-IR spectrometer on solid samples. Single crystal X-ray diffraction data were collected on Bruker Apex III-CCD detector using Mo-Kα radiation (λ = 0.71073 Å) or a Rigaku Oxford Diffraction XtaLAB Synergy with a HyPix-Arc 100 detector using Cu-Kα radiation (λ = 1.54184 Å). Crystals were selected under paratone oil, mounted on MiTeGen micromounts, and immediately placed in a cold stream of N_2. Structures were solved and refined using SHELXTL and figures produced using OLEX2.[3],[4]

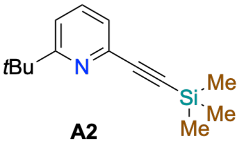
2. Experimental Section

2.1 Synthesis of ethynylsilanes

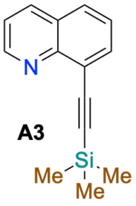
Ethynylsilanes **A1** and **A5** were purchased and used as received. Ethynylsilanes **A2**-**A4** were prepared by the procedures below.



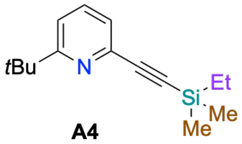
A1



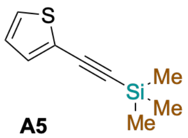
A2



A3

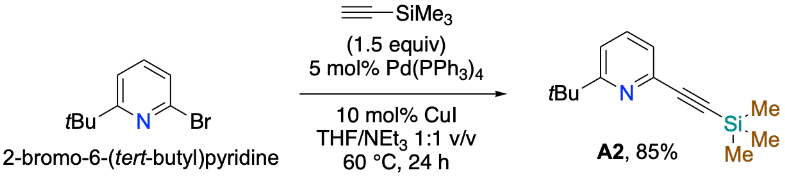


A4



A5

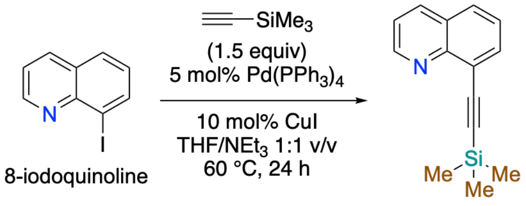
2.1.1 Synthesis of A2



To a stirred degassed THF (10 mL) solution of 2-bromo-6-(*tert*-butyl)pyridine (428 mg, 2.00 mmol), Pd(PPh$_3$)$_4$ (116 mg, 0.100 mmol, 5.00 mol%) and CuI (38.1 mg, 0.200 mmol, 10.0 mol%) were added under nitrogen, followed by 10 mL of degassed triethylamine. Trimethylsilylacetylene (427 μL, 3.00 mmol) was added dropwise over 2 min and the reaction mixture heated at 60 ºC for 24 hours. After consumption of the 2-bromo-6-(*tert*-butyl)pyridine (monitored by TLC), 10 mL of ethyl acetate was added to the reaction mixture. After filtering through a pad of celite, the volatiles were removed from the filtrate under vacuum and the crude purified by flash chromatography on silica gel (eluent: 5% ethyl acetate/hexanes), to give **A2** as yellow liquid. Yield: 85%, 394 mg; ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.53-7.50 (m, 1H), 7.26-7.24 (m, 2H), 1.34 (s, 9H), 0.25 (s, 9H) ppm; ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ = 169.9, 142.0, 136.1, 125.1, 118.8, 104.9, 93.5, 37.7, 30.3, 0.0 ppm; ^{29}Si{^{1}H} NMR (119 MHz, CDCl$_3$): δ = –17.0 ppm ; FT-IR (ranked intensity, cm^{-}

^{1}): 2958 (7), 1567 (4), 1441 (2), 1360 (13), 1296 (15), 1249 (3), 1165 (12), 1092 (14), 918 (5), 839 (1), 811 (8), 759 (6), 743 (11), 704 (9), 647 (10); HRMS (+ESI): calcd 232.1516 for $C_{14}H_{21}NSi$ $[M+H]^+$ found 232.1516.

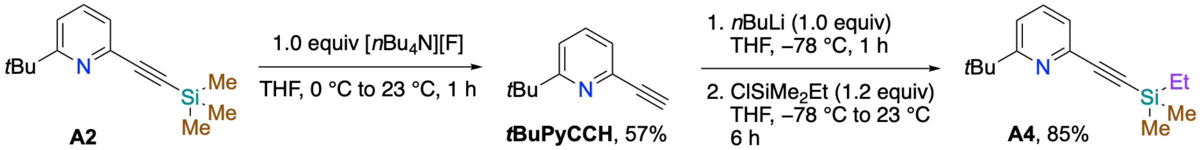
2.1.2 Synthesis of A3



A3, 56%

Sequentially, $Pd(PPh_3)_4$ (57.8 mg, 0.050 mmol, 5.00 mol%), CuI (19.1 mg, 0.100 mmol, 10.0 mol%), and 5.00 mL of degassed triethylamine were added to a degassed THF (5 mL) solution of 8-iodoquinoline (255 mg, 1.00 mmol). Trimethylsilylacetylene (214 μL, 1.50 mmol) was added dropwise under nitrogen over 2 min and the reaction stirred for 24 hours at 60 ºC. After the 8-iodoquinoline was consumed (monitored by TLC), 10 mL of ethyl acetate was added to the reaction mixture, and it was filtered through celite. The volatiles were stripped from the filtrate under vacuum and the residue purified by flash chromatography on silica gel (eluent: 10% ethyl acetate/hexanes), to give **A3** as a yellow liquid. Yield: 56%, 127 mg; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 9.04$ (dd, $J = 4$ and 2 Hz, 1H), 8.15 (dd, $J = 8$ and 2 Hz, 1H), 7.97-7.95 (m, 1H), 7.79 (dd, $J = 8$ and 2 Hz, 1H), 7.50-7.46 (m, 1H), 7.43 (dd, $J = 8$ and 4 Hz, 1H), 0.34 (s, 9H) ppm; $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): $\delta = 151.4$, 148.3, 136.6, 135.3, 128.8, 128.4, 126.1, 123.4, 121.7, 102.8, 100.9, 0.4 ppm; $^{29}Si\{^{1}H\}$ NMR (119 MHz, $CDCl_3$): $\delta = -17.4$ ppm; FT-IR (ranked intensity, cm^{-1}): 2958 (13), 2156 (11), 1591 (15), 1493 (5), 1382 (9), 1382 (10), 1248 (2), 1076 (6), 1052 (7), 828 (1), 790 (4), 756 (3), 726 (12), 641 (8), 446 (14); HRMS (+ESI): calcd 226.1047 for $C_{14}H_{16}NSi$ $[M+H]^+$ found 226.1054.

2.1.2 Synthesis of A4

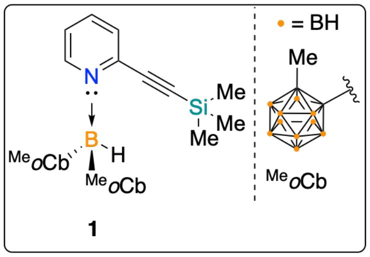


To a stirred THF (5 mL) solution of **A2** (231 mg, 1.00 mmol), TBAF (1.00 M in THF, 1.00 mL, 1.00 mmol) was added at 0 °C. The bath was removed and the mixture stirred for 1 h at 23 °C. The mixture was quenched by addition of water (5 mL) and extracted with EtOAc (3 × 5 mL). The organic layers were washed with brine (10 mL), dried over Na_2SO_4, and rotary evaporated. The crude was purified by flash column chromatography on silica gel (eluent: 10% ethyl acetate/hexanes) to afford ***t*BuPyCCH** as a yellow liquid. Yield: 57%, 91 mg; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57 (t, J = 8 Hz, 1H), 7.33-7.28 (m, 2H), 3.10 (s, 1H), 1.36 (s, 9H) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 170.1, 141.2, 136.3, 124.8, 119.3, 83.8, 76.1, 37.7, 30.2 ppm; FT-IR (ranked intensity, cm^{-1}): 3296 (8), 2957 (4), 1566 (1), 1479 (11), 1441 (3), 1360 (9), 1247 (13), 1165 (7), 1144 (14), 1089 (15), 988 (12), 894 (10), 811 (2), 744 (6), 648 (5); HRMS (+ESI): calcd 160.1121 for $C_{11}H_{14}N$ $[M+H]^+$ found 160.1121.

To a THF (5 mL) solution of ***t*BuPyCCH** (80 mg, 0.50 mmol), *n*BuLi (2.5 M in hexanes, 0.20 mL, 0.50 mmol) was added at –78 ºC and stirred for 1 hour. A THF solution (2 mL) of chlorodimethylethylsilane (85 μL, 0.60 mmol) was added drop-wise over 2 min at –78 ºC, the cold bath removed, and stirred for 4 hours at 23 ºC. The mixture was quenched by the addition of water (5 mL). The reaction mixture was extracted with EtOAc (3 × 5 mL), dried over Na_2SO_4, and evaporated in vacuo. The crude product was purified by column chromatography on silica gel (eluent: 5% ethyl acetate/hexanes) to afford **A4** as a yellow liquid. Yield: 85%, 104.0 mg; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53 (t, J = 8 Hz, 1H), 7.28-7.26 (m, 2H), 1.36 (s, 9H), 1.06 (t, J = 8 Hz, 3H), 0.70 (q, *J* = 8 Hz, 2H), 0.24 (s, 6H) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 169.8, 142.1, 136.1, 125.1, 118.8, 105.4, 92.7, 37.7, 30.3, 8.1, 7.5, –2.2 ppm; $^{29}Si\{^1H\}$ NMR (119 MHz, $CDCl_3$): δ = –13.5 ppm; FT-IR (ranked intensity, cm^{-1}): 2956 (8), 1567 (3), 1441 (2), 1361 (15), 1249 (5), 1165 (13), 1013 (14), 960 (11), 918 (6), 827 (10), 809 (1), 778 (4), 743 (9), 710 (7), 640 (12); HRMS (+ESI): calcd 246.1673 for $C_{15}H_{24}NSi$ $[M+H]^+$ found 246.1667.

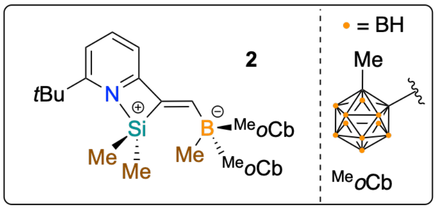
2.2 Reactions of ethynylsilanes with HB^{Me}*o*Cb$_2$

A benzene (1 mL) solution of ethynylsilane (**A1**-**A4**, 0.100 mmol) was added to a benzene solution (1 mL) of HB^{Me}*o*Cb$_2$ (32.6 mg, 0.100 mmol) at 23 ºC (70 ºC for **A3**) and stirred for 24 hours. The volume was reduced to ~0.5 mL under vacuum and 2 mL of *n*-pentane was added. The precipitate was collected by filtration through a small glass frit and the solids washed with *n*-pentane (2 × 1 mL). The residue was dried under vacuum to give **1**-**4** as solids.

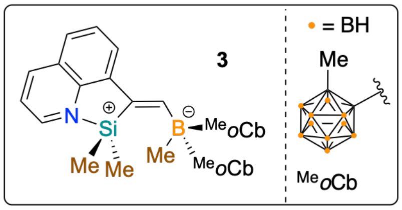


1: White solid; Yield: 92%, 46 mg; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.91 (d, *J* = 8 Hz, 1H), 8.17 (td, *J* = 8 and 2 Hz, 1H), 7.87 (dd, *J* = 8 and 4 Hz, 1H), 7.74-7.70 (m, 1H), 3.76 (br. s., 1H), 2.90-1.50 (m, 26H), 0.24 (s, 9H) ppm; $^1H\{^{11}B\}$ NMR (400 MHz, $CDCl_3$): δ = 8.91 (d, *J* = 4 Hz, 1H), 8.23-8.08 (td, *J* = 8 and 2 Hz, 1H), 7.86 (d, *J* = 8 Hz, 1H), 7.74-7.70 (m, 1H), 3.69 (s, 1H), 2.72 (s, 2H), 2.51 (s, 2H), 2.37 (s, 2H), 2.29 (s, 2H), 2.25 (s, 2H), 2.11 (s, 6H), 2.07 (s, 4H), 1.97 (s, 2H), 1.78 (s, 2H), 1.46 (s, 2H), 0.25 (s, 9H) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 151.9, 142.5, 141.0, 132.5, 123.8, 113.1, 98.6, 80.3, 26.3, –0.7 ppm; ^{11}B NMR (128 MHz, $CDCl_3$): δ = –0.2 (d, *J* = 147 Hz), –5.5 to –9.4 (m) ppm; $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ = –0.2 (s), –6.0 to

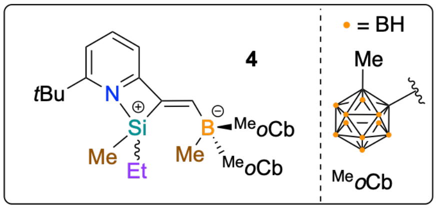
–9.1 (m) ppm; ^{29}Si{^{1}H} NMR (119 MHz, $CDCl_3$): δ = 14.7 ppm; FT-IR (ranked intensity, cm^{-1}): 2564 (2), 1610 (8), 1564 (11), 1488 (6), 1436 (10), 1250 (5), 1145 (9), 1103 (4), 843 (1), 1049 (12), 760 (3), 668 (14), 648 (7), 577 (13), 542 (15); HRMS(–ESI): calcd 502.5102 for $C_{16}H_{41}B_{21}NSi$ [M+H]$^{-}$ found 502.5147. Single crystals for X-ray diffraction studies were grown from a 1:1 dichloromethane/diethyl ether solution of **1** by vapor diffusion into *n*-pentane.



2: White solid; Yield: 88%, 49 mg. Compound **2** was also synthesized on a larger scale (236 mg, 85% yield) by reacting 0.50 mmol of **A2** and HB^{Me}*o*Cb_2 in C_6H_6 (5 mL) at 23 ºC for 24 hours. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19 (s, 1H), 8.14 (t, *J* = 8 Hz, 1H), 7.65 (d, *J* = 8 Hz, 1H), 7.47 (d, *J* = 8 Hz, 1H), 2.83-1.70 (m, 26H), 1.48 (s, 9H), 1.13 (s, 6H), 0.24 (s, 3H) ppm; ^{1}H{^{11}B} NMR (400 MHz, $CDCl_3$): δ = 8.19 (s, 1H), 8.14 (t, *J* = 8 Hz, 1H), 7.65 (d, *J* = 8 Hz, 1H), 7.47 (d, *J* = 8 Hz, 1H), 2.68 (s, 2H), 2.49 (s, 2H), 2.37 (s, 2H), 2.25 (s, 2H), 2.14 (s, 6H), 2.10 (s, 6H), 2.04 (br. s, 6H), 1.48 (s, 9H), 1.13 (s, 6H), 0.24 (s, 3H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 166.5, 145.9, 128.4, 127.0, 120.6, 114.7, 79.2, 37.3, 32.7, 30.4, 26.7, 2.5 ppm; ^{11}B NMR (128 MHz, $CDCl_3$): δ = –1.7 (d, *J* = 141 Hz), –5.4 to –9.3 (m) ppm; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ = –1.6 (s), –5.6 to –9.0 (m) ppm; ^{29}Si{^{1}H} NMR (119 MHz, $CDCl_3$): δ = 59.9 ppm; FT-IR (ranked intensity, cm^{-1}): 2564 (2), 1560 (4), 1551 (5), 1480 (15), 1456 (3), 1261 (6), 1179 (10), 1097 (12), 1046 (13), 941 (11), 865 (8), 816 (1), 733 (7), 688 (9), 431 (14); HRMS (+ESI): calcd 558.5728 for $C_{20}H_{49}B_{21}NSi$ [M+H]$^{+}$ found 558.5682. Single crystals for X-ray diffraction studies were grown by storing a benzene solution of **2** at 23 ºC.



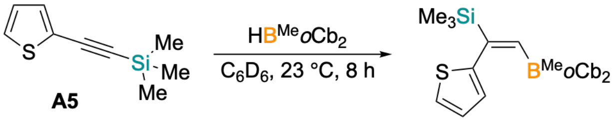
3: Yellow solid; Yield: 83%, 46 mg; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.90 (d, *J* = 8 Hz, 1H), 8.79 (d, *J* = 8 Hz, 1H), 8.46 (s, 1H), 8.25 (d, *J* = 4 Hz, 1H), 8.04-7.95 (m, 3H), 2.87-1.62 (m, 26H), 1.01 (s, 6H), 0.48 (s, 3H) ppm; ^{1}H{^{11}B} NMR (400 MHz, $CDCl_3$): δ = 8.90 (d, *J* = 8 Hz, 1H), 8.79 (d, *J* = 4 Hz, 1H), 8.46 (s, 1H), 8.25 (d, *J* = 4 Hz, 1H), 8.04-7.95 (m, 3H), 2.71 (s, 2H), 2.58 (s, 2H), 2.44 (s, 2H), 2.24 (s, 2H), 2.14 (s, 14H), 2.04 (s, 4H), 1.01 (s, 6H), 0.49 (s, 3H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 145.5, 143.4, 142.4, 132.6, 129.0, 128.5, 126.0, 124.4, 122.5, 119.8, 79.4, 26.9, 2.8 ppm; ^{11}B NMR (128 MHz, $CDCl_3$): δ = –1.6 (d, *J* = 146 Hz), –5.1 to –9.3 (m) ppm; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ = –1.7 (s), –5.5 to –9.9 (m) ppm; ^{29}Si{^{1}H} NMR (119 MHz, $CDCl_3$): δ = 29.5 ppm; FT-IR (ranked intensity, cm^{-1}): 3296 (8), 2957 (4), 1566 (1), 1479 (11), 1441 (3), 1360 (9), 1247 (13), 1165 (7), 1144 (14), 1089 (15), 988 (12), 894 (10), 811 (2), 744 (6), 648 (5); HRMS (–ESI): calcd 551.5180 for $C_{20}H_{42}B_{21}NSi$ $[M]^{-}$ found 551.5137. Single crystals for X-ray diffraction studies were grown from a chloroform solution of **3**.



4: White solid; Yield: 91%, 52 mg; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.21 (s, 1H), 8.14 (t, *J* = 8 Hz, 1H), 7.65 (dd, *J* = 8 and 1 Hz, 1H), 7.48 (dd, *J* = 8 and 1 Hz, 1H), 2.93-1.64 (m, 26H), 1.58-1.51 (m, 2H), 1.48 (s, 9H), 1.12 (s, 3H), 1.05 (t, *J* = 8 Hz, 3H), 0.24 (s, 3H) ppm; ^{1}H{^{11}B} NMR (400 MHz, $CDCl_3$): δ = 8.22 (s, 1H), 8.14 (t, *J* = 8 Hz, 1H), 7.65 (dd, *J* = 8 and 4 Hz, 1H), 7.48 (d,

J = 8 Hz, 1H), 2.80 (s, 1H), 2.60 (s, 1H), 2.50 (s, 2H), 2.39 (s, 2H), 2.25 (s, 2H), 2.13-2.05 (m, 14H), 2.03 (s, 4H), 1.57-1.52 (m, 2H), 1.49 (s, 9H), 1.12 (s, 3H), 1.05 (t, J = 8 Hz, 3H), 0.25 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 166.8, 166.2, 146.0, 125.9, 120.8, 114.5, 78.9, 77.5, 37.4, 30.4, 27.1, 26.7, 10.2, 6.4, 1.4 ppm; ^{11}B NMR (128 MHz, $CDCl_3$): δ = –1.6 (d, J = 114 Hz), –5.2 to –9.3 (m) ppm; $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ = –1.7 (s), –5.7 to –9.9 (m) ppm; $^{29}Si\{^1H\}$ NMR (119 MHz, $CDCl_3$): δ = 64.3 ppm; FT-IR (ranked intensity, cm^{-1}): 2955 (8), 2559 (1), 1601 (3), 1459 (9), 1383 (15), 1258 (5), 1181 (14), 1098 (7), 1045 (10), 954 (6), 811 (4), 734 (2), 651 (13), 487 (12), 425 (11); HRMS (–ESI): calcd 572.5885 for $C_{21}H_{51}B_{21}NSi$ $[M+H]^-$ found 572.5894. Single crystals for X-ray diffraction studies were grown from a dichloromethane solution of **4** by vapor diffusion into toluene.

2.3 Reaction of trimethyl(thiophen-2-ylethynyl)silane (A5) with $HB^{Me}oCb_2$



5, 95%

5: In an NMR tube, a benzene-d^6 (0.25 mL) solution of **A5** (0.050 mmol) was added to a benzene-d^6 solution (0.25 mL) of $HB^{Me}oCb_2$ (16.3 mg, 0.050 mmol) at 23 ºC and monitored by ^1H NMR spectroscopy over an 8-hour period. The 1,1-hydroboration product **5** was formed within 10 minutes and no change was observed after 8 hours. The volatiles were removed under vacuum and **5** was extracted with 1 mL of *n*-pentane. The volatiles were removed under vacuum to give **5** as thick yellow liquid. Yield: 95%, 24 mg; ^1H NMR (400 MHz, $CDCl_3$): δ = 6.70-6.63 (m, 2H), 6.59-6.56 (m, 1H), 6.42 (s, 1H), 3.35-2.11 (m, 20H), 1.62 (s, 6H), 0.02 (s, 8H) ppm; $^1H\{^{11}B\}$ NMR (400 MHz, $CDCl_3$): δ = 6.70-6.63 (m, 2H), 6.59-6.56 (m, 1H), 6.42 (s, 1H), 3.26 (s, 2H), 2.95-2.88 (m, 4H), 2.81 (s, 4H), 2.66 (s, 4H), 2.46 (s, 4H), 1.99 (s, 2H), 1.63 (s, 6H), 0.03 (s, 9H) ppm;

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 157. 6, 152.1, 146.5, 129.6, 127.2, 126.7, 80.1, 26.1, –1.5 ppm; ^{11}B NMR (128 MHz, $CDCl_3$): δ = 69.7 (br. s), 3.77 (d, J = 142 Hz), –1.2 to –19.4 (m) ppm; $^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$): δ = 69.7 (br. s), 3.77 (s), –1.2 to –19.4 (m) ppm; FT-IR (ranked intensity, cm^{-1}): 2952 (9), 2570 (1), 1448 (6), 1385 (15), 1248 (4), 1220 (13), 1053 (8), 1107 (5), 1064 (11), 836 (2), 732 (7), 704 (3), 499 (10), 471 (14), 416 (12); HRMS (–ESI): calcd 507.4714 for $C_{15}H_{39}B_{21}SSi$ $[M+H]^{-}$ found 507.4720.

2.4 Reaction of 2 with methanol to generate 6

To a stirred CH_2Cl_2 solution (2 mL) of **1** (0.10 mmol, 56 mg) MeOH (0.10 mmol, 4.0 μL) was added at 23 ºC and stirred for 10 minutes. The volatiles were removed under vacuum and the residue washed with *n*-pentane (2 × 1 mL). The white solid was dried under vacuum to give **6**. Yield: 88%, 52 mg; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.75 (br. s, 1H), 8.23 (t, J = 8 Hz, 1H), 7.85 (s, 1H), 7.81 (d, J = 8 Hz, 1H), 7.54 (d, J = 8 Hz, 1H), 3.46 (s, 3H), 2.78-1.72 (m, 26H), 1.54 (s, 9H), 0.57 (s, 6H), 0.32 (s, 3H) ppm; $^{1}H\{^{11}B\}$ NMR (400 MHz, $CDCl_3$): δ = 12.72 (br. s, 1H), 8.23 (t, J = 8 Hz, 1H), 7.84 (s, 1H), 7.81 (d, J = 8 Hz, 1H), 7.54 (d, J = 8 Hz, 1H), 3.46 (s, 3H), 2.77 (br. s, 2H), 2.38 (br. s, 4H), 2.26 (br. s, 2H), 2.15 (br. s, 8H), 2.07 (br. s, 10H), 1.54 (s, 9H), 0.58 (s, 6H), 0.33 (s, 3H) ppm; $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 163.8, 160.6, 145.3, 127.4, 124.5, 119.0, 79.8, 50.7, 36.5, 29.4, 26.5, 1.5 ppm; ^{11}B NMR (128 MHz, $CDCl_3$): δ = –1.6 (d, J = 119 Hz), –5.5 (d, J = 149 Hz), –8.7 (br. s.) ppm; $^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$): δ = –1.6 (br. s), –5.5 (br. s), –9.0 (br. s) ppm; $^{29}Si\{^{1}H\}$ NMR (119 MHz, $CDCl_3$): δ = 14.1 ppm; FT-IR (ranked intensity, cm^{-1}): 2941 (14), 2561 (1), 1613 (2), 1413 (12), 1257 (5), 1073 (4), 953 (9), 861 (12), 845 (11), 822 (7), 787 (3), 734 (6), 653 (15), 545 (10), 431 (8); HRMS (–ESI): calcd 588.5834 for $C_{21}H_{51}B_{21}NOSi$ $[M]^-$ found 588.5850. Single crystals for X-ray diffraction studies were grown from a 5:1 dichloromethane/*n*-pentane solution of **6** by vapor diffusion into toluene.

3. X-ray Crystallographic Data

Table S1: X-ray crystallographic details for **1**, **2**, **3**, **3′**, **4**, and **6**.

Compound	**1**	**2**	**3**	**3′**	**4**	**6**
CCDC	2523192	2523193	2523194	2523195	2523196	2523197
Empirical Formula	$C_{16}H_{40}B_{21}NSi$	$C_{32}H_{60}B_{21}NSi$	$C_{21}H_{43}B_{21}Cl_3NSi$	$C_{20}H_{42}B_{21}NSi$	$C_{21}H_{50}B_{21}NSi$	$C_{21}H_{52}B_{21}NOSi$
FW (g/mol)	501.59	713.91	671.01	551.64	571.72	589.73
Crystal System	monoclinic	triclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space Group	I2/a	*P–1*	$P2_1/c$	$P2_1/c$	*Cc*	$P2_1/c$
a (Å)	14.9895(2)	11.0604(8)	10.4054(16)	10.7274(3)	12.6734(7)	15.1522(2)
b (Å)	13.4010(2)	13.5354(11)	16.245(3)	28.5734(9)	22.6482(12)	16.8289(2)
c (Å)	33.0166(6)	15.5066(13)	21.694(3)	11.7289(4)	11.8929(6)	15.4035(3)
α (deg)	90	107.912(3)	90	90	90	90
β (deg)	96.005(2)	93.138(3)	100.359(5)	114.5888(1)	102.483(2)	113.168(2)
γ (deg)	90	100.623(3)	90	90	90	90
V (Å^3)	6595.79(18)	2155.6(3)	3607.3(10)	3269.13(18)	3332.9(3)	3611.05(11)
Z	8	2	4	4	4	4
D_c (g cm^{-3})	1.010	1.100	1.236	1.121	1.139	1.094
λ (Å)	1.54184	0.71073	0.71073	0.71073	0.71073	1.54184
Temp (K)	150	150	150	150	150	150
R1 [I>2(σ) I][a]	0.0496	0.0608	0.0595	0.0522	0.0519	0.0520
wR2 (F^2)[a]	0.1479	0.1708	0.1452	0.1192	0.1420	0.1526
GOF (S)[a]	1.113	1.047	1.058	1.112	1.056	1.094

[a] $R1(F[I > 2(I)]) = \sum\|F_o| - |F_c\|/ \sum |F_o|$; $wR2(F^2[\text{all data}]) = \{[w(F_o^2 - F_c^2)^2]/[w(F_o^2)^2]\}^{1/2}$; $S(\text{all data}) = [w(F_o^2 - F_c^2)^2 /(n - p)]^{1/2}$ (n = no. of data; p = no. of parameters varied; $w = 1/\sigma^2 (F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$ and a and b are constants suggested by the refinement program.

4. NMR and IR Spectra

Figure S1: ^{1}H NMR spectrum of **A2** in CDCl$_3$ (400 MHz)

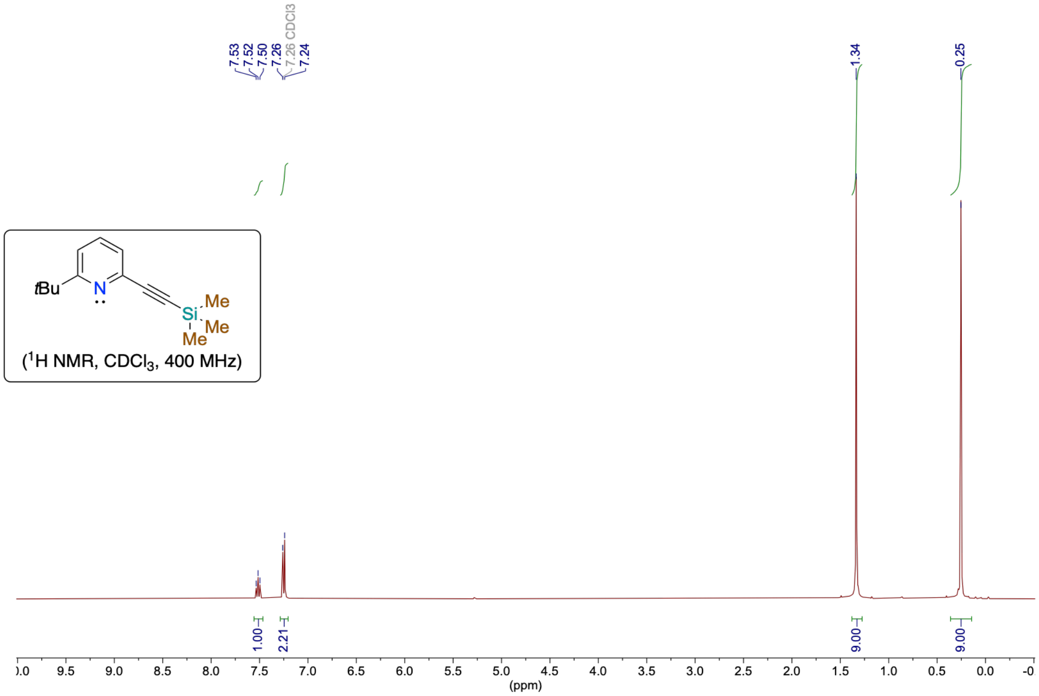


Figure S2: ^{13}C{^{1}H} NMR spectrum of **A2** in CDCl$_3$ (101 MHz)

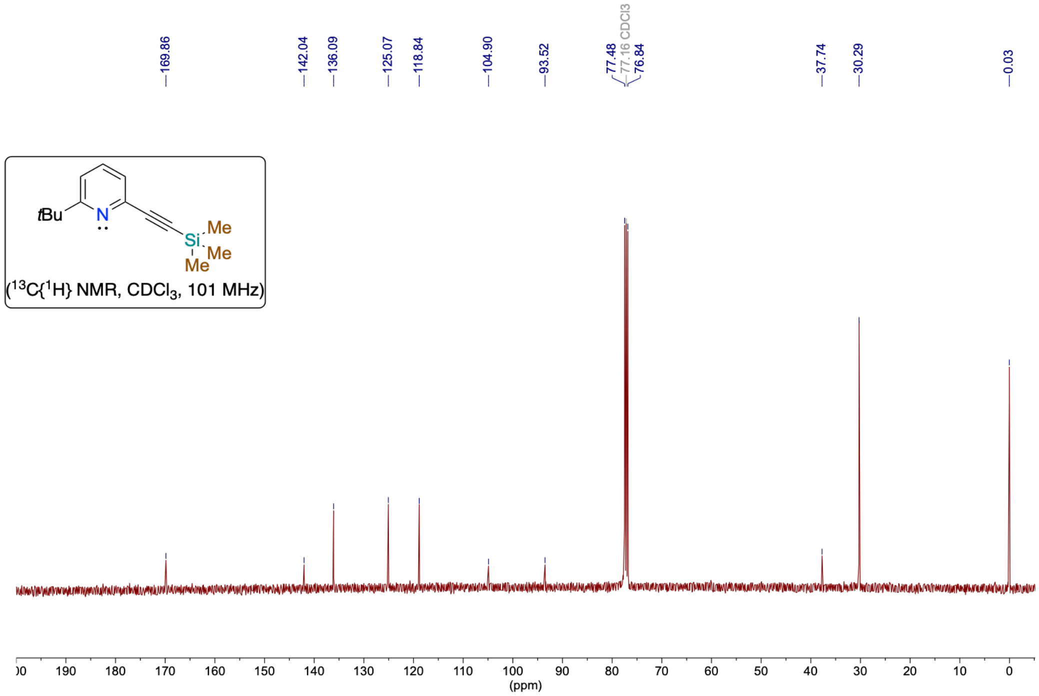


Figure S3: $^{29}Si\{^{1}H\}$ NMR spectrum of **A2** in $CDCl_3$ (119 MHz)

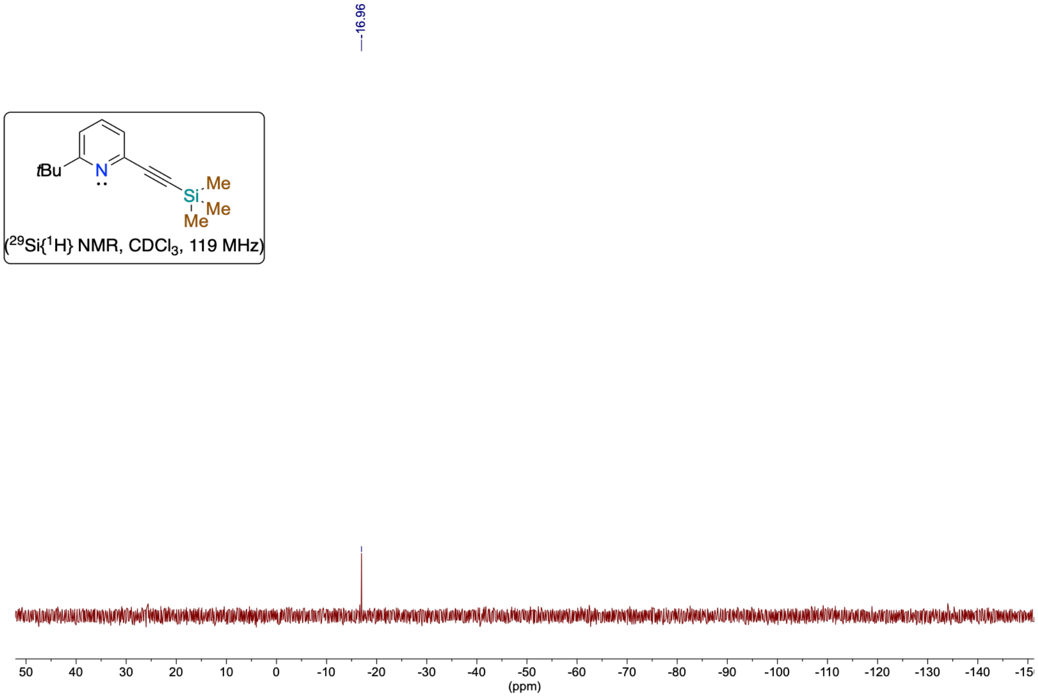


Figure S4: FT-IR spectrum of **A2**

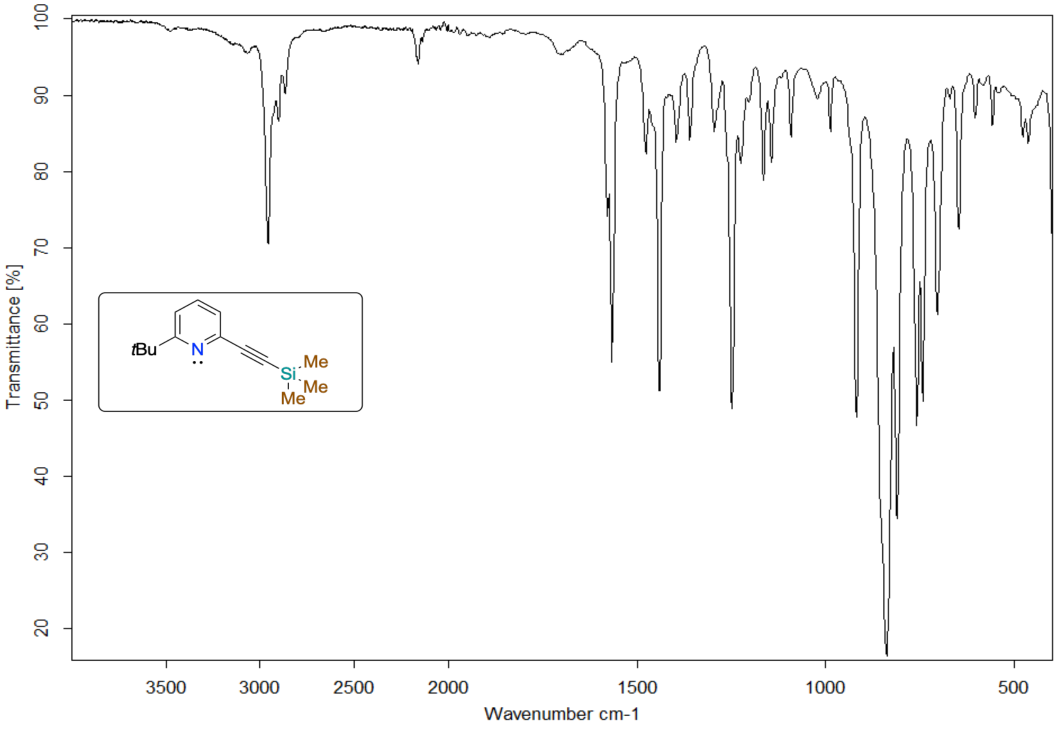


Figure S5: ^{1}H NMR spectrum of **A3** in CDCl$_3$ (400 MHz)

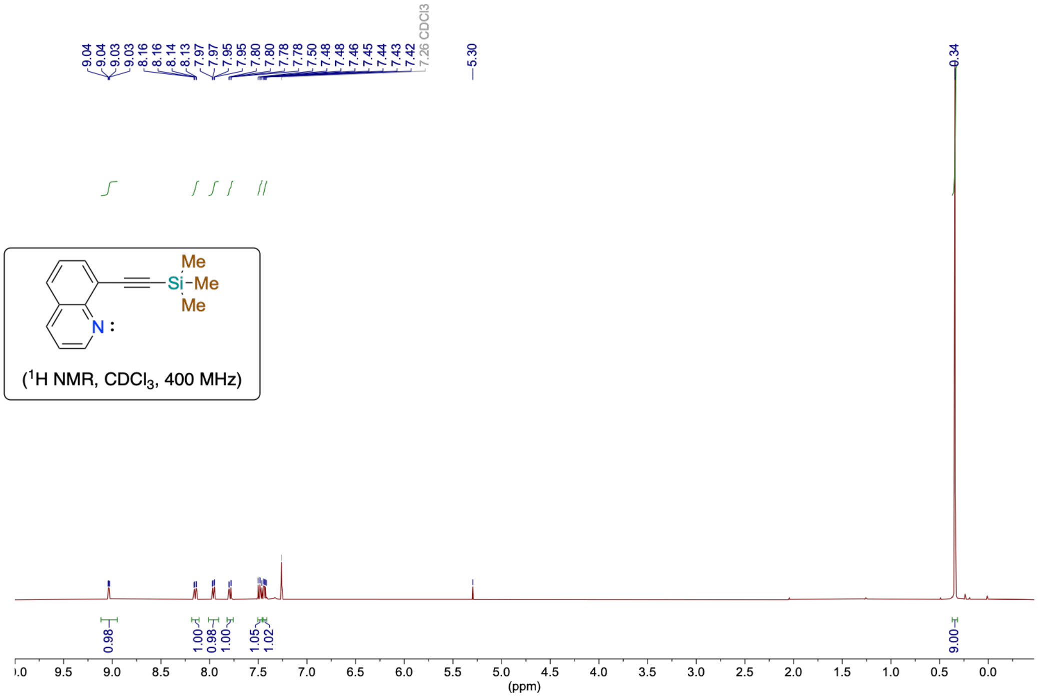


Figure S6: ^{13}C{^{1}H} NMR spectrum of **A3** in CDCl$_3$ (101 MHz)

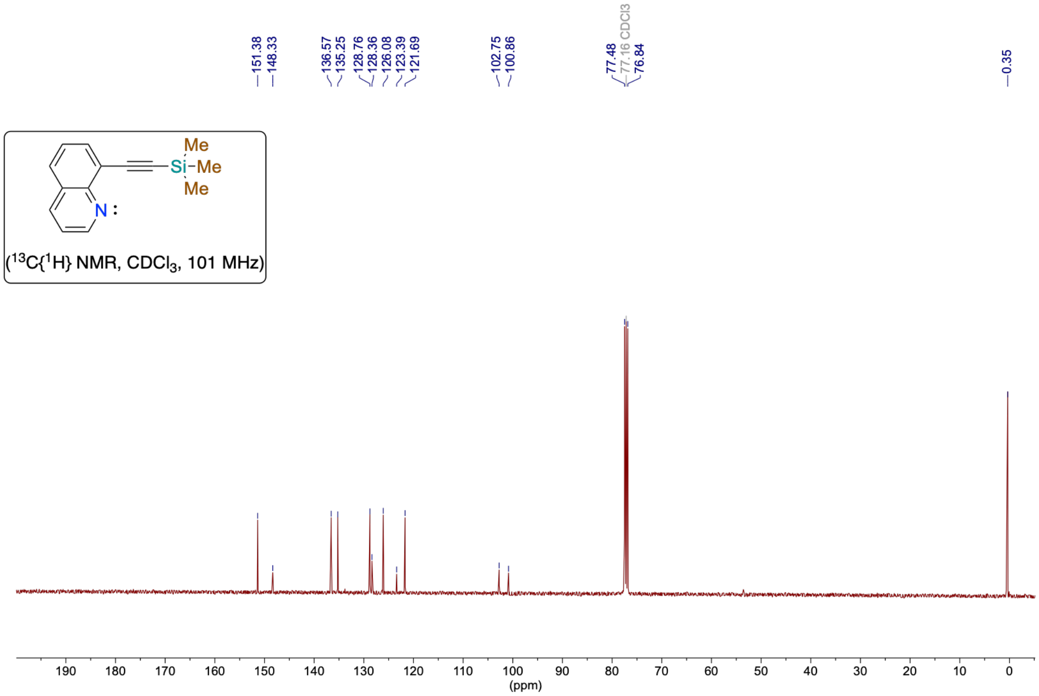


Figure S7: ^{29}Si{^{1}H} NMR spectrum of **A3** in CDCl$_3$ (119 MHz)

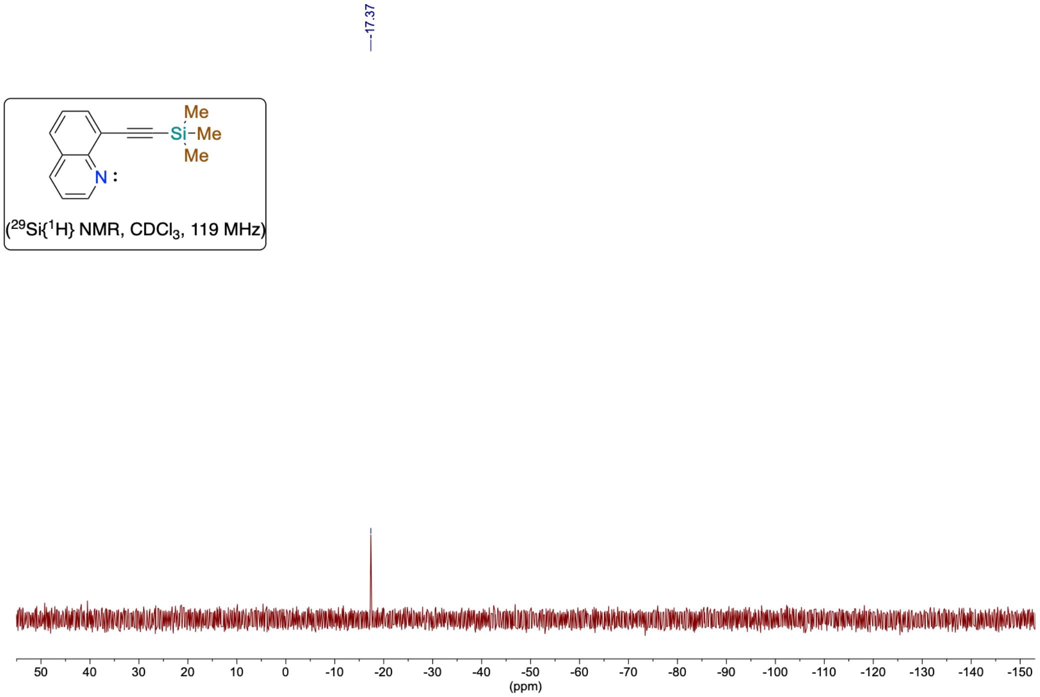


Figure S8: FT-IR spectrum of **A3**

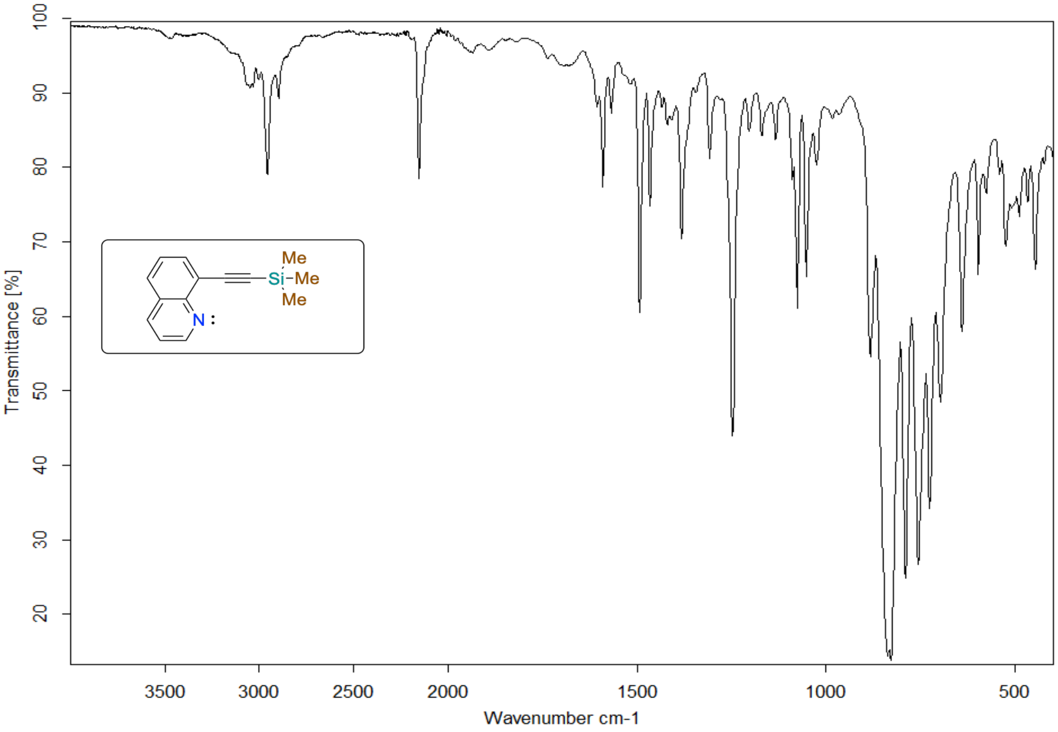


Figure S9: ^{1}H NMR spectrum of ***t*BuPyCCH** in $CDCl_3$ (400 MHz) [*hexanes]

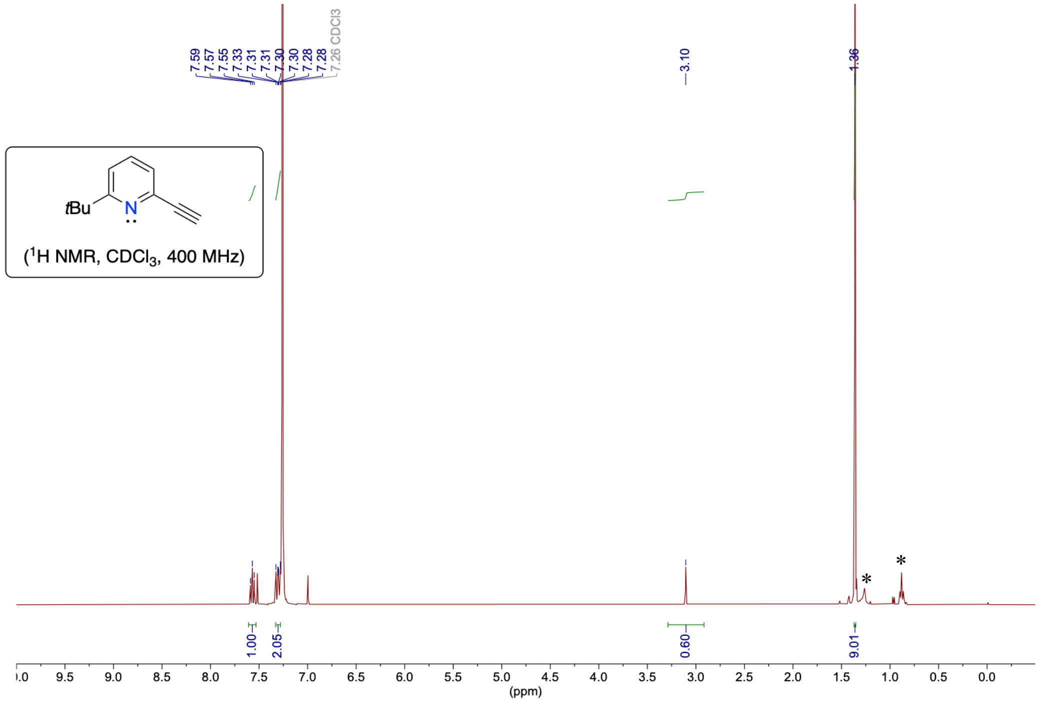


Figure S10: $^{13}C\{^{1}H\}$ NMR spectrum of ***t*BuPyCCH** in $CDCl_3$ (101 MHz) [*hexanes]

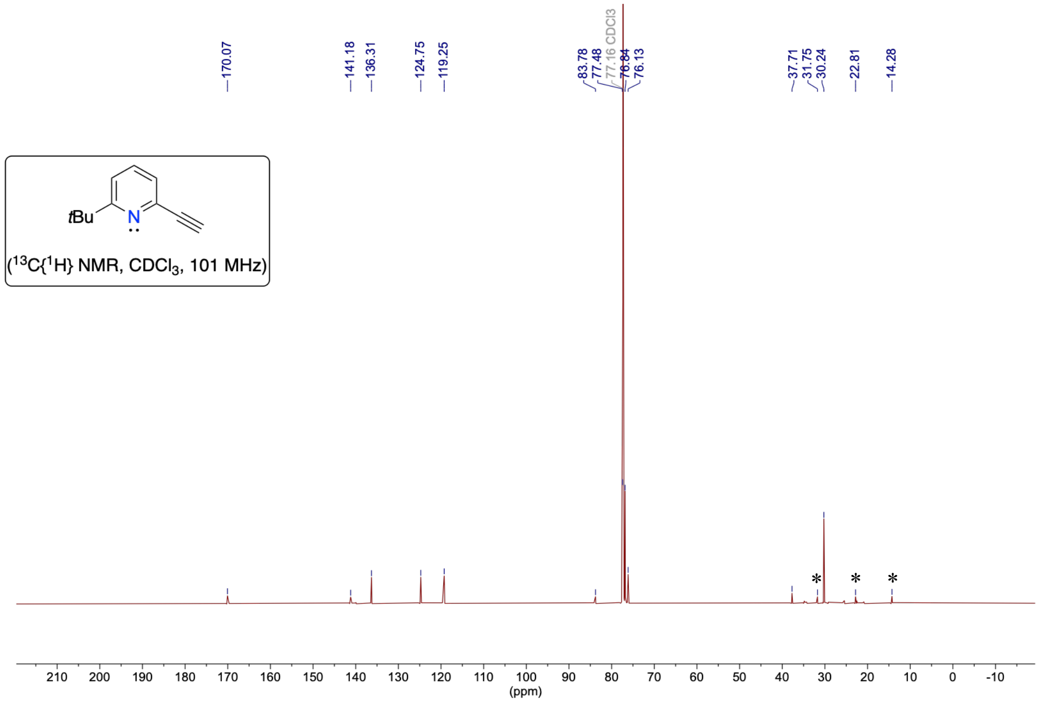


Figure S11: FT-IR spectrum of ***t*BuPyCCH**

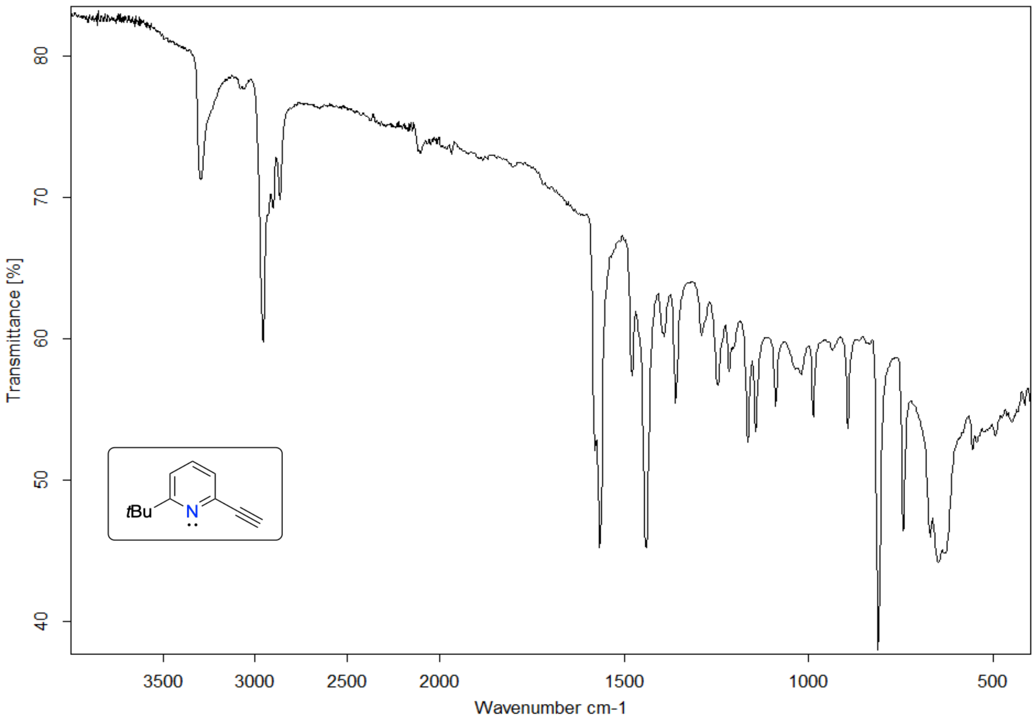


Figure S12: ^{1}H NMR spectrum of **A4** in CDCl$_3$ (400 MHz) [*hexanes]

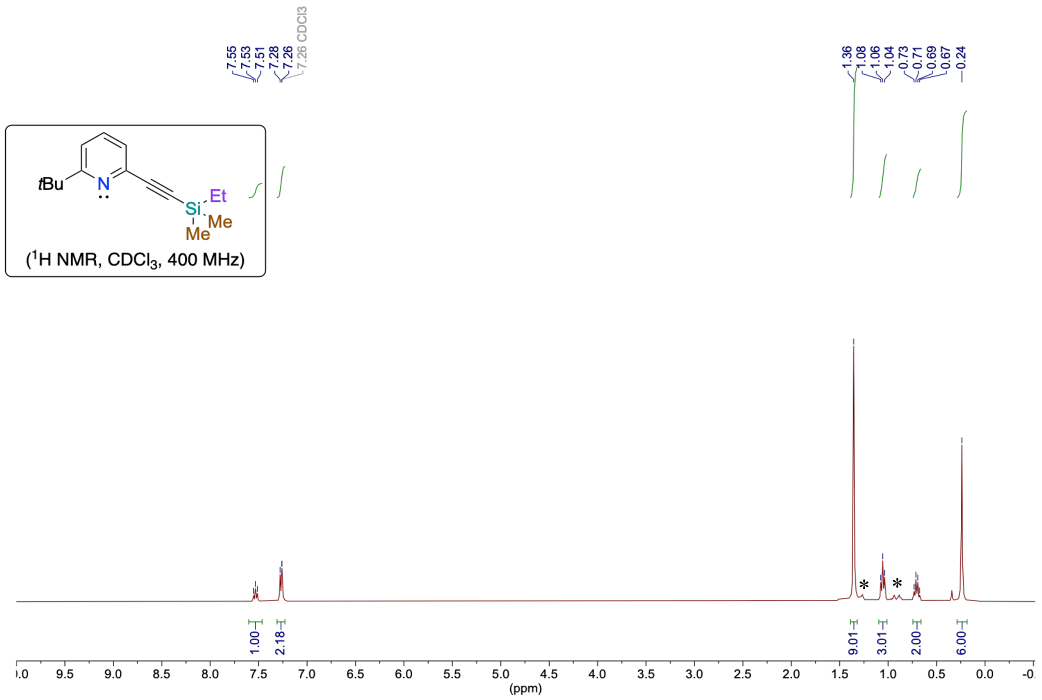


Figure S13: $^{13}C\{^1H\}$ NMR spectrum of **A4** in $CDCl_3$ (101 MHz) [*hexanes]

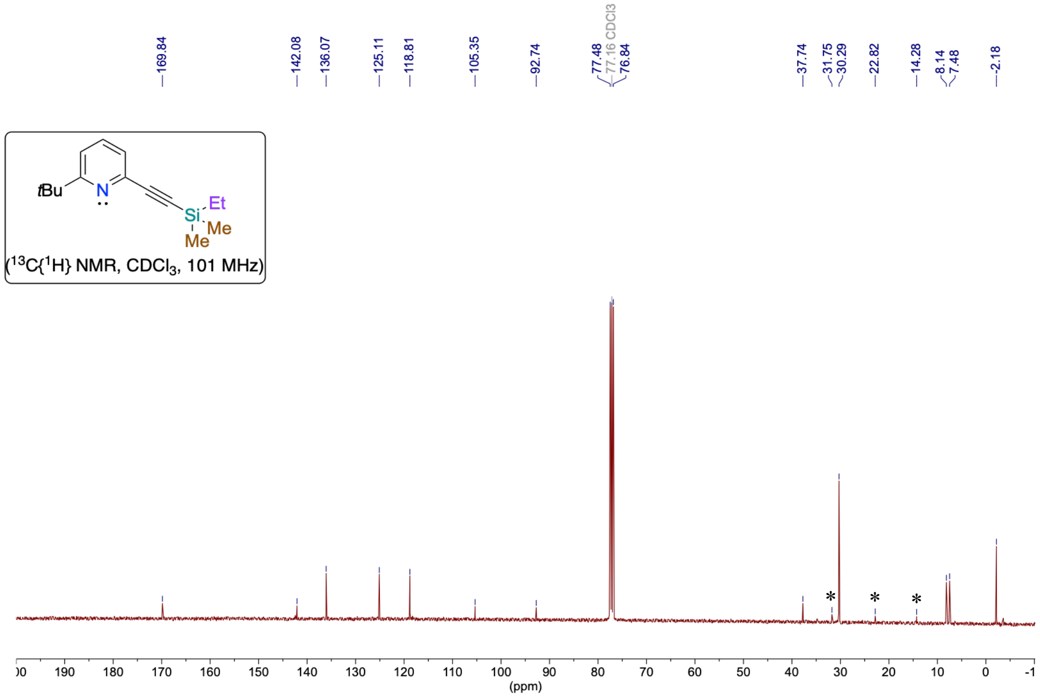


Figure S14: $^{29}Si\{^1H\}$ NMR spectrum of **A4** in $CDCl_3$ (119 MHz)

*

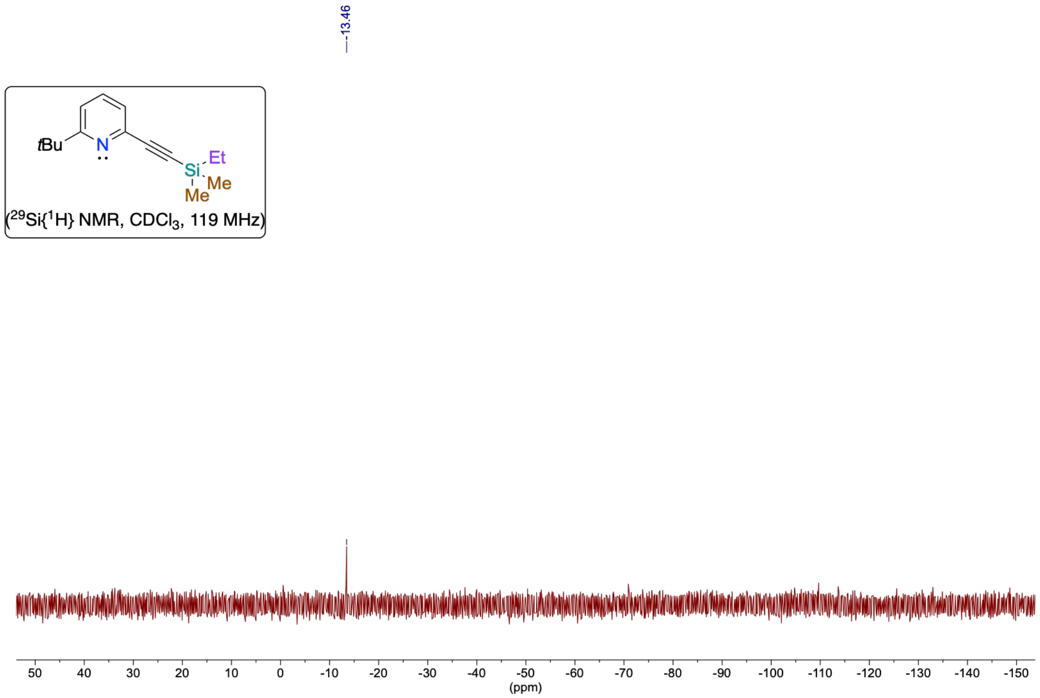


Figure S15: FT-IR spectrum of **A4**

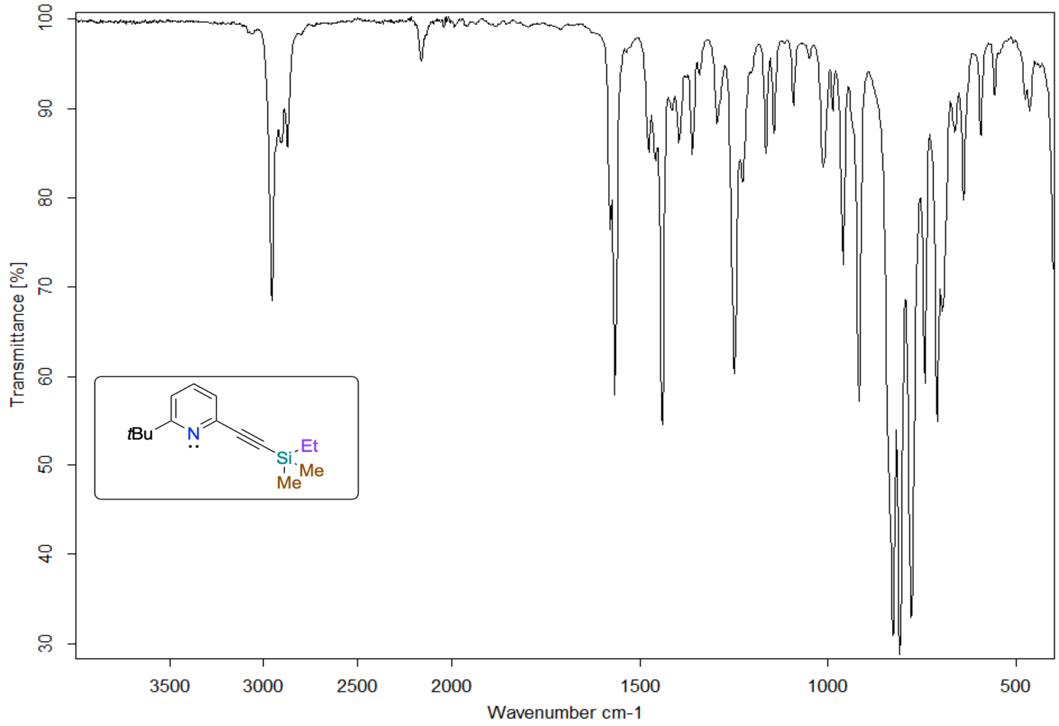


Figure S16: ^{1}H NMR spectrum of **1** in $CDCl_3$ (400 MHz)

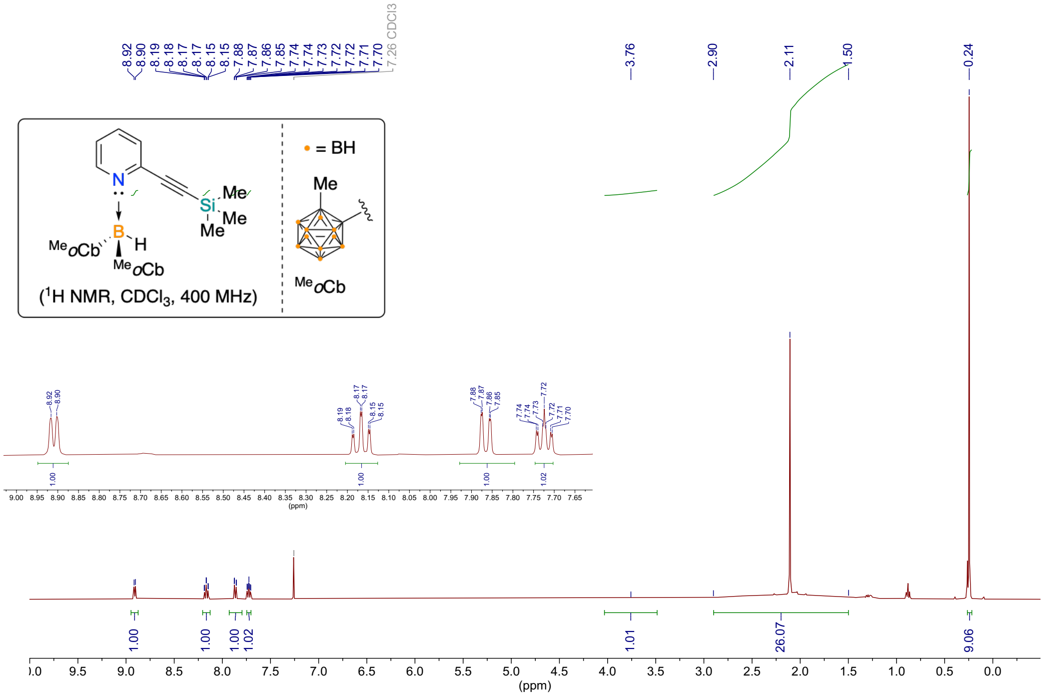


Figure S17: $^1H\{^{11}B\}$ NMR spectrum of **1** in $CDCl_3$ (400 MHz)

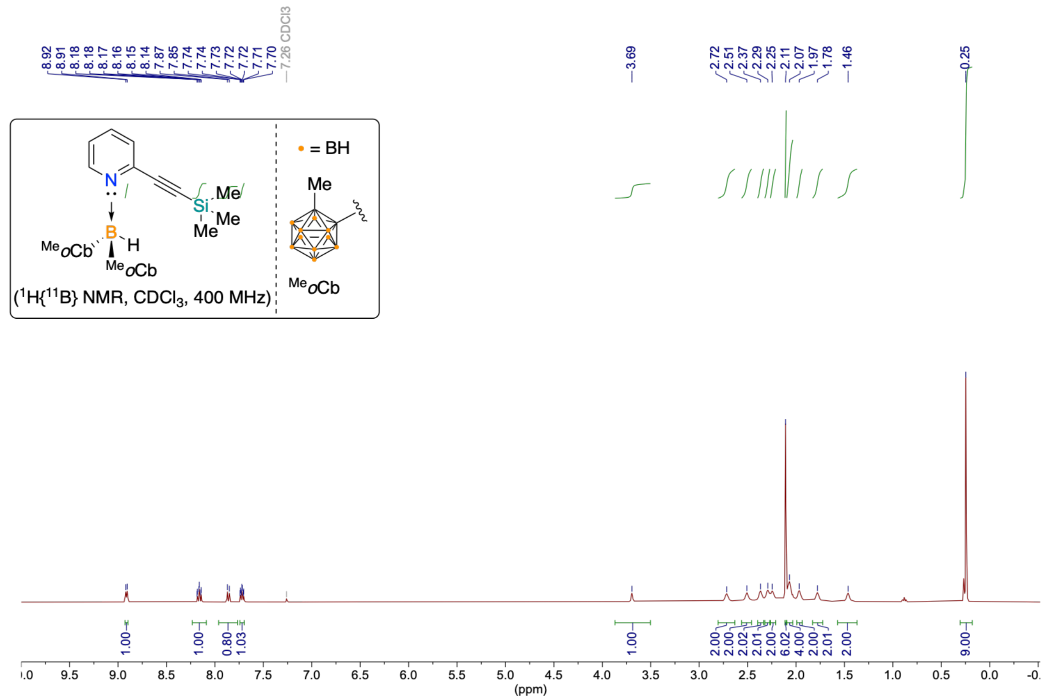


Figure S18: $^{13}C\{^1H\}$ NMR spectrum of **1** in $CDCl_3$ (101 MHz) [* *n*-pentane]

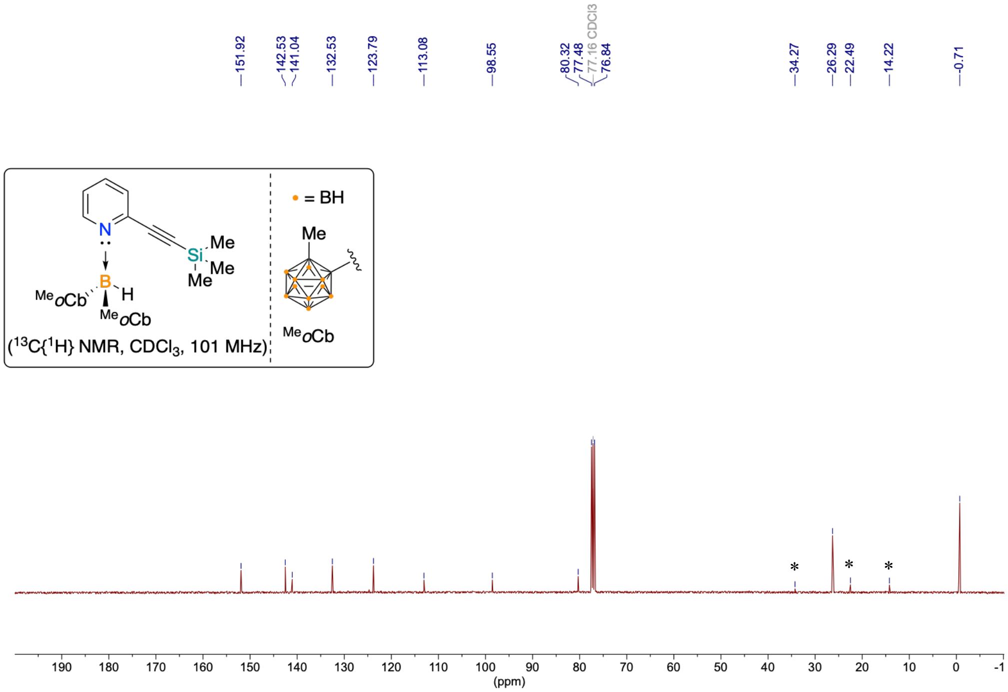


Figure S19: ^{11}B NMR spectrum of **1** in $CDCl_3$ (128 MHz)

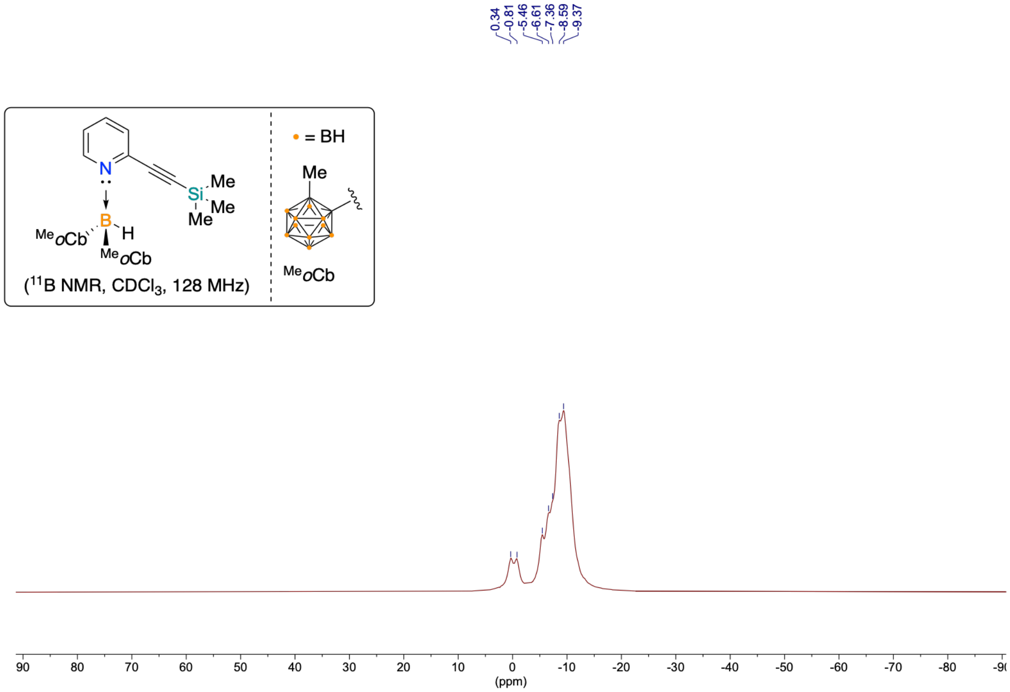


Figure S20: ^{11}B{^{1}H} NMR spectrum of **1** in $CDCl_3$ (128 MHz)

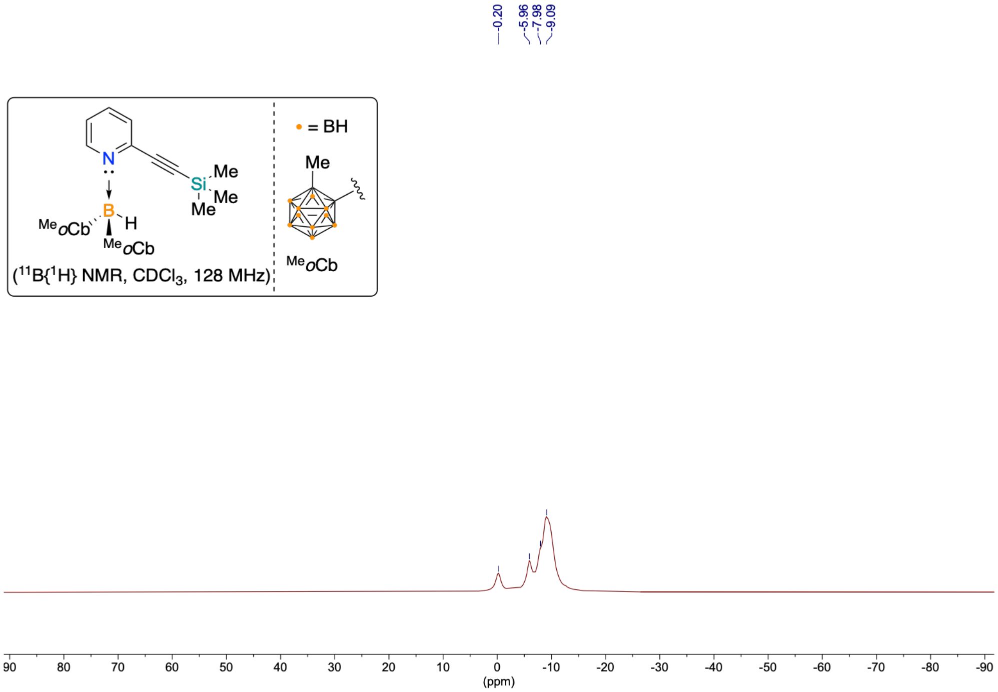


Figure S21: ^{29}Si{^{1}H} NMR spectrum of **1** in $CDCl_3$ (119 MHz)

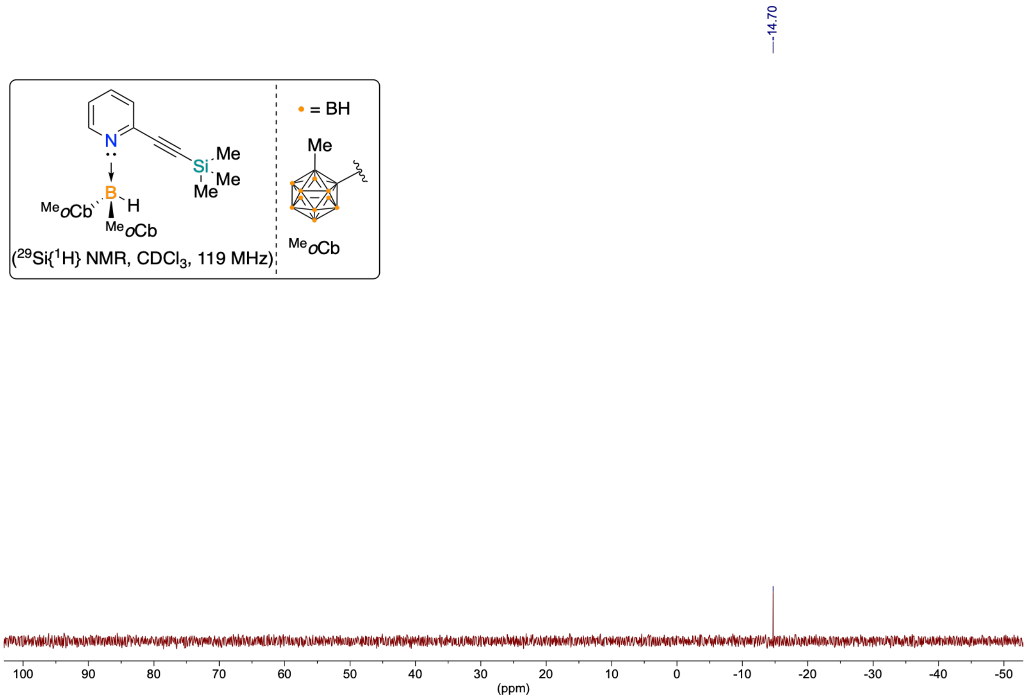


Figure S22: FT-IR spectrum of **1**

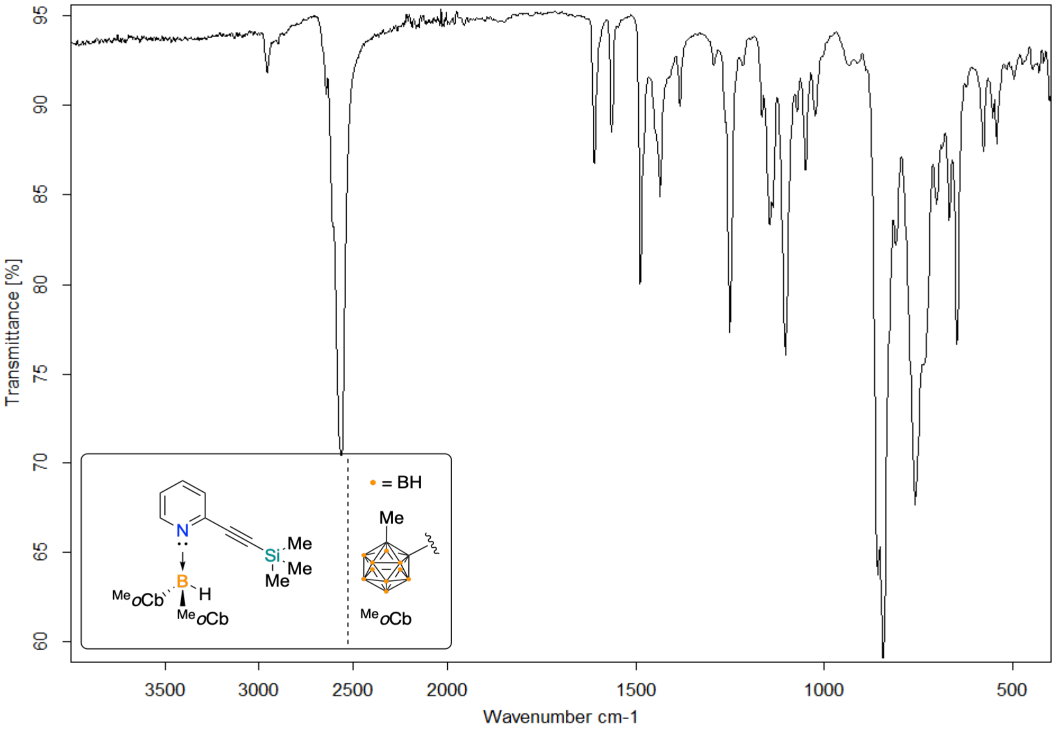


Figure S23: ^{1}H NMR spectrum of **2** in CDCl$_3$ (400 MHz)

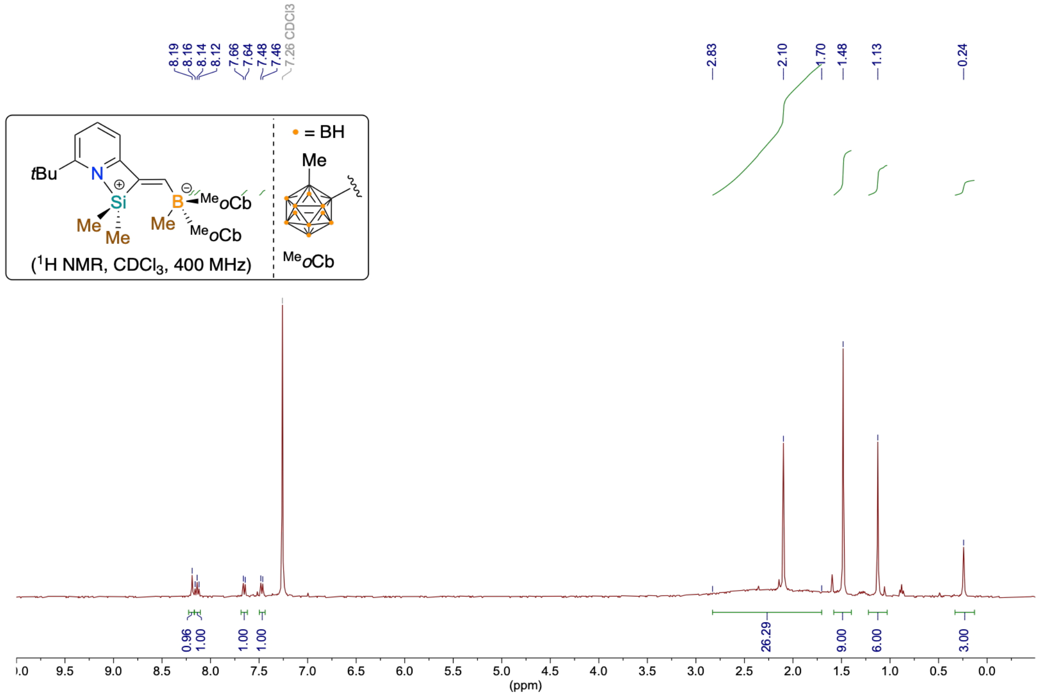


Figure S24: ^{1}H{^{11}B} NMR spectrum of **2** in CDCl$_3$ (400 MHz)

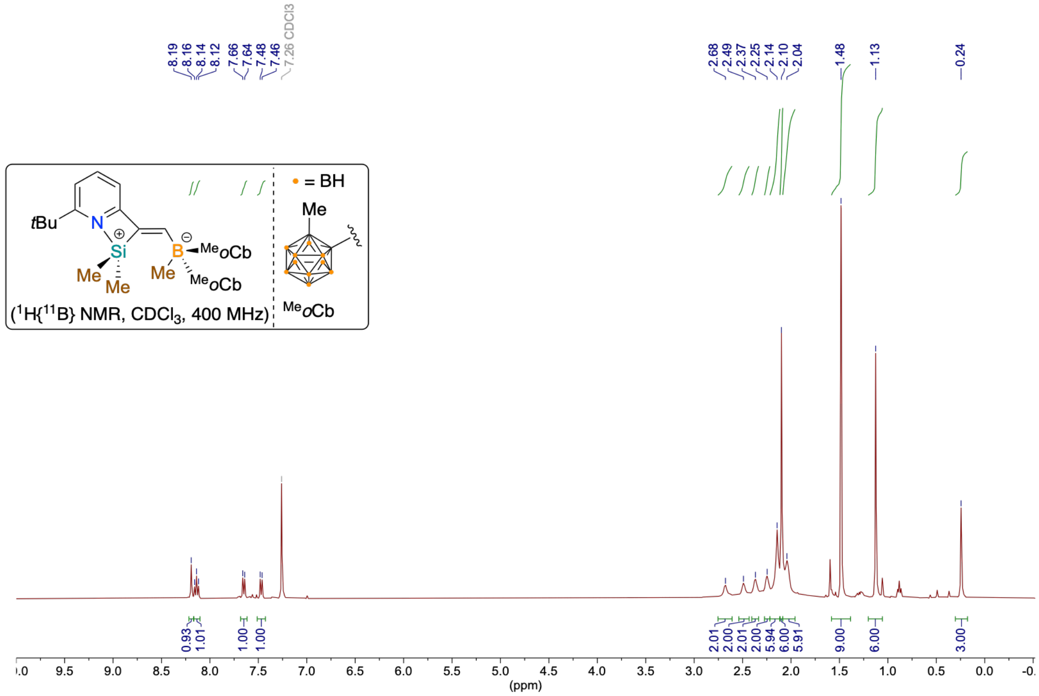


Figure S25: $^{13}C\{^1H\}$ NMR spectrum of **2** in $CDCl_3$ (101 MHz) [**n*-pentane]

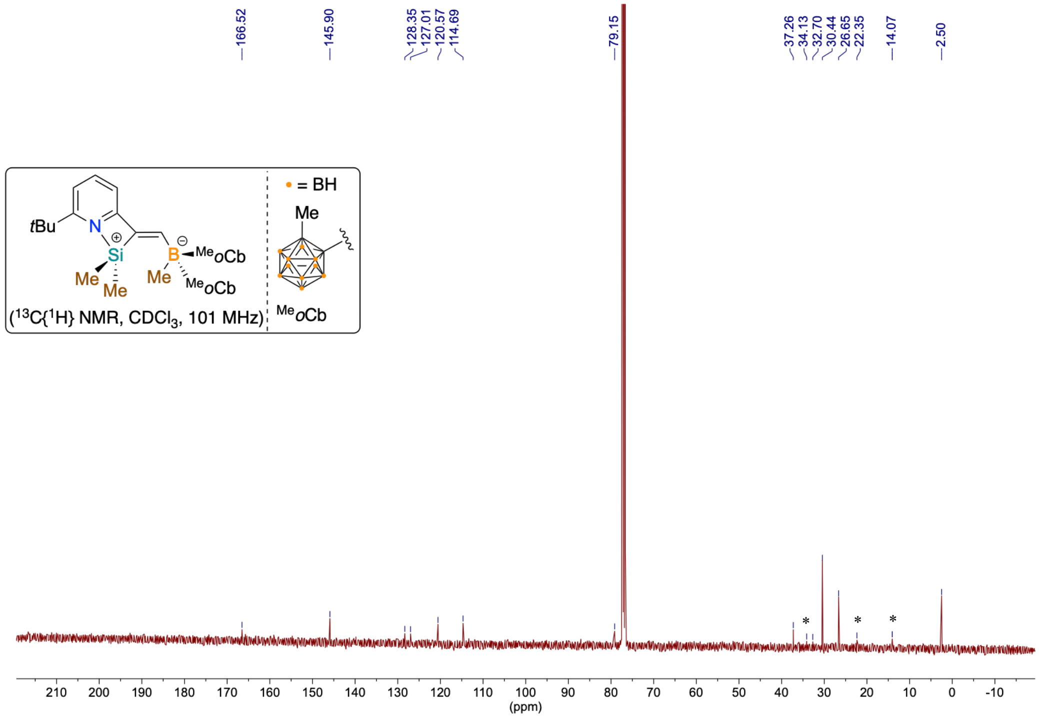


Figure S26: ^1H-$^{13}C\{^1H\}$ HSQC spectrum of **2** in $CDCl_3$ (400 MHz)

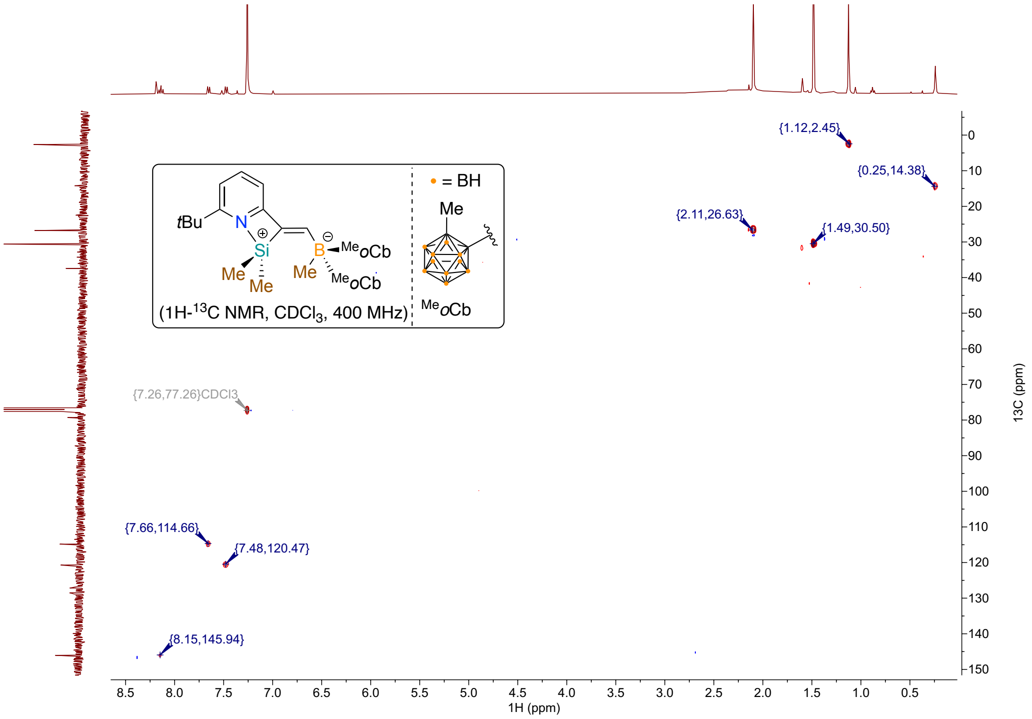


Figure S27: ^{11}B NMR spectrum of **2** in CDCl$_3$ (128 MHz)

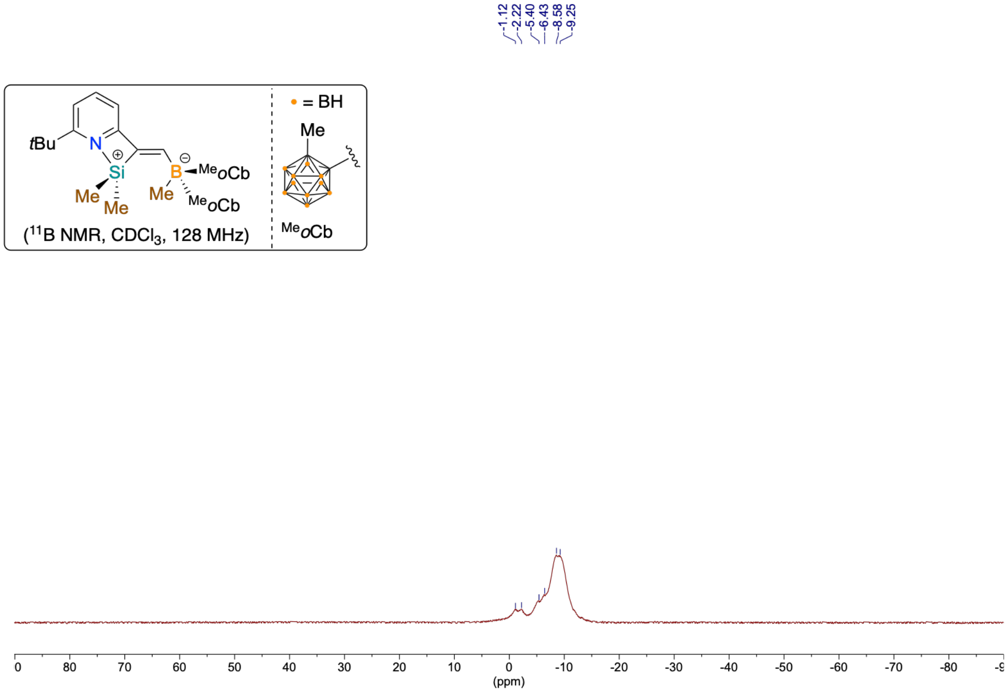


Figure S28: ^{11}B{^{1}H} NMR spectrum of **2** in CDCl$_3$ (128 MHz)

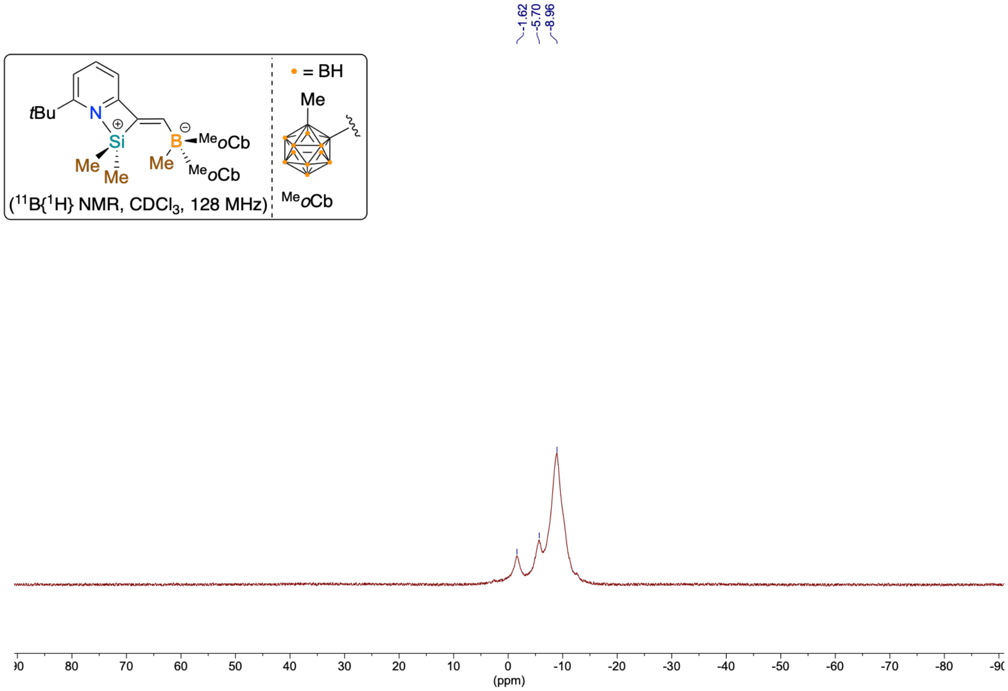


Figure S29: ^{29}Si{^{1}H} NMR spectrum of **2** in CDCl$_3$ (119 MHz)

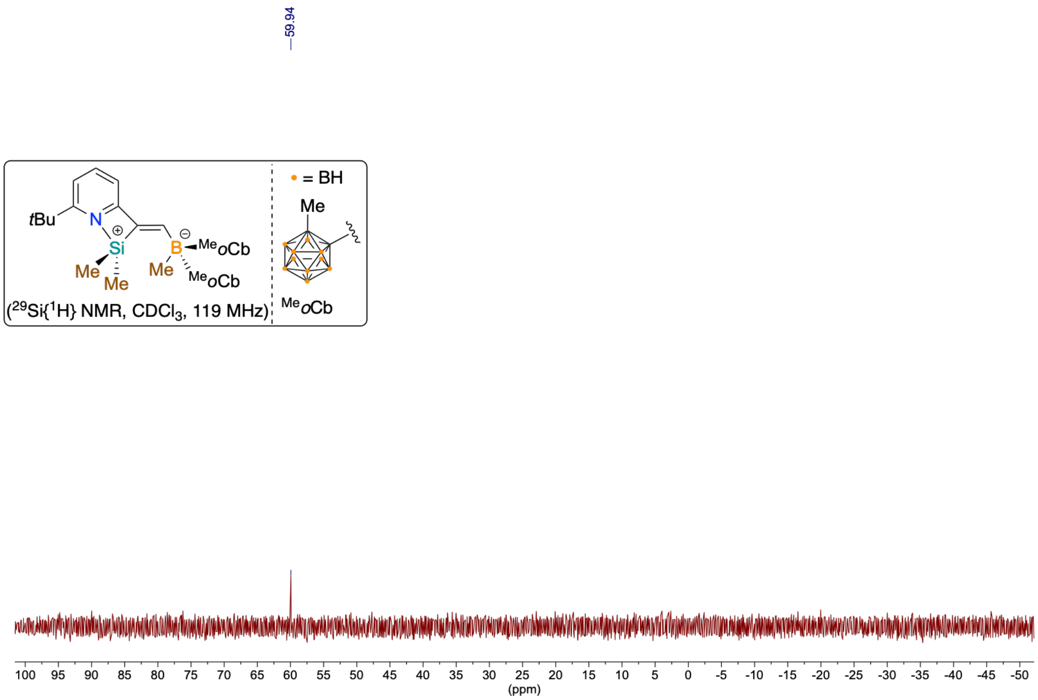


Figure S30: FT-IR spectrum of **2**

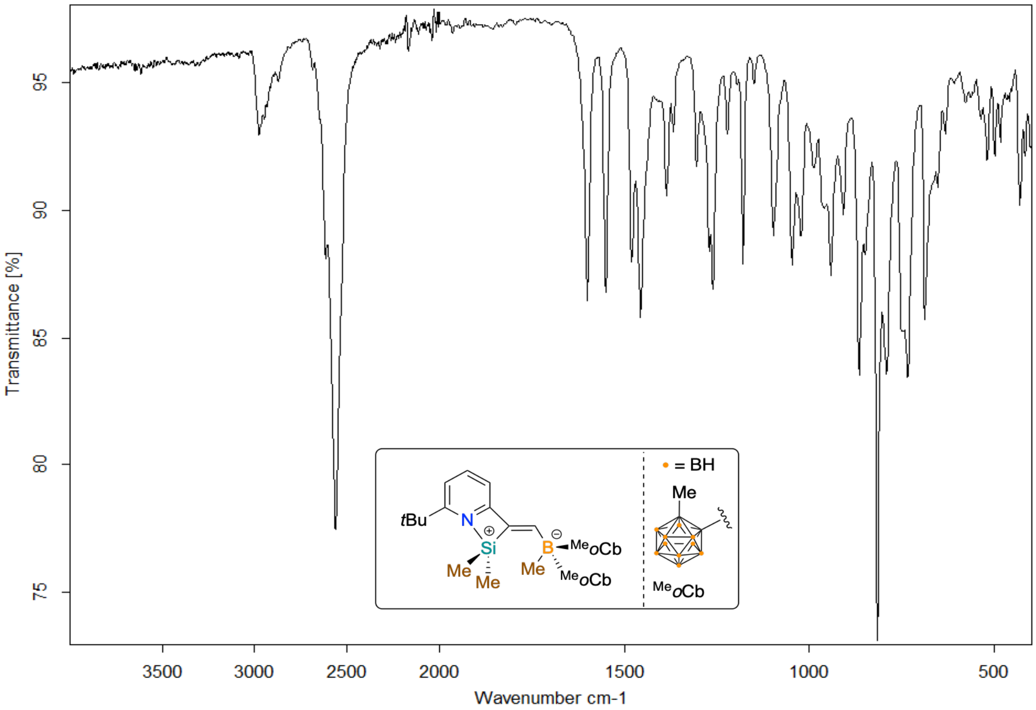


Figure S31: ^{1}H NMR spectrum of **3** in CDCl$_3$ (400 MHz) [*benzene]

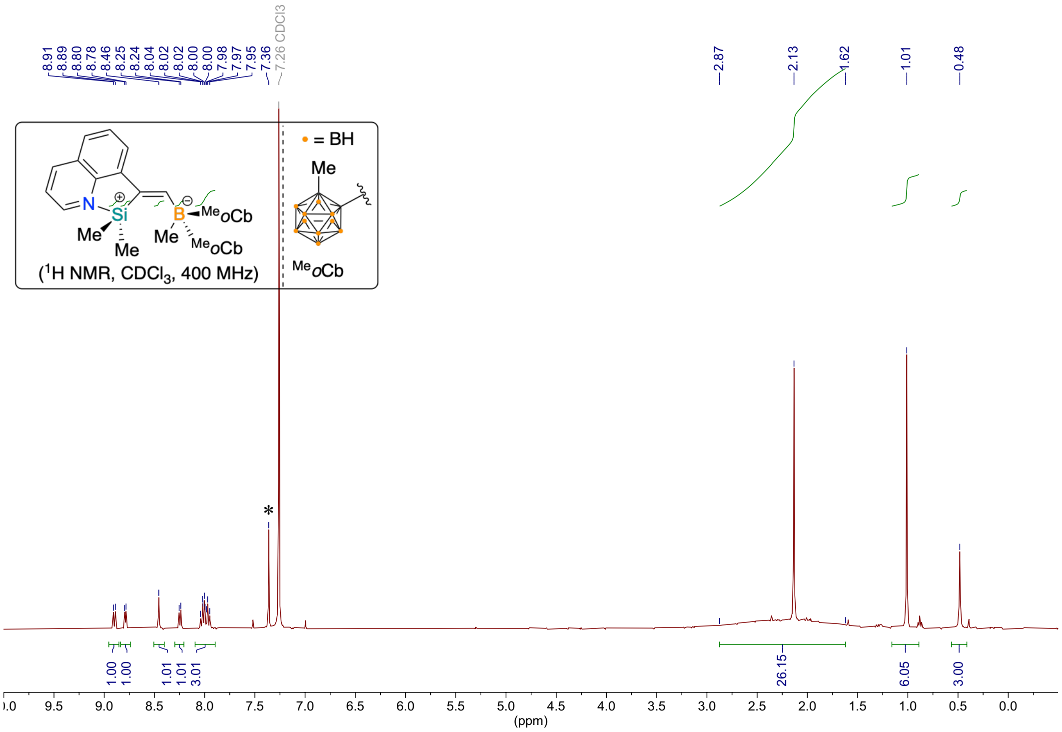


Figure S32: ^{1}H{^{11}B} NMR spectrum of **3** in CDCl$_3$ (400 MHz) [*benzene]

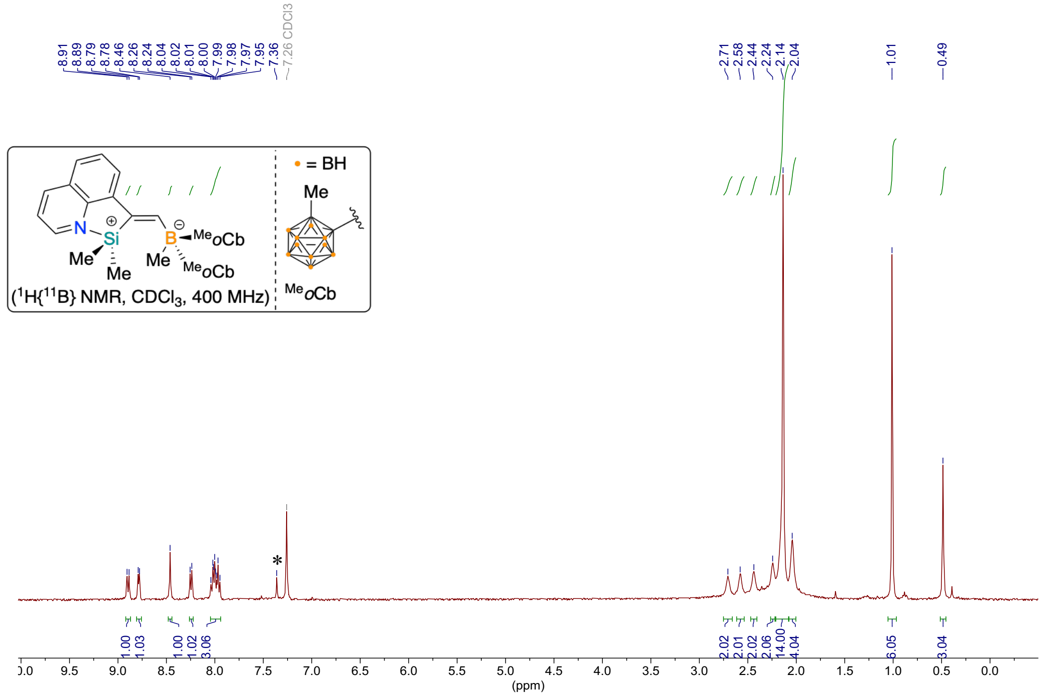


Figure S33: $^{13}C\{^{1}H\}$ NMR spectrum of **3** in $CDCl_3$ (101 MHz)

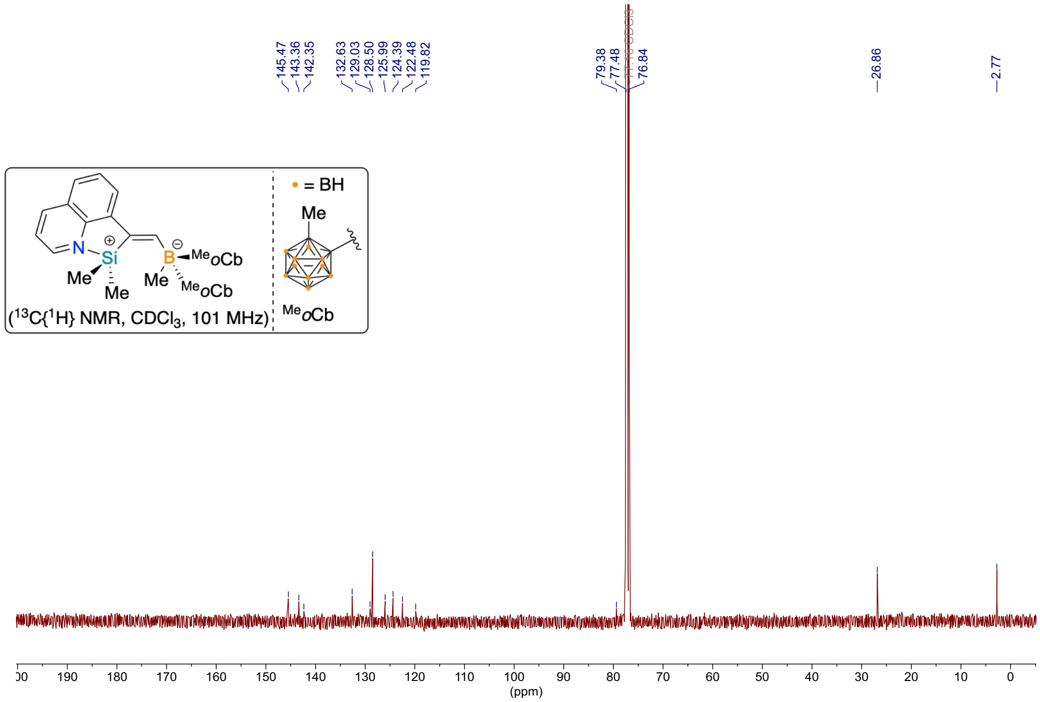


Figure S34: ^{1}H-$^{13}C\{^{1}H\}$ HSQC spectrum of **3** in $CDCl_3$ (400 MHz)

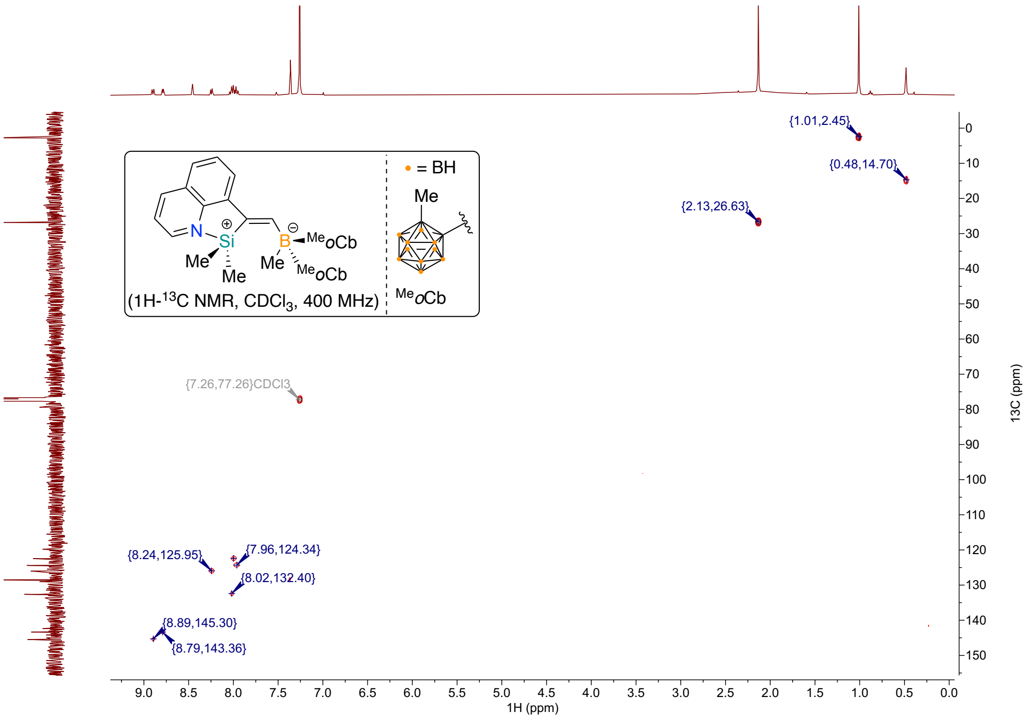


Figure S35: ^{11}B NMR spectrum of **3** in $CDCl_3$ (128 MHz)

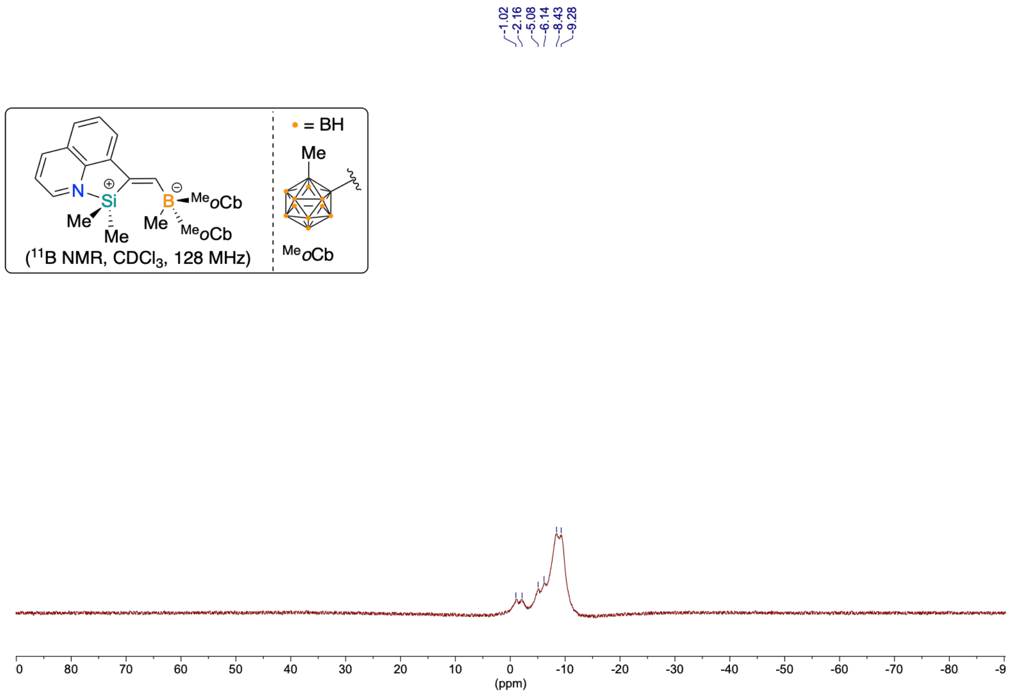


Figure S36: ^{11}B{^{1}H} NMR spectrum of **3** in $CDCl_3$ (128 MHz)

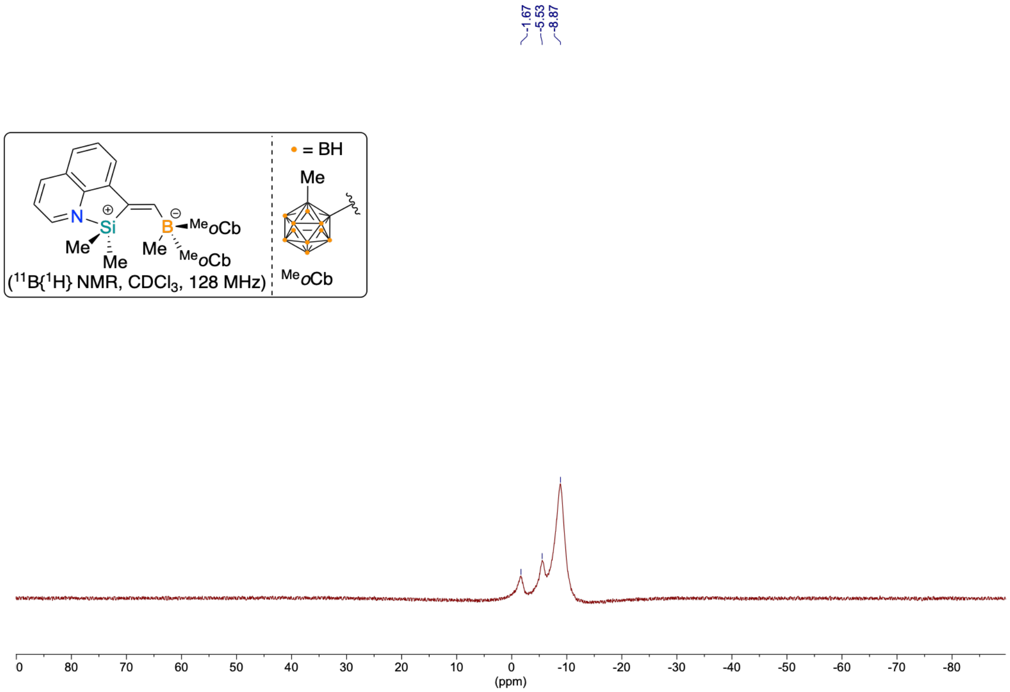


Figure S37: ^{29}Si{^{1}H} NMR spectrum of **3** in CDCl₃ (119 MHz)

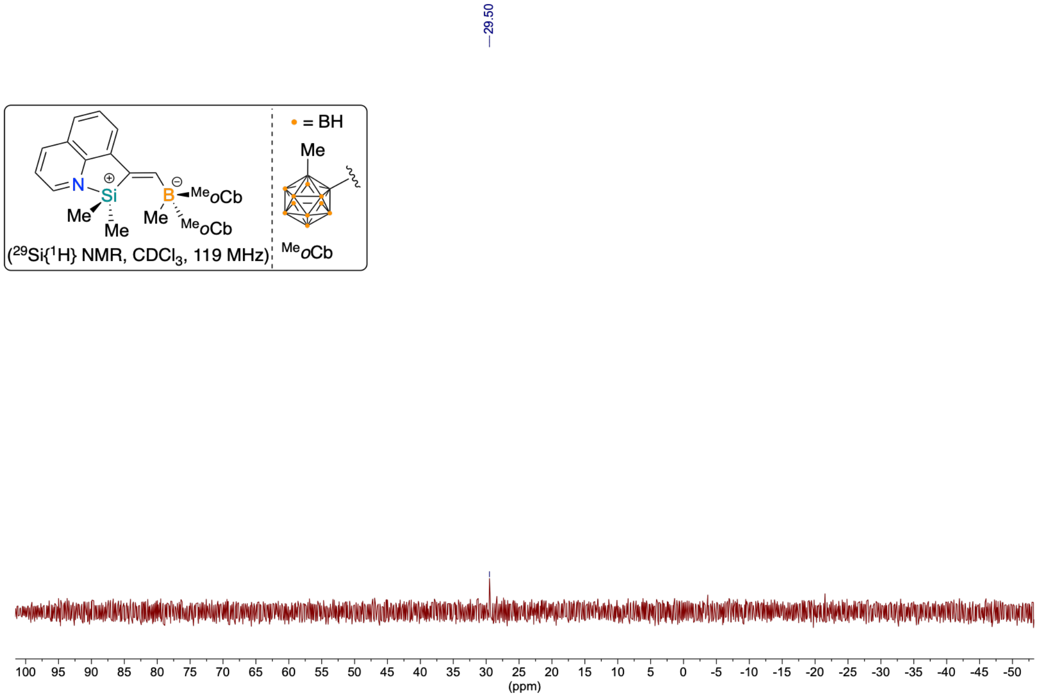


Figure S38: FT-IR spectrum of **3**

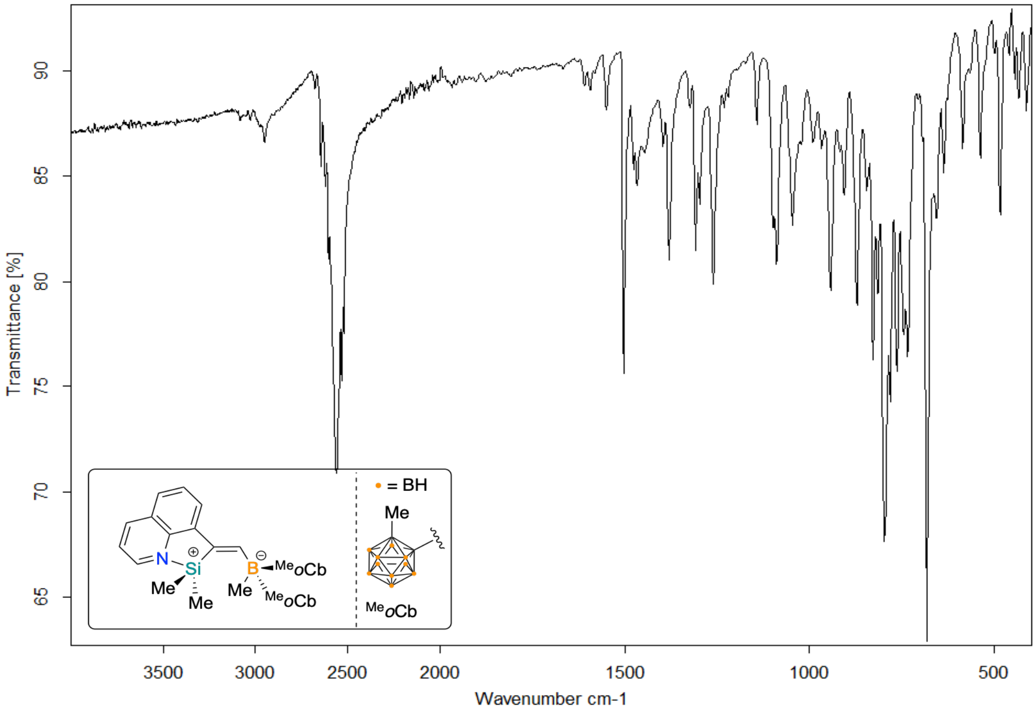


Figure S39: ^{1}H NMR spectrum of **4** in $CDCl_3$ (400 MHz)

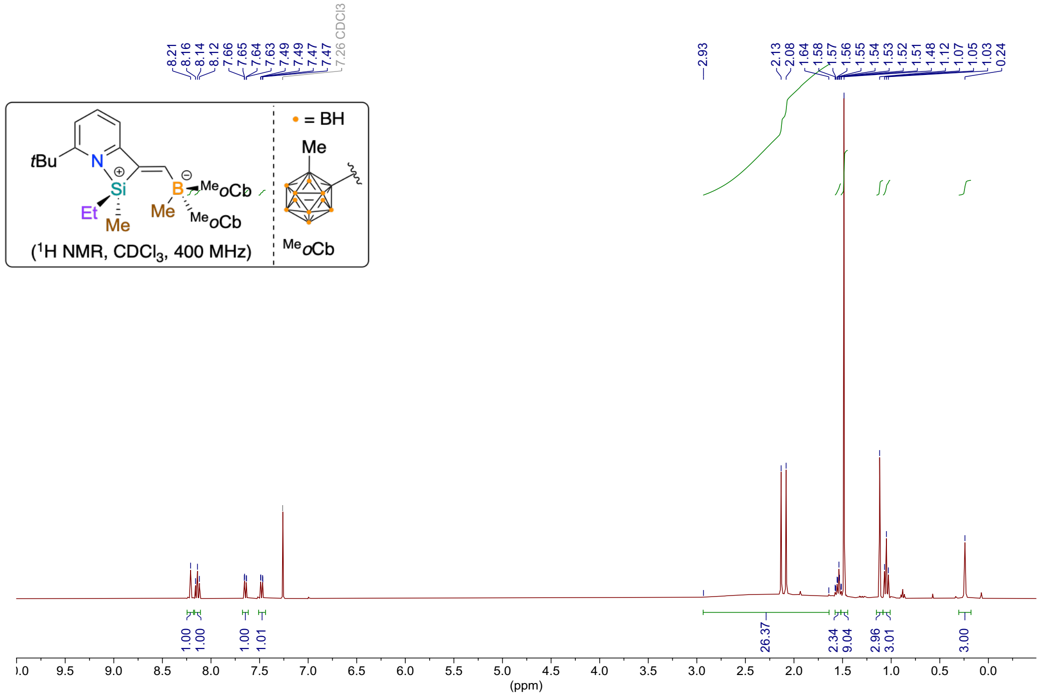


Figure S40: $^1H\{^{11}B\}$ NMR spectrum of **4** in $CDCl_3$ (400 MHz)

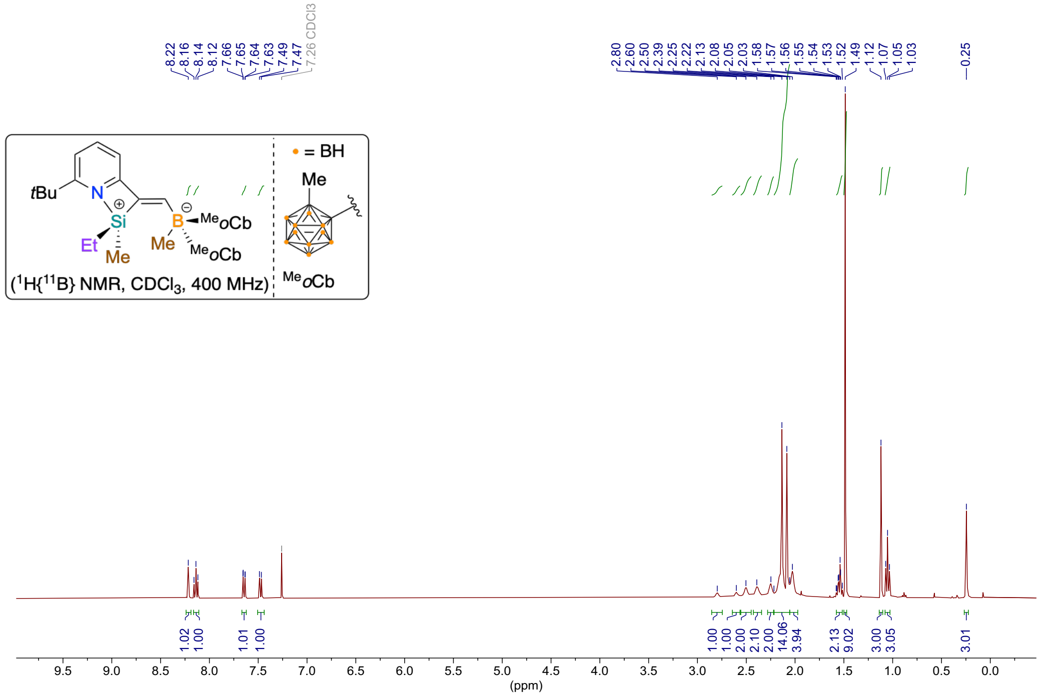


Figure S41: $^{13}C\{^1H\}$ NMR spectrum of **4** in $CDCl_3$ (101 MHz)

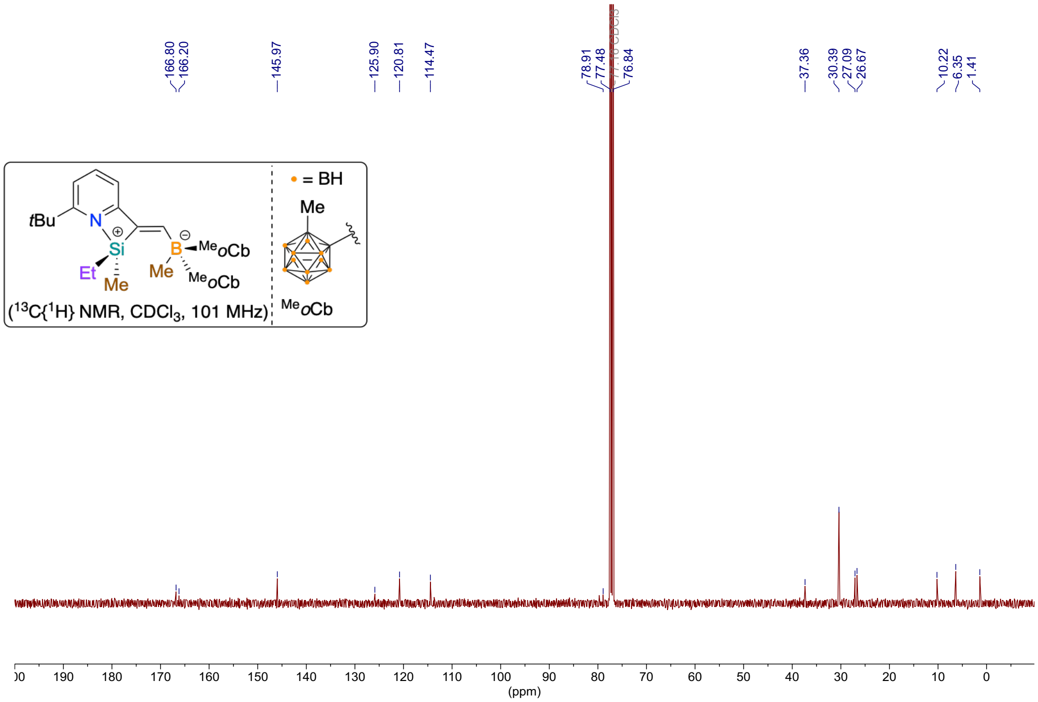


Figure S42: ^1H-$^{13}C\{^1H\}$ HSQC spectrum of **4** in $CDCl_3$ (400 MHz)

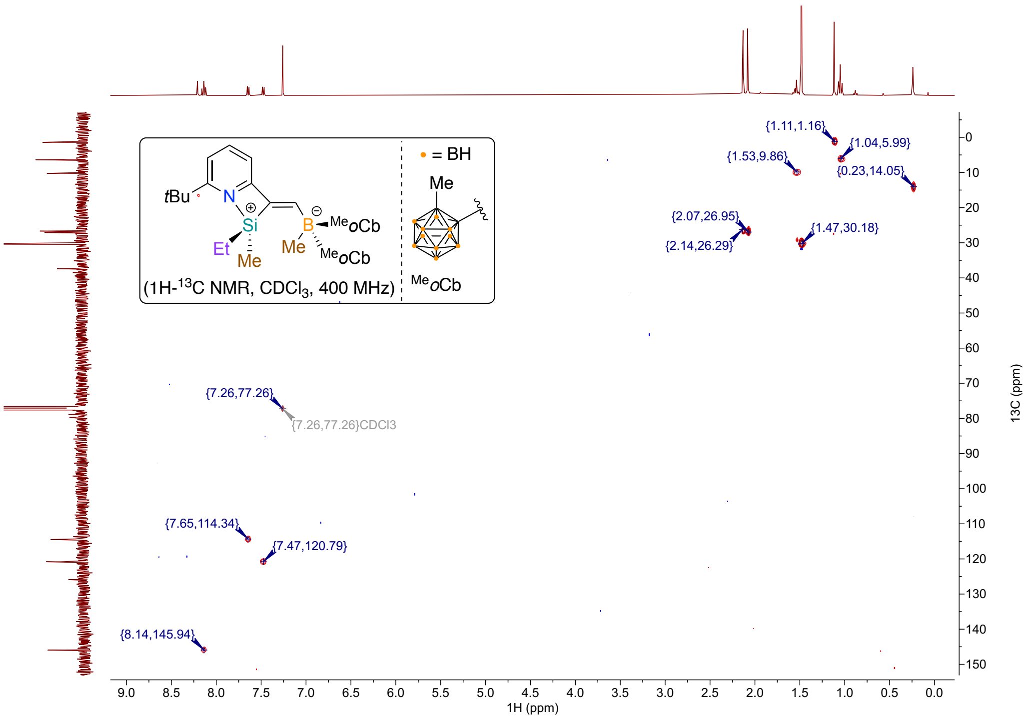


Figure S43: ^{11}B NMR spectrum of **4** in CDCl$_3$ (128 MHz)

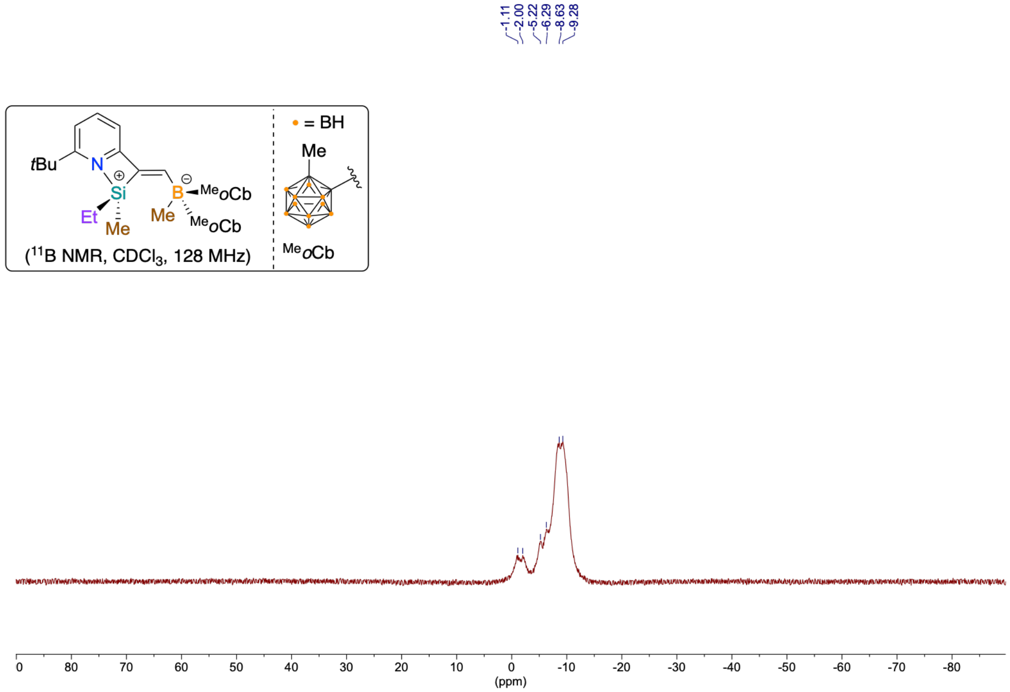


Figure S44: ^{11}B{^{1}H} NMR spectrum of **4** in CDCl$_3$ (128 MHz)

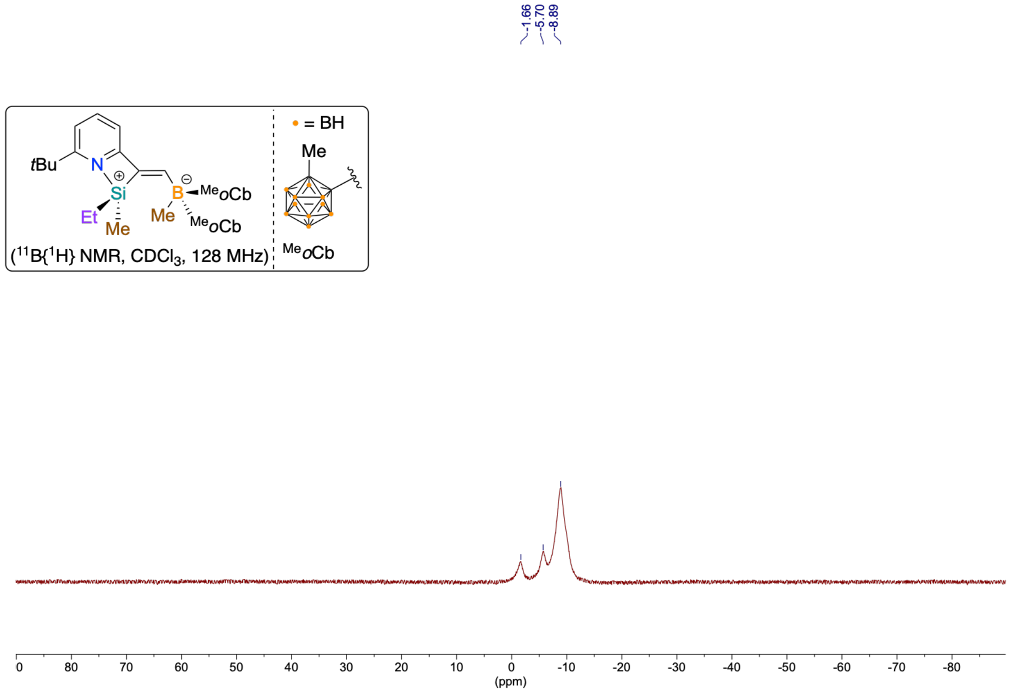


Figure S45: $^{29}Si\{^1H\}$ NMR spectrum of **4** in $CDCl_3$ (119 MHz)

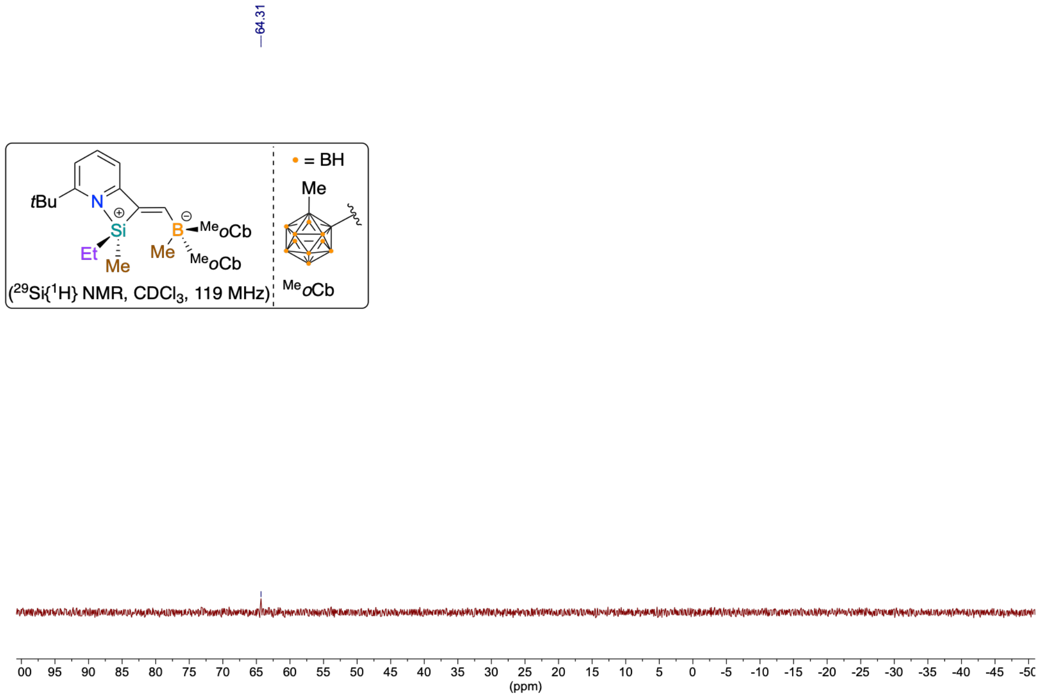


Figure S46: FT-IR spectrum of **4**

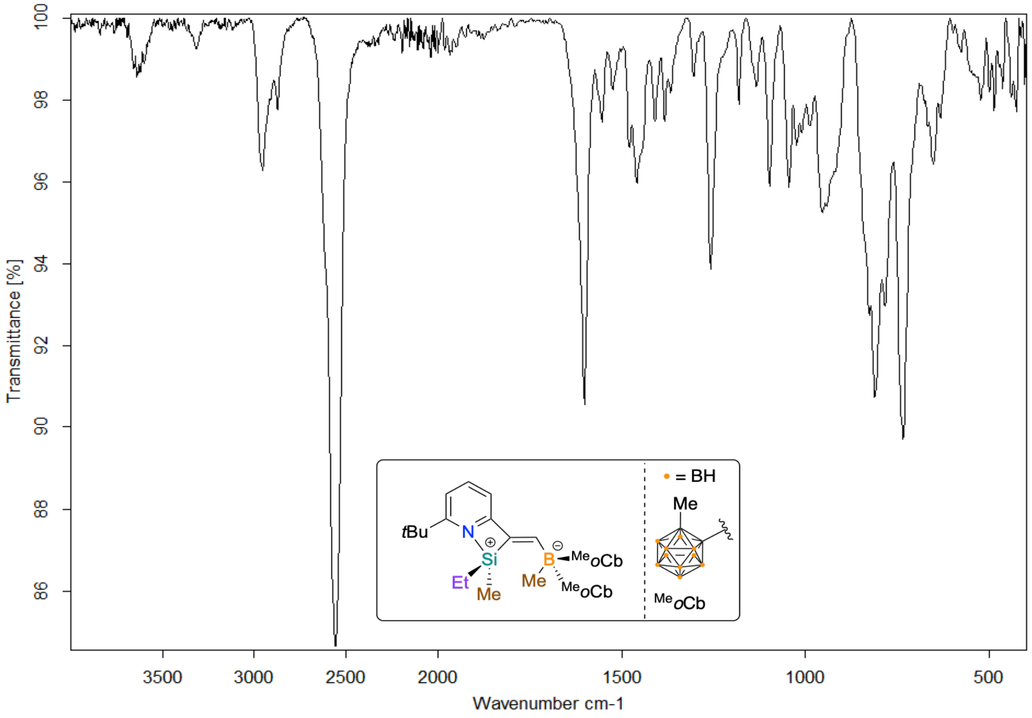


Figure S47: ^{1}H NMR spectrum of **5** in C_6D_6 (400 MHz)

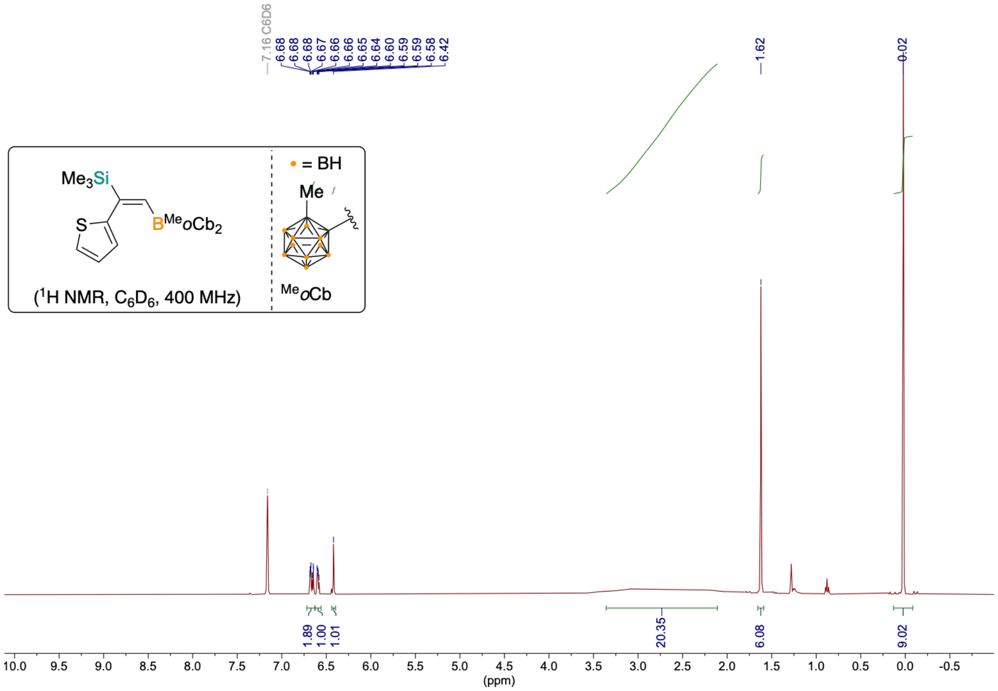


Figure S48: ^{1}H{^{11}B} NMR spectrum of **5** in C_6D_6 (400 MHz)

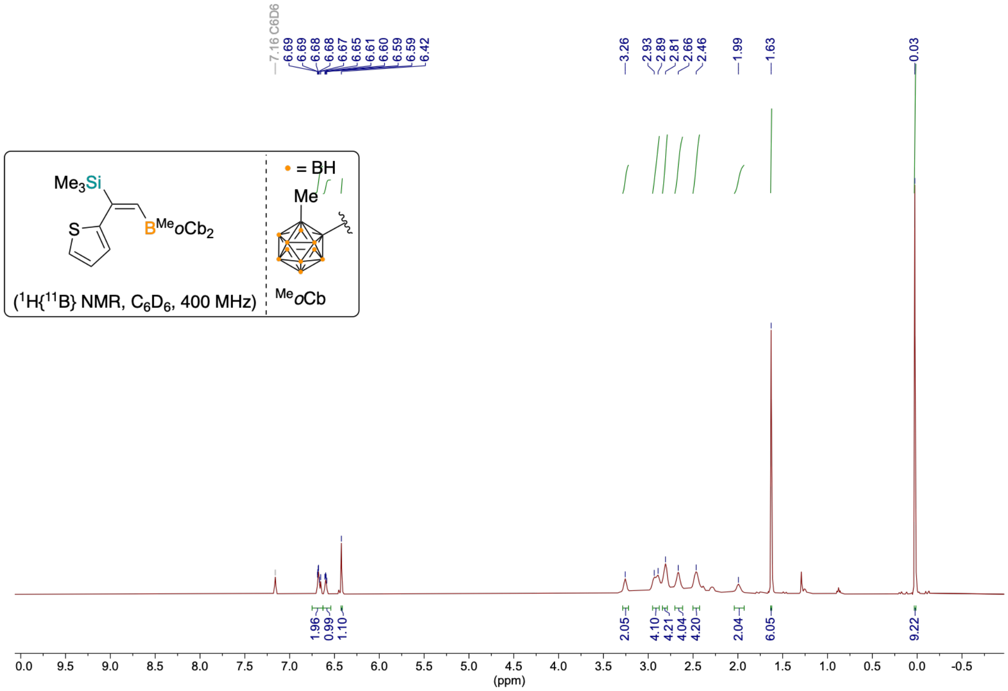


Figure S50: $^{13}C\{^{1}H\}$ NMR spectrum of **5** in C_6D_6 (101 MHz)

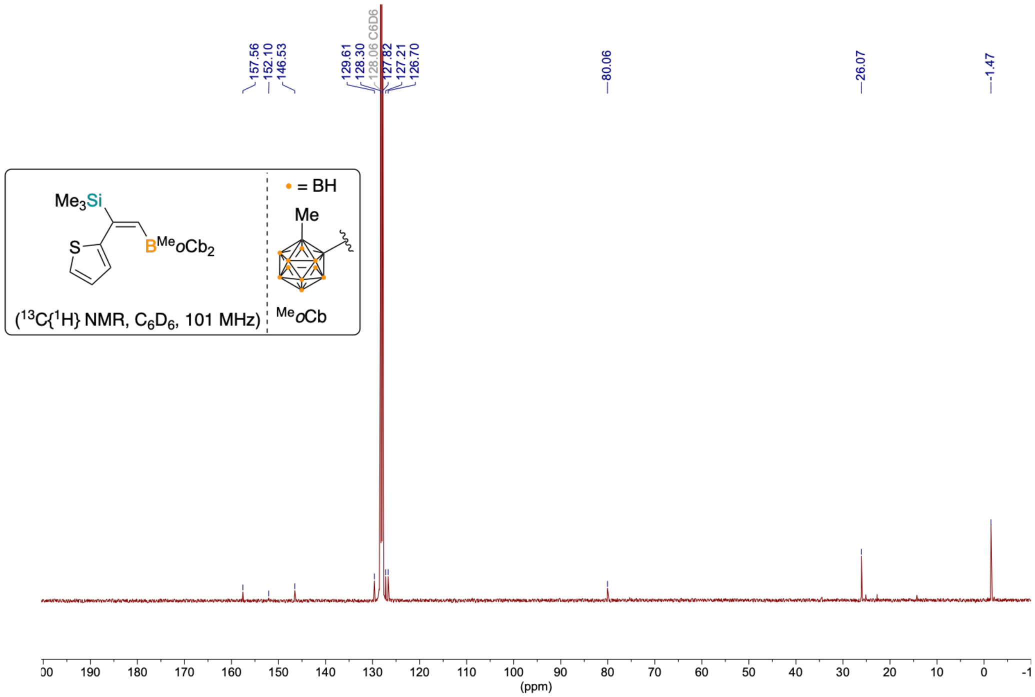


Figure S49: ^{1}H-$^{13}C\{^{1}H\}$ HSQC spectrum of **5** in C_6D_6 (400 MHz)

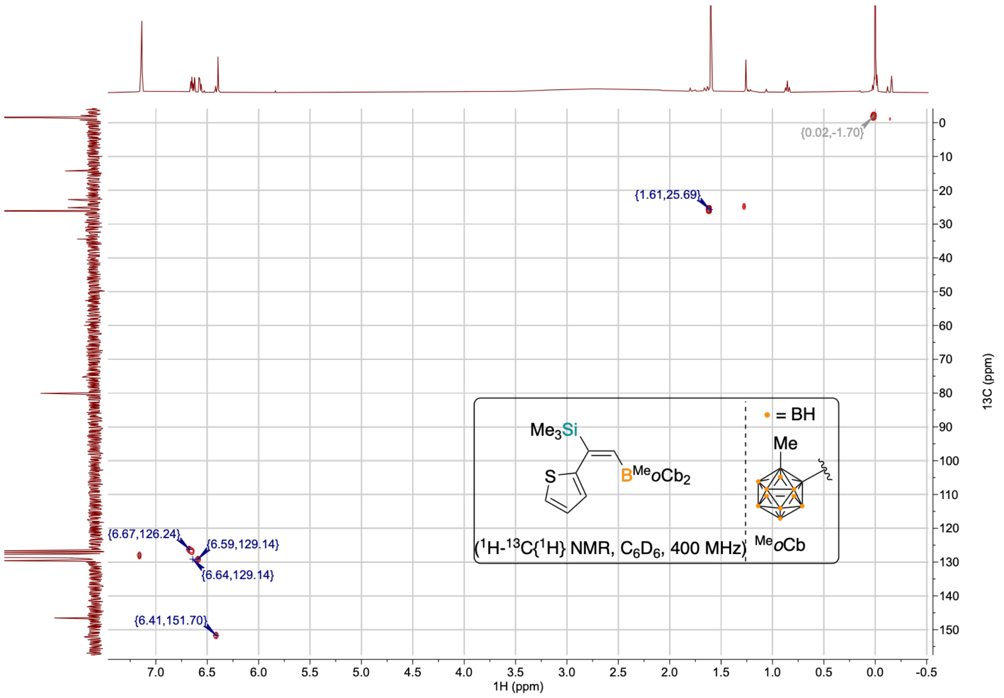


Figure S51: ^{11}B NMR spectrum of **5** in C_6D_6 (128 MHz)

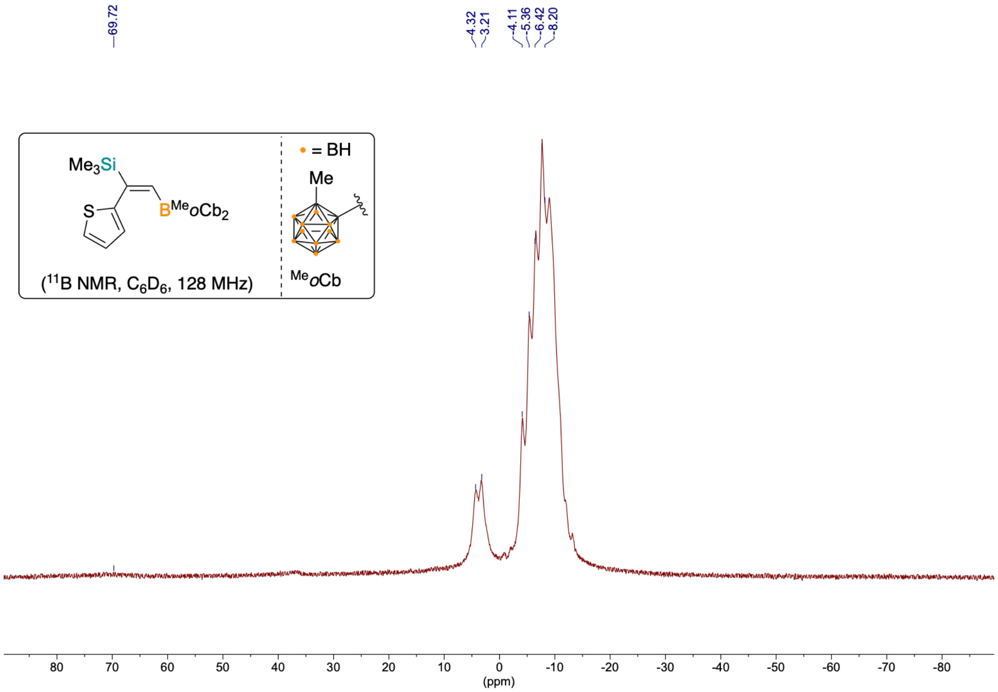


Figure S52: ^{11}B{^{1}H} NMR spectrum of **5** in C_6D_6 (128 MHz)

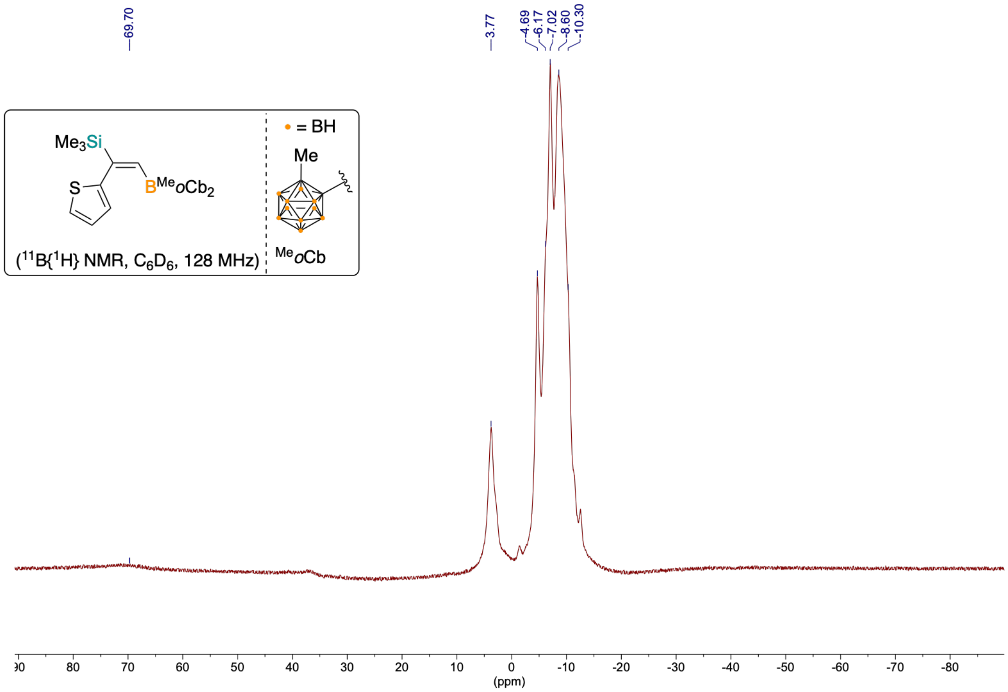


Figure S53: FT-IR spectrum of **5**

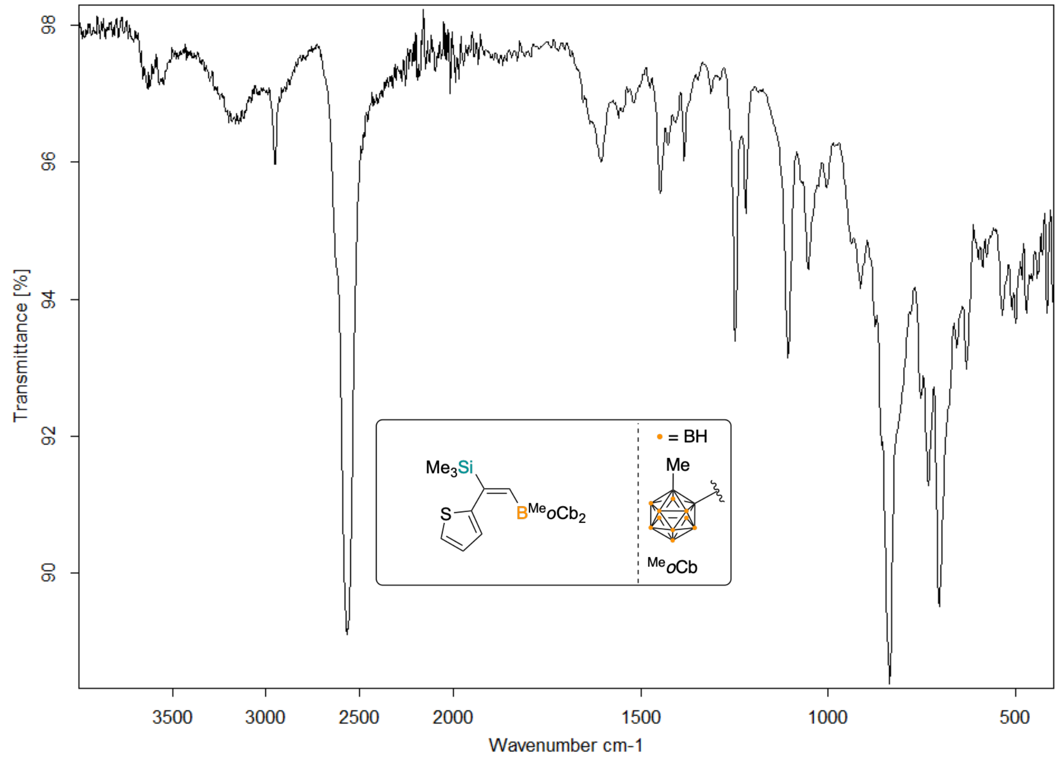


Figure S54: ^{1}H NMR spectrum of **6** in $CDCl_3$ (400 MHz)

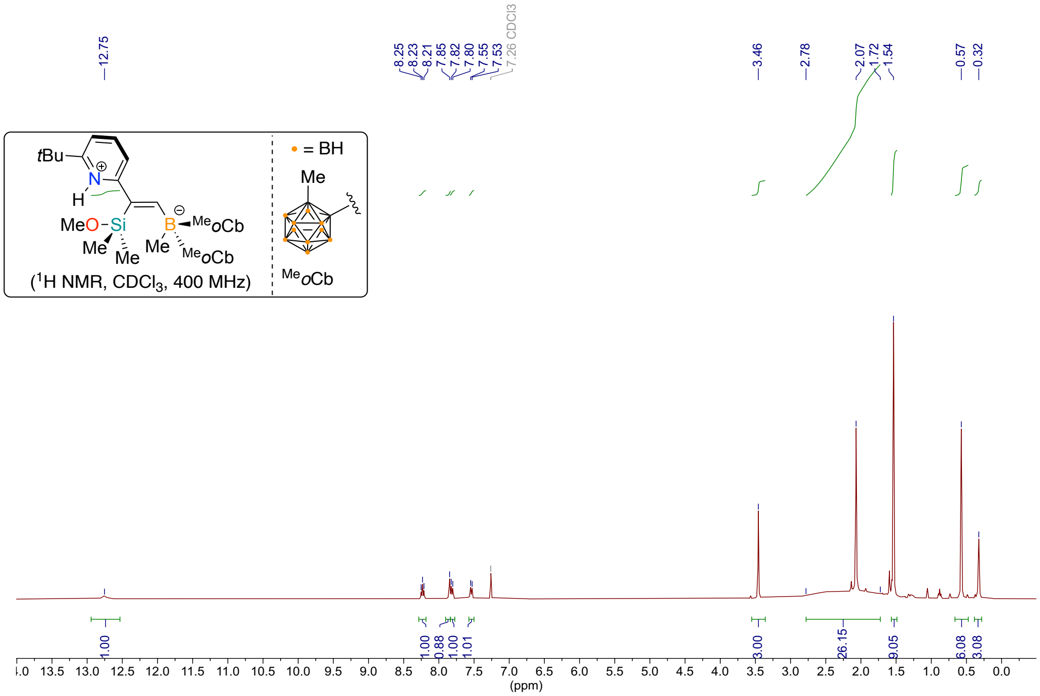


Figure S55: ^{1}H{^{11}B} NMR spectrum of **6** in CDCl$_3$ (400 MHz)

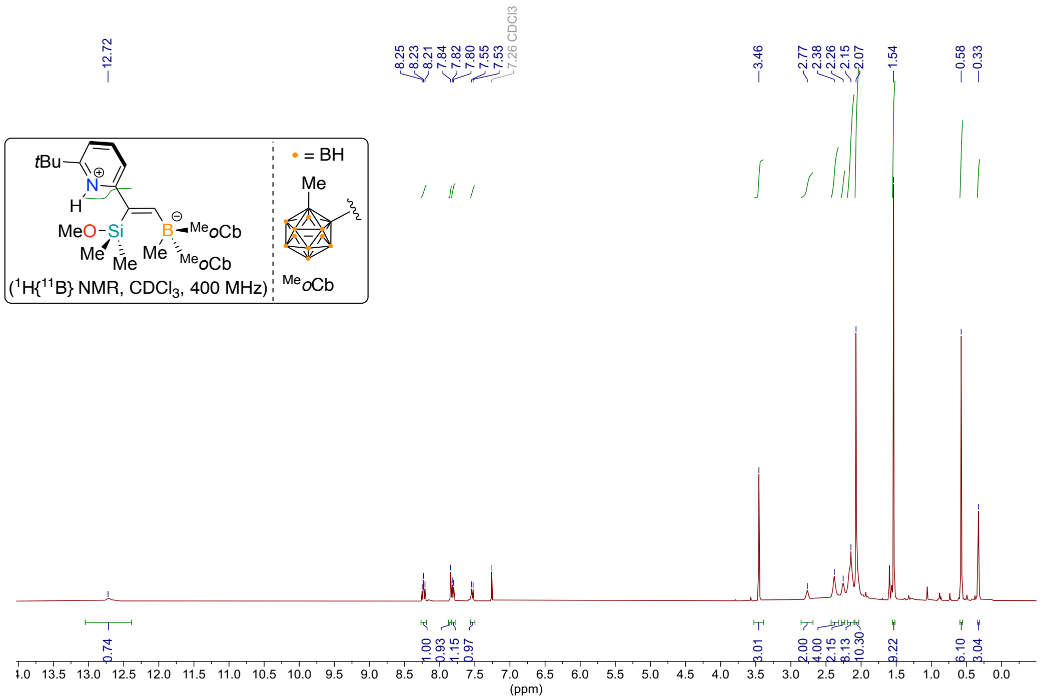


Figure S56: ^{13}C{^{1}H} NMR spectrum of **6** in CDCl$_3$ (101 MHz)

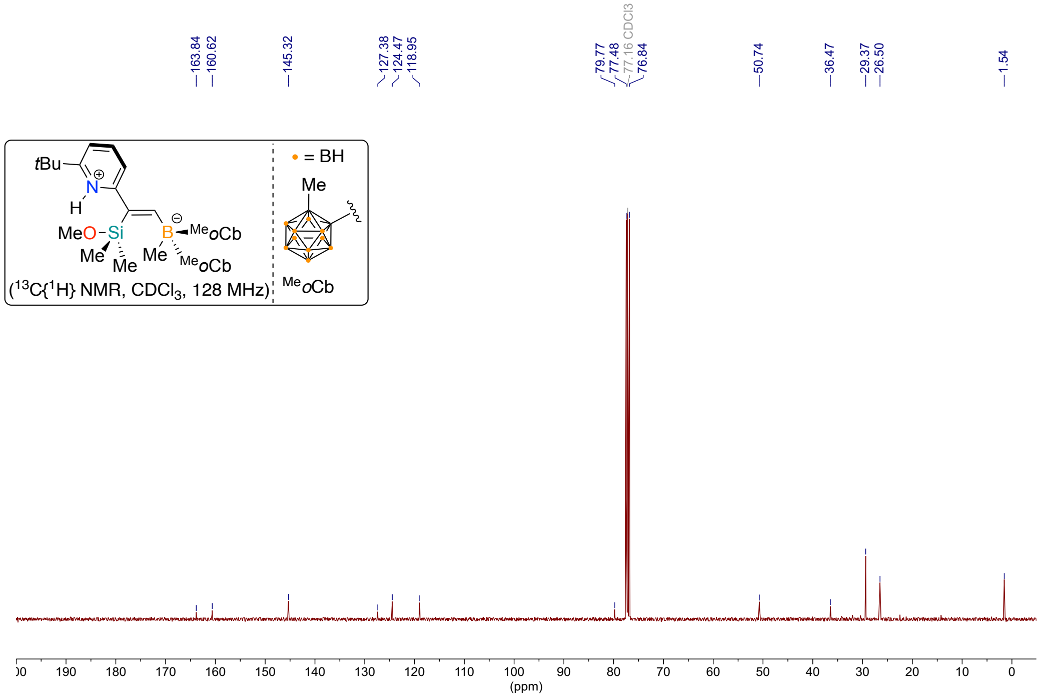


Figure S57: ^{1}H-^{13}C{^{1}H} HSQC spectrum of **6** in CDCl$_3$ (400 MHz)

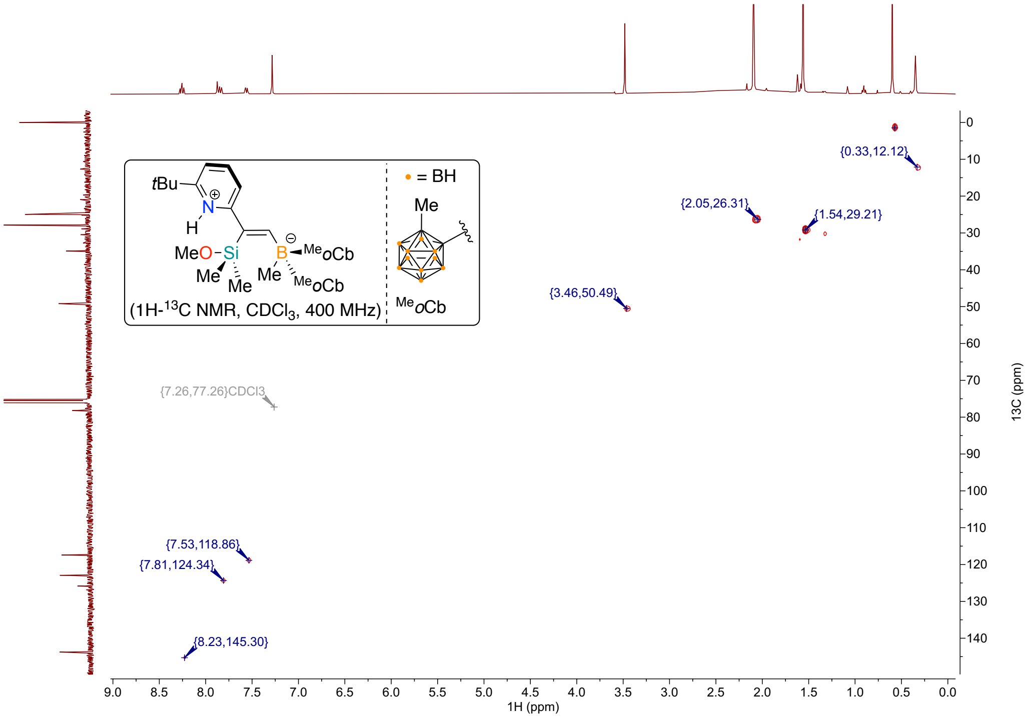


Figure S58: ^{11}B NMR spectrum of **6** in CDCl$_3$ (128 MHz)

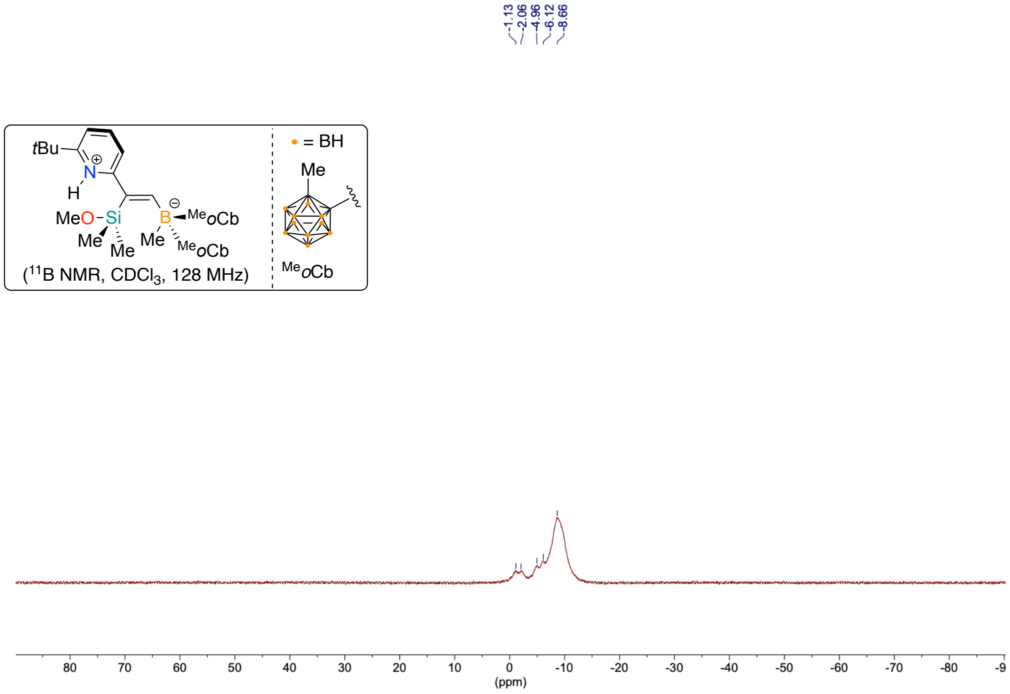


Figure S59: $^{11}B\{^1H\}$ NMR spectrum of **6** in $CDCl_3$ (128 MHz)

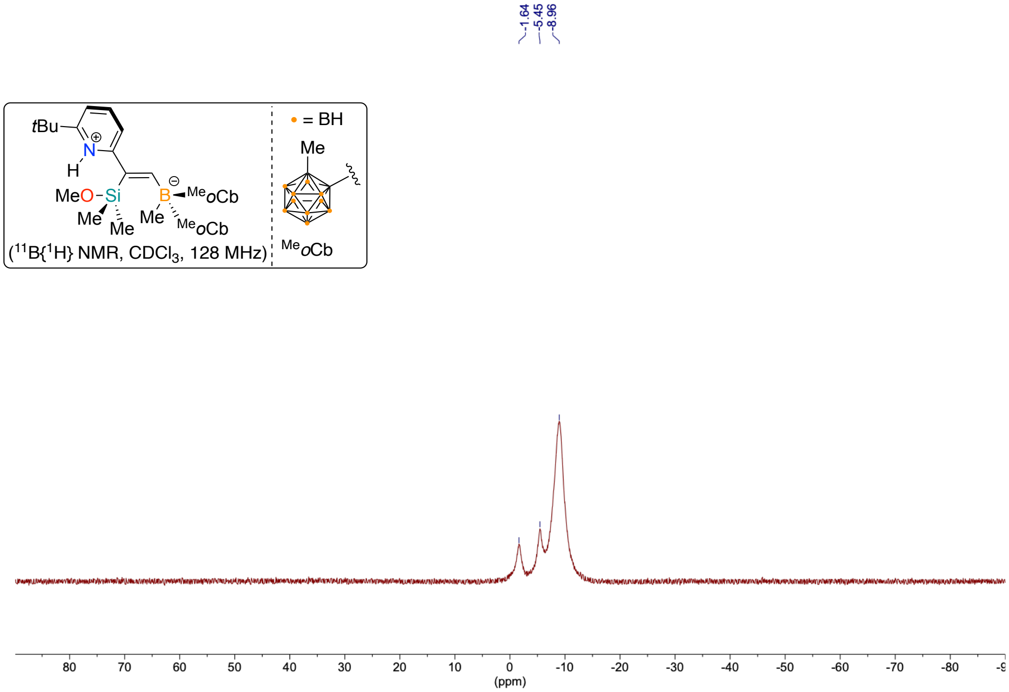


Figure S60: $^{29}Si\{^1H\}$ NMR spectrum of **6** in $CDCl_3$ (119 MHz)

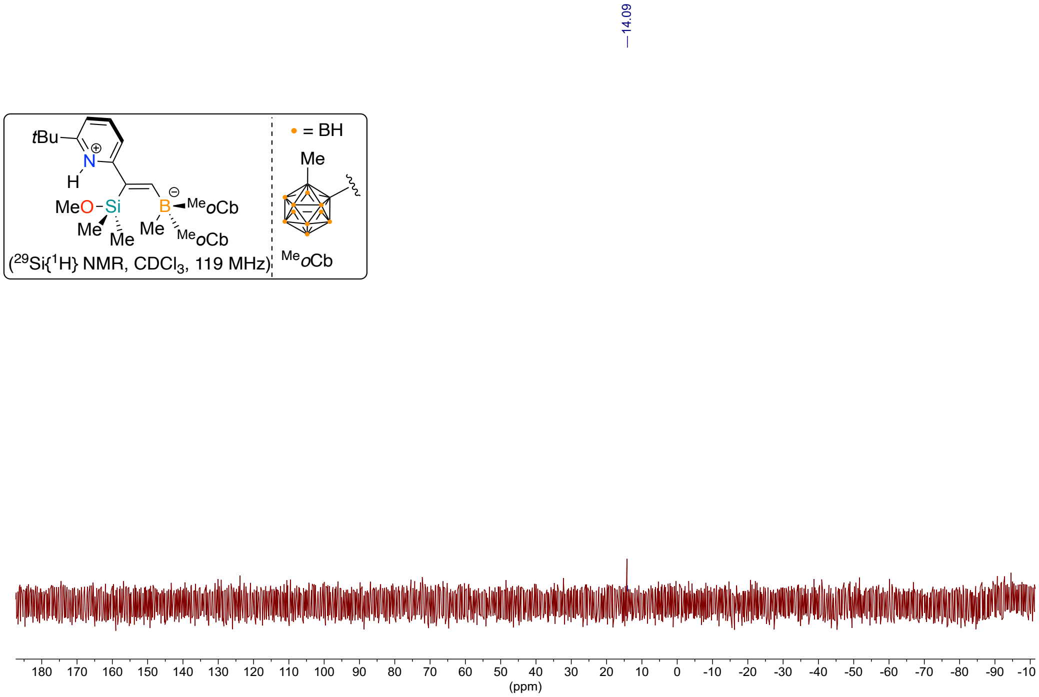
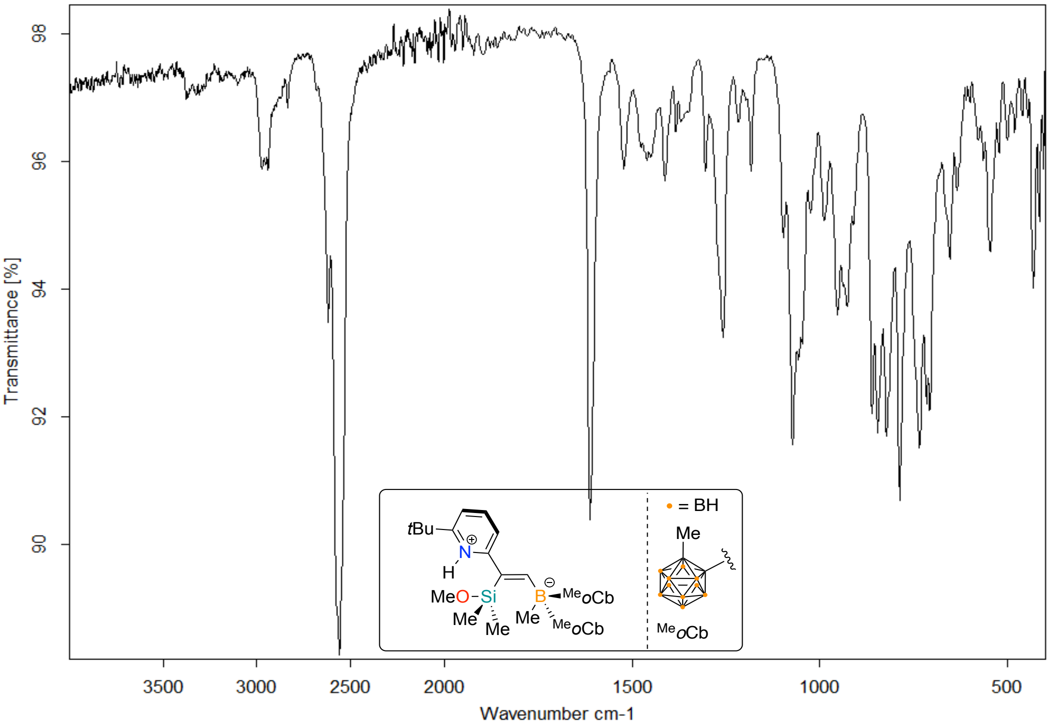


Figure S61: FT-IR spectrum of **5**



5. References

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