Supporting Information for:

Borenium-catalysed para-selective borylation of alkylarenes

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Supporting Information Contents:

I. Synthesis and characterization of new complexes

1. General information

Solvents were dried by reflux under N_2 atmosphere over calcium hydride and freshly distilled prior to use. Air-sensitive compounds were handled under N_2 atmosphere using standard Schlenk and glove-box techniques. NMR spectra were recorded on Bruker SPECT NMR (400 MHz for ^{1}H, 128 MHz for ^{11}B, 100 MHz for ^{13}C, 376 MHz for ^{19}F) and Bruker DMX500 NMR (500 MHz for ^{1}H and 160 MHz for ^{11}B) spectrometers. High-resolution mass spectra (HRMS) analyses were performed at Bruker micrOTOF II. Gas chromatography mass spectrometry (GCMS) analyses were performed at PerkinElmer 680-SQ 8T. GC analyses of headspace gas were obtained on a Shimadzu GC-2010 Plus gas chromatograph system. Gel Permeation Chromatography (GPC) was carried out using an Agilent Technologies 1260 Infinity equipped with three columns (Agilent PLgel (5μm, 103Å), Agilent PLgel (5μm, 106Å) and Agilent PLgel (10μm, MIXED BLS)) in a column oven, one differential refractometer and one UV Detector (λ = 260 nm). THF (HPLC Grade) was used as the eluent with a flow rate of 1 mL/min. Polystyrene standards (from Agilent Technologies, M_n = 162 ~ 6.57 × 10^6 g mol^{-1}) were used for calibration. 1-((pentafluorophenyl)methyl)-1H-imidazole, [1] 1-methyl-*o*-carborane,[2] $[IBn^{F}B(H)Cb^{Me}][B(C_6F_5)_4]$,[3] and $HBcat^{Cl}$[4] were prepared according to reported procedures.

2. Preparation of catecholboranes (HBcat^{R})

All the catecholboranes were synthesized following our reported preparation for 4-Cl-catecholborane (HBcat^{Cl}).[4] To a stirred, ice-bathed *n*-hexane solution of catechol (1.0 equiv) was added 10 M $Me_2S{\cdot}BH_3$ (1.5 equiv) dropwise via syringe, resulting in effervescence. Continuous stirring at 0 °C for one hour turned the reaction mixture to a clear colorless solution. Solvent and most unreacted $Me_2S{\cdot}BH_3$ were removed in vacuo, followed by the addition of a hexane solution of PPh_3 (3 mol%) to remove the residue $Me_2S{\cdot}BH_3$. Afterwards, hexane and Me_2S were removed in vacuo, and the catecholborane was obtained after trap-to-trap distillation at 35–80 °C under vacuum of 0.05 mbar as a clear colorless oil. NMR data of all catecholboranes are in agreement with literature.[5]

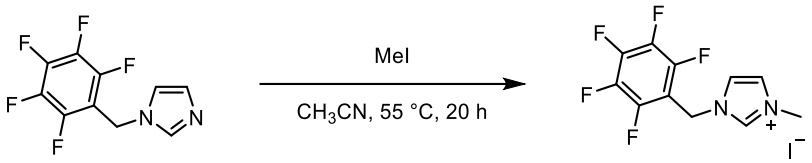
3,5-di(*tert*-butyl)-catecholborane. Prepared from 3,5-di(*tert*-butyl)-catechol (1.34 g, 6.03 mmol) and $Me_2S{\cdot}BH_3$ (0.9 mL, 9.00 mmol) according to the general procedure. The title product was isolated at 80 °C in 65% yield (903 mg).
^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.20 (d, J_{H-H} = 1.8 Hz, 1H), 7.10 (d, J_{H-H} = 1.8 Hz, 1H), 4.75 (br q, J_{B-H} = 197 Hz, 1H), 1.46 (s, 9H), 1.35 (s, 9H).
^{11}B NMR (128 MHz, $CDCl_3$): δ [ppm] = 28.3 (d, J_{B-H} = 195 Hz).

4-(*tert*-butyl)-catecholborane. Prepared from 4-(*tert*-butyl)-catechol (4.75 g, 28.6 mmol) and $Me_2S{\cdot}BH_3$ (4.2 mL, 42.0 mmol) according to the general procedure. The title product was isolated at 49 °C in 72% yield (4.1 g).
^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.35 (d, J_{H-H} = 1.5 Hz, 1H), 7.20 (d, J_{H-H} = 8.4 Hz, 1H), 7.16 (dd, J_{H-H} = 8.4 and 1.5 Hz, 1H), 4.75 (br q, J_{B-H} = 186 Hz, 1H), 1.35 (s, 9H).
^{11}B NMR (128 MHz, $CDCl_3$): δ [ppm] = 28.8 (d, J_{B-H} = 186 Hz).

4-methyl-catecholborane. Prepared from 4-methyl-catechol (1.37 g, 11.0 mmol) and $Me_2S{\cdot}BH_3$ (1.6 mL, 16.0 mmol) according to the general procedure. The title product was isolated at 40 °C in 41% yield (608 mg).
^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.15 (d, J_{H-H} = 8.1 Hz, 1H), 7.10 (s, 1H), 6.93 (d, J_{H-H} = 8.1 Hz, 1H), 4.74 (br q, J_{B-H} = 201 Hz, 1H), 2.40 (s, 3H).
^{11}B NMR (128 MHz, $CDCl_3$): δ [ppm] = 28.7 (d, J_{B-H} = 201 Hz).

3-fluoro-catecholborane.
Prepared from 3-fluoro-catechol (6.41 g, 50.0 mmol) and $Me_2S{\cdot}BH_3$ (7.5 mL, 75.0 mmol) according to the general procedure. The title product was isolated at 35 °C in 22% yield (1.51 g).
^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.12−7.06 (m, 2H), 6.98−6.92 (m, 1H), 4.79 (br q, J_{B-H} = 196 Hz, 1H.
^{11}B NMR (128 MHz, $CDCl_3$): δ [ppm] = 28.7 (d, J_{B-H} = 196 Hz).
^{19}F NMR (376 MHz, $CDCl_3$): δ [ppm] = -135.0 (m, 1F).

3. Synthesis of 3-methyl-1-((pentafluorophenyl)methyl)-1*H*-imidazol-3-ium iodide (IBn^{F}Me·HI)



IBn^{F}Me•HI

To a 25-mL flask containing a solution of 1-((pentafluorophenyl)methyl)-1*H*-imidazole (3.1 g, 12.5 mmol) in acetonitrile (5.0 mL) was added iodomethane (5.0 mL, 80.3 mmol, 6.4 equiv). The mixture was then stirred at 55 °C for 20 h. The resultant scarlet solution was concentrated and purified by recrystallization from Et_2O to afford **IBn^{F}Me·HI** as a yellowish solid (4.6 g, 94% yield).

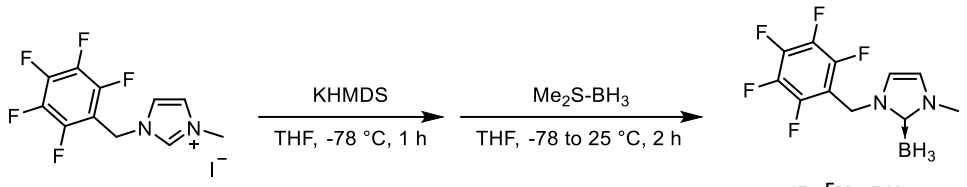
^{1}H NMR (400 MHz, DMSO-d_6): δ [ppm] = 9.22 (s, 1H), 7.79 (s, 1H), 7.75 (s, 1H), 5.63 (s, 2H), 3.85 (s, 3H).

^{13}C NMR (100 MHz, DMSO-d_6): δ [ppm] = 145.2 (dm, $^1J_{C-F}$ = 253 Hz), 141.3 (dm, $^1J_{C-F}$ = 250 Hz), 137.2 (dm, $^1J_{C-F}$ = 250 Hz), 137.2, 124.0, 122.6, 108.2, 39.9, 36.1.

^{19}F NMR (376 MHz, DMSO-d_6): δ [ppm] = -141.2 (m, 2F), -152.9 (t, $^3J_{F-F}$ = 22.3 Hz, 1F), -161.7 (m, 2F).

HRMS (m/z): $[M]^+$ calcd. For $C_{11}H_8F_5N_2^+$, 263.0608; found 263.0609.

4. Synthesis of IBn^{F}Me-BH$_3$.



IBn^{F}Me-BH$_3$

To a 250-mL three-neck flask containing a solution of **IBn^{F}Me·HI** (6.6 g, 16.9 mmol) in THF (65 mL) was added a THF solution of KHMDS (18.0 mL, 18.0 mmol, 1.06 equiv, 1.0 M in THF) at -78 °C. After one-hour stirring at -78 °C, a hexane solution of Me_2S-BH_3 (2.6 mL, 26.0 mmol, 1.5 equiv, 10 M in hexane) was slowly added to the reaction mixture at -78 °C. The resultant mixture was then warmed to room temperature and stirred for 2 h. After quenched by saturated NH_4Cl aqueous solution (15 mL) and extracted with CH_2Cl_2 (20 mL x 2). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (eluted with petroleum ether/AcOEt = 3/1) on silica gel to give **IBn^{F}Me-BH$_3$** as a white solid (3.5 g, 75 %).

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 6.83 (s, 1H), 6.82 (s, 2H), 5.45 (s, 2H), 3.74 (s, 3H), 1.04 (q, J_{B-H} = 86.8 Hz, 3H).

^{1}H{^{11}B} NMR (400 MHz, $CDCl_3$): δ [ppm] = 6.83 (s, 1H), 6.82 (s, 2H), 5.45 (s, 2H), 3.74 (s, 3H), 1.04 (s, 3H).

^{11}B NMR (128 MHz, $CDCl_3$): δ [ppm] = -37.7 (q, J_{B-H} = 86.8 Hz).

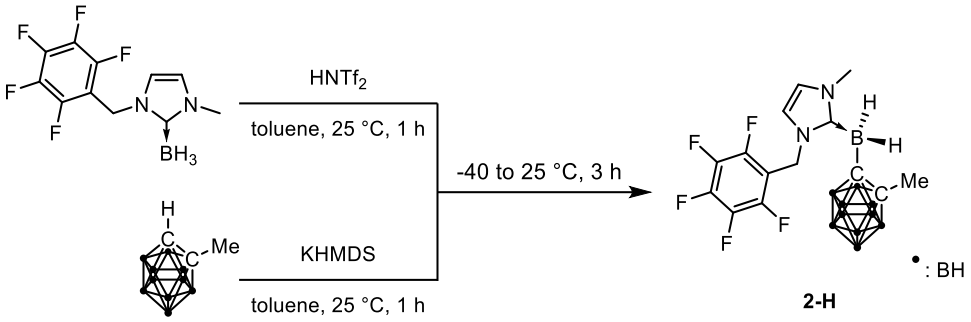
^{11}B{^{1}H} NMR (128 MHz, CDCl3, 298 K): δ [ppm] = -37.7 (s).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ [ppm] = 145.7 (dm, $^{1}J_{C-F}$ = 252 Hz, *o*-C_6F_5), 141.8 (dm, $^{1}J_{C-F}$ = 257 Hz, *p*-C_6F_5), 137.8 (dm, $^{1}J_{C-F}$ = 259 Hz, *m*-C_6F_5), 120.9 and 118.7 (*C*H=*C*H), 109.3 (m, *ipso*-C_6F_5), 40.1 (*CH$_2$*-C_6F_5), 36.2 (N*CH$_3$*).

^{19}F NMR (376 MHz, $CDCl_3$): δ [ppm] = -140.4 (m, 2F), -152.0 (t, $^{3}J_{F-F}$ = 20.8 Hz, 1F), -160.7 (m, 2F).

HRMS (m/z): $[M-H]^+$ calcd. For $C_{11}H_9BF_5N_2^+$, 275.0781; found 275.0779.

5. Synthesis of IBn^{F}Me-B(H)$_2$-Cb^{Me} (2-H).



A solution of KHMDS (1.7 g, 8.5 mmol, 1.4 equiv.) in toluene (5.0 mL) was added to a solution of 1-methyl-*o*-carborane (1.3 g, 8.2 mmol, 1.3 equiv.) in toluene (5.0 mL) at 25 °C, resulting in formation of a brownish yellow slurry. The reaction mixture was stirred at room temperature for 1 h. All volatiles were then removed in vacuo, and to the leftover was added 10.0 mL of toluene. Subsequently, to this pre-cooled (-40 °C) slurry was added a solution of [IBn^{F}Me-BH$_2$][NTf$_2$] in toluene (10.0 mL) at -40 °C which was *in situ* generated from **IBn^{F}Me-BH$_3$** (1.7 g, 6.2 mmol, 1.0 equiv.) and HNTf$_2$ (1.8 g, 6.4 mmol, 1.03 equiv.) at 25 °C. After warmed to room temperature, the resulting mixture was stirred for 3 h before quenched by saturated NH_4Cl aqueous solution (10 mL) and extracted with CH_2Cl_2 (20 mL x 2). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (eluted with petroleum ether/AcOEt = 4/1) on silica gel to give compound **2-H** as a white solid (1.5 g, 56 %).

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 6.98 (s, 1H), 6.90 (s, 1H), 5.53 (s, 2H), 3.87 (s, 3H), 2.10 (s, 3H).

^{1}H{^{11}B} NMR (400 MHz, $CDCl_3$): δ [ppm] = 6.98 (s, 1H), 6.90 (s, 1H), 5.53 (s, 2H), 3.87 (s, 3H), 2.34 (s, 2H, B*H*$_{Carborane}$), 2.26 (s, 2H, B*H*$_{Carborane}$), 2.10 (s, 3H, Cb^{Me}), 2.03 − 1.98 (m, 4H, B*H*$_2$ and B*H*$_{Carborane}$), 1.67 (s, 2H, B*H*$_{Carborane}$).

^{11}B NMR (128 MHz, $CDCl_3$): δ [ppm] = -3.8 − -11.1 (m, 10B, H*B*$_{Carborane}$), -25.0 (t, $^{1}J_{H-B}$ = 93.9 Hz, H_2B).

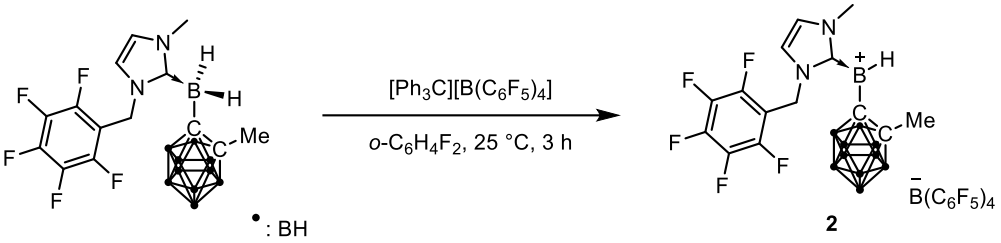
^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ [ppm] = -4.4 (s, 1B), -5.9 (s, 1B), -8.8 − -10.6 (m, 8B), -25.0 (s, 1B).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ [ppm] = 145.7 (dm, $^{1}J_{C-F}$ = 256 Hz, *o*-C_6F_5), 142.2 (dm, $^{1}J_{C-F}$ = 256 Hz, *p*-C_6F_5), 138.0 (dm, $^{1}J_{C-F}$ = 251 Hz, *m*-C_6F_5), 122.4 and 119.6 (*C*H=*C*H), 108.7 (m, *ipso*-C_6F_5), 75.4 (*C*CH_3), 40.9 (*CH*$_2$-C_6F_5), 37.1 (N*CH*$_3$), 24.6 (Cb^{CH3}).

^{19}F NMR (376 MHz, $CDCl_3$): δ [ppm] = -140.1 (m, 2F), -150.7 (t, $^{3}J_{F-F}$ = 20.8 Hz, 1F), -159.8 (m, 2F).

HRMS (m/z): $[M+H]^+$ calcd. For $C_{14}H_{23}B_{11}F_5N_2^+$, 435.2829; found 435.2830.

6. Synthesis of [IBn^{F}Me-B(H)-Cb^{Me}][B(C_6F_5)$_4$] (2).



To a solution of **2-H** (481.6 mg, 1.11 mmol) in *o*-$C_6H_4F_2$ (2.0 mL) was added a solution of [Ph_3C][B(C_6F_5)$_4$] (1039.1 mg, 1.13 mmol) in *o*-$C_6H_4F_2$ (2.0 mL). The resulting orange solution was stirred at room temperature for 5 min. Subsequently, hexane (8.0 mL) was added to the reaction mixture, leading to formation of an immiscible brown oil at the bottom of the flask. After vigorous stirring of 3 h, the oil was transformed into a yellow precipitate, which was filtered, washed with hexane (5.0 mL) and dried under vacuum, affording **2** as a yellow solid (1343.4 mg, 97 %).

^{1}H NMR (400 MHz, C_6D_5Br): δ [ppm] = 6.69 (s, 2H), 4.90 (s, 2H), 4.21 (br s, 1H), 3.60 (s, 3H), 1.98 (s, 3H).

^{1}H{^{11}B} NMR (400 MHz, C_6D_5Br): δ [ppm] = 6.69 (s, 2H), 4.91 (s, 2H), 4.21 (br s, 1H), 3.60 (s, 3H), 2.85 − 2.47 (m, 6H, B$H_{carborane}$), 2.16 − 1.84 (m, 7H, CCH_3 & B$H_{carborane}$).

^{11}B NMR (128 MHz, *o*-$C_6H_4F_2$): δ [ppm] = 6.4 to -13.6 (m, 10B), -16.2 (s, 1B, *B*(C_6F_5)$_4$). The signal of the borenium center was too broad to be observed.

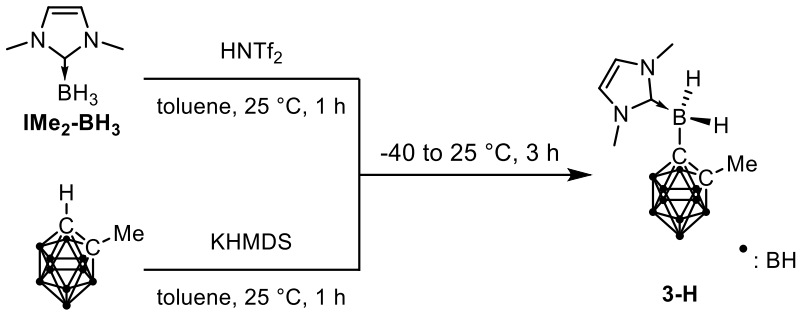
^{11}B{^{1}H} NMR (128 MHz, *o*-$C_6H_4F_2$): δ [ppm] = 4.6 (br s, 1B), -0.8 to -13.6 (m, 9B), -16.2 (s, 1B, *B*(C_6F_5)$_4$). The signal of the borenium center was too broad to be observed.

^{13}C{^{1}H} NMR (100 MHz, C_6D_5Br): δ [ppm] = 148.6 (dm, $^{1}J_{F-C}$ = 238 Hz, *o*-B(C_6F_5)$_4$), 145.2 (dm, $^{1}J_{F-C}$ = 244 Hz, *o*-C_6F_5), 141.8 (dm, $^{1}J_{F-C}$ = 242 Hz, *p*-C_6F_5), 140.3 (dm, $^{1}J_{F-C}$ = 244 Hz, *m*-C_6F_5), 138.5 (dm, $^{1}J_{F-C}$ = 247 Hz, *p*-B(C_6F_5)$_4$), 136.6 (dm, $^{1}J_{F-C}$ = 250 Hz, *m*-B(C_6F_5)$_4$), 125.9 and 125.8 (*C*H=*C*H), 105.6 (m, *ipso*-C_6F_5), 79.5 (*C*CH_3), 41.5 (*C*H_2-C_6F_5), 38.5 (N*C*H_3), 25.0 (Cb^{CH3}). Carbons attached to boron were not observed.

^{19}F NMR (376 MHz, C_6D_5Br): δ [ppm] = -133.25 (m, 8F), -163.26 (t, $^{3}J_{F-F}$ = 20.2 Hz), -167.25 (t, $^{3}J_{F-F}$ = 16.1 Hz).

HRMS (m/z): [M]$^{+}$ calcd. for $C_{14}H_{21}B_{11}F_5N_2^{+}$, 433.2667; found 433.2678.

7. Synthesis of IMe_2-$B(H)_2$-Cb^{Me} (3-H).



A solution of KHMDS (1290 mg, 6.5 mmol, 1.4 equiv.) in toluene (3.0 mL) was added to a solution of 1-methyl-*o*-carborane (973 mg, 6.1 mmol, 1.3 equiv.) in toluene (3.0 mL) at 25 °C, resulting in formation of a brownish yellow slurry. The reaction mixture was stirred at room temperature for 1 h. All volatiles were then removed in vacuo, and to the leftover was added 8.0 mL of toluene. Subsequently, to this pre-cooled (-40 °C) slurry was added a solution of $[IMe_2\text{-}BH_2][NTf_2]$ in toluene (8.0 mL) at -40 °C which was *in situ* generated from **IMe_2-BH_3** (527 mg, 4.8 mmol, 1.0 equiv.) and $HNTf_2$ (1410 mg, 5.0 mmol, 1.04 equiv.) at 25 °C. After warmed to room temperature, the resulting mixture was stirred for 3 h before quenched by saturated NH_4Cl aqueous solution (10 mL) and extracted with CH_2Cl_2 (20 mL x 2). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (eluted with petroleum ether/AcOEt = 4/1) on silica gel to give compound **3-H** as a white solid (836 mg, 66 %).

^1H NMR (400 MHz, $CDCl_3$): δ [ppm] = 6.93 (s, 2H), 3.83 (s, 6H), 2.09 (s, 3H).

$^1H\{^{11}B\}$ NMR (400 MHz, $CDCl_3$): δ [ppm] = 6.93 (s, 2H), 3.83 (s, 6H), 2.30 (s, 2H, $BH_{Carborane}$), 2.25 (s, 2H, $BH_{Carborane}$), 2.09 (m, 4H, Cb^{Me} and $BH_{Carborane}$), 2.02 (s, 2H, $BH_{Carborane}$), 1.94 (s, 1H, $BH_{Carborane}$), 1.86 (s, 2H, BH_2), 1.68 (s, 2H, $BH_{Carborane}$).

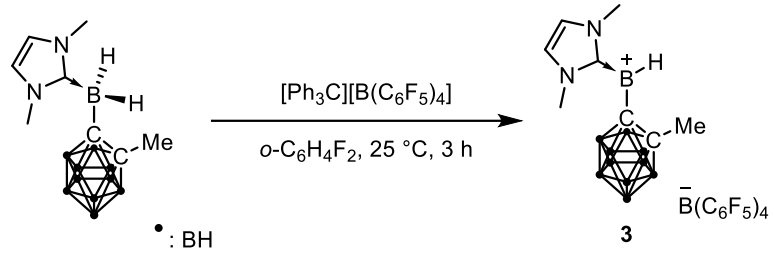
^{11}B NMR (128 MHz, $CDCl_3$): δ [ppm] = -3.9 − -11.2 (m, 10B, $HB_{Carborane}$), -25.0 (t, $^1J_{H-B}$ = 92.0 Hz, H_2B). The signal of the borenium center was too broad to be observed.

$^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ [ppm] = -4.5 (s, 1B), -6.0 (s, 1B), -7.6 − -10.6 (m, 8B), -25.0 (s, 1B). The signal of the borenium center was too broad to be observed.

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ [ppm] = 121.4 (*C*H=*C*H), 75.4 (*C*CH_3), 36.9 (N*C*H_3), 24.6 (Cb^{CH3}).

HRMS (m/z): $[M+H]^+$ calcd. For $C_8H_{24}B_{11}N_2^+$, 269.2978; found 269.2980.

8. Synthesis of [IMe$_2$-B(H)-Cb^{Me}][B(C$_6$F$_5$)$_4$] (3).



To a solution of **3-H** (260 mg, 0.98 mmol) in *o*-$C_6H_4F_2$ (2.0 mL) was added a solution of $[Ph_3C][B(C_6F_5)_4]$ (850 mg, 0.92 mmol) in *o*-$C_6H_4F_2$ (2.0 mL). The resulting orange solution was stirred at room temperature for 5 min. Subsequently, hexane (6.0 mL) was added to the reaction mixture, leading to formation of an immiscible brown oil at the bottom of the flask. After vigorous stirring of 3 h, the oil was transformed into a yellow precipitate, which was filtered, washed with hexane (5.0 mL) and dried under vacuum, affording **3** as a pale-yellow solid (886 mg, 94 %). Due to the low solubility of **3** in C_6D_5Br, the signals in the $^{13}C\{^1H\}$ NMR spectra of **3** are too weak to give any useful information.

^1H NMR (400 MHz, C_6D_5Br): δ [ppm] = 6.41 (s, 2H), 4.03 (br s, 1H), 3.26 (s, 6H), 1.82 (s, 3H).

$^1H\{^{11}B\}$ NMR (400 MHz, C_6D_5Br): δ [ppm] = 6.41 (s, 2H), 4.05 (br s, 1H), 3.26 (s, 6H), 2.89 (s, 1H, B$H_{carborane}$), 2.71 − 2.23 (m, 6H, B$H_{carborane}$), 2.16 − 1.80 (m, 6H, CCH_3 & B$H_{carborane}$).

^{11}B NMR (160 MHz, *o*-$C_6H_4F_2$): δ [ppm] = 3.1 (br s, 1B), -1.1 (d, J_{B-H} = 143 Hz, 1B), -6.2 (d, J_{B-H} = 139 Hz, 2B), -11.7 (m, 6B), -16.3 (s, $B(C_6F_5)_4$). The signal of the borenium center was not observed.

$^{11}B\{^1H\}$ NMR (160 MHz, *o*-$C_6H_4F_2$): δ [ppm] =3.2 (s, 1B), -1.1 (s, 1B), -6.1 (s, 2B), -11.7 (m, 6B), -16.3 (s, $B(C_6F_5)_4$). The signal of the borenium center was not observed.

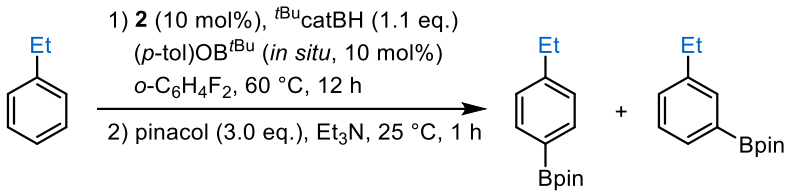
^{19}F NMR (376 MHz, *o*-$C_6H_4F_2$): *δ* [ppm] = -131.9 (m, 8F, C$F_{o\text{-Ph}}$), -161.7 (t, J_{F-F} = 20.8 Hz, 4F, C$F_{p\text{-Ph}}$), -165.8 (t, J_{F-F} = 18.2 Hz, 8F, C$F_{m\text{-Ph}}$).

HRMS (m/z): $[M]^+$ calcd. for $C_8H_{22}B_{11}^+$, 267.2816; found 267.2780.

II. General procedure for borylation of arenes

To a 10-mL flask containing an *o*-$C_6H_4F_2$ (0.2 mL) solution of *p*-cresol (0.05 mmol, 10 mol%) and arene (0.5 mmol, 1.0 equiv) was added a solution of HBcat$^{t\text{Bu}}$ (0.55 mmol, 1.1 equiv.) in *o*-$C_6H_4F_2$ (0.2 mL). Effervescence was immediately observed, and the resulting colorless solution was stirred at 25 °C for 1.0 h. Subsequently, a solution of **2** (0.05 mmol, 10 mol%) in *o*-$C_6H_4F_2$ (0.4 mL) was added to the flask. The reaction mixture was then heated to 60 °C for 12 h and quenched by successive addition of Et_3N (0.5 mL) and pinacol (1.65 mmol, 3.0 equiv.). After one hour of stirring, all volatiles were removed under reduced pressure, and the residue was purified by flash column chromatography over silica gel (eluted with petroleum ether/EtOAc = 70/1) to afford the borylated product. The product is a mixture of *meta*- and *para*-isomers which ratio was determined by the integration of their corresponding signals in the ^{1}H NMR spectrum. The calculation of the yield was based on the amount of arene applied.

Borylation of ethylbenzene.



74%, *para*/*meta* = 7:1

Prepared from **2** (53.8 mg, 0.048 mmol), *p*-cresol (5.8 mg,0.054 mmol), ethylbenzene (55.7 mg, 0.52 mmol) and HBcat$^{t\text{Bu}}$ (101.6 mg, 0.58 mmol) according to the general procedure. The borylation product was isolated as a colorless oil (90.1 mg, 74%).

The product is a mixture of two isomers, whose identities were determined by comparing the ^{1}H NMR spectrum of the product mixture with those reported in the literatures.[6,7] The chemical shifts of each isomer are presented as follows:

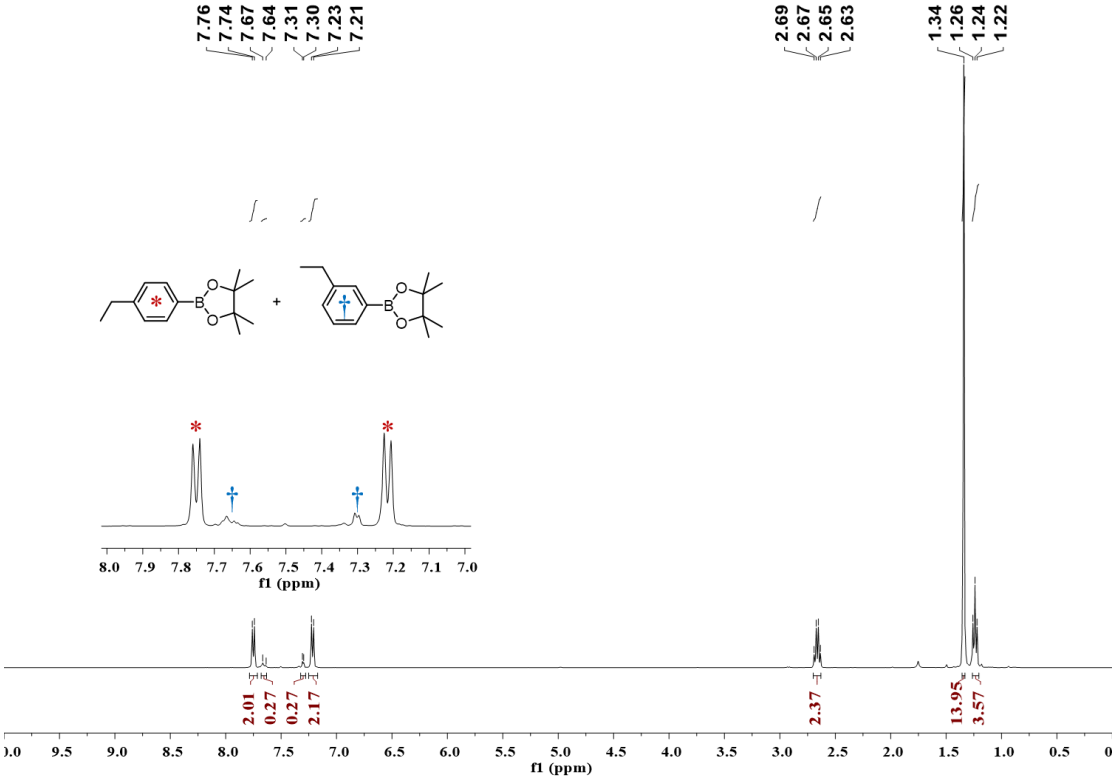


Figure S1. ^{1}H NMR spectrum of the borylation products of ethylbenzene in $CDCl_3$.

Para-isomer:

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.75 (d, *J* = 7.8 Hz, 2H), 7.22 (d, *J* = 7.8 Hz, 2H), 2.66 (q, *J* = 7.7 Hz, 2H), 1.34 (s, 12H), 1.24 (t, *J* = 7.7 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 147.8, 135.0, 127.5, 83.7, 29.2, 25.0, 15.6.

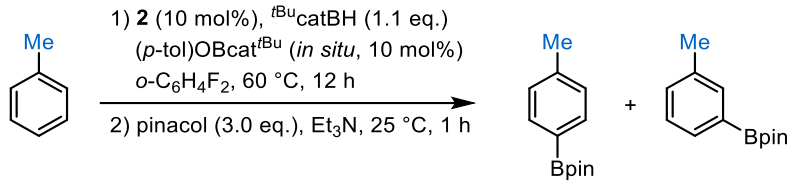
Meta-isomer:

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.67 – 7.64 (m, 2H), 7.31 – 7.30 (m, 2H), 2.66 (q, *J* = 7.7 Hz, 2H), 1.36 (s, 12H), 1.24 (t, *J* = 7.7 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 134.4, 132.2, 131.0, 127.9, 83.7, 28.9, 25.0, 15.8. The *ipso*-carbon was not observed.

HRMS (ESI) *m/z*: Calcd for $C_{14}H_{21}BO_2H^+$ $[M+H]^+$ 233.1715, found 233.1722.

Borylation of toluene.



53%, *para*/*meta* = 5:1

Prepared from **2** (58.8 mg, 0.053 mmol), *p*-cresol (6.0 mg,0.055 mmol), ethylbenzene (49.9 mg, 0.54 mmol) and HBcat$^{t\text{Bu}}$ (104.3 mg, 0.59 mmol) according to the general procedure. The borylation product was isolated as a colorless oil (62.4 mg, 53%).

The product is a mixture of two isomers, whose identities were determined by comparing the ^{1}H NMR spectrum of the product mixture with those reported in the literatures.[8,9] The chemical shifts of each isomer are presented as follows:

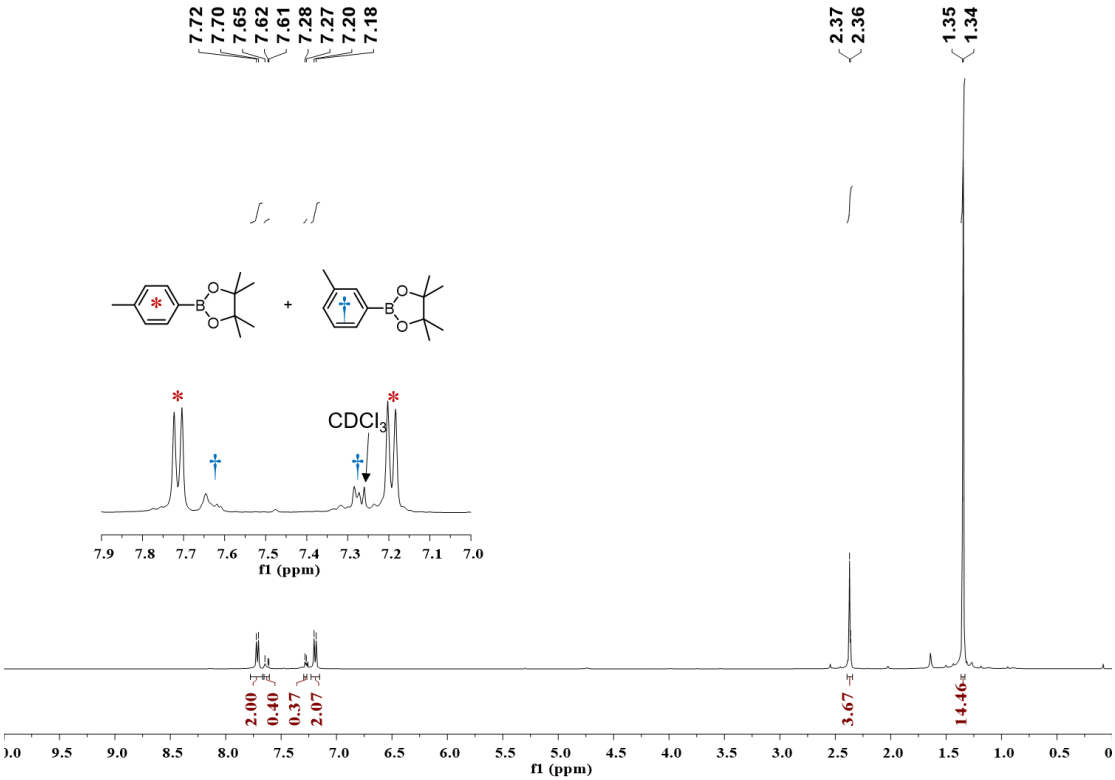


Figure S2. ^{1}H NMR spectrum of the borylation products of toluene in $CDCl_3$.

Para-isomer:

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.71 (d, *J* = 7.7 Hz, 2H), 7.19 (d, *J* = 7.7 Hz, 2H), 2.37 (s, 3H), 1.34 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 141.5, 134.9, 128.7, 83.8, 25.0, 21.9.

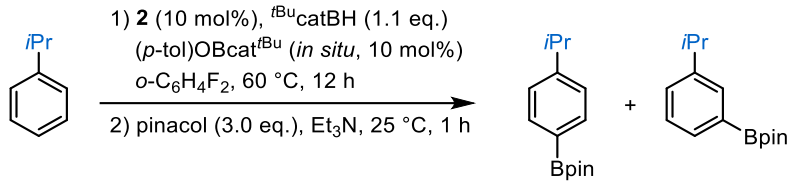
Meta-isomer:

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.65 – 7.61 (m, 2H), 7.28 – 7.27 (m, 2H), 2.36 (s, 3H), 1.35 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 137.3, 135.5, 132.2, 131.9, 127.8, 83.9, 25.0, 21.4.

HRMS (ESI) *m/z*: Calcd for $C_{13}H_{19}BO_2H^+$ $[M+H]^+$ 219.1559, found 219.1568.

Borylation of cumene.



74%, *para*/*meta* = 6:1

Prepared from **2** (55.6 mg, 0.050 mmol), *p*-cresol (5.6 mg,0.052 mmol), cumene (61.2 mg, 0.51 mmol) and HBcat$^{t\text{Bu}}$ (98.7 mg, 0.56 mmol) according to the general procedure. The borylation product was isolated as a white solid (92.6 mg, 74%).

The product is a mixture of two isomers, whose identities were determined by comparing the ^{1}H NMR spectrum of the product mixture with those reported in the literatures.[8,9] The chemical shifts of each isomer are presented as follows:

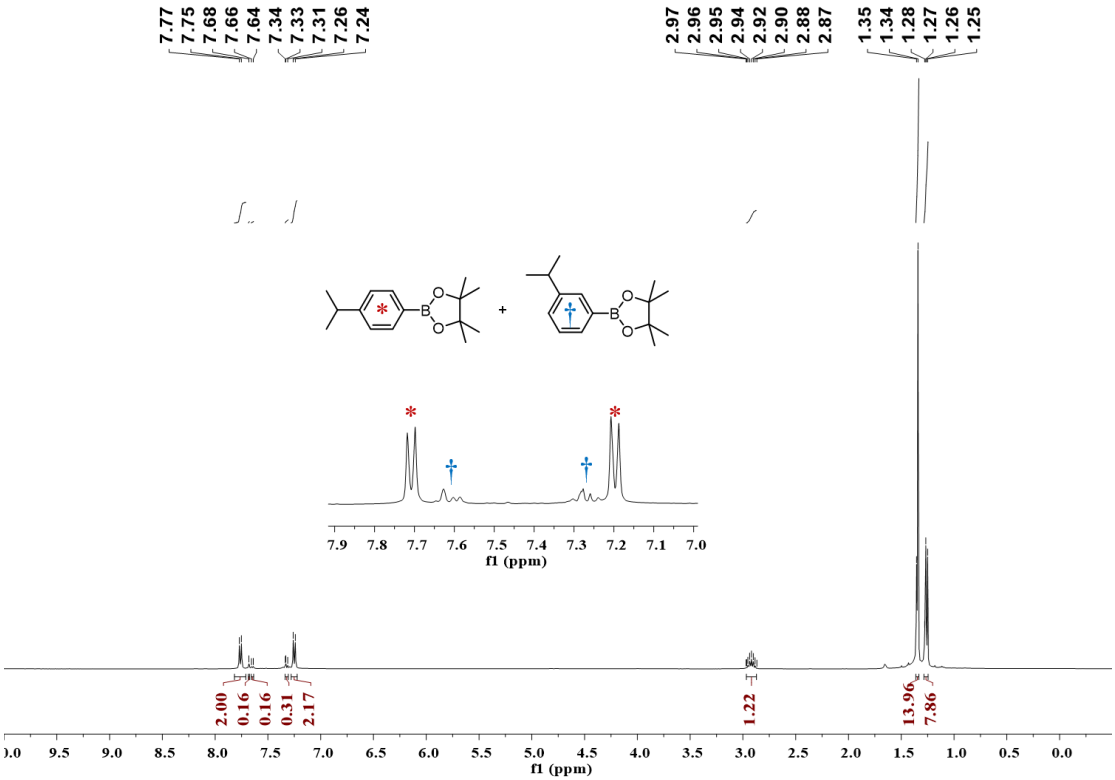


Figure S3. ^{1}H NMR spectrum of the borylation products of cumene in $CDCl_3$.

Para-isomer:

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.76 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 2.94 (m, 1H), 1.34 (s, 12H), 1.26 (d, *J* = 6.9 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 152.4, 135.1, 126.0, 83.8, 34.5, 25.0, 24.0.

HRMS (ESI) *m/z*: Calcd for $C_{15}H_{24}BO_2^+$ [M+H]$^+$ 247.1872, found 247.1858.

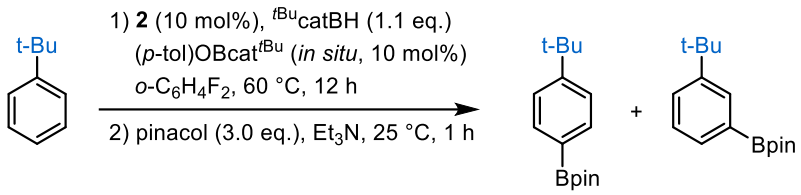
Meta-isomer:

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.68 (s, 1H), 7.65 (d, *J* = 6.7 Hz, 1H), 7.34–7.30 (m, 2H), 2.92 (m, 1H), 1.35 (s, 12H), 1.27 (d, *J* = 6.9 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 148.2, 133.0, 132.5, 129.5, 127.9, 83.7, 34.3, 25.0, 24.2.

HRMS (ESI) *m/z*: Calcd for $C_{15}H_{24}BO_2^+$ [M+H]$^+$ 247.1872, found 247.1858.

Borylation of *t*-butylbenzene.



80%, *para*/*meta* = 10:1

Prepared from **2** (57.2 mg, 0.052 mmol), *p*-cresol (6.5 mg, 0.060 mmol), *t*-butylbenzene (67.8 mg, 0.51 mmol) and HBcat$^{t\text{Bu}}$ (99.0 mg, 0.56 mmol) according to the general procedure. The borylation product was isolated as a white solid (104.8 mg, 80%).

The product is a mixture of two isomers, whose identities were determined by comparing the ^{1}H NMR spectrum of the product mixture with those reported in the literatures.[10,11] The chemical shifts of each isomer are presented as follows:

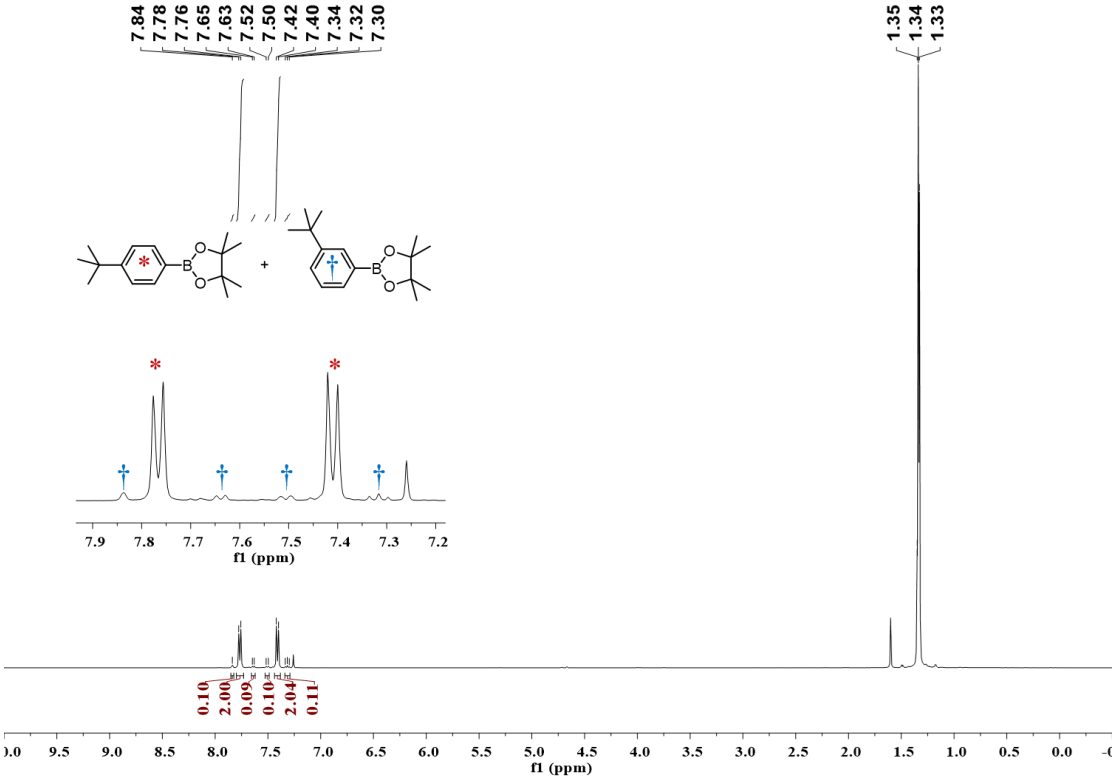


Figure S4. ^{1}H NMR spectrum of the borylation products of *t*-butylbenzene in $CDCl_3$.

Para-isomer:

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.77 (d, *J* = 8.1 Hz, 2H), 7.41 (d, *J* = 8.1 Hz, 2H), 1.34 (s, 12H), 1.33 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 154.6, 134.8, 124.8, 83.7, 35.0, 31.3, 25.0.

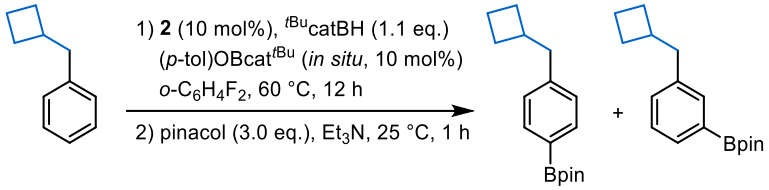
Meta-isomer:

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.84 (s, 1H), 7.64 (d, *J* = 7.3 Hz, 1H), 7.51 (d, *J* = 8.1 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 1.35 (s, 12H), 1.34 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 150.4, 132.2, 131.5, 128.5, 127.6, 83.8, 34.8, 31.6, 25.0.

HRMS (ESI) *m/z*: Calcd for $C_{16}H_{26}BO_2^+$ [M+H]$^+$ 261.2029, found 261.2042.

Borylation of (cyclobutylmethyl)benzene.



61%, *para*/*meta* = 5:1

Prepared from **2** (55.6 mg, 0.050 mmol), *p*-cresol (6.2 mg, 0.057 mmol), (cyclobutylmethyl)benzene (71.5 mg, 0.49 mmol) and HBcat$^{t\text{Bu}}$ (96.5 mg, 0.55 mmol) according to the general procedure. The borylation product was isolated as a colorless oil (80.6 mg, 61%).

The product was a mixture of two isomers, whose identities were determined by a series of 2D NMR analysis. The ratio of the two isomers was determined by the integration of their corresponding signals in the ^{1}H NMR spectrum. The chemical shifts of each isomer are presented as follows:

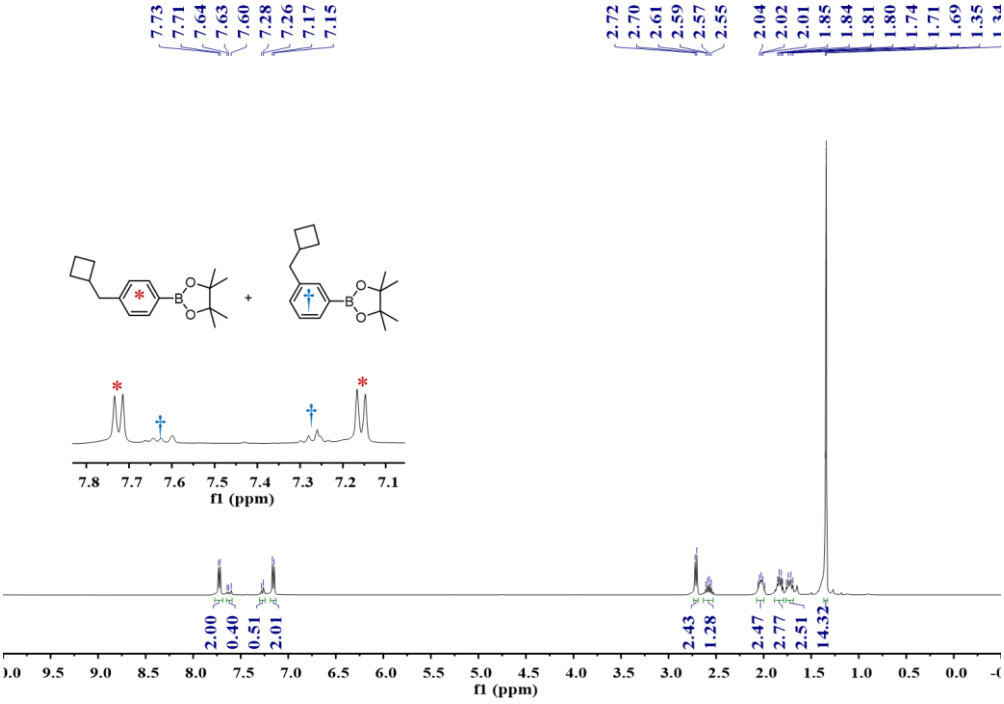


Figure S5. ^{1}H NMR spectrum of the borylation products of (cyclobutylmethyl)benzene in $CDCl_3$.

Para-isomer:

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.72 (d, *J* = 7.9 Hz, 2H), 7.16 (d, *J* = 7.9 Hz, 2H), 2.71 (d, *J* = 7.3 Hz, 2H), 2.61–2.55 (m, 1H), 2.06–1.99 (m, 2H), 1.85–1.80 (m, 2H), 1.76–1.69 (m, 2H), 1.34 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): 144.9, 134.9, 128.2, 83.7, 43.3, 37.3, 28.3, 25.0, 18.5.

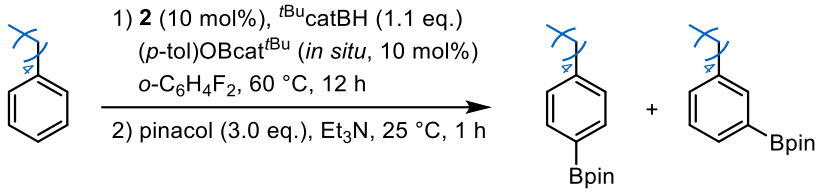
Meta-isomer:

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.64–7.60 (m, 2H), 7.28–7.26 (m, 2H), 2.71 (d, *J* = 7.3 Hz, 2H), 2.61–2.55 (m, 1H), 2.06–1.99 (m, 2H), 1.85–1.80 (m, 2H), 1.76–1.69 (m, 2H), 1.35 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): 144.9, 134.9, 128.2, 83.7, 43.3, 37.3, 28.3, 25.0, 18.5.

HRMS (ESI) *m/z*: Calcd for $C_{17}H_{26}BO_2^+$ [M+H]$^+$ 273.2029, found 273.2034.

Borylation of *n*-amylbenzene.



73%, *para*/*meta* = 5:1

Prepared from **2** (54.3 mg, 0.049 mmol), *p*-cresol (6.3 mg, 0.058 mmol), *n*-amylbenzene (71.2 mg, 0.48 mmol) and HBcat$^{t\text{Bu}}$ (93.8 mg, 0.53 mmol) according to the general procedure. The borylation product was isolated as a colorless oil (96.6 mg, 73%).

The product is a mixture of two isomers, whose identities were determined by comparing the ^{1}H NMR spectrum of the product mixture with those reported in the literatures.[12,13] The chemical shifts of each isomer are presented as follows:

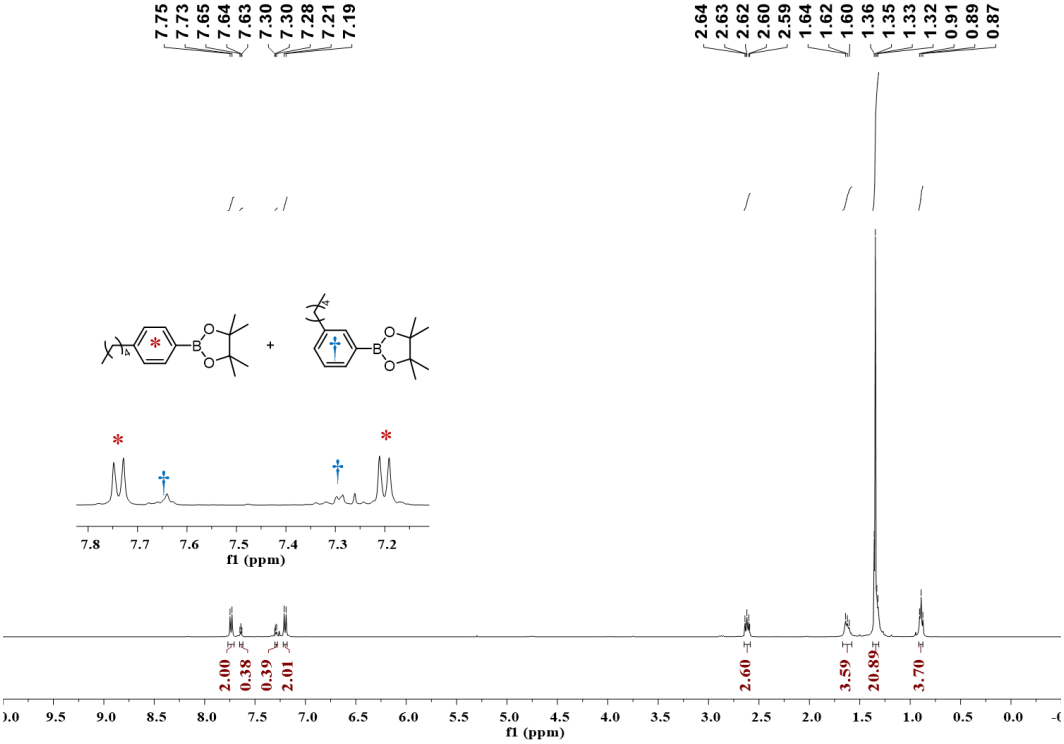


Figure S6. ^{1}H NMR spectrum of the borylation products of *n*-amylbenzene in $CDCl_3$.

Para-isomer:

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.74 (d, *J* = 8.0 Hz, 2H), 7.20 (d, J = 8.0 Hz, 2 H), 2.62 (t, *J* = 7.7 Hz, 2H), 1.64–1.60 (m, 2H), 1.35 (s, 12H), 1.34–1.30 (m, 4 H), 0.89 (t, *J* = 6.8 Hz, 3 H)

^{13}C NMR (100 MHz, $CDCl_3$): 146.6, 134.9, 128.0, 83.7, 36.3, 31.6, 31.2, 25.0, 22.7, 14.2.

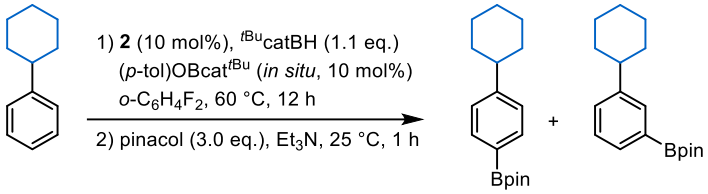
Meta-isomer:

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.65–7.63 (m, 2H), 7.30–7.28 (m, 2H), 2.61 (t, *J* = 7.7 Hz, 2H), 1.64–1.60 (m, 2H), 1.36 (s, 12H), 1.34–1.30 (m, 4 H), 0.89 (t, *J* = 6.8 Hz, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): 142.4, 134.9, 132.2, 131.5, 127.8, 83.8, 36.1, 31.8, 31.5, 25.0, 22.7, 14.3.

HRMS (ESI) *m/z*: Calcd for $C_{17}H_{28}BO_2^+$ $[M+H]^+$ 275.2185, found 275.2207.

Borylation of cyclohexylbenzene.



56%, *para*/*meta* = 6:1

Prepared from **2** (51.4 mg, 0.046 mmol), *p*-cresol (5.1 mg, 0.047 mmol), cyclohexylbenzene (79.8 mg, 0.50 mmol) and HBcat$^{t\text{Bu}}$ (97.1 mg, 0.55 mmol) according to the general procedure. The borylation product was isolated as a colorless oil (78.5 mg, 56%).

The product is a mixture of two isomers, whose identities were determined by comparing the ^{1}H NMR spectrum of the product mixture with those reported in the literatures.[14] The chemical shifts of each isomer are presented as follows:

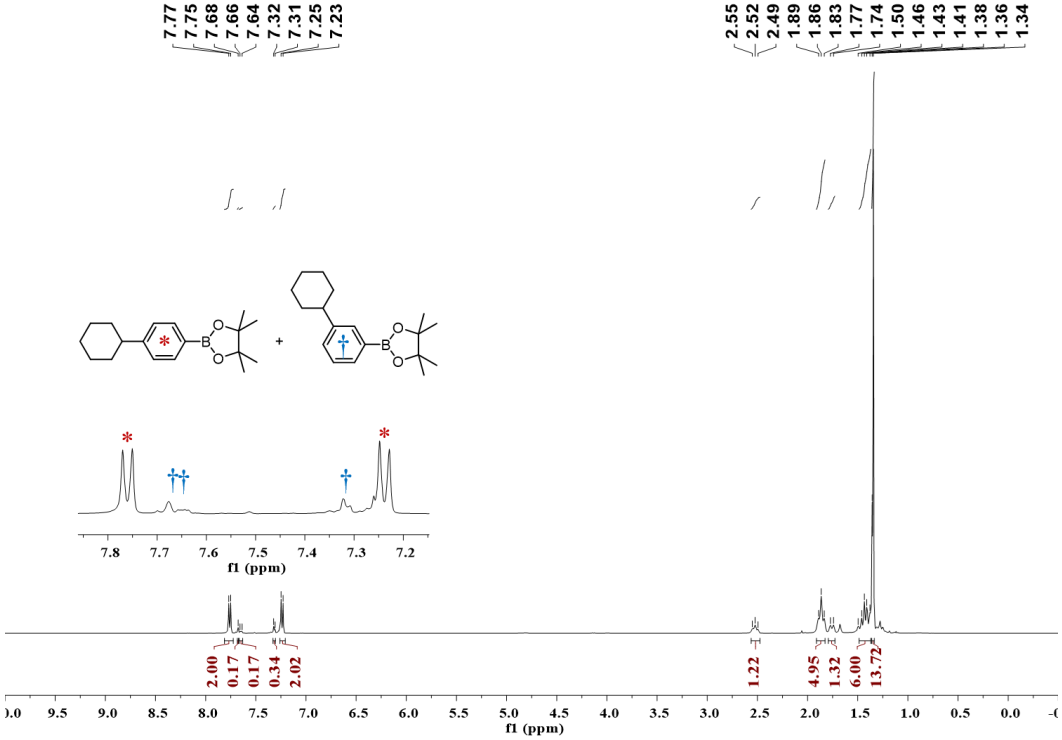


Figure S7. ^{1}H NMR spectrum of the borylation products of cyclohexylbenzene in $CDCl_3$.

Para-isomer:

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.76 (d, *J* = 7.9 Hz, 2H), 7.24 (d, J = 7.9 Hz, 2H), 2.55–2.49 (m, 1H), 1.89–1.83 (m, 4H), 1.77–1.74 (m, 1H), 1.50–1.38 (m, 5H), 1.34 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): 151.6, 135.0, 126.5, 83.7, 45.0, 34.4, 27.0, 26.3, 25.0.

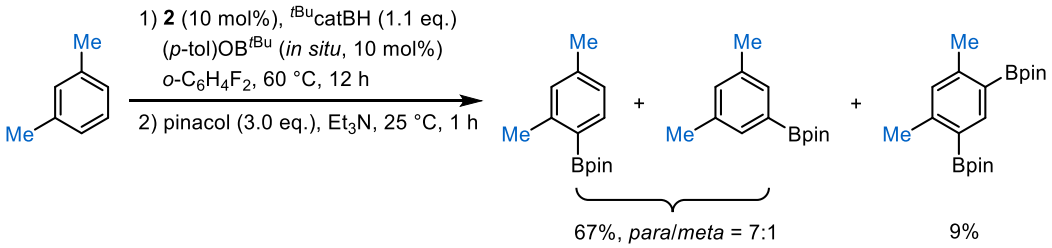
Meta-isomer:

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.68 (s, 1H), 7.66–7.64 (m, 1H), 7.32–7.31 (m, 2H), 2.55–2.49 (m, 1H), 1.89–1.83 (m, 4H), 1.77–1.74 (m, 1H), 1.50–1.38 (m, 5H), 1.36 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): 147.4, 133.4, 132.5, 129.9, 127.9, 83.8, 44.8, 34.5, 27.1, 26.3, 25.0.

HRMS (ESI) *m/z*: Calcd for $C_{18}H_{28}BO_2^+$ $[M+H]^+$ 287.2186, found 287.2181.

Borylation of *m*-xylene.



Prepared from **2** (54.9 mg, 0.049 mmol), *p*-cresol (5.4 mg, 0.050 mmol), *m*-xylene (54.8 mg, 0.52 mmol) and HBcat$^{t\text{Bu}}$ (107.6 mg, 0.61 mmol) according to the general procedure. The *mono*-borylated product was isolated as a colorless oil (79.8 mg, 67%), and 4,6-*di*-borylated product was also isolated as a colorless oil (9.5 mg, 9%).

The *mono*-borylated product is a mixture of two isomers, whose identities were determined by comparing the ^{1}H NMR spectrum of the product mixture with those reported in the literatures.[6, 15] The chemical shifts of each *mono*-borylated isomer are presented as follows:

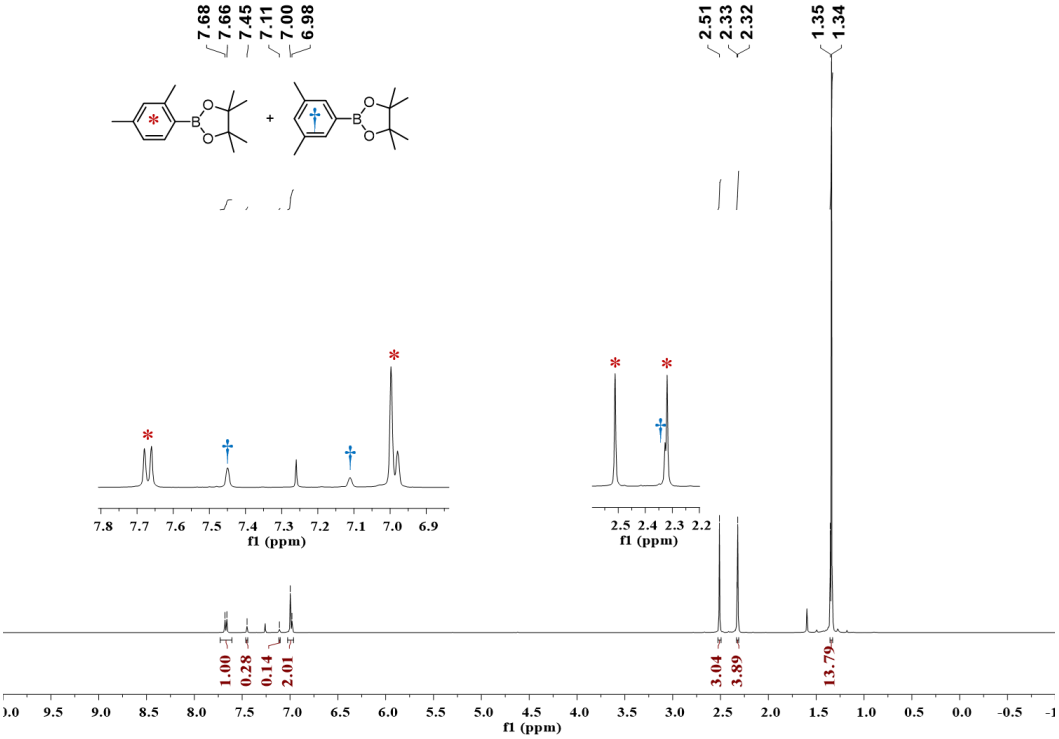


Figure S8. ^{1}H NMR spectrum of the *mono*-borylated products of *m*-xylene in $CDCl_3$.

2-(2,4-dimethylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.67 (d, *J* = 8.1 Hz, 1H), 7.00–6.98 (m, 2H), 2.51 (s, 3H), 2.32 (s, 3H), 1.34 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 145.1, 141.0, 136.2, 130.9, 125.7, 83.4, 25.0, 22.3, 21.6.

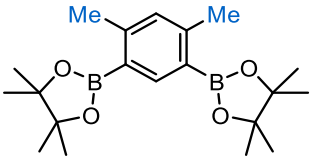
2-(3,5-dimethylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.45 (s, 2H), 7.11 (s, 1H), 2.33 (s, 6H), 1.35 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 137.3, 133.1, 132.5, 83.8, 25.0, 21.3.

HRMS (ESI) *m/z*: Calcd for $C_{14}H_{22}BO_2^+$ $[M+H]^+$ 233.1715, found 233.1722.

1,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,4-dimethylbenzene



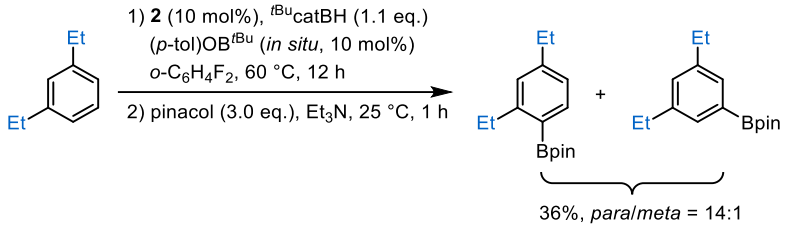
Prepared from **2** (55.5 mg, 0.050 mmol), *p*-cresol (5.5 mg, 0.051 mmol), *m*-xylene (53.1 mg, 0.50 mmol) and HBcat$^{t\text{Bu}}$ (221.0 mg, 1.26 mmol) according to the general procedure. The 4,6-*di*-borylated product was isolated as a colorless oil (125.1 mg, 70%). NMR data are in agreement with literature.[16]

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 8.13 (s, 1H), 6.98 (s, 1H), 2.51 (s, 6H), 1.34 (s, 24H).

^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 147.9, 143.8, 131.7, 83.3, 25.0, 22.5.

HRMS (ESI) *m/z*: Calcd for $C_{20}H_{32}B_2O_4Na^+$ $[M+Na]^+$ 381.2392, found 381.2391.

Borylation of 1,3-diethylbenzene.



Prepared from **2** (49.8 mg, 0.045 mmol), *p*-cresol (5.3 mg, 0.049 mmol), 1,3-diethylbenzene (67.9 mg, 0.51 mmol) and HBcat$^{t\text{Bu}}$ (101.3 mg, 0.58 mmol) according to the general procedure. The borylation product was isolated as a colorless oil (47.8 mg, 36%).

The product was a mixture of two isomers, whose identities were determined by a series of 2D NMR analysis. The ratio of the two isomers was determined by the integration of their corresponding signals in the ^{1}H NMR spectrum. The chemical shifts of each isomer are presented as follows:

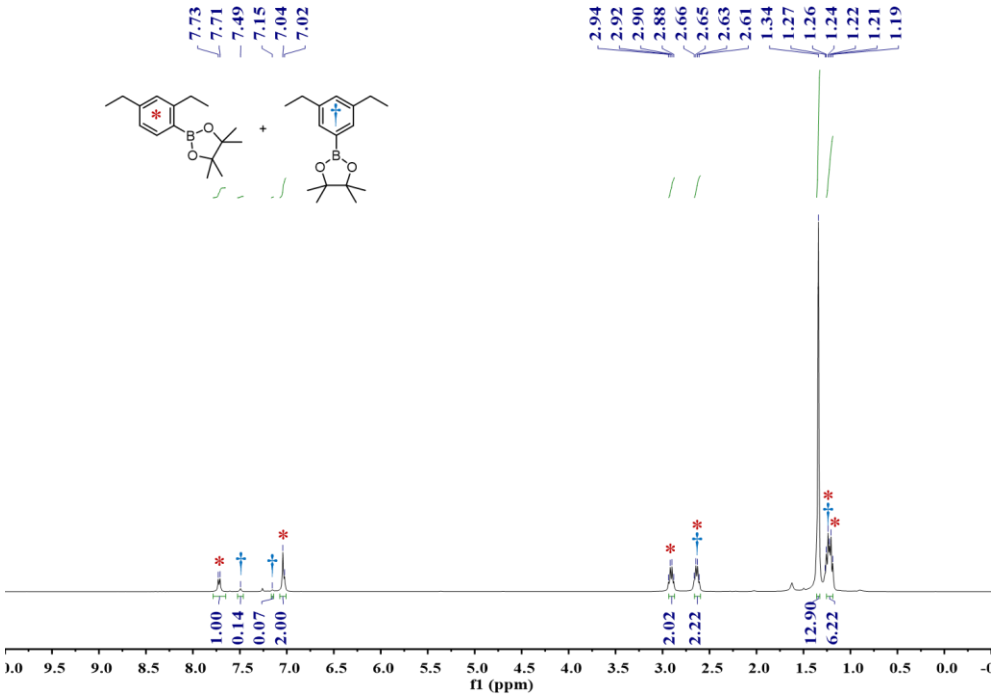


Figure S9. ^{1}H NMR spectrum of the *mono*-borylated products of 1,3-diethylbenzene in $CDCl_3$.

2-(2,4-diethylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.72 (d, *J* = 7.6 Hz, 1H), 7.07–7.01 (m, 2H), 2.91 (q, *J* = 7.3 Hz, 2H), 2.64 (q, *J* = 7.3 Hz, 2H), 1.34 (s, 12H), 1.26 (t, *J* = 7.3 Hz, 3H), 1.21 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 151.8, 147.5, 136.5, 128.3, 124.6, 83.3, 29.1, 29.0, 25.0, 17.4, 15.6.

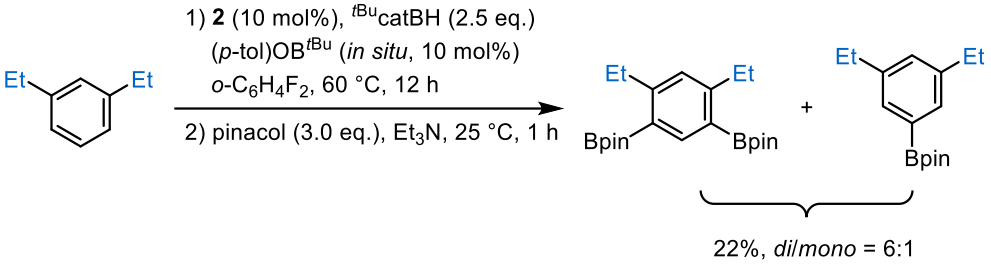
2-(3,5-diethylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.49 (s, 2H), 7.15 (s, 1H), 2.64 (q, *J* = 7.3 Hz, 2H), 1.34 (s, 12H), 1.26 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 143.7, 131.8, 130.8, 83.8, 28.9, 25.0, 15.9.

HRMS (ESI) *m/z*: Calcd for $C_{16}H_{25}BO_2Na^+$ [M+Na]$^+$ 283.1848, found 283.1840.

Di-borylation of 1,3-diethylbenzene.



Prepared from **2** (54.0 mg, 0.049 mmol), *p*-cresol (5.4 mg, 0.050 mmol), 1,3-diethylbenzene (67.7 mg, 0.50 mmol) and HBcat$^{t\text{Bu}}$ (220.3 mg, 1.25 mmol) according to the general procedure. The borylated product was isolated as a colorless oil (43.6 mg, 22%).

The product is a mixture of the 4,6-*di*-borylated product (major) and the 5-*mono*-borylated product (minor). The identity of the latter was confirmed by comparing its ^{1}H NMR spectrum with that found for the *mono*-borylation of 1,3-diethylbenzene. The ratio of the two component was determined by the integration of their corresponding signals in the ^{1}H NMR spectrum. The chemical shifts of each component are presented as follows:

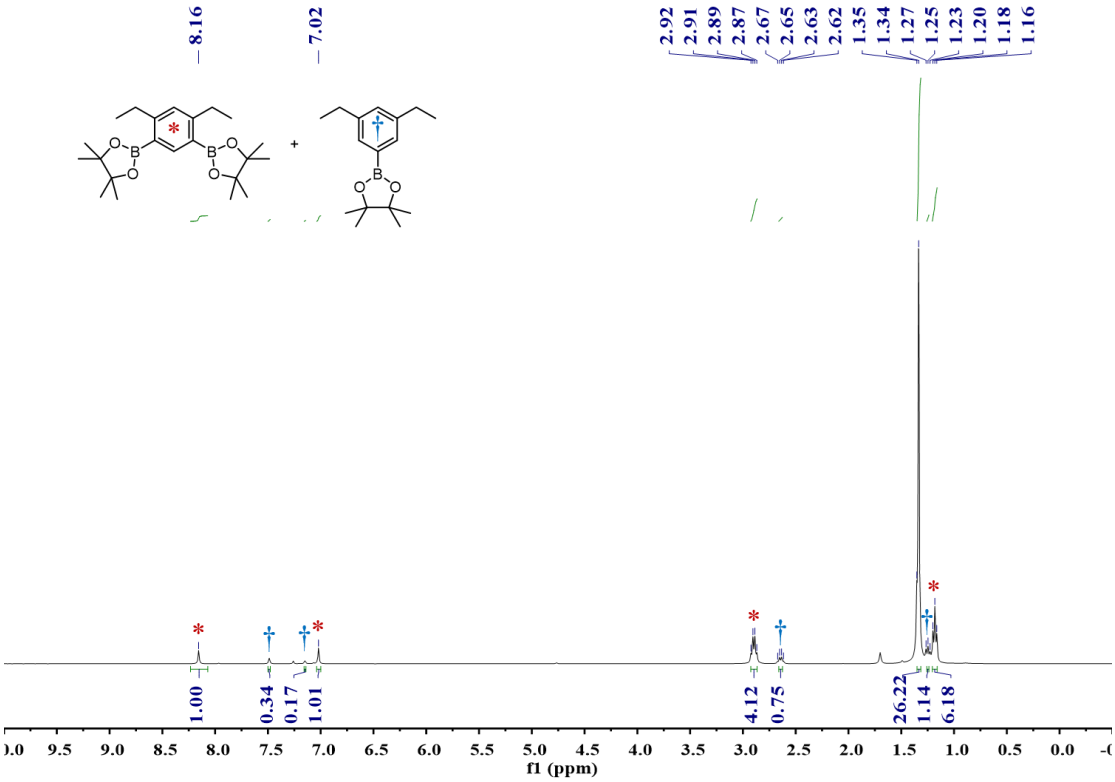


Figure S10. ^{1}H NMR spectrum of the borylated products of 1,3-diethylbenzene in $CDCl_3$.

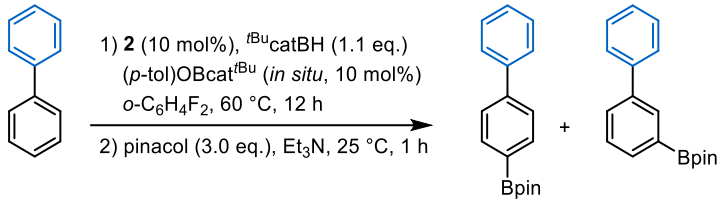
2,2'-(4,6-diethyl-1,3-phenylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 8.16 (s, 1H), 7.02 (s, 1H), 2.90 (q, *J* = 7.4 Hz, 4H), 1.34 (s, 12H), 1.18 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 154.7, 144.3, 129.0, 83.2, 29.2, 25.0, 17.2.

HRMS (ESI) *m/z*: Calcd for $C_{22}H_{36}B_2O_4Na^+$ $[M+Na]^+$ 409.2705, found 409.2707.

Borylation of biphenyl.



66%, *para*/*meta* = 17:1

Prepared from **2** (55.5 mg, 0.050 mmol), *p*-cresol (5.6 mg,0.052 mmol), biphenyl (77.9 mg, 0.50 mmol) and HBcat$^{t\text{Bu}}$ (97.7 mg, 0.55 mmol) according to the general procedure. The borylation product was isolated as a colorless oil (93.2 mg, 66%).

The product is a mixture of two isomers, whose identities were determined by comparing the ^{1}H NMR spectrum of the product mixture with those reported in the literatures.[17] The chemical shifts of each isomer are presented as follows:

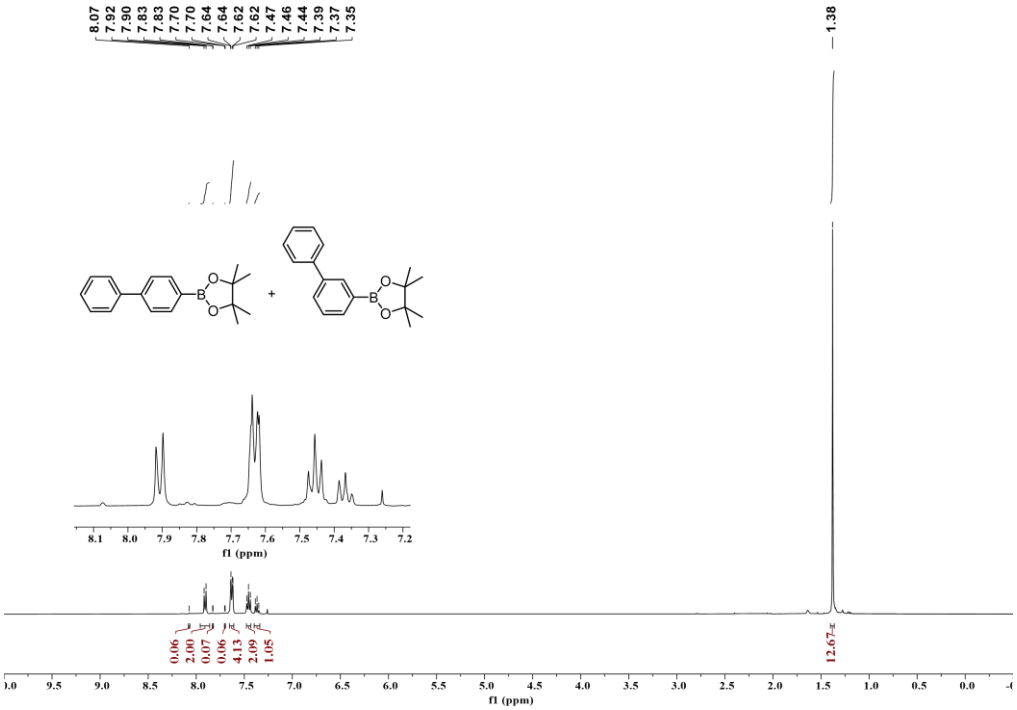


Figure S11. ^{1}H NMR spectrum of the borylated products of biphenyl in $CDCl_3$.

Para-isomer:

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.91 (d, *J* = 8.2 Hz, 2H), 7.64–7.62 (m, 4H), 7.47–7.44 (m, 2H), 7.37 (t, *J* = 7.8 Hz, 1H), 1.38 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 144.0, 141.2, 135.4, 128.8, 127.7, 127.4, 126.6, 84.0, 25.0.

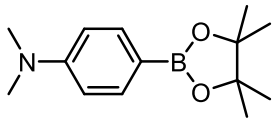
Meta-isomer:

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 8.07 (s, 1H), 7.83 (d, *J* = 7.4 Hz, 1H), 7.70 (d, *J* = 8.2 Hz, 1H), 7.64–7.62 (m, 2H), 7.47–7.44 (m, 3H), 7.37–7.35 (m, 1H), 1.38 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 141.2, 133.8, 133.7, 130.1, 128.9, 128.3, 127.4, 84.0, 25.0. Due to the low yield of *meta*-isomer, some signals in the ^{13}C{^{1}H} NMR spectra are too weak to be identified.

HRMS (ESI) *m/z*: Calcd for $C_{18}H_{22}BO_2^+$ [M+H]$^+$ 281.1716, found 281.1722.

N,N-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline



Prepared from **2** (54.1 mg, 0.045 mmol), N,N-dimethylaniline (54.1 mg, 0.45 mmol) and HBcat^{tBu} (86.4 mg, 0.49 mmol) according to the general procedure. The 4-borylated product was isolated as a white solid (68.0 mg, 65%). The chemical shifts are consistent with those reported in the literature.[18]

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.70 (d, *J* = 8.7 Hz, 2H), 6.70 (d, *J* = 8.7 Hz, 2H), 2.99 (s, 6H), 1.33 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 152.7, 136.3, 111.4, 83.3, 40.2, 25.0.

HRMS (ESI) *m/z*: Calcd for $C_{14}H_{23}BNO_2$ $[M+H]^+$ 248.1824, found 248.1834.

III. Procedure for borylation of polystyrene

To a 10-mL flask containing an *o*-$C_6H_4F_2$ (0.2 mL) solution of *p*-cresol (5.5 mg, 0.051 mmol, 10 mol%) was added a solution of $HBcat^{tBu}$ (97.1 mg, 0.55 mmol, 1.1 equiv.) in *o*-$C_6H_4F_2$ (0.4 mL). Effervescence was immediately observed, and the resulting colorless solution was stirred at 25 °C for 1.0 h. Subsequently, laboratory-grade polystyrene sample (52.0 mg) and a solution of **2** (55.7mg, 0.050 mmol, 10 mol%) in *o*-$C_6H_4F_2$ (0.4 mL) was added to the flask. The reaction mixture was then heated to 60 °C for 12 h and quenched by successive addition of Et_3N (0.5 mL) and pinacol (1.65 mmol, 3.0 equiv.). After one hour of stirring, all volatiles were removed under reduced pressure. The residue was then added CH_3OH (2.0 mL), followed by ultrasonication at room temperature for 10 minutes. The resultant suspension was filtered, and the filtrate was collected and dried at 60°C for 4 hours, yielding a white solid product (65.0 mg). The identities and regio-selectivity of the borylated phenyl rings in the product of the polystyrene borylation reaction were determined by comparing the ^{1}H NMR spectrum of the product with those previously reported in the literature.[19] The mol% of Bpin functionalized styrene unit was calculated from the ^{1}H NMR spectrum.

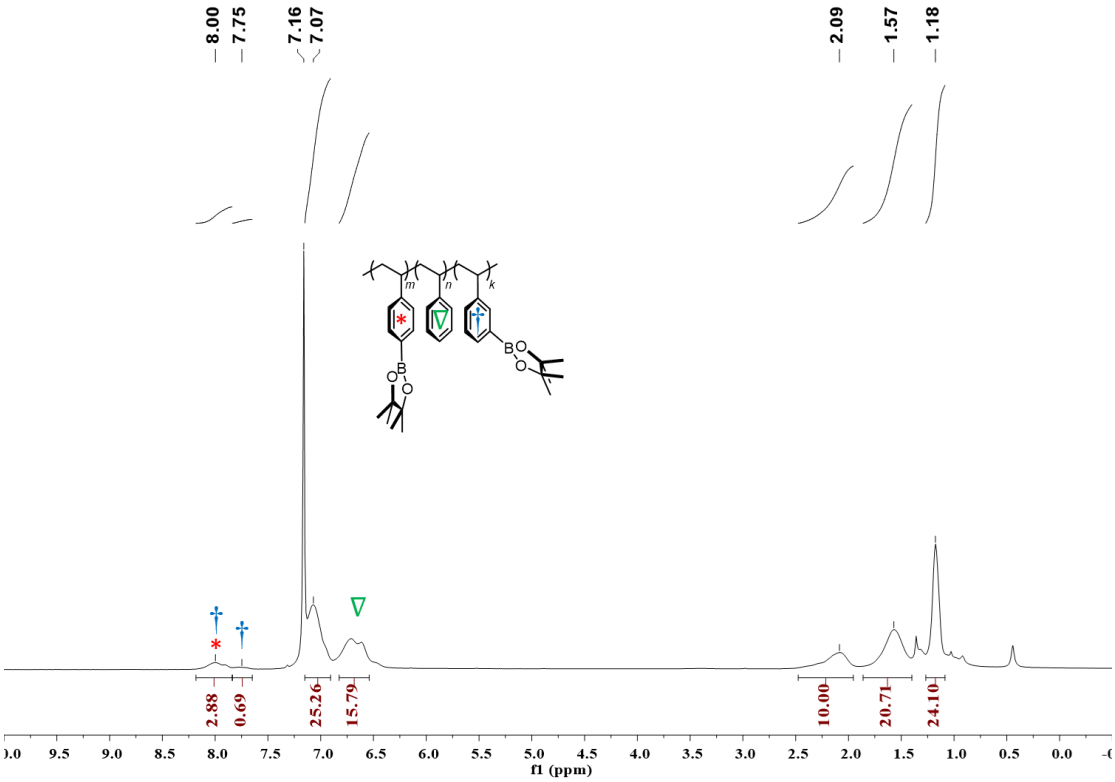
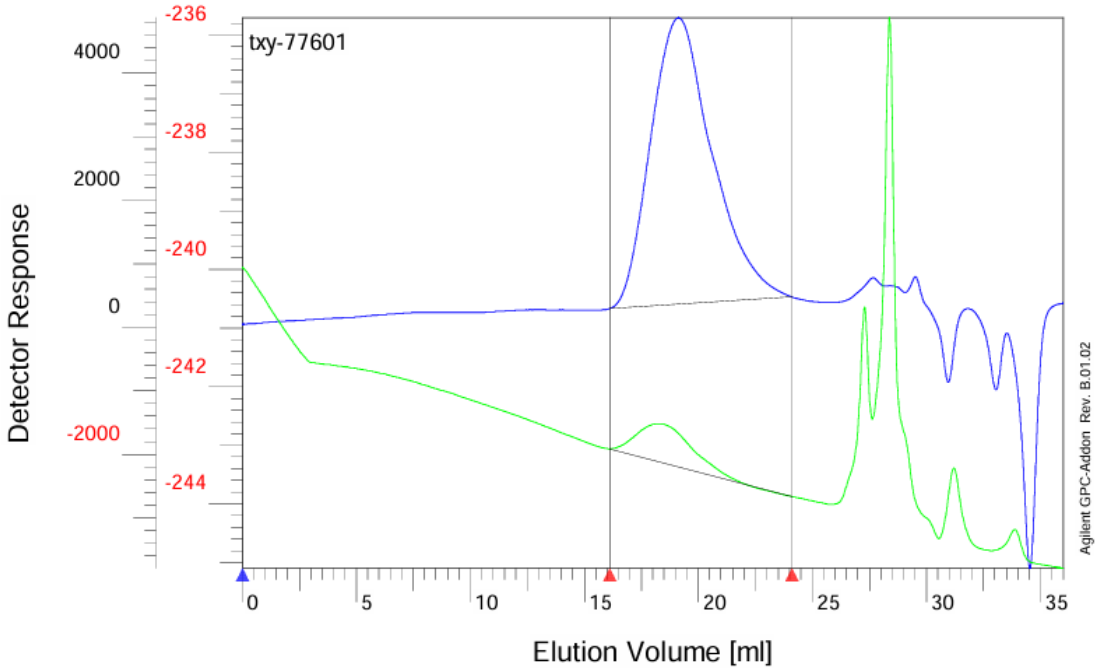
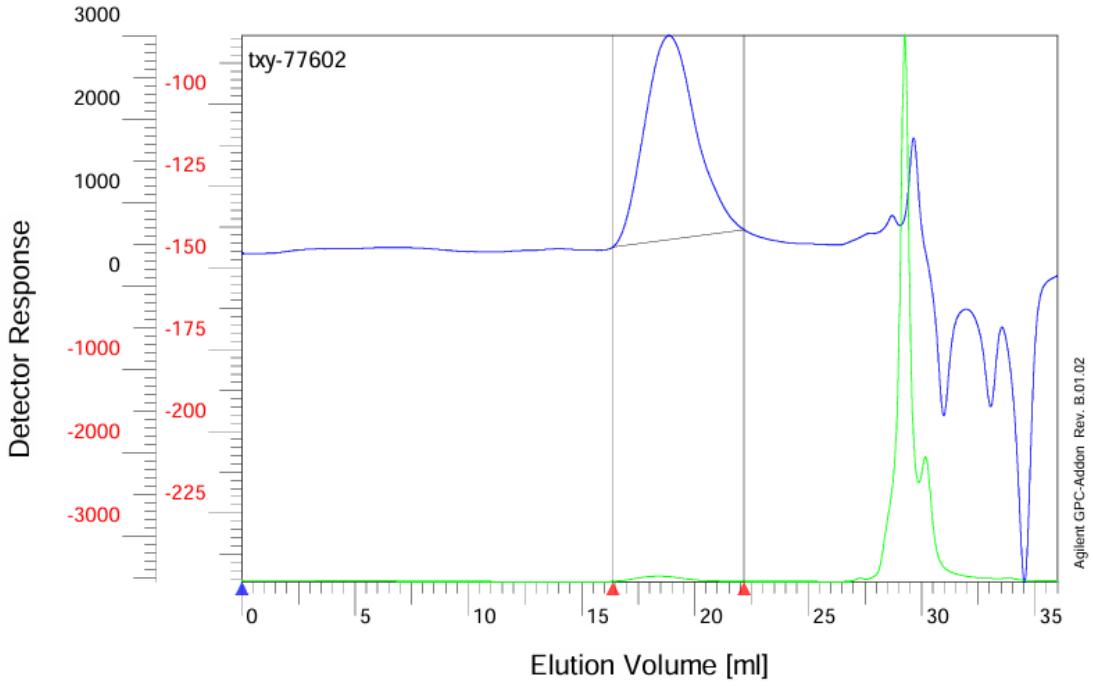


Figure S12. ^{1}H NMR spectrum of the borylated product from the borylation of laboratory-grade polystyrene in C_6D_6.



	RID1A	VWD1A	
Mn :	9.3942e4	1.7133e5	g/mol
Mw :	1.9368e5	2.9515e5	g/mol
Mz :	3.2915e5	4.5340e5	g/mol
Mv :	0.000000	0.000000	g/mol
D :	2.0617e0	1.7227e0	
[n]:	0.000000	0.000000	ml/g
Vp :	1.9123e1	1.8511e1	ml
Mp :	1.6716e5	2.5446e5	g/mol
A :	1.4096e4	1.8623e0	ml*V
10%	4.3584e4	8.1795e4	g/mol
30%	9.2465e4	1.5519e5	g/mol
50%	1.4729e5	2.3527e5	g/mol
70%	2.2726e5	3.5198e5	g/mol
90%	4.0534e5	5.9306e5	g/mol

Figure S13. GPC trace of laboratory-grade polystyrene



	RID1A	VWD1A	
Mn :	1.4578e5	1.9614e5	g/mol
Mw :	2.3112e5	3.0202e5	g/mol
Mz :	3.4053e5	4.2551e5	g/mol
Mv :	0.000000	0.000000	g/mol
D :	1.5854e0	1.5398e0	
[n]:	0.000000	0.000000	ml/g
Vp :	1.8843e1	1.8406e1	ml
Mp :	2.0237e5	2.7379e5	g/mol
A :	6.3577e3	4.1442e0	ml*V
10%	7.3430e4	1.0099e5	g/mol
30%	1.2985e5	1.7612e5	g/mol
50%	1.8905e5	2.5403e5	g/mol
70%	2.7282e5	3.6198e5	g/mol
90%	4.4671e5	5.7454e5	g/mol

Figure S14. GPC trace of the borylated product from the borylation of laboratory-grade polystyrene

IV. Confirmation of dihydrogen formation

To a 10-mL flask containing an *o*-$C_6H_4F_2$ (0.2 mL) solution of *p*-cresol (5.5 mg, 0.050 mmol, 10 mol%) was added a solution of HBcat$^{t\text{Bu}}$ (100.7 mg, 0.57 mmol, 1.1 equiv.) in *o*-$C_6H_4F_2$ (0.2 mL). Effervescence was immediately observed, and the resulting colorless solution was stirred at 25 °C. After stirring for 1 h, the system was degassed with three freeze-pump-thaw cycles. Subsequently, a solution of the borenium catalyst **2** (53.5mg, 0.048 mmol, 10 mol%) and ethylbenzene substrate (55.3mg, 0.52 mmol, 1.0 equiv) were then added, and the reaction flask was sealed and heated at 60 °C for 12 hours. After cooling the reaction mixture to 25 °C, the headspace content was analyzed by GC/FID.

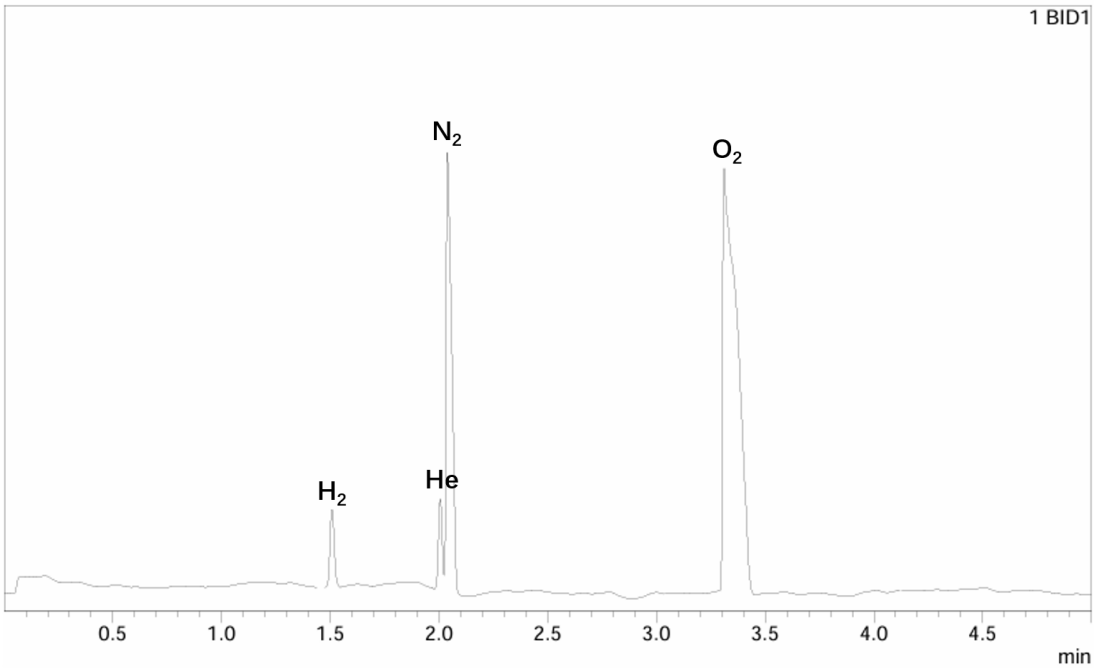


Figure S15. GC data for the headspace gas

V. References

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VI. NMR spectra

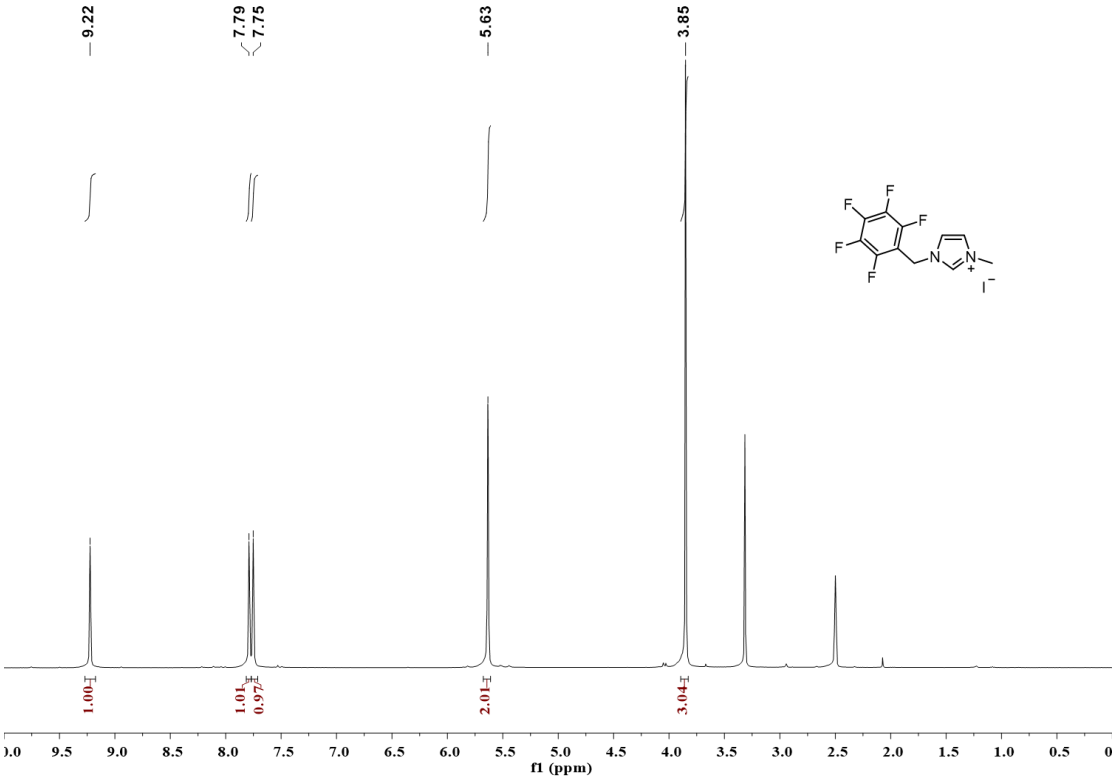

Figure S15. ^{1}H NMR spectrum of **IBn^{F}Me·HI** in DMSO-d_6.

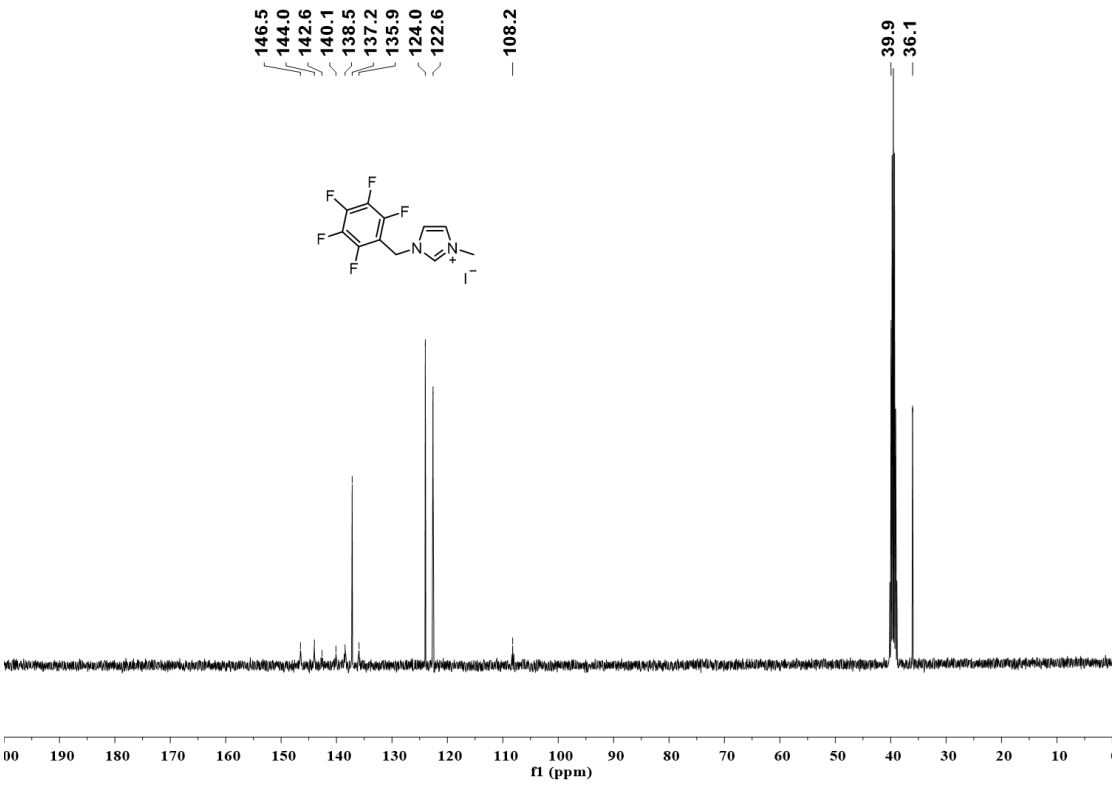

Figure S16. ^{13}C NMR spectrum of **IBn^{F}Me·HI** in DMSO-d_6.

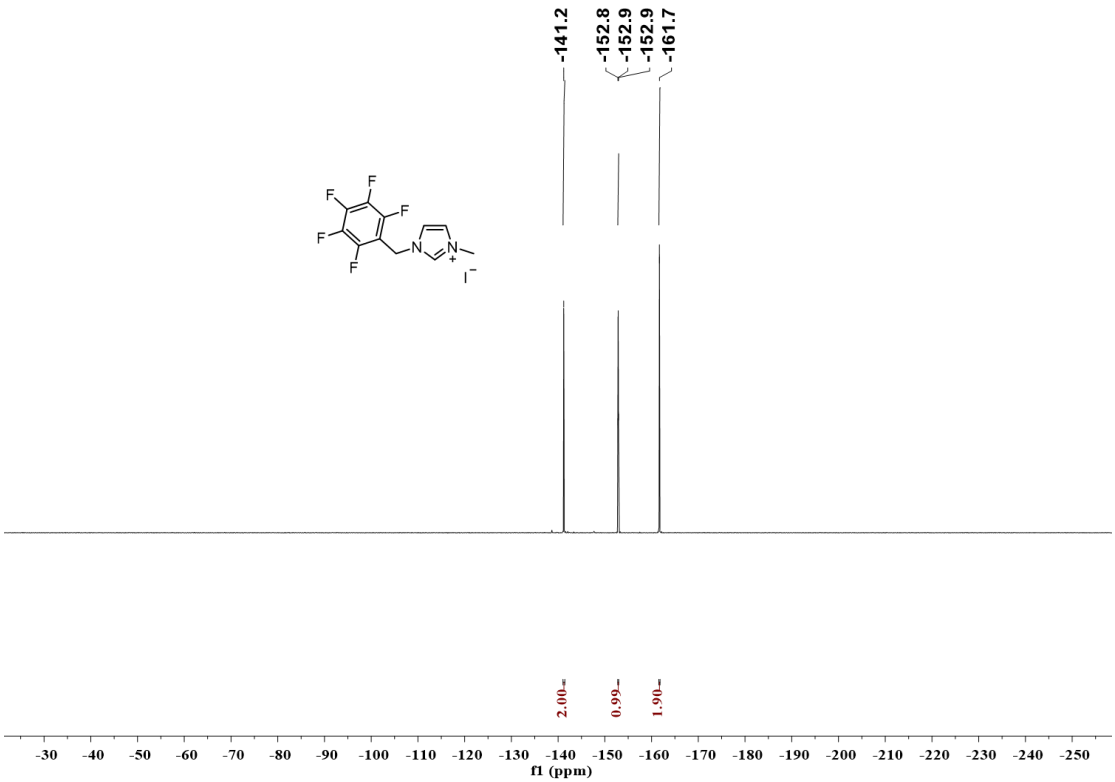

Figure S17. ^{19}F NMR spectrum of **IBn^{F}Me·HI** in DMSO-d_6.

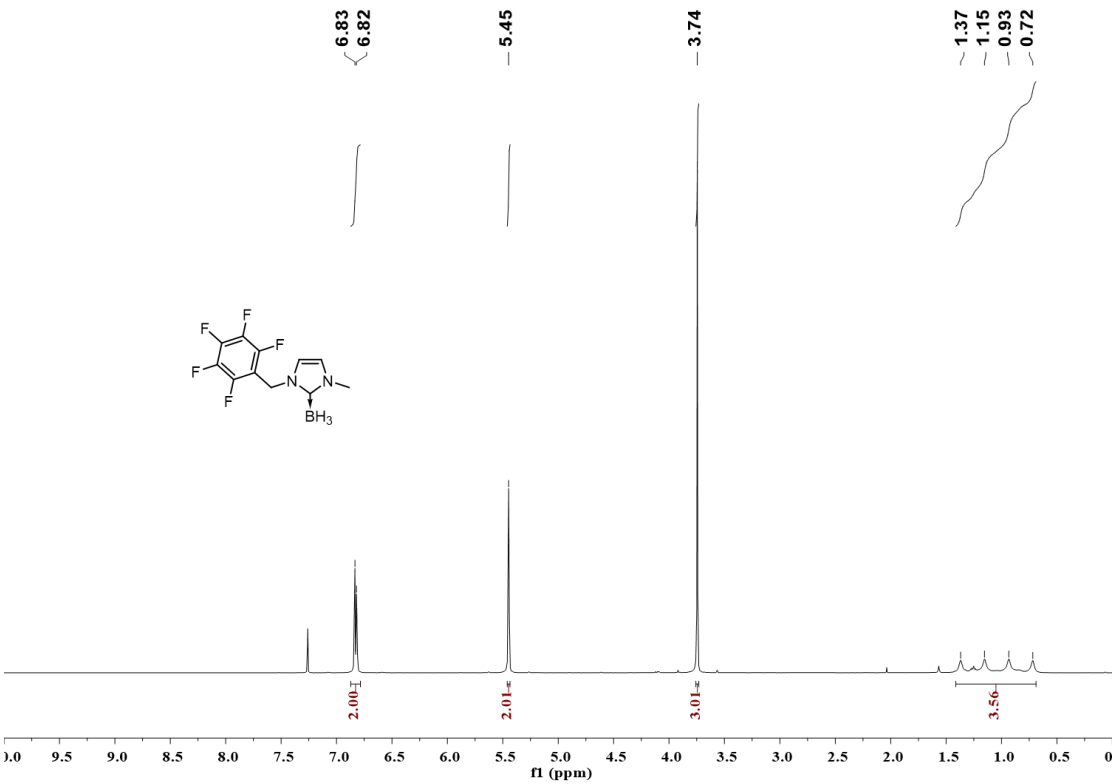

Figure S18. ^{1}H NMR spectrum of **IBn^{F}Me-BH$_3$** in $CDCl_3$.

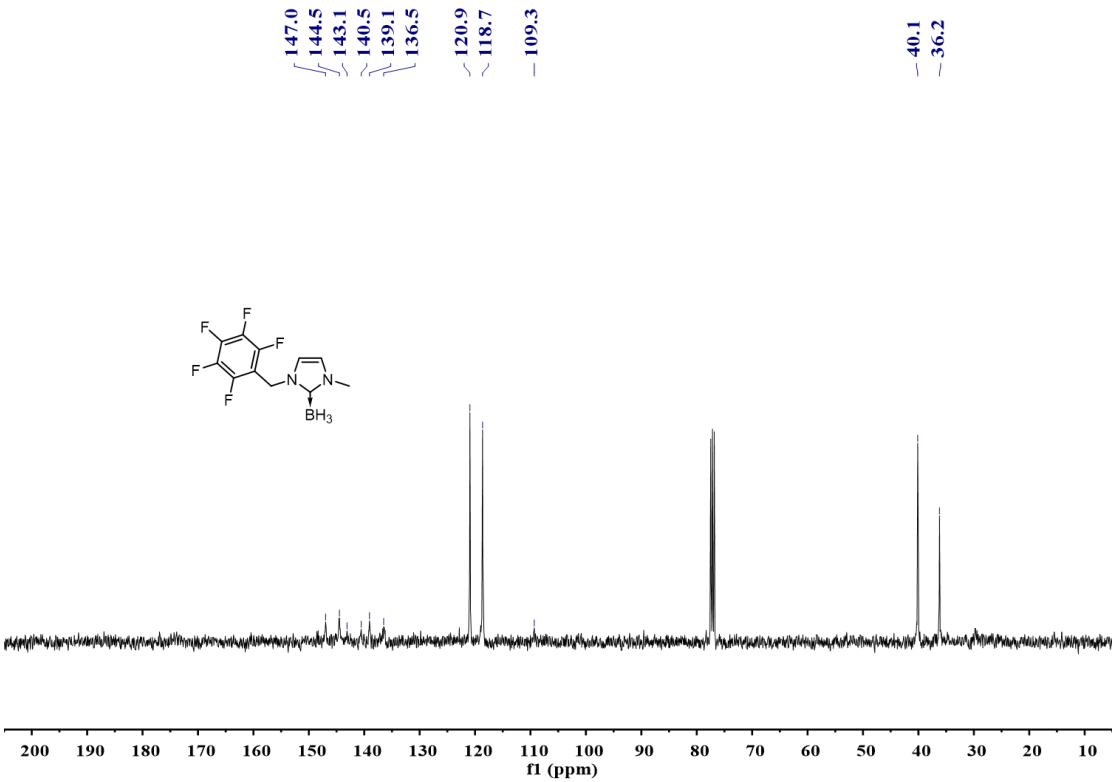

Figure S19. ^{13}C NMR spectrum of **IBn^{F}Me-BH$_3$** in $CDCl_3$.

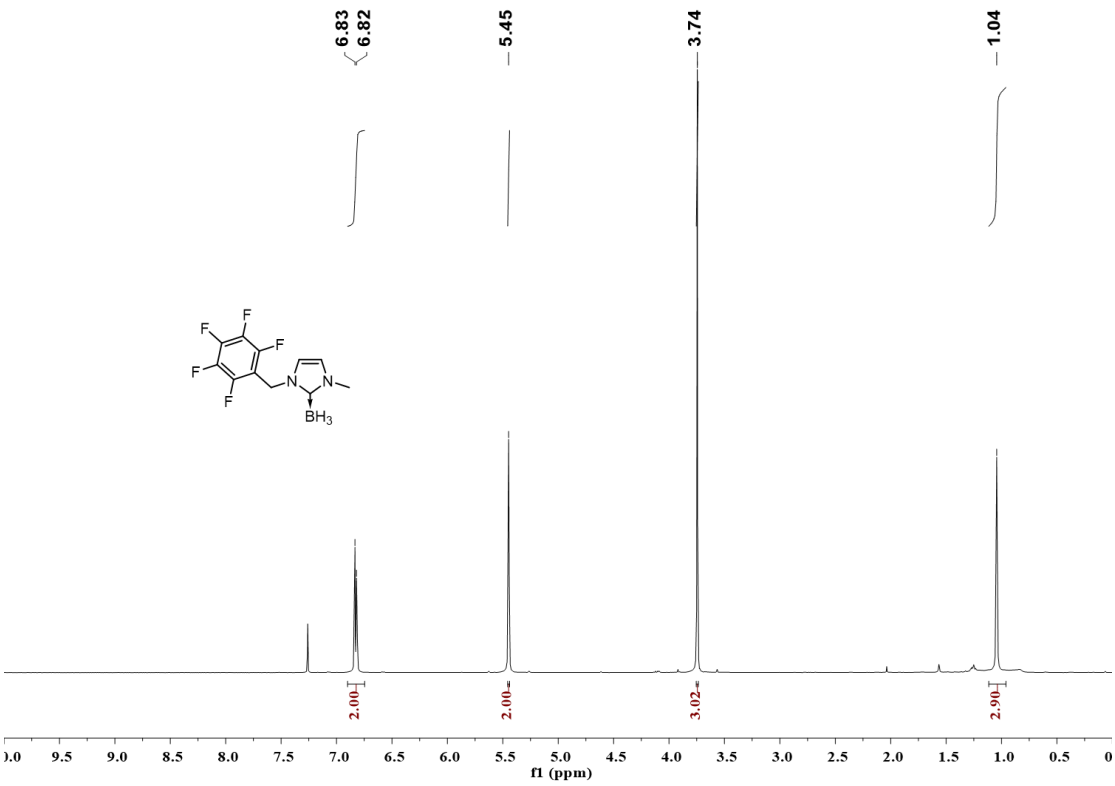

Figure S20. $^{1}H\{^{11}B\}$ NMR spectrum of **IBn^{F}Me-BH$_3$** in $CDCl_3$.

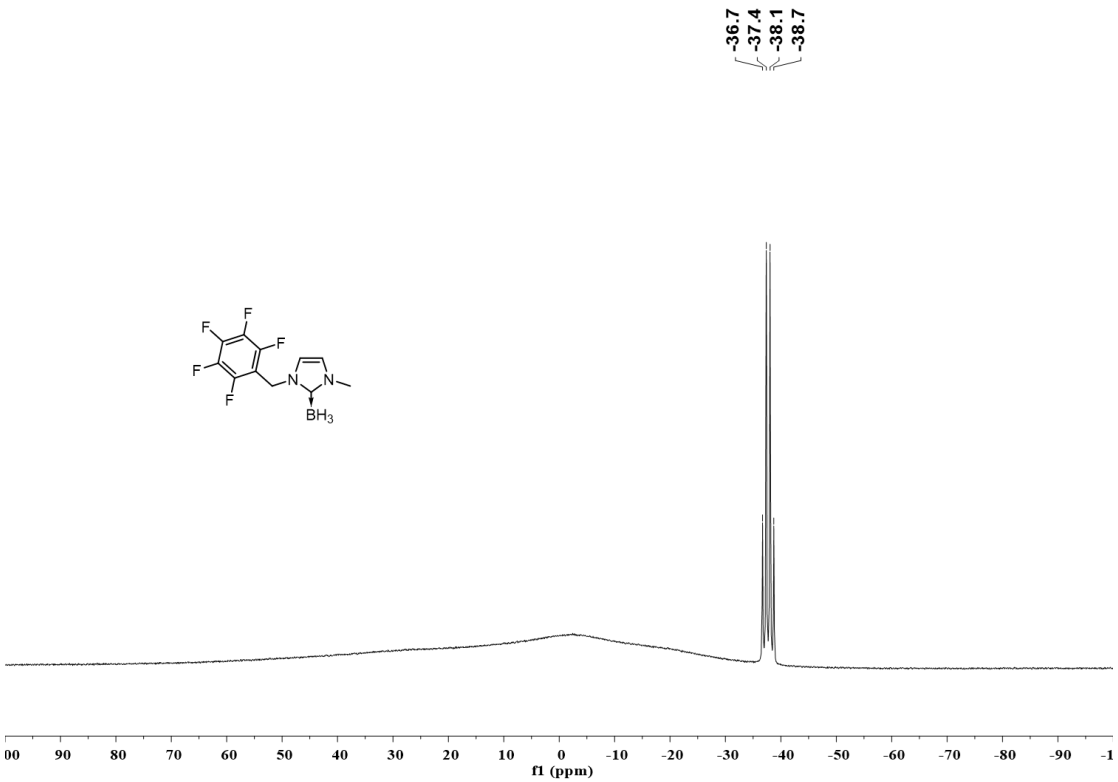

Figure S21. ^{11}B NMR spectrum of **IBn^{F}Me-BH$_3$** in $CDCl_3$.

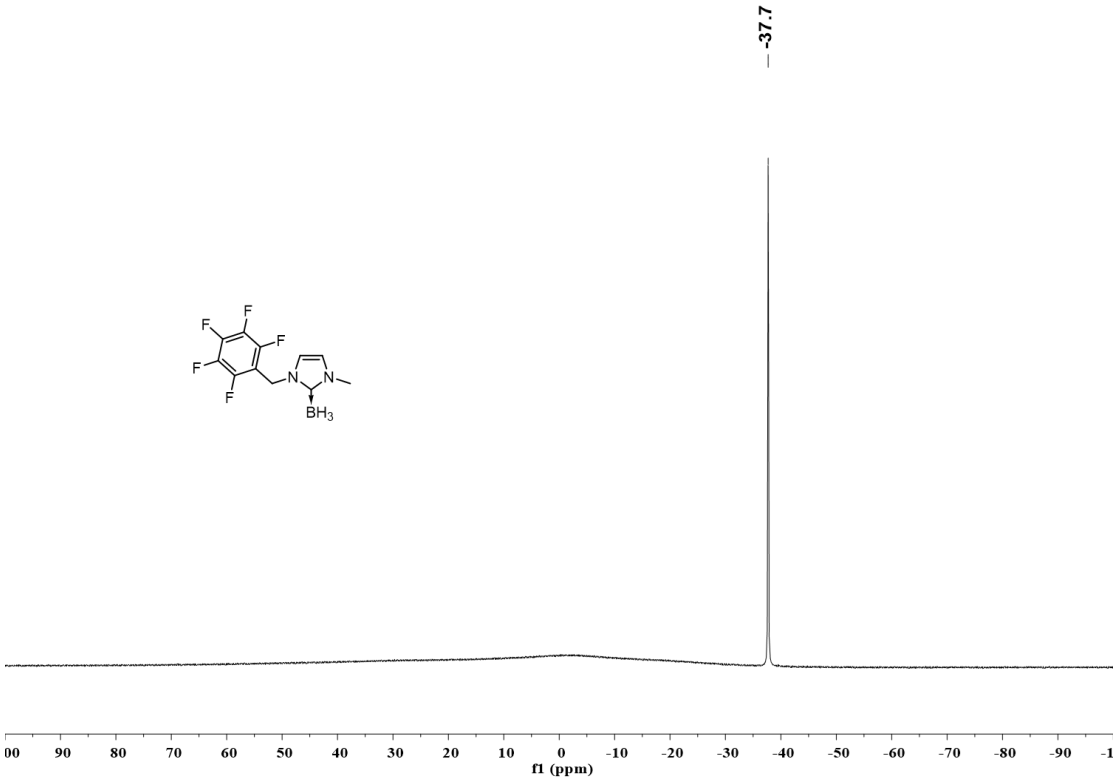

Figure S22. $^{11}B\{^{1}H\}$ NMR spectrum of **IBn^{F}Me-BH$_3$** in $CDCl_3$.

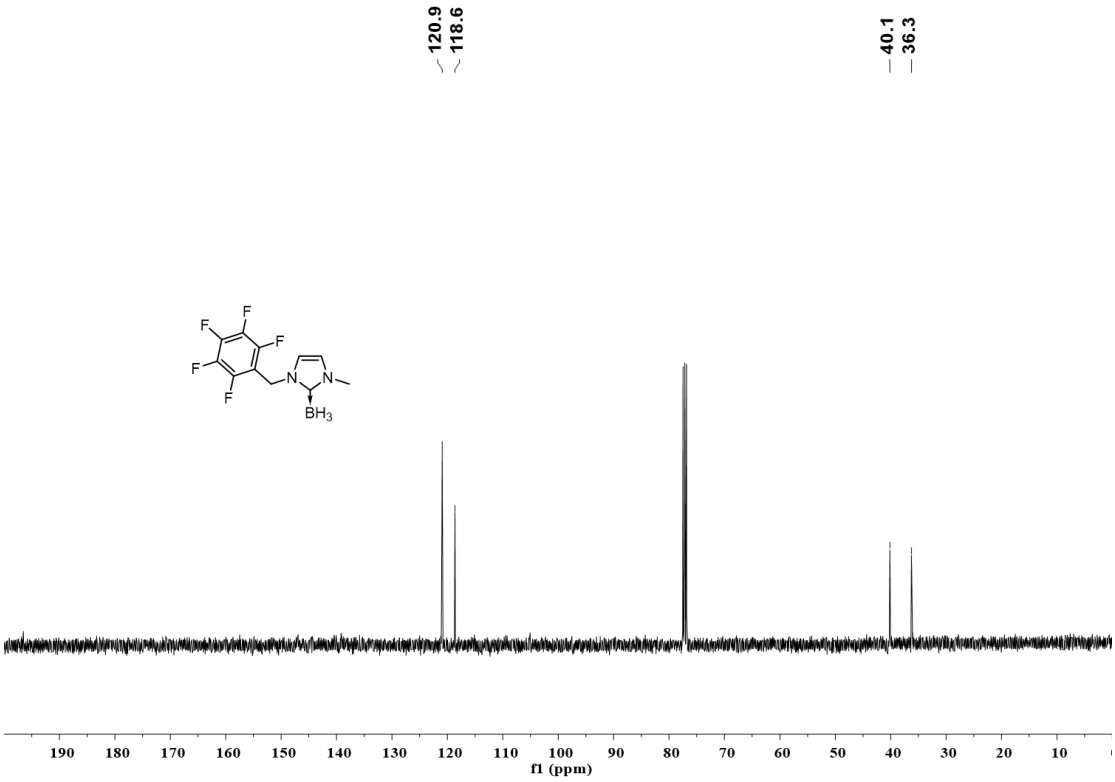

Figure S23. $^{13}C\{^{1}H\}$ NMR spectrum of **IBn^{F}Me-BH$_3$** in $CDCl_3$.

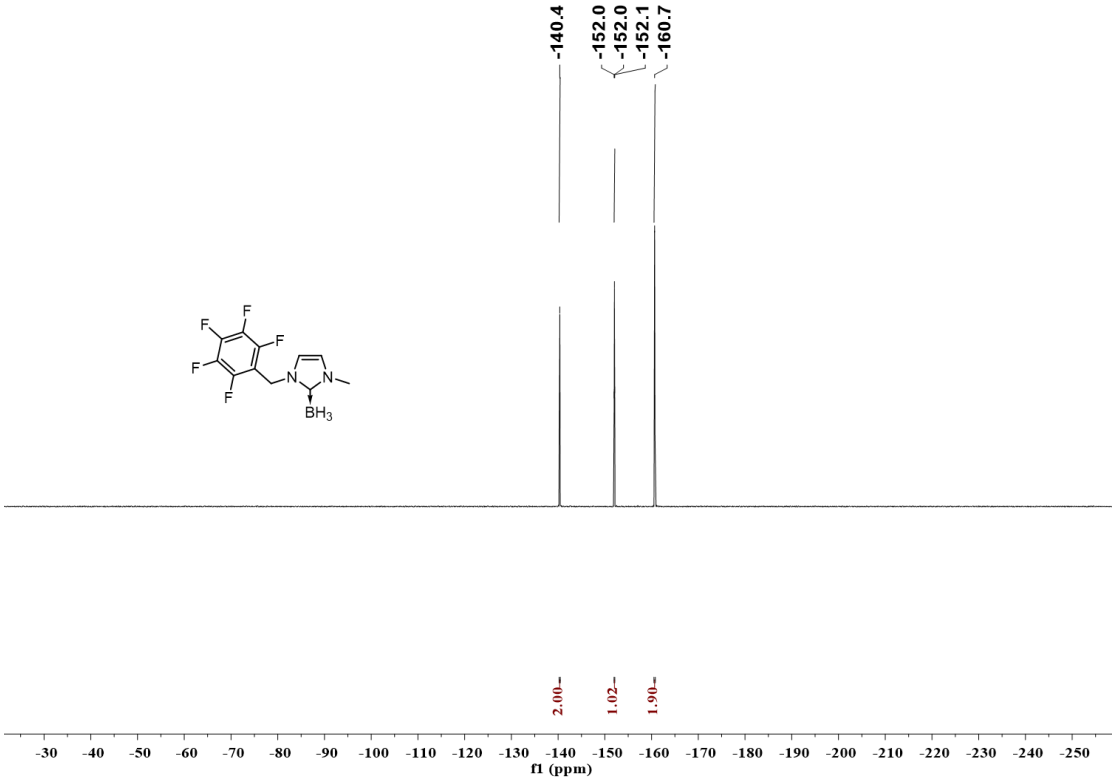

Figure S24. ^{19}F NMR spectrum of **IBn^{F}Me-BH$_3$** in $CDCl_3$.

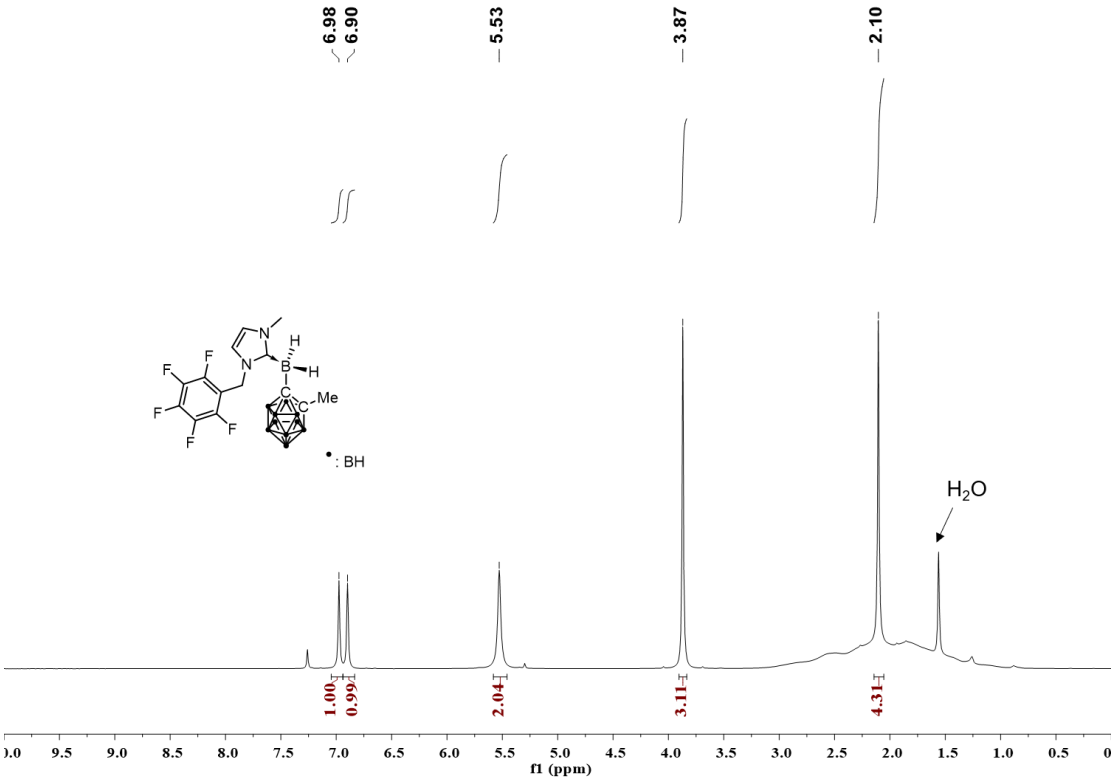

Figure S25. ^{1}H NMR spectrum of **2-H** in $CDCl_3$.

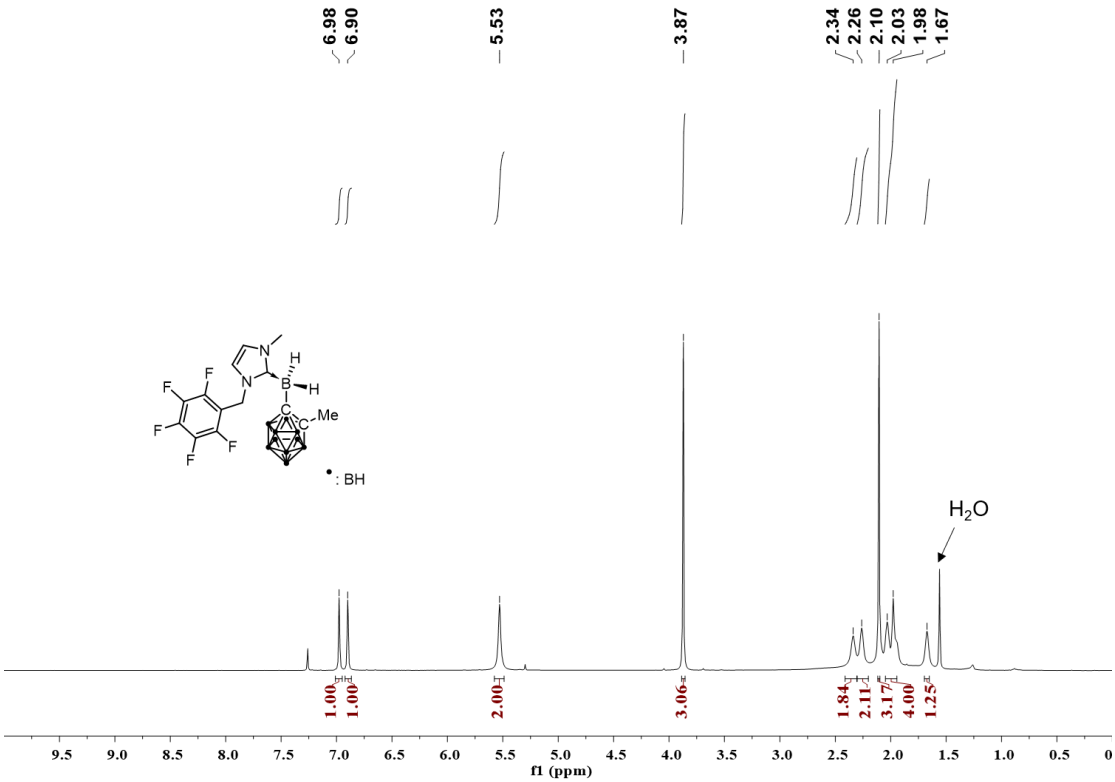

Figure S26. $^{1}H\{^{11}B\}$ NMR spectrum of **2-H** in $CDCl_3$.

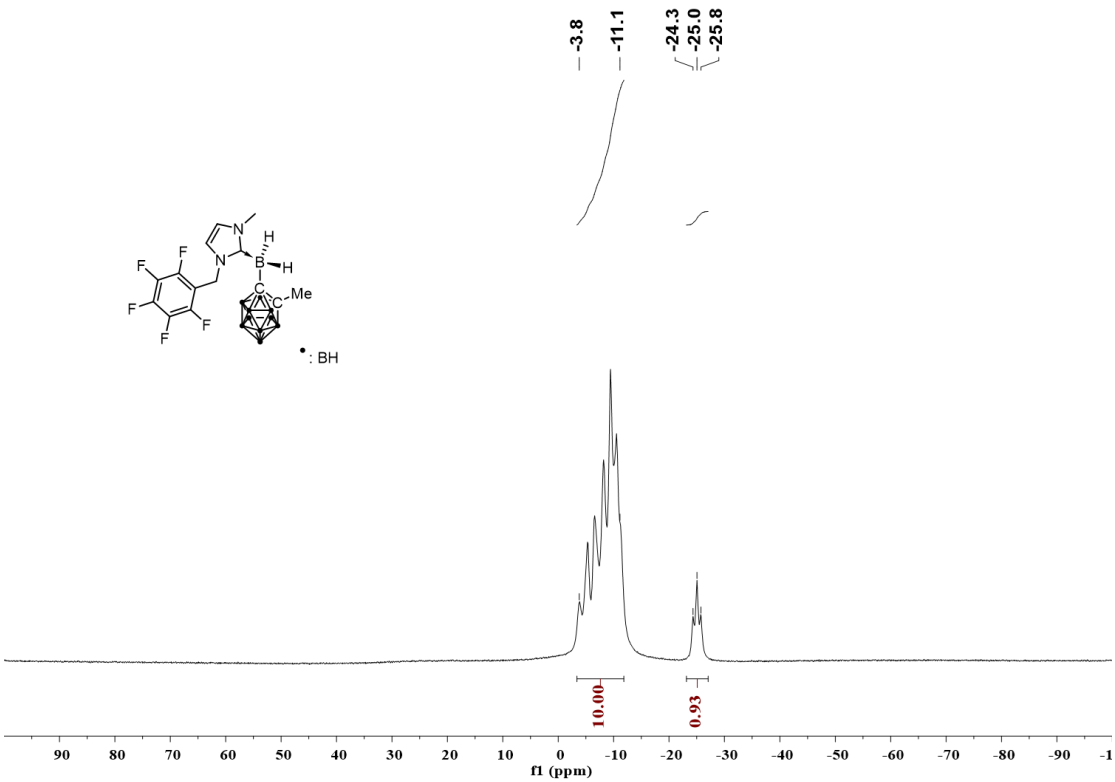

Figure S27. ^{11}B NMR spectrum of **2-H** in $CDCl_3$.

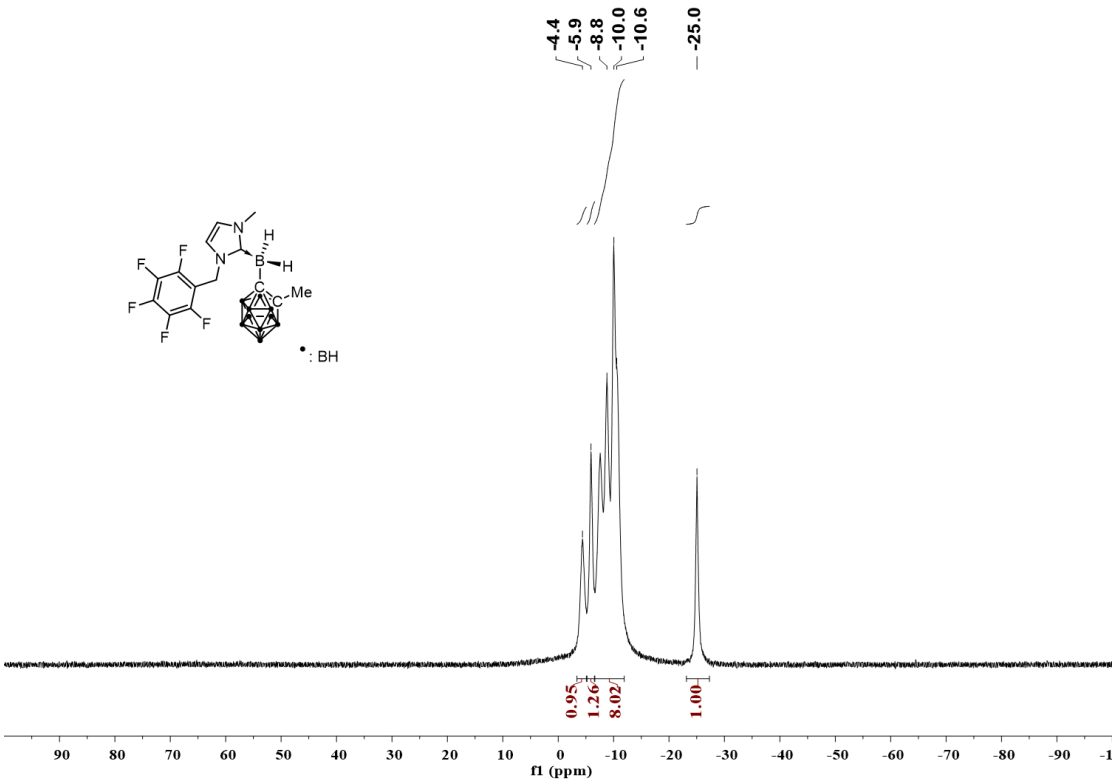

Figure S28. $^{11}B\{^1H\}$ NMR spectrum of **2-H** in $CDCl_3$.

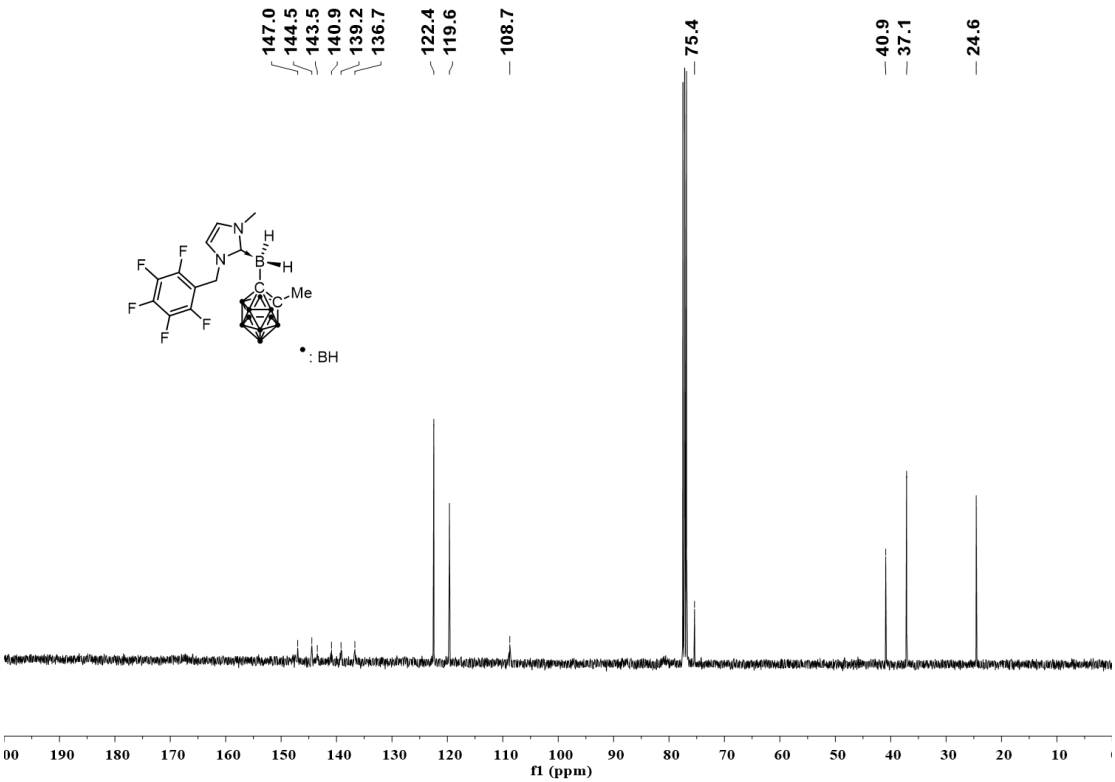

Figure S29. ^{13}C NMR spectrum of **2-H** in $CDCl_3$.

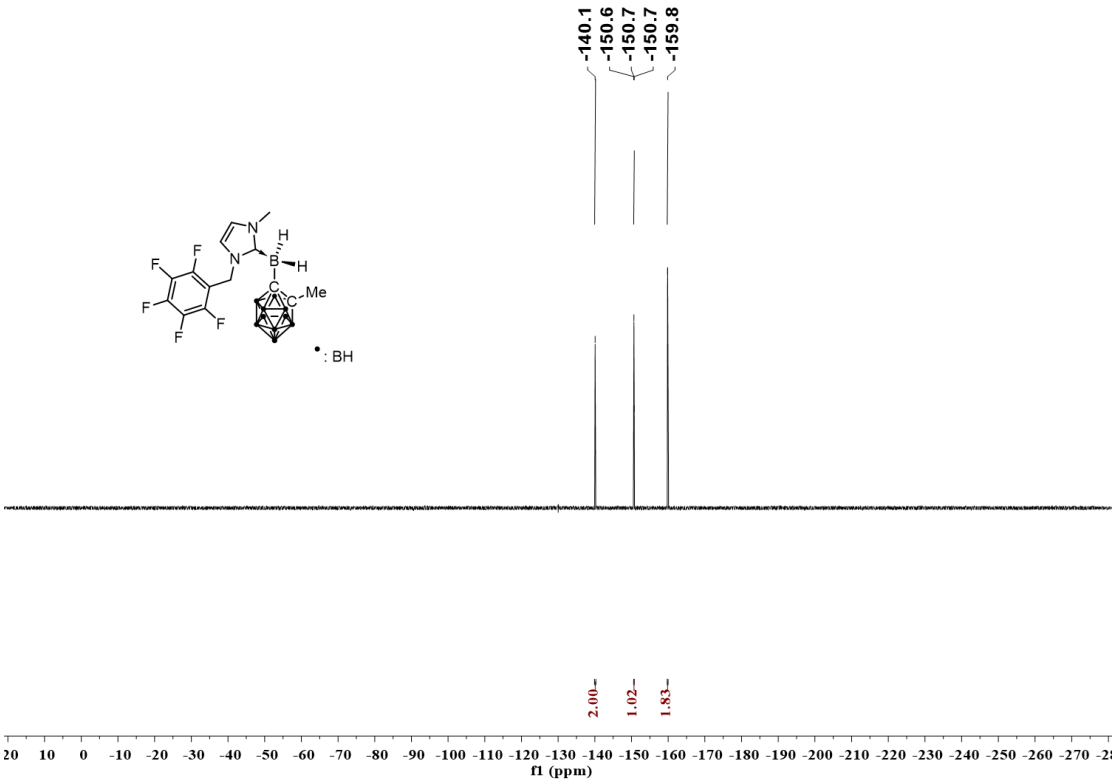

Figure S30. ^{19}F NMR spectrum of **2-H** in $CDCl_3$.

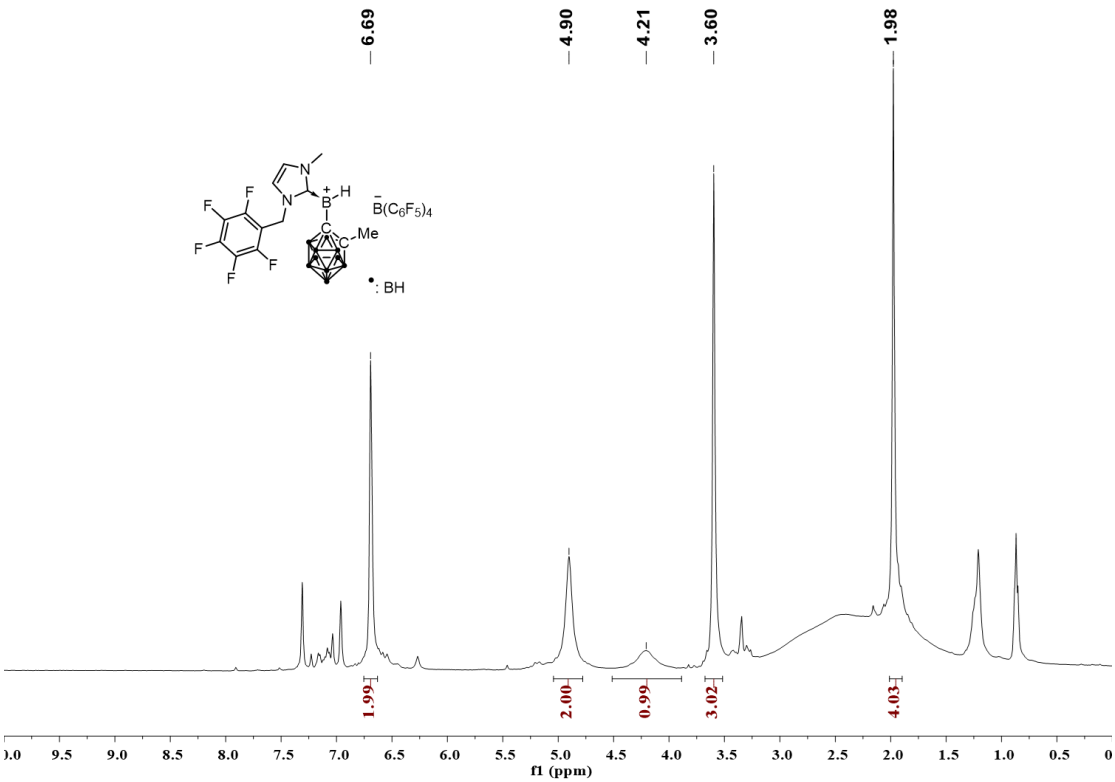

Figure S31. ^{1}H NMR spectrum of **2** in C_6D_5Br.

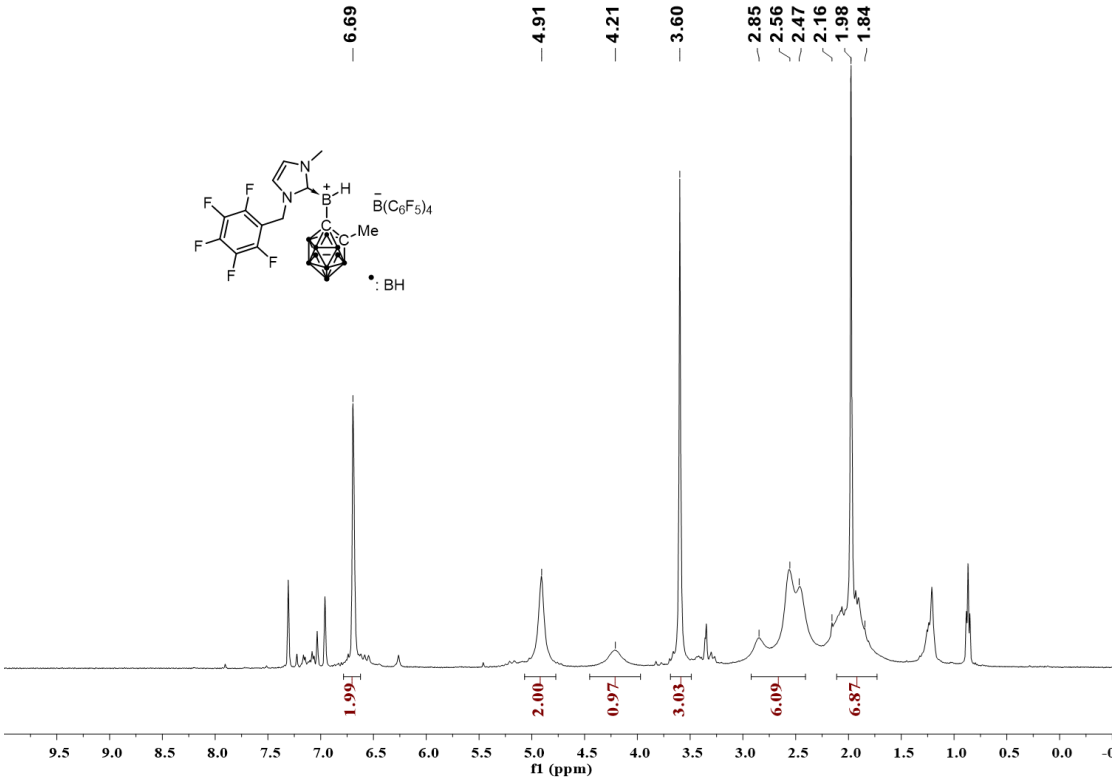

Figure S32. $^{1}H\{^{11}B\}$ NMR spectrum of **2** in C_6D_5Br.

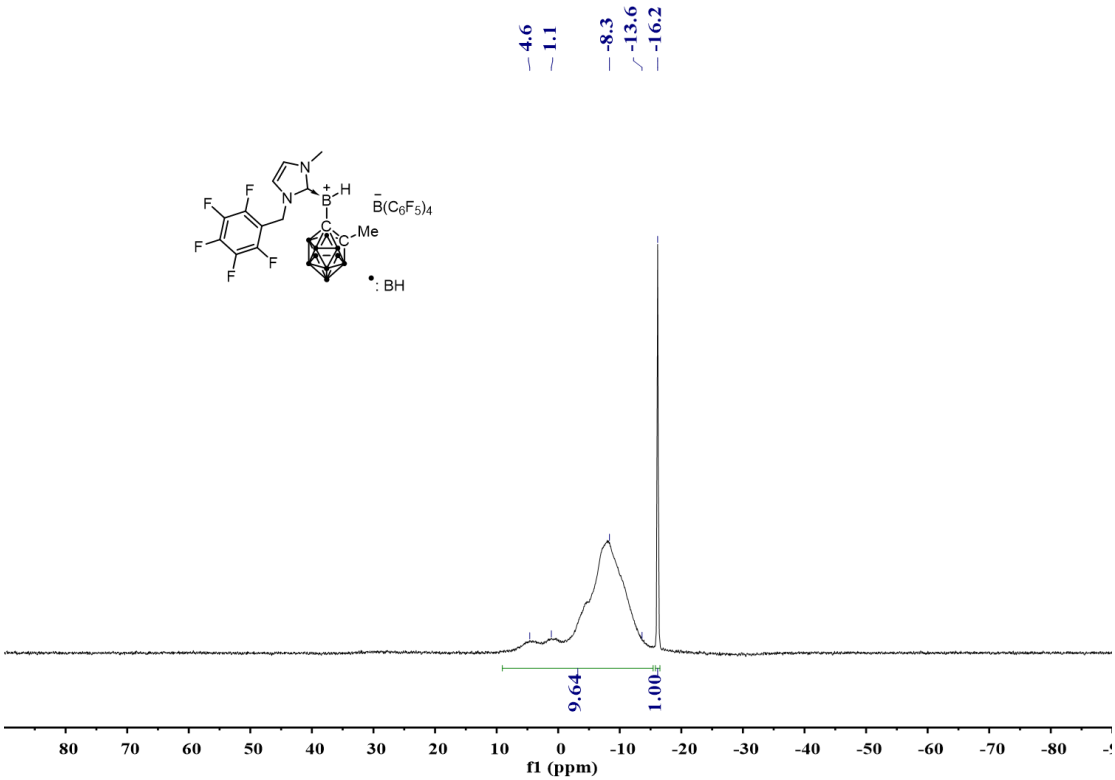

Figure S33. ^{11}B NMR spectrum of **2** in *o*-$C_6H_4F_2$.

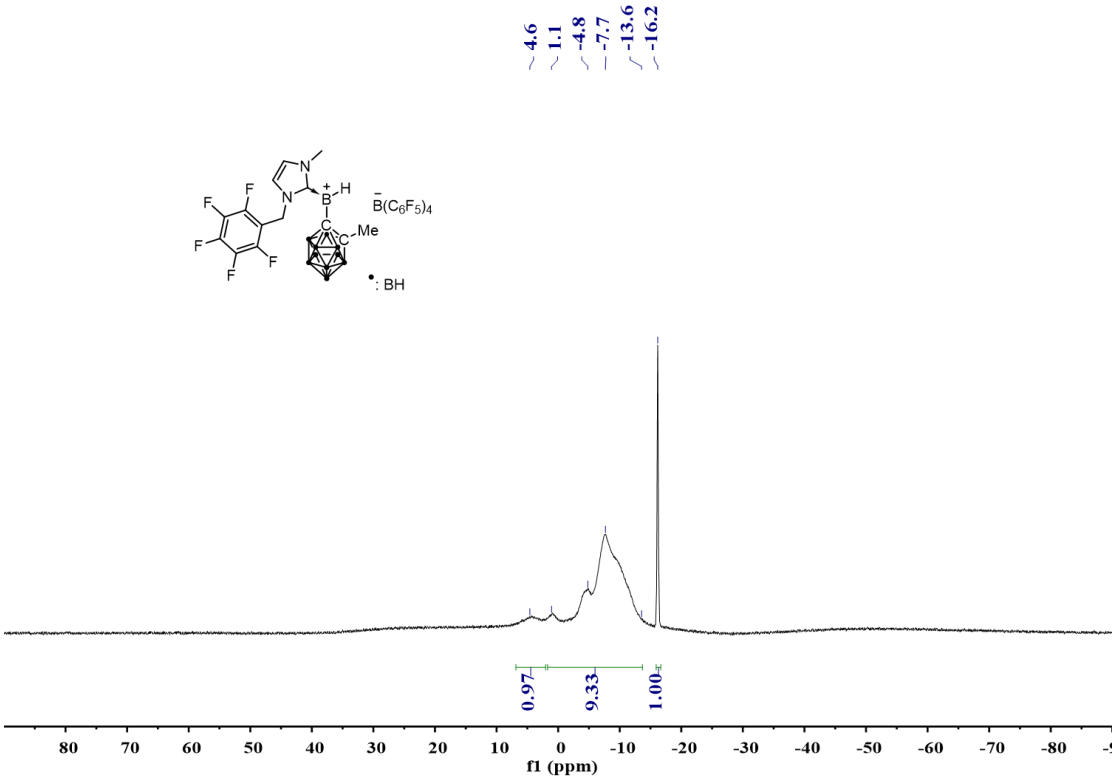

Figure S34. ^{11}B{^{1}H} NMR spectrum spectrum of **2** in *o*-$C_6H_4F_2$.

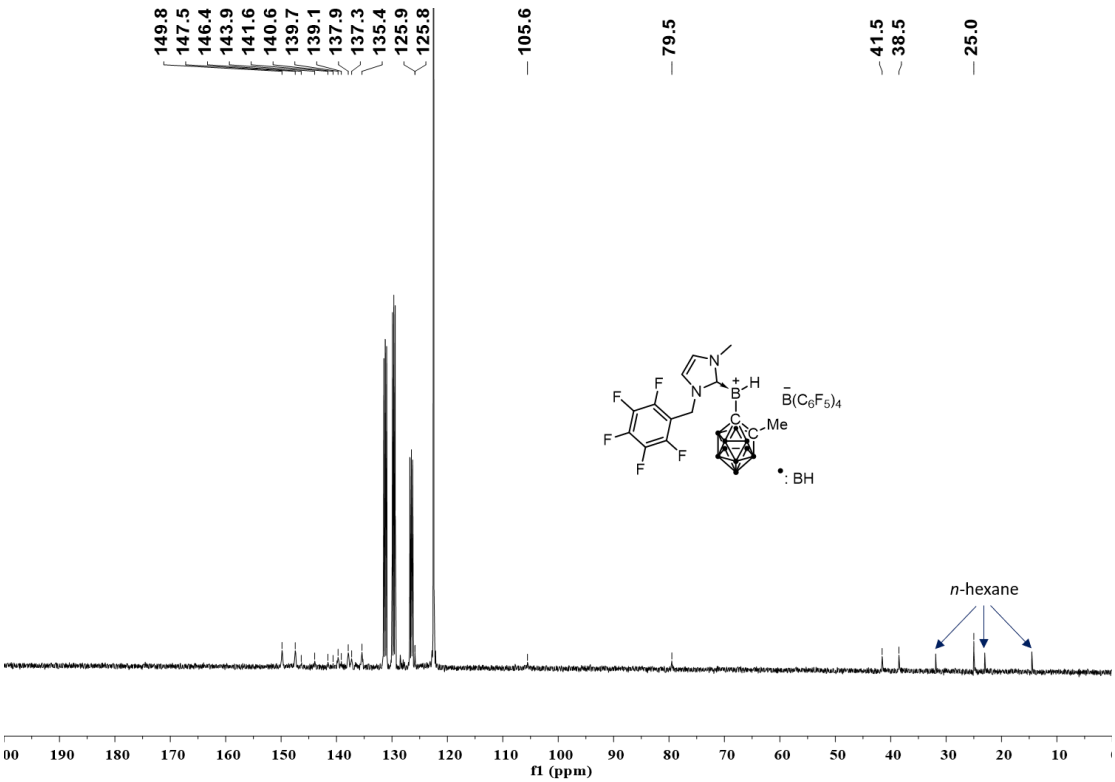

Figure S35. $^{13}C\{^{1}H\}$ NMR spectrum of **2** in C_6D_5Br.

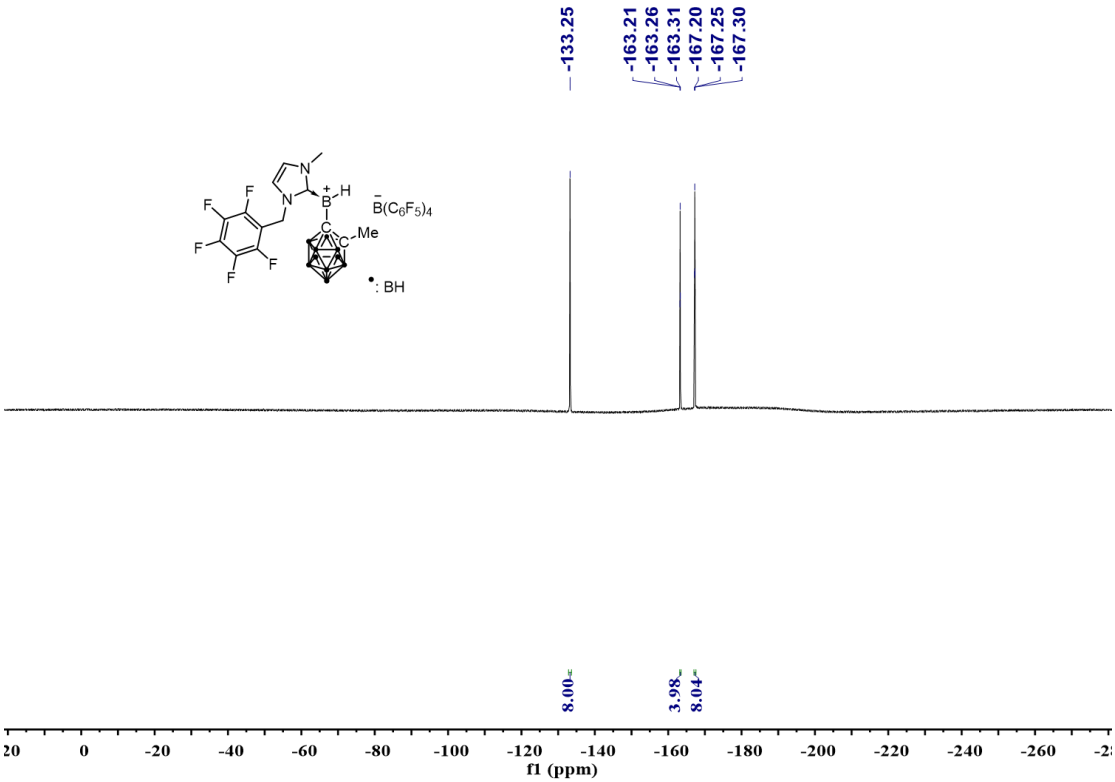

Figure S36. ^{19}F NMR spectrum of **2** in C_6D_5Br.

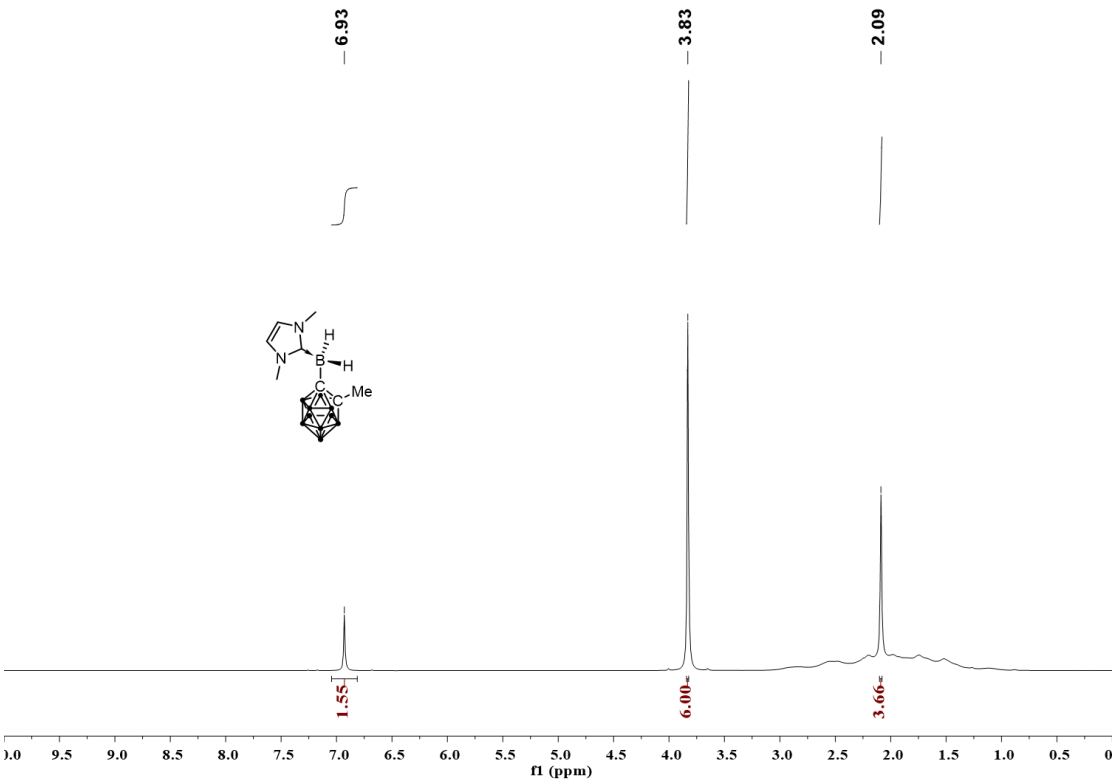

Figure S37. ^{1}H NMR spectrum of **3-H** in $CDCl_3$.

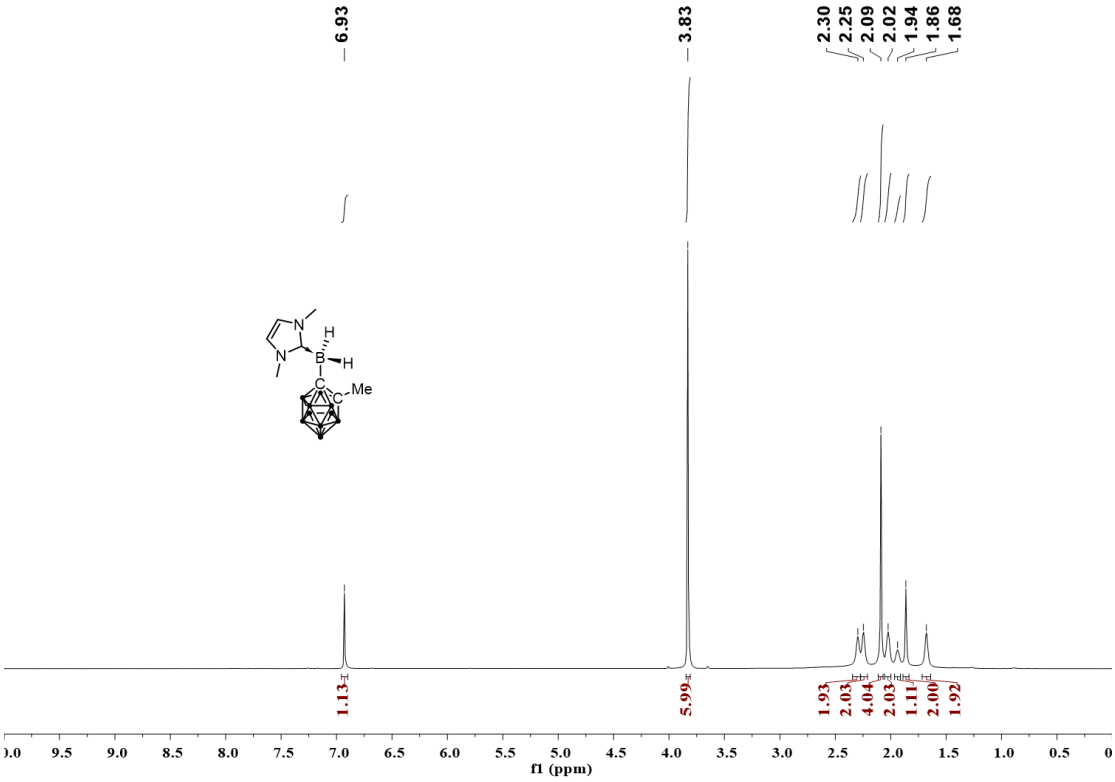

Figure S38. $^{1}H\{^{11}B\}$ NMR spectrum of **3-H** in $CDCl_3$.

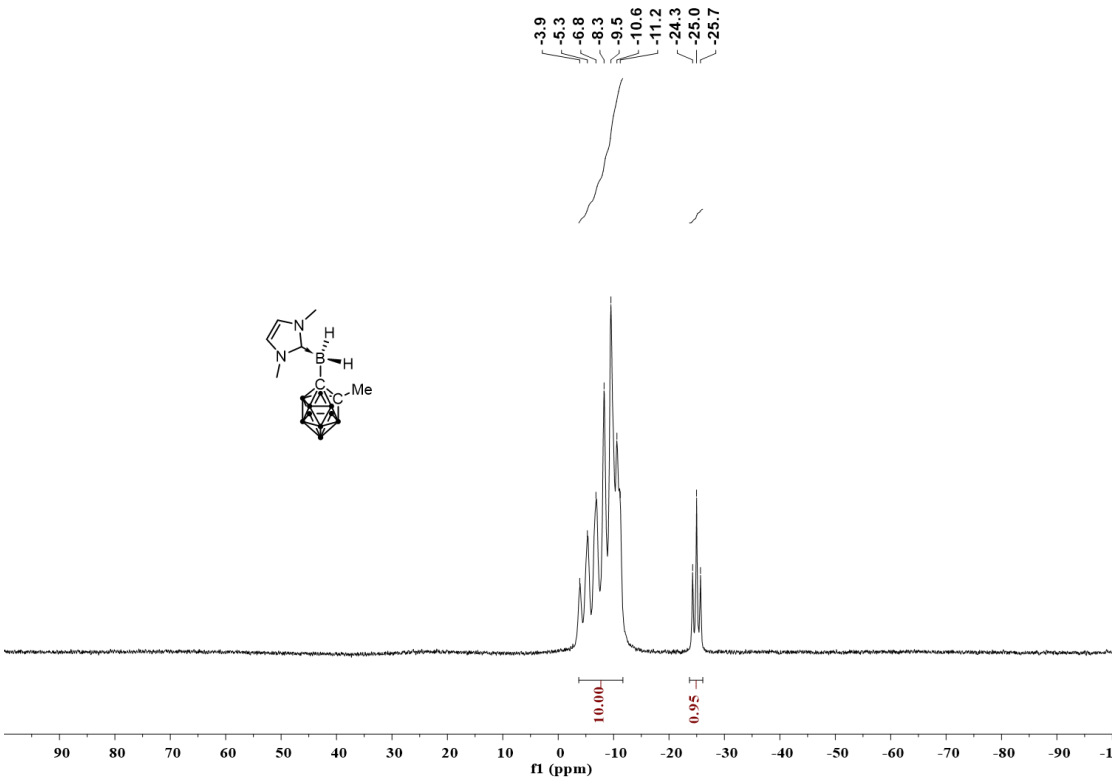

Figure S39. ^{11}B NMR spectrum of **3-H** in $CDCl_3$.

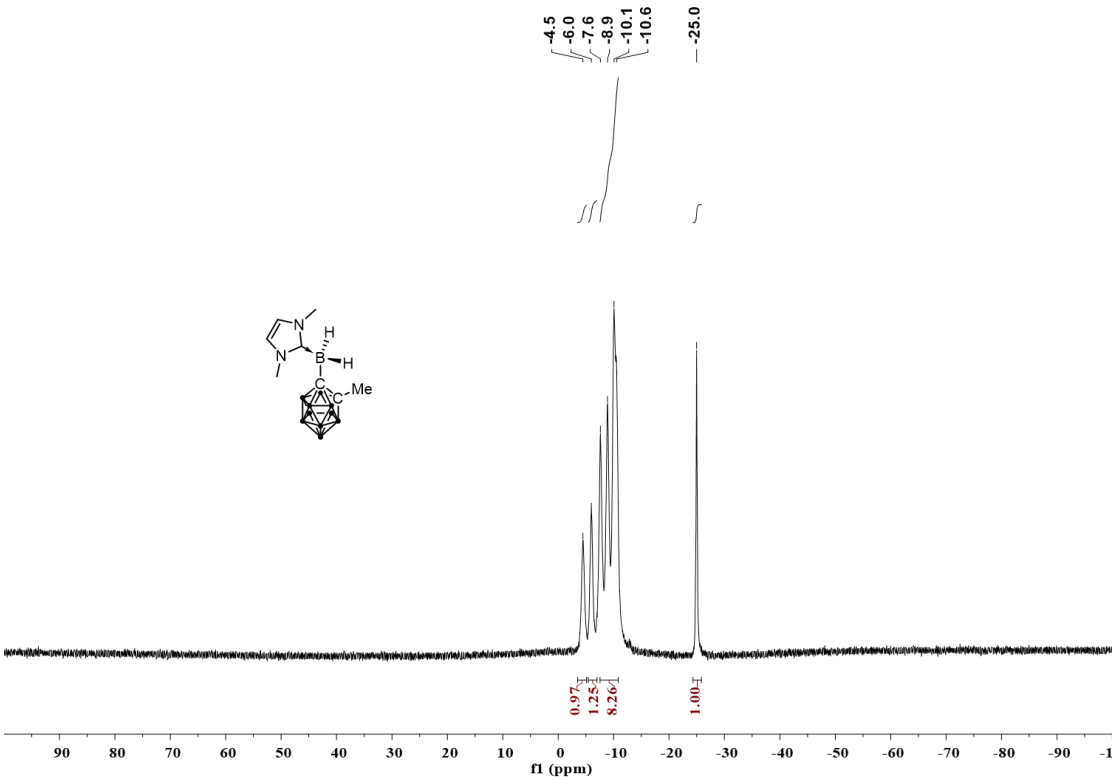

Figure S40. $^{11}B\{^1H\}$ NMR spectrum of **3-H** in $CDCl_3$.

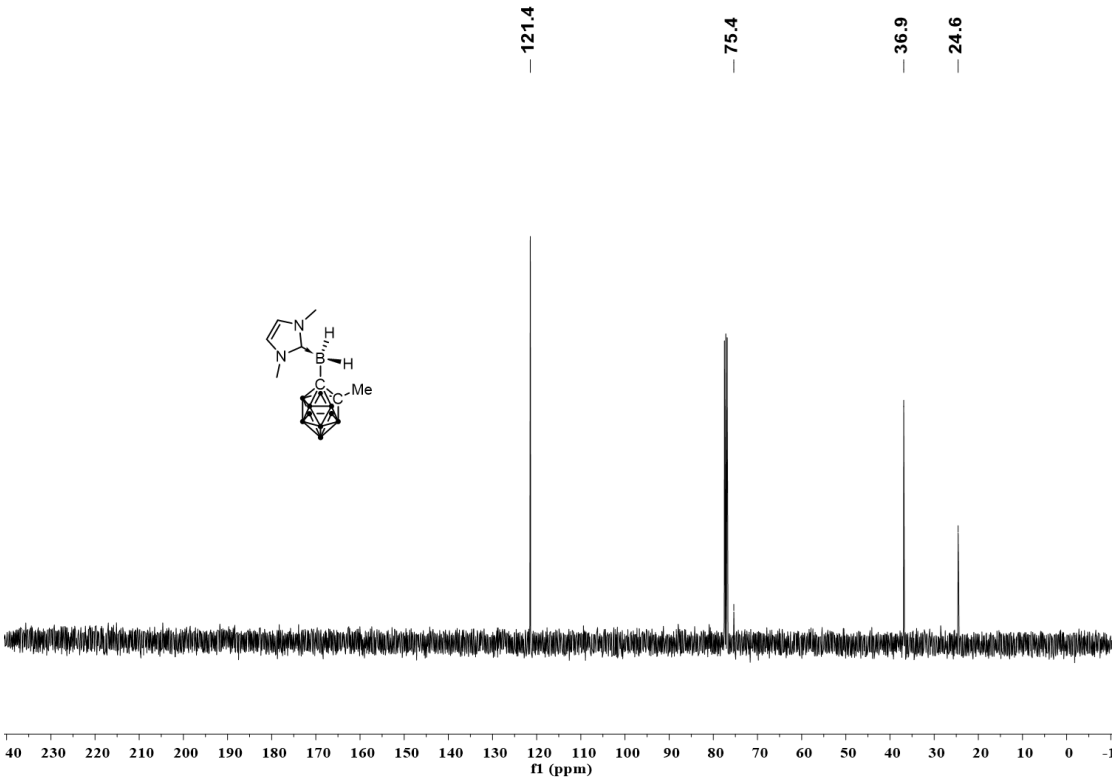

Figure S41. ^{13}C NMR spectrum of **3-H** in $CDCl_3$.

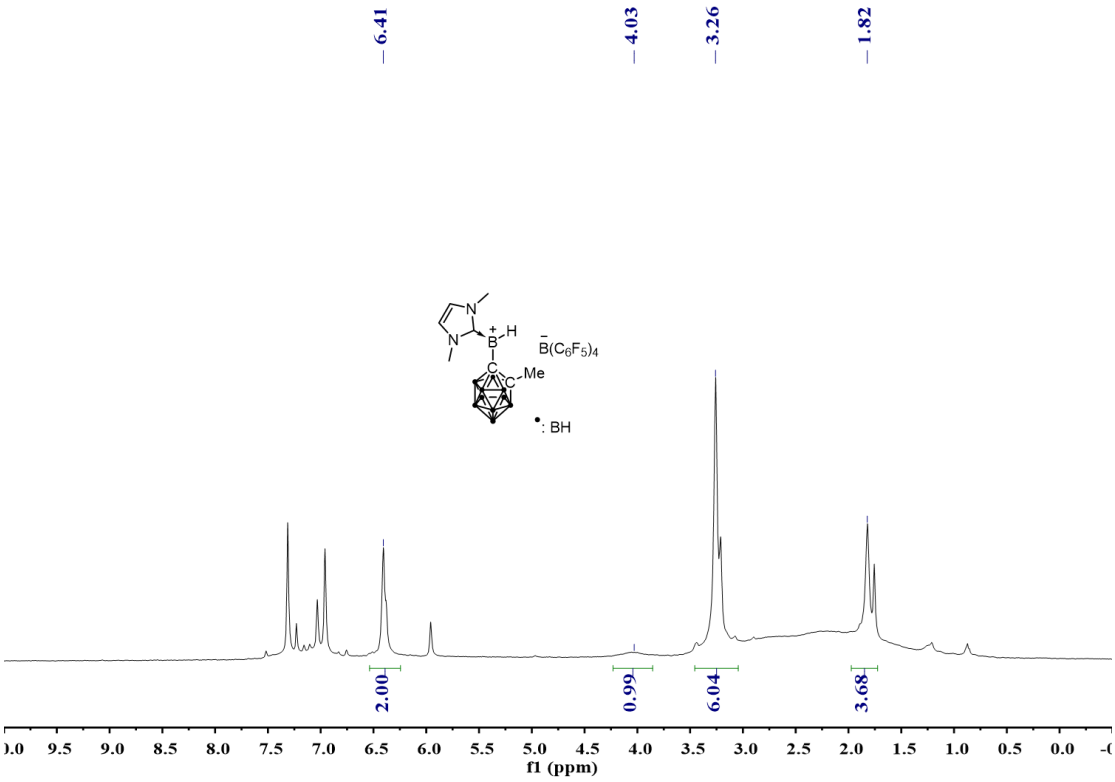

Figure S42. ^{1}H NMR spectrum of **3** in C_6D_5Br.

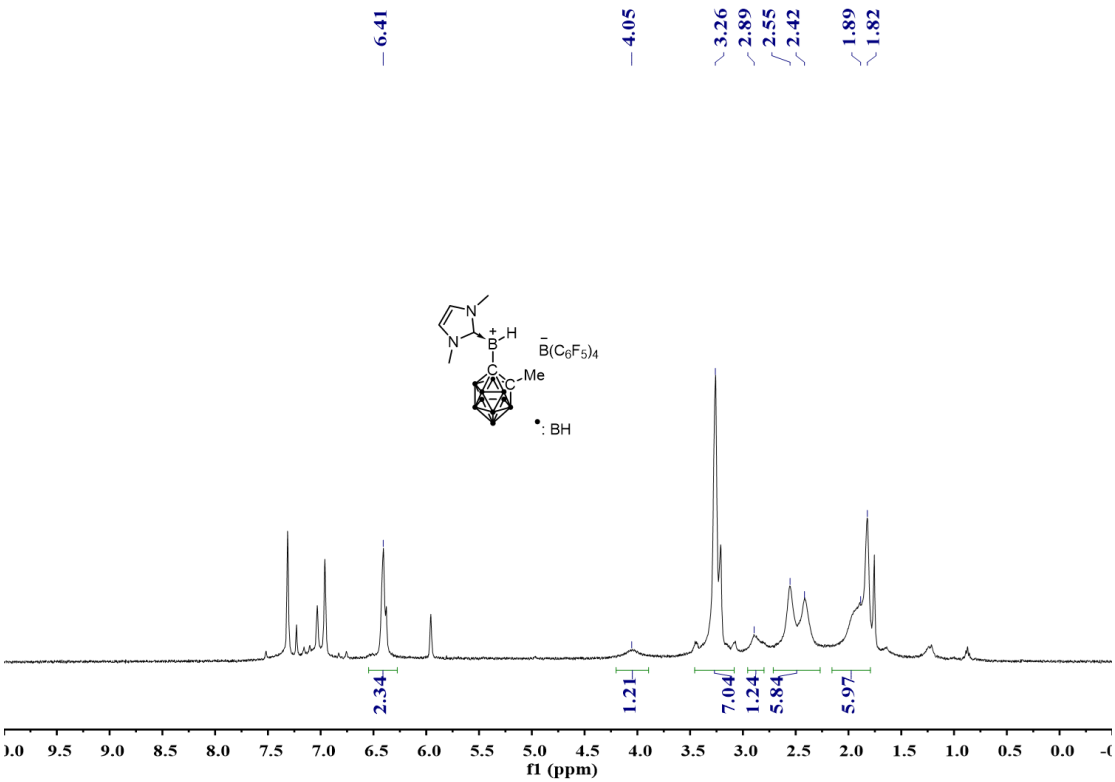

Figure S43. $^{1}H\{^{11}B\}$ NMR spectrum of **3** in C_6D_5Br.

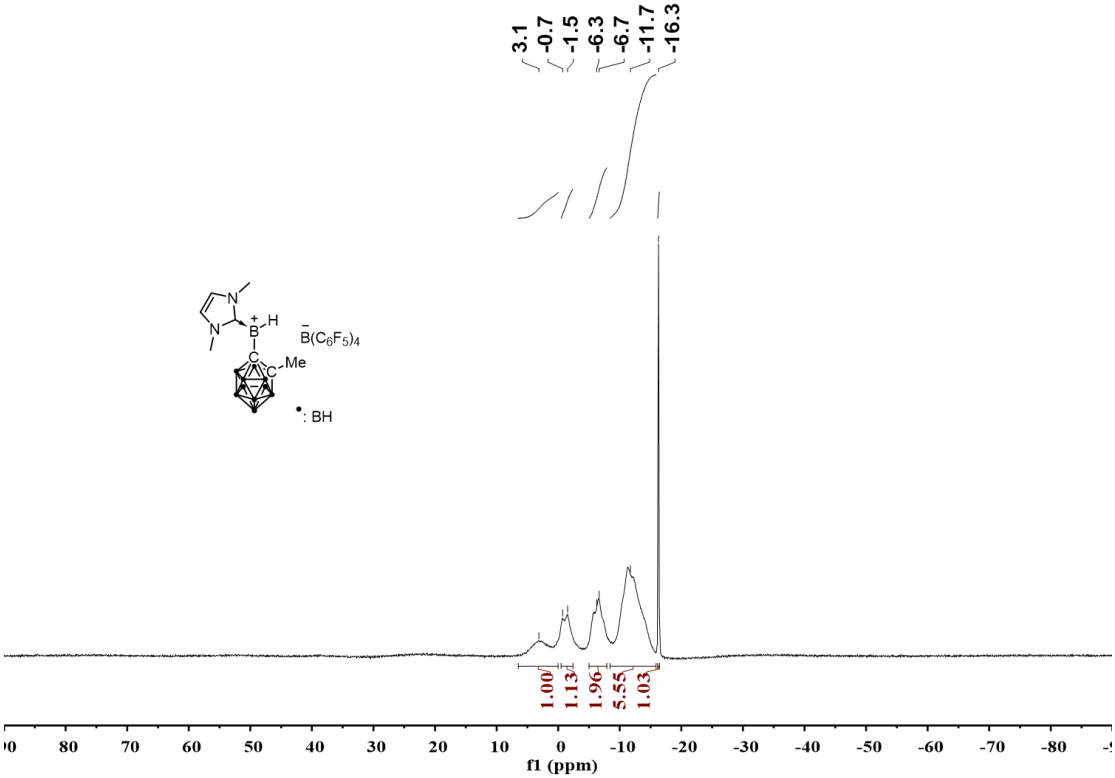

Figure S44. ^{11}B NMR spectrum of **3** in C_6D_5Br.

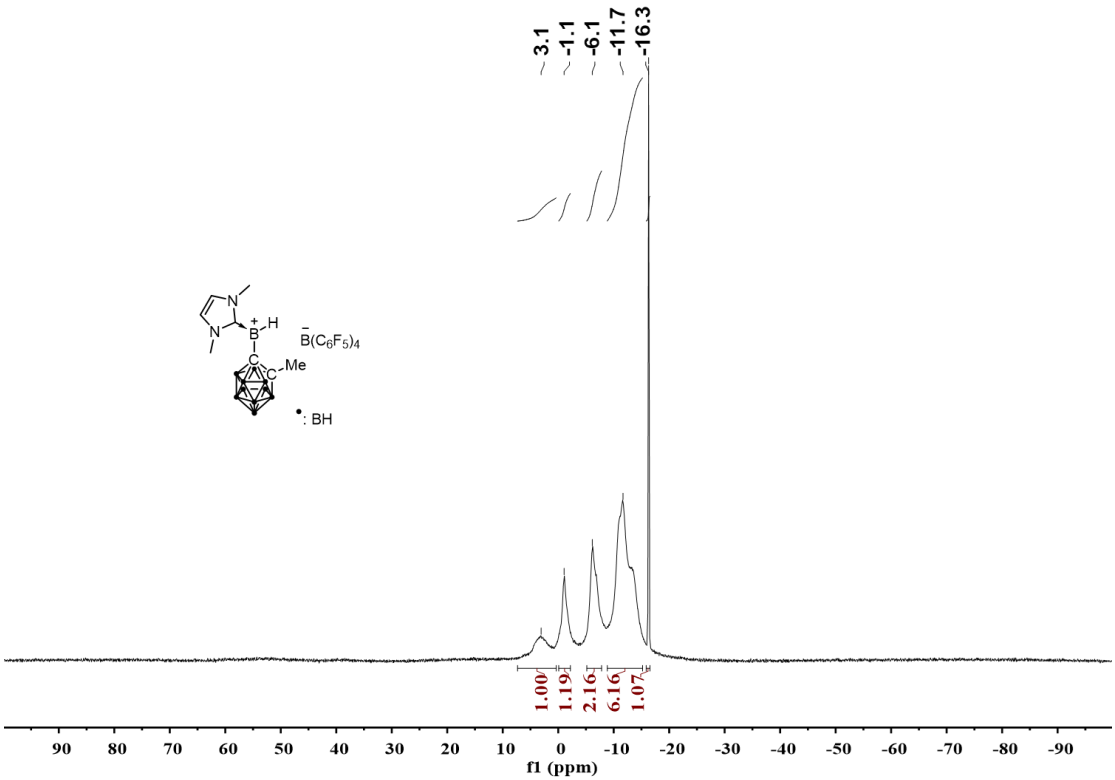

Figure S45. $^{11}B\{^{1}H\}$ NMR spectrum of **3** in C_6D_5Br.

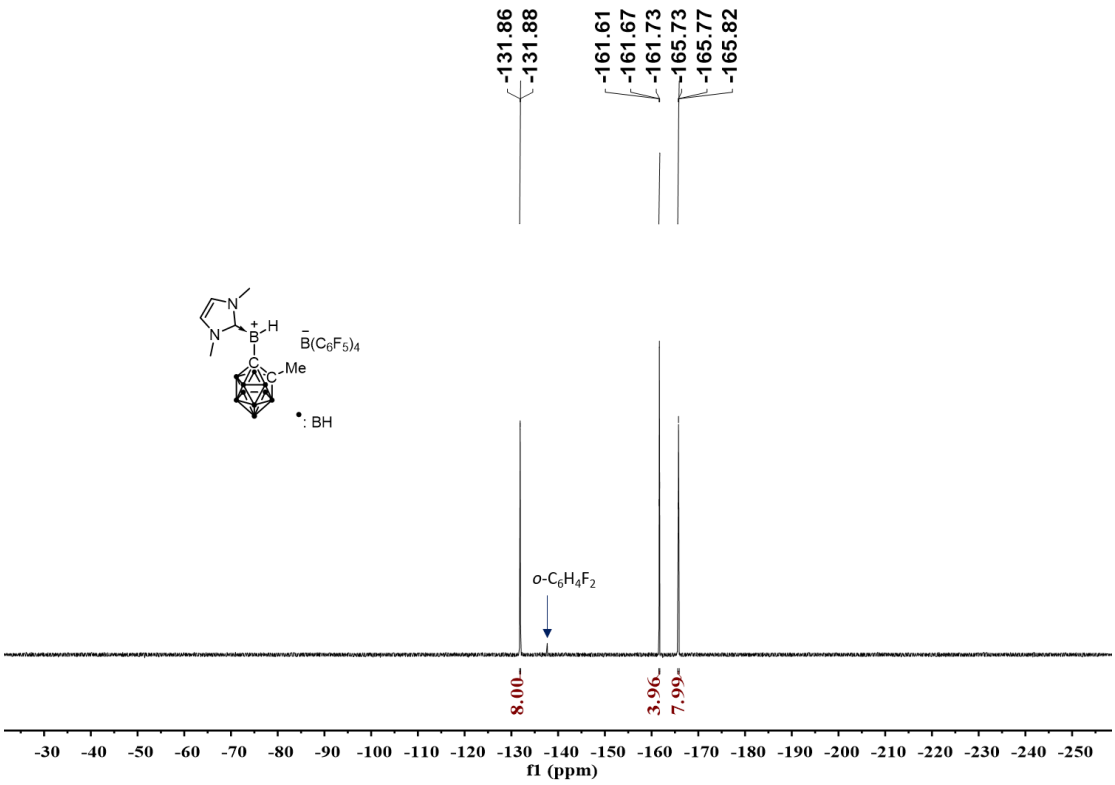

Figure S46. ^{19}F NMR spectrum of **2** in C_6D_5Br.

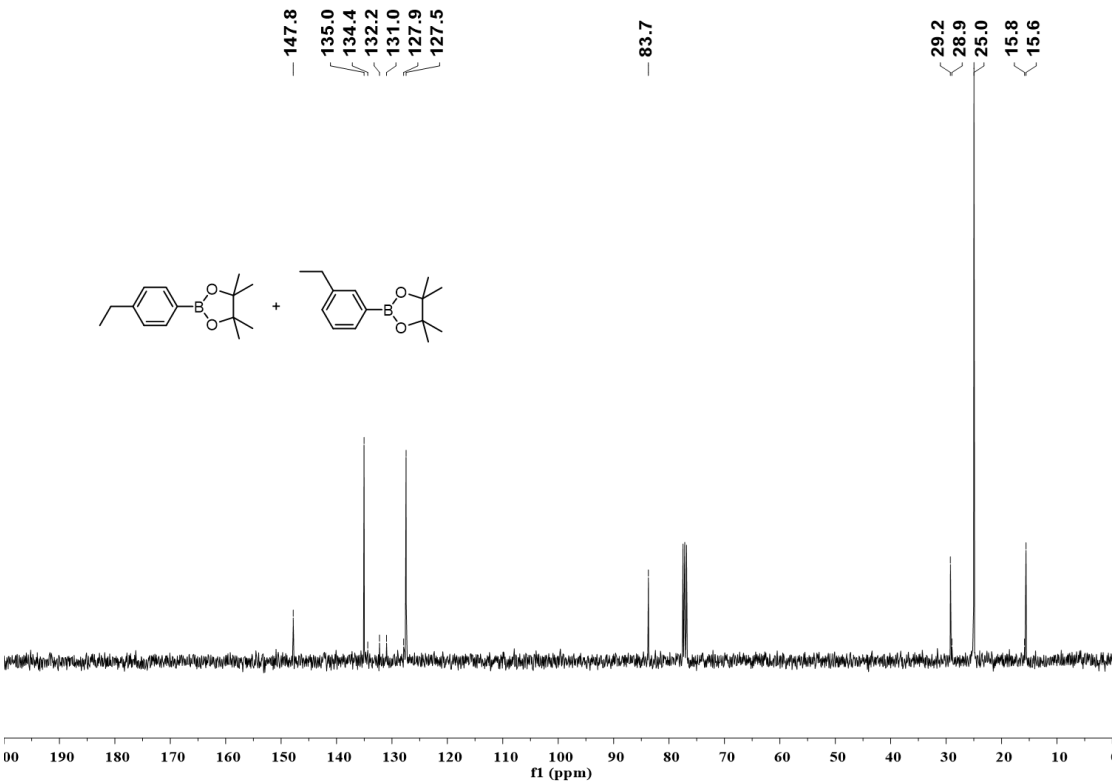

Figure S47. $^{13}C\{^{1}H\}$ NMR spectrum of the borylation products of ethylbenzene in $CDCl_3$.

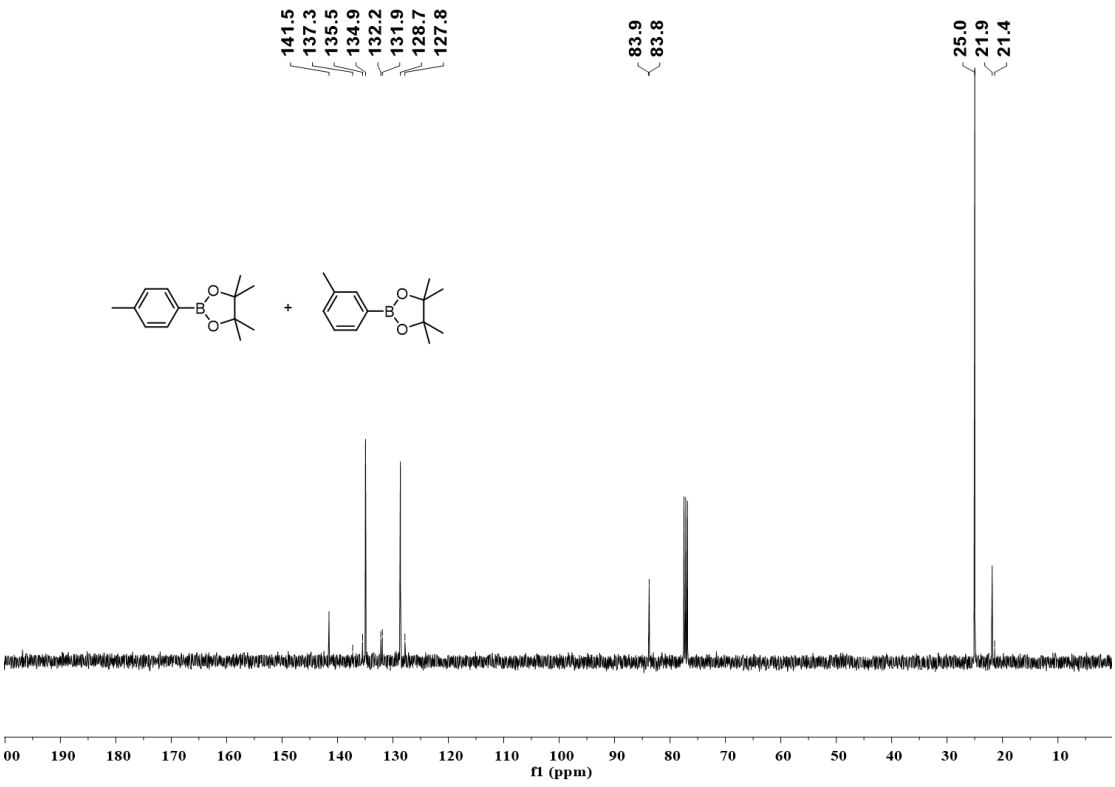

Figure S48. $^{13}C\{^{1}H\}$ NMR spectrum of the borylation products of toluene in $CDCl_3$.

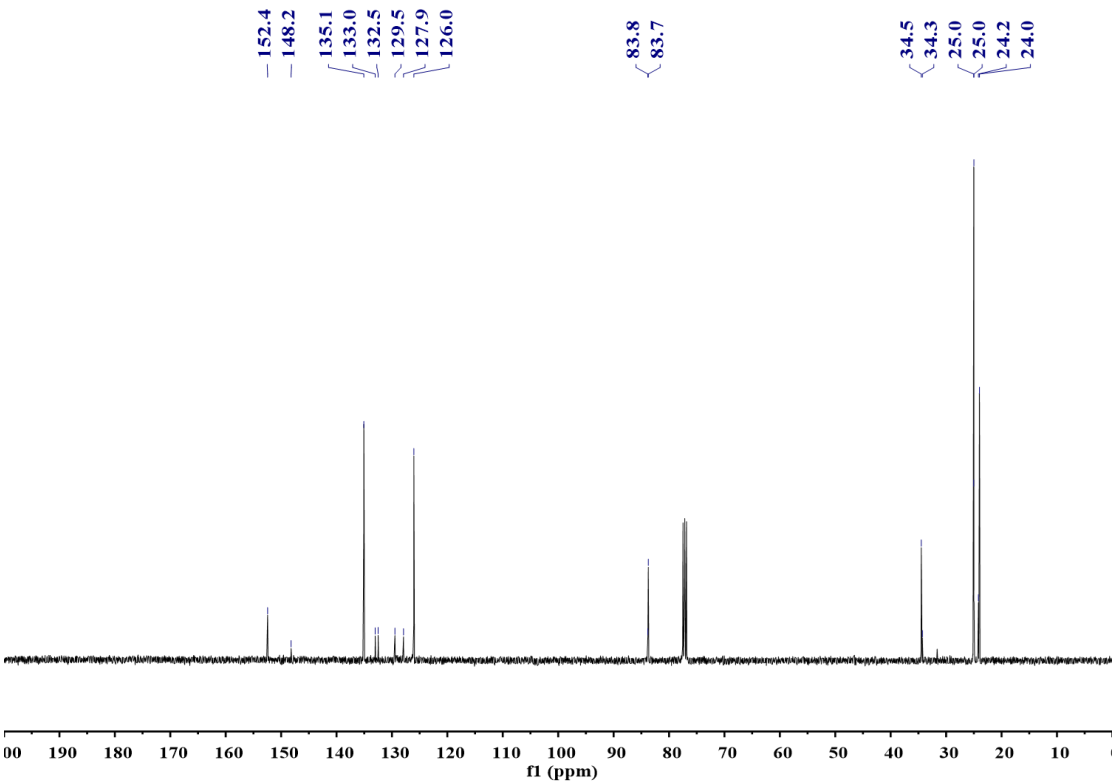

Figure S49. $^{13}C\{^{1}H\}$ NMR spectrum of the borylation products of cumene in $CDCl_3$.

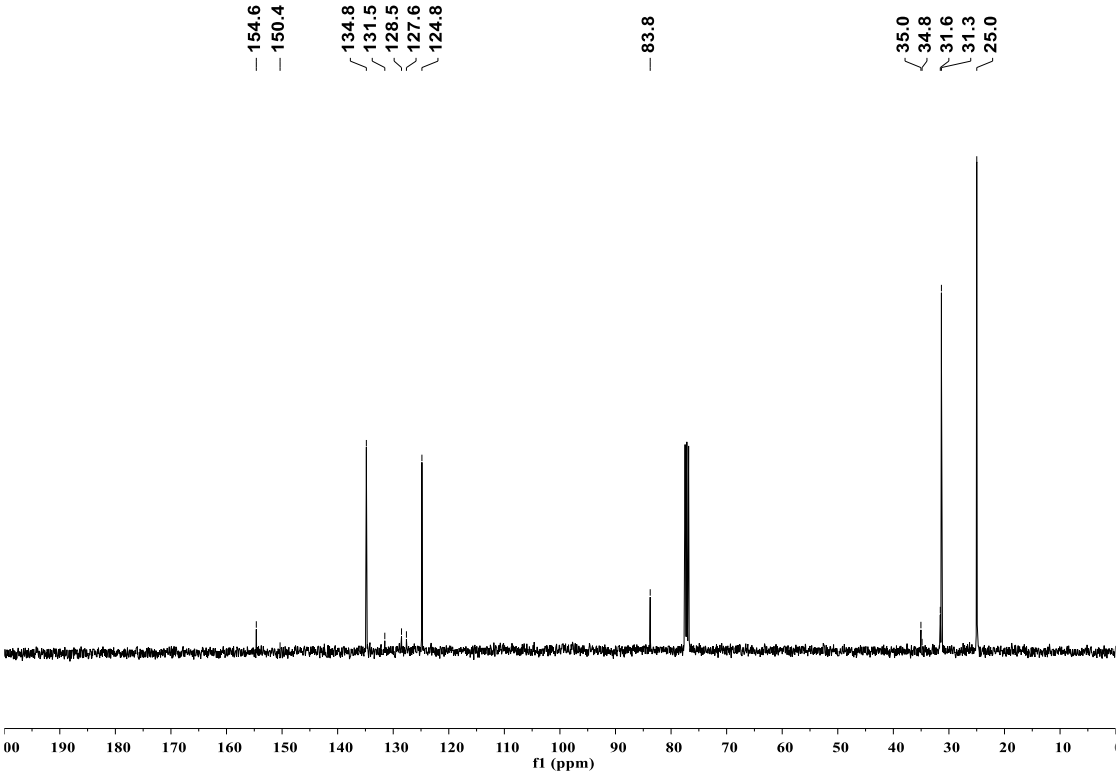

Figure S50. $^{13}C\{^{1}H\}$ NMR spectrum of the borylation products of *t*-butylbenzene in $CDCl_3$.

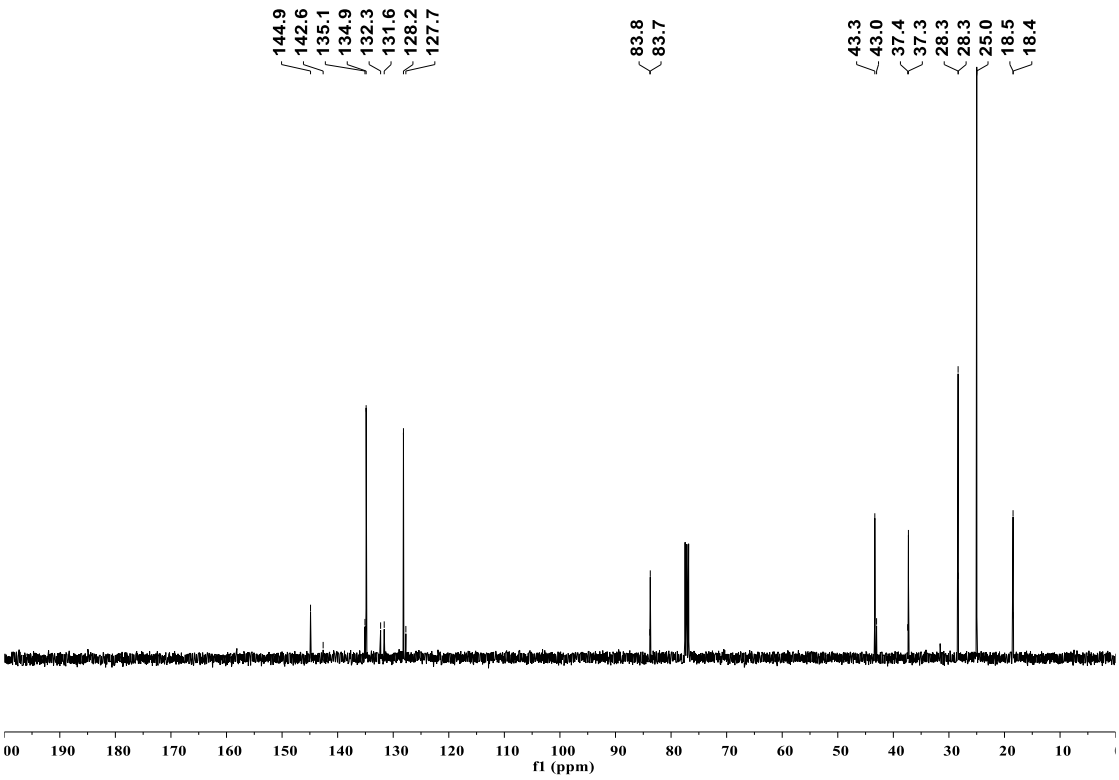

Figure S51. $^{13}C\{^{1}H\}$ NMR spectrum of the borylation products of (cyclobutylmethyl)benzene in $CDCl_3$.

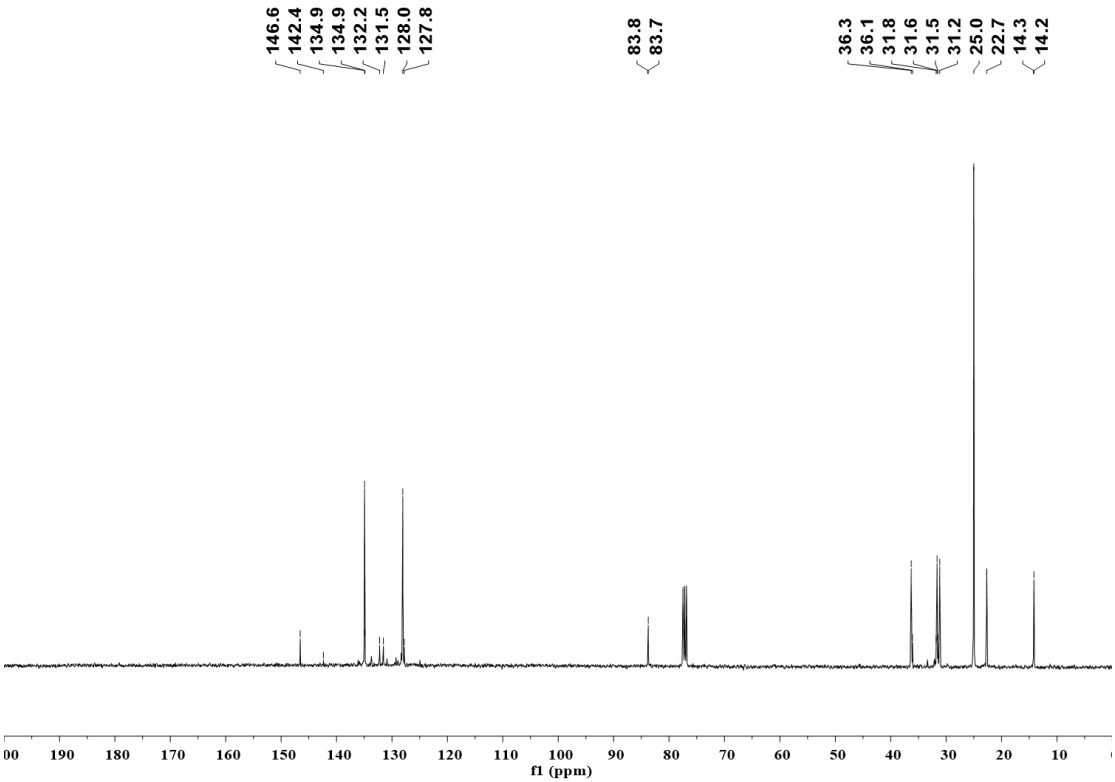

Figure S52. $^{13}C\{^{1}H\}$ NMR spectrum of the borylation products of *n*-amylbenzene in $CDCl_3$.

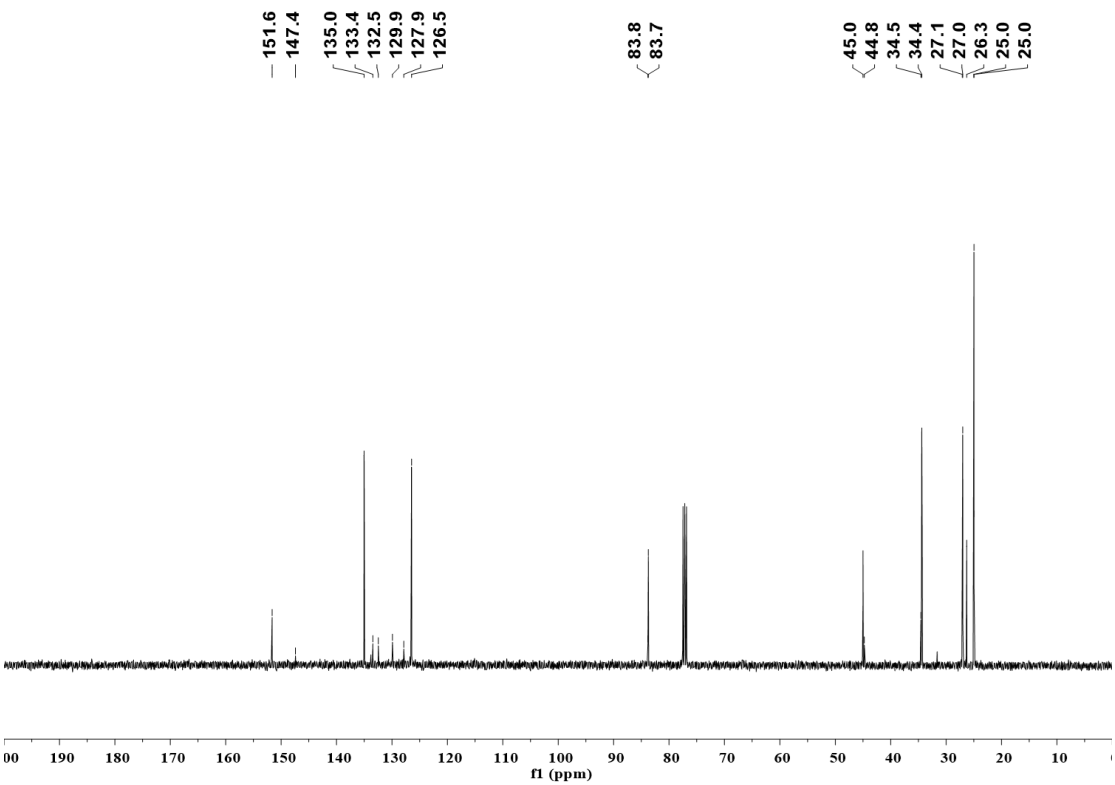

Figure S53. $^{13}C\{^{1}H\}$ NMR spectrum of the borylation products of cyclohexylbenzene in $CDCl_3$.

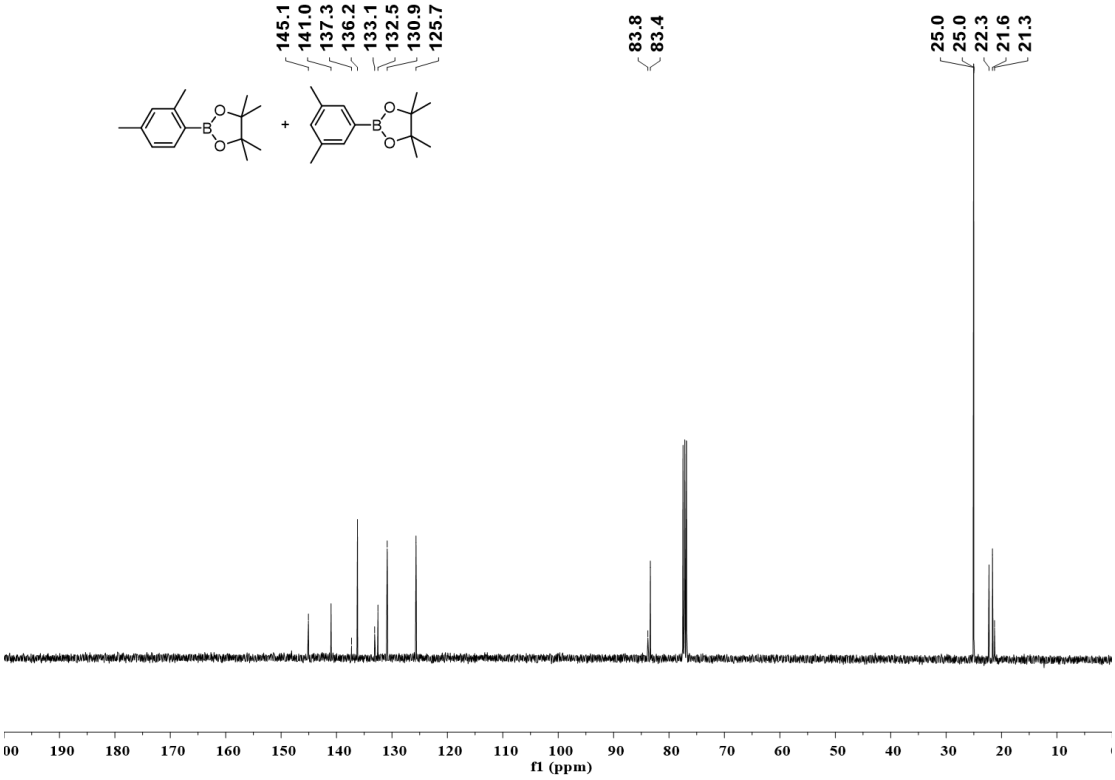

Figure S54. $^{13}C\{^{1}H\}$ NMR spectrum of the mono-borylated products of *m*-xylene in $CDCl_3$.

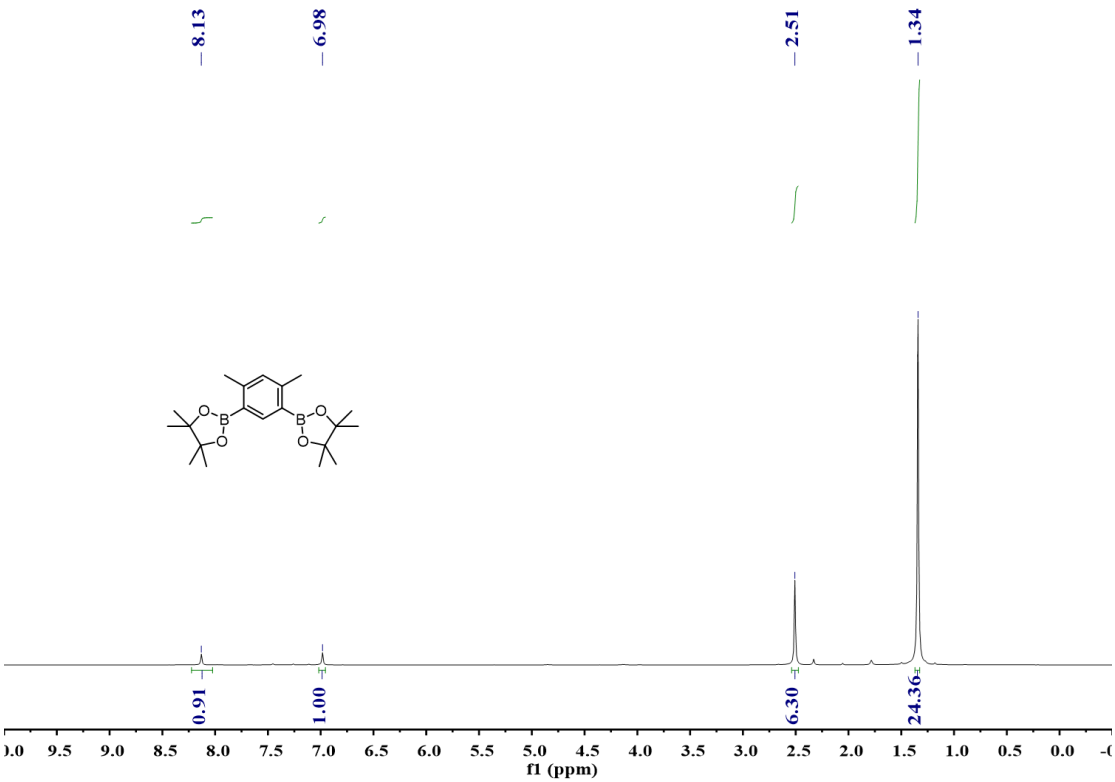

Figure S55. ^{1}H NMR spectrum of **5h** in $CDCl_3$.

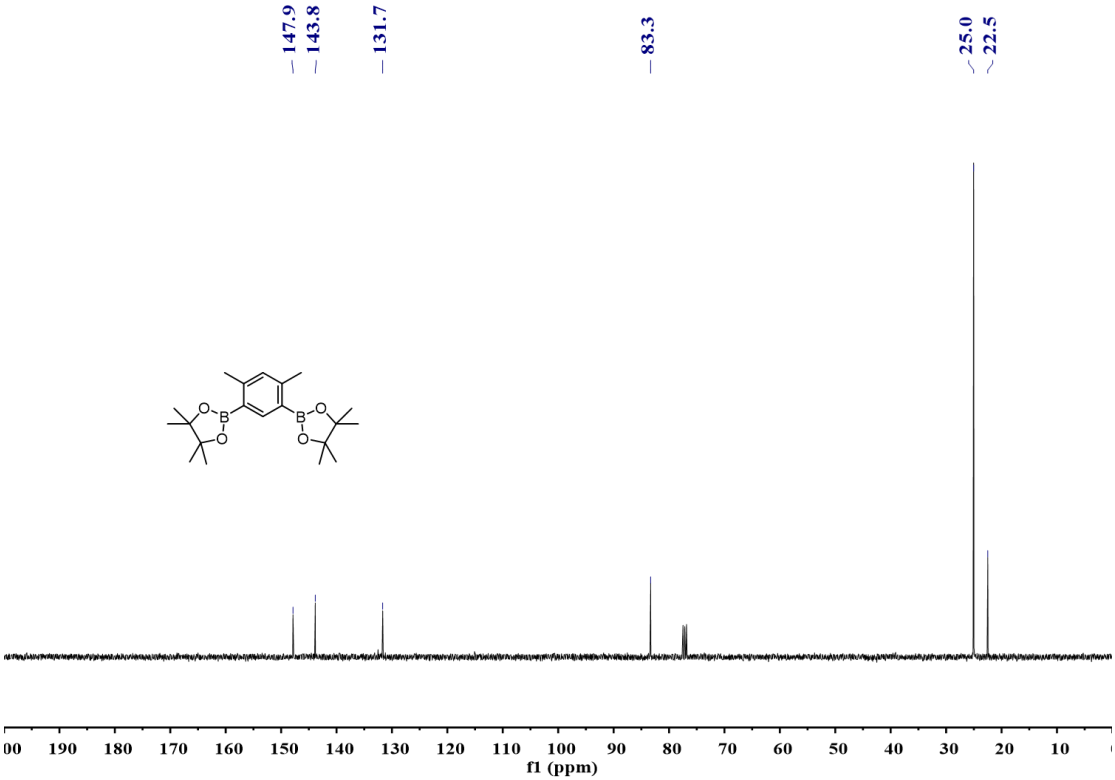

Figure S56. $^{13}C\{^{1}H\}$ NMR spectrum of **5h** in $CDCl_3$.

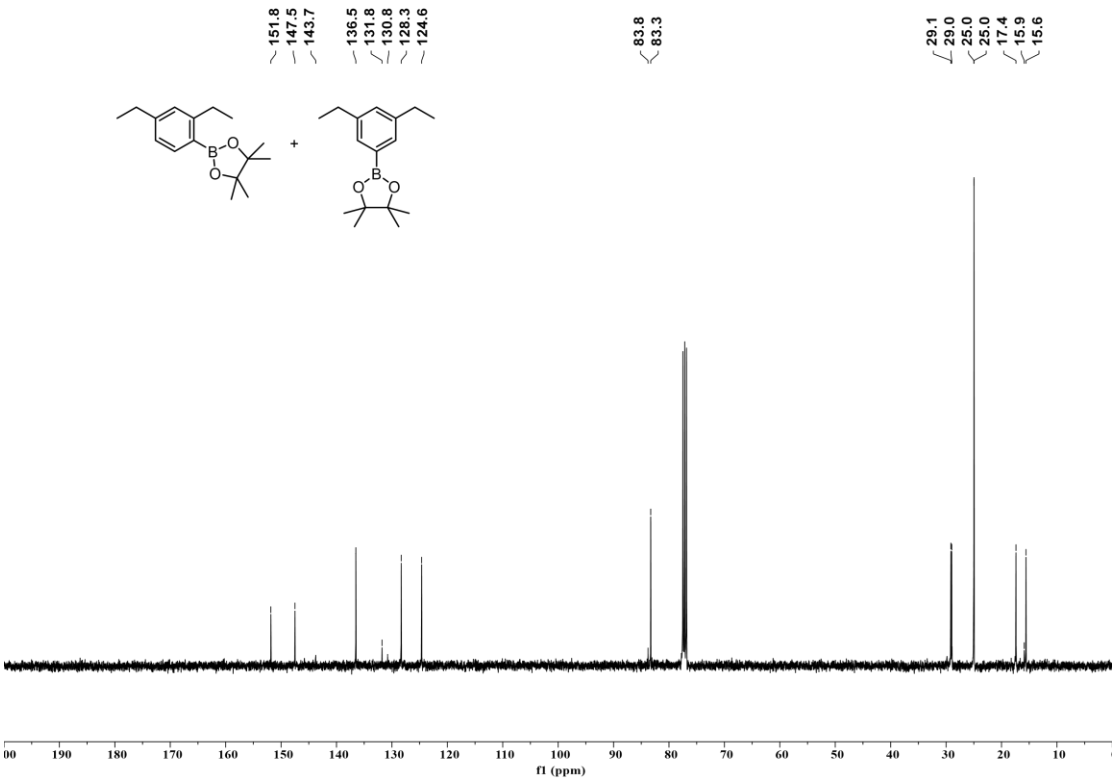

Figure S57. $^{13}C\{^{1}H\}$ NMR spectrum of the mono-borylated products of 1,3-diethylbenzene in $CDCl_3$.

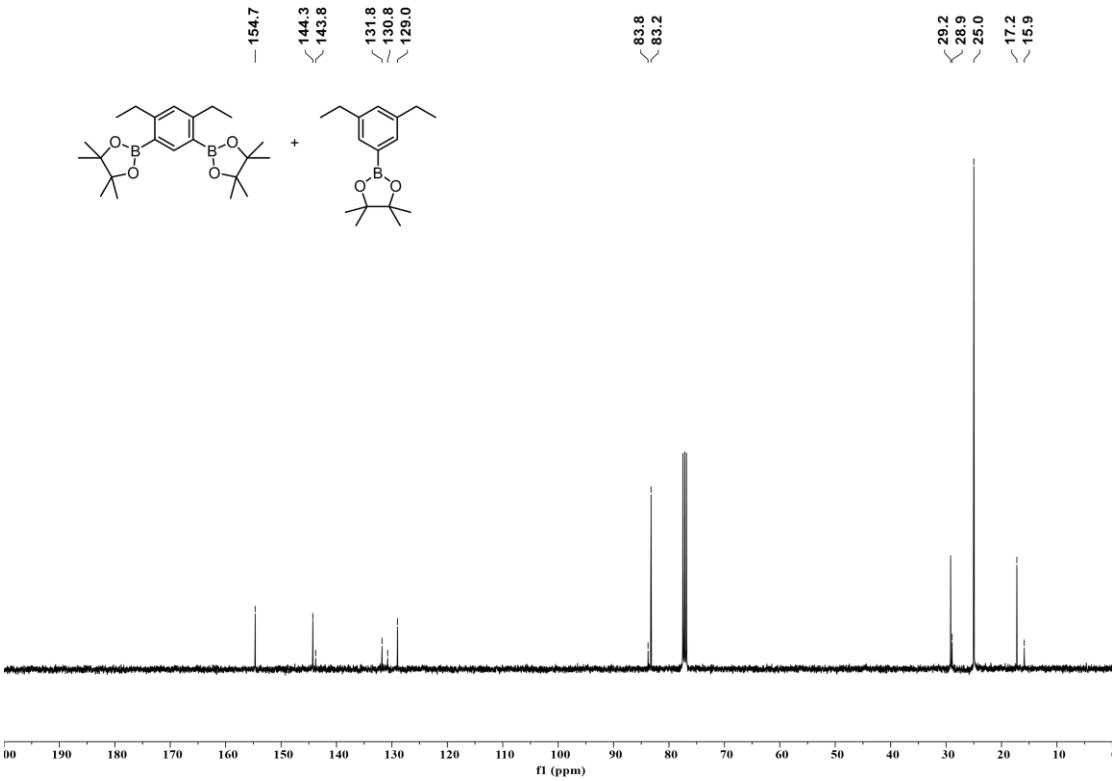

Figure S58. $^{13}C\{^{1}H\}$ NMR spectrum of the di-borylated products of 1,3-diethylbenzene in $CDCl_3$.

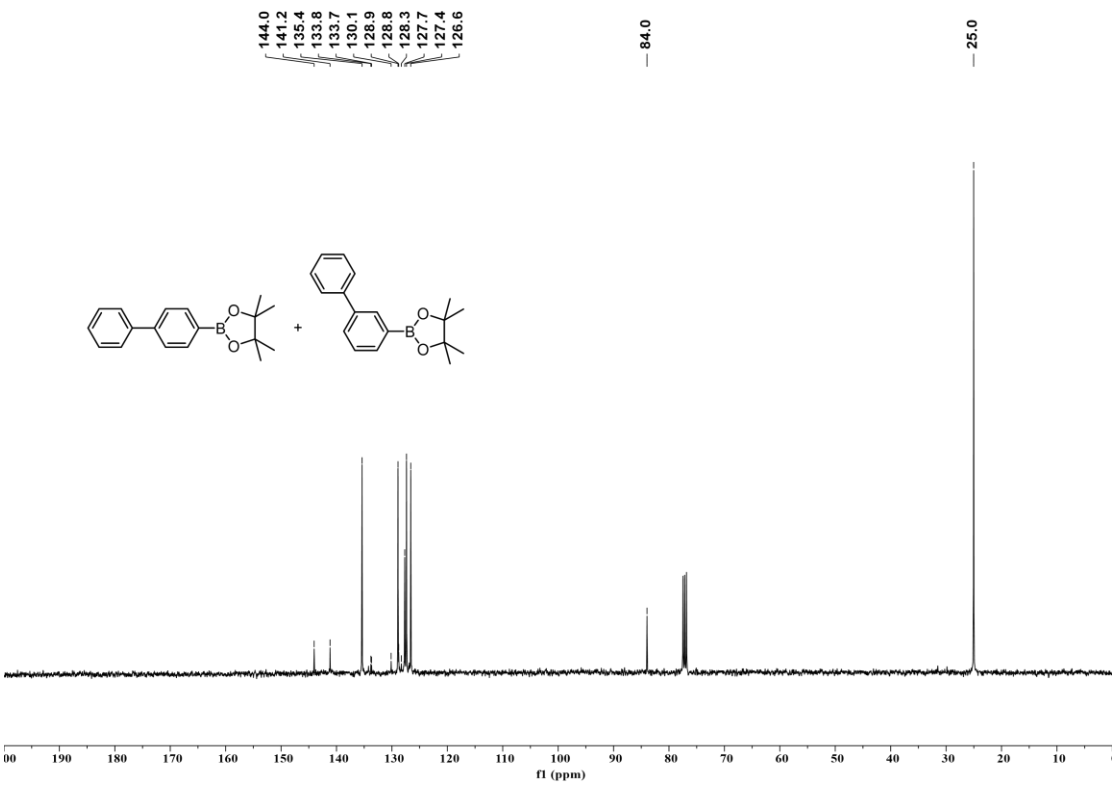

Figure S59. $^{13}C\{^{1}H\}$ NMR spectrum of the borylation products of biphenyl in $CDCl_3$.

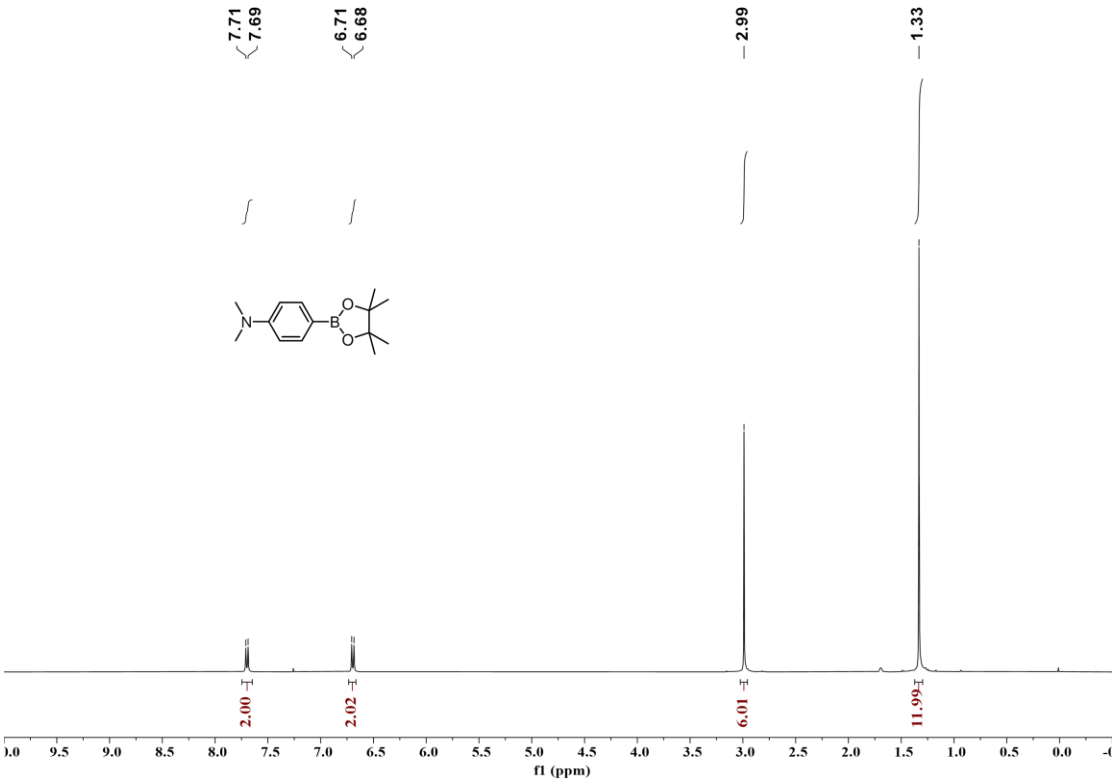

Figure S60. ^{1}H NMR spectrum of **5l** in $CDCl_3$.

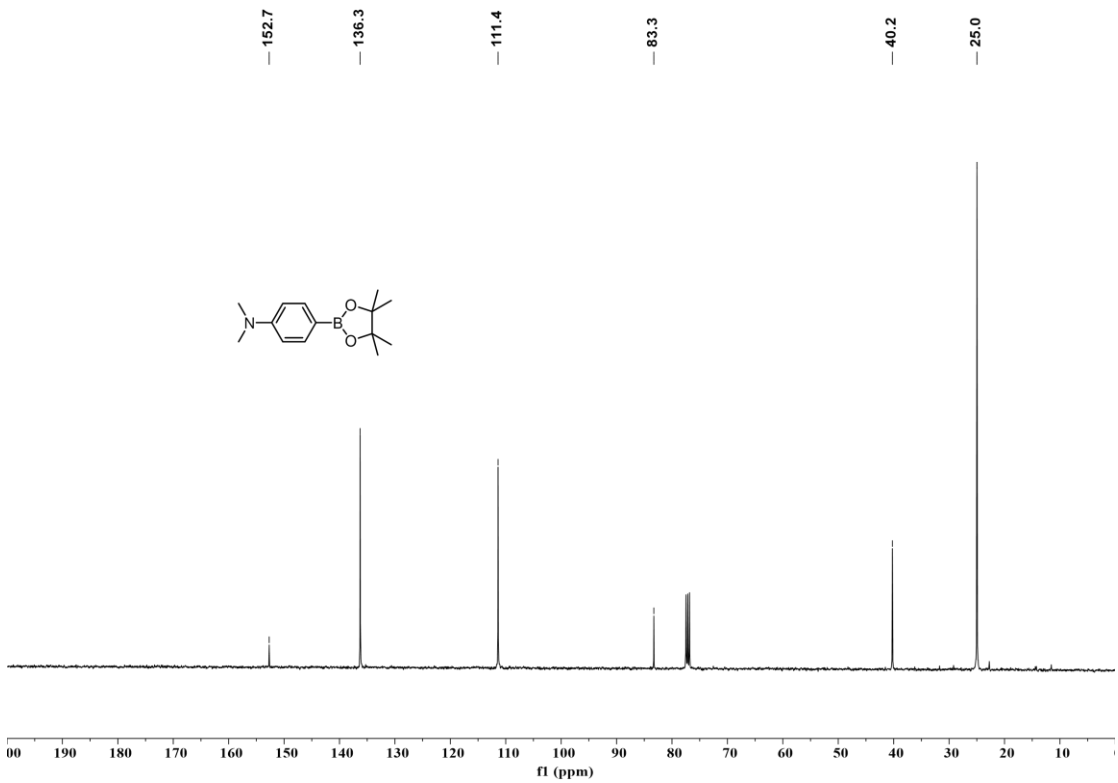

Figure S61. $^{13}C\{^{1}H\}$ NMR spectrum of **5l** in $CDCl_3$.