Electronic Supplementary Material (ESI) for Faraday Discussions.

Supporting Information

FBpin and its Adducts and their Role in Catalytic Borylations

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1 General Considerations

All reactions and subsequent manipulations involving organometallic reagents were performed under an argon atmosphere using standard Schlenk techniques or in a glovebox (Innovative Technology Inc. and Braun Uni Lab). All reactions were carried out in oven-dried glassware. Toluene, *n*-hexane, MeCN and THF were purified by distillation from an appropriate drying agent (sodium with benzophenone as indicator). C_6D_6 and CD_3CN were purchased from Sigma-Aldrich. *i*Pr_2Im,[S1] Me_2Im,[S1] Me*i*PrIm,[S1] *n*Pr_2Im,[S1] Mes_2Im[S2] and 2,3-bis(trimethylsilyloxy)-2,3-dimethylbutane[S3] were prepared according to published procedures. The diboron reagent B_2pin_2 was a generous gift from AllyChem Co. Ltd. Anhydrous NMe_4F is commercially available; for this work, however, it was synthesized according to a literature procedure.[S4] All other reagents were purchased from Aldrich or ABCR. NMR spectra were recorded at 298 K using Bruker Avance 200 (^{1}H, 200 MHz; ^{13}C, 50 MHz; ^{11}B, 64 MHz; ^{19}F, 188 MHz), Bruker Avance 400 (^{1}H, 400 MHz; ^{13}C, 100 MHz; ^{11}B, 128 MHz; ^{19}F, 376 MHz) or Bruker Avance 500 (^{1}H, 500 MHz; ^{13}C, 125 MHz; ^{11}B, 160 MHz; ^{19}F, 471 MHz) spectrometers. ^{1}H NMR chemical shifts are reported relative to TMS and were referenced *via* residual proton resonances of the corresponding deuterated solvent (C_6D_5H: 7.16 ppm; CD_2HCN: 1.94 ppm) whereas $^{13}C\{^1H\}$ NMR spectra are reported relative to TMS using the natural-abundance carbon resonances (C_6D_6: 128.0 ppm; CD_3CN: 1.32, 118.26 ppm).$^{19}F\{^1H\}$ NMR spectra are reported relative to external $CFCl_3$. Coupling constants are given in Hertz. Elemental analyses were performed in the microanalytical laboratory of the Institute of Inorganic Chemistry, Universität Würzburg, using an Elementar vario micro cube. High-resolution mass spectra were obtained using a Thermo Scientific Exactive Plus spectrometer equipped with an Orbitrap Mass Analyzer. Ionizations were accomplished in Liquid Injection Field Desorption Ionization mode using a LIFDI 700 from Linden CMS with 10 kV at the emitter and an accelerating voltage of 5 V.

2 Syntheses of Compounds

Preparation of pinacolatofluoroborane (FBpin)

This was prepared according to a modified literature procedure[S3]: 2,3-bis(trimethylsilyloxy)-2,3-dimethylbutane (2.00 g, 7.62 mmol, 1 equiv.) was dissolved in dichlorormethane (15 mL) and cooled to 0 °C. BF_3•OEt_2 (1.00 mL, 1.15 g, 8.10 mmol, 1.06 equiv.) was added slowly while the evolving Me_3SiF was condensed into a cooling trap at -196 °C. After complete addition, the reaction mixture was allowed to warm to 20 °C and was analyzed by *in situ* NMR-spectroscopy.

^{11}B NMR (128 MHz, CH_2Cl_2, 25 °C): δ_B / ppm = 20.6.

^{19}F NMR (376 MHz, CH_2Cl_2, 25 °C): δ_F / ppm = -151.9.

FBpin•*i*Pr$_2$Im 1

B_2pin_2 (500 mg, 1.97 mmol, 1 equiv.) and NMe_4F (183 mg, 1.97 mmol, 1 equiv.) were dissolved in 20 mL of THF and *i*Pr$_2$Im (300 µL, 300 mg, 1.97 mmol, 1 equiv.) was added to the reaction mixture, which immediately turned from colourless to bright yellow. The reaction mixture was heated in a sealed Schlenk tube at 70 °C for 16 h. The solvent was removed *in vacuo* and the residue was re-dissolved in 10 mL of *n*-hexane. A colourless solid precipitated, which was identified as [pinBF$_2$][NMe$_4$] **6**. The yellow mother liquor was cooled to -30 °C for 3 days to obtain the adduct FBpin·*i*Pr$_2$Im **1** as yellow crystals in low yield.

Yield: 65.0 mg (11%) of yellow crystals.

^{1}H NMR (500 MHz, C_6D_6, 25 °C): δ_H / ppm = 1.06 (d, $^3J_{HH}$ = 7 Hz, 12H, *i*Pr-C*H*$_3$), 1.20 (s, 6H, pin-C*H*$_3$), 1.57 (s, 6H,pin-C*H*$_3$), 6.02 (sept, $^3J_{HH}$ = 7 Hz, 2H, *i*Pr-C*H*), 6.39 (s, 2H, NC*H*C*H*N).

^{13}C{^{1}H} NMR (125 MHz, C_6D_6, 25 °C): δ_C / ppm = 23.2 (*i*Pr-*C*H$_3$), 26.1 (pin-*C*H$_3$), 26.4 (pin-*C*H$_3$), 49.3 (*i*Pr-*C*H), 79.1 (pin-*C*$_q$), 115.9 (N*CC*N), 162.3 (N*C*N) was observed with line broadening (lb 12).

^{11}B{^{1}H} NMR (160 MHz, C_6D_6, 25 °C): δ_B / ppm = 4.90 (d, $^1J_{BF}$ = 54 Hz).

^{19}F NMR (188 MHz, C_6D_6, 25 °C): δ_F / ppm = -130.9 (q, $^1J_{FB}$ = 54 Hz).

Elemental analysis calcd (%) for $C_{15}H_{28}O_2N_2BF$: C 60.42, H 9.46, N 9.39; found: C 60.91, H 9.65, N 9.20.

FBpin•Me$_2$Im 2

B_2pin_2 (500 mg, 1.97 mmol, 1 equiv.) and NMe_4F (183 mg, 1.97 mmol, 1 equiv.) were dissolved in 20 mL of THF and Me_2Im (189 µL, 189 mg, 1.97 mmol, 1 equiv.) was added to the reaction mixture, which immediately turned from colourless to red. The reaction mixture was heated at 70 °C for 16 h. The solvent was removed *in vacuo* and the residue was re-dissolved in 10 mL of *n*-hexane. A colourless solid precipitated, which was identified as a mixture of [pinBF$_2$][NMe$_4$] **6** and the adduct FBpin·Me$_2$Im **2**. Other unidentified boron containing species were present in solution. To separate the two compounds, the residue was re-dissolved in MeCN and FBpin·Me$_2$Im **2** crystallized at -30 °C in very low yield.

Yield: 40.0 mg (8%) of yellow crystals.

^{1}H NMR (200 MHz, MeCN-d$_3$, 25 °C): δ_H / ppm = 0.94 (s, 6 H, pin-C*H*$_3$), 1.13 (s, 6H, pin-C*H*$_3$), 3.90 (s, 6H, NC*H*$_3$), 6.98 (s, 2H, NC*H*C*H*N).

^{11}B{^{1}H} NMR (64 MHz, MeCN-d$_3$, 25 °C): δ_B / ppm = 4.27 (d, $^1J_{BF}$ = 54 Hz).

^{19}F NMR (188 MHz, MeCN-d$_3$, 25 °C): δ_F / ppm = -133.5 (q, $^1J_{FB}$ = 54 Hz).

FBpin•Me*i*Pr$_2$Im 3

B_2pin_2 (200 mg, 788 µmol, 1 equiv.) and NMe_4F (73.4 mg, 788 µmol, 1 equiv.) were dissolved in 20 mL of THF and Me*i*Pr$_2$Im (98.0 µL, 98.0 mg, 788 µmol, 1 equiv.) was added to the reaction mixture, which immediately turned from colourless to orange. The reaction mixture was heated at 70 °C for 16 h. The solvent was removed *in vacuo* and the residue was re-dissolved in 10 mL of *n*-hexane. A colourless solid precipitated, which was identified as [pinBF$_2$][NMe$_4$] **6**. The orange mother liquor was cooled to -30 °C to obtain the adduct FBpin·Me*i*Pr$_2$Im **3**.

Yield: 20.0 mg (9%) of an orange solid.

^{1}H NMR (200 MHz, C_6D_6, 25 °C): δ_H / ppm = 1.01 (d, $^3J_{HH}$ = 7 Hz, 6H, *i*Pr-C*H*$_3$), 1.20 (s, 6H, pin-C*H*$_3$), 1.60 (s, 6H, pin-C*H*$_3$), 3.55 (s, 6 H, Me-C*H*$_3$), 5.75 (d, $^3J_{HH}$ = 2 Hz, 1H, NC*H*CHN), 5.91 (sept, $^3J_{HH}$ = 7 Hz, 1H, *i*Pr-C*H*), 6.02 (d, $^3J_{HH}$ = 2 Hz, 1H, NCHC*H*N).

^{11}B{^{1}H} NMR (64 MHz, C_6D_6, 25 °C): δ_B / ppm = 4.81 (d, $^1J_{BF}$ = 54 Hz).

^{19}F NMR (188 MHz, C_6D_6, 25 °C): δ_F / ppm = -132.1 (q, $^1J_{FB}$ = 54 Hz).

FBpin•*n*Pr$_2$Im 4

B_2pin_2 (200 mg, 788 µmol, 1 equiv.) and NMe_4F (73.4 mg, 788 µmol, 1 equiv.) were dissolved in 20 mL of THF and *n*Pr$_2$Im (120 µL, 120 mg, 788 µmol, 1 equiv.) was added to the reaction mixture, which immediately turned from colourless to bright yellow. The reaction mixture was heated in a sealed Schlenk tube at 70 °C for 16 h. The solvent was removed *in vacuo* and the residue was re-dissolved in 10 mL of *n*-hexane. A yellow solid precipitated, which was identified as the adduct FBpin·*n*Pr$_2$Im **4**.

For X-ray diffraction: A saturated solution of FBpin·*n*Pr$_2$Im **4** in *n*-hexane was cooled to -30 °C to obtain single crystals for X-ray diffraction.

Yield: 213 mg (91%) of a colourless solid.

^{1}H NMR (500 MHz, CD_3CN, 25 °C): δ_H / ppm = 0.89 (t, $^3J_{HH}$ = 7 Hz, 6H, *n*Pr-C*H*$_3$), 0.93 (s, 6H, pin-C*H*$_3$), 1.12 (s, 6H, pin-C*H*$_3$), 1.79 (sext, $^3J_{HH}$ = 7 Hz, 4H, C*H*$_2$CH$_3$), 4.33 (t, $^3J_{HH}$ = 7 Hz, 4H, NC*H*$_2$), 7.04 (s, 2H, NC*H*C*H*N).

^{13}C{^{1}H} NMR (125 MHz, CD_3CN, 25 °C): δ_C / ppm = 11.1 (*n*Pr-*C*H$_3$), 25.0 (*C*H$_2$CH$_3$), 25.5 (pin-*C*H$_3$), 26.1 (pin-*C*H$_3$), 50.6 (N-*C*H$_2$), 79.4 (pin-*C*$_q$), 121.0 (N*CC*N), 162.2 (N*C*N) assigned *via* 2D NMR spectroscopy (HMBC).

^{11}B{^{1}H} NMR (160 MHz, CD_3CN, 25 °C): δ_B / ppm = 3.36 (d, $^1J_{BF}$ = 54 Hz).

^{19}F NMR (471 MHz, CD_3CN, 25 °C): δ_F / ppm = -131.0 (q, $^1J_{FB}$ = 54 Hz).

Elemental analysis calcd (%) for $C_{15}H_{28}O_2N_2BF$: C 60.42, H 9.46, N 9.39; found: C 60.16, H 9.39, N 9.47.

FBpin•Mes_2Im 5

2,3-Bis(trimethylsilyloxy)-2,3-dimethylbutane (267 mg, 1.02 mmol, 1 equiv.) was dissolved in CH_2Cl_2 (5 mL) and $BF_3{\cdot}OEt_2$ (126 µL, 145 mg, 1.02 mmol, 1 equiv.) was added. After 10 min at room temperature 1,3-dimesitylimidazoline-2-ylidene (310 mg, 1.02 mmol, 1 equiv.) was added. Immediate evaporation of the solvent *in vacuo* and washing of the residue with 10 mL of *n*-hexane and subsequent drying *in vacuo* yielded the product.

Yield: 254 mg (55%) of a colourless solid.

^{1}H NMR (500 MHz, C_6D_6, 25 °C): δ_H / ppm = 0.90 (s, 6H, pin-CH_3), 1.24 (s, 6H, pin-CH_3), 2.08 (s, 6H, *p*-Mes-CH_3), 2.18 (s, 12H, *o*-Mes-CH_3), 5.89 (s, 2H, NC*H*C*H*N), 6.75 (s, 4H, Mes-C*H*).

^{13}C{^{1}H} NMR (125 MHz, C_6D_6, 25 °C): δ_C / ppm = 18.1 (*o*-Mes-*C*H_3), 21.0 (*p*-Mes-*C*H_3), 26.3 (pin-*C*H_3), 26.7 (pin-*C*H_3), 78.7 (pin-C_q), 121.4 (N*CC*N), 129.0 (Mes-*C*H), 135.3 (*o*-Mes-C_q), 135.4 (*p*-Mes-C_q), 138.8 (Mes-C_{ipso}), 167.5 (N*C*N) assigned *via* 2D NMR spectroscopy (HMBC).

^{11}B{^{1}H} NMR (160 MHz, C_6D_6, 25 °C): δ_B / ppm = 4.34 (d, $^1J_{BF}$ = 54 Hz).

^{19}F NMR (471 MHz, C_6D_6, 25 °C): δ_F / ppm = -131.4 (q, $^1J_{FB}$ = 54 Hz).

Elemental analysis calcd (%) for $C_{27}H_{36}O_2N_2BF$: C 72.00, H 8.06, N 6.22; found: C 71.97, H 8.29, N 6.22.

HRMS-ASAP (m/z): $[M+H]^+$ calcd for $C_{27}H_{36}O_2N_2BF$, 451.2927; found, 451.2922.

[pinBF_2][NMe_4] 6

B_2pin_2 (200 mg, 0.79 mmol, 1 equiv.) and NMe_4F (73.4 mg, 0.79 mmol, 1 equiv.) were dissolved in 20 mL of THF and *i*Pr_2Im (120 µL, 120 mg, 0.79 mmol, 1 equiv.) was added to the reaction mixture, which immediately turned from colourless to bright yellow. The reaction mixture was heated in a sealed Schlenk tube at 70 °C for 16 h. The solvent was removed *in vacuo* and the residue was re-dissolved in 10 mL of *n*-hexane. A colourless solid precipitated, which was identified as [pinBF_2][NMe_4] **6**. The salt was collected by filtration, washed with THF (7 mL) and dried *in vacuo*.

Yield: 79.3 mg (42%) of a colourless solid.

^{1}H NMR (400 MHz, CD_3CN, 25 °C): δ_H / ppm = 1.00 (2, 12H, pin-CH_3), 1.60 (s, 12H, NCH_3).

^{13}C{^{1}H} NMR (100 MHz, CD_3CN, 25 °C): δ_C / ppm = 26.0 (pin-*C*H_3), 56.1 (N-*C*H_3), 78.1 (pin-C_q).

^{11}B{^{1}H} NMR (128 MHz, CD_3CN, 25 °C): δ_B / ppm = 5.02 (t, $^1J_{BF}$ = 21 Hz).

^{19}F NMR (376 MHz, CD_3CN, 25 °C): δ_F / ppm = -141.5 (q, $^1J_{FB}$ = 21 Hz).

Elemental analysis calcd (%) for $C_{10}H_{24}O_2NBF_2$: C 50.23, H 10.12, N 5.86; found: C 49.88, H 10.22, N 6.11.

HRMS-ESI pos (m/z): $[M]^+$ calcd for NC_4H_{12}, 74.0964; found, 74.0969.

HRMS-ESI neg (m/z): $[M]^-$ calcd for $C_6H_{12}BO_2F_2$, 165.0904; found, 165.0892.

[pinBF$_2$][N*n*Bu$_4$] 7

To a solution of B_2pin_2 (5.00 g, 19.7 mmol, 1 equiv.) in 15 mL of THF in a Schlenk flask, a tetrabutylammoniumfluoride solution in THF (39.4 mL, 39.4 mmol, 1.0 M, 2 equiv.) was added and the reaction mixture was heated at 80 °C for 2 days. The solvent was removed under reduced pressure and the resulting oil left to crystallize at room temperature for 3 days. The crude product was recrystallized several times from hot *n*-hexane.

Yield: 3.92 g (49%) of colourless needles.

^{1}H NMR (400 MHz, CD_3CN, 25 °C): δ_H / ppm = 0.96 (t, $^3J_{HH}$ = 7 Hz, 12H, CH_2CH_3), 0.99 (s, 12H, pin-CH_3), 1.35 (sext, $^3J_{HH}$ = 7 Hz, 8H, CH_2CH_3), 1.60 (m, 8H, N-CH_2CH_2), 3.10 (m, 8H, N-CH_2).

^{13}C{^{1}H} NMR (100 MHz, CD_3CN, 25 °C): δ_C / ppm = 13.8 (*n*BuCH_3), 20.3 (CH_2CH_3), 24.3 (N-CH_2CH_2), 26.1 (pin-CH_3), 59.3 (N-CH_2), 77.9 (pin-C_q).

^{11}B{^{1}H} NMR (128 MHz, CD_3CN, 25 °C): δ_B / ppm = 4.95 (t, $^1J_{BF}$ = 20 Hz).

^{19}F NMR (376 MHz, CD_3CN, 25 °C): δ_F / ppm = -142.2 (q, $^1J_{FB}$ = 20 Hz).

Elemental analysis calcd (%) for $C_{22}H_{48}O_2NBF_2$: C 64.85, H 11.88, N 3.44; found: C 65.13, H 12.10, N 3.51.

HRMS-ESI pos (m/z): $[M]^+$ calcd for $NC_{16}H_{36}$, 242.2853; found, 242.2835.

HRMS-ESI neg (m/z): $[M]^-$ calcd for $C_6H_{12}BO_2F_2$, 165.0904; found, 165.0891.

3 NMR Spectra

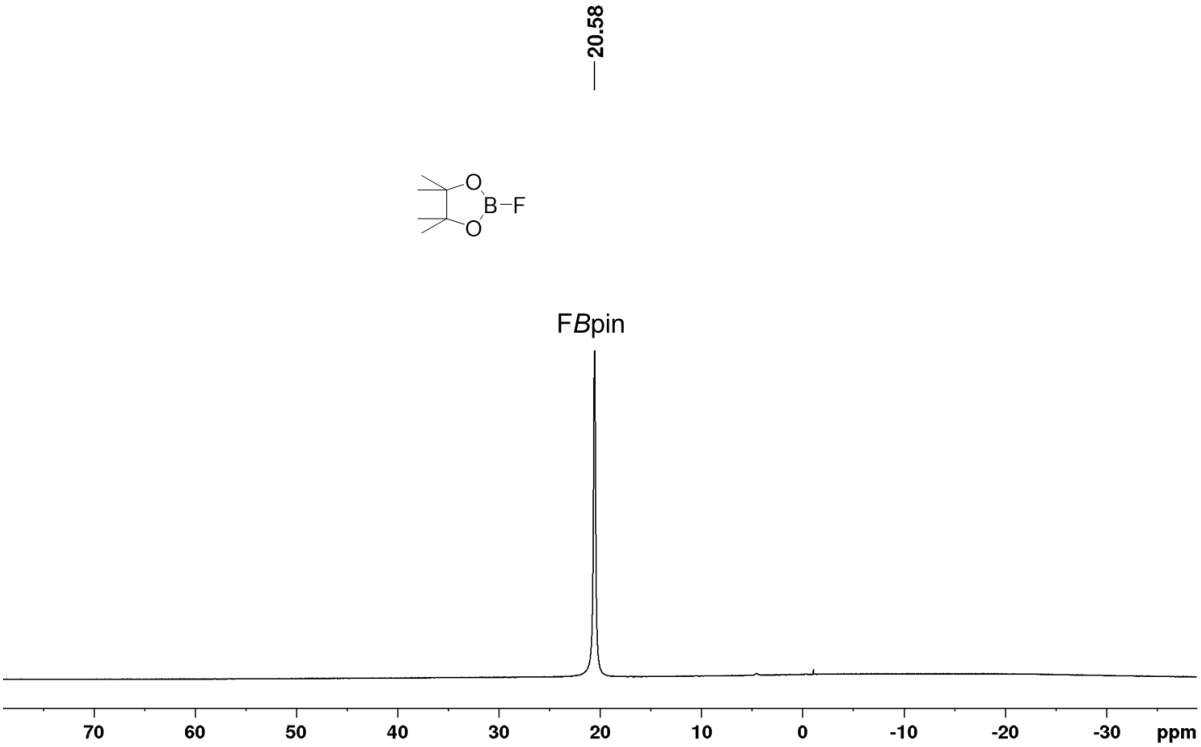

Figure S1. *In situ* ^{11}B NMR spectrum of FBpin in CH_2Cl_2 (128 MHz).

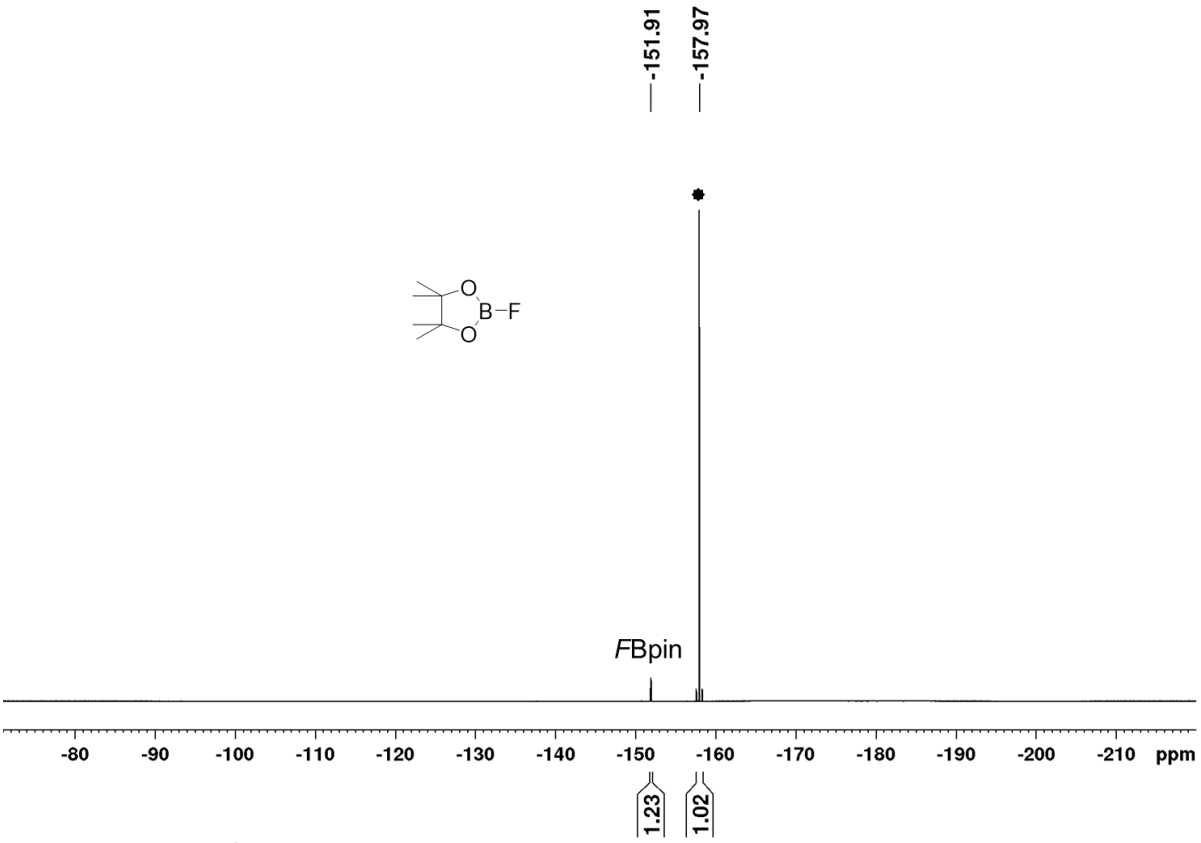

Figure S2. *In situ* ^{19}F NMR spectrum of FBpin in CH_2Cl_2 (128 MHz). (*= residual trimethylsilyl fluoride (TMSF))

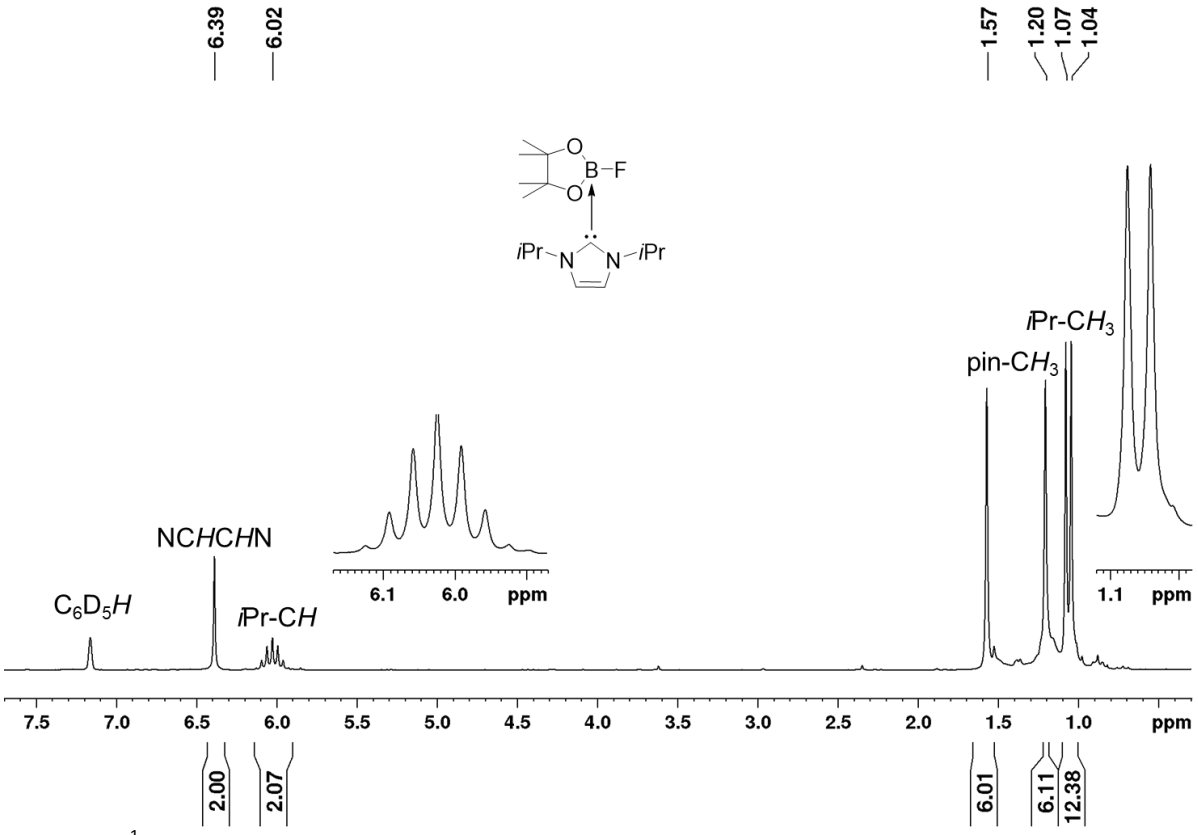

Figure S3. ^{1}H NMR spectrum of FBpin·*i*Pr$_2$Im **1** recorded in C_6D_6 (500 MHz).

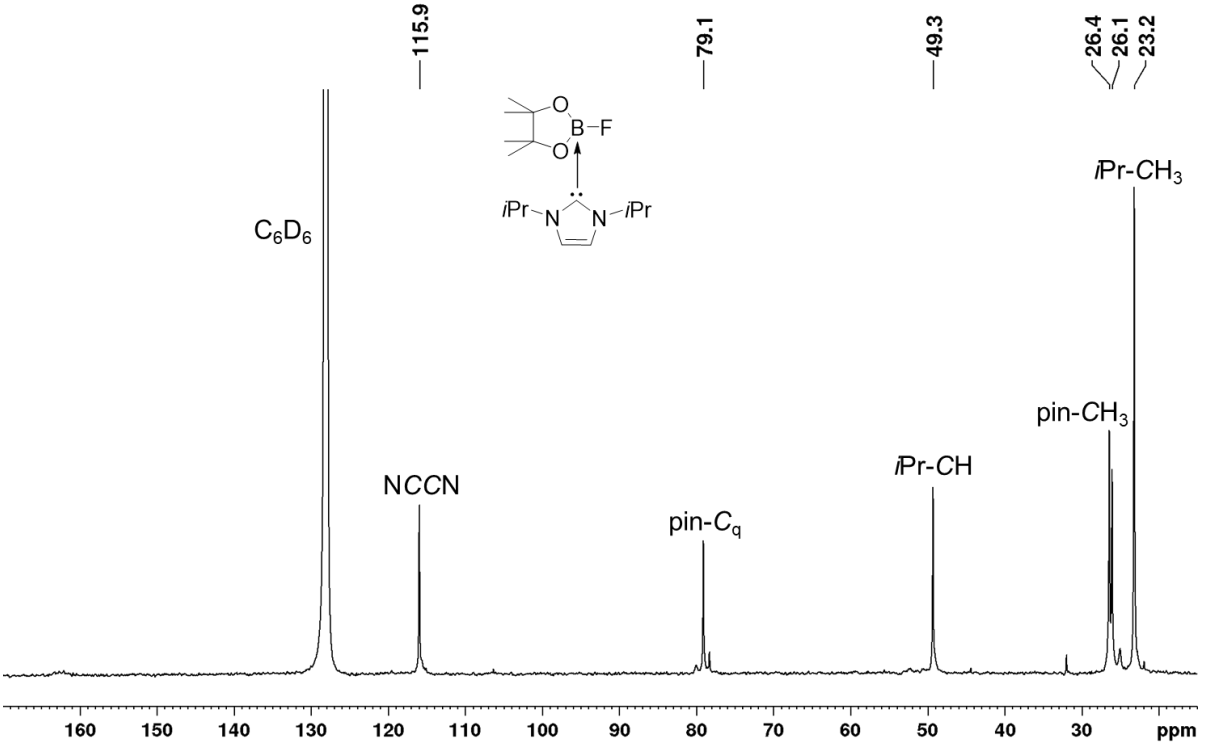

Figure S4. ^{13}C{^{1}H} NMR spectrum of FBpin·*i*Pr$_2$Im **1** recorded in C_6D_6 (125 MHz).

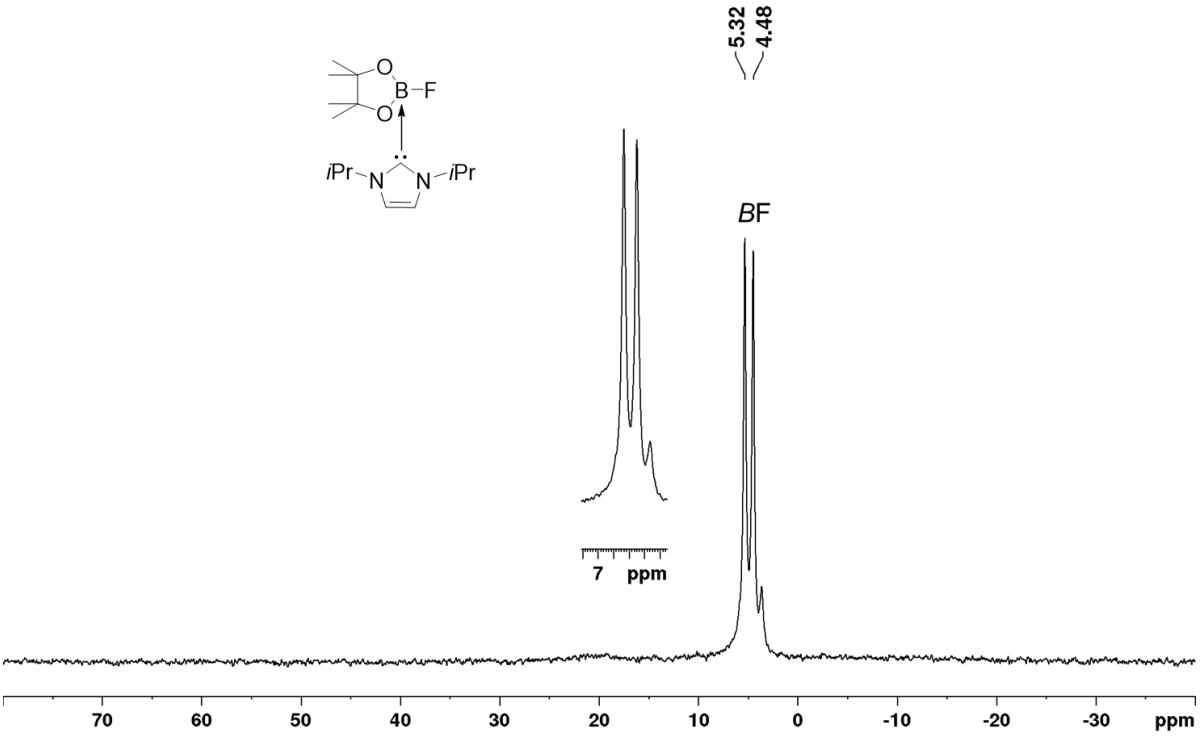

Figure S5. $^{11}B\{^{1}H\}$ NMR spectrum of FBpin·*i*Pr$_2$Im **1** recorded in C_6D_6 (160 MHz).

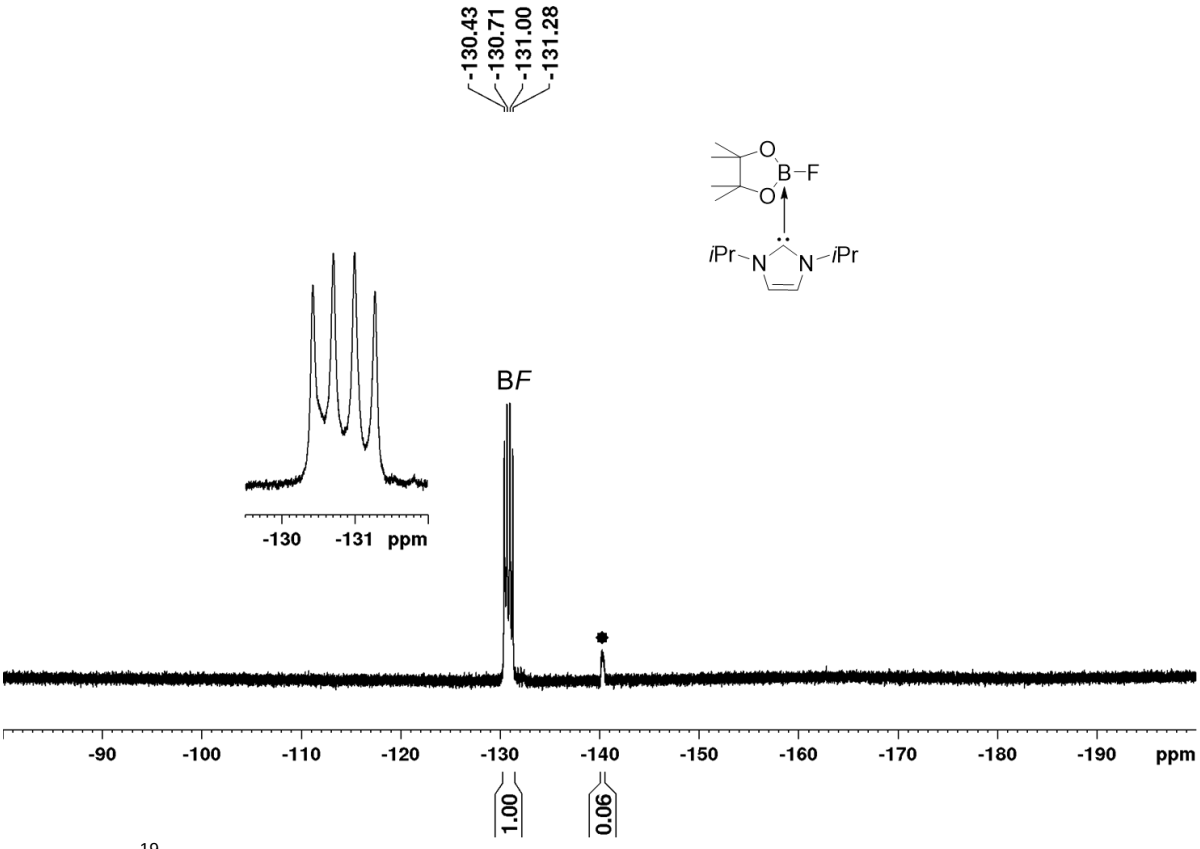

Figure S6. ^{19}F NMR spectrum of FBpin·*i*Pr$_2$Im **1** recorded in C_6D_6 (471 MHz). (*= [pinBF$_2$][NMe$_4$] **6**)

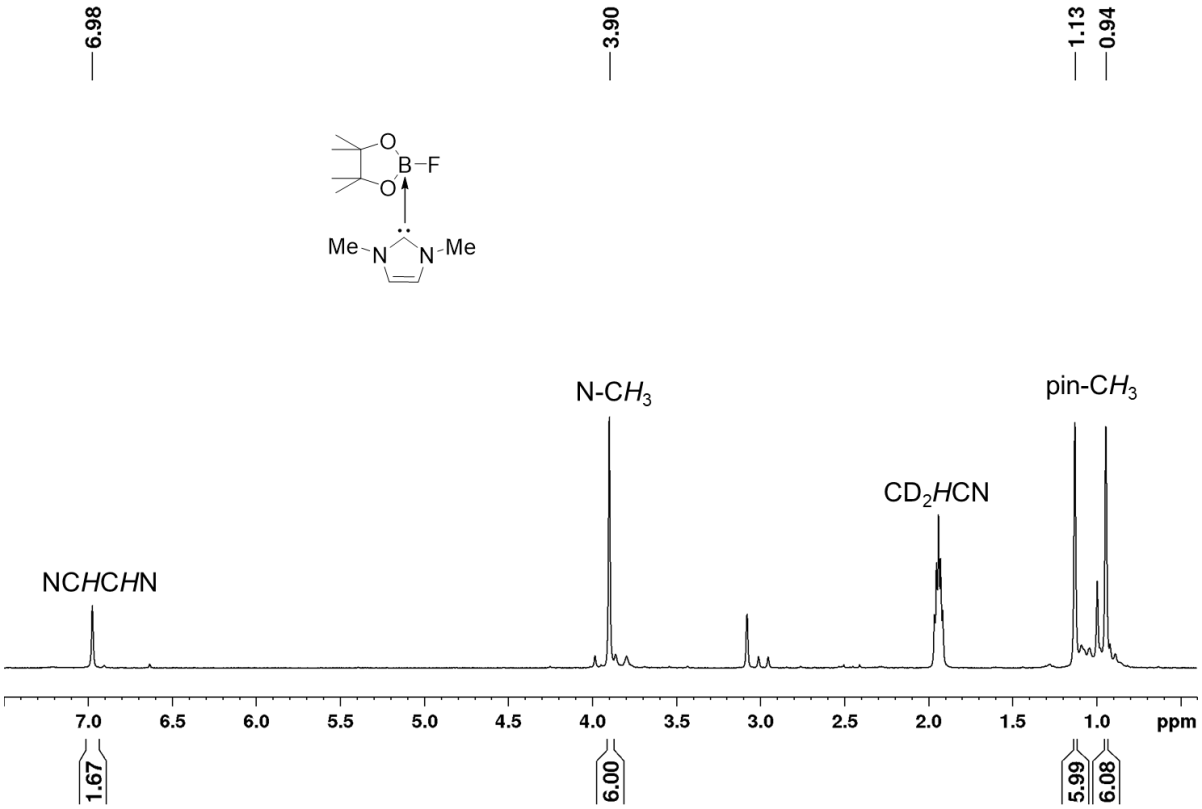

Figure S7. ^{1}H NMR spectrum of FBpin·Me$_2$Im **2** recorded in CD$_3$CN (200 MHz).

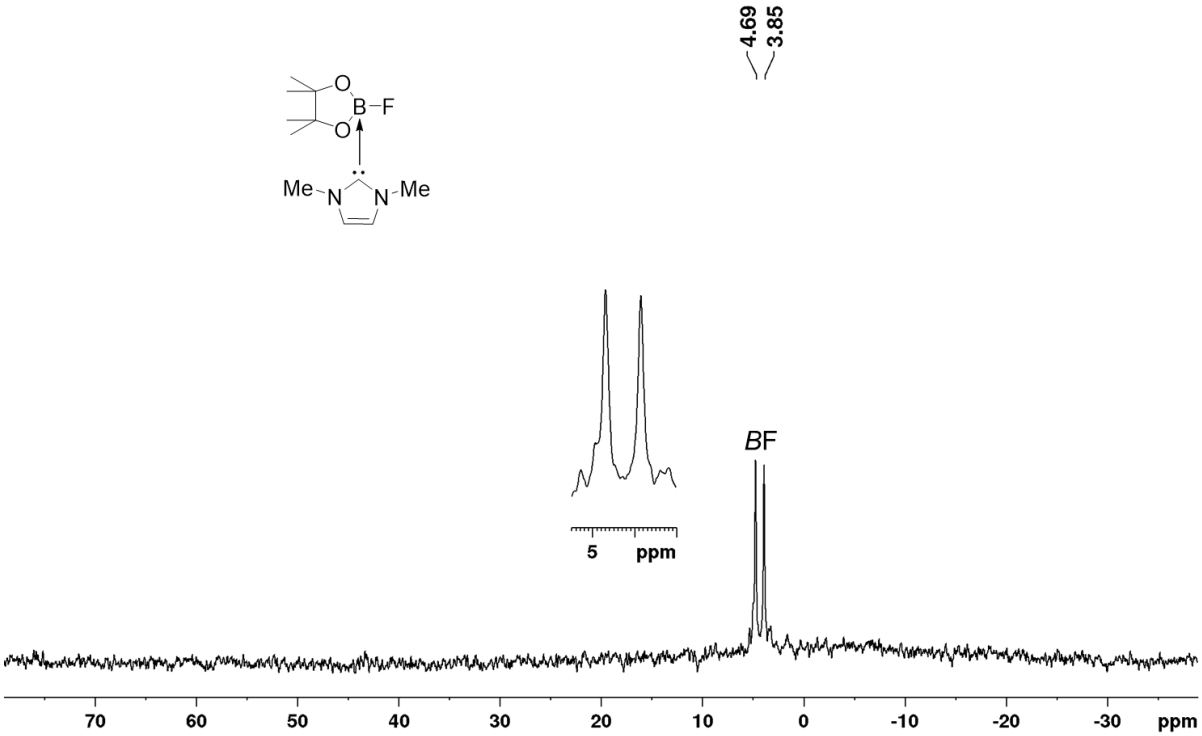

Figure S8. ^{11}B{^{1}H} NMR spectrum of FBpin·Me$_2$Im **2** recorded in CD$_3$CN (64 MHz).

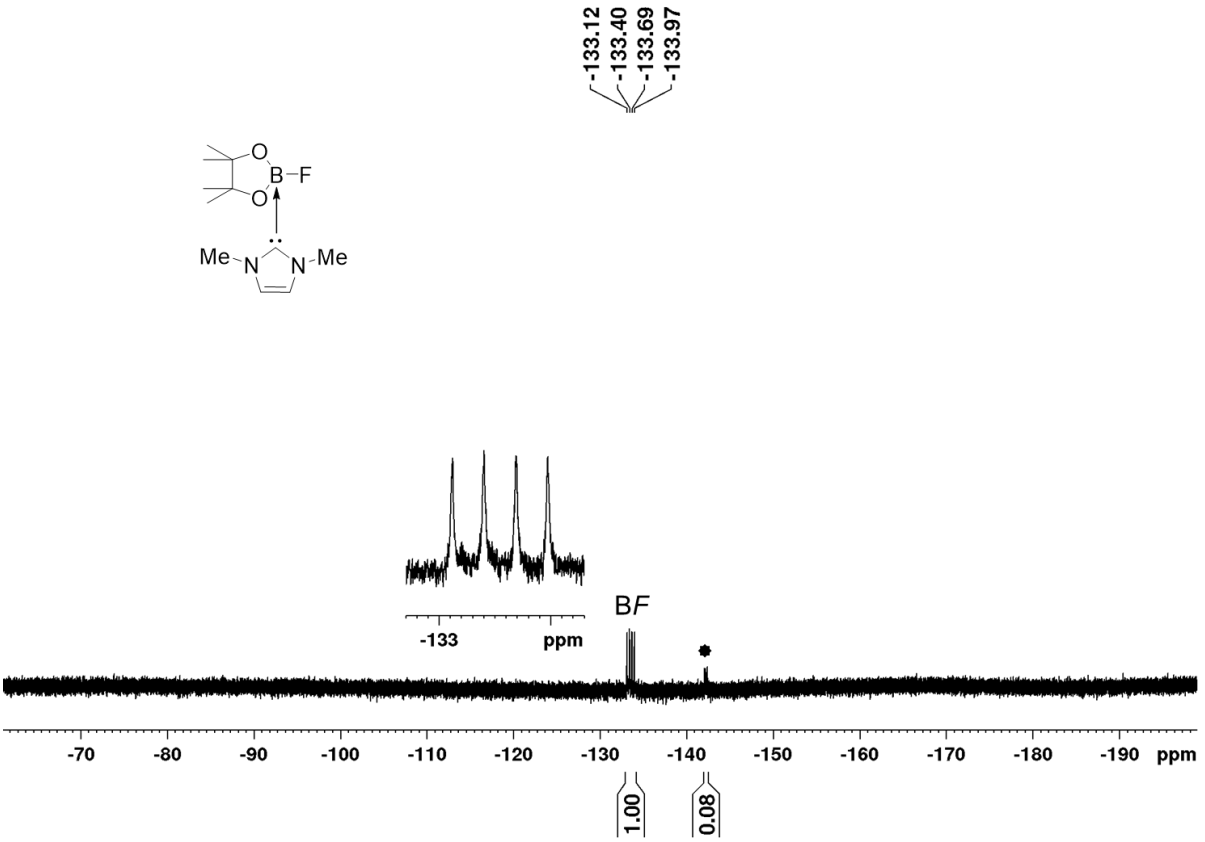

Figure S9. ^{19}F NMR spectrum of FBpin·Me_2Im **2** recorded in CD_3CN (188 MHz). (*= [pinBF_2][NMe_4] **6**)

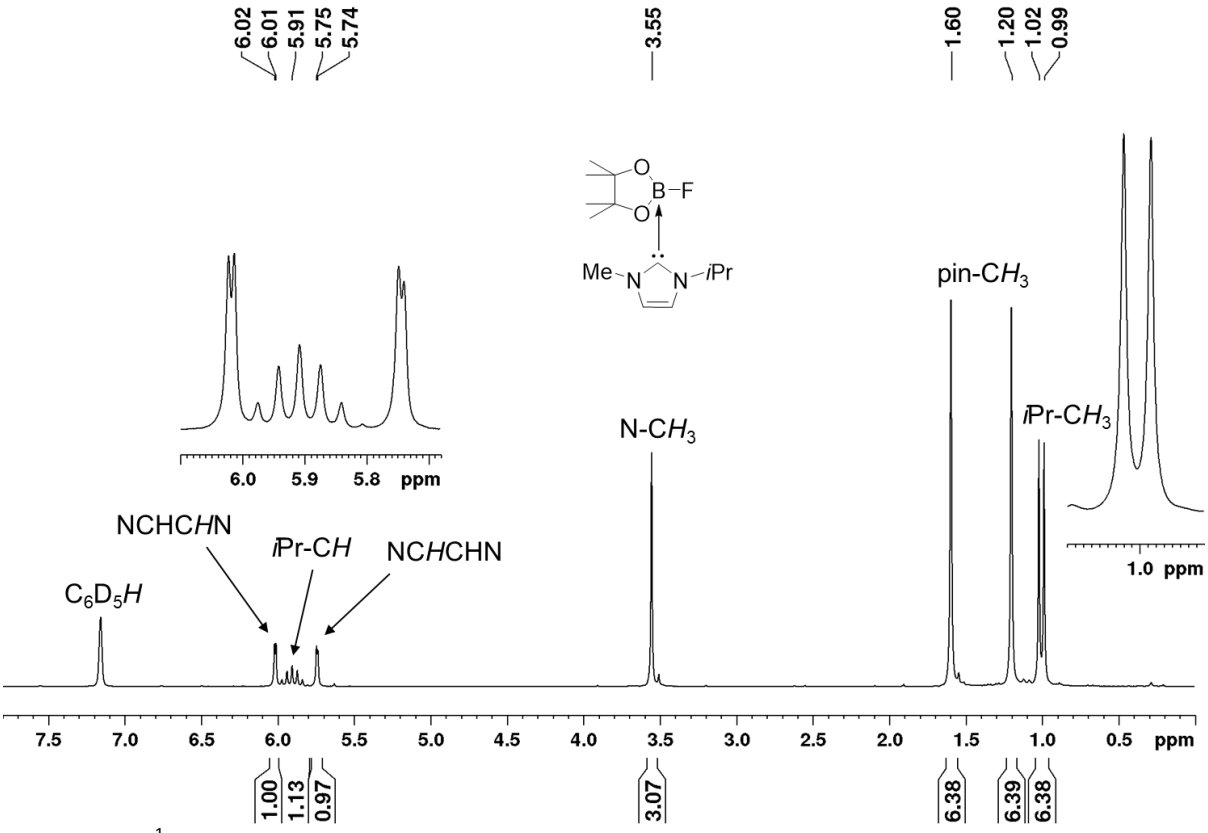

Figure S10. ^{1}H NMR spectrum of FBpin·Me*i*PrIm **3** recorded in C_6D_6 (200 MHz).

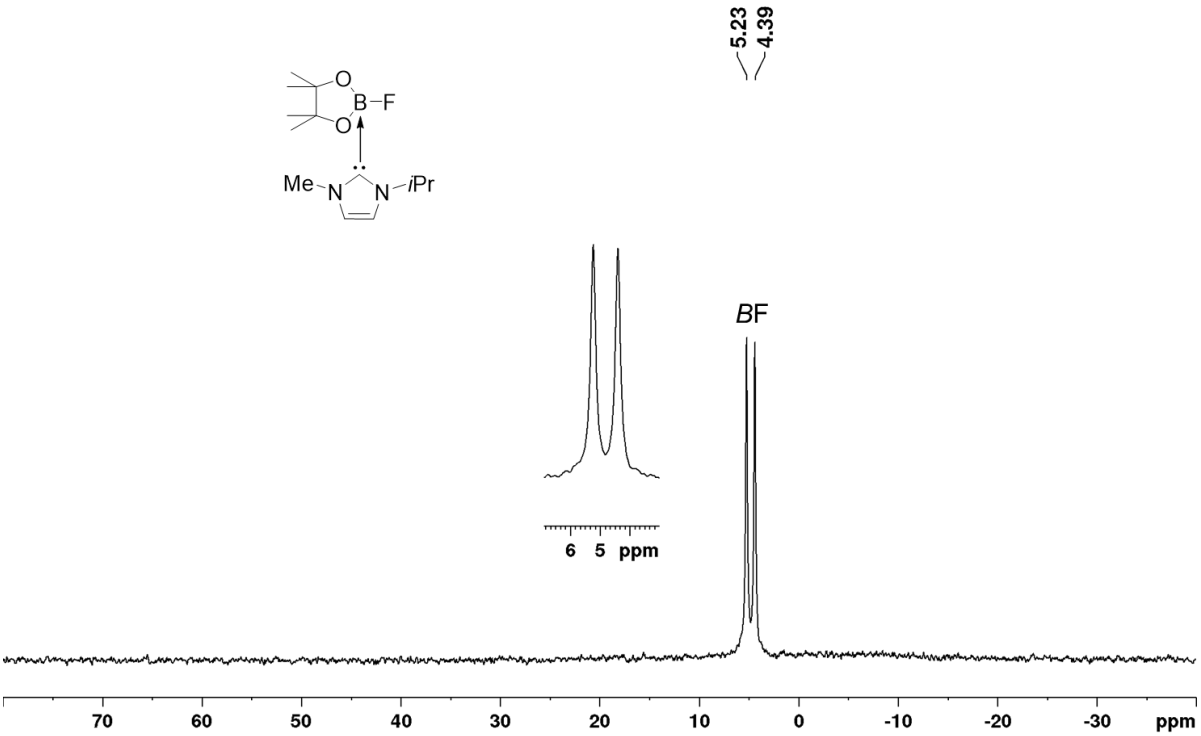

Figure S11. $^{11}B\{^{1}H\}$ NMR spectrum of FBpin·Me*i*PrIm **3** recorded in C_6D_6 (64 MHz).

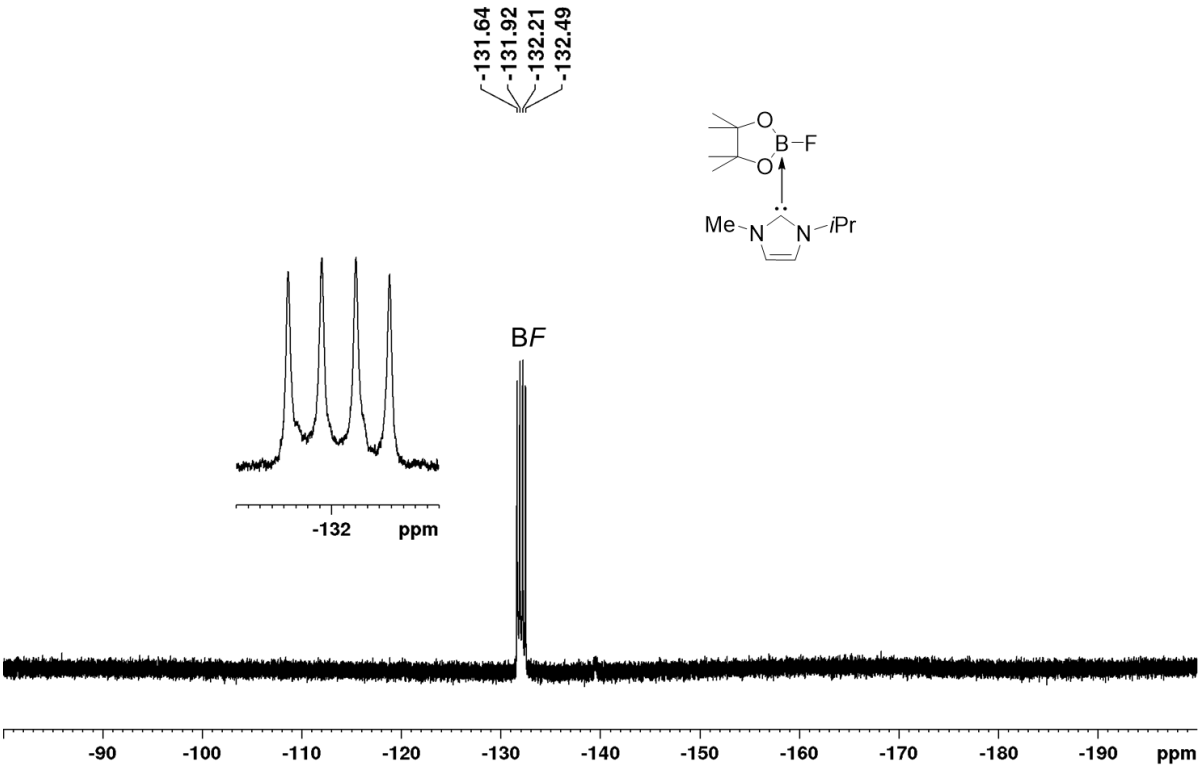

Figure S12. ^{19}F NMR spectrum of FBpin·Me*i*PrIm **3** recorded in C_6D_6 (188 MHz).

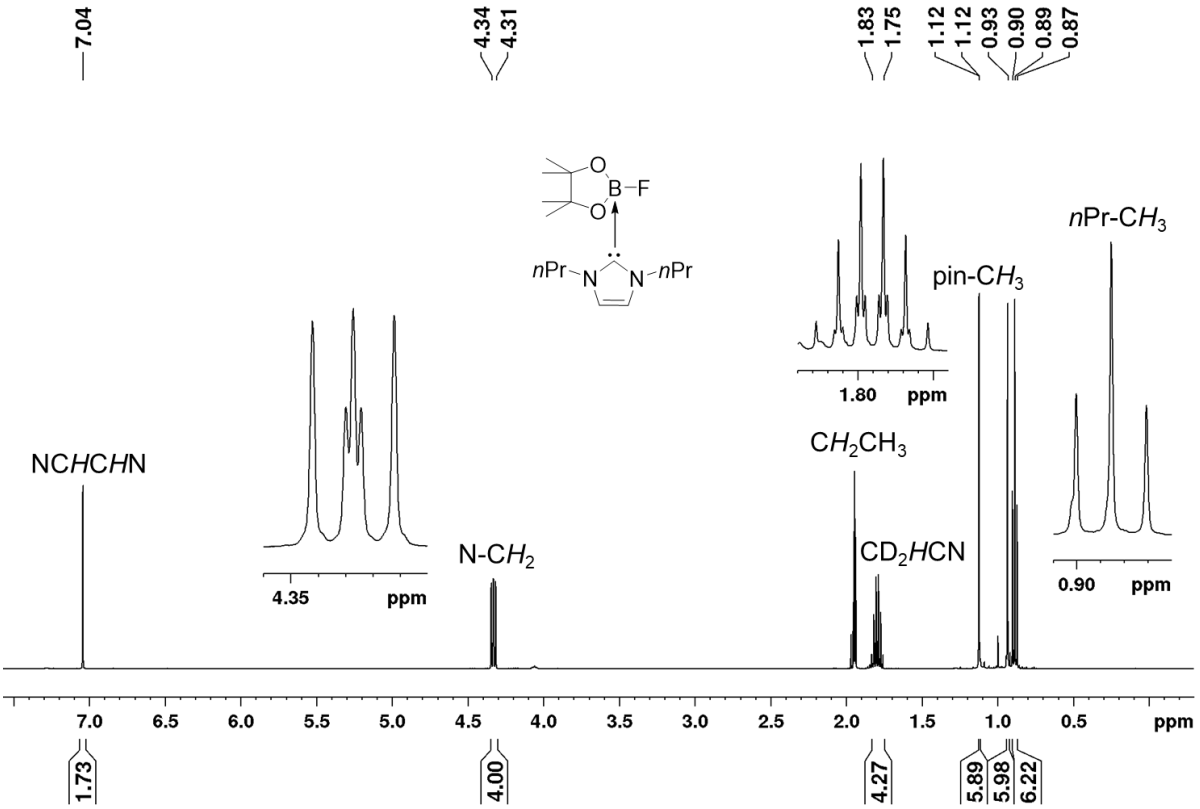

Figure S13. ^{1}H NMR spectrum of FBpin·*n*Pr$_2$Im **4** recorded in CD_3CN (500 MHz).

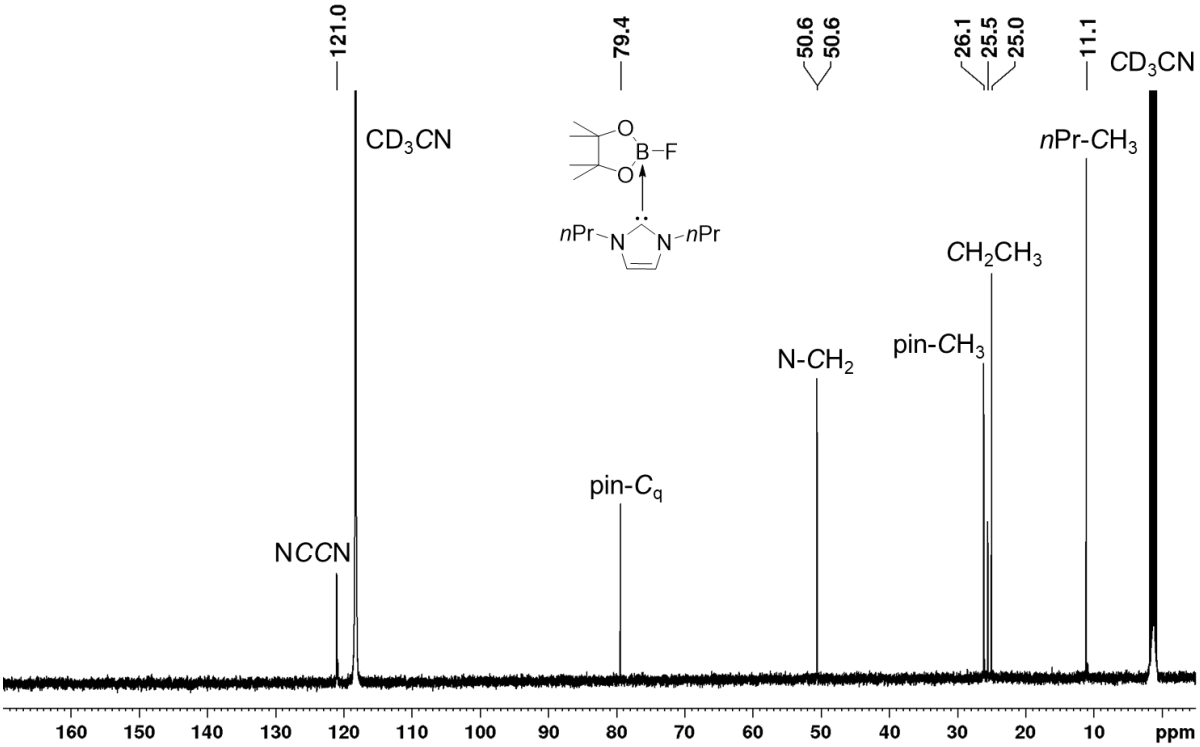

Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum of FBpin·*n*Pr$_2$Im **4** recorded in CD_3CN (125 MHz).

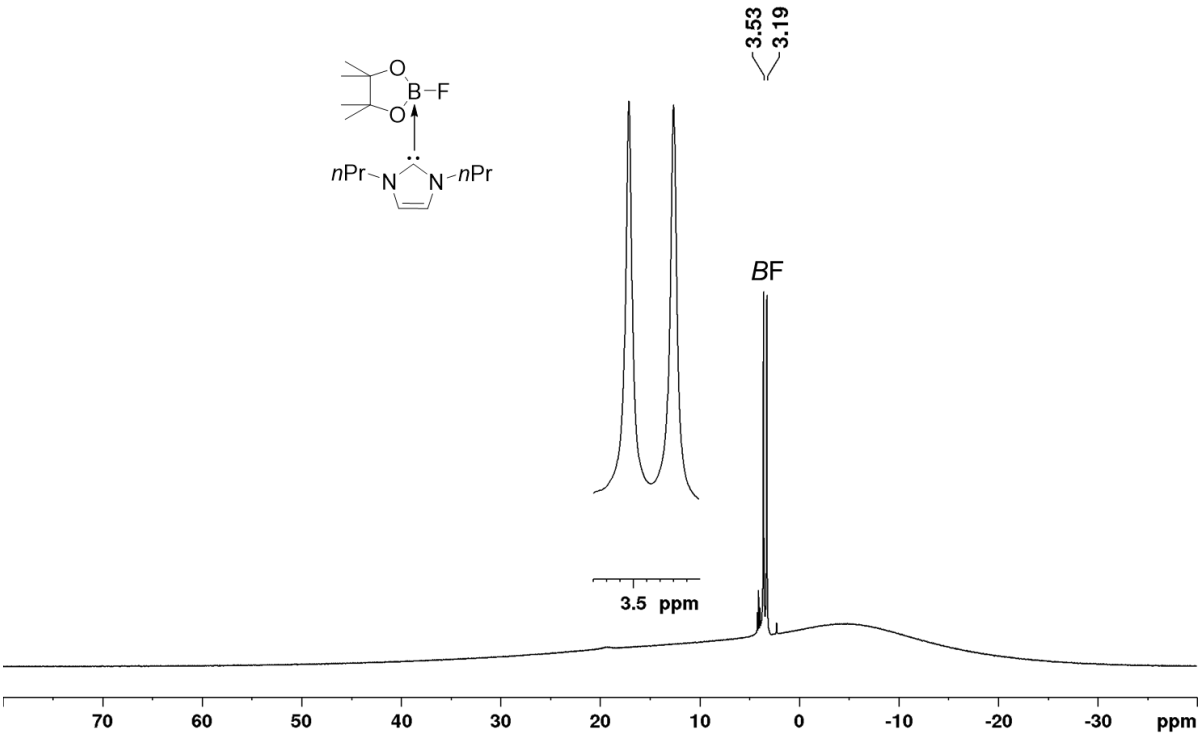

Figure S15. $^{11}B\{^{1}H\}$ NMR spectrum of FBpin·*n*Pr_2Im **4** recorded in CD_3CN (160 MHz).

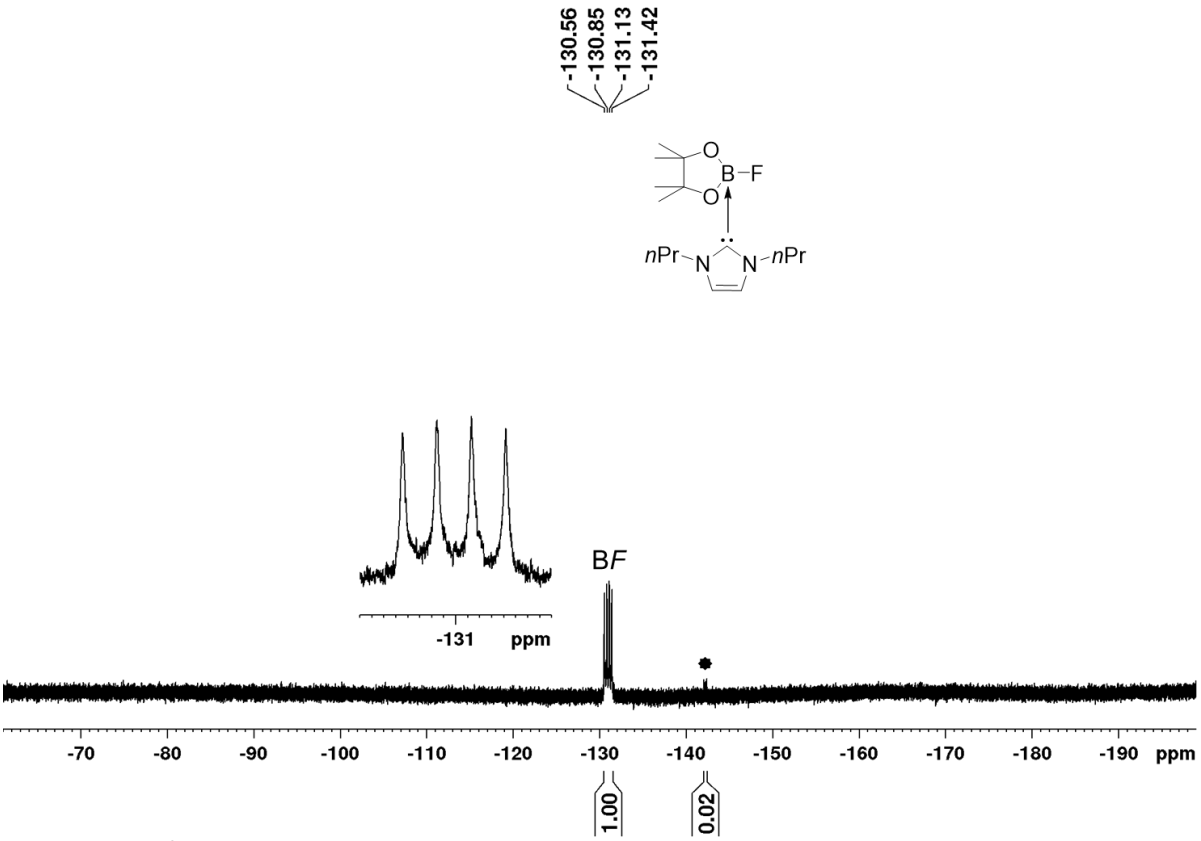

Figure S16. ^{19}F NMR spectrum of FBpin·*n*Pr_2Im **4** recorded in CD_3CN (471 MHz). (*= $[pinBF_2][NMe_4]$ **6**)

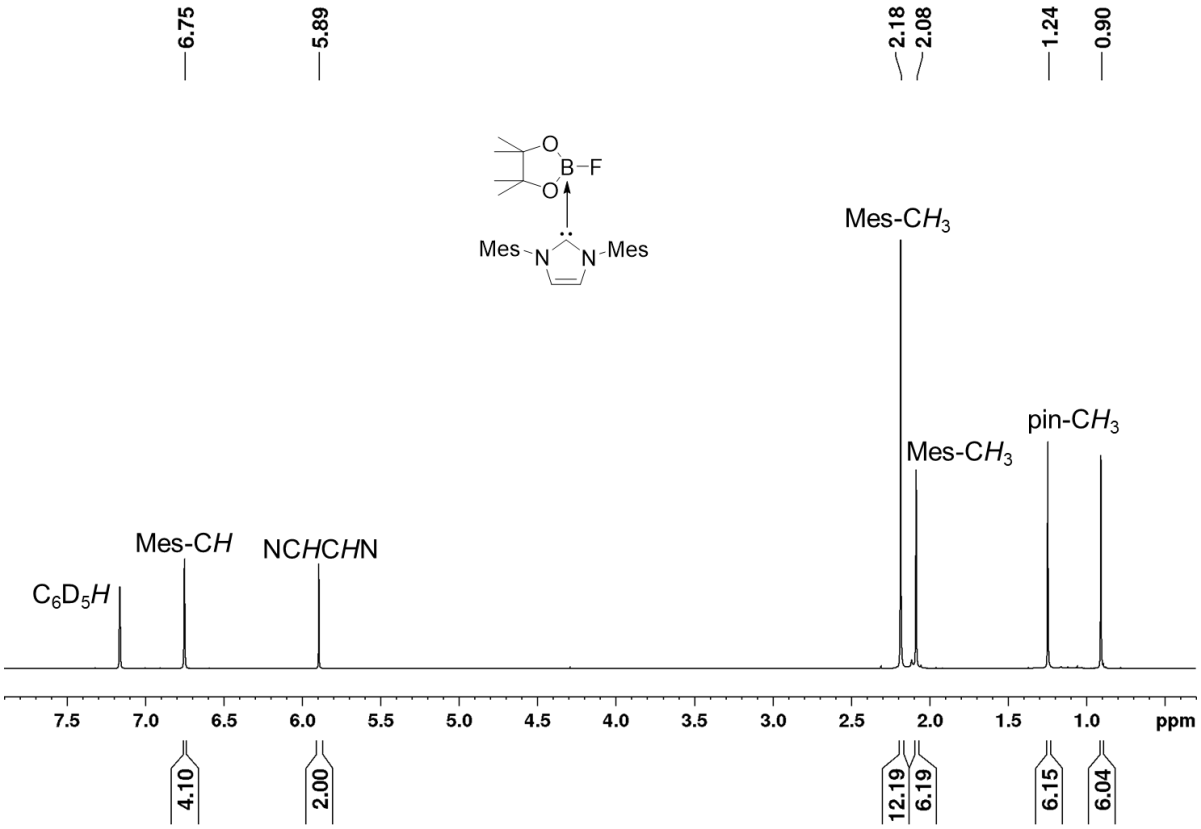

Figure S17. ^{1}H NMR spectrum of FBpin·Mes$_2$Im **5** recorded in C_6D_6 (500 MHz).

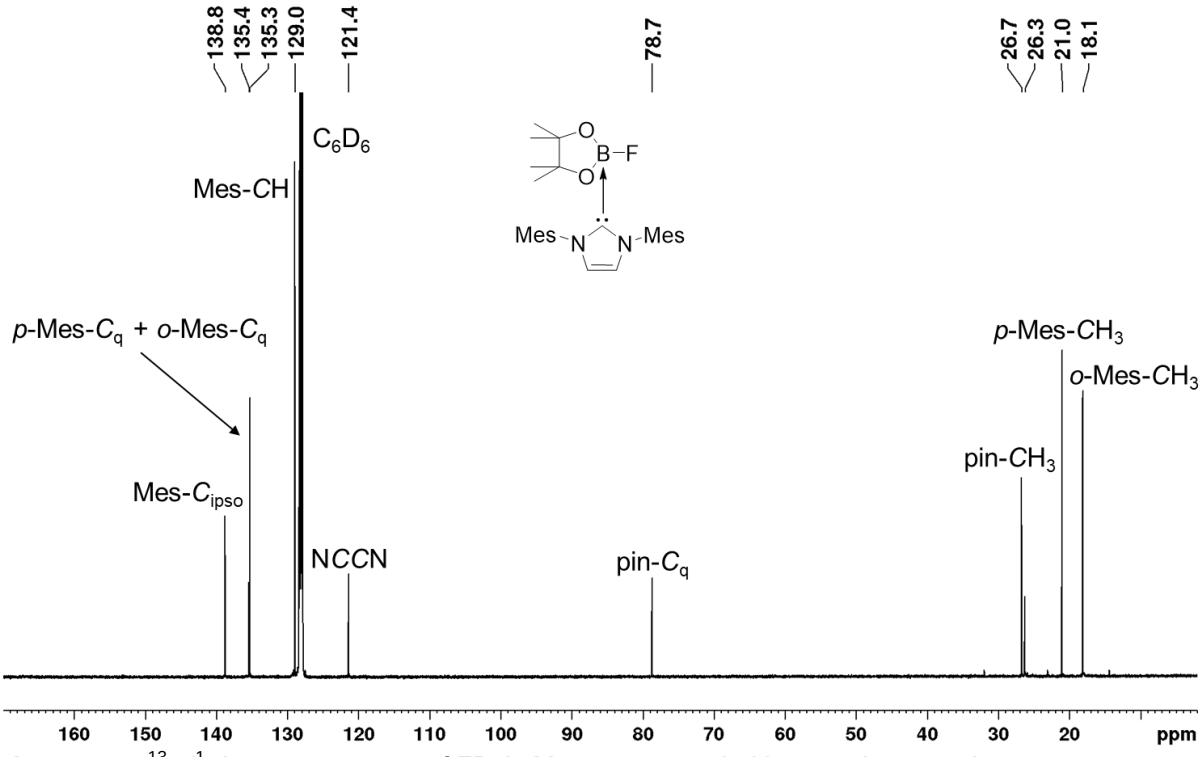

Figure S18. ^{13}C{^{1}H} NMR spectrum of FBpin·Mes$_2$Im **5** recorded in C_6D_6 (125 MHz).

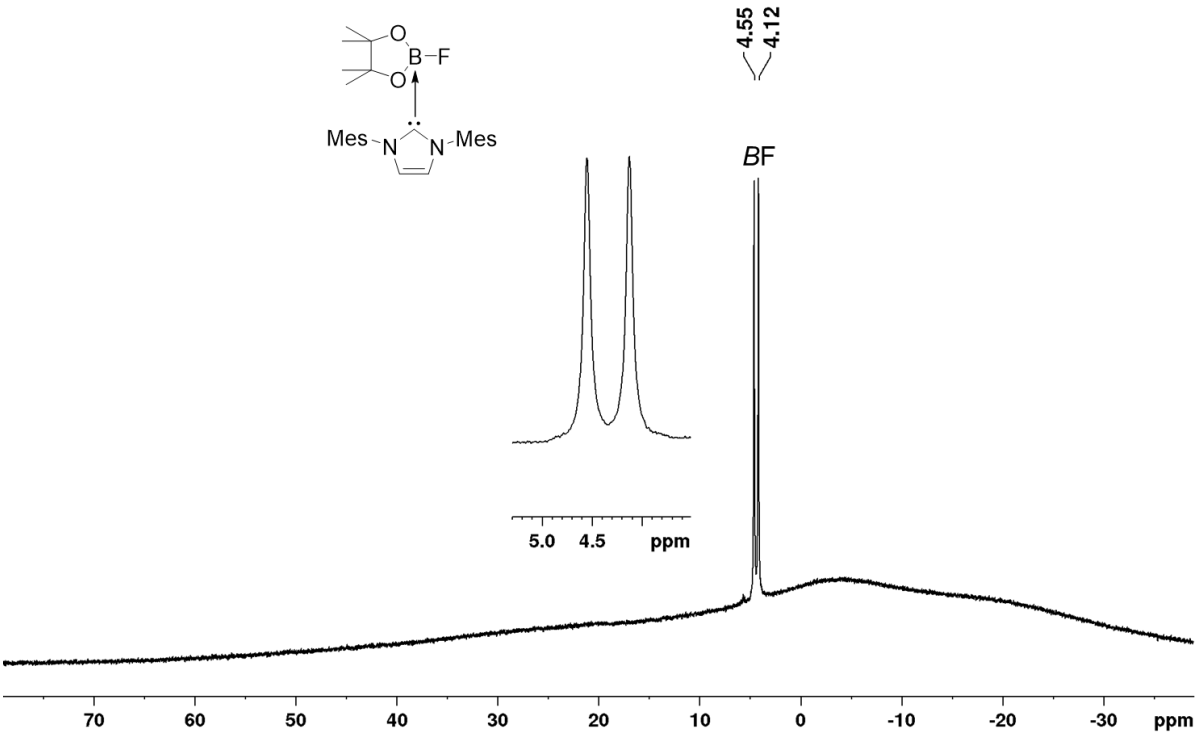

Figure S19. $^{11}B\{^{1}H\}$ NMR spectrum of FBpin·Mes_2Im **5** recorded in C_6D_6 (160 MHz).

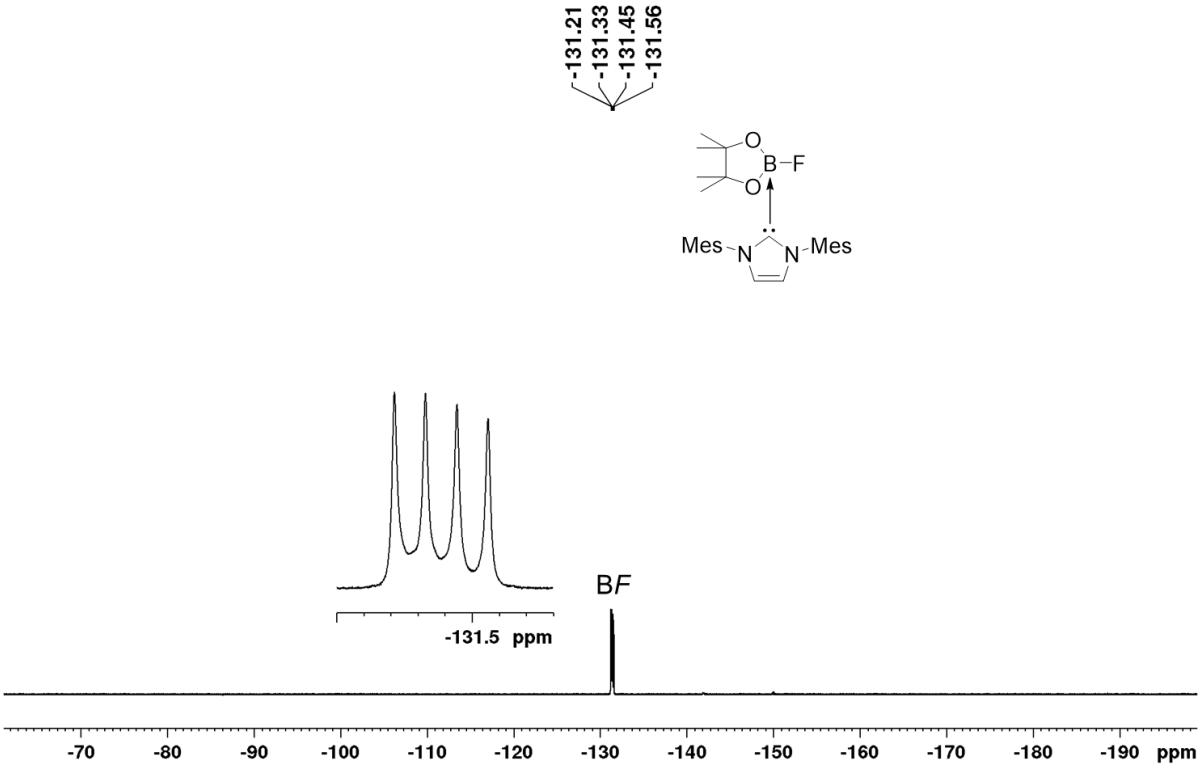

Figure S20. ^{19}F NMR spectrum of FBpin·Mes_2Im **5** recorded in C_6D_6 (471 MHz).

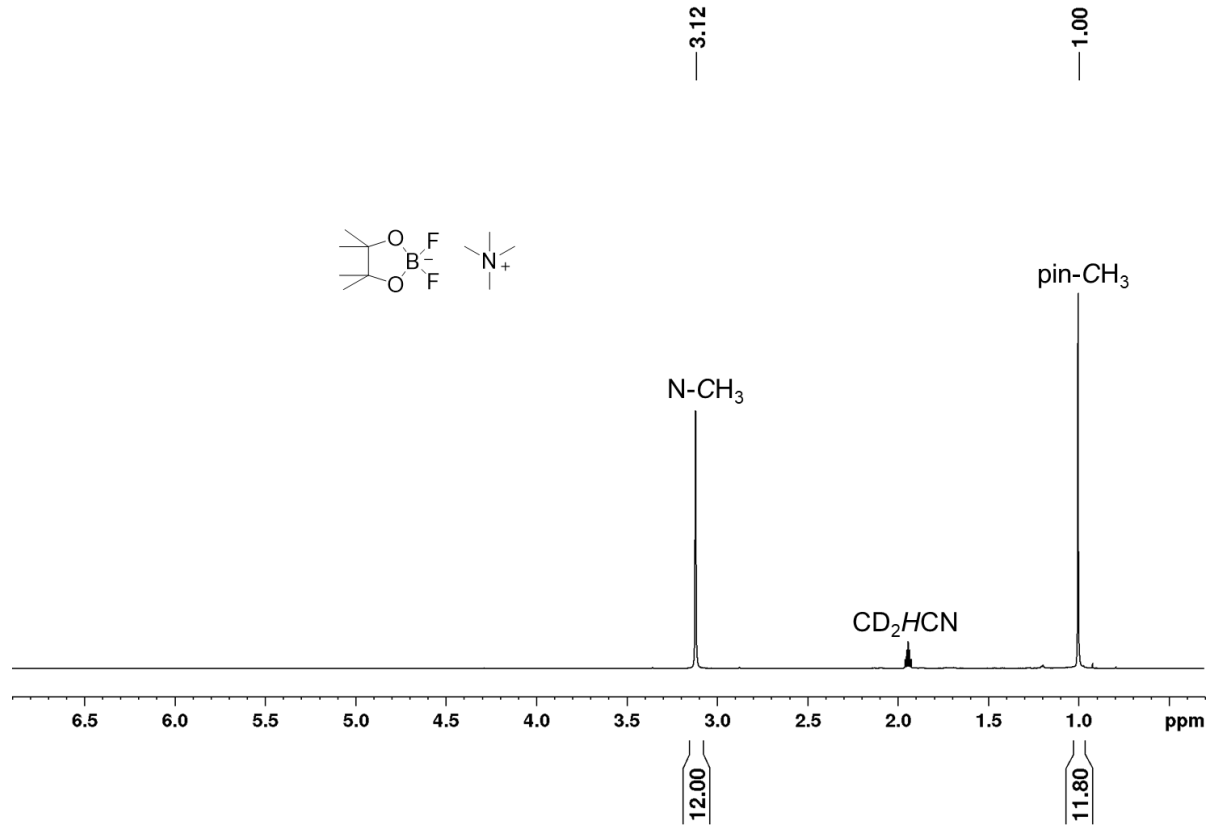

Figure S21. ^{1}H NMR spectrum of [pinBF$_2$][NMe$_4$] **6** recorded in CD$_3$CN (400 MHz).

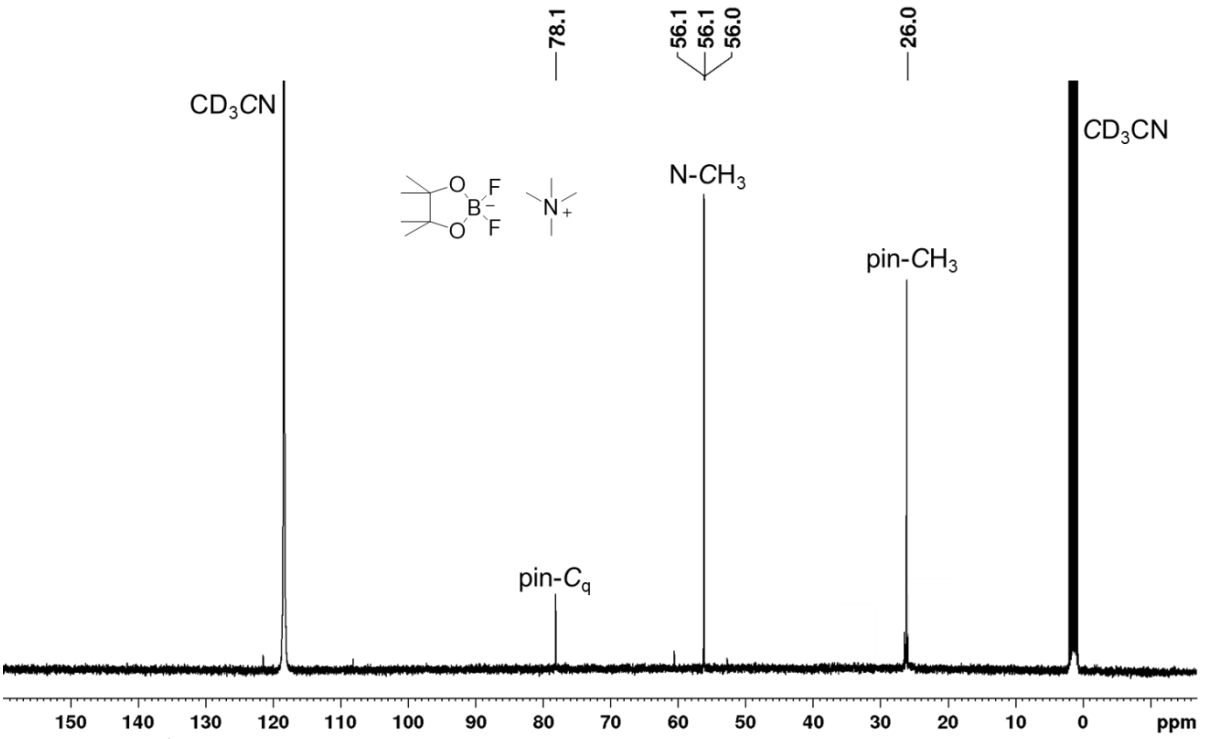

Figure S22. ^{13}C{^{1}H} NMR spectrum of [pinBF$_2$][NMe$_4$] **6** recorded in CD$_3$CN (100 MHz).

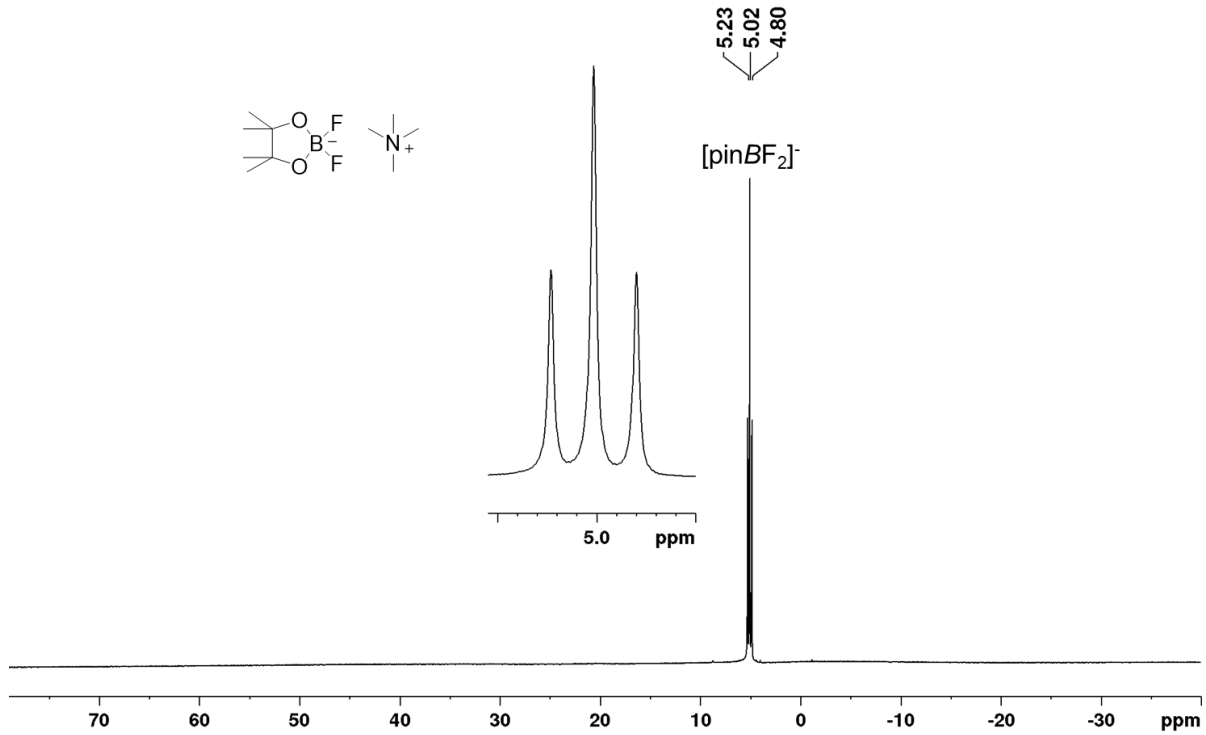

Figure S23. $^{11}B\{^{1}H\}$ NMR spectrum of $[pinBF_2][NMe_4]$ **6** recorded in CD_3CN (128 MHz).

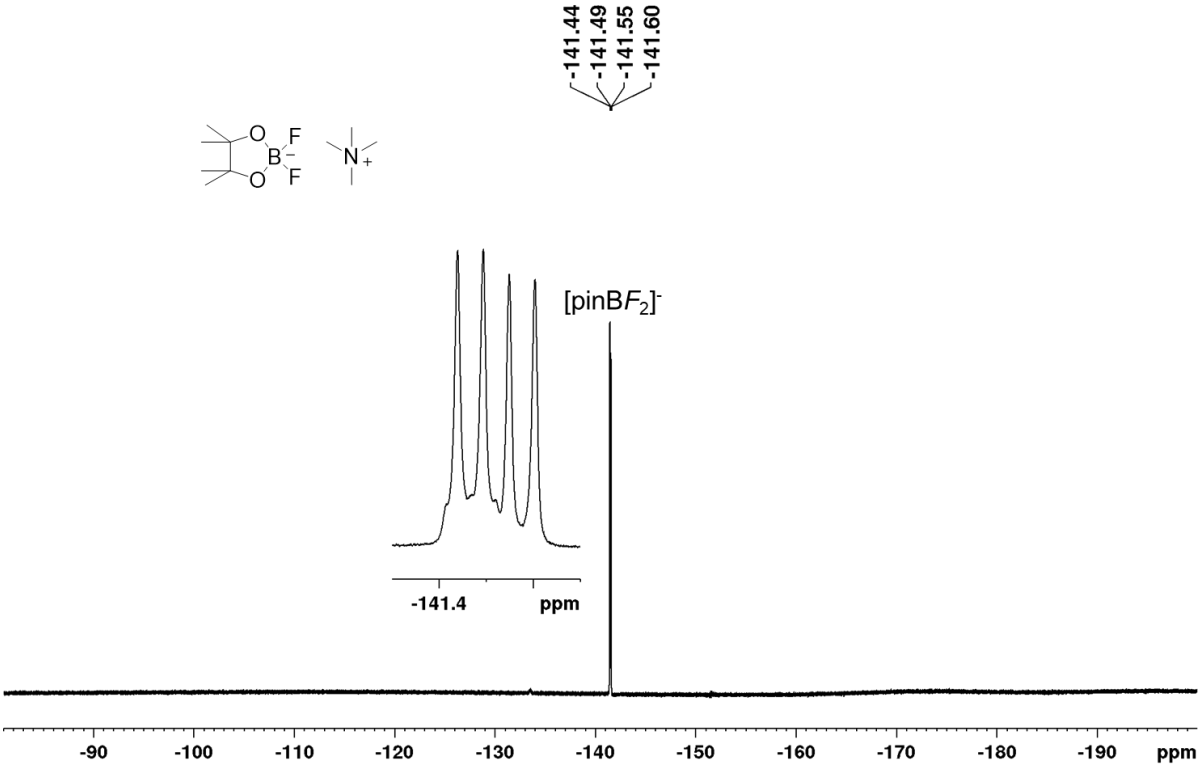

Figure S24. ^{19}F NMR spectrum of $[pinBF_2][NMe_4]$ **6** recorded in CD_3CN (376 MHz).

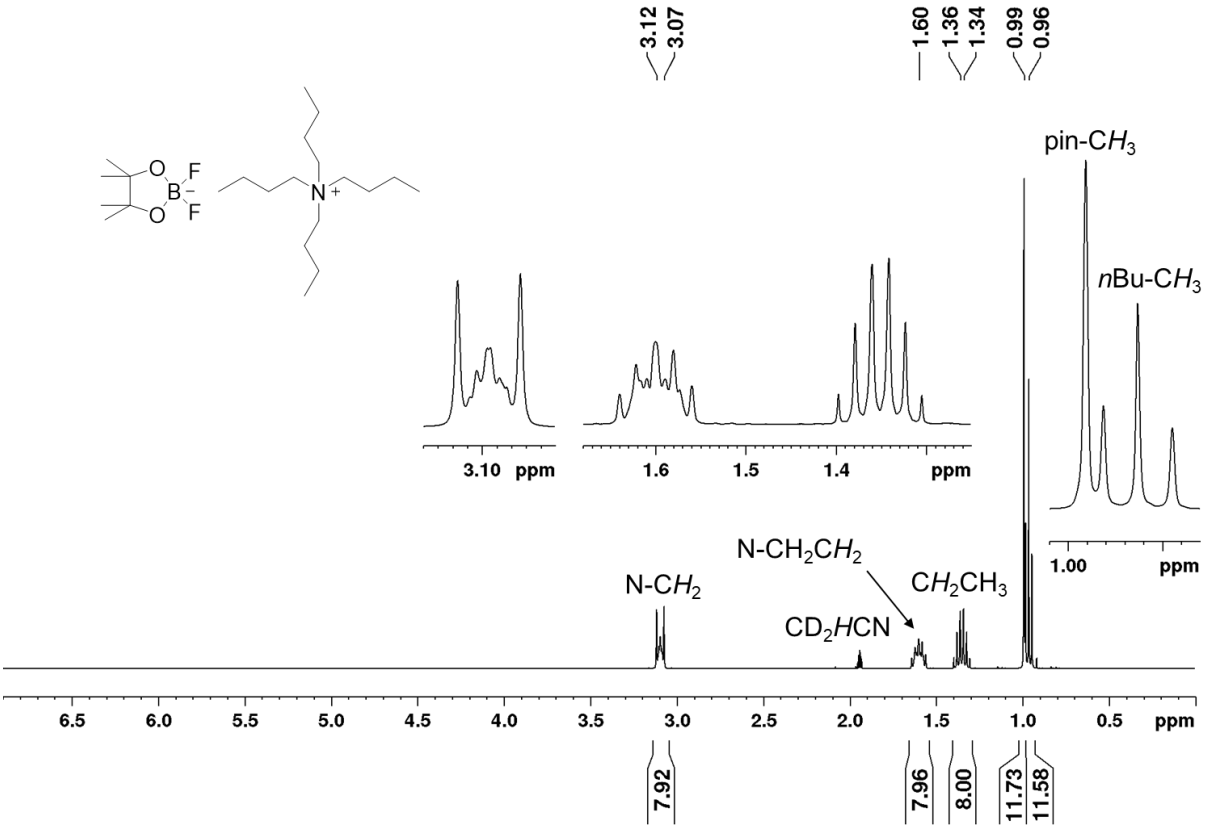

Figure S25. ^{1}H NMR spectrum of [pinBF$_2$][N*n*Bu$_4$] **7** recorded in CD$_3$CN (400 MHz).

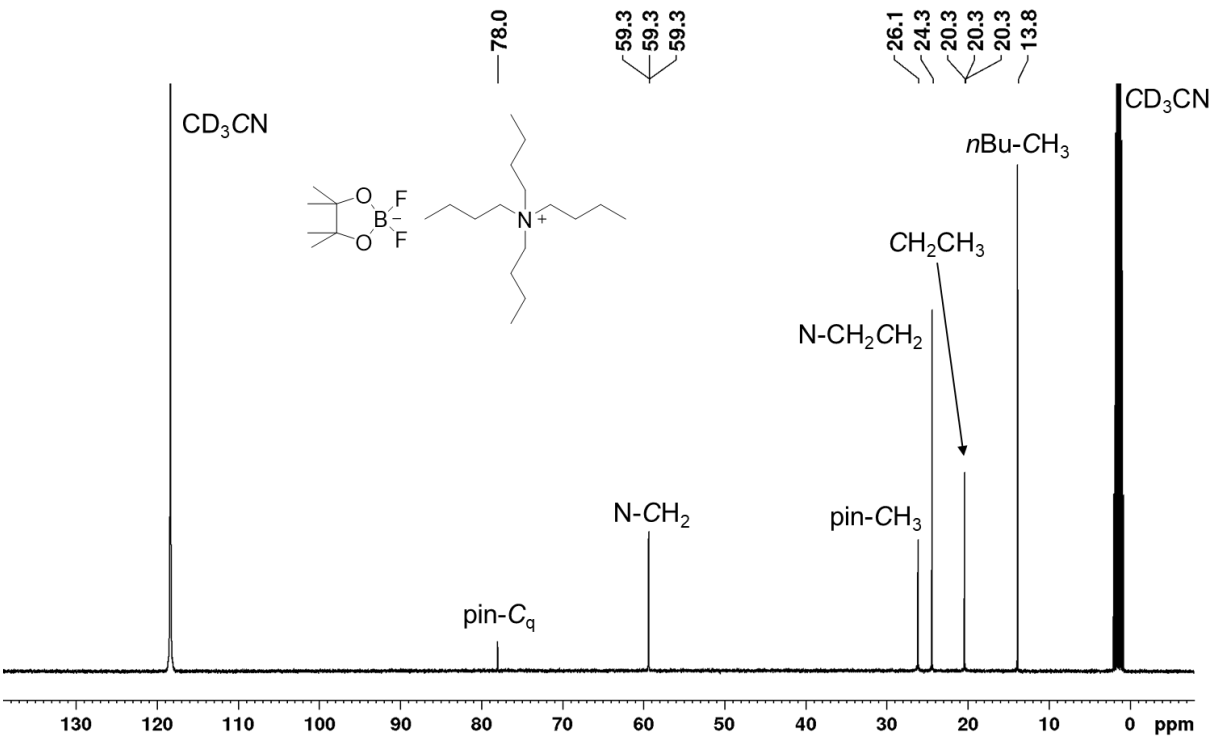

Figure S26. ^{13}C{^{1}H} NMR spectrum of [pinBF$_2$][N*n*Bu$_4$] **7** recorded in CD$_3$CN (100 MHz).

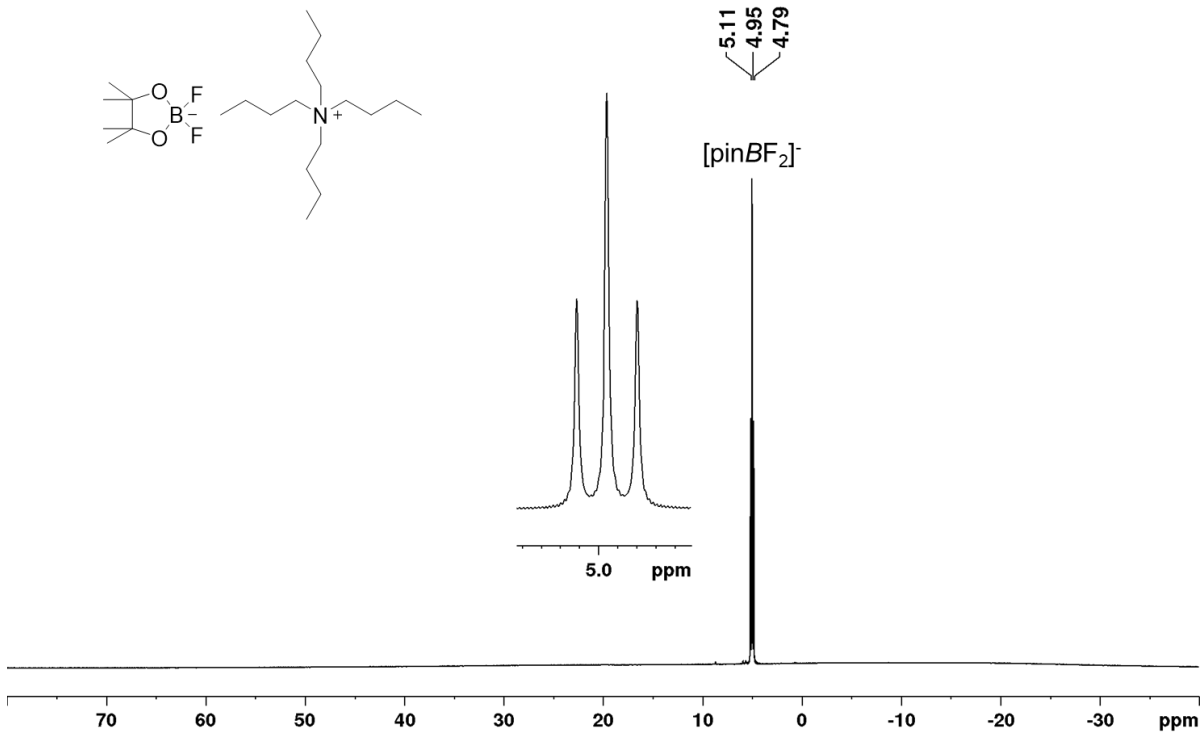

Figure S27. $^{11}B\{^{1}H\}$ NMR spectrum of [pinBF$_2$][N*n*Bu$_4$] **7** recorded in CD_3CN (128 MHz).

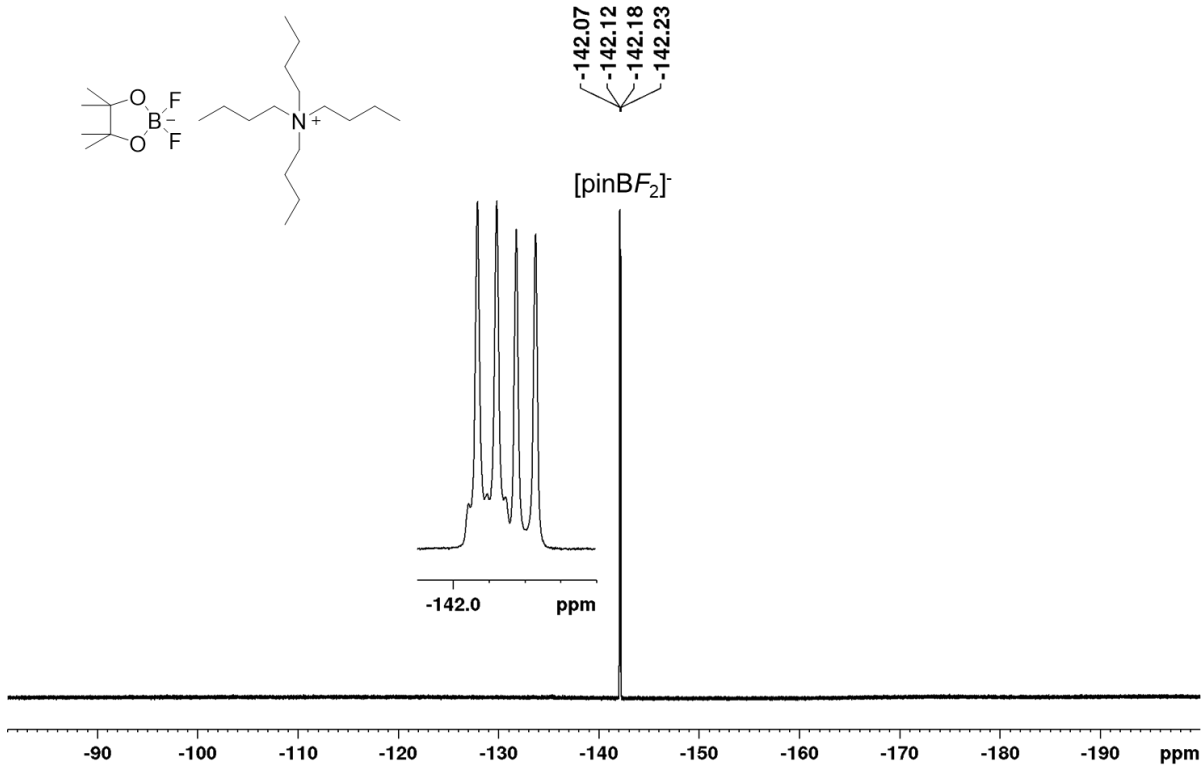

Figure S28. $^{19}F\{^{1}H\}$ NMR spectrum of [pinBF$_2$][N*n*Bu$_4$] **7** recorded in CD_3CN (376 MHz).

4 Crystallographic Details

Crystal data collection and processing parameters are given in Table S1. Crystals were immersed in a film of perfluoropolyether oil and mounted on a glass fiber or a MiTeGen sample holder, respectively. Diffraction data of **4** were collected on a Bruker X8 Apex-2 diffractometer with CCD area detector and graphite-monochromated Mo-Kα radiation, while diffraction data of **7** were collected on a Rigaku Oxford Diffraction XtaLAB Synergy diffractometer with a semiconductor HPA-detector (HyPix-6000) and multi-layer mirror monochromated CuKα radiation. The crystals were cooled using Oxford Cryosystem low-temperature devices. Data were collected at 100 K (**4**) and 250 K (**7**). Crystals of **7** are damaged at temperatures below 250 K, probably due to a phase transition. The images were processed with the Bruker software packages (**4**) or the CrysAlisPro software (**7**) and equivalent reflections were merged. Corrections for Lorentz-polarization effects and absorption were performed and the structures were solved using direct methods (**4**) or the intrinsic phasing method (SHELXT) (**7**).[S5] Subsequent difference Fourier syntheses revealed the positions of all other non-hydrogen atoms. Crystallographic calculations were performed using the SHELXTL software package.[S6] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned to idealized positions and were included in structure factors calculations. Due to the high data collection temperature, displacement parameters of the crystal structure of **7** are very large, and manifold disorder is observed as well, which required the use of several restraints in the refinement. This restricted the quality of the structure refinement of **7**, which nevertheless is good enough to serve as a proof for the connectivity present in the compound.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1912484 (**4**). Copies of the data can be obtained free of charge on application to CCDC.

Table S1. Crystallographic data collection parameters for FBpin•*n*Pr_2Im **4** and [pinBF_2][N*n*Bu_4] **7**.

	FBpin•*n*Pr_2Im **4**	[pinBF_2][N*n*Bu_4] **7**
Chemical formula	$C_{15}H_{28}BFN_2O_2$	$C_6H_{12}BF_2O_2 \cdot C_{16}H_{36}N$
Formula mass /g · mol^{-1}	298.20	407.42
Crystal size/mm^3	0.25x0.12x0.11	0.38x0.13x0.07
Crystal system	trigonal	triclinic
Space group, Z	*R*3*c*, 18	$P\bar{1}$, 4
a /Å	24.782(7)	10.5943(6)
b /Å	24.782(7)	16.1705(8)
c /Å	14.217(5)	16.8966(9)
α /°	90	68.662(5)
ß /°	90	83.756(5)
γ /°	120	80.229(5)
Volume /$Å^3$	7562(5)	2653.6(3)
ρ_{calcd} /g · cm^{-3}	1.179	1.020
T /K	100(2)	250(2)
μ /mm^{-1}, Radiation	0.084 MoK_α	0.577 CuK_α
Measured reflns	30064	30421
Indep. reflns	4103	9394
param./restraints	196 / 1	724 / 439
θ range /°	2.891 – 28.297	2.811 – 67.078
GoF on F^2	1.048	1.665
R_{int}	0.0368	0.0578
R_1 [$I > 2\sigma(I)$]	0.0312	0.1115
wR_2 (all data)	0.0743	0.3380
max / min peaks /e $Å^{-3}$	0.209, -0.150	0.204, -0.200

Note: The quality of the crystal structure refinement of **7** is restricted due to large vibrations and disorder at 250 K. We could not collect data below this temperature due to a destructive phase transition upon cooling. However, the quality is good enough to serve as a proof of the connectivity present in the compound.

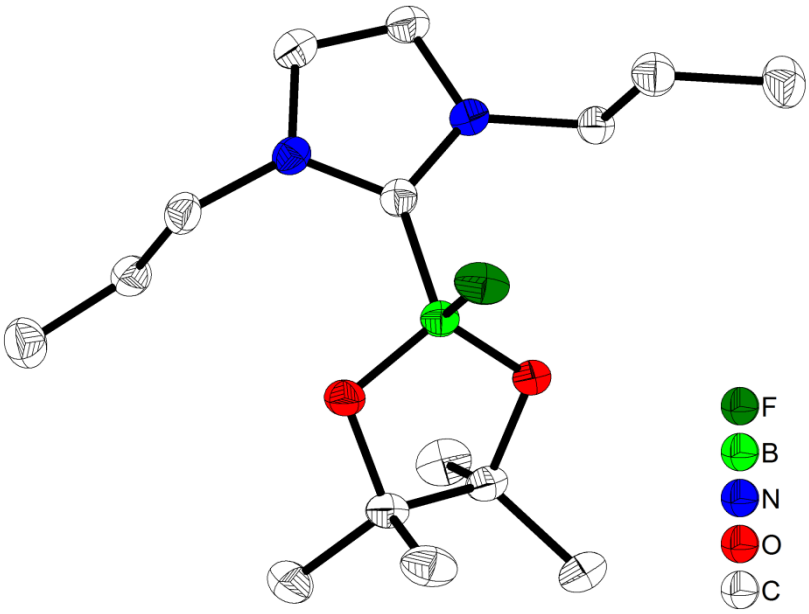

Figure S29. The solid state molecular structure of **4** determined by single-crystal X-ray diffraction at 100 K. All ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity.

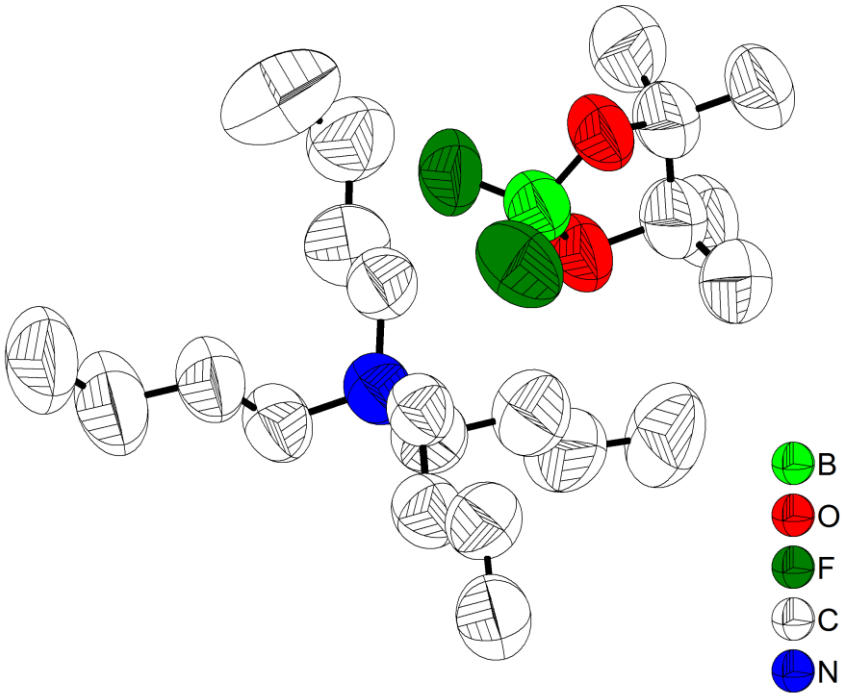

Figure S30. The solid state molecular structure of **7** determined by single-crystal X-ray diffraction at 250 K. All ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity. From each of the moieties only one of two symmetry-independent molecules is drawn. Molecules are partly or completely disordered and only the parts with the larger occupancies are shown.

5 Computational Details

Gas phase fluoride ion affinities (FIA) of were calculated using a procedure introduced by Krossing *et al.*[S7] The geometries were optimized at the (RI-)BP86/SV(P) level[S8-S10] using TURBOMOLE 7.0.[S11] Vibrational frequencies were calculated with the AOFORCE module and all structures represented true minima without imaginary frequencies. For the calculation of the free reaction enthalpy ΔG^{298}(THF) for the formation of B_2pin_2 and F_2Bpin^- the Conductor-like Screening Model (COSMO) was employed as a continuum solvation model for THF (ε = 7.25; r_f = 1.407).

Me_3SiF

Energy = -508.9271155174 h
NIMAG = 0

Si	-0.6817638	-1.3163335	0.0499658
F	-0.1290939	-0.5341248	-1.3015998
C	-2.5660682	-1.2780068	-0.0173774
H	-3.0102501	-1.7870672	0.8681264
H	-2.9472930	-0.2324063	-0.0331194
H	-2.9468248	-1.7910213	-0.9288260
C	-0.0175704	-3.0802082	-0.0173394
H	1.0953290	-3.0910141	-0.0319878
H	-0.3501709	-3.6688298	0.8678326
H	-0.3733580	-3.6102608	-0.9291458
C	-0.0172459	-0.3771029	1.5442025
H	-0.3517990	-0.8477276	2.4966185
H	1.0956907	-0.3613047	1.5470696
H	-0.3707817	0.6783081	1.5456800

Me_3Si^+

Energy = -408.8071293944 h
NIMAG = 0

Si	-0.4468135	-0.3727372	-0.0258993
C	0.4670176	1.2306376	-0.1059282
H	1.4212659	1.1496162	-0.6710316
H	-0.1608626	2.0473900	-0.5270188
H	0.7290701	1.5354477	0.9400059
C	0.4674959	-1.9757611	-0.1075818
H	-0.1580796	-2.7901457	-0.5367743
H	1.4253965	-1.8925851	-0.6660529
H	0.7219252	-2.2861108	0.9385919
C	-2.2818508	-0.3731890	0.1845650
H	-2.6458846	0.5380253	0.7089341
H	-2.7500090	-0.3695054	-0.8334554
H	-2.6464713	-1.2874825	0.7030453

BF_3

Energy = -324.3176047666 h
NIMAG = 0

B	0.0345590	-0.4632000	0.0000000
F	1.3582305	-0.4632000	-0.0000000
F	-0.6271947	-1.6095313	-0.0000000
F	-0.6271947	0.6831313	-0.0000000

$[BF_4]^-$

Energy = -424.2006088263 h
NIMAG = 0

B	0.0346275	-0.4632000	0.0000336
F	1.3717129	-0.4632000	0.4726593
F	-0.6339387	-1.6210805	0.4727203
F	-0.6339387	0.6946805	0.4727203
F	0.0346370	-0.4632000	-1.4180334

B_2Cat_2

Energy = -812.3161726714 h
NIMAG = 0

B	-1.7932937	-0.2788585	-0.4066037
B	-0.1057835	-0.3379279	-0.5367946
O	-2.4931140	0.4335982	0.5753749
O	-2.6855370	-0.9352228	-1.2636662
O	0.7846714	0.3195425	0.3214498
O	0.5961037	-1.0514602	-1.5163650
C	-3.8286843	0.2136739	0.3202608
C	-4.9465719	0.6952255	1.0042701
C	-3.9464188	-0.6239663	-0.8048201
C	-6.2057957	0.2980316	0.5087421
H	-4.8411877	1.3496871	1.8828495
C	-5.1880883	-1.0230618	-1.3031720
C	-6.3238525	-0.5421004	-0.6193490
H	-7.1181845	0.6527601	1.0153469
H	-5.2668631	-1.6786239	-2.1836769
H	-7.3265463	-0.8298538	-0.9753089
C	1.9311476	-0.8315716	-1.2584718
C	3.0504661	-1.3146786	-1.9389642
C	2.0465092	0.0073710	-0.1341149
C	4.3086552	-0.9177194	-1.4406868
H	2.9469388	-1.9702777	-2.8168654
C	3.2871759	0.4062720	0.3669884
C	4.4243931	-0.0762761	-0.3133306
H	5.2221107	-1.2737430	-1.9444125
H	3.3641230	1.0627336	1.2470357
H	5.4263607	0.2112034	0.0449425

[FB_2Cat_2]$^-$

Energy = -912.1964623369 h
NIMAG = 0

B	-1.6598656	0.6896619	-0.6552056
B	-0.0045639	1.1945702	-0.8620708
O	-2.5683413	1.1858199	0.3296212
O	-2.3423249	-0.3226409	-1.3933384
O	0.8012406	0.8403373	0.3883817
O	0.6992322	0.4075885	-1.9579029
C	-3.7370556	0.4968695	0.1862925
C	-4.9287879	0.6110944	0.9070971
C	-3.5991639	-0.4277306	-0.8718914
C	-5.9936199	-0.2398715	0.5328261
H	-5.0231424	1.3363973	1.7308897
C	-4.6466755	-1.2725970	-1.2476952
C	-5.8554273	-1.1631514	-0.5230621
H	-6.9504127	-0.1790649	1.0792309
H	-4.5242957	-1.9903187	-2.0744241
H	-6.7054170	-1.8142595	-0.7900184
C	1.7927134	-0.1516841	-1.4148218
C	2.7873528	-0.9098218	-2.0459216
C	1.8527759	0.1035918	-0.0101368
C	3.8506392	-1.4229863	-1.2578848
H	2.7315707	-1.0979659	-3.1315101
C	2.9049966	-0.4009958	0.7643319
C	3.9086982	-1.1732310	0.1228483
H	4.6396434	-2.0271604	-1.7406421
H	2.9406538	-0.1946094	1.8474661
H	4.7431734	-1.5813825	0.7208240
F	0.1132034	2.5809410	-1.1227835

FBpin

Energy = -510.7849039200 h
NIMAG = 0

B	1.2145331	-4.4771535	2.5388085
O	-0.1233075	-4.3951892	2.2432671
O	1.7651715	-5.7281864	2.4145563
C	0.7509255	-6.5565453	1.7659374
C	-0.5937815	-5.7716558	2.1029606
C	-1.6602461	-5.8149419	1.0068463
H	-1.9941733	-6.8592584	0.8198072
H	-2.5461090	-5.2229942	1.3237540
H	-1.2895575	-5.3842688	0.0546085
C	-1.2021551	-6.1705653	3.4574669
H	-1.9994645	-5.4431779	3.7220048
H	-1.6516716	-7.1864284	3.4257534
H	-0.4399221	-6.1479472	4.2660743
C	1.0833095	-6.5677593	0.2648039
H	2.1236587	-6.9339615	0.1293575
H	0.4006770	-7.2347077	-0.3046132
H	1.0230667	-5.5471033	-0.1711142
C	0.8351344	-7.9719485	2.3405225
H	0.0302548	-8.6171574	1.9247838
H	1.8130478	-8.4269933	2.0717072
H	0.7555907	-7.9721518	3.4465647
F	1.9283185	-3.4175050	2.9199426

[F_2Bpin]$^-$

Energy = -610.6448316411 h
NIMAG = 0

B	1.2736767	-4.3947426	2.5725517
O	-0.1402537	-4.4165713	2.1002173
O	1.7129794	-5.8183983	2.5217936
C	0.7585476	-6.5570483	1.7973838
C	-0.5854681	-5.7518171	2.0803771
C	-1.6752700	-5.9093199	1.0035962
H	-1.9969824	-6.9710303	0.8860647
H	-2.5699394	-5.3076912	1.2866550
H	-1.3190448	-5.5312122	0.0220168
C	-1.1853770	-6.1150966	3.4642655
H	-1.9661031	-5.3616599	3.7140833
H	-1.6494849	-7.1297452	3.4915629
H	-0.3962707	-6.0529648	4.2435202
C	1.1272960	-6.5362535	0.2905178
H	2.1779363	-6.8890373	0.1843181
H	0.4694699	-7.1866990	-0.3338934
H	1.0816513	-5.4947209	-0.0928498
C	0.7587862	-8.0146324	2.2946916
H	-0.0453779	-8.6209324	1.8148501
H	1.7379933	-8.4907596	2.0559810
H	0.6305736	-8.0560084	3.3970864
F	1.3869153	-3.9090238	3.8997694
F	2.0471463	-3.5655351	1.7217407

B_2pin_2

Energy = -821.9015536874 h
NIMAG = 0

B	1.2686903	-4.4356363	2.5855033
O	0.1609478	-4.3390805	1.7663841
O	1.5481843	-5.7375829	2.9519208
C	0.6874501	-6.6214420	2.1672525
C	-0.4861335	-5.6496296	1.7267118
B	2.1952998	-3.0843745	3.0918493
O	2.1491473	-2.5592569	4.3684305
O	3.0677687	-2.4022180	2.2666661
C	2.8957174	-1.3021625	4.3660627
C	3.8253143	-1.4615745	3.0906496
C	4.0483504	-0.1794668	2.2835079
H	4.5696769	0.5901596	2.8948421
H	4.6827001	-0.4018429	1.3981799
H	3.0933813	0.2470612	1.9151308
C	5.1744262	-2.1339851	3.3978644
H	5.6715199	-2.3980423	2.4395691
H	5.8510066	-1.4611882	3.9683679
H	5.0370789	-3.0720660	3.9772729
C	3.6369111	-1.1752246	5.7000383
H	4.2683629	-0.2593659	5.7190865
H	2.9009353	-1.1019094	6.5299102
H	4.2818956	-2.0550704	5.8986840
C	1.8579121	-0.1748278	4.2288487
H	1.1209354	-0.2614101	5.0561404
H	2.3296419	0.8302567	4.2851610
H	1.3007525	-0.2511815	3.2704802
C	-1.0270556	-5.8815112	0.3129991
H	-1.4759919	-6.8952079	0.2199606
H	-1.8187454	-5.1338680	0.0893999
H	-0.2344066	-5.7726897	-0.4547625
C	-1.6472406	-5.5971622	2.7344184
H	-2.3186531	-4.7531442	2.4661701
H	-2.2446242	-6.5346842	2.7257850
H	-1.2794184	-5.4211361	3.7680061
C	1.5360588	-7.1286663	0.9886533
H	2.4476835	-7.6231326	1.3880868
H	0.9822031	-7.8662745	0.3681119
H	1.8640694	-6.2919469	0.3352201
C	0.2618112	-7.7961593	3.0526289
H	-0.4455332	-8.4649502	2.5138760
H	1.1553938	-8.3955055	3.3320094
H	-0.2198242	-7.4523004	3.9904219

[FB_2pin_2]$^-$

Energy = -921.7451932971 h
NIMAG = 0

B	2.1598132	-4.7201209	1.5508016
O	0.7834253	-4.3759259	1.0319718
O	1.9363781	-5.9575785	2.3584786
C	0.7042902	-6.5308357	1.9723378
C	-0.1650869	-5.2517351	1.6006137
B	2.7538032	-3.3972353	2.5364172
O	2.3802795	-3.1650220	3.8778455
O	3.5777202	-2.3387138	2.1087995
C	2.7532020	-1.8247751	4.2555922
C	3.9148651	-1.5003343	3.2316642
C	3.9837341	-0.0415320	2.7599588
H	4.1810645	0.6535550	3.6085218
H	4.8089701	0.0712892	2.0219214
H	3.0437353	0.2665037	2.2575783
C	5.3034996	-1.9463689	3.7343549
H	6.0197082	-1.8995448	2.8849696
H	5.6865419	-1.3003773	4.5571651
H	5.2737884	-2.9990437	4.0885597
C	3.1630734	-1.8201425	5.7344814
H	3.5196249	-0.8144023	6.0558741
H	2.2863352	-2.0926725	6.3632152
H	3.9617938	-2.5630618	5.9374035
C	1.5123070	-0.9301578	4.0595697
H	0.6712254	-1.3528362	4.6514057
H	1.6876214	0.1182504	4.3927073
H	1.1978367	-0.9221728	2.9940767
C	-1.2875211	-5.5111876	0.5774754
H	-2.0275712	-6.2591586	0.9490710
H	-1.8320762	-4.5605785	0.3723577
H	-0.8695815	-5.8689779	-0.3869551
C	-0.7761749	-4.5897640	2.8627138
H	-1.1790632	-3.5927852	2.5726859
H	-1.6040483	-5.1852771	3.3156602
H	0.0174309	-4.4252278	3.6225074
C	0.9185926	-7.4600031	0.7486982
H	1.7154144	-8.1941719	1.0053306
H	-0.0012814	-8.0236930	0.4611277
H	1.2773169	-6.8705796	-0.1210923
C	0.1554646	-7.3680824	3.1427617
H	-0.8653250	-7.7652246	2.9302816
H	0.8300928	-8.2354843	3.3286926
H	0.1202385	-6.7687784	4.0768941
F	3.0159421	-4.9790350	0.4263042

B_2eg_2

Energy = -507.6289979322 h
NIMAG = 0

B	1.2744227	-4.4268037	2.5862510
O	0.1491273	-4.3244555	1.7938306
O	1.5748920	-5.7295487	2.9285294
C	0.6113347	-6.5980074	2.3055413
H	1.1407821	-7.2714795	1.5947200
H	0.1319250	-7.2276707	3.0872454
C	-0.3907038	-5.6438137	1.5967660
H	-0.4789121	-5.8402455	0.5054778
H	-1.4109540	-5.6847775	2.0400065
B	2.2007519	-3.0767955	3.0920739
O	2.1332676	-2.5386678	4.3611912
O	3.0915947	-2.4133723	2.2729338
C	3.0108772	-1.3996535	4.4199142
H	3.7225755	-1.5331171	5.2642577
H	2.4038129	-0.4880632	4.6190687
C	3.7139489	-1.3624623	3.0339552
H	3.5724459	-0.3962818	2.5014131
H	4.8065115	-1.5651845	3.1001245

$[FB_2eg_2]^-$

Energy = -607.4702563933 h
NIMAG = 0

B	2.0026893	-4.7109119	1.7780126
O	0.6310093	-4.3116567	1.2741086
O	1.7468762	-5.9196101	2.6232766
C	0.4677202	-6.3911540	2.3153559
H	0.4697522	-7.1296593	1.4584495
H	0.0079838	-6.9161547	3.1956256
C	-0.3139857	-5.1227916	1.9033392
H	-1.1770881	-5.3515233	1.2197804
H	-0.7501445	-4.6340107	2.8254258
B	2.6069581	-3.3624044	2.7227593
O	2.2532292	-3.1125097	4.0641412
O	3.3657084	-2.2796766	2.2361156
C	2.6920869	-1.8165354	4.4522302
H	3.2786291	-1.8773055	5.4014003
H	1.8076918	-1.1603915	4.6502492
C	3.5415252	-1.3042005	3.2567593
H	3.2066780	-0.3028189	2.8915576
H	4.6265378	-1.2164680	3.5167001
F	2.8276430	-5.0342174	0.6533131

B_2neop_2

Energy = -743.3229010306 h
NIMAG = 0

B	-4.1601945	0.1113751	0.1624164
O	-4.8259311	-1.0105220	-0.2869970
O	-4.8285927	1.1311626	0.8081333
C	-6.2346106	-1.1443078	-0.1036186
H	-6.7514377	-0.7674215	-1.0192888
H	-6.4580423	-2.2328231	-0.0218765
C	-6.2372820	1.0583685	1.0225719
H	-6.4626053	1.6290488	1.9526828
H	-6.7543742	1.5790855	0.1805239
C	-6.7580870	-0.3909631	1.1389973
C	-6.2372584	-1.0515738	2.4326796
H	-6.5989616	-0.5004524	3.3297211
H	-6.5952098	-2.1028426	2.5101211
H	-5.1268378	-1.0700851	2.4738956
C	-8.2967953	-0.3885803	1.1304388
H	-8.6973790	-1.4258951	1.1876433
H	-8.6994984	0.1734871	2.0032132
H	-8.7029915	0.0820529	0.2064240
B	-2.4553735	0.2353938	-0.0751657
O	-1.7906397	-0.7740061	-0.7406601
O	-1.7863455	1.3480714	0.3919518
C	-0.3828426	-0.6988185	-0.9601877
H	-0.1623618	-1.2530115	-1.9013725
H	0.1374868	-1.2350485	-0.1299479
C	-0.3782165	1.4831848	0.2053249
H	-0.1535654	2.5727034	0.1424537
H	0.1419194	1.0888924	1.1117315
C	0.1388737	0.7518904	-1.0530326
C	-0.3873117	1.4360379	-2.3322468
H	-1.4978857	1.4545213	-2.3689950
H	-0.0304383	2.4888507	-2.3914042
H	-0.0286224	0.9019653	-3.2407274
C	1.6775939	0.7481574	-1.0517367
H	2.0756653	0.2015589	-1.9363740
H	2.0787484	1.7860374	-1.0922210
H	2.0878048	0.2607059	-0.1382718

[FB_2neop_2]$^-$

Energy = -843.1629263378 h
NIMAG = 0

B	-4.9005953	0.2962541	-0.2848041
O	-5.4230544	-1.1002729	-0.2021648
O	-5.4360450	1.1189114	0.8395669
C	-6.8036613	-1.1972128	-0.0545024
H	-7.3528584	-0.8186370	-0.9640933
H	-7.0875735	-2.2798612	0.0618599
C	-6.8171583	1.0548198	0.9992709
H	-7.1126654	1.6568723	1.9028455
H	-7.3650848	1.5043088	0.1218794
C	-7.3382676	-0.4034915	1.1759144
C	-6.7737922	-1.0065396	2.4729229
H	-7.1132260	-0.4306210	3.3675441
H	-7.1009663	-2.0665649	2.6020275
H	-5.6642839	-0.9837210	2.4426936
C	-8.8718615	-0.4226681	1.1967808
H	-9.2658099	-1.4635606	1.2920531
H	-9.2757616	0.1682369	2.0543785
H	-9.2938942	0.0122557	0.2602439
B	-3.1490276	0.2846433	-0.2503937
O	-2.4230297	-0.7214877	-0.9086543
O	-2.4194913	1.3361939	0.3279026
C	-1.0176081	-0.6847751	-1.0298539
H	-0.7356927	-1.2097942	-1.9771215
H	-0.5448406	-1.2593155	-0.1903343
C	-1.0134596	1.4196410	0.2371718
H	-0.7268931	2.5012263	0.2584747
H	-0.5420737	0.9436114	1.1367483
C	-0.4460215	0.7509225	-1.0350599
C	-0.9112427	1.5099361	-2.2944050
H	-2.0197968	1.5487191	-2.3593269
H	-0.5320402	2.5580983	-2.2864187
H	-0.5318725	1.0132962	-3.2173911
C	1.0887782	0.7114294	-0.9738669
H	1.5137034	0.2003356	-1.8692690
H	1.5163258	1.7408031	-0.9407411
H	1.4488660	0.1663538	-0.0706173
F	-5.3591229	0.8855541	-1.5426608

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