

A green and facile photochemical thiolate-catalyze strategy for the borylation of aryl fluorides with NHC-borane

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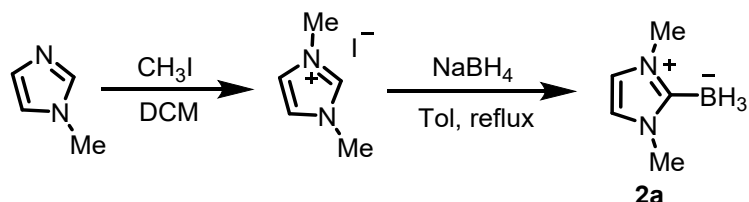
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1. General information

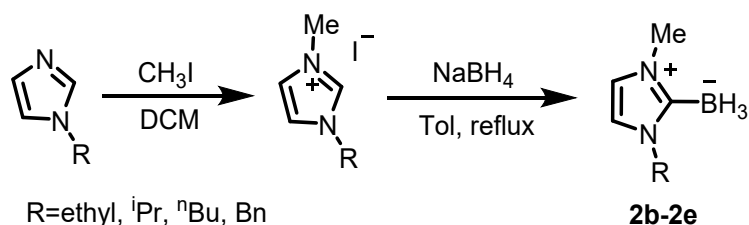
All reagents purchased commercially were used without further purification unless otherwise noted. The Blue LEDs were purchased from the supermarket. Thin-layer chromatography (TLC) analysis was performed by illumination with a UV lamp (254 nm), and flash column chromatography was carried out with 200–300 mesh silica gel. ^1H NMR, ^{13}C NMR, ^{11}B NMR and ^{19}F NMR spectra were recorded on 600 MHz spectrometer in CDCl_3 at room temperature. Chemical shifts (δ) are reported in ppm relative to the solvent peak. The ^{11}B and $^{11}\text{B}\{^1\text{H}\}$ NMR spectra were obtained at 128 or 193 MHz. All ^{11}B chemical shifts are referenced to $\text{BF}_3\cdot\text{OEt}_2$ (0.0 ppm), with a negative sign indicating an upfield shift. Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), with coupling constants (J) in hertz (Hz).

2. Synthesis of Starting Materials

2.1 Procedure for preparation of NHC-BH₃¹



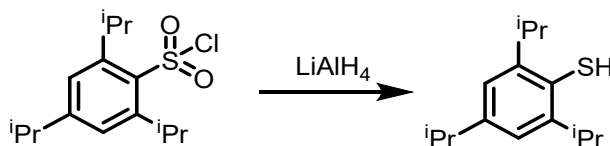
A 100 mL Schlenk-tube was charged with 1-methylimidazole (8.2 g, 100 mmol, 1.0 equiv.) in CH_2Cl_2 (20 mL) to which methyl iodide (16.9 g, 120 mmol, 1.2 equiv.) was added dropwise over 10 min at 0 °C. The mixture was allowed to stir for 2 h at room temperature. The crude product was then obtained after removing the solvent, and directly used for next step without further purification. Then the mixture was added 50 mL toluene and NaBH_4 (4.53 g, 120 mmol, 1.2 equiv.), and the mixture was placed in an oil bath and reacted at 120 °C for 24 h. The hot reaction solvent was cautiously decanted from the insoluble mixture, and the remaining residue was extracted with hot toluene (2×20 mL). The organic extracts were combined, evaporated, and further recrystallized over water to give the 5.3 g pure product as a fine white crystal in a 48% yield.



A 100 mL Schlenk-tube was charged with imidazole (10 mmol, 1.0 equiv.) in CH_2Cl_2 (20 mL) to which methyl iodide (1.7 g, 12 mmol, 1.2 equiv.) was added dropwise over 5 min at 0 °C. The mixture was allowed to stir for 2 h at room temperature. The crude product was then obtained after removing the solvent, and directly used for next step without further purification. Then the mixture was added 30 mL toluene and NaBH_4

(453 mg, 12 mmol, 1.2 equiv.), and the mixture was placed in an oil bath and reacted at 120 °C for 24 h. The hot reaction solvent was cautiously decanted from the insoluble mixture, and the remaining residue was extracted with hot toluene (2 × 20 mL). The organic extracts were combined, evaporated, purified by column chromatography (Petroleum ether: EtOAc) on silica gel to obtain the final products.

2.2 Preparation of TRIP thiol²



A 100 mL Schlenk-tube was charged with lithium aluminum hydride (LiAlH₄) (1.52 g, 40.0 mmol, 2.0 equiv.). Dry Et₂O (20 mL) was then added and cooled to 0 °C. To a mixture of 2,4,6-triisopropylbenzene-1-sulfonyl chloride (5.96 g, 20 mmol, 1.0 equiv.) in Et₂O (20 mL) was added slowly. After completion of the addition, an additional load of LiAlH₄ (0.76 g, 20 mmol, 1.0 equiv.) was added. The reaction was allowed to warm to rt and it was stirred overnight. Upon completion, the reaction was cooled to 0 °C and diluted with 40 mL Et₂O. The reaction was quenched with water (4 mL), 4 mL 15% (w/w) NaOH solution, and 10 mL water. The reaction was stirred for 30 min at 0 °C before MgSO₄ was added. The resulting white slurry was allowed to stir for 30 minutes at room temperature. The white solids were removed via filtration, with Et₂O washing. The filtrate was then concentrated and distilled at reduced pressure to provide 3.8 g of 2,4,6-triisopropyl-benzenethiol as colorless oil in 80% yield.

3. General Experimental Procedure for the defluoroborylation of polyfluoroarenes.

3.1 General Experimental Procedure for the defluoroborylation of polyfluoroarenes with NHC-borane 2a.

A 10 mL Schlenk-tube was charged with polyfluoroarene (0.2 mmol, 1.0 equiv.), NHC-borane **2a** (44 mg, 0.4 mmol, 2 equiv.), 2,4,6-triisopropyl-thiophenol (14 mg, 0.06 mmol, 0.3 equiv.) and pyridine (48 mg, 0.6 mmol, 3 equiv.) in dry THF (4 mL) with magnetic stirring under N₂ atmosphere. The tube was placed at a distance (app. 5 cm) from 10W blue LEDs (390-400 nm) lamp and the mixture was stirred for 24 h at 35-38 °C. Then the reaction was added 5 mL 1M HCl, extracted with DCM (3 × 10 mL), dried over anhydrous Na₂SO₄, and evaporated under reduced pressure. The residue was purified by column chromatography (Petroleum ether: EtOAc) on silica gel to obtain the products.

3.2 General Experimental Procedure for the defluoroborylation of pentafluoroanisole with NHC-borane 2b-2e.

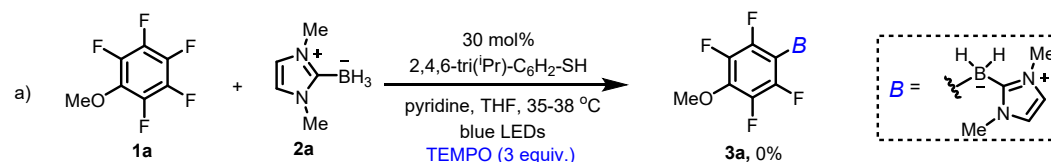
A 10 mL Schlenk-tube was charged with pentafluoroanisole (40 mg, 0.2 mmol, 1.0 equiv.), NHC-borane (0.4 mmol, 2 equiv.), 2,4,6-triisopropyl-thiophenol (14 mg, 0.06 mmol, 0.3 equiv.) and NaNH₂ (24 mg, 0.6 mmol, 3 equiv.) in dry THF (4 mL) with magnetic stirring under N₂ atmosphere. The tube was placed at a distance (app. 5 cm) from 10W blue LEDs (390-400 nm) lamp and the mixture was stirred for 24 h at 35-38

°C. Then the reaction was added 5 mL 1M HCl, extracted with DCM (3 × 10 mL), dried over anhydrous Na₂SO₄, and evaporated under reduced pressure. The residue was purified by column chromatography (Petroleum ether: EtOAc) on silica gel to obtain the products.

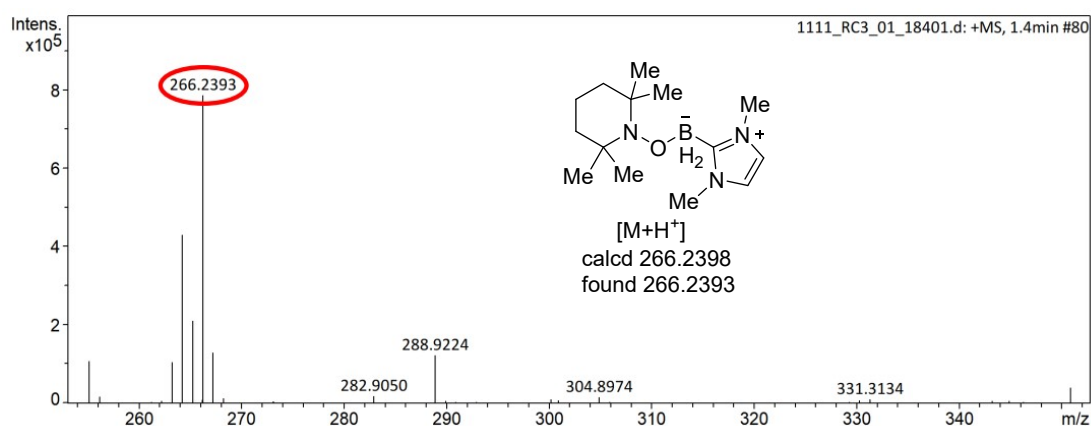
3.3 1 mmol scale reaction.

A 50 mL Schlenk-tube was charged with methyl 3,4,5-trifluorobenzoate (190 mg, 1 mmol, 1.0 equiv.), NHC-borane **2a** (220 mg, 2 mmol, 2 equiv.), 2,4,6-triisopropylthiophenol (70 mg, 0.3 mmol, 0.3 equiv.) and pyridine (480 mg, 6 mmol, 3 equiv.) in dry THF (20 mL) with magnetic stirring under N₂ atmosphere. The tube was placed at a distance (app. 5 cm) from 10W blue LEDs (390-400 nm) lamp and the mixture was stirred for 24 h at 35-38 °C. Then the reaction was added 10 mL 1M HCl, extracted with DCM (3 × 20 mL), dried over anhydrous Na₂SO₄, and evaporated under reduced pressure. The residue was purified by column chromatography (Petroleum ether: EtOAc) on silica gel to obtain the **3s** in 75% isolated yield.

4. Mechanistic Experiments.



A 10 mL Schlenk-tube was charged with 2,3,4,5,6-pentafluoroanisole (20 mg, 0.1 mmol, 1.0 equiv.), NHC-borane **2a** (22 mg, 0.2 mmol, 2 equiv.), 2,4,6-triisopropylthiophenol (7 mg, 0.03 mmol, 0.3 equiv.), pyridine (24 mg, 0.3 mmol, 3 equiv.) and TEMPO (47 mg, 0.3 mmol, 3.0 equiv.) in dry THF (2 mL) with magnetic stirring under N₂ atmosphere. The tube was placed at a distance (app. 5 cm) from 10W blue LEDs (390-400 nm) lamp and the mixture was stirred for 24 h at 35-38 °C. The desired product **3a** were not formed by TLC detected. And we found the boryl radical-trapping and thiyl radical-trapping products by HRMS.



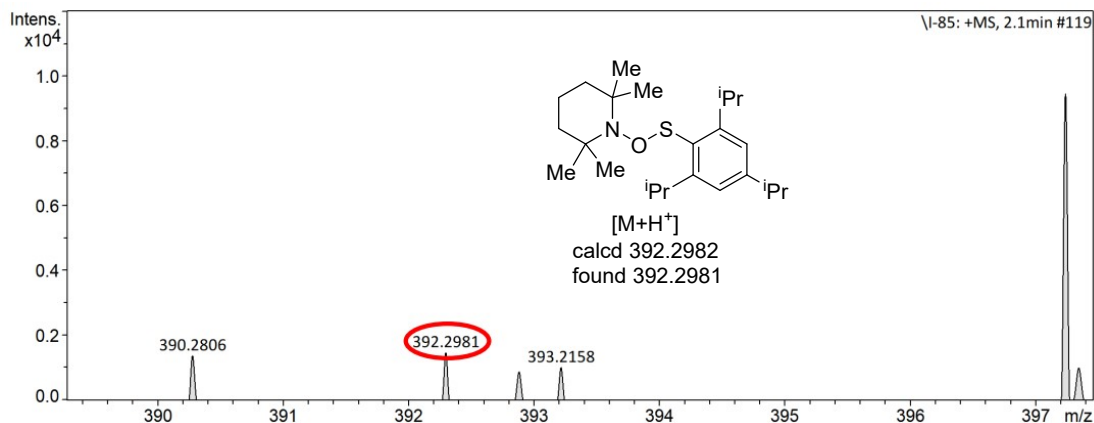
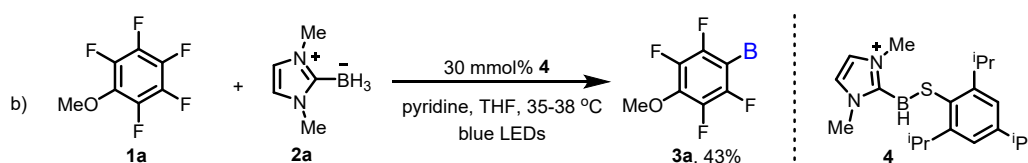
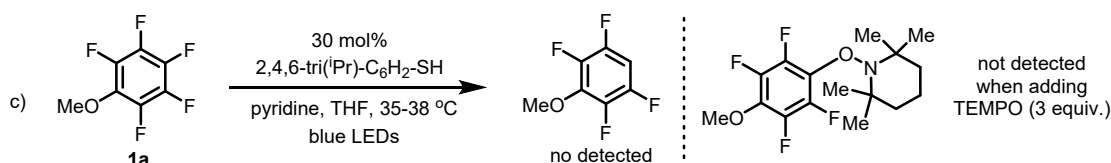


Figure S1. HRMS data of the reaction mixture



A 10 mL Schlenk-tube was charged with 2,3,4,5,6-pentafluoroanisole (20 mg, 0.1 mmol, 1.0 equiv.), NHC-borane **2a** (22 mg, 0.2 mmol, 2 equiv.), boryl sulphide **4** (10 mg, 0.03 mmol, 0.3 equiv.) and pyridine (24 mg, 0.3 mmol, 3 equiv.) in dry THF (2 mL) with magnetic stirring under N₂ atmosphere. The tube was placed at a distance (app. 5 cm) from 10W blue LEDs (390-400 nm) lamp and the mixture was stirred for 24 h at 35-38 °C. Then the reaction was added 5 mL 1M HCl, extracted with DCM (3 × 10 mL), dried over anhydrous Na₂SO₄, and evaporated under reduced pressure. Then the mixture was subjected to ¹H NMR to determine the yield (43%) using 1,3,5-methoxybenzenes as the internal standard.



A 10 mL Schlenk-tube was charged with 2,3,4,5,6-pentafluoroanisole (20 mg, 0.1 mmol, 1.0 equiv.), 2,4,6-triisopropylthiophenol (7 mg, 0.03 mmol, 0.3 equiv.) and pyridine (24 mg, 0.3 mmol, 3 equiv.) in dry THF (2 mL) with magnetic stirring under N₂ atmosphere. The tube was placed at a distance (app. 5 cm) from 10W blue LEDs (390-400 nm) lamp and the mixture was stirred for 24 h at 35-38 °C. The hydrodefluorination product could not be formed by TLC detected. When this control experiment was added the 3 equiv. TEMPO, the fluoroaryl radical adduct with TEMPO could not be detected by HRMS detected.

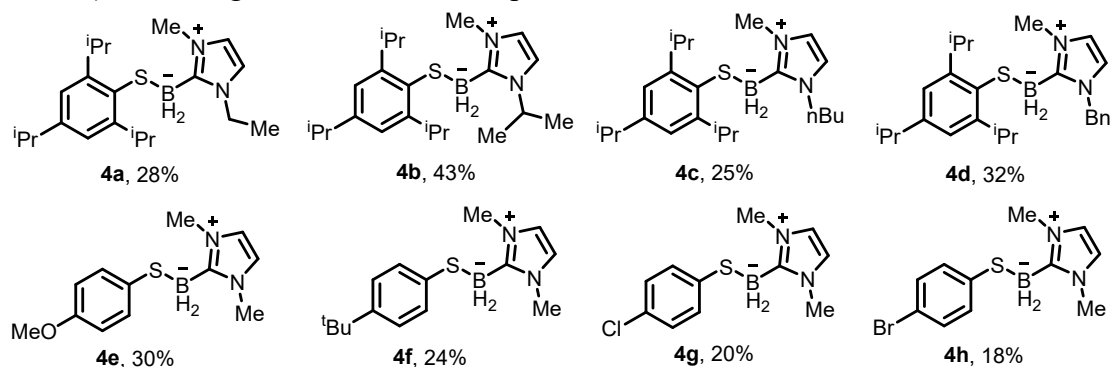
5. EPR spectrum experiment.

EPR experiments were carried out using an X-Band spectrometer (MS 400 Magnettech). The radicals were produced at room temperature under a light exposure

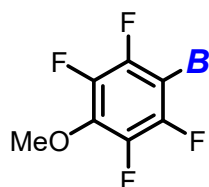
under N₂ and trapped by phenyl-N-^tbutylnitrone (PBN).

6. General Experimental Procedure for the formation of boryl sulfides

A 10 mL Schlenk-tube was charged with NHC-borane (0.5 mmol, 1 equiv.), thiol (0.5 mmol, 1 equiv.) in dry THF (5 mL) with magnetic stirring under N₂ atmosphere. The tube was placed at a distance (app. 5 cm) from 10W blue LEDs (390-400 nm) lamp and the mixture was stirred for 24 h. Then the reaction was added 5 mL H₂O, extracted with DCM (3 × 20 mL), dried over anhydrous Na₂SO₄, and evaporated under reduced pressure. The residue was purified by column chromatography (Petroleum ether: EtOAc) on silica gel to obtain the final products.



7. Characterization data of products.



(1,3-dimethyl-1H-imidazol-3-ium-2-yl)(2,3,5,6-tetrafluoro-4-methoxyphenyl) dihydroborate (**3a**): Colorless liquid (44 mg, 76% yield); Gradient eluent: EtOAc/petroleum ether: 1/4 to 1/2.

¹H NMR (600 MHz, CDCl₃) δ 6.85 (s, 2H), 3.96 (s, 2H), 3.89 (s, 1H), 3.74 (s, 6H), 2.17 (dd, *J* = 177.1, 87.8 Hz, 3H).

¹⁹F NMR (565 MHz, CDCl₃) δ -134.45 – -134.49 (m, 2F), -160.29 (dd, *J* = 24.7, 10.7 Hz, 2F);

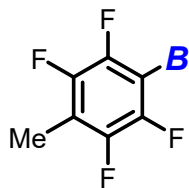
¹³C NMR (151 MHz, CDCl₃) δ 149.0 – 148.8 (m), 147.5 – 147.3 (m), 141.5 – 141.3 (m), 139.8 – 139.7 (m), 134.7 – 134.6 (m), 120.6, 62.1, 35.9.

¹¹B NMR (193 MHz, CDCl₃) δ -32.54 (t, *J* = 90.7 Hz).

¹¹B{¹H} NMR (193 MHz, CDCl₃) δ -32.54.

¹H{¹¹B} NMR (600 MHz, CDCl₃) δ 6.85 (s, 2H), 3.96 (s, 2H), 3.89 (s, 1H), 3.74 (s, 6H), 2.18 (s, 2H).

Characterization agrees with previous reports for this compound.³



(1,3-dimethyl-1H-imidazol-3-ium-2-yl)(2,3,5,6-tetrafluoro-4-methylphenyl) dihydroborate (**3b**): White solid (37 mg, 68% yield); Gradient eluent: EtOAc/petroleum ether: 1/4 to 1/2.

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 6.84 (s, 2H), 3.75 (s, 6H), 2.16 (s, 2H), 2.08 (s, 1H).

$^{19}\text{F NMR}$ (565 MHz, CDCl_3) δ -135.14 – -135.31 (m, 2F), -147.21 (dd, $J = 24.7$, 14.3 Hz, 2F).

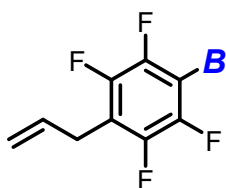
$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 148.7 – 148.5 (m), 147.2 – 146.9 (m), 145.4 – 145.3 (m), 143.8 – 143.7 (m), 120.5, 111.0 (t, $J = 19.6$ Hz), 35.9, 7.3.

$^{11}\text{B NMR}$ (193 MHz, CDCl_3) δ -32.39 (t, $J = 88.8$ Hz).

$^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3) δ -32.39.

$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3) δ 6.84 (s, 2H), 3.75 (s, 6H), 2.16 (s, 2H), 2.08 (s, 1H).

Characterization agrees with previous reports for this compound.³



(4-allyl-2,3,5,6-tetrafluorophenyl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl) dihydroborate (**3c**): Colorless liquid (49 mg, 82% yield); Gradient eluent: EtOAc/petroleum ether: 1/4 to 1/2.

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 6.84 (s, 2H), 5.94 – 5.85 (m, 1H), 5.05 – 4.98 (m, 2H), 3.75 (s, 6H), 3.35 (dd, $J = 46.2$, 6.2 Hz, 2H), 2.22 (dd, $J = 176.6$, 87.0 Hz, 2H).

$^{19}\text{F NMR}$ (565 MHz, CDCl_3) δ -134.53 – -134.57 (m, 2F), -147.98 (dd, $J = 24.7$, 14.3 Hz, 2F).

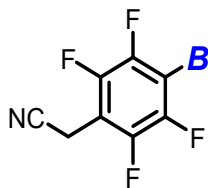
$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 148.8 – 148.6 (m), 147.2 – 147.0 (m), 145.2 – 144.9 (m), 143.5 – 143.3 (m), 134.7 (d, $J = 111.9$ Hz), 120.5 (d, $J = 13.5$ Hz), 115.7 (d, $J = 86.9$ Hz), 113.2 (t, $J = 23.2$ Hz), 36.0, 26.8 (t, $J = 2.9$ Hz).

$^{11}\text{B NMR}$ (193 MHz, CDCl_3) -32.36 (t, $J = 88.8$ Hz).

$^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3) δ -32.36.

$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3) δ 6.84 (s, 2H), 5.93 – 5.85 (m, 1H), 5.06 – 4.98 (m, 2H), 3.75 (s, 6H), 3.35 (dd, $J = 47.3$, 6.1 Hz, 2H), 2.22 (s, 2H).

HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ cacl. for $\text{C}_{14}\text{H}_{15}\text{BF}_4\text{N}_2\text{Na}^+$ 321.1157; found: 321.1149.



(4-(cyanomethyl)-2,3,5,6-tetrafluorophenyl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl) dihydroborate (**3d**): Colorless liquid (52 mg, 88% yield); Gradient eluent: EtOAc/petroleum ether: 1/2 to 1/1.

^1H NMR (600 MHz, CDCl_3) δ 6.87 (s, 2H), 3.75 (s, 6H), 3.70 (s, 2H), 2.21 (dd, $J = 179.2, 86.6$ Hz, 2H).

^{19}F NMR (565 MHz, CDCl_3) δ -132.53 (s, 2F), 145.76 (dd, $J = 24.0, 13.8$ Hz, 2F).

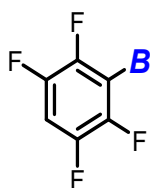
^{13}C NMR (151 MHz, CDCl_3) δ 148.9 – 148.7 (m), 147.3 – 147.1 (m), 144.8 – 144.6 (m), 143.2 – 143.0 (m), 120.7, 116.1 (d, $J = 96.5$ Hz), 104.0 (t, $J = 22.2$ Hz), 36.0, 11.3.

^{11}B NMR (193 MHz, CDCl_3) δ -32.35 (t, $J = 90.7$ Hz).

$^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3) δ -32.36.

$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3) δ 6.87 (s, 2H), 3.75 (s, 6H), 3.70 (s, 2H), 2.21 (s, 2H).

Characterization agrees with previous reports for this compound.³



(1,3-dimethyl-1H-imidazol-3-ium-2-yl)(2,3,5,6-tetrafluorophenyl) dihydroborate (**3e**): White solid (39 mg, 76% yield); Gradient eluent: EtOAc/petroleum ether: 1/4 to 1/2.

^1H NMR (600 MHz, CDCl_3) δ 6.85 (s, 2H), 6.73 – 6.67 (m, 1H), 3.75 (s, 6H), 2.23 (dd, $J = 177.8, 87.9$ Hz, 2H).

^{19}F NMR (565 MHz, CDCl_3) δ -133.95 – -134.11 (m, 2F), -142.40 (dd, $J = 24.5, 14.3$ Hz, 2F).

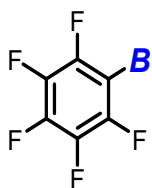
^{13}C NMR (151 MHz, CDCl_3) δ 148.8 – 148.6 (m), 147.2 – 147.0 (m), 146.3 – 146.2 (m), 144.7 – 144.5 (m), 101.6 (t, $J = 29.0$ Hz), 36.0.

^{11}B NMR (193 MHz, CDCl_3) δ -32.27 (t, $J = 89.7$ Hz).

$^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3) δ -32.26.

$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3) δ 6.85 (s, 2H), 6.73 – 6.67 (m, 1H), 3.75 (s, 6H), 2.23 (s, 2H).

Characterization agrees with previous reports for this compound.³



(1,3-dimethyl-1H-imidazol-3-ium-2-yl)(perfluorophenyl) dihydroborate (**3f**): White

solid (43 mg, 78% yield); Gradient eluent: EtOAc/petroleum ether: 1/4 to 1/2.

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 6.86 (s, 2H), 3.75 (s, 6H), 2.18 (dd, $J = 179.2, 88.8$ Hz, 3H).

$^{19}\text{F NMR}$ (565 MHz, CDCl_3) δ -133.10 – -133.14 (m, 2F), -161.91 (t, $J = 20.2$ Hz, 1F), -165.14 (dt, $J = 24.7, 9.1$ Hz, 2F).

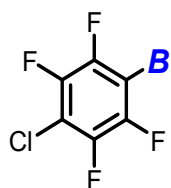
$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 148.8 – 148.5 (m), 147.2 – 146.9 (m), 139.0 – 138.7 (m), 137.7 – 137.2 (m), 136.2 – 135.8 (m), 120.7, 36.0.

$^{11}\text{B NMR}$ (193 MHz, CDCl_3) δ -32.59 (d, $J = 90.7$ Hz).

$^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3) δ -32.59.

$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3) δ 6.86 (s, 2H), 3.75 (s, 6H), 2.19 (s, 2H).

Characterization agrees with previous reports for this compound.³



(4-chloro-2,3,5,6-tetrafluorophenyl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl) dihydroborate (**3g**): White solid (39 mg, 67% yield); Gradient eluent: EtOAc/petroleum ether: 1/4 to 1/2.

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 6.87 (s, 2H), 3.75 (s, 6H), 2.42 – 1.98 (m, 2H).

$^{19}\text{F NMR}$ (565 MHz, CDCl_3) δ -132.13 (d, $J = 13.4$ Hz, 2F), -144.81 (td, $J = 14.2, 5.1$ Hz, 2F).

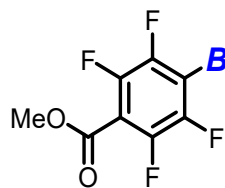
$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 149.0 – 148.8 (m), 147.5 – 147.2 (m), 144.2 – 144.0 (m), 142.6 – 142.4 (m), 120.7, 106.8 – 106.5 (m), 36.0.

$^{11}\text{B NMR}$ (193 MHz, CDCl_3) δ -32.39 (t, $J = 88.8$ Hz).

$^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3) δ -32.40.

$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3) δ 6.86 (s, 2H), 3.75 (s, 6H), 2.20 (s, 2H).

Characterization agrees with previous reports for this compound.³



(1,3-dimethyl-1H-imidazol-3-ium-2-yl)(2,3,5,6-tetrafluoro-4-(methoxycarbonyl)phenyl)dihydroborate (**3h**): White solid (50 mg, 79% yield); Gradient eluent: EtOAc/petroleum ether: 1/2 to 1/1.

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 6.87 (s, 2H), 3.92 (s, 3H), 3.74 (s, 6H), 2.44 – 2.00 (m, 2H).

$^{19}\text{F NMR}$ (565 MHz, CDCl_3) δ -132.74 (s, 2F), -142.66 – -142.82 (m, 2F).

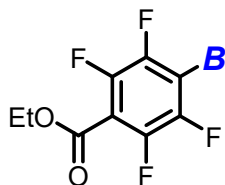
$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 161.8 – 161.5 (m), 149.0 – 148.7 (m), 147.4 – 147.2 (m), 145.2 – 144.9 (m), 143.4 – 143.1 (m), 120.6, 107.9 (t, $J = 15.9$ Hz), 52.7, 36.0.

$^{11}\text{B NMR}$ (193 MHz, CDCl_3) δ -32.25 (t, $J = 90.7$ Hz).

$^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3) δ -32.25.

$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3) δ 6.87 (s, 2H), 3.92 (s, 3H), 3.74 (s, 6H), 2.22 (s, 2H).

Characterization agrees with previous reports for this compound.³



(1,3-dimethyl-1H-imidazol-3-ium-2-yl)(4-(ethoxycarbonyl)-2,3,5,6-tetrafluorophenyl) dihydroborate (**3i**): White solid (50 mg, 76% yield); Gradient eluent: DCM/petroleum ether: 1/2 to 1/1.

^1H NMR (600 MHz, CDCl_3) δ 6.87 (s, 2H), 4.38 (q, $J = 7.1$ Hz, 2H), 3.73 (s, 6H), 2.22 (dd, $J = 178.4, 84.6$ Hz, 2H), 1.36 (t, $J = 7.1$ Hz, 3H).

^{19}F NMR (565 MHz, CDCl_3) δ -132.84 (s, 2F), -143.05 (dd, $J = 21.8, 11.6$ Hz, 2F).

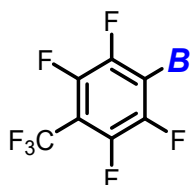
^{13}C NMR (151 MHz, CDCl_3) δ 161.2 – 161.1 (m), 148.9 – 148.7 (m), 147.4 – 147.1 (m), 145.0 – 144.8 (m), 143.3 – 143.1 (m), 120.7, 108.4 (t, $J = 15.1$ Hz), 61.9, 36.0, 14.1.

^{11}B NMR (193 MHz, CDCl_3) δ -32.26 (t, $J = 90.7$ Hz).

$^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3) δ -32.26.

$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3) δ 6.87 (s, 2H), 4.38 (q, $J = 7.1$ Hz, 2H), 3.73 (s, 6H), 2.22 (s, 2H), 1.36 (t, $J = 7.1$ Hz, 3H).

Characterization agrees with previous reports for this compound.³



(1,3-dimethyl-1H-imidazol-3-ium-2-yl)(2,3,5,6-tetrafluoro-4-(trifluoromethyl) phenyl) dihydroborate (**3j**): White solid (55 mg, 84% yield); Gradient eluent: EtOAc/petroleum ether: 1/2 to 1/1.

^1H NMR (600 MHz, CDCl_3) δ 6.89 (s, 2H), 3.75 (s, 6H), 2.23 (dd, $J = 178.2, 88.6$ Hz, 3H).

^{19}F NMR (565 MHz, CDCl_3) δ -55.99 (t, $J = 19.8$ Hz, 3F), -131.96 (s, 2F), -144.41 – -144.59 (m, 2F).

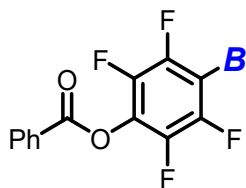
^{13}C NMR (151 MHz, CDCl_3) δ 149.2 – 148.9 (m), 147.5 – 147.3 (m), 144.1 – 143.9 (m), 142.4 – 142.2 (m), 122.5 (q, $J = 90.1$ Hz), 120.8, 36.0.

^{11}B NMR (193 MHz, CDCl_3) δ -32.29 (t, $J = 90.7$ Hz).

$^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3) δ -32.29.

$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3) δ 6.88 (s, 2H), 3.75 (s, 6H), 2.24 (s, 2H).

Characterization agrees with previous reports for this compound.³



(4-(benzoyloxy)-2,3,5,6-tetrafluorophenyl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl) dihydroborate (**3k**): White solid (65 mg, 86% yield); Gradient eluent: EtOAc/petroleum ether: 1/4 to 1/2.

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 8.22 – 8.16 (m, 2H), 7.65 (q, $J = 7.9$ Hz, 1H), 7.51 (q, $J = 7.7$ Hz, 2H), 6.86 (s, 2H), 3.77 (s, 6H), 2.24 (dd, $J = 179.1, 83.4$ Hz, 2H).

$^{19}\text{F NMR}$ (565 MHz, CDCl_3) δ -133.52 (d, $J = 18.5$ Hz, 2F), -156.48 (td, $J = 13.4, 4.2$ Hz, 2F).

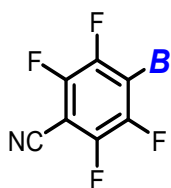
$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 163.4, 149.1 – 148.5 (m), 147.3 – 147.0 (m), 142.8 – 142.5 (m), 141.0 – 140.6 (m), 139.2 – 139.0, 134.2, 130.6, 128.7, 127.9, 120.7, 36.0.

$^{11}\text{B NMR}$ (193 MHz, CDCl_3) δ -32.42 (t, $J = 79.1$ Hz).

$^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3) δ -32.46.

$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3) δ 8.23 – 8.17 (m, 2H), 7.65 (q, $J = 7.8$ Hz, 1H), 7.51 (q, $J = 7.6$ Hz, 2H), 6.85 (d, $J = 17.6$ Hz, 2H), 3.76 (d, $J = 14.7$ Hz, 6H), 2.25 (s, 2H).

Characterization agrees with previous reports for this compound.³



(4-cyano-2,3,5,6-tetrafluorophenyl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl) dihydroborate (**3l**): White solid (21 mg, 37% yield); Gradient eluent: DCM/petroleum ether: 1/2 to 1/1.

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 6.90 (s, 2H), 3.74 (s, 6H), 2.23 (dd, $J = 180.4, 88.6$ Hz, 3H).

$^{19}\text{F NMR}$ (565 MHz, CDCl_3) δ -130.45 (s, 2F), -136.21 – -136.43 (m, 2F).

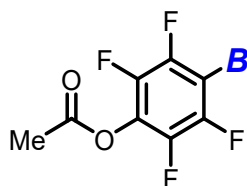
$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 148.6 – 148.4 (m), 147.2 – 147.0 (m), 147.0 – 146.9 (m), 145.5 – 145.3 (m), 120.9, 109.2 (t, $J = 4.5$ Hz), 89.3 – 89.1 (m), 36.1.

$^{11}\text{B NMR}$ (193 MHz, CDCl_3) δ -32.11 (t, $J = 90.7$ Hz).

$^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3) δ -32.12.

$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3) δ 6.90 (s, 2H), 3.74 (s, 6H), 2.23 (s, 2H).

Characterization agrees with previous reports for this compound.³



(4-acetoxy-2,3,5,6-tetrafluorophenyl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)

dihydroborate (**3m**): Colorless liquid (51 mg, 81% yield); Gradient eluent: DCM/petroleum ether: 1/2 to 1/1. Gradient eluent: EtOAc/petroleum ether: 1/4 to 1/2. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 6.85 (s, 2H), 3.75 (s, 6H), 2.35 (s, 3H), 2.12 (dd, $J = 126.1, 86.0$ Hz, 2H).

$^{19}\text{F NMR}$ (565 MHz, CDCl_3) δ -133.55 – -133.75 (m, 2F), -156.83 (td, $J = 13.4, 4.1$ Hz).

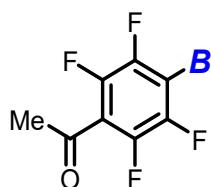
$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 167.5, 151.1 – 150.8 (m), 148.7 – 148.5 (m), 147.3 – 146.9 (m), 140.7 – 140.4 (m), 139.0 – 138.8 (m), 120.7, 36.0, 20.1.

$^{11}\text{B NMR}$ (193 MHz, CDCl_3) δ -32.48 (t, $J = 92.6$ Hz).

$^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3) δ -32.47.

$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3) δ 6.85 (s, 2H), 3.75 (s, 6H), 2.35 (s, 3H), 2.21 (s, 2H).

HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ cacl. for $\text{C}_{13}\text{H}_{13}\text{BF}_4\text{N}_2\text{NaO}_2^+$ 339.0898; found: 339.0892.



(4-acetyl-2,3,5,6-tetrafluorophenyl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)dihydroborate (**3n**): White solid (21 mg, 35% yield); Gradient eluent: DCM/petroleum ether: 1/2 to 1/1. Gradient eluent: EtOAc/petroleum ether: 1/2 to 1/1. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 6.88 (s, 2H), 3.75 (s, 6H), 2.57 (t, $J = 2.0$ Hz, 3H), 2.22 (dd, $J = 178.2, 92.5$ Hz, 2H).

$^{19}\text{F NMR}$ (565 MHz, CDCl_3) δ -132.84 (s, 2F), -144.54 (dd, $J = 24.3, 14.1$ Hz, 2F).

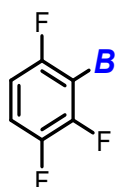
$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 193.7, 149.0 – 148.8 (m), 147.4 – 147.2 (m), 144.5 – 144.3 (m), 142.8 – 142.6 (m), 120.7, 115.6 – 115.3 (m), 36.0, 32.5 (t, $J = 3.0$ Hz).

$^{11}\text{B NMR}$ (193 MHz, CDCl_3) δ -32.25 (t, $J = 92.6$ Hz).

$^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3) δ -32.26.

$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3) δ 6.87 (s, 2H), 3.75 (s, 6H), 2.57 (t, $J = 1.9$ Hz, 3H), 2.23 (s, 2H).

Characterization agrees with previous reports for this compound.³



(1,3-dimethyl-1H-imidazol-3-ium-2-yl)(2,3,6-trifluorophenyl)dihydroborate (**3o**): Colorless liquid (26 mg, 54% yield); Gradient eluent: EtOAc/petroleum ether: 1/2 to 1/1.

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 6.83 (s, 2H), 6.80 – 6.74 (m, 1H), 6.61 – 6.55 (m, 1H), 3.75 (s, 6H), 2.22 (dd, $J = 176.3, 88.7$ Hz, 2H).

¹⁹F NMR (565 MHz, CDCl₃) δ -108.93 (s, 1F), -128.09 (d, *J* = 21.8 Hz, 1F), -145.80 (dd, *J* = 23.8, 16.3 Hz, 1F).

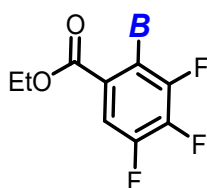
¹³C NMR (151 MHz, CDCl₃) δ 161.2 (dd, *J* = 234.1, 13.6 Hz), 153.5 – 151.8 (m), 148.0 – 146.2 (m), 120.5, 112.6 – 112.4 (m), 109.3 – 109.0 (m), 36.0.

¹¹B NMR (193 MHz, CDCl₃) δ -32.33 (t, *J* = 90.7 Hz).

¹¹B{¹H} NMR (193 MHz, CDCl₃) δ -32.33.

¹H{¹¹B} NMR (600 MHz, CDCl₃) δ 6.83 (s, 2H), 6.77 (tt, *J* = 9.3, 4.6 Hz, 1H), 6.58 (ddd, *J* = 10.9, 6.4, 2.0 Hz, 1H), 3.76 (s, 6H), 2.22 (s, 2H).

Characterization agrees with previous reports for this compound.⁴



(1,3-dimethyl-1H-imidazol-3-ium-2-yl)(6-(ethoxycarbonyl)-2,3,4-trifluorophenyl) dihydroborate (**3p**): Colorless liquid (42 mg, 67% yield); Gradient eluent: EtOAc/petroleum ether: 1/2 to 1/1.

¹H NMR (600 MHz, CDCl₃) δ 7.17 (ddd, *J* = 8.2, 4.7, 2.0 Hz, 1H), 6.86 (s, 2H), 4.34 (q, *J* = 7.1 Hz, 2H), 3.73 (s, 6H), 2.43 – 1.99 (m, 2H), 1.36 (t, *J* = 7.1 Hz, 3H).

¹⁹F NMR (565 MHz, CDCl₃) δ -108.30 (d, *J* = 13.2 Hz, 1F), -127.05 (d, *J* = 21.7 Hz, 1F), -143.12 (dd, *J* = 22.5, 16.3 Hz, 1F).

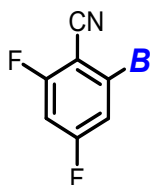
¹³C NMR (151 MHz, CDCl₃) δ 163.7 (q, *J* = 3.5 Hz), 160.1 (ddd, *J* = 235.6, 14.4, 3.0 Hz), 154.2 – 152.4 (m), 146.9 (ddd, *J* = 250.7, 18.1, 3.0 Hz), 120.6, 116.2 (t, *J* = 9.1 Hz), 110.8 (dd, *J* = 31.7, 3.0 Hz), 61.3, 36.0, 14.2.

¹¹B NMR (193 MHz, CDCl₃) δ -32.24 (t, *J* = 88.8 Hz).

¹¹B{¹H} NMR (193 MHz, CDCl₃) δ -32.24.

¹H{¹¹B} NMR (600 MHz, CDCl₃) δ 7.19 – 7.15 (m, 1H), 6.86 (s, 2H), 4.34 (q, *J* = 7.1 Hz, 2H), 3.73 (s, 6H), 2.21 (s, 2H), 1.36 (t, *J* = 7.1 Hz, 3H).

Characterization agrees with previous reports for this compound.⁴



(2-cyano-3,5-difluorophenyl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)dihydroborate (**3q**): White solid (37 mg, 75% yield); Gradient eluent: EtOAc/petroleum ether: 1/2 to 1/1.

¹H NMR (600 MHz, CDCl₃) δ 6.94 (d, *J* = 8.1 Hz, 1H), 6.91 (s, 2H), 6.56 (td, *J* = 9.0, 2.4 Hz, 1H), 3.70 (s, 6H), 2.41 (dd, *J* = 175.7, 87.1 Hz, 2H).

¹⁹F NMR (565 MHz, CDCl₃) δ -103.80 (d, *J* = 10.1 Hz, 1F), -105.10 (d, *J* = 10.0 Hz, 1F).

¹³C NMR (151 MHz, CDCl₃) δ 165.5 – 163.5 (m), 122.8, 121.0, 117.8 (d, *J* = 18.1

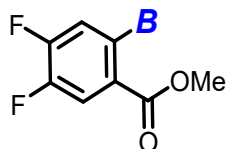
Hz), 115.4, 101.1 (dd, $J = 10.6, 3.0$ Hz), 100.1 (q, $J = 17.1$ Hz), 36.4.

^{11}B NMR (193 MHz, CDCl_3) δ -25.65 (t, $J = 86.9$ Hz).

$^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3) δ -25.66.

$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3) δ 6.93 (dd, $J = 9.1, 1.9$ Hz, 1H), 6.91 (s, 2H), 6.56 (td, $J = 9.0, 2.4$ Hz, 1H), 3.70 (s, 6H), 2.41 (s, 2H).

Characterization agrees with previous reports for this compound.⁴



(4,5-difluoro-2-(methoxycarbonyl)phenyl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)dihydroborate (**3r**): White solid (19 mg, 34% yield); Gradient eluent: EtOAc/petroleum ether: 1/2 to 1/1.

^1H NMR (600 MHz, CDCl_3) δ 7.30 (dd, $J = 8.6, 5.6$ Hz, 1H), 7.07 (d, $J = 8.3$ Hz, 1H), 6.86 (s, 2H), 3.87 (s, 3H), 3.72 (s, 6H), 2.25 (dd, $J = 174.0, 87.7$ Hz, 2H).

^{19}F NMR (565 MHz, CDCl_3) δ -113.05 (d, $J = 19.1$ Hz, 2F), -119.18 (d, $J = 19.5$ Hz, 2F).

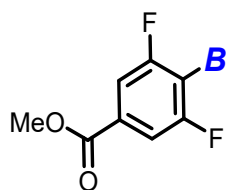
^{13}C NMR (151 MHz, CDCl_3) δ 164.9 (dd, $J = 4.5, 3.0$ Hz), 161.4 (d, $J = 234.1$ Hz), 157.7 (d, $J = 255.2$ Hz), 124.4 (dd, $J = 21.1, 12.1$ Hz), 120.6, 115.7 (d, $J = 28.7$ Hz), 114.8 (dd, $J = 12.5, 8.3$ Hz), 52.0, 36.1.

^{11}B NMR (193 MHz, CDCl_3) δ -27.98 (t, $J = 86.9$ Hz).

$^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3) δ -27.98.

$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3) δ 7.30 (dd, $J = 8.6, 5.6$ Hz, 1H), 7.07 (dd, $J = 11.3, 4.8$ Hz, 1H), 6.86 (s, 2H), 3.87 (s, 3H), 3.72 (s, 6H), 2.25 (s, 2H).

Characterization agrees with previous reports for this compound.⁴



(2,6-difluoro-4-(methoxycarbonyl)phenyl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)dihydroborate (**3s**): White solid (49 mg, 88% yield); Gradient eluent: DCM/petroleum ether: 1/2 to 1/1.

^1H NMR (600 MHz, CDCl_3) δ 7.30 (dd, $J = 6.0, 1.6$ Hz, 2H), 6.83 (s, 2H), 3.85 (s, 3H), 3.72 (s, 6H), 2.21 (dd, $J = 176.2, 86.0$ Hz, 2H).

^{19}F NMR (565 MHz, CDCl_3) δ -102.24 (s, 2F).

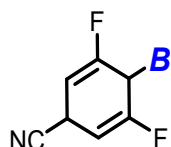
^{13}C NMR (151 MHz, CDCl_3) δ 166.2 (t, $J = 3.8$ Hz), 166.0 (dd, $J = 240.09, 16.6$ Hz), 128.5 (t, $J = 10.8$ Hz), 120.5, 111.0 (dd, $J = 25.7, 7.6$ Hz), 52.1, 35.9.

^{11}B NMR (193 MHz, CDCl_3) δ -32.30 (t, $J = 88.8$ Hz).

$^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3) δ -32.30.

$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3) δ 7.30 (dd, $J = 5.9, 1.6$ Hz, 2H), 6.83 (s, 2H), 3.85 (s, 3H), 3.72 (s, 6H), 2.21 (s, 2H).

Characterization agrees with previous reports for this compound.⁴



(4-cyano-2,6-difluorocyclohexa-2,5-dien-1-yl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl) dihydroborate (**3t**): White solid (18 mg, 36% yield); Gradient eluent: DCM/petroleum ether: 1/2 to 1/1.

¹H NMR (600 MHz, CDCl₃) δ 6.89 (s, 2H), 4.80 (dt, *J* = 9.9, 4.9 Hz, 2H), 3.98 (d, *J* = 3.7 Hz, 1H), 3.79 (s, 6H), 2.54 (s, 1H), 1.78 (d, *J* = 93.9 Hz, 2H).

¹⁹F NMR (565 MHz, CDCl₃) δ -99.16 (s, 2F).

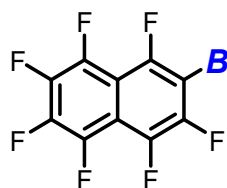
¹³C NMR (151 MHz, CDCl₃) δ 168.2 (dd, *J* = 259.7, 19.6 Hz), 121.3, 119.1, 89.8 (dd, *J* = 22.7 Hz), 36.2, 26.4 (t, *J* = 12.1 Hz).

¹¹B NMR (193 MHz, CDCl₃) δ -27.58 (t, *J* = 88.8 Hz).

¹¹B{¹H} NMR (193 MHz, CDCl₃) δ -27.58.

¹H{¹¹B} NMR (600 MHz, CDCl₃) δ 6.89 (s, 2H), 4.80 (dt, *J* = 9.9, 4.9 Hz, 2H), 4.00 – 3.95 (m, 1H), 3.79 (s, 6H), 2.54 (dq, *J* = 10.1, 5.0 Hz, 1H), 1.78 (s, 2H).

Characterization agrees with previous reports for this compound.⁴



(1,3-dimethyl-1H-imidazol-3-ium-2-yl)(perfluoronaphthalen-2-yl)dihydroborate (**3u**): White solid (23 mg, 32% yield); Gradient eluent: EtOAc/petroleum ether: 1/2 to 1/1.

¹H NMR (600 MHz, CDCl₃) δ 6.89 (s, 2H), 3.79 (s, 6H), 2.32 (dd, *J* = 178.3, 87.0 Hz, 3H).

¹⁹F NMR (565 MHz, CDCl₃) δ -110.74 (d, *J* = 70.5 Hz, 1F), -125.71 (s, 1F), -146.19 (dt, *J* = 71.2, 16.8 Hz, 1F), -148.51 (dtd, *J* = 20.4, 16.3, 3.4 Hz, 1F), -153.39 (dt, *J* = 55.7, 19.9 Hz, 1F), -158.71 (t, *J* = 18.6 Hz, 1F), -159.66 (t, *J* = 18.7 Hz).

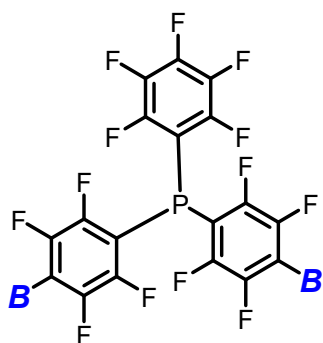
¹³C NMR (151 MHz, CDCl₃) δ 154.5 – 154.1 (m), 152.8 – 151.9 (m), 150.7 – 150.4 (m), 141.8 – 141.5 (m), 140.7 – 139.6 (m), 139.1 – 138.8 (m), 137.4 – 137.1 (m), 120.7, 36.0.

¹¹B NMR (193 MHz, CDCl₃) δ -32.18 (t, *J* = 86.9 Hz).

¹¹B{¹H} NMR (193 MHz, CDCl₃) δ -32.19.

¹H{¹¹B} NMR (600 MHz, CDCl₃) δ 6.89 (s, 2H), 3.79 (s, 6H), 2.33 (s, 2H).

Characterization agrees with previous reports for this compound.³



(4-(bis(perfluorophenyl)phosphanyl)-2,3,5,6-tetrafluorophenyl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)dihydroborate (**3v**): Colorless liquid (86 mg, 60% yield); Gradient eluent: DCM/petroleum ether: 1/2 to 1/1.

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 6.86 (s, 2H), 3.73 (s, 6H), 2.21 (dd, $J = 176.3, 78.0$ Hz, 2H).

$^{31}\text{P NMR}$ (243 MHz, CDCl_3) δ -74.41 – -75.01 (m).

$^{19}\text{F NMR}$ (565 MHz, CDCl_3) δ -130.32 – -130.50 (m, 2F), -132.76 (dd, $J = 22.9, 11.4$ Hz, 4F), -134.45 – -134.62 (m, 4F), -151.15 (t, $J = 20.6$ Hz, 1F), -161.36 (dt, $J = 22.2, 7.2$ Hz, 2F).

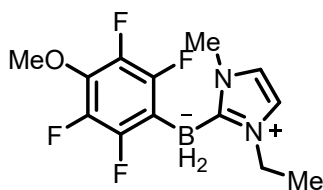
$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 149.0 – 148.3 (m), 147.7 – 147.2 (m), 147.0 – 145.8 (m), 143.1 – 141.2 (m), 138.3 – 136.4 (m), 120.7, 108.0 – 107.5 (m), 104.9 – 104.5 (m), 36.0.

$^{11}\text{B NMR}$ (193 MHz, CDCl_3) δ -32.20 (t, $J = 88.8$ Hz).

$^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3) δ -32.19.

$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3) δ 6.85 (s, 2H), 3.73 (s, 6H), 2.21 (s, 2H).

HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ cacl. for $\text{C}_{28}\text{H}_{20}\text{B}_2\text{F}_{13}\text{N}_4\text{NaP}^+$ 735.1296; found: 735.1287.



(3-ethyl-1-methyl-1H-imidazol-3-ium-2-yl)(2,3,5,6-tetrafluoro-4-methoxyphenyl)dihydroborate (**3w**): Colorless liquid (53 mg, 88% yield); Gradient eluent: EtOAc/petroleum ether: 1/4 to 1/2.

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 6.90 – 6.85 (m, 2H), 4.18 (qd, $J = 7.3, 2.5$ Hz, 2H), 3.92 (d, $J = 42.5$ Hz, 3H), 3.73 (s, 3H), 2.19 (dd, $J = 177.1, 86.4$ Hz, 3H), 1.32 (dd, $J = 13.4, 7.2$ Hz, 2H).

$^{19}\text{F NMR}$ (565 MHz, CDCl_3) δ -134.46 – -134.63 (m, 2F), -165.31 (dd, $J = 25.6, 20.5$ Hz, 2F).

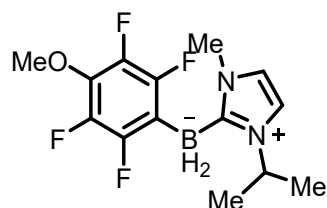
$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 149.0 – 148.7 (m), 147.5 – 147.2 (m), 141.5 – 141.2 (m), 139.9 – 139.6 (m), 135.0 – 134.5 (m), 120.9, 118.5, 62.1, 43.7, 35.8, 15.5.

$^{11}\text{B NMR}$ (193 MHz, CDCl_3) δ -32.49 (t, $J = 88.8$ Hz).

$^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3) δ -32.50.

$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3) δ 6.88 (d, $J = 17.7$ Hz, 2H), 4.18 (qd, $J = 7.3, 2.2$ Hz, 2H), 3.92 (d, $J = 42.6$ Hz, 3H), 3.73 (s, 3H), 2.19 (s, 2H), 1.32 (dd, $J = 13.6, 7.1$ Hz, 3H).

HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ cacl. for $\text{C}_{13}\text{H}_{15}\text{BF}_4\text{N}_2\text{NaO}^+$ 325.1106; found: 325.1104.



(3-isopropyl-1-methyl-1H-imidazol-3-ium-2-yl)(2,3,5,6-tetrafluoro-4-methoxyphenyl) dihydroborate (**3x**): Colorless liquid (53 mg, 83% yield); Gradient eluent: EtOAc/petroleum ether: 1/4 to 1/2.

^1H NMR (600 MHz, CDCl_3) δ 6.96 – 6.94 (m, 1H), 6.88 (s, 1H), 5.10 (dq, $J = 13.4, 6.7$ Hz, 1H), 3.92 (d, $J = 44.0$ Hz, 3H), 3.74 (s, 3H), 2.20 (dd, $J = 177.8, 85.5$ Hz, 2H), 1.33 – 1.31 (m, 6H).

^{19}F NMR (565 MHz, CDCl_3) δ -157.03 (d, $J = 20.2$ Hz, 2F), -160.31 (dd, $J = 24.6, 10.7$ Hz, 2F).

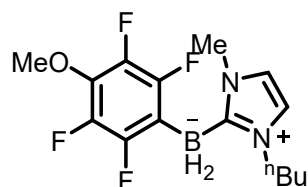
^{13}C NMR (151 MHz, CDCl_3) δ 149.0 – 148.6 (m), 147.5 – 147.1 (m), 141.6 – 141.2 (m), 139.9 – 139.6 (m), 134.7 – 134.4 (m), 121.2, 115.2, 62.1, 49.8, 35.7, 22.9.

^{11}B NMR (193 MHz, CDCl_3) δ -32.44 (t, $J = 90.7$ Hz).

$^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3) δ -32.44.

$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3) δ 6.95 (s, 1H), 6.88 (s, 1H), 5.10 (dq, $J = 13.3, 6.7$ Hz, 1H), 3.92 (d, $J = 44.0$ Hz, 3H), 3.74 (s, 3H), 2.20 (s, 2H), 1.34 – 1.31 (m, 6H).

HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ cacl. for $\text{C}_{14}\text{H}_{17}\text{BF}_4\text{N}_2\text{NaO}^+$ 339.1262; found: 339.1253.



(3-butyl-1-methyl-1H-imidazol-3-ium-2-yl)(2,3,5,6-tetrafluoro-4-methoxyphenyl) dihydroborate (**3y**): Colorless liquid (52 mg, 79% yield); Gradient eluent: EtOAc/petroleum ether: 1/4 to 1/2.

^1H NMR (600 MHz, CDCl_3) δ 6.87 (s, 1H), 6.85 (s, 1H), 4.10 (t, $J = 7.6$ Hz, 2H), 3.92 (d, $J = 42.8$ Hz, 3H), 3.73 (s, 3H), 2.19 (dd, $J = 177.6, 84.9$ Hz, 2H), 1.68 – 1.61 (m, 2H), 1.30 (dt, $J = 14.6, 7.5$ Hz, 2H), 0.90 (t, $J = 7.4$ Hz, 3H).

^{19}F NMR (565 MHz, CDCl_3) δ -134.37 – -134.57 (m, 2F) -160.32 (dd, $J = 24.6, 10.8$ Hz, 2F).

^{13}C NMR (151 MHz, CDCl_3) δ 149.0 – 148.7 (m), 147.5 – 147.1 (m), 141.5 – 141.2 (m), 139.9 – 139.6 (m), 134.8 – 134.5 (m), 120.7, 119.2, 62.1, 48.5, 35.9, 32.4, 19.7,

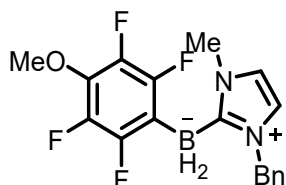
13.6.

^{11}B NMR (193 MHz, CDCl_3) δ -32.44 (t, J = 88.8 Hz).

$^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3) δ -32.45.

$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3) δ 6.86 (d, J = 10.0 Hz, 2H), 4.10 (t, J = 7.6 Hz, 2H), 3.92 (d, J = 42.9 Hz, 3H), 3.73 (s, 3H), 2.19 (s, 2H), 1.68 – 1.61 (m, 2H), 1.30 (dt, J = 14.8, 7.4 Hz, 2H), 0.90 (t, J = 7.4 Hz, 3H).

HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ cacl. for $\text{C}_{15}\text{H}_{19}\text{BF}_4\text{N}_2\text{NaO}^+$ 353.1419; found: 353.1415.



(3-benzyl-1-methyl-1H-imidazol-3-ium-2-yl)(2,3,5,6-tetrafluoro-4-methoxyphenyl)dihydroborate (**3z**): Colorless liquid (58 mg, 80% yield); Gradient eluent: EtOAc/petroleum ether: 1/4 to 1/2.

^1H NMR (600 MHz, CDCl_3) δ 7.30 (q, J = 6.4 Hz, 3H), 7.14 – 7.10 (m, 2H), 6.86 (s, 1H), 6.75 (d, J = 1.8 Hz, 1H), 5.33 (s, 2H), 3.90 (d, J = 50.6 Hz, 3H), 3.80 (s, 3H), 2.31 (dd, J = 177.6, 85.7 Hz, 2H).

^{19}F NMR (565 MHz, CDCl_3) δ -133.62 (d, J = 25.4 Hz, 2F), -160.23 (dd, J = 24.7, 10.7 Hz, 2F).

^{13}C NMR (151 MHz, CDCl_3) δ 149.0 – 148.6 (m), 147.6 – 147.2 (m), 141.7 – 141.2 (m), 139.8 – 139.6 (m), 135.4, 134.8 – 134.5 (m), 128.6, 128.3, 127.6, 121.1, 119.3, 62.1, 52.1, 36.1.

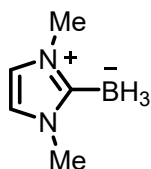
^{11}B NMR (193 MHz, CDCl_3) δ -32.28 (t, J = 88.8 Hz).

$^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3) δ -32.29.

$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3) δ 7.32 – 7.27 (m, 3H), 7.13 (d, J = 4.7 Hz, 2H), 6.86 (s, 1H), 6.75 (s, 1H), 5.33 (s, 2H), 3.90 (d, J = 50.6 Hz, 3H), 3.80 (s, 3H), 2.32 (s, 2H).

HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ cacl. for $\text{C}_{18}\text{H}_{17}\text{BF}_4\text{N}_2\text{NaO}^+$ 387.1262; found: 387.1252.

8. Characterization data of starting materials and boryl sulfides.



(1,3-dimethyl-1H-imidazol-3-ium-2-yl)trihydroborate (**2a**): white solid (5.3 g, 47% yield).

^1H NMR (600 MHz, CDCl_3) δ 6.79 (s, 2H), 3.71 (s, 6H), 0.99 (dd, J = 172.7, 86.3 Hz, 3H).

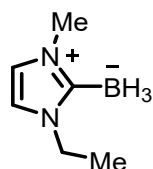
^{13}C NMR (151 MHz, CDCl_3) δ 112.0, 35.9.

^{11}B NMR (193 MHz, CDCl_3) δ -37.49 (q, J = 86.9 Hz).

$^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3) δ -37.48.

$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3) δ 6.79 (s, 2H), 3.71 (s, 6H), 0.99 (dd, J = 55.1, 27.9 Hz, 3H).

Characterization agrees with previous reports for this compound.¹



(1-ethyl-3-methyl-1H-imidazol-3-ium-2-yl)trihydroborate (**2b**): white solid (0.35 g, 28% yield); Gradient eluent: EtOAc/petroleum ether: 1/5 to 1/4.

^1H NMR (600 MHz, CDCl_3) δ 6.82 (d, J = 1.9 Hz, 1H), 6.80 (d, J = 1.9 Hz, 1H), 4.14 (q, J = 7.3 Hz, 2H), 3.70 (s, 3H), 1.36 (t, J = 7.3 Hz, 3H), 1.00 (dd, J = 172.6, 86.2 Hz, 3H).

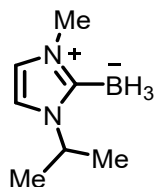
^{13}C NMR (151 MHz, CDCl_3) δ 120.2, 118.1, 43.7, 35.8, 15.4.

^{11}B NMR (193 MHz, CDCl_3) δ -37.48 (q, J = 83.6 Hz).

$^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3) δ -37.48.

$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3) δ 6.82 (d, J = 1.9 Hz, 1H), 6.80 (d, J = 1.9 Hz, 1H), 4.14 (q, J = 7.3 Hz, 2H), 3.70 (s, 3H), 1.36 (t, J = 7.3 Hz, 3H), 1.17 – 0.82 (m, 3H).

Characterization agrees with previous reports for this compound.¹



(1-isopropyl-3-methyl-1H-imidazol-3-ium-2-yl)trihydroborate (**2c**): white solid (0.35 g, 28% yield); Gradient eluent: EtOAc/petroleum ether: 1/5 to 1/4.

^1H NMR (600 MHz, CDCl_3) δ 6.88 (d, J = 2.0 Hz, 1H), 6.81 (d, J = 2.0 Hz, 1H), 5.05 (dt, J = 13.5, 6.8 Hz, 1H), 3.72 (s, 3H), 1.37 (d, J = 6.8 Hz, 6H), 1.02 (dd, J = 172.6, 86.2 Hz, 3H).

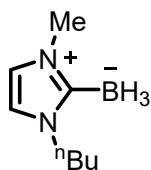
^{13}C NMR (151 MHz, CDCl_3) δ 120.4, 114.6, 49.6, 35.7, 22.7.

^{11}B NMR (193 MHz, CDCl_3) δ -37.40 (q, J = 86.2 Hz).

$^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3) δ -37.40.

$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3) δ 6.88 (d, J = 2.0 Hz, 1H), 6.81 (d, J = 2.0 Hz, 1H), 5.04 (dq, J = 13.5, 6.8 Hz, 1H), 3.71 (s, 3H), 1.37 (d, J = 6.8 Hz, 6H), 1.18 – 0.85 (m, 3H).

Characterization agrees with previous reports for this compound.¹



(1-butyl-3-methyl-1H-imidazol-3-ium-2-yl)trihydroborate (**2d**): white solid (0.40 g, 26% yield); Gradient eluent: EtOAc/petroleum ether: 1/5 to 1/4.

^1H NMR (600 MHz, CDCl_3) δ 6.79 (q, $J = 1.9$ Hz, 2H), 4.08 – 4.04 (m, 2H), 3.68 (s, 3H), 1.74 – 1.68 (m, 2H), 1.35 – 1.27 (m, 2H), 1.20 – 0.76 (m, 6H).

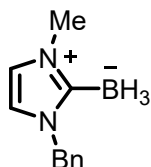
^{13}C NMR (151 MHz, CDCl_3) δ 112.0, 118.8, 48.5, 35.8, 32.2, 19.7, 13.6.

^{11}B NMR (193 MHz, CDCl_3) δ -37.36 (q, $J = 86.9$ Hz).

$^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3) δ -37.36.

$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3) δ 6.79 (dd, $J = 3.8, 1.9$ Hz, 2H), 4.08 – 4.04 (m, 2H), 3.68 (s, 3H), 1.74 – 1.68 (m, 2H), 1.35 – 1.28 (m, 2H), 1.14 – 0.80 (m, 6H).

Characterization agrees with previous reports for this compound.¹



(1-benzyl-3-methyl-1H-imidazol-3-ium-2-yl)trihydroborate (**2e**): white solid (0.66 g, 36% yield); Gradient eluent: EtOAc/petroleum ether: 1/5 to 1/4.

^1H NMR (600 MHz, CDCl_3) δ 7.32 (dt, $J = 14.4, 7.6$ Hz, 3H), 7.27 (d, $J = 7.9$ Hz, 2H), 6.79 (d, $J = 1.9$ Hz, 1H), 6.71 (d, $J = 1.9$ Hz, 1H), 5.30 (s, 2H), 3.75 (s, 3H), 1.15 (dd, $J = 173.1, 86.2$ Hz, 3H).

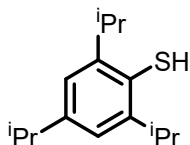
^{13}C NMR (151 MHz, CDCl_3) δ 136.0, 128.9, 128.3, 120.5, 118.6, 52.1, 36.0.

^{11}B NMR (193 MHz, CDCl_3) δ -37.05 (q, $J = 86.9$ Hz).

$^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3) δ -37.05.

$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3) δ 7.35 – 7.29 (m, 3H), 7.27 (d, $J = 7.4$ Hz, 2H), 6.79 (d, $J = 1.9$ Hz, 1H), 6.71 (d, $J = 1.9$ Hz, 1H), 5.30 (s, 2H), 3.74 (s, 3H), 1.29 – 1.01 (m, 3H).

Characterization agrees with previous reports for this compound.¹

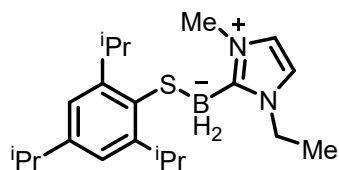


2,4,6-triisopropylbenzenethiol. Colorless liquid (3.8 g, 80% yield).

^1H NMR (600 MHz, CDCl_3) δ 7.03 (s, 2H), 3.58 – 3.50 (m, 2H), 3.10 (s, 1H), 2.90 (dq, $J = 13.8, 6.9$ Hz, 1H), 1.29 (dd, $J = 11.1, 6.9$ Hz, 18H).

^{13}C NMR (151 MHz, CDCl_3) δ 148.1, 147.1, 124.3, 121.4, 34.2, 31.8, 24.1, 23.3.

Characterization agrees with previous reports for this compound.²



(1-ethyl-3-methyl-1H-imidazol-3-ium-2-yl)((2,4,6-triisopropylphenyl)thio) dihydroborate (**4a**): white solid (50 mg, 28% yield); Gradient eluent: EtOAc/petroleum ether: 1/4 to 1/2.

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 6.83 (s, 2H), 6.79 (d, $J = 1.8$ Hz, 1H), 6.74 (d, $J = 1.7$ Hz, 1H), 3.91 – 3.82 (m, 4H), 3.38 (s, 3H), 2.81 (dt, $J = 13.8, 6.9$ Hz, 1H), 2.38 (d, $J = 131.1$ Hz, 2H), 1.20 (d, $J = 6.9$ Hz, 6H), 1.15 (t, $J = 7.3$ Hz, 3H), 1.08 (d, $J = 7.0$ Hz, 12H).

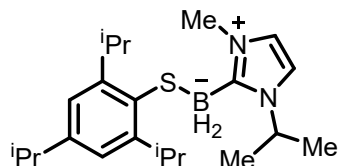
$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 152.2, 146.0, 135.2, 120.9, 120.5, 118.4, 43.4, 35.3, 34.2, 31.2, 24.2, 24.2, 15.2.

$^{11}\text{B NMR}$ (193 MHz, CDCl_3) δ -23.23 (t, $J = 99.4$ Hz).

$^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3) δ -23.25.

$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3) δ 6.83 (s, 2H), 6.79 (d, $J = 1.6$ Hz, 1H), 6.74 (d, $J = 1.6$ Hz, 1H), 3.90 – 3.84 (m, 4H), 3.38 (s, 3H), 2.81 (dt, $J = 13.8, 6.9$ Hz, 1H), 2.38 (s, 2H), 1.20 (d, $J = 6.9$ Hz, 6H), 1.15 (t, $J = 7.3$ Hz, 3H), 1.08 (d, $J = 7.0$ Hz, 12H).

HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ cacl'd. for $\text{C}_{21}\text{H}_{35}\text{BN}_2\text{NaS}^+$ 381.2506; found: 381.2477.



(1-isopropyl-3-methyl-1H-imidazol-3-ium-2-yl)((2,4,6-triisopropylphenyl)thio) dihydroborate (**4b**): white solid (80 mg, 43% yield); Gradient eluent: EtOAc/petroleum ether: 1/4 to 1/2.

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 6.83 (d, $J = 4.0$ Hz, 3H), 6.77 (d, $J = 1.7$ Hz, 1H), 4.71 (dt, $J = 13.5, 6.7$ Hz, 1H), 3.89 (dt, $J = 13.8, 6.9$ Hz, 2H), 3.41 (s, 3H), 2.80 (dt, $J = 13.8, 6.9$ Hz, 1H), 2.42 (d, $J = 105.0$ Hz, 2H), 1.19 (d, $J = 7.0$ Hz, 6H), 1.10 (d, $J = 6.8$ Hz, 6H), 1.06 (d, $J = 7.1$ Hz, 12H).

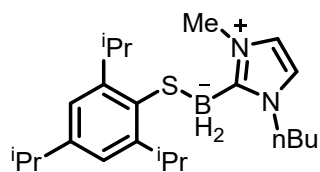
$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 152.2, 145.9, 135.0, 121.3, 120.6, 115.2, 49.8, 35.2, 34.2, 31.1, 24.2, 24.2, 22.6.

$^{11}\text{B NMR}$ (193 MHz, CDCl_3) δ -23.35 (t, $J = 103.3$ Hz).

$^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3) δ -23.17.

$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3) δ 6.83 (s, 3H), 6.77 (s, 1H), 4.71 (dt, $J = 13.1, 6.4$ Hz, 1H), 3.89 (dt, $J = 13.7, 6.8$ Hz, 2H), 3.42 (s, 3H), 2.80 (dt, $J = 13.7, 6.8$ Hz, 1H), 2.42 (s, 2H), 1.19 (d, $J = 7.0$ Hz, 6H), 1.11 (d, $J = 6.8$ Hz, 6H), 1.07 (d, $J = 7.1$ Hz, 12H).

HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ cacl'd. for $\text{C}_{22}\text{H}_{37}\text{BN}_2\text{NaS}^+$ 395.2663; found: 395.2658.



(1-butyl-3-methyl-1H-imidazol-3-ium-2-yl)((2,4,6-triisopropylphenyl)thio) dihydroborate (**4c**): white solid (48 mg, 25% yield); Gradient eluent: EtOAc/petroleum ether: 1/4 to 1/2.

¹H NMR (600 MHz, CDCl₃) δ 6.84 (s, 2H), 6.75 (dd, *J* = 15.9, 1.7 Hz, 2H), 3.85 (dt, *J* = 13.8, 6.9 Hz, 2H), 3.76 – 3.72 (m, 2H), 3.41 (s, 3H), 2.85 – 2.77 (m, 1H), 2.37 (d, *J* = 144.5 Hz, 2H), 1.57 (dd, *J* = 9.4, 5.8 Hz, 2H), 1.25 (dd, *J* = 14.9, 7.4 Hz, 2H), 1.21 (d, *J* = 6.9 Hz, 6H), 1.09 (d, *J* = 6.9 Hz, 12H), 0.88 (t, *J* = 7.4 Hz, 3H).

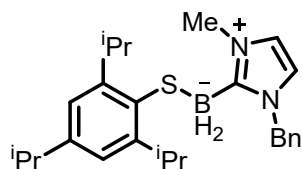
¹³C NMR (151 MHz, CDCl₃) δ 152.2, 146.0, 135.3, 120.6, 120.4, 119.0, 48.2, 35.4, 34.1, 32.1, 31.2, 24.2, 24.2, 19.8, 13.6.

¹¹B NMR (193 MHz, CDCl₃) δ -23.18 (t, *J* = 106.4 Hz).

¹¹B{¹H} NMR (193 MHz, CDCl₃) δ -23.06.

¹H{¹¹B} NMR (600 MHz, CDCl₃) δ 6.84 (s, 2H), 6.76 (d, *J* = 1.8 Hz, 1H), 6.74 (d, *J* = 1.7 Hz, 1H), 3.85 (dt, *J* = 13.8, 6.9 Hz, 2H), 3.77 – 3.72 (m, 2H), 3.41 (s, 3H), 2.81 (hept, *J* = 6.8 Hz, 1H), 2.38 (s, 2H), 1.57 (t, *J* = 7.6 Hz, 2H), 1.25 (dd, *J* = 14.9, 7.5 Hz, 2H), 1.21 (d, *J* = 6.9 Hz, 6H), 1.09 (d, *J* = 6.9 Hz, 12H), 0.88 (t, *J* = 7.4 Hz, 3H).

HRMS (ESI-TOF) *m/z*: [M + Na]⁺ cacl'd. for C₂₃H₃₉BN₂NaS⁺ 409.2819; found:409.2816.



(1-benzyl-3-methyl-1H-imidazol-3-ium-2-yl)((2,4,6-triisopropylphenyl)thio) dihydroborate (**4d**): white solid (67 mg, 32% yield); Gradient eluent: EtOAc/petroleum ether: 1/4 to 1/2.

¹H NMR (600 MHz, CDCl₃) δ 7.32 (d, *J* = 5.1 Hz, 3H), 7.18 – 7.13 (m, 2H), 6.87 (s, 2H), 6.70 (s, 1H), 6.56 (s, 1H), 4.87 (s, 2H), 3.89 (dt, *J* = 13.8, 6.9 Hz, 2H), 3.43 (s, 3H), 2.84 (dt, *J* = 13.5, 6.8 Hz, 1H), 2.52 (d, *J* = 120.6 Hz, 2H), 1.24 (d, *J* = 6.9 Hz, 6H), 1.09 (d, *J* = 6.9 Hz, 12H).

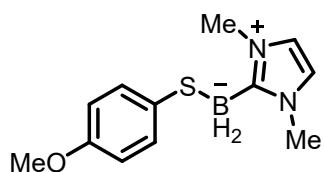
¹³C NMR (151 MHz, CDCl₃) δ 152.3, 146.2, 135.2, 135.0, 128.9, 128.8, 128.5, 120.8, 120.5, 118.8, 51.8, 35.5, 34.2, 31.3, 24.3, 24.2.

¹¹B NMR (193 MHz, CDCl₃) δ -23.13 (t, *J* = 96.5 Hz).

¹¹B{¹H} NMR (193 MHz, CDCl₃) δ -23.17.

¹H{¹¹B} NMR (600 MHz, CDCl₃) δ 7.32 (d, *J* = 5.2 Hz, 3H), 7.17 – 7.14 (m, 2H), 6.87 (s, 2H), 6.70 (s, 1H), 6.56 (s, 1H), 4.88 (s, 2H), 3.89 (dt, *J* = 13.7, 6.8 Hz, 2H), 3.43 (s, 3H), 2.84 (dt, *J* = 13.5, 6.8 Hz, 1H), 2.51 (s, 2H), 1.23 (d, *J* = 6.9 Hz, 6H), 1.09 (d, *J* = 6.9 Hz, 12H).

HRMS (ESI-TOF) m/z : $[M + Na]^+$ cacl. for $C_{26}H_{37}BN_2NaS^+$ 443.2663; found: 443.2653.



(1,3-dimethyl-1H-imidazol-3-ium-2-yl)((4-methoxyphenyl)thio)dihydroborate (**4e**): Colorless liquid (37 mg, 30% yield); Gradient eluent: EtOAc/petroleum ether: 1/4 to 1/2.

1H NMR (600 MHz, $CDCl_3$) δ 7.22 (d, $J = 8.7$ Hz, 2H), 6.80 (s, 2H), 6.67 (d, $J = 8.7$ Hz, 2H), 3.74 (s, 3H), 3.66 (s, 6H), 2.57 (dd, $J = 199.3, 84.0$ Hz, 2H).

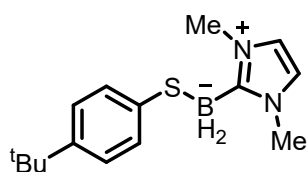
^{13}C NMR (151 MHz, $CDCl_3$) δ 156.9, 133.2, 133.1, 120.7, 113.8, 55.3, 36.1.

^{11}B NMR (193 MHz, $CDCl_3$) δ -23.70 (d, $J = 107.1$ Hz).

$^{11}B\{^1H\}$ NMR (193 MHz, $CDCl_3$) δ -23.70

$^1H\{^{11}B\}$ NMR (600 MHz, $CDCl_3$) δ 7.22 (d, $J = 8.6$ Hz, 2H), 6.79 (s, 2H), 6.67 (d, $J = 8.6$ Hz, 2H), 3.73 (s, 3H), 3.65 (s, 6H), 2.57 (s, 2H).

HRMS (ESI-TOF) m/z : $[M + Na]^+$ cacl. for $C_{12}H_{17}BN_2NaOS^+$ 271.1047; found: 271.1053.



((4-(tert-butyl)phenyl)thio)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)dihydroborate (**4f**): Colorless liquid (33 mg, 24% yield); Gradient eluent: EtOAc/petroleum ether: 1/4 to 1/2.

1H NMR (600 MHz, $CDCl_3$) δ 7.27 (d, $J = 8.1$ Hz, 2H), 7.13 (d, $J = 8.3$ Hz, 2H), 6.81 (s, 2H), 3.71 (s, 6H), 2.60 (dd, $J = 194.8, 82.2$ Hz, 2H), 1.26 (s, 9H).

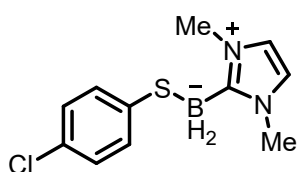
^{13}C NMR (151 MHz, $CDCl_3$) δ 146.4, 139.0, 130.8, 125.0, 120.8, 36.1, 34.2, 31.4.

^{11}B NMR (193 MHz, $CDCl_3$) δ -24.28 (t, $J = 100.4$ Hz).

$^{11}B\{^1H\}$ NMR (193 MHz, $CDCl_3$) δ -24.33.

$^1H\{^{11}B\}$ NMR (600 MHz, $CDCl_3$) δ 7.27 (d, $J = 8.0$ Hz, 2H), 7.13 (d, $J = 8.3$ Hz, 2H), 6.81 (s, 2H), 3.71 (s, 6H), 2.60 (s, 2H), 1.26 (s, 9H).

HRMS (ESI-TOF) m/z : $[M + Na]^+$ cacl. for $C_{15}H_{23}BN_2NaS^+$ 297.1567; found: 297.1565.



((4-chlorophenyl)thio)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)dihydroborate (**4g**): Colorless liquid (25 mg, 20% yield); Gradient eluent: EtOAc/petroleum ether: 1/4 to 1/2.

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.30 (d, $J = 8.3$ Hz, 2H), 7.07 (d, $J = 8.3$ Hz, 2H), 6.84 (s, 2H), 3.75 (s, 6H), 2.57 (dd, $J = 146.0, 50.6$ Hz, 2H).

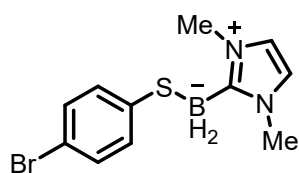
$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 141.5, 132.1, 128.9, 127.9, 120.9, 36.2.

$^{11}\text{B NMR}$ (193 MHz, CDCl_3) δ -24.39 (t, $J = 103.3$ Hz).

$^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3) δ -24.40.

$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3) δ 7.30 (d, $J = 8.3$ Hz, 2H), 7.07 (d, $J = 8.3$ Hz, 2H), 6.84 (s, 2H), 3.75 (s, 6H), 2.60 (s, 2H).

HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ cacl. for $\text{C}_{11}\text{H}_{14}\text{BClN}_2\text{NaS}^+$ 275.0551; found: 275.0557.



((4-bromophenyl)thio)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)dihydroborate (**4h**): Colorless liquid (30 mg, 18% yield); Gradient eluent: EtOAc/petroleum ether: 1/4 to 1/2.

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.24 (d, $J = 6.0$ Hz, 2H), 7.21 (d, $J = 8.4$ Hz, 2H), 6.84 (s, 2H), 3.76 (s, 6H), 2.58 (dd, $J = 153.6, 48.4$ Hz, 2H).

$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 142.3, 132.4, 130.8, 121.0, 116.7, 36.2.

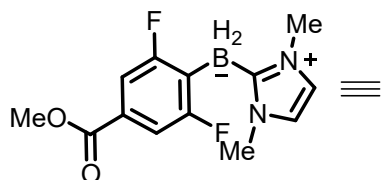
$^{11}\text{B NMR}$ (193 MHz, CDCl_3) δ -24.47 (d, $J = 100.4$ Hz).

$^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3) δ -24.47.

$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3) δ 7.24 (d, $J = 6.0$ Hz, 2H), 7.21 (d, $J = 8.5$ Hz, 2H), 6.84 (s, 2H), 3.76 (s, 6H), 2.60 (s, 2H).

HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ cacl. for $\text{C}_{11}\text{H}_{14}\text{BBBrN}_2\text{NaS}^+$ 319.0046; found: 319.0042.

9. The crystallographic data



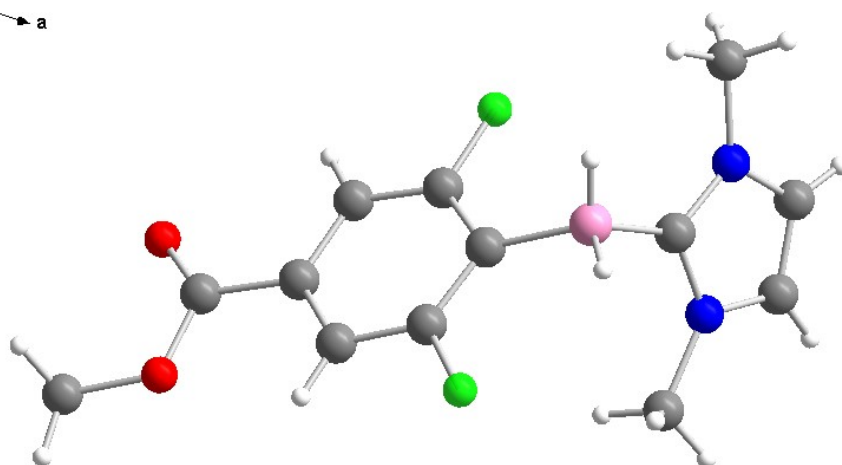
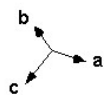


Table S1

CCDC Number	2286018
Empirical formula	C ₁₃ H ₁₅ BF ₂ N ₂ O ₂
Formula weight	280.08
Temperature/K	293(2)
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	12.3113(4)
b/Å	7.3110(3)
c/Å	15.6195(5)
α/°	90
β/°	97.042(3)
γ/°	90
Volume/Å ³	1395.27(9)
Z	4
ρ _{calc} /g/cm ³	1.333
μ/mm ⁻¹	0.909
F(000)	584.0
Crystal size/mm ³	0.01 × 0.01 × 0.01
Radiation	Cu Kα (λ = 1.54184)
2θ range for data collection/°	7.234 to 143.024
Index ranges	-13 ≤ h ≤ 15, -8 ≤ k ≤ 8, -19 ≤ l ≤ 15
Reflections collected	5541
Independent reflections	2637 [R _{int} = 0.0160, R _{sigma} = 0.0220]

Data/restraints/parameters 2637/0/184
 Goodness-of-fit on F² 1.040
 Final R indexes [I>=2σ (I)] R₁ = 0.0515, wR₂ = 0.1491
 Final R indexes [all data] R₁ = 0.0641, wR₂ = 0.1600
 Largest diff. peak/hole / e Å⁻³ 0.25/-0.24

^[a]R₁ = $\sum ||F_o| - |F_c|| / \sum |F_o|$; wR₂ = $\{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$

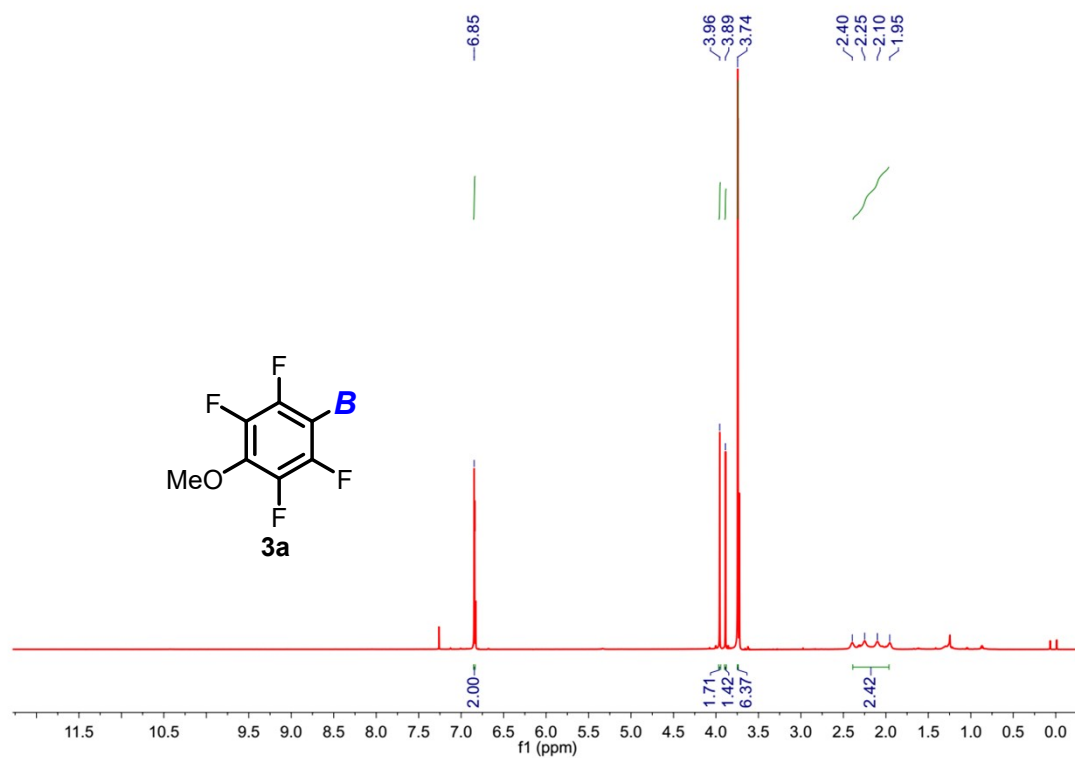
Table S2

Bond Lengths			Bond Angles			
C6	C1	1.381 (3)	C6	C1	C2	111.64 (19)
C2	C1	1.389 (3)	C6	C1	B7	125.3 (2)
C1	B7	1.632 (3)	C2	C1	B7	123.06 (19)
C8	B7	1.596 (3)	C1	B7	C8	110.93 (17)

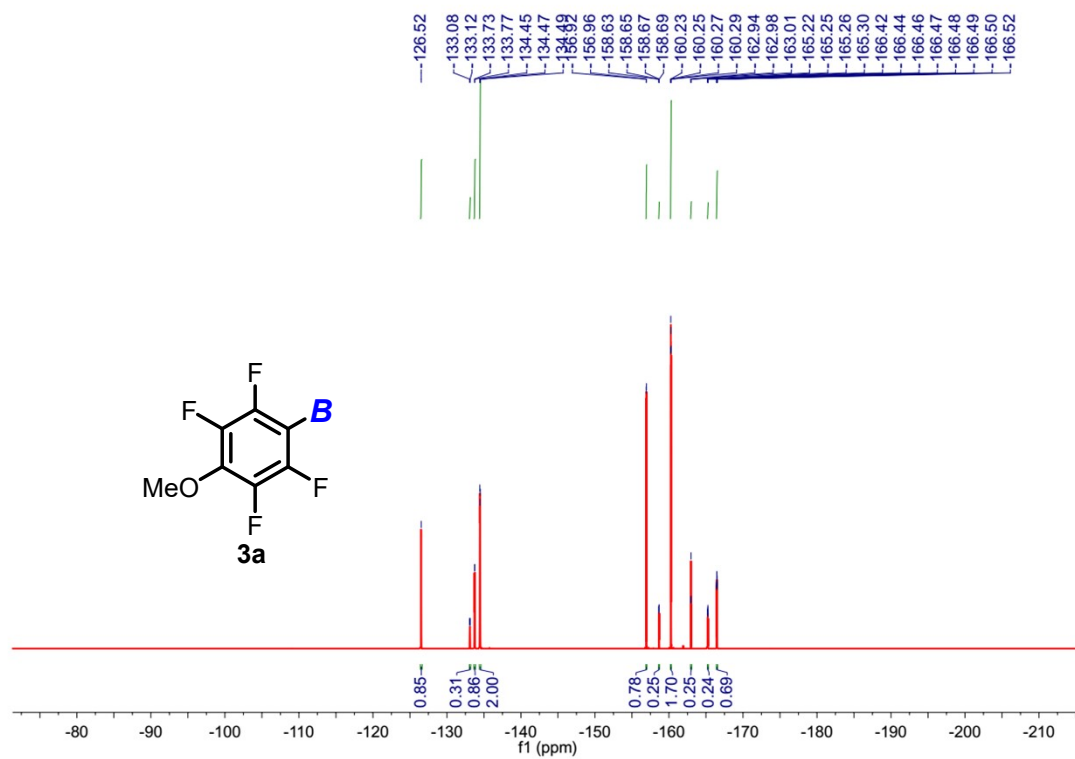
10. References:

1. S. Gardner, T. Kawamoto, and D. P. Curran, Synthesis of 1,3-Dialkylimidazol-2-ylidene Boranes from 1,3-Dialkylimidazolium Iodides and Sodium Borohydride, *J. Org. Chem.*, 2015, **80**, 9794-9797.
2. D. C. Miller, J. M. Ganley, A. J. Musacchio, T. C. Sherwood, W. R. Ewing and R. R. Knowles, Anti-Markovnikov Hydroamination of Unactivated Alkenes with Primary Alkyl Amines, *J. Am. Chem. Soc.*, 2019, **141**, 16590-16594.
3. P.-J. Xia, Z.-P. Ye, Y.-Z. Hu, J.-A. Xiao, K. Chen, H.-Y. Xiang, X.-Q. Chen and H. Yang, Photocatalytic C-F Bond Borylation of Polyfluoroarenes with NHC-boranes, *Org. Lett.*, 2020, **22**, 1742-1747.
4. W. Xu, H. Jiang, J. Leng, H.-W. Ong and J. Wu, Visible-Light-Induced Selective Defluoroborylation of Polyfluoroarenes, gem-Difluoroalkenes, and Trifluoromethylalkenes, *Angew. Chem., Int. Ed.*, 2020, **59**, 4009-4016.

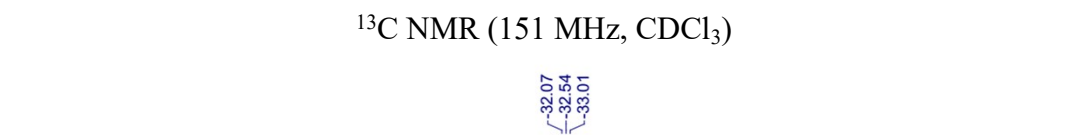
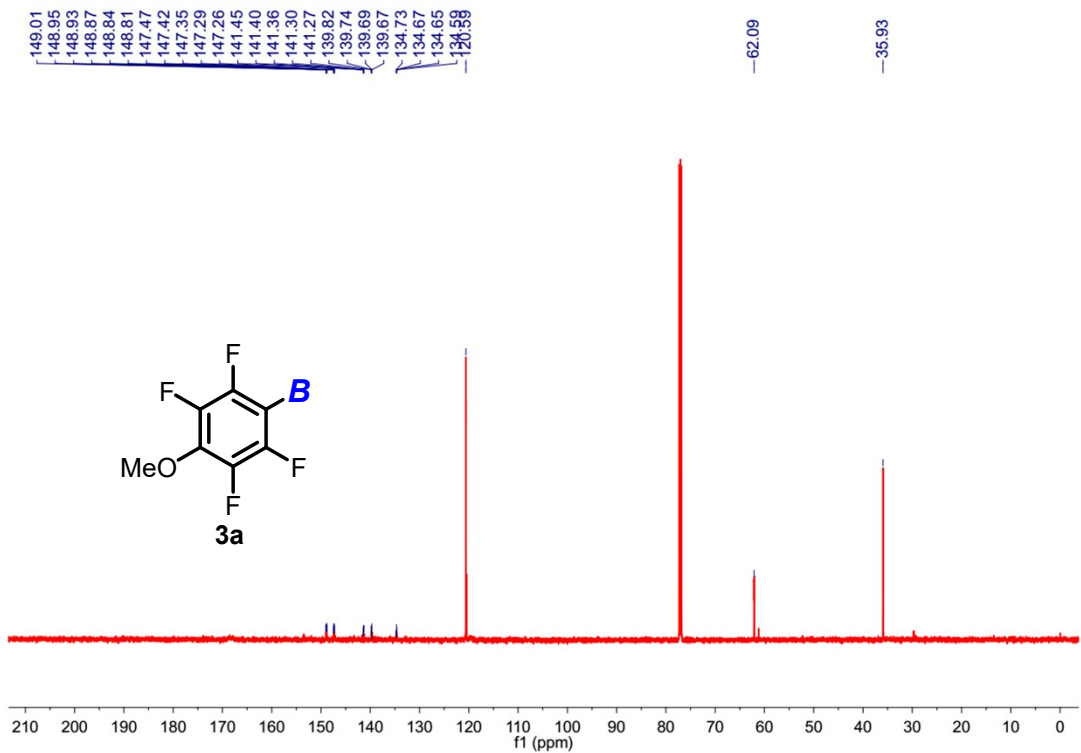
11. NMR Spectra

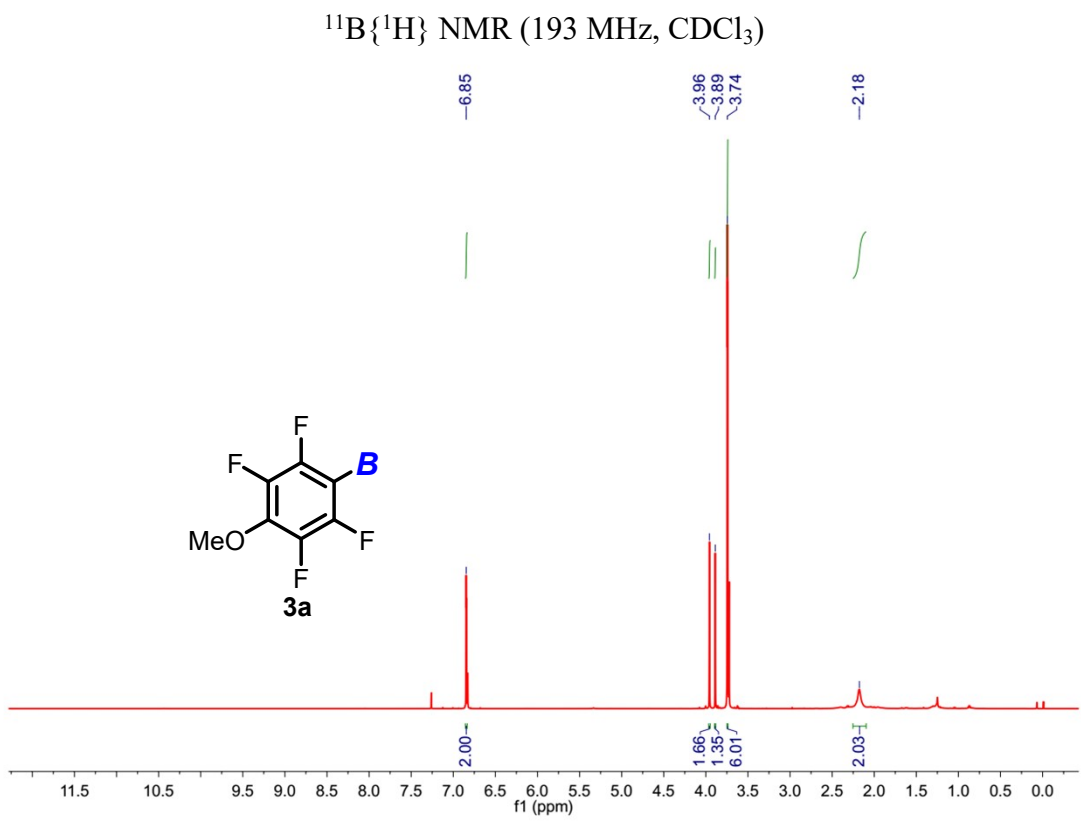
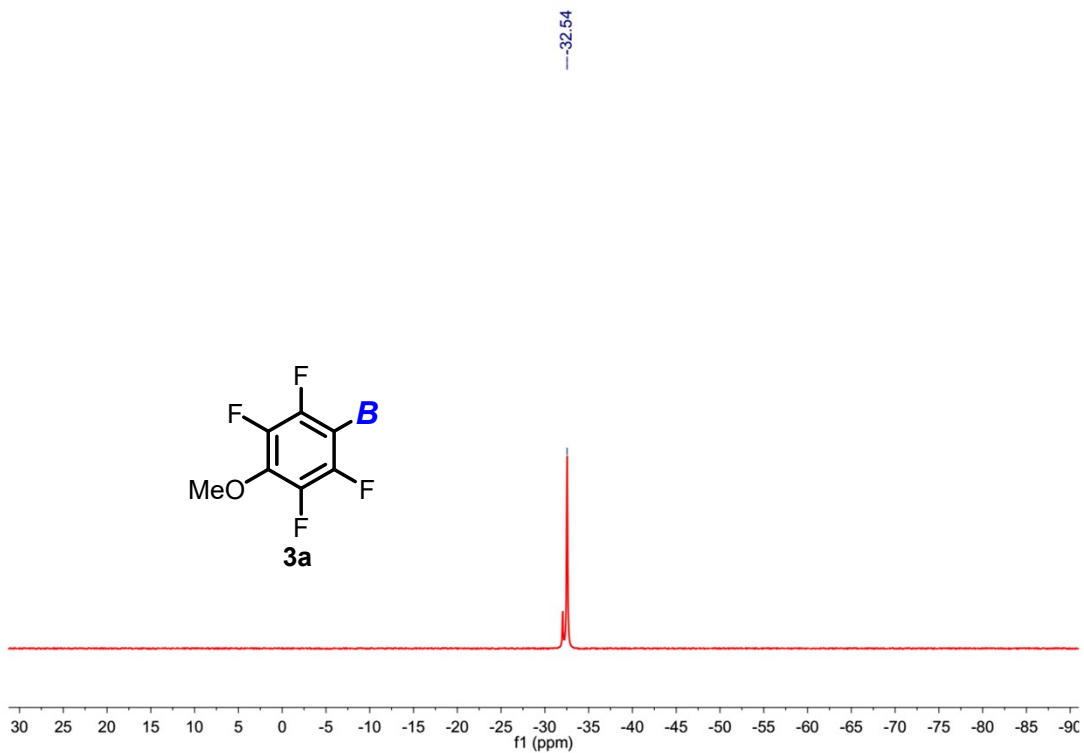


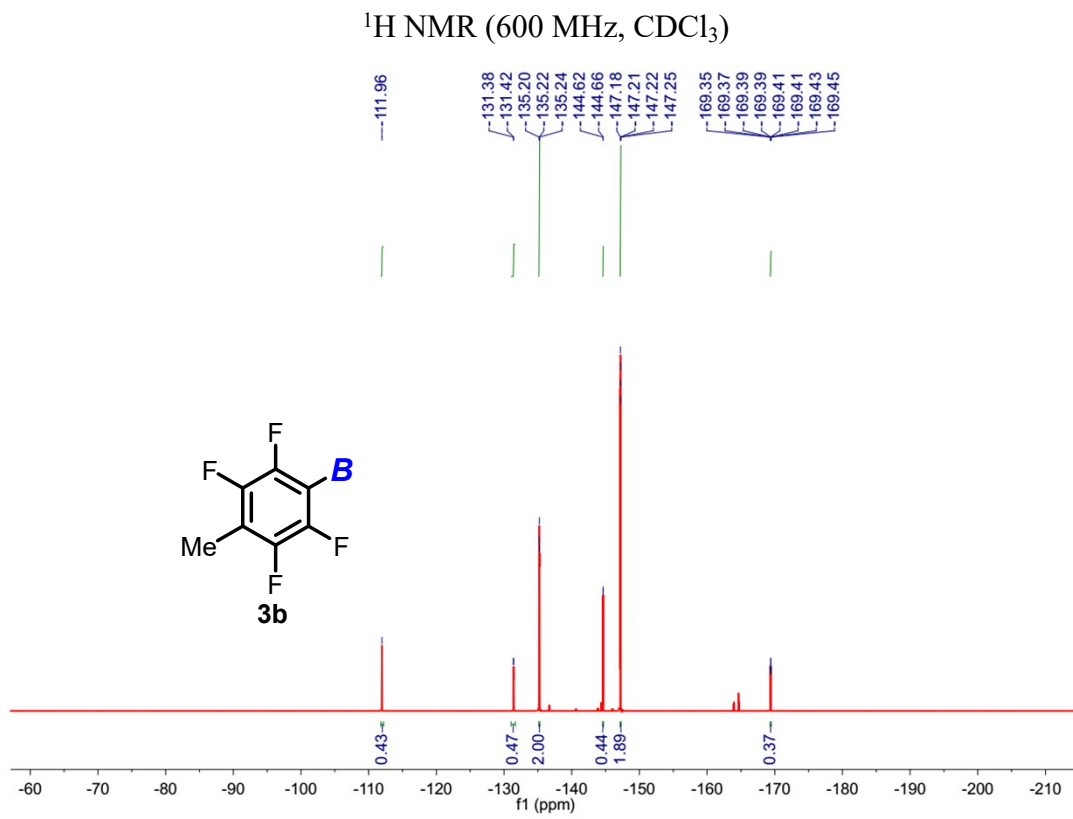
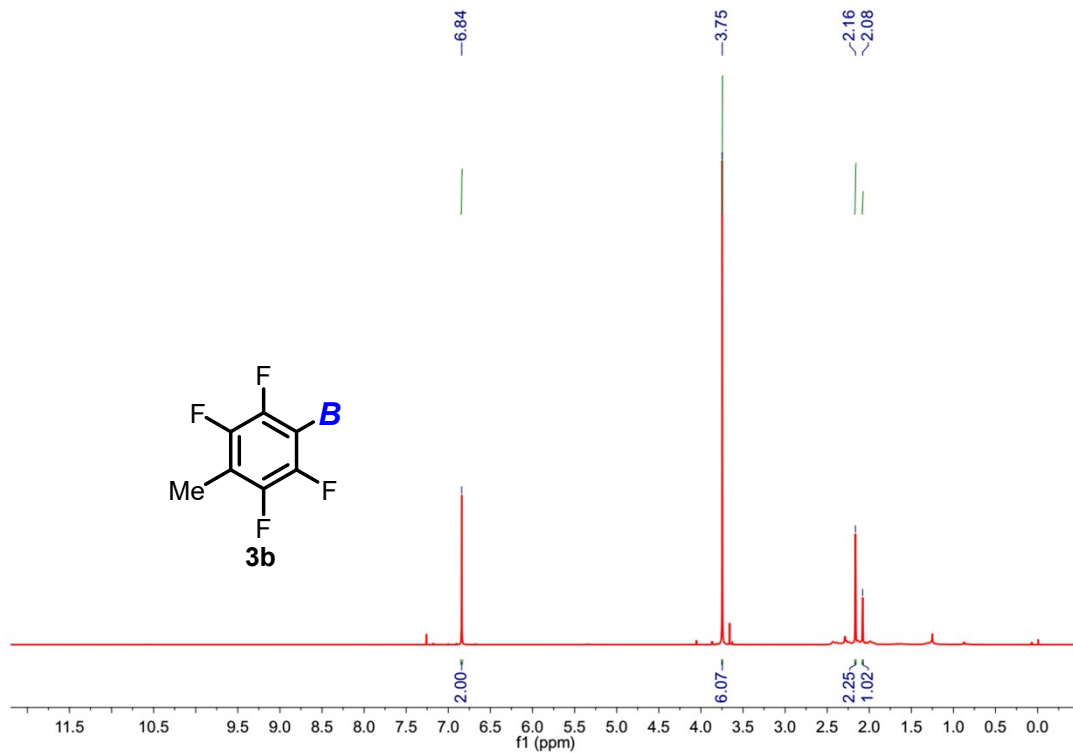
¹H NMR (600 MHz, CDCl₃)

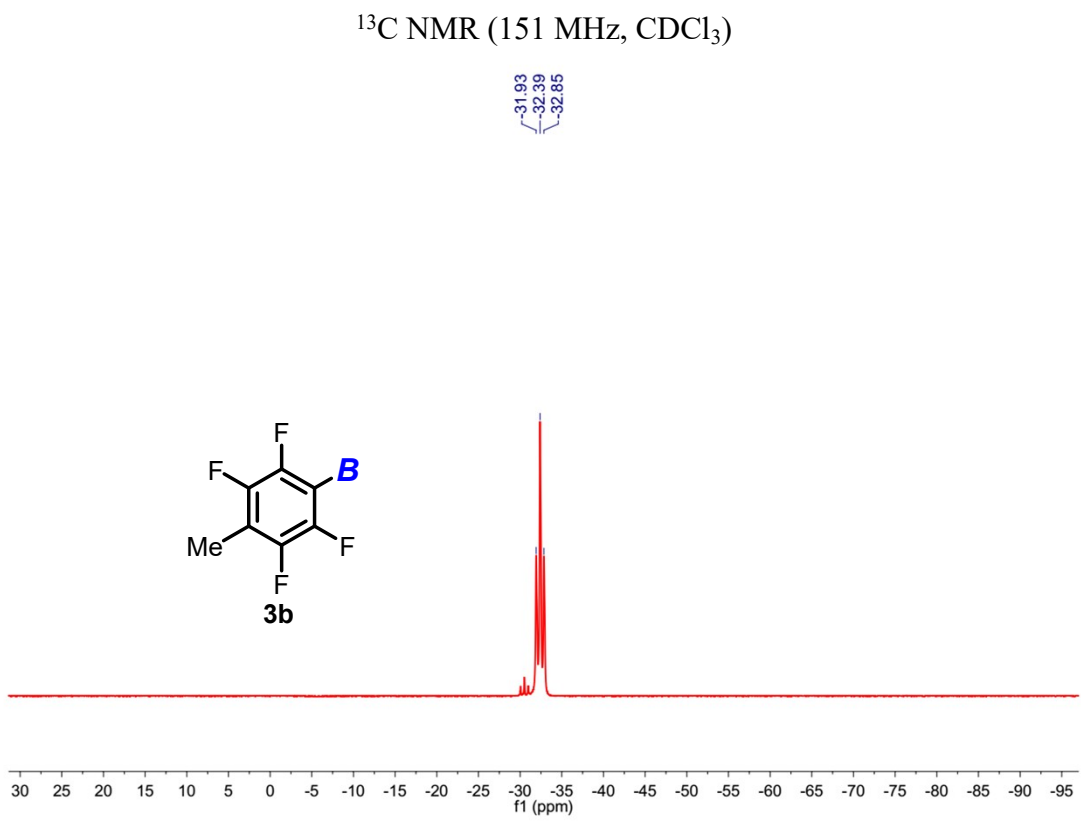
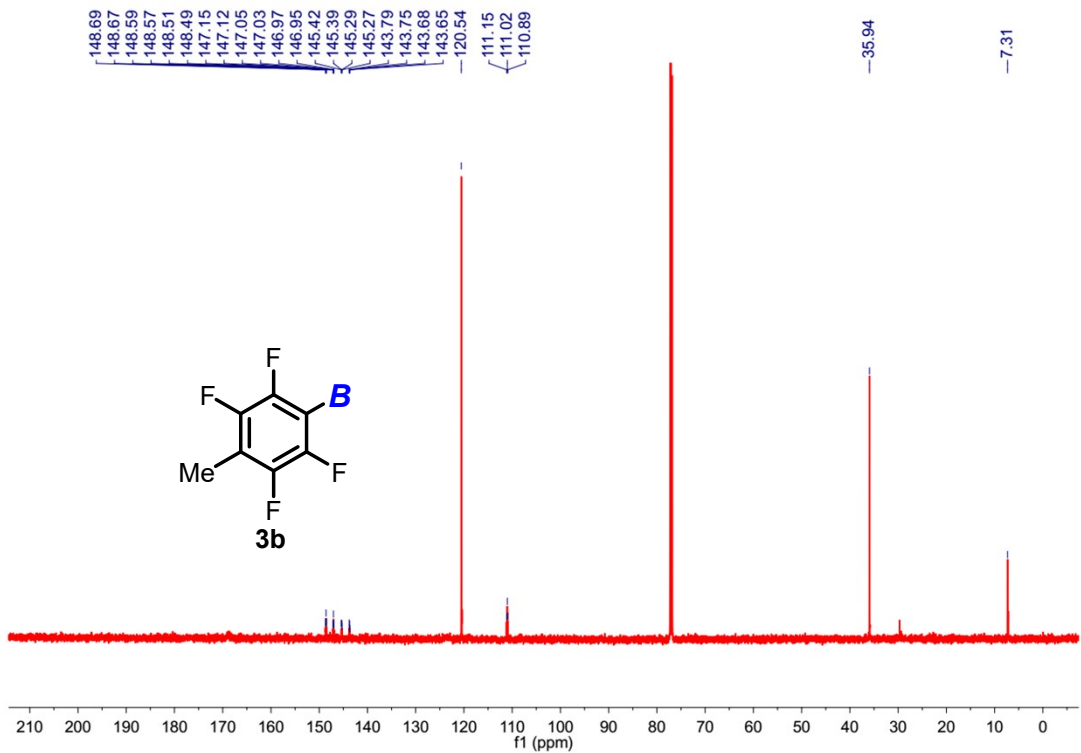


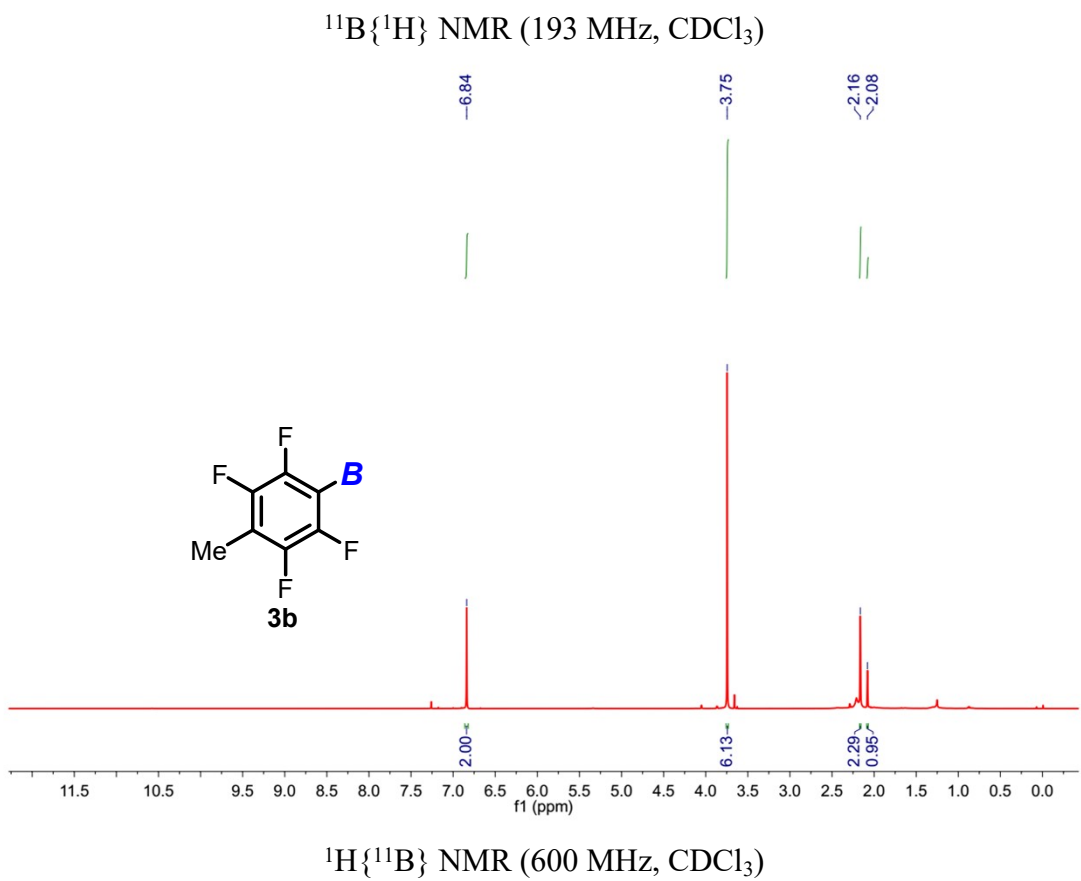
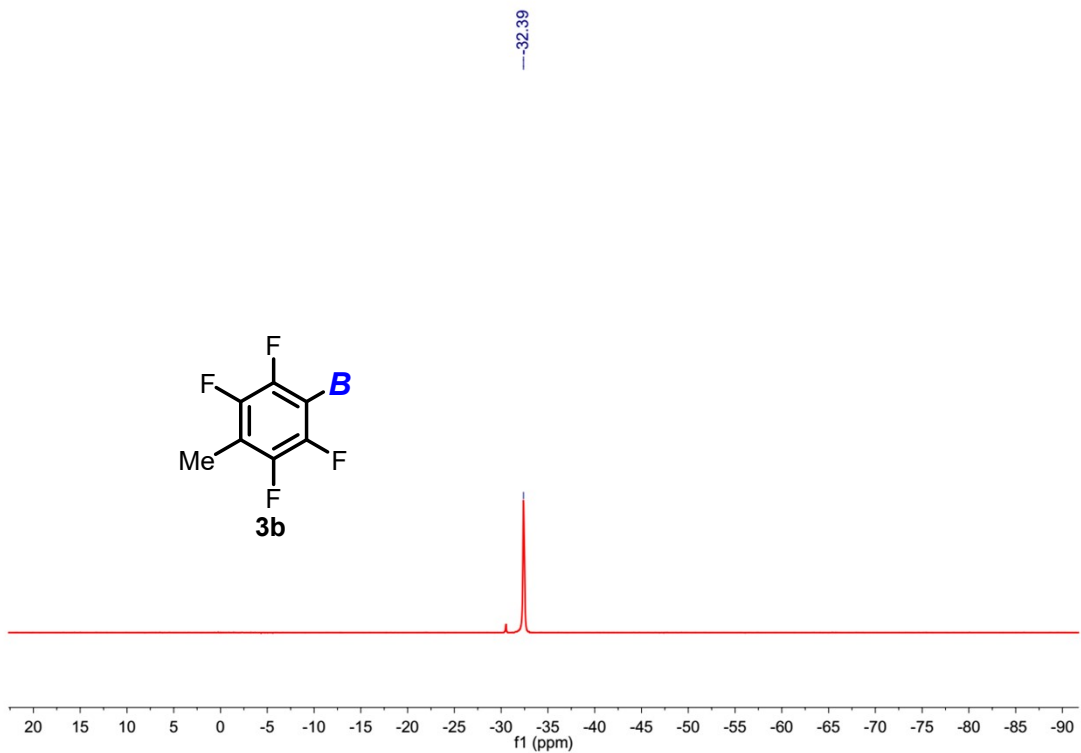
¹⁹F NMR (565 MHz, CDCl₃)

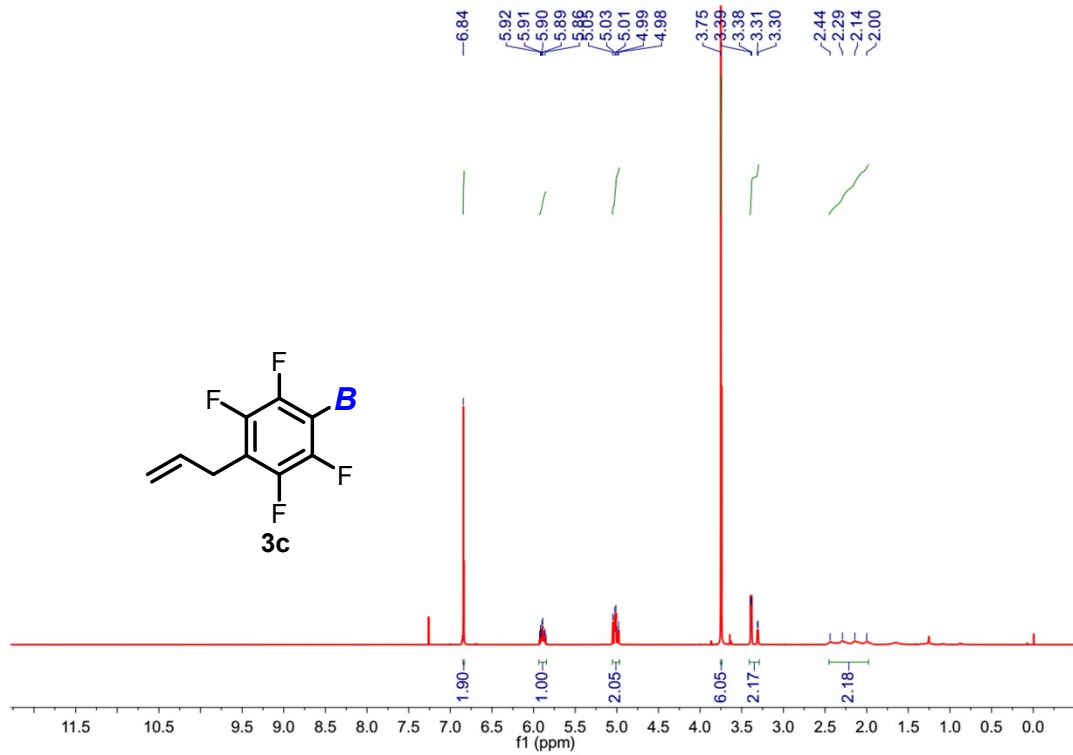




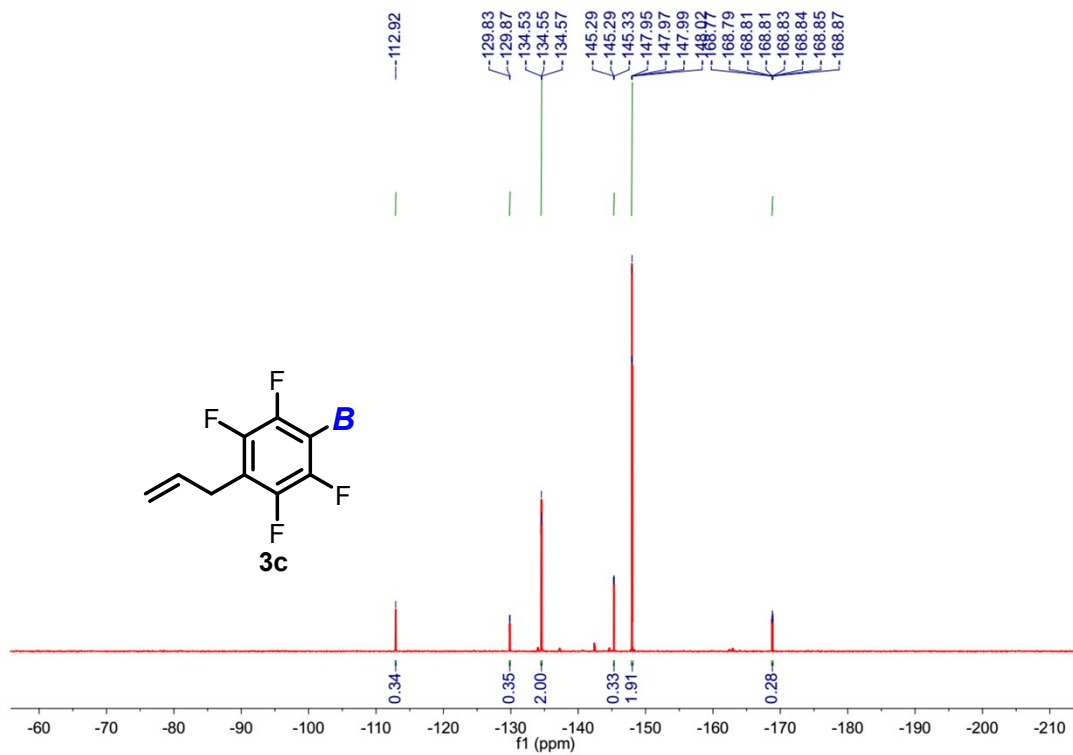




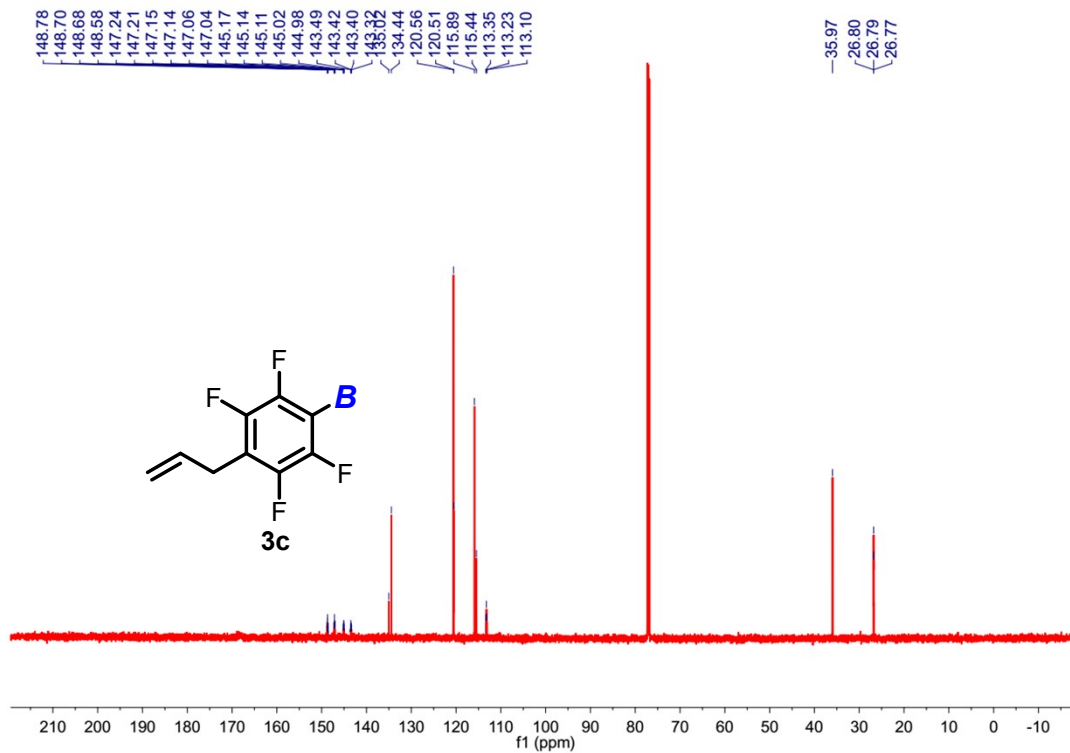




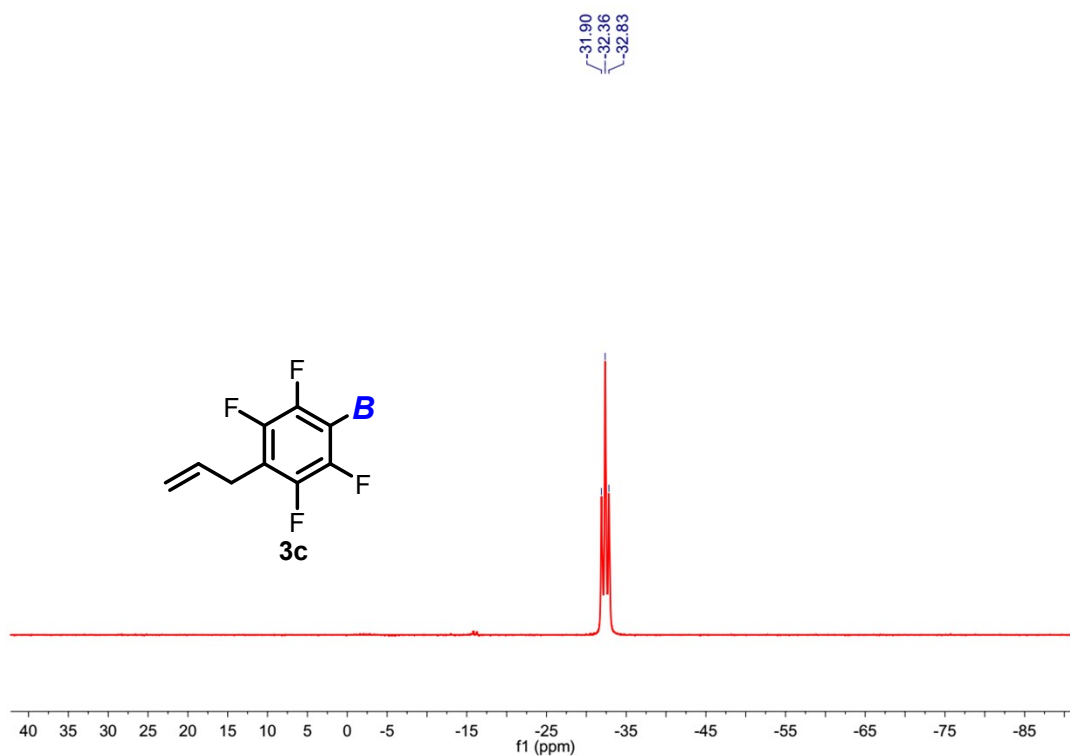
¹H NMR (600 MHz, CDCl₃)



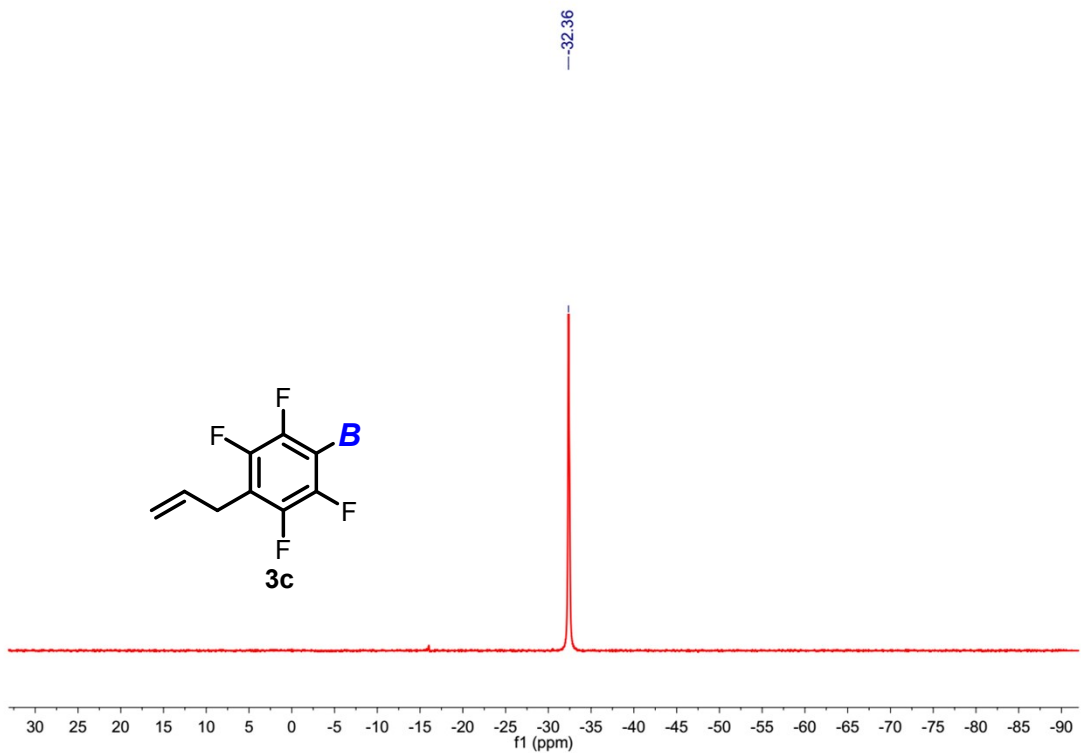
¹⁹F NMR (565 MHz, CDCl₃)



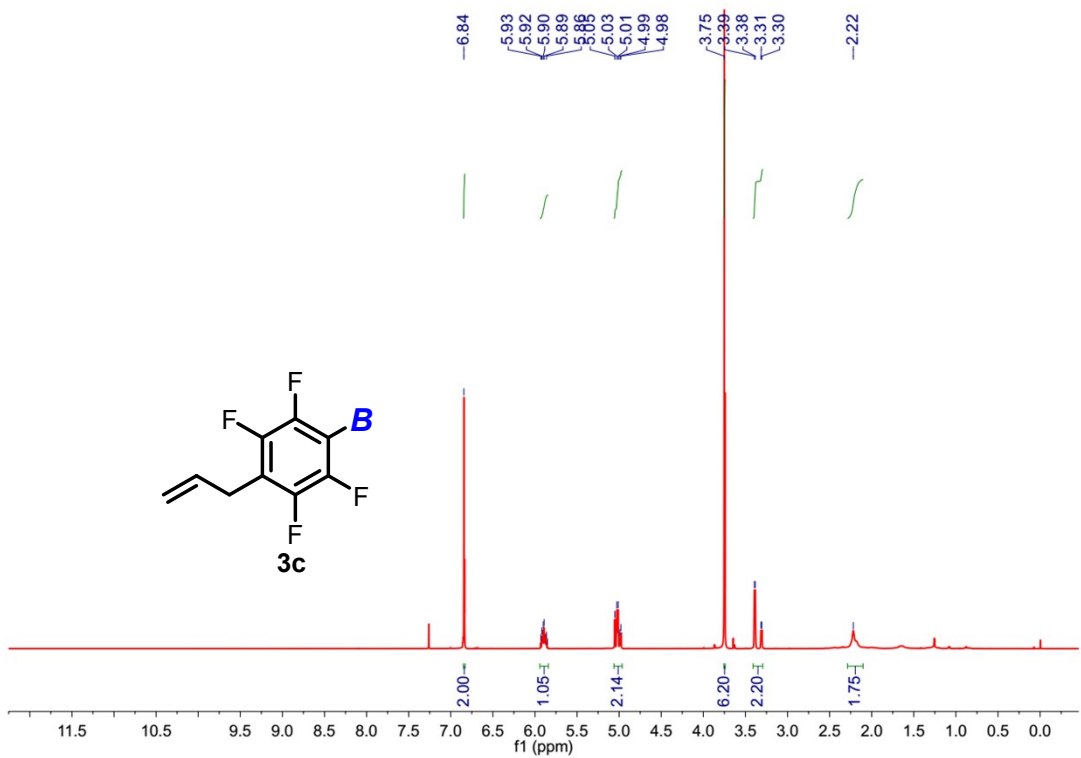
^{13}C NMR (151 MHz, CDCl_3)



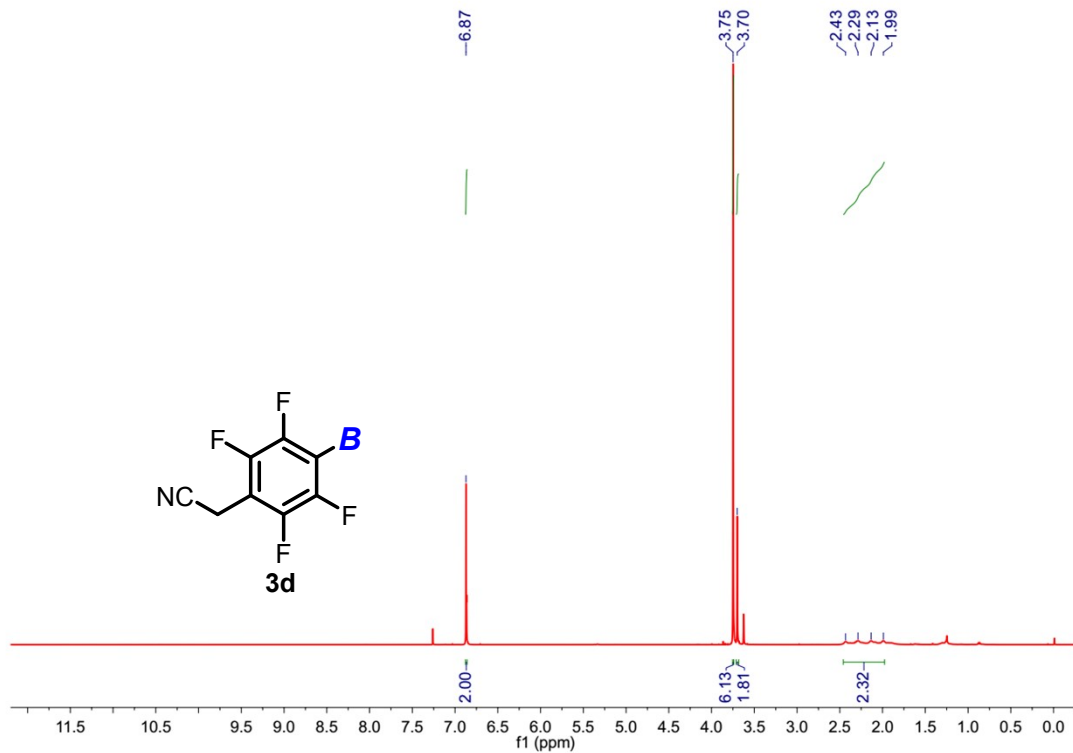
^{11}B NMR (193 MHz, CDCl_3)



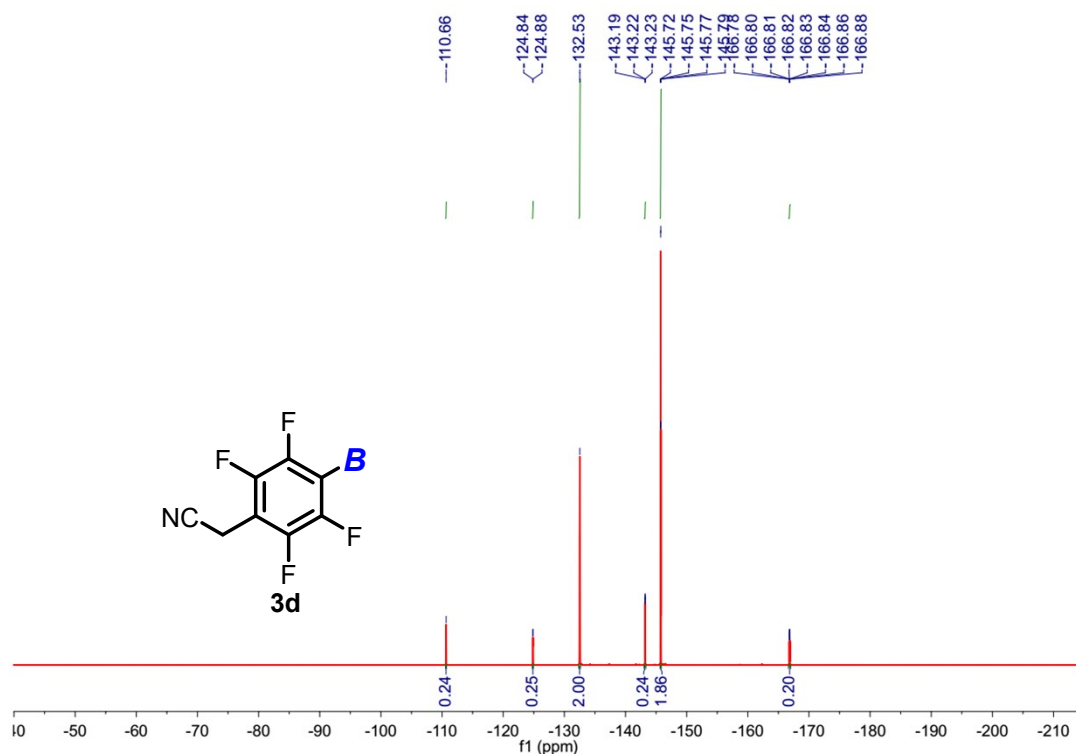
$^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3)



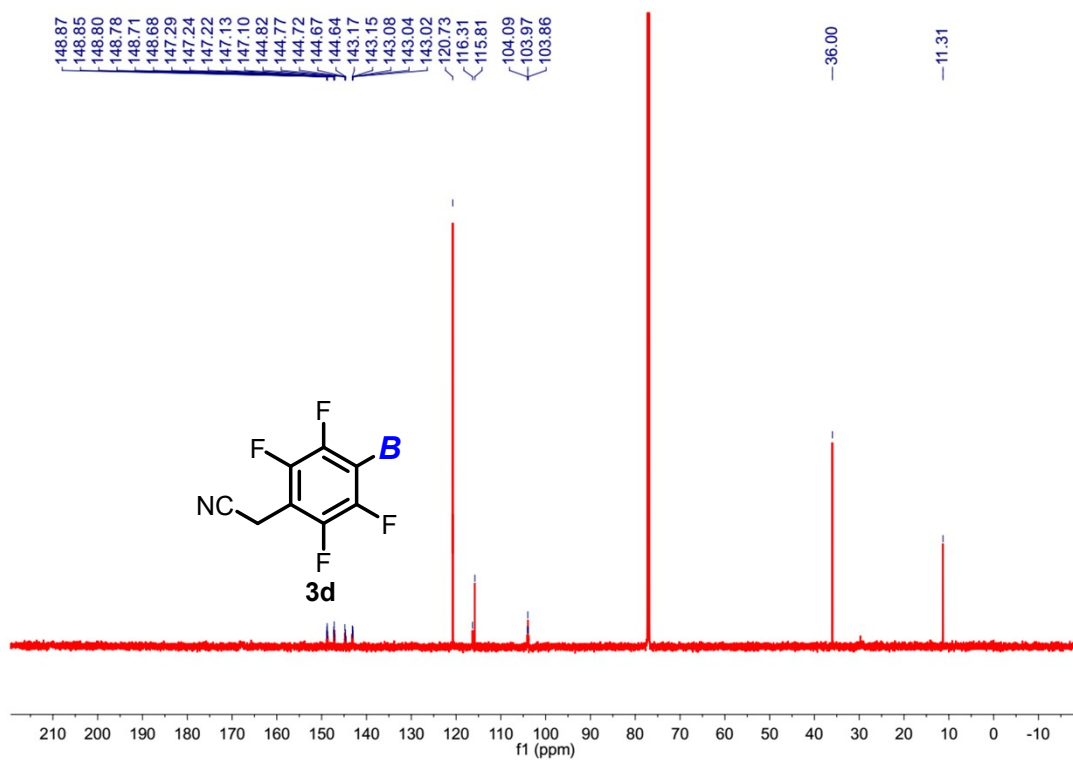
$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3)



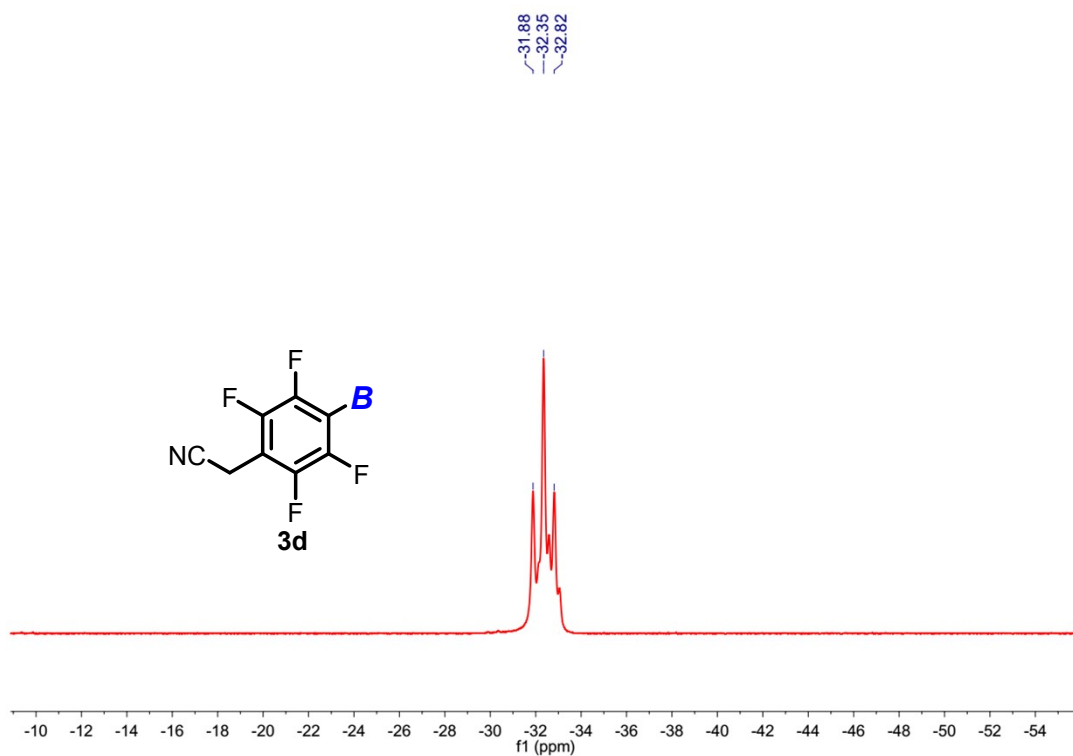
¹H NMR (600 MHz, CDCl₃)



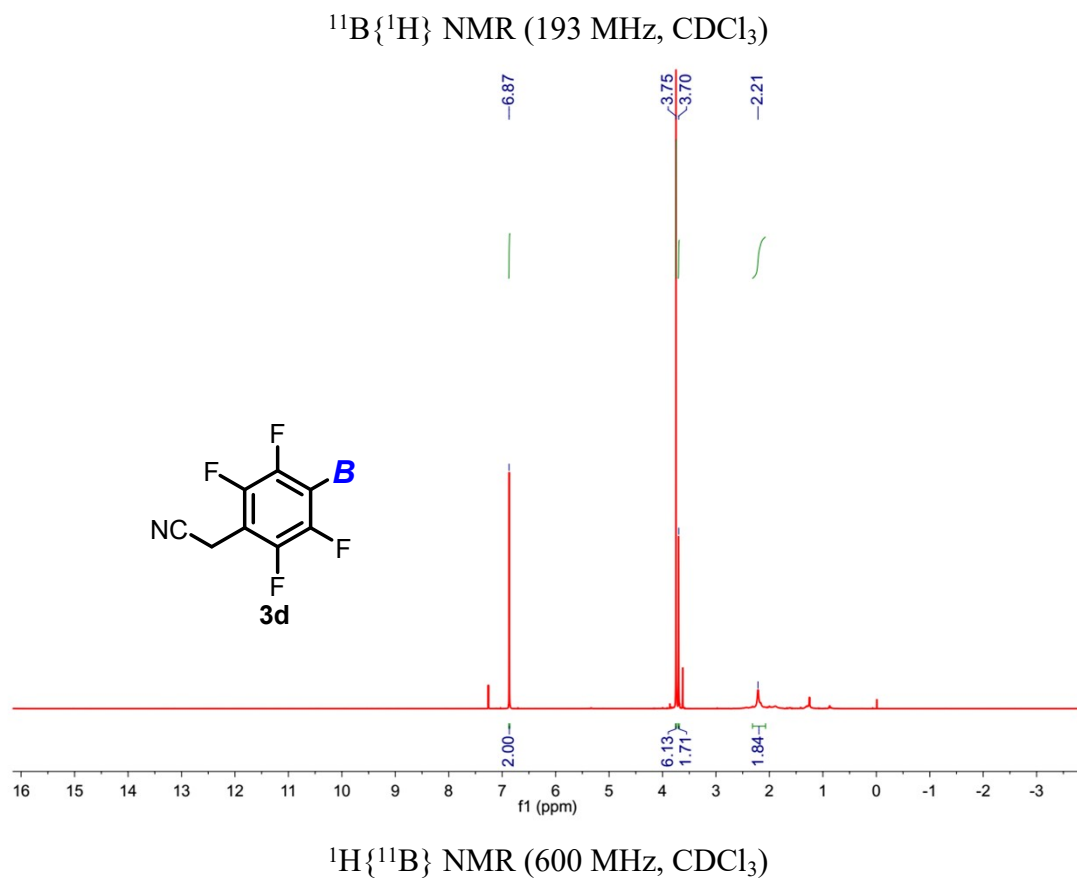
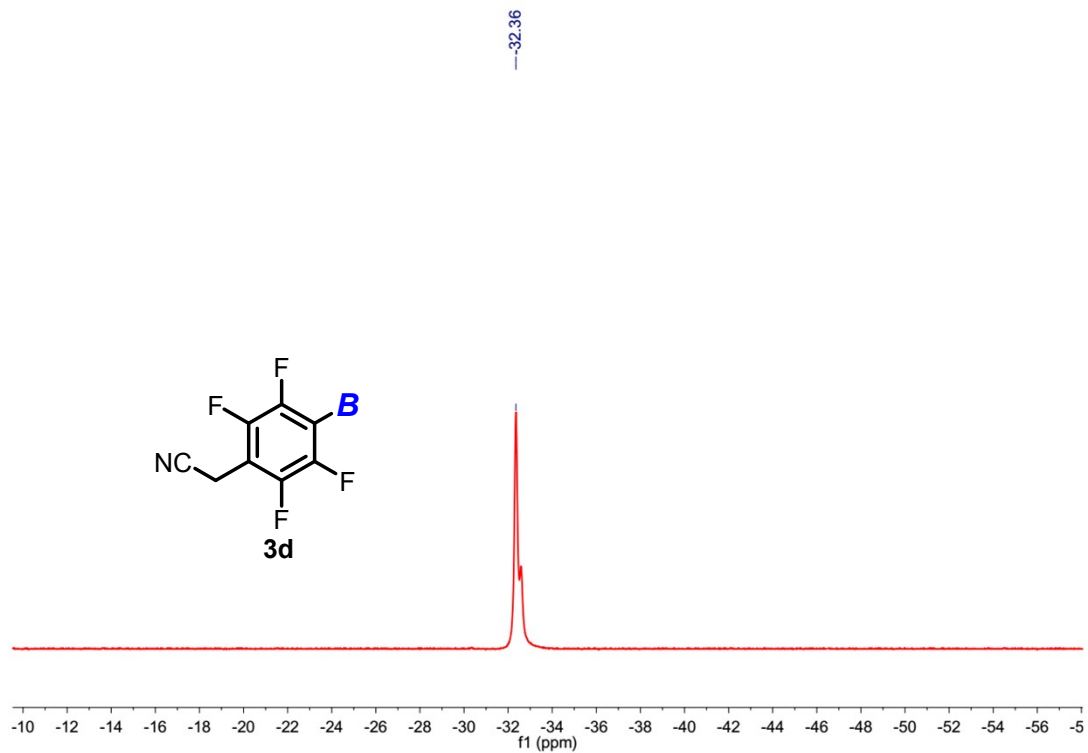
¹⁹F NMR (565 MHz, CDCl₃)

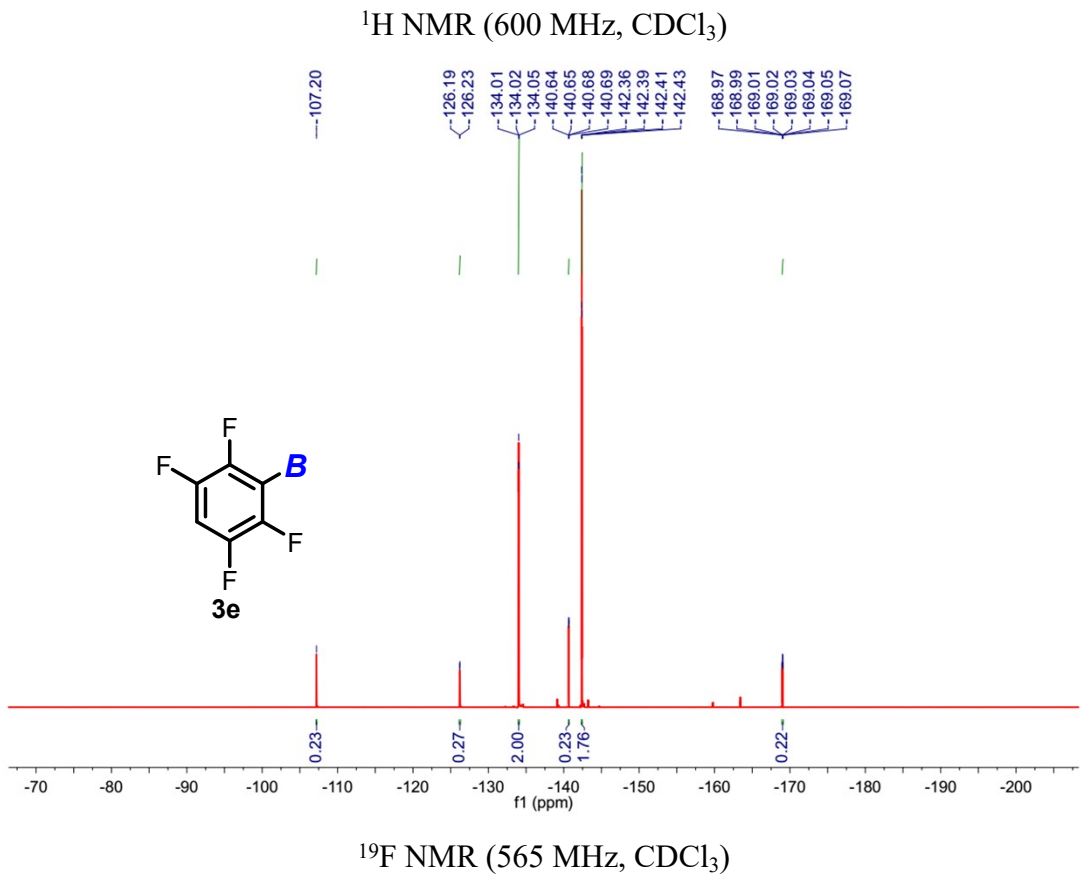
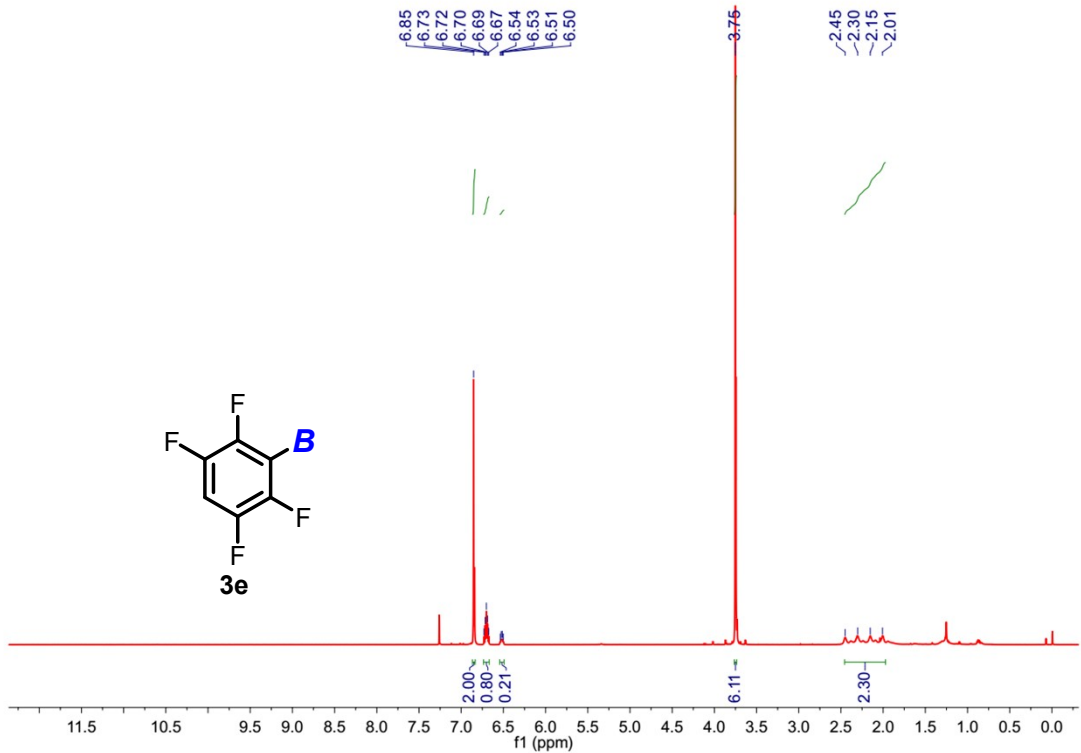


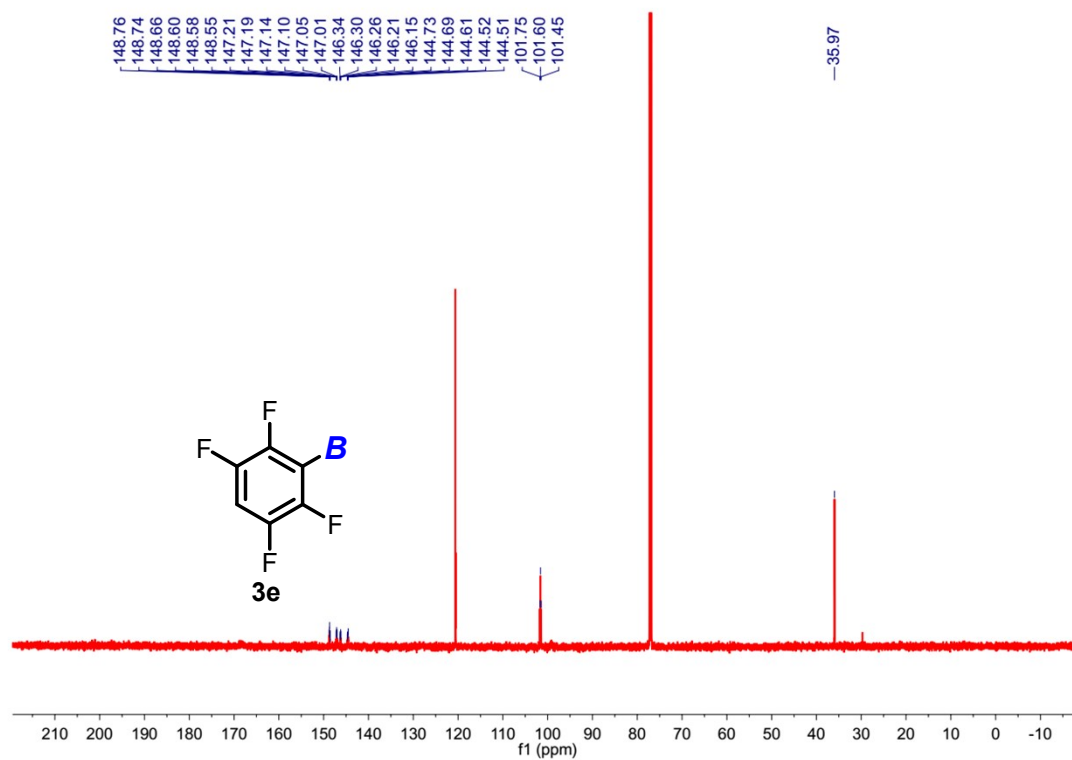
^{13}C NMR (151 MHz, CDCl_3)



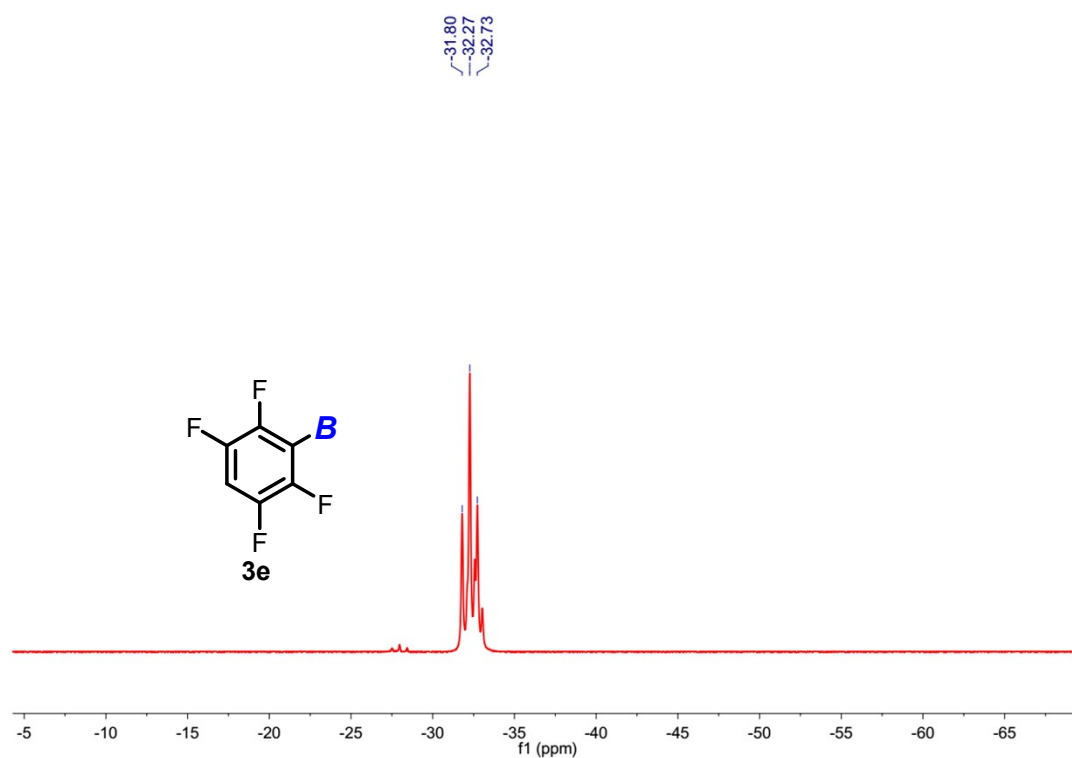
^{11}B NMR (193 MHz, CDCl_3)



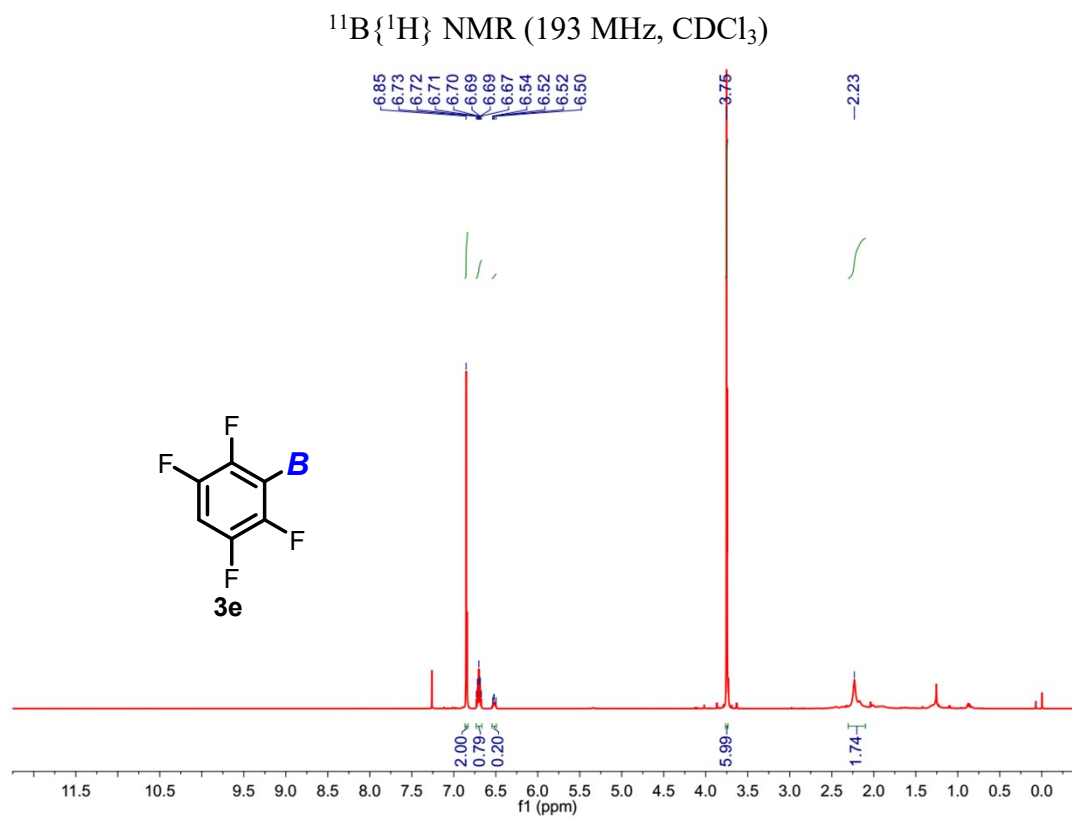
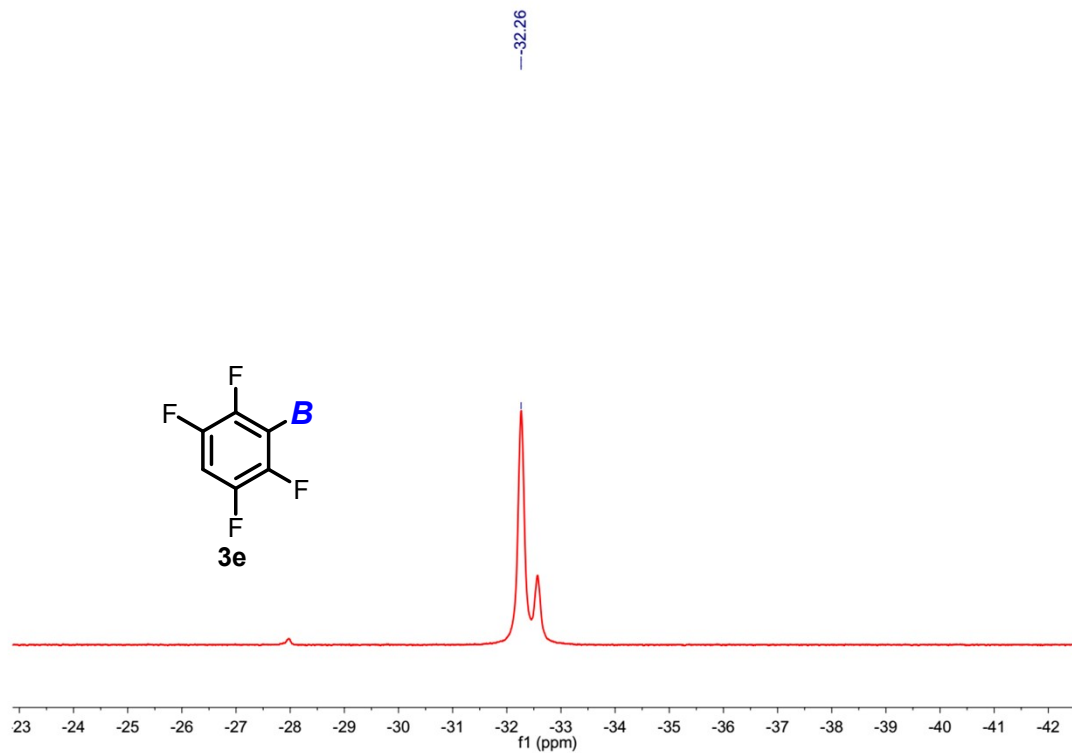


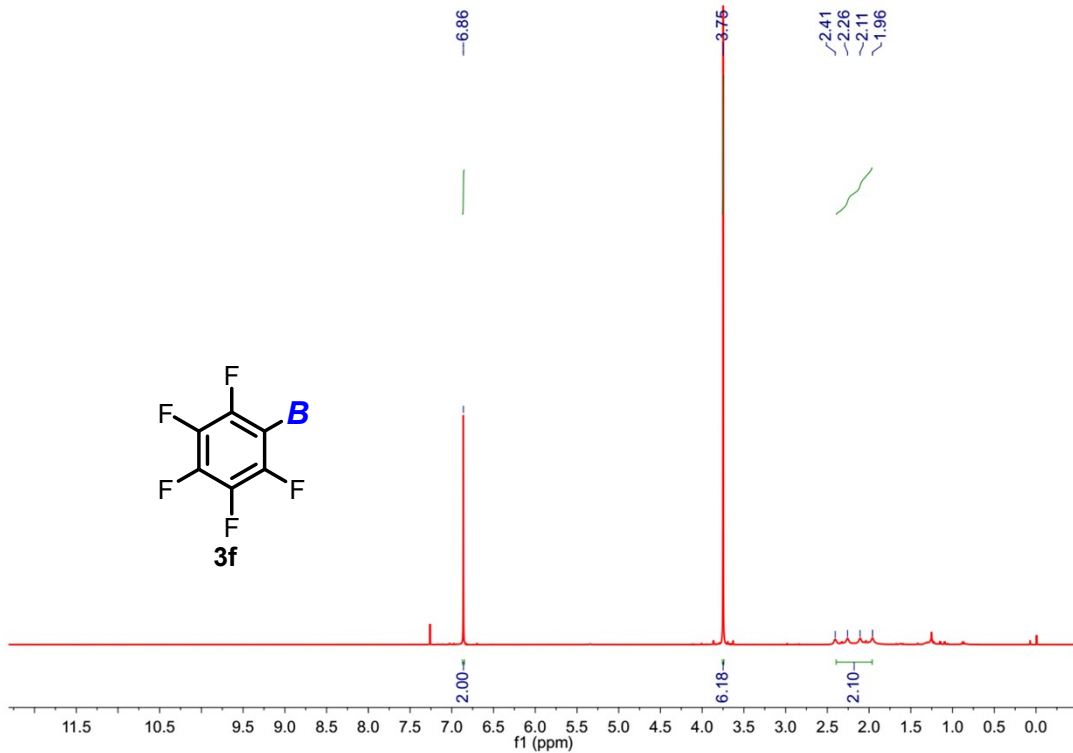


^{13}C NMR (151 MHz, CDCl_3)

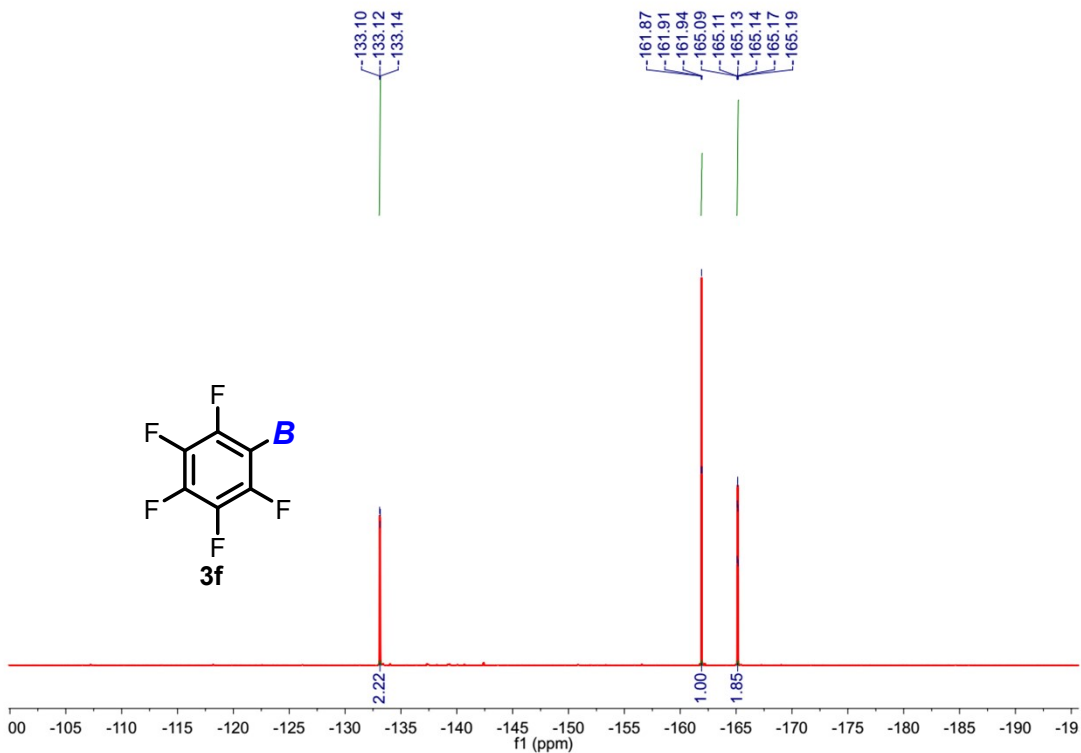


^{11}B NMR (193 MHz, CDCl_3)

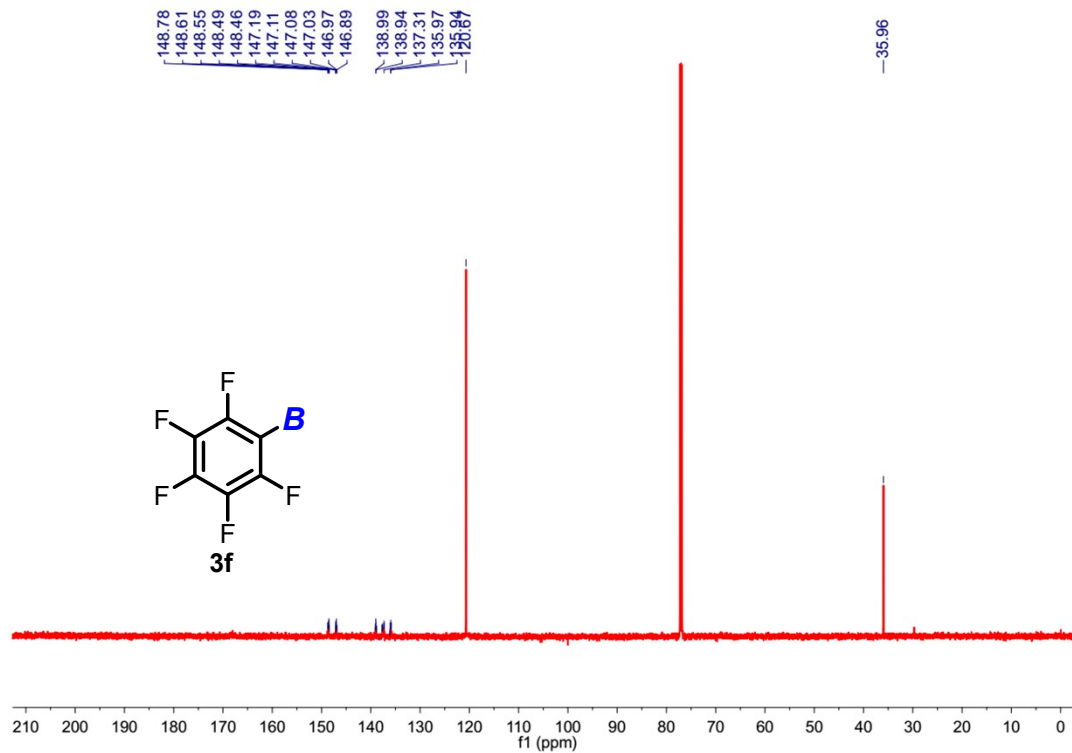




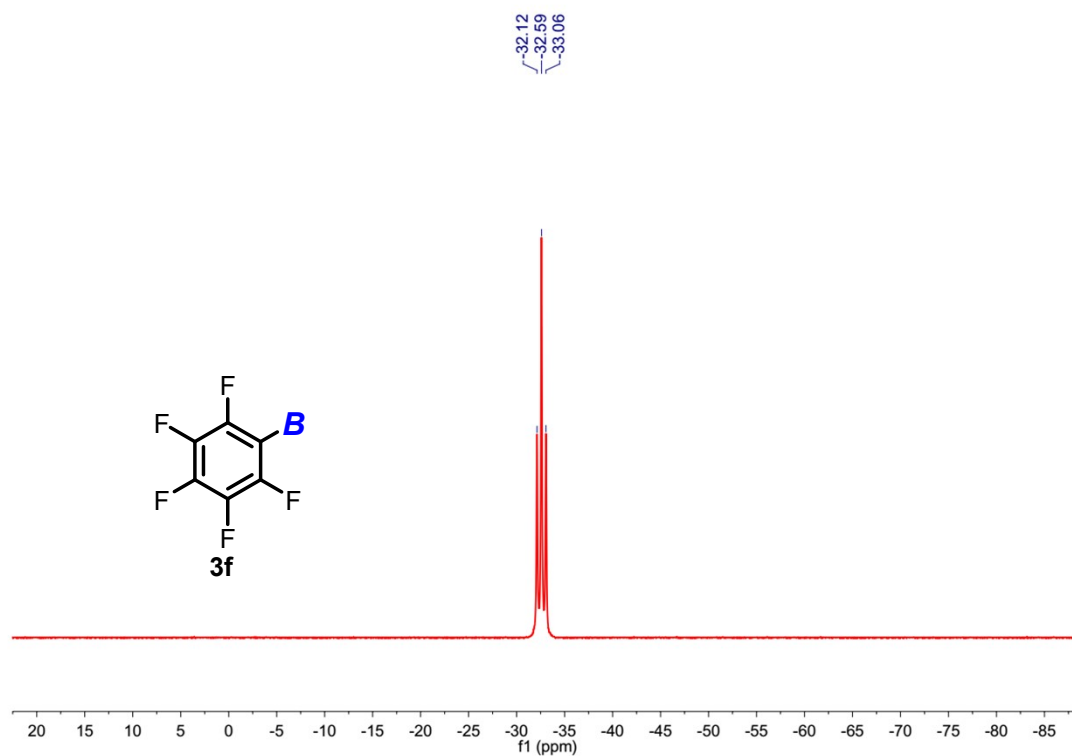
¹H NMR (600 MHz, CDCl₃)



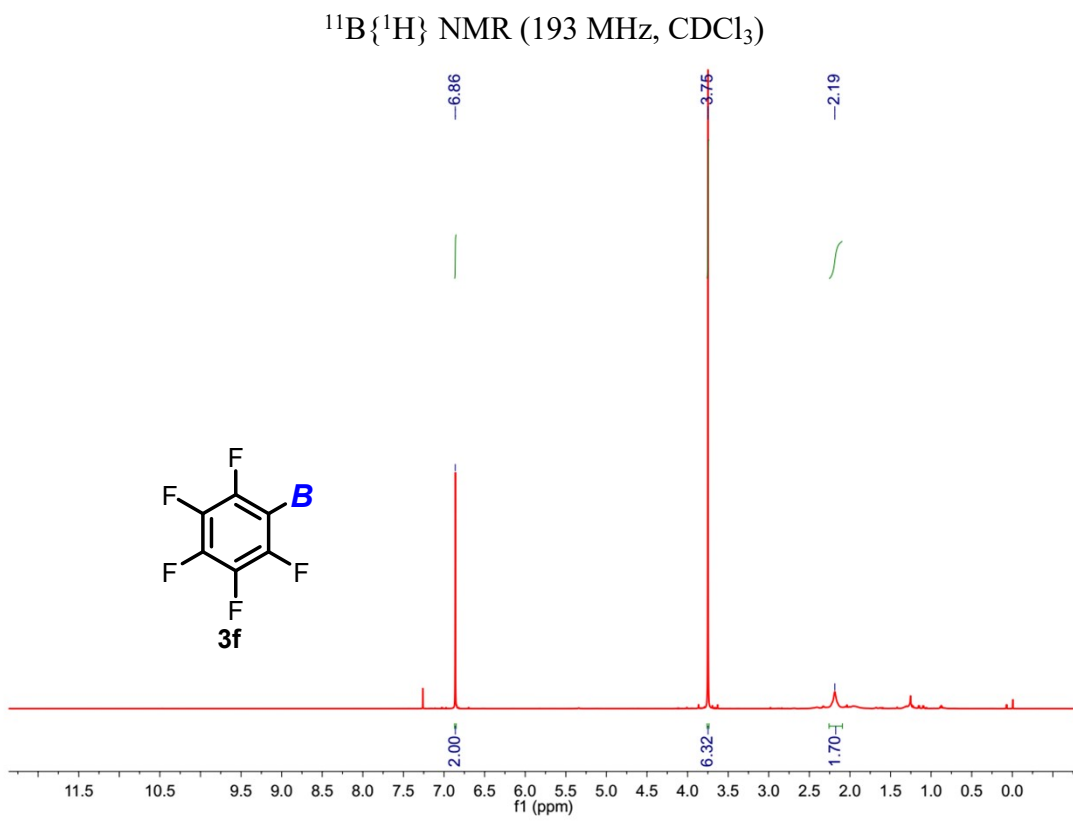
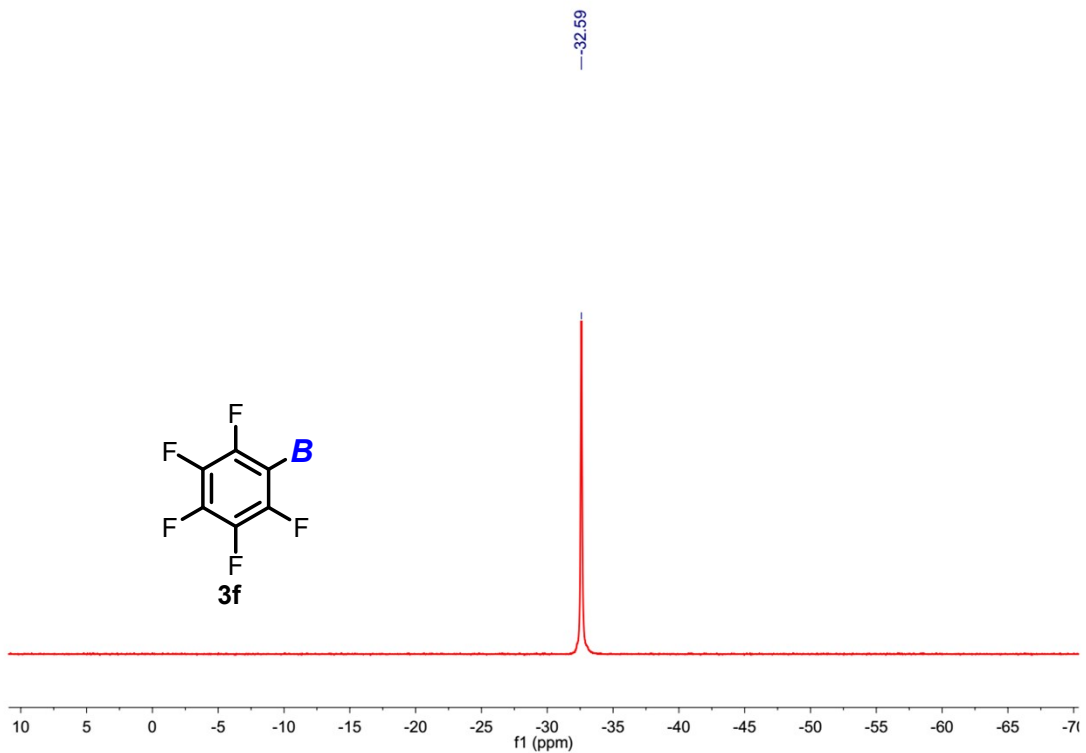
¹⁹F NMR (565 MHz, CDCl₃)

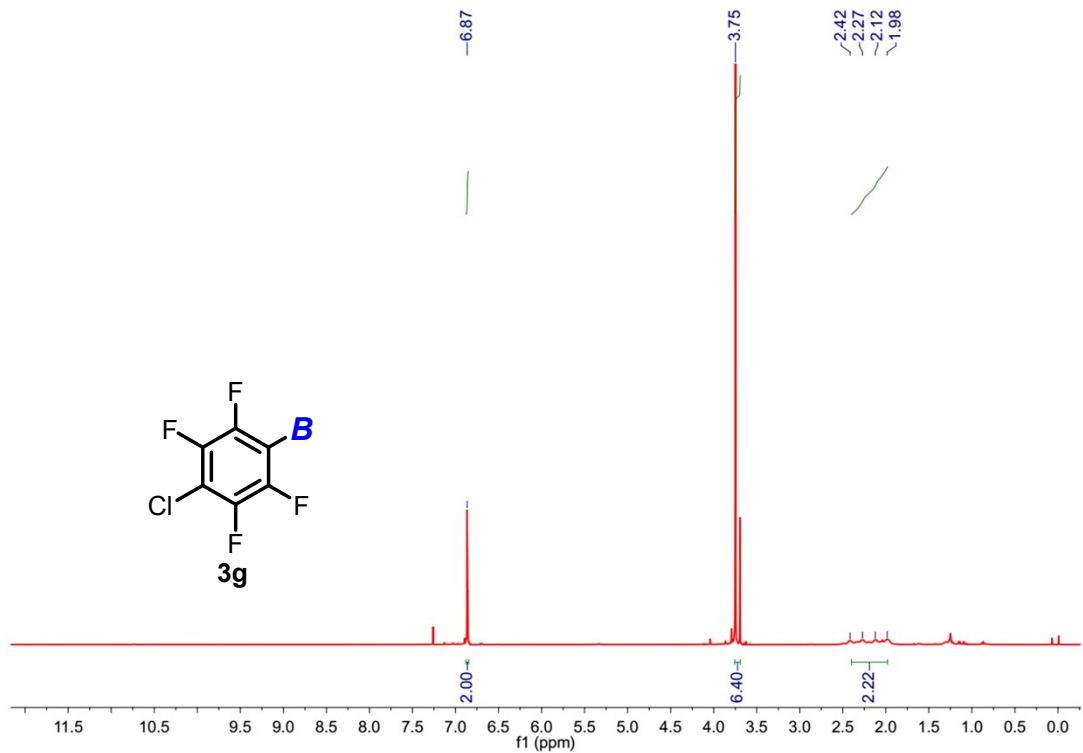


^{13}C NMR (151 MHz, CDCl_3)

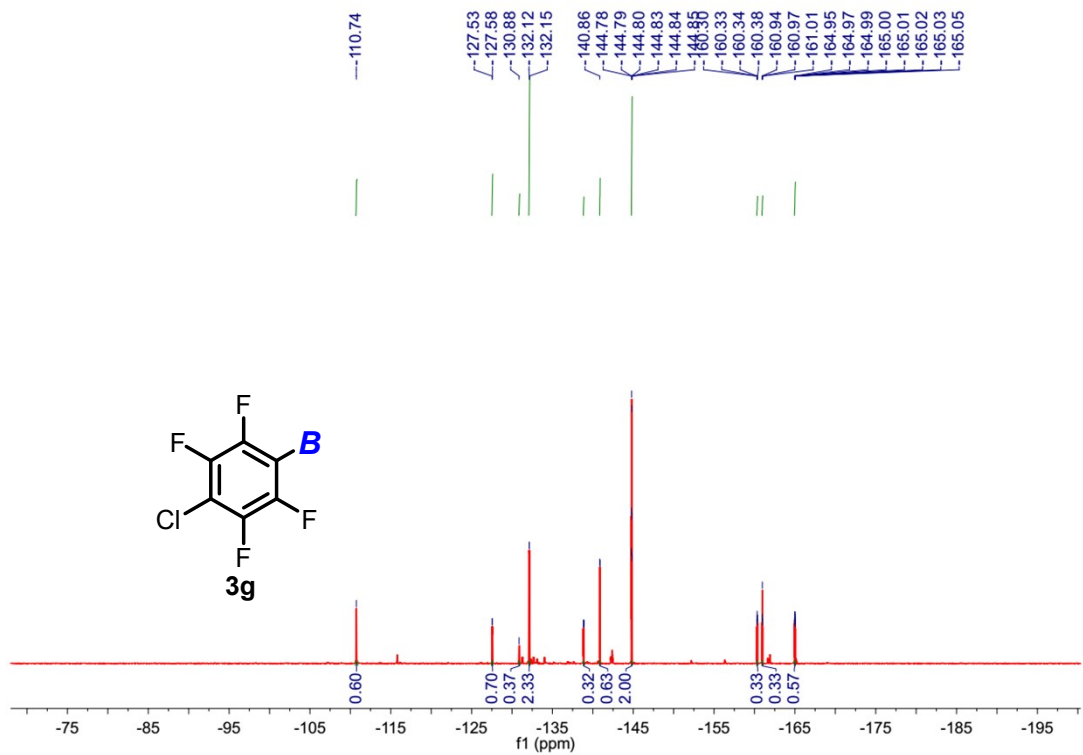


^{11}B NMR (193 MHz, CDCl_3)

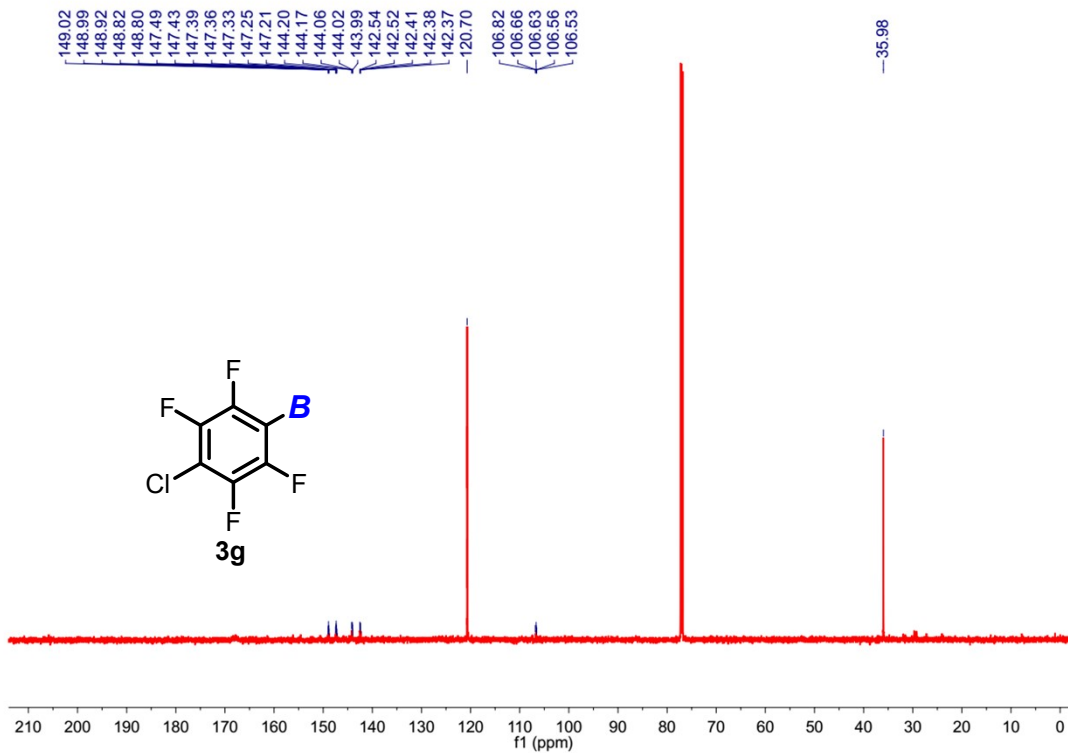




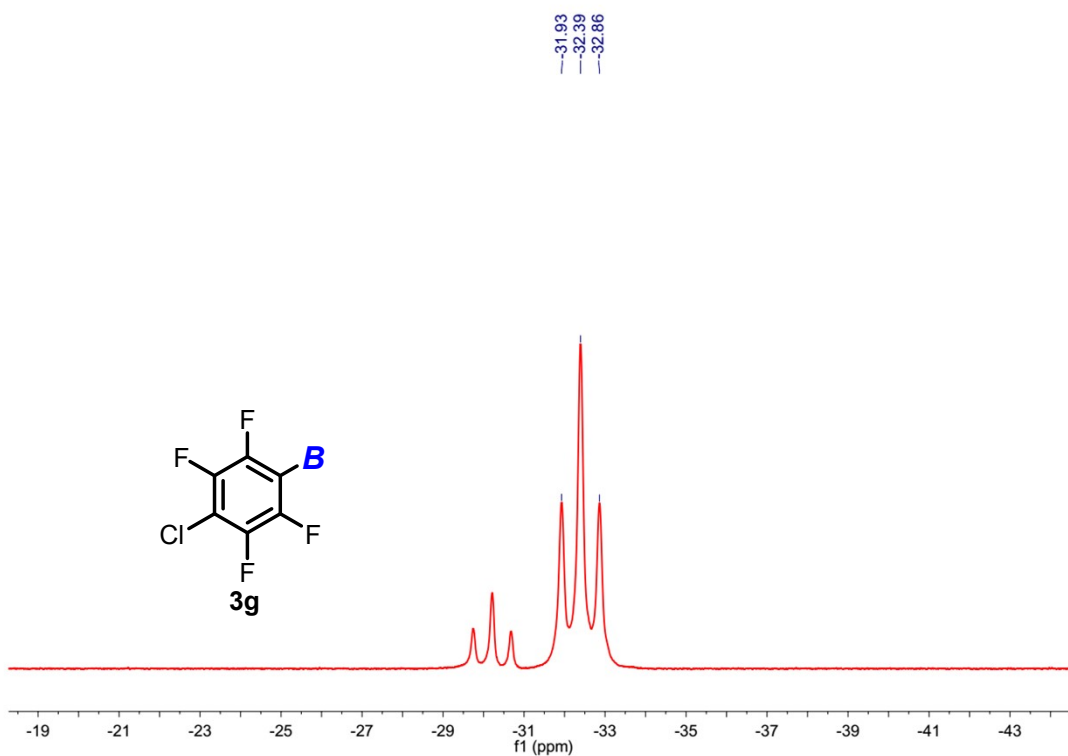
$^1\text{H NMR}$ (600 MHz, CDCl_3)



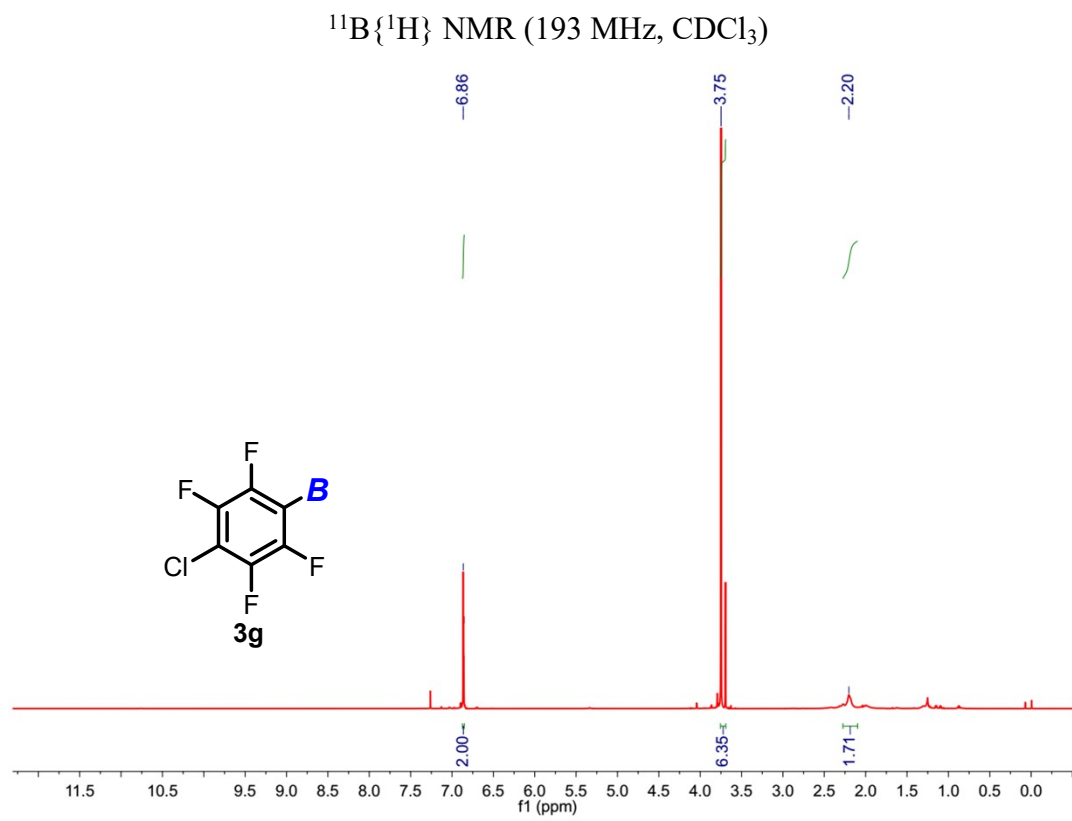
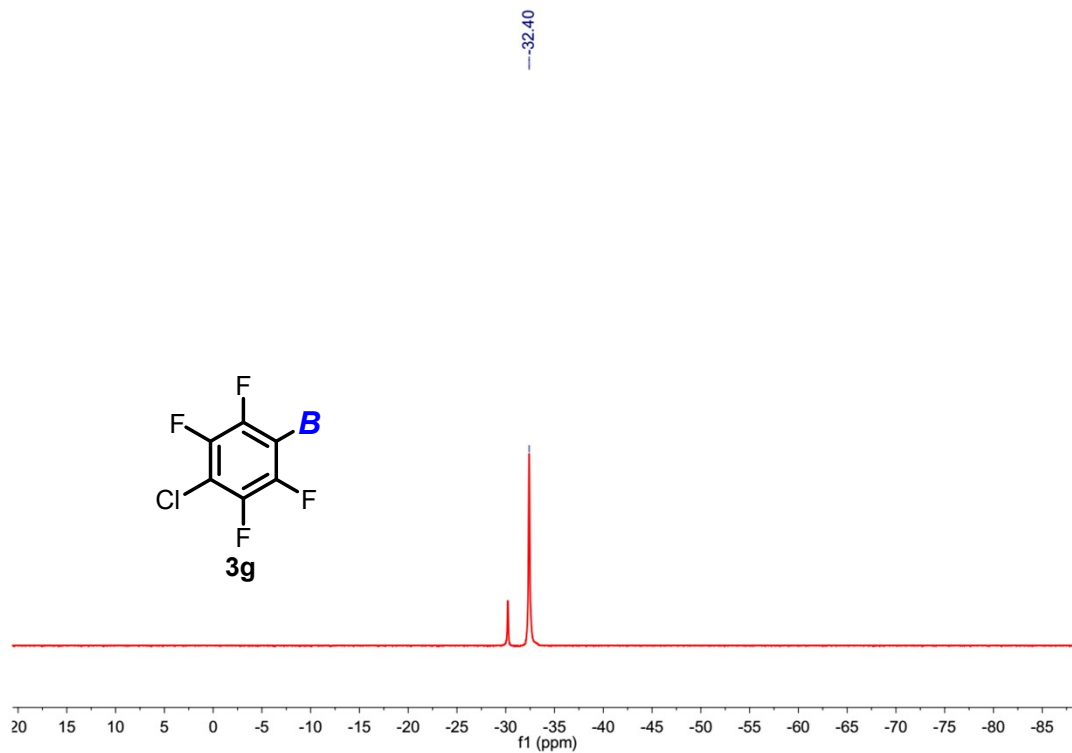
$^{19}\text{F NMR}$ (565 MHz, CDCl_3)

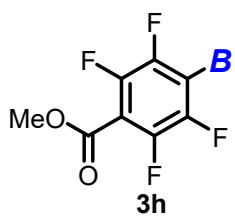
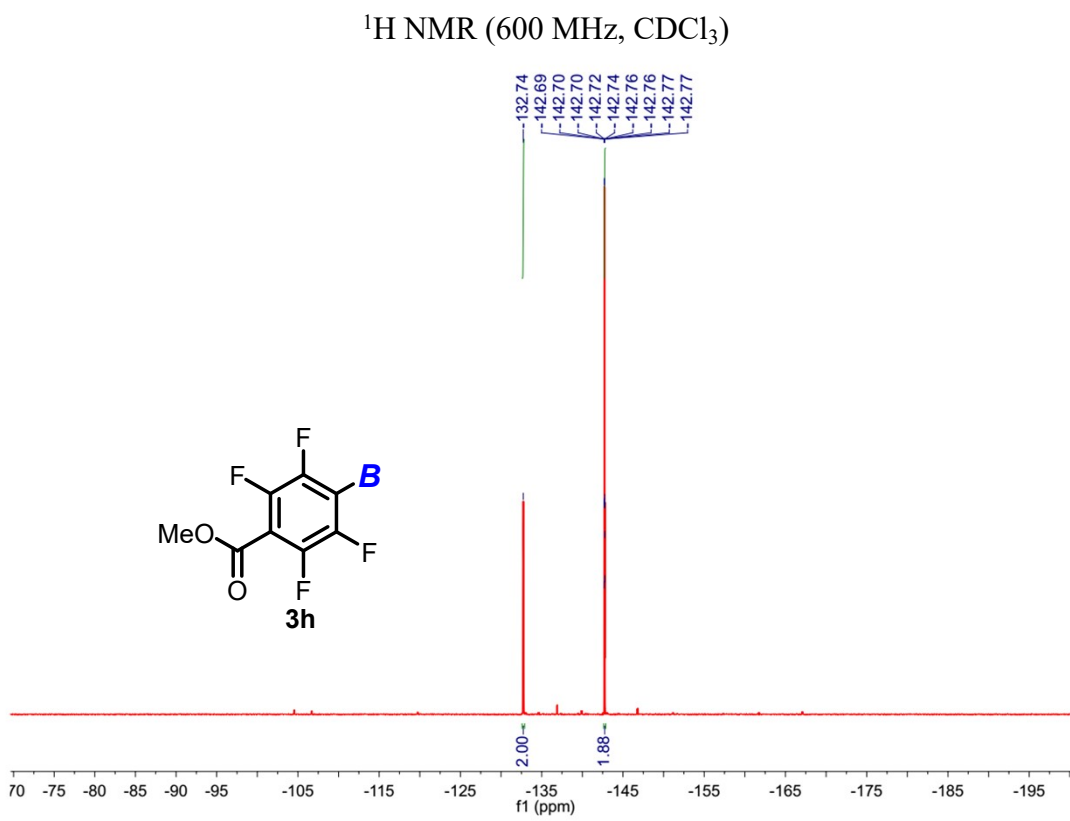
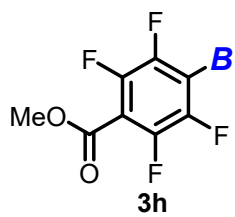
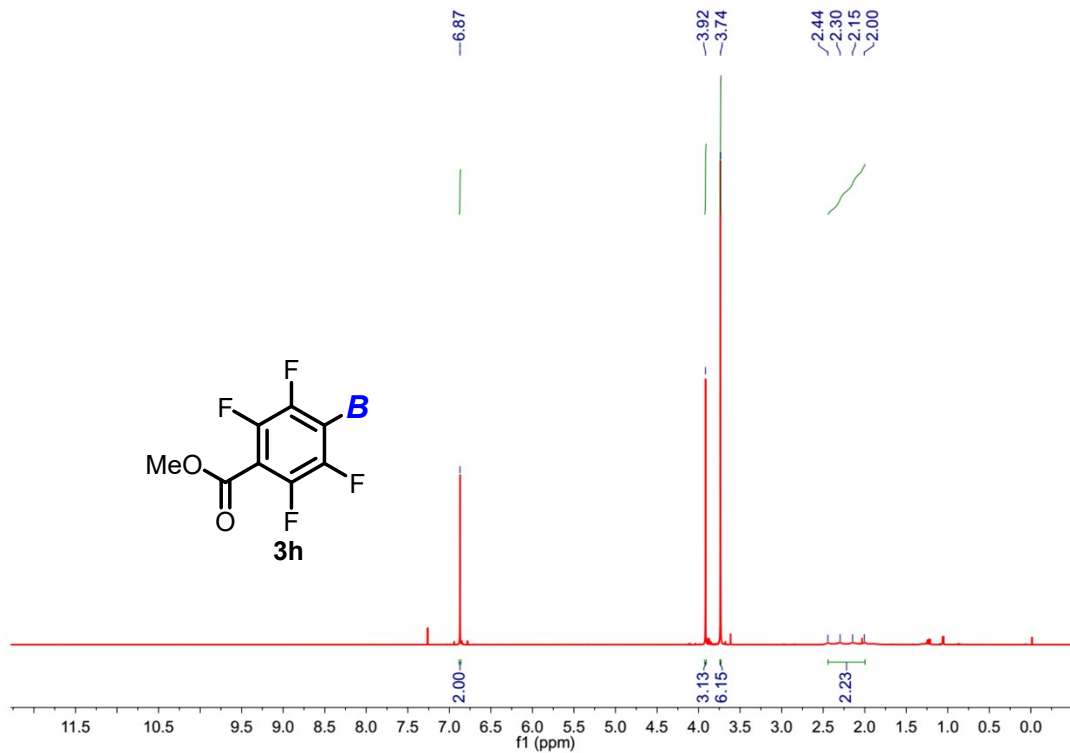


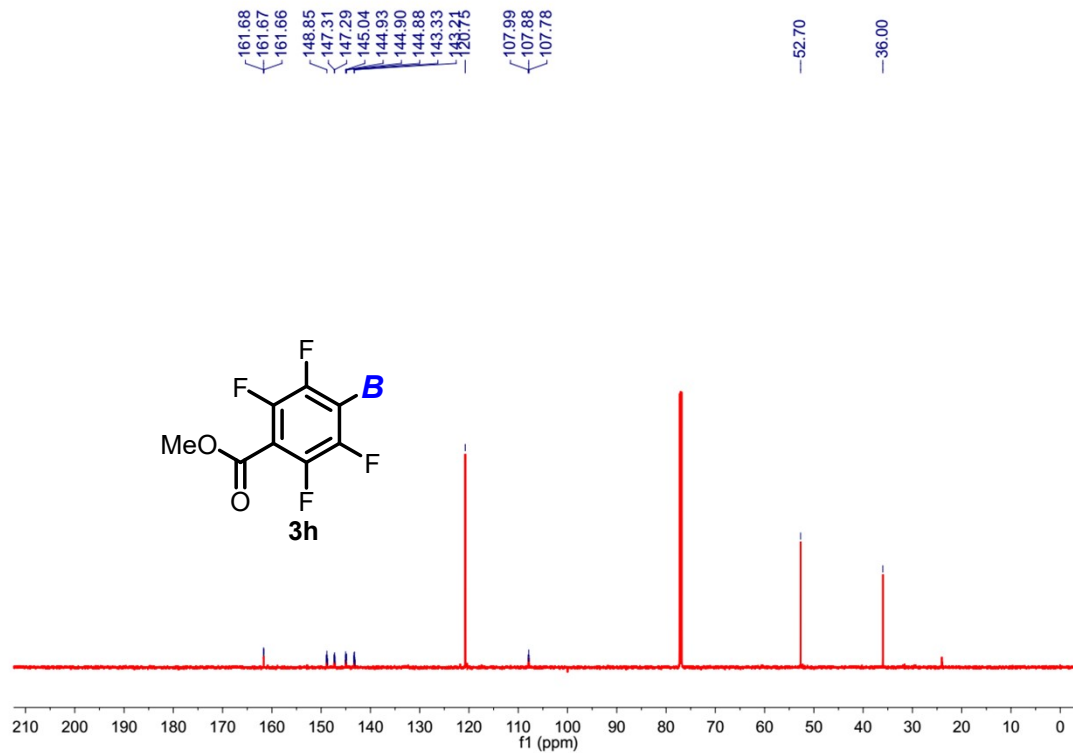
^{13}C NMR (151 MHz, CDCl_3)



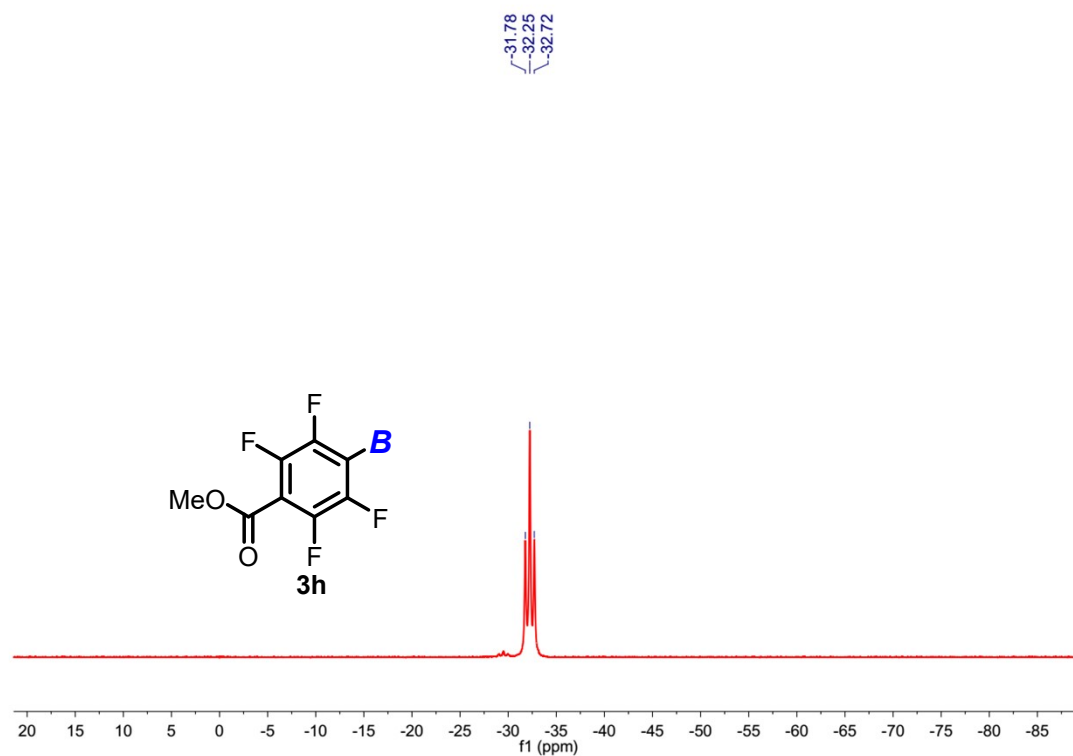
^{11}B NMR (193 MHz, CDCl_3)



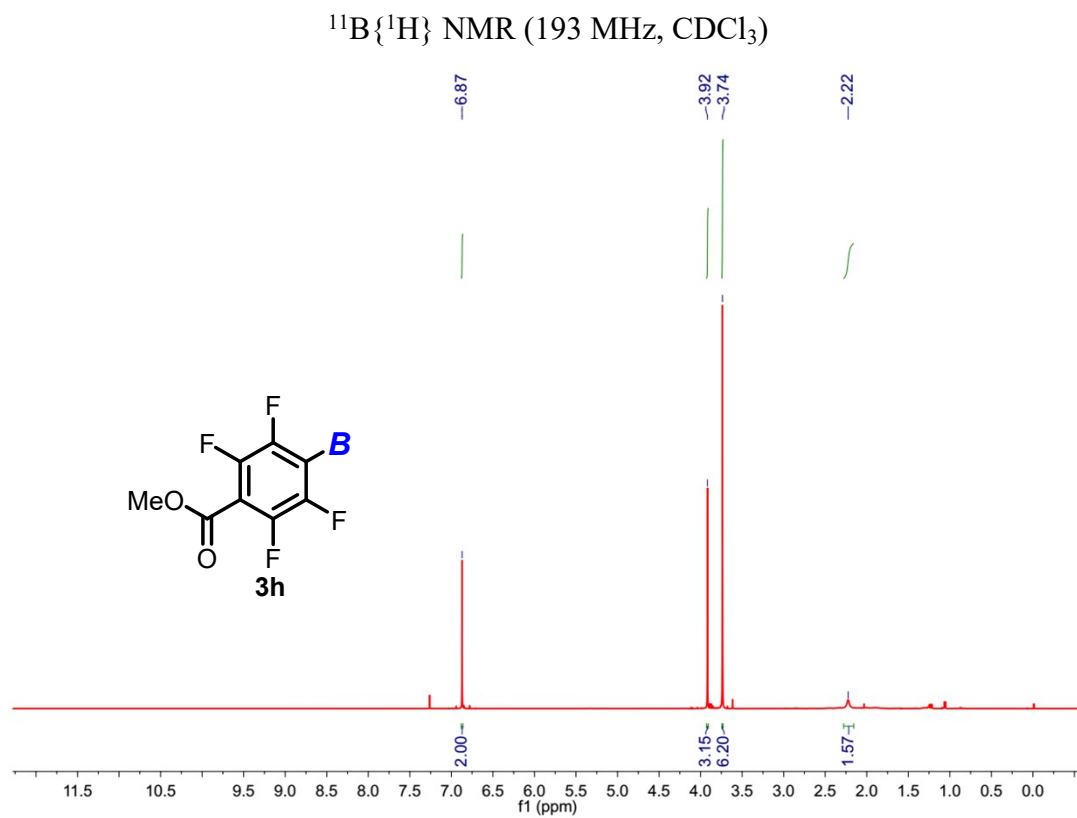
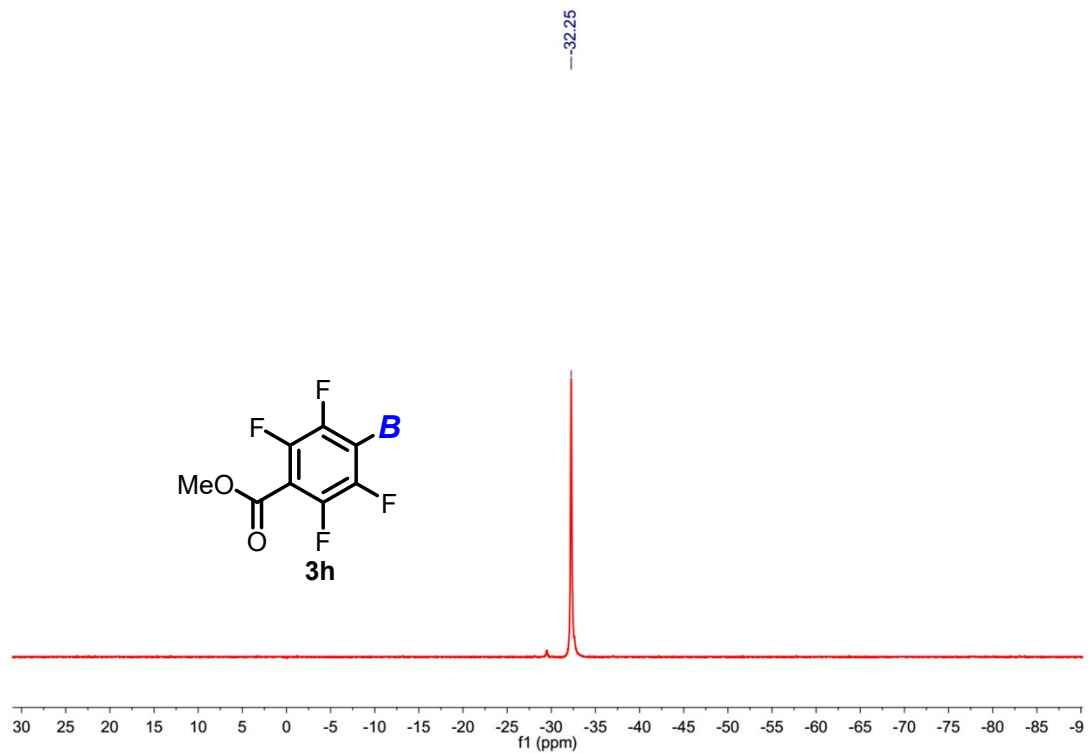


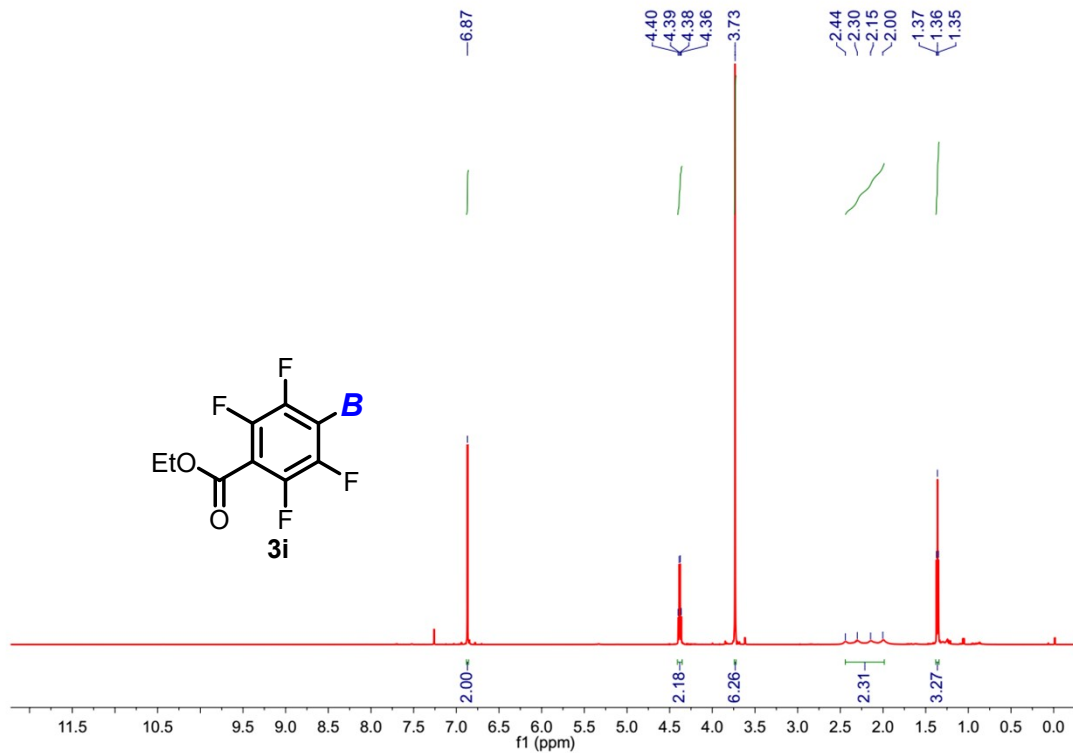


^{13}C NMR (151 MHz, CDCl_3)

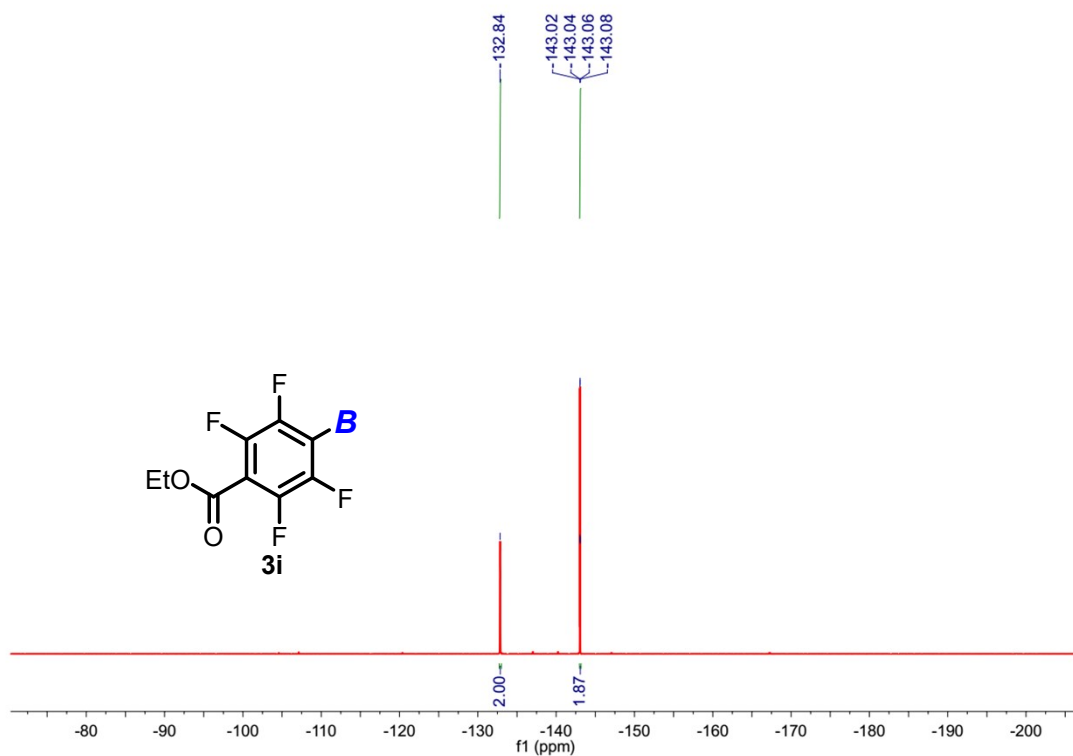


^{11}B NMR (193 MHz, CDCl_3)

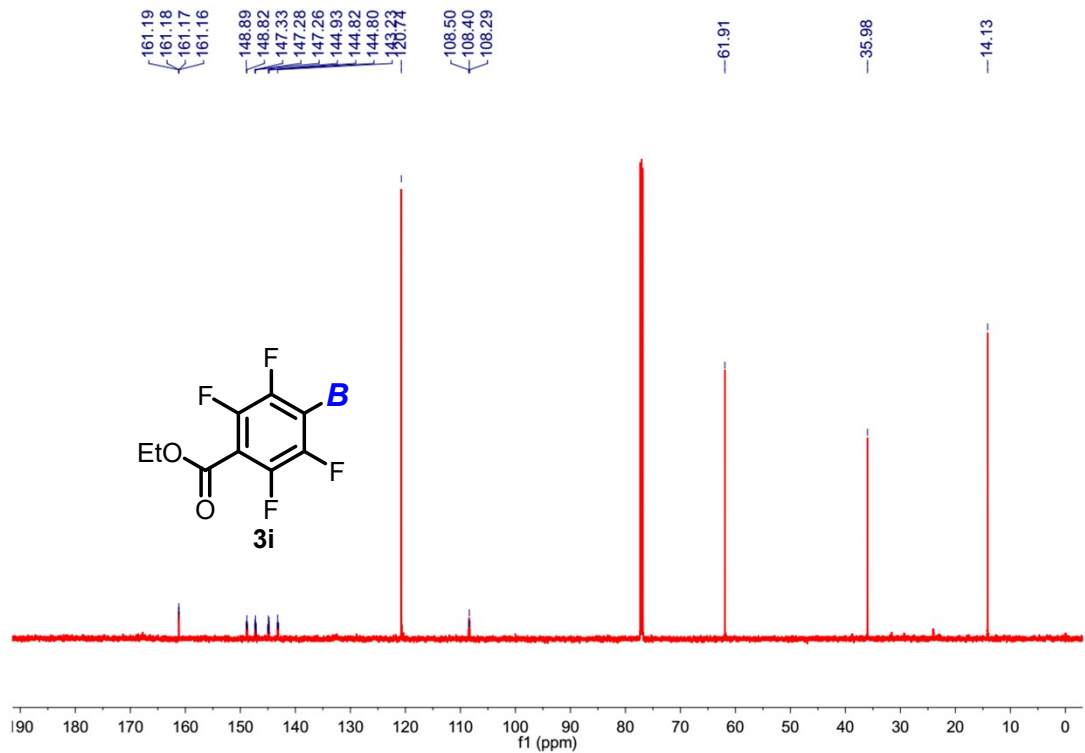




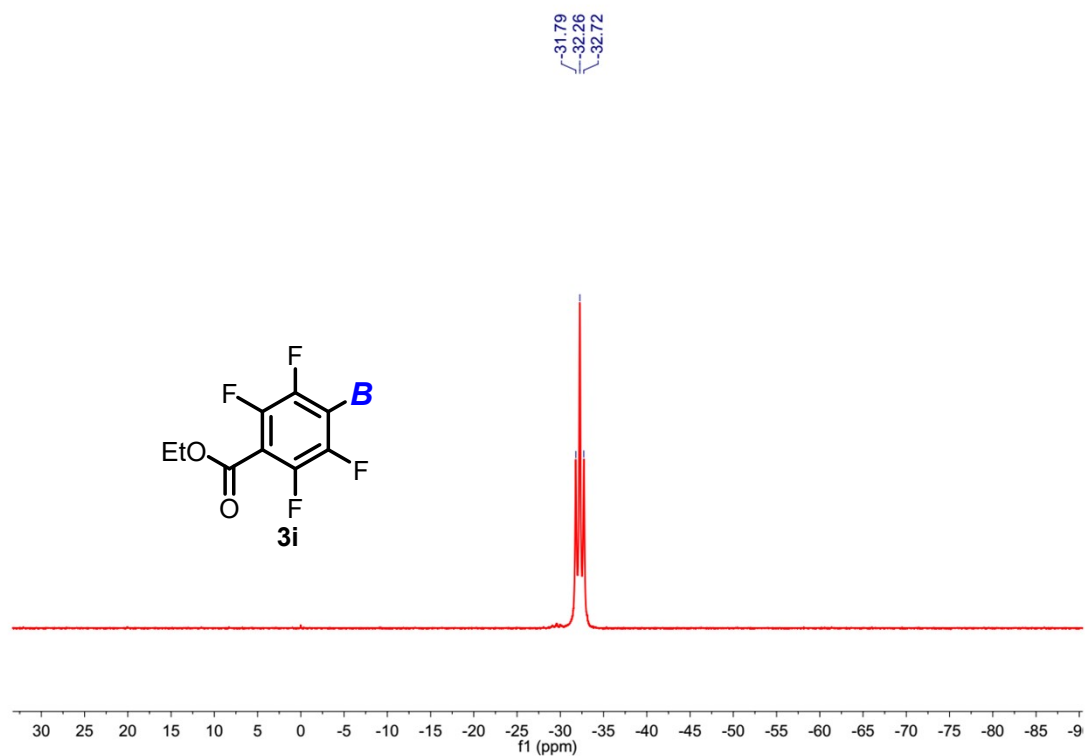
¹H NMR (600 MHz, CDCl₃)



¹⁹F NMR (565 MHz, CDCl₃)

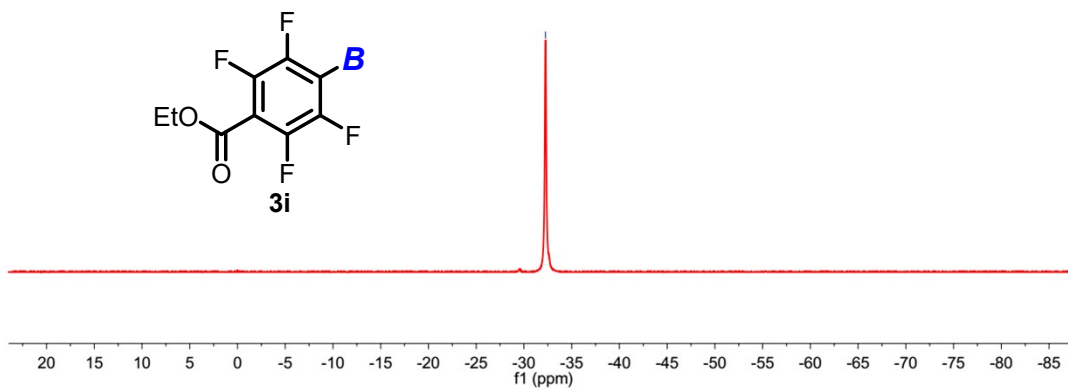


^{13}C NMR (151 MHz, CDCl_3)

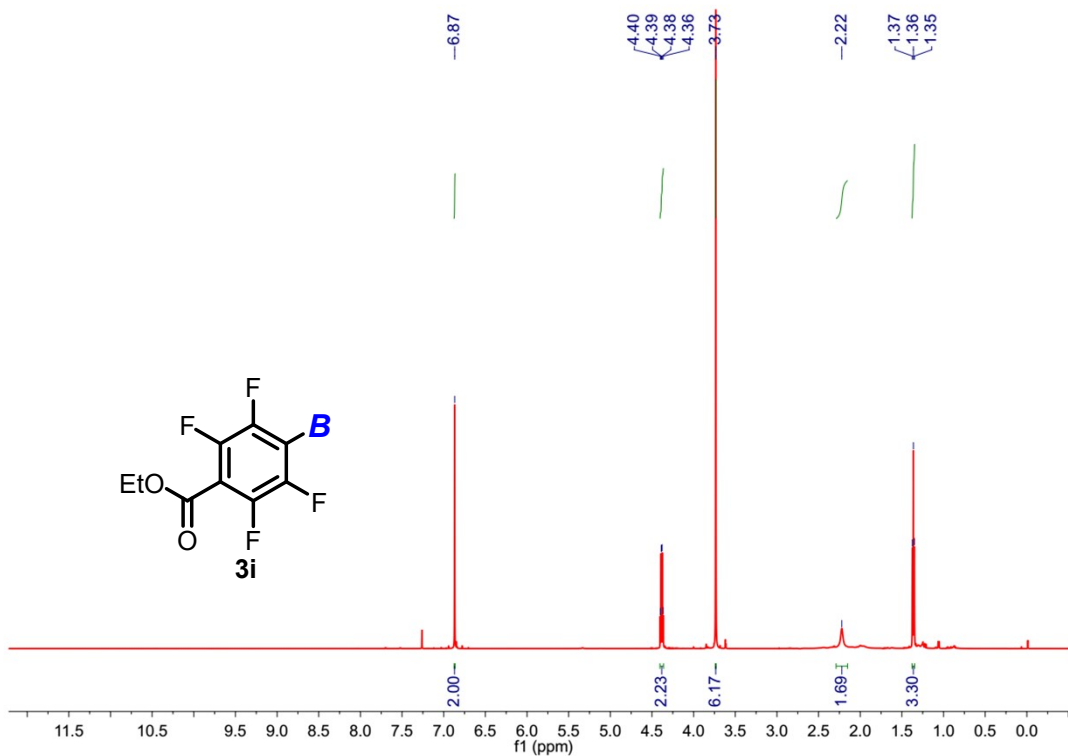


^{11}B NMR (193 MHz, CDCl_3)

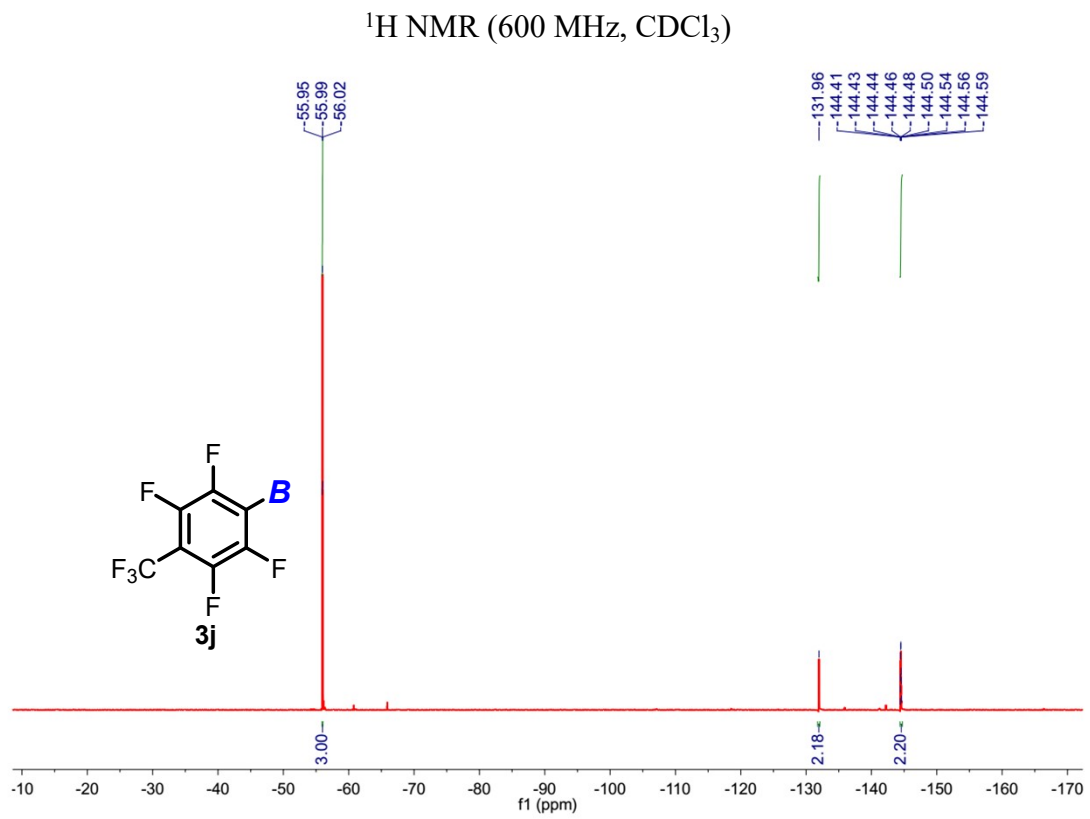
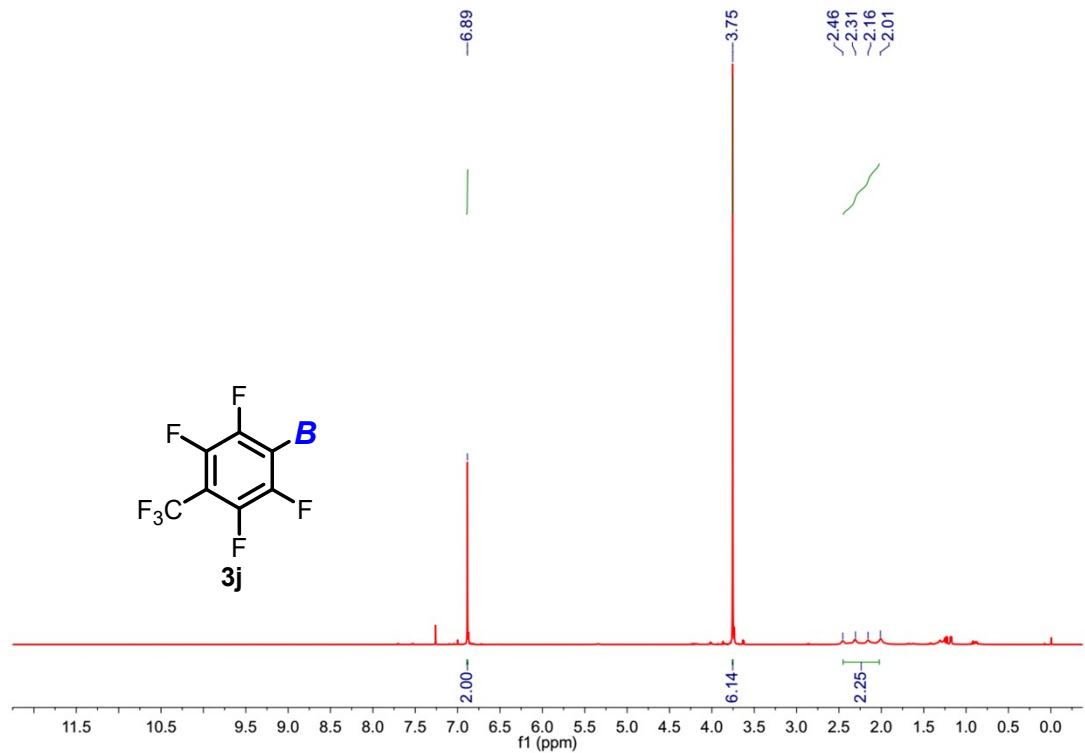
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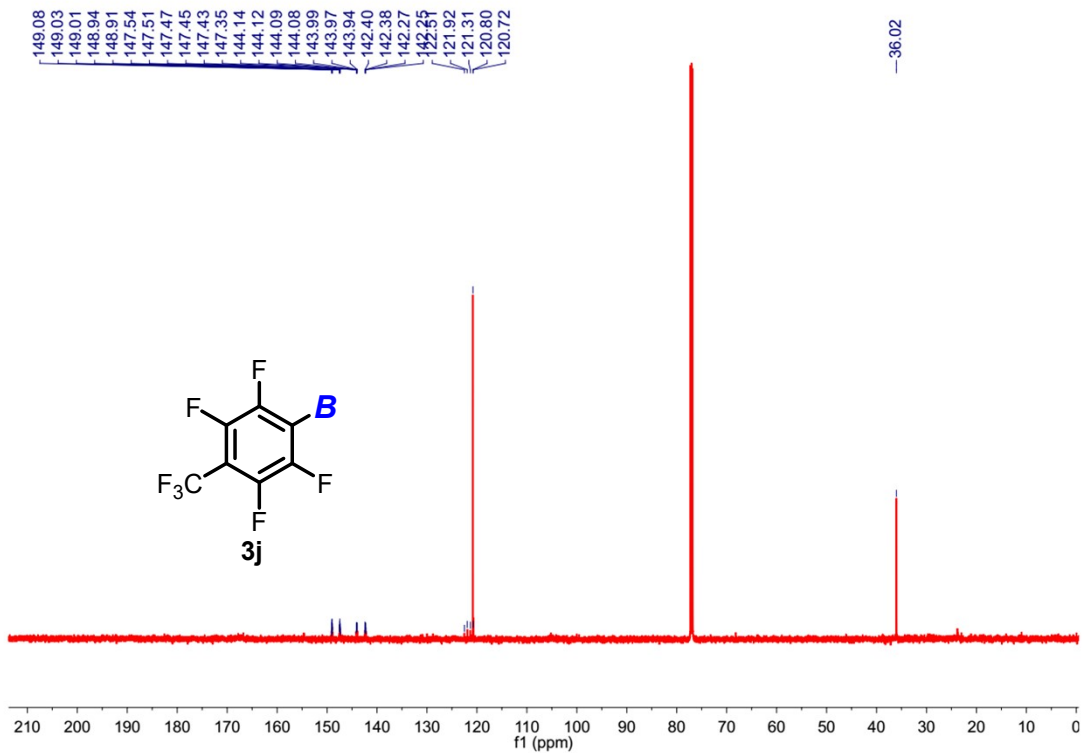


$^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3)

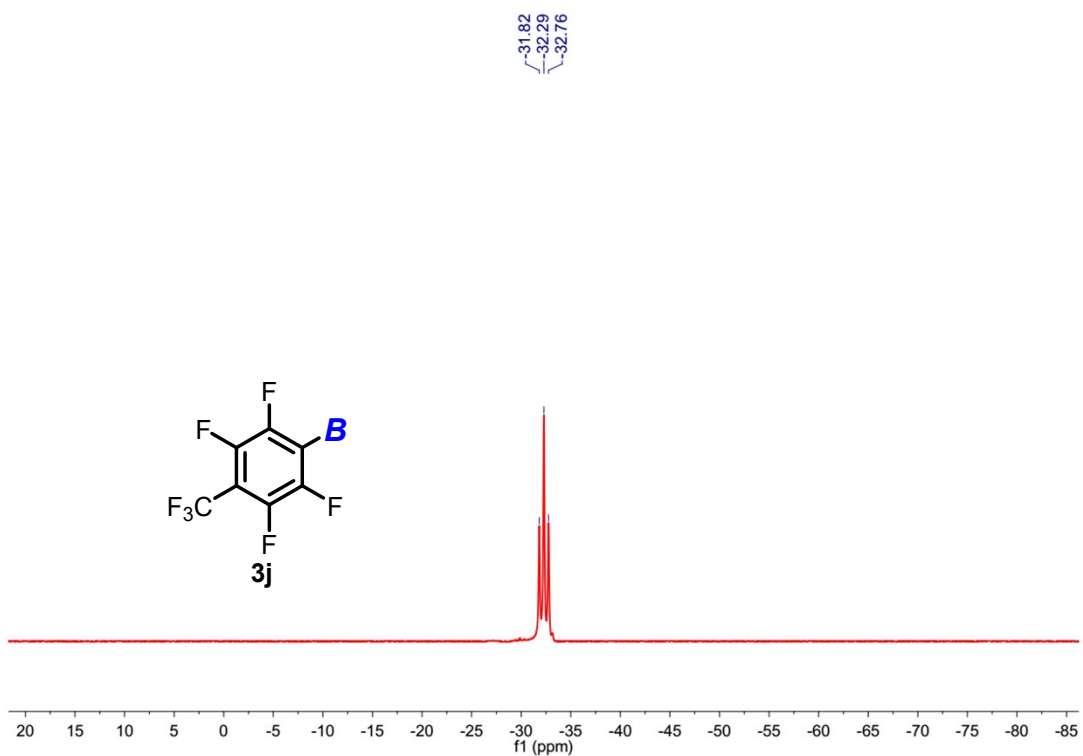


$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3)

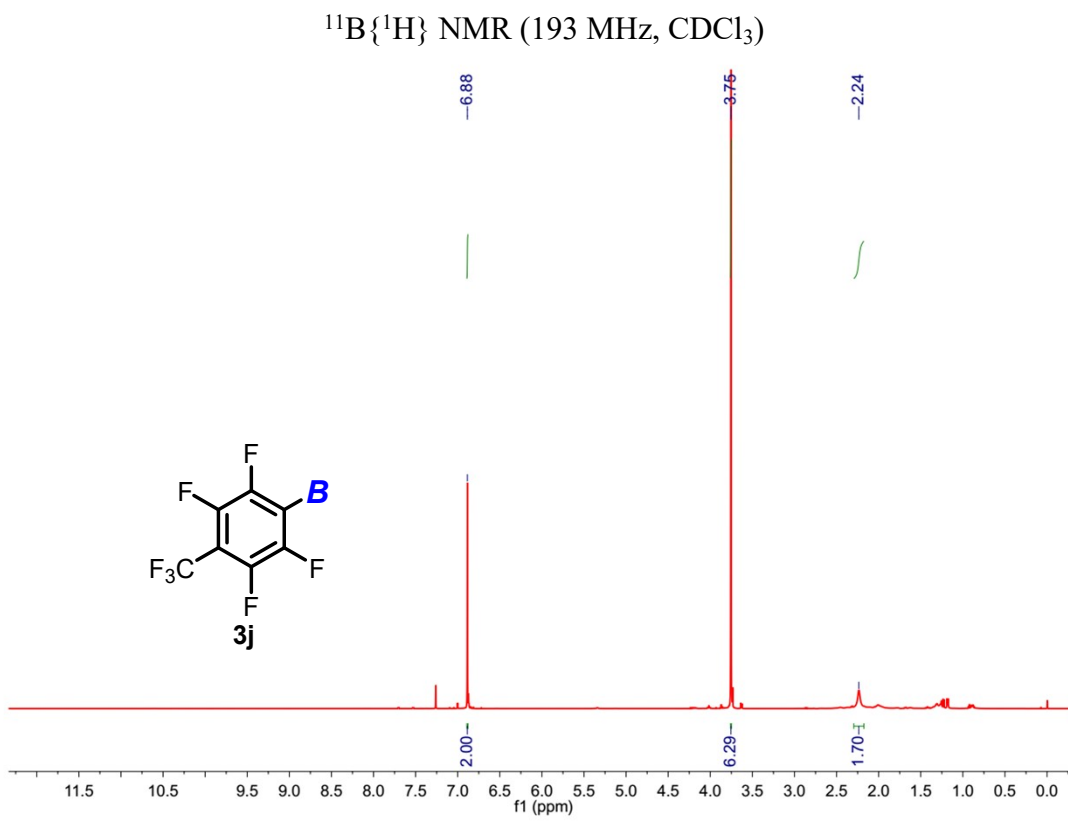
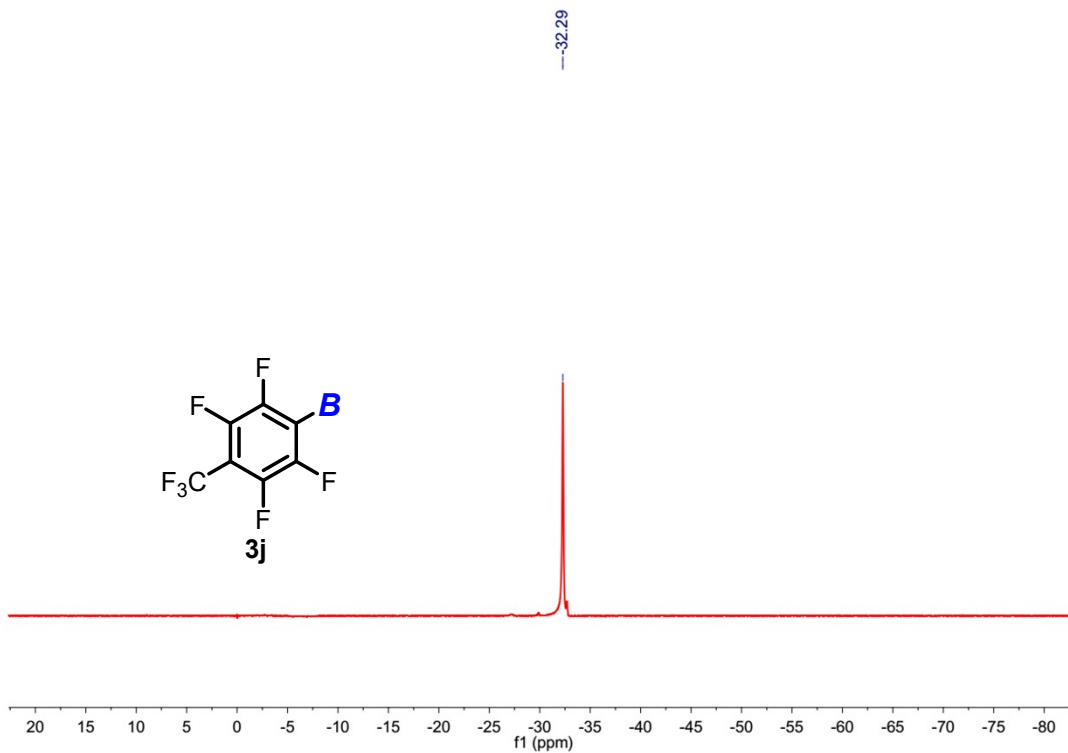


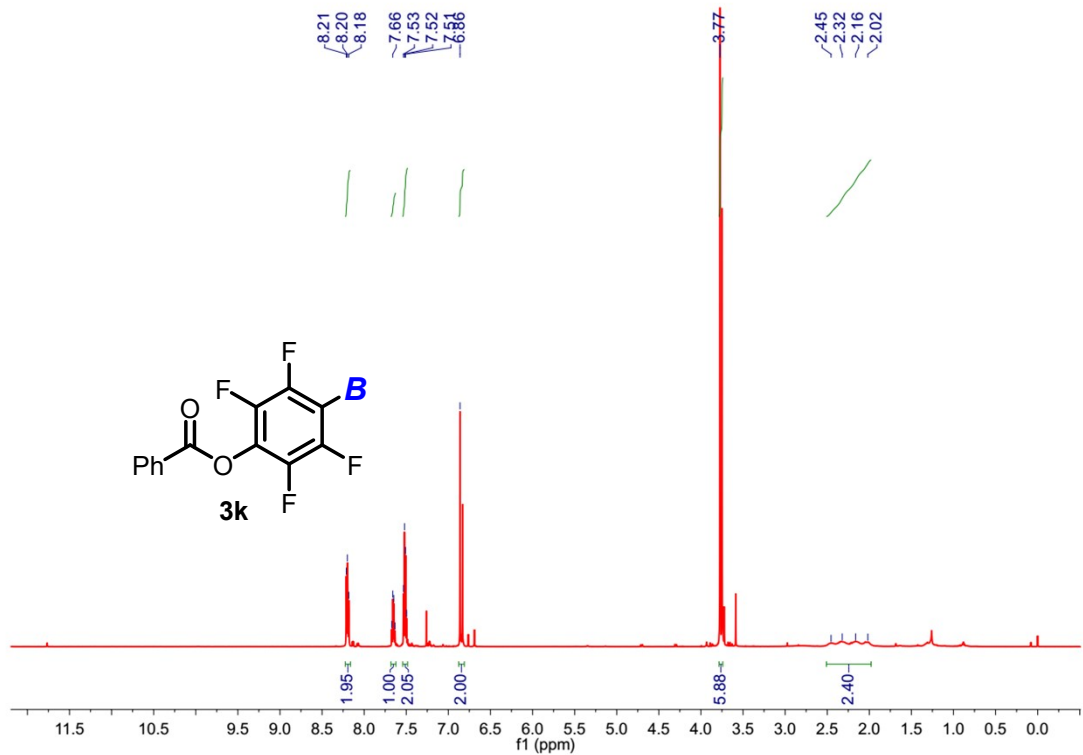


^{13}C NMR (151 MHz, CDCl_3)

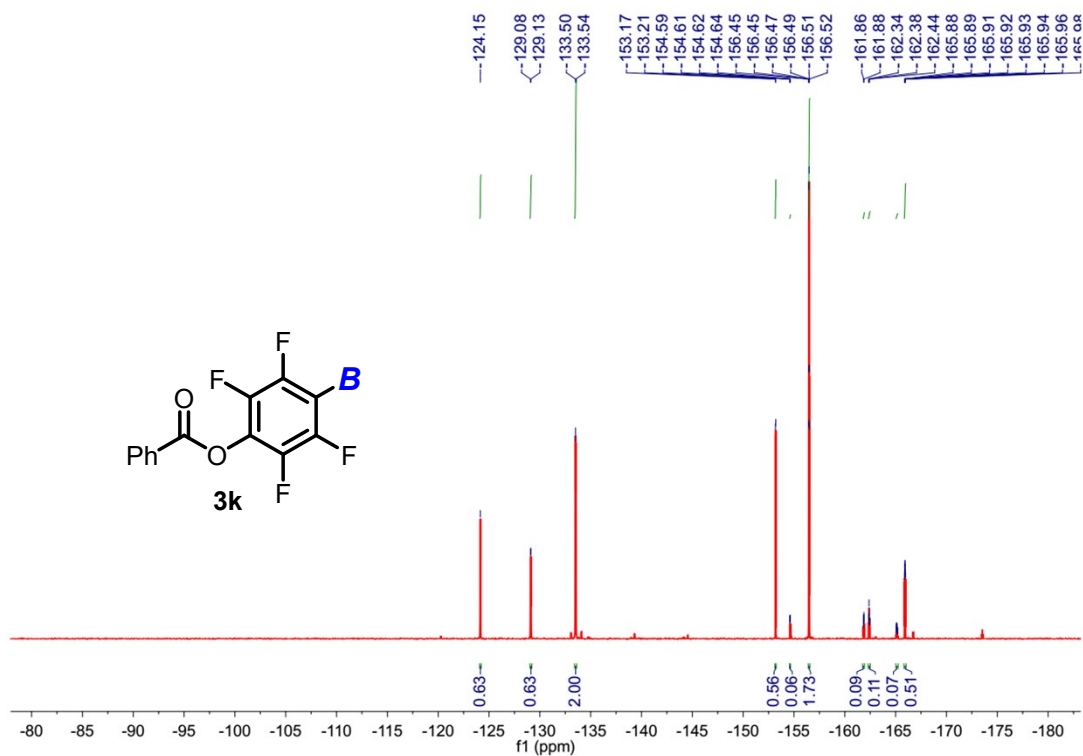


^{11}B NMR (193 MHz, CDCl_3)

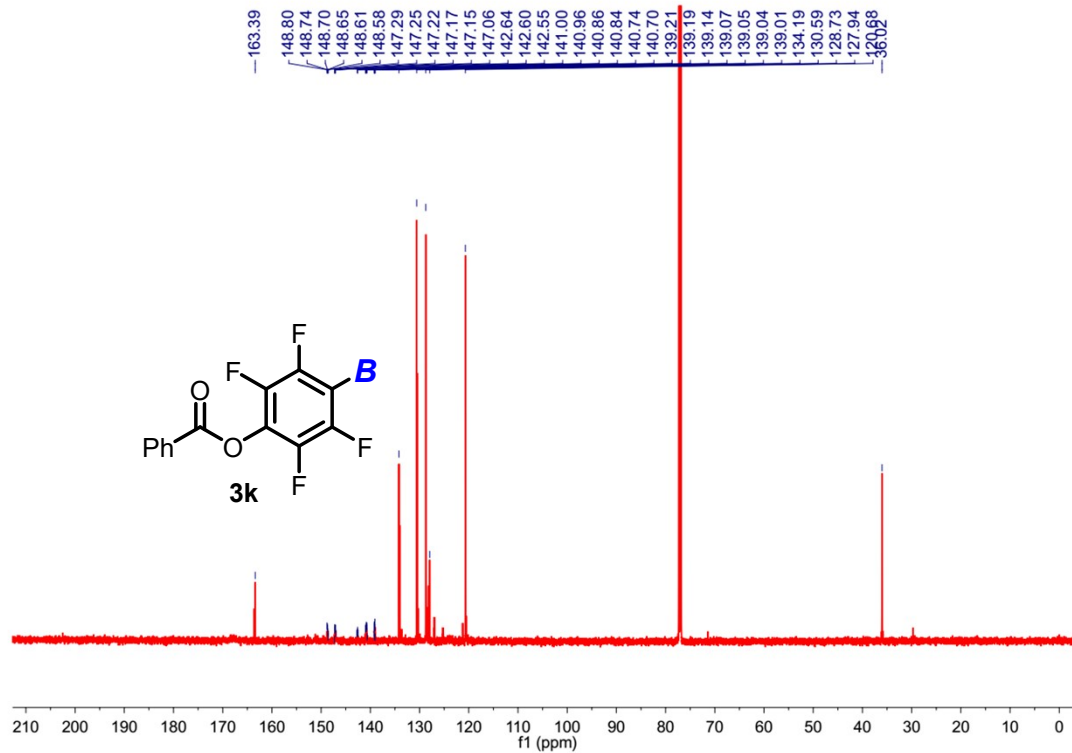




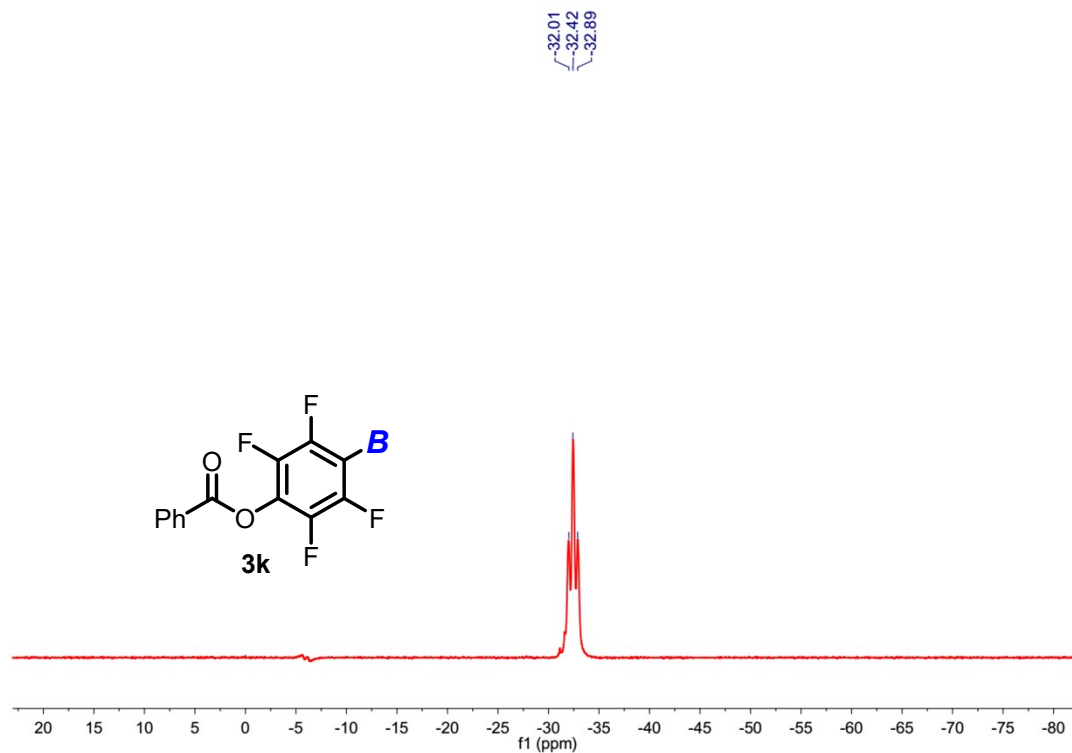
¹H NMR (600 MHz, CDCl₃)



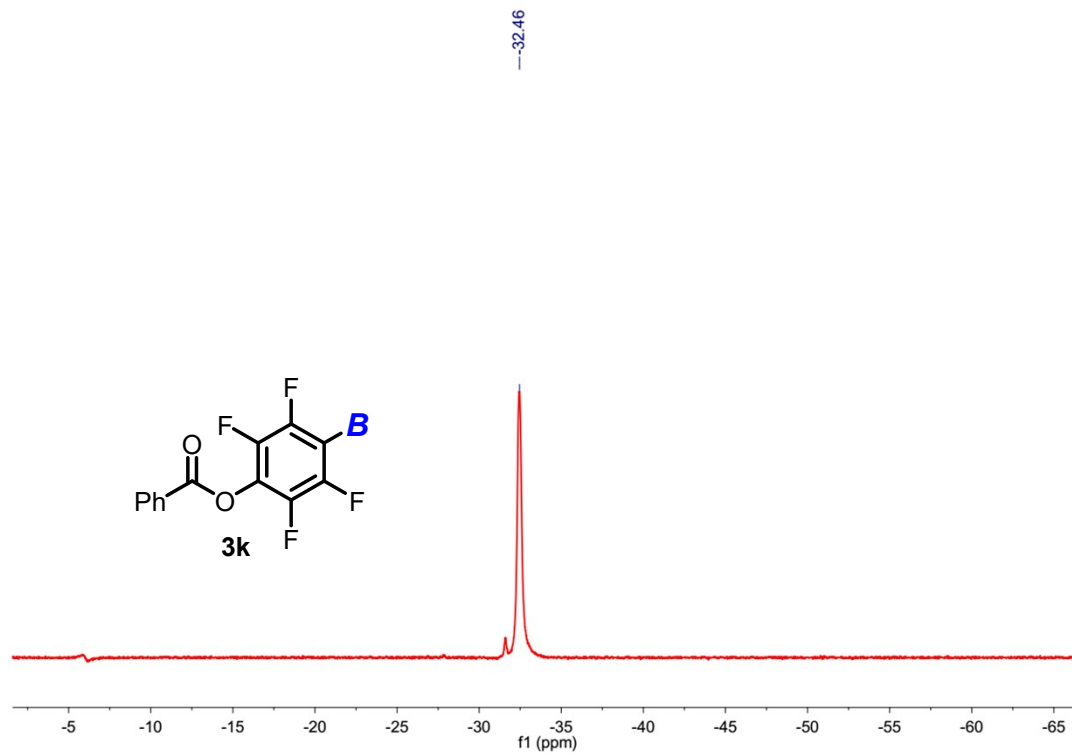
¹⁹F NMR (565 MHz, CDCl₃)



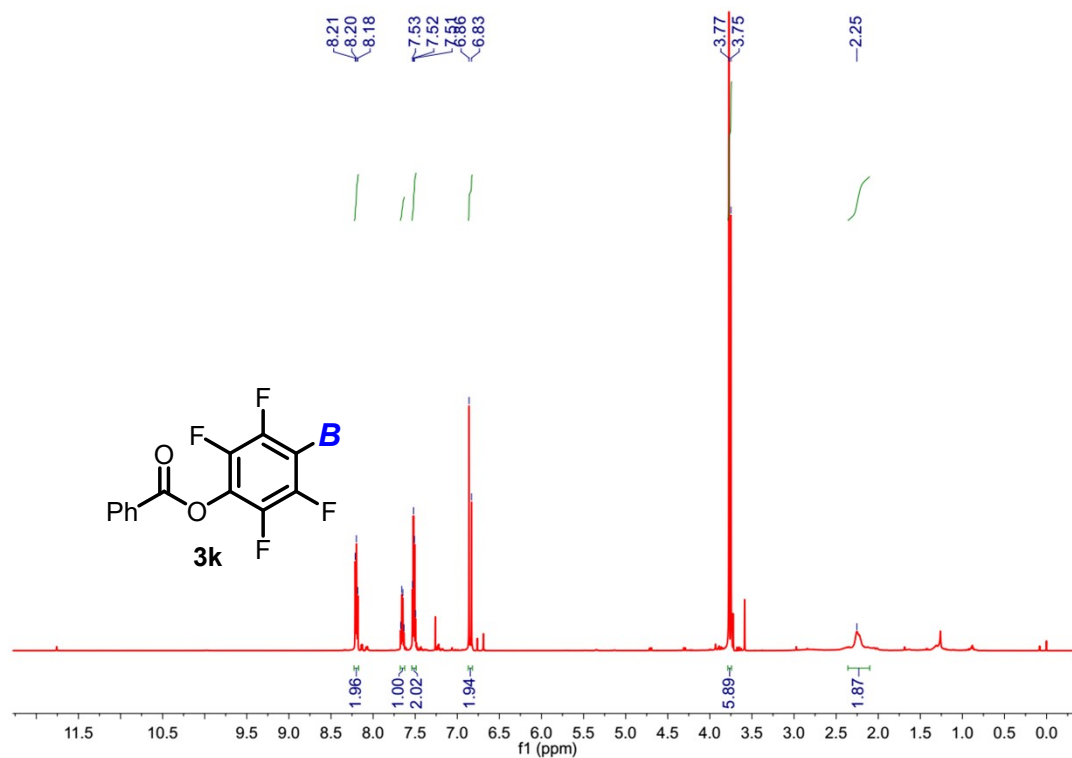
¹³C NMR (151 MHz, CDCl₃)



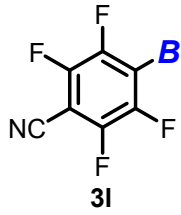
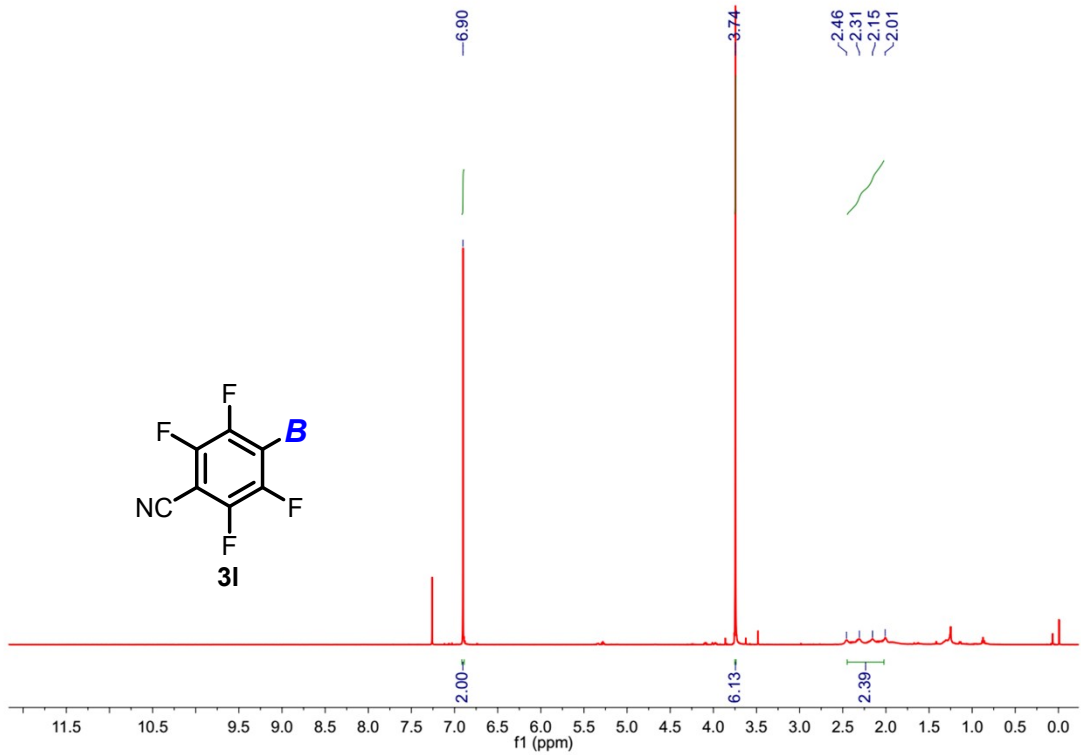
¹¹B NMR (193 MHz, CDCl₃)



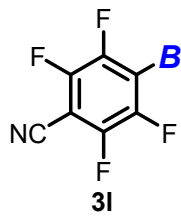
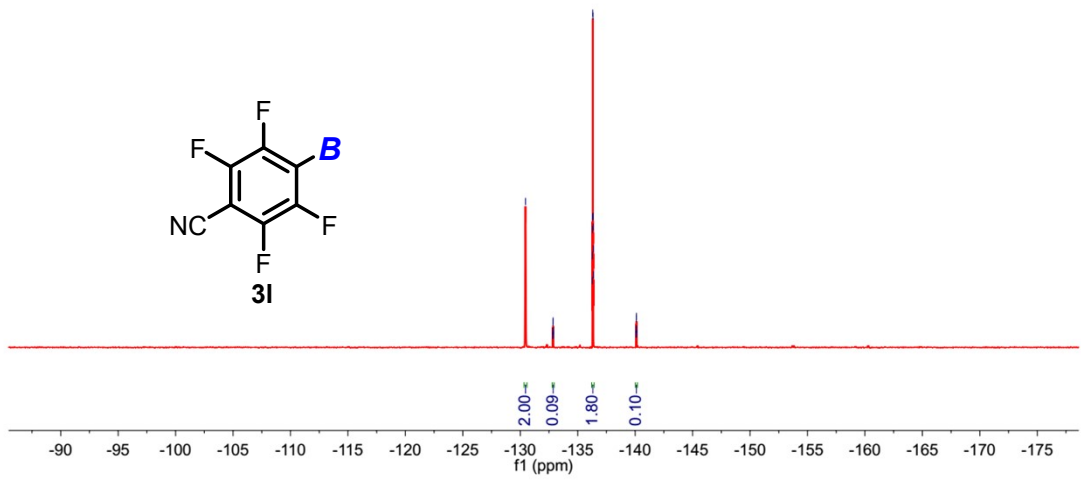
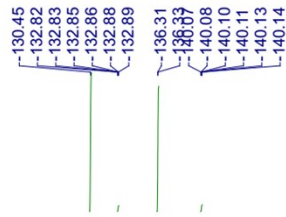
$^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3)



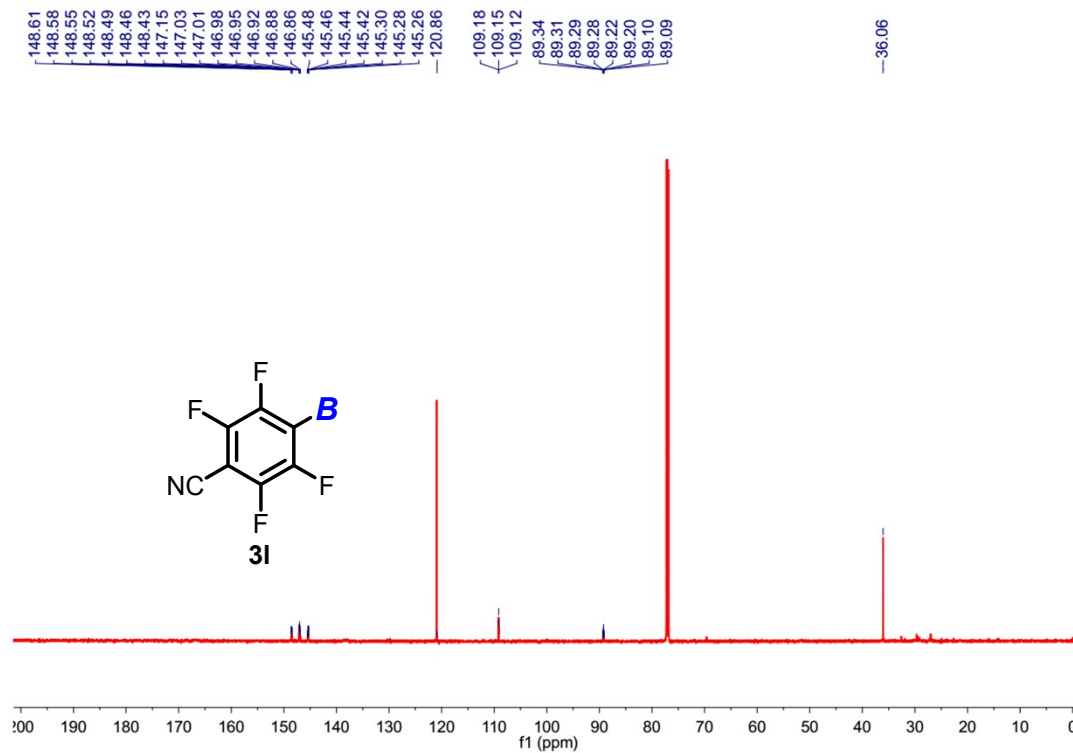
$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3)



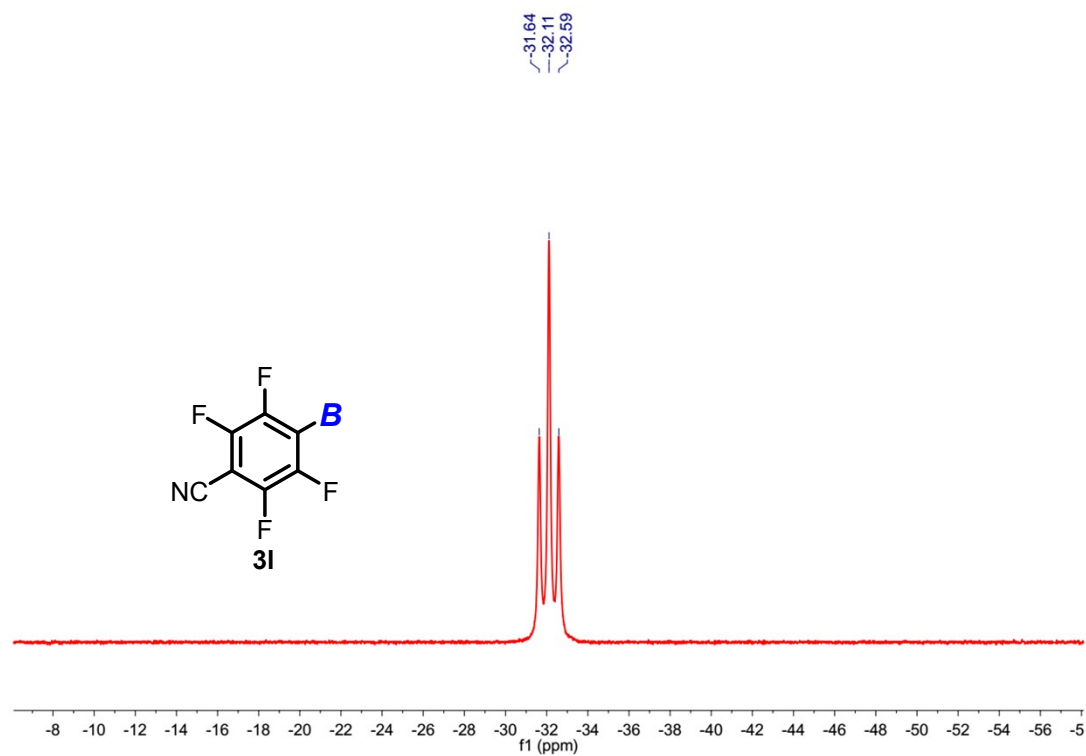
¹H NMR (600 MHz, CDCl₃)



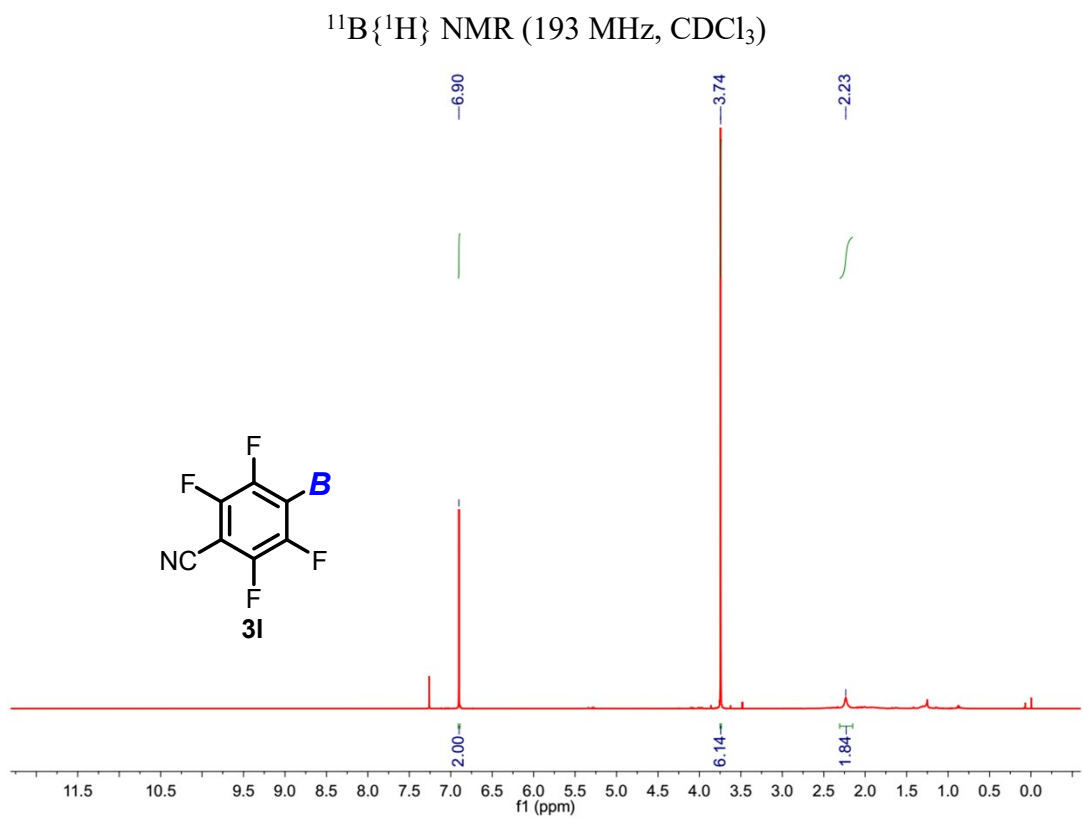
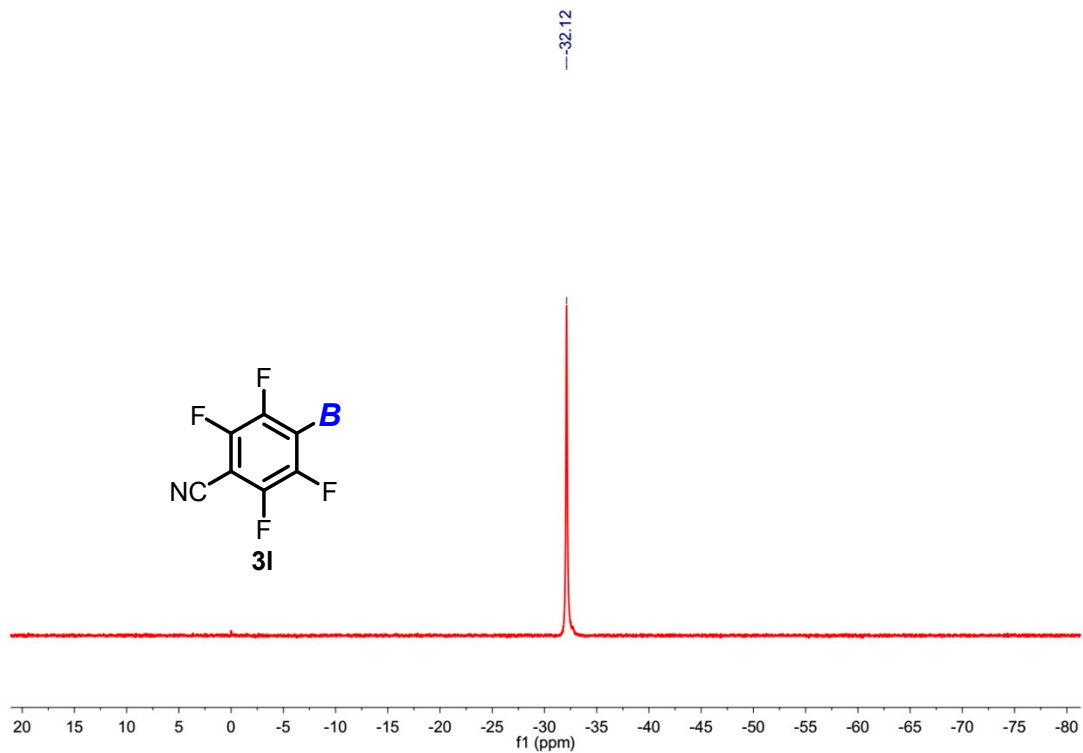
¹⁹F NMR (565 MHz, CDCl₃)



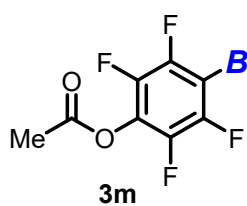
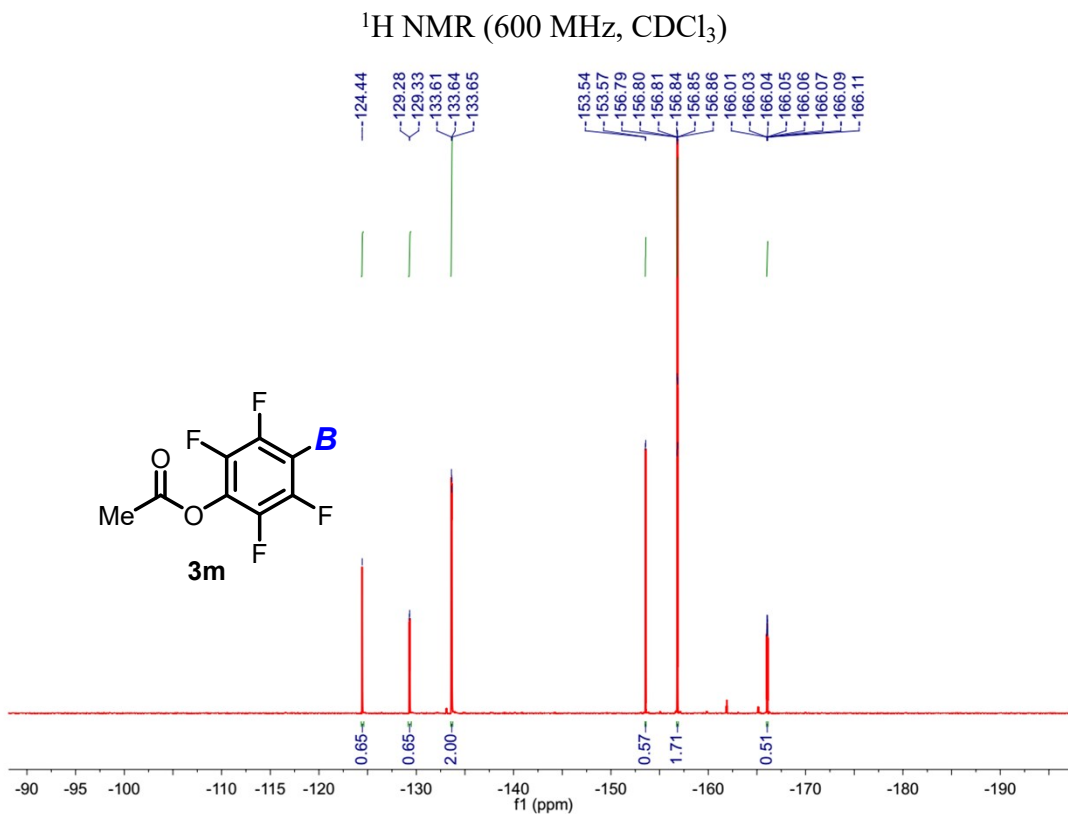
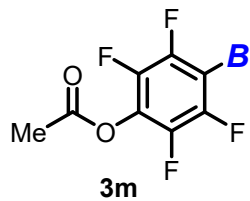
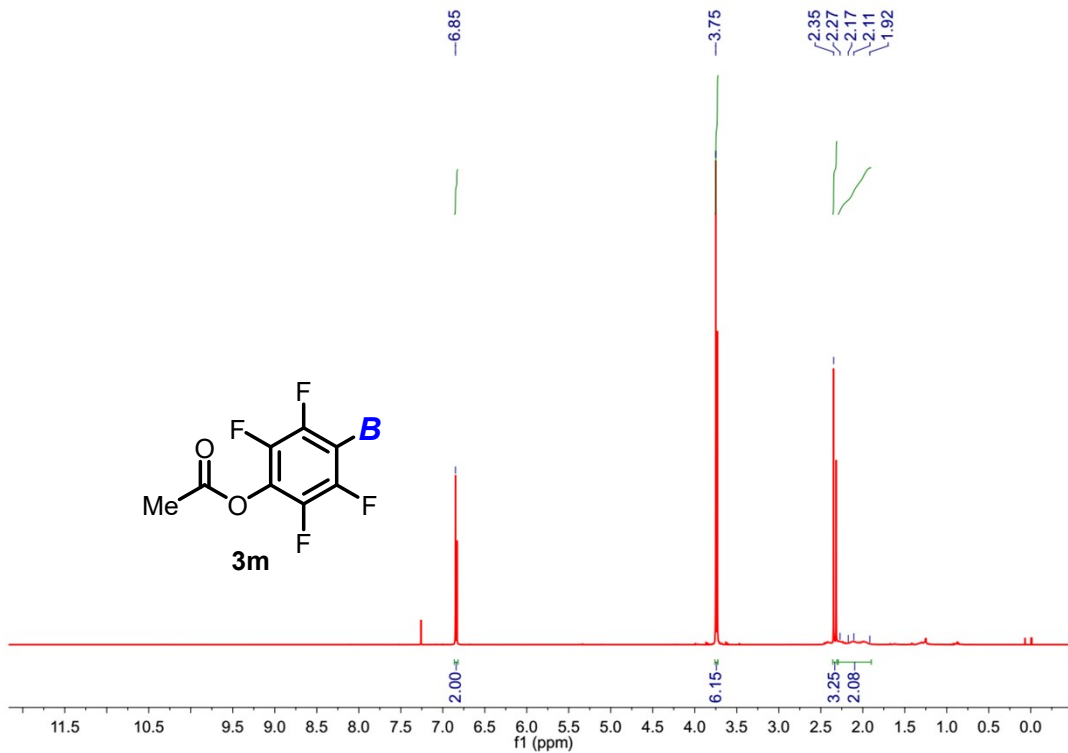
¹³C NMR (151 MHz, CDCl₃)

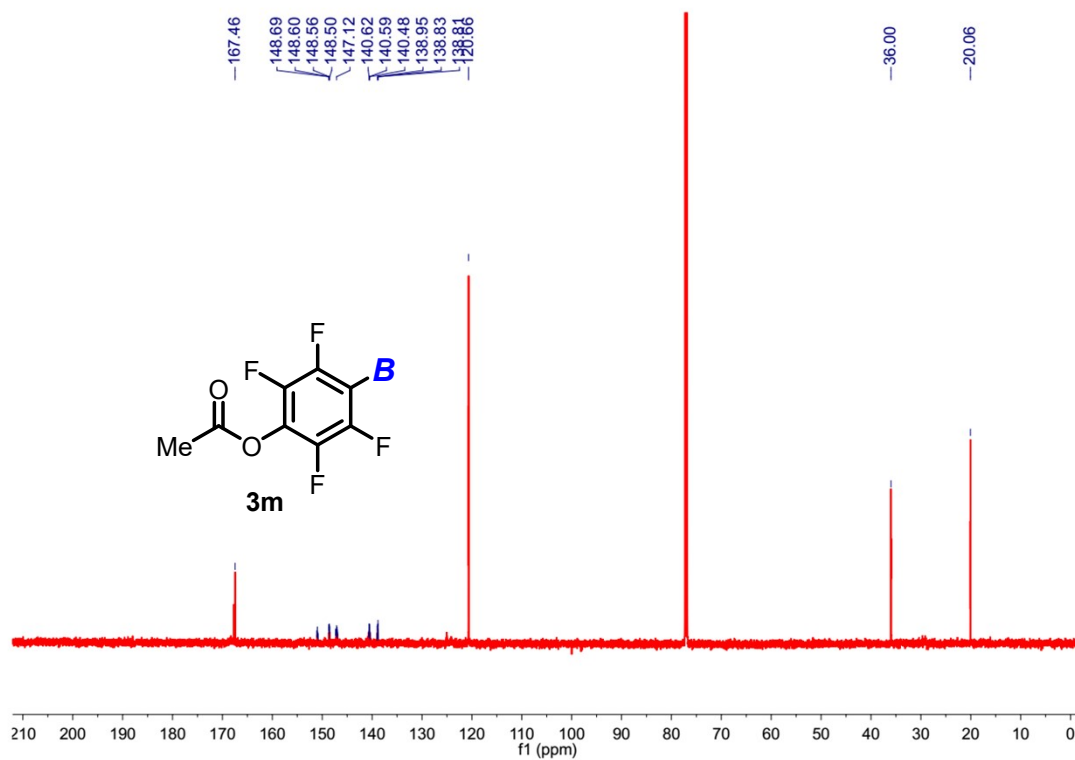


¹¹B NMR (193 MHz, CDCl₃)

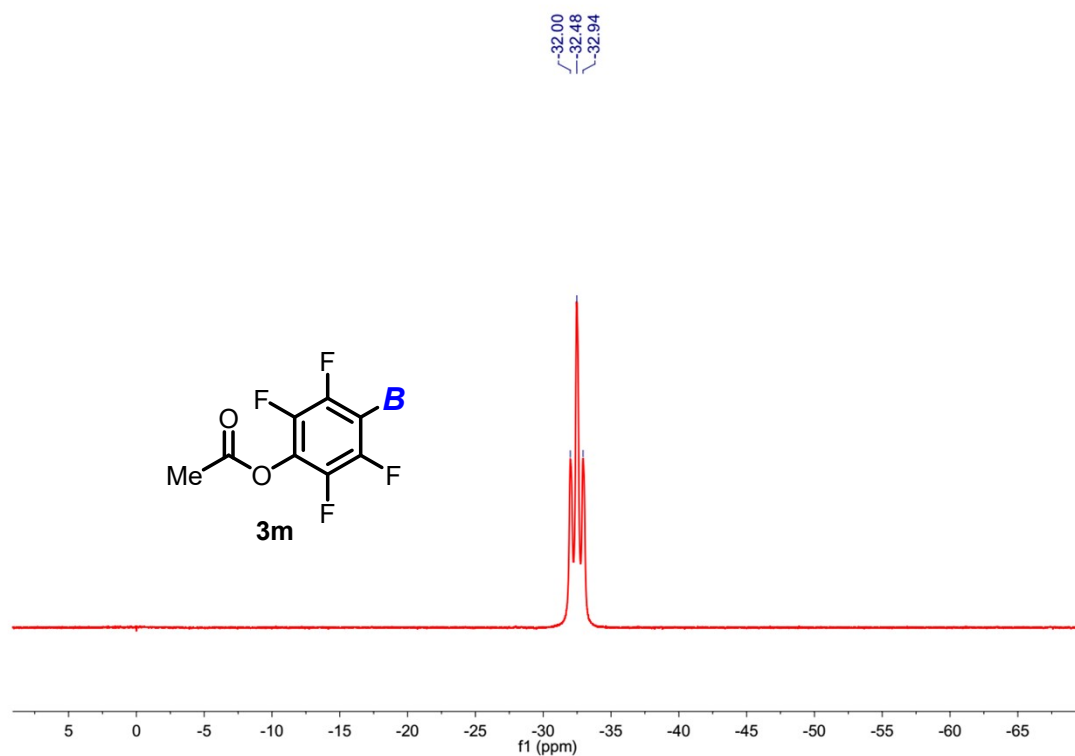


$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3)

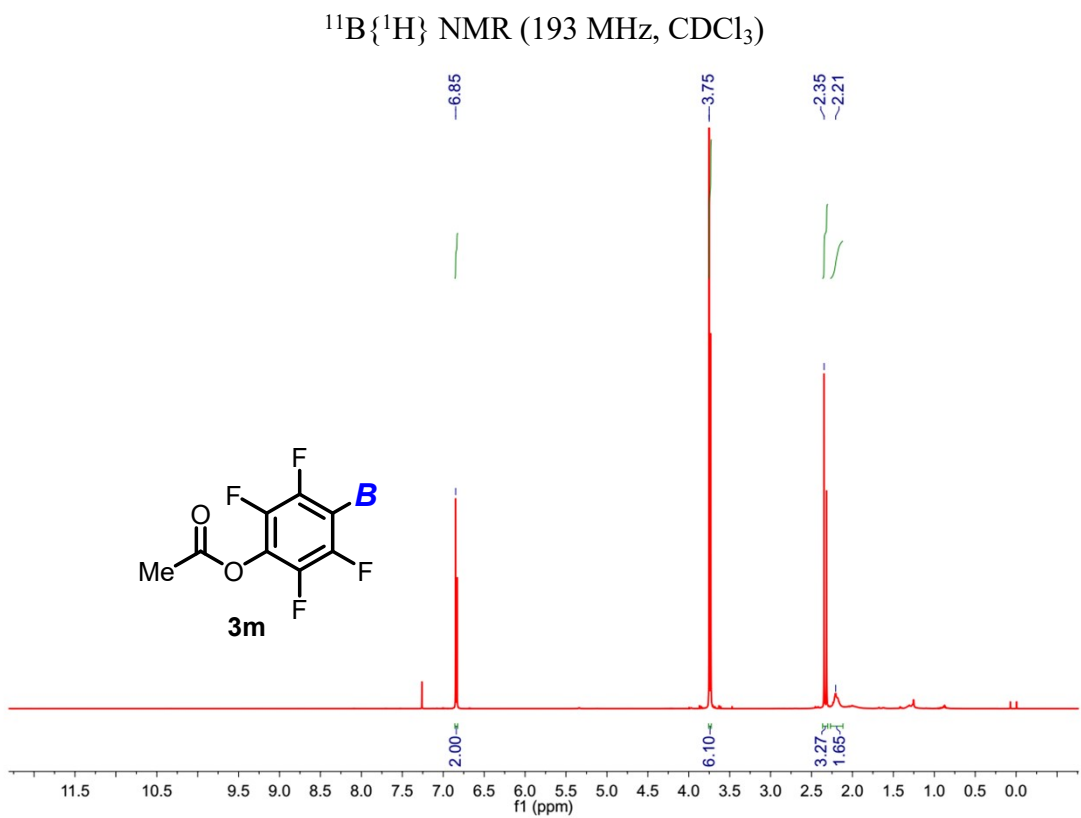
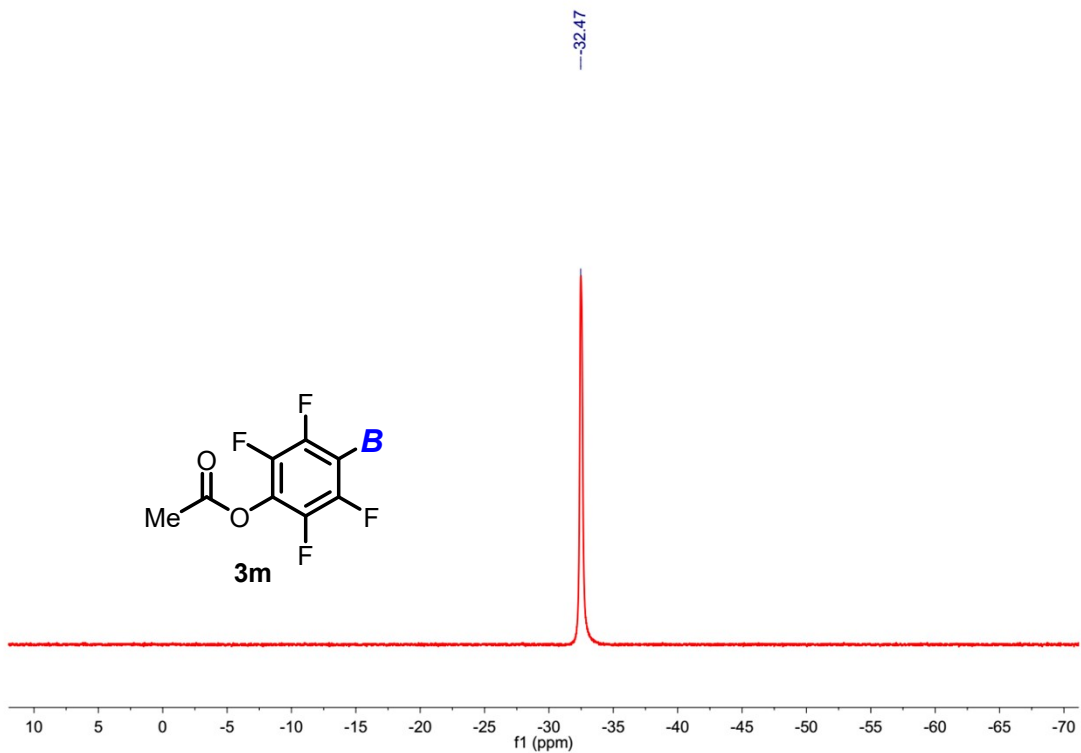


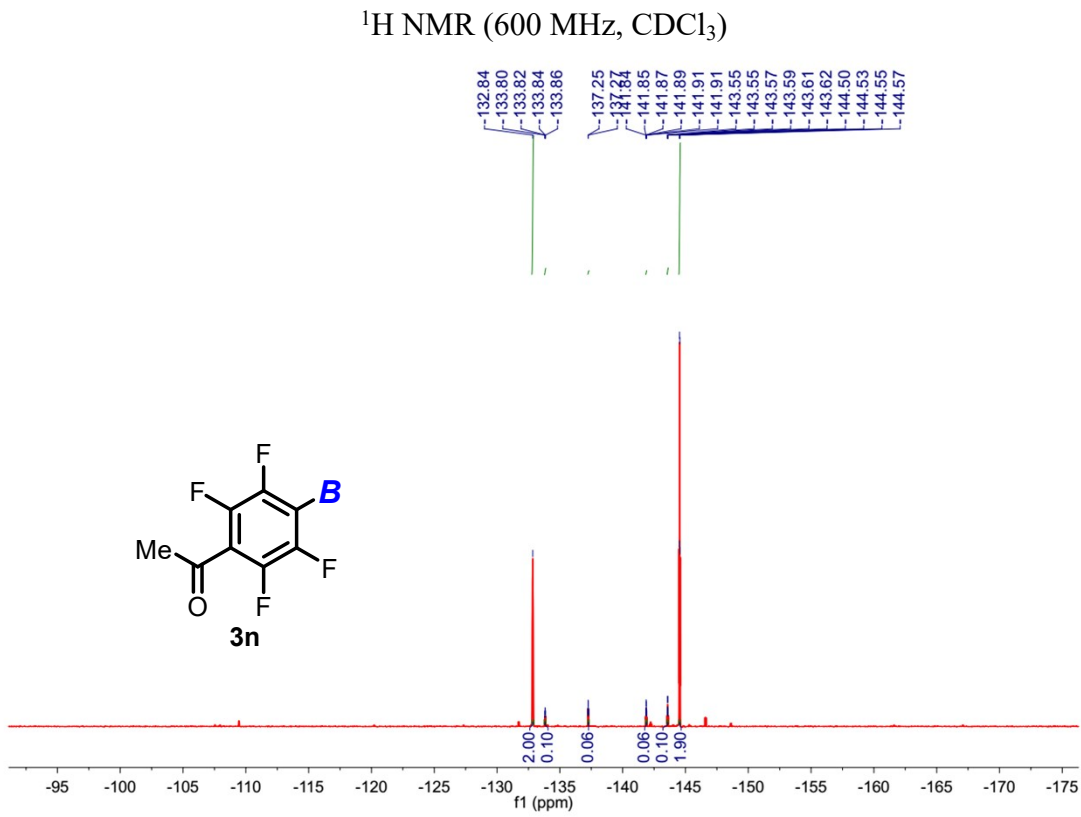
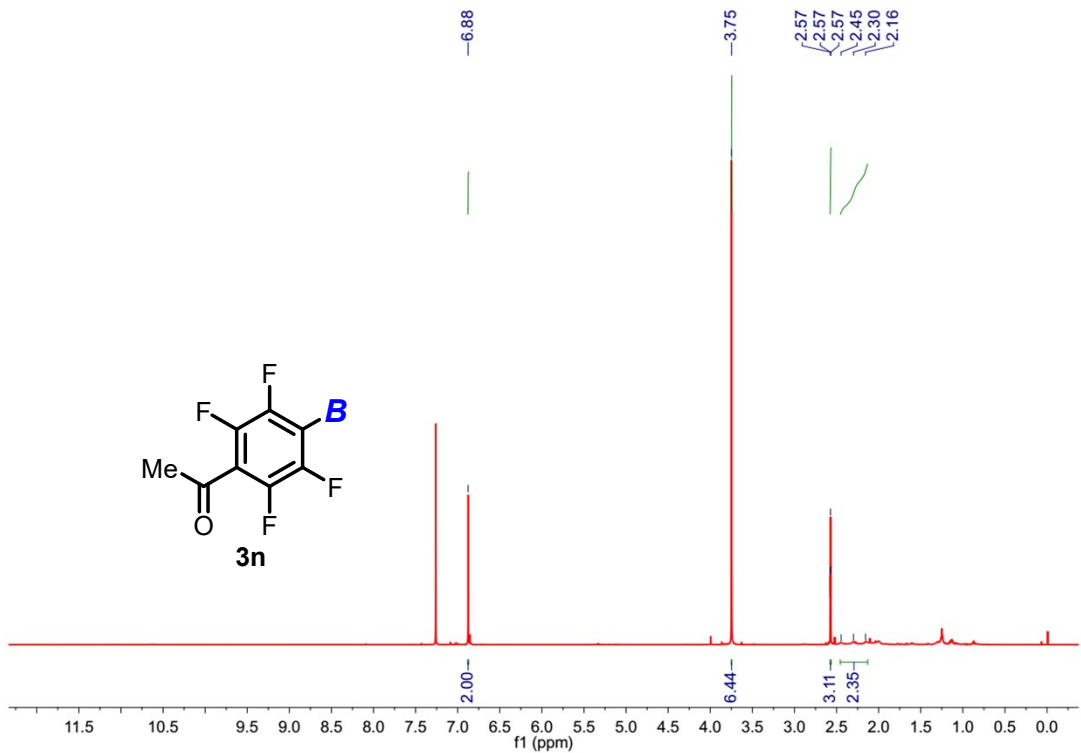


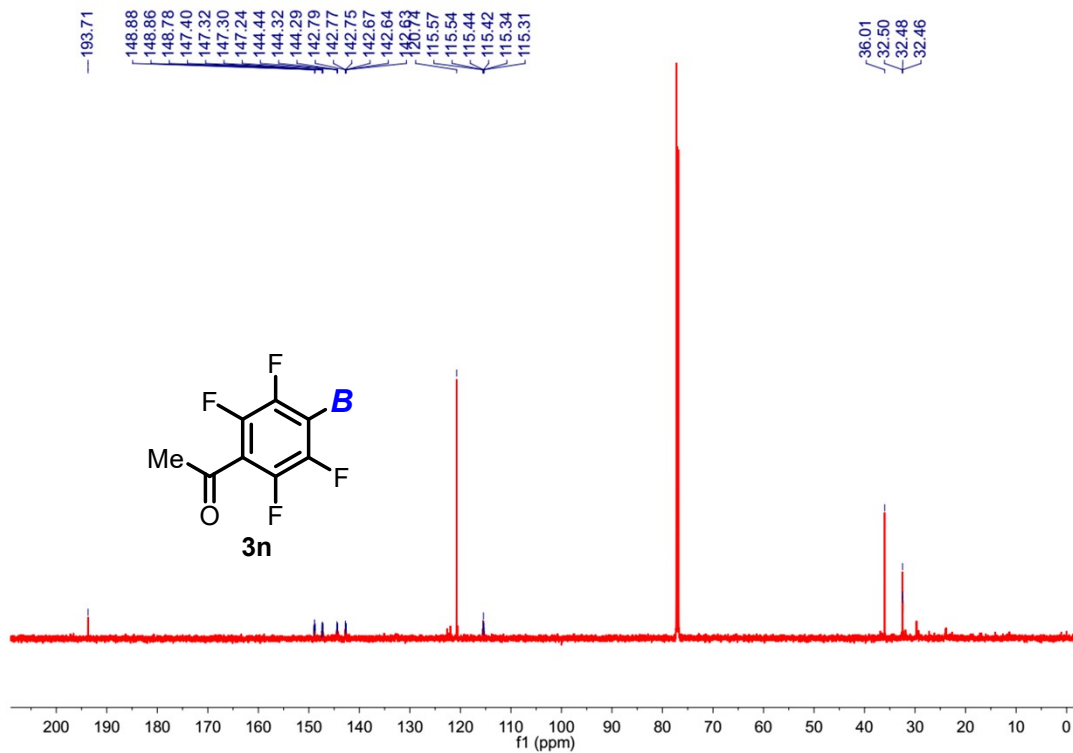
^{13}C NMR (151 MHz, CDCl_3)



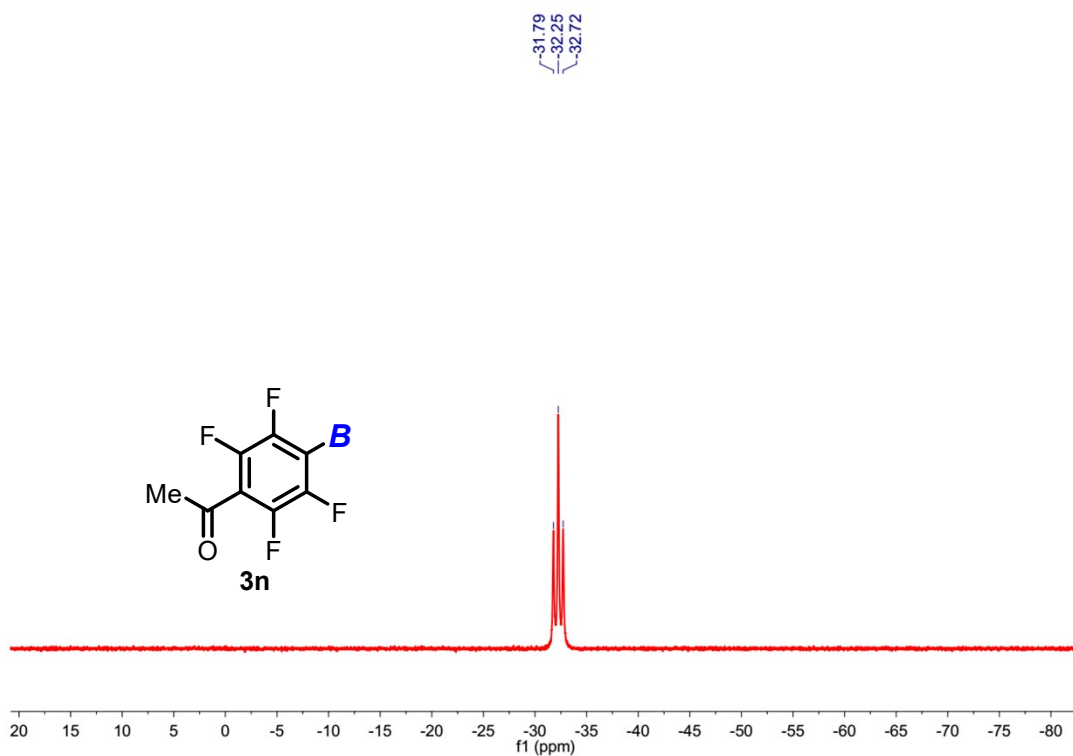
^{11}B NMR (193 MHz, CDCl_3)



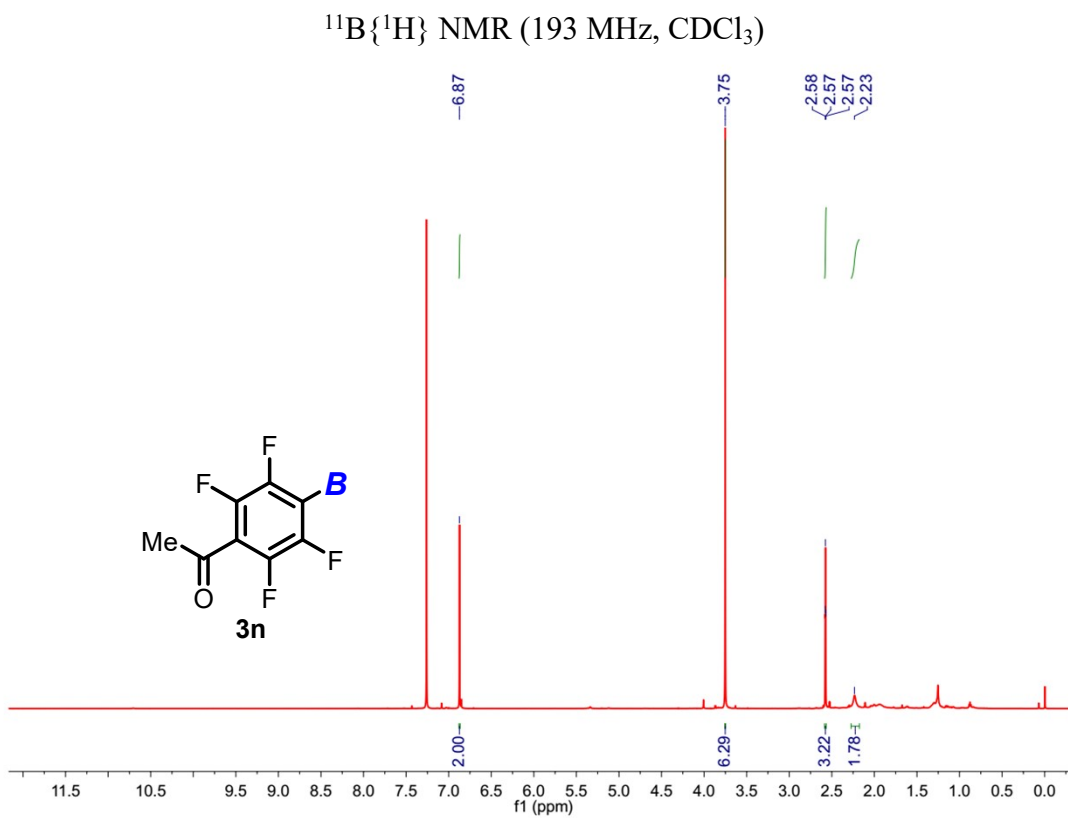
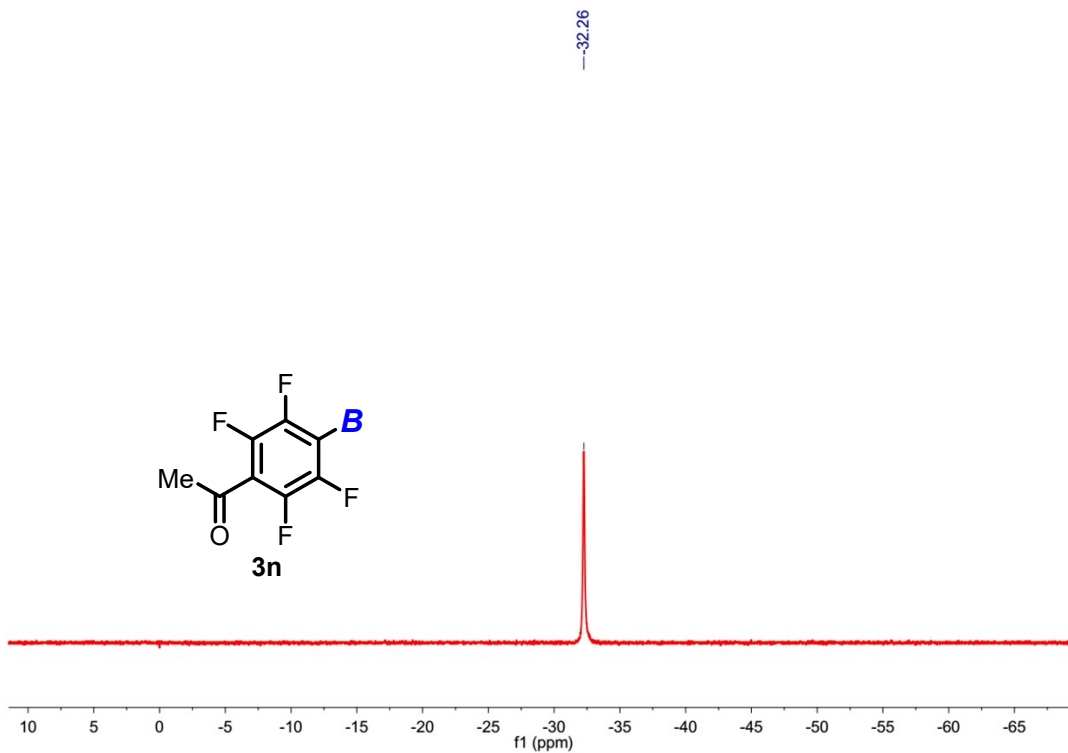


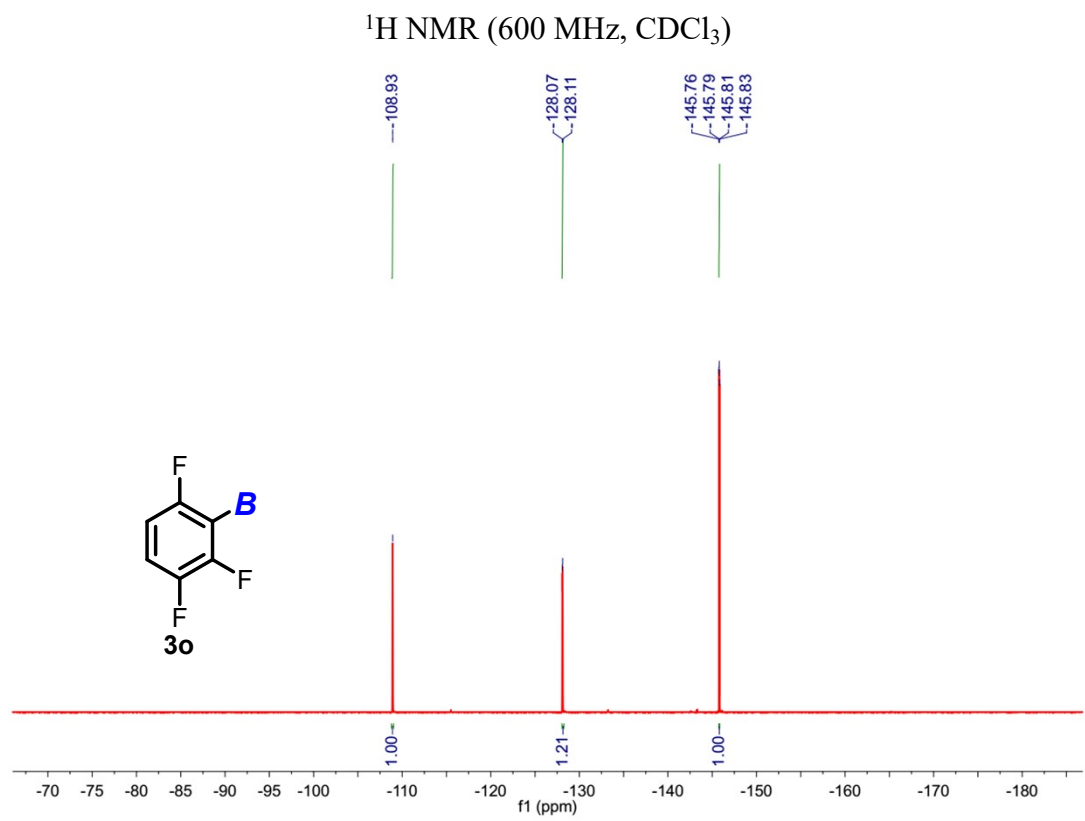
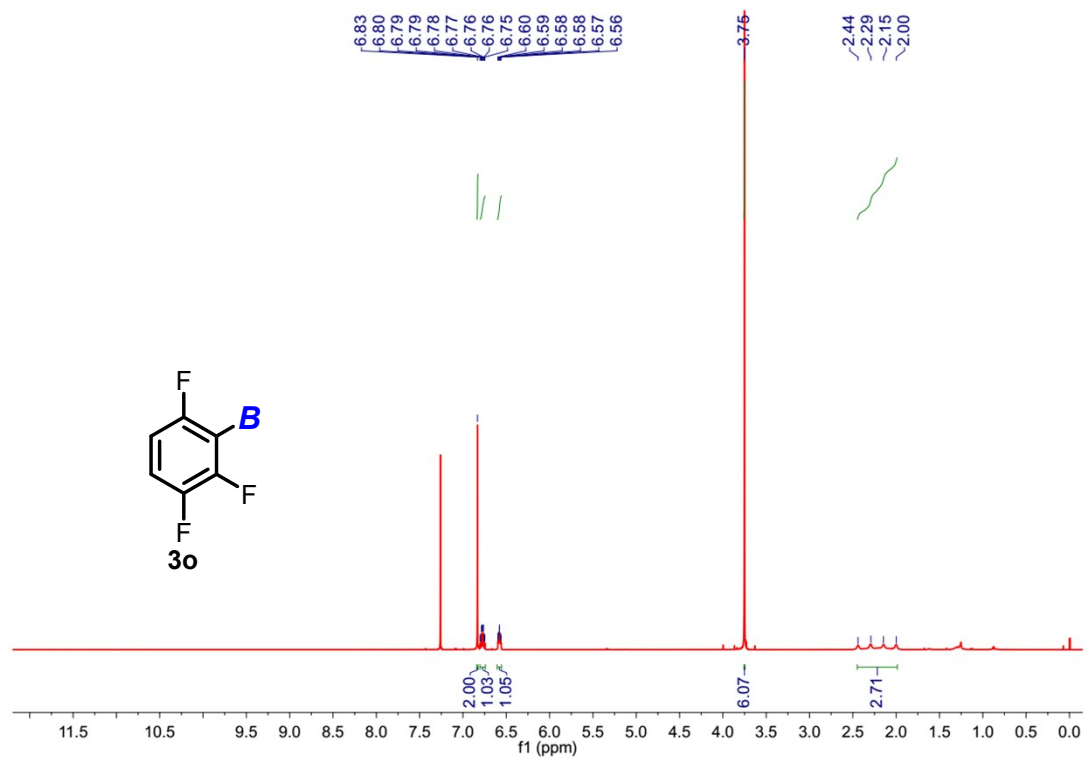


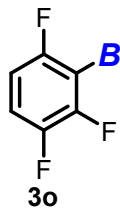
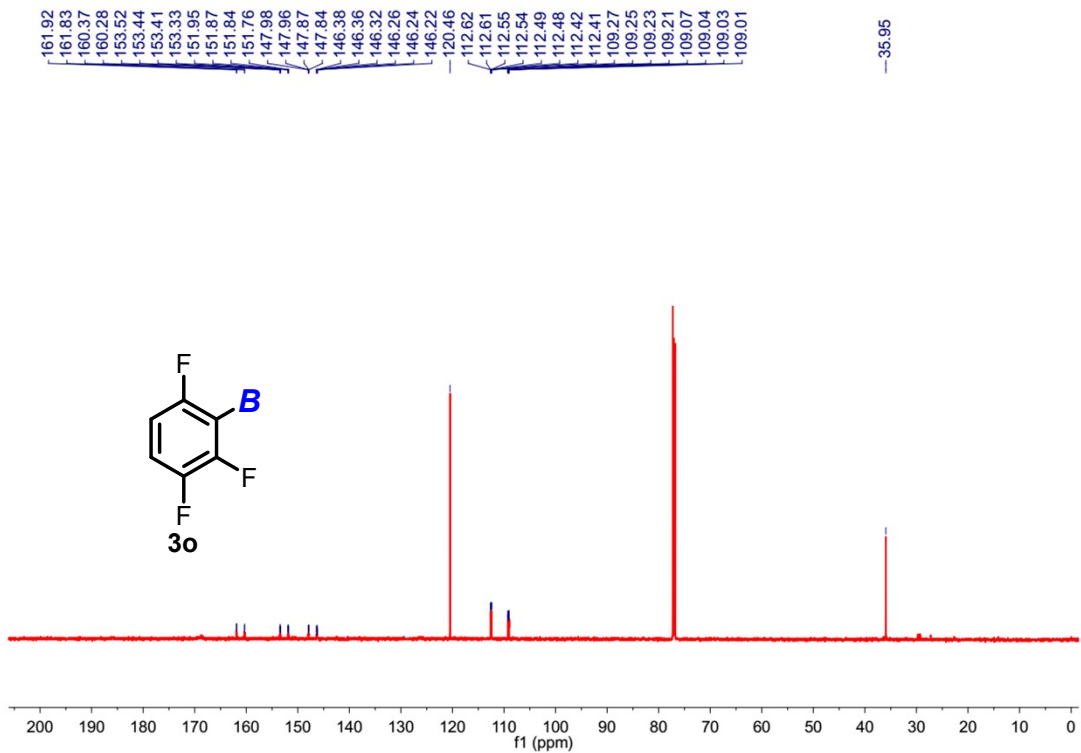
^{13}C NMR (151 MHz, CDCl_3)



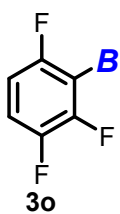
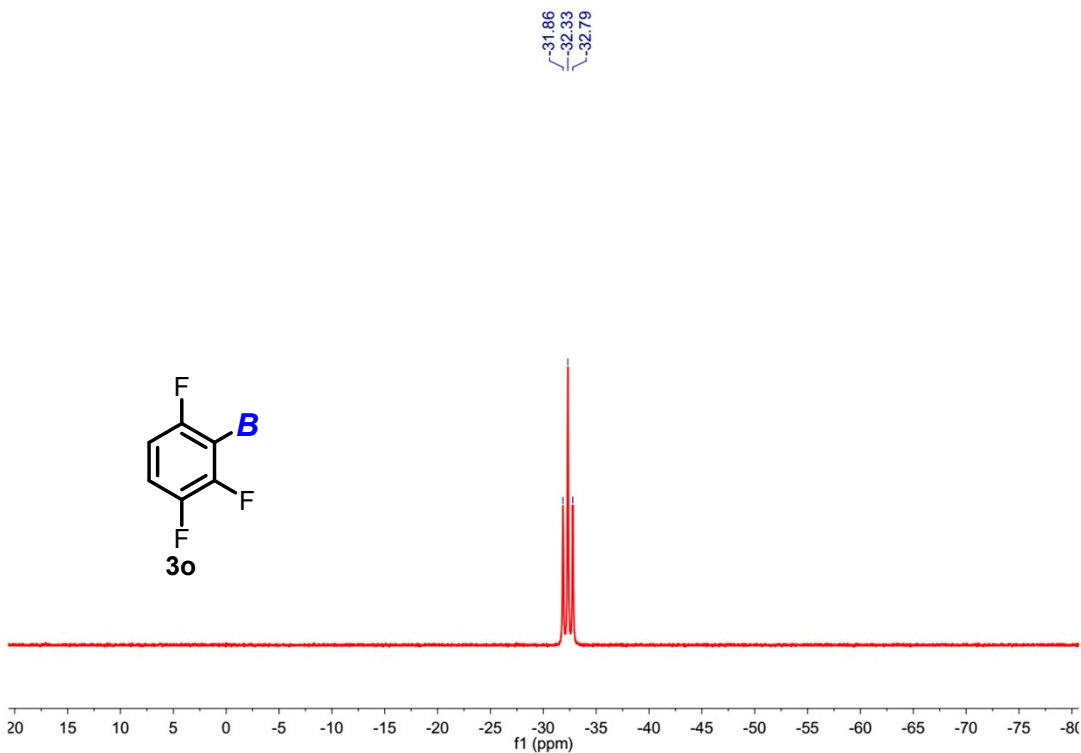
^{11}B NMR (193 MHz, CDCl_3)



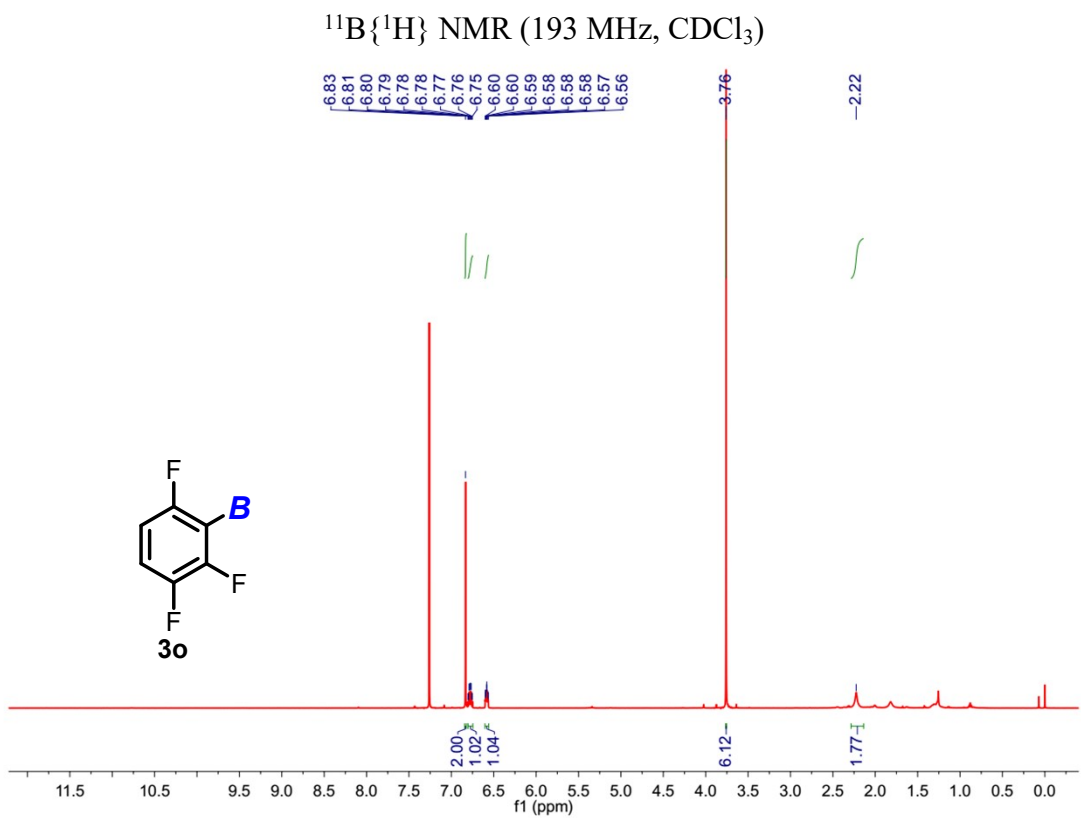
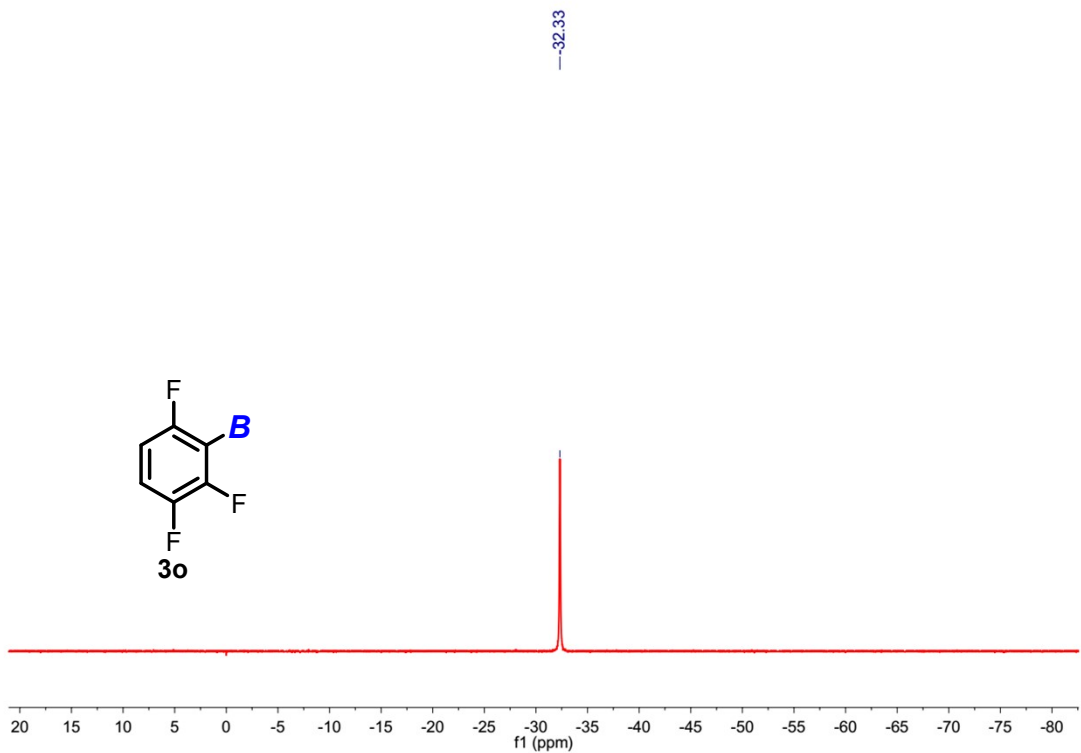




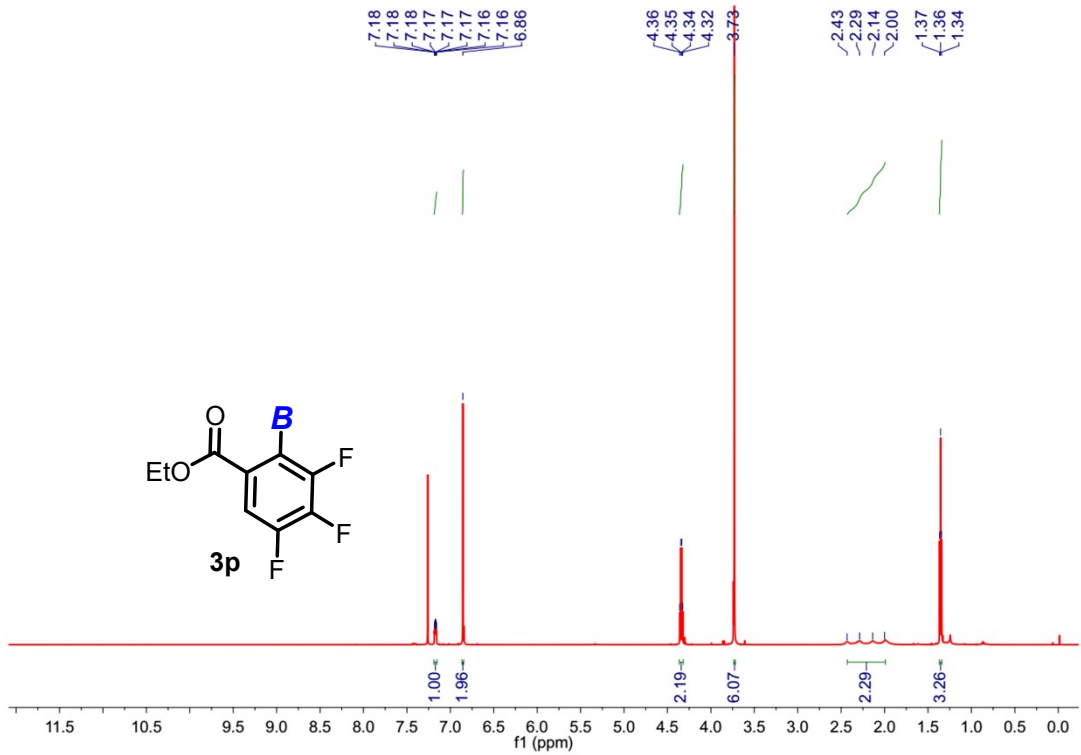
^{13}C NMR (151 MHz, CDCl_3)



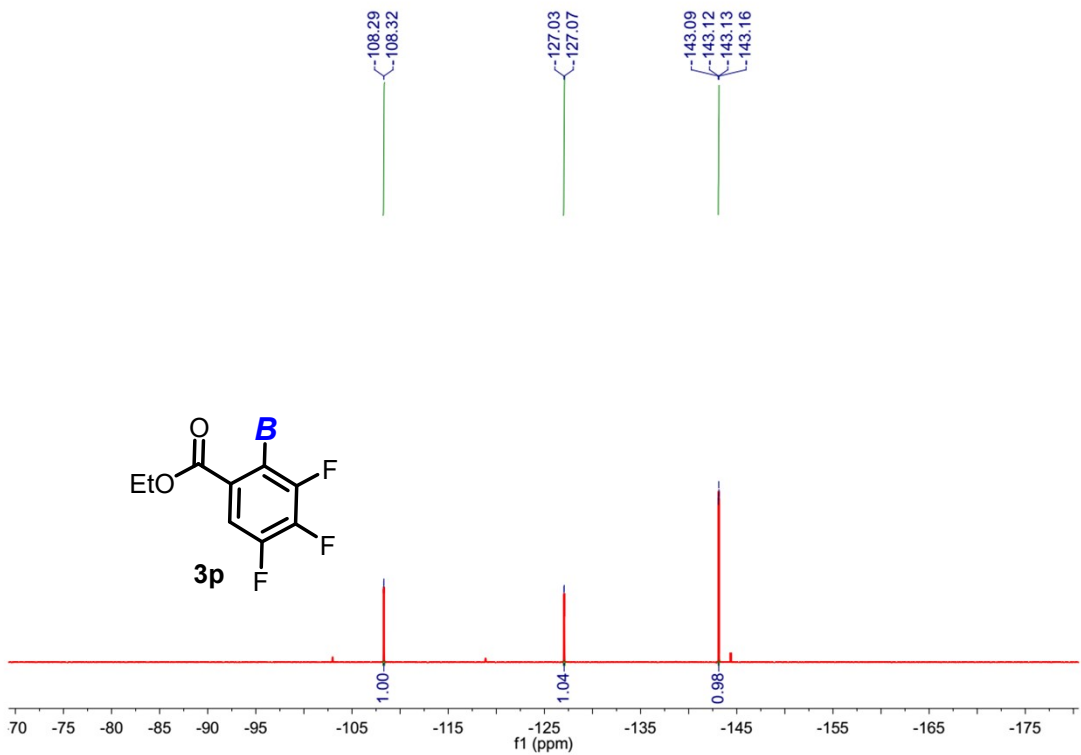
^{11}B NMR (193 MHz, CDCl_3)



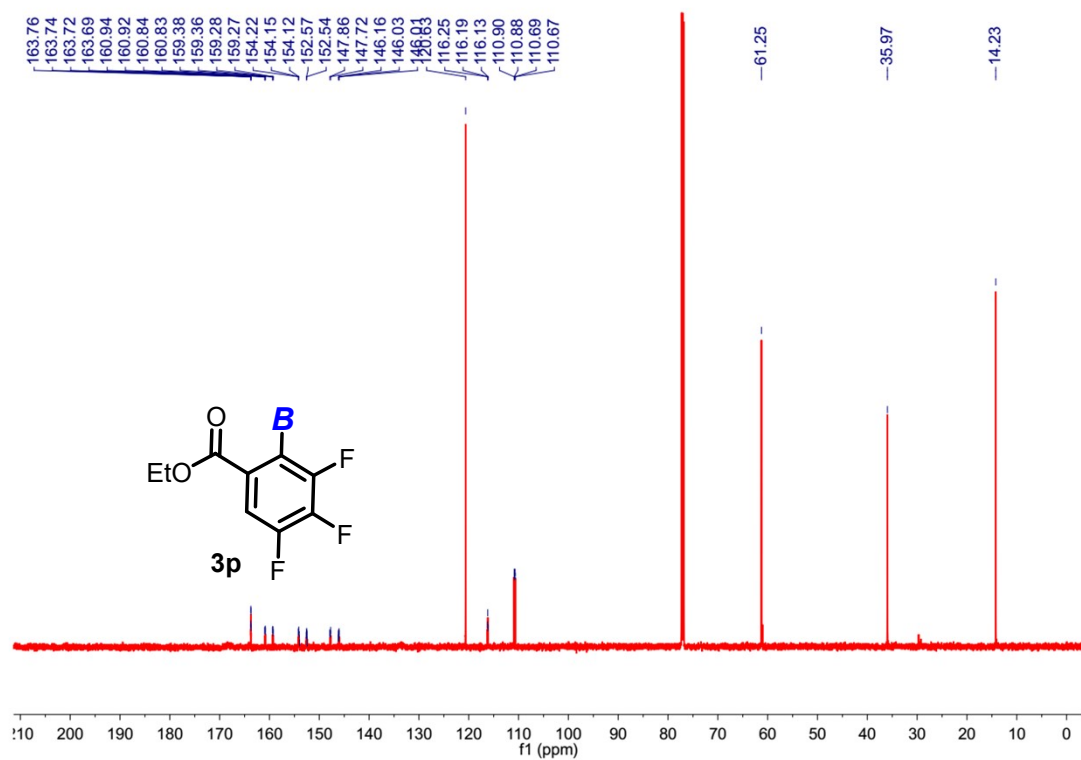
$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3)



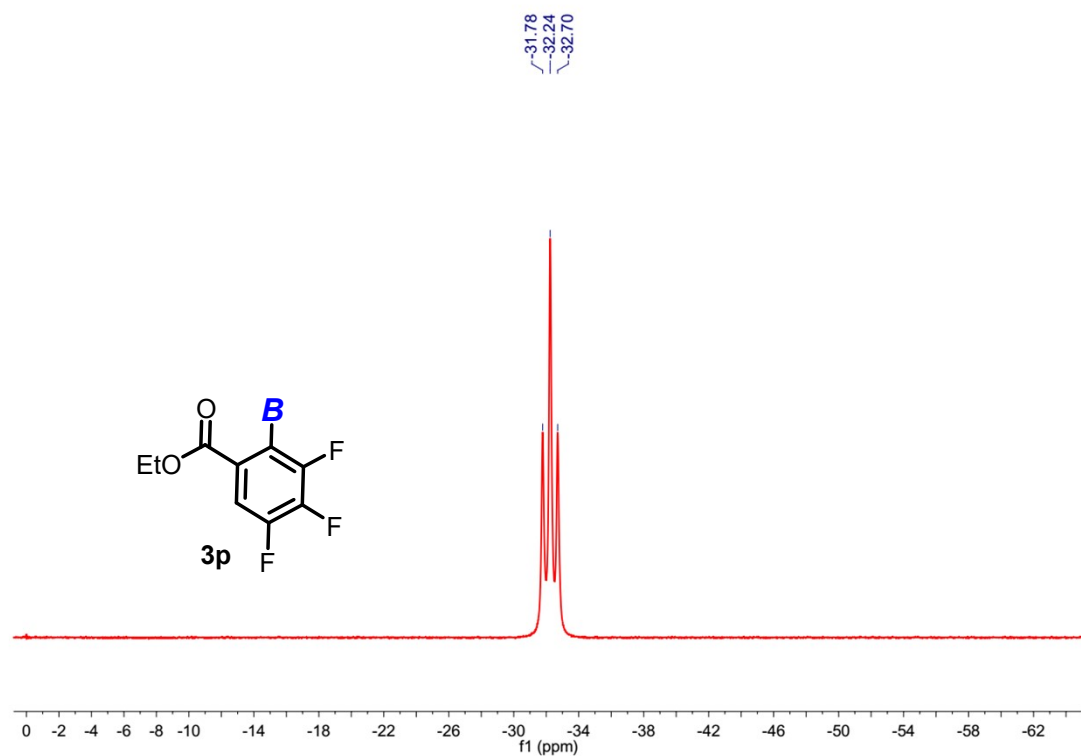
¹H NMR (600 MHz, CDCl₃)



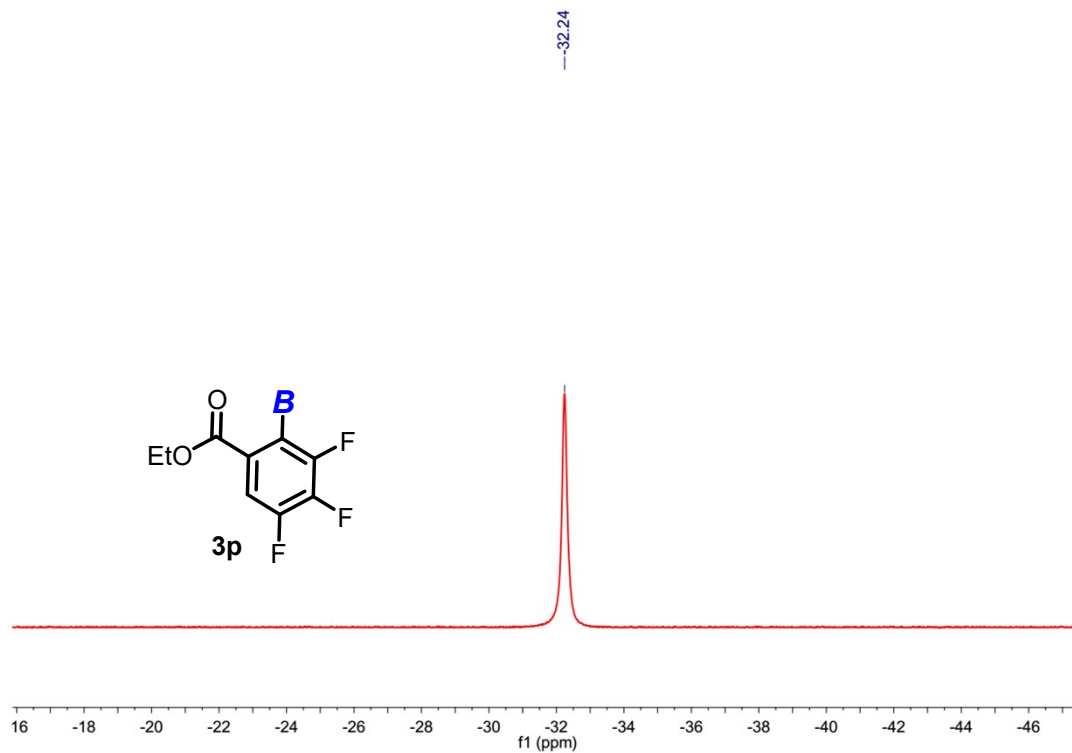
¹⁹F NMR (565 MHz, CDCl₃)



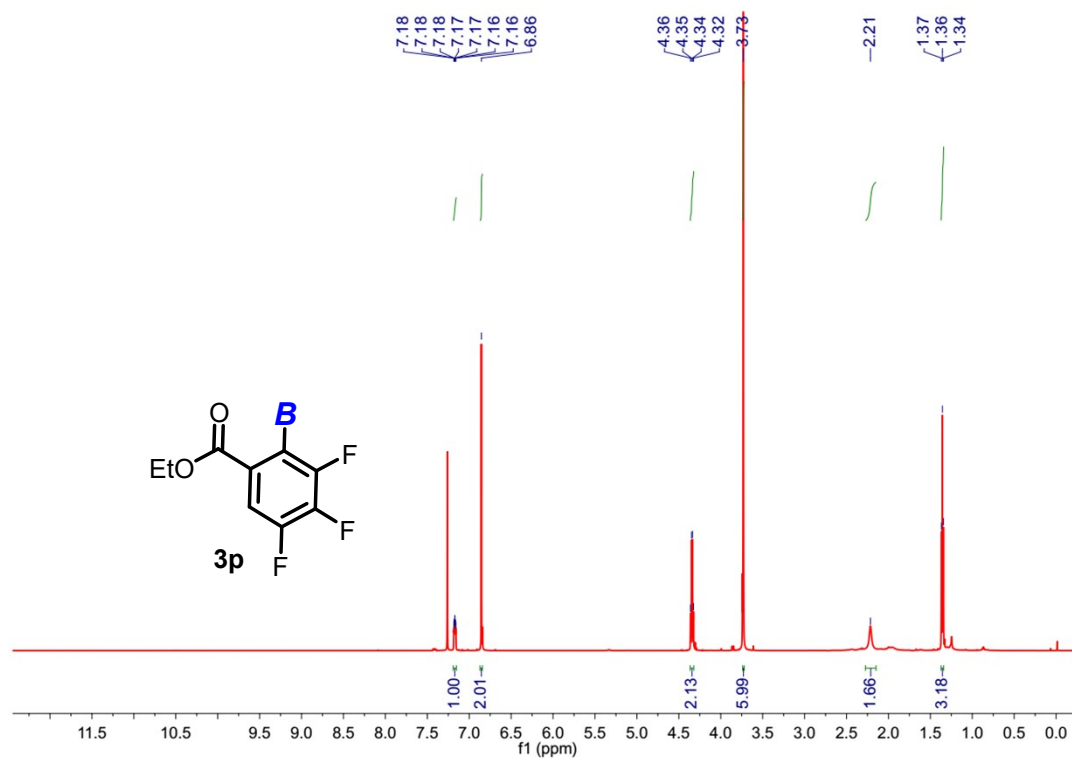
¹³C NMR (151 MHz, CDCl₃)



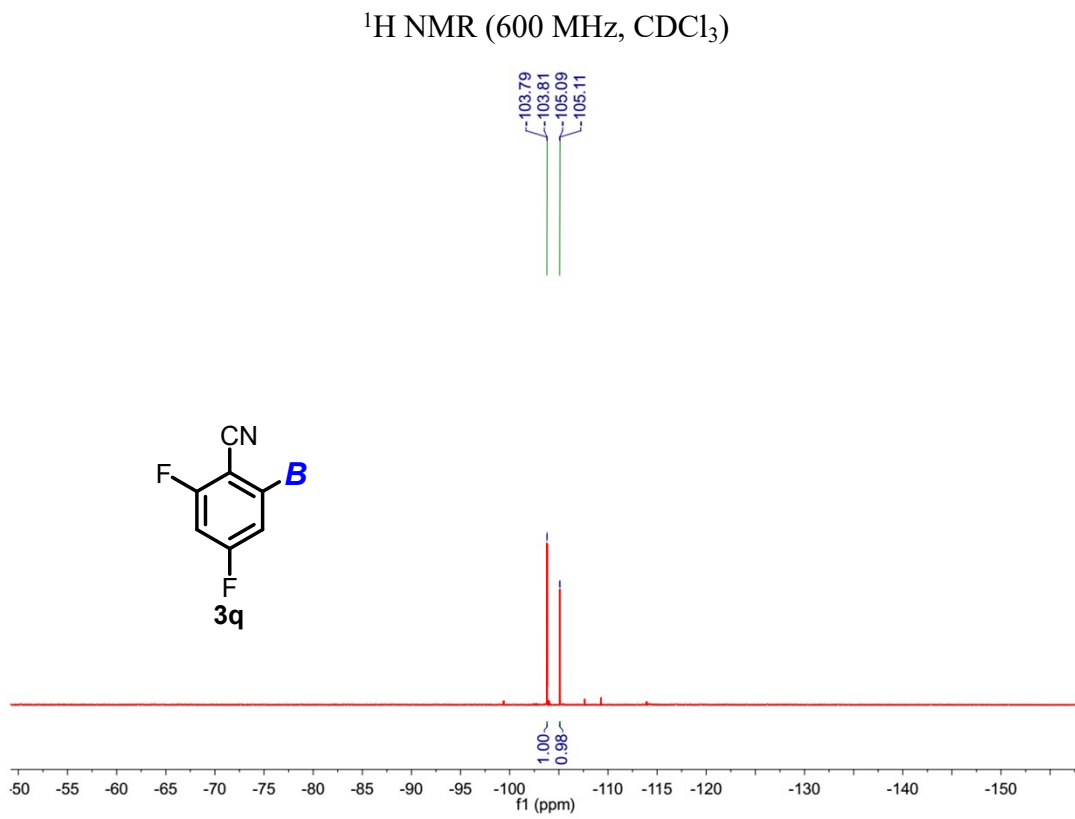
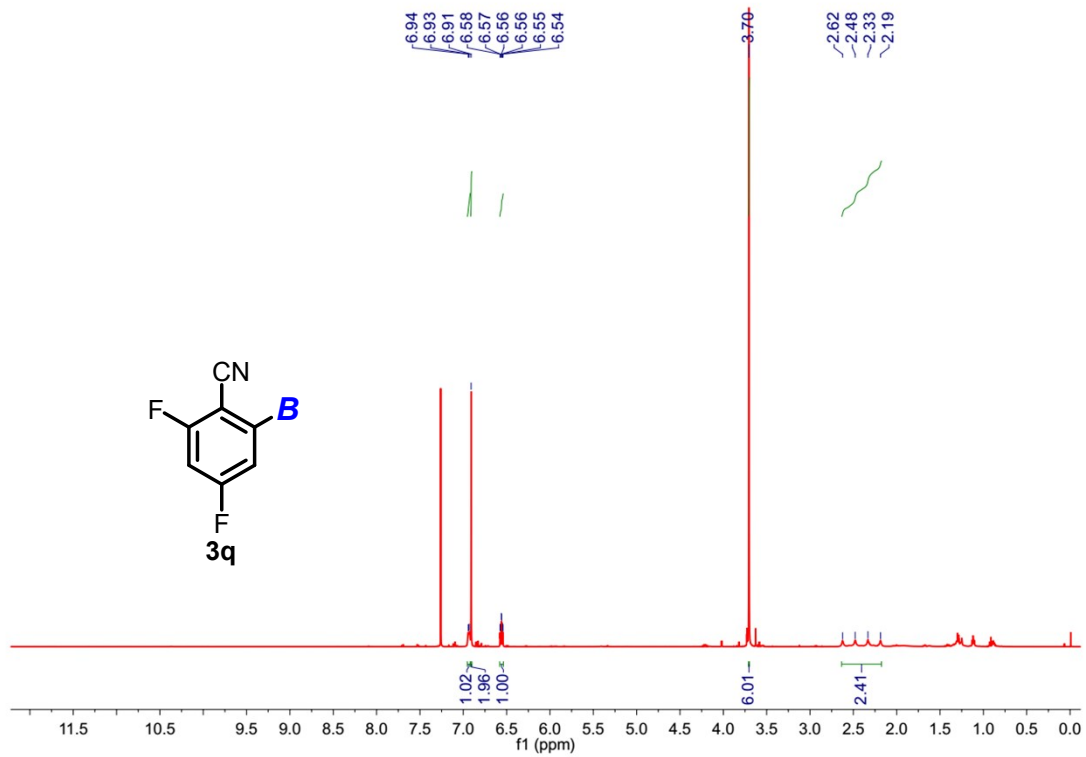
¹¹B NMR (193 MHz, CDCl₃)

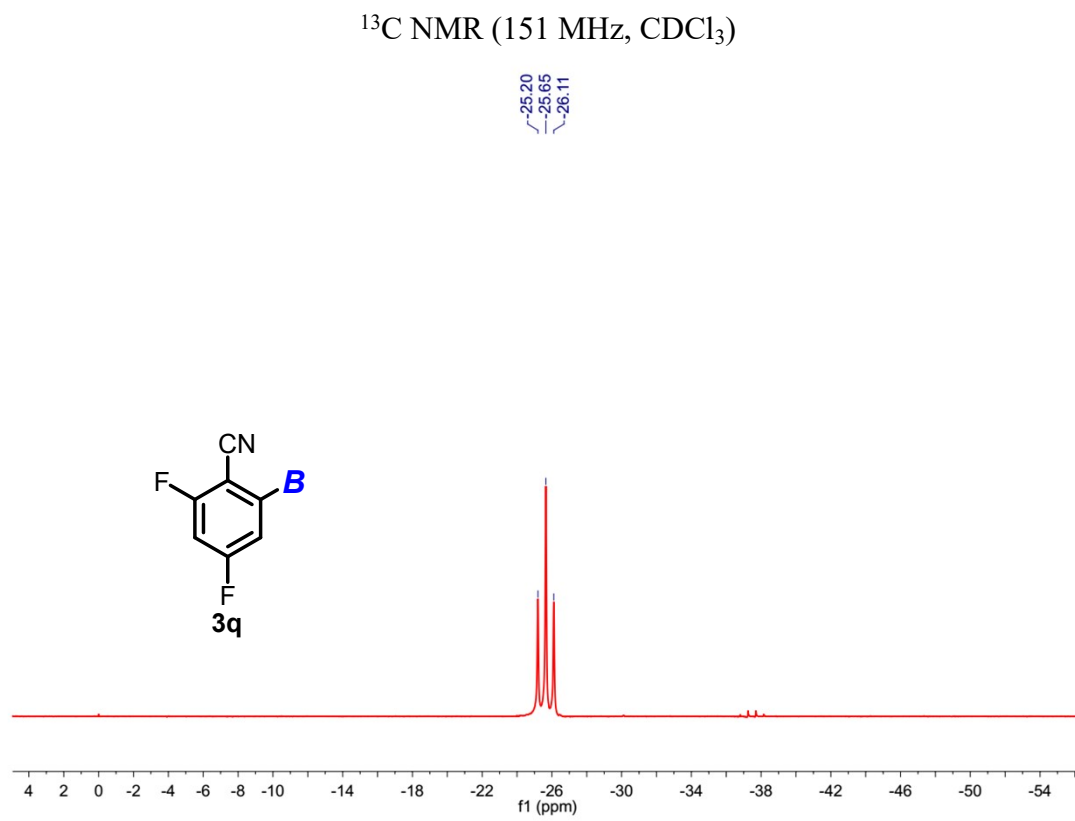
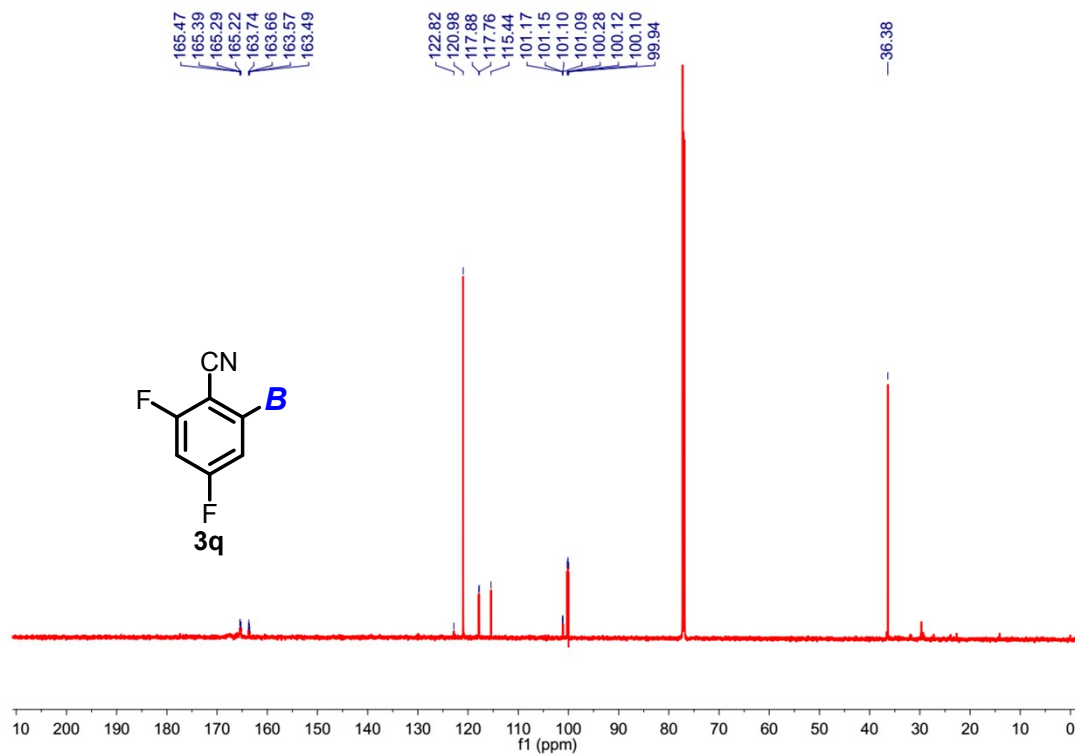


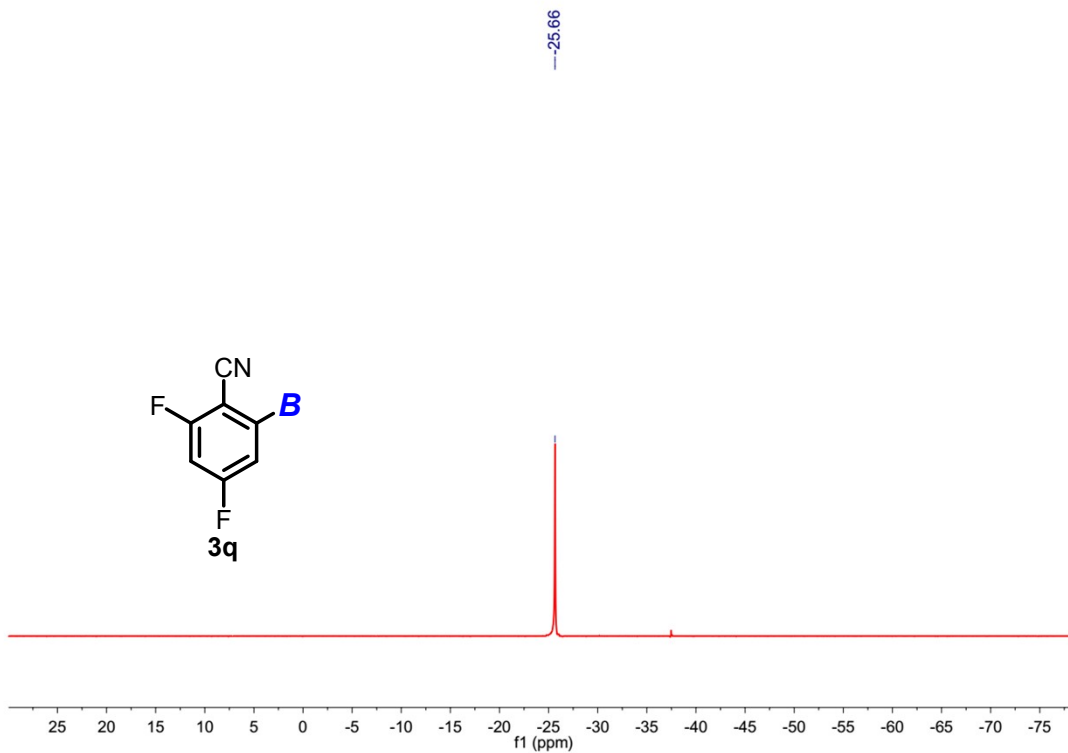
$^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3)



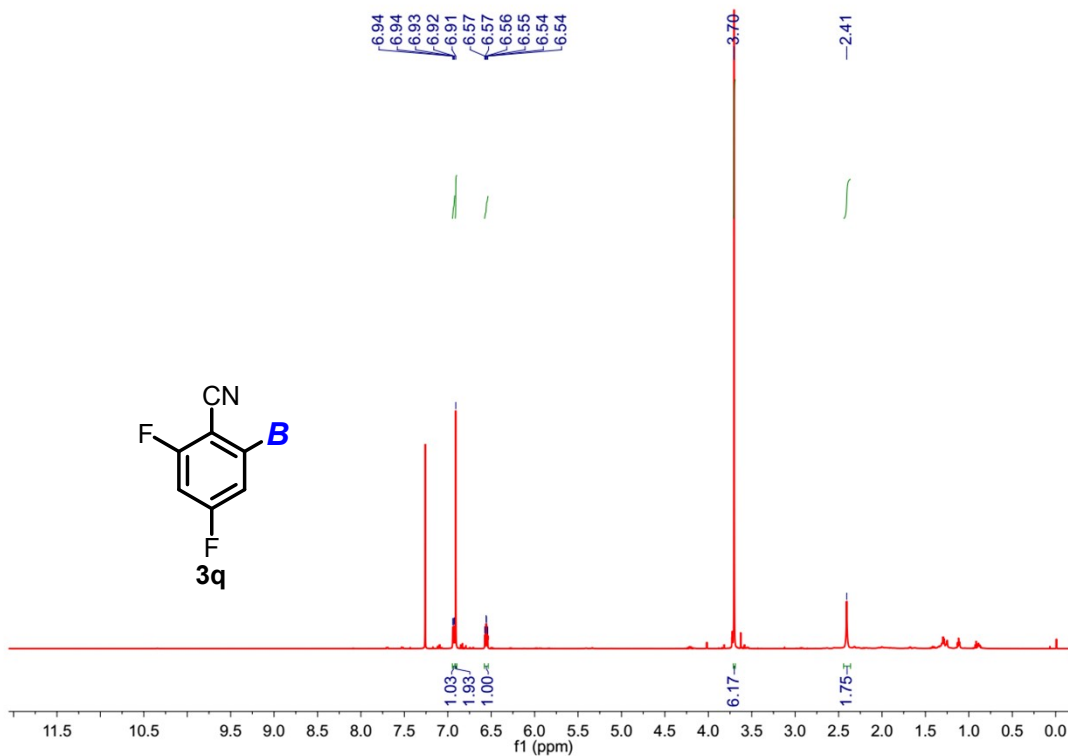
$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3)



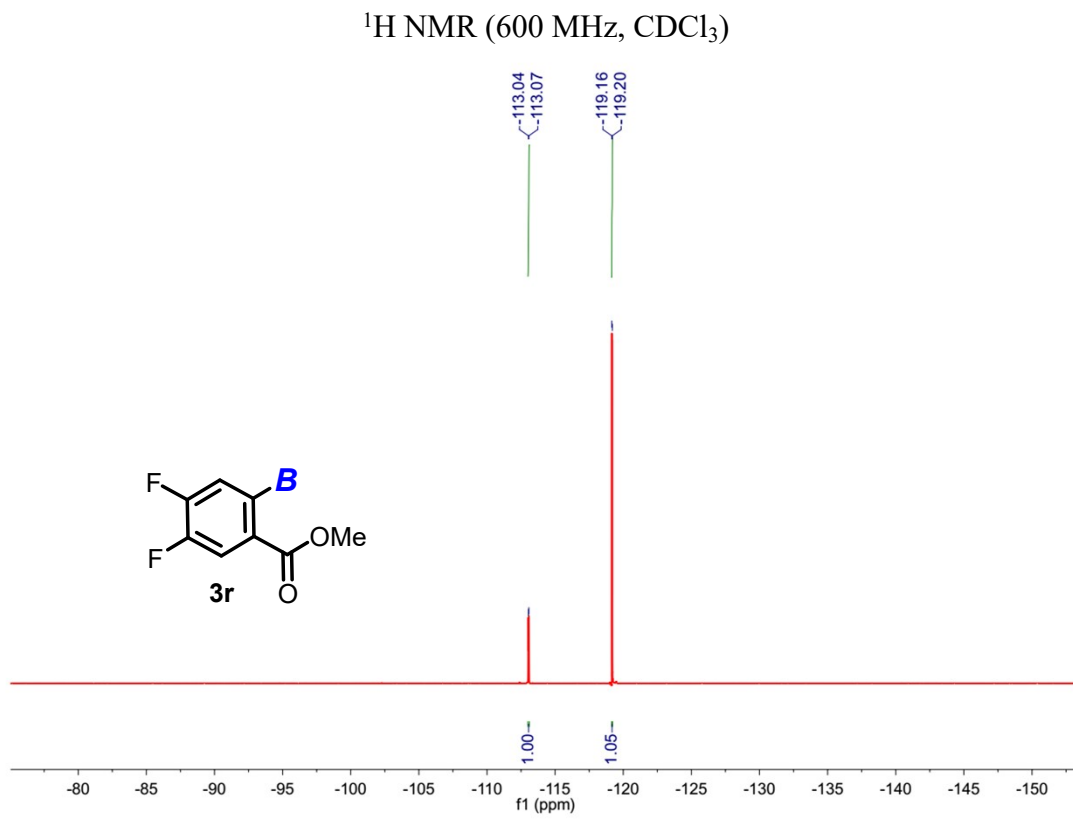
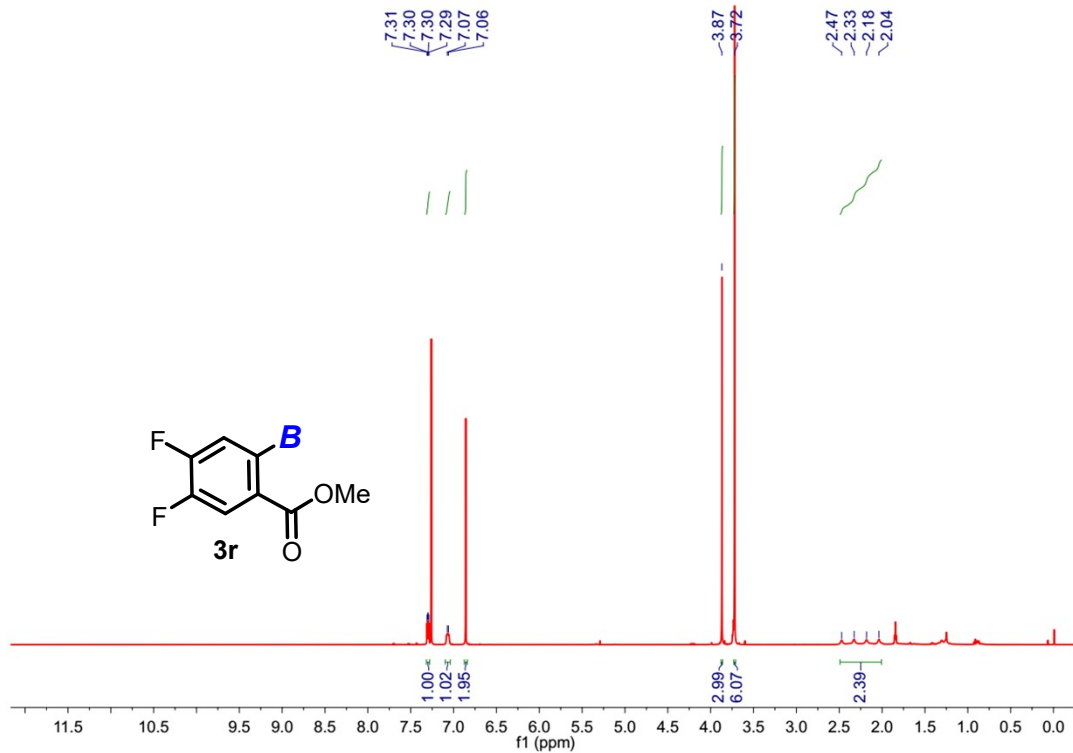


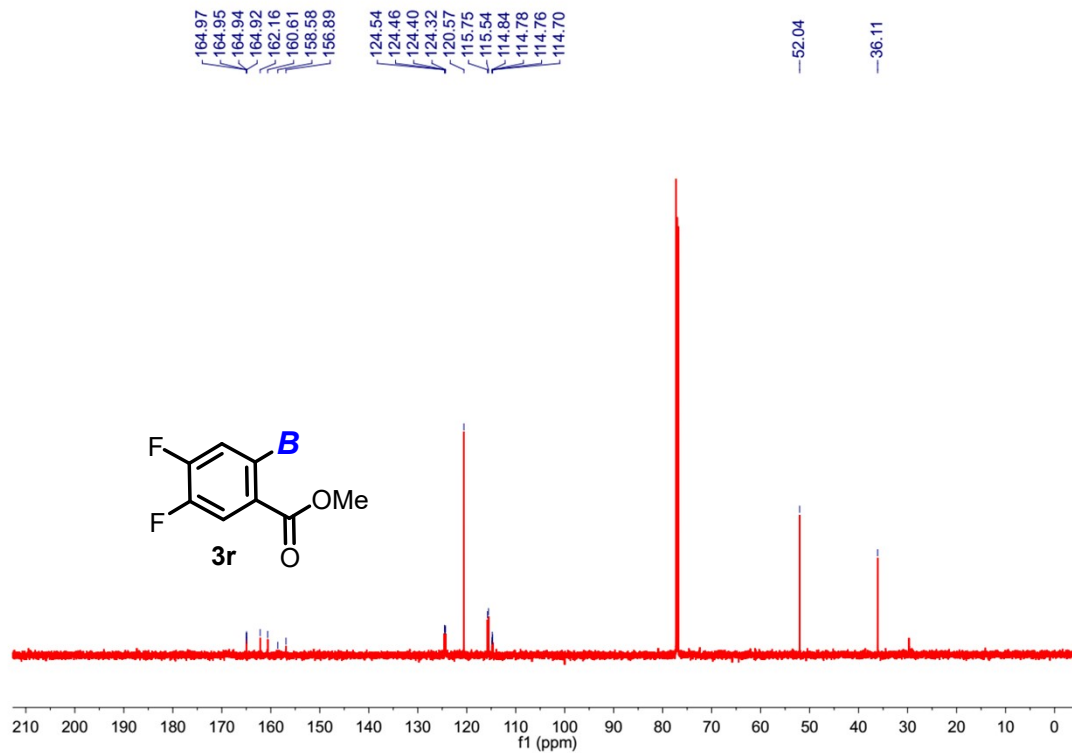


$^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3)

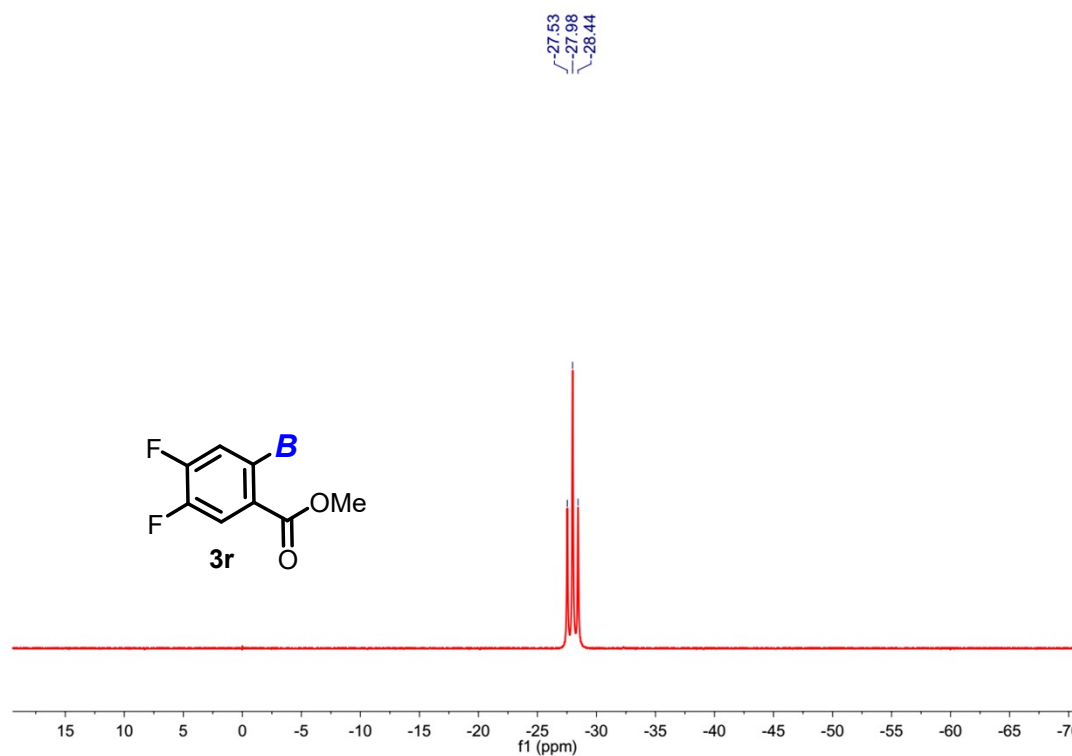


$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3)

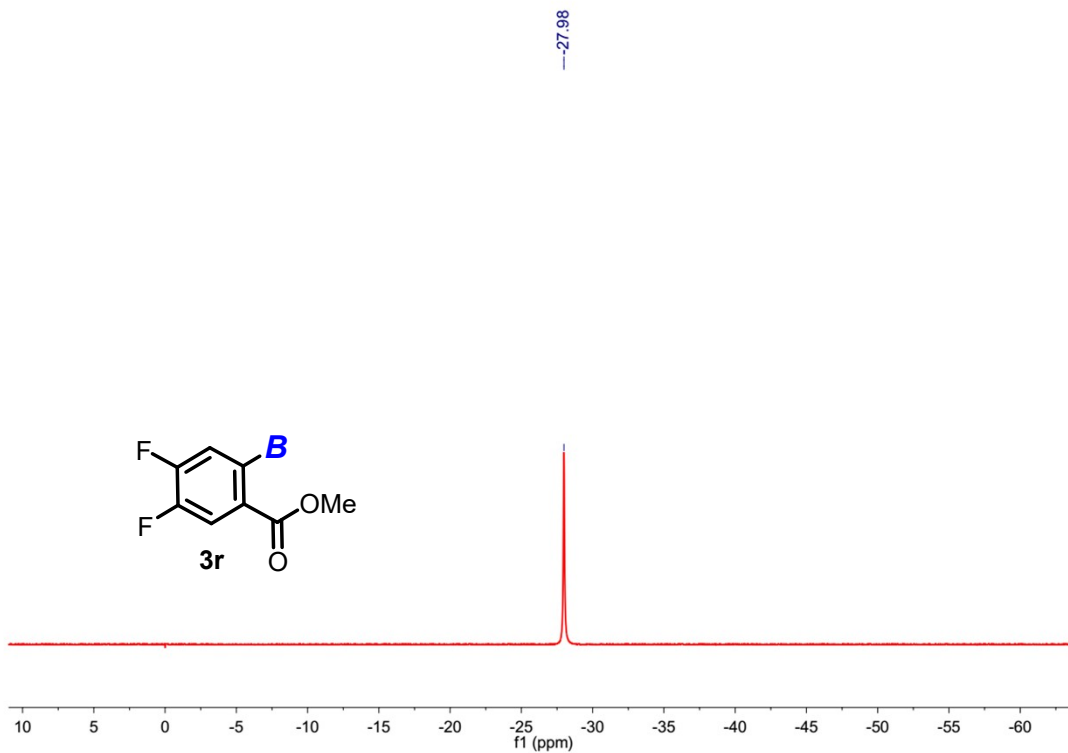




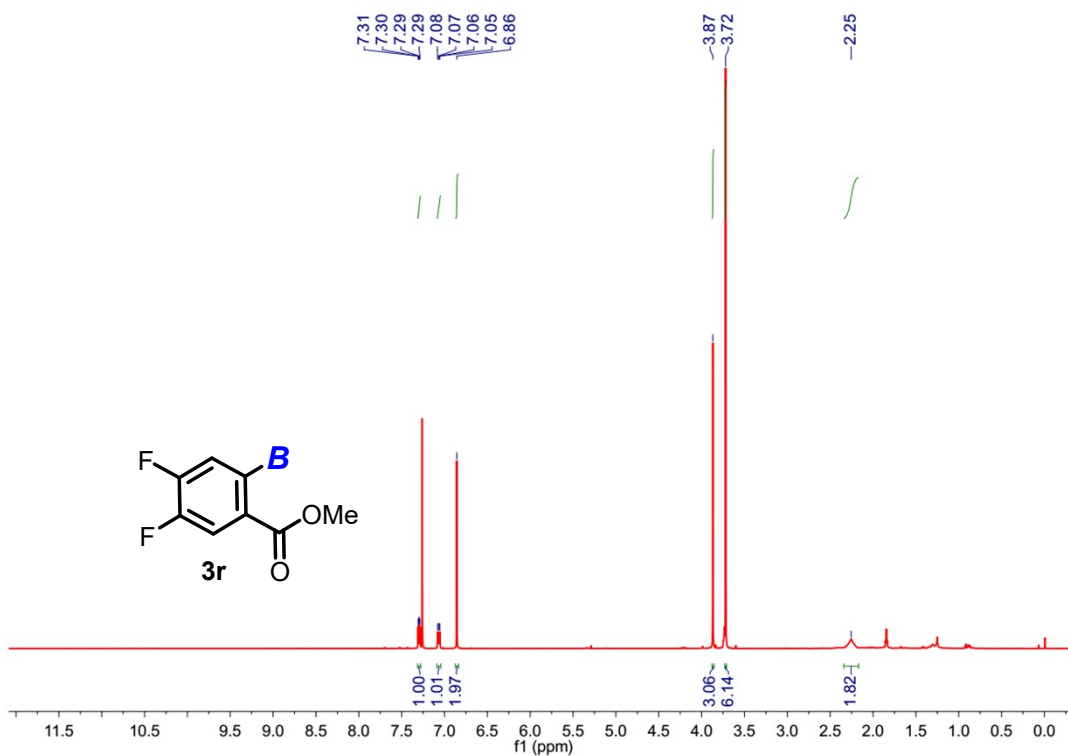
^{13}C NMR (151 MHz, CDCl_3)



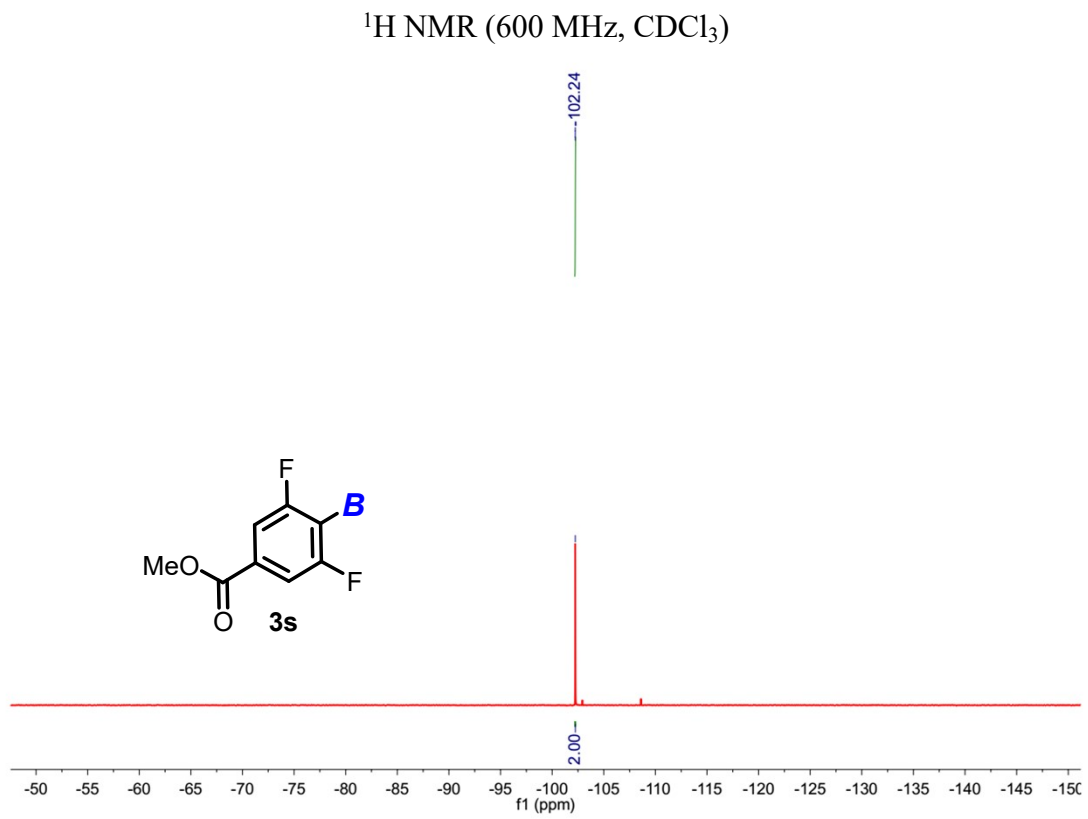
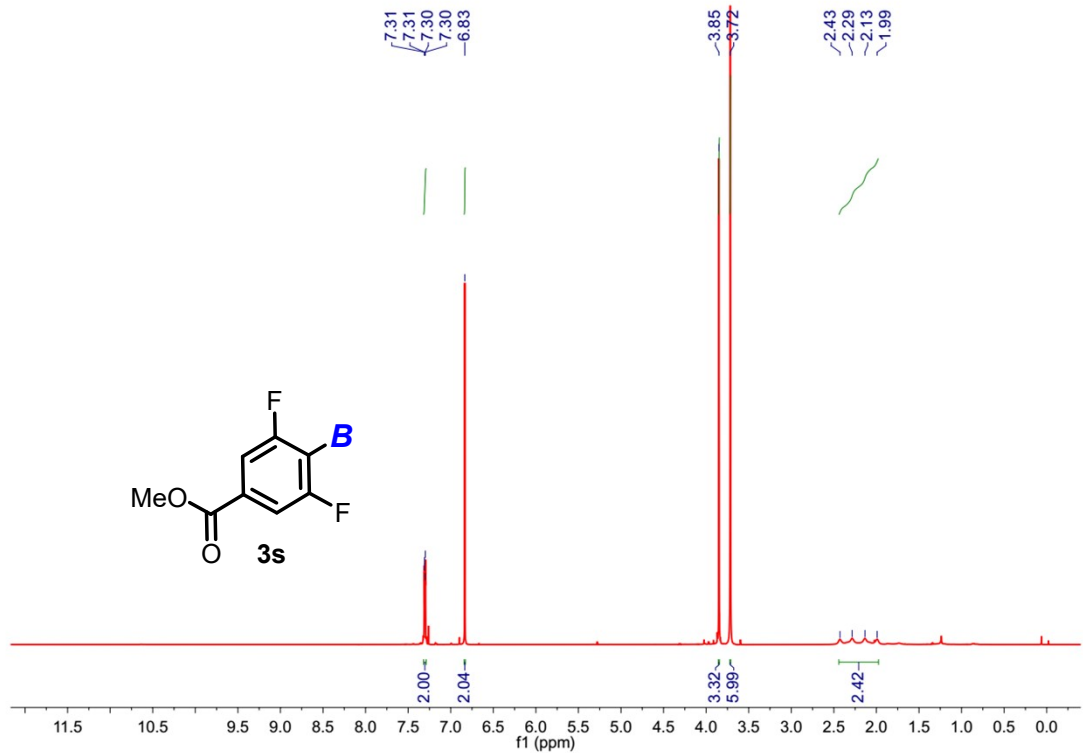
^{11}B NMR (193 MHz, CDCl_3)

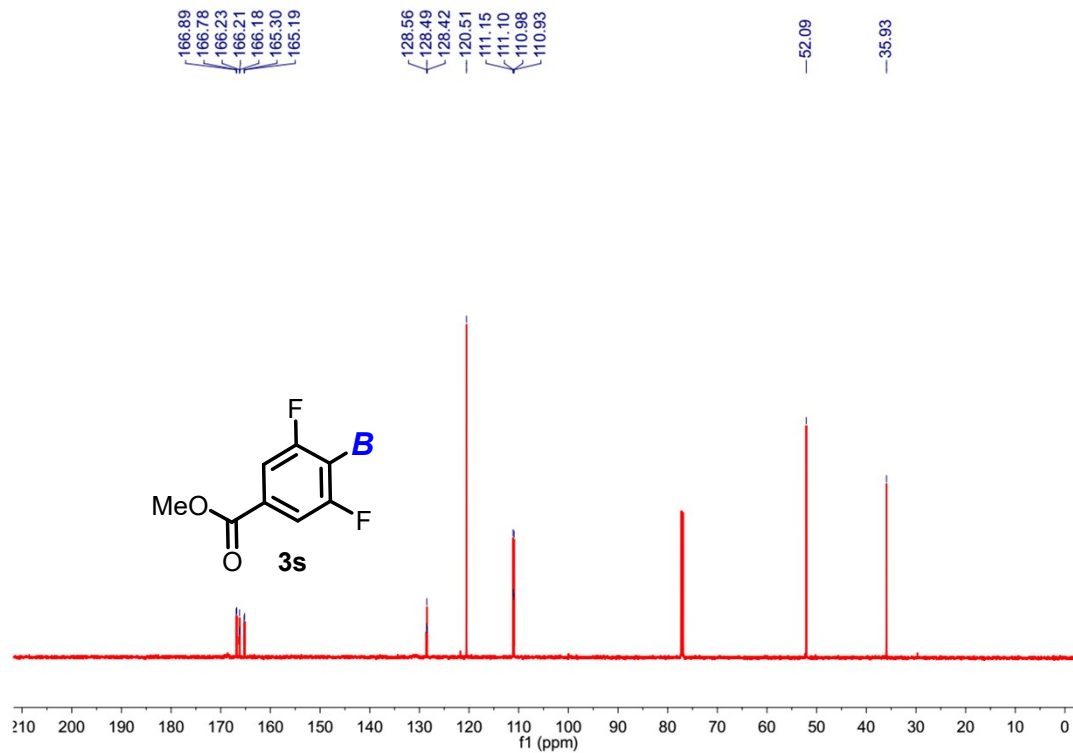


$^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3)

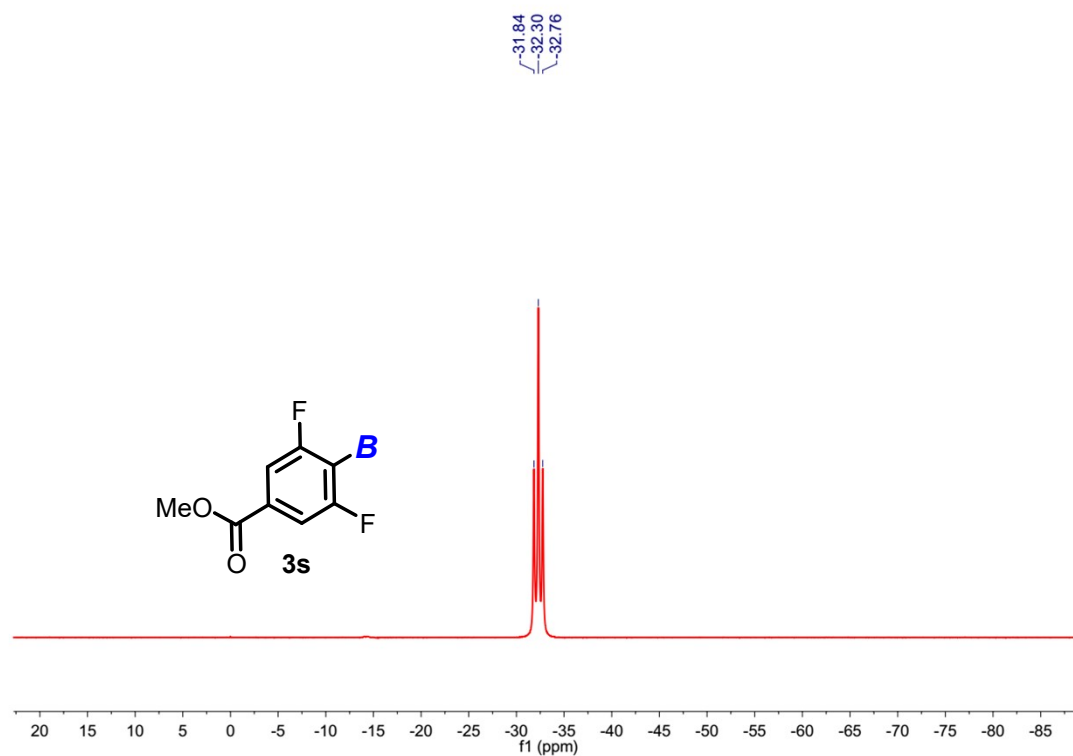


$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3)

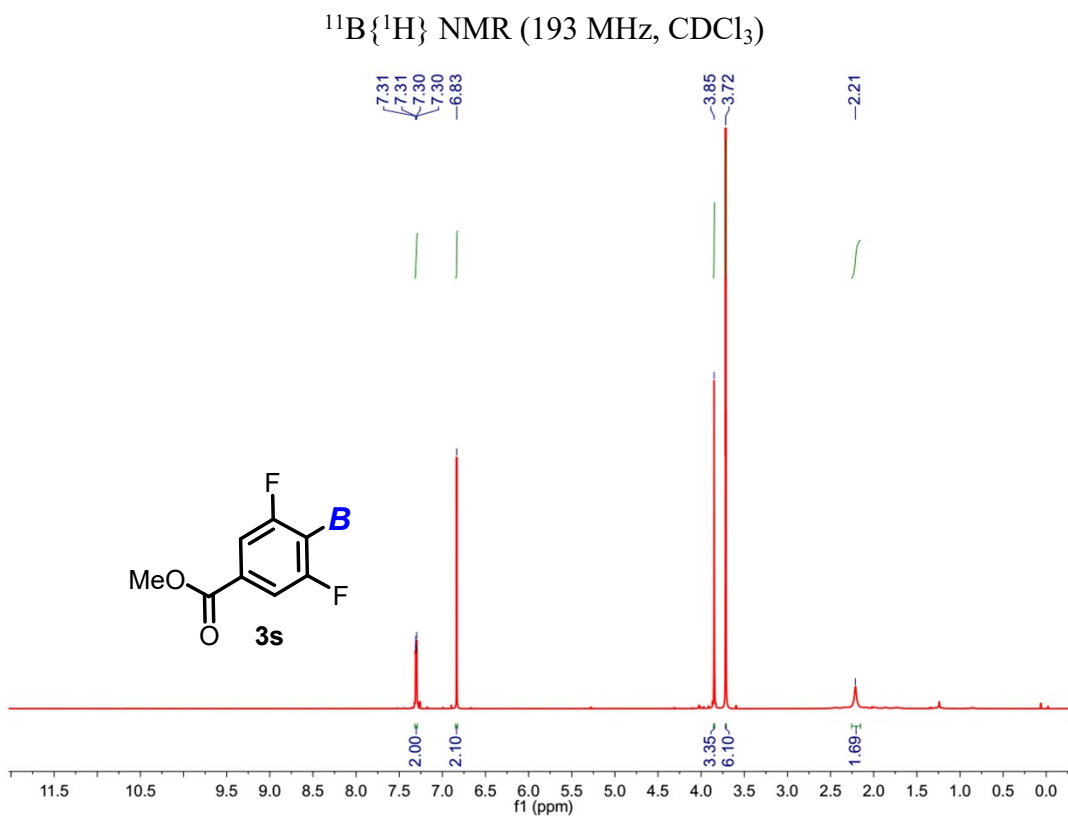
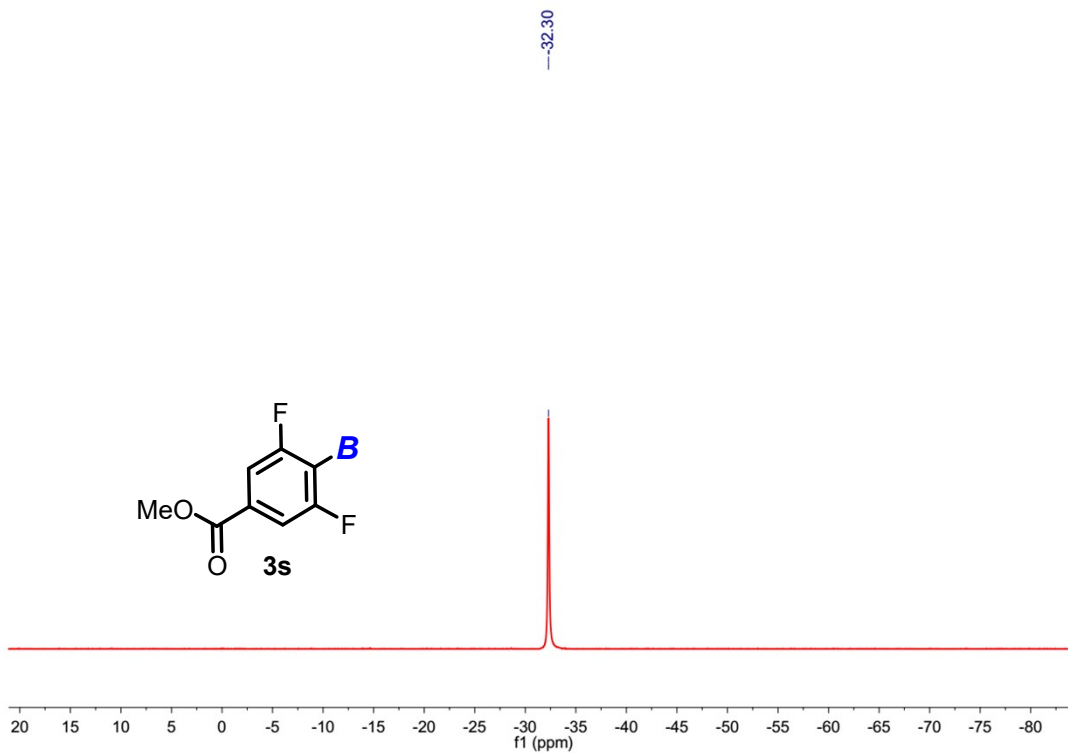




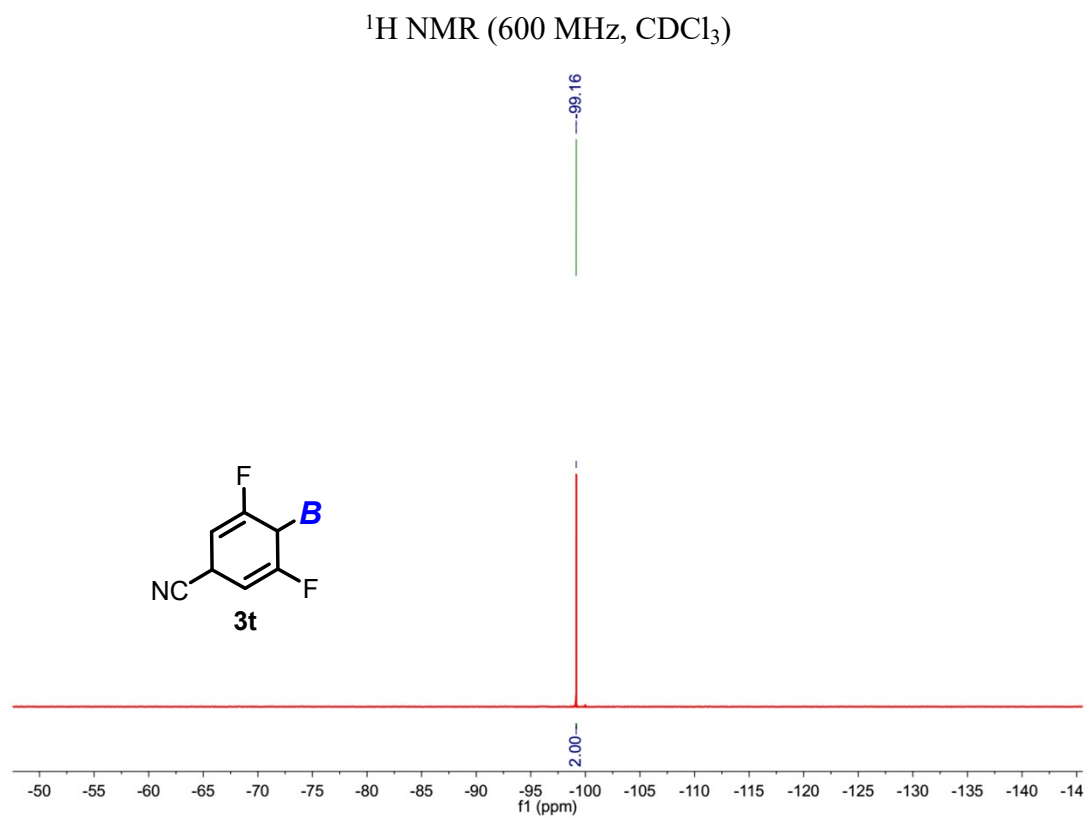
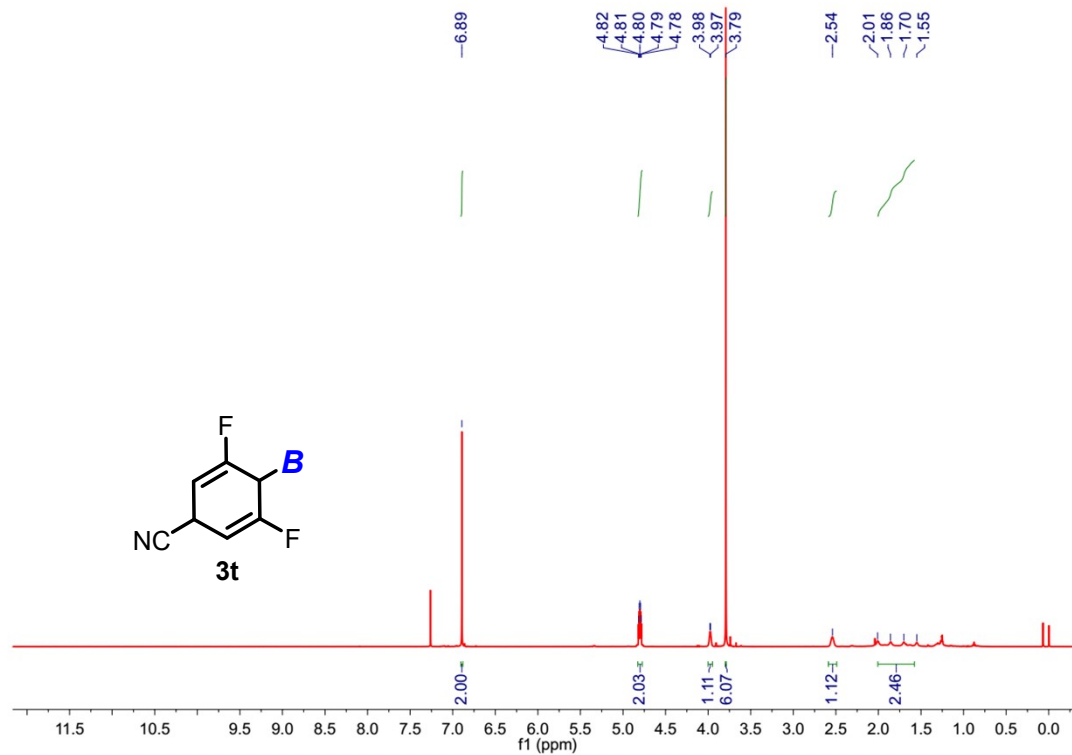
^{13}C NMR (151 MHz, CDCl_3)

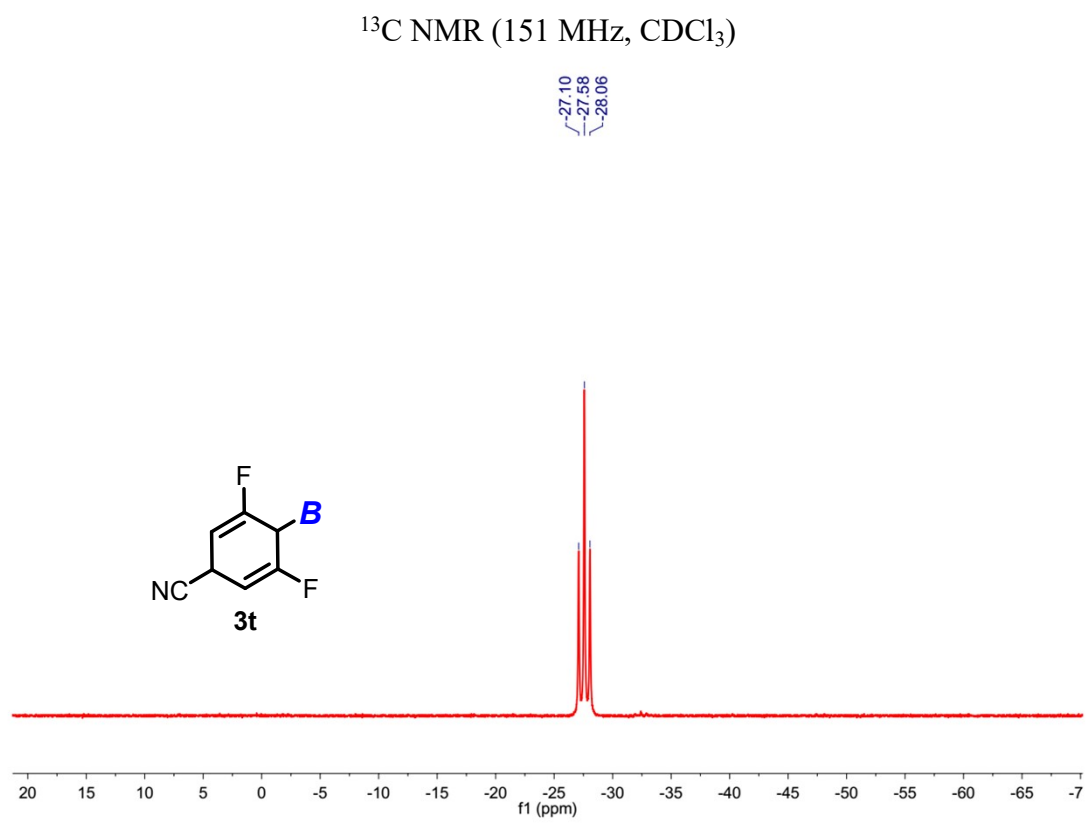
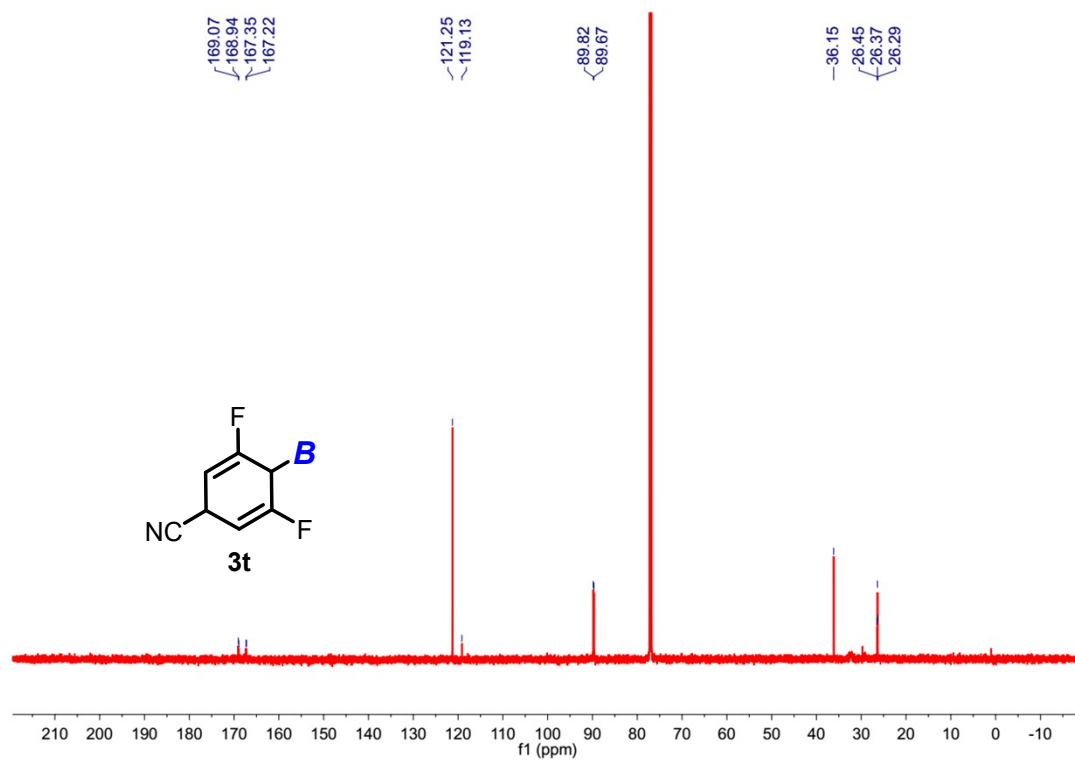


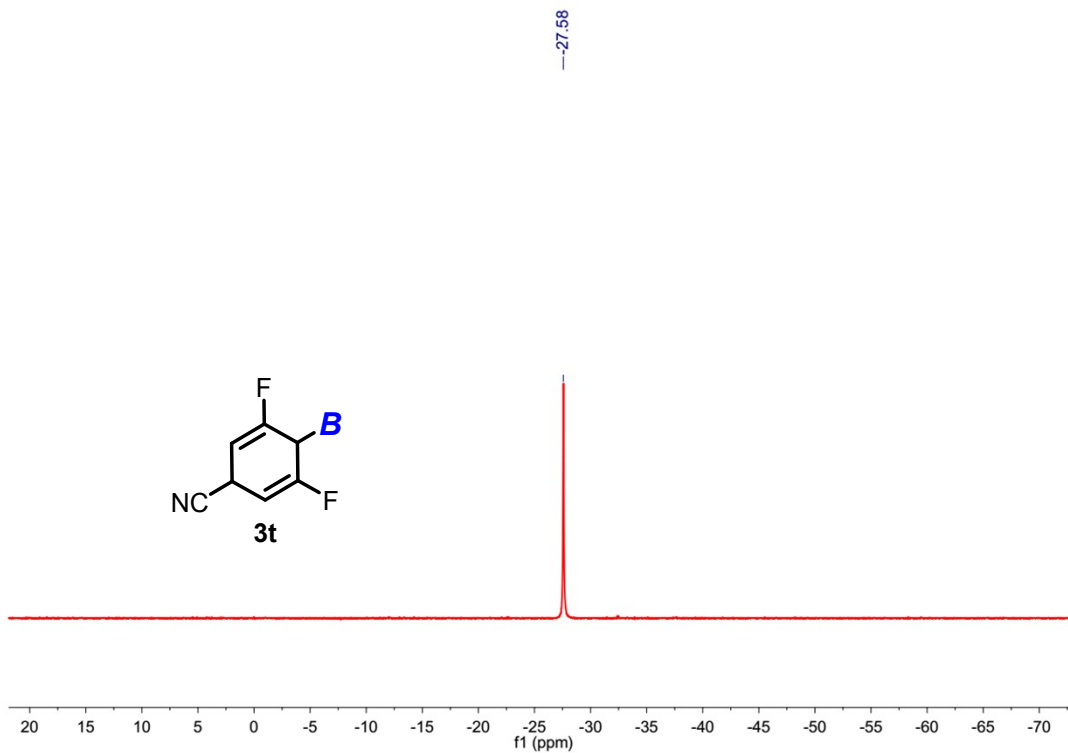
^{11}B NMR (193 MHz, CDCl_3)



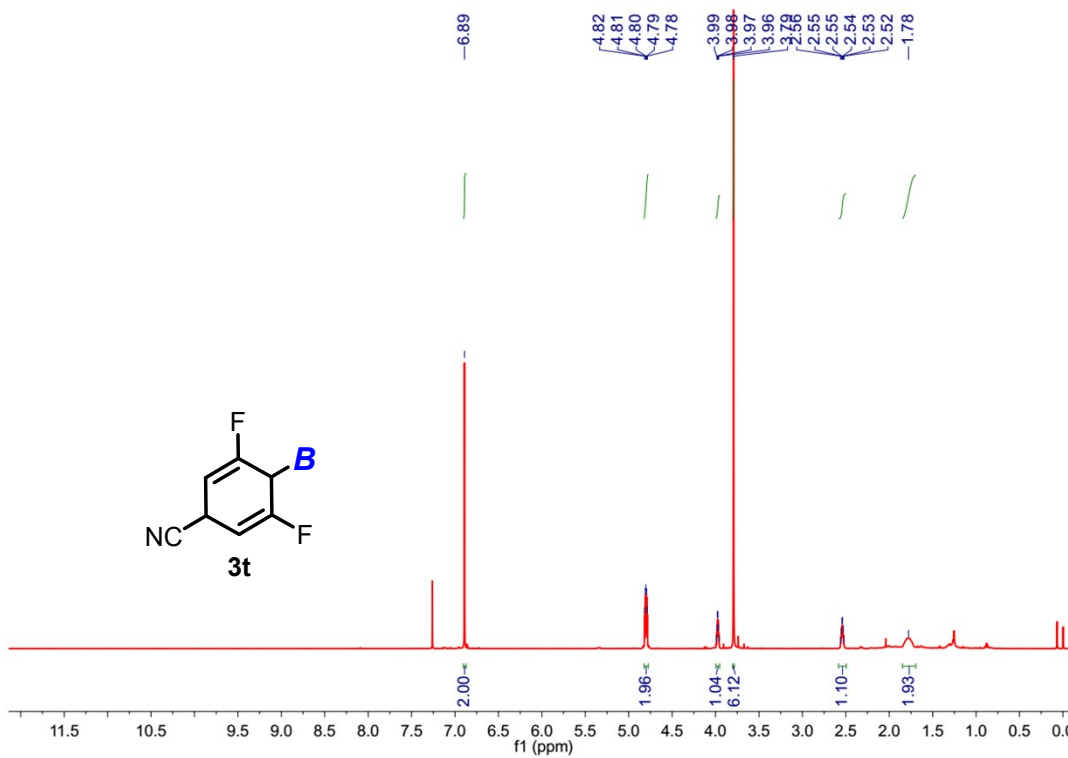
$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3)



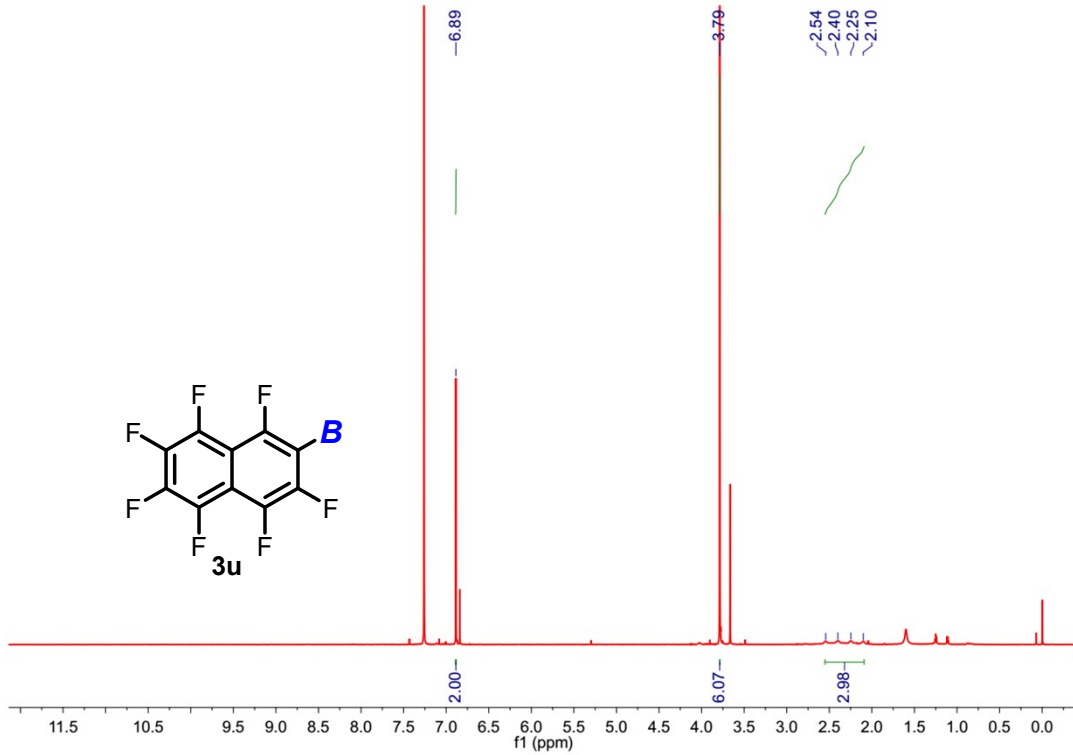




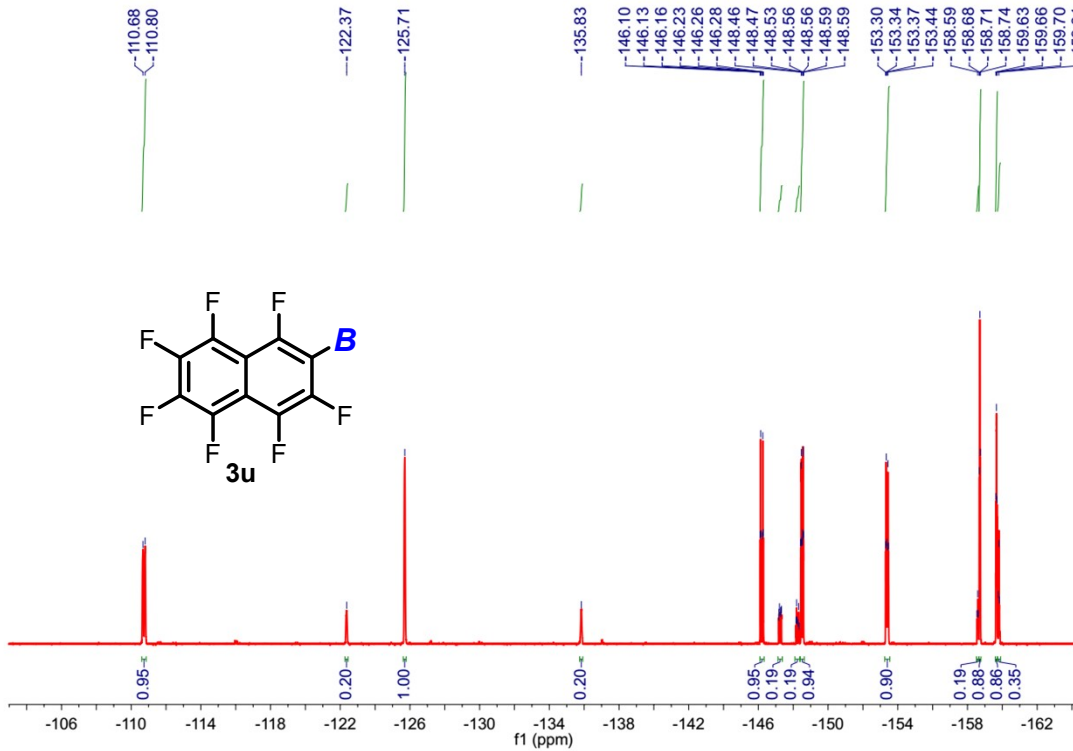
$^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3)



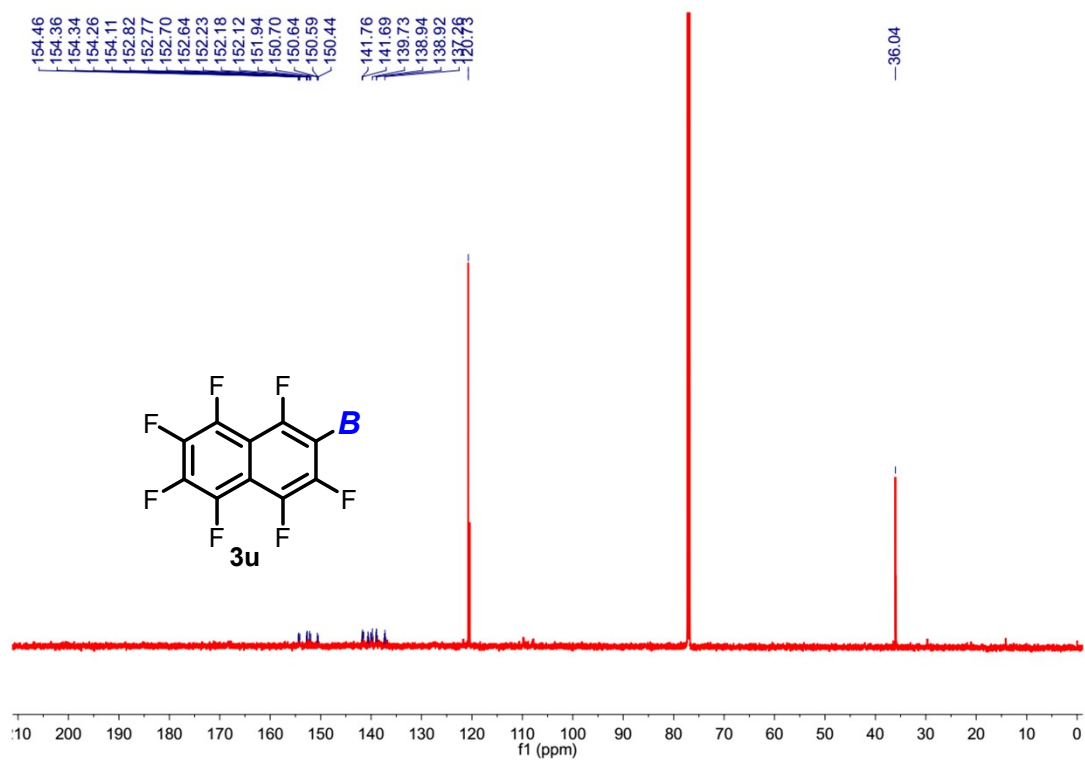
$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3)



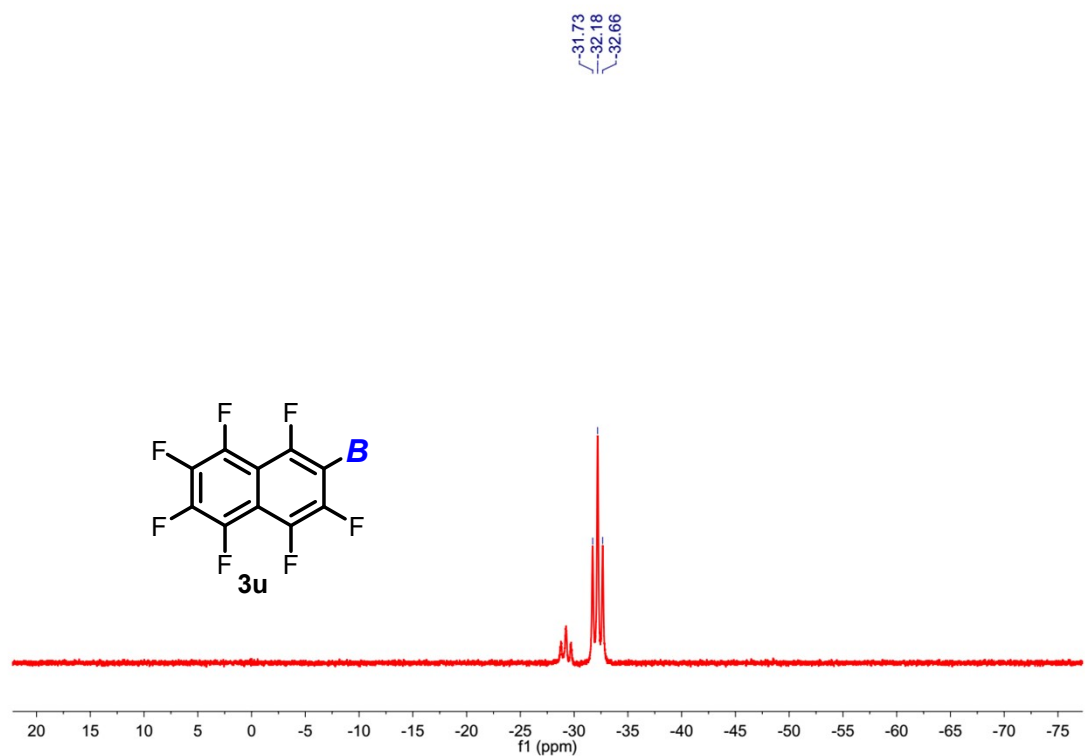
¹H NMR (600 MHz, CDCl₃)



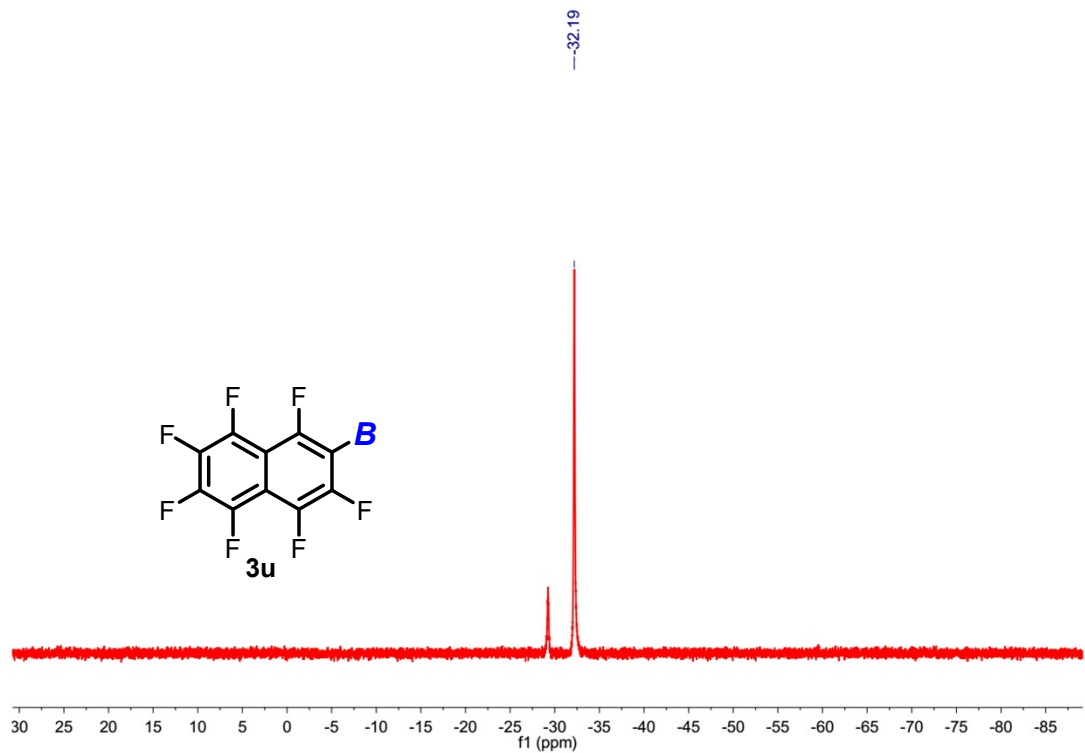
¹⁹F NMR (565 MHz, CDCl₃)



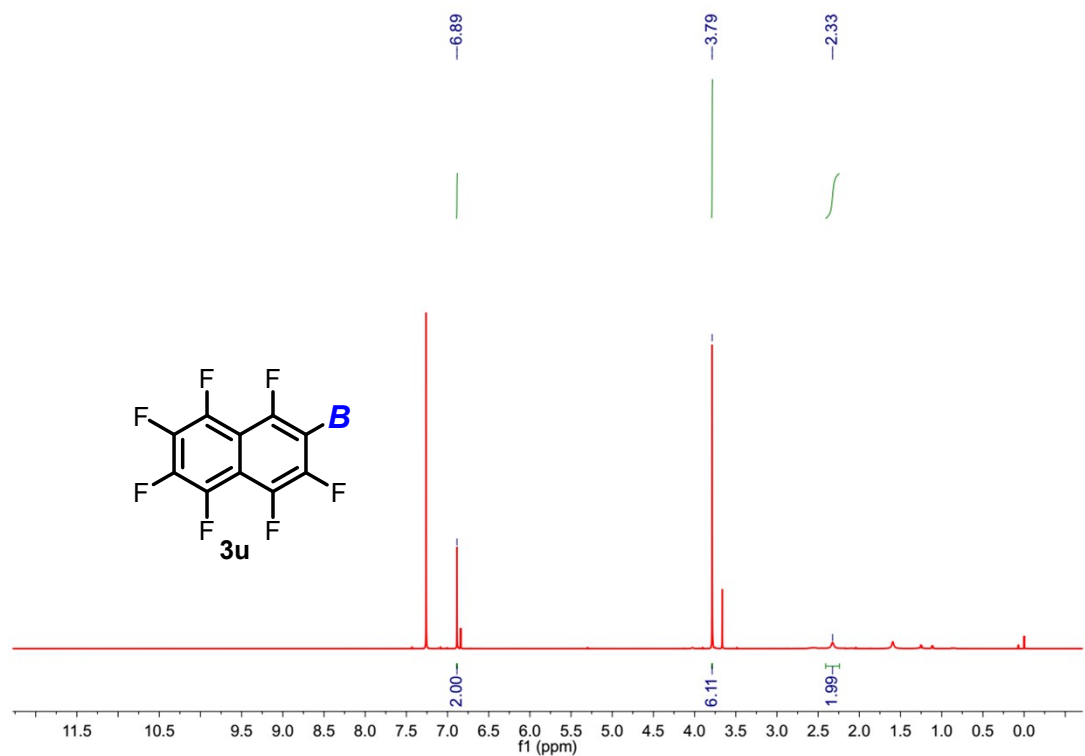
^{13}C NMR (151 MHz, CDCl_3)



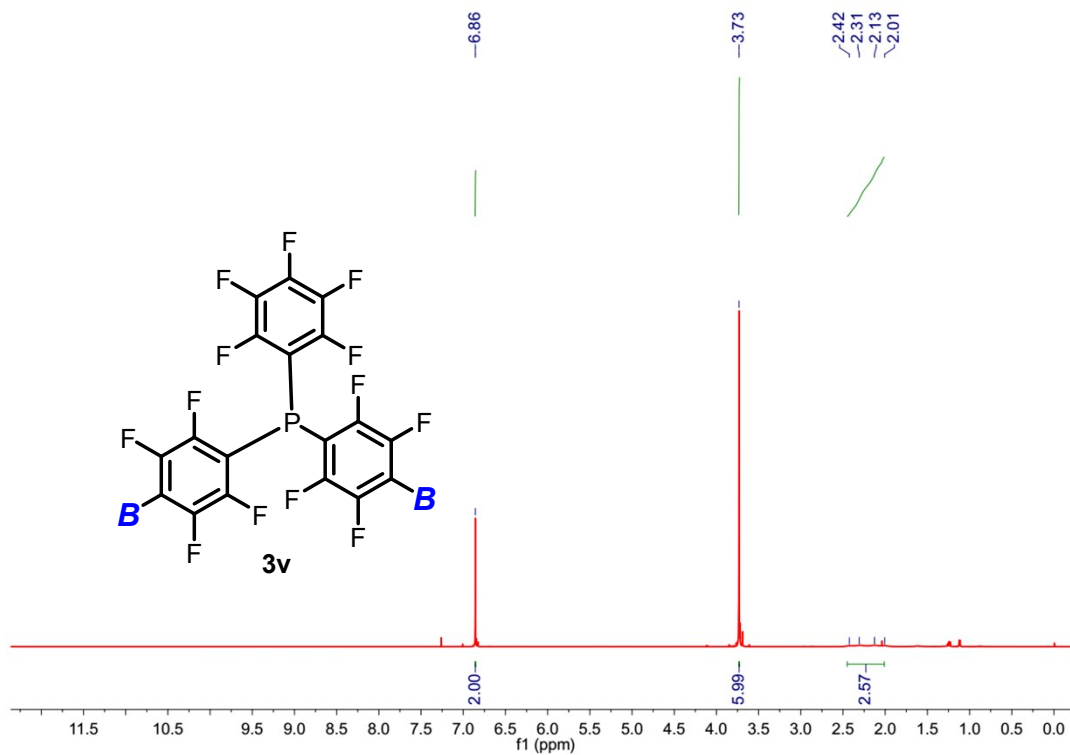
^{11}B NMR (193 MHz, CDCl_3)



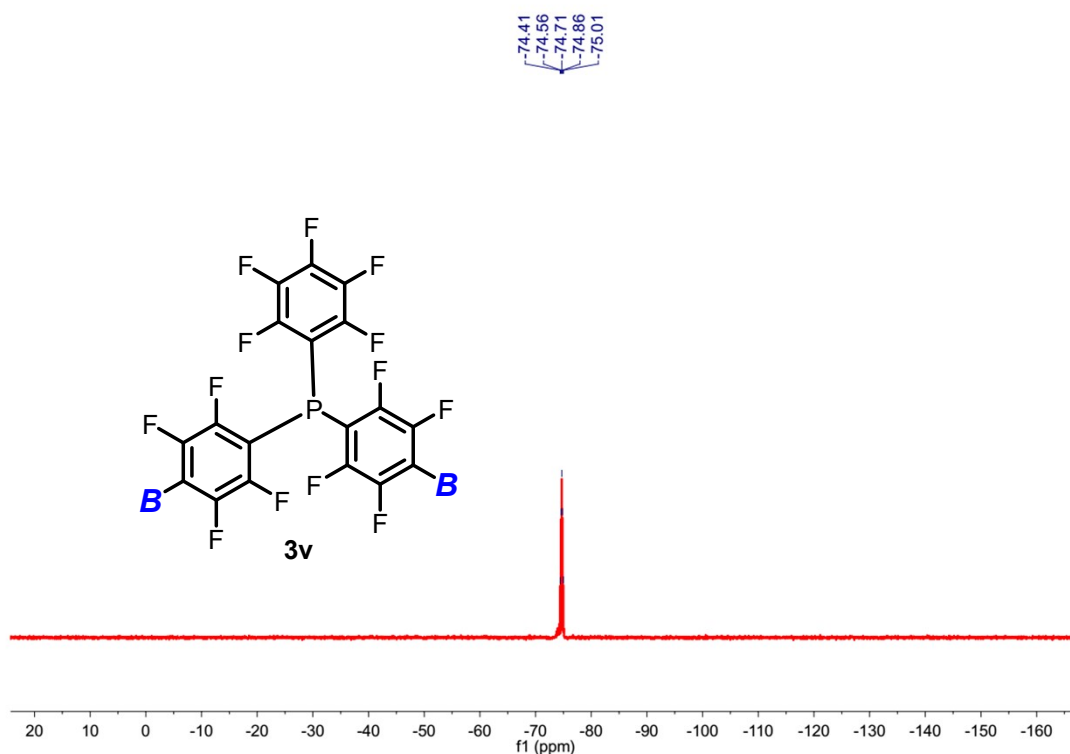
$^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3)



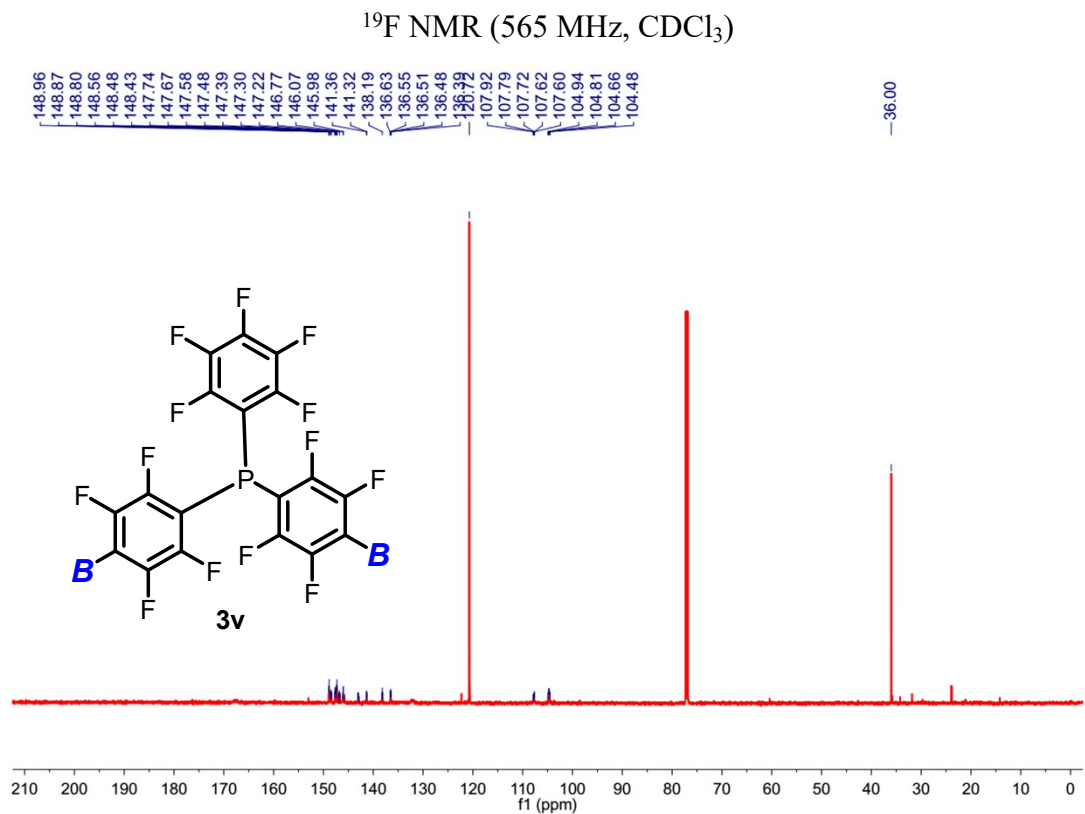
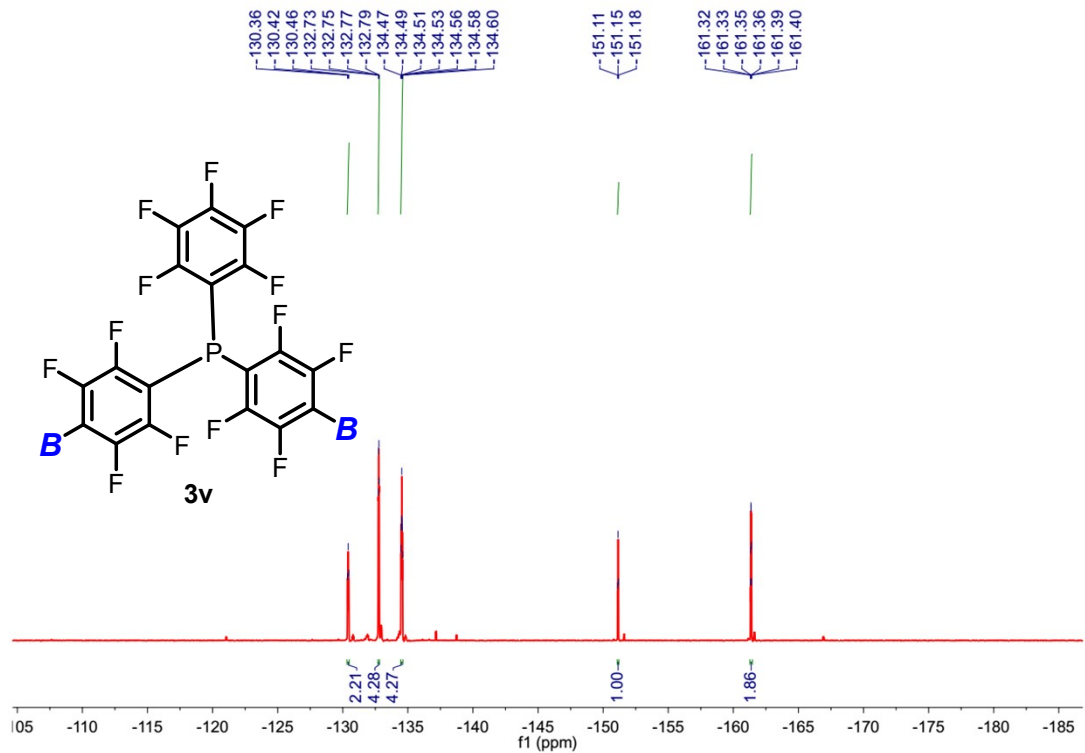
$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3)

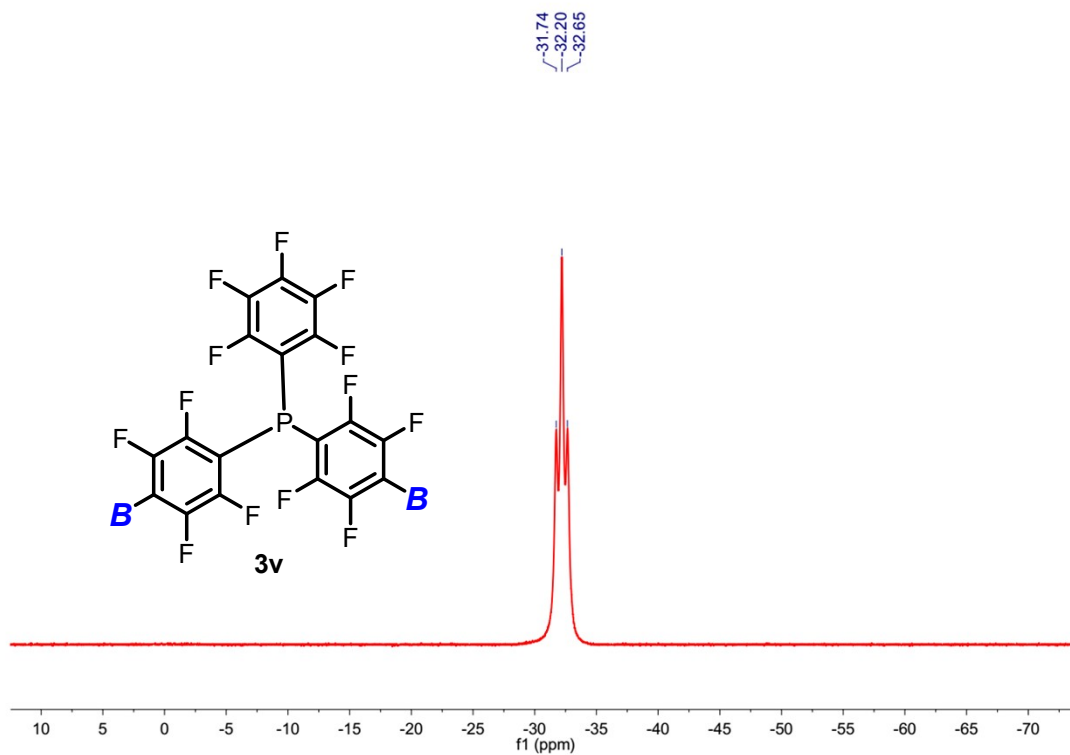


$^1\text{H NMR}$ (600 MHz, CDCl_3)

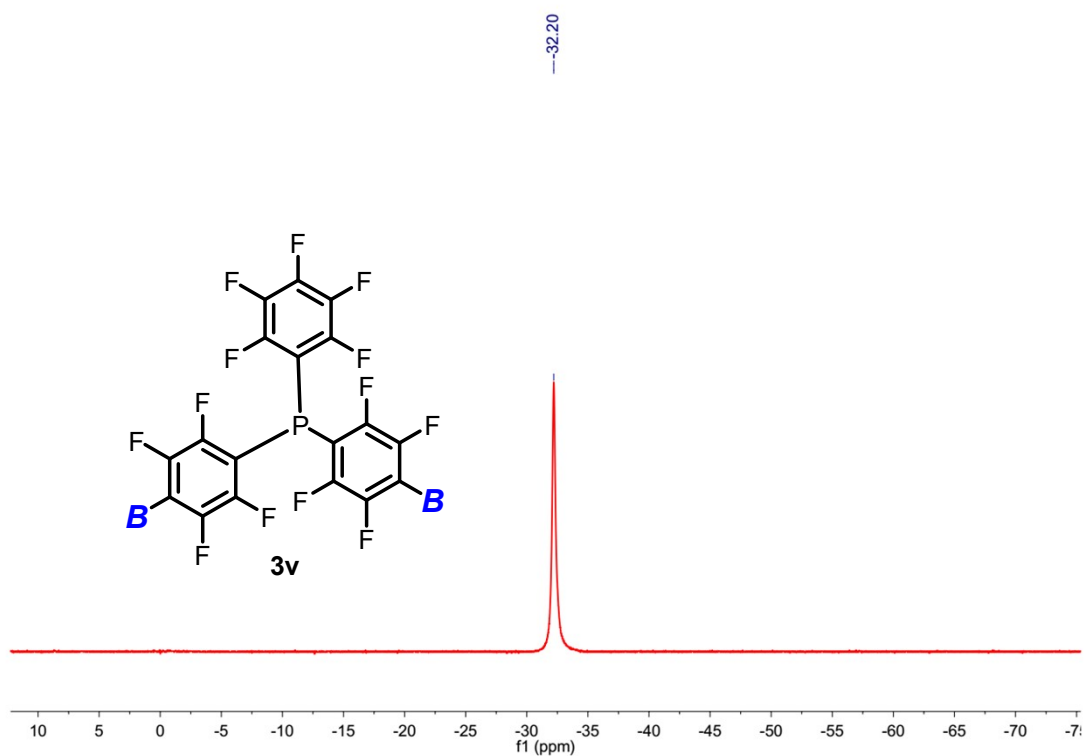


$^{31}\text{P NMR}$ (243 MHz, CDCl_3)

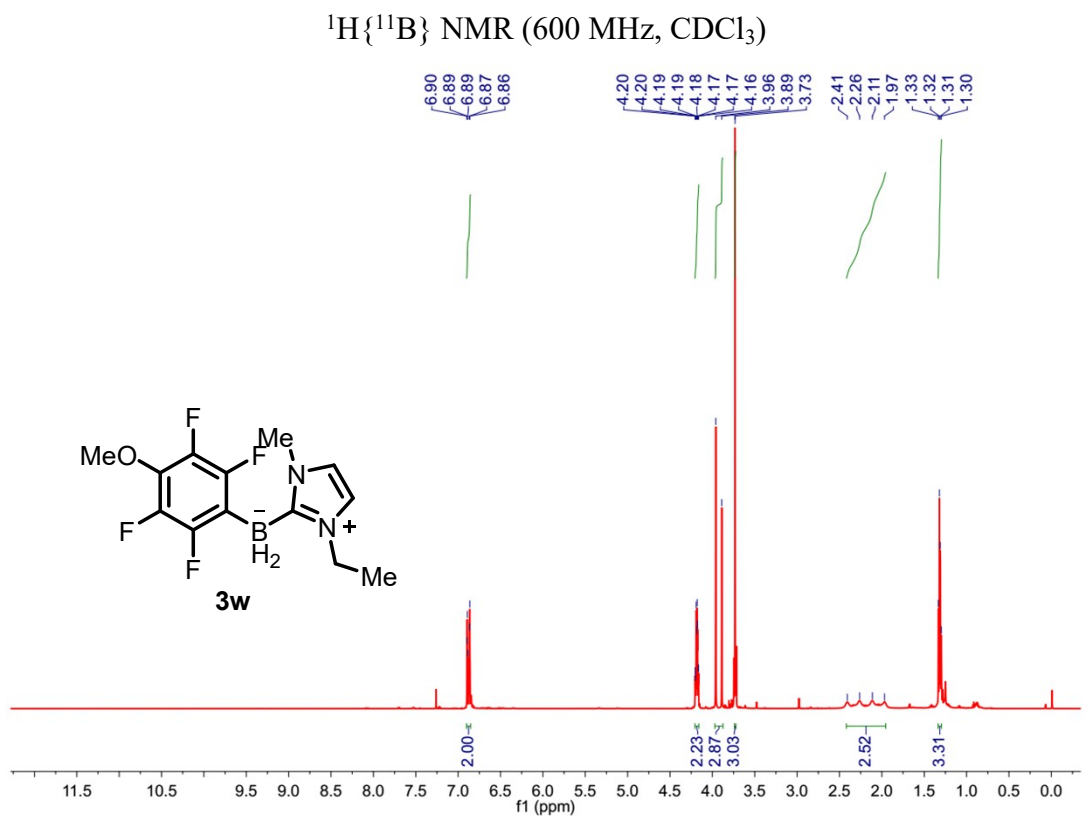
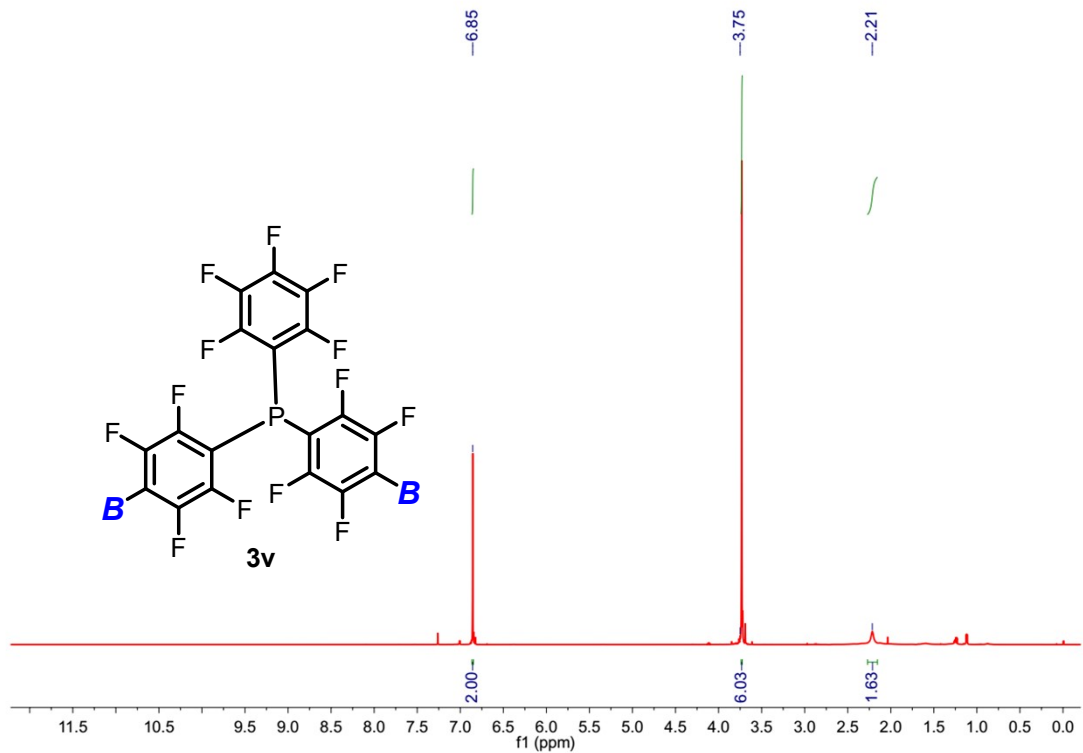




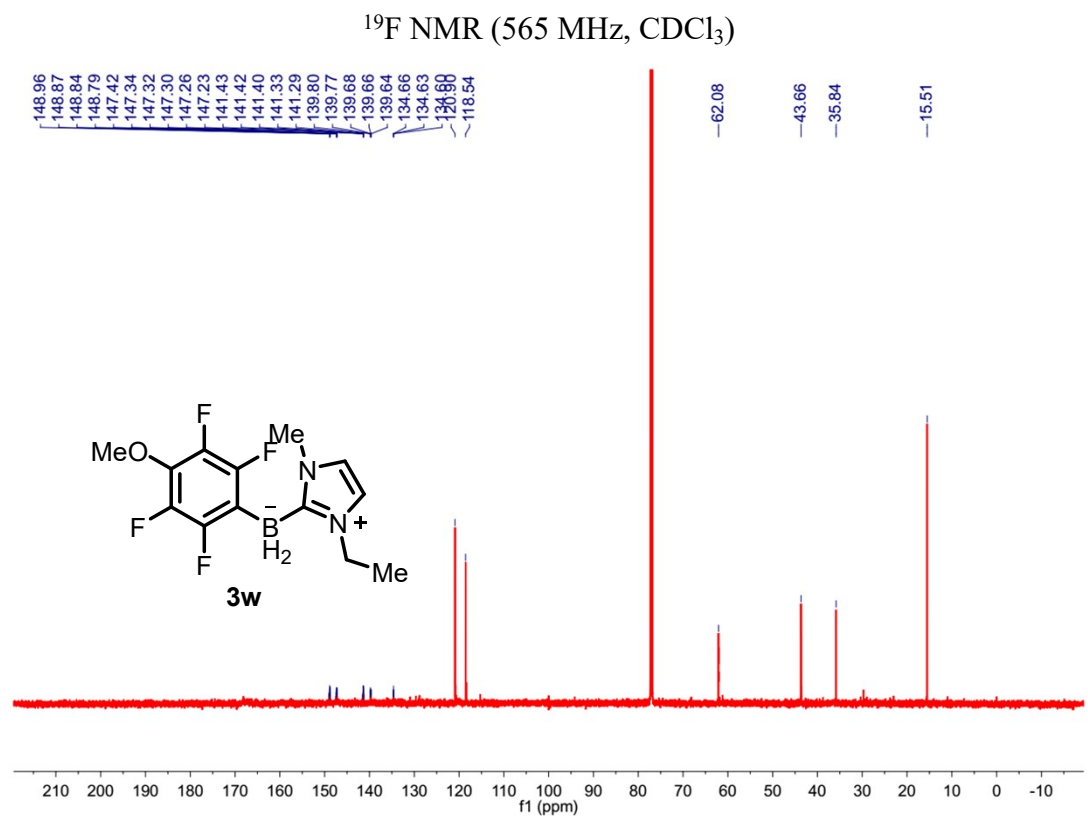
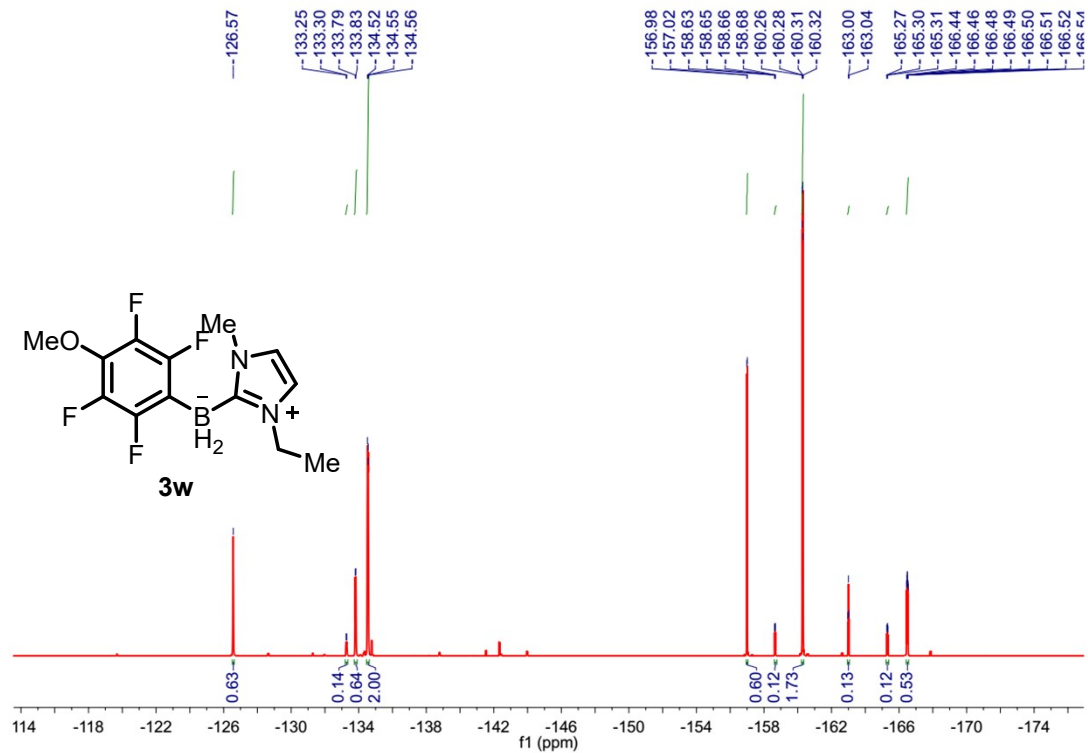
^{11}B NMR (193 MHz, CDCl_3)

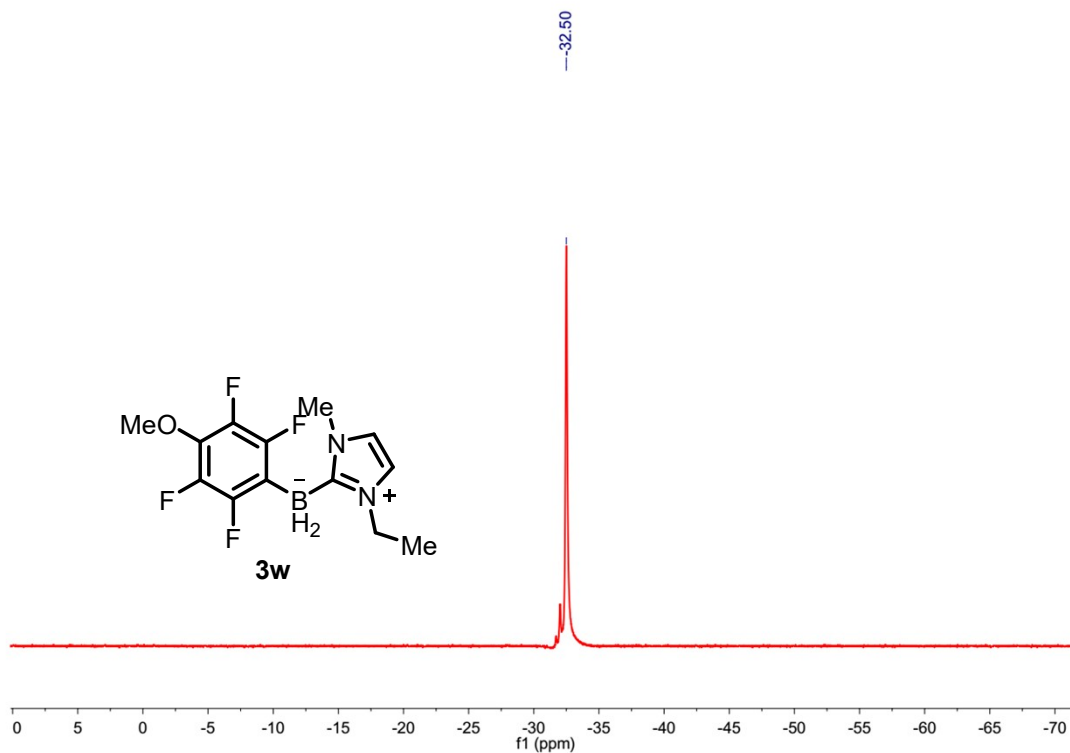
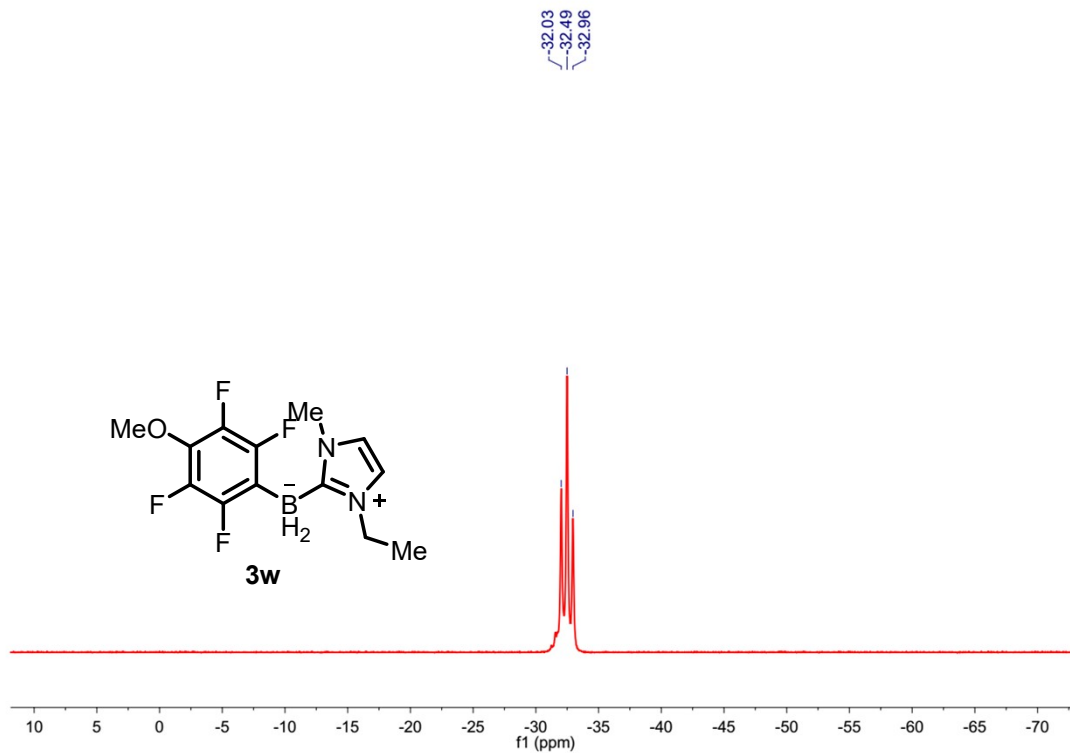


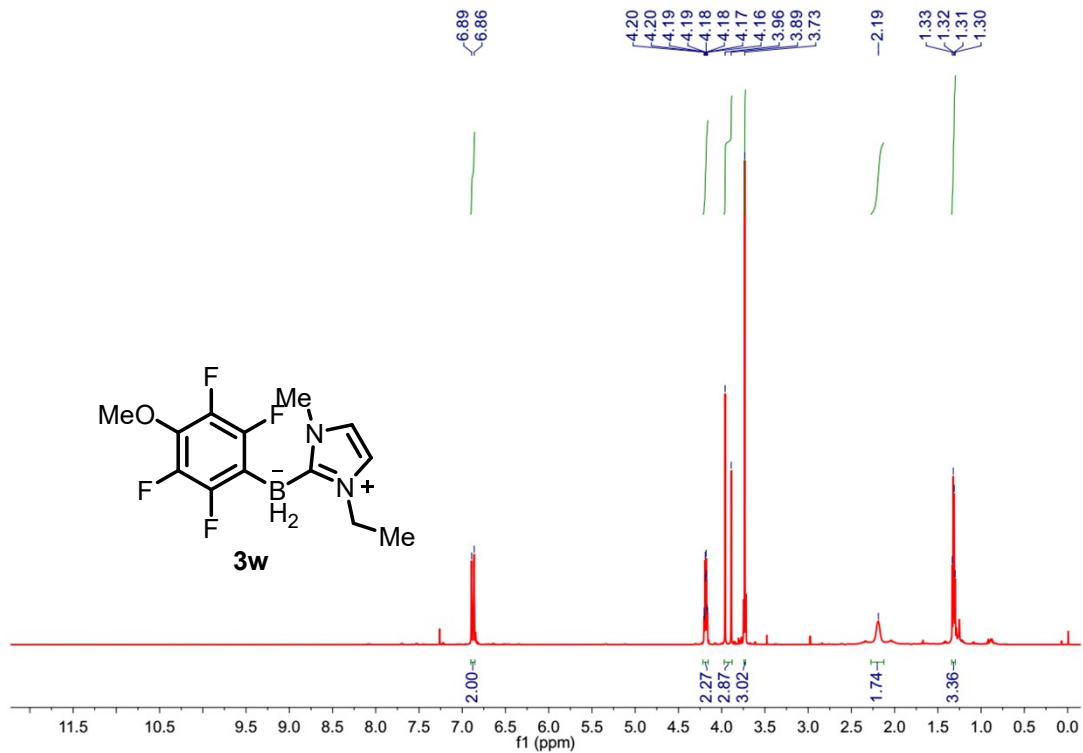
$^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3)



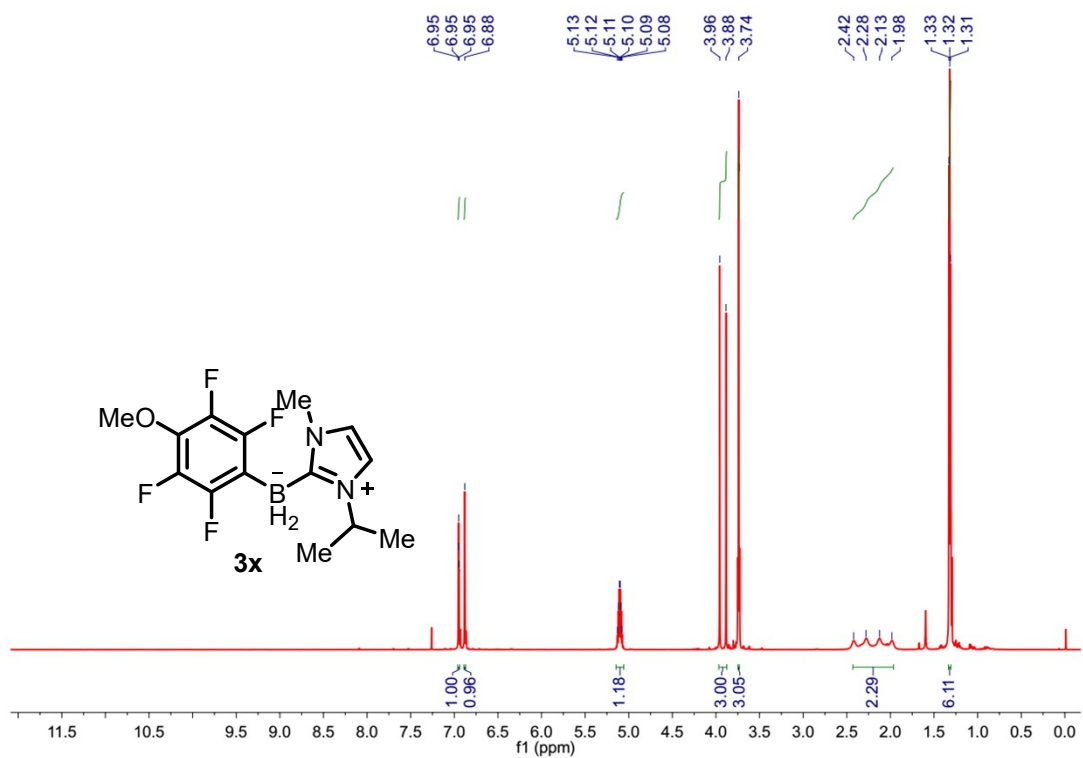
^1H NMR (600 MHz, CDCl_3)



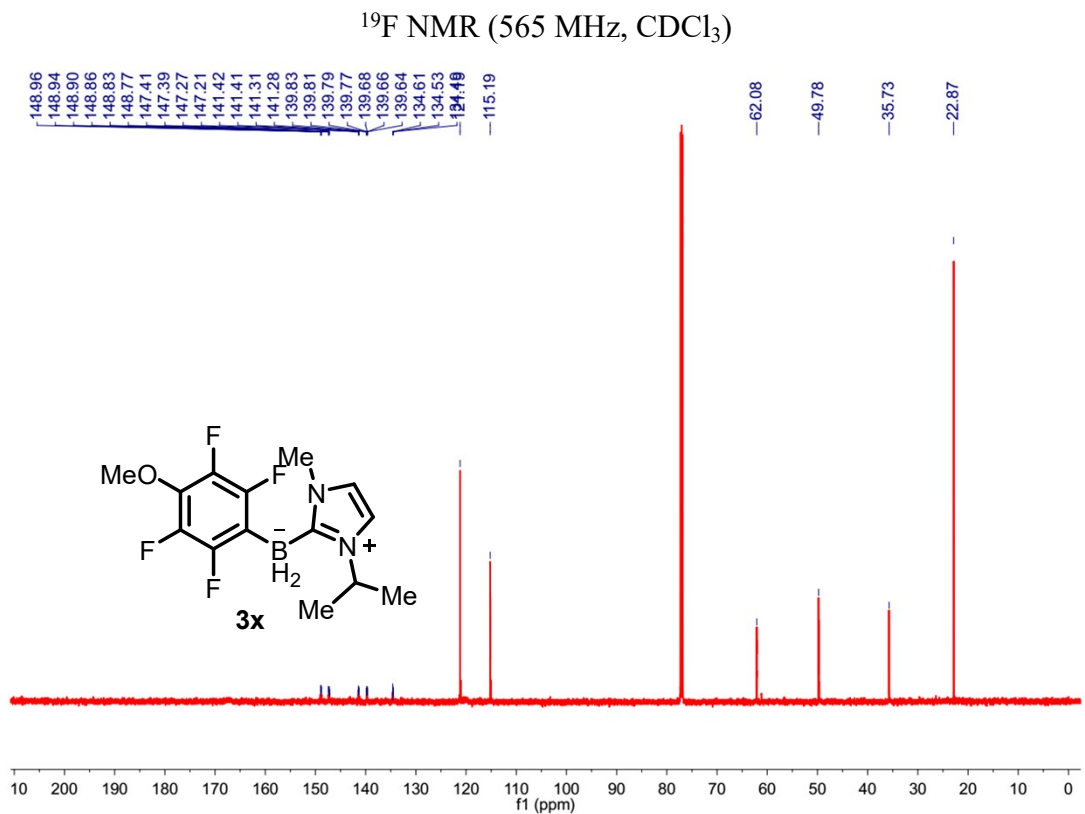
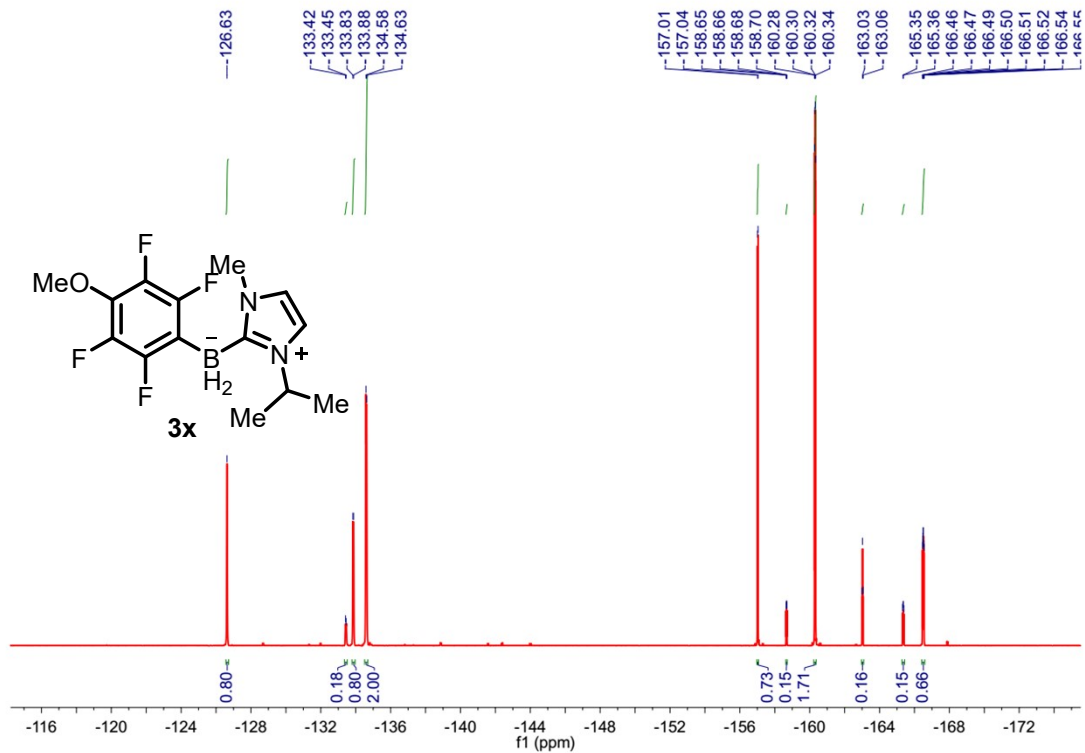


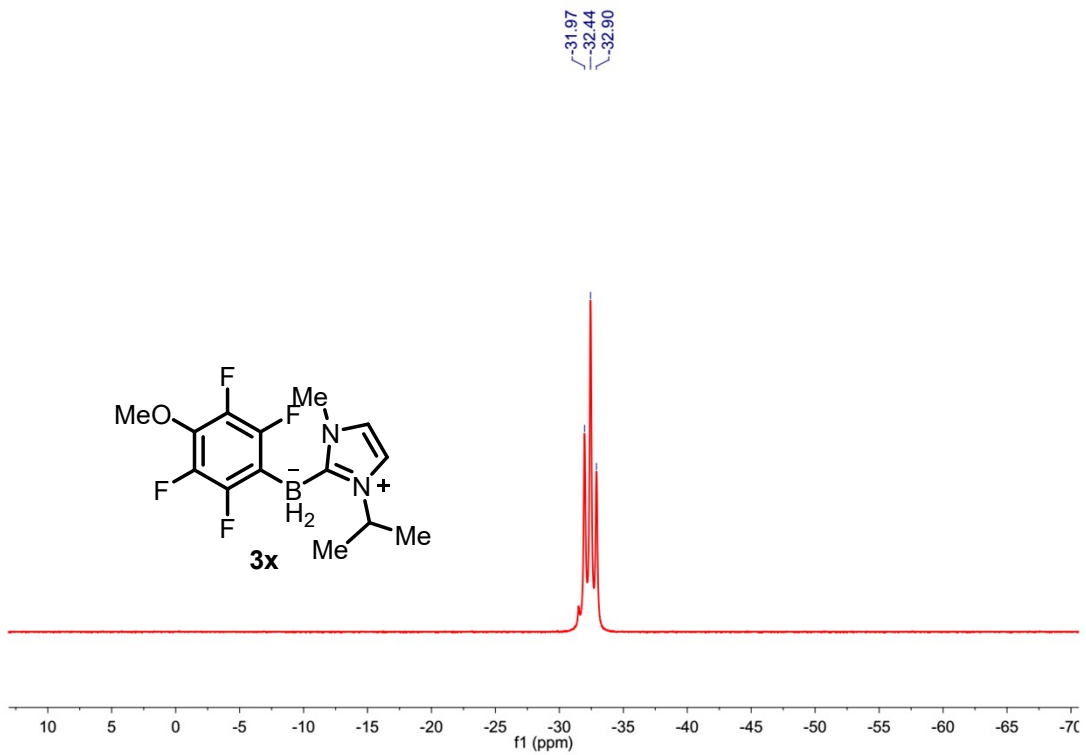


$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3)

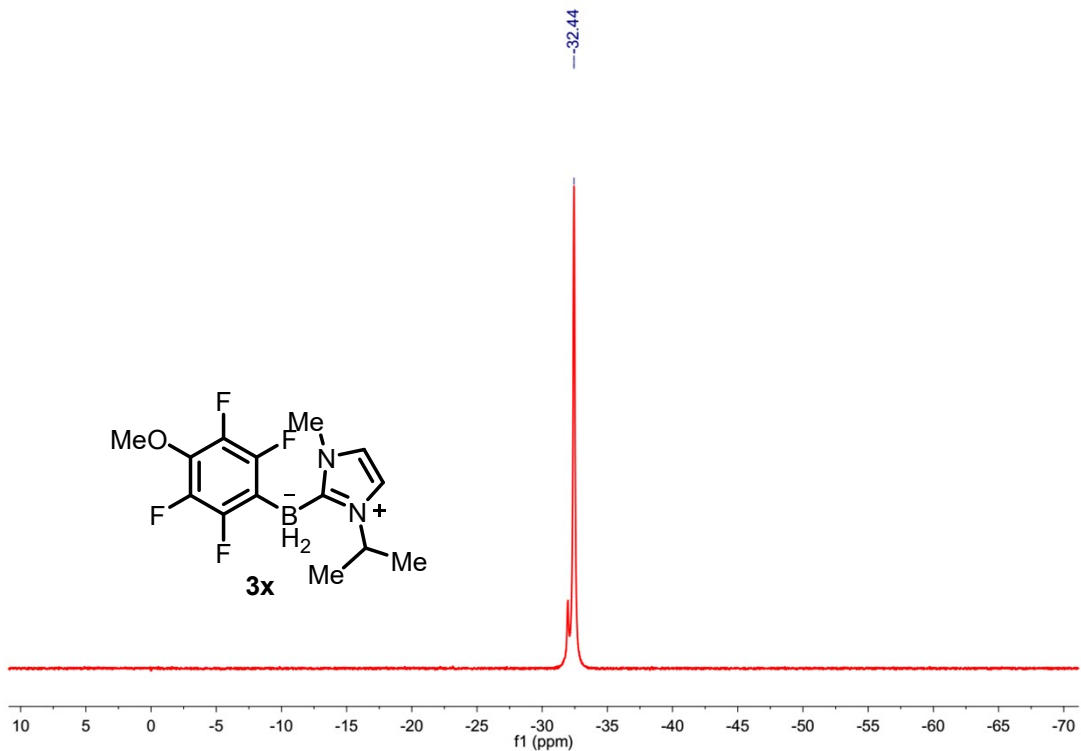


^1H NMR (600 MHz, CDCl_3)

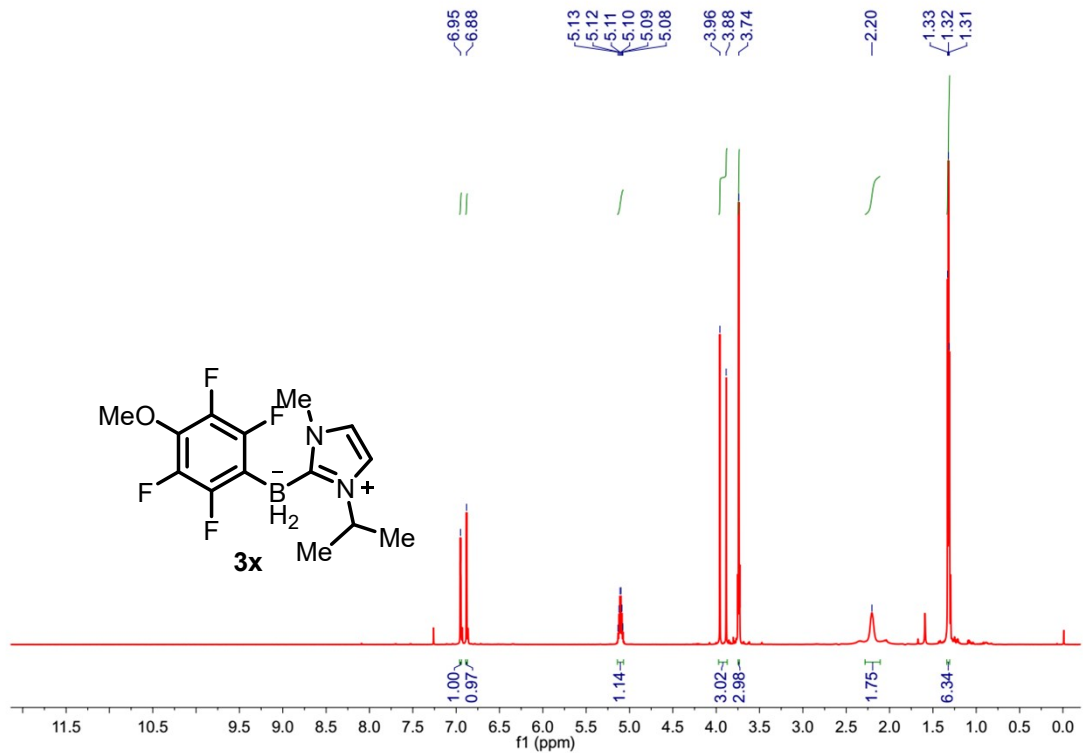




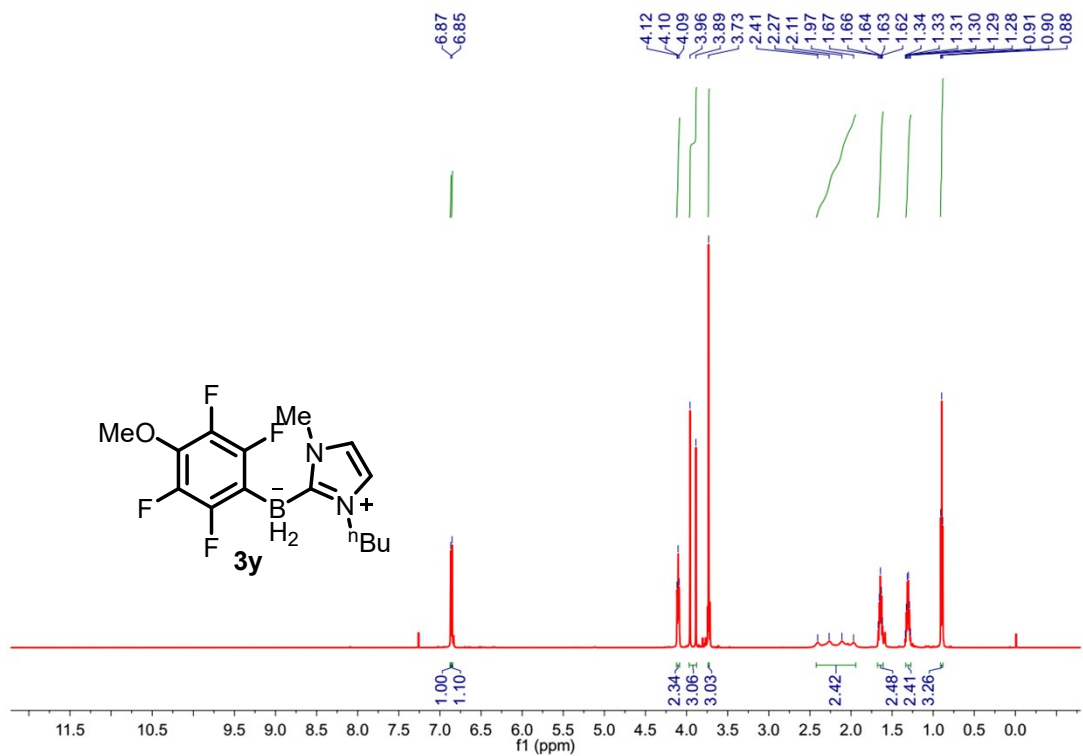
¹¹B NMR (193 MHz, CDCl₃)



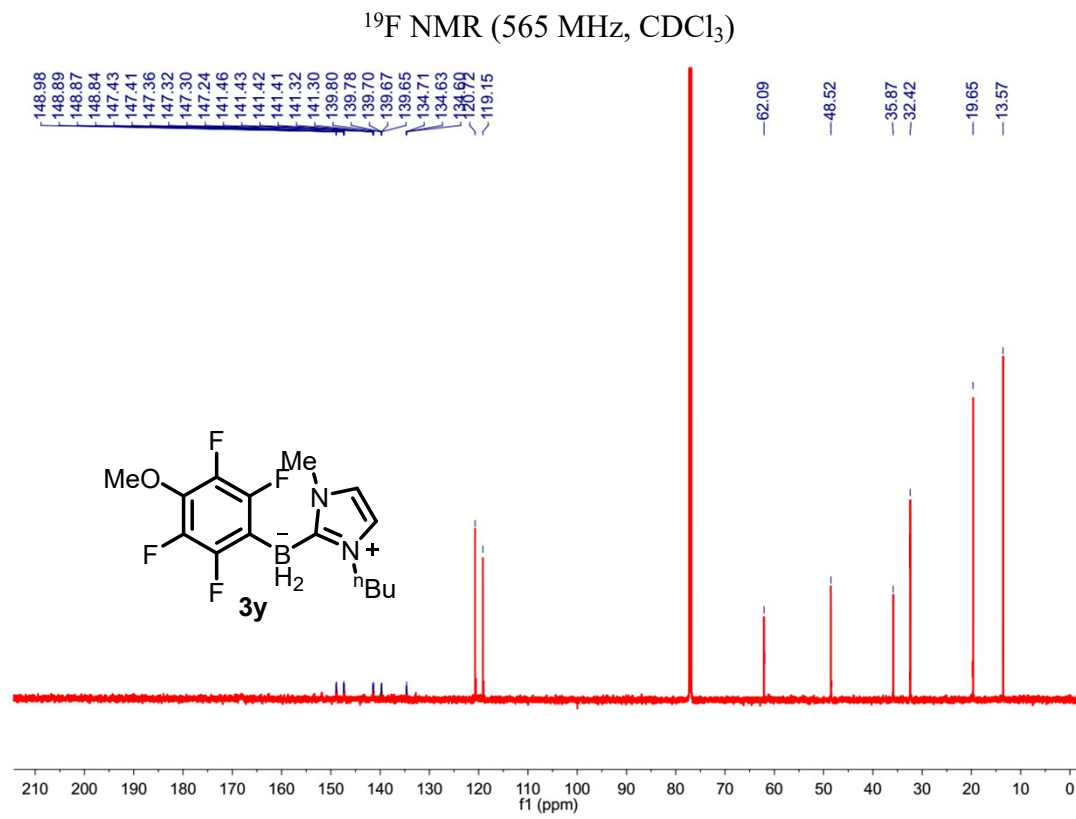
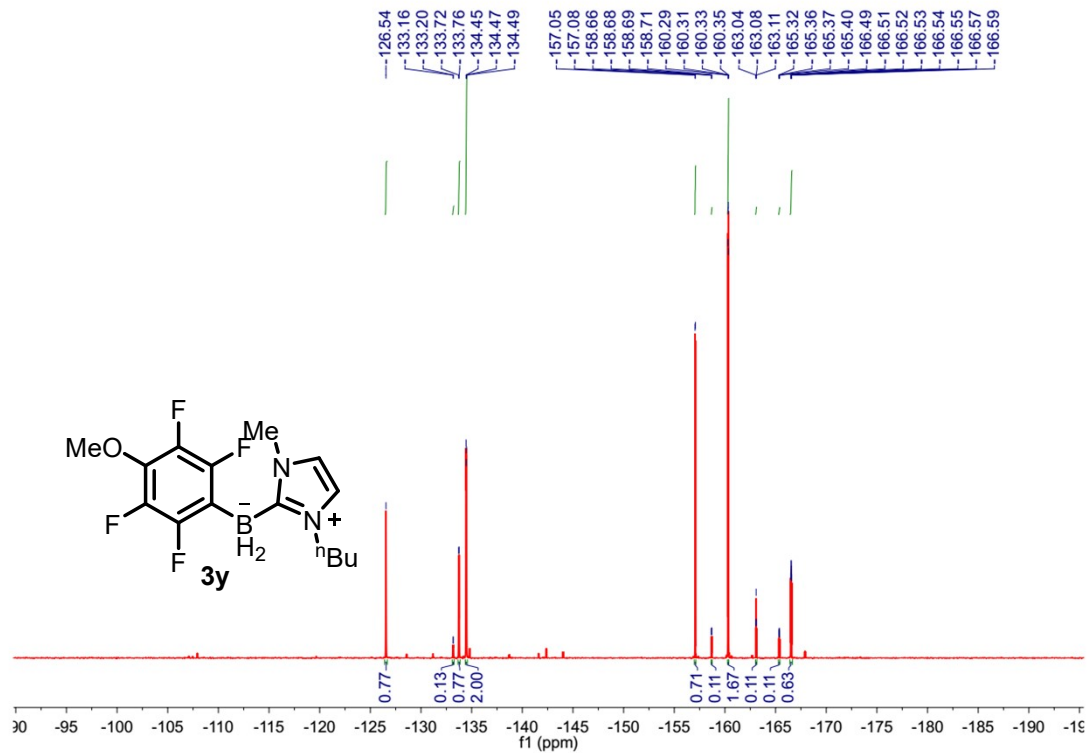
¹¹B{¹H} NMR (193 MHz, CDCl₃)

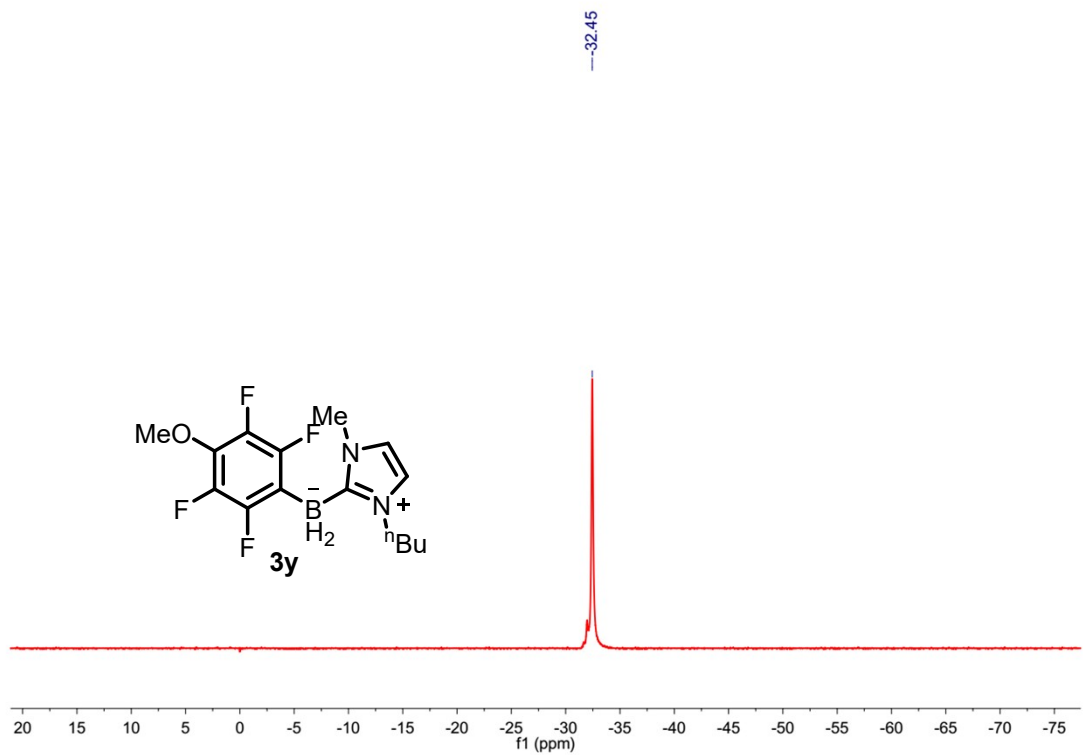
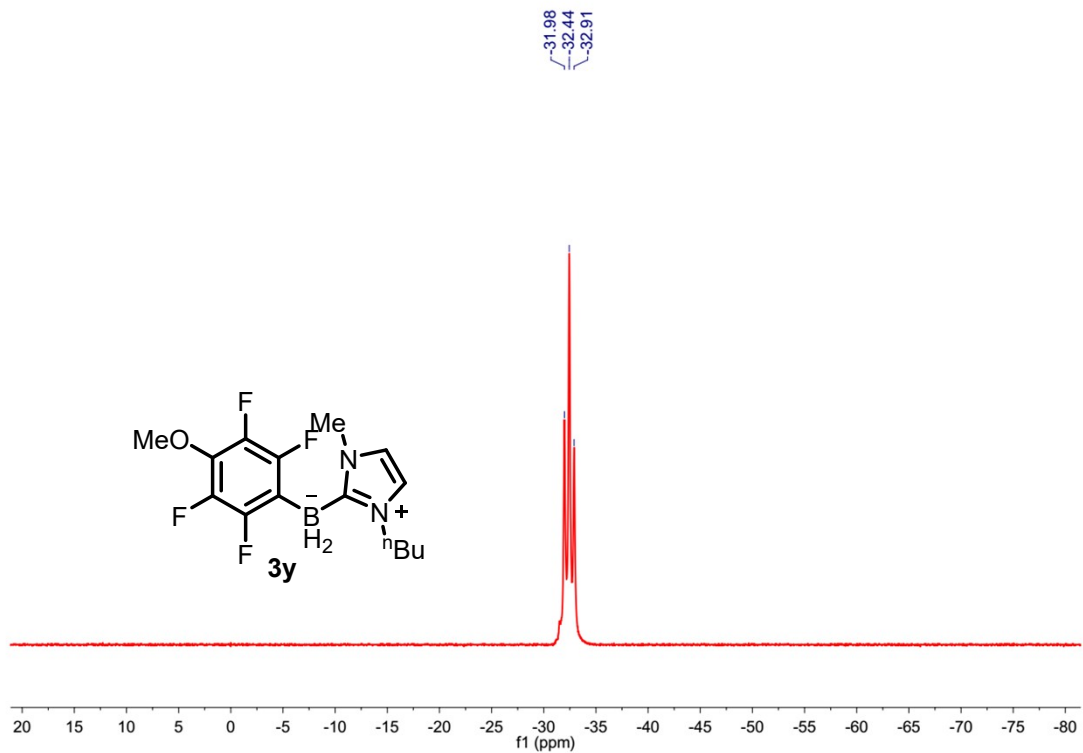


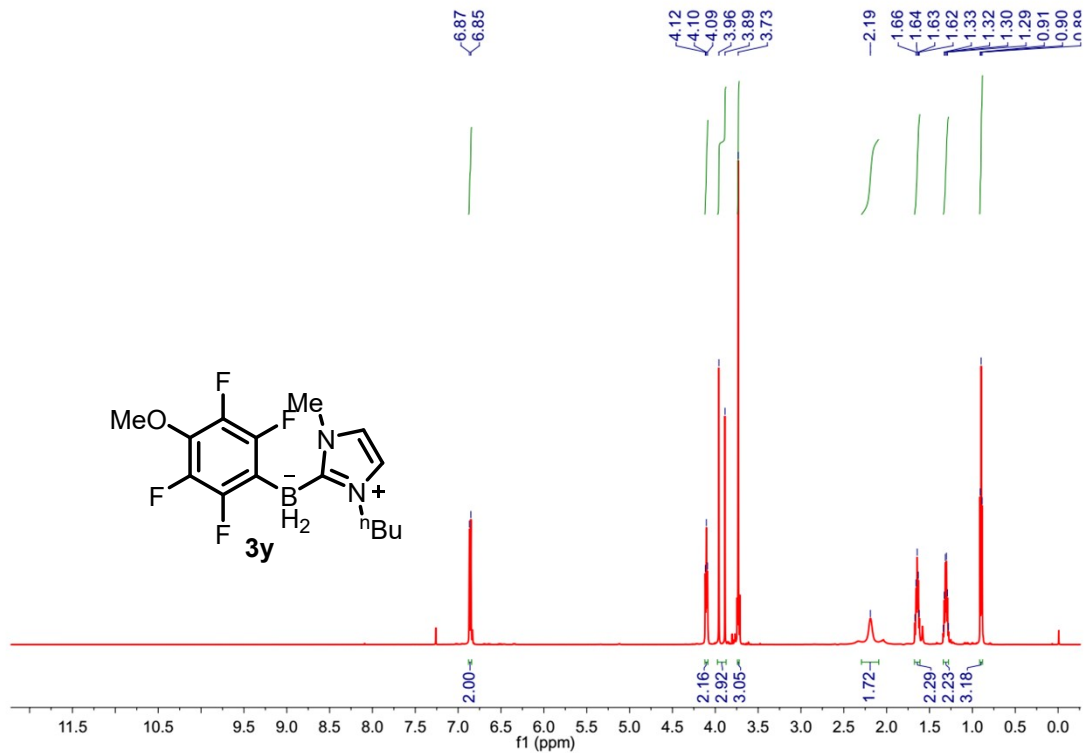
$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3)



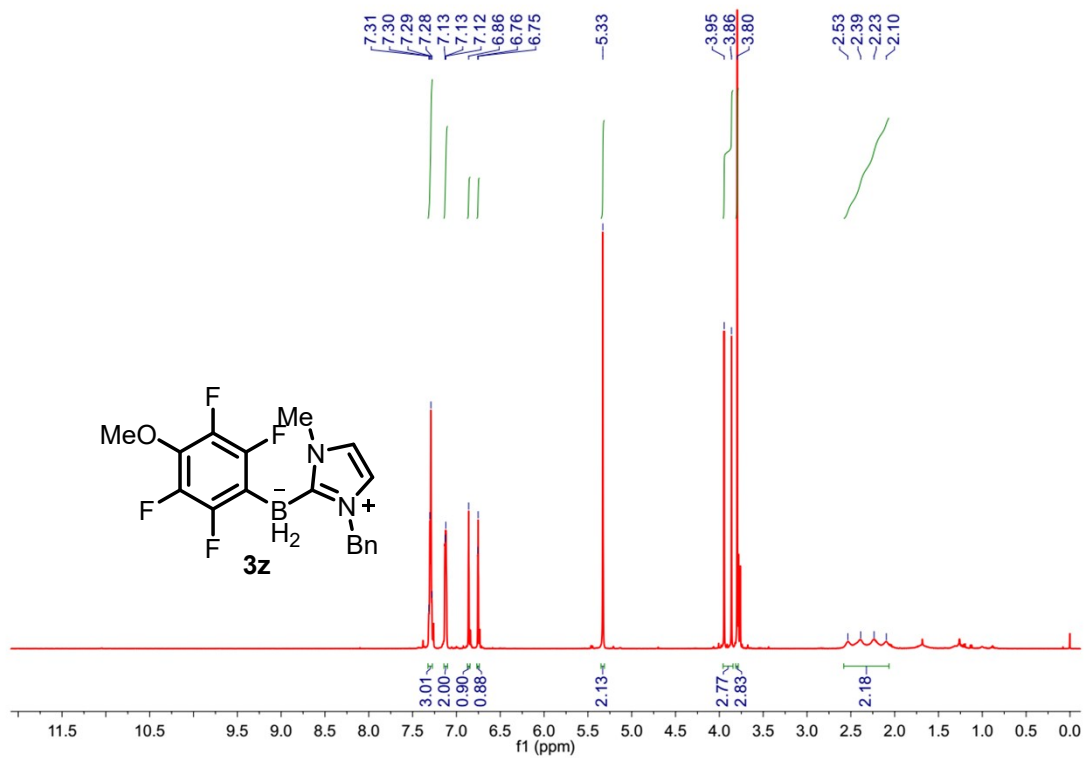
^1H NMR (600 MHz, CDCl_3)



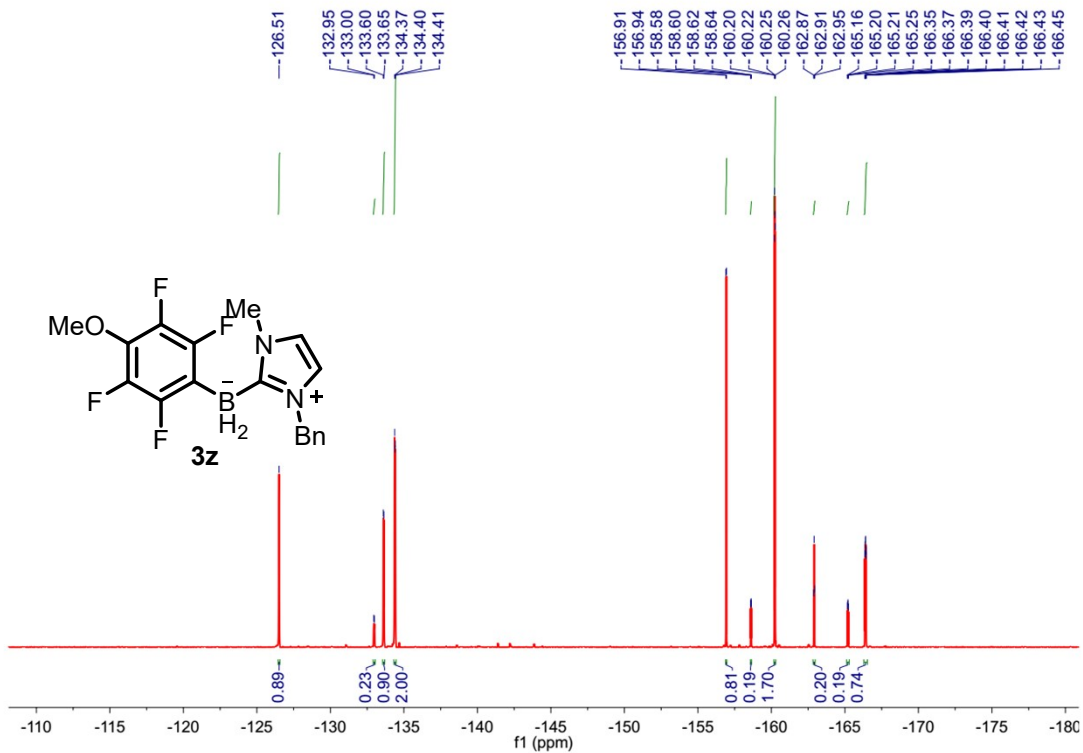




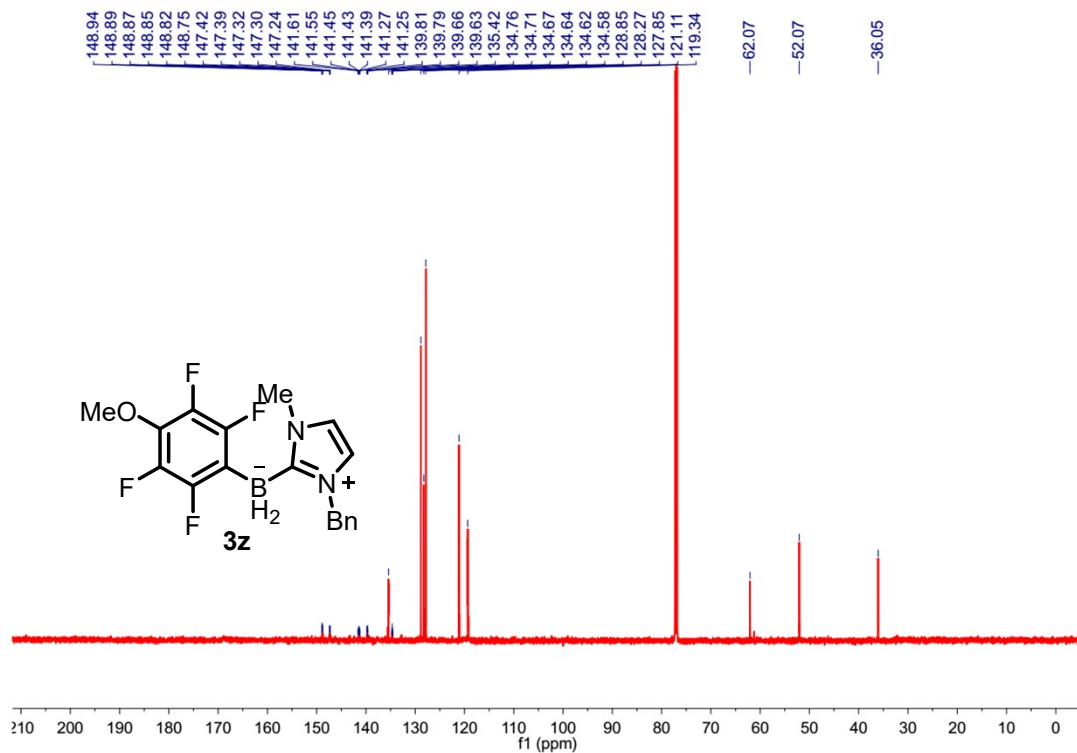
$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3)



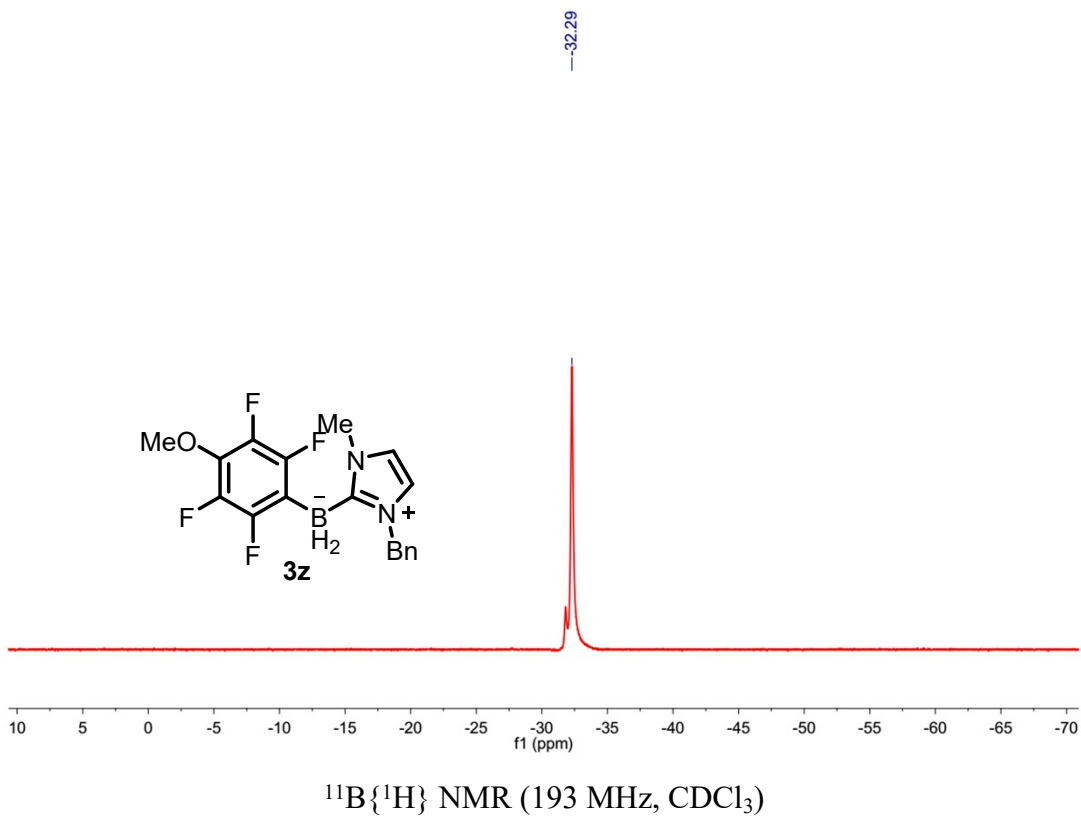
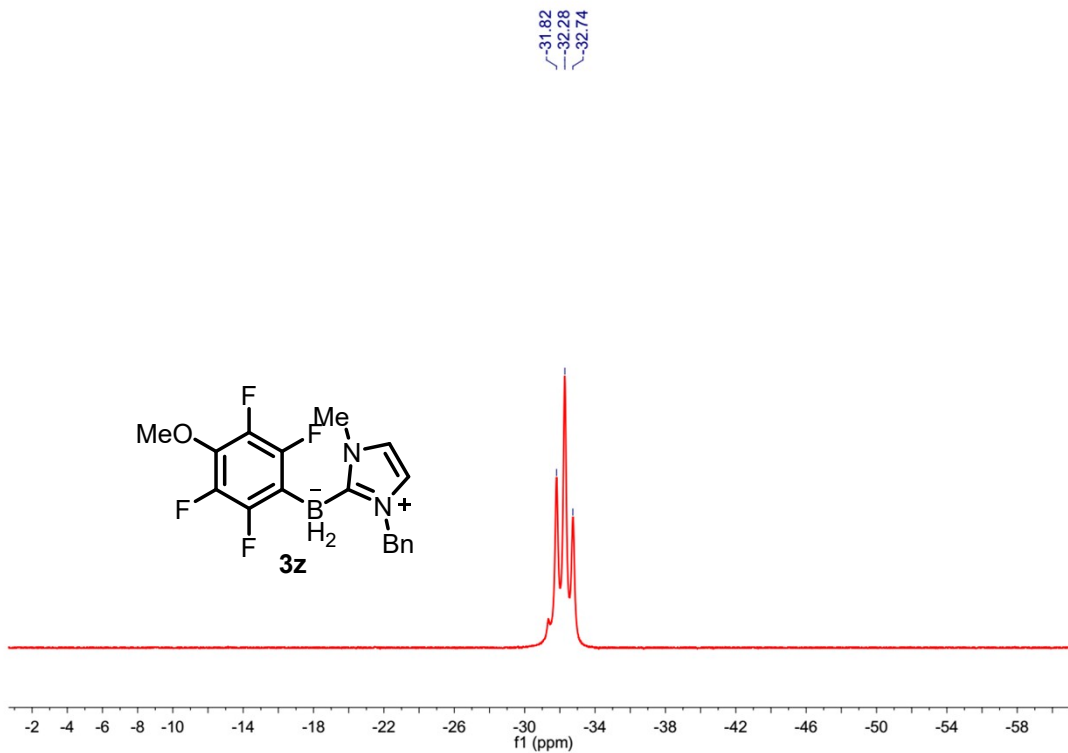
^1H NMR (600 MHz, CDCl_3)

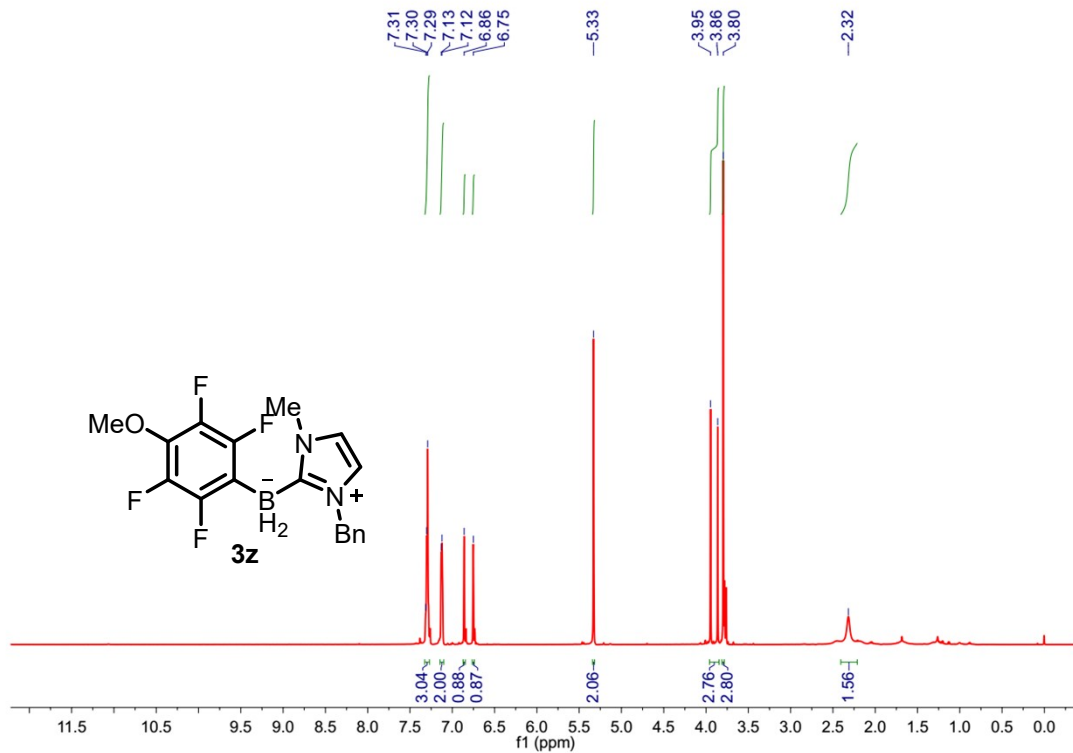


¹⁹F NMR (565 MHz, CDCl₃)

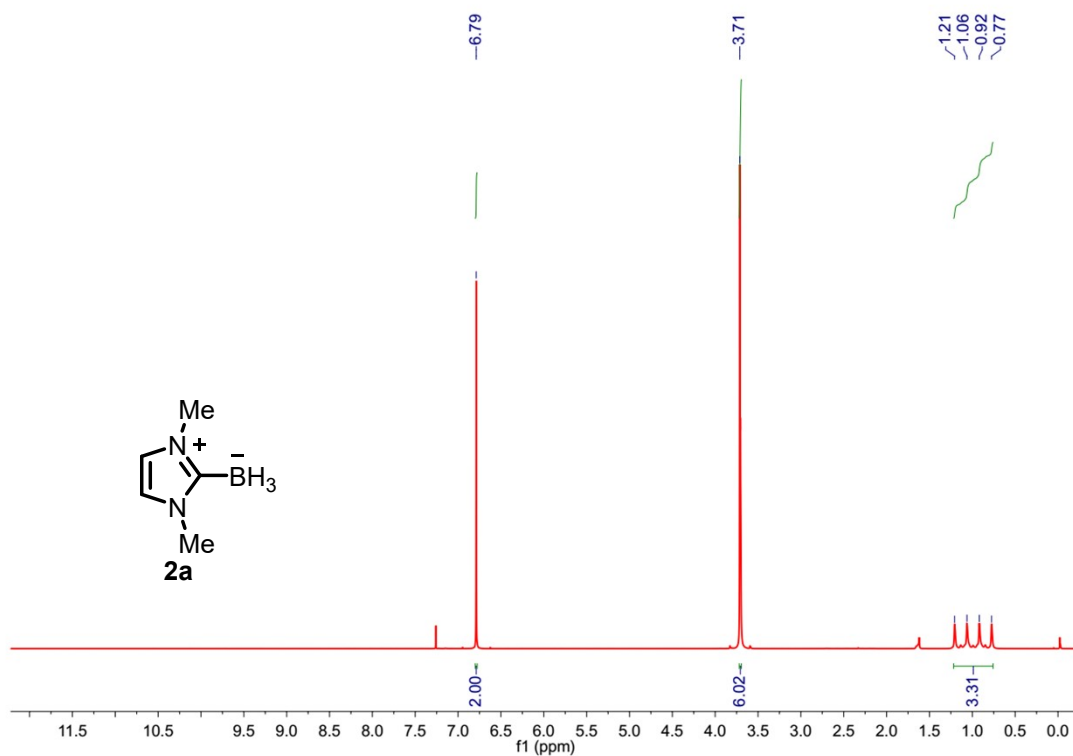


¹³C NMR (151 MHz, CDCl₃)

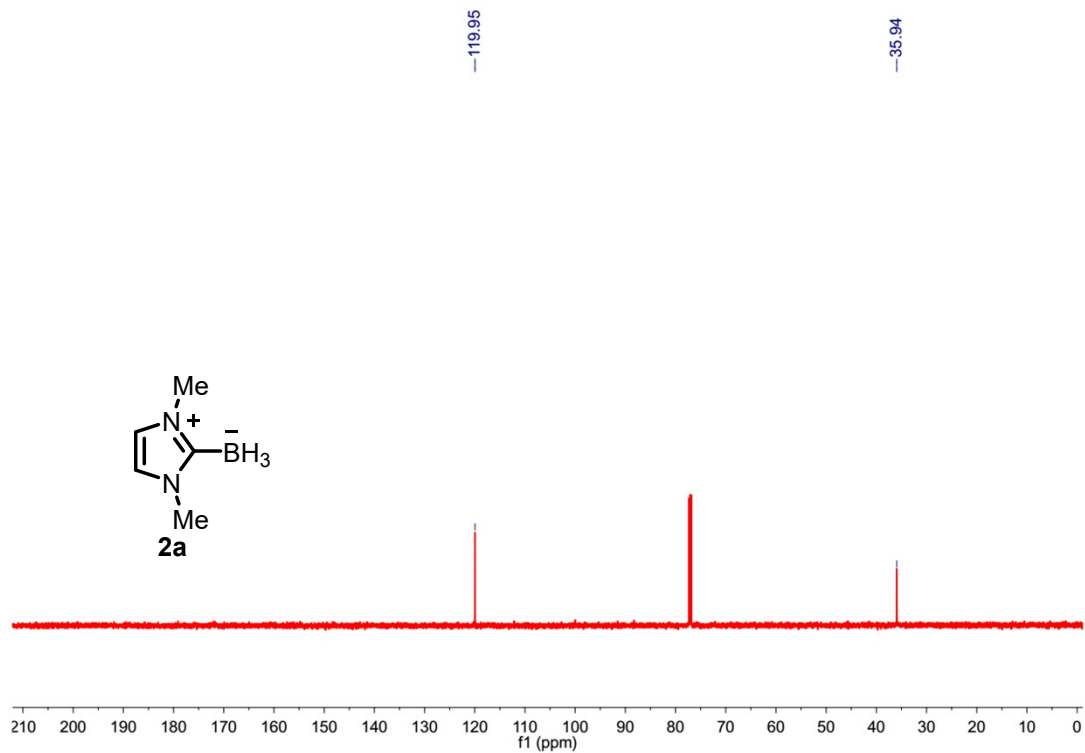




$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3)

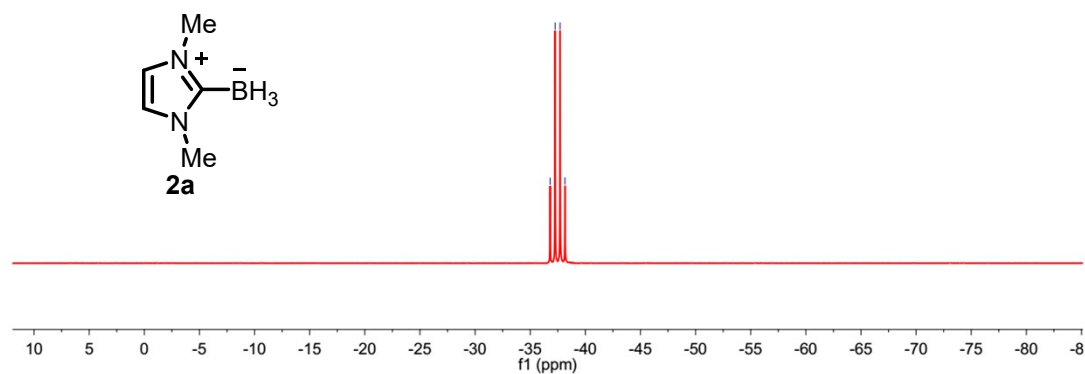


^1H NMR (600 MHz, CDCl_3)

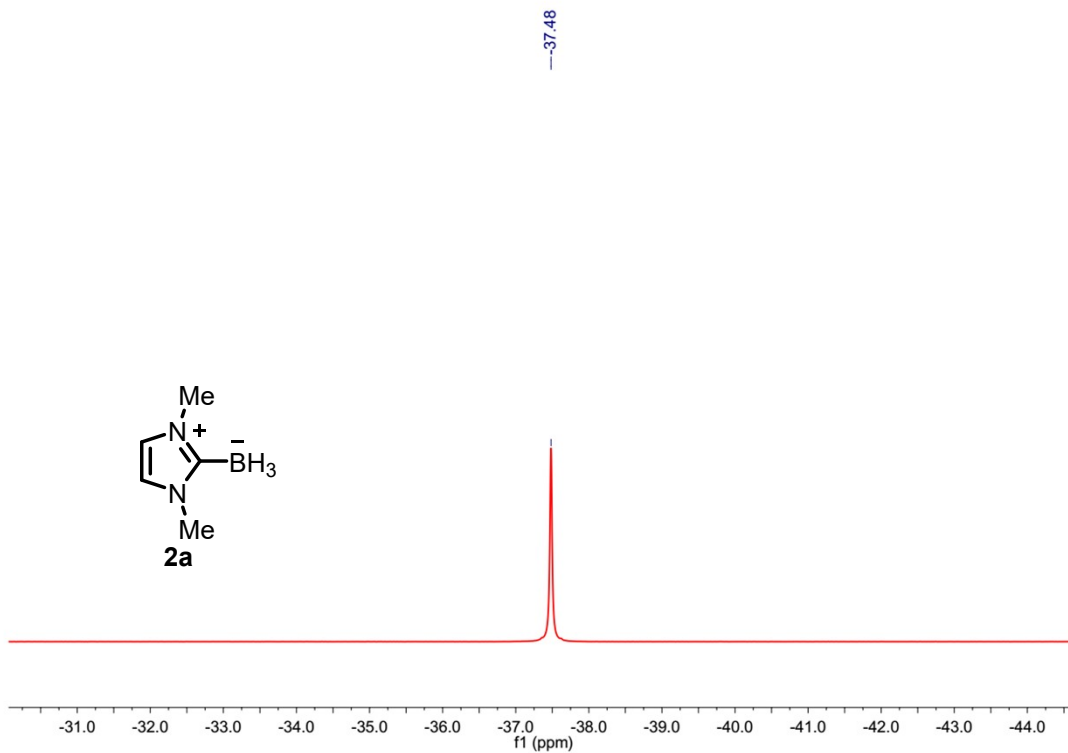


^{13}C NMR (151 MHz, CDCl_3)

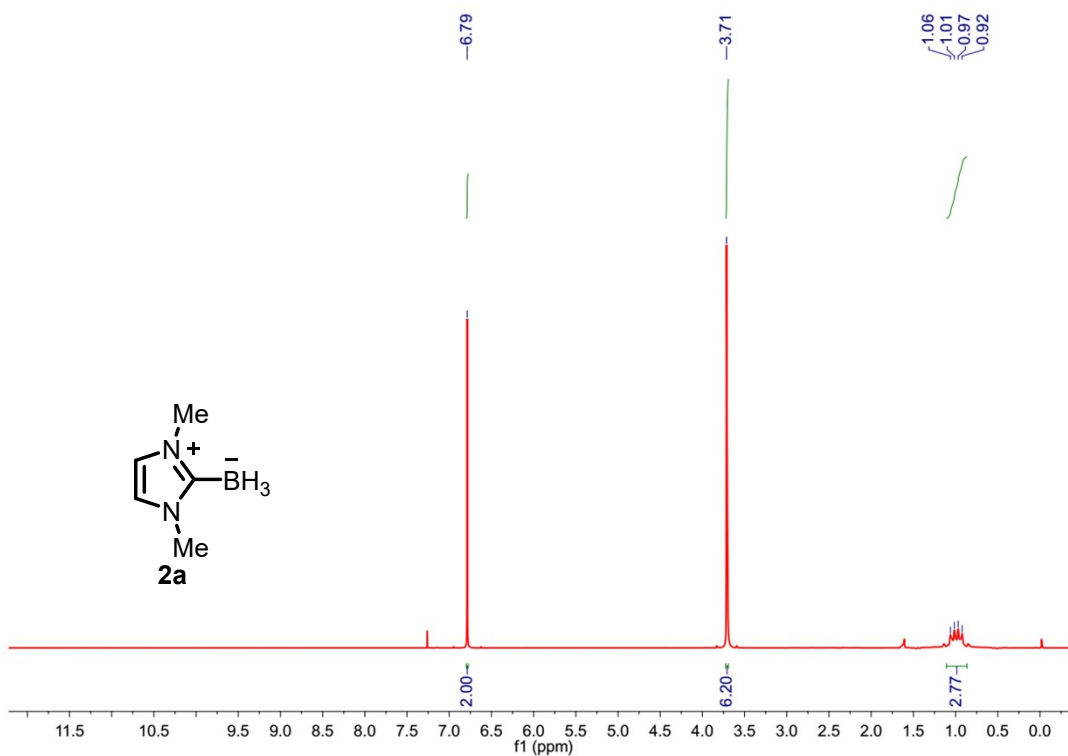
36.81
37.26
37.71
38.16



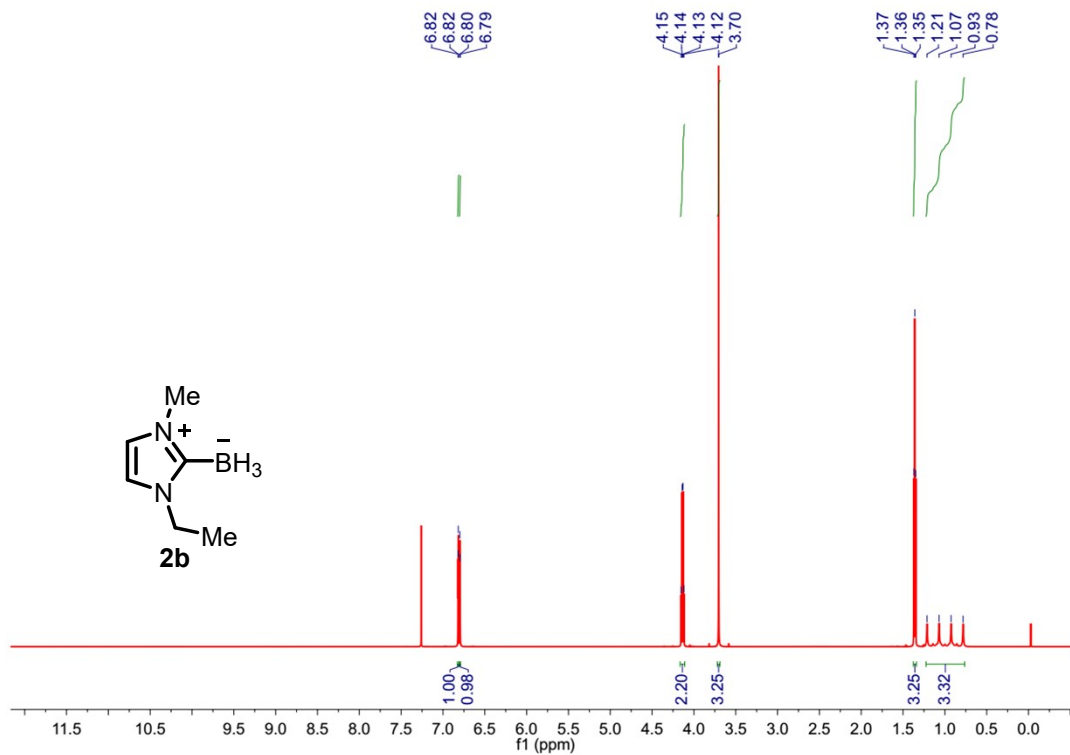
^{11}B NMR (193 MHz, CDCl_3)



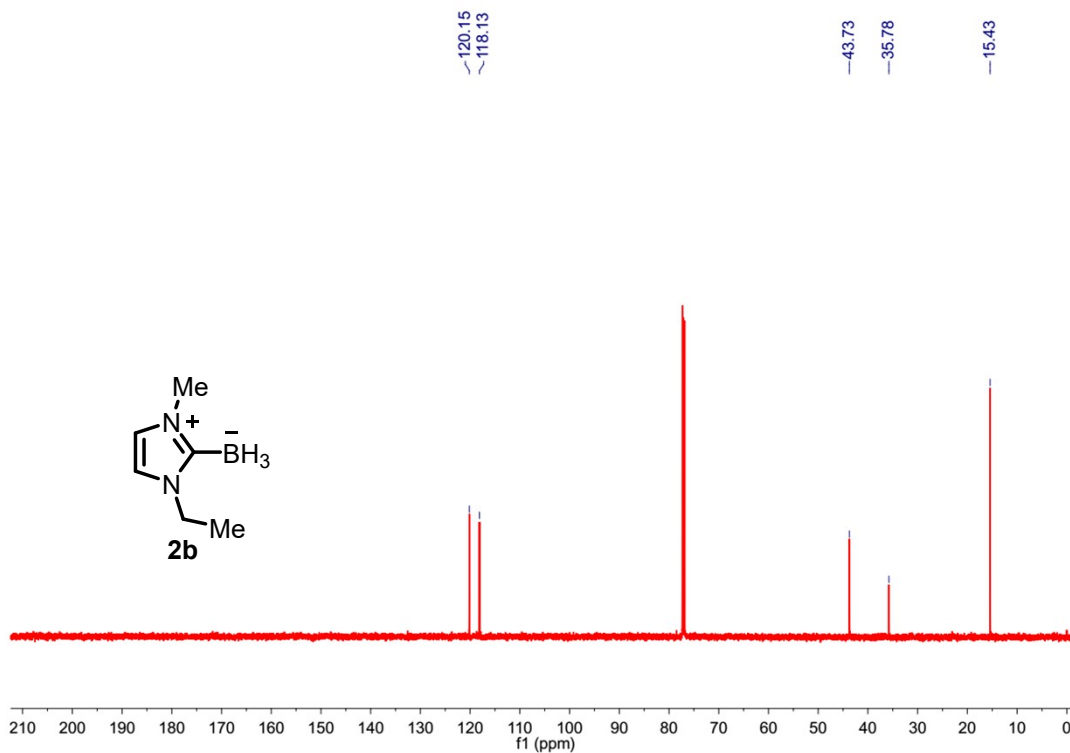
$^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl₃)



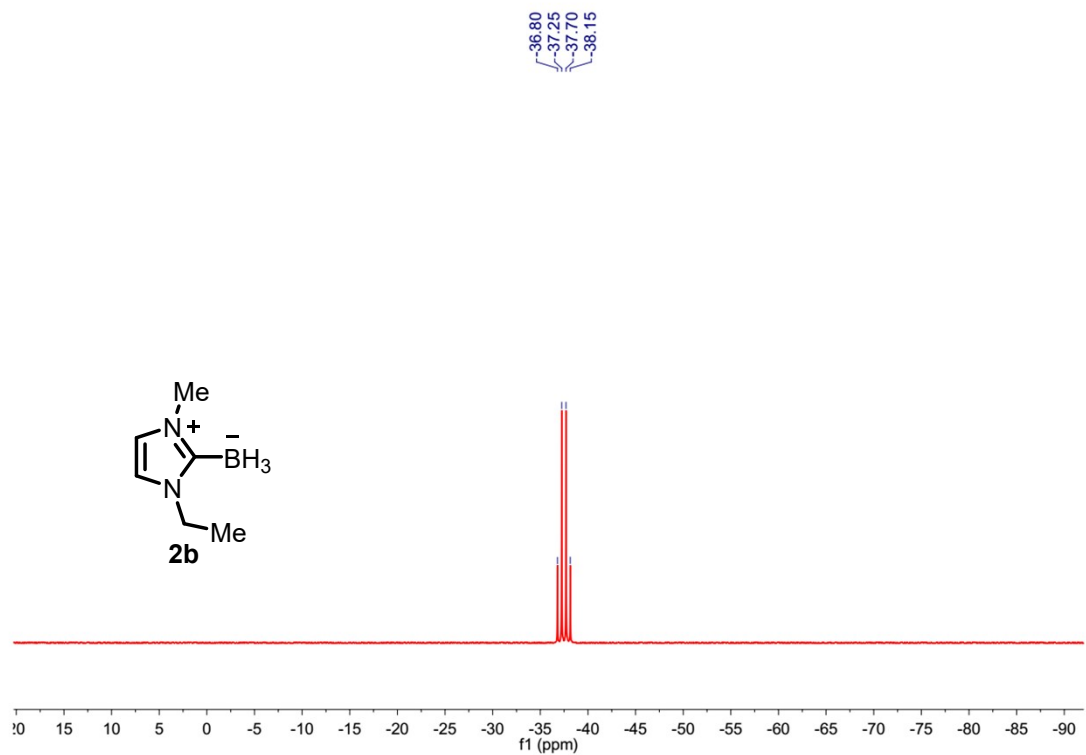
$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl₃)



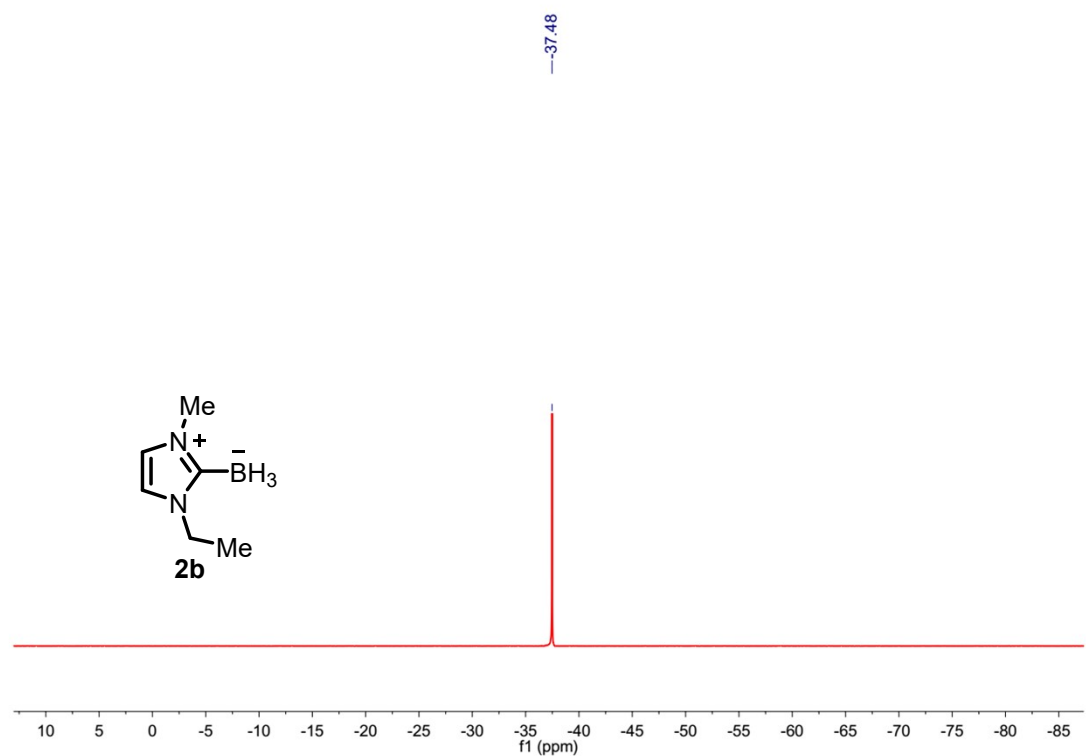
$^1\text{H NMR}$ (600 MHz, CDCl_3)



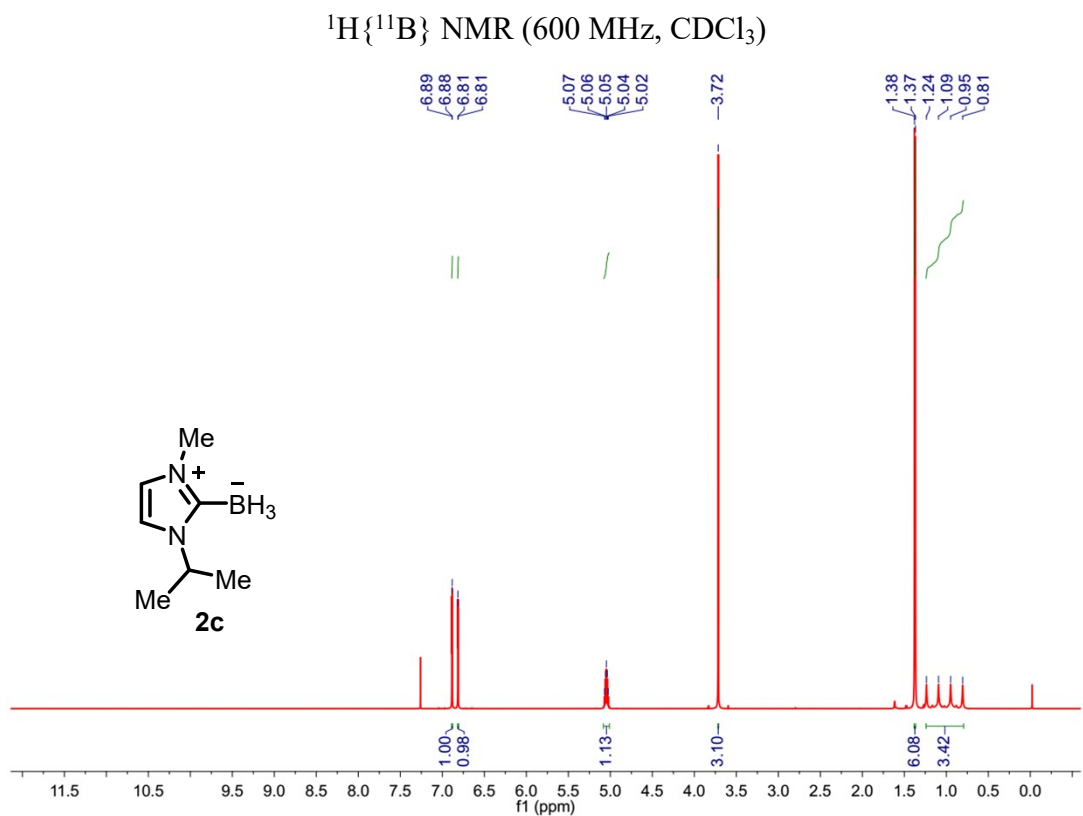
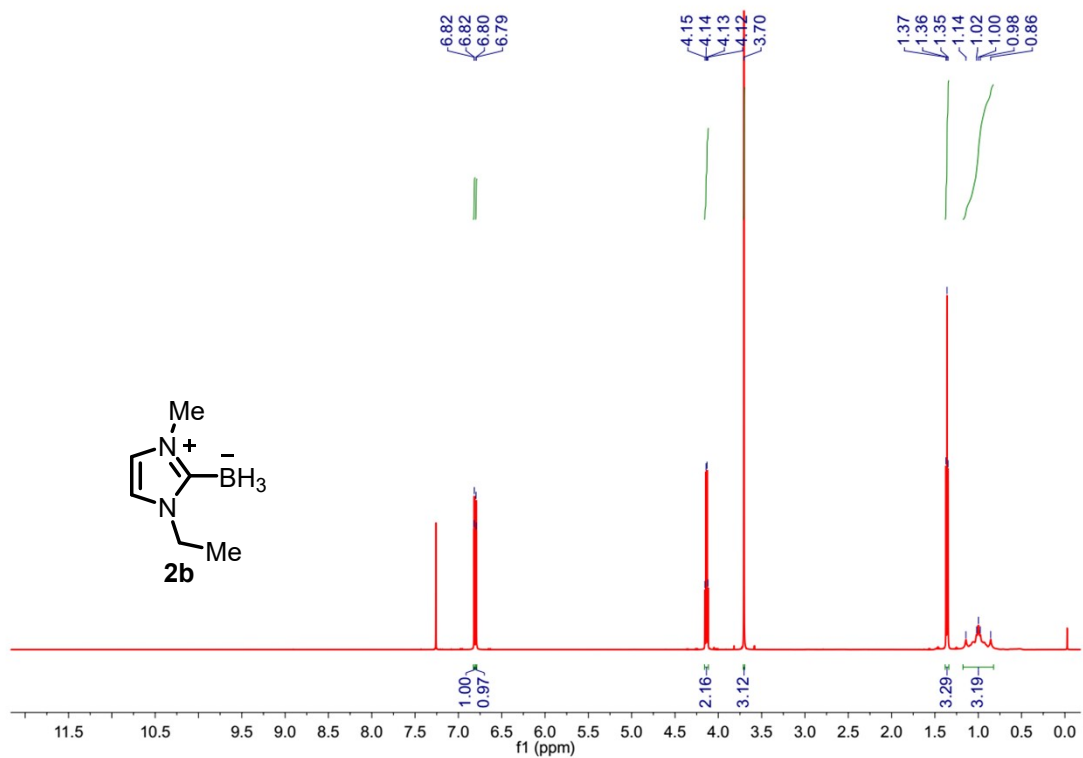
$^{13}\text{C NMR}$ (151 MHz, CDCl_3)

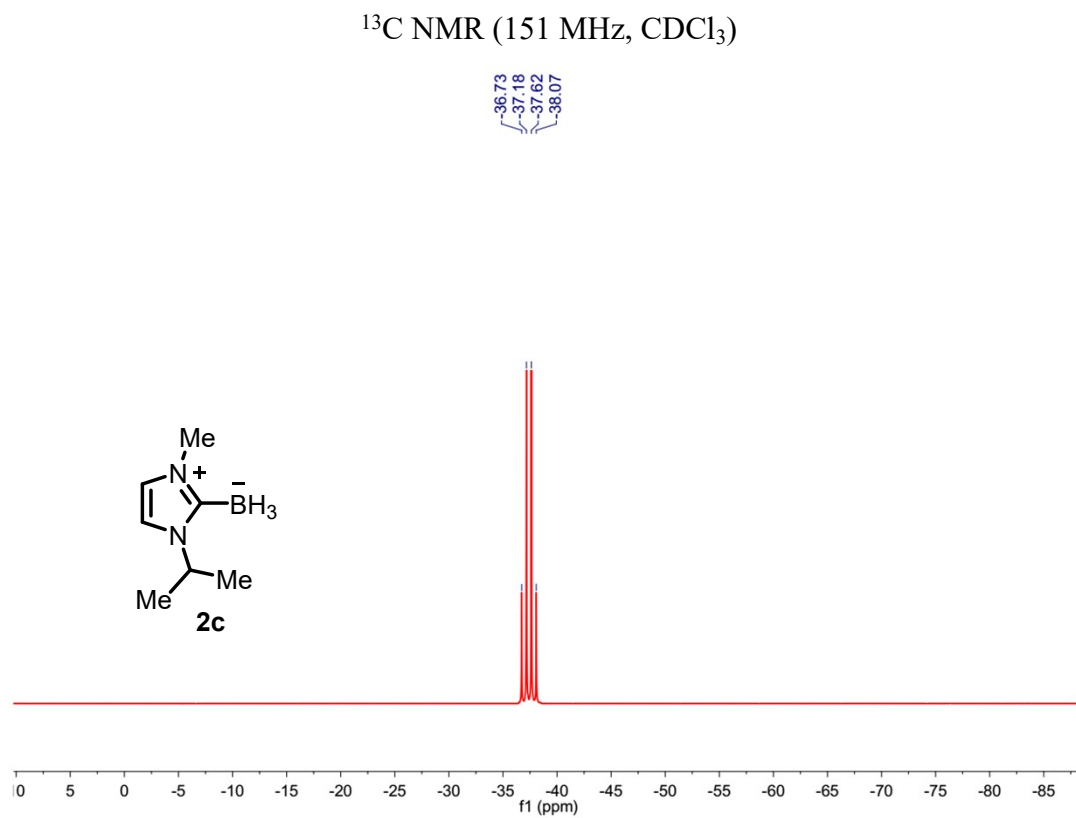
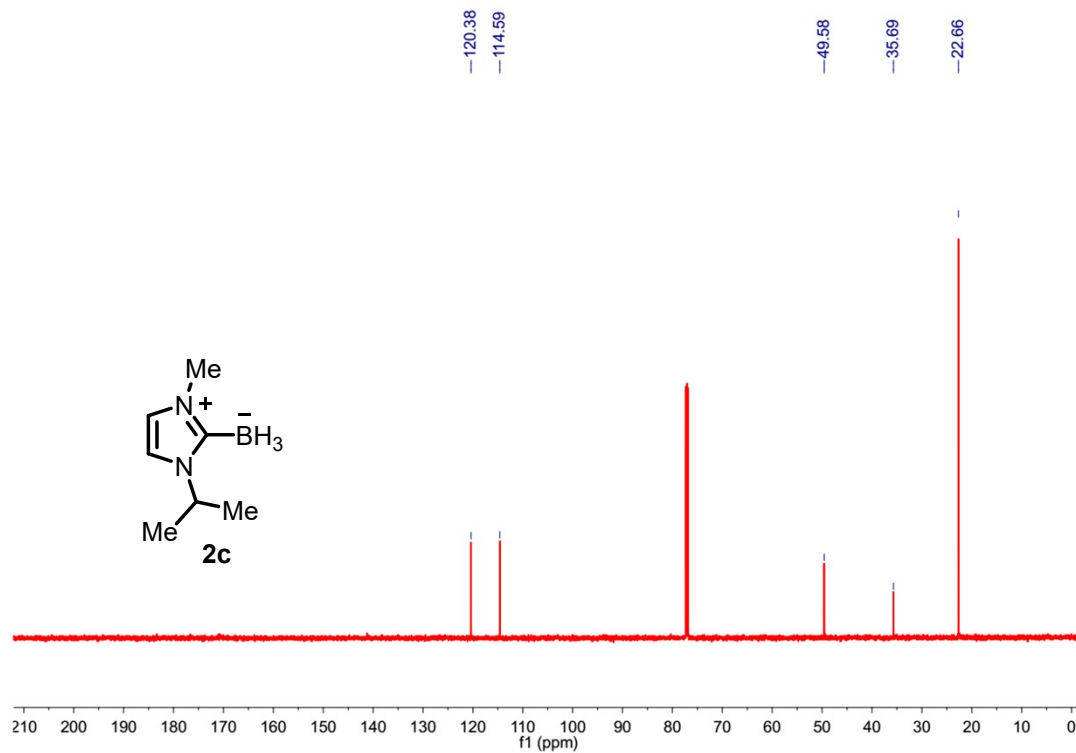


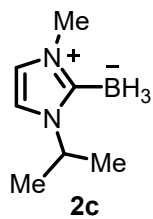
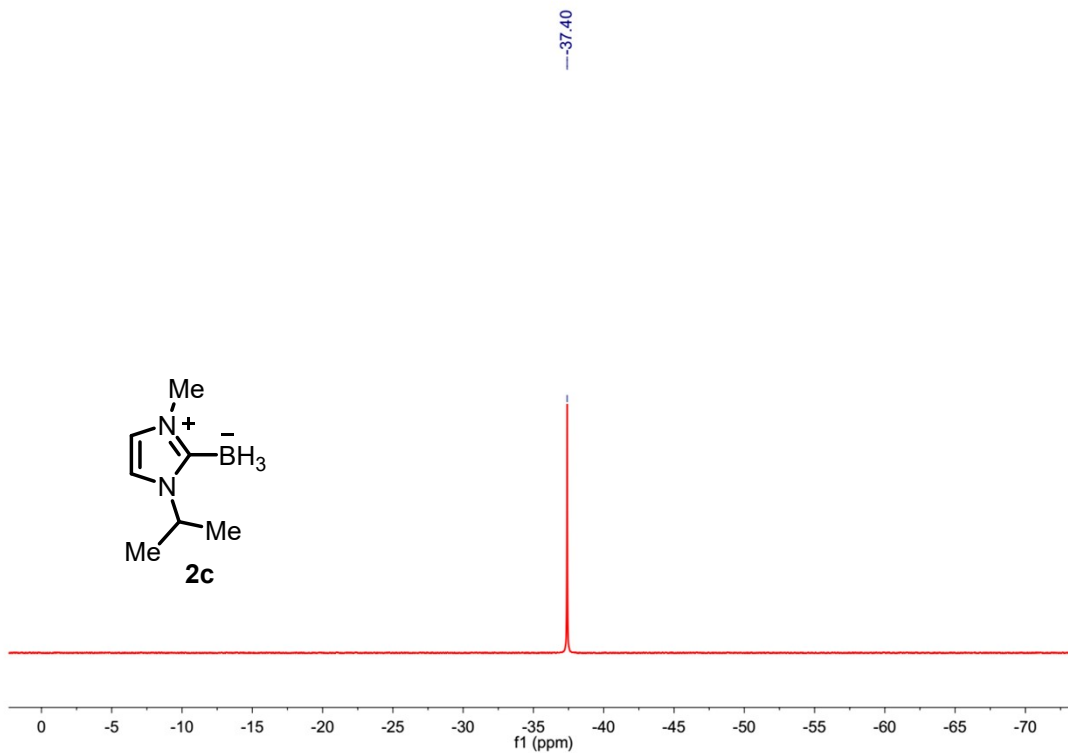
¹¹B NMR (193 MHz, CDCl₃)



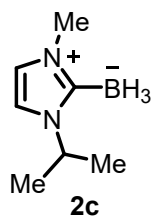
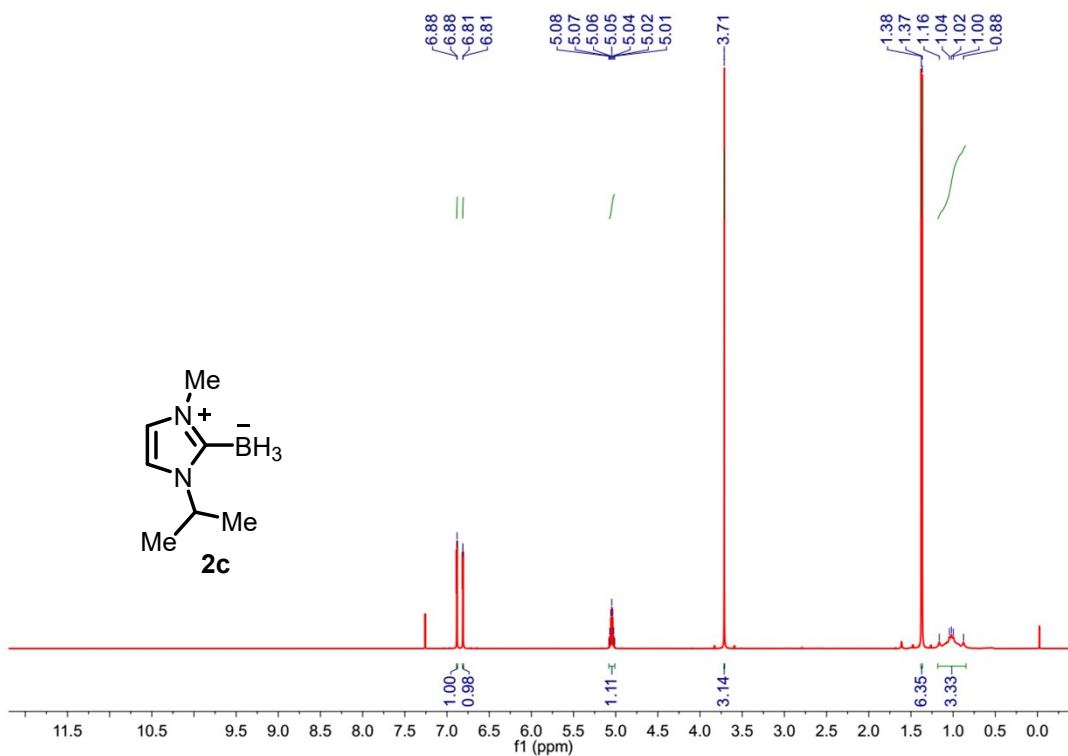
¹¹B{¹H} NMR (193 MHz, CDCl₃)



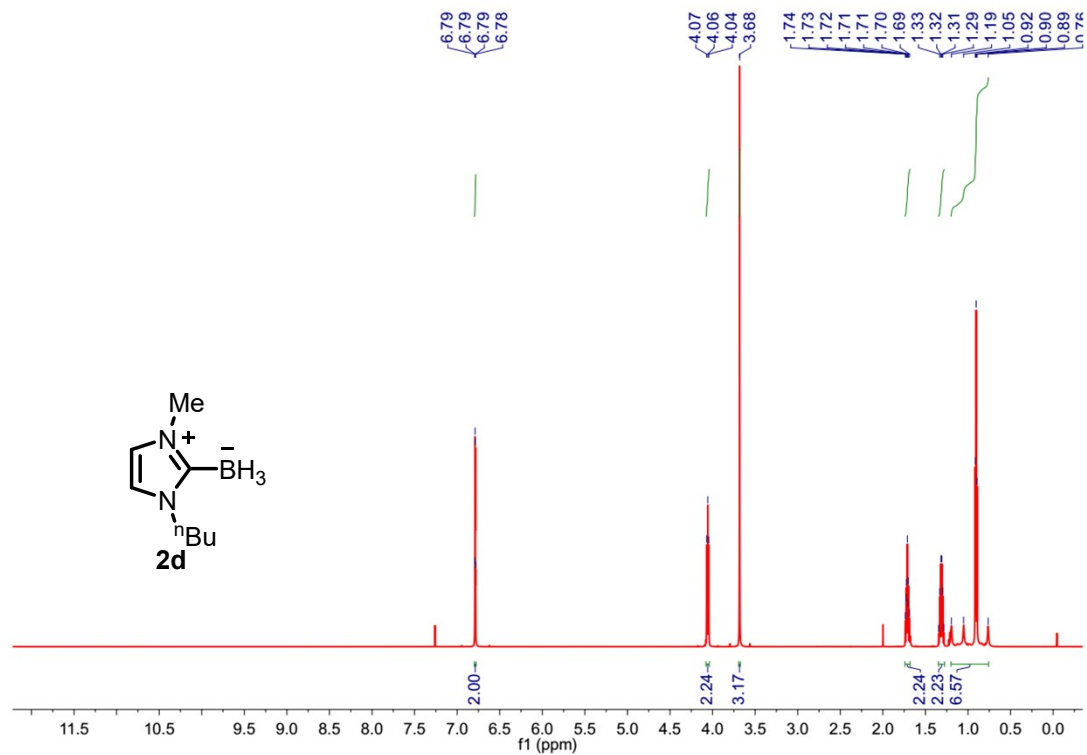




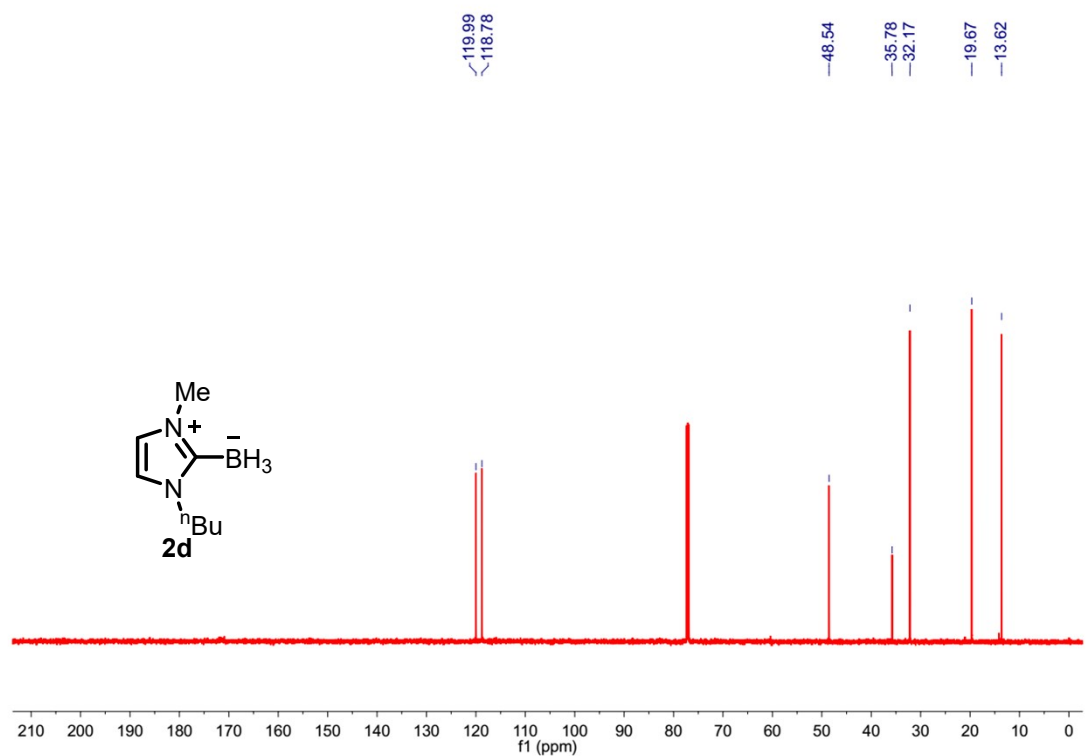
$^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3)



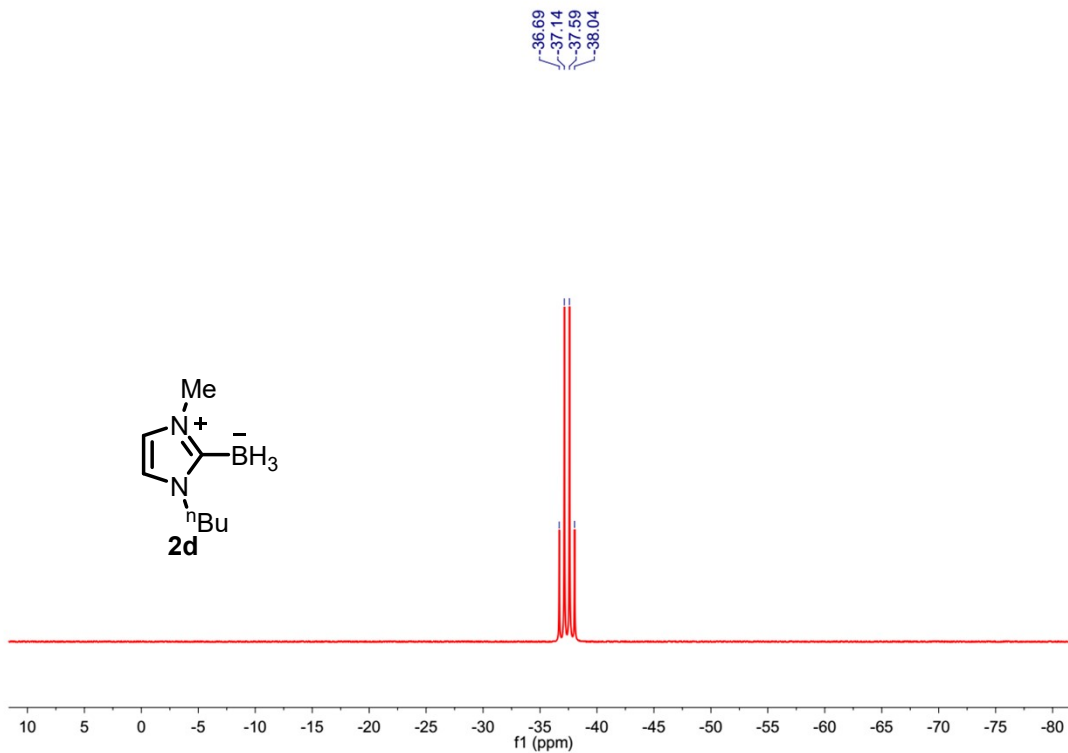
$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3)



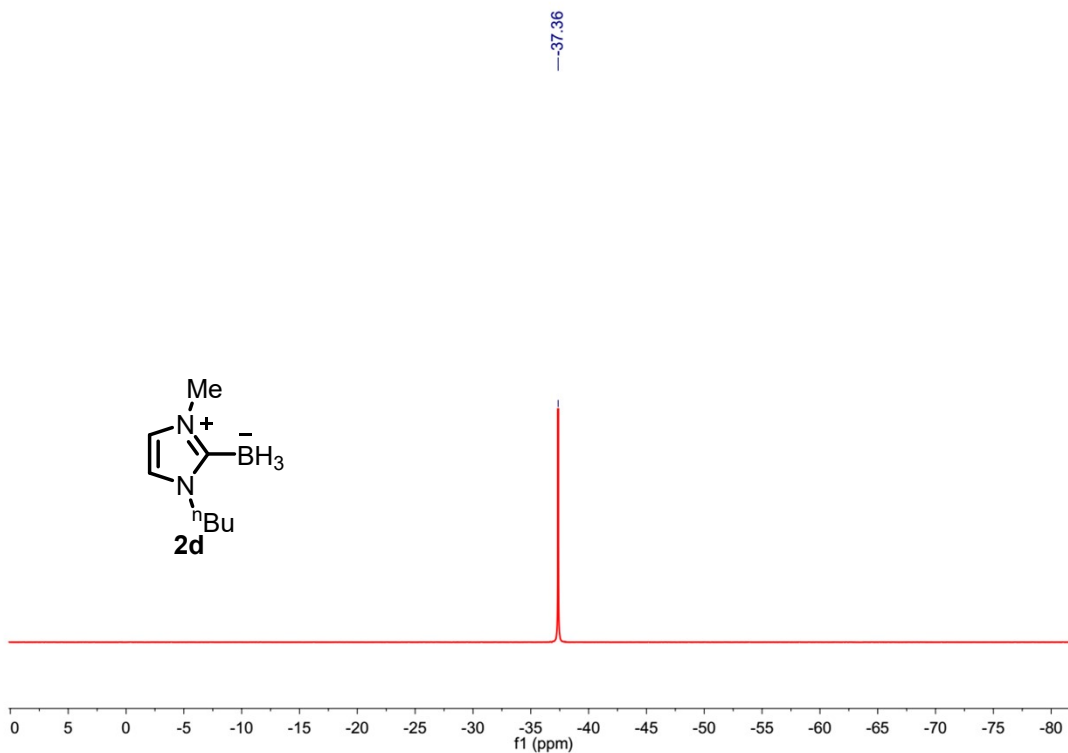
¹H NMR (600 MHz, CDCl₃)



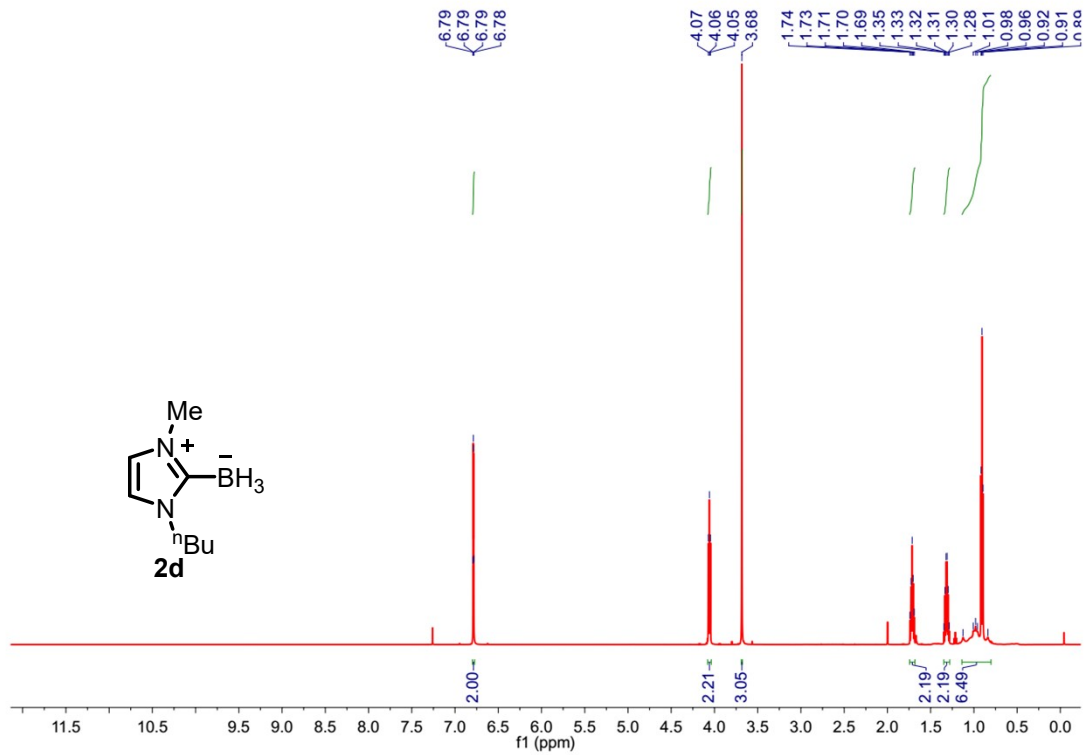
¹³C NMR (151 MHz, CDCl₃)



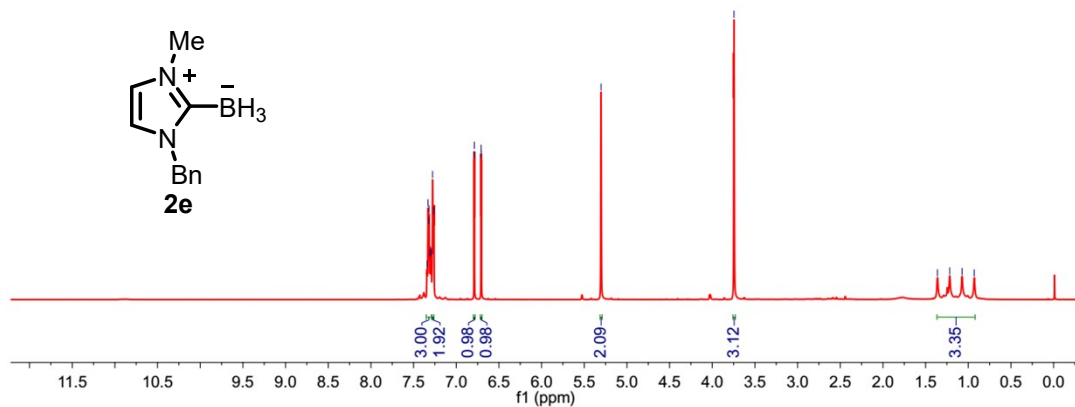
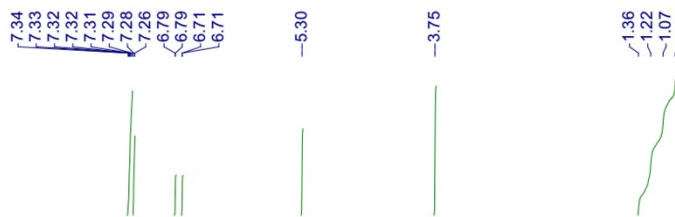
¹¹B NMR (193 MHz, CDCl₃)



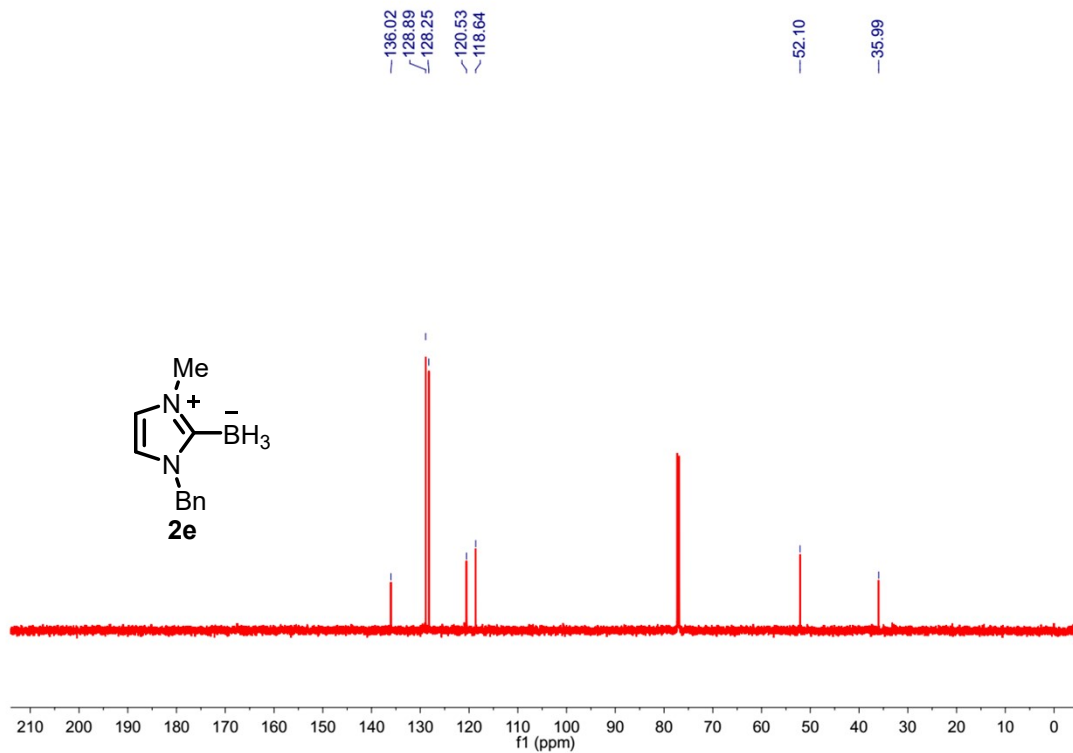
¹¹B{¹H} NMR (193 MHz, CDCl₃)



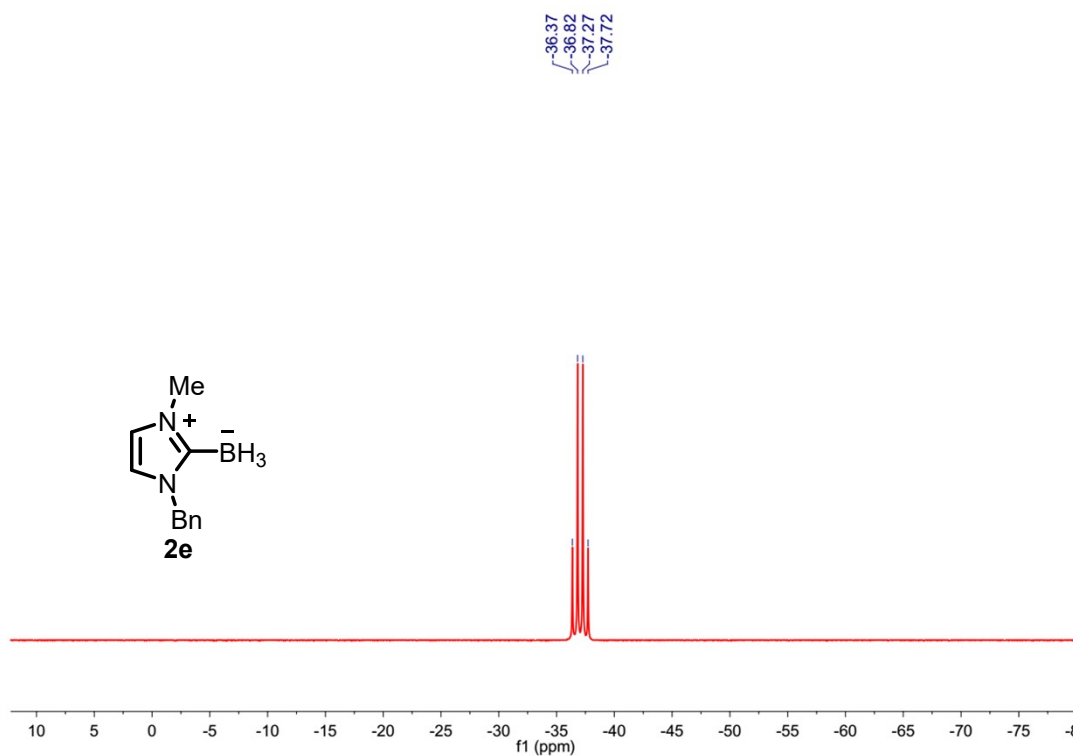
$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3)



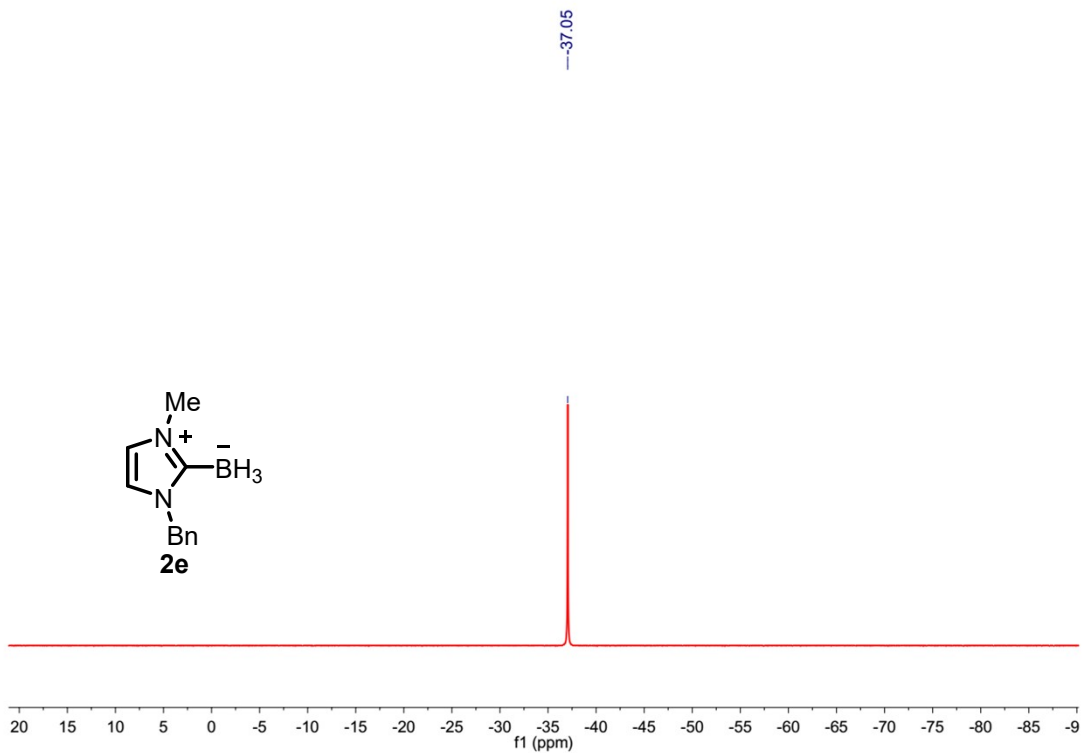
^1H NMR (600 MHz, CDCl_3)



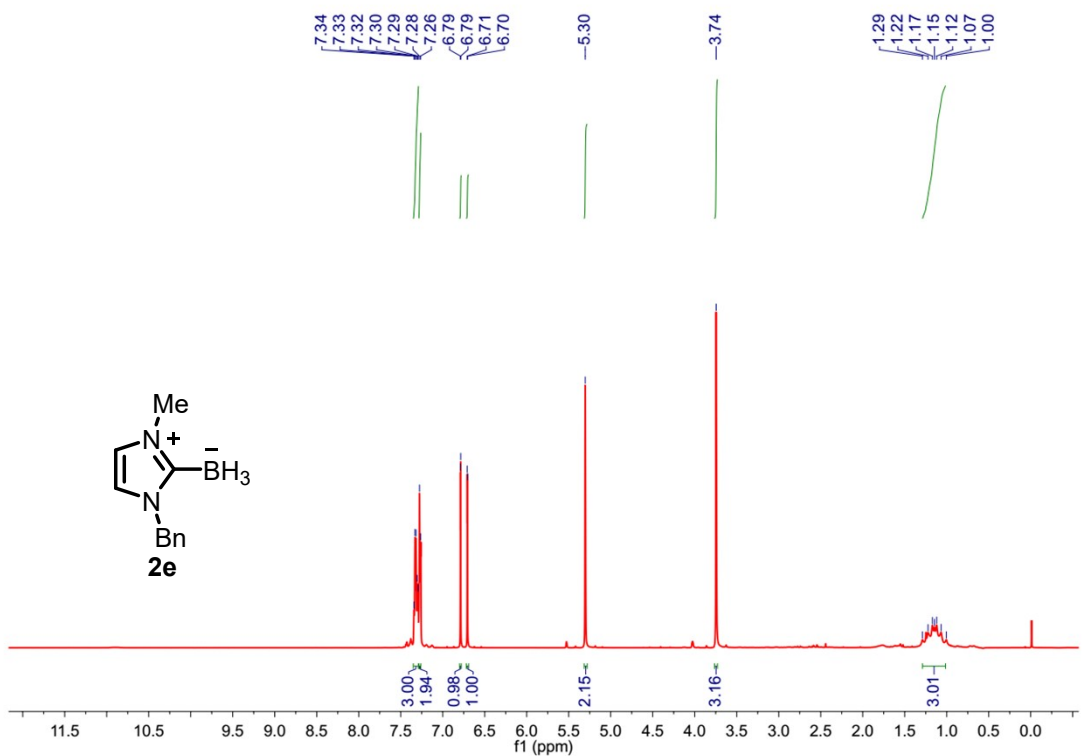
^{13}C NMR (151 MHz, CDCl_3)



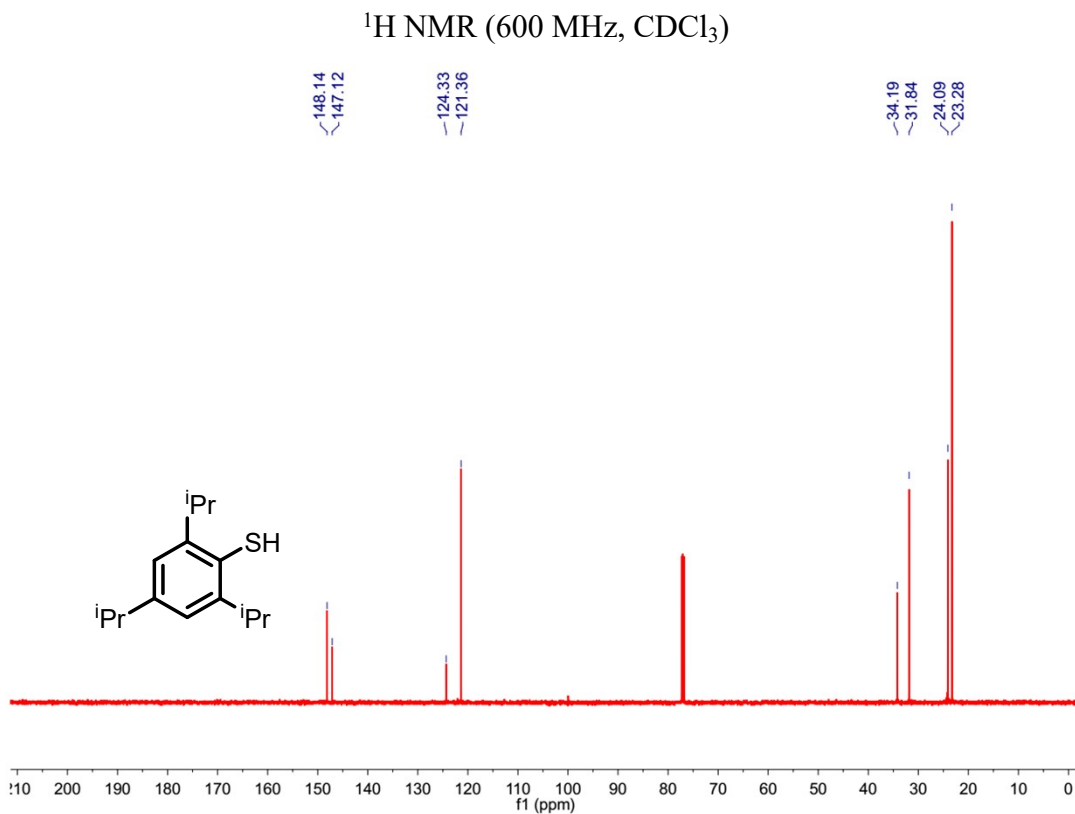
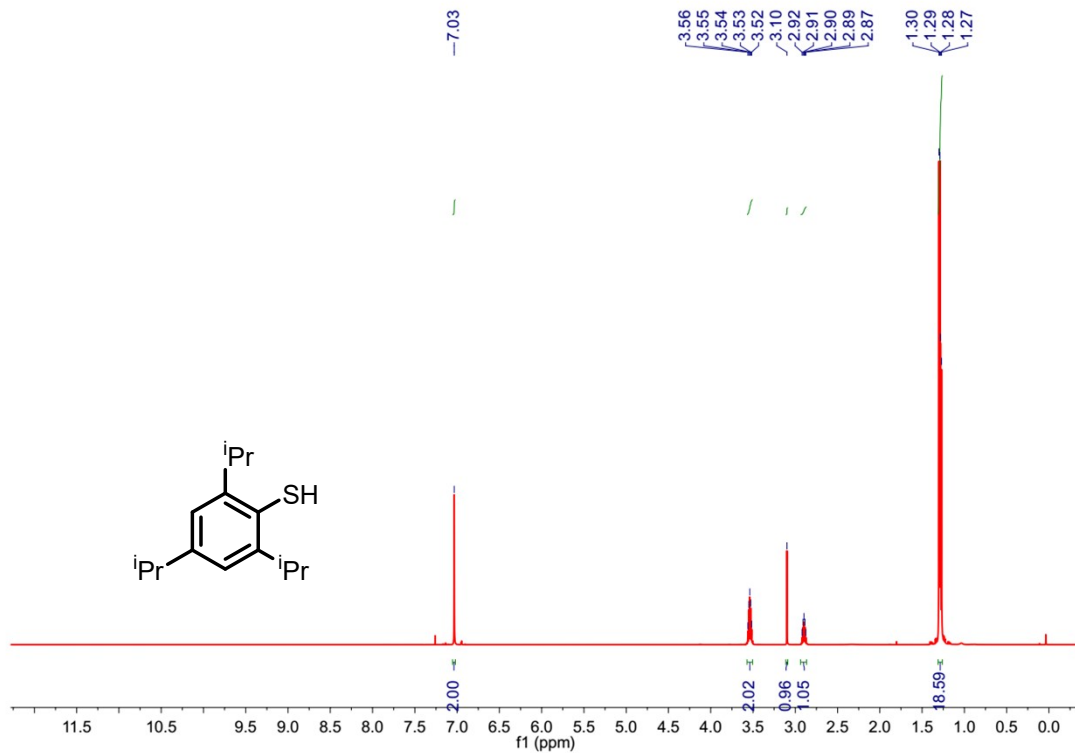
^{11}B NMR (193 MHz, CDCl_3)

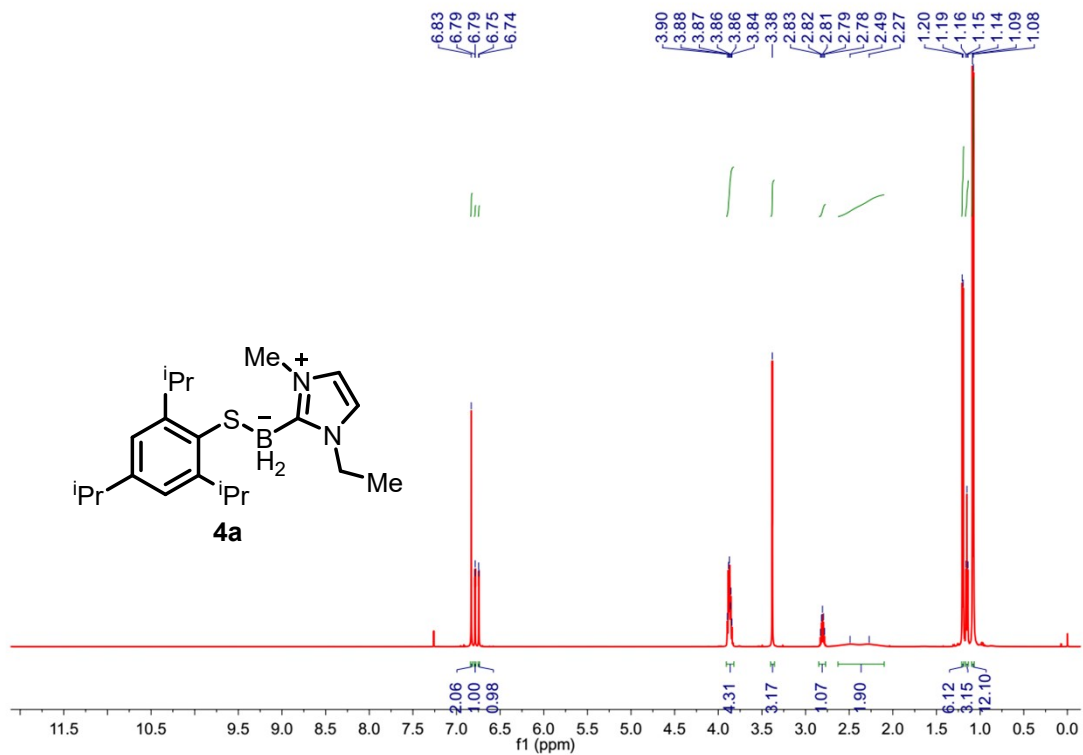


$^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3)

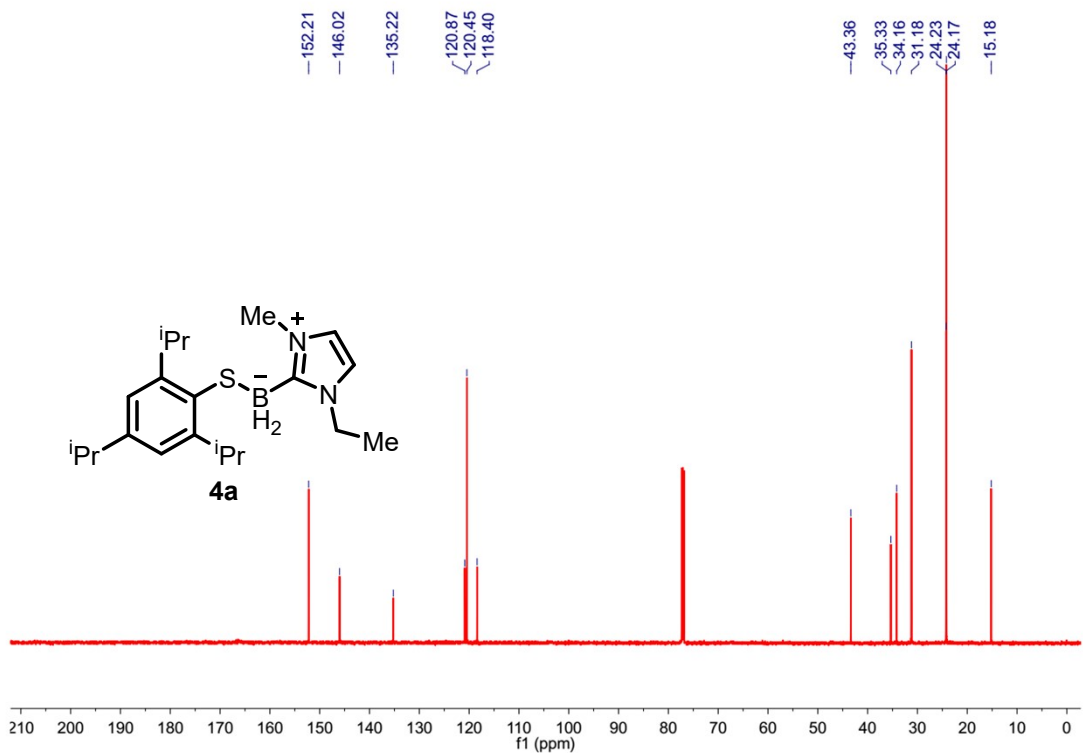


$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3)

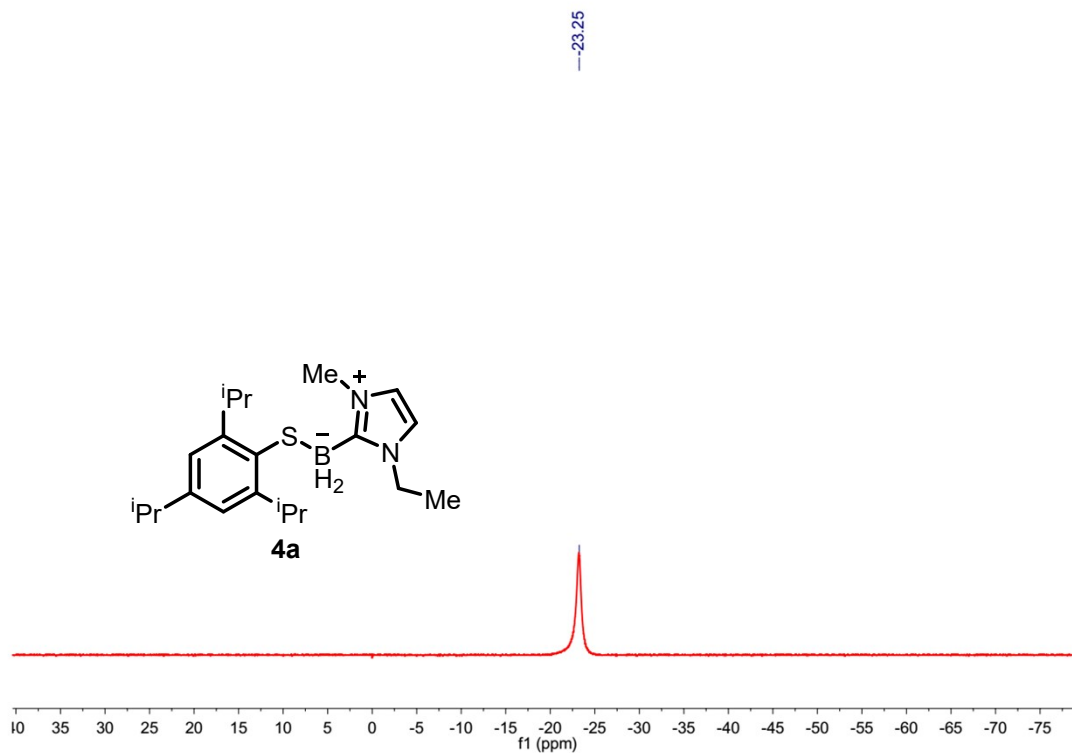
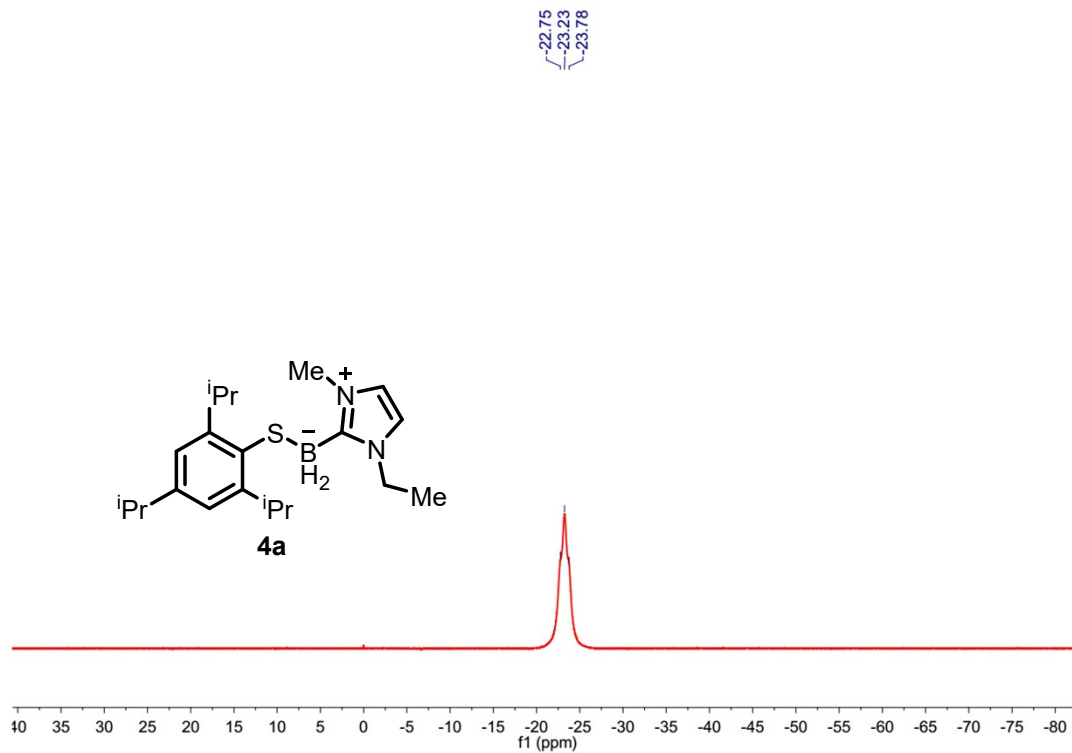


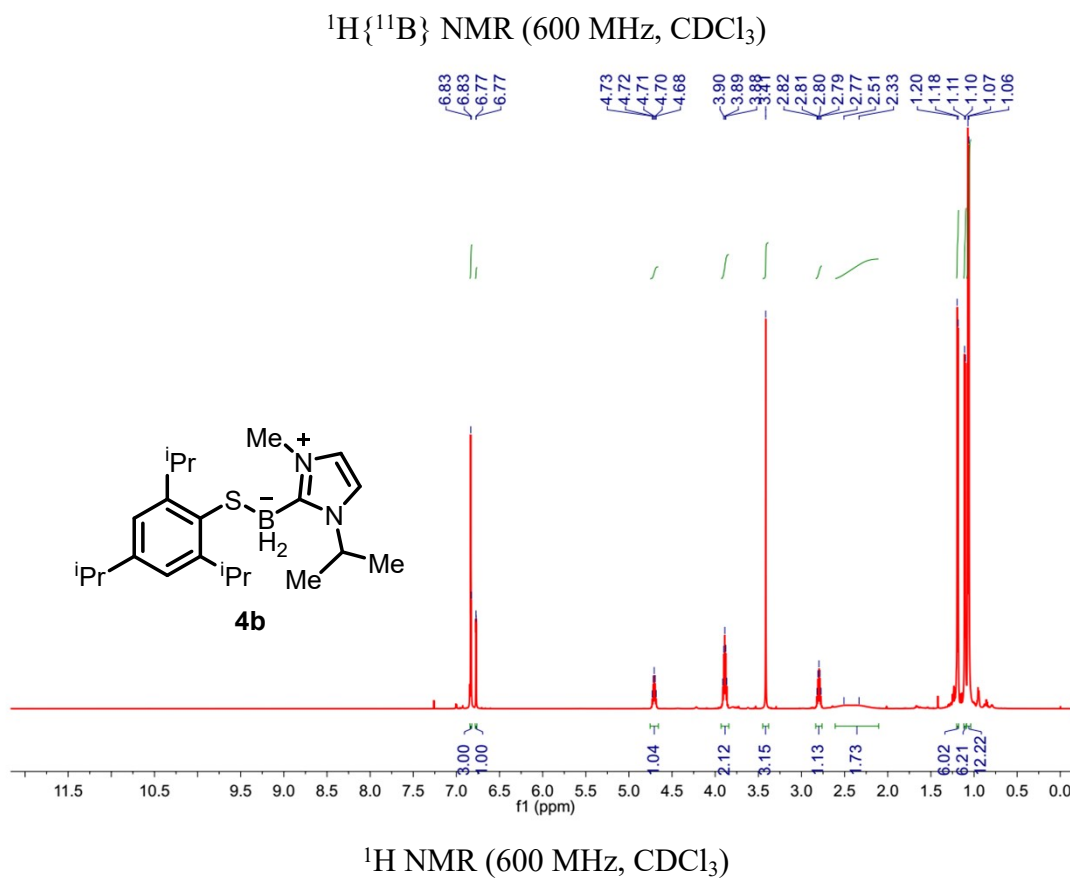
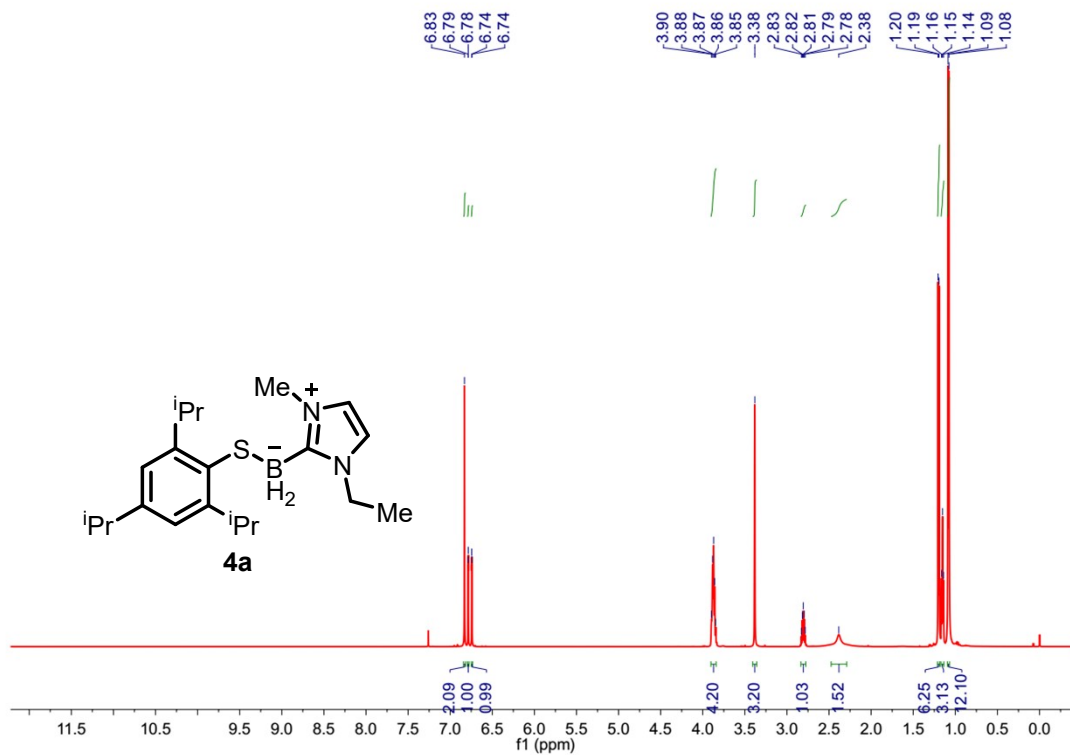


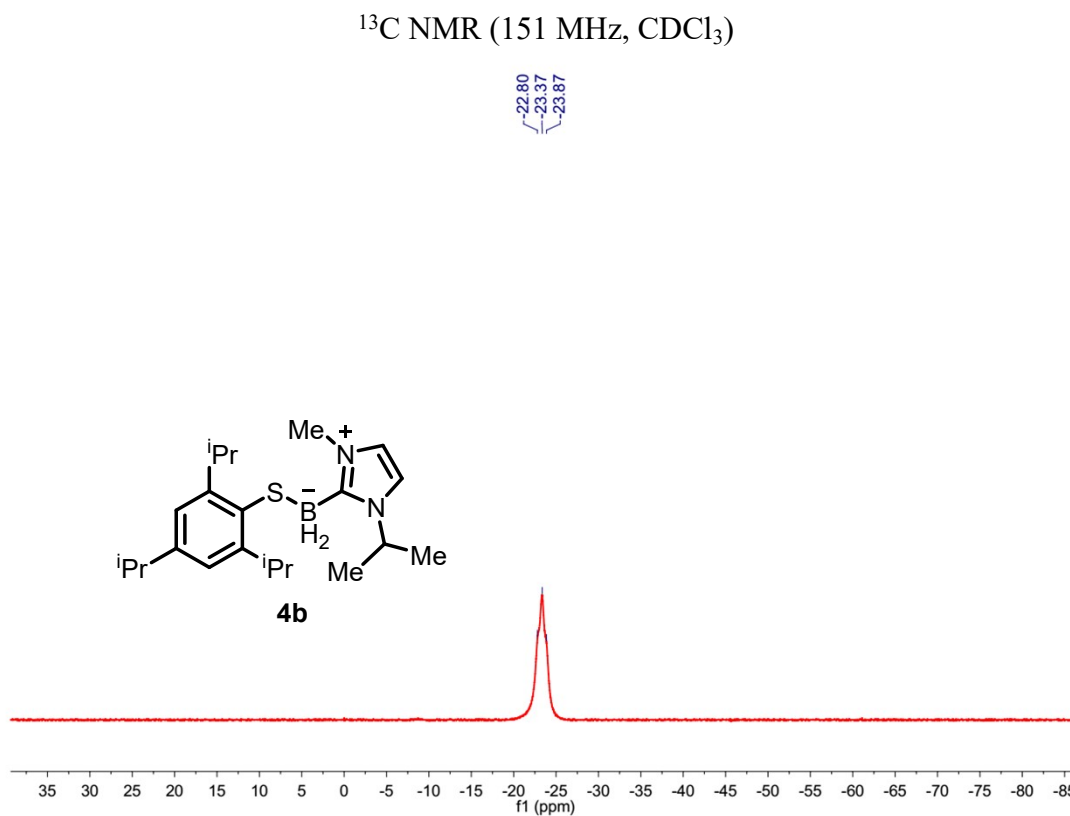
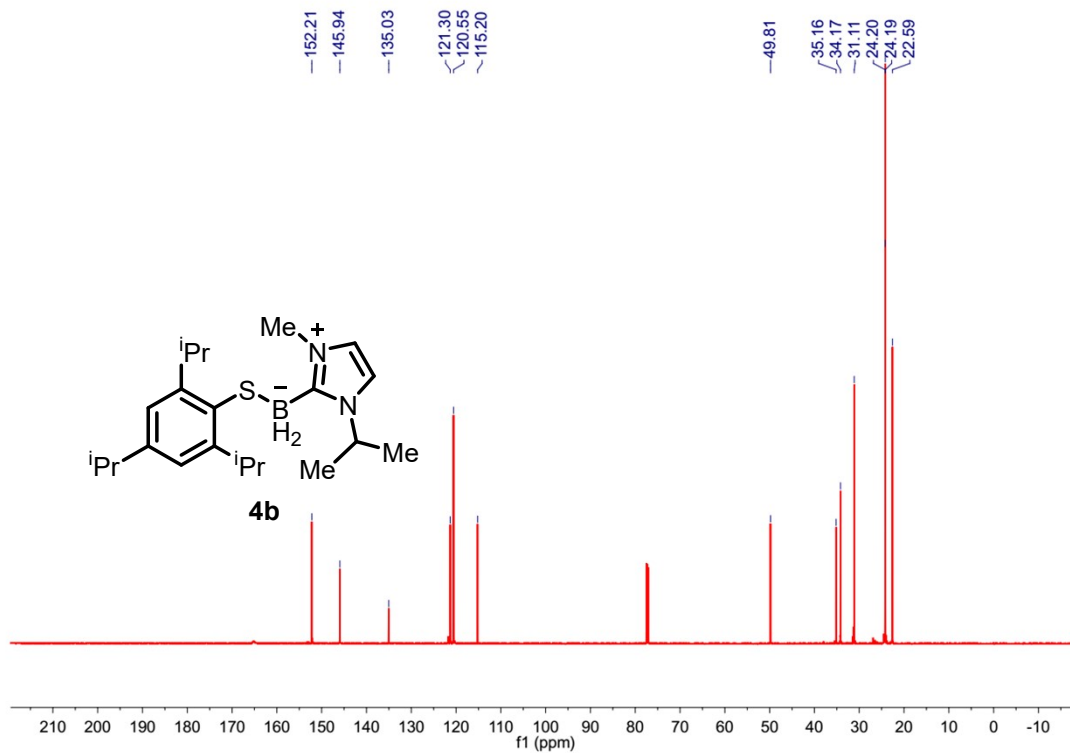
¹H NMR (600 MHz, CDCl₃)

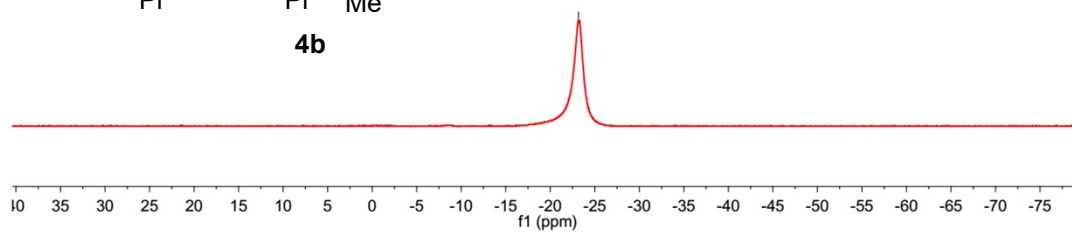
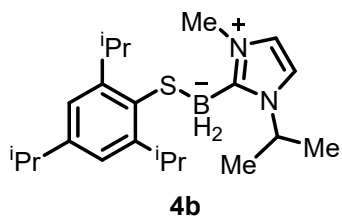


¹³C NMR (151 MHz, CDCl₃)

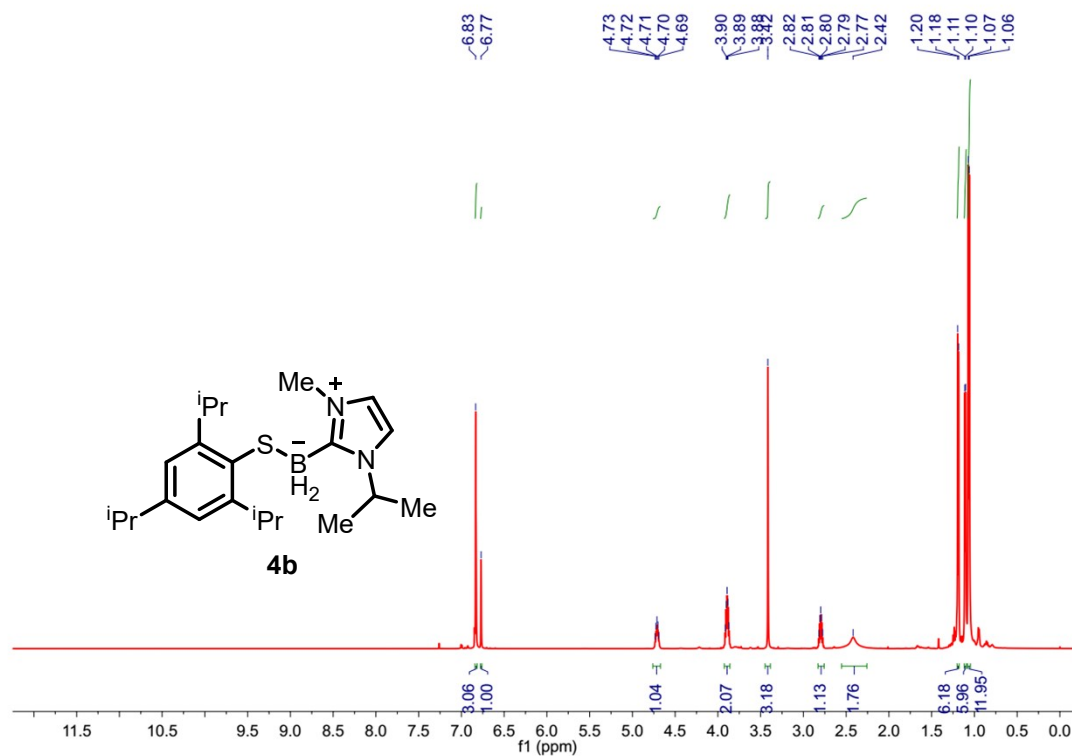




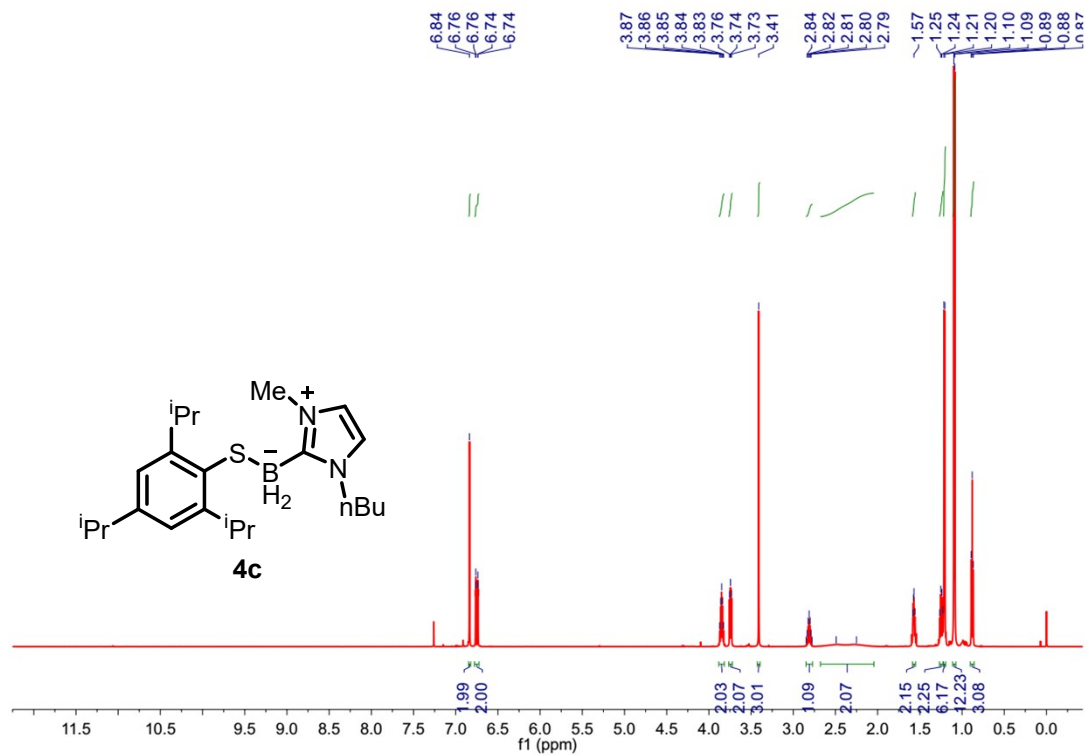




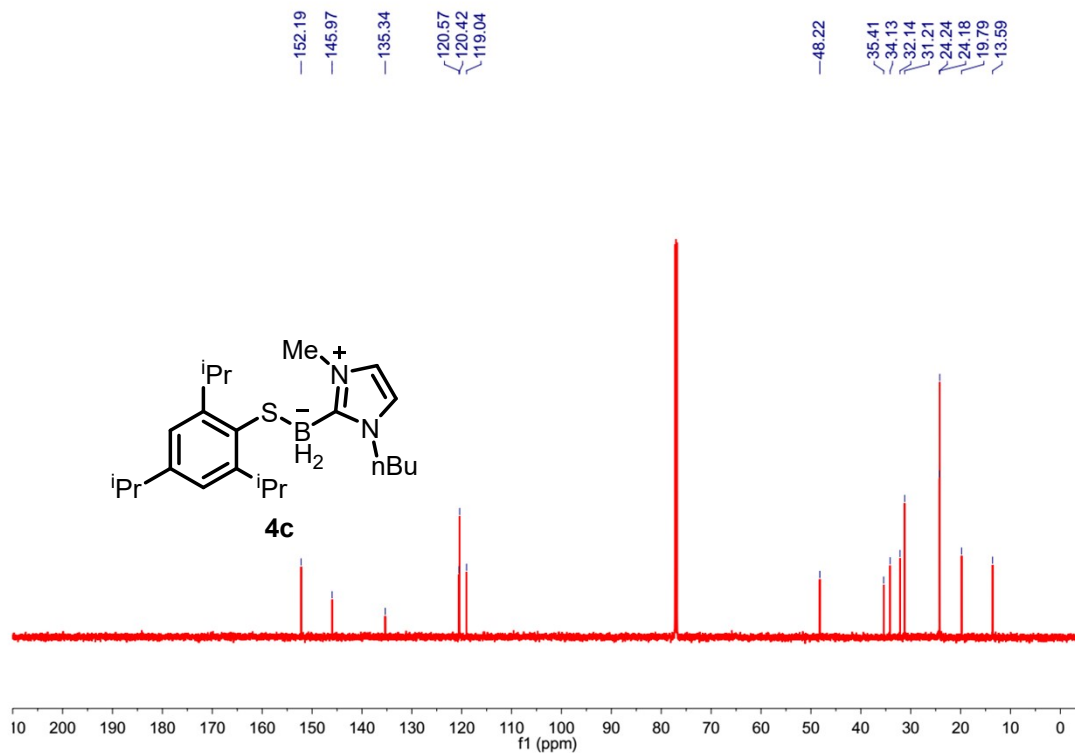
$^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3)



$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3)

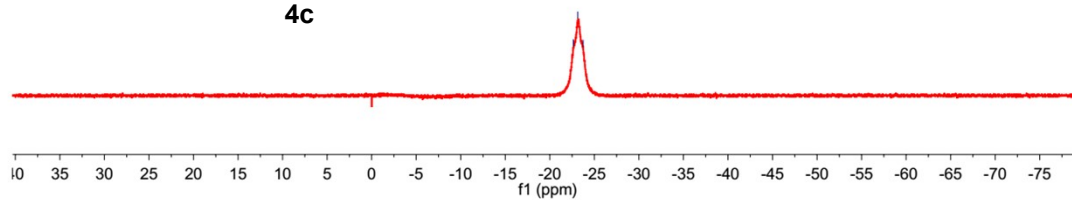
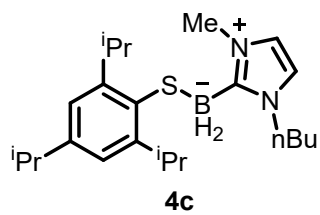


^1H NMR (600 MHz, CDCl_3)



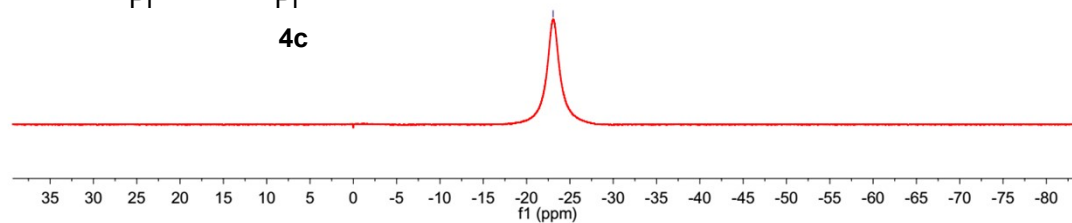
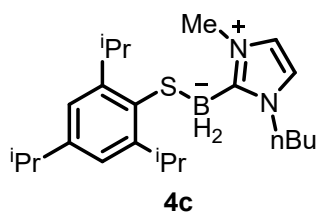
^{13}C NMR (151 MHz, CDCl_3)

22.64
23.14
23.74

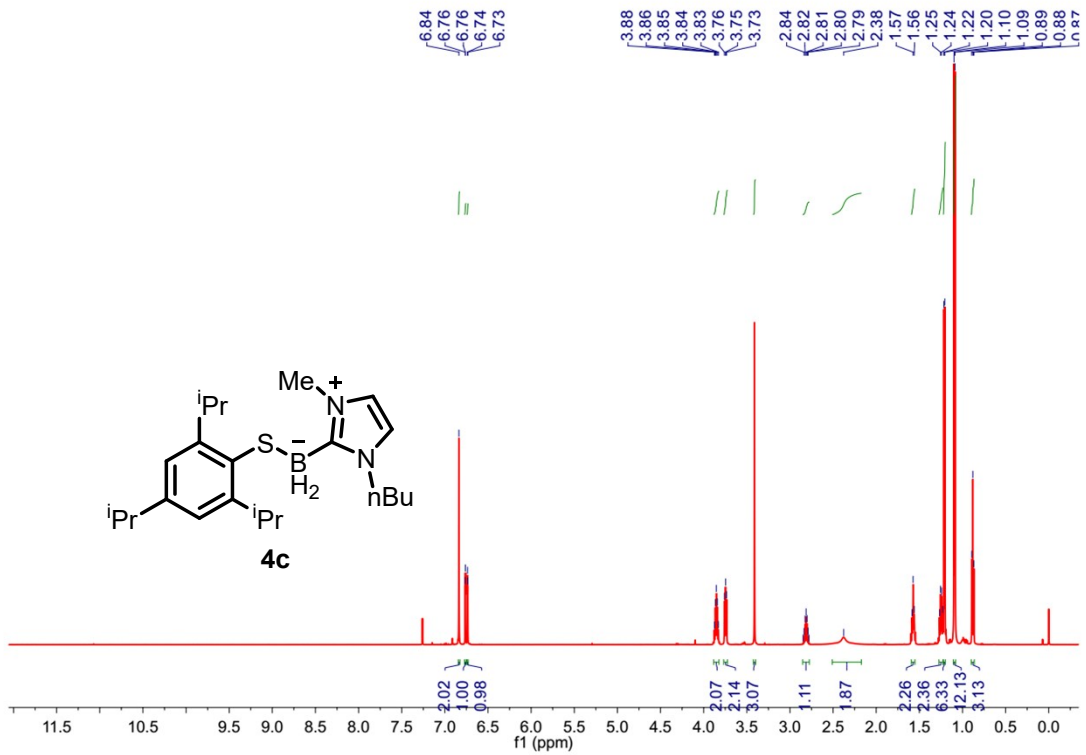


^{11}B NMR (193 MHz, CDCl_3)

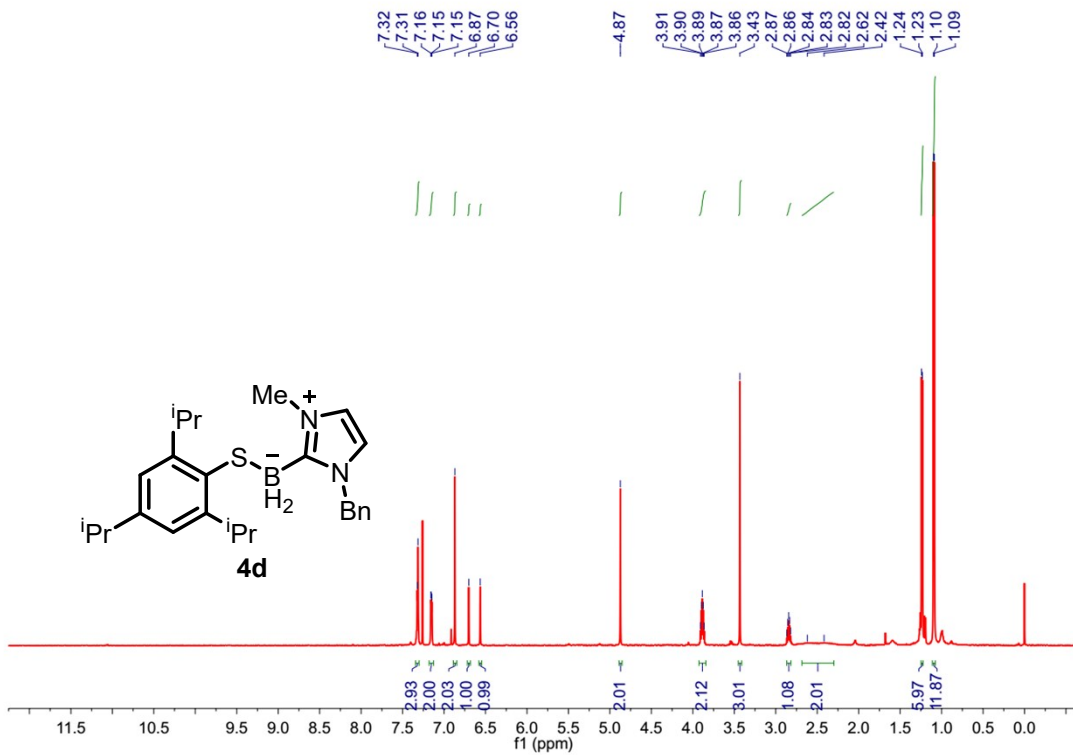
23.06



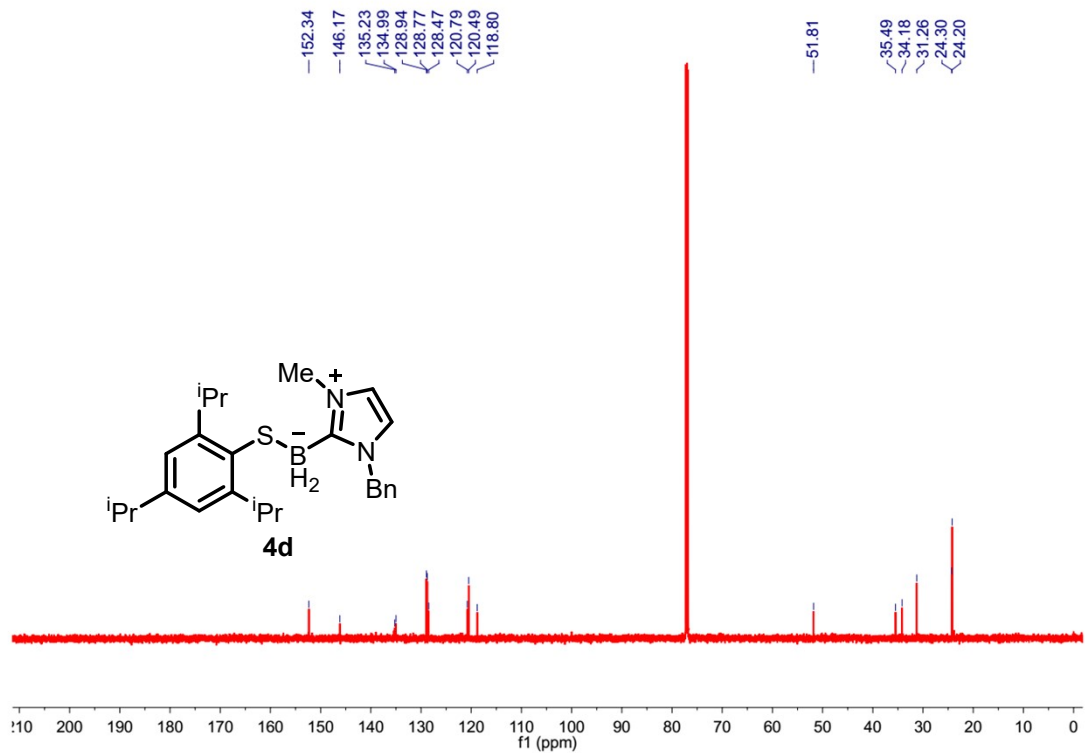
$^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3)



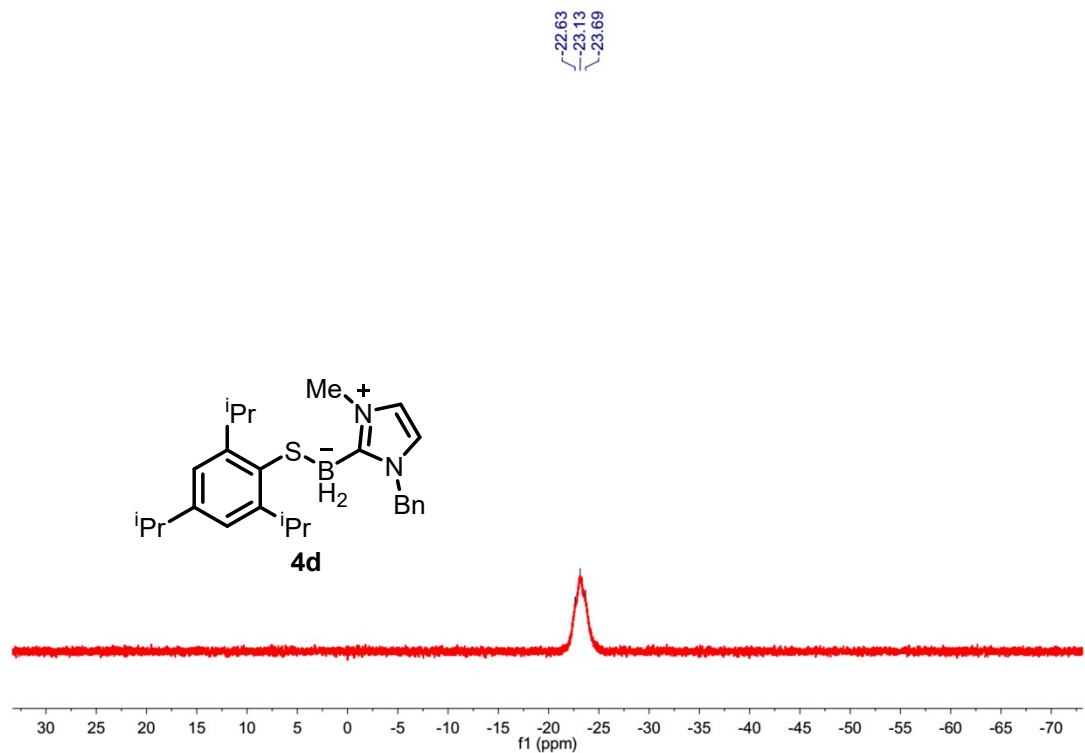
$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3)



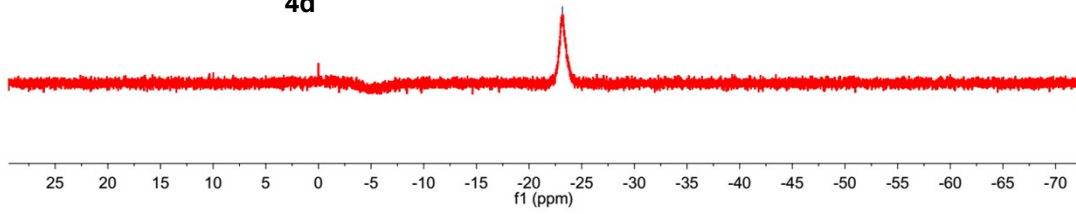
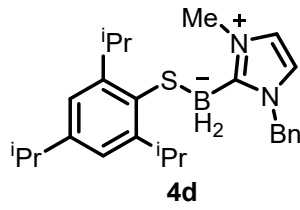
^1H NMR (600 MHz, CDCl_3)



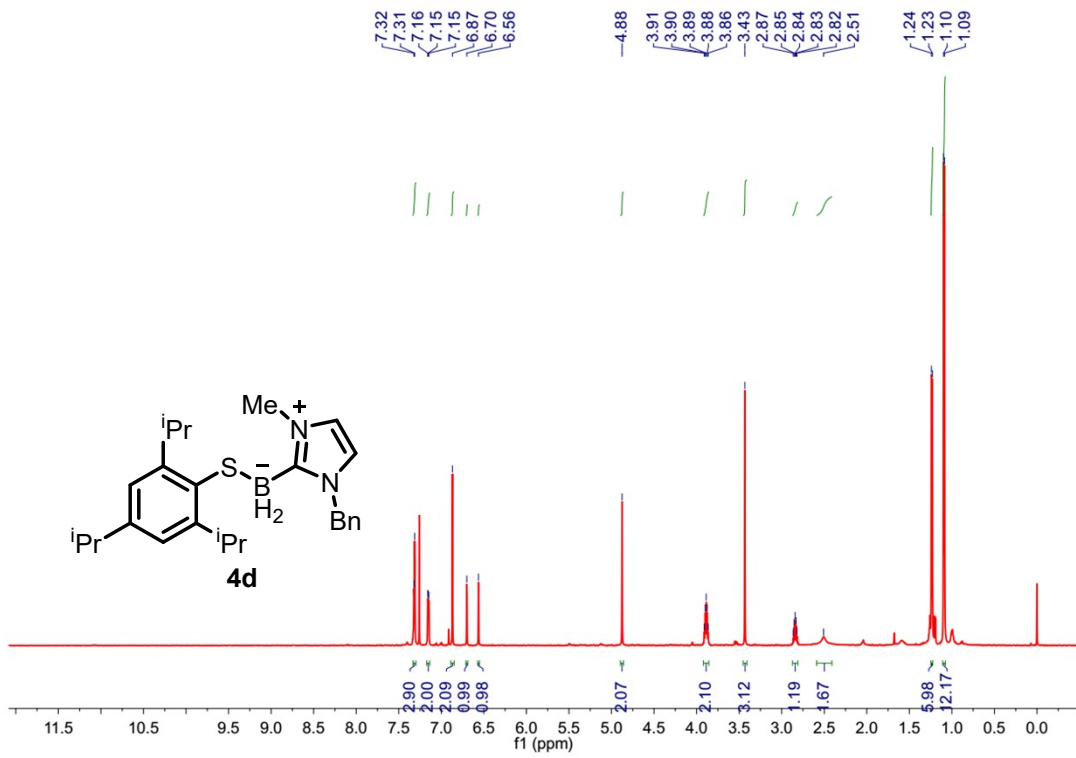
¹³C NMR (151 MHz, CDCl₃)



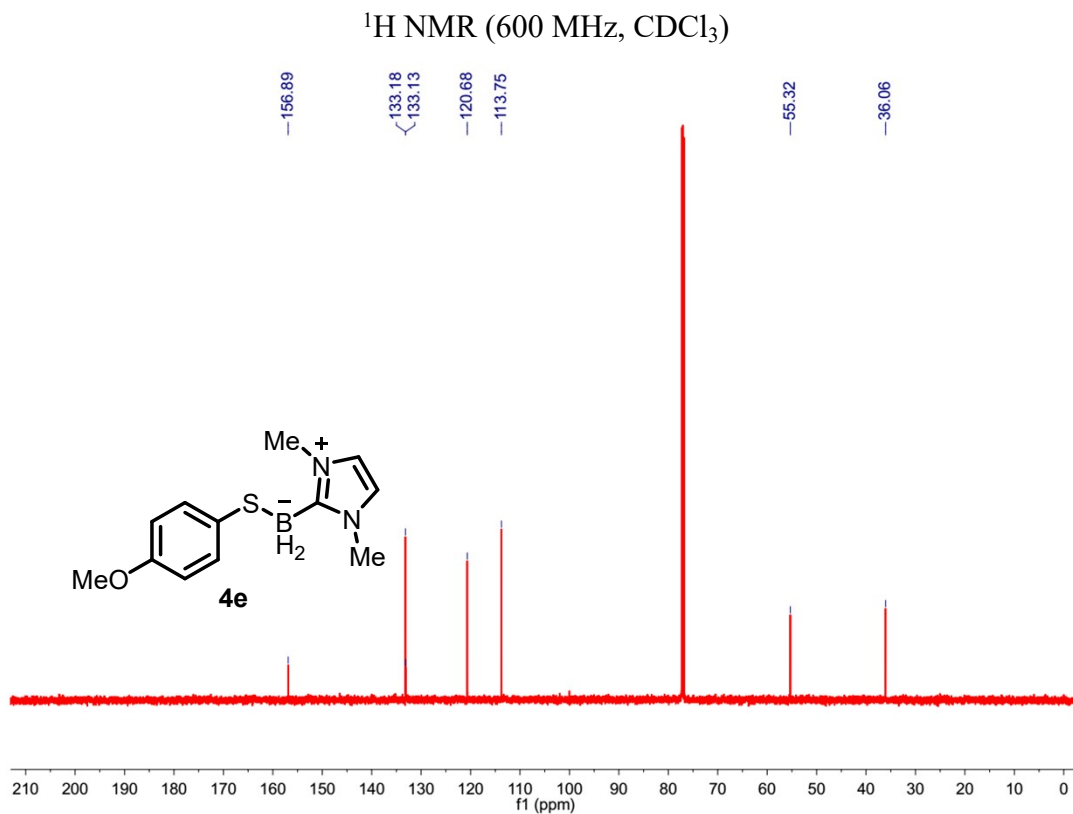
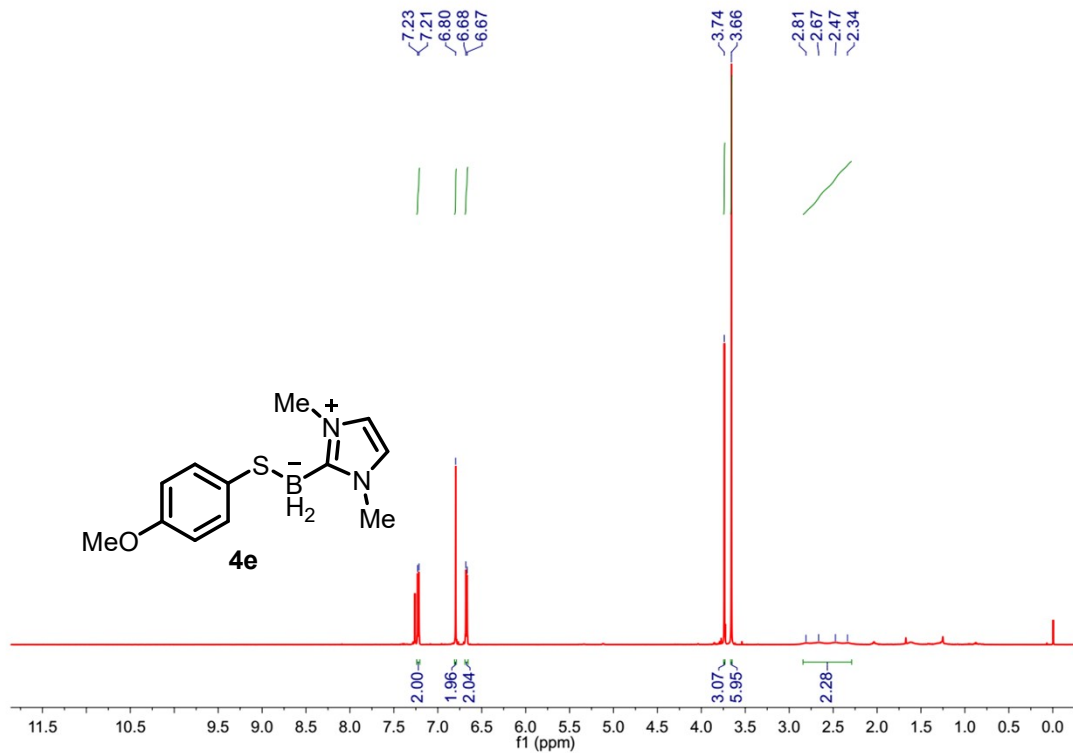
¹¹B NMR (193 MHz, CDCl₃)

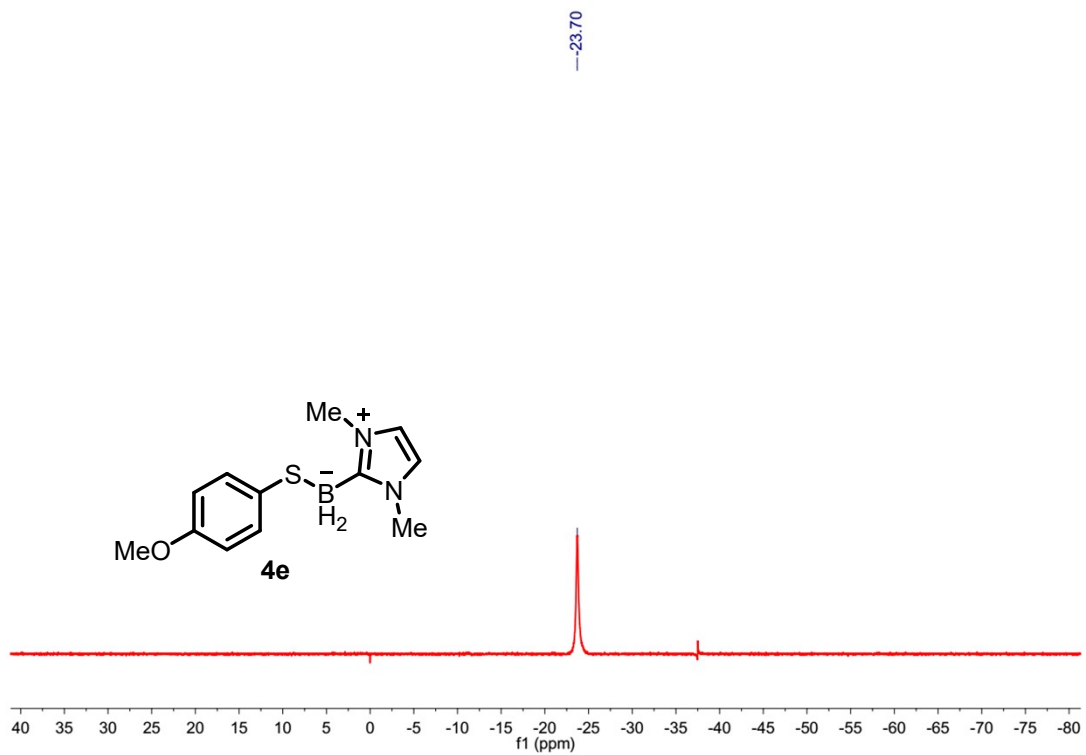
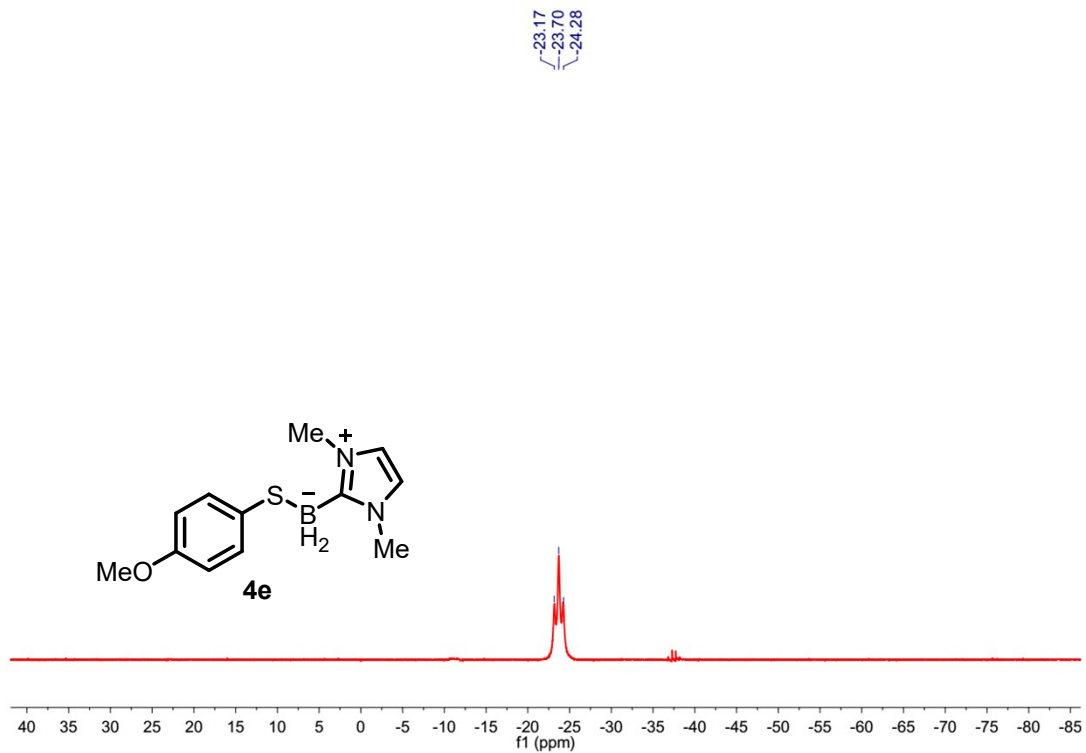


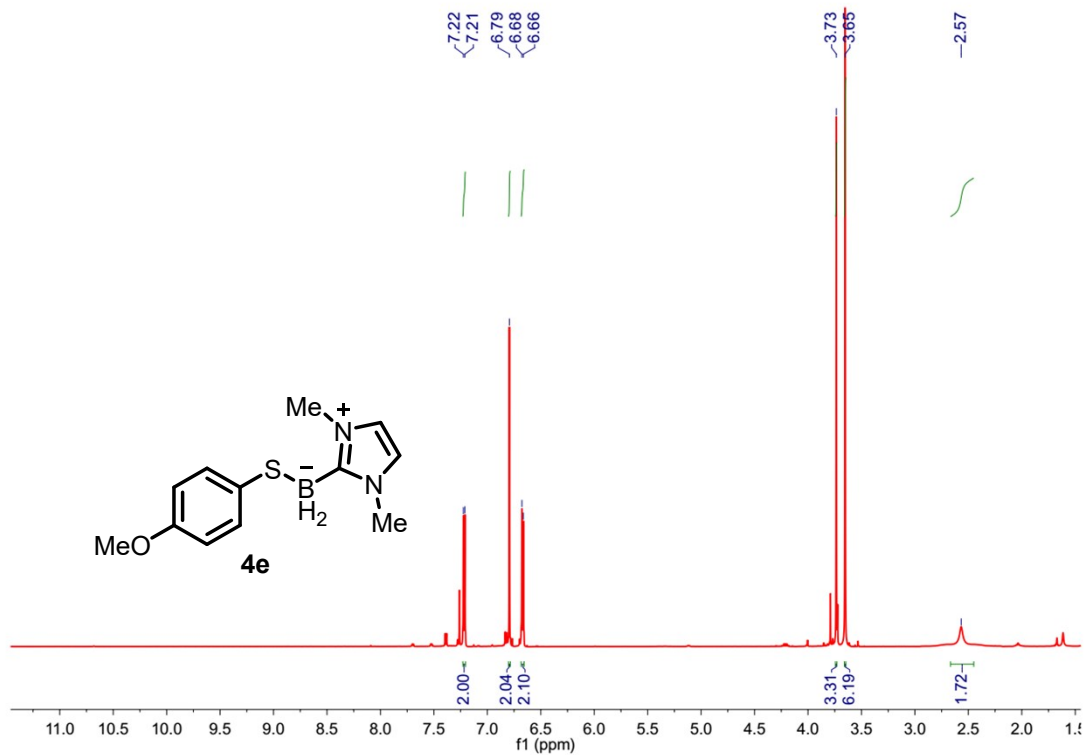
$^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3)



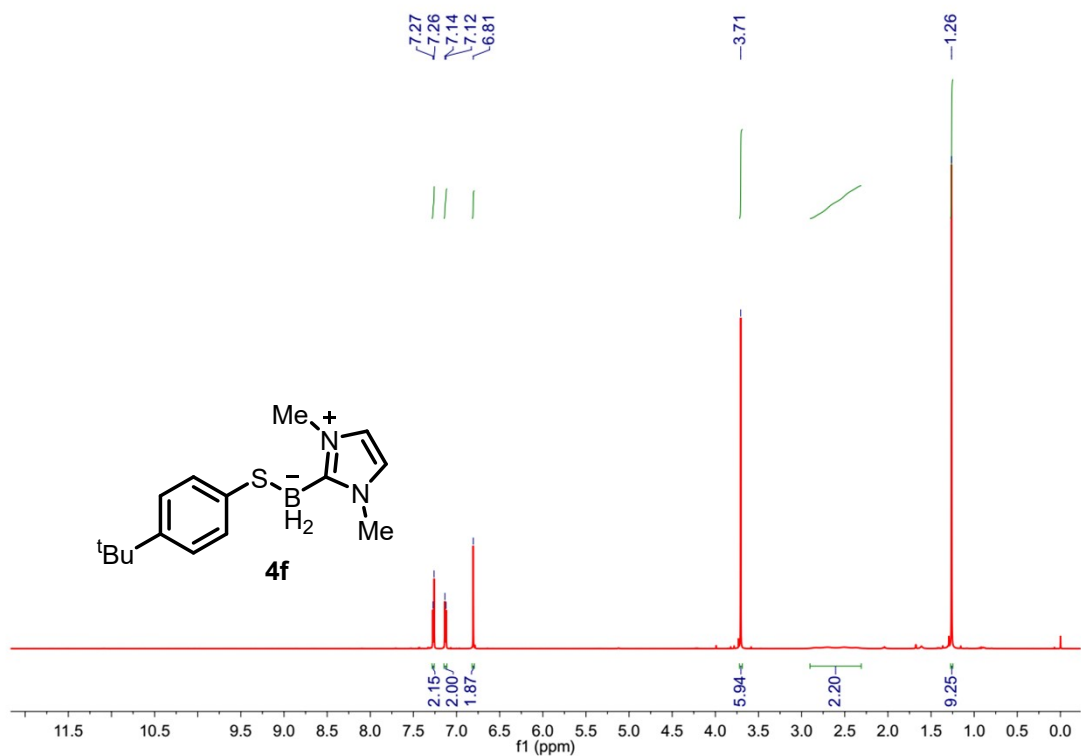
$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3)



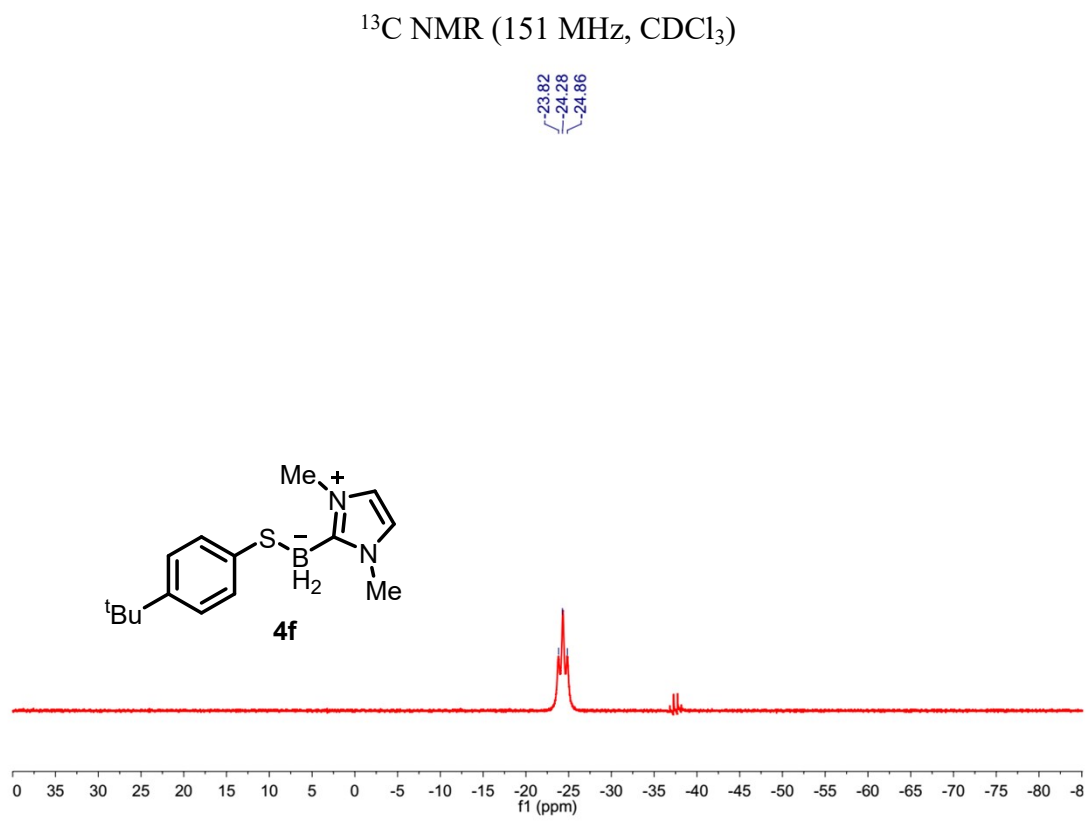
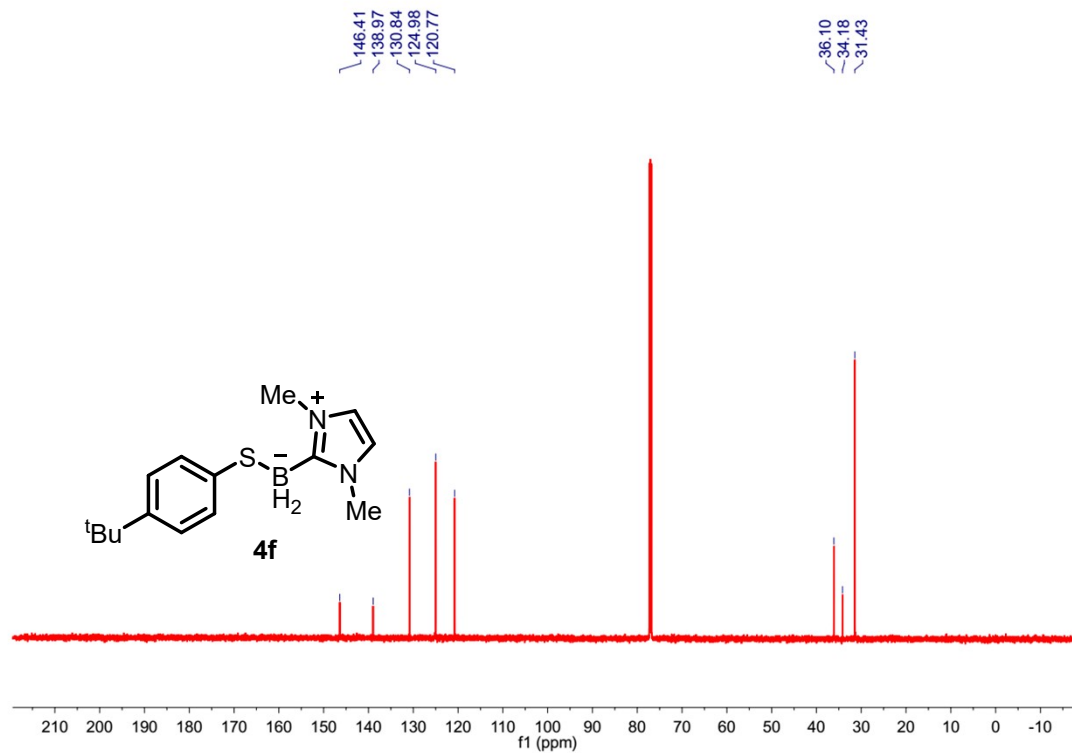


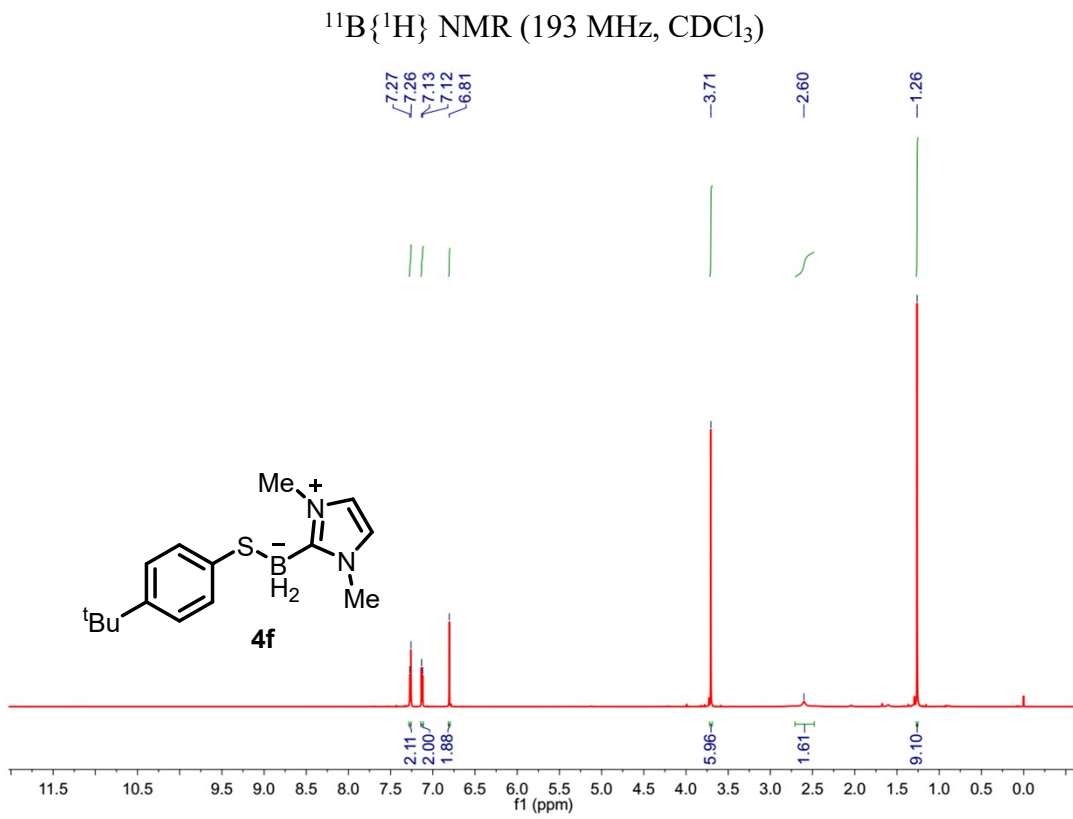
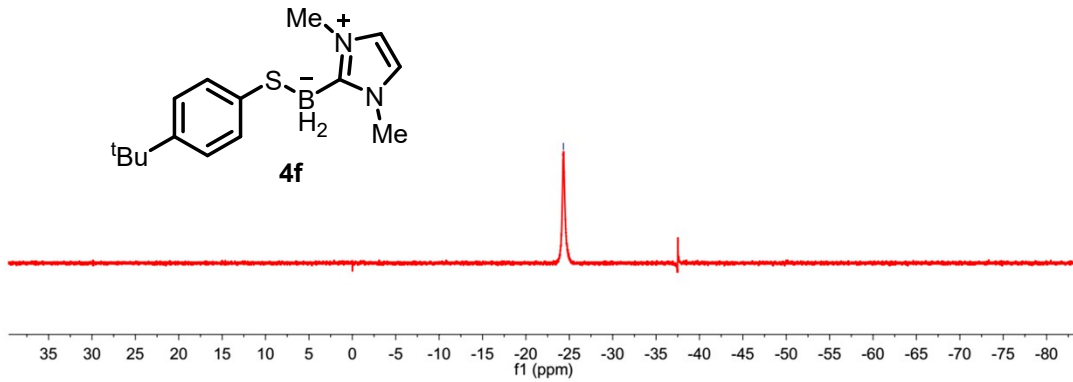


$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3)

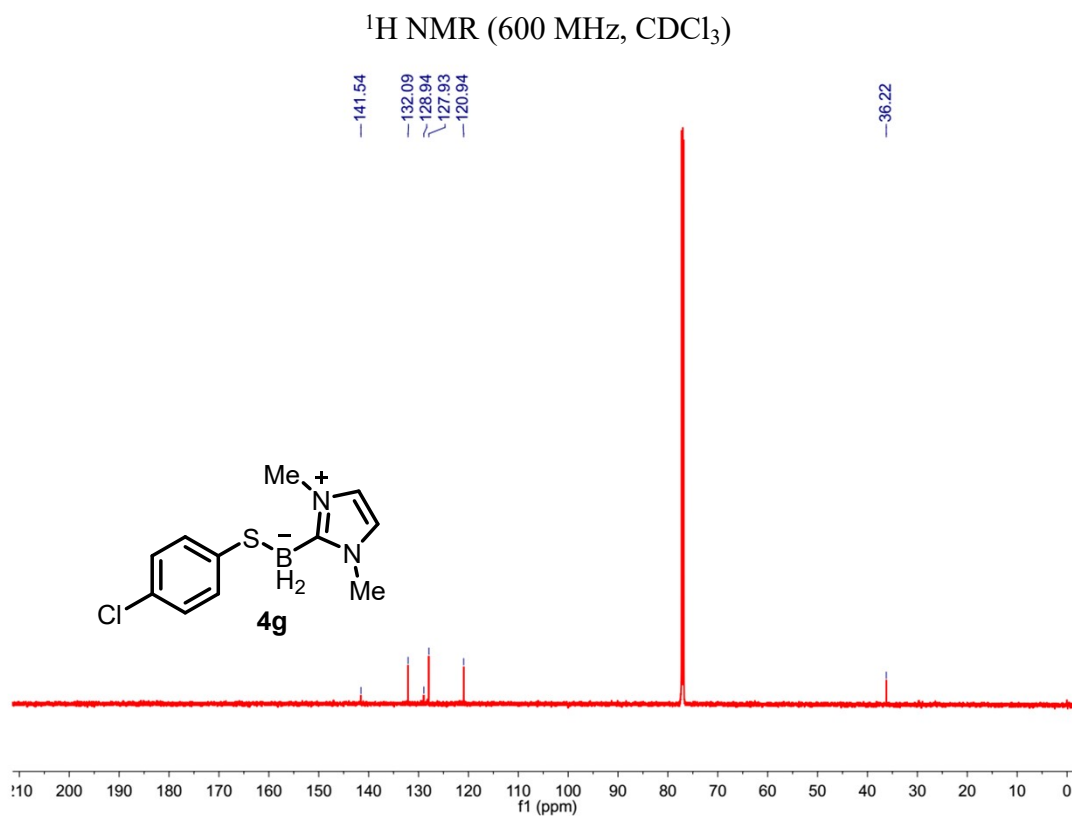
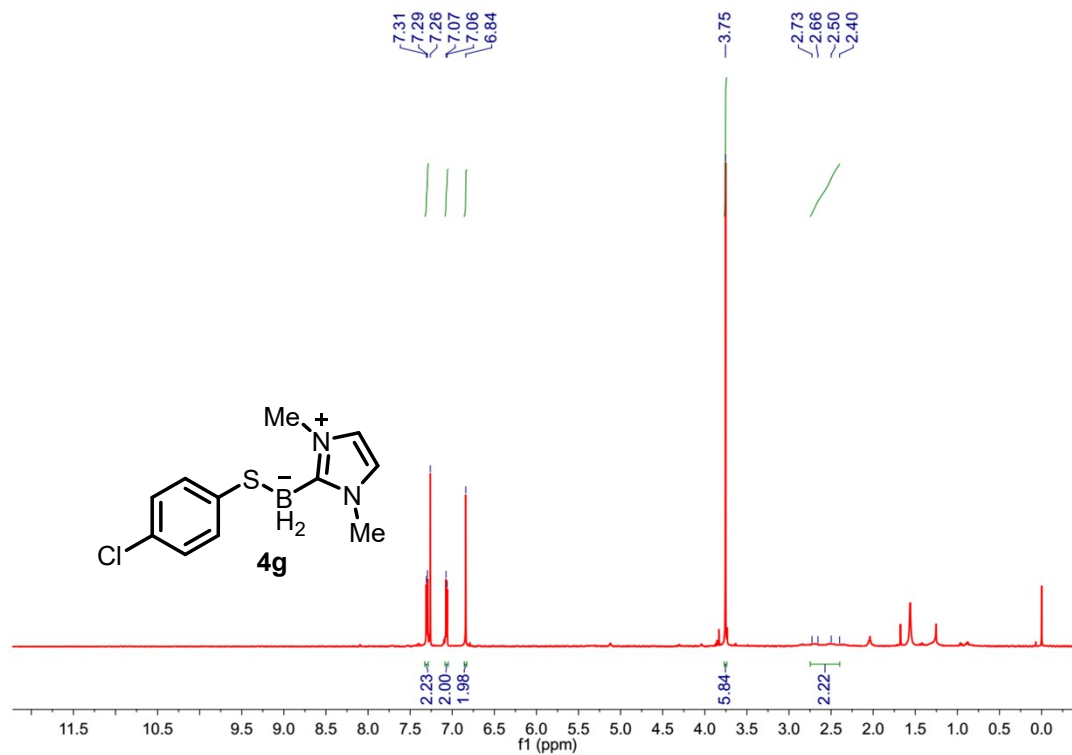


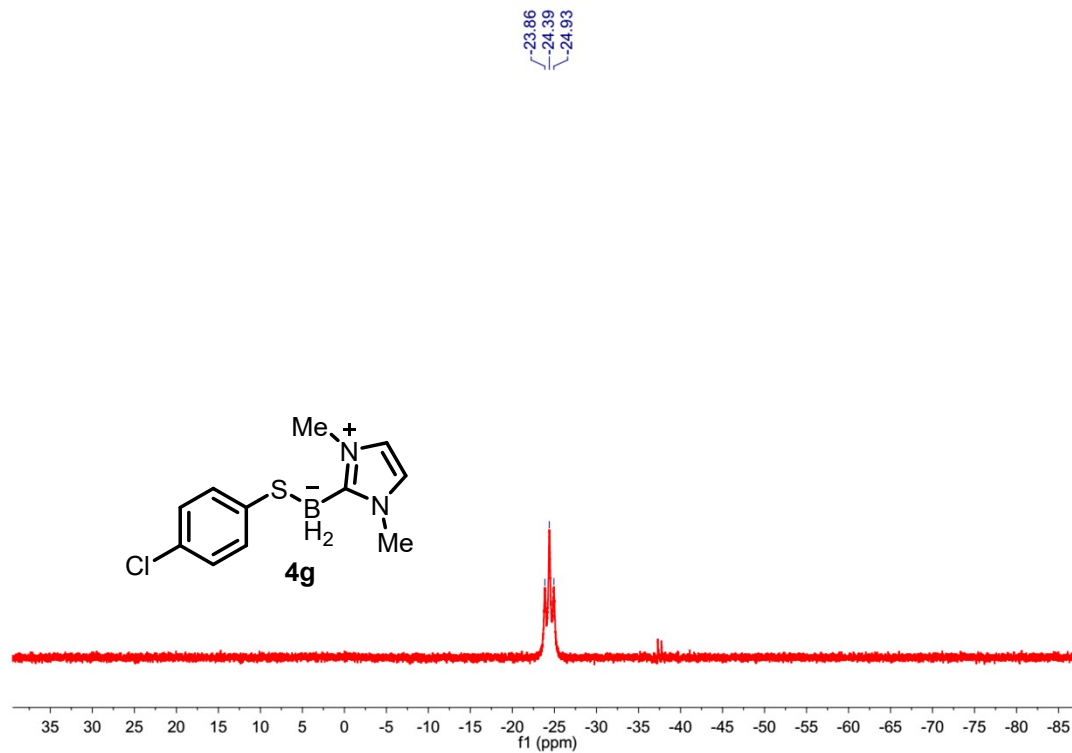
^1H NMR (600 MHz, CDCl_3)



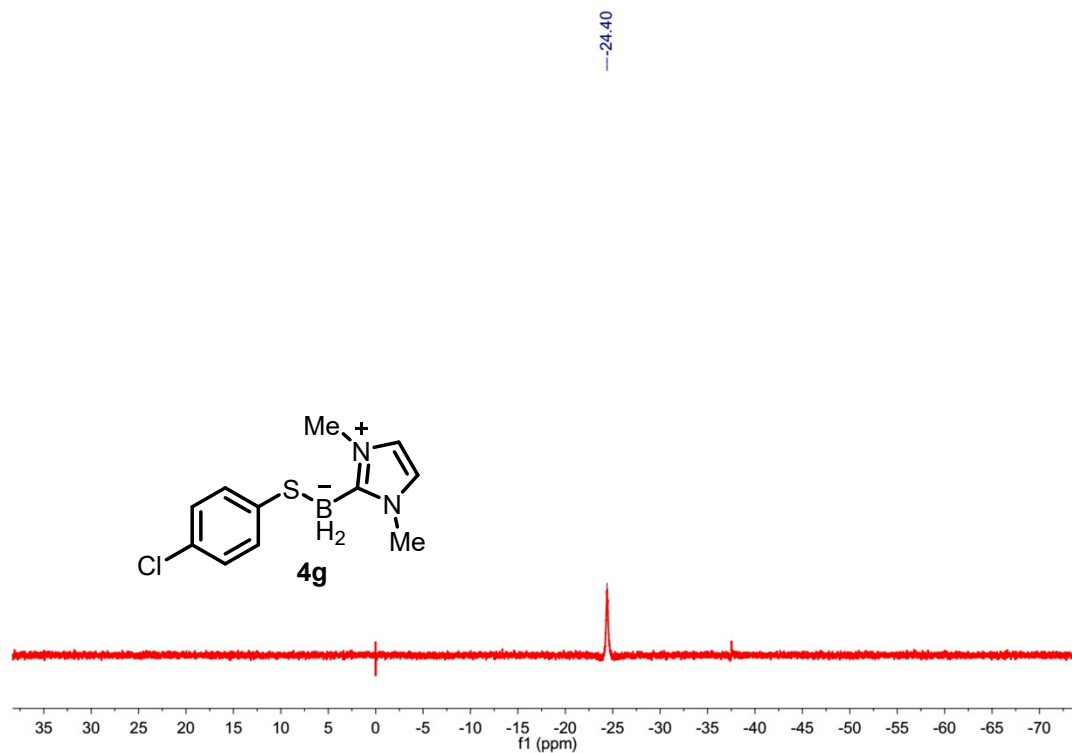


$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3)

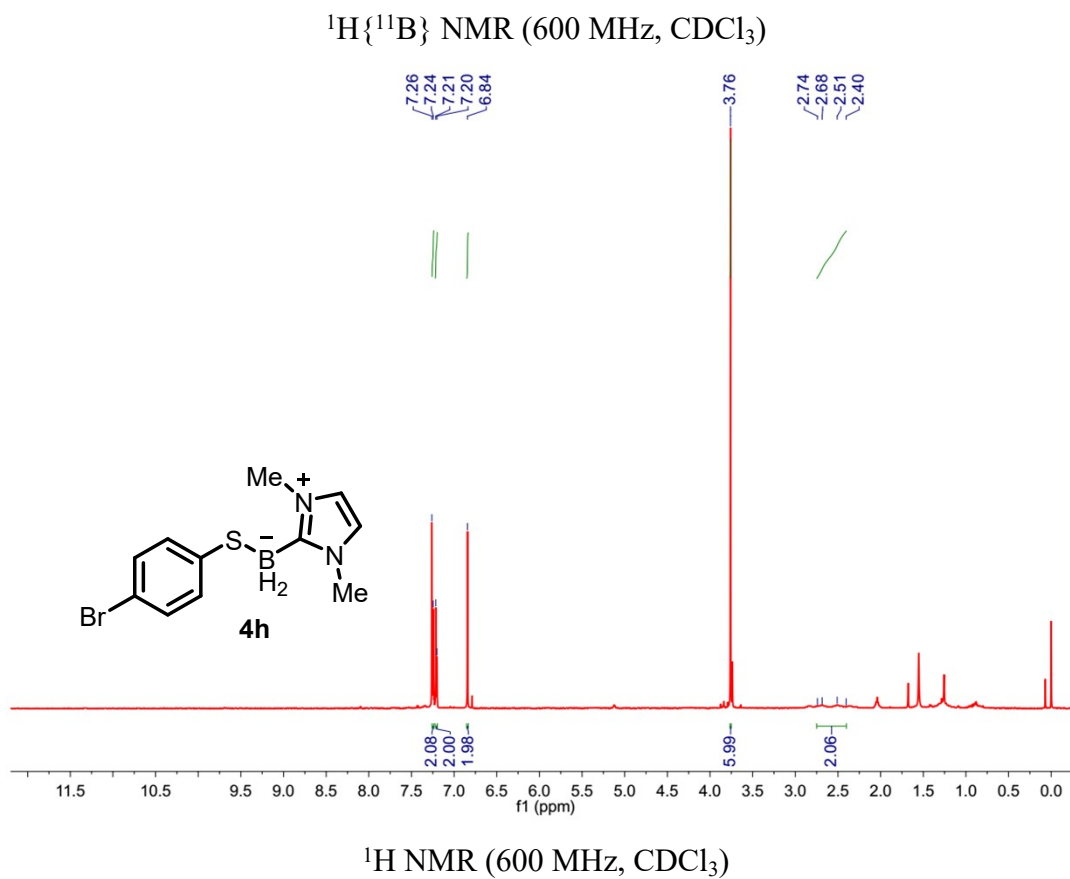
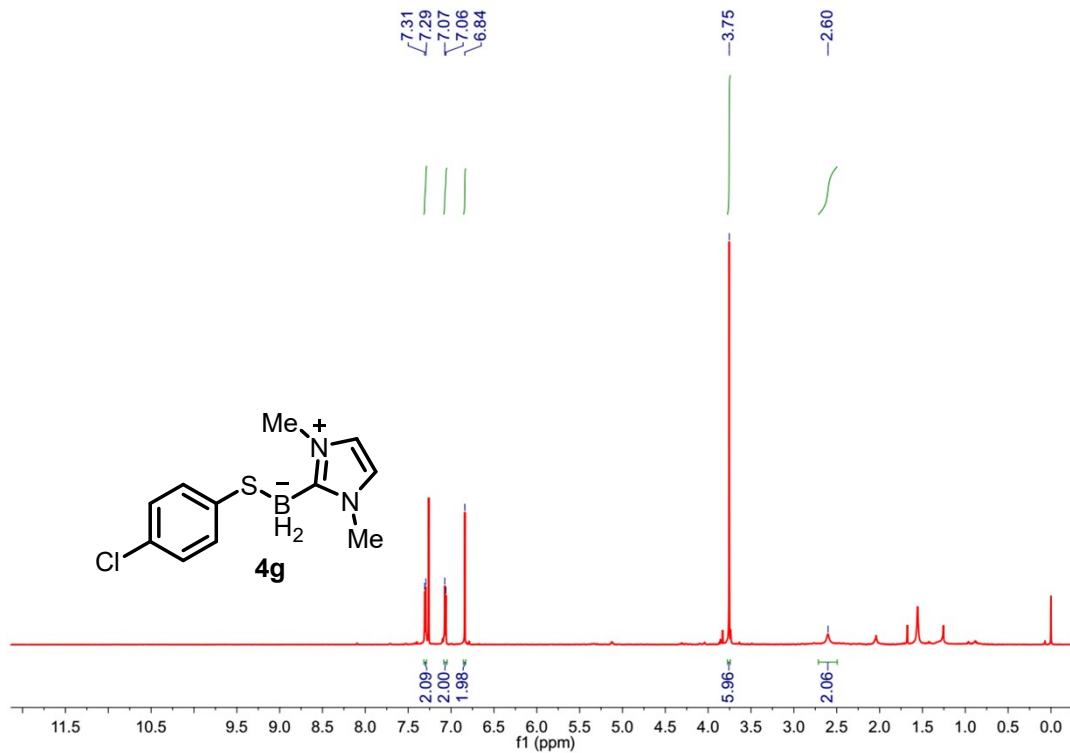


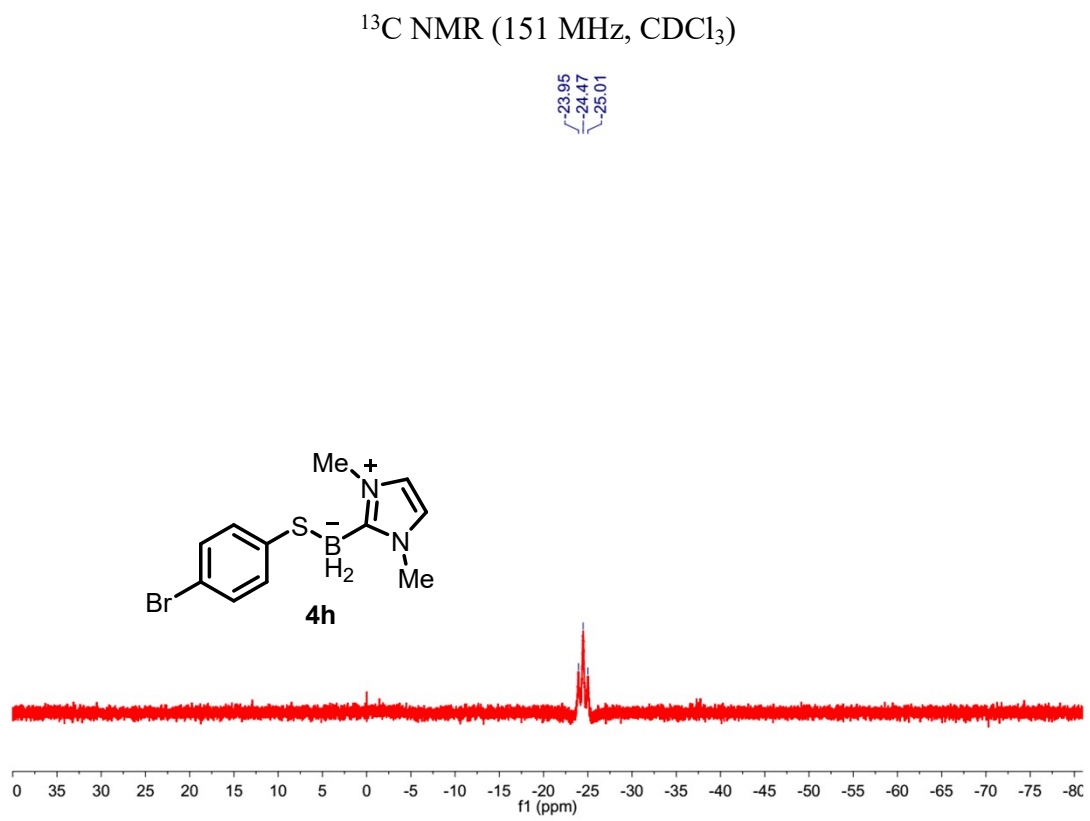
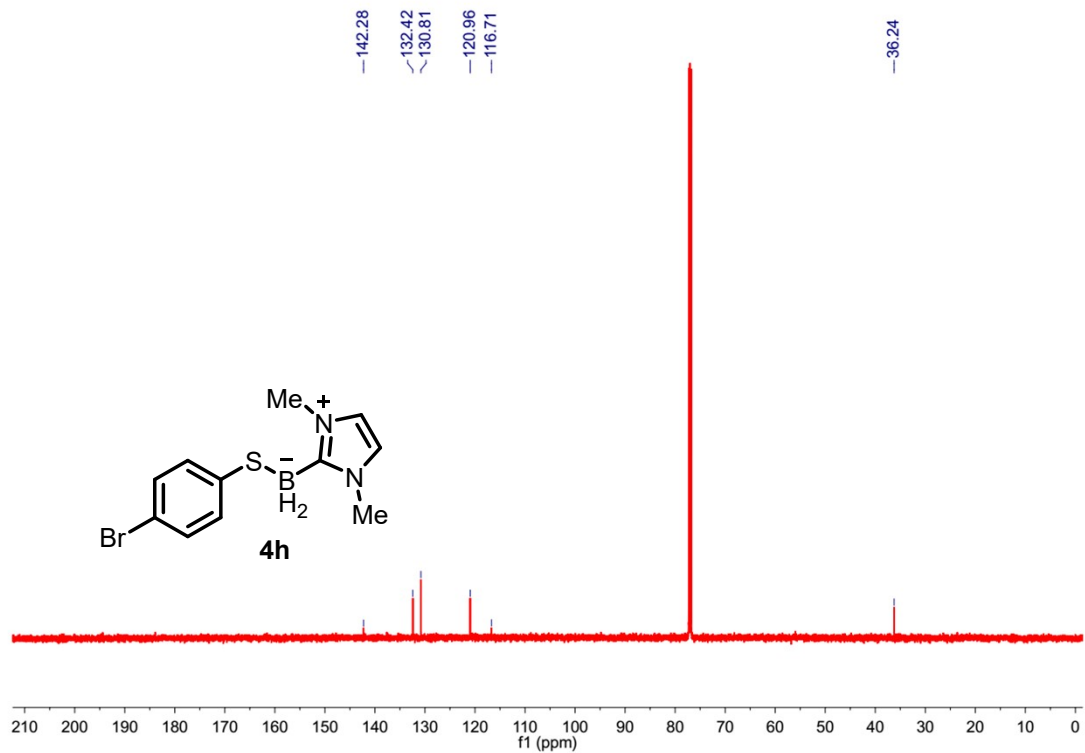


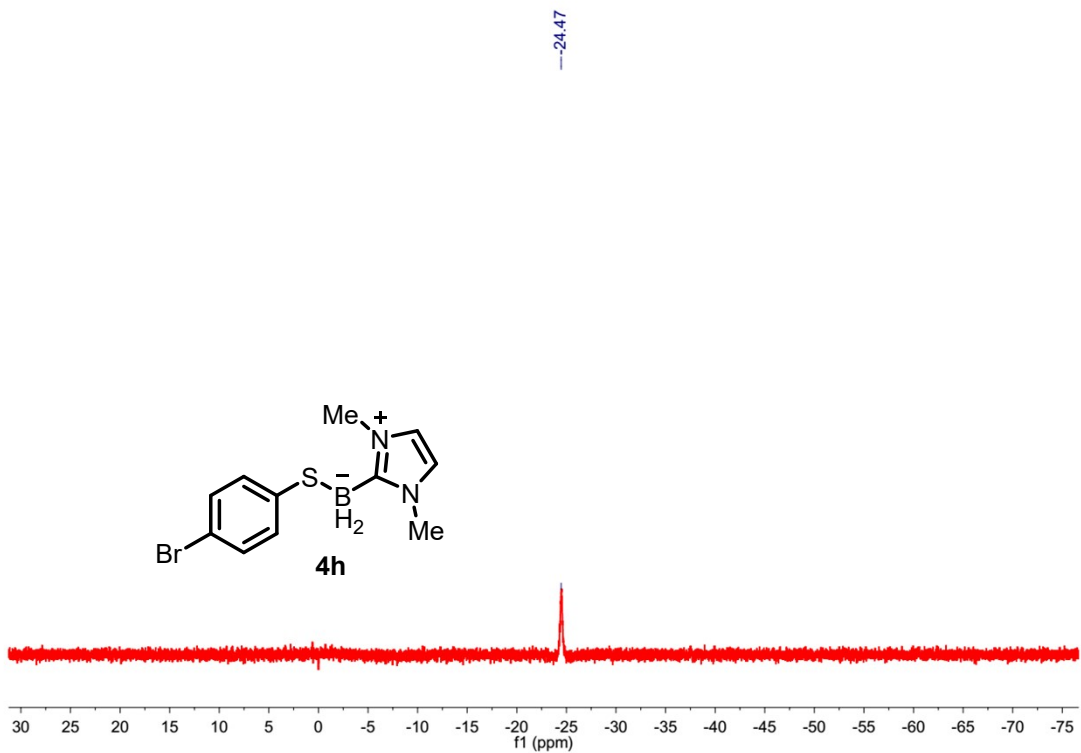
^{11}B NMR (193 MHz, CDCl_3)



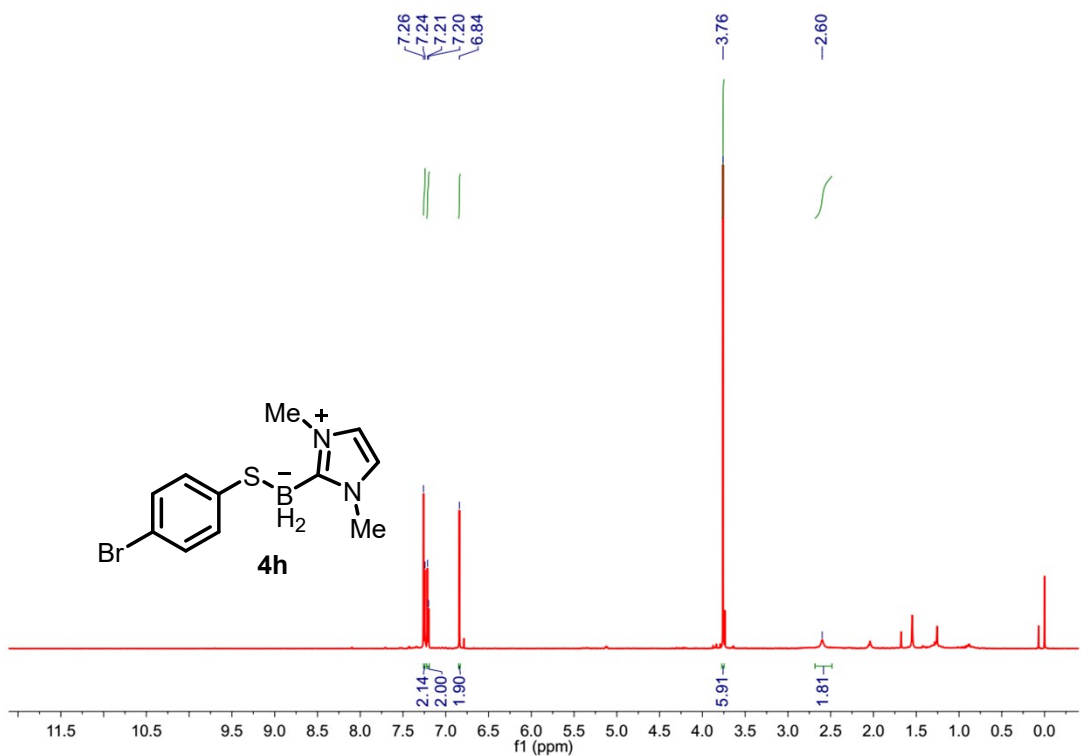
$^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3)







$^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3)



$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3)