

Visible-light-Induced 1,2-Diphenyldisulfane-Catalyzed Regioselective Hydroboration of Electron-Deficient Alkenes

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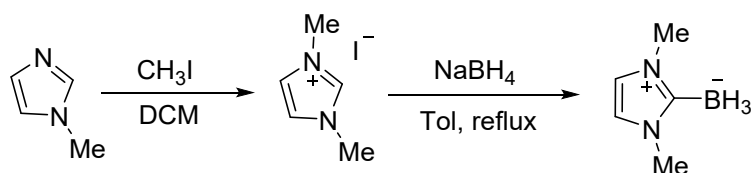
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1. General information

All the reagents were purchased from commercial suppliers and used without further purification, unless otherwise stated. Reactions were monitored by thin layer chromatography (TLC) using performed on commercial silica gel plates, and flash column chromatography was performed with 200–300 mesh silica gel. The CFL lamp and Blue LEDs were purchased from the supermarket. ^1H NMR, ^{13}C NMR, ^{11}B NMR and ^{19}F NMR spectra were recorded on 600 MHz spectrometer in CDCl_3 or DMSO 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), q (quartet), with coupling constants (J) in hertz (Hz).

2. Synthesis of Starting Materials

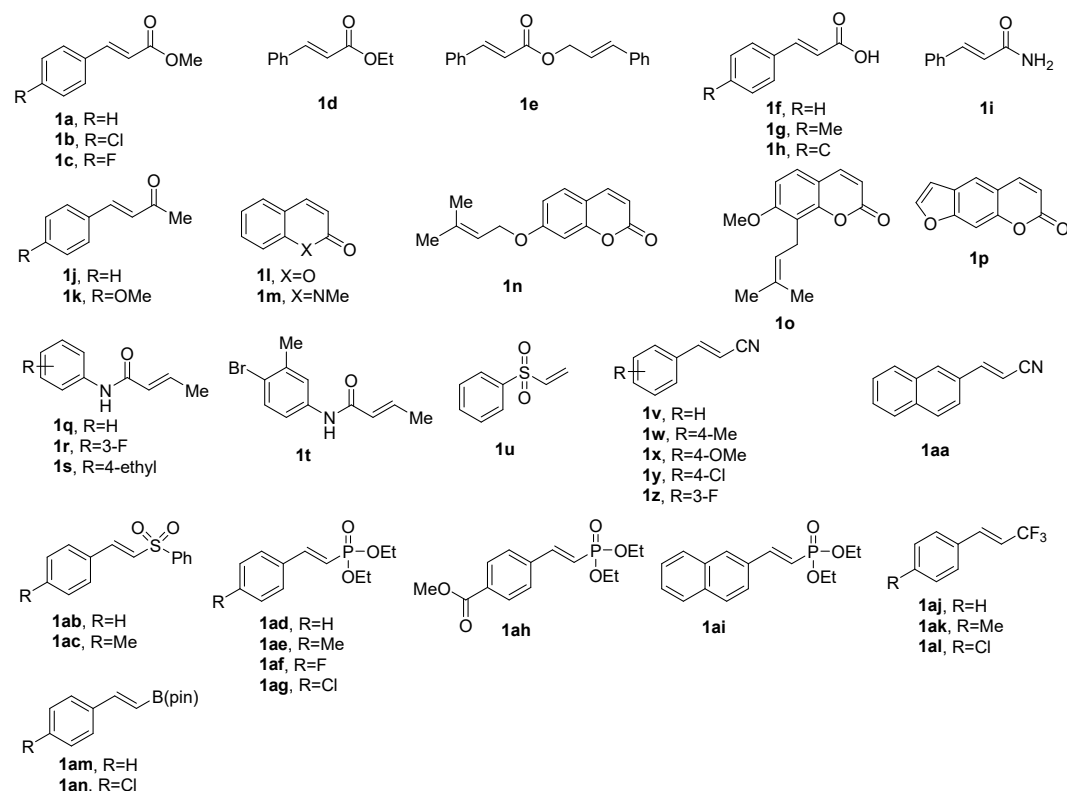
2.1 Procedure for preparation of NHC-BH₃ using the literature report¹



A 100 mL Schlenk-tube was charged with 1-methylimidazole (8.2 g, 100 mmol, 1.0 equiv.) and DCM (20 mL) was added. Iodomethane (16.9 g, 120 mmol, 1.2 equiv.) was subsequently added slowly over 10 min at 0 °C. Then the reaction was left to stir at room temperature for 2 hours. After this time the solvent was removed under vacuum and got the crude product, which toluene (50 mL) and NaBH₄ (4.53 g, 120 mmol, 1.2 equiv.) was then added. And the mixture was heated at 120 °C for 24 h. The hot reaction solvent was cautiously decanted from the insoluble mixture, then the reaction flask was washed with hot toluene (2 × 20 mL). The organic extracts were combined, evaporated, and purified by recrystallization from boiling water to give the 5.3 g pure product as a fine white crystal in a 48% yield.

2.2 Starting electron-deficient alkenes

1n, 1q-1t, 1w-1an were synthetic, others were purchased



2.3 Procedure for the Synthesis of 1n²

To a 50 mL Schlenk flask equipped with 7-hydroxycoumarin (486 mg, 3.0 mmol, 1.0 equiv.), 1-chloro-3-methylbut-2-ene (374mg, 3.6 mmol, 1.2 equiv.), and potassium carbonate (1.24 g, 9 mmol, 3.0 equiv.) in DMF (15 mL). The mixture was stirred at 100 °C for 10 h. After the starting material was consumed, monitored by TLC. The mixture was cooled to room temperature and dissolved in ethyl acetate. The organic layer was washed with water, dried over Na₂SO₄, filtered and concentrated under reduced pressure. The residue was purified by column chromatography (Petroleum ether: EtOAc) on silica gel to obtain the product **1n**.

2.4 Procedure for the Synthesis of 1q-1t³

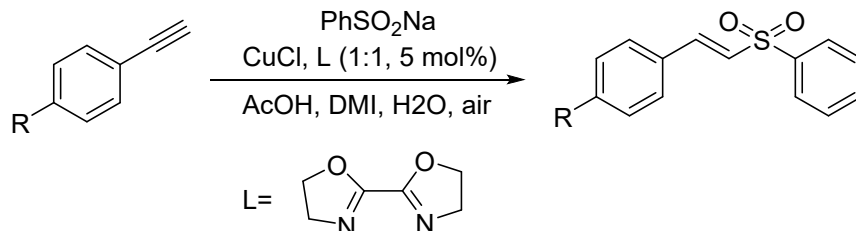
To a 50 mL Schlenk flask equipped with aniline (3.0 mmol, 1.0 equiv.), potassium carbonate (420 mg, 3.0 mmol, 1.0 equiv.) in DCM (15 mL), which crotonyl chloride (374 mg, 3.6 mmol, 1.2 equiv.) was added by syringe under N₂ atmosphere. After the starting material was consumed, monitored by TLC. The mixture was poured into H₂O, extracted with ethyl acetate (3 × 15 mL), dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The residue was purified by column chromatography (Petroleum ether: EtOAc) on silica gel to obtain the products **1q-1t**.

2.5 Procedure for the Synthesis of 1w-1aa¹⁰

To a 50 mL Schlenk flask equipped with NaH (3.6 mmol, 1.2 equiv.) in dry THF, which was added diethyl(cyanomethyl)phosphonate (3.6 mmol, 1.2 equiv.) at 0 °C under N₂ atmosphere. The reaction was stirred at room temperature for 0.5 h before adding the solution of aldehyde (3 mmol, 1.0 equiv.). The starting material was consumed, monitored by TLC. The mixture was quenched with saturated NH₄Cl (aq.). The mixture

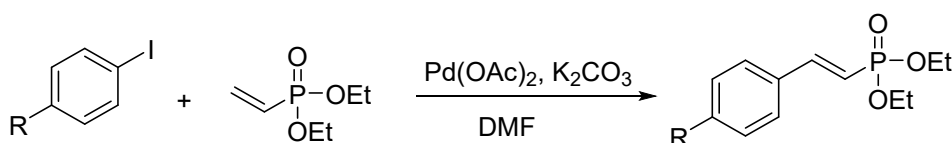
was extracted with ethyl acetate (3 × 15 mL), the organic layer was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography (Petroleum ether: EtOAc) on silica gel to obtain the products **1w-1aa**.

2.6 Procedure for the Synthesis of **1ab**, **1ac**⁷



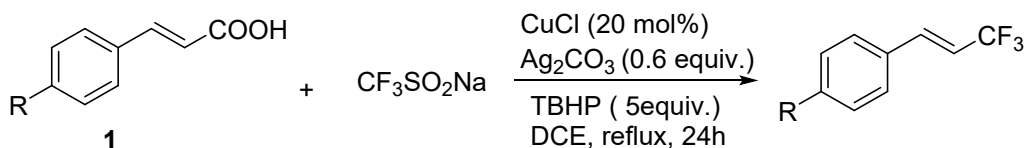
To a 50 mL Schlenk flask equipped with ethynylbenzene (3.0 mmol, 1.0 equiv.), PhSO₂Na (3.6 mmol, 1.2 equiv.), CuCl (0.15 mmol, 0.05 equiv.), 4,4',5,5'-tetrahydro-2,2'-bioxazole (0.15 mmol, 0.05 equiv.) in AcOH (3 mL), DMI (3 mL), H₂O (3 mL). The mixture was stirred at 60 °C for 18 h under air atmosphere. After the mixture was poured into H₂O, extracted with ethyl acetate (3 × 15 mL), dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The residue was purified by column chromatography (Petroleum ether: EtOAc) on silica gel to obtain the products **1ab**, **1ac**.

2.7 Procedure for the Synthesis of **1ad-1ai**⁶



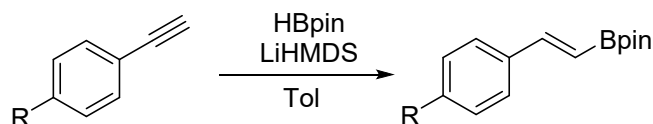
To a 20 mL pressure equipped with aryl iodide (3.0 mmol, 1.0 equiv.), diethyl vinylphosphonate (3.0 mmol, 1.0 equiv.), Pd(OAc)₂ (0.06 mmol, 0.02 equiv.), K₂CO₃ (3.0 mmol, 1.0 equiv.) in DMF (10 mL). The reaction was heated at 110 °C for 10 h. Then the mixture was poured into H₂O, extracted with ethyl acetate (3 × 15 mL), dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The residue was purified by column chromatography (Petroleum ether: EtOAc) on silica gel to obtain the products **1ad-1ai**.

2.8 Procedure for the Synthesis of **1aj-1al**⁵



To a 50 mL Schlenk flask equipped with substrate **1** (3.0 mmol, 1.0 equiv.), CuCl (0.6 mmol, 0.2 equiv.), Ag₂CO₃ (1.8 mmol, 0.6 equiv.), and NaSO₂CF₃ (9.0 mmol, 3.0 equiv.) in DCE (15 mL) at 0 °C, which was slowly added TBHP (15 mmol, 5.0 equiv.). The reaction was heated under refluxing for 24h. Then the mixture was extracted with ethyl acetate (3 × 15 mL), the organic layer was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography (Petroleum ether: EtOAc) on silica gel to obtain the products **1aj-1al**.

2.9 Procedure for the Synthesis of **1am**, **1an**⁸



To a 50 mL Schlenk flask equipped with ethynylbenzene (3.0 mmol, 1.0 equiv.), HBpin (3.6 mmol, 1.2 equiv.), LiHMDS (0.3 mmol, 0.1 equiv.) in toluene (15 mL). The mixture was stirred at 80 °C for 18 h under N₂ atmosphere. After the mixture was poured into H₂O, extracted with ethyl acetate (3 × 15 mL), dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The residue was purified by column chromatography (Petroleum ether: EtOAc) on silica gel to obtain the products **1am**, **1an**.

3. Procedure for the hydroboration of electron-deficient alkenes.

3.1 General Procedure for the hydroboration of **1a-1e**, **1i-1p**, **1u**, **1v-1aa**.

To a 10 mL Schlenk flask equipped with alkenes (0.2 mmol, 1.0 equiv.), NHC-borane (28.6 mg, 0.26 mmol, 1.3 equiv.), PhSSPh (4.4 mg, 0.02 mmol, 0.1 equiv.) in EtOH (2 mL) under N₂ atmosphere. Then the reaction was placed at a distance (app. 5 cm) from 23W CFL lamp and the mixture was stirred for 24 h at room temperature. Then the reaction was concentrated under reduced pressure. The residue was purified by column chromatography (Petroleum ether: EtOAc) on silica gel to obtain the products **3a-3e**, **3i-3p**, **3u**, **3v-3aa**.

3.2 General Procedure for the hydroboration of **1f-1h**.

To a 10 mL Schlenk flask equipped with alkenes (0.2 mmol, 1.0 equiv.), NHC-borane (28.6 mg, 0.26 mmol, 1.3 equiv.), PhSSPh (4.4 mg, 0.02 mmol, 0.1 equiv.) in MeCN (2 mL) under N₂ atmosphere. Then the reaction was placed at a distance (app. 5 cm) from 23W CFL lamp and the mixture was stirred for 24 h at room temperature. Then the reaction was added 5 mL H₂O, extracted with DCM (3 × 10 mL), dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The residue was purified by column chromatography (Petroleum ether: EtOAc) on silica gel to obtain the products **3f-3h**.

3.3 General Procedure for the hydroboration of **1q**, **1s**.

To a 10 mL Schlenk flask equipped with alkenes (0.2 mmol, 1.0 equiv.), NHC-borane (44 mg, 0.4 mmol, 2 equiv.), PhSSPh (8.8 mg, 0.04 mmol, 0.2 equiv.) and THF (2 mL) under N₂ atmosphere. Then the reaction was placed at a distance (app. 5 cm) from 10W blue LEDs (410-420 nm) lamp and the mixture was stirred for 24 h at room temperature. Then the reaction was added 5 mL H₂O, extracted with DCM (3 × 10 mL), dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The residue was purified by column chromatography (Petroleum ether: EtOAc) on silica gel to obtain the products **3q**, **3s**.

3.4 General Procedure for the hydroboration of **1r**, **1t**.

To a 10 mL Schlenk flask equipped with alkenes (0.2 mmol, 1.0 equiv.), NHC-borane (44 mg, 0.4 mmol, 2 equiv.), PhSSPh (8.8 mg, 0.04 mmol, 0.2 equiv.) and THF (2 mL) under N₂ atmosphere. Then the reaction was placed at a distance (app. 5 cm) from 23W CFL lamp and the mixture was stirred for 24 h at room temperature. Then the reaction

was added 5 mL H₂O, extracted with DCM (3 × 10 mL), dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The residue was purified by column chromatography (Petroleum ether: EtOAc) on silica gel to obtain the products **3r**, **3t**.

3.5 General Procedure for the hydroboration of **1ab**, **1ac**, **1aj-1al**, **1am**, **1an**.

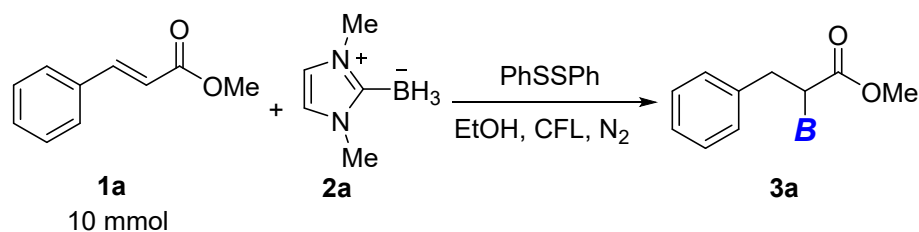
To a 10 mL Schlenk flask equipped with alkenes (0.2 mmol, 1.0 equiv.), NHC-borane (44 mg, 0.4 mmol, 2 equiv.), PhSSPh (8.8 mg, 0.04 mmol, 0.2 equiv.) and THF (2 mL) under N₂ atmosphere. Then the reaction was placed at a distance (app. 5 cm) from 10W blue LEDs (410-420 nm) lamp and the mixture was stirred for 24 h at room temperature. Then the reaction was added 5 mL H₂O, extracted with DCM (3 × 10 mL), dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The residue was purified by column chromatography (Petroleum ether: EtOAc) on silica gel to obtain the products **3ab**, **3ac**, **3aj-3al**, **3am**, **3an**.

3.6 General Procedure for the hydroboration of **1ad-1ai**.

To a 10 mL Schlenk flask equipped with alkenes (0.2 mmol, 1.0 equiv.), NHC-borane (28.6 mg, 0.26 mmol, 1.3 equiv.), PhSSPh (4.4 mg, 0.02 mmol, 0.1 equiv.) and in THF (2 mL) under N₂ atmosphere. Then the reaction was placed at a distance (app. 5 cm) from 10W blue LEDs (410-420 nm) lamp and the mixture was stirred for 24 h at room temperature. Then the reaction was added 5 mL H₂O, extracted with DCM (3 × 10 mL), dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The residue was purified by column chromatography (Petroleum ether: EtOAc) on silica gel to obtain the products **3ad-3ai**.

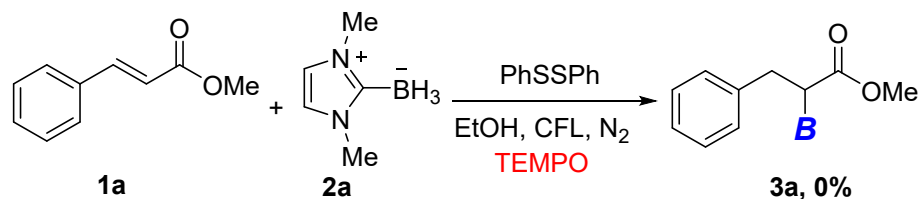
4. Gram scale and mechanistic experiments.

4.1 Gram scale experiment procedure.



To a 100 mL Schlenk flask equipped with **1a** (10 mmol, 1.0 equiv.), NHC-borane (1.43 g, 13 mmol, 1.3 equiv.), PhSSPh (220 mg, 1 mmol, 0.1 equiv.) in EtOH (50 mL) under N₂ atmosphere. Then the reaction was placed at a distance (app. 5 cm) from 23W CFL lamp and the mixture was stirred for 24 h at room temperature. Then the reaction was concentrated under reduced pressure. The residue was purified by column chromatography (Petroleum ether: EtOAc) on silica gel to obtain the products **3a** in 70% yield.

4.2 radical trapping experiment procedure.



To a 10 mL Schlenk flask equipped with **1a** (0.2 mmol, 1.0 equiv.), NHC-borane (28.6

mg, 0.26 mmol, 1.3 equiv.), PhSSPh (4.4 mg, 0.02 mmol, 0.1 equiv.) and TEMPO (47 mg, 0.6 mmol, 3.0 equiv.) in EtOH (2 mL) under N₂ atmosphere. Then the reaction was placed at a distance (app. 5 cm) from 23W CFL lamp and the mixture was stirred for 24 h at room temperature. No desired product was obtained by TLC detected and we found the boryl radical, thiyl radical, and intermediate A radical-trapping products.

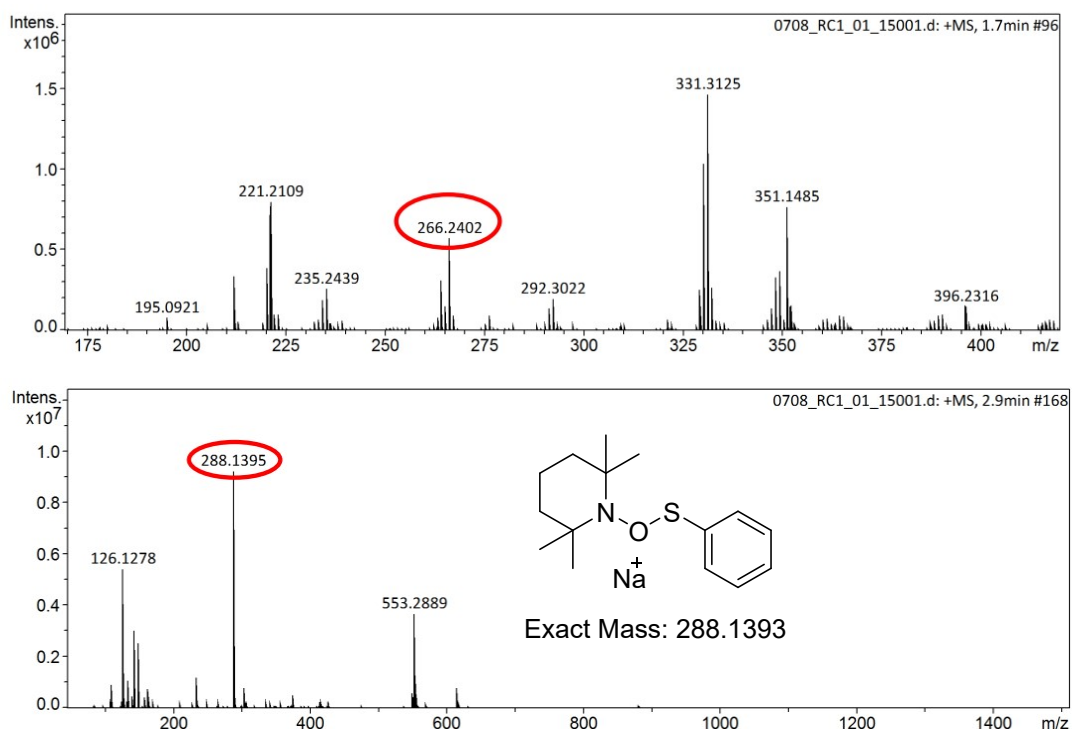
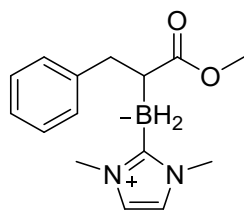
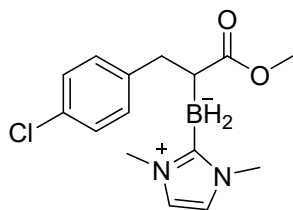


Figure S1. HRMS data of the reaction mixture

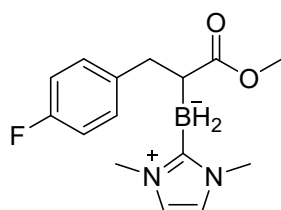
5. Characterization data of products.



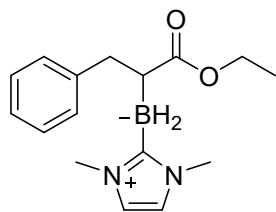
(1,3-dimethyl-1H-imidazol-3-ium-2-yl)(1-methoxy-1-oxo-3-phenylpropan-2-yl) dihydroborate (**3a**): Colorless liquid (50 mg, 92% yield); Gradient eluent: EtOAc/petroleum ether: 1/2 to 1/1; ¹H NMR (600 MHz, CDCl₃) δ 7.19 (d, *J* = 4.5 Hz, 4H), 7.10 – 7.06 (m, 1H), 6.79 (s, 2H), 3.71 (s, 6H), 3.36 (s, 3H), 3.11 (dd, *J* = 14.3, 10.2 Hz, 1H), 2.70 (dd, *J* = 14.3, 4.2 Hz, 1H), 2.19 (s, 1H), 1.88 – 1.39 (m, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 181.94, 144.74, 128.46, 127.91, 125.06, 120.46, 50.37, 39.11, 35.97. ¹¹B NMR (193 MHz, CDCl₃) δ -25.00 (t, *J* = 89.7 Hz). ¹¹B{¹H} NMR (193 MHz, CDCl₃) δ -25.0. ¹H{¹¹B} NMR (600 MHz, CDCl₃) δ 7.19 (d, *J* = 4.4 Hz, 4H), 7.10 – 7.06 (m, 1H), 6.79 (s, 2H), 3.71 (s, 6H), 3.36 (s, 3H), 3.11 (dd, *J* = 14.3, 10.2 Hz, 1H), 2.70 (dd, *J* = 14.3, 4.3 Hz, 1H), 2.21-2.17 (m, 1H), 1.76 – 1.52 (m, 2H). Characterization agrees with previous reports for this compound.⁴



(3-(4-chlorophenyl)-1-methoxy-1-oxopropan-2-yl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)dihydroborate (**3b**): Colorless liquid (50 mg, 82% yield); Gradient eluent: EtOAc/petroleum ether: 1/3 to 1/2; ^1H NMR (600 MHz, CDCl_3) δ 7.13 (q, $J = 8.5$ Hz, 4H), 6.81 (s, 2H), 3.72 (s, 6H), 3.34 (s, 3H), 3.04 (dd, $J = 14.3, 10.3$ Hz, 1H), 2.67 (dd, $J = 14.4, 4.2$ Hz, 1H), 2.13 (s, 1H), 1.87 – 1.39 (m, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 181.6, 143.25, 130.61, 129.88, 127.92, 120.46, 50.39, 38.45, 35.99. ^{11}B NMR (193 MHz, CDCl_3) δ -25.09 (t, $J = 90.7$ Hz). $^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3) δ -25.0. $^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3) δ 7.13 (q, $J = 8.5$ Hz, 4H), 6.81 (s, 2H), 3.71 (s, 6H), 3.34 (s, 3H), 3.04 (dd, $J = 14.3, 10.3$ Hz, 1H), 2.67 (dd, $J = 14.4, 4.3$ Hz, 1H), 2.15 – 2.11 (m, 1H), 1.74 – 1.51 (m, 2H). HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{15}\text{H}_{20}\text{BClN}_2\text{NaO}_2$ 329.1199; found: 329.1195.

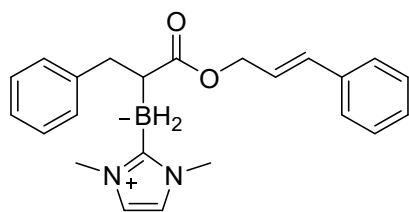


(1,3-dimethyl-1H-imidazol-3-ium-2-yl)(3-(4-fluorophenyl)-1-methoxy-1-oxopropan-2-yl)dihydroborate (**3c**): Colorless liquid (43 mg, 74% yield); Gradient eluent: EtOAc/petroleum ether: 1/2 to 1/1; ^1H NMR (600 MHz, CDCl_3) δ 7.13 (dd, $J = 8.4, 5.7$ Hz, 2H), 6.86 (t, $J = 8.8$ Hz, 2H), 6.81 (s, 2H), 3.72 (s, 6H), 3.35 (s, 3H), 3.05 (dd, $J = 14.3, 10.3$ Hz, 1H), 2.67 (dd, $J = 14.3, 4.1$ Hz, 1H), 2.13 (s, 1H), 1.94 – 1.44 (m, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 181.76, 161.67, 160.06, 140.36, 129.74 (d, $J = 7.6$ Hz), 120.45, 114.47 (d, $J = 21.1$ Hz), 50.36, 38.28, 35.98. ^{11}B NMR (193 MHz, CDCl_3) δ -25.11 (t, $J = 90.7$ Hz). $^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3) δ -25.11. $^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3) δ 7.13 (dd, $J = 8.4, 5.7$ Hz, 2H), 6.86 (t, $J = 8.8$ Hz, 2H), 6.81 (s, 2H), 3.72 (s, 6H), 3.35 (s, 3H), 3.05 (dd, $J = 14.3, 10.2$ Hz, 1H), 2.67 (dd, $J = 14.4, 4.3$ Hz, 1H), 2.13 (td, $J = 10.6, 5.0$ Hz, 1H), 1.60 (d, $J = 19.2$ Hz, 2H). ^{19}F NMR (565 MHz, CDCl_3) δ -119.13. HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{15}\text{H}_{20}\text{BFN}_2\text{NaO}_2$ 313.1494; found: 313.1496.



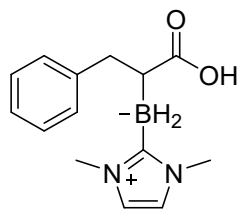
(1,3-dimethyl-1H-imidazol-3-ium-2-yl)(1-ethoxy-1-oxo-3-phenylpropan-2-yl) dihydroborate (**3d**): Colorless liquid (41.2 mg, 72% yield); Gradient eluent: EtOAc/petroleum ether: 1/3 to 1/2; ^1H NMR (600 MHz, CDCl_3) δ 7.22 – 7.17 (m, 4H), 7.08 (t, $J = 6.6$ Hz, 1H), 6.80 (s, 2H), 3.80 (dd, $J = 15.1, 7.3$ Hz, 2H), 3.73 (s, 6H), 3.11 (dd, $J = 14.3, 10.3$ Hz, 1H), 2.71 (dd, $J = 14.3, 4.0$ Hz, 1H), 2.19 (s, 1H), 1.86 – 1.40 (m, 2H), 0.97 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 181.59, 144.87, 128.54, 127.83, 124.98, 120.36, 58.52, 39.15, 36.02, 14.33. ^{11}B NMR (193 MHz, CDCl_3) δ -25.00 (t, $J = 89.7$ Hz). $^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3) δ -25.00. $^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3) δ 7.21 – 7.17 (m, 4H), 7.08 (t, $J = 6.7$ Hz, 1H), 6.80 (s, 2H), 3.80 (ddd, $J = 26.2, 10.8, 7.1$ Hz, 2H), 3.73 (s, 6H), 3.11 (dd, $J = 14.3, 10.3$ Hz, 1H), 2.71 (dd, $J = 14.3, 4.2$ Hz, 1H), 2.19 (dt, $J = 10.3, 5.1$ Hz, 1H), 1.62 (d, $J = 13.9$ Hz, 2H), 0.97 (t, $J = 7.1$ Hz, 3H).

Characterization agrees with previous reports for this compound.⁴

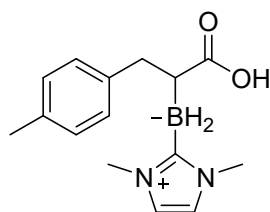


(1-(cinnamyloxy)-1-oxo-3-phenylpropan-2-yl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl) dihydroborate (**3e**): Colorless liquid (53 mg, 71% yield); Gradient eluent: EtOAc/petroleum ether: 1/3 to 1/2; ^1H NMR (600 MHz, CDCl_3) δ 7.32 – 7.29 (m, 4H), 7.23 (dd, $J = 6.8, 3.0$ Hz, 3H), 7.19 (t, $J = 7.6$ Hz, 2H), 7.09 (t, $J = 7.2$ Hz, 1H), 6.71 (s, 2H), 6.42 (d, $J = 15.9$ Hz, 1H), 6.01 (dt, $J = 15.9, 6.2$ Hz, 1H), 4.48 (ddd, $J = 13.2, 6.4, 1.3$ Hz, 1H), 4.41 (ddd, $J = 13.2, 6.1, 1.4$ Hz, 1H), 3.71 (s, 6H), 3.15 (dd, $J = 14.3, 10.2$ Hz, 1H), 2.76 (dd, $J = 14.3, 4.1$ Hz, 1H), 2.27 (s, 1H), 1.46 (dd, $J = 97.8, 48.3$ Hz, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 181.27, 144.76, 136.63, 132.55, 128.58, 128.56, 127.91, 127.76, 126.44, 125.07, 124.74, 120.35, 63.31, 39.19, 36.07. ^{11}B NMR (193 MHz, CDCl_3) δ -24.96 (t, $J = 91.1$ Hz). $^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3) δ -24.95. $^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3) δ 7.32 – 7.29 (m, 4H), 7.24 (dd, $J = 10.8, 5.2$ Hz, 3H), 7.19 (t, $J = 7.6$ Hz, 2H), 7.09 (t, $J = 7.2$ Hz, 1H), 6.71 (s, 2H), 6.43 (d, $J = 15.9$ Hz, 1H), 6.01 (dt, $J = 15.9, 6.2$ Hz, 1H), 4.48 (ddd, $J = 13.2, 6.4, 1.1$ Hz, 1H), 4.41 (dd, $J = 13.2, 6.0$ Hz, 1H), 3.71 (s, 6H), 3.15 (dd, $J = 14.3, 10.2$ Hz, 1H), 2.76 (dd, $J = 14.3, 4.2$ Hz, 1H), 2.26 (td, $J = 10.4, 5.1$ Hz, 1H), 1.64 (s, 2H).

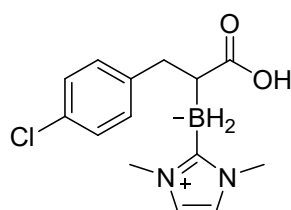
Characterization agrees with previous reports for this compound.⁴



(1-carboxy-2-phenylethyl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)dihydroborate (**3f**): White solid (41.5 mg, 81% yield); Gradient eluent: EtOAc/petroleum ether: 1/2 to 2/1; ^1H NMR (600 MHz, CDCl_3) δ 7.22 (q, $J = 4.2$ Hz, 2H), 7.22 (s, 2H), 7.11 (ddd, $J = 8.5, 6.3, 2.2$ Hz, 1H), 6.68 (s, 2H), 3.62 (s, 6H), 3.05 (dd, $J = 14.5, 10.5$ Hz, 1H), 2.73 (dd, $J = 14.6, 4.0$ Hz, 1H), 2.17 (s, 1H), 1.92 – 1.42 (m, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 188.67, 144.74, 128.59, 127.87, 125.08, 120.51, 38.64, 35.84. ^{11}B NMR (193 MHz, CDCl_3) δ -24.58 (t, $J = 89.7$ Hz). $^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3) δ -24.58. $^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3) δ 7.22 (q, $J = 4.2$ Hz, 2H), 7.22 (s, 2H), 7.11 (dt, $J = 8.4, 2.0$ Hz, 1H), 6.68 (s, 2H), 3.62 (s, 6H), 3.05 (dd, $J = 14.5, 10.4$ Hz, 1H), 2.73 (dd, $J = 14.6, 4.0$ Hz, 1H), 2.17 (td, $J = 10.2, 4.8$ Hz, 1H), 1.65 (d, $J = 39.8$ Hz, 2H). Characterization agrees with previous reports for this compound.⁹

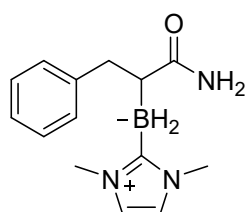


(1-carboxy-2-(p-tolyl)ethyl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)dihydroborate (**3g**): White solid (30 mg, 55% yield); Gradient eluent: EtOAc/petroleum ether: 1/2 to 2/1; ^1H NMR (600 MHz, CDCl_3) δ 7.12 (d, $J = 7.9$ Hz, 2H), 7.03 (d, $J = 7.8$ Hz, 2H), 6.69 (s, 2H), 3.64 (s, 6H), 3.01 (dd, $J = 14.5, 10.5$ Hz, 1H), 2.68 (dd, $J = 14.6, 3.8$ Hz, 1H), 2.29 (s, 3H), 2.16 (s, 1H), 1.92 – 1.41 (m, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 188.57, 141.65, 134.28, 128.55, 128.44, 120.47, 38.20, 35.87, 21.01. ^{11}B NMR (193 MHz, CDCl_3) δ -24.60 (t, $J = 89.7$ Hz). $^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3) δ -24.61. $^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3) δ 7.12 (d, $J = 7.9$ Hz, 2H), 7.02 (d, $J = 7.9$ Hz, 2H), 6.69 (s, 2H), 3.64 (s, 6H), 3.02 (dd, $J = 14.5, 10.5$ Hz, 1H), 2.68 (dd, $J = 14.6, 3.9$ Hz, 1H), 2.29 (s, 3H), 2.15 (td, $J = 10.3, 4.8$ Hz, 1H), 1.64 (d, $J = 38.3$ Hz, 2H). HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd. for $\text{C}_{15}\text{H}_{21}\text{BN}_2\text{NaO}_2$ 295.1588; found: 295.1587.



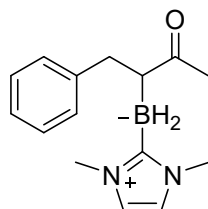
(1-carboxy-2-(4-chlorophenyl)ethyl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)

dihydroborate (**3h**): White solid (40 mg, 53% yield); Gradient eluent: EtOAc/petroleum ether: 1/2 to 2/1; ^1H NMR (600 MHz, CDCl_3) δ 7.16 (q, $J = 8.6$ Hz, 4H), 6.75 (s, 2H), 3.65 (s, 6H), 2.99 (dd, $J = 14.5, 10.5$ Hz, 1H), 2.69 (dd, $J = 14.5, 4.1$ Hz, 1H), 2.11 (s, 1H), 1.96 – 1.60 (m, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 187.72, 143.15, 130.62, 130.04, 127.84, 120.52, 38.05, 35.87. ^{11}B NMR (193 MHz, CDCl_3) δ -24.71 (t, $J = 93.6$ Hz). $^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3) δ -24.74. $^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3) δ 7.16 (q, $J = 8.6$ Hz, 4H), 6.75 (s, 2H), 3.65 (s, 6H), 2.99 (dd, $J = 14.5, 10.5$ Hz, 1H), 2.69 (dd, $J = 14.5, 4.2$ Hz, 1H), 2.11 (dd, $J = 12.4, 7.9$ Hz, 1H), 1.63 (d, $J = 36.5$ Hz, 2H). HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ cacl. for $\text{C}_{15}\text{H}_{21}\text{BN}_2\text{NaO}_2$ 315.1042; found: 315.1030.



(1-amino-1-oxo-3-phenylpropan-2-yl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl) dihydroborate (**3i**): Colorless liquid (36.3 mg, 71% yield); Gradient eluent: DCM/MeOH: 30/1 to 10/1; ^1H NMR (600 MHz, CDCl_3) δ 7.18 (d, $J = 4.5$ Hz, 4H), 7.07 (dt, $J = 8.6, 4.4$ Hz, 1H), 6.73 (s, 2H), 5.27 (s, 2H), 3.69 (s, 6H), 2.94 (dd, $J = 14.4, 10.1$ Hz, 1H), 2.71 (dd, $J = 14.4, 4.7$ Hz, 1H), 2.07 (s, 1H), 1.84 – 1.41 (m, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 185.16, 144.24, 128.38, 127.95, 125.16, 120.56, 39.67, 36.13. ^{11}B NMR (193 MHz, CDCl_3) δ -24.59 (t, $J = 88.8$ Hz). $^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3) δ -24.59. $^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3) δ 7.18 (d, $J = 4.6$ Hz, 4H), 7.07 (dt, $J = 8.6, 4.5$ Hz, 1H), 6.73 (s, 2H), 5.26 (s, 2H), 3.69 (s, 6H), 2.95 (dd, $J = 14.4, 10.0$ Hz, 1H), 2.71 (dd, $J = 14.4, 4.8$ Hz, 1H), 2.07 (dq, $J = 10.2, 5.2$ Hz, 1H), 1.63 (d, $J = 4.6$ Hz, 2H).

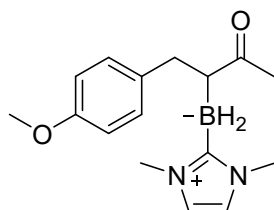
Characterization agrees with previous reports for this compound.⁴



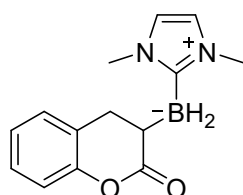
(1,3-dimethyl-1H-imidazol-3-ium-2-yl)(3-oxo-1-phenylbutan-2-yl)dihydroborate (**3j**): Colorless liquid (30.2 mg, 59% yield); Gradient eluent: EtOAc/petroleum ether: 1/2 to 1/1; ^1H NMR (600 MHz, CDCl_3) δ 7.17 (t, $J = 7.5$ Hz, 2H), 7.12 (d, $J = 7.0$ Hz, 2H), 7.07 (t, $J = 7.2$ Hz, 1H), 6.79 (s, 2H), 3.71 (s, 6H), 3.09 (dd, $J = 14.6, 9.6$ Hz, 1H), 2.65 (dd, $J = 14.6, 4.6$ Hz, 1H), 2.58 (s, 1H), 2.01 (s, 3H), 1.85 – 1.51 (m, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 217.42, 144.40, 128.27, 127.95, 125.05, 120.62, 38.35, 36.16, 28.29. ^{11}B NMR (193 MHz, CDCl_3) δ -25.35 (t, $J = 89.7$ Hz). $^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz,

CDCl₃) δ -25.35. ¹H{¹¹B} NMR (600 MHz, CDCl₃) δ 7.17 (t, *J* = 7.5 Hz, 2H), 7.11 (d, *J* = 7.2 Hz, 2H), 7.06 (t, *J* = 7.2 Hz, 1H), 6.79 (s, 2H), 3.71 (s, 6H), 3.09 (dd, *J* = 14.6, 9.6 Hz, 1H), 2.65 (dd, *J* = 14.6, 4.7 Hz, 1H), 2.57 (td, *J* = 10.1, 5.0 Hz, 1H), 2.00 (s, 3H), 1.61 (d, *J* = 33.7 Hz, 2H).

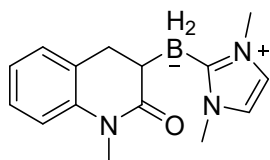
Characterization agrees with previous reports for this compound.⁴



(1,3-dimethyl-1H-imidazol-3-ium-2-yl)(1-(4-methoxyphenyl)-3-oxobutan-2-yl) dihydroborate (**3k**): Colorless liquid (24 mg, 42% yield); Gradient eluent: EtOAc/petroleum ether: 1/2 to 1/1; ¹H NMR (600 MHz, CDCl₃) δ 7.03 (d, *J* = 8.6 Hz, 2H), 6.79 (s, 2H), 6.72 (d, *J* = 8.6 Hz, 2H), 3.73 (s, 3H), 3.70 (s, 6H), 3.01 (dd, *J* = 14.4, 9.7 Hz, 1H), 2.57 (dd, *J* = 14.4, 4.5 Hz, 1H), 2.53 (s, 1H), 1.98 (s, 3H), 1.86 – 1.38 (m, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 217.51, 157.18, 136.62, 129.10, 120.64, 113.38, 55.22, 37.43, 36.15, 28.33. ¹¹B NMR (193 MHz, CDCl₃) δ -25.36 (t, *J* = 89.7 Hz). ¹¹B{¹H} NMR (193 MHz, CDCl₃) δ -25.36. ¹H{¹¹B} NMR (600 MHz, CDCl₃) δ 7.02 (d, *J* = 8.6 Hz, 2H), 6.79 (s, 2H), 6.72 (d, *J* = 8.6 Hz, 2H), 3.73 (s, 3H), 3.70 (s, 6H), 3.01 (dd, *J* = 14.5, 9.6 Hz, 1H), 2.57 (dd, *J* = 14.5, 4.7 Hz, 1H), 2.52 (td, *J* = 9.9, 5.0 Hz, 1H), 1.98 (s, 3H), 1.59 (d, *J* = 28.3 Hz, 2H). HRMS (ESI-TOF) *m/z*: [M + Na]⁺ calcd for C₁₆H₂₃BN₂NaO₂ 309.1745; found: 309.1745.

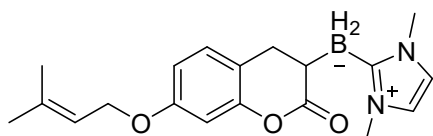


(1,3-dimethyl-1H-imidazol-3-ium-2-yl)(2-oxochroman-3-yl)dihydroborate (**3l**): White solid (39 mg, 76% yield); Gradient eluent: EtOAc/petroleum ether: 1/1 to 2/1; ¹H NMR (600 MHz, CDCl₃) δ 7.12 (dd, *J* = 13.2, 7.5 Hz, 2H), 6.99 (t, *J* = 7.8 Hz, 1H), 6.88 (d, *J* = 8.0 Hz, 1H), 6.77 (s, 2H), 3.65 (s, 6H), 3.24 (d, *J* = 12.3 Hz, 1H), 2.71 (d, *J* = 15.2 Hz, 1H), 2.37 (s, 1H), 1.77 – 1.28 (m, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 178.24, 152.38, 128.45, 126.83, 124.07, 123.32, 120.69, 115.43, 35.97, 30.63. ¹¹B NMR (193 MHz, CDCl₃) δ -26.07 (t, *J* = 91.3 Hz). ¹¹B{¹H} NMR (193 MHz, CDCl₃) δ -26.07. ¹H{¹¹B} NMR (600 MHz, CDCl₃) δ 7.12 (dd, *J* = 13.1, 7.5 Hz, 2H), 6.99 (t, *J* = 7.8 Hz, 1H), 6.88 (d, *J* = 7.9 Hz, 1H), 6.76 (s, 2H), 3.65 (s, 6H), 3.24 (dd, *J* = 15.2, 6.2 Hz, 1H), 2.71 (d, *J* = 15.2 Hz, 1H), 2.37 (dd, *J* = 12.8, 5.9 Hz, 1H), 1.47 (d, *J* = 32.7 Hz, 2H). Characterization agrees with previous reports for this compound.⁴



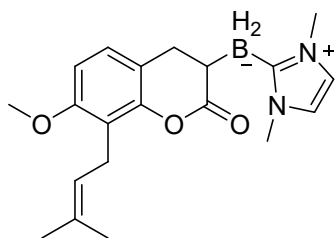
(1,3-dimethyl-1H-imidazol-3-ium-2-yl)(1-methyl-2-oxo-1,2,3,4-tetrahydroquinolin-3-yl)dihydroborate (**3m**): White solid (49.1 mg, 92% yield); Gradient eluent: EtOAc/petroleum ether: 1/1 to 2/1; ^1H NMR (600 MHz, CDCl_3) δ 7.14 (t, $J = 7.9$ Hz, 1H), 7.10 (d, $J = 7.2$ Hz, 1H), 6.91 (t, $J = 7.3$ Hz, 1H), 6.82 (d, $J = 8.0$ Hz, 1H), 6.73 (s, 2H), 3.60 (s, 6H), 3.23 (s, 3H), 3.20 (d, $J = 14.7$ Hz, 1H), 2.61 (d, $J = 14.8$ Hz, 1H), 2.24 (s, 1H), 1.60-1.10 (m, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 180.17, 141.17, 127.97, 127.94, 126.11, 121.69, 120.30, 112.96, 35.80, 32.48, 29.10. ^{11}B NMR (193 MHz, CDCl_3) δ -27.81 (t, $J = 90.7$ Hz). $^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3) δ -26.81. $^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3) δ 7.14 (t, $J = 7.9$ Hz, 1H), 7.10 (d, $J = 7.2$ Hz, 1H), 6.91 (t, $J = 7.3$ Hz, 1H), 6.82 (d, $J = 8.0$ Hz, 1H), 6.73 (s, 2H), 3.59 (s, 6H), 3.23 (s, 3H), 3.20 (q, $J = 14.7$ Hz, 1H), 2.61 (d, $J = 14.8$ Hz, 1H), 2.24 (dd, $J = 11.7, 5.6$ Hz, 1H), 1.35 (d, $J = 39.3$ Hz, 2H).

Characterization agrees with previous reports for this compound.⁹

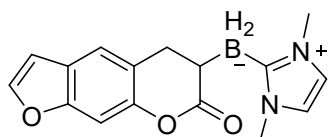


(1,3-dimethyl-1H-imidazol-3-ium-2-yl)(7-((3-methylbut-2-en-1-yl)oxy)-2-oxochroman-3-yl)dihydroborate (**3n**): White solid (47.9 mg, 70% yield); Gradient eluent: EtOAc/petroleum ether: 1/1 to 2/1; ^1H NMR (600 MHz, CDCl_3) δ 7.01 (d, $J = 8.2$ Hz, 1H), 6.77 (s, 2H), 6.58 (dd, $J = 8.2, 2.5$ Hz, 1H), 6.49 (d, $J = 2.5$ Hz, 1H), 5.47 (t, $J = 7.3$ Hz, 1H), 4.46 (d, $J = 6.7$ Hz, 2H), 3.67 (s, 6H), 3.16 (dd, $J = 14.5, 5.0$ Hz, 1H), 2.64 (d, $J = 14.9$ Hz, 1H), 2.34 (s, 1H), 1.78 (s, 3H), 1.72 (s, 3H), 1.66 – 1.25 (m, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 178.26, 157.93, 152.95, 138.11, 128.69, 120.65, 119.70, 116.00, 109.60, 102.36, 64.94, 36.01, 29.88, 25.85, 18.22. ^{11}B NMR (193 MHz, CDCl_3) δ -26.00 (t, $J = 91.7$ Hz). $^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3) δ -25.99. $^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3) δ 7.01 (d, $J = 8.2$ Hz, 1H), 6.77 (s, 2H), 6.58 (dd, $J = 8.2, 2.5$ Hz, 1H), 6.49 (d, $J = 2.5$ Hz, 1H), 5.47 (t, $J = 6.7$ Hz, 1H), 4.46 (d, $J = 6.7$ Hz, 2H), 3.67 (s, 6H), 3.16 (dd, $J = 14.9, 6.1$ Hz, 1H), 2.64 (d, $J = 14.9$ Hz, 1H), 2.35 (dd, $J = 12.4, 6.0$ Hz, 1H), 1.78 (s, 3H), 1.72 (s, 3H), 1.48 (d, $J = 26.1$ Hz, 2H).

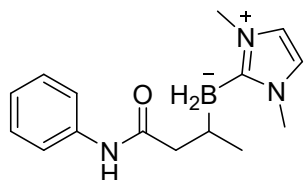
HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ cacl. for $\text{C}_{19}\text{H}_{25}\text{BN}_2\text{NaO}_3$ 363.1850; found: 363.1837.



(1,3-dimethyl-1H-imidazol-3-ium-2-yl)(7-methoxy-8-(3-methylbut-2-en-1-yl)-2-oxochroman-3-yl)dihydroborate (**3o**): White solid (65.3 mg, 92% yield); Gradient eluent: EtOAc/petroleum ether: 1/1 to 2/1; ^1H NMR (600 MHz, CDCl_3) δ 6.92 (d, $J = 8.2$ Hz, 1H), 6.76 (s, 2H), 6.55 (d, $J = 8.3$ Hz, 1H), 5.18 (t, $J = 7.0$ Hz, 1H), 3.79 (s, 3H), 3.65 (s, 6H), 3.40 (dd, $J = 14.0, 7.5$ Hz, 1H), 3.32 (dd, $J = 14.0, 6.6$ Hz, 1H), 3.17 (dd, $J = 14.2, 4.8$ Hz, 1H), 2.65 (d, $J = 14.8$ Hz, 1H), 2.31 (s, 1H), 1.77 (s, 3H), 1.63 (s, 3H), 1.56 – 1.29 (m, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 178.35, 156.31, 150.56, 131.02, 125.44, 122.92, 120.60, 116.95, 116.52, 105.43, 55.79, 35.93, 30.48, 25.82, 22.26, 17.91. ^{11}B NMR (193 MHz, CDCl_3) δ -26.12 (t, $J = 91.7$ Hz). $^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3) δ -26.11. $^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3) δ 6.92 (d, $J = 8.2$ Hz, 1H), 6.76 (s, 2H), 6.54 (d, $J = 8.2$ Hz, 1H), 5.18 (t, $J = 7.0$ Hz, 1H), 3.79 (s, 3H), 3.65 (s, 6H), 3.40 (dd, $J = 14.0, 7.4$ Hz, 1H), 3.32 (dd, $J = 14.0, 6.6$ Hz, 1H), 3.17 (dd, $J = 14.7, 6.0$ Hz, 1H), 2.65 (d, $J = 14.6$ Hz, 1H), 2.32 (dd, $J = 12.1, 5.8$ Hz, 1H), 1.77 (s, 3H), 1.63 (s, 3H), 1.44 (d, $J = 35.9$ Hz, 2H). HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ cacl. for $\text{C}_{20}\text{H}_{29}\text{BN}_2\text{NaO}_3$ 377.2007; found: 377.2008.

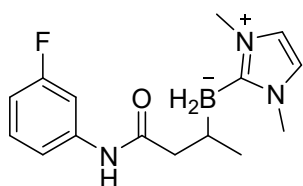


(1,3-dimethyl-1H-imidazol-3-ium-2-yl)(7-oxo-6,7-dihydro-5H-furo[3,2-g]chromen-6-yl)dihydroborate (**3p**): White solid (52.1 mg, 88% yield); Gradient eluent: EtOAc/petroleum ether: 1/1 to 2/1; ^1H NMR (600 MHz, CDCl_3) δ 7.54 (d, $J = 2.2$ Hz, 1H), 7.34 (s, 1H), 7.09 (s, 1H), 6.78 (s, 2H), 6.68 (dd, $J = 2.1, 0.8$ Hz, 1H), 3.68 (s, 6H), 3.34 (d, $J = 10.8$ Hz, 1H), 2.84 (d, $J = 14.8$ Hz, 1H), 2.39 (s, 1H), 1.60 – 1.13 (m, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 178.39, 153.75, 150.37, 144.74, 123.11, 120.63, 120.04, 119.61, 106.27, 98.70, 36.01, 30.87. ^{11}B NMR (193 MHz, CDCl_3) δ -26.25 (t, $J = 90.7$ Hz). $^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3) δ -26.26. $^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3) δ 7.54 (d, $J = 2.1$ Hz, 1H), 7.34 (s, 1H), 7.09 (s, 1H), 6.78 (s, 2H), 6.68 (d, $J = 1.2$ Hz, 1H), 3.68 (s, 6H), 3.34 (dd, $J = 14.7, 5.8$ Hz, 1H), 2.84 (d, $J = 14.8$ Hz, 1H), 2.39 (dd, $J = 12.9, 5.5$ Hz, 1H), 1.47 (d, $J = 59.1$ Hz, 2H). HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ cacl. for $\text{C}_{16}\text{H}_{17}\text{BN}_2\text{NaO}_3$ 319.1224; found: 319.1221.

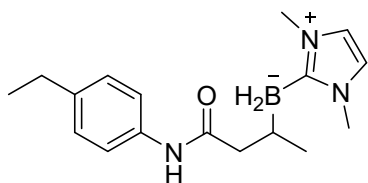


(1,3-dimethyl-1H-imidazol-3-ium-2-yl)(4-oxo-4-(phenylamino)butan-2-yl)dihydroborate (**3q**): White solid (36 mg, 38% yield); Gradient eluent: EtOAc/petroleum ether: 2/1 to 1/1; ^1H NMR (600 MHz, CDCl_3) δ 7.83 (s, 1H), 7.53 (d, $J = 7.9$ Hz, 2H), 7.28 (d, $J = 7.7$ Hz, 2H), 7.03 (t, $J = 7.4$ Hz, 1H), 6.79 (s, 2H), 3.76 (s, 6H), 2.32 (dd, J

= 13.8, 7.3 Hz, 1H), 2.24 (dd, $J = 13.6, 6.8$ Hz, 1H), 1.76 – 1.35 (m, 2H), 1.19 (s, 1H), 0.84 (d, $J = 6.6$ Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 174.65, 138.77, 128.82, 123.38, 120.32, 119.60, 48.69, 36.14, 22.57. ^{11}B NMR (193 MHz, CDCl_3) δ -24.03 (t, $J = 84.0$ Hz). $^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3) δ -24.03. $^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3) δ 7.82 (s, 1H), 7.53 (d, $J = 7.9$ Hz, 2H), 7.29 – 7.26 (m, 2H), 7.03 (t, $J = 7.3$ Hz, 1H), 6.79 (s, 2H), 3.76 (s, 6H), 2.32 (dd, $J = 13.9, 7.4$ Hz, 1H), 2.24 (dd, $J = 13.9, 6.9$ Hz, 1H), 1.58 – 1.40 (m, 2H), 1.18 (td, $J = 13.1, 6.6$ Hz, 1H), 0.84 (d, $J = 6.9$ Hz, 3H). HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{15}\text{H}_{22}\text{BN}_3\text{NaO}$ 294.1754; found: 294.1750.



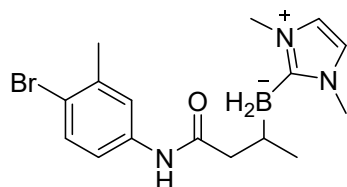
(1,3-dimethyl-1H-imidazol-3-ium-2-yl)(4-((3-fluorophenyl)amino)-4-oxobutan-2-yl) dihydroborate (**3r**): White solid (38 mg, 66% yield); Gradient eluent: EtOAc/petroleum ether: 1/3 to 1/2; ^1H NMR (600 MHz, CDCl_3) δ 8.07 (s, 1H), 7.54 (d, $J = 11.3$ Hz, 1H), 7.19 (td, $J = 8.1, 6.5$ Hz, 1H), 7.14 (dd, $J = 7.7, 1.0$ Hz, 1H), 6.79 (s, 2H), 6.73 – 6.69 (m, 1H), 3.74 (s, 6H), 2.32 (dd, $J = 13.8, 7.5$ Hz, 1H), 2.26 (dd, $J = 13.8, 6.6$ Hz, 1H), 1.56 (dd, $J = 163.4, 74.7$ Hz, 2H), 1.16 (d, $J = 4.4$ Hz, 1H), 0.81 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 174.86, 163.02 (d, $J = 241.6$ Hz), 140.39 (d, $J = 12.1$ Hz), 129.77 (d, $J = 9.1$ Hz), 120.37, 114.72, 109.90 (d, $J = 241.6$ Hz), 106.93 (d, $J = 27.2$ Hz), 48.66, 36.11, 22.51. ^{11}B NMR (193 MHz, CDCl_3) δ -24.04 (t, $J = 84.2$ Hz). $^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3) δ -24.04. $^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3) δ 8.05 (s, 1H), 7.53 (d, $J = 11.2$ Hz, 1H), 7.21 – 7.17 (m, 1H), 7.14 (d, $J = 8.2$ Hz, 1H), 6.79 (s, 2H), 6.71 (td, $J = 8.6, 2.0$ Hz, 1H), 3.74 (s, 6H), 2.31 (dd, $J = 13.9, 7.5$ Hz, 1H), 2.26 (dd, $J = 13.9, 6.7$ Hz, 1H), 1.59 – 1.40 (m, 2H), 1.20 – 1.14 (m, 1H), 0.82 (d, $J = 7.0$ Hz, 3H). HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{15}\text{H}_{21}\text{BFN}_3\text{NaO}$ 312.1659; found: 312.1656.



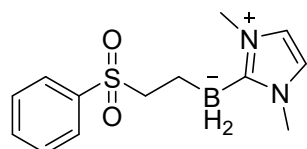
(1,3-dimethyl-1H-imidazol-3-ium-2-yl)(4-((4-ethylphenyl)amino)-4-oxobutan-2-yl) dihydroborate (**3s**): White solid (20 mg, 33% yield); Gradient eluent: EtOAc/petroleum ether: 1/1 to 2/1; ^1H NMR (600 MHz, CDCl_3) δ 7.72 (s, 1H), 7.43 (d, $J = 8.3$ Hz, 2H), 7.11 (d, $J = 8.3$ Hz, 2H), 6.79 (s, 2H), 3.76 (s, 6H), 2.59 (q, $J = 7.6$ Hz, 2H), 2.31 (dd, $J = 13.8, 7.3$ Hz, 1H), 2.22 (dd, $J = 13.6, 6.8$ Hz, 1H), 1.83 – 1.46 (m, 2H), 1.20 (d, $J = 7.6$ Hz, 3H), 1.18 – 1.15 (m, 1H), 0.84 (d, $J = 6.6$ Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 174.47, 139.41, 136.37, 128.13, 120.30, 119.78, 48.62, 36.15, 28.30, 22.56, 15.74.

^{11}B NMR (193 MHz, CDCl_3) δ -24.03 (t, J = 83.3 Hz). $^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3) δ -24.03. $^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3) δ 7.71 (s, 1H), 7.44 (d, J = 8.2 Hz, 2H), 7.11 (d, J = 8.3 Hz, 2H), 6.79 (s, 2H), 3.77 (s, 6H), 2.59 (q, J = 7.6 Hz, 2H), 2.31 (dd, J = 13.9, 7.3 Hz, 1H), 2.22 (dd, J = 13.9, 7.0 Hz, 1H), 1.59 – 1.41 (m, 2H), 1.21 (d, J = 7.6 Hz, 3H), 1.19 – 1.15 (m, 1H), 0.85 (d, J = 6.9 Hz, 3H).

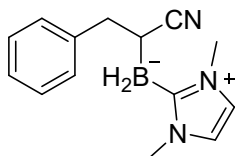
HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{17}\text{H}_{26}\text{BN}_3\text{NaO}$ 322.2061; found: 322.2060.



(4-((4-bromo-3-methylphenyl)amino)-4-oxobutan-2-yl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)dihydroborate (**3t**): White solid (31.8 mg, 44% yield); Gradient eluent: EtOAc/petroleum ether: 1/3 to 1/1; ^1H NMR (600 MHz, CDCl_3) δ 7.87 (s, 1H), 7.47 (d, J = 1.9 Hz, 1H), 7.39 (d, J = 8.6 Hz, 1H), 7.26 (dd, J = 8.3, 2.3 Hz, 1H), 6.80 (s, 2H), 3.75 (s, 6H), 2.34 (s, 3H), 2.32 – 2.28 (m, 1H), 2.24 (dd, J = 13.6, 6.5 Hz, 1H), 1.66 – 1.33 (m, 2H), 1.16 (d, J = 4.3 Hz, 1H), 0.81 (d, J = 6.8 Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 174.68, 138.18, 138.03, 132.38, 121.77, 120.35, 118.59, 118.29, 48.69, 36.14, 23.02, 22.53. ^{11}B NMR (193 MHz, CDCl_3) δ -24.07 (t, J = 85.0 Hz). $^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3) δ -24.06. $^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3) δ 7.86 (s, 1H), 7.47 (s, 1H), 7.39 (d, J = 8.6 Hz, 1H), 7.25 (d, J = 7.0 Hz, 1H), 6.80 (s, 2H), 3.75 (s, 6H), 2.34 (s, 3H), 2.30 (dd, J = 13.9, 7.5 Hz, 1H), 2.24 (dd, J = 13.9, 6.7 Hz, 1H), 1.59 – 1.39 (m, 2H), 1.15 (dt, J = 13.4, 6.7 Hz, 1H), 0.82 (d, J = 6.9 Hz, 3H). HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{16}\text{H}_{23}\text{BBrN}_3\text{NaO}$ 386.1010; found: 386.1004.

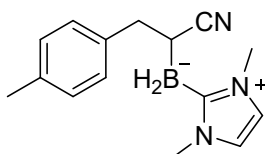


(1,3-dimethyl-1H-imidazol-3-ium-2-yl)(2-(phenylsulfonyl)ethyl)dihydroborate (**3u**): Colorless liquid (32.7 mg, 59% yield); Gradient eluent: EtOAc/petroleum ether: 1/1 to 2/1; ^1H NMR (600 MHz, CDCl_3) δ 7.87 (dd, J = 8.3, 1.2 Hz, 2H), 7.59 – 7.57 (m, 1H), 7.51 (dd, J = 10.0, 3.6 Hz, 2H), 6.80 (s, 2H), 3.69 (s, 6H), 3.06 – 3.03 (m, 2H), 1.65 – 1.30 (m, 2H), 0.67 (s, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 139.90, 132.86, 128.84, 128.11, 123.18, 120.43, 60.23, 35.93. ^{11}B NMR (193 MHz, CDCl_3) δ -27.88 (t, J = 86.3 Hz). $^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3) δ -27.87. $^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3) δ 7.88 (d, J = 7.3 Hz, 2H), 7.57 (d, J = 7.4 Hz, 1H), 7.51 (t, J = 7.7 Hz, 2H), 6.80 (s, 2H), 3.70 (s, 6H), 3.07 – 3.02 (m, 2H), 1.33 (d, J = 20.1 Hz, 2H), 0.74 – 0.62 (m, 2H). HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd. for $\text{C}_{13}\text{H}_{19}\text{BN}_2\text{NaO}_2\text{S}$ 301.1153; found: 301.1153.



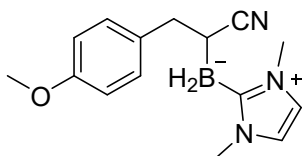
(1-cyano-2-phenylethyl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)dihydroborate (**3v**): Colorless liquid (36.4 mg, 76% yield); Gradient eluent: EtOAc/petroleum ether: 1/2 to 1/1; ^1H NMR (600 MHz, CDCl_3) δ 7.28 (d, $J = 4.6$ Hz, 4H), 7.18 (dt, $J = 8.6, 3.7$ Hz, 1H), 6.85 (s, 2H), 3.83 (s, 6H), 2.87 (dd, $J = 14.0, 4.6$ Hz, 1H), 2.81 (dd, $J = 13.8, 10.5$ Hz, 1H), 1.88 (s, 1H), 1.83 – 1.34 (m, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 142.51, 129.11, 128.55, 128.25, 125.97, 120.97, 40.03, 36.39. ^{11}B NMR (193 MHz, CDCl_3) δ -25.89 (t, $J = 90.7$ Hz). $^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3) δ -25.89. $^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3) δ 7.28 (d, $J = 4.5$ Hz, 4H), 7.18 (dd, $J = 7.6, 4.2$ Hz, 1H), 6.85 (s, 2H), 3.83 (s, 6H), 2.87 (dd, $J = 14.0, 4.8$ Hz, 1H), 2.82 (dd, $J = 13.9, 10.3$ Hz, 1H), 1.88 (qd, $J = 9.9, 4.8$ Hz, 1H), 1.69 (d, $J = 39.0$ Hz, 2H).

Characterization agrees with previous reports for this compound.⁴



(1-cyano-2-(p-tolyl)ethyl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)dihydroborate (**3w**) : Colorless liquid (40.4 mg, 80% yield); Gradient eluent: EtOAc/petroleum ether: 1/2 to 1/1; ^1H NMR (600 MHz, CDCl_3) δ 7.18 (d, $J = 7.9$ Hz, 2H), 7.09 (d, $J = 7.8$ Hz, 2H), 6.86 (s, 2H), 3.84 (s, 6H), 2.83 (dd, $J = 14.0, 4.5$ Hz, 1H), 2.77 (dd, $J = 13.8, 10.5$ Hz, 1H), 2.31 (s, 3H), 1.86 (s, 1H), 1.79-1.49 (m, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 139.47, 135.33, 129.19, 128.95, 128.40, 120.94, 39.62, 36.40, 21.07. ^{11}B NMR (193 MHz, CDCl_3) δ -25.91 (t, $J = 90.7$ Hz). $^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3) δ -25.91. $^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3) δ 7.18 (d, $J = 7.9$ Hz, 2H), 7.09 (d, $J = 7.8$ Hz, 2H), 6.86 (s, 2H), 3.84 (s, 6H), 2.83 (dd, $J = 14.0, 4.8$ Hz, 1H), 2.77 (dd, $J = 13.9, 10.5$ Hz, 1H), 2.31 (s, 3H), 1.86 (qd, $J = 10.0, 4.7$ Hz, 1H), 1.68 (d, $J = 41.9$ Hz, 2H).

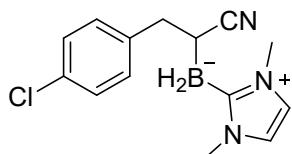
Characterization agrees with previous reports for this compound.⁴



(1-cyano-2-(4-methoxyphenyl)ethyl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)dihydroborate (**3x**): Colorless liquid (47.7 mg, 89% yield); Gradient eluent: EtOAc/petroleum ether: 1/2 to 1/1; ^1H NMR (600 MHz, CDCl_3) δ 7.19 (d, $J = 8.6$ Hz, 2H), 6.85 (s, 2H), 6.82 (d, $J = 8.6$ Hz, 2H), 3.82 (s, 6H), 3.77 (s, 3H), 2.81 (dd, $J = 14.0, 4.6$ Hz, 1H), 2.74 (dd, $J = 14.0, 10.4$ Hz, 1H), 1.83 (s, 1H), 1.79 – 1.22 (m, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 157.88, 134.74, 129.47, 129.22, 120.96, 113.66, 55.25, 39.16, 36.38. ^{11}B NMR (193 MHz, CDCl_3) δ -25.97 (t, $J = 90.7$ Hz). $^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3) δ -25.97. $^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3) δ 7.19 (d, $J = 8.5$ Hz,

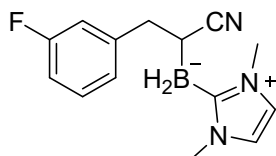
2H), 6.85 (s, 2H), 6.82 (d, $J = 8.5$ Hz, 2H), 3.82 (s, 6H), 3.77 (s, 3H), 2.81 (dd, $J = 14.1$, 4.8 Hz, 1H), 2.74 (dd, $J = 13.9$, 10.5 Hz, 1H), 1.83 (td, $J = 12.1$, 4.7 Hz, 1H), 1.67 (d, $J = 40.8$ Hz, 2H).

Characterization agrees with previous reports for this compound.⁴



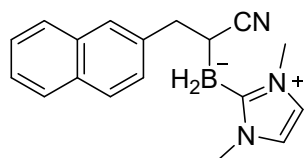
(2-(4-chlorophenyl)-1-cyanoethyl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)dihydroborate (**3y**): Colorless liquid (38.3 mg, 70% yield); Gradient eluent: EtOAc/petroleum ether: 1/2 to 1/1; ¹H NMR (600 MHz, CDCl₃) δ 7.22 (q, $J = 8.5$ Hz, 4H), 6.87 (s, 2H), 3.83 (s, 6H), 2.83 (dd, $J = 14.0$, 4.6 Hz, 1H), 2.77 (dd, $J = 13.9$, 10.3 Hz, 1H), 1.82 (s, 1H), 1.77 – 1.32 (m, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 140.90, 131.63, 129.98, 128.79, 128.30, 120.99, 39.30, 36.39. ¹¹B NMR (193 MHz, CDCl₃) δ -26.00 (t, $J = 91.7$ Hz). ¹¹B{¹H} NMR (193 MHz, CDCl₃) δ -25.99. ¹H{¹¹B} NMR (600 MHz, CDCl₃) δ 7.22 (q, $J = 8.5$ Hz, 4H), 6.86 (s, 2H), 3.83 (s, 6H), 2.83 (dd, $J = 14.1$, 4.9 Hz, 1H), 2.77 (dd, $J = 14.0$, 10.3 Hz, 1H), 1.82 (ddd, $J = 12.7$, 9.8, 4.7 Hz, 1H), 1.66 (d, $J = 39.4$ Hz, 2H).

HRMS (ESI-TOF) m/z : [M + Na]⁺ calcd for C₁₄H₁₇BClN₃Na 296.1096; found: 296.1099.



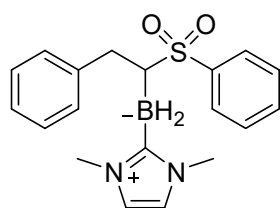
(1-cyano-2-(3-fluorophenyl)ethyl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)dihydroborate (**3z**): Colorless liquid (34.5 mg, 67% yield); Gradient eluent: EtOAc/petroleum ether: 1/2 to 1/1; ¹H NMR (600 MHz, CDCl₃) δ 7.23 (dd, $J = 14.0$, 7.9 Hz, 1H), 7.05 (d, $J = 7.6$ Hz, 1H), 6.97 (d, $J = 10.0$ Hz, 1H), 6.87 (s, 2H), 6.86 (dd, $J = 8.4$, 4.2 Hz, 1H), 3.83 (s, 6H), 2.86 (dd, $J = 14.1$, 4.7 Hz, 1H), 2.80 (dd, $J = 14.0$, 10.4 Hz, 1H), 1.86 (s, 1H), 1.78 – 1.39 (m, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 162.81 (d, $J = 244.6$ Hz), 145.05 (d, $J = 7.6$ Hz), 129.62 (d, $J = 7.6$ Hz), 128.75, 124.28 (d, $J = 3.0$ Hz), 121.00, 115.32 (d, $J = 21.1$ Hz), 112.81 (d, $J = 21.1$ Hz), 39.70 (d, $J = 1.5$ Hz), 36.39. ¹¹B NMR (193 MHz, CDCl₃) δ -25.94 (t, $J = 90.7$ Hz). ¹¹B{¹H} NMR (193 MHz, CDCl₃) δ -25.94. ¹H{¹¹B} NMR (600 MHz, CDCl₃) δ 7.23 (dd, $J = 14.0$, 7.9 Hz, 1H), 7.05 (d, $J = 7.6$ Hz, 1H), 6.97 (d, $J = 10.0$ Hz, 1H), 6.87 (s, 2H), 6.86 (dd, $J = 8.4$, 4.2 Hz, 1H), 3.83 (s, 6H), 2.86 (dd, $J = 14.1$, 4.9 Hz, 1H), 2.80 (dd, $J = 14.0$, 10.3 Hz, 1H), 1.86 (ddd, $J = 12.7$, 9.9, 4.8 Hz, 1H), 1.67 (d, $J = 40.8$ Hz, 2H). ¹⁹F NMR (565 MHz, CDCl₃) δ -114.06.

Characterization agrees with previous reports for this compound.⁴



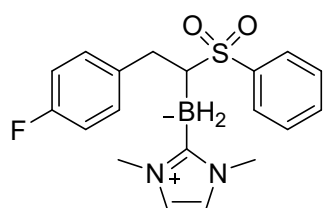
(1-cyano-2-(naphthalen-2-yl)ethyl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl) dihydroborate (**3aa**): Colorless liquid (44.9 mg, 78% yield); Gradient eluent: EtOAc/petroleum ether: 1/2 to 1/1; ^1H NMR (600 MHz, CDCl_3) δ 7.77 (dd, $J = 12.6, 8.7$ Hz, 3H), 7.71 (s, 1H), 7.45 – 7.37 (m, 3H), 6.78 (s, 2H), 3.81 (s, 6H), 3.00 (qd, $J = 14.1, 7.6$ Hz, 2H), 1.97 (s, 1H), 1.92 – 1.50 (m, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 140.06, 133.64, 132.17, 129.09, 127.77, 127.67, 127.60, 127.49, 126.64, 125.75, 125.09, 120.94, 40.19, 36.39. ^{11}B NMR (193 MHz, CDCl_3) δ -25.84 (t, $J = 90.7$ Hz). $^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3) δ -25.85. $^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3) δ 7.80 (d, $J = 8.9$ Hz, 2H), 7.46 (dd, $J = 8.4, 6.6$ Hz, 1H), 7.45 – 7.39 (m, 2H), 6.80 (s, 2H), 3.83 (s, 6H), 3.05 (dd, $J = 14.1, 5.0$ Hz, 1H), 3.00 (dd, $J = 14.0, 10.2$ Hz, 1H), 1.99 (qd, $J = 9.9, 4.8$ Hz, 1H), 1.72 (d, $J = 42, 2$ Hz).

Characterization agrees with previous reports for this compound.¹⁰



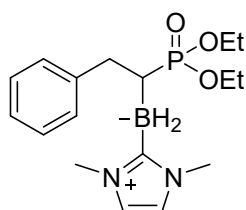
(1,3-dimethyl-1H-imidazol-3-ium-2-yl)(2-phenyl-(phenylsulfonyl) vinyl) dihydroborate (**3ab**): Colorless liquid (34 mg, 48% yield); Gradient eluent: EtOAc/petroleum ether: 1/4 to 1/2; ^1H NMR (600 MHz, CDCl_3) δ 7.84 (d, $J = 7.3$ Hz, 2H), 7.52 (t, $J = 7.4$ Hz, 1H), 7.46 (t, $J = 7.5$ Hz, 2H), 7.11 (t, $J = 7.3$ Hz, 2H), 7.05 (t, $J = 7.3$ Hz, 1H), 6.90 (d, $J = 7.1$ Hz, 2H), 6.76 (s, 2H), 3.65 (s, 6H), 2.86 (d, $J = 10.0$ Hz, 1H), 2.77 – 2.69 (m, 2H), 1.66 (dd, $J = 181.0, 96.7$ Hz, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 141.25, 141.23, 132.05, 128.90, 128.59, 128.10, 127.85, 125.55, 120.49, 37.43, 35.98. ^{11}B NMR (193 MHz, CDCl_3) δ -29.56 (t, $J = 90.7$ Hz). $^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3) δ -29.56. $^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3) δ 7.84 (d, $J = 7.3$ Hz, 2H), 7.52 (t, $J = 7.4$ Hz, 1H), 7.46 (t, $J = 7.5$ Hz, 2H), 7.11 (t, $J = 7.3$ Hz, 2H), 7.05 (t, $J = 7.3$ Hz, 1H), 6.90 (d, $J = 7.2$ Hz, 2H), 6.76 (s, 2H), 3.65 (s, 6H), 2.90 – 2.83 (dd, $J = 9.0, 5.1$ Hz, 1H), 2.78 – 2.68 (m, 2H), 1.64 (d, $J = 178.7$ Hz, 2H).

Characterization agrees with previous reports for this compound.¹⁰



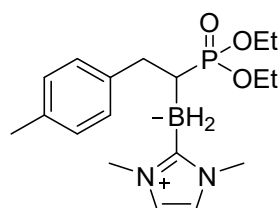
(1,3-dimethyl-1H-imidazol-3-ium-2-yl)(2-(4-fluorophenyl)-1-(phenylsulfonyl) vinyl) dihydroborate

dihydroborate (**3ac**): Colorless liquid (33.5 mg, 45% yield); Gradient eluent: EtOAc/petroleum ether: 1/2 to 1/1; ^1H NMR (600 MHz, CDCl_3) δ 7.81 (d, $J = 7.1$ Hz, 2H), 7.52 (t, $J = 7.4$ Hz, 1H), 7.46 (t, $J = 7.6$ Hz, 2H), 6.89 – 6.82 (m, 2H), 6.82 – 6.74 (m, 3H), 6.78 (s, 2H), 3.67 (s, 6H), 2.79 (d, $J = 11.5$ Hz, 1H), 2.75 – 2.69 (m, 1H), 2.65 (s, 1H), 1.99 – 1.93 (m, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 161.06 (d, $J = 243.1$ Hz), 141.23, 136.89 (d, $J = 3.0$ Hz), 132.10, 130.26 (d, $J = 7.6$ Hz), 128.62, 128.01, 120.54, 114.59, 114.45, 36.70, 35.99. ^{11}B NMR (193 MHz, CDCl_3) δ -29.56 (t, $J = 90.7$ Hz). $^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3) δ -29.57. $^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3) δ 7.81 (d, $J = 7.2$ Hz, 2H), 7.52 (t, $J = 7.4$ Hz, 1H), 7.46 (t, $J = 7.5$ Hz, 2H), 6.85 (dd, $J = 8.5$, 5.6 Hz, 2H), 6.82 – 6.75 (m, 3H), 6.78 (s, 2H), 3.67 (s, 6H), 2.79 (dd, $J = 13.1$, 3.0 Hz, 1H), 2.72 (dd, $J = 13.0$, 9.4 Hz, 1H), 2.66 (dt, $J = 12.3$, 3.2 Hz, 1H), 1.64 (d, $J = 187.7$ Hz, 2H). ^{19}F NMR (565 MHz, CDCl_3) δ -117.98. HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{19}\text{H}_{22}\text{BFN}_2\text{NaO}_2\text{S}$ 395.1377; found: 395.1383.



(1-(diethoxyphosphoryl)-2-phenylethyl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)dihydroborate (**3ad**): Colorless liquid (31.3 mg, 45% yield); Gradient eluent: Dichloromethane/ methanol: 40/1 to 20/1; ^1H NMR (600 MHz, CDCl_3) δ 7.20 – 7.16 (m, 4H), 7.08 (t, $J = 6.6$ Hz, 1H), 6.67 (s, 2H), 4.05 (p, $J = 7.1$ Hz, 2H), 3.92 – 3.85 (m, 2H), 3.58 (s, 6H), 3.15 (t, $J = 13.7$ Hz, 1H), 2.61 (dd, $J = 22.3$, 12.3 Hz, 1H), 1.88 – 1.43 (m, 2H), 1.34 – 1.30 (m, 1H), 1.25 (t, $J = 7.1$ Hz, 3H), 1.16 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 144.10 (d, $J = 16.6$ Hz), 128.96, 127.65, 125.04, 120.12, 61.04 (d, $J = 7.6$ Hz), 60.01 (d, $J = 6.0$ Hz), 36.68 (d, $J = 4.5$ Hz), 35.85, 16.62 (d, $J = 6.0$ Hz), 16.47 (d, $J = 6.0$ Hz). ^{11}B NMR (193 MHz, CDCl_3) δ -28.61 (t, $J = 86.9$ Hz). $^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3) δ -28.60. $^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3) δ 7.20 – 7.16 (m, 4H), 7.07 (t, $J = 6.7$ Hz, 1H), 6.67 (s, 2H), 4.05 (p, $J = 7.1$ Hz, 2H), 3.92 – 3.85 (m, 2H), 3.58 (s, 6H), 3.15 (td, $J = 14.2$, 4.1 Hz, 1H), 2.61 (td, $J = 12.6$, 9.7 Hz, 1H), 1.67 – 1.36 (m, 2H), 1.34 – 1.31 (m, 1H), 1.25 (t, $J = 7.1$ Hz, 3H), 1.16 (t, $J = 7.0$ Hz, 3H). ^{31}P NMR (243 MHz, CDCl_3) δ 44.09.

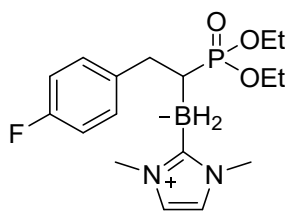
Characterization agrees with previous reports for this compound.¹⁰



(1-(diethoxyphosphoryl)-2-(p-tolyl)ethyl)(1,3-dimethyl-1H-imidazol-3-ium-2-

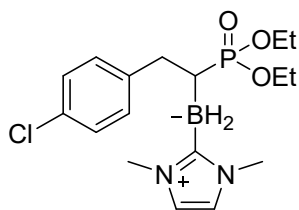
yl)dihydroborate (**3ae**): Colorless liquid (40 mg, 55% yield); Gradient eluent: Dichloromethane/ methanol: 40/1 to 20/1; ^1H NMR (600 MHz, CDCl_3) δ 7.07 (d, $J = 7.8$ Hz, 2H), 6.97 (d, $J = 7.7$ Hz, 2H), 6.66 (s, 2H), 4.03 (p, $J = 7.1$ Hz, 2H), 3.92 – 3.83 (m, 2H), 3.09 (t, $J = 13.0$ Hz, 1H), 2.56 (dd, $J = 22.4, 12.3$ Hz, 1H), 2.25 (s, 3H), 1.86 – 1.36 (m, 2H), 1.32 – 1.27 (m, 1H), 1.23 (t, $J = 7.1$ Hz, 3H), 1.15 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 140.91 (d, $J = 16.6$ Hz), 134.26, 128.77, 128.31, 120.09, 60.99 (d, $J = 7.6$ Hz), 59.99 (d, $J = 6.0$ Hz), 36.14 (d, $J = 4.5$ Hz), 35.87, 20.98, 16.59 (d, $J = 6.0$ Hz), 16.46 (dd, $J = 6.0$ Hz). ^{11}B NMR (193 MHz, CDCl_3) δ -28.57 (t, $J = 88.2$ Hz). $^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3) δ -28.57. $^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3) δ 7.07 (d, $J = 7.8$ Hz, 2H), 6.98 (d, $J = 7.7$ Hz, 2H), 6.66 (s, 2H), 4.03 (p, $J = 7.1$ Hz, 2H), 3.91 – 3.84 (m, 2H), 3.58 (s, 6H), 3.10 (td, $J = 14.4, 4.0$ Hz, 1H), 2.56 (dd, $J = 22.3, 12.5$ Hz, 1H), 2.26 (s, 3H), 1.64 – 1.34 (m, 2H), 1.30 (dd, $J = 17.6, 6.7$ Hz, 1H), 1.23 (t, $J = 7.0$ Hz, 3H), 1.15 (t, $J = 7.1$ Hz, 3H). ^{31}P NMR (243 MHz, CDCl_3) δ 44.29.

HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{18}\text{H}_{30}\text{BN}_2\text{NaO}_3\text{P}$ 387,1979; found: 387.1967.

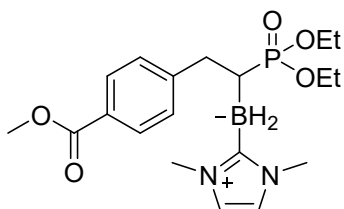


(1-(diethoxyphosphoryl)-2-(4-fluorophenyl)ethyl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)dihydroborate (**3af**): Colorless liquid (46 mg, 63% yield); Gradient eluent: Dichloromethane/ methanol: 40/1 to 20/1; ^1H NMR (600 MHz, CDCl_3) δ 7.17 – 7.13 (m, 2H), 6.86 (t, $J = 8.3$ Hz, 2H), 6.69 (s, 2H), 4.04 – 3.99 (m, 2H), 3.89 – 3.82 (m, 2H), 3.59 (s, 6H), 3.08 (t, $J = 13.0$ Hz, 1H), 2.58 (dd, $J = 22.4, 12.7$ Hz, 1H), 1.84 – 1.36 (m, 2H), 1.22 (t, $J = 7.1$ Hz, 4H), 1.14 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 160.85 (d, $J = 241.6$ Hz), 139.74 (d, $J = 15.1$ Hz), 130.26 (d, $J = 7.6$ Hz), 120.17, 114.22 (d, $J = 21.1$ Hz), 61.02 (d, $J = 7.6$ Hz), 60.00 (d, $J = 6.0$ Hz), 35.90 (d, $J = 4.5$ Hz), 35.86, 16.58 (d, $J = 6.0$ Hz), 16.45 (d, $J = 6.0$ Hz). ^{11}B NMR (193 MHz, CDCl_3) δ -28.65 (t, $J = 87.8$ Hz). $^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3) δ -28.65. $^1\text{H}\{^{11}\text{B}\}$ (600 MHz, CDCl_3) δ 7.15 (dd, $J = 8.3, 5.7$ Hz, 2H), 6.86 (t, $J = 8.7$ Hz, 2H), 6.69 (s, 2H), 4.01 (p, $J = 7.0$ Hz, 2H), 3.89 – 3.82 (m, 2H), 3.59 (s, 6H), 3.08 (t, $J = 13.7$ Hz, 1H), 2.58 (dd, $J = 22.3, 12.8$ Hz, 1H), 1.83 – 1.32 (m, 2H), 1.22 (t, $J = 7.1$ Hz, 4H), 1.14 (t, $J = 7.1$ Hz, 3H). ^{19}F NMR (565 MHz, CDCl_3) δ -119.00. ^{31}P NMR (243 MHz, CDCl_3) δ 43.78.

HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{17}\text{H}_{27}\text{BFN}_2\text{NaO}_3\text{P}$ 391.1729; found: 391.1732.

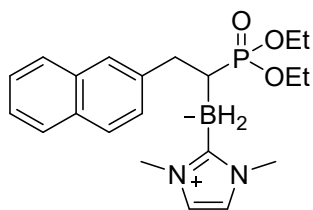


(2-(4-chlorophenyl)-1-(diethoxyphosphoryl)ethyl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)dihydroborate (**3ag**): Colorless liquid (46.4 mg, 60% yield); Gradient eluent: Dichloromethane/ methanol: 40/1 to 20/1; ^1H NMR (600 MHz, CDCl_3) δ 7.15 – 7.11 (m, 4H), 6.69 (s, 2H), 4.01 (p, $J = 7.1$ Hz, 2H), 3.88 – 3.81 (m, 2H), 3.59 (s, 6H), 3.07 (td, $J = 14.4, 3.4$ Hz, 1H), 2.57 (dd, $J = 22.3, 12.9$ Hz, 1H), 1.84 – 1.31 (m, 2H), 1.26 – 1.19 (m, 4H), 1.13 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 142.65 (d, $J = 16.6$ Hz), 130.61, 130.38, 127.64, 120.18, 61.01 (d, $J = 6.0$ Hz), 60.02 (d, $J = 6.0$ Hz), 36.11 (d, $J = 4.5$ Hz), 35.88, 16.58 (d, $J = 6.0$ Hz), 16.45 (d, $J = 7.6$ Hz). ^{11}B NMR (193 MHz, CDCl_3) δ -28.63 (t, $J = 88.8$ Hz). $^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3) δ -28.62. $^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3) δ 7.18 – 7.14 (m, 4H), 6.72 (s, 2H), 4.04 (p, $J = 7.1$ Hz, 2H), 3.91 – 3.85 (m, 2H), 3.62 (s, 6H), 3.10 (td, $J = 14.4, 4.4$ Hz, 1H), 2.60 (td, $J = 13.0, 9.3$ Hz, 1H), 1.44 (dd, $J = 81.7, 62.9$ Hz, 2H), 1.24 (t, $J = 7.1$ Hz, 4H), 1.16 (t, $J = 7.1$ Hz, 3H). ^{31}P NMR (243 MHz, CDCl_3) δ 43.63. HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{17}\text{H}_{27}\text{BClN}_2\text{NaO}_3\text{P}$ 407.1433; found:407.1429.



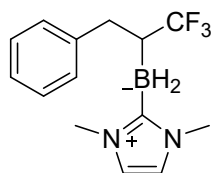
(1-(diethoxyphosphoryl)-2-(4-(methoxycarbonyl)phenyl)ethyl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)dihydroborate (**3ah**): Colorless liquid (36 mg, 44% yield); Gradient eluent: Dichloromethane/ methanol: 40/1 to 20/1; ^1H NMR (600 MHz, CDCl_3) δ 7.87 (d, $J = 8.0$ Hz, 2H), 7.28 (d, $J = 8.0$ Hz, 2H), 6.69 (s, 2H), 4.03 (p, $J = 7.0$ Hz, 2H), 3.89 – 3.84 (m, 5H), 3.59 (s, 6H), 3.16 (t, $J = 13.9$ Hz, 1H), 2.67 (dd, $J = 22.3, 12.6$ Hz, 1H), 1.32 – 1.28 (m, 1H), 1.23 (t, $J = 7.0$ Hz, 3H), 1.14 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 167.41, 150.04 (d, $J = 16.6$ Hz), 129.05, 127.02, 120.20, 61.08 (d, $J = 6.0$ Hz), 60.09 (d, $J = 7.6$ Hz), 51.88, 36.87 (d, $J = 4.5$ Hz), 35.89, 16.59 (d, $J = 6.0$ Hz), 16.46 (d, $J = 6.0$ Hz). ^{11}B NMR (193 MHz, CDCl_3) δ -28.62 (t, $J = 88.8$ Hz). $^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3) δ -28.62. $^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3) δ 7.87 (d, $J = 8.1$ Hz, 2H), 7.28 (d, $J = 8.1$ Hz, 2H), 6.69 (s, 2H), 4.03 (p, $J = 7.1$ Hz, 2H), 3.90 – 3.84 (m, 5H), 3.60 (s, 6H), 3.17 (td, $J = 14.3, 4.1$ Hz, 1H), 2.67 (td, $J = 12.8, 9.7$ Hz, 1H), 1.62 – 1.35 (m, 2H), 1.31 – 1.27 (m, 1H), 1.23 (d, $J = 7.1$ Hz, 3H), 1.15 (t, $J = 7.1$ Hz, 3H). ^{31}P NMR (243 MHz, CDCl_3) δ 43.39.

Characterization agrees with previous reports for this compound.¹⁰



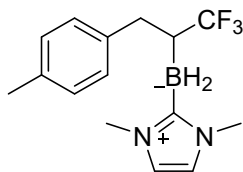
(1-(diethoxyphosphoryl)-2-(naphthalen-2-yl)ethyl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)dihydroborate (**3ai**): Colorless liquid (26 mg, 33% yield); Gradient eluent: Dichloromethane/ methanol: 40/1 to 20/1; ^1H NMR (600 MHz, CDCl_3) δ 7.74 (dd, $J = 15.8, 8.0$ Hz, 2H), 7.68 (d, $J = 8.4$ Hz, 1H), 7.63 (s, 1H), 7.42 – 7.34 (m, 3H), 6.61 (s, 2H), 4.09 (p, $J = 7.1$ Hz, 2H), 3.96 – 3.89 (m, 2H), 3.56 (s, 6H), 3.32 (t, $J = 14.2$ Hz, 1H), 2.79 (dd, $J = 23.0, 11.1$ Hz, 1H), 1.43 (d, $J = 23.3$ Hz, 1H), 1.26 (t, $J = 7.1$ Hz, 3H), 1.18 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 141.69, 141.58, 133.48, 131.76, 128.03, 127.45, 127.01, 126.91, 125.48, 124.65, 120.08, 61.09 (d, $J = 6.0$ Hz), 60.07 (d, $J = 6.0$ Hz), 36.87 (d, $J = 4.5$ Hz), 35.87, 16.64 (d, $J = 6.0$ Hz), 16.50 (d, $J = 6.0$ Hz). ^{11}B NMR (193 MHz, CDCl_3) δ -28.57 (t, $J = 88.8$ Hz). $^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3) δ -28.59. $^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3) δ 7.74 (dd, $J = 15.6, 8.0$ Hz, 2H), 7.68 (d, $J = 8.4$ Hz, 1H), 7.63 (s, 1H), 7.41 – 7.35 (m, 3H), 6.61 (s, 2H), 4.09 (p, $J = 7.1$ Hz, 2H), 3.93 (qd, $J = 7.2, 2.8$ Hz, 2H), 3.56 (s, 6H), 3.33 (td, $J = 14.3, 3.8$ Hz, 1H), 2.82 – 2.75 (m, 1H), 1.46 – 1.42 (m, 1H), 1.26 (t, $J = 7.1$ Hz, 3H), 1.18 (t, $J = 7.1$ Hz, 3H). ^{31}P NMR (243 MHz, CDCl_3) δ 43.92.

Characterization agrees with previous reports for this compound.¹⁰



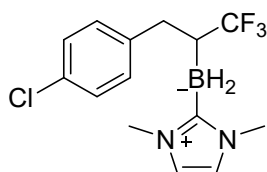
(1,3-dimethyl-1H-imidazol-3-ium-2-yl)(1,1,1-trifluoro-3-phenylpropan-2-yl)dihydroborate (**3aj**): Colorless liquid (32 mg, 57% yield); Gradient eluent: EtOAc/petroleum ether: 1/4 to 1/2; ^1H NMR (600 MHz, CDCl_3) δ 7.22 (d, $J = 4.4$ Hz, 4H), 7.14 – 7.10 (m, 1H), 6.71 (s, 2H), 3.58 (s, 6H), 3.02 (d, $J = 12.9$ Hz, 1H), 2.62 (t, $J = 11.1$ Hz, 1H), 1.64 (s, 1H), 1.64 – 1.32 (m, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 143.45, 133.79 (q, $J = 279.3$ Hz), 129.04, 127.79, 125.20, 120.26, 36.66 (q, $J = 4.0$ Hz), 35.67. ^{11}B NMR (193 MHz, CDCl_3) δ -28.70 (t, $J = 87.6$ Hz). $^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3) δ -28.71. $^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3) δ 7.22 (d, $J = 4.3$ Hz, 4H), 7.14 – 7.10 (m, 1H), 6.71 (s, 2H), 3.58 (s, 6H), 3.02 (dd, $J = 13.4, 4.6$ Hz, 1H), 2.62 (dd, $J = 13.4, 8.7$ Hz, 1H), 1.67 – 1.61 (m, 1H), 1.42 (d, $J = 94.0$ Hz, 2H). ^{19}F NMR (565 MHz, CDCl_3) δ -64.82.

Characterization agrees with previous reports for this compound.¹⁰



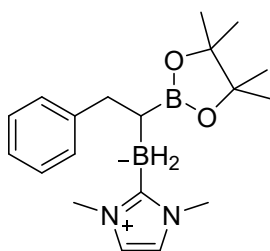
(1,3-dimethyl-1H-imidazol-3-ium-2-yl)(1,1,1-trifluoro-3-(p-tolyl)propan-2-yl)dihydroborate (**3ak**): Colorless liquid (45 mg, 76% yield); Gradient eluent: EtOAc/petroleum ether: 1/4 to 1/2; ^1H NMR (600 MHz, CDCl_3) δ 7.12 (d, $J = 7.9$ Hz, 2H), 7.04 (d, $J = 7.9$ Hz, 2H), 6.72 (s, 2H), 3.60 (s, 6H), 2.98 (d, $J = 12.8$ Hz, 1H), 2.60 (dd, $J = 12.9, 8.7$ Hz, 1H), 2.30 (s, 3H), 1.63 (s, 1H), 1.58 – 1.27 (m, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 140.34, 132.93 (q, $J = 279.3$ Hz), 134.46, 128.87, 128.49, 120.24, 36.22 (q, $J = 4.0$ Hz), 35.70, 21.02. $^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3) δ -28.63. $^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3) δ 7.11 (d, $J = 7.4$ Hz, 2H), 7.04 (d, $J = 7.4$ Hz, 2H), 6.72 (s, 2H), 3.60 (s, 6H), 2.98 (dd, $J = 13.5, 4.5$ Hz, 1H), 2.59 (dd, $J = 13.4, 8.5$ Hz, 1H), 2.30 (s, 3H), 1.63 (dd, $J = 11.6, 4.2$ Hz, 1H), 1.42 (d, $J = 93.3$ Hz, 2H). ^{19}F NMR (565 MHz, CDCl_3) δ -64.71.

HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{15}\text{H}_{20}\text{BF}_3\text{N}_2\text{Na}$ 319.1564; found: 319.1560.



(3-(4-chlorophenyl)-1,1,1-trifluoropropan-2-yl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)dihydroborate (**3al**): ^1H NMR (600 MHz, CDCl_3) δ 7.18 (q, $J = 8.4$ Hz, 4H), 6.74 (s, 2H), 3.59 (s, 6H), 2.96 (d, $J = 12.8$ Hz, 1H), 2.59 (dd, $J = 12.8, 8.8$ Hz, 1H), 1.56 (s, 1H), 1.47 – 1.26 (m, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 141.97, 133.02 (q, $J = 277.84$ Hz), 130.79, 130.49, 127.81, 120.33, 36.05 (q, $J = 4.0$ Hz), 35.69. ^{11}B NMR (193 MHz, CDCl_3) δ -28.78 (t, $J = 87.6$ Hz). $^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3) δ -28.79. $^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3) δ 7.18 (q, $J = 8.5$ Hz, 4H), 6.74 (s, 2H), 3.60 (s, 6H), 2.96 (dd, $J = 13.4, 4.7$ Hz, 1H), 2.59 (dd, $J = 13.4, 8.6$ Hz, 1H), 1.57 (dtd, $J = 16.1, 8.2, 4.2$ Hz, 1H), 1.38 (d, $J = 107.7$ Hz, 2H). ^{19}F NMR (565 MHz, CDCl_3) δ -64.77.

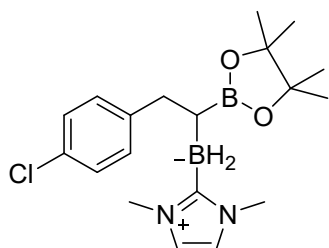
Characterization agrees with previous reports for this compound.¹⁰



(1,3-dimethyl-1H-imidazol-3-ium-2-yl)(2-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)dihydroborate (**3am**): Colorless liquid (39 mg, 57% yield); Gradient eluent: Dichloromethane; ^1H NMR (600 MHz, CDCl_3) δ 7.13 (dt, $J = 15.1, 7.5$

Hz, 4H), 7.00 (t, $J = 7.1$ Hz, 1H), 6.72 (s, 2H), 3.74 (s, 6H), 2.86 (dd, $J = 14.1, 10.9$ Hz, 1H), 2.38 (dd, $J = 14.0, 5.4$ Hz, 1H), 1.87 – 1.46 (m, 2H), 1.14 (s, 6H), 1.08 (s, 6H), 0.60 (s, 1H). ^{13}C NMR (151 MHz, CDCl_3) δ 147.58, 128.20, 127.55, 124.36, 120.07, 81.47, 39.13, 36.14, 24.94, 24.49. ^{11}B NMR (193 MHz, CDCl_3) δ 36.12, -26.65 (t, $J = 86.7$ Hz). $^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3) δ -26.65. $^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3) δ 7.13 (dt, $J = 15.1, 7.5$ Hz, 4H), 6.99 (t, $J = 7.1$ Hz, 1H), 6.71 (s, 2H), 3.73 (s, 6H), 2.85 (dd, $J = 14.1, 10.7$ Hz, 1H), 2.38 (dd, $J = 14.1, 5.5$ Hz, 1H), 1.52 (d, $J = 14.1$ Hz, 2H), 1.14 (s, 6H), 1.08 (s, 6H), 0.60 (td, $J = 10.8, 5.3$ Hz, 1H).

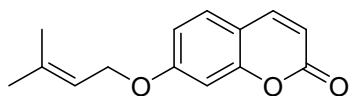
Characterization agrees with previous reports for this compound.¹⁰



(2-(4-chlorophenyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)(1,3-dimethyl-1H-imidazol-3-ium-2-yl)dihydroborate (**3an**): Colorless liquid (50.4 mg, 67% yield); Gradient eluent: Dichloromethane; ^1H NMR (600 MHz, CDCl_3) δ 7.07 (s, 4H), 6.73 (s, 2H), 3.73 (s, 6H), 2.79 (dd, $J = 13.7, 11.0$ Hz, 1H), 2.34 (dd, $J = 14.1, 5.3$ Hz, 1H), 1.78 – 1.31 (m, 2H), 1.12 (s, 6H), 1.05 (s, 6H), 0.53 (s, 1H). ^{13}C NMR (151 MHz, CDCl_3) δ 146.18, 129.82, 129.60, 127.51, 120.13, 81.53, 38.57, 36.15, 24.96, 24.47. ^{11}B NMR (193 MHz, CDCl_3) δ 35.60, -26.68 (t, $J = 86.7$ Hz). $^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3) δ -26.68. $^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3) δ 7.06 (s, 4H), 6.72 (s, 2H), 3.71 (s, 6H), 2.78 (t, $J = 12.6$ Hz, 1H), 2.33 (dd, $J = 13.6, 5.4$ Hz, 1H), 1.48 (d, $J = 20.0$ Hz, 2H), 1.10 (s, 6H), 1.04 (s, 6H), 0.51 (s, 1H).

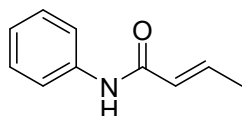
HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{19}\text{H}_{29}\text{BClN}_2\text{NaO}_3$ 397.2001; found: 397.2000.

6.Characterization data of starting materials

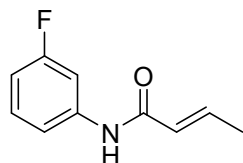


7-((3-methylbut-2-en-1-yl)oxy)-2H-chromen-2-one (**1n**): White solid (503 mg, 75% yield); Gradient eluent: EtOAc/petroleum ether: 1/3 to 1/2; ^1H NMR (600 MHz, CDCl_3) δ 7.62 (d, $J = 9.5$ Hz, 1H), 7.35 (d, $J = 8.6$ Hz, 1H), 6.84 (dd, $J = 8.6, 2.2$ Hz, 1H), 6.81 (s, 1H), 6.23 (d, $J = 9.4$ Hz, 1H), 5.46 (t, $J = 6.7$ Hz, 1H), 4.57 (d, $J = 6.7$ Hz, 2H), 1.80 (s, 3H), 1.76 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 162.14, 161.30, 155.88, 143.47, 139.30, 128.71, 118.64, 113.22, 112.97, 112.44, 101.57, 65.44, 25.83, 18.30.

Characterization agrees with previous reports for this compound.²

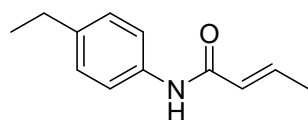


(*E*)-*N*-phenylbut-2-enamide (**1q**): White solid (338 mg, 70% yield); Gradient eluent: EtOAc/petroleum ether: 1/5 to 1/4; ¹H NMR (600 MHz, CDCl₃) δ 8.12 (s, 1H), 7.59 (d, *J* = 7.3 Hz, 2H), 7.28 (t, *J* = 7.9 Hz, 2H), 7.08 (t, *J* = 7.3 Hz, 1H), 6.95 (dq, *J* = 13.8, 6.9 Hz, 1H), 6.02 (dd, *J* = 15.1, 1.6 Hz, 1H), 1.83 (dd, *J* = 6.9, 1.6 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 164.59, 141.34, 138.23, 128.92, 125.66, 124.23, 120.26, 17.82. Characterization agrees with previous reports for this compound.¹¹



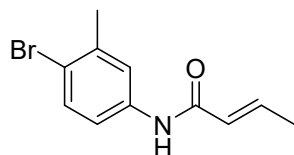
(*E*)-*N*-(3-fluorophenyl)but-2-enamide (**1r**): White solid (430 mg, 80% yield); Gradient eluent: EtOAc/petroleum ether: 1/5 to 1/4; ¹H NMR (600 MHz, CDCl₃) δ 8.04 (s, 1H), 7.53 (d, *J* = 10.0 Hz, 1H), 7.22 (s, 2H), 6.97 (dd, *J* = 13.9, 6.6 Hz, 1H), 6.78 (s, 1H), 5.99 (d, *J* = 15.1 Hz, 1H), 1.86 (d, *J* = 4.4 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 164.57, 162.95 (d, *J* = 244.6 Hz), 142.22, 139.69 (d, *J* = 10.6 Hz), 130.00 (d, *J* = 9.1 Hz), 125.22, 115.43, 110.93 (d, *J* = 21.1 Hz), 107.61 (d, *J* = 28.7 Hz), 17.85. ¹⁹F NMR (565 MHz, CDCl₃) δ -111.53.

HRMS (ESI-TOF) *m/z*: [M + Na]⁺ cacl. for C₁₀H₁₀FN₂NaO 202.0639; found: 202.0635.

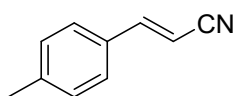


(*E*)-*N*-(4-ethylphenyl)but-2-enamide (**1s**): White solid (454 mg, 80% yield); Gradient eluent: EtOAc/petroleum ether: 1/5 to 1/4; ¹H NMR (600 MHz, CDCl₃) δ 8.15 (s, 1H), 7.50 (d, *J* = 7.8 Hz, 2H), 7.10 (d, *J* = 8.2 Hz, 2H), 6.94 (dq, *J* = 13.8, 6.8 Hz, 1H), 6.02 (dd, *J* = 15.1, 1.6 Hz, 1H), 2.59 (q, *J* = 7.6 Hz, 2H), 1.83 (dd, *J* = 6.9, 1.6 Hz, 3H), 1.20 (t, *J* = 7.6 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 164.50, 140.92, 140.23, 135.89, 128.21, 125.78, 120.40, 28.33, 17.79, 15.66.

HRMS (ESI-TOF) *m/z*: [M + Na]⁺ cacl. for C₁₂H₁₅NNaO 212.1046; found: 212.1043.

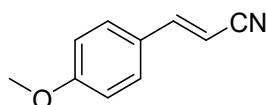


(*E*)-*N*-(4-bromo-3-methylphenyl)but-2-enamide (**1t**): White solid (607 mg, 80% yield); Gradient eluent: EtOAc/petroleum ether: 1/5 to 1/4; ¹H NMR (600 MHz, CDCl₃) δ 7.72 (s, 1H), 7.48 (s, 1H), 7.40 (d, *J* = 8.6 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 1H), 6.96 (dq, *J* = 13.8, 6.9 Hz, 1H), 5.95 (dd, *J* = 15.1, 1.6 Hz, 1H). ¹³C NMR (151 MHz, CDCl₃) δ 164.29, 141.91, 138.49, 137.26, 132.56, 125.29, 122.32, 119.46, 119.10, 23.01, 17.88. HRMS (ESI-TOF) *m/z*: [M + Na]⁺ cacl. for C₁₁H₁₂BrNNaO 275.9994; found: 275.9994.



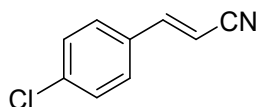
(*E*)-3-(*p*-tolyl)acrylonitrile (**1w**): White solid (146 mg, 34% yield); Gradient eluent: EtOAc/petroleum ether: 1/20 to 1/15; ^1H NMR (600 MHz, CDCl_3) δ 7.37 (d, $J = 17.4$ Hz, 1H), 7.35 (d, $J = 8.4$ Hz, 2H), 7.21 (d, $J = 8.0$ Hz, 2H), 5.82 (d, $J = 16.6$ Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 150.55, 141.86, 130.90, 129.85, 127.36, 118.45, 95.09, 21.53.

Characterization agrees with previous reports for this compound.¹²



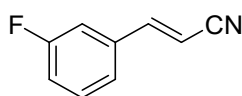
(*E*)-3-(*p*-tolyl)acrylonitrile (**1x**): White solid (143 mg, 30% yield); Gradient eluent: EtOAc/petroleum ether: 1/20 to 1/15; ^1H NMR (600 MHz, CDCl_3) δ 7.40 – 7.36 (m, 2H), 7.31 (d, $J = 16.6$ Hz, 1H), 6.94 – 6.86 (m, 2H), 5.70 (d, $J = 16.6$ Hz, 1H), 3.83 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 162.08, 150.05, 129.13, 126.36, 118.77, 114.55, 93.34, 55.48.

Characterization agrees with previous reports for this compound.¹²



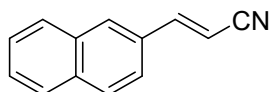
(*E*)-3-(4-chlorophenyl)acrylonitrile (**1y**): White solid (196 mg, 40% yield); Gradient eluent: EtOAc/petroleum ether: 1/20 to 1/15; ^1H NMR (600 MHz, CDCl_3) δ 7.39 (s, 4H), 7.35 (d, $J = 16.6$ Hz, 1H), 5.86 (d, $J = 16.6$ Hz, 1H). ^{13}C NMR (151 MHz, CDCl_3) δ 149.14, 137.32, 132.00, 129.47, 128.56, 117.84, 97.03.

Characterization agrees with previous reports for this compound.¹²



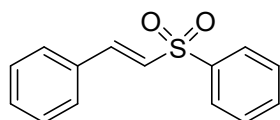
(*E*)-3-(3-fluorophenyl)acrylonitrile (**1z**): White solid (198 mg, 45% yield); Gradient eluent: EtOAc/petroleum ether: 1/20 to 1/15; ^1H NMR (600 MHz, CDCl_3) δ 7.39 (q, $J = 7.2$ Hz, 1H), 7.37 (d, $J = 16.8$ Hz, 1H), 7.23 (d, $J = 7.7$ Hz, 1H), 7.14 (t, $J = 8.7$ Hz, 2H), 5.89 (d, $J = 16.6$ Hz, 1H). ^{13}C NMR (151 MHz, CDCl_3) δ 149.20 (d, $J = 3.0$ Hz), 135.62 (d, $J = 7.6$ Hz), 130.81 (d, $J = 9.1$ Hz), 123.43 (d, $J = 3.0$ Hz), 118.17 (d, $J = 21.1$ Hz), 117.61, 113.82, 113.67, 97.99.

Characterization agrees with previous reports for this compound.¹²



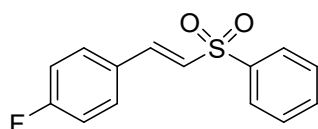
(*E*)-3-(naphthalen-2-yl)acrylonitrile (**1aa**): White solid (525 mg, 69% yield); Gradient eluent: EtOAc/petroleum ether: 1/20 to 1/15; ^1H NMR (600 MHz, CDCl_3) δ 7.86 – 7.81 (m, 4H), 7.56 – 7.51 (m, 4H), 5.96 (d, $J = 16.6$ Hz, 1H). ^{13}C NMR (151 MHz, CDCl_3) δ 150.61, 134.55, 133.10, 131.00, 129.71, 129.10, 128.74, 127.87, 127.13, 127.13, 122.22, 118.35, 96.32.

Characterization agrees with previous reports for this compound.¹²



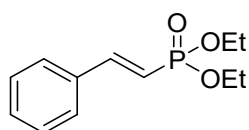
(*E*)-2-(phenylsulfonyl)vinylbenzene (**1ab**): White solid (190 mg, 26% yield); Gradient eluent: EtOAc/petroleum ether: 1/20 to 1/10; ^1H NMR (600 MHz, CDCl_3) δ 7.95 (dd, $J = 8.4, 1.2$ Hz, 2H), 7.69 (d, $J = 15.4$ Hz, 1H), 7.62 (t, $J = 7.4$ Hz, 1H), 7.55 (t, $J = 7.7$ Hz, 2H), 7.49 (dd, $J = 7.8, 1.5$ Hz, 2H), 7.43 – 7.37 (m, 3H), 6.86 (d, $J = 15.4$ Hz, 1H). ^{13}C NMR (151 MHz, CDCl_3) δ 142.53, 140.74, 133.41, 132.38, 131.25, 129.36, 129.12, 128.60, 127.68, 127.30.

Characterization agrees with previous reports for this compound.⁷



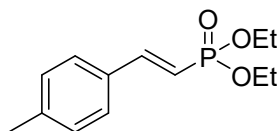
(*E*)-1-fluoro-4-(2-(phenylsulfonyl)vinyl)benzene (**1ac**): White solid (408 mg, 52% yield); Gradient eluent: EtOAc/petroleum ether: 1/20 to 1/10; ^1H NMR (600 MHz, CDCl_3) δ 7.95 (dd, $J = 8.4, 1.2$ Hz, 2H), 7.65 (d, $J = 15.3$ Hz, 1H), 7.62 (d, $J = 7.4$ Hz, 1H), 7.56 (t, $J = 7.7$ Hz, 2H), 7.48 (dd, $J = 8.7, 5.3$ Hz, 2H), 7.09 (t, $J = 8.6$ Hz, 2H), 6.79 (d, $J = 15.4$ Hz, 1H). ^{13}C NMR (151 MHz, CDCl_3) δ 141.18, 140.66, 133.46, 130.63 (d, $J = 9.1$ Hz), 129.39, 128.66, 127.68, 127.07, 116.44, 116.29.

Characterization agrees with previous reports for this compound.⁷



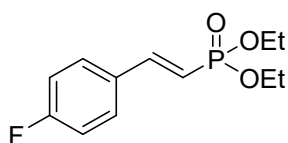
diethyl (*E*)-styrylphosphonate (**1ad**): Yellow oil (144 mg, 60% yield); Gradient eluent: EtOAc/petroleum ether: 1/4 to 1/2; ^1H NMR (600 MHz, CDCl_3) δ 7.55 – 7.46 (m, 3H), 7.38 (dd, $J = 5.0, 1.9$ Hz, 3H), 6.25 (t, $J = 17.6$ Hz, 1H), 4.21 – 4.04 (m, 4H), 1.35 (t, $J = 7.1$ Hz, 6H). ^{13}C NMR (151 MHz, CDCl_3) δ 148.78 (d, $J = 6.0$ Hz), 134.95 (d, $J = 22.7$ Hz), 130.25, 128.87, 127.72, 114.97 (d, $J = 191.8$ Hz), 61.86 (d, $J = 6.0$ Hz), 16.42 (d, $J = 6.0$ Hz). ^{31}P NMR (243 MHz, CDCl_3) δ 19.52.

Characterization agrees with previous reports for this compound.⁶



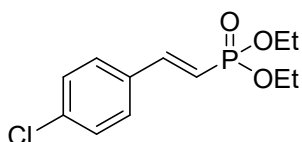
diethyl (*E*)-(4-methylstyryl)phosphonate (**1ae**): White solid (525 mg, 69% yield); Gradient eluent: EtOAc/petroleum ether: 1/4 to 1/2; ^1H NMR (600 MHz, CDCl_3) δ 7.44 (dd, $J = 22.5, 17.5$ Hz, 1H), 7.36 (d, $J = 7.9$ Hz, 2H), 7.15 (d, $J = 7.8$ Hz, 2H), 6.16 (t, $J = 17.7$ Hz, 1H), 4.19 – 4.01 (m, 4H), 2.33 (s, 3H), 1.31 (t, $J = 7.1$ Hz, 6H). ^{13}C NMR (151 MHz, CDCl_3) δ 148.80 (d, $J = 6.0$ Hz), 140.62, 132.13 (d, $J = 24.2$ Hz), 129.55, 127.69, 112.49 (d, $J = 193.3$ Hz), 61.79 (d, $J = 6.0$ Hz), 21.39, 16.38 (d, $J = 6.0$ Hz). ^{31}P NMR (243 MHz, CDCl_3) δ 20.01.

Characterization agrees with previous reports for this compound.⁶



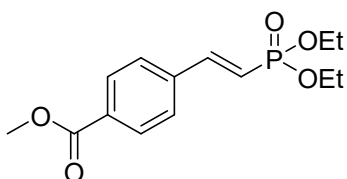
diethyl (*E*)-(3-fluorostyryl)phosphonate (**1af**): Yellow oil (215 mg, 83% yield); Gradient eluent: EtOAc/petroleum ether: 1/4 to 1/2; ^1H NMR (600 MHz, CDCl_3) δ 7.45 (ddd, $J = 28.2, 13.9, 9.9$ Hz, 3H), 7.05 (t, $J = 8.6$ Hz, 2H), 6.15 (t, $J = 17.3$ Hz, 1H), 4.16 – 4.07 (m, 4H), 1.33 (t, $J = 7.1$ Hz, 6H). ^{13}C NMR (151 MHz, CDCl_3) δ 163.85 (d, $J = 250.7$ Hz), 147.39 (d, $J = 6.0$ Hz), 131.12 (d, $J = 24.2$ Hz), 129.58 (d, $J = 7.6$ Hz), 115.97 (d, $J = 22.7$ Hz), 113.75 (d, $J = 194.8$ Hz), 61.87 (d, $J = 6.0$ Hz), 16.39 (d, $J = 7.6$ Hz). ^{31}P NMR (243 MHz, CDCl_3) δ 19.24. ^{19}F NMR (565 MHz, CDCl_3) δ -109.87.

Characterization agrees with previous reports for this compound.⁶



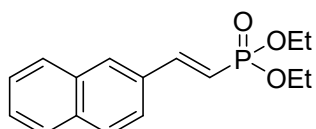
diethyl (*E*)-(4-chlorostyryl)phosphonate (**1ag**): White solid (493 mg, 60% yield); Gradient eluent: EtOAc/petroleum ether: 1/4 to 1/2; ^1H NMR (600 MHz, CDCl_3) δ 7.43 (d, $J = 17.7$ Hz, 1H), 7.39 (d, $J = 7.6$ Hz, 2H), 7.32 (d, $J = 6.9$ Hz, 2H), 6.20 (t, $J = 16.9$ Hz, 1H), 4.15 – 4.04 (m, 4H), 1.32 (t, $J = 7.1$ Hz, 6H). ^{13}C NMR (151 MHz, CDCl_3) δ 147.20 (d, $J = 7.6$ Hz), 136.11, 133.34 (d, $J = 24.2$ Hz), 129.10, 128.88, 115.41 (d, $J = 191.8$ Hz), 61.92 (d, $J = 4.5$ Hz), 16.39 (d, $J = 6.0$ Hz). ^{31}P NMR (243 MHz, CDCl_3) δ 18.91.

Characterization agrees with previous reports for this compound.⁶



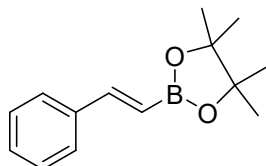
methyl (*E*)-4-(2-(diethoxyphosphoryl)vinyl)benzoate (**1ah**): White solid (626 mg, 70% yield); Gradient eluent: EtOAc/petroleum ether: 1/4 to 1/2; ^1H NMR (600 MHz, CDCl_3) δ 8.05 (d, $J = 8.2$ Hz, 2H), 7.56 (d, $J = 7.9$ Hz, 2H), 7.52 (q, $J = 3.3$ Hz, 1H), 6.37 (t, $J = 17.3$ Hz, 1H), 4.20 – 4.10 (m, 4H), 3.93 (s, 3H), 1.36 (t, $J = 7.1$ Hz, 6H). ^{13}C NMR (151 MHz, CDCl_3) δ 166.45, 147.21 (d, $J = 6.0$ Hz), 139.01 (d, $J = 24.2$ Hz), 131.39, 130.11, 127.59, 117.02 (d, $J = 190.3$ Hz), 62.03 (d, $J = 6.0$ Hz), 52.30, 16.43 (d, $J = 6.0$ Hz). ^{31}P NMR (243 MHz, CDCl_3) δ 18.34.

Characterization agrees with previous reports for this compound.⁶



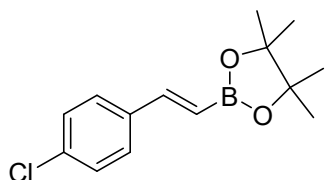
diethyl (*E*)-2-(naphthalen-2-yl)vinylphosphonate (**1ai**): White solid (470 mg, 54% yield); Gradient eluent: EtOAc/petroleum ether: 1/4 to 1/2; ^1H NMR (600 MHz, CDCl_3) δ 7.89 (s, 1H), 7.85 – 7.80 (m, 3H), 7.70 – 7.62 (m, 2H), 7.52 – 7.47 (m, 2H), 6.36 (t, $J = 17.5$ Hz, 1H), 4.21 – 4.10 (m, 4H), 1.37 (t, $J = 7.1$ Hz, 6H). ^{13}C NMR (151 MHz, CDCl_3) δ 148.79 (d, $J = 7.6$ Hz), 134.21, 133.24, 132.31 (d, $J = 24.2$ Hz), 129.48, 128.68, 128.60, 127.78, 127.23, 126.74, 123.21, 114.05 (d, $J = 191.8$ Hz), 61.93 (d, $J = 6.0$ Hz), 16.45 (d, $J = 7.6$ Hz). ^{31}P NMR (243 MHz, CDCl_3) δ 19.63.

Characterization agrees with previous reports for this compound.⁶



(*E*)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane (**1am**): White solid (130 mg, 25% yield); Gradient eluent: EtOAc/petroleum ether: 1/50 to 1/25; ^1H NMR (600 MHz, CDCl_3) δ 7.50 (d, $J = 7.3$ Hz, 2H), 7.41 (d, $J = 18.4$ Hz, 1H), 7.34 (t, $J = 7.4$ Hz, 2H), 7.29 (t, $J = 7.3$ Hz, 1H), 6.18 (d, $J = 18.4$ Hz, 1H), 1.32 (s, 12H). ^{13}C NMR (151 MHz, CDCl_3) δ 149.54, 137.50, 128.92, 128.59, 127.08, 83.37, 24.84. ^{11}B NMR (193 MHz, CDCl_3) δ 30.05.

Characterization agrees with previous reports for this compound.⁸



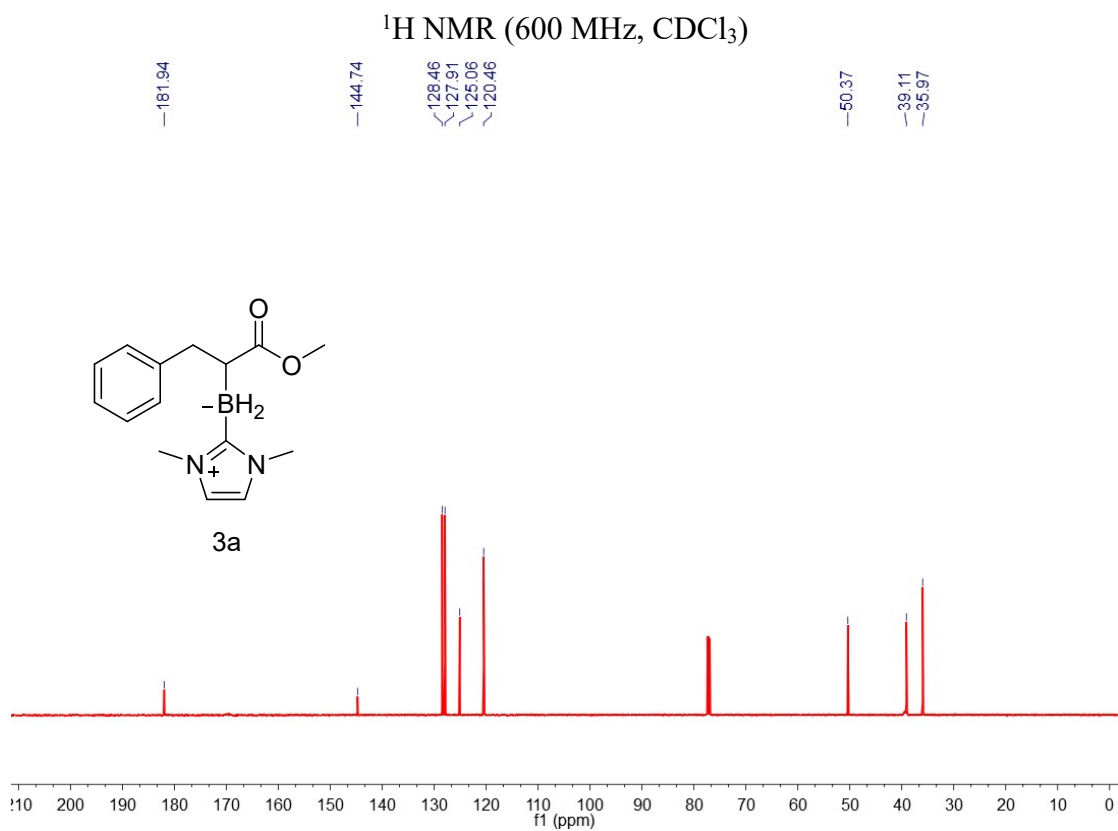
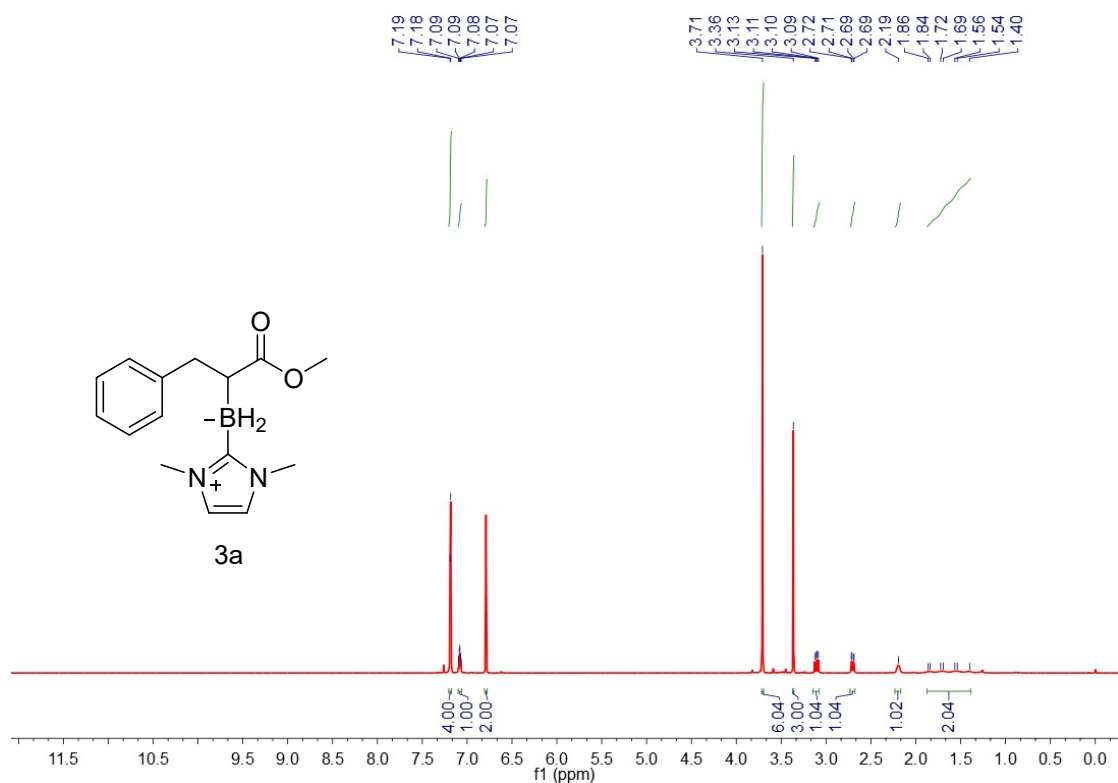
(*E*)-2-(4-chlorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1an**): White solid (182 mg, 23% yield); Gradient eluent: EtOAc/petroleum ether: 1/50 to 1/25; ^1H NMR (600 MHz, CDCl_3) δ 7.41 (d, $J = 8.5$ Hz, 2H), 7.33 (d, $J = 18.4$ Hz, 1H), 7.30 (d, $J = 8.5$ Hz, 2H), 6.13 (d, $J = 18.4$ Hz, 1H), 1.31 (s, 12H). ^{13}C NMR (151 MHz, CDCl_3) δ 152.69,

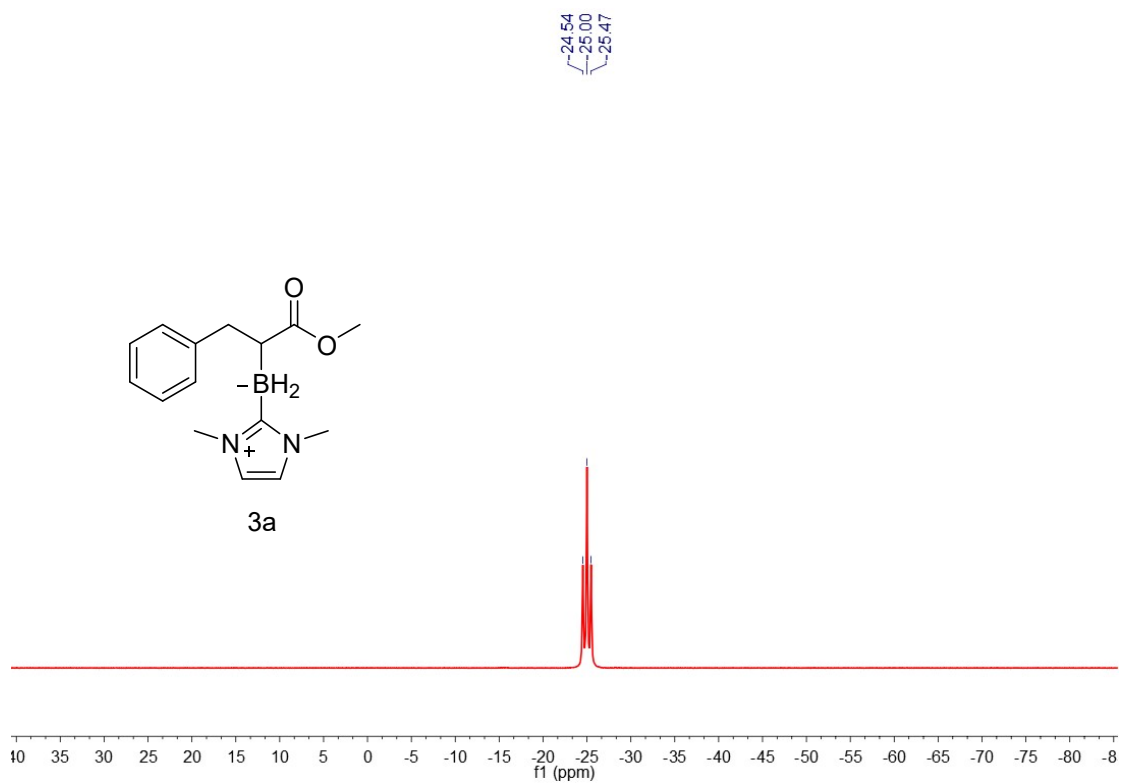
148.04, 144.59, 128.81, 128.24, 83.48, 24.82. ^{11}B NMR (193 MHz, CDCl_3) δ 30.31.
Characterization agrees with previous reports for this compound.⁸

6. References:

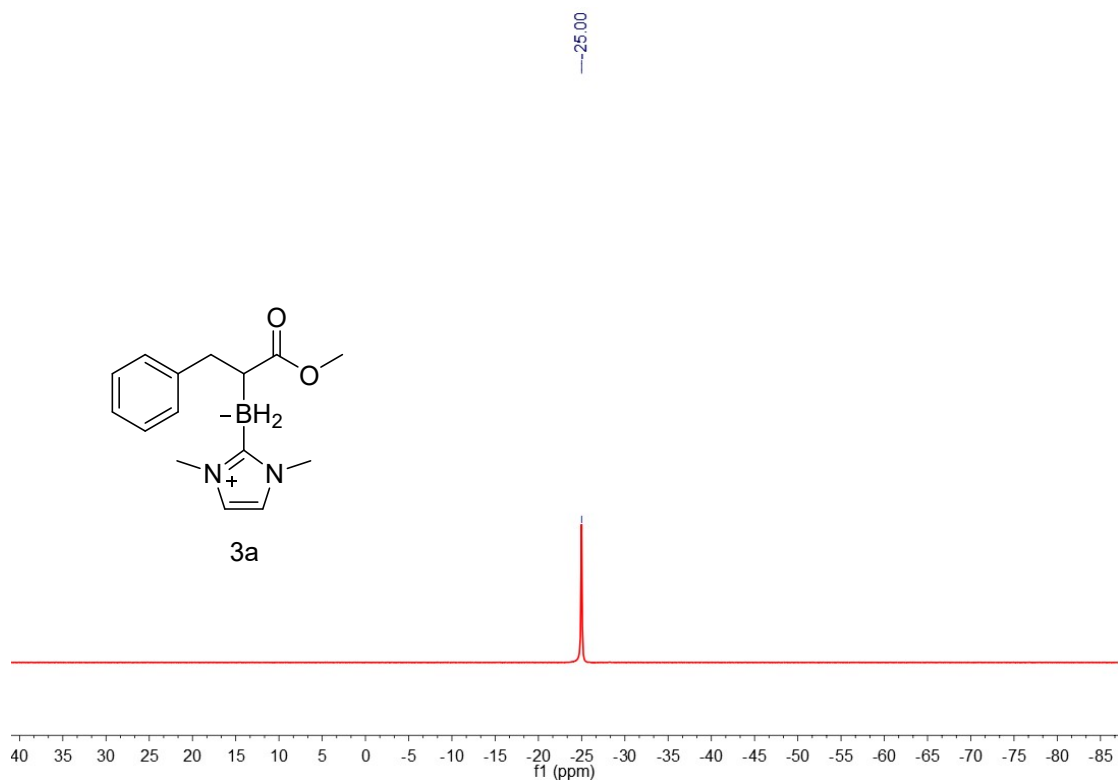
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7. NMR Spectra

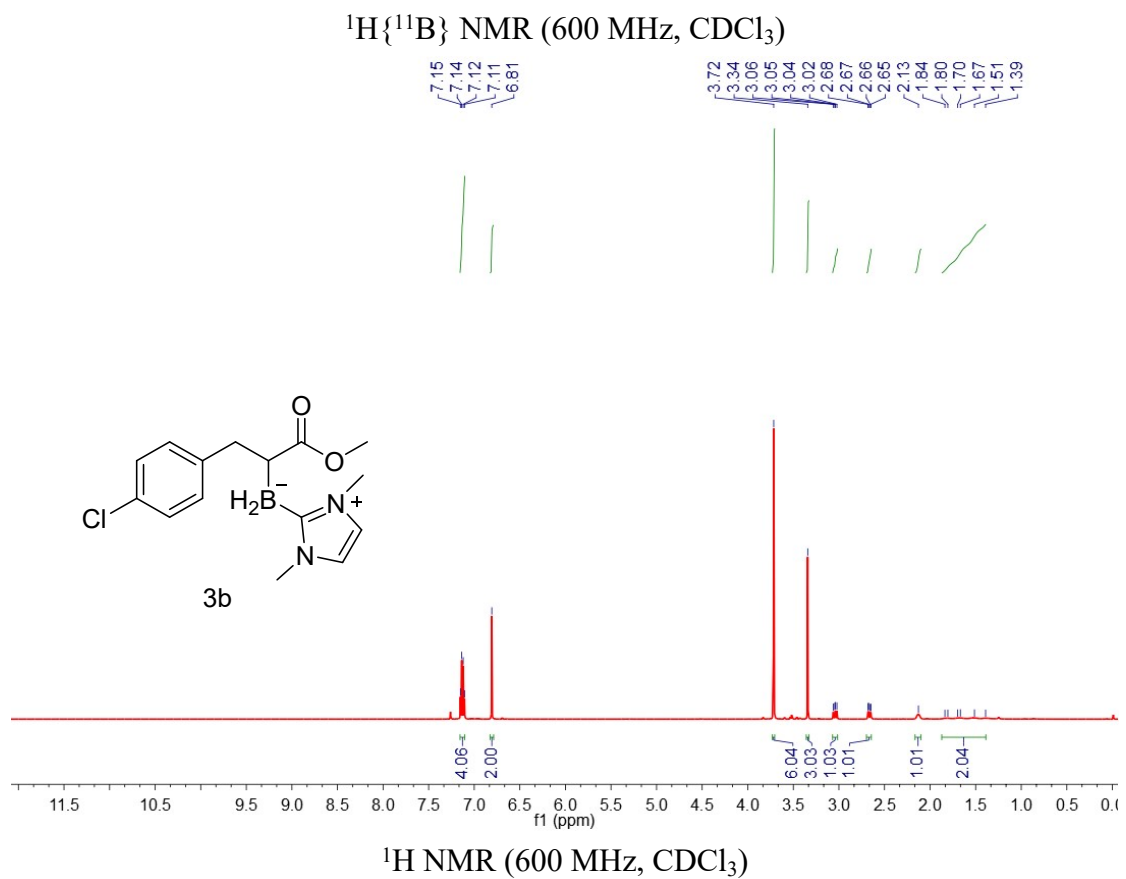
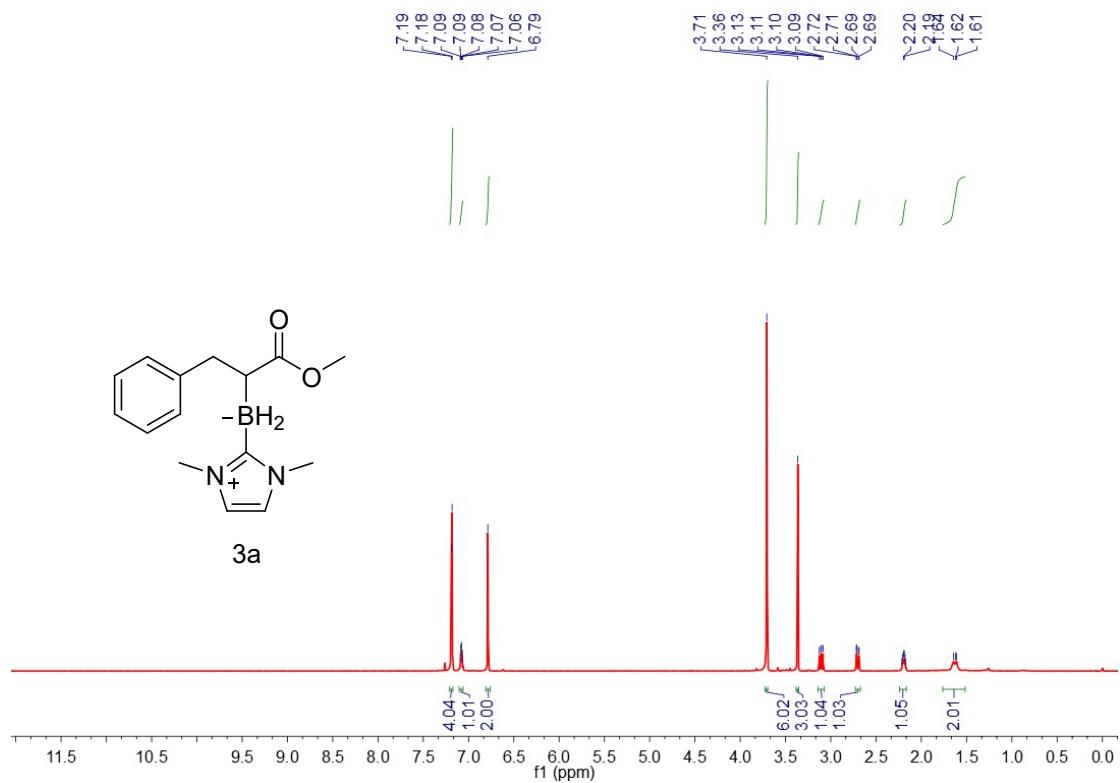


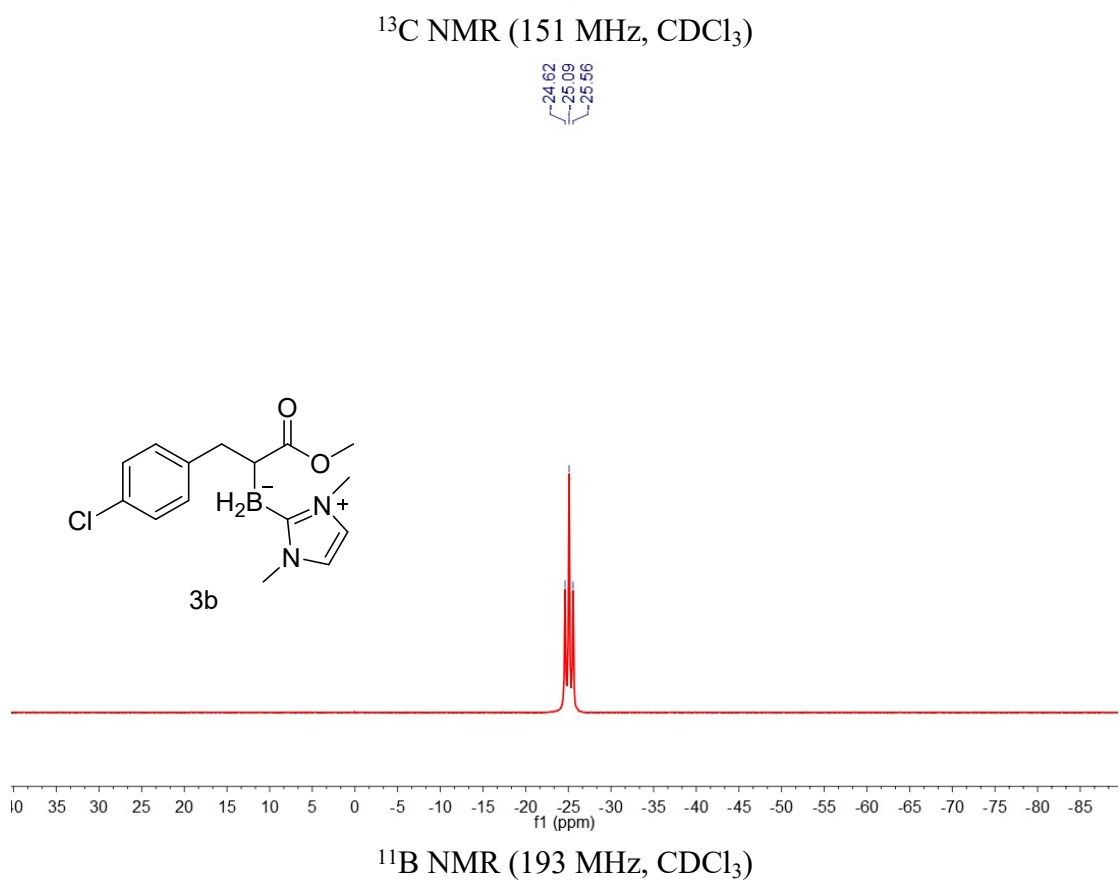
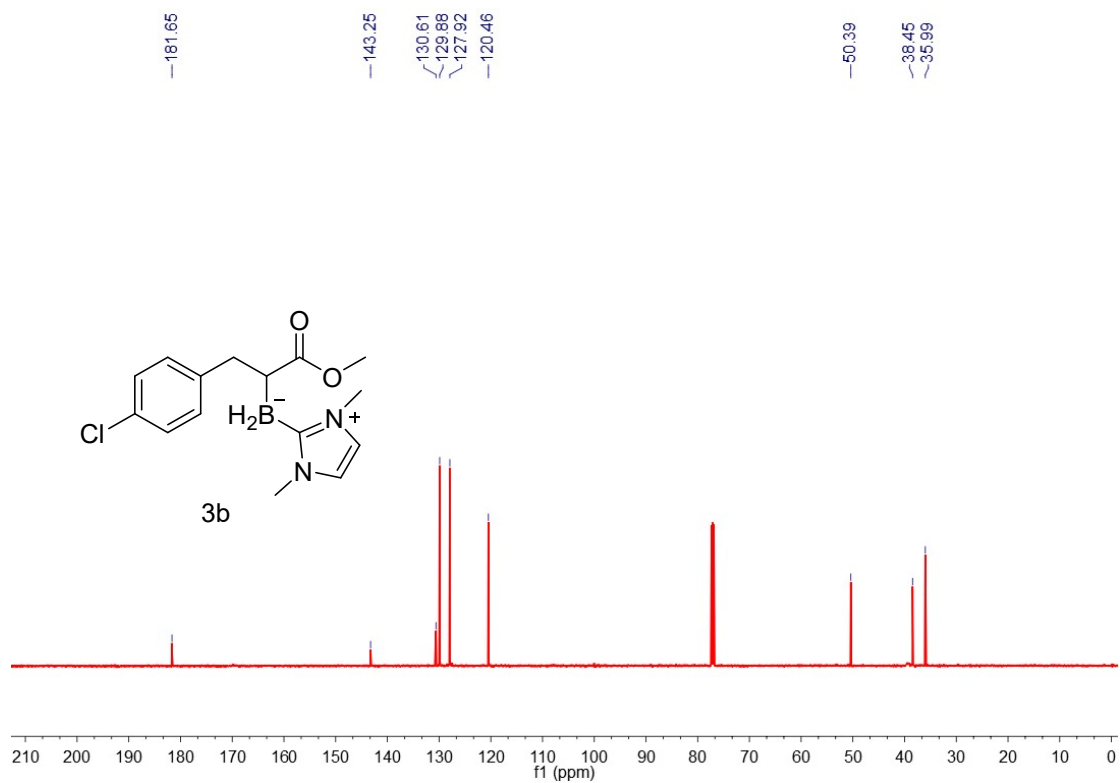


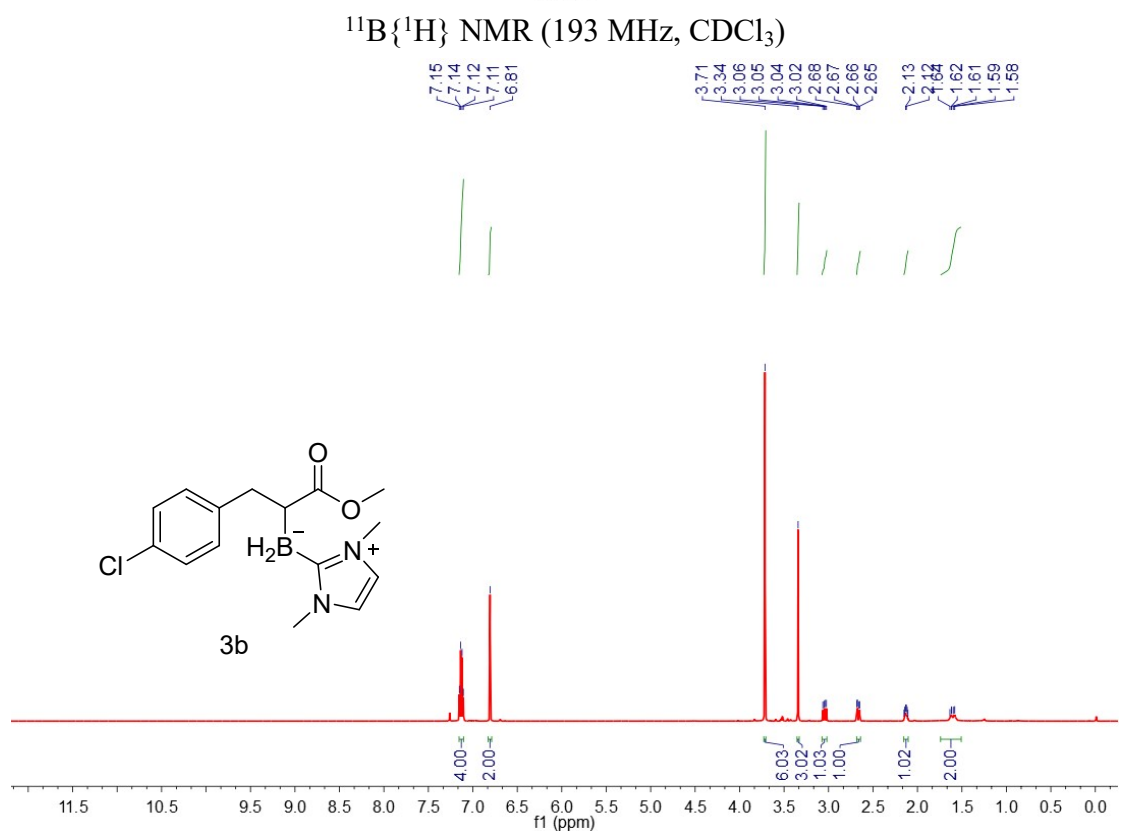
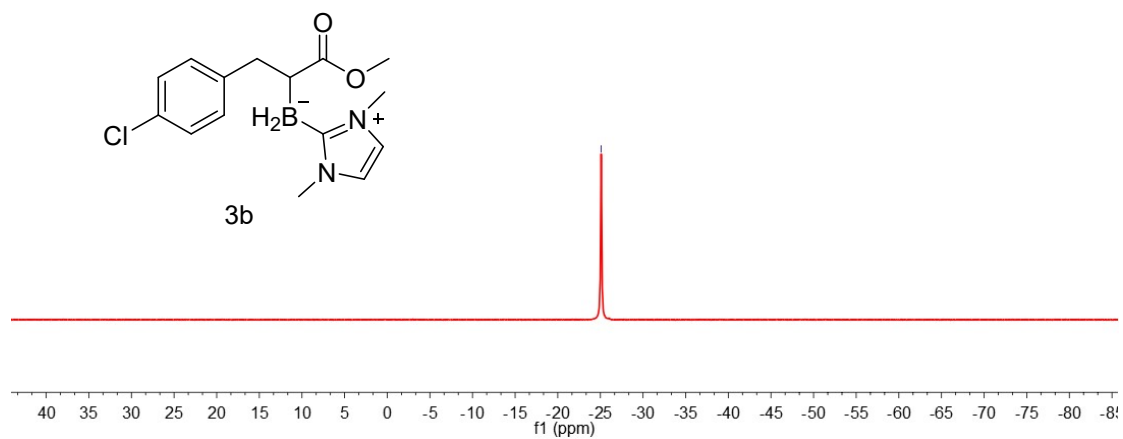
^{11}B NMR (193 MHz, CDCl_3)

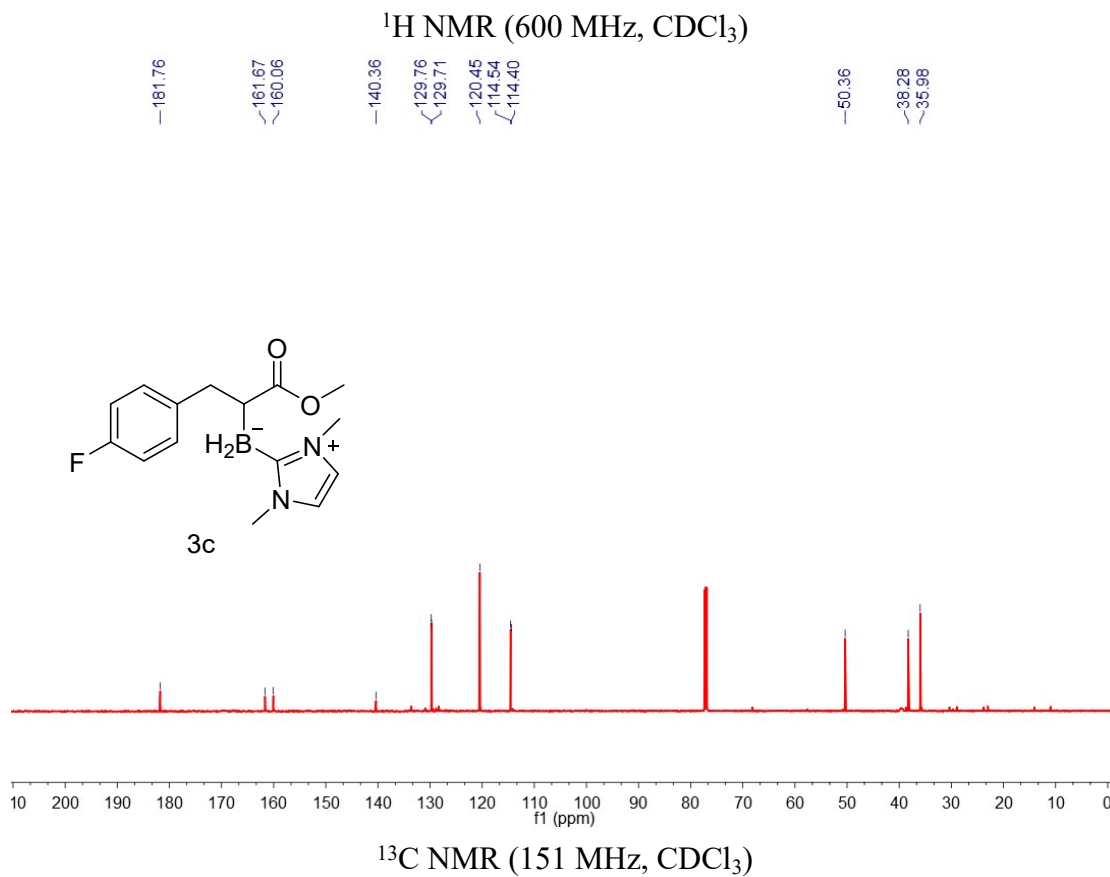
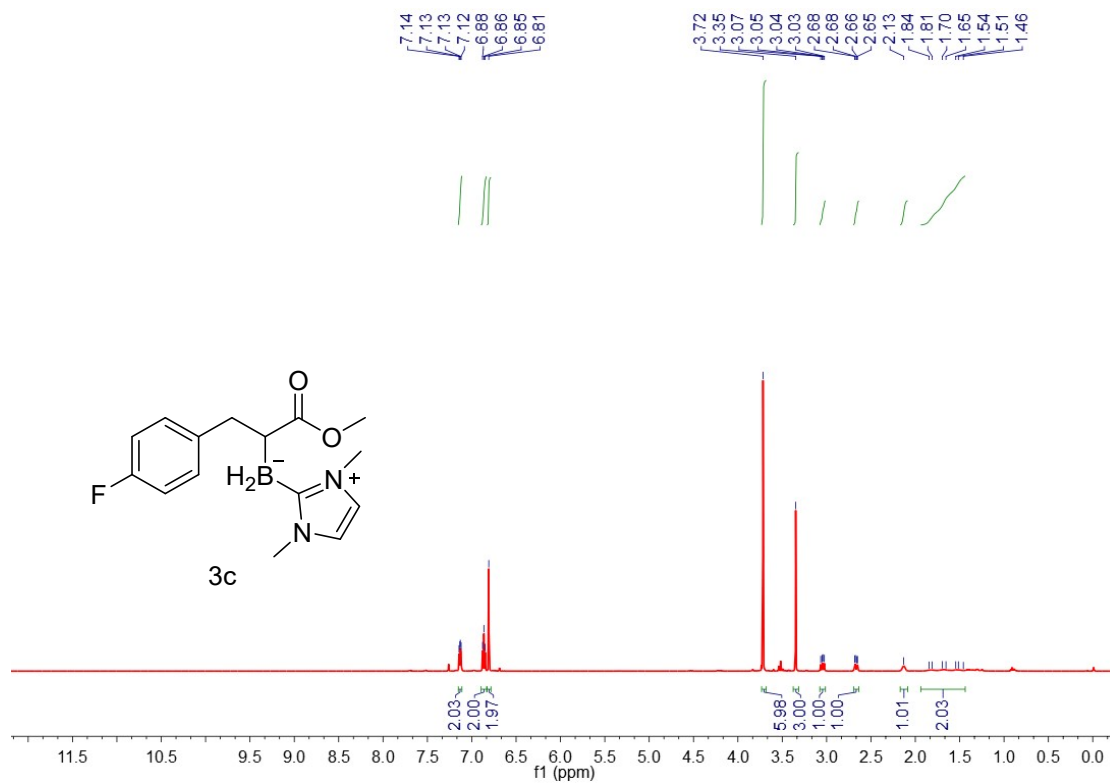


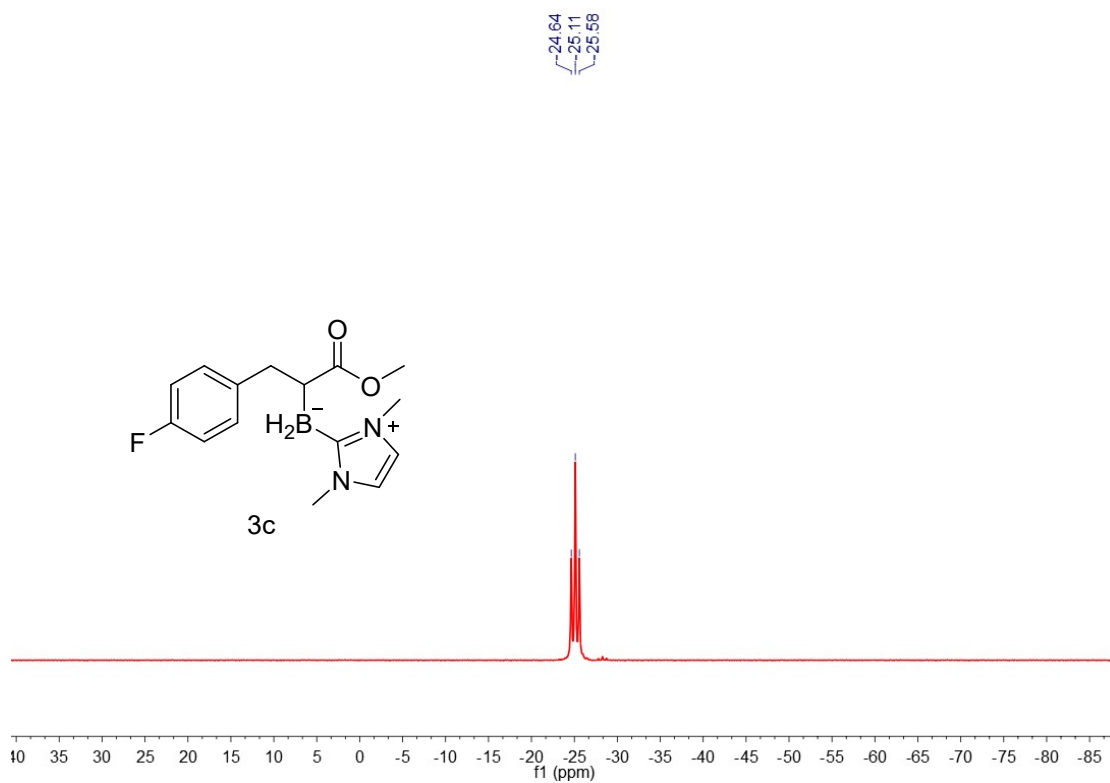
$^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3)



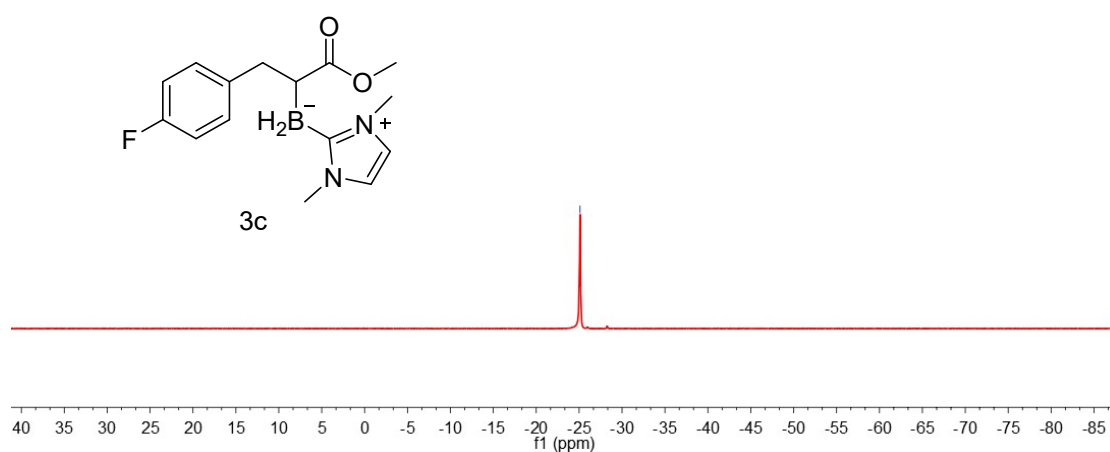




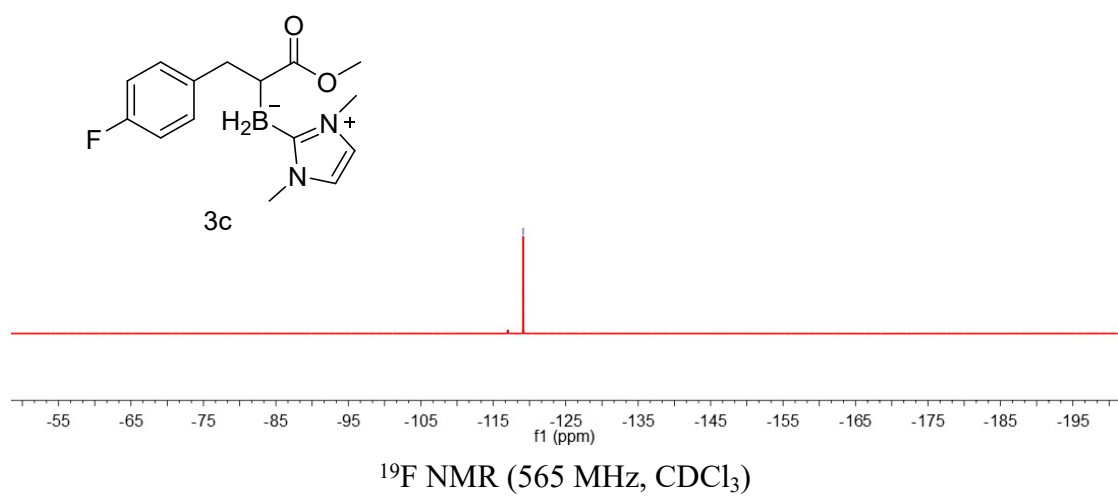
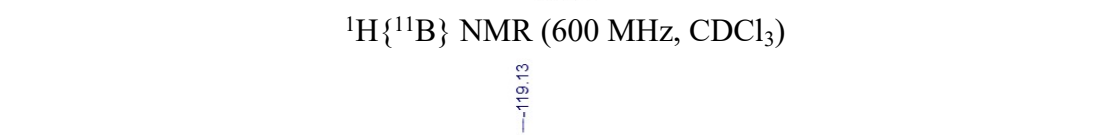
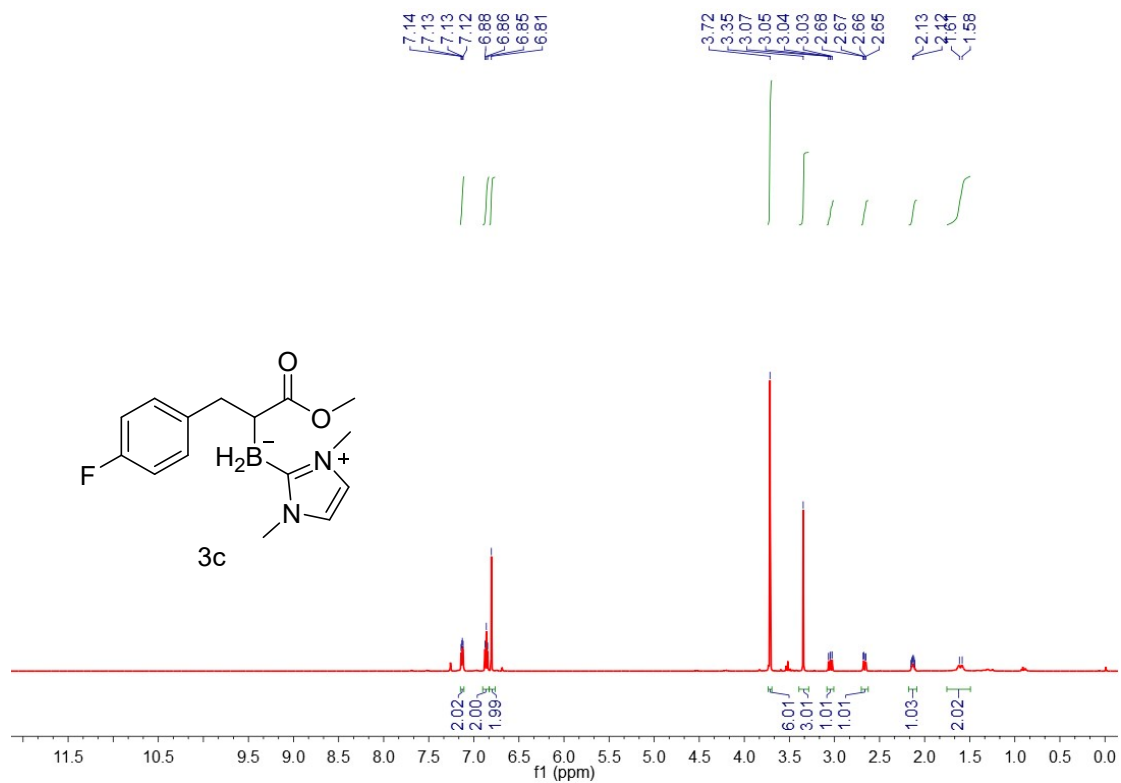


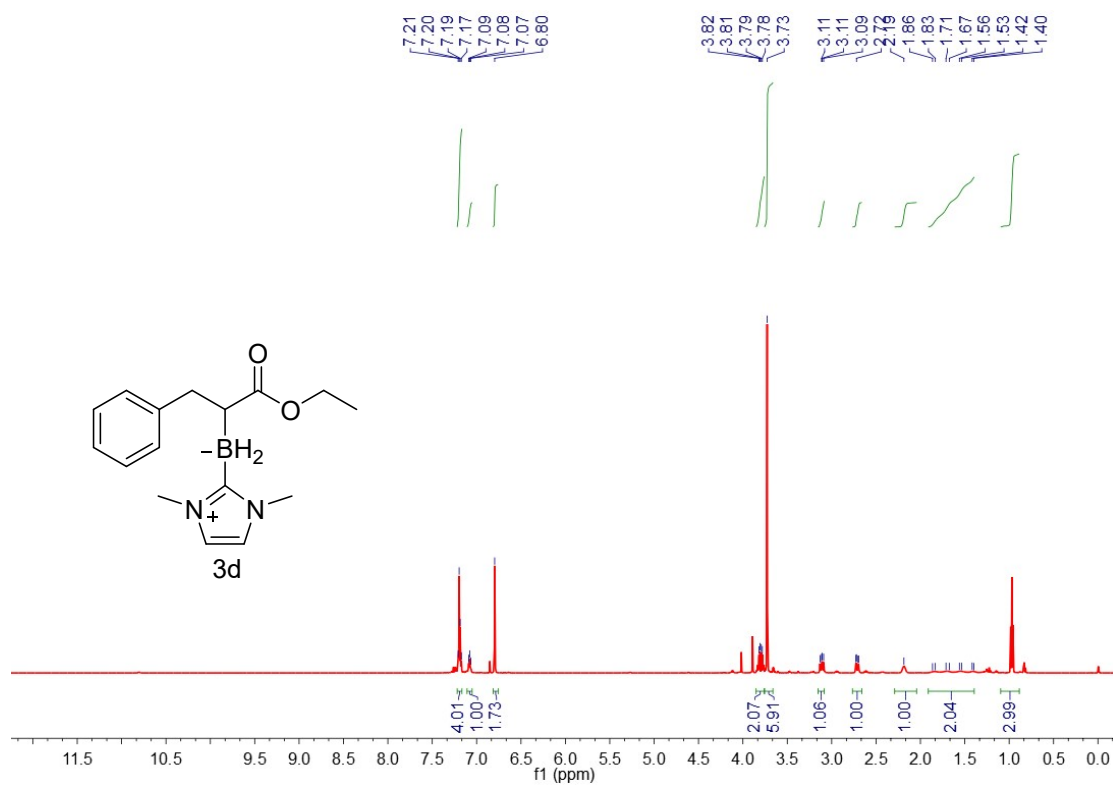


^{11}B NMR (193 MHz, CDCl_3)

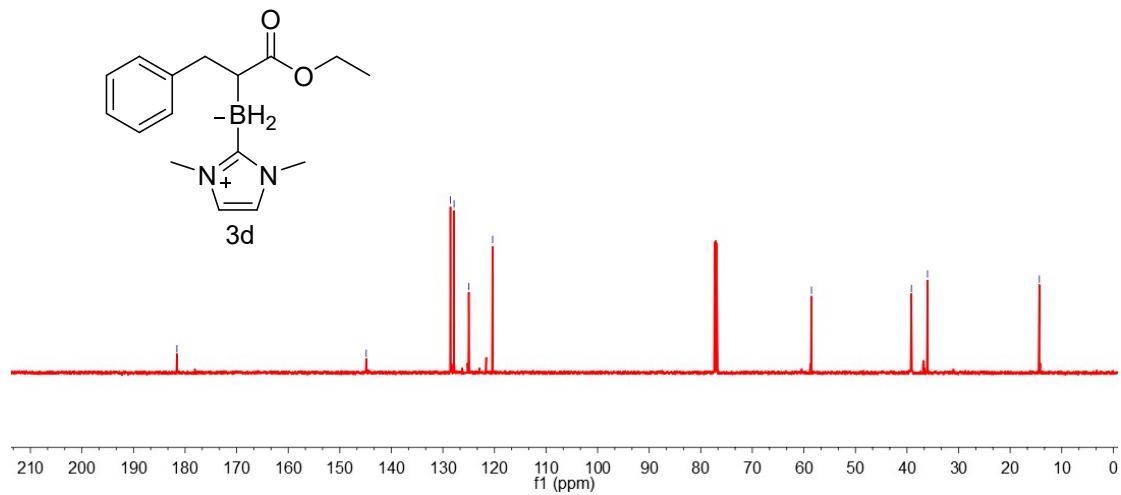


$^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3)

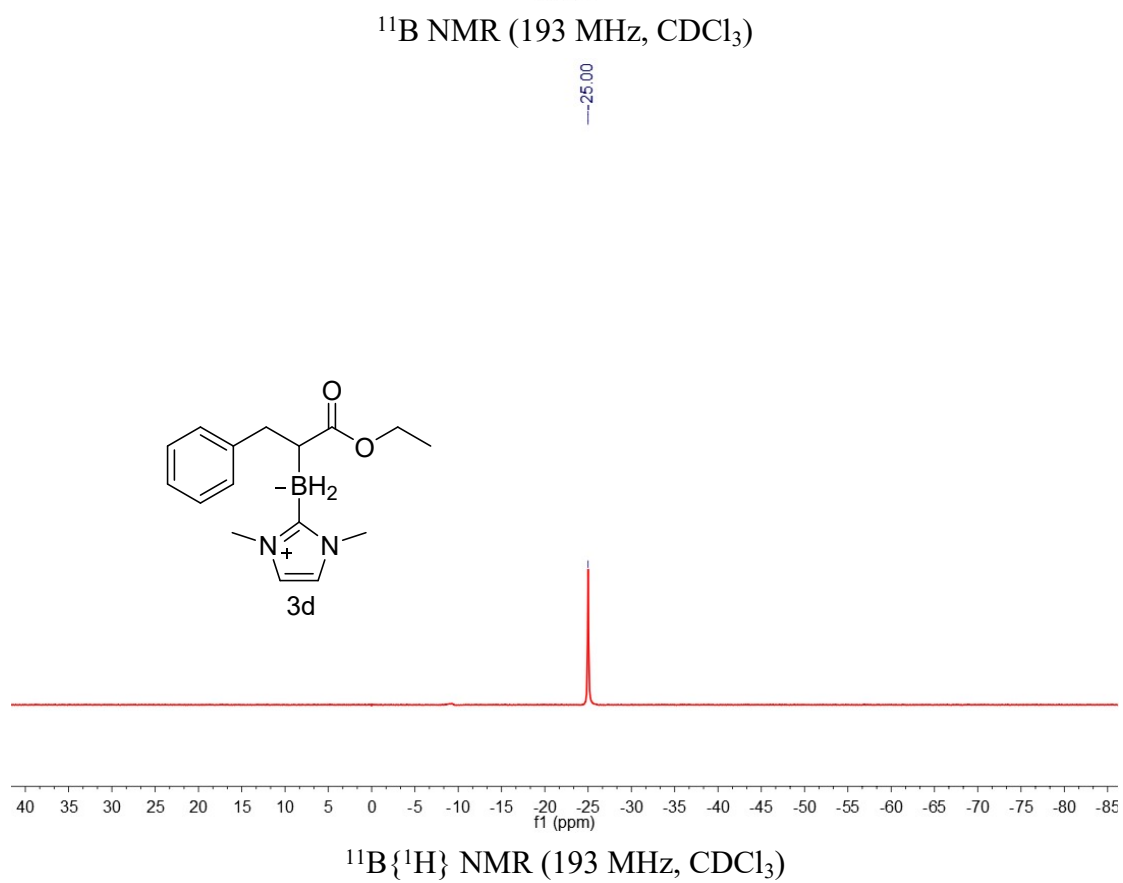
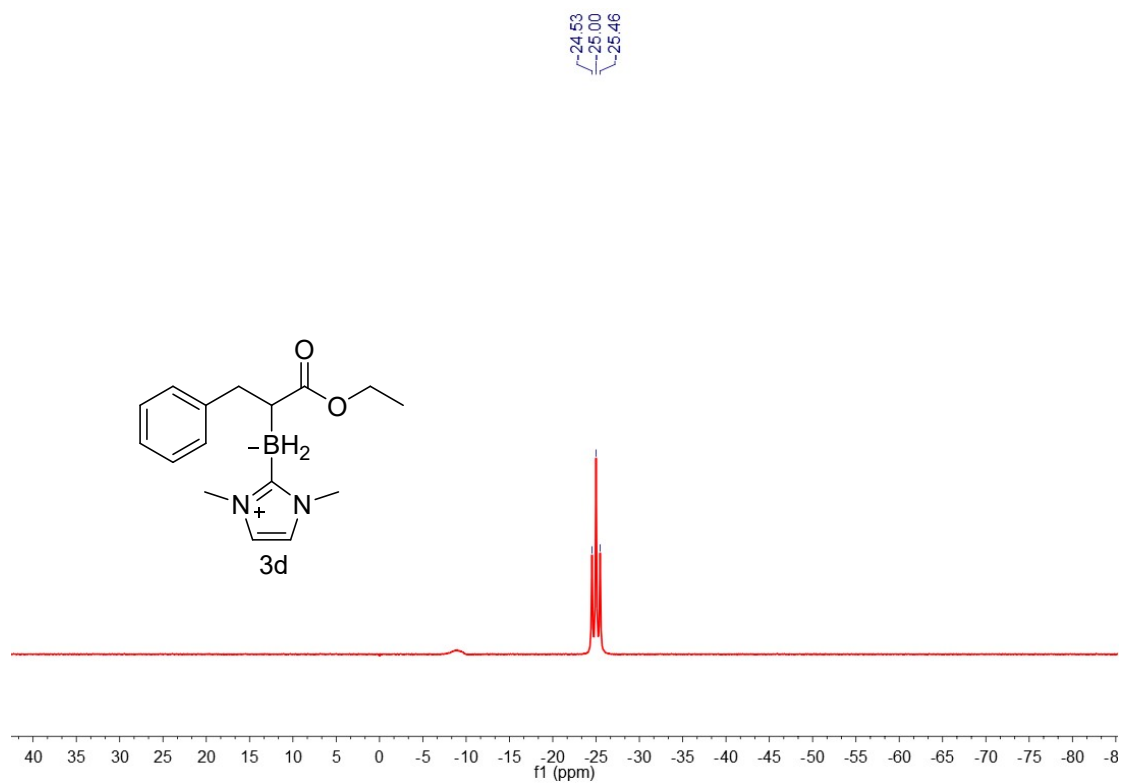


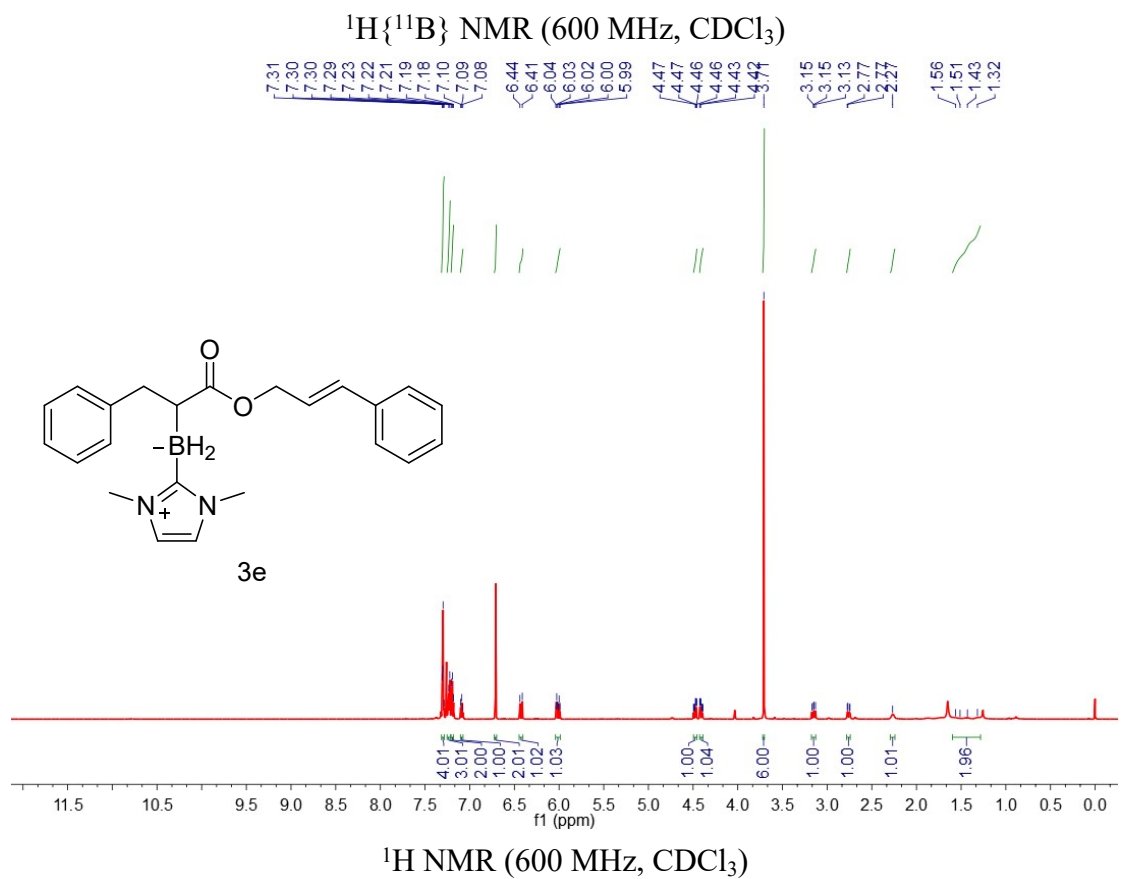
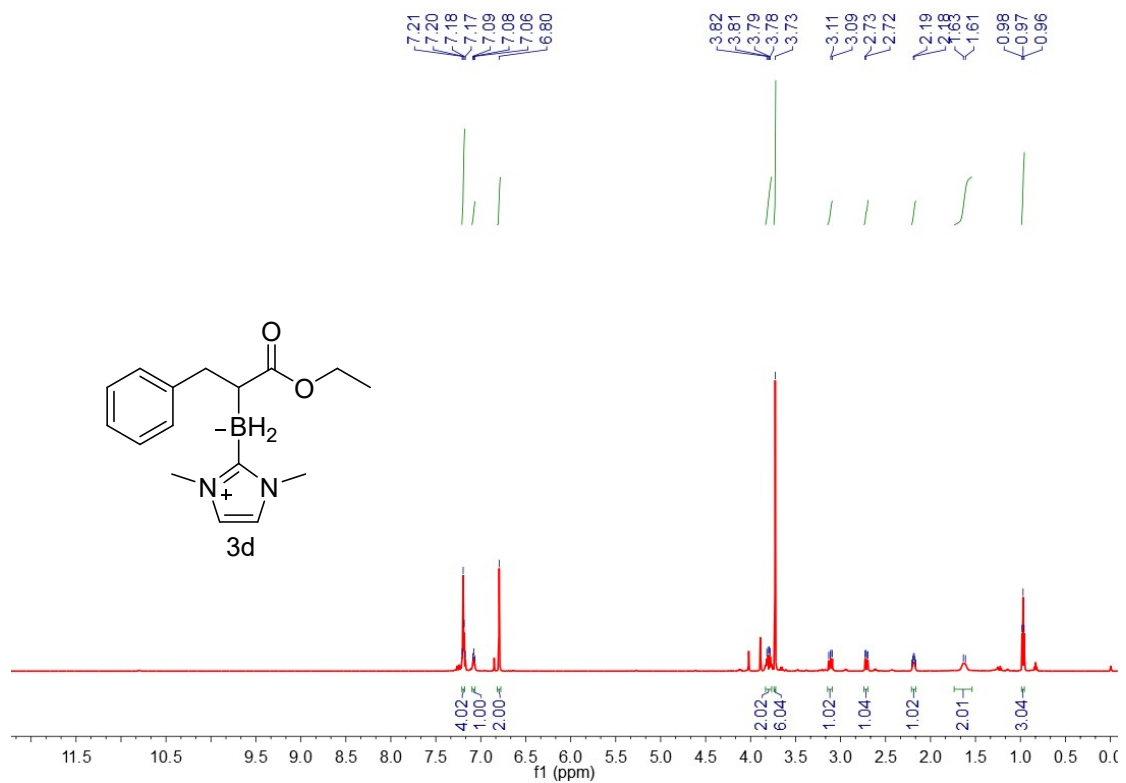


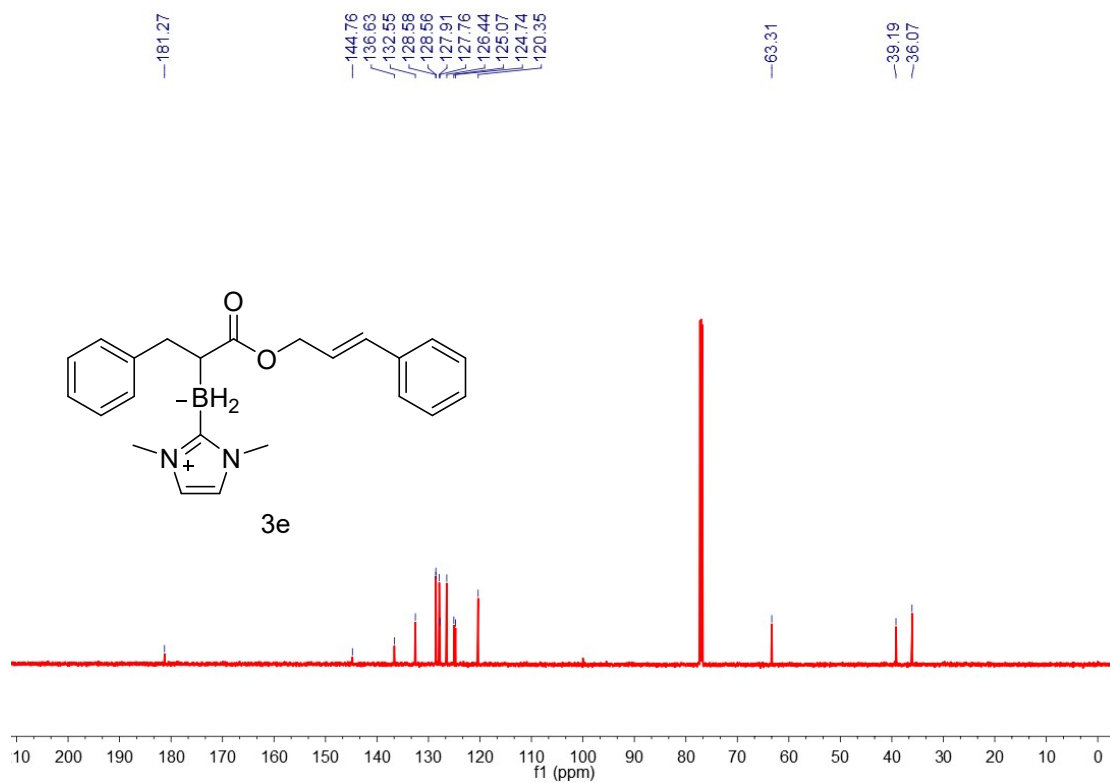
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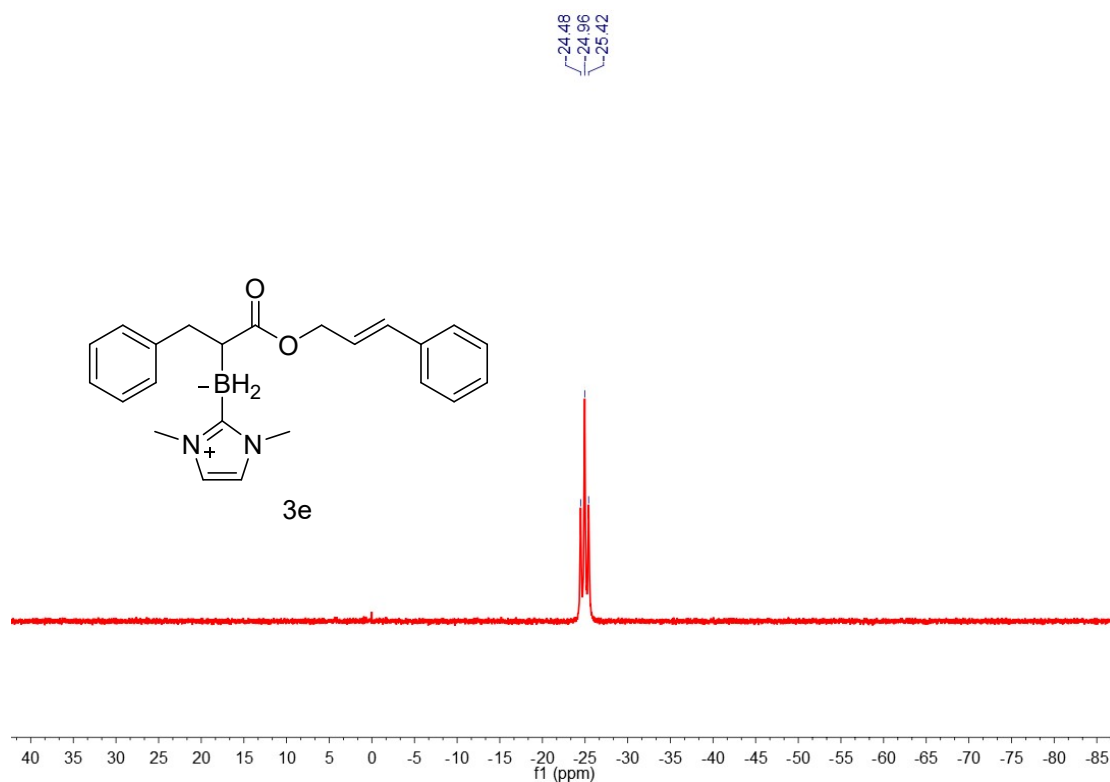
¹³C NMR (151 MHz, CDCl₃)



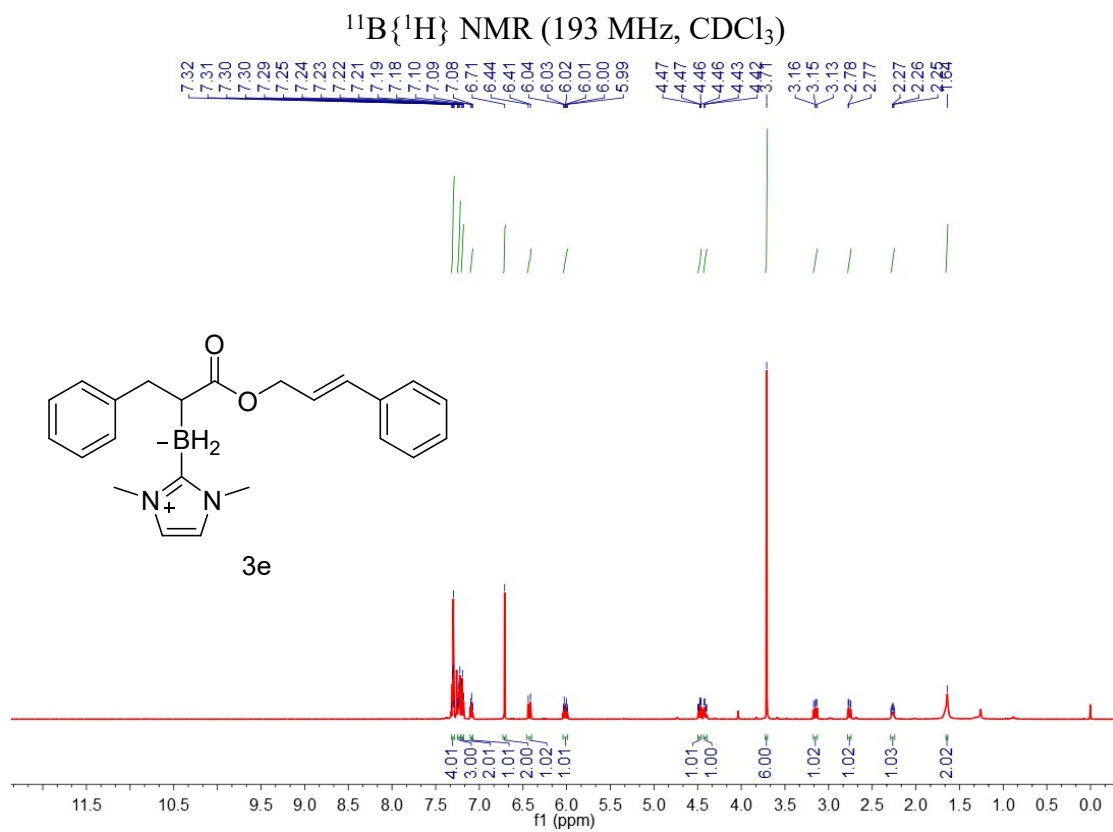
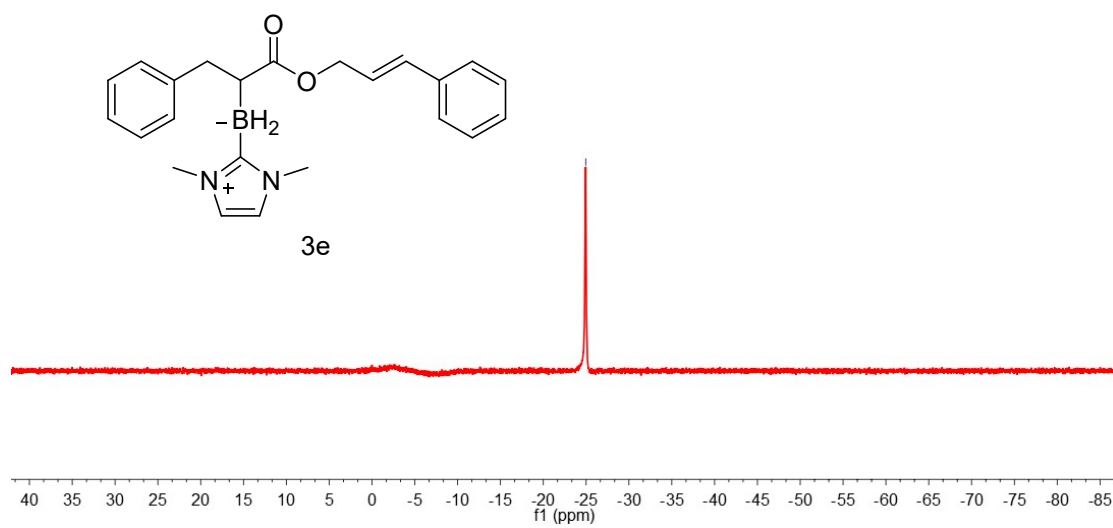


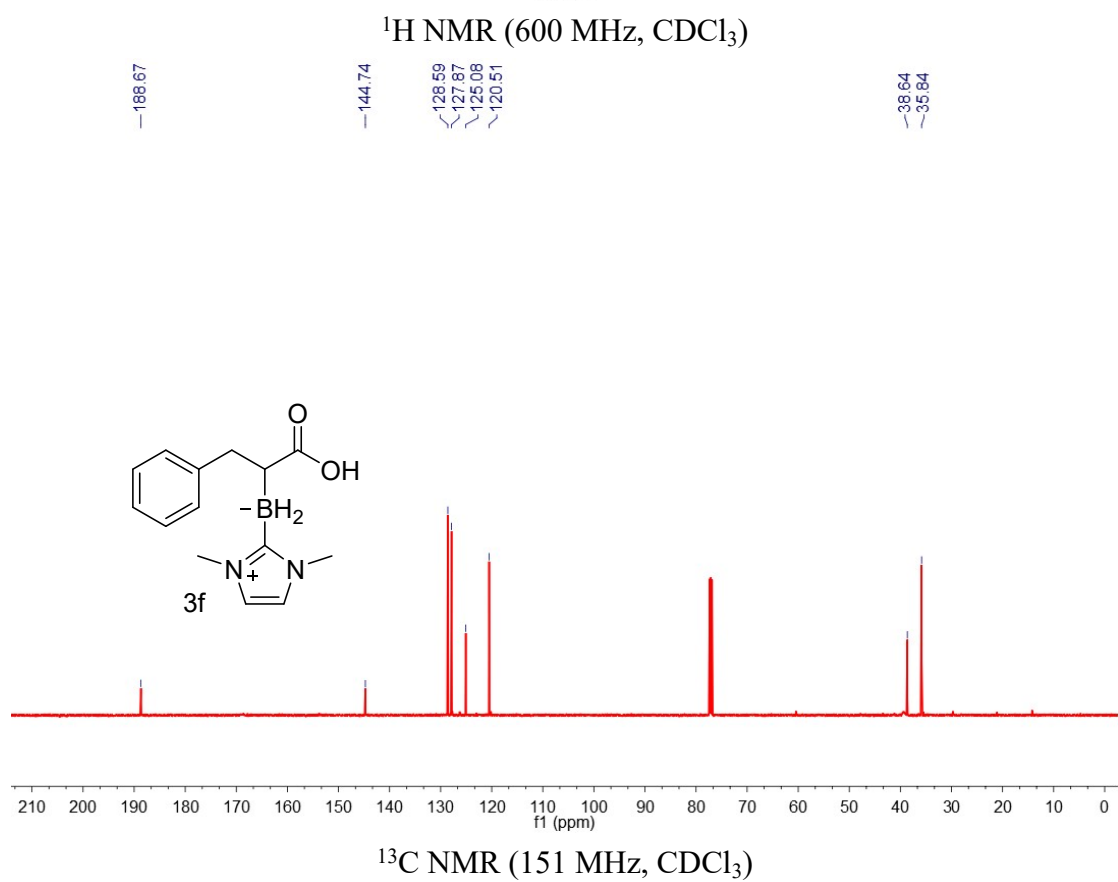
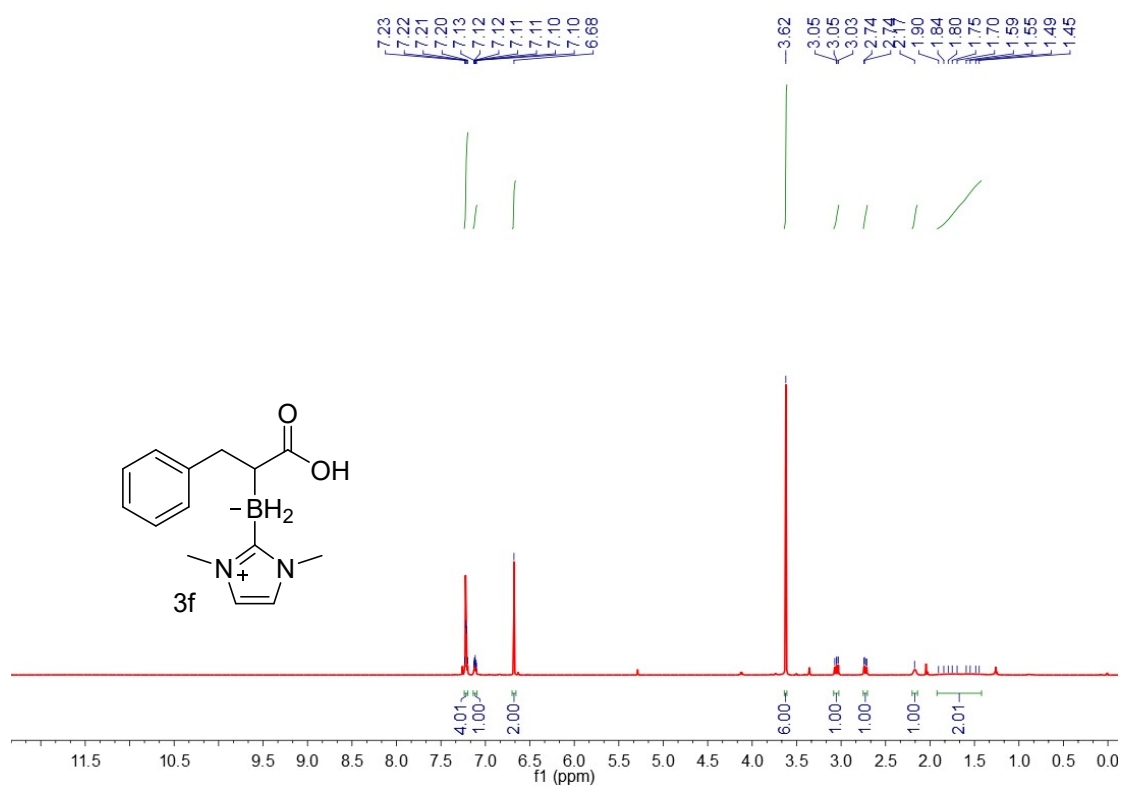


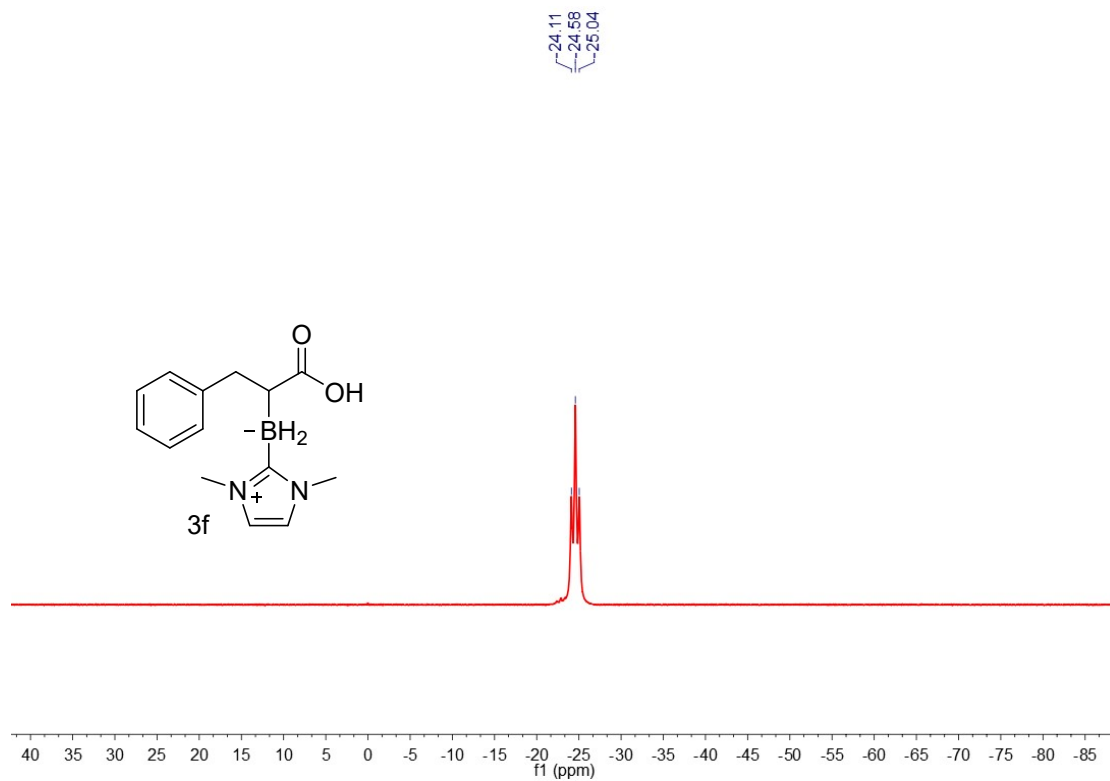
^{13}C NMR (151 MHz, CDCl_3)



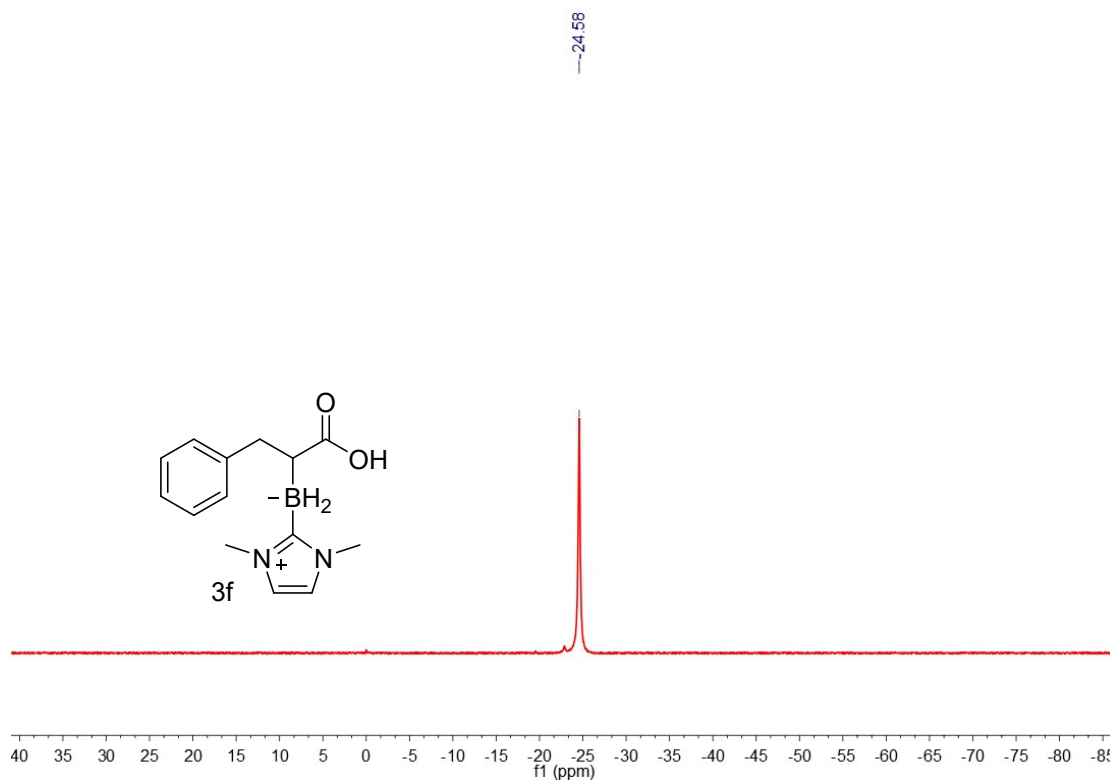
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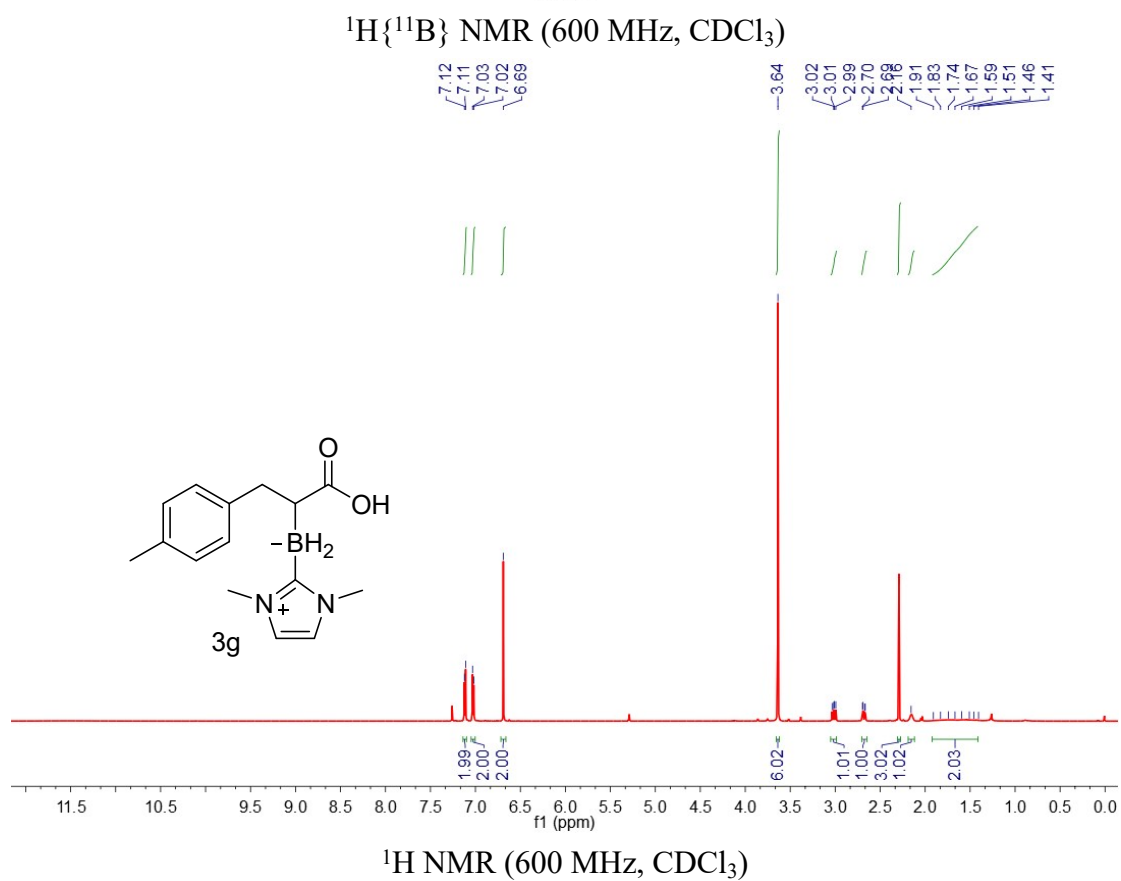
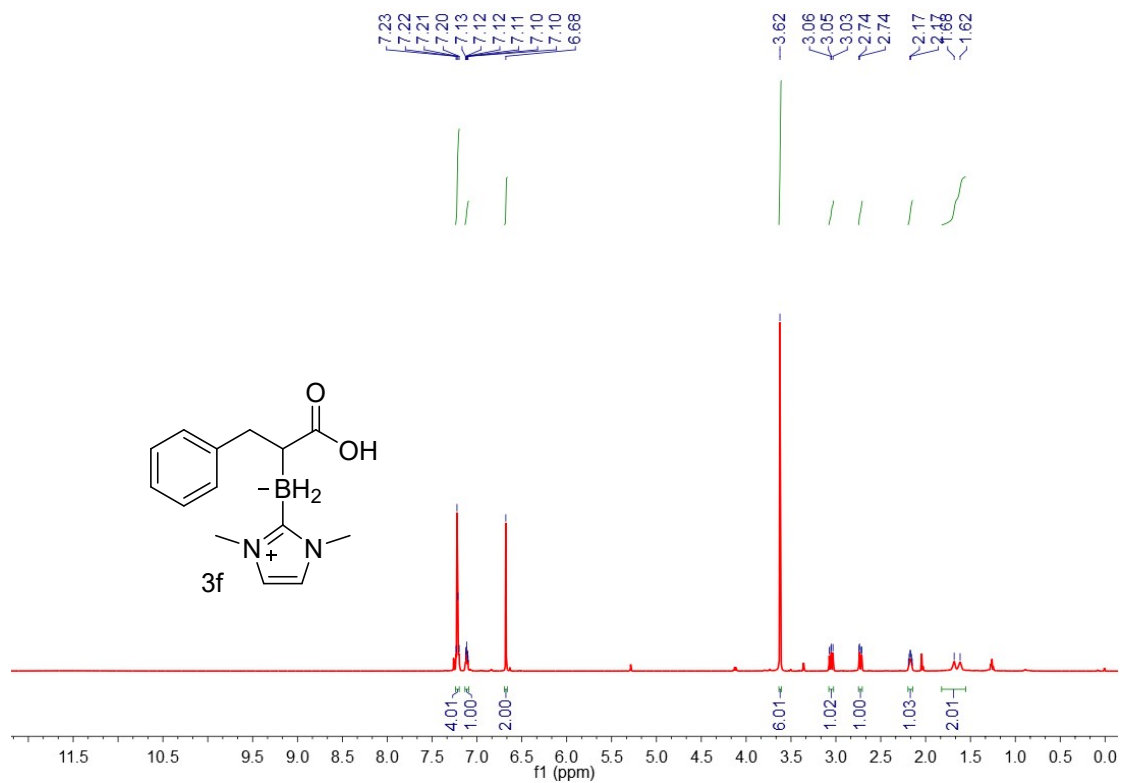


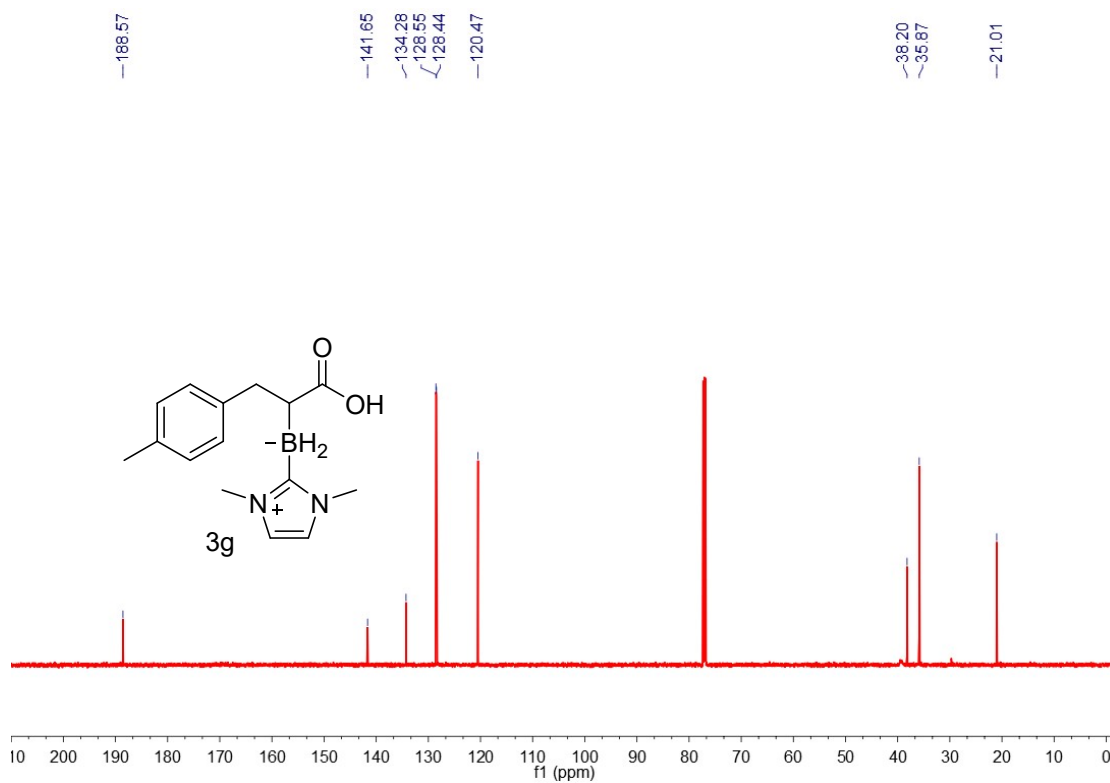


¹¹B NMR (193 MHz, CDCl₃)



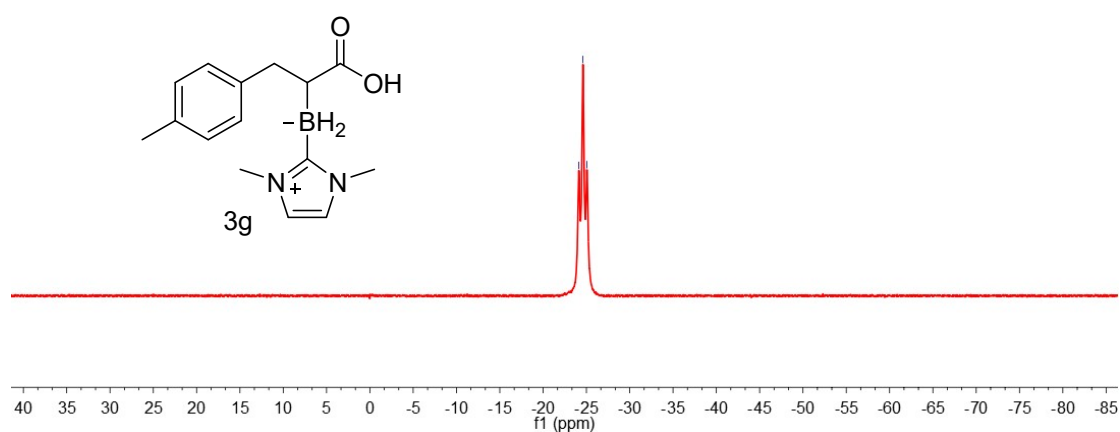
¹¹B{¹H} NMR (193 MHz, CDCl₃)



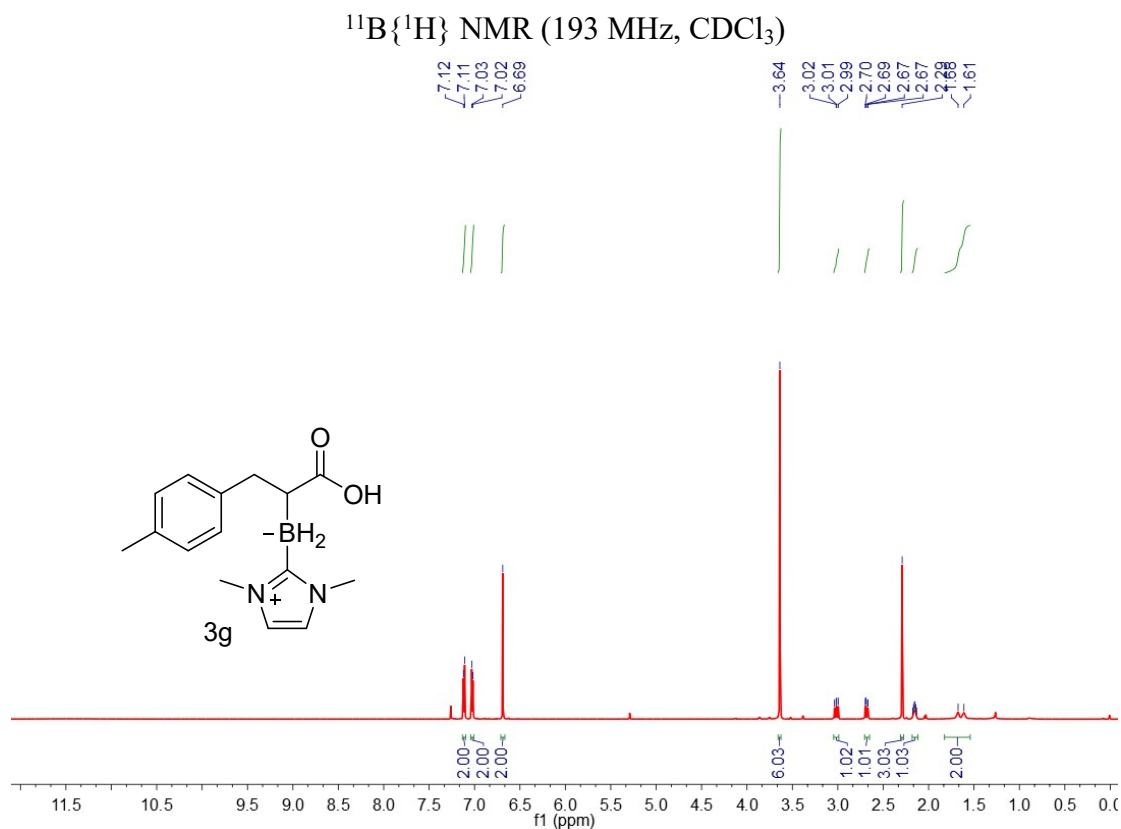
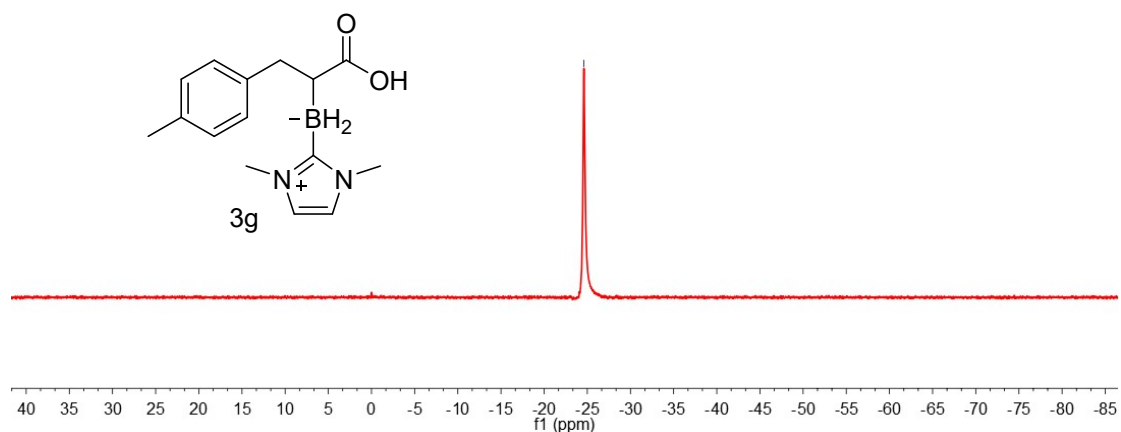


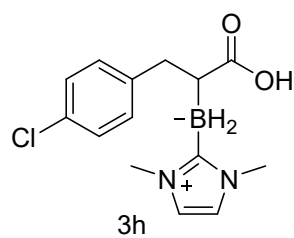
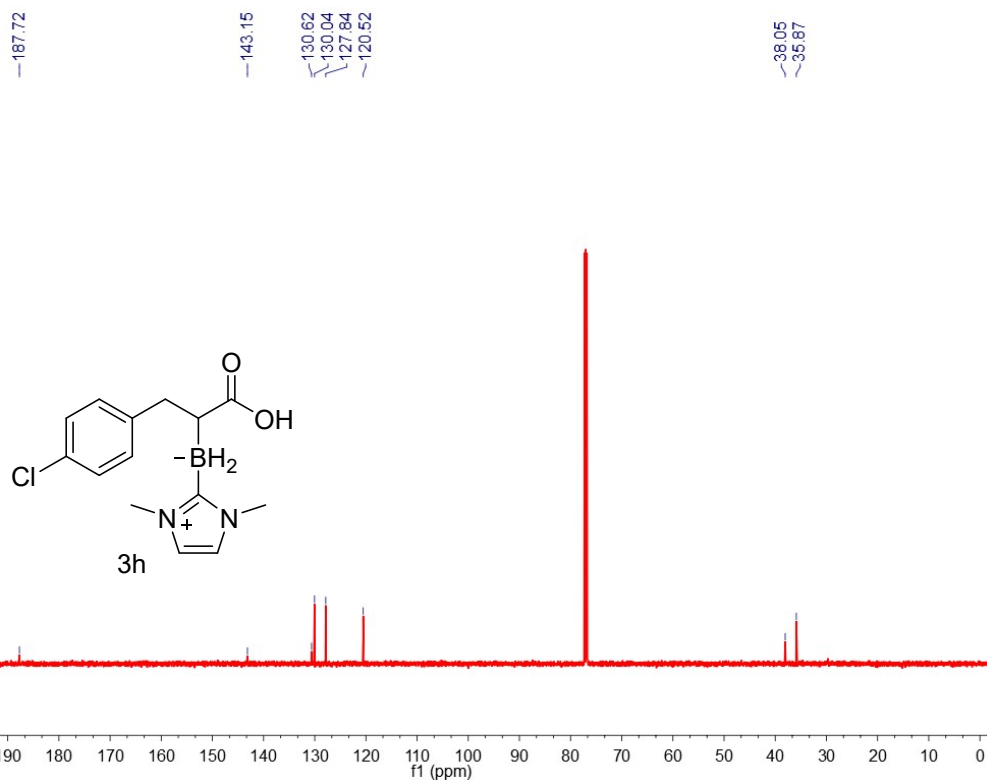
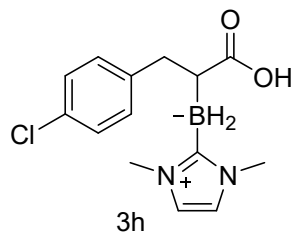
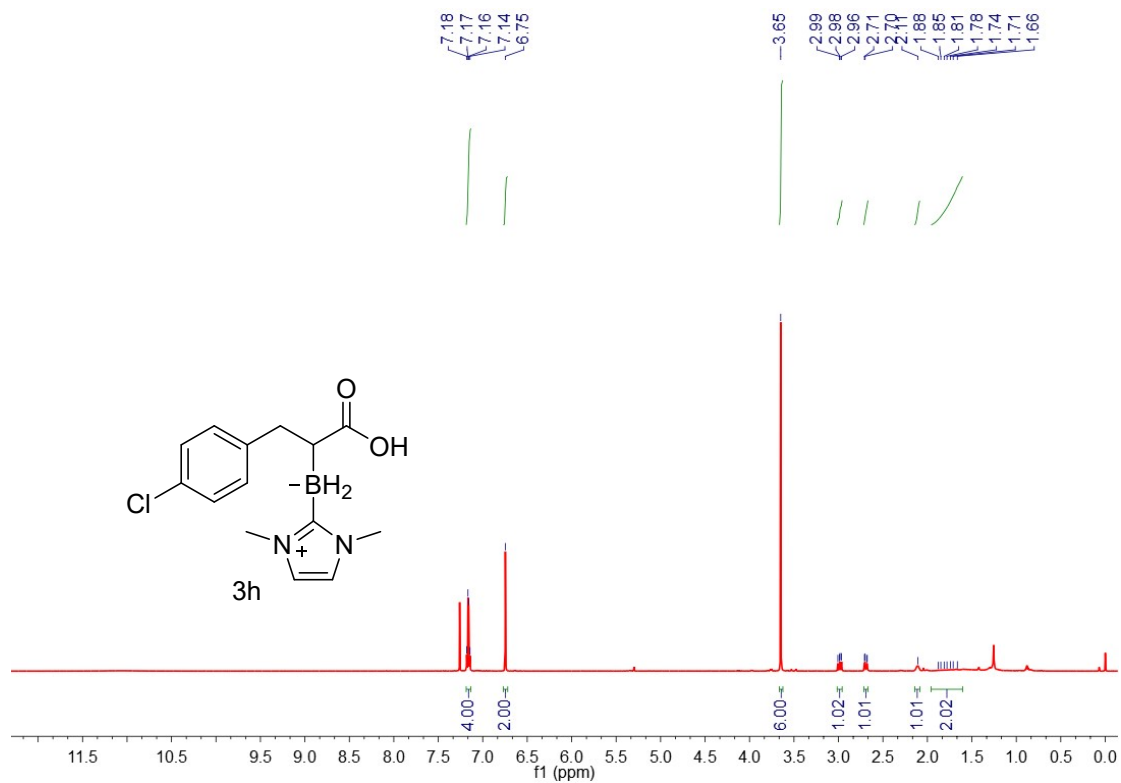
¹³C NMR (151 MHz, CDCl₃)

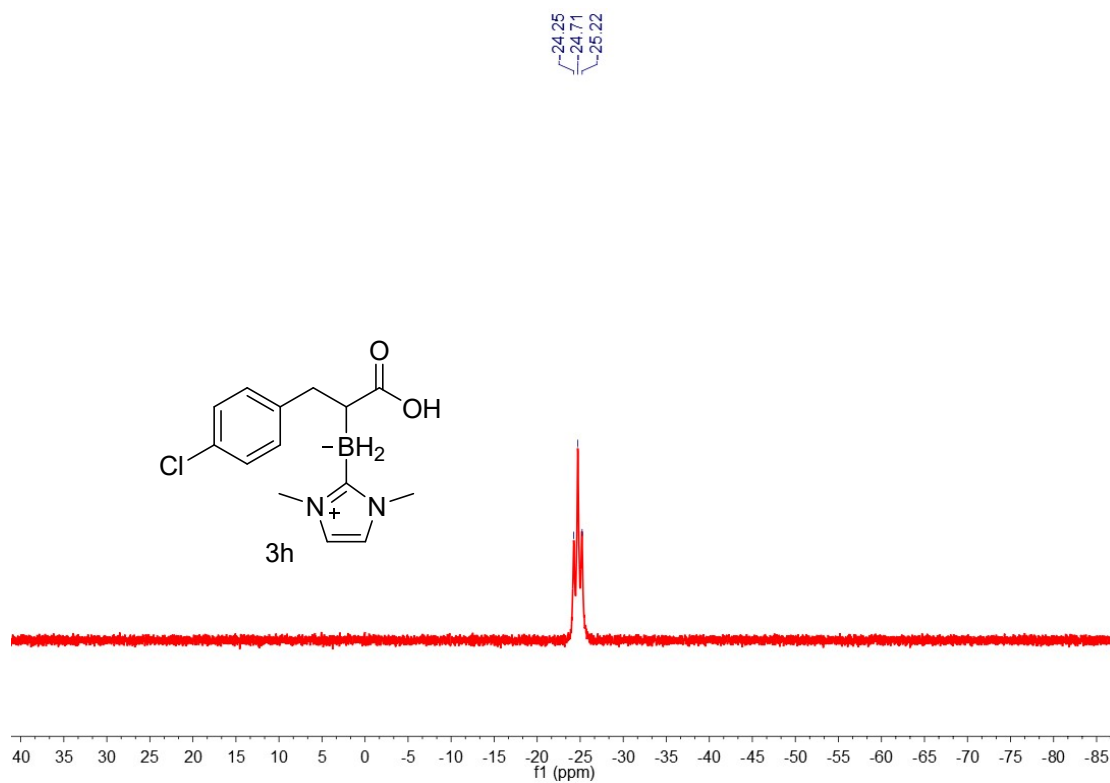
24.13
24.60
25.06



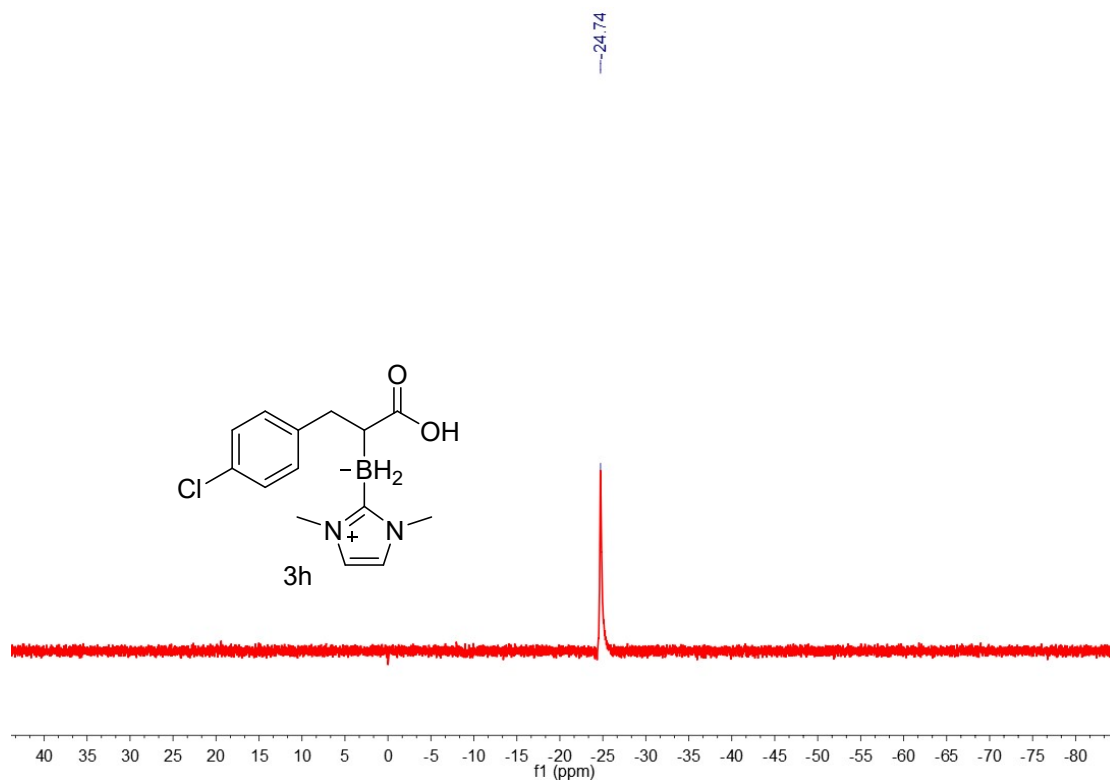
¹¹B NMR (193 MHz, CDCl₃)



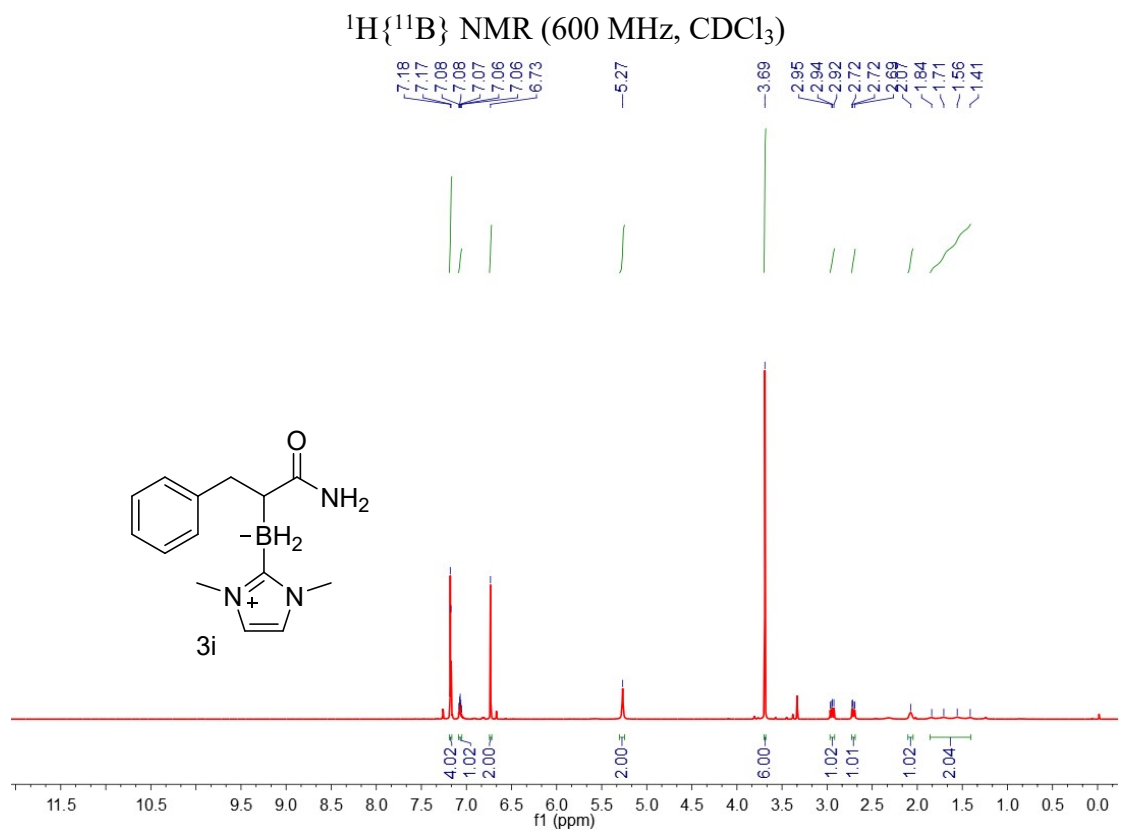
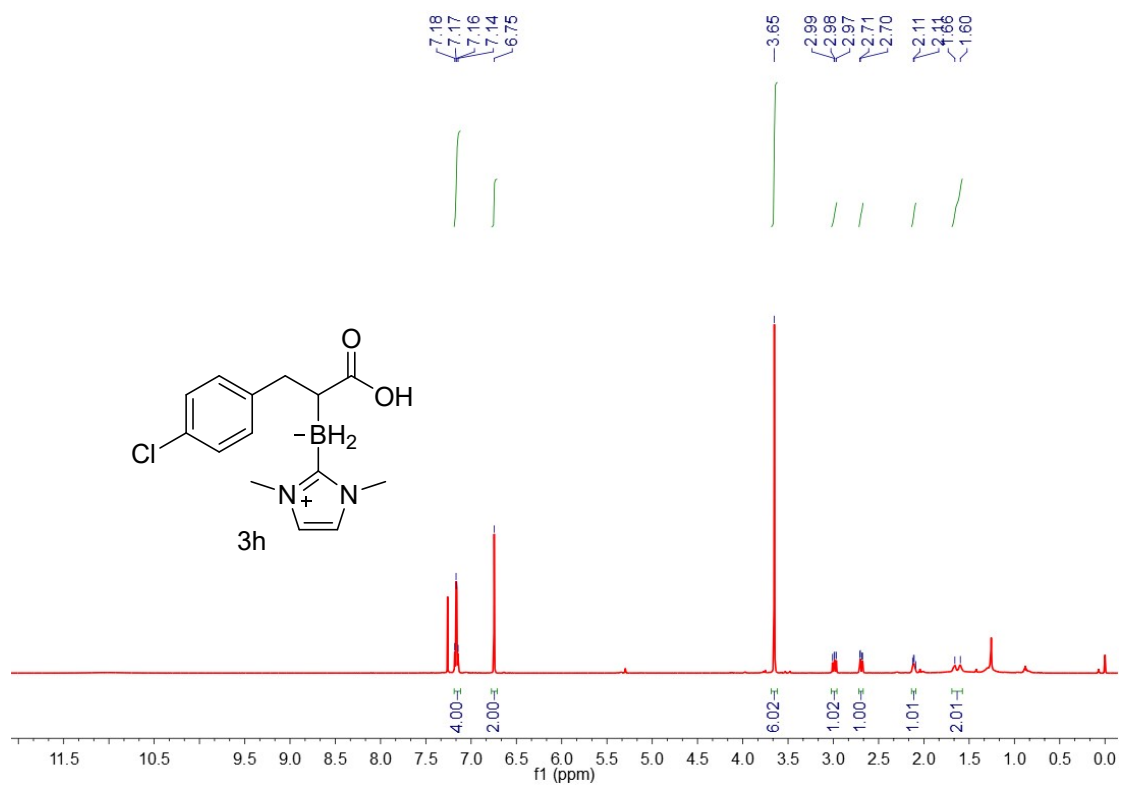


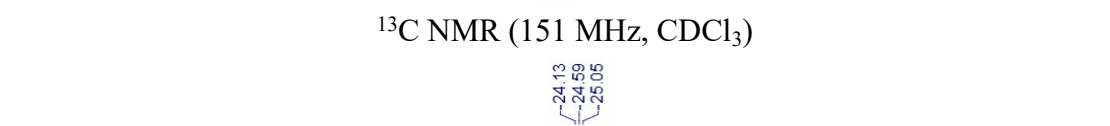
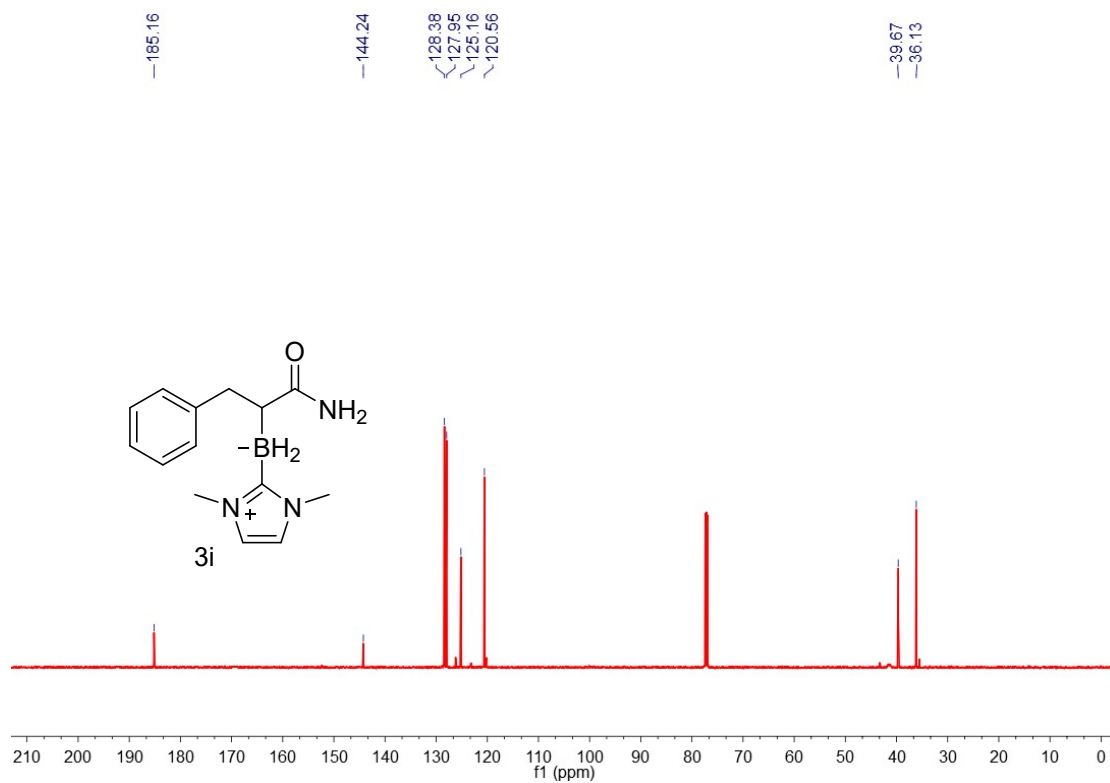


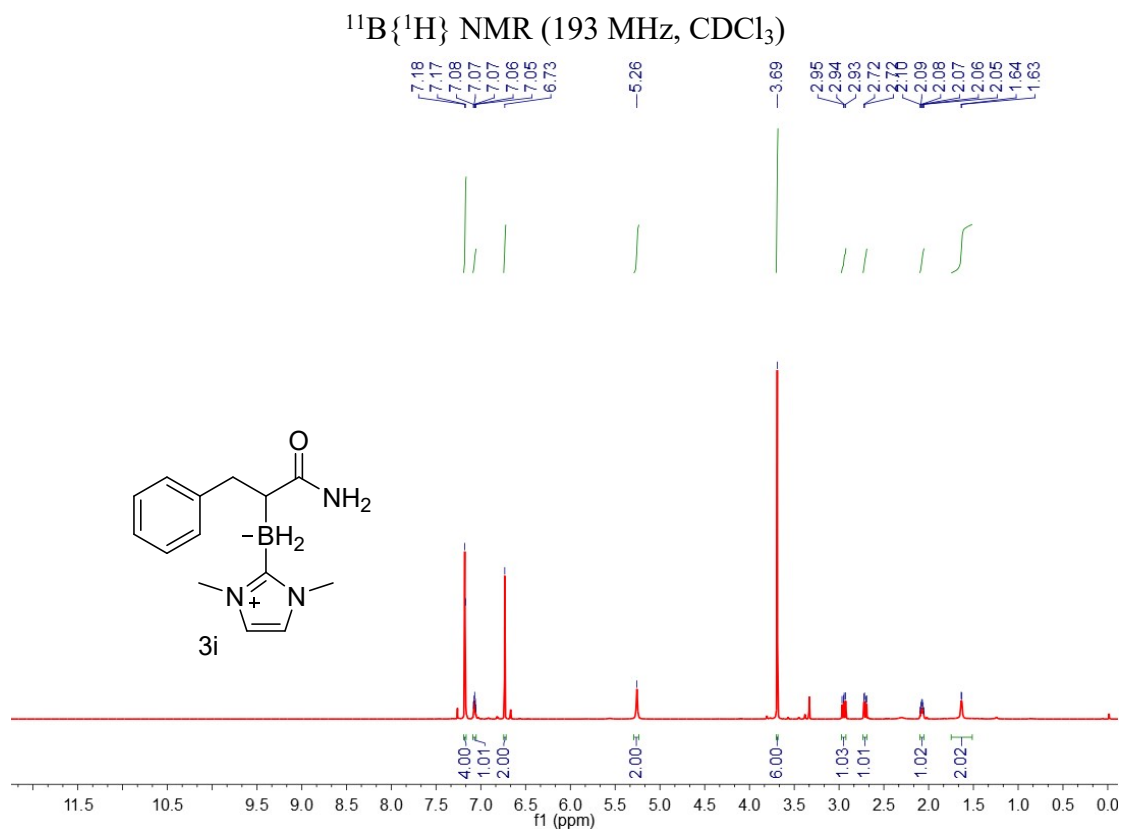
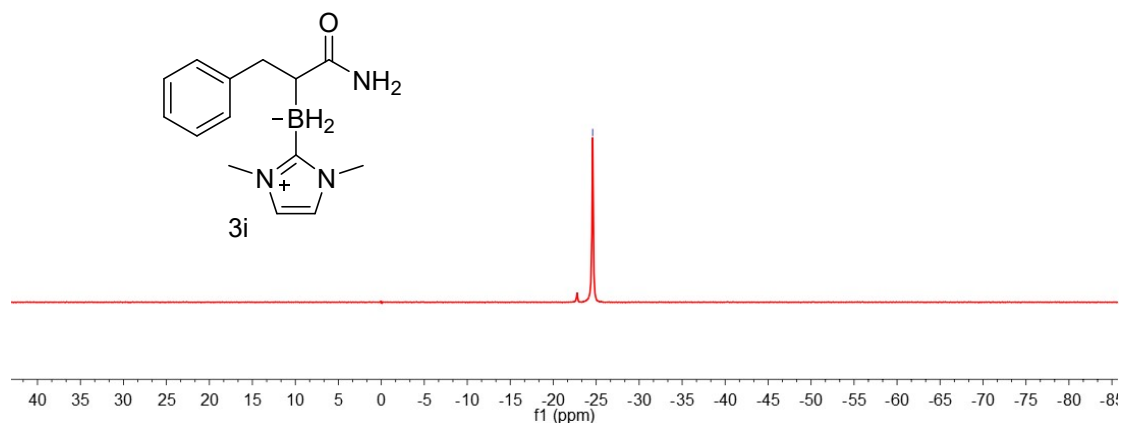
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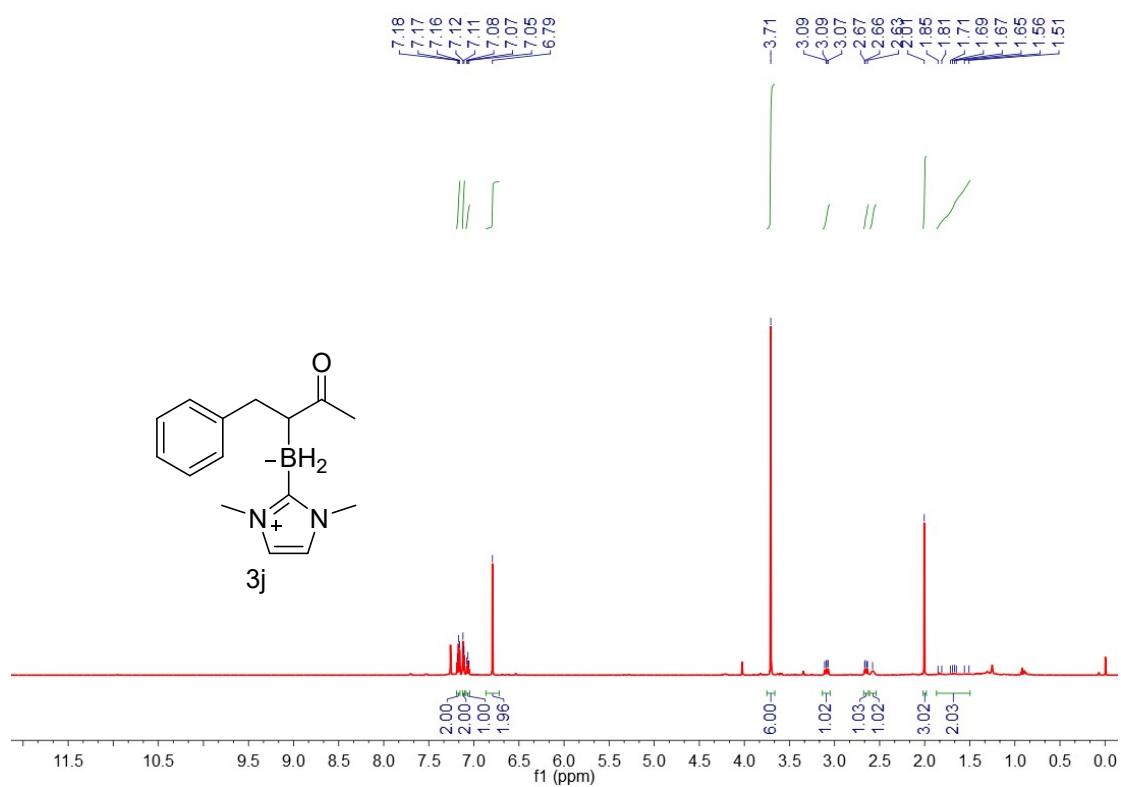


¹¹B{¹H} NMR (193 MHz, CDCl₃)

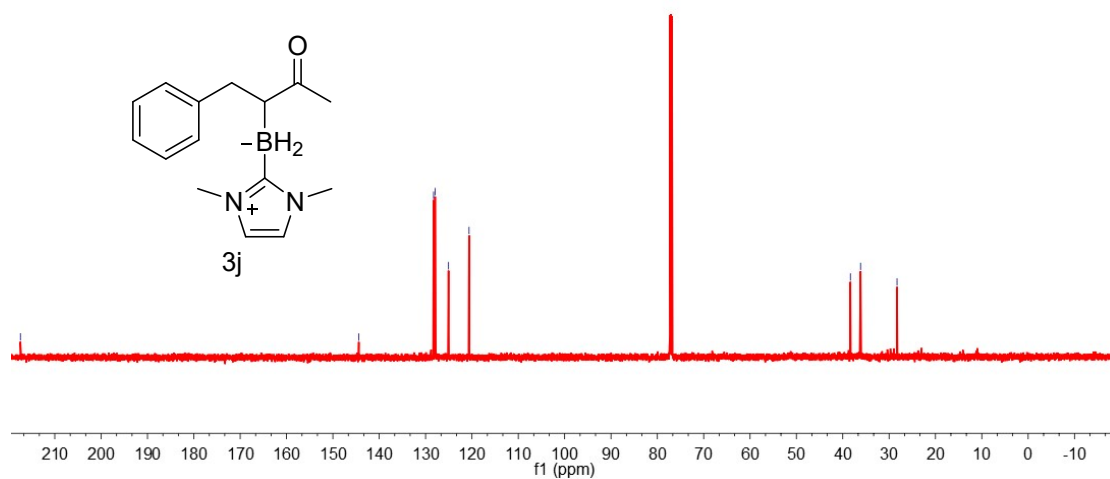




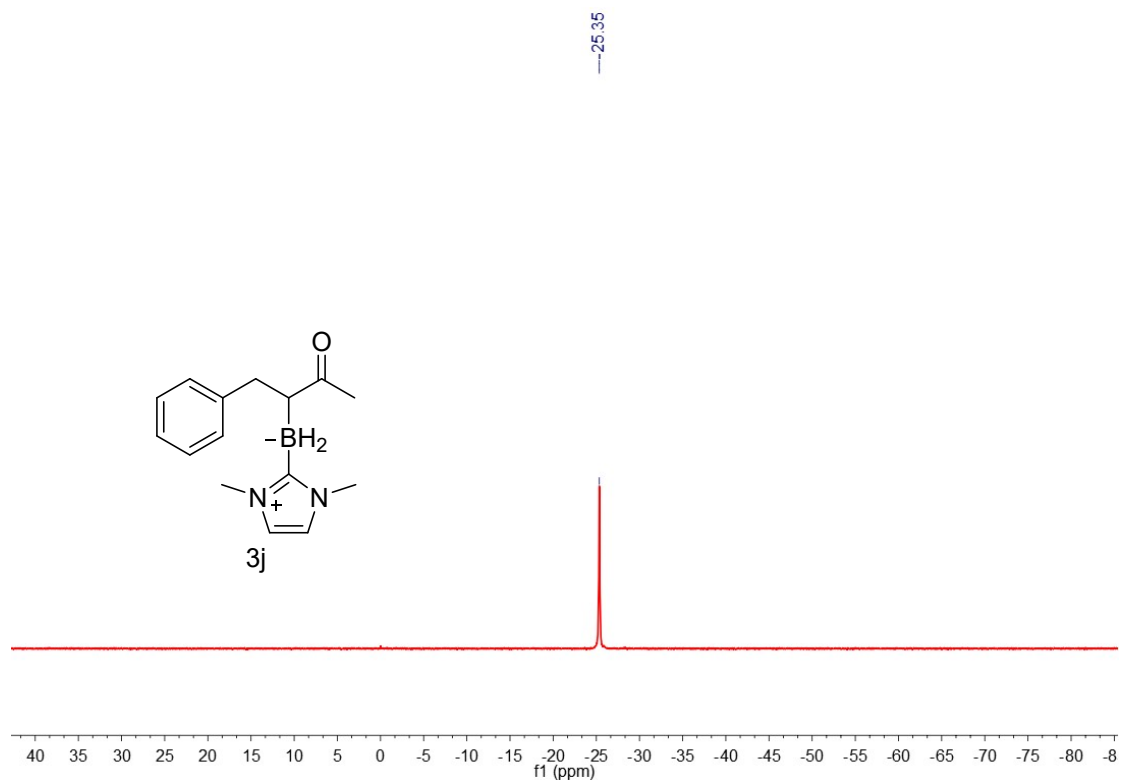
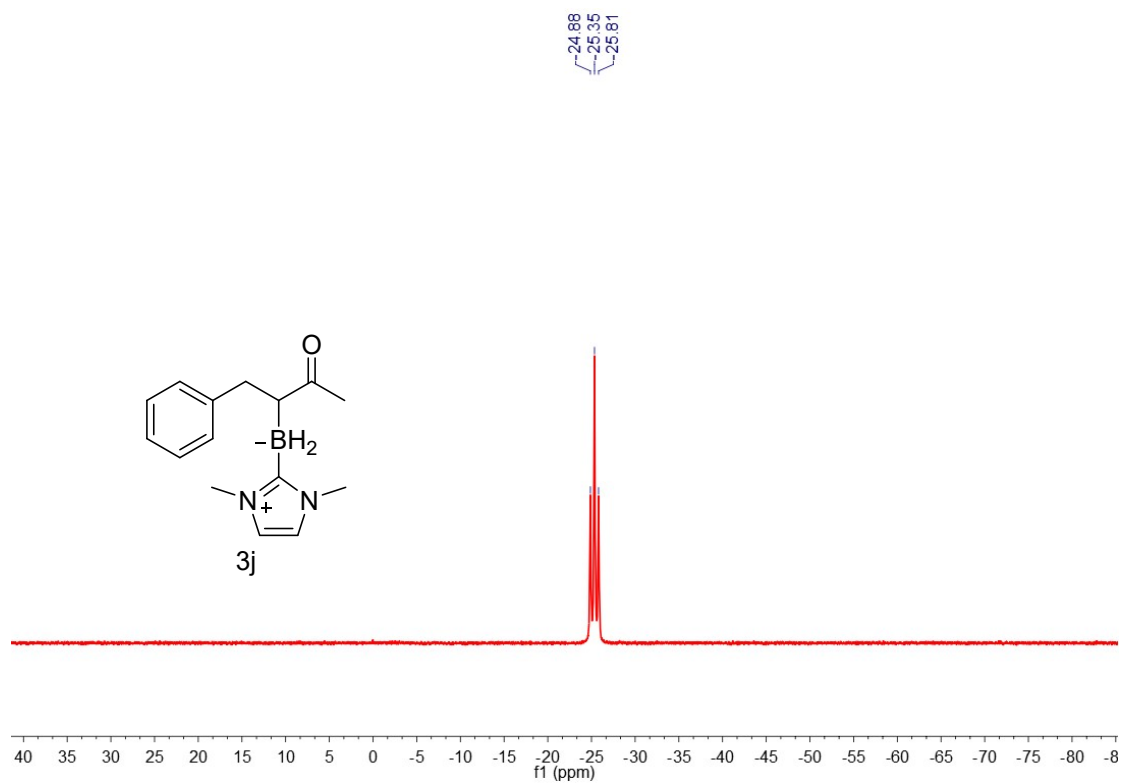


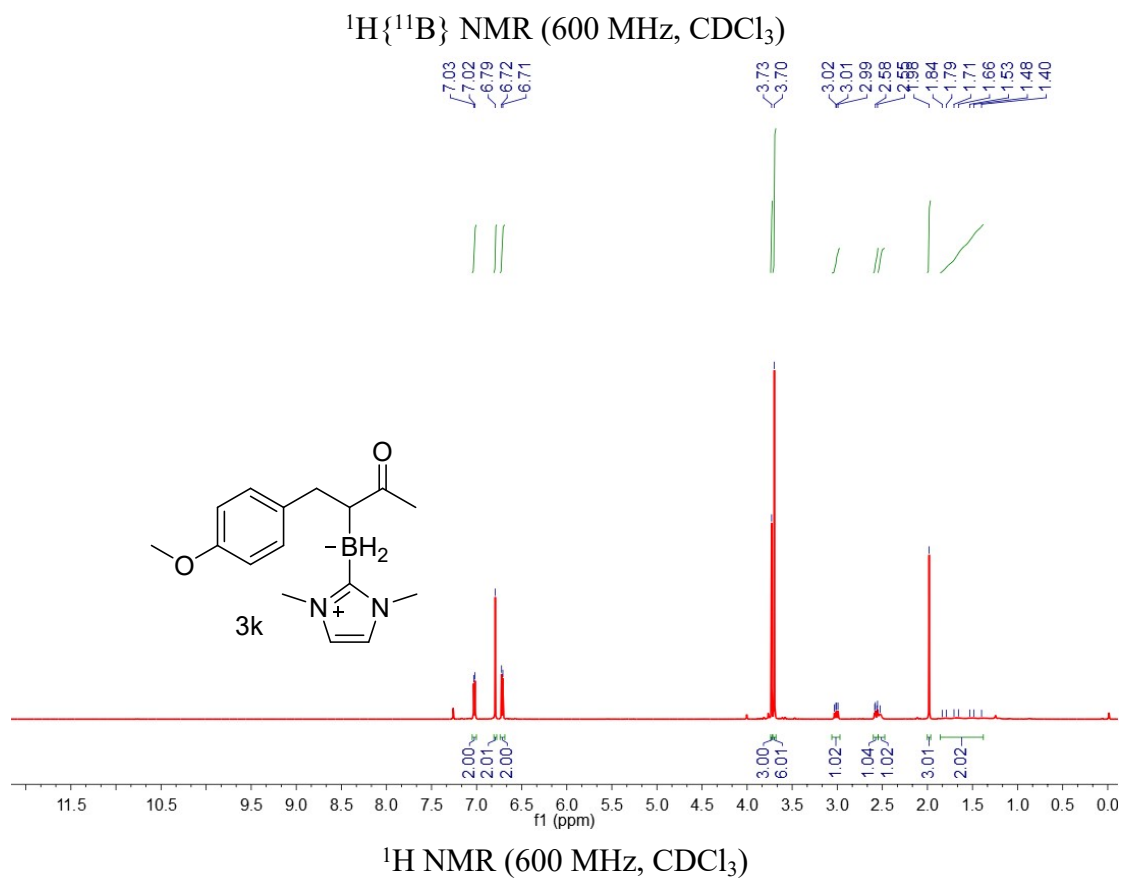
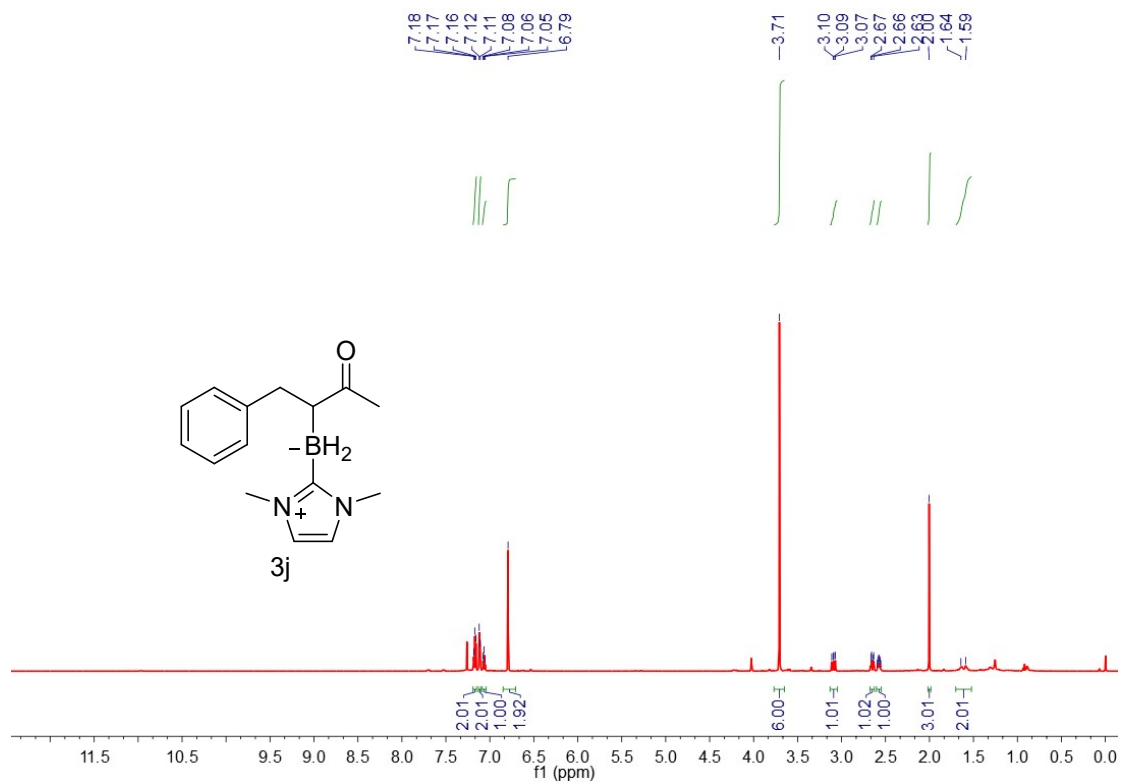


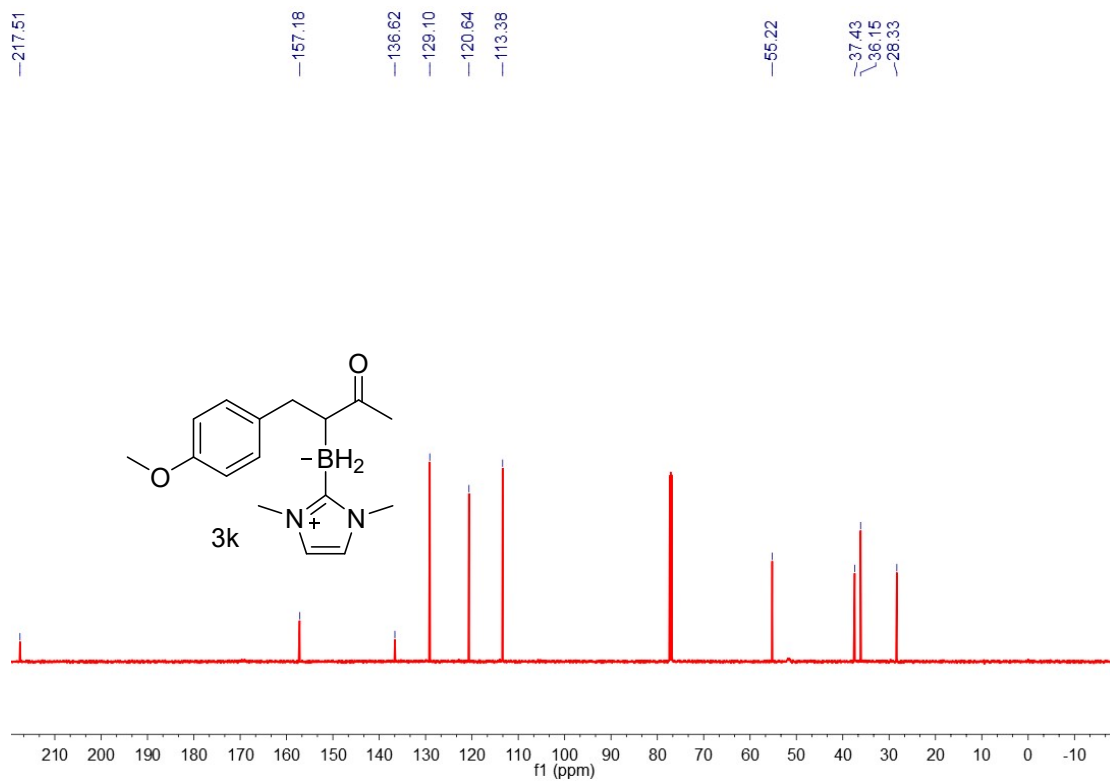
¹H NMR (600 MHz, CDCl₃)



¹³C NMR (151 MHz, CDCl₃)

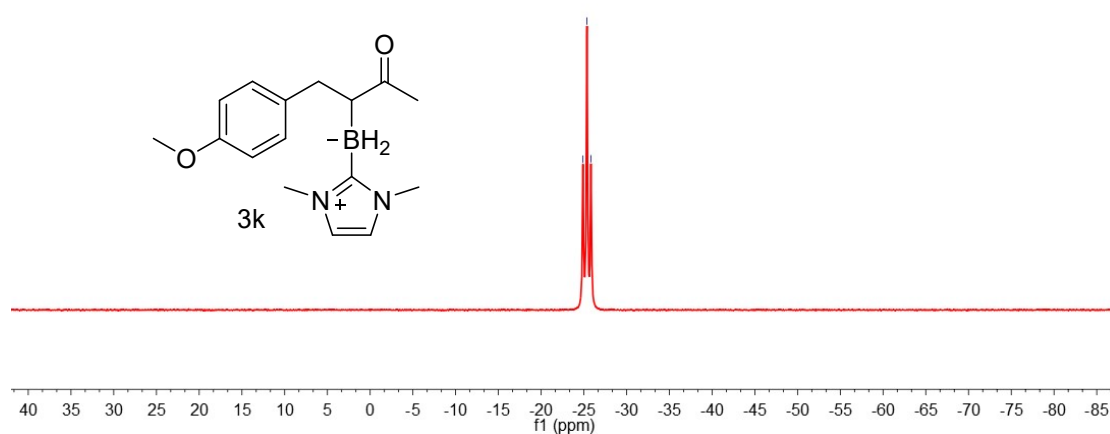




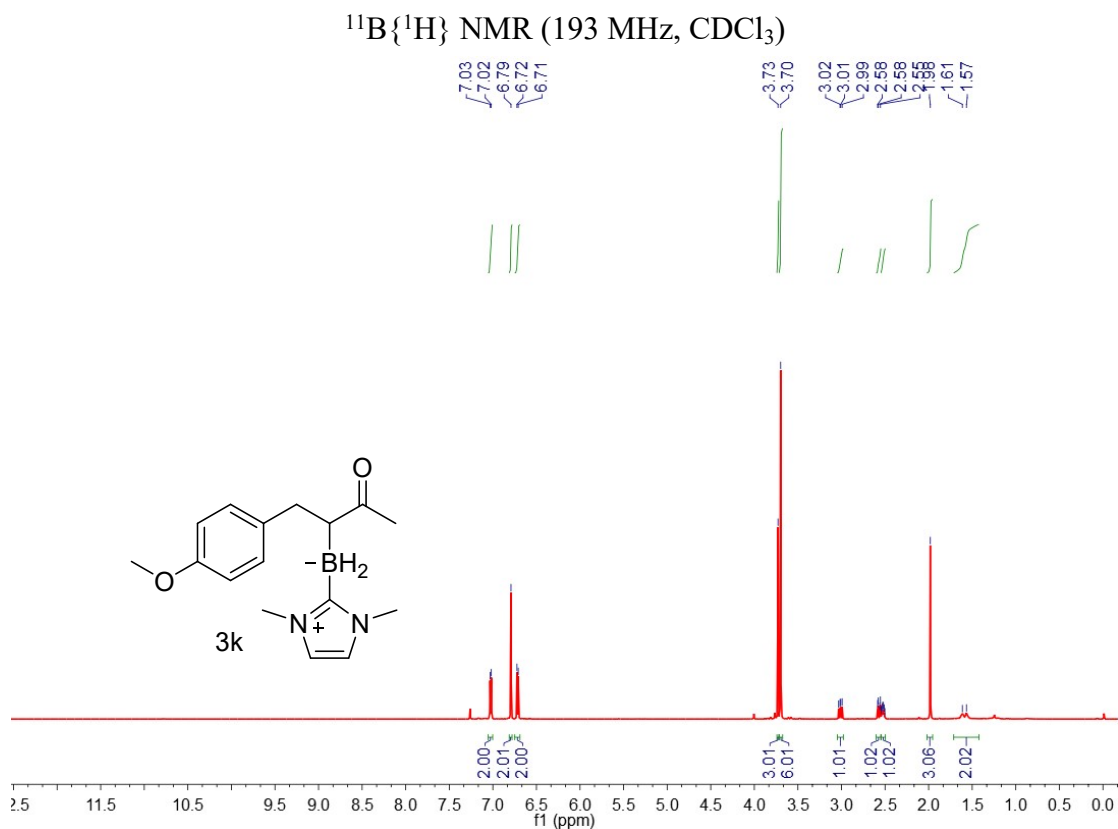
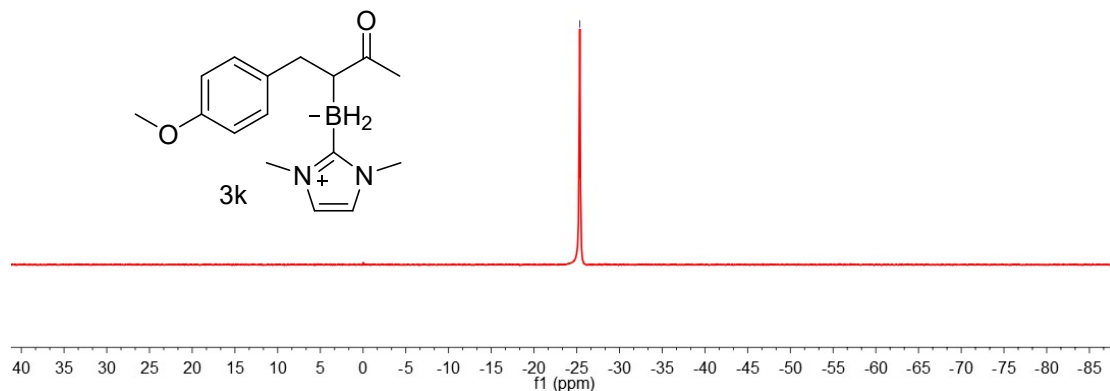


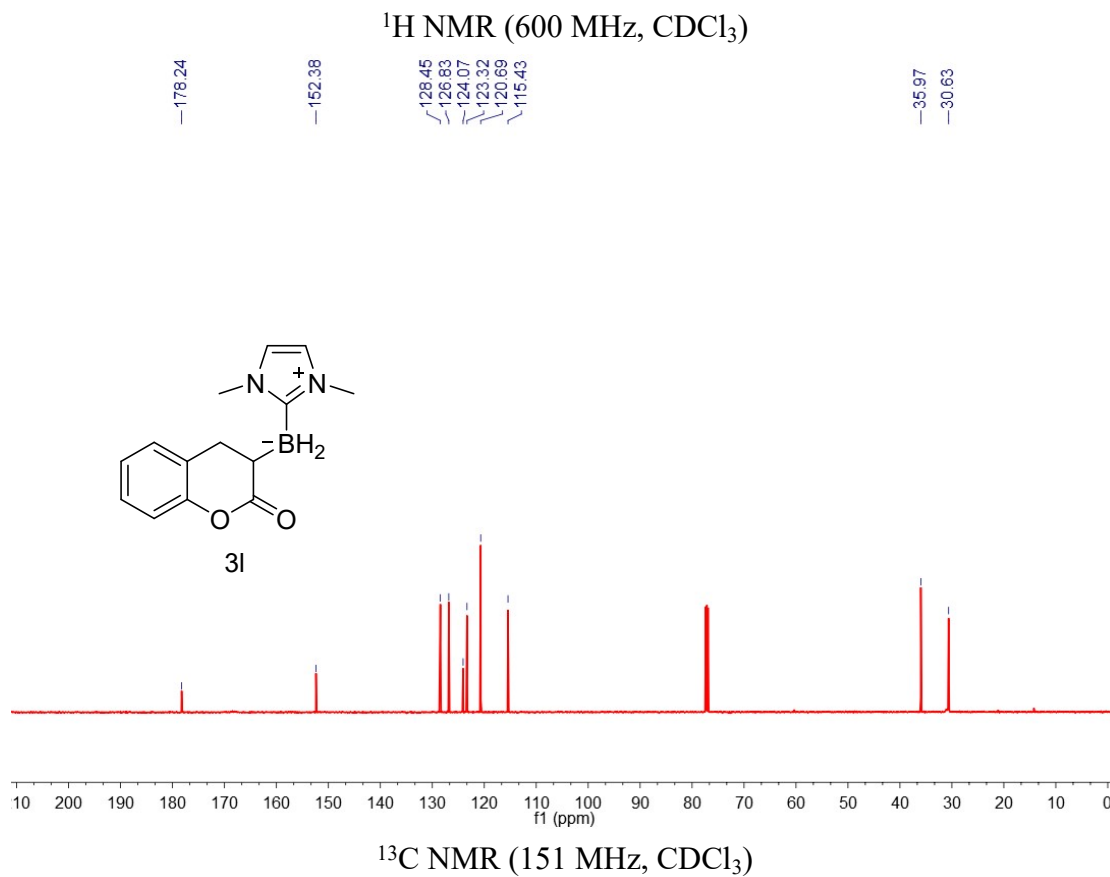
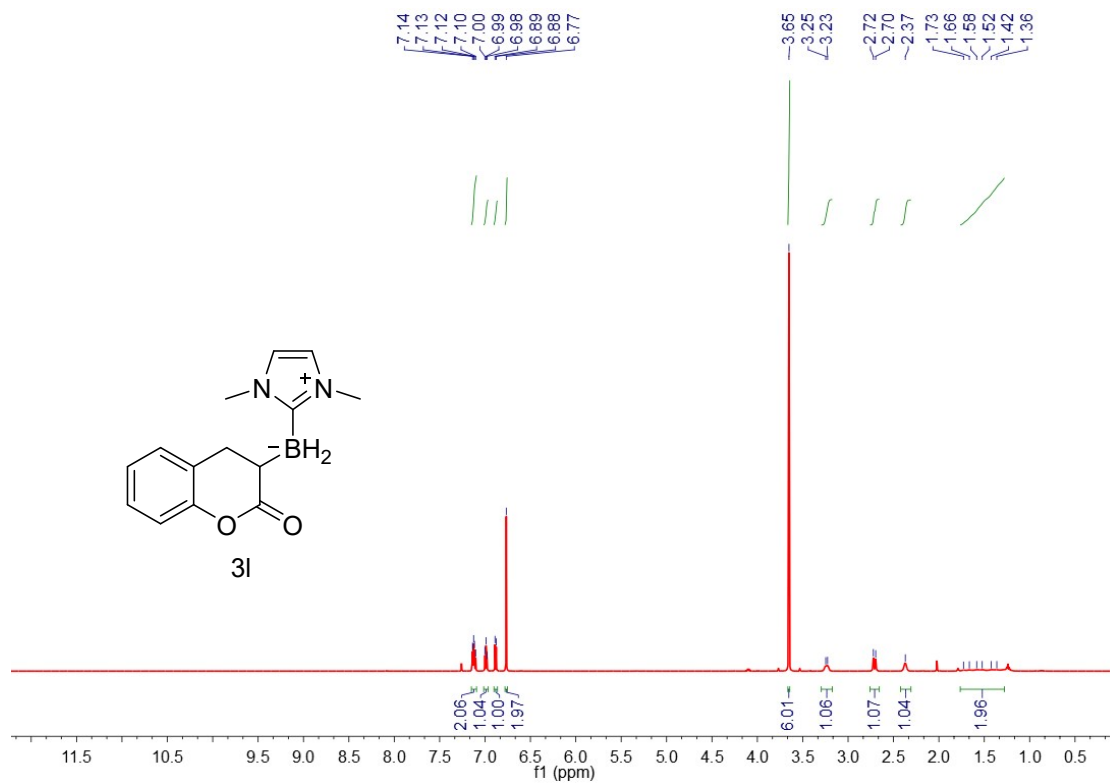
^{13}C NMR (151 MHz, CDCl_3)

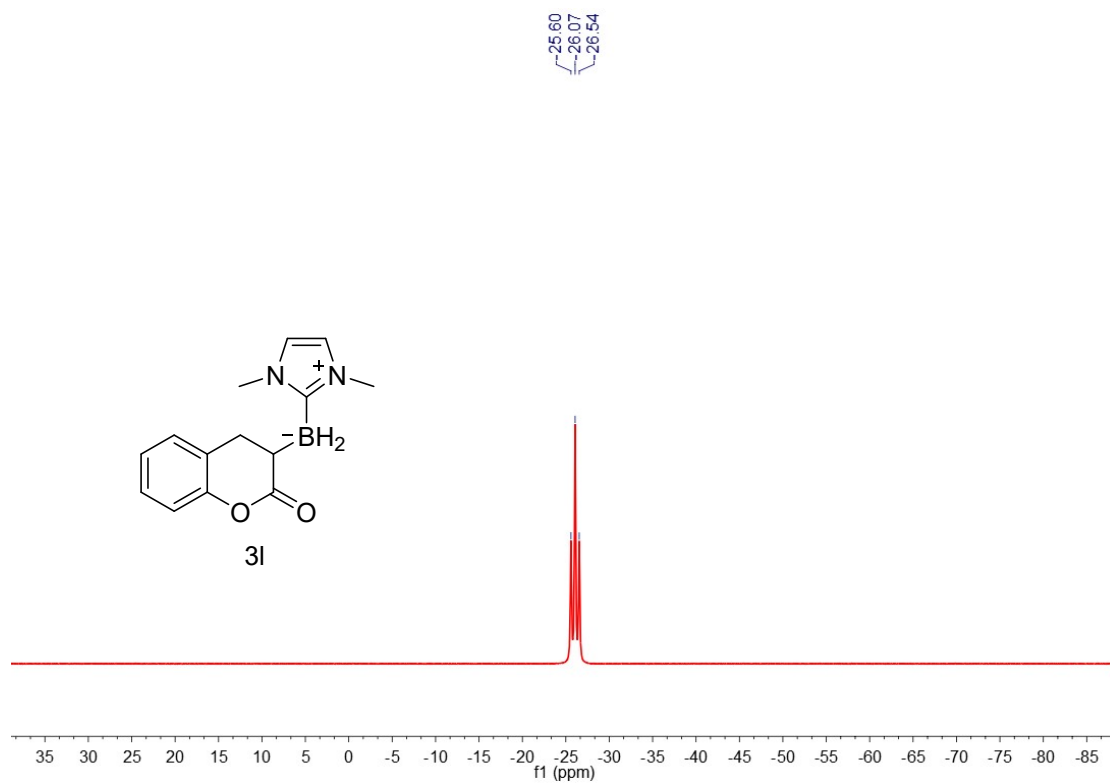
24.90
25.36
25.83



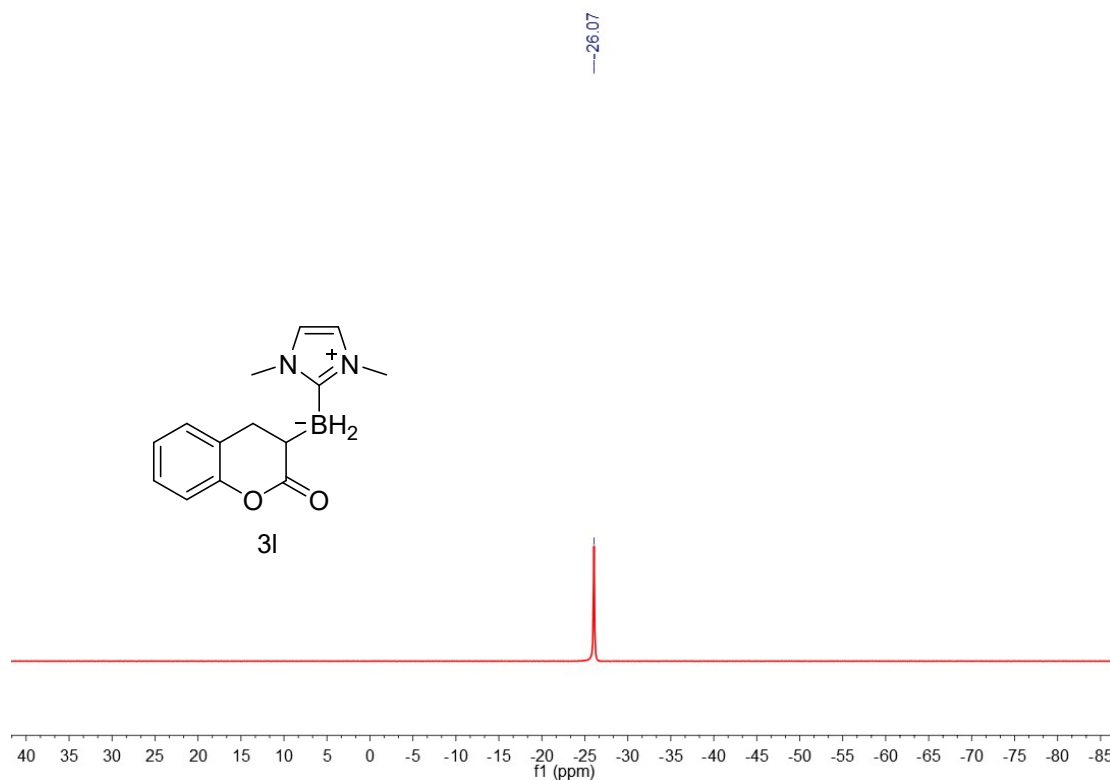
^{11}B NMR (193 MHz, CDCl_3)



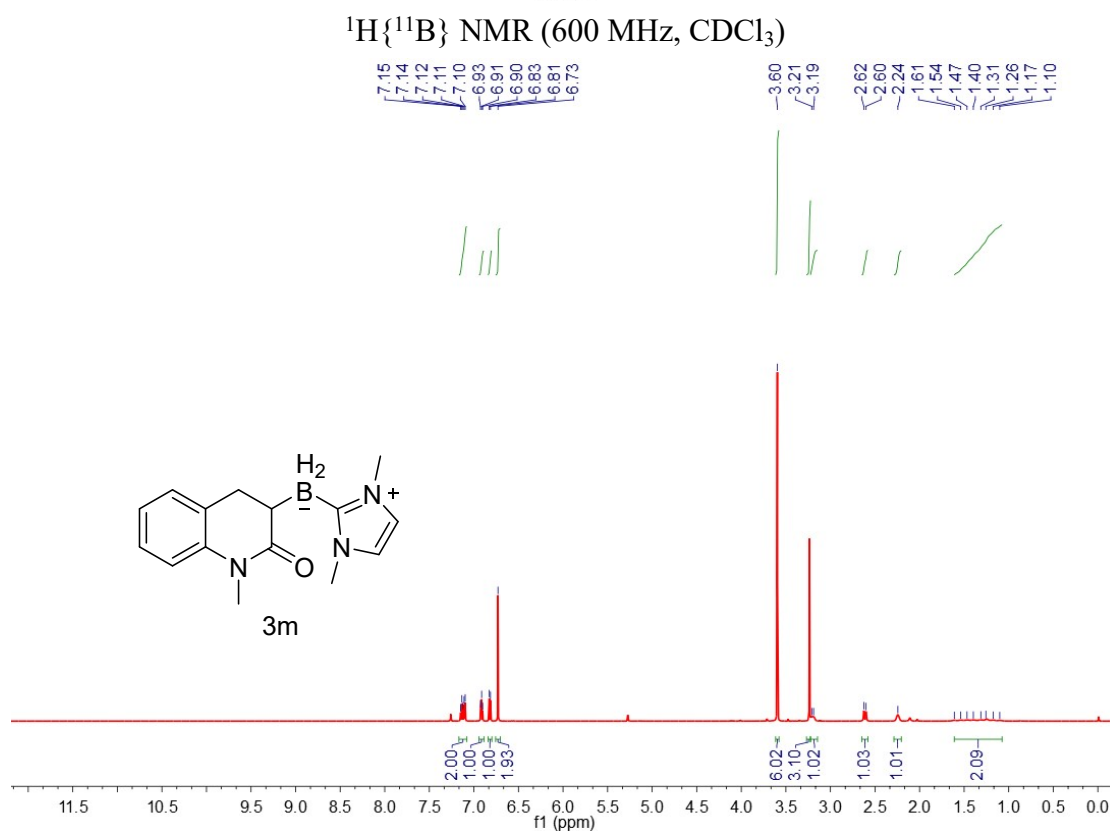
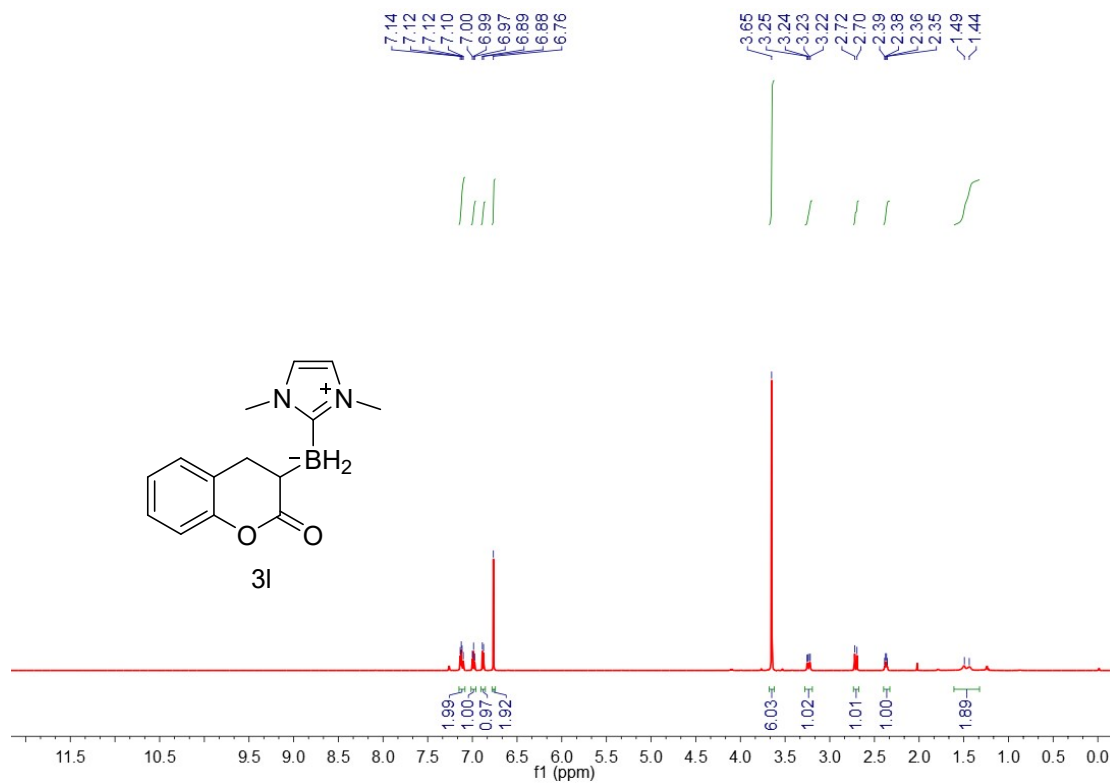


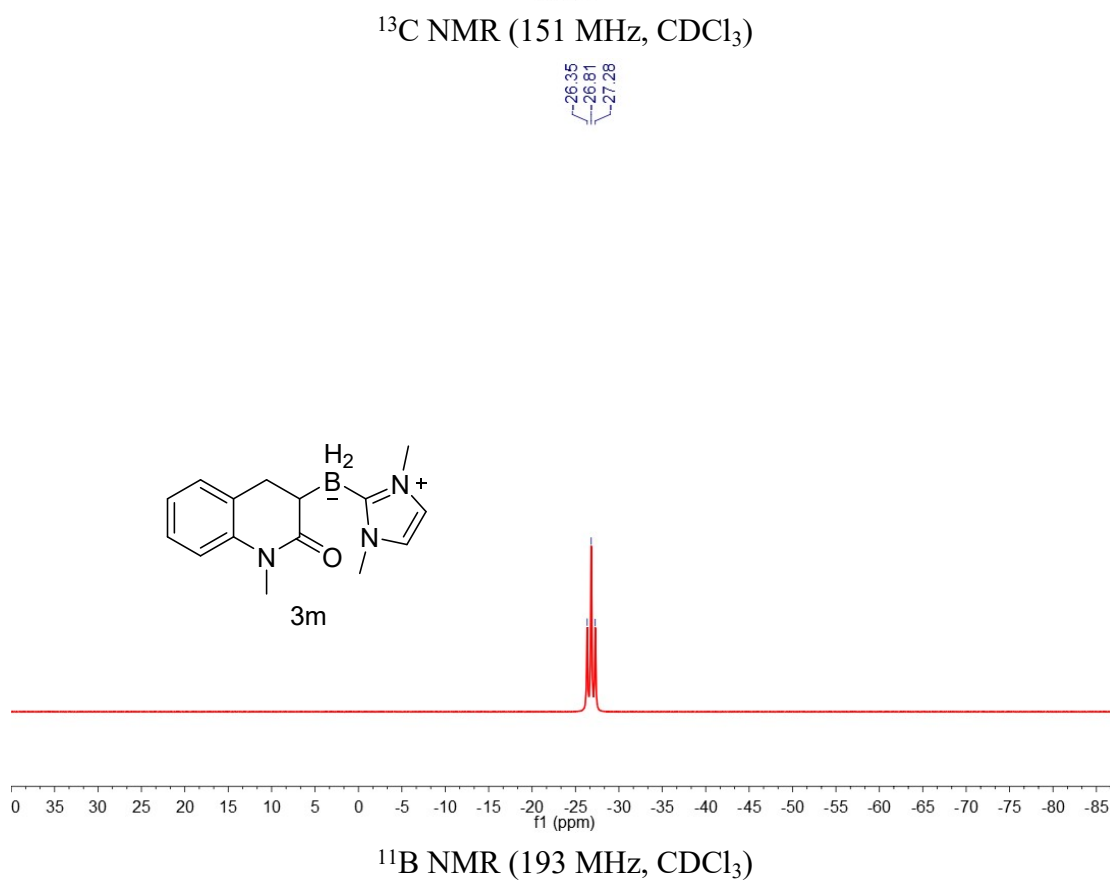
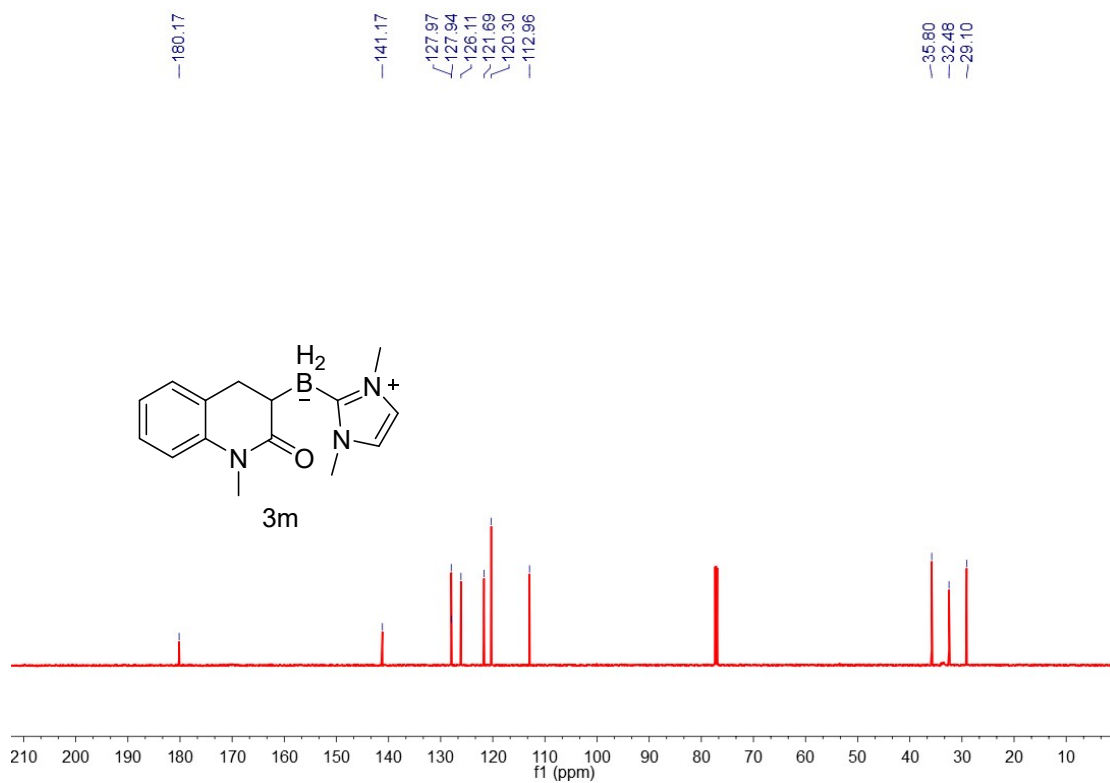


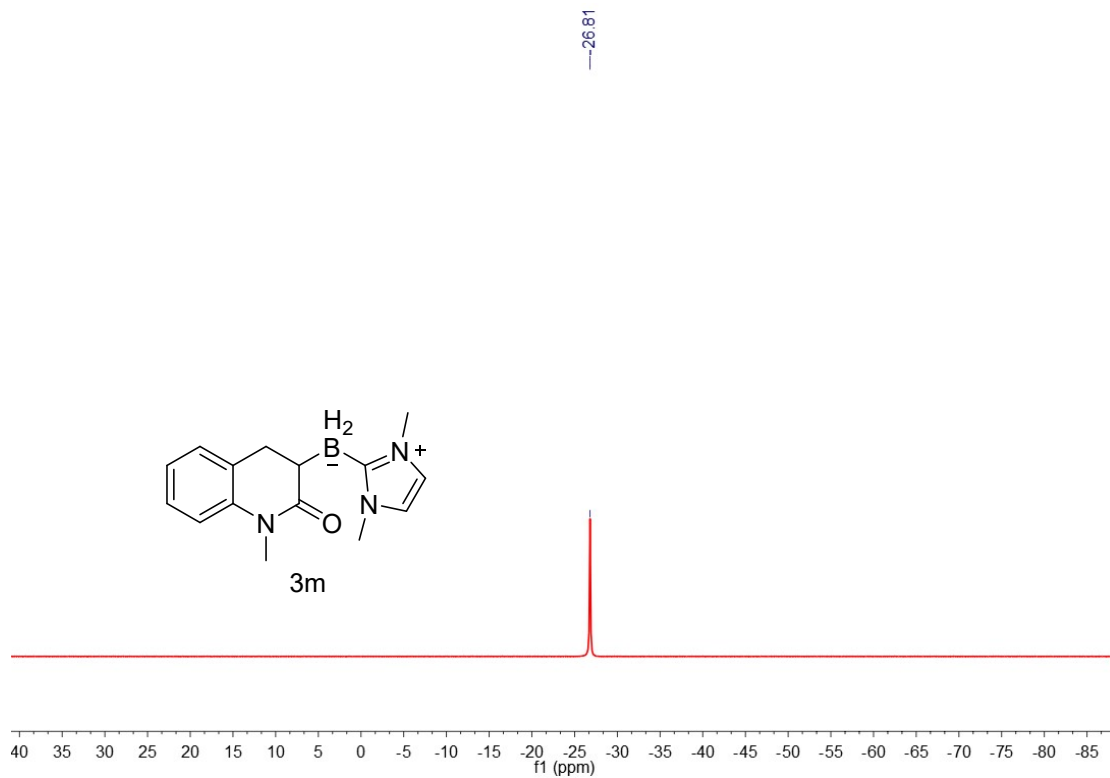
^{11}B NMR (193 MHz, CDCl_3)



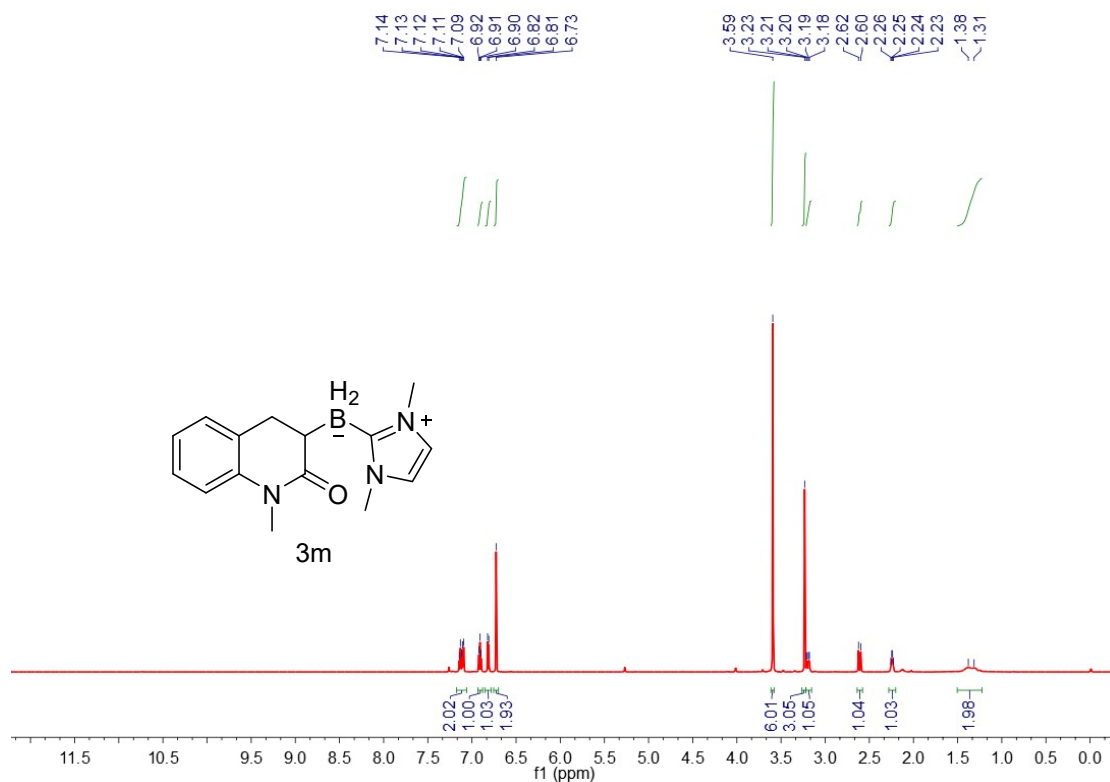
$^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3)



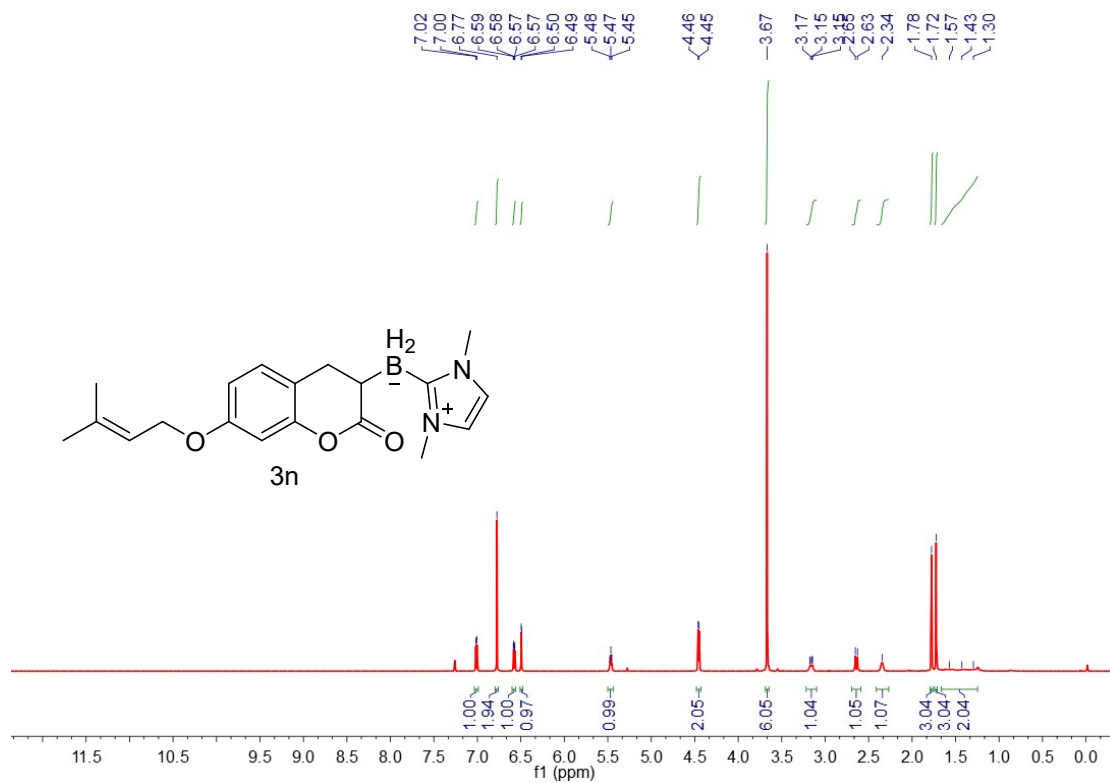




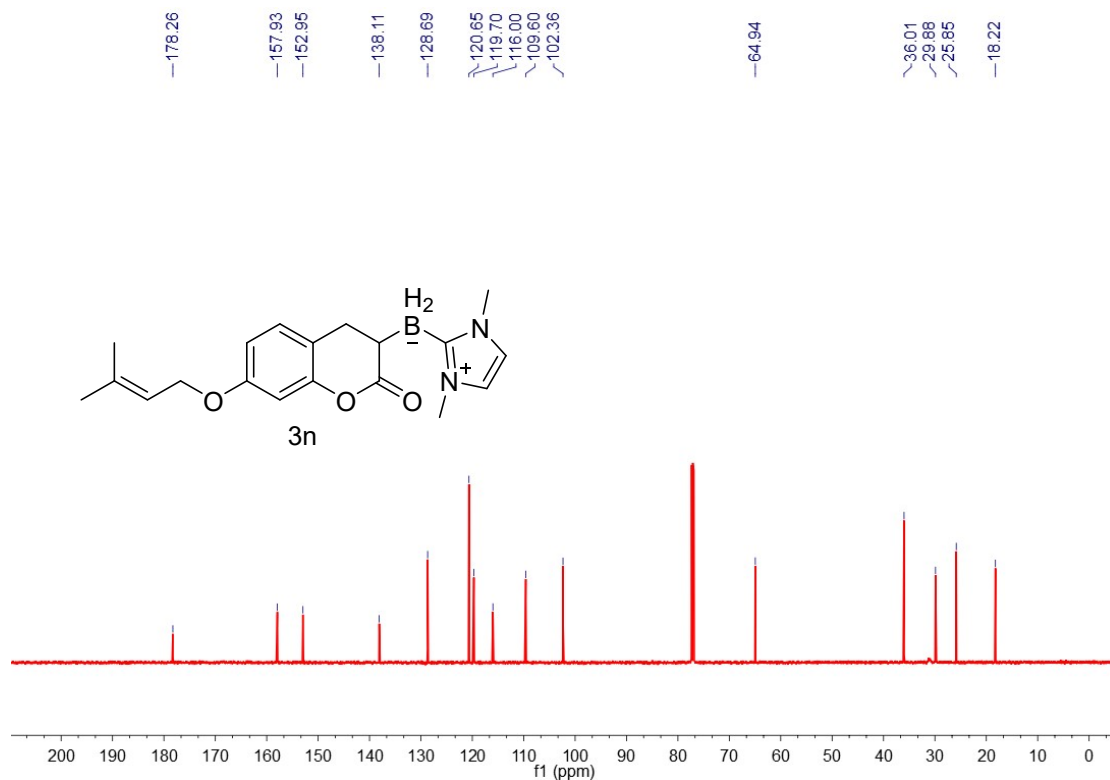
$^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3)



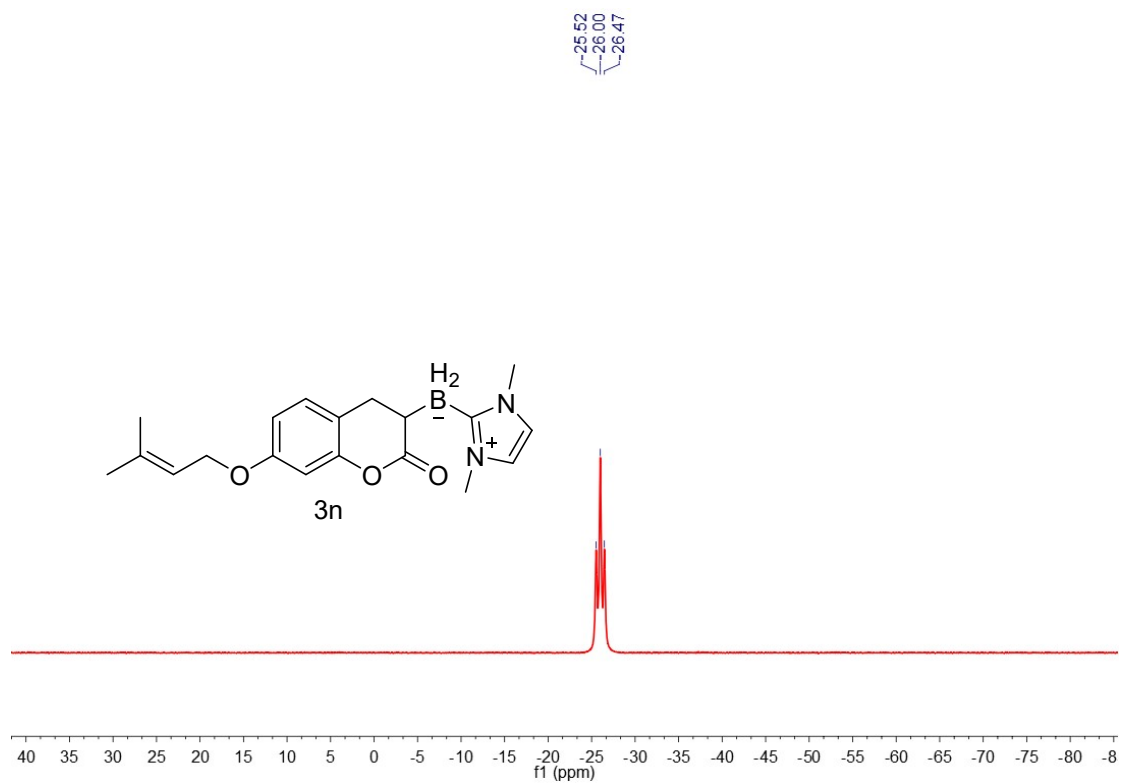
$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3)



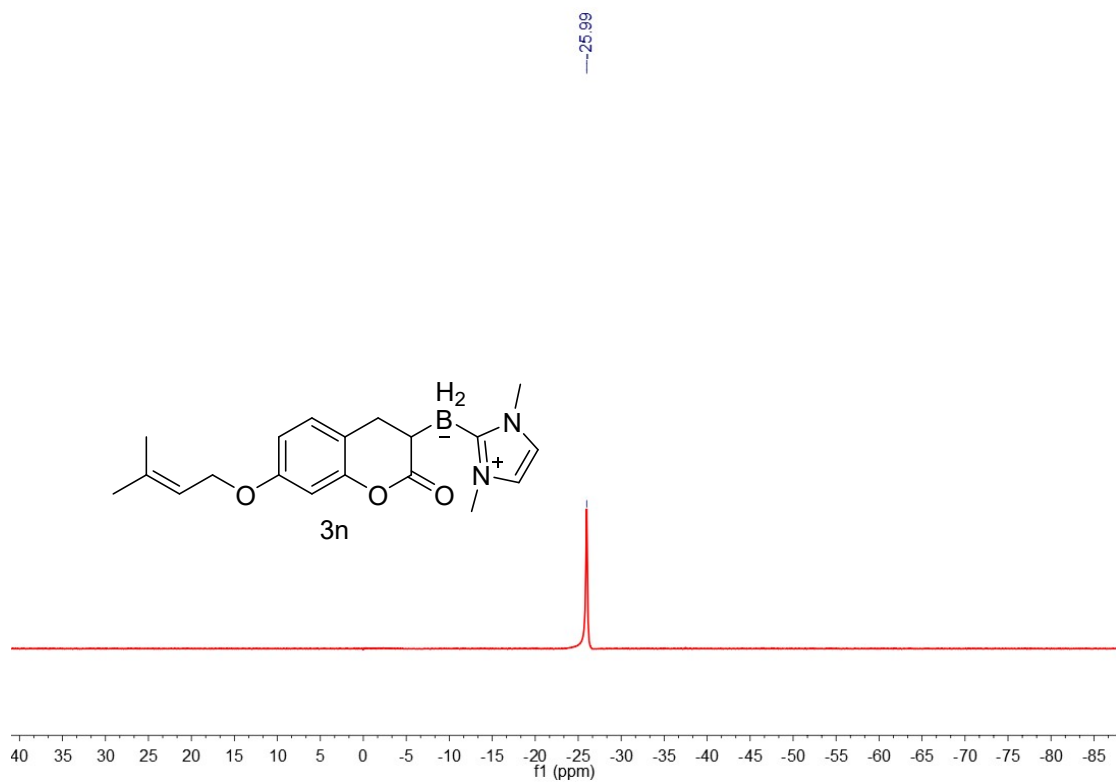
¹H NMR (600 MHz, CDCl₃)



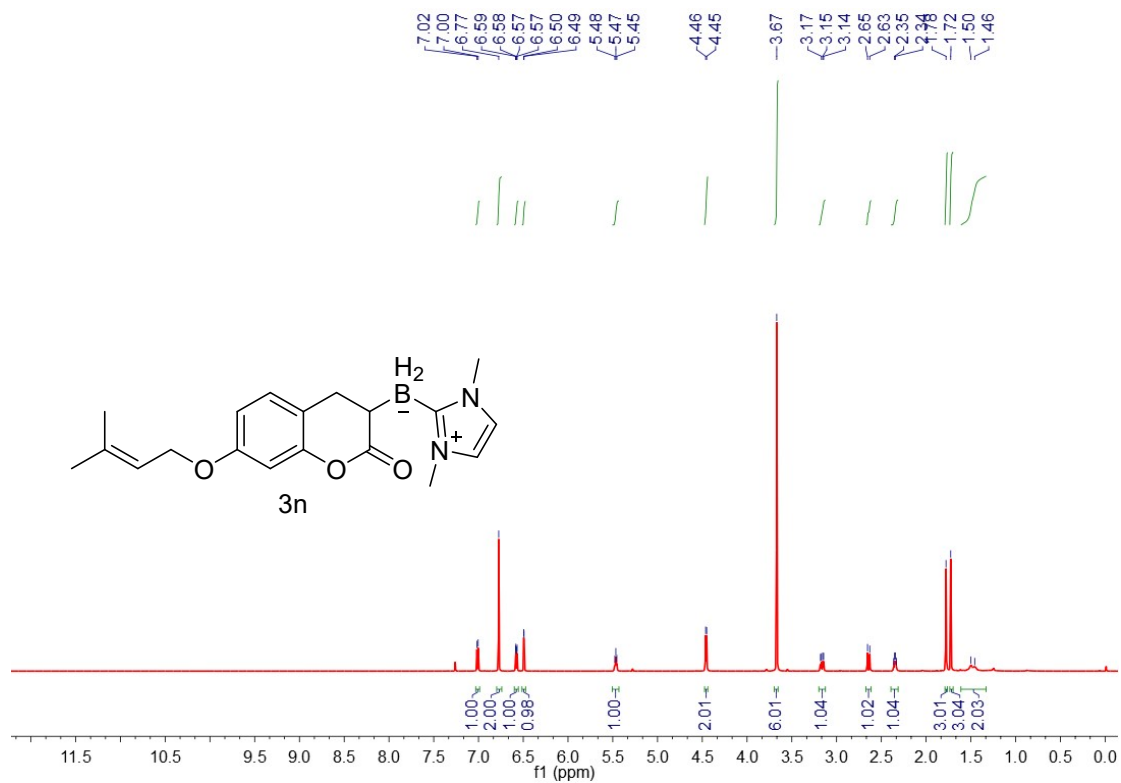
¹³C NMR (151 MHz, CDCl₃)



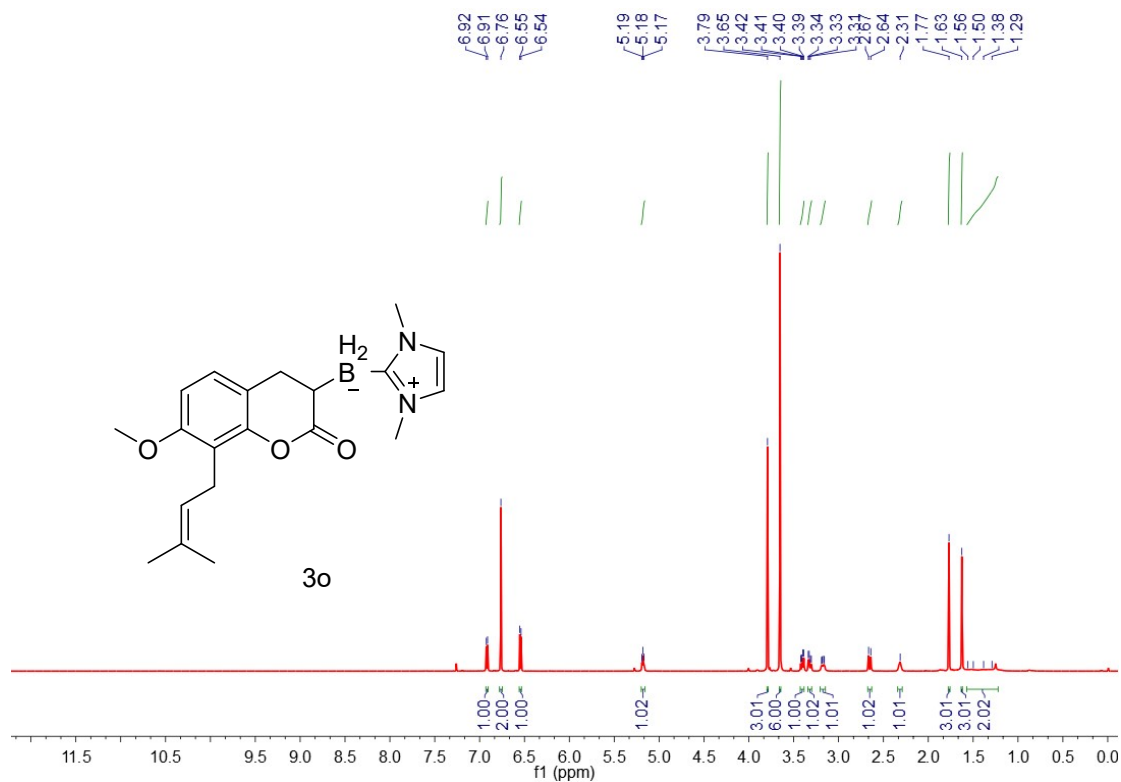
¹¹B NMR (193 MHz, CDCl₃)



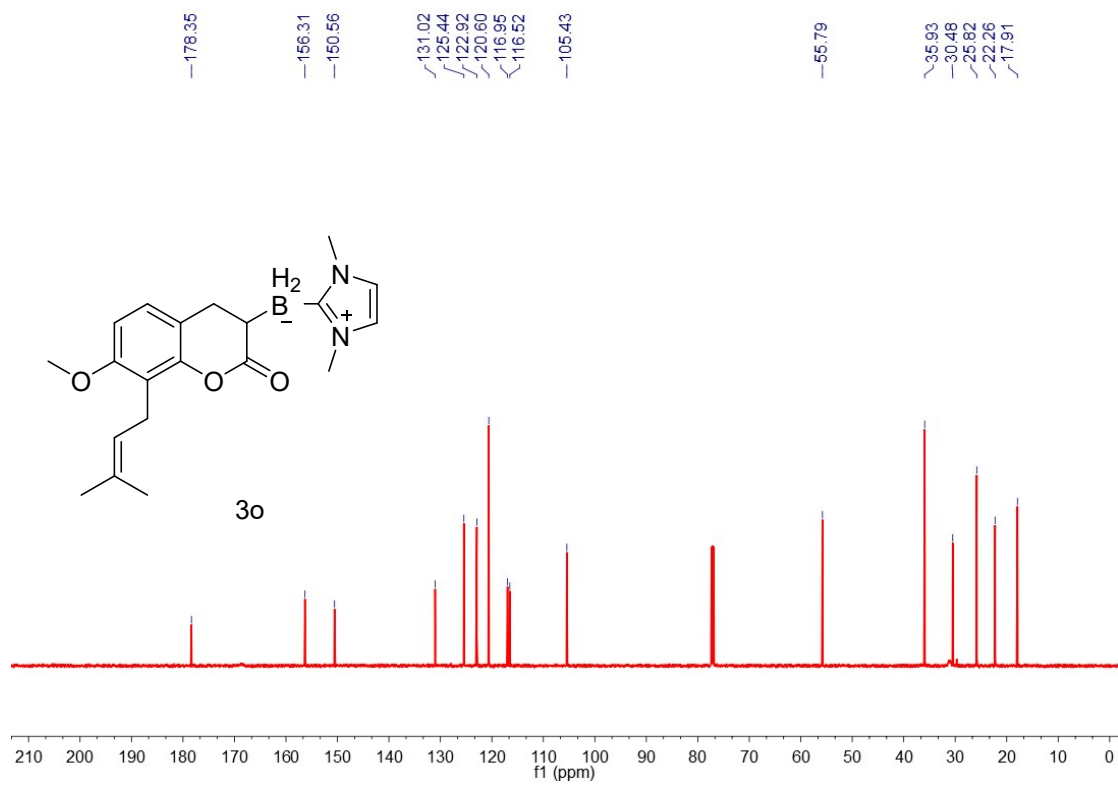
¹¹B{¹H} NMR (193 MHz, CDCl₃)



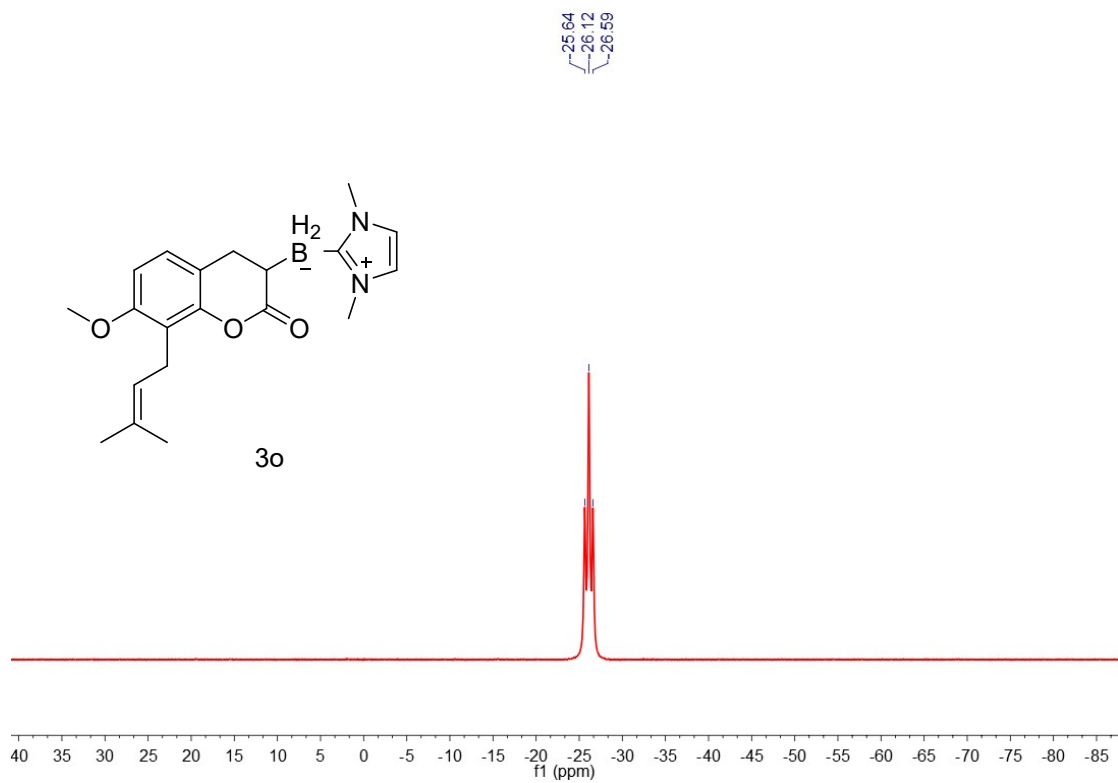
$^1\text{H}\{^1\text{B}\}$ NMR (600 MHz, CDCl_3)



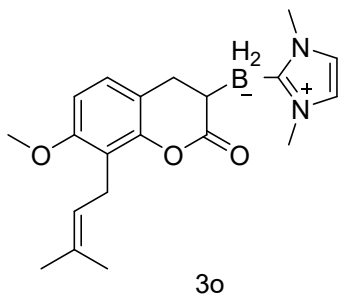
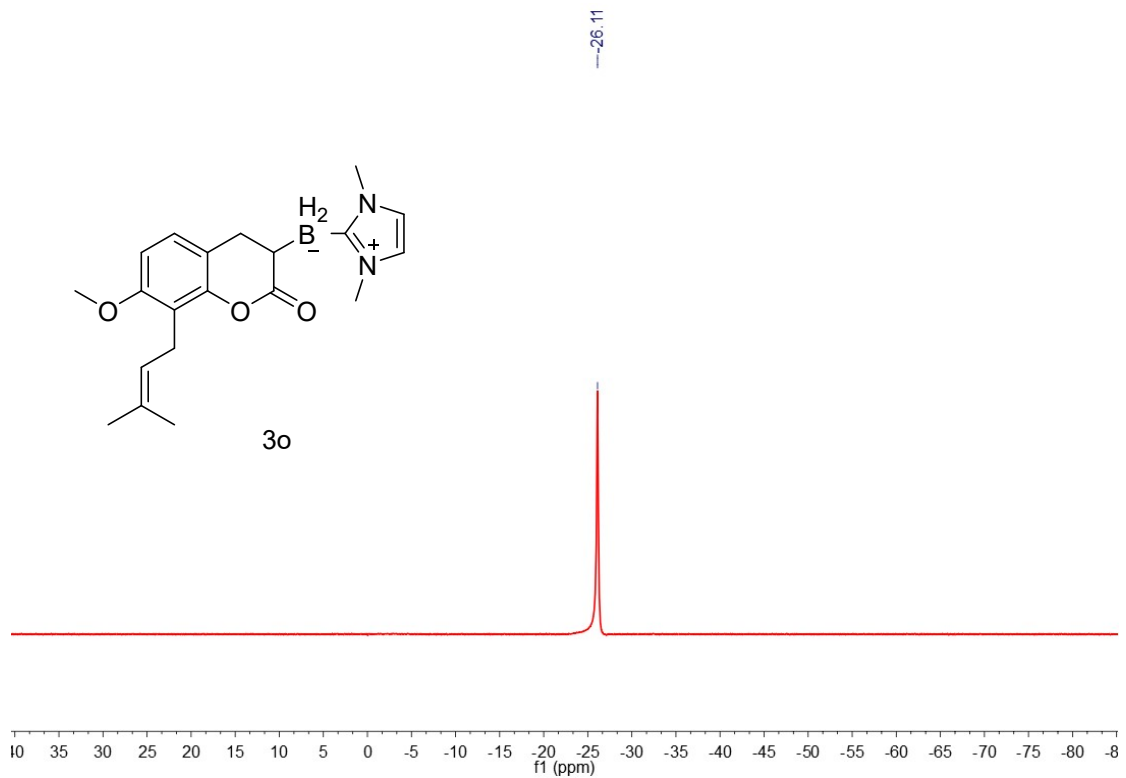
^1H NMR (600 MHz, CDCl_3)



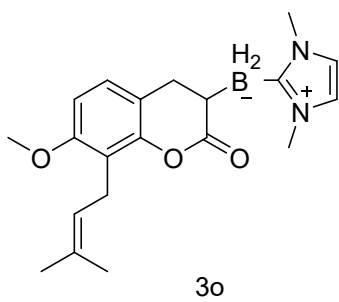
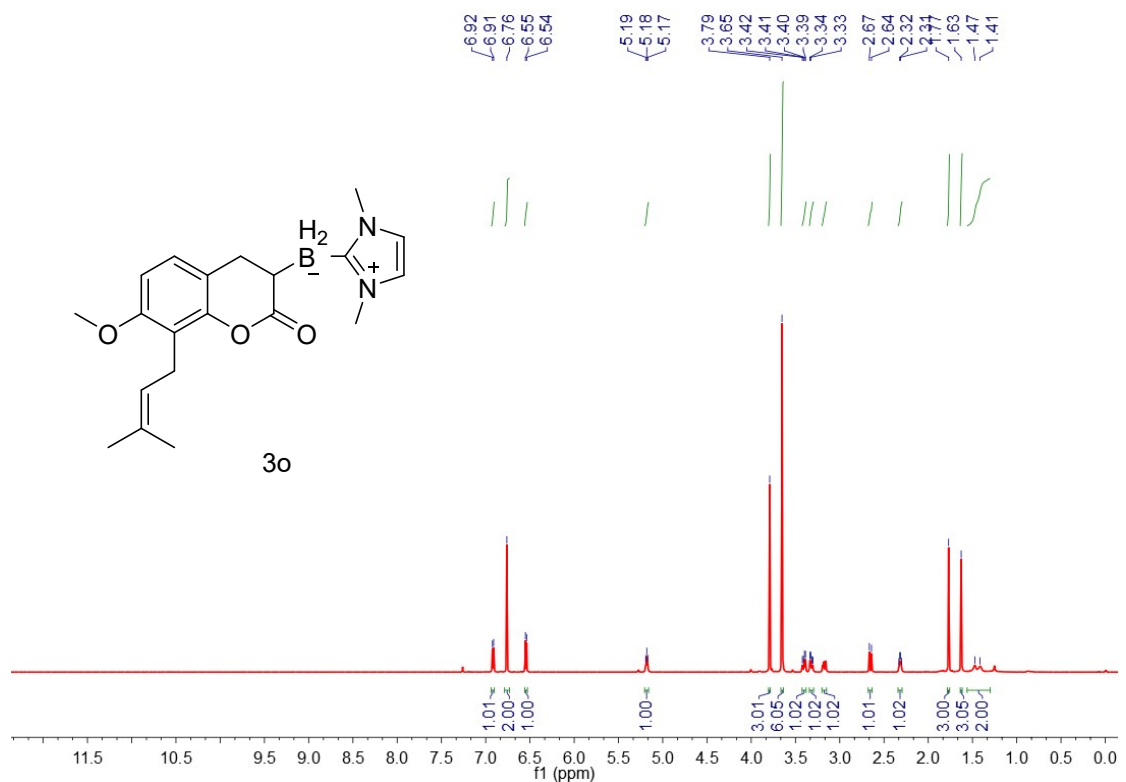
^{13}C NMR (151 MHz, CDCl_3)



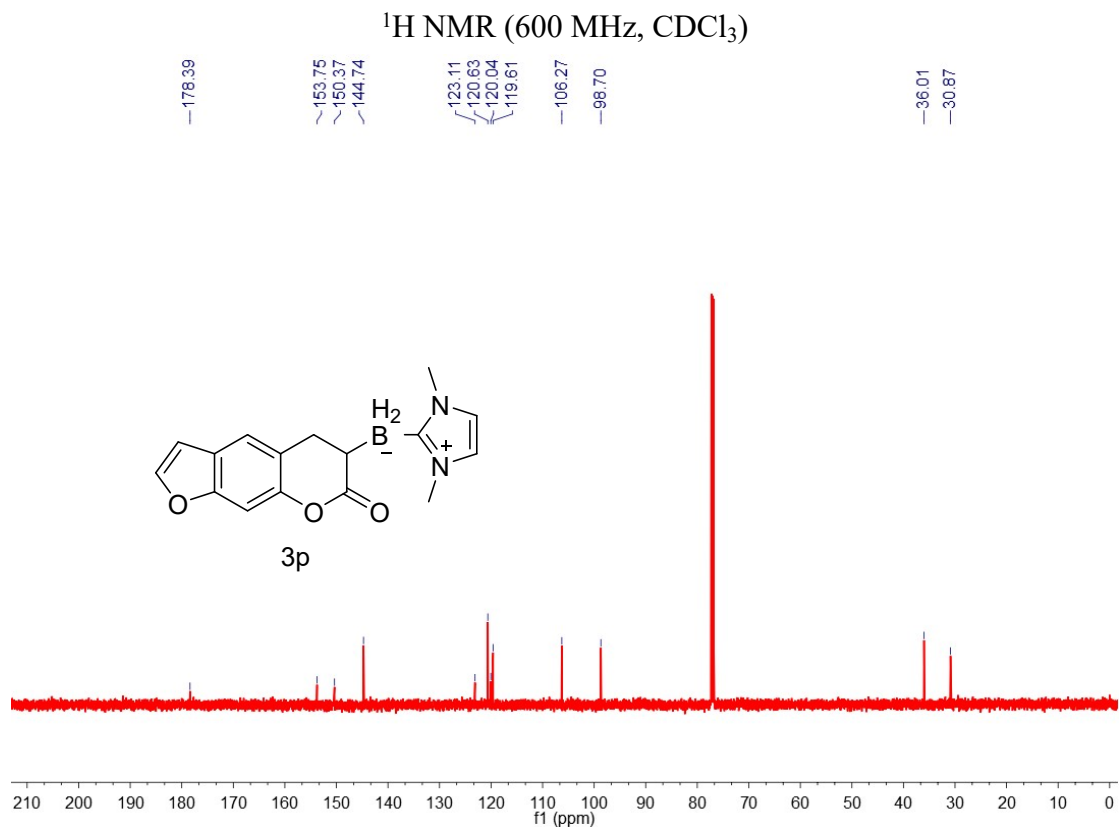
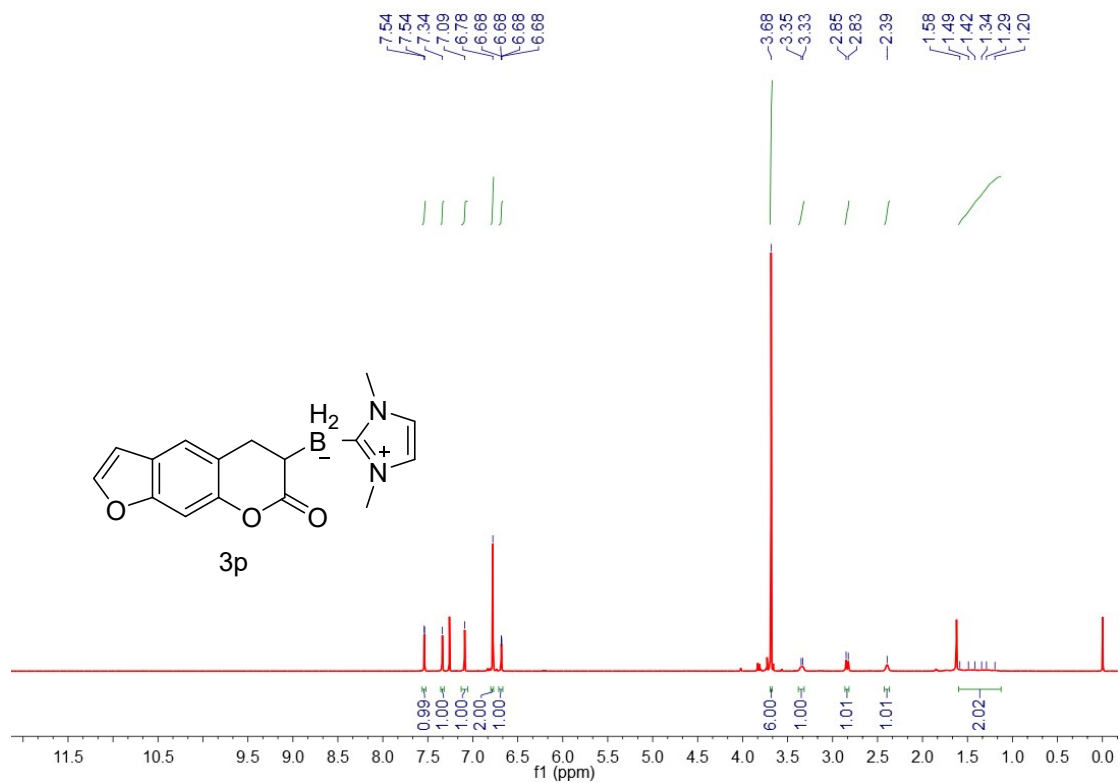
^{11}B NMR (193 MHz, CDCl_3)

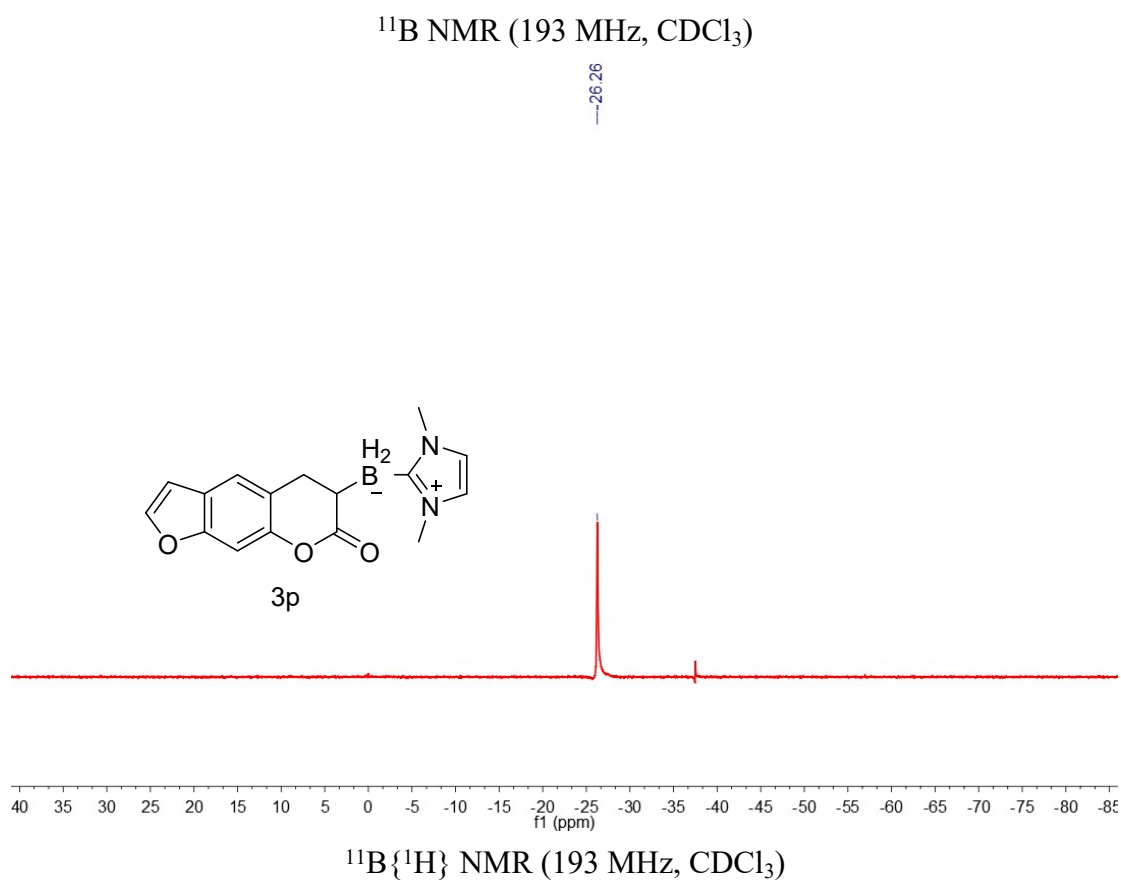
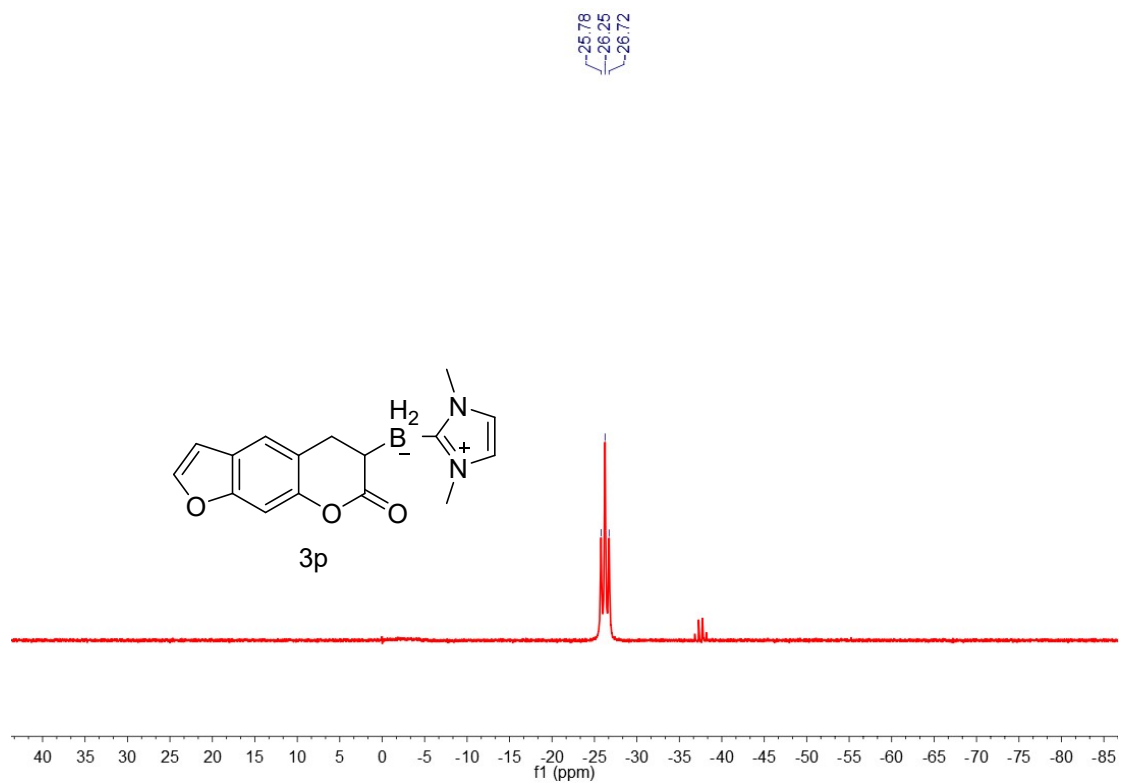


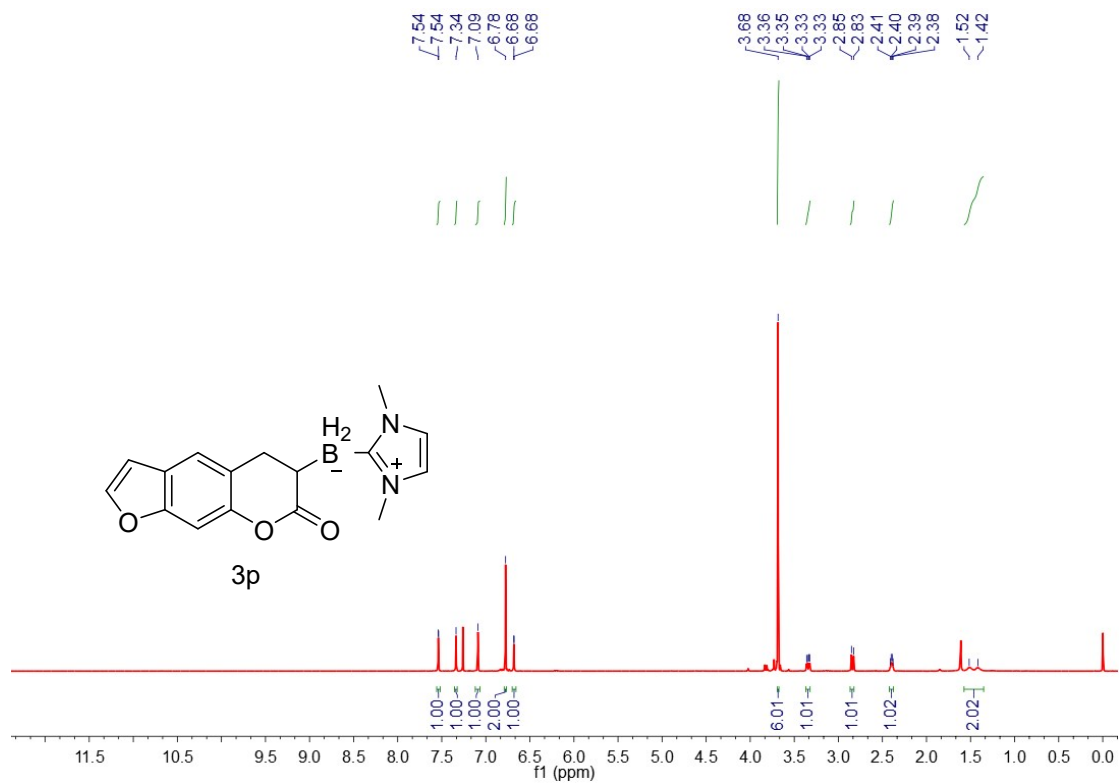
$^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3)



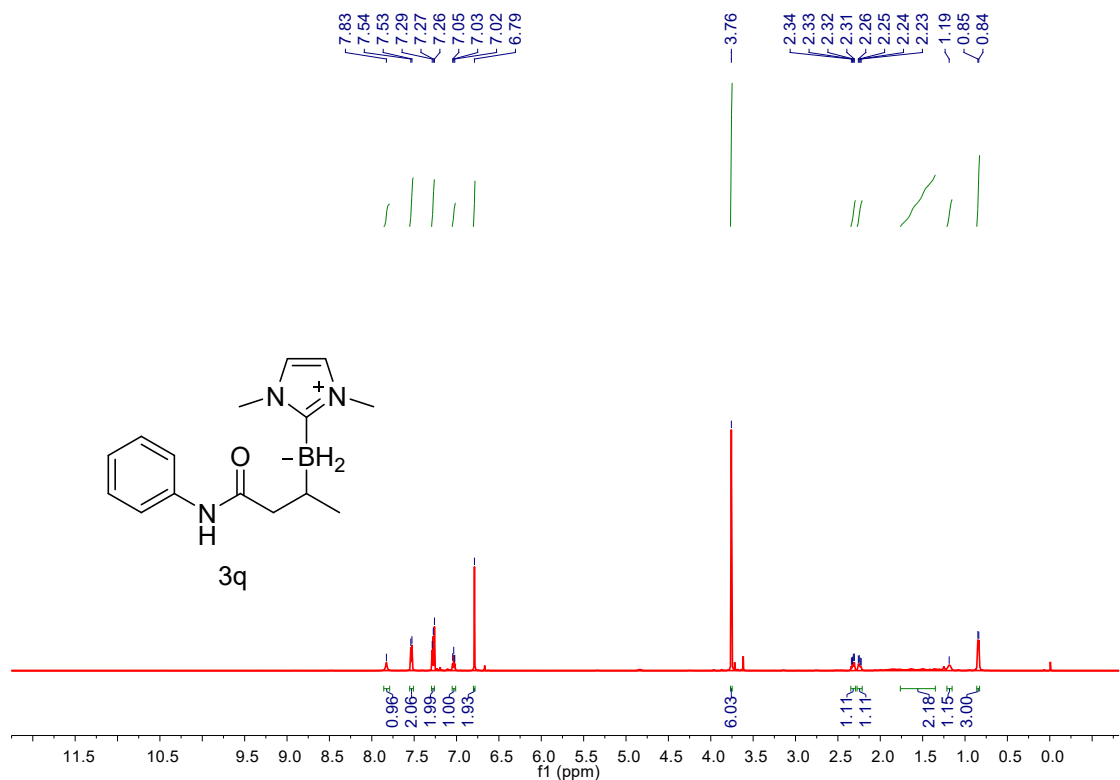
$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3)



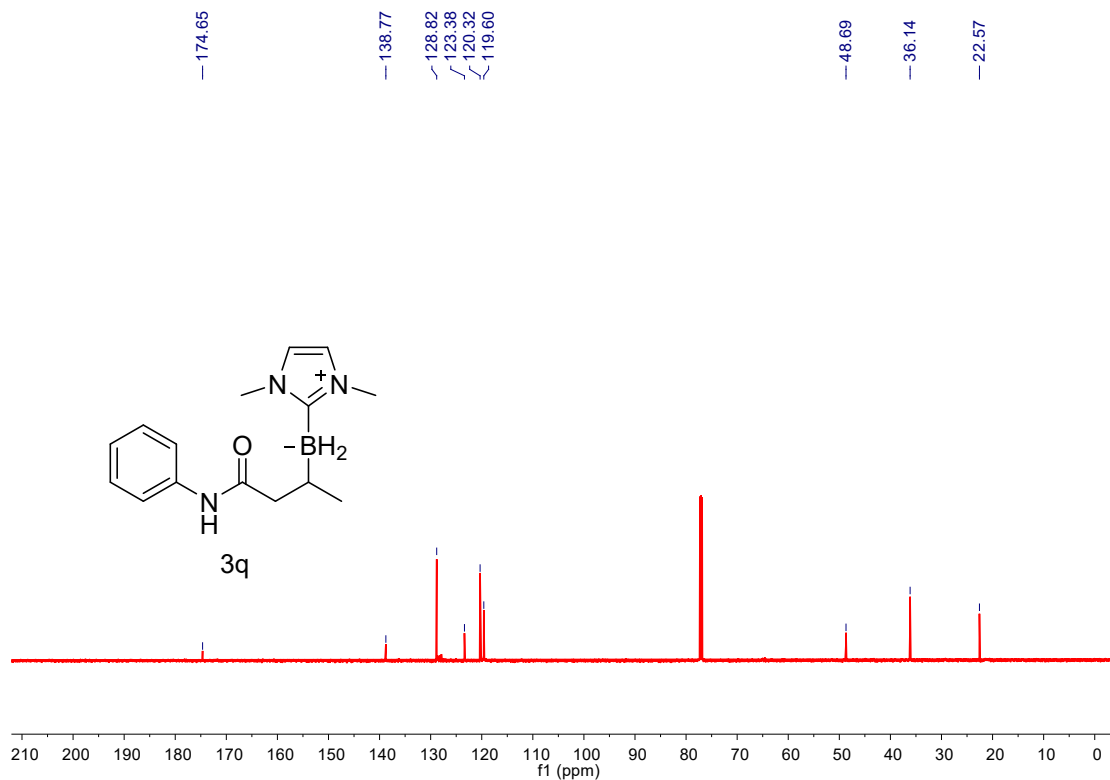




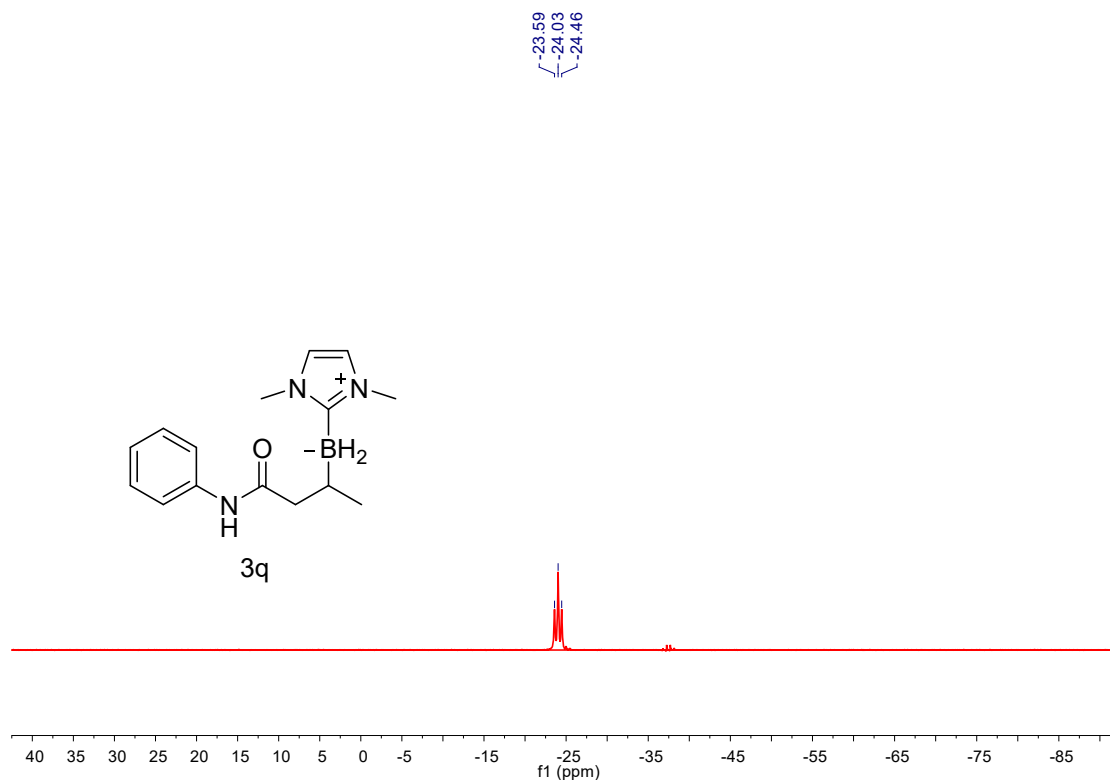
$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3)



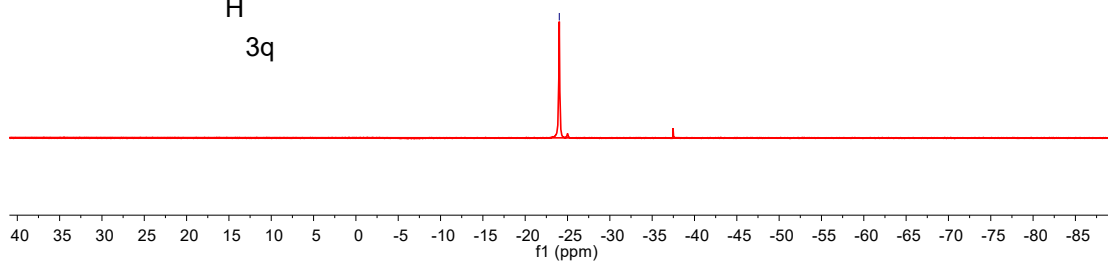
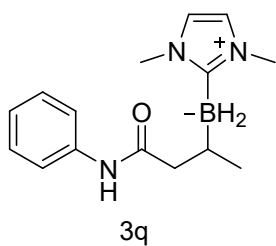
^1H NMR (600 MHz, CDCl_3)



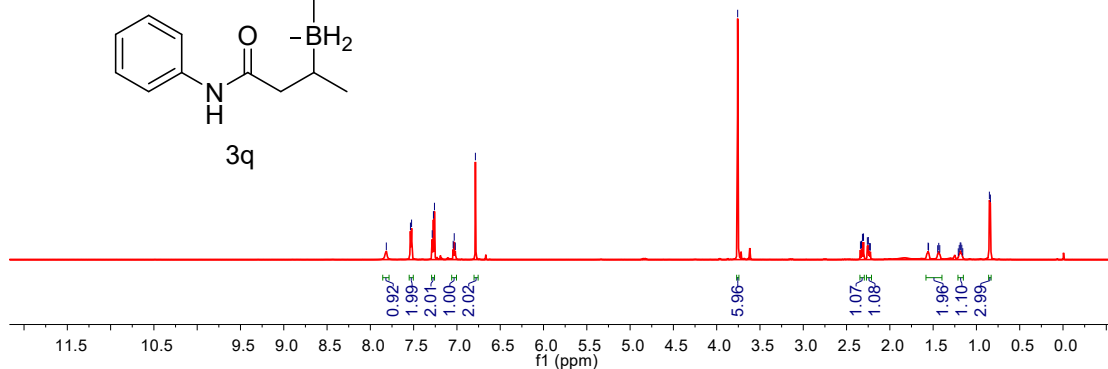
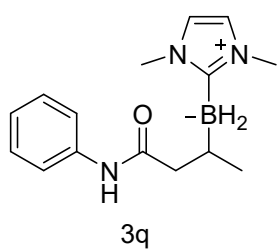
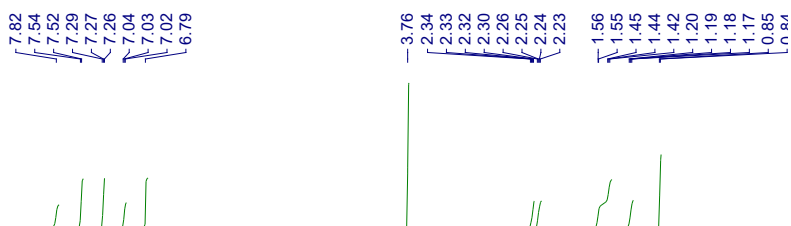
^{13}C NMR (151 MHz, CDCl_3)



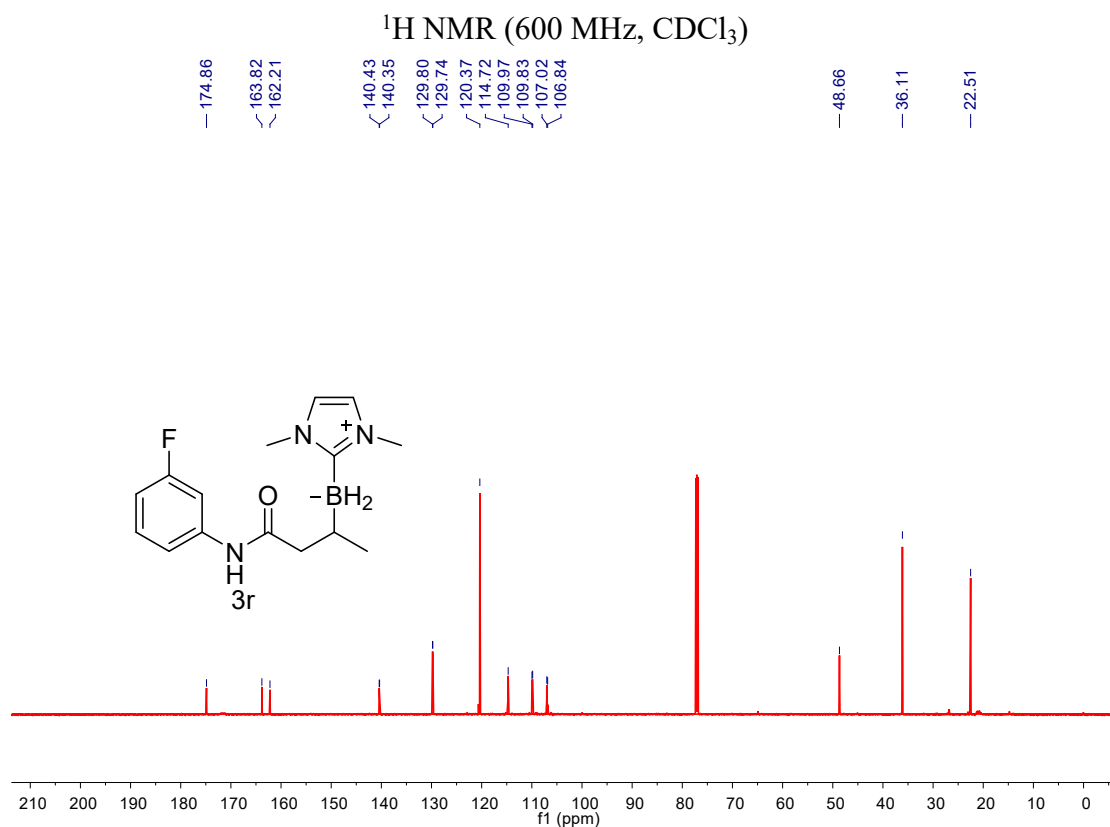
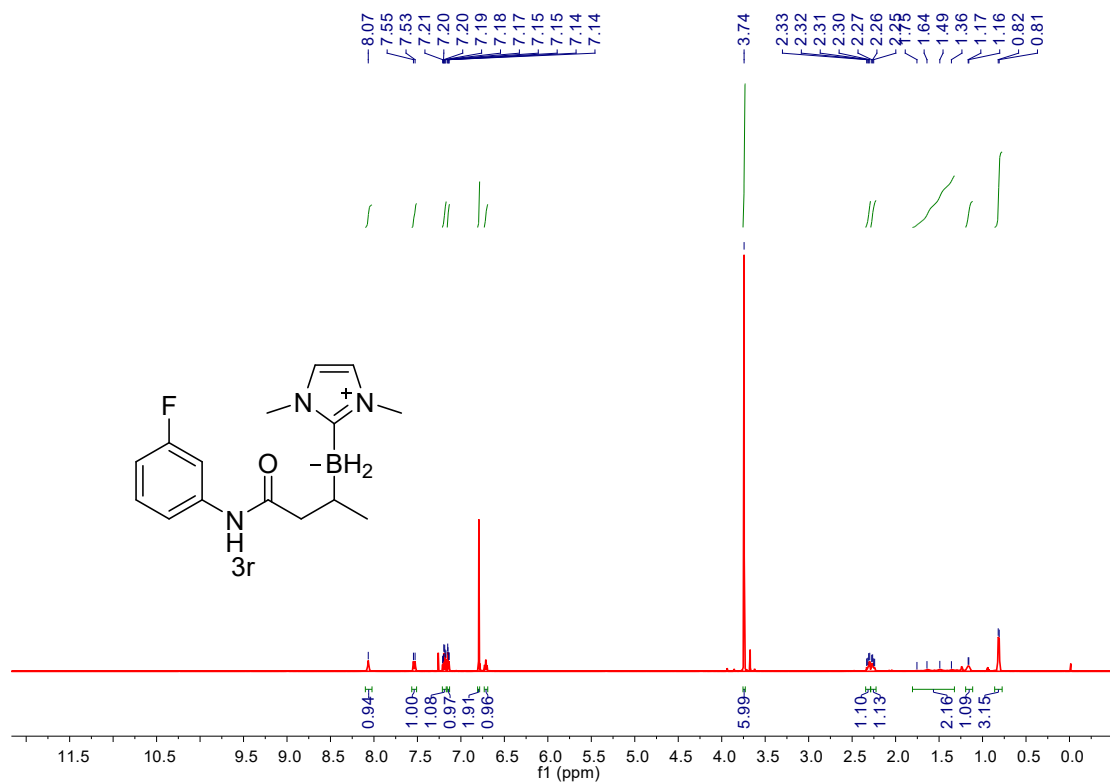
^{11}B NMR (193 MHz, CDCl_3)



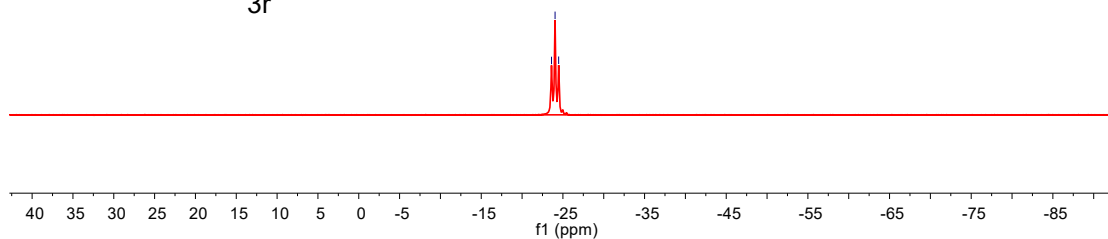
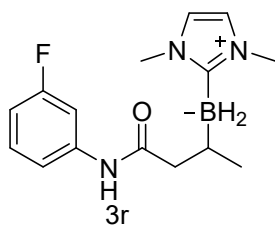
$^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3)



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

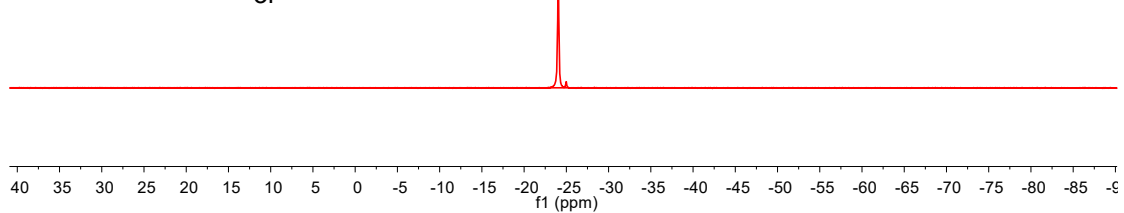
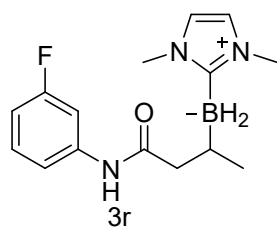


-23.60
-24.04
-24.48

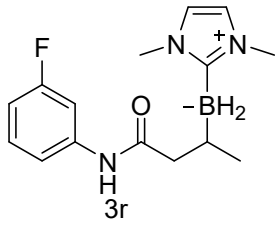
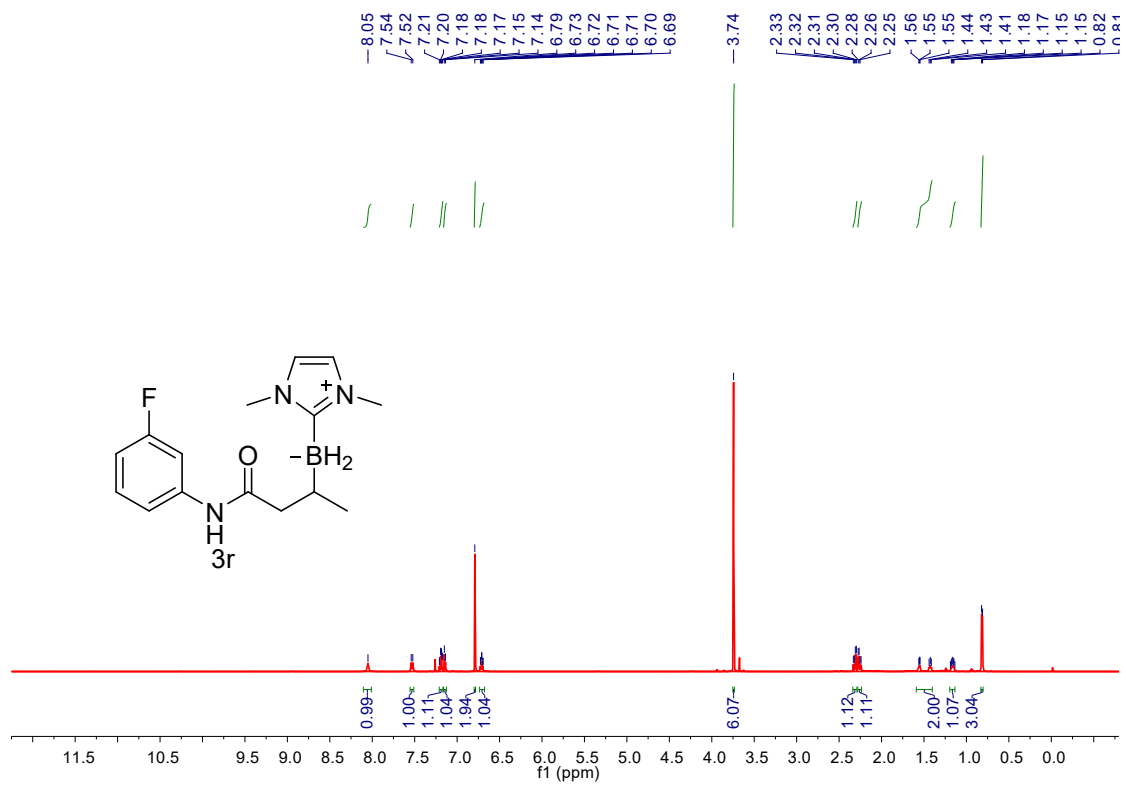


^{11}B NMR (193 MHz, CDCl_3)

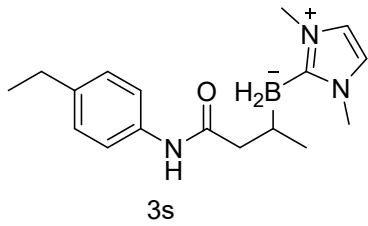
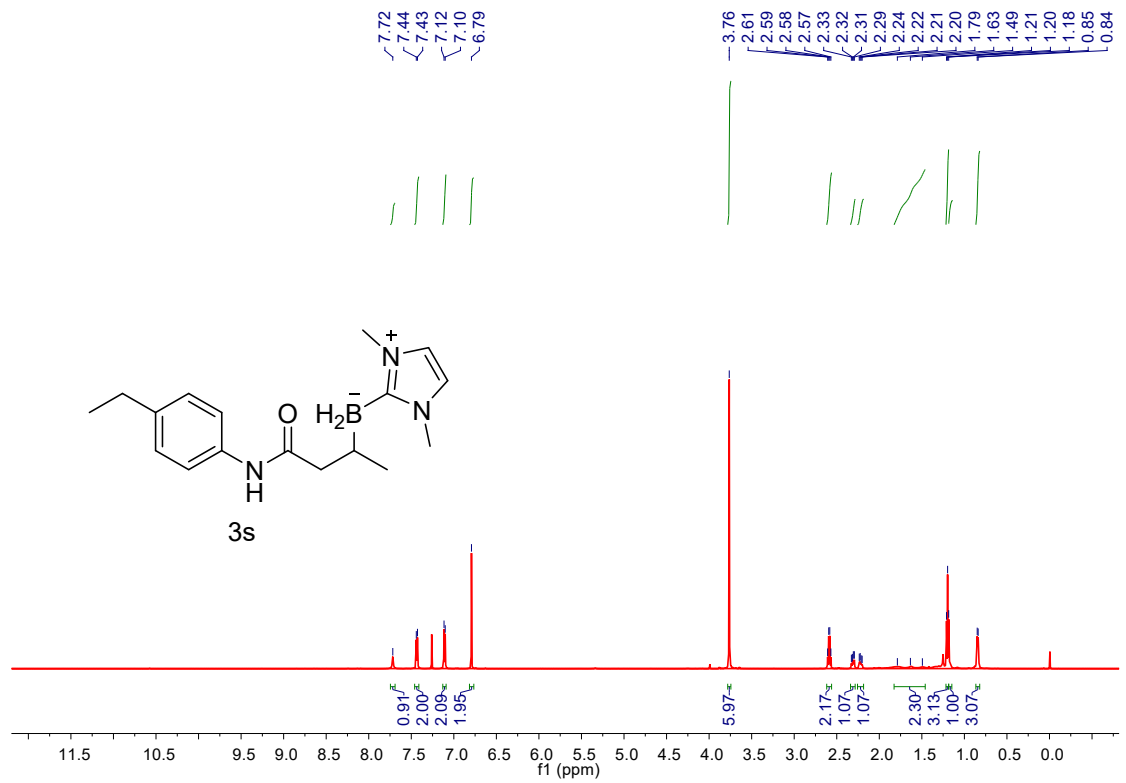
-24.04



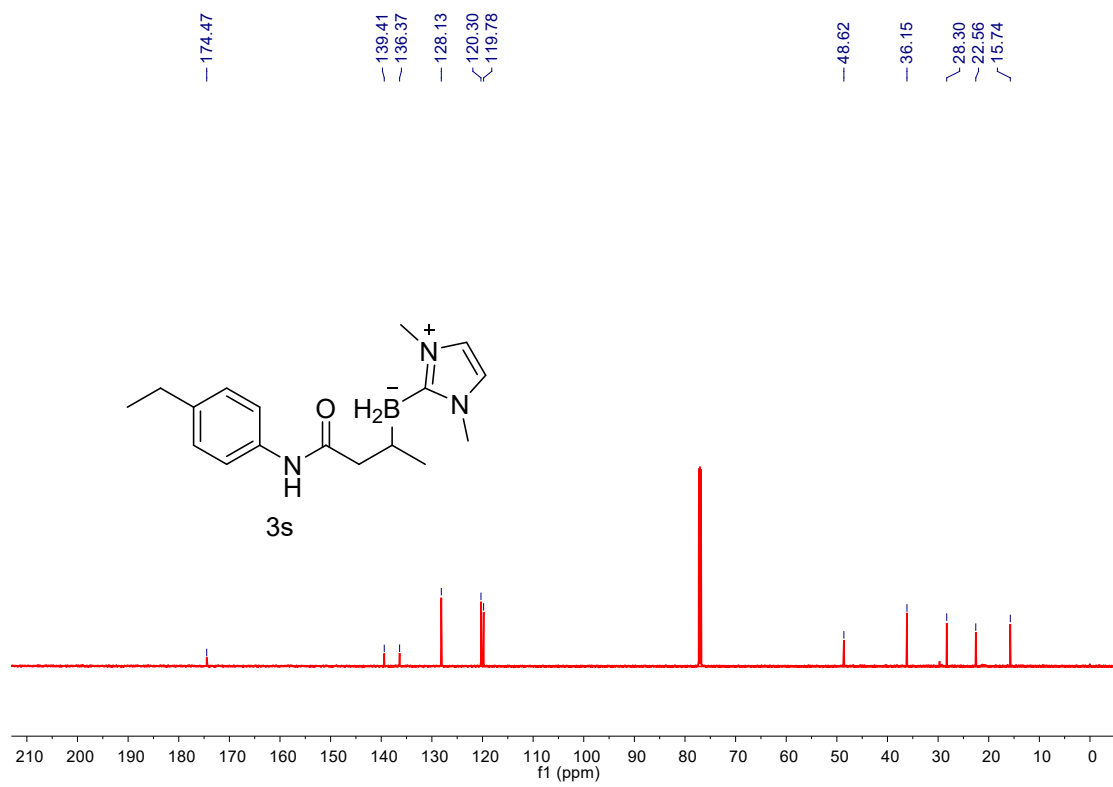
$^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3)



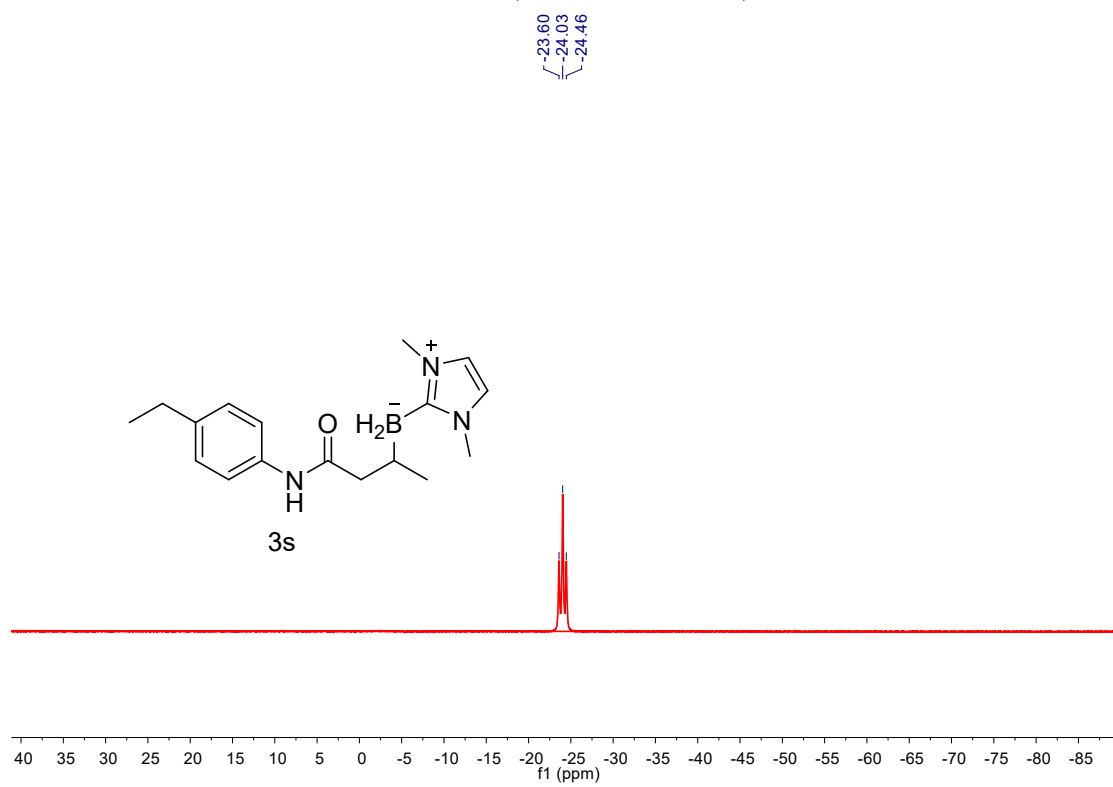
¹H{¹¹B} NMR (600 MHz, CDCl₃)



¹H NMR (600 MHz, CDCl₃)

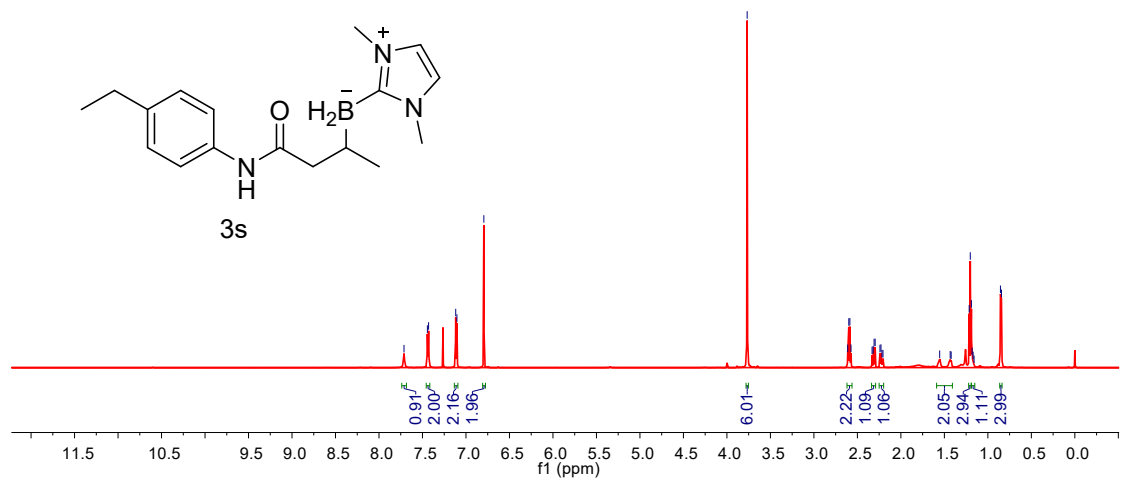
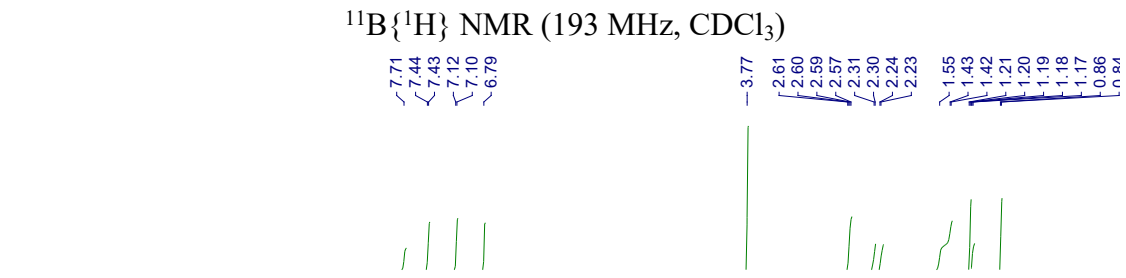
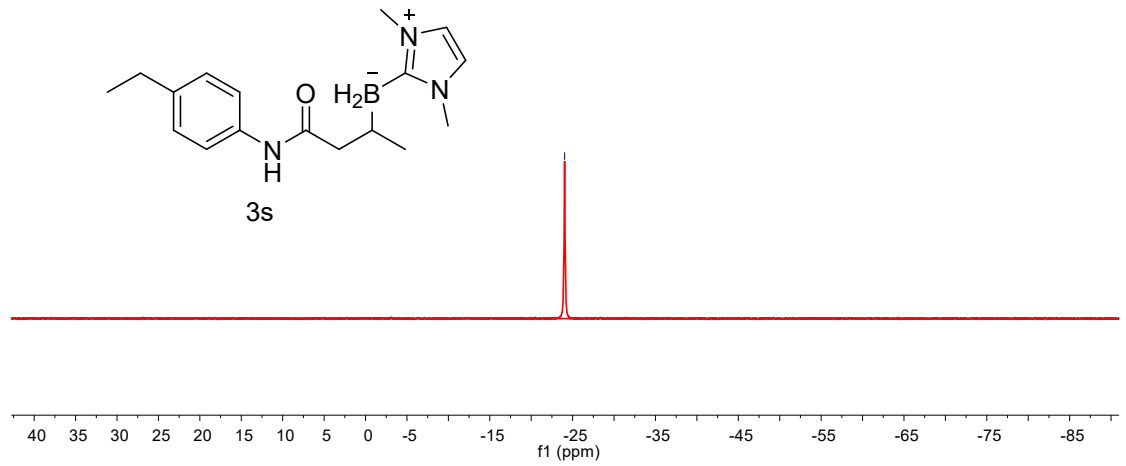


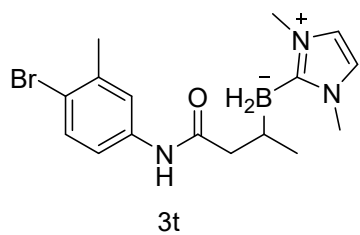
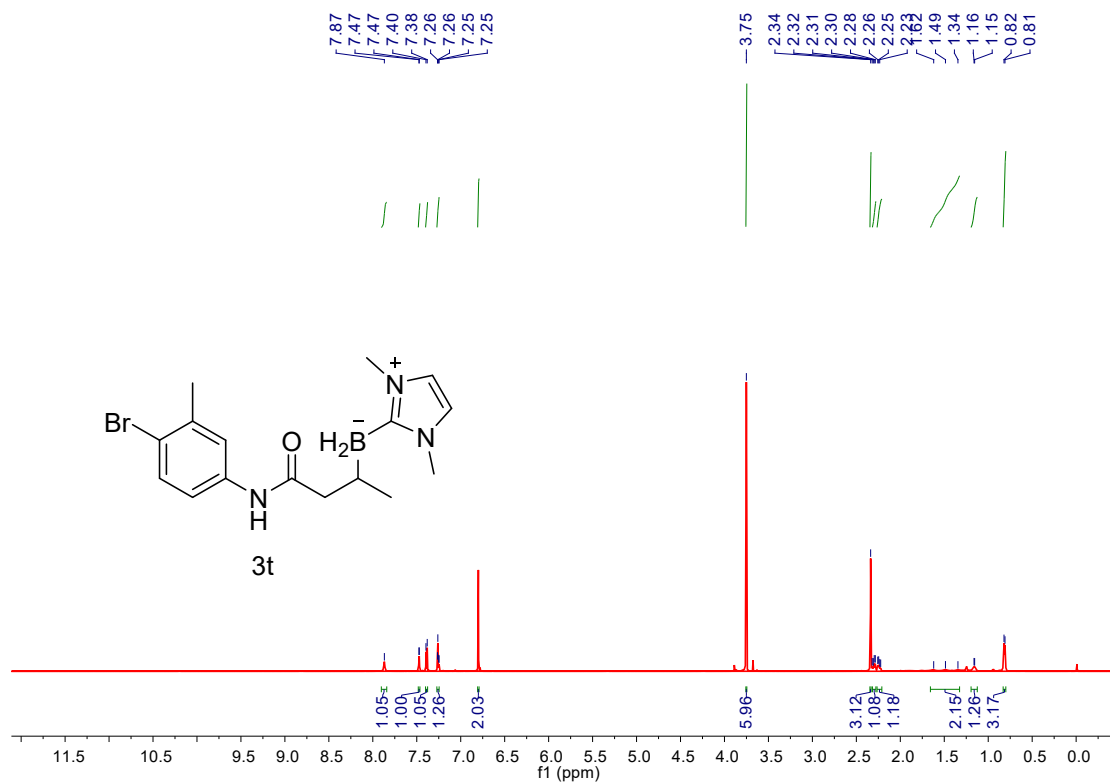
¹³C NMR (151 MHz, CDCl₃)



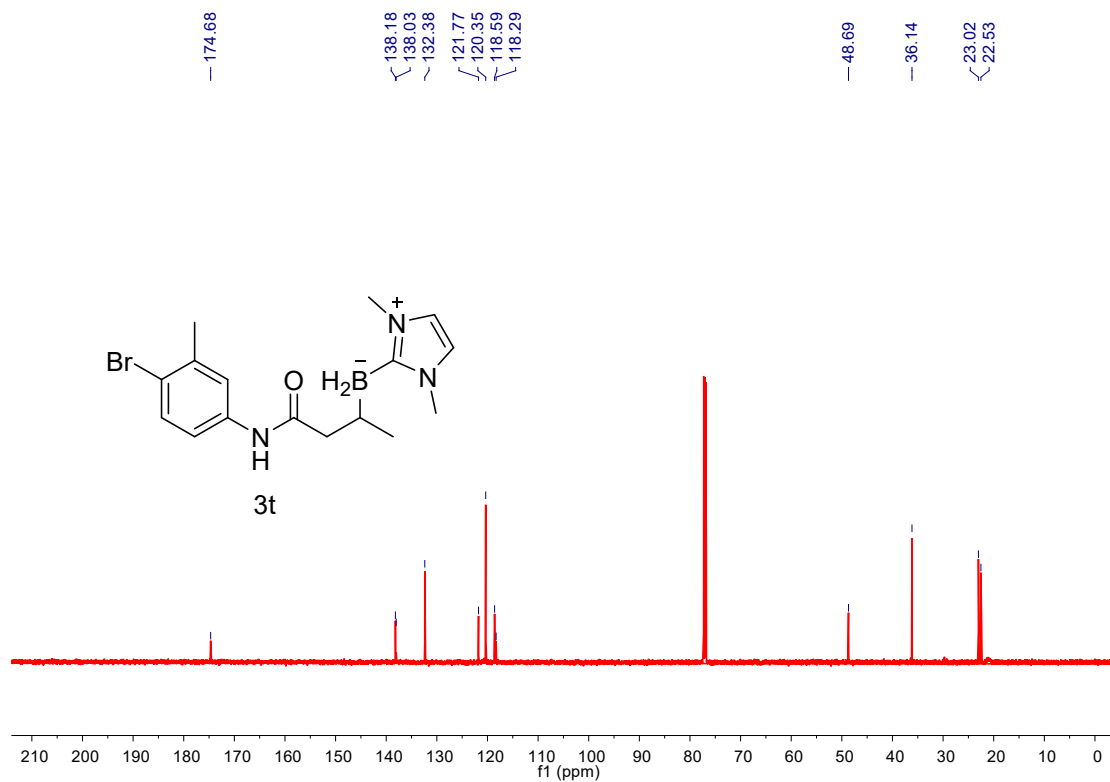
¹¹B NMR (193 MHz, CDCl₃)

--24.03

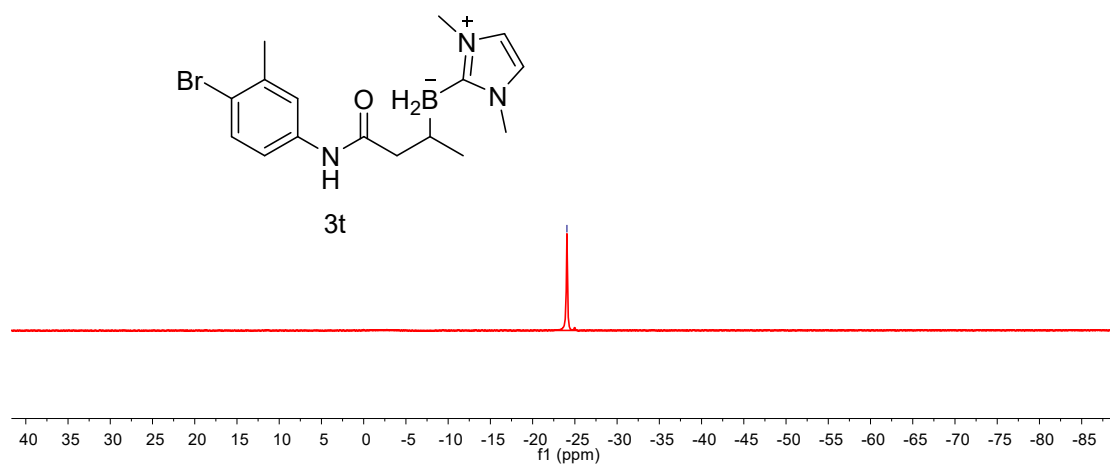
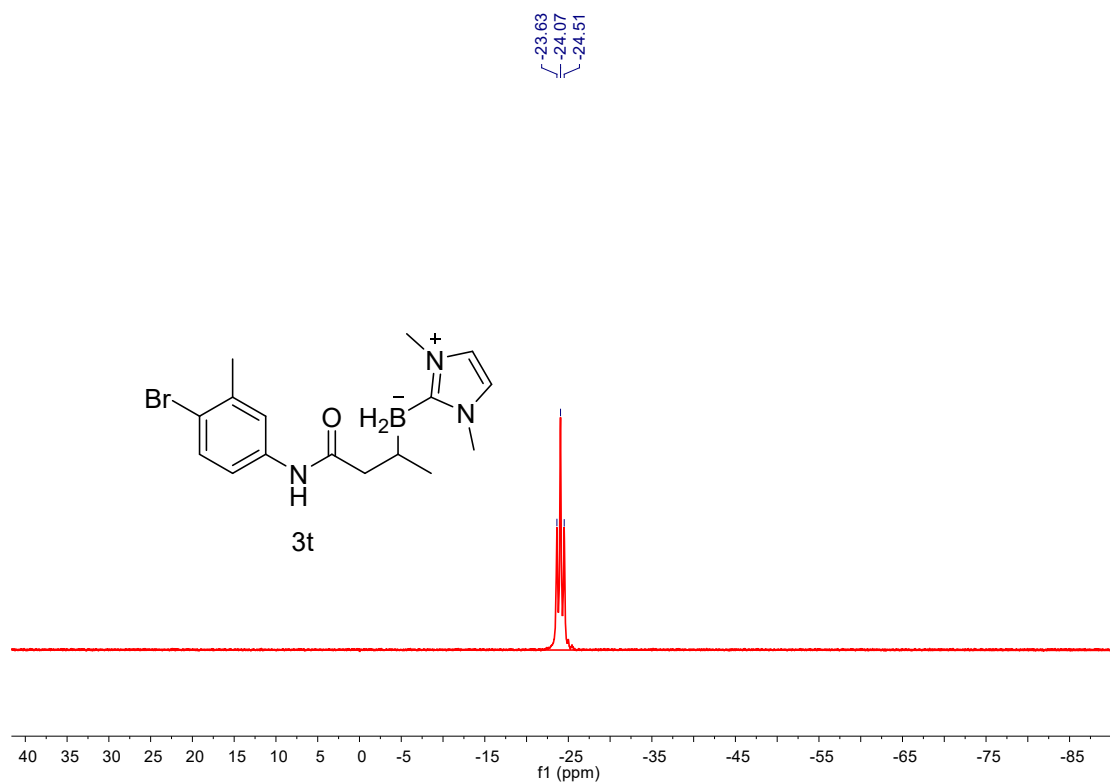


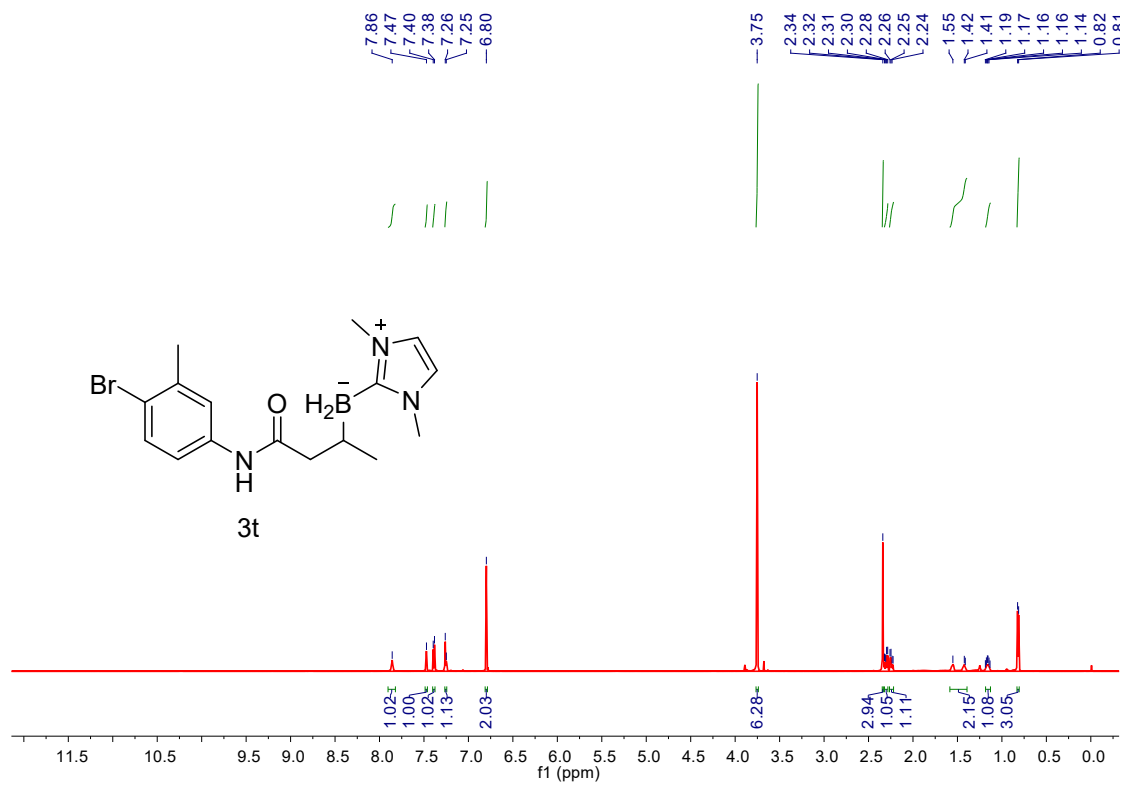


¹H NMR (600 MHz, CDCl₃)

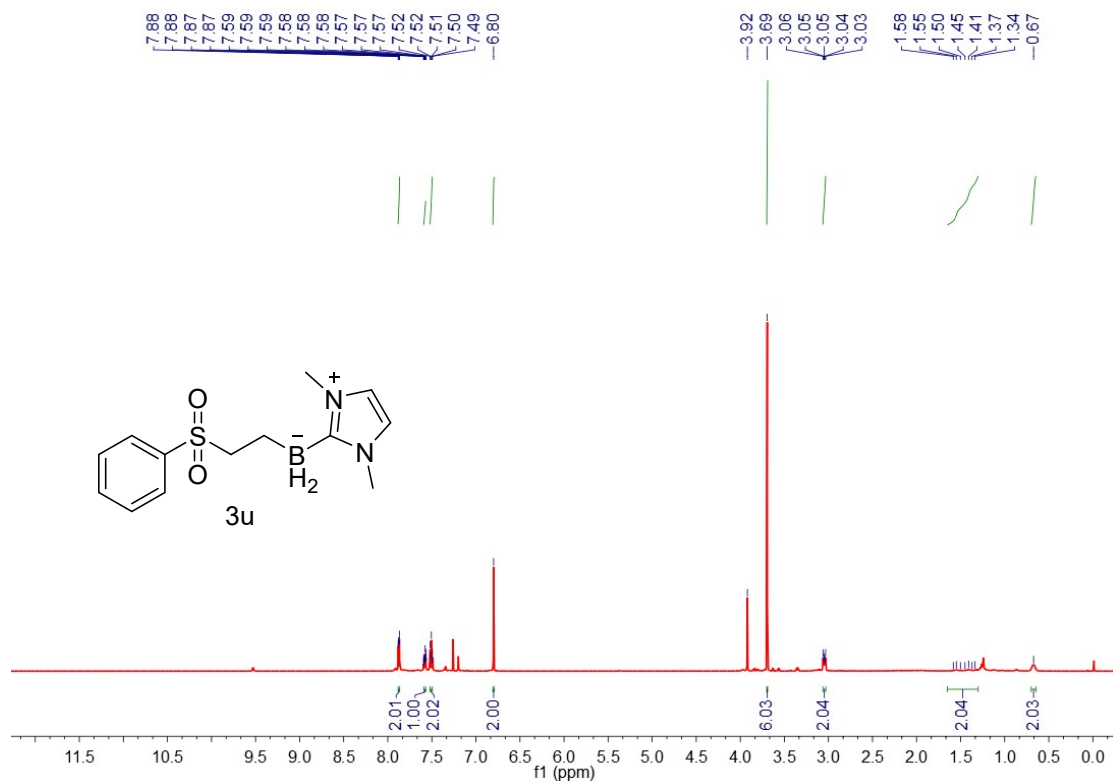


¹³C NMR (151 MHz, CDCl₃)

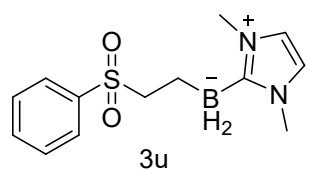
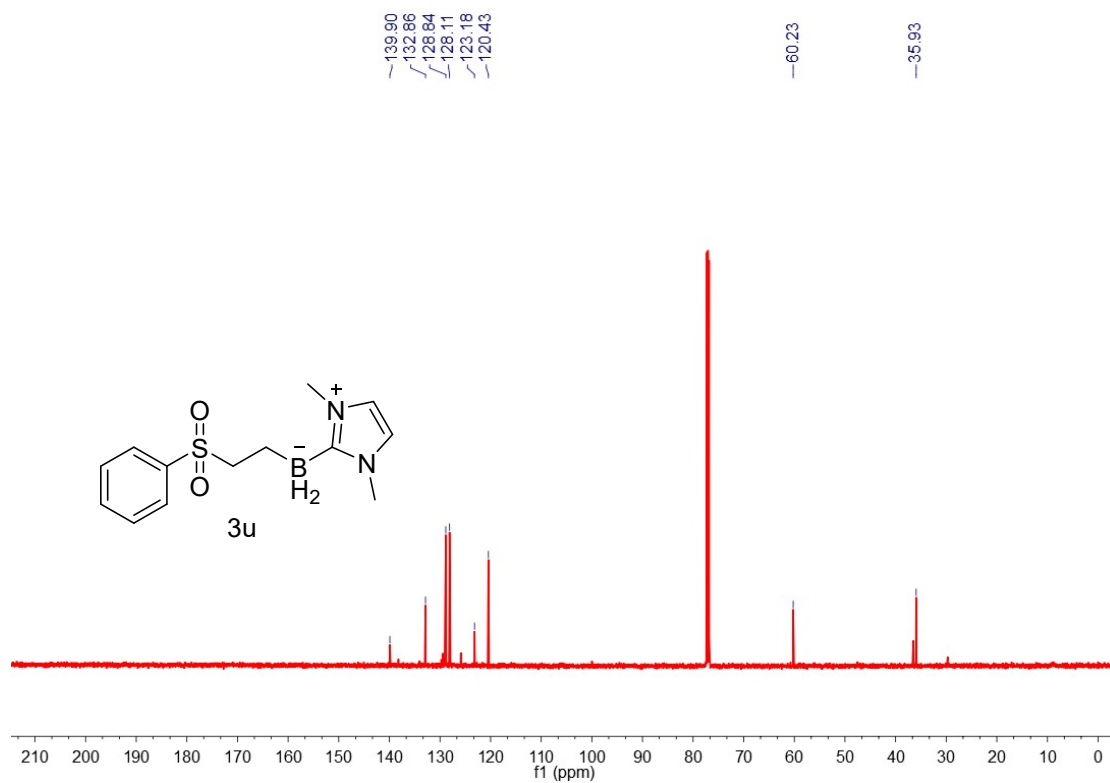




$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3)

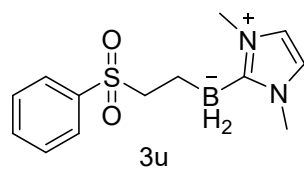
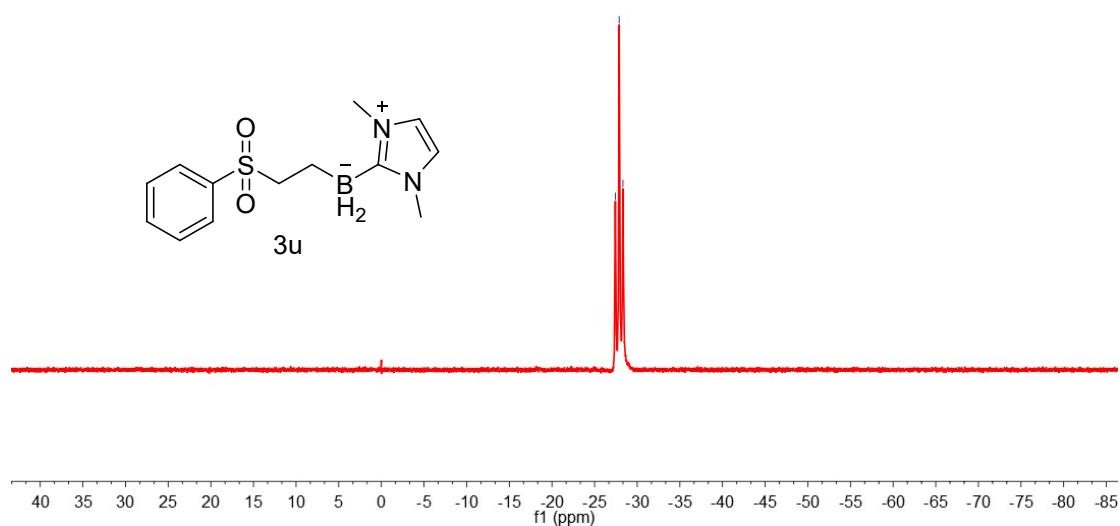


^1H NMR (600 MHz, CDCl_3)

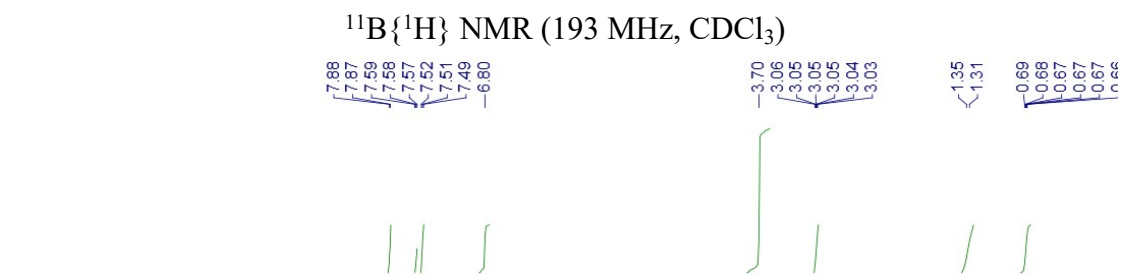
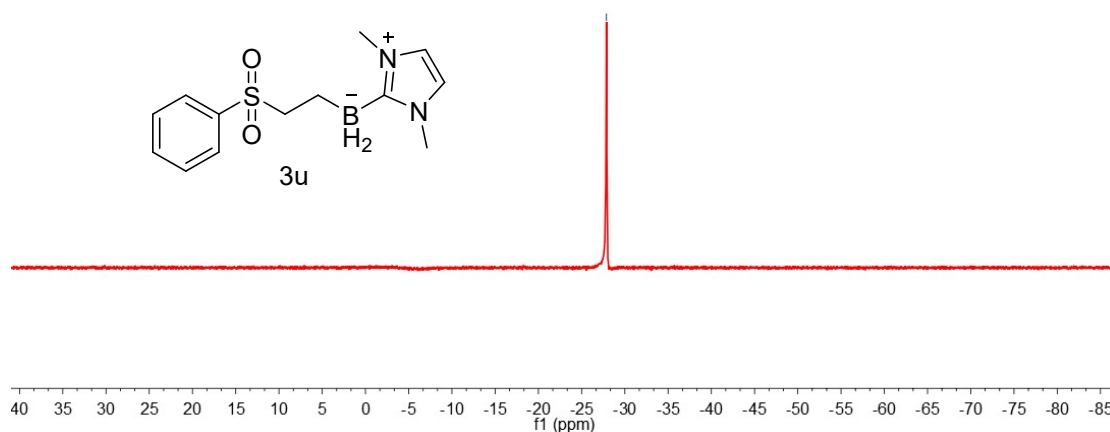


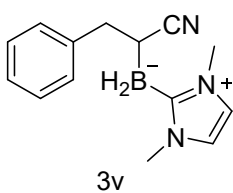
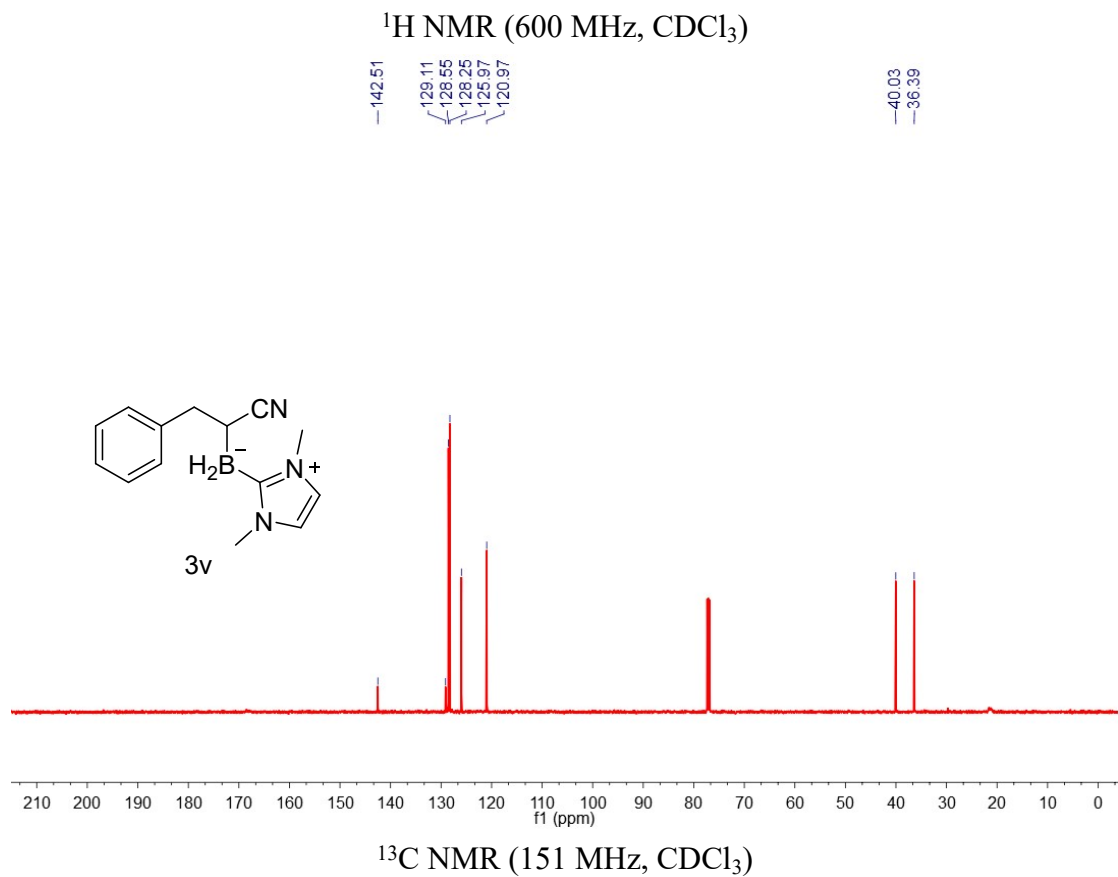
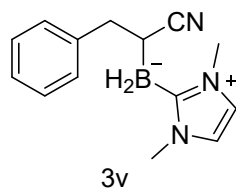
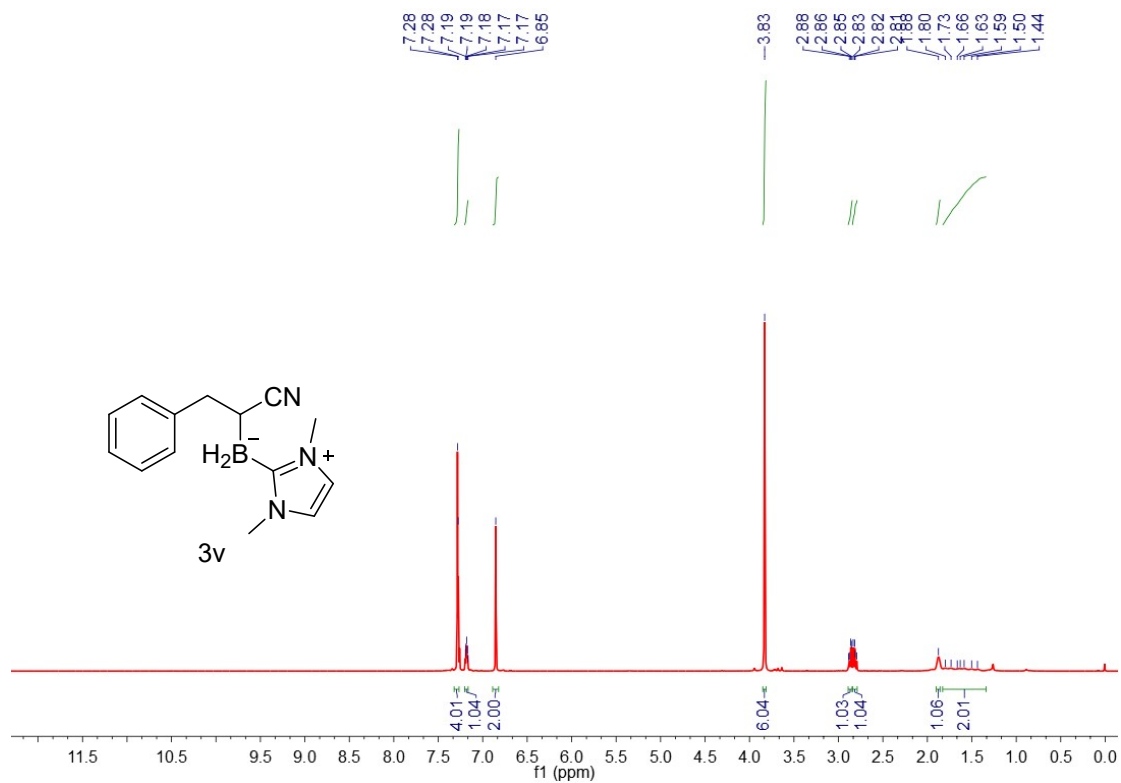
^{13}C NMR (151 MHz, CDCl_3)

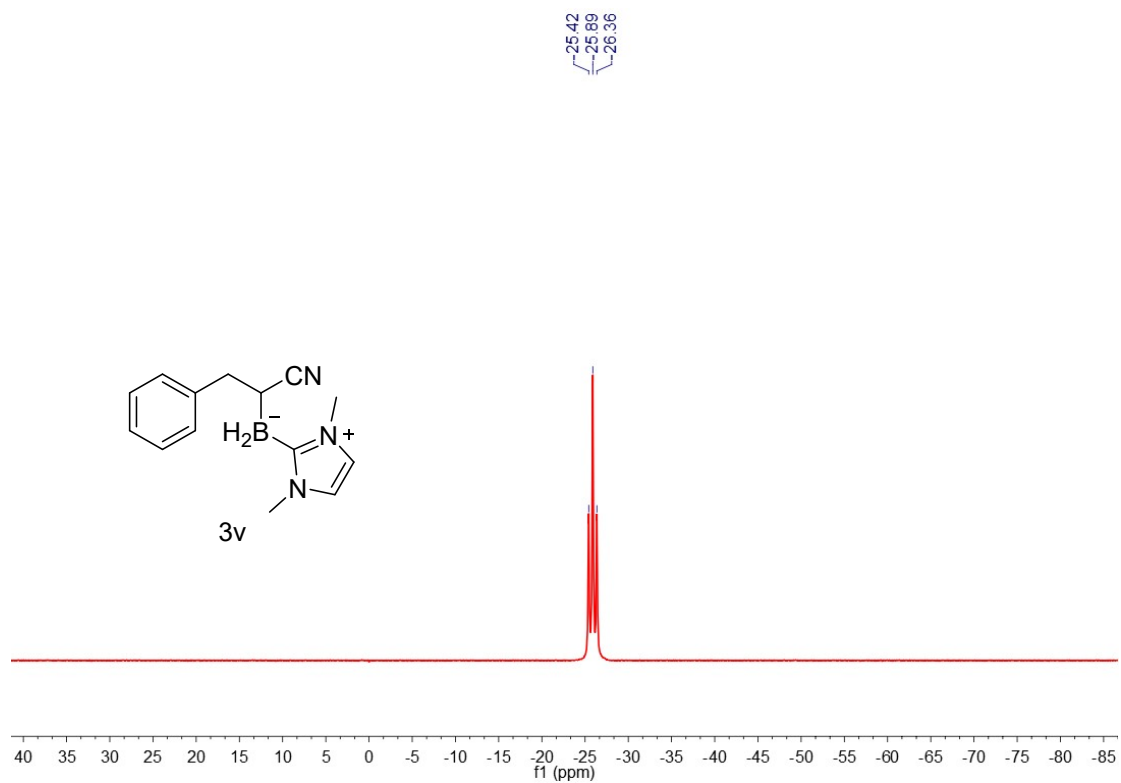
27.43
27.88
28.33



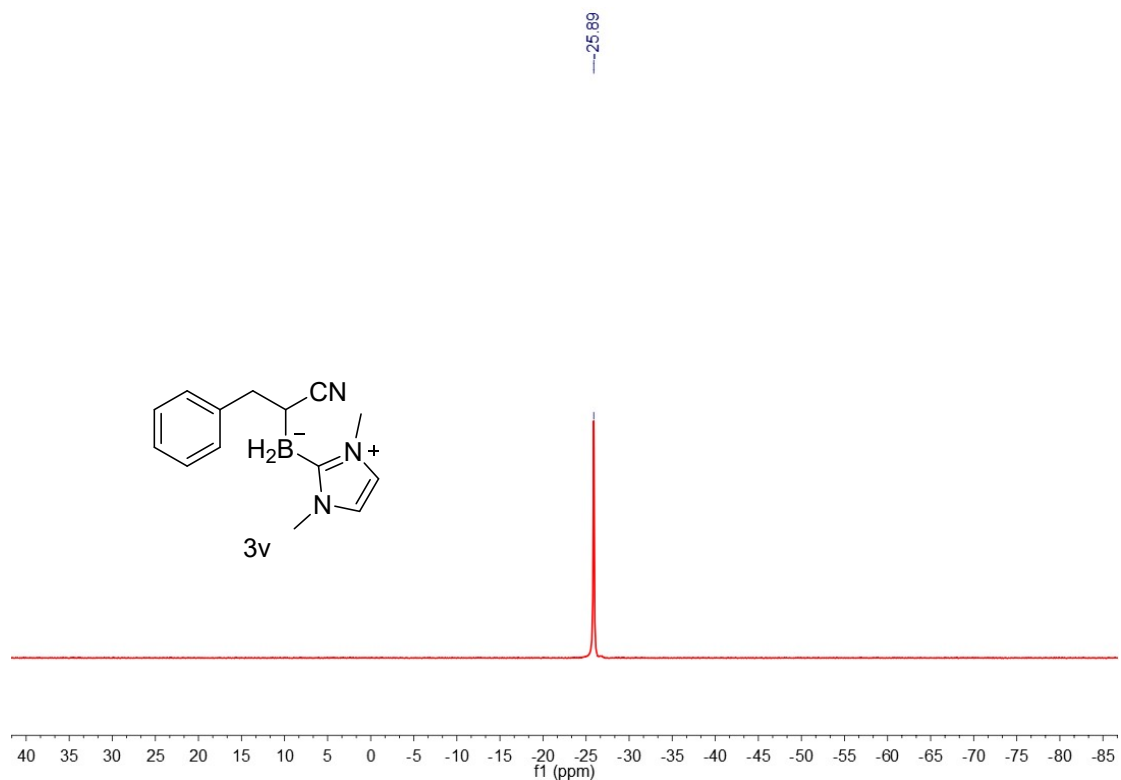
^{11}B NMR (193 MHz, CDCl_3)



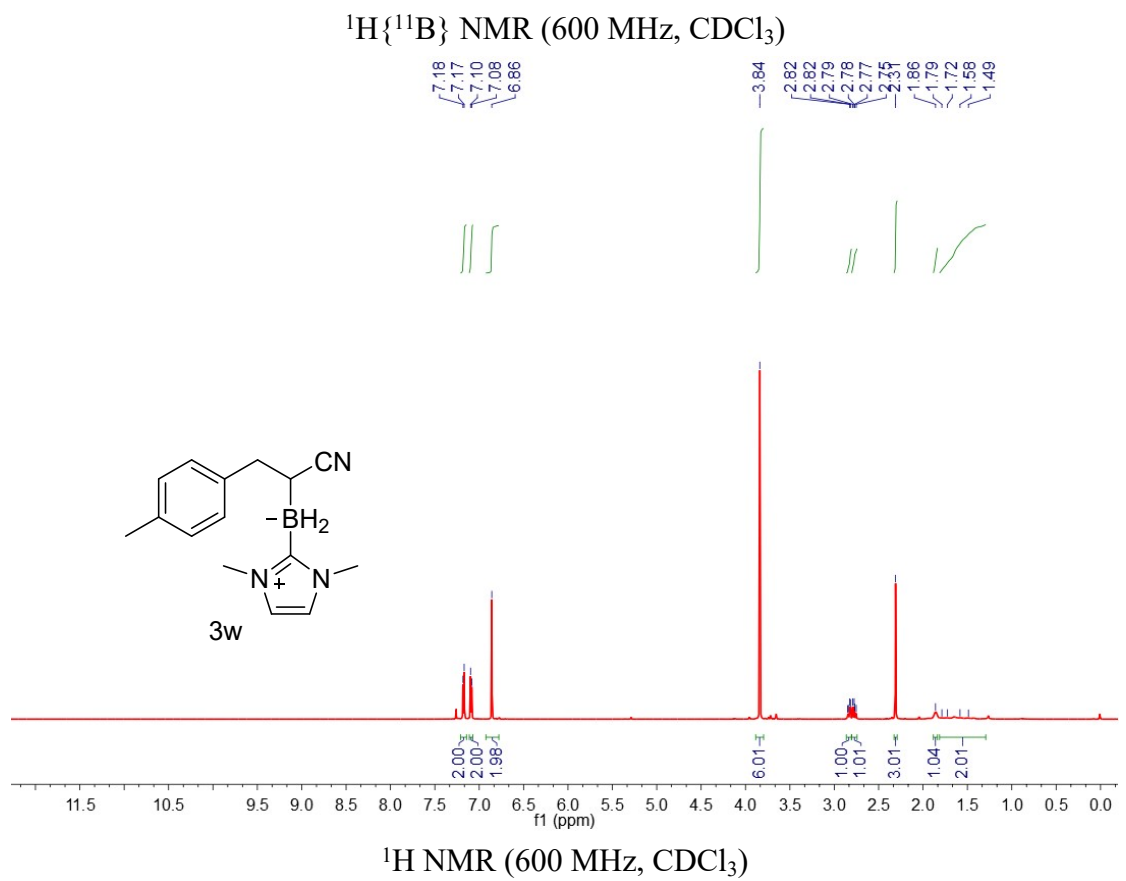
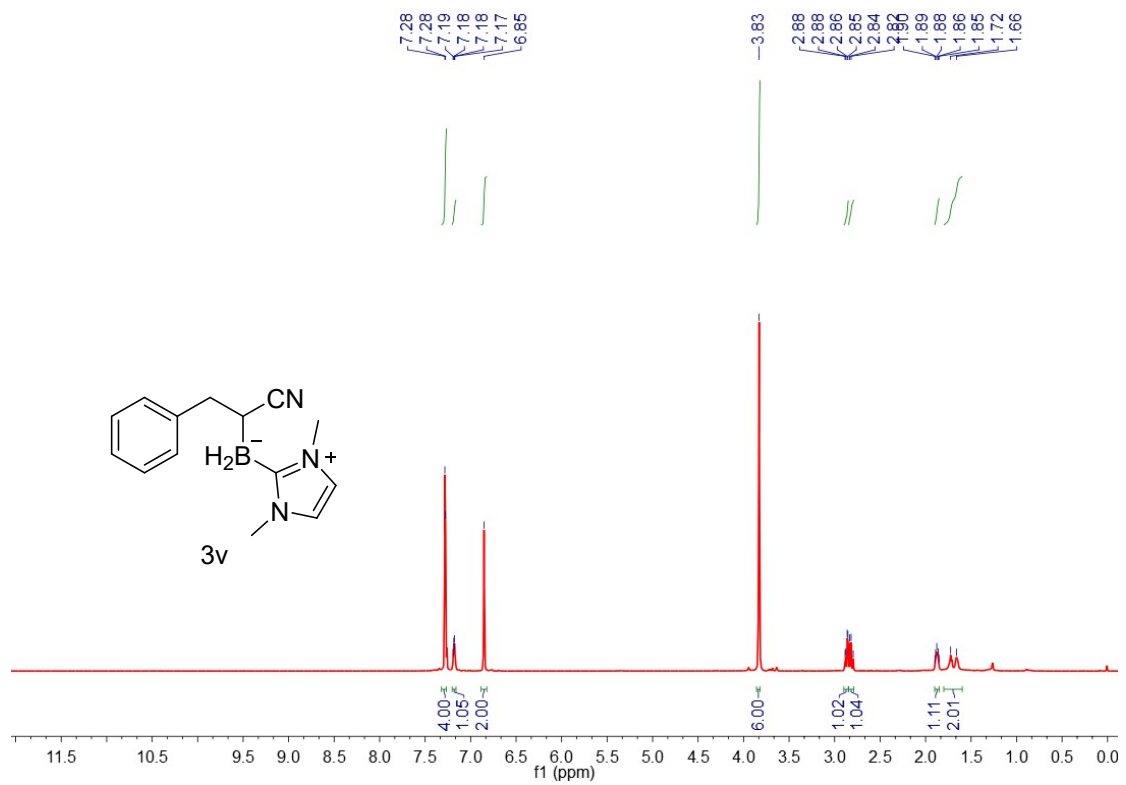


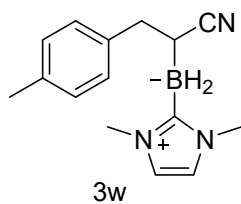
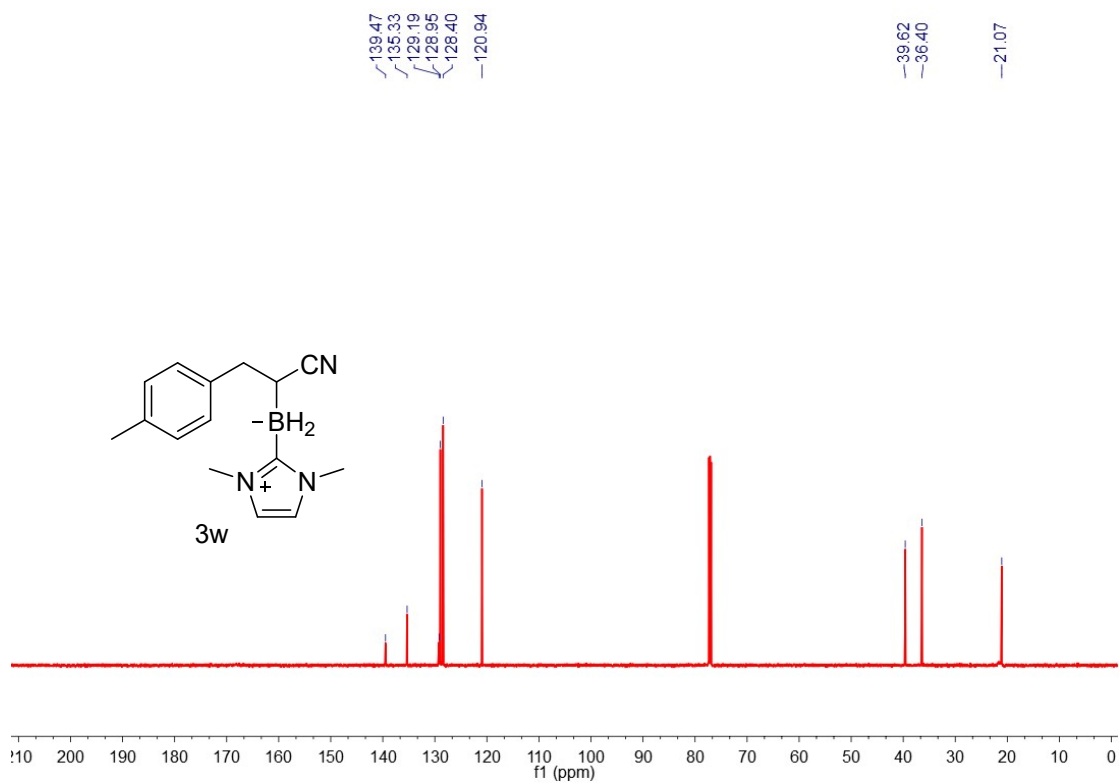


^{11}B NMR (193 MHz, CDCl_3)



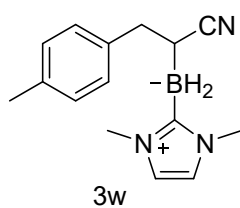
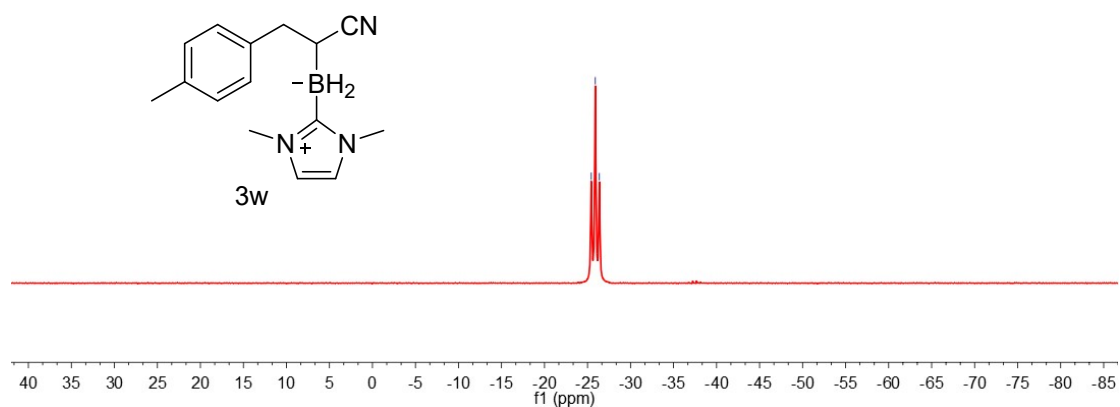
$^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3)





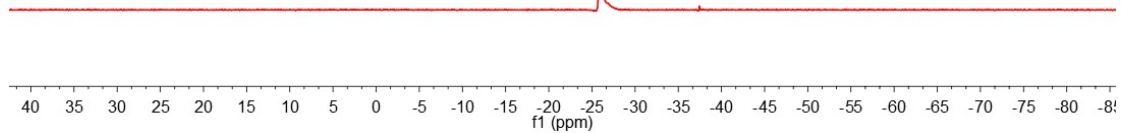
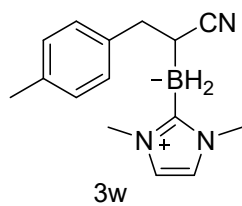
^{13}C NMR (151 MHz, CDCl_3)

25.44
25.91
26.38

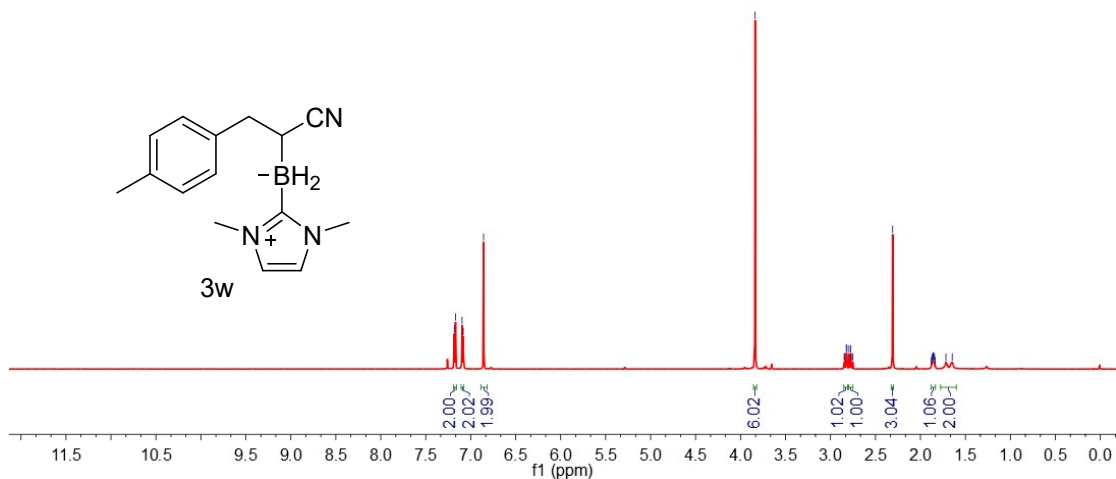
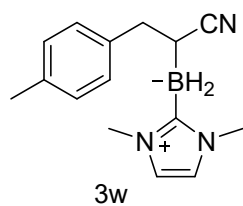
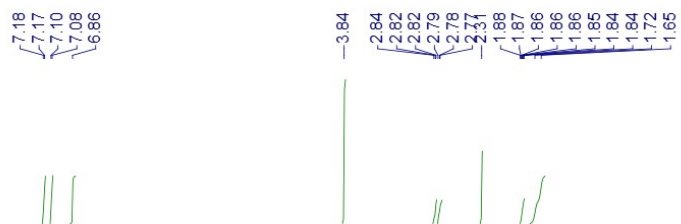


^{11}B NMR (193 MHz, CDCl_3)

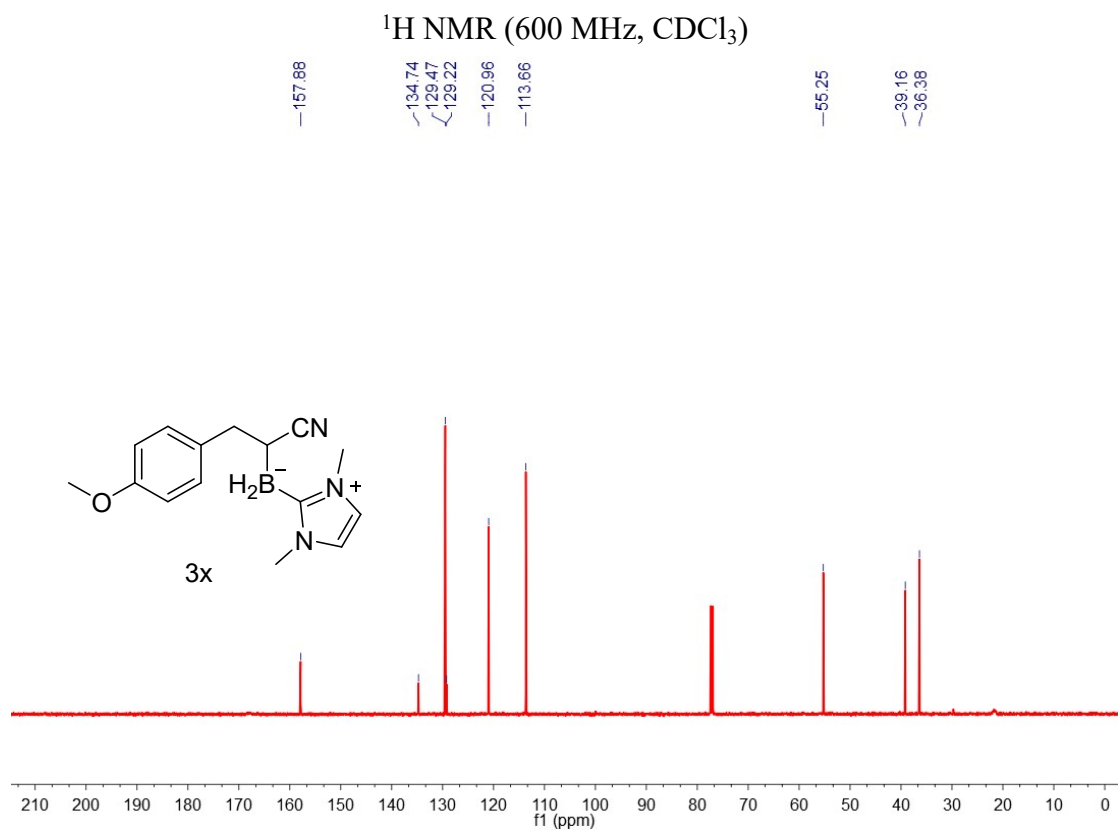
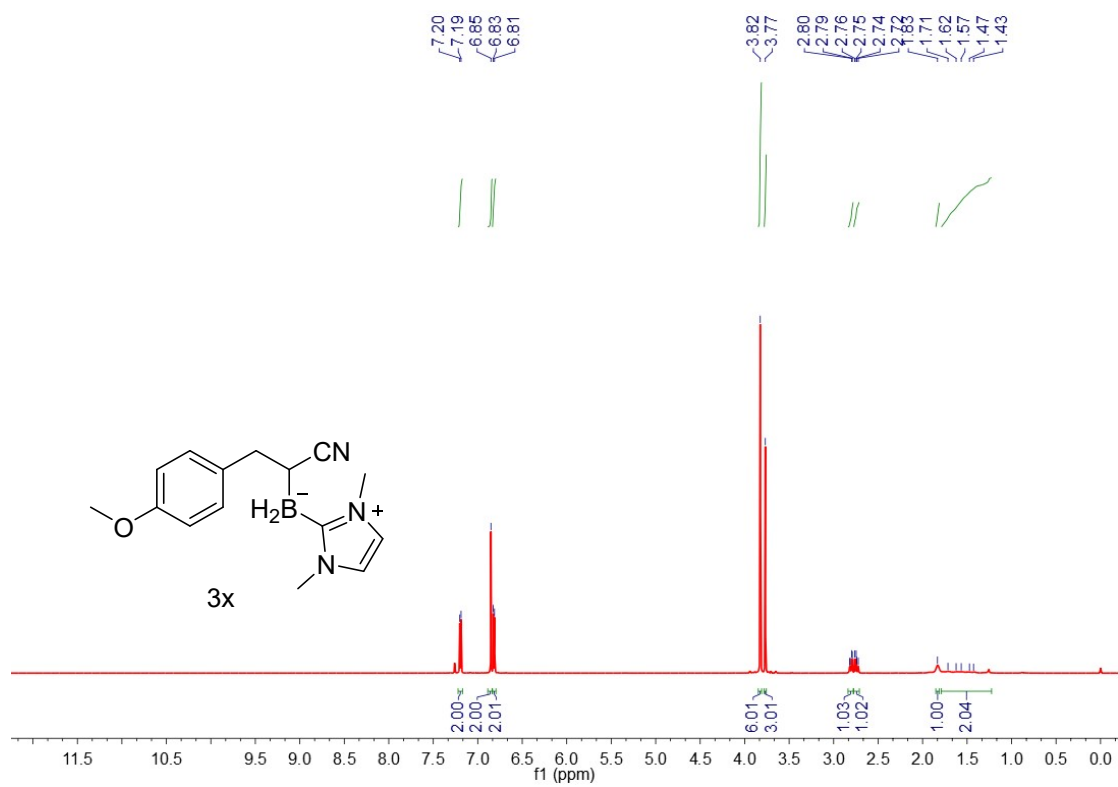
--25.91

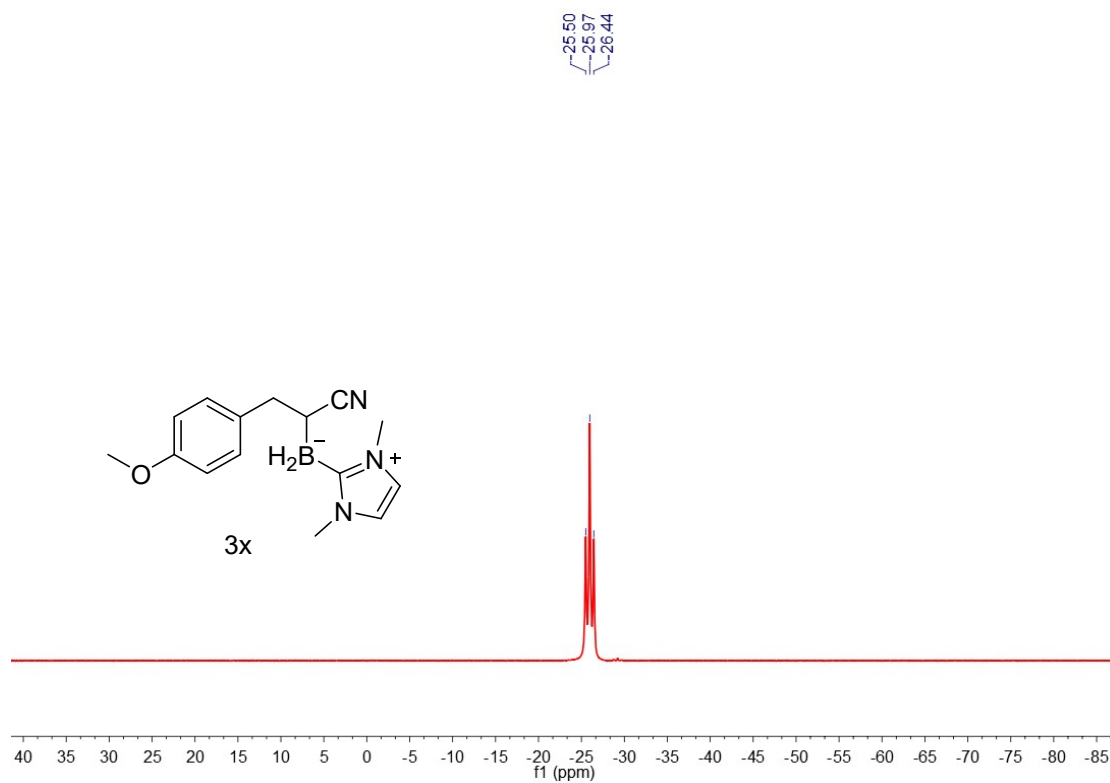


$^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3)

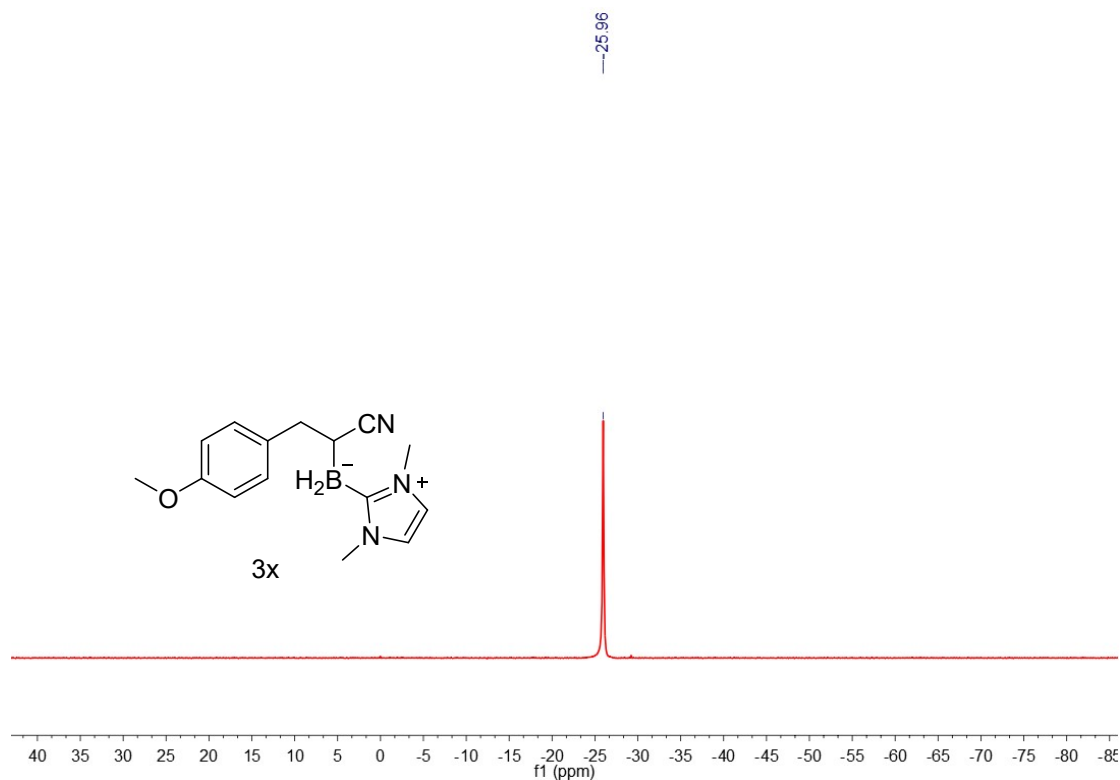


$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3)

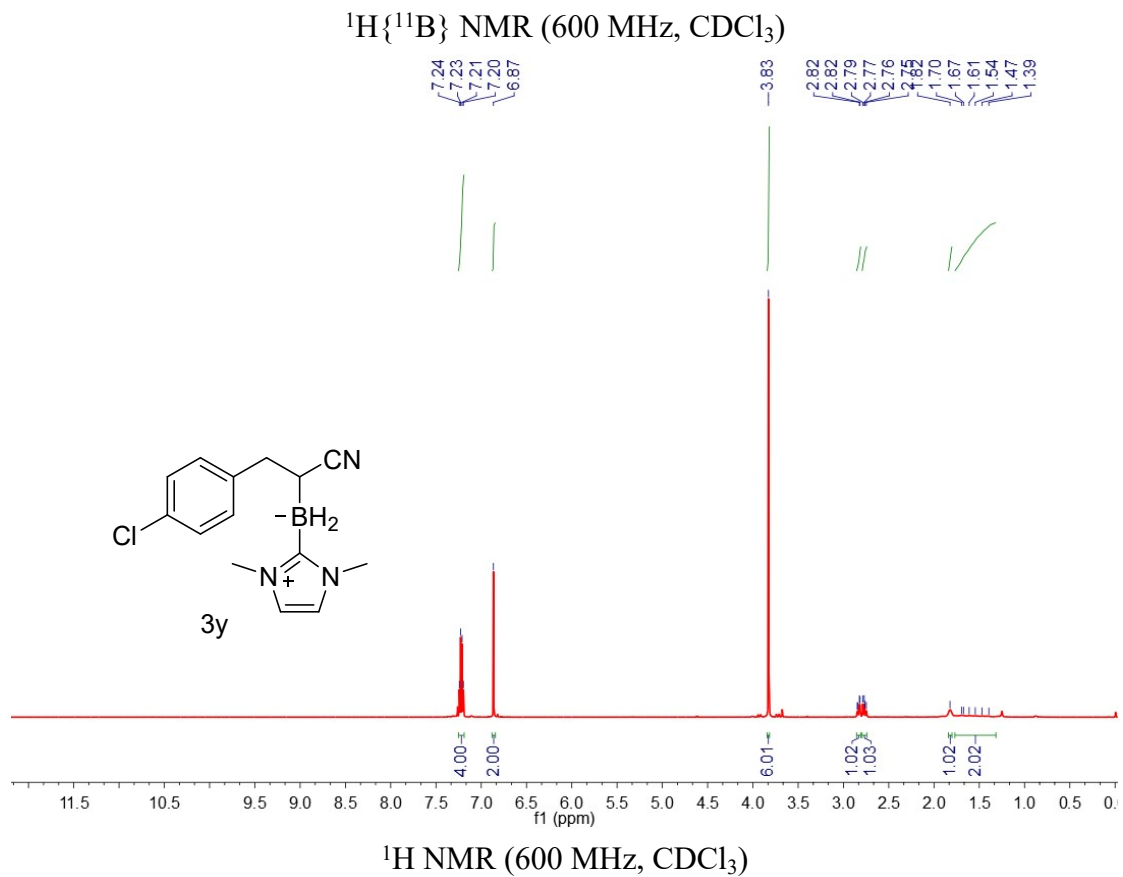
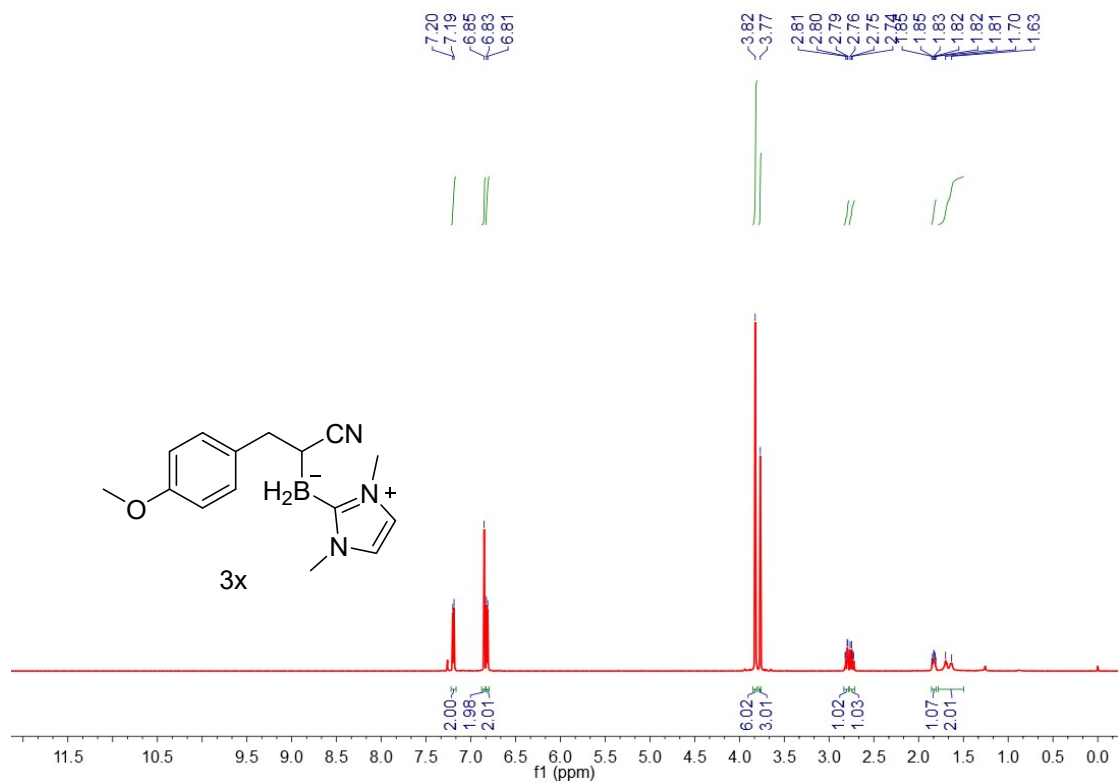


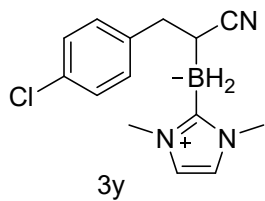
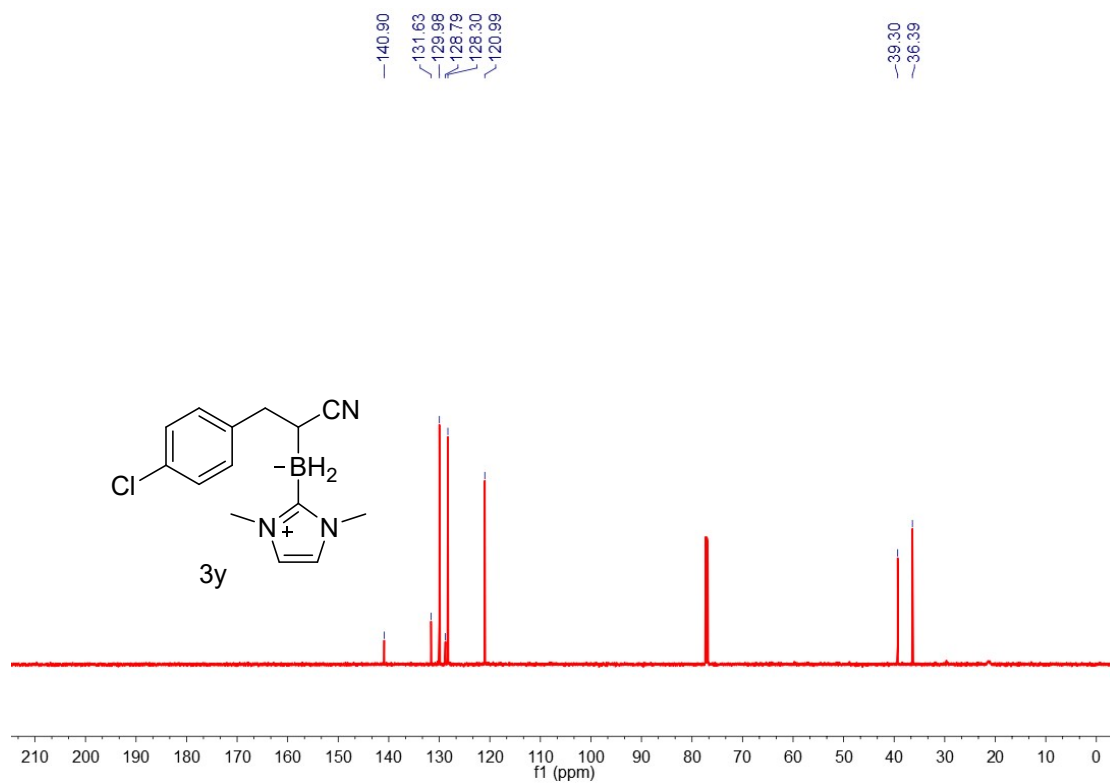


^{11}B NMR (193 MHz, CDCl_3)



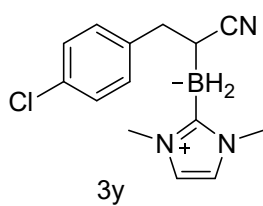
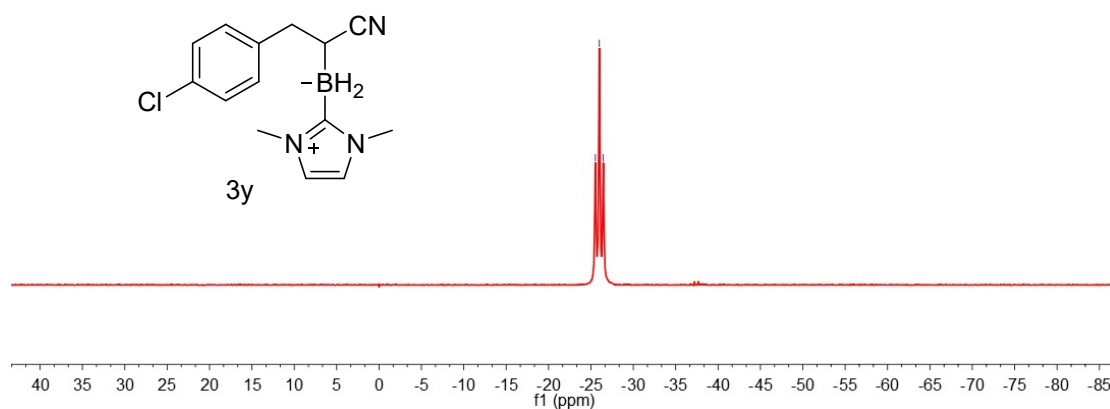
$^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3)



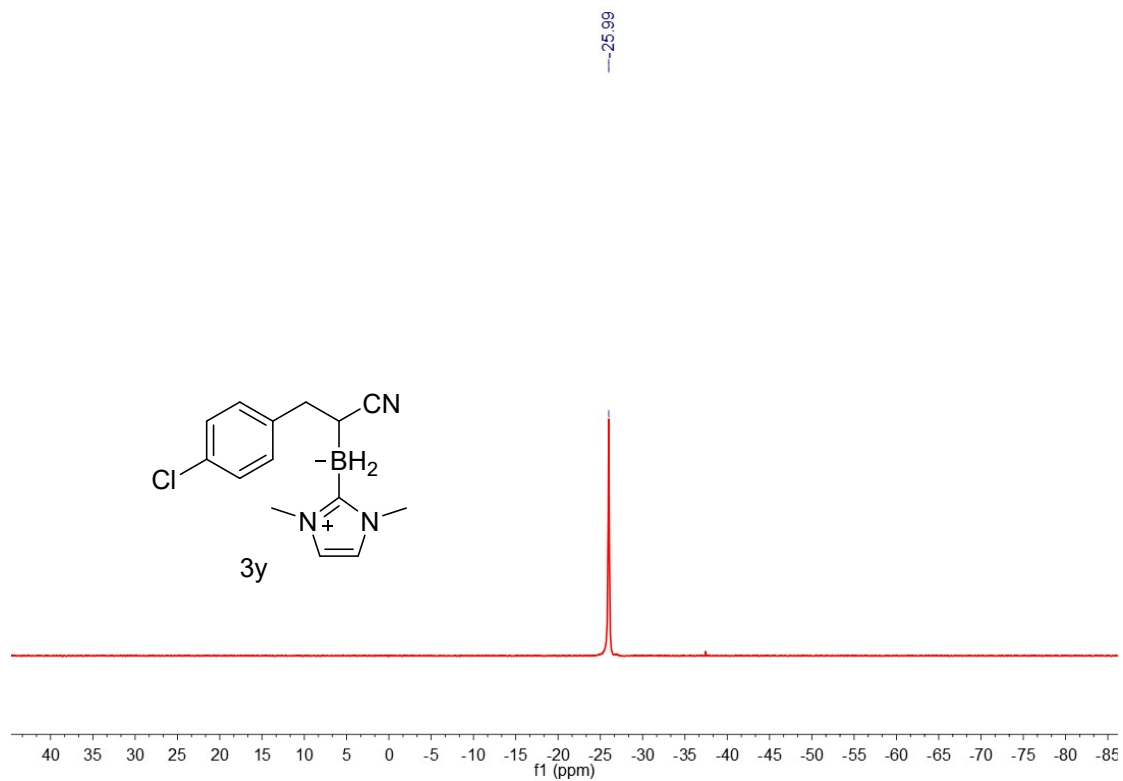


^{13}C NMR (151 MHz, CDCl_3)

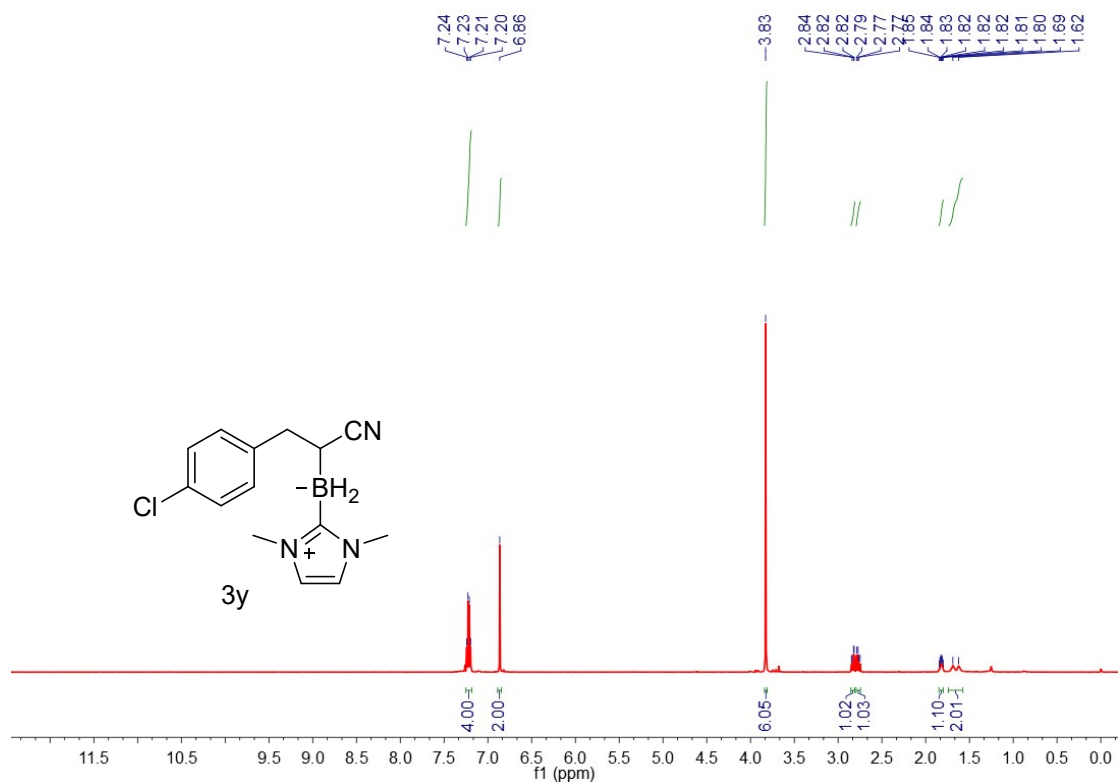
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26.00
26.47



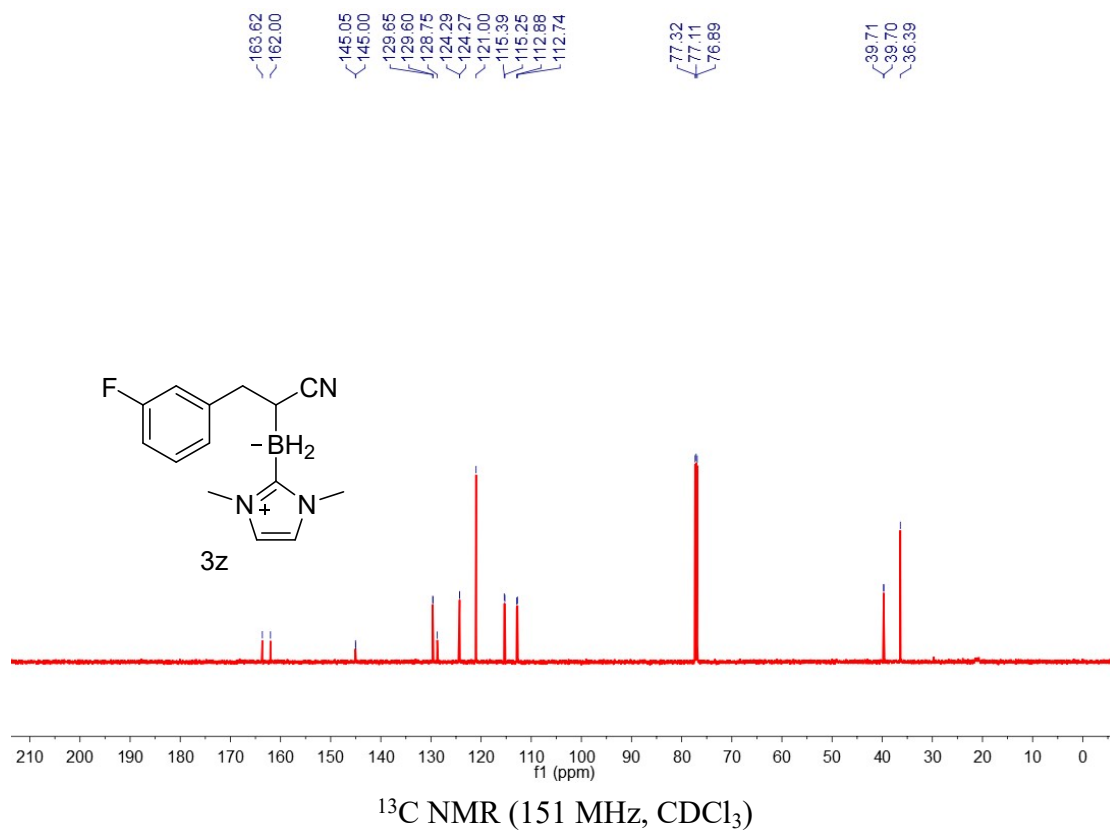
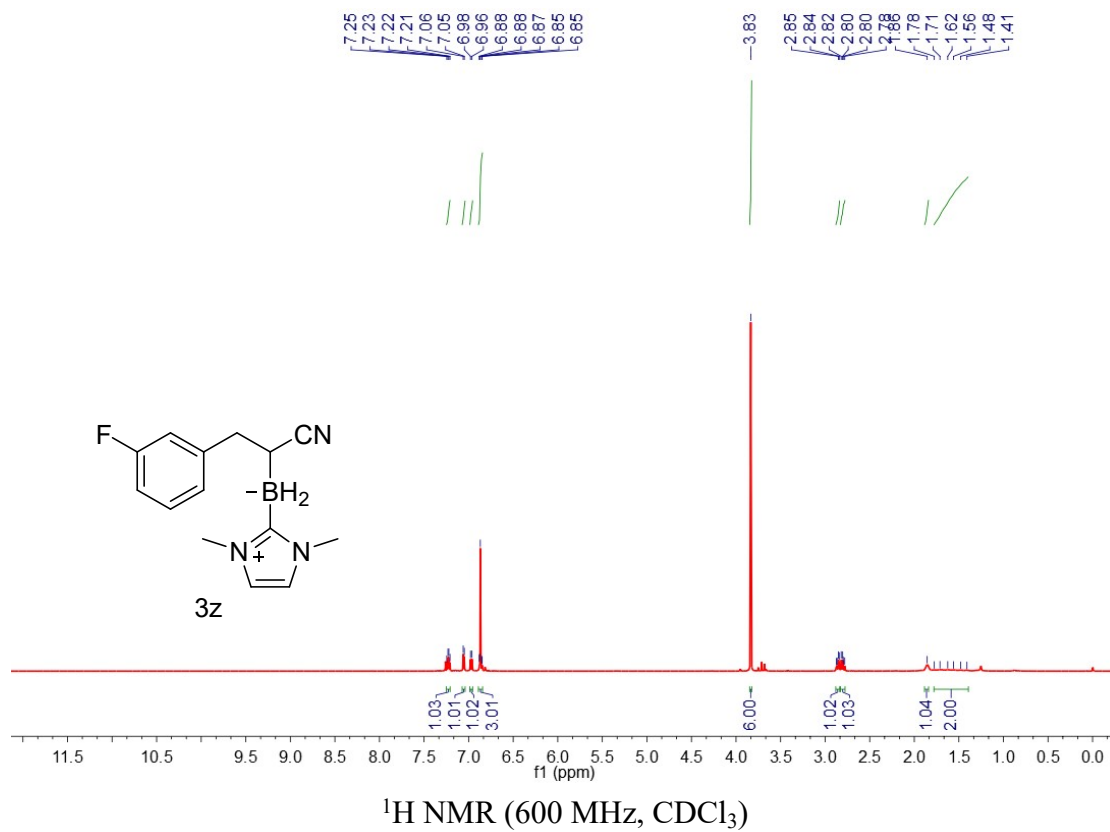
^{11}B NMR (193 MHz, CDCl_3)

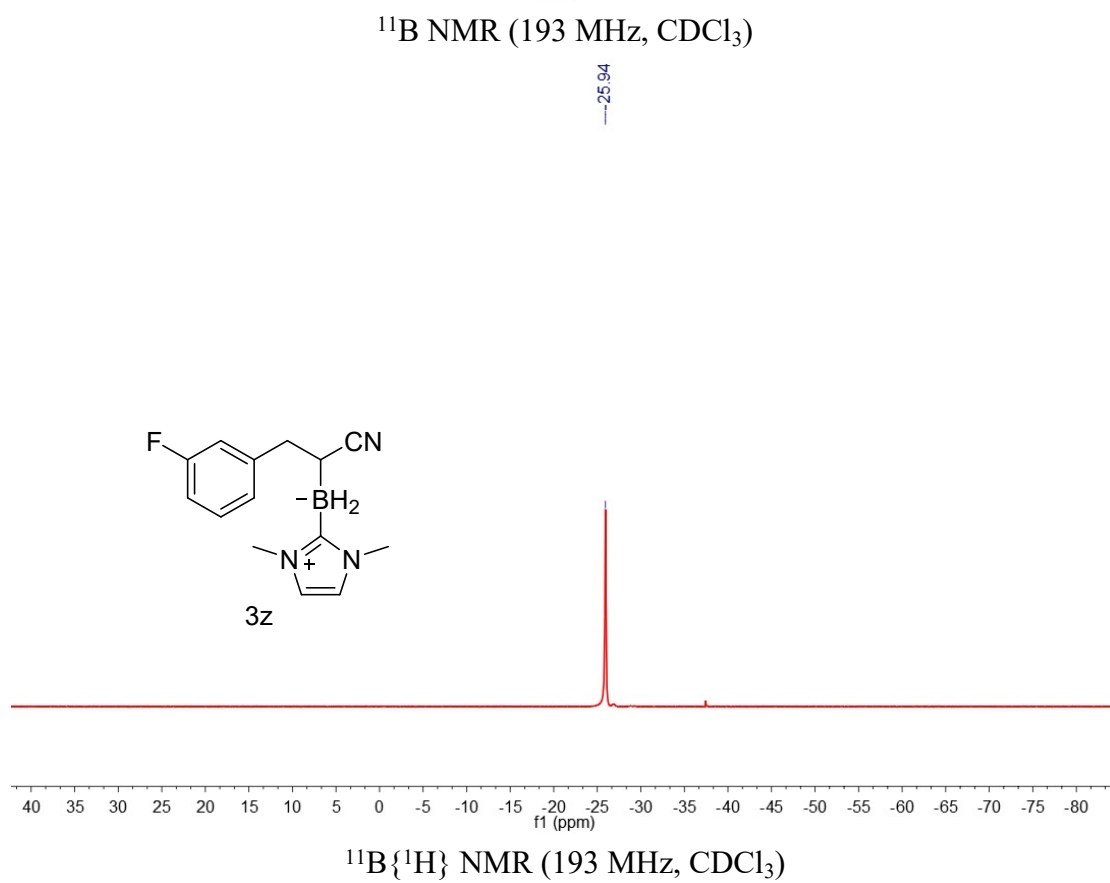
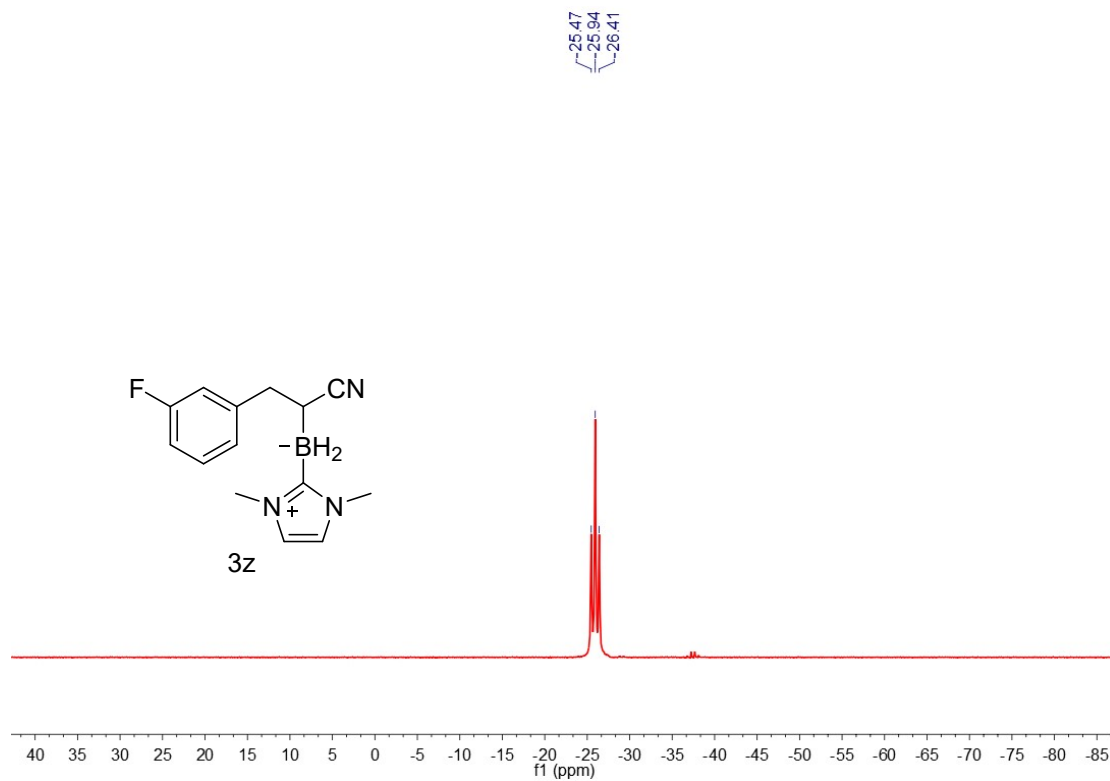


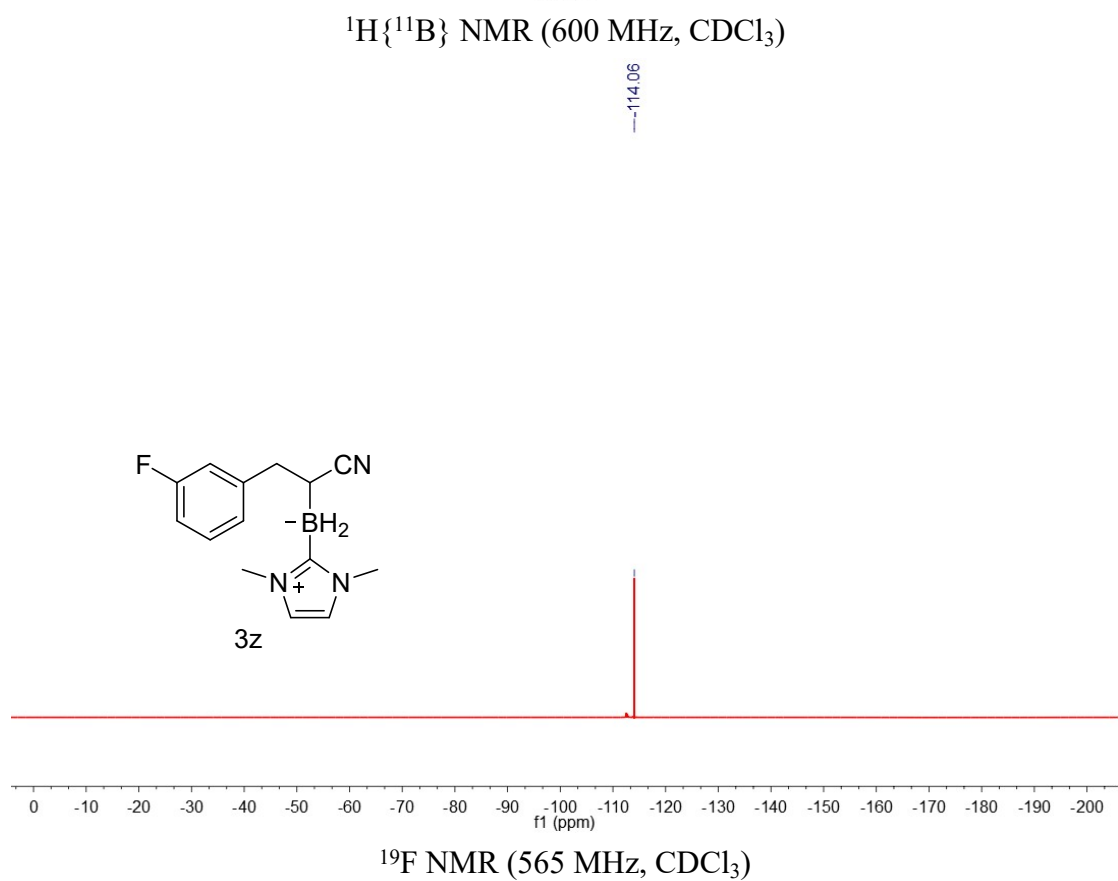
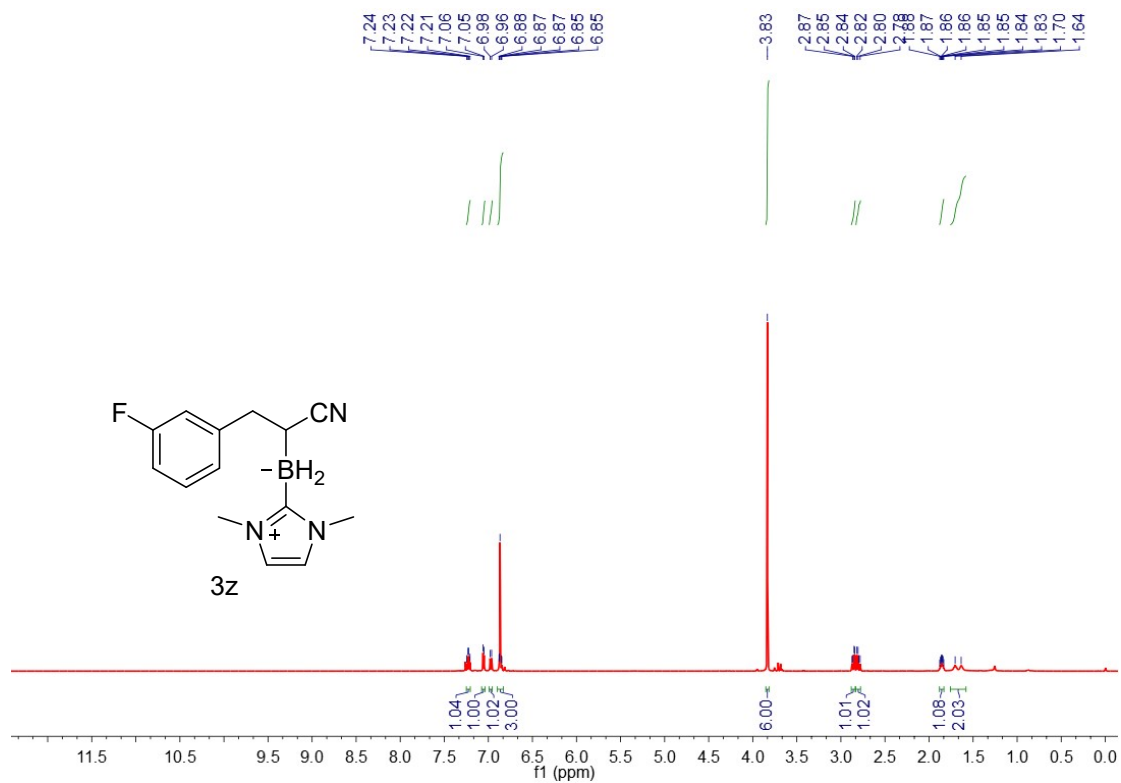
$^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3)

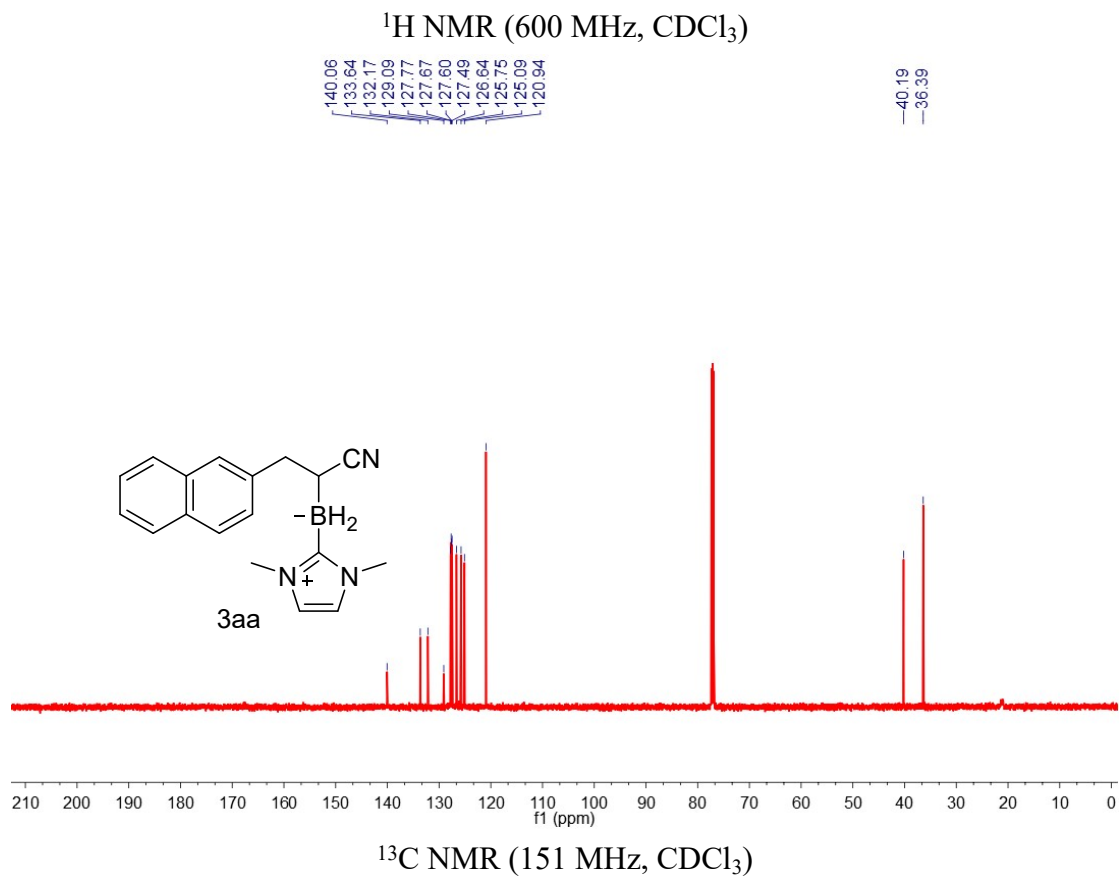
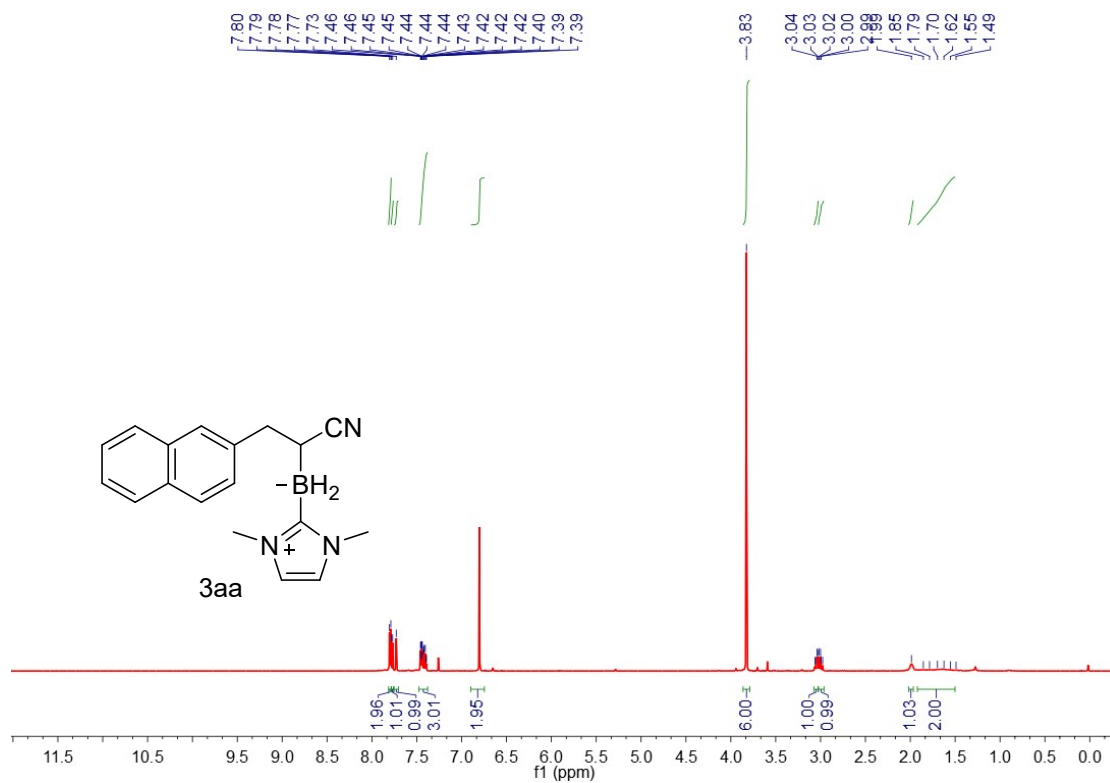


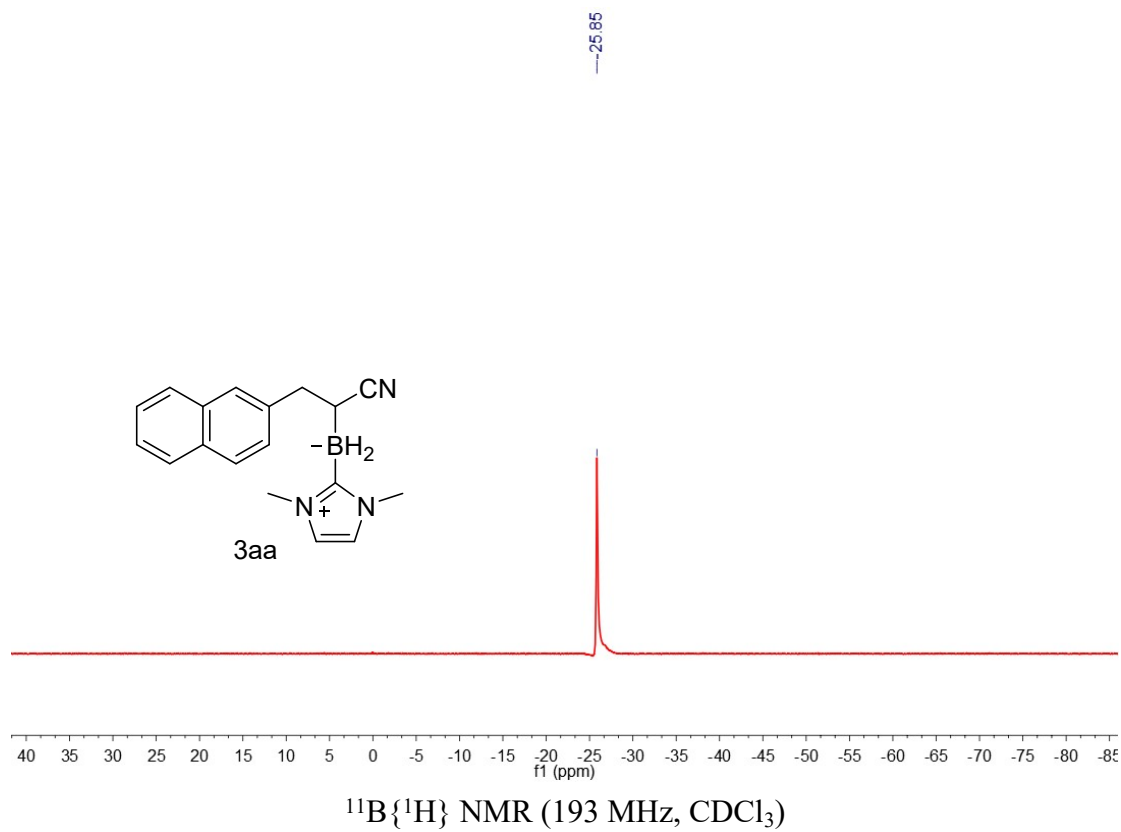
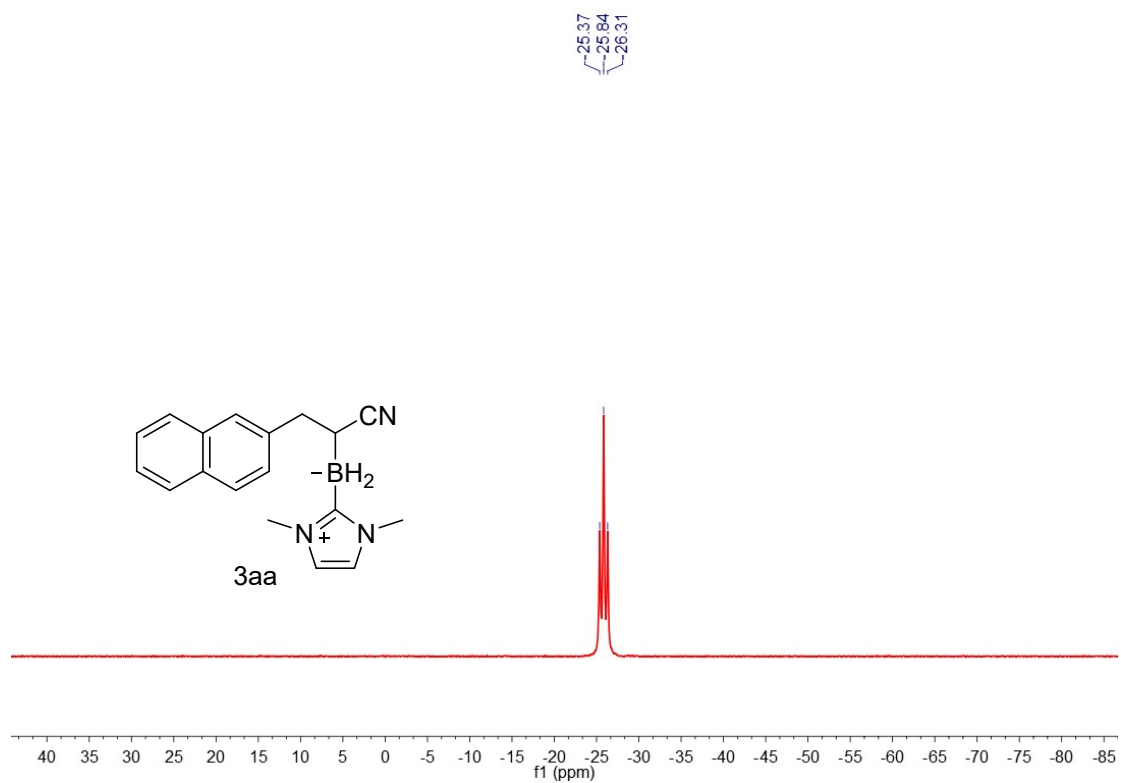
$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3)

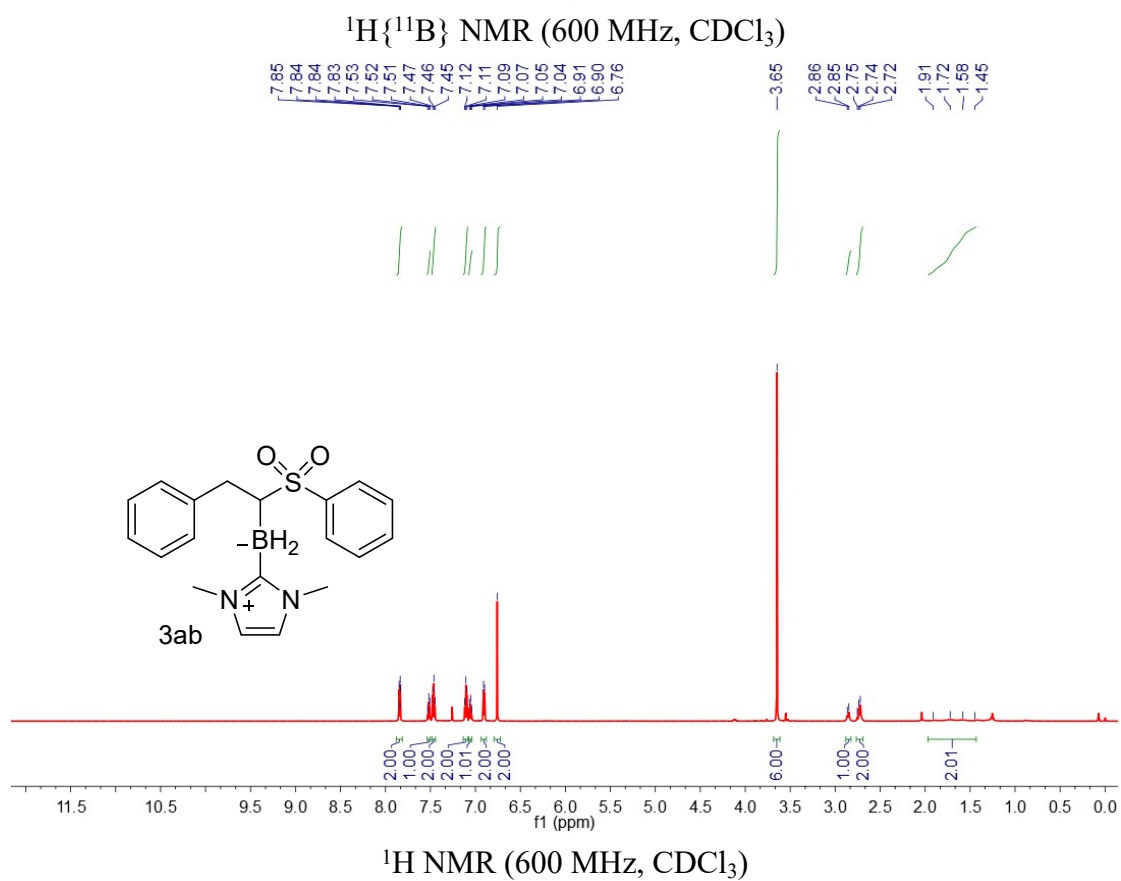
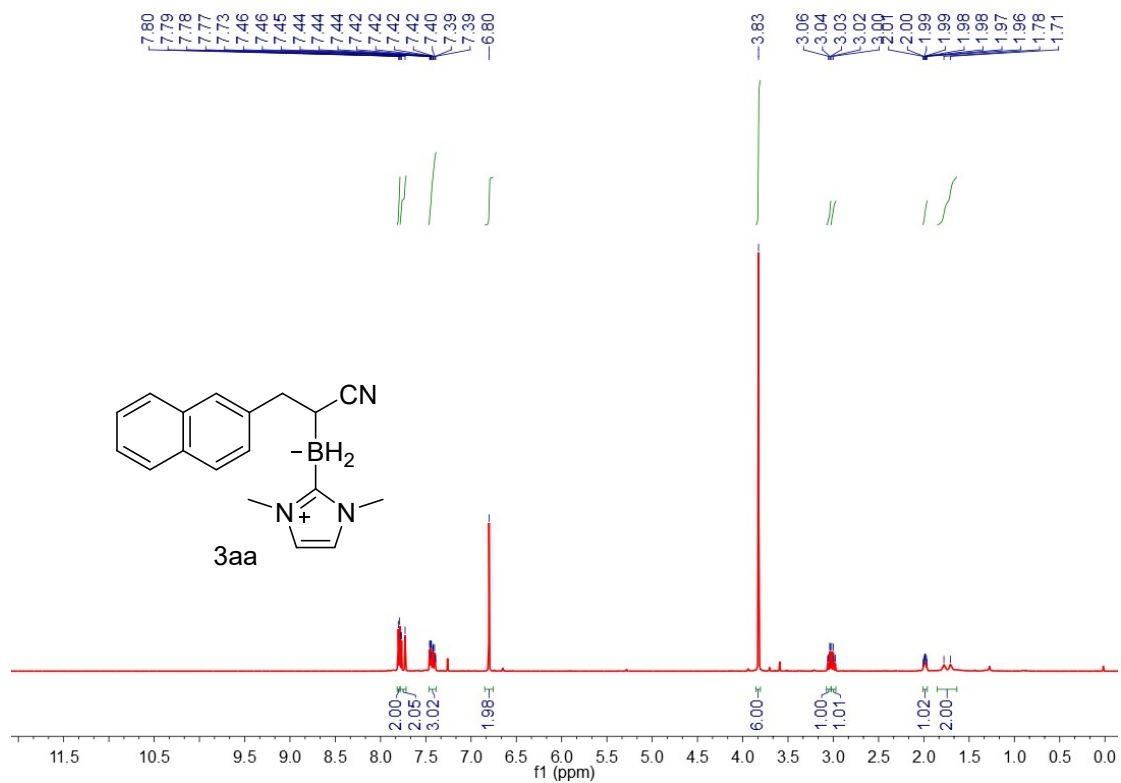


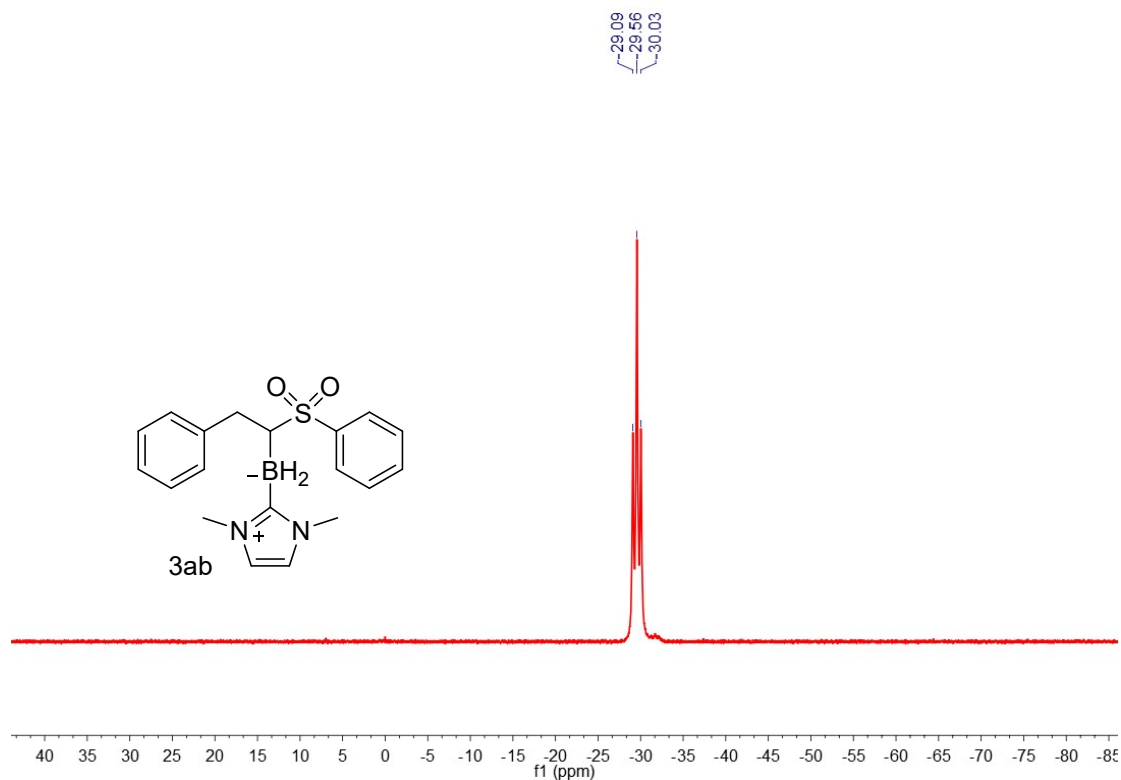
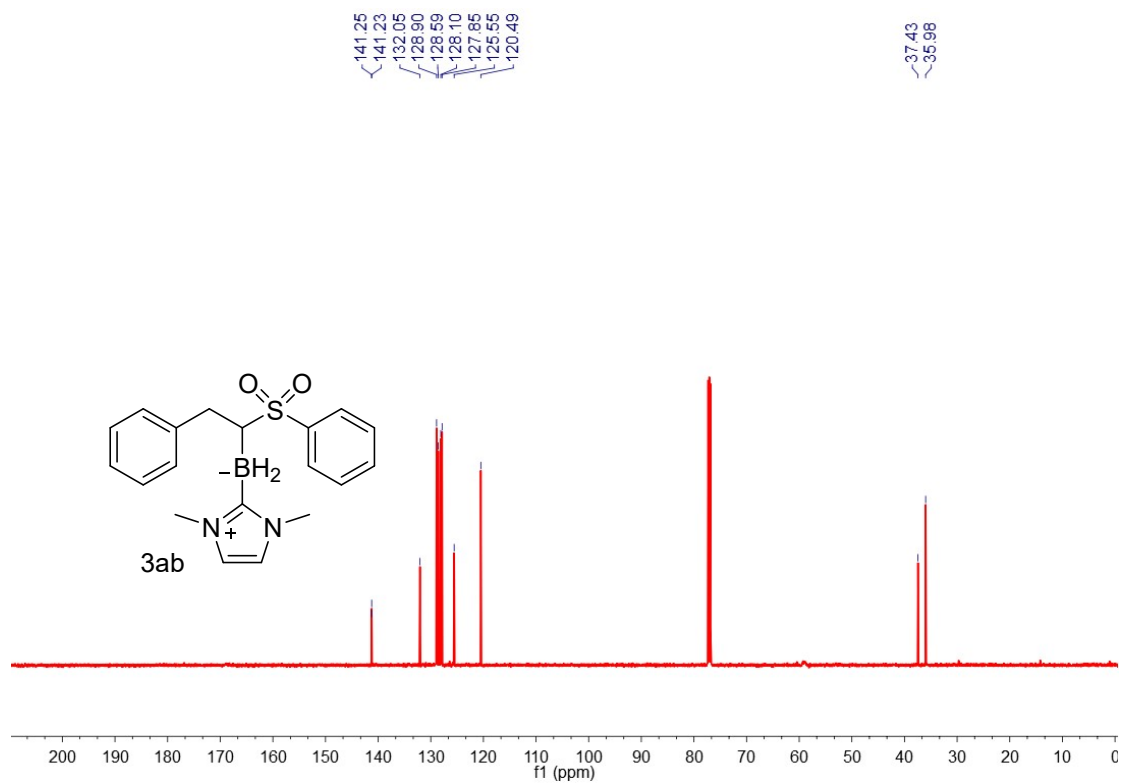


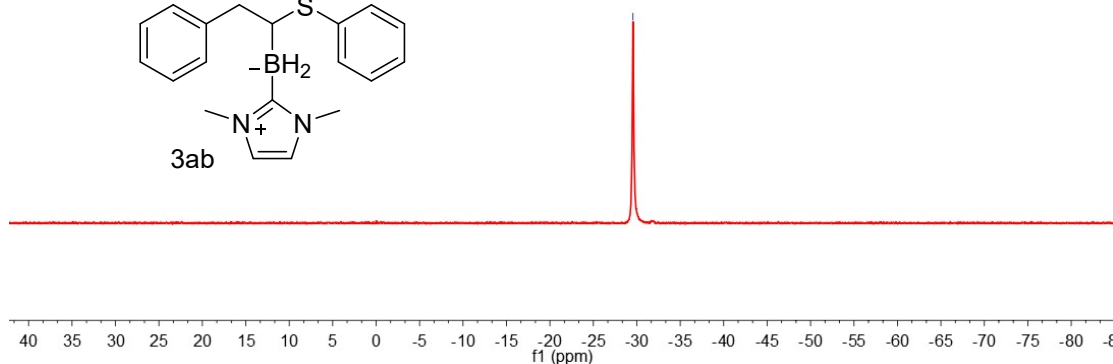
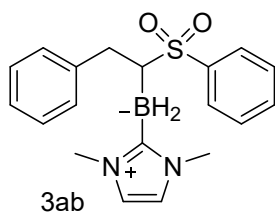




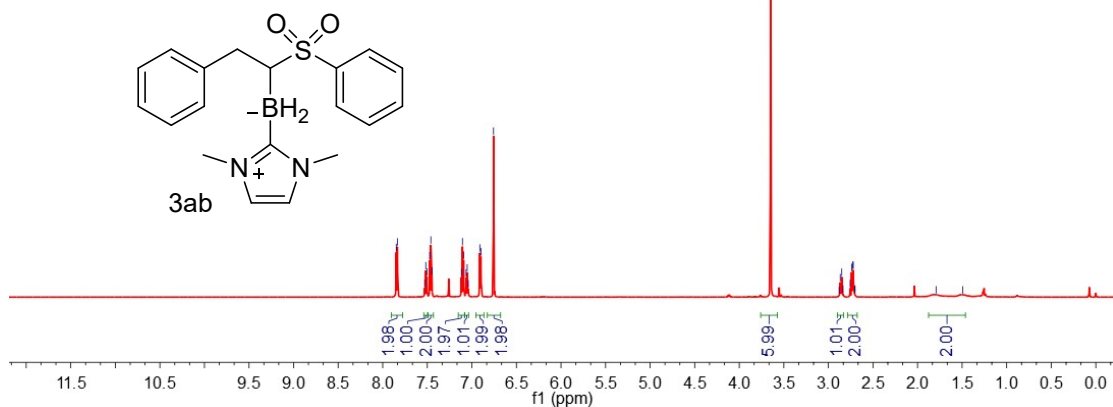
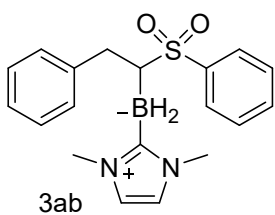
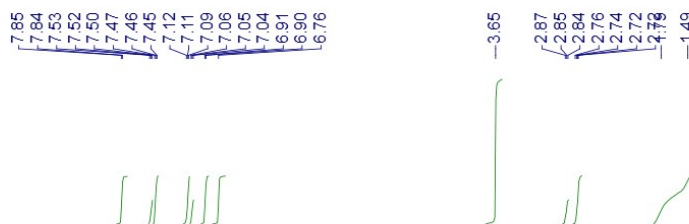




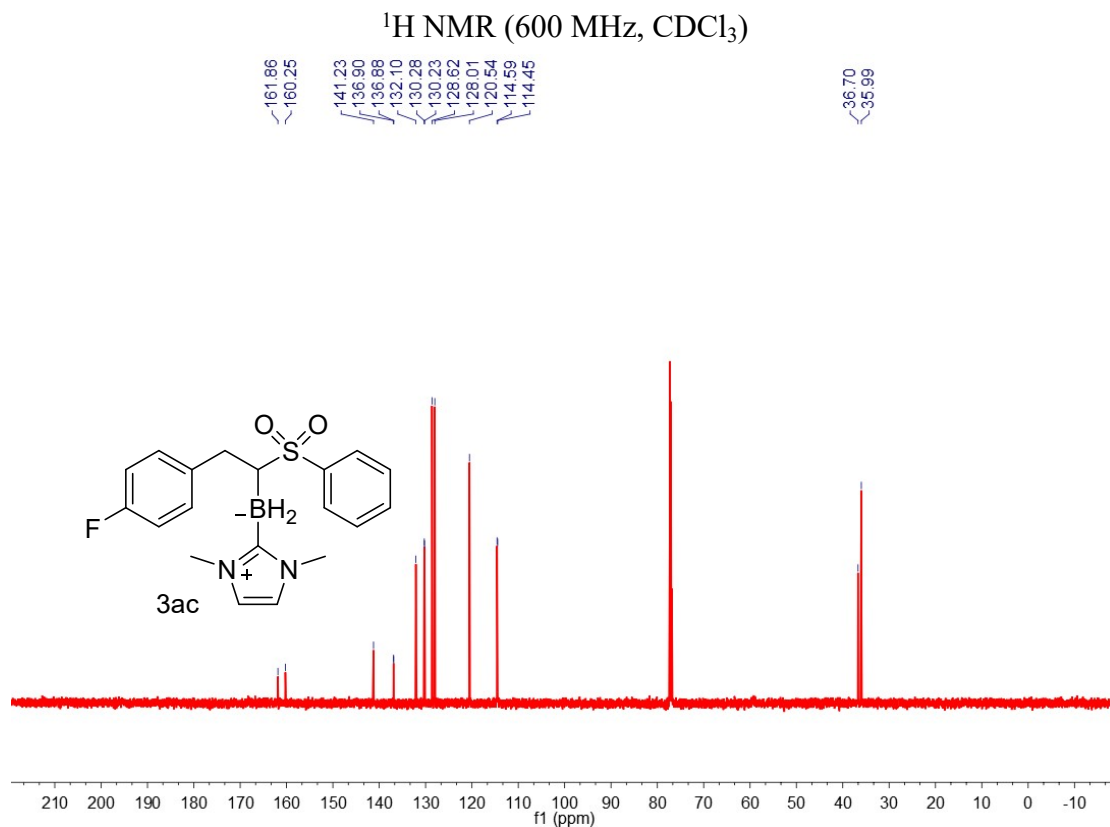
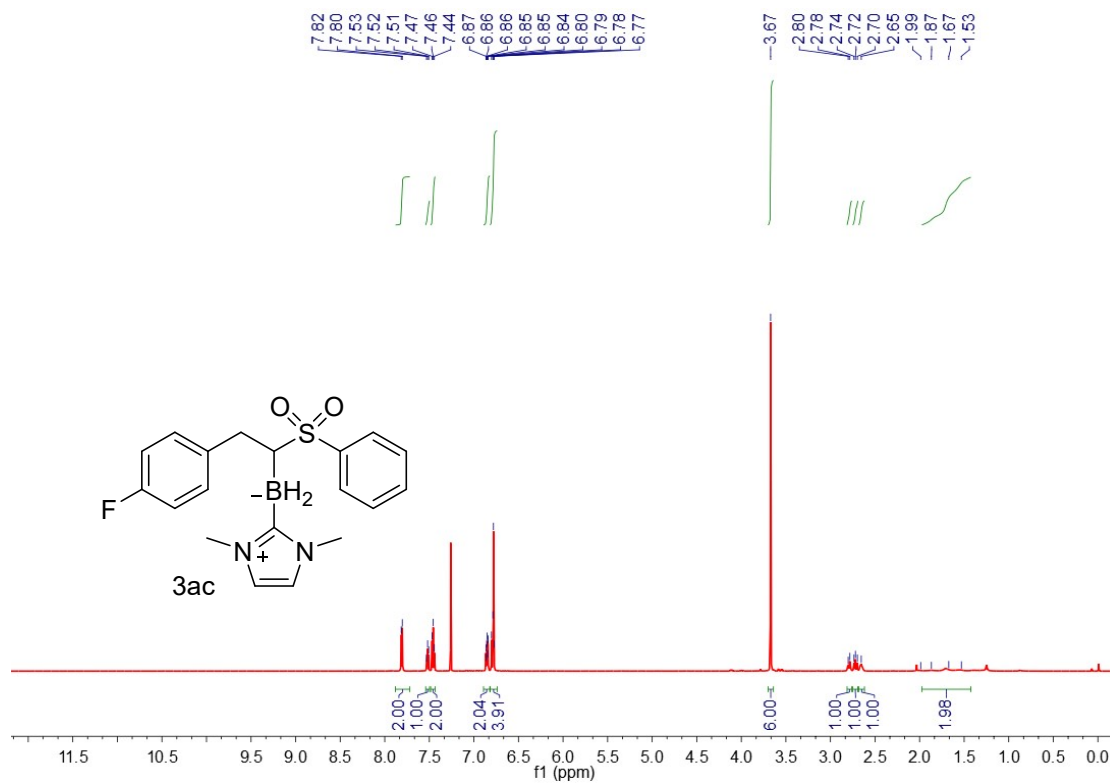


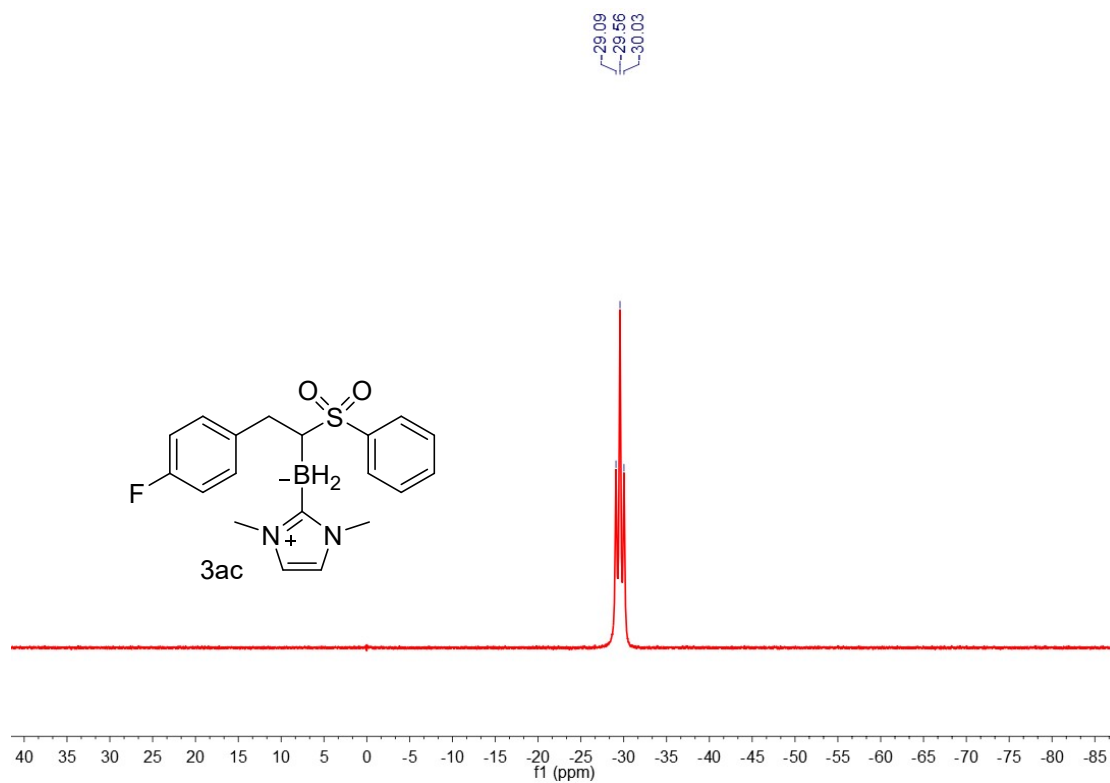


$^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3)

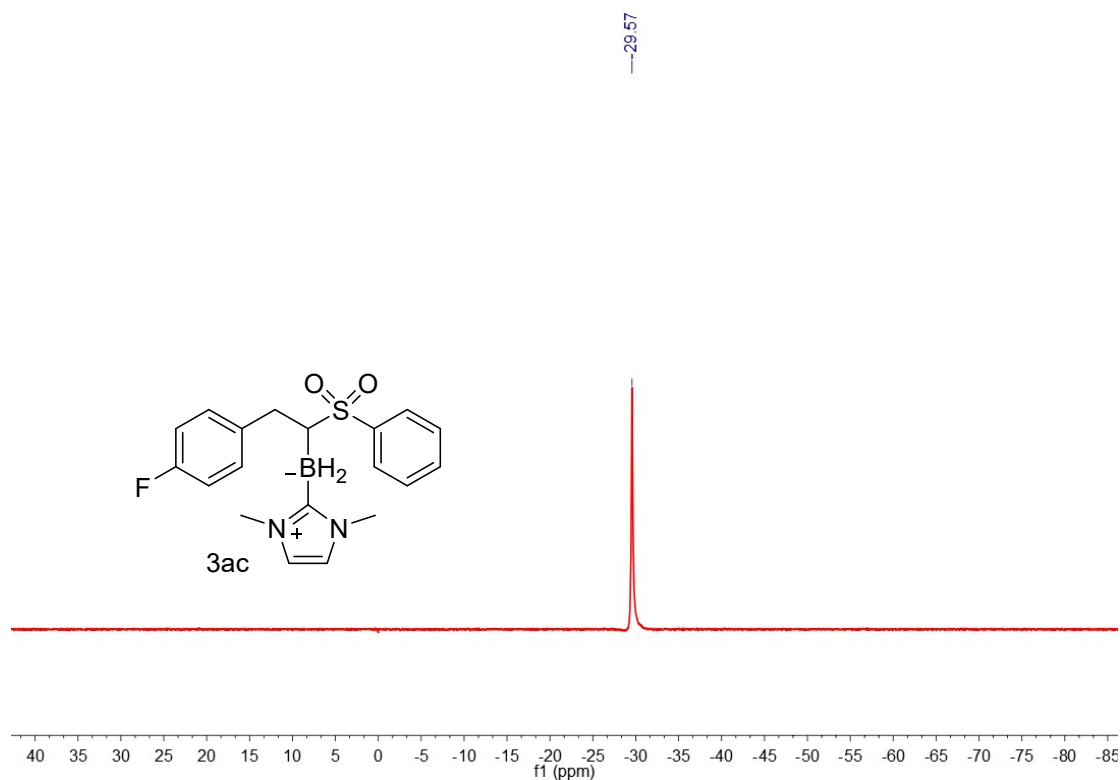


$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3)

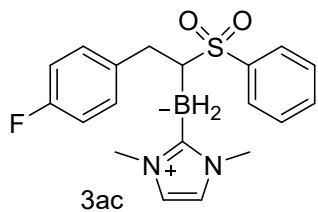
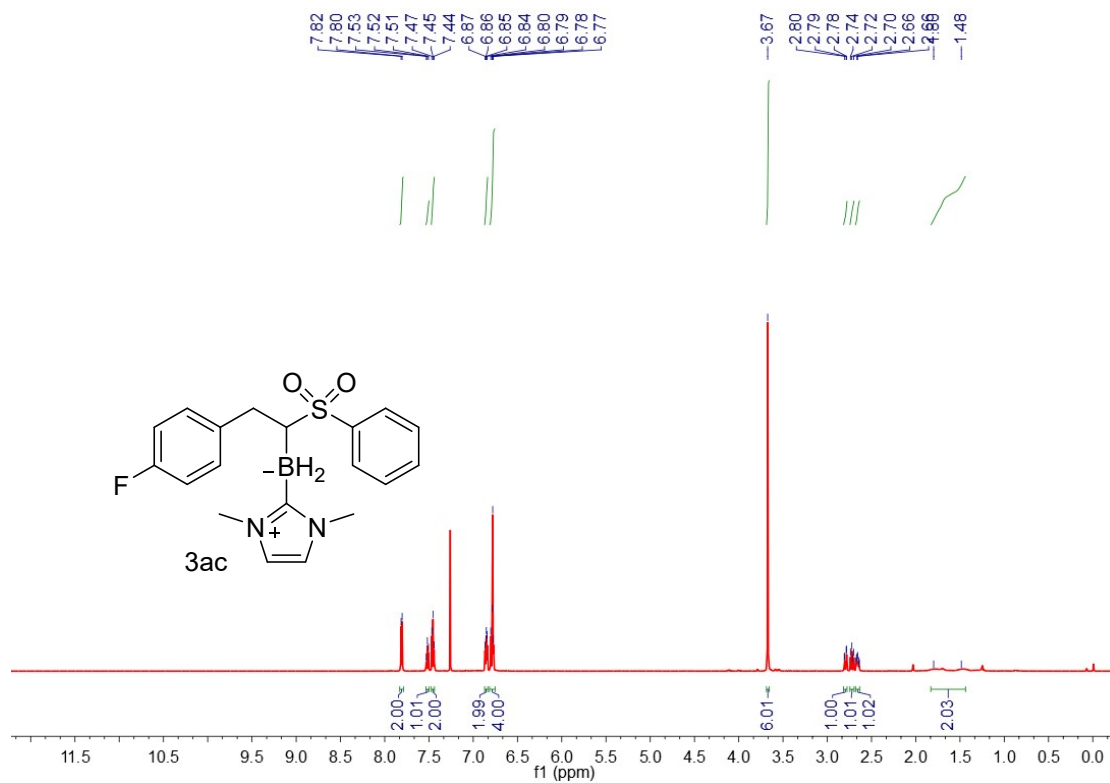




^{11}B NMR (193 MHz, CDCl_3)

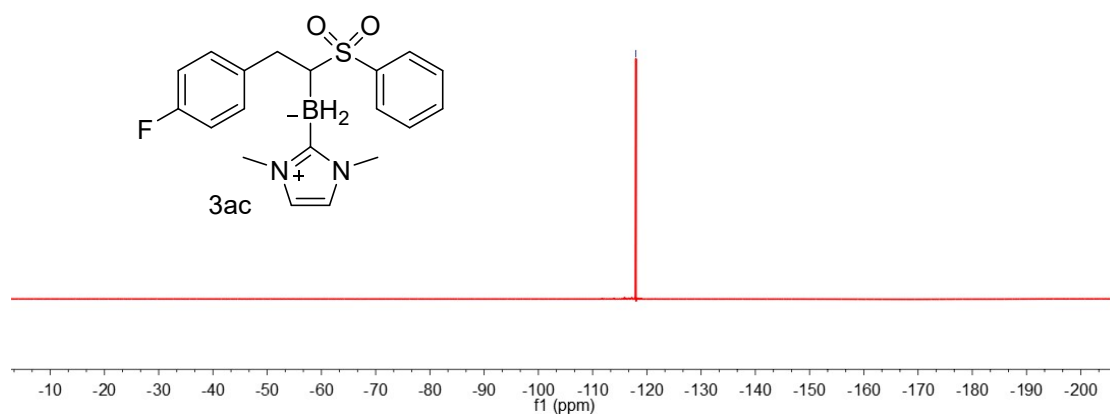


$^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3)

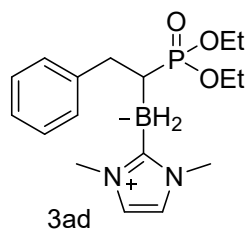
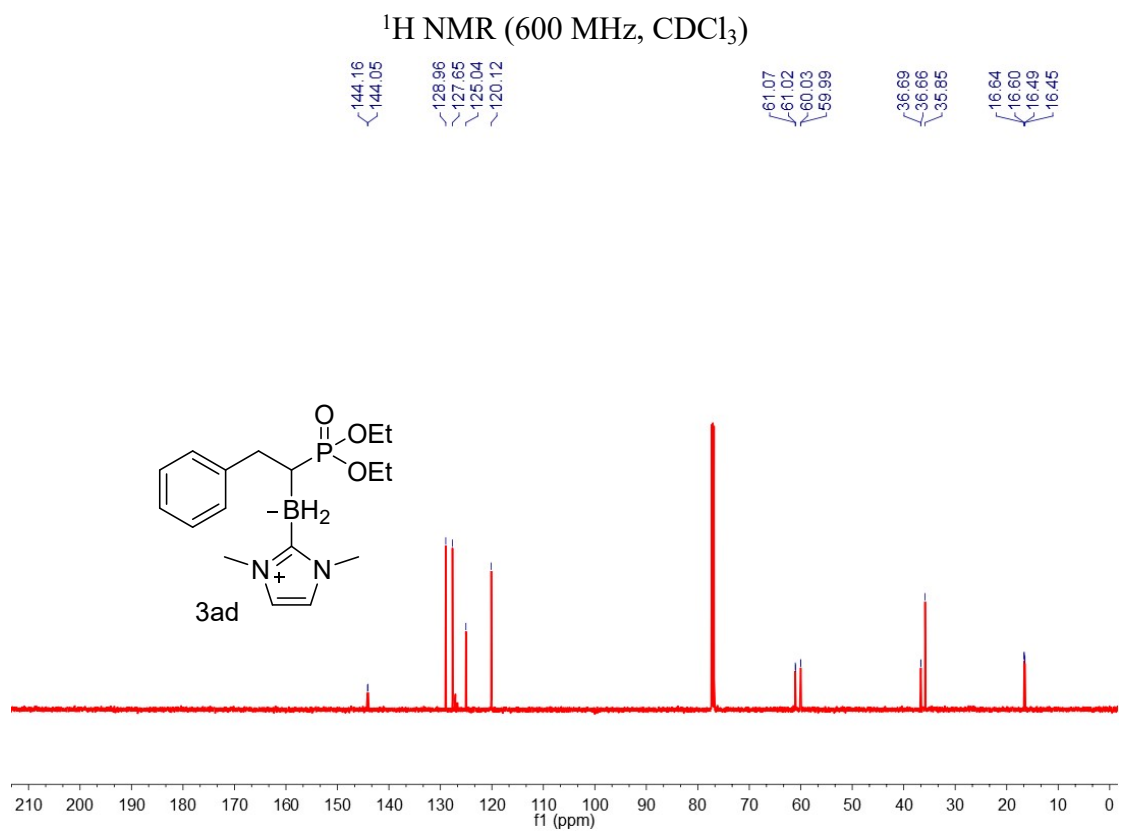
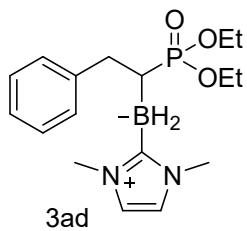
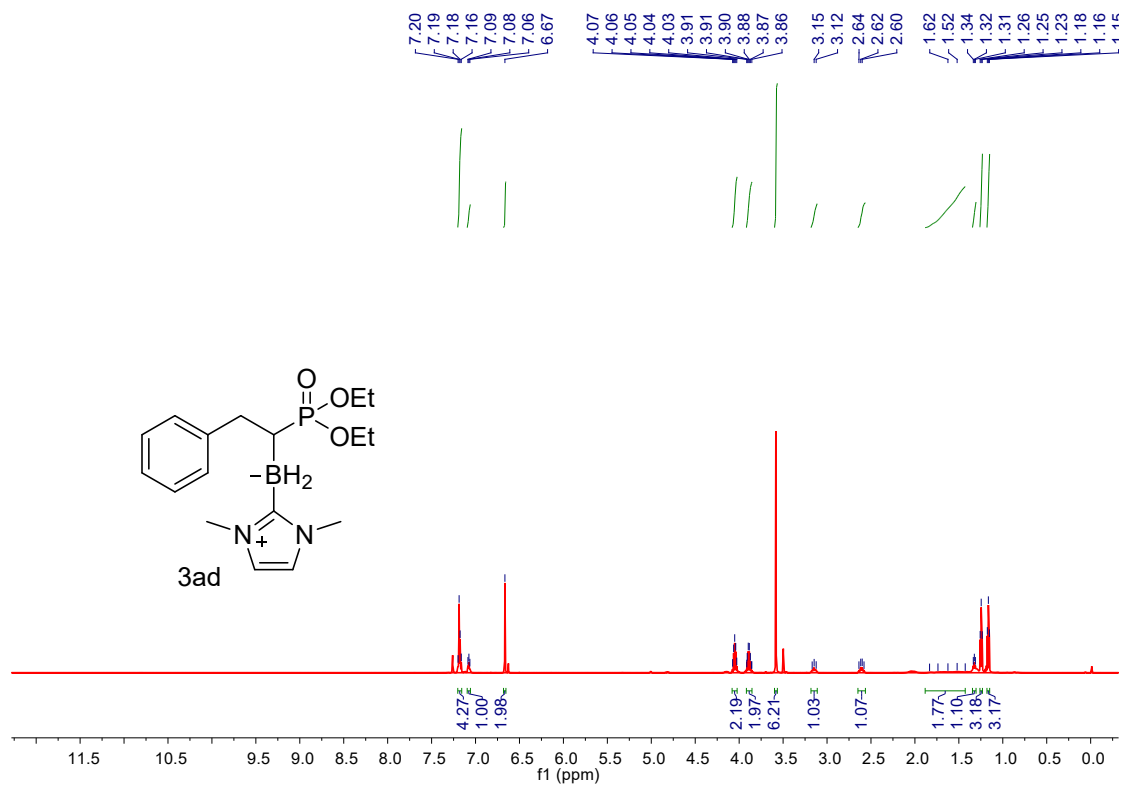


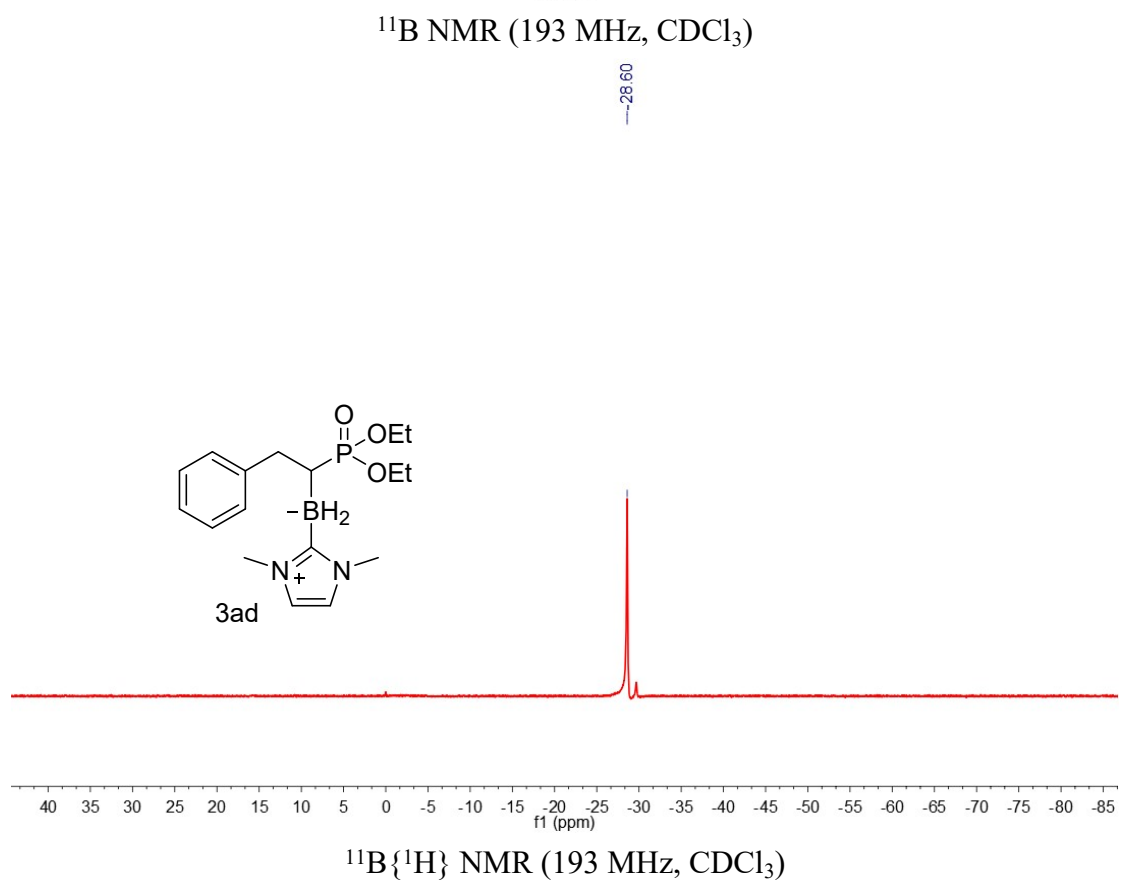
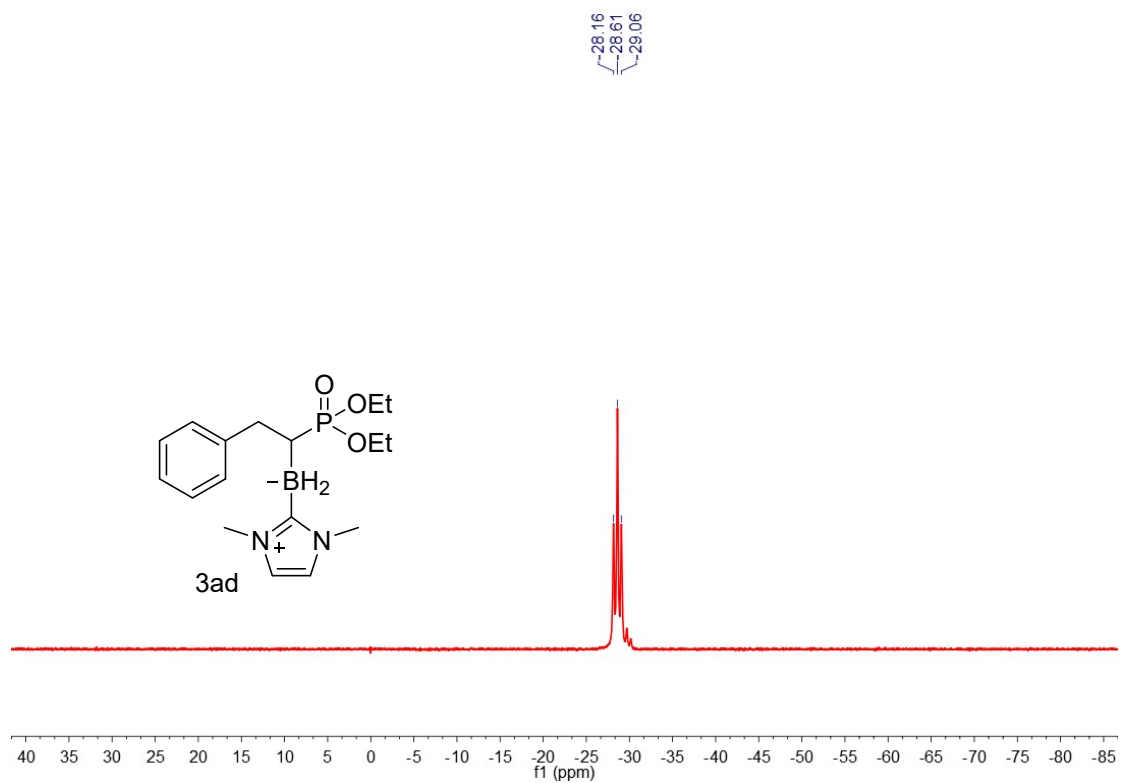
$^1\text{H}\{^1\text{B}\}$ NMR (600 MHz, CDCl_3)

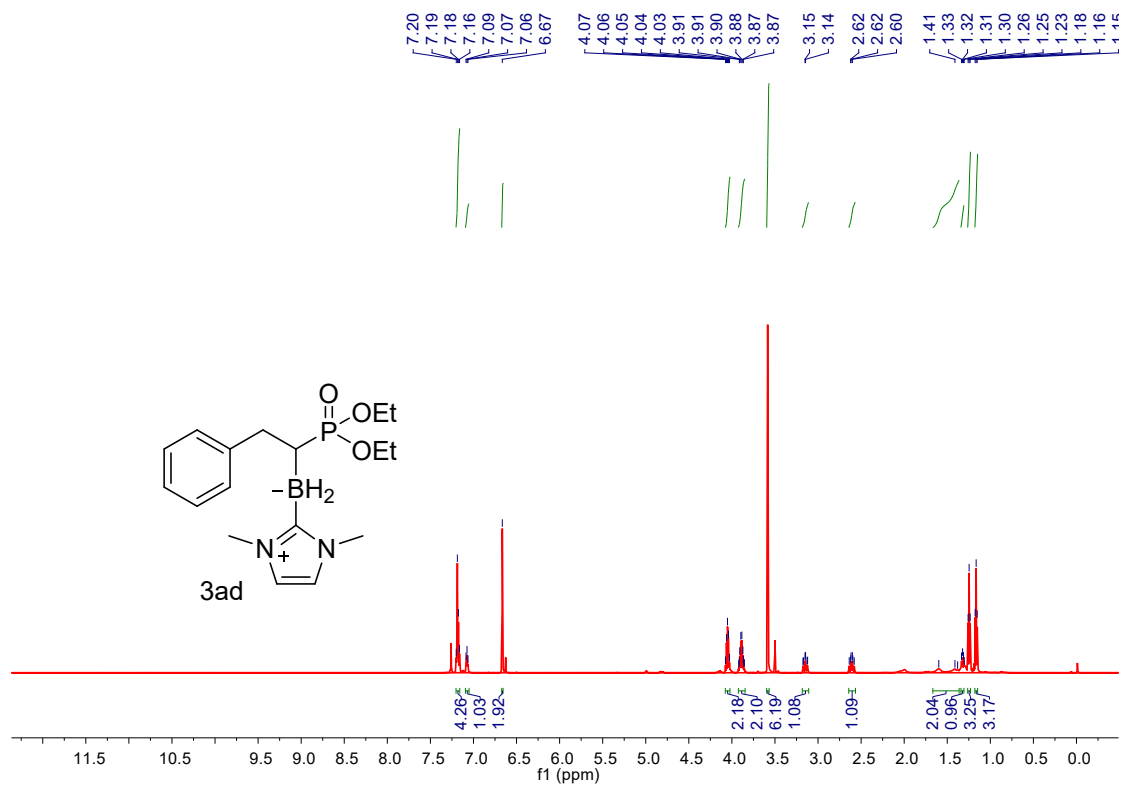
—117.98



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

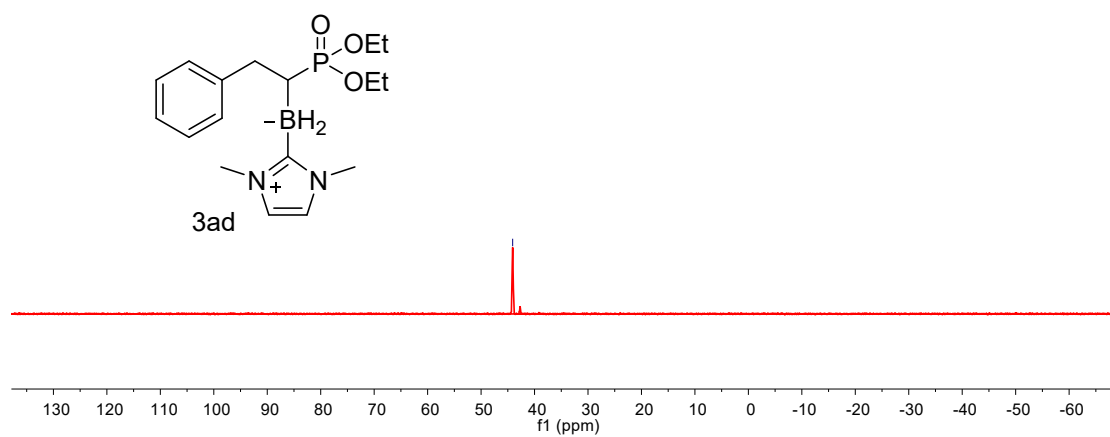




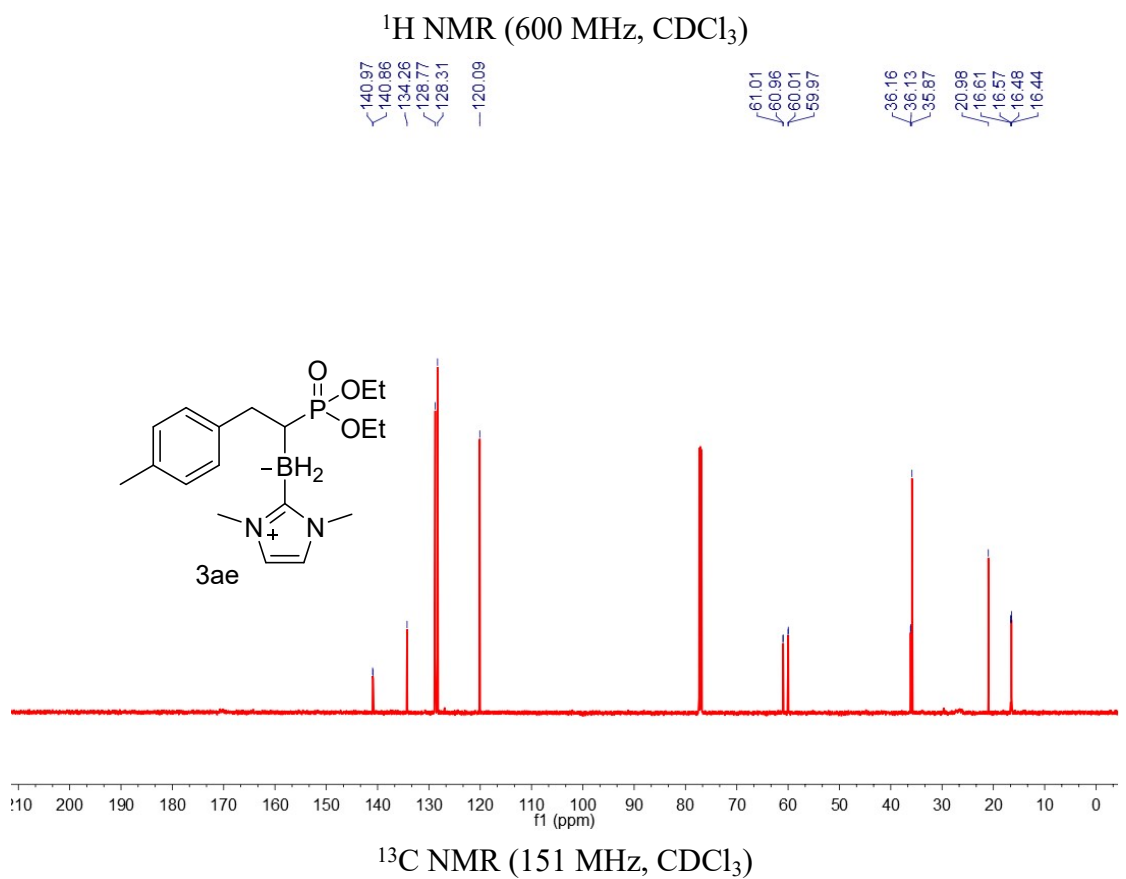
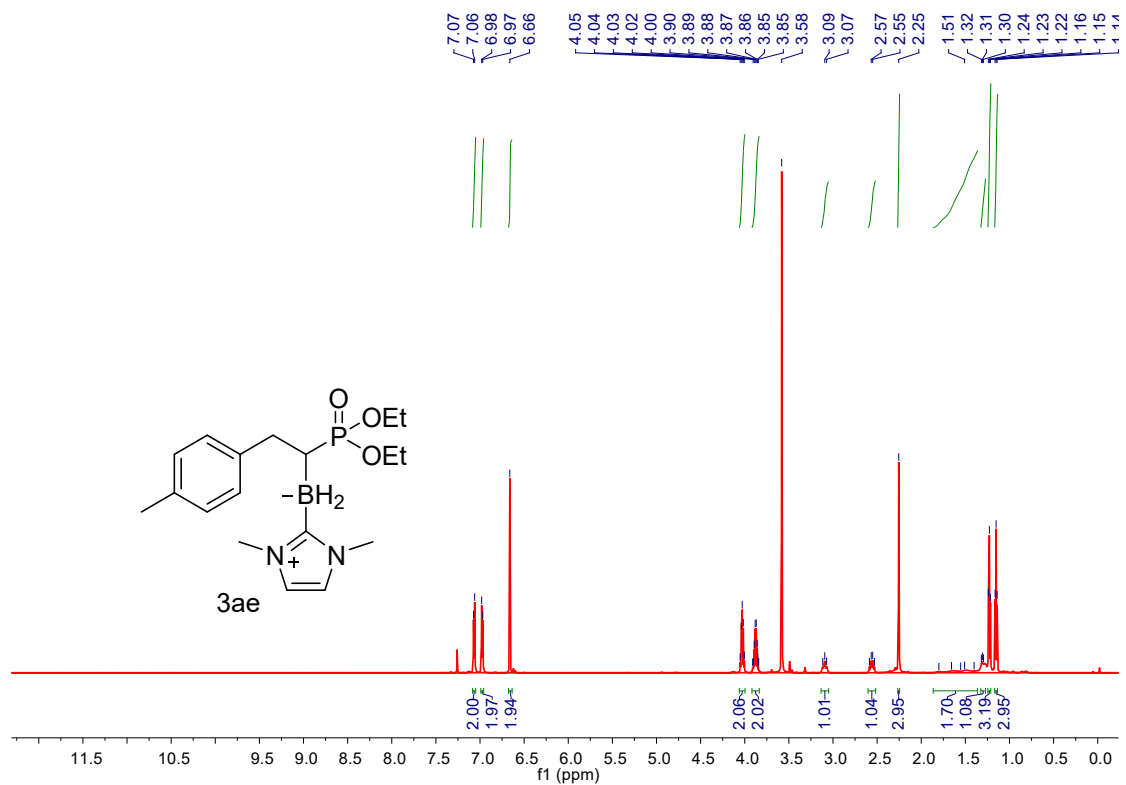


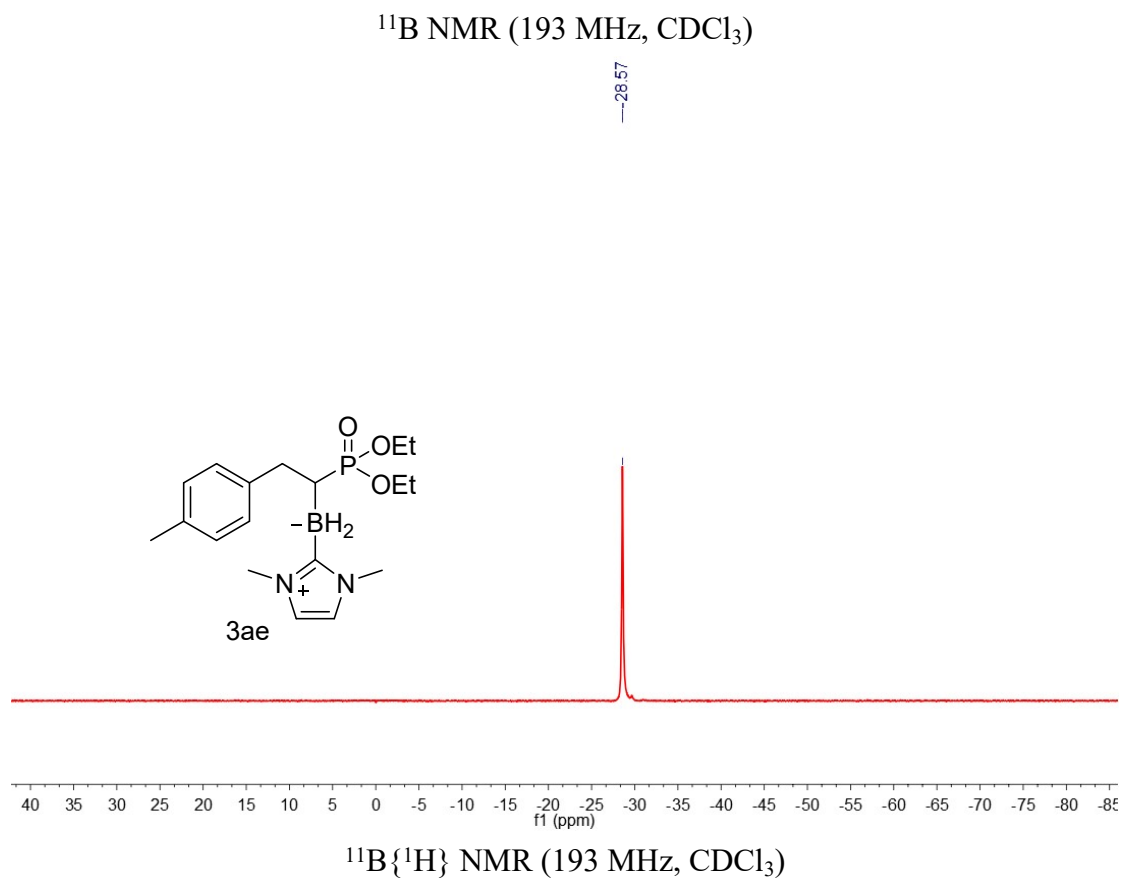
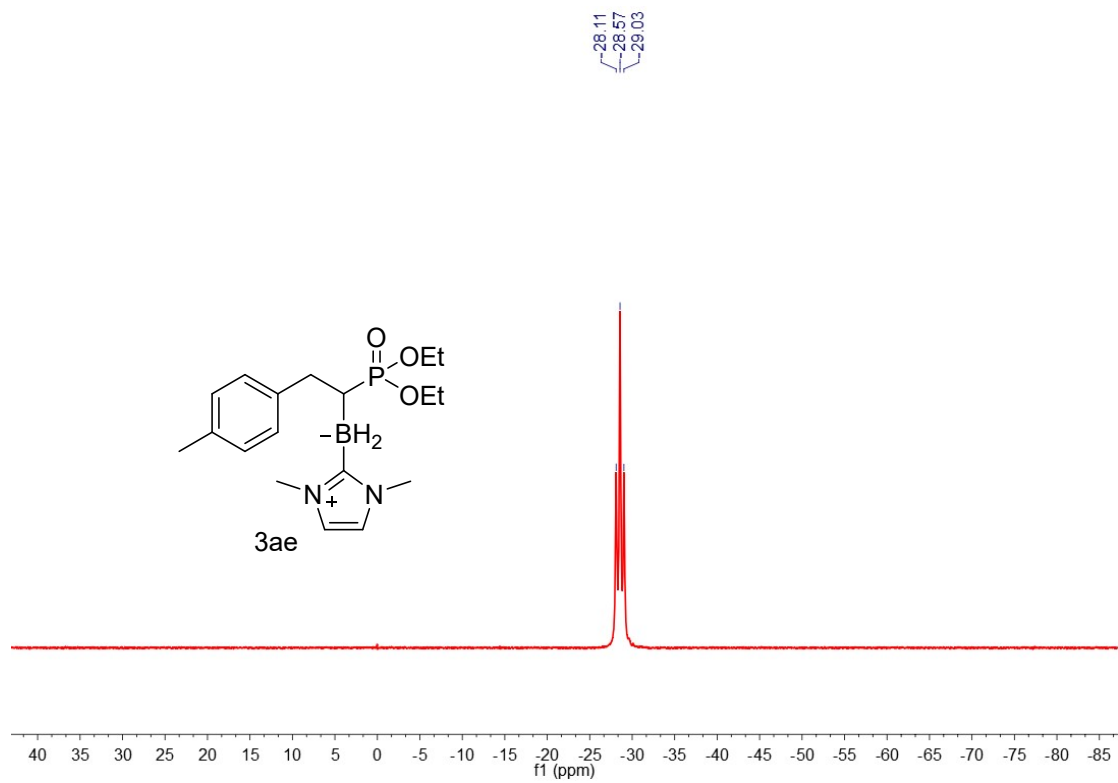
$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3)

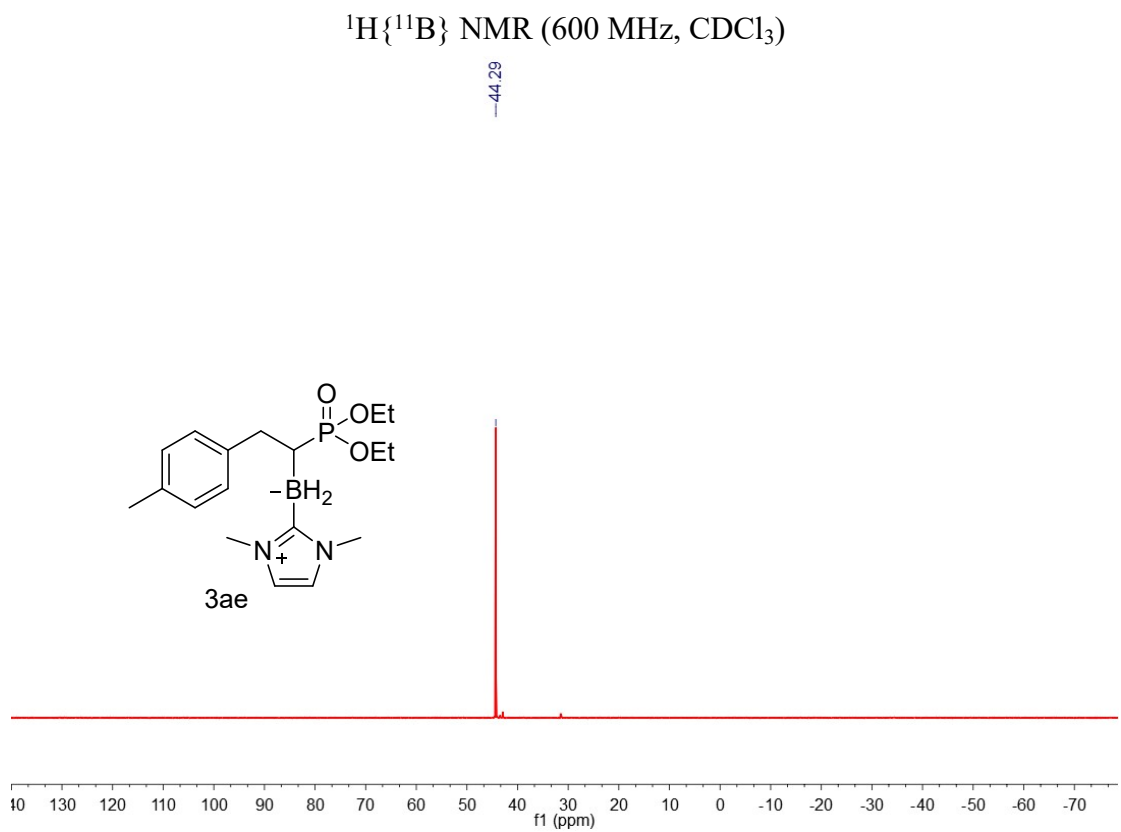
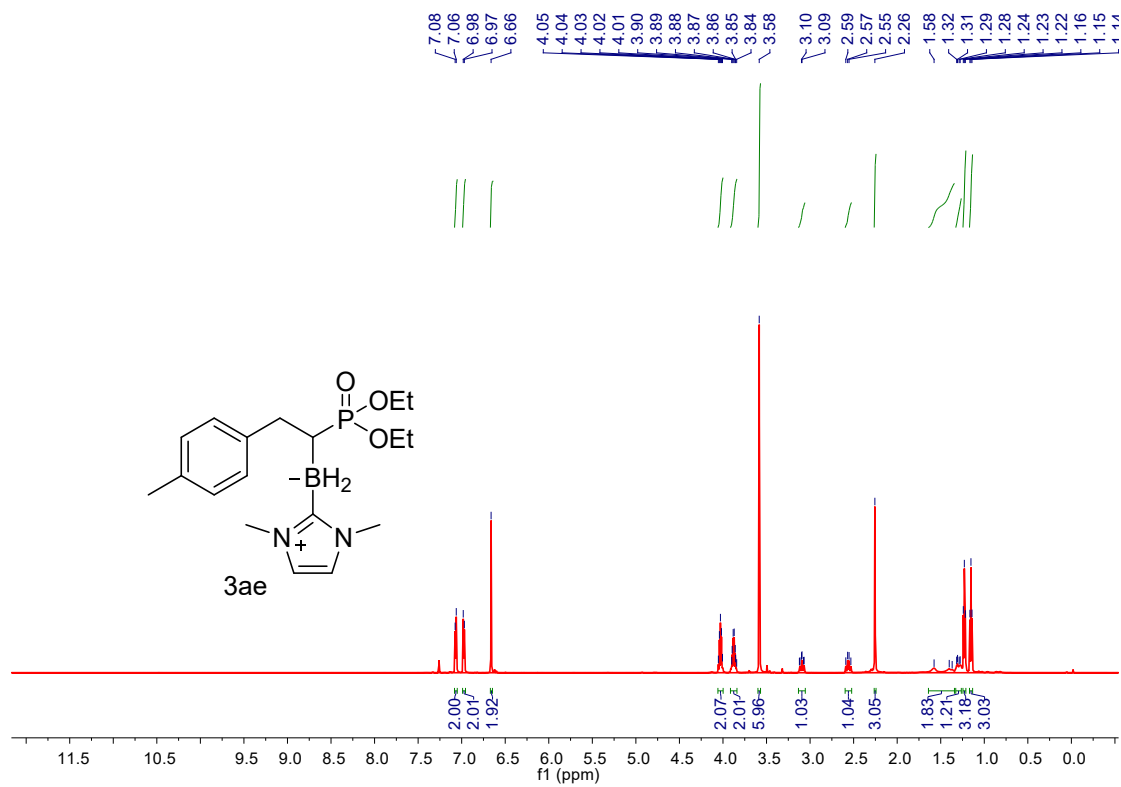
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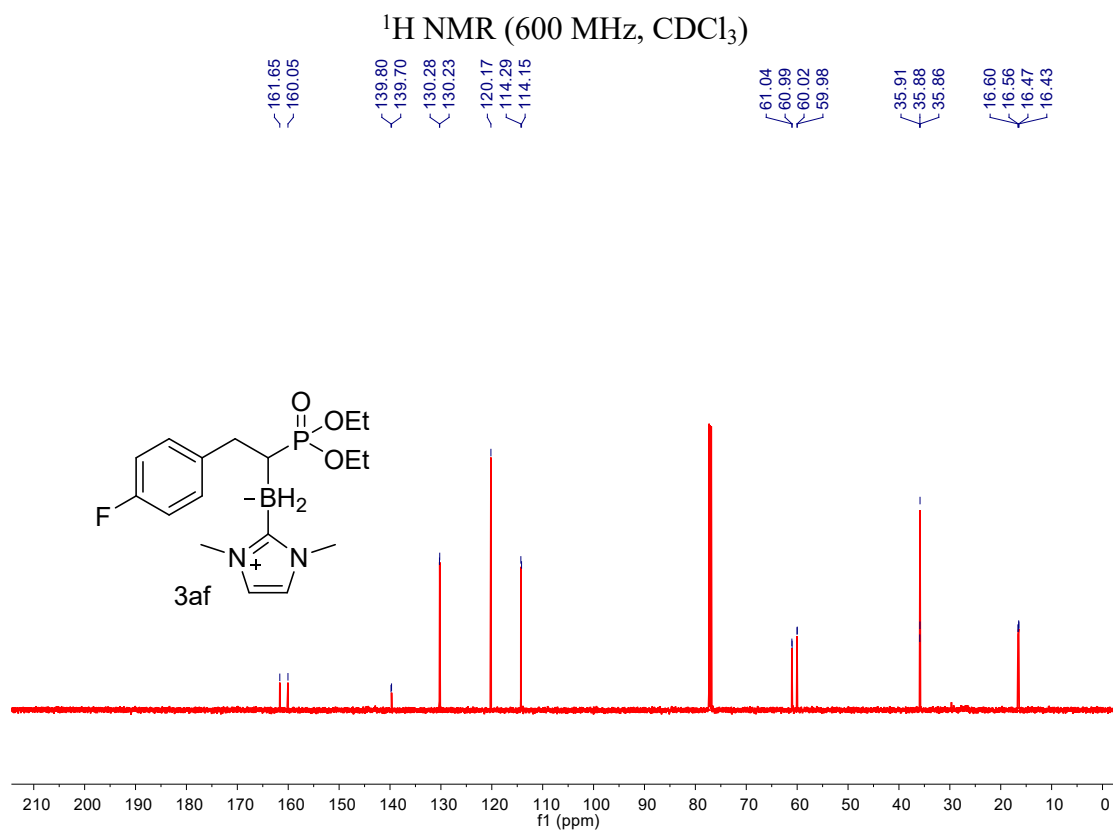
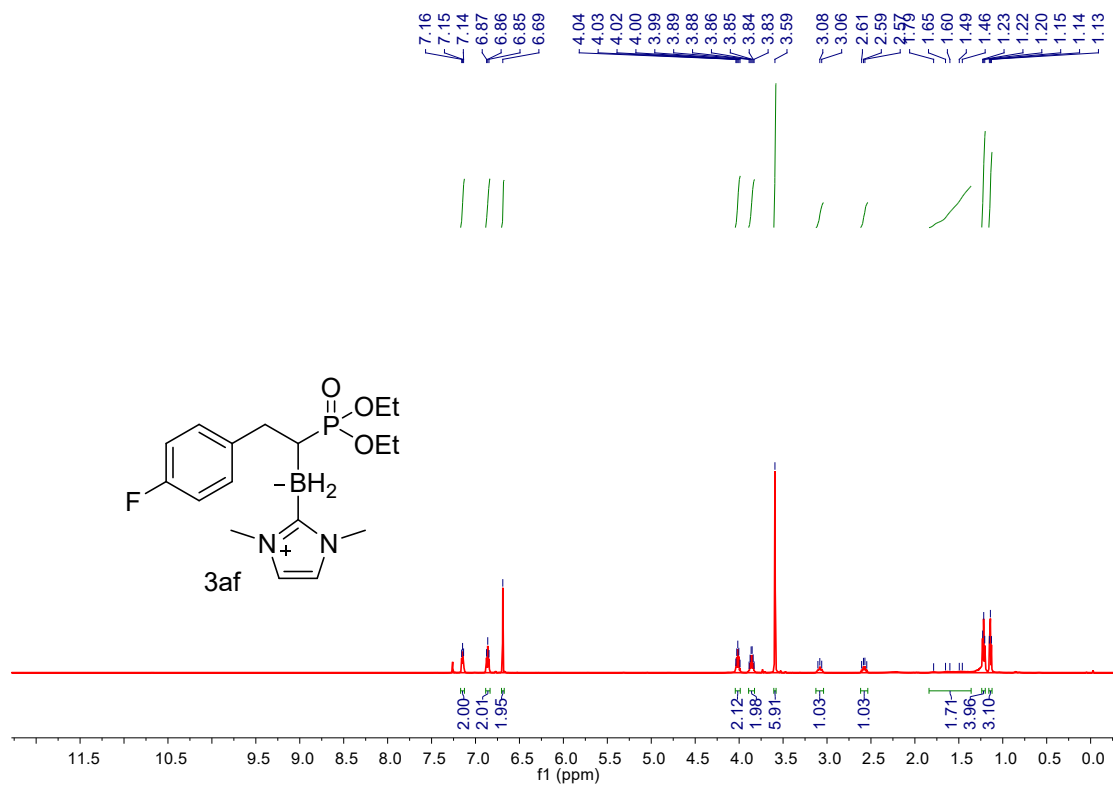


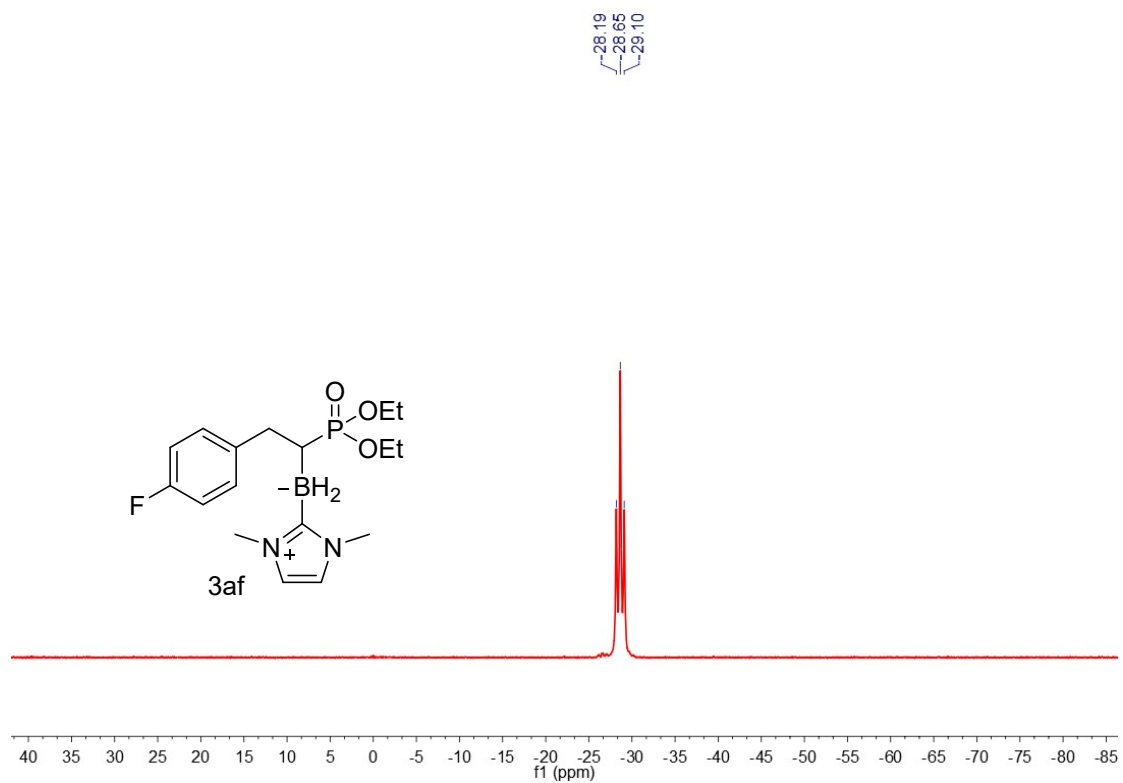
^{31}P NMR (243 MHz, CDCl_3)



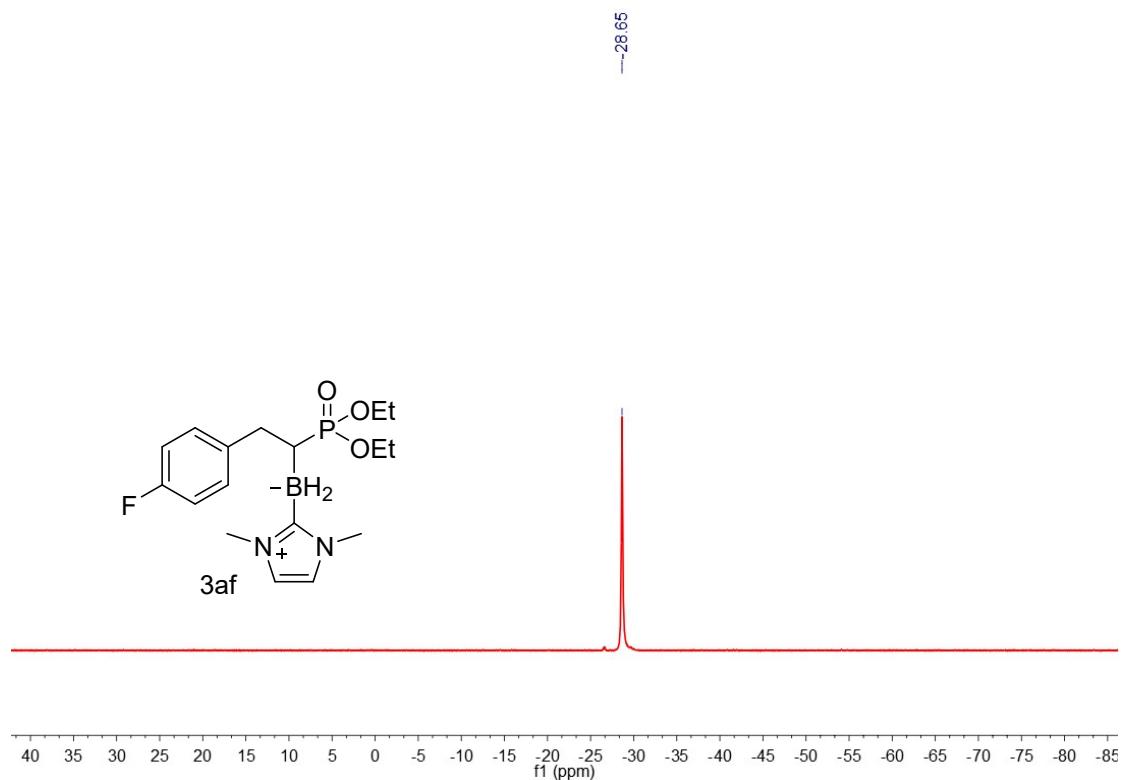




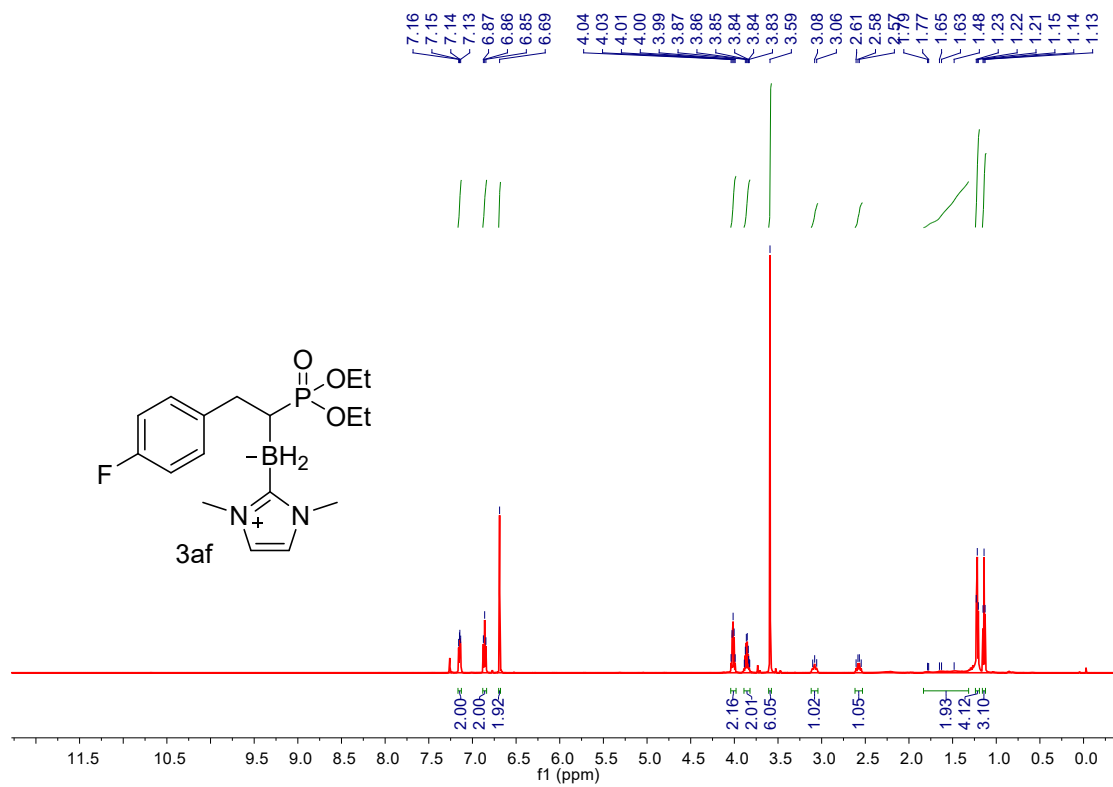




^{11}B NMR (193 MHz, CDCl_3)

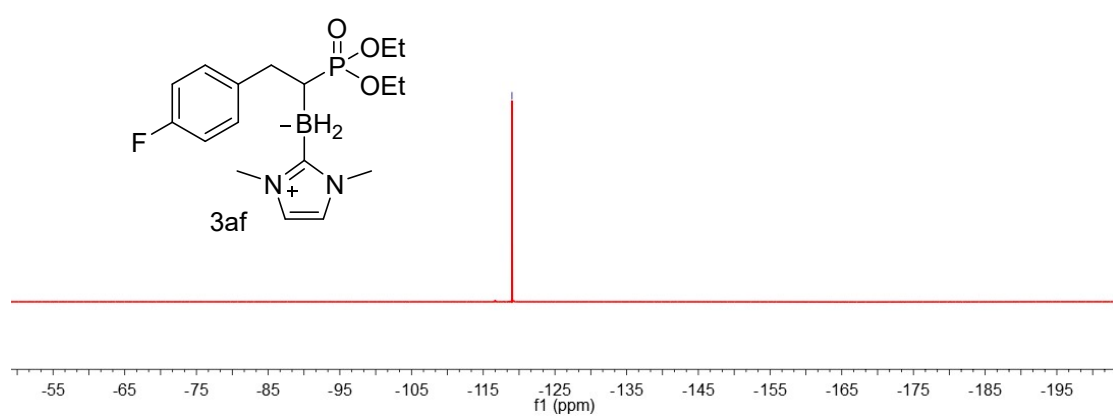


$^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3)



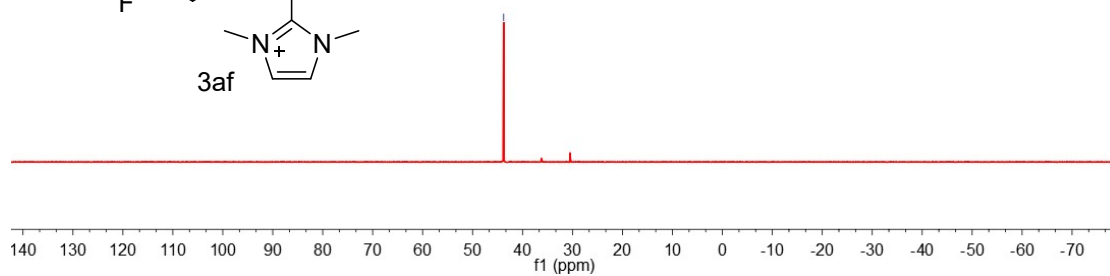
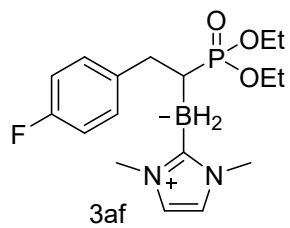
$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3)

-119.00

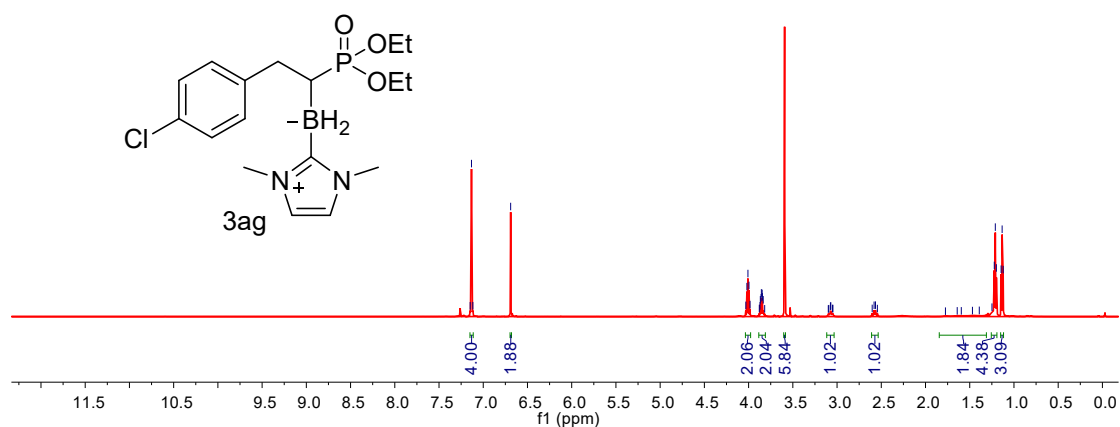
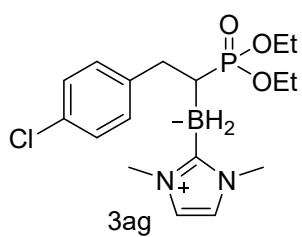
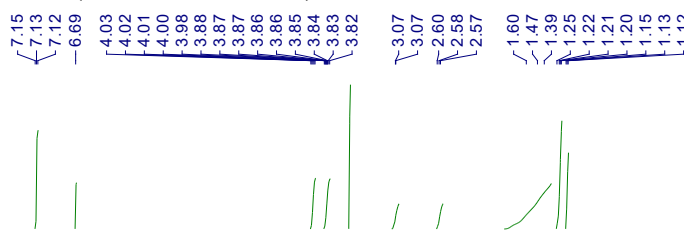


^{19}F NMR (565 MHz, CDCl_3)

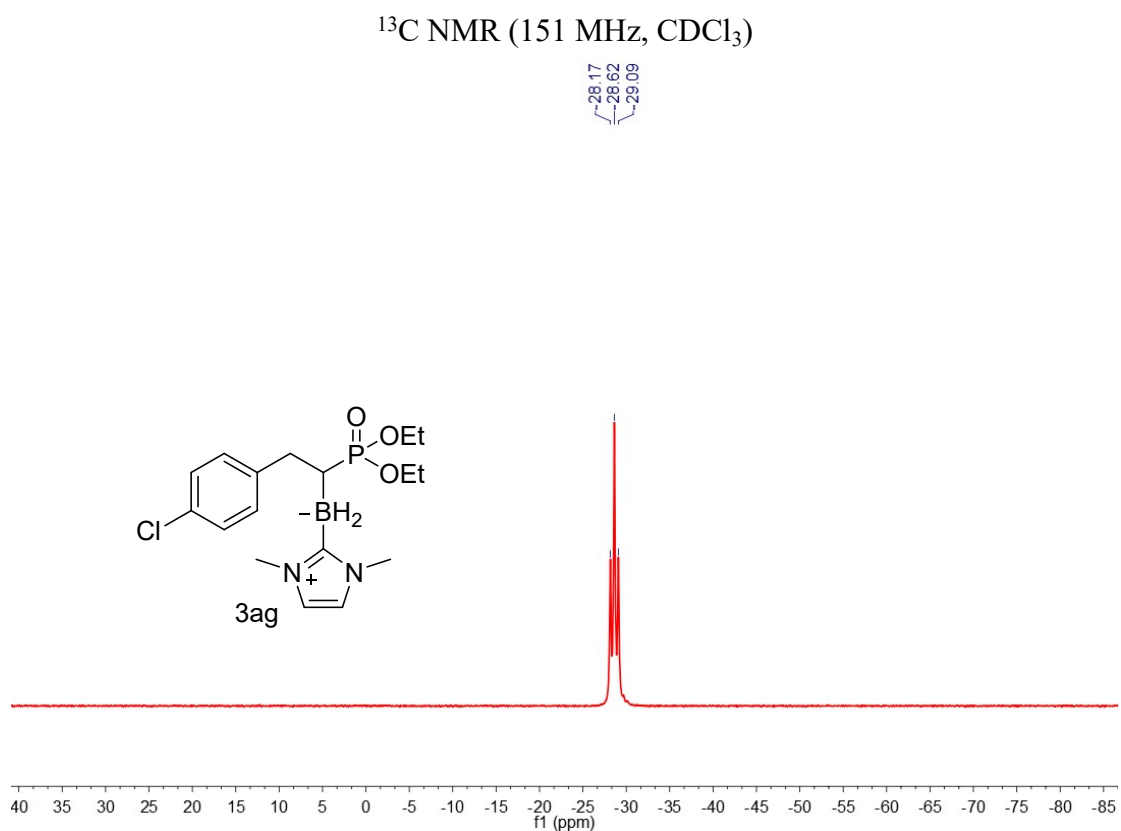
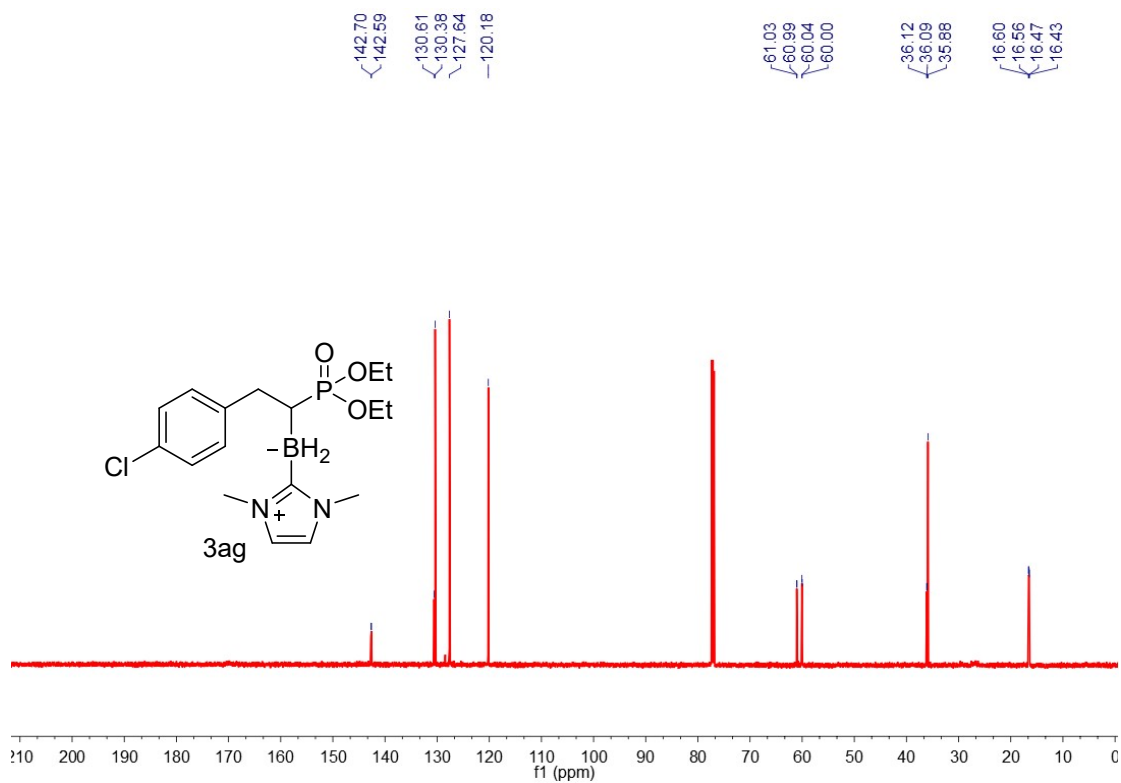
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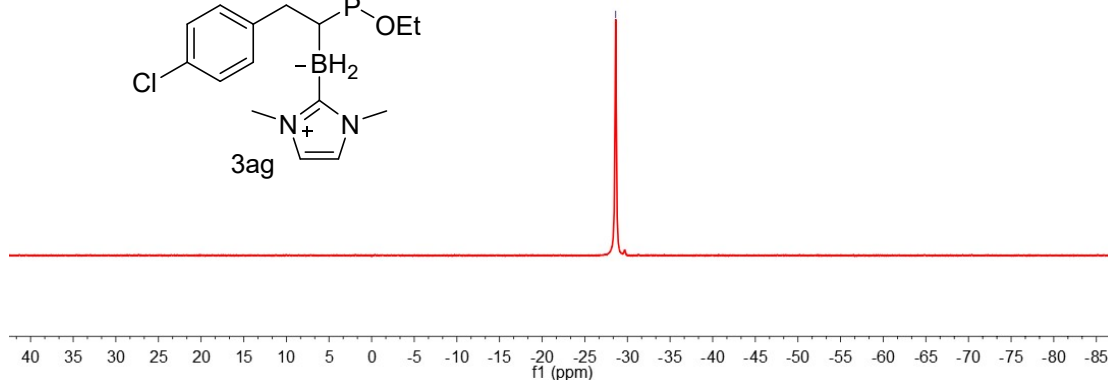
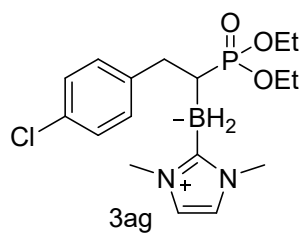


^{31}P NMR (243 MHz, CDCl_3)



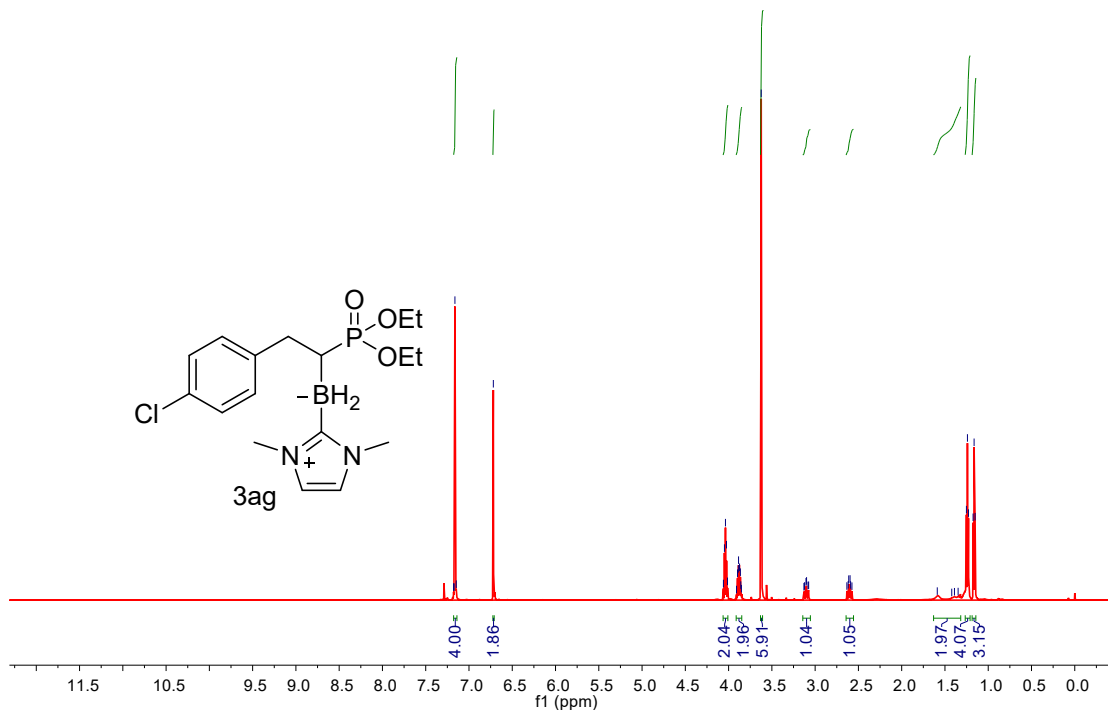
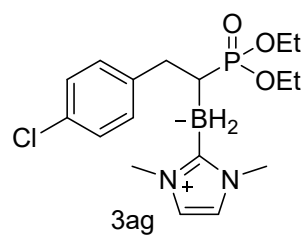
^1H NMR (600 MHz, CDCl_3)



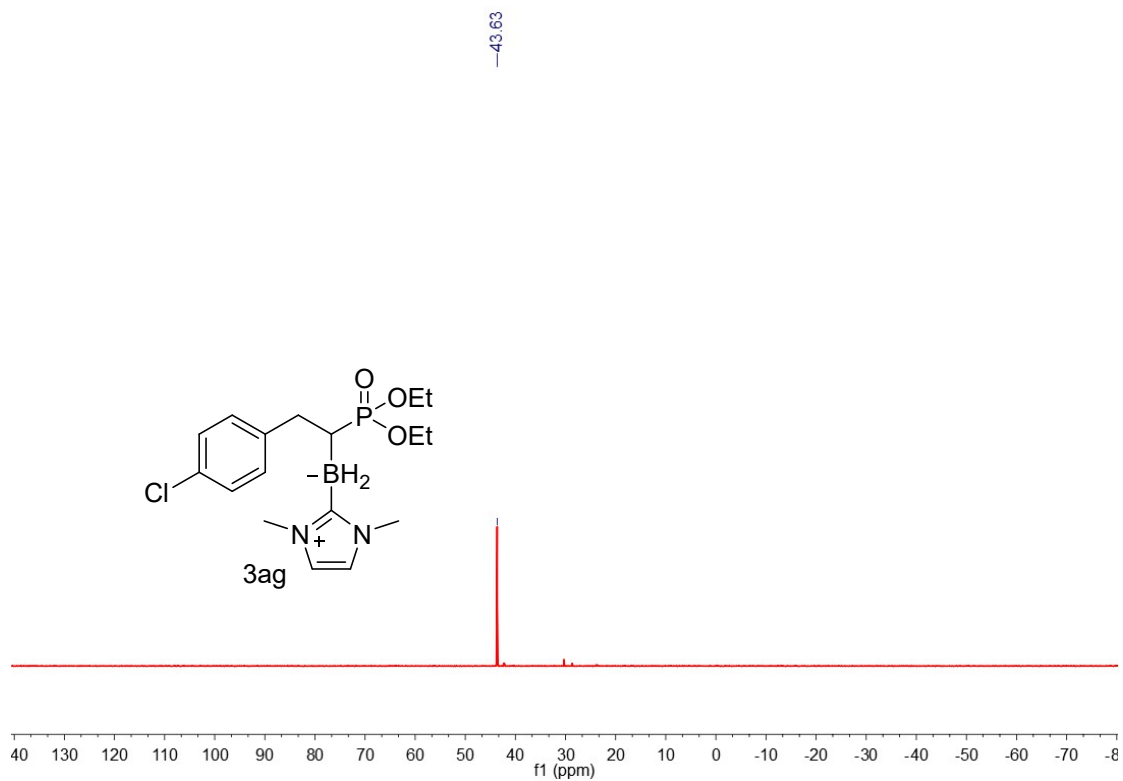


$^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3)

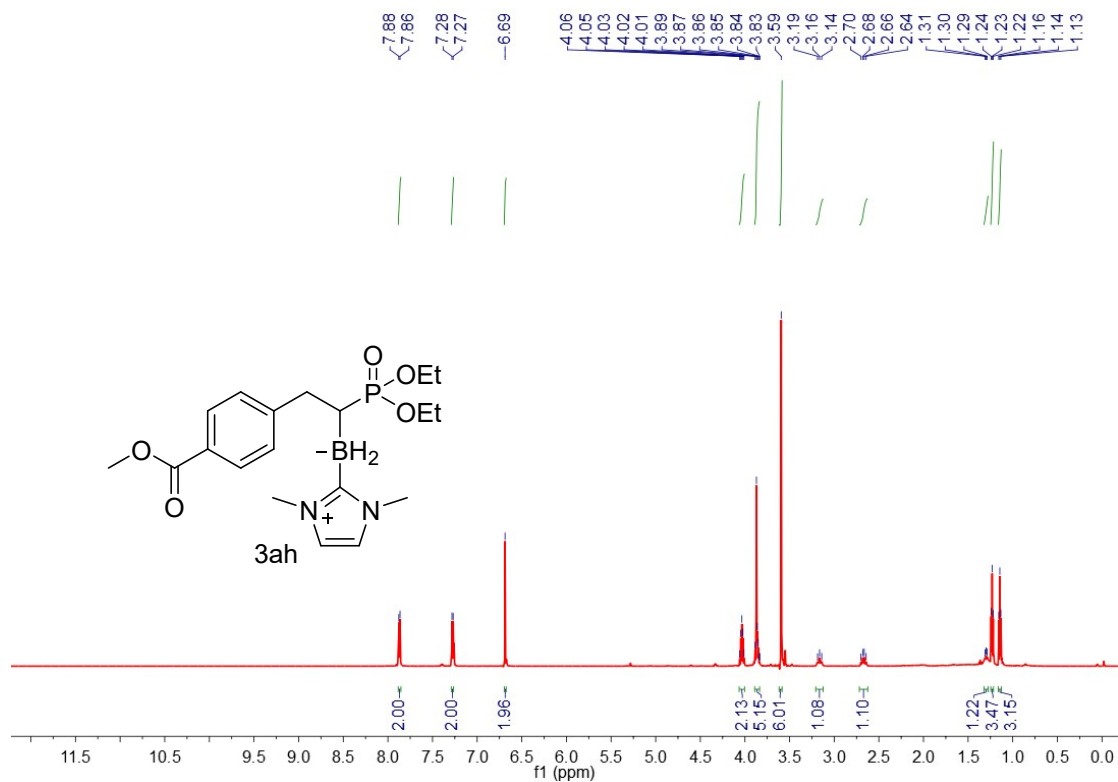
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3.86
3.85
3.62
3.11
3.10
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1.15



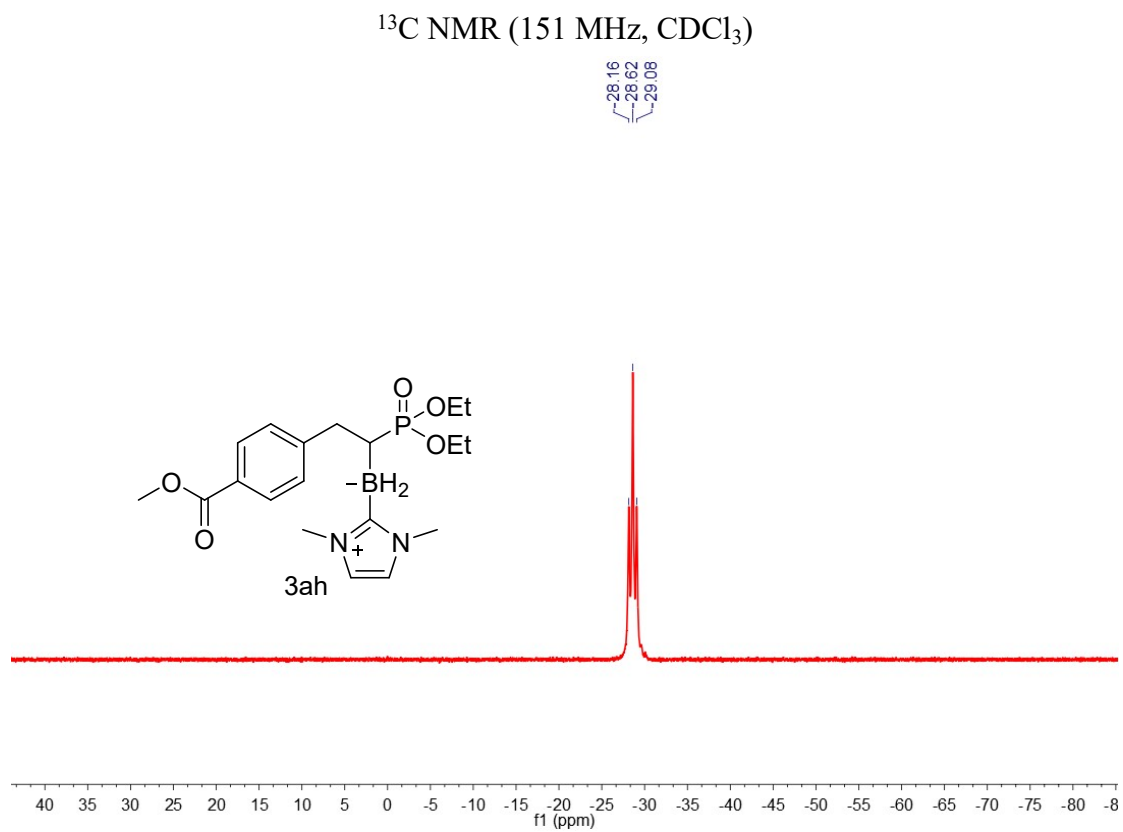
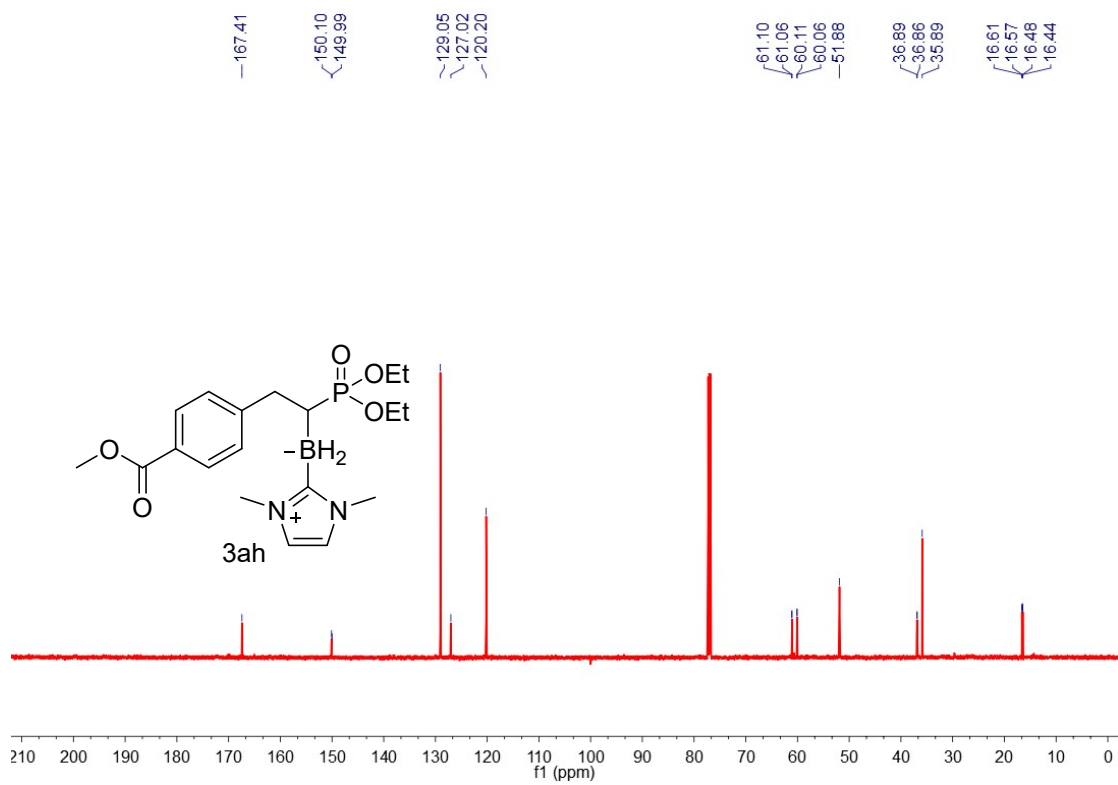
$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3)

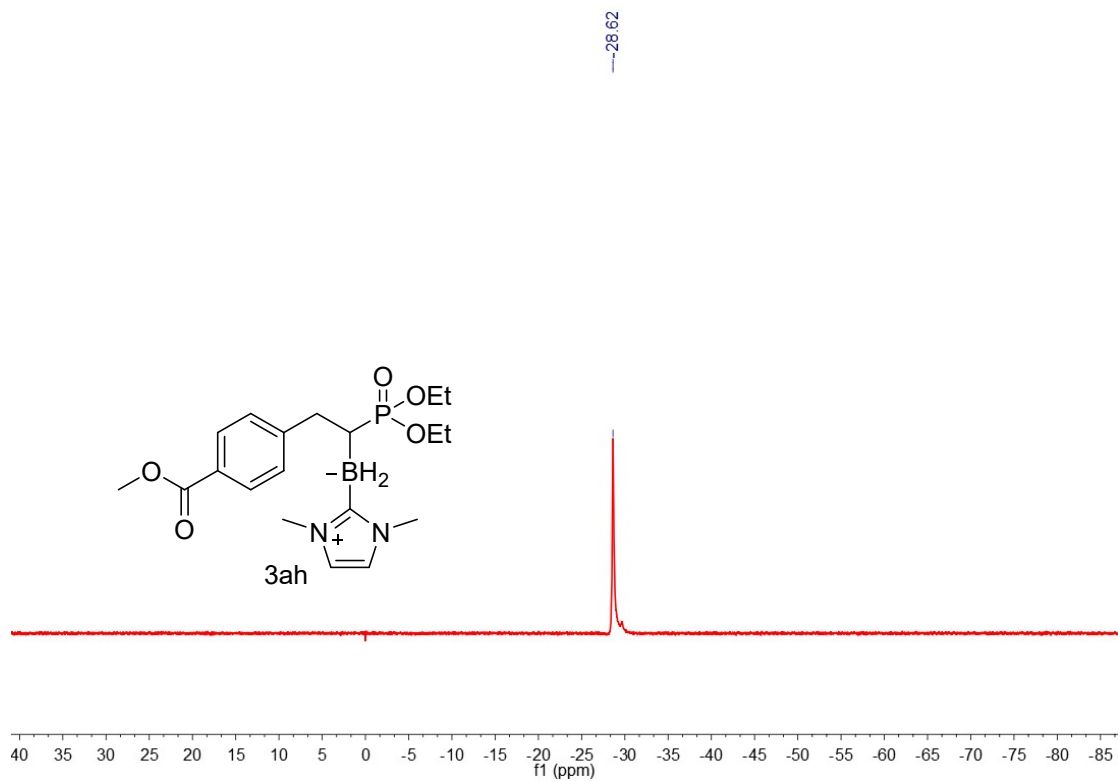


³¹P NMR (243 MHz, CDCl₃)

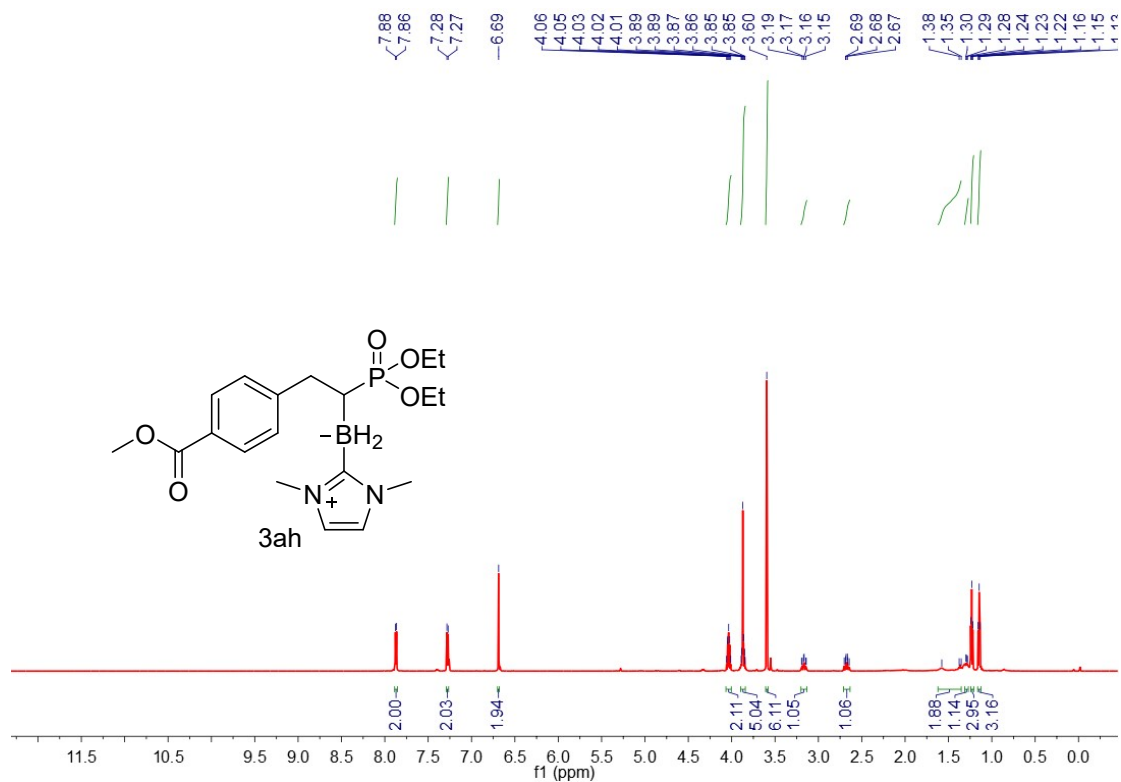


¹H NMR (600 MHz, CDCl₃)

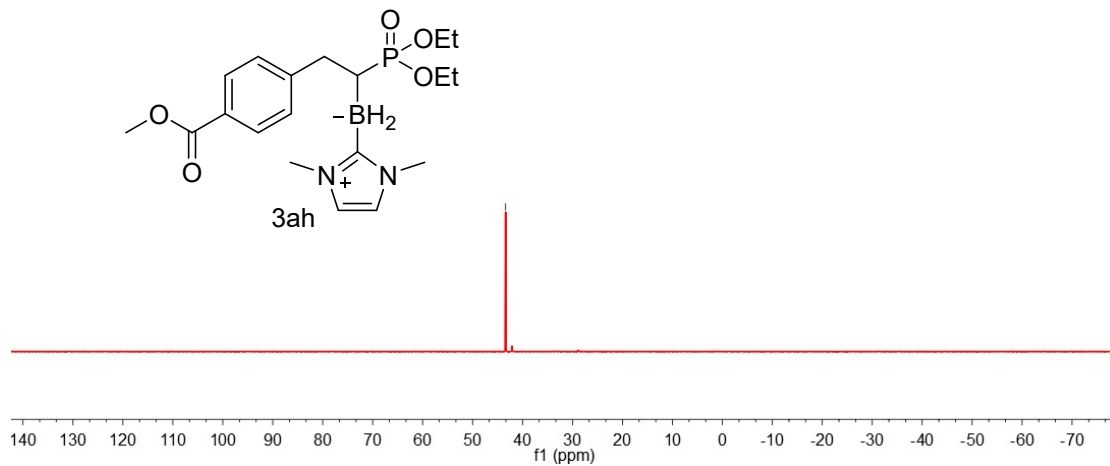




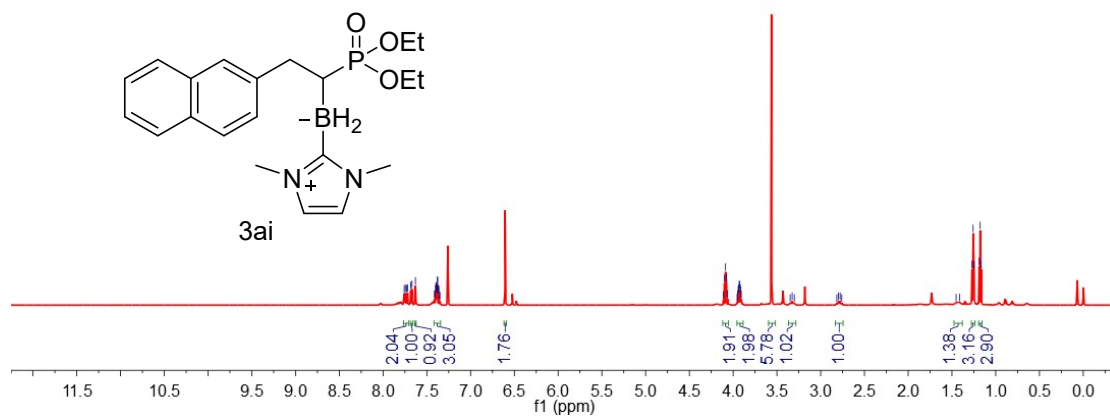
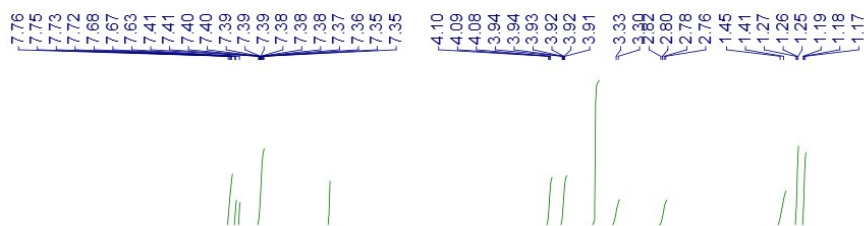
$^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3)



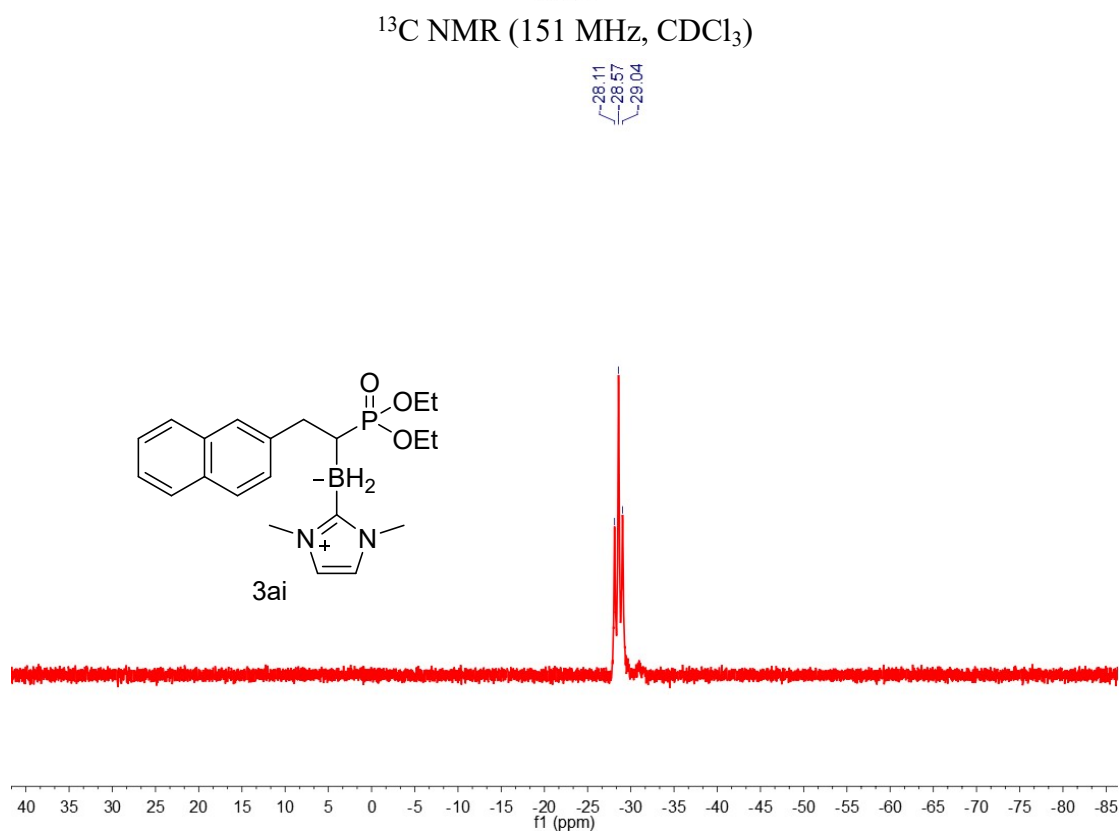
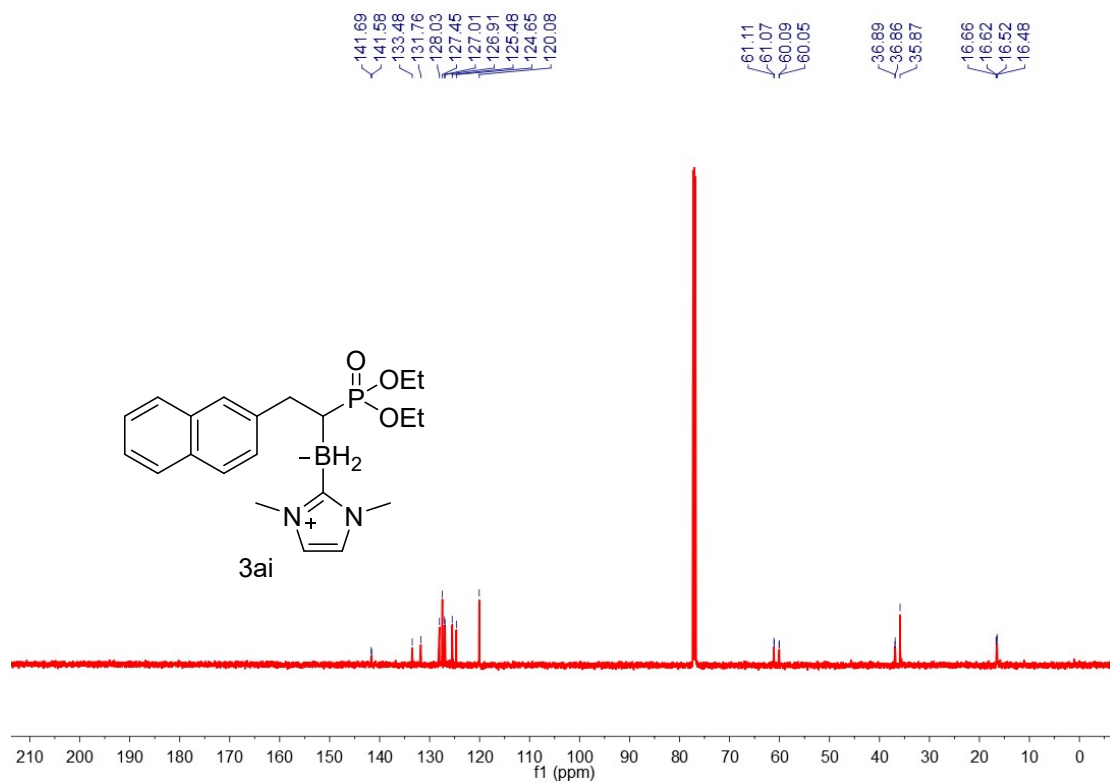
$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3)

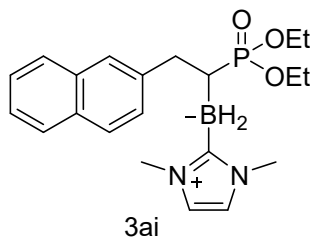
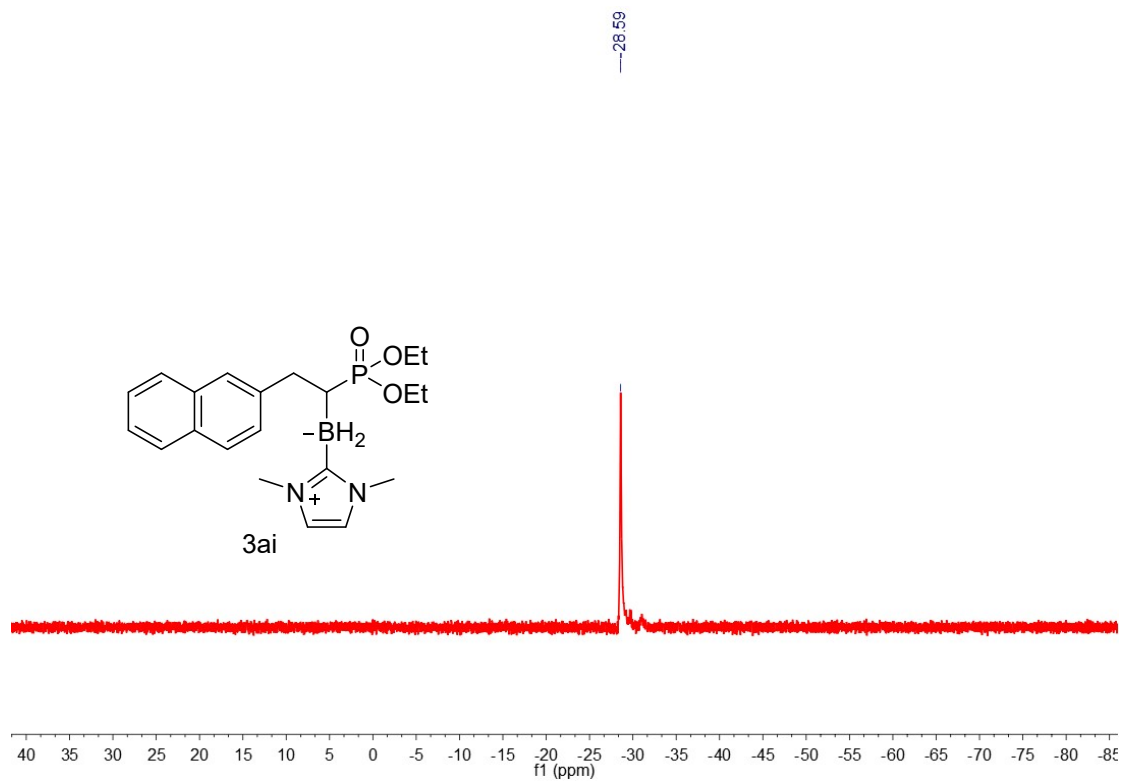


³¹P NMR (243 MHz, CDCl₃)

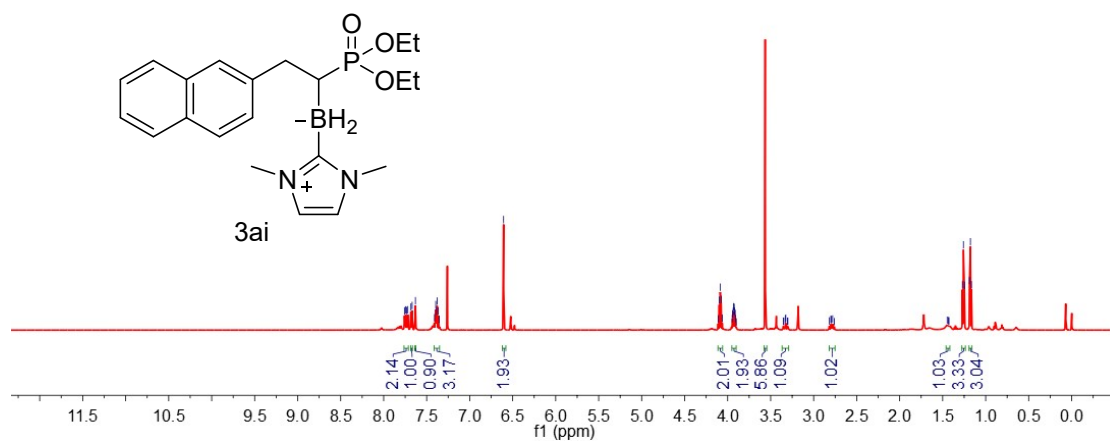
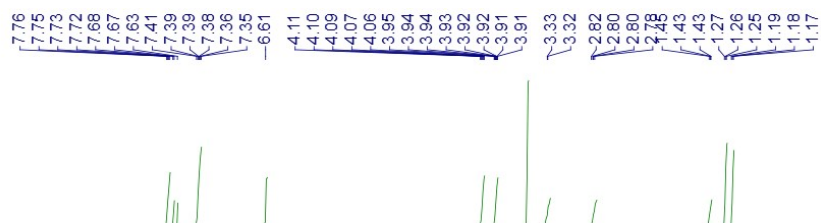


¹H NMR (600 MHz, CDCl₃)



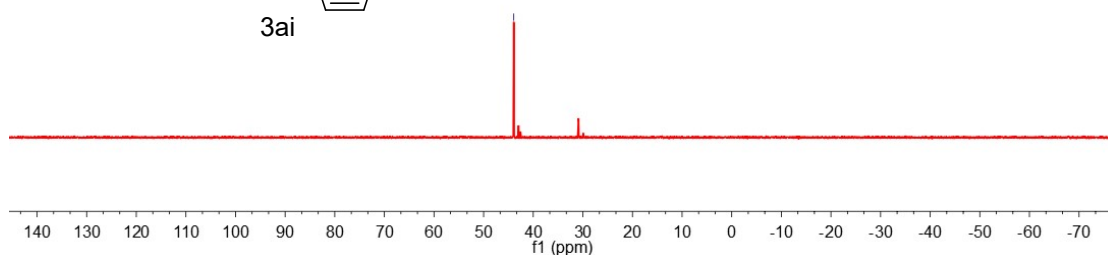
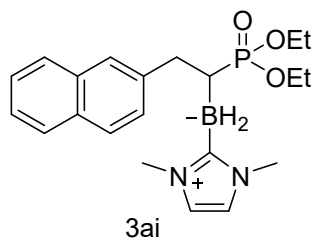


$^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3)

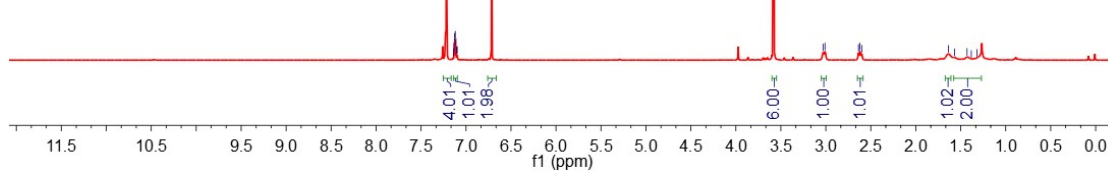
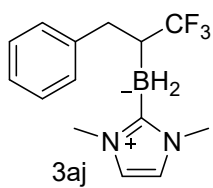
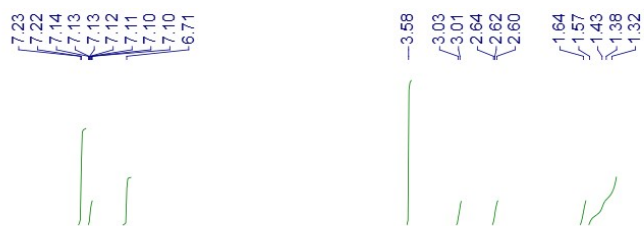


$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3)

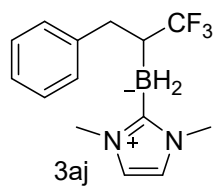
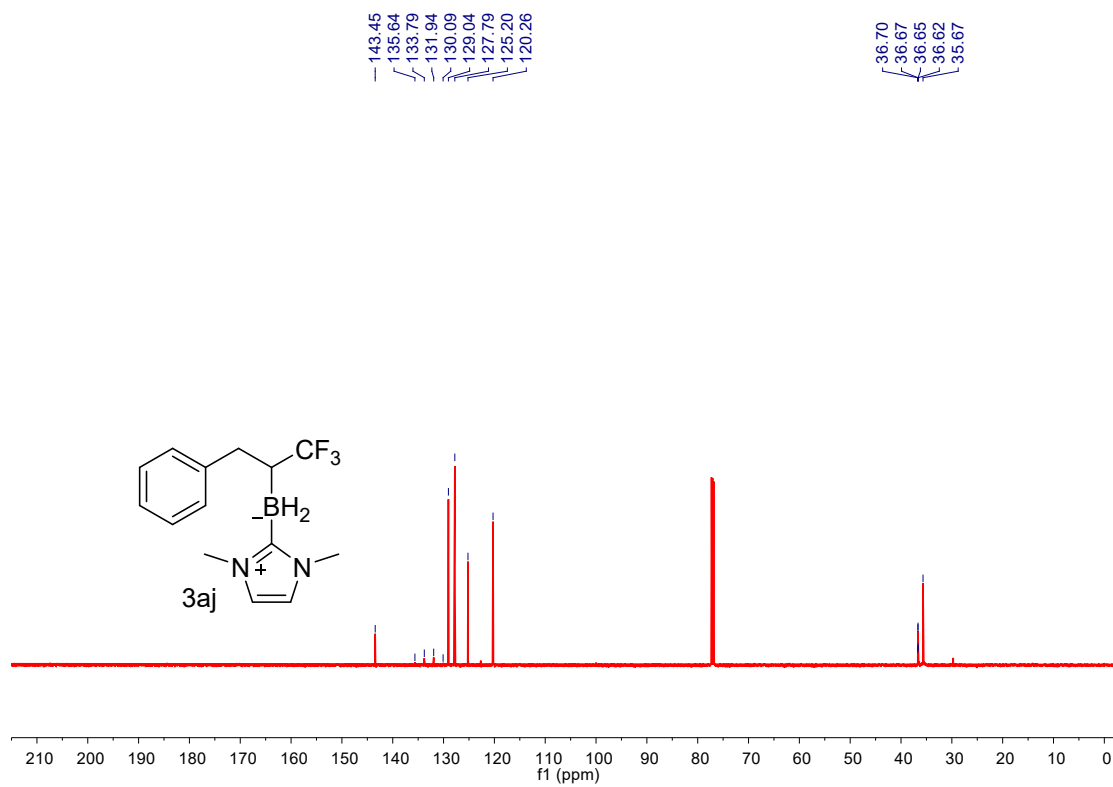
-43.92



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

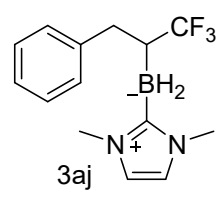
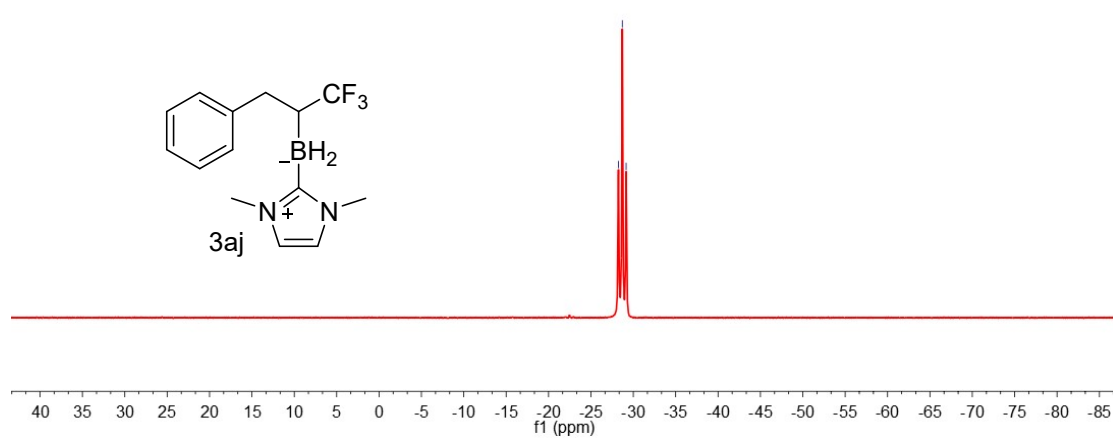


^1H NMR (600 MHz, CDCl_3)

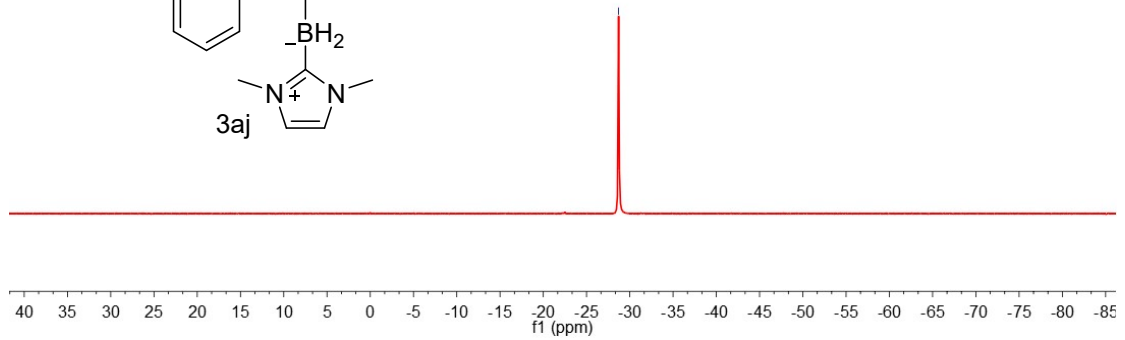
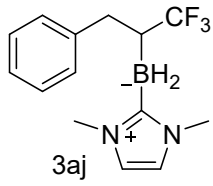


¹³C NMR (151 MHz, CDCl₃)

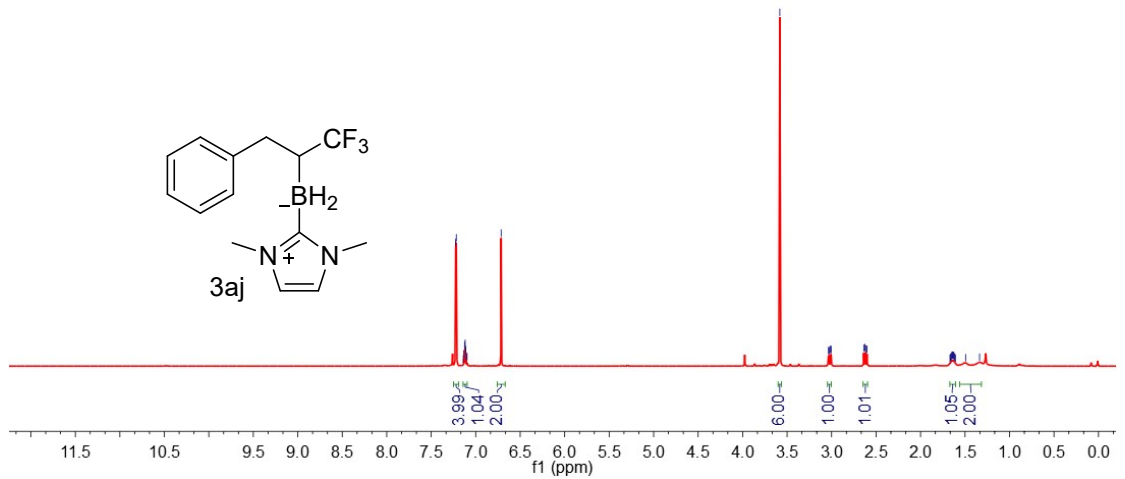
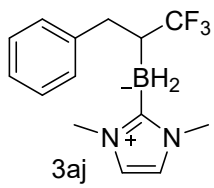
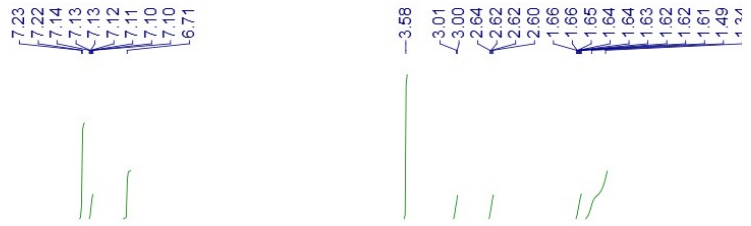
28.25
28.70
29.16



¹¹B NMR (193 MHz, CDCl₃)

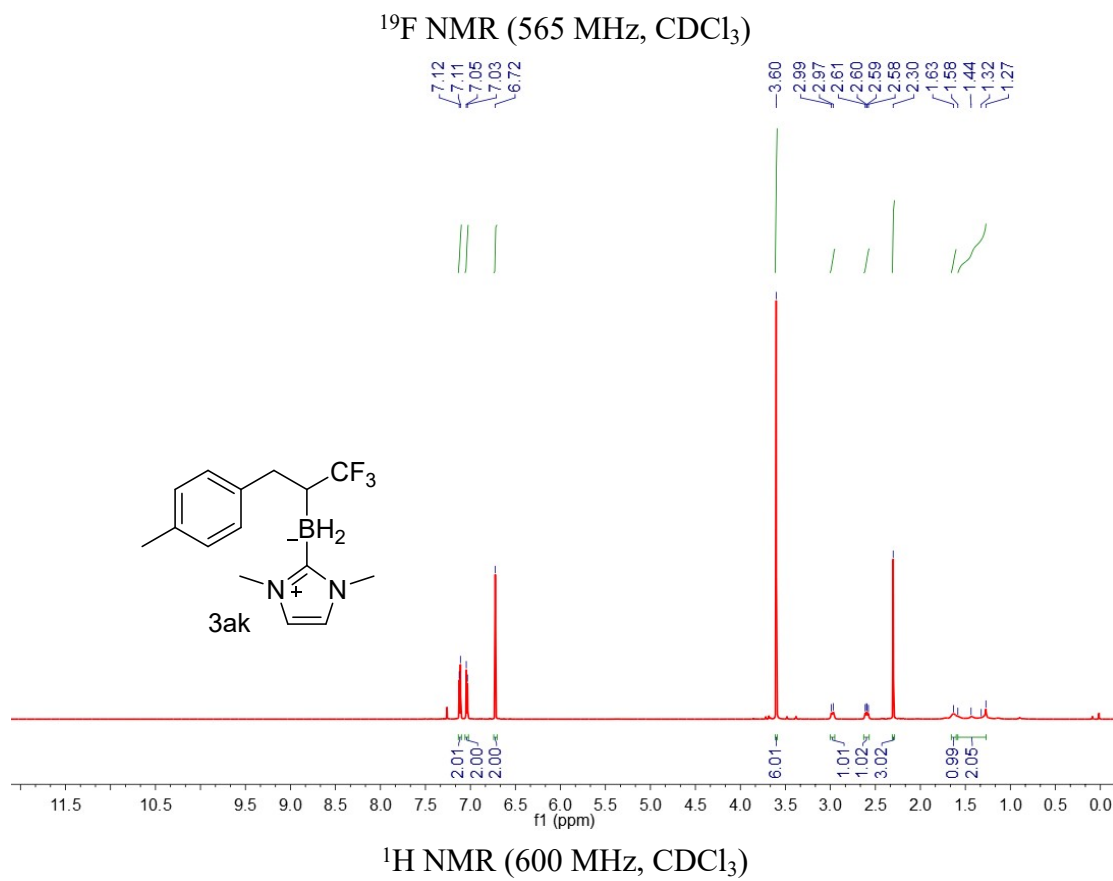
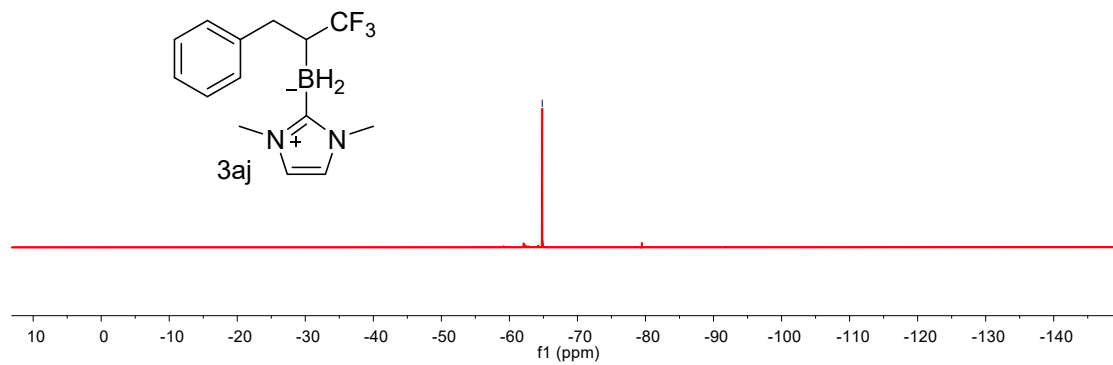


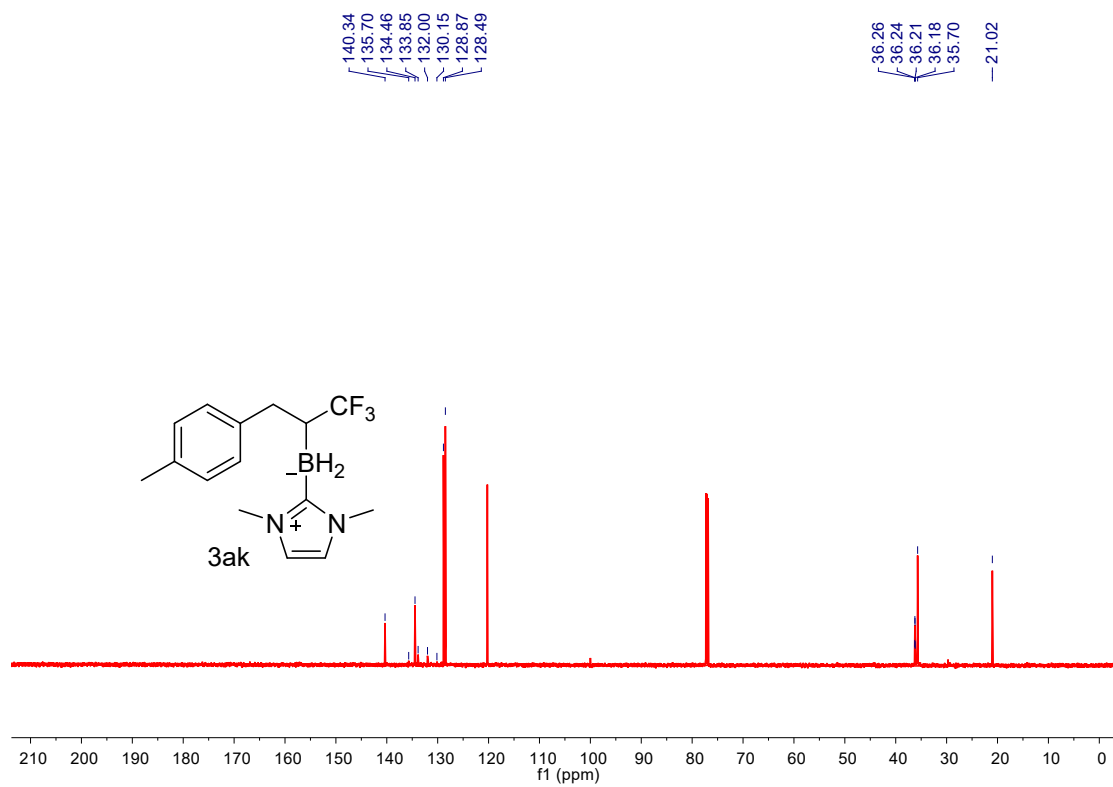
$^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3)



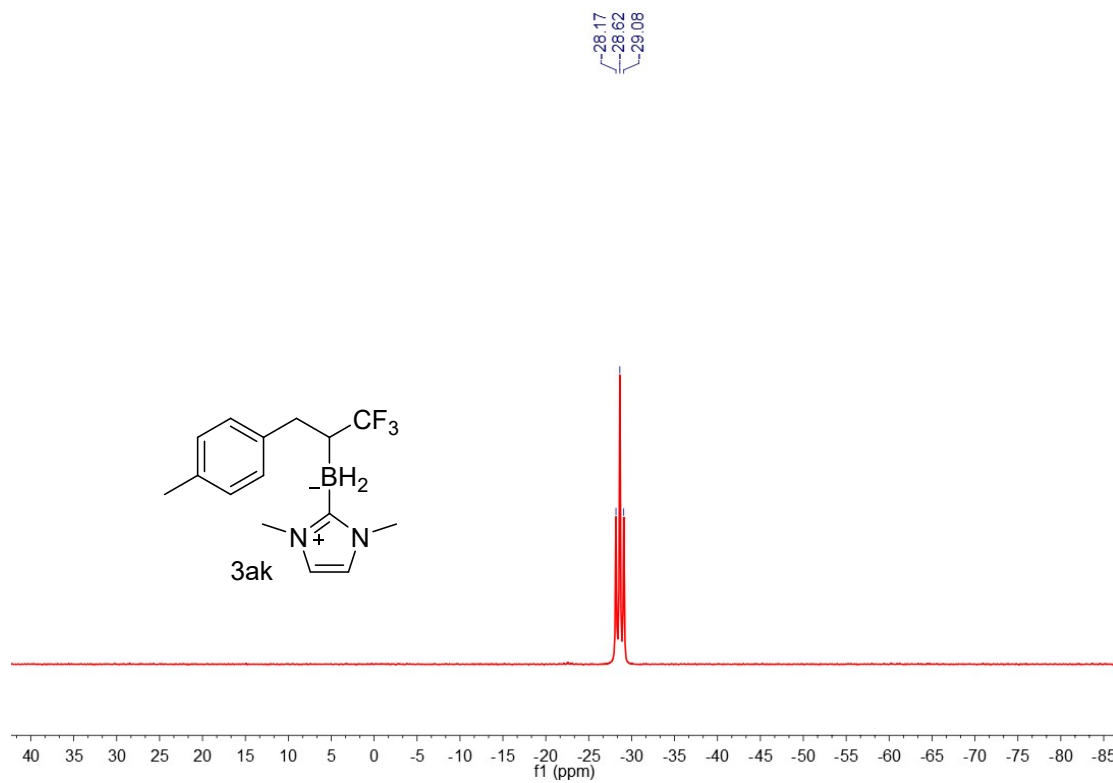
$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3)

--64.82

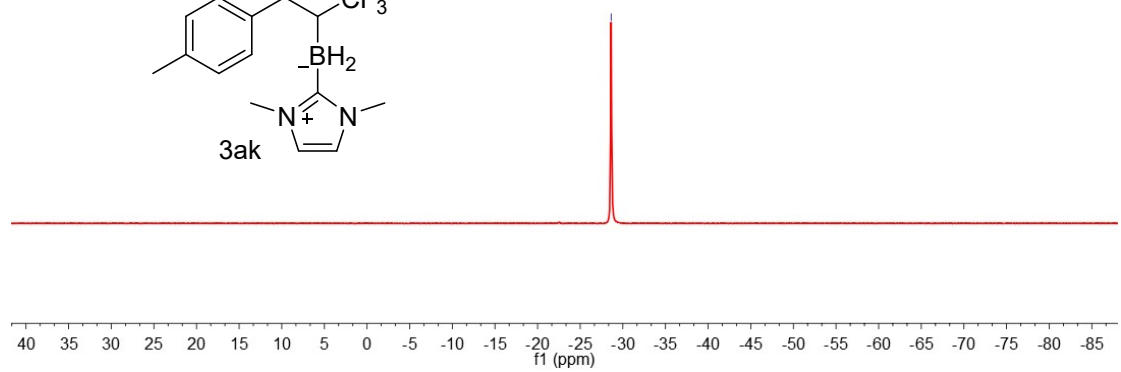
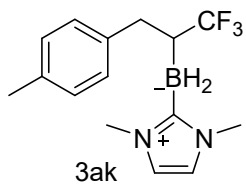




¹³C NMR (151 MHz, CDCl₃)

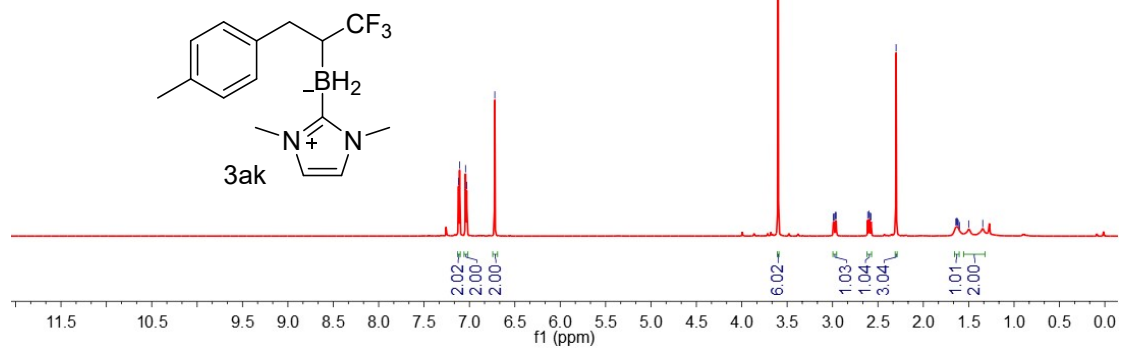
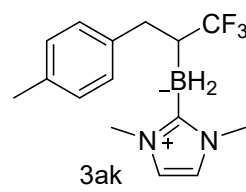


¹¹B NMR (193 MHz, CDCl₃)

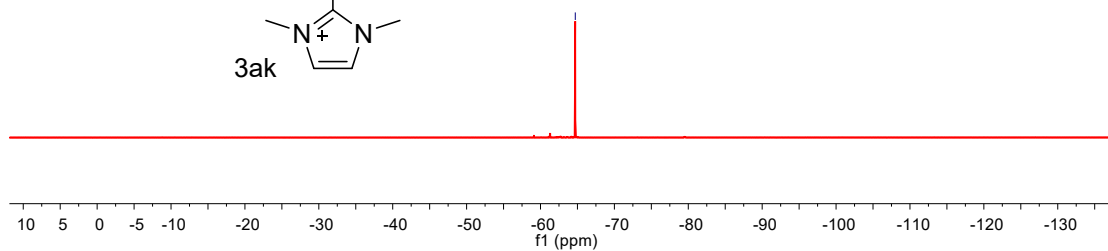
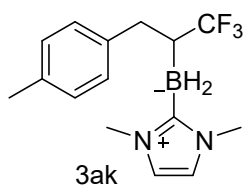


$^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3)

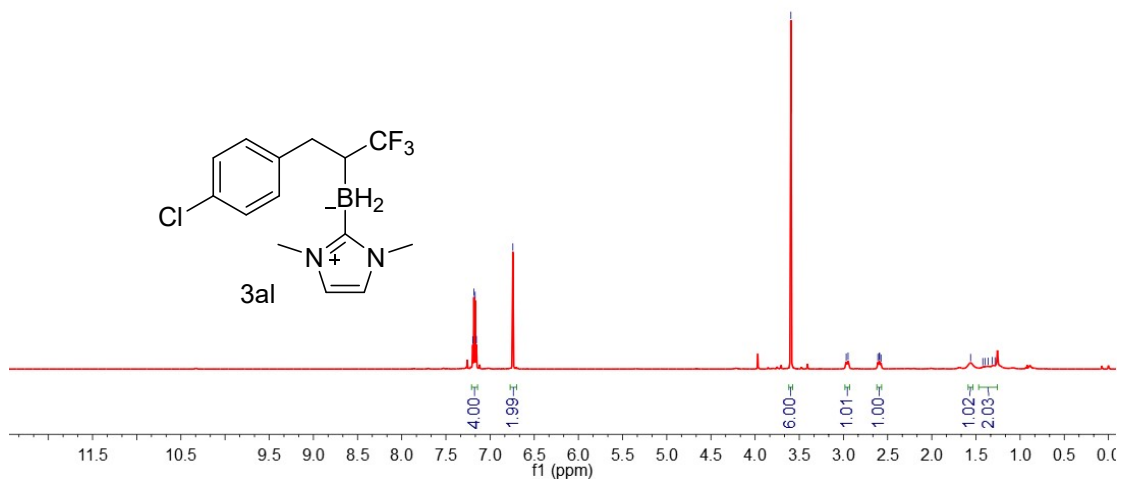
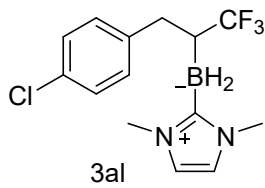
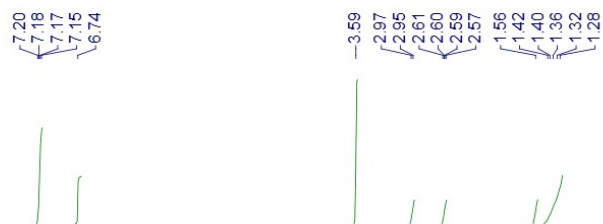
7.12, 7.11, 7.04, 7.03, 6.72, -3.60, 2.97, 2.96, 2.61, 2.60, 2.59, 2.58, 2.30, 1.63, 1.62, 1.60, 1.50, 1.35



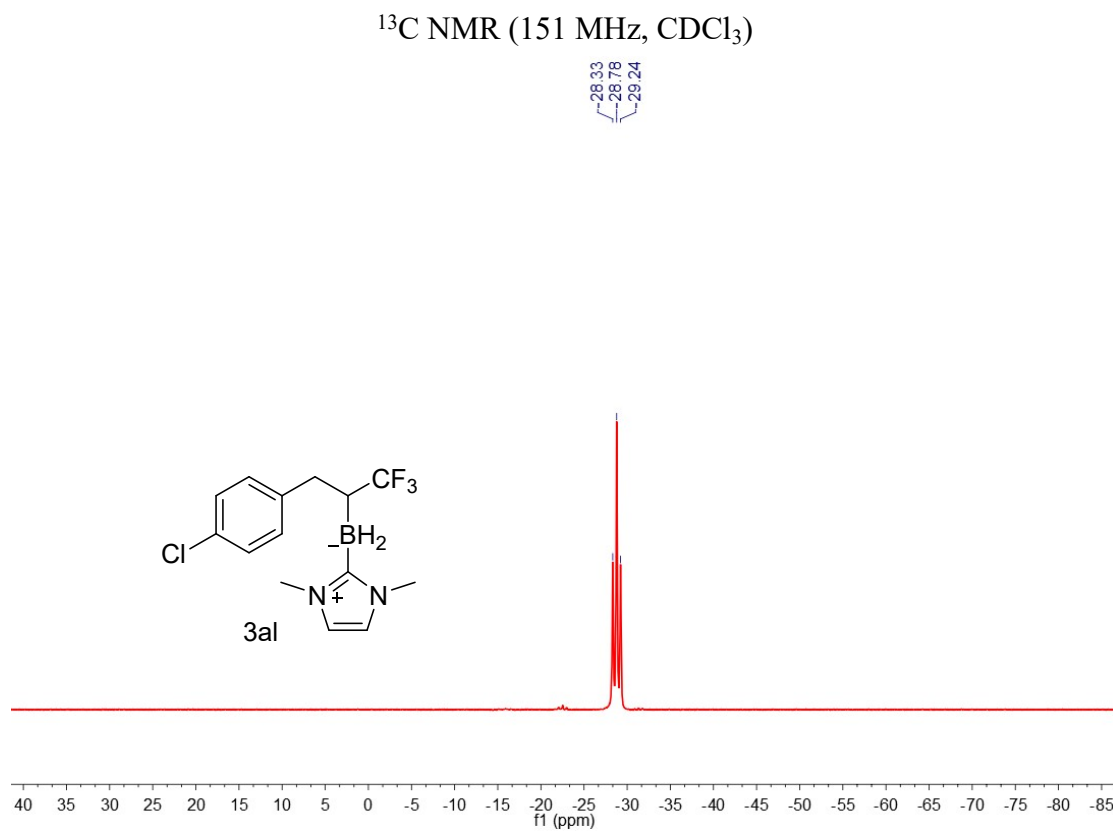
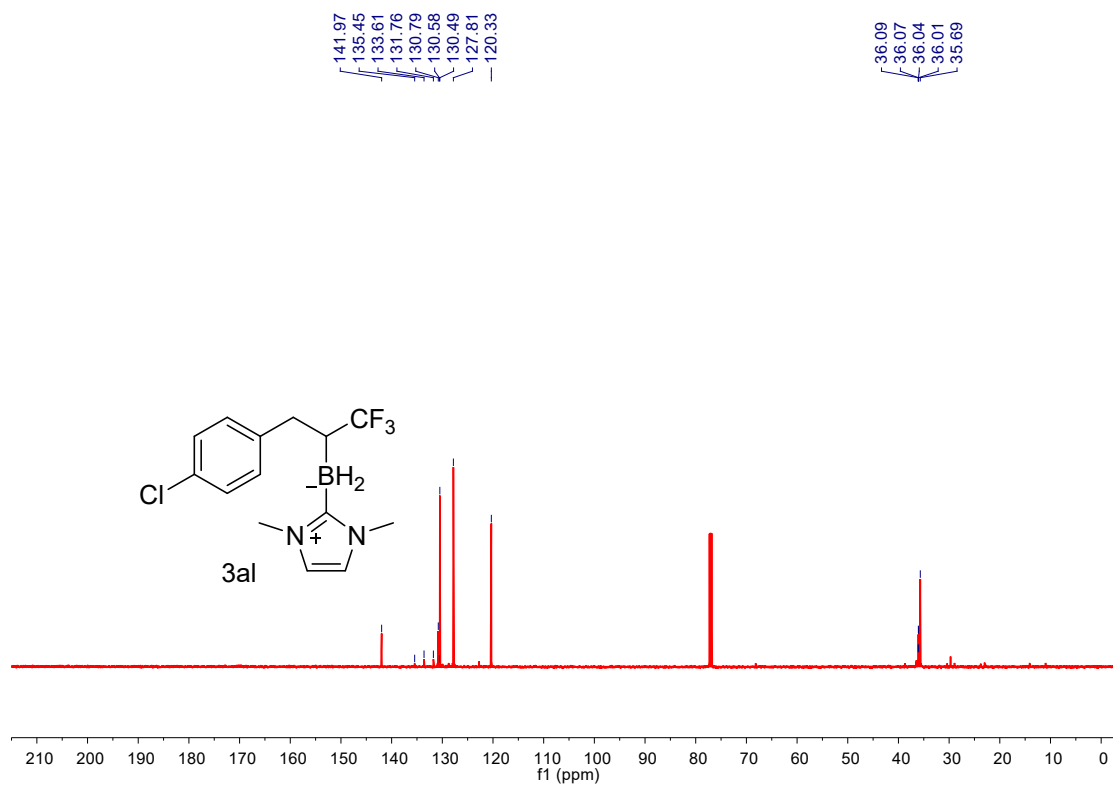
$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3)

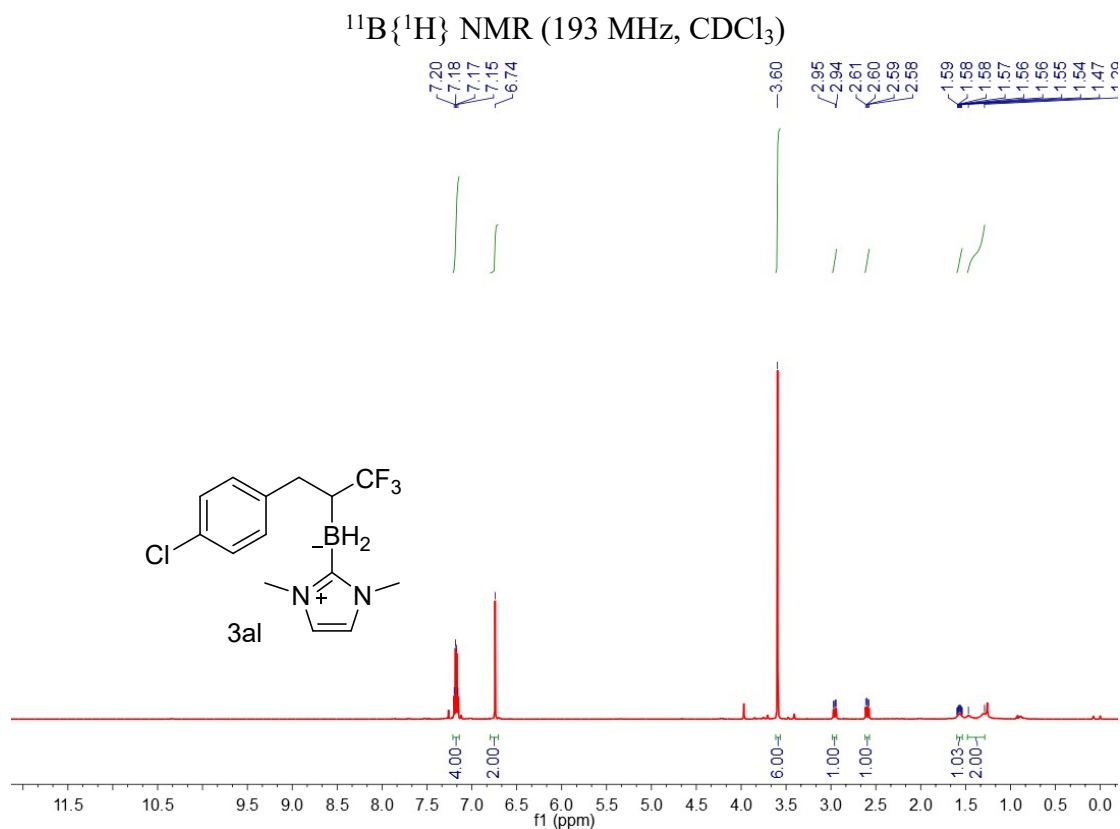
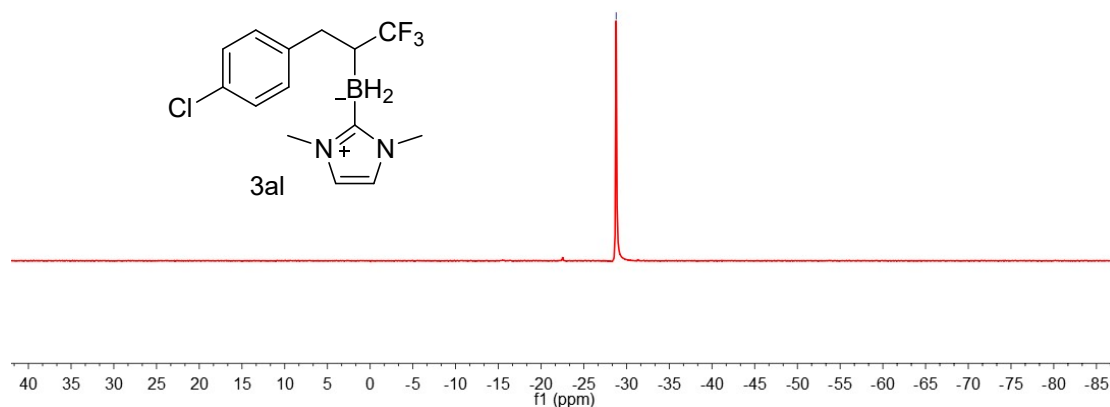


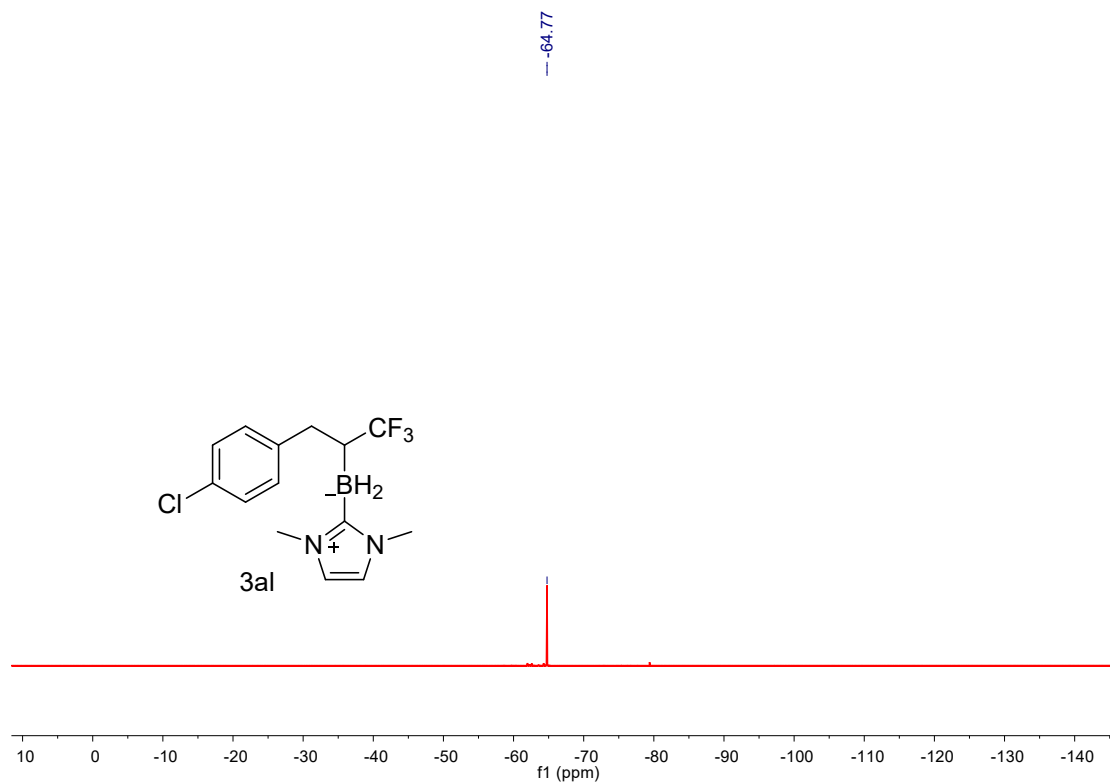
^{19}F NMR (565 MHz, CDCl_3)



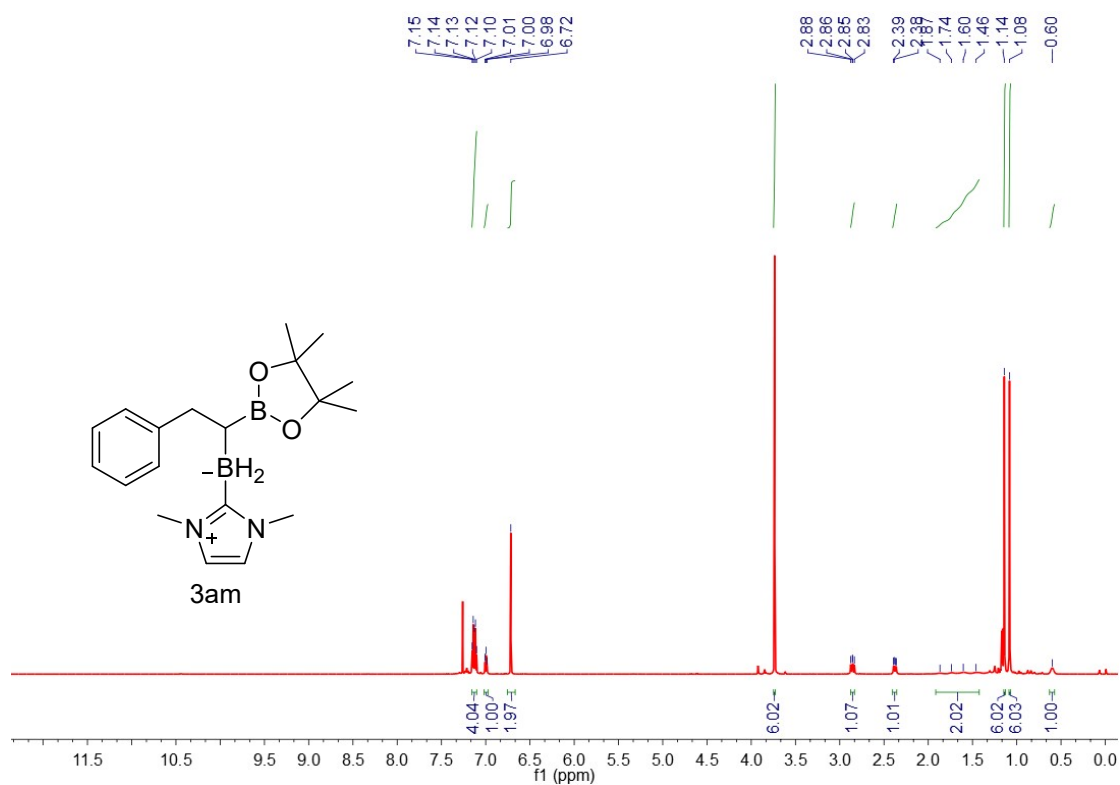
^{19}F NMR (565 MHz, CDCl_3)



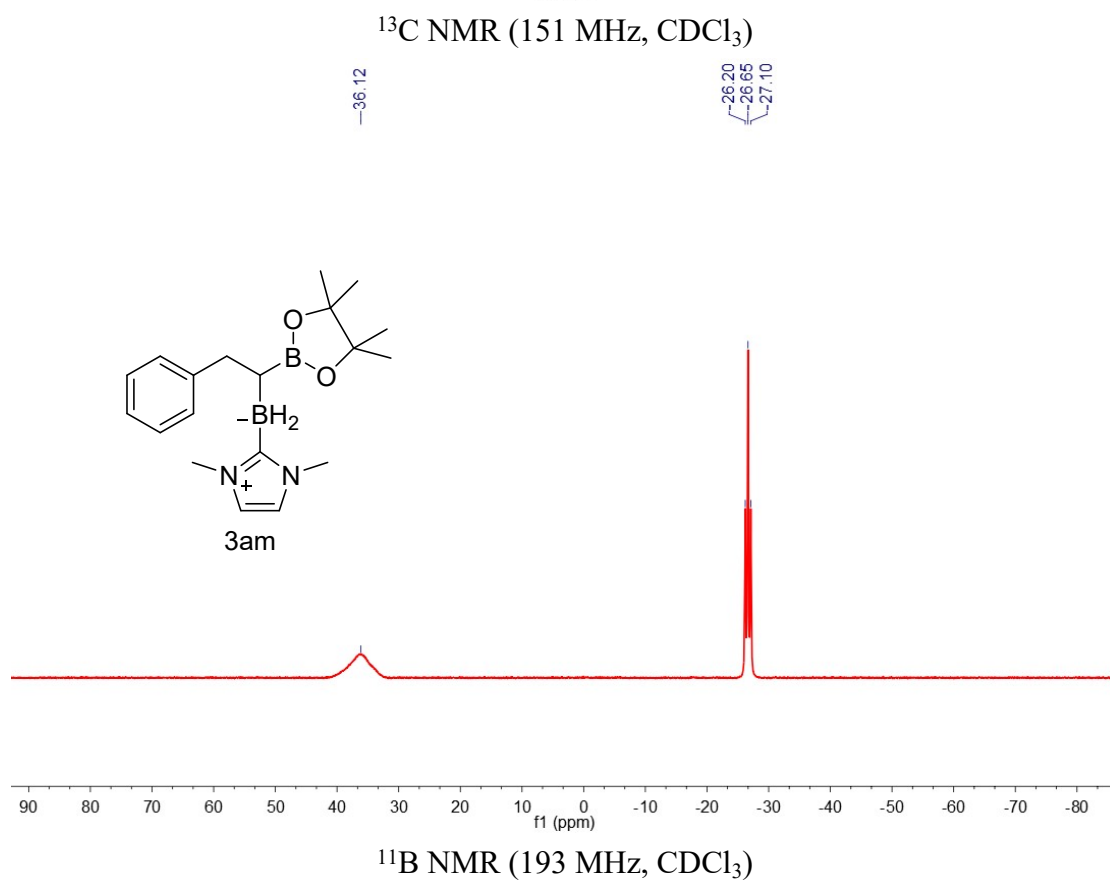
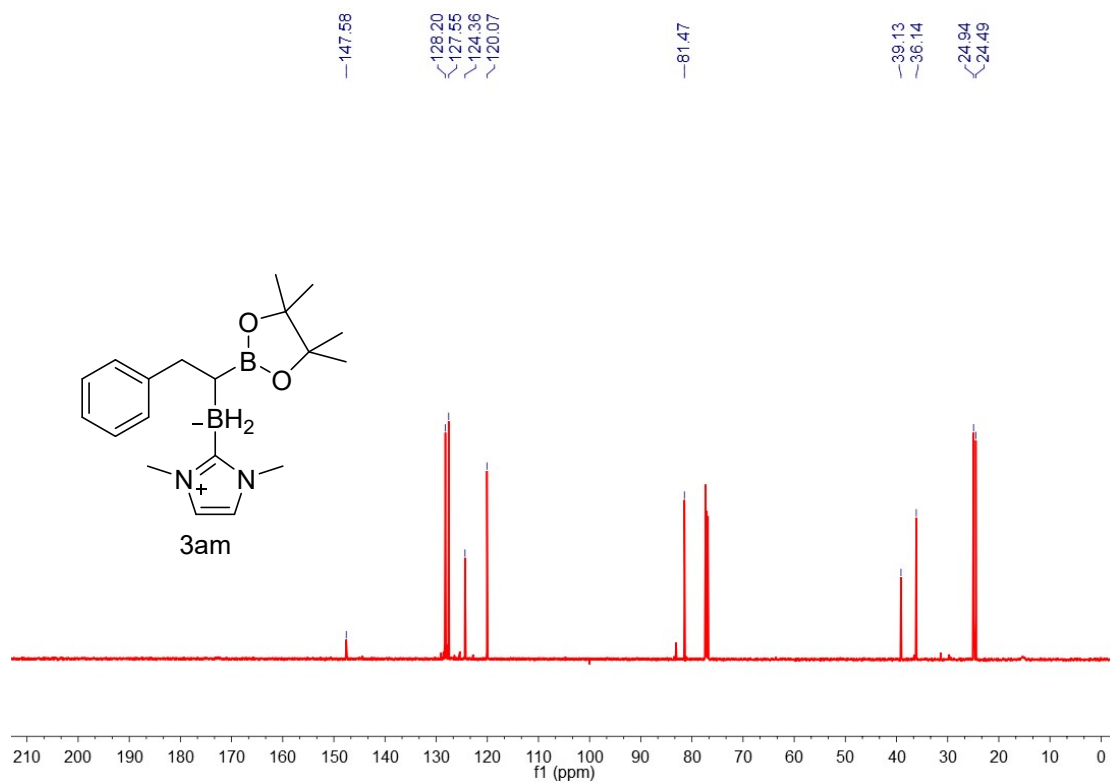


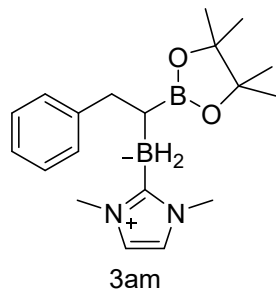
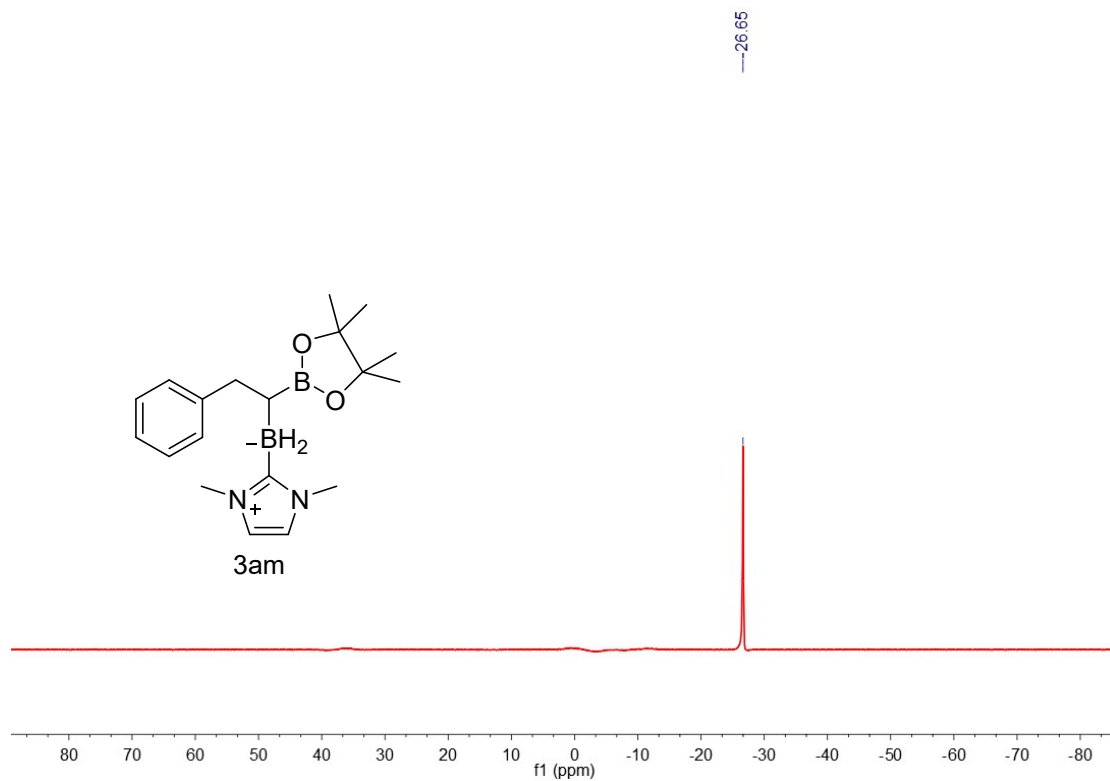


^{19}F NMR (565 MHz, CDCl_3)

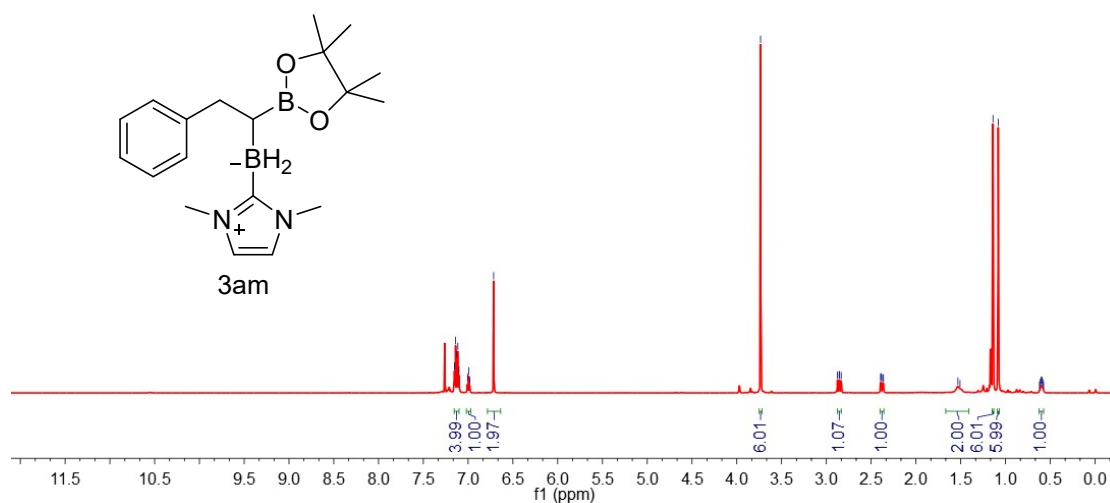
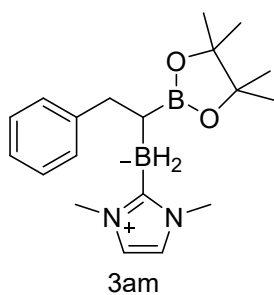
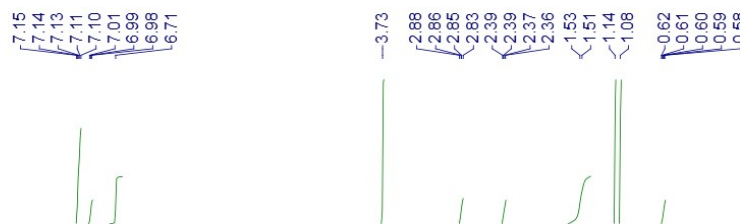


^1H NMR (600 MHz, CDCl_3)

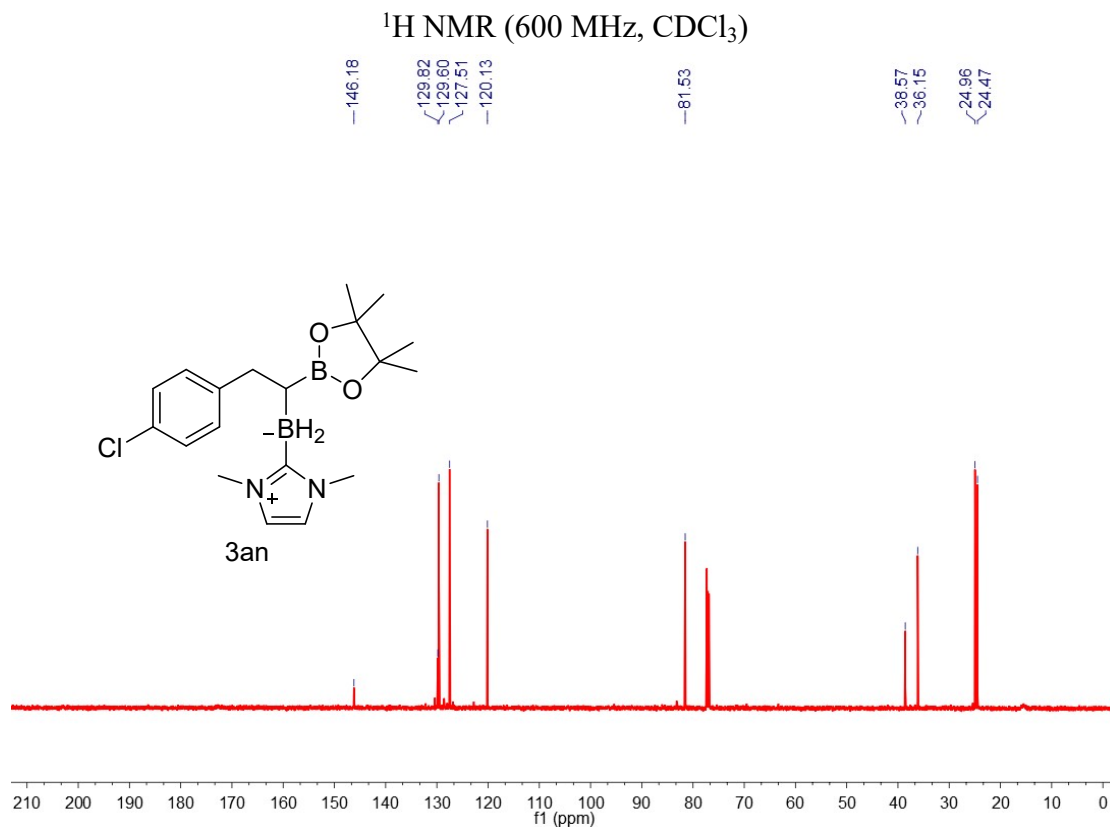
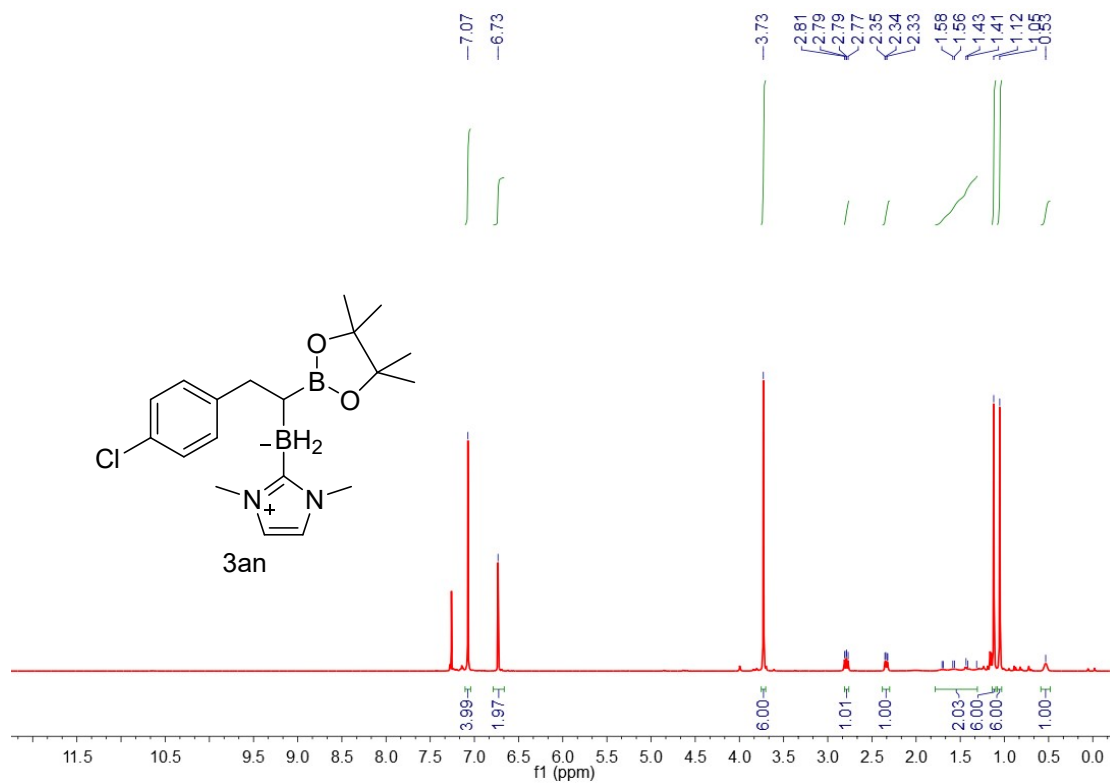


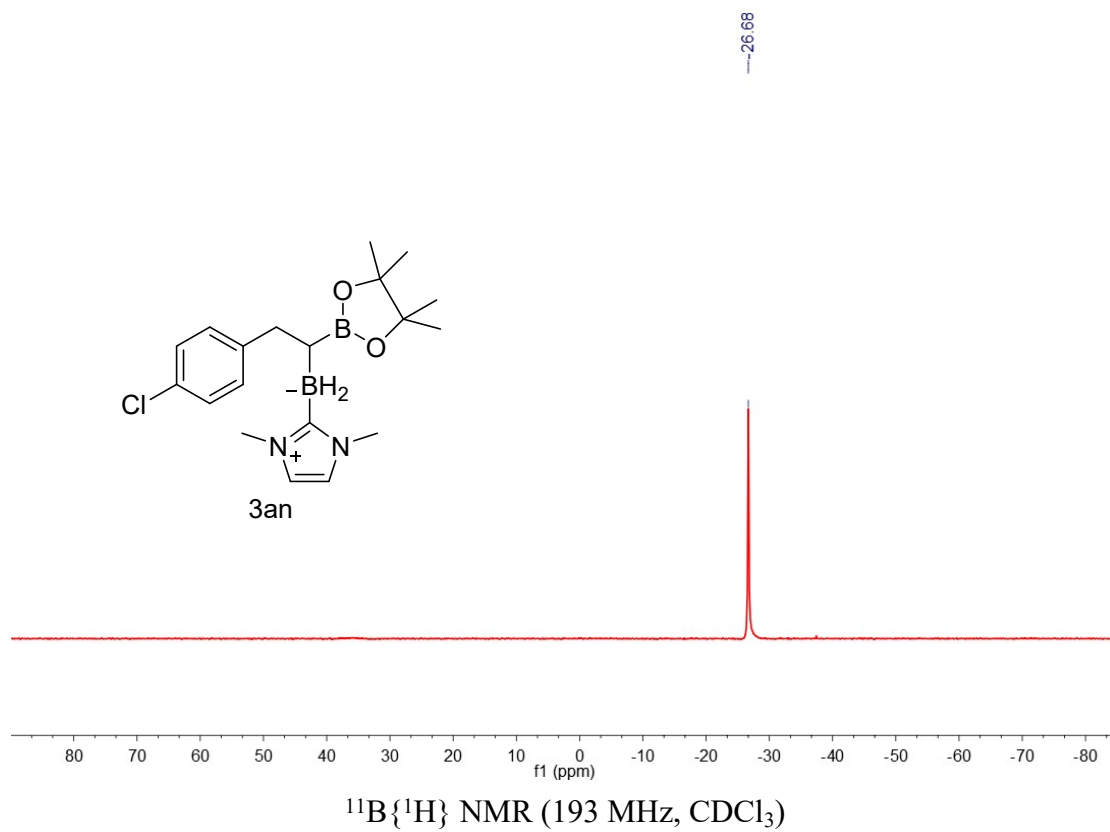
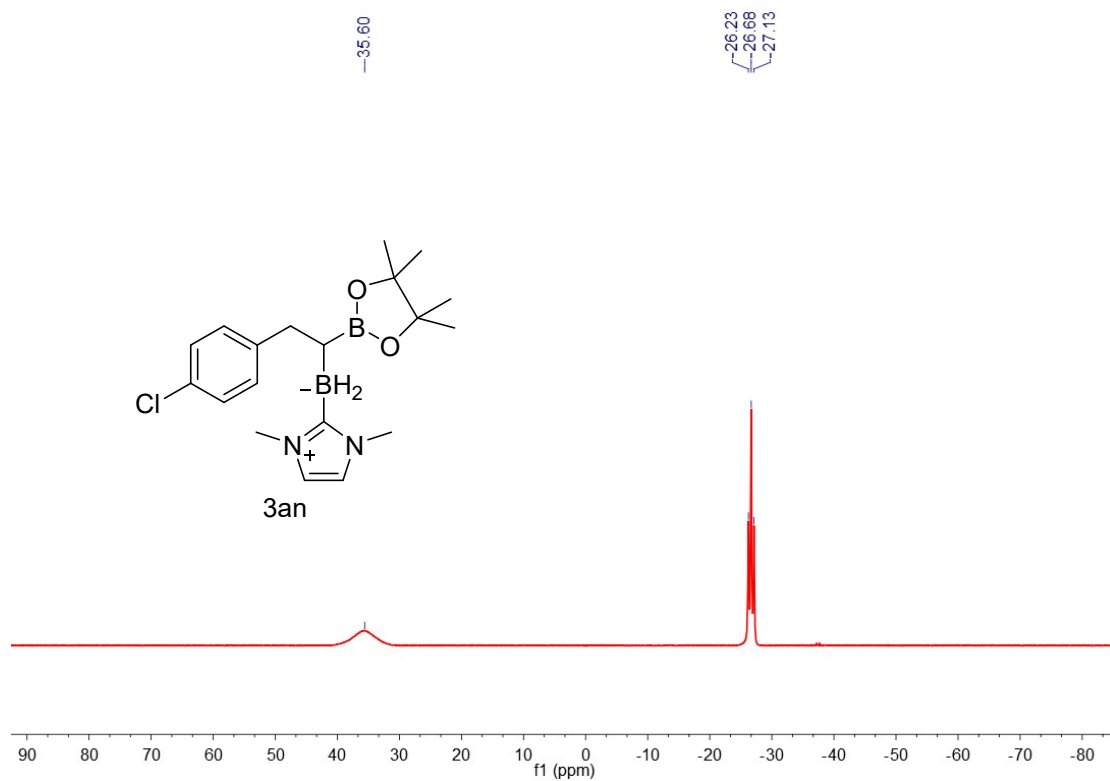


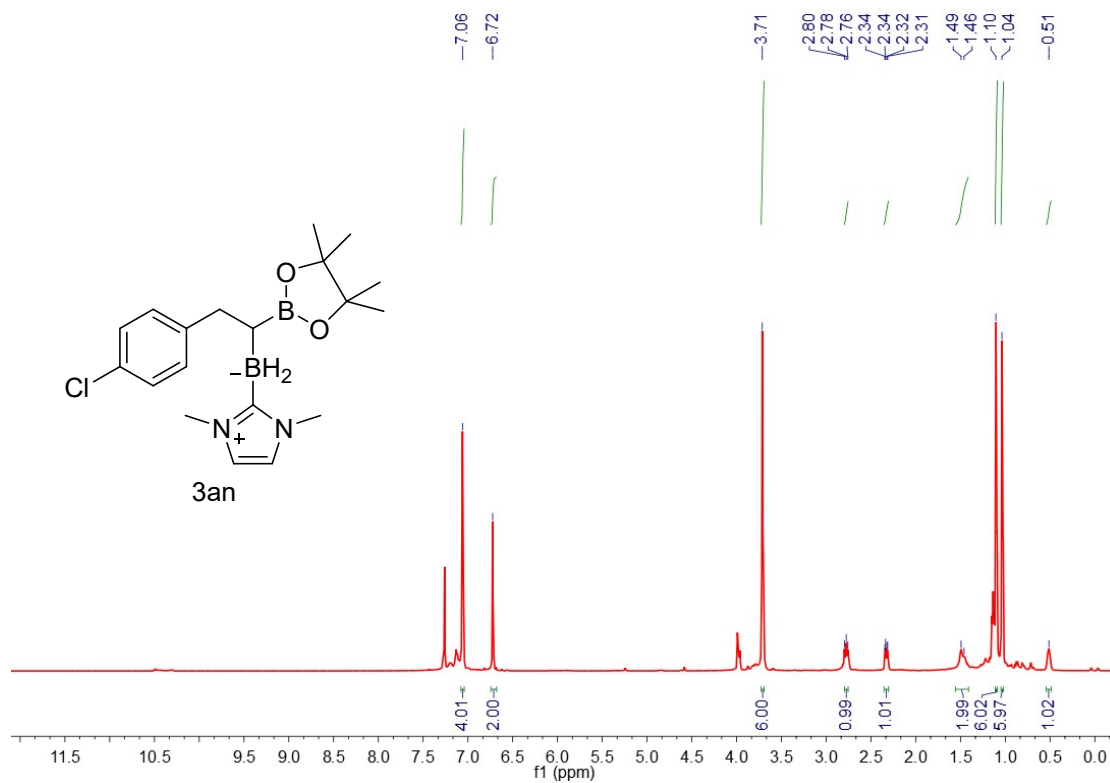
$^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, CDCl_3)



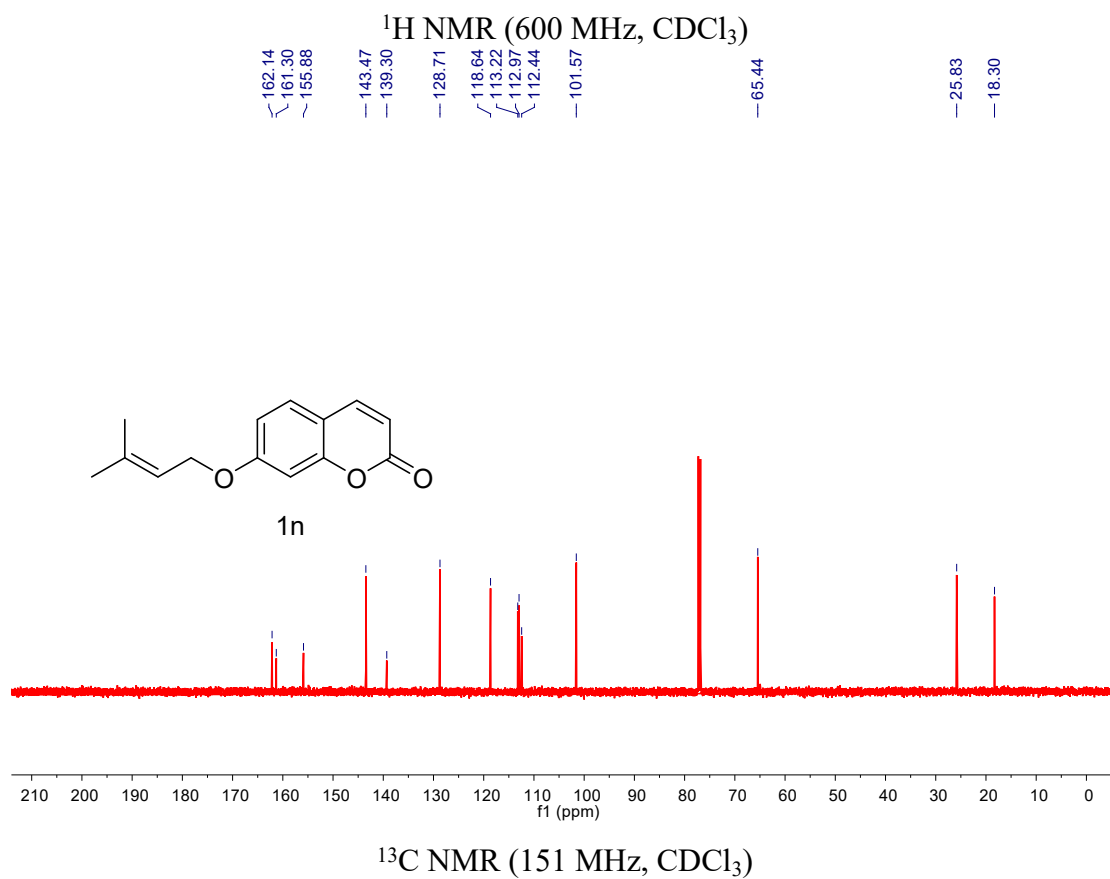
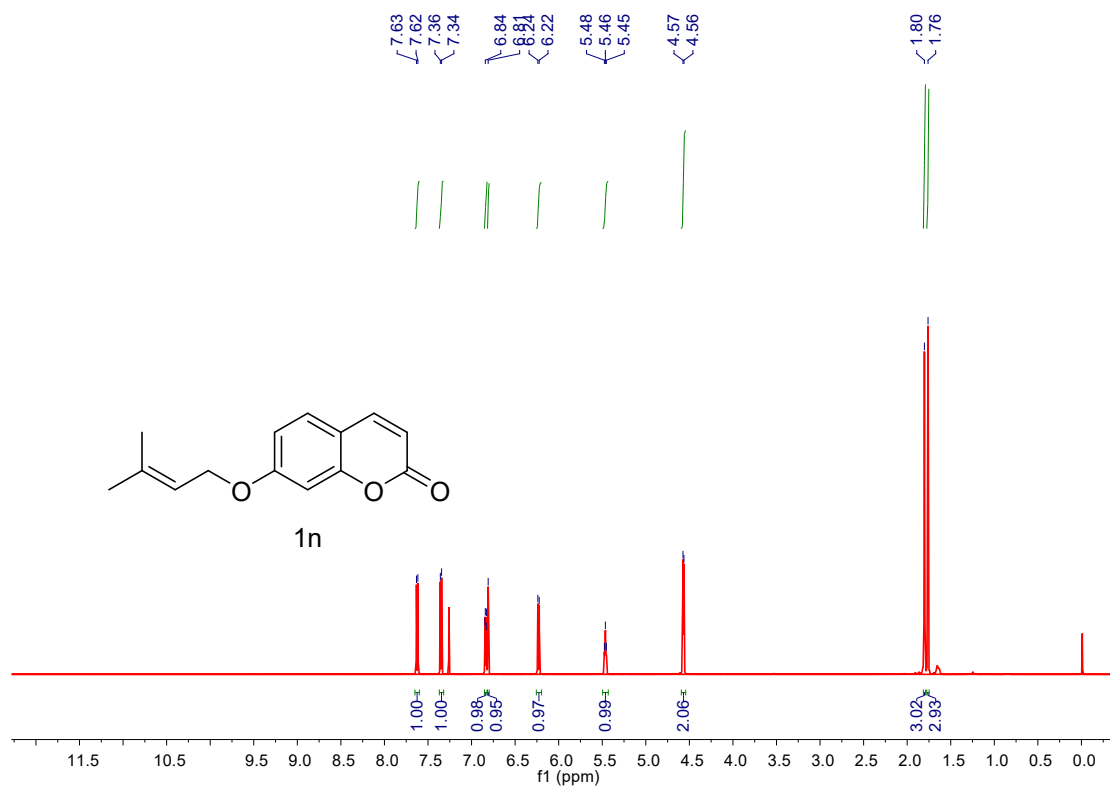
$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3)

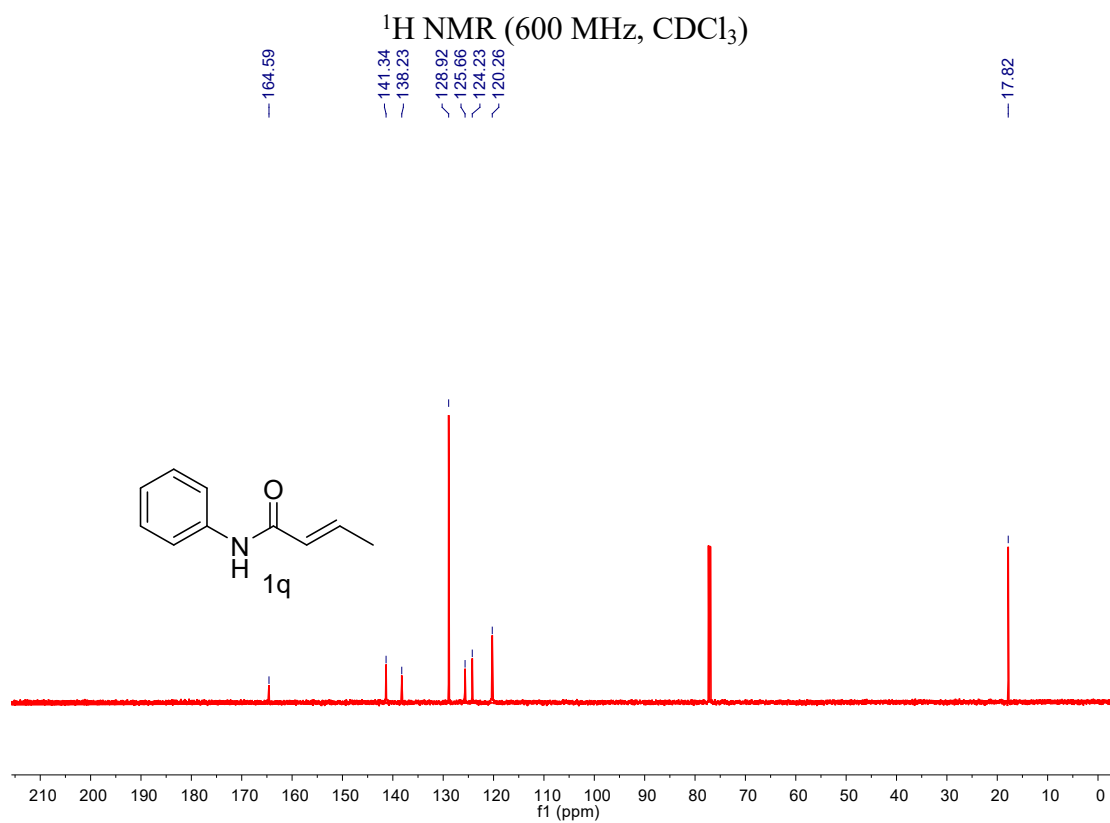
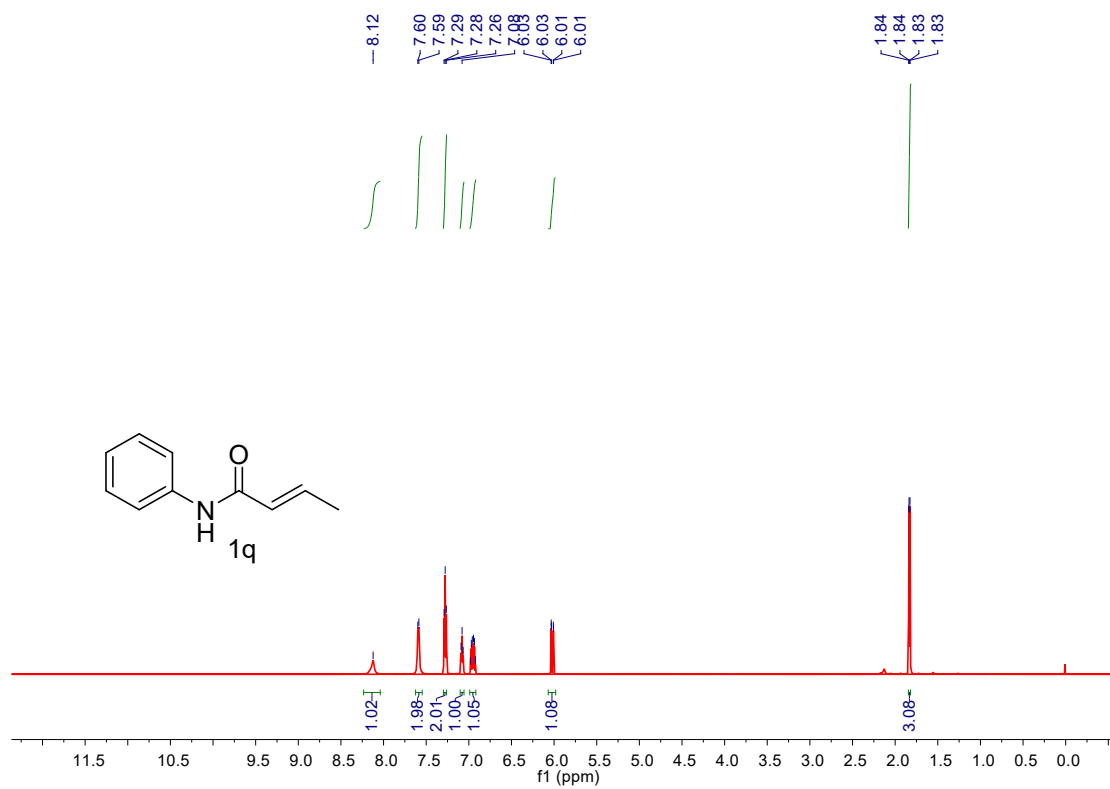


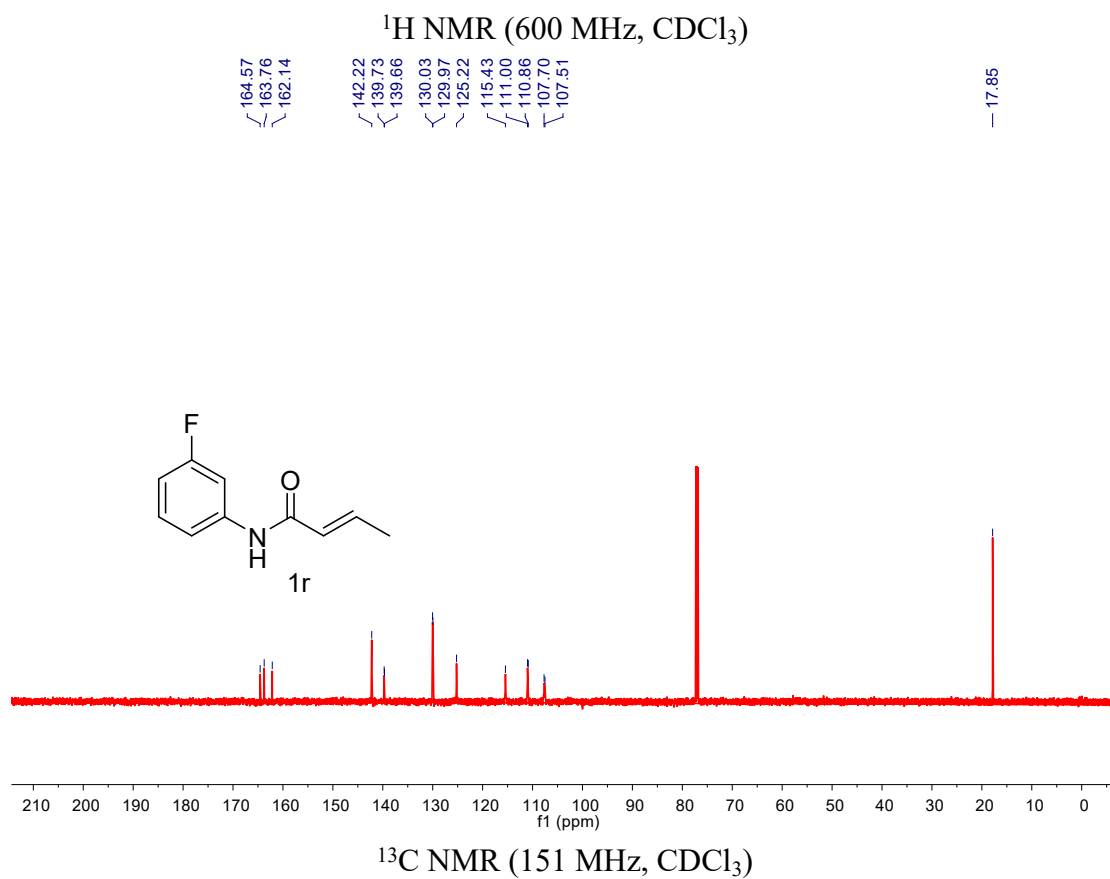
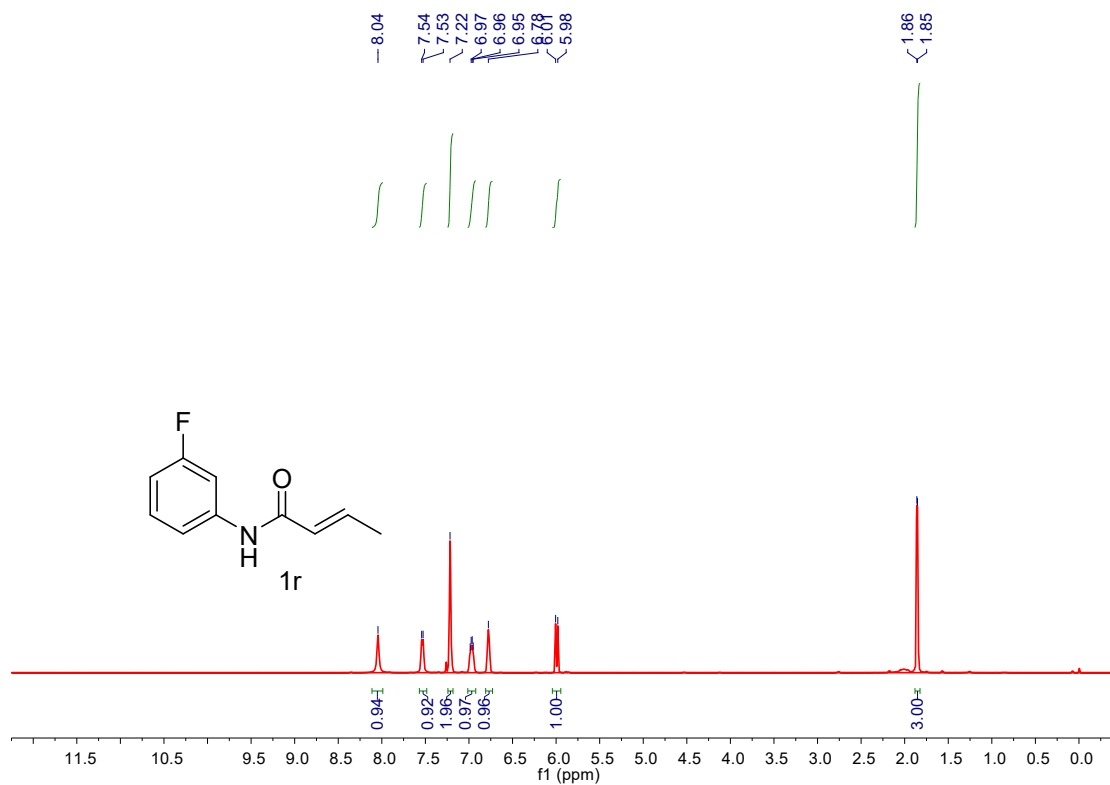


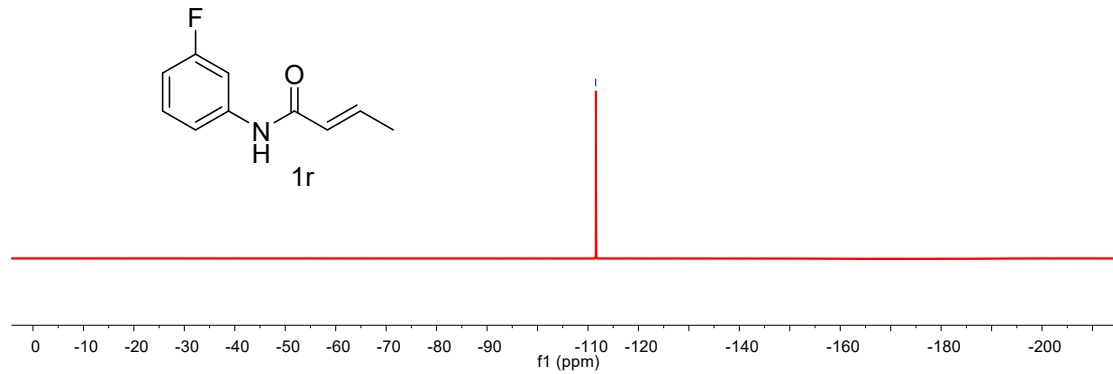


$^1\text{H}\{^{11}\text{B}\}$ NMR (600 MHz, CDCl_3)





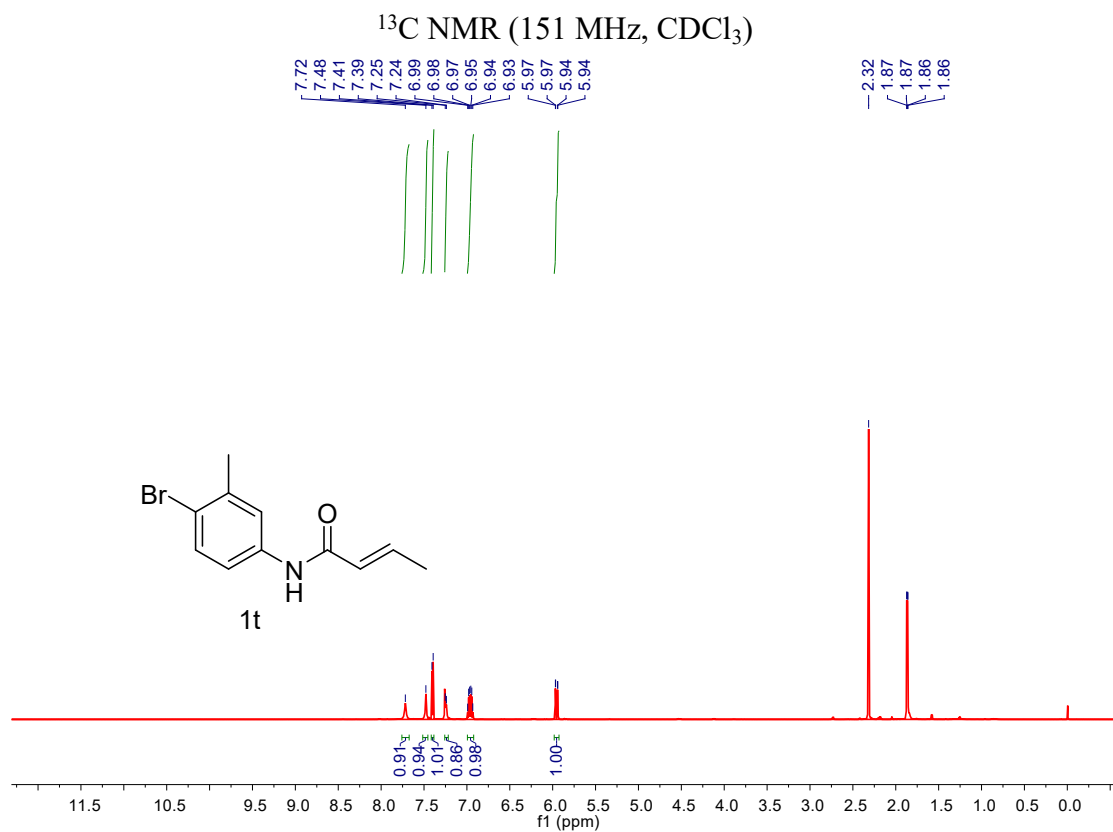
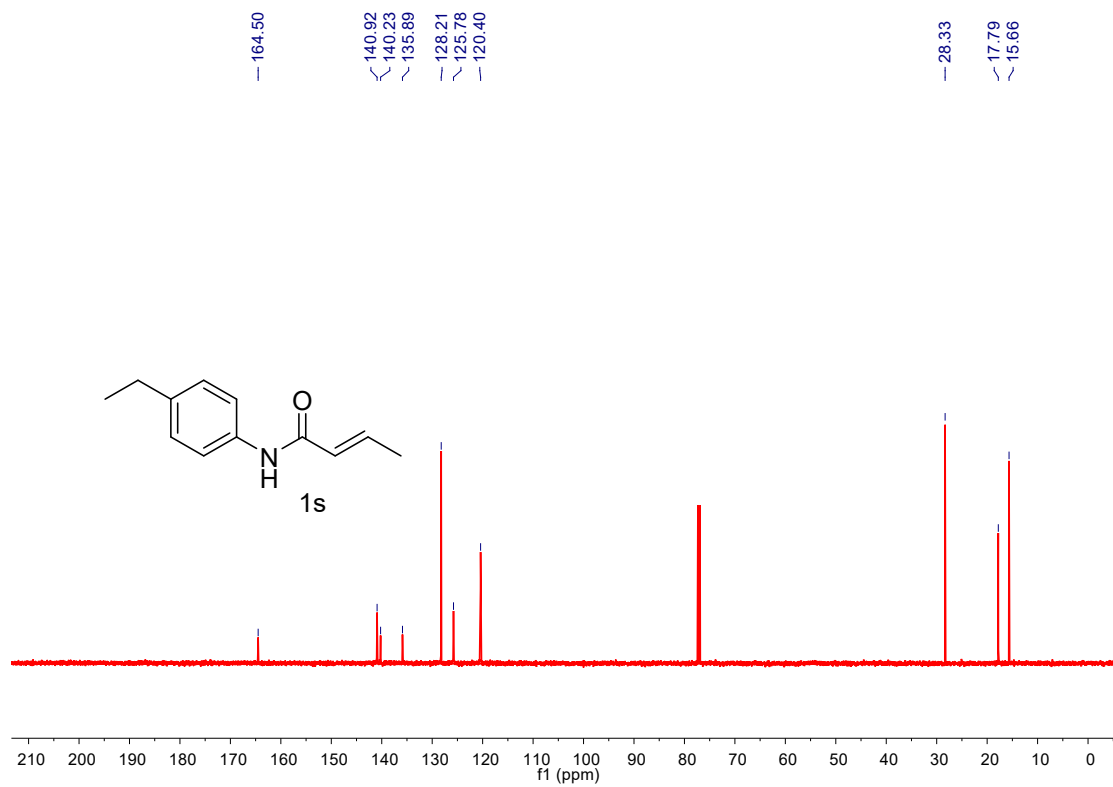


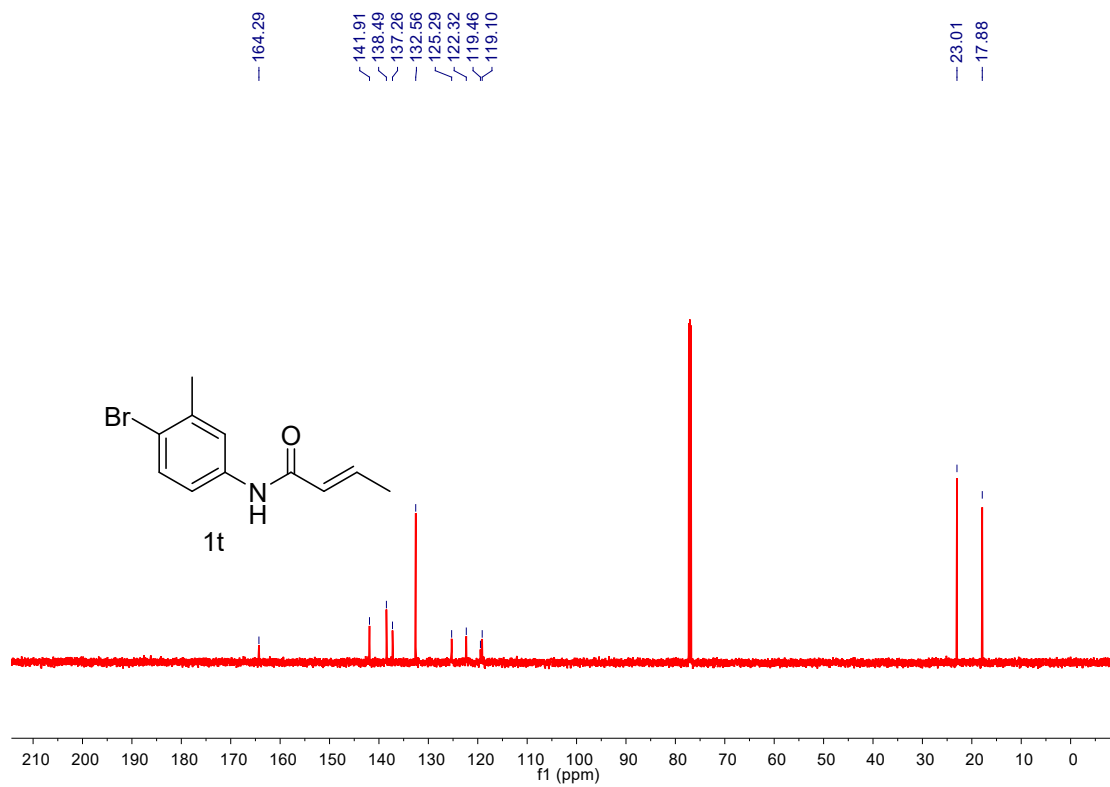


¹⁹F NMR (565 MHz, CDCl₃)

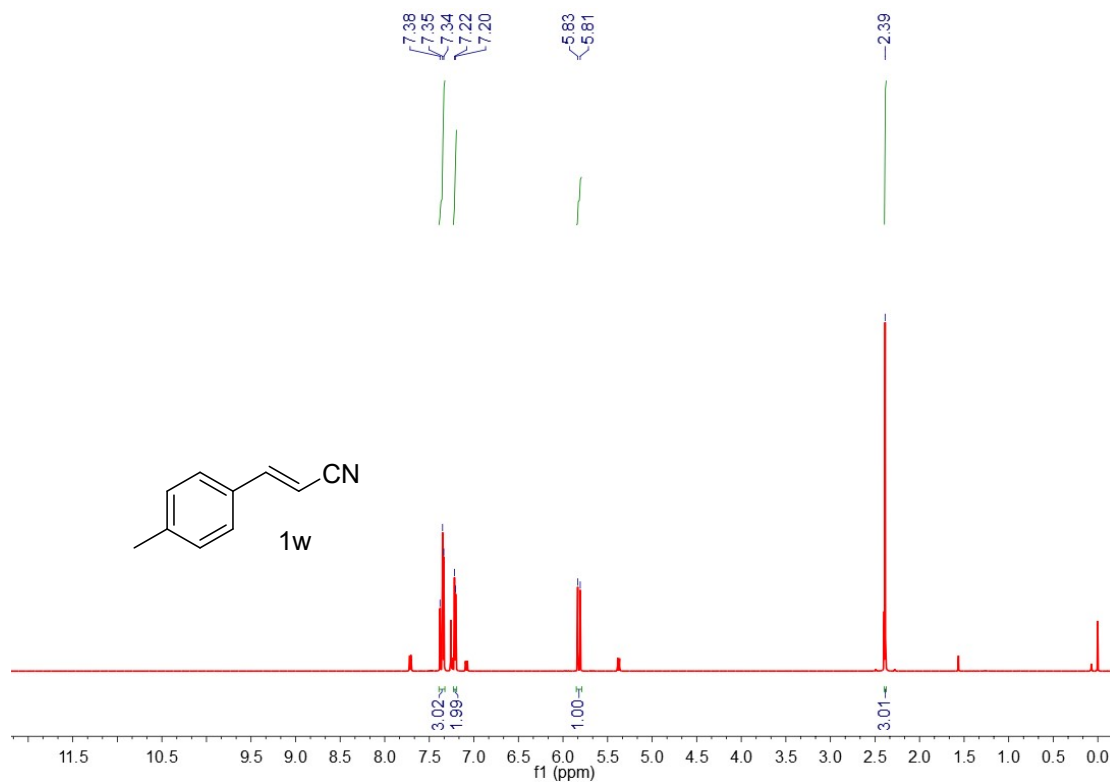


¹H NMR (600 MHz, CDCl₃)

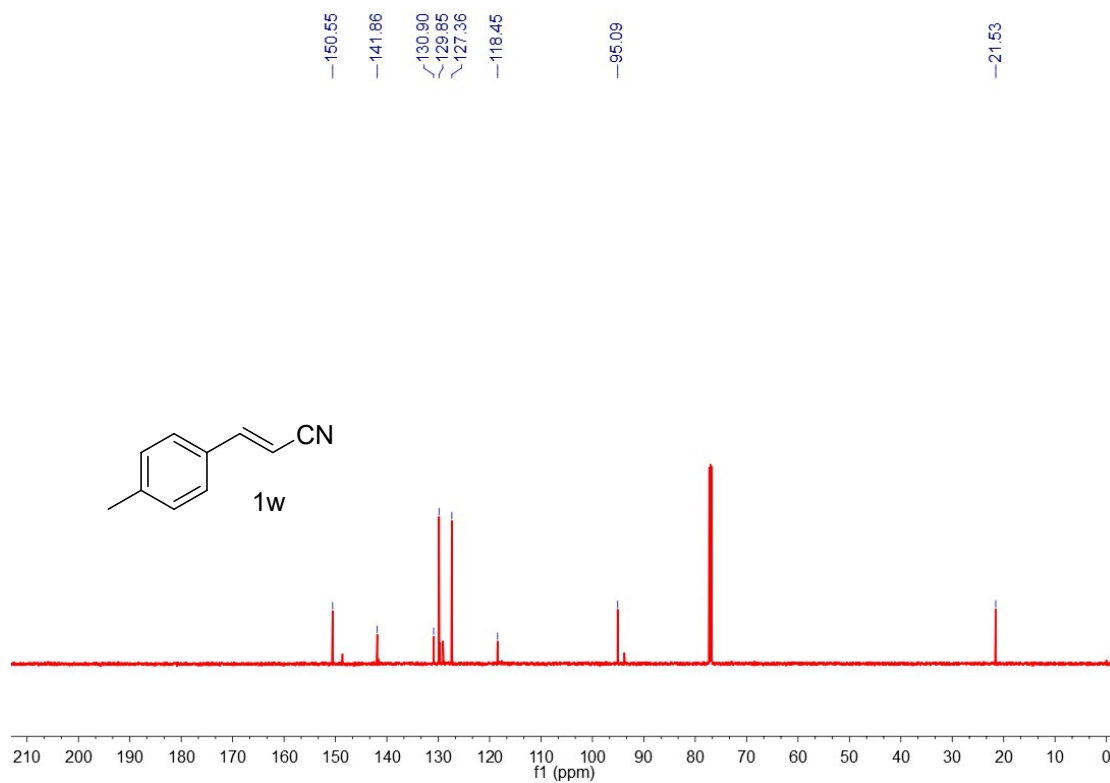




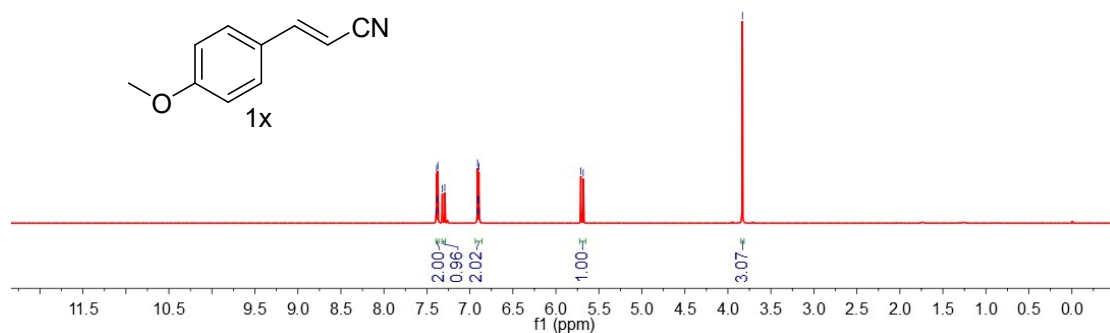
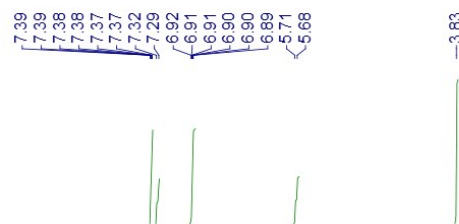
^{13}C NMR (151 MHz, CDCl_3)



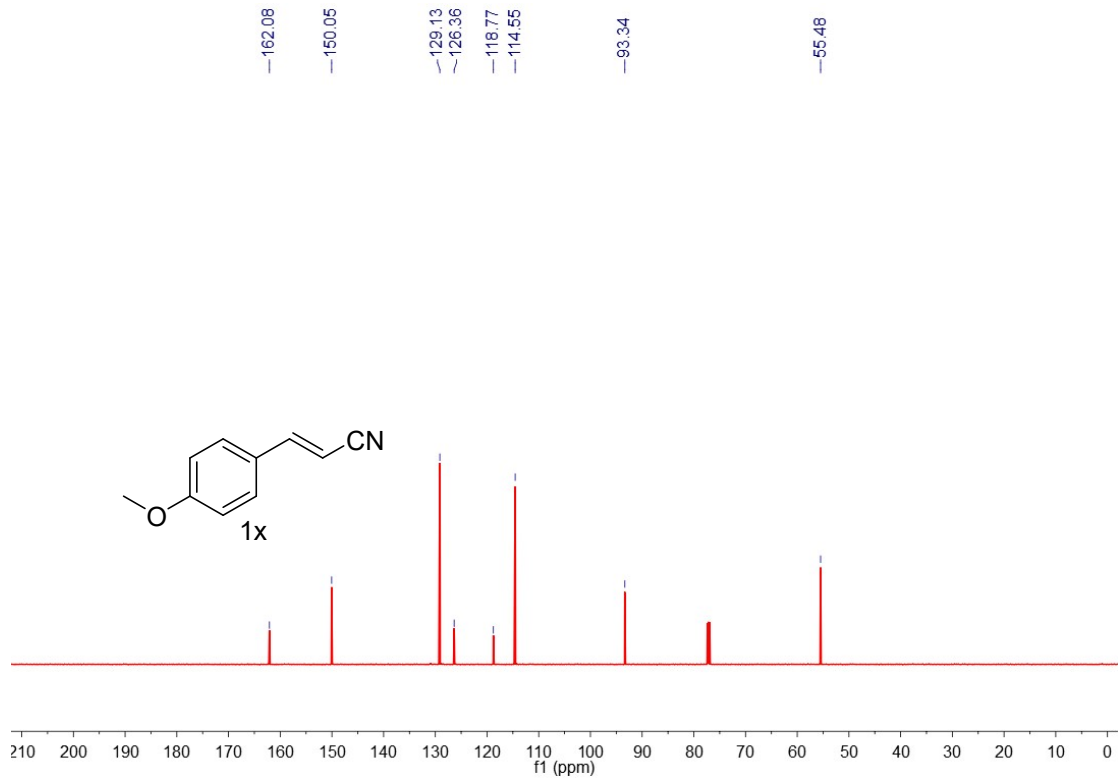
^1H NMR (600 MHz, CDCl_3)



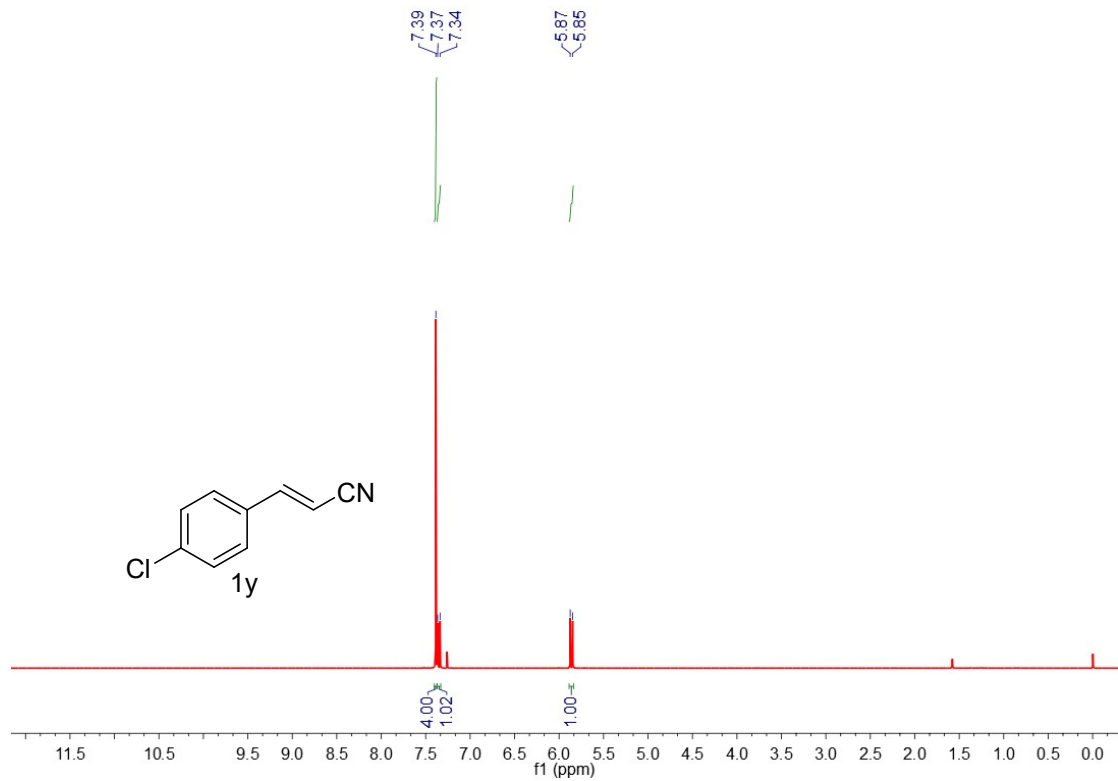
^{13}C NMR (151 MHz, CDCl_3)



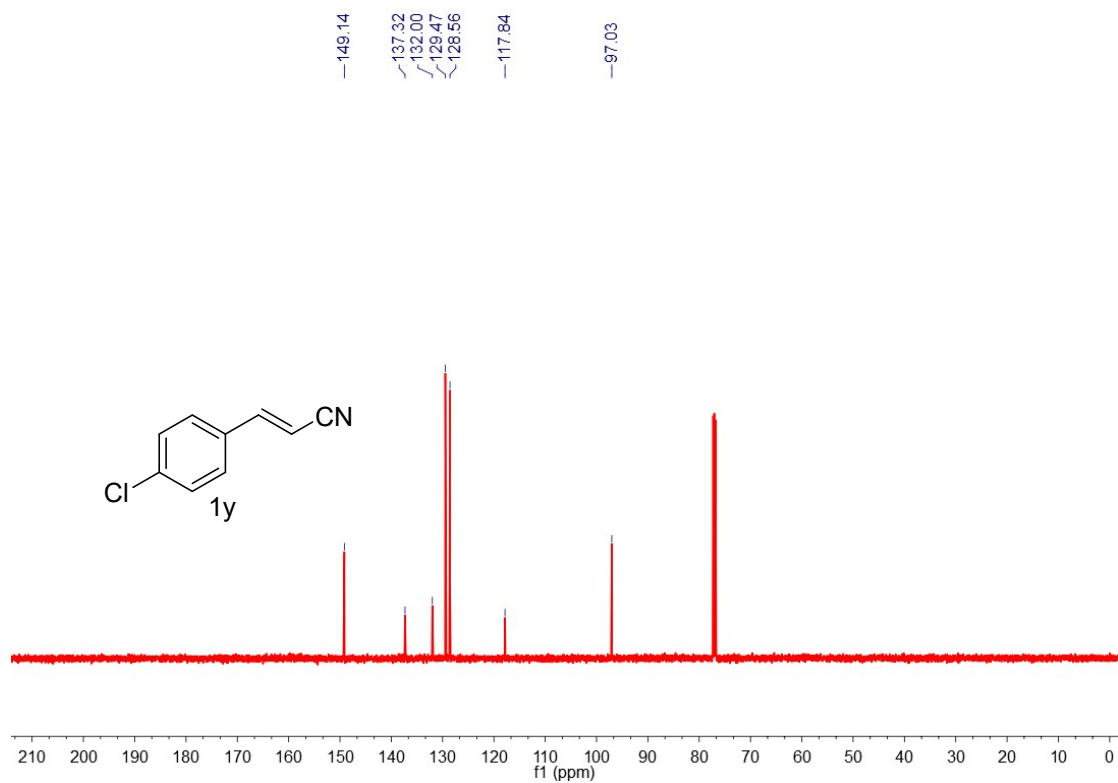
^1H NMR (600 MHz, CDCl_3)



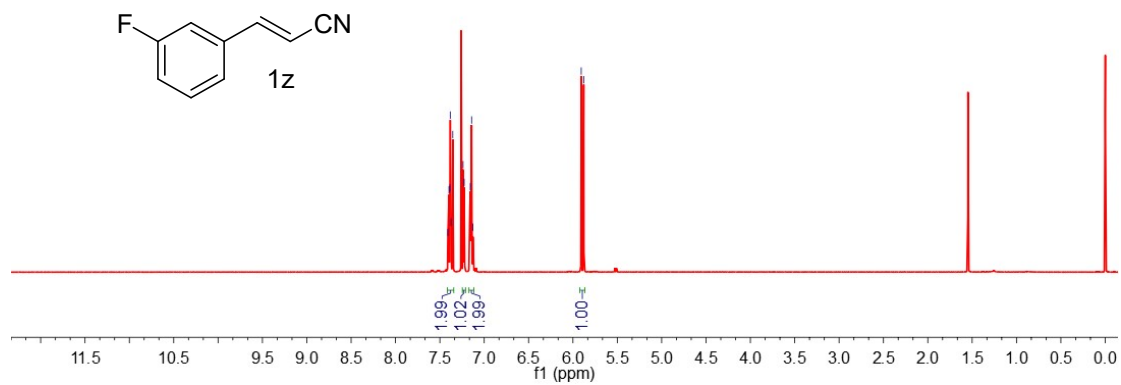
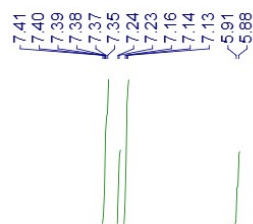
^{13}C NMR (151 MHz, CDCl_3)



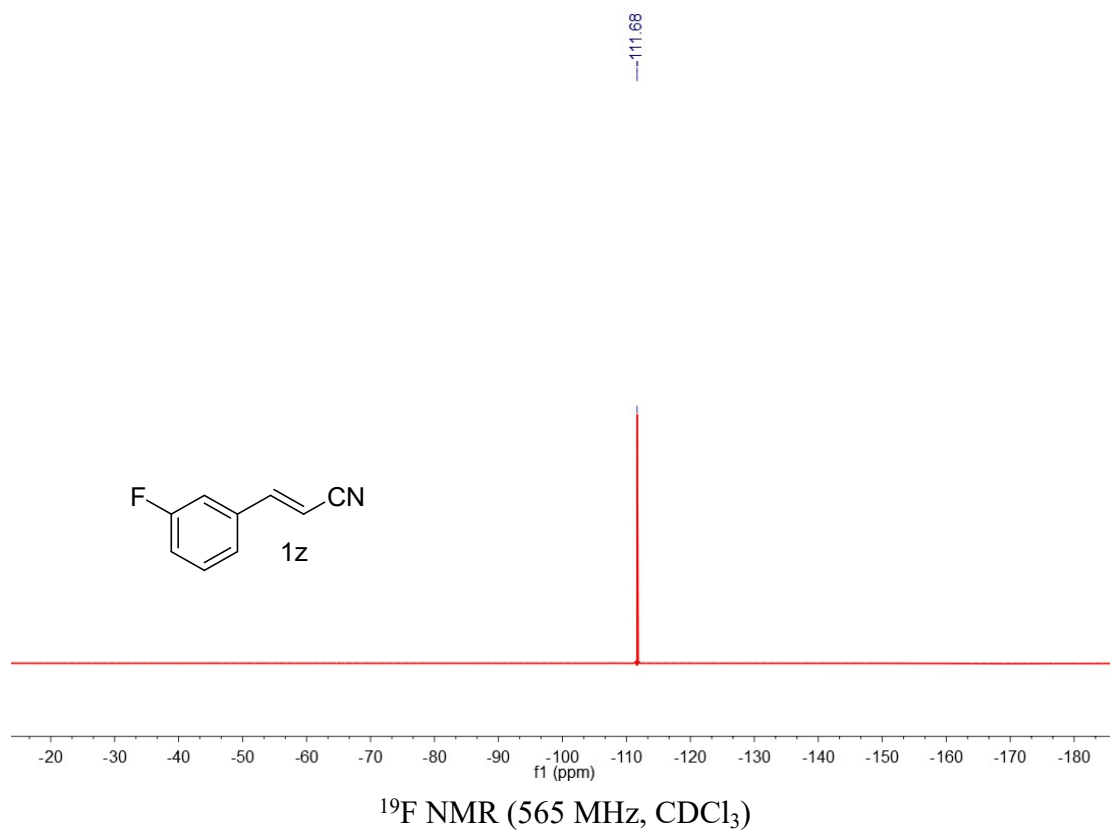
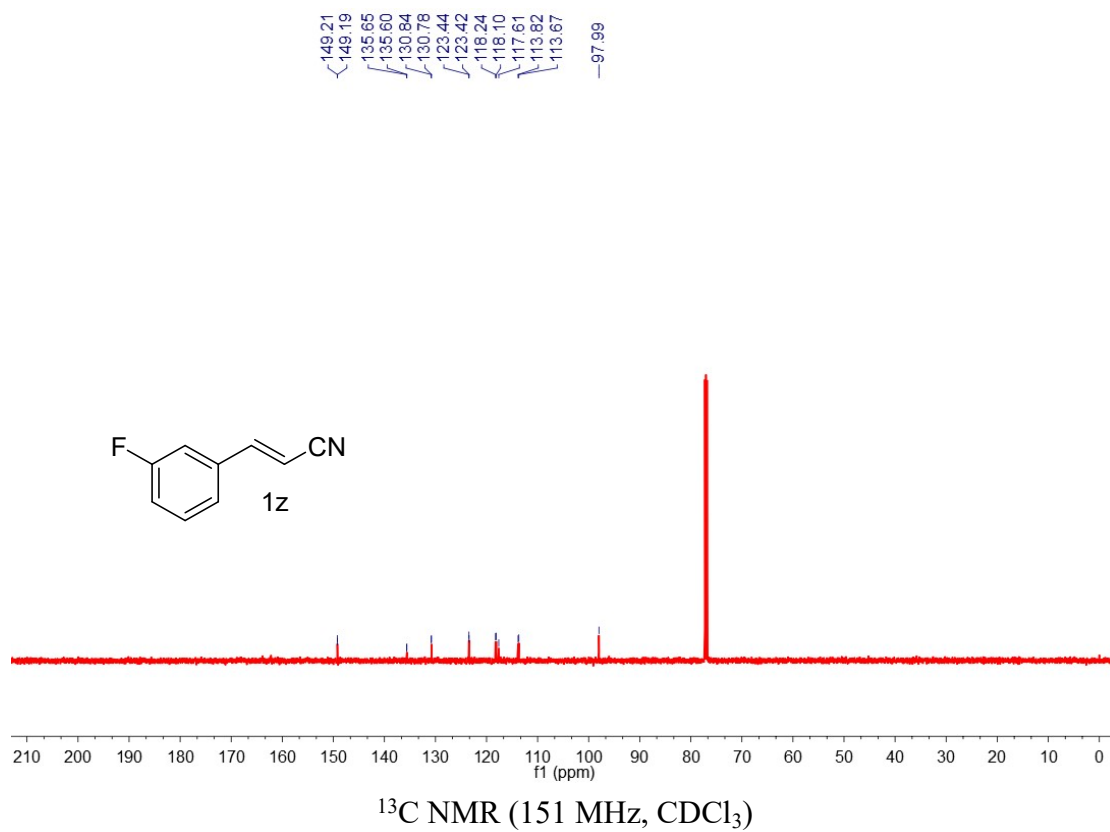
^1H NMR (600 MHz, CDCl_3)

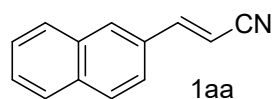
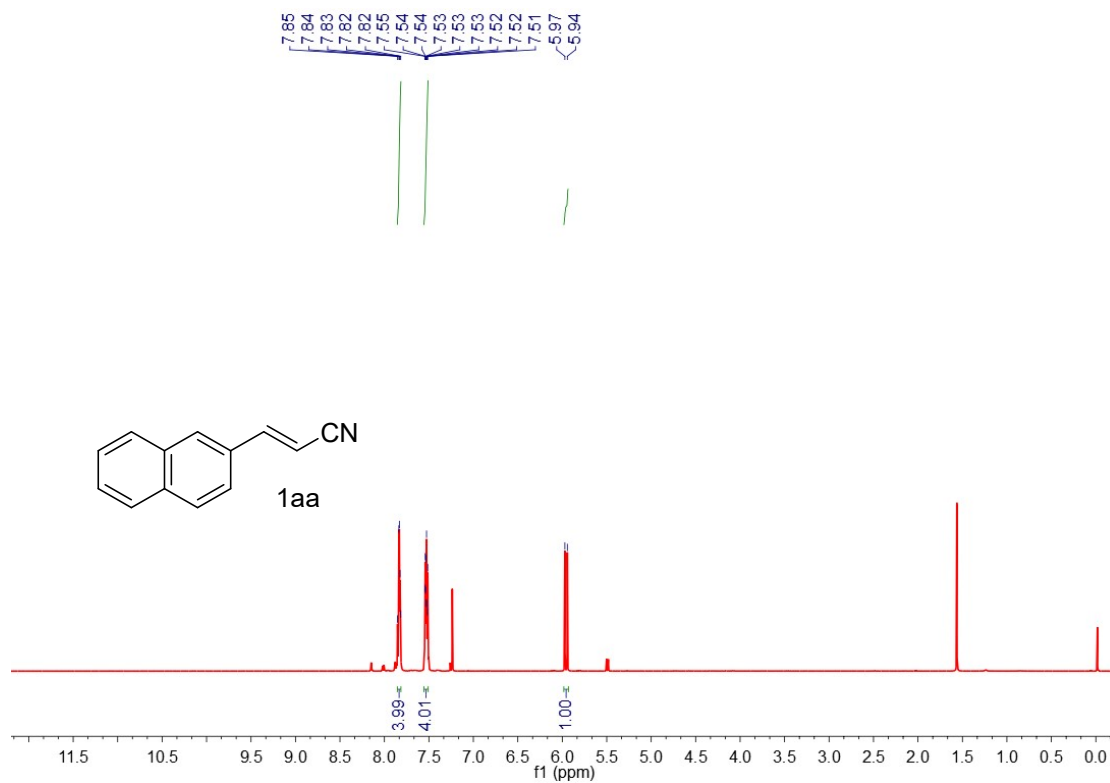


^{13}C NMR (151 MHz, CDCl_3)

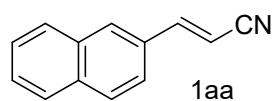
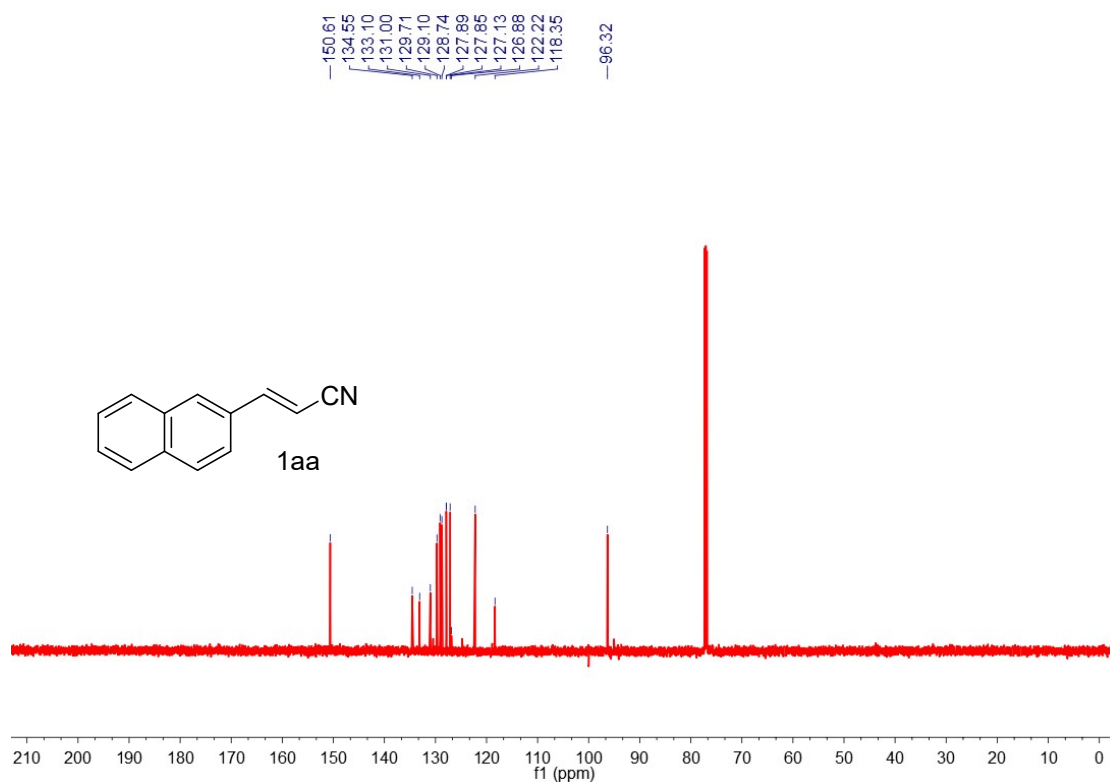


^1H NMR (600 MHz, CDCl_3)

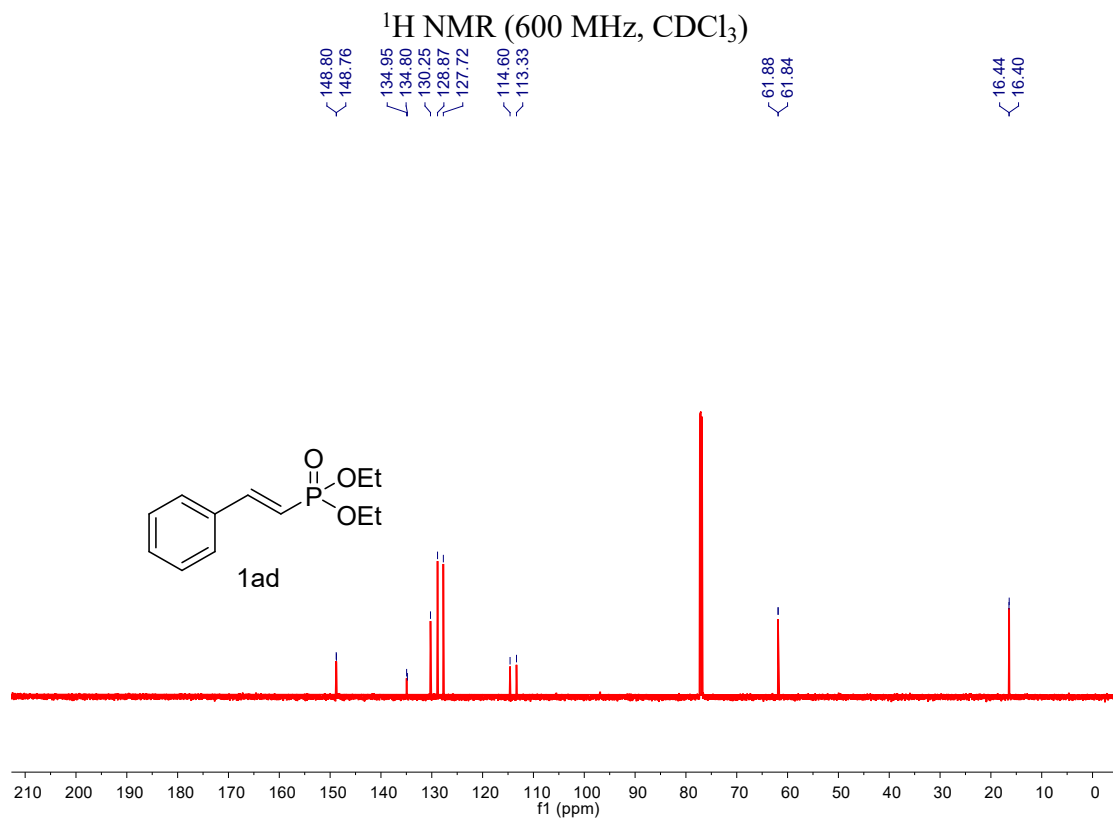
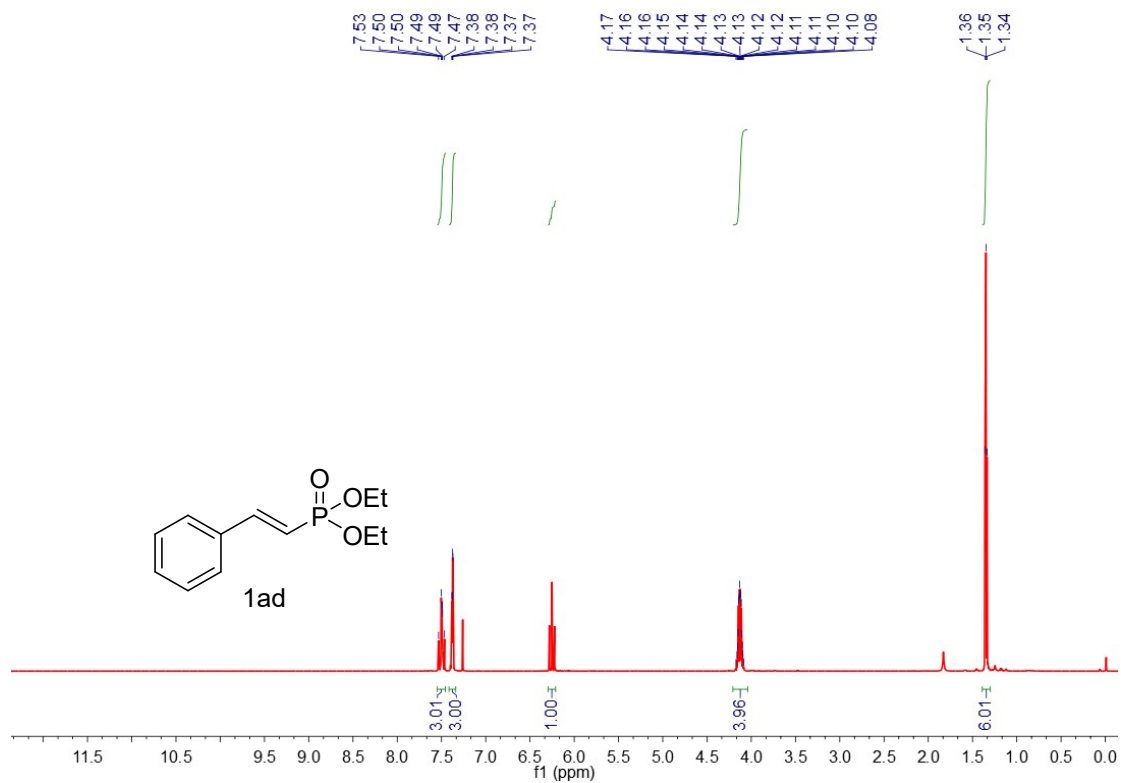


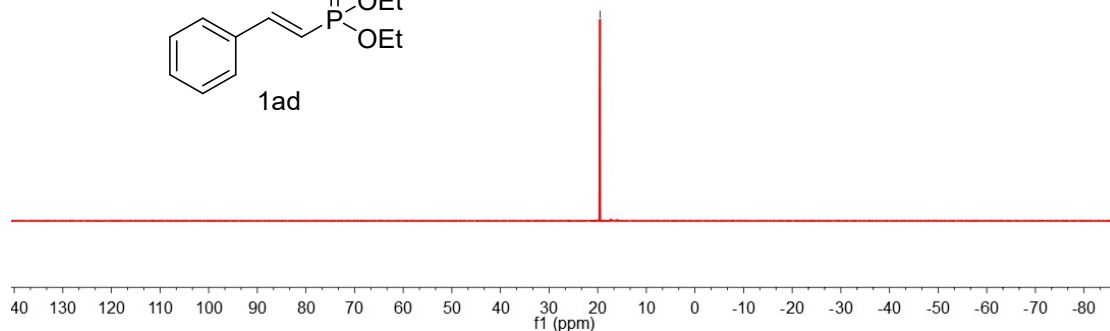
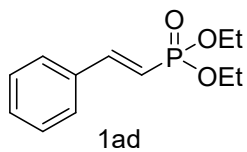


$^1\text{H NMR}$ (600 MHz, CDCl_3)



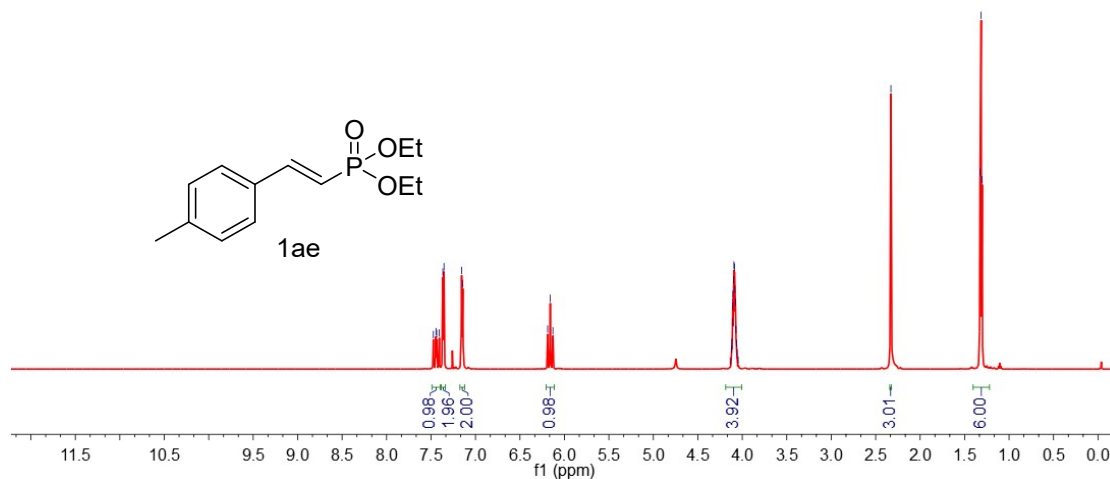
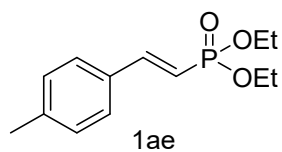
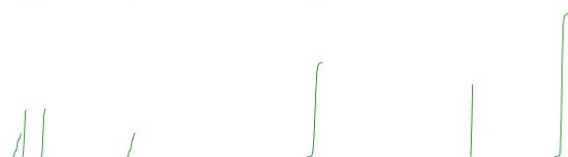
$^{13}\text{C NMR}$ (151 MHz, CDCl_3)



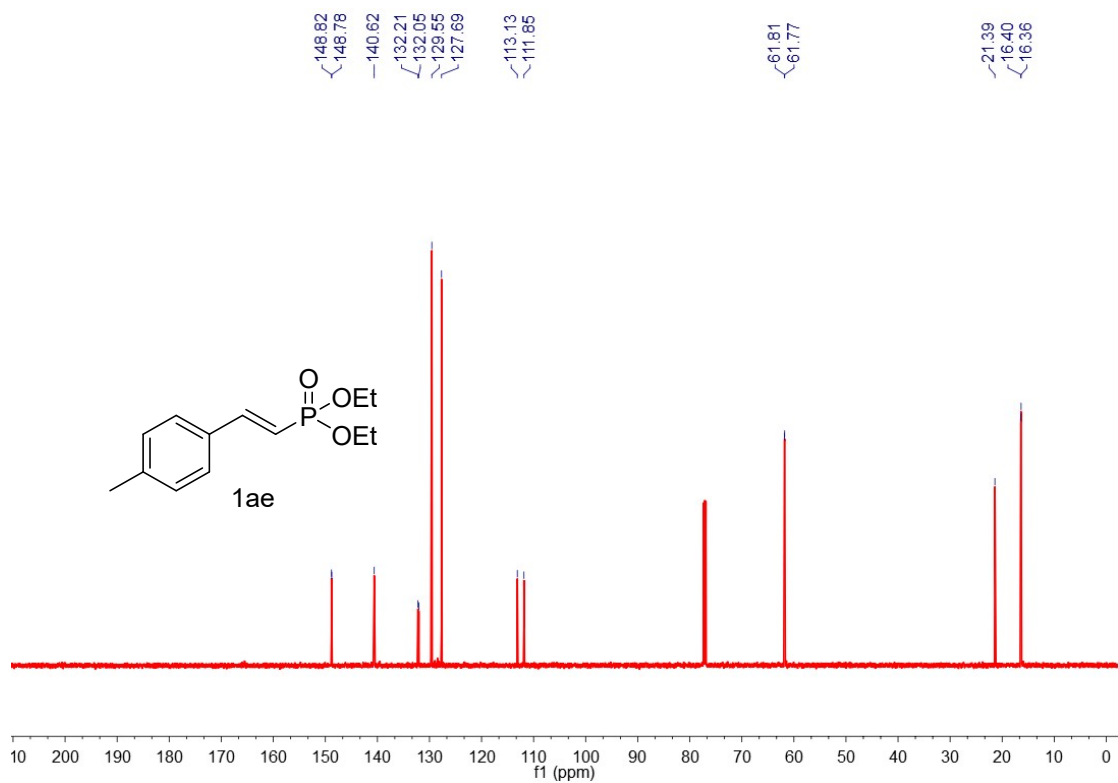


^{31}P NMR (243 MHz, CDCl_3)

7.47, 7.44, 7.41, 7.37, 7.35, 7.14, 6.19, 6.16, 6.13, 4.14, 4.12, 4.12, 4.11, 4.11, 4.10, 4.09, 4.08, 4.08, 4.07, 4.06, 4.06, 4.05, -2.33, 1.33, 1.31, 1.30

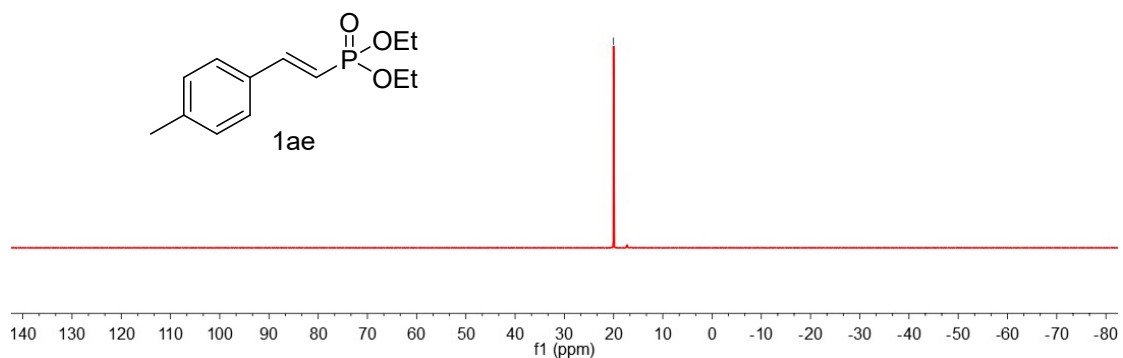


^1H NMR (600 MHz, CDCl_3)

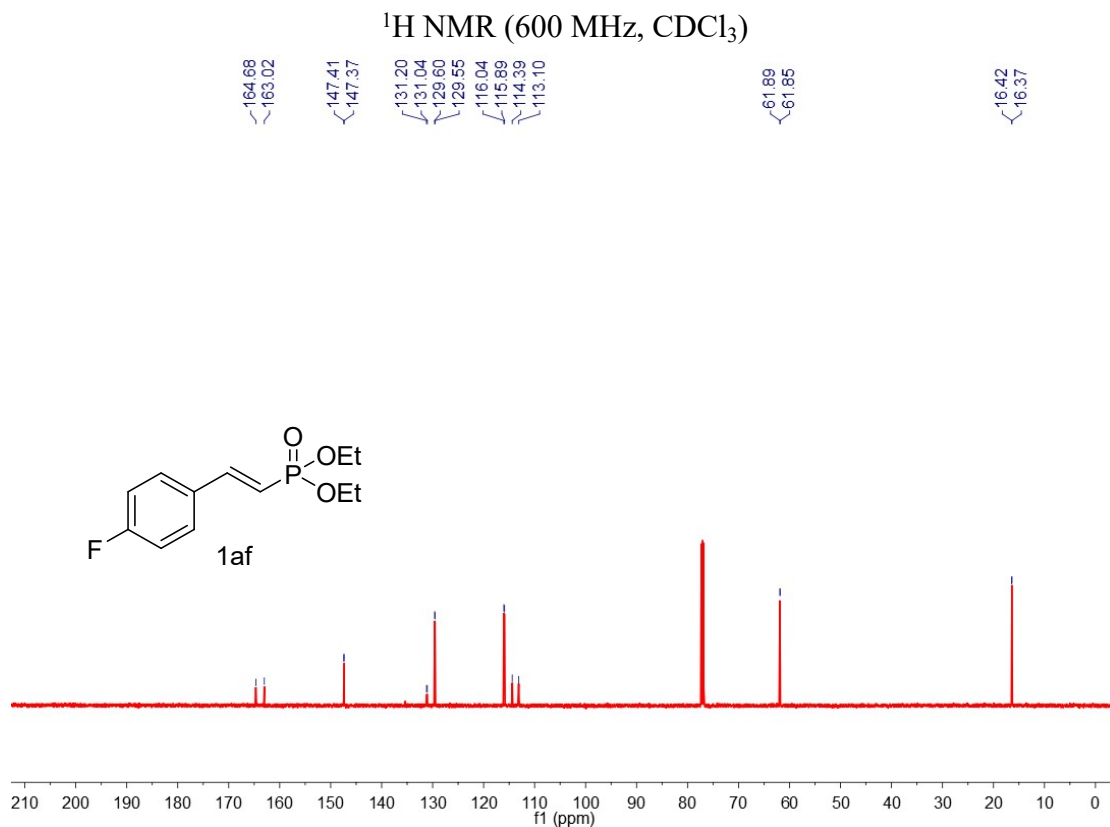
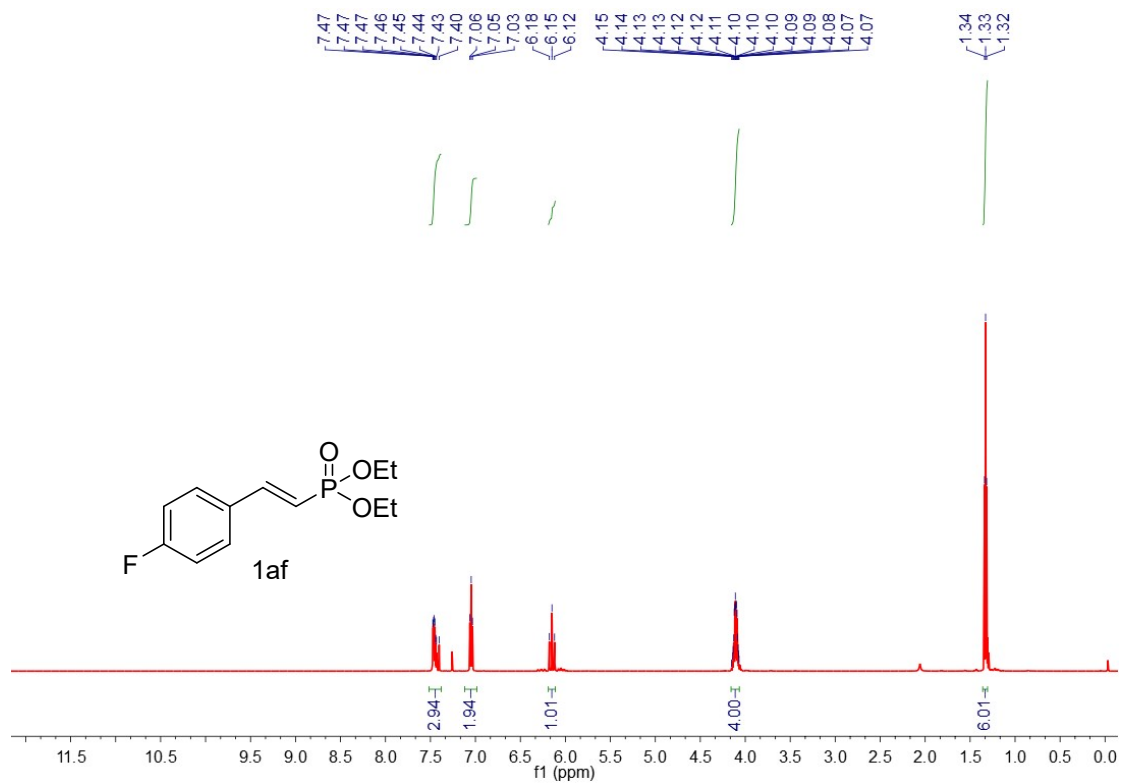


^{13}C NMR (151 MHz, CDCl_3)

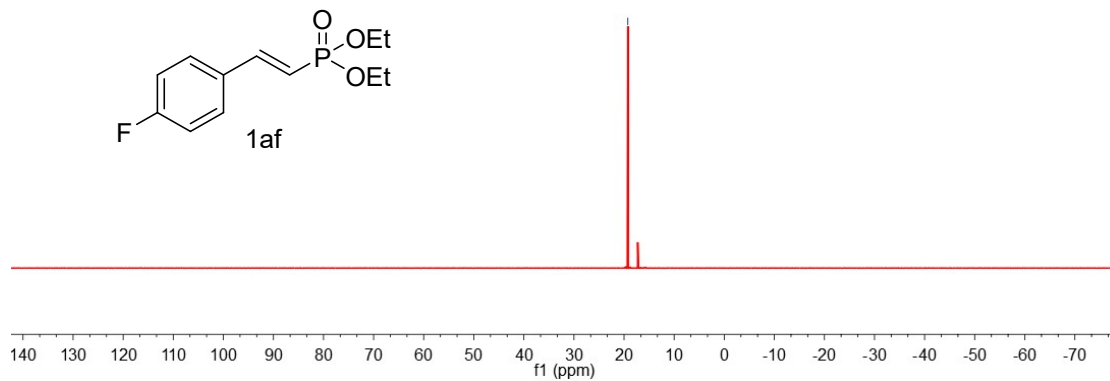
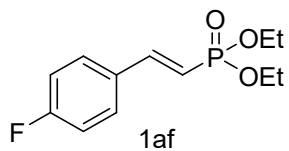
-20.01



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

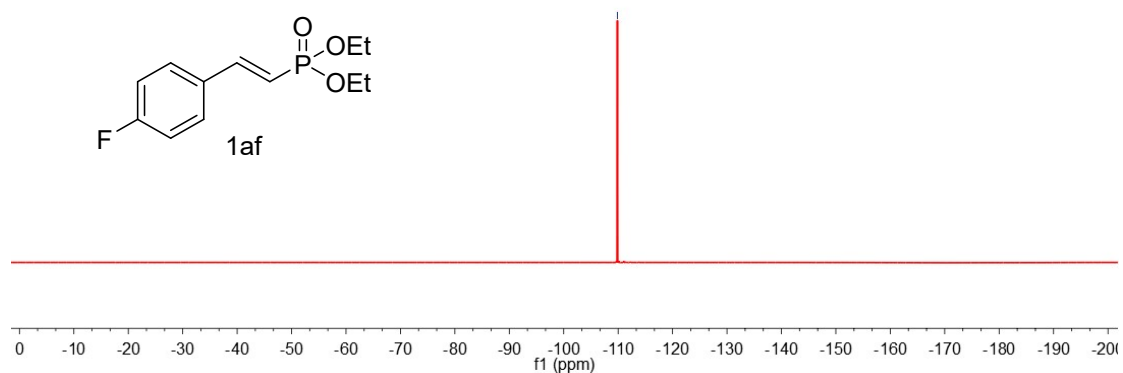
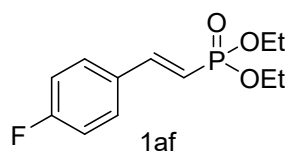


-19.24

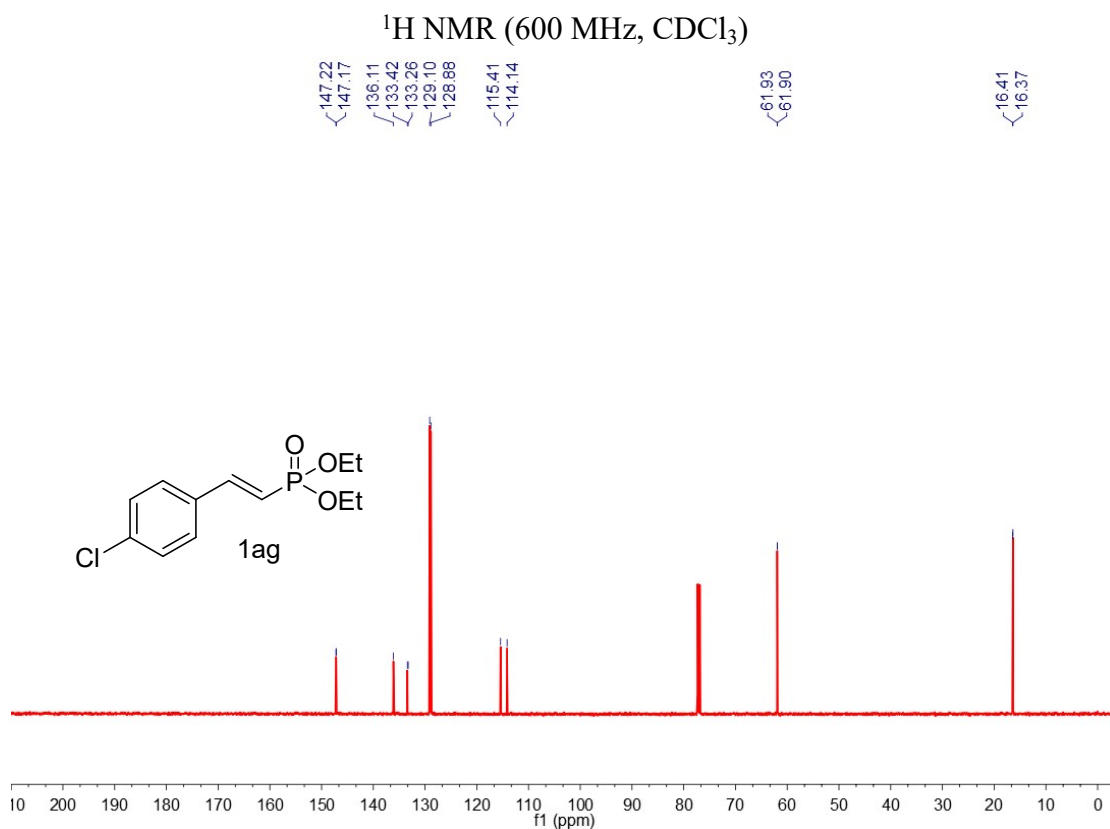
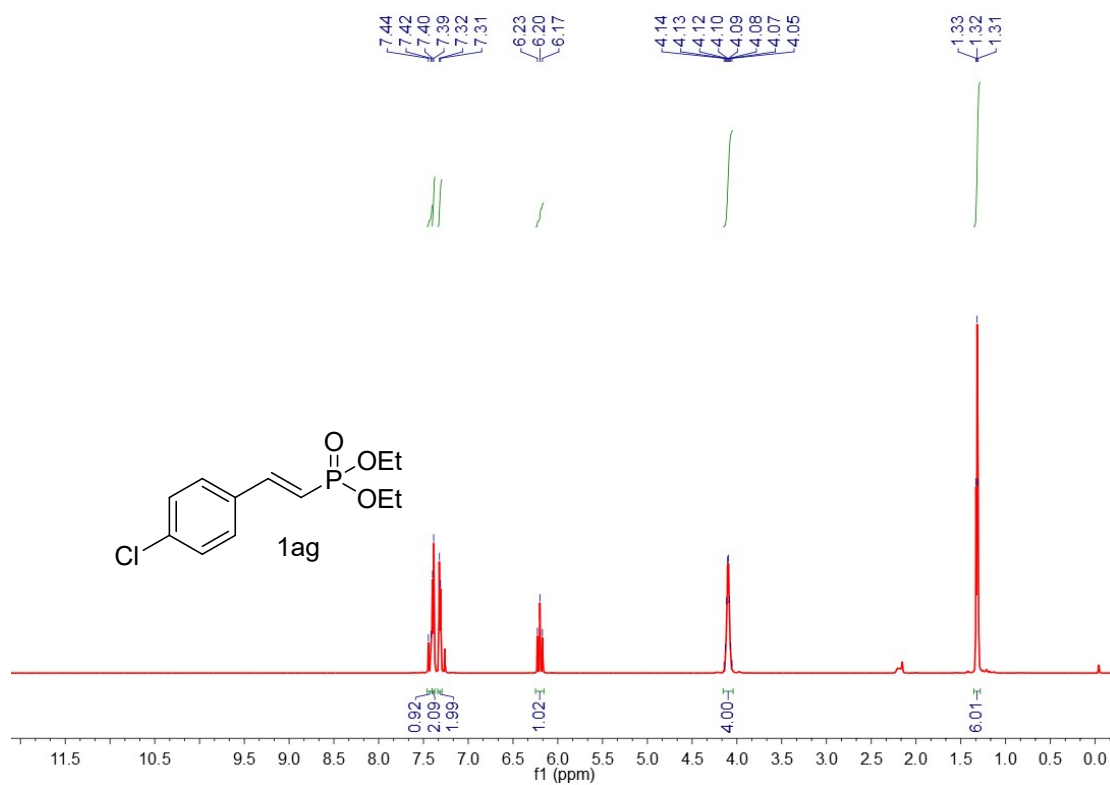


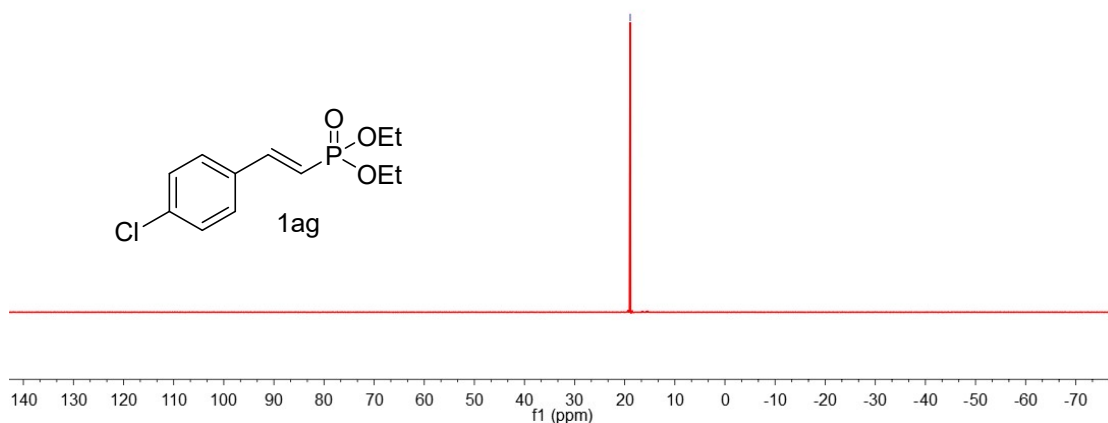
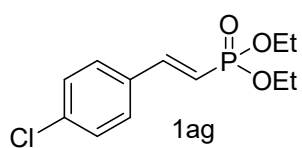
^{31}P NMR (243 MHz, CDCl_3)

-109.87



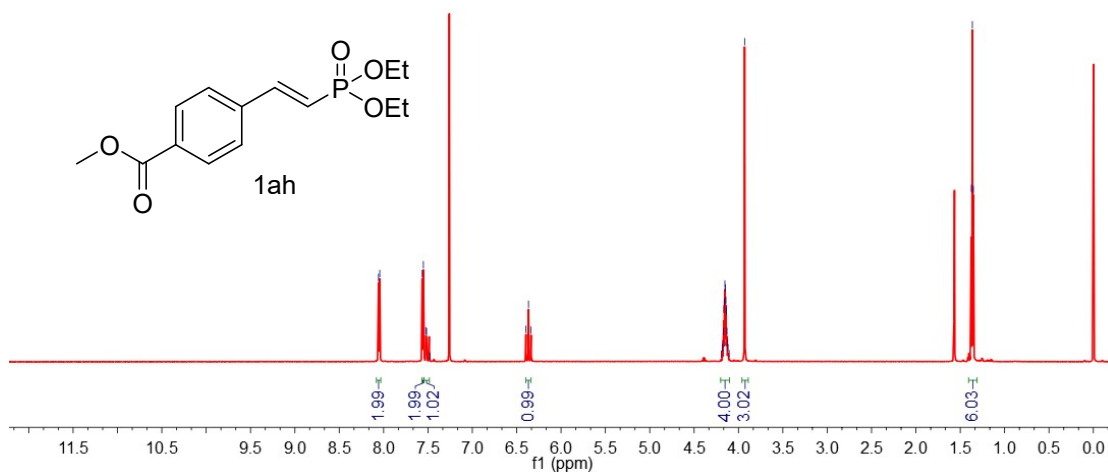
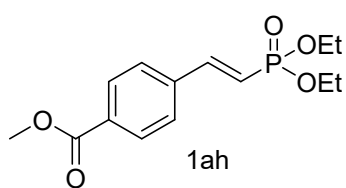
^{19}F NMR (565 MHz, CDCl_3)



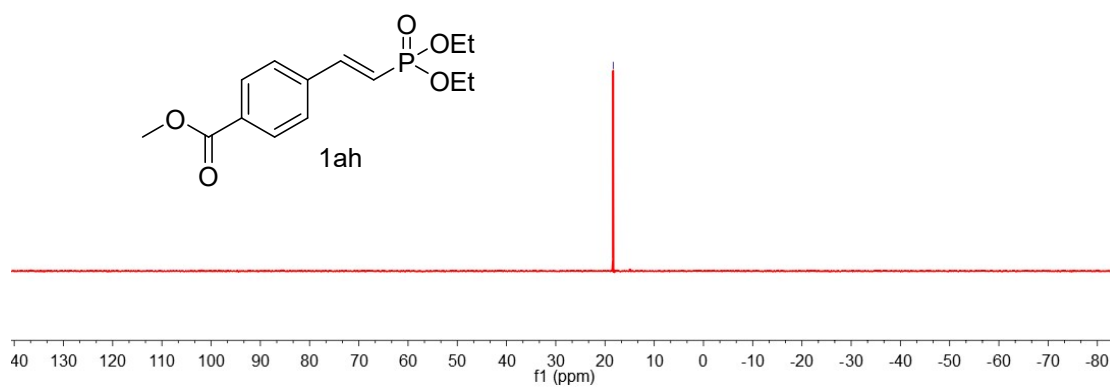
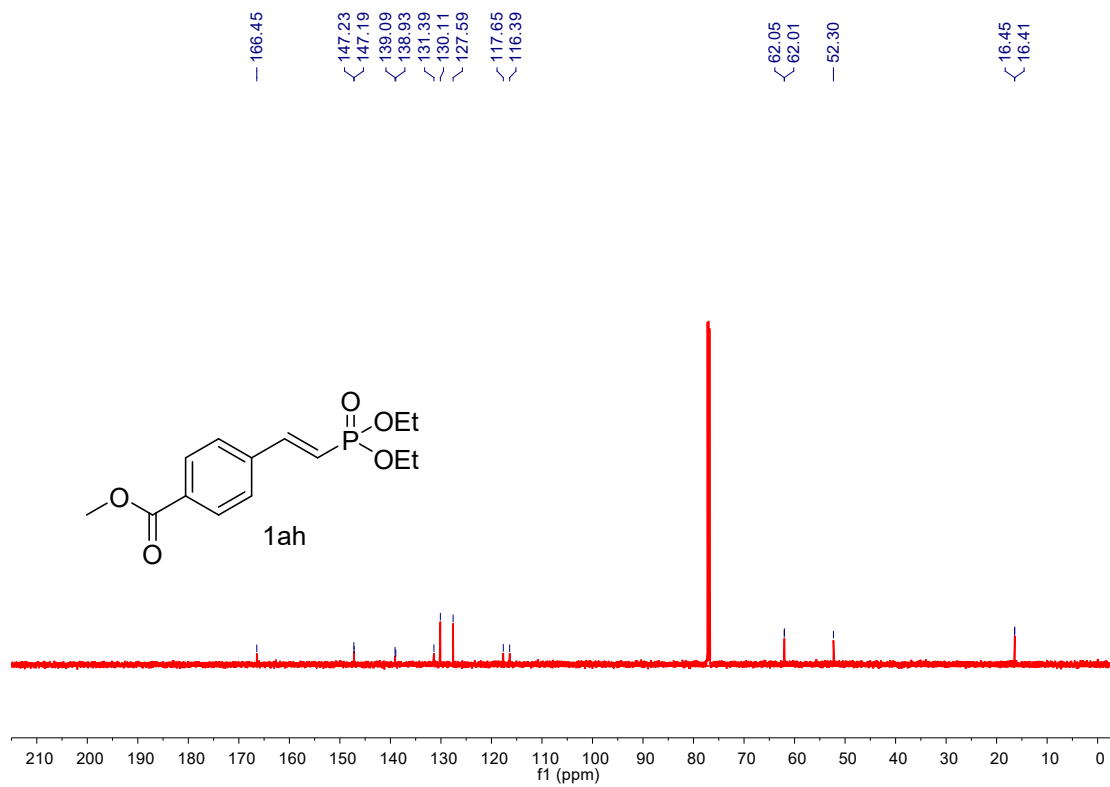


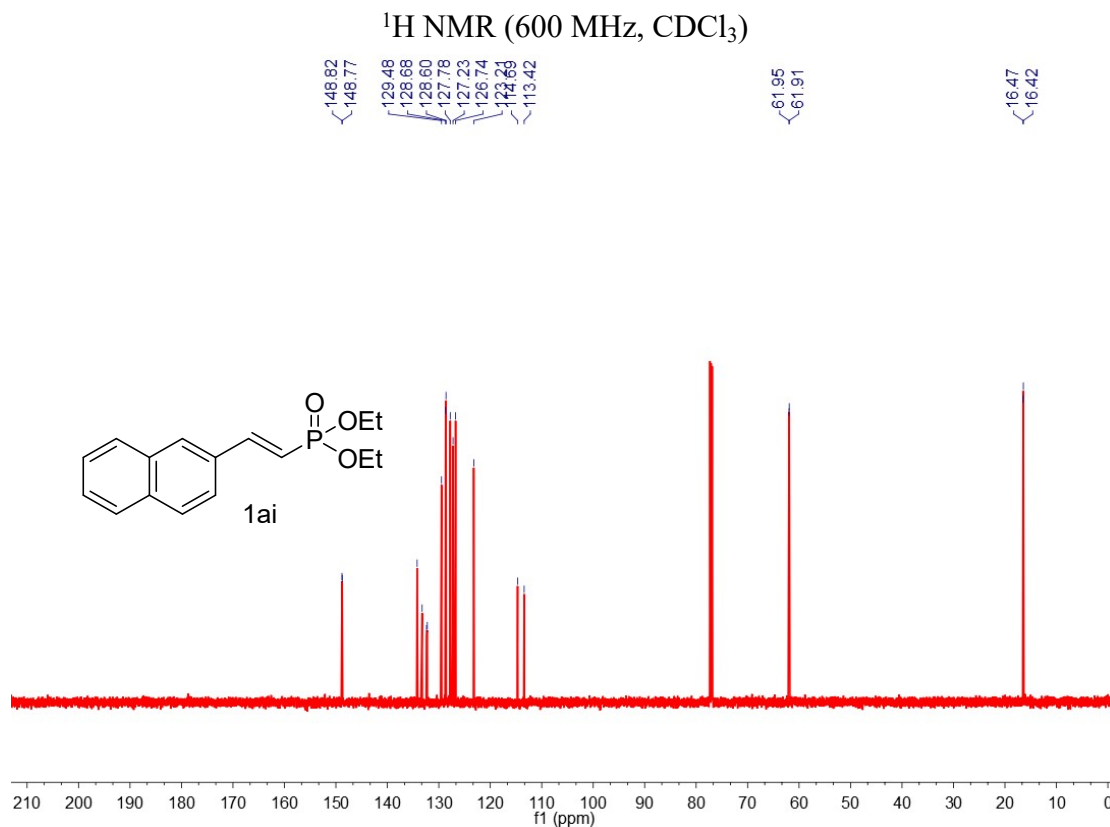
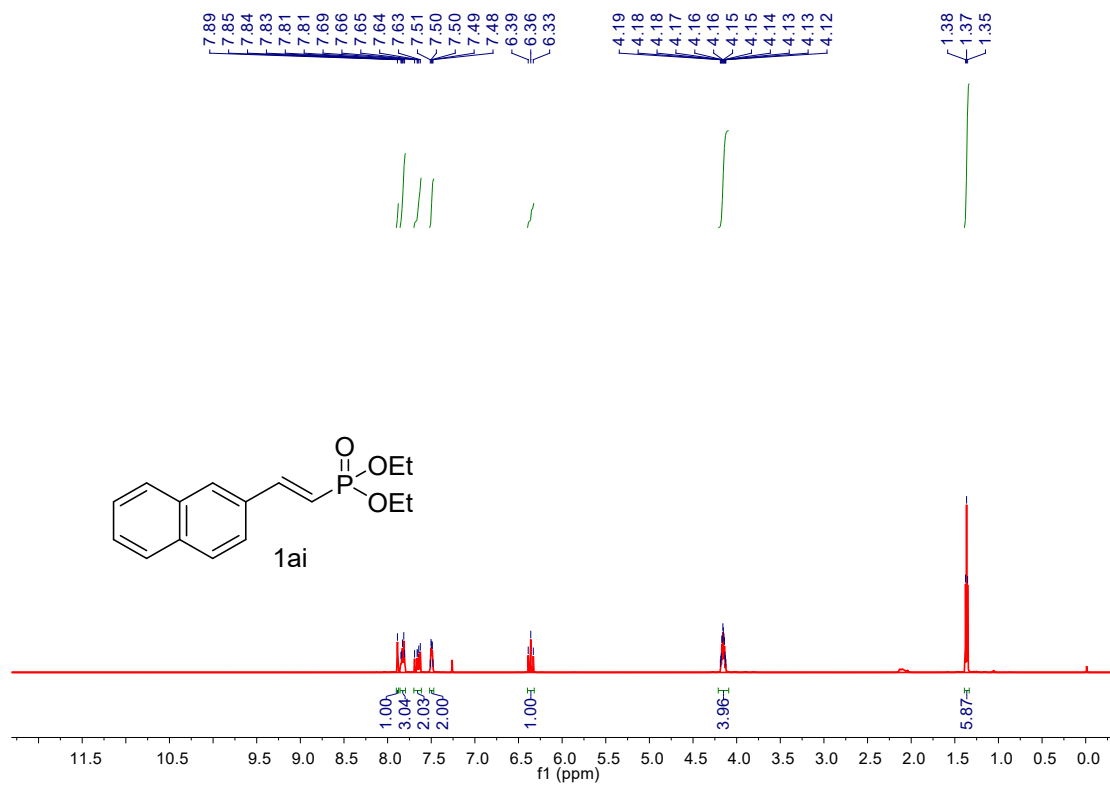
^{31}P NMR (243 MHz, CDCl_3)

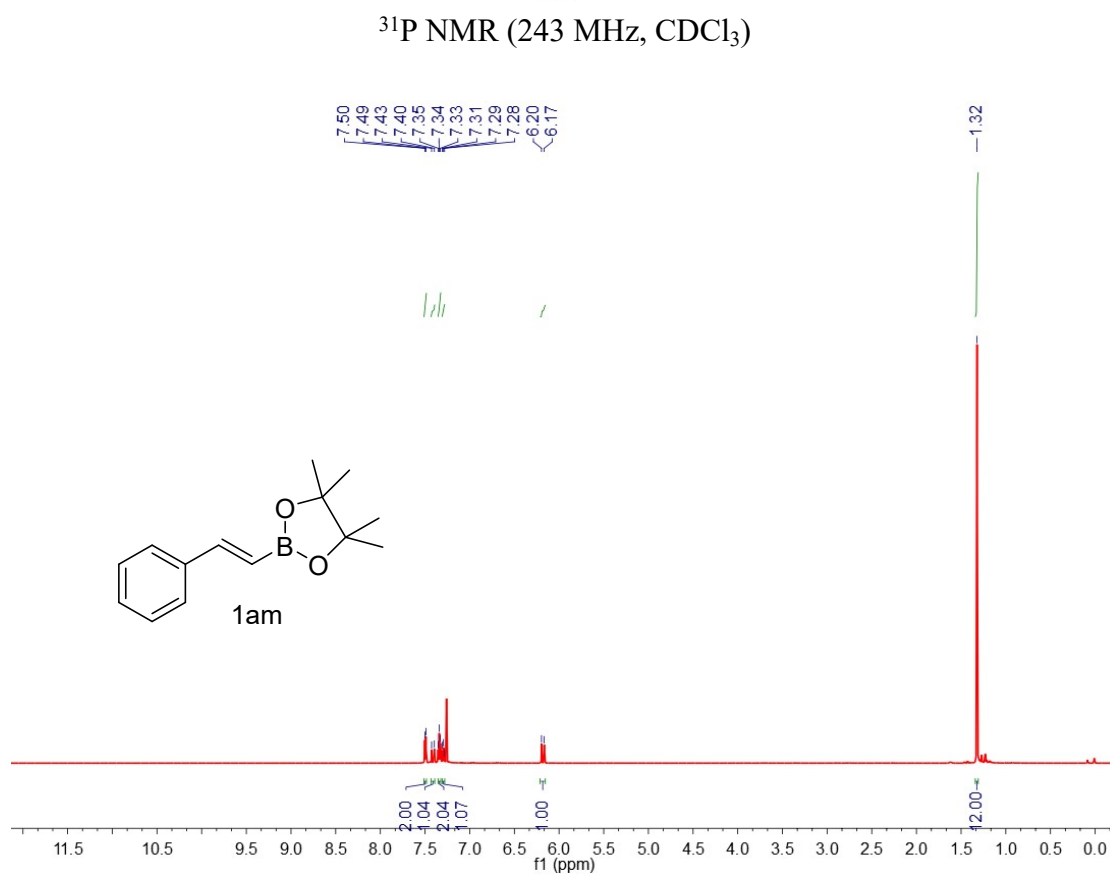
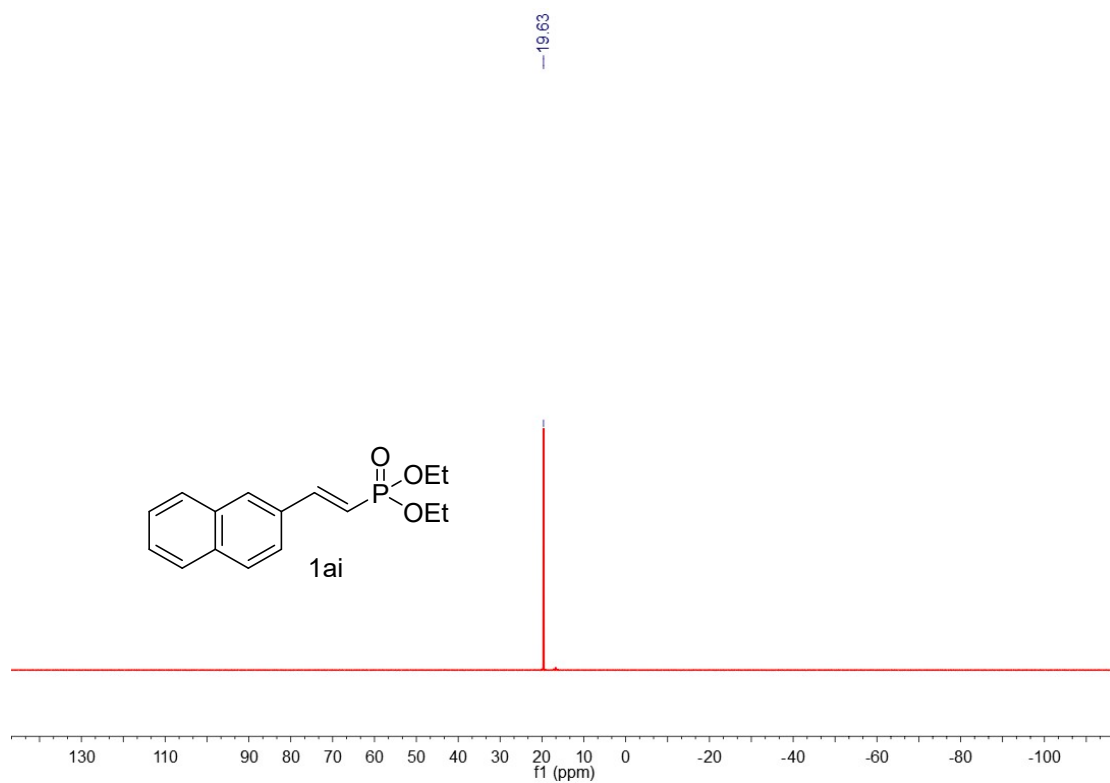
8.06, 8.04, 7.56, 7.52, 7.48, 6.40, 6.37, 6.34, 4.19, 4.18, 4.18, 4.17, 4.17, 4.16, 4.15, 4.14, 4.13, 4.13, 4.12, 4.12, 4.11, 4.11, 3.93, 1.38, 1.36, 1.35

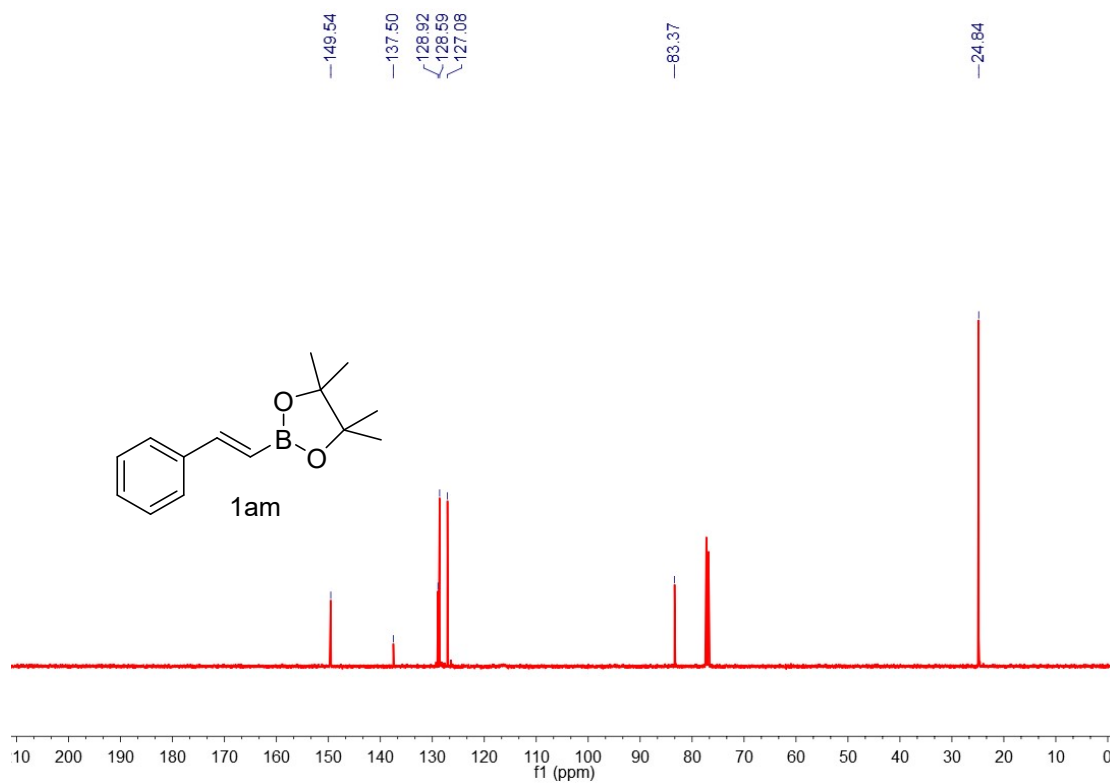


^1H NMR (600 MHz, CDCl_3)

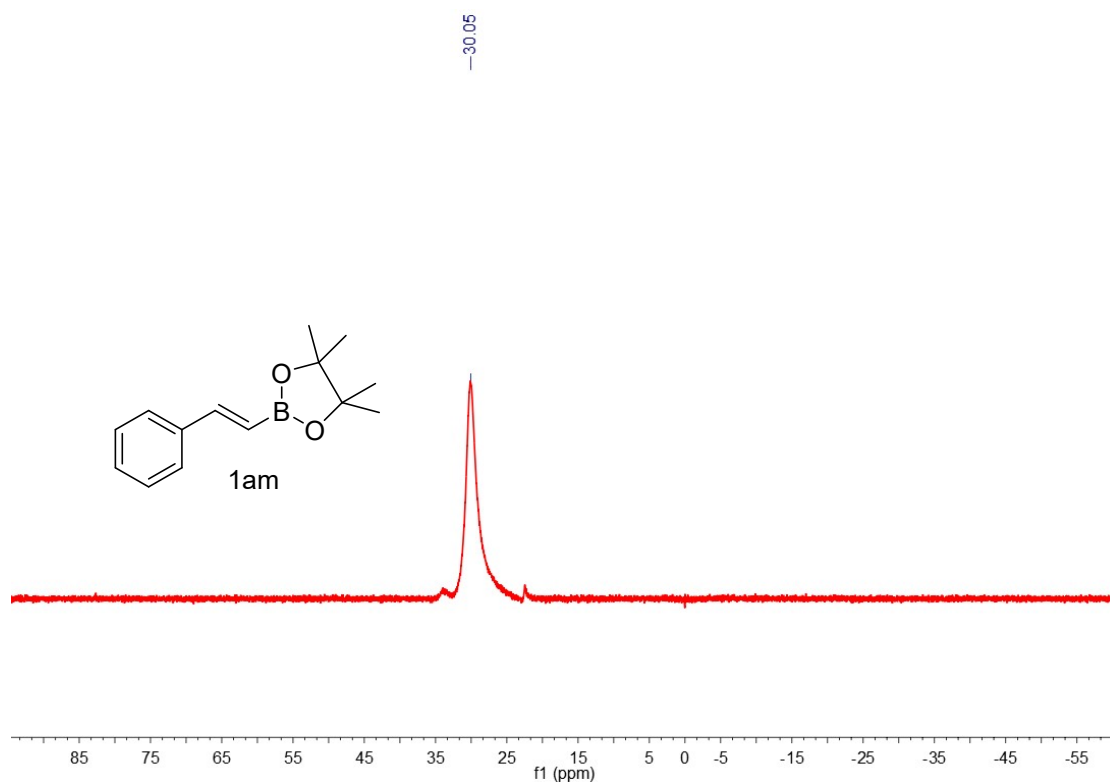




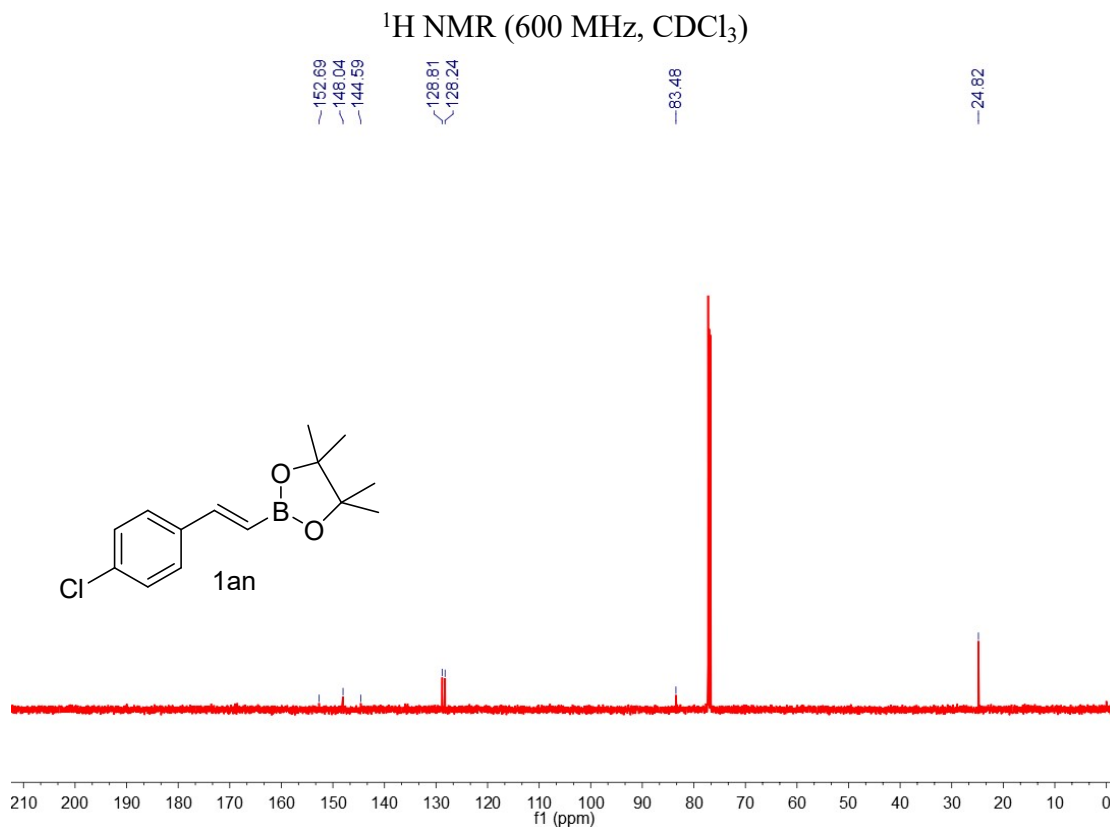
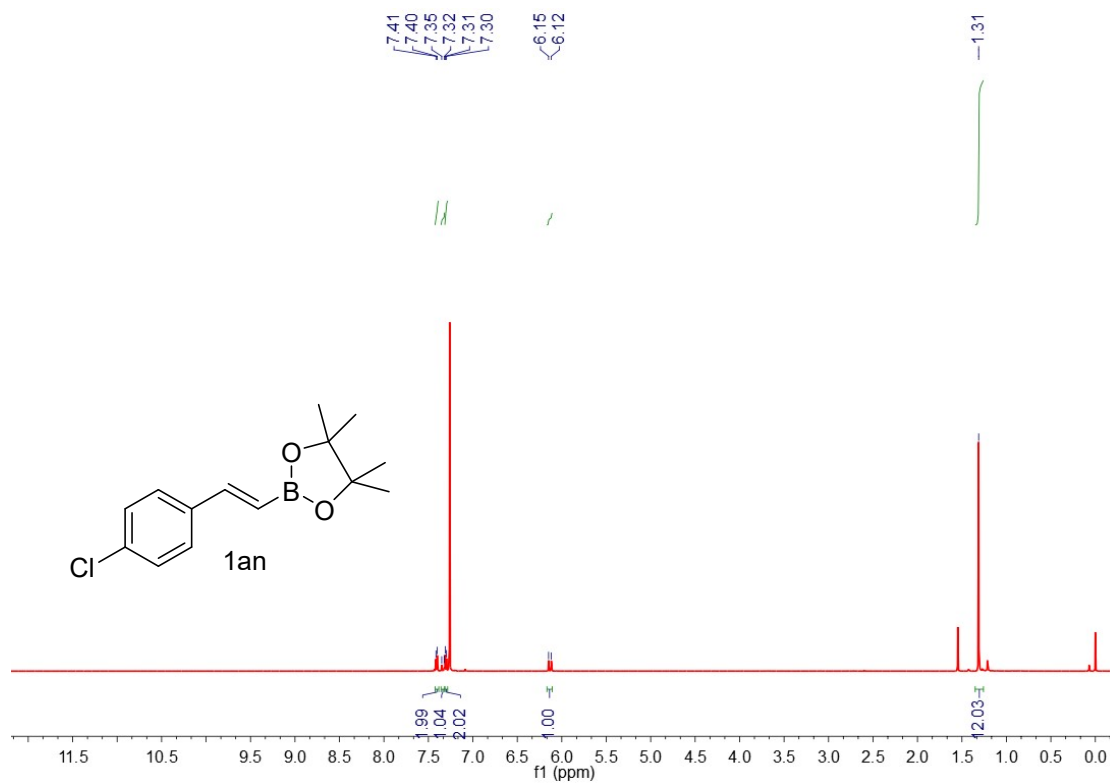


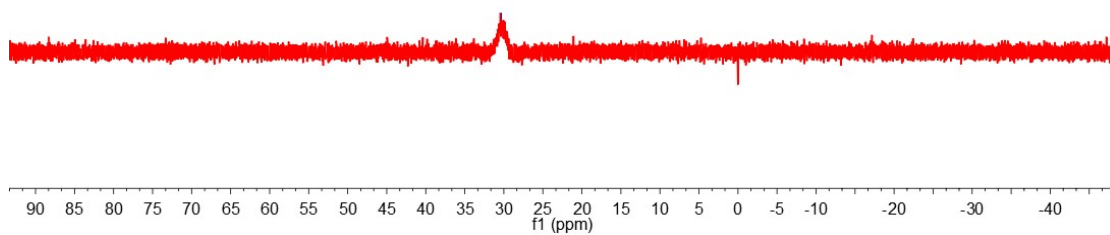
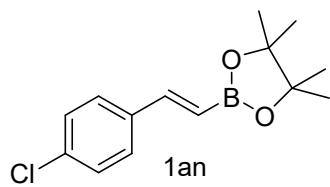


¹³C NMR (151 MHz, CDCl₃)



¹¹B NMR (193 MHz, CDCl₃)





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