

# Supporting Information

## Ozonolysis of Unsaturated Organotrifluoroborates

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### **Contents:**

Experimental Procedure and Compound Characterization .....	S2
NMR spectra .....	S13

**General Methods and Materials.**  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{19}\text{F}$  NMR spectra were measured on spectrometers at 500.13, 125.75, and 470.55 Hz, respectively.  $^{11}\text{B}$  spectra at 64.2 Hz were obtained on a spectrometer equipped with the appropriate decoupling accessories. The melting points were uncorrected. CI mass spectra were obtained at 70 eV with direct inlet injection.

**Potassium 3-Methylbut-3-enyl Trifluoroborate (1).** To a solution of trimethyl borate (26.3 g, 256 mmol) in THF (185 mL) was added dropwise 3-methylbut-3-enylmagnesium bromide (1.0 M THF solution, 200 mL, 200 mmol) at  $-78\text{ }^\circ\text{C}$ . The resulting suspension was stirred for 20 min at  $-78\text{ }^\circ\text{C}$  and then allowed to warm to rt for 1 h. The mixture was then cooled to  $0\text{ }^\circ\text{C}$  and  $\text{KHF}_2$  (86.0 g, 906 mmol) was added followed by the addition of  $\text{H}_2\text{O}$  (150 mL) over 30 min. After stirring at rt for 20 min, the solution was concentrated and the crude material was dissolved in acetone, filtered and concentrated. The resulting white solid was purified by dissolving in hot acetone and precipitating with  $\text{Et}_2\text{O}$  to afford the alkenyl trifluoroborate **1** as a white solid (18.57 g, 118.2 mmol, 59%). mp  $>250\text{ }^\circ\text{C}$ ; IR (KBr) =  $1652\text{ cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz, acetone- $d^6$ ):  $\delta$  0.25 – 0.34 (m, 2H), 1.66 (s, 3H), 1.94 (t,  $J = 8.6\text{ Hz}$ , 2H), 4.49 (s, 1H), 4.59 (s, 1H);  $^{13}\text{C}$  NMR (125.8 MHz, acetone- $d^6$ ):  $\delta$  22.3, 33.9, 106.7, 151.1;  $^{19}\text{F}$  NMR (471 MHz, acetone- $d^6$ ):  $\delta$   $-142.1$ ;  $^{11}\text{B}$  NMR (64.2 MHz, acetone- $d^6$ ):  $\delta$  5.38; HRMS (ESI): calcd for  $\text{C}_5\text{H}_9\text{BF}_3$  ( $\text{M}^+$ ) 137.0749, found 137.0751.

**Potassium 3-Oxobutyl Trifluoroborate (2) via method A.** To a solution of potassium trifluoroborate **1** (0.101 g, 0.643 mmol) in an acetone/ $\text{H}_2\text{O}$  mixture (30%  $\text{H}_2\text{O}$  in acetone,

7 mL) at  $-70\text{ }^{\circ}\text{C}$  was applied a flow of ozone for 14 min. The solution was then degassed with  $\text{N}_2$  for 15 min followed by the addition of  $\text{H}_2\text{O}$  (1 mL). This was allowed to warm to rt while stirring. Following solvent removal the resulting white solid was purified by dissolving in hot acetone and precipitating with  $\text{Et}_2\text{O}$ , affording the trifluoroborate **2** as a white solid (0.072 g, 0.453 mmol, 70%). mp  $>250\text{ }^{\circ}\text{C}$ ; IR (KBr) =  $1714\text{ cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz, acetone- $d^6$ ):  $\delta$  0.41 (m, 2H), 2.02 (s, 3H), 2.29 (t,  $J = 7.8\text{ Hz}$ , 2H);  $^{13}\text{C}$  NMR (125.8 MHz, acetone- $d^6$ ):  $\delta$  28.3, 40.7, 212.9;  $^{19}\text{F}$  NMR (471 MHz, acetone- $d^6$ ):  $\delta$   $-142.3$ ;  $^{11}\text{B}$  NMR (64.2 MHz, acetone- $d^6$ ):  $\delta$  5.65.

**Tetrabutylammonium 4-Vinylphenyltrifluoroborate (3).** To a slurry of potassium 4-vinylphenyl trifluoroborate<sup>1</sup> **5** (54 mg, 0.33 mmol) in  $\text{H}_2\text{O}$  (1 mL) and  $\text{CH}_2\text{Cl}_2$  (2 mL) was added a solution of (*n*-Bu)<sub>4</sub>NOH (0.2 mL, 0.49 mmol, 1.6M solution) with stirring. The biphasic solution was stirred for 0.5 h. The layers were separated. The aqueous layer was extracted with  $\text{CH}_2\text{Cl}_2$  after which the combined organic layers were washed with  $\text{H}_2\text{O}$ , dried ( $\text{MgSO}_4$ ) and concentrated under high vacuum to afford the alkenyl product **3** (98 mg, 0.27 mmol, 81%). IR (neat) =  $1627, 1602\text{ cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz, acetone- $d^6$ ):  $\delta$  0.85 (t,  $J = 7.1\text{ Hz}$ , 12H), 1.15 – 1.23 (m, 8H), 1.23 – 1.33 (m, 8H), 2.77 (t,  $J = 7.3\text{ Hz}$ , 8H), 5.05 (d,  $J = 11.4\text{ Hz}$ , 1H), 5.59 (d,  $J = 18.0\text{ Hz}$ , 1H), 6.59 (dd,  $J = 18.8, 10.8\text{ Hz}$ , 1H), 7.17 (d,  $J = 7.3\text{ Hz}$ , 2H), 7.45 (d,  $J = 7.5\text{ Hz}$ , 2H);  $^{13}\text{C}$  NMR (125.8 MHz, acetone- $d^6$ ):  $\delta$  13.6, 19.4, 23.6, 57.9, 111.3, 124.7, 132.1, 134.8, 137.8;  $^{19}\text{F}$  NMR (471 MHz, acetone- $d^6$ ):  $\delta$   $-142.15$ ;  $^{11}\text{B}$  NMR (64.2 MHz, acetone- $d^6$ ):  $\delta$  2.45; HRMS (ESI): calcd for  $\text{C}_8\text{H}_7\text{BF}_3$  ( $\text{M}^-$ ) 171.0593, found 171.0595.

**Tetrabutylammonium 4-Formylphenyl Trifluoroborate (4) via procedure B<sup>a</sup>.** To a solution of tetrabutylammonium 4-vinylphenyl trifluoroborate **3** (85 mg, 0.2 mmol) and 4-methylmorpholine *N*-oxide (100 mg, 1.0 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (3 mL) was applied a flow of ozone at -78 °C until the solution appeared light blue in color. The solution was degassed and then washed with H<sub>2</sub>O (3 X 5 mL) and brine to give the product **4** (63 mg, 0.15 mmol, 76%) following solvent removal. IR (neat) = 1693 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 0.93 (t, *J* = 7.3, 12H), 1.30 – 1.36 (m, 8H), 1.43 – 1.53 (m, 8H), 3.05 (t, *J* = 7.9 Hz, 8H), 7.71 (d, *J* = 7.8 Hz, 2H), 7.76 (d, *J* = 7.8 Hz, 2H), 9.93 (s, 1H); <sup>13</sup>C NMR (125.8 MHz, CDCl<sub>3</sub>): δ 14.0, 20.0, 24.14, 58.9, 128.9, 132.7, 133.9, 193.9; <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>): δ -142.8; <sup>11</sup>B NMR (64.2 MHz, CDCl<sub>3</sub>): δ 3.34; HRMS (ESI): calcd for C<sub>7</sub>H<sub>5</sub>BF<sub>3</sub>O (M<sup>-</sup>) 173.0385, found 173.0381.

**Tetrabutylammonium 4-Formylphenyl Trifluoroborate (4) via procedure B<sup>b</sup>.** To a solution of potassium 4-vinylphenyl trifluoroborate **5** (209 mg, 1.0 mmol) in 50% DMF/Et<sub>3</sub>N (4 mL) was added sufficient Sudan III to create a light pink colored solution. A flow of ozone was applied at 0 °C during which a white vapor was evolved. The ozone flow was continued until both the pink color of the solution faded and the white vapor cleared, after which the solution was degassed with nitrogen. CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was added to the solution leading to the precipitation of white crystals which were washed with ether to give the aldehyde. Further purification was achieved by creating a slurry of the aldehyde in H<sub>2</sub>O (1 mL) and CH<sub>2</sub>Cl<sub>2</sub> (2 mL) to which was added a solution of (*n*-Bu)<sub>4</sub>NOH (0.63 mL, 1.0 mmol, 1.6M solution) with stirring. The biphasic solution was stirred for 0.5 h. The layers were separated. The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub>

after which the combined organic layers were washed with H<sub>2</sub>O, dried (MgSO<sub>4</sub>) and concentrated under high vacuum to afford the aldehyde **4** (168 mg, 0.79 mmol, 79%).

**Tetrabutylammonium 4-Formylphenyl Trifluoroborate (4) via procedure B<sup>c</sup>.** To a solution of potassium 4-vinylphenyl trifluoroborate **5** (49 mg, 0.25 mmol) in 40% DMF/DCM (1.25 mL) was added sufficient Sudan III to create a light pink colored solution. A flow of ozone was applied at -78 °C until the pink color faded, after which the solution was degassed with nitrogen. To this solution was added (*n*-Bu)<sub>4</sub>NOH (0.16 mL, 0.25 mmol, 1.6M solution) with stirring, which was continued for 1 hour. The solution was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 X 5 mL), after which the organic layers were washed with H<sub>2</sub>O (3 X 5 mL) and with brine to give **4** (69 mg, 0.17 mmol, 72%) following solvent removal.

**Tetrabutylammonium Dec-9-enyl Trifluoroborate (6).** Potassium dec-9-enyl trifluoroborate<sup>1</sup> (0.161 g, 0.654 mmol) was slurried in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) after which tetrabutylammonium hydroxide (0.453 g, 0.437 mmol, 40% solution by weight) was added while stirring. Stirring was continued until the white solid was completely taken into solution. The reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 X 20 mL) and washed with H<sub>2</sub>O (3 X 20 mL) to give tetrabutylammonium trifluoroborate **6** as a colorless oil (0.236 g, 0.52 mmol, 81%) following solvent removal. IR (neat) = 1638 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 0.18 – 0.27 (m, 2H), 1.00 (t, *J* = 7.3, 12H), 1.20 – 1.38 (m, 12H), 1.40 – 1.46 (m, 8H), 1.59 – 1.65 (m, 8H), 2.01 (q, *J* = 7.0 Hz, 2H), 3.23 (t, *J* = 8.33 Hz, 8H), 4.90 (d, *J* = 10.0 Hz, 1H) 4.97 (d, *J* = 16.2 Hz, 1H), 5.78 (dddd, *J* = 6.7, 6.7, 10.2,

16.9 Hz, 1H);  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.0, 20.0, 24.3, 26.4, 29.5, 29.8, 30.1, 30.4, 34.27, 34.33, 59.0, 114.3, 139.8;  $^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ ):  $\delta$  -140.3;  $^{11}\text{B}$  NMR (64.2 MHz,  $\text{CDCl}_3$ ):  $\delta$  5.5; Anal. Calcd for  $\text{C}_{26}\text{H}_{55}\text{BF}_3\text{N}$ : C, 69.47; H, 12.33. Found: C, 66.72; H, 12.12.

**Tetrabutylammonium 8-Formyloctyl Trifluoroborate (7) via procedure B<sup>d</sup>.** To a solution of tetrabutylammonium trifluoroborate **6** (68 mg, 0.15 mmol), pyridine (38 mg, 0.45 mmol) and pyridine *N*-oxide (33 mg, 0.3 mmol) in  $\text{CH}_2\text{Cl}_2$  (5 mL) was applied a flow of ozone at  $-78\text{ }^\circ\text{C}$  until the solution turned light blue in color. This was degassed with nitrogen followed by the addition of 1.0 M  $\text{CuSO}_4$  (3 mL) at  $0\text{ }^\circ\text{C}$ . The organic layer was extracted and washed with a pH 7 buffer, after which the solvent was removed to give aldehyde **7** as product (51 mg, 0.11 mmol, 75%). IR (neat) =  $1721\text{ cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.17 – 0.23 (m, 2H), 0.99 (t,  $J = 7.3$ , 12H), 1.20 – 1.38 (m, 12H), 1.40 – 1.46 (m, 8H), 1.57 – 1.62 (m, 8H), 2.38 (t,  $J = 7.36$  Hz, 2H), 3.23 (t,  $J = 8.7$  Hz, 8H), 9.74 (s, 1H);  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.0, 20.0, 22.5, 24.3, 26.3, 29.7, 29.9, 30.2, 34.1, 44.4, 59.0, 203.7;  $^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ ):  $\delta$  -140.2;  $^{11}\text{B}$  NMR (64.2 MHz,  $\text{CDCl}_3$ ):  $\delta$  5.35; HRMS (ESI): calcd for  $\text{C}_9\text{H}_{17}\text{BF}_3\text{O}$  ( $\text{M}^-$ ) 209.1324, found 209.1333.

**Tetrabutylammonium 8-Formyloctyl Trifluoroborate (7) via procedure D.** To a solution of tetrabutylammonium trifluoroborate **6** (0.285 g, 0.632 mmol) in  $\text{CH}_2\text{Cl}_2$  (2.85 mL) at  $-78\text{ }^\circ\text{C}$  was applied a flow of ozone until the solution became blue in color. The reaction mixture was immediately degassed with  $\text{N}_2$  for 15 min after which Zn (0.204 g,

3.15 mmol) in acetic acid (0.0265g, 4.42 mmol) was added dropwise with stirring. The solution was allowed to warm to rt and stirring was continued for 2 h (the reaction progress was followed by  $^1\text{H}$  NMR). The reaction mixture was passed through a pad of Celite to remove the Zn after which  $\text{NaHCO}_3$  was added dropwise over 15 min. The reaction mixture was extracted with  $\text{CH}_2\text{Cl}_2$  (3 X 5 mL) and then the combined organic extracts were washed with  $\text{H}_2\text{O}$  (3 X 5 mL), dried ( $\text{MgSO}_4$ ), and filtered. Solvent was removed to give the trifluoroborate **7** as a colorless oil (0.269 g, 0.601 mmol, 95%).

**Tetrabutylammonium (Cyclohex-3-enyl)methyltrifluoroborate (8)**. To a slurry of potassium (cyclohex-3-enyl)methyltrifluoroborate<sup>1</sup> (23 mg, 0.11 mmol) in  $\text{H}_2\text{O}$  (2 mL) and  $\text{CH}_2\text{Cl}_2$  (2 mL) was added a solution of (*n*-Bu)<sub>4</sub>NOH (0.07 mL, 0.11 mmol, 1.6M solution) with stirring. The biphasic solution was stirred until the potassium organotrifluoroborate was taken up into solution. The layers were separated. The aqueous layer was extracted with  $\text{CH}_2\text{Cl}_2$  (3 X 5 mL) after which the combined organic layers were washed with  $\text{H}_2\text{O}$  (3 X 5 mL), dried ( $\text{MgSO}_4$ ) and concentrated under high vacuum to afford the alkenyl product **8** (42 mg, 0.1 mmol, 93%). IR (neat) = 1644  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.16 – 0.26 (m, 2H), 0.96 (t,  $J = 7.6$ , 12H), 1.10 – 1.21 (m, 1H), 1.36 – 1.43 (m, 8H), 1.55 – 1.62 (m, 10H), 1.83 (d,  $J = 12.1$  Hz, 1H), 1.96 (s, 2H), 2.18 (d,  $J = 12.1$  Hz, 1H), 3.19 (t,  $J = 8.1$  Hz, 8H), 5.57 (m, 2H);  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ ):  $\delta$  13.6, 19.7, 23.9, 26.2, 31.1, 32.5, 35.3, 58.6, 126.6, 128.4;  $^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ ):  $\delta$  -137.2;  $^{11}\text{B}$  NMR (64.2 MHz,  $\text{CH}_2\text{Cl}_2$ ):  $\delta$  3.06; HRMS (ESI): calcd for  $\text{C}_7\text{H}_{11}\text{BF}_3$  (M) 163.0906, found 163.0908.

**Tetrabutylammonium 4-formyl-2-(formylmethy)butyltrifluoroborate (9) via**

**procedure B<sup>e</sup>.** To a solution of Tetrabutylammonium (cyclohex-3-enyl)methyltrifluoroborate **8** (52 mg, 0.13 mmol) and pyridine (5 mg, 0.07 mmol) in CDCl<sub>3</sub> (5 mL) was applied a flow of ozone at -78 °C until the solution turned light blue in color. This was degassed with nitrogen after which the solution was washed with 1.0 M CuSO<sub>4</sub> (2 X 5 mL) and with a pH 7 buffer (3 X 5 mL). The solvent was removed to give dialdehyde **9** as the product (44 mg, 0.1 mmol, 79%). IR (neat) = 1717 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 0.21 – 0.31 (m, 1H), 0.35 – 0.45 (m, 1H), 0.98 (t, *J* = 7.6, 12H), 1.37 – 1.44 (m, 8H), 1.57 – 1.68 (m, 10H), 2.14 (ddd, *J* = 13.6, 6.8, 6.8 Hz, 1H), 2.41 (ddd, *J* = 15.6, 6.1, 2.2 Hz, 2H), 2.43 (t, *J* = 6.6 Hz, 2H), 3.21 (t, *J* = 8.1 Hz, 8H), 9.72 (s, 1H), 9.76 (s, 1H); <sup>13</sup>C NMR (125.8 MHz, CDCl<sub>3</sub>): δ 13.6, 19.7, 23.9, 29.7, 30.6, 41.7, 50.8, 58.7, 204.1, 206.2; <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>): δ -137.3; <sup>11</sup>B NMR (64.2 MHz, CDCl<sub>3</sub>): δ 4.38; HRMS (ESI): calcd for C<sub>7</sub>H<sub>11</sub>BF<sub>3</sub>O<sub>2</sub> (M<sup>-</sup>) 195.0804, found 195.0808.

**Tetrabutylammonium 4-Butenyltrifluoroborate (10).** To a slurry of Potassium 4-butenyltrifluoroborate<sup>1</sup> (33 mg, 0.20 mmol) in H<sub>2</sub>O (2 mL) and CH<sub>2</sub>Cl<sub>2</sub> (2 mL) was added a solution of (*n*-Bu)<sub>4</sub>NOH (0.12 mL, 0.2 mmol, 1.6M solution) with stirring. The biphasic solution was stirred until the potassium organotrifluoroborate was taken up into solution. The layers were separated. The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 X 5 mL) after which the combined organic layers were washed with H<sub>2</sub>O (3 X 5 mL), dried (MgSO<sub>4</sub>) and concentrated under high vacuum to afford the alkenyl product **10** (72 mg, 0.20 mmol, 100%). IR (neat) = 1636 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 0.29 - 0.34 (m,



2H), 0.97 (t,  $J = 7.3$ , 12H), 1.42 (m, 8H), 1.61 (m, 8H), 2.1 (q,  $J = 7.0$  Hz, 2H), 3.22 (t,  $J = 8.33$  Hz, 8H), 4.72 (d,  $J = 10.0$ , 1H), 4.90 (d,  $J = 17.0$ , 1H), 5.96 – 6.01 (m, 1H);  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ ):  $\delta$  13.6, 19.7, 24.0, 30.5, 58.7, 110.3, 145.3;  $^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ ):  $\delta$  -140.8;  $^{11}\text{B}$  NMR (64.2 MHz,  $\text{CDCl}_3$ ):  $\delta$  4.85; HRMS (ESI): calcd for  $\text{C}_4\text{H}_7\text{BF}_3$  ( $M^-$ ) 123.0595, found 123.0599.

**Tetrabutylammonium 3-Formylpropyltrifluoroborate (11) via procedure B<sup>b</sup>.** To a solution of potassium 4-butenyltrifluoroborate<sup>1</sup> (76 mg, 0.47 mmol) in 50% DMF/ $\text{Et}_3\text{N}$  (1 mL) was added sufficient Sudan III to create a light pink colored solution. A flow of ozone was applied at 0 °C during which a white vapor was evolved. The ozone flow was continued until both the pink color of the solution had faded and the white vapor cleared after which the solution was degassed with nitrogen. To this solution was added (*n*-Bu)<sub>4</sub>NOH (0.32 ml, 0.5 mmol, 1.6M solution) with stirring, which was continued for 1 hour. The solution was extracted with  $\text{CH}_2\text{Cl}_2$  (3 X 5 mL), after which the organic layers were washed with  $\text{H}_2\text{O}$  (3 X 5 mL) and with brine to give **11** (62 mg, 0.38 mmol, 80%) following removal of solvent. IR (neat) = 1716  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.42 (m, 2H), 0.94 (t,  $J = 7.3$ , 12H), 1.38 (m, 8H), 1.58 (m, 8H), 2.2 (q,  $J = 7.0$  Hz, 2H), 3.18 (t,  $J = 8.33$  Hz, 8H), 9.68 (s, 1H);  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ ):  $\delta$  13.6, 19.6, 23.9, 40.9, 58.6, 208.8;  $^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ ):  $\delta$  -141.6;  $^{11}\text{B}$  NMR (64.2 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.27; HRMS (ESI): calcd for  $\text{C}_3\text{H}_5\text{BF}_3\text{O}$  ( $M^-$ ) 125.0385, found 125.0391.

**Tetrabutylammonium 2-Formethyltrifluoroborate (11) via procedure B<sup>d</sup>.** To a solution of tetrabutylammonium 4-butenyltrifluoroborate **10** (52 mg, 0.14 mmol),

pyridine (38 mg, 0.45 mmol) and pyridine *N*-oxide (33 mg, 0.3 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) was applied a flow of ozone at -78 °C until the solution turned light blue in color. This was degassed with nitrogen followed by the addition of 1.0 M CuSO<sub>4</sub> (3 mL) at 0 °C. The organic layer was extracted and washed with a pH 7 buffer, after which the solvent was removed to give aldehyde **11** as product (42 mg, 0.11 mmol, 82%).

**Tetrabutylammonium 2-Formethyltrifluoroborate (11) via procedure C.** To a solution of tetrabutylammonium 4-butenyltrifluoroborate **10** (75 mg, 0.2 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (2 mL) was applied a flow of ozone at -78 °C until the solution turned blue in color. The solution was degassed followed by the addition of pyridine (158 mg, 0.4 mmol) with stirring which was continued 24 hours. To this was added 1.0 M CuSO<sub>4</sub> (3 mL) at 0 °C. The organic layer was extracted and washed with a pH 7 buffer, after which the solvent was removed to give aldehyde **11** as product (38 mg, 0.14 mmol, 71%)

**Tetrabutylammonium 3-Methylbut-3-enyl Trifluoroborate (12).** Potassium trifluoroborate **1** (0.157 g, 1.00 mmol) was slurried in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) after which tetrabutylammonium hydroxide (0.265 g, 1.02 mmol, 40% solution by weight) was added while stirring, which was continued until **1** was completely taken into solution. This solution was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 X 20 mL) and washed with H<sub>2</sub>O (3 X 20 mL) to provide tetrabutylammonium trifluoroborate **12** as a colorless liquid (0.268 g, 0.703 mmol, 70%) following solvent removal. IR (neat) = 1644 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 0.27 – 0.36 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 12H), 1.36 – 1.42 (m, 8H), 1.55 – 1.61 (m, 8H), 1.67 (s, 3H), 1.99 (t, *J* = 9.4 Hz, 2H), 3.19 (t, *J* = 9.6 Hz, 8H), 4.50 (s, 1H), 4.61

(s, 1H);  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.0, 20.0, 23.0, 24.2, 34.7, 58.9, 106.6, 152.3;  $^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ ):  $\delta$  -140.4;  $^{11}\text{B}$  NMR (64.2 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.54; Anal. Calcd for  $\text{C}_{21}\text{H}_{45}\text{BF}_3\text{N}$ : C, 66.48; H, 11.96. Found: C, 66.51; H, 12.07.

**Tetrabutylammonium 3-Oxobutyl Trifluoroborate (13) via procedure B<sup>a</sup>.** To a solution of tetrabutylammonium 3-methylbut-3-enyl trifluoroborate **12** (66 mg, 0.17 mmol) and 4-methylmorpholine *N*-oxide (117 mg, 0.85 mmol) in  $\text{CH}_2\text{Cl}_2$  (2 mL) was applied a flow of ozone at  $-78$  °C until the solution appeared light blue in color. The solution was degassed and then washed with  $\text{H}_2\text{O}$  and brine to give the product **13** (59 mg, 0.15 mmol, 89%) following solvent removal. IR (neat) =  $1721\text{ cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.17 – 0.23 (m, 2H), 1.0 (t,  $J = 7.3$ , 12H), 1.37 – 1.49 (m, 8H), 1.60 – 1.69 (m, 8H), 2.07 (s, 3H), 2.38 (t,  $J = 8.9$  Hz, 2H), 3.22 (t,  $J = 8.7$  Hz, 8H);  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.0, 20.0, 23.7, 24.2, 29.2, 41.8, 59.0, 210.0;  $^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ ):  $\delta$  -140.8;  $^{11}\text{B}$  NMR (64.2 MHz,  $\text{CDCl}_3$ ):  $\delta$  5.38; Anal. Calcd for  $\text{C}_{20}\text{H}_{43}\text{BF}_3\text{NO}$ : C, 62.99; H, 11.36. Found: C, 63.40; H, 10.99.

**Tetrabutylammonium 3-Oxobutyl Trifluoroborate (13) via procedure D.** To a solution of tetrabutylammonium trifluoroborate **12** (0.089 g, 0.235 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 mL) at  $-78$  °C was applied a flow of ozone until the solution became blue in color. The reaction mixture was immediately degassed with  $\text{N}_2$  for 15 min after which Zn (0.060 g, 0.923 mmol) in acetic acid (0.100 g, 1.67 mmol) was added dropwise with stirring. The solution was allowed to warm to rt, and stirring was continued for 2 h (the reaction progress was followed by  $^1\text{H}$  NMR). The reaction mixture was filtered to remove the Zn

after which 1.0 M NaHCO<sub>3</sub> was added over 15 min. The reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 X 5 mL) and then the combined organic extracts were washed H<sub>2</sub>O (3 X 5 mL), dried (MgSO<sub>4</sub>), and filtered. Solvent was removed to give the trifluoroborate **13** as a colorless oil (0.085 g, 0.223 mmol, 95%).

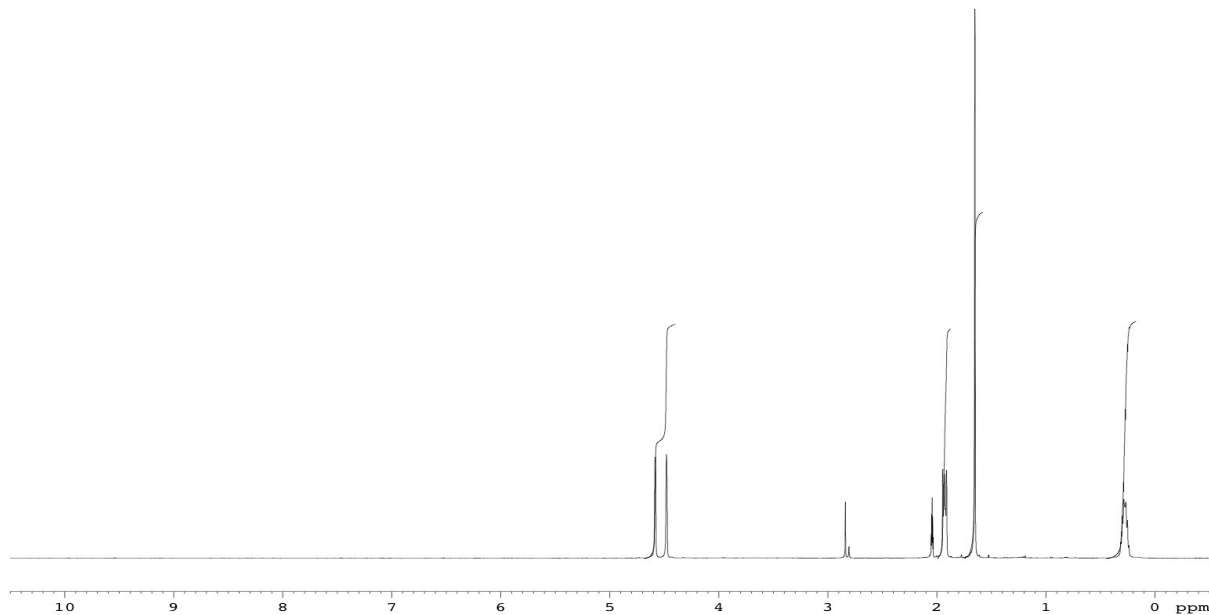
**(E)-Tetrabutylammonium 4-(3-Methoxy-3-oxoprop-1-enyl)phenyltrifluoroborate**

**(14)**. To a round bottomed flask containing tetrabutylammonium 4-formylphenyl trifluoroborate **4** (412 mg, 1.0 mmol) and methyl (triphenylphosphoranylidene) acetate (434 mg, 1.3 mmol) was added H<sub>2</sub>O (5 mL) with stirring. The temperature of the solution was raised to 90 °C for 2 h after which the heat was removed and the solution was allowed to reach room temperature. The reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 X 10 mL) and the combined organic phases were then washed with NaOH (2M, 2 X 5 mL), H<sub>2</sub>O (2 X 10 mL), and dried over MgSO<sub>4</sub>. This was filtered and concentrated to give a white solid that was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (2 mL) and reprecipitated using diethyl ether. The white crystals were washed with diethyl ether to give the product **14** (282 mg, 0.6 mmol, 61%). IR (neat) = 1633, 1706 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 0.87 (t, *J* = 7.3 Hz, 12H), 1.16 – 1.26 (m, 8H), 1.32 – 1.35 (m, 8H), 2.88 (t, *J* = 8.7 Hz, 8H), 6.33 (d, *J* = 16.0 Hz, 1H), 7.31 (d, *J* = 8 Hz, 2H), 7.54 (d, *J* = 8 Hz, 2H), 7.61 (d, *J* = 17.0 Hz, 1H); <sup>13</sup>C NMR (125.8 MHz, CDCl<sub>3</sub>): δ 13.6, 19.5, 23.7, 51.5, 58.2, 115.3, 126.7, 131.6, 132.4, 146.4, 167.9; <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>): δ -142.5; <sup>11</sup>B NMR (64.2 MHz, CDCl<sub>3</sub>): δ 2.31.

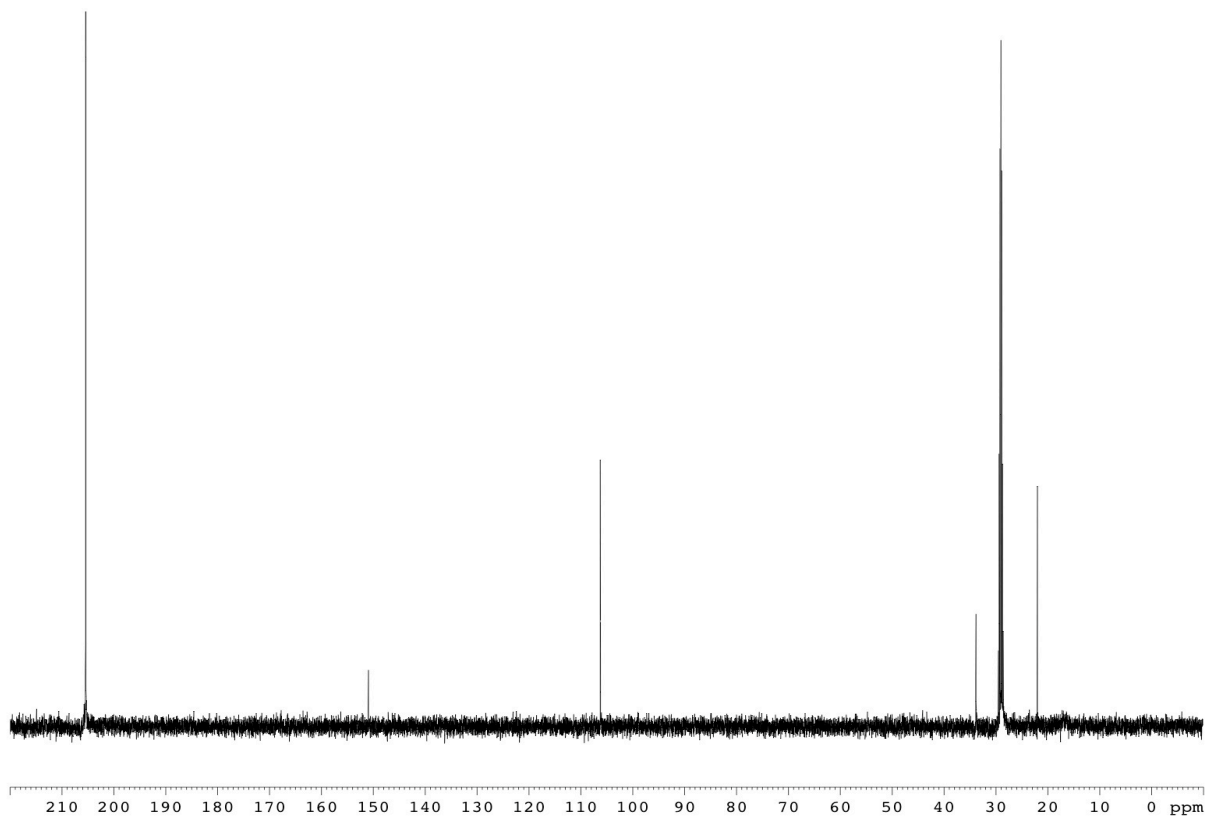
Reference:

1) Molander, G. A., Figueroa, R. *Org Lett*, **2006**, 8, 75.

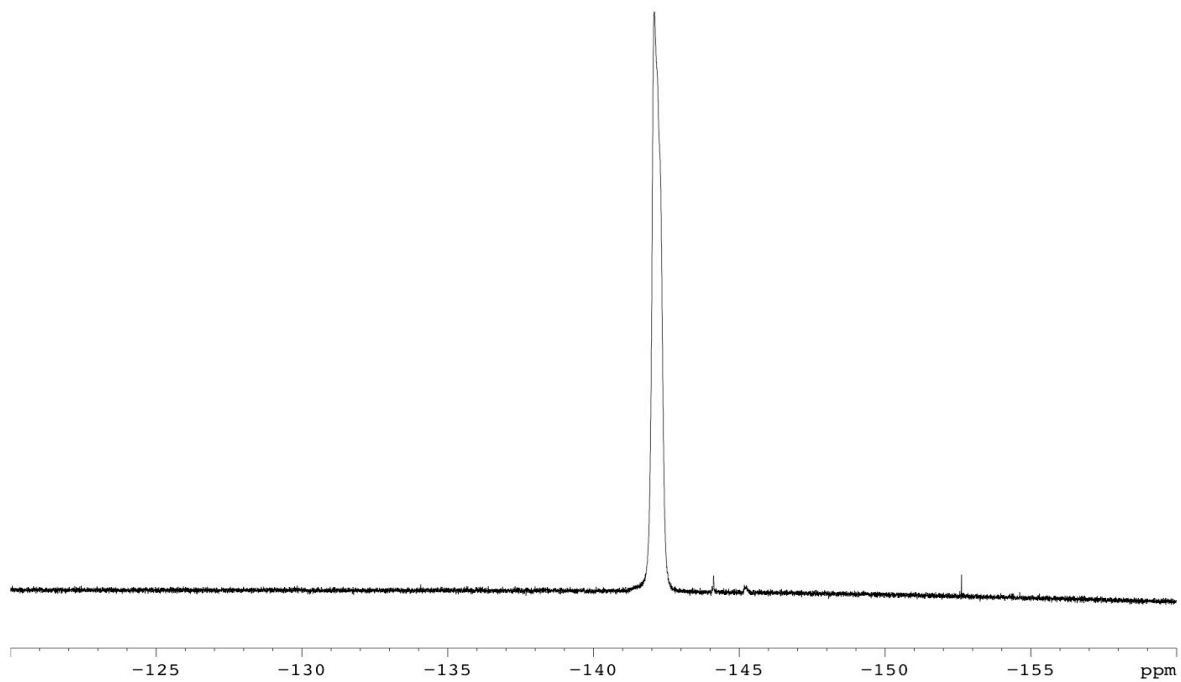
Potassium 3-Methylbut-3-enyl Trifluoroborate (**1**)



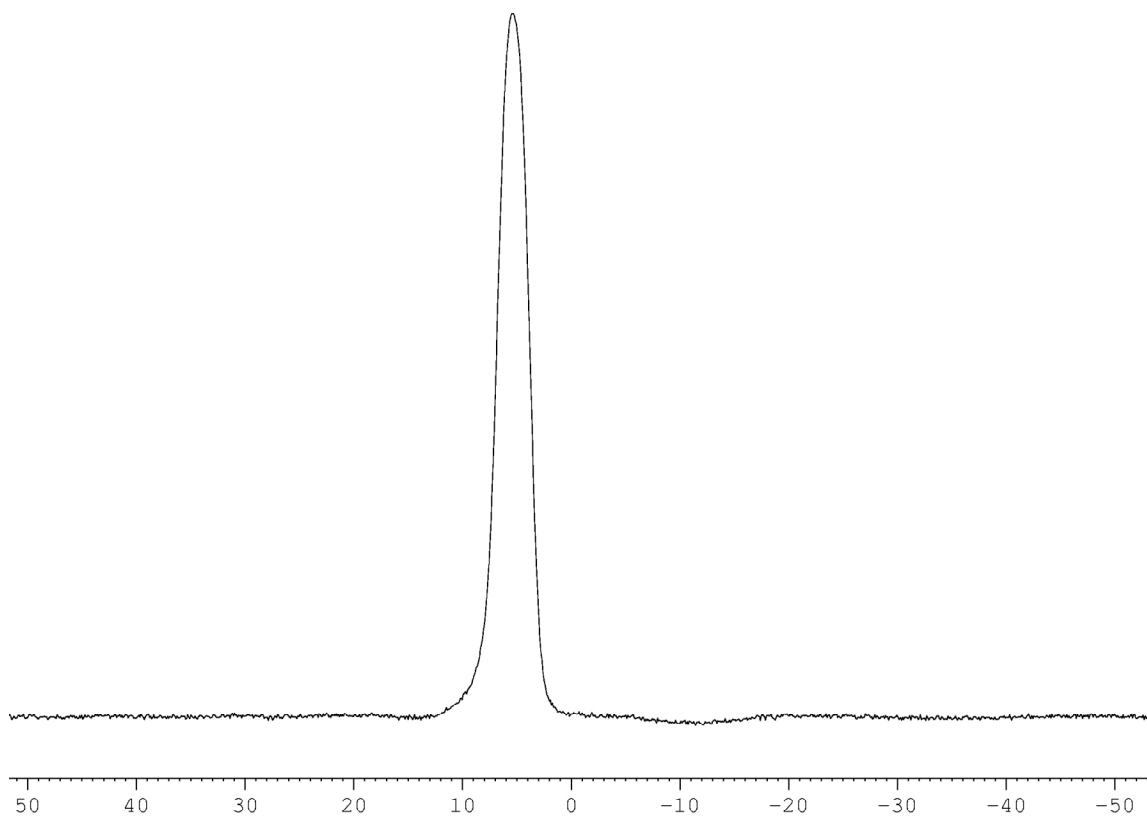
500 MHz <sup>1</sup>H NMR of Compound (**1**) in Acetone-*d*<sub>6</sub>



126 MHz <sup>13</sup>C NMR of Compound (**1**) in Acetone-*d*<sub>6</sub>

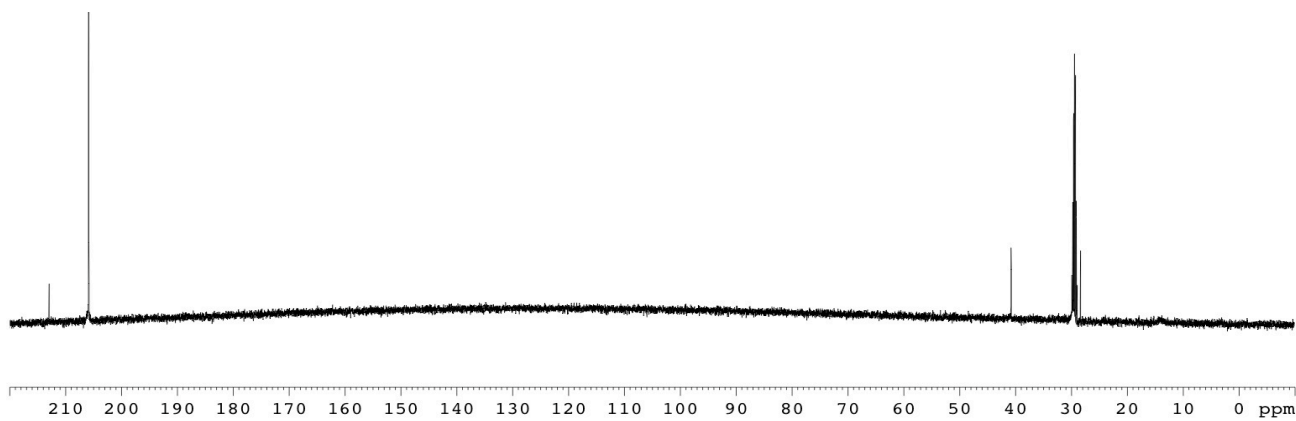
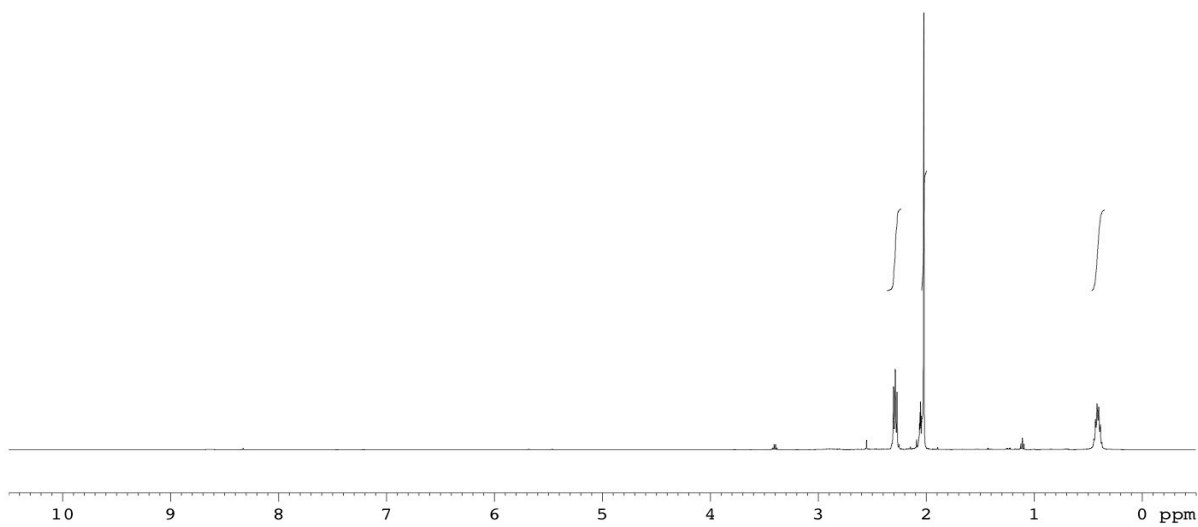


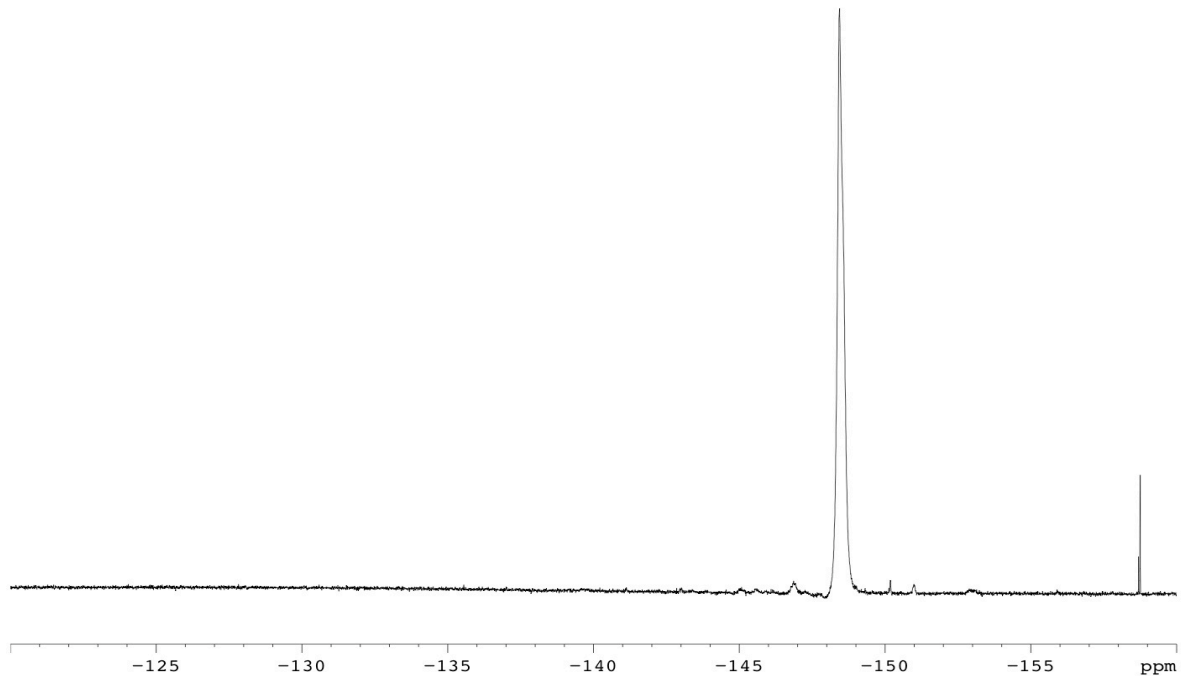
471 MHz  $^1\text{F}$  NMR of Compound (**1**) in Acetone- $d_6$



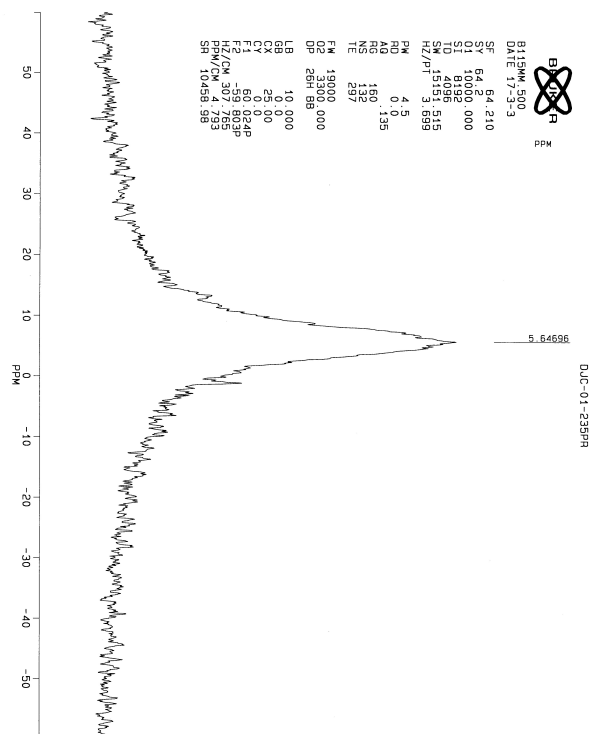
128 MHz  $^1\text{B}$  NMR of Compound (**1**) in Acetone- $d_6$

Potassium 3-Oxobutyl Trifluoroborate (**2**)





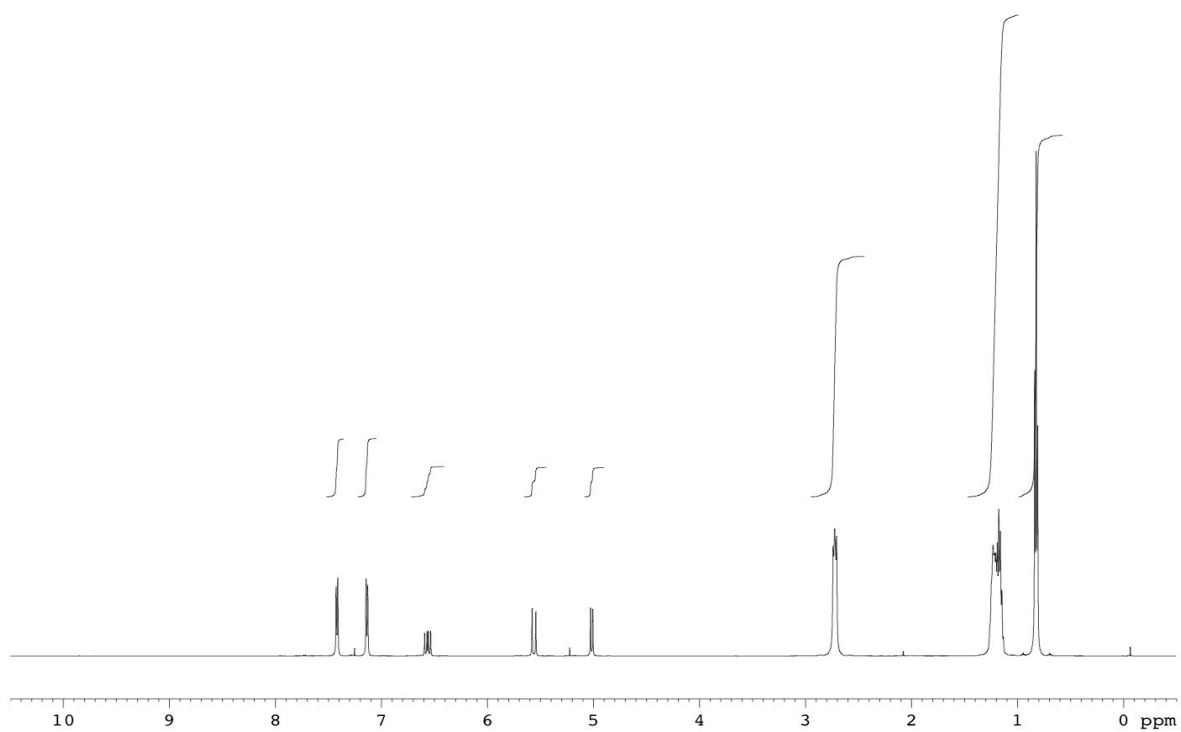
471 MHz  $^1\text{F}$  NMR of Compound (2) in Acetone- $d_6$



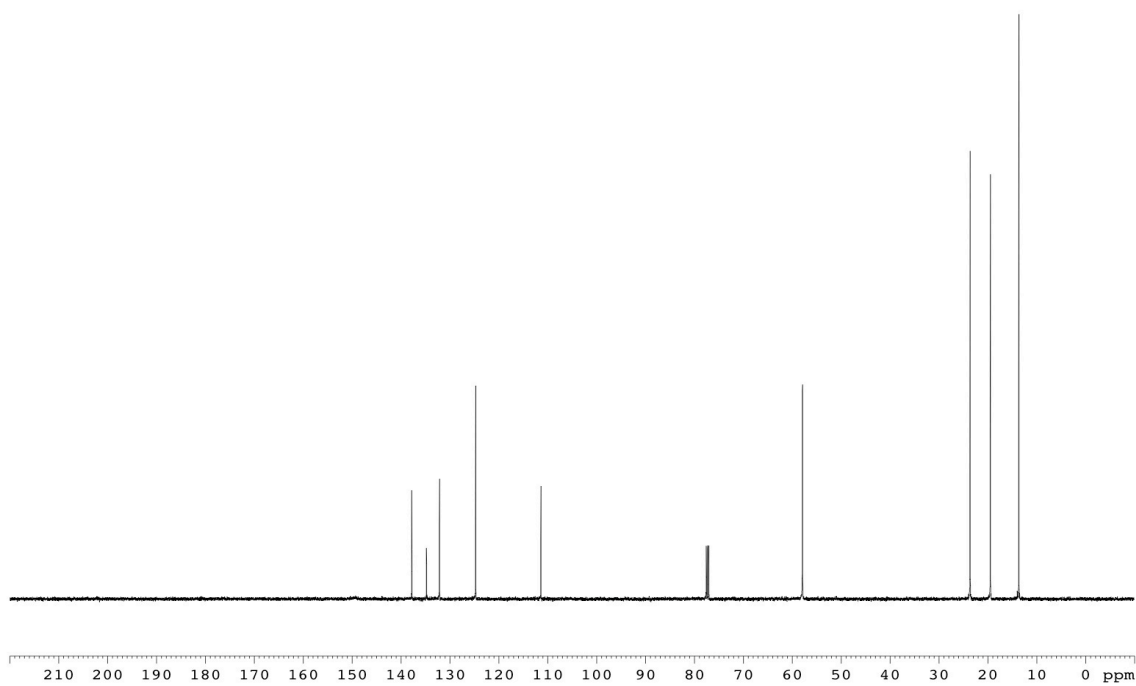
128 MHz  $^1\text{B}$  NMR of Compound (2) in Acetone- $d_6$



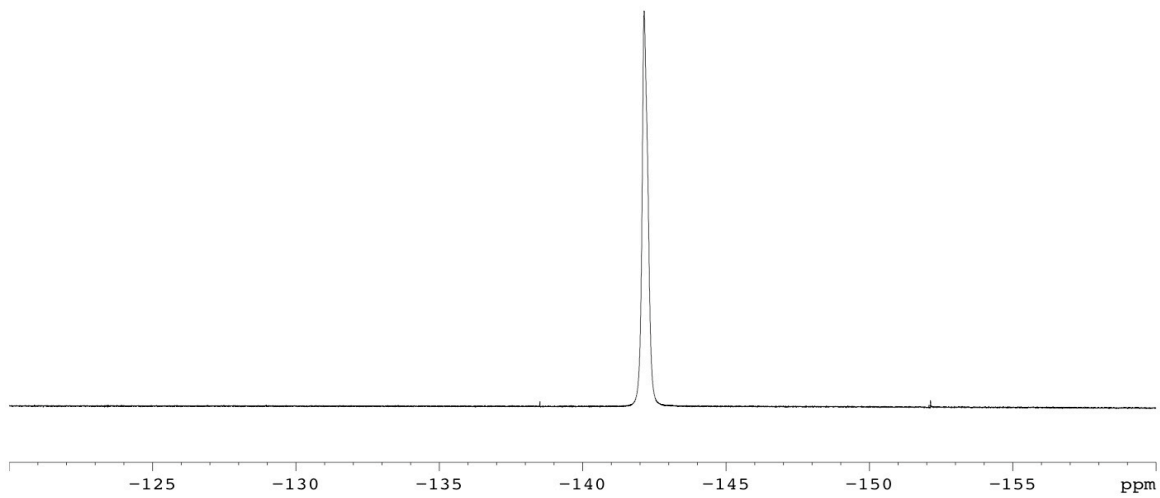
Tetrabutylammonium 4-Vinylphenyltrifluoroborate (**3**)



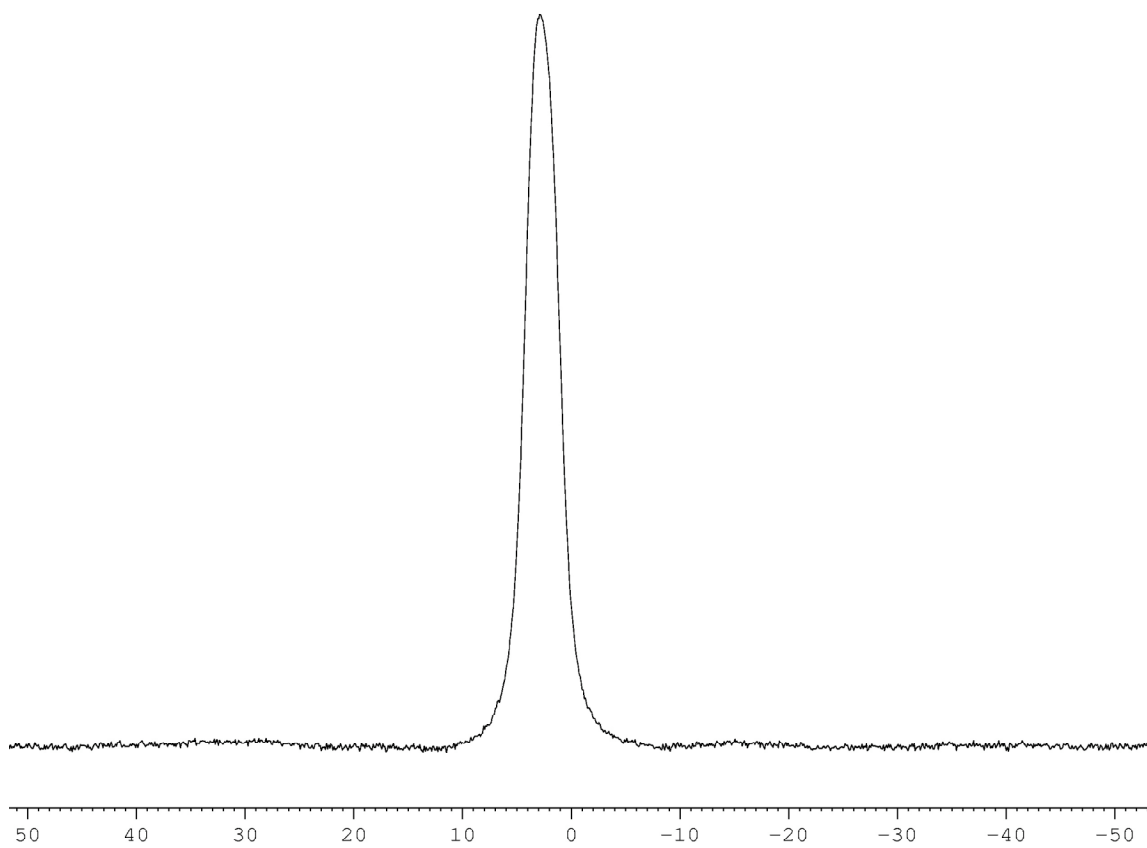
500 MHz  $^1\text{H}$  NMR of Compound (**3**) in  $\text{CDCl}_3$



126 MHz  $^{13}\text{C}$  NMR of Compound (**3**) in  $\text{CDCl}_3$

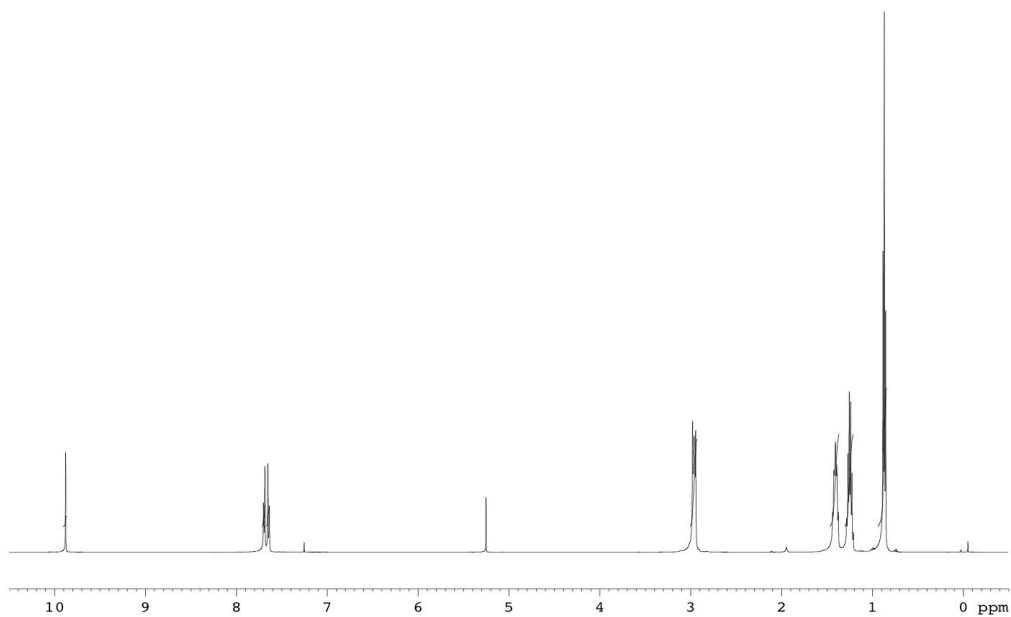


471 MHz  $^1\text{F}$  NMR of Compound (**3**) in  $\text{CDCl}_3$

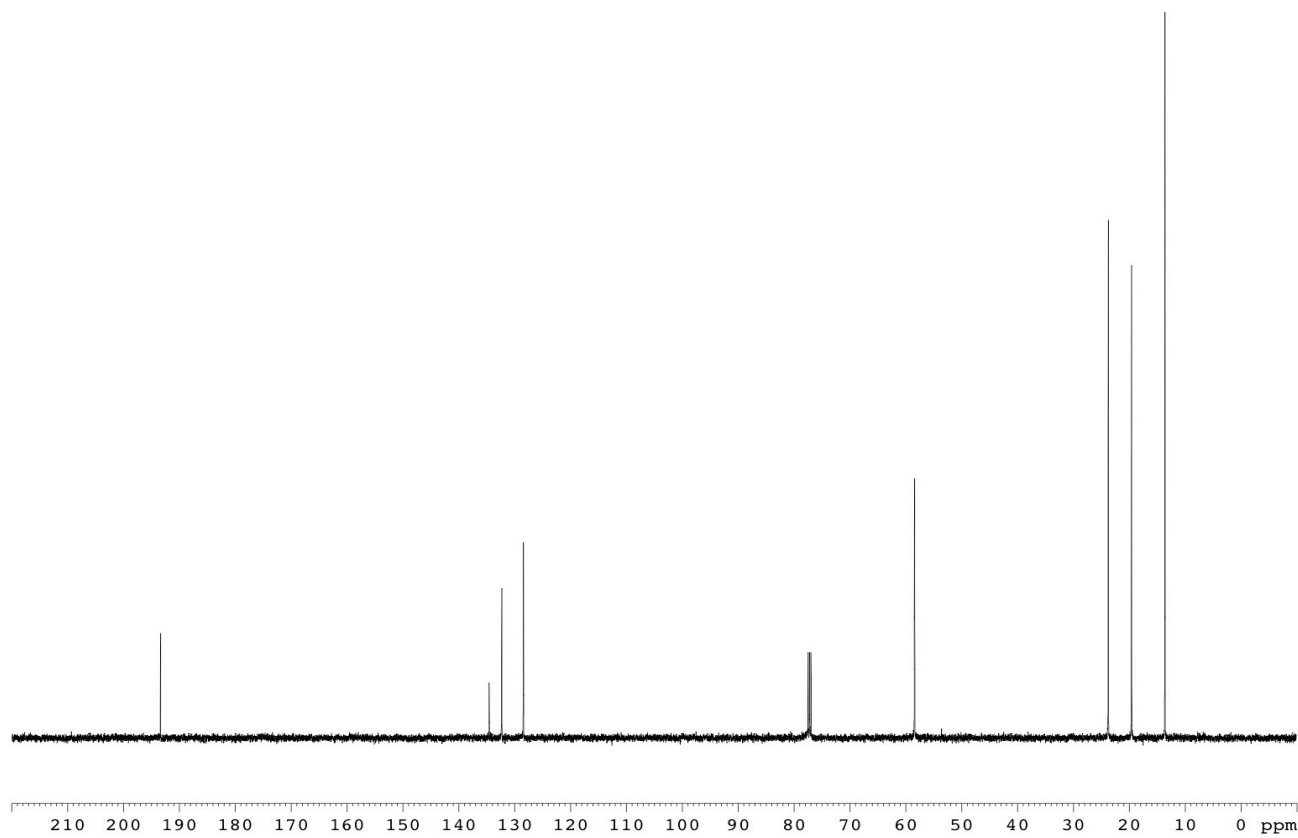


128 MHz  $^1\text{B}$  NMR of Compound (**3**) in  $\text{CDCl}_3$

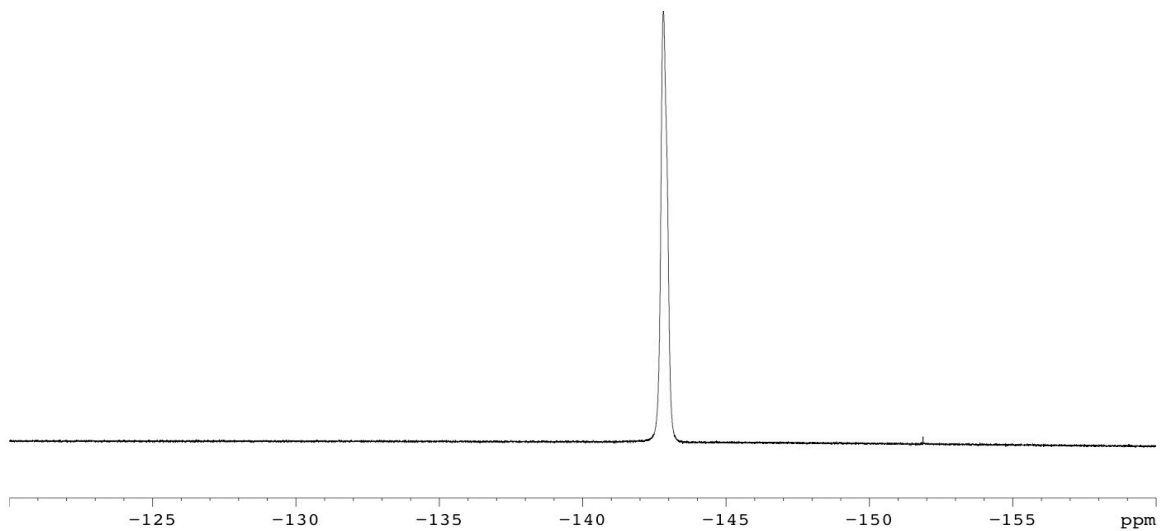
Tetrabutylammonium 4-Formylphenyl Trifluoroborate (**4**)



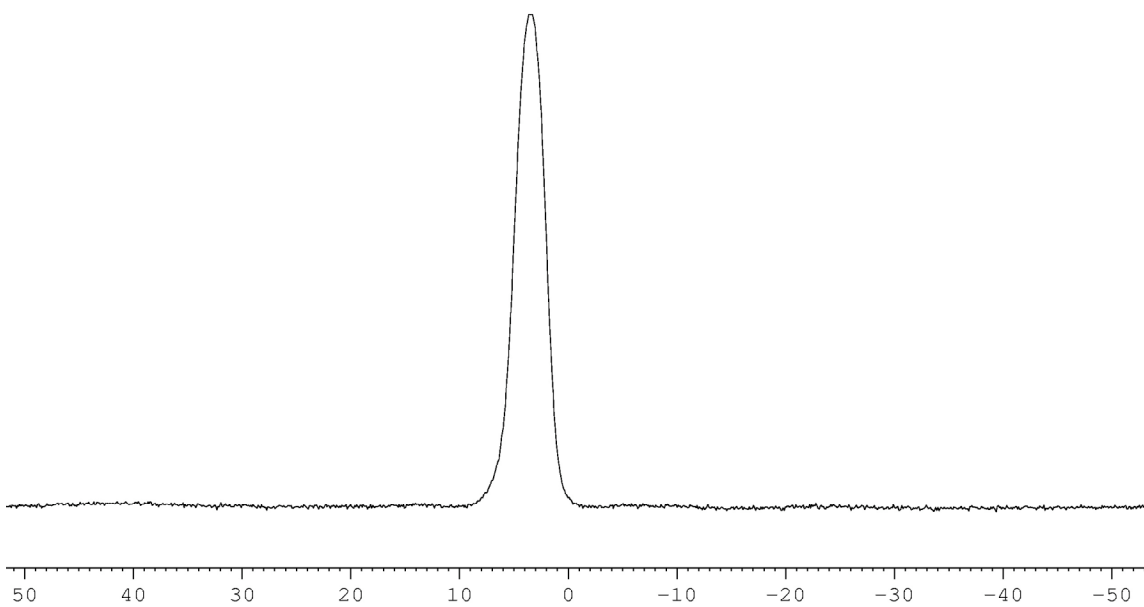
500 MHz  $^1\text{H}$  NMR of Compound (**4**) in  $\text{CDCl}_3$



126 MHz  $^{13}\text{C}$  NMR of Compound (**4**) in  $\text{CDCl}_3$

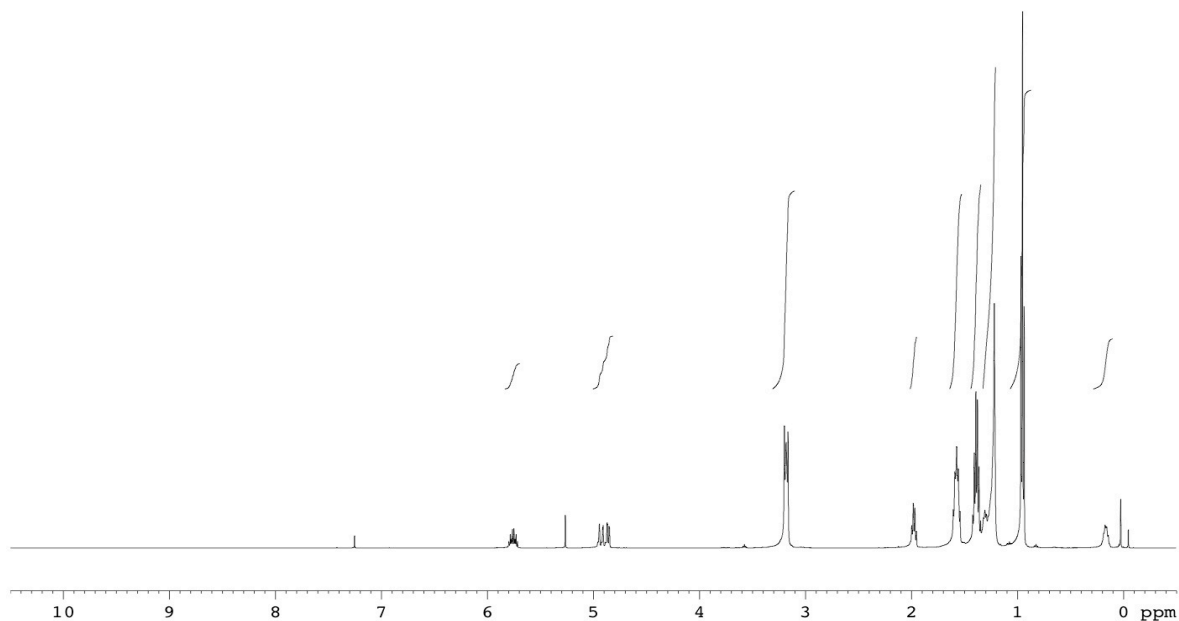


471 MHz  $^1\text{F}$  NMR of Compound (**4**) in  $\text{CDCl}_3$

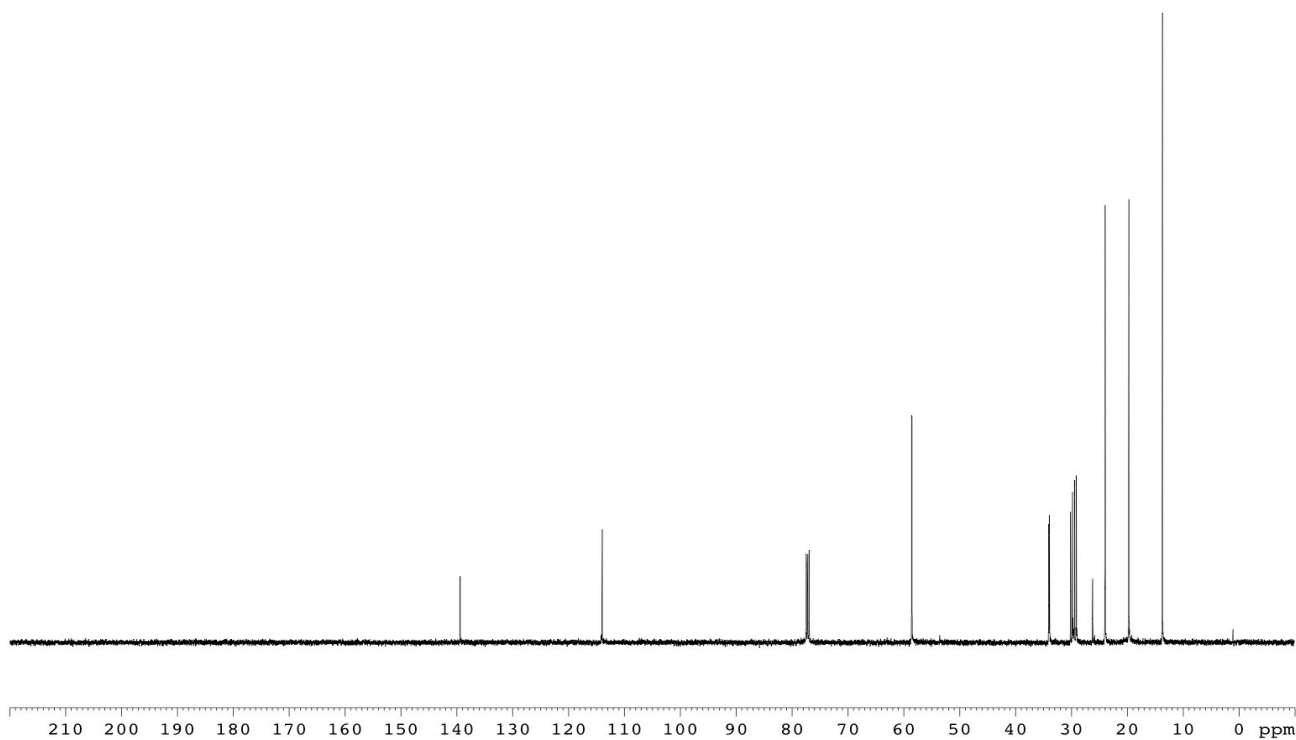


128 MHz  $^1\text{B}$  NMR of Compound (**4**) in  $\text{CDCl}_3$

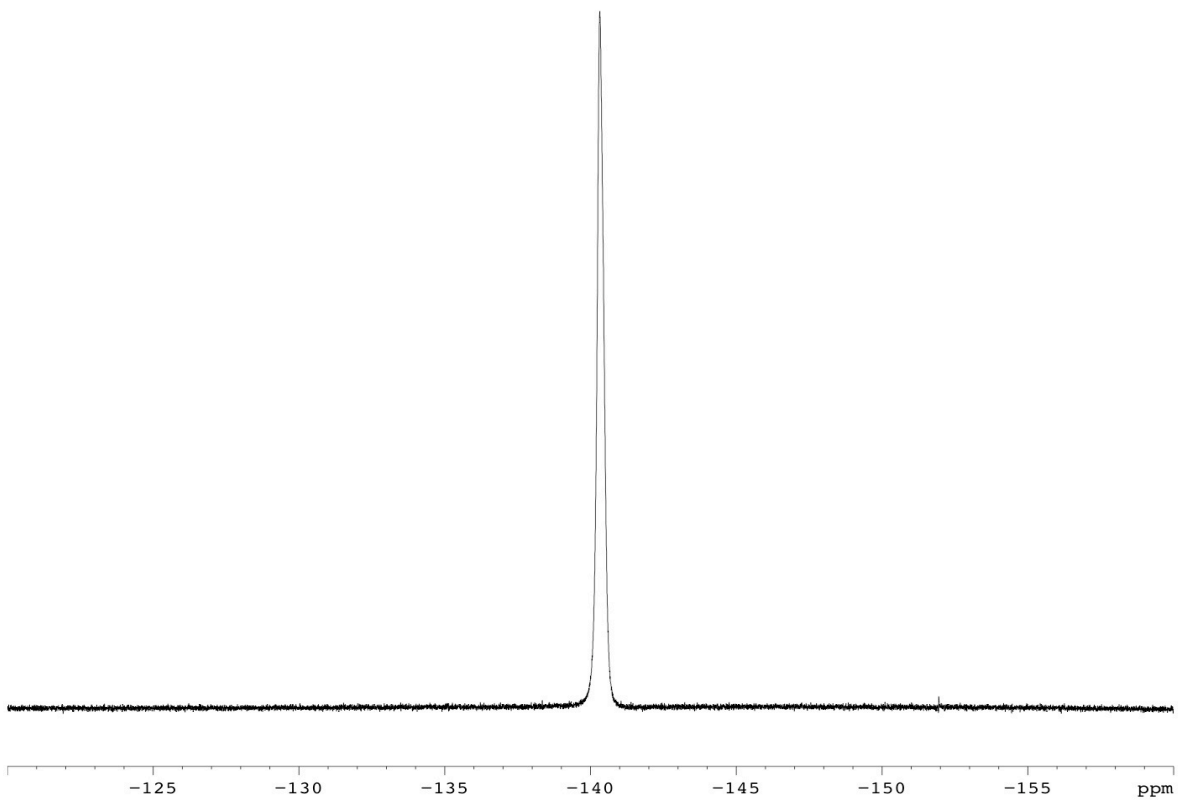
Tetrabutylammonium Dec-9-enyl Trifluoroborate (**6**)



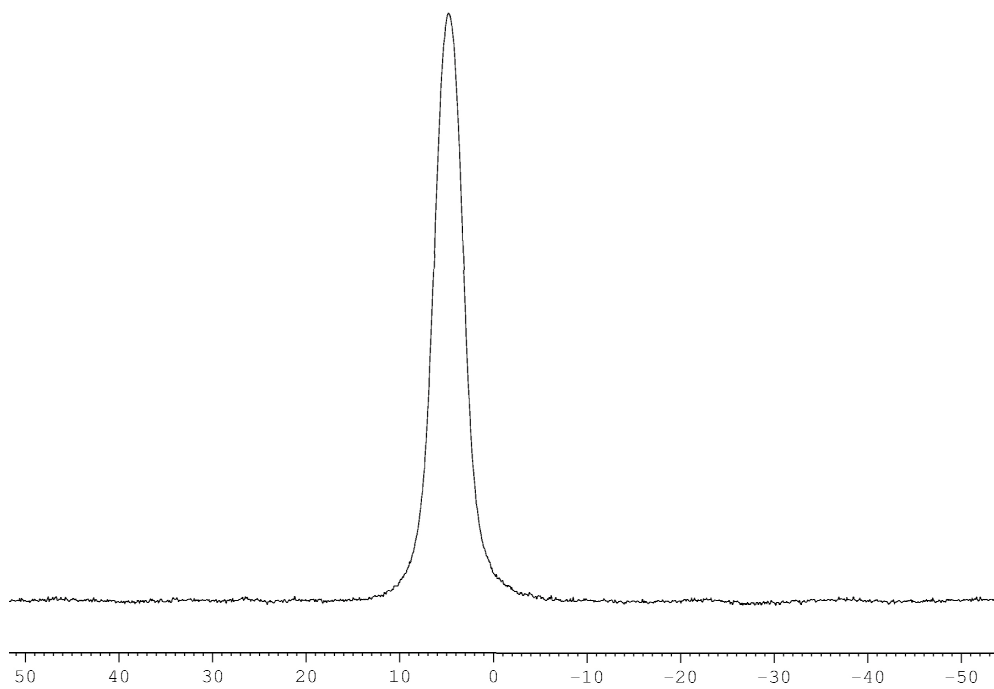
500 MHz  $^1\text{H}$  NMR of Compound (**6**) in  $\text{CDCl}_3$



126 MHz  $^{13}\text{C}$  NMR of Compound (**6**) in  $\text{CDCl}_3$

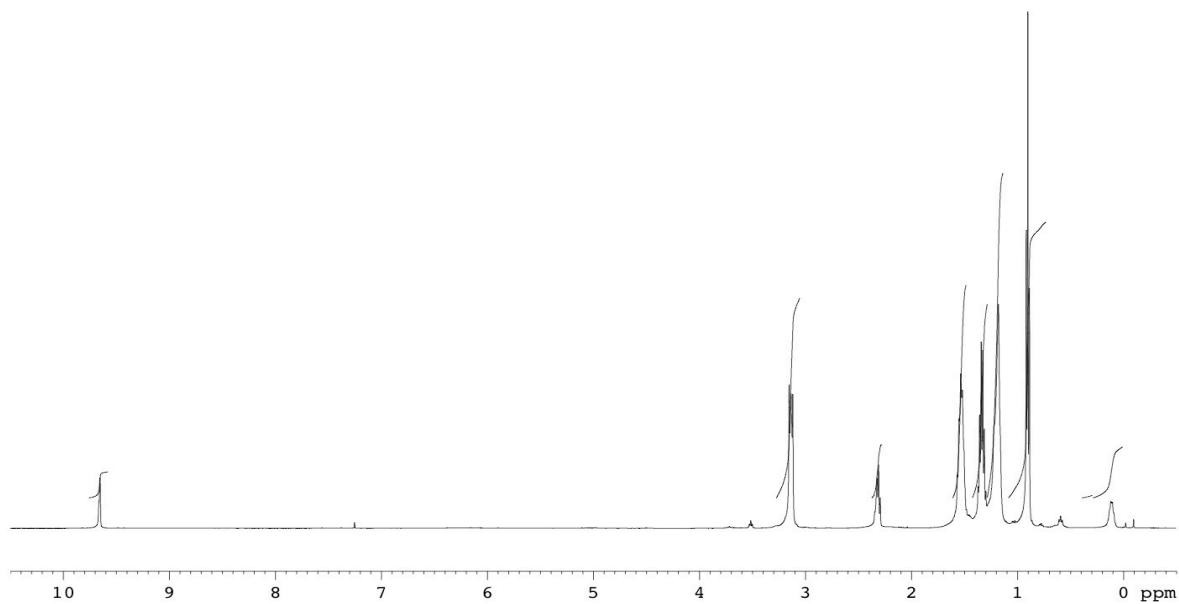


471 MHz  $^1\text{F}$  NMR of Compound (**6**) in  $\text{CDCl}_3$

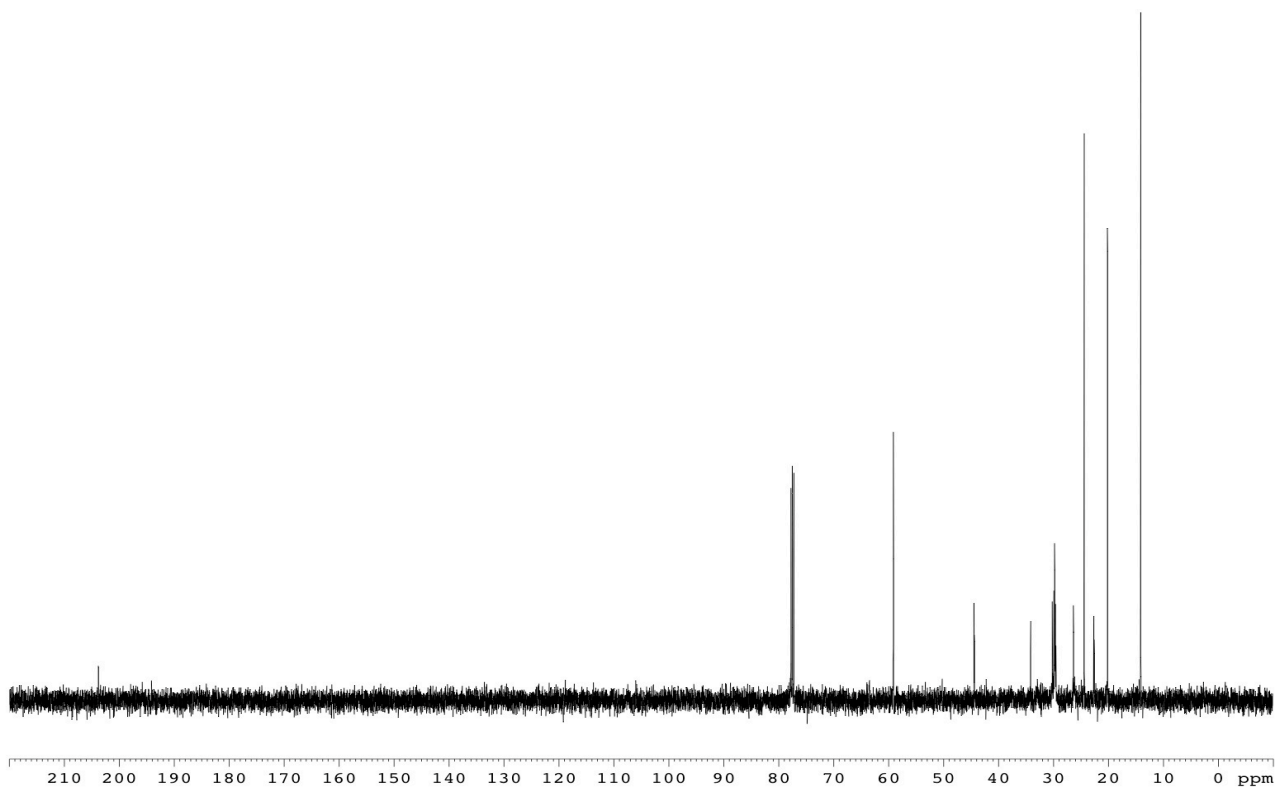


128 MHz  $^1\text{B}$  NMR of Compound (**6**) in  $\text{CDCl}_3$

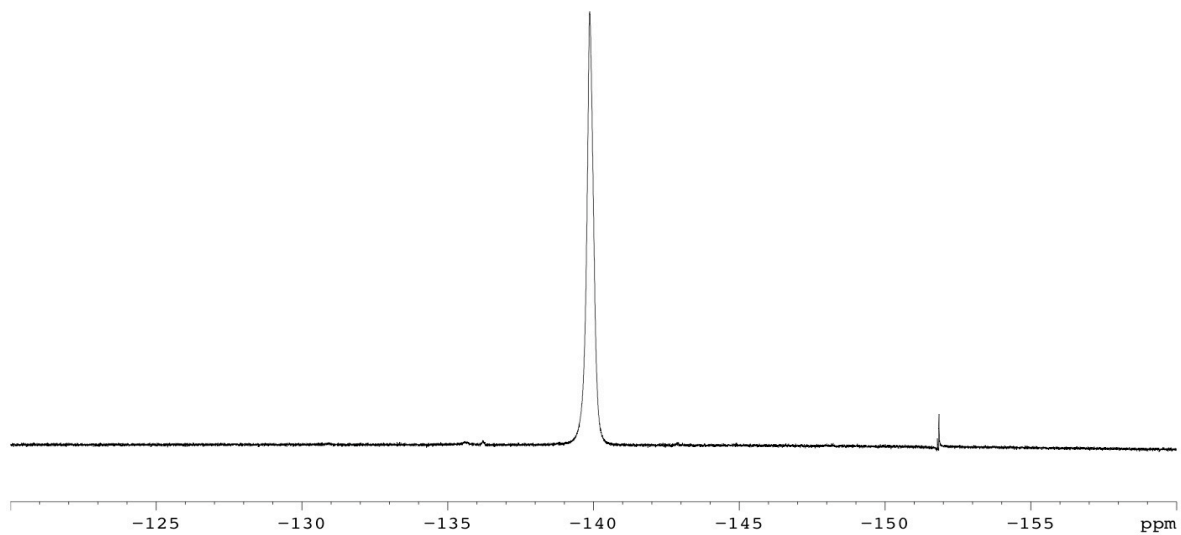
Tetrabutylammonium 8-Formyloctyl Trifluoroborate (7)



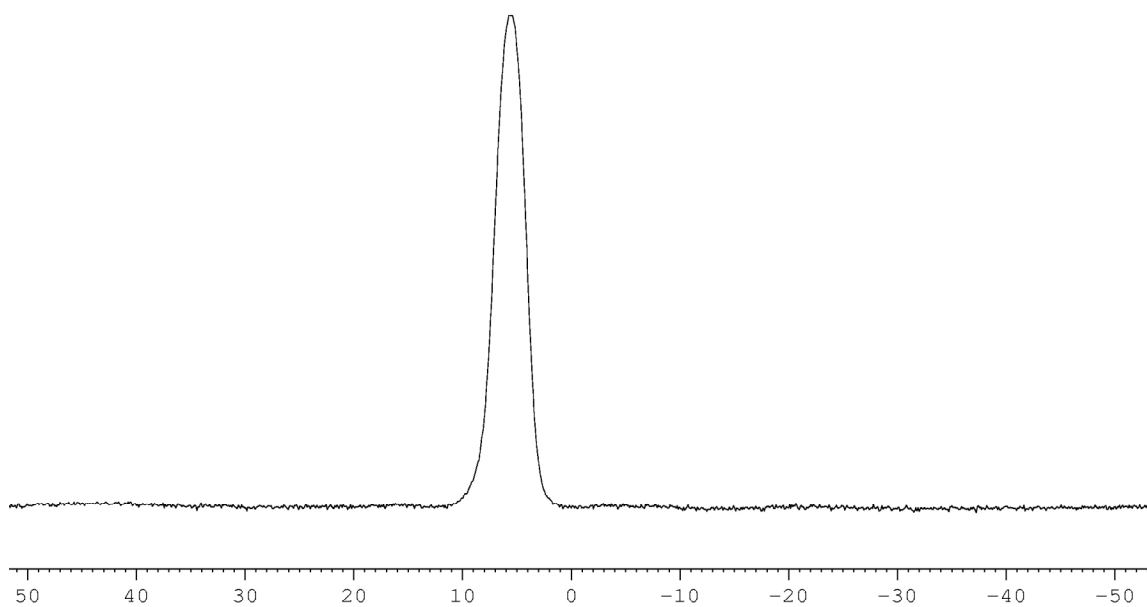
500 MHz <sup>1</sup>H NMR of Compound (7) in CDCl<sub>3</sub>



126 MHz <sup>13</sup>C NMR of Compound (7) in CDCl<sub>3</sub>



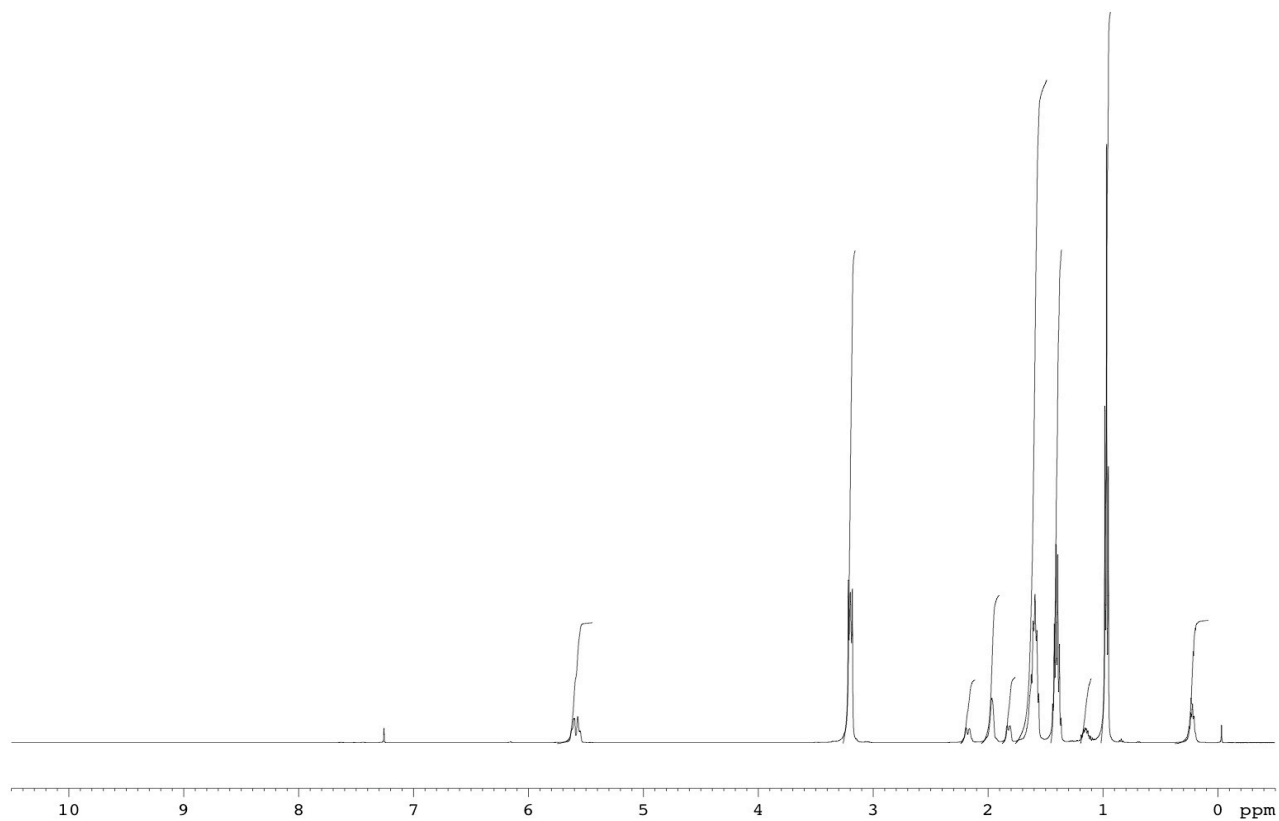
471 MHz  $^1\text{F}$  NMR of Compound (7) in  $\text{CDCl}_3$



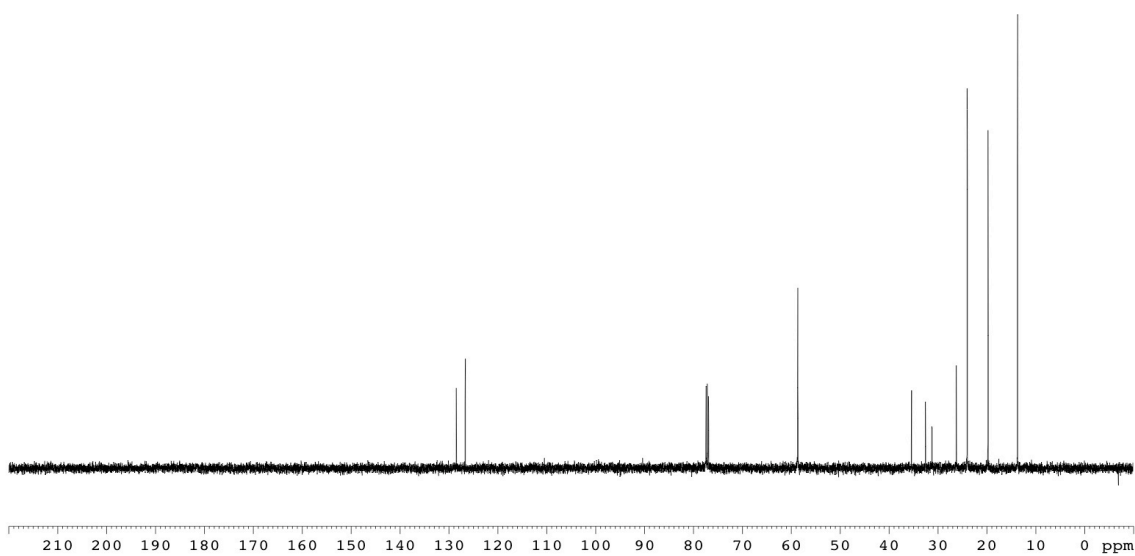
128 MHz  $^1\text{B}$  NMR of Compound (7) in  $\text{CDCl}_3$



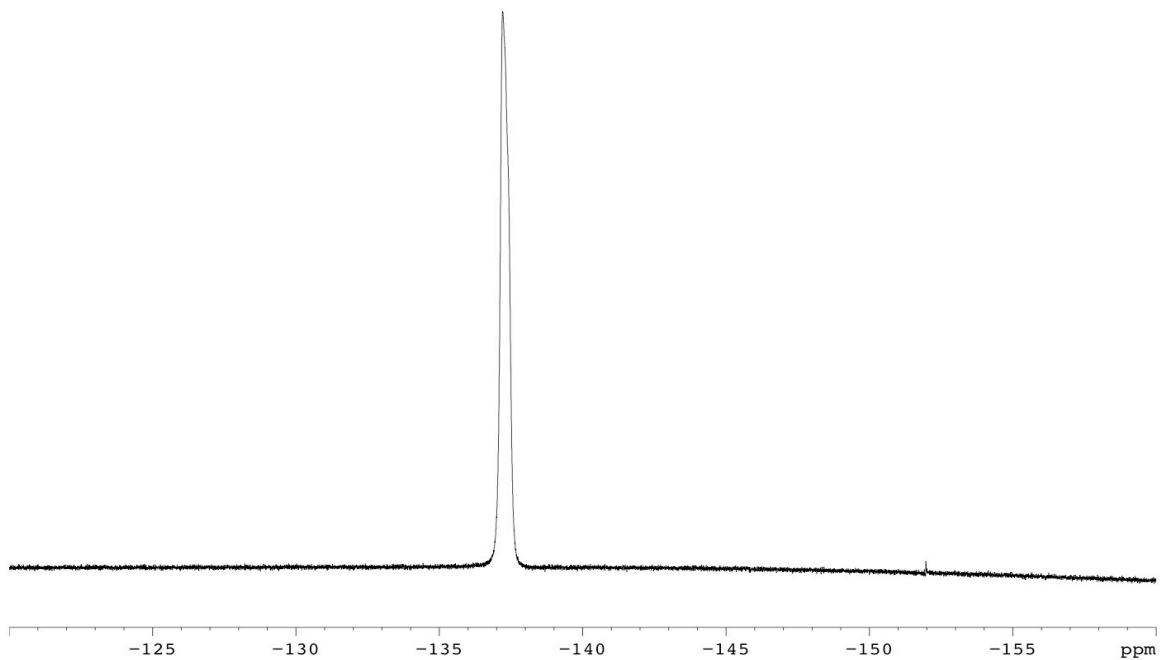
Tetrabutylammonium (Cyclohex-3-enyl)methyltrifluoroborate (**8**)



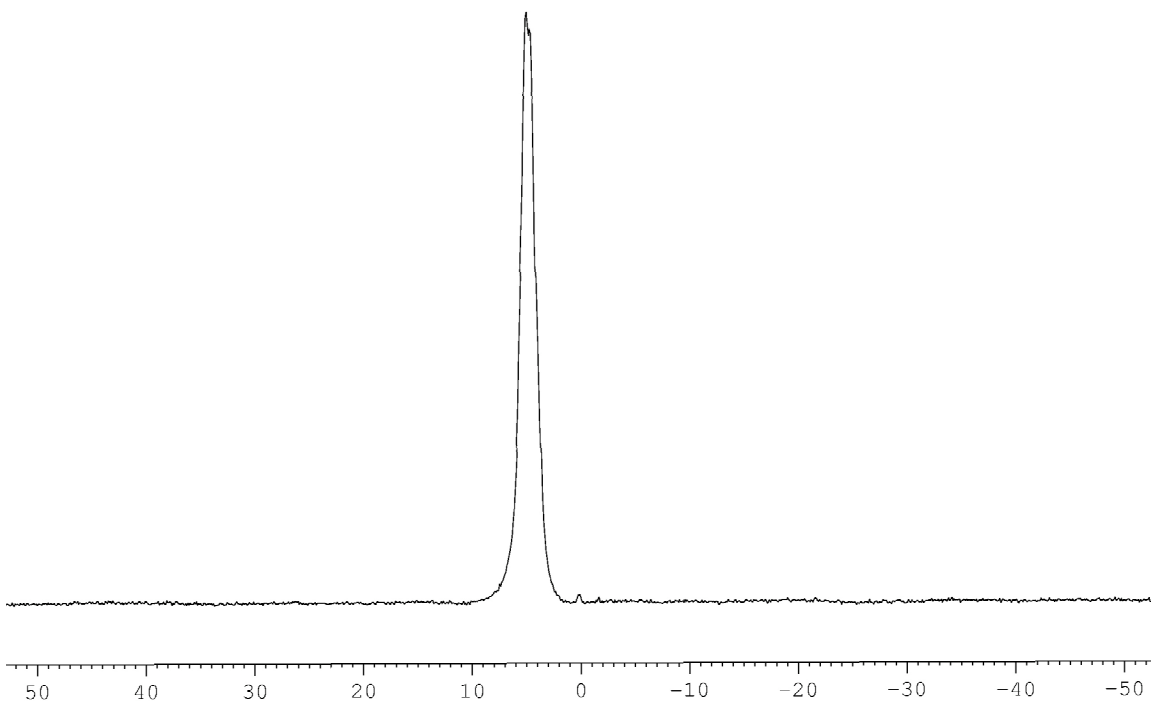
500 MHz  $^1\text{H}$  NMR of Compound (**8**) in  $\text{CDCl}_3$



126 MHz  $^{13}\text{C}$  NMR of Compound (**8**) in  $\text{CDCl}_3$

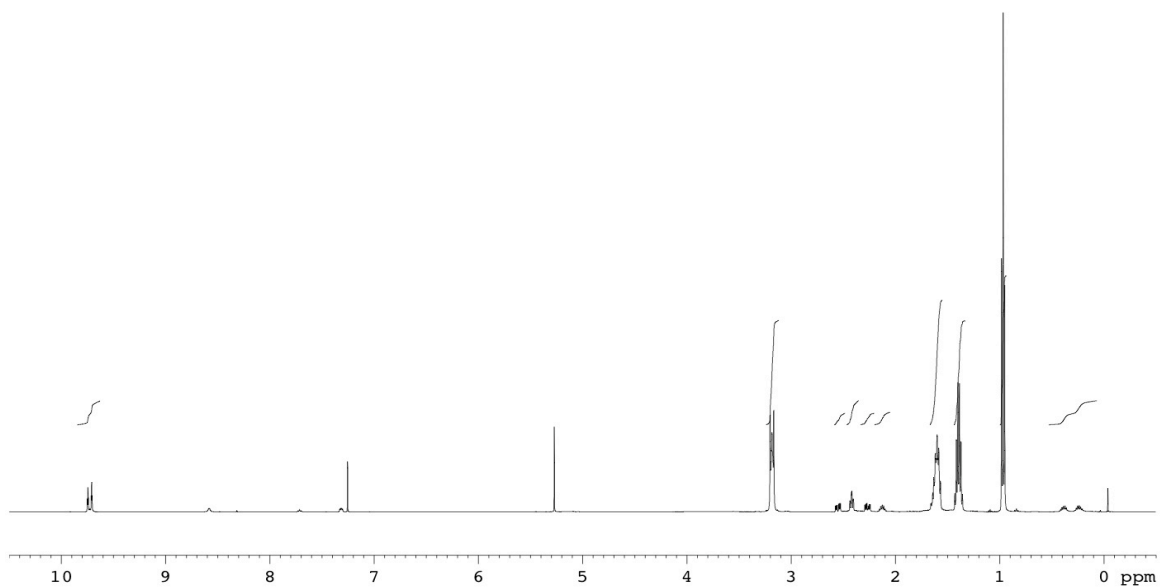


471 MHz  $^1\text{F}$  NMR of Compound (**8**) in  $\text{CDCl}_3$

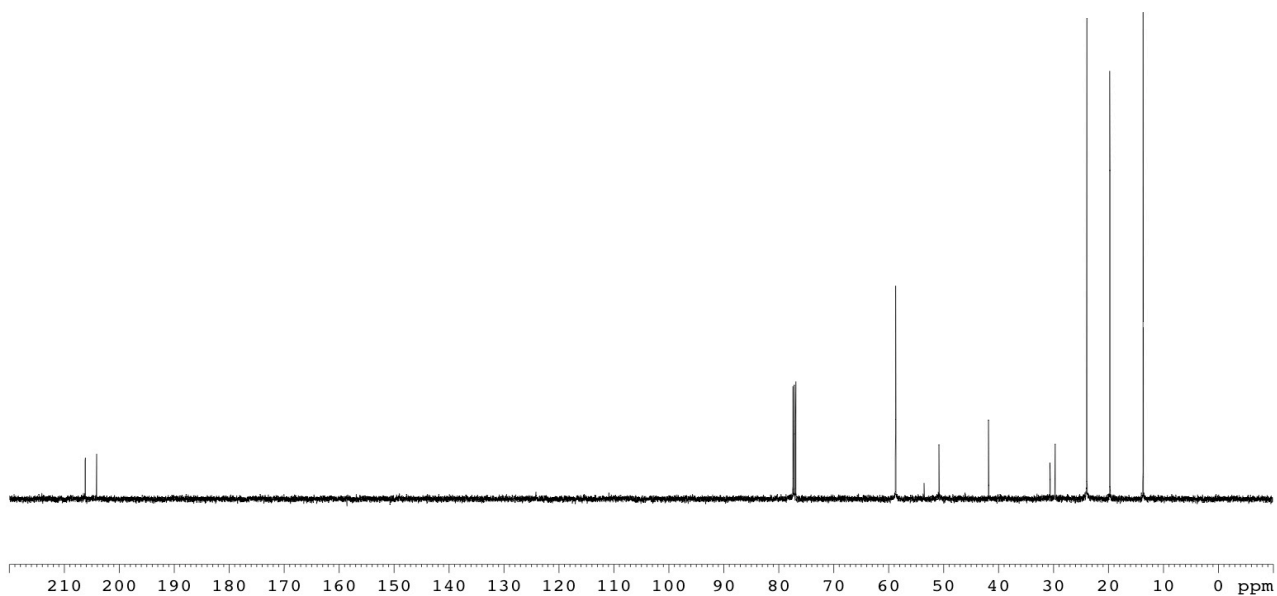


128 MHz  $^1\text{B}$  NMR of Compound (**8**) in  $\text{CDCl}_3$

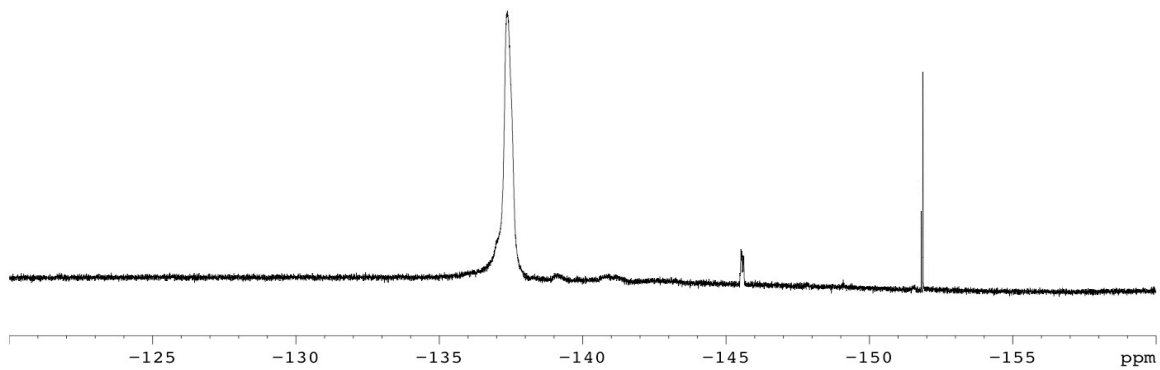
Tetrabutylammonium 4-formyl-2-(formylmethy)butyltrifluoroborate (**9**)



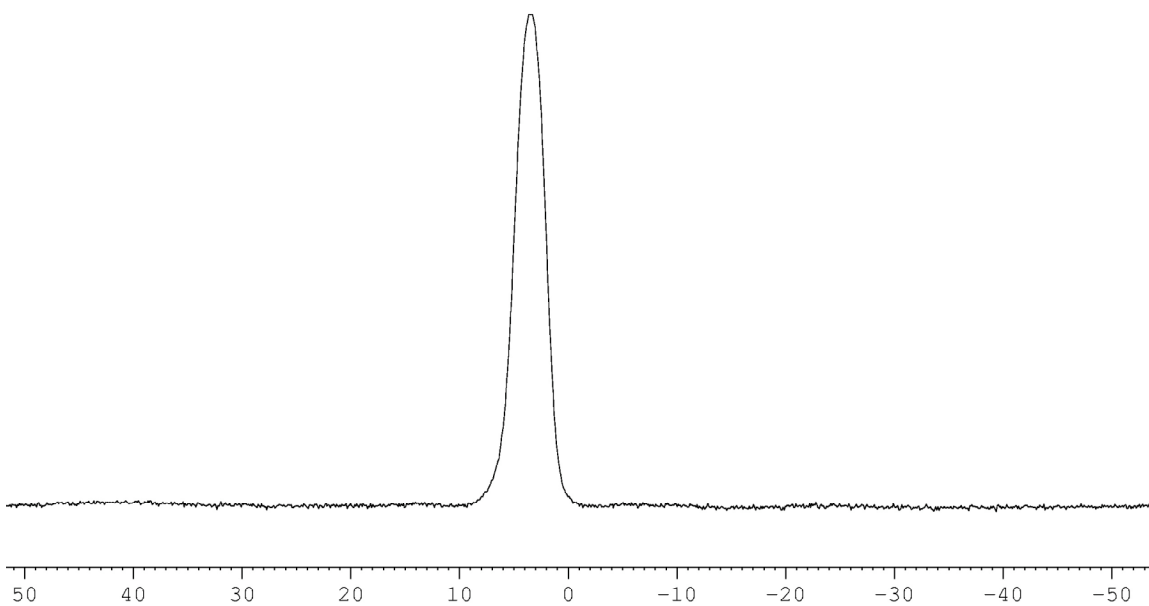
500 MHz <sup>1</sup>H NMR of Compound (**9**) in CDCl<sub>3</sub>



126 MHz <sup>13</sup>C NMR of Compound (**9**) in CDCl<sub>3</sub>

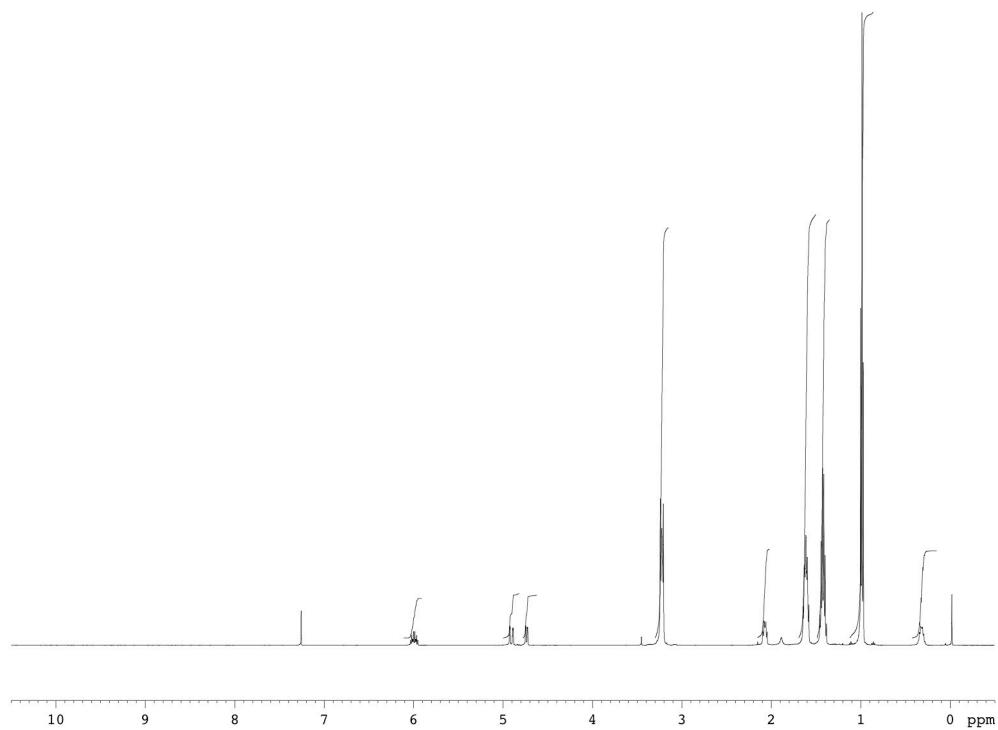


471 MHz  $^1\text{F}$  NMR of Compound (**9**) in  $\text{CDCl}_3$

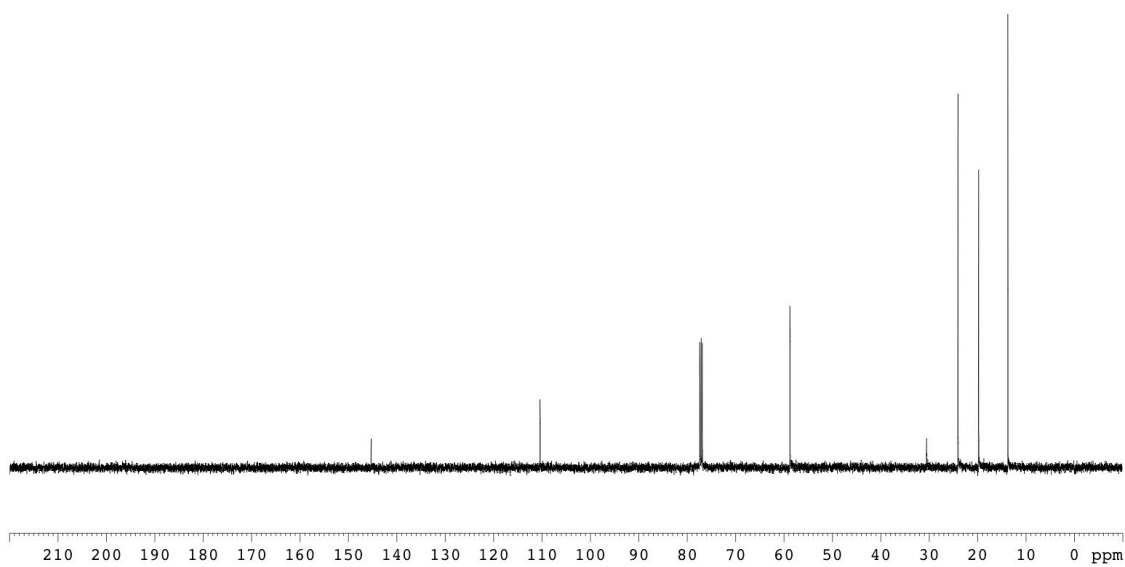


128 MHz  $^1\text{B}$  NMR of Compound (**9**) in  $\text{CDCl}_3$

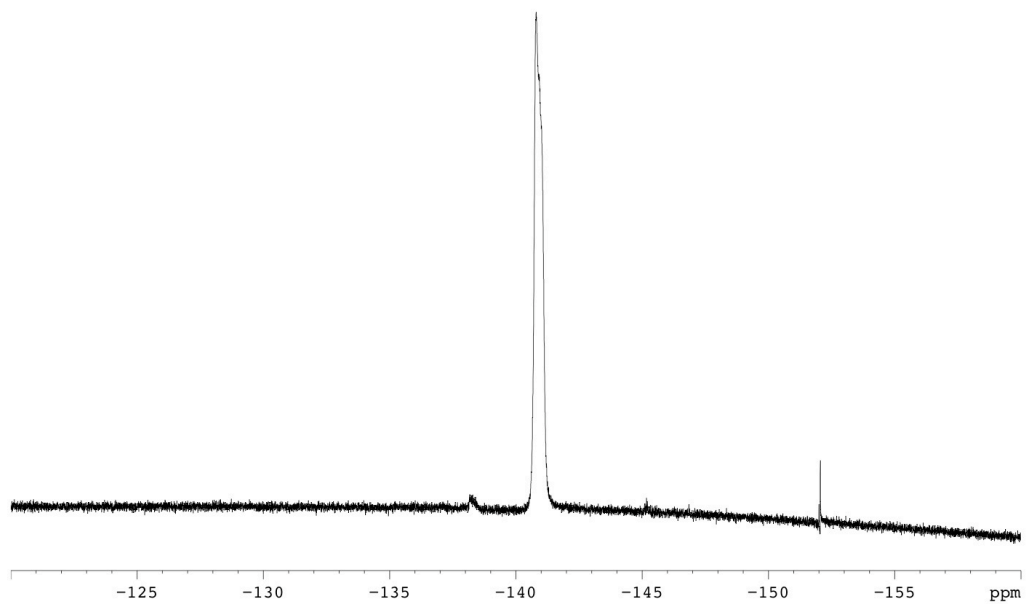
Tetrabutylammonium 4-butenyl Trifluoroborate (**10**)



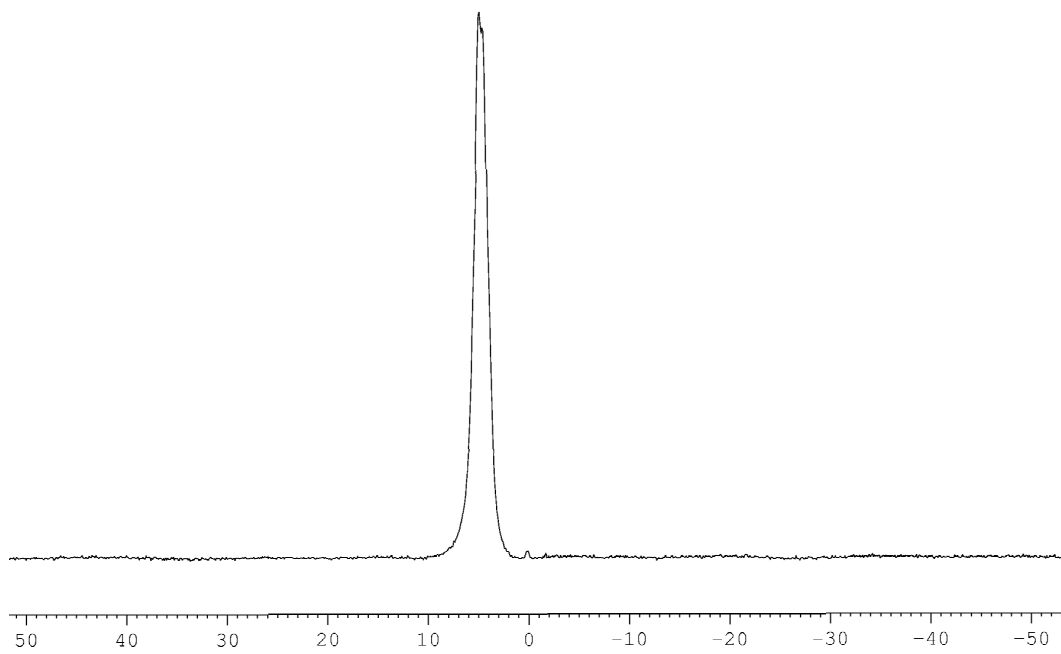
500 MHz  $^1\text{H}$  NMR of Compound (**10**) in  $\text{CDCl}_3$



126 MHz  $^{13}\text{C}$  NMR of Compound (**10**) in  $\text{CDCl}_3$

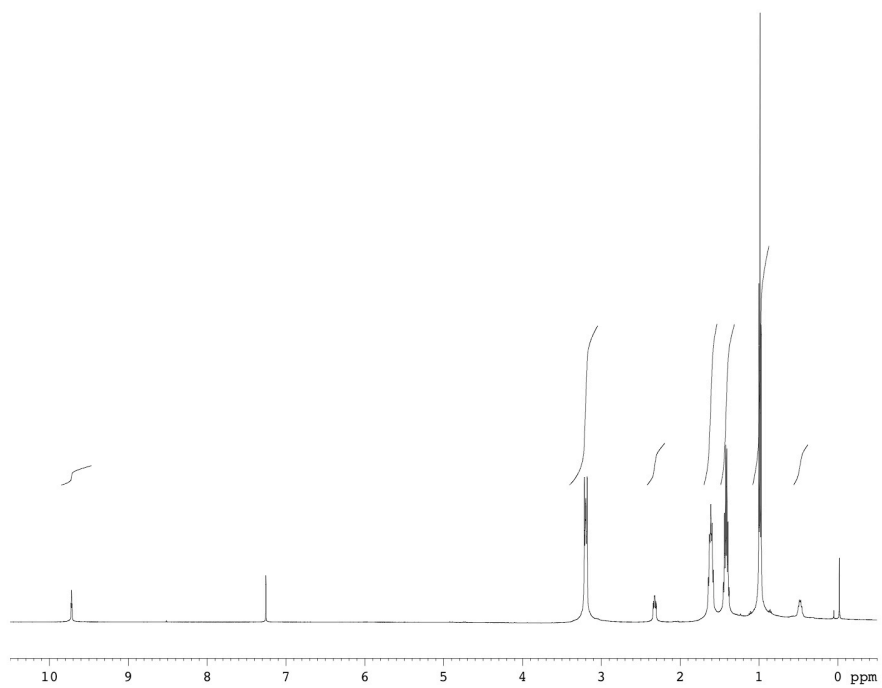


471 MHz  $^1\text{F}$  NMR of Compound (**10**) in  $\text{CDCl}_3$

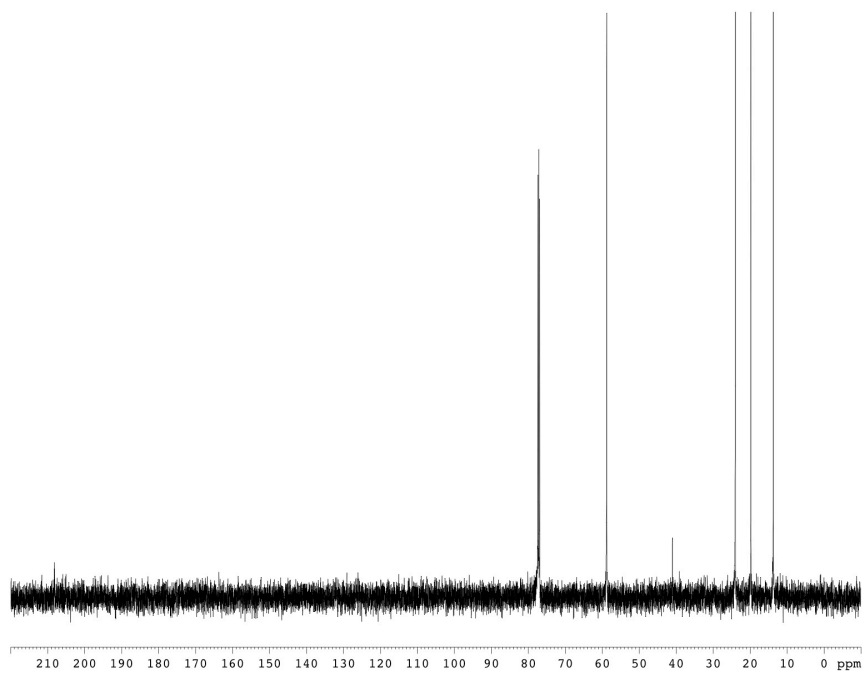


128 MHz  $^1\text{B}$  NMR of Compound (**10**) in  $\text{CDCl}_3$

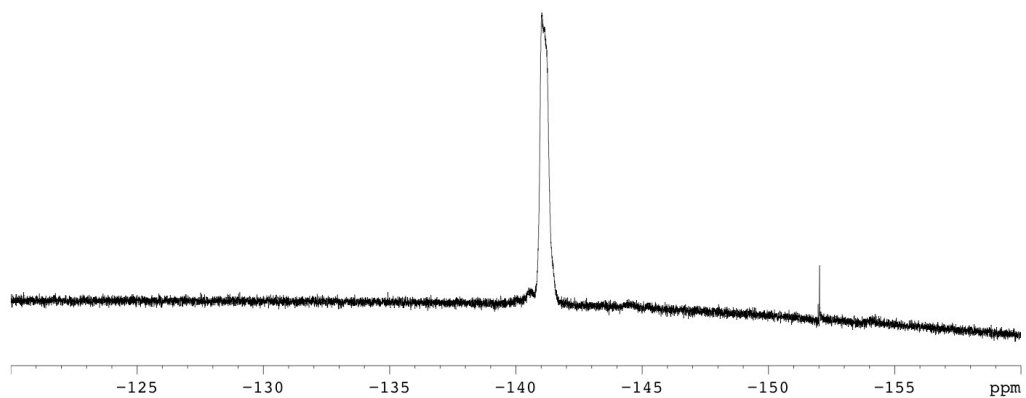
Tetrabutylammonium 2-formethyl Trifluoroborate (**11**)



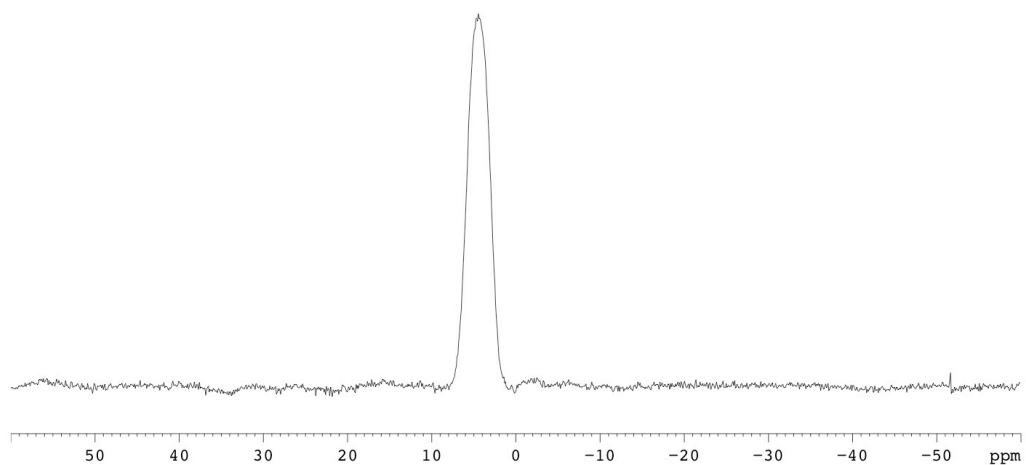
500 MHz  $^1\text{H}$  NMR of Compound (**11**) in  $\text{CDCl}_3$



126 MHz  $^{13}\text{C}$  NMR of Compound (**11**) in  $\text{CDCl}_3$



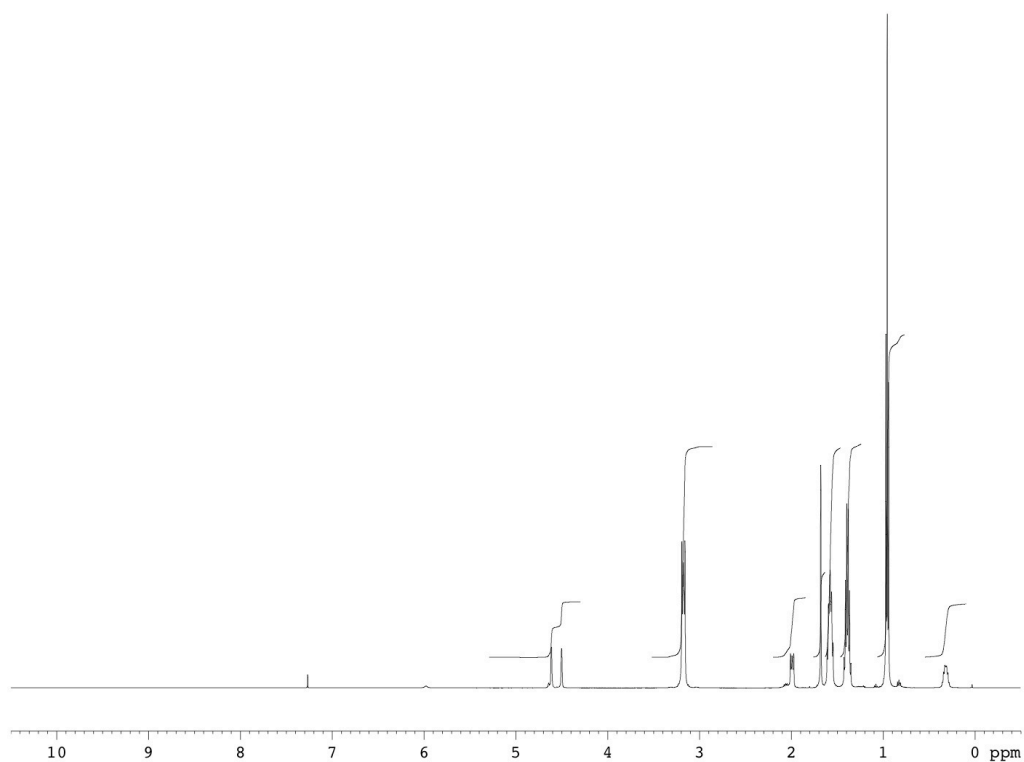
471 MHz  $^1\text{F}$  NMR of Compound (**11**) in  $\text{CDCl}_3$



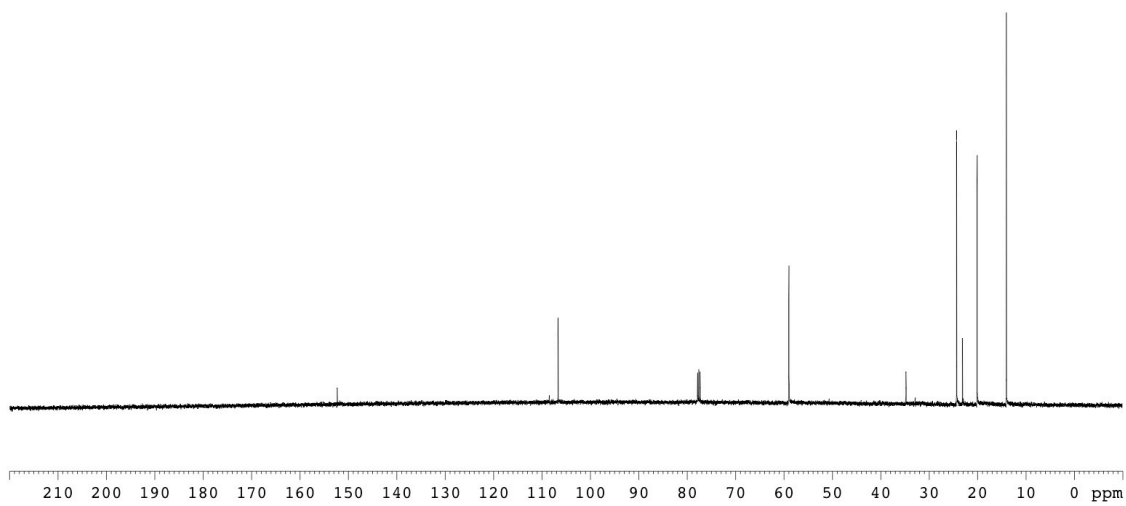
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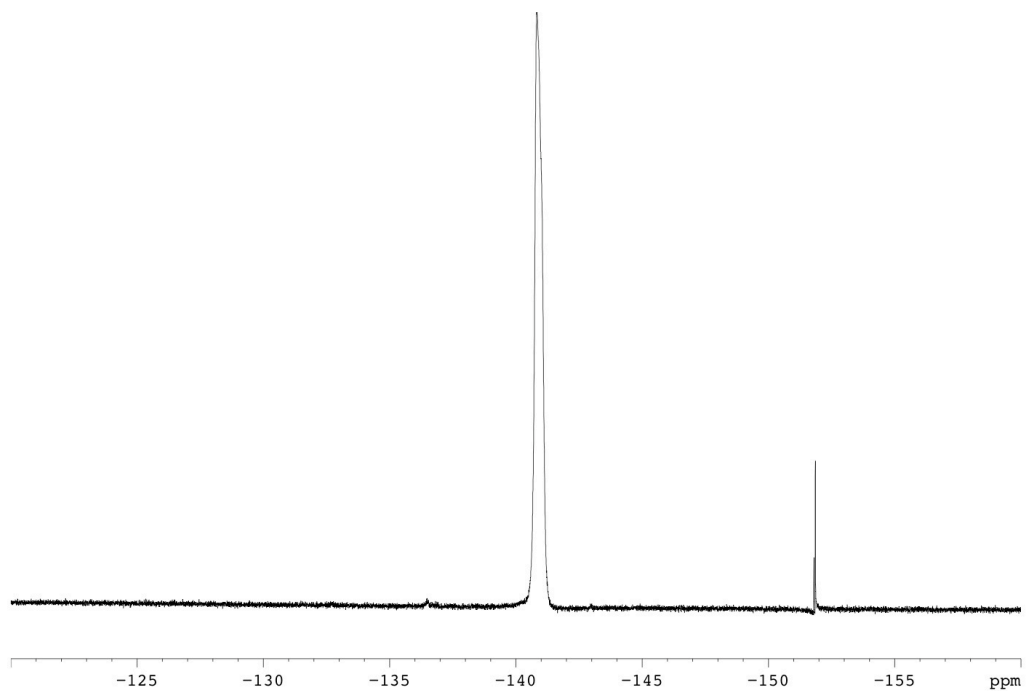
Tetrabutylammonium 3-Methylbut-3-enyl Trifluoroborate (**12**)



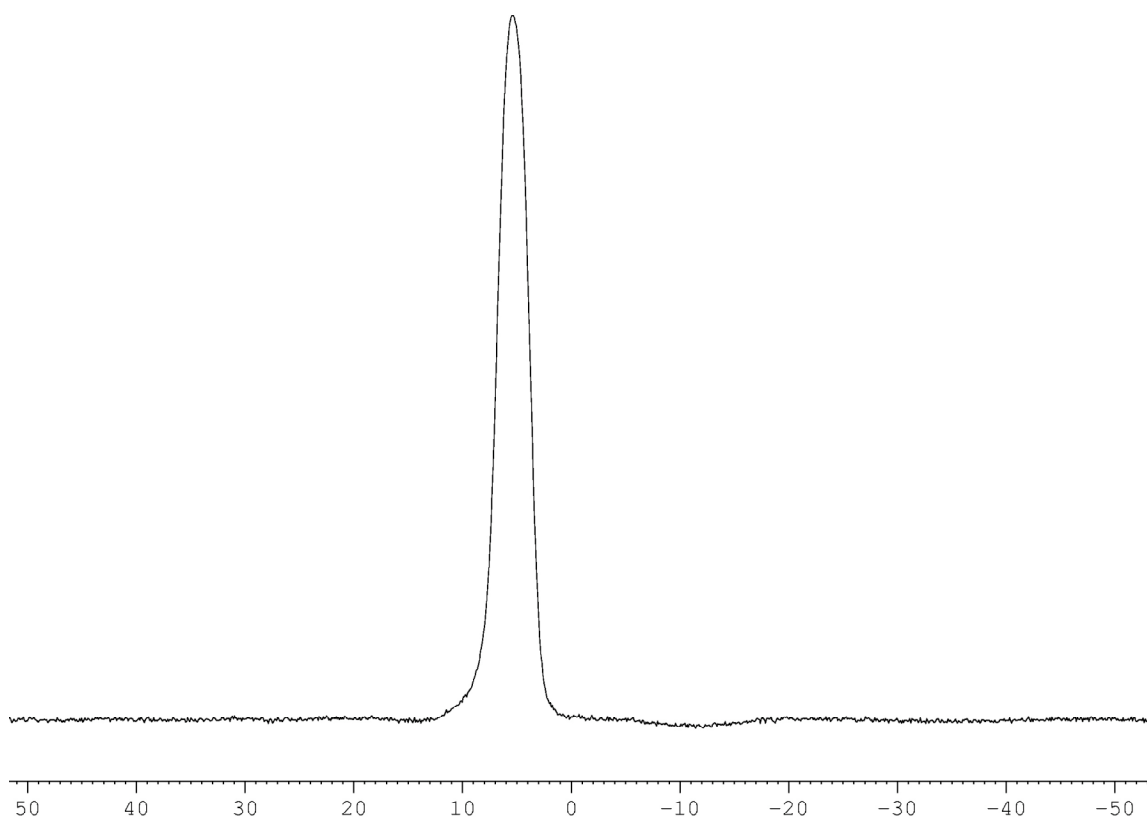
500 MHz  $^1\text{H}$  NMR of Compound (**12**) in  $\text{CDCl}_3$



126 MHz  $^{13}\text{C}$  NMR of Compound (**12**) in  $\text{CDCl}_3$

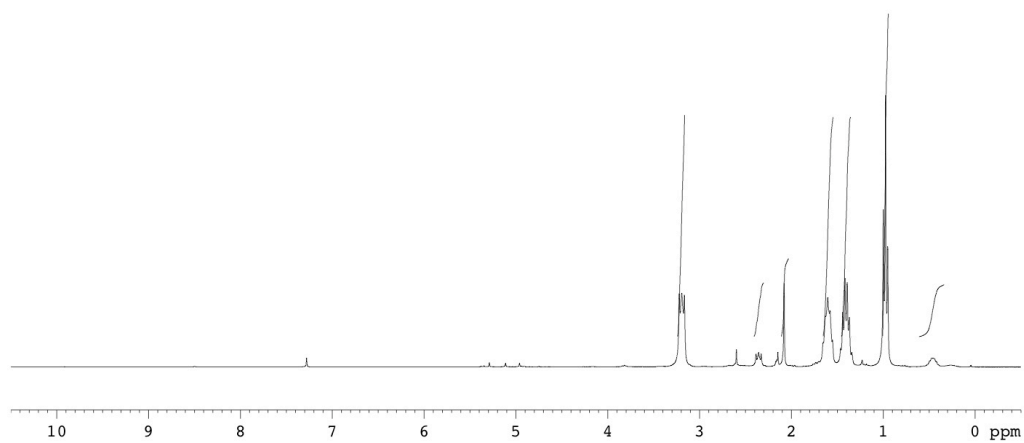


471 MHz  $^1\text{F}$  NMR of Compound (**12**) in  $\text{CDCl}_3$

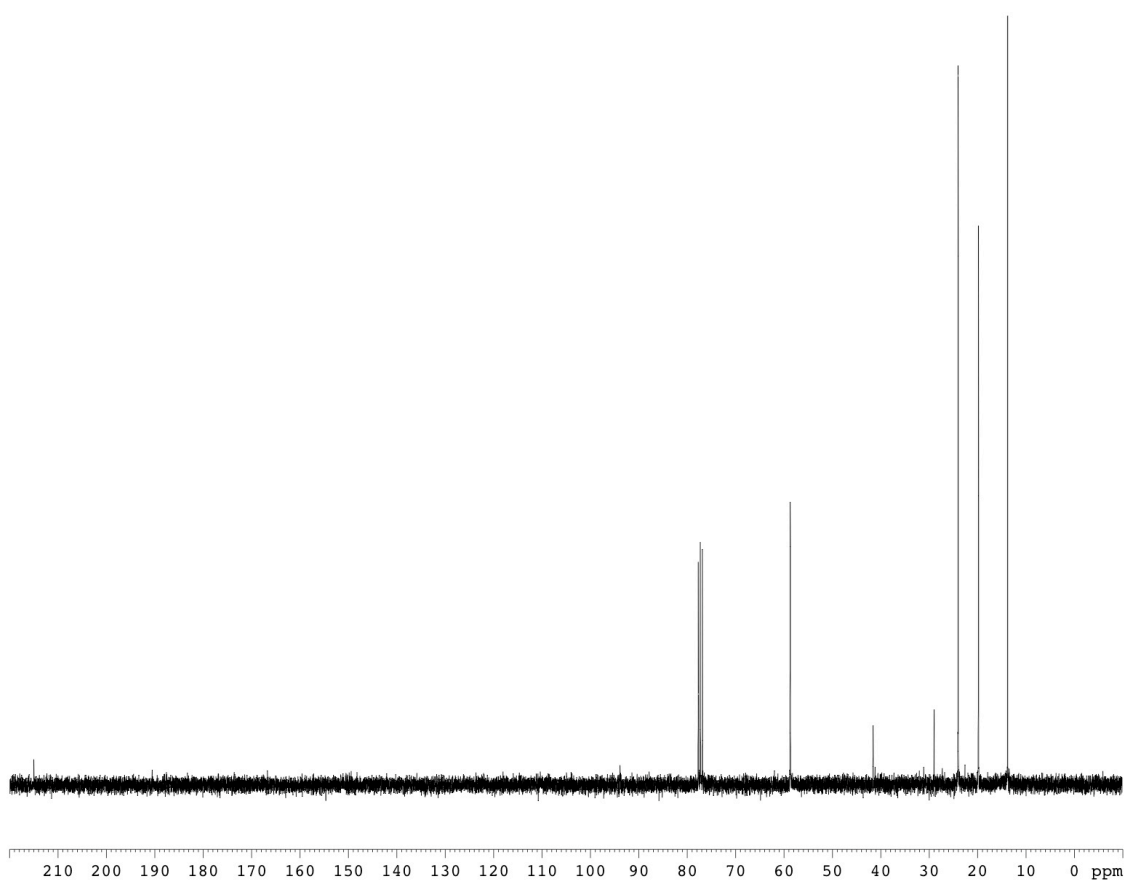


128 MHz  $^1\text{B}$  NMR of Compound (**12**) in  $\text{CDCl}_3$

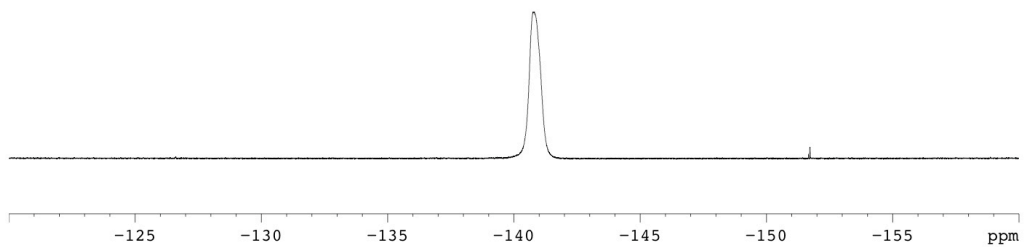
Tetrabutylammonium 3-oxobutyl Trifluoroborate (**13**)



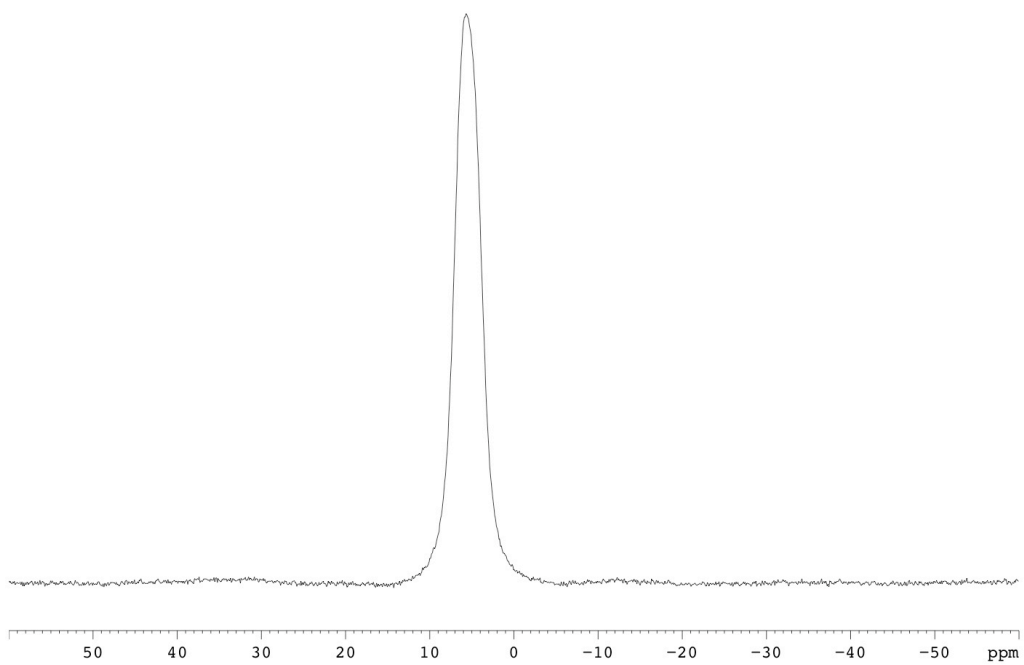
500 MHz  $^1\text{H}$  NMR of Compound (**13**) in  $\text{CDCl}_3$



126 MHz  $^{13}\text{C}$  NMR of Compound (**13**) in  $\text{CDCl}_3$

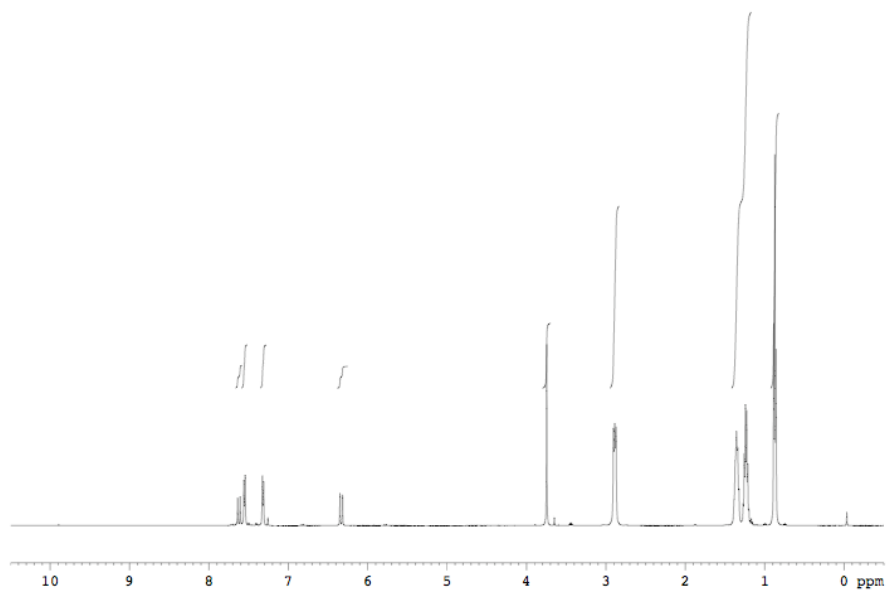


471 MHz  $^1\text{F}$  NMR of Compound (**13**) in  $\text{CDCl}_3$

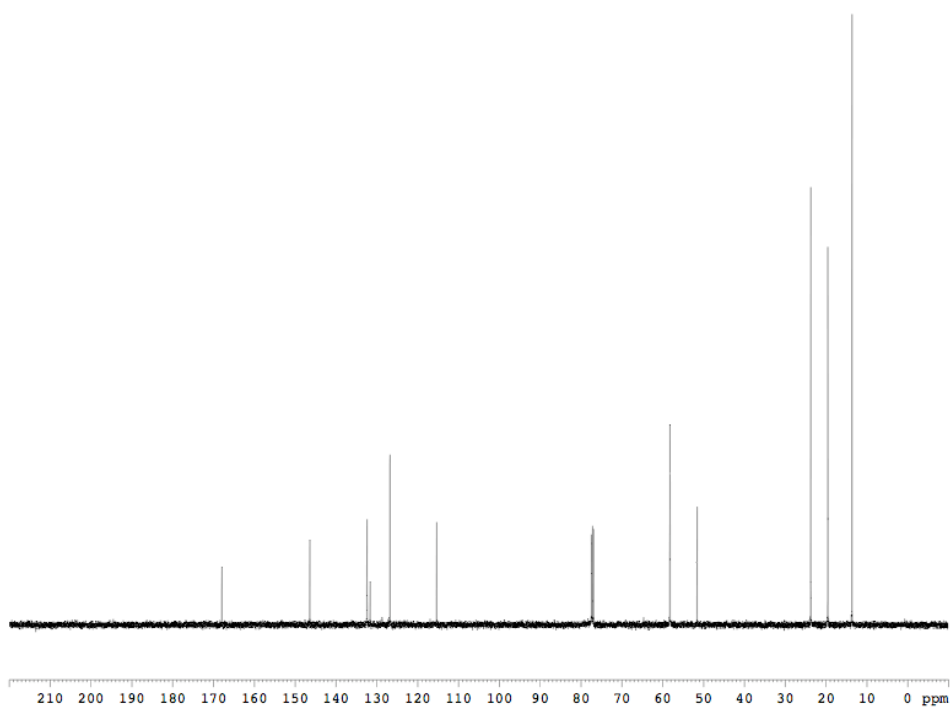


128 MHz  $^1\text{B}$  NMR of Compound (**13**) in  $\text{CDCl}_3$

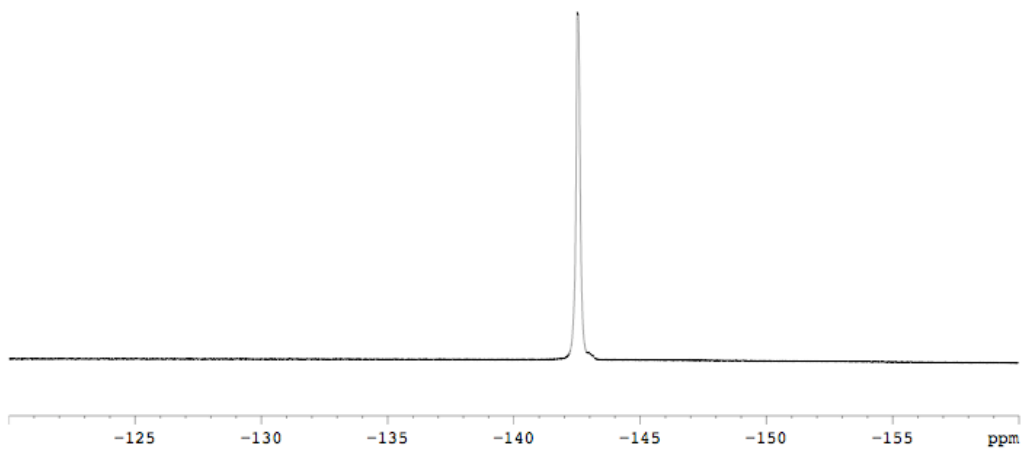
(*E*)-Tetrabutylammonium 4-(3-Methoxy-3-oxoprop-1-enyl)phenyltrifluoroborate (**14**)



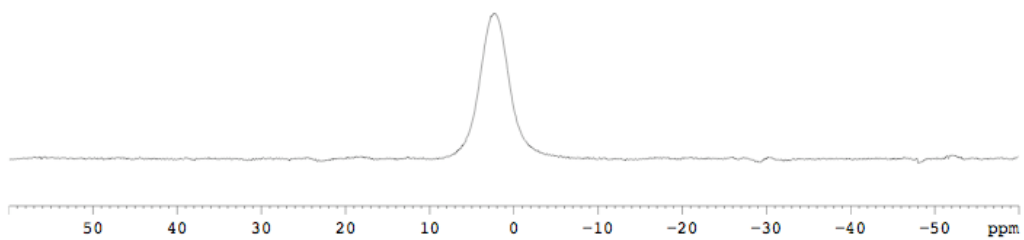
500 MHz <sup>1</sup>H NMR of Compound (**14**) in CDCl<sub>3</sub>



126 MHz <sup>13</sup>C NMR of Compound (**14**) in CDCl<sub>3</sub>



471 MHz  $^1\text{F}$  NMR of Compound (**14**) in  $\text{CDCl}_3$



128 MHz  $^1\text{B}$  NMR of Compound (**14**) in  $\text{CDCl}_3$