

## **Palladium-Catalyzed Borylation of Aryl and Heteroaryl Halides Utilizing Tetrakis(dimethylamino)diborane: One Step Greener**

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### **Supporting Information**

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#### **General Considerations**

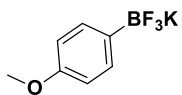
**Reagents:** All reactions were carried out under an atmosphere of argon. Methanol (anhydrous) was thoroughly degassed (1 h) with argon directly before use. All aryl halides were purchased from commercial sources and used as received. KOAc was dried in an oven overnight before use. All reagents (with the exception of the aryl halides) were stored in a bench-top desiccator. Tetrakis(dimethylamino)diboron was distilled (104 °C, 0.5 torr) and thoroughly degassed with argon before storing in a glovebox and put under argon atmosphere before each use. The XPhos version of the palladium preformed catalyst is currently available from commercial sources (CAS 1310584-14-5).

**Analytical Methods:** All new compounds were characterized by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR,  $^{11}\text{B}$  NMR (when applicable),  $^{19}\text{F}$  NMR, IR spectroscopy, high-resolution mass spectrometry, and melting point determination (for solids). All known compounds were characterized by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR,  $^{11}\text{B}$  NMR, and  $^{19}\text{F}$  NMR and compared to literature values.  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{11}\text{B}$ , and  $^{19}\text{F}$  were recorded at 500 MHz, 125.8 MHz, 128.4 MHz, 282 (or 338.8) MHz, respectively. Melting points are uncorrected.

**General Procedure A: Pd Catalyzed Borylation of Aryl Halides and their Conversion to Trifluoroborates.** To an oven dried glass vessel capable of being sealed with a Teflon cap (for microwave vials) was added X-Phos palladium(II) biphenyl preformed catalyst (5.89 mg, 7.5  $\mu\text{mol}$ ), X-Phos (7.14 mg, 15  $\mu\text{mol}$ ), and KOAc (441 mg, 4.5 mmol). The vessel was sealed and then evacuated and backfilled with Ar (process was repeated four times). MeOH (7.5 mL degassed) was added via syringe followed by the addition of the halide (1.5 mmol) in a similar manner (solid halides were added with the other solid reagents before sealing). tetrakis(dimethylamino)diboron (890 mg, 1.03 mL, 4.5 mmol) was added dropwise, and the reaction mixture was allowed to stir at rt for 5 min. The reaction was then added to a preheated oil bath warmed to 60  $^\circ\text{C}$  and heated at this temperature until the starting material was consumed (as monitored by GC). The reaction was cooled to rt then filtered through a thin pad of Celite (eluting with 5 x 10 mL of EtOAc), and concentrated. The crude reaction was dissolved in EtOAc (10 mL) and then transferred to a separatory funnel followed by the addition of saturated aqueous  $\text{NaHCO}_3$  (10 mL). The layers were separated and the organic layer was washed once with brine. The combined aqueous layers were further extracted with EtOAc (3 x 5

mL). The combined organics were dried ( $\text{Na}_2\text{SO}_4$ ) and concentrated. The concentrated crude reaction (unless otherwise indicated) was taken up in MeOH (~15 mL or enough to make a free-flowing solution) and cooled to 0 °C. To this cooled mixture was added 4.5 equivalents of a 4.5 M aqueous  $\text{KHF}_2$  solution (1 mL), and the reaction was stirred for 10 min at 0 °C before removing the bath and allowing the mixture to stir at rt for 20 min (or until the conversion to the corresponding trifluoroborate was achieved as determined by  $^{11}\text{B}$  NMR). The resulting mixture was then concentrated and then lyophilized overnight to remove any traces of water. The compound was purified with continuous Soxhlet extraction (overnight) with acetone (150 mL). The collected solvent was filtered through a thin pad of Celite, rinsed with hot acetone (3 x 5 mL), then concentrated until a minimal volume of acetone remained (~3 mL). The addition of  $\text{Et}_2\text{O}$  (~25 mL) led to the precipitation of the desired product. The collected solid was washed with  $\text{Et}_2\text{O}$ . Further purification (to remove small organic or boron containing impurities) could be realized via trituration of the solid with  $\text{Et}_2\text{O}$ .

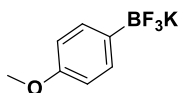
#### General Procedure A with Aryl Halides:



**Potassium 4-Methoxyphenyl-trifluoroborate (Table 1, entry 1).<sup>1</sup>**

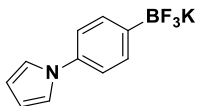
Following general procedure A, a mixture of 4-chloroanisole (214 mg, 183  $\mu\text{L}$ , 1.5 mmol), XPhos-Pd-G2 preformed catalyst (5.89 mg, 7.5  $\mu\text{mol}$ ), XPhos (7.14 mg, 15  $\mu\text{mol}$ ), KOAc (441 mg, 4.5 mmol), and tetrakis(dimethylamino)diboron (890 mg, 1.03 mL, 4.5 mmol), was heated to 60 °C in MeOH (7.5 mL) for 5 h. The title compound was

obtained as a white solid in 94% yield (302 mg). mp > 225 °C. Spectral data were in accordance with those of published results. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ 7.22 (d, *J* = 7.9 Hz, 2H), 6.65 (d, *J* = 7.8 Hz, 2H), 3.66 (s, 3H). <sup>13</sup>C NMR (125.8 MHz, DMSO-*d*<sub>6</sub>) δ 157.8, 132.9, 112.5, 55.1. <sup>11</sup>B NMR (128.4 MHz, acetone-*d*<sub>6</sub>) δ 4.23 (m). <sup>19</sup>F NMR (338.8 MHz, acetone-*d*<sub>6</sub>) δ -141.8.



**Potassium 4-Methoxyphenyl-trifluoroborate (Table 1, entry 1<sup>a</sup>).**<sup>1</sup>

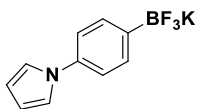
Following general procedure A, a mixture of 4-chloroanisole (214 mg, 183 μL, 1.5 mmol), XPhos-Pd-G2 preformed catalyst (5.89 mg, 7.5 μmol), XPhos (7.14 mg, 15 μmol), KOAc (441 mg, 4.5 mmol), and tetrakis(dimethylamino)diboron (890 mg, 1.03 mL, 4.5 mmol), was heated to 60 °C in MeOH (3 mL) for 5 h. The title compound was obtained as a white solid in 94% yield (300 mg). mp > 225 °C. Spectral data were in accordance with those of published results. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ 7.20 (d, *J* = 7.7 Hz, 2H), 6.64 (d, *J* = 7.7 Hz, 2H), 3.65 (s, 3H). <sup>13</sup>C NMR (125.8 MHz, DMSO-*d*<sub>6</sub>) δ 157.8, 132.8, 112.4, 55.1. <sup>11</sup>B NMR (128.4 MHz, acetone-*d*<sub>6</sub>) δ 4.3 (m). <sup>19</sup>F NMR (338.8 MHz, acetone-*d*<sub>6</sub>) δ -141.8.



**Potassium 4-(1H-Pyrrol-1-yl)phenyl-trifluoroborate (Table 1, entry**

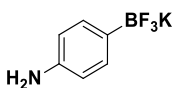
**2).**<sup>1</sup> Following general procedure A, a mixture of 1-(4-chlorophenyl)-1H-pyrrole (267 mg, 1.5 mmol), XPhos-Pd-G2 preformed catalyst (5.89 mg, 7.5 μmol), XPhos (7.14 mg,

15  $\mu\text{mol}$ ), KOAc (441 mg, 4.5 mmol), and tetrakis(dimethylamino)diboron (890 mg, 1.03 mL, 4.5 mmol), was heated to 60  $^{\circ}\text{C}$  in MeOH (7.5 mL) for 3 h. The title compound was obtained as a white solid in 96% yield (358 mg). Spectral data were in accordance with those published. mp > 225  $^{\circ}\text{C}$ .  $^1\text{H}$  NMR (500 MHz, acetone- $d_6$ )  $\delta$  7.57 (d,  $J$  = 7.9 Hz, 2H), 7.25 (d,  $J$  = 8.0 Hz, 2H), 7.15 (t,  $J$  = 2.1 Hz, 2H), 6.22 (t,  $J$  = 2.1 Hz, 2H).  $^{13}\text{C}$  NMR (125.8 MHz, acetone- $d_6$ )  $\delta$  139.4, 133.6, 119.6, 119.0, 110.3.  $^{11}\text{B}$  NMR (128.4 MHz, acetone- $d_6$ )  $\delta$  4.1.  $^{19}\text{F}$  NMR (282 MHz, acetone- $d_6$ )  $\delta$  -141.7.



**Potassium 4-(1H-Pyrrol-1-yl)phenyl-trifluoroborate (Table 1, entry**

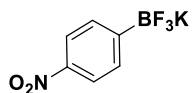
**2 $^{\circ}$** ).<sup>1</sup> Following general procedure A, but in a round bottom flask with a reflux condenser (under an atmosphere of argon), a mixture of 1-(4-chlorophenyl)-1H-pyrrole (267 mg, 1.5 mmol), XPhos-Pd-G2 preformed catalyst (5.89 mg, 7.5  $\mu\text{mol}$ ), XPhos (7.14 mg, 15  $\mu\text{mol}$ ), KOAc (441 mg, 4.5 mmol), and tetrakis(dimethylamino)diboron (890 mg, 1.03 mL, 4.5 mmol), was heated to 60  $^{\circ}\text{C}$  in MeOH (7.5 mL) for 3 h. The title compound was obtained as a white solid in 93% yield (347 mg). Spectral data were in accordance with those published. mp > 225  $^{\circ}\text{C}$ .  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  7.39 (d,  $J$  = 8.0 Hz, 2H), 7.26 (d,  $J$  = 8.0 Hz, 2H), 7.25 (t,  $J$  = 2.0 Hz, 2H), 6.21 (t,  $J$  = 2.0 Hz, 2H).  $^{13}\text{C}$  NMR (125.8 MHz, DMSO- $d_6$ )  $\delta$  137.6, 132.4, 118.8, 117.7, 109.6.  $^{11}\text{B}$  NMR (128.4 MHz, acetone- $d_6$ )  $\delta$  4.1.  $^{19}\text{F}$  NMR (282 MHz, acetone- $d_6$ )  $\delta$  -142.4.



**Potassium 4-Aminophenyl-trifluoroborate (Table 1, entry 3).**<sup>2</sup>

Following general procedure A, a mixture of 4-chloroaniline (214 mg, 1.5 mmol),

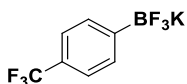
XPhos-Pd-G2 preformed catalyst (5.89 mg, 7.5  $\mu\text{mol}$ ), XPhos (7.14 mg, 15  $\mu\text{mol}$ ), KOAc (441 mg, 4.5 mmol), and tetrakis(dimethylamino)diboron (890 mg, 1.03 mL, 4.5 mmol), was heated to 60  $^{\circ}\text{C}$  in MeOH (7.5 mL) for 7 h. After the standard Soxhlet purification (without filtration through celite after Soxhlet), the trifluoroborate was concentrated and then taken up in 10 mL of MeCN (10 mL), and  $\text{K}_2\text{CO}_3$  (726 mg, 5.25 mmol) was added. The mixture was stirred under an atmosphere of argon for 18 h. The mixture was then concentrated *in vacuo*, acetone (20 mL) was added, and the mixture was sonicated and filtered through a short pad of Celite, rinsing with additional hot acetone (3 x 15 mL). The combined filtrate was concentrated. The trifluoroborate was then dissolved in a minimal amount of acetone (3 mL), and  $\text{Et}_2\text{O}$  (15 mL) was added to obtain an off white precipitate that was filtered and dried *in vacuo*. The title compound was obtained as a tan solid in 39% yield (116 mg). Spectral data were in accordance with those published. mp > 225  $^{\circ}\text{C}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}d_6$ )  $\delta$  6.99 (d,  $J = 7.7$  Hz, 2H), 6.35 (d,  $J = 7.7$  Hz, 2H), 4.40 (s, 2H).  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{DMSO-}d_6$ )  $\delta$  145.5, 131.9, 113.0.  $^{11}\text{B}$  NMR (128.4 MHz,  $\text{acetone-}d_6$ )  $\delta$  1.4 (q,  $J = 55.5$  Hz).  $^{19}\text{F}$  NMR (282 MHz,  $\text{acetone-}d_6$ )  $\delta$  -141.4.



**Potassium (4-Nitrophenyl)trifluoroborate (Table 1, entry 4).<sup>1</sup>**

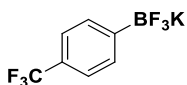
Following general procedure A, a mixture of 1-bromo-4-nitrobenzene (303 mg, 1.5 mmol), XPhos-Pd-G2 preformed catalyst (5.89 mg, 7.5  $\mu\text{mol}$ ), XPhos (7.14 mg, 15  $\mu\text{mol}$ ), KOAc (441 mg, 4.5 mmol), and tetrakis(dimethylamino)diboron (890 mg, 1.03 mL, 4.5 mmol), was heated to 60  $^{\circ}\text{C}$  in MeOH (7.5 mL) for 3.5 h. The title compound

was obtained as a light reddish-brown solid in 56% yield (192 mg). Spectral data were in accordance with those of published results. mp > 225 °C.  $^1\text{H}$  NMR (500 MHz, acetone- $d_6$ )  $\delta$  7.97 (d,  $J$  = 7.7 Hz, 2H), 7.68 (d,  $J$  = 7.4 Hz, 2H).  $^{13}\text{C}$  NMR (125.8 MHz, DMSO- $d_6$ )  $\delta$  146.4, 132.8, 121.8.  $^{11}\text{B}$  NMR (128.4 MHz, acetone- $d_6$ )  $\delta$  3.4 (q,  $J$  = 50.5 Hz).  $^{19}\text{F}$  NMR (338.8 MHz, acetone- $d_6$ )  $\delta$  -143.9.



**Potassium (4-(Trifluoromethyl)phenyl)trifluoroborate (Table 1, entry**

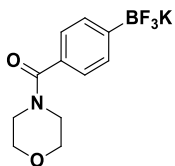
**5).**<sup>1</sup> Following general procedure A, a mixture of 4-trifluoromethylchlorobenzene (200  $\mu\text{L}$ , 1.5 mmol), XPhos-Pd-G2 preformed catalyst (5.89 mg, 7.5  $\mu\text{mol}$ ), XPhos (7.14 mg, 15  $\mu\text{mol}$ ), KOAc (441 mg, 4.5 mmol), and tetrakis(dimethylamino)diboron (890 mg, 1.03 mL, 4.5 mmol), was heated to 60 °C in MeOH (7.5 mL) for 2.5 h. The title compound was obtained as a white solid in 97% yield (365 mg). Spectral data were in accordance with those published. mp > 225 °C.  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  7.51 (d,  $J$  = 7.4 Hz, 2H), 7.40 (d,  $J$  = 7.5 Hz, 2H).  $^{13}\text{C}$  NMR (125.8 Hz, DMSO- $d_6$ )  $\delta$  132.3, 132.3, 126.8, 126.6, 126.3, 124.6, 123.4, 123.3, 100.1.  $^{11}\text{B}$  NMR (128.4 MHz, acetone- $d_6$ )  $\delta$  3.8 (m).  $^{19}\text{F}$  NMR (338.8 MHz, acetone- $d_6$ )  $\delta$  -62.5, -143.3.



**Potassium (4-(Trifluoromethyl)phenyl)trifluoroborate (Table 1, entry**

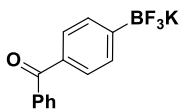
**5<sup>d</sup>).**<sup>1</sup> Following general procedure A, a mixture of 4-trifluoromethylchlorobenzene (1.33 mL, 10 mmol), XPhos-Pd-G2 preformed catalyst (40 mg, 0.05 mmol), XPhos (48 mg, 0.1 mmol), KOAc (2.94 g, 30 mmol), and tetrakis(dimethylamino)diboron (6.9 mL, 30 mmol), was heated to 60 °C in MeOH (7.5 mL) for 2.5 h. The title compound was obtained as a white solid in 98% yield (2.48 g). Spectral data were in accordance with

those published. mp > 225 °C.  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  7.55 (d,  $J$  = 7.0 Hz, 2H), 7.43 (d,  $J$  = 7.0 Hz, 2H).  $^{13}\text{C}$  NMR (125.8 MHz, DMSO- $d_6$ )  $\delta$  131.8, 128.4, 126.2, 126.1, 125.9, 124.1, 122.8, 121.9.  $^{11}\text{B}$  NMR (128.4 MHz, acetone- $d_6$ )  $\delta$  3.8.  $^{19}\text{F}$  NMR (282 MHz, acetone- $d_6$ )  $\delta$  -62.5, -143.2.



**Potassium 4-(Morpholine-4-carbonyl)phenyl-trifluoroborate (Table 1,**

**entry 6).**<sup>3</sup> Following general procedure A, a mixture of (4-chlorophenyl)(morpholino)methanone (340 mg, 1.5 mmol), XPhos-Pd-G2 preformed catalyst (5.89 mg, 7.5  $\mu\text{mol}$ ), XPhos (7.14 mg, 15  $\mu\text{mol}$ ), KOAc (441 mg, 4.5 mmol), and tetrakis(dimethylamino)diboron (890 mg, 1.03 mL, 4.5 mmol), was heated to 60 °C in MeOH (7.5 mL) for 5.5 h. The title compound was obtained as a white solid in 85% yield (380 mg). Spectral data were in accordance with those published. mp > 225 °C.  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  7.36 (d,  $J$  = 7.5 Hz, 2H), 7.12 (d,  $J$  = 7.4 Hz, 2H), 3.56 (s, 8H).  $^{13}\text{C}$  NMR (125.8 MHz, DMSO- $d_6$ )  $\delta$  170.9, 132.7, 131.7, 131.7, 125.7, 66.8.  $^{11}\text{B}$  NMR (128.4 MHz, acetone- $d_6$ )  $\delta$  3.8 (m).  $^{19}\text{F}$  NMR (338.8 MHz, acetone- $d_6$ )  $\delta$  -143.1.

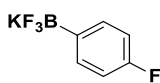


**Potassium 4-Benzoylphenyl-trifluoroborate (Table 1, entry 7).**<sup>1</sup>

Following general procedure A, a mixture of 4-chlorobenzophenone (325 mg, 1.5 mmol), XPhos-Pd-G2 preformed catalyst (5.89 mg, 7.5  $\mu\text{mol}$ ), XPhos (7.14 mg, 15  $\mu\text{mol}$ ), KOAc (441 mg, 4.5 mmol), and tetrakis(dimethylamino)diboron (890 mg, 1.03 mL, 4.5

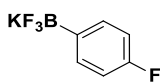


mmol), was heated to 60 °C in MeOH (7.5 mL) for 2.5 h. The title compound was obtained as a white solid in 92% yield (397 mg). Spectral data were in accordance with those published. mp = 220 °C dec. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ 7.73 – 7.69 (m, 2H), 7.64 (t, *J* = 7.4 Hz, 2H), 7.65 – 7.57 (m, 1H), 7.56 – 7.51 (m, 4H). <sup>13</sup>C NMR (125.8 MHz, DMSO-*d*<sub>6</sub>) δ 196.4, 138.0, 134.0, 132.1, 131.3, 129.4, 128.4, 128.1. <sup>11</sup>B NMR (128.4 MHz, acetone-*d*<sub>6</sub>) δ 4.0. <sup>19</sup>F NMR (282 MHz, acetone-*d*<sub>6</sub>) δ -143.2.



**Potassium (4-Fluorophenyl)trifluoroborate (Table 1, entry 8).<sup>1</sup>**

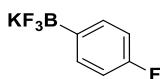
Following general procedure A, a mixture of 1-chloro-4-fluorobenzene (196 mg, 159 μL, 1.5 mmol), XPhos-Pd-G2 preformed catalyst (5.89 mg, 7.5 μmol), XPhos (7.14 mg, 15 μmol), KOAc (441 mg, 4.5 mmol), and tetrakis(dimethylamino)diboron (890 mg, 1.03 mL, 4.5 mmol), was heated to 60 °C in MeOH (7.5 mL) for 3 h. The title compound was obtained as a white solid in 97% yield (295 mg). Spectral data were in accordance with those published. mp > 225 °C. <sup>1</sup>H NMR (500 MHz, acetone-*d*<sub>6</sub>) δ 7.46 (t, *J* = 7.1 Hz, 2H), 6.82 (t, *J* = 8.9 Hz, 2H). <sup>13</sup>C NMR (125.8 MHz, DMSO-*d*<sub>6</sub>) δ 162.5, 160.6, 133.4 (d, *J* = 5.5 Hz), 113.3 (d, *J* = 18.4 Hz). <sup>11</sup>B NMR (128.4 MHz, acetone-*d*<sub>6</sub>) δ 4.0 (q, *J* = 53 Hz). <sup>19</sup>F NMR (338.8 MHz, acetone-*d*<sub>6</sub>) δ -120.4, -142.4.



**Potassium (4-Fluorophenyl)trifluoroborate (Table 1, entry 8<sup>a</sup>).<sup>1</sup>**

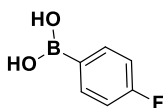
Following general procedure A, a mixture of 1-chloro-4-fluorobenzene (196 mg, 159 μL, 1.5 mmol), XPhos-Pd-G2 preformed catalyst (5.89 mg, 7.5 μmol), XPhos (7.14 mg, 15 μmol), KOAc (441 mg, 4.5 mmol), and tetrakis(dimethylamino)diboron (890 mg, 1.03

mL, 4.5 mmol), was heated to 60 °C in MeOH (3 mL) for 4.5 h. The title compound was obtained as a white solid in 97% yield (295mg). Spectral data were in accordance with those published. mp > 225 °C. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ 7.30 (t, *J* = 7.2 Hz, 2H), 6.84 (t, *J* = 8.9 Hz, 2H). <sup>13</sup>C NMR (125.8 MHz, DMSO-*d*<sub>6</sub>) δ 160.5, 160.6, 133.4 (m, *J* = 7.7 Hz), 113.3 (d, *J* = 18.4 Hz). <sup>11</sup>B NMR (128.4 MHz, acetone-*d*<sub>6</sub>) δ 4.0 (q, *J* = 53 Hz). <sup>19</sup>F NMR (338.8 MHz, acetone-*d*<sub>6</sub>) δ -120.4, -142.4.

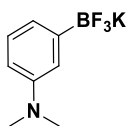


**Potassium (4-Fluorophenyl)trifluoroborate (Table 1, entry 8<sup>e</sup>).**<sup>1</sup>

Following general procedure A, a mixture of Pd(OAc)<sub>2</sub> (16.8 mg, 75 μmol), XPhos (107 mg, 225 μmol), and KOAc (441 mg, 4.5 mmol) was heated in MeOH (2 mL) at 60 °C for 30 min. The reaction was cooled to rt, a needle attached to a manifold under argon was inserted into the septa, and 1-chloro-4-fluorobenzene (196 mg, 159 μL, 1.5 mmol) was added neat via syringe followed by the dropwise addition of tetrakis(dimethylamino)diboron (890 mg, 1.03 mL, 4.5 mmol) in a solution of MeOH (5.5 mL) The needle was removed and the reaction was heated to 60 °C for an additional 2.5 h. See general procedure A for work-up. The title compound was obtained as a white solid in 87% yield (263 mg). Spectral data were in accordance with those published. mp > 225 °C. <sup>1</sup>H NMR (500 MHz, acetone-*d*<sub>6</sub>) δ 7.45 (t, *J* = 6.9 Hz, 2H), 6.81 (t, *J* = 8.9 Hz, 2H). <sup>13</sup>C NMR (125.8 MHz, acetone-*d*<sub>6</sub>) δ 162.9, 160.9, 133.3 (d, *J* = 5.14 Hz), 112.8 (d, *J* = 19.27 Hz). <sup>11</sup>B NMR (128.4 MHz, acetone-*d*<sub>6</sub>) δ 4.0 (q, *J* = 51 Hz). <sup>19</sup>F NMR (338.8 MHz, acetone-*d*<sub>6</sub>) δ -119.9, -142.1.

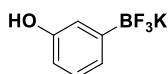


**(4-Fluorophenyl)boronic Acid (Table 1, entry 8<sup>f</sup>).**<sup>4</sup> Following general procedure A, a mixture of 1-chloro-4-fluorobenzene (196 mg, 159  $\mu$ L, 1.5 mmol), XPhos-Pd-G2 preformed catalyst (5.89 mg, 7.5  $\mu$ mol), XPhos (7.14 mg, 15  $\mu$ mol), KOAc (441 mg, 4.5 mmol), and tetrakis(dimethylamino)diboron (890 mg, 1.03 mL, 4.5 mmol), was heated to 60  $^{\circ}$ C in MeOH (7.5 mL) for 2.5 h. The reaction was cooled to rt and filtered through a pad of celite, rinsing with EtOAc (3 x 10 mL). After concentrating the reaction to dryness, EtOAc (10 mL) and 1 M HCl (10 mL) was added and the reaction stirred at rt for 30 min. The mixture was then added to a separatory funnel and the aq layer was removed. The organic layer was washed with brine, and the combined aqueous layers were extracted with EtOAc (3 x 10 mL). The combined organics were dried ( $\text{Na}_2\text{SO}_4$ ) and concentrated under vacuum. The crude boronic acid was then lyophilized overnight to remove any remaining water. To the dried solid was added hexanes (15 mL) and sonicated ( $\sim$  1 min) affording a white solid that was filtered and rinsed with hexanes (10 mL). The title compound was obtained as a white solid in 85% yield ( $\sim$ 90% pure, 178 mg). Spectral data were in accordance with those published. mp  $>$  225  $^{\circ}$ C.  $^1\text{H}$  NMR (500 MHz, acetone- $d_6$ )  $\delta$  7.89 (t,  $J$  = 7.0 Hz, 2H), 7.16 (t,  $J$  = 8.6 Hz, 2H).  $^{13}\text{C}$  NMR (125.8 MHz, DMSO- $d_6$ )  $\delta$  165.10, 163.16, 136.22, 114.84.  $^{11}\text{B}$  NMR (128.4 MHz, acetone- $d_6$ )  $\delta$  29.1 (m).



**(3-(Dimethylamino)phenyl)trifluoroborate (Table 1, entry 9).**<sup>2</sup> Following general procedure A, a mixture of 4-bromobenzaldehyde (277 mg, 1.5 mmol), XPhos-Pd-

G2 preformed catalyst (5.89 mg, 7.5  $\mu\text{mol}$ ), XPhos (7.14 mg, 15  $\mu\text{mol}$ ), KOAc (441 mg, 4.5 mmol), and tetrakis(dimethylamino)diboron (890 mg, 1.03 mL, 4.5 mmol), was heated to 60  $^{\circ}\text{C}$  in MeOH (7.5 mL) for 6 h. The title compound was obtained as a white solid in 90% yield (306 mg). mp > 225  $^{\circ}\text{C}$ .  $^1\text{H}$  NMR (500 MHz, acetone- $d_6$ )  $\delta$  8.20 (s, 1H), 7.71 (t,  $J = 7.1$  Hz, 2H), 7.20 (t,  $J = 7.4$  Hz, 2H), 3.81 (s, 6H).  $^{13}\text{C}$  NMR (125.8 MHz, DMSO- $d_6$ )  $\delta$  168.1, 136.9, 132.9, 132.9, 128.1, 127.1, 126.7, 52.2).  $^{11}\text{B}$  NMR (128.4 MHz, acetone- $d_6$ )  $\delta$  3.8 (m).  $^{19}\text{F}$  NMR (338.8 MHz, acetone- $d_6$ )  $\delta$  -143.2.



**Potassium (3-Hydroxyphenyl)trifluoroborate (Table 1, entry 10).**<sup>5</sup>

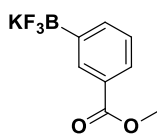
Following general procedure A, a mixture of 3-chlorophenol (193 mg, 160  $\mu\text{L}$ , 1.5 mmol), XPhos-Pd-G2 preformed catalyst (5.89 mg, 7.5  $\mu\text{mol}$ ), XPhos (7.14 mg, 15  $\mu\text{mol}$ ), KOAc (441 mg, 4.5 mmol), and tetrakis(dimethylamino)diboron (890 mg, 1.03 mL, 4.5 mmol), was heated to 60  $^{\circ}\text{C}$  in MeOH (7.5 mL) for 5 h. The title compound was obtained as a white solid in 84% yield (252 mg). Spectral data were in accordance with those published. mp = 185  $^{\circ}\text{C}$  dec.  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  8.51 (s, 1H), 6.87 (t,  $J = 7.5$  Hz, 1H), 6.80 – 6.72 (m, 2H), 6.42 (d,  $J = 7.5$  Hz, 1H).  $^{13}\text{C}$  NMR (125.8 MHz, DMSO- $d_6$ )  $\delta$  156.3, 127.7, 122.9, 119.0, 112.5.  $^{11}\text{B}$  NMR (128.4 MHz, acetone- $d_6$ )  $\delta$  4.1.  $^{19}\text{F}$  NMR (282 MHz, acetone- $d_6$ )  $\delta$  -141.9.



**Potassium 3-Formylphenyl-trifluoroborate (Table 1, entry 11).**<sup>6</sup> Following

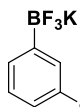
general procedure A, a mixture of 2-(3-bromophenyl)-1,3-dioxolane (344 mg, 130 mL,

1.5 mmol), XPhos-Pd-G2 preformed catalyst (5.89 mg, 7.5  $\mu\text{mol}$ ), XPhos (7.14 mg, 15  $\mu\text{mol}$ ), KOAc (441 mg, 4.5 mmol), and tetrakis(dimethylamino)diboron (890 mg, 1.03 mL, 4.5 mmol), was heated to 60  $^{\circ}\text{C}$  in MeOH (7.5 mL) for 5 h. After the standard workup, the concentrated crude boronic acid was taken up in acetone (5 mL) to which HCl (1 mL, 1 M) was added. The mixture was stirred for 1 h at which time EtOAc (5 mL) was added, and the organic phase was separated. The aqueous phase was extracted with EtOAc (4 x 5 mL). The combined organic layers were washed with brine, dried ( $\text{MgSO}_4$ ), filtered, and concentrated in vacuo. The crude mixture was then converted to the potassium trifluoroborate salt following General Procedure A. The title compound was obtained as a white solid in 96% yield (305 mg). Spectral data were in accordance with those published. mp = 179  $^{\circ}\text{C}$  dec.  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO}-d_6$ )  $\delta$  9.95 (s, 1H), 7.89 (s, 1H), 7.67 (d,  $J = 7.2$  Hz, 1H), 7.60 (d,  $J = 7.6$  Hz, 1H), 7.34 (t,  $J = 7.4$  Hz, 1H).  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{DMSO}-d_6$ )  $\delta$  194.3, 137.9, 134.7, 133.4, 127.1, 126.3.  $^{11}\text{B}$  NMR (128.4 MHz,  $\text{acetone}-d_6$ )  $\delta$  4.0.  $^{19}\text{F}$  NMR (282 MHz,  $\text{acetone}-d_6$ )  $\delta$  -142.8.

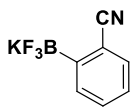


**Potassium (3-(Methoxycarbonyl)phenyl)trifluoroborate (Table 1, entry 12).**<sup>1</sup> Following general procedure A, a mixture of methyl 3-bromobenzoate (323 mg, 1.5 mmol), XPhos-Pd-G2 preformed catalyst (5.89 mg, 7.5  $\mu\text{mol}$ ), XPhos (7.14 mg, 15  $\mu\text{mol}$ ), KOAc (441 mg, 4.5 mmol), and tetrakis(dimethylamino)diboron (890 mg, 1.03 mL, 4.5 mmol), was heated to 60  $^{\circ}\text{C}$  in MeOH (7.5 mL) for 3 h. The title compound was obtained as a white solid in 84% yield (216 mg). mp > 225  $^{\circ}\text{C}$ . Spectral data were in accordance with those of published results.  $^1\text{H}$  NMR (500 MHz,  $\text{acetone}-d_6$ )  $\delta$  8.20 (s,

1H), 7.71 (t,  $J = 7.3$  Hz, 2H), 7.21 (t,  $J = 7.4$  Hz, 1H), 3.81, (s, 3H).  $^{13}\text{C}$  NMR (125.8 MHz, DMSO- $d_6$ )  $\delta$  168.1, 136.9, 132.1, 128.1, 127.1, 126.7, 52.2.  $^{11}\text{B}$  NMR (128.4 MHz, acetone- $d_6$ )  $\delta$  3.9.  $^{19}\text{F}$  NMR (338.8 MHz, acetone- $d_6$ )  $\delta$  -143.2.

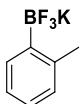


**Potassium (3-Cyanophenyl)trifluoroborate (Table 1, entry 13).**<sup>2</sup> Following general procedure A, a mixture of 3-bromobenzonitrile (273 mg, 1.5 mmol), XPhos-Pd-G2 preformed catalyst (5.89 mg, 7.5  $\mu\text{mol}$ ), XPhos (7.14 mg, 15  $\mu\text{mol}$ ), KOAc (441 mg, 4.5 mmol), and tetrakis(dimethylamino)diboron (890 mg, 1.03 mL, 4.5 mmol), was heated to 60  $^{\circ}\text{C}$  in MeOH (7.5 mL) for 6 h. The title compound was obtained as a white solid in 91% yield (286 mg). Spectral data were in accordance with those of a commercially available sample. mp = 200 – 201  $^{\circ}\text{C}$ .  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  7.72 – 7.56 (m, 2H), 7.50 (d,  $J = 7.4$  Hz, 1H), 7.32 (t,  $J = 7.4$  Hz, 1H).  $^{13}\text{C}$  NMR (125.8 MHz, DMSO- $d_6$ )  $\delta$  136.1, 134.7, 129.0, 127.5, 120.3, 109.4.  $^{11}\text{B}$  NMR (128.4 MHz, acetone- $d_6$ )  $\delta$  0.7 (q,  $J = 49.5$  Hz).  $^{19}\text{F}$  NMR (338.8 MHz, acetone- $d_6$ )  $\delta$  -143.8.

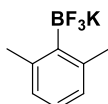


**Potassium (2-Cyanophenyl)trifluoroborate (Table 1, entry 14).**<sup>1</sup> Following general procedure A, a mixture of 2-bromobenzonitrile (273 mg, 1.5 mmol), XPhos-Pd-G2 preformed catalyst (5.89 mg, 7.5  $\mu\text{mol}$ ), XPhos (7.14 mg, 15  $\mu\text{mol}$ ), KOAc (441 mg, 4.5 mmol), and tetrakis(dimethylamino)diboron (890 mg, 1.03 mL, 4.5 mmol), was heated to 60  $^{\circ}\text{C}$  in MeOH (7.5 mL) for 7 h. The title compound was obtained as a white solid in 4% yield (12.5 mg). Spectral data were in accordance with those published. mp =

230 °C dec. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ 7.52 (d, *J* = 7.1 Hz, 1H), 7.50 (d, *J* = 7.7 Hz, 1H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.22 (td, *J* = 7.5, 1.3 Hz, 1H). <sup>13</sup>C NMR (125.8 MHz, DMSO-*d*<sub>6</sub>) δ 132.3, 132.0, 130.6, 126.0, 121.0, 114.3. <sup>11</sup>B NMR (128.4 MHz, acetone-*d*<sub>6</sub>) δ 0.11 (q, *J* = 50.0 Hz). <sup>19</sup>F NMR (282 MHz, acetone-*d*<sub>6</sub>) δ -142.9.

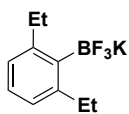


**Potassium o-Tolyltrifluoroborate (Table 1, entry 15).**<sup>1</sup> Following general procedure A, a mixture of 1-bromo-2-methylbenzene (256 mg, 180 μL, 1.5 mmol), XPhos-Pd-G2 preformed catalyst (5.89 mg, 7.5 μmol), XPhos (7.14 mg, 15 μmol), KOAc (441 mg, 4.5 mmol), and tetrakis(dimethylamino)diboron (890 mg, 1.03 mL, 4.5 mmol), was heated to 60 °C in MeOH (7.5 mL) for 26 h. The title compound was obtained as an off-white solid in 75% yield (224 mg). Spectral data were in accordance with those of published results. mp 210-213 °C. <sup>1</sup>H NMR (500 MHz, acetone-*d*<sub>6</sub>) δ 7.46 (d, *J* = 6.1 Hz, 1H), 6.88 (d, *J* = 13.0 Hz, 3H), 2.38 (s, 3H). <sup>13</sup>C NMR (125.8 MHz, DMSO-*d*<sub>6</sub>) δ 141.1, 132.2, 128.8, 125.6, 123.9, 22.3. <sup>11</sup>B NMR (128.4 MHz, acetone-*d*<sub>6</sub>) δ 4.3 (q, *J* = 57.6 Hz). <sup>19</sup>F NMR (338.8 MHz, acetone-*d*<sub>6</sub>) δ -140.6.



**Potassium (2,6-Dimethylphenyl)trifluoroborate (Table 1, entry 16).**<sup>1</sup> Following general procedure A, a mixture of 2-chloro-1,3-dimethylbenzene (211 mg, 1.5 mmol), XPhos-Pd-G2 preformed catalyst (5.89 mg, 7.5 μmol), XPhos (7.14 mg, 15 μmol), KOAc (441 mg, 4.5 mmol), and tetrakis(dimethylamino)diboron (890 mg, 1.03 mL, 4.5 mmol), was heated to 60 °C in MeOH (7.5 mL) for 22 h. The title compound was

obtained as a white solid in 81% yield (259 mg). Spectral data were in accordance with those of published results. mp > 225 °C. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ 6.80 – 6.74 (m, 1H), 6.67 (d, *J* = 7.4 Hz, 2H), 2.30 (s, 6H). <sup>13</sup>C NMR (125.8 MHz, DMSO-*d*<sub>6</sub>) δ 140.9, 126.5, 124.5, 23.3 (d, *J* = 2.52 Hz). <sup>11</sup>B NMR (128.4 MHz, acetone-*d*<sub>6</sub>) δ 4.8 (q, *J* = 56.3 Hz). <sup>19</sup>F NMR (282 MHz, acetone-*d*<sub>6</sub>) δ -132.3.



**Potassium (2,6-Diethylphenyl)trifluoroborate (Table 1, entry 17).**

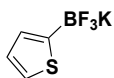
Following general procedure A, a mixture of 2-bromo-1,3-diethylbenzene (253 μL, 1.5 mmol), XPhos-Pd-G2 preformed catalyst (5.89 mg, 7.5 μmol), XPhos (7.14 mg, 15 μmol), KOAc (441 mg, 4.5 mmol), and tetrakis(dimethylamino)diboron (890 mg, 1.03 mL, 4.5 mmol), was heated to 60 °C in MeOH (7.5 mL) for 22 h. The title compound was obtained as a white solid in 43% yield (156 mg). Spectral data were in accordance with those of published results. mp > 225 °C. <sup>1</sup>H NMR (500 MHz, acetone-*d*<sub>6</sub>) δ 6.84 (t, *J* = 7.4 Hz, 1H), 6.71 (d, *J* = 7.4 Hz, 2H), 2.72 (q, *J* = 7.4 Hz, 4H), 1.06 (t, *J* = 7.4 Hz, 6H). <sup>13</sup>C NMR (125.8 MHz, DMSO-*d*<sub>6</sub>) δ 147.9, 125.3, 124.8, 28.9, 17.7. <sup>11</sup>B NMR (128.4 MHz, acetone-*d*<sub>6</sub>) δ 4.7 (q, *J* = 56.5 Hz). <sup>19</sup>F NMR (282 MHz, acetone-*d*<sub>6</sub>) δ -131.1.



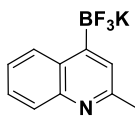
**Potassium 3-Trifluoroborato-thiophene (Table 2, entry 1).**<sup>2</sup> Following general procedure A, a mixture of 3-chlorothiophene (140 μL, 1.5 mmol), XPhos-Pd-G2 preformed catalyst (5.89 mg, 7.5 μmol), XPhos (7.14 mg, 15 μmol), KOAc (441 mg, 4.5 mmol), and tetrakis(dimethylamino)diboron (890 mg, 1.03 mL, 4.5 mmol), was heated to



60 °C in MeOH (7.5 mL) for 5 h. The title compound was obtained as a pale yellow solid in 45% yield (127 mg). Spectral data were in accordance with those published. mp > 225 °C. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ 7.19 (s, 1H), 7.03 (s, 1H), 7.01 (d, *J* = 4.6 Hz, 1H). <sup>13</sup>C NMR (125.8 MHz, DMSO-*d*<sub>6</sub>) δ 131.9, 124.4, 122.6. <sup>11</sup>B NMR (128.4 MHz, acetone-*d*<sub>6</sub>) δ 0.7 (q, *J* = 47.9 Hz). <sup>19</sup>F NMR (282 MHz, acetone-*d*<sub>6</sub>) δ -139.1.

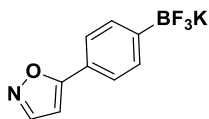


**Potassium 2-Trifluoroborato-thiophene (Table 2, entry 2).**<sup>6</sup> Following general procedure A, a mixture of 2-chlorothiophene (140 μL, 1.5 mmol), XPhos-Pd-G2 preformed catalyst (5.89 mg, 7.5 μmol), XPhos (7.14 mg, 15 μmol), KOAc (441 mg, 4.5 mmol), and tetrakis(dimethylamino)diboron (890 mg, 1.03 mL, 4.5 mmol), was heated to 60 °C in MeOH (7.5 mL) for 5 h. The title compound was obtained as a pale yellow solid in 5% yield (13 mg). Spectral data were in accordance with those published. mp = 240 °C dec. <sup>1</sup>H NMR (500 MHz, acetone-*d*<sub>6</sub>) δ 7.13 (d, *J* = 4.3 Hz, 1H), 6.95 (s, 1H), 6.88 (s, 1H). <sup>13</sup>C NMR (125.8 MHz, acetone-*d*<sub>6</sub>) δ 127.2, 126.1, 123.5. <sup>11</sup>B NMR (128.4 MHz, acetone-*d*<sub>6</sub>) δ 0.4 (q, *J* = 48.0 Hz). <sup>19</sup>F NMR (282 MHz, acetone-*d*<sub>6</sub>) δ -137.5.



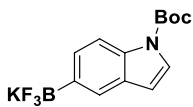
**Potassium (2-Methylquinolin-4-yl)trifluoroborate (Table 2, entry 3).** Following general procedure B, a mixture of 4-chloroquinoline (266 mg, 302 μL, 1.5 mmol), XPhos-Pd-G2 preformed catalyst (5.89 mg, 7.5 μmol), XPhos (7.14 mg, 15 μmol), KOAc (441 mg, 4.5 mmol), and tetrakis(dimethylamino)diboron (890 mg, 1.03 mL, 4.5 mmol), was heated to 60 °C in MeOH (7.5 mL) for 11 h. The title compound was

obtained as a white solid in 58% yield (218 mg) as a mixture of the trifluoroborate and internal salt. As such, reasonable NMR spectra could not be obtained.



**(4-(Isoxazol-5-yl)phenyl)trifluoroborate (Table 2, entry 4).<sup>2</sup>**

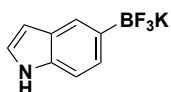
Following general procedure A, a mixture of 5-(4-bromophenyl)isoxazole (336 mg, 1.5 mmol), XPhos-Pd-G2 preformed catalyst (5.89 mg, 7.5  $\mu$ mol), XPhos (7.14 mg, 15  $\mu$ mol), KOAc (441 mg, 4.5 mmol), and tetrakis(dimethylamino)diboron (890 mg, 1.03 mL, 4.5 mmol), was heated to 60 °C in MeOH (7.5 mL) for 5.5 h. The title compound was obtained as an orange solid in 37% yield (140 mg) as a mixture of product and unidentified impurities. mp = 220 °C dec. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  8.57 (s, 1H), 7.61 (d, *J* = 7.7 Hz, 2H), 7.47 (d, *J* = 7.6 Hz, 2H), 6.85 (s, 1H). <sup>13</sup>C NMR (125.8 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  169.7, 151.5, 132.0, 123.7, 98.3. <sup>11</sup>B NMR (128.4 MHz, acetone-*d*<sub>6</sub>)  $\delta$  0.82. <sup>19</sup>F NMR (338.8 MHz, acetone-*d*<sub>6</sub>)  $\delta$  -143.2.



**Potassium 1-(*tert*-Butoxycarbonyl)-indol-5-yl-trifluoroborate (Table**

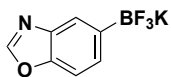
**2, entry 5).<sup>7</sup>** Following general procedure A, a mixture of 1-(*tert*-butoxycarbonyl)-5-bromoindole (445 mg, 1.5 mmol), XPhos-Pd-G2 preformed catalyst (5.89 mg, 7.5  $\mu$ mol), XPhos (7.14 mg, 15  $\mu$ mol), KOAc (441 mg, 4.5 mmol), and tetrakis(dimethylamino)diboron (890 mg, 1.03 mL, 4.5 mmol), was heated to 60 °C in MeOH (7.5 mL) for 4.5 h. The title compound was obtained as a white solid in 96% yield (464 mg). Spectral data were in accordance with those published. mp = 186 °C dec. <sup>1</sup>H

NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ 7.83 (d, *J* = 8.0 Hz, 1H), 7.56 (s, 1H), 7.49 (d, *J* = 3.5 Hz, 1H), 7.35 (d, *J* = 8.2 Hz, 1H), 6.57 (d, *J* = 3.5 Hz, 1H), 1.62 (s, 9H). <sup>13</sup>C NMR (125.8 MHz, DMSO-*d*<sub>6</sub>) δ 149.4, 133.3, 129.2, 128.3, 124.2, 123.6, 112.6, 107.9, 82.9, 27.8. <sup>11</sup>B NMR (128.4 MHz, acetone-*d*<sub>6</sub>) δ 4.7. <sup>19</sup>F NMR (282 MHz, acetone-*d*<sub>6</sub>) δ -141.5.



**Potassium 1H-Indol-5-yl-trifluoroborate (Table 2, entry 6).**<sup>8</sup> Following

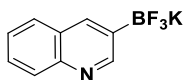
general procedure A, a mixture of 5-bromoindole (294 mg, 1.5 mmol), XPhos-Pd-G2 preformed catalyst (5.89 mg, 7.5 μmol), XPhos (7.14 mg, 15 μmol), KOAc (441 mg, 4.5 mmol), and tetrakis(dimethylamino)diboron (890 mg, 1.03 mL, 4.5 mmol), was heated to 60 °C in MeOH (7.5 mL) for 6 h. The title compound was obtained as a white solid in 70% yield (233 mg). Spectral data were in accordance with those published. mp = 240 °C dec. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ 10.56 (s, 1H), 7.51 (s, 1H), 7.14 – 7.12 (m, 3H), 6.25 (s, 1H). <sup>13</sup>C NMR (125.8 MHz, DMSO-*d*<sub>6</sub>) δ 135.5, 127.6, 126.1, 123.6, 123.1, 109.7, 101.1. <sup>11</sup>B NMR (128.4 MHz, acetone-*d*<sub>6</sub>) δ 2.2. <sup>19</sup>F NMR (282 MHz, acetone-*d*<sub>6</sub>) δ -140.6.



**Potassium 5-Trifluoroborato-benzoxazole (Table 2, entry 7).**<sup>2</sup> Following

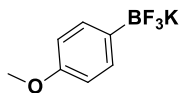
general procedure A, a mixture of 5-chlorobenzoxazole (231 mg, 1.5 mmol), XPhos-Pd-G2 preformed catalyst (5.89 mg, 7.5 μmol), XPhos (7.14 mg, 15 μmol), KOAc (441 mg, 4.5 mmol), and tetrakis(dimethylamino)diboron (890 mg, 1.03 mL, 4.5 mmol), was heated to 60 °C in MeOH (7.5 mL) for 5 h. The title compound was obtained as a brick red solid in 36% yield (122 mg). mp = 200 °C dec. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ

8.51 (s, 1H), 7.65 (s, 1H), 7.43 (q,  $J = 8.0$  Hz, 2H).  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{DMSO-}d_6$ )  $\delta$  152.5, 148.1, 138.7, 128.9, 122.0, 108.6.  $^{11}\text{B}$  NMR (128.4 MHz,  $\text{acetone-}d_6$ )  $\delta$  1.1 (q,  $J = 51.7$  Hz).  $^{19}\text{F}$  NMR (282 MHz,  $\text{acetone-}d_6$ )  $\delta$  -142.0.



**Potassium (Quinolin-3-yl)trifluoroborate (Table 2, entry 8).<sup>8</sup>**

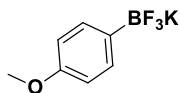
Following general procedure B, a mixture of 3-bromoquinoline (312 mg, 202  $\mu\text{L}$ , 1.5 mmol), XPhos-Pd-G2 preformed catalyst (5.89 mg, 7.5  $\mu\text{mol}$ ), XPhos (7.14 mg, 15  $\mu\text{mol}$ ), KOAc (441 mg, 4.5 mmol), and tetrakis(dimethylamino)diboron (890 mg, 1.03 mL, 4.5 mmol), was heated to 60  $^\circ\text{C}$  in MeOH (7.5 mL) for 5 h. The title compound was obtained as a white solid in 64% yield (225 mg). Spectral data were in accordance with those published. mp > 225  $^\circ\text{C}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}d_6$ )  $\delta$  8.86 (s, 1H), 8.11 (s, 1H), 7.89 (d,  $J = 8.3$  Hz, 1H), 7.83 (d,  $J = 7.9$  Hz, 1H), 7.58 (t,  $J = 7.4$  Hz, 1H), 7.46 (t,  $J = 7.2$  Hz, 1H).  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{DMSO-}d_6$ )  $\delta$  155.2, 146.8, 137.4, 128.5, 128.2, 127.6, 127.4, 125.1.  $^{11}\text{B}$  NMR (128.4 MHz,  $\text{acetone-}d_6$ )  $\delta$  0.85 (q,  $J = 49.3$ ).  $^{19}\text{F}$  NMR (282 MHz,  $\text{acetone-}d_6$ )  $\delta$  -142.6.



**Potassium 4-Methoxyphenyl-trifluoroborate (Table 3, entry 2).<sup>1</sup>**

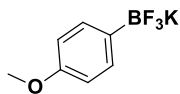
Following general procedure A, a mixture of 4-bromoanisole (280 mg, 187  $\mu\text{L}$ , 1.5 mmol), XPhos-Pd-G2 preformed catalyst (5.89 mg, 7.5  $\mu\text{mol}$ ), XPhos (7.14 mg, 15  $\mu\text{mol}$ ), KOAc (441 mg, 4.5 mmol), and tetrakis(dimethylamino)diboron (890 mg, 1.03 mL, 4.5 mmol), was heated to 60  $^\circ\text{C}$  in MeOH (7.5 mL) for 5 h. The title compound was obtained as a white solid in 87% yield (279 mg). Spectral data were in accordance with

those of published results. mp > 225 °C. <sup>1</sup>H NMR (500 MHz, acetone-*d*<sub>6</sub>) δ 7.37 (d, *J* = 7.7 Hz, 2H), 6.67 (d, *J* = 7.8 Hz, 2H), 3.69 (s, 3H). <sup>13</sup>C NMR (125.8 MHz, DMSO-*d*<sub>6</sub>) δ 157.8, 132.9, 112.5, 55.1. <sup>11</sup>B NMR (128.4 MHz, acetone-*d*<sub>6</sub>) δ 4.3 (m). <sup>19</sup>F NMR (338.8 MHz, acetone-*d*<sub>6</sub>) δ -141.8.



**Potassium 4-Methoxyphenyl-trifluoroborate (Table 3, entry 3).<sup>1</sup>**

Following general procedure A, a mixture of 4-iodoanisole (349 mg, 1.5 mmol), XPhos-Pd-G2 preformed catalyst (5.89 mg, 7.5 μmol), XPhos (7.14 mg, 15 μmol), KOAc (441 mg, 4.5 mmol), and tetrakis(dimethylamino)diboron (890 mg, 1.03 mL, 4.5 mmol), was heated to 60 °C in MeOH (7.5 mL) for 9 h. The title compound was obtained as a white solid in 51% yield (163 mg). Spectral data were in accordance with those of published results. mp > 225 °C. <sup>1</sup>H NMR (500 MHz, acetone-*d*<sub>6</sub>) δ 7.37 (d, *J* = 7.2 Hz, 2H), 6.67 (d, *J* = 7.2 Hz, 2H), 3.69 (s, 3H). <sup>13</sup>C NMR (125.8 MHz, DMSO-*d*<sub>6</sub>) δ 157.8, 132.8, 112.5, 55.1. <sup>11</sup>B NMR (128.4 MHz, acetone-*d*<sub>6</sub>) δ 4.3 (m). <sup>19</sup>F NMR (338.8 MHz, acetone-*d*<sub>6</sub>) δ -141.8.



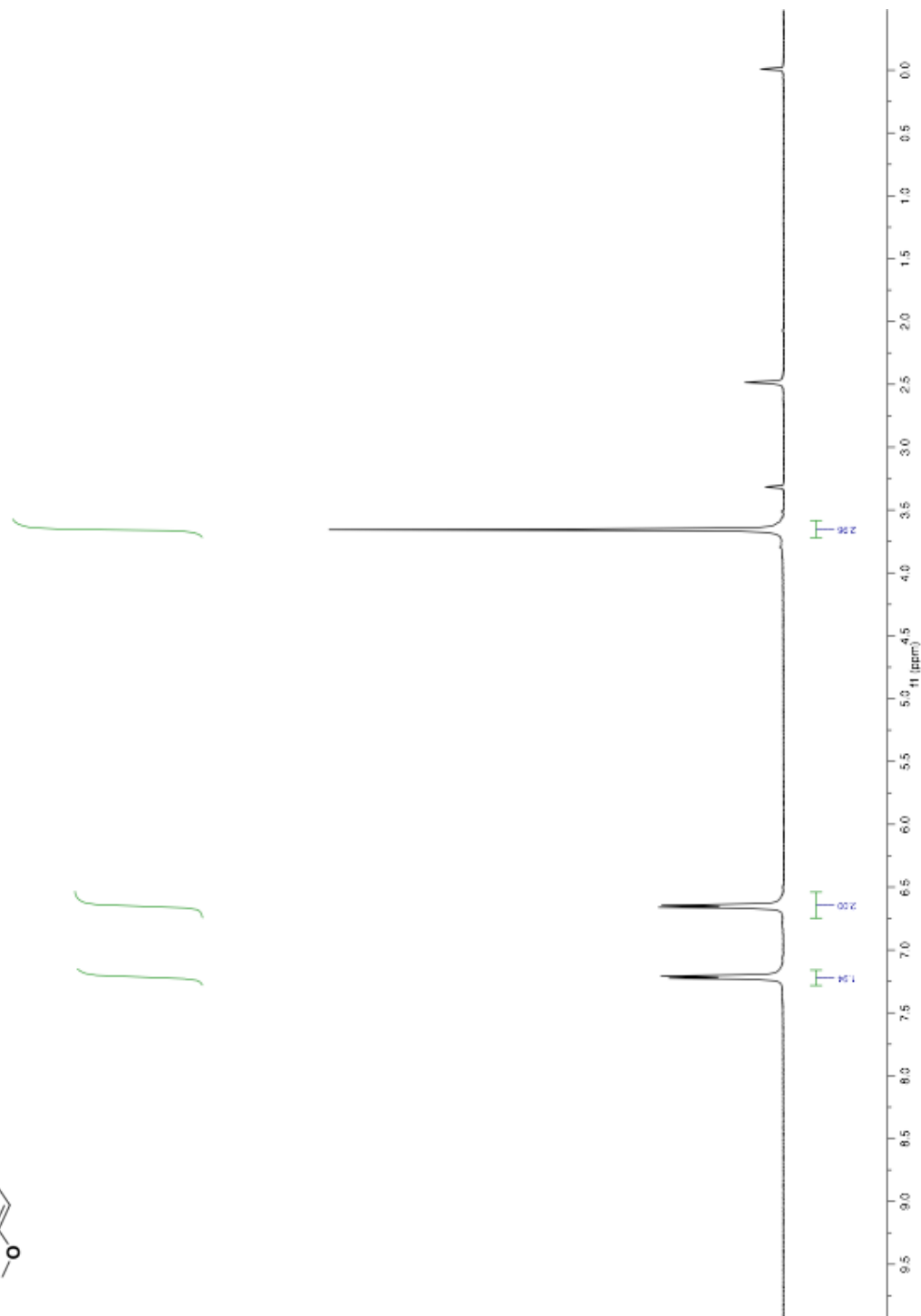
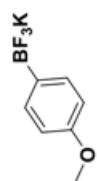
**Potassium 4-Methoxyphenyl-trifluoroborate (Table 3, entry 4).<sup>1</sup>**

Following general procedure A, a mixture 4-methoxyphenyl trifluoromethanesulfonate (384 mg, 271 μL, 1.5 mmol), XPhos-Pd-G2 preformed catalyst (5.89 mg, 7.5 μmol), XPhos (7.14 mg, 15 μmol), KOAc (441 mg, 4.5 mmol), and tetrakis(dimethylamino)diboron (890 mg, 1.03 mL, 4.5 mmol), was heated to 60 °C in

MeOH (7.5 mL) for 6.5 h. The title compound was obtained as a white solid in 98% yield (314 mg). Spectral data were in accordance with those of published results. mp > 225 °C.  $^1\text{H}$  NMR (500 MHz, acetone- $d_6$ )  $\delta$  7.37 (d,  $J$  = 7.5 Hz, 2H), 6.67 (d,  $J$  = 7.6 Hz, 2H), 3.69 (s, 3H).  $^{13}\text{C}$  NMR (125.8 MHz, DMSO- $d_6$ )  $\delta$  157.80, 132.84, 112.45, 55.12.  $^{11}\text{B}$  NMR (128.4 MHz, acetone- $d_6$ )  $\delta$  4.3 (m).  $^{19}\text{F}$  NMR (338.8 MHz, acetone- $d_6$ )  $\delta$  -141.8.

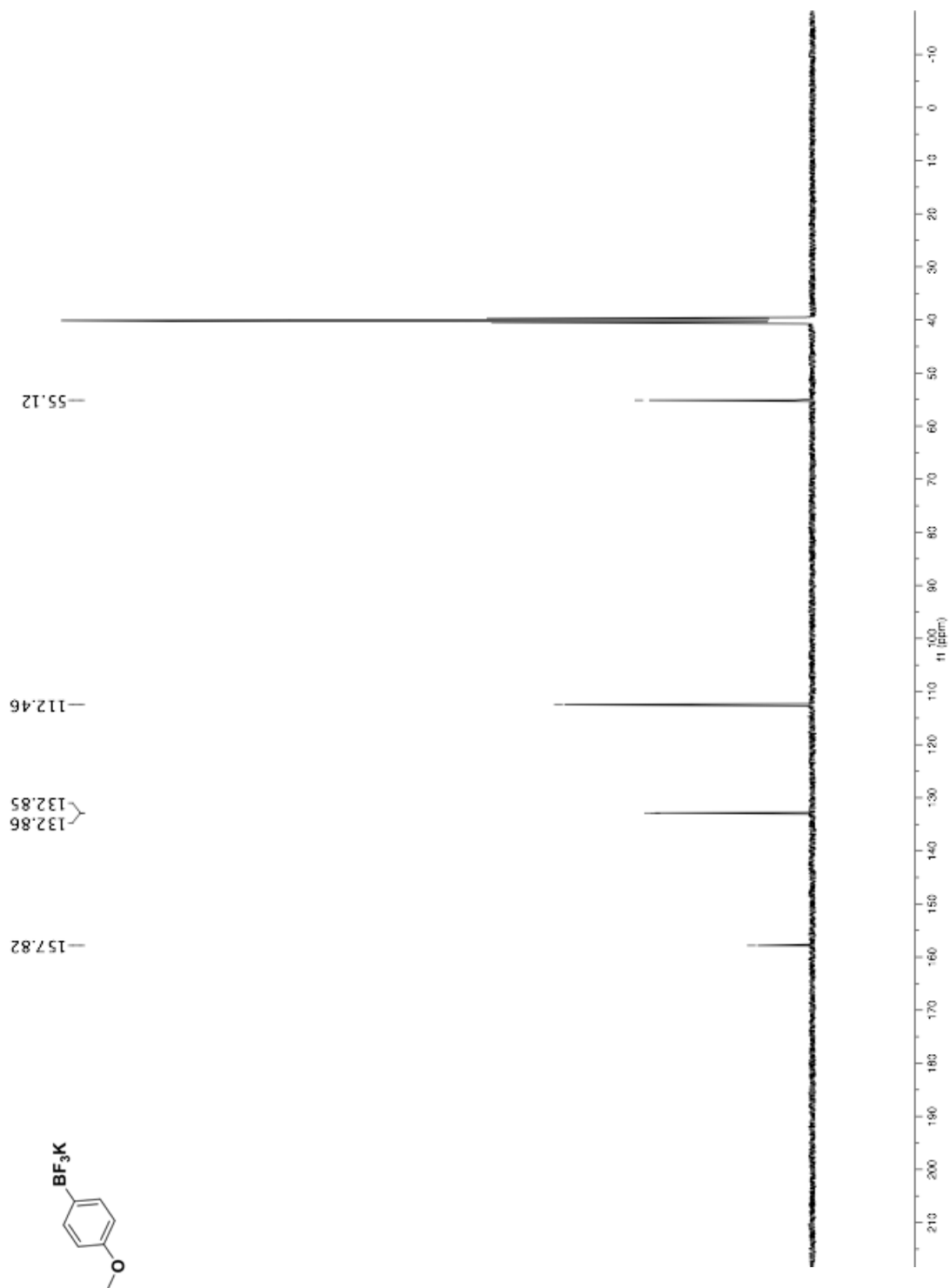
## References:

- (1) Molander, G. A.; Trice, S. L. J.; Dreher, S. D. *J. Am. Chem. Soc.* **2010**, *132*, 17701-17703.
- (2) Molander, G. A.; Trice, S. L. J.; Kennedy, S. M.; Dreher, S. D.; Tudge, M. T. *J. Am. Chem. Soc.* Submitted for publication.
- (3) Schmidt, B.; Hoelter, F. *Org. Biomol. Chem.* **2011**, *9*, 4914 - 4920.
- (4) Molander, G. A.; Cavalcanti, L. N.; Canturk, B.; Pan, P.; Kennedy, L. E. *J. Org. Chem.* **2009**, *74*, 7364-7369.
- (5) Park, Y. H.; Ahn, H. R.; Canturk, B.; Jeon, S.; Lee, S.; Kang, H.; Molander, G. A.; Ham, J. *Org. Lett.* **2008**, *10*, 1215-1218.
- (6) Oliveira, R. A.; Silva, R. O.; Menezes, P. H.; Molander, G. A. *Magn. Reson. Chem.* **2009**, *47*, 873 - 878.
- (7) Delcamp, J. H.; Brucks, A. P.; White, M. C. *J. Am. Chem. Soc.* **2008**, *130*, 11270 - 11271.
- (8) Molander, G. A.; Canturk, B.; Kennedy, L. E. *J. Org. Chem.* **2009**, *74*, 973 - 980.

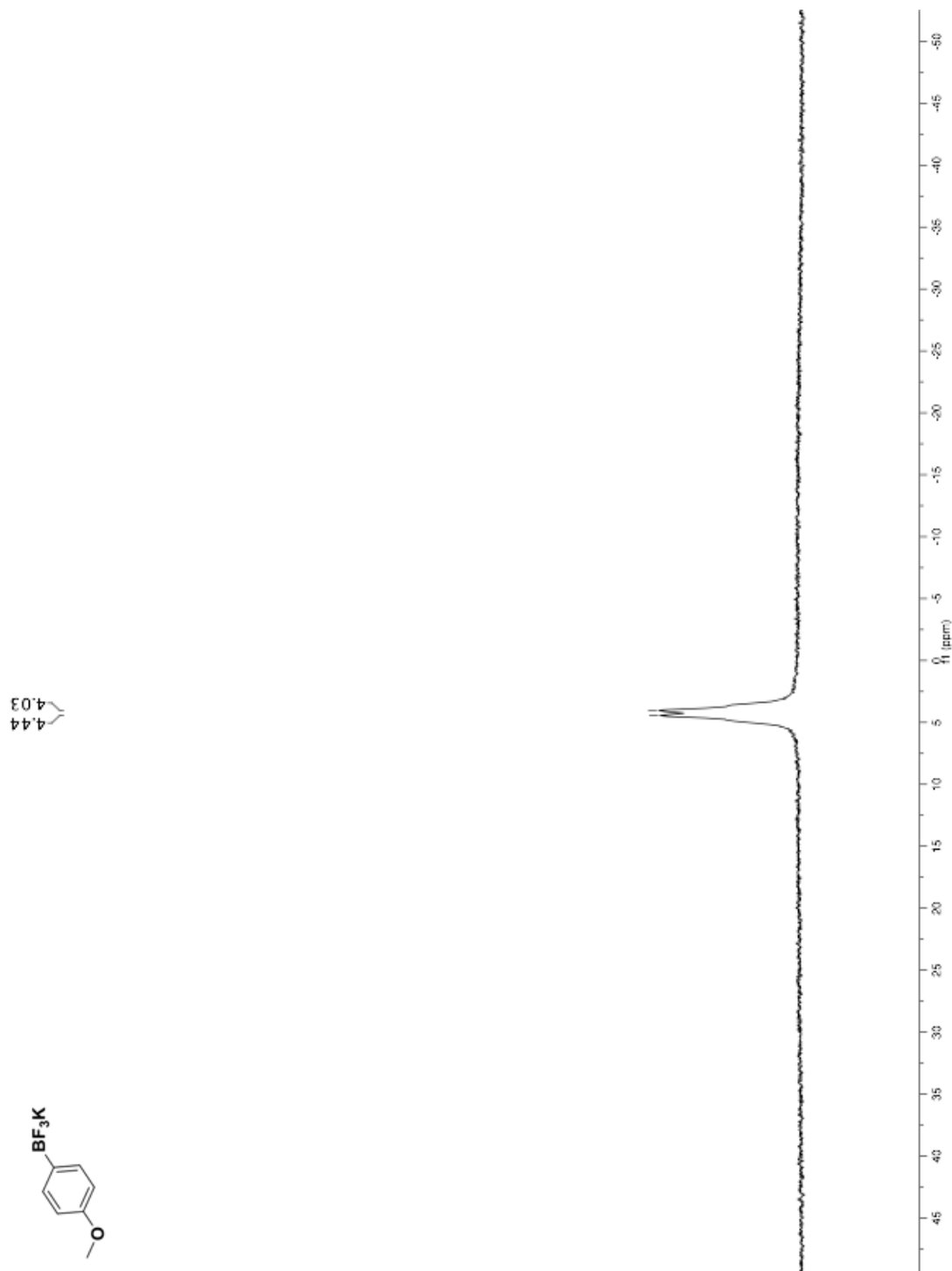


<sup>1</sup>H NMR Spectra (500 MHz, acetone-*d*<sub>6</sub>) **Potassium 4-Methoxyphenyl-trifluoroborate** (Table 1, entry 1)

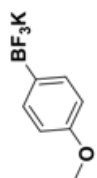




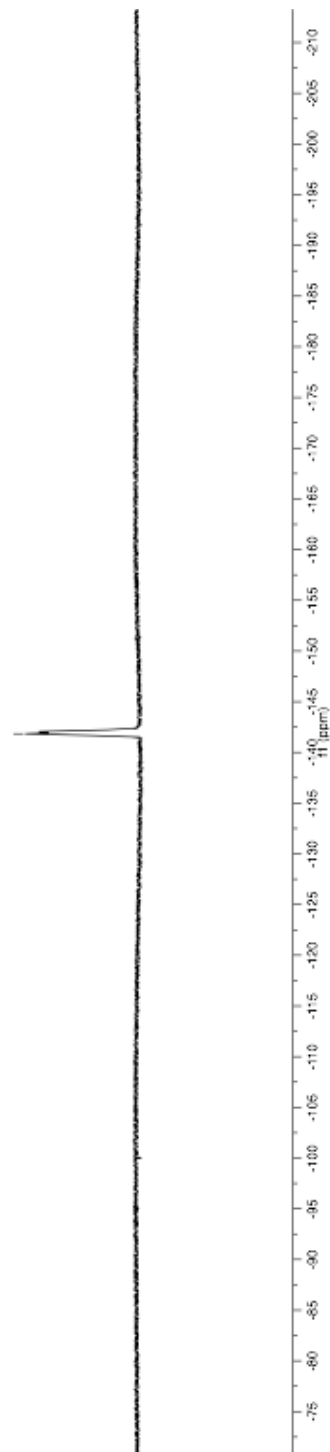
$^{13}\text{C}$  NMR Spectra (125.8 MHz,  $\text{DMSO-}d_6$ ) Potassium 4-Methoxyphenyl-trifluoroborate (Table 1, entry 1)



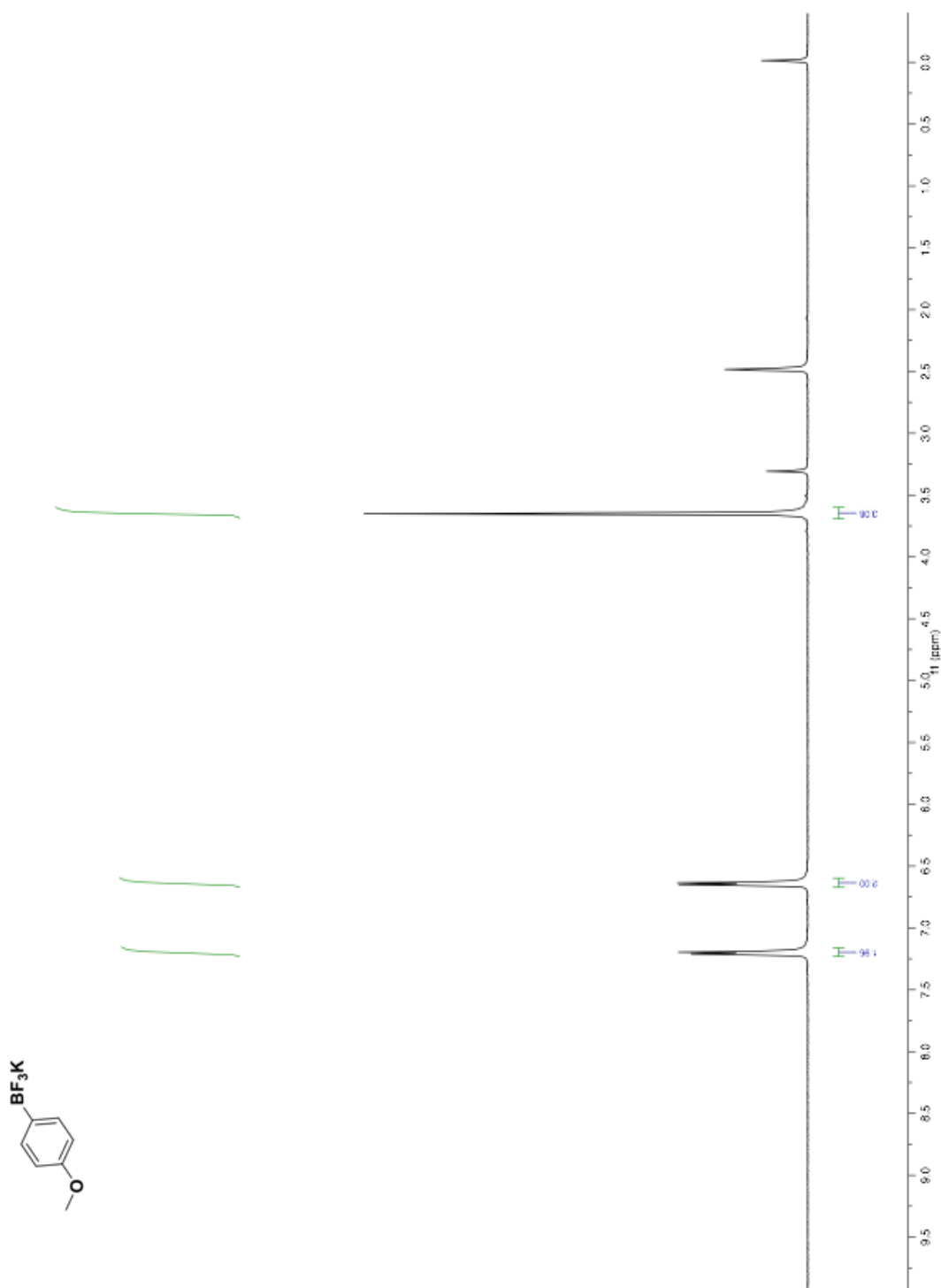
$^{11}\text{B}$  NMR Spectra (128.4 MHz, acetone- $d_6$ ) **Potassium 4-Methoxyphenyltrifluoroborate (Table 1, entry 1)**



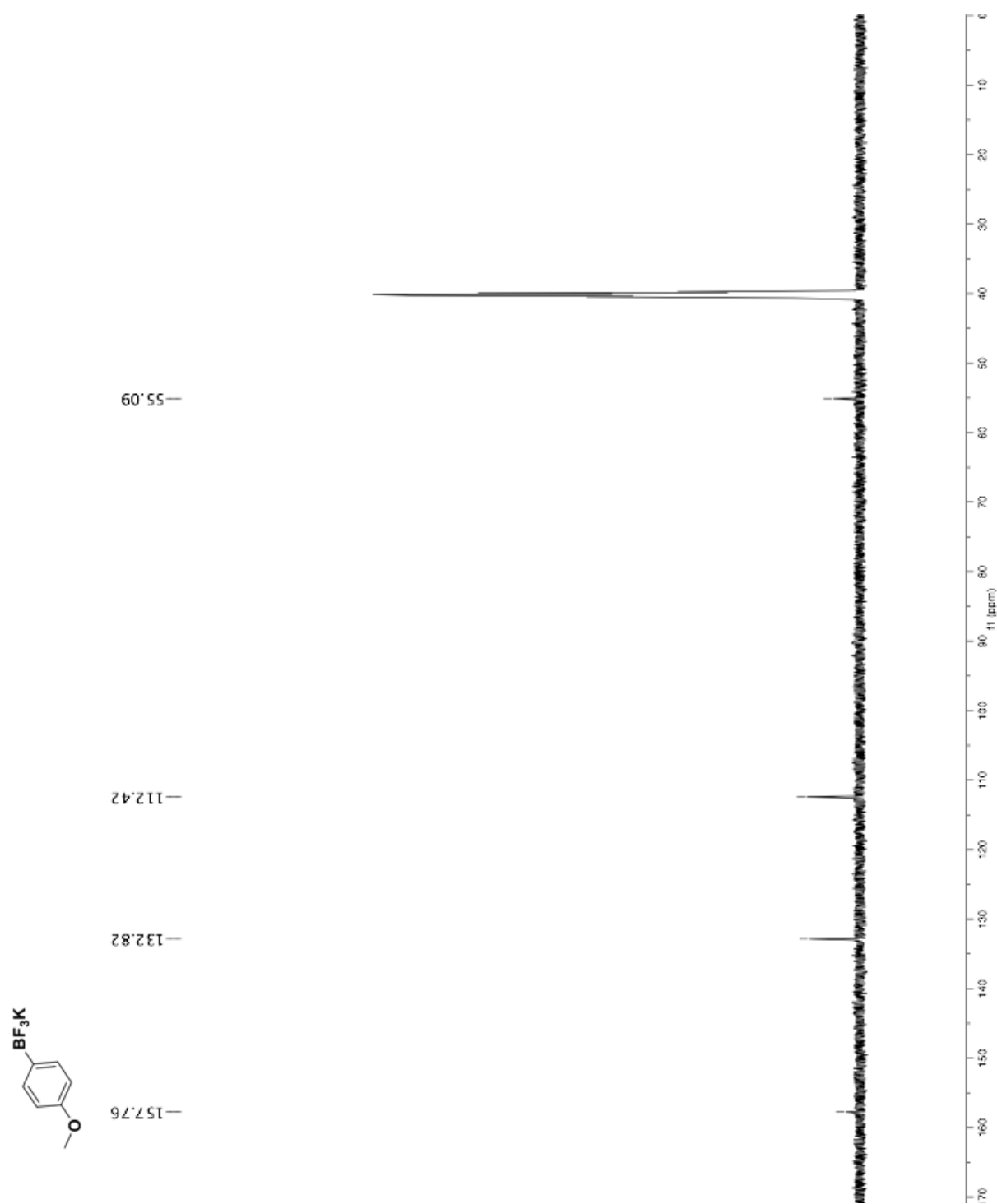
—141.84



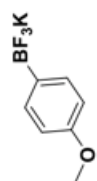
$^{19}\text{F}$  NMR Spectra (338.8 MHz, acetone- $d_6$ ) **Potassium 4-Methoxyphenyltrifluoroborate** (Table 1, entry 1)



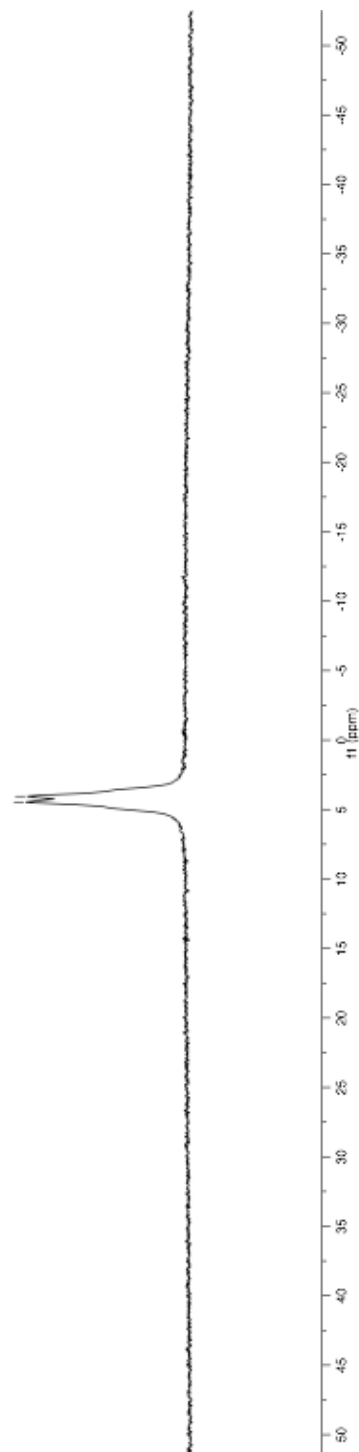
<sup>1</sup>H NMR Spectra (500 MHz, acetone-*d*<sub>6</sub>) Potassium 4-Methoxyphenyl-trifluoroborate (Table 1, entry 1<sup>a</sup>)



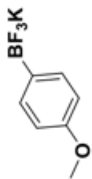
$^{13}\text{C}$  NMR Spectra (125.8 MHz,  $\text{DMSO-}d_6$ ) Potassium 4-Methoxyphenyltrifluoroborate (Table 1, entry 1<sup>a</sup>)



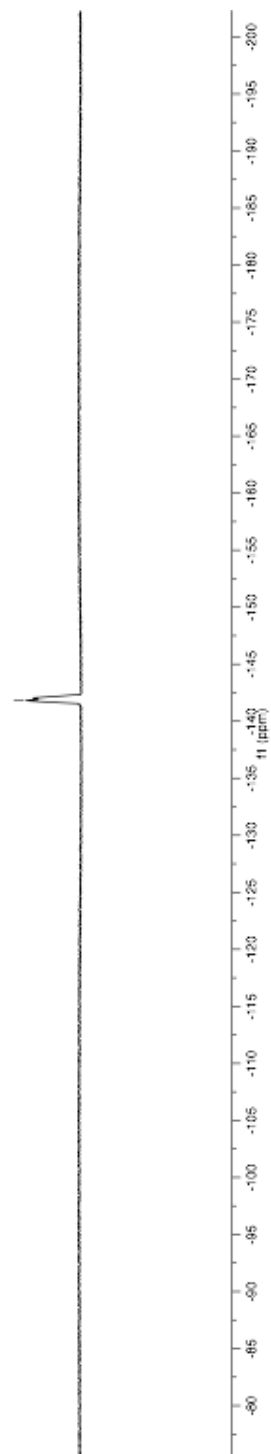
4.46  
4.06



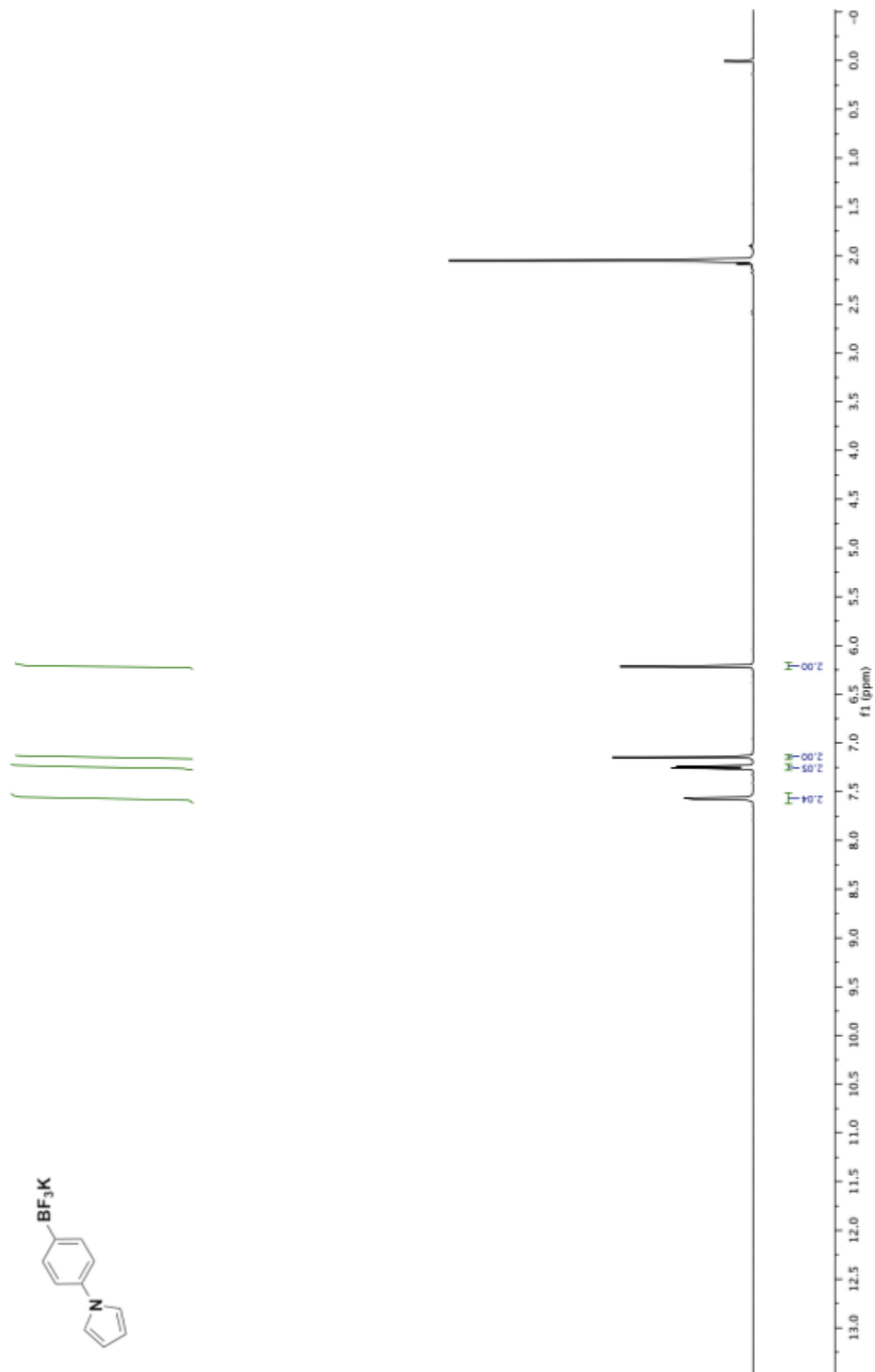
<sup>11</sup>B NMR Spectra (128.4 MHz, acetone-*d*<sub>6</sub>) **Potassium 4-Methoxyphenyltrifluoroborate (Table 1, entry 1<sup>a</sup>)**



—141.82

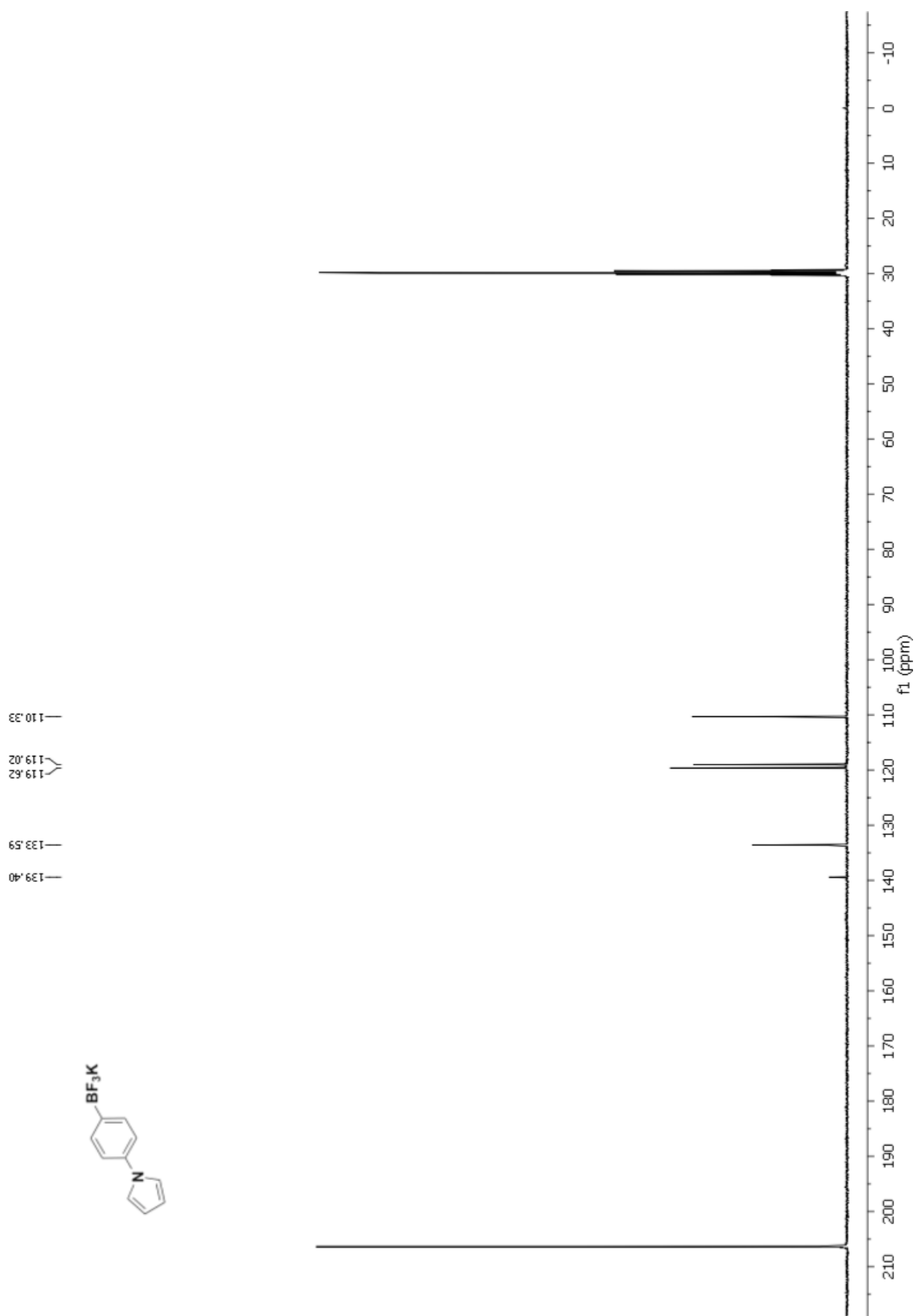


$^{19}\text{F}$  NMR Spectra (338.8 MHz, acetone- $d_6$ ) Potassium 4-Methoxyphenyltrifluoroborate (Table 1, entry 1<sup>a</sup>)

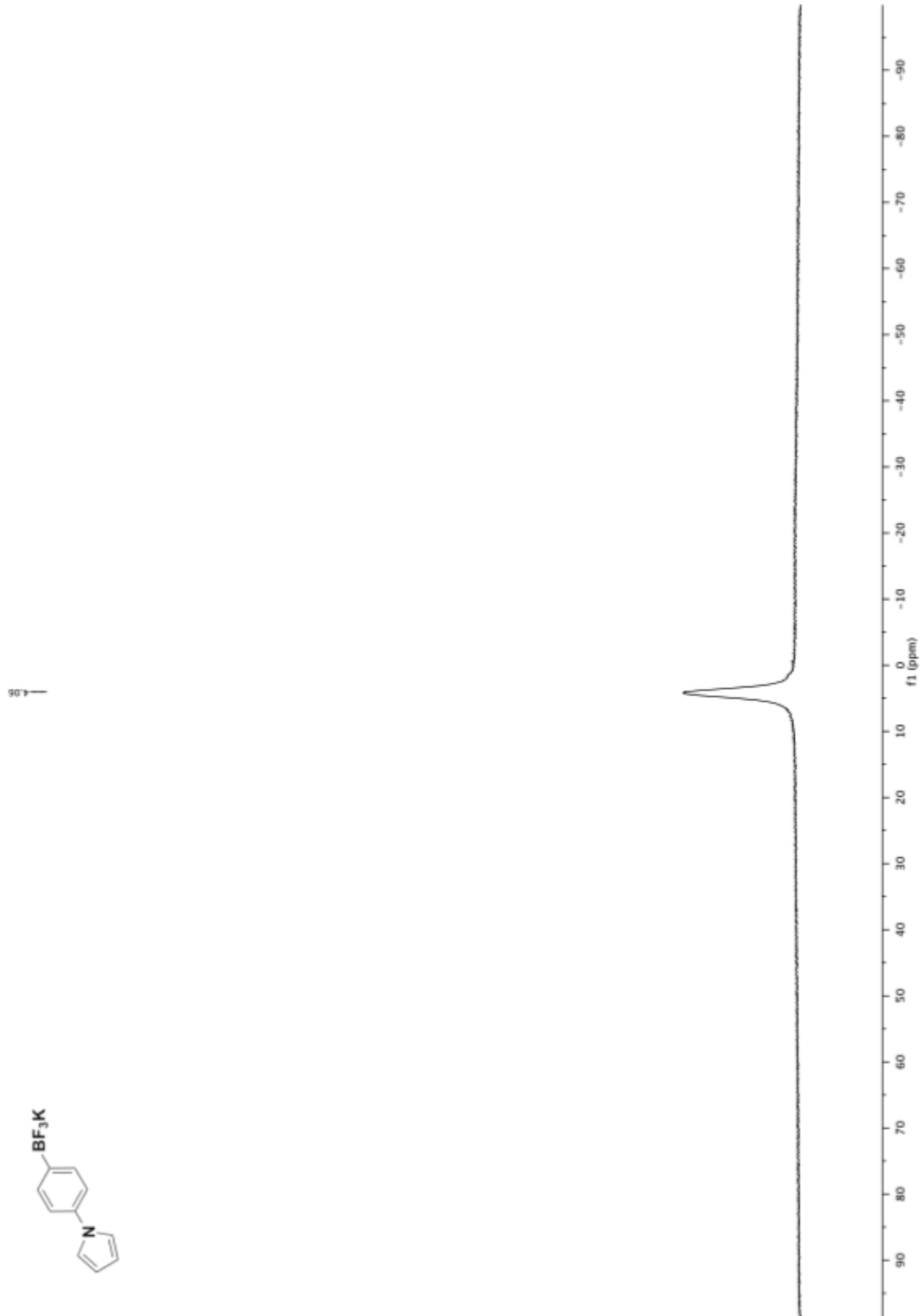


<sup>1</sup>H NMR Spectra (500 MHz, DMSO-d<sub>6</sub>) Potassium 4-(1H-Pyrrol-1-yl)phenyl-trifluoroborate (Table 1, entry 2)

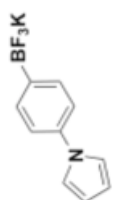




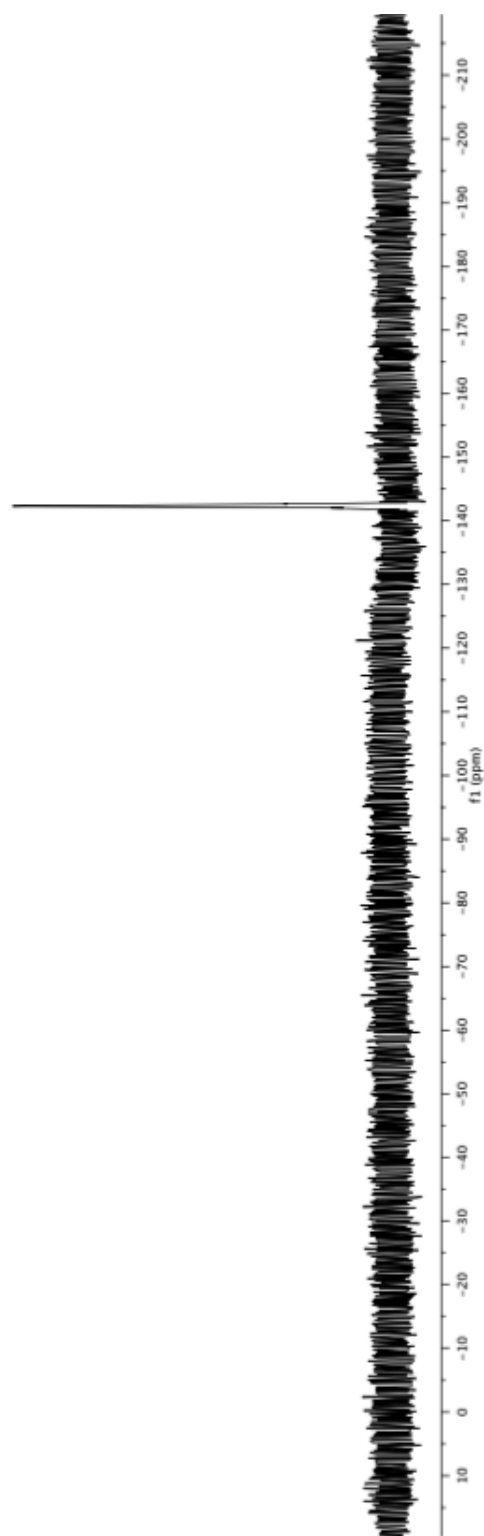
$^{13}\text{C}$  NMR Spectra (125.8 MHz,  $\text{DMSO-}d_6$ ) Potassium 4-(1H-Pyrrol-1-yl)phenyl-trifluoroborate (Table 1, entry 2)



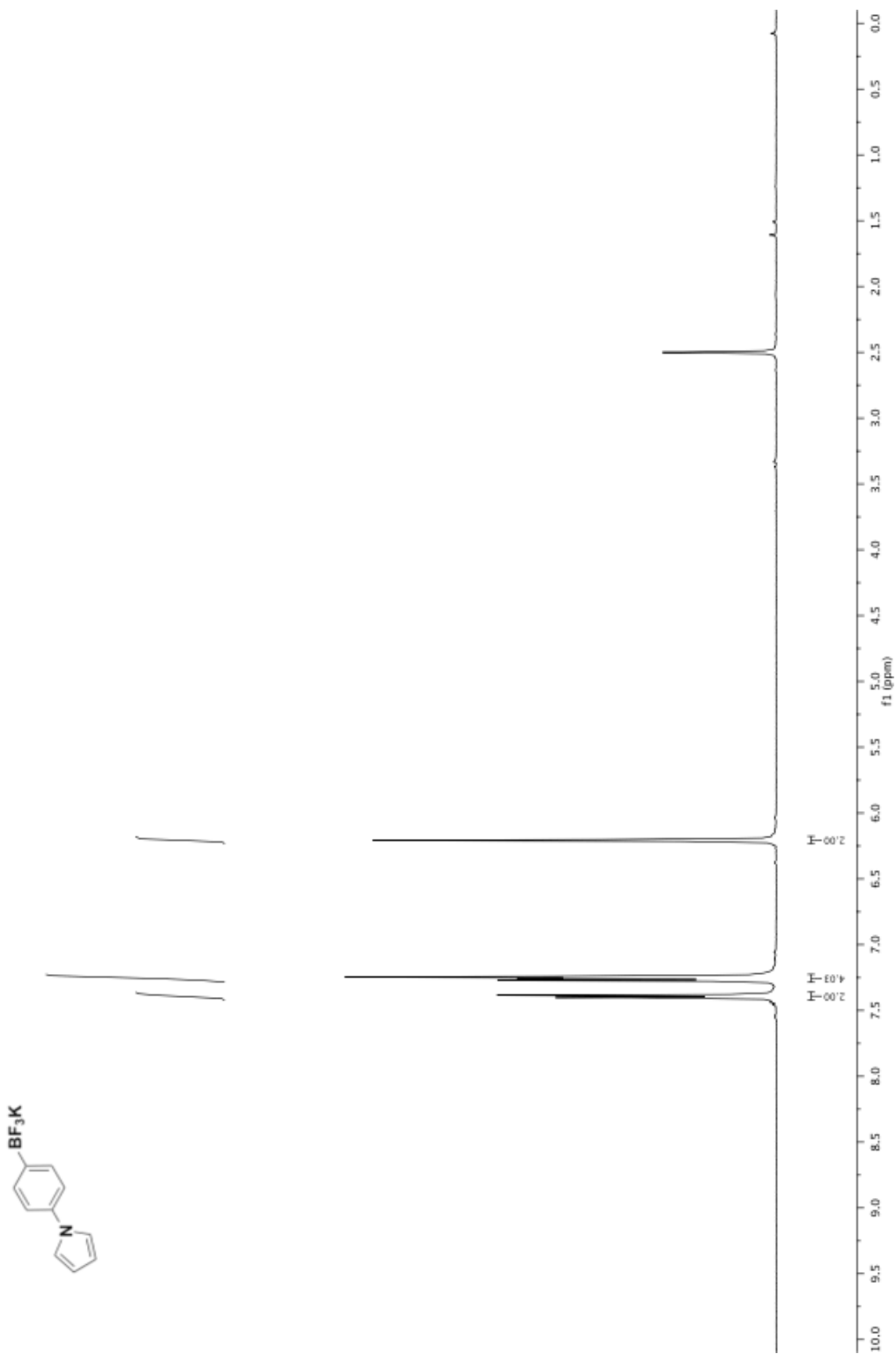
$^{11}\text{B}$  NMR Spectra (128.4 MHz, acetone- $d_6$ ) **Potassium 4-(1H-Pyrrol-1-yl)phenyl-trifluoroborate (Table 1, entry 2)**



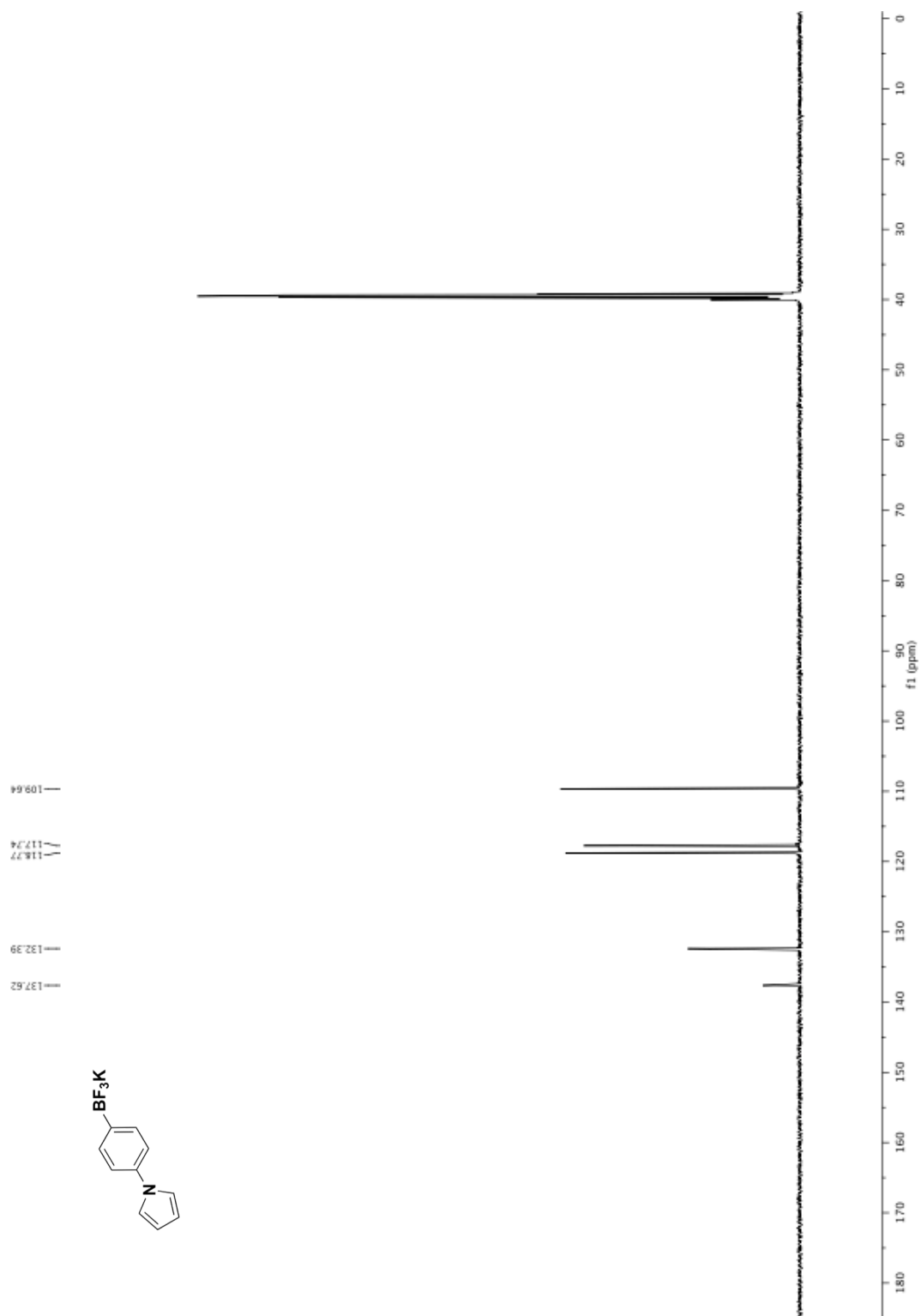
SE291 —  
— 142.35



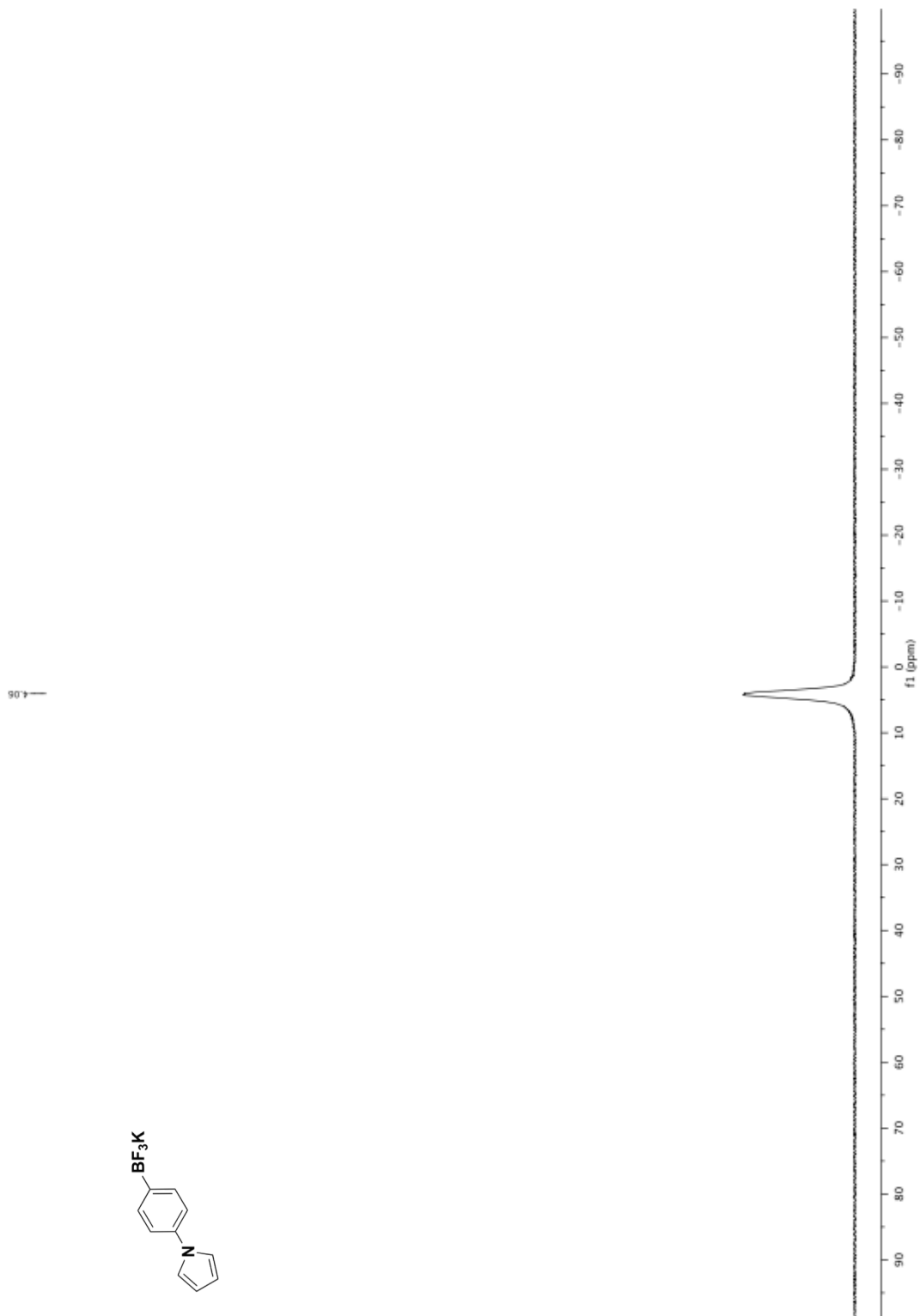
<sup>19</sup>F NMR Spectra (282 MHz, acetone-*d*<sub>6</sub>) **Potassium 4-(1H-Pyrrol-1-yl)phenyltrifluoroborate (Table 1, entry 2)**



<sup>1</sup>H NMR Spectra (500 MHz, DMSO-*d*<sub>6</sub>) Potassium 4-(1H-Pyrrol-1-yl)phenyltrifluoroborate (Table 1, entry 2<sup>d</sup>)

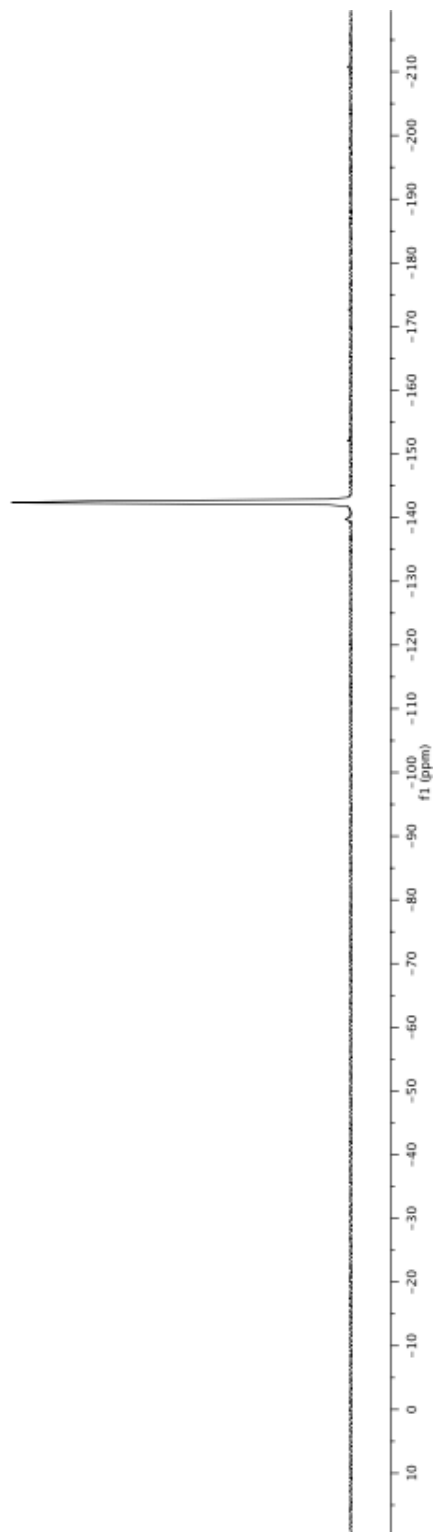
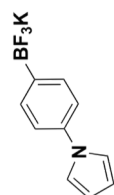


$^{13}\text{C}$  NMR Spectra (125.8 MHz,  $\text{DMSO-}d_6$ ) Potassium 4-(1H-Pyrrol-1-yl)phenyl-trifluoroborate (Table 1, entry 2<sup>d</sup>)

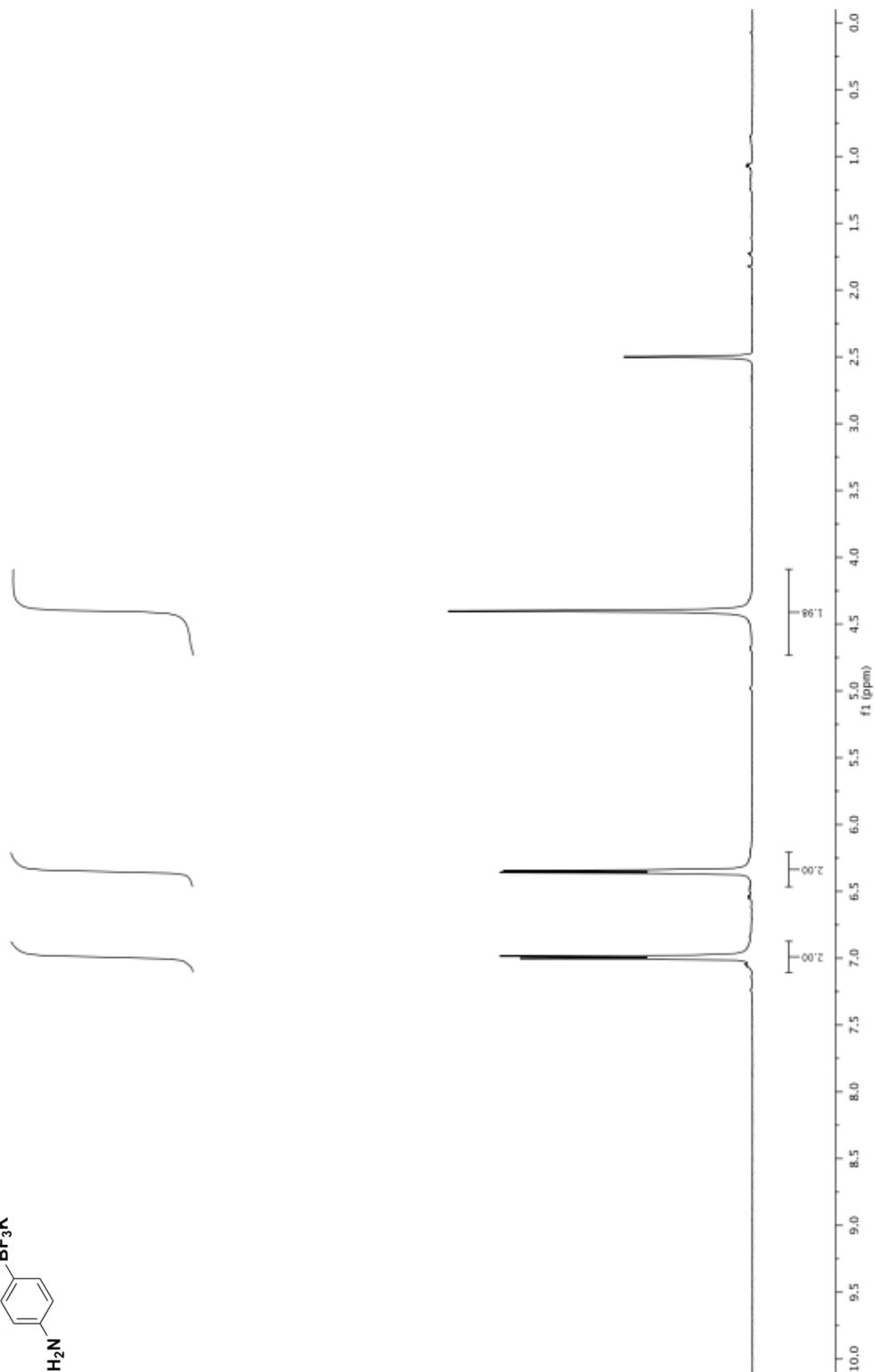
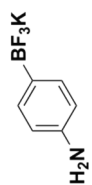


$^{11}\text{B}$  NMR Spectra (128.4 MHz, acetone- $d_6$ ) Potassium 4-(1H-Pyrrol-1-yl)phenyltrifluoroborate (Table 1, entry 2<sup>d</sup>)

95211

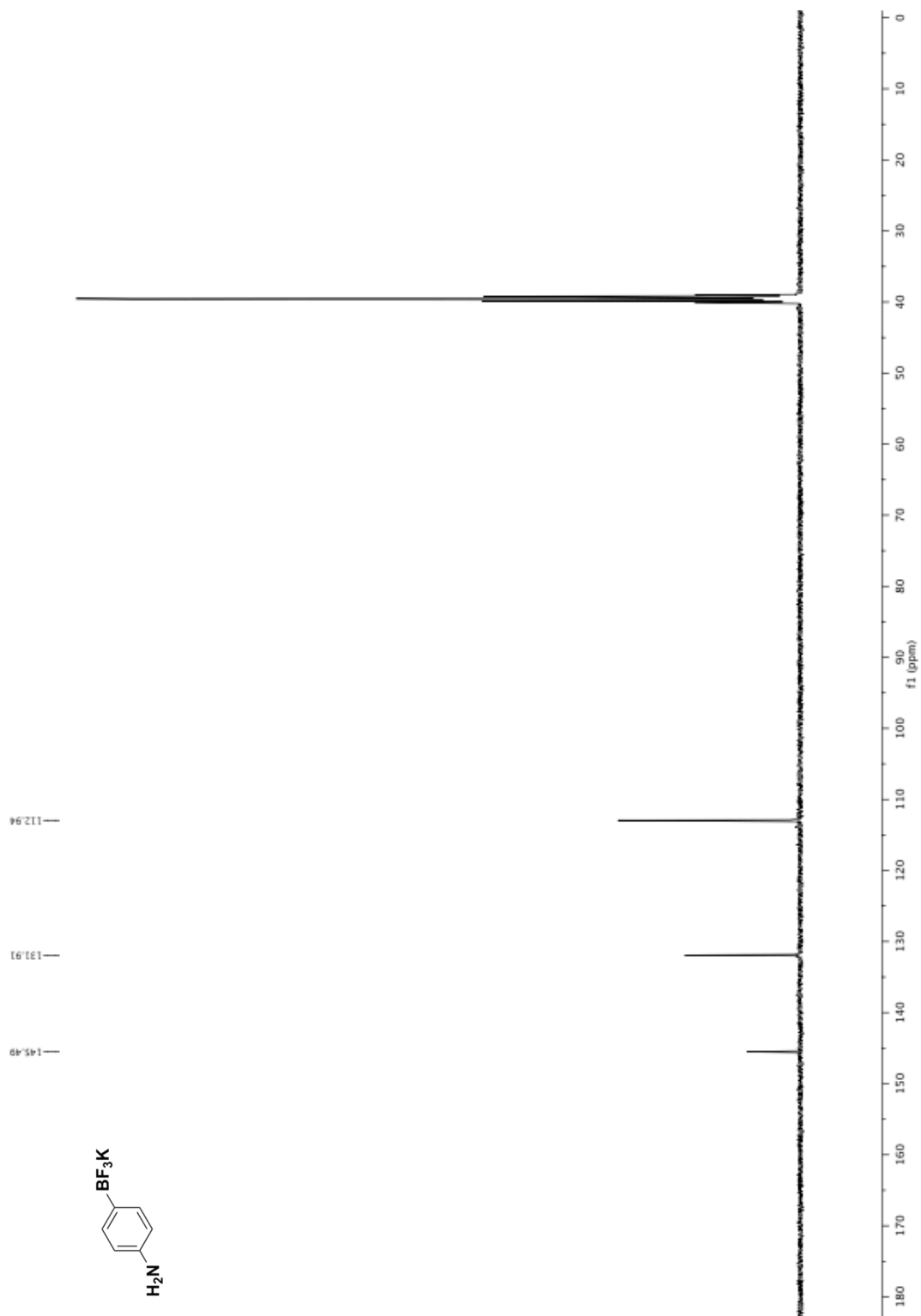


<sup>19</sup>F NMR Spectra (282 MHz, acetone-*d*<sub>6</sub>) Potassium 4-(1H-Pyrrol-1-yl)phenyltrifluoroborate (Table 1, entry 2<sup>d</sup>)

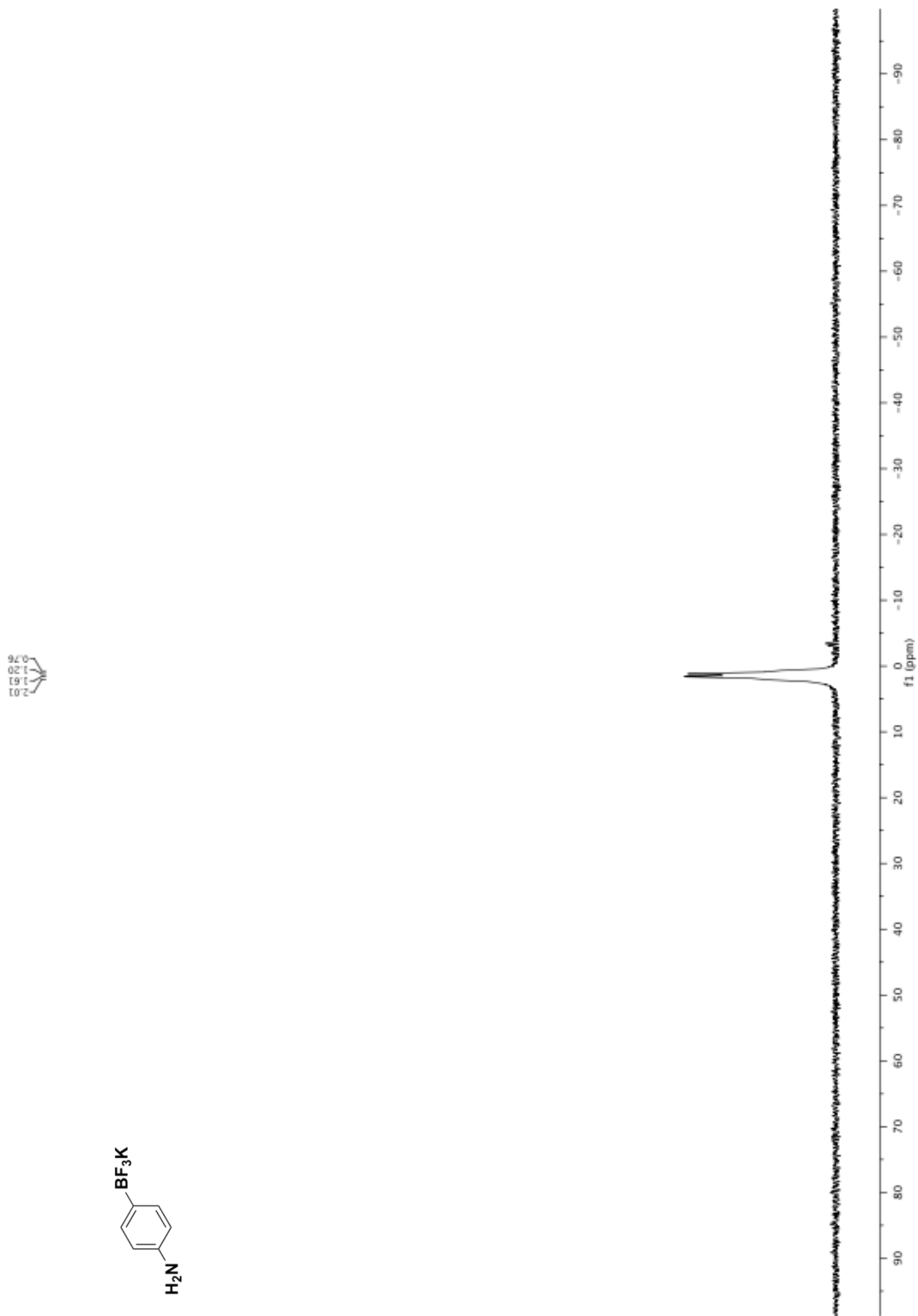


<sup>1</sup>H NMR Spectra (500 MHz, DMSO-*d*<sub>6</sub>) **Potassium 4-Aminophenyl-trifluoroborate** (Table 1, entry 3)

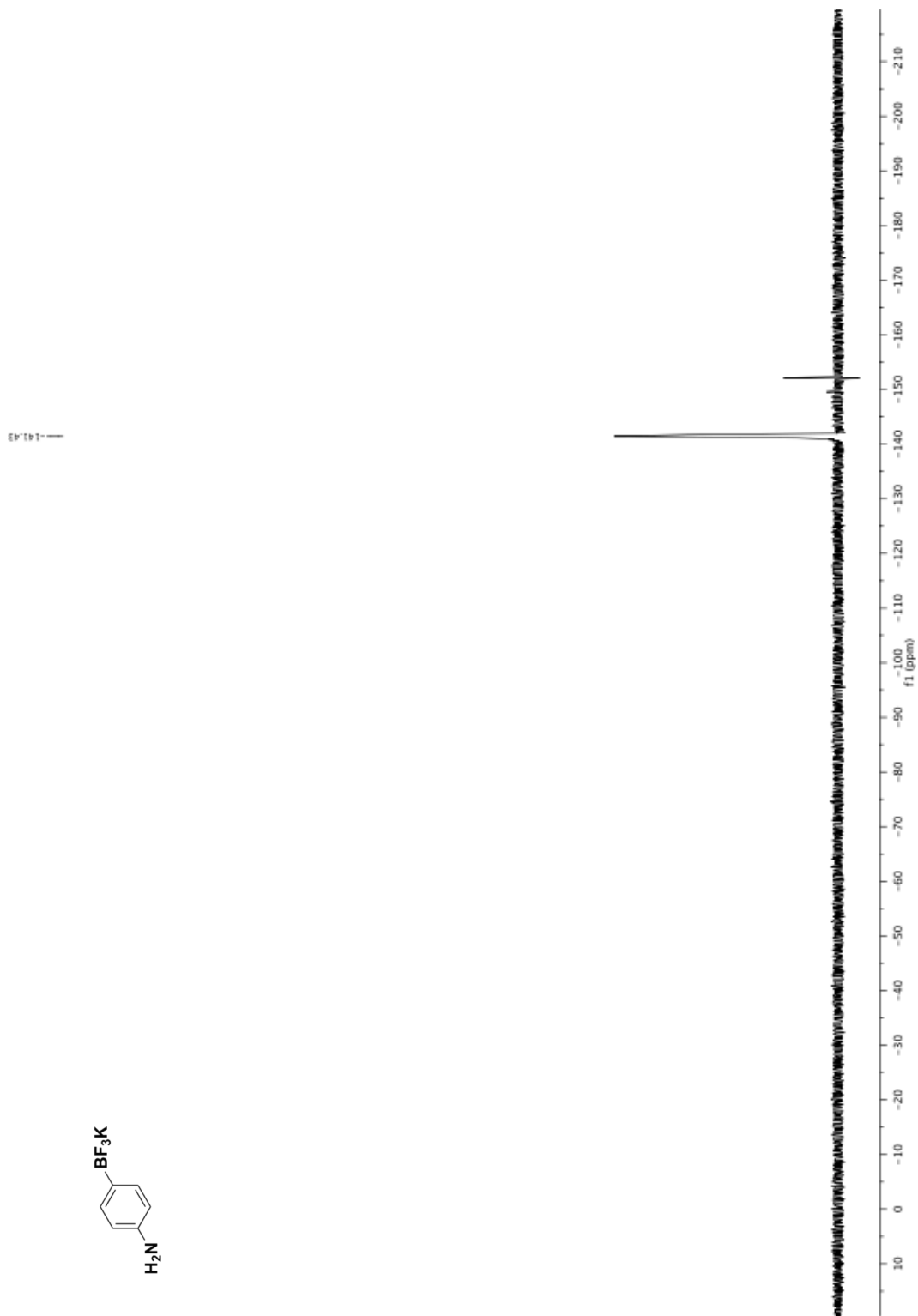




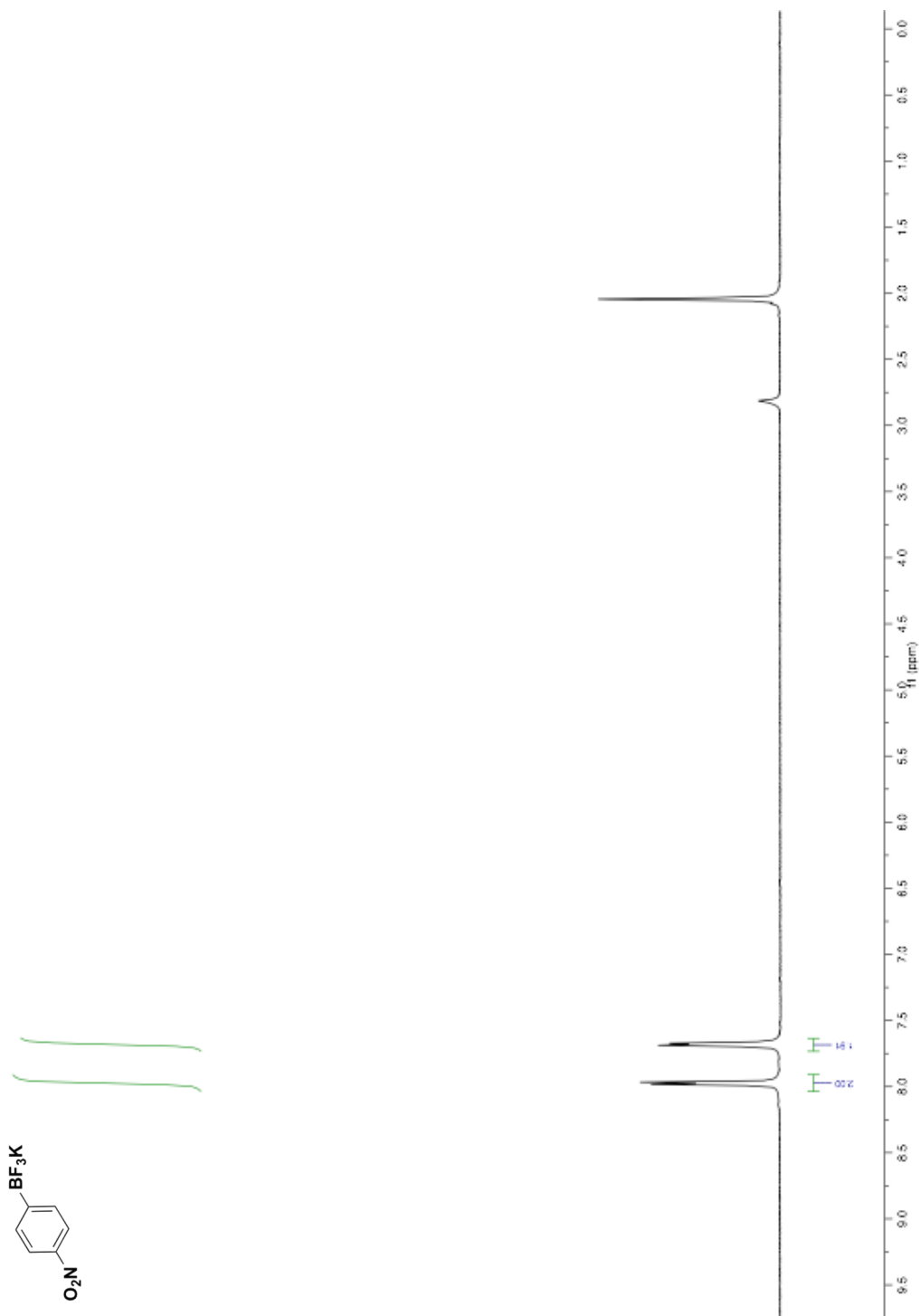
$^{13}\text{C}$  NMR Spectra (125.8 MHz,  $\text{DMSO-}d_6$ ) Potassium 4-Aminophenyl-trifluoroborate (Table 1, entry 3)



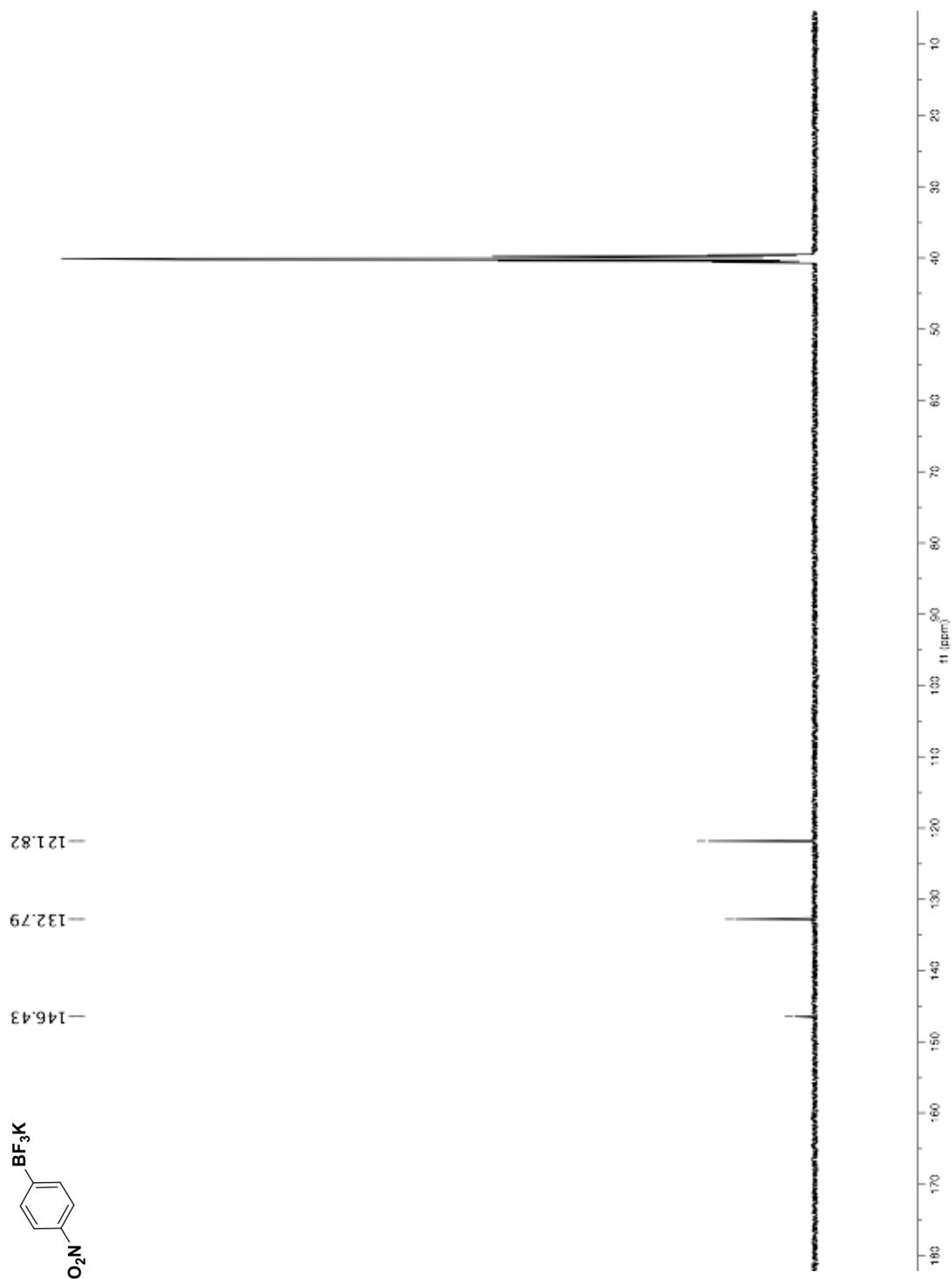
<sup>11</sup>B NMR Spectra (128.4 MHz, acetone-*d*<sub>6</sub>) **Potassium 4-Aminophenyl-trifluoroborate** (Table 1, entry 3)



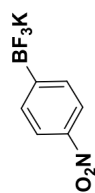
<sup>19</sup>F NMR Spectra (282 MHz, acetone-*d*<sub>6</sub>) Potassium 4-Aminophenyl-trifluoroborate (Table 1, entry 3)



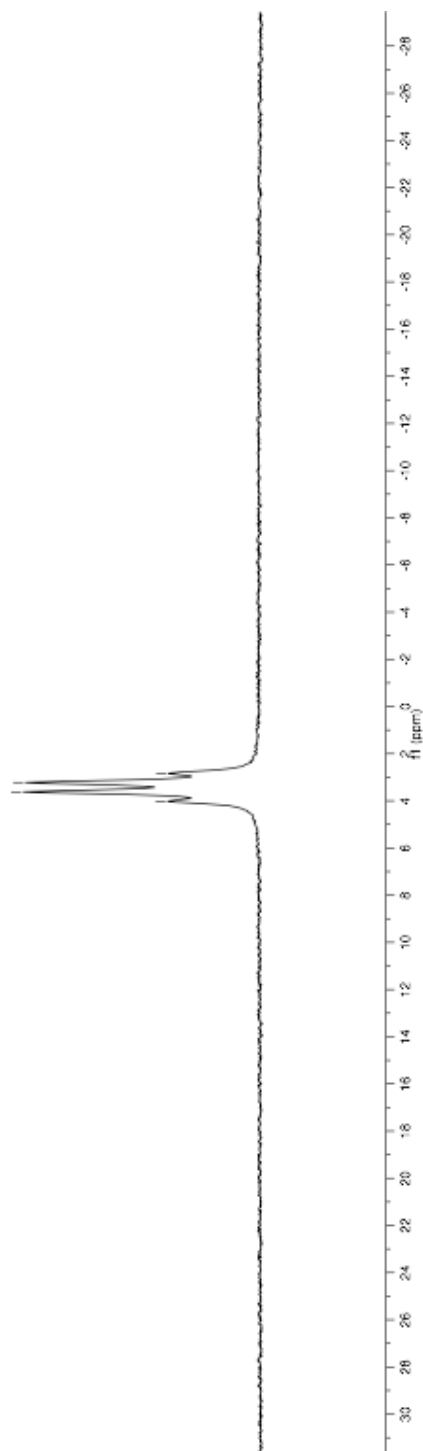
<sup>1</sup>H NMR Spectra (500 MHz, acetone-*d*<sub>6</sub>) **Potassium (4-Nitrophenyl)trifluoroborate** (Table 1, entry 4)



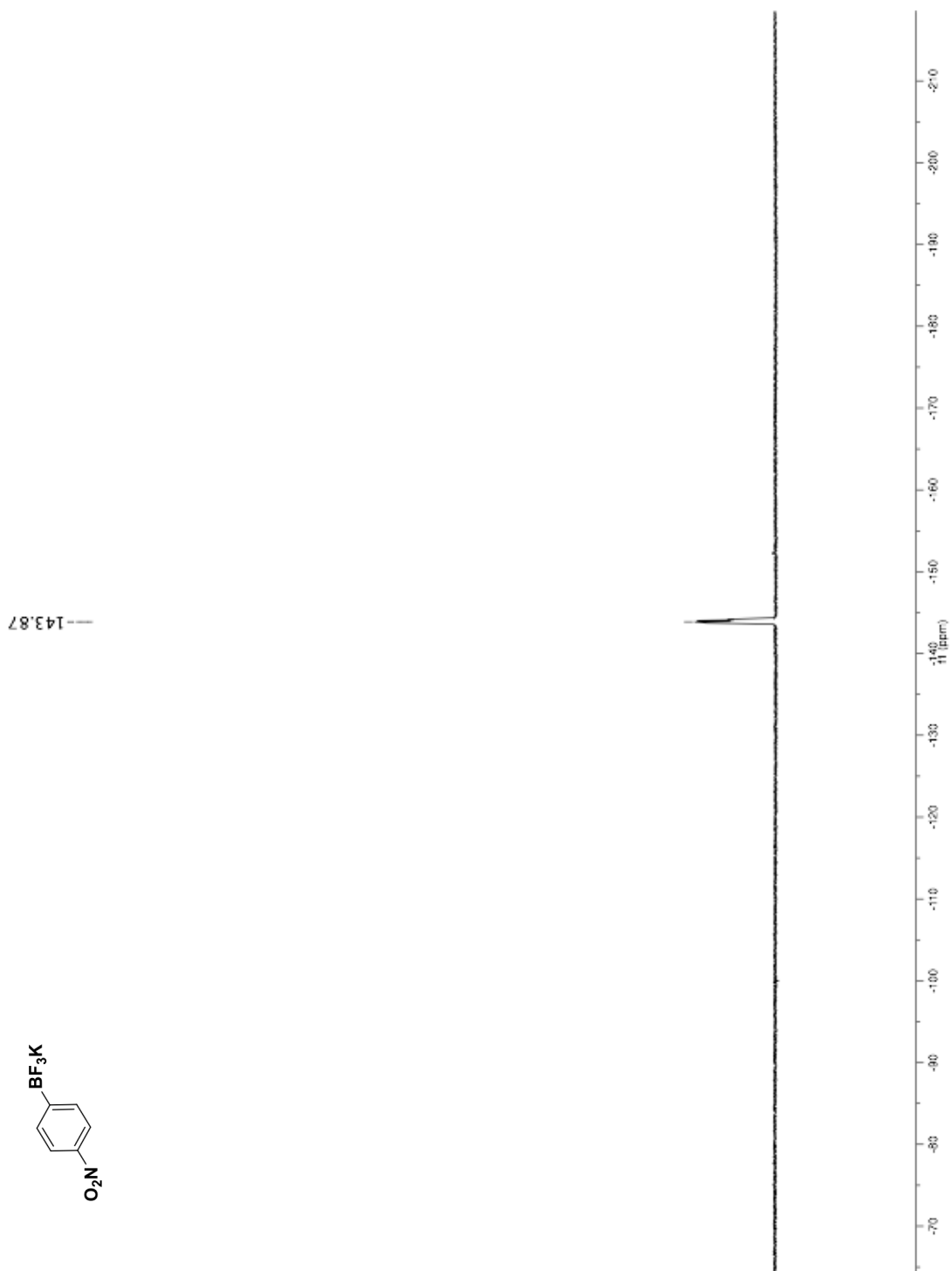
$^{13}\text{C}$  NMR Spectra (125.8 MHz,  $\text{DMSO-}d_6$ ) Potassium (4-Nitrophenyl)trifluoroborate (Table 1, entry 4)



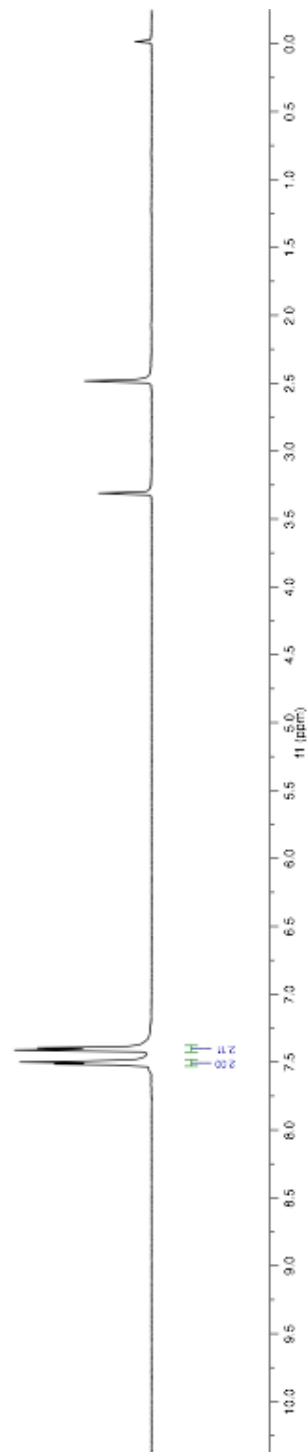
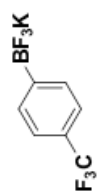
4.02  
3.62  
3.22  
2.84



$^{11}\text{B}$  NMR Spectra (128.4 MHz, acetone- $d_6$ ) **Potassium (4-Nitrophenyl)trifluoroborate** (Table 1, entry 4)



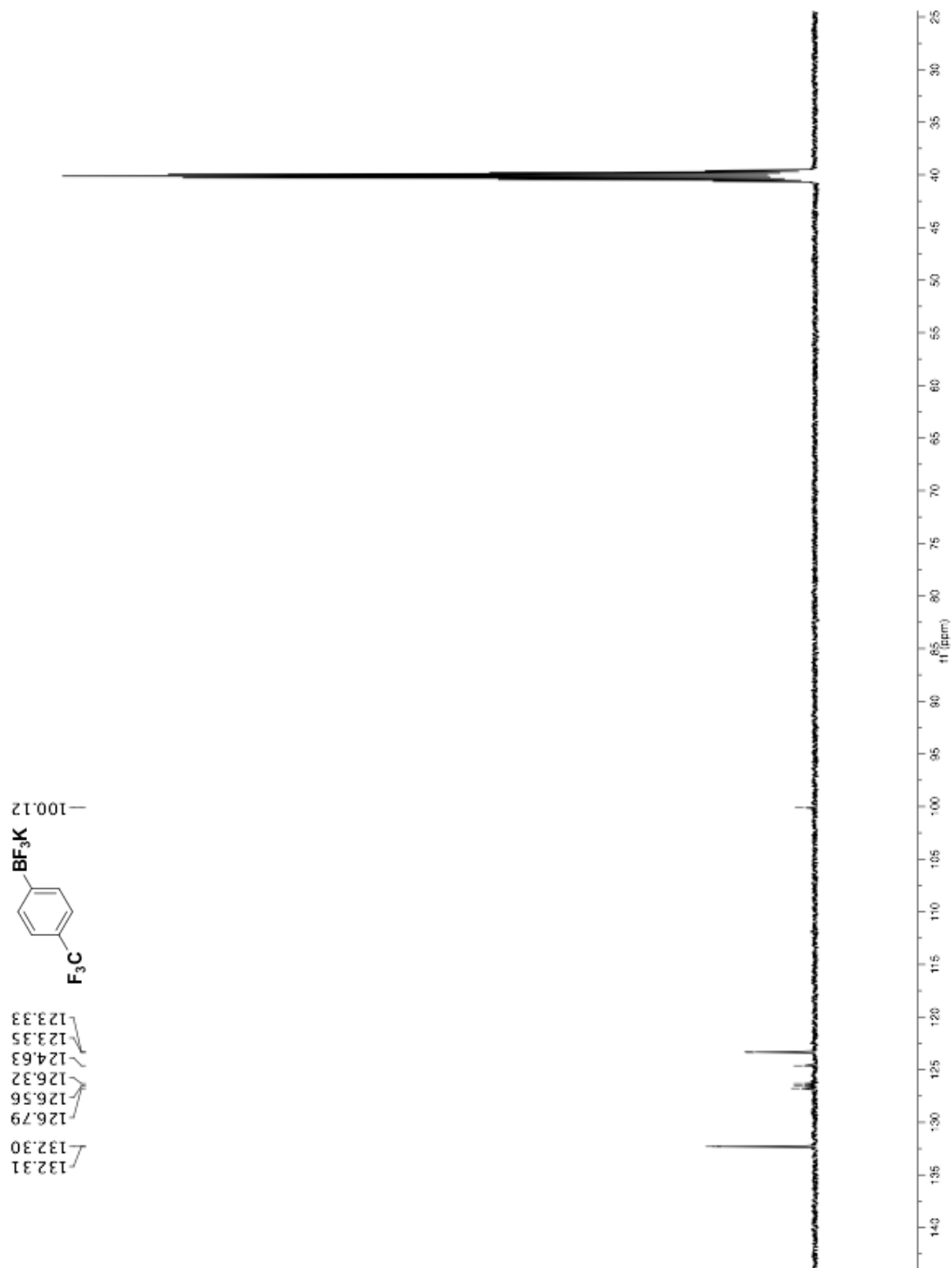
$^{19}\text{F}$  NMR Spectra (338.8 MHz, acetone- $d_6$ ) Potassium (4-Nitrophenyl)trifluoroborate (Table 1, entry 4)



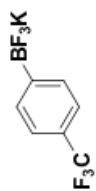
$^1H$  NMR Spectra (500 MHz,  $DMSO-d_6$ )  
(Trifluoromethyl)phenyltrifluoroborate (Table 1, entry 5)

Potassium (4-

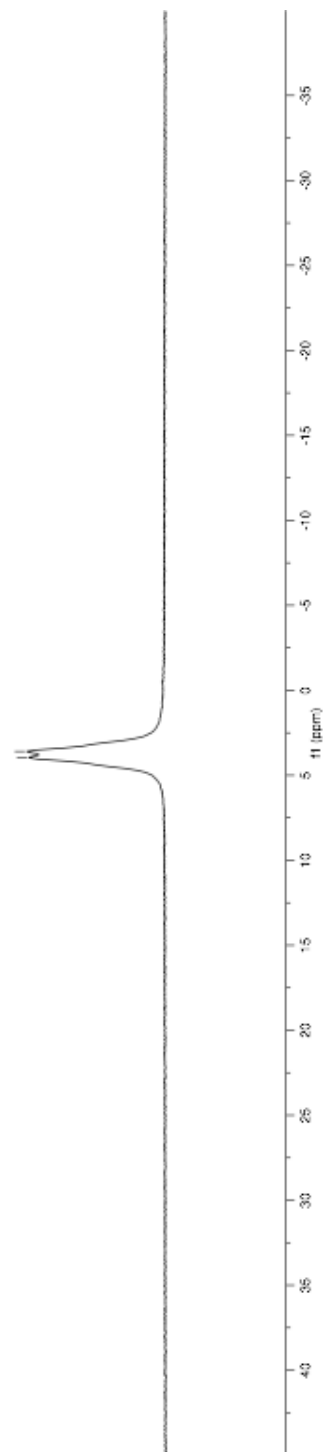




<sup>13</sup>C NMR Spectra (125.8 Hz, DMSO-*d*<sub>6</sub>) Potassium (4-(Trifluoromethyl)phenyl)trifluoroborate (Table 1, entry 5)

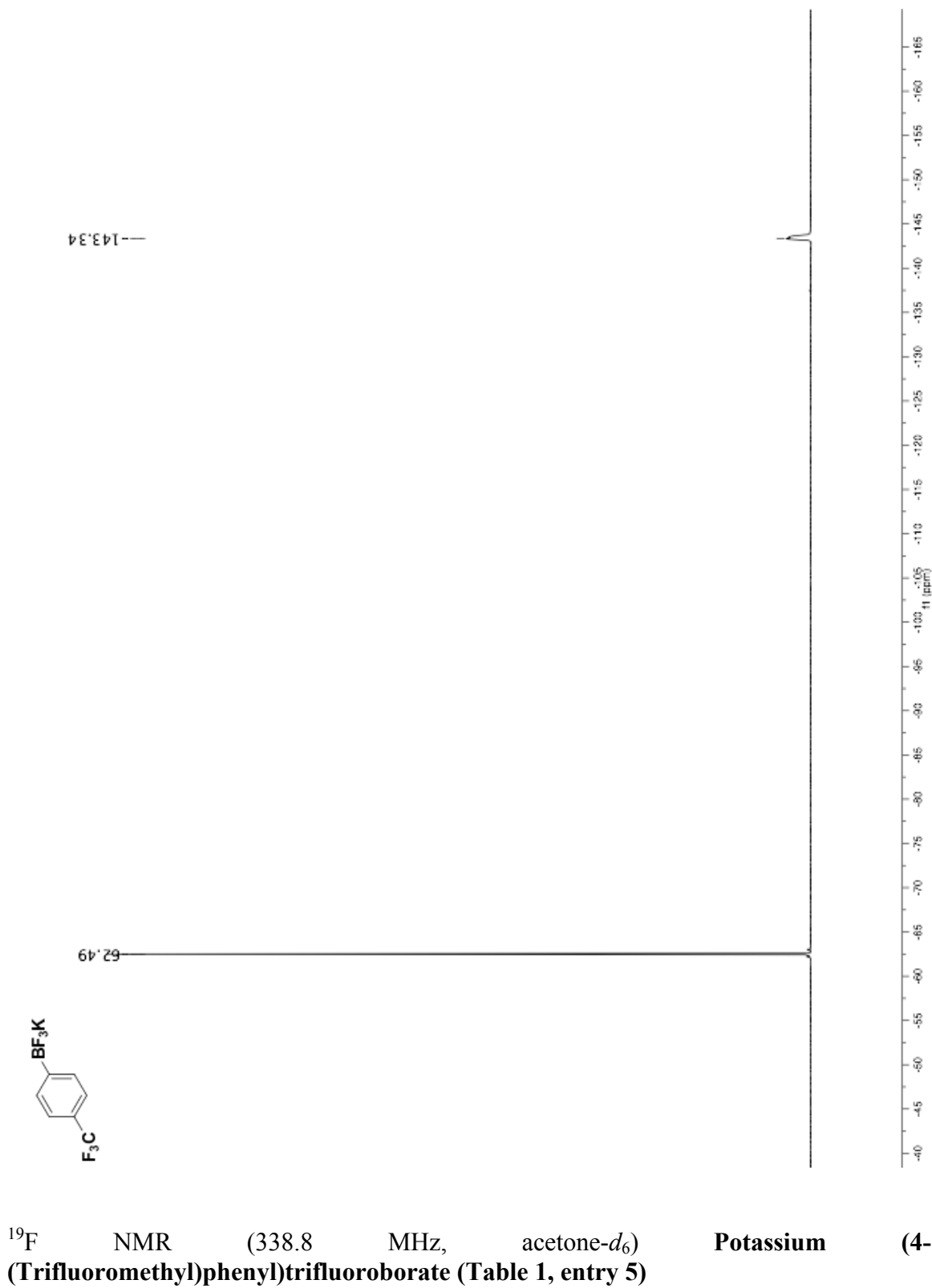


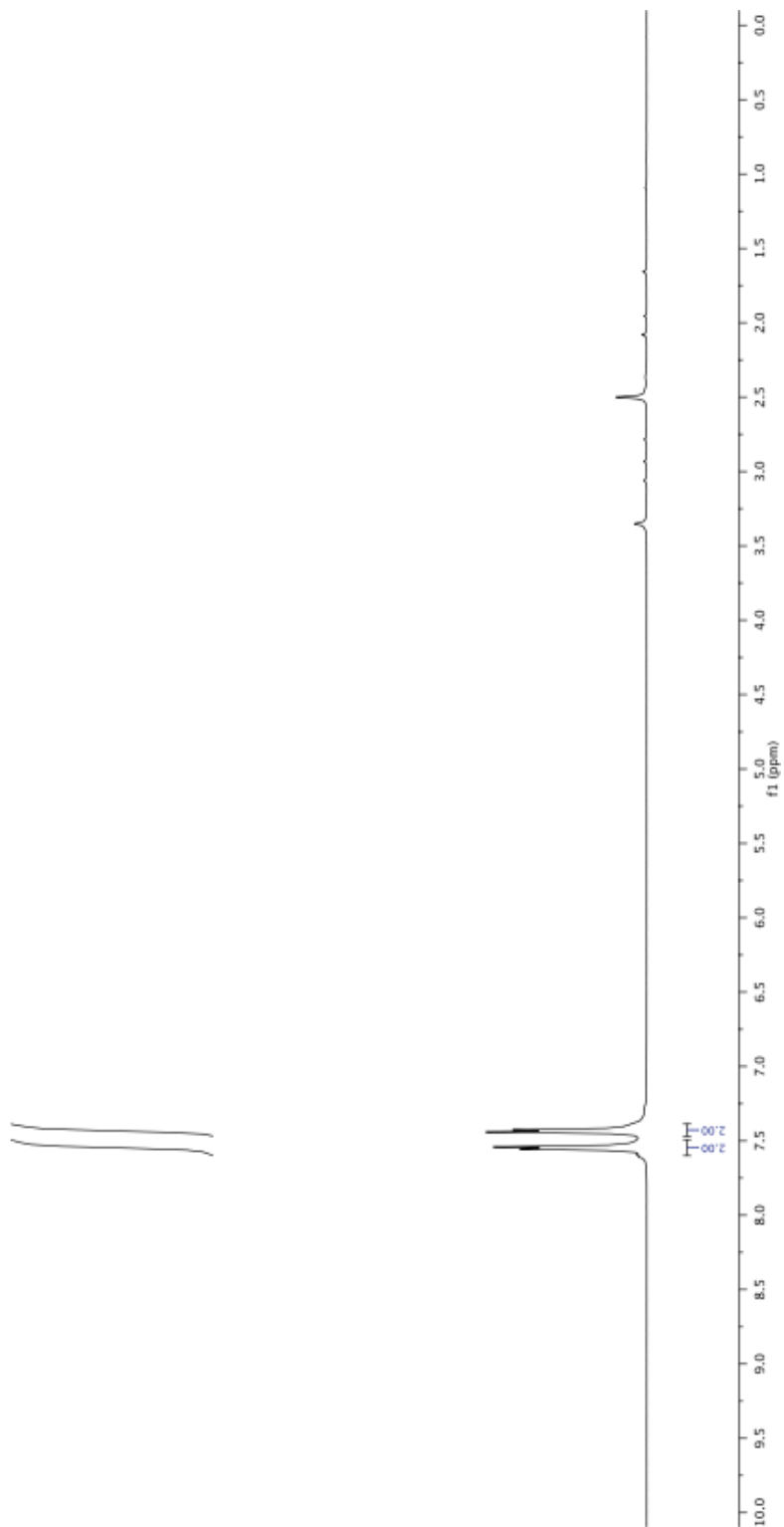
3.96  
3.98



$^{11}\text{B}$  NMR (128.4 MHz, acetone- $d_6$ )  
(Trifluoromethyl)phenyltrifluoroborate (Table 1, entry 5)

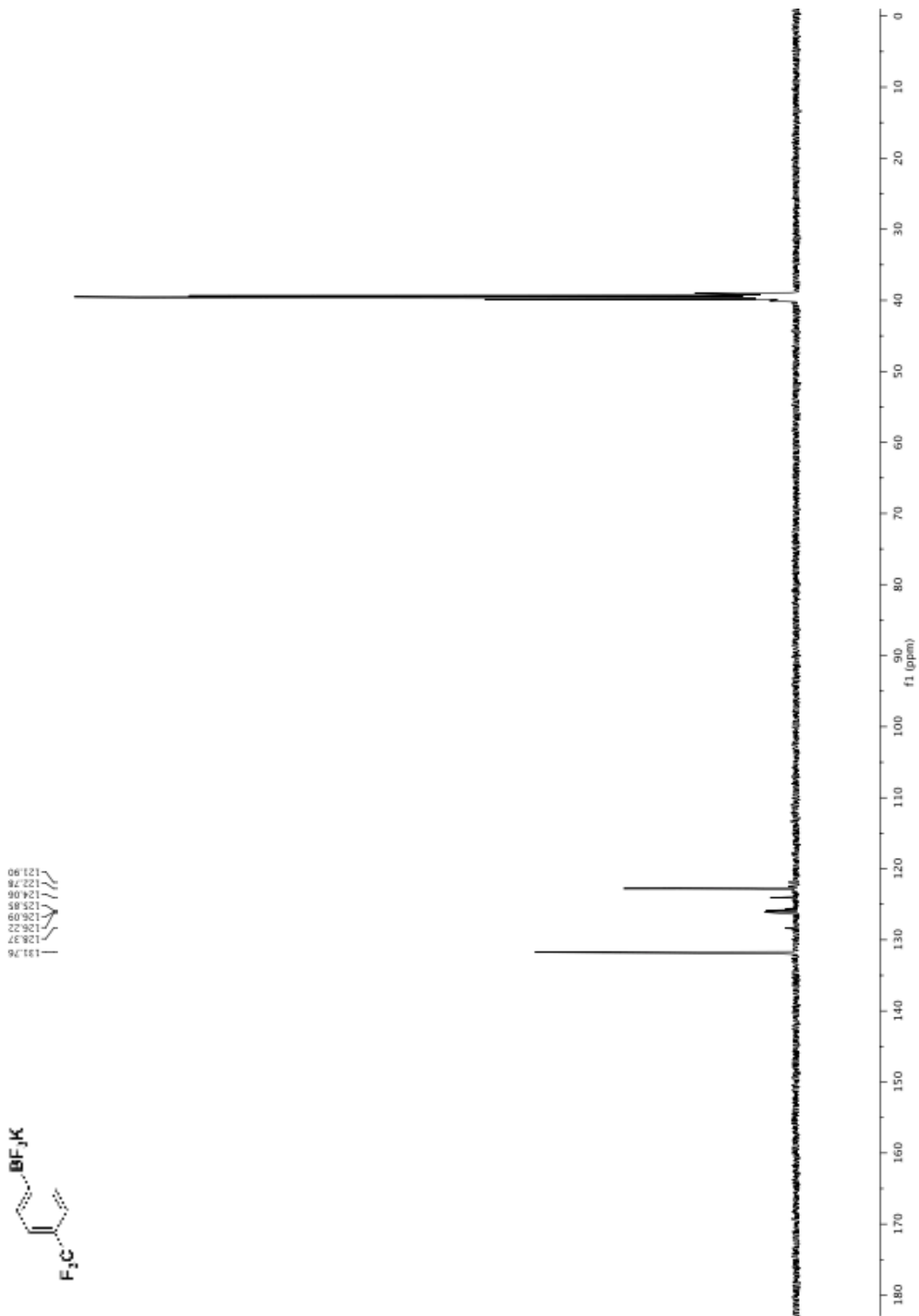
Potassium (4-





<sup>1</sup>H NMR Spectra (500 MHz, DMSO-*d*<sub>6</sub>)

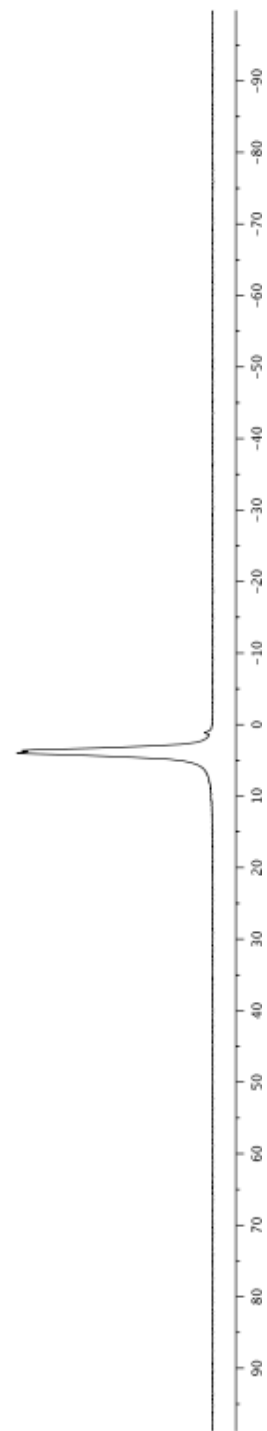
Potassium (4-



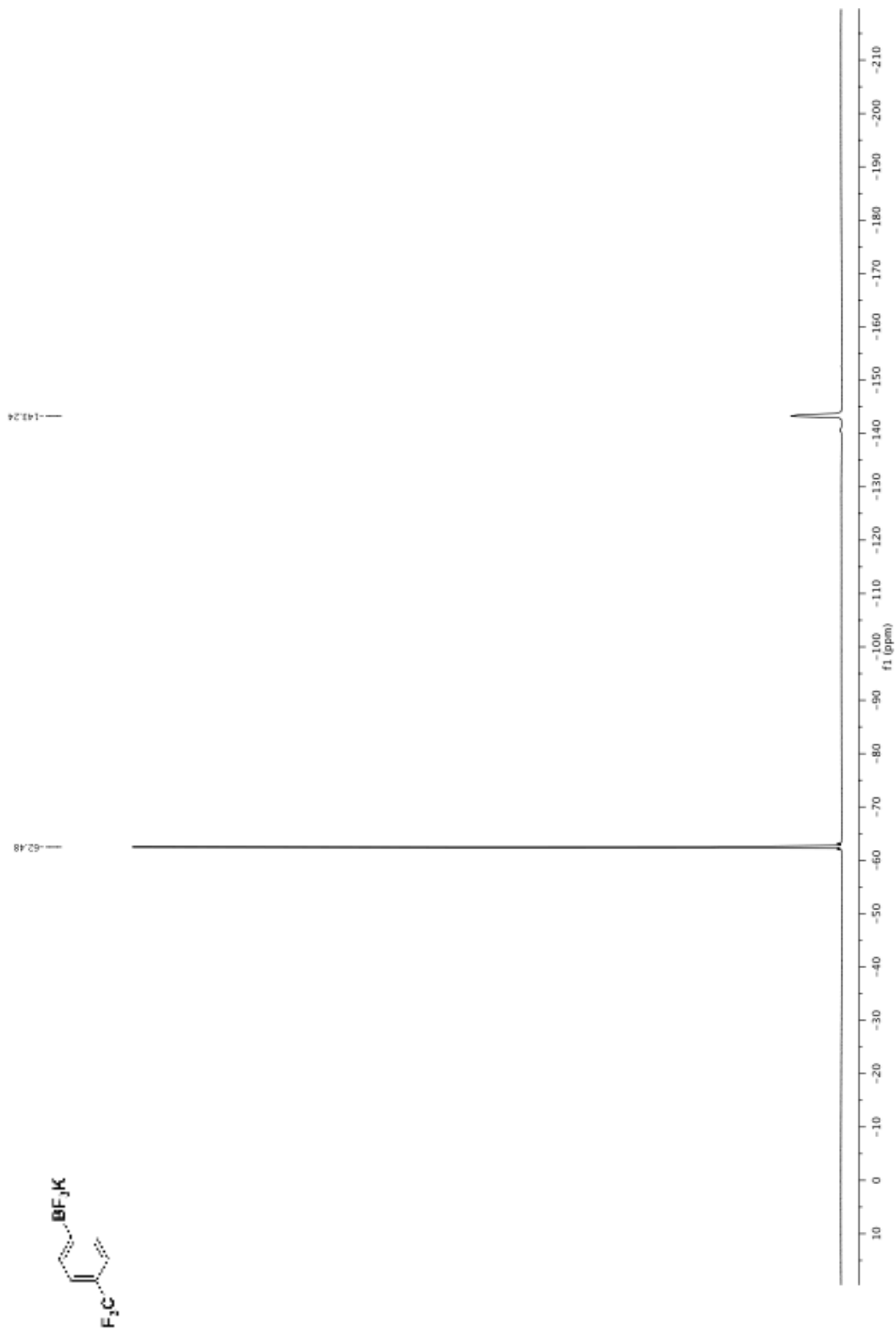
<sup>13</sup>C NMR Spectra (125.8 MHz, DMSO-*d*<sub>6</sub>) Potassium (4-(Trifluoromethyl)phenyl)trifluoroborate (Table 1, entry 5<sup>e</sup>)



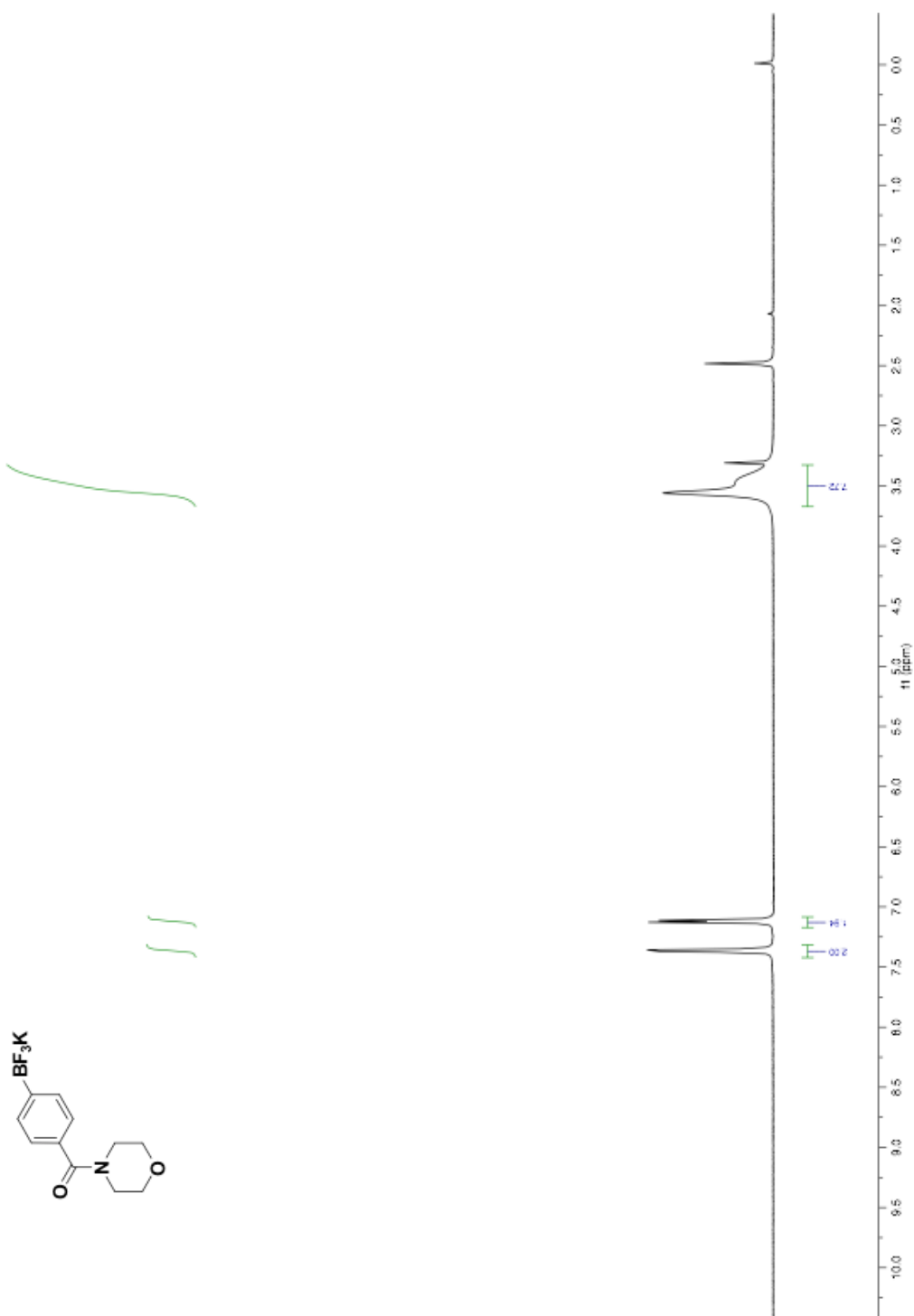
197  
198



$^{11}\text{B}$  NMR Spectra (128.4 MHz, acetone- $d_6$ ) Potassium (4-(Trifluoromethyl)phenyl)trifluoroborate (Table 1, entry 5<sup>e</sup>)

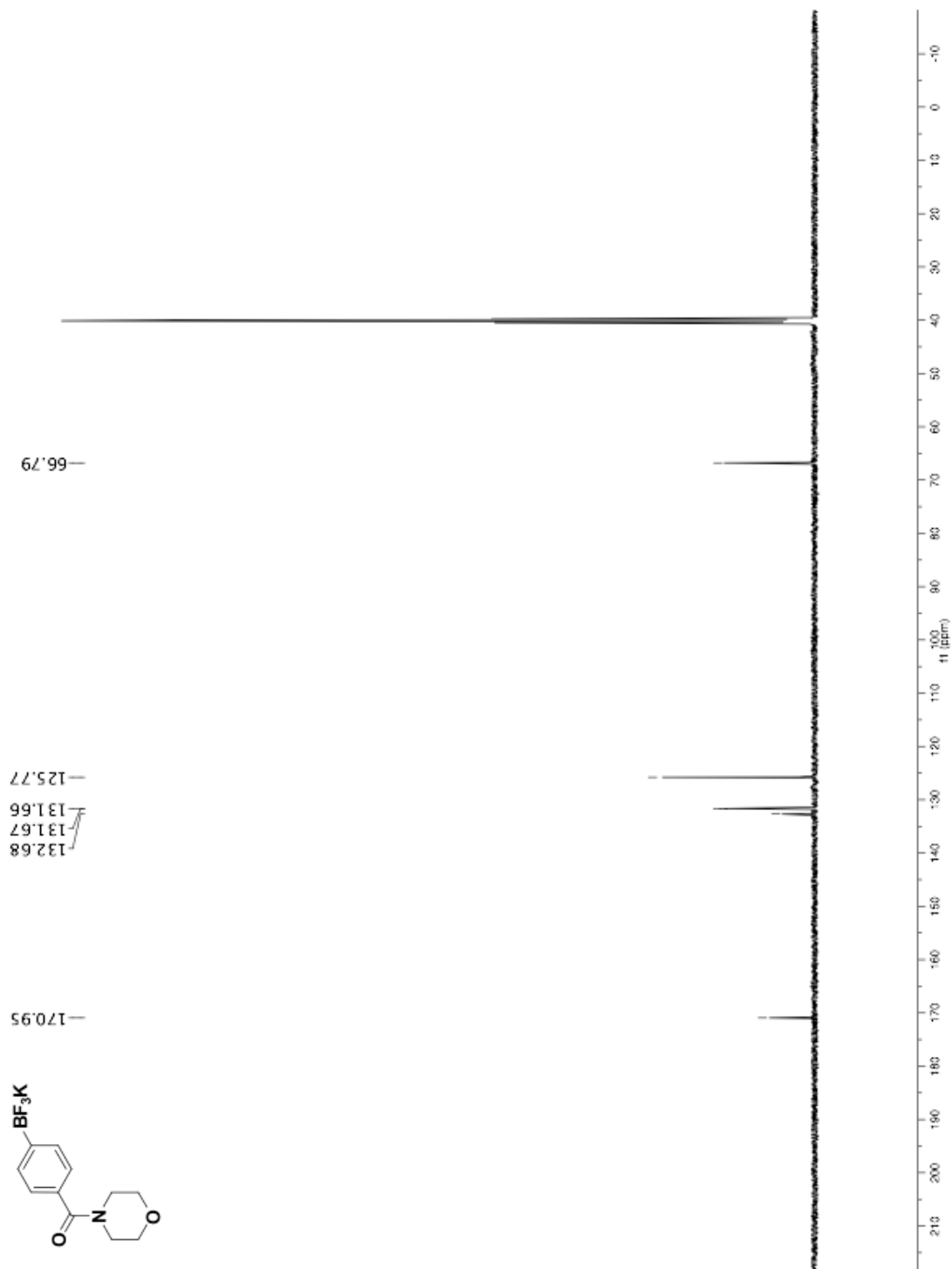


$^{19}\text{F}$  NMR Spectra (282 MHz, acetone- $d_6$ ) Potassium (4-(Trifluoromethyl)phenyl)trifluoroborate (Table 1, entry 5<sup>c</sup>)

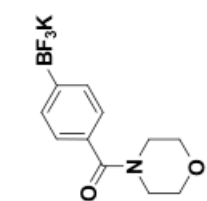


<sup>1</sup>H NMR Spectra (500 MHz, DMSO-*d*<sub>6</sub>) Potassium 4-(Morpholine-4-carbonyl)phenyltrifluoroborate (Table 1, entry 6)

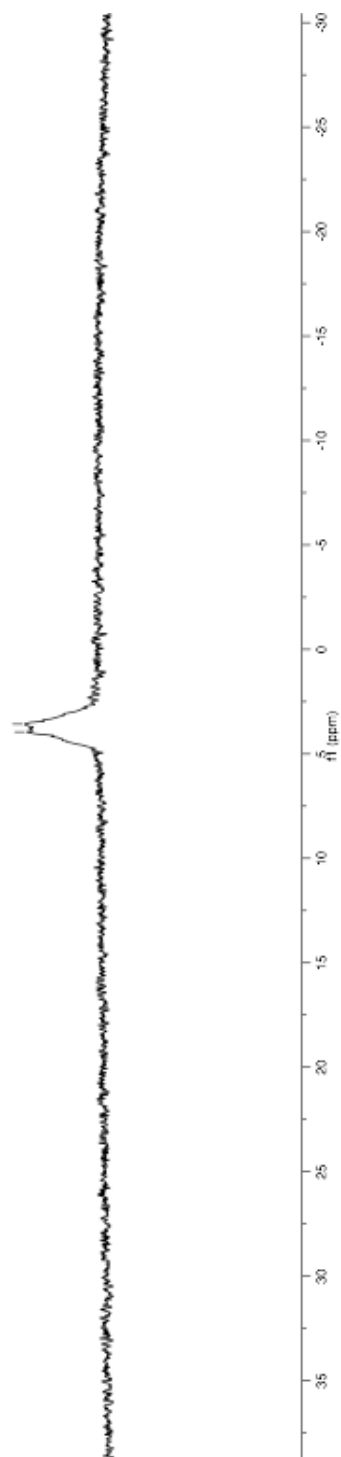




<sup>13</sup>C NMR Spectra (125.8 MHz, DMSO-*d*<sub>6</sub>) Potassium 4-(Morpholine-4-carbonyl)phenyl-trifluoroborate (Table 1, entry 6)

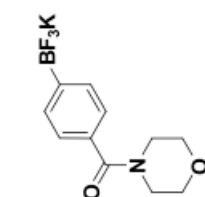


3.95  
3.57

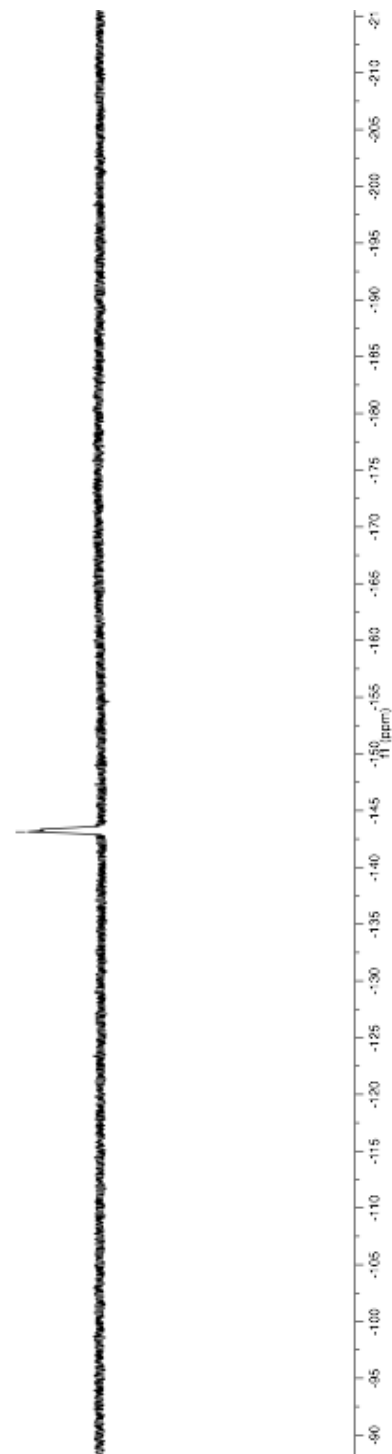


<sup>11</sup>B NMR Spectra (128.4 MHz, acetone-*d*<sub>6</sub>) **Potassium 4-(Morpholine-4-carbonyl)phenyl-trifluoroborate (Table 1, entry 6)**

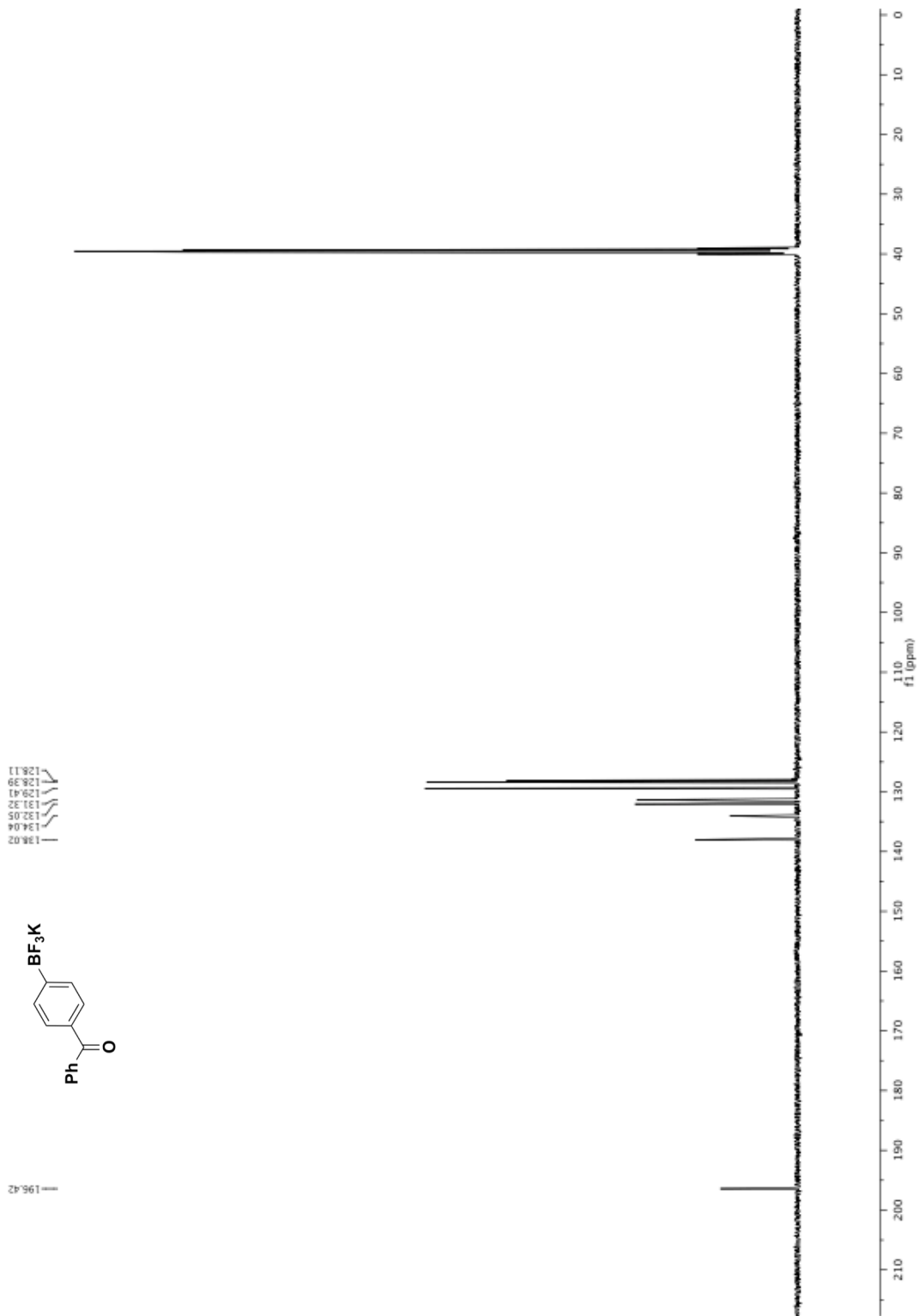
**<sup>19</sup>F NMR Spectra (338.8 MHz, DMSO-*d*<sub>6</sub>) Potassium 4-(Morpholine-4-carbonyl)phenyl-trifluoroborate (Table 1, entry 6)**



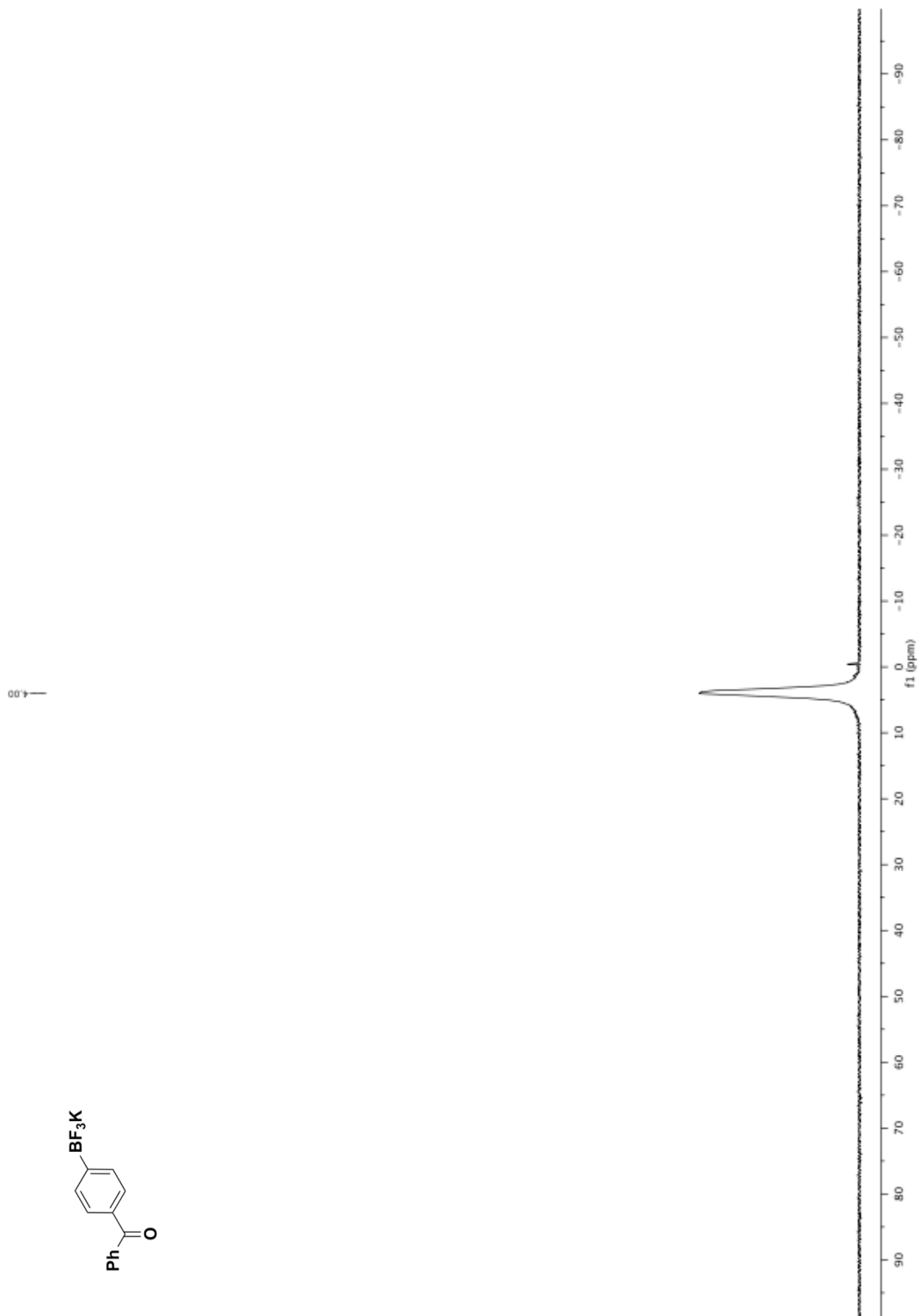
—143.14



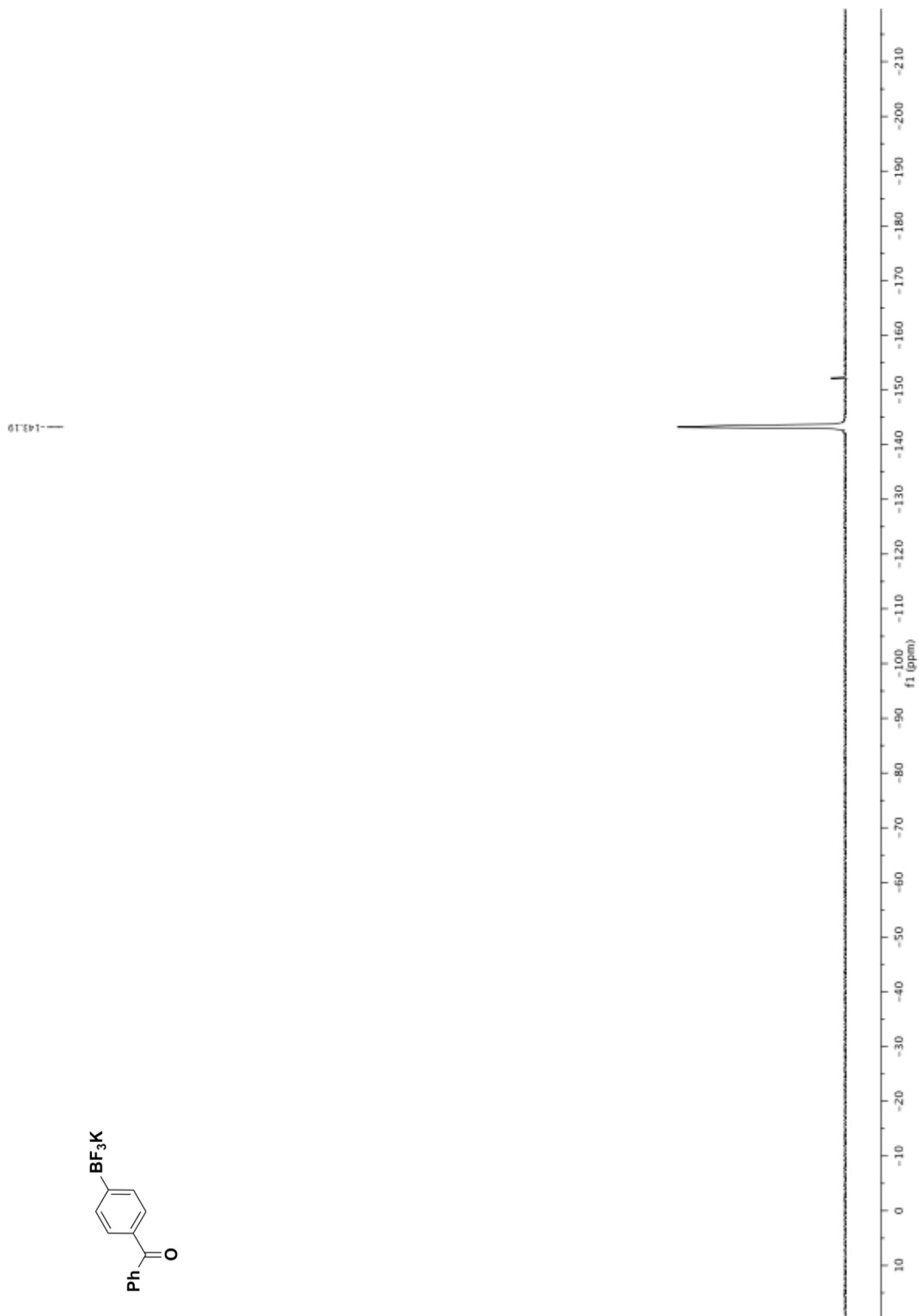




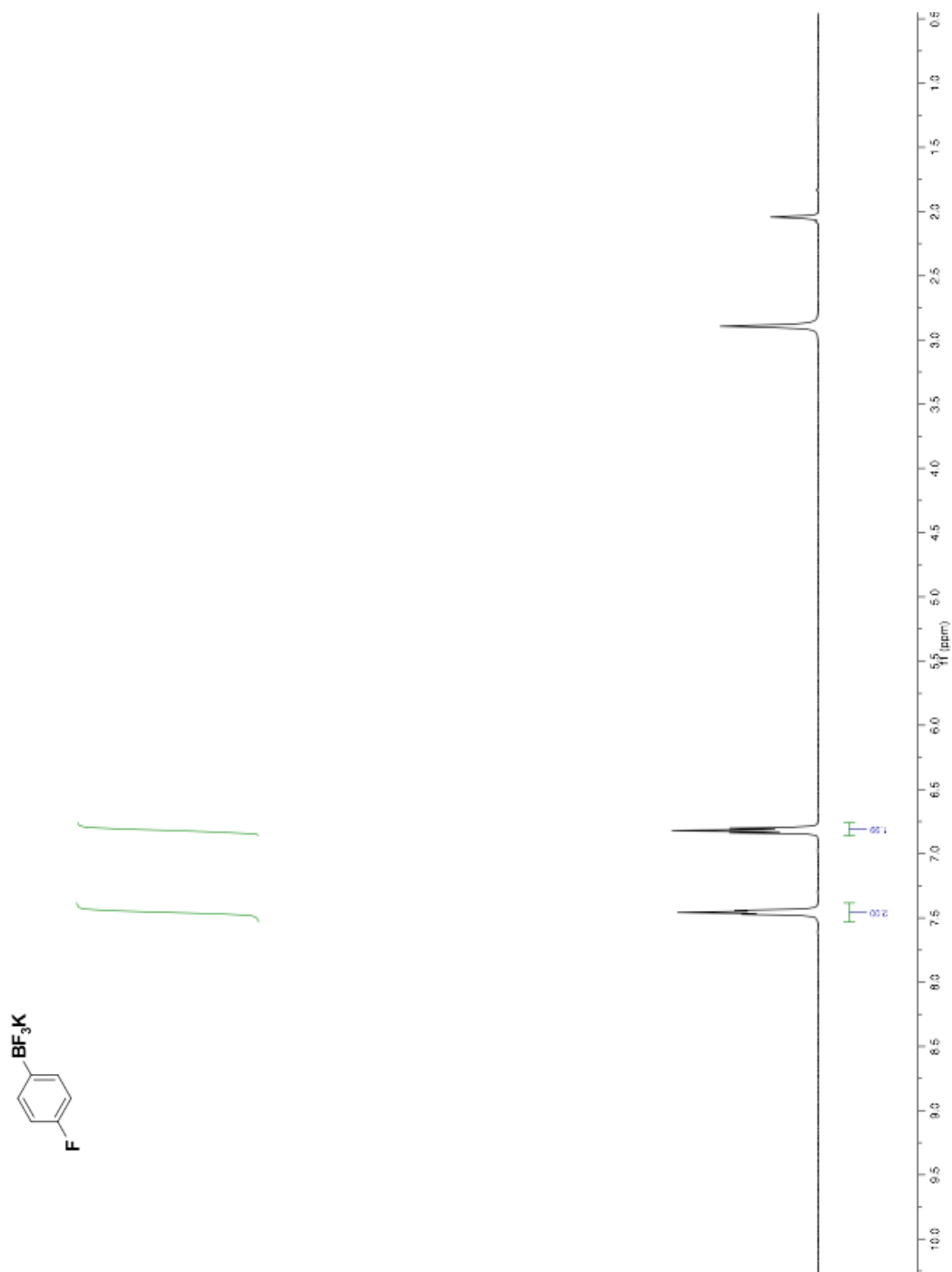
<sup>13</sup>C NMR Spectra (125.8 MHz, DMSO-*d*<sub>6</sub>) Potassium 4-Benzoylphenyl-trifluoroborate (Table 1, entry 7)



$^{11}\text{B}$  NMR Spectra (128.4 MHz, acetone- $d_6$ ) Potassium 4-Benzoylphenyltrifluoroborate (Table 1, entry 7)

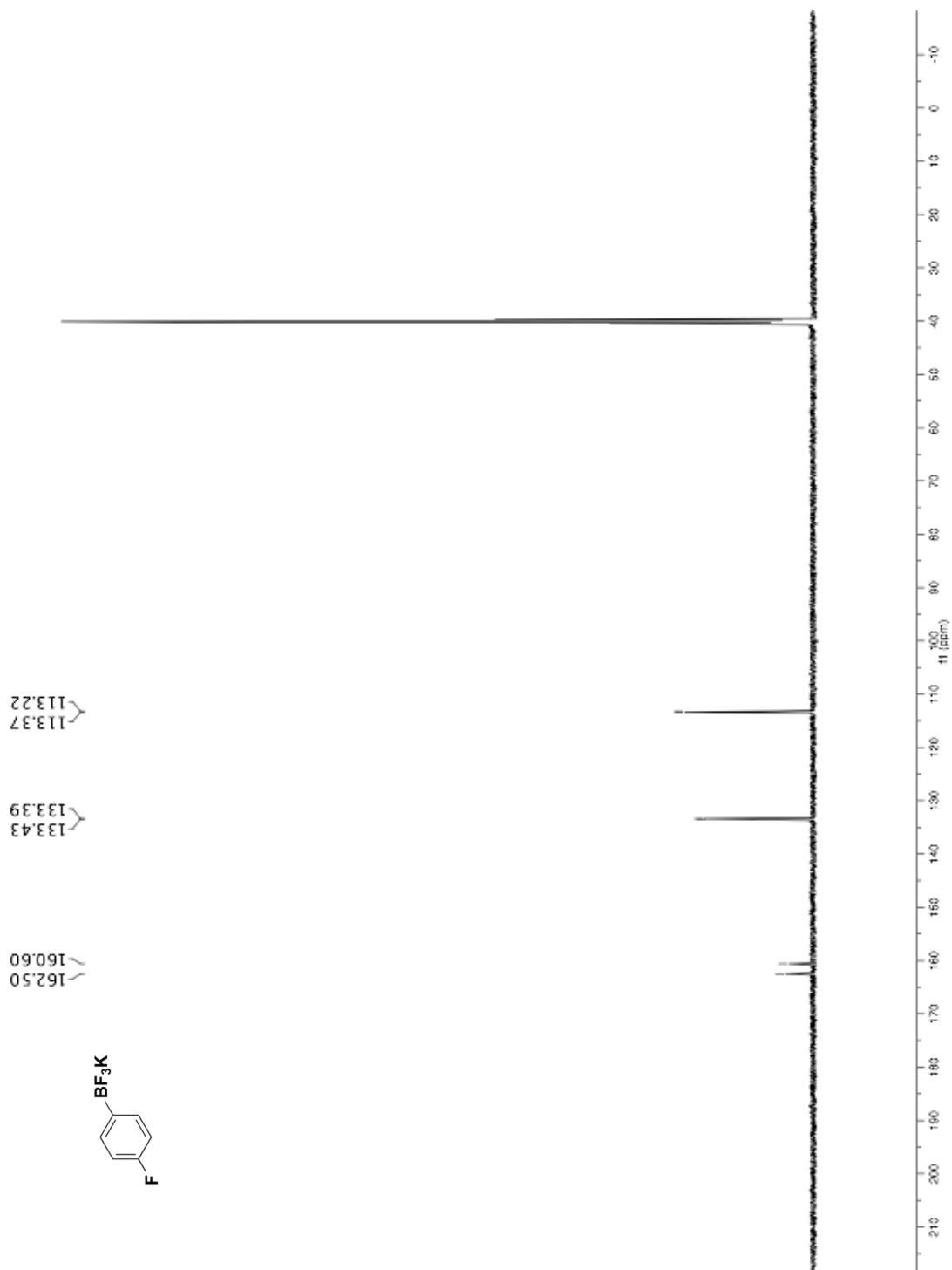


$^{19}\text{F}$  NMR Spectra (282 MHz, acetone- $d_6$ ) **Potassium 4-Benzoylphenyl-trifluoroborate** (Table 1, entry 7)

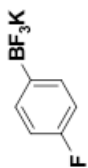


$^1\text{H}$  NMR Spectra (500 MHz, acetone- $d_6$ ) Potassium (4-Fluorophenyl)trifluoroborate (Table 1, entry 8)

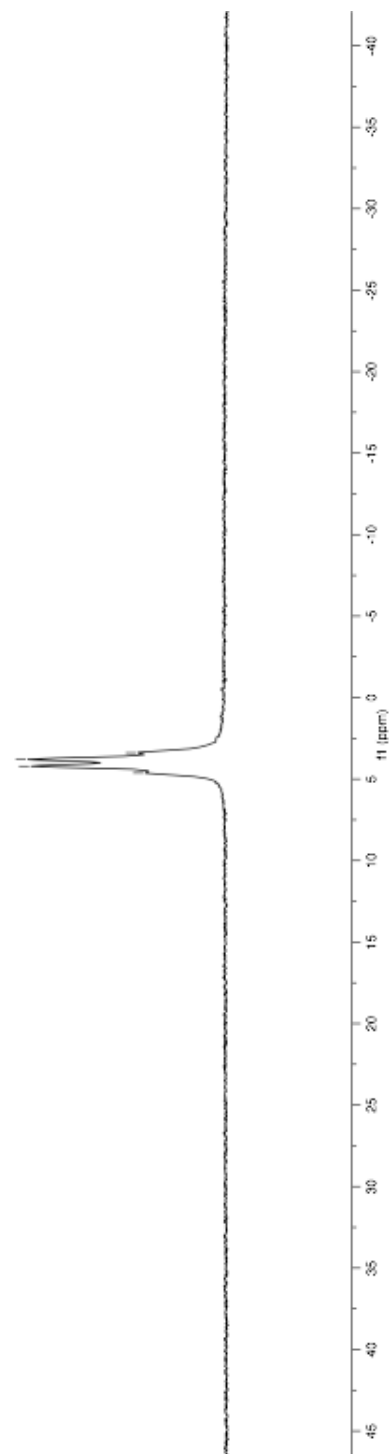




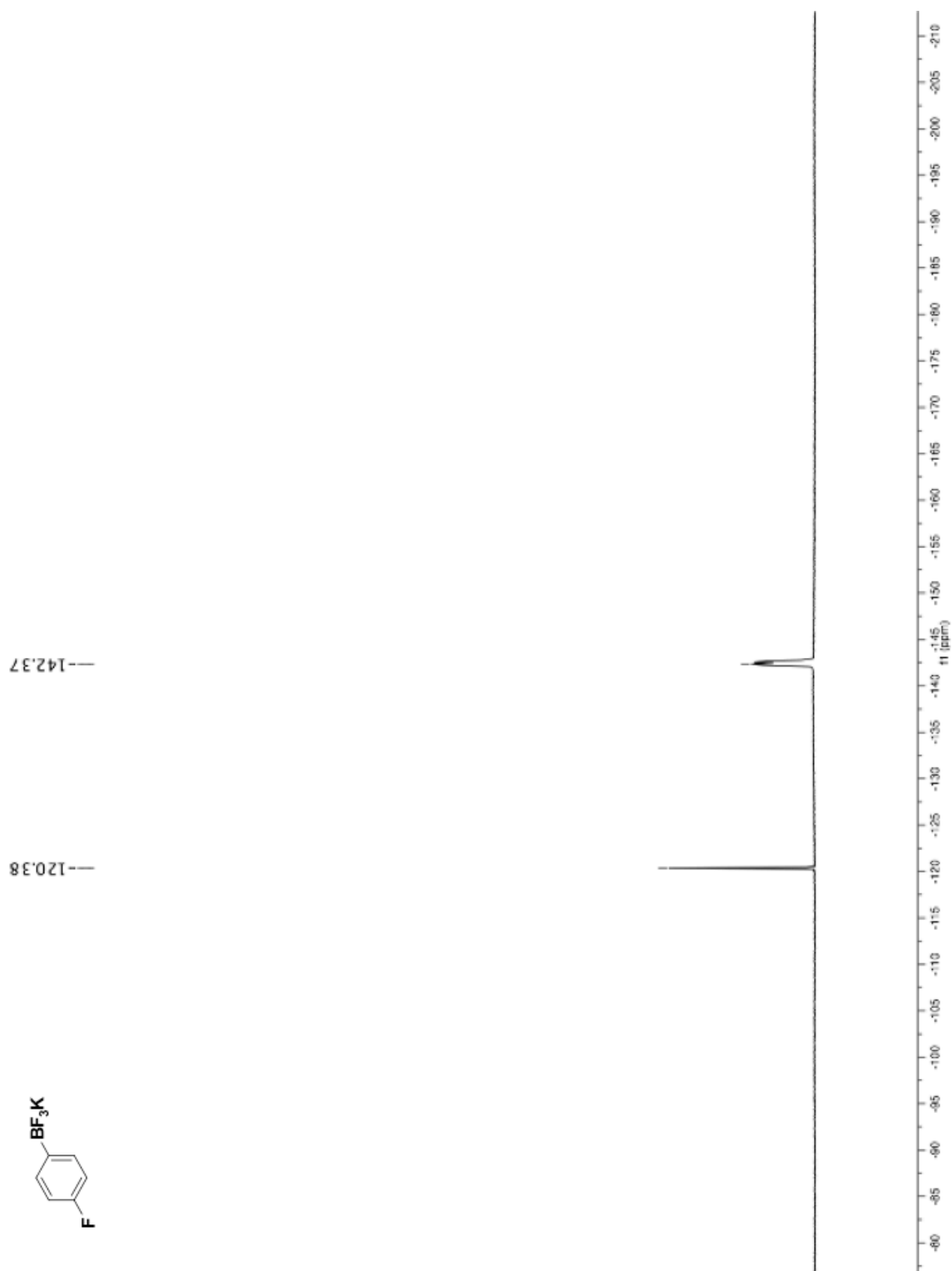
$^{13}\text{C}$  NMR Spectra (125.8 MHz, DMSO- $d_6$ ) Potassium (4-Fluorophenyl)trifluoroborate (Table 1, entry 8)



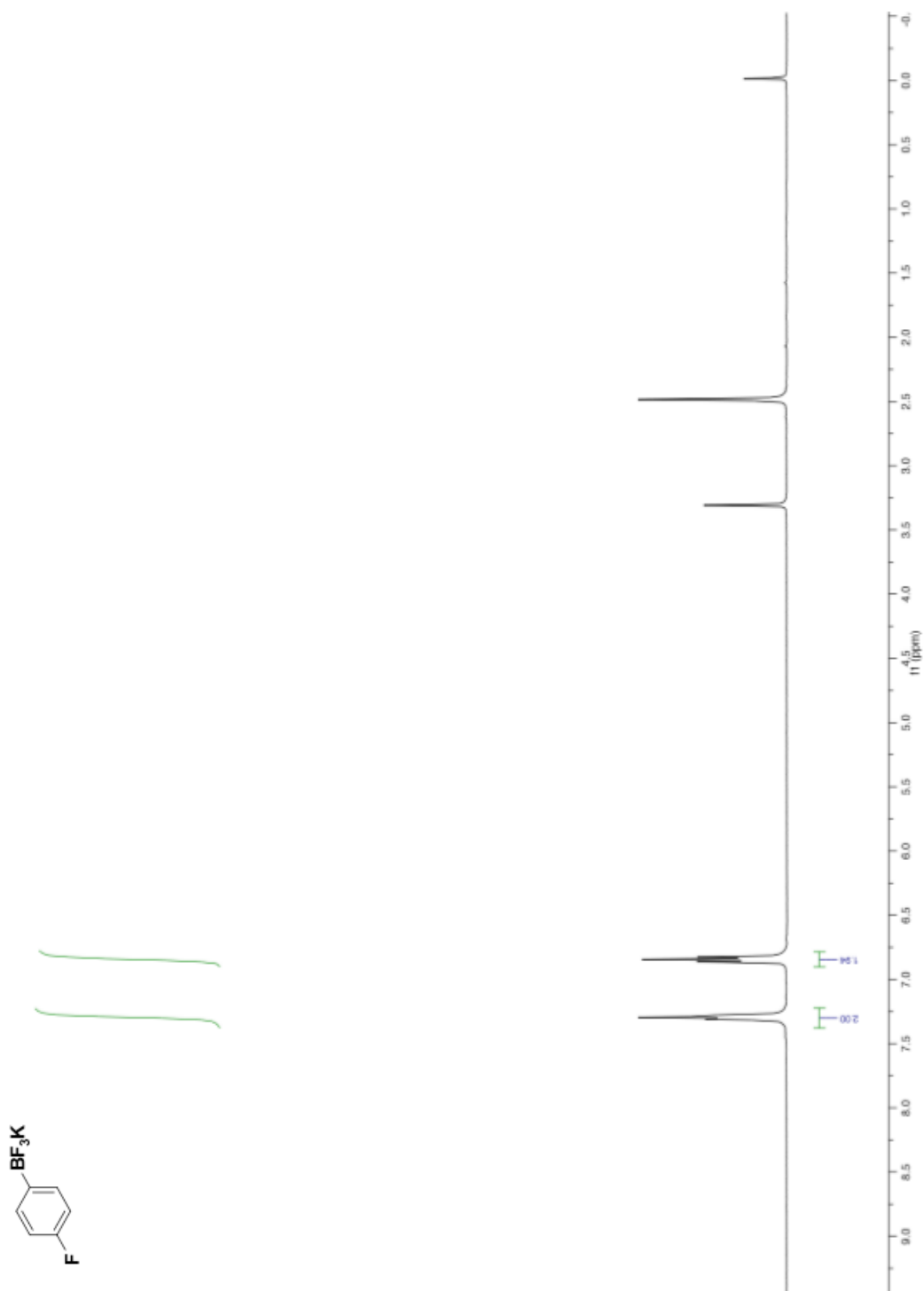
4.63  
4.21  
3.80  
3.39



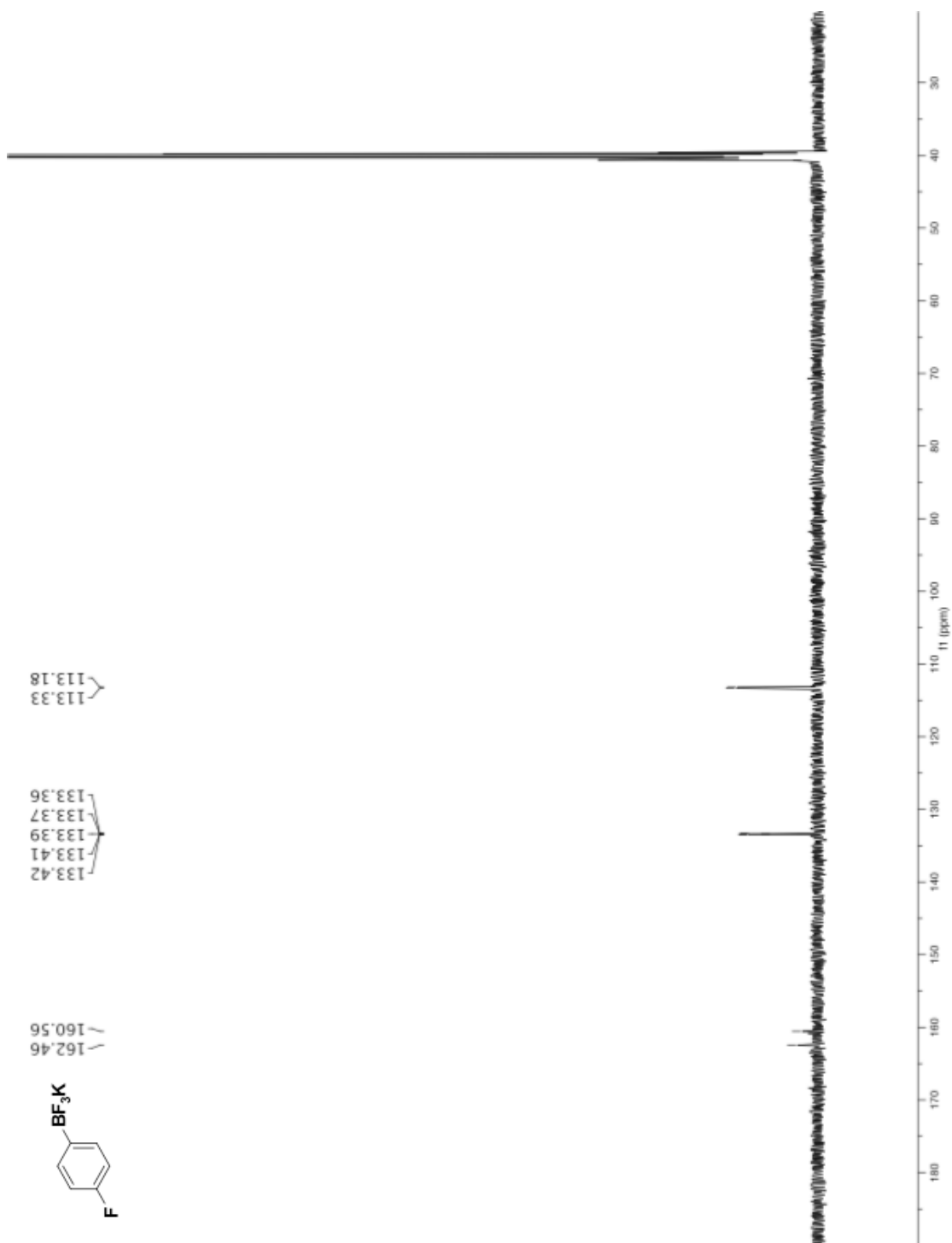
<sup>11</sup>B NMR (128.4 MHz, acetone-*d*<sub>6</sub>) Potassium (4-Fluorophenyl)trifluoroborate (Table 1, entry 8)



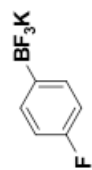
$^{19}\text{F}$  NMR Spectra (338.8 MHz, acetone- $d_6$ ) Potassium (4-Fluorophenyl)trifluoroborate (Table 1, entry 8)



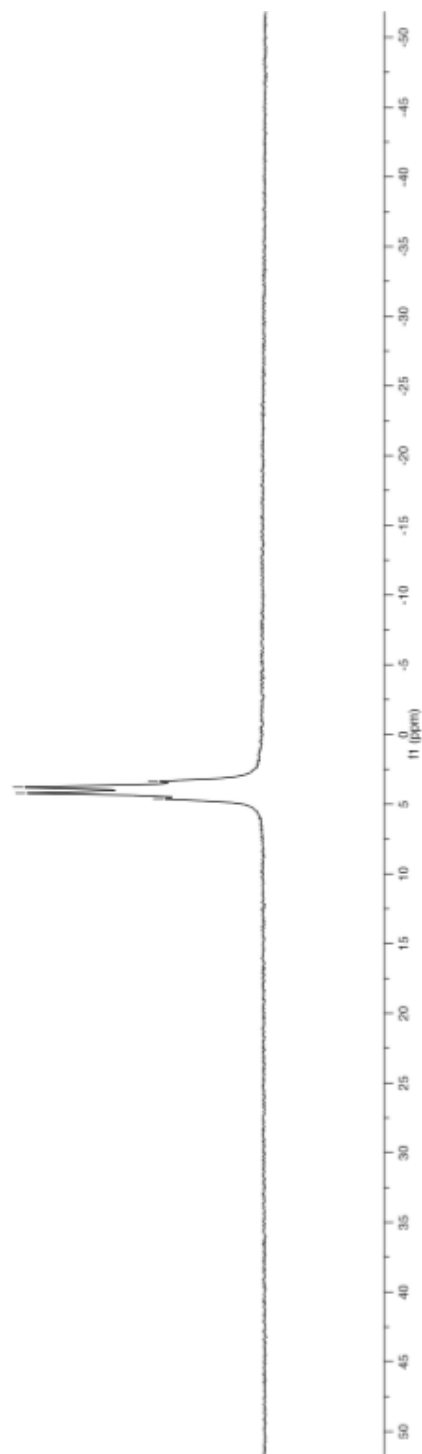
$^1\text{H}$  NMR Spectra (500 MHz,  $\text{DMSO-}d_6$ ) Potassium (4-Fluorophenyl)trifluoroborate (Table 1, entry 8<sup>a</sup>)



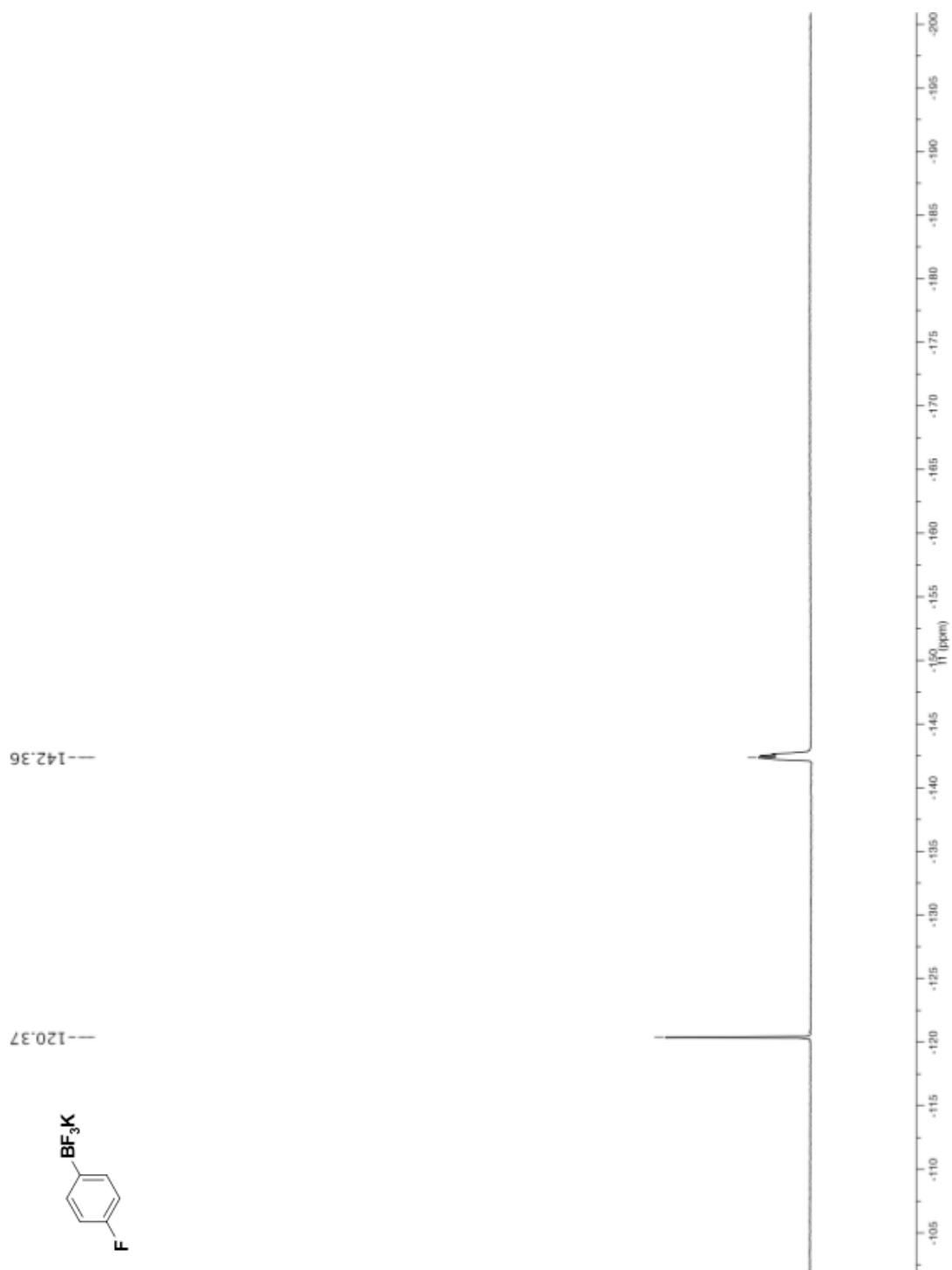
$^{13}\text{C}$  NMR Spectra (125.8 MHz,  $\text{DMSO-}d_6$ ) Potassium (4-Fluorophenyl)trifluoroborate (Table 1, entry 8<sup>a</sup>)



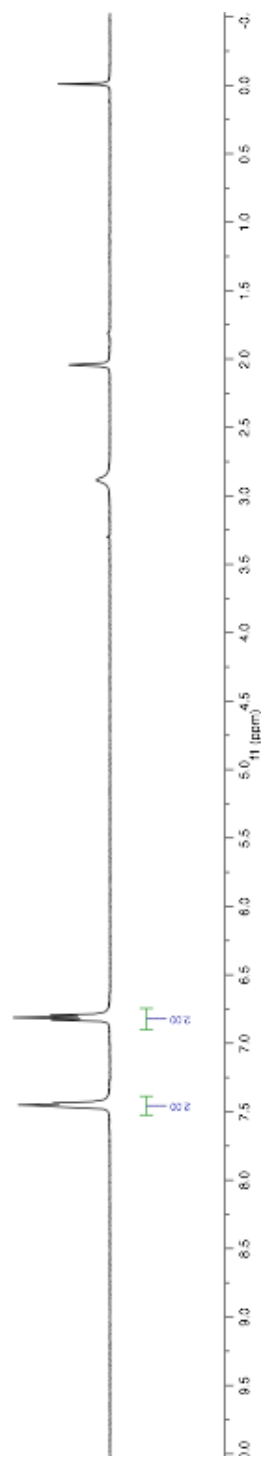
4.62  
4.21  
3.79  
3.38



$^{11}\text{B}$  NMR (128.4 MHz, acetone- $d_6$ ) Potassium (4-Fluorophenyl)trifluoroborate (Table 1, entry 8<sup>a</sup>)

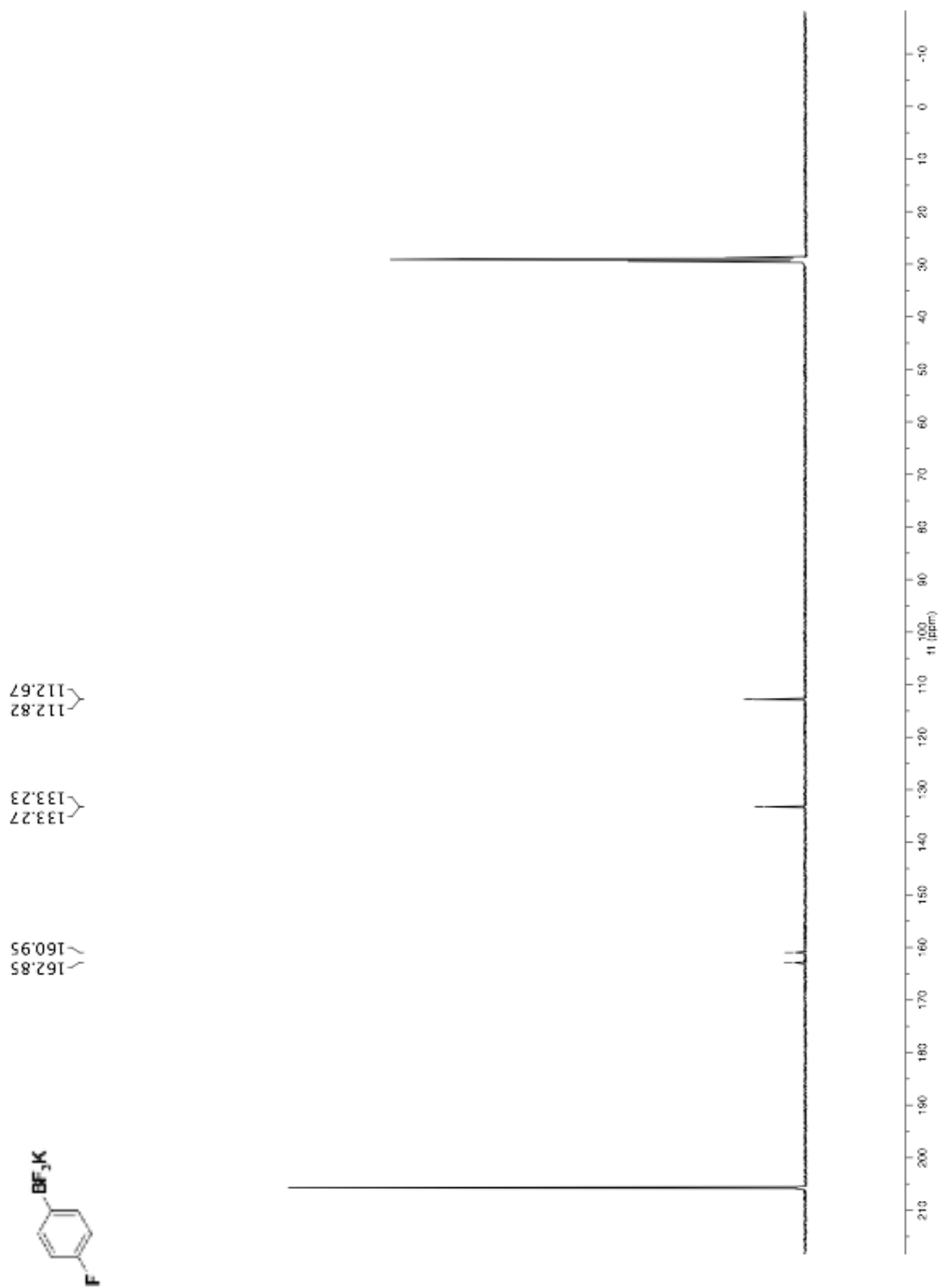


$^{19}\text{F}$  NMR Spectra (338.8 MHz, acetone- $d_6$ ) Potassium (4-Fluorophenyl)trifluoroborate (Table 1, entry 8<sup>a</sup>)

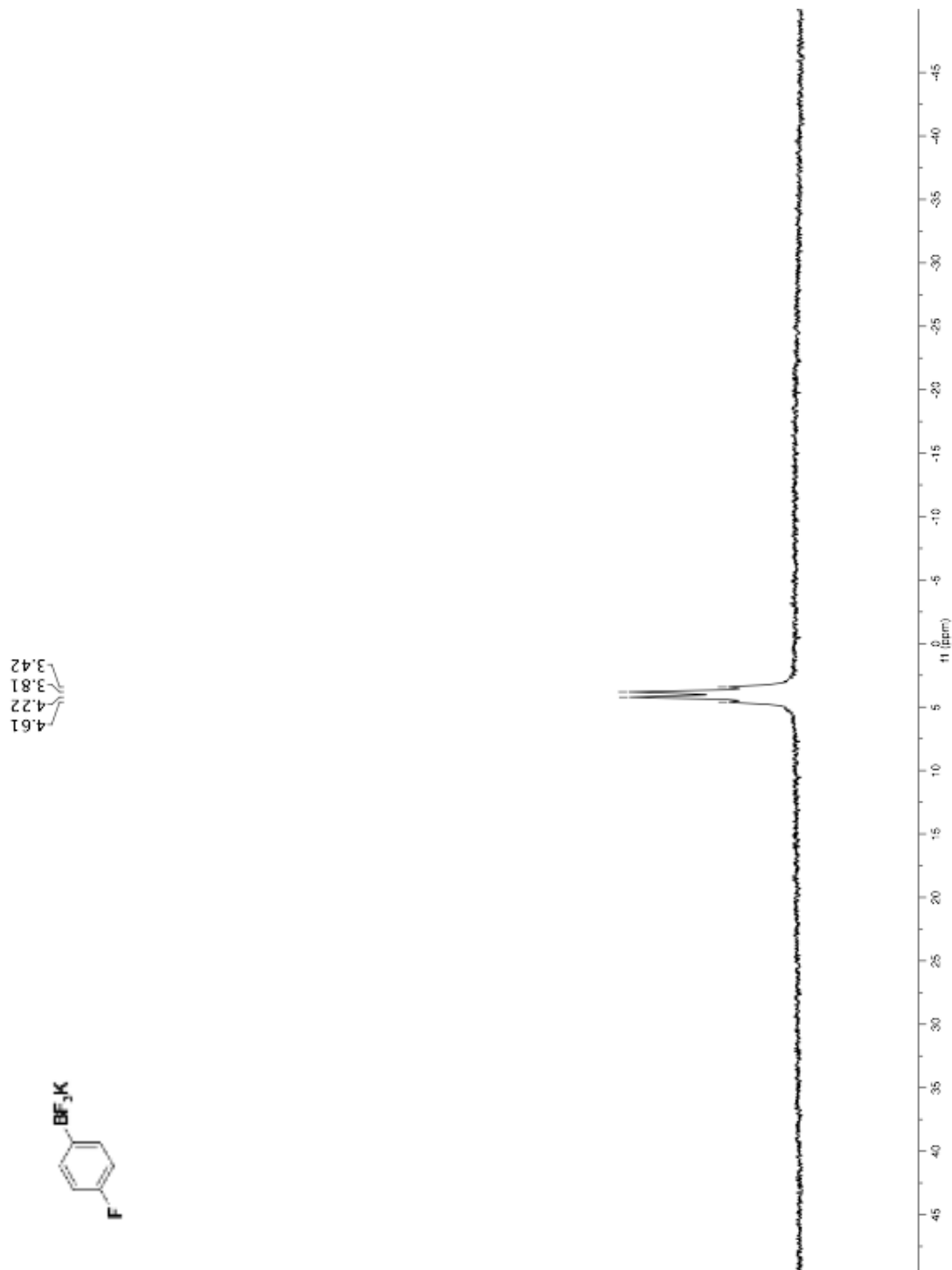


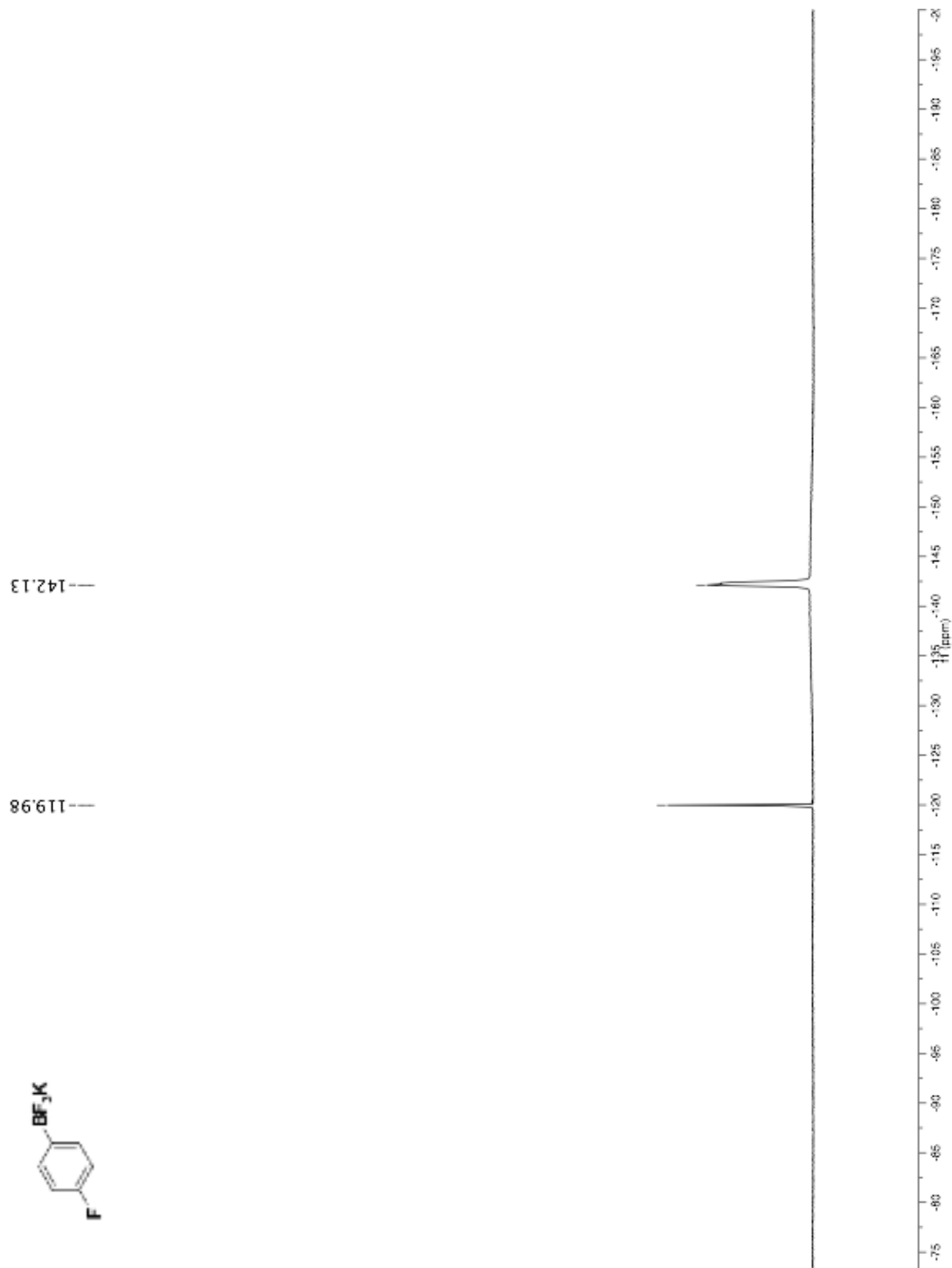
<sup>1</sup>H NMR Spectra (500 MHz, acetone-*d*<sub>6</sub>) **Potassium (4-Fluorophenyl)trifluoroborate** (Table 1, entry 8<sup>b</sup>)



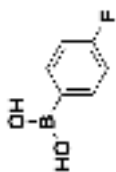


<sup>13</sup>C NMR Spectra (125.8 MHz, Acetone-*d*<sub>6</sub>) Potassium (4-Fluorophenyl)trifluoroborate (Table 1, entry 8<sup>b</sup>)

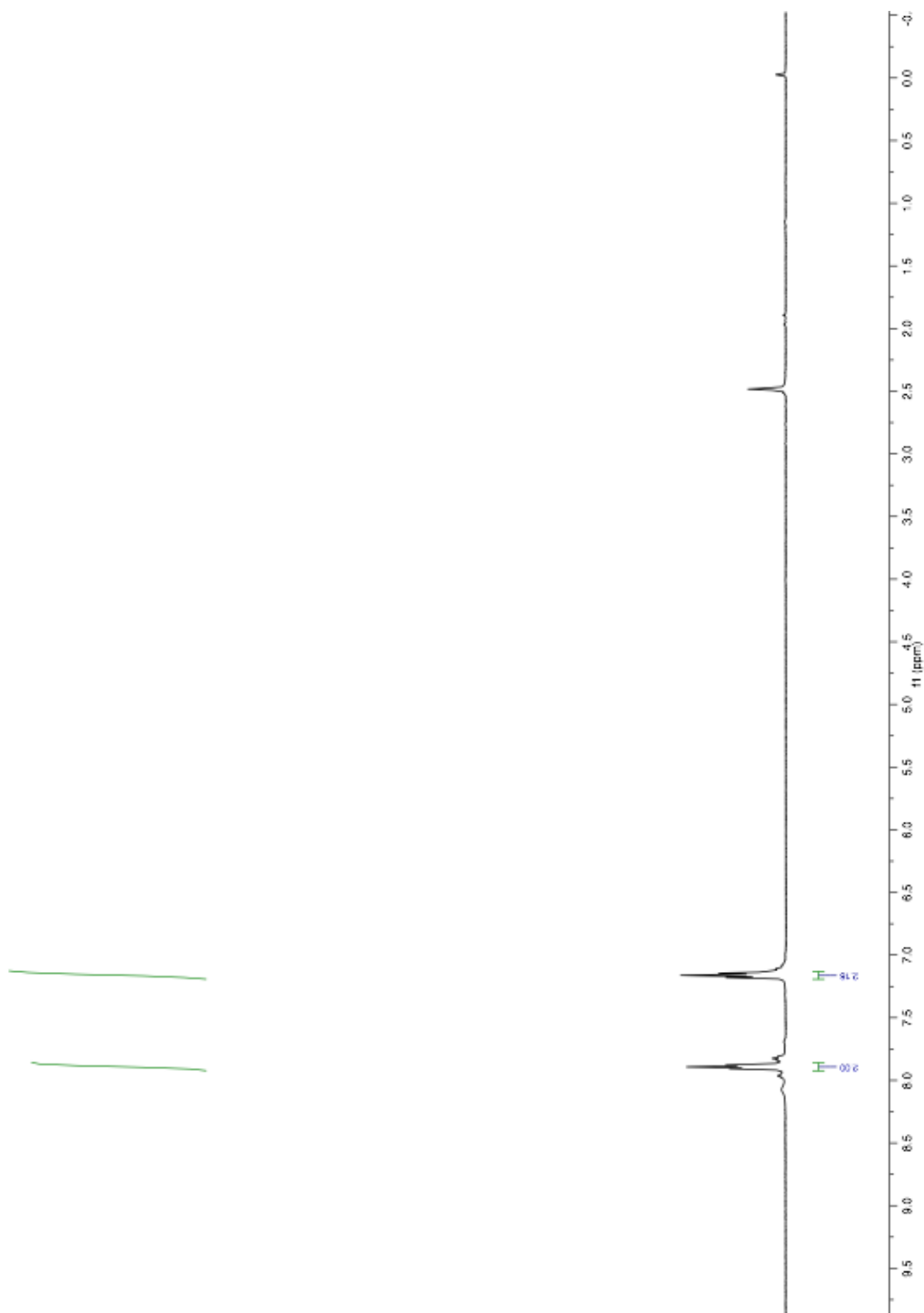


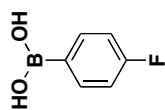


$^{19}\text{F}$  NMR Spectra (338.8 MHz, acetone- $d_6$ ) Potassium (4-Fluorophenyl)trifluoroborate (Table 1, entry 8<sup>b</sup>)

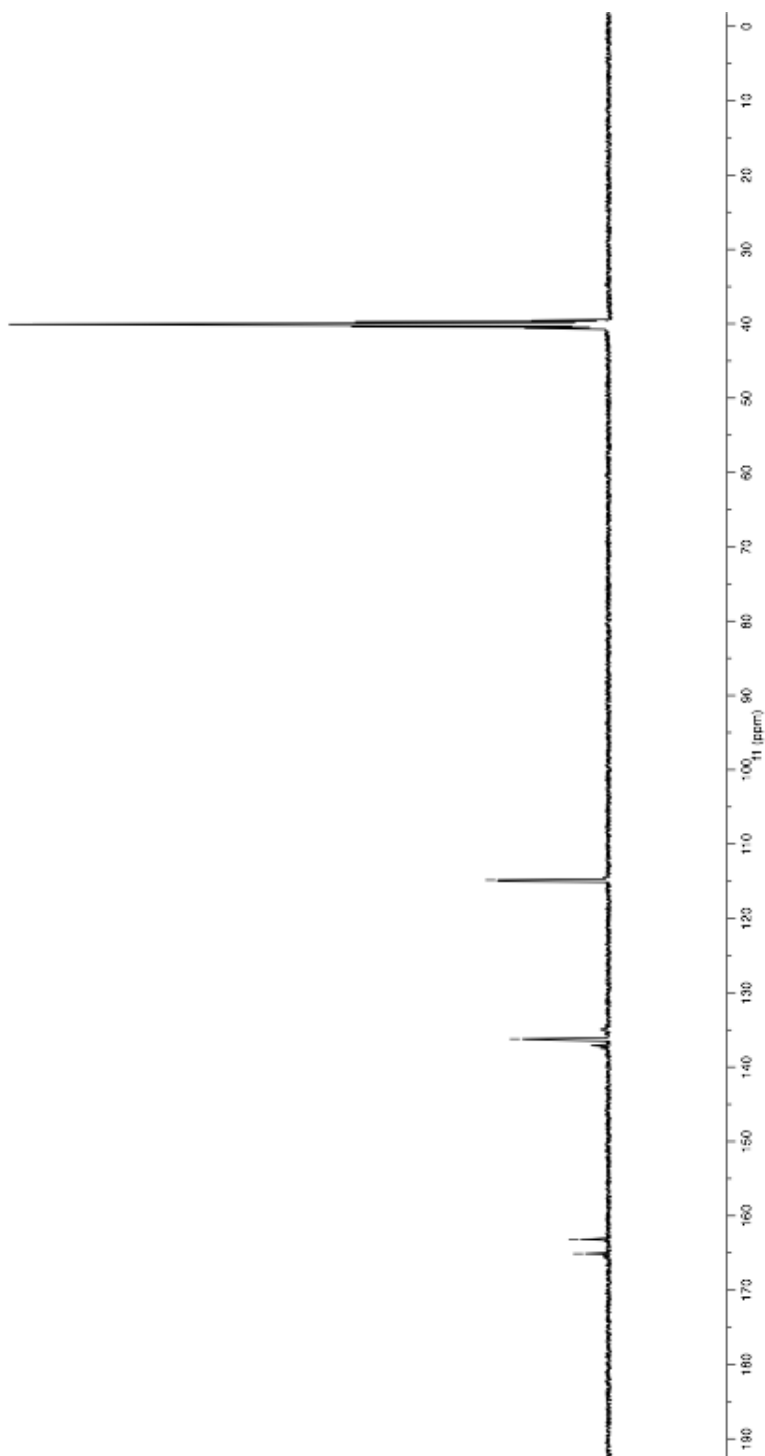


<sup>1</sup>H NMR Spectra (500 MHz, acetone-*d*<sub>6</sub>) (4-Fluorophenyl)boronic acid (Table 1, entry 8<sup>f</sup>)

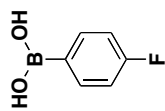




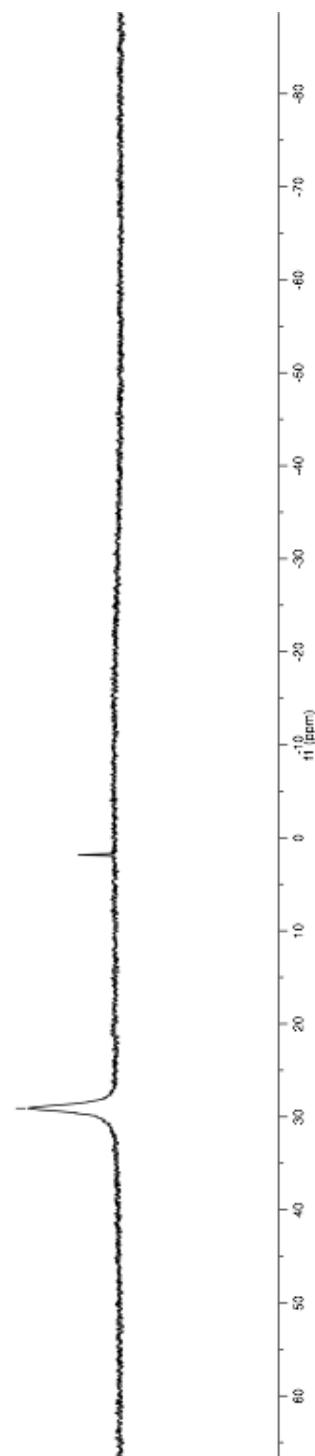
165.10  
163.16  
136.22  
114.84



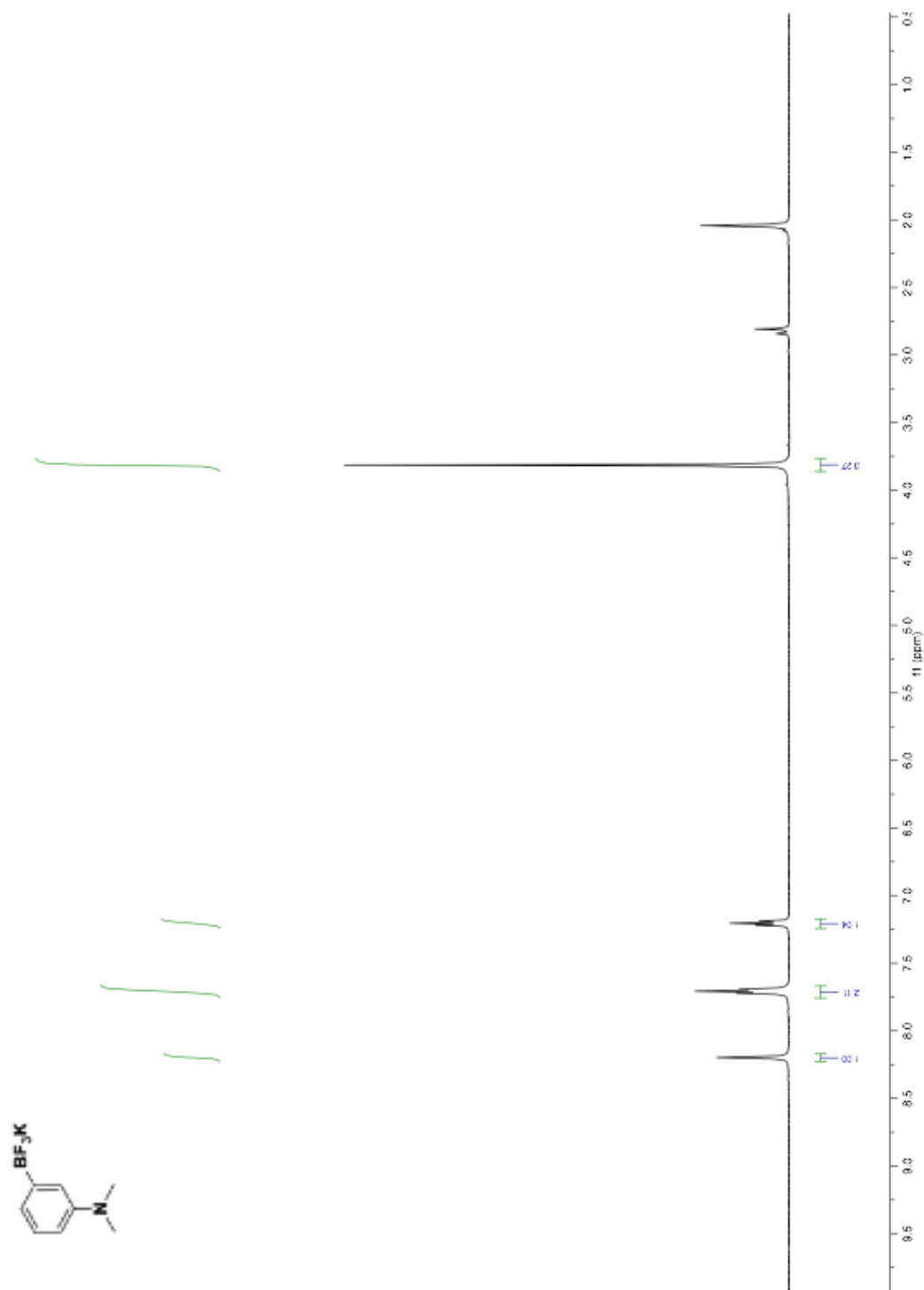
<sup>13</sup>C NMR Spectra (125.8 MHz, DMSO-*d*<sub>6</sub>) (4-Fluorophenyl)boronic acid (Table 1, entry 8<sup>f</sup>)



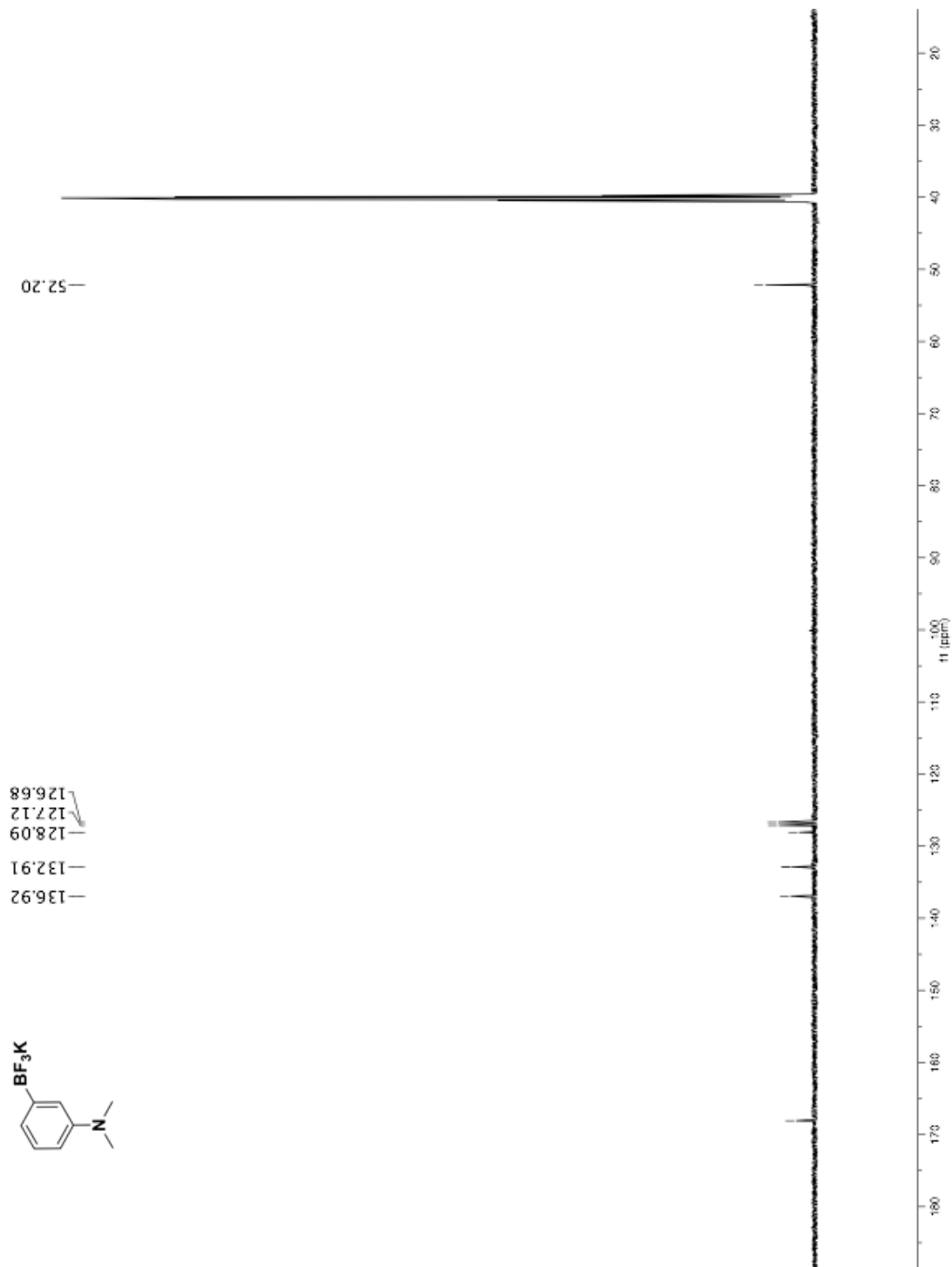
—29.09



$^{11}\text{B}$  NMR (128.4 MHz, acetone- $d_6$ ) (4-Fluorophenyl)boronic acid (Table 1, entry 8<sup>f</sup>)

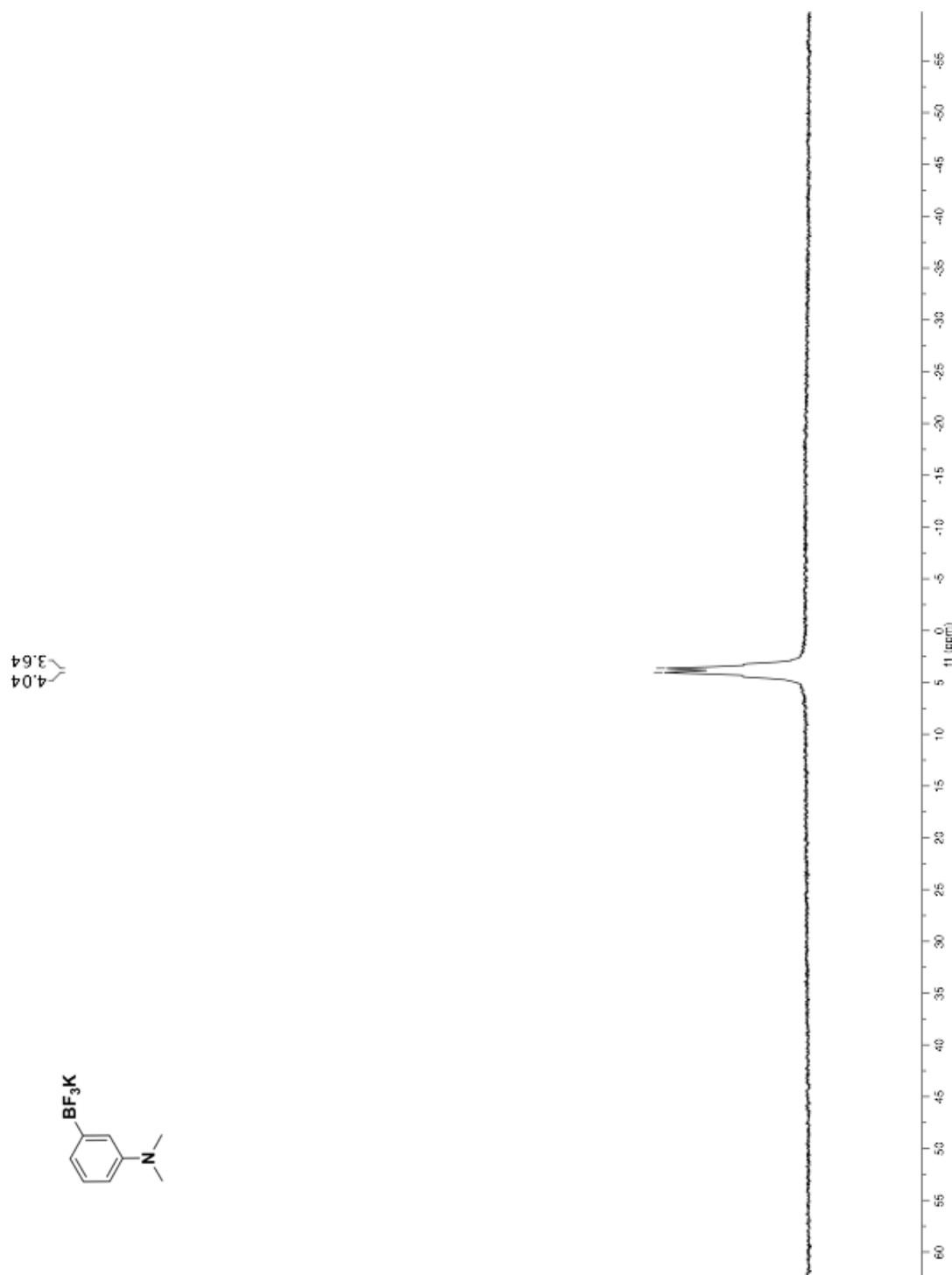


<sup>1</sup>H NMR Spectra (500 MHz, acetone-*d*<sub>6</sub>) **(3-(Dimethylamino)phenyl)trifluoroborate** (Table 1, entry 9)

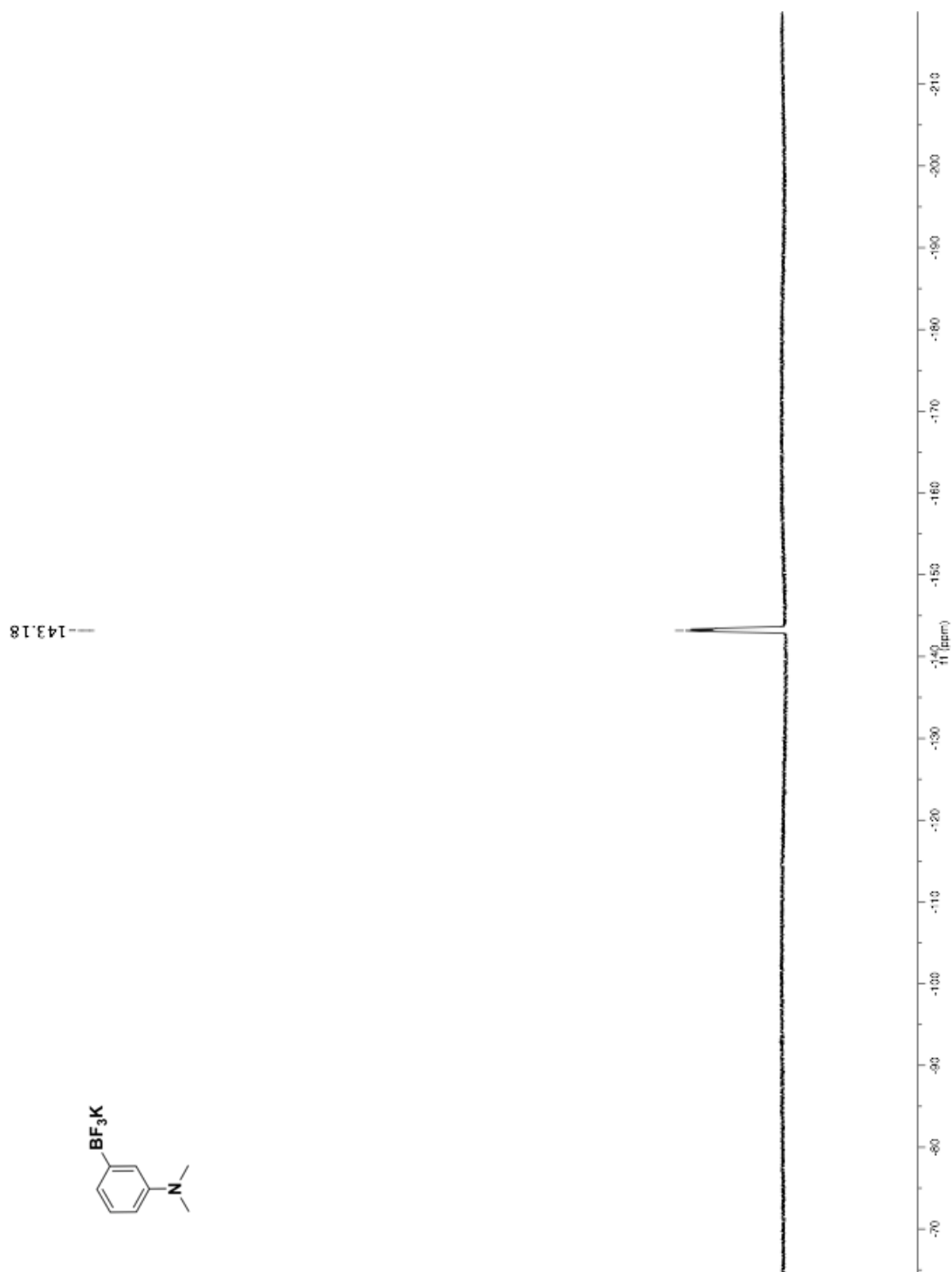


<sup>13</sup>C NMR Spectra (125.8 MHz, DMSO-*d*<sub>6</sub>) **(3-(Dimethylamino)phenyl)trifluoroborate** (Table 1, entry 9)

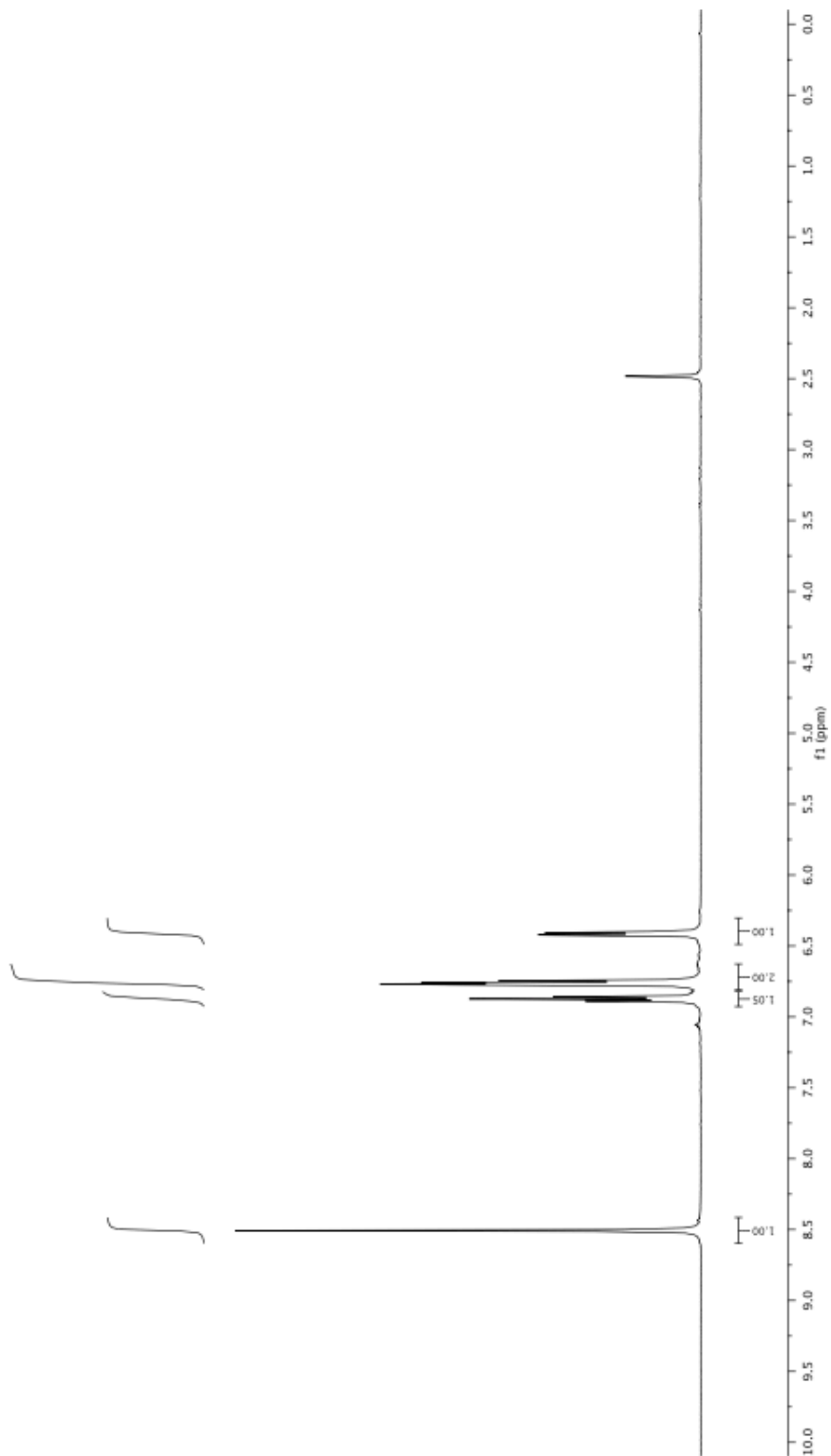
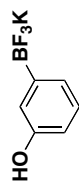




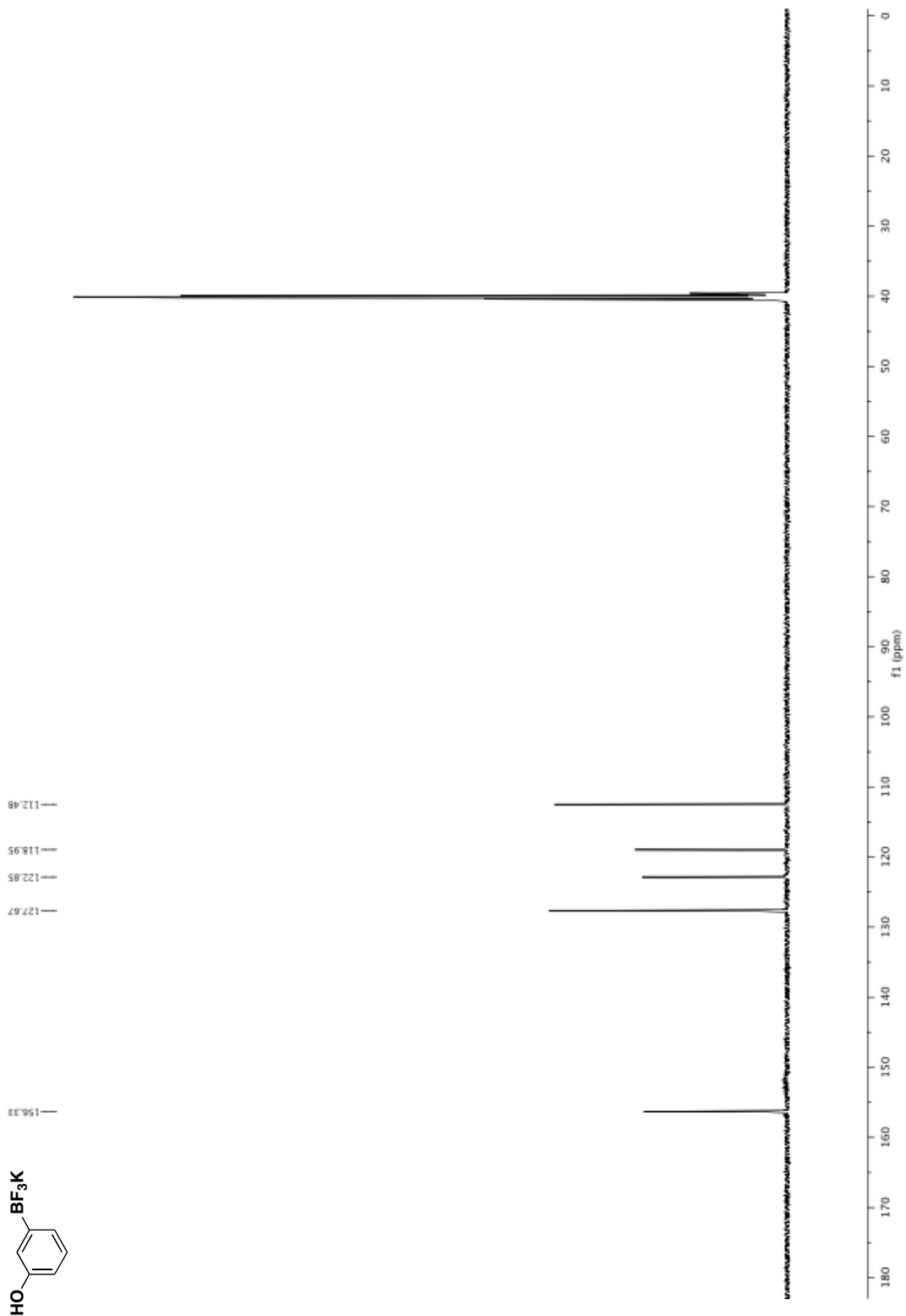
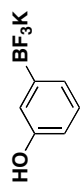
$^{11}\text{B}$  NMR (128.4 MHz, acetone- $d_6$ ) (3-(Dimethylamino)phenyl)trifluoroborate (Table 1, entry 9)



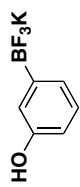
$^{19}\text{F}$  NMR Spectra (338.8 MHz, acetone- $d_6$ ) **(3-(Dimethylamino)phenyl)trifluoroborate** (Table 1, entry 9)



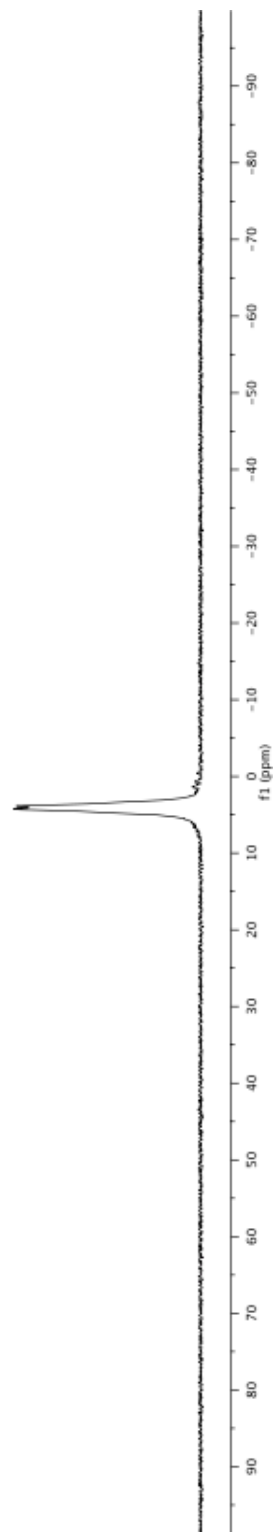
$^1\text{H}$  NMR Spectra (500 MHz,  $\text{DMSO-}d_6$ ) Potassium (3-Hydroxyphenyl)trifluoroborate (Table 1, entry 10)



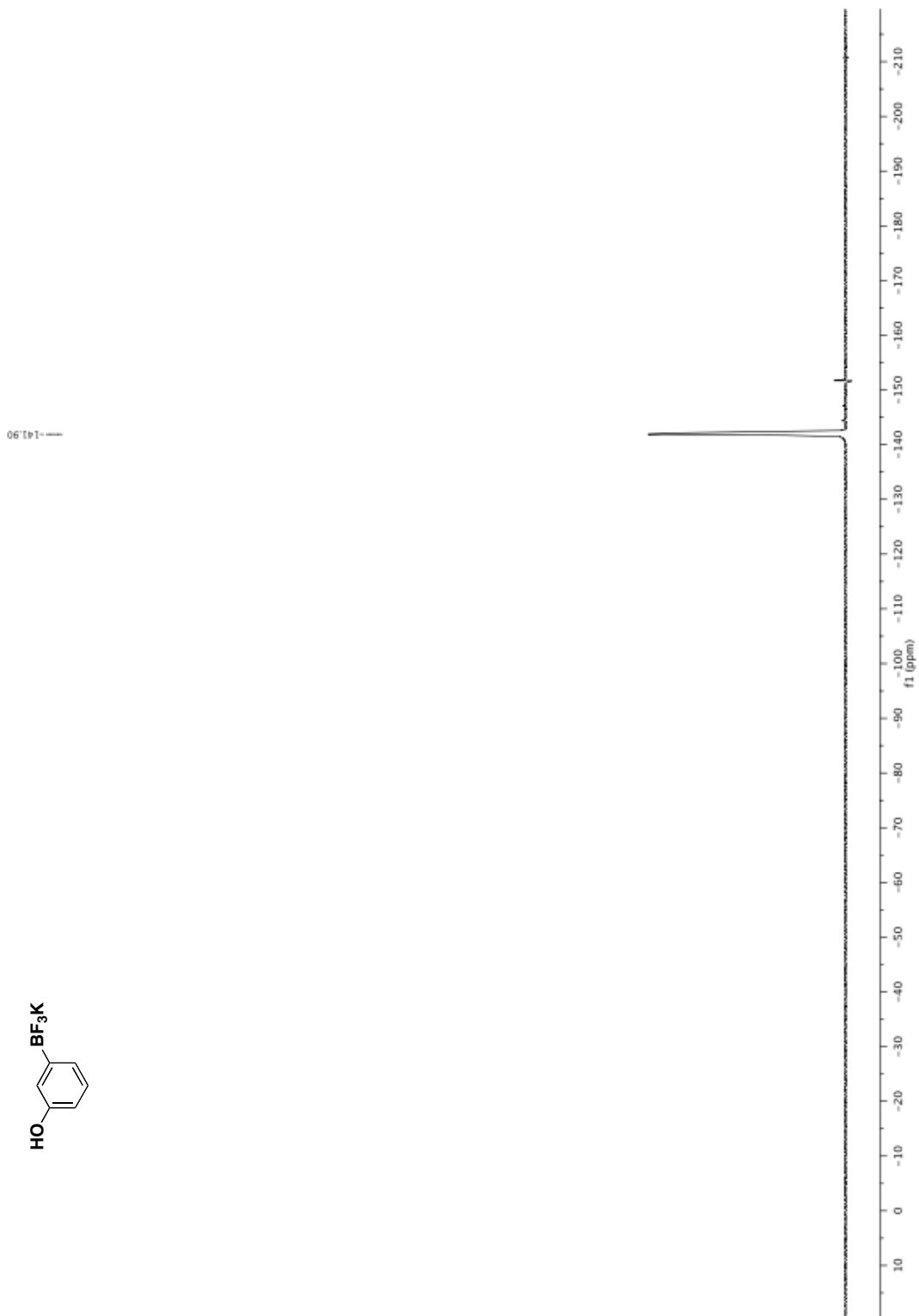
$^{13}\text{C}$  NMR Spectra (125.8 MHz,  $\text{DMSO-}d_6$ ) Potassium (3-Hydroxyphenyl)trifluoroborate (Table 1, entry 10)



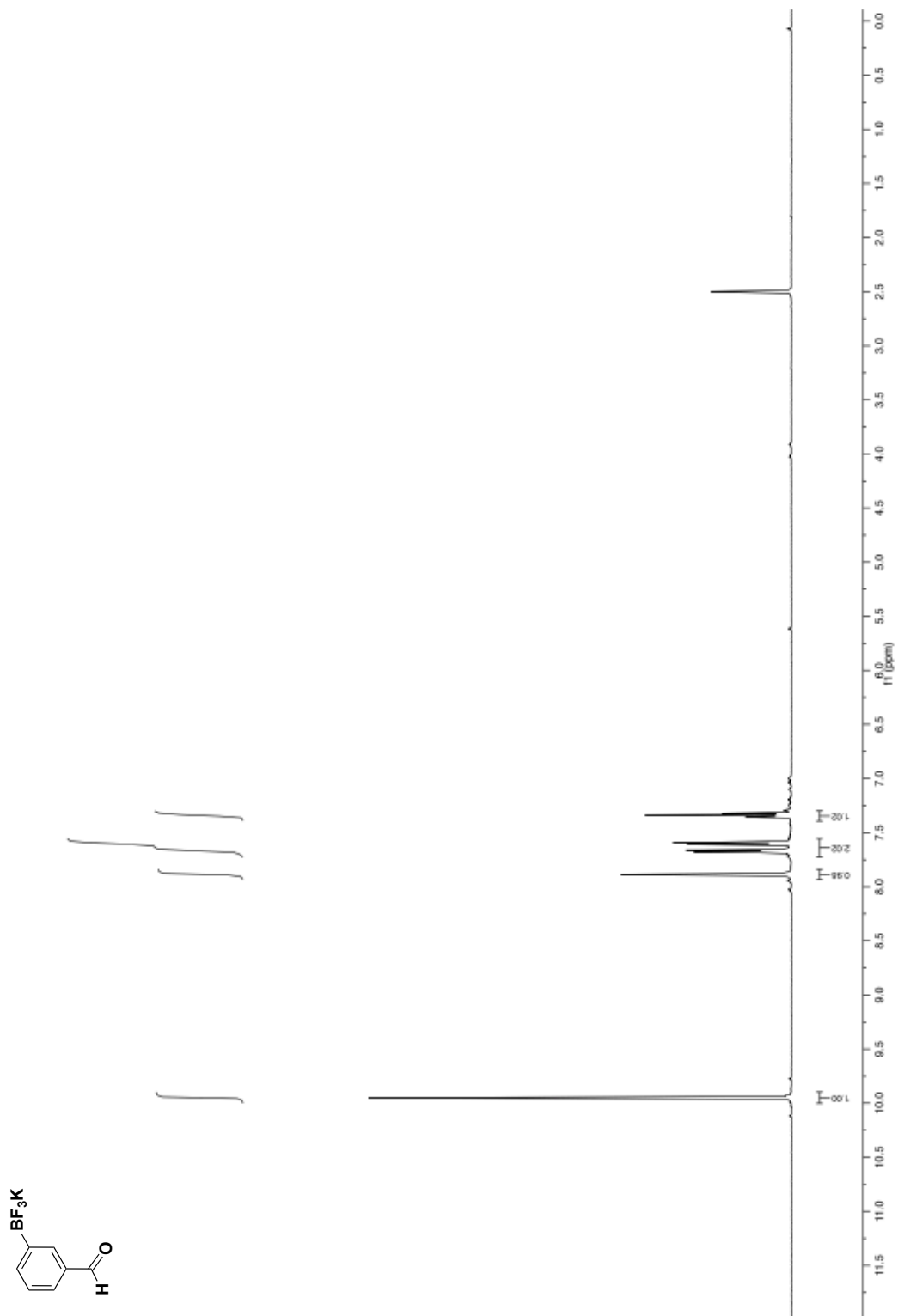
1.24  
3.89



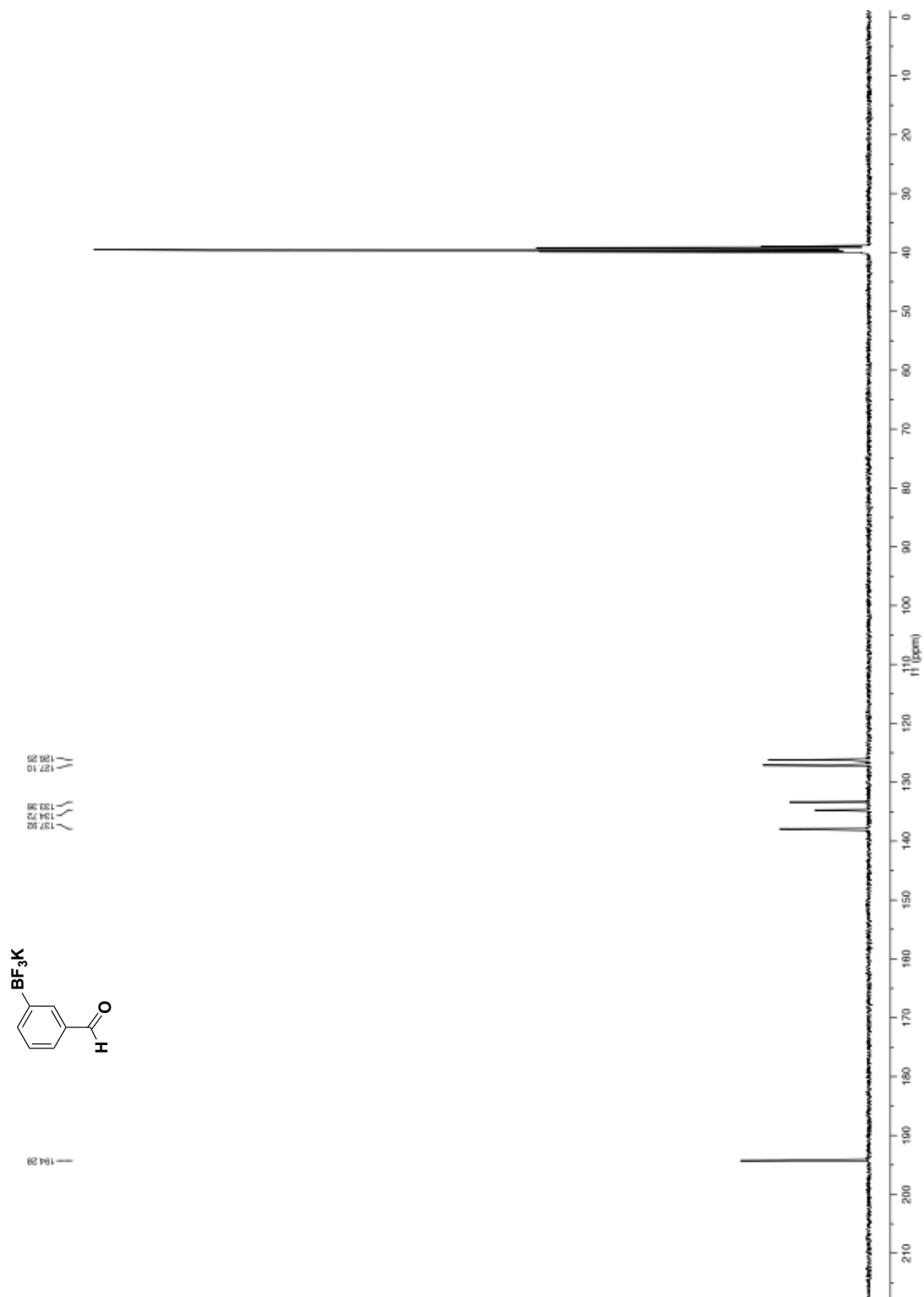
$^{11}\text{B}$  NMR (128.4 MHz, acetone- $d_6$ ) **Potassium (3-Hydroxyphenyl)trifluoroborate**  
(Table 1, entry 10)



$^{19}\text{F}$  NMR Spectra (282 MHz, acetone- $d_6$ ) Potassium (3-Hydroxyphenyl)trifluoroborate (Table 1, entry 10)

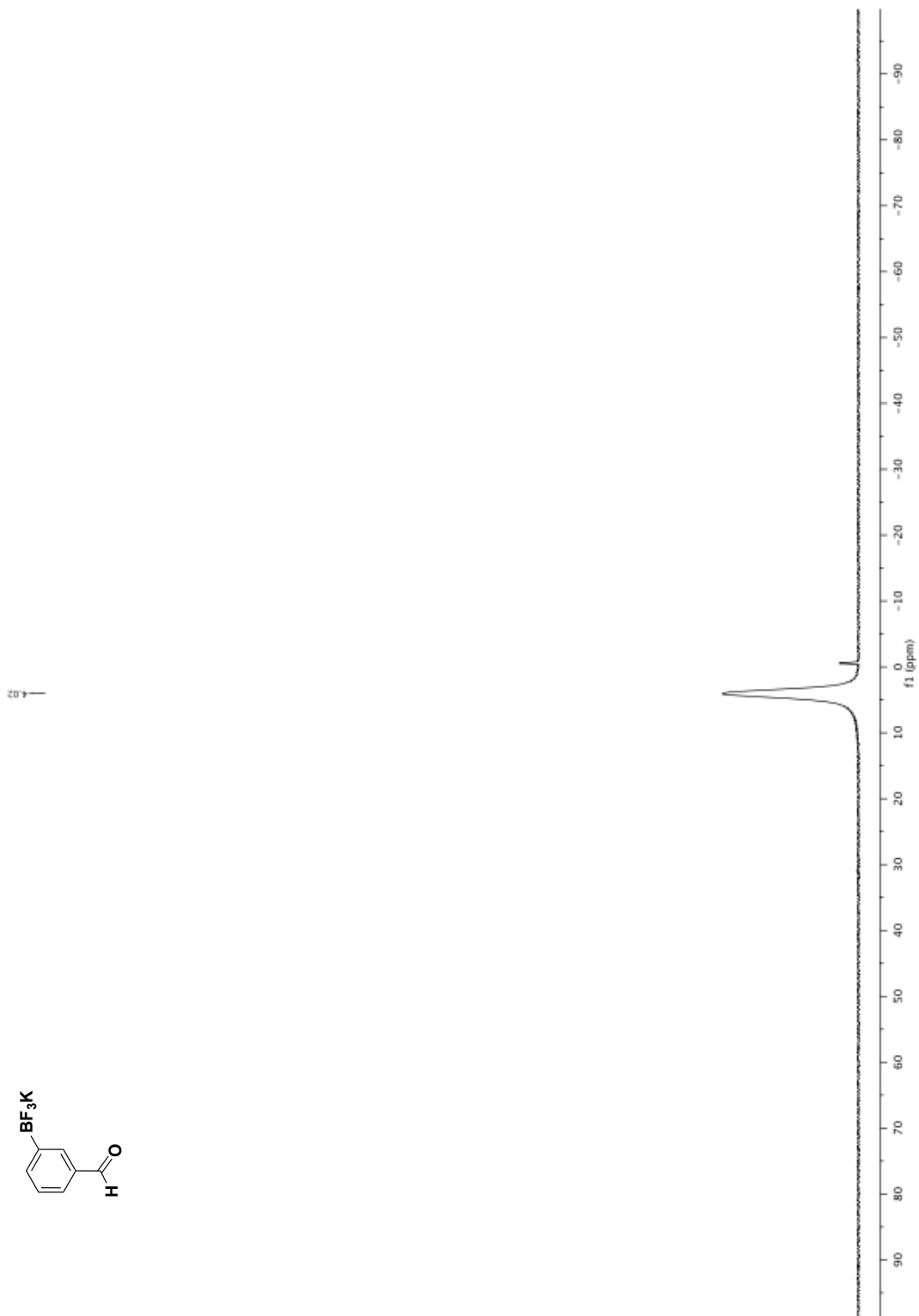


<sup>1</sup>H NMR Spectra (500 MHz, DMSO-*d*<sub>6</sub>) Potassium 3-Formylphenyl-trifluoroborate (Table 1, entry 11)

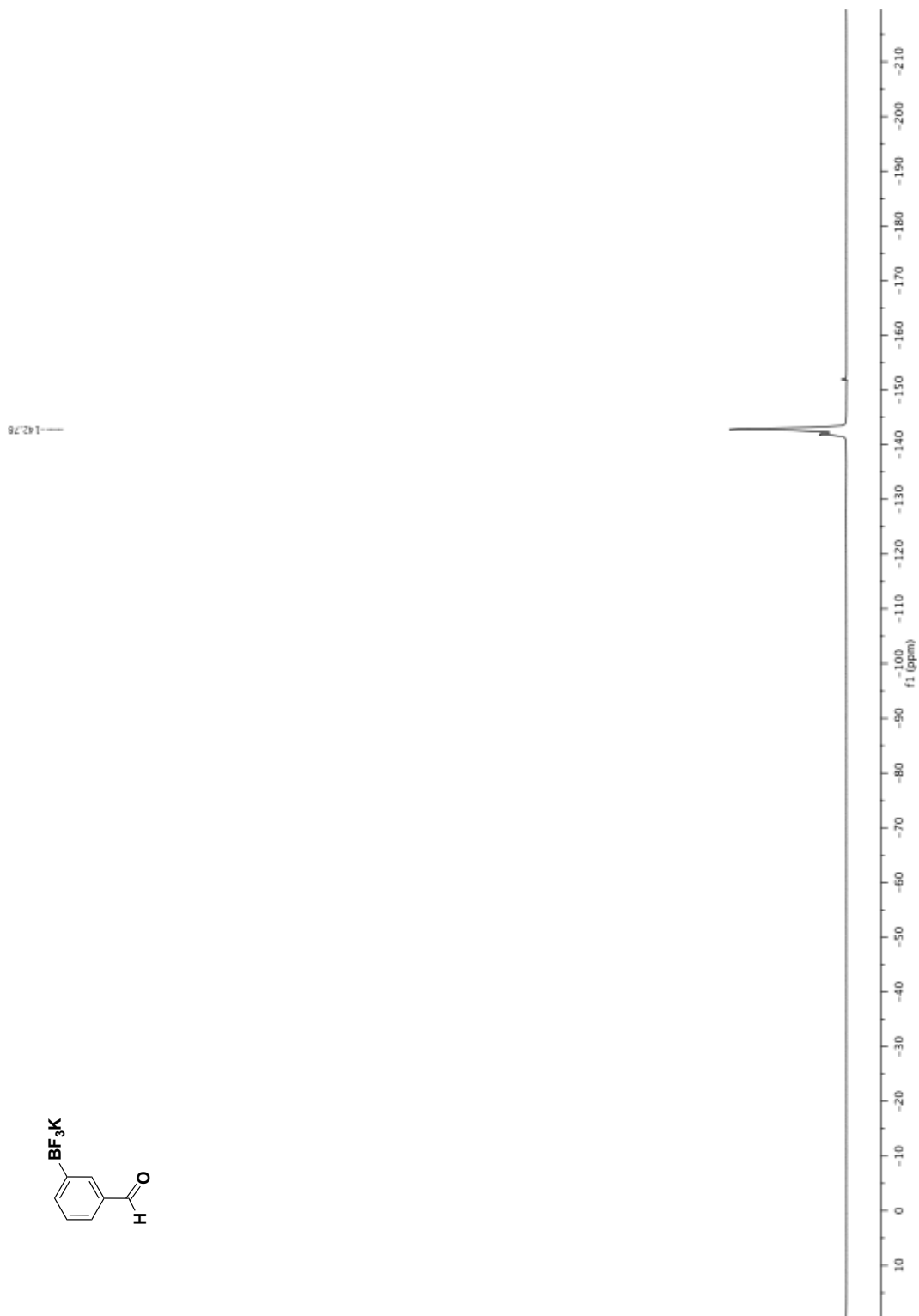


<sup>13</sup>C NMR Spectra (125.8 MHz, DMSO-*d*<sub>6</sub>) Potassium 3-Formylphenyl-trifluoroborate (Table 1, entry 11)<sup>6</sup>

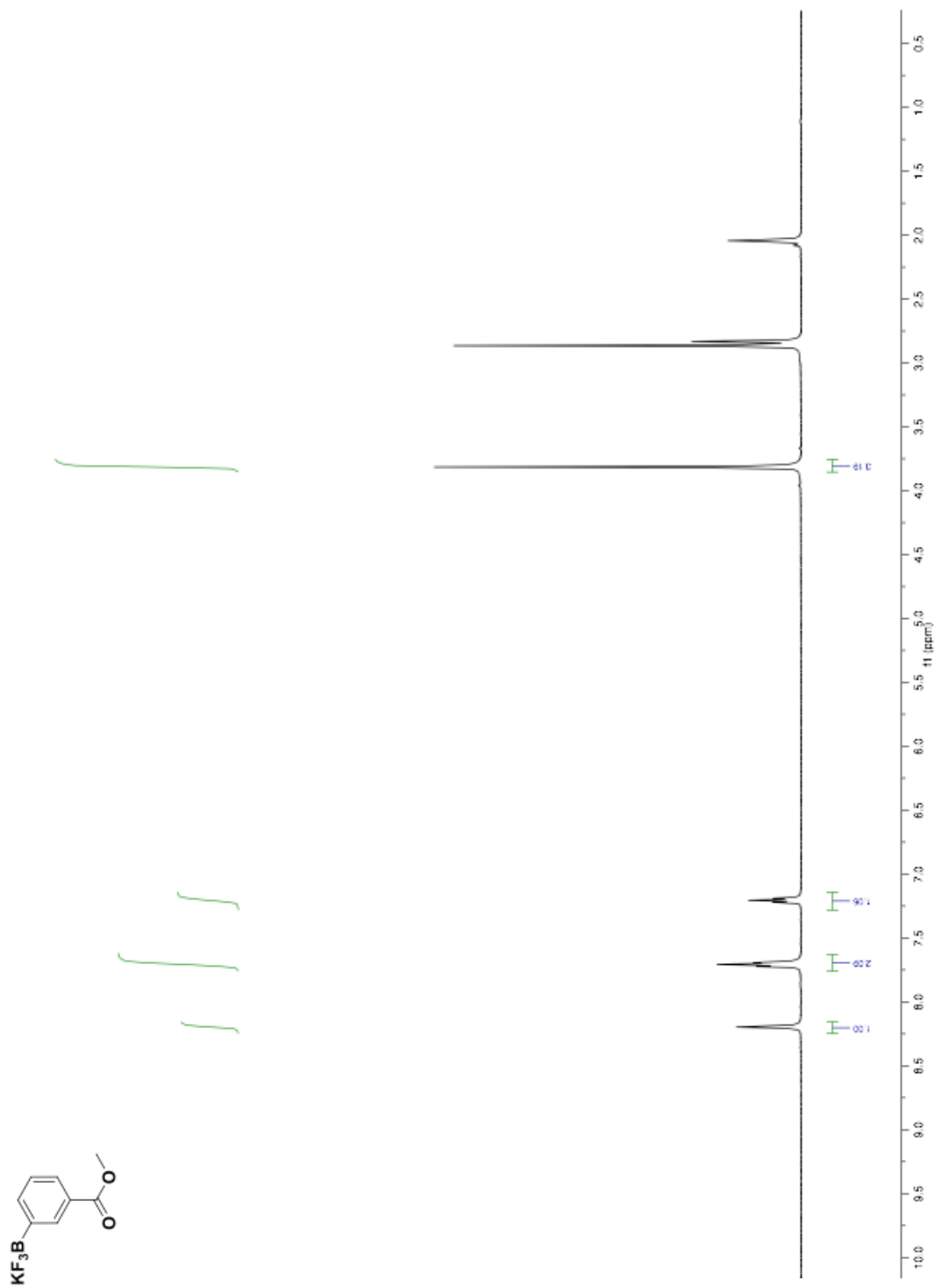




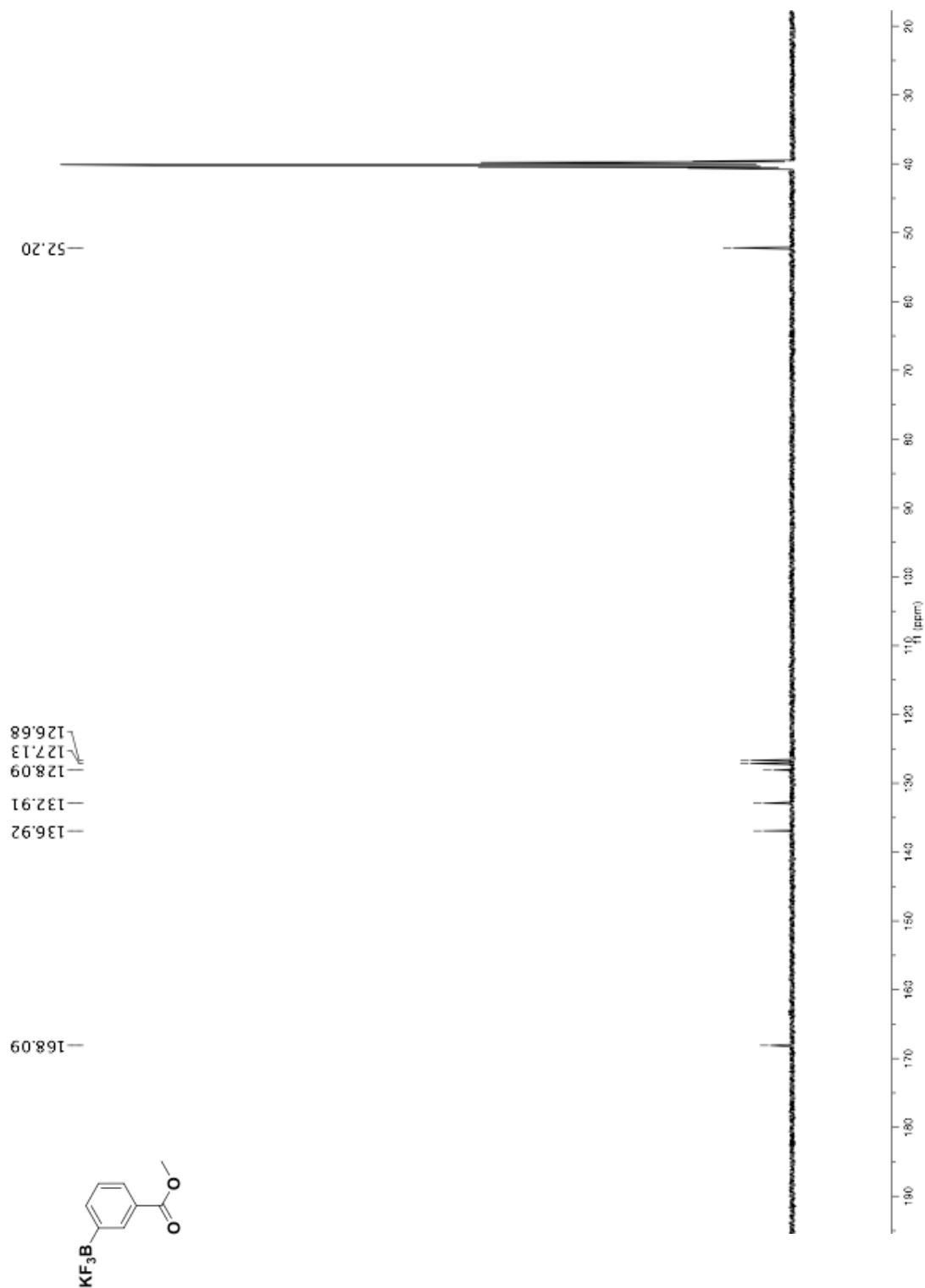
$^{11}\text{B}$  NMR (128.4 MHz, acetone- $d_6$ ) Potassium 3-Formylphenyl-trifluoroborate (Table 1, entry 11)



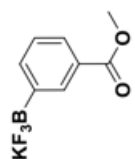
$^{19}\text{F}$  NMR Spectra (282 MHz, acetone- $d_6$ ) **Potassium 3-Formylphenyl-trifluoroborate**  
(Table 1, entry 11)



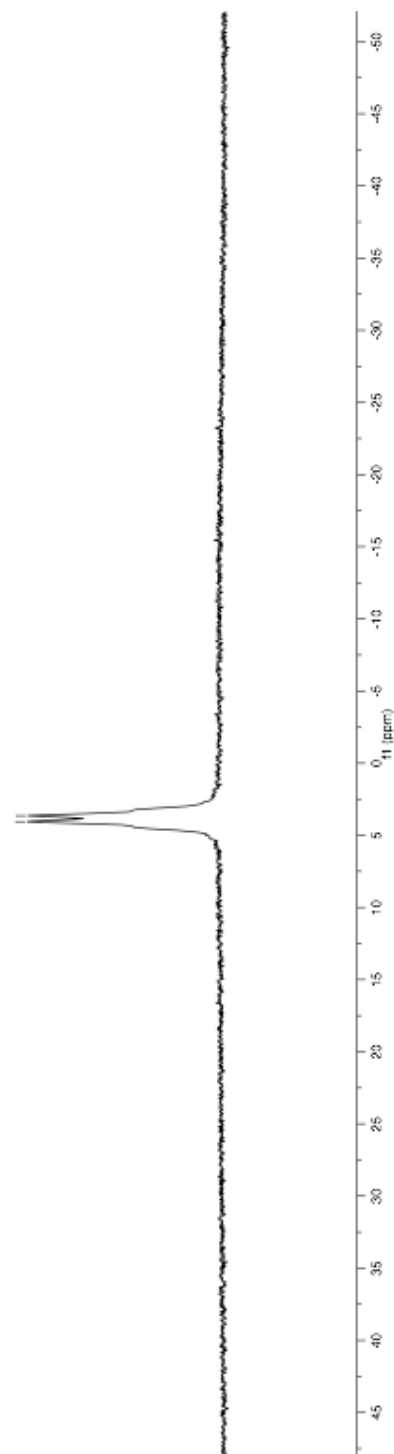
<sup>1</sup>H NMR Spectra (500 MHz, acetone-*d*<sub>6</sub>) Potassium (3-(Methoxycarbonyl)phenyl)trifluoroborate (Table 1, entry 12) (3-



<sup>13</sup>C NMR Spectra (125.8 MHz, DMSO-*d*<sub>6</sub>) Potassium (3-(Methoxycarbonyl)phenyl)trifluoroborate (Table 1, entry 12)

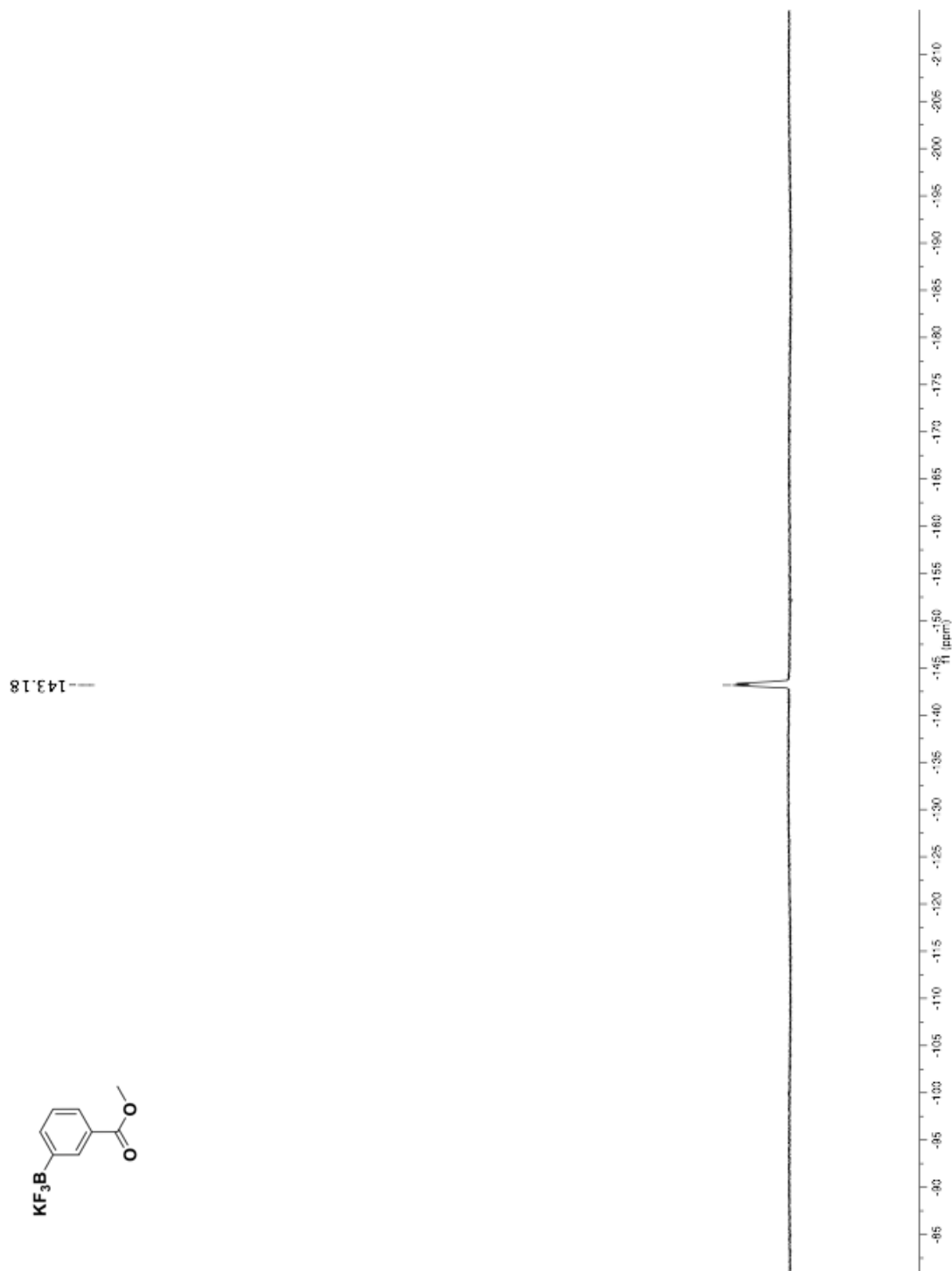


4.06  
3.65



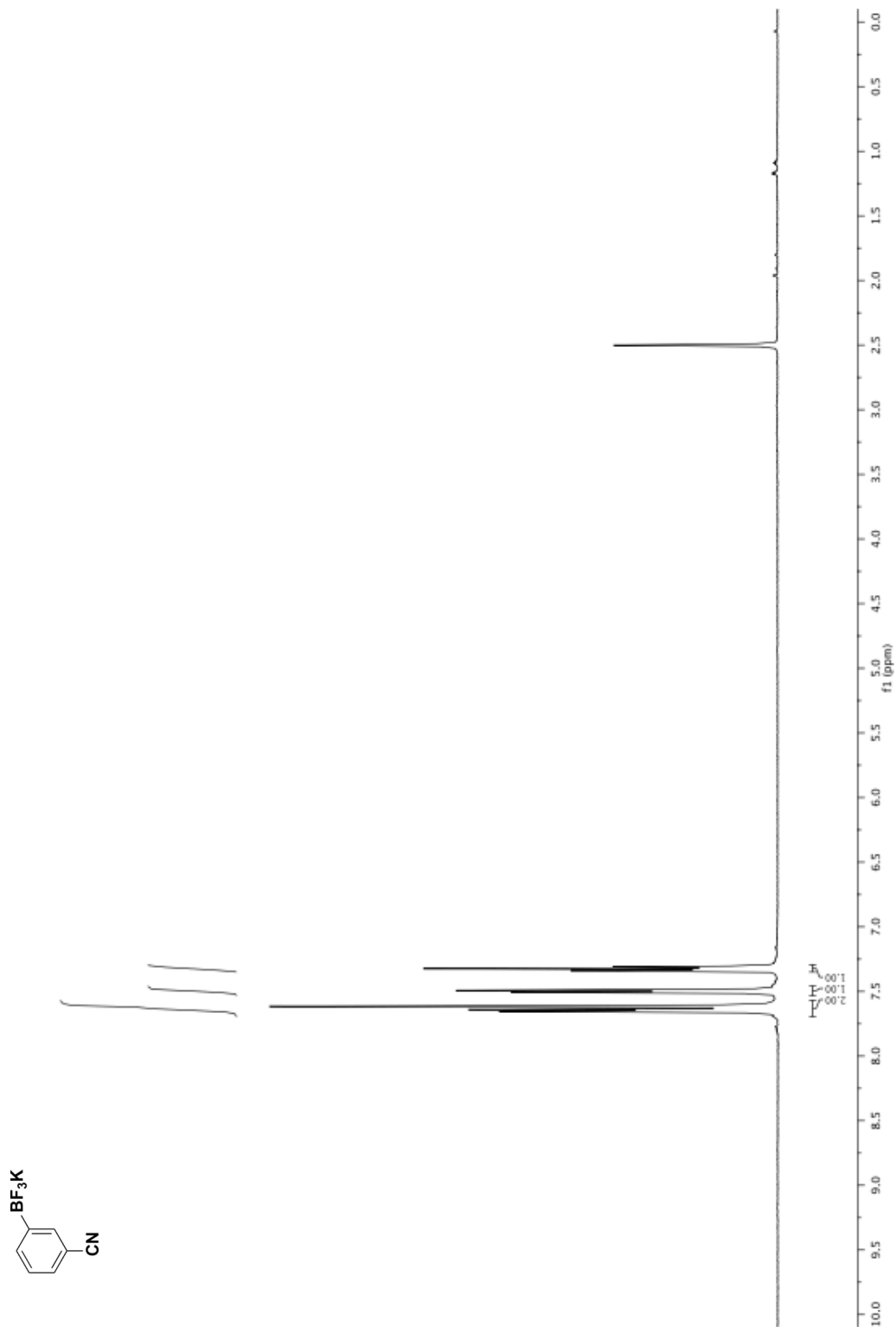
$^{11}\text{B}$  NMR (128.4 MHz, acetone- $d_6$ )  
(Methoxycarbonyl)phenyltrifluoroborate (Table 1, entry 12)

Potassium (3-

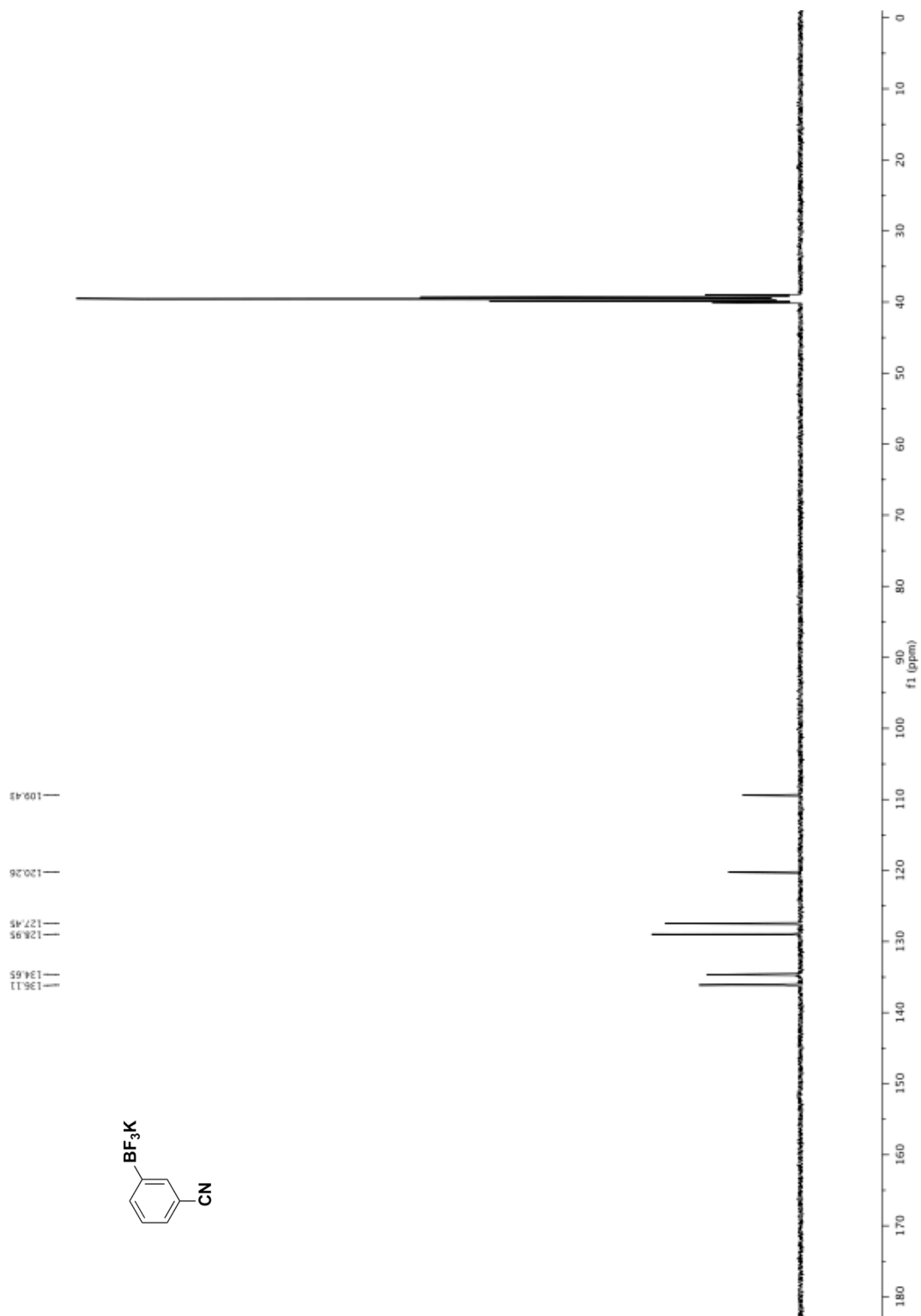


$^{19}\text{F}$  NMR Spectra (338.8 MHz, acetone- $d_6$ )  
(Methoxycarbonyl)phenyltrifluoroborate (Table 1, entry 12)

Potassium (3-

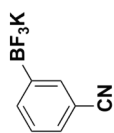
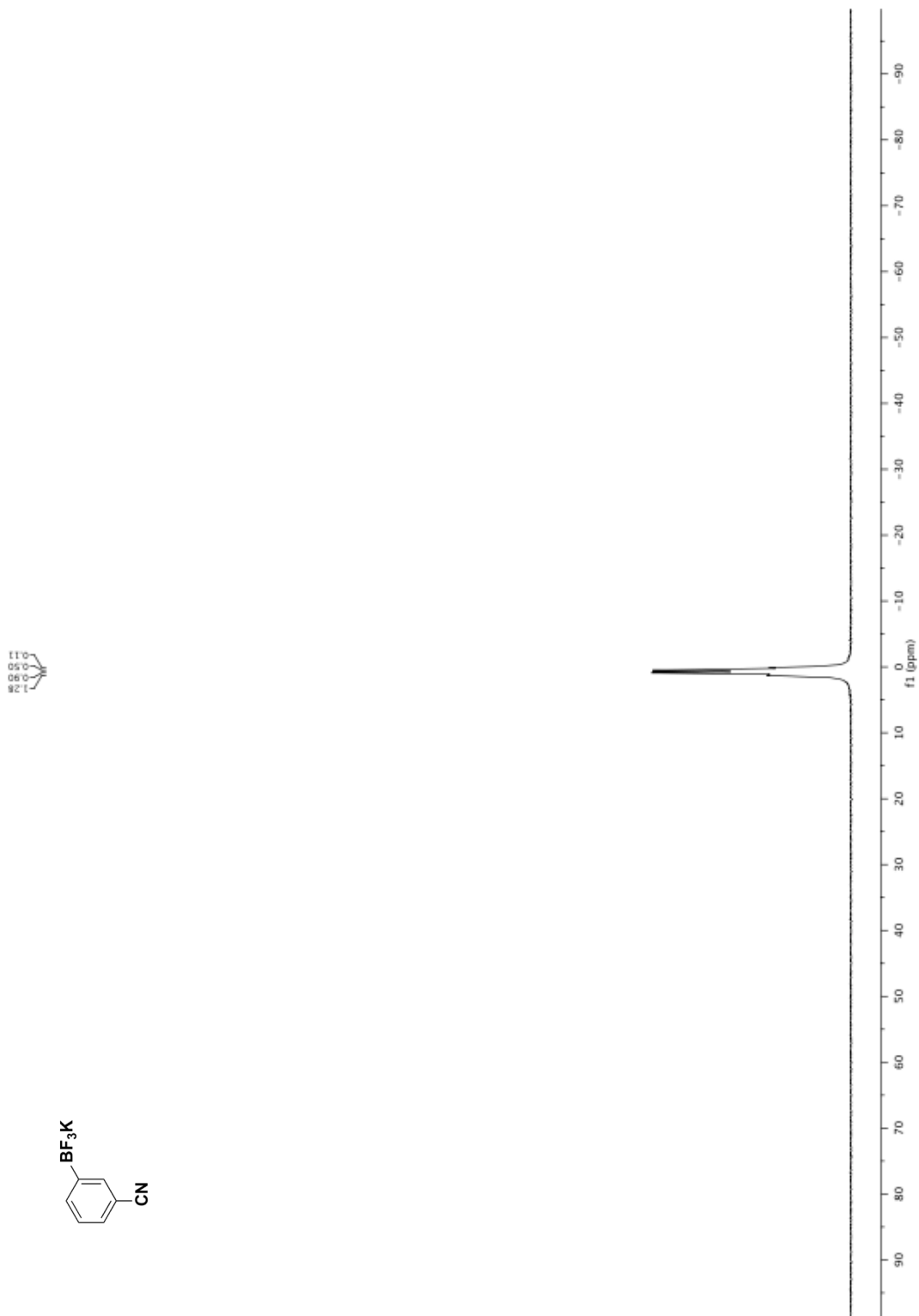


<sup>1</sup>H NMR Spectra (500 MHz, DMSO-*d*<sub>6</sub>) Potassium (3-Cyanophenyl)trifluoroborate (Table 1, entry 13)



$^{13}\text{C}$  NMR Spectra (125.8 MHz, DMSO-*d*<sub>6</sub>) Potassium (3-Cyanophenyl)trifluoroborate (Table 1, entry 13)

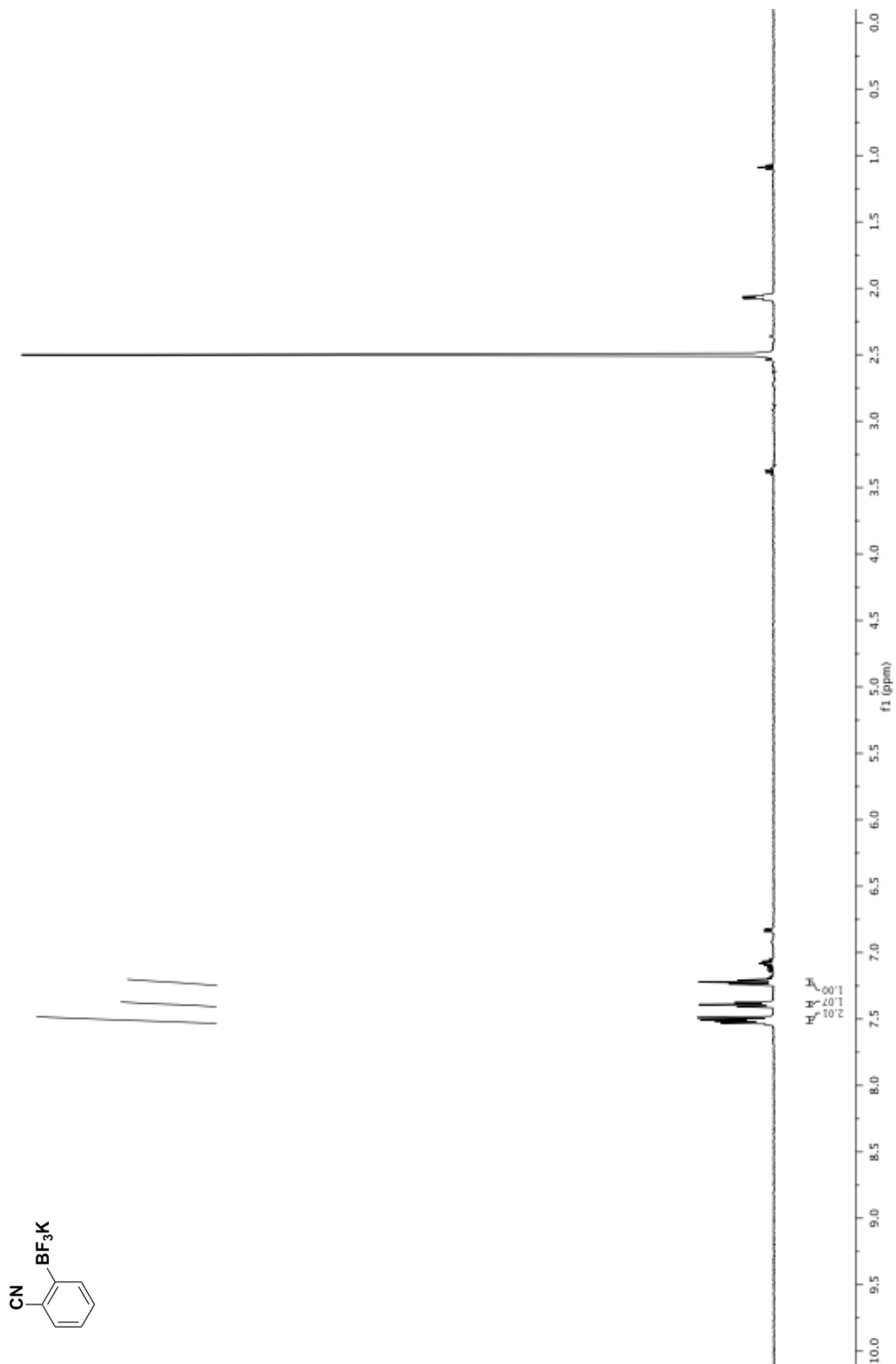




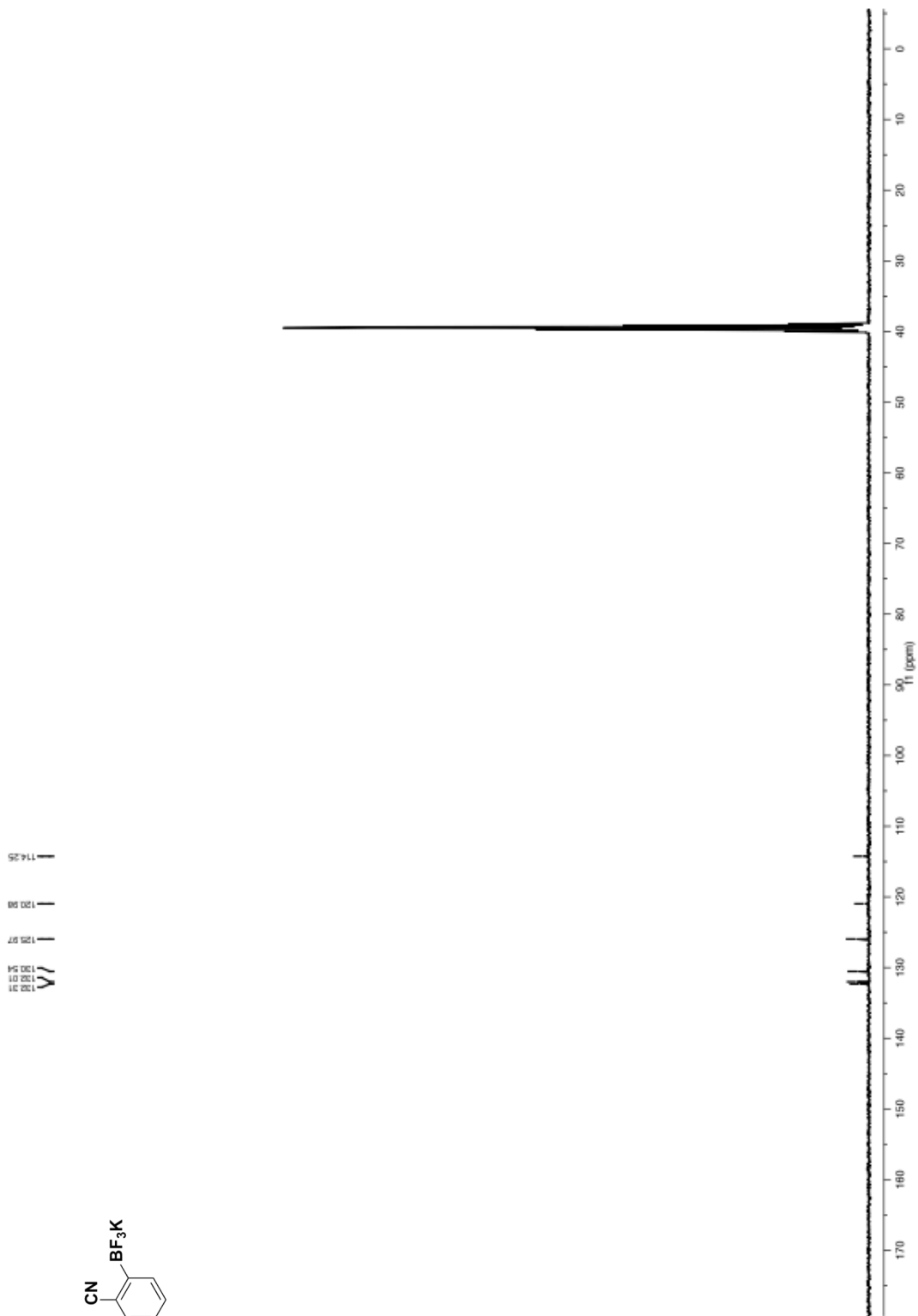
$^{11}\text{B}$  NMR (128.4 MHz, acetone-*d*<sub>6</sub>) Potassium (3-Cyanophenyl)trifluoroborate (Table 1, entry 13)



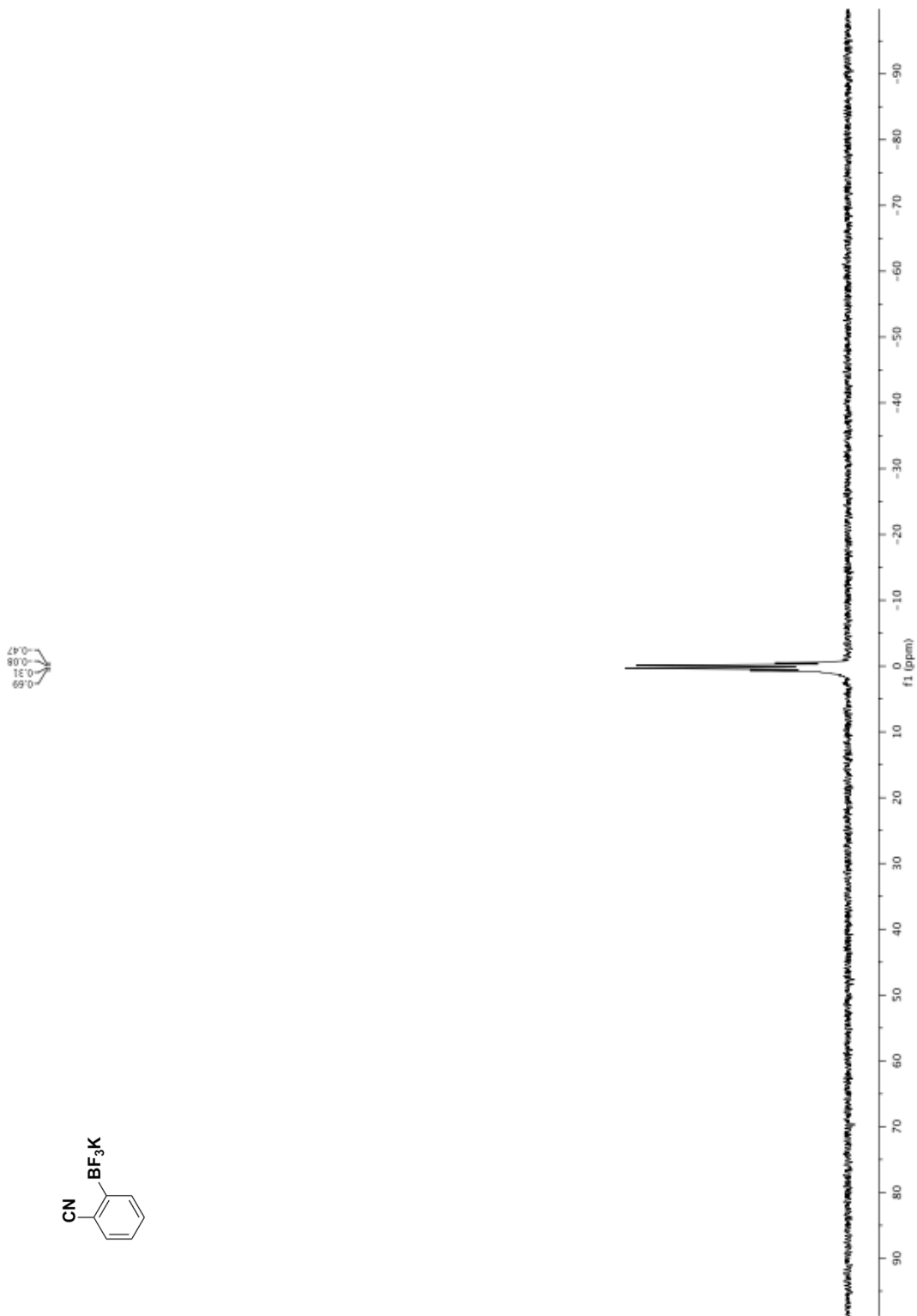
$^{19}\text{F}$  NMR Spectra (338.8 MHz, acetone- $d_6$ ) Potassium (3-Cyanophenyl)trifluoroborate (Table 1, entry 13)

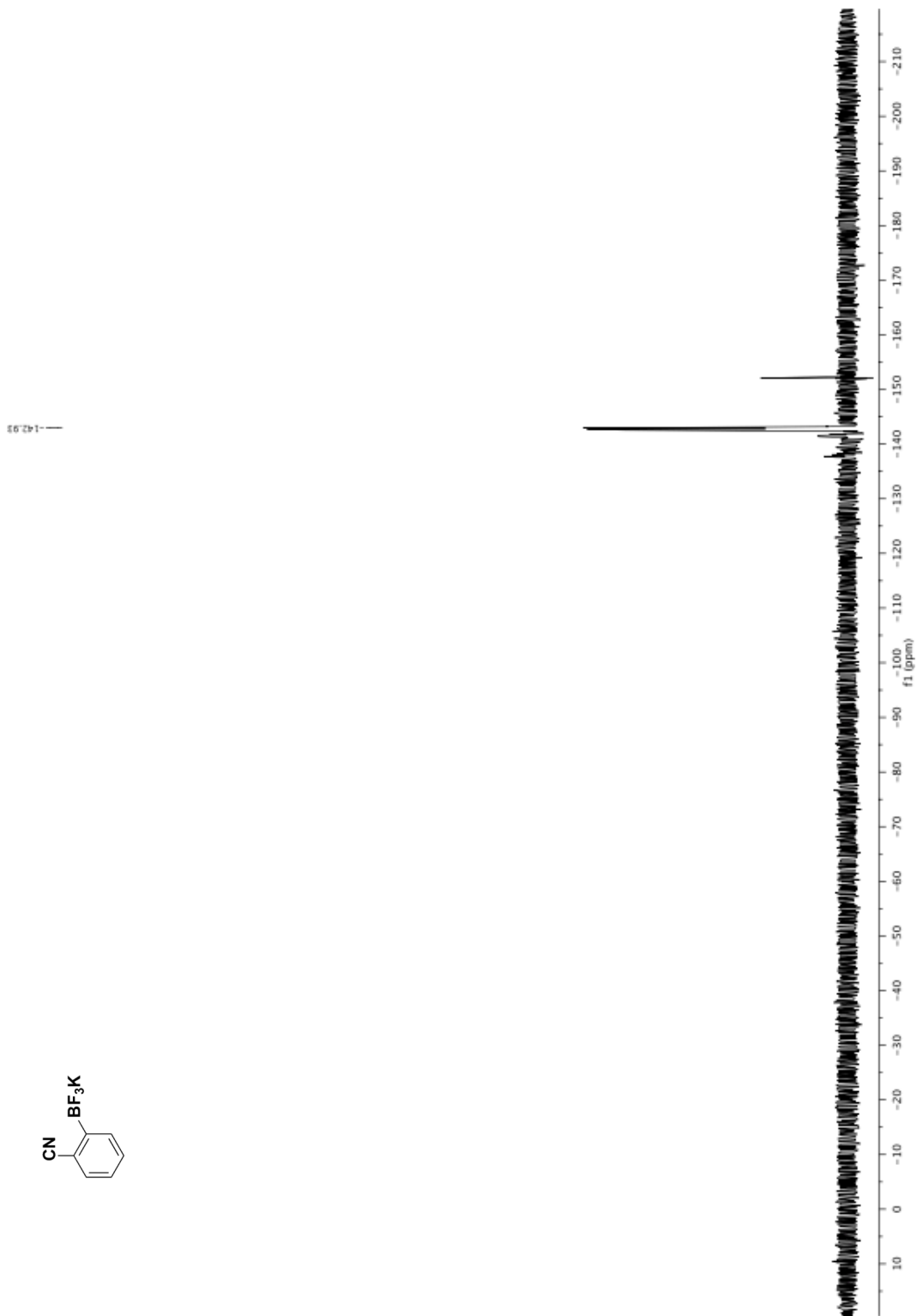


<sup>1</sup>H NMR Spectra (500 MHz, DMSO-*d*<sub>6</sub>) Potassium (2-Cyanophenyl)trifluoroborate (Table 1, entry 14)

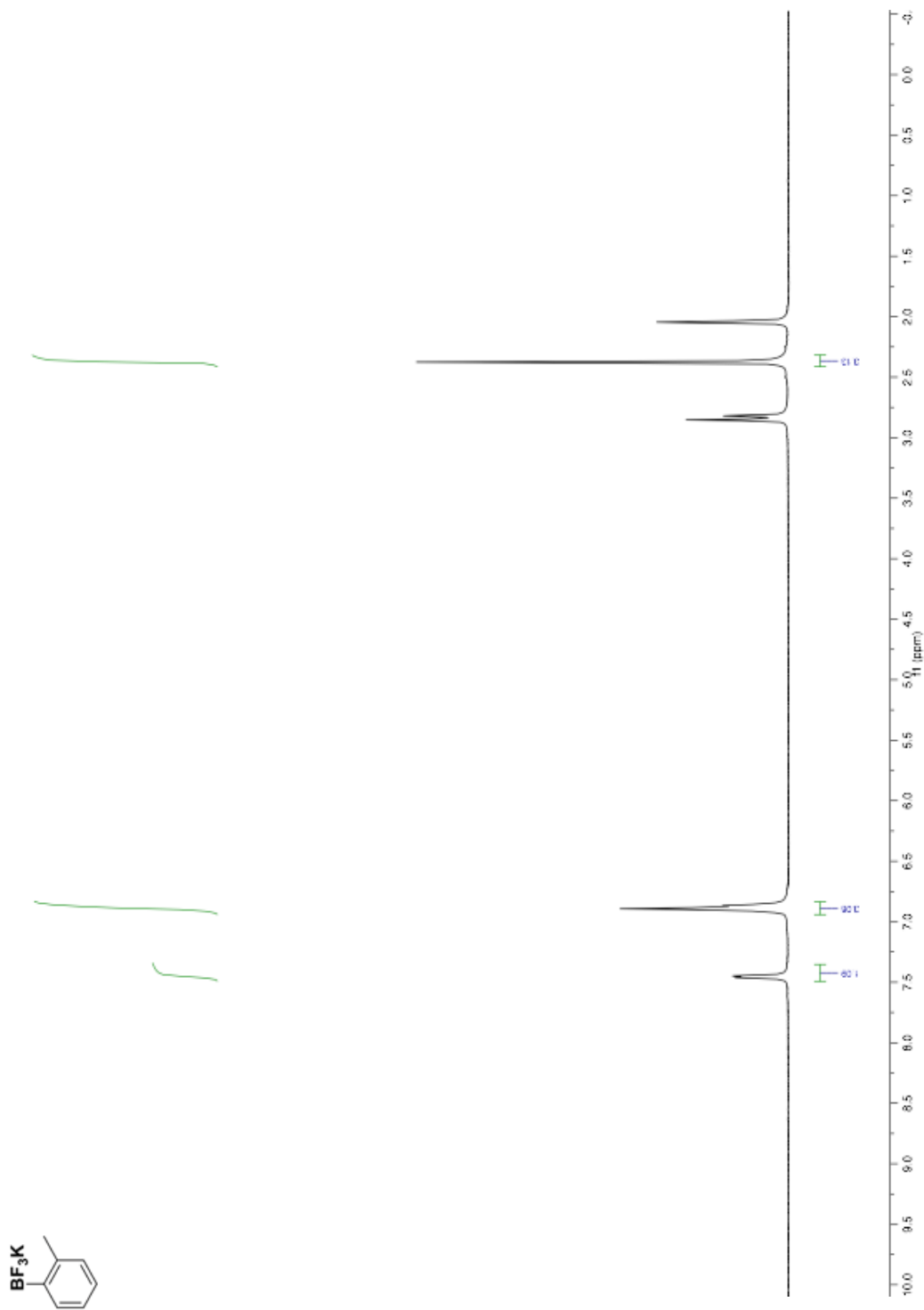


<sup>13</sup>C NMR Spectra (125.8 MHz, DMSO-*d*<sub>6</sub>) **Potassium (2-Cyanophenyl)trifluoroborate** (Table 1, entry 14)

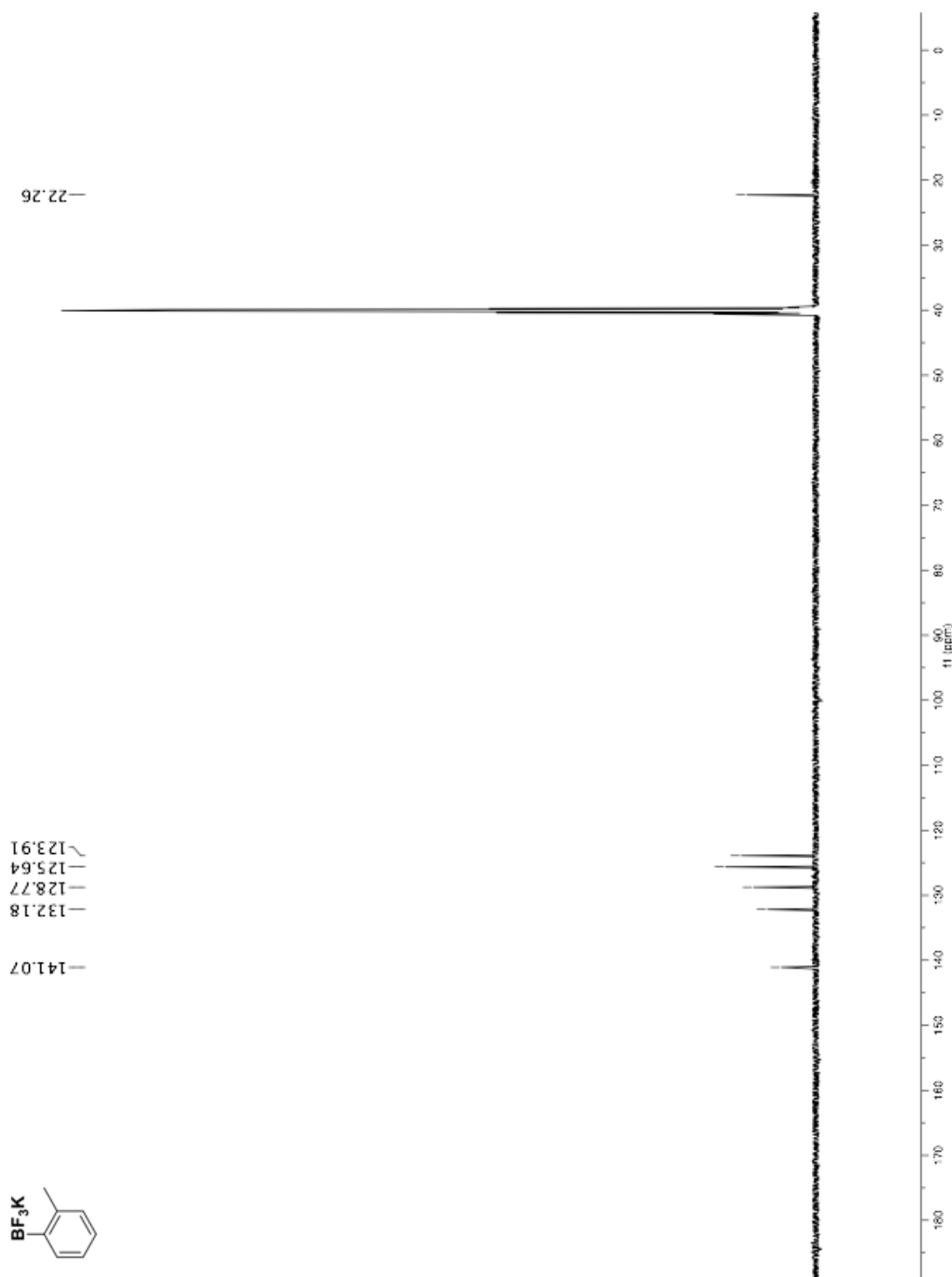




<sup>19</sup>F NMR Spectra (282 MHz, acetone-*d*<sub>6</sub>) **Potassium (2-Cyanophenyl)trifluoroborate** (Table 1, entry 14)

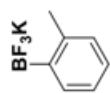


<sup>1</sup>H NMR Spectra (500 MHz, acetone-*d*<sub>6</sub>) **Potassium *o*-Tolyltrifluoroborate (Table 1, entry 15)**

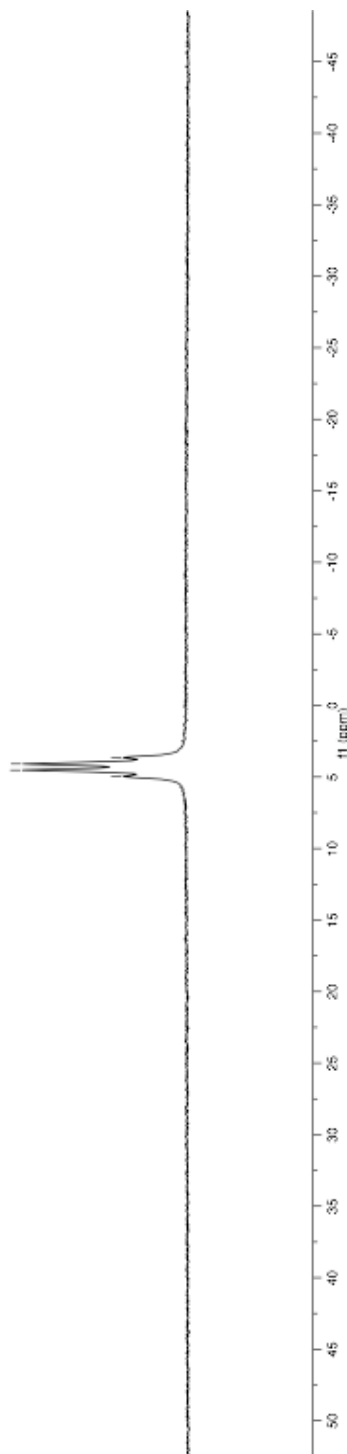


$^{13}\text{C}$  NMR Spectra (125.8 MHz,  $\text{DMSO-}d_6$ ) Potassium o-Tolyltrifluoroborate (Table 1, entry 15)

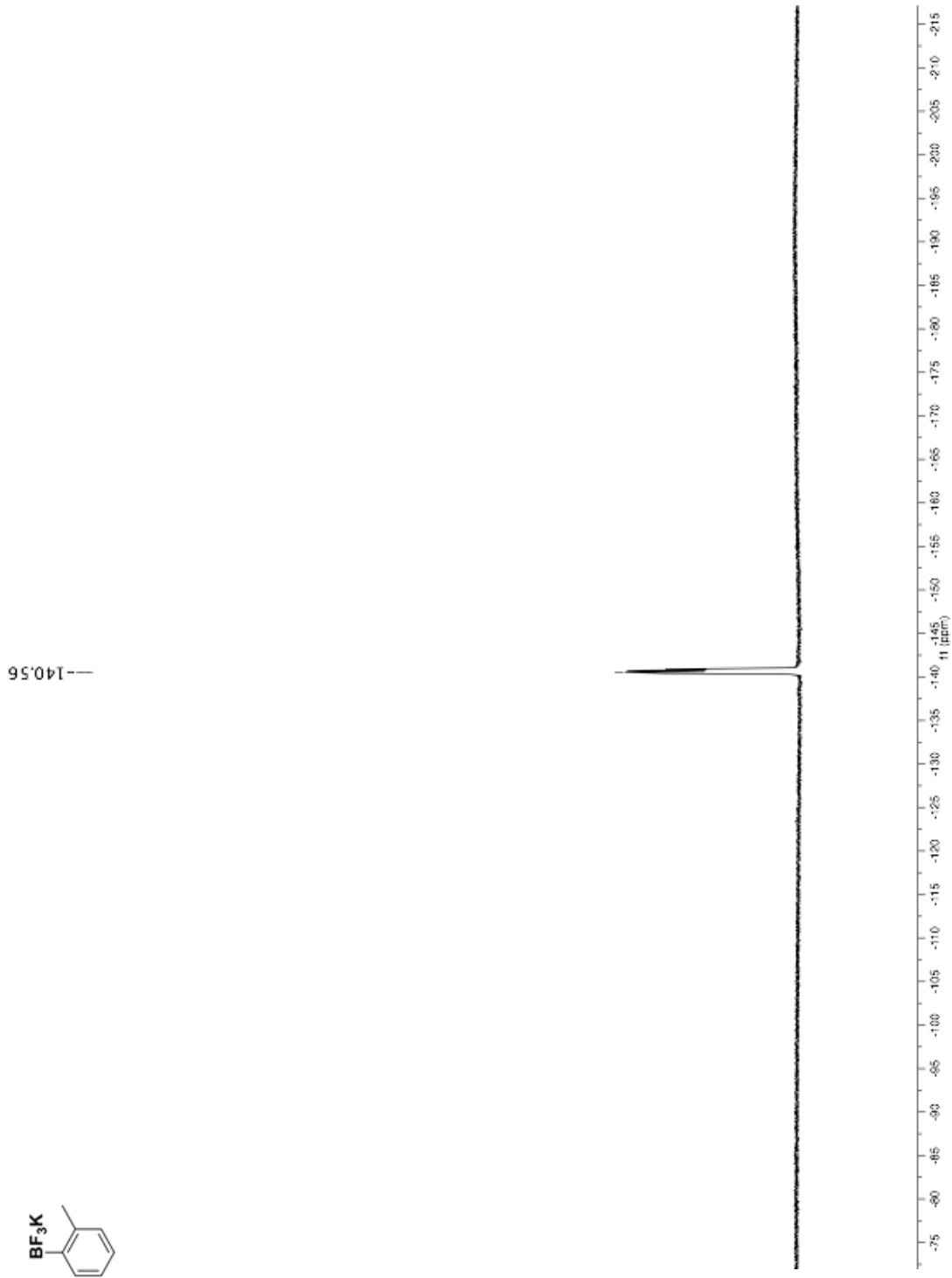




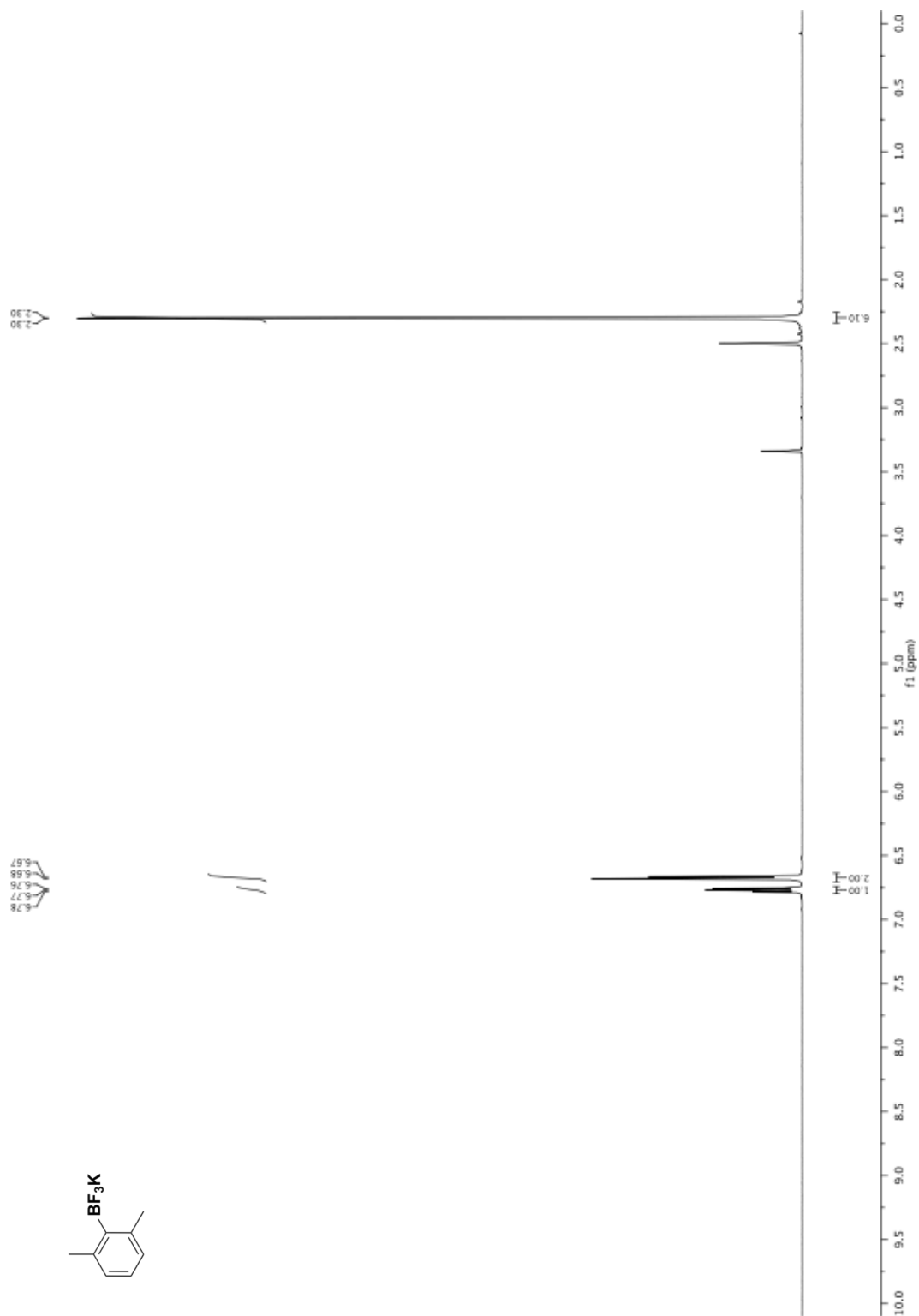
4.97  
4.52  
4.08  
3.64



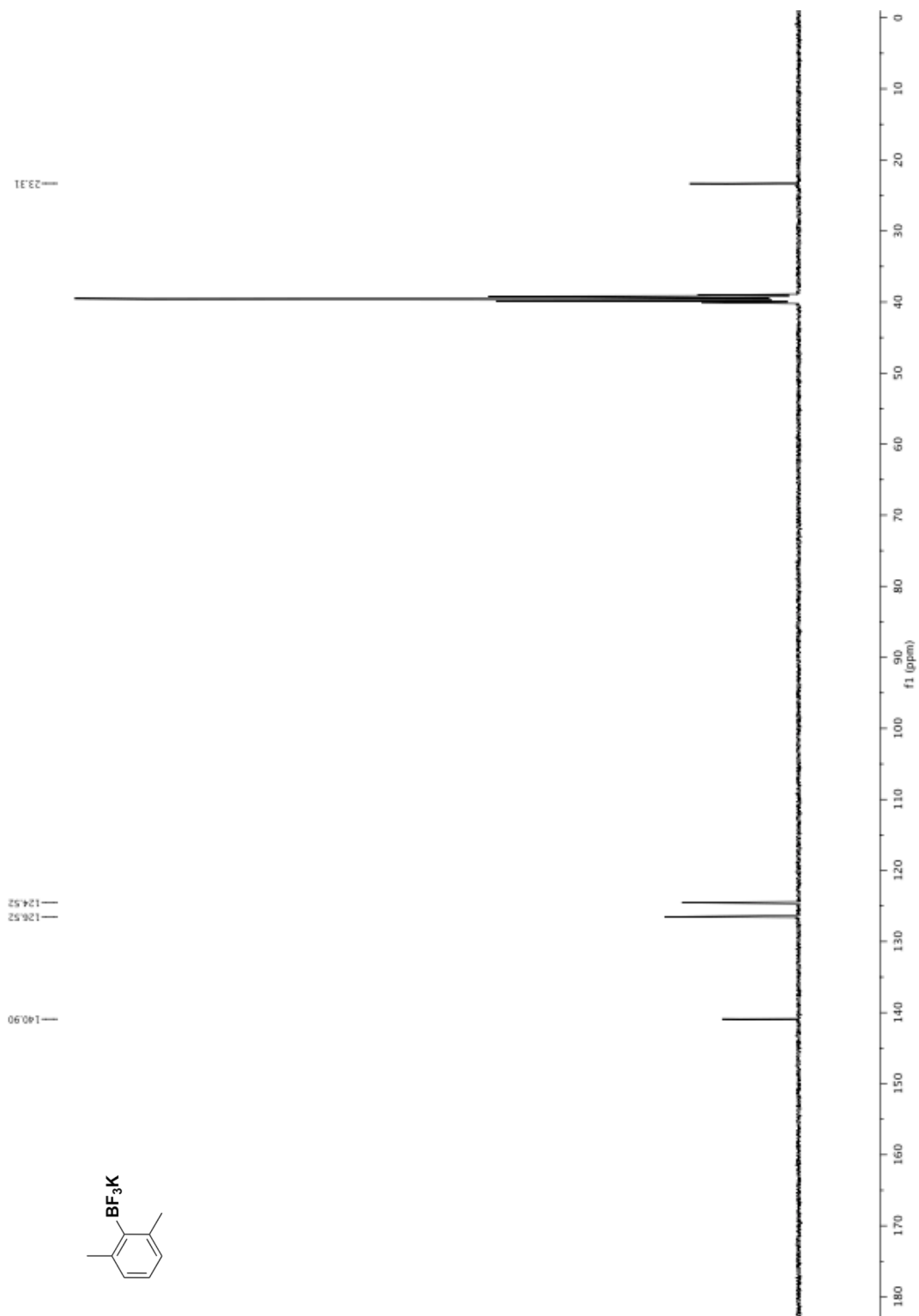
<sup>11</sup>B NMR (128.4 MHz, acetone-*d*<sub>6</sub>) Potassium o-Tolyltrifluoroborate (Table 1, entry 15)



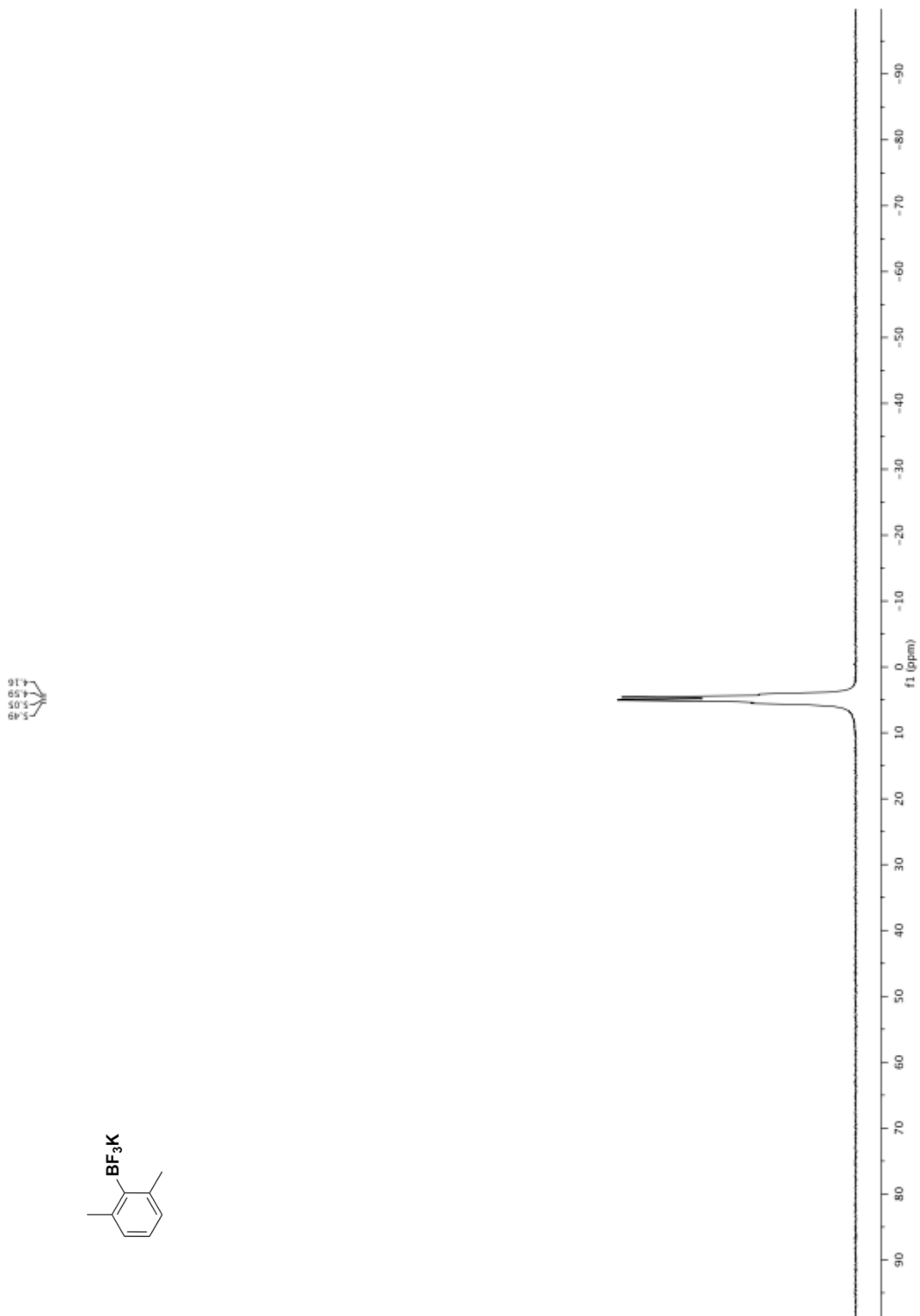
$^{19}\text{F}$  NMR Spectra (338.8 MHz, acetone- $d_6$ ) Potassium *o*-Tolyltrifluoroborate (Table 1, entry 15)



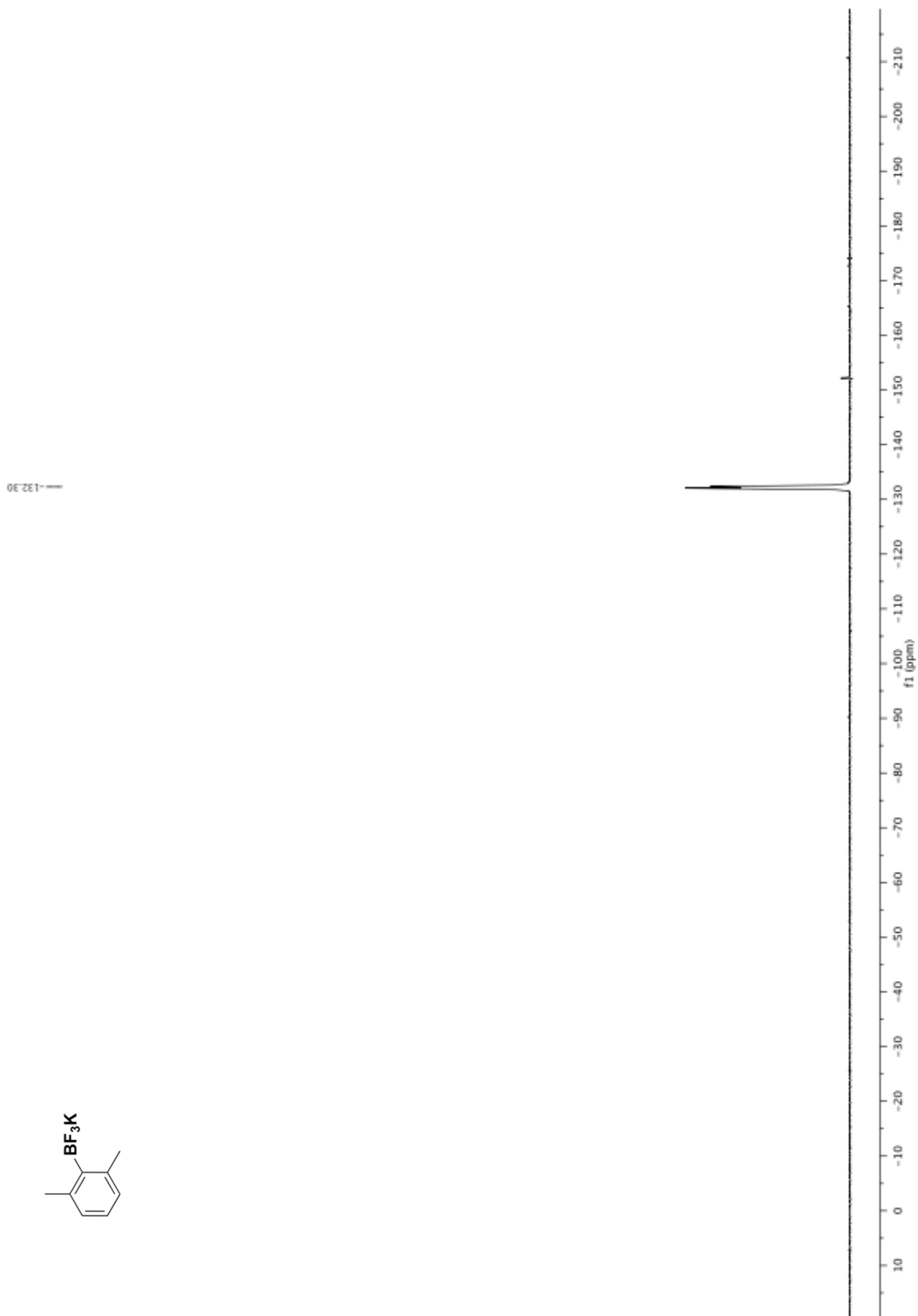
$^1\text{H}$  NMR Spectra (500 MHz,  $\text{DMSO-}d_6$ ) Potassium (2,6-Dimethylphenyl)trifluoroborate (Table 1, entry 16)



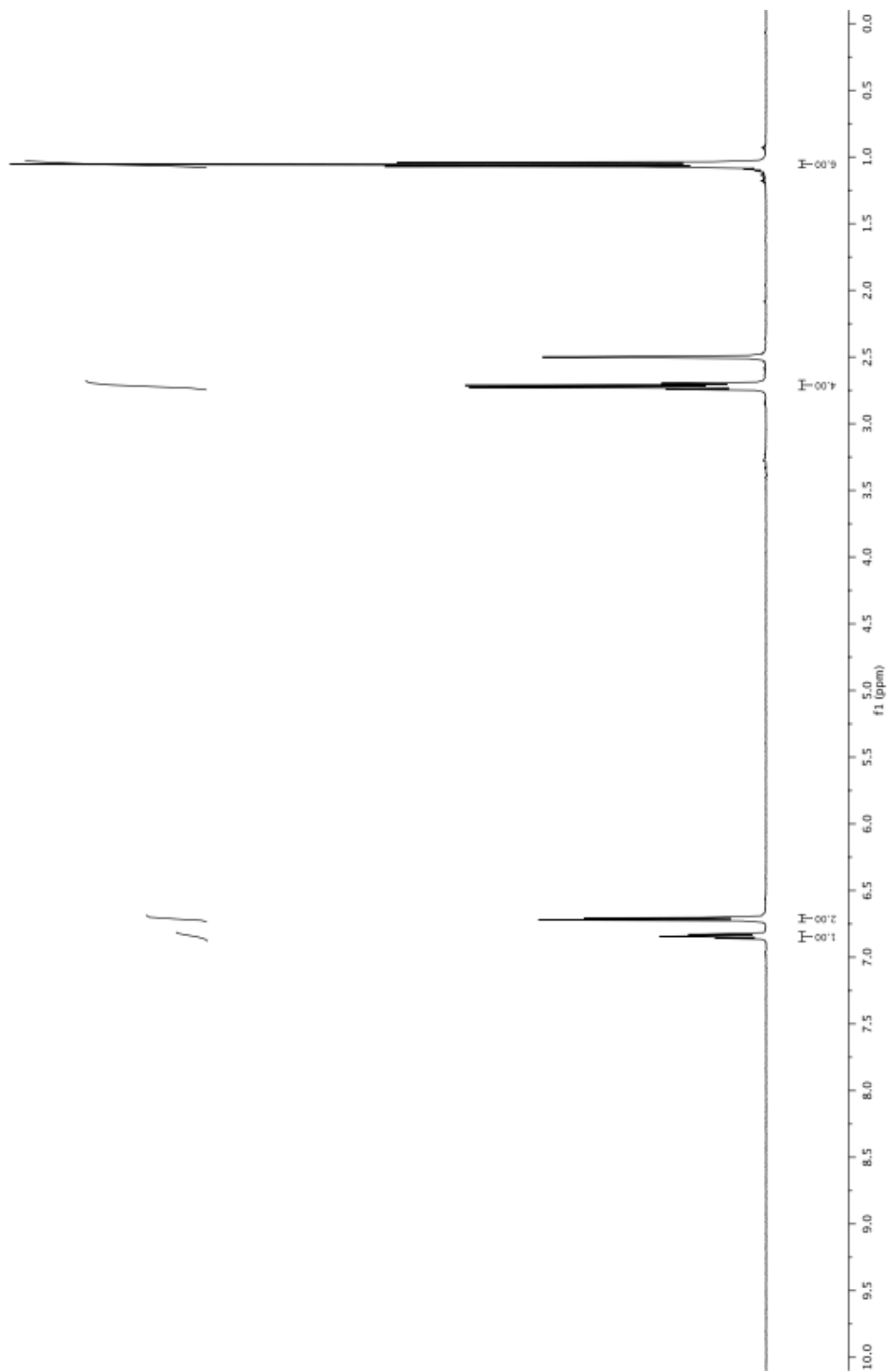
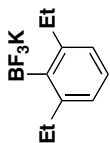
<sup>13</sup>C NMR Spectra (125.8 MHz, DMSO-*d*<sub>6</sub>) Potassium (2,6-Dimethylphenyl)trifluoroborate (Table 1, entry 16)



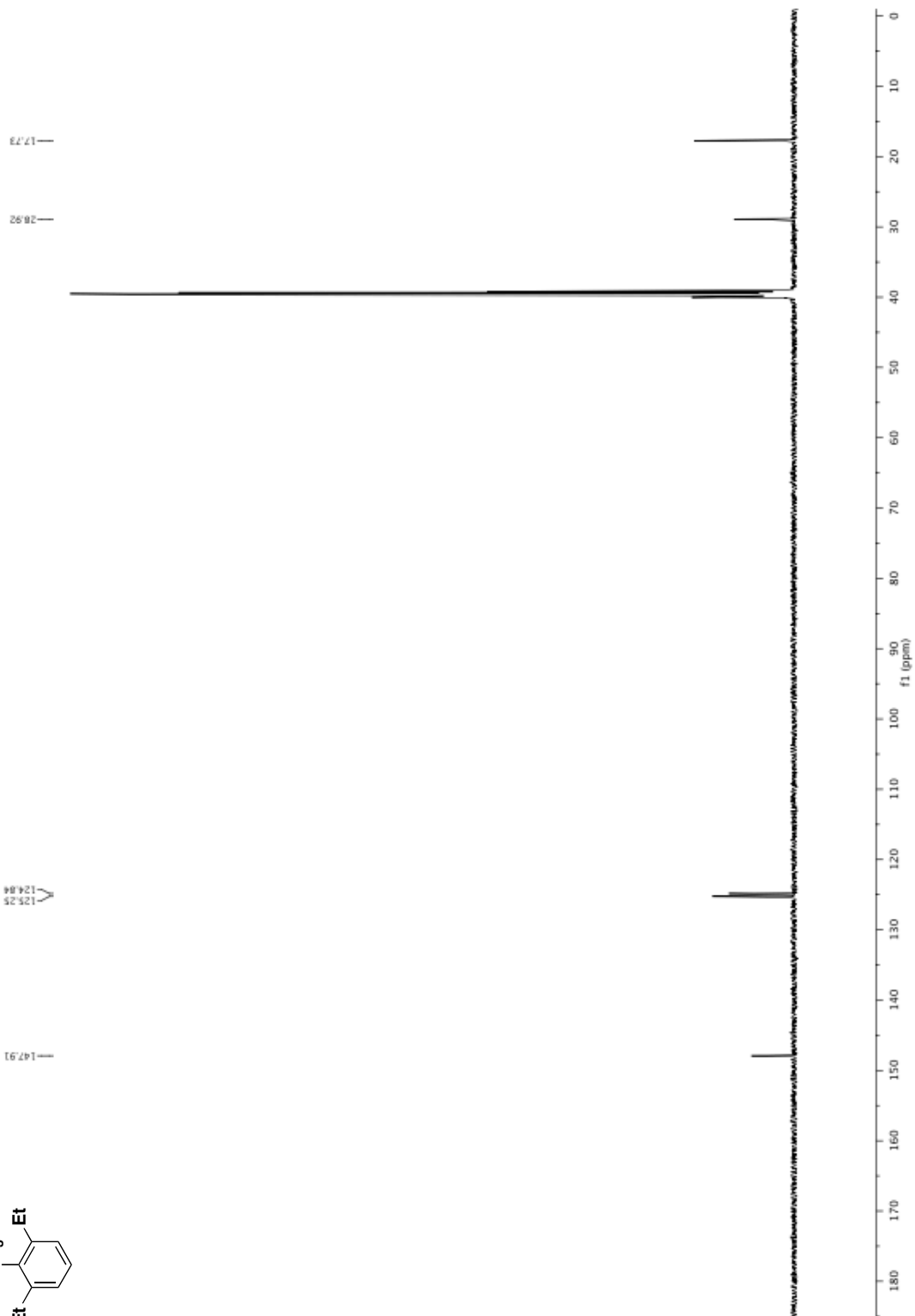
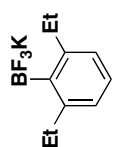
$^{11}\text{B}$  NMR (128.4 MHz, acetone- $d_6$ ) Potassium (2,6-Dimethylphenyl)trifluoroborate (Table 1, entry 16)



$^{19}\text{F}$  NMR Spectra (282 MHz, acetone- $d_6$ ) Potassium (2,6-Dimethylphenyl)trifluoroborate (Table 1, entry 16)

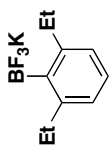


<sup>1</sup>H NMR Spectra (500 MHz, DMSO-*d*<sub>6</sub>) Potassium (2,6-diethylphenyl)trifluoroborate (Table 1, entry 17)

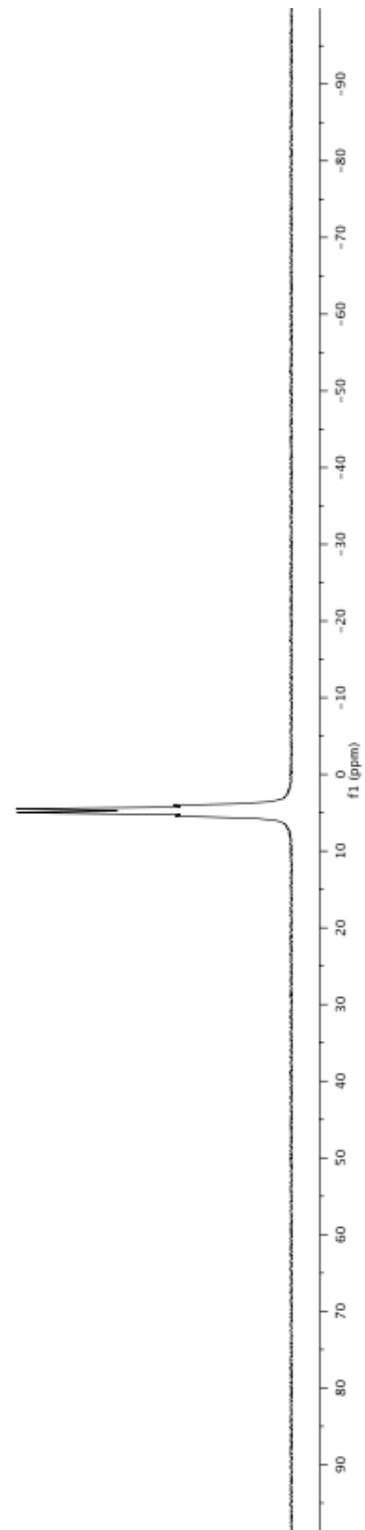


<sup>13</sup>C NMR Spectra (125.8 MHz, DMSO-*d*<sub>6</sub>) Potassium (2,6-diethylphenyl)trifluoroborate (Table 1, entry 17)

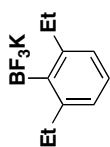




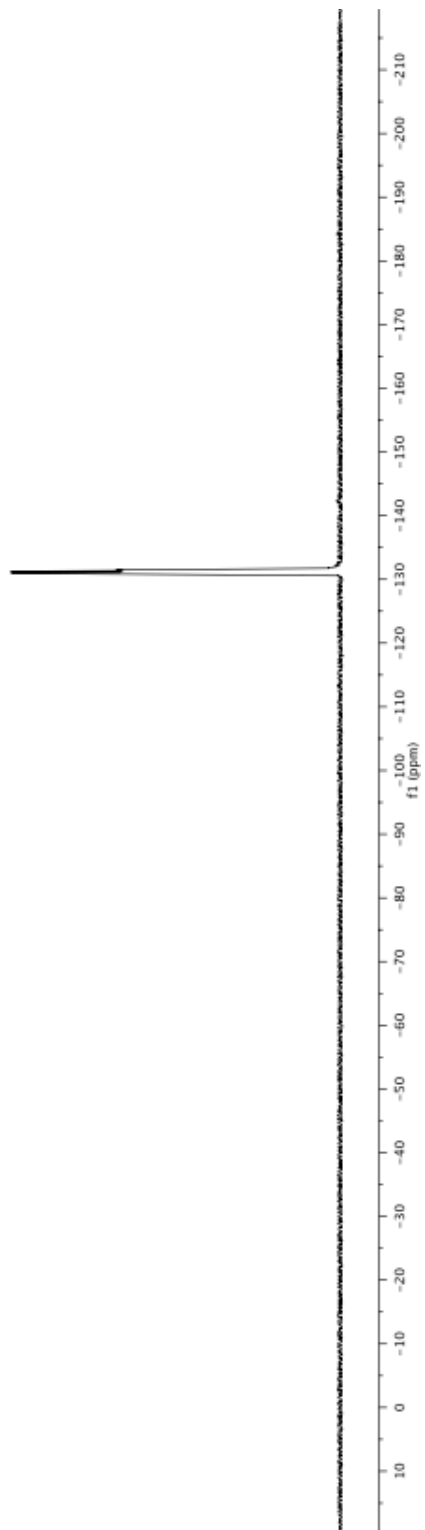
5.40  
4.96  
4.50  
4.05



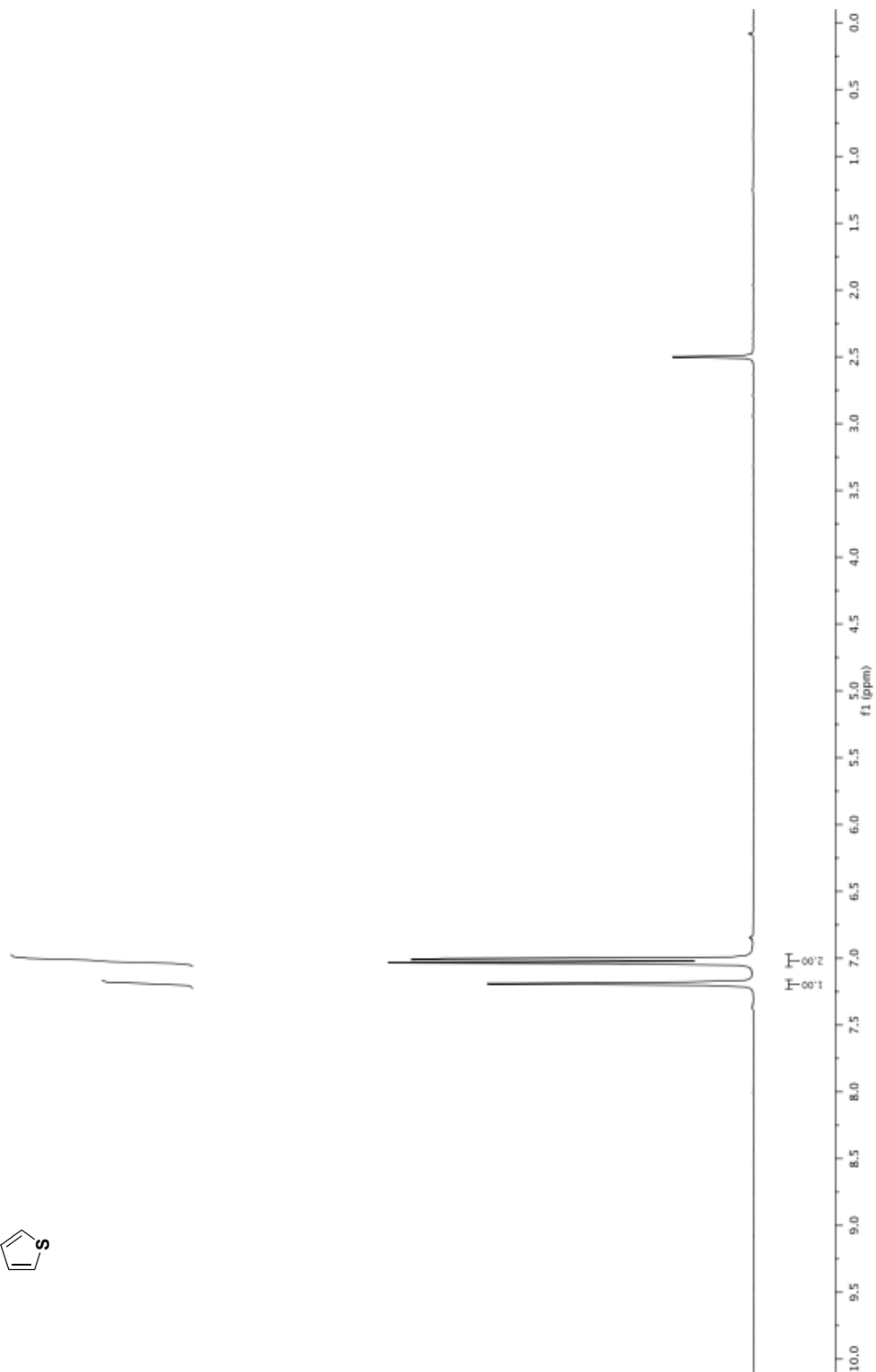
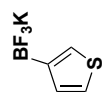
$^{11}\text{B}$  NMR (128.4 MHz, acetone- $d_6$ ) **Potassium (2,6-diethylphenyl)trifluoroborate**  
(Table 1, entry 17)



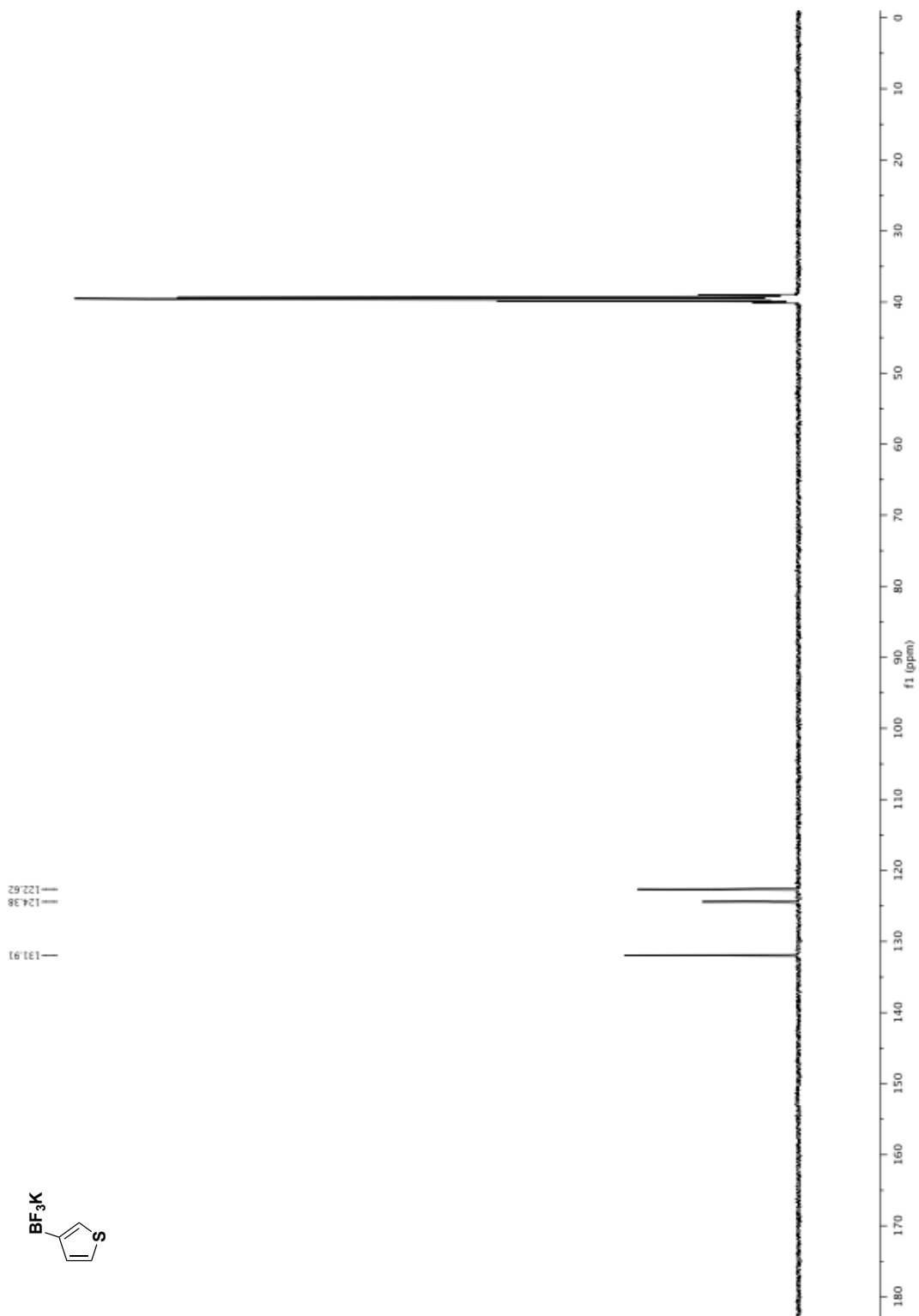
—131.02



<sup>19</sup>F NMR Spectra (282 MHz, acetone-*d*<sub>6</sub>) **Potassium (2,6-diethylphenyl)trifluoroborate**  
(Table 1, entry 17)

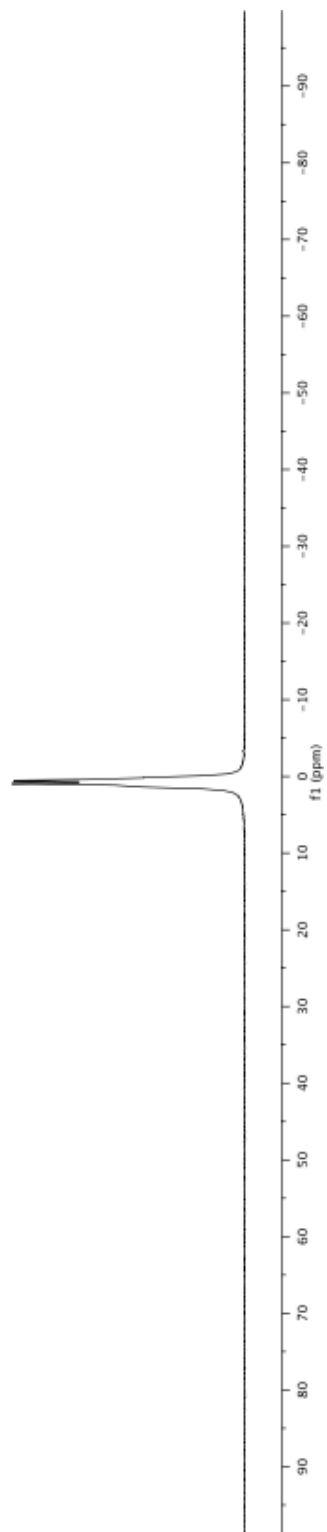


<sup>1</sup>H NMR Spectra (500 MHz, DMSO-*d*<sub>6</sub>) **Potassium 3-Trifluoroborato-thiophene** (Table 2, entry 1)

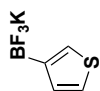


<sup>13</sup>C NMR Spectra (125.8 MHz, DMSO-*d*<sub>6</sub>) **Potassium 3-Trifluoroborato-thiophene**  
(Table 2, entry 1)

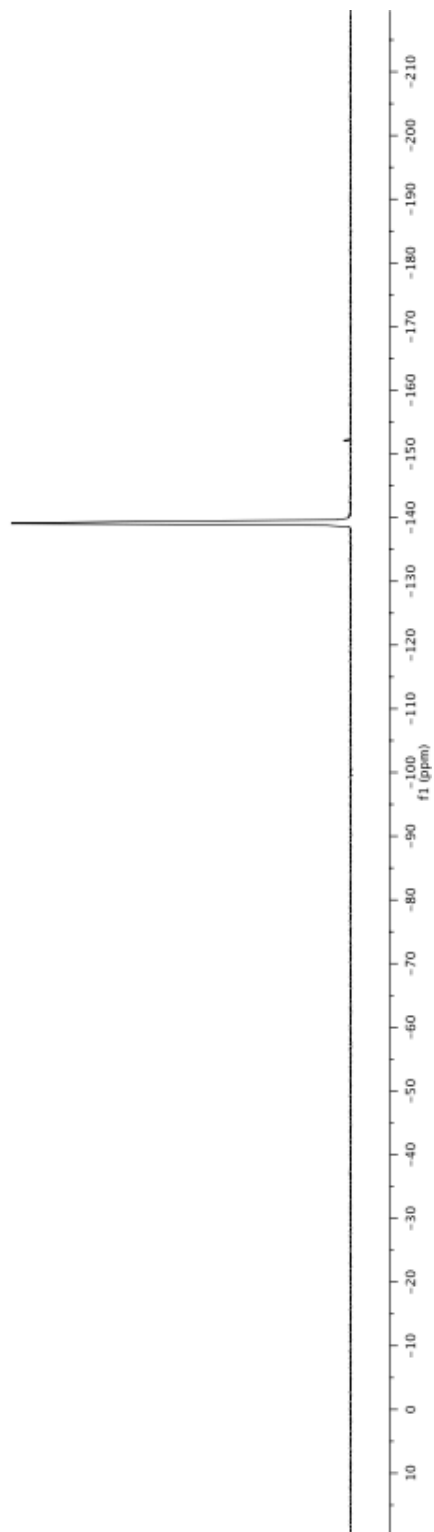
110  
950  
800  
650



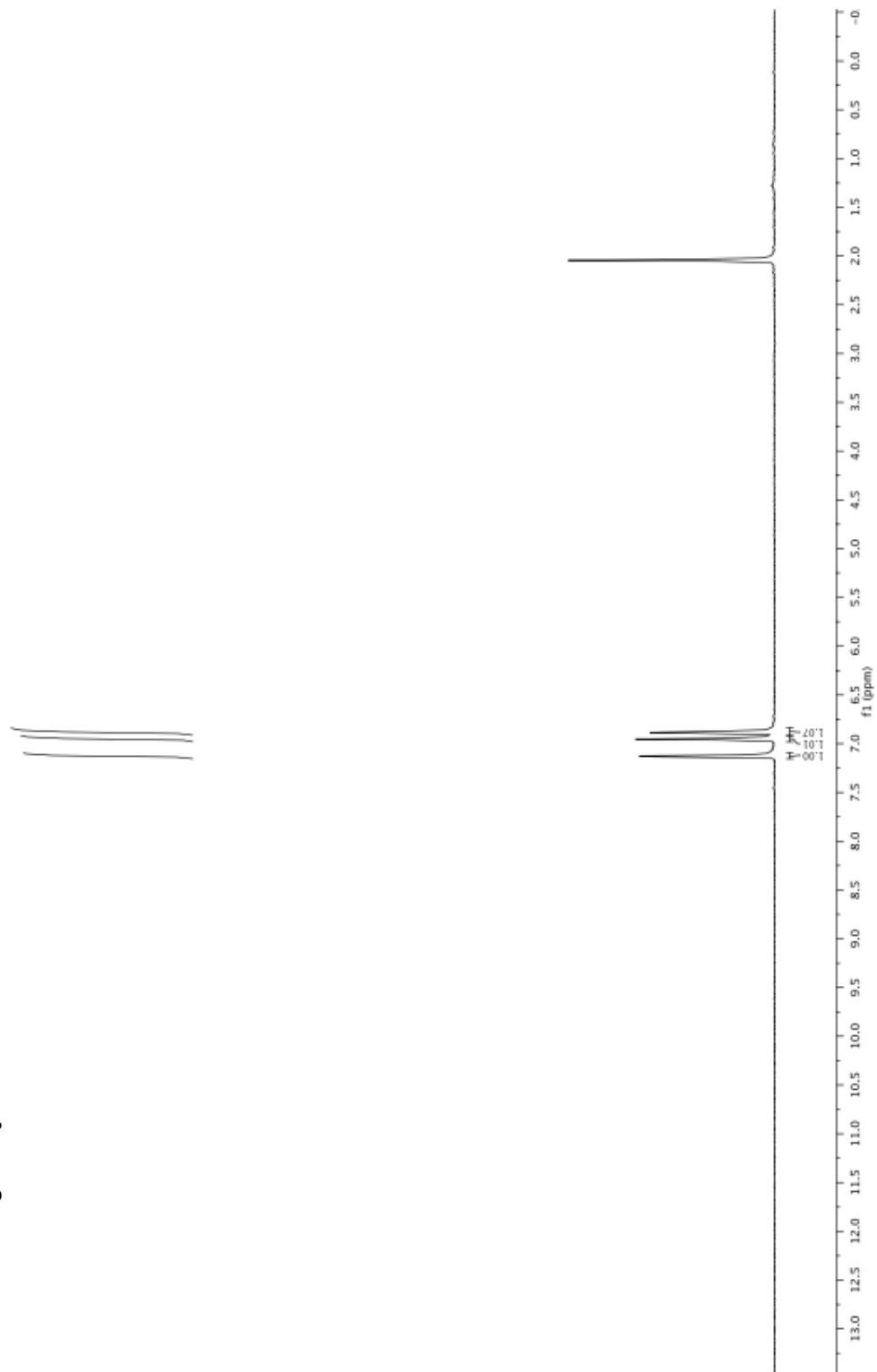
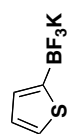
$^{11}\text{B}$  NMR (128.4 MHz, acetone- $d_6$ ) **Potassium 3-Trifluoroborato-thiophene (Table 2, entry 1)**



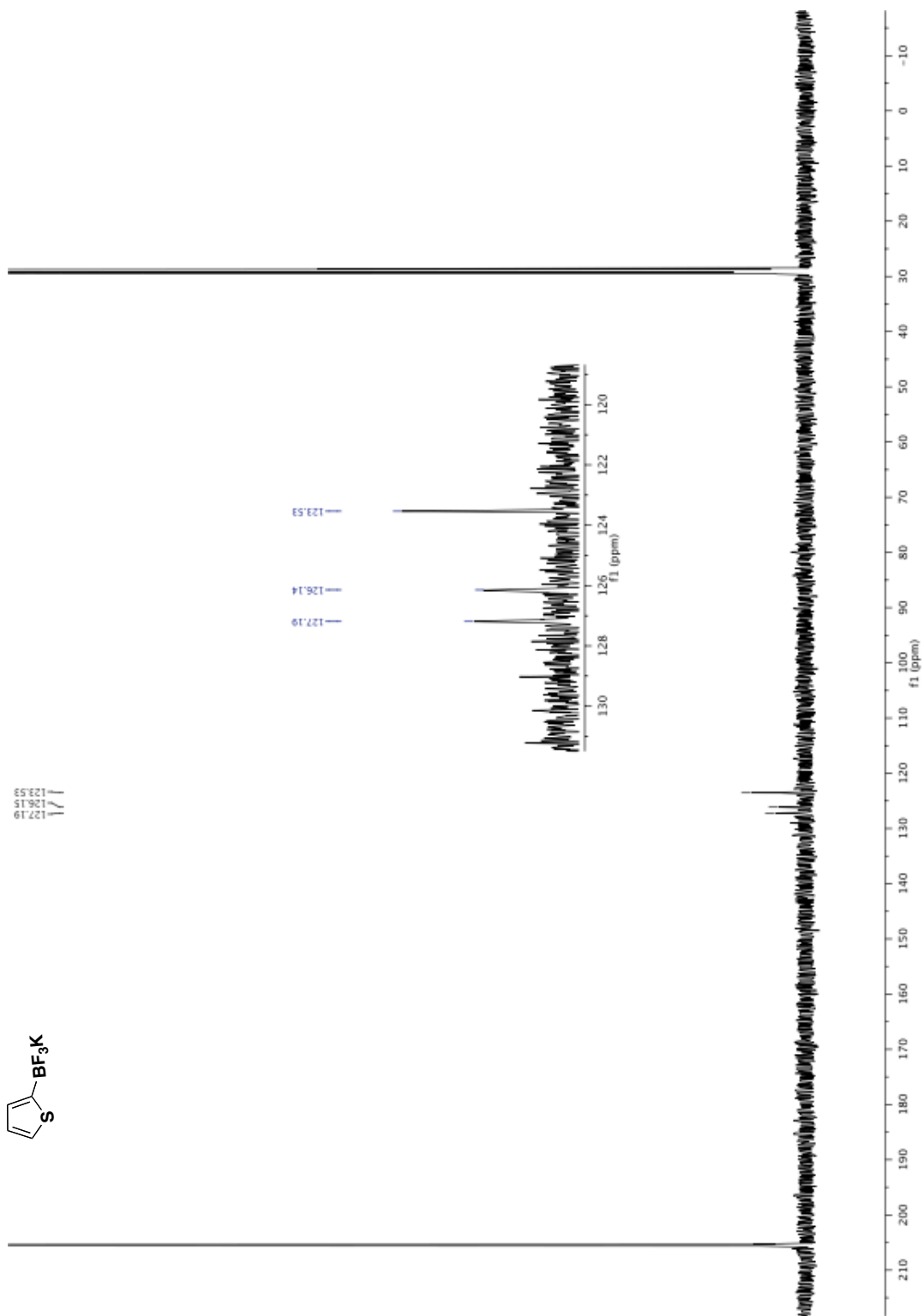
607651



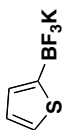
<sup>19</sup>F NMR Spectra (282 MHz, acetone-*d*<sub>6</sub>) **Potassium 3-Trifluoroborato-thiophene** (Table 2, entry 1)



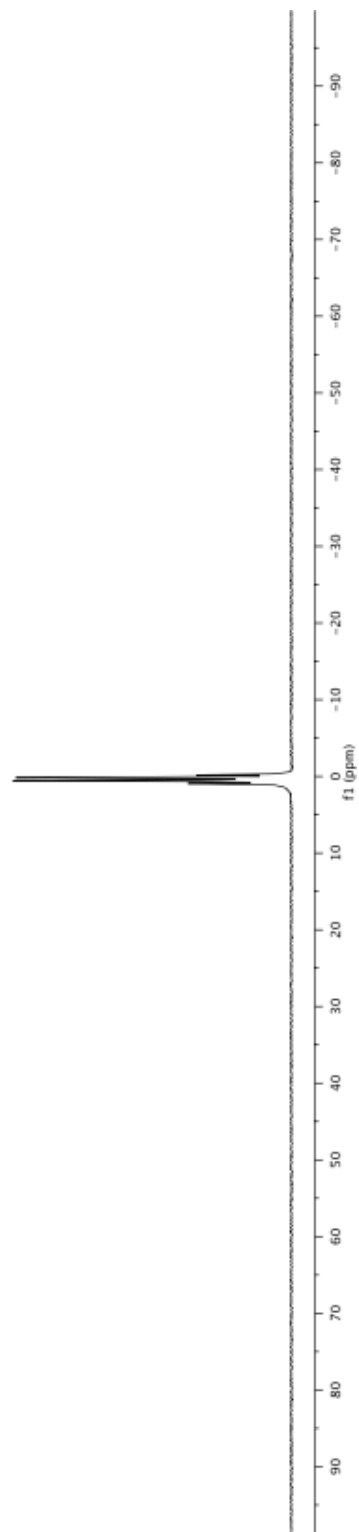
$^1\text{H}$  NMR Spectra (500 MHz, acetone- $d_6$ ) Potassium 2-Trifluoroborato-thiophene (Table 2, entry 2)



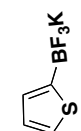




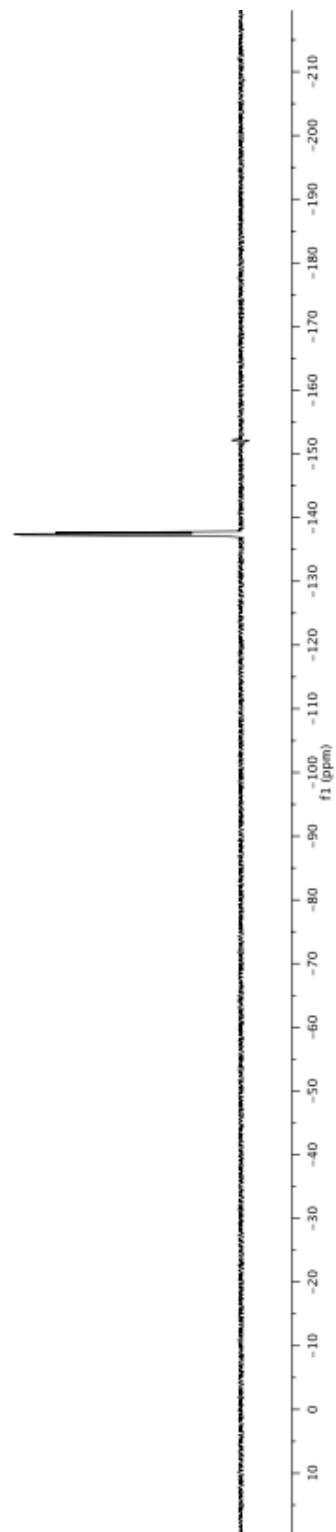
61.0  
81.0  
95.0  
86.0



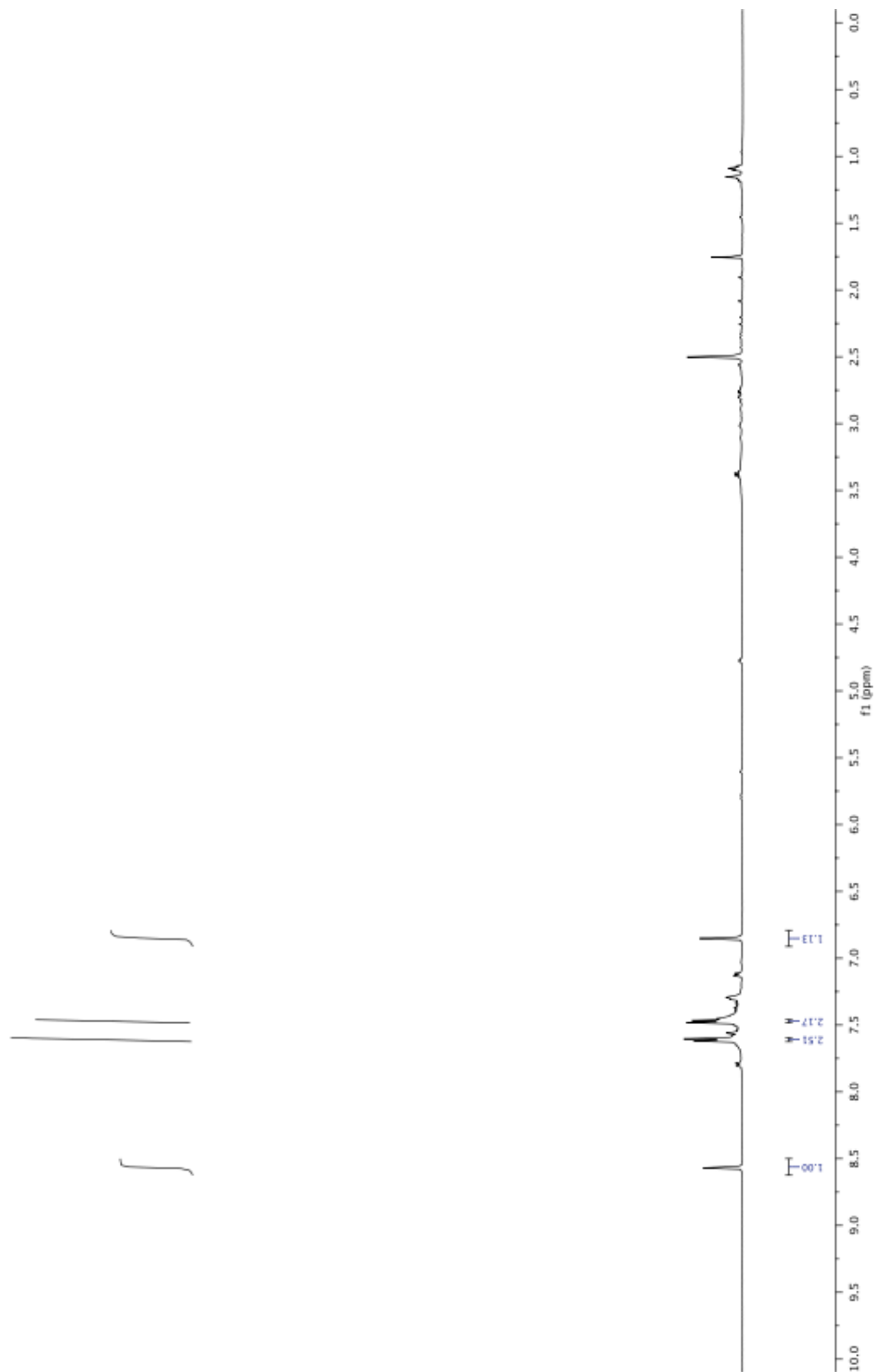
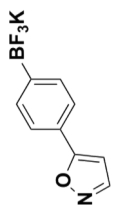
$^{11}\text{B}$  NMR (128.4 MHz, acetone- $d_6$ ) Potassium 2-Trifluoroborato-thiophene (Table 2, entry 2)



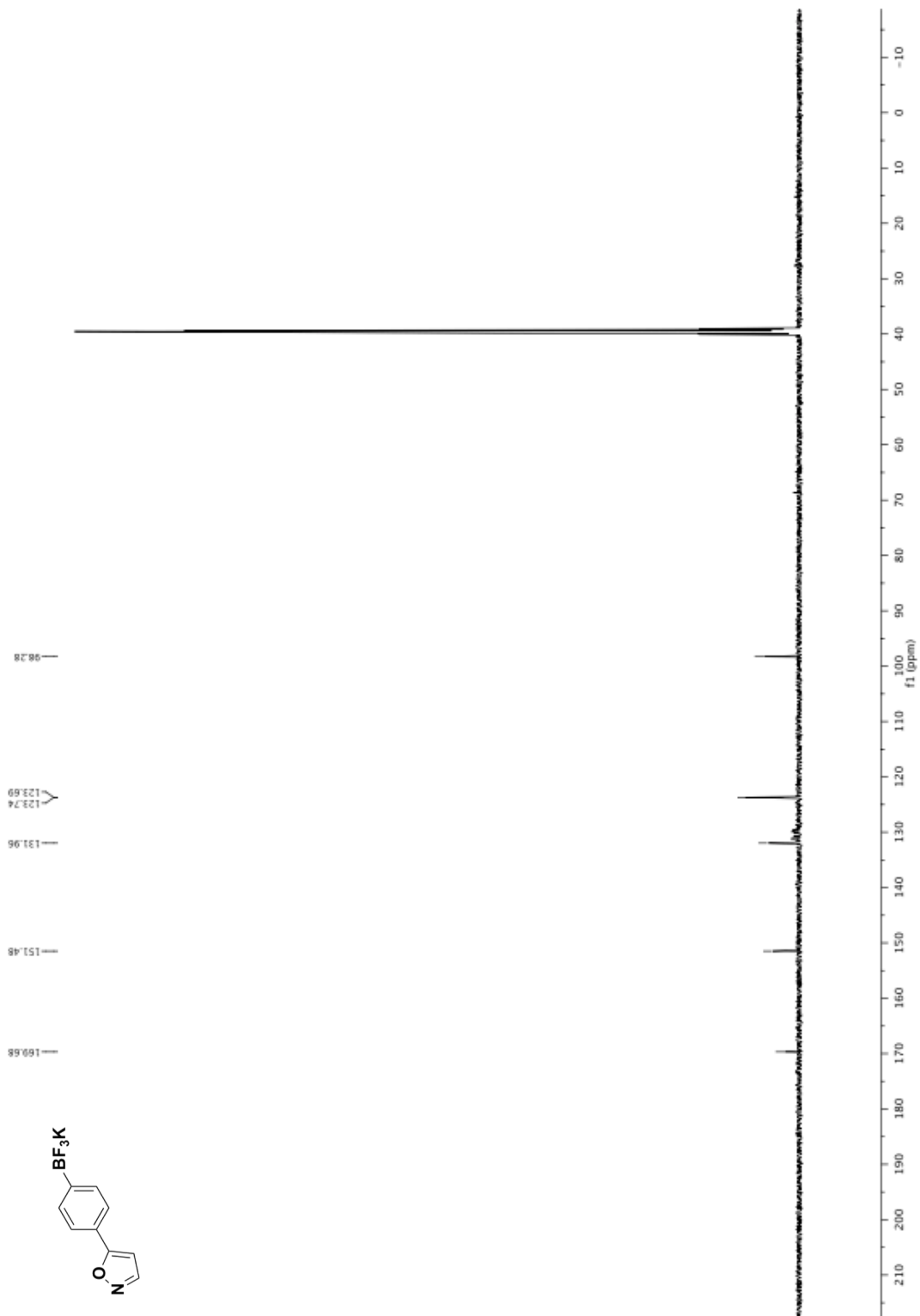
—137.46



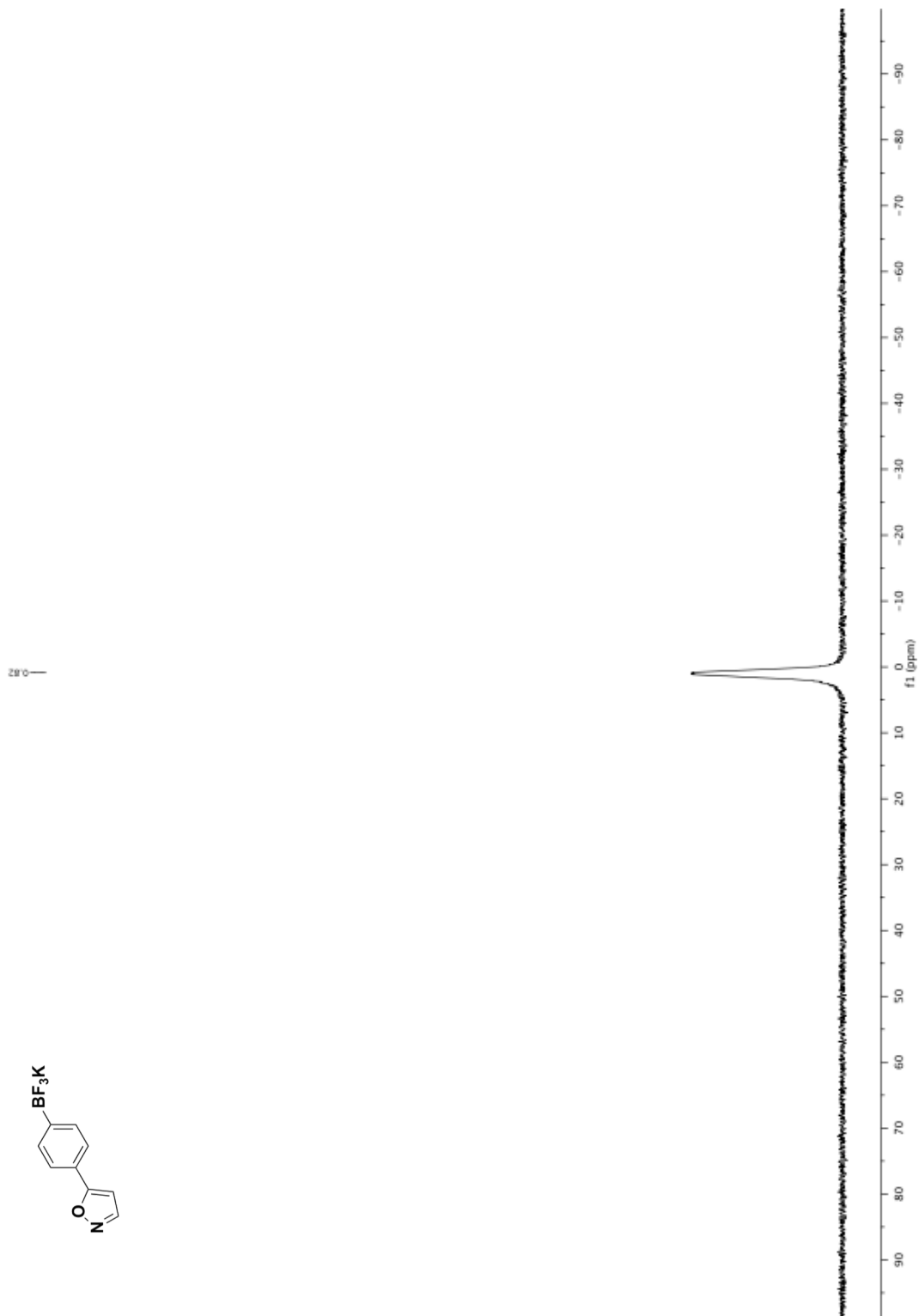
$^{19}\text{F}$  NMR Spectra (282 MHz, acetone- $d_6$ ) **Potassium 2-Trifluoroborato-thiophene**  
(Table 2, entry 2)



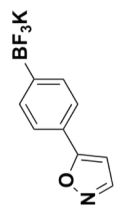
<sup>1</sup>H NMR Spectra (500 MHz, DMSO-*d*<sub>6</sub>) (4-(Isoxazol-5-yl)phenyl)trifluoroborate (Table 2, entry 4)



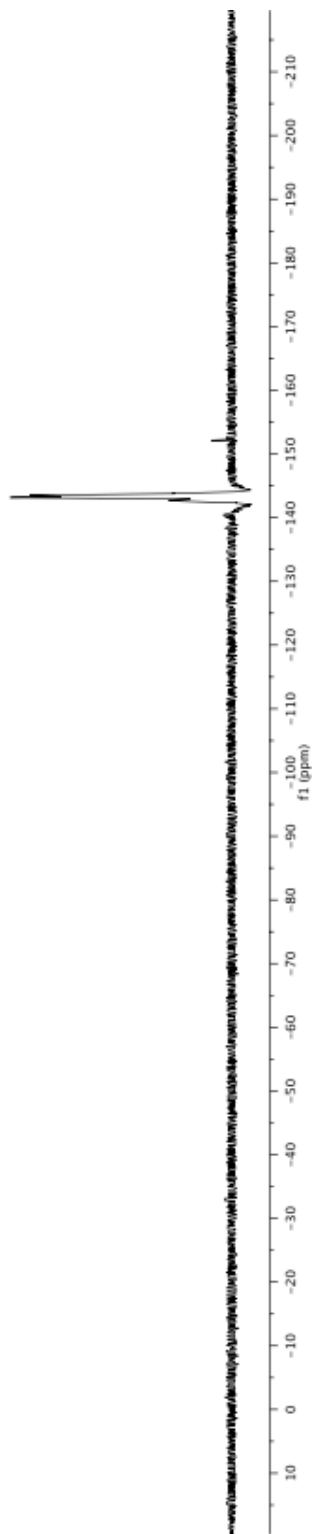
$^{13}\text{C}$  NMR Spectra (125.8 MHz,  $\text{DMSO-}d_6$ ) (4-(Isoxazol-5-yl)phenyl)trifluoroborate (Table 2, entry 4)



$^{11}\text{B}$  NMR (128.4 MHz, acetone- $d_6$ ) (4-(Isoxazol-5-yl)phenyl)trifluoroborate (Table 2, entry 4)

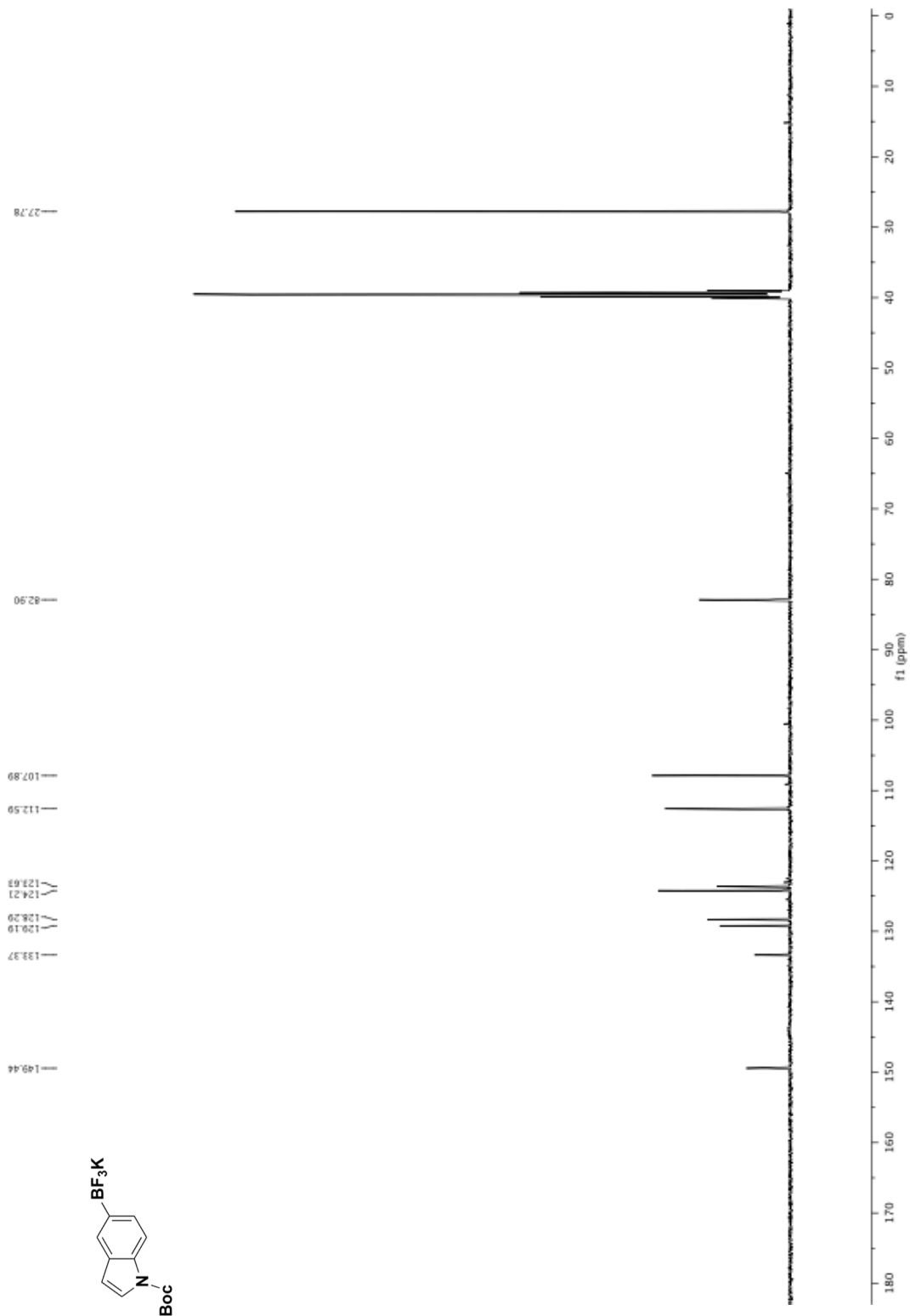


9TEPT1



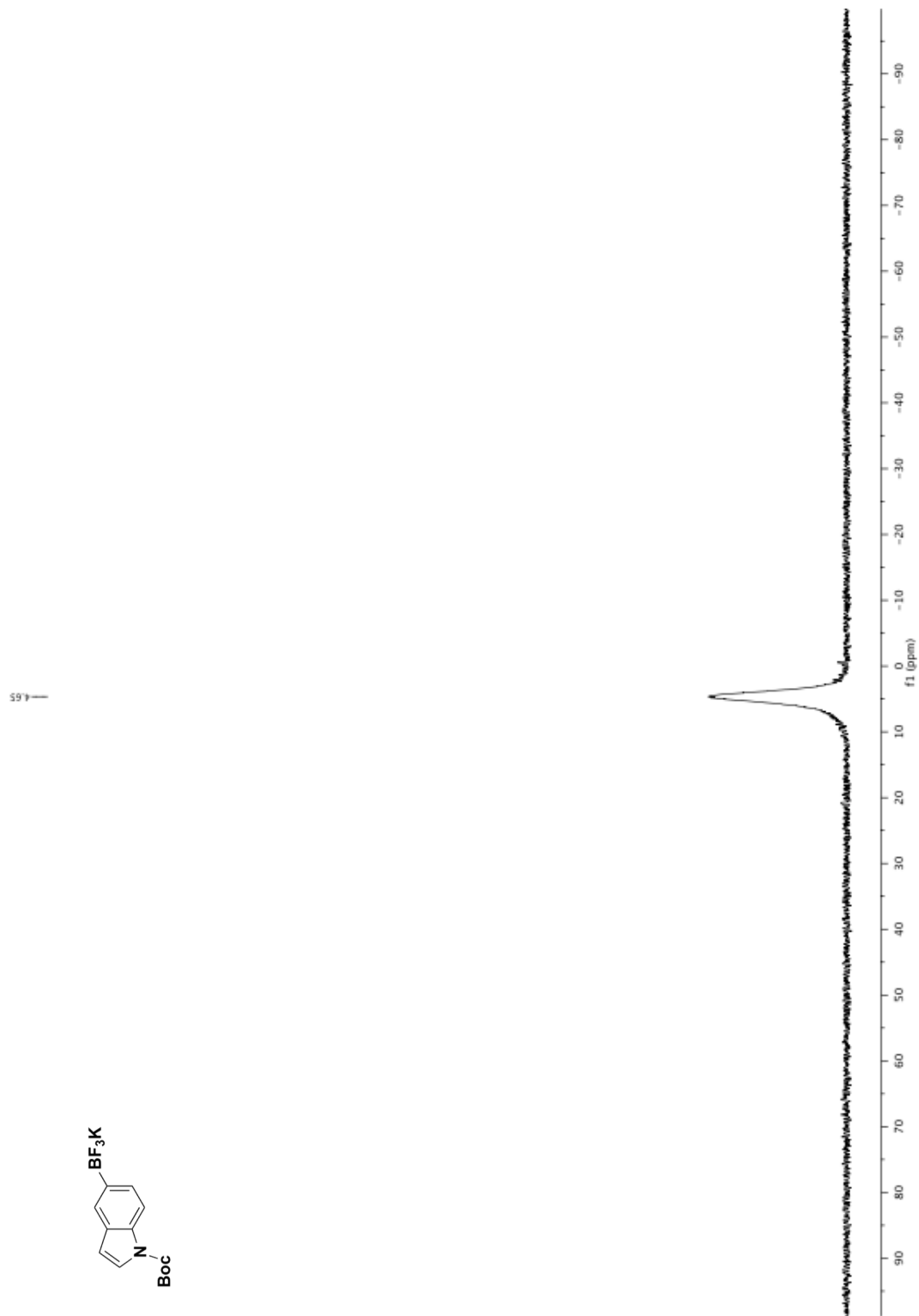
<sup>19</sup>F NMR Spectra (282 MHz, acetone-*d*<sub>6</sub>) (4-(Isoxazol-5-yl)phenyl)trifluoroborate (Table 2, entry 4)



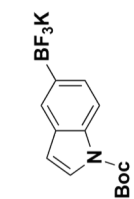


<sup>13</sup>C NMR Spectra (125.8 MHz, DMSO-*d*<sub>6</sub>) Potassium 1-(*tert*-Butoxycarbonyl)-indol-5-yl-trifluoroborate (Table 2, entry 5)

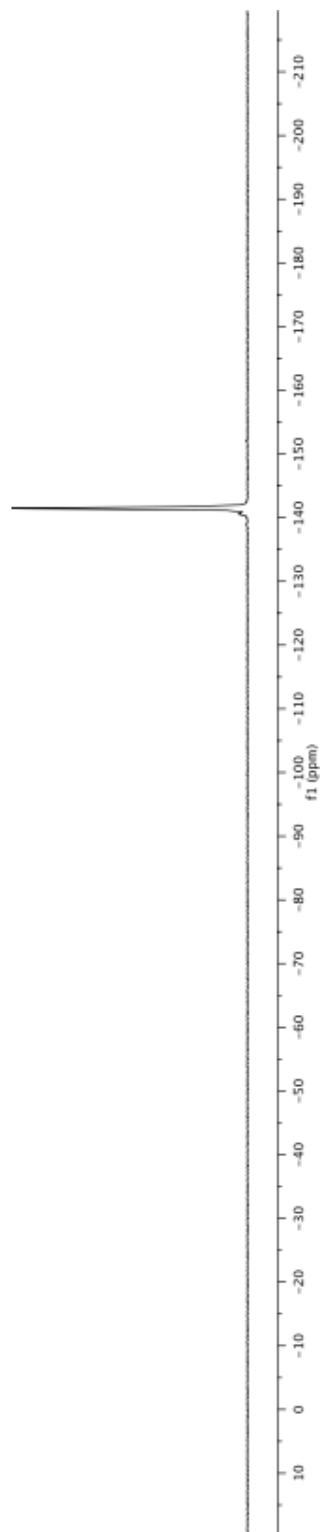




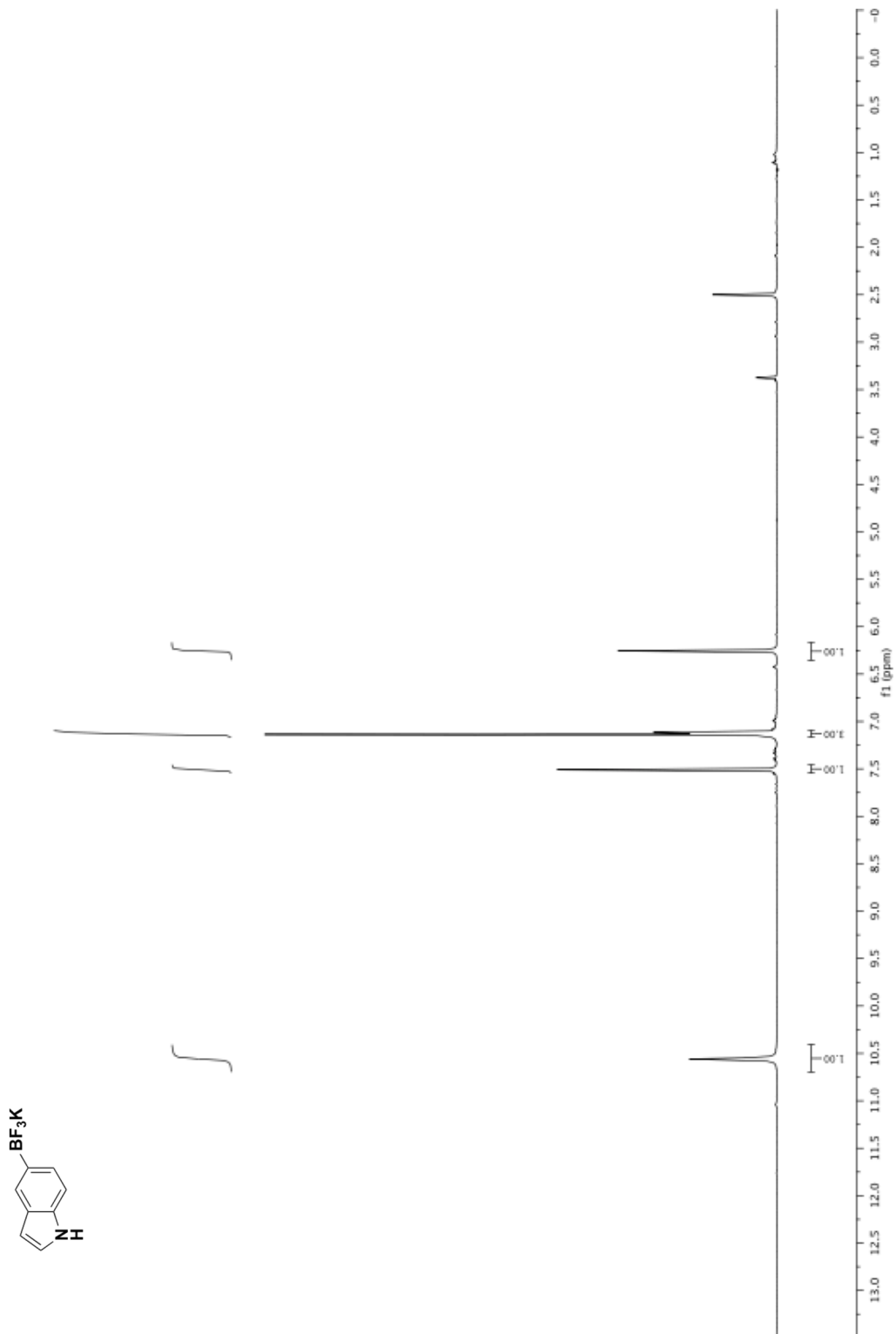
$^{11}\text{B}$  NMR (128.4 MHz, acetone- $d_6$ ) Potassium 1-(*tert*-Butoxycarbonyl)-indol-5-yl-trifluoroborate (Table 2, entry 5)



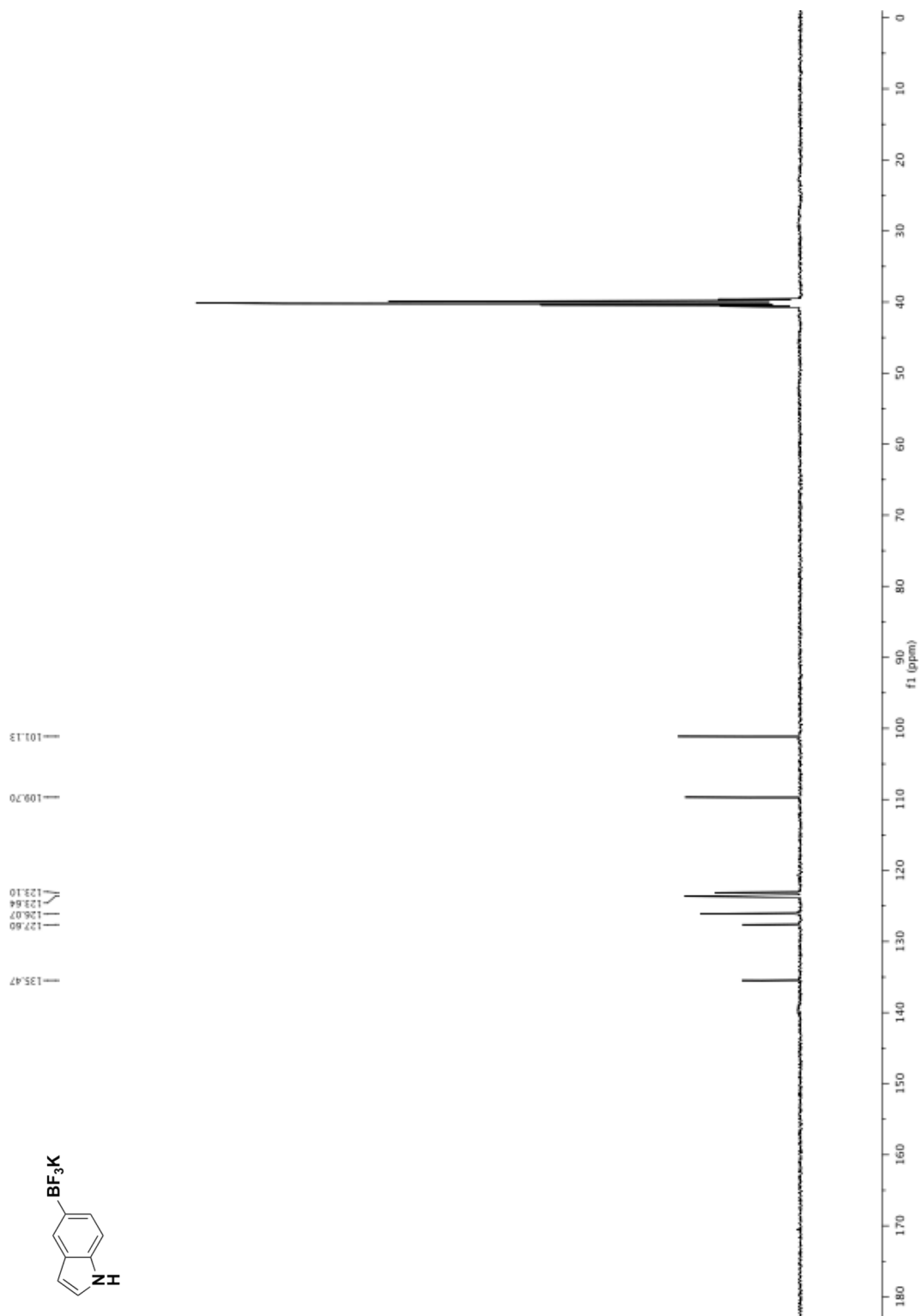
—141.47



<sup>19</sup>F NMR Spectra (282 MHz, acetone-*d*<sub>6</sub>) Potassium 1-(*tert*-Butoxycarbonyl)-indol-5-yl-trifluoroborate (Table 2, entry 5)

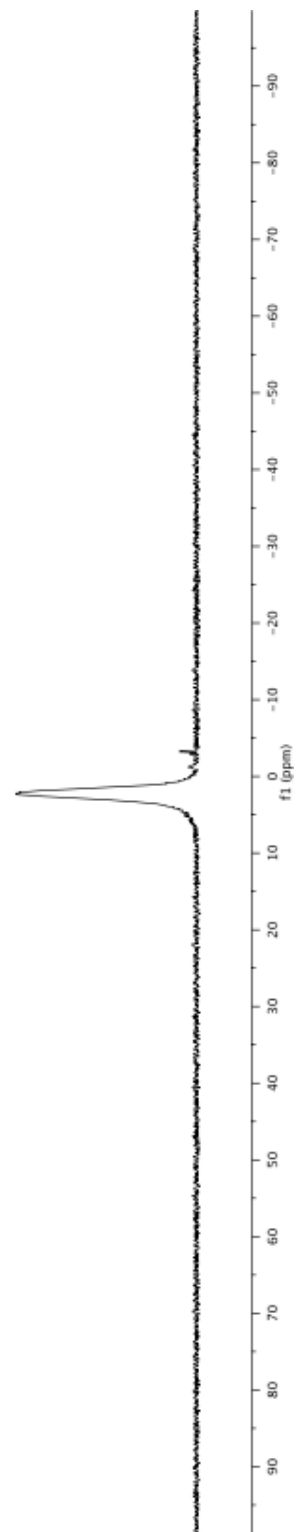
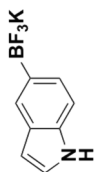


<sup>1</sup>H NMR Spectra (500 MHz, DMSO-*d*<sub>6</sub>) Potassium 1H-indol-5-yl-trifluoroborate (Table 2, entry 6)

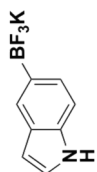


<sup>13</sup>C NMR Spectra (125.8 MHz, DMSO-*d*<sub>6</sub>) Potassium 1H-indol-5-yl-trifluoroborate (Table 2, entry 6)

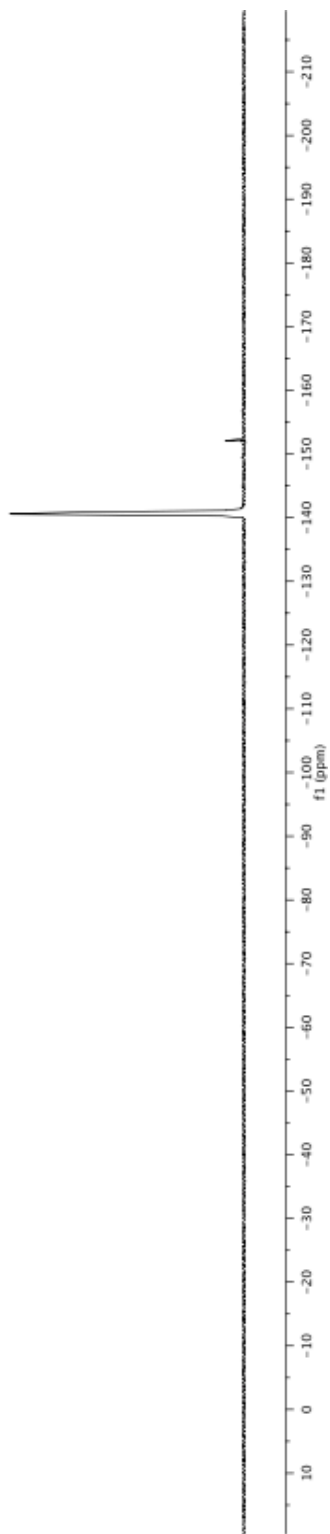
—224—



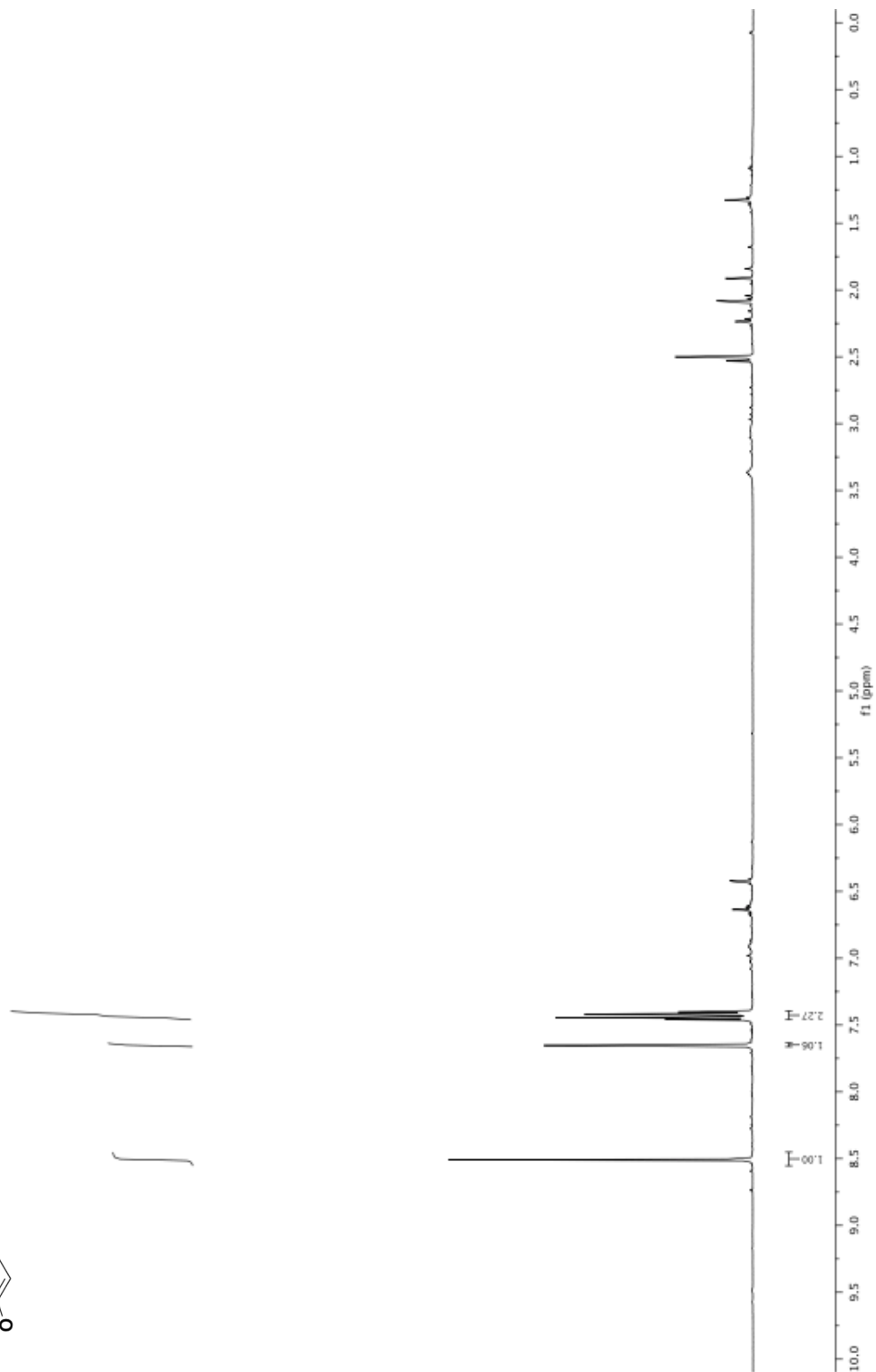
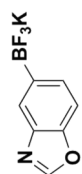
$^{11}\text{B}$  NMR (128.4 MHz, acetone- $d_6$ ) Potassium 1H-indol-5-yl-trifluoroborate (Table 2, entry 6)



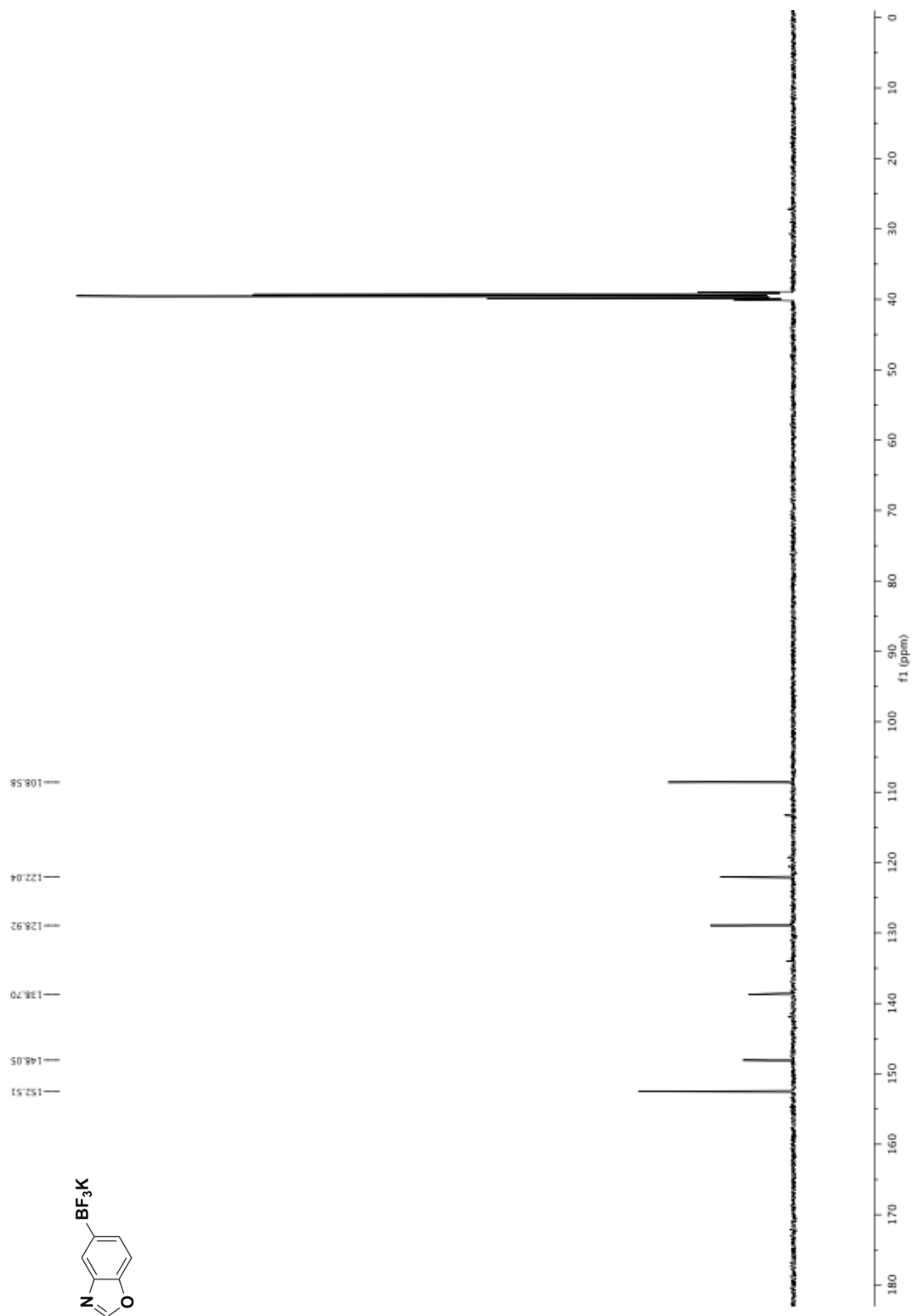
09'061-



$^{19}\text{F}$  NMR Spectra (282 MHz, acetone- $d_6$ ) Potassium 1H-indol-5-yl-trifluoroborate (Table 2, entry 6)

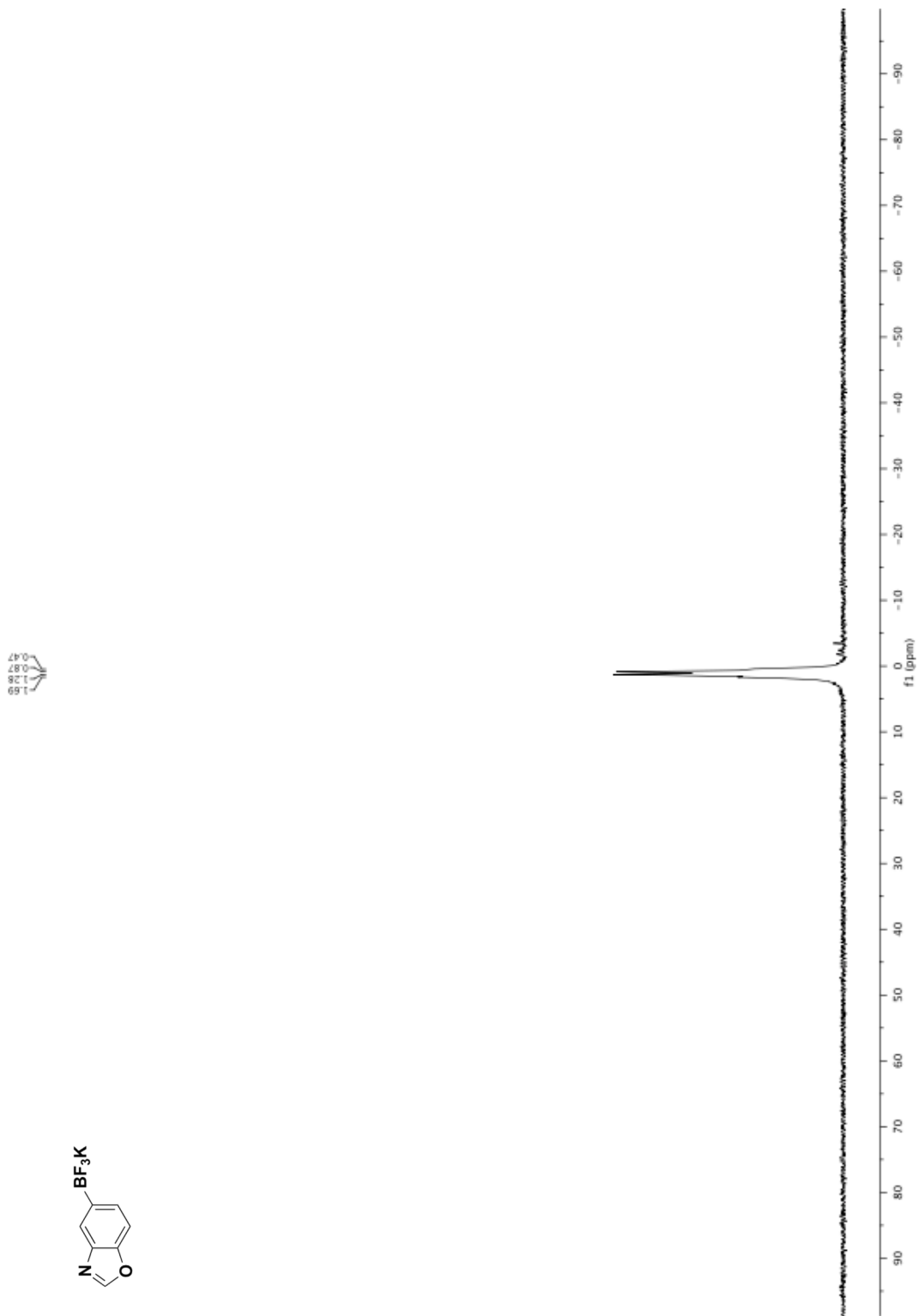


<sup>1</sup>H NMR Spectra (500 MHz, DMSO-*d*<sub>6</sub>) Potassium 5-Trifluoroborato-benzoxazole (Table 2, entry 7)

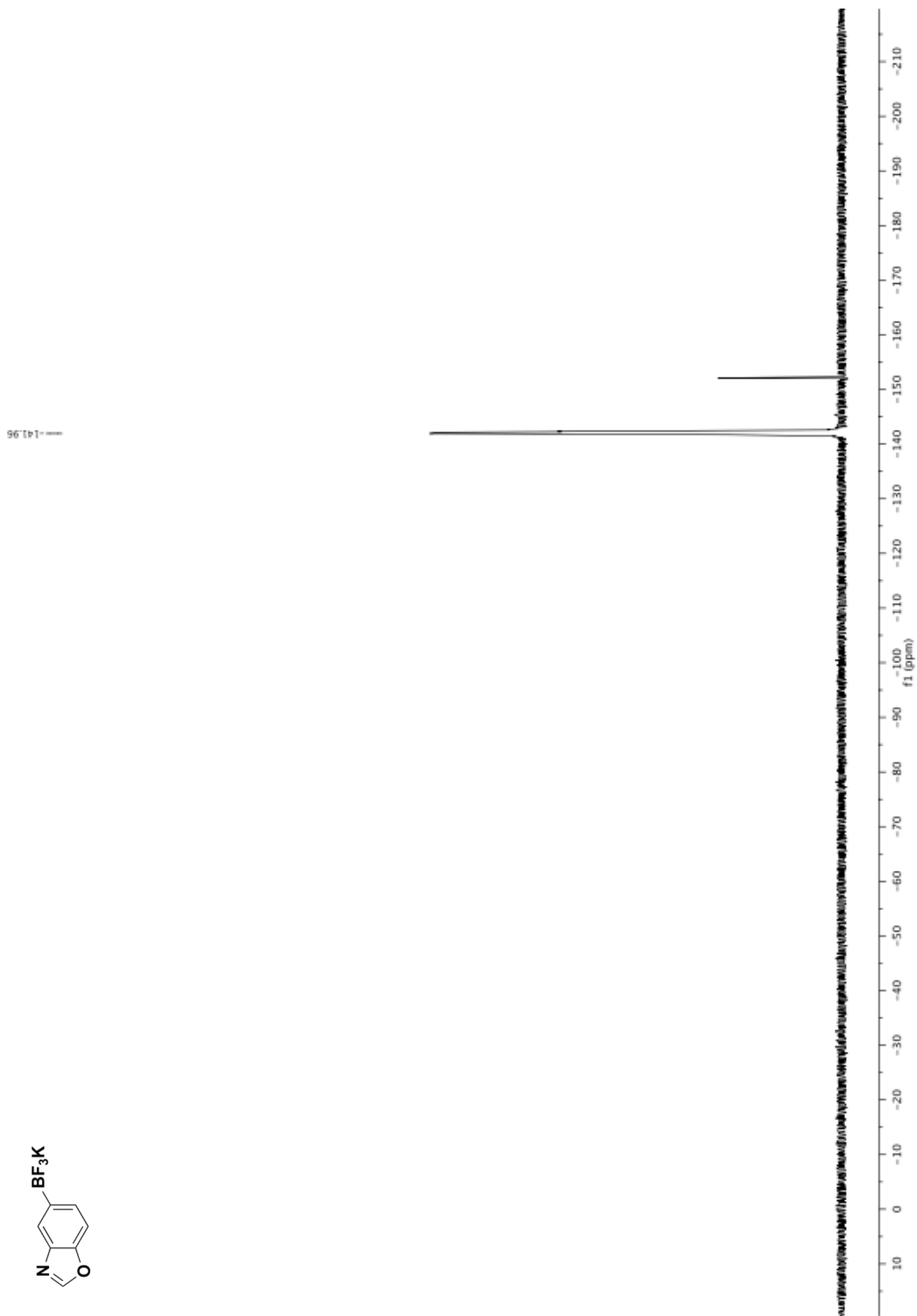
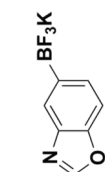


$^{13}\text{C}$  NMR Spectra (125.8 MHz,  $\text{DMSO-}d_6$ ) **Potassium 5-Trifluoroborato-benzoxazole** (Table 2, entry 7)

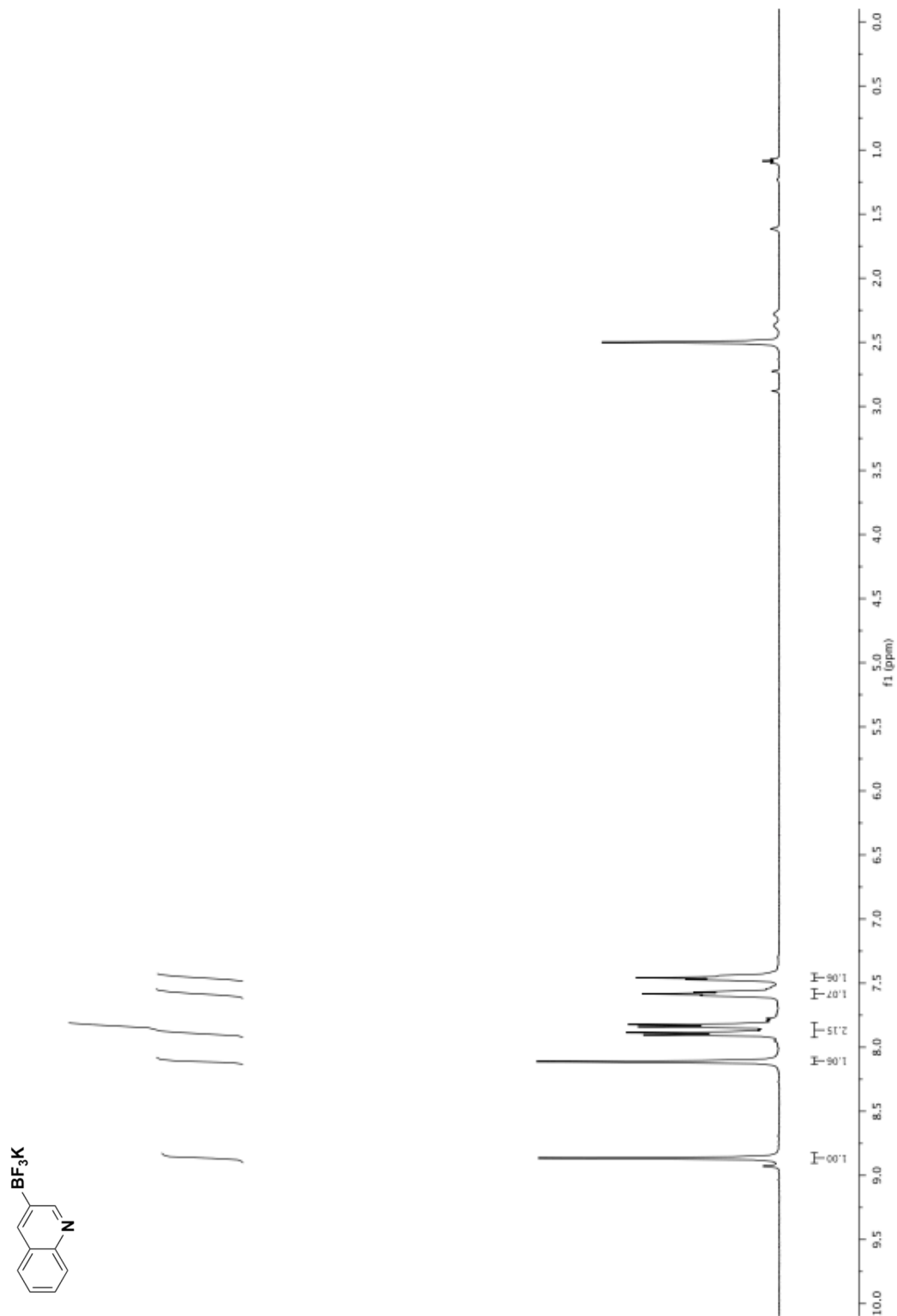




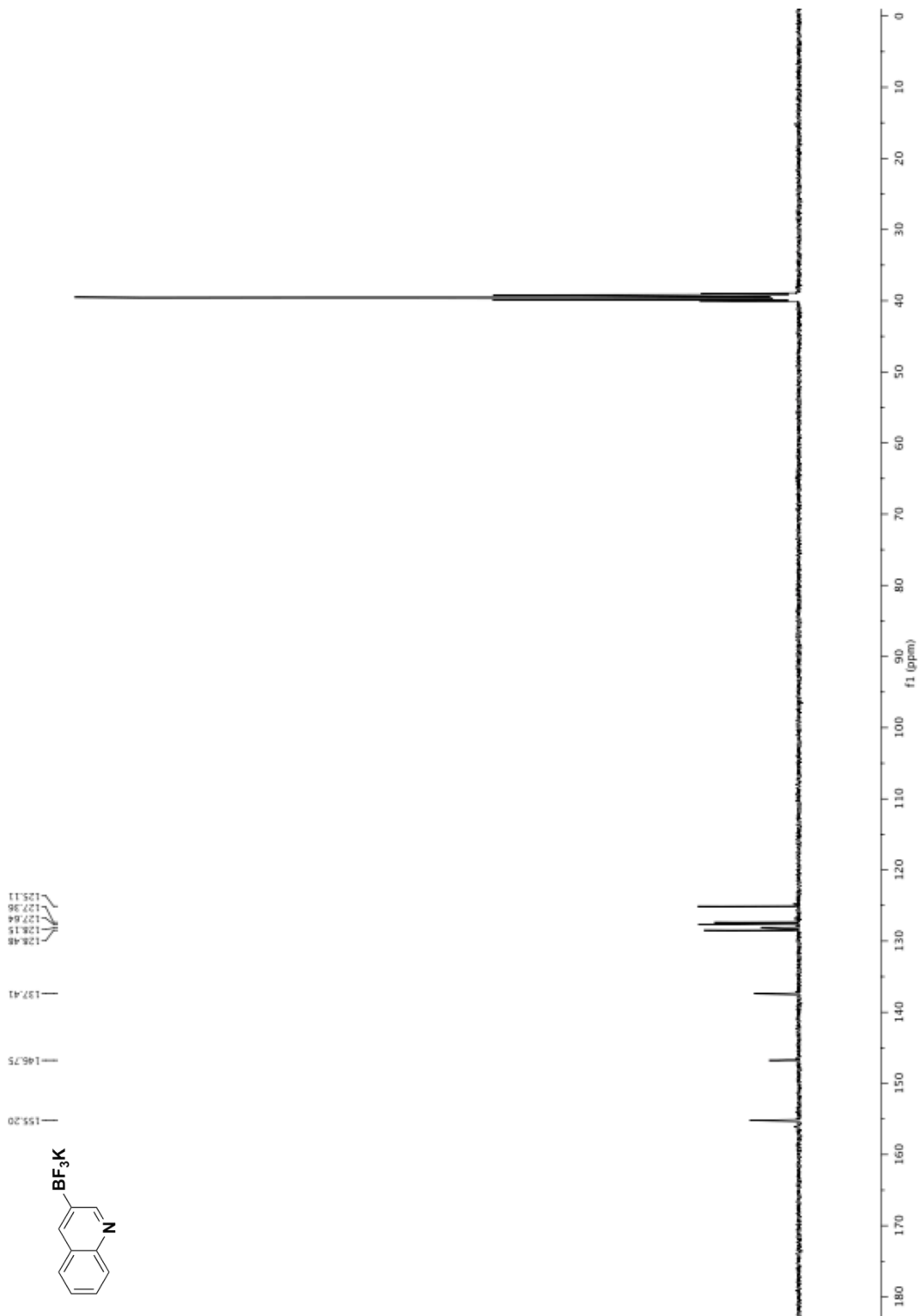
$^{11}\text{B}$  NMR (128.4 MHz, acetone- $d_6$ ) Potassium 5-Trifluoroborato-benzoxazole (Table 2, entry 7)



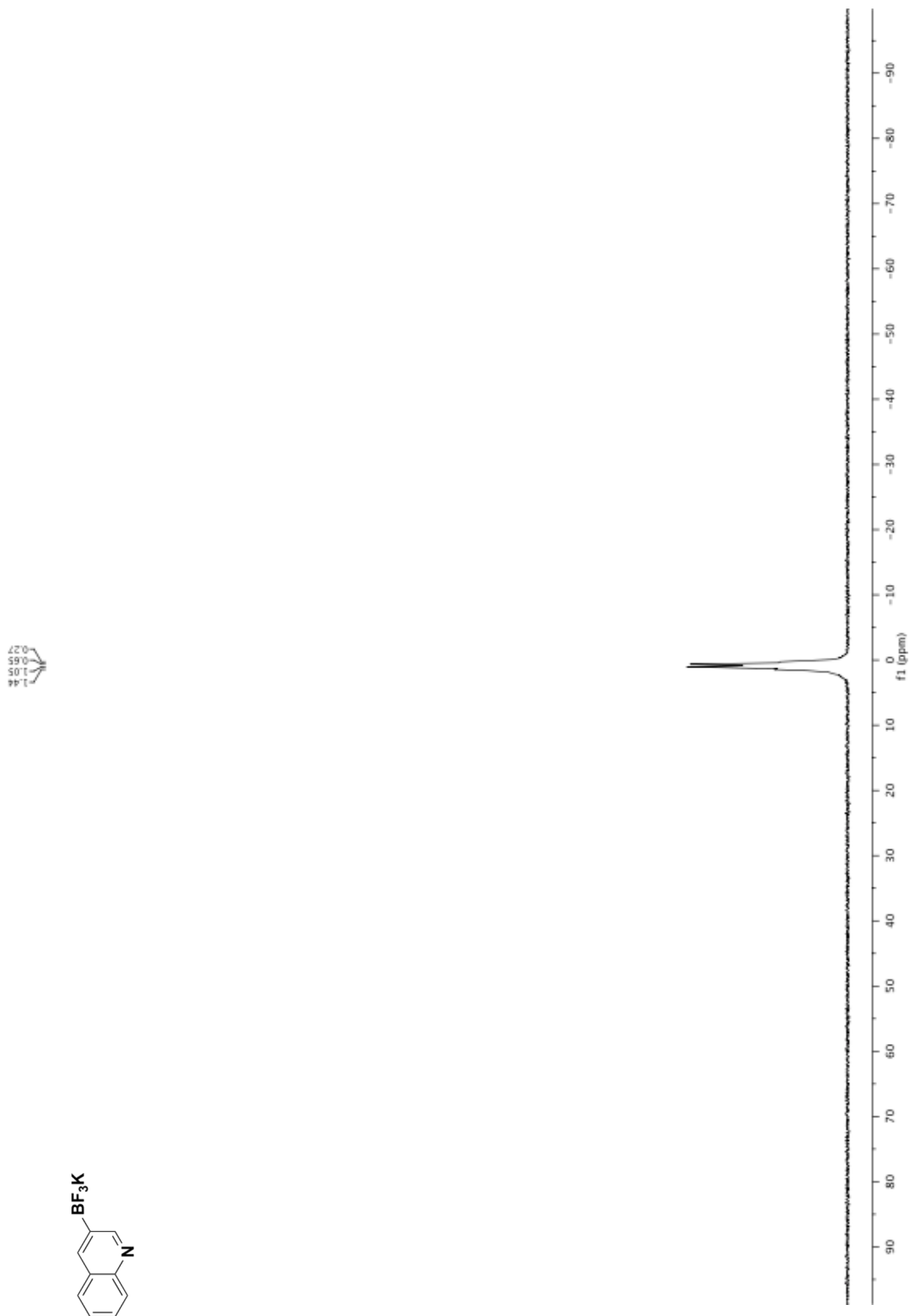
$^{19}\text{F}$  NMR Spectra (282 MHz, acetone- $d_6$ ) Potassium 5-Trifluoroborato-benzoxazole (Table 2, entry 7)



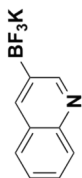
<sup>1</sup>H NMR Spectra (500 MHz, DMSO-*d*<sub>6</sub>) Potassium (Quinolin-3-yl)trifluoroborate (Table 2, entry 8)



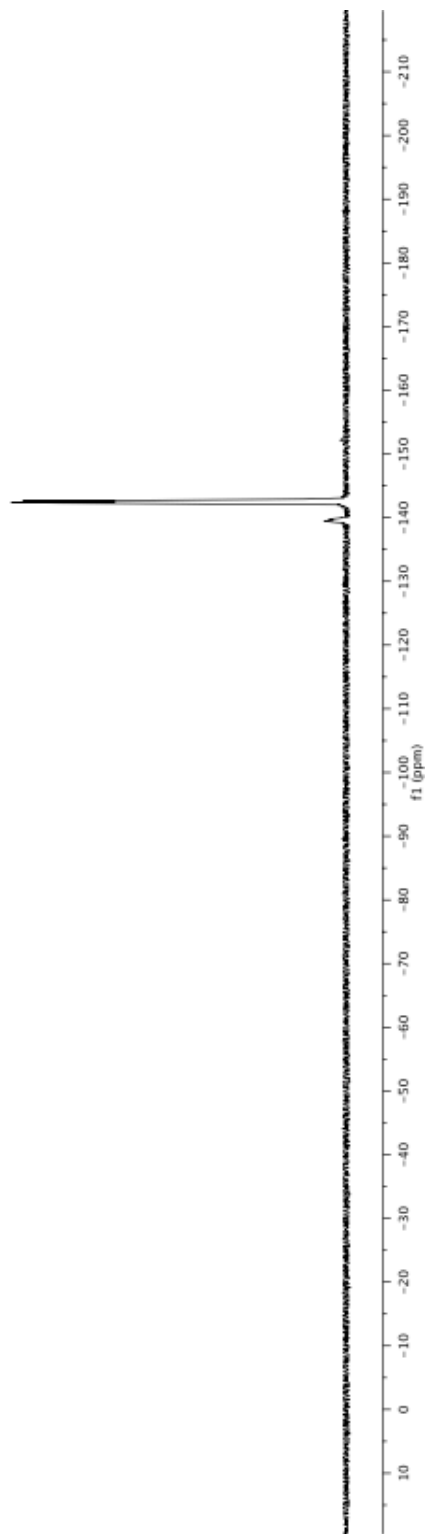
$^{13}\text{C}$  NMR Spectra (125.8 MHz,  $\text{DMSO-}d_6$ ) Potassium (Quinolin-3-yl)trifluoroborate (Table 2, entry 8)



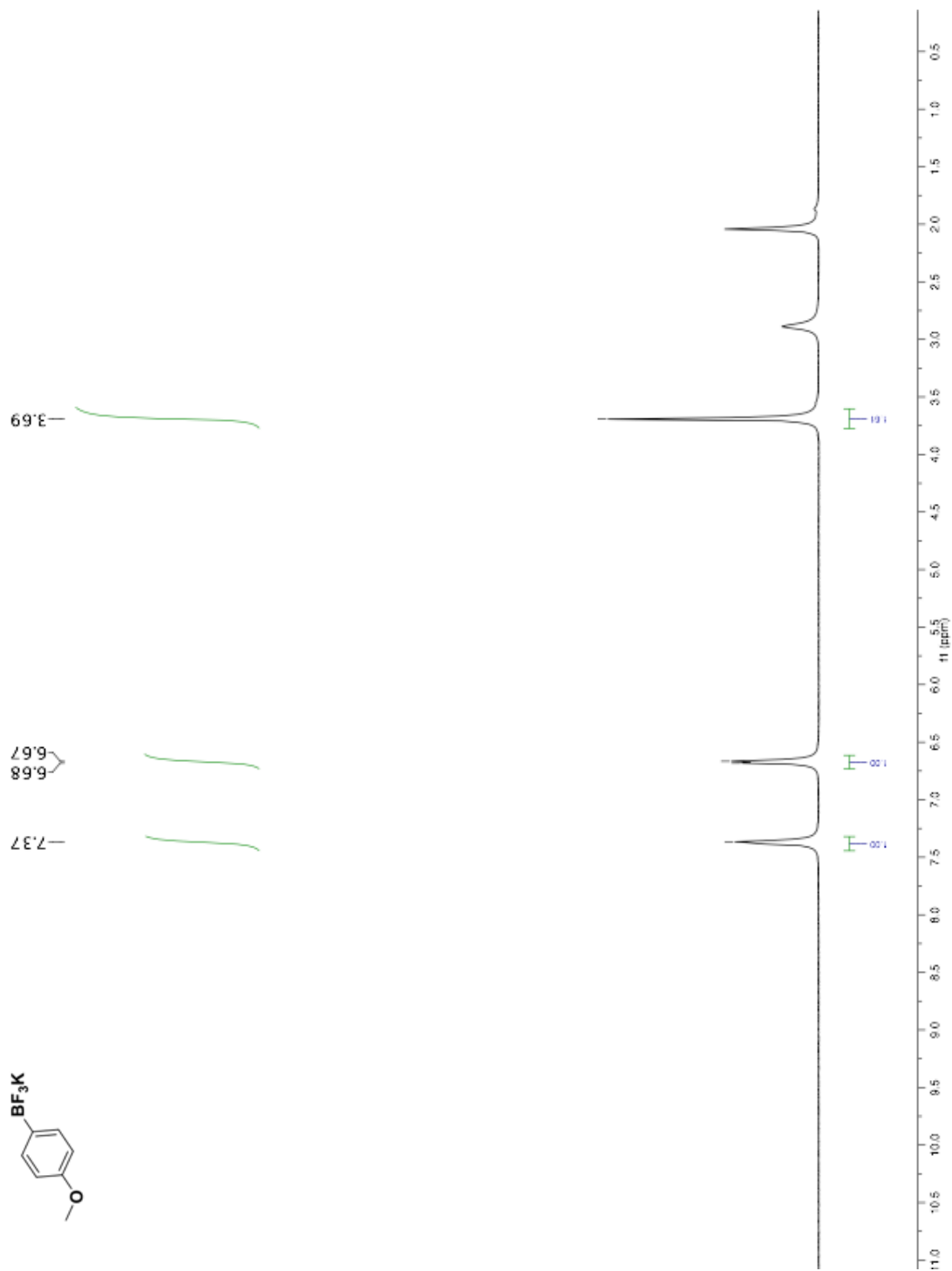
$^{11}\text{B}$  NMR (128.4 MHz, acetone- $d_6$ ) Potassium (Quinolin-3-yl)trifluoroborate (Table 2, entry 8)



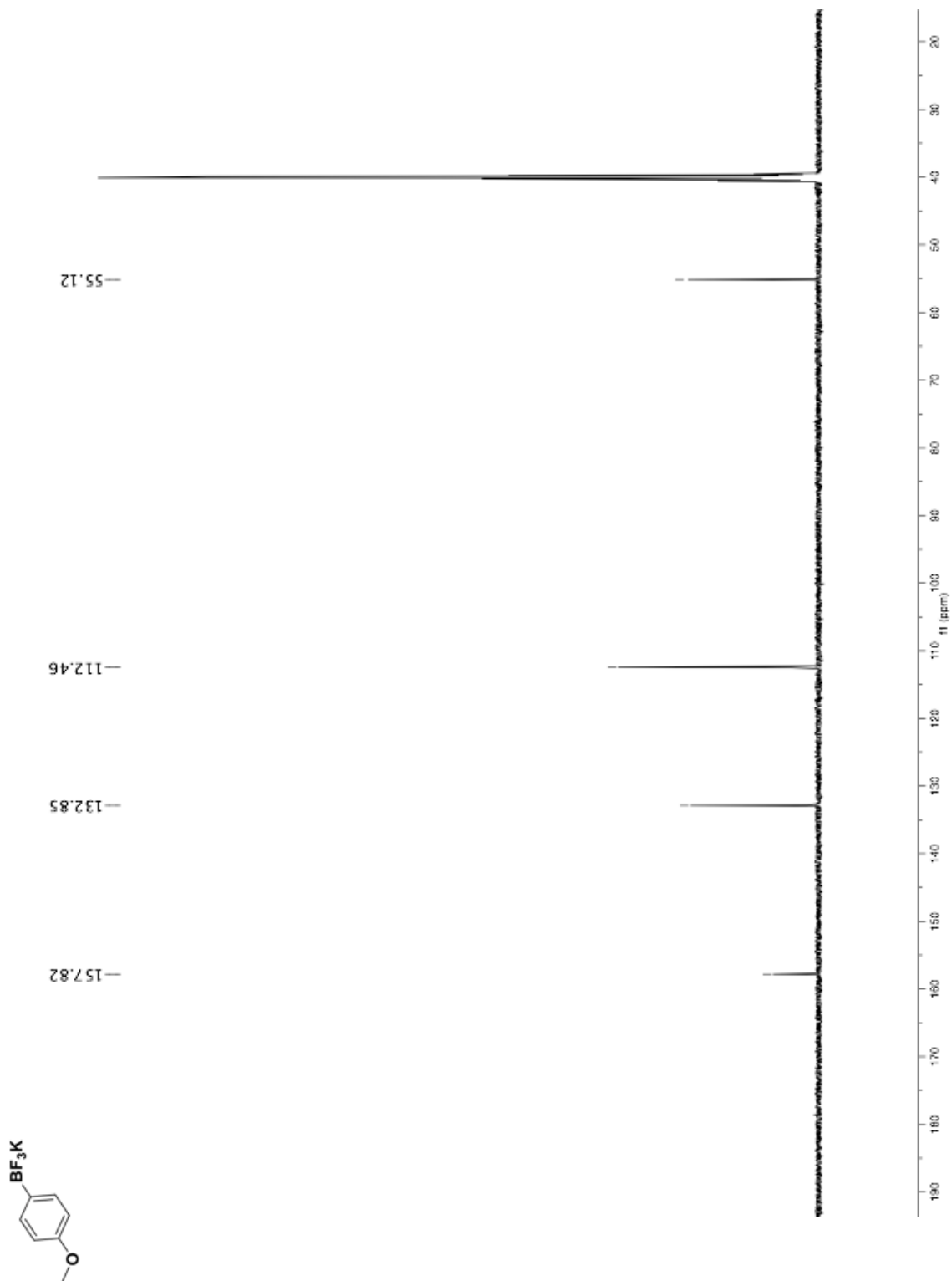
19F



$^{19}\text{F}$  NMR Spectra (282 MHz, acetone- $d_6$ ) Potassium (Quinolin-3-yl)trifluoroborate (Table 2, entry 8)

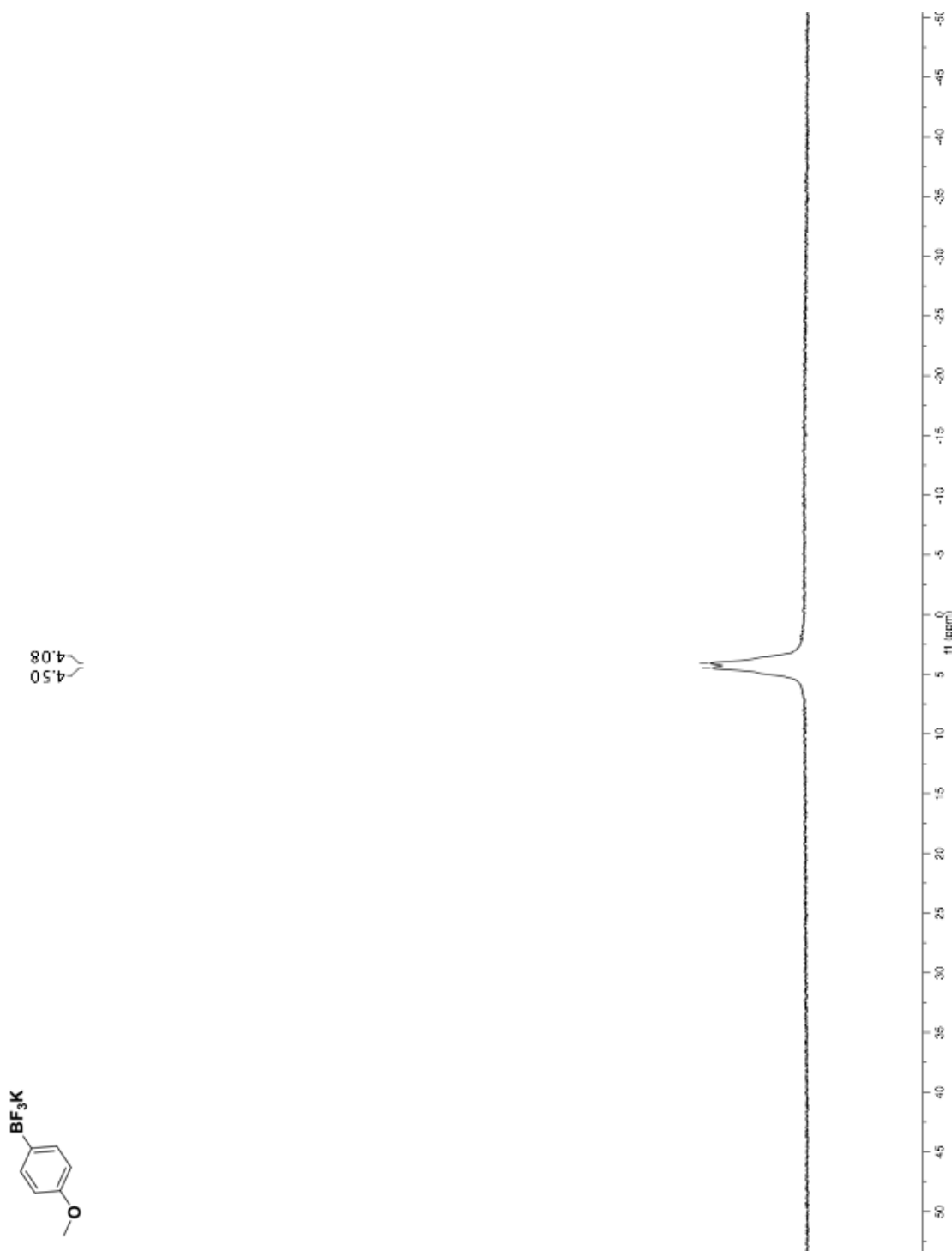


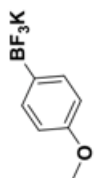
<sup>1</sup>H NMR Spectra (500 MHz, DMSO-*d*<sub>6</sub>) Potassium 4-Methoxyphenyl-trifluoroborate (Table 3, entry 2)



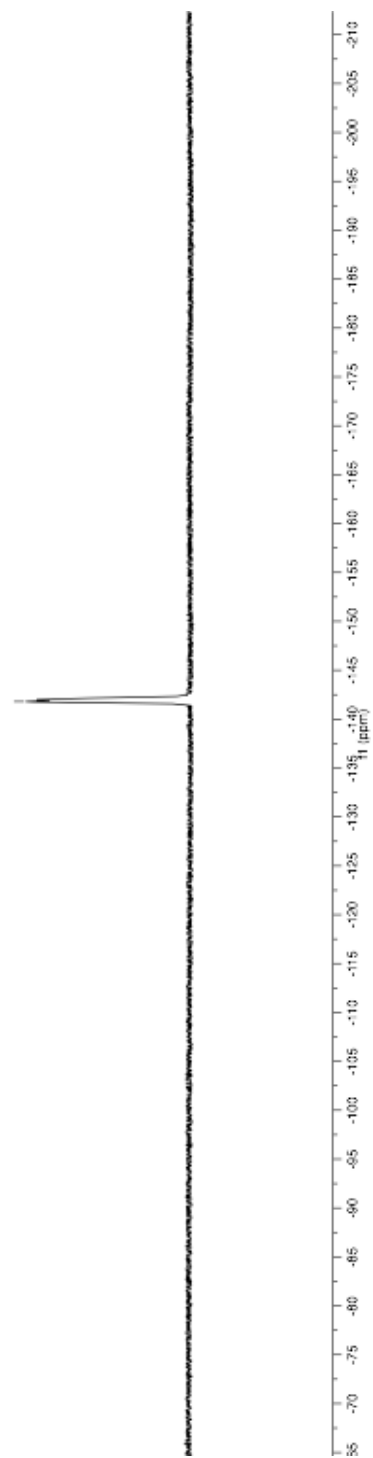
$^{13}\text{C}$  NMR Spectra (125.8 MHz,  $\text{DMSO-}d_6$ ) Potassium 4-Methoxyphenyltrifluoroborate (Table 3, entry 2)



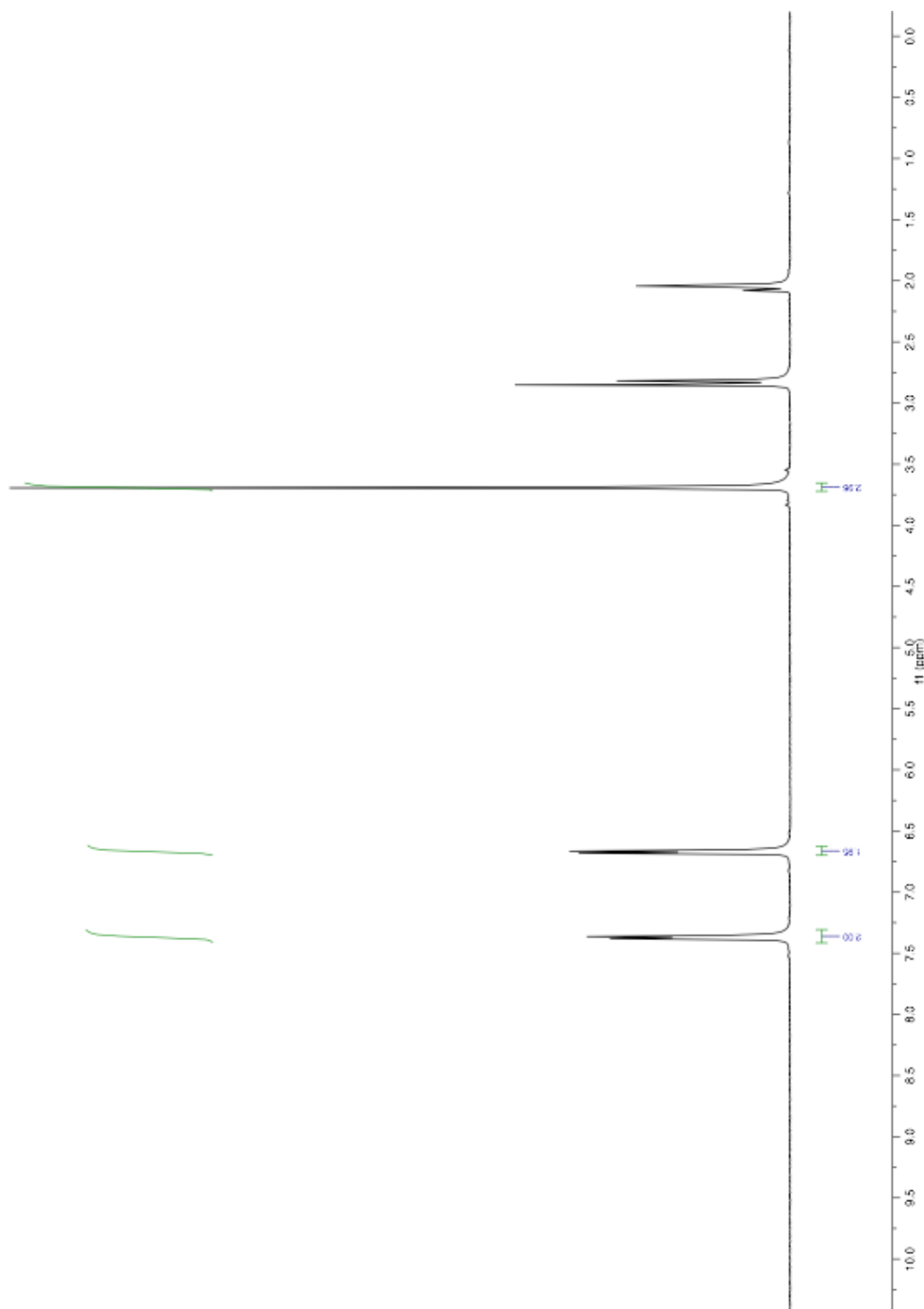
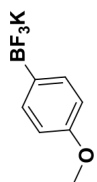




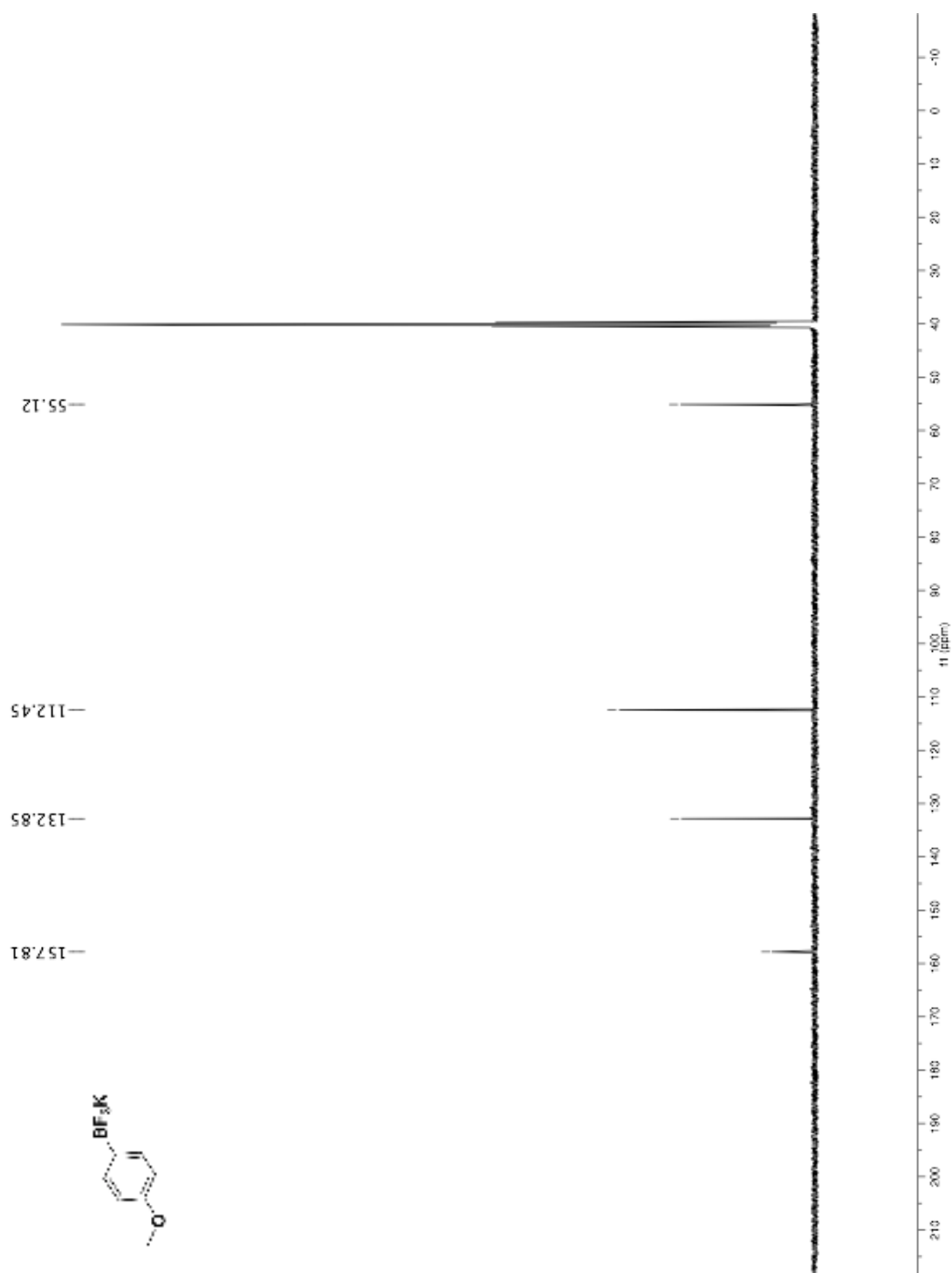
—141.80



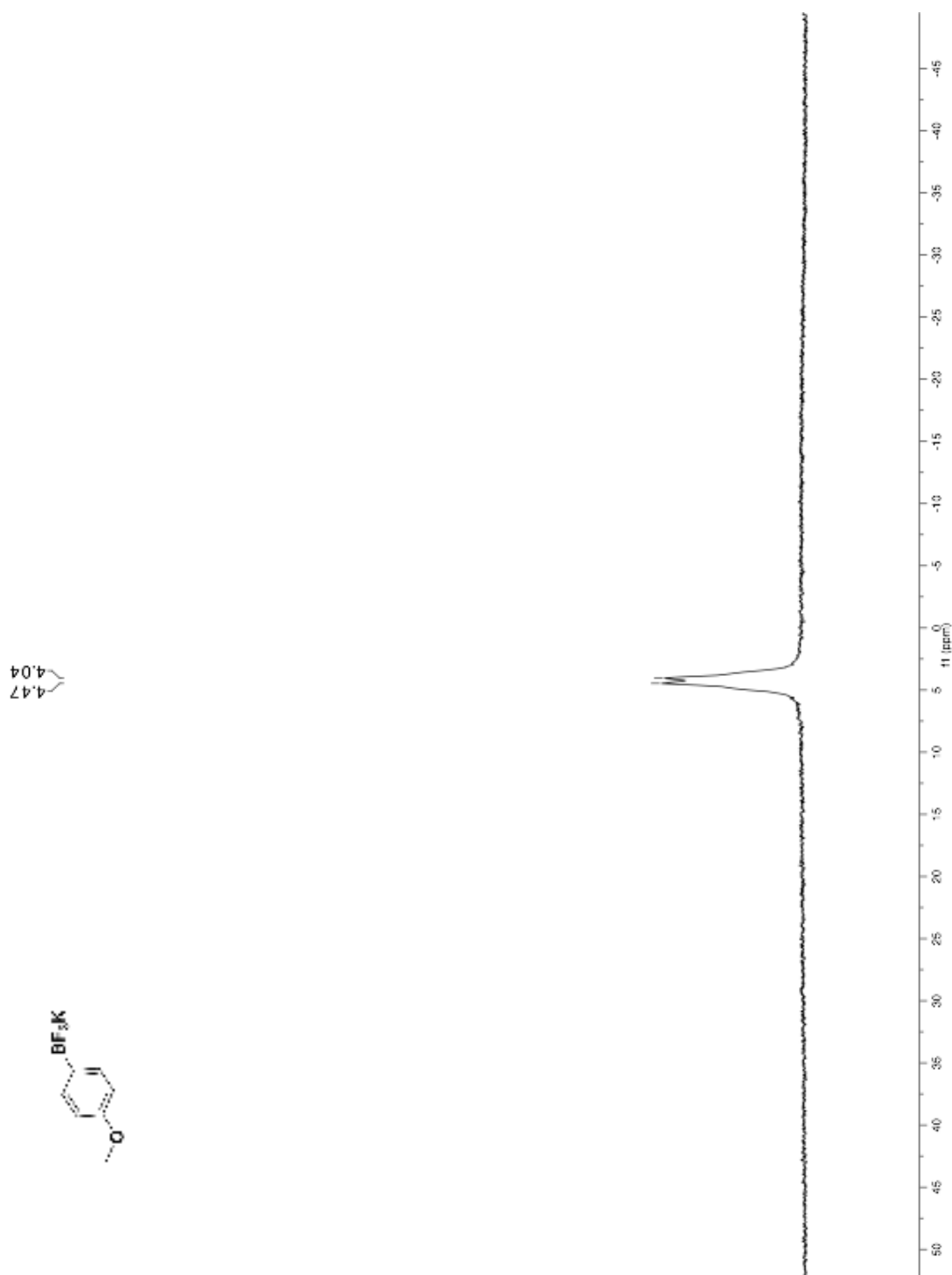
<sup>19</sup>F NMR Spectra (338.8 MHz, acetone-*d*<sub>6</sub>) Potassium 4-Methoxyphenyltrifluoroborate (Table 3, entry 2)



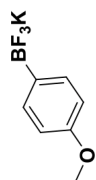
<sup>1</sup>H NMR Spectra (500 MHz, Acetone-*d*<sub>6</sub>) Potassium 4-Methoxyphenyl-trifluoroborate (Table 3, entry 3)



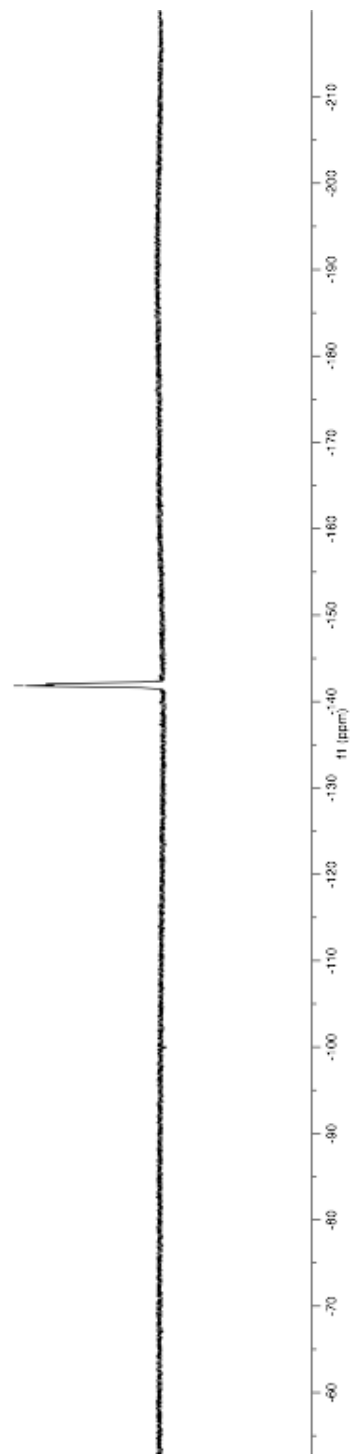
$^{13}\text{C}$  NMR Spectra (125.8 MHz,  $\text{DMSO-}d_6$ ) Potassium 4-Methoxyphenyltrifluoroborate (Table 3, entry 3)



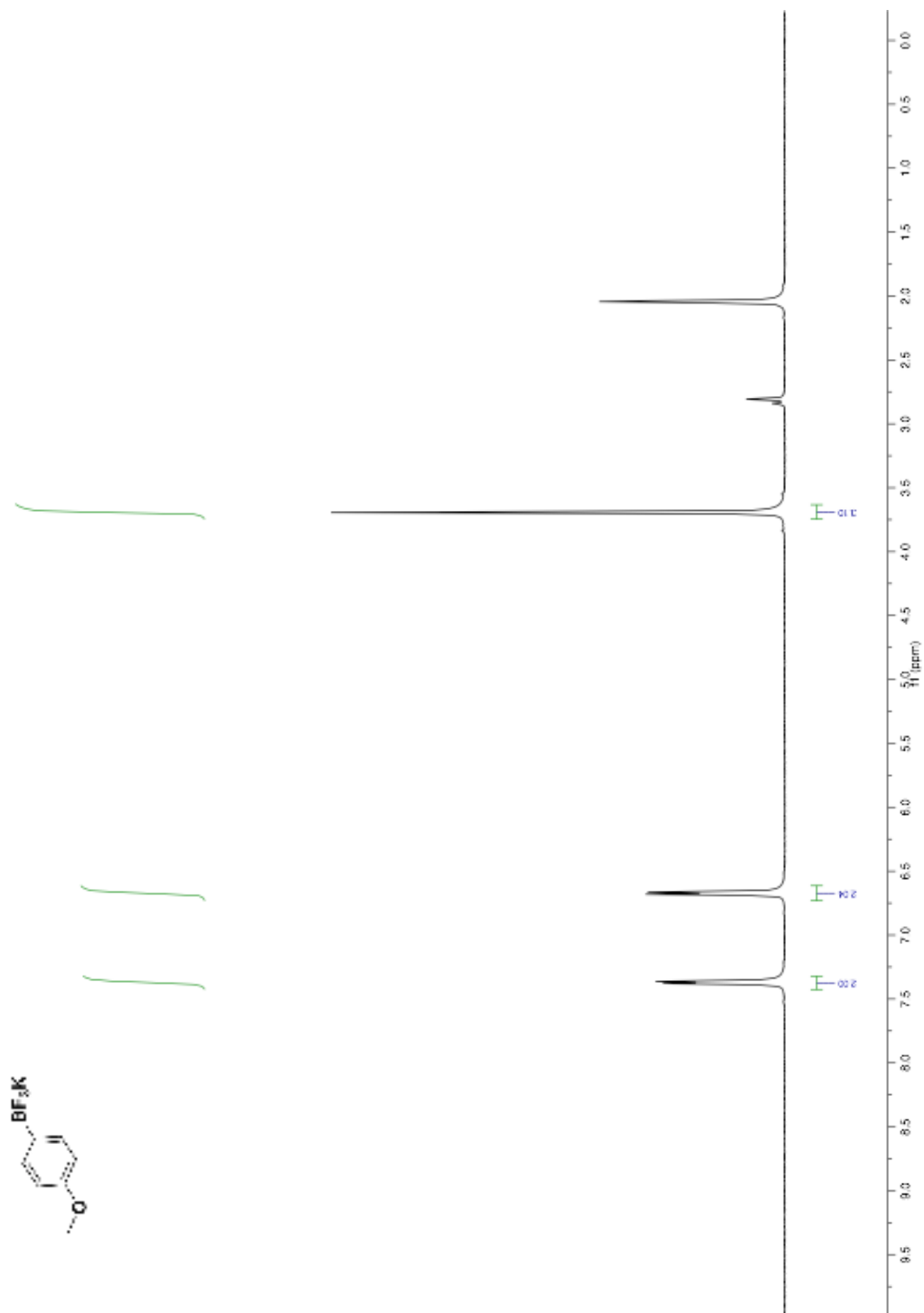
$^{11}\text{B}$  NMR (128.4 MHz, acetone- $d_6$ ) Potassium 4-Methoxyphenyl-trifluoroborate (Table 3, entry 3)



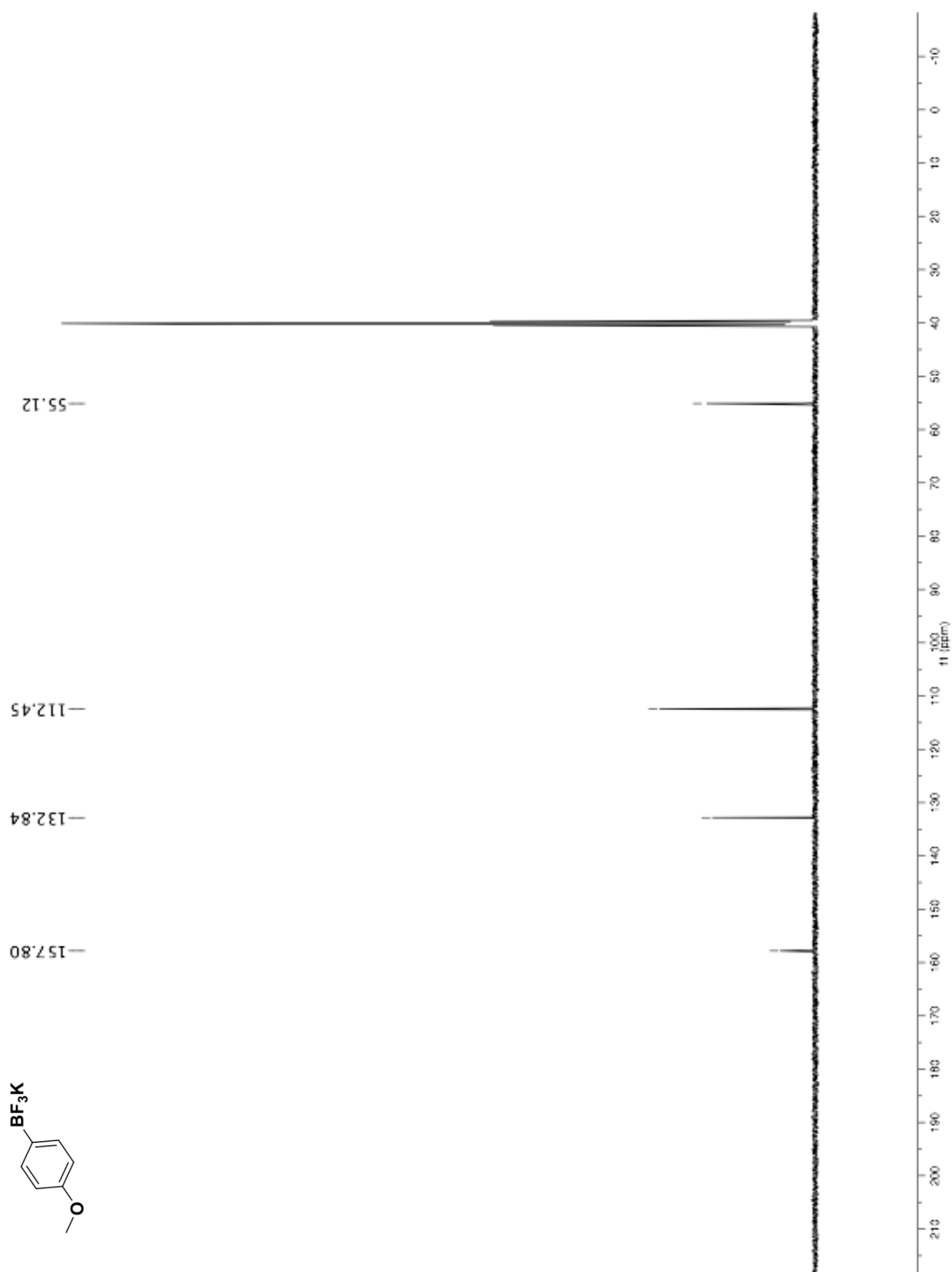
—141.82



$^{19}\text{F}$  NMR Spectra (338.8 MHz, acetone- $d_6$ ) Potassium 4-Methoxyphenyltrifluoroborate (Table 3, entry 3)

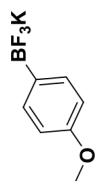


<sup>1</sup>H NMR Spectra (500 MHz, DMSO-*d*<sub>6</sub>) Potassium 4-Methoxyphenyl-trifluoroborate (Table 3, entry 4)

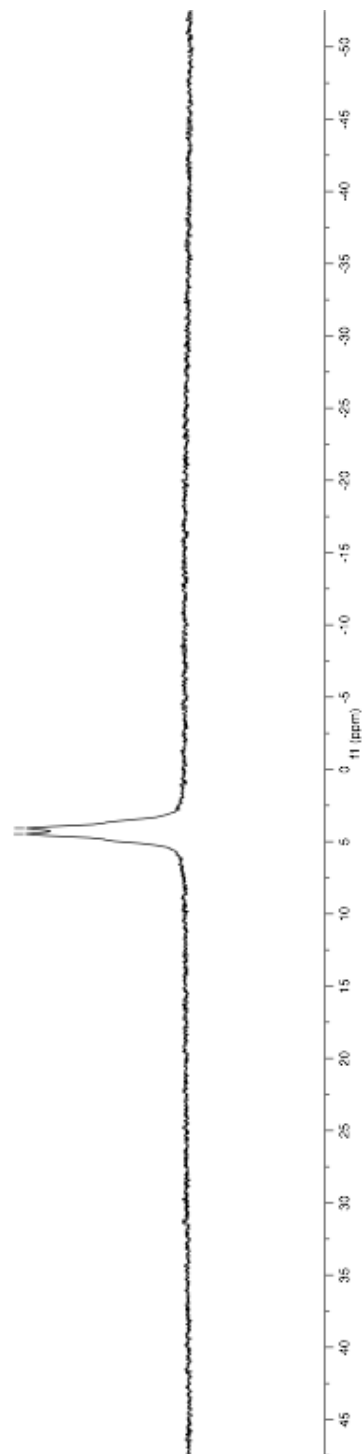


$^{13}\text{C}$  NMR Spectra (125.8 MHz,  $\text{DMSO-}d_6$ ) Potassium 4-Methoxyphenyltrifluoroborate (Table 3, entry 4)

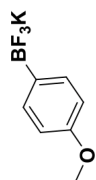




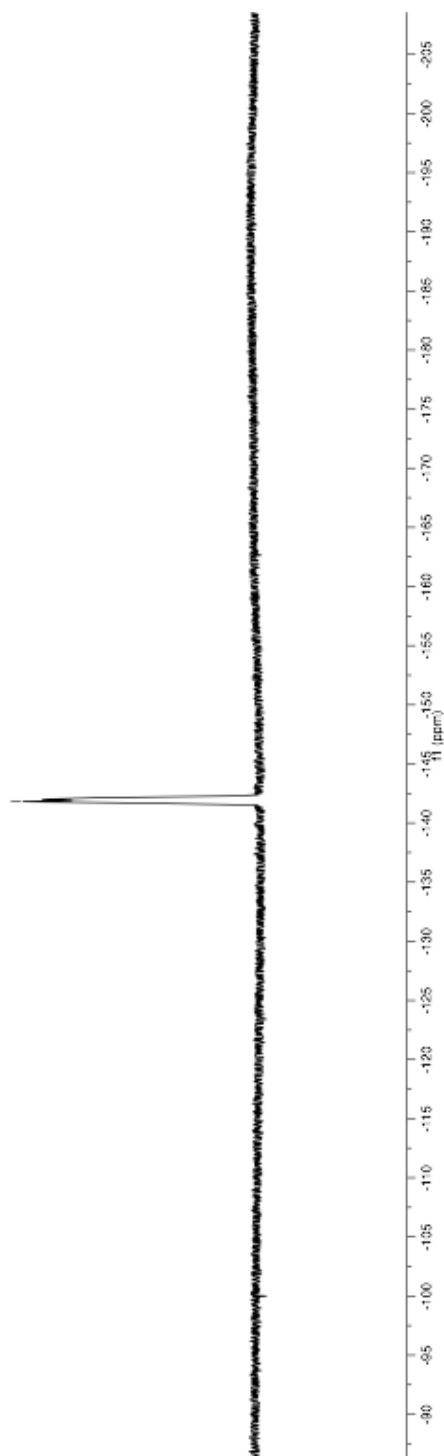
4.47  
4.07



$^{11}\text{B}$  NMR (128.4 MHz, acetone- $d_6$ ) Potassium 4-Methoxyphenyl-trifluoroborate (Table 3, entry 4)



—141.82



<sup>19</sup>F NMR Spectra (338.8 MHz, acetone-*d*<sub>6</sub>) Potassium 4-Methoxyphenyltrifluoroborate (Table 3, entry 4)