

Scope of the Palladium-Catalyzed Aryl Borylation Utilizing Bis-Boronic Acid

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Supporting Information

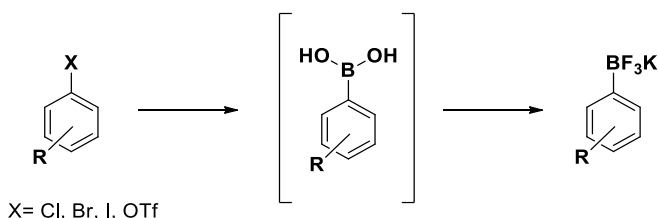
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General Considerations

Reagents: All reactions were carried out under an atmosphere of argon. Ethanol (200 proof, non-anhydrous) was thoroughly degassed (1 h) with argon directly before use. All aryl halides were purchased from commercial sources and used as received. KOAc, K₃PO₄, and K₂CO₃ were dried in an oven overnight before use. All reagents (with the exception of the aryl halides) were stored in a bench-top desiccator. Bis-boronic acid was provided by BASF (and is now commercially available, CAS 13675-18-8). The XPhos version of the palladium preformed catalyst is now available from commercial sources

(CAS 1310584-14-5). The cataCXium A palladium preformed catalyst was prepared by Matt Tudge of Merck Process Chemistry.

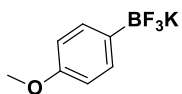
Analytical Methods: All new compounds were characterized by ^1H NMR, ^{13}C NMR, ^{11}B NMR (when applicable), ^{19}F NMR (when applicable), IR spectroscopy, high-resolution mass spectrometry, and melting point determination (for solids). All known compounds were characterized by ^1H NMR and ^{13}C NMR and compared to literature values. ^1H , ^{13}C , ^{11}B , and ^{19}F were recorded at 500 MHz, 125.8 MHz, 128.4 MHz, and 282 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 μmol), X-Phos (7.14 mg, 15 μmol), $\text{B}_2(\text{OH})_4$ (405 mg, 4.5 mmol), and KOAc (441 mg, 4.5 mmol). The vessel was sealed and then evacuated and backfilled with Ar (process was repeated four times). EtOH (15 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). The reaction was then heated to 80 $^\circ\text{C}$ until consumption of starting material (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 H_2O (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 (Na₂SO₄) 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 KHF₂ 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 ¹¹B 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 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 Et₂O (~25 mL) led to the precipitation of the desired product. The collected solid was washed with Et₂O. Further purification (to remove small organic or boron containing impurities) could be realized via trituration of the solid with Et₂O.

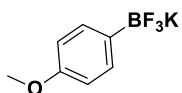
General Procedure A with Aryl Chlorides:



Potassium 4-Methoxyphenyl-trifluoroborate (Table 1, entry 1).¹

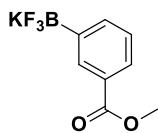
Following general procedure A, a mixture of 4-chloroanisole (214 mg, 183 μ L, 1.5 mmol), XPhos palladium(II) biphenyl preformed catalyst (5.89 mg, 7.5 μ mol), XPhos (7.14 mg, 15 μ mol), KOAc (441 mg, 4.5 mmol), and B₂(OH)₄ (405 mg, 4.5 mmol), was heated to 80 °C in EtOH (15 mL) for 2 h. The title compound was obtained as a white solid in 93% yield (298 mg). mp > 225 °C. Spectral data were in accordance with those of published results. ¹H NMR (500 MHz, acetone-*d*₆) δ 7.37 (d, *J* = 7.8 Hz, 2H), 6.67 (d, *J* =

7.9 Hz, 2H), 3.69 (s, 3H). ^{13}C NMR (125.8 MHz, acetone- d_6) δ 158.0, 132.7, 111.9, 54.2.



Potassium 4-Methoxyphenyl-trifluoroborate (Table 1, entry 1^e).¹

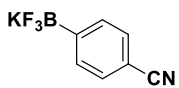
A mixture of Pd(OAc)₂ (1.68 mg, 7.5 μmol), XPhos (10.71 mg, 22.5 μmol), and KOAc (441 mg, 4.5 mmol) was heated to 80 °C in EtOH (3 mL) for 20 min. The reaction was cooled to rt, a needle attached to a manifold under argon was inserted into the septa and 4-chloroanisole (214 mg, 183 μL , 1.5 mmol) was added neat via syringe followed by the addition of a solution of B₂(OH)₄ (405 mg, 4.5 mmol) in EtOH (12 mL). The needle was removed, and the reaction was heated to 80 °C for an additional 1 h. See general procedure A for work-up. The title compound was obtained as a white solid in 95% yield (306 mg). Spectral data were in accordance with those of published results. mp > 225 °C. ^1H NMR (500 MHz, DMSO- d_6) δ 7.21 (d, J = 7.4 Hz, 2H), 6.65 (d, J = 7.5 Hz, 2H), 3.65 (s, 3H). ^{13}C NMR (125.8 MHz, DMSO- d_6) δ 157.8, 132.9, 112.5, 55.1.



Potassium (3-(Methoxycarbonyl)phenyl)trifluoroborate (Table 1, entry

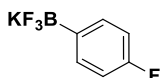
2).¹ Following general procedure A, a mixture of methyl 3-chlorobenzoate (256 mg, 208 μL , 1.5 mmol), XPhos palladium(II) biphenyl preformed catalyst (5.89 mg, 7.5 μmol), XPhos (7.14 mg, 15 μmol), KOAc (441 mg, 4.5 mmol), and B₂(OH)₄ (405 mg, 4.5 mmol), was heated to 80 °C in EtOH (15 mL) for 2.5 h. The title compound was obtained as a white solid in 97% yield (351 mg). mp > 225 °C. Spectral data were in accordance with those of published results. ^1H NMR (500 MHz, acetone- d_6) δ 8.23 (s, 1H), 7.74 (t, J

= 7.4 Hz, 2H), 7.24 (t, $J = 7.4$ Hz, 1H), 3.85 (s, 3H). ^{13}C NMR (125.8 MHz, DMSO- d_6) δ 167.9, 136.8, 132.8, 127.9, 126.9, 126.5, 52.1.



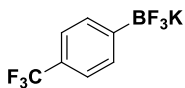
Potassium (4-Cyanophenyl)trifluoroborate (Table 1, entry 3).¹

Following general procedure A, a mixture of 4-chlorobenzonitrile (206 mg, 1.5 mmol), XPhos palladium(II) biphenyl preformed catalyst (5.89 mg, 7.5 μmol), XPhos (7.14 mg, 15 μmol), KOAc (441 mg, 4.5 mmol), and $\text{B}_2(\text{OH})_4$ (405 mg, 4.5 mmol), was heated to 80 $^\circ\text{C}$ in EtOH (15 mL) for 1 h. The title compound was obtained as a white solid in 81% yield (255 mg). Spectral data were in accordance with those of published results. mp > 225 $^\circ\text{C}$. ^1H NMR (500 MHz, acetone- d_6) δ 7.65 (d, $J = 7.6$ Hz, 2H), 7.48 (d, $J = 7.7$ Hz, 2H). ^{13}C NMR (125.8 MHz, DMSO- d_6) δ 132.5, 130.4, 120.5, 108.1.



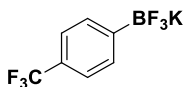
Potassium (4-Fluorophenyl)trifluoroborate (Table 1, entry 4).¹

Following general procedure A, a mixture of 1-chloro-4-fluorobenzene (196 mg, 1.5 mmol), XPhos palladium(II) biphenyl preformed catalyst (5.89 mg, 7.5 μmol), XPhos (7.14 mg, 15 μmol), KOAc (441 mg, 4.5 mmol), and $\text{B}_2(\text{OH})_4$ (405 mg, 4.5 mmol), was heated to 80 $^\circ\text{C}$ in EtOH (15 mL) for 2.5 h. The title compound was obtained as a white solid in 98% yield (297 mg). Spectral data were in accordance with those published. mp > 225 $^\circ\text{C}$. ^1H NMR (500 MHz, acetone- d_6) δ 7.47 (t, $J = 7.1$ Hz, 2H), 6.83 (t, $J = 9.0$ Hz, 2H). ^{13}C NMR (125.8 MHz, DMSO- d_6) δ 161.9, 160.1, 132.9 (d, $J = 5.9$ Hz), 112.77 (d, $J = 18.4$ Hz).



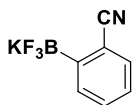
Potassium (4-(Trifluoromethyl)phenyl)trifluoroborate (Table 1, entry

5).¹ Following general procedure A, a mixture of 4-trifluoromethylchlorobenzene (270 mg, 203 μ L, 1.5 mmol), XPhos palladium(II) biphenyl preformed catalyst (5.89 mg, 7.5 μ mol), XPhos (7.14 mg, 15 μ mol), KOAc (441 mg, 4.5 mmol), and B₂(OH)₄ (405 mg, 4.5 mmol), was heated to 80 °C in EtOH (15 mL) for 2.5 h. The title compound was obtained as a white solid in 91% yield (344 mg). Spectral data were in accordance with those published. mp > 225 °C. ¹H NMR (500 MHz, acetone-*d*₆) δ 7.67 (d, *J* = 7.5 Hz, 2H), 7.41 (d, *J* = 7.5 Hz, 2H). ¹³C NMR (125.8 MHz, acetone-*d*₆) δ 132.1, 126.5, 124.4, 122.9.



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

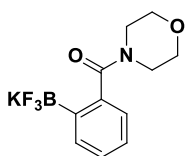
5^b).¹ Following general procedure A, a mixture of 1-chloro-4-(trifluoromethyl)benzene (2.166 g, 1.6 mL, 12 mmol), B₂(OH)₄ (3.24 g, 36 mmol), X-Phos (11.42 mg, 0.024 mmol), X-Phos palladium(II) biphenyl preformed catalyst (9.43 mg, 0.012 mmol), and KOAc (3.5 g, 36 mmol) was heated to 80 °C in EtOH (24 mL) for 3 h. The title compound was obtained as an off-white solid in 88% yield (2.6 g). Spectral data were in accordance with those of published results. mp > 225 °C. ¹H NMR (500 MHz, acetone-*d*₆) δ 7.64 (d, *J* = 7.5 Hz, 2H), 7.40 (d, *J* = 7.5 Hz, 2H). ¹³C NMR (125.8 MHz, DMSO-*d*₆) δ 175.0, 132.31, 126.9, 126.8, 126.6, 126.4, 126.1, 124.6, 123.4, 123.34.



Potassium (2-Cyanophenyl)trifluoroborate (Table 1, entry 6).¹ Following

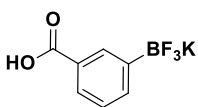
general procedure A, a mixture of 2-chlorobenzonitrile (207 mg, 1.5 mmol), XPhos palladium(II) biphenyl preformed catalyst (5.89 mg, 7.5 μ mol), XPhos (7.14 mg, 15

μmol), KOAc (441 mg, 4.5 mmol), and $\text{B}_2(\text{OH})_4$ (405 mg, 4.5 mmol), was heated to 80 °C in EtOH (15 mL) for 1 h. The title compound was obtained as a white solid in 27% yield (80 mg). Spectral data were in accordance with those published. mp = 185 °C dec. ^1H NMR (500 MHz, acetone- d_6) δ 7.67 (d, J = 7.4 Hz, 1H), 7.49 (d, J = 7.6 Hz, 1H), 7.39 (t, J = 7.5 Hz, 1H), 7.22 (t, J = 7.5 Hz, 1H). ^{13}C NMR (125.8 MHz, DMSO- d_6) δ 132.9, 132.65, 131.2, 126.6, 121.6, 114.9.



Potassium 2-(Morpholine-4-carbonyl)phenyl-trifluoroborate (Table 1,

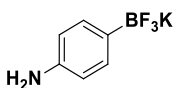
entry 7). Following general procedure A, a mixture of (2-chlorophenyl)(morpholino)methanone (338 mg, 1.5 mmol), XPhos palladium(II) biphenyl preformed catalyst (5.89 mg, 7.5 μmol), XPhos (7.14 mg, 15 μmol), KOAc (441 mg, 4.5 mmol), and $\text{B}_2(\text{OH})_4$ (405 mg, 4.5 mmol), was heated to 80 °C in EtOH (15 mL) for 4 h. The title compound was obtained as an inseparable mixture of the trifluoroborate and the protodeboronated product. As a result, reasonable spectra for this compound could not be obtained.



Potassium 3-Trifluoroborato-benzoic acid (Table 1, entry 8).²

Following general procedure A, a mixture of 3-chlorobenzoic acid (235 mg, 1.5 mmol), XPhos palladium(II) biphenyl preformed catalyst (5.89 mg, 7.5 μmol), XPhos (7.14 mg, 15 μmol), KOAc (441 mg, 4.5 mmol), and $\text{B}_2(\text{OH})_4$ (405 mg, 4.5 mmol), was heated to 80 °C in EtOH (15 mL) for 5 h. After the standard workup (using sat. aq NH_4Cl solution instead of H_2O during the aqueous workup), the crude boronic ester was converted to the potassium trifluoroborate salt. The title compound was obtained as a white solid in 44%

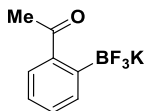
yield (150 mg). mp = 192 °C dec. ^1H NMR (500 MHz, acetone- d_6) δ 8.24 (s, 1H), 7.76 (d, $J = 7.7$ Hz, 1H), 7.70 (d, $J = 7.2$ Hz, 1H), 7.21 (t, $J = 7.5$ Hz, 1H). ^{13}C NMR (125.8 MHz, DMSO- d_6) δ 168.8, 135.9, 132.6, 128.7, 126.3. ^{11}B NMR (128.4 MHz, DMSO- d_6) δ 3.1. ^{19}F NMR (282 MHz, DMSO- d_6) δ -139.6. IR (dry film): 3047, 3000 (OH, br), 1686, 1316, 1278, 1208, 992, 949, 908, 820, 748, 715 cm^{-1} . HRMS (ES-) calcd. for $\text{C}_7\text{H}_5\text{BF}_3\text{O}_2$ (M-K) 189.0335, found 189.0341.



Potassium 4-Aminophenyl-trifluoroborate (Table 1, entry 9). Following

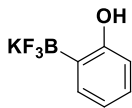
general procedure A, a mixture of 4-chloroaniline (214 mg, 1.5 mmol), XPhos palladium(II) biphenyl preformed catalyst (5.89 mg, 7.5 μmol), XPhos (7.14 mg, 15 μmol), KOAc (441 mg, 4.5 mmol), and $\text{B}_2(\text{OH})_4$ (405 mg, 4.5 mmol), was heated to 80 °C in EtOH (15 mL) for 1 h. After the standard workup (using sat. aq NaHCO_3 solution instead of H_2O during the aqueous workup), the crude boronic acid was converted to the potassium trifluoroborate salt. After the standard purification, the trifluoroborate was taken up in 10 mL MeCN (10 mL), and K_2CO_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, 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 the minimal amount of acetone (3 mL), and Et_2O (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 68% yield (204 mg). mp = 210 °C dec. ^1H NMR (500 MHz, DMSO- d_6) δ 6.98 (d, $J = 7.6$ Hz, 2H), 6.35 (d, $J = 7.6$ Hz, 2H), 4.41 (s, 2H). ^{13}C NMR (125.8 MHz, DMSO- d_6) δ 145.7, 131.9, 113.1. ^{11}B NMR (128.4 MHz, acetone- d_6) δ 3.6 (q, $J = 49.7$ Hz). ^{19}F NMR (282 MHz, DMSO- d_6) δ -137.7. IR (dry film): 3432, 3395, 3314, 3209, 3014,

1607, 1512, 1498, 1413, 1214, 966, 915, 828 cm^{-1} . HRMS (ES-) calcd. for $\text{C}_6\text{H}_6\text{BF}_3\text{N}$ (M-K) 160.0545, found 160.0552.



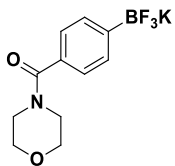
Potassium 2-Acetylphenyl-trifluoroborate (Table 1, entry 10).³ Following

general procedure A, a mixture of 2-chloroacetophenone (232 mg, 200 μL , 1.5 mmol), XPhos palladium(II) biphenyl preformed catalyst (5.89 mg, 7.5 μmol), XPhos (7.14 mg, 15 μmol), KOAc (441 mg, 4.5 mmol), and $\text{B}_2(\text{OH})_4$ (405 mg, 4.5 mmol), was heated to 80 $^\circ\text{C}$ in MeOH (15 mL) for 2 h. The title compound was obtained as a white solid in 15% yield (51 mg) as a 2:5 mixture of alcohol to ketone. Spectral data were in accordance with those published. Reasonable spectra for mixture of products could not be obtained.



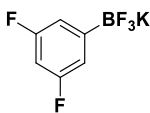
2-Hydroxyphenyltrifluoroborate (Table 1, entry 11).⁴ Following general

procedure A, a mixture of 2-chlorophenol (193 mg, 155 μL , 1.5 mmol), XPhos palladium(II) biphenyl preformed catalyst (5.89 mg, 7.5 μmol), XPhos (7.14 mg, 15 μmol), KOAc (441 mg, 4.5 mmol), and $\text{B}_2(\text{OH})_4$ (405 mg, 4.5 mmol), was heated to 80 $^\circ\text{C}$ in EtOH (15 mL) for 1.5 h. The title compound was obtained as a white solid in 17% yield (50 mg). Spectral data were in accordance with those of published results. mp = 195 $^\circ\text{C}$ dec. ^1H NMR (500 MHz, acetone- d_6) δ 7.50 (dd, J = 11.3 Hz, 1H), 7.28 (s, 1H), 6.88 (t, J = 7.4 Hz, 1H), 6.58 (t, J = 7.1 Hz, 1H), 6.50 (d, J = 7.9 Hz, 1H). ^{13}C NMR (125.8 MHz, DMSO- d_6) δ 159.9, 133.5, 127.5, 118.9, 113.8.



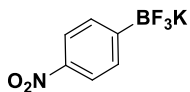
Potassium 4-(Morpholine-4-carbonyl)phenyl-trifluoroborate (Table 1,

entry 12).⁵ Following general procedure A, a mixture of (4-chlorophenyl)(morpholino)methanone (340 mg, 1.5 mmol), XPhos palladium(II) biphenyl preformed catalyst (5.89 mg, 7.5 μ mol), XPhos (7.14 mg, 15 μ mol), KOAc (441 mg, 4.5 mmol), and bis-boronic acid (405 mg, 4.5 mmol), was heated to 80 °C in EtOH (15 mL) for 1.5 h. The title compound was obtained as a white solid in 81% yield (362 mg). Spectral data were in accordance with those published. mp > 225 °C. ¹H NMR (500 MHz, DMSO-*d*₆) δ 7.39 (d, *J* = 7.8 Hz, 2H), 7.14 (d, *J* = 7.6 Hz, 2H), 3.58 (s, 8H). ¹³C NMR (125.8 MHz, DMSO-*d*₆) δ 170.4, 132.1, 131.1, 125.2, 66.2.



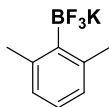
Potassium 3,5-Difluorophenyl-trifluoroborate (Table 1, entry 13).⁶

Following general procedure A, a mixture of 1-chloro-3,5-difluorobenzene (223 mg, 168 mL, 1.5 mmol), XPhos palladium(II) biphenyl preformed catalyst (5.89 mg, 7.5 μ mol), XPhos (7.14 mg, 15 μ mol), KOAc (441 mg, 4.5 mmol), and B₂(OH)₄ (405 mg, 4.5 mmol), was heated to 80 °C in EtOH (15 mL) for 1 h. The title compound was obtained as a white solid in 77% yield (256 mg). Spectral data were in accordance with those published. mp > 225 °C. ¹H NMR (500 MHz, DMSO-*d*₆) δ 6.84 (d, *J* = 7.4 Hz, 2H), 6.76 – 6.73 (m, 1H). ¹³C NMR (125.8 MHz, DMSO-*d*₆) δ 161.9 (d, *J* = 245.5 Hz), 112.9 (d, *J* = 15.8 Hz), 100.0 (t, *J* = 25.8 Hz).



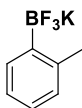
Potassium (4-Nitrophenyl)trifluoroborate (Table 1, entry 14).¹

Following general procedure A, a mixture of 1-chloro-4-nitrobenzene (236 mg, 1.5 mmol), XPhos palladium(II) biphenyl preformed catalyst (5.89 mg, 7.5 μ mol), XPhos (7.14 mg, 15 μ mol), KOAc (441 mg, 4.5 mmol), and B₂(OH)₄ (405 mg, 4.5 mmol), was heated to 80 °C in EtOH (15 mL) for 2 h. The title compound was obtained as a light reddish-brown solid in 64% yield (220 mg). Spectral data were in accordance with those of published results. mp > 225 °C. ¹H NMR (500 MHz, acetone-*d*₆) δ 8.00 (d, *J* = 8.1 Hz, 2H), 7.71 (d, *J* = 8.0 Hz, 2H). ¹³C NMR (125.8 MHz, DMSO-*d*₆) δ 146.3, 132.6, 121.7.



Potassium (2,6-Dimethylphenyl)trifluoroborate (Table 1, entry 15).¹

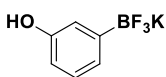
Following general procedure A, a mixture of 2-chloro-1,3-dimethylbenzene (211 mg, 1.5 mmol), XPhos palladium(II) biphenyl preformed catalyst (5.89 mg, 7.5 μ mol), XPhos (7.14 mg, 15 μ mol), KOAc (441 mg, 4.5 mmol), and B₂(OH)₄ (405 mg, 4.5 mmol), was heated to 80 °C in EtOH (15 mL) for 4.5 h. The title compound was obtained as a white solid in 53% yield (167 mg). Spectral data were in accordance with those of published results. mp > 225 °C. ¹H NMR (500 MHz, acetone-*d*₆) δ 6.82 – 6.77 (m, 1H), 6.72 (d, *J* = 7.3 Hz, 2H), 2.41 (s, 6H). ¹³C NMR (125.8 MHz, DMSO-*d*₆) δ 141.4, 126.9, 124.9, 23.8 (d, *J* = 2.52 Hz).



Potassium *o*-Tolyltrifluoroborate (Table 1, entry 16).¹

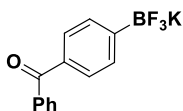
Following general procedure A, a mixture of 1-chloro-2-methylbenzene (190 mg, 176 μ L, 1.5 mmol), XPhos palladium(II) biphenyl preformed catalyst (5.89 mg, 7.5 μ mol), XPhos (7.14 mg,

15 μmol), KOAc (441 mg, 4.5 mmol), and $\text{B}_2(\text{OH})_4$ (405 mg, 4.5 mmol), was heated to 80 $^\circ\text{C}$ in EtOH (15 mL) for 3.5 h. After the standard workup (using sat. aq. NaHCO_3 solution instead of H_2O during the aqueous workup), the title compound was obtained as a white solid in 95% yield (281 mg). Spectral data were in accordance with those of published results. mp = 210 $^\circ\text{C}$ dec. ^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ 7.29 (s, 1H), 6.96 – 6.79 (m, 3H), 2.26 (s, 3H). ^{13}C NMR (125.8 MHz, $\text{DMSO-}d_6$) δ 140.9, 132.0 (d, J = 2.52 Hz), 128.6, 125.5, 123.8, 22.1.



Potassium (3-Hydroxyphenyl)trifluoroborate (Table 1, entry 18).⁴

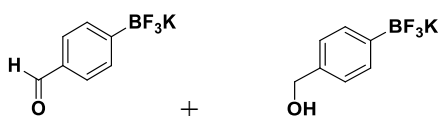
Following general procedure A, a mixture of 3-chlorophenol (193 mg, 160 μL , 1.5 mmol), XPhos palladium(II) biphenyl preformed catalyst (5.89 mg, 7.5 μmol), XPhos (7.14 mg, 15 μmol), KOAc (441 mg, 4.5 mmol), and $\text{B}_2(\text{OH})_4$ (405 mg, 4.5 mmol), was heated to 80 $^\circ\text{C}$ in EtOH (15 mL) for 2.5 h. The title compound was obtained as a white solid in 98% yield (294 mg). Spectral data were in accordance with those published. mp = 185 $^\circ\text{C}$ dec. ^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ 8.54 (s, 1H), 6.89 (t, J = 7.4 Hz, 1H), 6.81 – 6.75 (m, 2H), 6.43 (d, J = 7.7 Hz, 1H). ^{13}C NMR (125.8 MHz, $\text{DMSO-}d_6$) δ 155.8, 127.1, 122.3, 118.4, 111.9.



Potassium 4-Benzoylphenyl-trifluoroborate (Table 1, entry 19).¹

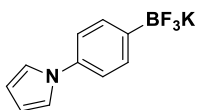
Following general procedure A, a mixture of 4-chlorobenzophenone (325 mg, 1.5 mmol), XPhos palladium(II) biphenyl preformed catalyst (5.89 mg, 7.5 μmol), XPhos (7.14 mg, 15 μmol), KOAc (441 mg, 4.5 mmol), and $\text{B}_2(\text{OH})_4$ (405 mg, 4.5 mmol), was heated to

80 °C in MeOH (15 mL) for 1.25 h. The title compound was obtained as a white solid in 91% yield (395 mg) as a 1:23 mixture of alcohol to ketone. Spectral data were in accordance with those published. mp = 220 °C dec. ¹H NMR (500 MHz, acetone-*d*₆) δ 7.75 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.65 (d, *J* = 8.1 Hz, 2H), 7.65 – 7.57 (m, 1H), 7.58 (d, *J* = 7.8 Hz, 2H), 7.52 (t, *J* = 7.6 Hz, 2H). ¹³C NMR (125.8 MHz, acetone-*d*₆) δ 197.3, 139.6, 135.6, 132.6, 132.3, 130.4, 128.9.



Potassium 4-Formylphenyl-trifluoroborate and

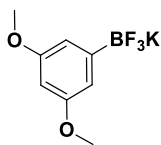
Potassium 4-(Hydroxymethyl)phenyl-trifluoroborate (Table 1, entry 20).¹ Following general procedure A, a mixture of 4-chlorobenzaldehyde (21 mg, 1.5 mmol), XPhos palladium(II) biphenyl preformed catalyst (5.89 mg, 7.5 μmol), XPhos (7.14 mg, 15 μmol), KOAc (441 mg, 4.5 mmol), and B₂(OH)₄ (405 mg, 4.5 mmol), was heated to 80 °C in MeOH (15 mL) for 20 h. The title compounds were obtained as a white solid in 80% yield (238 mg) as a 1:2 mixture of aldehyde to alcohol.



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

21).¹ Following general procedure A, a mixture of 1-(4-chlorophenyl)-1H-pyrrole (267 mg, 1.5 mmol), XPhos palladium(II) biphenyl preformed catalyst (5.89 mg, 7.5 μmol), XPhos (7.14 mg, 15 μmol), KOAc (441 mg, 4.5 mmol), and B₂(OH)₄ (405 mg, 4.5 mmol), was heated to 80 °C in EtOH (15 mL) for 1 h. The title compound was obtained as a white solid in 86% yield (320 mg). Spectral data were in accordance with those published. mp > 225 °C. ¹H NMR (500 MHz, acetone-*d*₆) δ 7.67 (d, *J* = 7.4 Hz, 2H), 7.49

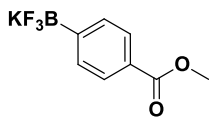
(d, $J = 7.6$ Hz, 2H), 7.39 (t, $J = 7.5$ Hz, 2H), 7.22 (t, $J = 7.5$ Hz, 2H). ^{13}C NMR (125.8 MHz, acetone- d_6) δ 139.4, 133.6, 119.6, 119.0, 110.3.



Potassium 3,5-Dimethoxyphenyl-trifluoroborate (Table 1, entry 22).¹

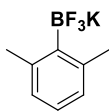
Following general procedure A, a mixture of 3,5-dimethoxychlorobenzene (259 mg, 1.5 mmol), XPhos palladium(II) biphenyl preformed catalyst (5.89 mg, 7.5 μmol), XPhos (7.14 mg, 15 μmol), KOAc (441 mg, 4.5 mmol), and $\text{B}_2(\text{OH})_4$ (405 mg, 4.5 mmol), was heated to 80 $^\circ\text{C}$ in EtOH (15 mL) for 2 h. The title compound was obtained as a white solid in 99% yield (367 mg). Spectral data were in accordance with those published. mp = 236 $^\circ\text{C}$ dec. ^1H NMR (500 MHz, acetone- d_6) δ 6.66 (d, $J = 2.5$ Hz, 2H), 6.19 (t, $J = 2.0$ Hz, 1H), 3.68 (s, 6H). ^{13}C NMR (125.8 Hz, acetone- d_6) δ 159.9, 109.1, 98.1, 54.3.

General Procedure A with Aryl Bromides:



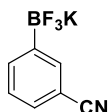
Potassium (4-(Methoxycarbonyl)phenyl)trifluoroborate (Table 2,

entry 1). Following general procedure A, a mixture of methyl 4-bromobenzoate (322 mg, 1.5 mmol), XPhos palladium(II) biphenyl preformed catalyst (5.89 mg, 7.5 μmol), XPhos (7.14 mg, 15 μmol), KOAc (441 mg, 4.5 mmol), and $\text{B}_2(\text{OH})_4$ (405 mg, 4.5 mmol), was heated to 80 $^\circ\text{C}$ in EtOH (15 mL) for 3 h. The title compound was obtained as a white solid in 93% yield (337 mg). Spectral data were in accordance with those of a commercially available sample. mp > 225 $^\circ\text{C}$. ^1H NMR (500 MHz, acetone- d_6) δ 7.76 (d, $J = 7.4$ Hz, 2H), 7.58 (d, $J = 7.3$ Hz, 2H), 3.81 (s, 3H). ^{13}C NMR (125.8 MHz, DMSO- d_6) δ 167.7, 132.0, 127.8, 127.0, 52.2.

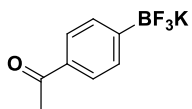


Potassium (2,6-Dimethylphenyl)trifluoroborate (Table 2, entry 2).¹

Following general procedure A, a mixture of 2-bromo-1,3-dimethylbenzene (277.6 mg, 200 μ L, 1.5 mmol), XPhos palladium(II) biphenyl preformed catalyst (5.89 mg, 7.5 μ mol), XPhos (7.14 mg, 15 μ mol), KOAc (441 mg, 4.5 mmol), and B₂(OH)₄ (405 mg, 4.5 mmol), was heated to 80 °C in EtOH (15 mL) for 5 h. The title compound was obtained as a white solid in 42% yield (132 mg). Spectral data were in accordance with those of published results. mp > 225 °C. ¹H NMR (500 MHz, acetone-*d*₆) δ 6.80 – 6.74 (m, 1H), 6.70 (d, *J* = 7.2 Hz, 2H), 2.36 (s, 6H). ¹³C NMR (125.8 MHz, acetone-*d*₆) δ 141.6, 126.8, 124.9, 22.9 (d, *J* = 2.52 Hz).

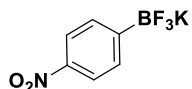


Potassium (3-Cyanophenyl)trifluoroborate (Table 2, entry 3). Following general procedure A, a mixture of 3-bromobenzonitrile (273 mg, 1.5 mmol), XPhos palladium(II) biphenyl preformed catalyst (5.89 mg, 7.5 μ mol), XPhos (7.14 mg, 15 μ mol), KOAc (441 mg, 4.5 mmol), and B₂(OH)₄ (405 mg, 4.5 mmol), was heated to 80 °C in EtOH (15 mL) for 5 h. The title compound was obtained as a white solid in 94% yield (296 mg). Spectral data were in accordance with those of a commercially available sample. mp = 175 °C dec. ¹H NMR (500 MHz, acetone-*d*₆) δ 7.75 (s, 2H), 7.41 (d, *J* = 7.5 Hz, 1H), 7.28 (t, *J* = 7.6 Hz, 1H). ¹³C NMR (125.8 MHz, acetone-*d*₆) δ 136.3, 135.3, 128.8, 127.3, 120.3, 110.2.



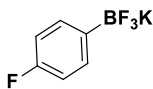
Potassium (4-Acetylphenyl)trifluoroborate (Table 2, entry 4).⁷

Following general procedure A, a mixture of 1-(4-bromophenyl)ethanone (298.5 mg, 1.5 mmol), XPhos palladium(II) biphenyl preformed catalyst (5.89 mg, 7.5 μ mol), XPhos (7.14 mg, 15 μ mol), KOAc (441 mg, 4.5 mmol), and B₂(OH)₄ (405 mg, 4.5 mmol), was heated to 80 °C in EtOH (15 mL) for 2 h. The title compound was obtained as a white solid in 95% yield (323 mg) as a mixture of the ketone (86%) and palladium-hydride reduced (alcohol) product (9%). mp > 225 °C. ¹H NMR (500 MHz, acetone-*d*₆) δ 7.73 (d, *J* = 7.6 Hz, 2H), 7.58 (d, *J* = 7.5 Hz, 2H), 2.49 (s, 3H). ¹³C NMR (125.8 MHz, DMSO-*d*₆) δ 198.8, 134.9, 132.0, 126.9, 27.1.



Potassium (4-Nitrophenyl)trifluoroborate (Table 2, entry 5).¹

Following general procedure A, a mixture of 1-bromo-4-nitrobenzene (303 mg, 1.5 mmol), XPhos palladium(II) biphenyl preformed catalyst (5.89 mg, 7.5 μ mol), XPhos (7.14 mg, 15 μ mol), KOAc (441 mg, 4.5 mmol), and B₂(OH)₄ (405 mg, 4.5 mmol), was heated to 80 °C in EtOH (15 mL) for 4 h. The title compound was obtained as a light reddish-brown solid in 65% yield (220 mg) as a mixture of the nitro (45%) and palladium-hydride reduced (aniline) product (20%). Spectral data were in accordance with those of published results. mp > 225 °C. ¹H NMR (500 MHz, acetone-*d*₆) δ 7.97 (d, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 7.7 Hz, 2H). ¹³C NMR (125.8 MHz, DMSO-*d*₆) δ 146.4, 132.7, 121.8.



Potassium (4-Fluorophenyl)trifluoroborate (Table 2, entry 6).¹

Following general procedure A, a mixture of 1-bromo-4-fluorobenzene (262 mg, 165 μ L, 1.5 mmol

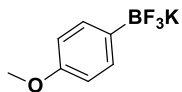
XPhos palladium(II) biphenyl preformed catalyst (5.89 mg, 7.5 μmol), XPhos (7.14 mg, 15 μmol), KOAc (441 mg, 4.5 mmol), and $\text{B}_2(\text{OH})_4$ (405 mg, 4.5 mmol), was heated to 80 $^\circ\text{C}$ in EtOH (15 mL) for 4 h. The title compound was obtained as a white solid in 95% yield (288 mg). Spectral data were in accordance with those of published results. mp = 210 $^\circ\text{C}$ dec. ^1H NMR (500 MHz, acetone- d_6) δ 7.45 (t, J = 7.2 Hz, 2H), 6.81 (t, J = 9.0 Hz, 2H). ^{13}C NMR (125.8 MHz, DMSO- d_6) δ 162.4, 160.6, 133.4 (d, J = 6.3 Hz), 113.26 (d, J = 17.6 Hz).



Potassium 3-Formylphenyl-trifluoroborate (Table 2, entry 7).⁸ Following

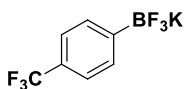
general procedure A, a mixture of 2-(3-bromophenyl)-1,3-dioxolane (344 mg, 130 mL, 1.5 mmol), XPhos palladium(II) biphenyl preformed catalyst (5.89 mg, 7.5 μmol), XPhos (7.14 mg, 15 μmol), KOAc (441 mg, 4.5 mmol), and $\text{B}_2(\text{OH})_4$ (405 mg, 4.5 mmol), was heated to 80 $^\circ\text{C}$ in MeOH (15 mL) for 2.5 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 (MgSO_4), filtered, and concentrated in vacuo. The crude mixture was then converted to the potassium trifluoroborate salt. The title compound was obtained as a white solid in 87% yield (277 mg). Spectral data were in accordance with those published. mp = 179 $^\circ\text{C}$ dec. ^1H NMR (500 MHz, DMSO- d_6) δ 9.93 (s, 1H), 7.87 (s, 1H), 7.65 (d, J = 7.2 Hz, 1H), 7.58 (d, J = 7.6 Hz, 1H), 7.32 (t, J = 7.4 Hz, 1H). ^{13}C NMR (125.8 MHz, DMSO- d_6) δ 194.9, 138.5, 135.3, 133.9, 127.7, 126.8. ^{11}B NMR (128.4 MHz, DMSO- d_6) δ 3.1. ^{19}F NMR (282 MHz, DMSO- d_6) δ -139.7. IR (dry film): 3058, 3030, 2819, 2726, 1712, 1594, 1246, 1151,

1005, 978, 962 cm^{-1} . HRMS (ES-) calcd. for $\text{C}_7\text{H}_5\text{BF}_3\text{O}$ (M-K) 173.0386, found 173.0381.



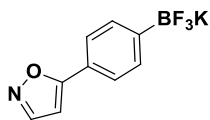
Potassium 4-Methoxyphenyl-trifluoroborate (Table 2, entry 8).¹

Following general procedure A, a mixture of 4-bromoanisole (214 mg, 182 μL , 1.5 mmol), XPhos palladium(II) biphenyl preformed catalyst (5.89 mg, 7.5 μmol), XPhos (7.14 mg, 15 μmol), KOAc (441 mg, 4.5 mmol), and $\text{B}_2(\text{OH})_4$ (405 mg, 4.5 mmol), was heated to 80 $^\circ\text{C}$ in EtOH (15 mL) for 4 h. The title compound was obtained as a white solid in 94% yield (289 mg). Spectral data were in accordance with those of published results. mp > 225 $^\circ\text{C}$. ^1H NMR (500 MHz, acetone- d_6) δ 7.37 (d, J = 8.1 Hz, 2H), 6.67 (d, J = 8.1 Hz, 2H), 3.69 (s, 3H). ^{13}C NMR (125.8 MHz, acetone- d_6) δ 158.0, 132.7, 111.9, 54.2.



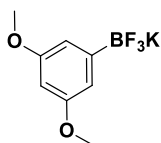
Potassium (4-(Trifluoromethyl)phenyl)trifluoroborate (Table 2, entry 9).¹

Following general procedure A, a mixture of 1-bromo-4-(trifluoromethyl)benzene (337 mg, 210 μL , 1.5 mmol), XPhos palladium(II) biphenyl preformed catalyst (5.89 mg, 7.5 μmol), XPhos (7.14 mg, 15 μmol), KOAc (441 mg, 4.5 mmol), and $\text{B}_2(\text{OH})_4$ (405 mg, 4.5 mmol), was heated to 80 $^\circ\text{C}$ in EtOH (15 mL) for 3 h. The title compound was obtained as an off-white solid in 88% yield (332 mg). Spectral data were in accordance with those of published results. mp > 225 $^\circ\text{C}$. ^1H NMR (500 MHz, acetone- d_6) δ 7.64 (d, J = 7.6 Hz, 2H), 7.39 (d, J = 7.8 Hz, 2H). ^{13}C NMR (125.8 MHz, acetone- d_6) δ 132.1, 127.1, 126.9, 126.6, 124.4, 122.8.



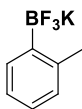
(4-(Isoxazol-5-yl)phenyl)trifluoroborate (Table 2, entry 10).

Following general procedure A, a mixture of 5-(4-bromophenyl)isoxazole (336 mg, 1.5 mmol), CatacxiumA palladium(II) biphenyl preformed catalyst (50 mg, 75 μ mol), DIEA (581 mg, 785 μ L, 4.5 mmol), and $B_2(OH)_4$ (405 mg, 4.5 mmol), was heated to 50 $^{\circ}C$ in MeOH (7.5 mL) for 4 h. After the standard workup (using sat. aq $NaHCO_3$ solution instead of H_2O during the aqueous workup), the title compound was obtained as a yellow solid in 85% yield (298 mg). mp > 225 $^{\circ}C$. 1H NMR (500 MHz, acetone- d_6) δ 8.36 (s, 1H), 7.61 (s, 4H), 6.66 (s, 1H). ^{13}C NMR (125.8 MHz, DMSO- d_6) δ 170.3, 152.1, 132.6, 124.3, 98.9. ^{19}F NMR (282 MHz, DMSO- d_6) δ -143.1. ^{11}B NMR (128.4 MHz, Acetone- d_6) δ 3.3. IR (dry film): 1468, 1213. HRMS (ES-) calcd. for $C_9H_6BF_3NO$: 212.0463 (M-K), found 212.0495.



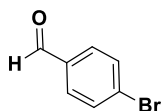
Potassium (3,5-Dimethoxyphenyl)trifluoroborate (Table 2, entry 11).¹

Following general procedure A, a mixture of 1-bromo-3,5-dimethoxybenzene (326 mg, 1.5 mmol), XPhos palladium(II) biphenyl preformed catalyst (5.89 mg, 7.5 μ mol), XPhos (7.14 mg, 15 μ mol), KOAc (441 mg, 4.5 mmol), and $B_2(OH)_4$ (405 mg, 4.5 mmol), was heated to 80 $^{\circ}C$ in EtOH (15 mL) for 4 h. The title compound was obtained as an off-white solid in 98% yield (375 mg). Spectral data were in accordance with those of published results. mp > 225 $^{\circ}C$. 1H NMR (500 MHz, acetone- d_6) δ 6.66 (s, 2H), 6.16 (t, J = 2.3 Hz, 1H), 3.68 (s, 6H). ^{13}C NMR (125.8 MHz, acetone- d_6) δ 159.9, 109.1, 97.9, 54.3.



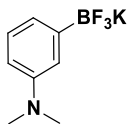
Potassium o-Tolyltrifluoroborate (Table 2, entry 12).¹

Following general procedure A, a mixture of 1-bromo-2-methylbenzene (256 mg, 1.5 mmol), XPhos palladium(II) biphenyl preformed catalyst (5.89 mg, 7.5 μ mol), XPhos (7.14 mg, 15 μ mol), KOAc (441 mg, 4.5 mmol), and B₂(OH)₄ (405 mg, 4.5 mmol), was heated to 80 °C in EtOH (15 mL) for 9 h. The title compound was obtained as an off-white solid in 80% yield (239 mg). Spectral data were in accordance with those of published results. mp = 215 °C dec. ¹H NMR (500 MHz, acetone-*d*₆) δ 7.46 (d, *J* = 6.7 Hz, 1H), 6.95 – 6.81 (m, 3H), 2.38 (s, 3H). ¹³C NMR (125.8 MHz, acetone-*d*₆) δ 141.1, 132.1, 128.3, 125.2, 123.4, 21.4.



Potassium (4-Formylphenyl)trifluoroborate (Table 2, entry 13).¹

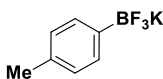
Following general procedure A, a mixture of 4-bromobenzaldehyde (277 mg, 1.5 mmol), XPhos palladium(II) biphenyl preformed catalyst (5.89 mg, 7.5 μ mol), XPhos (7.14 mg, 15 μ mol), KOAc (441 mg, 4.5 mmol), and B₂(OH)₄ (405 mg, 4.5 mmol), was heated to 80 °C in MeOH (15 mL) for 4 h. The title compound was obtained as a white solid in 75% yield (240 mg) as a mixture of the aldehyde (45%) and palladium-hydride reduced (alcohol) product (30%). A reasonable spectra could not be obtained.



(3-(Dimethylamino)phenyl)trifluoroborate (Table 2, entry 14).

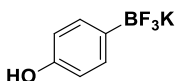
Following general procedure A, a mixture of 4-bromobenzaldehyde (277 mg, 1.5 mmol), XPhos palladium(II) biphenyl preformed catalyst (5.89 mg, 7.5 μ mol), XPhos (7.14 mg, 15 μ mol), KOAc (441 mg, 4.5 mmol), and B₂(OH)₄ (405 mg, 4.5 mmol), was heated to 80

°C in EtOH (15 mL) for 4 h. After the standard workup (using sat. aq NaHCO₃ solution instead of H₂O during the aqueous workup), the title compound was obtained as a pale pink solid in 94% yield (320 mg). mp 185–187 °C. ¹H NMR (500 MHz, acetone-*d*₆) δ 6.99 (s, 1H), 6.95 (t, *J* = 7.6 Hz, 1H), 6.87 (d, *J* = 7.0 Hz, 1H), 6.52 – 6.47 (m, 1H), 2.83 (s, 6H). ¹³C NMR (125.8 MHz, acetone-*d*₆) δ 150.0, 126.9, 121.4, 121.4, 117.2, 117.2, 110.9, 40.6. ¹⁹F NMR (282 MHz, acetone-*d*₆) δ -142.2. ¹¹B NMR (128.4 MHz, acetone-*d*₆) δ 4.1. IR (dry film): 1597, 1217. HRMS (ES-) calcd. for C₈H₁₀BF₃N: 188.0888 (M-K), found 188.0876.



Potassium *p*-Tolyl-trifluoroborate (Table 2, entry 15).⁸

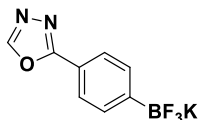
Following general procedure A, a mixture of 4-bromotoluene (257 mg, 1.5 mmol), XPhos palladium(II) biphenyl preformed catalyst (5.89 mg, 7.5 μmol), XPhos (7.14 mg, 15 μmol), KOAc (441 mg, 4.5 mmol), and B₂(OH)₄ (405 mg, 4.5 mmol), was heated to 80 °C in EtOH (15 mL) for 2.5 h. The title compound was obtained as a white solid in 90% yield (268 mg). Spectral data were in accordance with those published. mp > 225 °C. ¹H NMR (500 MHz, acetone-*d*₆) δ 7.35 (d, *J* = 7.4 Hz, 2H), 6.91 (d, *J* = 7.4 Hz, 2H), 2.21 (s, 3H). ¹³C NMR (125.8 MHz, DMSO-*d*₆) δ 133.82, 131.96, 127.53, 21.61.



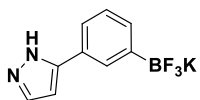
Potassium 4-hydroxyphenyl-trifluoroborate (Table 2, entry 17).⁴

Following general procedure A, a mixture of 4-bromophenol (260 mg, 1.5 mmol), XPhos palladium(II) biphenyl preformed catalyst (5.89 mg, 7.5 μmol), XPhos (7.14 mg, 15 μmol), KOAc (441 mg, 4.5 mmol), and B₂(OH)₄ (405 mg, 4.5 mmol), was heated to 80 °C in EtOH (15 mL) for 2 h. After the standard workup (using sat. aq NaHCO₃ solution instead of H₂O during the aqueous workup), the crude boronic acid was converted to the

potassium trifluoroborate salt. The title compound was obtained as a white solid in 98% yield (295 mg). Spectral data were in accordance with those published. mp > 225 °C. ¹H NMR (500 MHz, DMSO-*d*₆) δ 8.55 (s, 1H), 7.09 (d, *J* = 8.0 Hz, 2H), 6.49 (d, *J* = 7.8 Hz, 2H). ¹³C NMR (125.8 MHz, DMSO-*d*₆) δ 154.9, 132.3, 113.4.

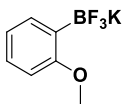


Potassium 4-(1,3,4-Oxadiazol-2-yl)phenyl-trifluoroborate (Table 2, entry 18). Following general procedure A, a mixture of 2-(4-bromophenyl)-1,3,4-oxadiazole (338 mg, 1.5 mmol), XPhos palladium(II) biphenyl preformed catalyst (5.89 mg, 7.5 μmol), XPhos (7.14 mg, 15 μmol), KOAc (441 mg, 4.5 mmol), and B₂(OH)₄ (405 mg, 4.5 mmol), was heated to 80 °C in EtOH (15 mL) for 1.5 h. After the standard workup (using sat. aq NaHCO₃ solution instead of H₂O during the aqueous workup), the crude boronic acid was converted to the potassium trifluoroborate salt. The title compound was obtained as a white solid in 34% yield (130 mg). mp = 230 °C dec. ¹H NMR (500 MHz, DMSO-*d*₆) δ 9.24 (s, 1H), 7.78 (d, *J* = 7.7 Hz, 2H), 7.54 (d, *J* = 8.0 Hz, 2H). ¹³C NMR (125.8 MHz, DMSO-*d*₆) δ 164.6, 153.9, 132.1, 124.7, 120.0. ¹¹B NMR (128.4 MHz, DMSO-*d*₆) δ 3.8–3.4 (m). ¹⁹F NMR (282 MHz, DMSO-*d*₆) δ -143.6. IR (dry film): 3594, 3347, 3140, 3047, 2365, 2333, 1652, 1520, 1213, 1068, 958, 842, 746, 639 cm⁻¹.



Potassium 3-(1H-Pyrazol-5-yl)phenyl-trifluoroborate (Table 2, entry 19). Following general procedure A, a mixture of 5-(3-bromophenyl)-1H-pyrazole (335 mg, 1.5 mmol), XPhos palladium(II) biphenyl preformed catalyst (5.89 mg, 7.5 μmol), XPhos (7.14 mg, 15 μmol), KOAc (441 mg, 4.5 mmol), and B₂(OH)₄ (405 mg, 4.5

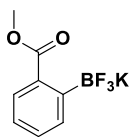
mmol), was heated to 80 °C in EtOH (15 mL) for 2.5 h. After the standard workup (using sat. aq NaHCO₃ solution instead of H₂O during the aqueous workup), the crude boronic acid was converted to the potassium trifluoroborate salt. After the standard purification, the trifluoroborate was taken up in CH₃CN (10 mL), and K₂CO₃ (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, 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 the minimal amount of acetone (3 mL), and Et₂O (15 mL) was added to obtain an off white precipitate that was filtered and dried *in vacuo*. The title compound was obtained as a white solid in 79% yield (297 mg). mp = 191 °C dec. ¹H NMR (500 MHz, DMSO-*d*₆) δ 12.89 (d, *J* = 149.0 Hz, 1H), 7.76 (s, 1H), 7.60 (s, 1H), 7.47 (d, *J* = 6.5 Hz, 1H), 7.30 (d, *J* = 7.0 Hz, 1H), 7.15 (t, *J* = 7.3 Hz, 1H), 6.59 – 6.48 (d, *J* = 5 Hz, 1H). ¹³C NMR (125.8 MHz, DMSO-*d*₆) δ 131.0, 128.6, 126.7, 122.3, 101.3. ¹¹B NMR (128.4 MHz, DMSO-*d*₆) δ 3.5. ¹⁹F NMR (282 MHz, DMSO-*d*₆) δ -138.9. IR (dry film): 3598, 3394, 3051, 1664, 1522, 1397, 1348, 1225, 1212, 995, 958, 895, 798, 744, 701, 681 cm⁻¹. HRMS (ES-) calcd. for C₉H₇BF₃N₂ (M-K) 211.0654, found 211.0663.



Potassium 2-methoxyphenyl-trifluoroborate (Table 2, entry 20).⁹

Following general procedure A, a mixture of 2-bromoanisole (323 mg, 188 μL, 1.5 mmol), XPhos palladium(II) biphenyl preformed catalyst (5.89 mg, 7.5 μmol), XPhos (7.14 mg, 15 μmol), KOAc (441 mg, 4.5 mmol), and B₂(OH)₄ (405 mg, 4.5 mmol), was heated to 80 °C in EtOH (15 mL) for 1.5 h. The title compound was obtained as a white solid in 86% yield (276 mg). Spectral data were in accordance with those published. mp

> 225 °C. ¹H NMR (500 MHz, DMSO-*d*₆) δ 7.29 (dd, *J* = 7.0, 1.7 Hz, 1H), 7.03 – 7.01 (m, 1H), 6.74 – 6.65 (m, 2H), 3.62 (s, 3H). ¹³C NMR (125.8 MHz, DMSO-*d*₆) δ 162.5, 133.2, 126.6, 119.2, 109.6, 54.7.



Potassium 2-Methoxycarbonylphenyl-trifluoroborate (Table 2, entry

21).¹ Following general procedure A, a mixture of methyl-2-chlorobenzoate (323 mg, 215 μL, 1.5 mmol), XPhos palladium(II) biphenyl preformed catalyst (5.89 mg, 7.5 μmol), XPhos (7.14 mg, 15 μmol), KOAc (441 mg, 4.5 mmol), and B₂(OH)₄ (405 mg, 4.5 mmol), was heated to 80 °C in MeOH (15 mL) for 6 h. The title compound was obtained as a white solid in 64% yield (234 mg). Spectral data were in accordance with those published. mp = 240 °C dec. ¹H NMR (500 MHz, DMSO-*d*₆) δ 7.48 (d, *J* = 7.1 Hz, 1H), 7.22 (m, 2H), 7.12 (t, *J* = 7.4 Hz, 1H), 3.68 (s, 3H). ¹³C NMR (125.8 MHz, DMSO-*d*₆) δ 172.8, 137.1, 133.3, 128.9, 126.4, 125.5, 51.9.

Preparation of μ-Chlorodimer and Precatalysts:

Step 1.

Isopropyl acetate (600 mL) was charged to a 1 L 3-necked round bottomed flask fitted with an overhead stirrer, N₂ inlet and thermocouple. To this was added MeOH (35.9 mL, 0.866 mol) followed by TMS-Cl (85 mL, 0.665 mol). The solution was aged at 22 °C for 1 h before adding 2-aminobiphenyl (75 g, 0.443 mol). The 2-aminobiphenyl hydrochloride formed a thick slurry, which was stirred continuously for 3 h. The solid was collected by filtration, washed with IPAc (3 x 100 mL) and dried via pulling N₂ through the cake for 24 h. 90 g (99%) of the title compound was isolated.

Step 2.

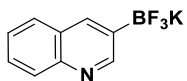
To a 3-necked round bottomed flask fitted with an overhead stirrer, N₂ inlet and thermocouple was added 2-aminobiphenyl hydrochloride (99.9 g, 0.486 mol) and THF (1000 mL). The solution was sparged with N₂ for 10 min before adding Pd(OAc)₂ (109 g, 0.486 mol). The slurry was heated to 60 °C for 75 min before cooling to 20 °C, at which point a thick seed bed formed. Heptane (500 mL) was added over 5 min and the slurry was aged for 15 min. The solid was collected by filtration and washed with 2:1 THF / heptane (2 x 500 mL) then MeOH (500 mL). The pale yellow solid was then dried for 24 h by pulling N₂ through the cake. (149 g, 95 wt%, 94% yield). Note: The wt was determined via H¹ NMR against 1,3,5-trimethoxybenzene as an internal standard. 4 wt % THF was observed.

CataCXium A Precatalyst Synthesis:

To a 500 mL 3-necked round bottomed flask fitted with an overhead stirrer under a N₂ atmosphere was added μ -chlorodimer (30 g, 90 wt%, 0.0435 mol), degassed acetone (200 mL) and CataCXium A (32.8 g, 0.091 mol). The reaction was aged for 24 h, after which time the solid was collected via filtration and washed with degassed acetone (2 x 50 mL). The solid was dried for 24 h via pulling N₂ through the cake. 56 g (96% yield) of the desired material was isolated.

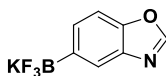
General procedure B: Pd catalyzed borylation of heteroaryl halides and their conversion to trifluoroborates. To an oven dried glass vessel capable of being sealed with a Teflon cap (for microwave vials) was added CataciumA palladium(II) biphenyl preformed catalyst (50 mg, 75 μ mol) and B₂(OH)₄ (405 mg, 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) and DIEA (784 μ L, 4.5 mmol) in a similar manner (solid halides were added with the other solid reagents before sealing). The reaction was then heated to 50 $^{\circ}$ C until the consumption of 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 EtOAc), and concentrated. The crude reaction was dissolved in EtOAc (10 mL) and then transferred to a separatory funnel followed by the addition of sat. NaHCO₃ (10 mL). The layers were separated and the aqueous layer was further extracted with EtOAc (3 x 5 mL). The combined organics were dried (Na₂SO₄) 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 $^{\circ}$ C. To this cooled mixture was added 4.5 equivalents of a 4.5 M aq KHF₂ solution (1 mL), and the reaction was stirred for 10 min at 0 $^{\circ}$ 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 ¹¹B 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 Et₂O (~25 mL) led to the precipitation of the desired product. The collected solid was washed with Et₂O. Further purification (to remove small organic or boron containing impurities) could be realized via trituration of the solid with Et₂O.

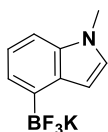


Potassium (Quinolin-3-yl)trifluoroborate (Table 4, entry 1). Following general procedure B, a mixture of 3-bromoquinoline (312 mg, 202 μ L, 1.5 mmol),

CataciumA palladium(II) biphenyl preformed catalyst (50 mg, 75 μ mol), DIEA (581 mg, 785 μ L, 4.5 mmol), and $B_2(OH)_4$ (405 mg, 4.5 mmol), was heated to 50 $^{\circ}C$ in MeOH (7.5 mL) for 5 h. The title compound was obtained as a white solid in 78% yield (275 mg) as a mixture of the trifluoroborate and internal salt. As such, reasonable NMR spectra could not be obtained and the compound was subjected to a two-step, one-pot borylation/Suzuki reaction (*vide infra*).

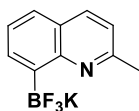


Potassium 5-Trifluoroborato-benzoxazole (Table 4, entry 2). Following general procedure A, a mixture of 5-chlorobenzoxazole (231 mg, 1.5 mmol), XPhos palladium(II) biphenyl preformed catalyst (5.89 mg, 7.5 μ mol), XPhos (7.14 mg, 15 μ mol), KOAc (441 mg, 4.5 mmol), and $B_2(OH)_4$ (405 mg, 4.5 mmol), was heated to 80 $^{\circ}C$ in EtOH (15 mL) for 1.5 h. After the standard workup (using sat. aq $NaHCO_3$ solution instead of H_2O during the aqueous workup), the crude boronic acid was converted to the potassium trifluoroborate salt. The title compound was obtained as a pale yellow solid in 81% yield (275 mg). mp = 215 $^{\circ}C$ dec. 1H NMR (500 MHz, $DMSO-d_6$) δ 8.51 (s, 1H), 7.68 (s, 1H), 7.45 (q, J = 8.1 Hz, 2H). ^{13}C NMR (125.8 MHz, $DMSO-d_6$) δ 152.5, 148.1, 138.7, 128.9, 122.1, 108.6. ^{11}B NMR (128.4 MHz, $DMSO-d_6$) δ 2.7. ^{19}F NMR (282 MHz, $DMSO-d_6$) δ -141.8--142.1 (m). IR (dry film): 3120, 3051, 1688, 1610, 1524, 1409, 1245, 1132, 1070, 988, 956, 876, 806, 650 cm^{-1} . HRMS (ES-) calcd. for $C_7H_4BF_3NO$ (M-K) 186.0338, found 186.0347.



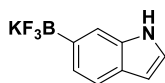
Potassium (2-Methylquinolin-8-yl)trifluoroborate (Table 4, entry 3). Following general procedure A, a mixture of 4-chloro-1-methyl-1H-indole (315 mg, 216

μL , 1.5 mmol), XPhos palladium(II) biphenyl preformed catalyst (5.89 mg, 7.5 μmol), XPhos (7.14 mg, 15 μmol), KOAc (441 mg, 4.5 mmol), and $\text{B}_2(\text{OH})_4$ (405 mg, 4.5 mmol), was heated to 80 $^\circ\text{C}$ in EtOH (15 mL) for 5 h. The title compound was obtained as a peach solid in 80% yield (285 mg). mp > 225 $^\circ\text{C}$. ^1H NMR (500 MHz, acetone- d_6) δ 7.17 (d, $J = 6.7$ Hz, 1H), 7.06 (d, $J = 8.0$ Hz, 1H), 6.97 (d, $J = 7.4$ Hz, 1H), 6.94 (d, $J = 3.0$ Hz, 1H), 6.71 (s, 1H), 3.71 (s, 3H). ^{13}C NMR (125.8 MHz, DMSO) δ 136.1, 132.2, 127.2, 122.2 (d, $J = 2.52$ Hz), 120.7, 106.7, 104.1, 32.8. ^{19}F NMR (282 MHz, acetone- d_6) δ -139.9. ^{11}B NMR (128.4 MHz, acetone- d_6) δ 4.09. IR (dry film): 2348, 1514. HRMS (ES-) calcd. for $\text{C}_9\text{H}_8\text{BF}_3\text{N}$: 198.07029 (M-K), found 198.0702.



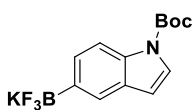
Potassium (2-Methylquinolin-8-yl)trifluoroborate (Table 4, entry 4).

Following general procedure A, a mixture of 8-chloro-2-methylquinoline (266 mg, 1.5 mmol), procedure A, a mixture of 4-chloro-1-methyl-1H-indole (315 mg, 216 μL , 1.5 mmol), XPhos palladium(II) biphenyl preformed catalyst (5.89 mg, 7.5 μmol), XPhos (7.14 mg, 15 μmol), KOAc (441 mg, 4.5 mmol), and $\text{B}_2(\text{OH})_4$ (405 mg, 4.5 mmol), was heated to 80 $^\circ\text{C}$ in EtOH (15 mL) for 2 h. The title compound was obtained as a yellow solid in 52% yield (194 mg). mp > 225 $^\circ\text{C}$. ^1H NMR (500 MHz, acetone- d_6) δ 8.05 (d, $J = 8.3$ Hz, 1H), 7.98 (d, $J = 6.5$ Hz, 1H), 7.60 (d, $J = 7.9$ Hz, 1H), 7.33 (t, $J = 7.3$ Hz, 1H), 7.21 (d, $J = 8.3$ Hz, 1H), 2.70 (s, 3H). ^{13}C NMR (125.8 MHz, DMSO- d_6) δ 156.4, 151.7, 136.7, 133.4, 126.3, 126.2, 125.3, 120.9, 25.7. ^{19}F NMR (282 MHz, acetone- d_6) δ -138.8. ^{11}B NMR (128.4 MHz, acetone- d_6) δ 3.9. IR (dry film): 2924, 2340. HRMS (ES-) calcd. for $\text{C}_{10}\text{H}_8\text{BF}_3\text{N}$: 210.0696 (M-K), found 210.0702.



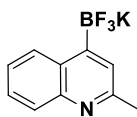
Potassium 1H-indol-6-yl-trifluoroborate (Table 4, entry 5).¹⁰

Following general procedure A, a mixture of 6-chloroindole (230 mg, 1.5 mmol), XPhos palladium(II) biphenyl preformed catalyst (5.89 mg, 7.5 μ mol), XPhos (7.14 mg, 15 μ mol), KOAc (441 mg, 4.5 mmol), and B₂(OH)₄ (405 mg, 4.5 mmol), was heated to 80 °C in EtOH (15 mL) for 1.5 h. After the standard workup (using sat. aq NaHCO₃ solution instead of H₂O during the aqueous workup), the crude boronic acid was converted to the potassium trifluoroborate salt. The title compound was obtained as a white solid in 78% yield (261 mg). Spectral data were in accordance with those published. mp > 225 °C. ¹H NMR (500 MHz, DMSO-*d*₆) δ 10.55 (s, 1H), 7.33 (s, 1H), 7.23 (d, *J* = 7.8 Hz, 1H), 7.09 (t, *J* = 2.6 Hz, 1H), 7.00 (d, *J* = 7.8 Hz, 1H), 6.23 (s, 1H). ¹³C NMR (125.8 MHz, DMSO-*d*₆) δ 136.2, 125.7, 123.2, 122.9, 117.8, 113.9, 100.4.



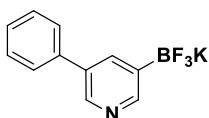
Potassium 1-(*tert*-Butoxycarbonyl)-indol-5-yl-trifluoroborate (Table

4, entry 6).¹¹ Following general procedure A, a mixture of 1-(*tert*-butoxycarbonyl)-5-bromoindole (445 mg, 1.5 mmol), XPhos palladium(II) biphenyl preformed catalyst (5.89 mg, 7.5 μ mol), XPhos (7.14 mg, 15 μ mol), KOAc (441 mg, 4.5 mmol), and B₂(OH)₄ acid (405 mg, 4.5 mmol), was heated to 80 °C in EtOH (15 mL) for 1.5 h. After the standard workup (using sat. aq NaHCO₃ solution instead of H₂O during the aqueous workup), the crude boronic acid was converted to the potassium trifluoroborate salt. The title compound was obtained as a white solid in 93% yield (449 mg). Spectral data were in accordance with those published. mp = 188 °C dec. ¹H NMR (500 MHz, DMSO-*d*₆) δ 7.80 (d, *J* = 8.0 Hz, 1H), 7.52 (s, 1H), 7.48 (d, *J* = 3.5 Hz, 1H), 7.31 (d, *J* = 8.1 Hz, 1H), 6.56 (d, *J* = 3.5 Hz, 1H), 1.62 (s, 9H). ¹³C NMR (125.8 MHz, DMSO-*d*₆) δ 149.4, 133.4, 129.2, 128.3, 124.2, 123.6, 112.6, 107.9, 82.9, 27.8.



Potassium (2-Methylquinolin-4-yl)trifluoroborate (Table 4, entry 7).

Following general procedure B, a mixture of 4-chloroquinoline (266 mg, 302 μ L, 1.5 mmol), CataxiumA palladium(II) biphenyl preformed catalyst (50 mg, 75 μ mol), DIEA (581 mg, 785 μ L, 4.5 mmol), and $B_2(OH)_4$ (405 mg, 4.5 mmol), was heated to 50 $^{\circ}$ C in MeOH (7.5 mL) for 1.5 h. The title compound was obtained as a white solid in 47% yield (175 mg) as a mixture of the trifluoroborate and internal salt. As such, reasonable NMR spectra could not be obtained, and the compound was subjected to a two-step, one-pot borylation/Suzuki reaction (*vide infra*).

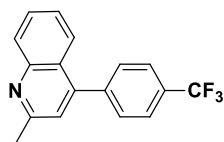


Potassium (5-Phenylpyridin-3-yl)trifluoroborate (Table 4, entry 8).

Following general procedure B, 3-bromo-5-phenylpyridine (351 mg, 1.5 mmol), CataxiumA palladium(II) biphenyl preformed catalyst (50 mg, 75 μ mol), DIEA (581 mg, 785 μ L, 4.5 mmol), and $B_2(OH)_4$ (405 mg, 4.5 mmol), was heated to 50 $^{\circ}$ C in MeOH (7.5 mL) for 1 h. After the standard workup (using sat. aq. $NaHCO_3$ solution instead of H_2O during the aqueous workup), the title compound was obtained as an off-white solid in 61% yield (238 mg) as a mixture of the trifluoroborate and internal salt. As such, reasonable NMR spectra could not be obtained and the compound was subjected to a two-step, one-pot borylation/Suzuki reaction (*vide infra*).

General procedure C: Pd catalyzed borylation of heteroaryl halides and their Suzuki coupling with aryl or heteroaryl halides.

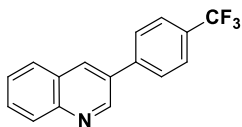
To an oven dried glass vessel capable of being sealed with a Teflon cap (for microwave vials) was added CataciumA palladium(II) biphenyl preformed catalyst (50 mg, 75 μmol) and $\text{B}_2(\text{OH})_4$ (405 mg, 4.5 mmol). The vessel was sealed and then evacuated and backfilled with Ar (process was repeated four times). MeOH (7.5 mL, degassed) was added via syringe followed by the addition of the halide (1.5 mmol) and DIEA (784 μL , 4.5 mmol) in a similar manner (solid halides were added with the other solid reagents before sealing). The reaction was then heated to 50 $^\circ\text{C}$ until consumption of starting material (as monitored by GC). Subsequently, a needle attached to a manifold under argon was added to the septum and 3 equiv (4.5 mL, 4.5 mmol) of 1.0 M degassed aqueous K_3PO_4 was added via syringe followed by the addition of the second halide (1.5 mmol) in a similar manner (in a solution of 500 μL degassed EtOH or THF if solid). The manifold needle was removed and the reaction was further heated to 50 $^\circ\text{C}$ for 15 h. The reaction was cooled to rt, filtered through a thin pad of Celite (eluting with 5 x 10 mL EtOAc) and concentrated. The crude solid was extracted with EtOAc (3x 5 mL), the combined organics were dried (Na_2SO_4) and then concentrated under reduced pressure. The desired compound was purified by column chromatography, eluting with EtOAc/hexane unless otherwise indicated.



2-Methyl-4-(4-(trifluoromethyl)phenyl)quinoline (Table 5, entry

1).¹² Following general procedure C, a mixture of 4-chloroquinoline (266 mg, 302 μL , 1.5 mmol), CataciumA palladium(II) biphenyl preformed catalyst (50 mg, 75 μmol), DIEA (581 mg, 785 μL , 4.5 mmol), and $\text{B}_2(\text{OH})_4$ (405 mg, 4.5 mmol), and were heated to 50 $^\circ\text{C}$ in MeOH (7.5 mL) for 1.5 h. Subsequently, a needle attached to a manifold under argon was added to the septum and 3 equiv (4.5 mL, 4.5 mmol) of 1.0 M degassed

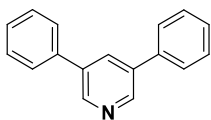
aqueous K_3PO_4 was added via syringe followed by the addition of 1-chloro-4-(trifluoromethyl)benzene (271 mg, 200 μ L, 1.5 mmol). The manifold needle was removed and the reaction was further heated to 50 $^{\circ}C$ for 15 h. The crude product was purified via flash chromatography on silica gel (0-10% EtOAc/hexane) to provide the title compound as off-white crystals in 64% yield (236 mg). Spectral data in accordance with those of published results. mp 106-109 $^{\circ}C$. 1H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, $J = 8.4$ Hz, 1H), 7.79 (d, $J = 8.0$ Hz, 2H), 7.78 – 7.70 (m, 2H), 7.62 (d, $J = 8.0$ Hz, 2H), 7.46 (t, $J = 7.5$ Hz, 1H), 7.23 (s, 1H), 2.80 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 158.7, 148.5, 147.1, 141.9, 131.1, 130.8, 130.6, 130.3, 130.0, 129.7, 129.4, 127.5, 126.3, 125.7, 125.7, 125.6, 125.6, 125.3, 125.2, 124.8, 123.1, 122.3, 120.9, 25.5.



3-(4-(Trifluoromethyl)phenyl)quinoline (Table 5, entry 2).

Following general procedure C, 3-bromo-5-phenylpyridine (351 mg, 1.5 mmol), CataciumA palladium(II) biphenyl preformed catalyst (50 mg, 75 μ mol), DIEA (581 mg, 785 μ L, 4.5 mmol), and $B_2(OH)_4$ (405 mg, 4.5 mmol), was heated to 50 $^{\circ}C$ in MeOH (7.5 mL) for 5 h. Subsequently, a needle attached to a manifold under argon was added to the septum and 3 equiv (4.5 mL, 4.5 mmol) of 1.0 M degassed aqueous K_3PO_4 was added via syringe followed by the addition of 1-chloro-4-(trifluoromethyl)benzene (271 mg, 200 μ L, 1.5 mmol). The manifold needle was removed and the reaction was further heated to 50 $^{\circ}C$ for 15 h. The crude product was purified via flash chromatography on silica gel (0-10% EtOAc/hexane) to provide the title compound as a pale yellow solid in 60% yield (245 mg). mp = 135-137 $^{\circ}C$. 1H NMR (500 MHz, $CDCl_3$) δ 9.18 (d, $J = 2.2$ Hz, 1H), 8.34 (d, $J = 1.7$ Hz, 1H), 8.17 (d, $J = 8.5$ Hz, 1H), 7.91 (d, $J = 8.1$ Hz, 1H), 7.85 – 7.81 (m, 2H), 7.81 – 7.75 (m, 3H), 7.62 (t, $J = 7.5$ Hz, 1H). ^{13}C NMR (125.8 MHz,

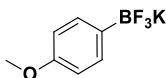
CDCl₃) δ 149.6, 147.9, 141.6, 133.9, 132.6, 130.5, 130.2, 130.1, 129.9, 129.5, 128.3, 127.9, 127.9, 127.5, 126.3, 126.3, 126.3, 126.2, 125.4, 123.2, 100.1. IR (dry film): 2912, 2365. HRMS (ES+) calcd. for C₁₆H₁₀F₃N: 274.0844 (M+H), found 274.0857.



3,5-Diphenylpyridine (Table 5, entry 3).¹³ Following general

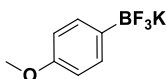
procedure C, 3-bromo-5-phenylpyridine (351 mg, 1.5 mmol), CatacxiuMA palladium(II) biphenyl preformed catalyst (50 mg, 75 μ mol), DIEA (581 mg, 785 μ L, 4.5 mmol), and B₂(OH)₄ (405 mg, 4.5 mmol), was heated to 50 °C in MeOH (7.5 mL) for 1 h. Subsequently, a needle attached to a manifold under argon was added to the septum and 3 equiv (4.5 mL, 4.5 mmol) of 1.0 M degassed aqueous K₃PO₄ was added via syringe followed by the addition of 1-bromobenzene (235 mg, 158 μ L, 1.5 mmol). The manifold needle was removed and the reaction was further heated to 50 °C for 15 h. The crude product was purified via flash chromatography on silica gel (0-40% EtOAc/hexane) to provide the title compound as a pale yellow solid in 68% yield (236 mg). Spectral data in accordance with that of published results. mp 133-136 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.83 (s, 2H), 8.05 (s, 1H), 7.65 (d, *J* = 7.4 Hz, 4H), 7.51 (t, *J* = 7.5 Hz, 4H), 7.44 (t, *J* = 7.3 Hz, 2H). ¹³C NMR (125.8 MHz, CDCl₃) δ 147.2, 137.9, 136.8, 133.1, 129.3, 128.4, 127.4.

General Procedure A with Aryl Electrophiles:



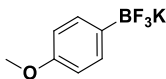
Potassium 4-Methoxyphenyl-trifluoroborate (Table 6, entry 1).¹ See

data for Table 1, entry 1.



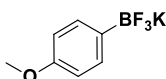
Potassium 4-Methoxyphenyl-trifluoroborate (Table 6, entry 2).¹ See

data for Table 2, entry 8.



Potassium 4-Methoxyphenyl-trifluoroborate (Table 6, entry 3).¹

Following general procedure A, a mixture of 4-iodoanisole (351 mg, 1.5 mmol), XPhos palladium(II) biphenyl preformed catalyst (5.89 mg, 7.5 μ mol), XPhos (7.14 mg, 15 μ mol), KOAc (441 mg, 4.5 mmol), and B₂(OH)₄ (405 mg, 4.5 mmol), was heated to 80 °C in EtOH (15 mL) for 1 h. The title compound was obtained as a white solid in 73% yield (234 mg). Spectral data were in accordance with those published. mp > 225 °C. ¹H NMR (500 MHz, DMSO-*d*₆) δ 7.25 (d, *J* = 8.1 Hz, 2H), 6.68 (d, *J* = 8.0 Hz, 2H), 3.66 (s, 3H). ¹³C NMR (125.8 MHz, DMSO-*d*₆) δ 157.4, 132.4, 111.9, 54.6.



Potassium 4-Methoxyphenyl-trifluoroborate (Table 6, entry 5).¹

Following general procedure A, a mixture of 4-methoxyphenyltrifluoromethanesulfonate (384 mg, 1.5 mmol), XPhos palladium(II) biphenyl preformed catalyst (5.89 mg, 7.5 μ mol), XPhos (7.14 mg, 15 μ mol), KOAc (441 mg, 4.5 mmol), and B₂(OH)₄ (405 mg, 4.5 mmol), was heated to 80 °C in EtOH (15 mL) for 2 h. The title compound was obtained as a white solid in 99% yield (318 mg). Spectral data were in accordance with those published. mp > 225 °C. ¹H NMR (500 MHz, DMSO-*d*₆) δ 7.25 (d, *J* = 8.1 Hz, 2H), 6.68 (d, *J* = 8.0 Hz, 2H), 3.66 (s, 2H). ¹³C NMR (125.8 MHz, DMSO-*d*₆) δ 157.4, 132.4, 111.9, 54.6.

Kinetics Experiments:

Time course studies were run under general reaction conditions provided above and from previously described experimentals¹ on 0.5 mmol scale at 80 °C over the course of 4 h. A Chemspeed SLT 100 removed 30 uL aliquots t(0) and every 15 min thereafter. Samples were quenched into MeCN (700 µL) with 6 equiv of pinacol. At the completion of the reaction, the diluted samples were analyzed by HPLC.

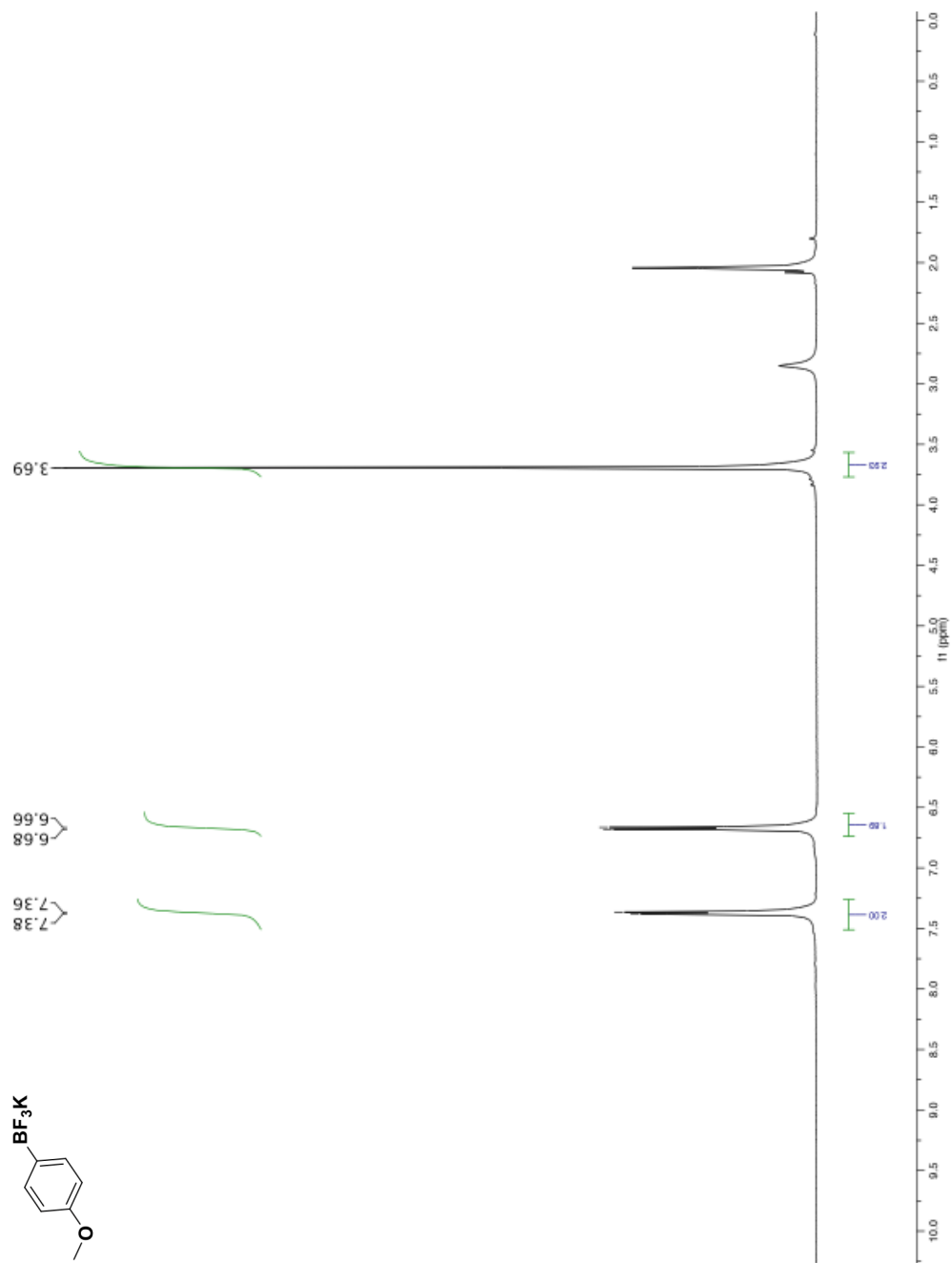
Inhibitory Experiments:

Bromide ion inhibitory experiments studies were run under general reaction conditions (vida supra) on 0.5 mmol scale at 80 °C over the course of 5 h. To the corresponding reactions were added 1, 5, or 10 equiv of tetra-*n*-butylammonium bromide (TBAB). A Chemspeed SLT 100 removed 30 uL aliquots t(0) every 5 minutes for 1 h, then samples were removed every 10 min for 2 h thereafter. Samples were quenched into MeCN (700 µL) with 6 equiv of pinacol. At the completion of the reaction, the diluted samples were analyzed by HPLC.

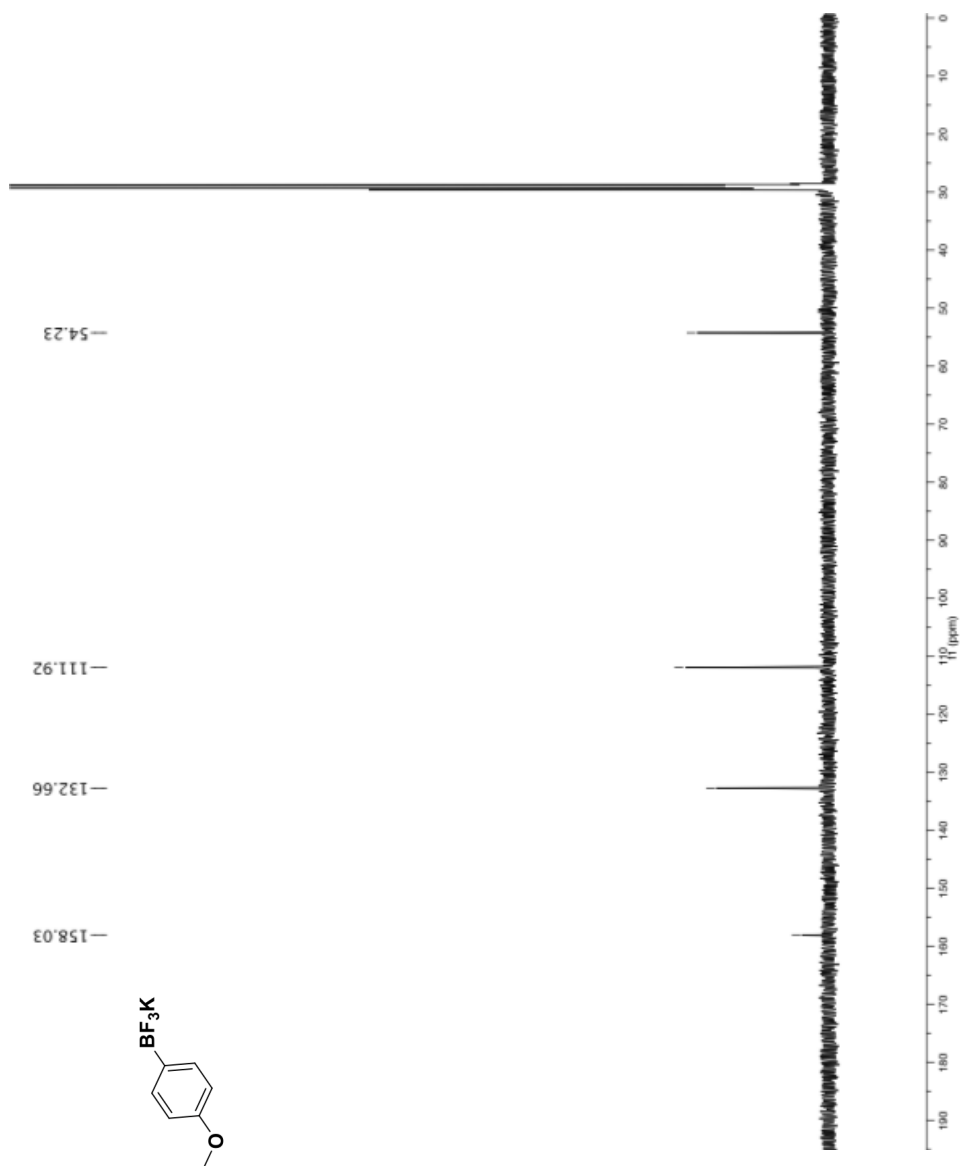
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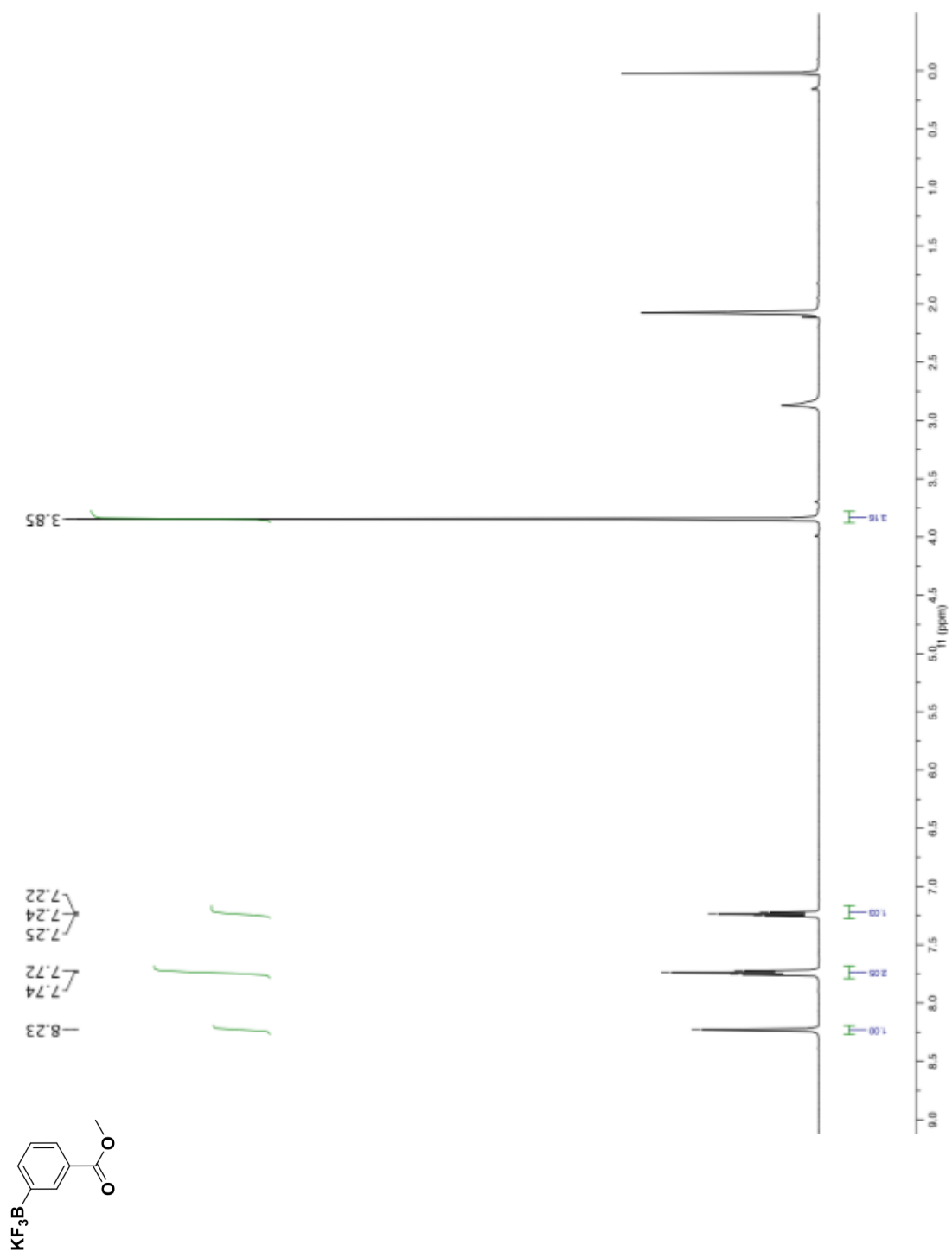
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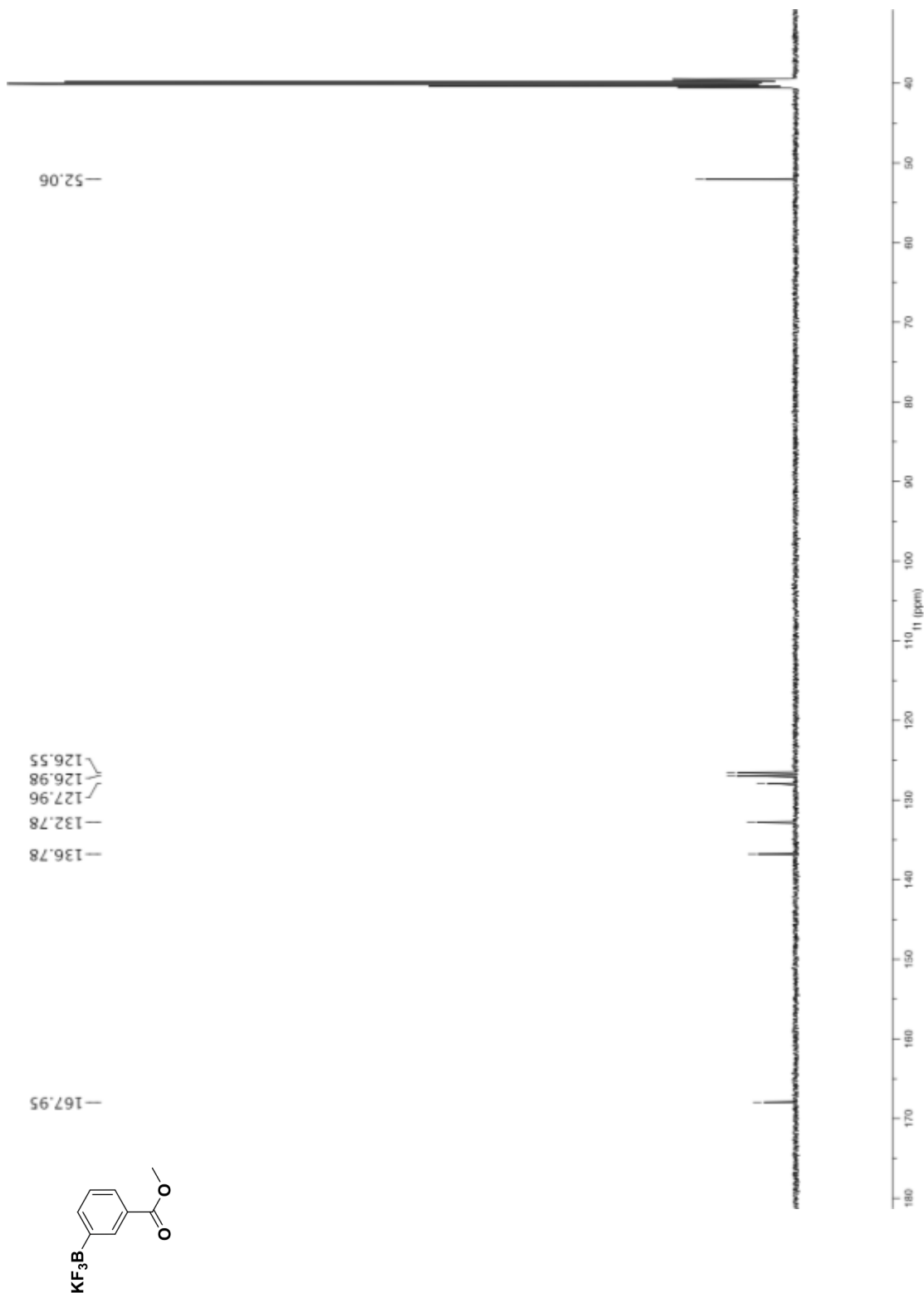
¹H NMR Spectra (500 MHz, acetone-*d*₆) **Potassium 4-Methoxyphenyl-trifluoroborate** (Table 1, entry 1)



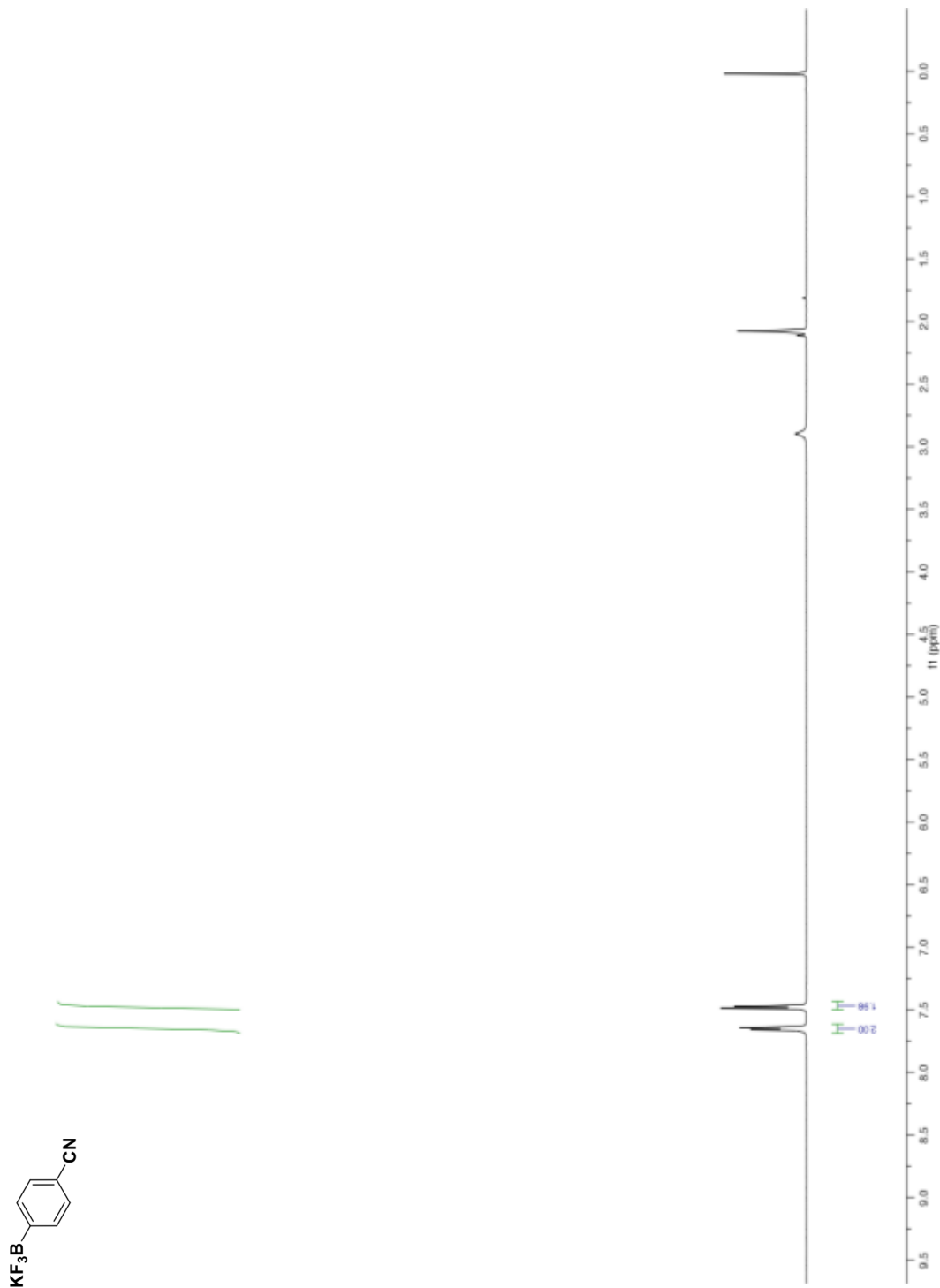
^{13}C NMR Spectra (125.8 MHz, acetone- d_6) Potassium 4-Methoxyphenyltrifluoroborate (Table 1, entry 1)



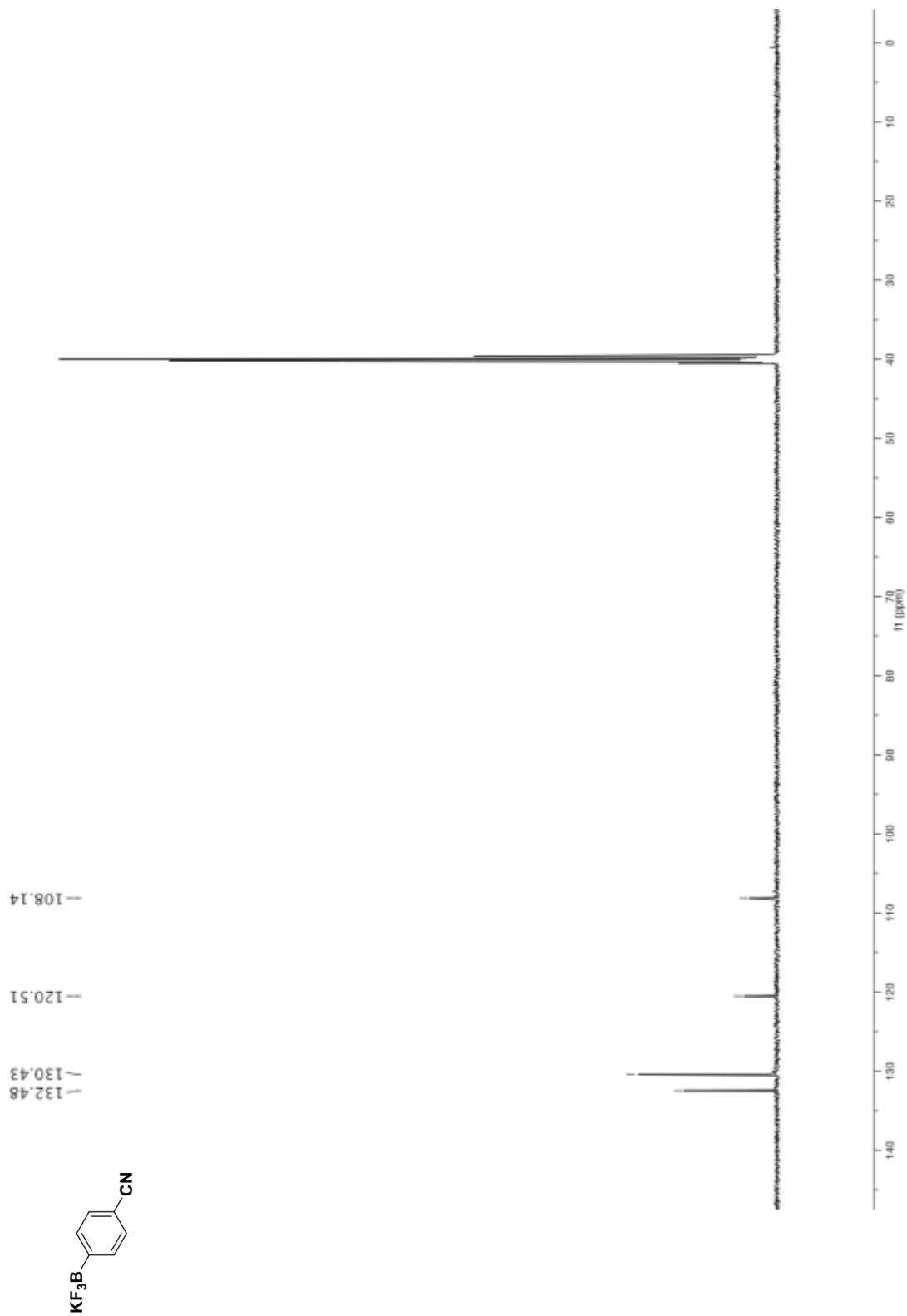
¹H NMR Spectra (500 MHz, acetone-*d*₆) Potassium (3-(Methoxycarbonyl)phenyl)trifluoroborate (Table 1, entry 2).



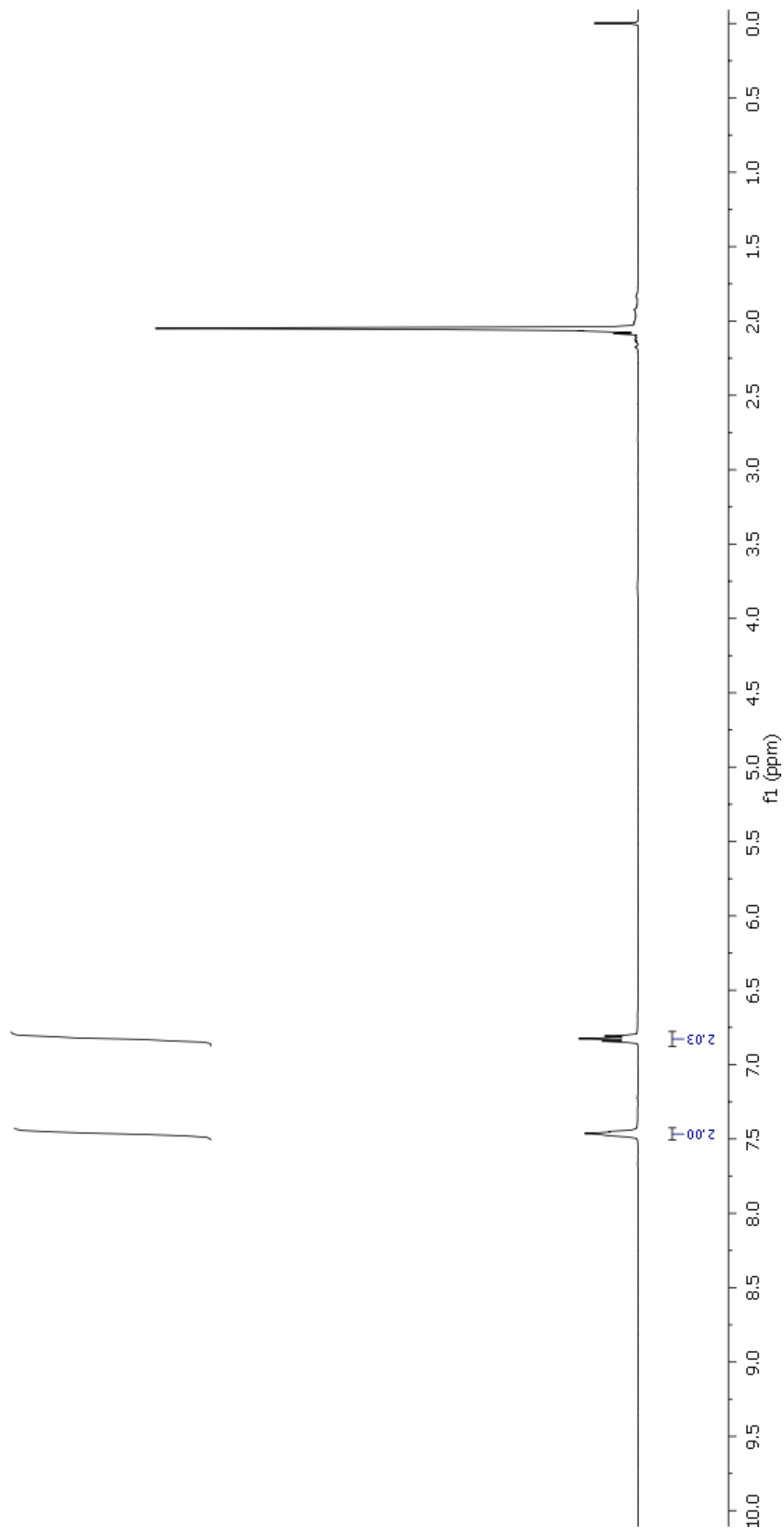
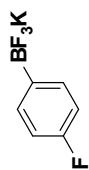
^{13}C NMR Spectra (125.8 MHz, $\text{DMSO-}d_6$) Potassium (3-(Methoxycarbonyl)phenyl)trifluoroborate (Table 1, entry 2).



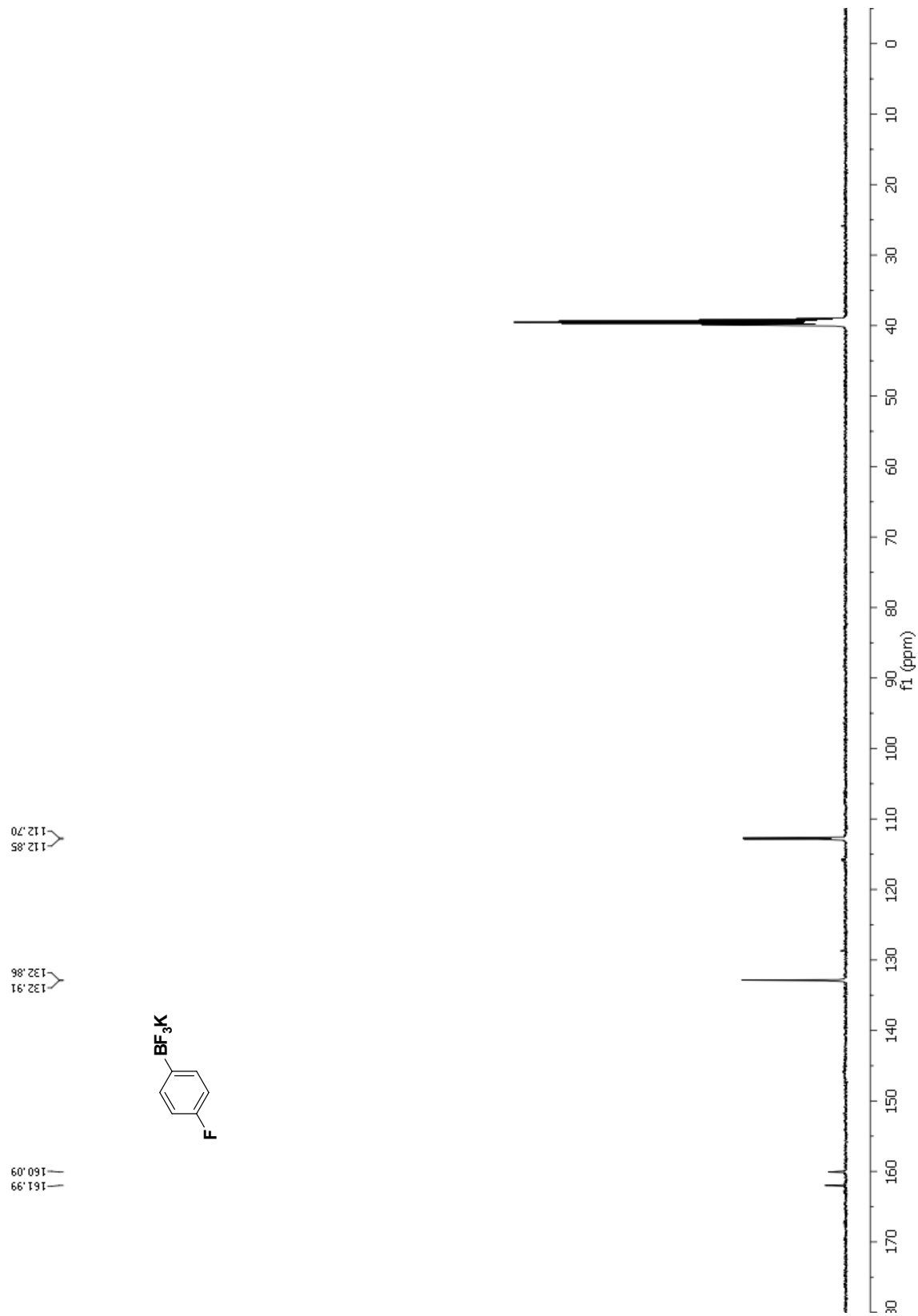
¹H NMR Spectra (500 MHz, acetone-*d*₆) Potassium (4-Cyanophenyl)trifluoroborate (Table 1, entry 3).



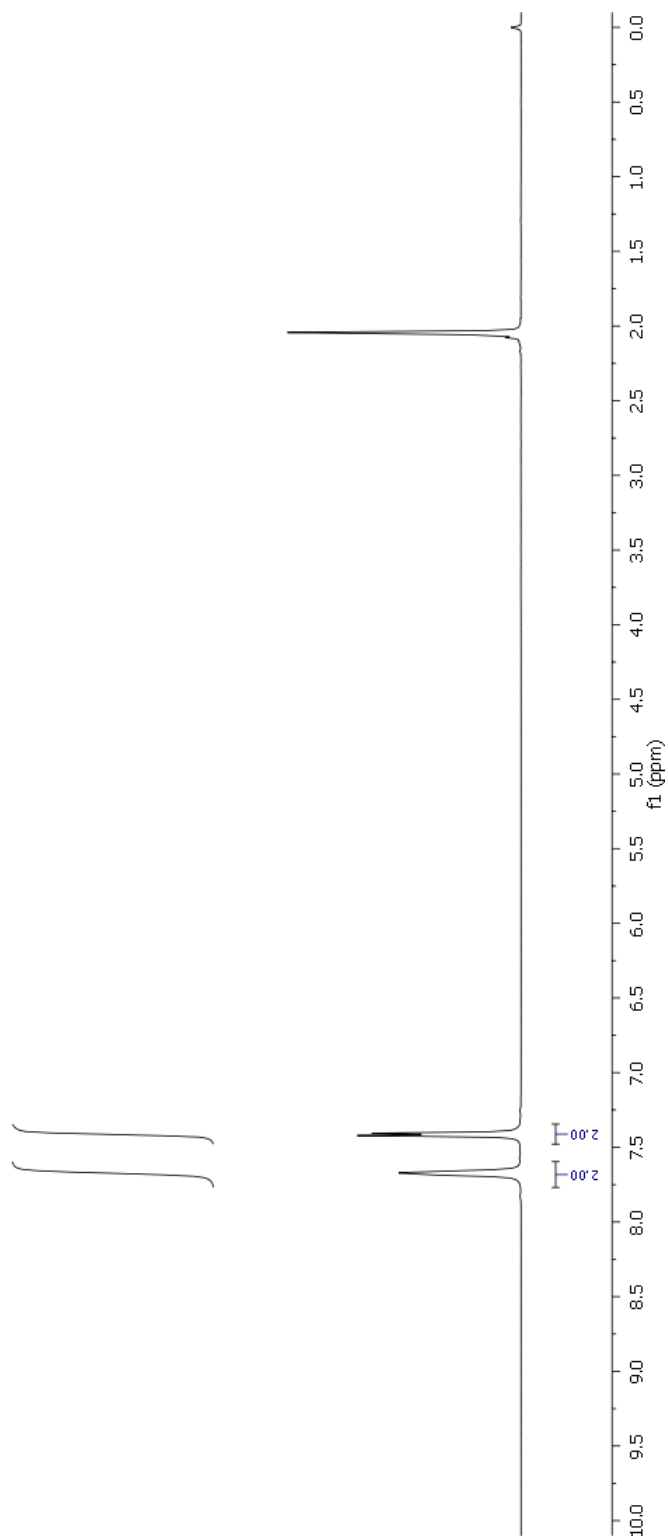
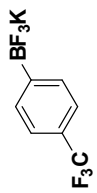
¹³C NMR Spectra (125.8 MHz, DMSO-*d*₆) Potassium (4-Cyanophenyl)trifluoroborate (Table 1, entry 3).



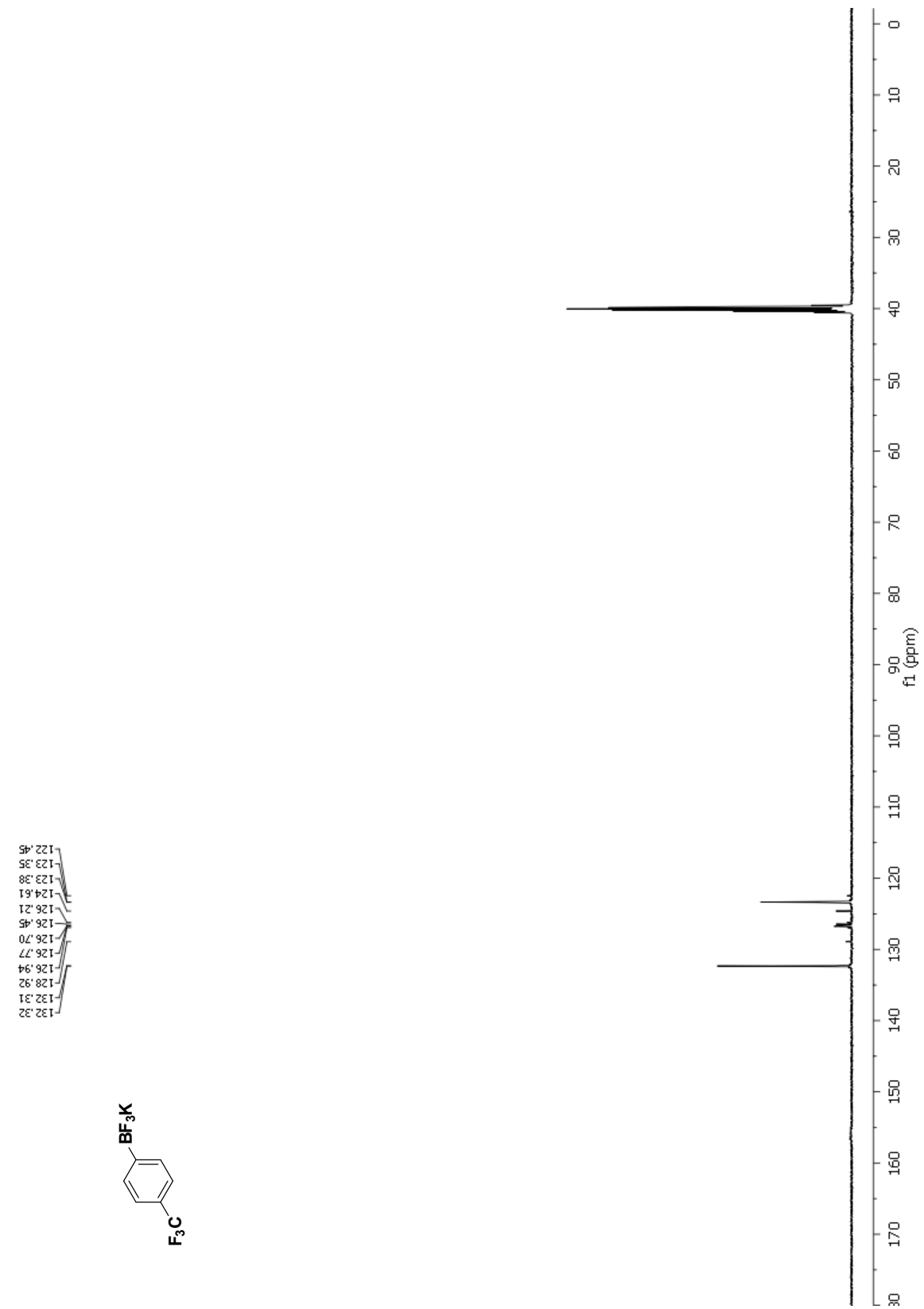
^1H NMR Spectra (500 MHz, acetone- d_6) **Potassium (4-Fluorophenyl)trifluoroborate** (Table 1, entry 4)



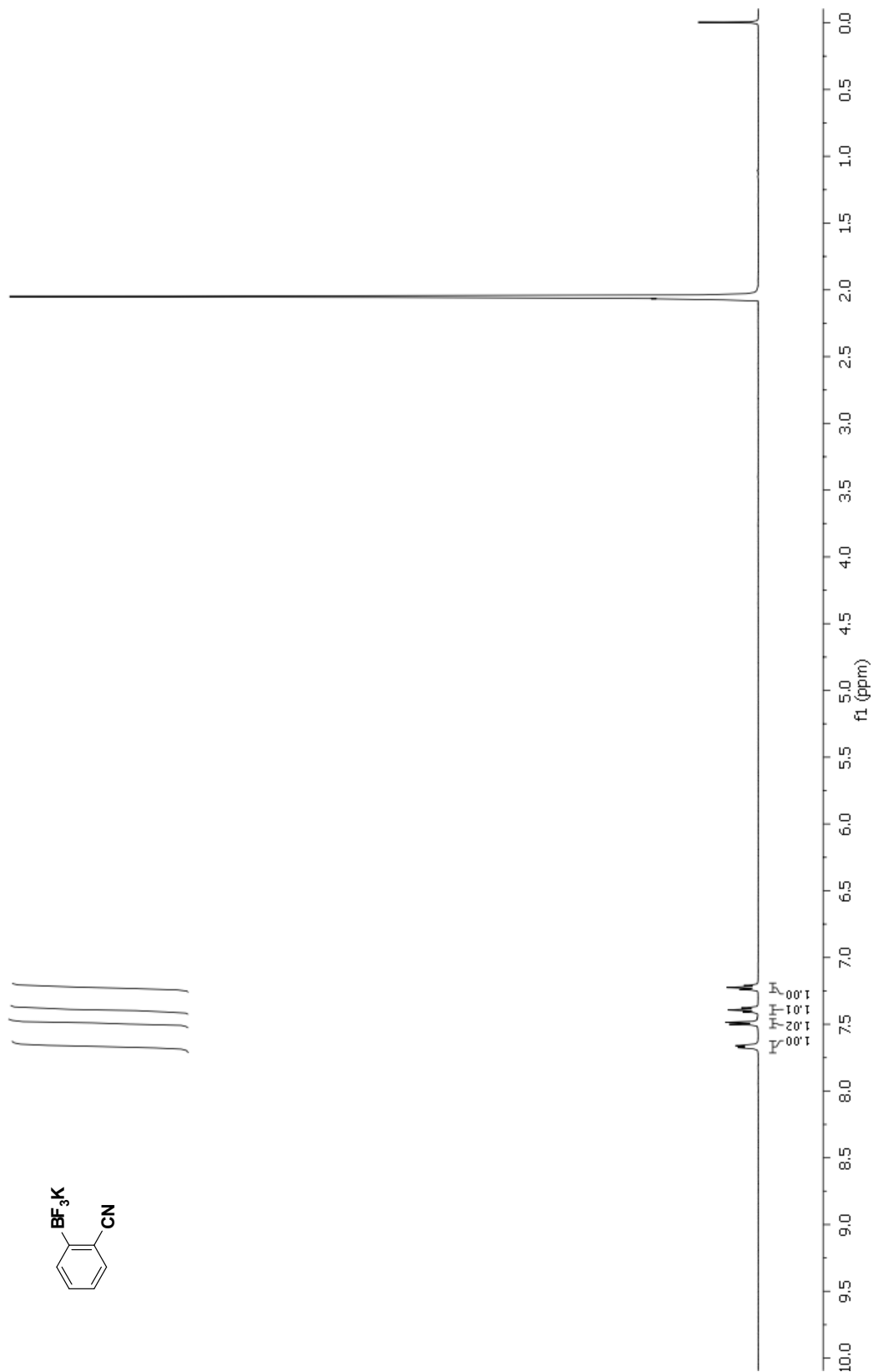
^{13}C NMR Spectra (125.8 MHz, $\text{DMSO-}d_6$) Potassium (4-Fluorophenyl)trifluoroborate (Table 1, entry 4)



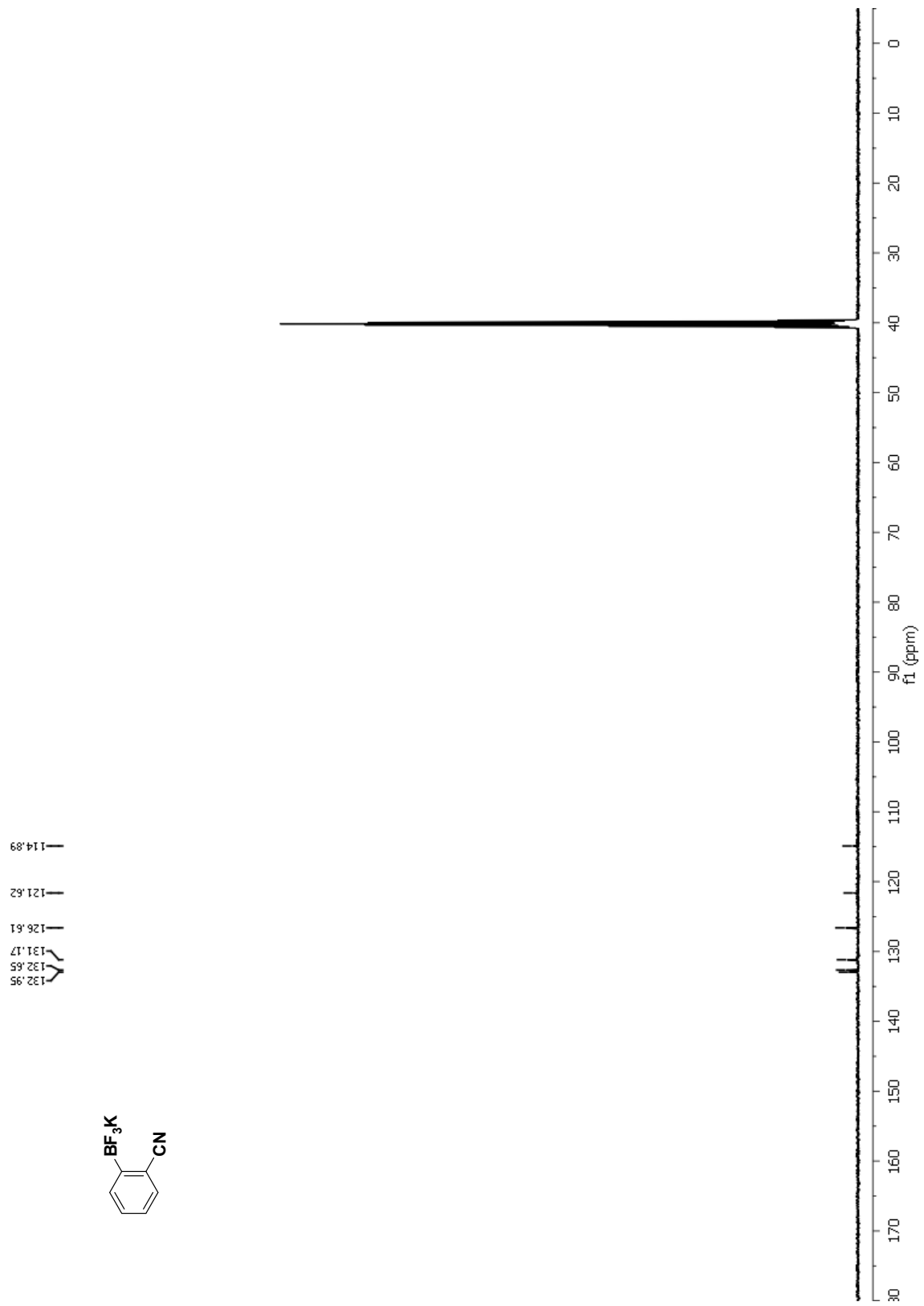
^1H NMR Spectra (500 MHz, acetone- d_6) Potassium (4-(Trifluoromethyl)phenyl)trifluoroborate (Table 1, entry 5)



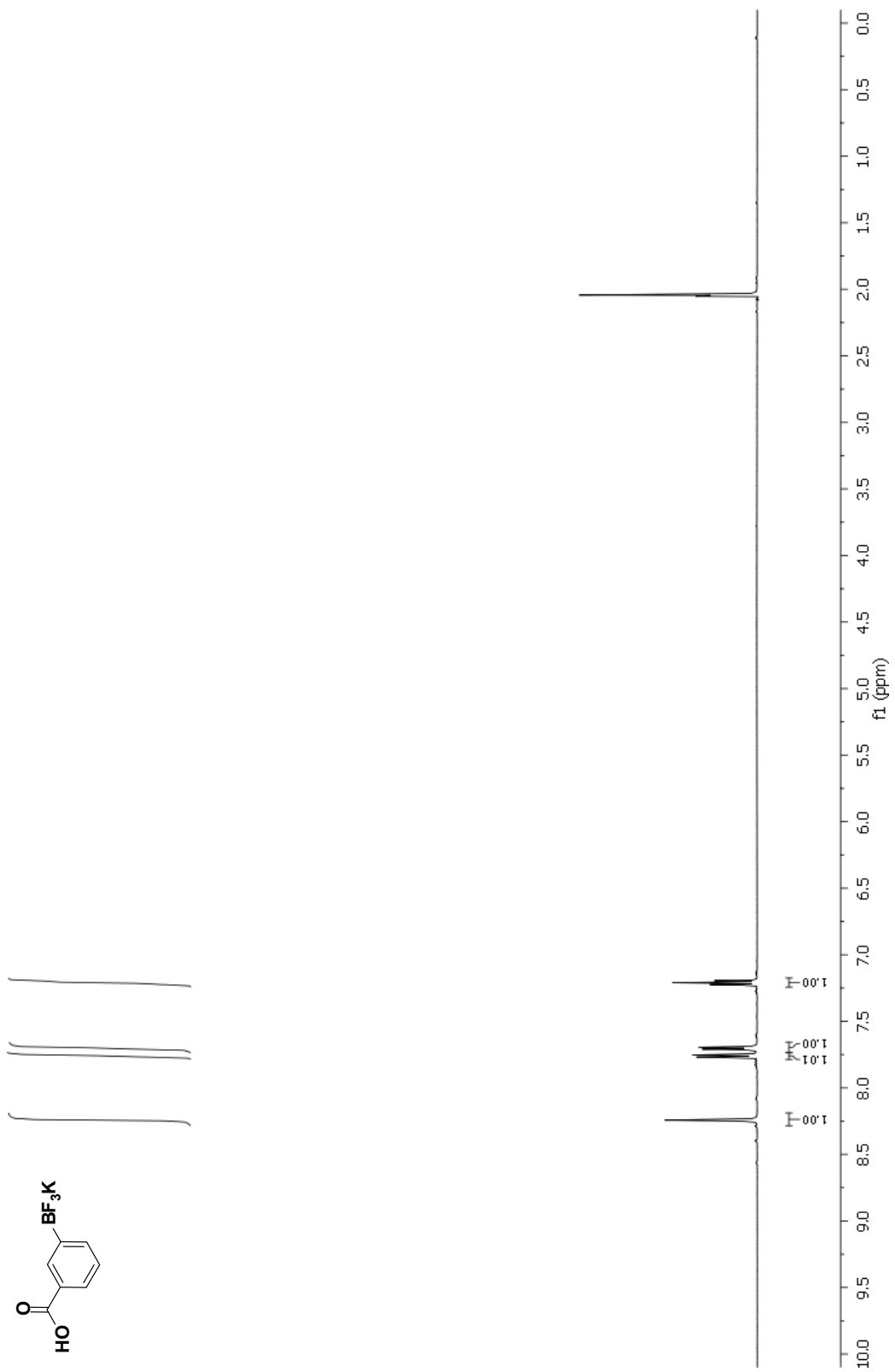
¹³C NMR Spectra (125.8 Hz, DMSO-*d*₆) Potassium (4-(Trifluoromethyl)phenyl)trifluoroborate (Table 1, entry 5)



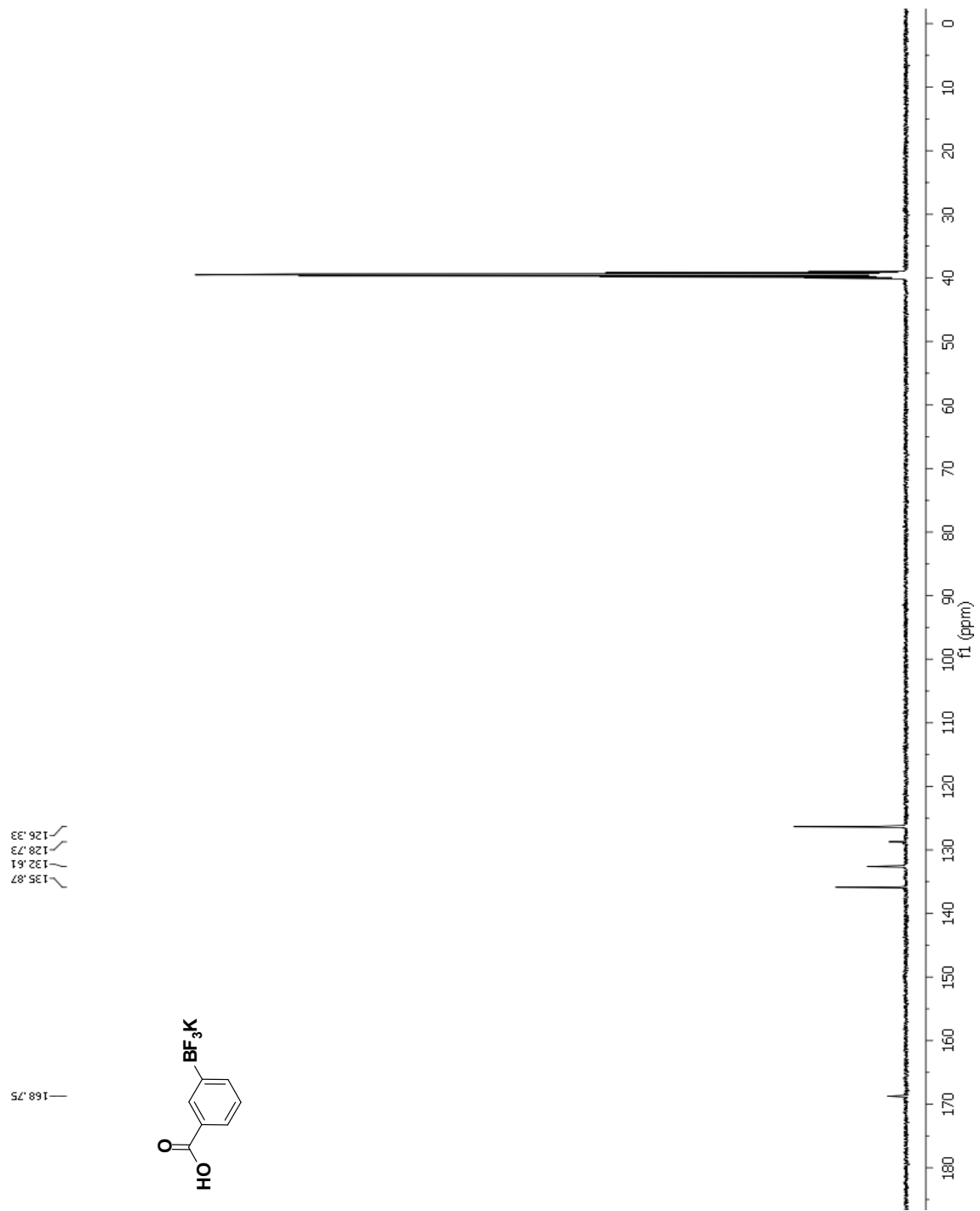
¹H NMR Spectra (500 MHz, acetone-*d*₆) Potassium (2-Cyanophenyl)trifluoroborate (Table 1, entry 6)



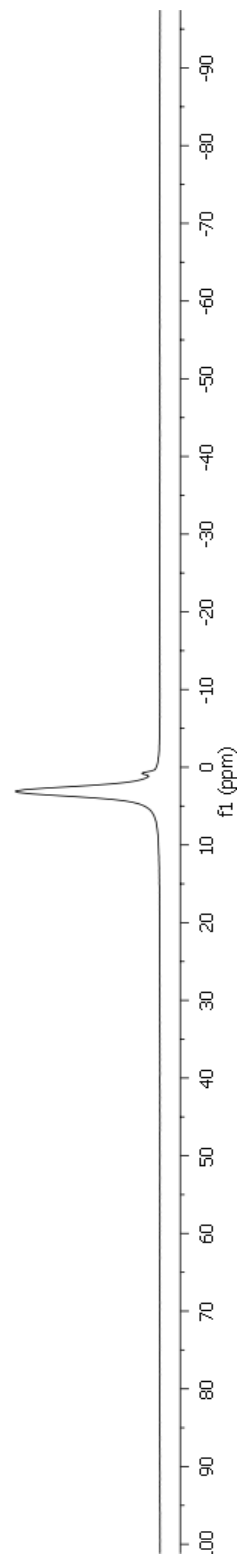
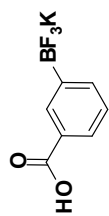
¹³C NMR Spectra (125.8 MHz, DMSO-*d*₆) Potassium (2-Cyanophenyl)trifluoroborate (Table 1, entry 6)



¹H NMR (500 MHz, acetone-*d*₆) Potassium 3-Trifluoroborato-benzoic acid (Table 1, entry 8)

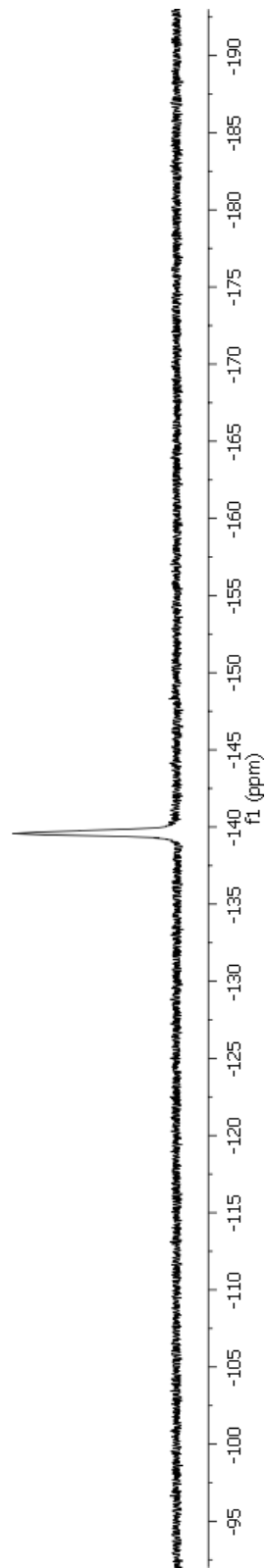
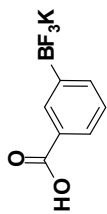


3.12

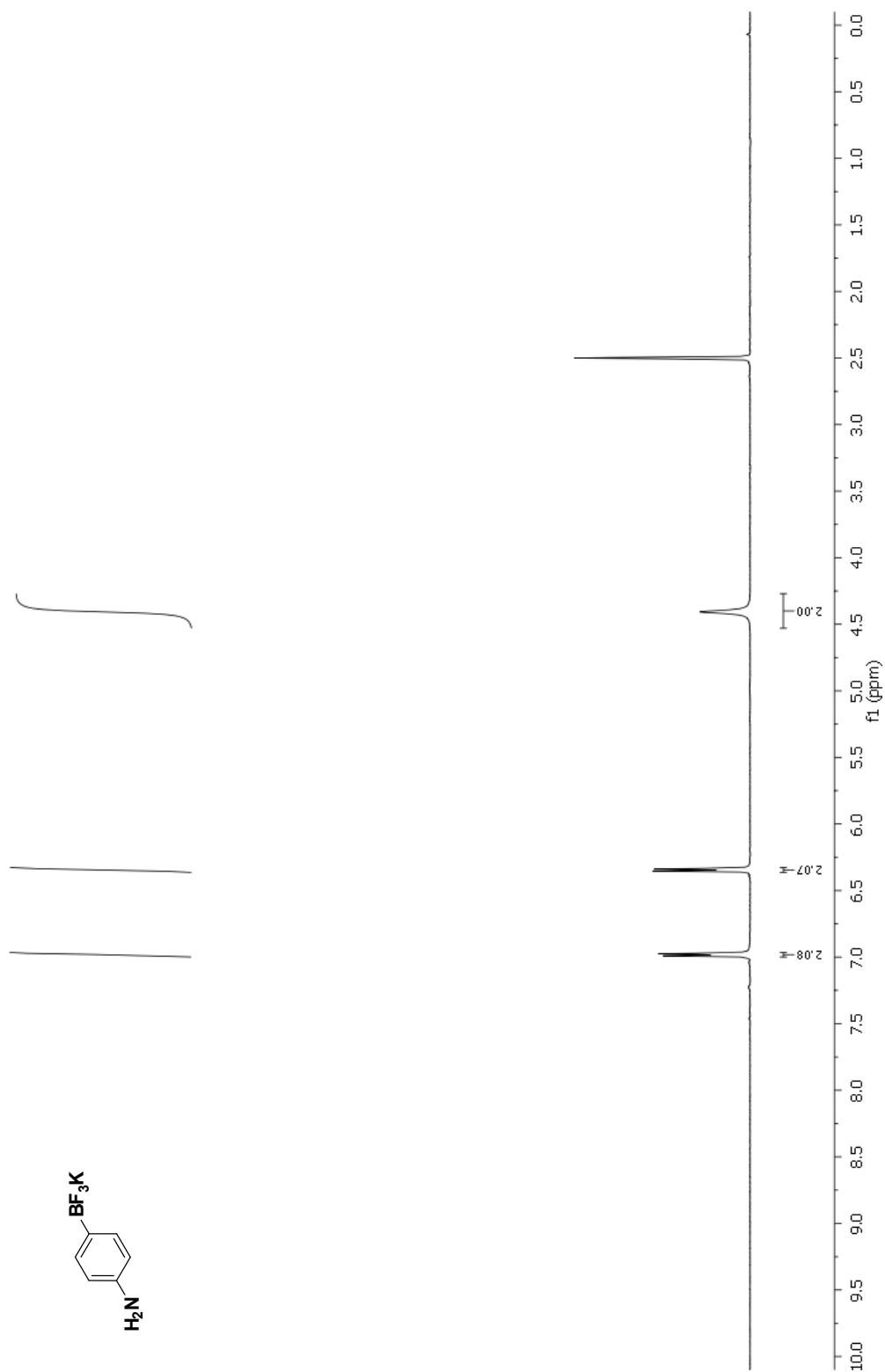


^{11}B NMR (128.4 MHz, $\text{DMSO-}d_6$) Potassium 3-Trifluoroborato-benzoic acid (Table 1, entry 8)

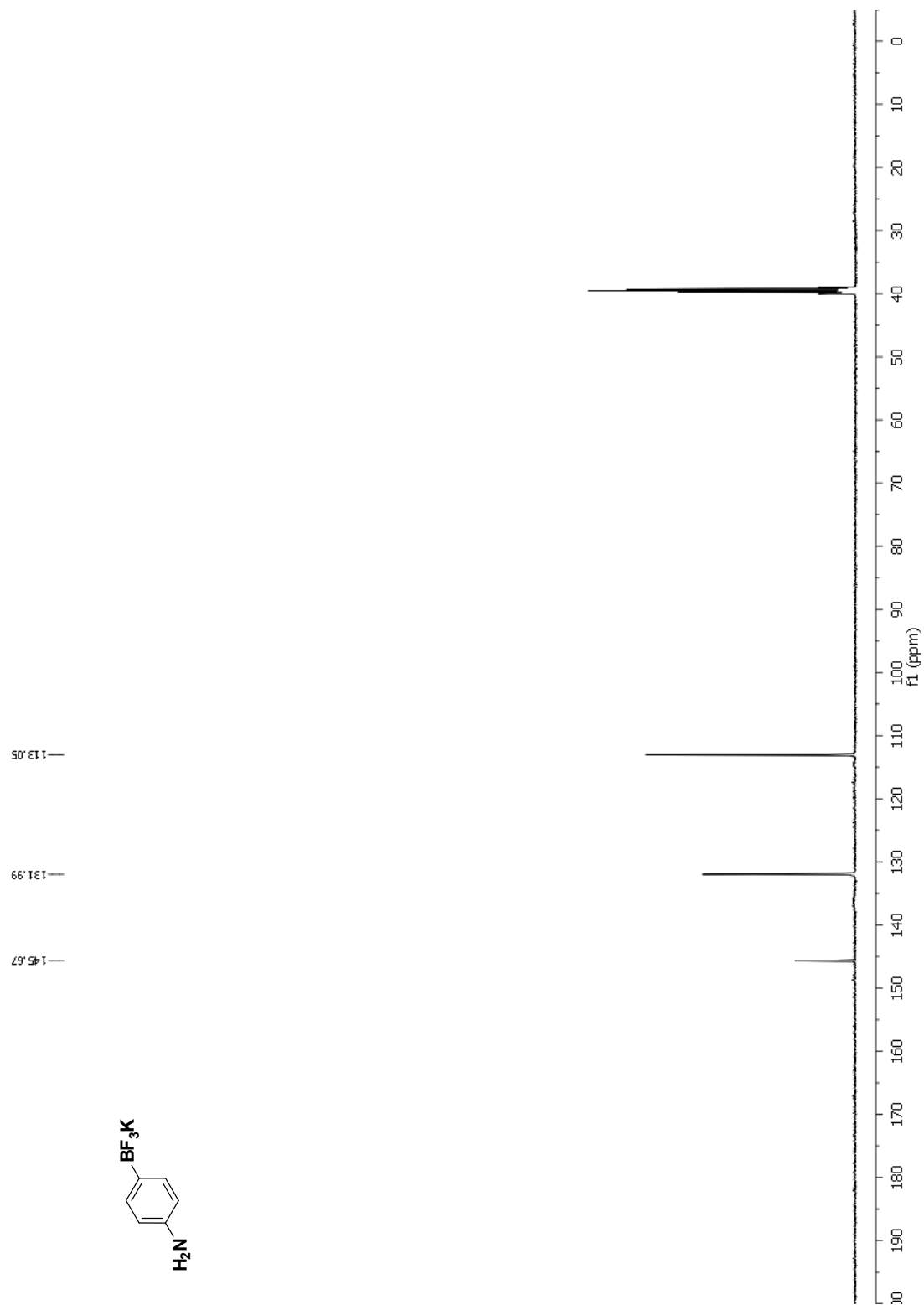
—139.57



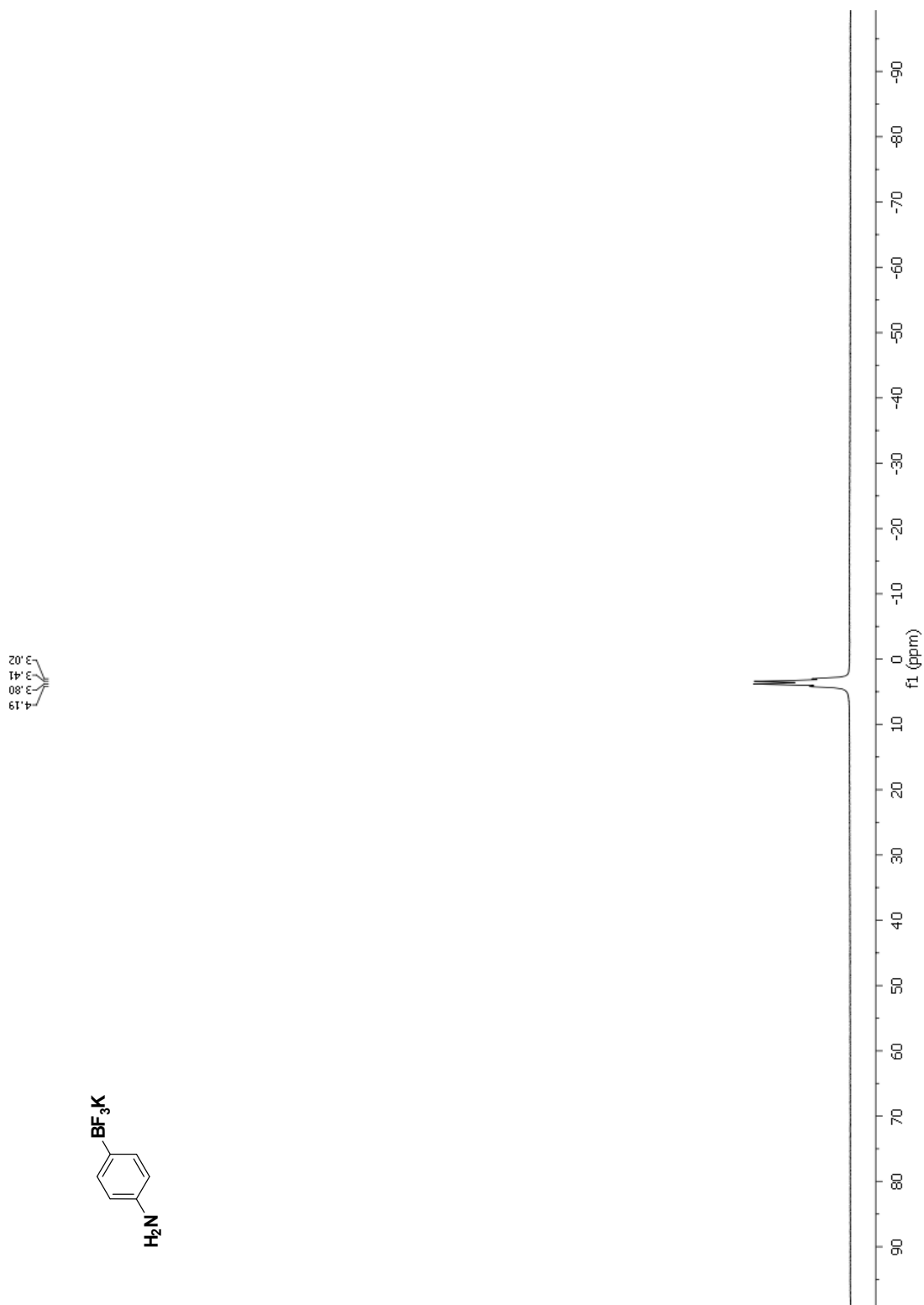
^{19}F NMR (282 MHz, $\text{DMSO-}d_6$) Potassium 3-Trifluoroborato-benzoic acid (Table 1, entry 8)



¹H NMR Spectra (500 MHz, DMSO-*d*₆) **Potassium 4-Aminophenyl-trifluoroborate** (Table 1, entry 9)

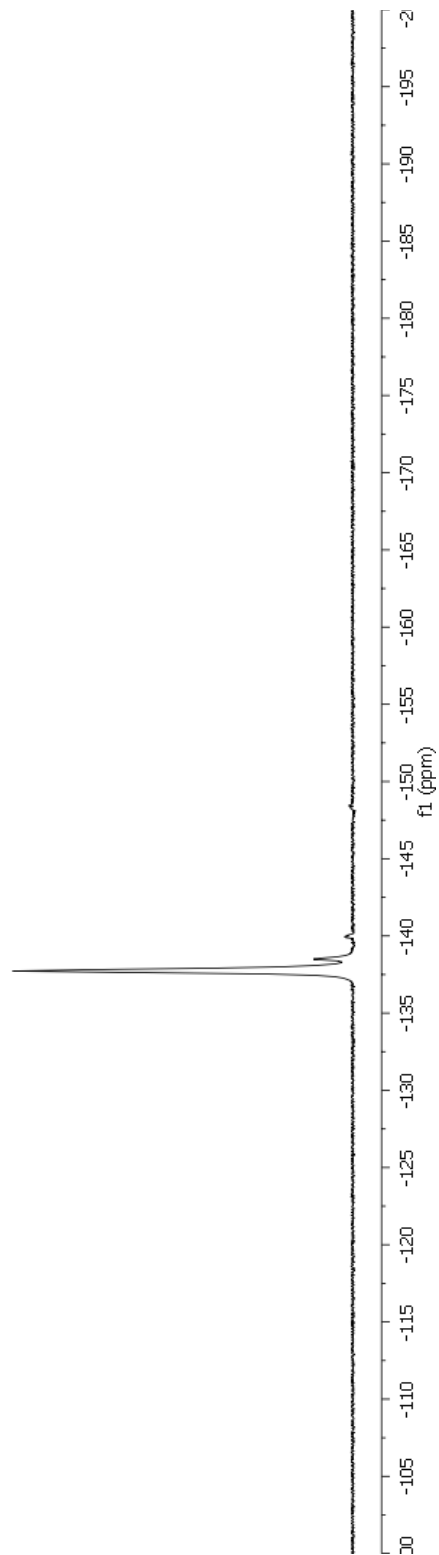
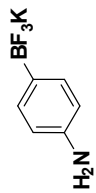


^{13}C NMR Spectra (125.8 MHz, $\text{DMSO-}d_6$) Potassium 4-Aminophenyl-trifluoroborate (Table 1, entry 9)

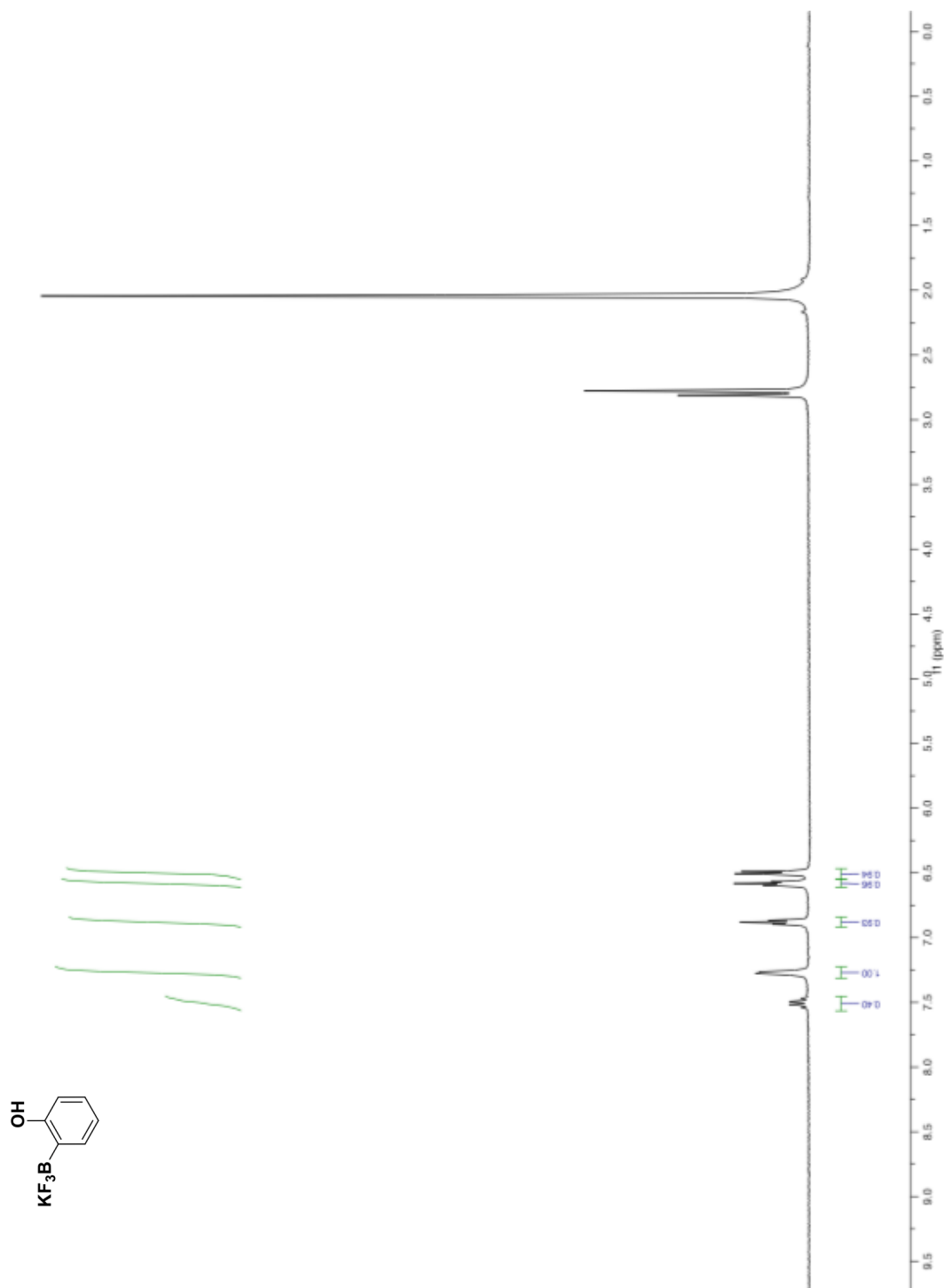


^{11}B NMR Spectra (128.4 MHz, $\text{DMSO-}d_6$) **Potassium 4-Aminophenyl-trifluoroborate**
(Table 1, entry 9)

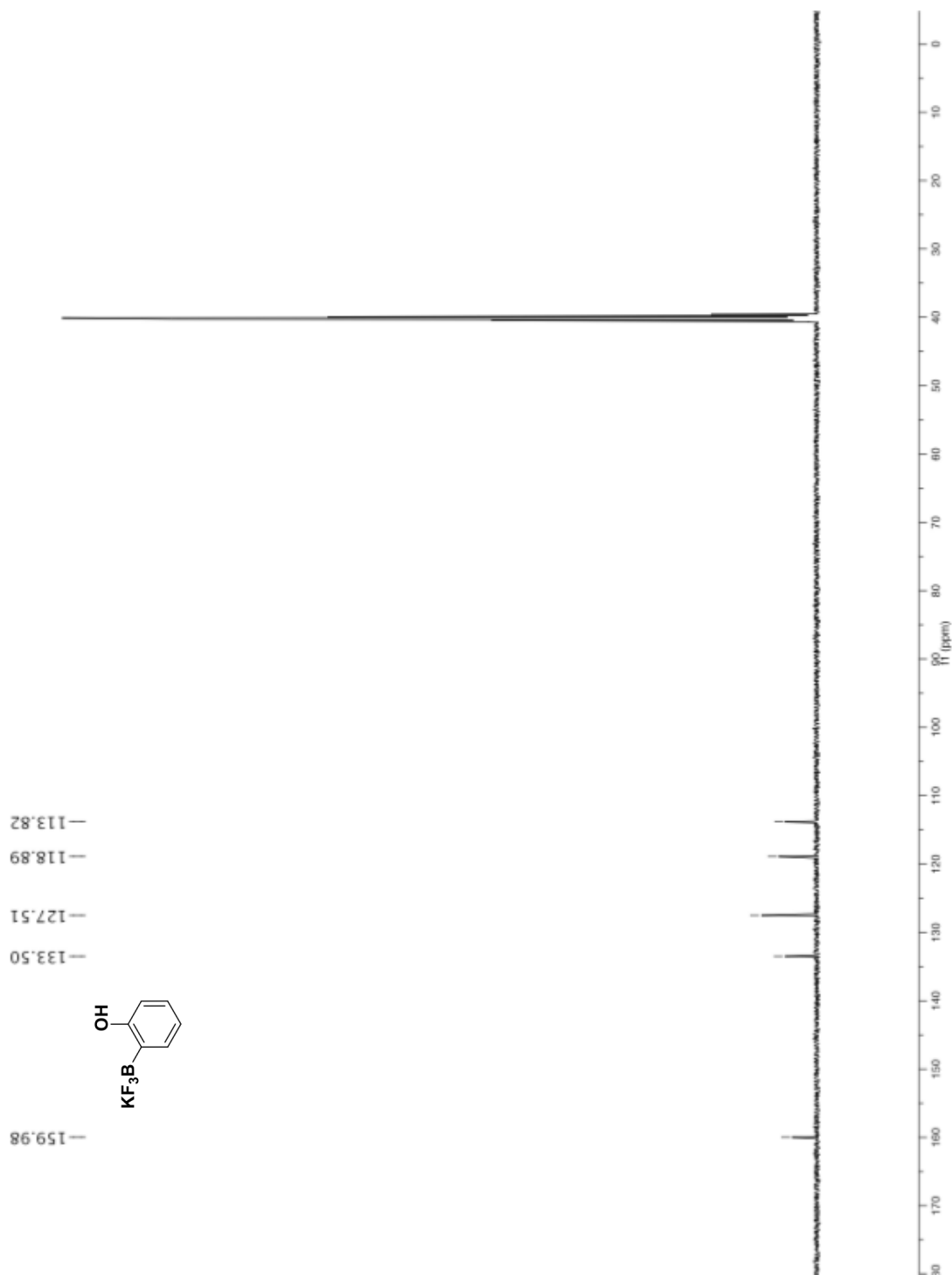
—137.72



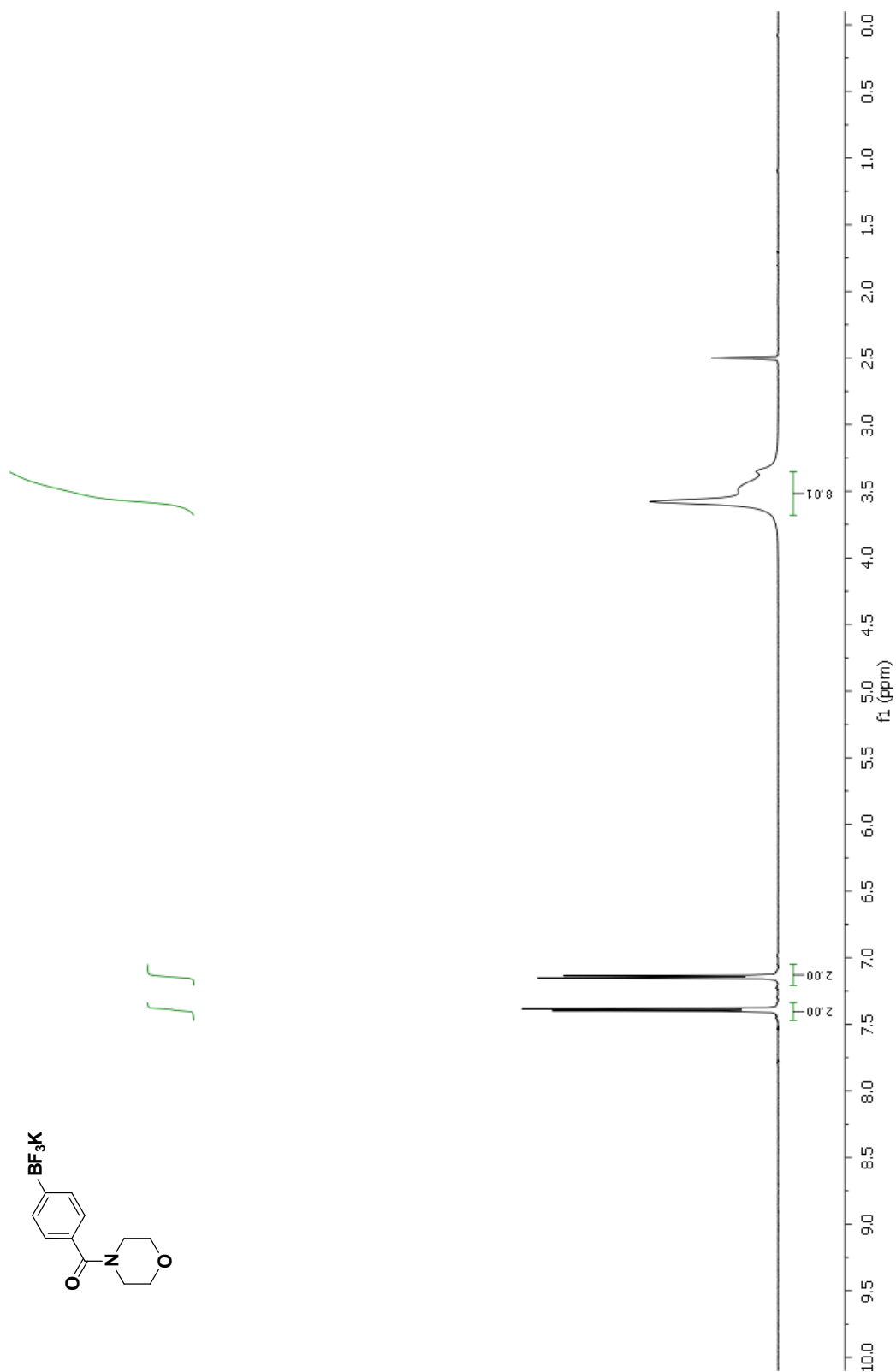
¹⁹F NMR Spectra (282 MHz, DMSO-*d*₆) **Potassium 4-Aminophenyl-trifluoroborate**
(Table 1, entry 9)



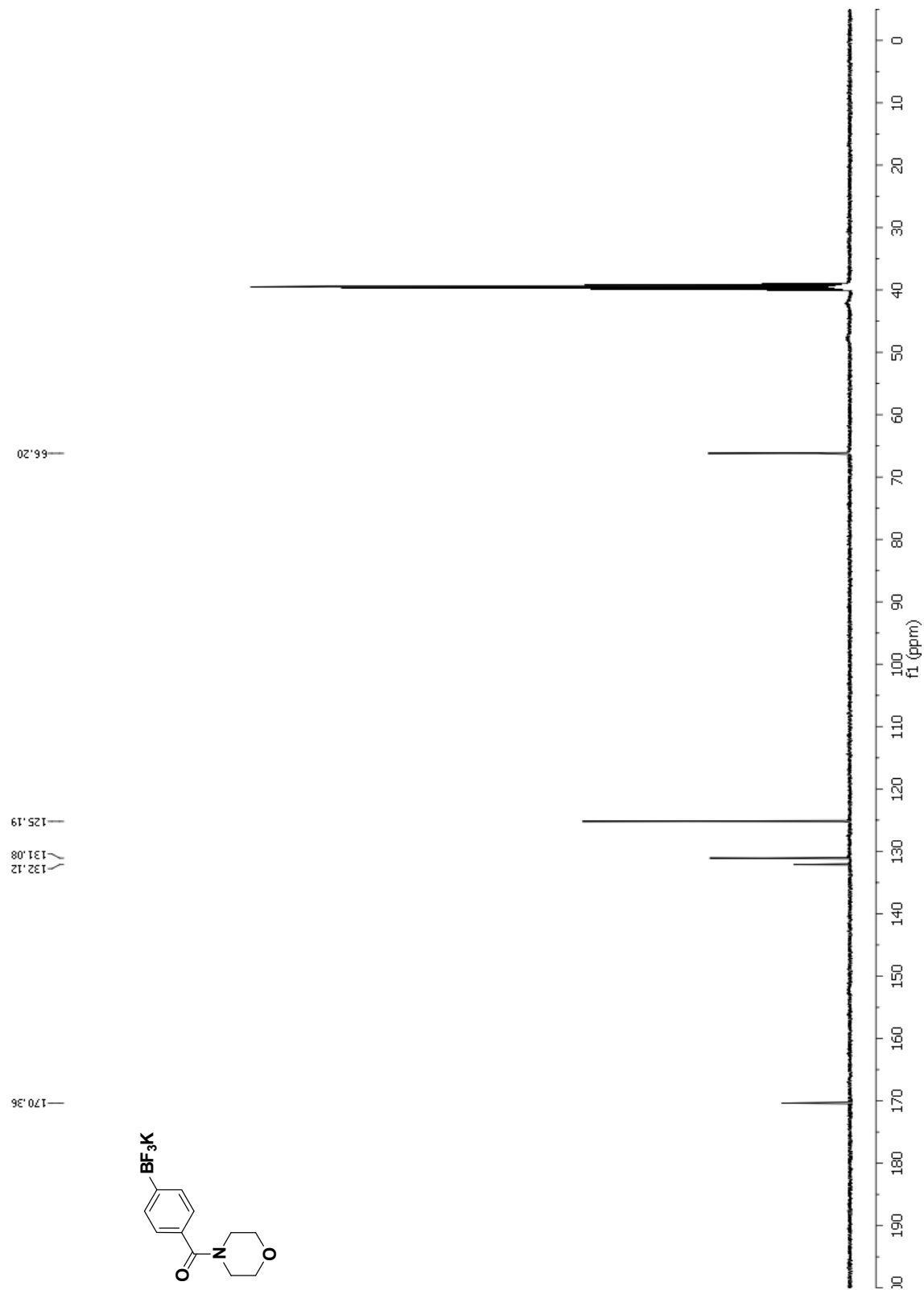
¹H NMR Spectra (500 MHz, acetone-*d*₆) **2-Hydroxyphenyltrifluoroborate (Table 1, entry 11).**



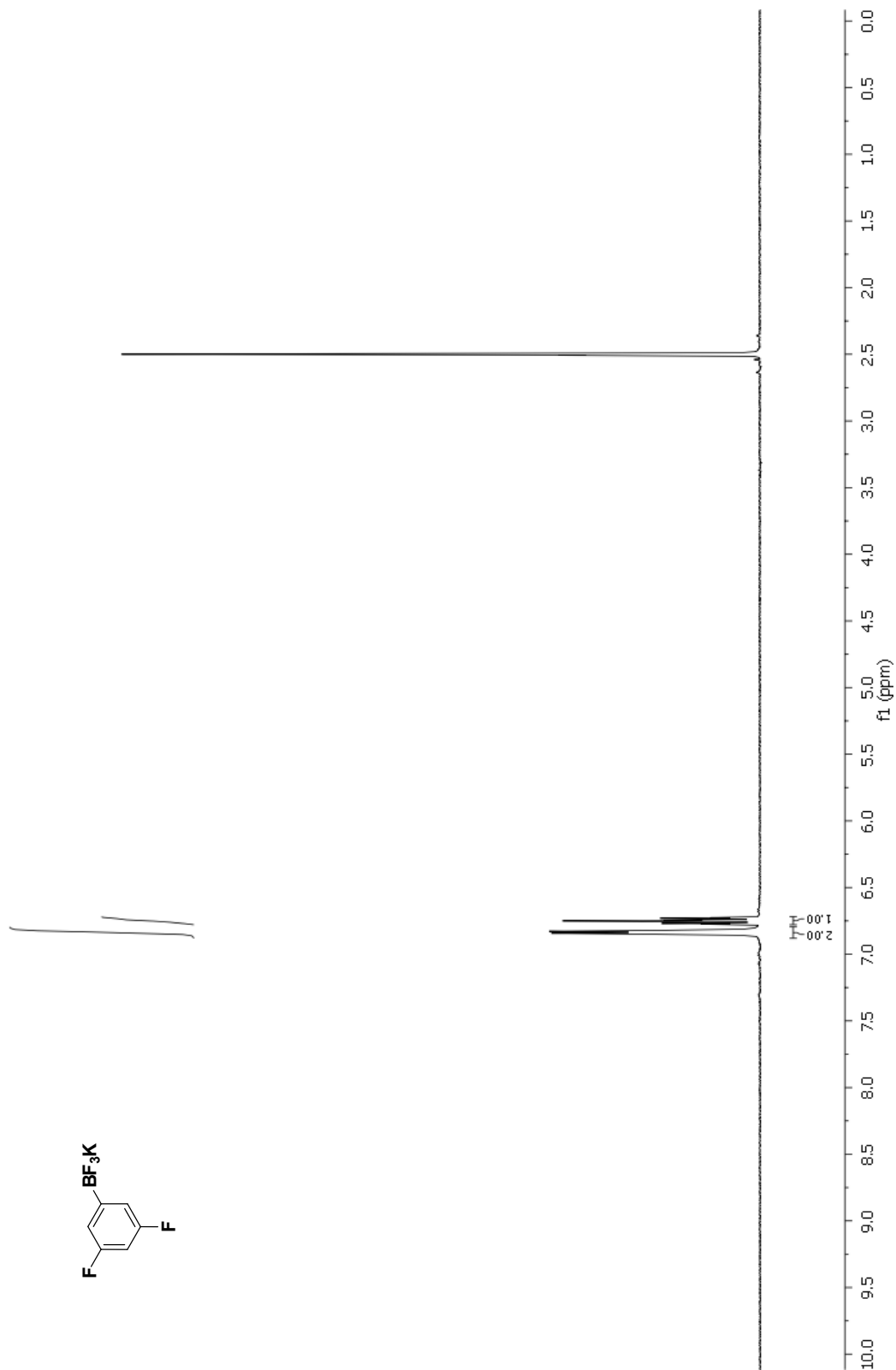
^{13}C NMR Spectra (125.8 MHz, $\text{DMSO-}d_6$) 2-Hydroxyphenyltrifluoroborate (Table 1, entry 11).



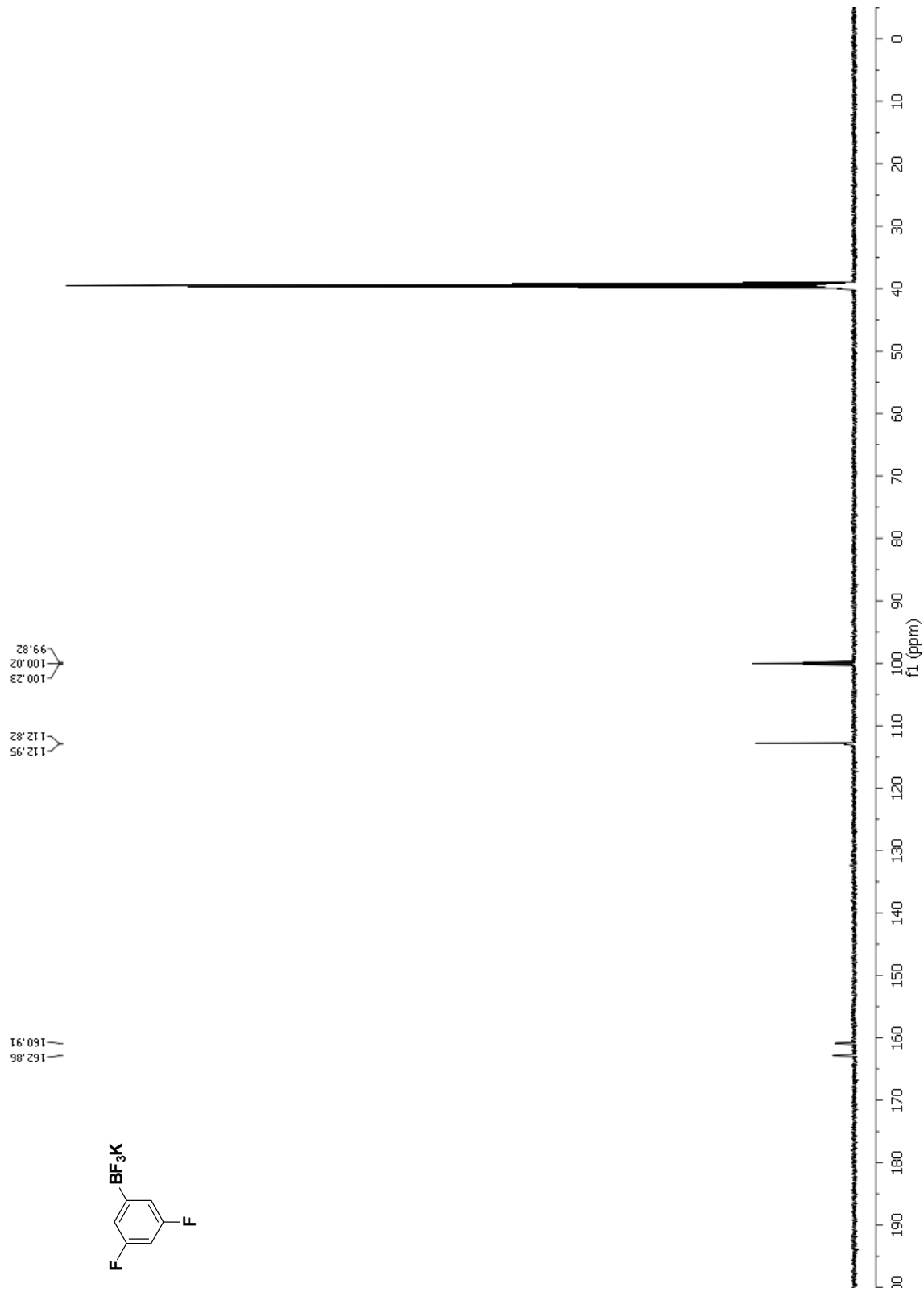
¹H NMR Spectra (500 MHz, DMSO-*d*₆) Potassium 4-(Morpholine-4-carbonyl)phenyltrifluoroborate (Table 1, entry 12)



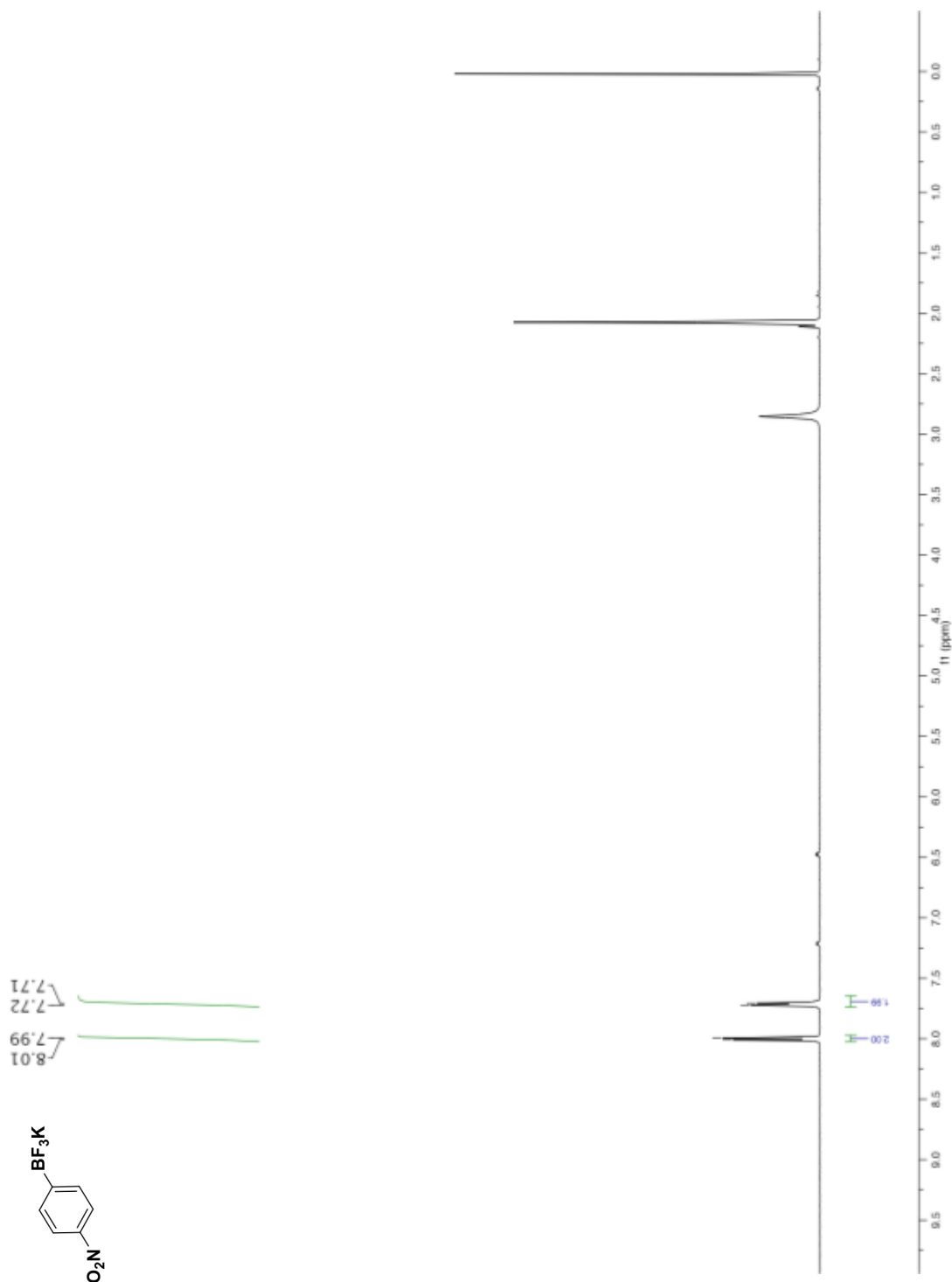
¹³C NMR Spectra (125.8 MHz, DMSO-*d*₆) Potassium 4-(Morpholine-4-carbonyl)phenyl-trifluoroborate (Table 1, entry 12)



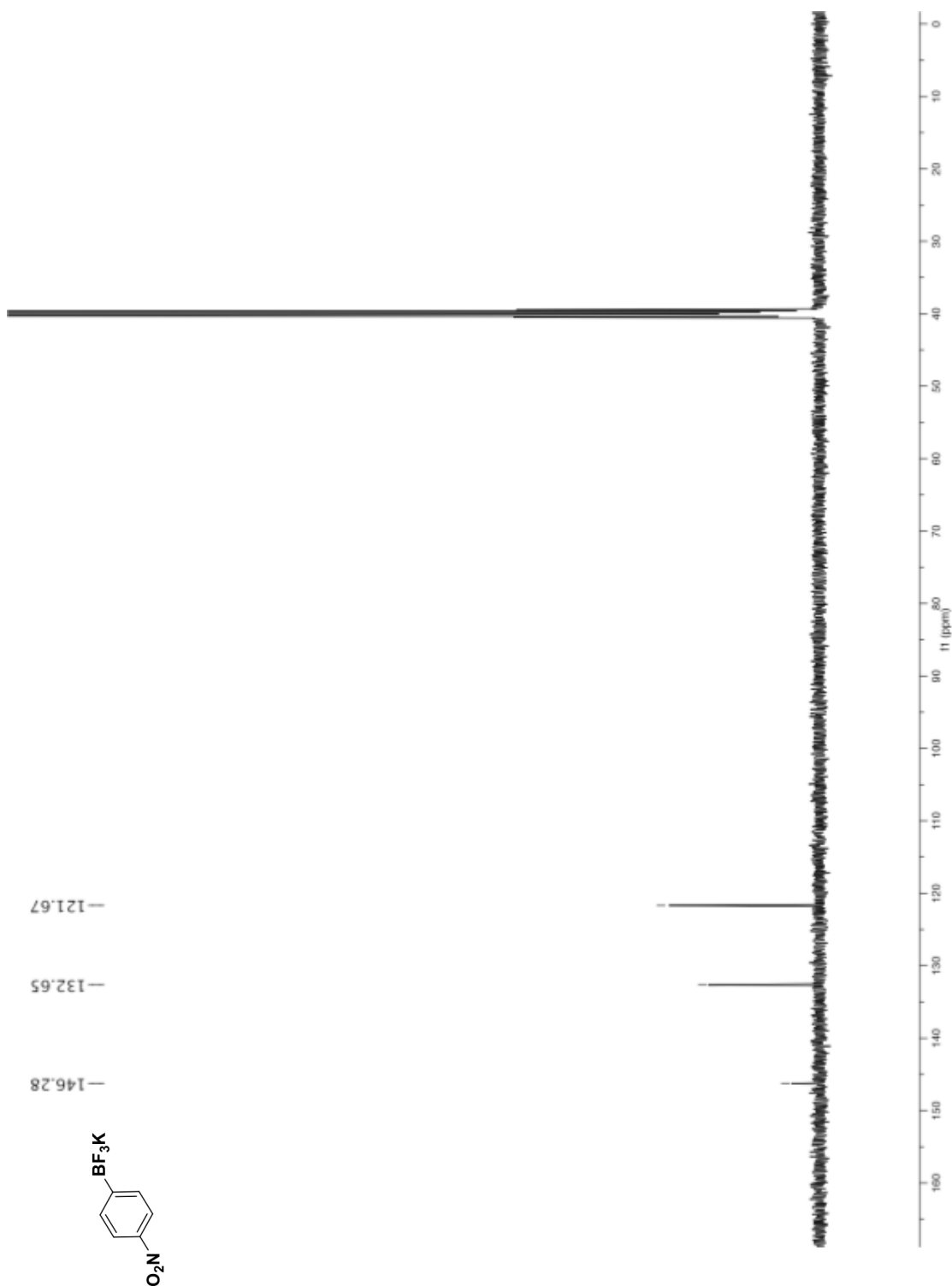
¹H NMR Spectra (500 MHz, DMSO-*d*₆) Potassium 3,5-Difluorophenyl-trifluoroborate (Table 1, entry 13)



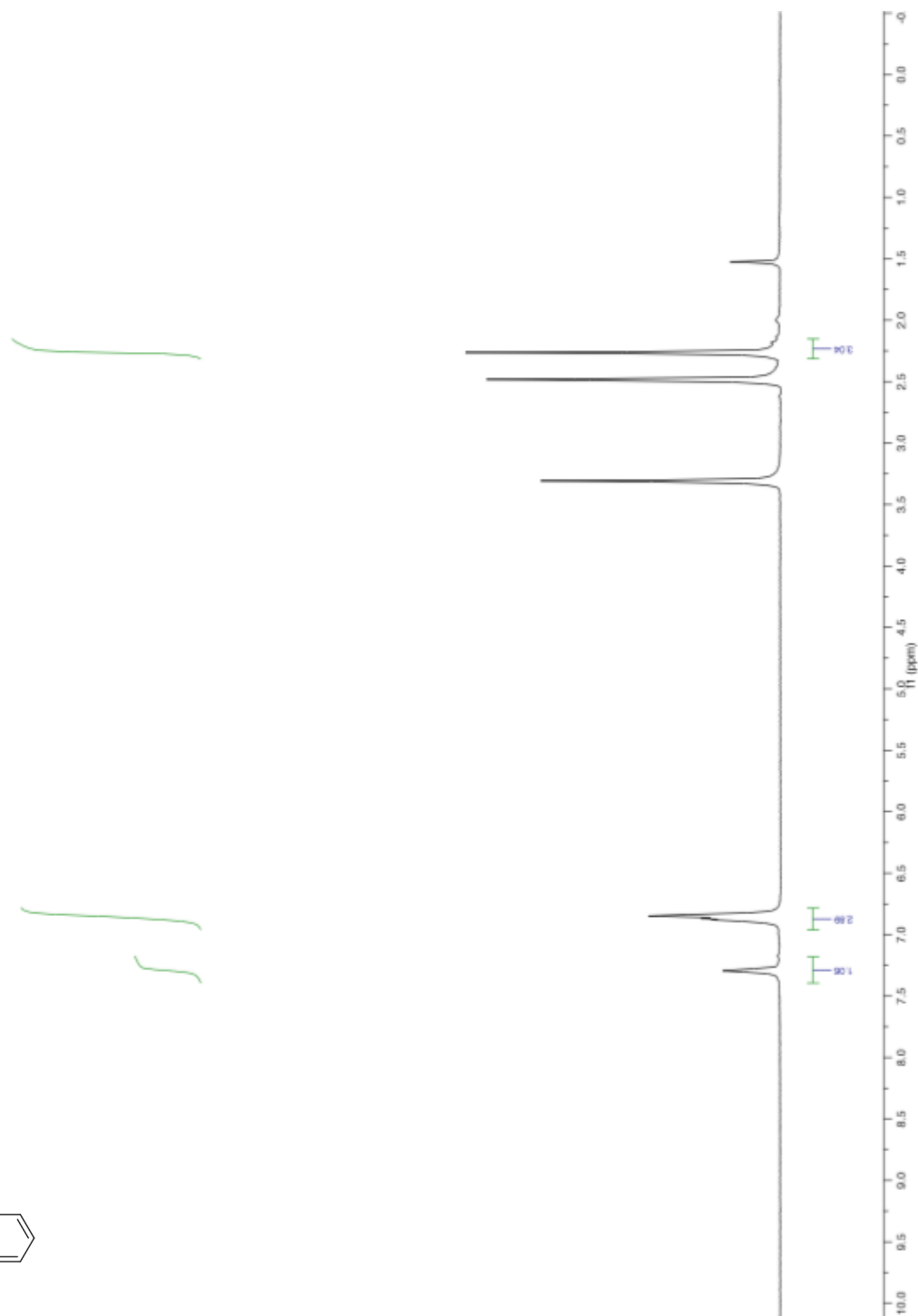
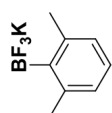
¹H NMR Spectra (500 MHz, DMSO-*d*₆) Potassium 3,5-Difluorophenyl-trifluoroborate (Table 1, entry 13)



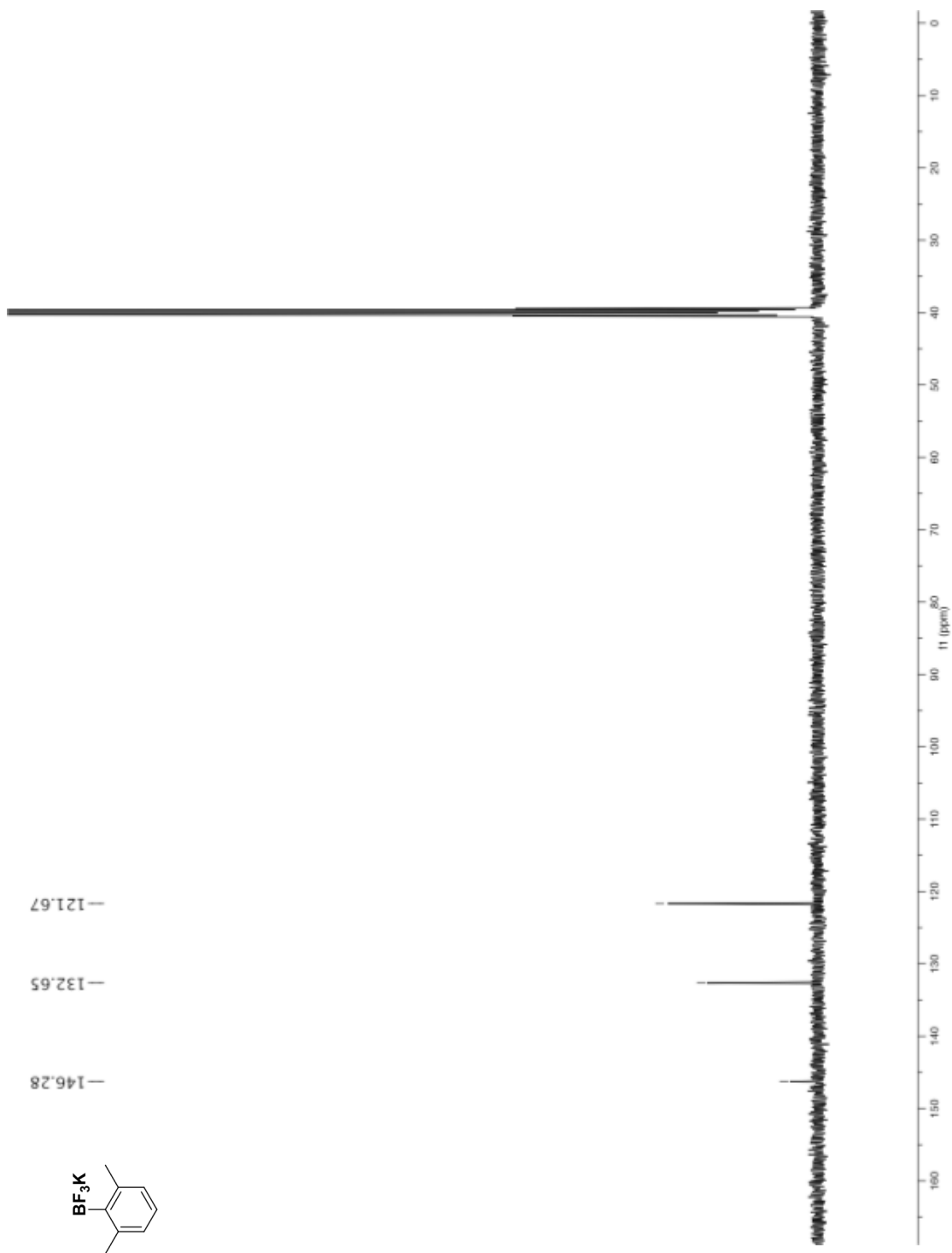
¹H NMR (500 MHz, acetone-*d*₆) Potassium (4-Nitrophenyl)trifluoroborate (Table 1, entry 14).



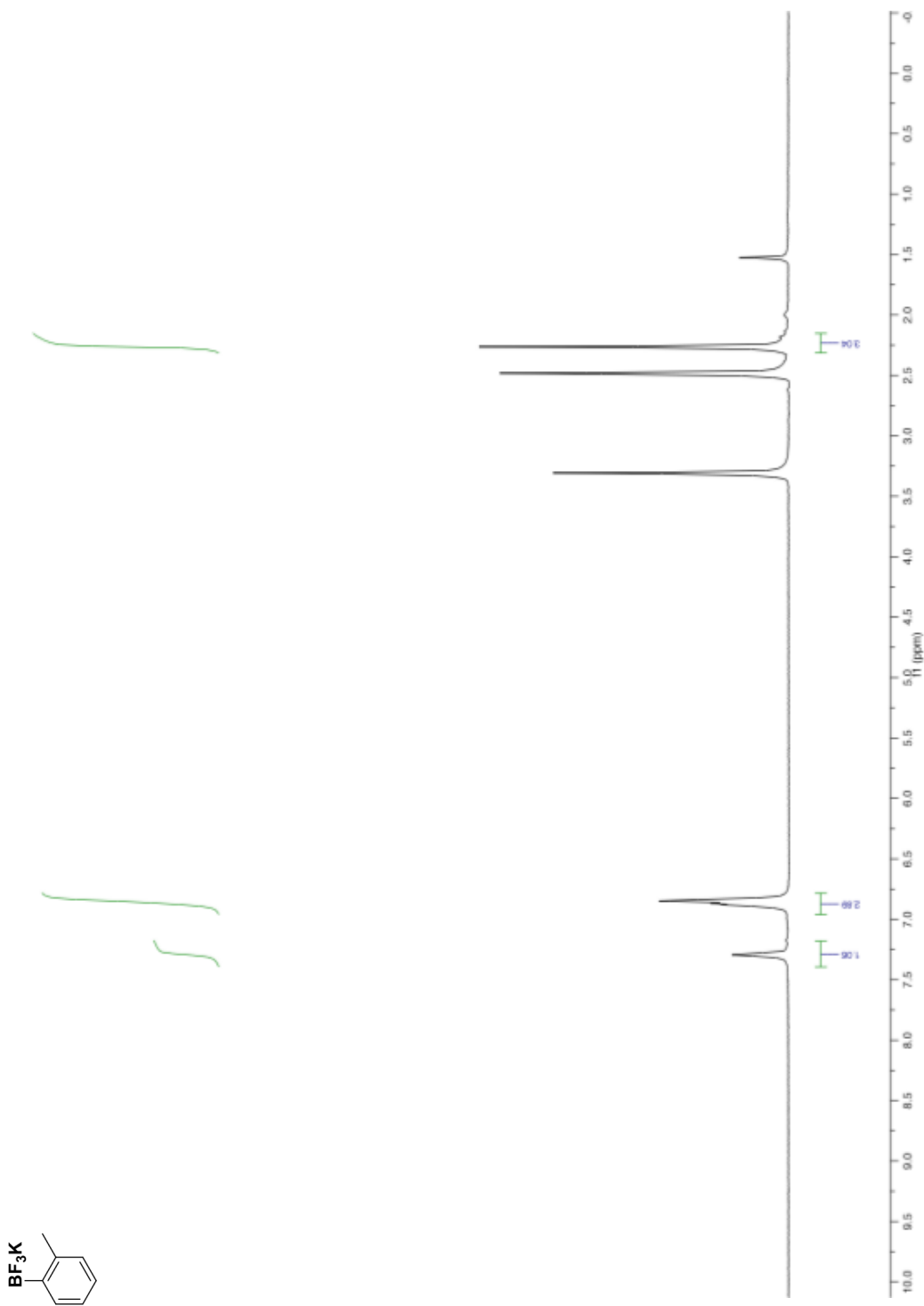
^{13}C NMR (125.8 MHz, $\text{DMSO-}d_6$) Potassium (4-Nitrophenyl)trifluoroborate (Table 1, entry 14).



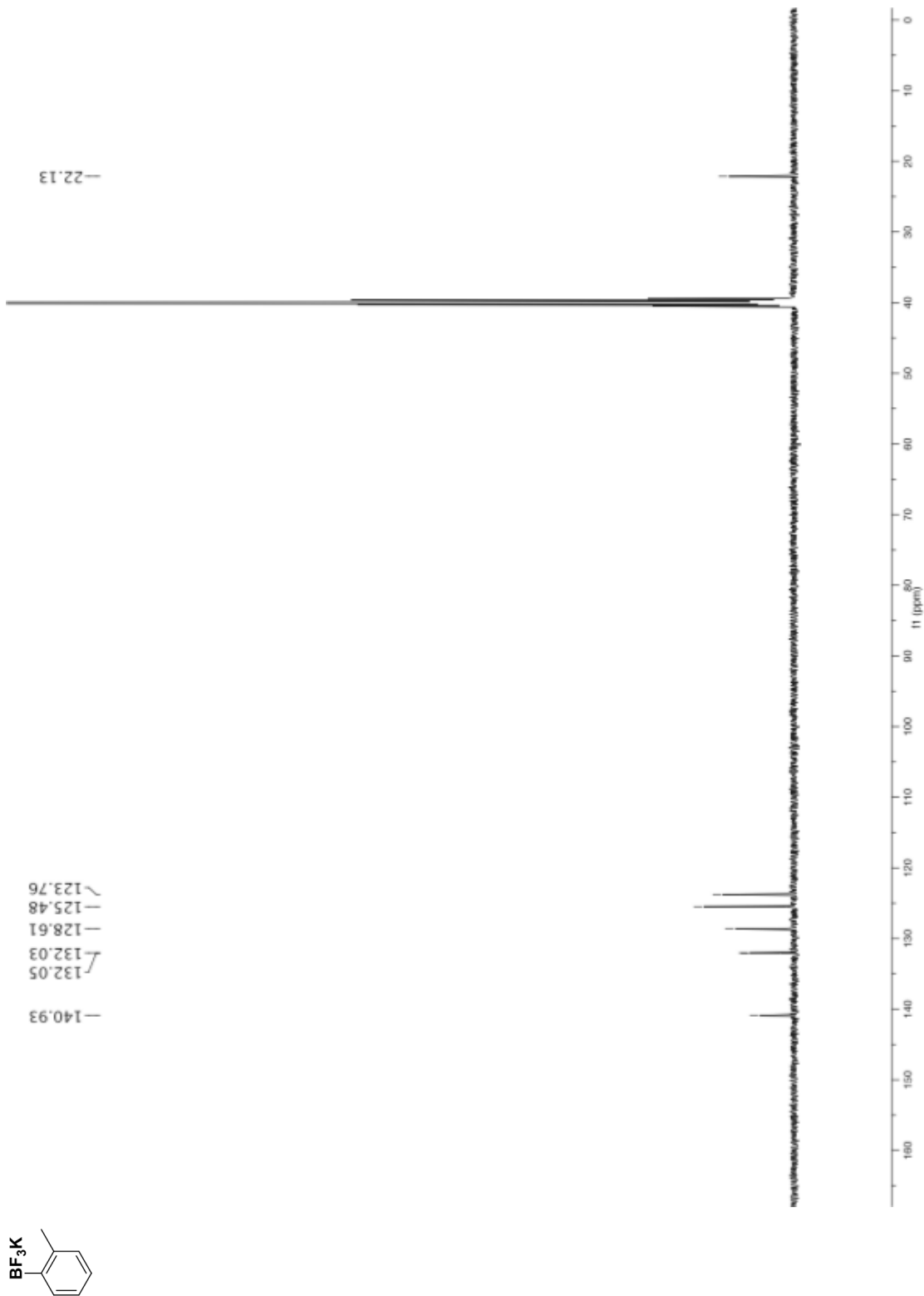
¹H NMR (500 MHz, acetone-*d*₆) (2,6-Dimethylphenyl)trifluoroborate (Table 1, entry 15).



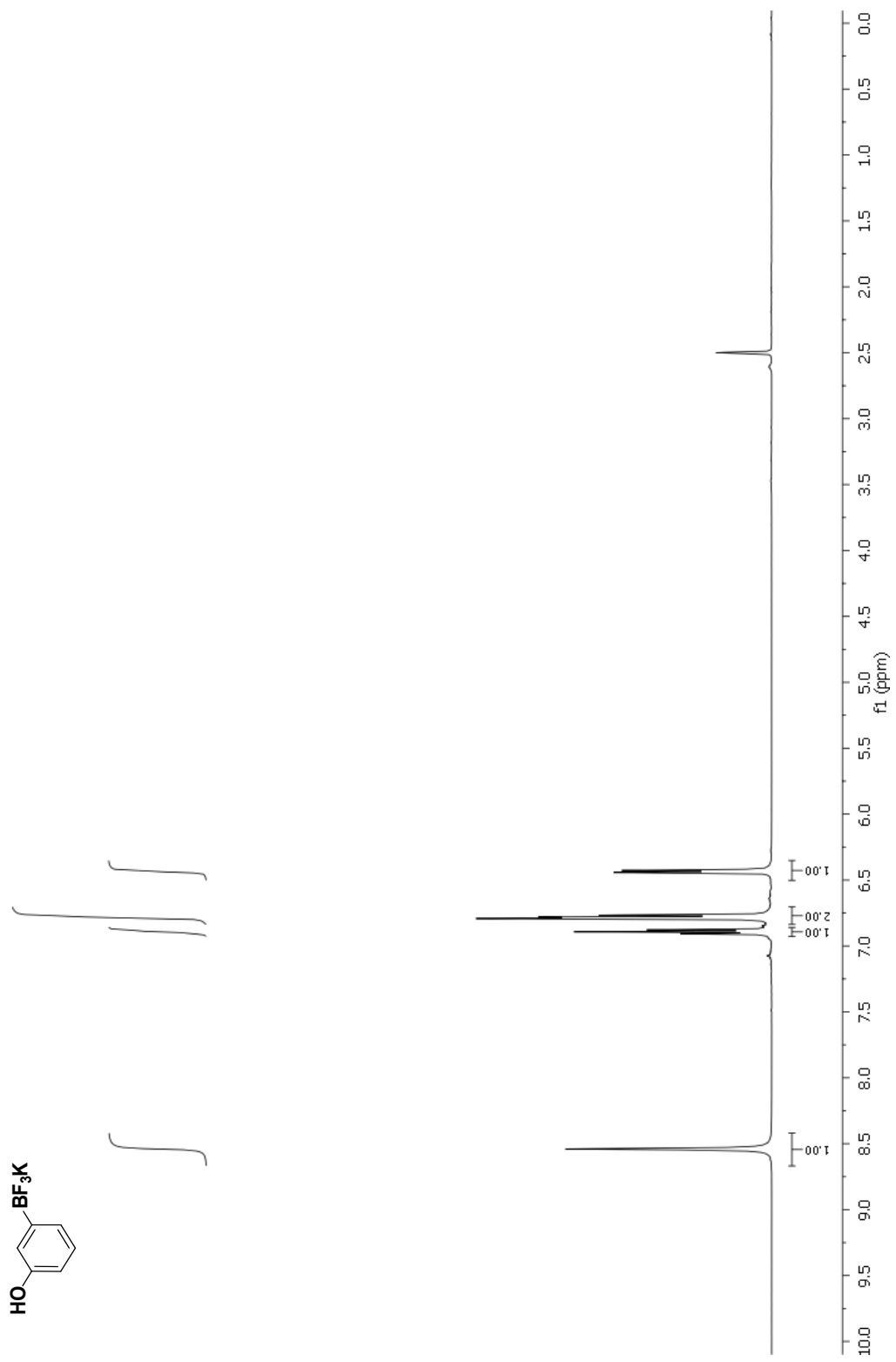
^{13}C NMR (125.8 MHz, $\text{DMSO-}d_6$) (2,6-Dimethylphenyl)trifluoroborate (Table 1, entry 15).



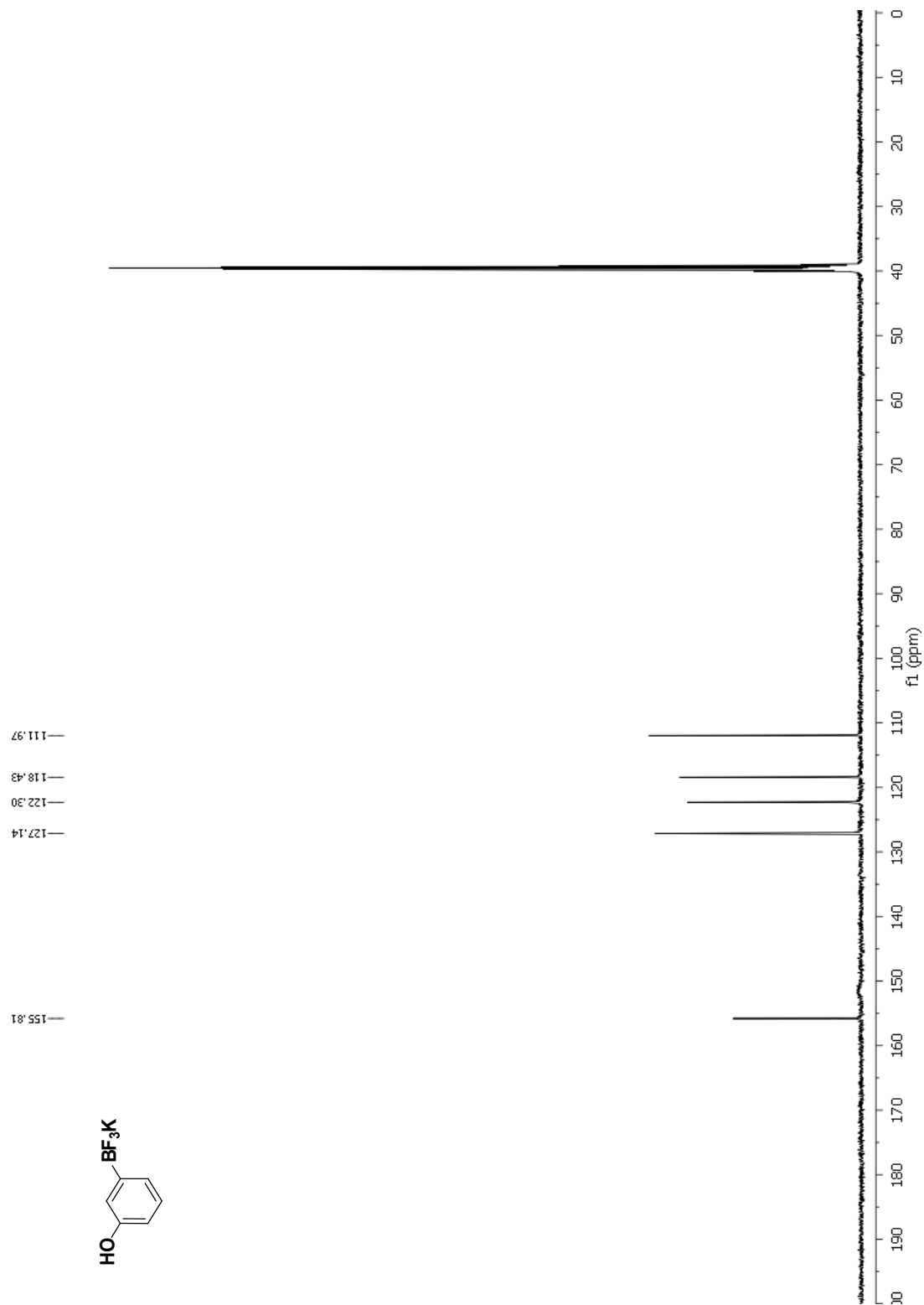
¹H NMR (500 MHz, acetone-*d*₆) Potassium *o*-Tolyltrifluoroborate (Table 1, entry 16).



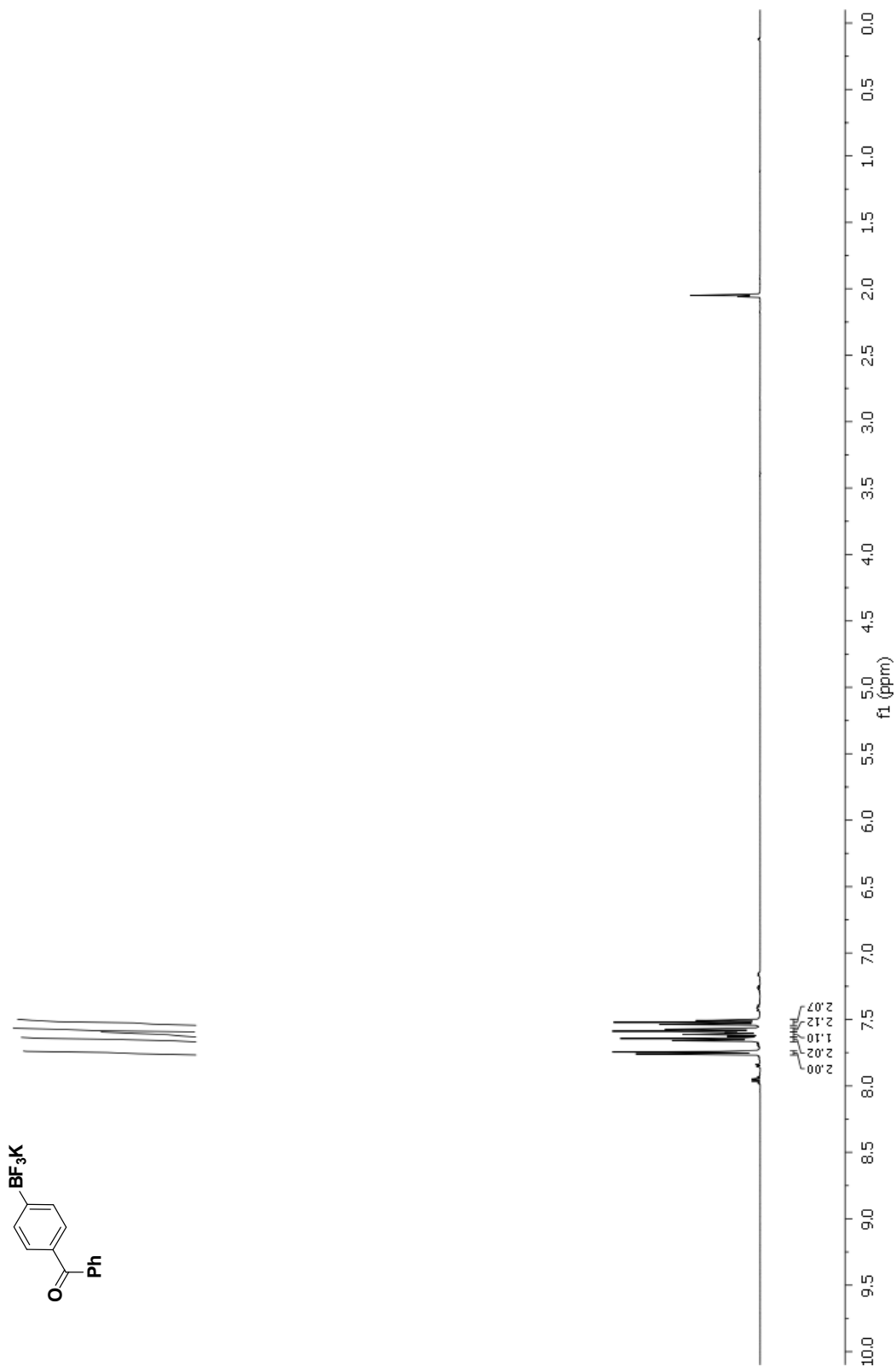
¹³C NMR 125.8 MHz, DMSO-*d*₆) Potassium *o*-Tolyltrifluoroborate (Table 1, entry 16).



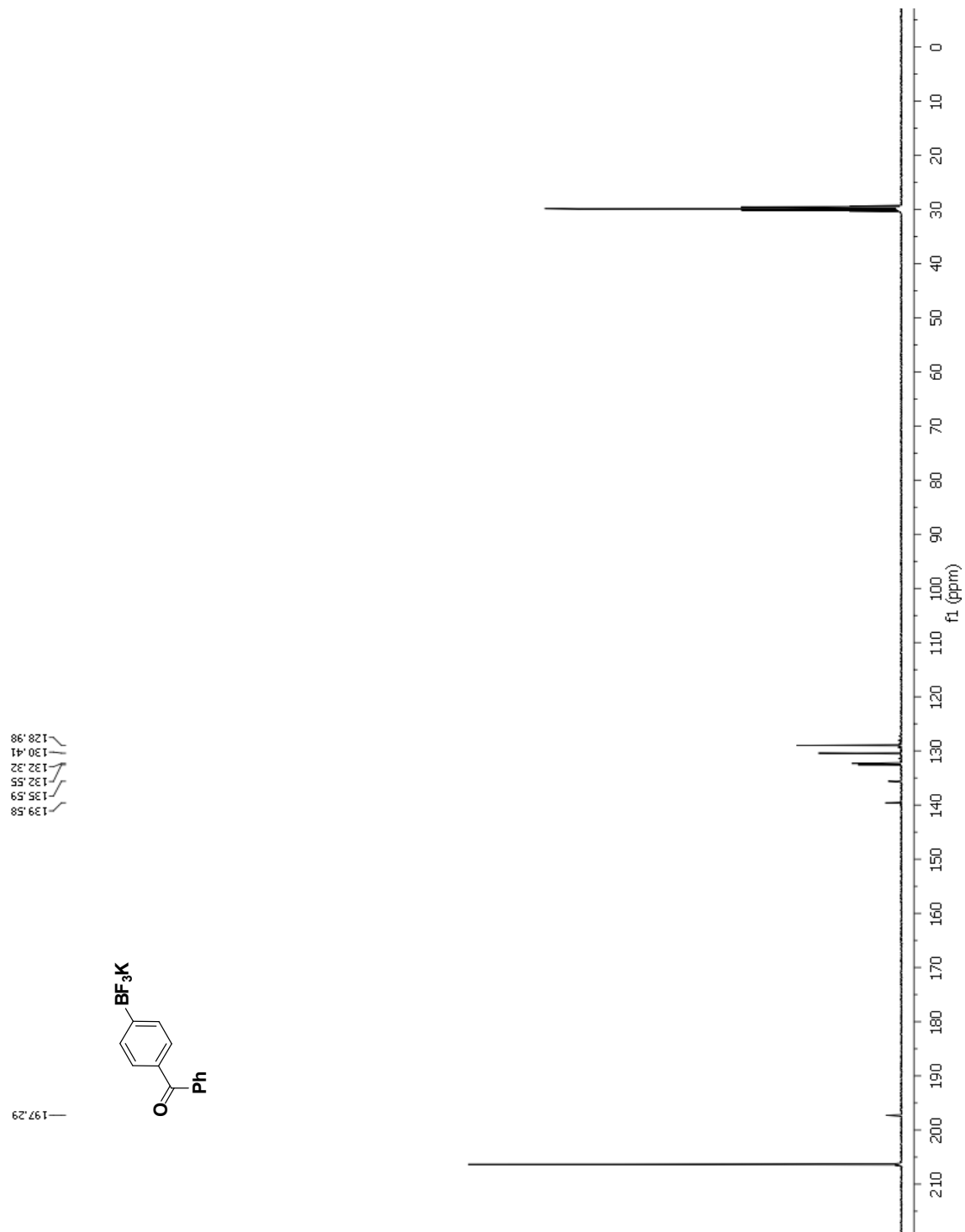
¹H NMR Spectra (500 MHz, DMSO-*d*₆) Potassium 3-Hydroxyphenyl-trifluoroborate (Table 1, entry 18)



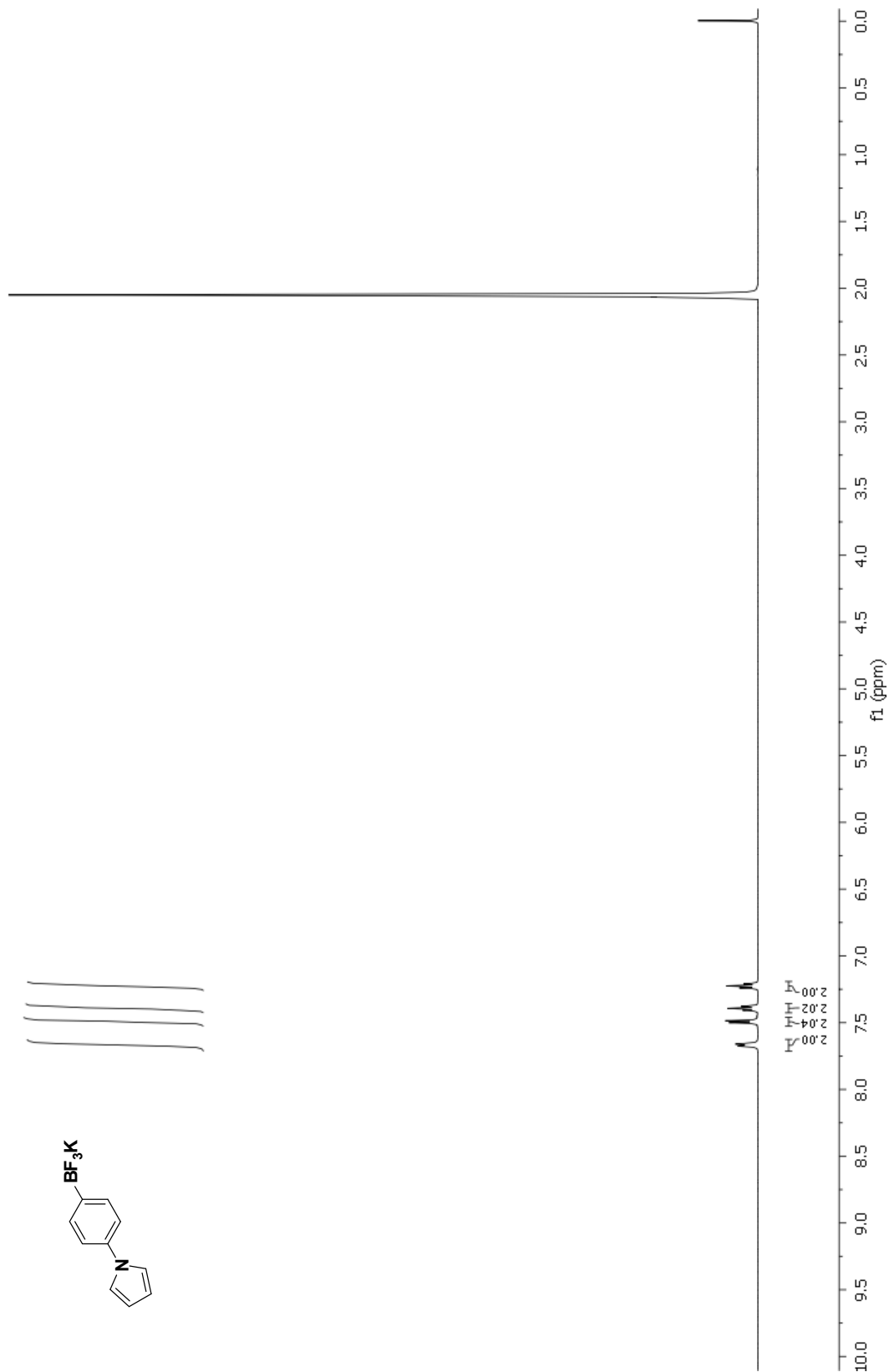
¹³C NMR Spectra (125.8 MHz, DMSO-*d*₆) Potassium 3-Hydroxyphenyltrifluoroborate (Table 1, entry 18)



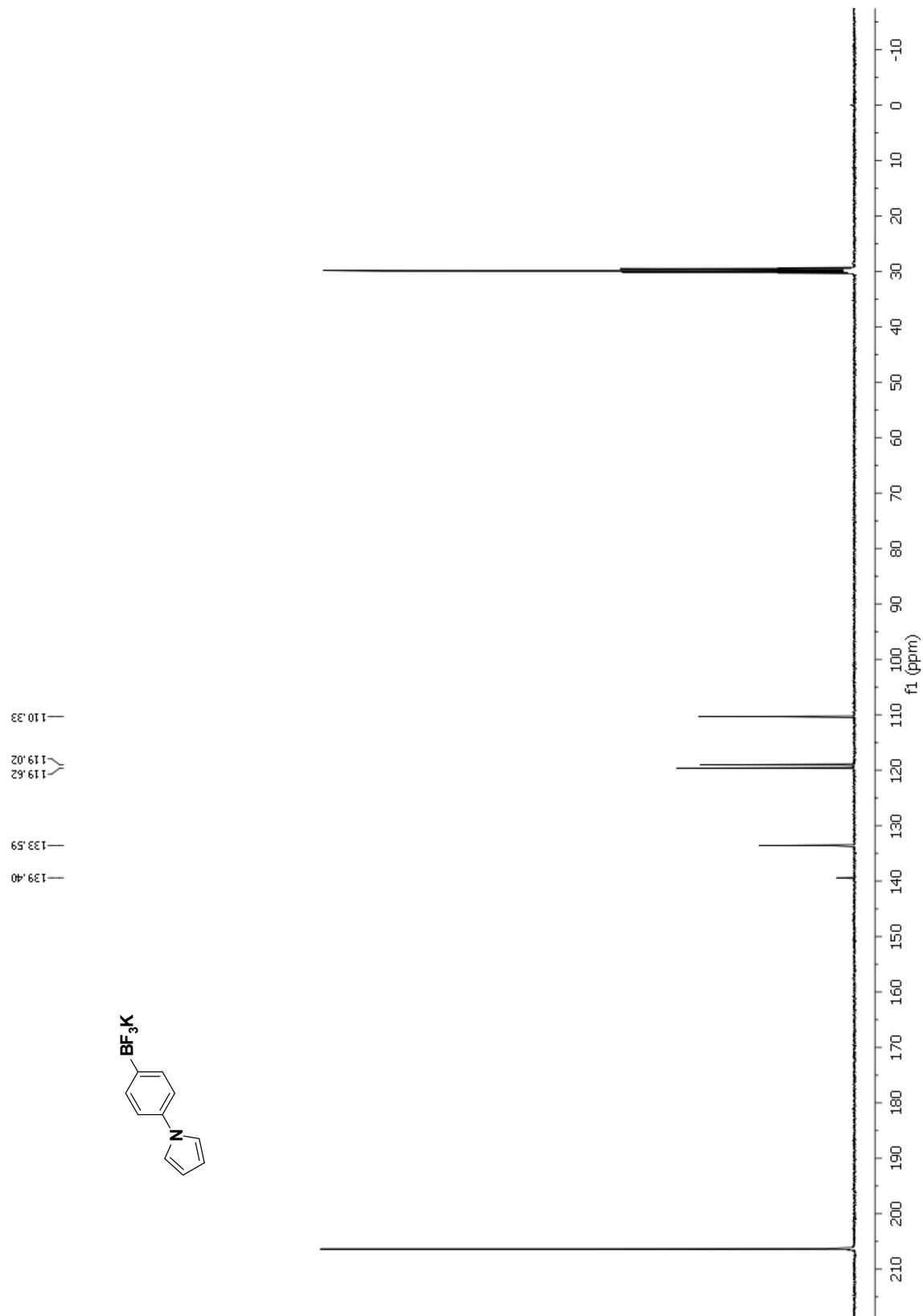
¹H NMR Spectra (500 MHz, acetone-*d*₆) **Potassium 4-Benzoylphenyl-trifluoroborate** (Table 1, entry 19)



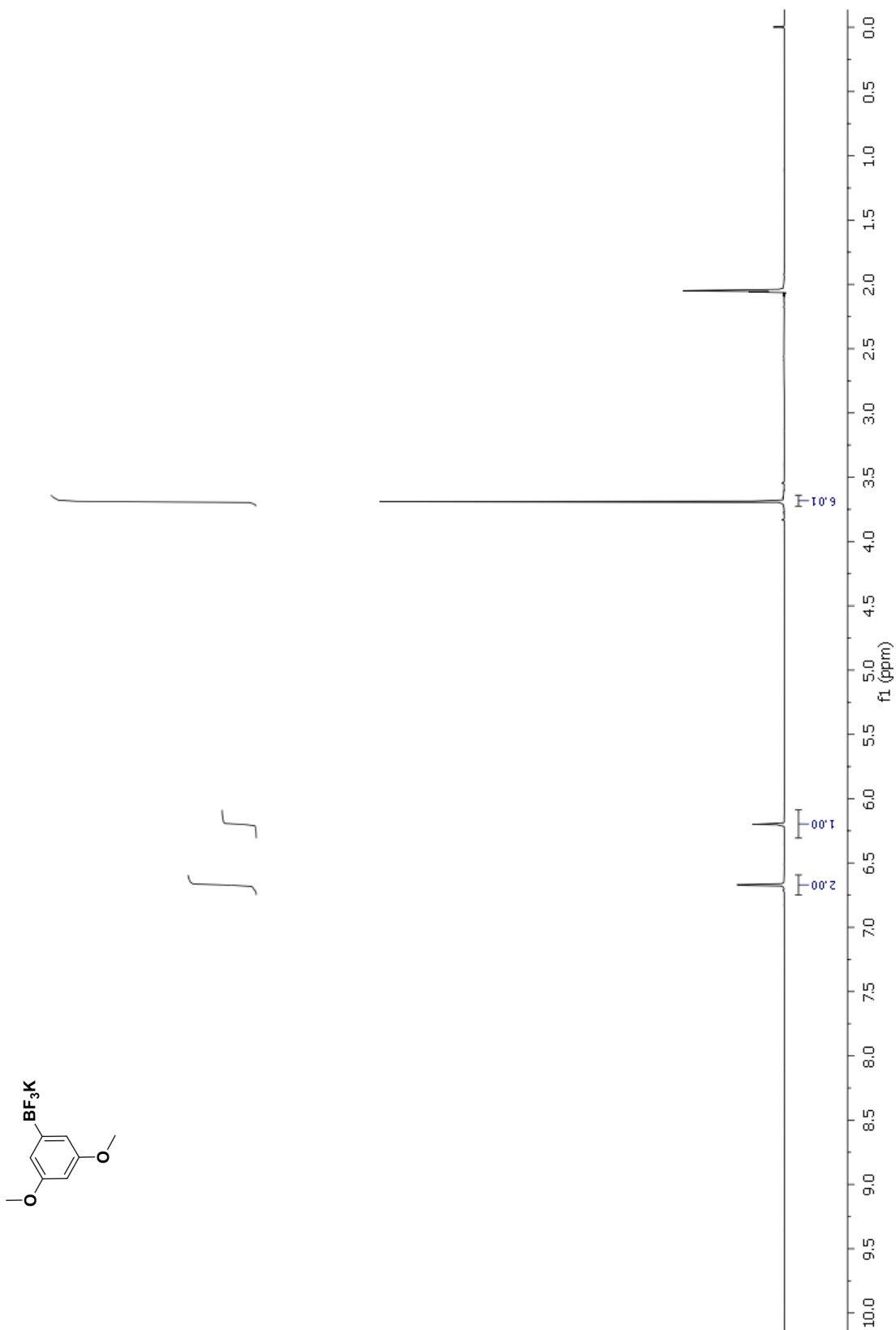
¹³C NMR Spectra (125.8 MHz, acetone-*d*₆) **Potassium 4-Benzoylphenyltrifluoroborate** (Table 1, entry 19)



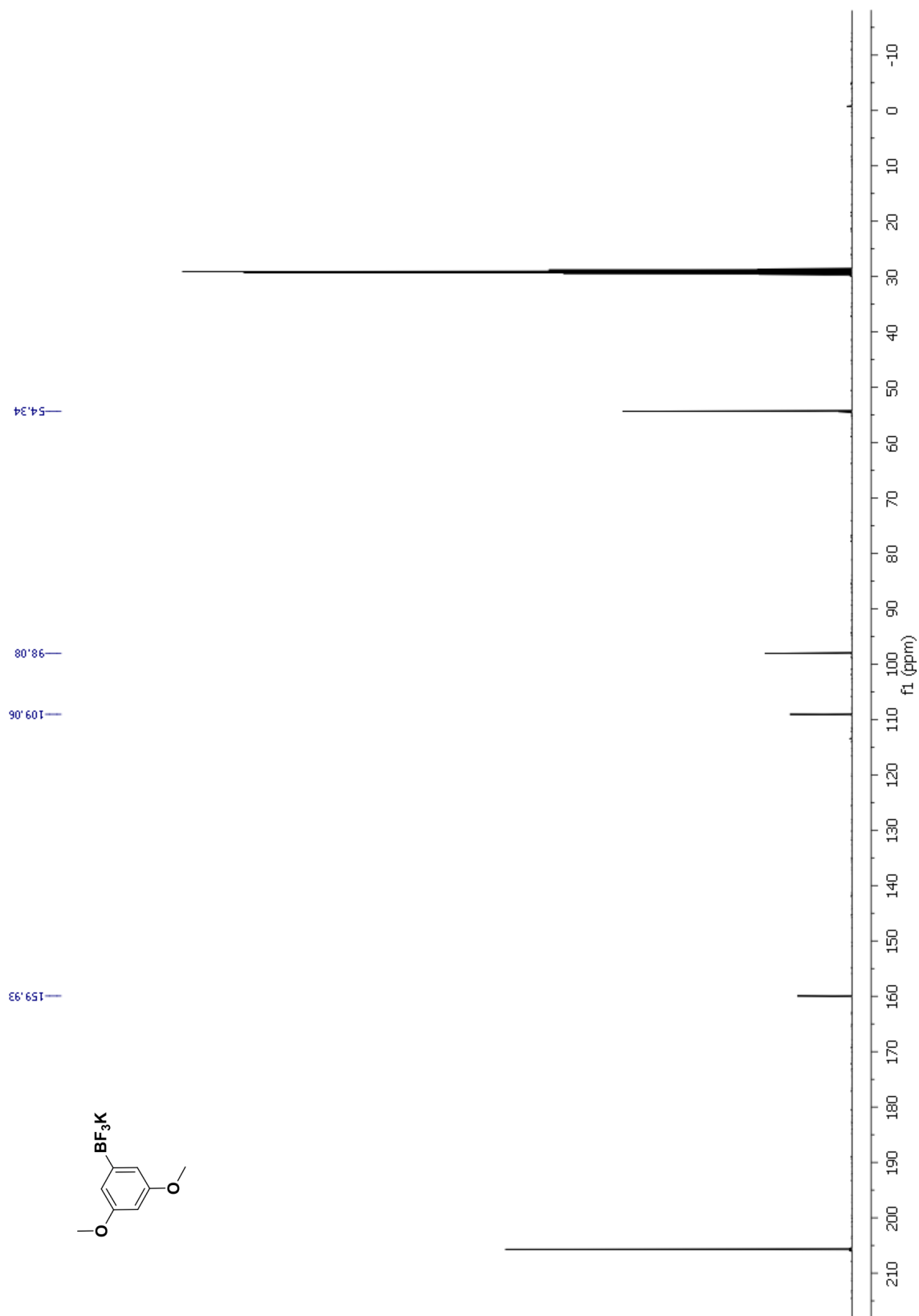
¹H NMR (500 MHz, acetone-*d*₆) Potassium 4-(1H-Pyrrol-1-yl)phenyl-trifluoroborate (Table 1, entry 21)



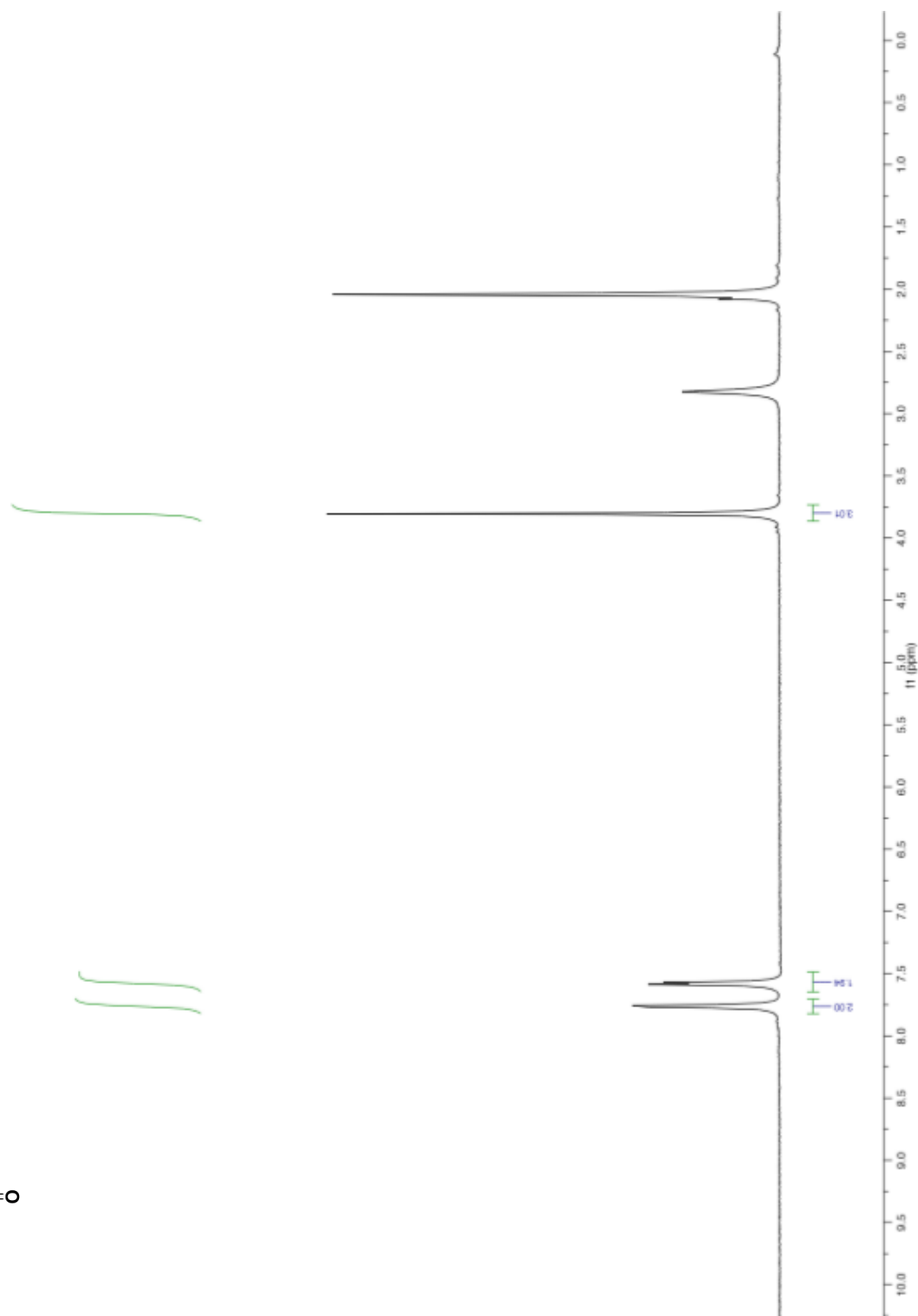
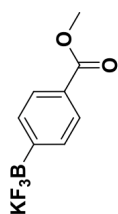
¹³C NMR Spectra (125.8 MHz, acetone-*d*₆) Potassium 4-(1H-Pyrrol-1-yl)phenyltrifluoroborate (Table 1, entry 21)



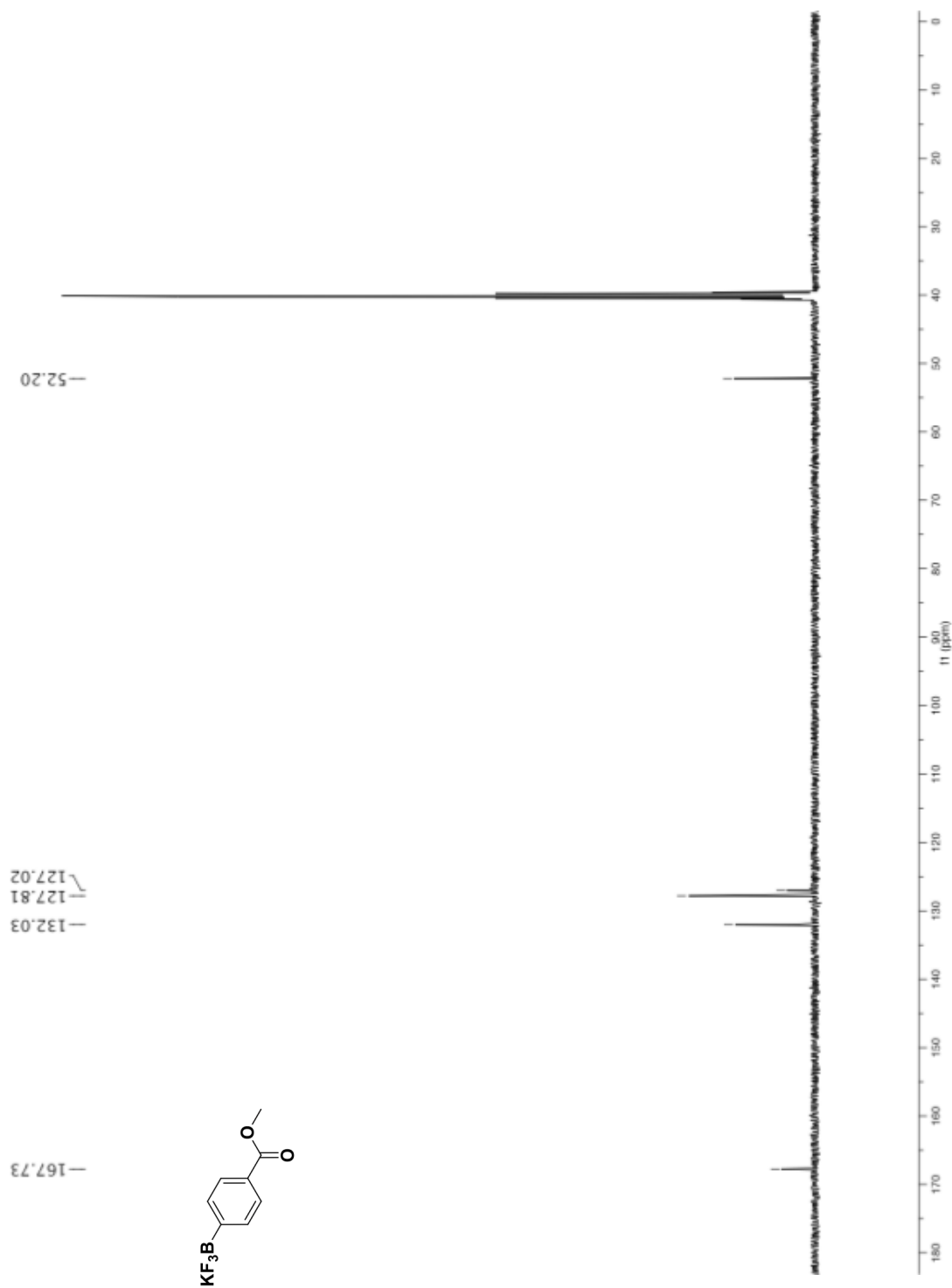
¹H NMR Spectra (500 MHz, acetone-*d*₆) Potassium 3,5-Dimethoxyphenyltrifluoroborate (Table 1, entry 22)



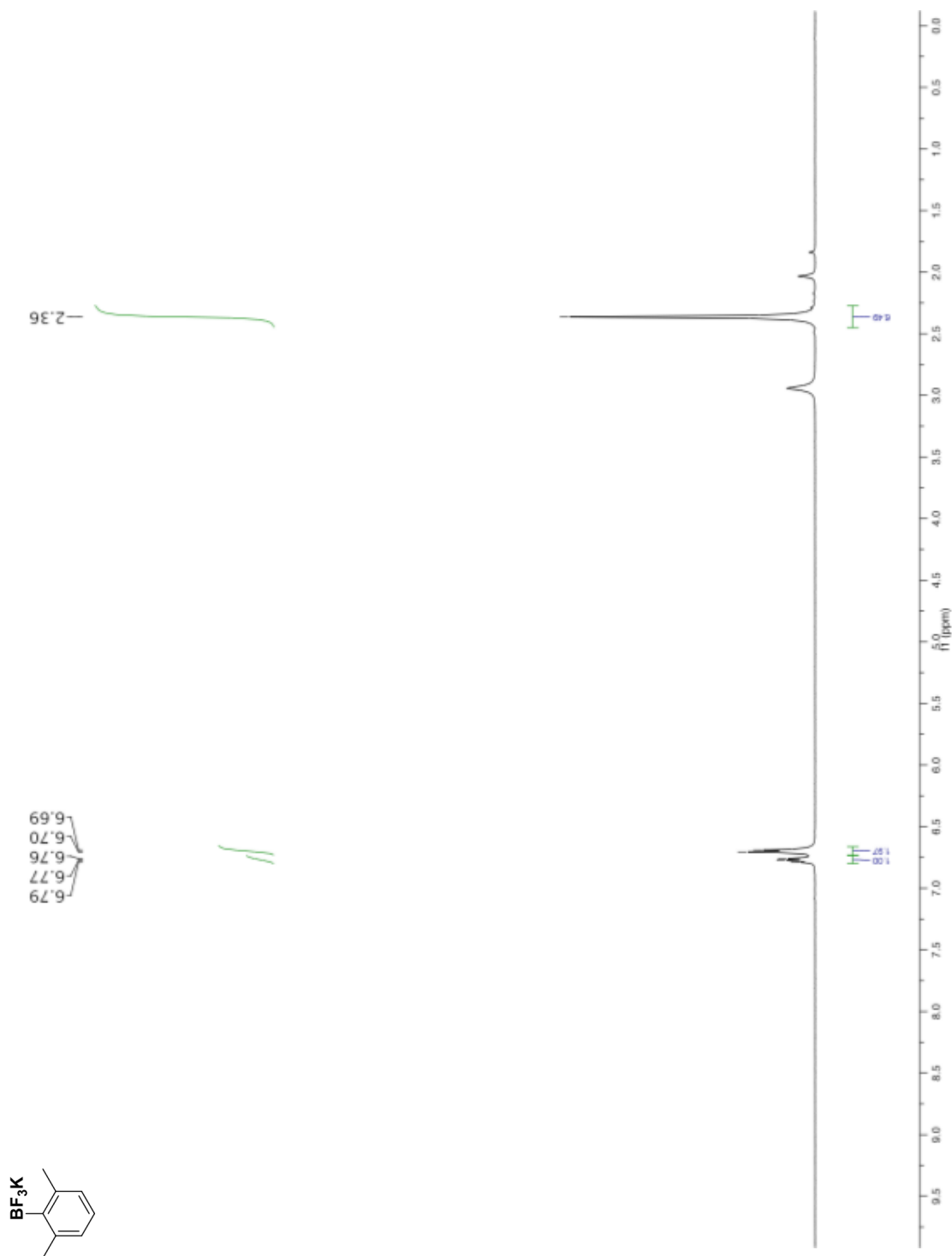
^{13}C NMR Spectra (125.8 MHz, acetone- d_6) Potassium 3,5-Dimethoxyphenyltrifluoroborate (Table 1, entry 22)



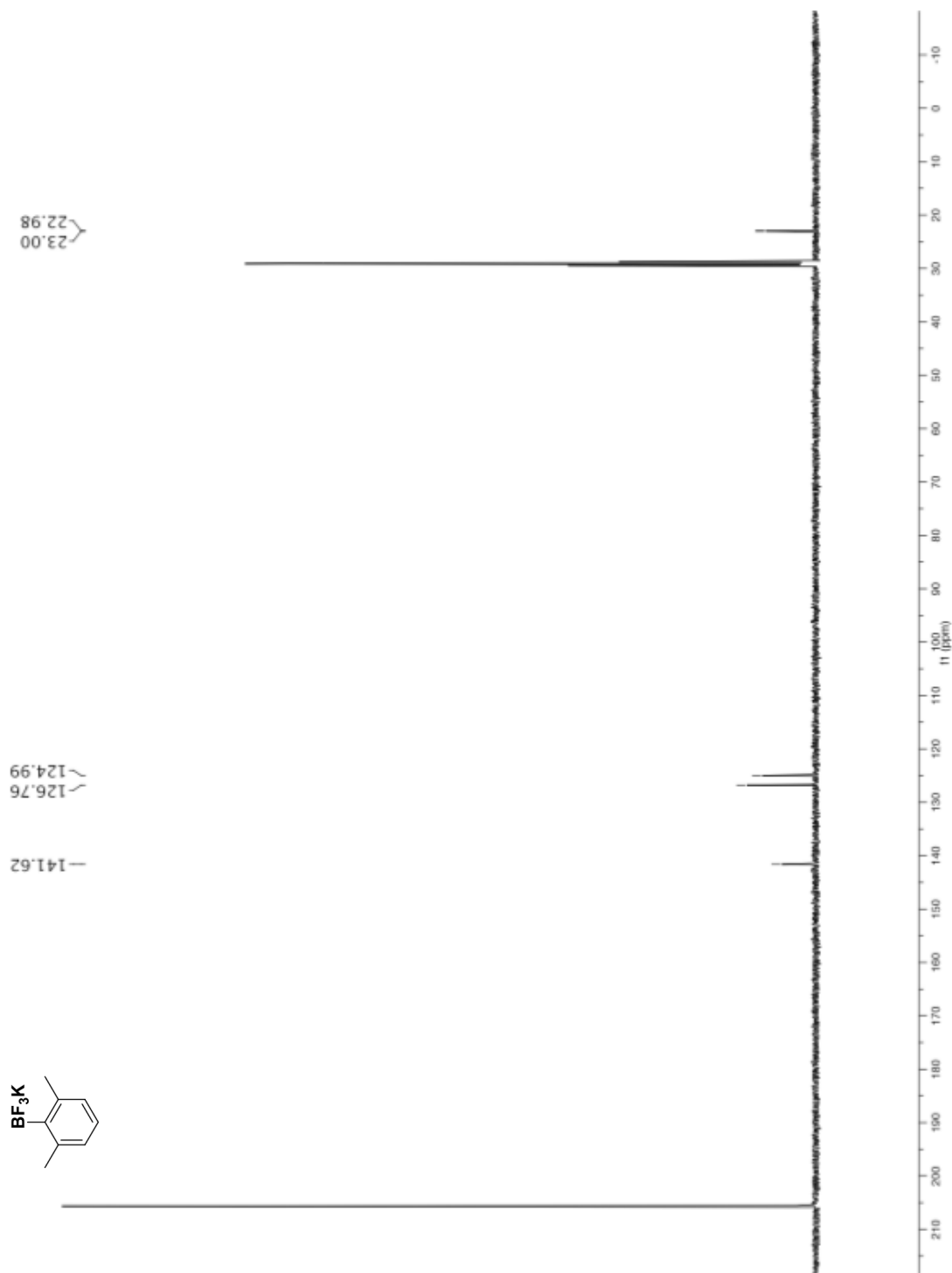
^1H NMR Spectra (500 MHz, acetone- d_6) Potassium (4-(Methoxycarbonyl)phenyl)trifluoroborate (Table 2, entry 1).



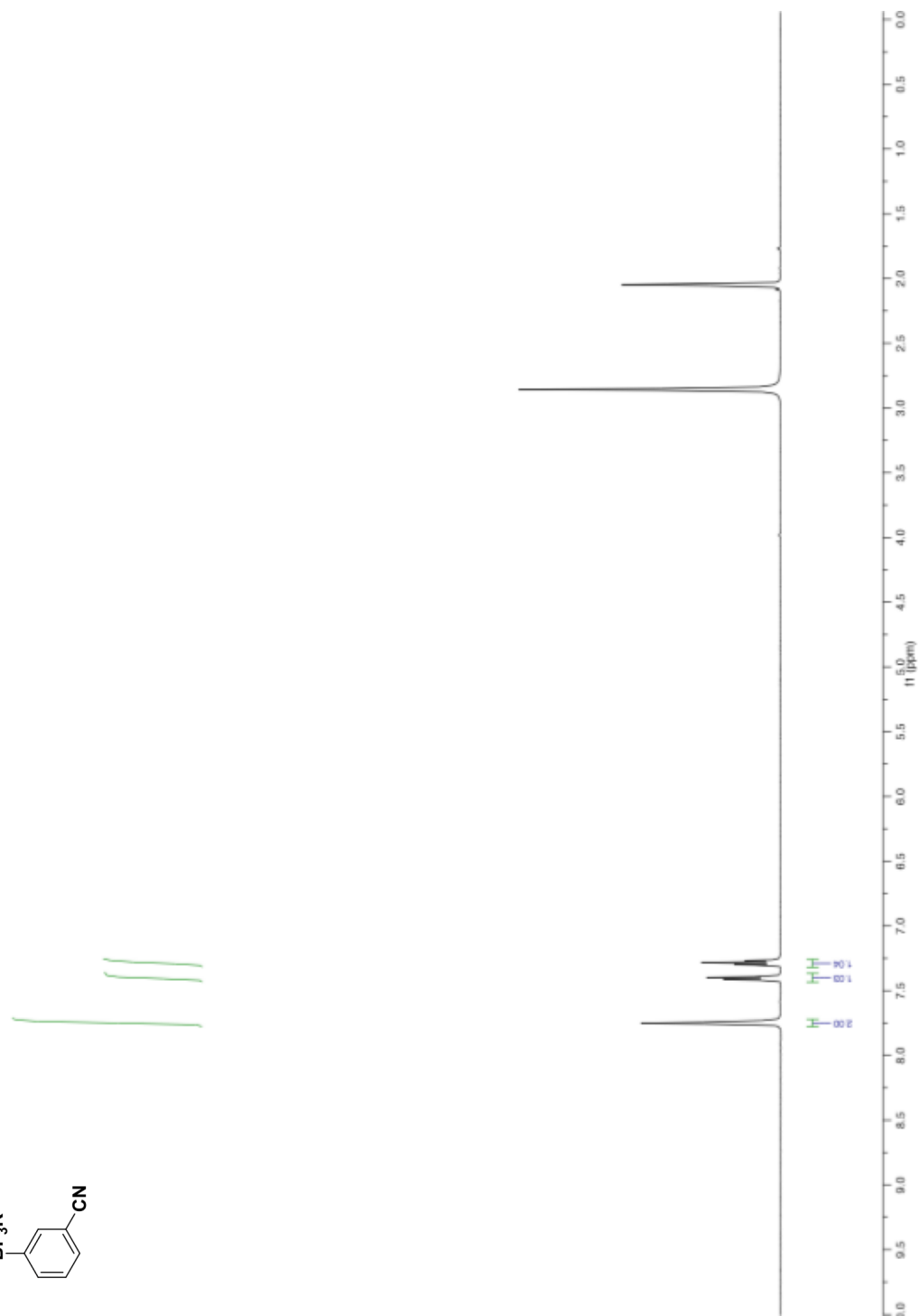
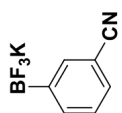
¹³C NMR Spectra (125.8 MHz, DMSO-*d*₆) Potassium (4-(Methoxycarbonyl)phenyl)trifluoroborate (Table 2, entry 1).



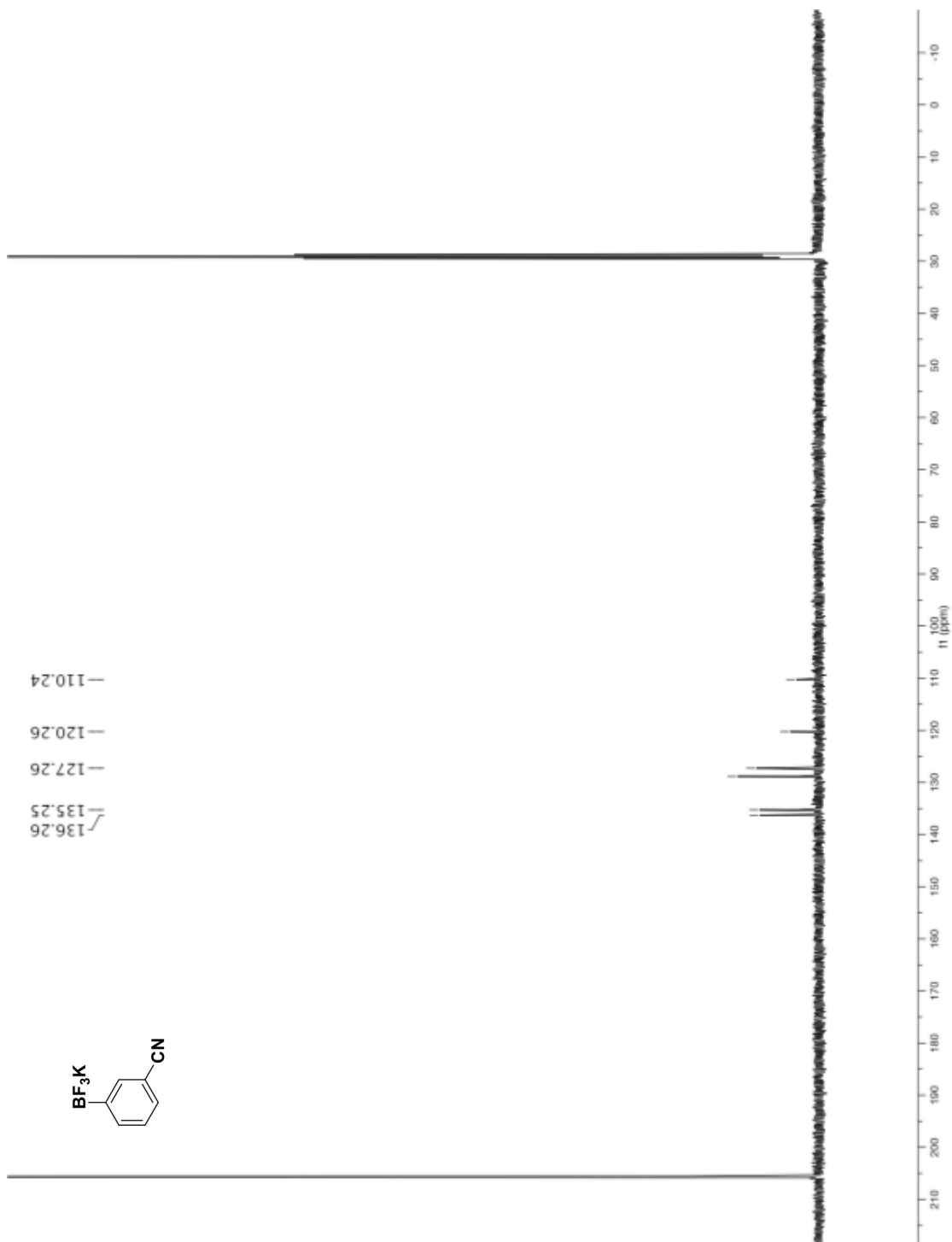
^1H NMR Spectra (500 MHz, acetone- d_6) Potassium (2,6-Dimethylphenyl)trifluoroborate (Table 2, entry 2).



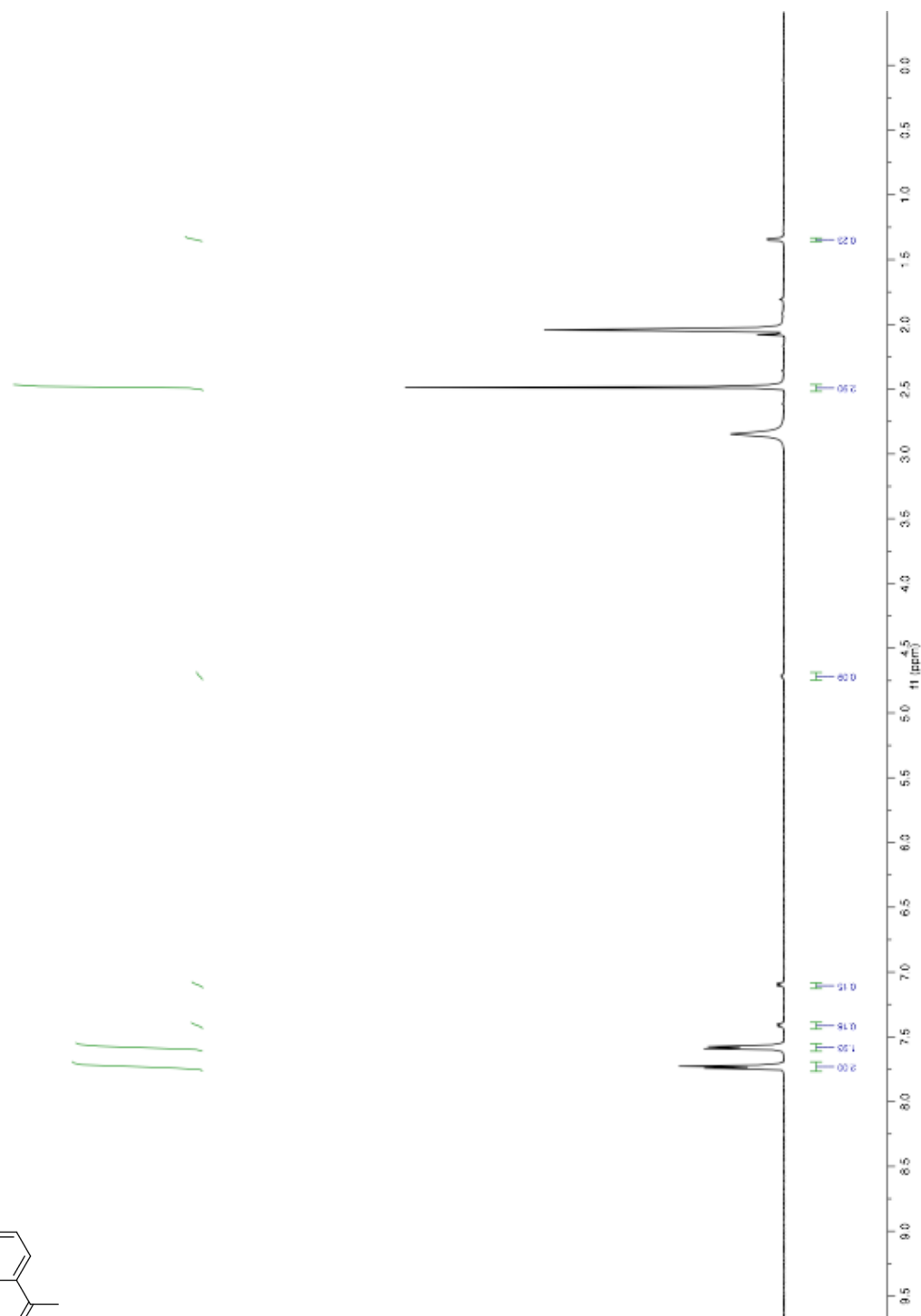
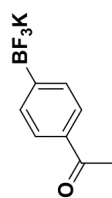
^{13}C NMR Spectra (125.8 MHz, $\text{DMSO-}d_6$) Potassium (2,6-Dimethylphenyl)trifluoroborate (Table 2, entry 2).



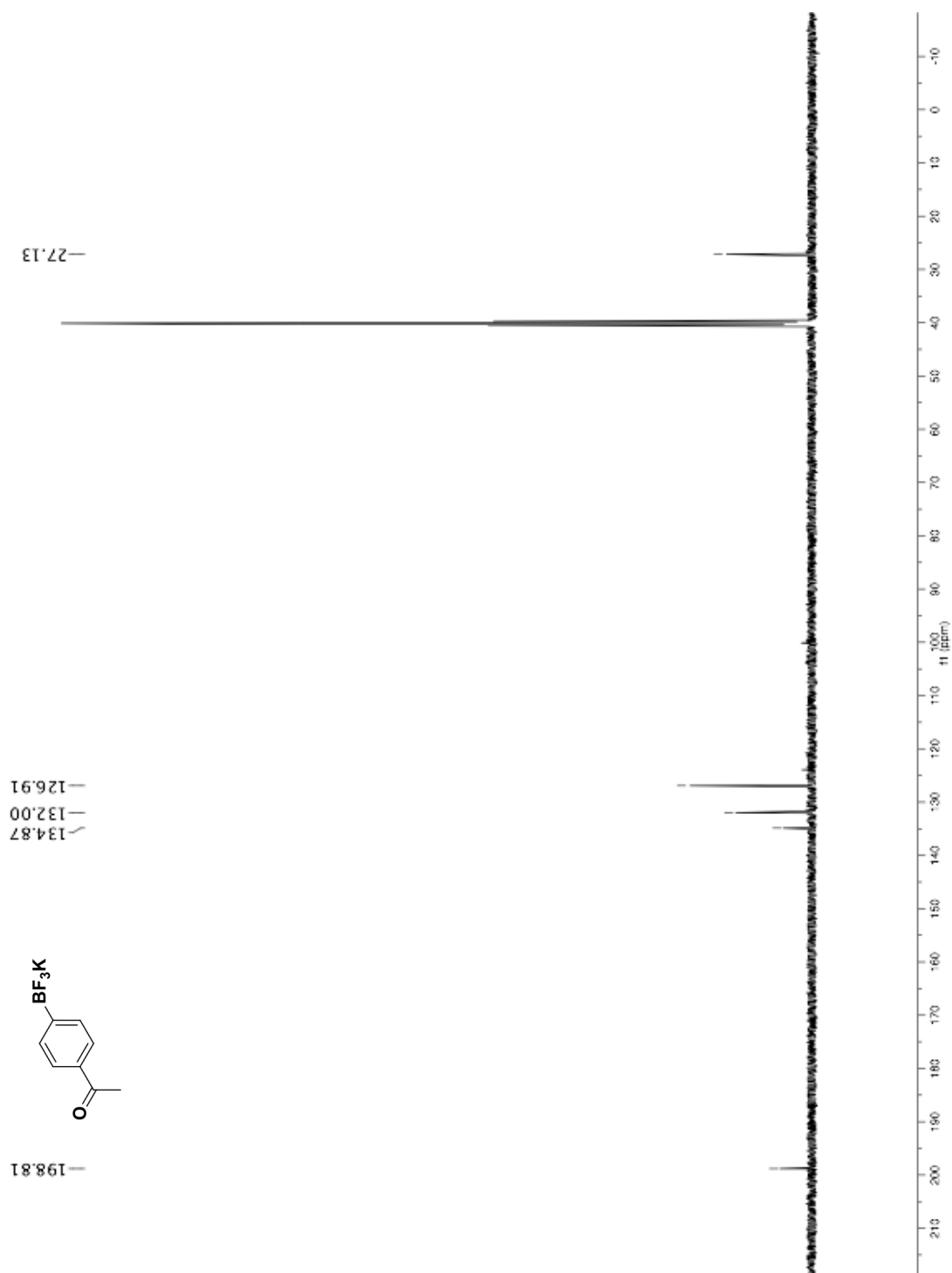
¹H NMR Spectra (500 MHz, acetone-*d*₆) **Potassium (3-Cyanophenyl)trifluoroborate (Table 2, entry 3).**



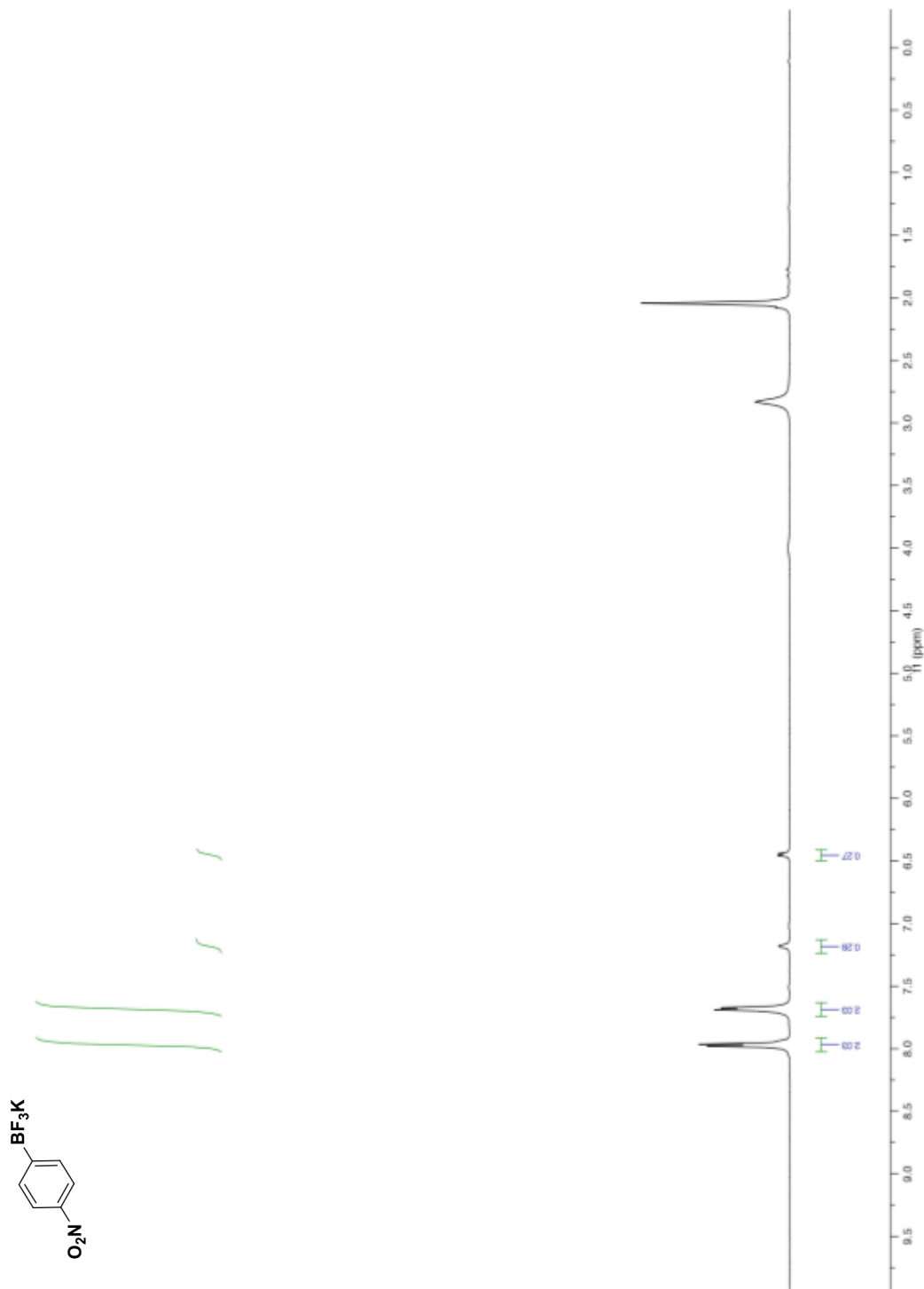
¹³C NMR Spectra (125.8 MHz, acetone-*d*₆) **Potassium (3-Cyanophenyl)trifluoroborate (Table 2, entry 3).**



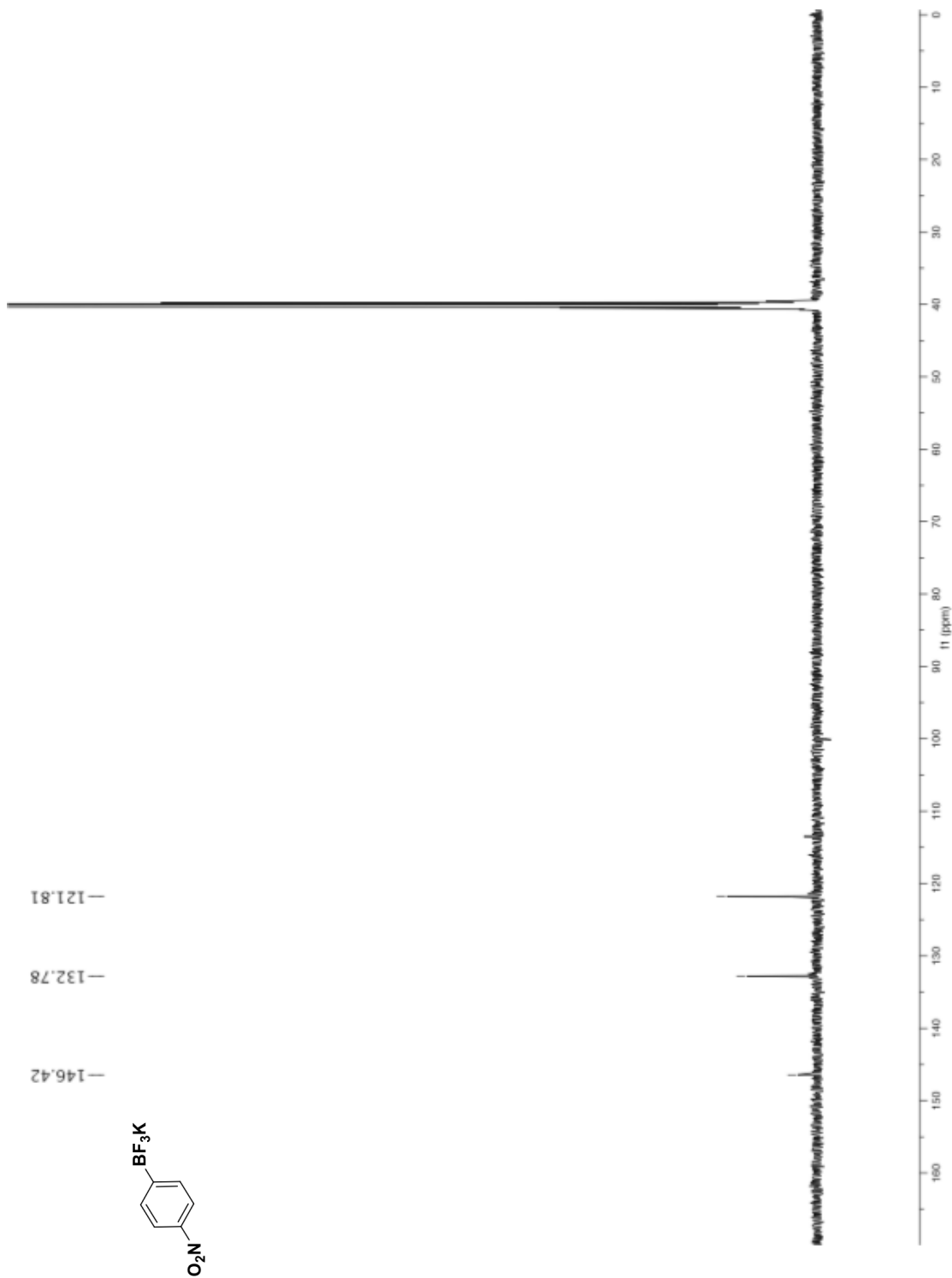
¹H NMR Spectra (500 MHz, acetone-*d*₆) Potassium (4-Acetylphenyl)trifluoroborate (Table 2, entry 4).



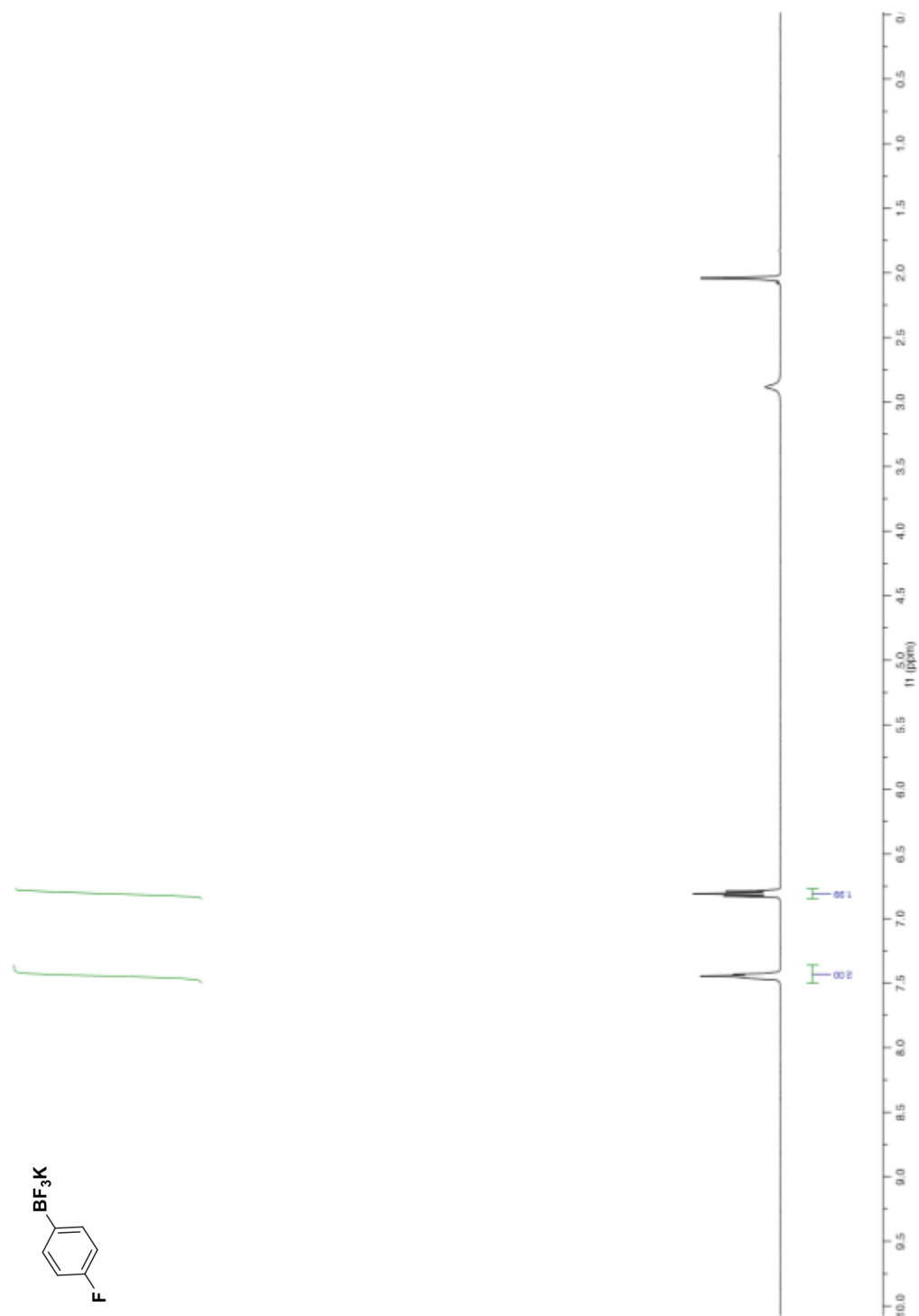
^{13}C NMR Spectra (125.8 MHz, $\text{DMSO-}d_6$) Potassium (4-Acetylphenyl)trifluoroborate (Table 2, entry 4).



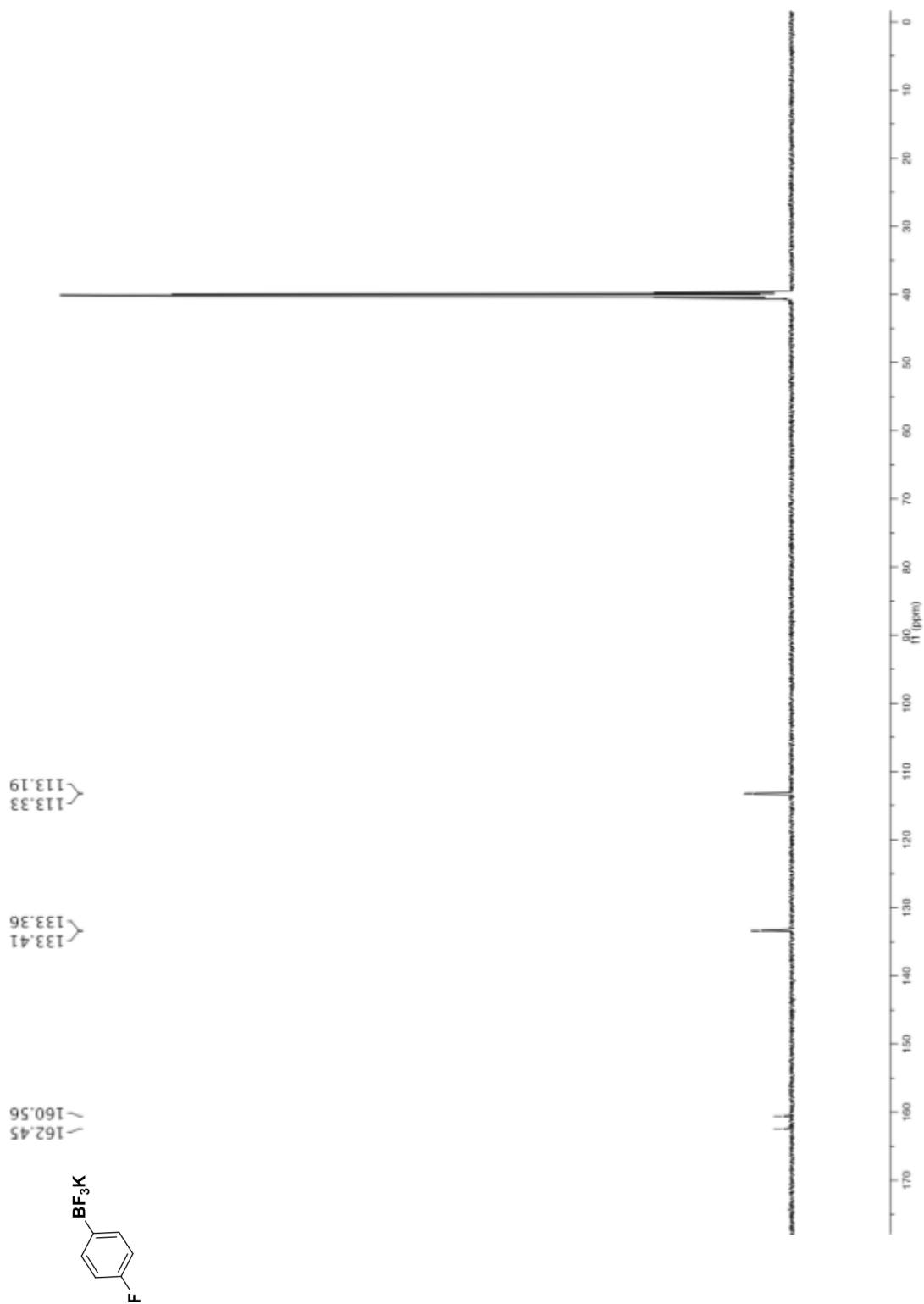
¹H NMR Spectra (500 MHz, acetone-*d*₆) Potassium (4-Nitrophenyl)trifluoroborate (Table 2, entry 5).



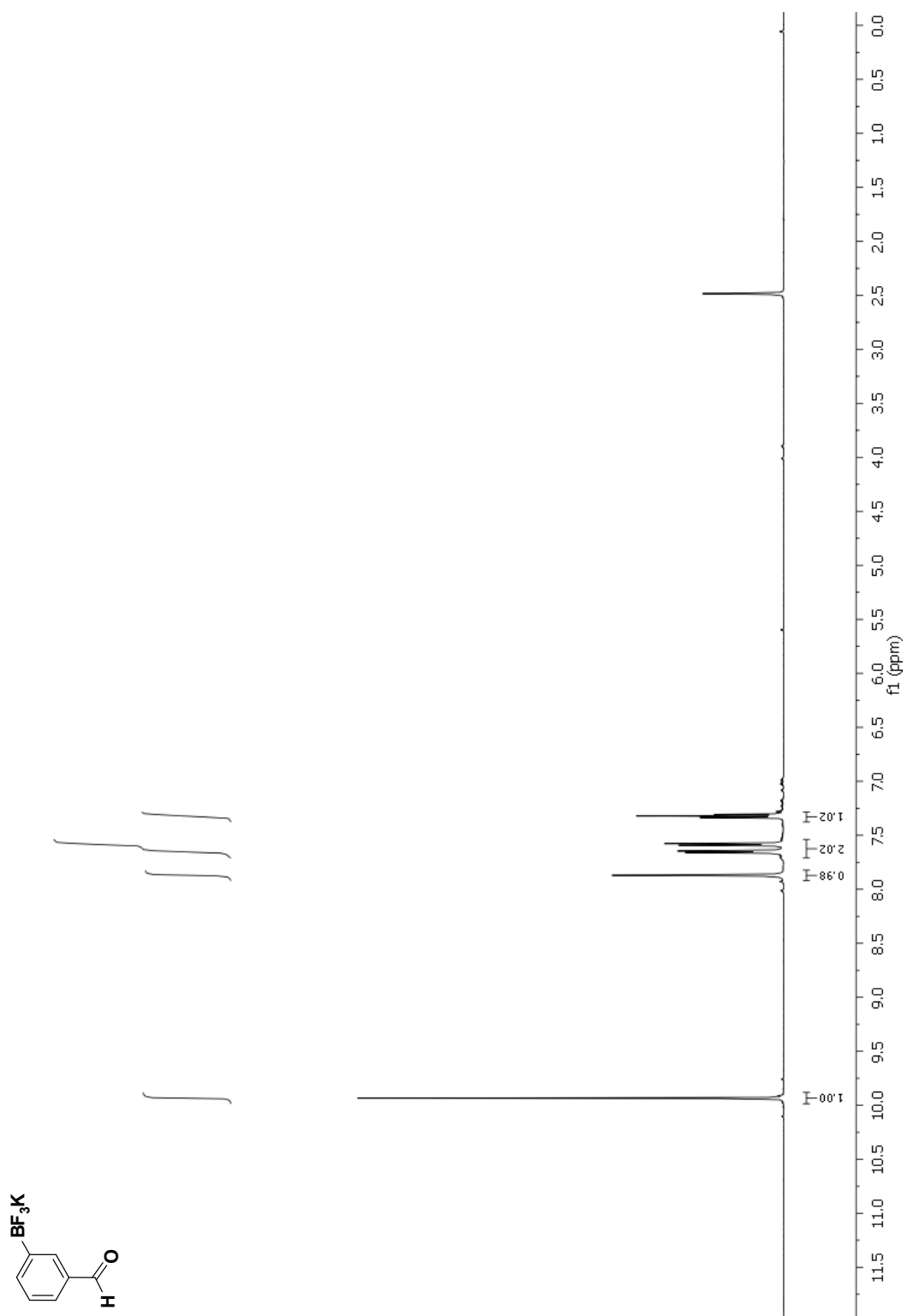
^{13}C NMR Spectra (500 MHz, $\text{DMSO-}d_6$) Potassium (4-Nitrophenyl)trifluoroborate (Table 2, entry 5).



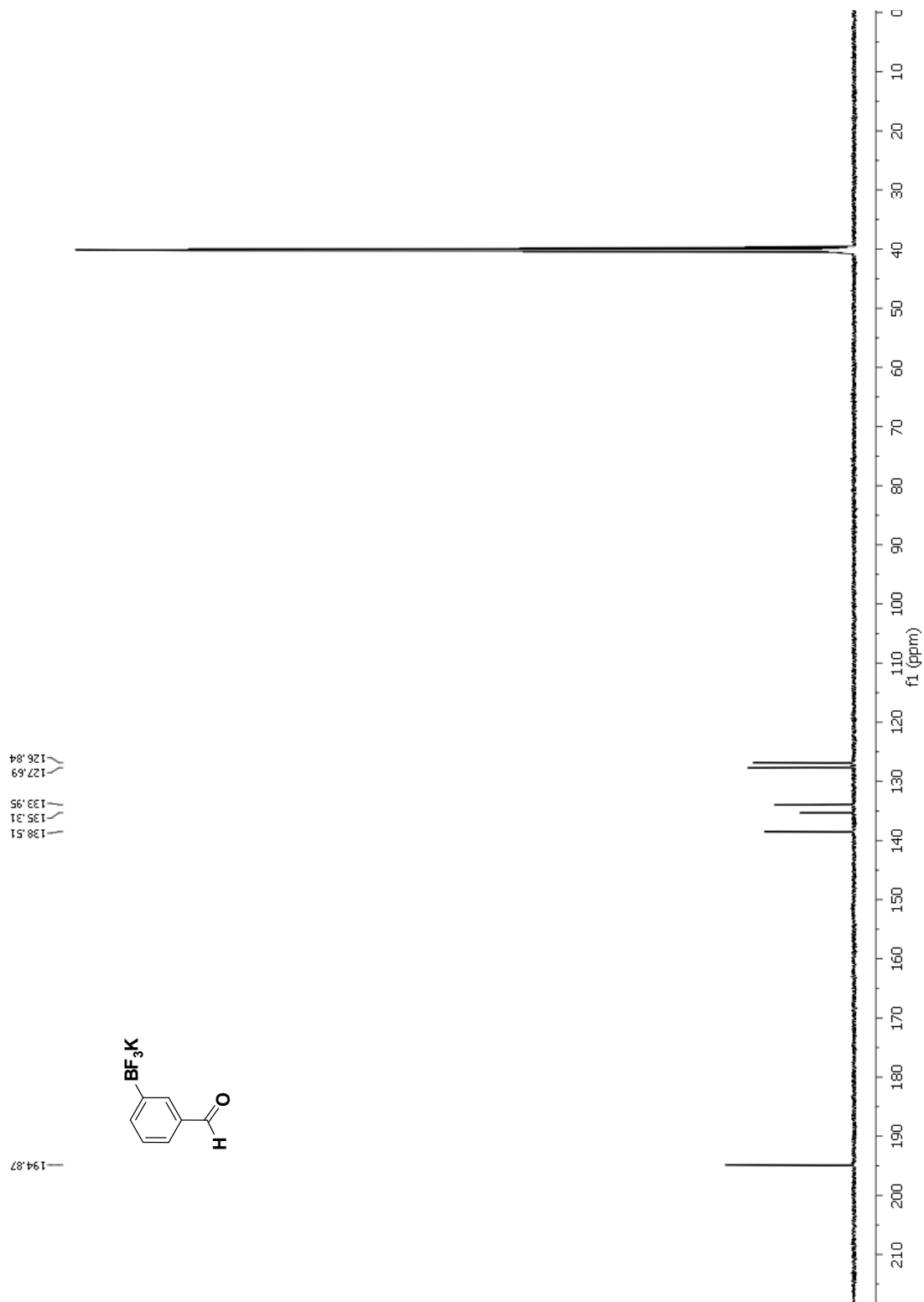
¹H NMR Spectra (500 MHz, acetone-*d*₆) **Potassium (4-Fluorophenyl)trifluoroborate (Table 2, entry 6).**



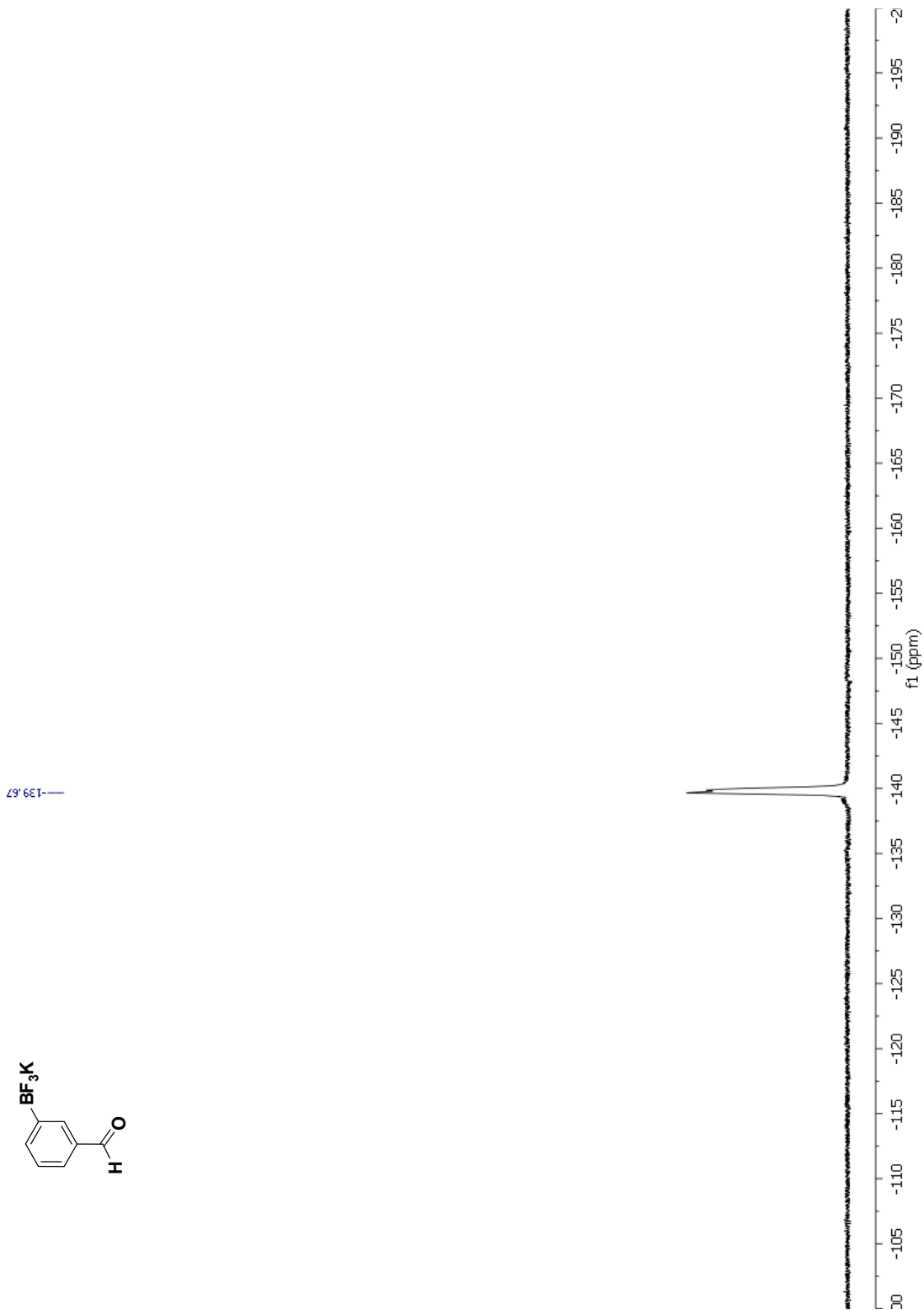
¹³C NMR Spectra (125.8 MHz, DMSO-*d*₆) Potassium (4-Fluorophenyl)trifluoroborate (Table 2, entry 6)



¹H NMR Spectra (500 MHz, DMSO-*d*₆) Potassium 3-Formylphenyl-trifluoroborate (Table 2, entry 7)

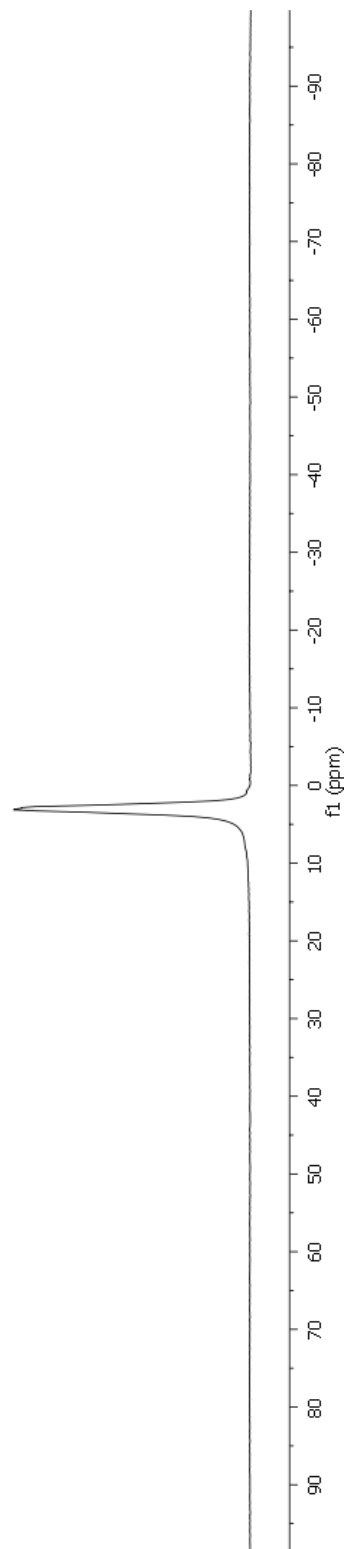
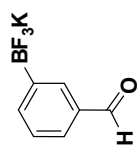


¹³C NMR Spectra (125.8 MHz, DMSO-*d*₆) Potassium 3-Formylphenyl-trifluoroborate (Table 2, entry 7)

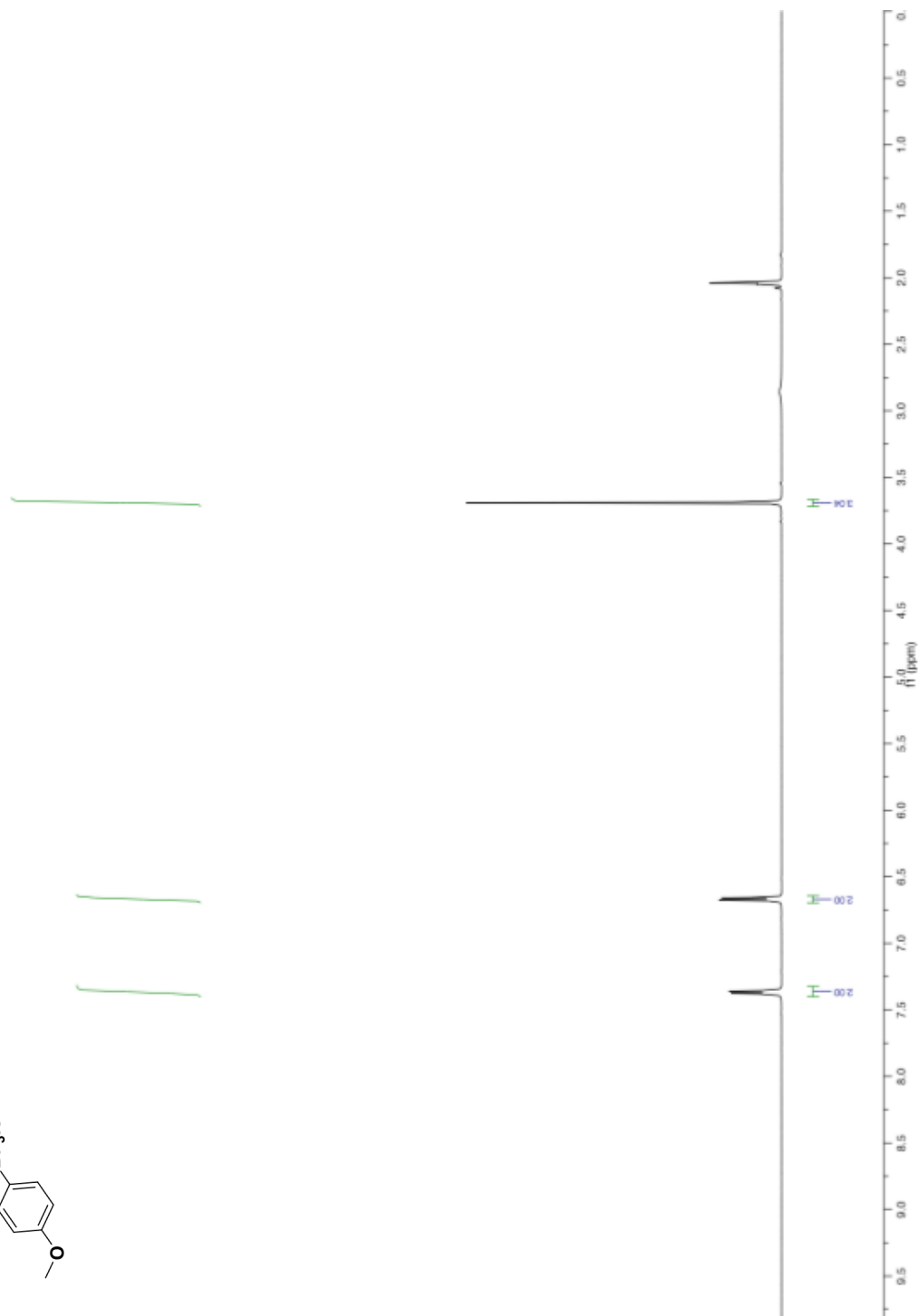
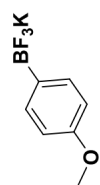


^{19}F NMR Spectra (282 MHz, $\text{DMSO-}d_6$) Potassium 3-Formylphenyl-trifluoroborate (Table 2, entry 7)

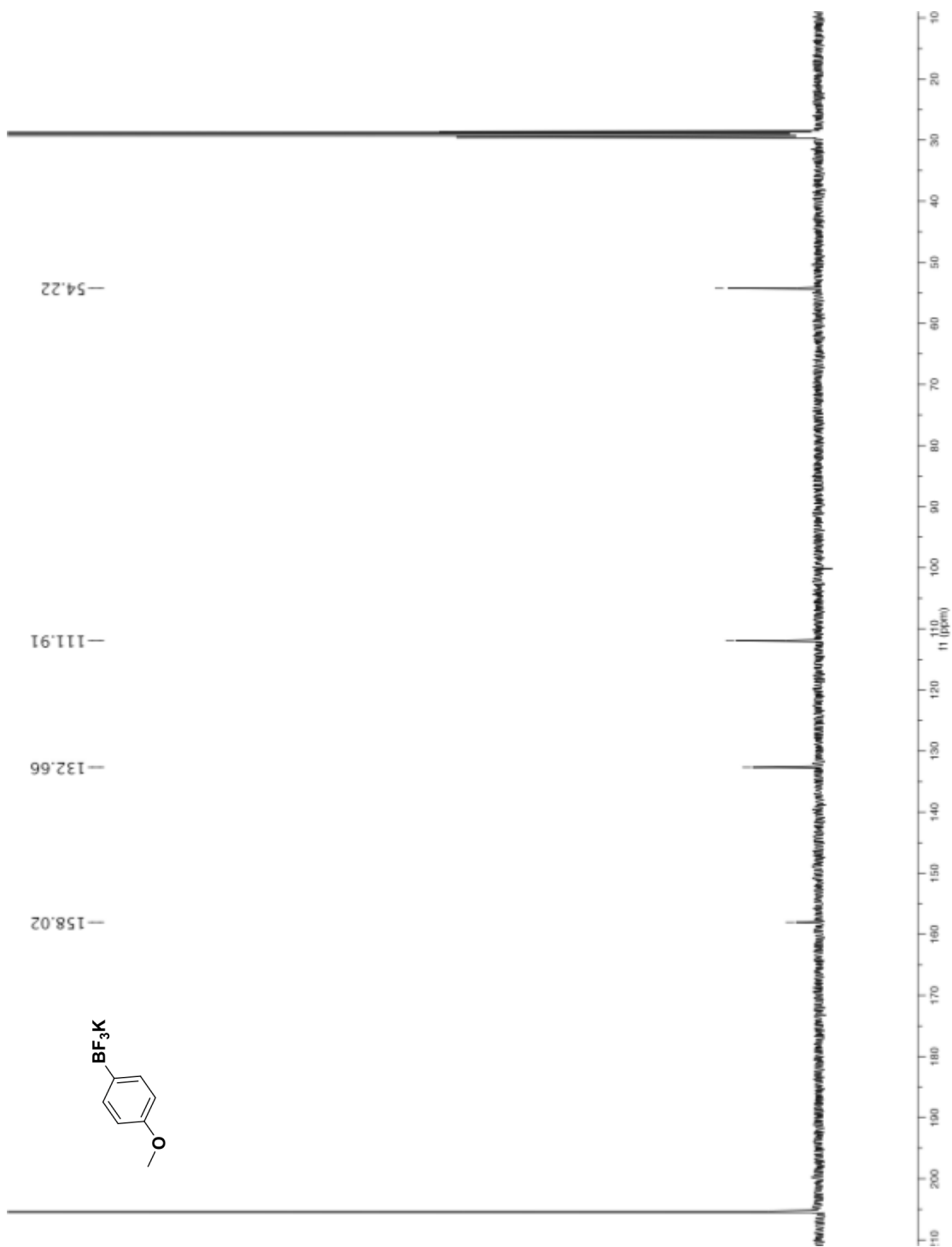
3.12



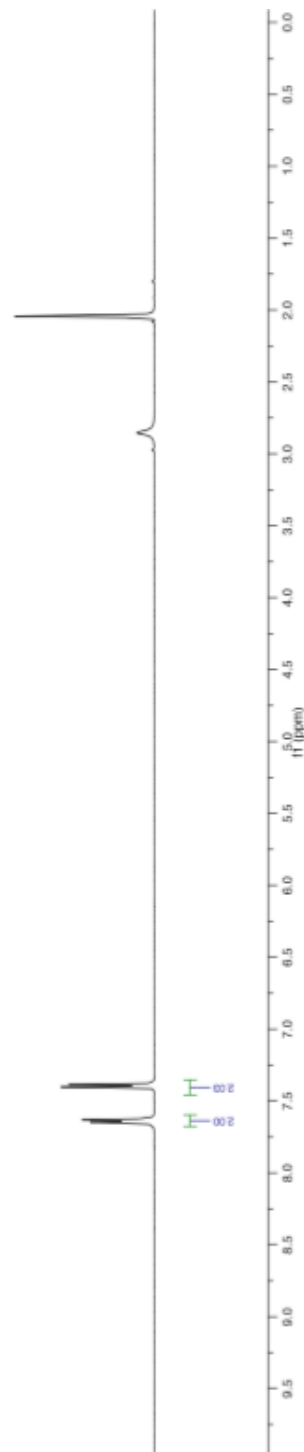
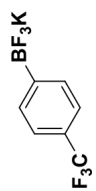
^{11}B NMR Spectra (128.4 MHz, $\text{DMSO-}d_6$) Potassium 3-Formylphenyl-trifluoroborate (Table 2, entry 7)



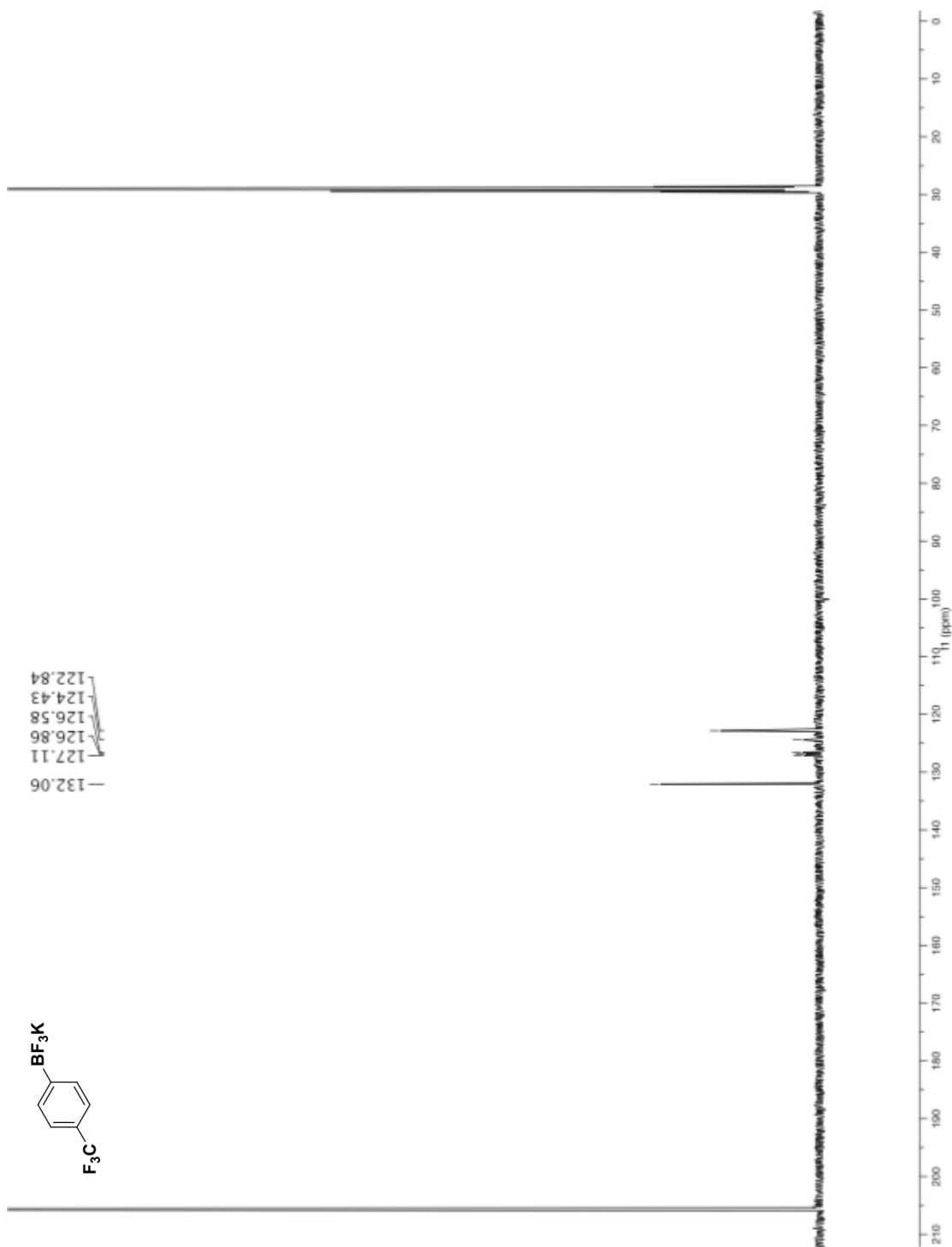
¹H NMR Spectra (500 MHz, acetone-*d*₆) **Potassium 4-Methoxyphenyl-trifluoroborate (Table 2, entry 8).**



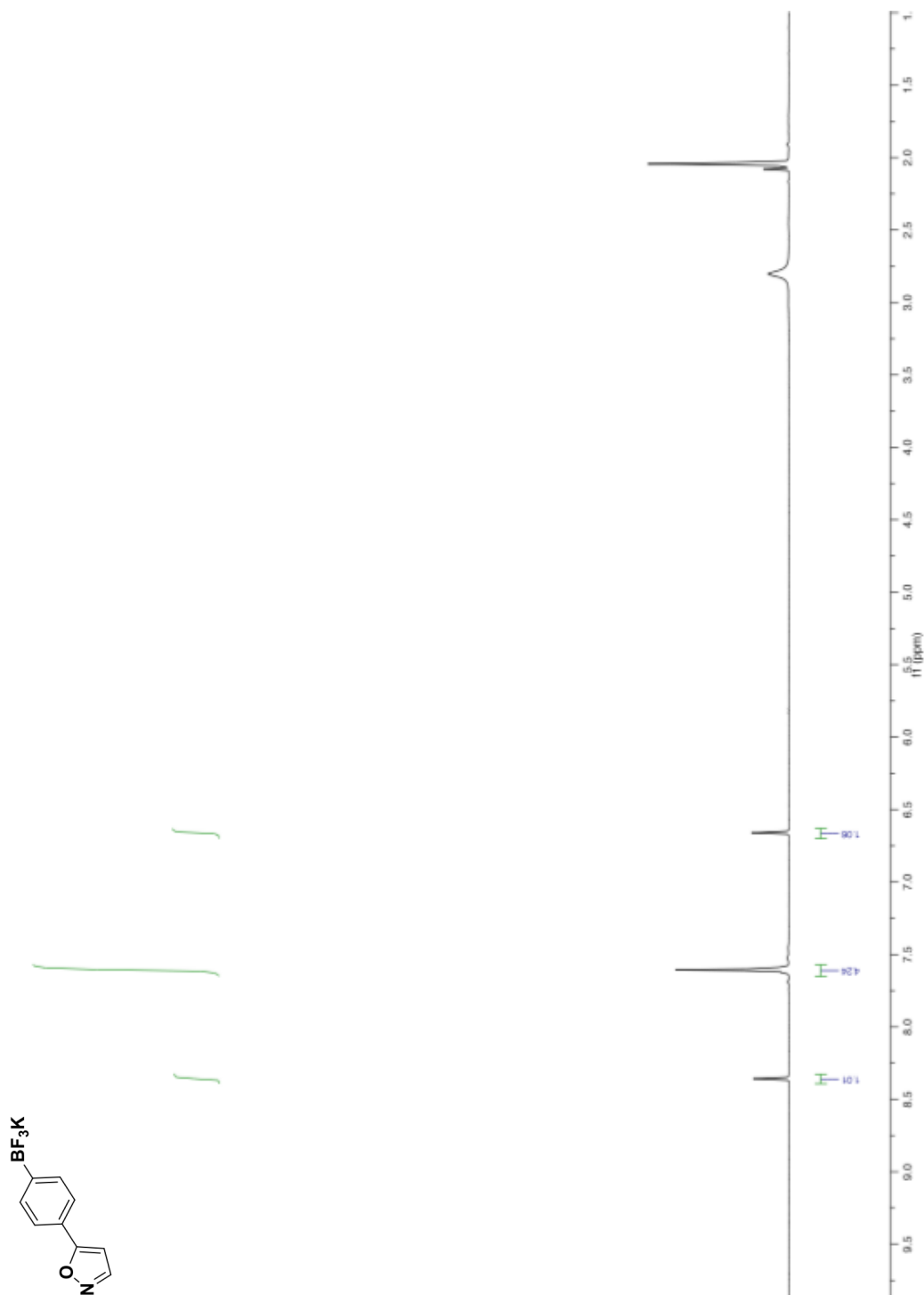
^{13}C NMR Spectra (125.8 MHz, acetone- d_6) Potassium 4-Methoxyphenyltrifluoroborate (Table 2, entry 8).



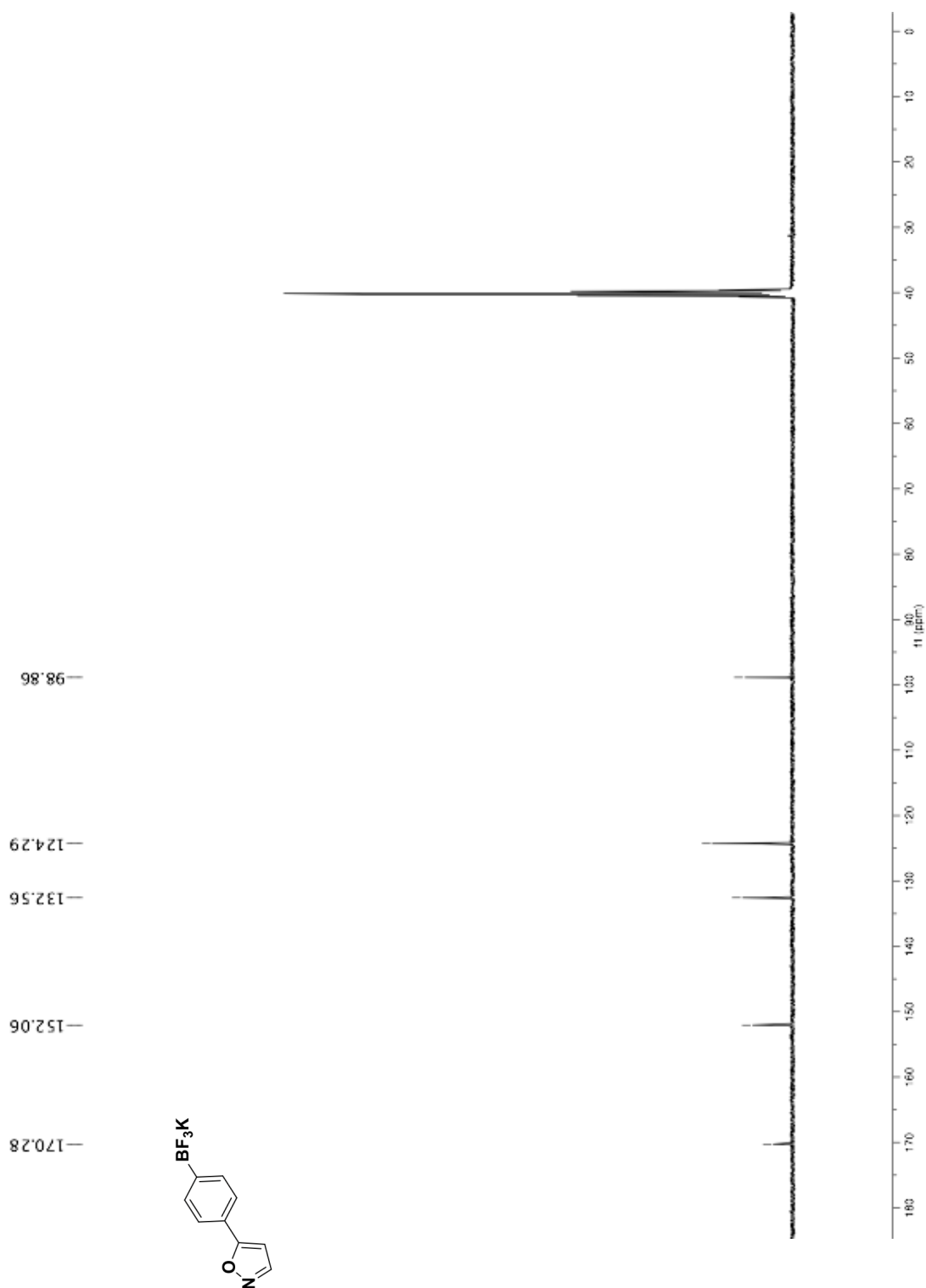
^1H NMR Spectra (500 MHz, acetone-d_6) Potassium (4-(Trifluoromethyl)phenyl)trifluoroborate (Table 2, entry 9).



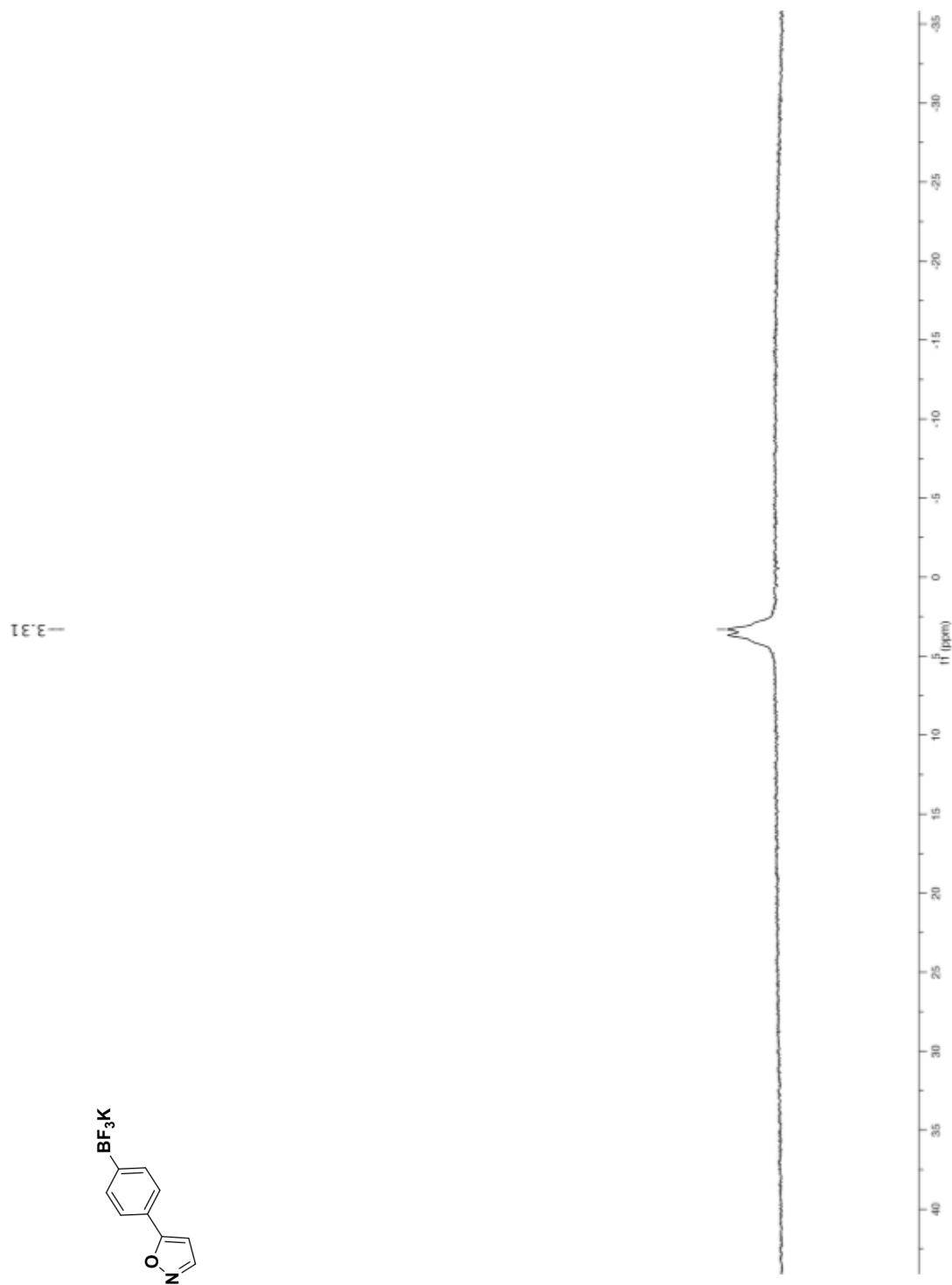
¹H NMR Spectra (500 MHz, acetone-*d*₆) Potassium (4-(Trifluoromethyl)phenyl)trifluoroborate (Table 2, entry 9).



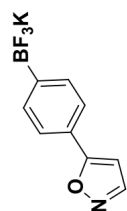
¹H NMR Spectra (500 MHz, acetone-*d*₆) (4-(Isoxazol-5-yl)phenyl)trifluoroborate (Table 2, entry 10).



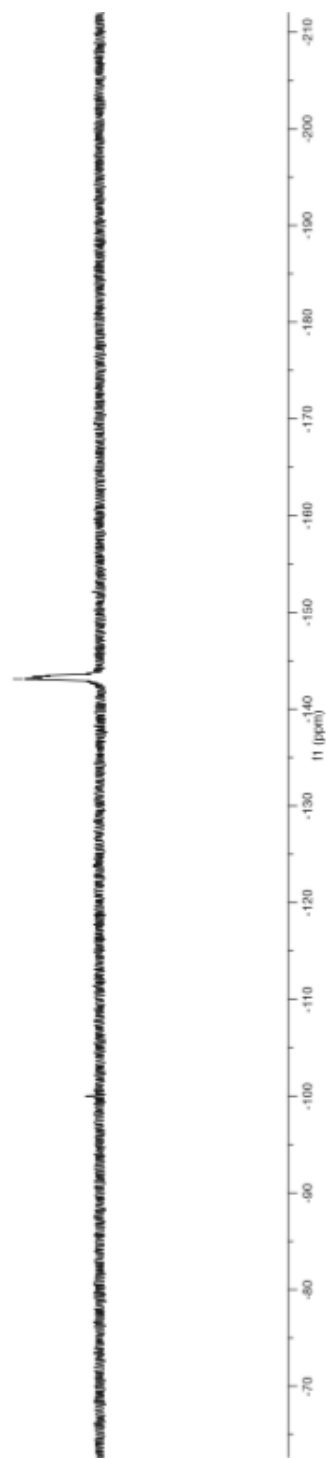
¹³C NMR Spectra (125.8 MHz, DMSO-*d*₆) (4-(Isoxazol-5-yl)phenyl)trifluoroborate (Table 2, entry 10).



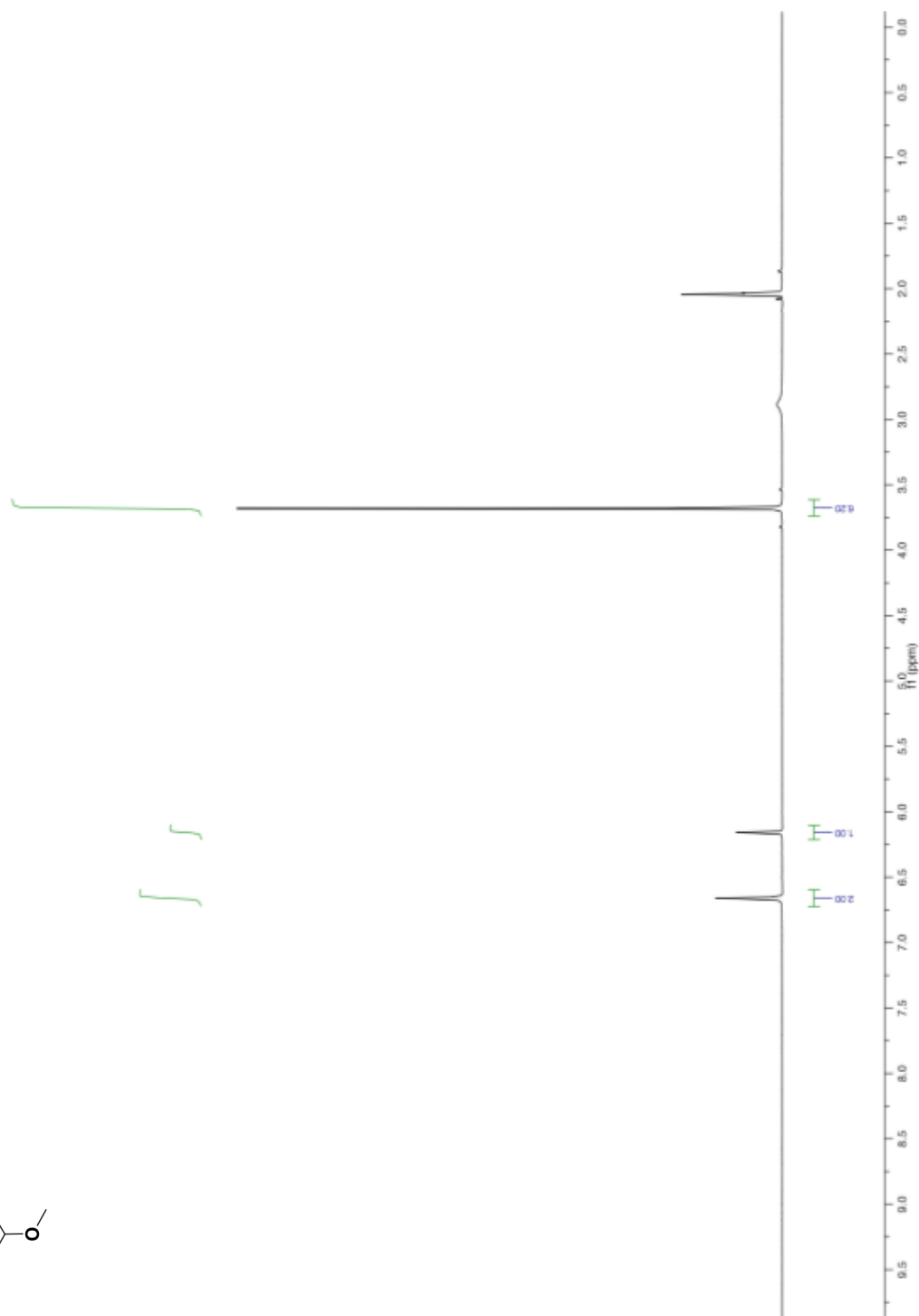
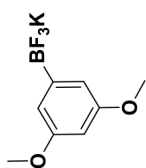
^{11}B NMR Spectra (128.4 MHz, acetone- d_6) (4-(Isoxazol-5-yl)phenyl)trifluoroborate (Table 2, entry 10).



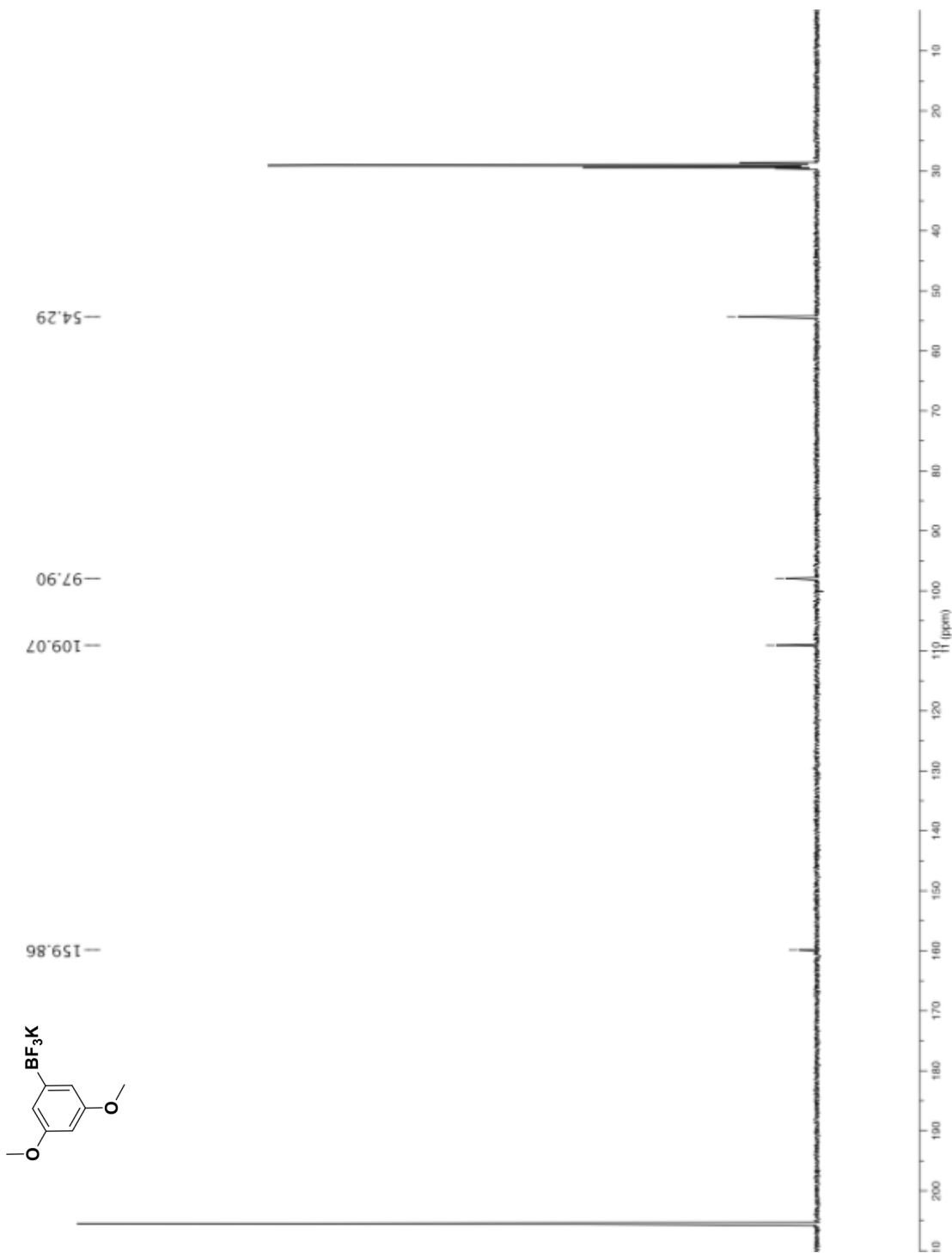
--143.11



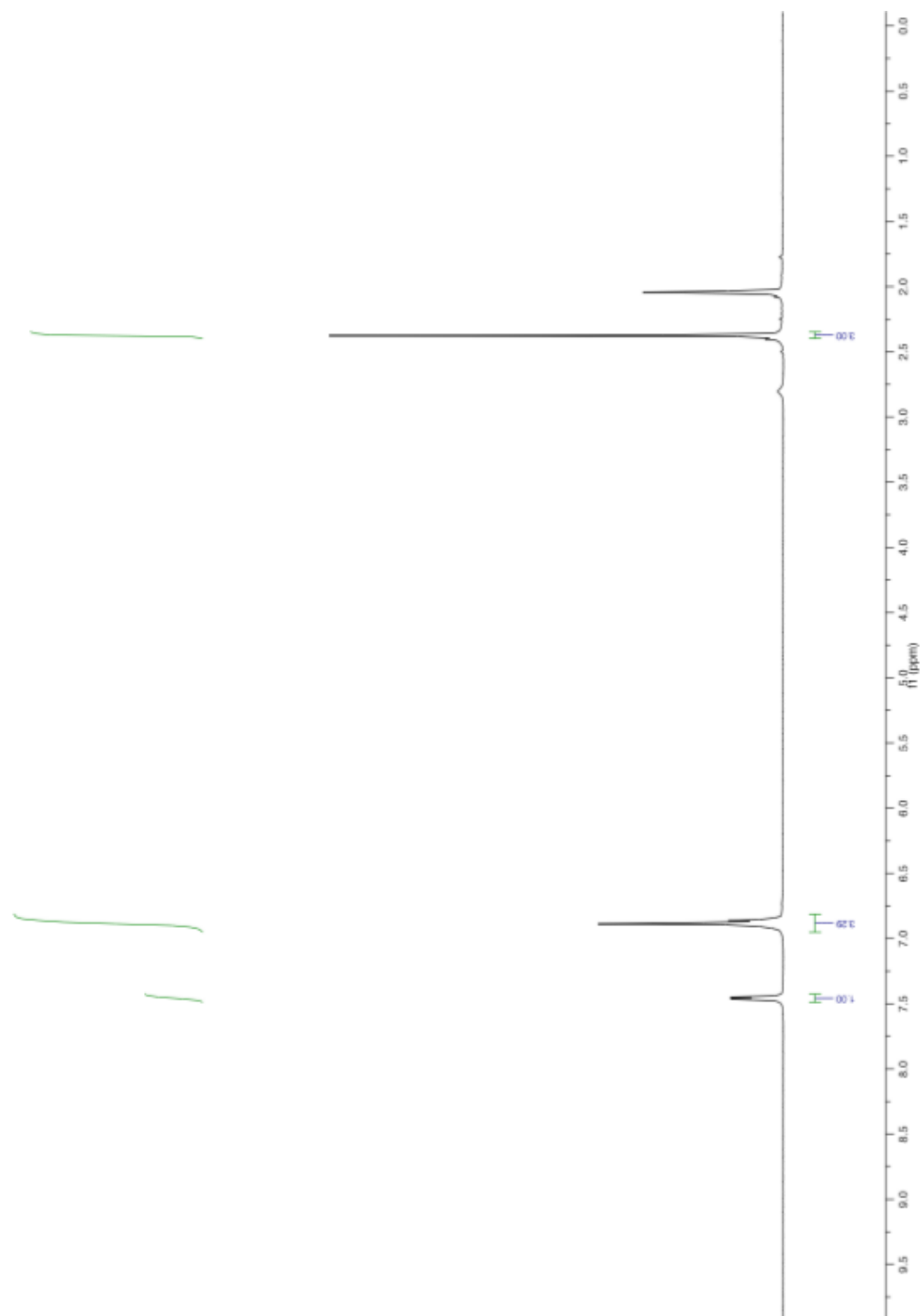
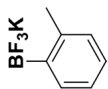
¹⁹F NMR Spectra (282 MHz, acetone-*d*₆) **(4-(Isoxazol-5-yl)phenyl)trifluoroborate** (Table 2, entry 10).



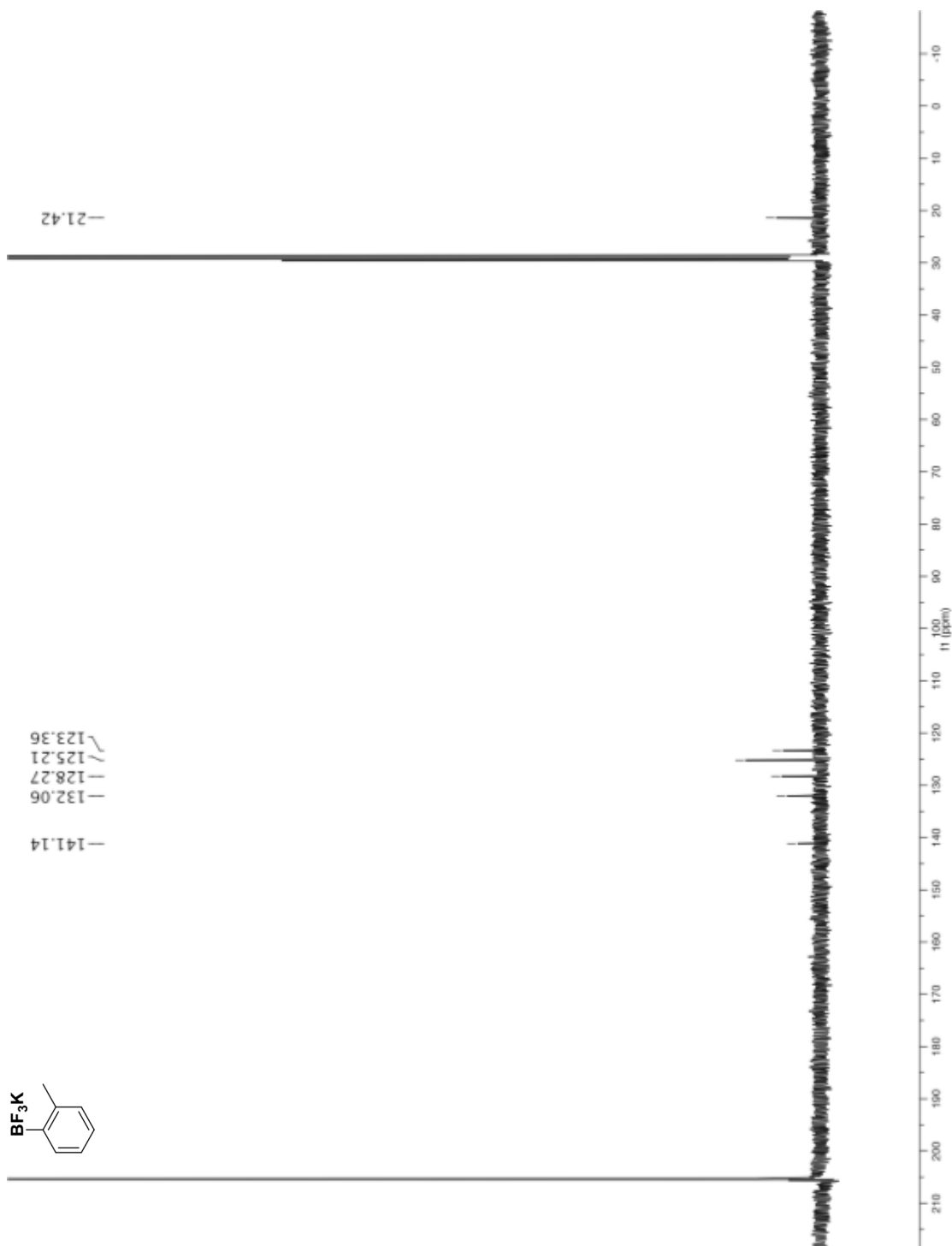
¹H NMR Spectra (500 MHz, acetone-*d*₆) Potassium (3,5-Dimethoxyphenyl)trifluoroborate (Table 2, entry 11).



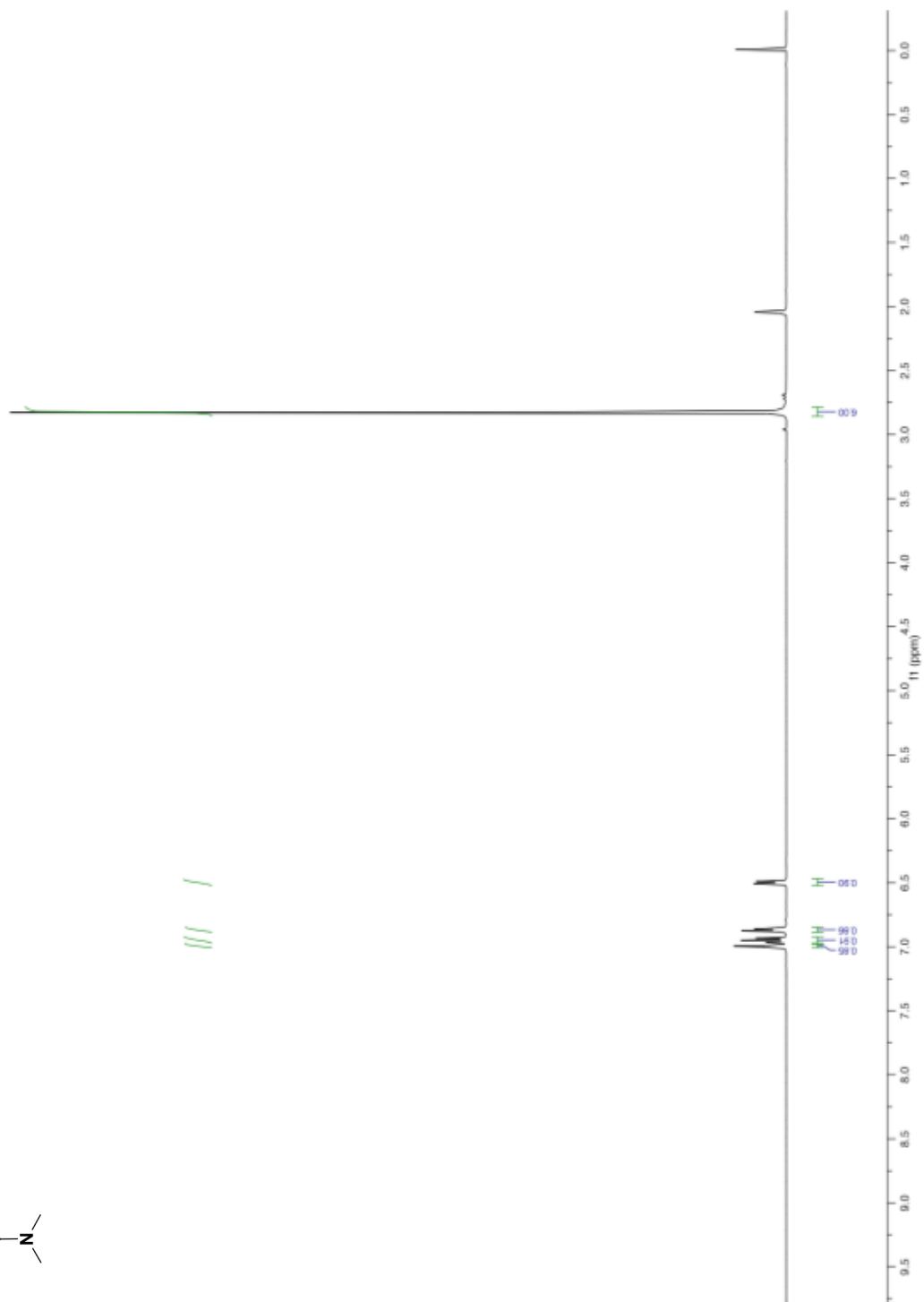
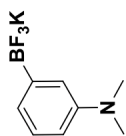
^{13}C NMR Spectra (125.8 MHz, acetone- d_6) Potassium (3,5-Dimethoxyphenyl)trifluoroborate (Table 2, entry 11).



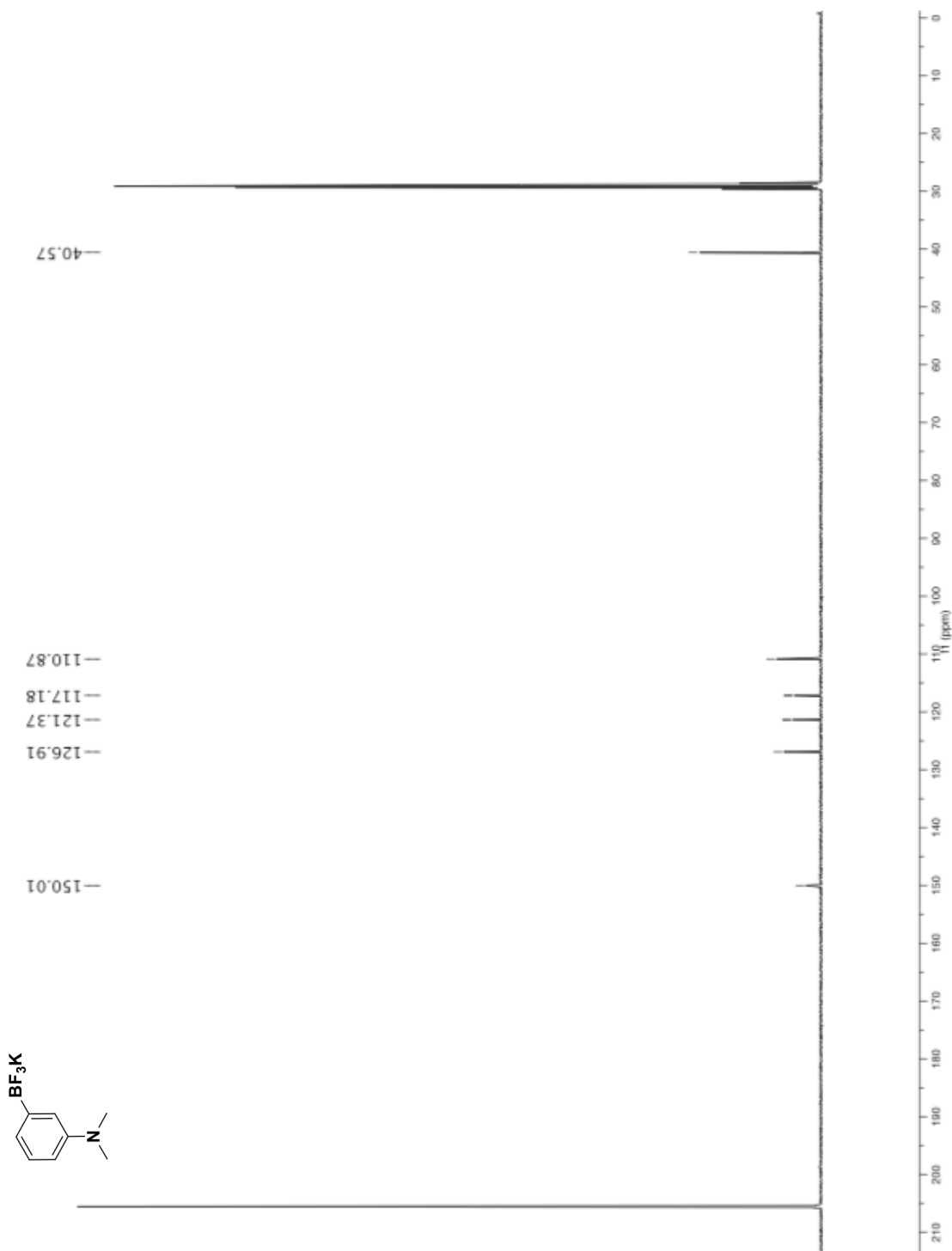
¹H NMR Spectra (500 MHz, acetone-*d*₆) Potassium *o*-Tolyltrifluoroborate (Table 2, entry 12).



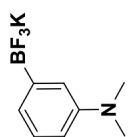
^{13}C NMR Spectra (125.8 MHz, acetone- d_6) Potassium *o*-Tolyltrifluoroborate (Table 2, entry 12).



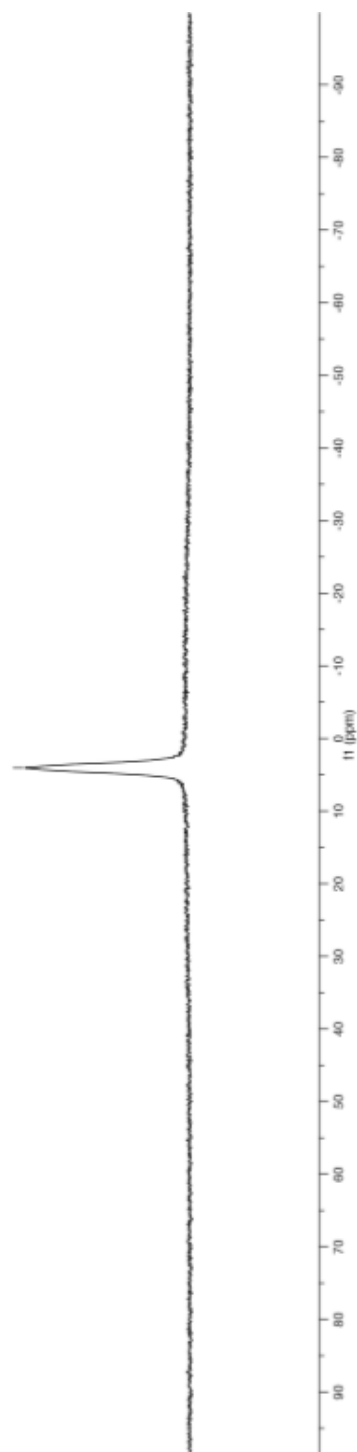
¹H NMR Spectra (500 MHz, acetone-*d*₆) (3-(Dimethylamino)phenyl)trifluoroborate (Table 2, entry 14).



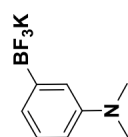
^{13}C NMR Spectra (125.8 MHz, acetone- d_6) (3-(Dimethylamino)phenyl)trifluoroborate (Table 2, entry 14).



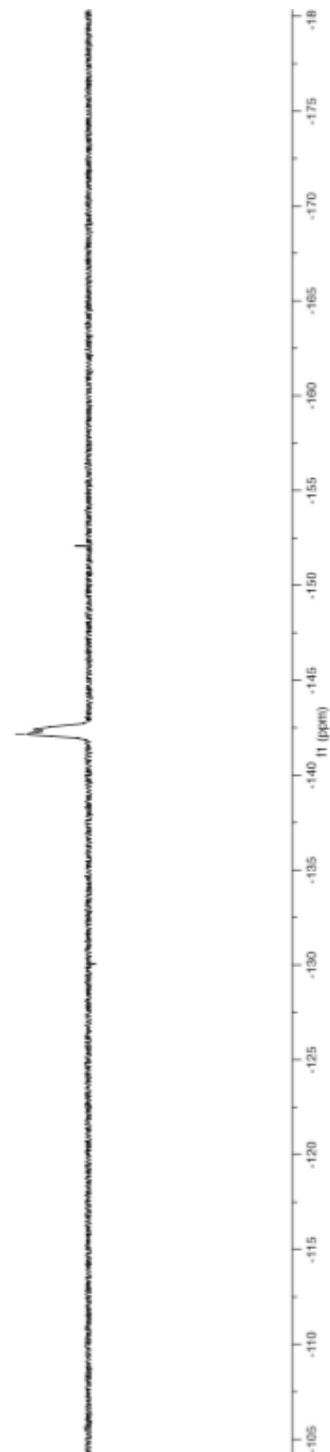
-4.05



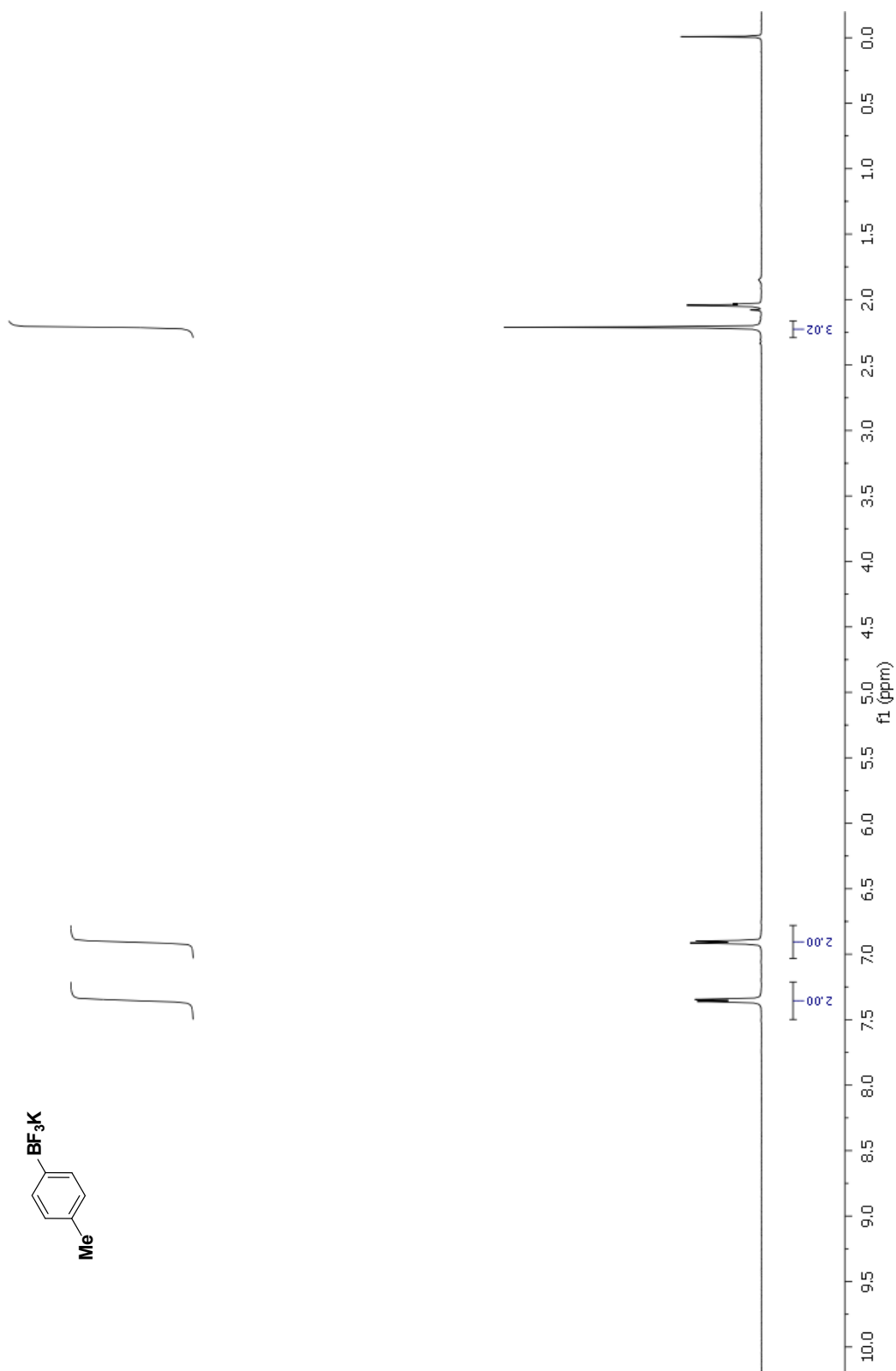
^{11}B NMR Spectra (128.4 MHz, acetone- d_6) (3-(Dimethylamino)phenyl)trifluoroborate (Table 2, entry 14).



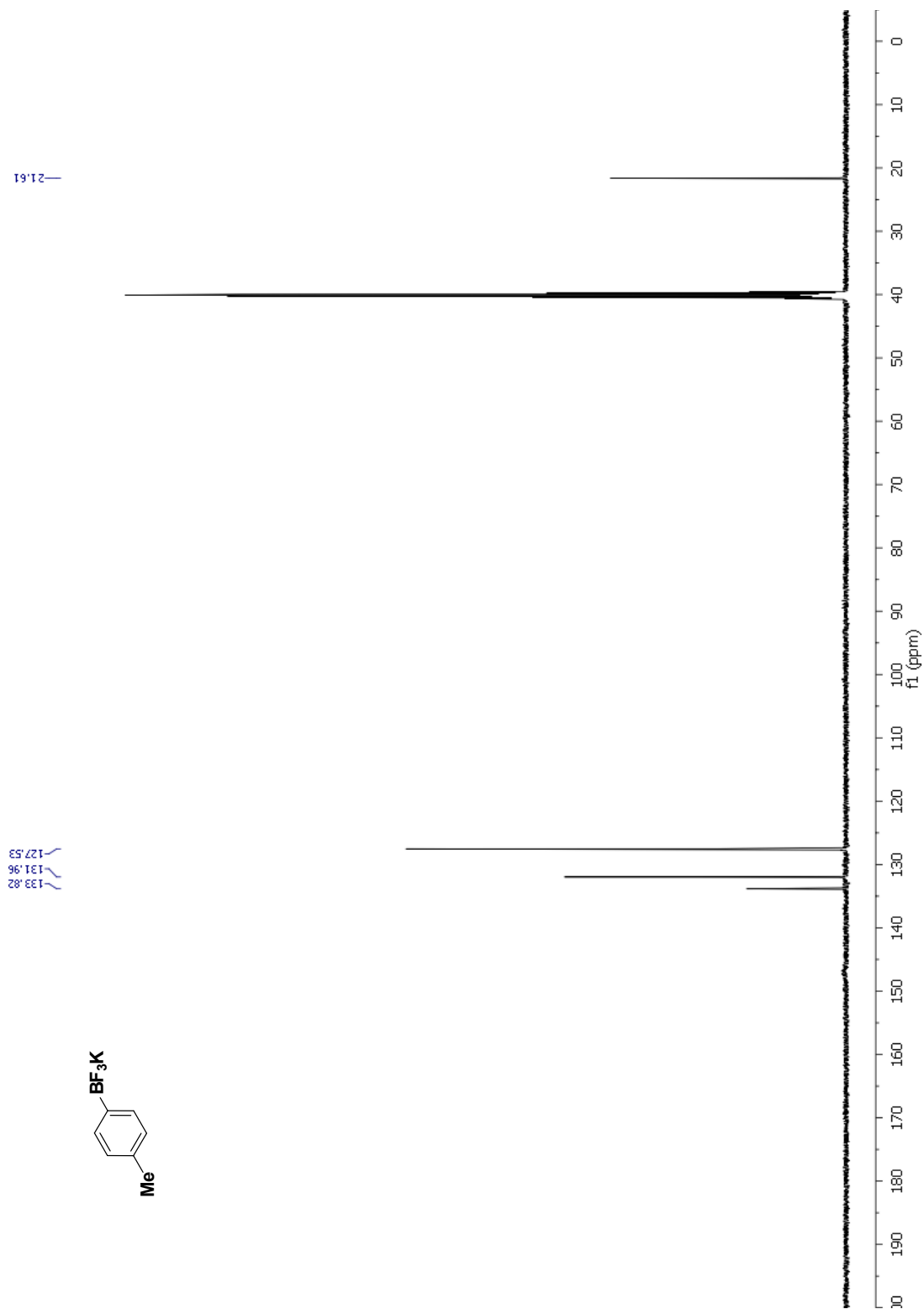
--142.18



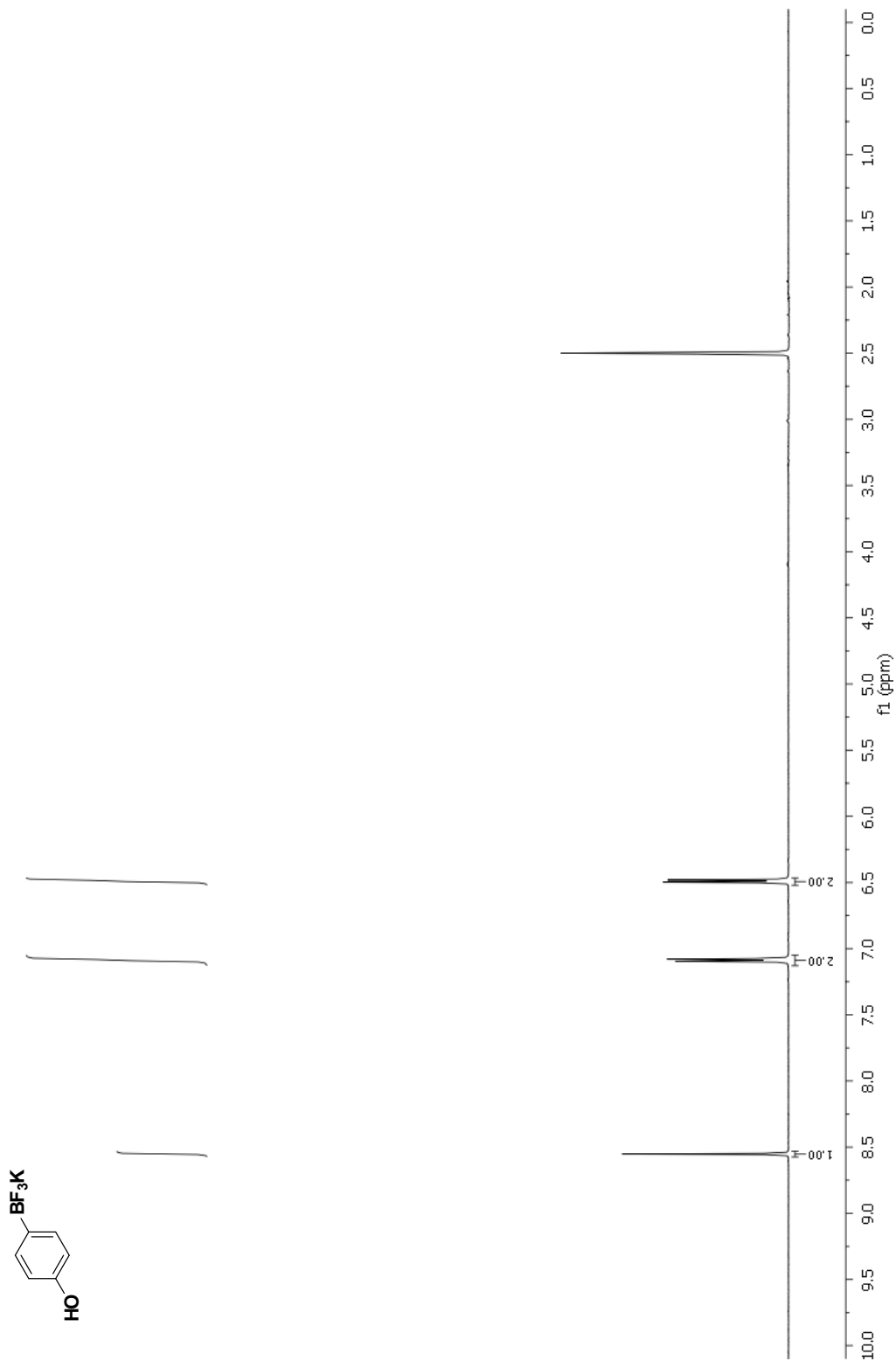
¹⁹F NMR Spectra (282 MHz, acetone-*d*₆) **(3-(Dimethylamino)phenyl)trifluoroborate** (Table 2, entry 14).



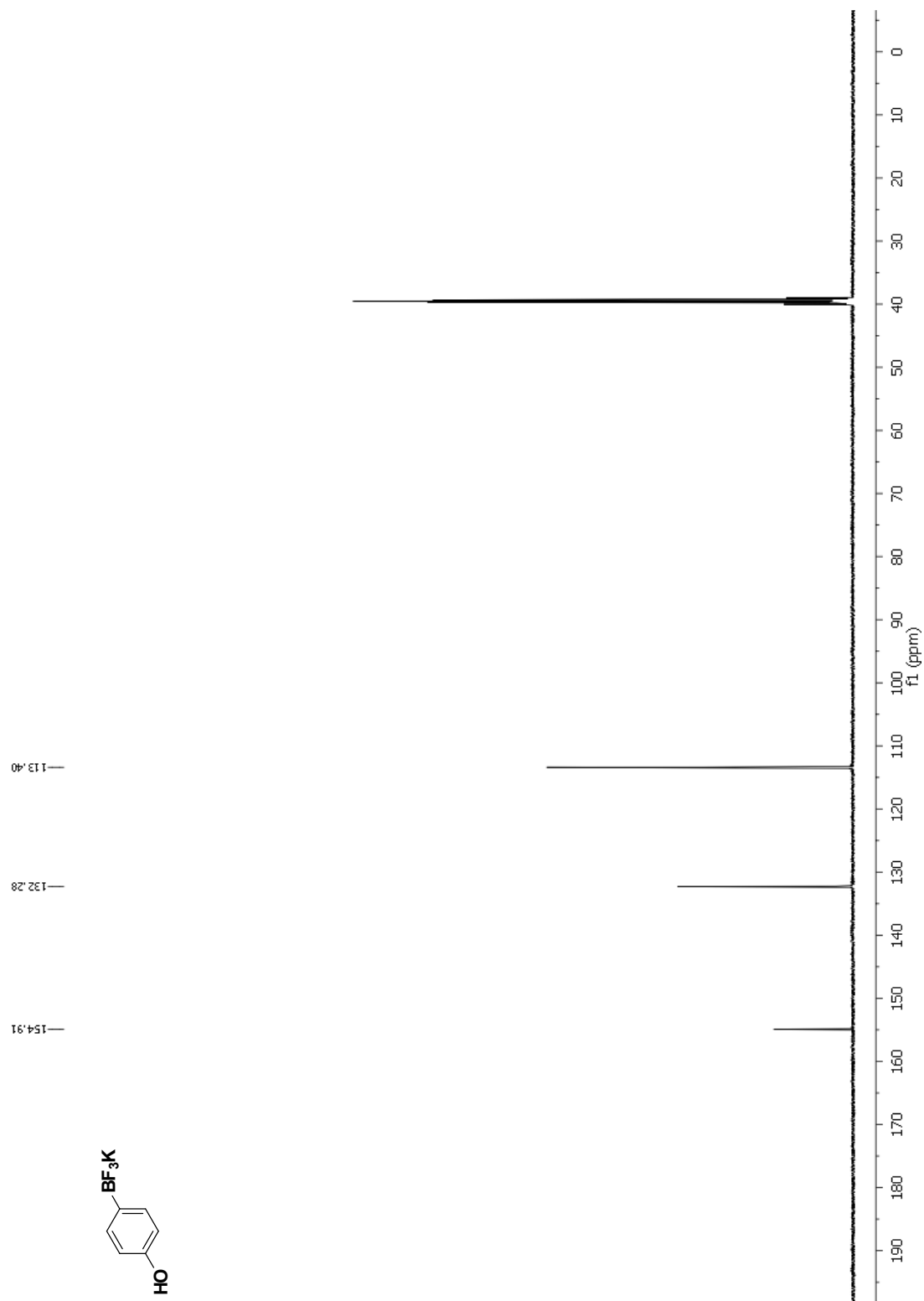
¹H NMR Spectra (500 MHz, acetone-*d*₆) Potassium *p*-Tolyl-trifluoroborate (Table 2, entry 15)



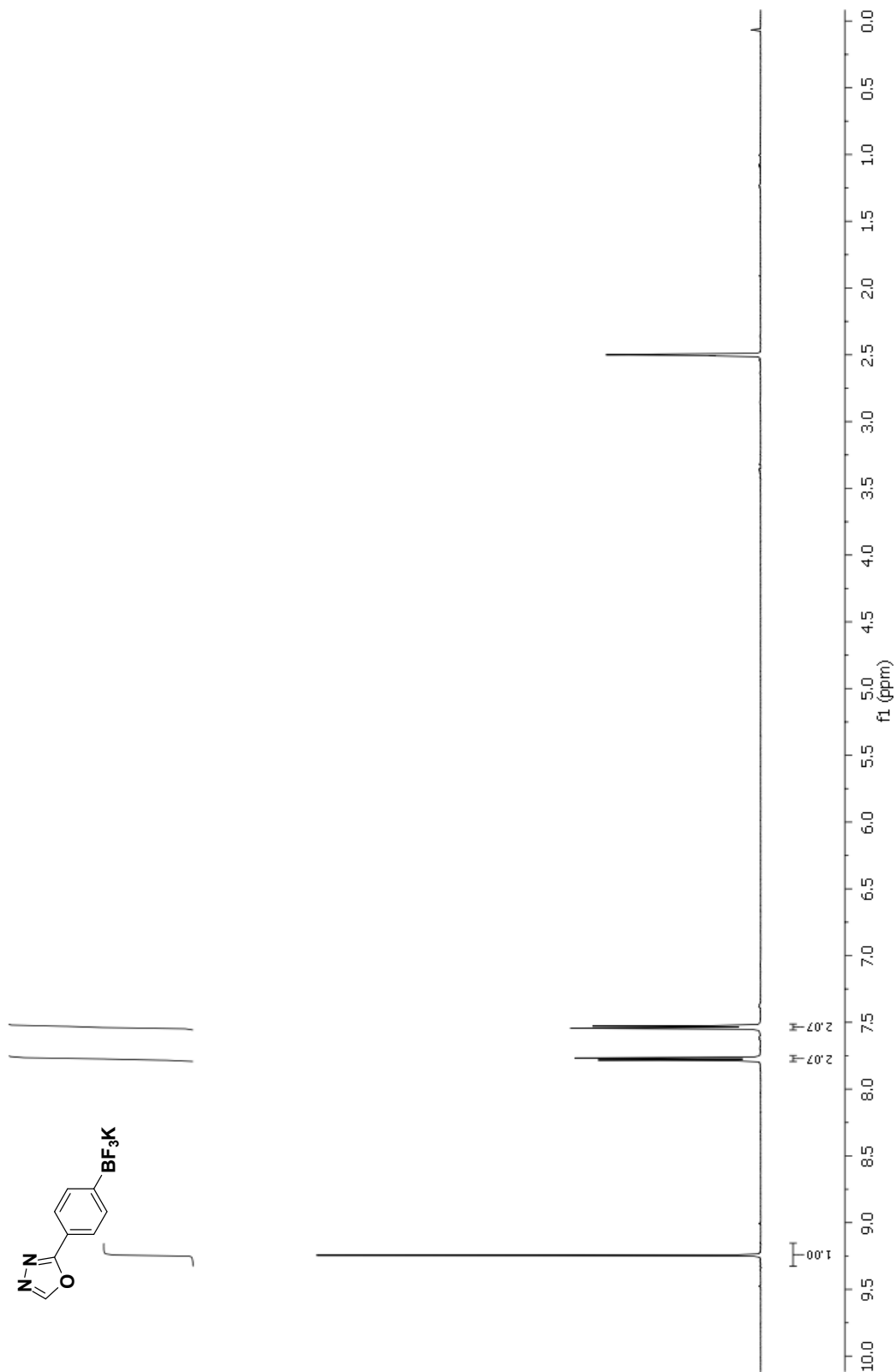
^{13}C NMR Spectra (125.8 MHz, acetone- d_6) Potassium *p*-Tolyl-trifluoroborate (Table 2, entry 15)



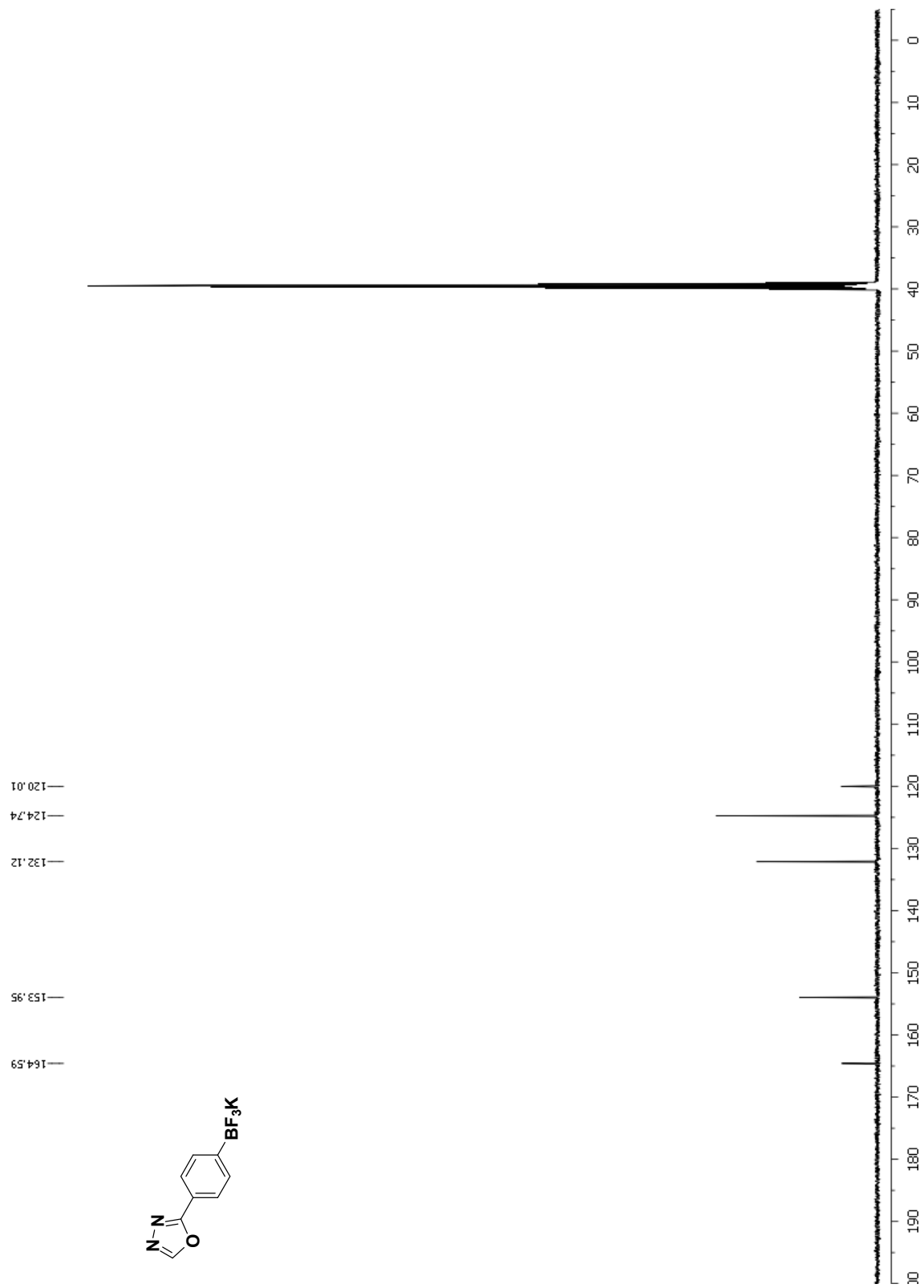
¹H NMR Spectra (500 MHz, DMSO-*d*₆) Potassium 4-Hydroxyphenyl-trifluoroborate (Table 2, entry 17)



^{13}C NMR Spectra (125.8 MHz, $\text{DMSO-}d_6$) Potassium 4-Hydroxyphenyltrifluoroborate (Table 2, entry 17)

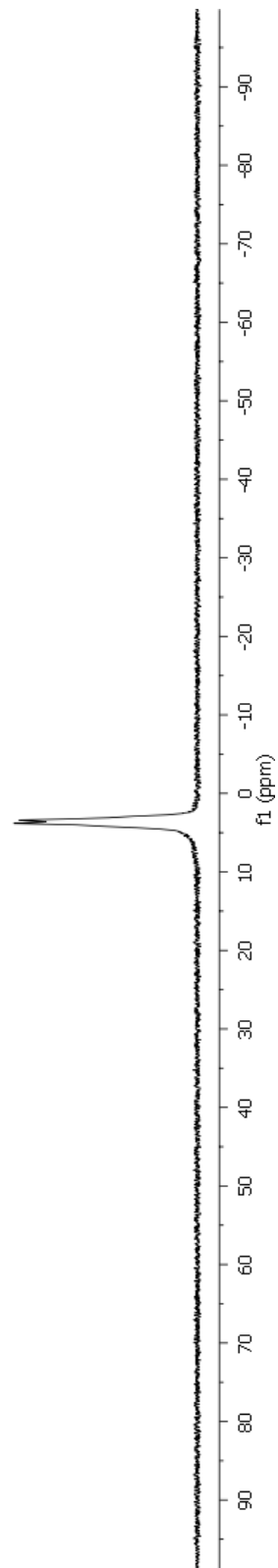
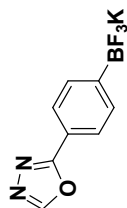


¹H NMR Spectra (500 MHz, DMSO-*d*₆) Potassium 4-(1,3,4-Oxadiazol-2-yl)phenyltrifluoroborate (Table 2, entry 18)



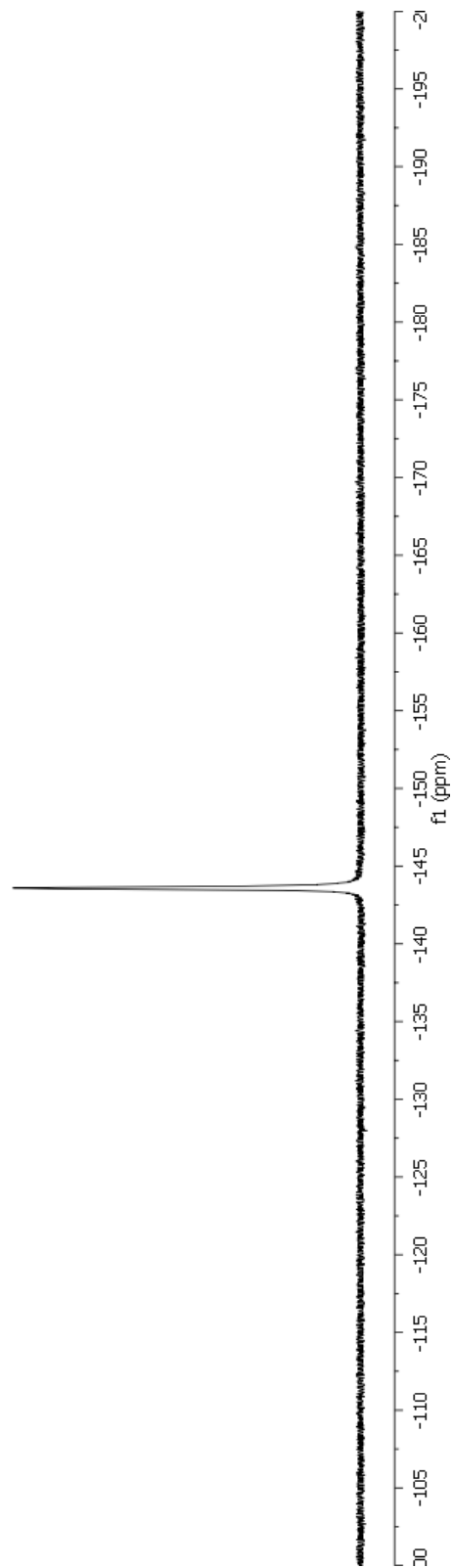
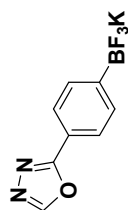
^{13}C NMR Spectra (125.8 MHz, $\text{DMSO-}d_6$) Potassium 4-(1,3,4-Oxadiazol-2-yl)phenyltrifluoroborate (Table 2, entry 18)

3.40
1.81

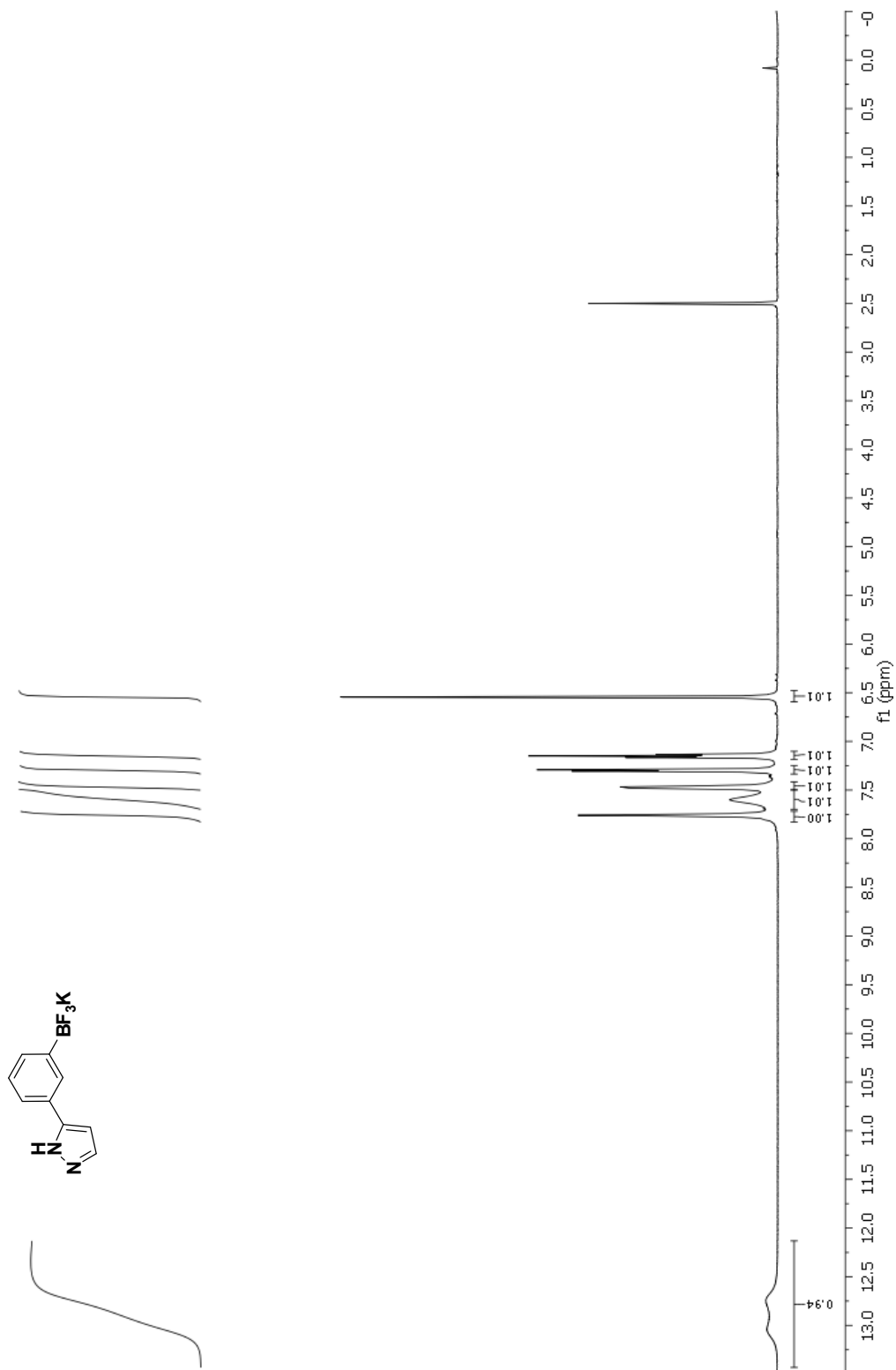


¹¹B NMR Spectra (128.4 MHz, DMSO-*d*₆) Potassium 4-(1,3,4-Oxadiazol-2-yl)phenyltrifluoroborate (Table 2, entry 18)

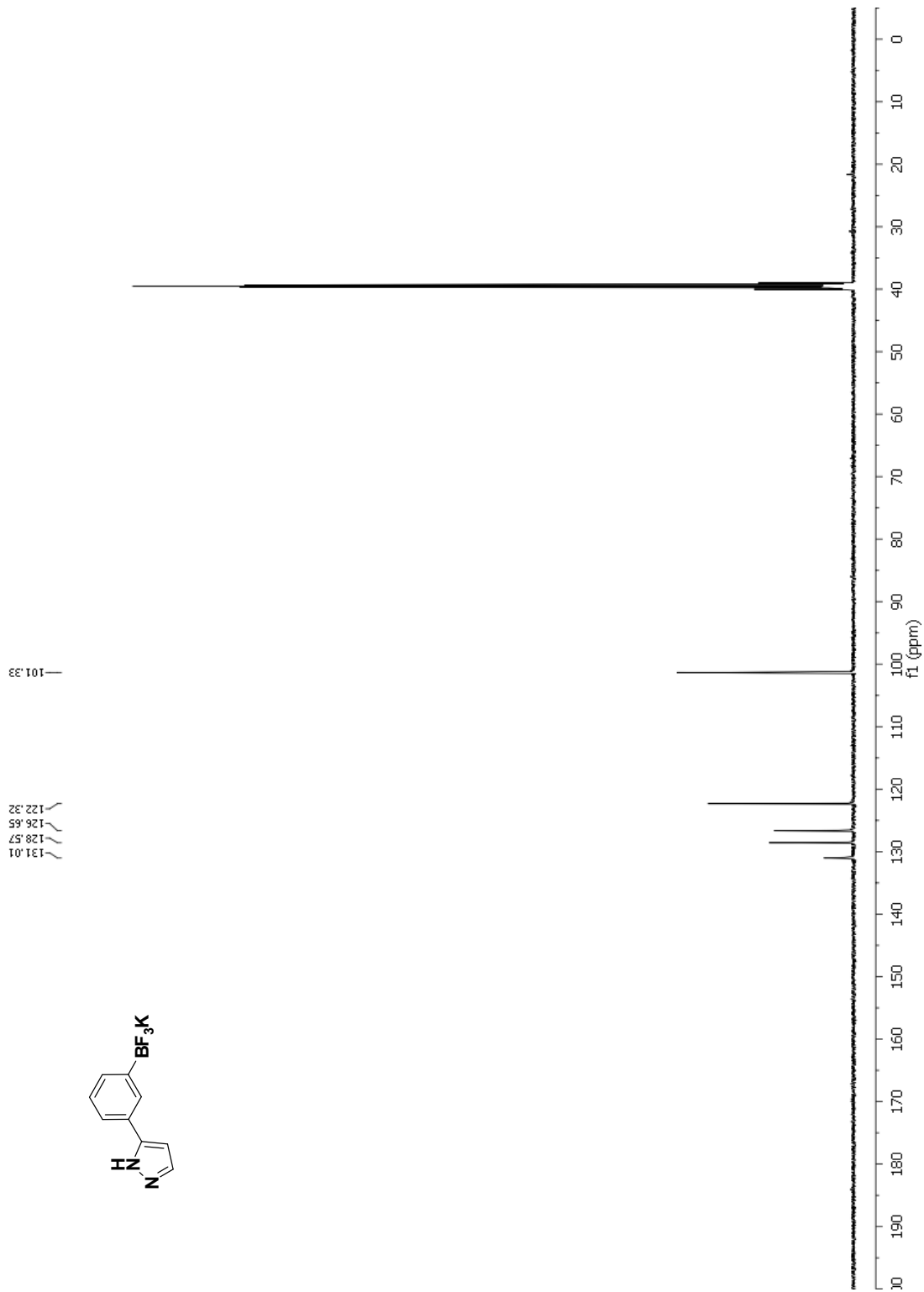
—143.59



¹⁹F NMR Spectra (282 MHz, DMSO-*d*₆) Potassium 4-(1,3,4-Oxadiazol-2-yl)phenyltrifluoroborate (Table 2, entry 18)

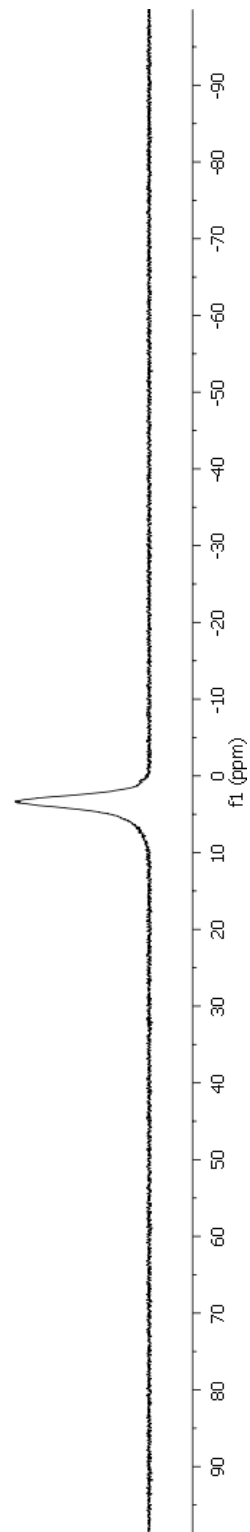
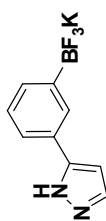


¹H NMR Spectra (500 MHz, DMSO-*d*₆) Potassium 3-(1H-Pyrazol-5-yl)phenyl-trifluoroborate (Table 2, entry 19)



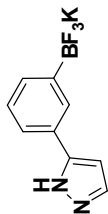
¹³C NMR Spectra (125.8 MHz, DMSO-*d*₆) Potassium 3-(1H-Pyrazol-5-yl)phenyl-trifluoroborate (Table 2, entry 19)

3.49

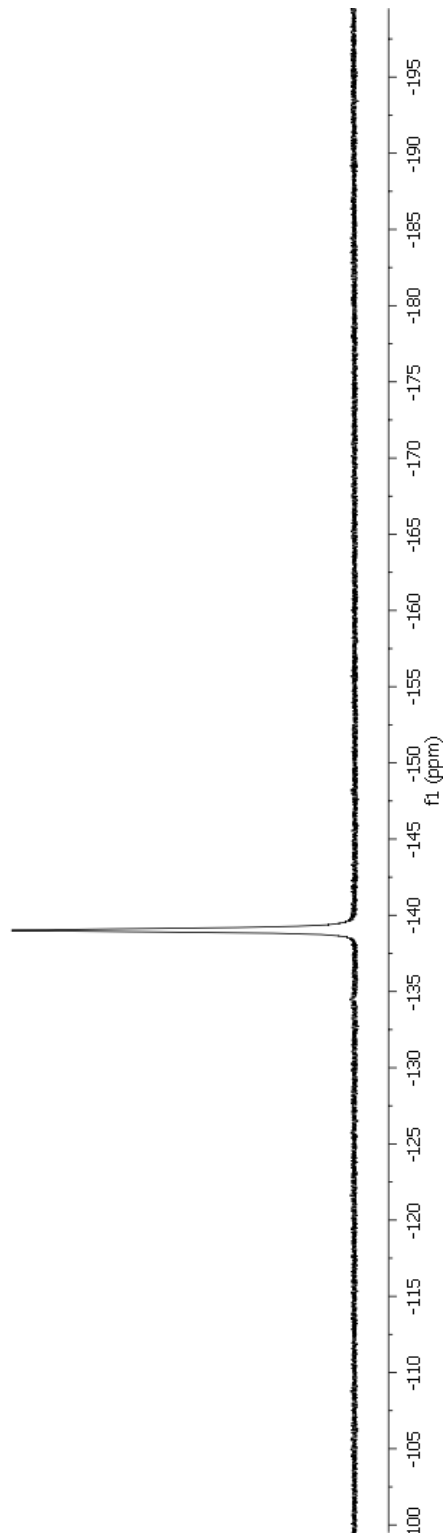


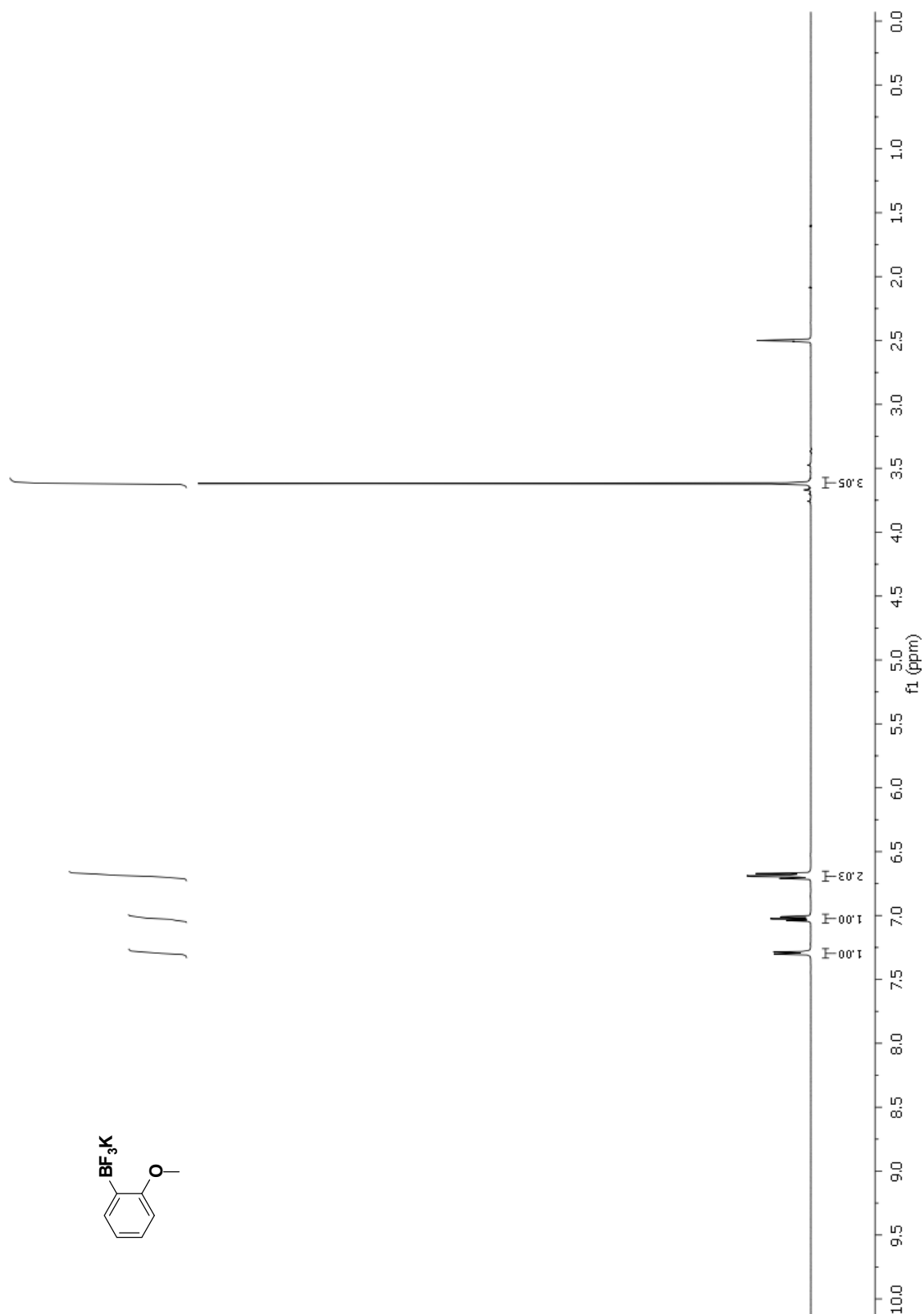
¹¹B NMR Spectra (128.4 MHz, DMSO-*d*₆) Potassium 3-(1H-Pyrazol-5-yl)phenyltrifluoroborate (Table 2, entry 19)

86.138.98

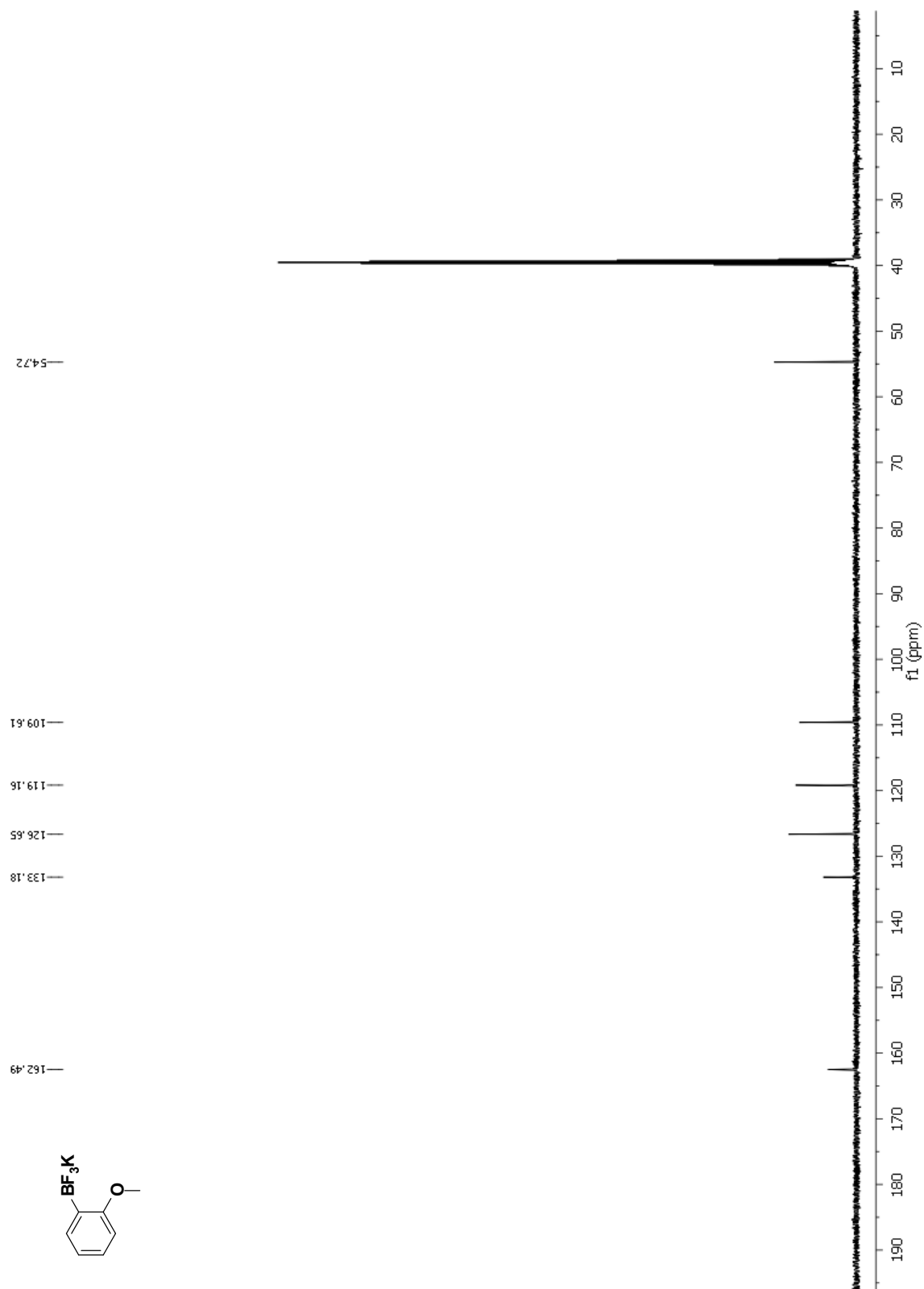


¹¹F NMR Spectra (282 MHz, DMSO-*d*₆) Potassium 3-(1H-Pyrazol-5-yl)phenyltrifluoroborate (Table 2, entry 19)

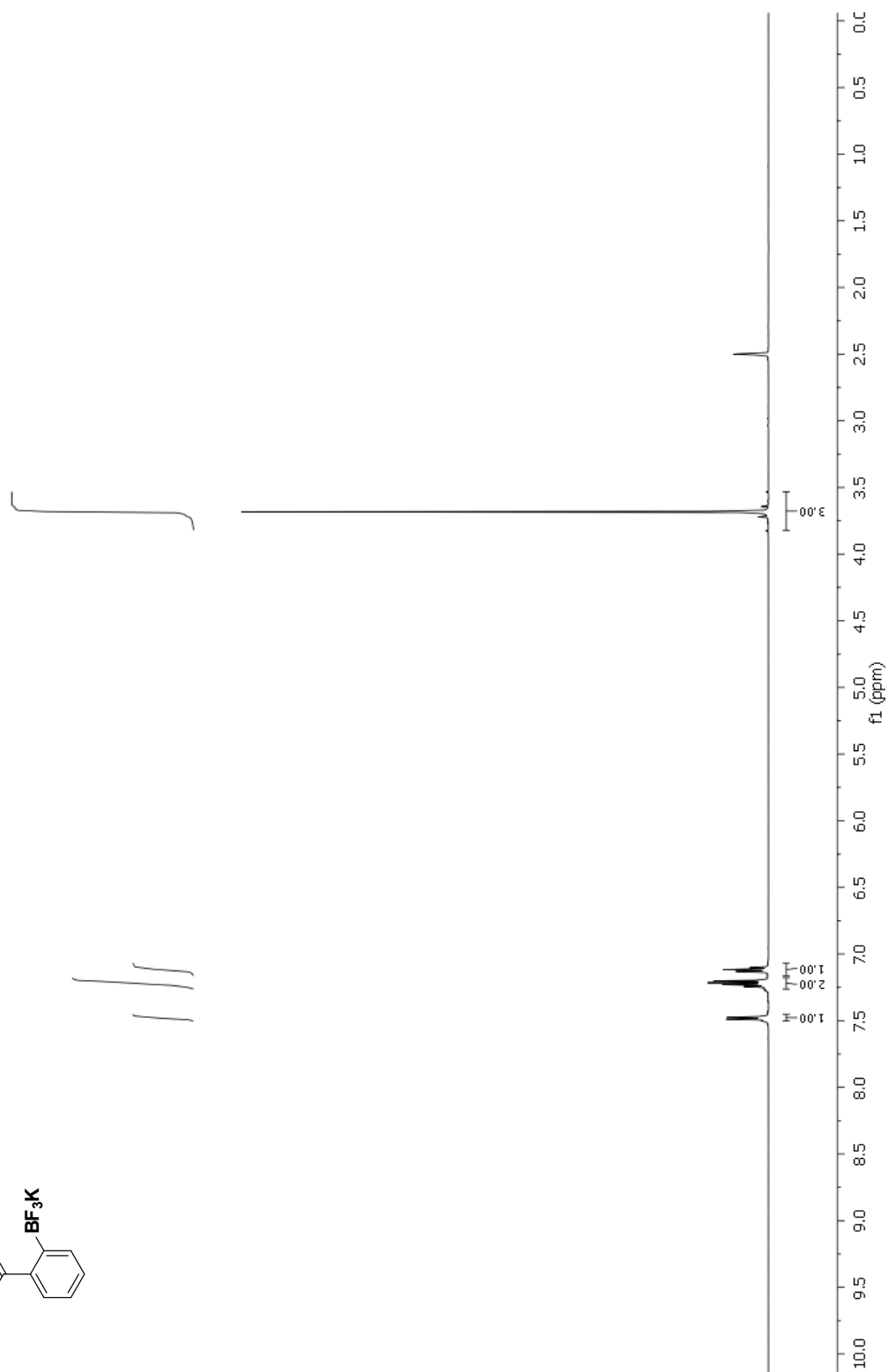
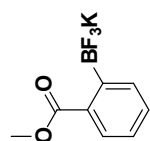




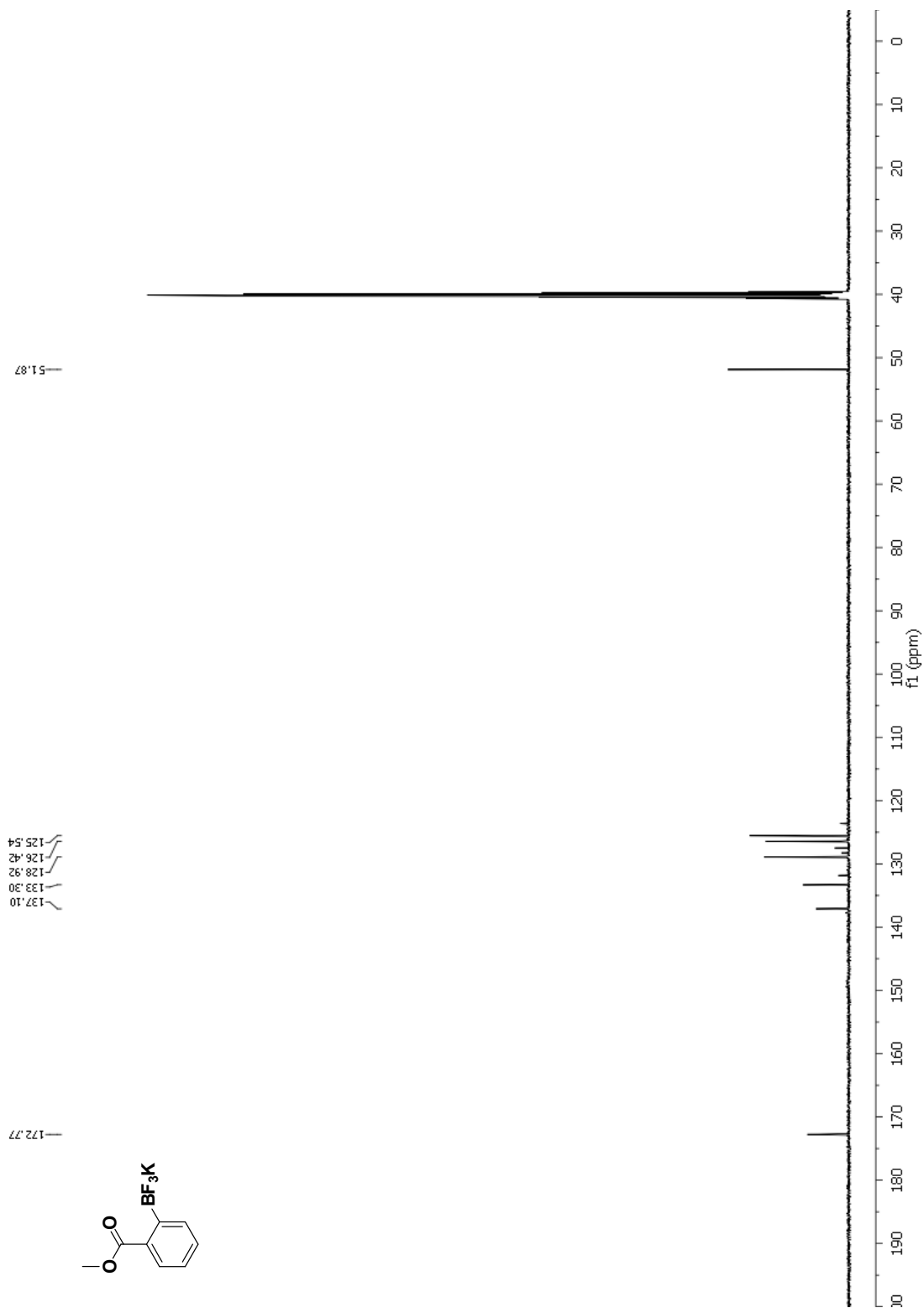
¹H NMR Spectra (500 MHz, DMSO-*d*₆) **Potassium 2-Methoxyphenyl-trifluoroborate (Table 2, entry 20)**



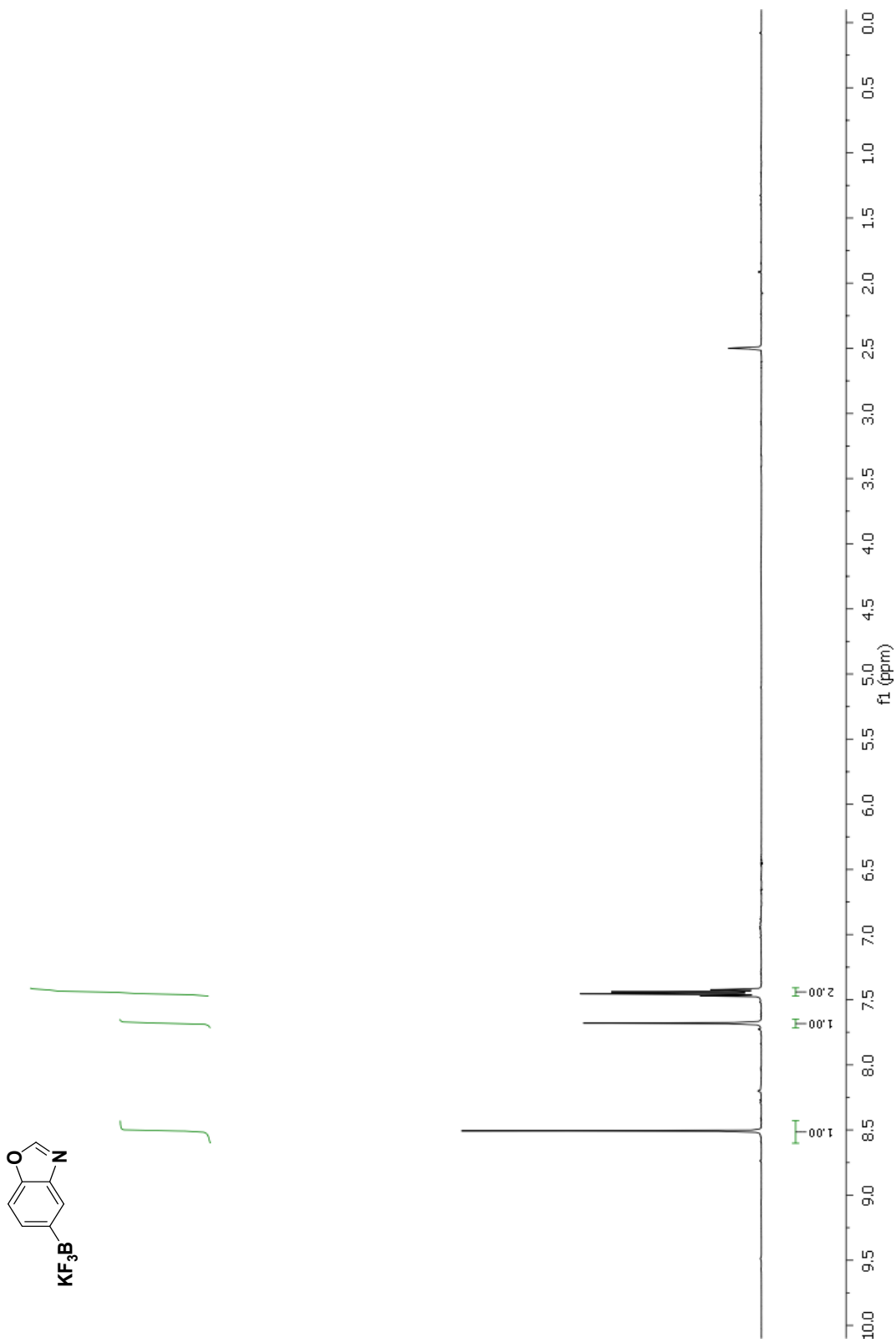
¹³C NMR Spectra (125.8 MHz, DMSO-*d*₆) Potassium 2-Methoxyphenyltrifluoroborate (Table 2, entry 20)



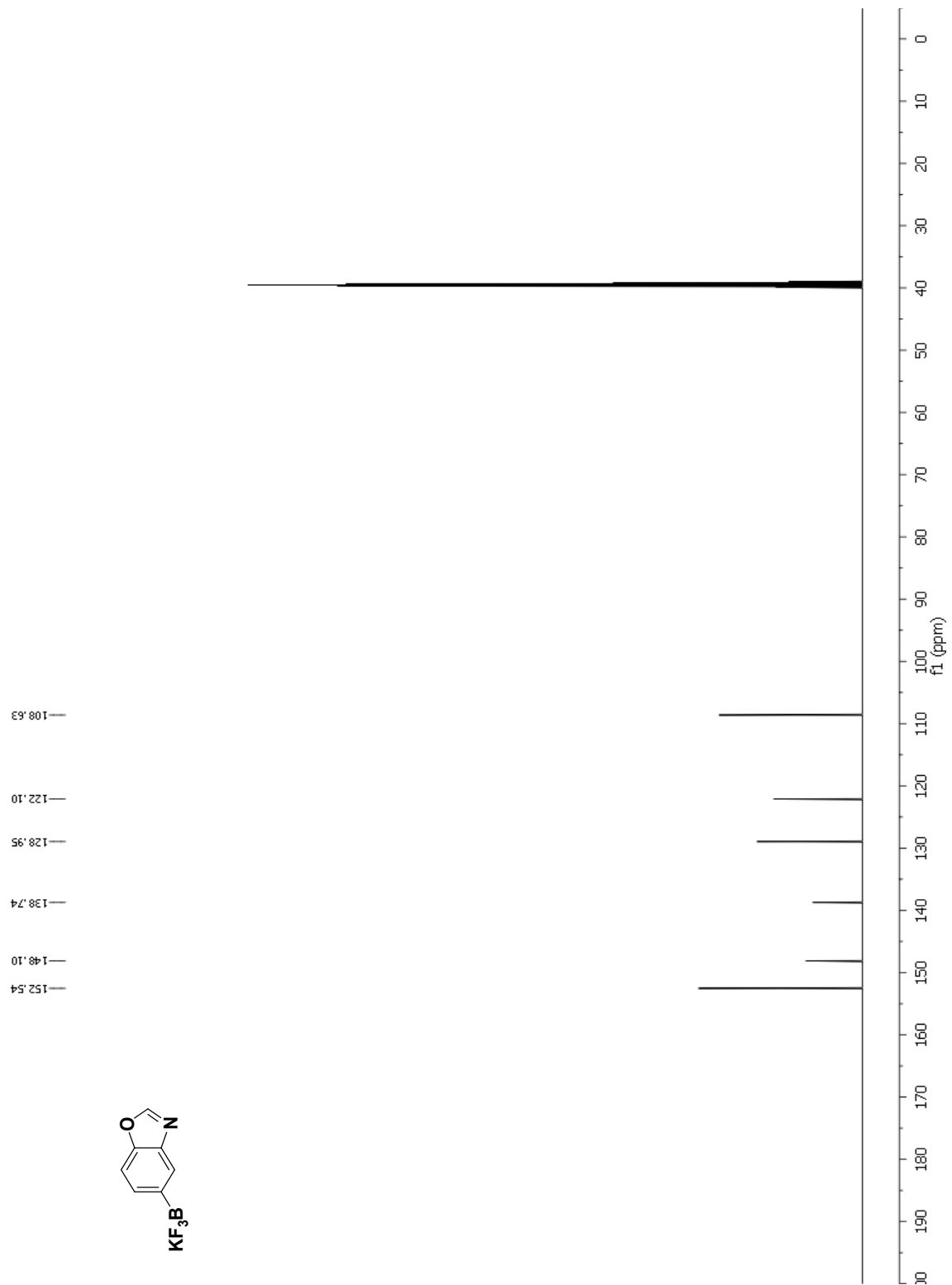
¹H NMR Spectra (500 MHz, DMSO-*d*₆) Potassium 2-(Methoxycarbonyl)phenyltrifluoroborate (Table 1, entry 21)



¹³C NMR Spectra (125.8 MHz, DMSO-*d*₆) Potassium 2-(Methoxycarbonyl)phenyltrifluoroborate (Table 1, entry 21)

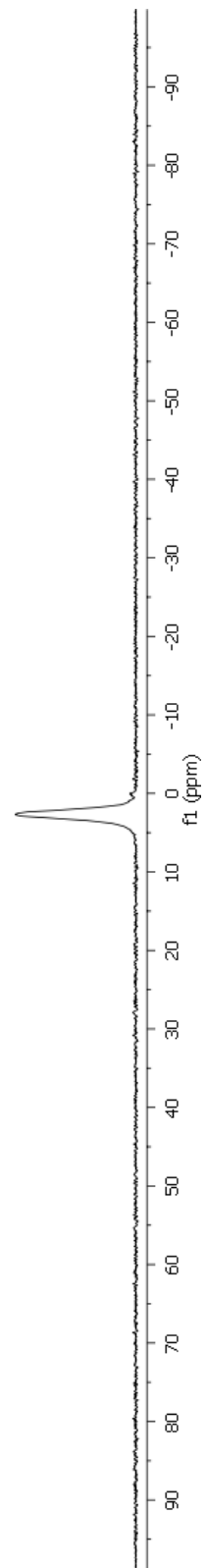
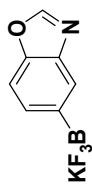


¹H NMR Spectra (500 MHz, DMSO-*d*₆) **Potassium 5-Trifluoroborato-benzoxazole** (Table 4, entry 2)



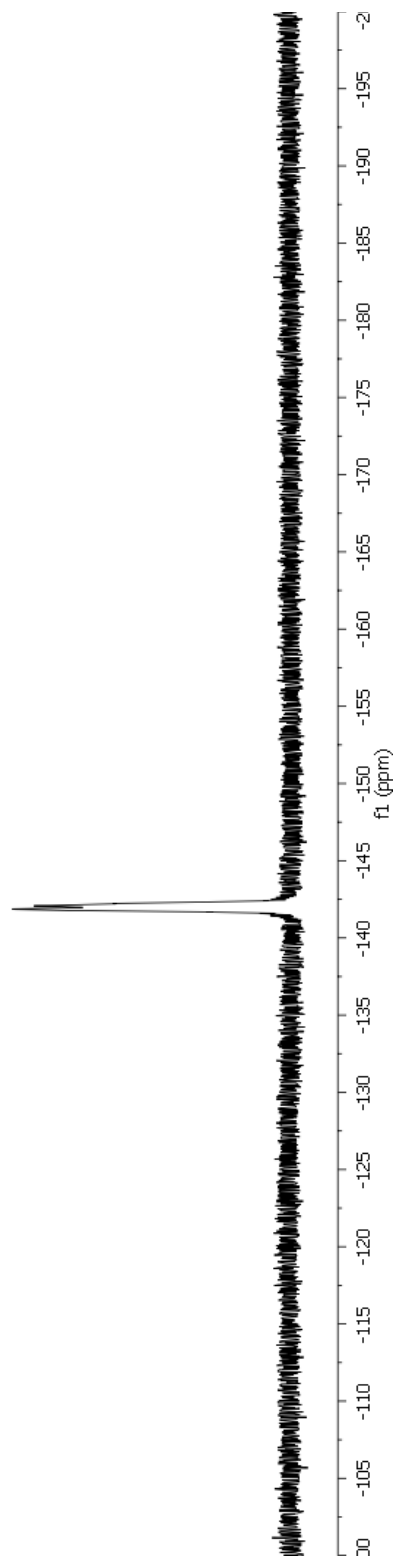
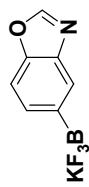
¹³C NMR Spectra (500 MHz, DMSO-*d*₆) Potassium 5-Trifluoroborato-benzoxazole (Table 4, entry 2)

—2.66

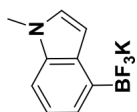


^{11}B NMR Spectra (128.4 MHz, $\text{DMSO-}d_6$) **Potassium 5-Trifluoroborato-benzoxazole** (Table 4, entry 2)

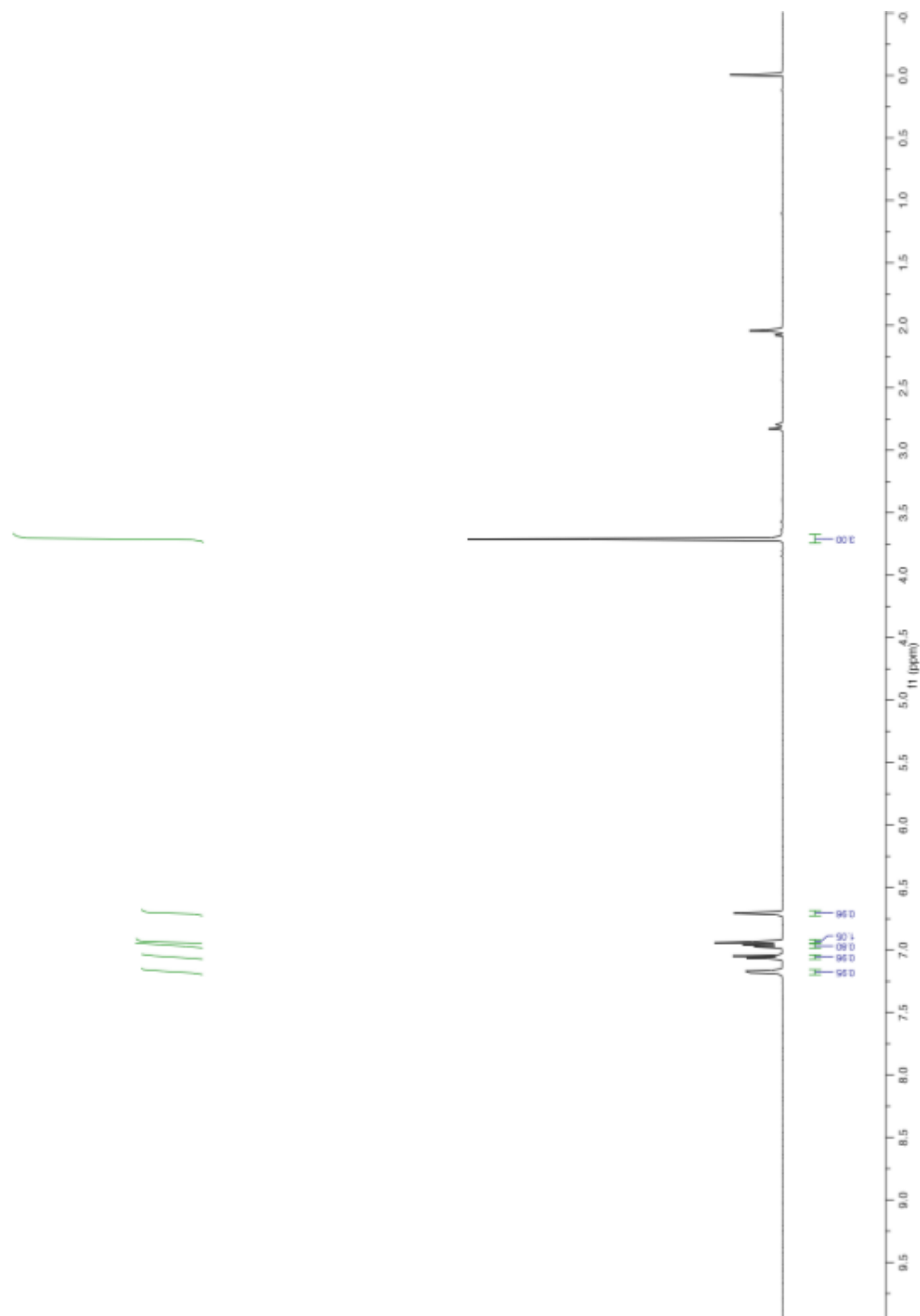
-141.85
-142.08

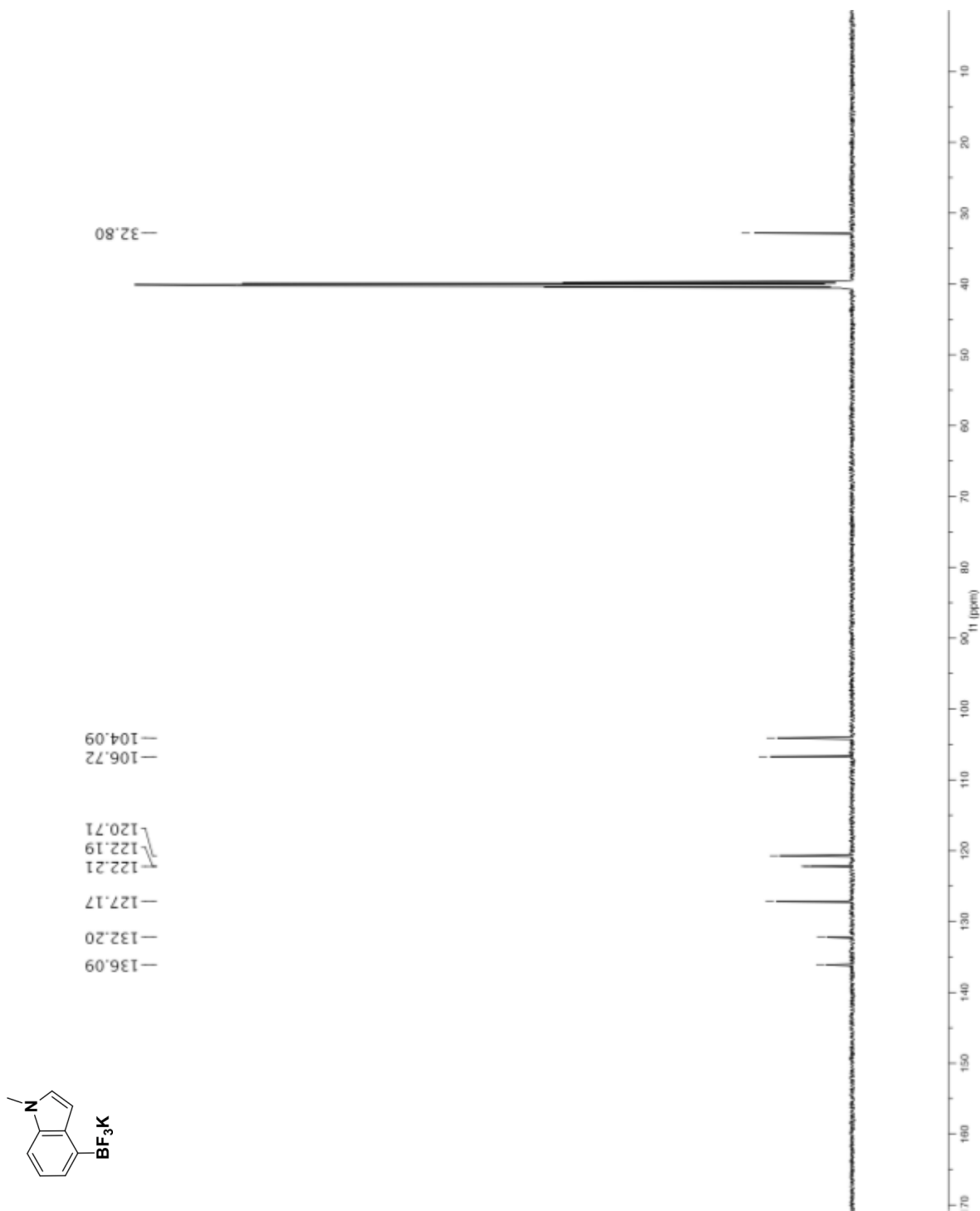


^{19}F NMR Spectra (282 MHz, $\text{DMSO-}d_6$) Potassium 5-Trifluoroborato-benzoxazole (Table 4, entry 2)

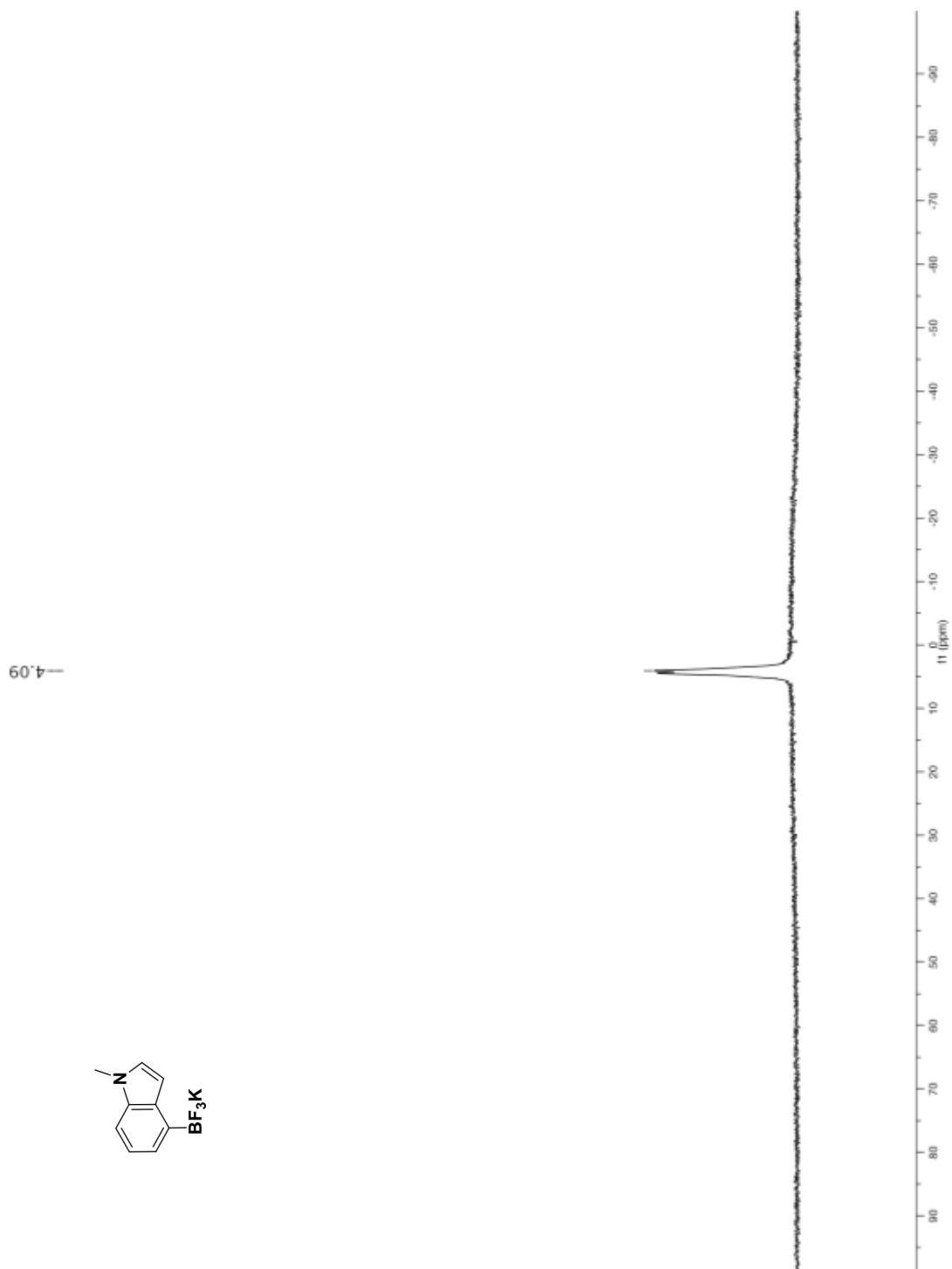


¹H NMR Spectra (500 MHz, acetone-*d*₆) **Potassium (2-Methylquinolin-8-yl)trifluoroborate (Table 4, entry 3).**

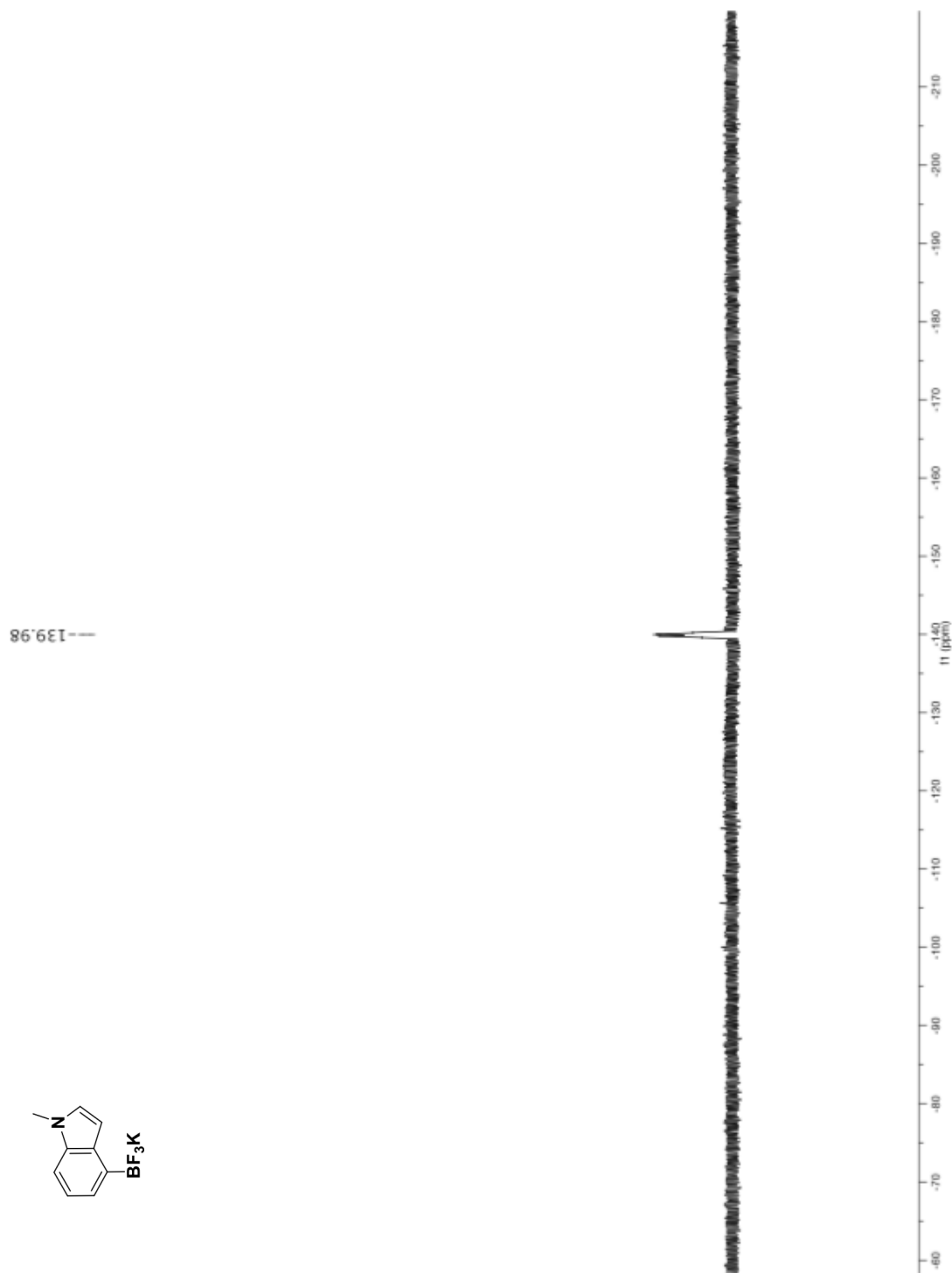




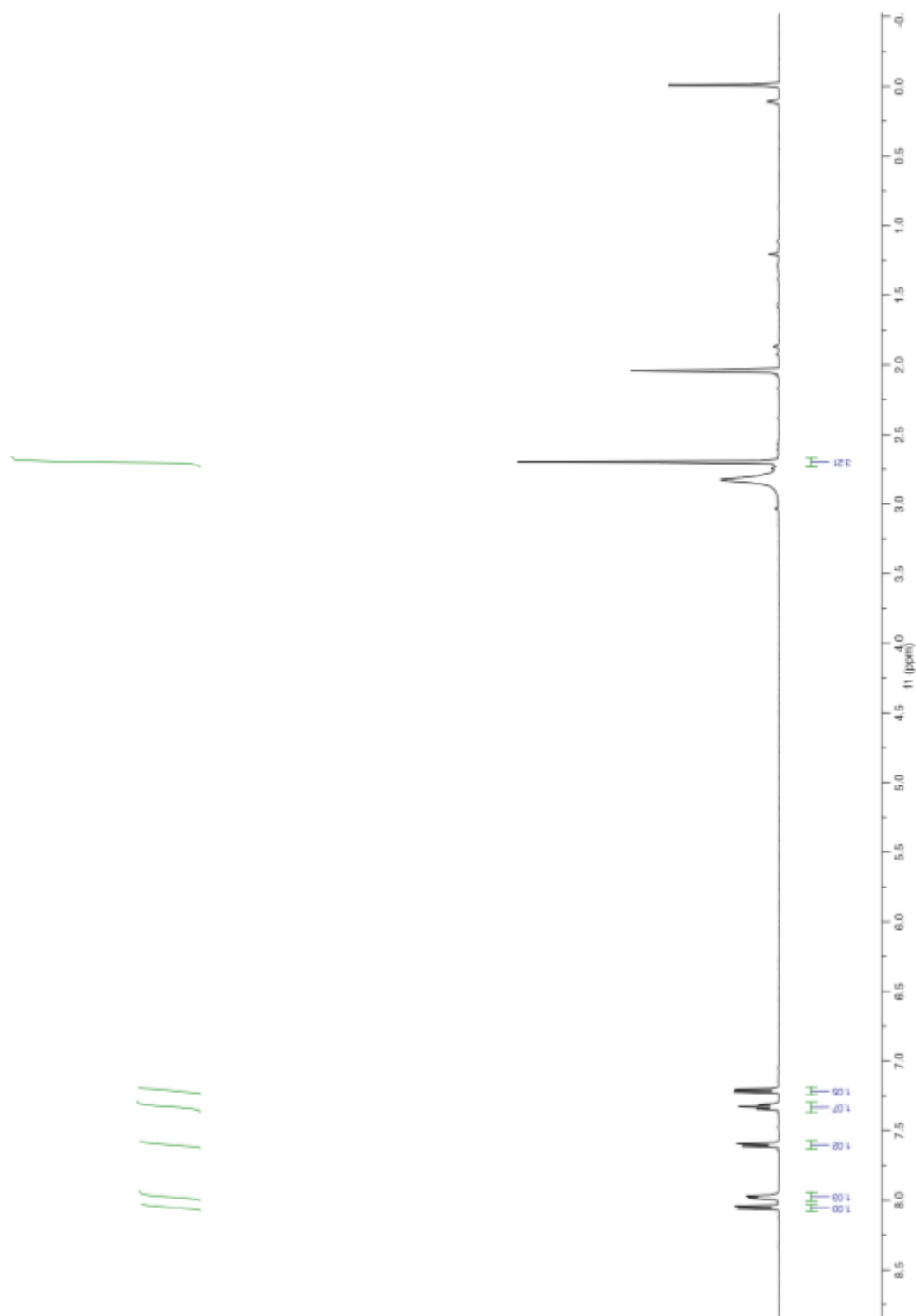
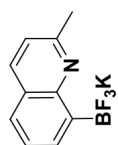
¹³C NMR Spectra (125.8 MHz, DMSO-*d*₆) Potassium (2-Methylquinolin-8-yl)trifluoroborate (Table 4, entry 3).



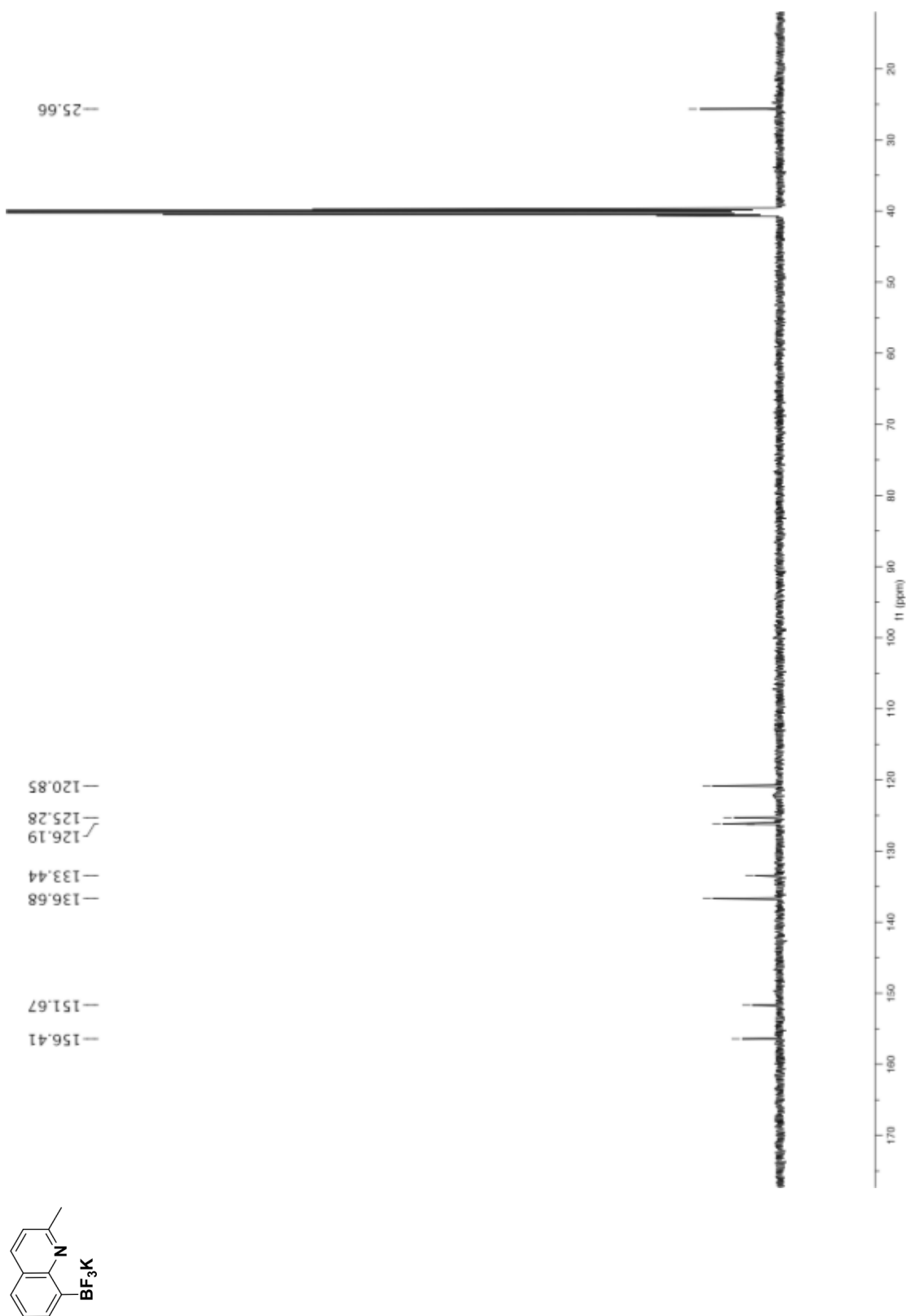
^{11}B NMR Spectra (128.4 MHz, acetone- d_6) **Potassium (2-Methylquinolin-8-yl)trifluoroborate (Table 4, entry 3).**



^{19}F NMR Spectra (282 MHz, acetone- d_6) Potassium (2-Methylquinolin-8-yl)trifluoroborate (Table 4, entry 3).

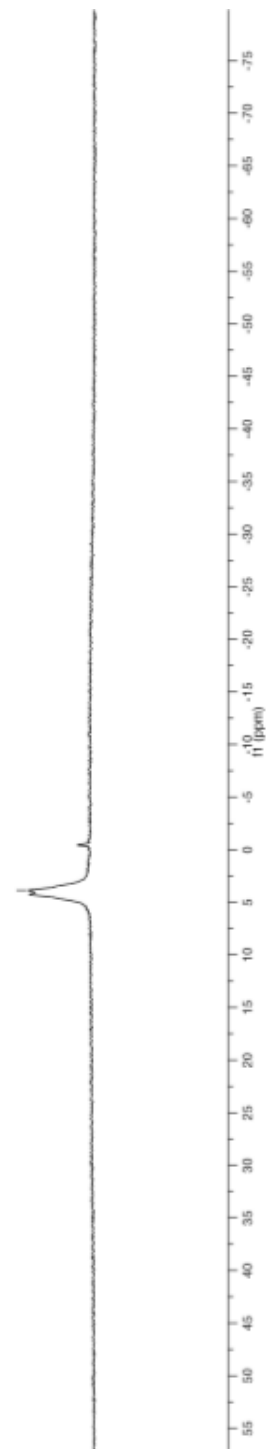
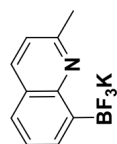


¹H NMR Spectra (500 MHz, acetone-d₆) Potassium (2-Methylquinolin-8-yl)trifluoroborate (Table 4, entry 4).

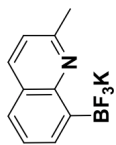


¹³C NMR Spectra (125.8 MHz, DMSO-*d*₆) Potassium (2-Methylquinolin-8-yl)trifluoroborate (Table 4, entry 4).

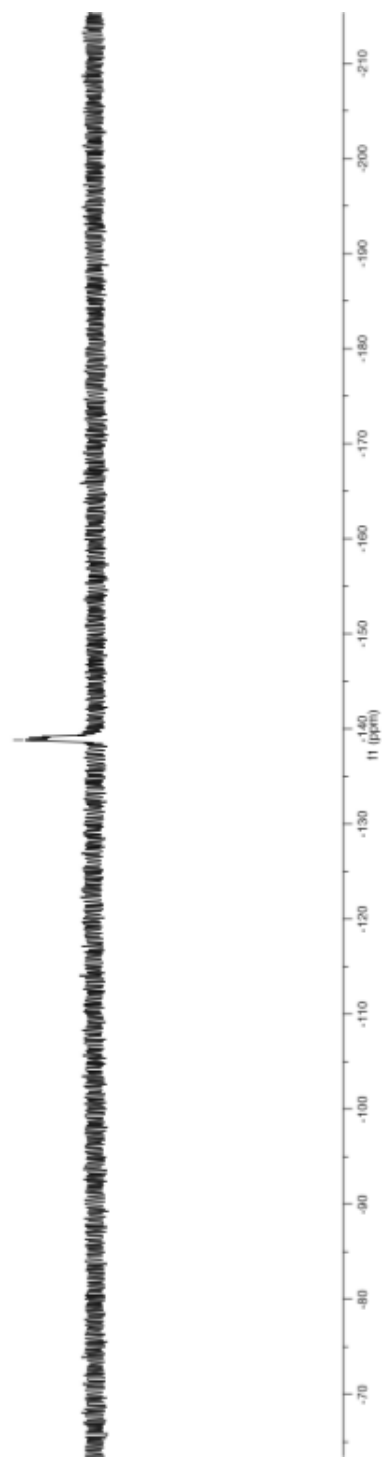
—3.86



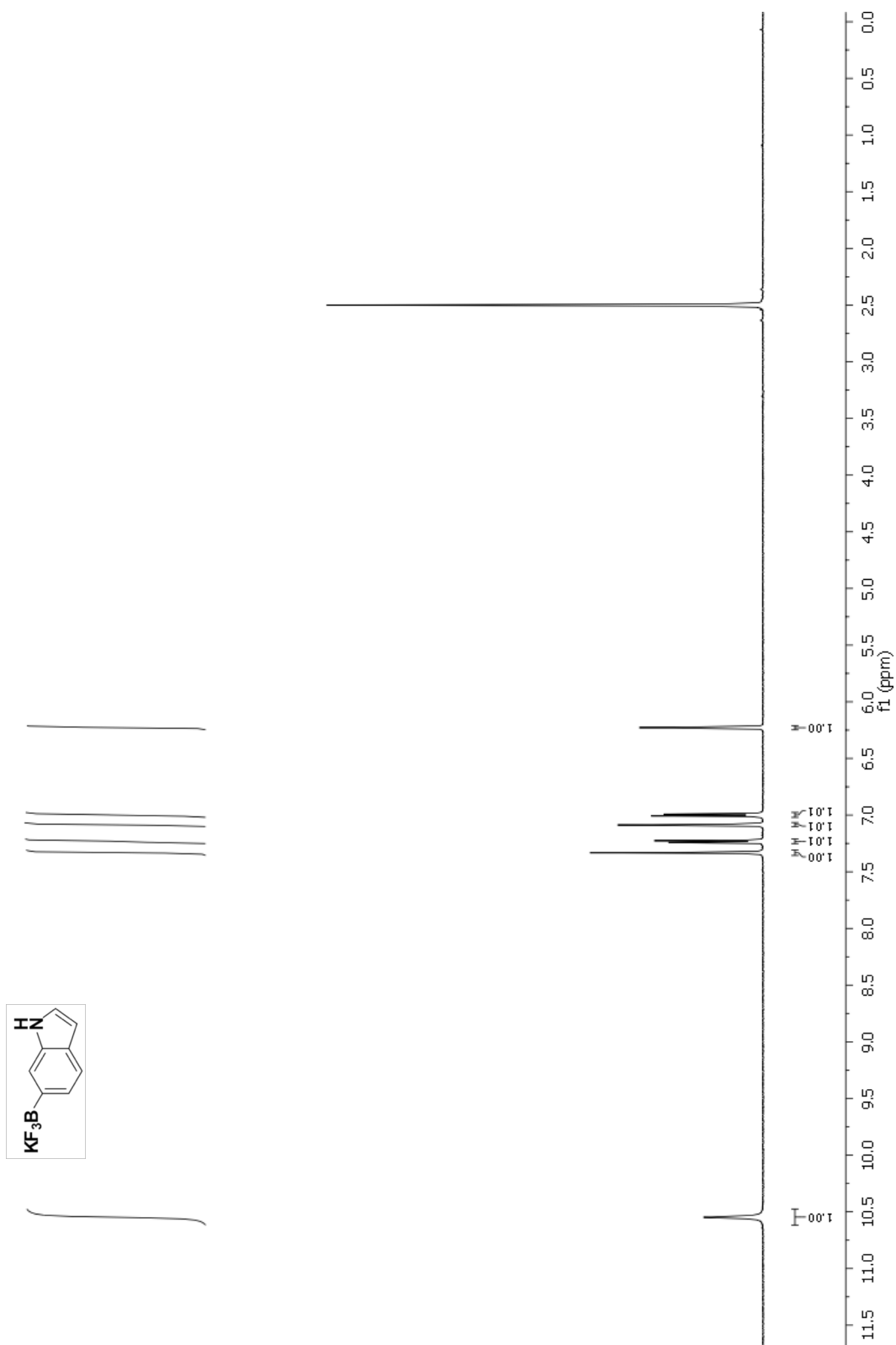
^{11}B NMR Spectra (128.4 MHz, acetone- d_6) **Potassium (2-Methylquinolin-8-yl)trifluoroborate (Table 4, entry 4).**



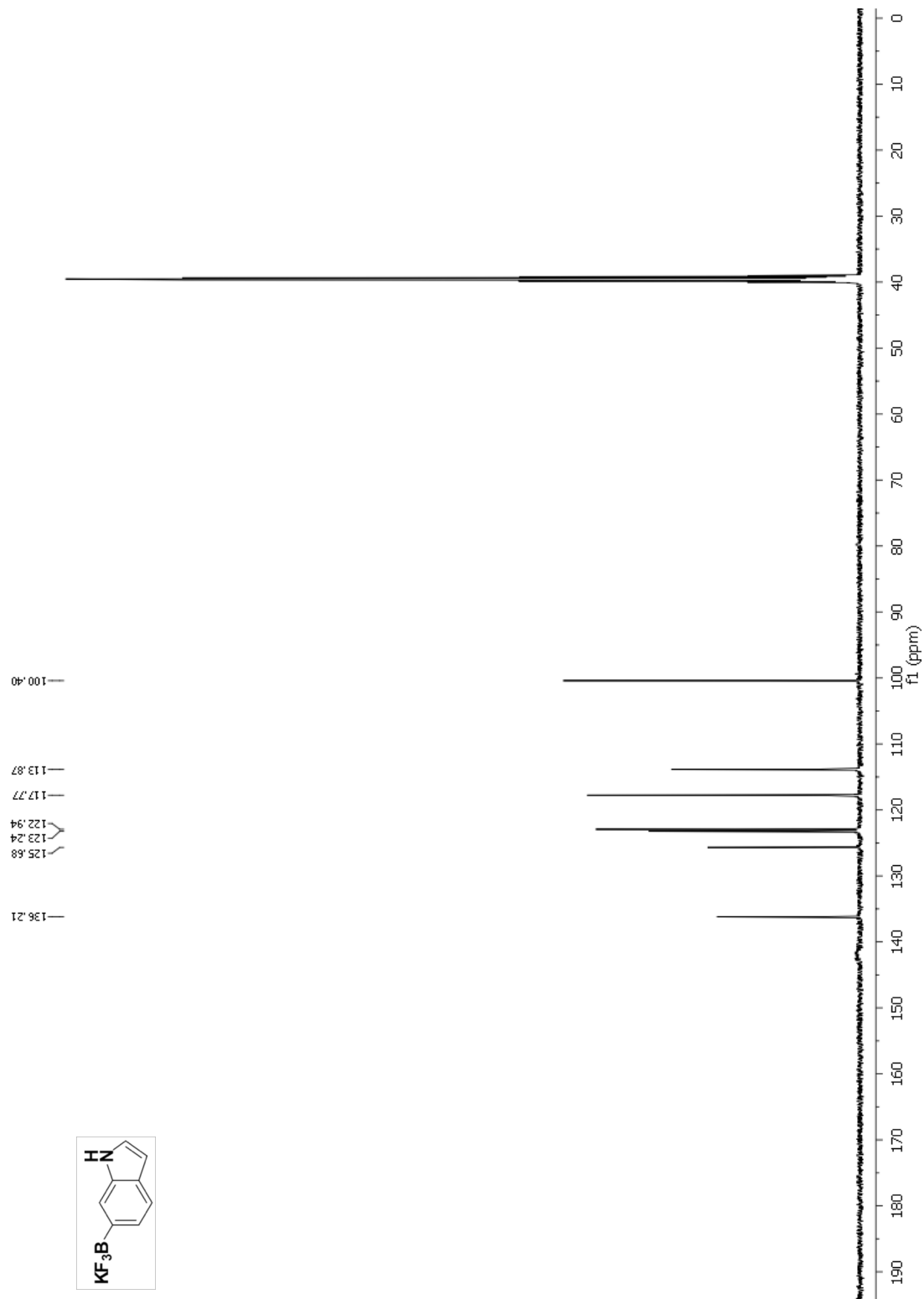
--138.82



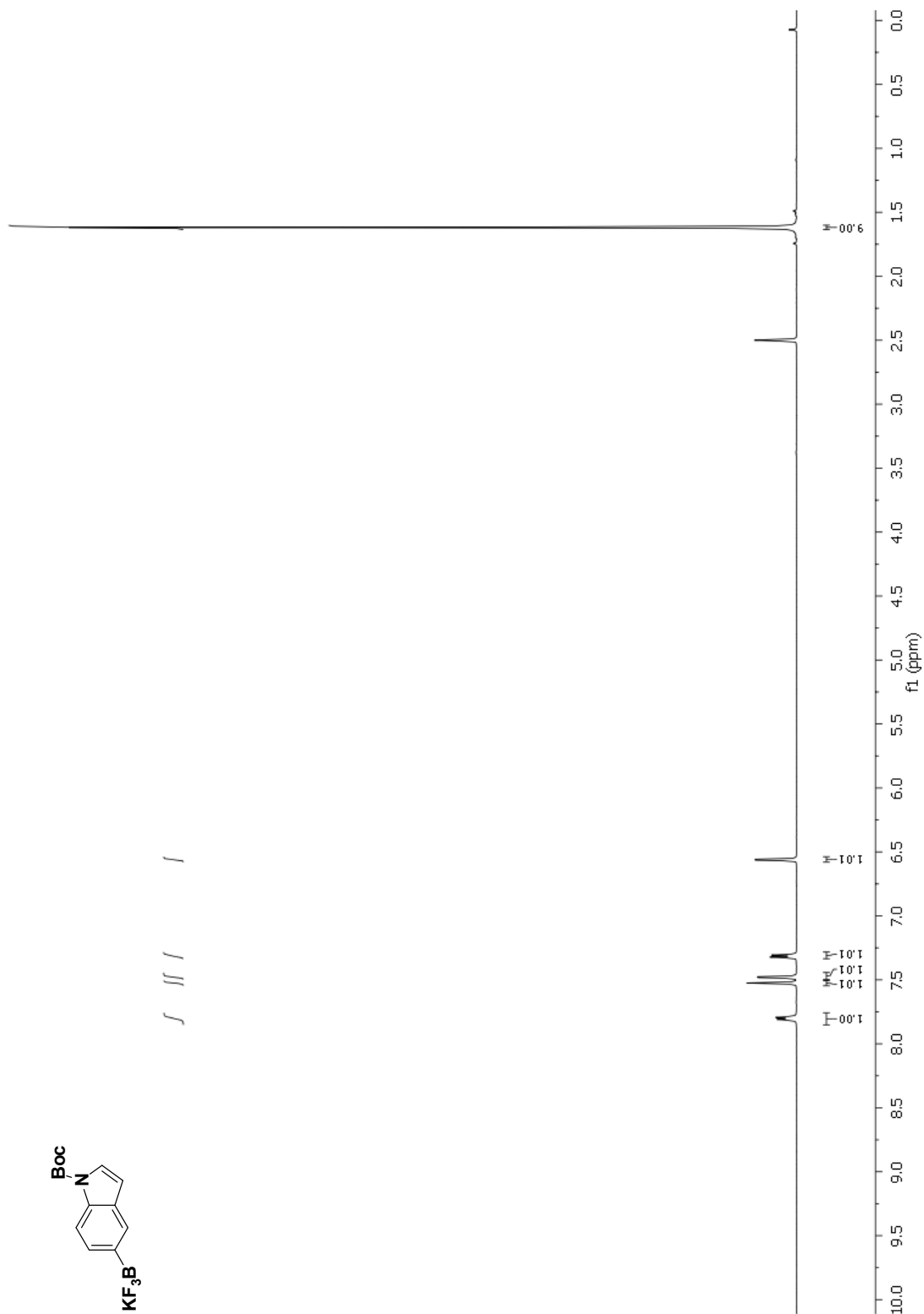
¹⁹F NMR Spectra (282 MHz, acetone-*d*₆) **Potassium (2-Methylquinolin-8-yl)trifluoroborate** (Table 4, entry 4).



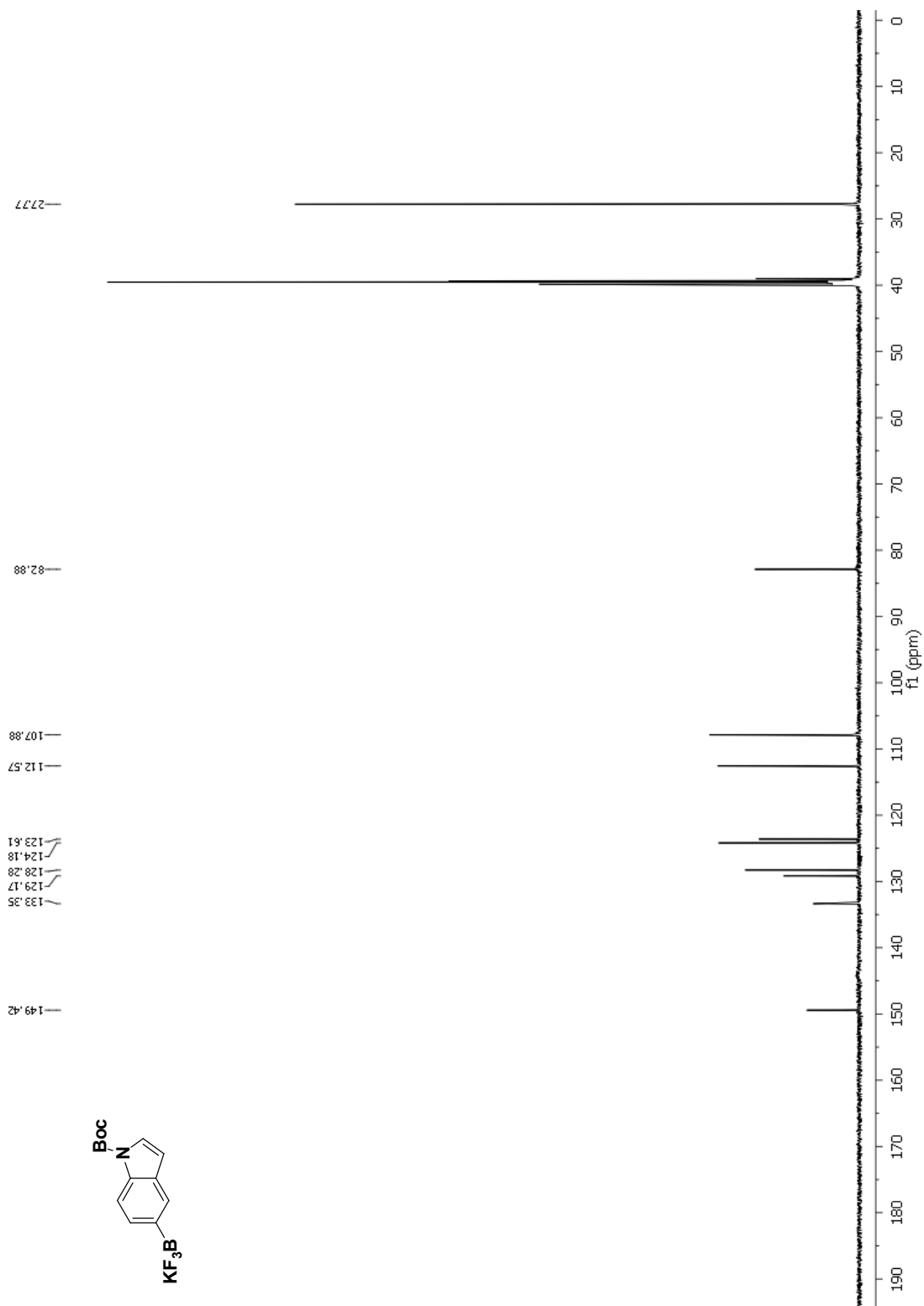
¹H NMR Spectra (500 MHz, DMSO-*d*₆) Potassium 1H-Indol-5-yl-trifluoroborate (Table 4, entry 5)



¹³C NMR Spectra (125.8 MHz, DMSO-*d*₆) Potassium 1H-Indol-5-yl-trifluoroborate (Table 4, entry 5)



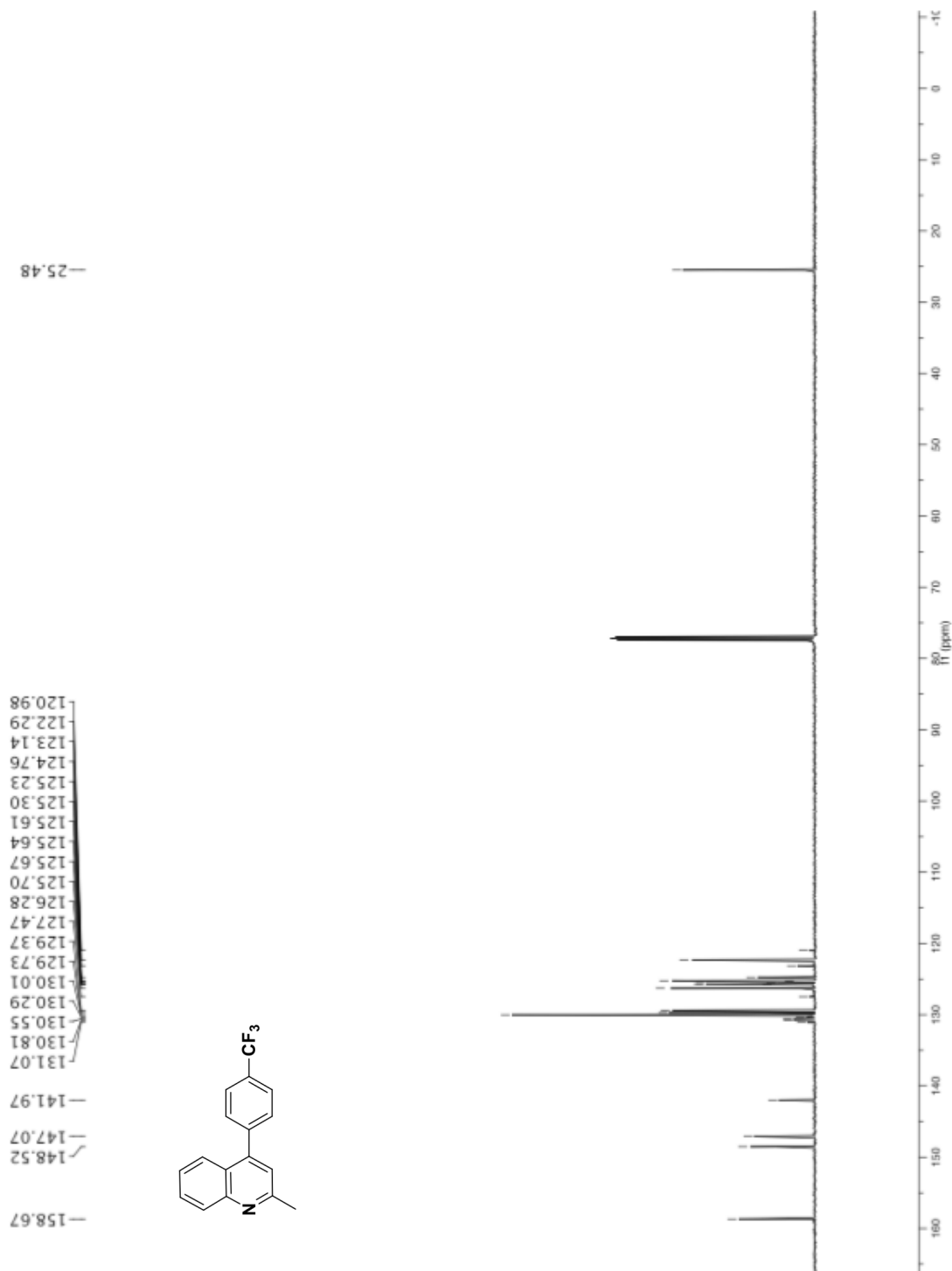
¹H NMR Spectra (500 MHz, DMSO-*d*₆) Potassium 1-(*tert*-Butoxycarbonyl)-indol-5-yl-trifluoroborate (Table 4, entry 6)



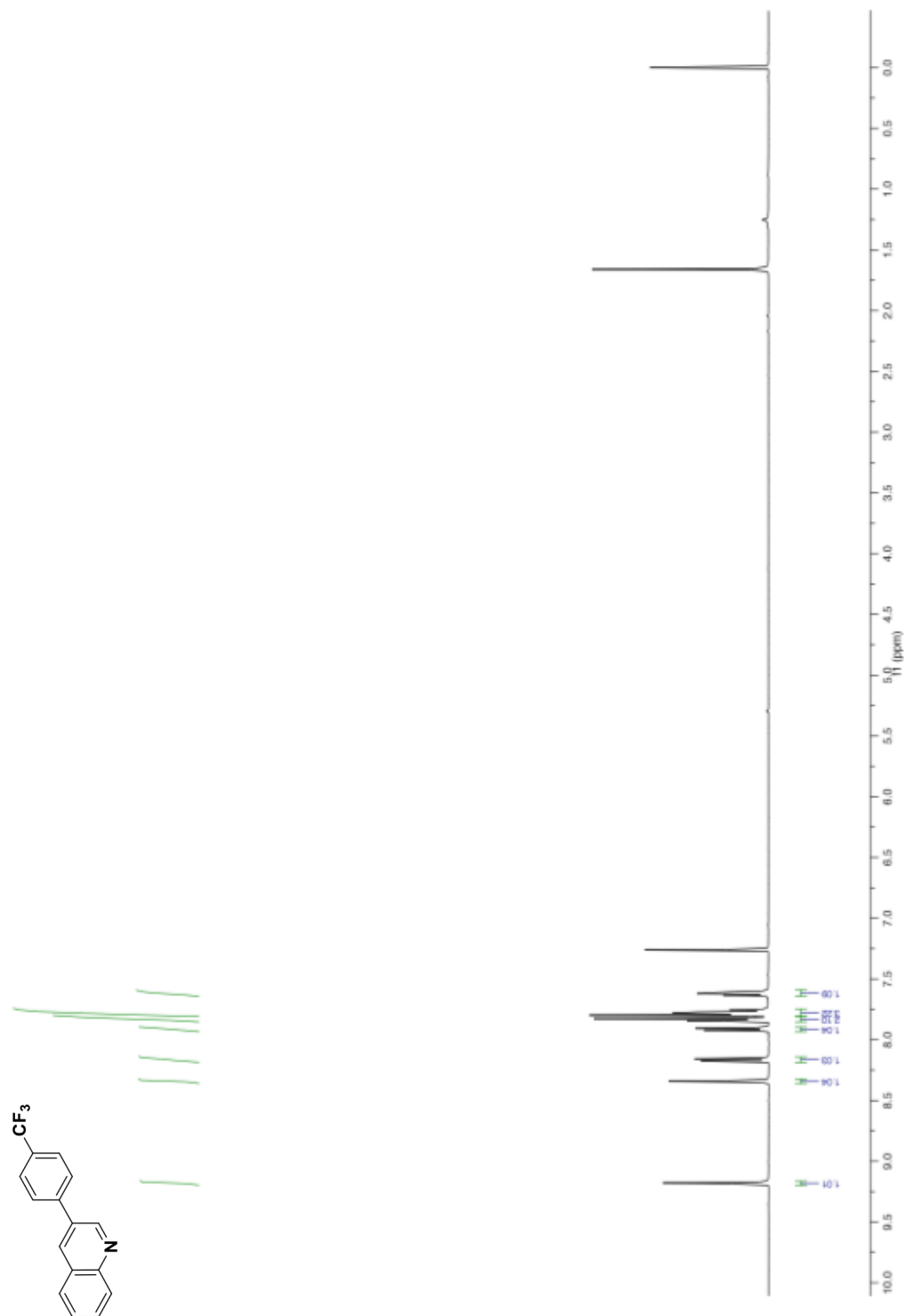
¹³C NMR Spectra (125.8 MHz, DMSO-*d*₆) Potassium 1-(*tert*-Butoxycarbonyl)-indol-5-yl-trifluoroborate (Table 4, entry 6)



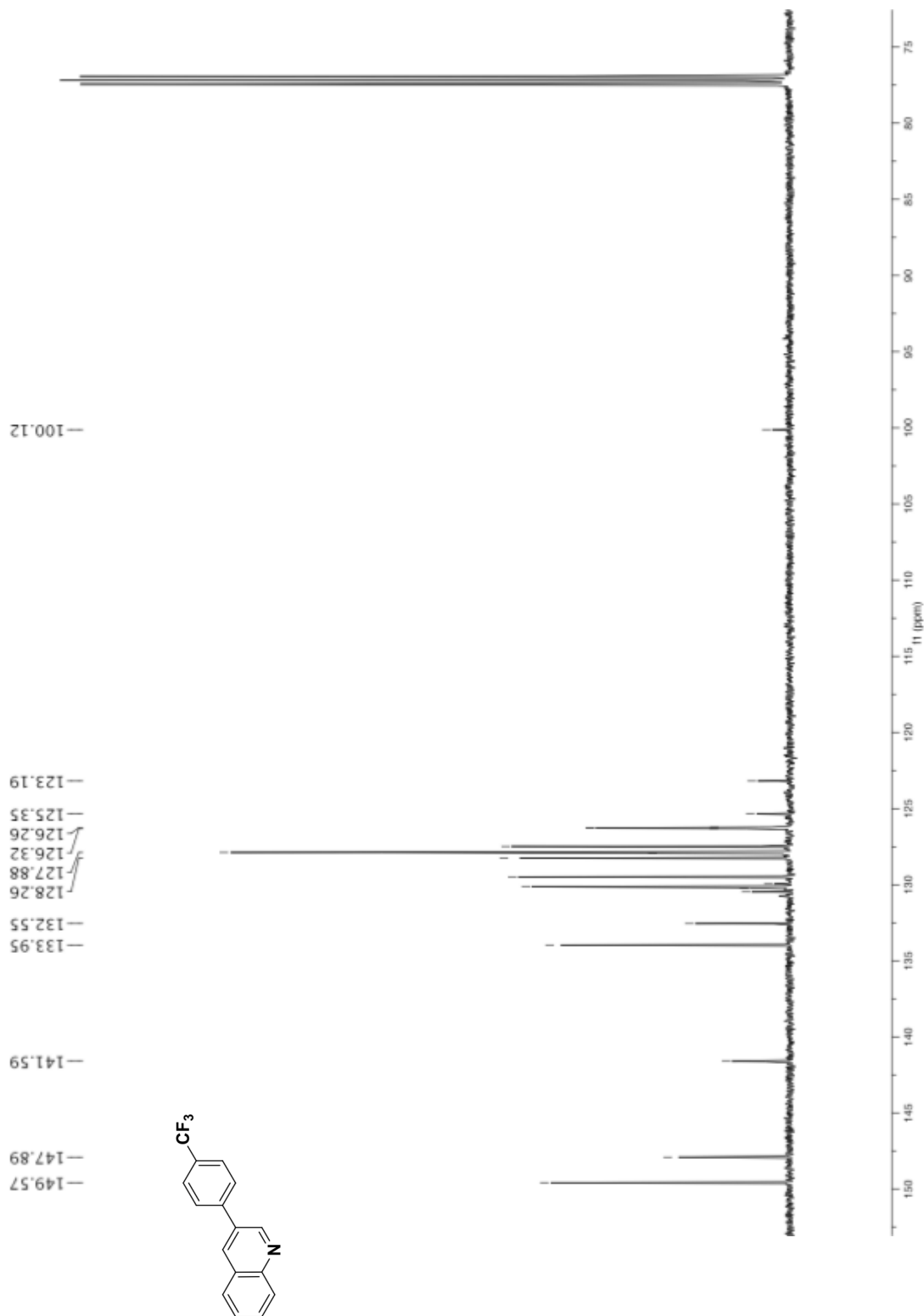
¹H NMR Spectra (500 MHz, CDCl₃) **2-Methyl-4-(4-(trifluoromethyl)phenyl)quinoline** (Table 5, entry 1).



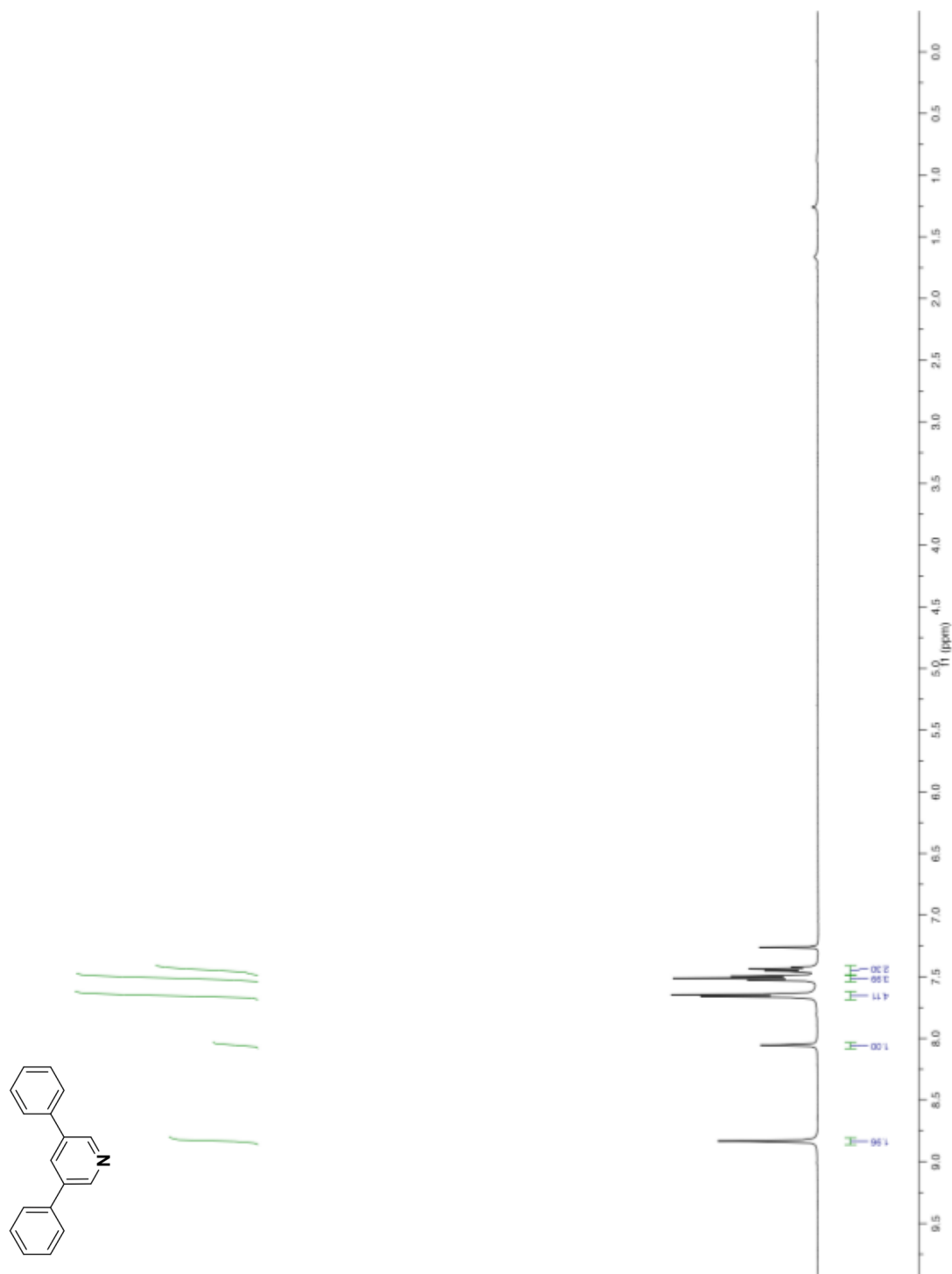
¹³C NMR Spectra (125.8 MHz, CDCl₃) 2-Methyl-4-(4-(trifluoromethyl)phenyl)quinoline (Table 5, entry 1).



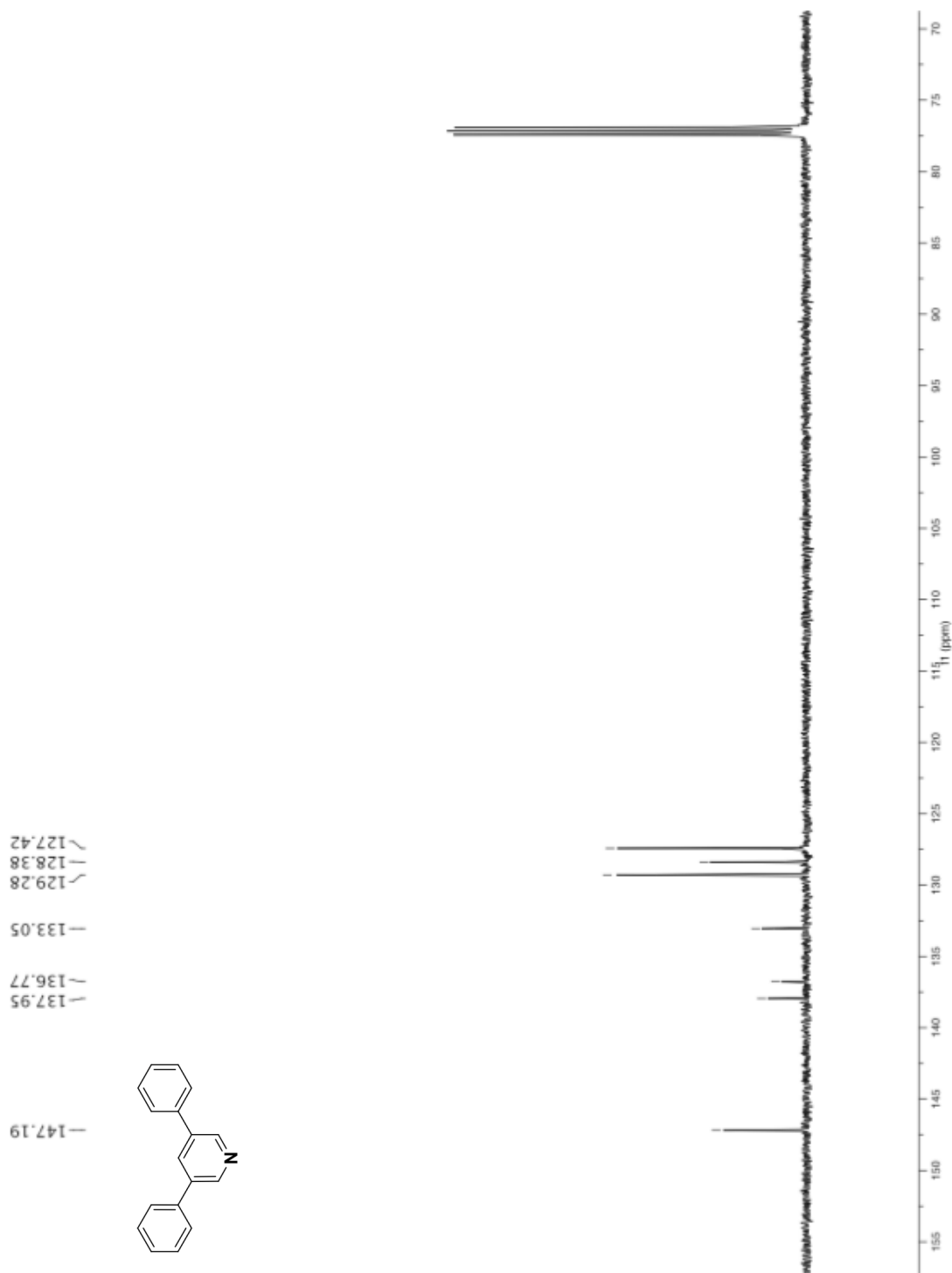
^1H NMR Spectra (500 MHz, CDCl_3) 3-(4-(Trifluoromethyl)phenyl)quinoline (Table 5, entry 2).



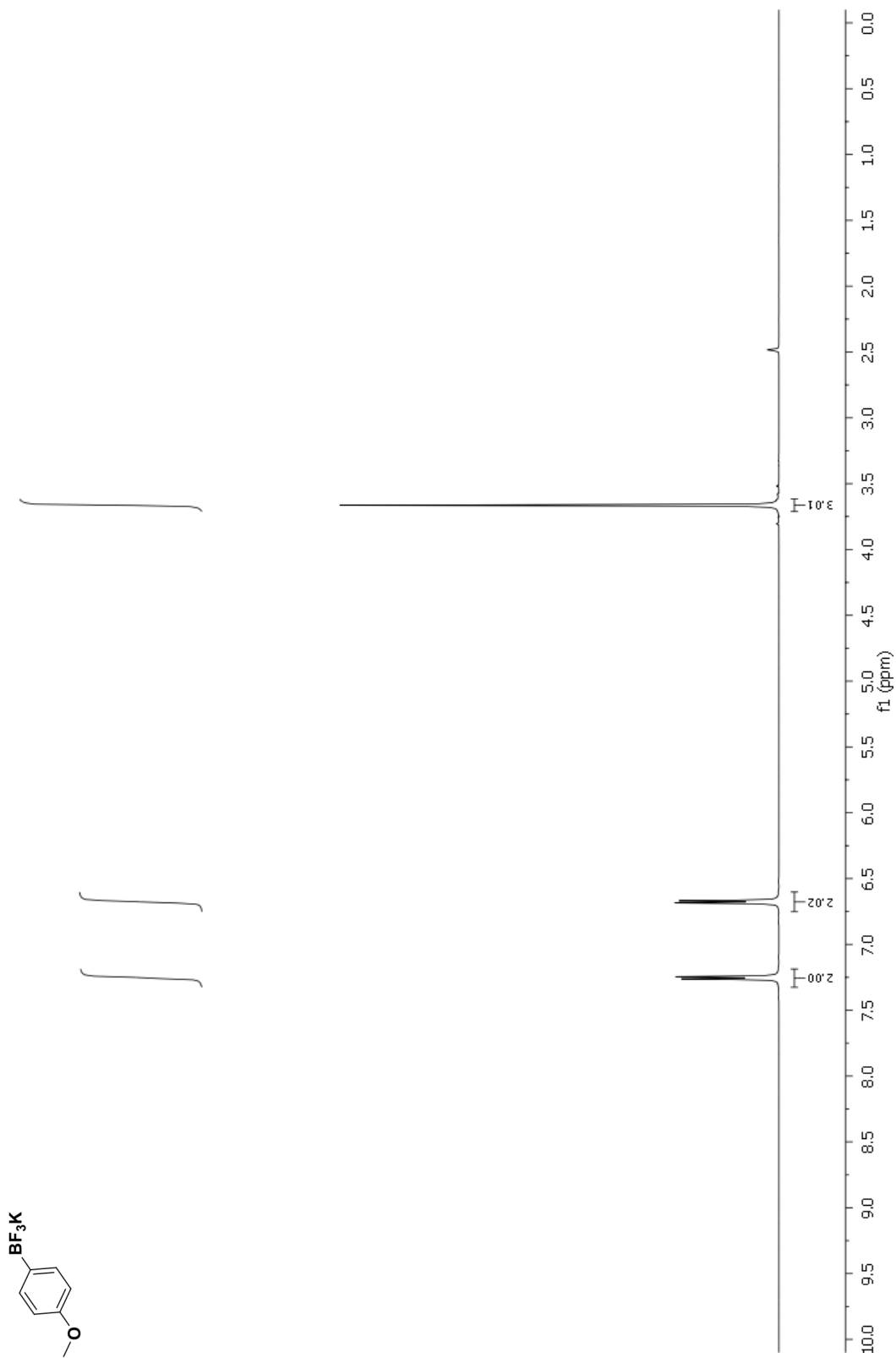
¹³C NMR Spectra (125.8 MHz, CDCl₃) 3-(4-(Trifluoromethyl)phenyl)quinoline (Table 5, entry 2).



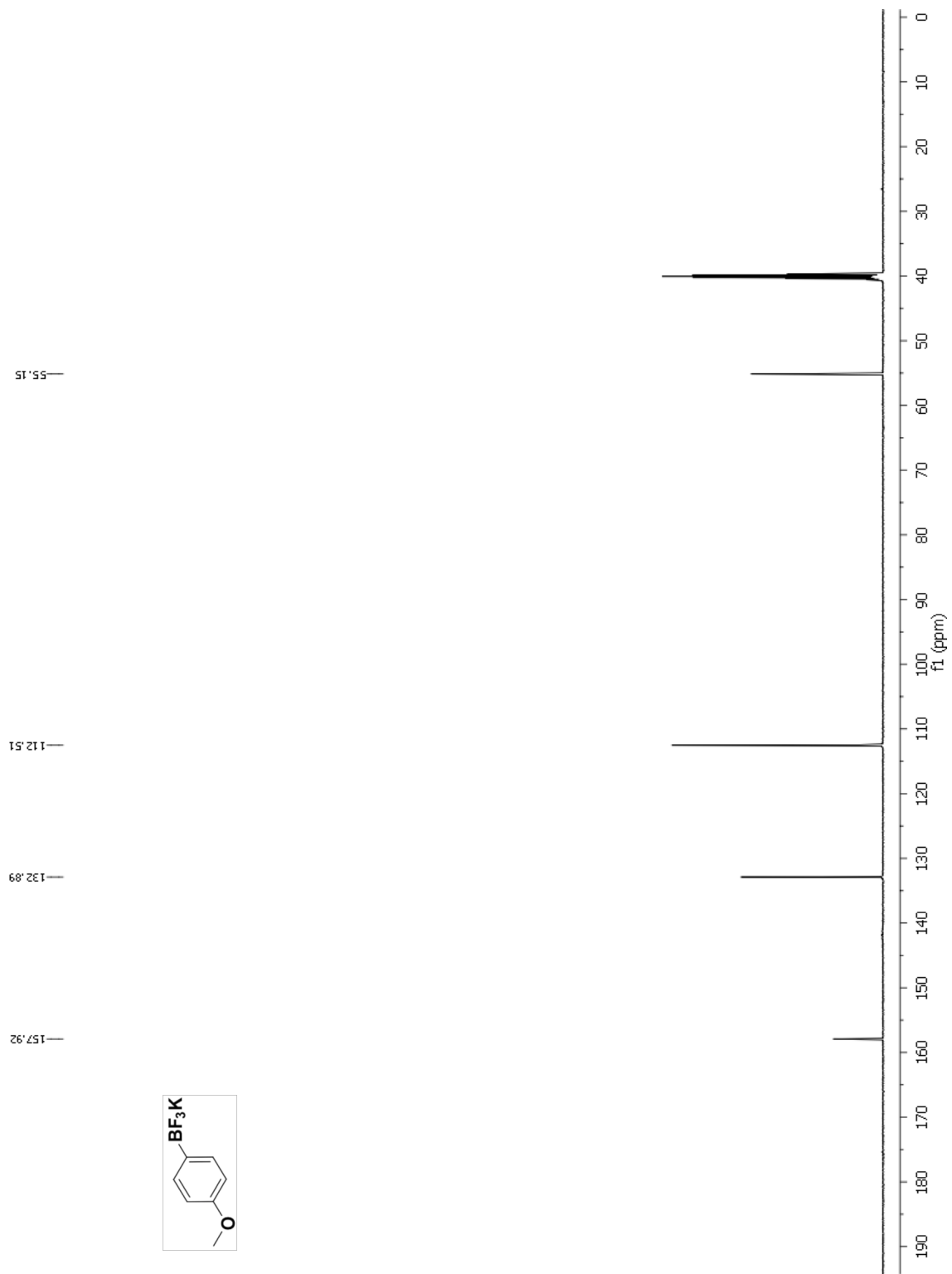
¹H NMR Spectra (500 MHz, CDCl₃) 3,5-Diphenylpyridine (Table 5, entry 3).



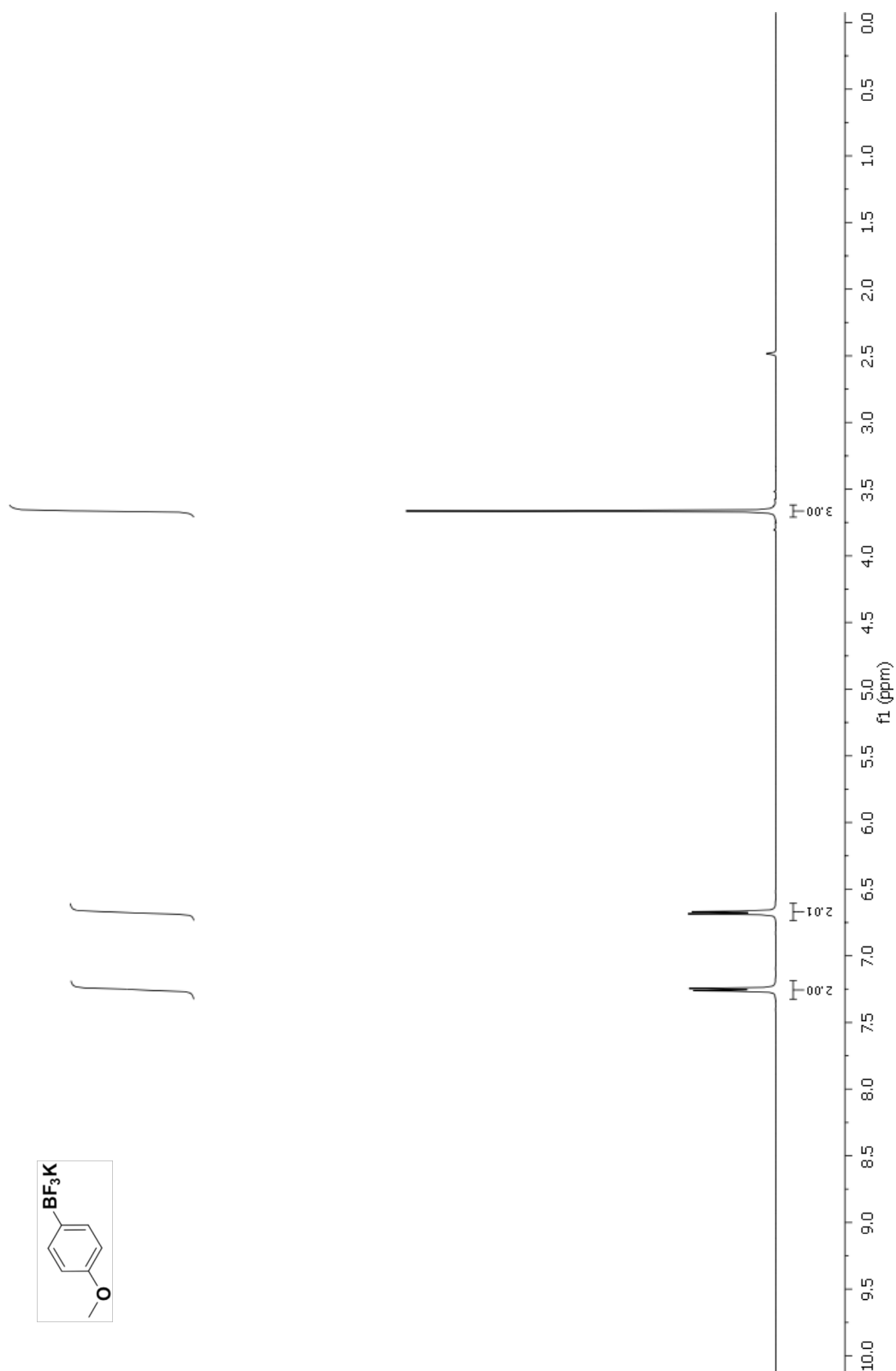
^{13}C NMR Spectra (125.8 MHz, CDCl₃) **3,5-Diphenylpyridine** (Table 5, entry 3).



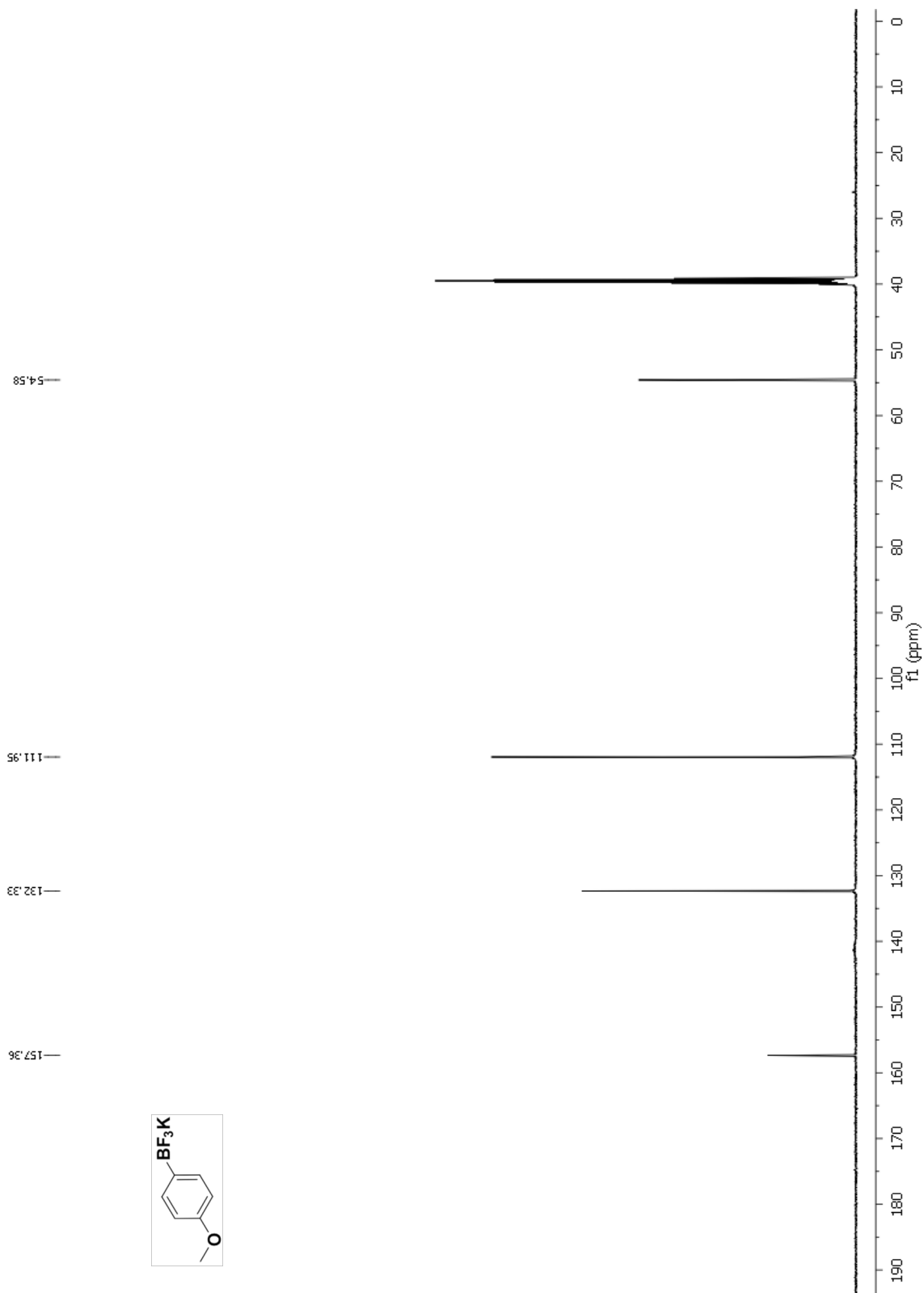
¹H NMR Spectra (500 MHz, DMSO-*d*₆) Potassium 4-Methoxyphenyl-trifluoroborate (Table 6, entry 3)



^{13}C NMR Spectra (125.8 MHz, $\text{DMSO-}d_6$) Potassium 4-Methoxyphenyltrifluoroborate (Table 6, entry 3)



¹H NMR Spectra (500 MHz, DMSO-*d*₆) **Potassium 4-Methoxyphenyl-trifluoroborate**
(Table 6, entry 5)



^{13}C NMR Spectra (125.8 MHz, $\text{DMSO-}d_6$) Potassium 4-Methoxyphenyl-trifluoroborate (Table 6, entry 5)