# Palladium-Catalyzed, Direct Boronic Acid Synthesis from Aryl Chlorides: A Simplified Route to Diverse Boronate Ester Derivatives

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## Supporting Information

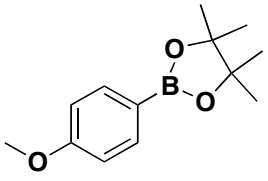
**General Considerations**

**Reagents:** All reactions were carried out under an atmosphere of nitrogen. Ethanol (200 proof) was thoroughly degassed with nitrogen directly before use. All aryl chlorides, (X-Phos) palladium(II) phenethylamine, and X-Phos were purchased from commercial sources and used as received. KOAc and $K_2CO_3$ were dried in an oven overnight before use. All reagents (with exception to the aryl chlorides), were stored in a bench-top desiccator. Tetrahydroxydiboron was synthesized according to literature procedures.[1,2]

**Ananlytical Methods:** All new compounds were characterized by $^{1}H$ 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 $^{1}H$ NMR and $^{13}C$ NMR and compared to literature values. $^{1}H$, $^{13}C$, $^{11}B$, and $^{19}F$ were recorded at 500 MHz, 125.8 MHz, 128.4 MHz, and 470.8 MHz, respectively. Melting points are uncorrected.

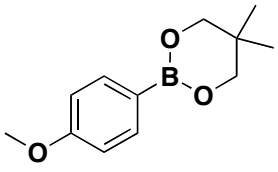
**General procedure A: Pd catalyzed boration of 4-chloroanisole and its conversion to boronate esters.** To an oven-dried glass vessel capable of being sealed with a Teflon cap (for microwave vials) was added (X-Phos) palladium(II) phenethylamine chloride (7.38 mg, 0.01 mmol), X-Phos (9.52 mg, 0.02 mmol), tetrahydroxydiboron, (133.5 mg, 1.5 mmol), KOAc (294 mg, 3 mmol), and NaO*t*-Bu (1 mg, 0.01 mmol). The vessel was sealed and then evacuated and backfilled with $N_2$ (process was repeated three times). EtOH (10 mL degassed) was added via syringe followed by the addition of 4-chloroanisole (1 mmol) in a similar manner. The reaction was then heated to 80 ºC for 18

hours. The reaction was cooled to rt then filtered through a thin pad of Celite (eluting with 100 mL EtOAc) and concentrated. To the crude concentrated reaction was added in equal parts 1 M aqueous HCl and EtOAc (25 mL each). This mixture was stirred 30 min before being added to a separatory funnel. The aqueous layer was removed, and the organic layer was washed once with brine. The organic layer was collected and the combined aqueous layers were further extracted with EtOAc (3 x 10 mL). The combined organics were dried ($Na_2SO_4$) and then concentrated under reduced pressure. The crude mixture was taken up in $CH_2Cl_2$, the corresponding diol was added (1.35 mmol), and the crude reaction was allowed to stir at rt. At completion of the reaction (as monitored by $^{11}B$ NMR in the reaction solvent), the reaction was concentrated, and the desired compound was purified by automated flash column chromatography with pre-packed silica gel columns, eluting with a gradient of EtOAc/hexane unless otherwise indicated.

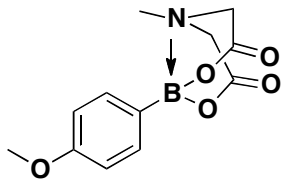



**2-(4-Methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 1, entry 1).**[3] Following general procedure A, a mixture of 4-chloroanisole (75 mg, 64 μL, 0.526 mmol), tetrahydroxydiboron (71 mg, 0.79 mmol), X-Phos (4.75 mg, 0.1 mmol), (X-Phos) palladium(II) phenethylamine chloride (3.9 mg, 0.0053 mmol), KOAc (155 mg, 1.58 mmol), and NaO*t*-Bu (0.5 mg, 0.005 mmol) was heated to 80 ºC for 18 h. After acidic work-up, the crude reaction was taken up in $CH_2Cl_2$. Pinacol (55 mg, 0.47 mmol) was added, and the reaction was allowed to stir overnight at rt. The crude product was purified via flash chromatography on silica gel (0-5% EtOAc/hexane) to provide the

title compound in 90% yield (111 mg) as a colorless oil. Spectral data were in accordance with those published. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, $J$ = 8.6 Hz, 2H), 6.91 (d, $J$ = 8.7 Hz, 2H), 3.84 (s, 3H), 1.35 (d, $J$ = 4.5 Hz, 12H). $^{13}$C NMR (125.8 MHz, $CDCl_3$) δ 162.07, 136.42, 113.22, 83.45, 54.98, 24.77.

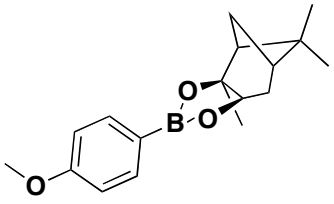


**2-(4-Methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane (Table 1, entry 2).**[3] Following general procedure A, a mixture of 4-chloroanisole (150 mg, 128 μL, 1.05 mmol), tetrahydroxydiboron (141 mg, 1.58 mmol), X-Phos (10 mg, 0.02 mmol), (X-Phos) palladium(II) phenethylamine chloride (7.4 mg, 0.01 mmol), KOAc (310 mg, 3.16 mmol), and NaO*t*-Bu (1.0 mg, 0.01 mmol) was heated to 80 ºC for 18 h. After acidic work-up, the crude reaction was taken up in $CH_2Cl_2$. 2,2-Dimethylpropane-1,3-diol (98 mg, 0.95 mmol) was added, and the reaction was allowed to stir overnight at rt. The crude product was purified via flash chromatography on silica gel (0-5% EtOAc/hexane) to provide the title compound in 87% yield (202.5mg) as a colorless oil. Spectral data were in accordance with those published. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, $J$ = 8.3 Hz, 2H), 6.90 (d, $J$ = 8.4 Hz, 2H), 3.83 (s, 3H), 3.76 (s, 4H), 1.03 (s, 6H). $^{13}$C NMR (125.8 MHz, $CDCl_3$) δ 161.89, 135.66, 113.29, 72.40, 55.19, 32.03, 22.06.



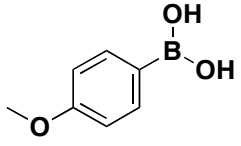
**2-(4-Methoxyphenyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (Table 1, entry 3).** Following general procedure A, a mixture of 4-chloroanisole

(410 mg, 350 μL, 2.87 mmol), tetrahydroxydiboron (387 mg, 4.3 mmol), X-Phos (27 mg, 0.057 mmol), (X-Phos) palladium(II) phenethylamine chloride (21.2 mg, 0.0287 mmol), KOAc (845 mg, 8.61 mmol), and NaO*t*-Bu (2.75 mg, 0.0287 mmol) was heated to 80 ºC for 18 h. After acidic work-up, the crude reaction was taken up in a 0.5 M (95:5 toluene:DMSO) solution, and *N*-methylaminodiacetic acid (440 mg, 3 mmol) was added. The reaction was fitted with a toluene-filled Dean-Stark trap with an attached reflux condenser and heated at reflux for 14 h. The crude reaction was concentrated until a chunky, wet solid was obtained. This solid was suspended in acetone (3 mL) and then $Et_2O$ was added in 5 mL portions (25 mL total), precipitating the solid. The solid was filtered, rinsed with $Et_2O$ (5 mL), and dried overnight to provide the title compound in 85% yield (642 mg) as a gray powder,[4] mp >220 °C. $^1$H NMR (500 MHz, $d_6$-DMSO) δ 7.35 (d, $J$ = 8.4 Hz, 2H), 6.92 (d, $J$ = 8.5 Hz, 2H), 4.30 (d, $J$ = 17.2 Hz, 2H), 4.07 (d, $J$ = 17.2 Hz, 2H), 3.75 (s, 3H), 2.48 (s, 3H). $^{13}$C NMR (125.8 MHz, $d_6$-DMSO) δ 169.76, 160.29, 134.13, 113.66, 62.01, 55.20, 47.84. $^{11}$B NMR (128.4 MHz, $d_6$-DMSO) δ 10.54. IR (KBr) 2960, 1764, 1324, 1217. HRMS (ES-) calcd. for $C_{12}H_{13}BNO_5$ (M-H) 262.0965 found 262.0887.



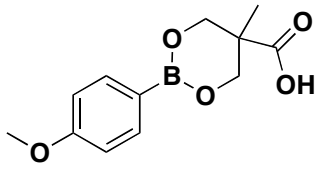

**(3a*S*,4*S*,6*R*,6a*R*)-2-(4-Methoxyphenyl)-3a,5,5-trimethyltetrahydro-3a*H*-4,6-methanocyclopenta[*d*][1,3,2]dioxaborole (Table 1 entry 4).** Following general procedure A, a mixture of 4-chloroanisole (150 mg, 128 μL, 1.05 mmol), tetrahydroxydiboron (141 mg, 1.58 mmol), X-Phos (10 mg, 0.021 mmol), (X-Phos) palladium(II) phenethylamine chloride (7.4 mg, 0.01 mmol), KOAc (310 mg,

3.16 mmol), and NaO*t*-Bu (1.0 mg, 0.01 mmol) was heated to 80 ºC for 18 h. After acidic work-up, the crude reaction was taken up in $CH_2Cl_2$. (1*S*,2*S*,3*R*,4*R*)-2,5,5-Trimethylbicyclo[2.1.1]hexane-2,3-diol (148 mg, 0.95 mmol) was added, and the reaction was allowed to stir overnight at rt. The crude product was purified via flash chromatography on silica gel (0-5% EtOAc/hexane) to provide the title compound in 75% yield (216 mg) as a colorless oil. $^1$H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.6 Hz, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 4.45 – 4.39 (m, 1H), 3.83 (s, 3H), 2.41 (ddd, *J* = 11.2, 7.1, 2.1 Hz, 1H), 2.26 – 2.18 (m, 1H), 2.14 (t, *J* = 5.5 Hz, 1H), 1.99 – 1.89 (m, 2H), 1.47 (s, 3H), 1.31 (s, 3H), 1.23 (t, *J* = 8.7 Hz, 1H), 0.89 (s, 3H). $^{13}$C NMR (125.8 MHz, $CDCl_3$) δ 136.52, 113.37, 86.06, 78.15, 55.10, 51.49, 39.57, 38.21, 35.65, 28.74, 27.13, 26.50, 24.07. $^{11}$B NMR (128.4 MHz, $CDCl_3$) δ 29.71. IR (neat) 2915, 1605, 1249**.** HRMS (ES+) calcd. for $C_{17}H_{24}BO_3$ (M+H) 287.1740, found 287.1819.



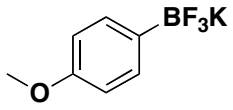

**(4-Methoxyphenyl)boronic acid (Table 1, entry 5).**[3] Following general procedure A, a mixture of 4-chloroanisole (214 mg, 182 μL, 1.5 mmol), tetrahydroxydiboron (201 mg, 2.25 mmol), X-Phos (14.3 mg, 0.03 mmol), (X-Phos) palladium(II) phenethylamine chloride (11.08 mg, 0.015 mmol), KOAc (442 mg, 4.5 mmol), and NaO*t*-Bu (1.44 mg, 0.015 mmol) was heated to 80 ºC for 18 h. After acidic work-up, the crude reaction was concentrated and dried overnight. The crude boronic acid was washed with hexane to afford the title compound in 82% yield (187 mg) as a white solid. Spectral data were in accordance with those published. $^1$H NMR (500 MHz,

$CDCl_3$) δ 8.16 (d, *J* = 7.9 Hz, 2H), 7.01 (d, *J* = 7.9 Hz, 2H), 3.88 (s, 3H). $^{13}C$ NMR (125.8 MHz, $CDCl_3$) δ 163.33, 137.65, 113.65, 55.31.

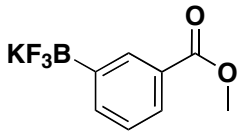



**2-(4-Methoxyphenyl)-5-methyl-1,3,2-dioxaborinane-5-carboxylic Acid (Table 1, entry 6).** Following general procedure A, a mixture of 4-chloroanisole (214 mg, 182 μL, 1.5 mmol), tetrahydroxydiboron (201 mg, 2.25 mmol), X-Phos (14.3 mg, 0.03 mmol), (X-Phos) palladium(II) phenethylamine chloride (11.08 mg, 0.015 mmol), KOAc (442 mg, 4.5 mmol), and NaO*t*-Bu (1.44 mg, 0.015 mmol) was heated to 80 ºC for 18 h. After acidic work-up, the crude reaction was taken up in $CH_2Cl_2$, 3-hydroxy-2-(hydroxymethyl)-2-methylpropanoic acid (250 mg, 1.86 mmol) was added, and the reaction was allowed to stir overnight at rt. To the concentrated crude reaction was added $Et_2O$ (10 mL) until a white solid precipitated out. The solid was filtered off, the reaction was concentrated, and the process was repeated until no additional precipitate was observed. The combined solids were dried overnight to provide the title compound in 72% yield (270 mg) as a white, free-flowing, low-melting powder. $^1H$ NMR (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.2 Hz, 2H), 6.87 (d, *J* = 8.2 Hz, 2H), 4.42 (d, *J* = 11.0 Hz, 2H), 3.90 (d, *J* = 11.0 Hz, 2H), 3.82 (s, 3H), 1.24 (s, 3H). $^{13}C$ NMR (125.8 MHz, $CDCl_3$) δ 179.15, 161.88, 135.69, 113.18, 99.99, 67.49, 55.07, 43.98, 18.19. $^{11}B$ NMR (128.4 MHz, $d_6$-DMSO) δ 26.28. IR (KBr) 2912, 1693, 1252, 1178. HRMS (CI+) calcd. for $C_{12}H_{16}BO_5$ 251.1013 (M+H), found 251.1091.

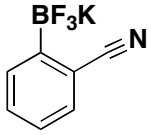
**General procedure B: Pd catalyzed boration of aryl chlorides and their conversion to trifluoroborates.** To an oven dried glass vessel capable of being sealed with a Teflon cap (for microwave vials) was added (X-Phos) palladium(II) phenethylamine chloride (14.8 mg, 20 μmol), X-Phos (19 mg, 40 μmol), tetrahydroxydiboron (270 mg, 3 mmol), KOAc (590 mg, 6 mmol), and NaO*t*-Bu (2 mg, 20 μmol). The vessel was sealed and then evacuated and backfilled with $N_2$ (process was repeated three times). EtOH (20 mL degassed) was added via syringe followed by the addition of the chloride (2 mmol) in a similar manner (solid chlorides were added with the other solid reagents before sealing). The reaction was then heated to 80 ºC for 18 h. The reaction was cooled to rt then filtered through a thin pad of Celite (eluting with 100 mL EtOAc), 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 ºC. To this cooled mixture was added 3.5 equivalents of a 4.5 M aqueous $KHF_2$ solution, and the reaction was stirred for 10 min at 0 ºC before removing the bath and allowing the mixture to stir at rt for 20 min (or until the conversion to the corresponding trifluoroborate was achieved as determined by $^{11}B$ NMR). After conversion, the mixture was concentrated under reduced pressure, and then further dried under high vacuum overnight to remove any traces of water. The compound was purified with continuous Soxhlet extraction (overnight) with acetone (100 mL). The collected solvent was concentrated and then dissolved in a minimal volume of acetone (~3 mL). The addition of $Et_2O$ (~25 mL) led to the precipitation of the desired product. The collected solid was washed with $Et_2O$. Further purification (to remove small organic or boron containing impurities) could be realized via trituration of the solid with $Et_2O$.



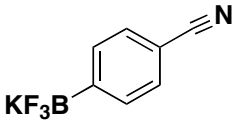

**Potassium 4-Methoxyphenyl-trifluoroborate (Table 2, entry 1).**[5] Following general procedure B, a mixture of 4-chloroanisole (855 mg, 730 μL, 6 mmol), tetrahydroxydiboron (804 mg, 9 mmol), X-Phos (57.2 mg, 0.12 mmol), (X-Phos) palladium(II) phenethylamine chloride (44.28 mg, 0.06 mmol), KOAc (1.76 g, 18 mmol), and NaO*t*-Bu (5.76 mg, 0.06 mmol) was heated to 80 ºC for 18 h. The title compound was obtained as a white solid in 92% yield (1.18 g). Spectral data were in accordance with those published. $^{1}$H NMR (500 MHz, $d_6$-DMSO) δ 7.22 (d, $J$ = 8.2 Hz, 2H), 6.66 (d, $J$ = 8.1 Hz, 2H), 3.51 (s, 3H). $^{13}$C NMR (125.8 MHz, $d_6$-DMSO) δ 157.58, 132.62, 112.22, 54.89.



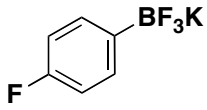

**Potassium (3-(Methoxycarbonyl)phenyl)trifluoroborate (Table 2, entry 2).** Following general procedure B, a mixture of methyl 3-chlorobenzoate (341 mg, 278 μL, 2 mmol), tetrahydroxydiboron (270 mg, 3 mmol), X-Phos (19 mg, 40 μmol), (X-Phos) palladium(II) phenethylamine chloride (14.8 mg, 20 μmol), KOAc (590 mg, 6 mmol), and NaO*t*-Bu (2 mg, 20 μmol) was heated to 80 ºC for 18 h. The title compound was obtained as a white solid in 76% yield (369 mg). mp >220 °C. $^{1}$H NMR (500 MHz, $d_6$-DMSO) δ 8.00 (s, 1H), 7.67 (d, $J$ = 6.7 Hz, 1H), 7.58 (d, $J$ = 6.9 Hz, 1H), 7.24 (t, $J$ = 7.4 Hz, 1H), 3.81 (s, 3H). $^{13}$C NMR (125.8 MHz, $d_6$-DMSO) δ 167.86, 136.69, 132.69, 127.87, 126.89, 126.46, 51.96. $^{11}$B NMR (128.4 MHz, $d_6$-DMSO) δ 1.28. $^{19}$F NMR (470.8 MHz, $d_6$-DMSO) δ -139.69. IR (KBr) 1721, 1560, 1188**.** HRMS (ES-) calcd. for $C_8H_7BF_3O_2$ (M-K) 203.0491, found 203.0491.



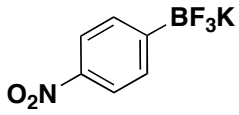

**Potassium (2-Cyanophenyl)trifluoroborate (Table 2, entry 3)** Following general procedure B, a mixture of 2-chlorobenzonitrile (275 mg, 2 mmol), tetrahydroxydiboron (270 mg, 3 mmol), X-Phos (19 mg, 40 μmol), (X-Phos) palladium(II) phenethylamine chloride (14.8 mg, 20 μmol), KOAc (590 mg, 6 mmol), and NaO*t*-Bu (2 mg, 20 μmol) was heated to 80 ºC for 18 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 (4-Cyanophenyl)trifluoroborate (Table 2, entry 4).** Following general procedure B, a mixture of 4-chlorobenzonitrile (206 mg, 1.5 mmol), tetrahydroxydiboron (403 mg, 4.5 mmol), X-Phos (14.8 mg, 30 μmol), (X-Phos) palladium(II) phenethylamine chloride (11.08 mg, 15 μmol), KOAc (442 mg, 4.5 mmol), and NaO*t*-Bu (1.44 mg, 15 μmol) was heated to 80 ºC for 18 h. The concentrated crude reaction was taken up in MeOH (15 mL) and $KHF_2$ (2.2 mL of a 4.5 M aqueous solution, 6.5 equiv) was added. The title compound was obtained as a white solid in 57% yield (180 mg). mp >220 °C. $^1$H NMR (500 MHz, $d_6$-acetone) δ 7.62 (s, 2H), 7.45 (s, 2H). $^{13}$C NMR (125.8 MHz, $d_6$-DMSO) δ 132.63, 130.57, 120.64, 108.29. IR (KBr) 2232, 1566. HRMS (ES-) calcd. for $C_7H_4BF_3N$ (M-K) 170.0389, found 170.0389.

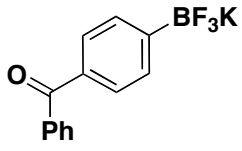



**Potassium (4-Fluorophenyl)trifluoroborate (Table 2, entry 5).**[5] Following general procedure B, a mixture of 1-chloro-4-fluorobenzene (261 mg, 213 μL, 2 mmol), tetrahydroxydiboron (270 mg, 3 mmol), X-Phos (19 mg, 40 μmol), (X-Phos) palladium(II) phenethylamine chloride (14.8 mg, 20 μmol), KOAc (590 mg, 6 mmol), and NaO*t*-Bu (2 mg, 20 μmol) was heated to 80 ºC for 18 h. The title compound was obtained as a white solid in 80% yield (209 mg). Spectral data were in accordance with those published. $^{1}$H NMR (500 MHz, $d_6$-acetone) δ 7.42 (s, 2H), 6.78 (t, $J$ = 8.5 Hz, 2H). $^{13}$C NMR (125.8 MHz, $d_6$-DMSO) δ 161.93, 160.03, 132.84 (d, $J$ = 5.9 Hz), 112.71 (d, $J$ = 18.4 Hz)

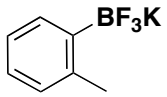



**Potassium (4-Nitrophenyl)trifluoroborate (Table 2, entry 6).** Following general procedure B, a mixture of 1-chloro-4-nitrobenzene (236 mg, 1.5 mmol), tetrahydroxydiboron (403 mg, 4.5 mmol), X-Phos (14.8 mg, 30 μmol), (X-Phos) palladium(II) phenethylamine chloride (11.08 mg, 15 μmol), KOAc (442 mg, 4.5 mmol), and NaO*t*-Bu (1.44 mg, 15 μmol) was heated to 80 ºC for 4 h. The concentrated crude reaction was taken up in MeOH (15 mL) and $KHF_2$ (2.2 mL of a 4.5 M aqueous solution, 6.5 equiv) was added. The title compound was obtained as a light yellow solid in 58% yield (200 mg). mp >220 °C. $^{1}$H NMR (500 MHz, $d_6$-DMSO) δ 7.96 (d, $J$ = 8.0 Hz, 2H), 7.55 (d, $J$ = 8.0 Hz, 2H). $^{13}$C NMR (125.8 MHz, $d_6$-DMSO) δ 146.16, 132.53, 121.54. $^{11}$B NMR (128.4 MHz, $d_6$-DMSO) δ 2.72. $^{19}$F NMR (470.8 MHz, $d_6$-DMSO) δ -140.21.

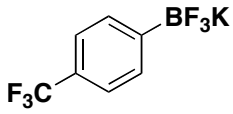
IR (KBr) 1514, 1359**.** HRMS (ES-) calcd. for $C_6H_4BF_3NO_2$ (M-K) 190.0287, found 190.0287.



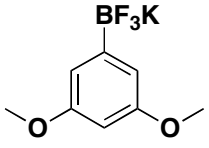

**Potassium (4-Benzoylphenyl)trifluoroborate (Table 2, entry 7).** Following general procedure B, a mixture of (4-chlorophenyl)(phenyl)methanone (433 mg, 2 mmol), tetrahydroxydiboron (540 mg, 6 mmol), X-Phos (14.8 mg, 40 μmol), (X-Phos) palladium(II) phenethylamine chloride (11.08 mg, 20 μmol), KOAc (590 mg, 6 mmol), and NaO*t*-Bu (2 mg, 20 μmol) was heated to 80 ºC for 18 h. The concentrated crude reaction was taken up in MeOH (15 mL) and $KHF_2$ (2.2 mL of a 4.5 M aqueous solution, 6.5 equiv) was added. After precipitation with ether, the solid was taken up in $CH_3CN$ (20 mL) and oven-dried $K_2CO_3$ (970 mg, 7 mmol) was added and the reaction was stirred overnight. The mixture was concentrated then the desired compound was obtained via hot filtration with acetone (3 x 20 mL). The title compound was obtained as a white solid in 90% yield (518 mg) as a mixture of the ketone (84%) and hydrate (16%). mp >220 °C. $^1$H NMR (500 MHz, $d_6$-acetone) δ 7.71 (d, $J$ = 7.2 Hz, 2H), 7.60 (d, $J$ = 7.6 Hz, 2H), 7.57 – 7.54 (m, 1H), 7.54 (s, 2H), 7.49 (t, $J$ = 7.5 Hz, 2H). $^{13}$C NMR (125.8 MHz, $d_6$-DMSO) δ 196.92, 138.52, 132.54, 131.82, 129.90, 128.88, 128.60, 128.33. $^{11}$B NMR (128.4 MHz, $d_6$-DMSO) δ 2.14. $^{19}$F NMR (470.8 MHz, $d_6$-DMSO) δ -138.80, -139.83. IR (KBr) 1654**.** HRMS (ES-) calcd. for $C_{13}H_9BF_3O$ (M-K) 249.0699, found 249.0684.



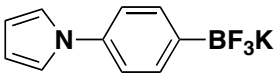

**Potassium o-Tolyltrifluoroborate (Table 2, entry 8).**[5] Following general procedure B, a mixture of 1-chloro-2-methylbenzene (190 mg, 176 μL, 1.5 mmol), tetrahydroxydiboron (403 mg, 4.5 mmol), X-Phos (14.8 mg, 30 μmol), (X-Phos) palladium(II) phenethylamine chloride (11.08 mg, 15 μmol), KOAc (442 mg, 4.5 mmol), and NaO*t*-Bu (1.44 mg, 15 μmol) was heated to 80 ºC for 18 h. The concentrated crude reaction was taken up in MeOH (15 mL) and $KHF_2$ (2.2 mL of a 4.5 M aqueous solution, 6.5 equiv) was added. The title compound was obtained as a white solid in 75% yield (222 mg). Spectral data were in accordance with those published. $^1$H NMR (500 MHz, $d_6$-acetone) δ 7.47 (d, $J$ = 6.8 Hz, 1H), 6.96 – 6.86 (m, 3H), 2.39 (s, 3H). $^{13}$C NMR (125.8 MHz, $d_6$-acetone) δ 140.89, 131.80, 128.15, 125.23, 123.24, 21.15.




**Potassium (4-(Trifluoromethyl)phenyl)trifluoroborate (Table 2, entry 9).**[5] Following general procedure B, a mixture of 1-chloro-4-(trifluoromethyl)benzene (271 mg, 210 μL, 1.5 mmol), tetrahydroxydiboron (403 mg, 4.5 mmol), X-Phos (14.8 mg, 30 μmol), (X-Phos) palladium(II) phenethylamine chloride (11.08 mg, 15 μmol), KOAc (442 mg, 4.5 mmol), and NaO*t*-Bu (1.44 mg, 15 μmol) was heated to 80 ºC for 18 h. The concentrated crude reaction was taken up in MeOH (15 mL) and $KHF_2$ (2.2 mL of a 4.5 M aqueous solution, 6.5 equiv) was added. The title compound was obtained as an off-white solid in 82% yield (310 mg). Spectral data were in accordance with those published. $^1$H NMR (500 MHz, $d_6$-DMSO) δ 7.52 (d, $J$ = 7.5 Hz, 2H), 7.41 (d, $J$ = 7.6 Hz, 2H).

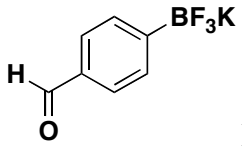


**Potassium (3,5-Dimethoxyphenyltrifluoroborate (Table 2, entry 10).**[6] Following general procedure B, a mixture of 1-chloro-3,5-dimethoxybenzene (345 mg, 2 mmol), tetrahydroxydiboron (270 mg, 3 mmol), X-Phos (19 mg, 40 μmol), (X-Phos) palladium(II) phenethylamine chloride (14.8 mg, 20 μmol), KOAc (590 mg, 6 mmol), and NaO*t*-Bu (2 mg, 20 μmol) was heated to 80 ºC for 18 h. The title compound was obtained as a white solid in 92% yield (445 mg). Spectral data were in accordance with those published. $^{1}$H NMR (500 MHz, $d_6$-DMSO) δ 6.48 (s, 2H), 6.14 (s, 1H), 3.66 (s, 6H). $^{13}$C NMR (125.8 MHz, $d_6$-DMSO) δ 159.27, 108.75, 99.66, 97.76, 54.69.



**Potassium (4-(1H-Pyrrol-1-yl)phenyltrifluoroborate (Table 2, entry 11).** Following general procedure B, a mixture of 1-(4-chlorophenyl)-1H-pyrrole (355 mg, 2 mmol), tetrahydroxydiboron (270 mg, 3 mmol), X-Phos (19 mg, 40 μmol), (X-Phos) palladium(II) phenethylamine chloride (14.8 mg, 20 μmol), KOAc (590 mg, 6 mmol), and NaO*t*-Bu (2 mg, 20 μmol) was heated to 80 ºC for 18 h. The title compound was obtained as an off-white solid in 84% yield (314 mg). mp >220 °C. $^{1}$H NMR (500 MHz, $d_6$-DMSO) δ 7.39 (d, $J$ = 7.6 Hz, 2H), 7.25 (dd, $J$ = 8.0 Hz, 5.2, 4H), 6.20 (d, $J$ = 1.9 Hz, 2H). $^{13}$C NMR (125.8 MHz, $d_6$-DMSO) δ 137.57, 132.34, 118.73, 117.70, 109.58. $^{11}$B NMR (128.4 MHz, $d_6$-DMSO) δ 1.65. $^{19}$F NMR (470.8 MHz, $d_6$-DMSO) δ -

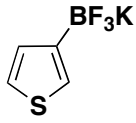
138.98. IR (KBr) 1604, 1328. HRMS (ES-) calcd. for $C_{10}H_8BF_3N$ (M-K) 210.0702, found 210.0702.




**Potassium (4-Formylphenyl)trifluoroborate (Table 2, entry 12)**.[5] Following general procedure B, a mixture of 1-chloro-2-methylbenzene (190 mg, 176 μL, 1.5 mmol), tetrahydroxydiboron (403 mg, 4.5 mmol), X-Phos (14.8 mg, 30 μmol), (X-Phos) palladium(II) phenethylamine chloride (11.08 mg, 15 μmol), KOAc (442 mg, 4.5 mmol), and NaO*t*-Bu (1.44 mg, 15 μmol) was heated to 80 ºC for 18 h. The reaction was cooled to rt then filtered through a thin pad of Celite (eluting with 100 mL EtOAc) and concentrated. To the crude concentrated reaction was added in equal parts 1 M aqueous HCl and EtOAc (20 mL each). This mixture was stirred 20 min before being added to a separatory funnel. The aqueous layer was removed, and the organic layer was washed once with brine. The organic layer was collected and the combined aqueous layers were further extracted with EtOAc (3 x 10 mL). The combined organics were dried ($Na_2SO_4$) and then concentrated under reduced pressure. The concentrated crude reaction was taken up in MeOH (15 mL) and $KHF_2$ (1 mL of a 4.5 M aqueous solution, 3 equiv) was added. After precipitation with $Et_2O$ (~20 mL), the solid taken up in $CH_3CN$ (15 mL) and 3.5 equiv oven-dried $K_2CO_3$ (725 mg, 5.25 mmol) was added and the reaction was stirred overnight. The mixture was concentrated and the desired compound was obtained via hot filtration with acetone (3 x 20 mL). The title compound was obtained as an off-white solid in 80% yield (258 mg) as a mixture of the aldehyde (83%) and hydrate (17%). Spectral data were in accordance with those published. $^1$H NMR (500 MHz, $d_6$-DMSO) δ

10.37 (s, 1H), 8.14 (d, $J$ = 7.3 Hz, 2H), 8.10 (d, $J$ = 7.6 Hz, 2H). $^{13}$C NMR (125.8 MHz, $d_6$-Acetone) δ 193.45, 128.54, 125.84, 65.43. mp >220 °C. IR (KBr) 1686. HRMS (ES-) calcd. for $C_7H_5BF_3O$ (M-K) 173.0386, found 173.0386.


**Potassium (2,6-Dimethylphenyl)trifluoroborate (Table 2, entry 13).**[5] Following general procedure B, a mixture of 2-chloro-1,3-dimethylbenzene (211 mg, 199 μL, 1.5 mmol), tetrahydroxydiboron (403 mg, 4.5 mmol), X-Phos (14.8 mg, 30 μmol), (X-Phos) palladium(II) phenethylamine chloride (11.08 mg, 15 μmol), KOAc (442 mg, 4.5 mmol), and NaO*t*-Bu (1.44 mg, 15 μmol) was heated to 80 ºC for 18 h. The concentrated crude reaction was taken up in MeOH (15 mL) and $KHF_2$ (2.2 mL of a 4.5 M aqueous solution, 6.5 equiv) was added. The title compound was obtained as a white solid in 50% yield (160 mg). Spectral data were in accordance with those published. $^1$H NMR (500 MHz, $d_6$-DMSO) δ 6.77 (t, $J$ = 7.3 Hz, 1H), 6.68 (d, $J$ = 7.2 Hz, 2H), 2.31 (s, 6H). $^{13}$C NMR (125.8 MHz, $d_6$-DMSO) δ 140.88, 126.50, 124.51, 23.30, 23.28.

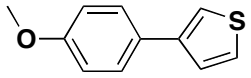



**Potassium Thiophen-3-yltrifluoroborate (Table 2, entry 14).**[5] Following general procedure B, a mixture of 3-chlorothiophene (178 mg, 140 μL, 1.5 mmol), tetrahydroxydiboron (403 mg, 4.5 mmol), X-Phos (44.4 mg, 90 μmol), (X-Phos) palladium(II) phenethylamine chloride (33.24 mg, 45 μmol), KOAc (442 mg, 4.5 mmol), and NaO*t*-Bu (4.32 mg, 45 μmol) was heated to 50 ºC for 24 h. The concentrated crude reaction was taken up in MeOH (15 mL) and 6.5 equiv (2.2 mL) of a 4.5 M aqueous $KHF_2$ solution was added. The title compound was obtained as a white solid in 65%

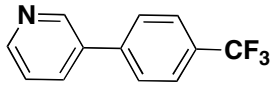
yield (185 mg). Spectral data were in accordance with those published. $^{1}$H NMR (500 MHz, $d_6$-DMSO) δ 7.17 (s, 1H), 7.00 (s, 2H). $^{13}$C NMR (125.8 MHz, $d_6$-DMSO) δ 131.87, 124.17, 122.46.

**General procedure C: Pd catalyzed boration of aryl chlorides and their Suzuki coupling with aryl or heteroaryl chlorides**

To an oven dried glass vessel capable of being sealed with a Teflon cap (for microwave vials) was added (X-Phos) palladium(II) phenethylamine chloride (27.6 mg, 37.5 μmol), X-Phos (35.7 mg, 75 μmol), tetrahydroxydiboron (402 mg, 4.5 mmol), KOAc (442 mg, 4.5 mmol), and NaO*t*-Bu (3.6 mg, 37.5 μmol). The vessel was sealed and then evacuated and backfilled with $N_2$ (process was repeated three times). EtOH (15 mL degassed) was added via syringe followed by the addition of the first chloride (1.5 mmol) in a similar manner (solid chlorides were added with the other solid reagents before sealing). The reaction was then heated to 80 ºC for 2 h, then a nitrogen needle was added to the septum and 3 equiv (2.5 mL, 4.5 mmol) of 1.8 M aqueous $K_2CO_3$ was added via syringe followed by the addition of the second chloride (1.5 mmol) in a similar manner (in a solution of 500 μL of EtOH if the chloride was a solid). The nitrogen needle was removed and the reaction was further heated to 80 ºC for 15 h. The reaction was cooled to rt then filtered through a thin pad of Celite (eluting with 100 mL EtOAc) and concentrated. The crude solid was extracted with EtOAc (3 x 10 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.

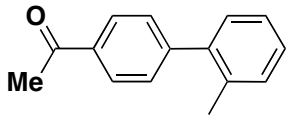


**3-(4-Methoxyphenyl)thiophene (Table 3 entry 1).** Following general procedure C, a mixture of 4-chloroanisole (214 mg, 182.5 μL, 1.5 mmol), tetrahydroxydiboron (202 mg, 2.25 mmol), X-Phos (35.7 mg, 75 μmol), (X-Phos) palladium(II) phenethylamine chloride (27.6 mg, 37.5 μmol), KOAc (442 mg, 4.5 mmol), and NaO*t*-Bu (3.6 mg, 37.5 μmol) was heated to 80 ºC for 2 h. At this point, a nitrogen needle was inserted followed by the addition of 3-chlorothiophene (177.87 mg, 140 μL, 1.5 mmol) and aq $K_2CO_3$ (1.8 M, 2.5 mL) via syringe. The crude product was purified via flash chromatography on silica gel (0-5% EtOAc/hexane) to provide the title compound in 85% yield (243 mg) as a white solid. mp 122-125 °C. $^1$H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.9 Hz, 2H), 7.36 (d, *J* = 6.3 Hz, 3H), 6.95 (d, *J* = 7.9 Hz, 2H), 3.85 (s, 3H). $^{13}$C NMR (125.8 MHz, $CDCl_3$) δ 158.99, 142.12, 128.85, 127.66, 126.35, 126.17, 119.04, 114.31, 55.42. IR (neat) 1606, 1503, 1248. HRMS (ES+) calcd. for $C_{11}H_{11}OS$ (M+H) 191.0452, found 191.0501.

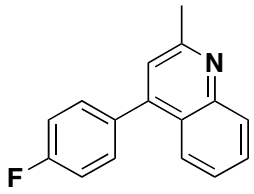


**3-(4-(Trifluoromethyl)phenyl)pyridine (Table 3 entry 2).** Following general procedure C, a mixture of 1-chloro-4-(trifluoromethyl)benzene (271 mg, 200 μL, 1.5 mmol), tetrahydroxydiboron (402 mg, 4.5 mmol), X-Phos (35.7 mg, 75 μmol), (X-Phos) palladium(II) phenethylamine chloride (27.6 mg, 37.5 μmol), KOAc (442 mg, 4.5 mmol), and NaO*t*-Bu (3.6 mg, 37.5 μmol) was heated to 80 ºC for 2 h. At this point, a nitrogen needle was inserted followed by the addition of 3-chloropyridine (170.25 mg, 143 μL, 1.5 mmol) and aq $K_2CO_3$ (1.8 M, 2.5 mL) via syringe. The crude product was purified via flash chromatography on silica gel (0-50% EtOAc/hexane) to

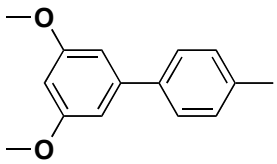
provide the title compound in 90% yield (303 mg) as yellow solid. mp 65-68 °C. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.87 (s, 1H), 8.66 (s, 1H), 7.90 (d, *J* = 7.6 Hz, 1H), 7.75 (d, *J* = 7.4 Hz, 2H), 7.70 (d, *J* = 7.6 Hz, 2H), 7.41 (s, 1H). $^{13}$C NMR (125.8 MHz, $CDCl_3$) δ 149.52, 148.48, 141.53, 135.88, 134.64, 130.21 (q, *J* = 32.6 Hz), 127.63, 126.13 (q, *J* = 3.7 Hz), 125.19, 123.91, 123.20. IR (neat) 1586, 1105. HRMS (ES+) calcd. for $C_{12}H_9F_3N$ (M+H) 224.0609, found 224.0687.




**1-(2'-Methyl-[1,1'-biphenyl]-4-yl)ethanone (Table 3 entry 3).** Following general procedure C, a mixture of 1-chloro-2-methylbenzene (189 mg, 175.3 μL, 1.5 mmol), tetrahydroxydiboron (402 mg, 4.5 mmol), X-Phos (35.7 mg, 75 μmol), (X-Phos) palladium(II) phenethylamine chloride (27.6 mg, 37.5 μmol), KOAc (442 mg, 4.5 mmol), and NaO*t*-Bu (3.6 mg, 37.5 μmol) was heated to 80 ºC for 2 h. At this point, a nitrogen needle was inserted followed by the addition of acetophenone (180 mg, 195 μL, 1.5 mmol) and aq $K_2CO_3$ (1.8 M, 2.5 mL) via syringe. The crude product was purified via flash chromatography on silica gel (0-5% EtOAc/hexane) to provide the title compound in 63% yield (198 mg) as a colorless oil. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.2 Hz, 2H), 7.44 (d, *J* = 8.2 Hz, 2H), 7.35 – 7.23 (m, 4H), 2.66 (s, 3H), 2.29 (s, 3H). $^{13}$C NMR (125.8 MHz, $CDCl_3$) δ 197.91, 147.06, 140.84, 135.70, 135.23, 130.62, 129.58, 129.55, 128.31, 128.00, 126.03, 26.72, 20.47. IR (neat) 3018, 1683, 1358, 1401. HRMS (ES+) calcd. for $C_{12}H_{15}O$ (M+H) 211.1045, found 211.1123.




**4-(4-Fluorophenyl)-2-methylquinoline (Table 3 entry 4).** Following general procedure C, a mixture 1-chloro-4-fluorobenzene (196 mg, 160 μL, 1.5 mmol), tetrahydroxydiboron (402 mg, 4.5 mmol), X-Phos (35.7 mg, 75 μmol), (X-Phos) palladium(II) phenethylamine chloride (27.6 mg, 37.5 μmol), KOAc (442 mg, 4.5 mmol), and NaO*t*-Bu (3.6 mg, 37.5 μmol) was heated to 80 ºC for 2 h. At this point, a nitrogen needle was inserted followed by the addition of 4-chloro-2-methylquinoline (266 mg, 302 μL, 1.5 mmol) and aq $K_2CO_3$ (1.8 M, 2.5 mL) via syringe. The crude product was purified via flash chromatography on silica gel (0-30% EtOAc/hexane) to provide the title compound in 60% yield (212 mg) as a colorless oil. $^1$H NMR (500 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 8.3 Hz, 1H), 7.71 – 7.66 (m, 1H), 7.47 – 7.41 (m, 3H), 7.20 (dd, *J* = 10.4, 6.9 Hz, 3H), 2.77 (s, 3H). $^{13}$C NMR (125.8 MHz, $CDCl_3$) δ 163.91, 161.94, 158.57, 148.49, 147.49, 134.18, 131.25 (d, *J* = 7.9 Hz), 129.34 (d, *J* = 34.0 Hz), 125.95, 125.42, 125.12, 122.34, 115.66 (d, *J* = 21.4 Hz), 25.40. IR (neat) 3064, 1606, 1498, 1413, 1224. HRMS (CI+) calcd. for $C_{16}H_{13}FN$ (M+H) 238.0954, found 238.1032.




**3,5-Dimethoxy-4'-methyl-1,1'-biphenyl (Table 3 entry 5).** Following general procedure C, a mixture 1-chloro-3,5-dimethoxybenzene (244 mg, 1.41 mmol), tetrahydroxydiboron (380 mg, 4.23 mmol), X-Phos (33.55 mg, 70.5 μmol), (X-

Phos) palladium(II) phenethylamine chloride (26 mg, 35 μmol), KOAc (414 mg, 4.23 mmol), and NaO*t*-Bu (3.36 mg, 35 μmol) was heated to 80 ºC for 2 h. At this point, a nitrogen needle was inserted followed by the addition of 1-chloro-4-methylbenzene (178 mg, 166 μL, 1.41 mmol) and aq $K_2CO_3$ (1.8 M, 2.5 mL) via syringe. The crude product was purified via flash chromatography on silica gel (0-3% EtOAc/hexane) to provide the title compound in 55% yield (175 mg) as a colorless oil. $^1$H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.7 Hz, 2H), 7.23 (d, *J* = 7.6 Hz, 2H), 6.72 (s, 2H), 6.45 (s, 1H), 3.83 (s, 6H), 2.39 (s, 3H). $^{13}$C NMR (125.8 MHz, $CDCl_3$) δ 183.17, 165.56, 160.46, 159.50, 151.55, 149.16, 127.43, 121.18, 77.53, 43.24. IR (neat) 2937, 2836, 1595, 1154. HRMS (CI+) calcd. for $C_{15}H_{17}O_2$ (M+H) 229.1150, found 229.1224.

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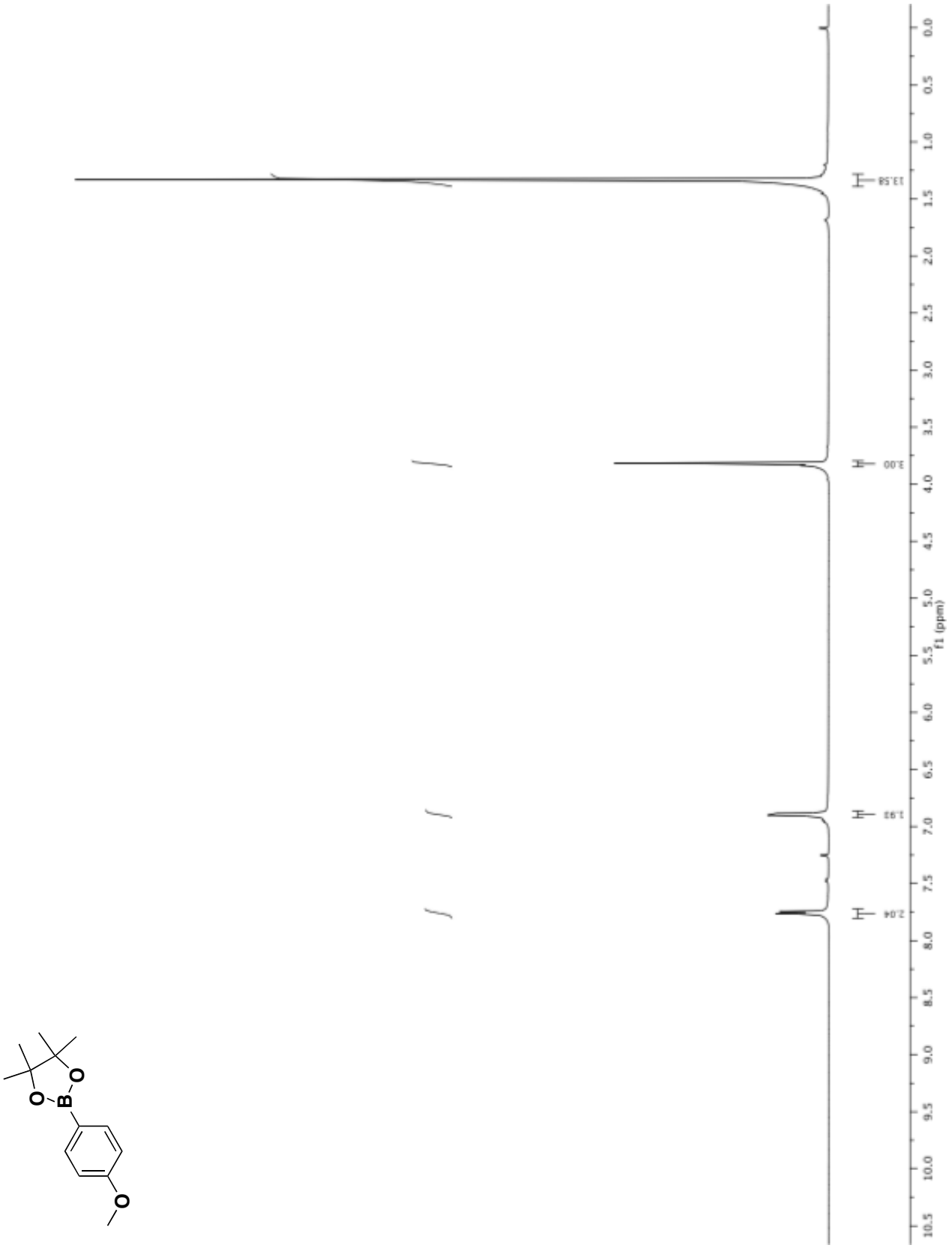
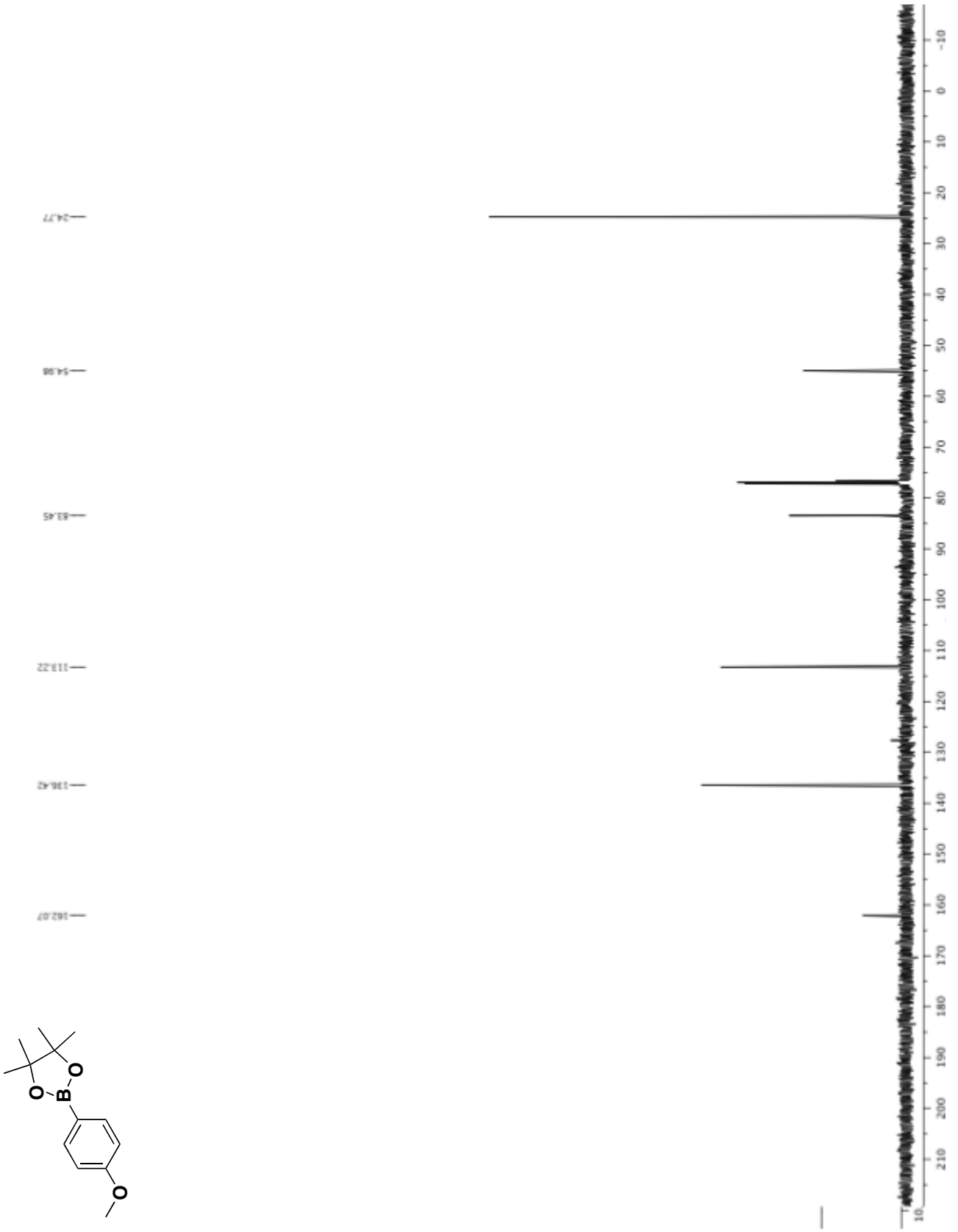
(5) Oliveira, R.; Silva, R.; Molander, G.; Menezes, P. *Magn. Reson. Chem.* **2009***, 47,* 873-878.

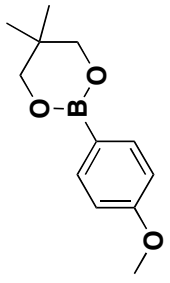
(6) Murphy, J.; Tzschucke, C., Hartwig, J. *Org. Lett.* **2007**, *9*, 757-760.

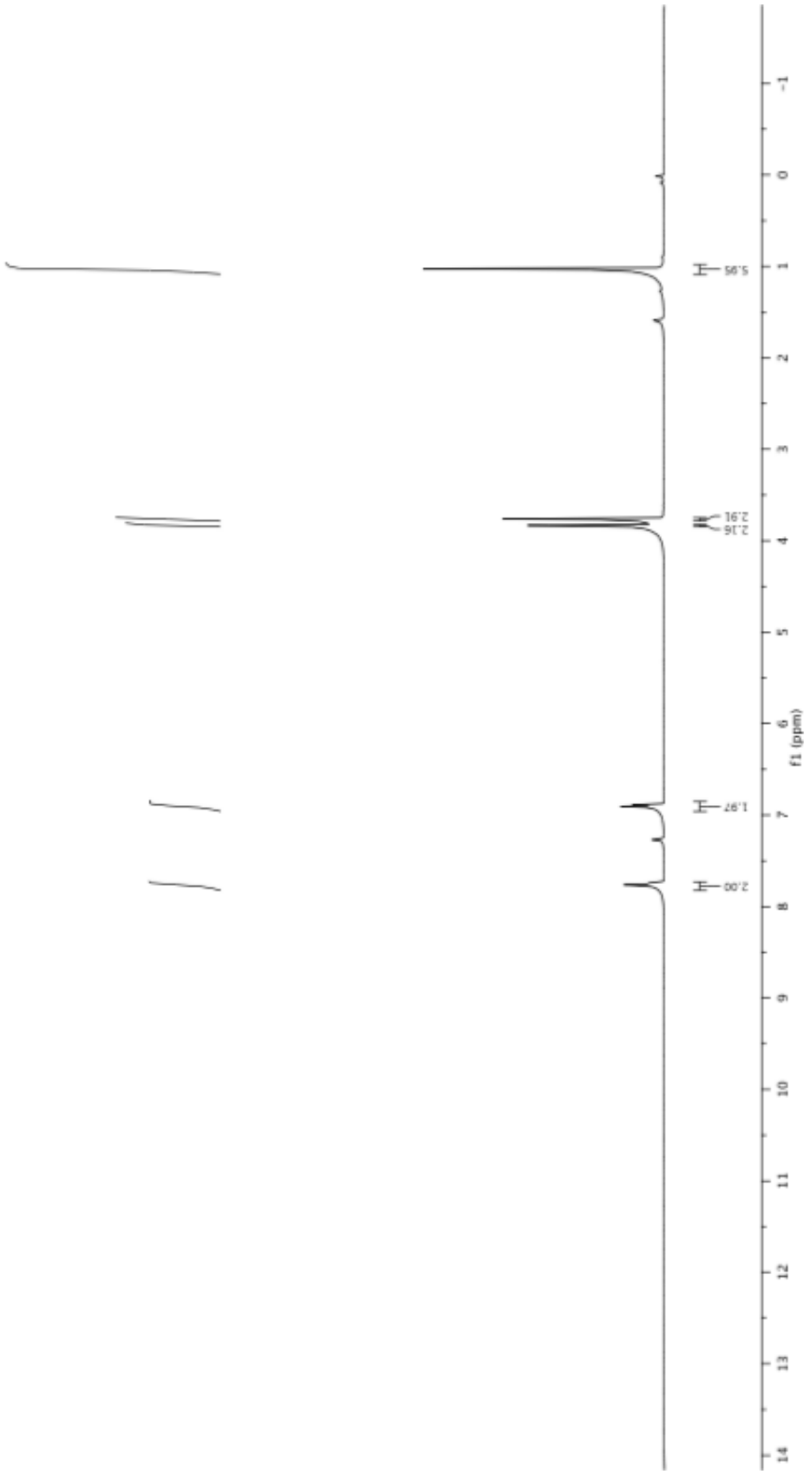



$^1$H NMR Spectra (500 MHz, $CDCl_3$), **2-(4-Methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 1, entry 1)**

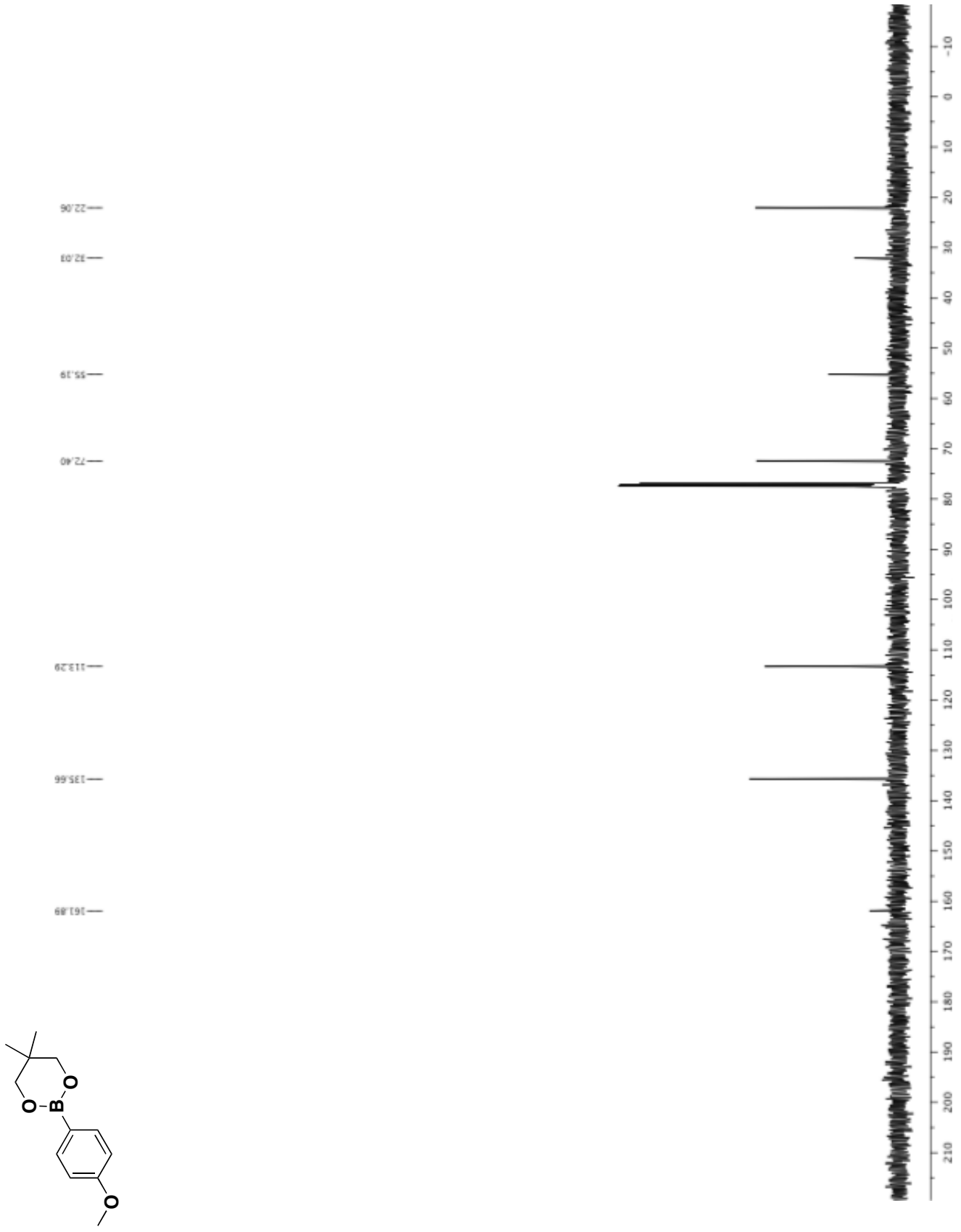



$^{13}C$ NMR Spectra (125.8 MHz, $CDCl_3$), **2-(4-Methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 1, entry 1)**

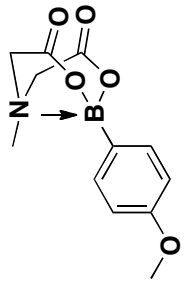


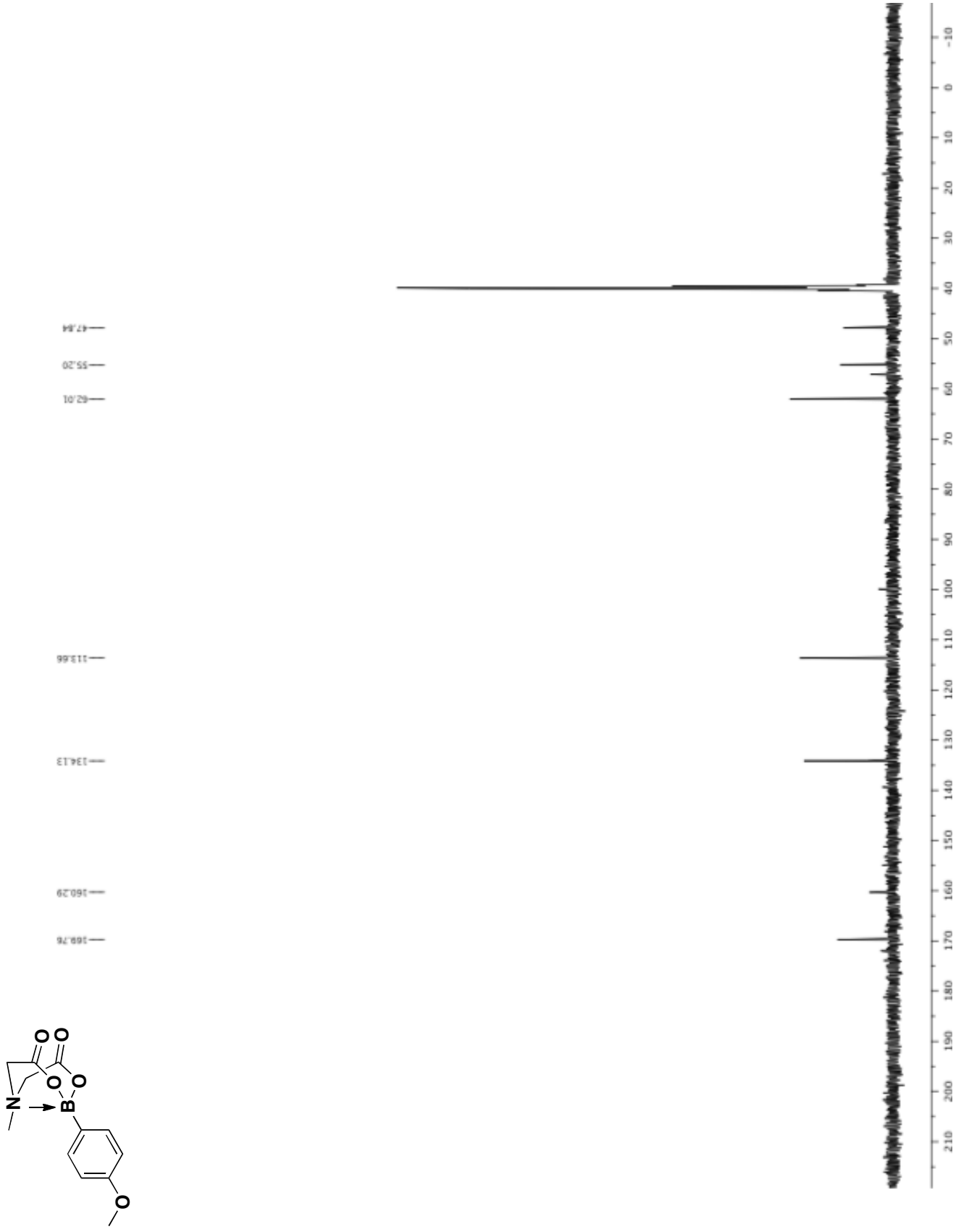

$^{1}$H NMR Spectra (500 MHz, $CDCl_3$), **(2-(4-Methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane (Table 1, entry 2)**



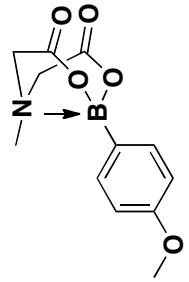

$^{13}C$ NMR Spectra (125.8 MHz, $CDCl_3$), **(2-(4-Methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane (Table 1, entry 2)**

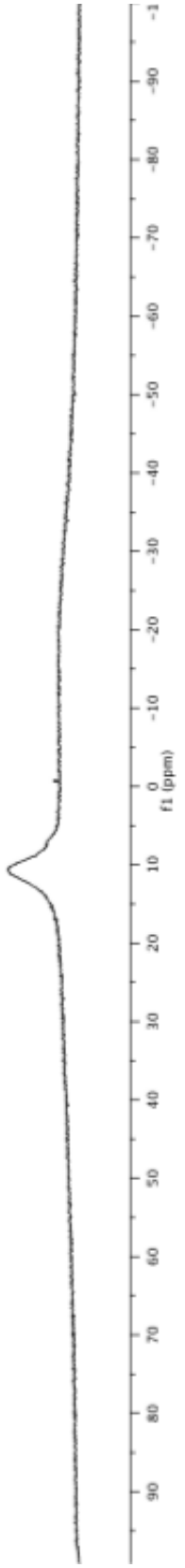



$^1$H NMR Spectra (500 MHz, $d_6$-DMSO), **2-(4-Methoxyphenyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (Table 1, entry 3)**

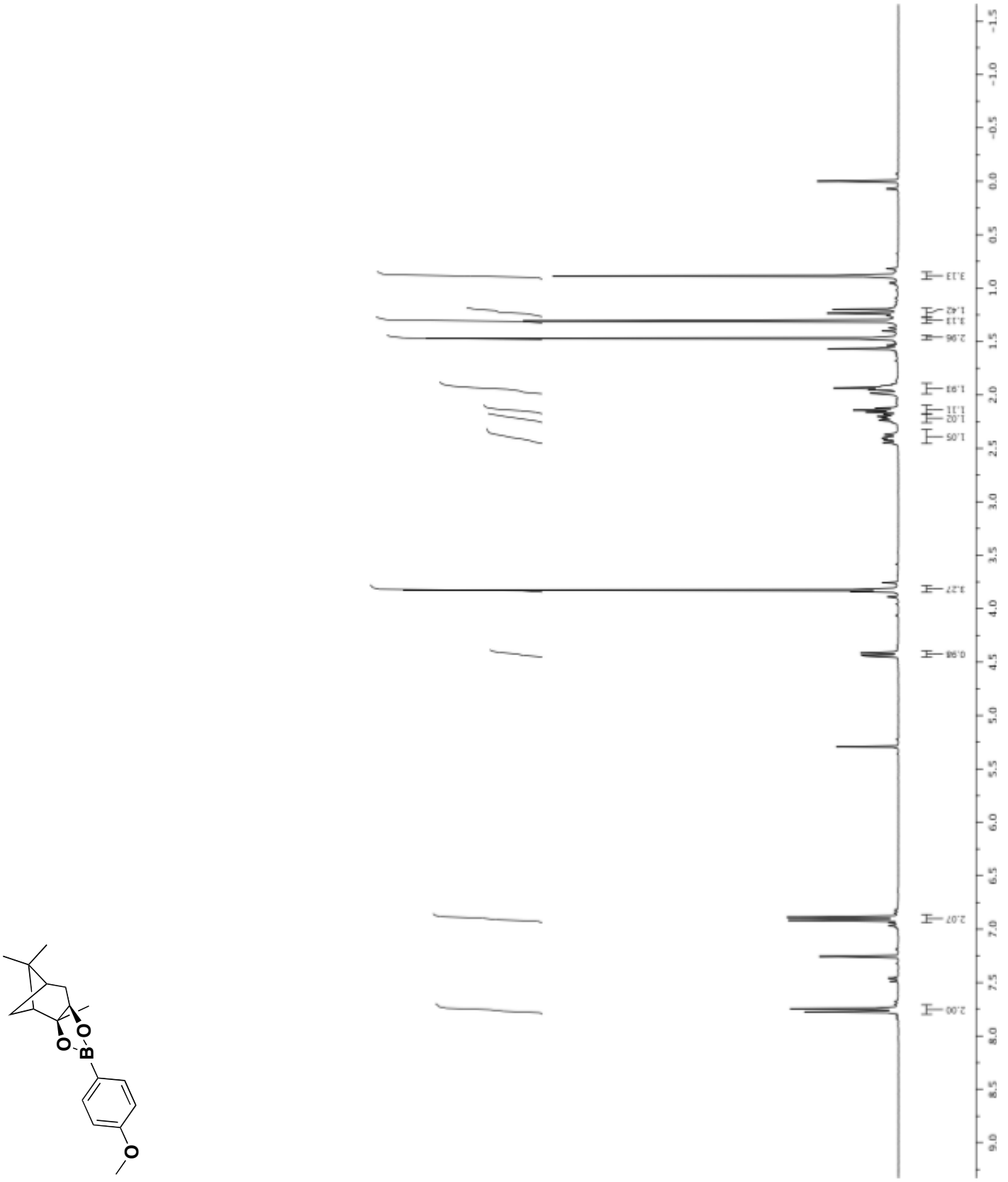



$^{13}$C NMR Spectra (125.8 MHz, $d_6$-DMSO), **2-(4-Methoxyphenyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (Table 1, entry 3)**

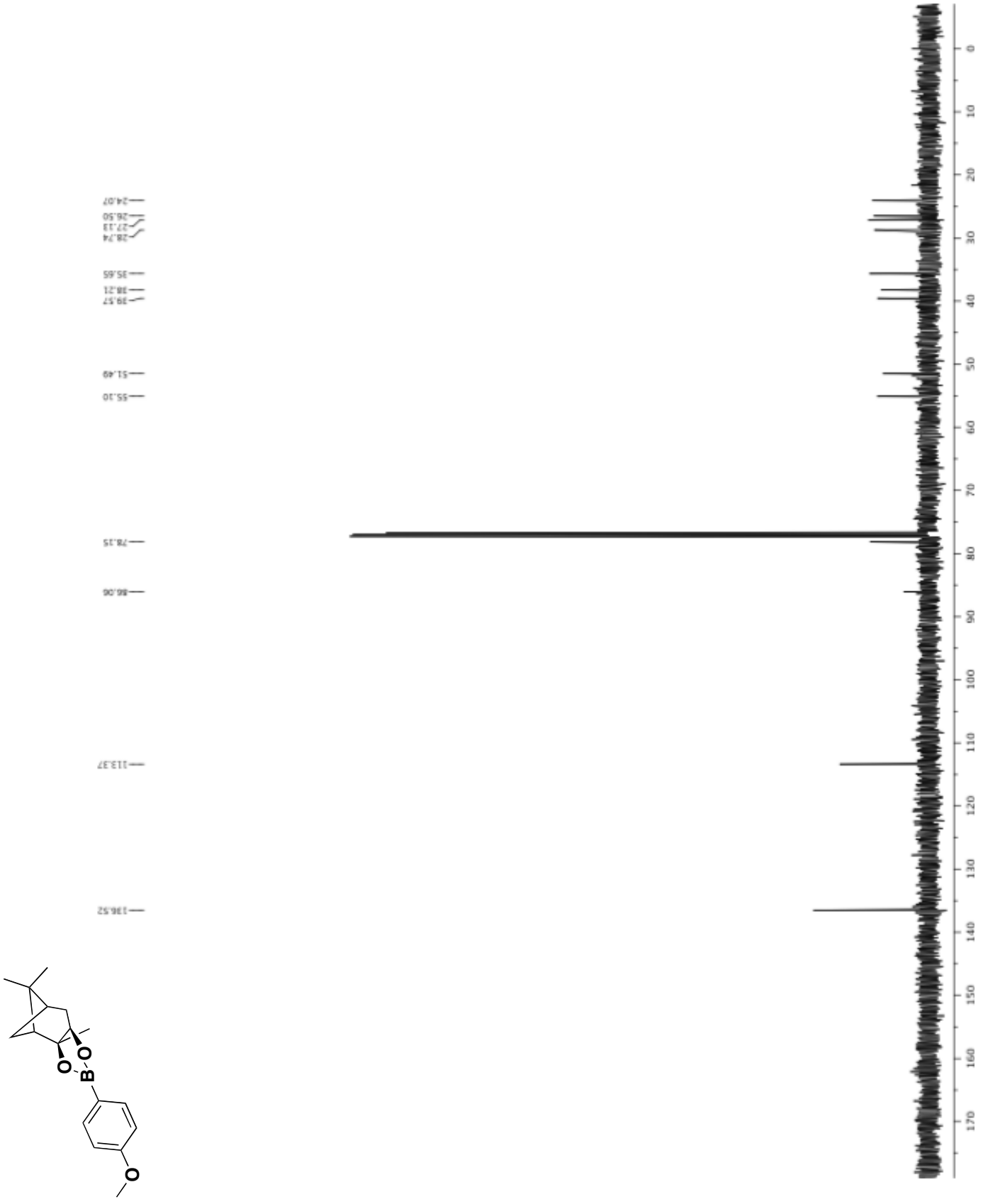




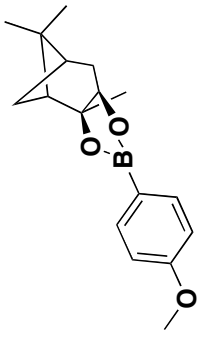

$^{11}$B NMR Spectra (128.4 MHz, $d_6$-DMSO), **2-(4-Methoxyphenyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (Table 1, entry 3)**



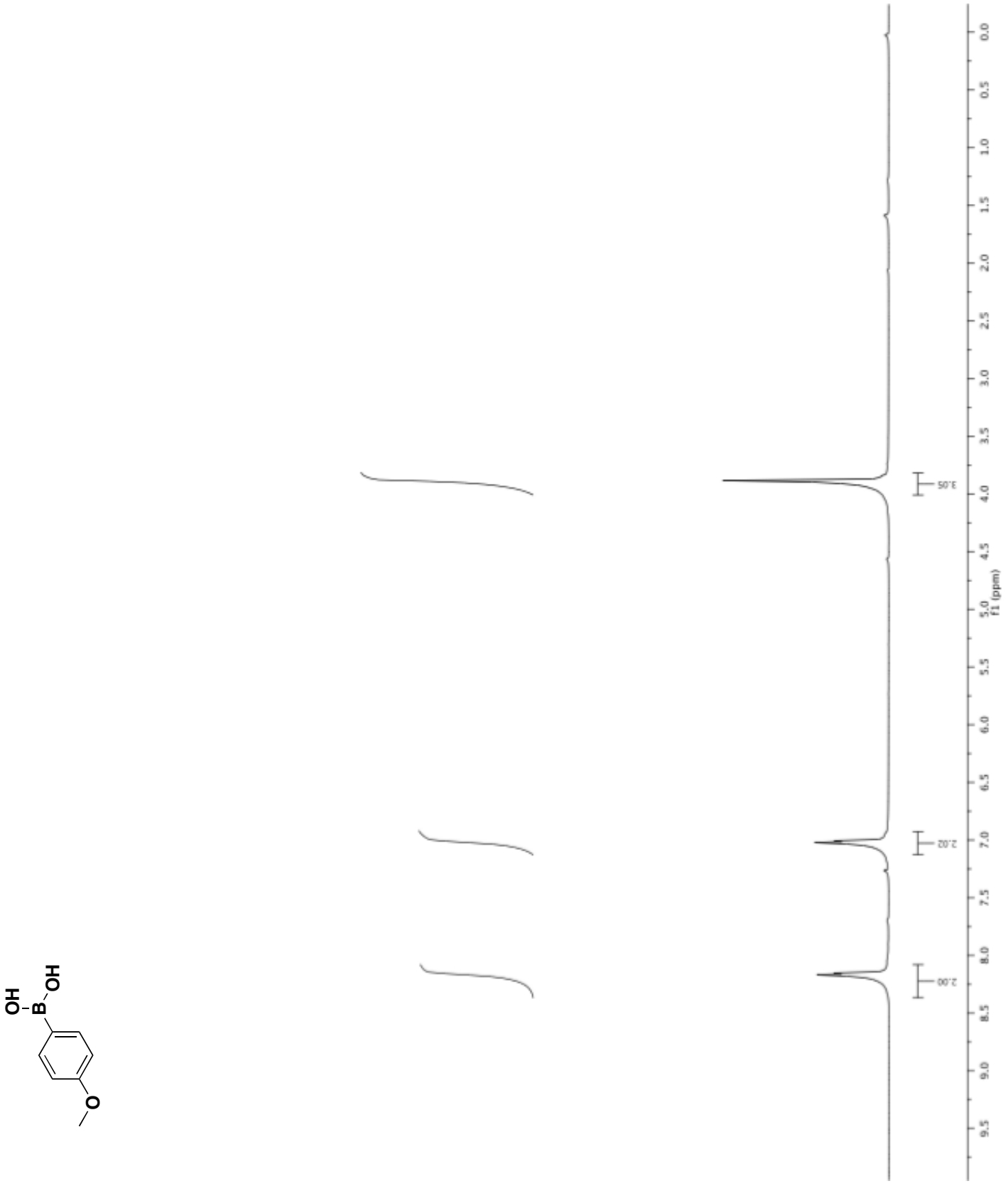
$^{1}$H NMR Spectra (500 MHz, $CDCl_3$), **(3a*S*,4*S*,6*R*,6a*R*)-2-(4-Methoxyphenyl)-3a,5,5-trimethyltetrahydro-3a*H*-4,6-methanocyclopenta[*d*][1,3,2]dioxaborole (Table 1 entry 4)**



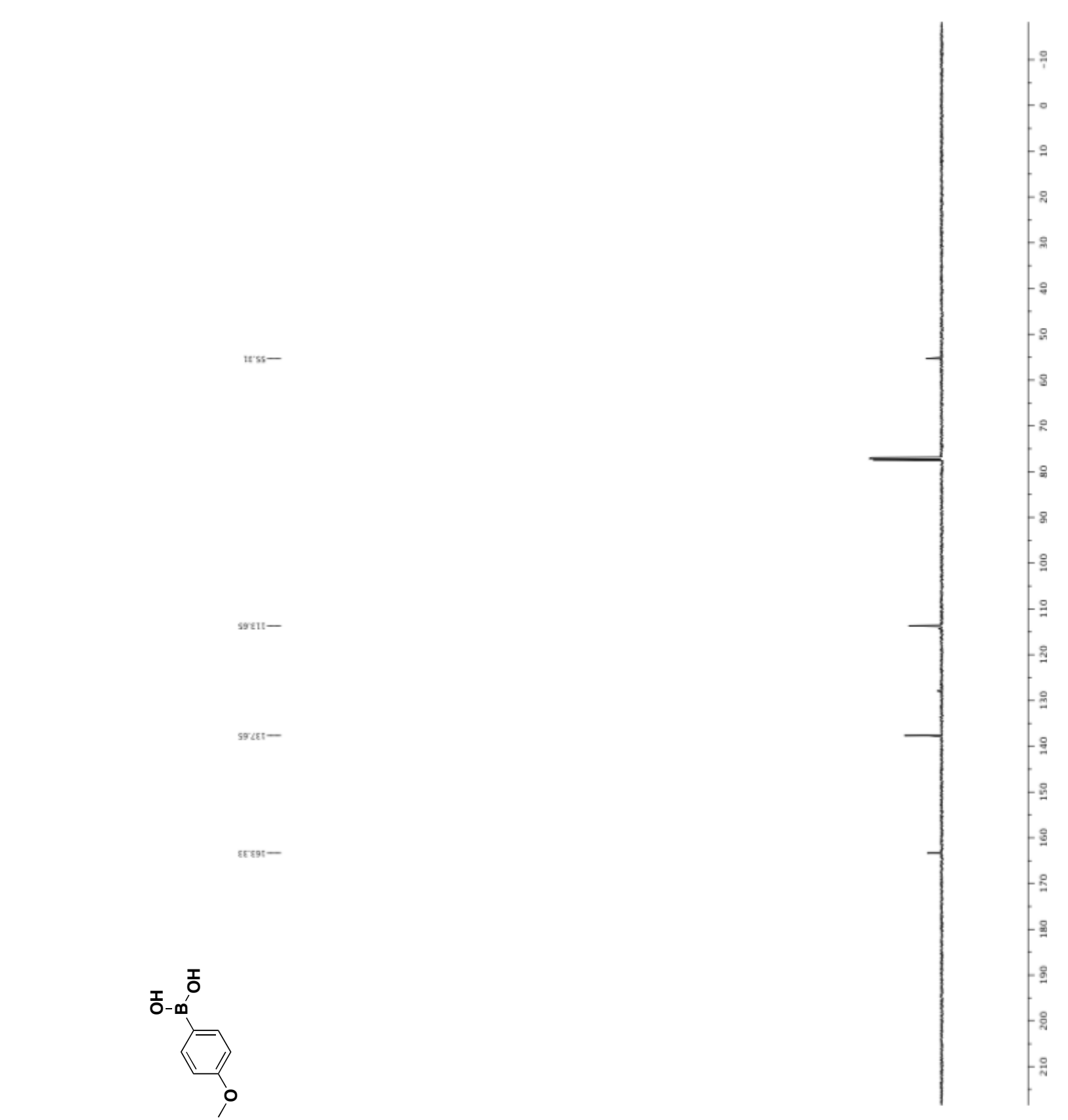

$^{13}$C NMR Spectra (125.8 MHz, $CDCl_3$), **(3a*S*,4*S*,6*R*,6a*R*)-2-(4-Methoxyphenyl)-3a,5,5-trimethyltetrahydro-3a*H*-4,6-methanocyclopenta[*d*][1,3,2]dioxaborole (Table 1 entry 4)**



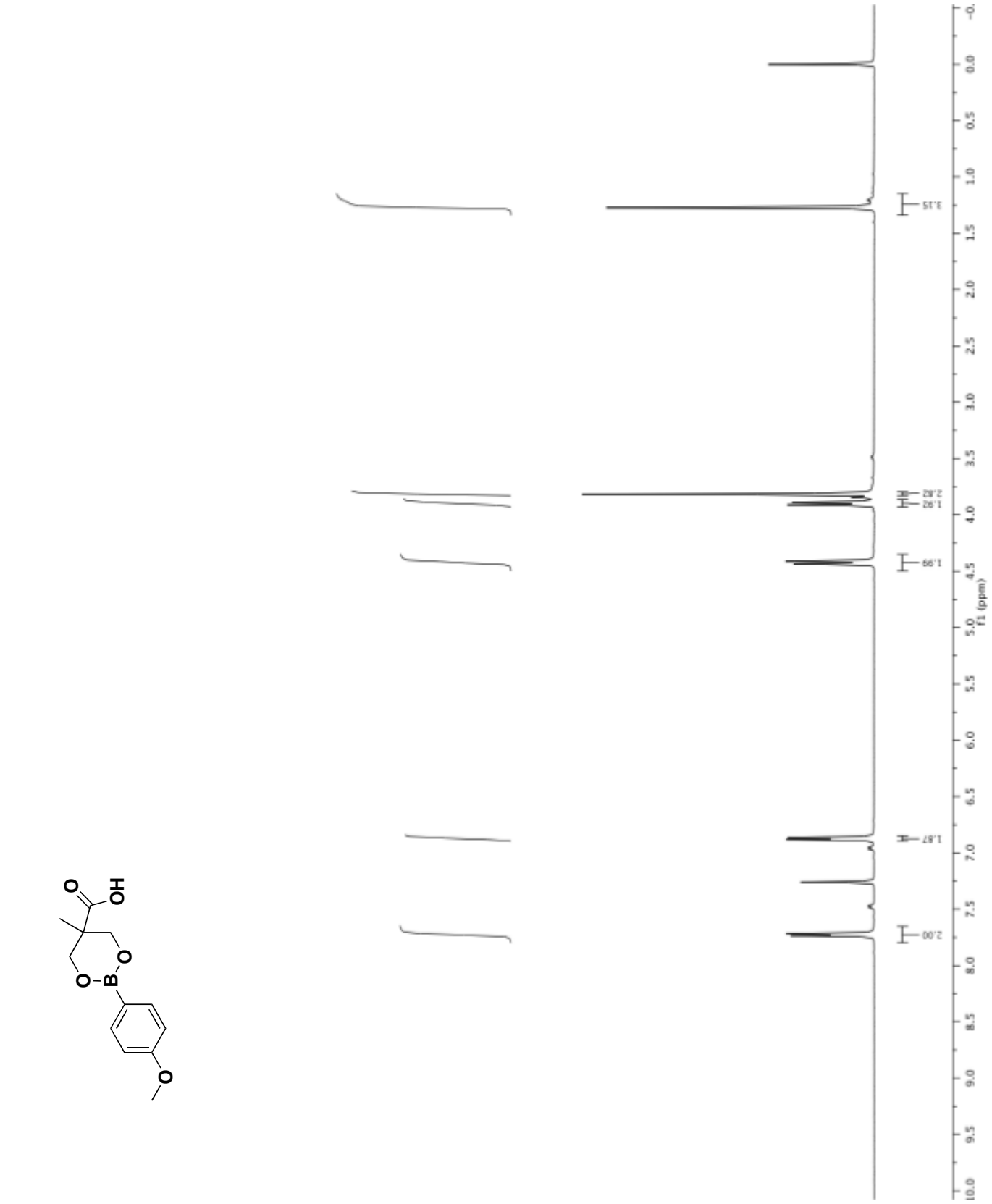
$^{11}$B NMR Spectra (128.4 MHz, $CDCl_3$), **(3a*S*,4*S*,6*R*,6a*R*)-2-(4-Methoxyphenyl)-3a,5,5-trimethyltetrahydro-3a*H*-4,6-methanocyclopenta[*d*][1,3,2]dioxaborole (Table 1 entry 4)**



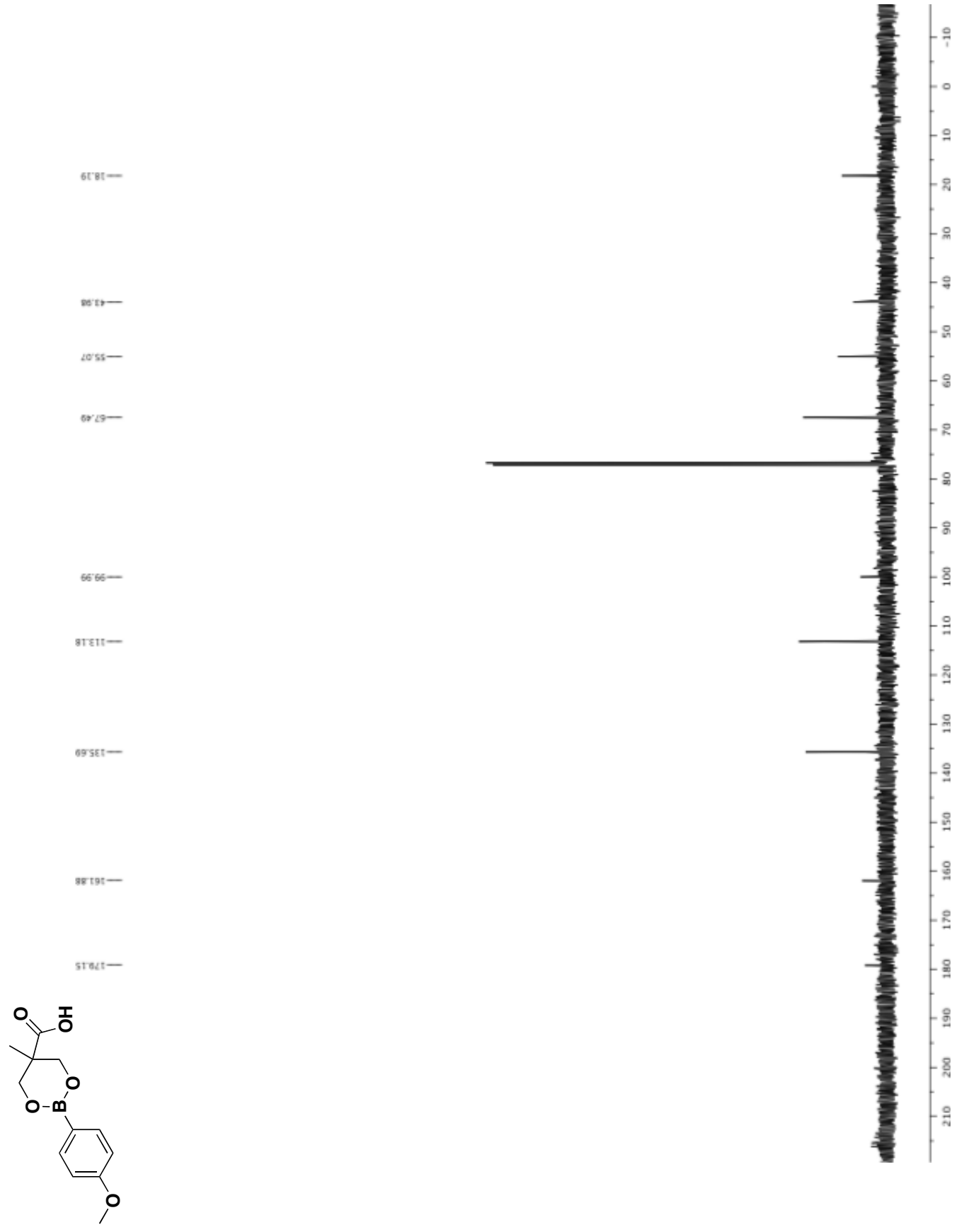

$^{1}$H NMR Spectra (500 MHz, $CDCl_3$), **(4-Methoxyphenyl)boronic acid (Table 1, entry 5)**



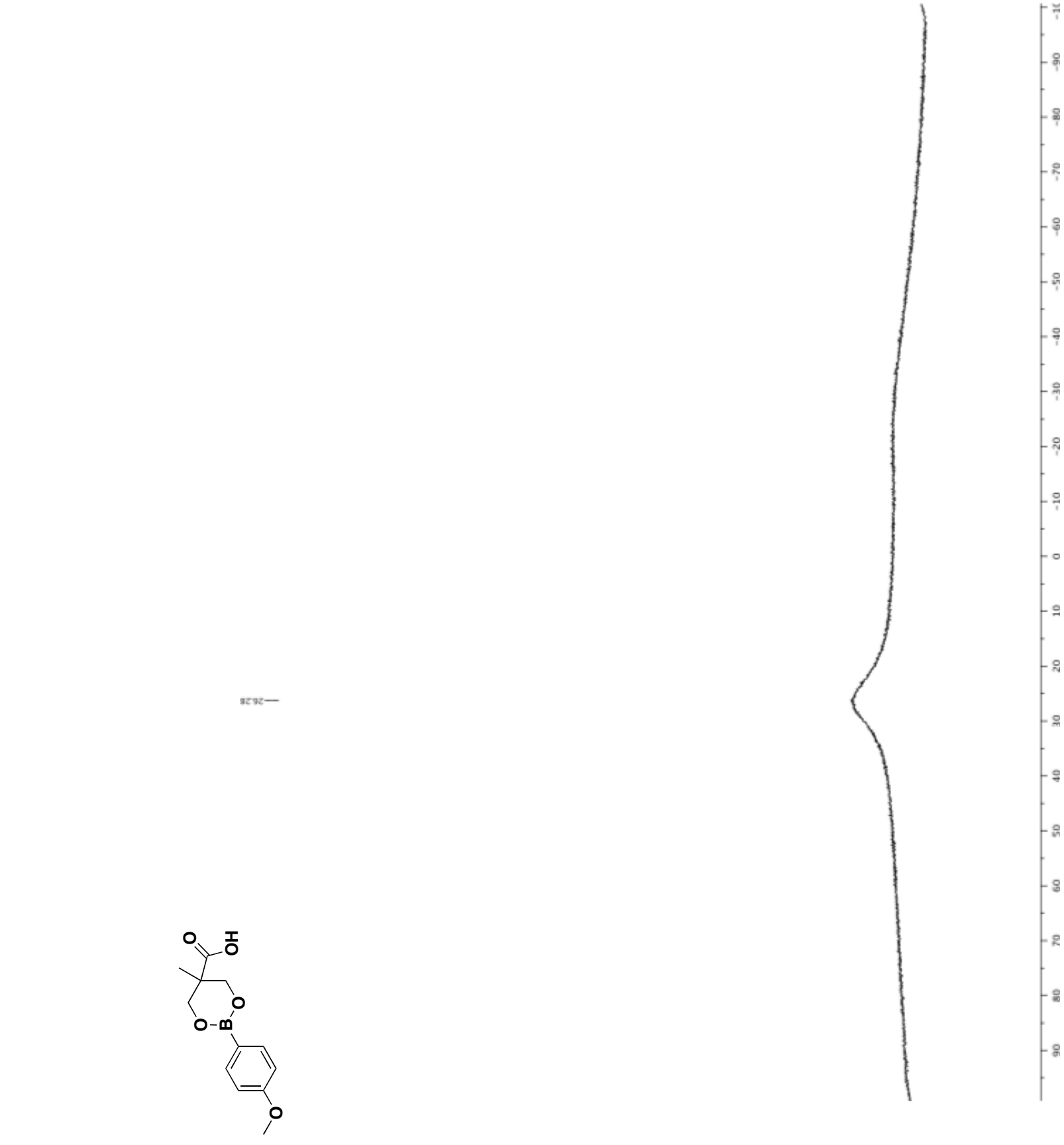

$^{13}C$ NMR Spectra (125.8 MHz, $CDCl_3$), **(4-Methoxyphenyl)boronic acid (Table 1, entry 5)**



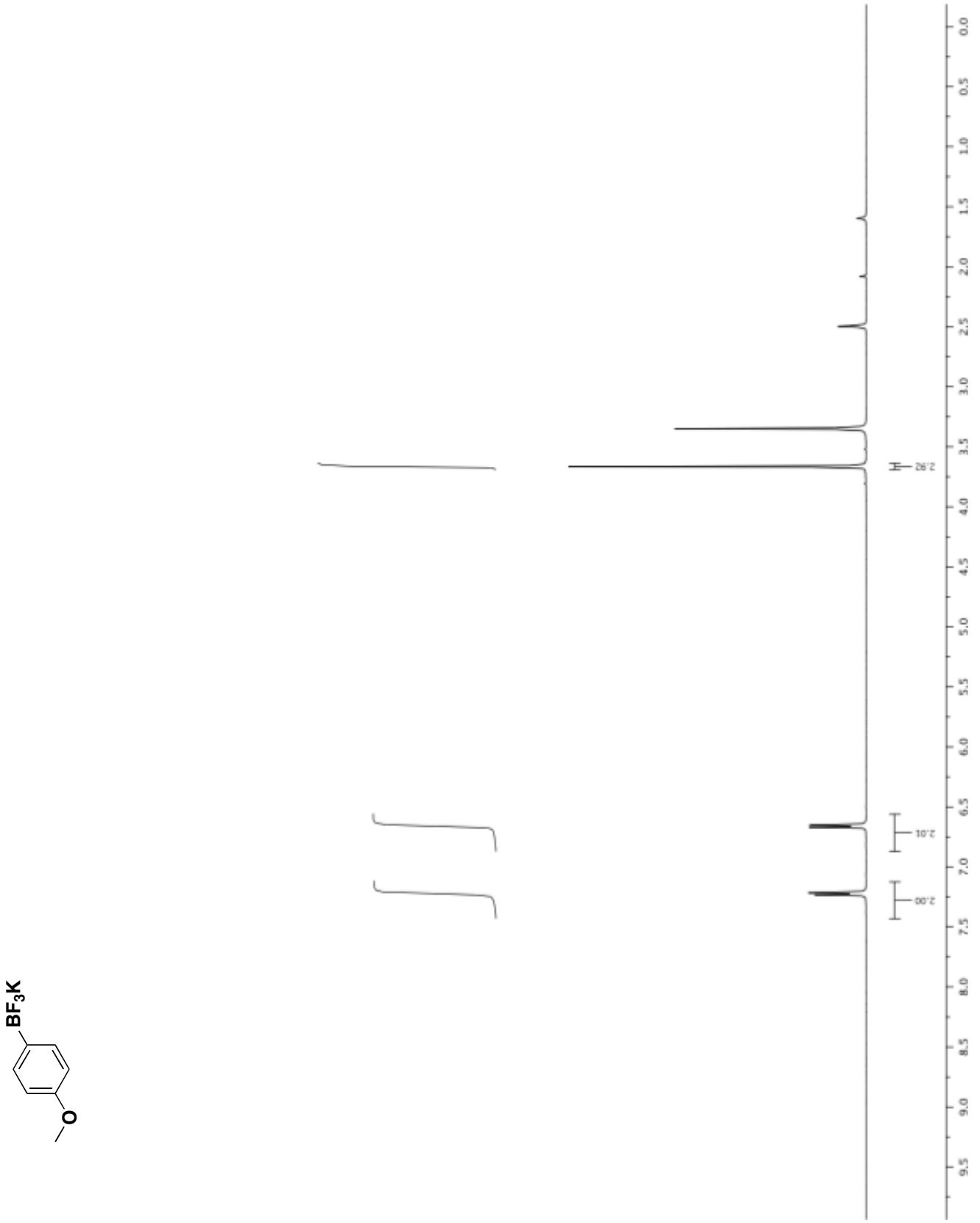

$^1$H NMR Spectra (500 MHz, $CDCl_3$), **2-(4-Methoxyphenyl)-5-methyl-1,3,2-dioxaborinane-5-carboxylic acid (Table 1, entry 6)**



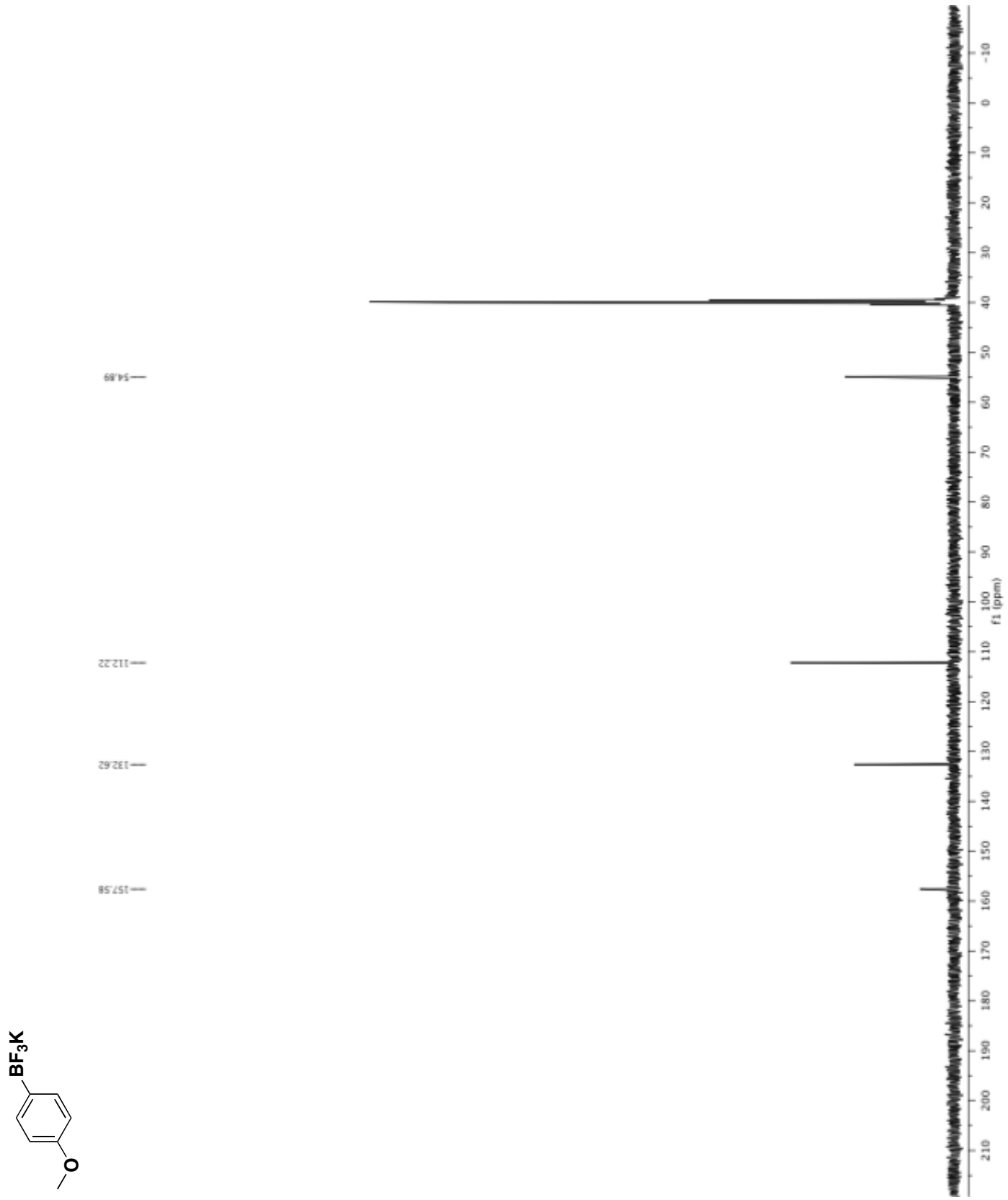

$^{13}C$ NMR Spectra (125.8 MHz, $CDCl_3$), **2-(4-Methoxyphenyl)-5-methyl-1,3,2-dioxaborinane-5-carboxylic acid (Table 1, entry 6)**



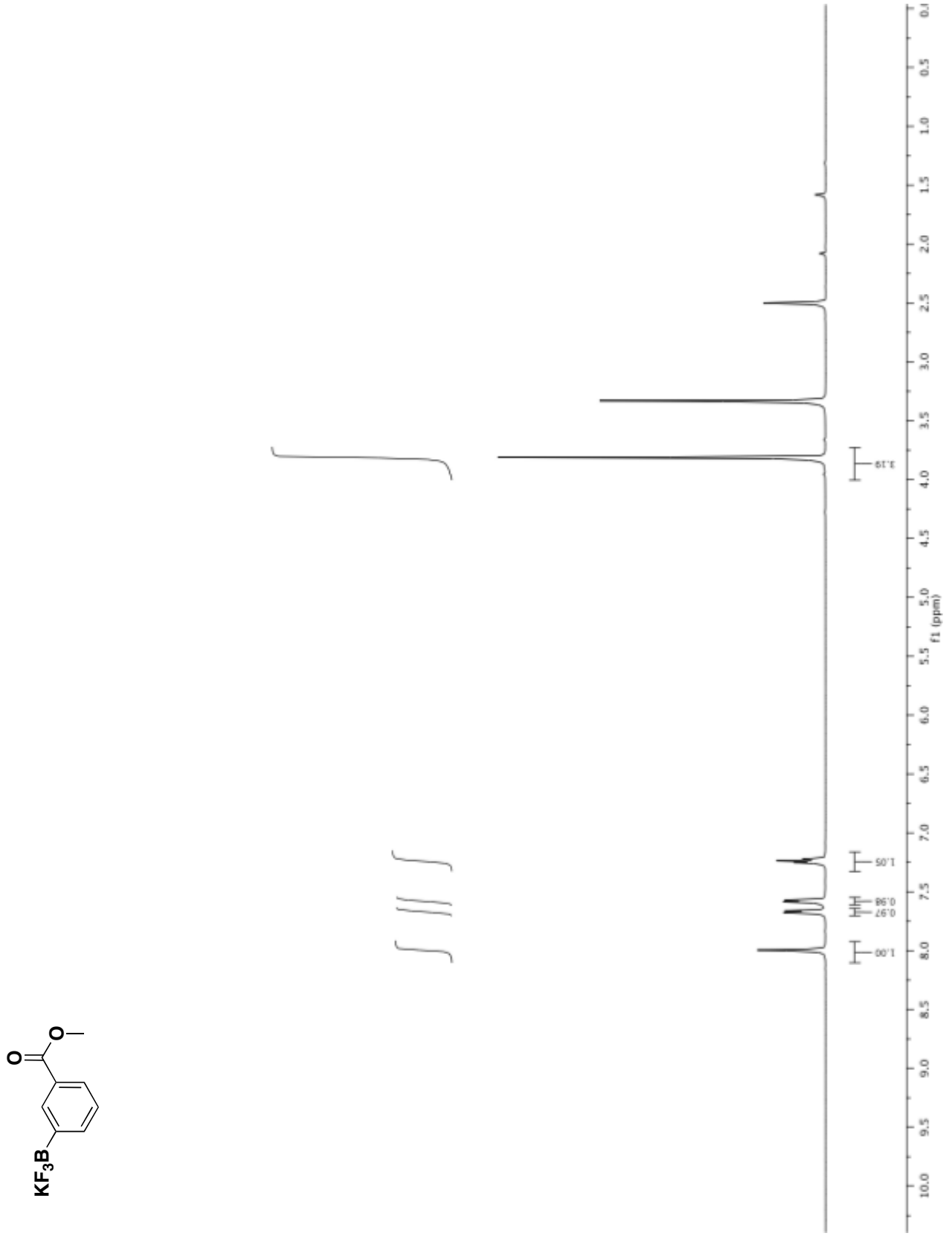
$^{11}$B NMR Spectra (128.4 MHz $d_6$-DMSO), **2-(4-Methoxyphenyl)-5-methyl-1,3,2-dioxaborinane-5-carboxylic acid (Table 1, entry 6)**



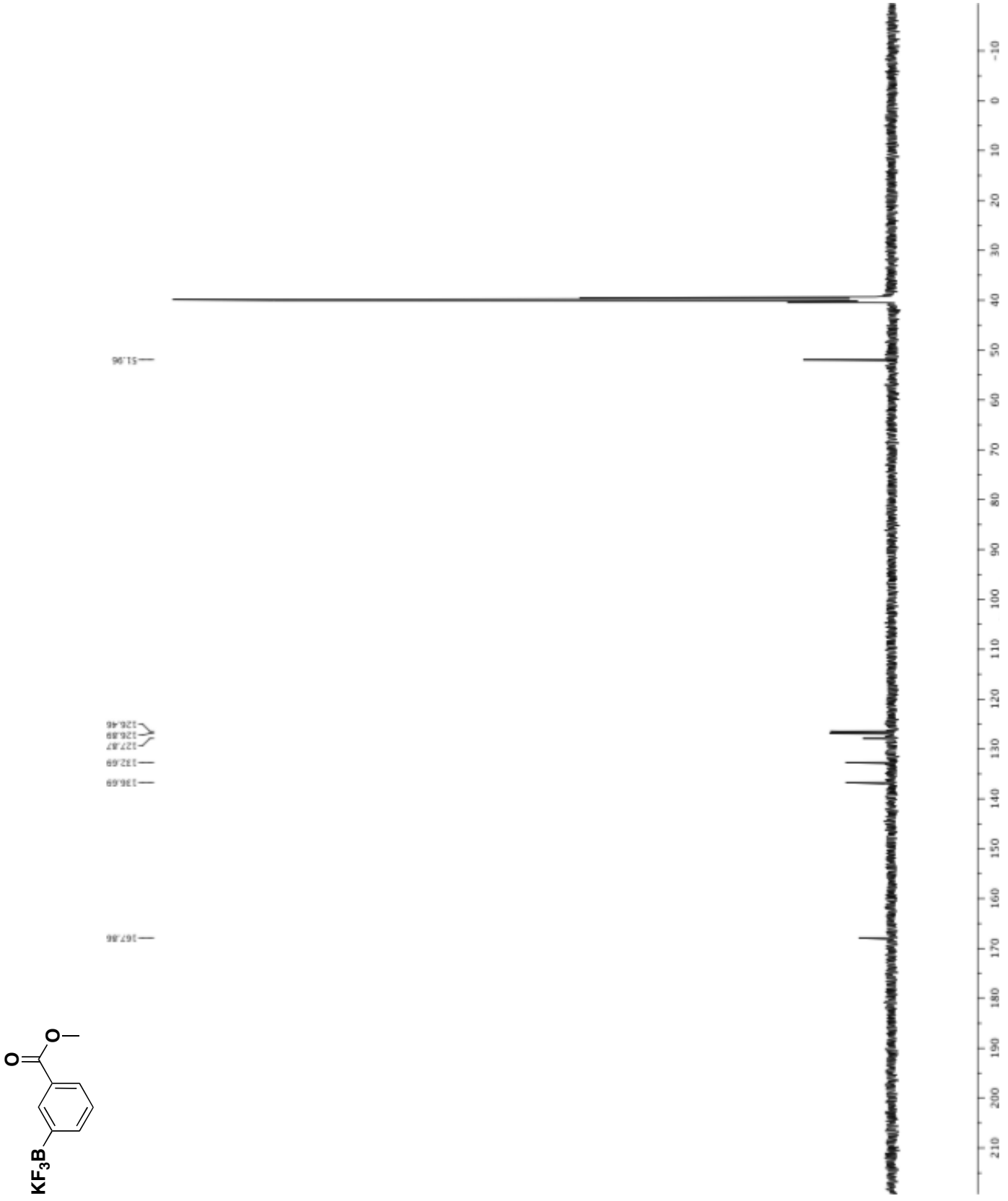

$^{1}$H NMR Spectra (500 MHz, $d_6$-DMSO), **Potassium 4-Methoxy-trifluoroborate (Table 2, entry 1)**



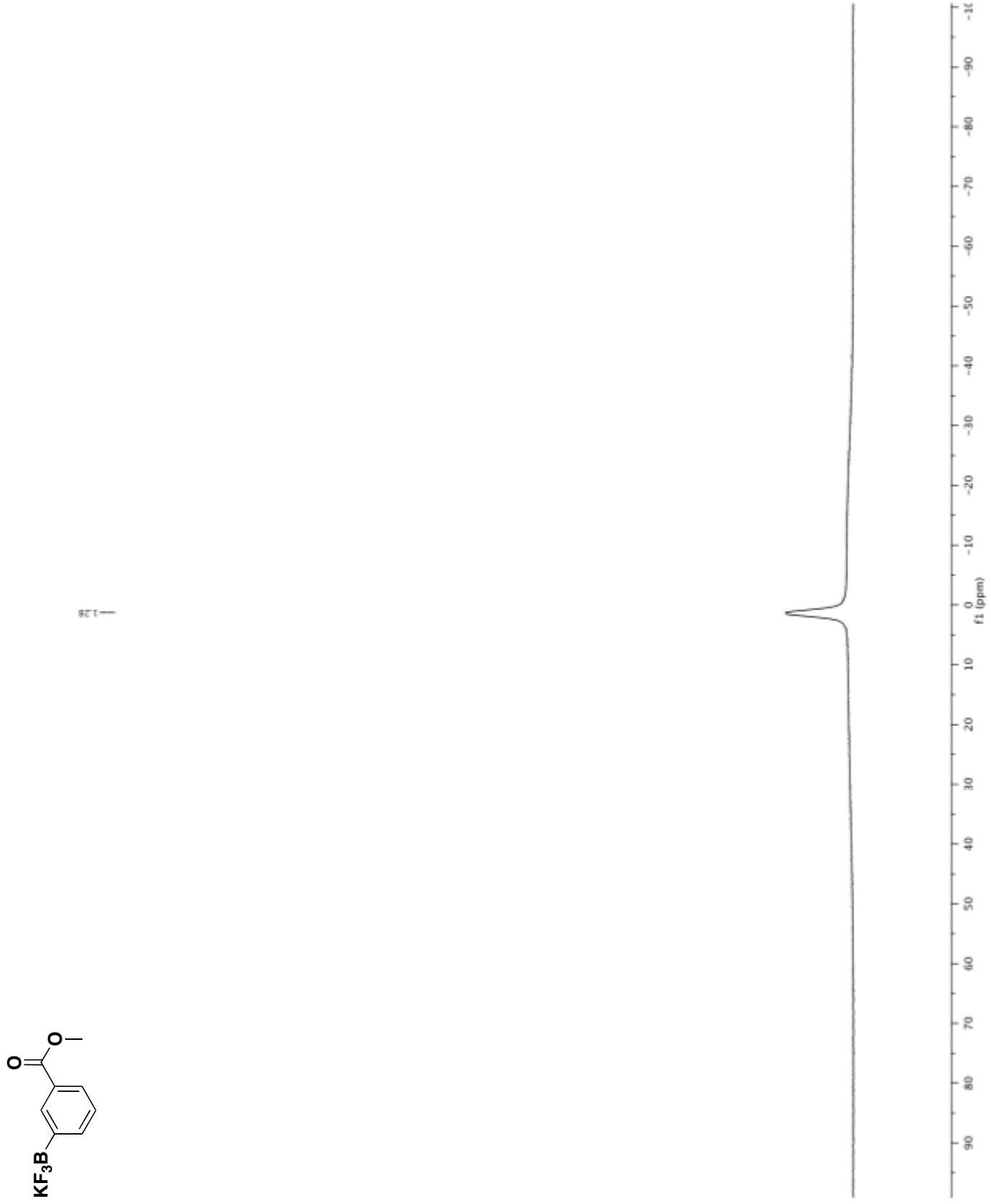

$^{13}$C NMR Spectra (125.8 MHz, $d_6$-DMSO), **Potassium 4-Methoxy-trifluoroborate (Table 2, entry 1)**



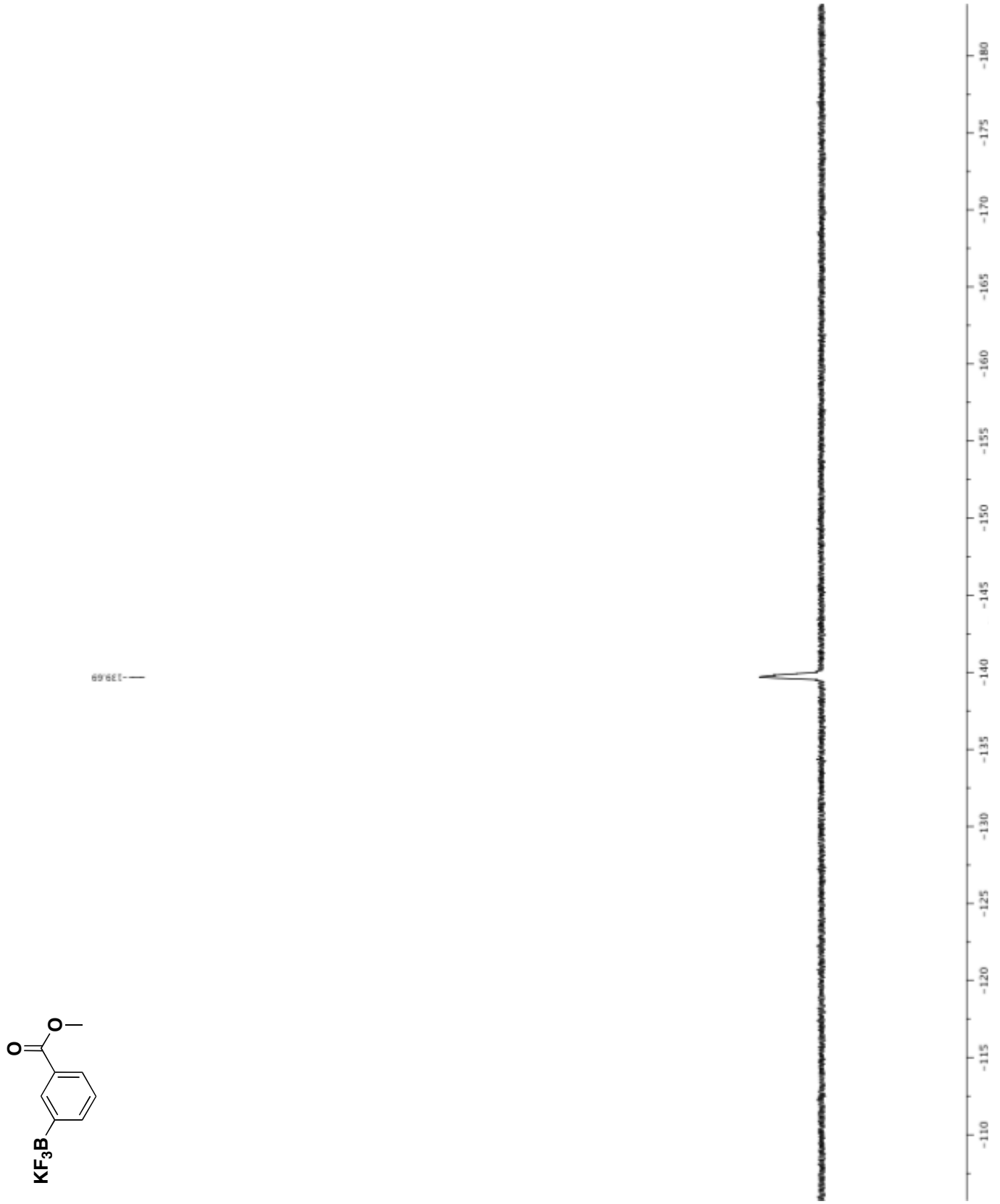

$^1$H NMR Spectra (500 MHz, $d_6$-DMSO), **Potassium (3-(Methoxycarbonyl)phenyl)trifluoroborate (Table 2, entry 2)**



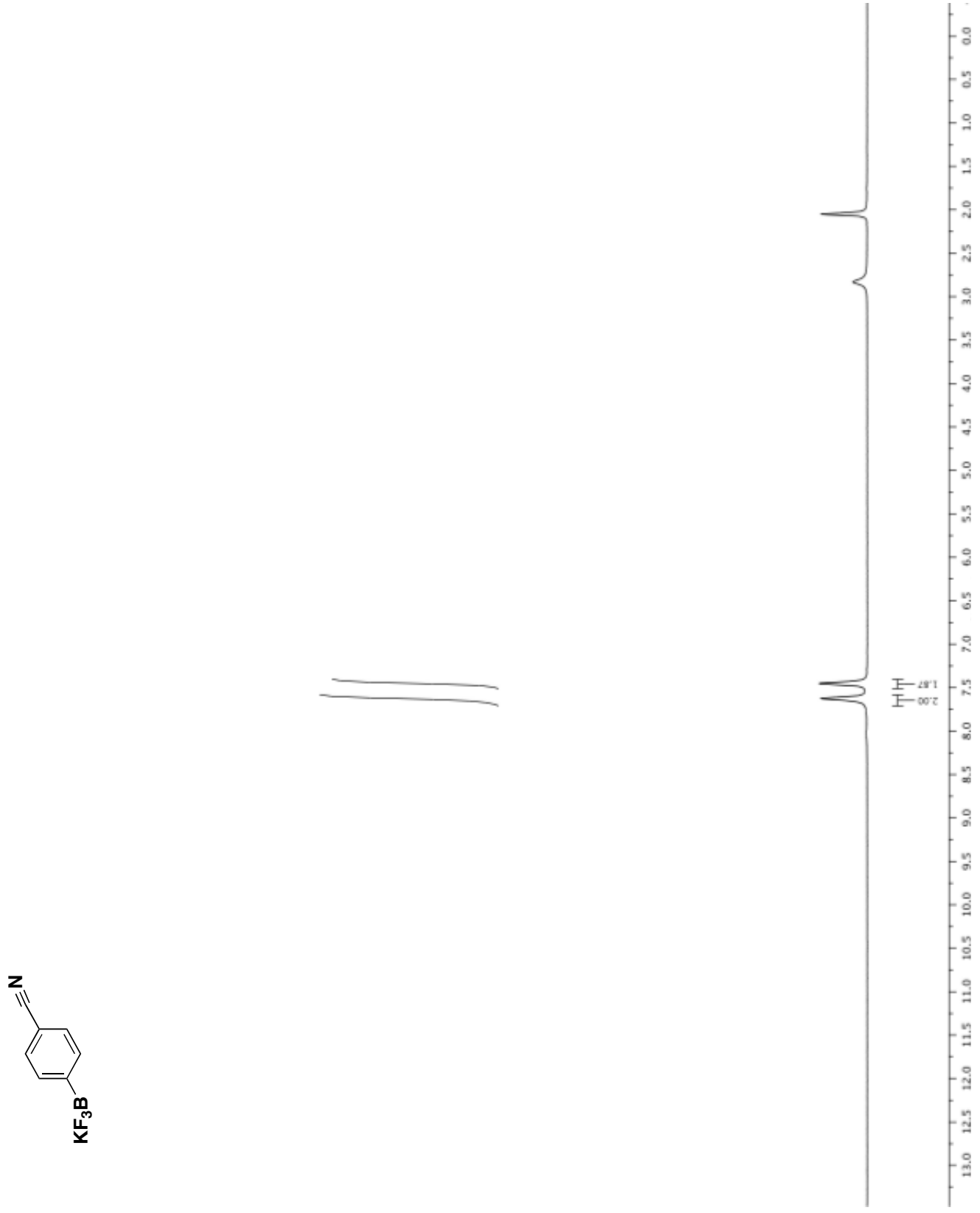

$^{13}C$ NMR Spectra (125.8 MHz, $d_6$-DMSO), **Potassium (3-(Methoxycarbonyl)phenyl)trifluoroborate (Table 2, entry 2)**



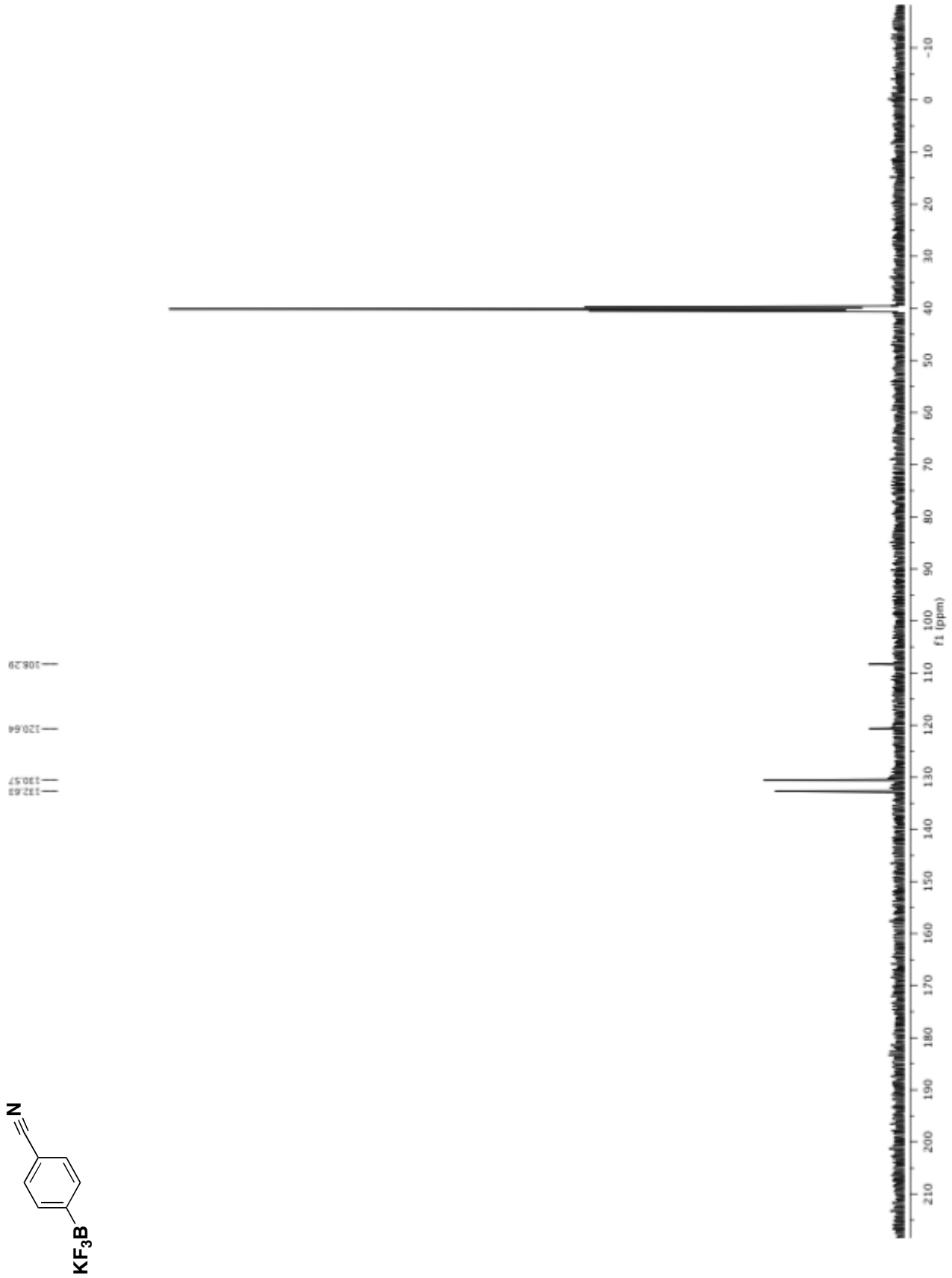

$^{11}$B NMR Spectra (128.4 MHz, $d_6$-DMSO), **Potassium (3-(Methoxycarbonyl)phenyl)trifluoroborate (Table 2, entry 2)**



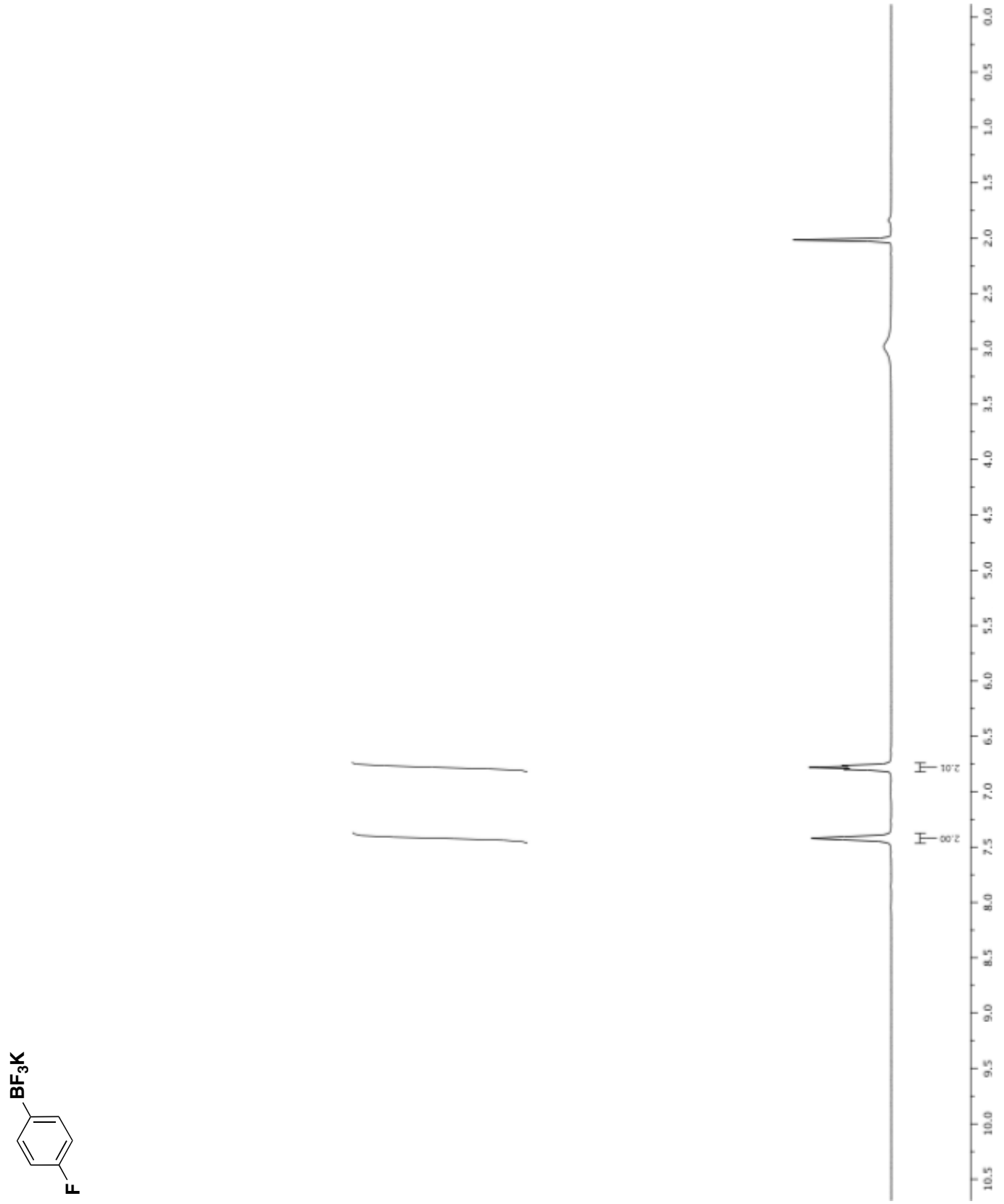

$^{19}$F NMR Spectra (470.8 MHz, $d_6$-DMSO), **Potassium (3-(Methoxycarbonyl)phenyl)trifluoroborate (Table 2, entry 2)**



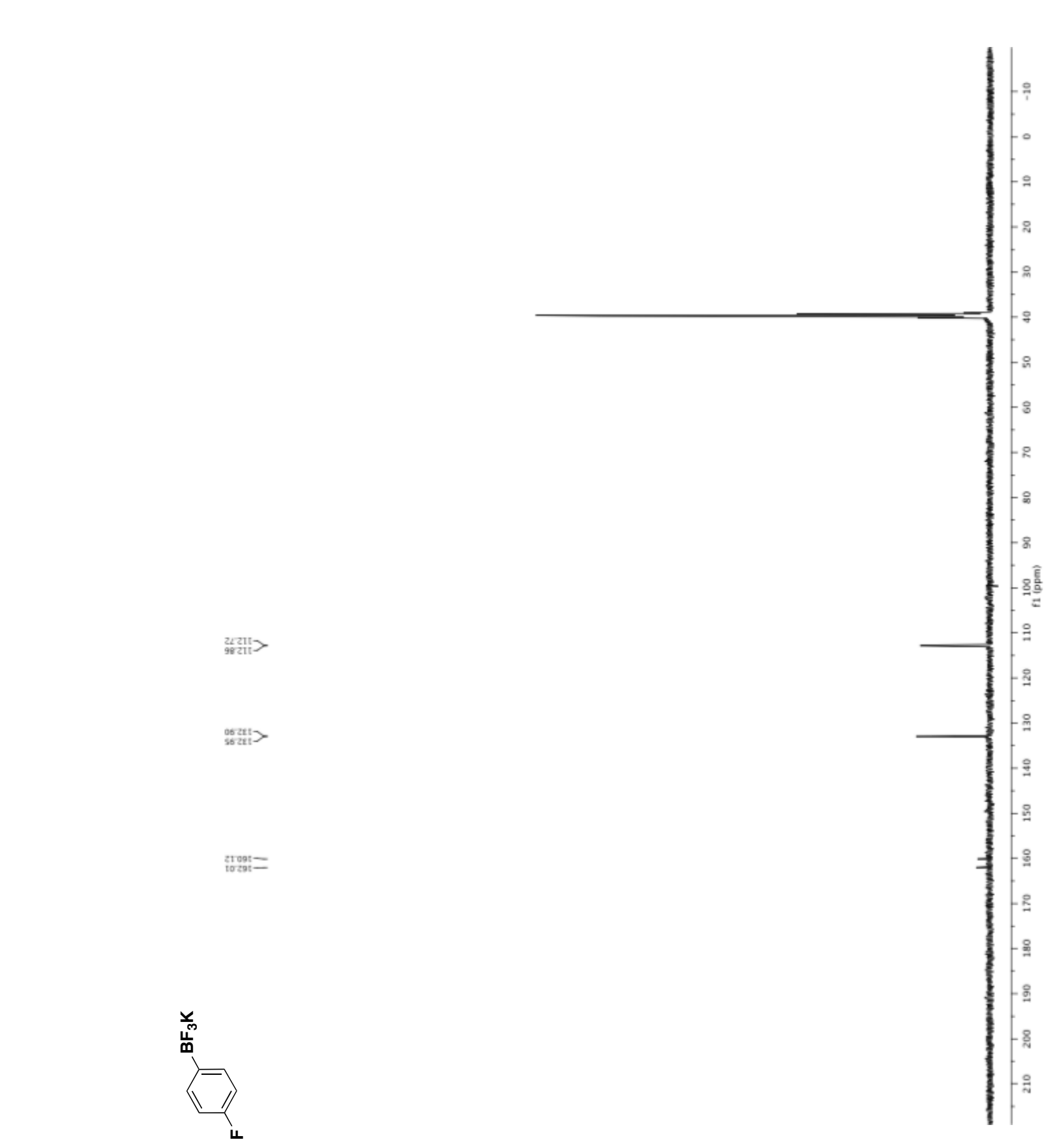

$^1$H NMR Spectra (500 MHz, $d_6$-Acetone), **Potassium (2-Cyanophenyl)trifluoroborate (Table 2, entry 3)**



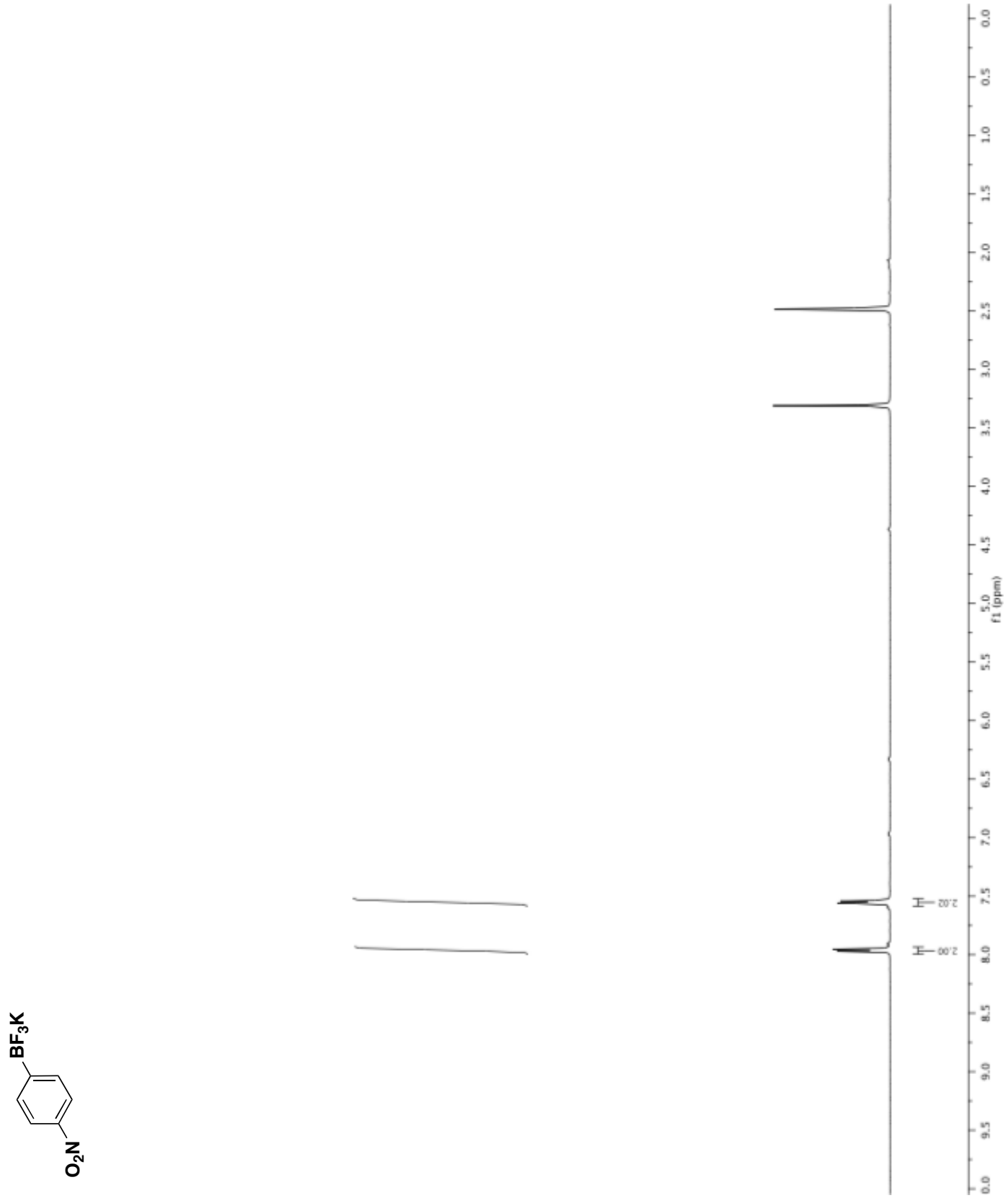

$^{13}$C NMR Spectra (125.8 MHz, $d_6$-DMSO), **Potassium (2-Cyanophenyl)trifluoroborate (Table 2, entry 3)**



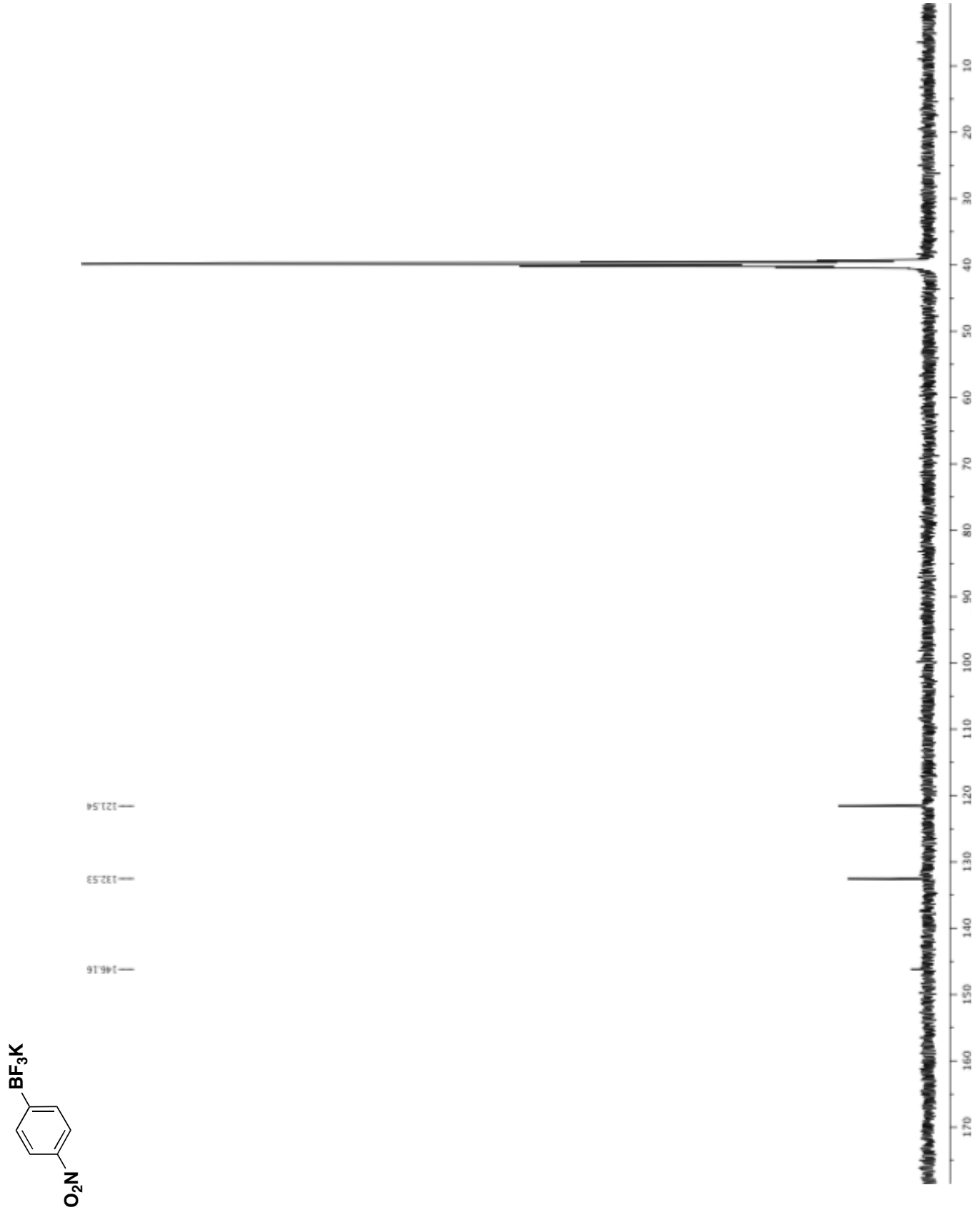

$^{1}$H NMR Spectra (500 MHz, $d_6$-Acetone), **Potassium (4-Fluorophenyl)trifluoroborate (Table 2, entry 5)**



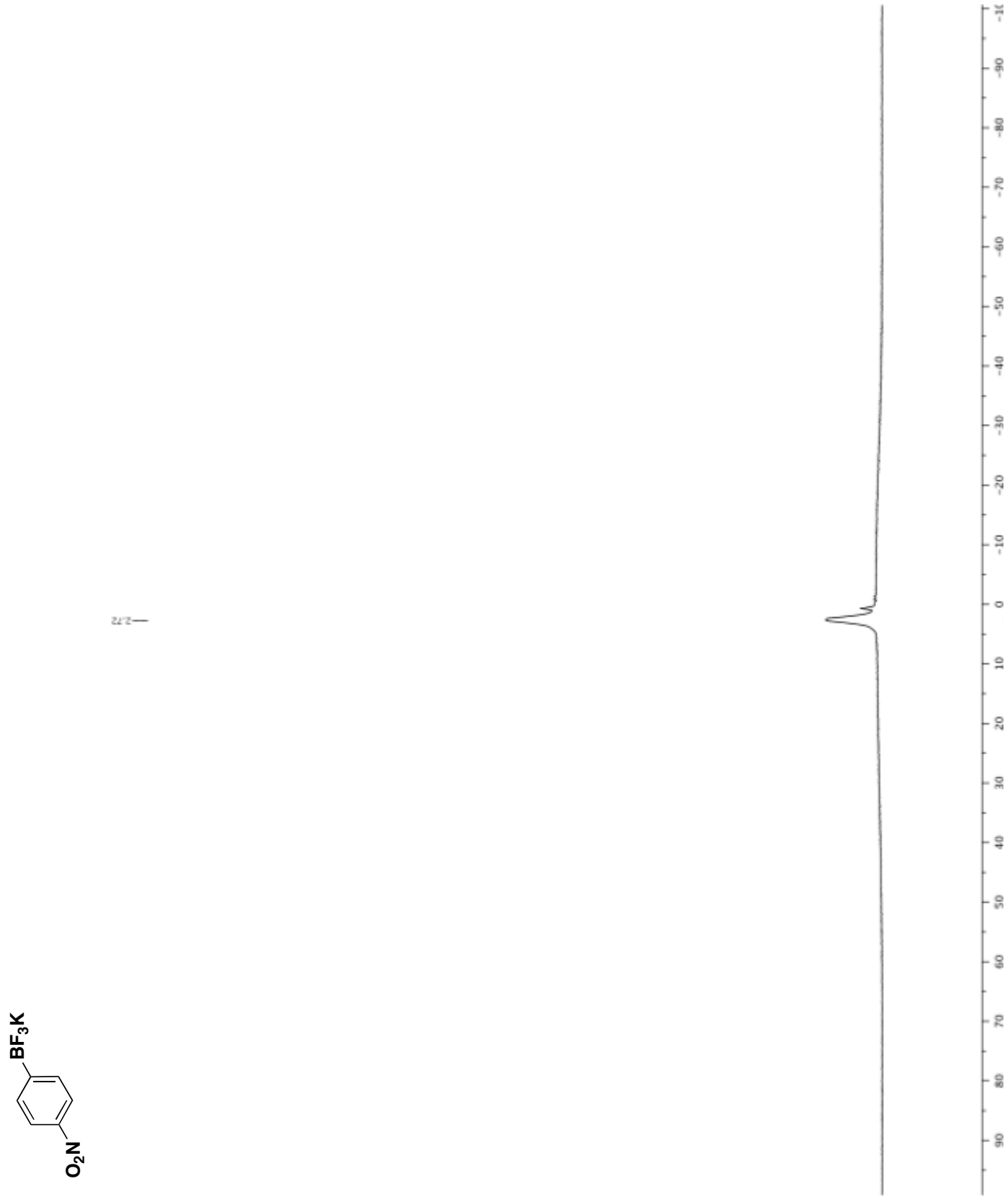

$^{13}$C NMR Spectra (125.8 MHz, $d_6$-DMSO), **Potassium (4-Fluorophenyl)trifluoroborate (Table 2, entry 5)**



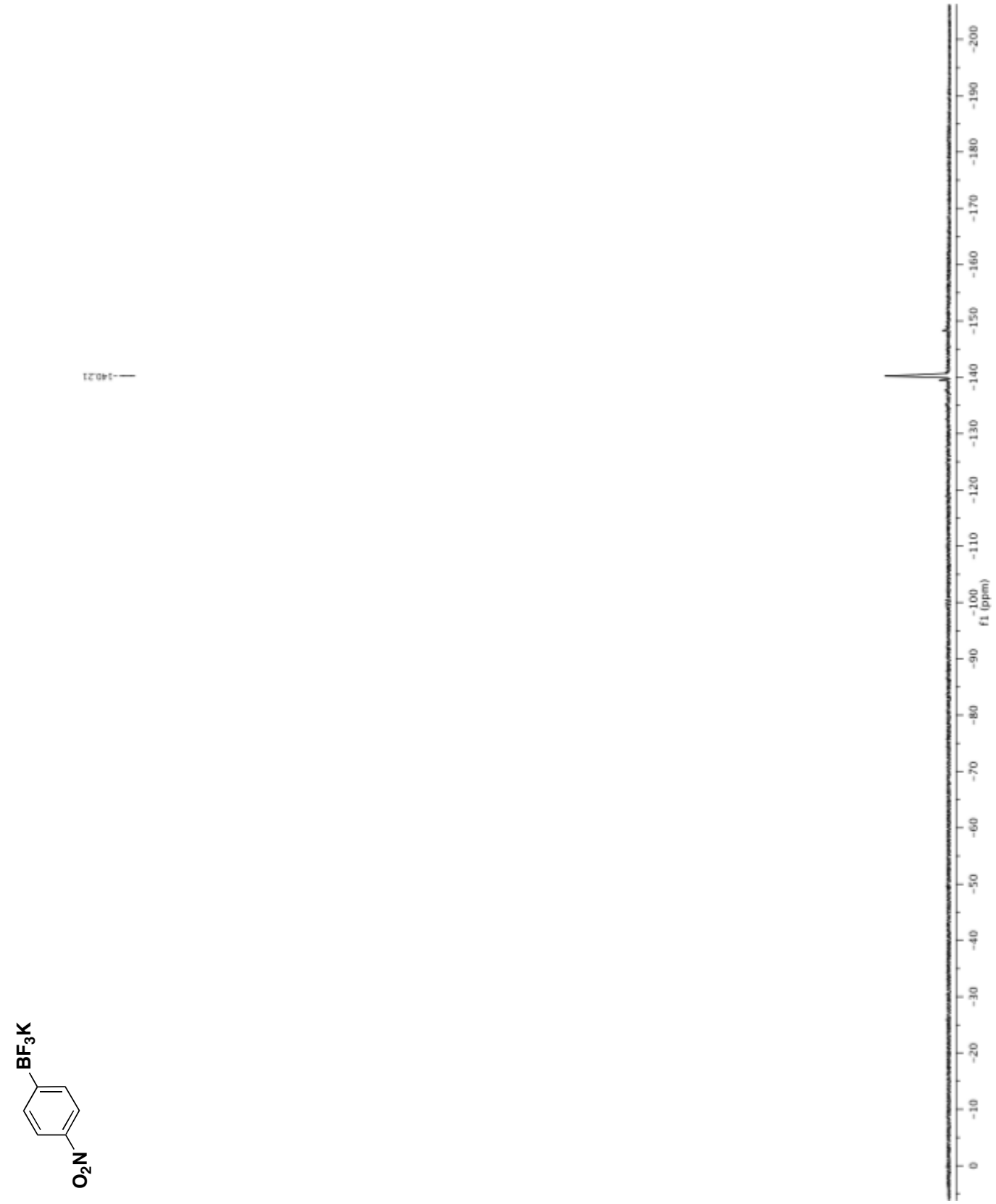

$^{1}$H NMR Spectra (500 MHz, $d_6$-DMSO), **Potassium (4-Nitrophenyl)trifluoroborate (Table 2, entry 6)**



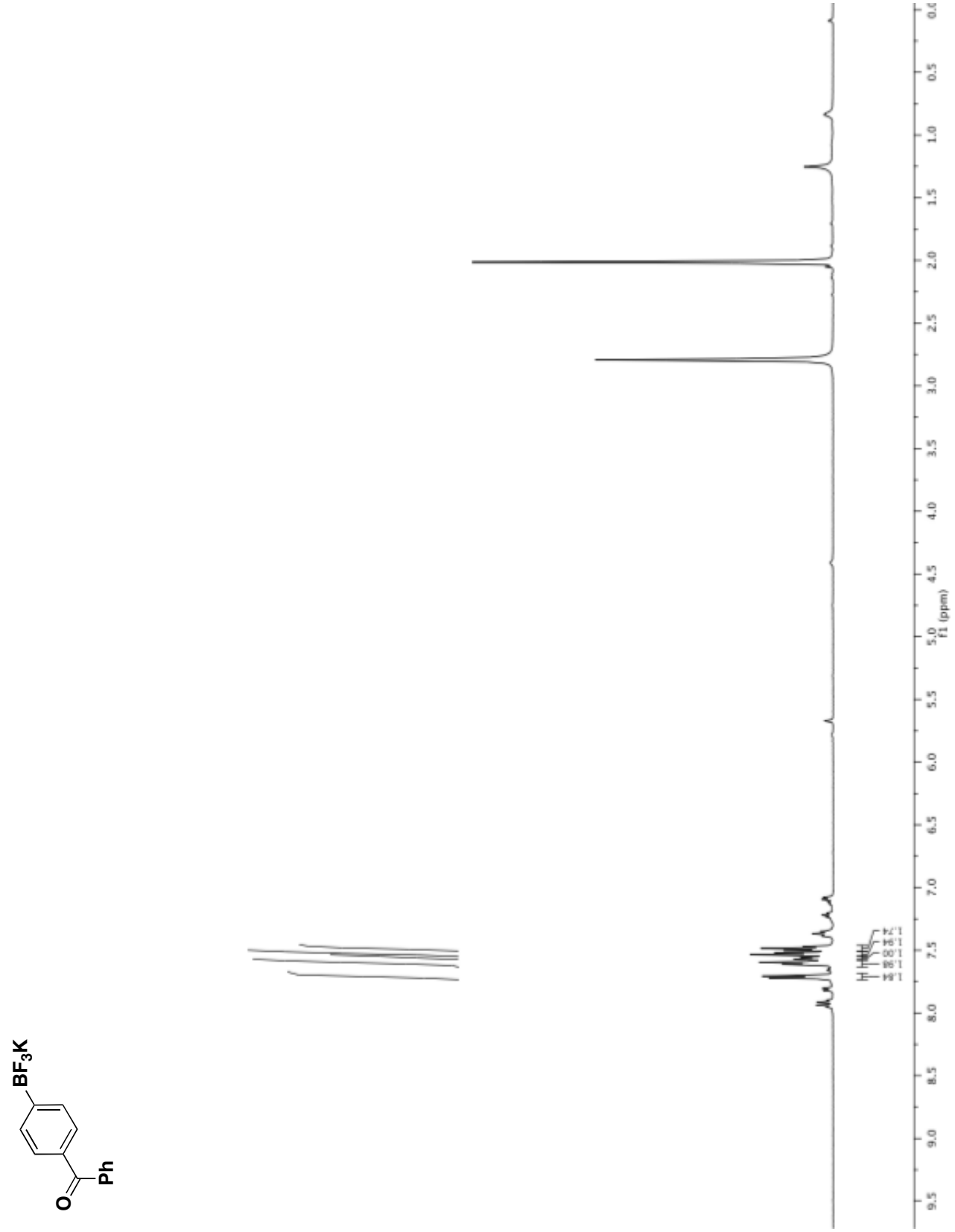

$^{13}$C NMR Spectra (125.8 MHz, $d_6$-DMSO), **Potassium (4-Nitrophenyl)trifluoroborate (Table 2, entry 6)**



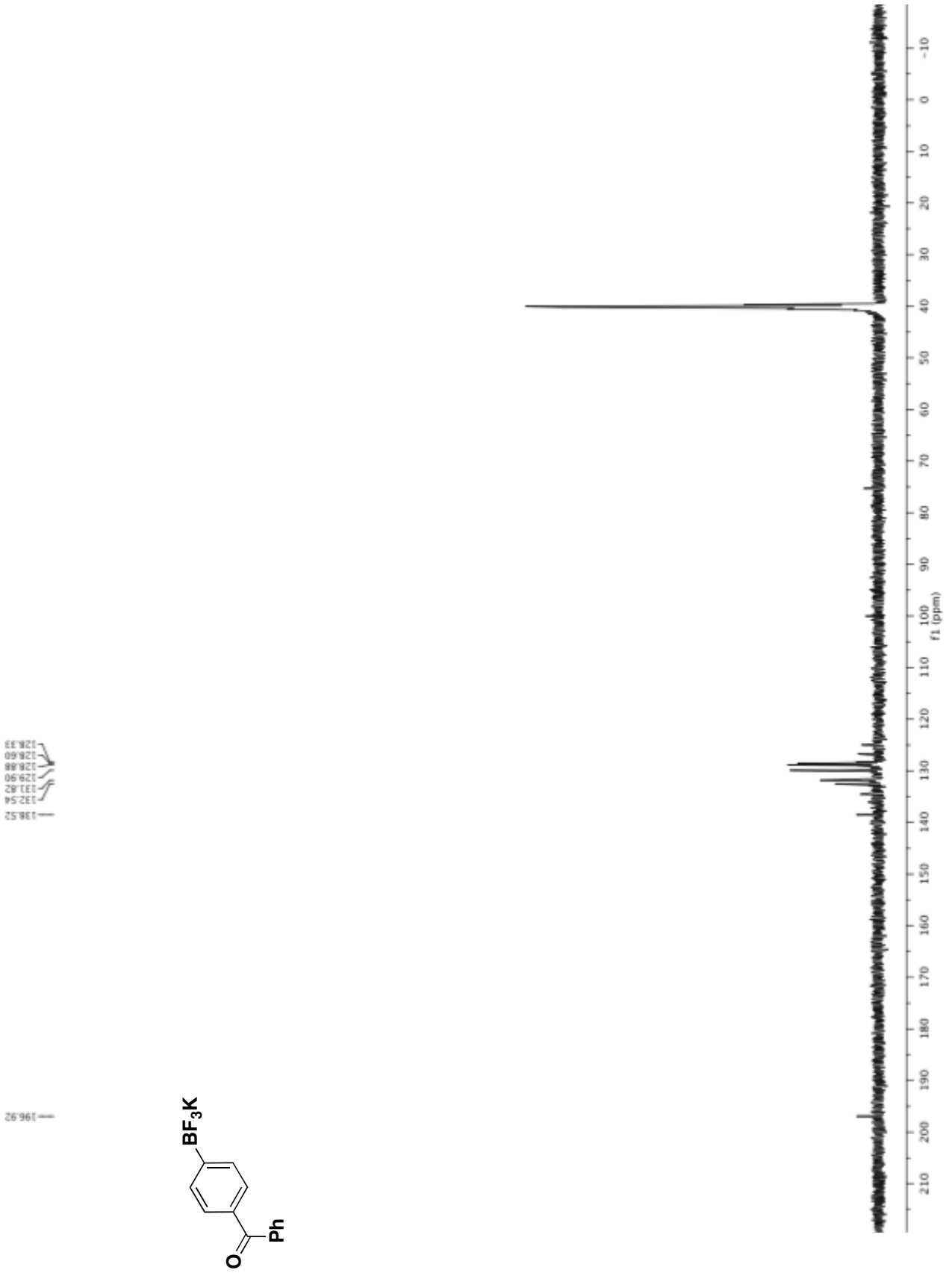

$^{11}$B NMR Spectra (128.4 MHz, $d_6$-DMSO), **Potassium (4-Nitrophenyl)trifluoroborate (Table 2, entry 6)**



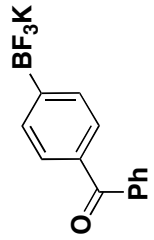

$^{19}$F NMR Spectra (470.8 MHz, $d_6$-DMSO), **Potassium (4-Nitrophenyl)trifluoroborate (Table 2, entry 6)**

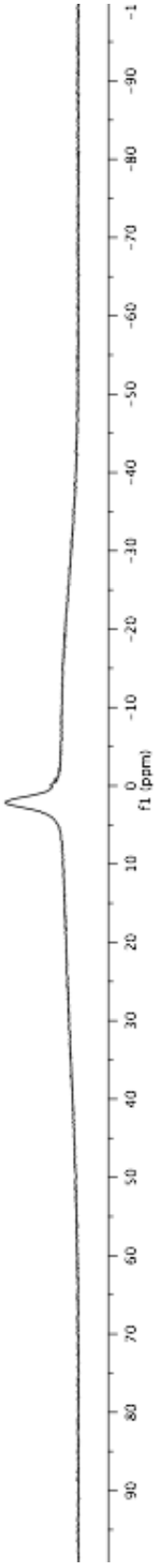



$^{1}$H NMR Spectra (500 MHz, $d_6$-Acetone), **Potassium (4-Benzoylphenyl)trifluoroborate (Table 2, entry 7)**

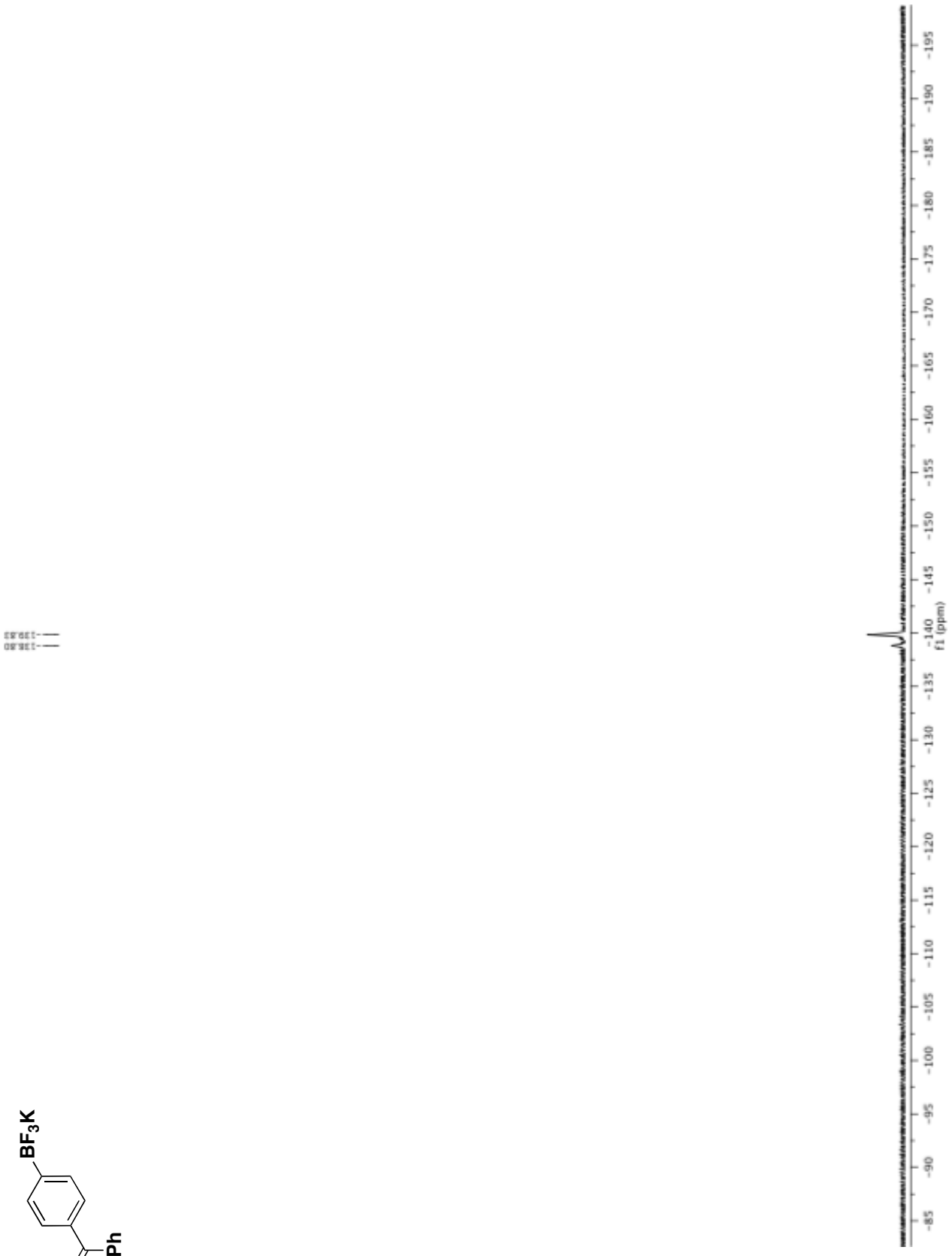



$^{13}$C NMR Spectra (125.8 MHz, $d_6$-DMSO), **Potassium (4-Benzoylphenyl)trifluoroborate (Table 2, entry 7)**



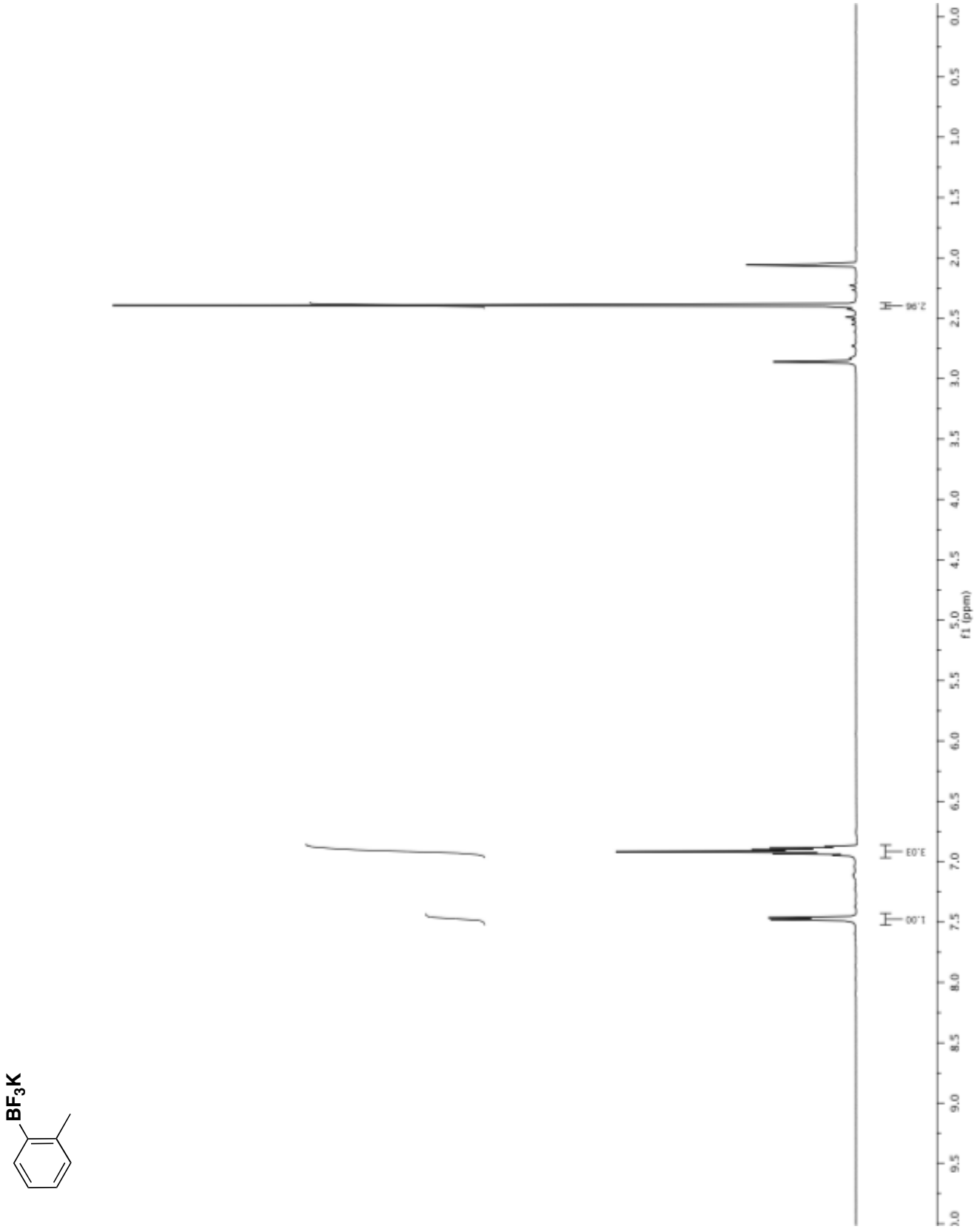

$^{11}$B NMR Spectra (128.4 MHz, $d_6$-DMSO), **Potassium (4-Benzoylphenyl)trifluoroborate (Table 2, entry 7)**



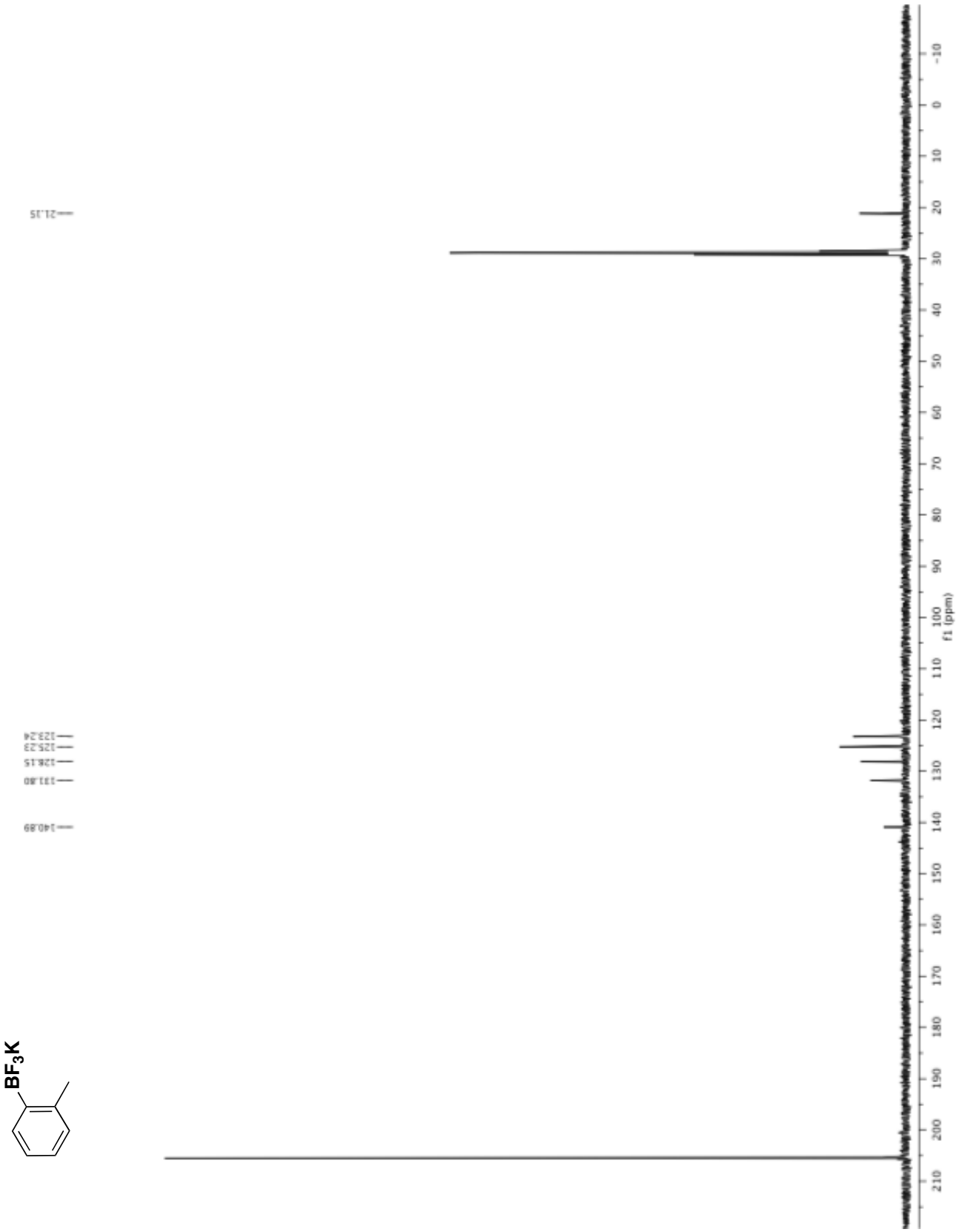




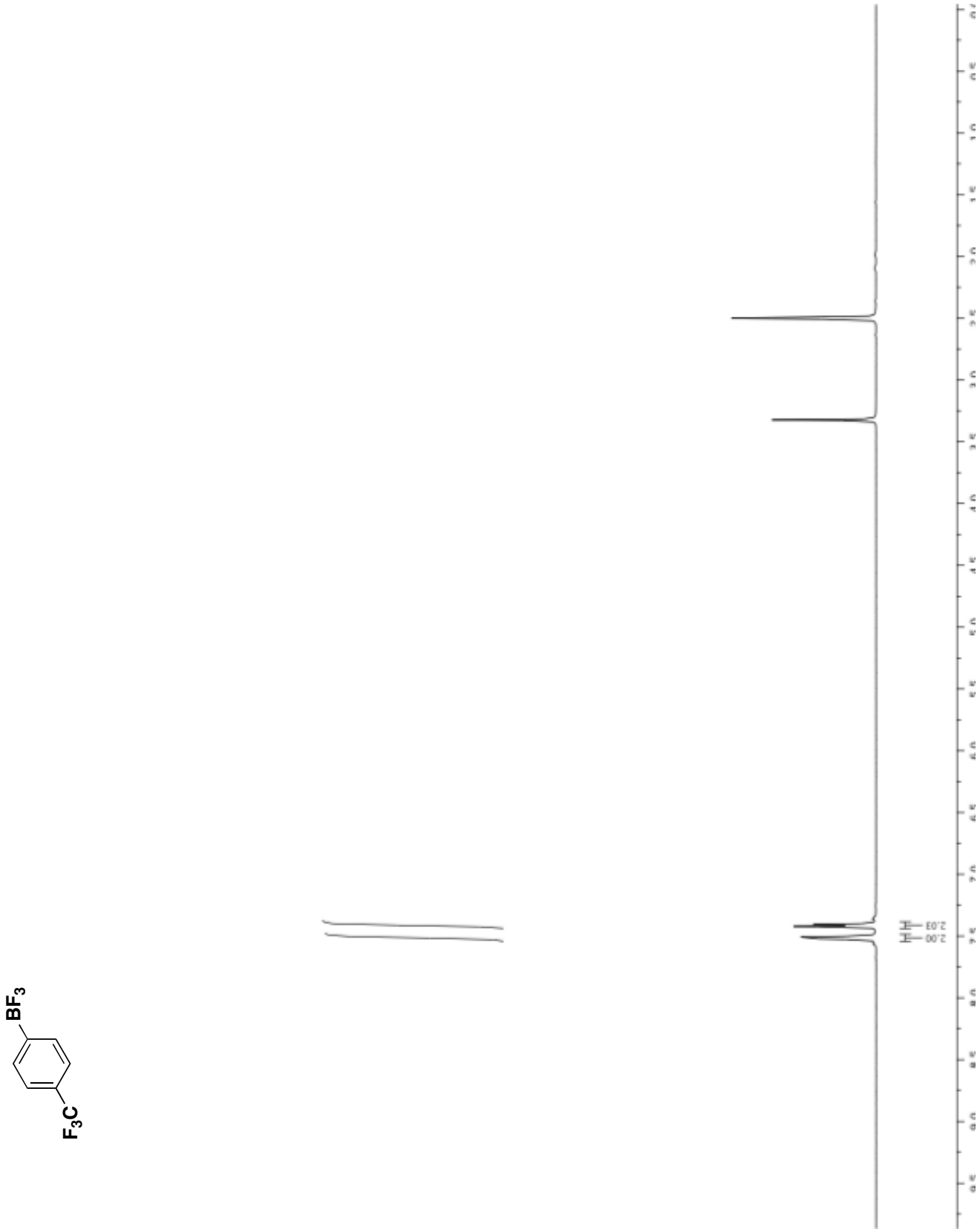
$^{19}F$ NMR Spectra (470.8 MHz, $d_6$-DMSO), **Potassium (4-Benzoylphenyl)trifluoroborate (Table 2, entry 7)**



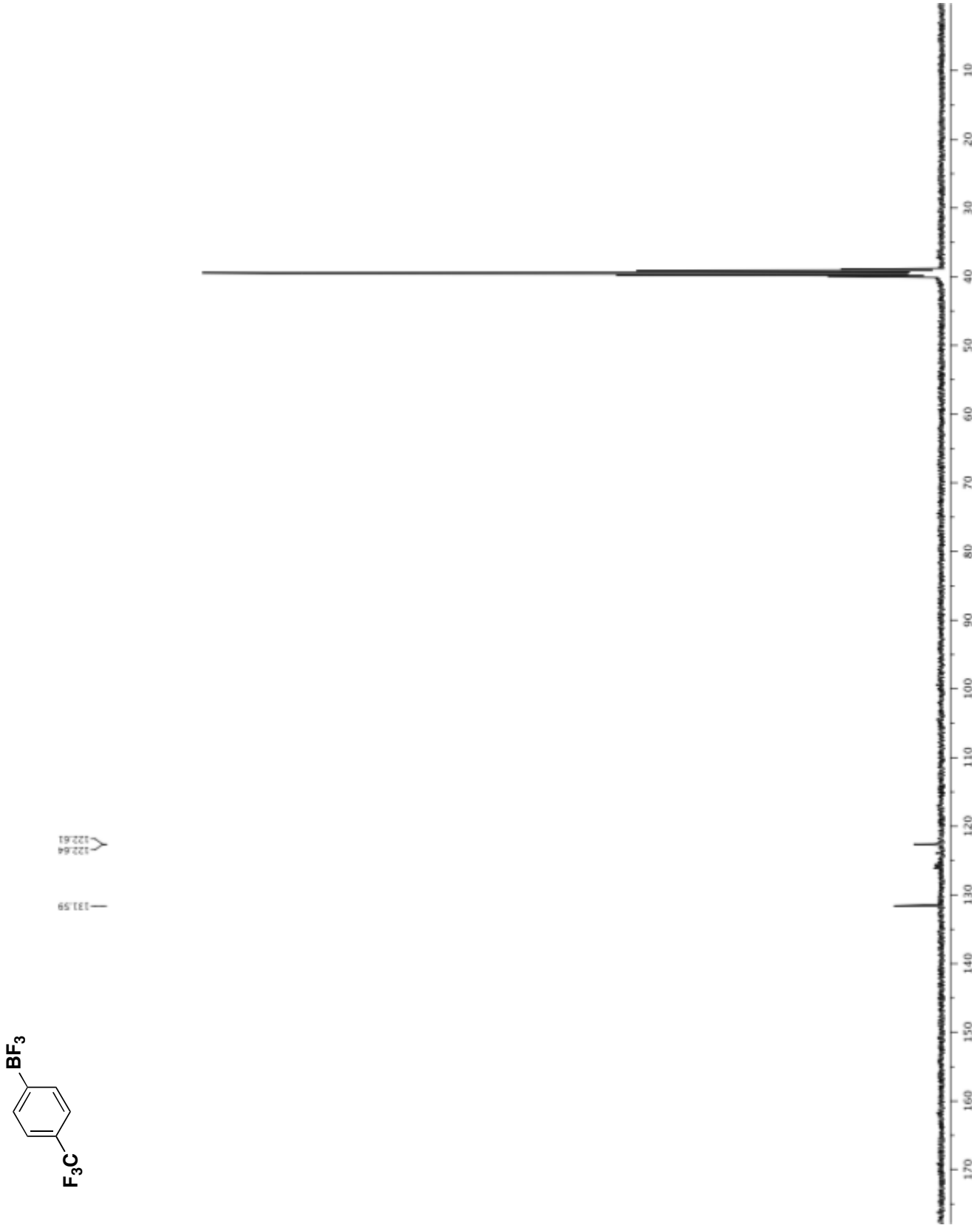

$^{1}$H NMR Spectra (500 MHz, $d_6$-Acetone), **Potassium o-Tolyltrifluoroborate (Table 2, entry 8)**



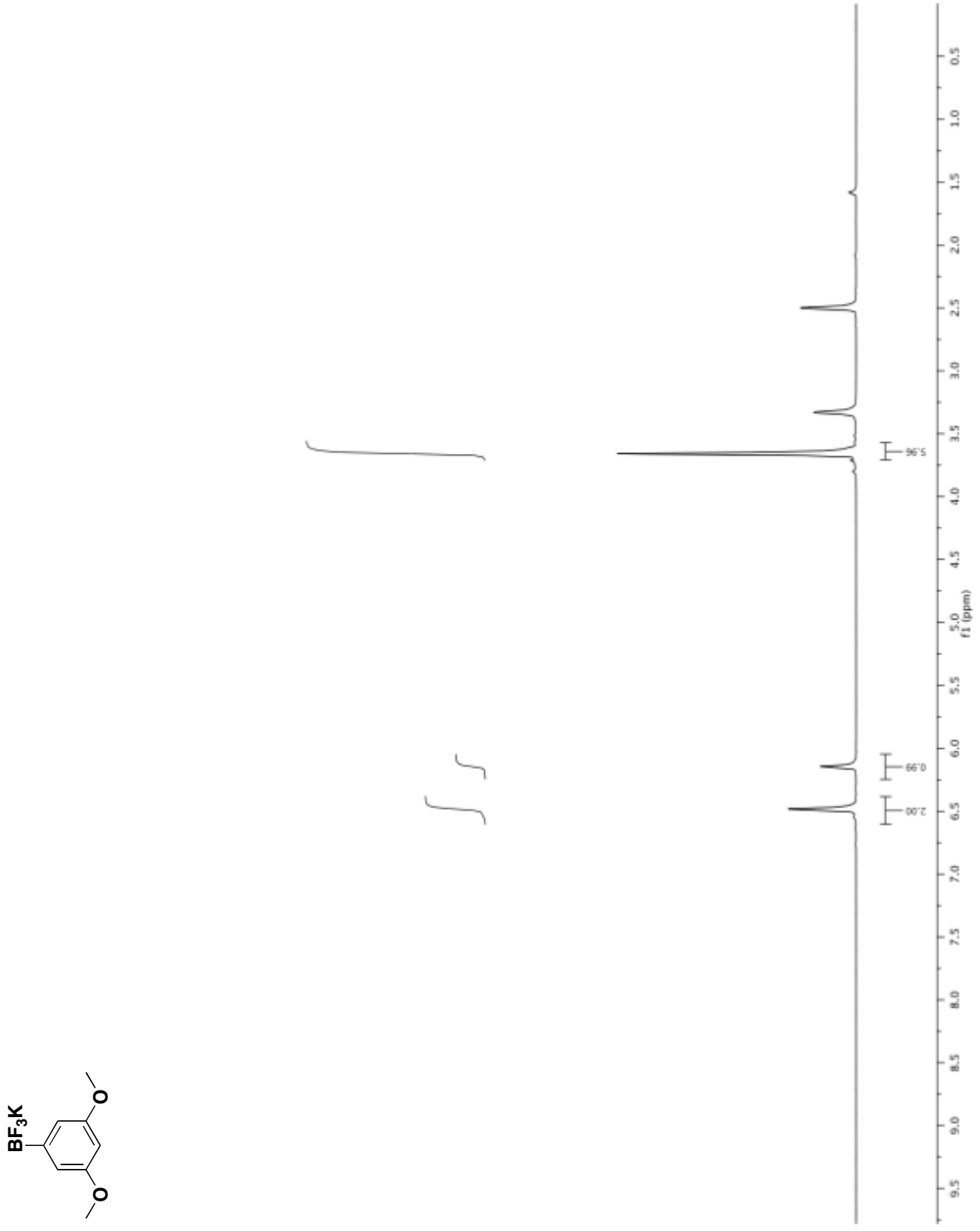

$^{13}$C NMR Spectra (125.8 MHz, $d_6$-Acetone) ,**Potassium o-Tolyltrifluoroborate (Table 2, entry 8)**



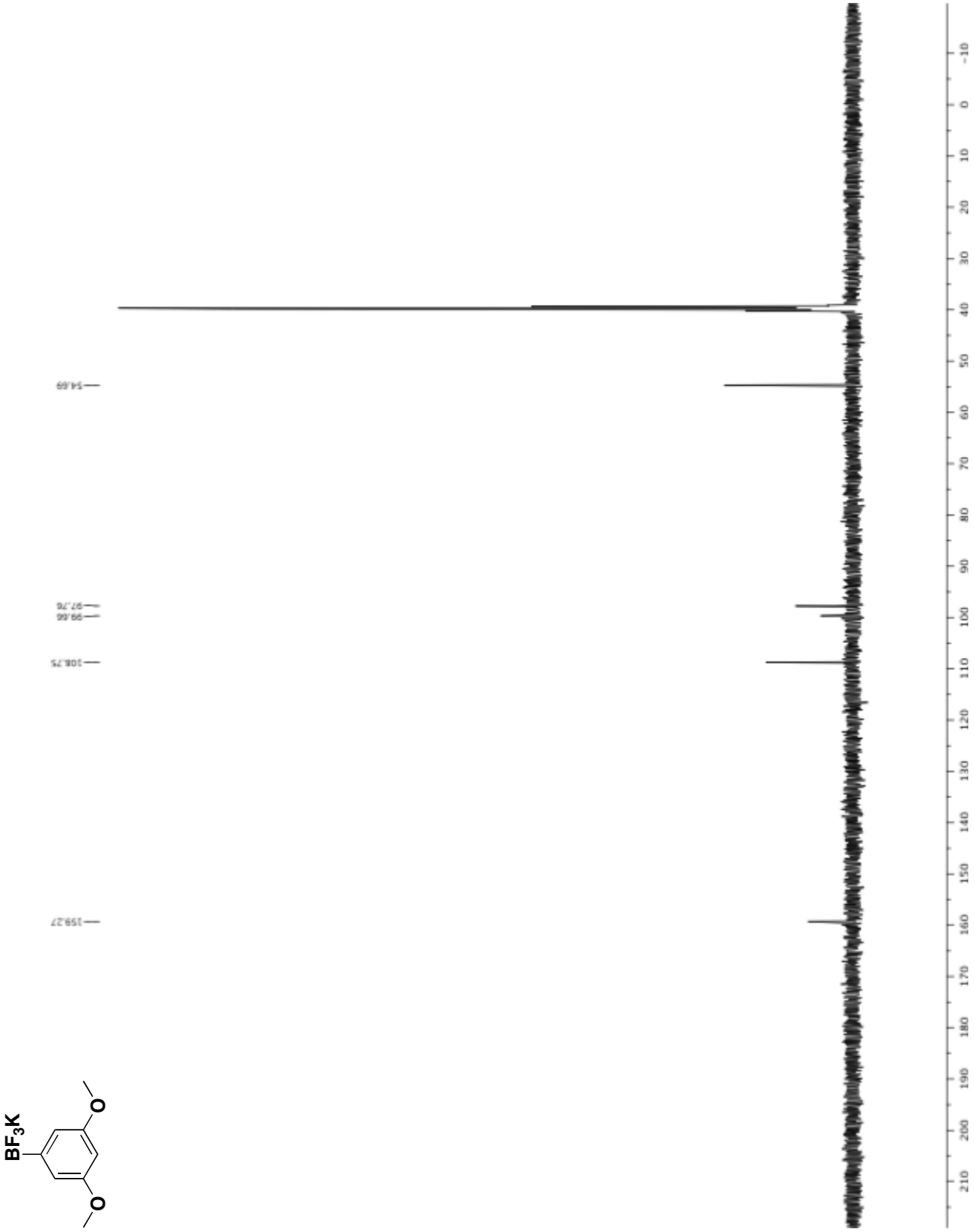

$^{1}$H NMR Spectra (500 MHz, $d_6$-DMSO), **Potassium (4-(Trifluoromethyl)phenyl)trifluoroborate (Table 2, entry 9)**



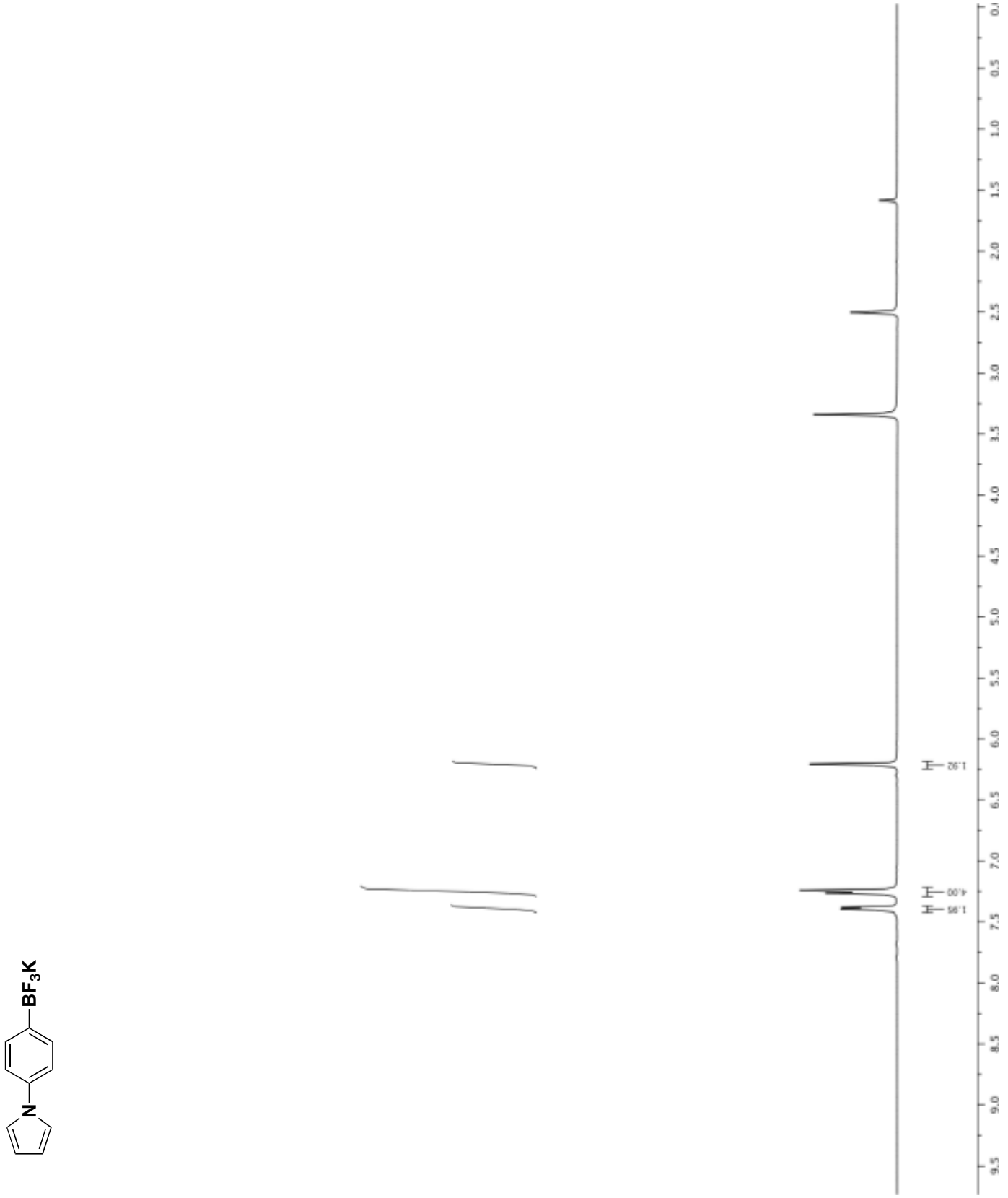

$^{13}C$ NMR Spectra (125.8 MHz, $d_6$-DMSO), **Potassium (4-(trifluoromethyl)phenyl)trifluoroborate (Table 2, entry 9)**



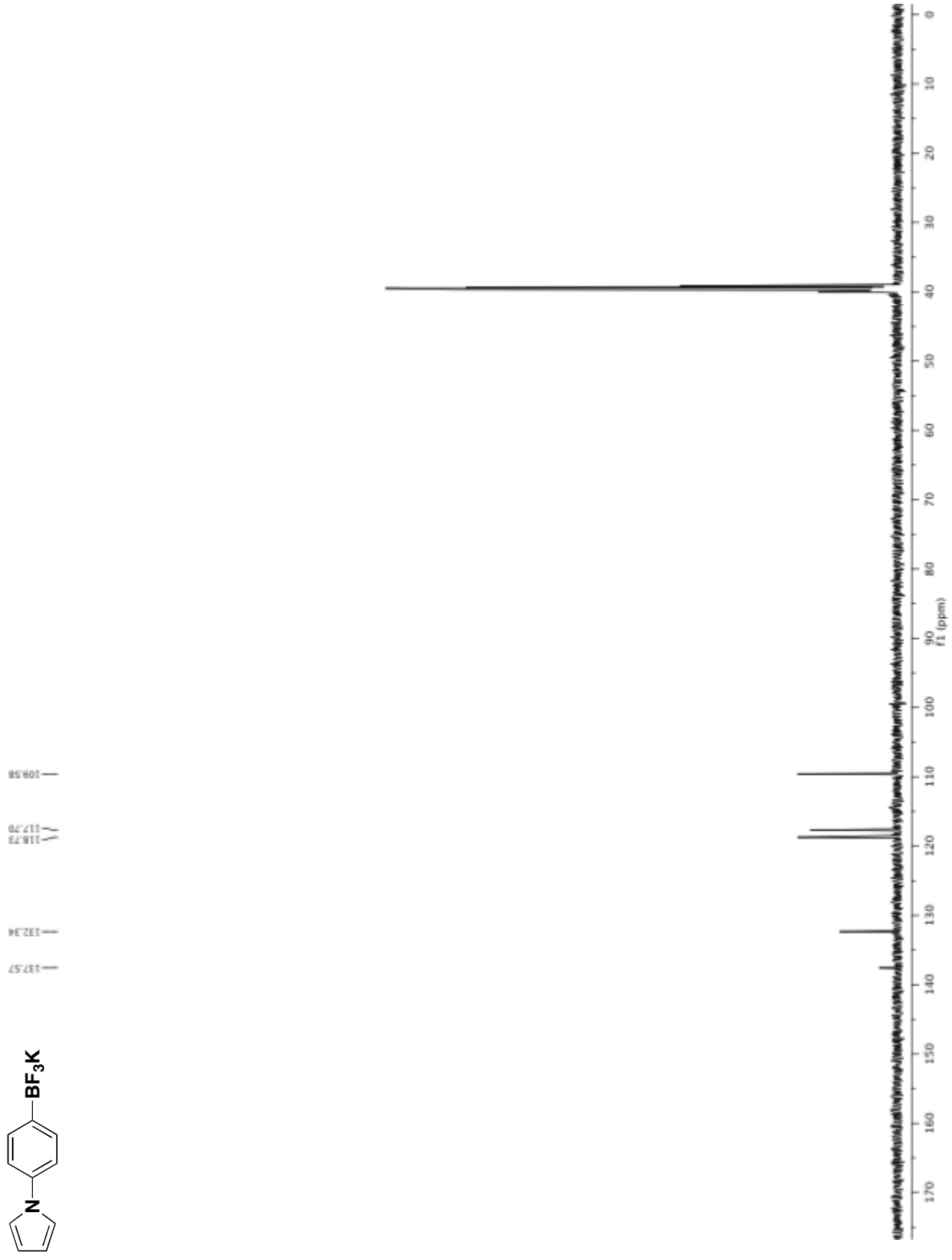

$^1$H NMR Spectra (500 MHz, $d_6$-DMSO), **Potassium (3,5-Dimethoxyphenyltrifluoroborate (Table 2, entry 10)**



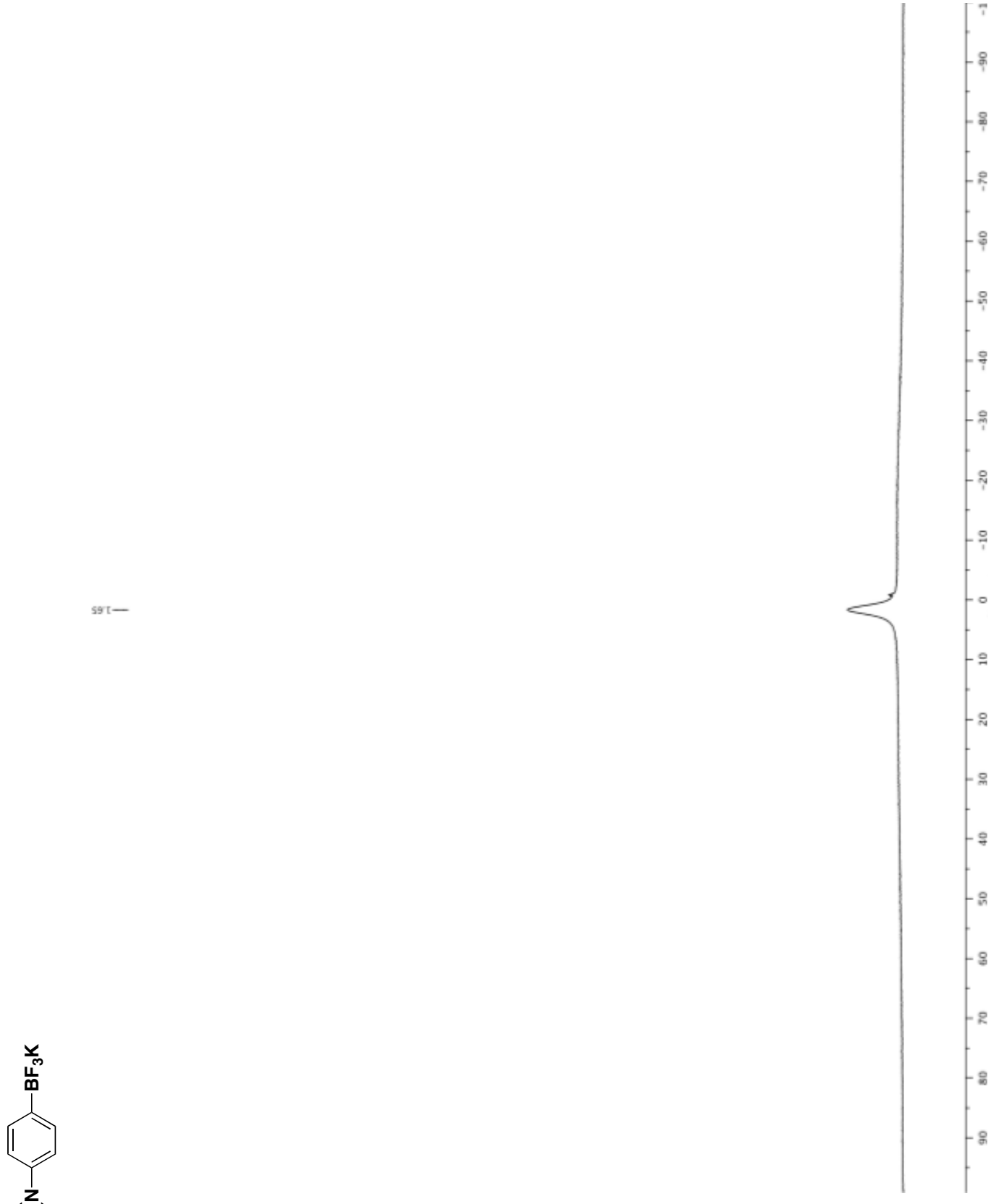

$^{13}C$ NMR Spectra (125.8 MHz, $d_6$-DMSO), **Potassium (3,5-Dimethoxyphenyltrifluoroborate (Table 2, entry 10)**




$^1$H NMR Spectra (500 MHz, $d_6$-DMSO**), Potassium (4-(1H-Pyrrol-1-yl)phenyltrifluoroborate (Table 2, entry 11)**

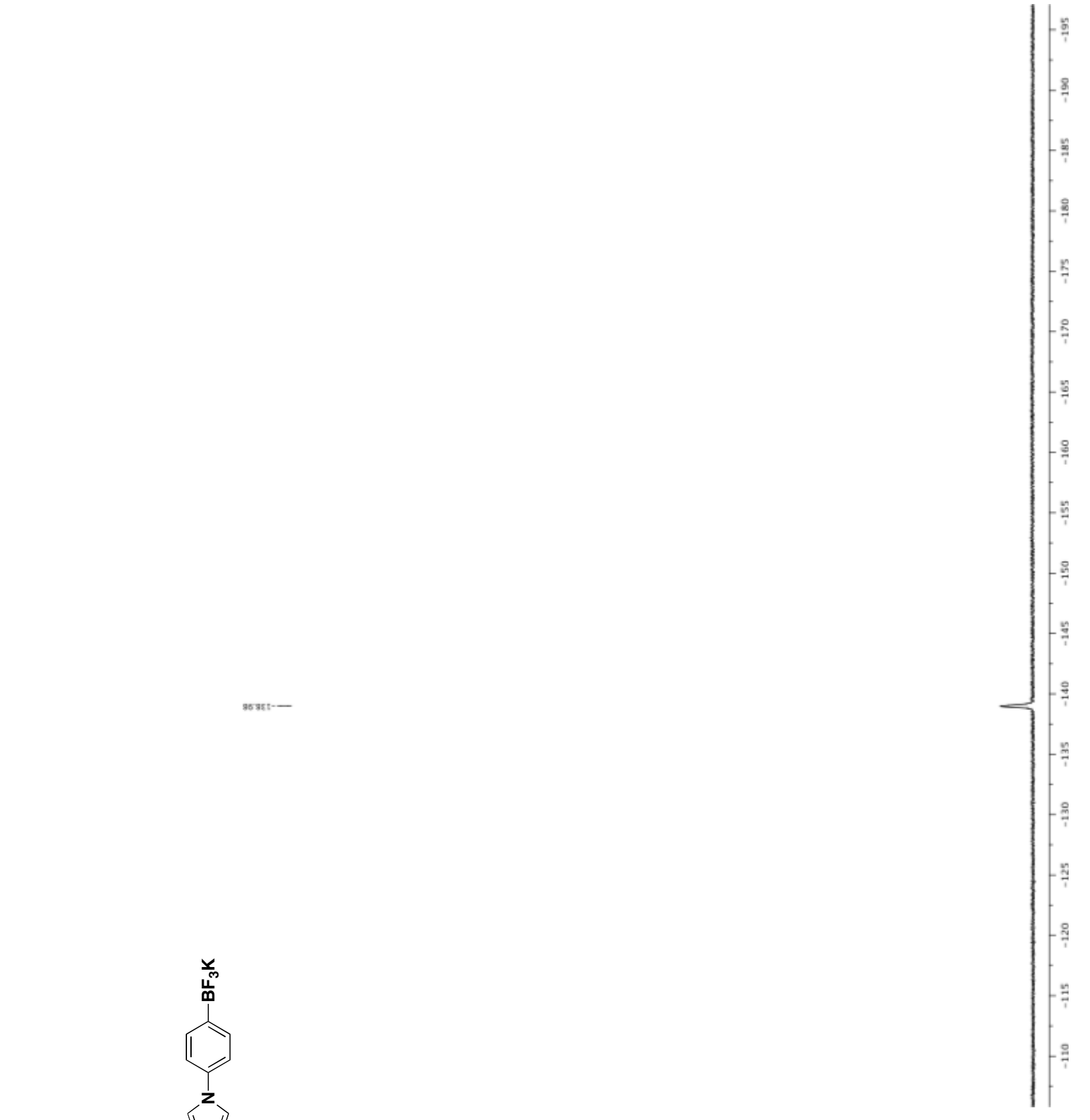



$^{13}$C NMR Spectra (125.8 MHz, $d_6$-DMSO**), Potassium (4-(1H-Pyrrol-1-yl)phenyltrifluoroborate (Table 2, entry 11)**





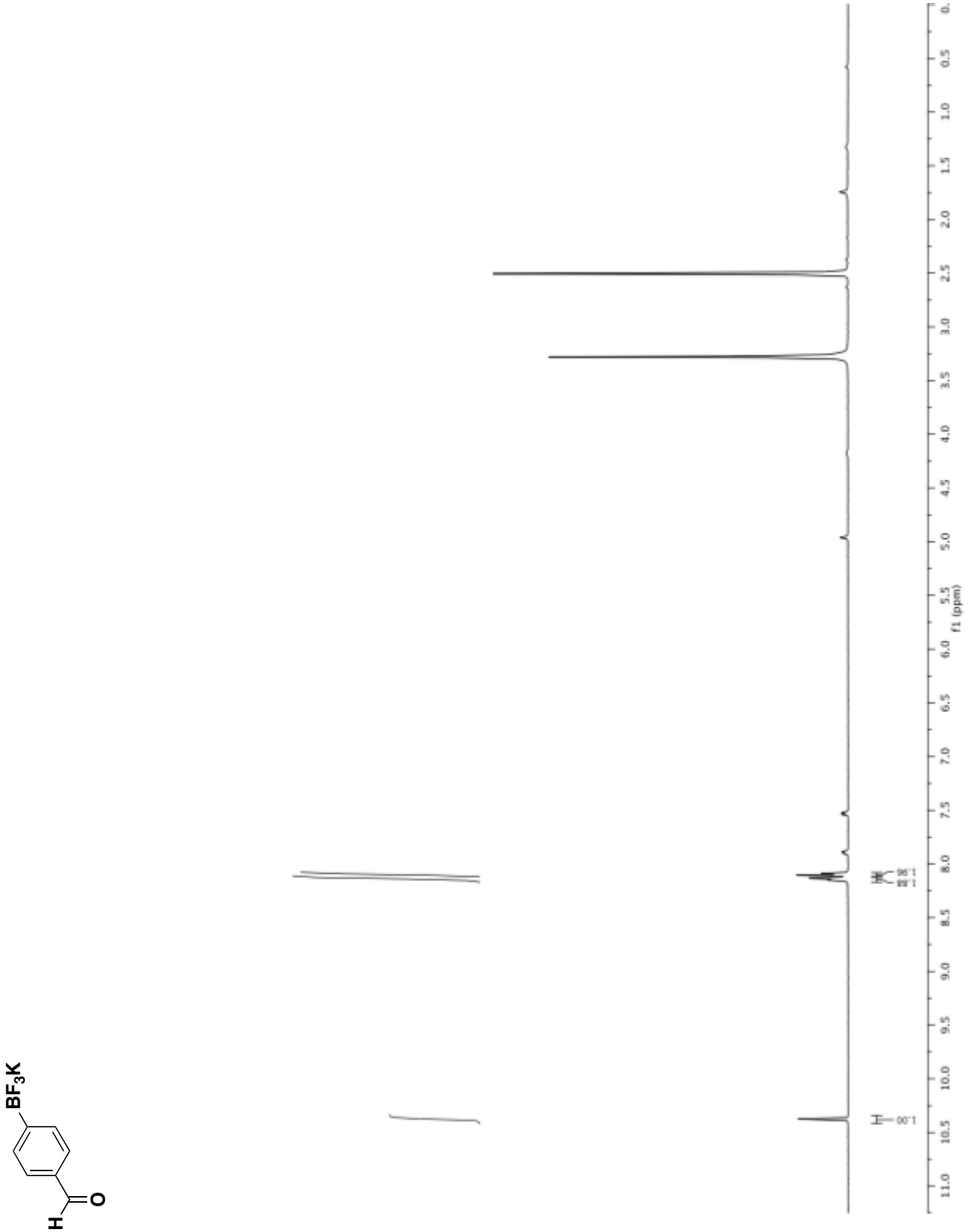

$^{11}$B NMR Spectra (128.4 MHz, $d_6$-DMSO**), Potassium (4-(1H-Pyrrol-1-yl)phenyltrifluoroborate (Table 2, entry 11)**



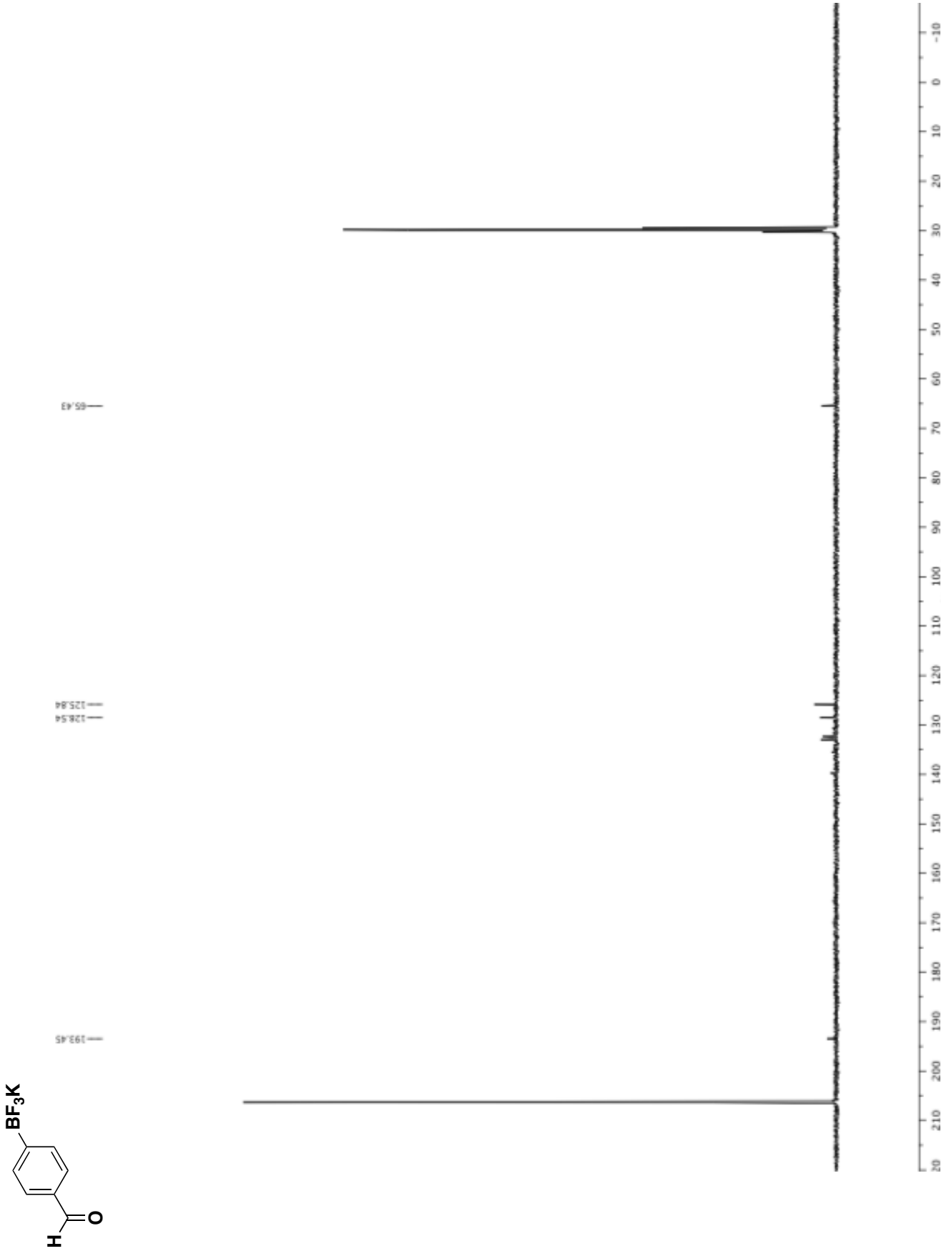




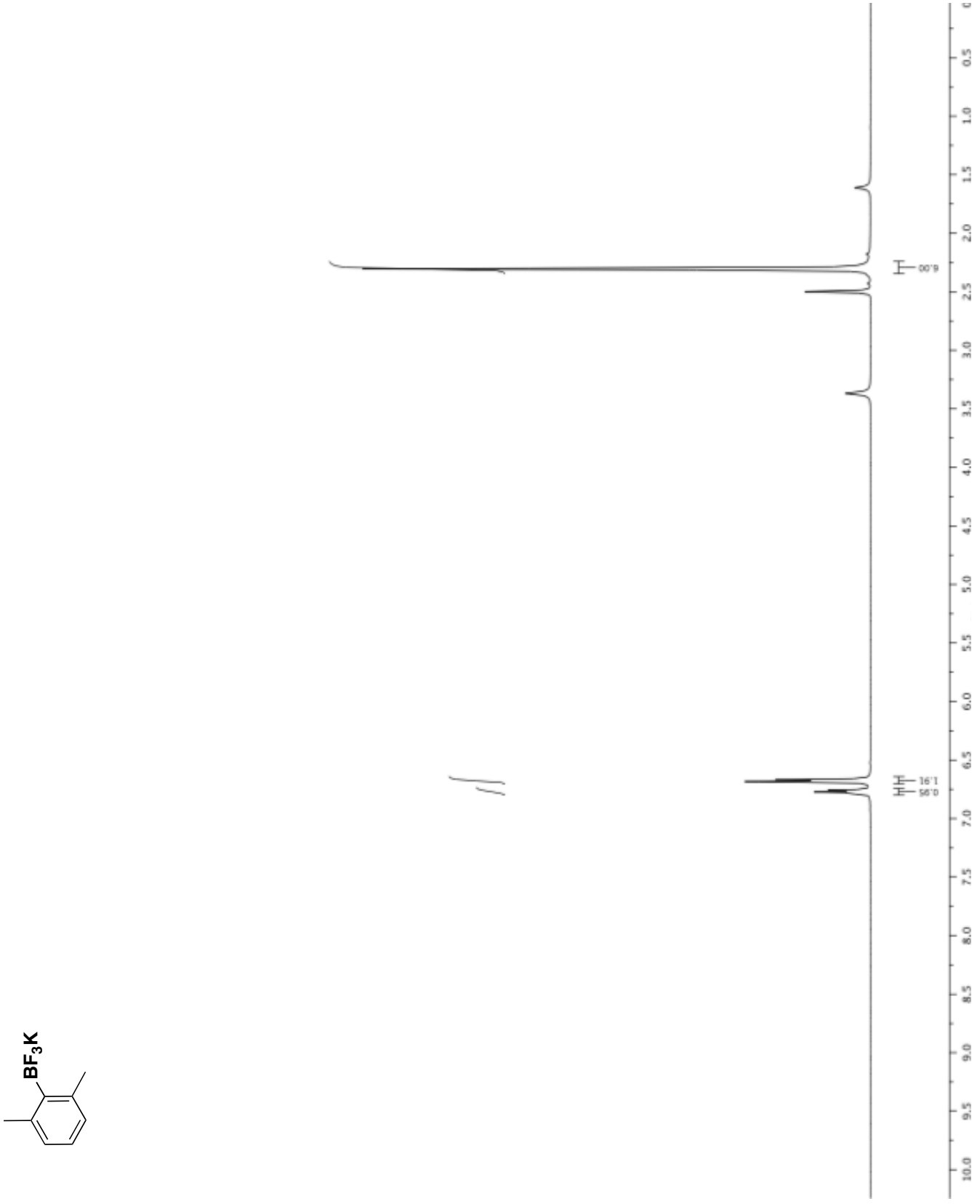
$^{19}$F NMR Spectra (470.8 MHz, $d_6$-DMSO**), Potassium (4-(1H-Pyrrol-1-yl)phenyltrifluoroborate (Table 2, entry 11)**



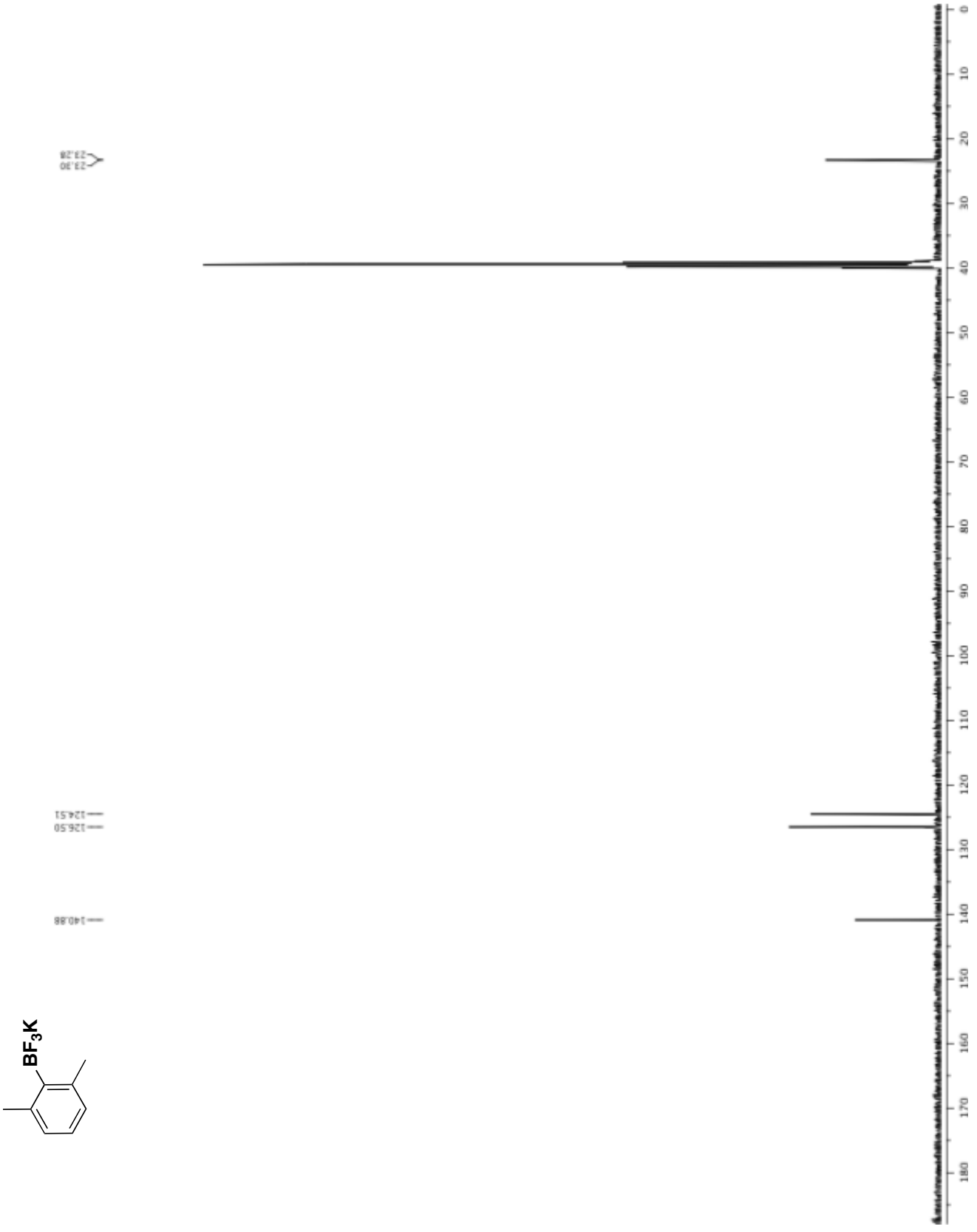

$^1$H NMR Spectra (500 MHz, $d_6$-DMSO**), Potassium (4-Formylphenyl)trifluoroborate (Table 2, entry 12)**



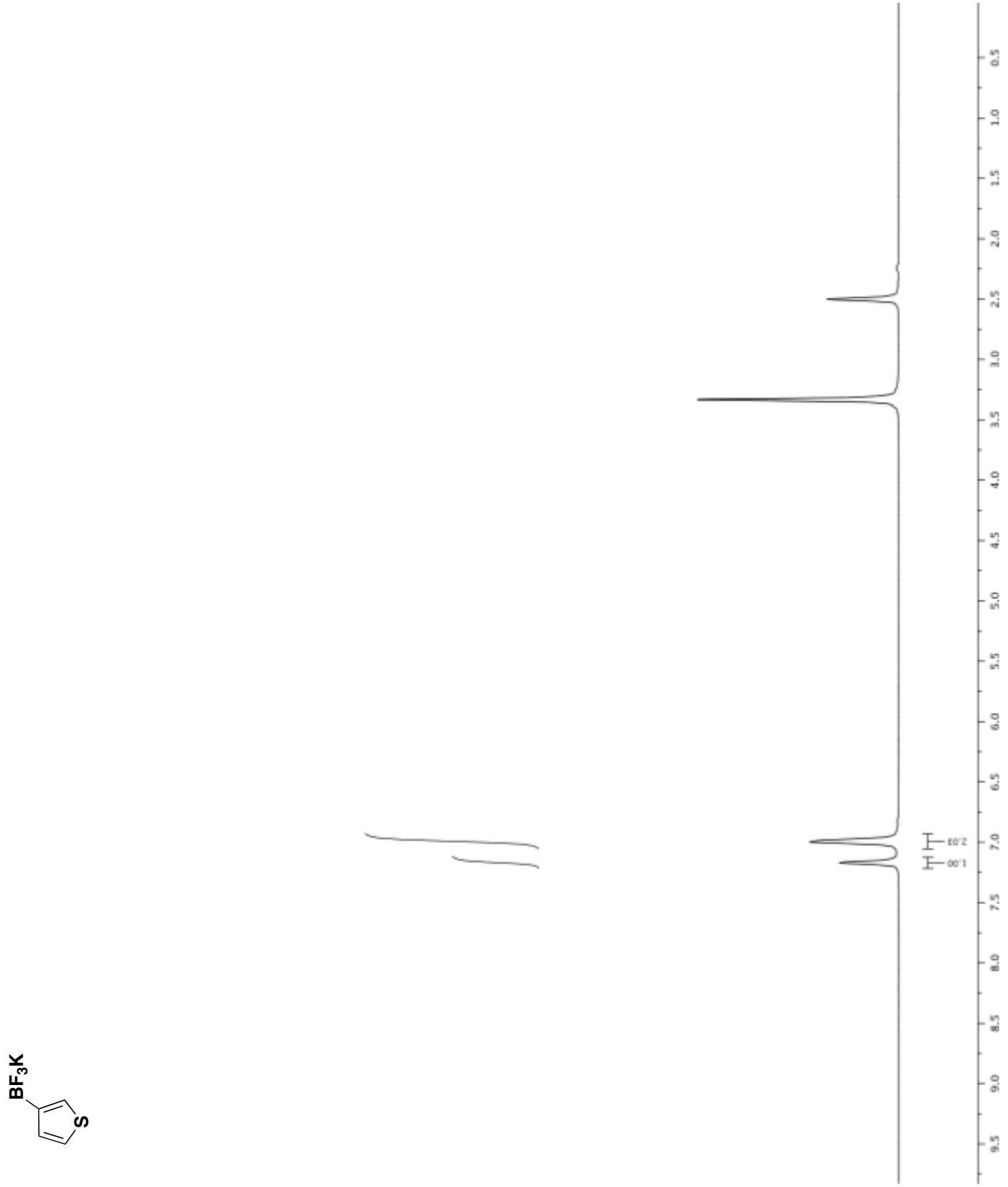

$^{13}$C NMR Spectra (500 MHz, $d_6$-Acetone**), Potassium (4-Formylphenyl)trifluoroborate (Table 2, entry 12)**



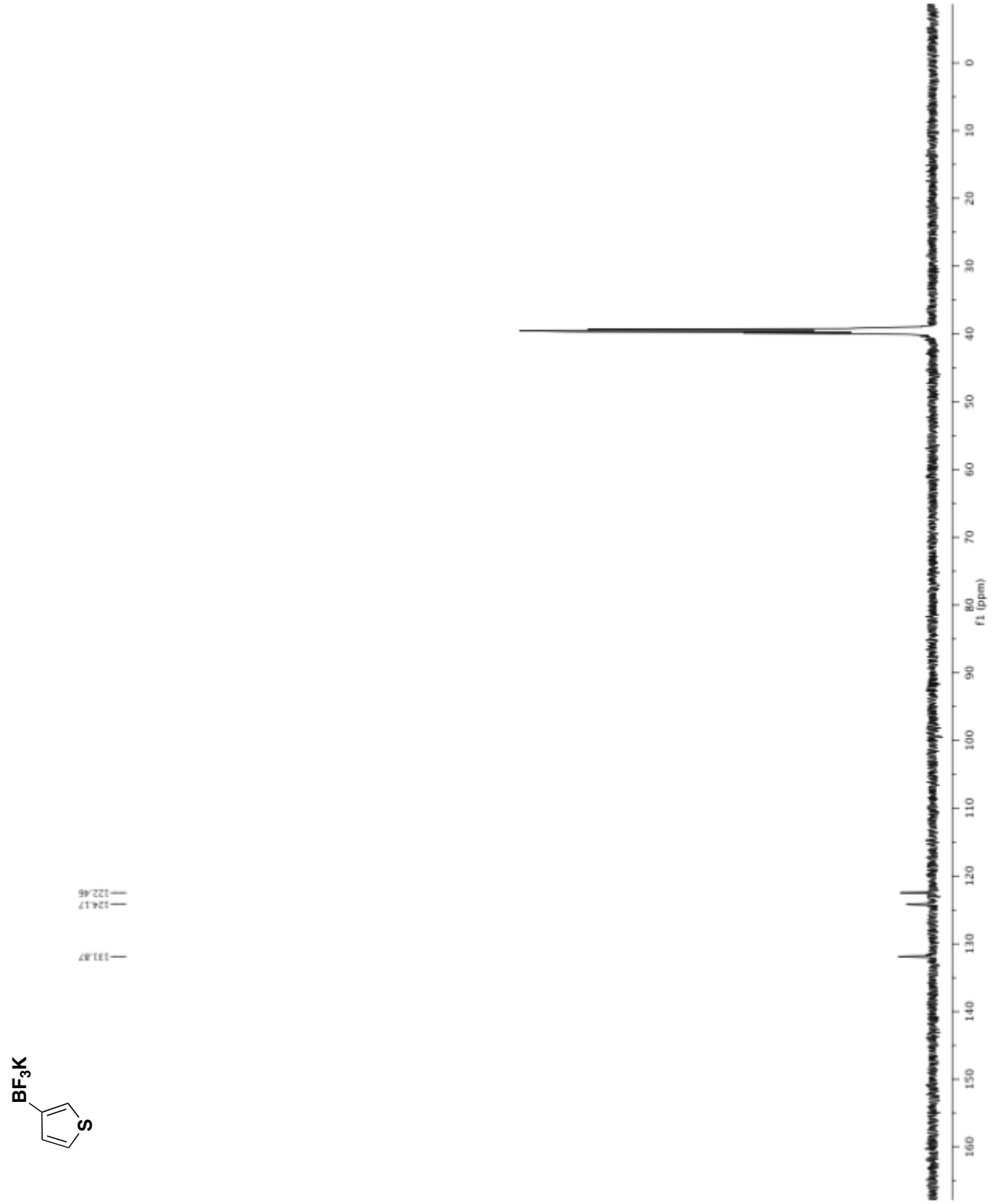

$^1$H NMR Spectra (500 MHz, $d_6$-DMSO**), Potassium (2,6-Dimethylphenyl)trifluoroborate (Table 2, entry 13)**



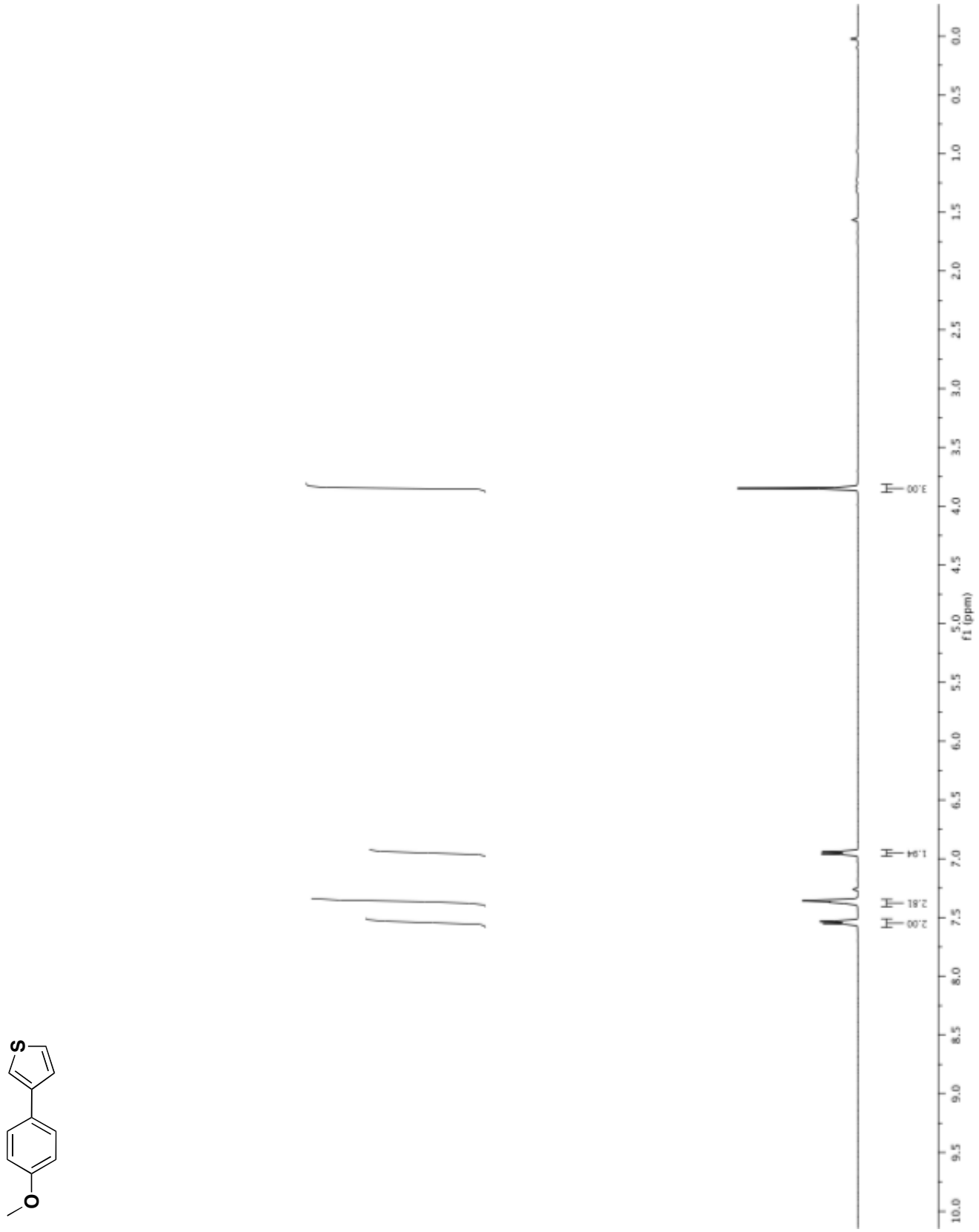

$^{13}C$ NMR Spectra (125.8 MHz, $d_6$-DMSO**), Potassium (2,6-Dimethylphenyl)trifluoroborate (Table 2, entry 13)**



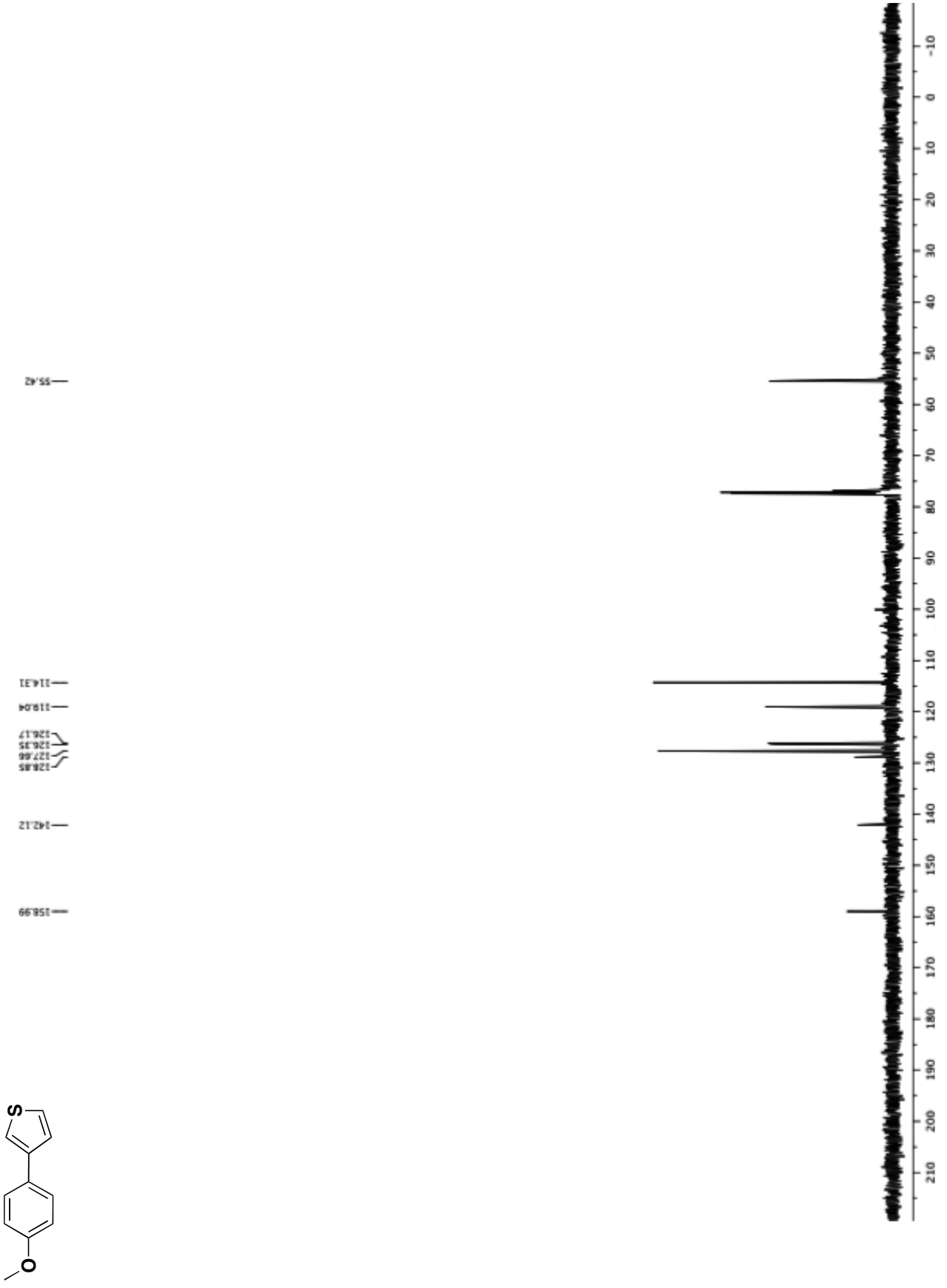

$^{1}$H NMR Spectra (500 MHz, $d_6$-DMSO**), Potassium Thiophen-3-yltrifluoroborate (Table 2, entry 14)**



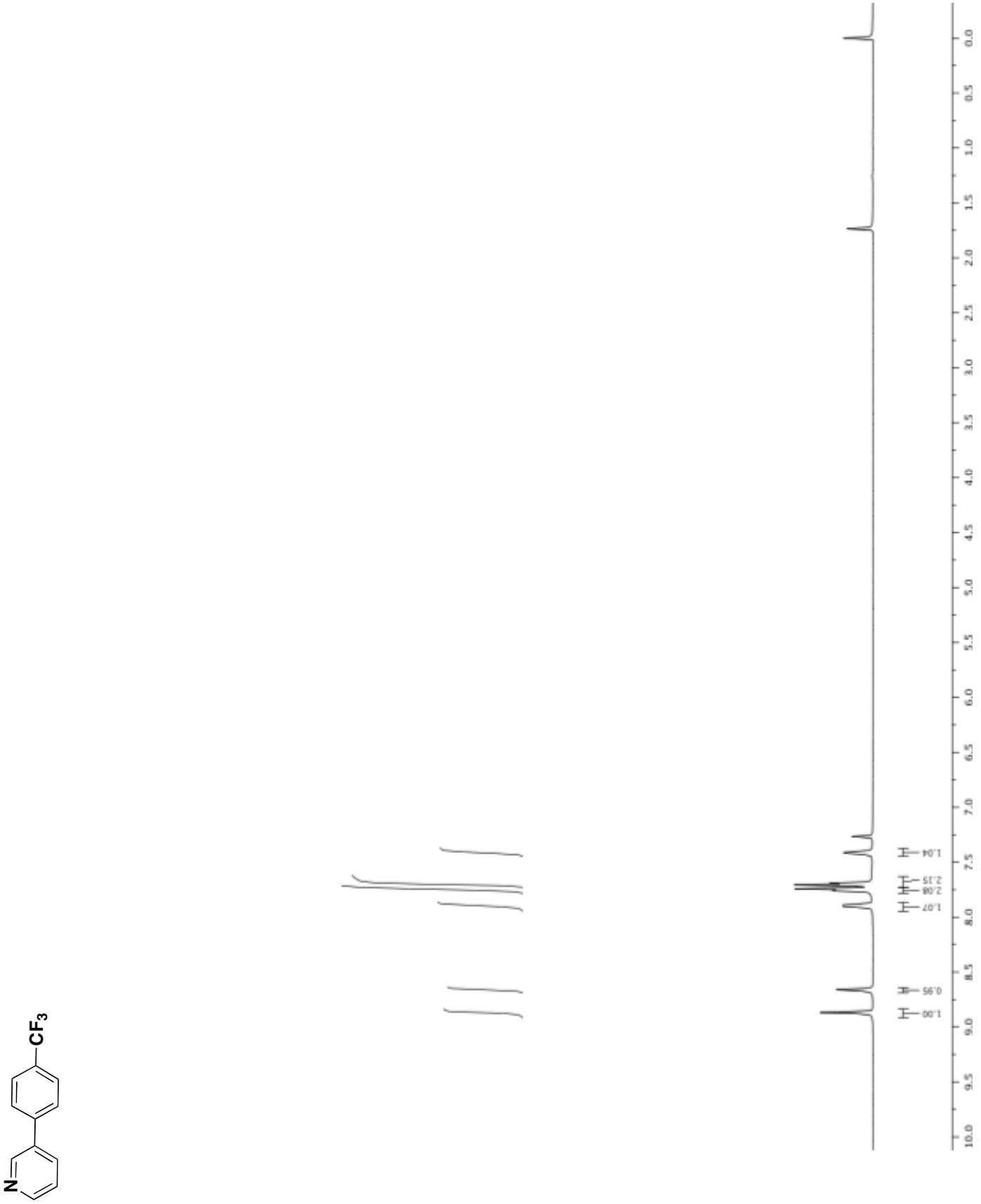

$^{13}$C NMR Spectra (125.8 MHz, $d_6$-DMSO**), Potassium Thiophen-3-yltrifluoroborate (Table 2, entry 14)**



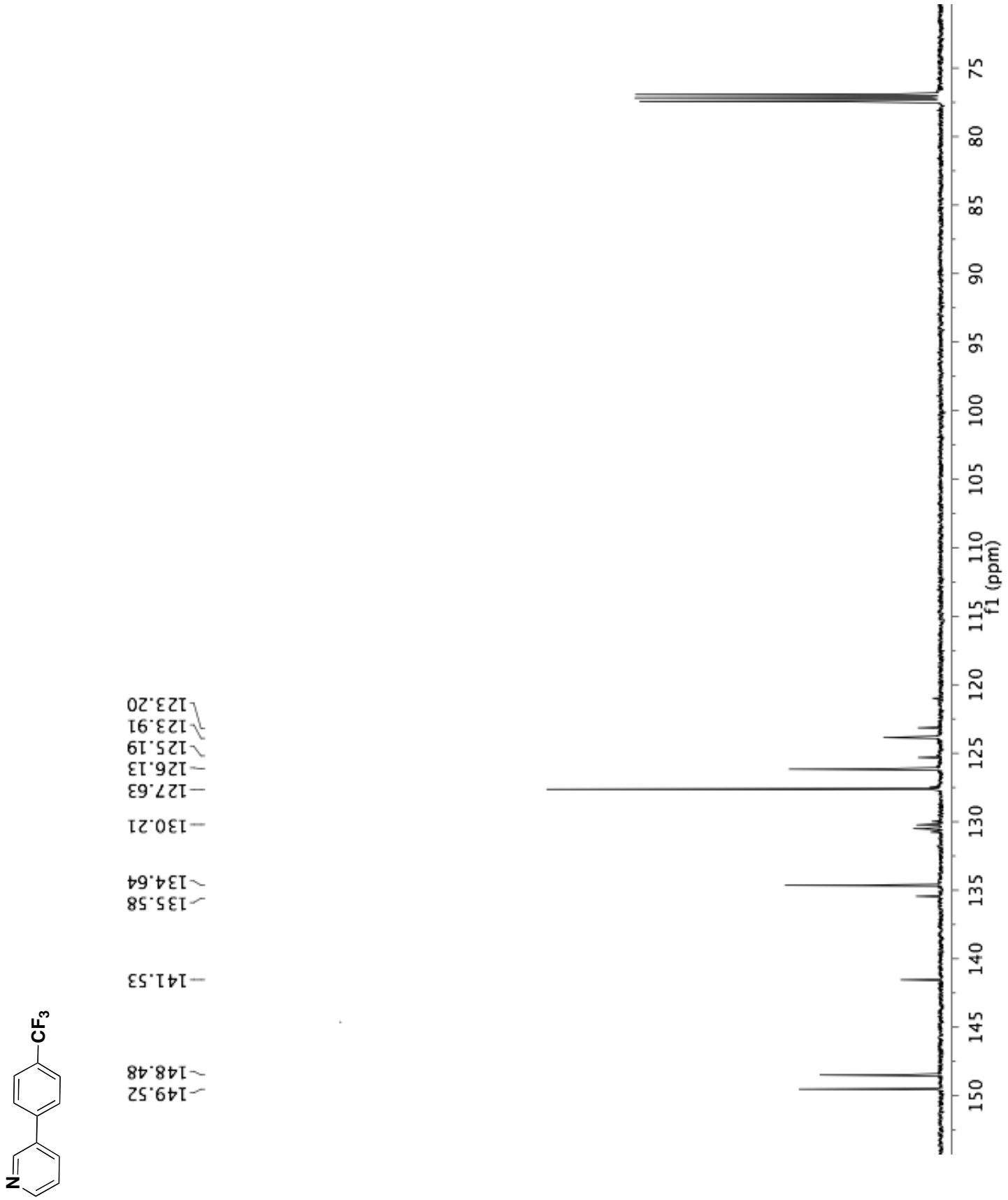

$^1$H NMR Spectra (500 MHz, $CDCl_3$)**, 3-(4-Methoxyphenyl)thiophene (Table 3 entry 1)**



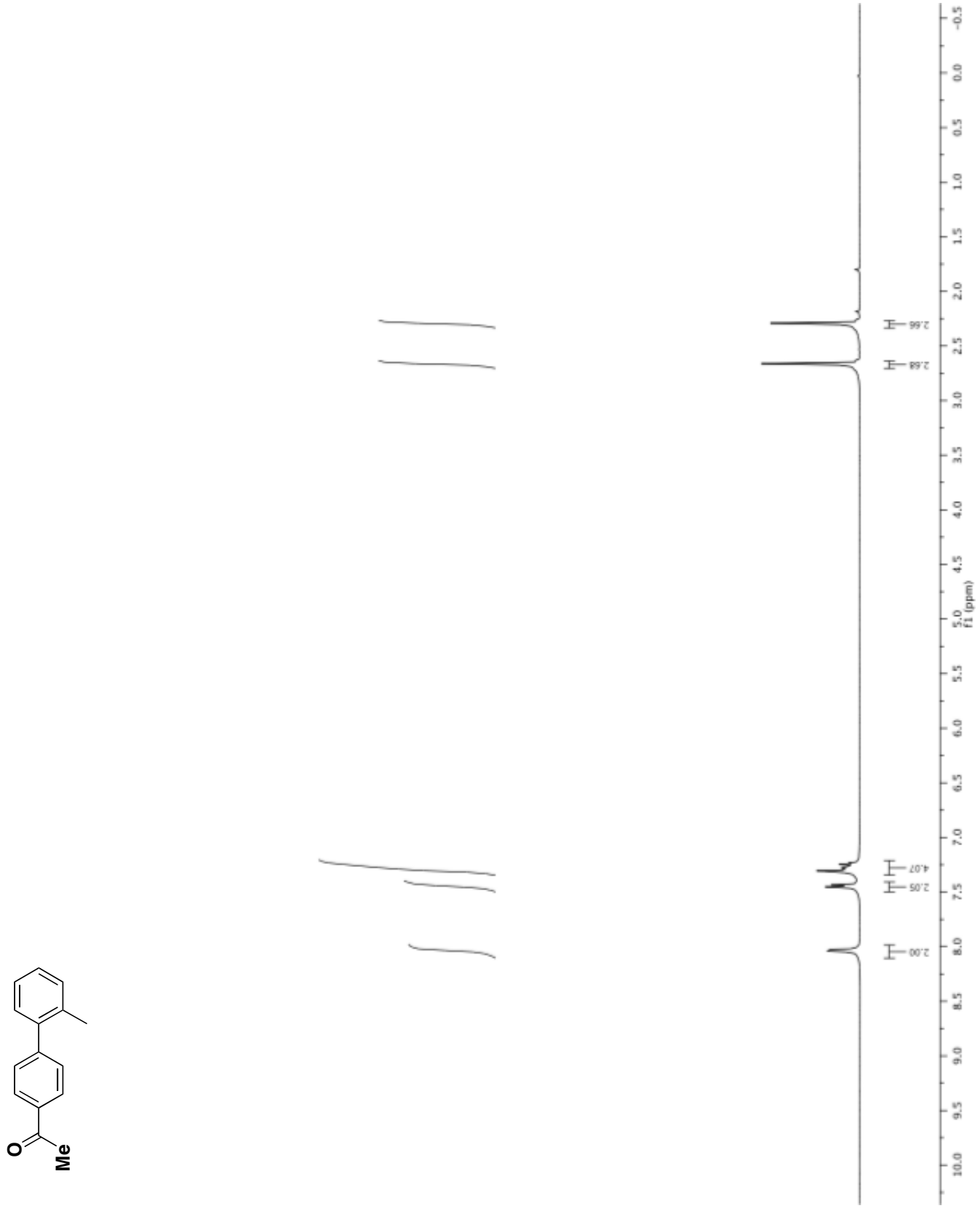

$^{13}$C NMR Spectra (125.8 MHz, $CDCl_3$)**, 3-(4-Methoxyphenyl)thiophene (Table 3 entry 1)**



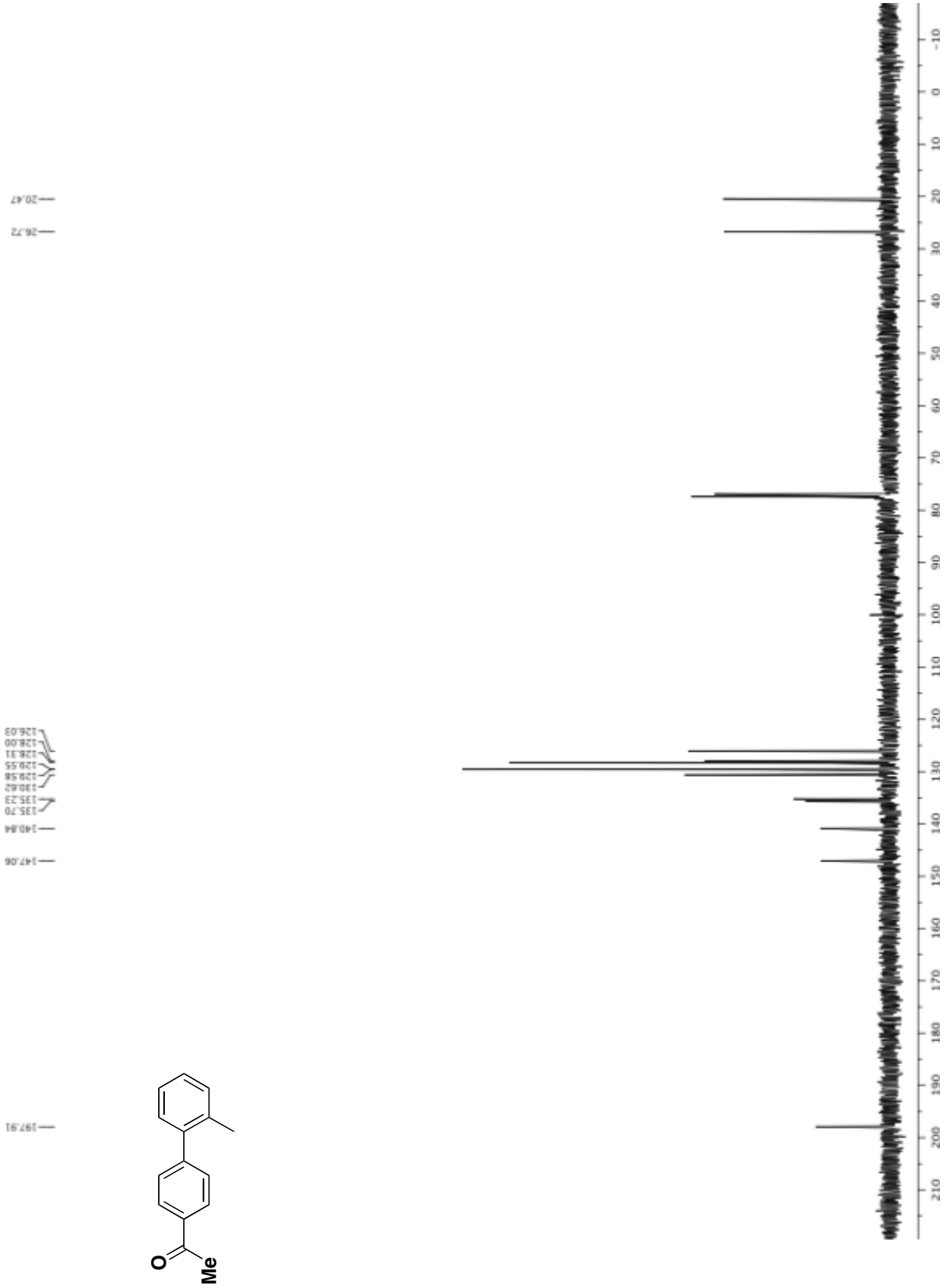

$^{1}$H NMR Spectra (500 MHz, $CDCl_3$)**, 3-(4-(Trifluoromethyl)phenyl)pyridine (Table 3 entry 2)**



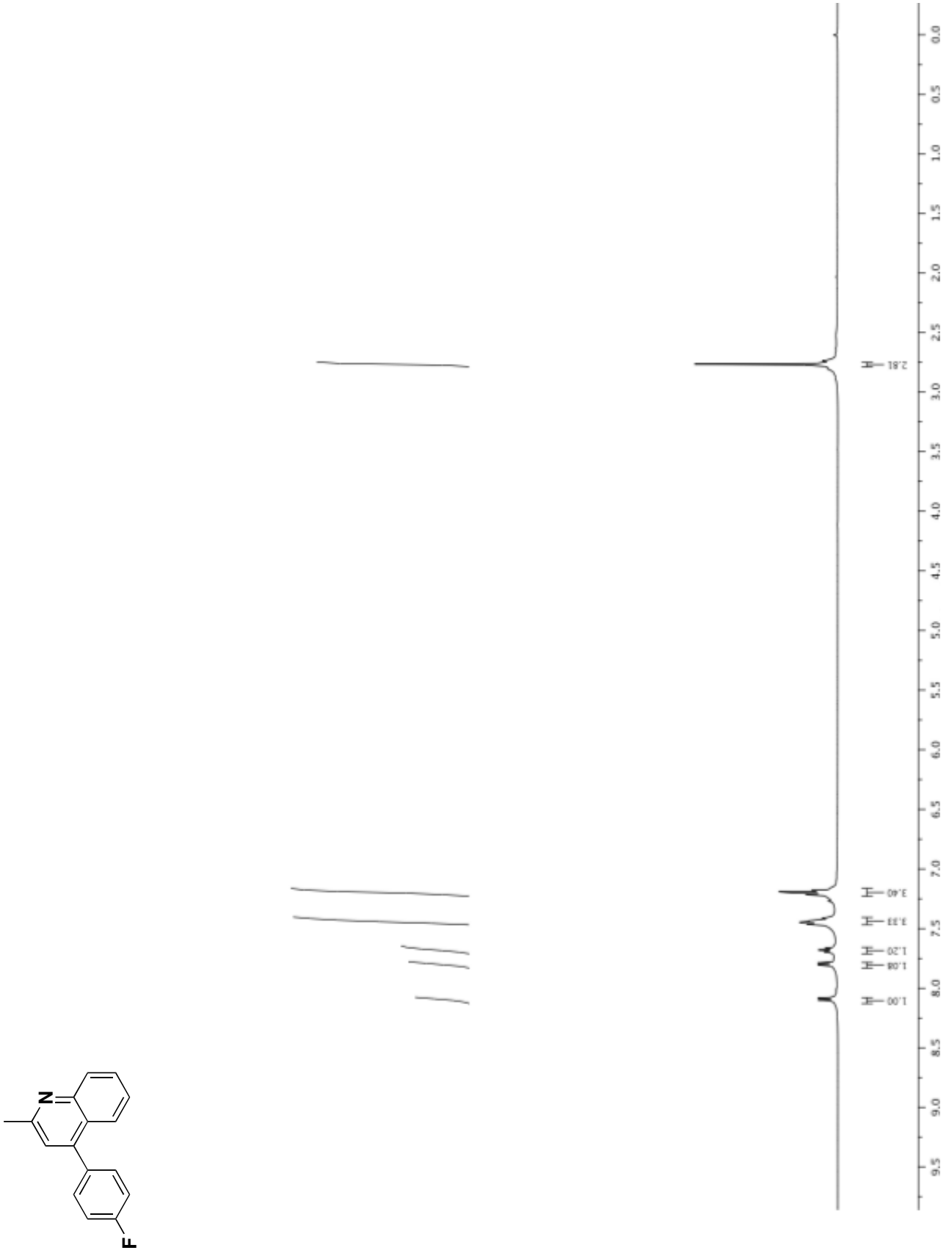

$^{13}$C NMR Spectra (125.8 MHz, $CDCl_3$)**, 3-(4-(Trifluoromethyl)phenyl)pyridine (Table 3 entry 2)**



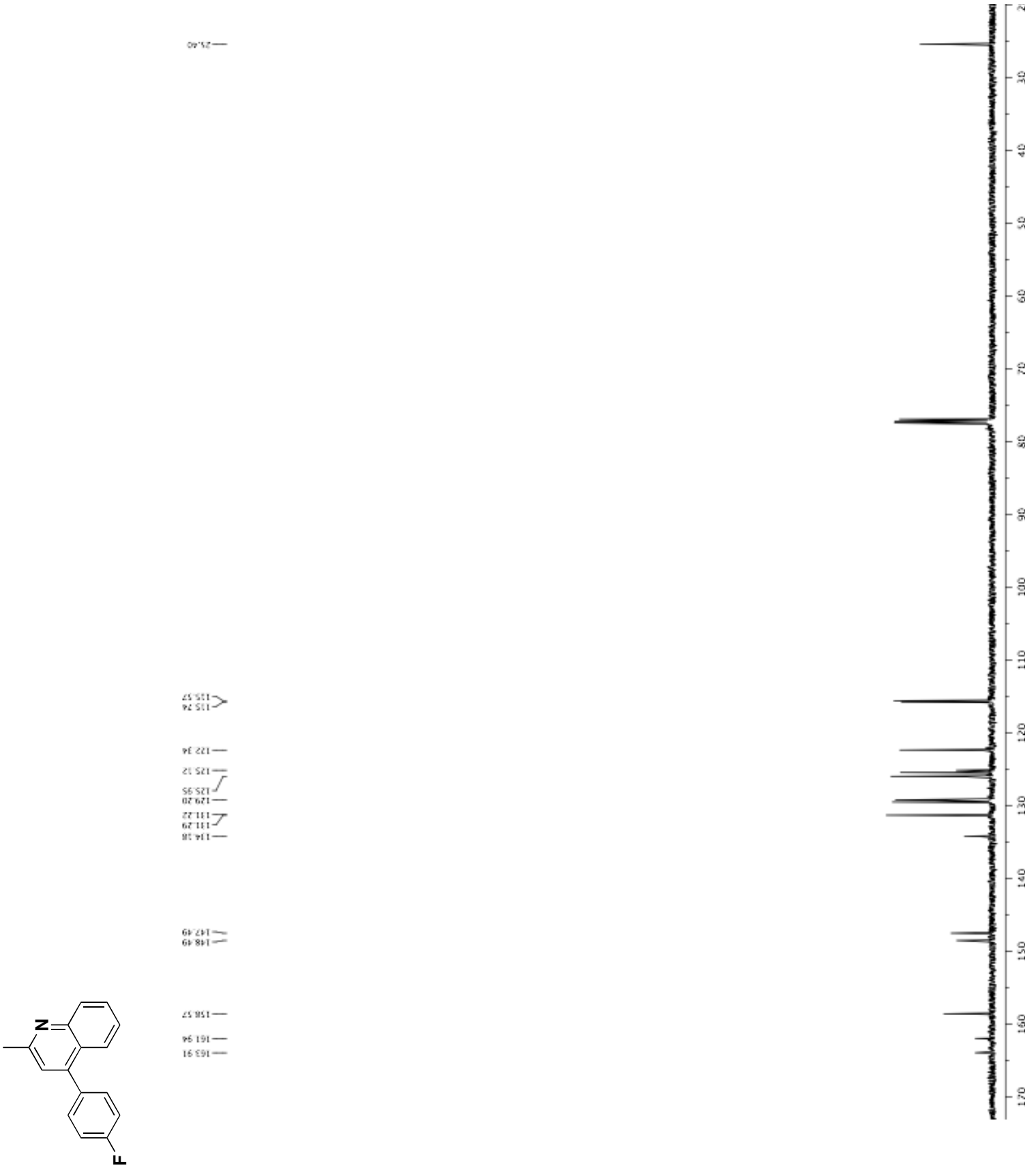

$^{1}$H NMR Spectra (500 MHz, $CDCl_3$)**, 1-(2'-Methyl-[1,1'-biphenyl]-4-yl)ethanone (Table 3 entry 3)**



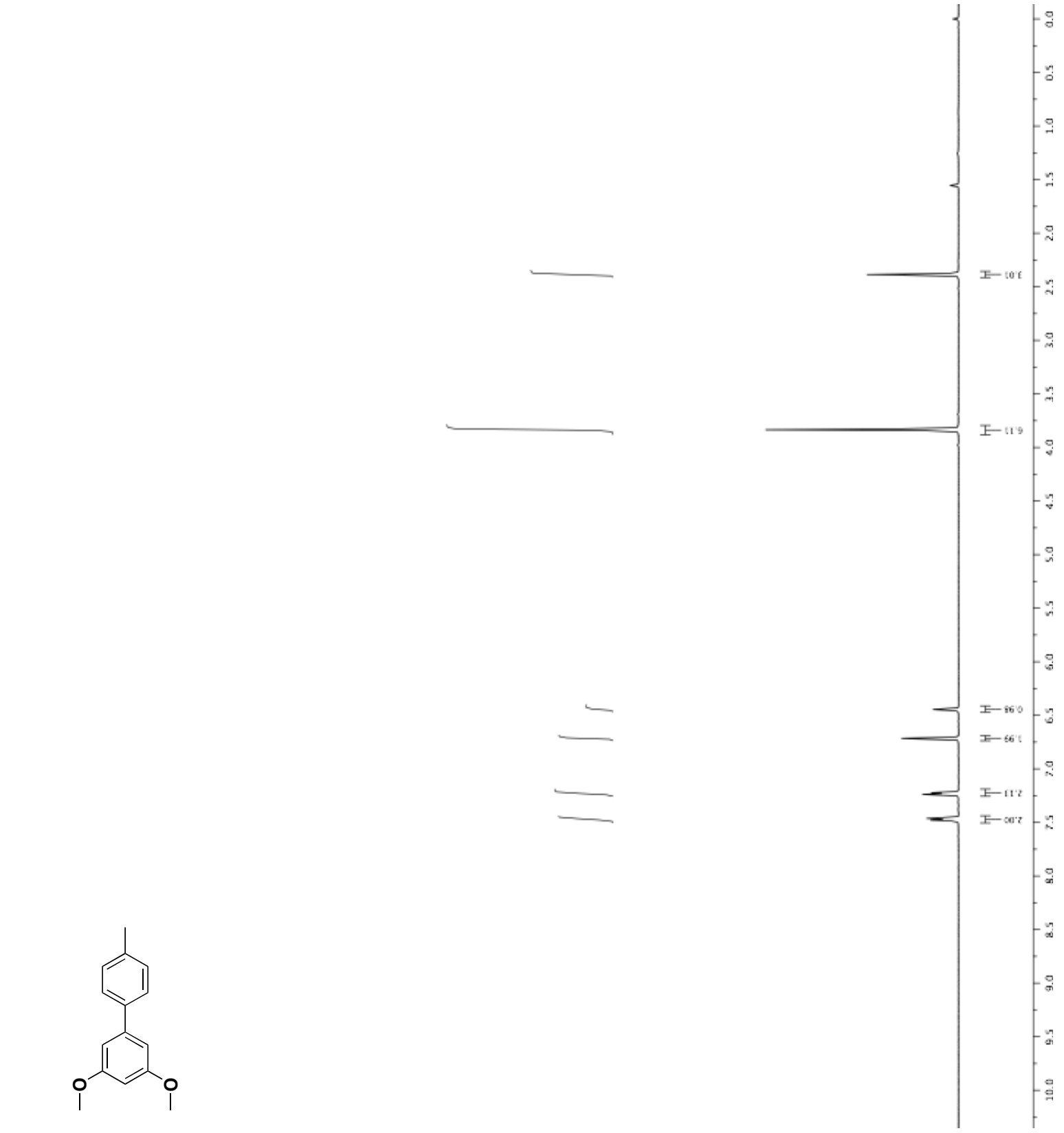

$^{13}$C NMR Spectra (125.8 MHz, $CDCl_3$**), 1-(2'-Methyl-[1,1'-biphenyl]-4-yl)ethanone (Table 3 entry 3)**



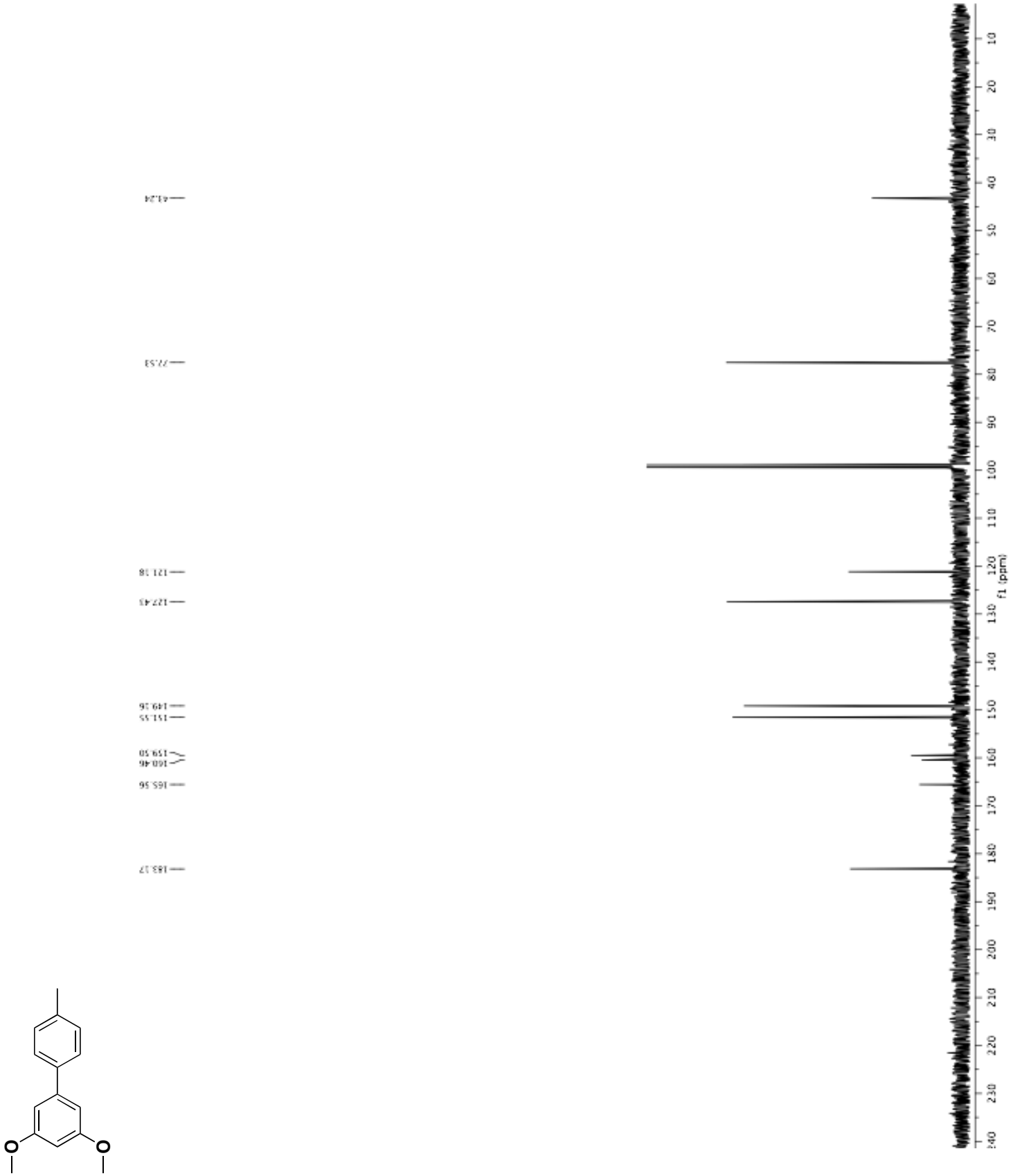

$^{1}$H NMR Spectra (500 MHz, $CDCl_3$)**, 4-(4-Fluorophenyl)-2-methylquinoline (Table 3 entry 4)**




$^{13}C$ NMR Spectra (125.8 MHz, $CDCl_3$)**, 4-(4-Fluorophenyl)-2-methylquinoline (Table 3 entry 4)**



$^{1}$H NMR Spectra (500 MHz, $CDCl_3$), **3,5-Dimethoxy-4'-methyl-1,1'-biphenyl (Table 3 entry 5)**




$^{13}C$ NMR Spectra (125.8 MHz, $CDCl_3$)**, 3,5-Dimethoxy-4'-methyl-1,1'-biphenyl (Table 3 entry 5)**