

**Solvent-free palladium-catalyzed C–O cross-coupling of (hetero)aryl halides with primary alcohols**

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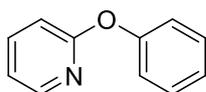
### *General information*

Reagents: Aryl halides and phenols were purchased from either Aldrich or Alfa Aesar and were used without further purification or were purified by common procedures. Phosphine ligands (DalChem) were used as purchased. Only freshly synthesized  $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$  was used. Cesium carbonate ( $\text{Cs}_2\text{CO}_3$ ) was purchased from Aldrich and was finely ground (with a mortar and pestle) prior to use. Silica gel chromatography purifications were performed by flash chromatography using EM Science silica gel 60 (230-400 mesh). All other reagents were commercially available and were used without further purification. Analytical methods: All new compounds were characterized by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, and High Resolution Mass Spectrometry (HRMS) spectroscopy. Chemicals and solvents were obtained from commercial sources and used without further purification. NMR spectra were obtained on a Bruker "Ascend™ 400" (400 MHz  $^1\text{H}$ , 101 MHz  $^{13}\text{C}$ ). The chemical shifts are frequency referenced relative to the residual undeuterated solvent peaks. Coupling constants  $J$  are given in Hertz as positive values regardless of their real individual signs. The multiplicity of the signals is indicated as "s", "d", "t" or "m" for singlet, doublet, triplet or multiplet, respectively. The abbreviation "br" is given for broadened signals. High Resolution Mass Spectrometry spectra were carried out using AB Sciex TripleTOF 5600+ supported TurboV ESI ionization source.

### *General Procedure*

An oven-dried screw-cap tube was cooled to room temperature under argon pressure and charged with aryl halide (1.0 mmol), phenol or alcohol (1.2 mmol) and the ligand (2 mol%),  $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$  (10 mg, 1 mol%). The mixture was mixed thoroughly followed by addition of  $\text{Cs}_2\text{CO}_3$  (650 mg, 2.0 mmol). The tube was sealed and placed in a pre-heated oil bath at  $110^\circ\text{C}$  and stirred for 18 h. Then the mixture was allowed to cool to room temperature, and the resulting dark heterogeneous substance was treated with water (10 ml) and ethyl acetate (10 ml). The organic phase was collected, filtered through a small pad of Celite and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel.

2-Phenoxy pyridine (**1a**)



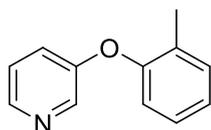
Yield 120 mg (70%), yellow oil.

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.21 (d,  $J = 4.7$  Hz, 1H), 7.68 (t,  $J = 8.7$  Hz, 1H), 7.40 (t,  $J = 8.0$  Hz, 2H), 7.20 (t,  $J = 7.4$  Hz, 1H), 7.15 (d,  $J = 8.5$  Hz, 2H), 7.02 – 6.97 (m, 1H), 6.90 (d,  $J = 8.3$  Hz, 1H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  163.8, 154.3, 147.8, 139.6, 129.8, 124.8, 121.3, 118.6, 111.6.

The NMR data are in agreement with previously reported.<sup>S1</sup>

3-(*o*-Tolyloxy)pyridine (**1b**)



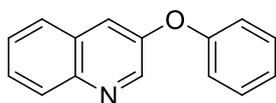
Yield 111 mg (60%), yellow oil.

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*) 8.33 (d,  $J = 15.9$  Hz, 2H), 7.30 – 7.26 (m, 1H), 7.26 – 7.14 (m, 3H), 7.12 (t,  $J = 7.4$  Hz, 1H), 6.92 (d,  $J = 8.0$  Hz, 1H), 2.23 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  153.6, 143.5, 140.0, 131.9, 130.1, 127.6, 125.0, 124.2, 124.0, 119.9, 16.2.

The NMR data are in agreement with previously reported.<sup>S1</sup>

3-Phenoxyquinoline (**1c**)



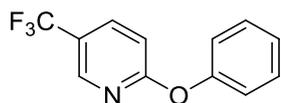
Yield 124 mg (56%), white solid, m.p. 66-67 °C (lit. data: m.p. 64-67°C).<sup>S2</sup>

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.83 (s, 1H), 8.11 (d,  $J = 8.4$  Hz, 1H), 7.67 (d,  $J = 8.1$  Hz, 1H), 7.63 (t,  $J = 7.3$  Hz, 1H), 7.54 – 7.50 (m, 2H), 7.41 (t,  $J = 8.0$  Hz, 2H), 7.21 (t,  $J = 7.4$  Hz, 1H), 7.11 (d,  $J = 7.8$  Hz, 2H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  156.3, 151.2, 145.2, 144.7, 130.3, 129.3, 128.7, 128.0, 127.4, 127.2, 124.5, 120.4, 119.4.

The NMR data are in agreement with previously reported.<sup>S2</sup>

*2-Phenoxy-5-(trifluoromethyl)pyridine (1d)*



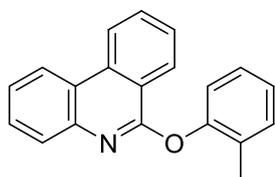
Yield 160 mg (67%), yellow oil.

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.45 (s, 1H), 7.89 (d,  $J$  = 8.6 Hz, 1H), 7.43 (t,  $J$  = 7.6 Hz, 2H), 7.26 (t,  $J$  = 6.4 Hz, 1H), 7.15 (d,  $J$  = 8.1 Hz, 2H), 7.00 (d,  $J$  = 8.7 Hz, 1H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  166.0, 153.3, 145.68, 136.8, 130.0, 125.7, 123.84 (d,  $J$  = 271.3 Hz), 121.6, 111.4.

HRMS calc. for  $\text{C}_{12}\text{H}_8\text{F}_3\text{NO}$   $[\text{M}+\text{H}]^+$  240.0630; found 240.0632.

*6-(o-Tolyloxy)phenanthridine (1e)*



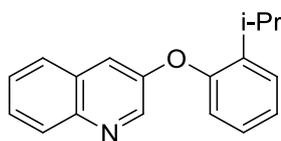
Yield 178 mg (62%), white solid, m.p. 99-101°C

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.56 (d,  $J$  = 8.1 Hz, 1H), 8.50 (d,  $J$  = 8.3 Hz, 1H), 8.38 (d,  $J$  = 8.0 Hz, 1H), 7.80 (t,  $J$  = 8.1 Hz, 1H), 7.70 (d,  $J$  = 8.0 Hz, 1H), 7.66 (t,  $J$  = 7.5 Hz, 1H), 7.51 (t,  $J$  = 8.0 Hz, 1H), 7.44 (t,  $J$  = 8.0 Hz, 1H), 7.29 (d,  $J$  = 7.5 Hz, 1H), 7.28 – 7.24 (m, 2H), 7.19 – 7.15 (m, 1H), 2.21 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  158.3, 152.1, 143.1, 135.5, 131.3, 131.2, 131.0, 128.8, 128.6, 127.6, 126.9, 125.3, 125.0, 123.0, 122.7, 122.1, 122.1, 119.9, 16.7.

HRMS calc. for  $\text{C}_{20}\text{H}_{16}\text{NO}$   $[\text{M}+\text{H}]^+$  286.1230; found 286.1226.

*3-(2-Isopropylphenoxy)quinoline (1f)*



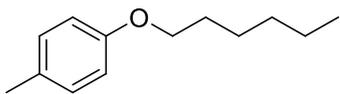
Yield 131.7 mg (50%), white solid, m.p. 90-91 °C (lit. data: m.p. 96-97°C).<sup>S2</sup>

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.87 – 8.82 (m, 1H), 8.11 (d,  $J$  = 8.4 Hz, 1H), 7.65 – 7.59 (m, 2H), 7.50 (t,  $J$  = 7.5 Hz, 1H), 7.44 – 7.40 (m, 1H), 7.35 (d,  $J$  = 2.6 Hz, 1H), 7.25 – 7.21 (m, 2H), 7.00 – 6.96 (m, 1H), 3.28 (p,  $J$  = 6.9 Hz, 1H), 1.25 (s, 3H), 1.24 (s, 3H)

$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  152.6, 152.3, 144.6, 144.3, 140.6, 129.2, 128.8, 127.7, 127.6, 127.4, 127.4, 127.0, 125.4, 120.3, 118.3, 27.3, 23.2.

The NMR data are in agreement with previously reported.<sup>S2</sup>

*1-(Hexyloxy)-4-methylbenzene (2a)*



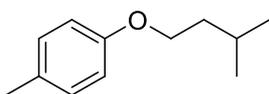
Yield 125 mg (55%) colorless oil.

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.10 (d,  $J$  = 8.2 Hz, 2H), 6.83 (d,  $J$  = 8.3 Hz, 2H), 3.96 (t,  $J$  = 6.6 Hz, 2H), 2.32 (s, 3H), 1.84 – 1.76 (m, 2H), 1.52 – 1.44 (m, 2H), 1.43 – 1.34 (m, 4H), 0.95 (t,  $J$  = 6.0 Hz, 3H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  157.2, 130.0, 129.7, 114.5, 68.2, 31.8, 29.5, 25.9, 22.8, 20.6, 14.2.

The NMR data are in agreement with previously reported.<sup>S3</sup>

*1-(3-Methylbutoxy)-4-methylbenzene (2b)*



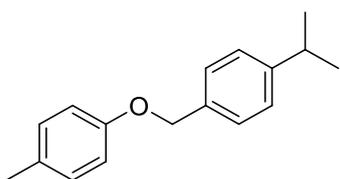
Yield 114.1 mg (55%) colorless oil.

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.09 (d,  $J$  = 8.2 Hz, 2H), 6.82 (d,  $J$  = 8.6 Hz, 2H), 3.98 (t,  $J$  = 6.7 Hz, 2H), 2.30 (s, 3H), 1.89 – 1.82 (m, 1H), 1.76 – 1.63 (m, 2H), 0.99 (s, 3H), 0.98 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  157.2, 130.0, 129.8, 114.5, 66.5, 38.2, 25.2, 22.8, 20.6.

HRMS calc. for  $\text{C}_{12}\text{H}_{18}\text{O}$   $[\text{M}]^+$  178.1357; found 178.1348.

*1-Isopropyl-4-(p-tolyloxymethyl)benzene (2c)*



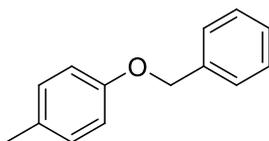
Yield 149 mg (62%), white solid, m.p. 69-70°C

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.37 (d,  $J$  = 7.7 Hz, 2H), 7.31 – 7.23 (m, 2H), 7.10 (d,  $J$  = 8.1 Hz, 2H), 6.90 (d,  $J$  = 8.4 Hz, 2H), 5.01 (s, 2H), 2.94 (p,  $J$  = 6.9 Hz, 1H), 2.31 (s, 3H), 1.28 (d,  $J$  = 6.9 Hz, 6H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  157.0, 148.8, 134.7, 130.2, 130.0, 127.8, 126.8, 114.8, 70.2, 34.1, 24.1, 20.6.

HRMS calc. for  $\text{C}_{12}\text{H}_{12}\text{O}_2$   $[\text{M}]^+$  240.1514; found 240.1506.

*1-Benzoyloxy-4-methylbenzene (2d)*



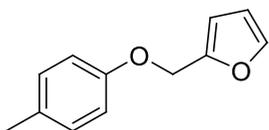
Yield 119 mg (60%), white solid, m.p. 39-40°C (lit. data: m.p. 41-42°C).<sup>S4</sup>

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.47 (d, *J* = 7.2 Hz, 2H), 7.42 (t, *J* = 7.4 Hz, 2H), 7.35 (t, *J* = 7.1 Hz, 1H), 7.12 (d, *J* = 8.1 Hz, 2H), 6.92 (d, *J* = 8.2 Hz, 2H), 5.07 (s, 2H), 2.33 (s, 3H).

<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*) δ 156.8, 137.4, 130.3, 130.0, 128.7, 128.0, 127.57, 114.8, 70.2, 20.6.

The NMR data are in agreement with previously reported.<sup>S5</sup>

*2-(p-Tolyloxymethyl)furan (2e)*



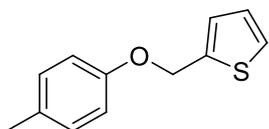
Yield 122.3 mg (65%), white solid, m.p. 49-51°C.

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.45 (s, 1H), 7.10 (d, *J* = 7.7 Hz, 2H), 6.89 (d, *J* = 7.5 Hz, 2H), 6.40 (d, *J* = 22.1 Hz, 2H), 4.98 (s, 2H), 2.30 (s, 3H).

<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*) δ 156.4, 150.7, 143.1, 130.6, 130.0, 115.0, 110.60, 109.9, 62.8, 20.6.

HRMS calc. for C<sub>17</sub>H<sub>20</sub>O [M]<sup>+</sup> 188.0837; found 188.0829.

*2-(p-Tolyloxymethyl)thiophene (2f)*



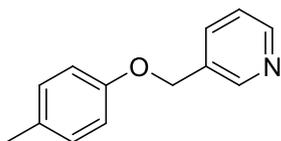
Yield 159.3 mg (78%), white solid, m.p. 39-41°C.

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.32 (d, *J* = 5.1 Hz, 1H), 7.09 (d, *J* = 8.3 Hz, 3H), 7.03 – 6.97 (m, 1H), 6.89 (d, *J* = 8.4 Hz, 2H), 5.20 (s, 2H), 2.30 (s, 3H).

<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*) δ 156.4, 139.8, 130.7, 130.1, 126.9, 126.8, 126.2, 115.1, 65.3, 20.6.

HRMS calc. for C<sub>12</sub>H<sub>12</sub>OS [M]<sup>+</sup> 204.0608; found 204.0601.

*3-(p-Tolyloxymethyl)pyridine (2g)*



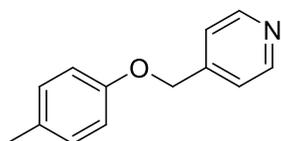
Yield 179.3 mg (90%), yellow oil.

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.68 (s, 1H), 8.58 (s, 1H), 7.77 (d,  $J = 7.8$  Hz, 1H), 7.33 – 7.29 (m, 1H), 7.10 (d,  $J = 8.2$  Hz, 2H), 6.87 (d,  $J = 8.6$  Hz, 2H), 5.05 (s, 2H), 2.29 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  156.4, 149.3, 149.0, 135.4, 130.8, 130.1, 123.6, 114.8, 67.7, 20.6.

HRMS calc. for  $\text{C}_{13}\text{H}_{14}\text{NO}$   $[\text{M}+\text{H}]^+$  200.1069; found 200.1070.

*4-(p-Tolyloxymethyl)pyridine (2h)*



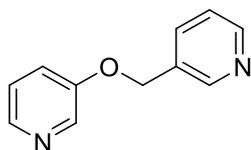
Yield 109.58 mg (55%), white solid, m.p. 72-73°C.

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.61 (d,  $J = 5.1$  Hz, 2H), 7.37 (d,  $J = 5.6$  Hz, 2H), 7.10 (d,  $J = 8.2$  Hz, 2H), 6.85 (d,  $J = 8.5$  Hz, 2H), 5.07 (s, 2H), 2.29 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  156.2, 149.8, 147.0, 130.9, 130.2, 121.7, 114.8, 68.3, 20.6.

HRMS calc. for  $\text{C}_{13}\text{H}_{14}\text{NO}$   $[\text{M}+\text{H}]^+$  200.1069; found 200.1074.

*3-(Pyridin-3-ylmethoxy)pyridine (2i)*



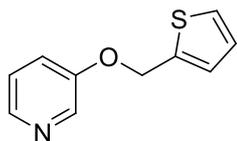
Yield 130 mg (70%), yellow oil.

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.65 (s, 1H), 8.56 (d,  $J = 3.7$  Hz, 1H), 8.36 (d,  $J = 2.4$  Hz, 1H), 8.22 (d,  $J = 3.1$  Hz, 1H), 7.74 (d,  $J = 7.8$  Hz, 1H), 7.34 – 7.27 (m, 1H), 7.25 – 7.16 (m, 2H), 5.08 (s, 2H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  154.6, 149.8, 149.0, 142.8, 138.2, 135.3, 131.8, 124.0, 123.6, 121.6, 67.9.

HRMS calc. for  $\text{C}_{11}\text{H}_{10}\text{N}_2\text{O}$   $[\text{M}+\text{H}]^+$  187.0866; found 188.0861.

3-(Thiophen-2-ylmethoxy)pyridine (**2j**)



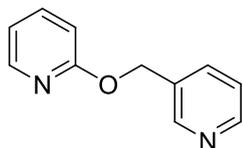
Yield 143 mg (75%), colorless oil.

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.27 – 8.13 (m, 1H), 7.58 (t,  $J$  = 8.6 Hz, 1H), 7.31 (d,  $J$  = 5.6 Hz, 1H), 7.17 (d,  $J$  = 3.1 Hz, 1H), 7.06 – 6.97 (m, 1H), 6.95 – 6.85 (m, 1H), 6.79 (d,  $J$  = 8.3 Hz, 1H), 5.57 (s, 2H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  163.2, 146.8, 139.6, 138.8, 127.6, 126.7, 126.4, 117.2, 111.5, 62.1.

HRMS calc. for  $\text{C}_{11}\text{H}_{10}\text{N}_2\text{O}$   $[\text{M}+\text{H}]^+$  192.0477; found 192.0478.

2-(Pyridin-3-ylmethoxy)pyridine (**2k**)



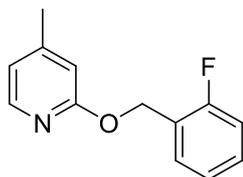
Yield 151 mg (81%), yellow oil.

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.63 (s, 1H), 8.55 (d,  $J$  = 4.6 Hz, 1H), 8.34 (s, 1H), 8.20 (d,  $J$  = 5.4 Hz, 1H), 7.72 (d,  $J$  = 7.8 Hz, 1H), 7.28 (dd,  $J$  = 7.8, 4.9 Hz, 1H), 7.23 – 7.14 (m, 2H), 5.06 (s, 2H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  163.3, 149.7, 149.3, 146.9, 138.9, 135.8, 133.1, 123.5, 117.3, 111.4, 65.0.

HRMS calc. for  $\text{C}_{11}\text{H}_{10}\text{N}_2\text{O}$   $[\text{M}+\text{H}]^+$  187.0866; found 188.0861.

2-(2-Fluorobenzoyloxy)-4-methylpyridine (**2l**)



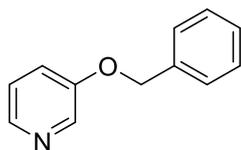
Yield 191 mg (88%), colorless oil.

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.01 (d,  $J$  = 5.2 Hz, 1H), 7.48 (t,  $J$  = 7.4 Hz, 1H), 7.31 – 7.22 (m, 1H), 7.11 (d,  $J$  = 15.0 Hz, 1H), 7.05 (t,  $J$  = 9.1 Hz, 1H), 6.70 (d,  $J$  = 5.1 Hz, 1H), 6.60 (s, 1H), 5.42 (s, 2H), 2.27 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  161.03 (d,  $J$  = 247.6 Hz), 130.35 (d,  $J$  = 4.1 Hz), 129.64 (d,  $J$  = 8.1 Hz), 124.83 (d,  $J$  = 14.5 Hz), 124.13 (d,  $J$  = 3.7 Hz), 115.43 (d,  $J$  = 21.1 Hz).

HRMS calc. for  $\text{C}_{13}\text{H}_{12}\text{FNO}$   $[\text{M}+\text{H}]^+$  218.0976; found 218.0972.

3-(Benzyloxy)pyridine (**2m**)



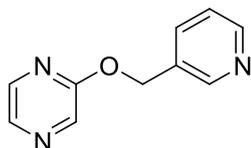
Yield 98 mg (53%), yellow oil.

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.40 (s, 1H), 8.24 (s, 1H), 7.45 – 7.33 (m, 5H), 7.27 – 7.18 (m, 2H), 5.11 (s, 2H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  155.0, 142.4, 138.4, 136.2, 128.8, 128.4, 127.6, 123.97, 121.7, 70.4.

The NMR data are in agreement with previously reported.<sup>S6</sup>

2-(Pyridin-3-ylmethoxy)pyrazine (**2n**)



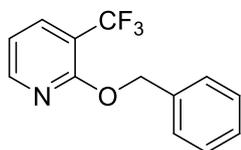
Yield 98 mg (52%), yellow solid, m.p. 52-54°C.

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.71 (s, 1H), 8.57 (d,  $J = 4.7$  Hz, 1H), 8.27 (s, 1H), 8.14 (d,  $J = 2.7$  Hz, 1H), 8.10 – 8.05 (m, 1H), 7.77 (d,  $J = 7.8$  Hz, 1H), 7.32 – 7.27 (m, 1H), 5.40 (s, 2H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  159.7, 149.8, 149.7, 140.5, 137.2, 136.1, 136.0, 132.0, 123.5, 65.4.

HRMS calc. for  $\text{C}_{10}\text{H}_{10}\text{N}_3\text{O}$   $[\text{M}+\text{H}]^+$  188.0818; found 188.0819.

2-(benzyloxy)-3-(trifluoromethyl)pyridine (**2o**)



Yield 96 mg (38%), colorless oil.

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.33 (dd,  $J = 5.1, 1.8$  Hz, 1H), 7.88 (d,  $J = 7.4$  Hz, 1H), 7.48 (d,  $J = 7.5$  Hz, 2H), 7.38 (t,  $J = 7.5$  Hz, 2H), 7.31 (t,  $J = 7.2$  Hz, 1H), 6.98 (dd,  $J = 7.2, 5.4$  Hz, 1H), 5.54 (s, 2H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  160.4, 150.6, 136.9, 136.6 (q,  $J = 4.8$  Hz), 128.6, 127.9, 127.4, 123.2 (q,  $J = 271.8$  Hz), 116.3, 113.6 (d,  $J = 33.1$  Hz), 68.0.

HRMS calc. for  $\text{C}_{13}\text{H}_{10}\text{F}_3\text{NO}$   $[\text{M}+\text{H}]^+$  254.0787; found 254.0789.

## References

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- S2. C. H. Burgos, T. E. Barder, X. Huang and S. L. Buchwald, *Angew. Chem., Int. Ed.*, 2006, **45**, 4321.
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# NMR and HRMS spectra

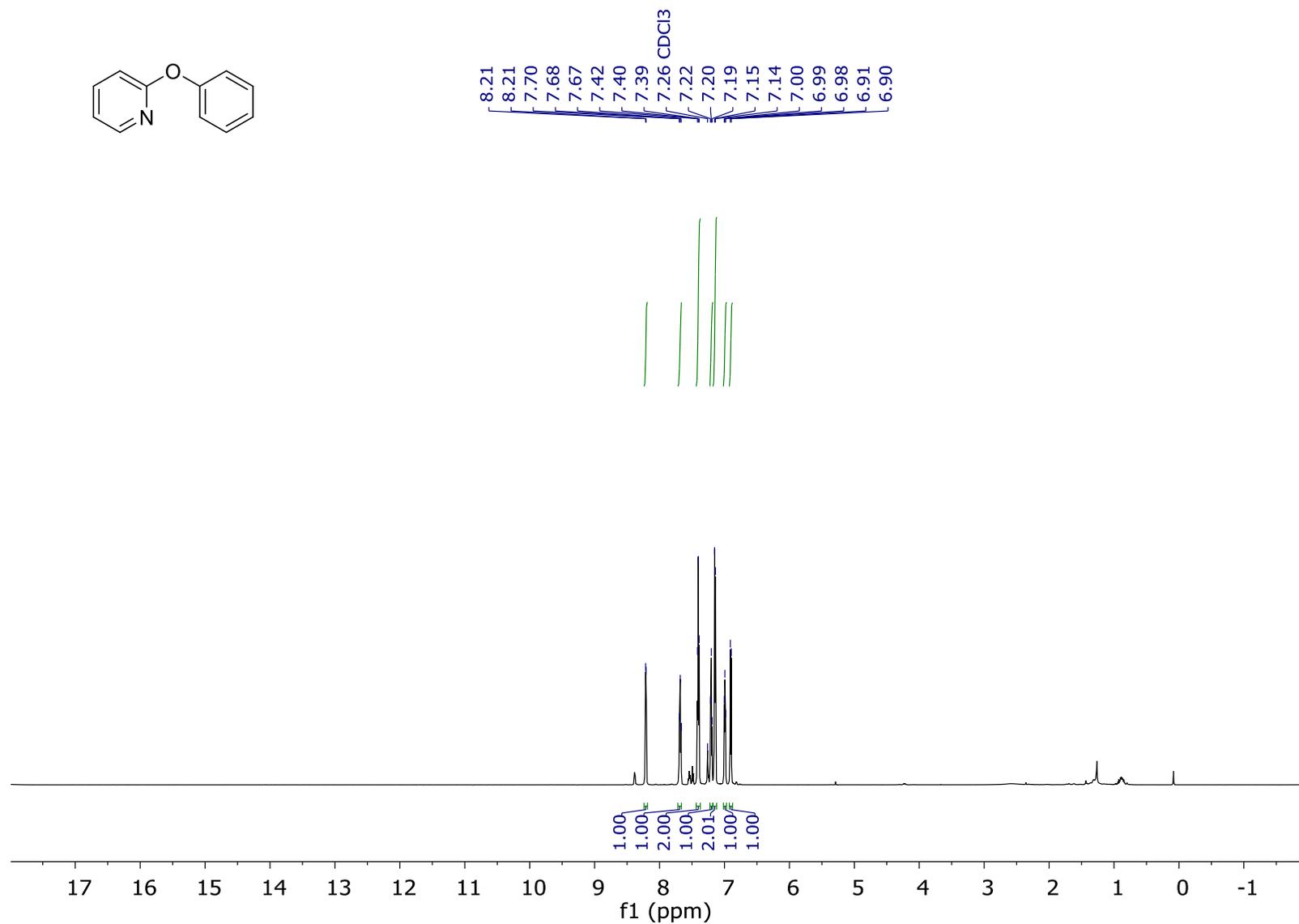
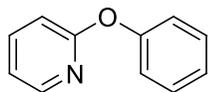


Figure S1. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) of 2-phenoxy pyridine (1a).

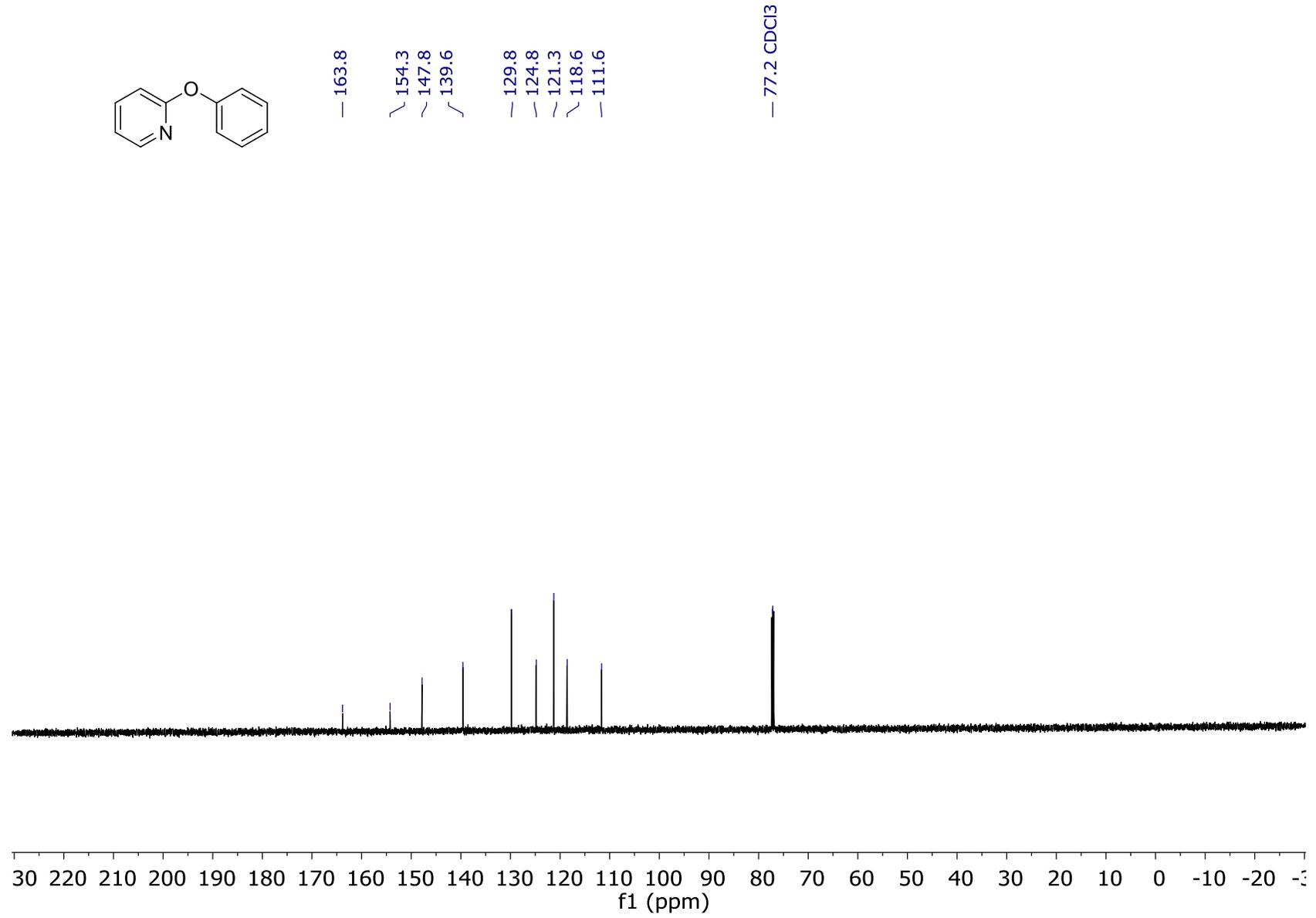


Figure S2.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform-*d*) of 2-phenoxy pyridine (1a).

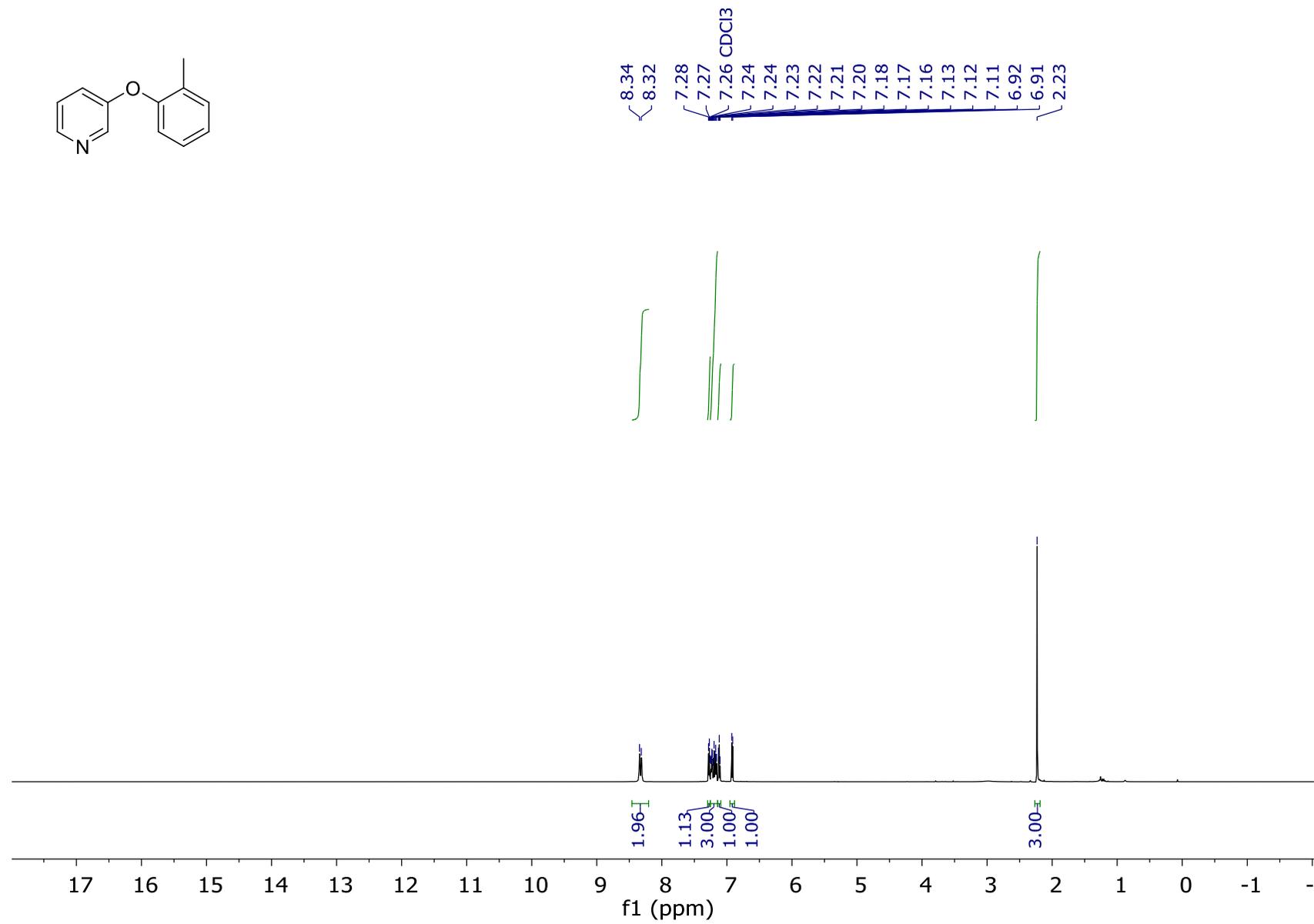


Figure S3. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) of 3-(*o*-tolylloxy)pyridine (1b).

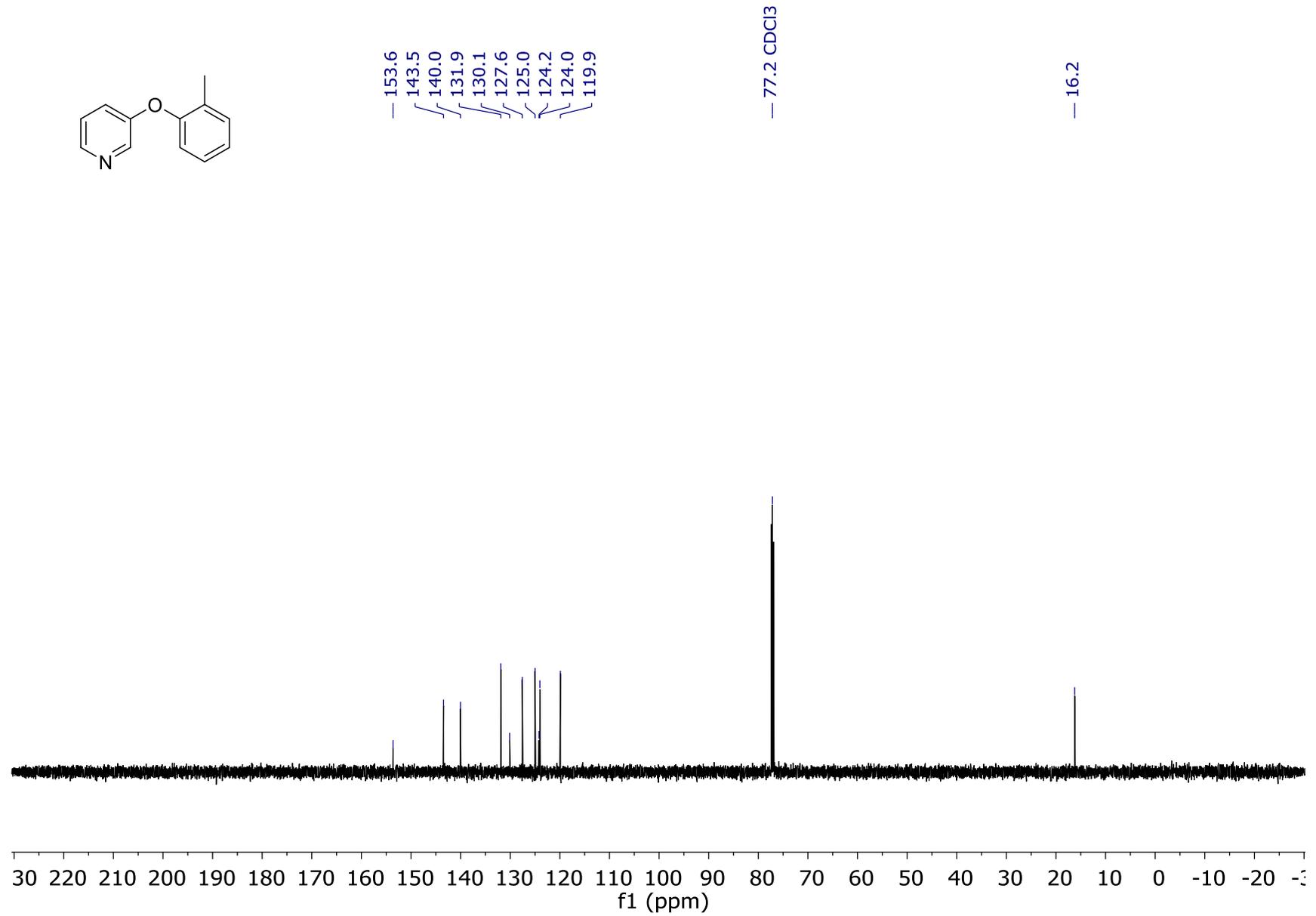


Figure S4.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform-*d*) of 3-(*o*-toloxy)pyridine (1b).

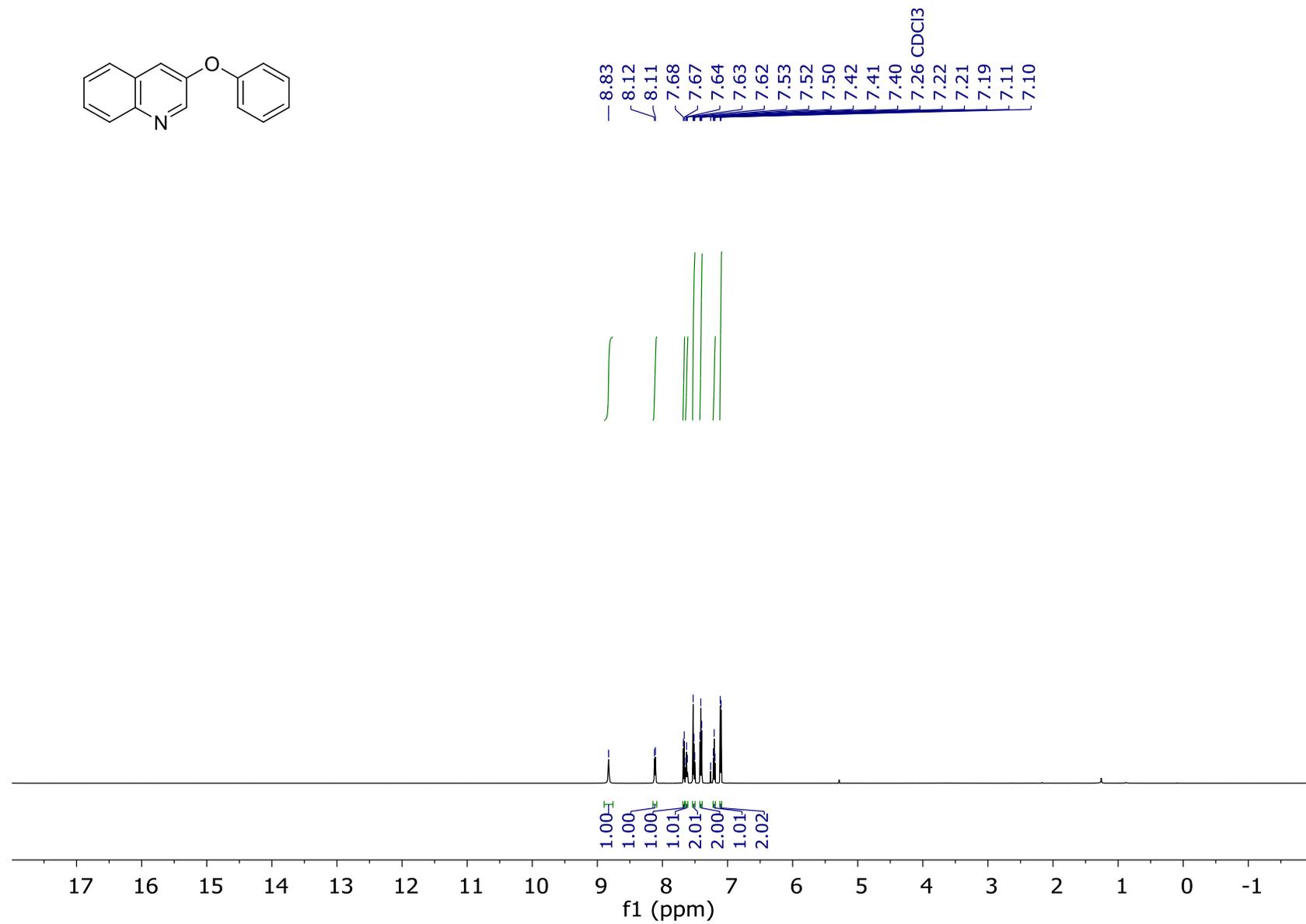


Figure S5.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*) of 3-phenoxyquinoline (1c).

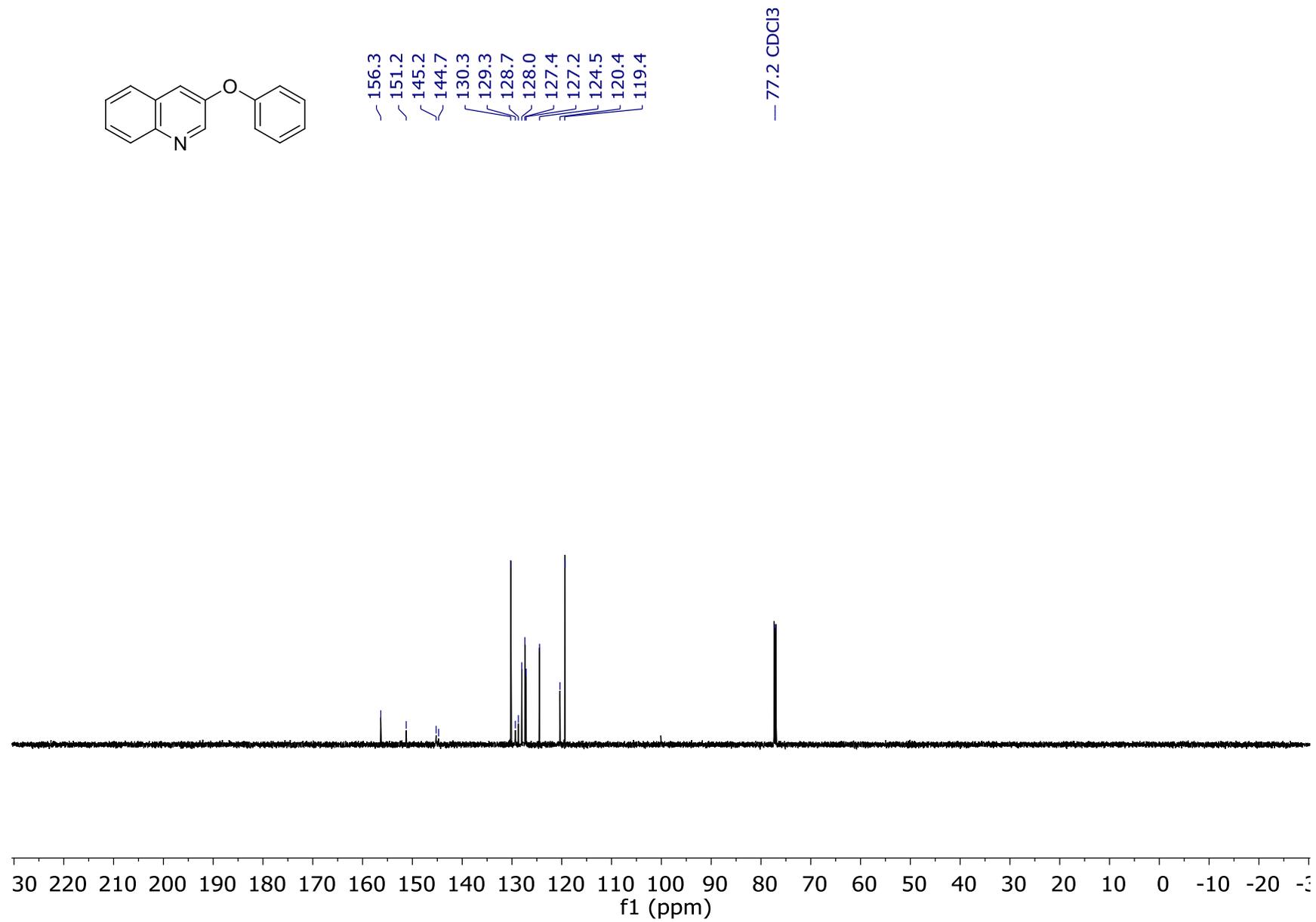


Figure S6.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform-*d*) of 3-phenoxyquinoline (1c).

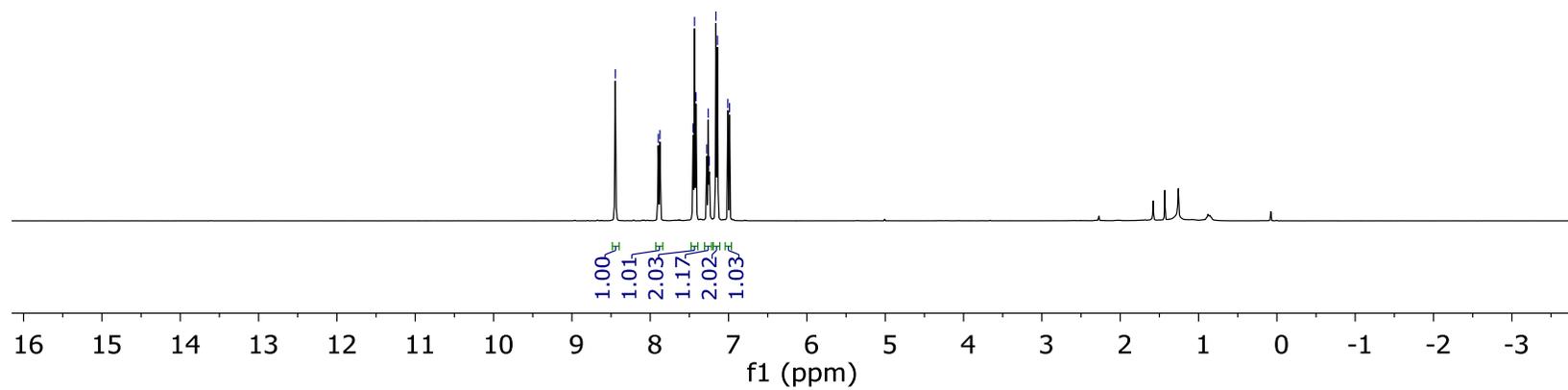
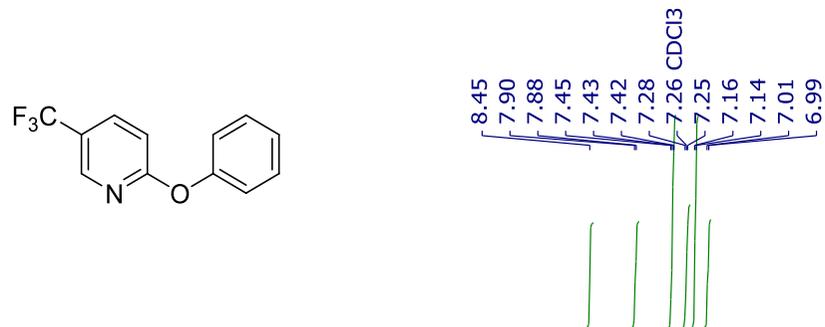


Figure S7.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*) of 2-phenoxy-5-(trifluoromethyl)pyridine (1d).

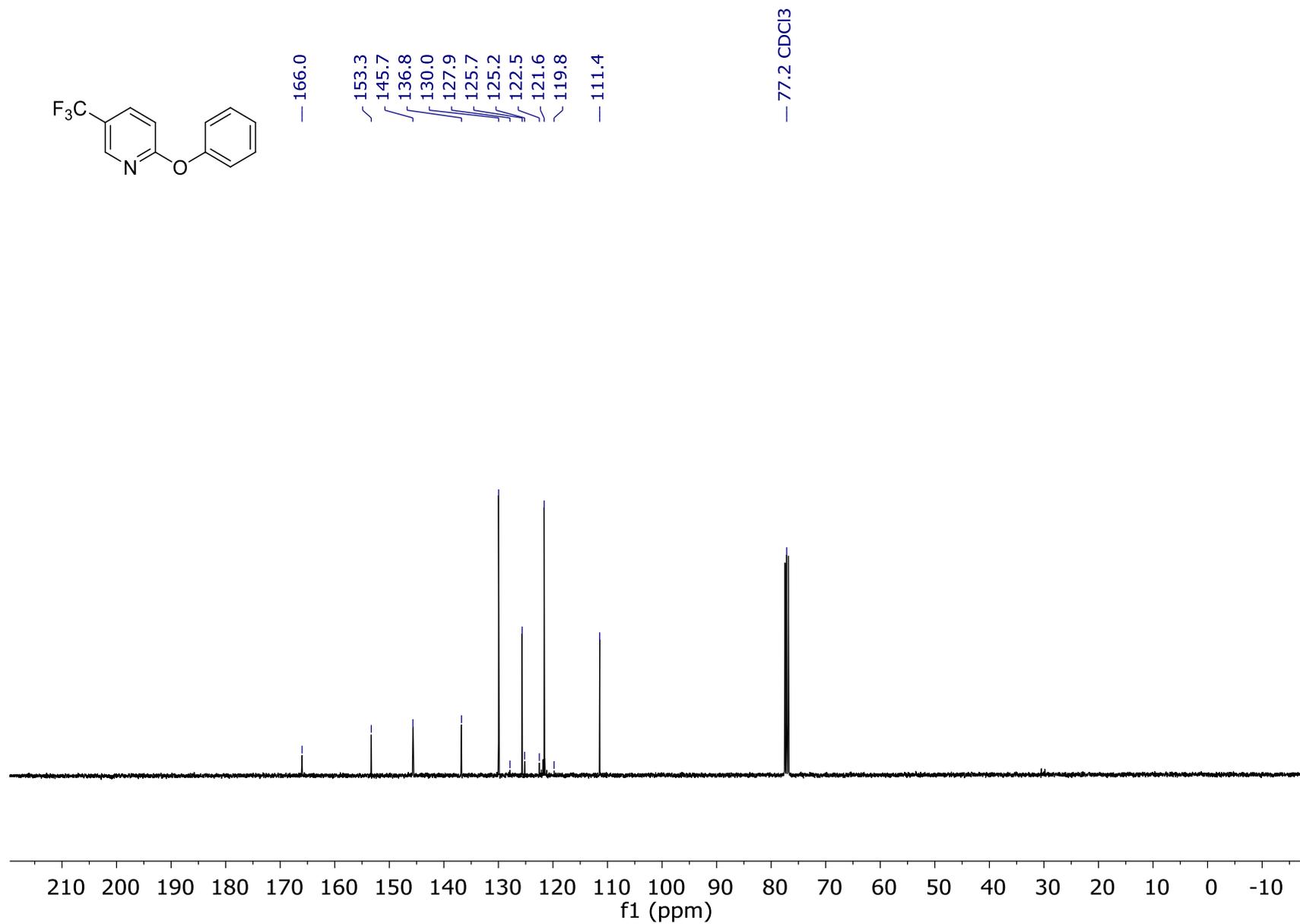


Figure S8.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform-*d*) of 2-phenoxy-5-(trifluoromethyl)pyridine (1d).

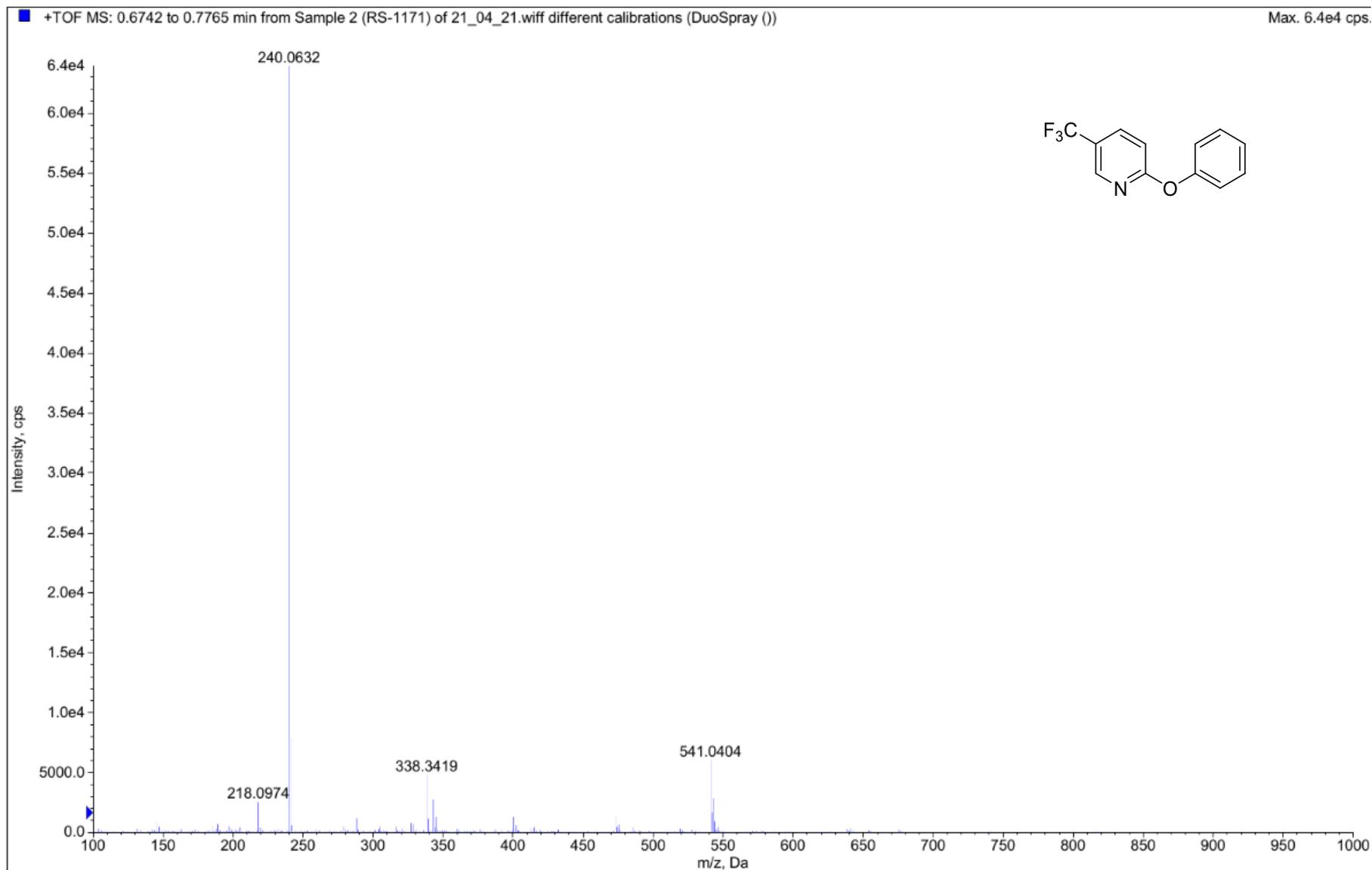


Figure S9. HRMS spectra of 2-phenoxy-5-(trifluoromethyl)pyridine (1d).

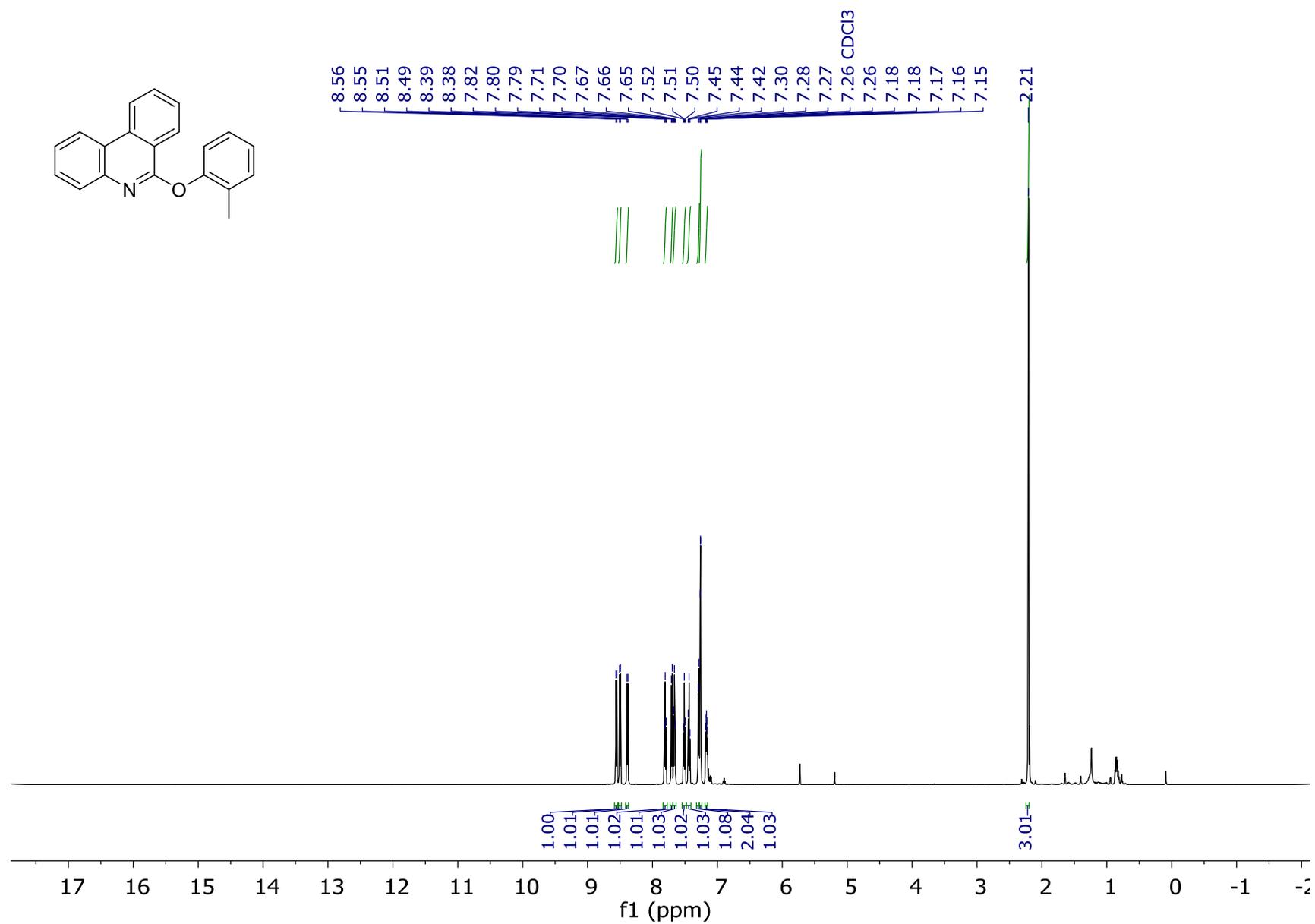


Figure S10. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) of 6-(o-tolyloxy)phenanthridine (1e).

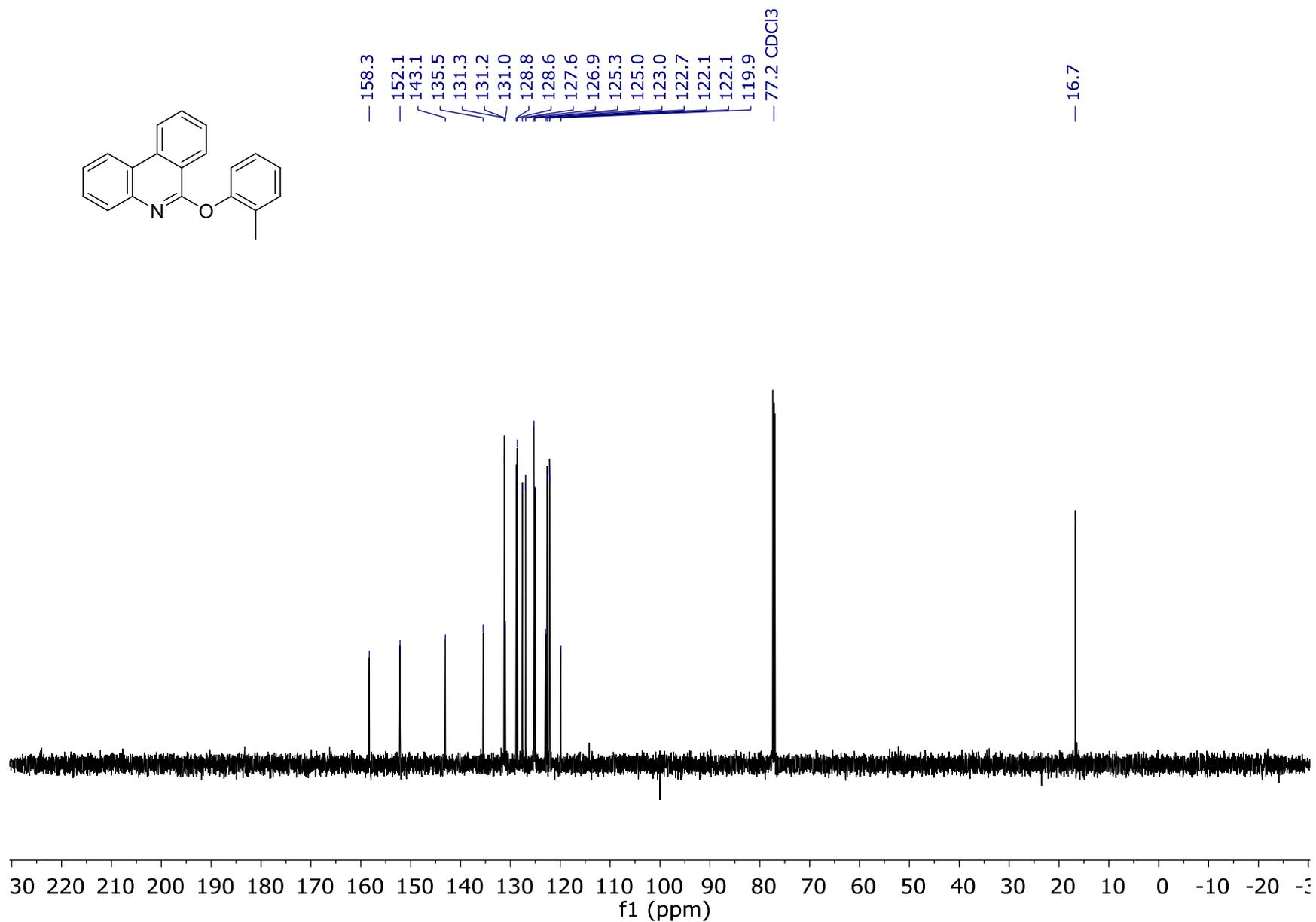
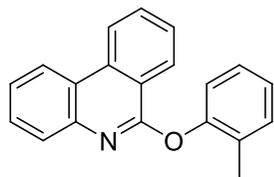


Figure S11.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform-*d*) of 6-(*o*-tolylloxy)phenanthridine (1e).

+TOF MS: 0.7393 to 0.8323 min from Sample 3 (RS-1134) of 21\_04\_21.wiff different calibrations (DuoSpray ())

Max. 1.6e5 cps.

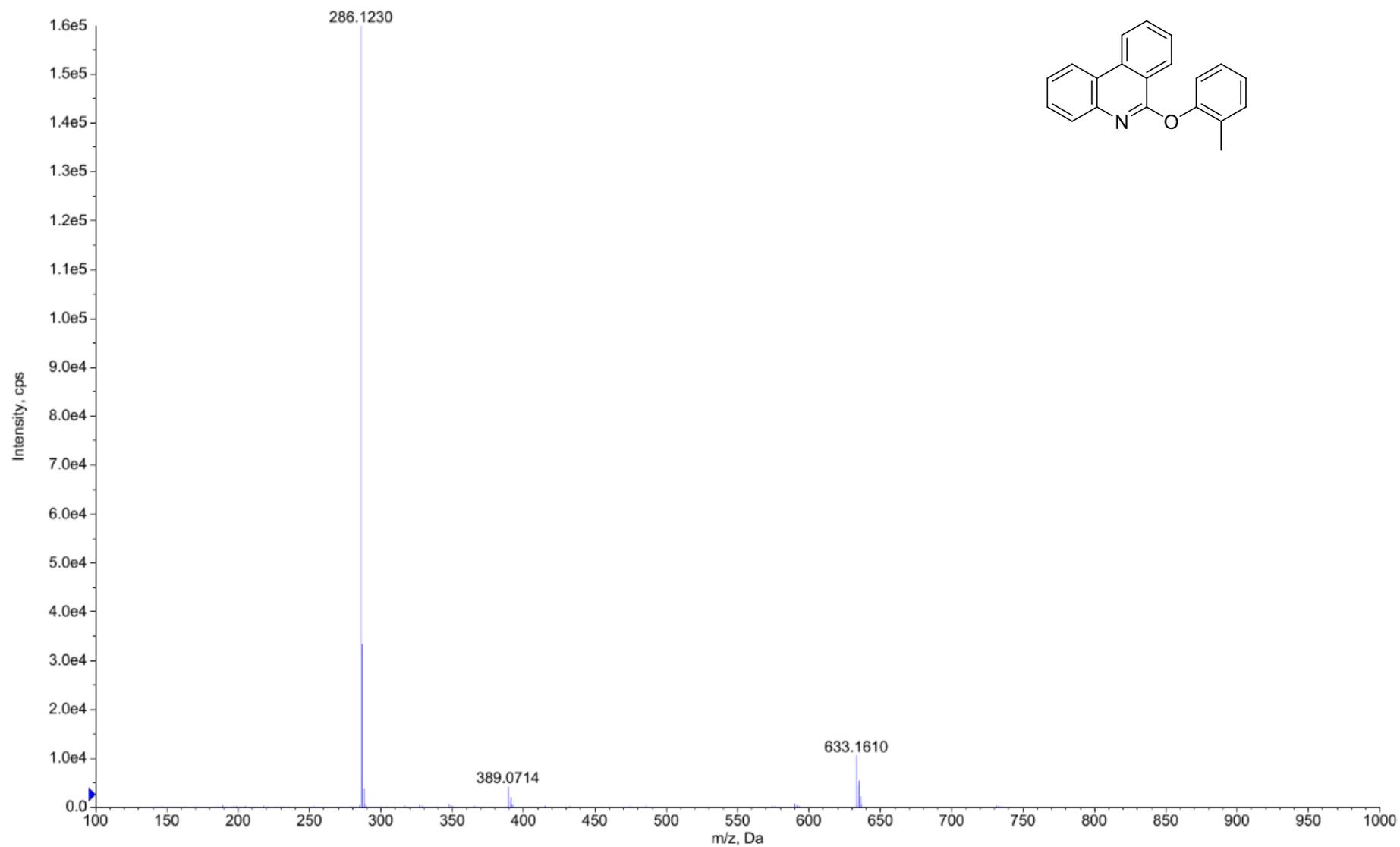


Figure S12. HRMS spectra of 6-(o-tolyloxy)phenanthridine (1e).

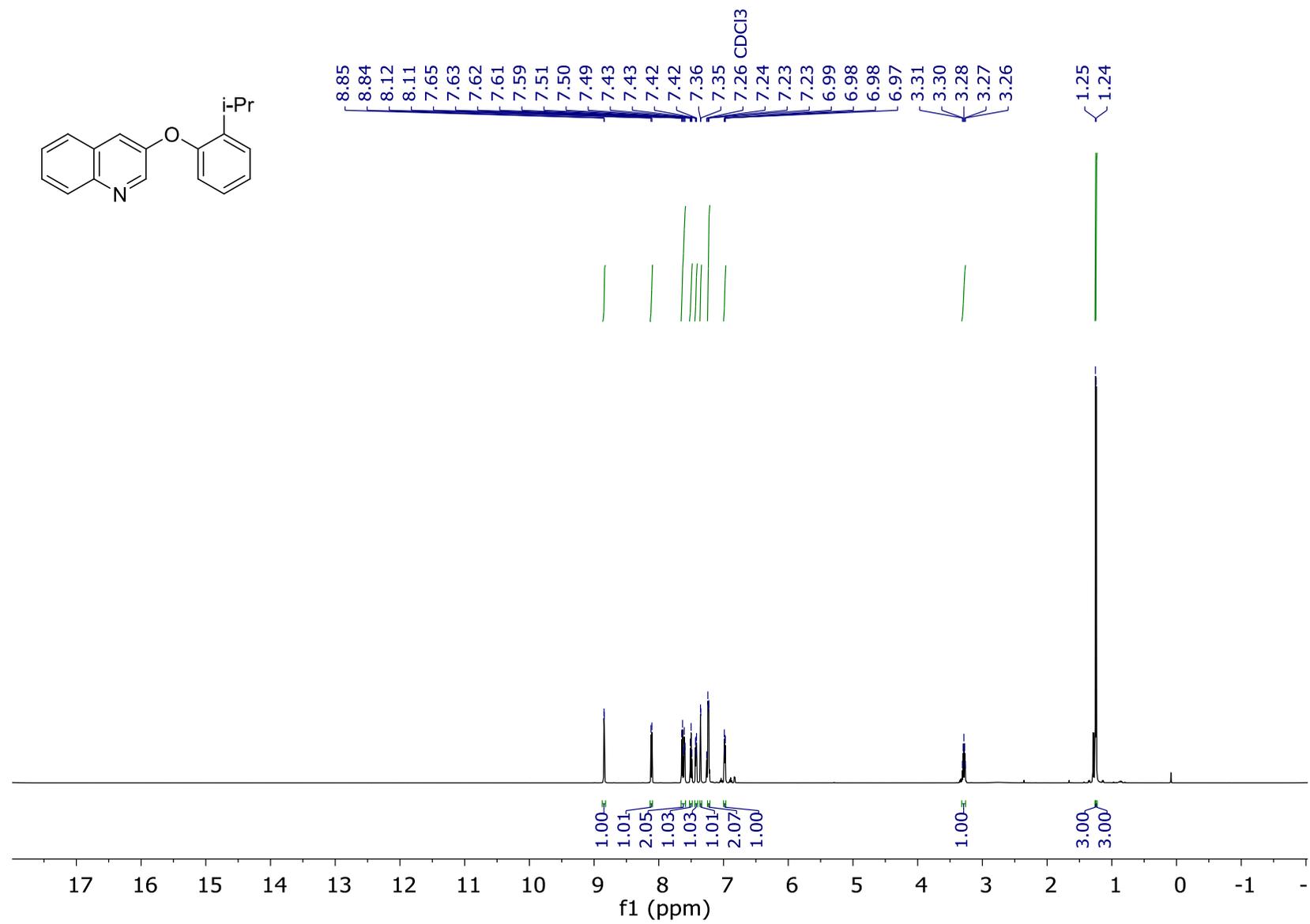


Figure S13. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) of 3-(2-isopropylphenoxy)quinoline (1f).

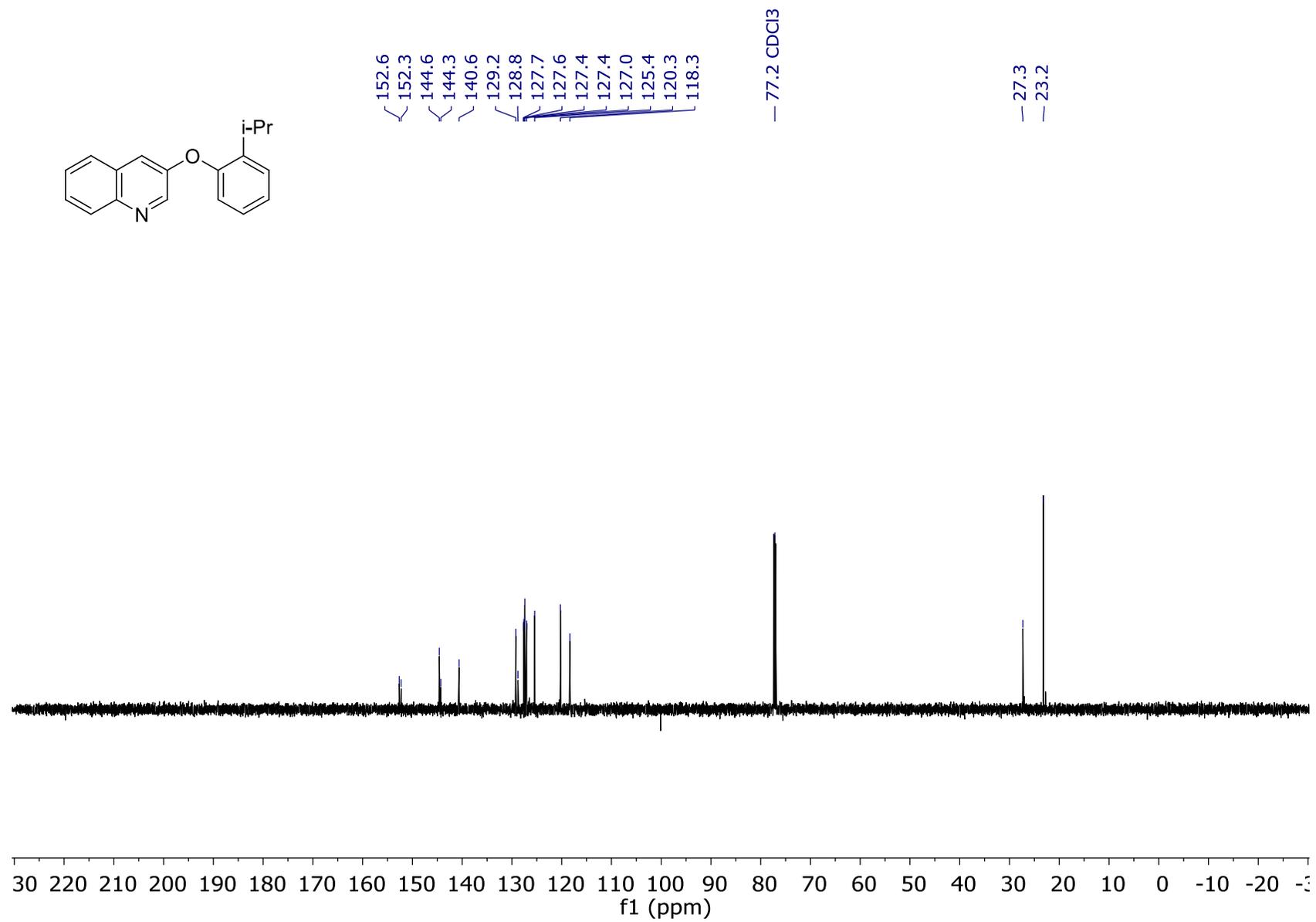


Figure S14.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform-*d*) of 3-(2-isopropylphenoxy)quinoline (1f).

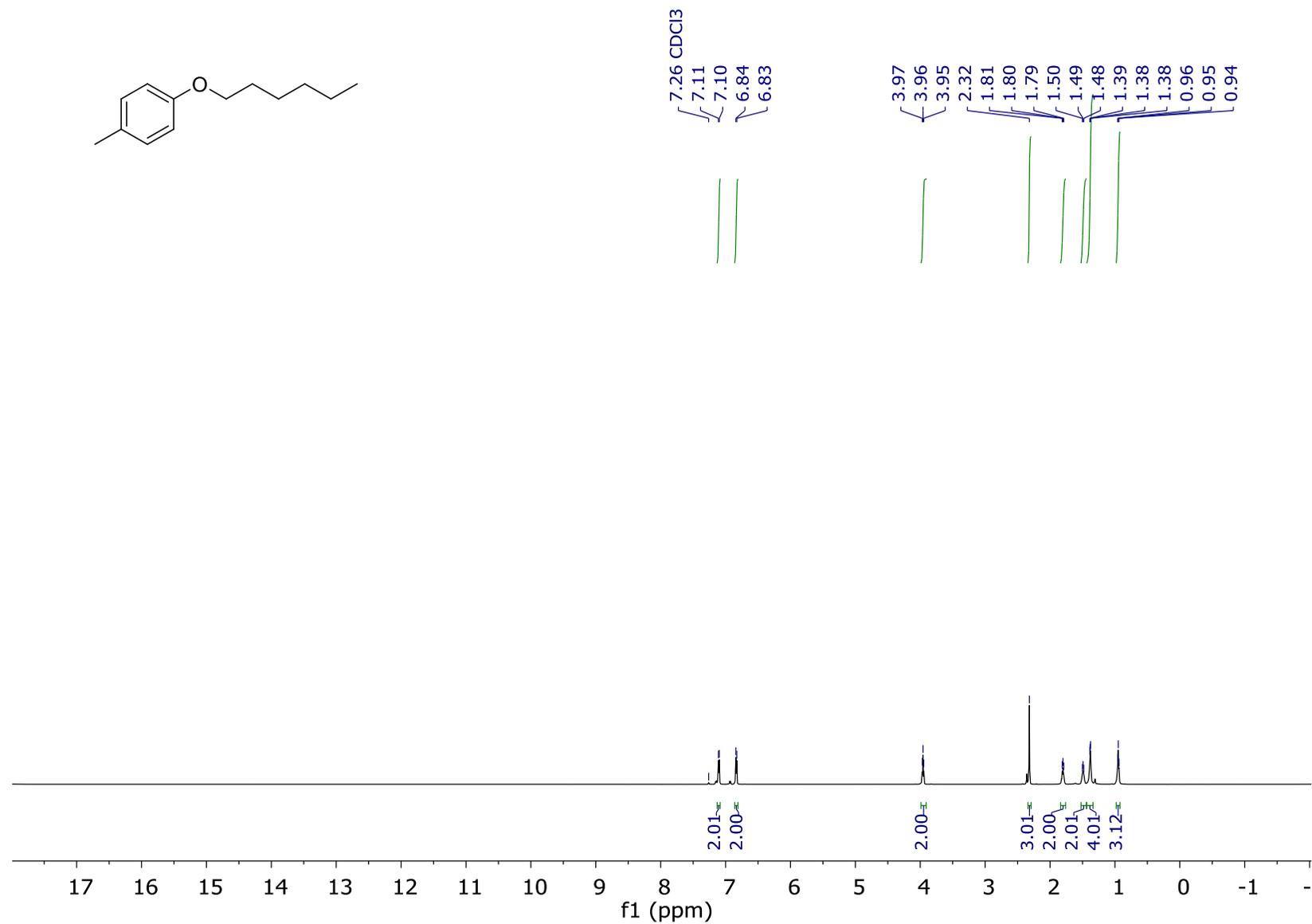


Figure S15. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) of 1-(hexyloxy)-4-methylbenzene (2a).

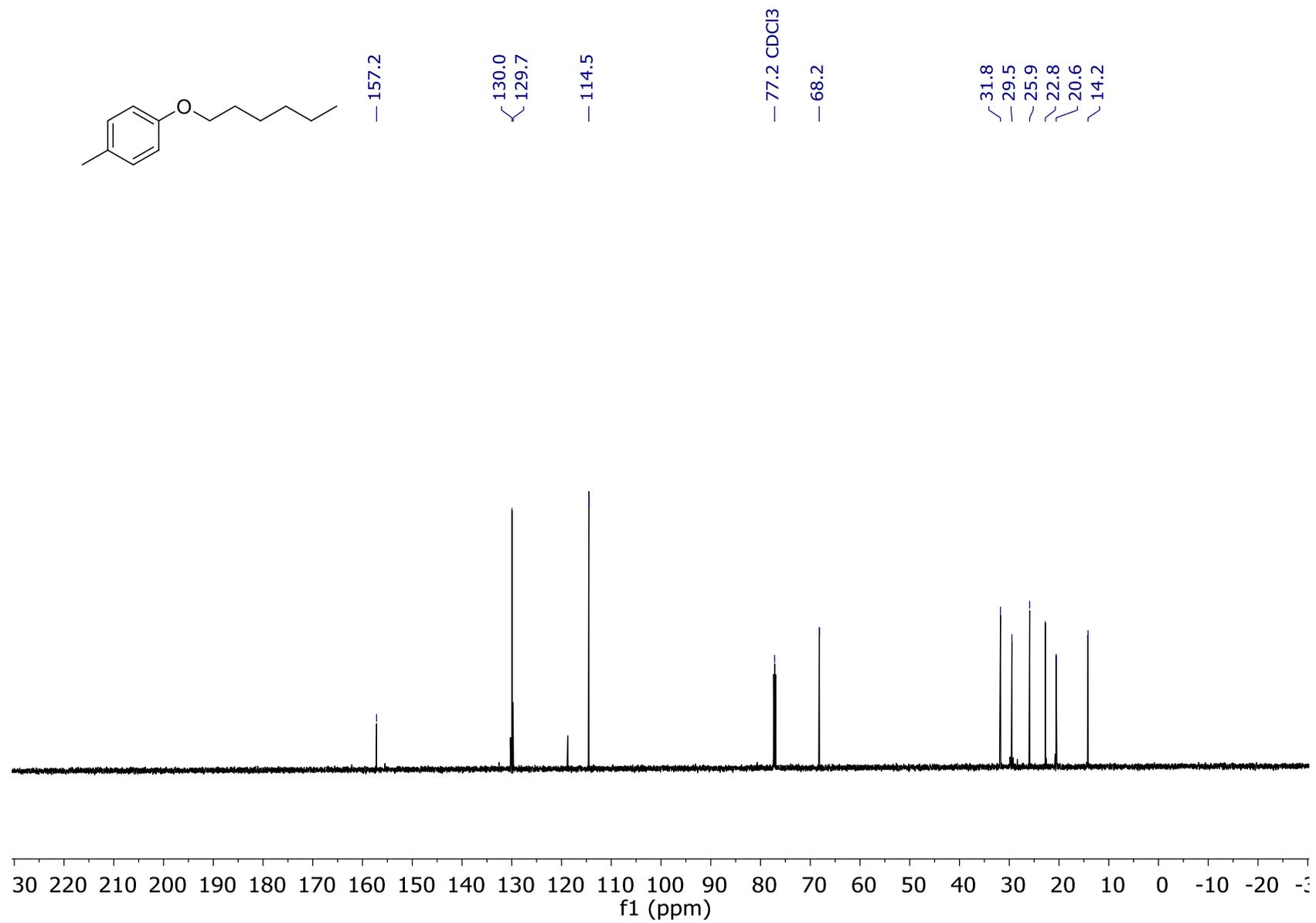


Figure S16.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform-*d*) of 1-(hexyloxy)-4-methylbenzene (2a).

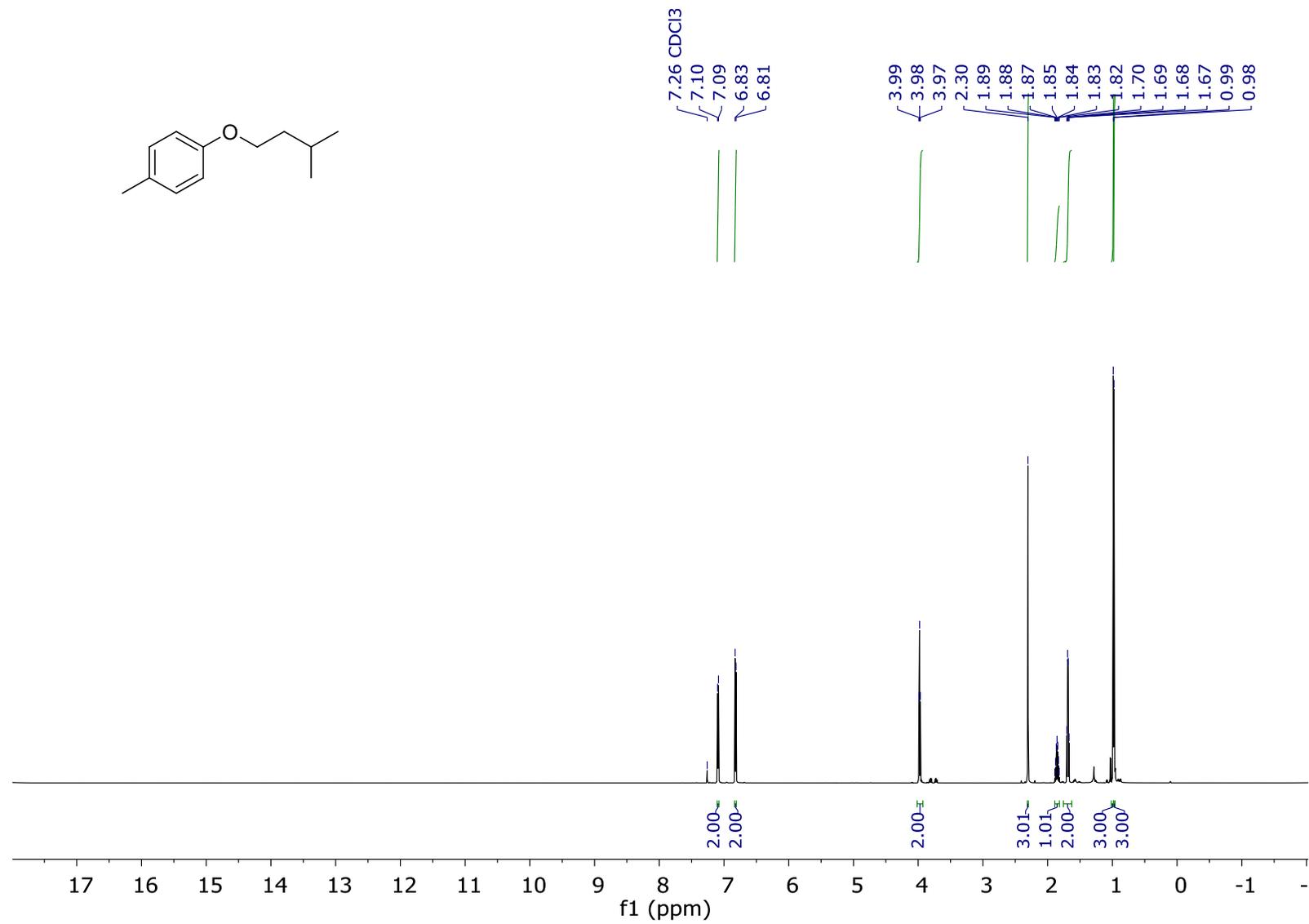


Figure S17. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) of 1-(isopentyloxy)-4-methylbenzene (2b).

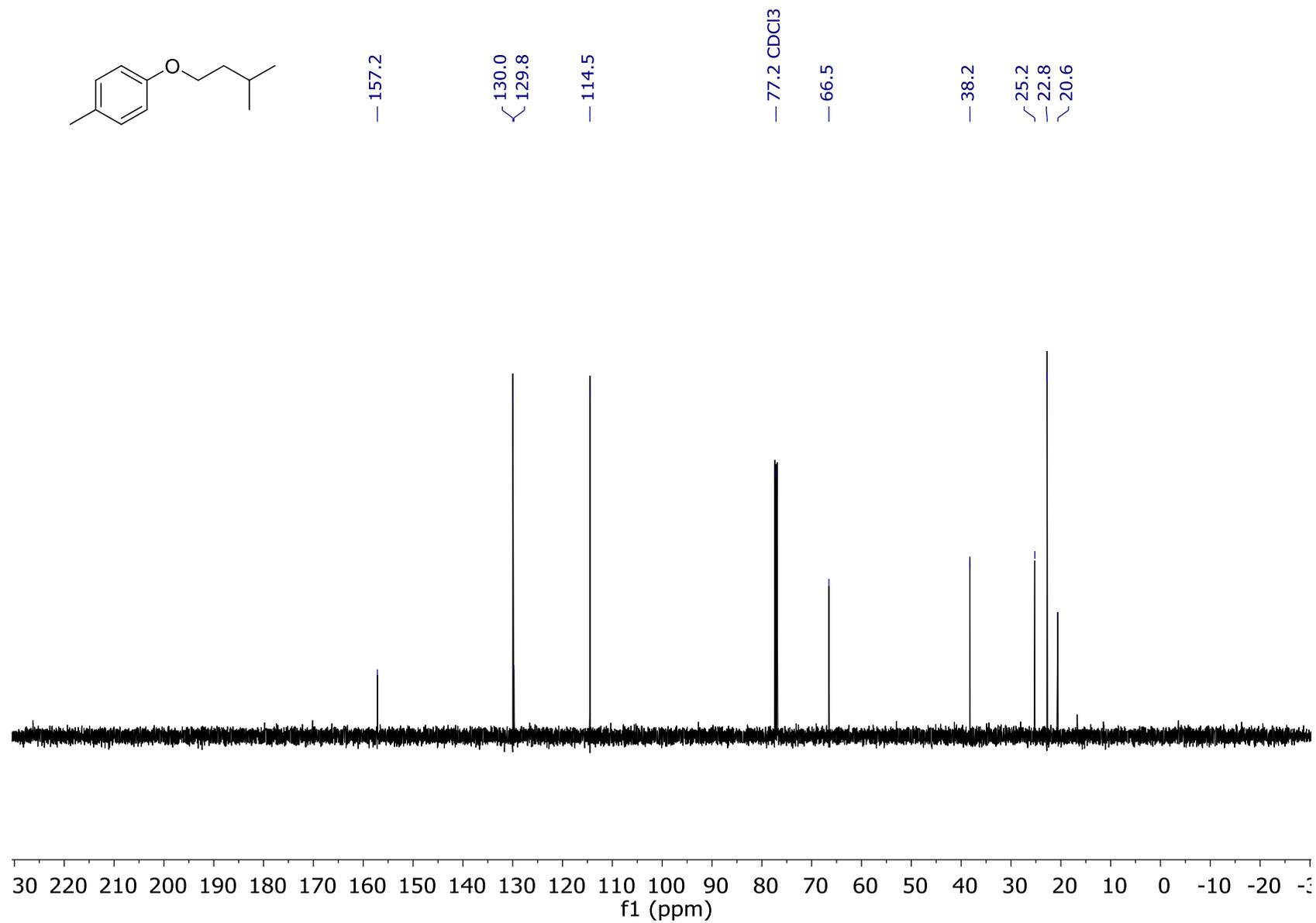
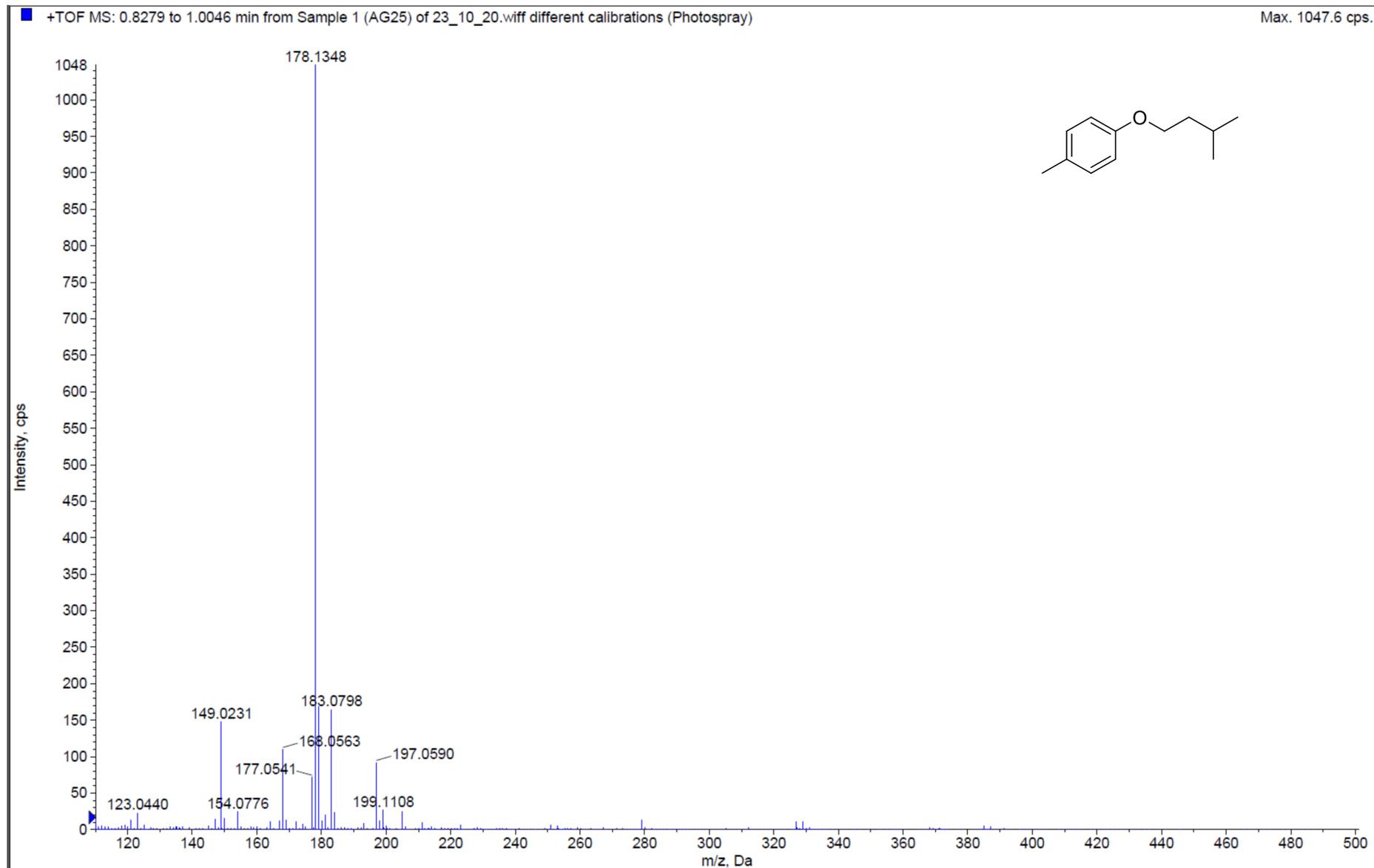


Figure S18.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform-*d*) of 1-(isopentyloxy)-4-methylbenzene (2b).



**Figure S19. HRMS Spectra of of 1-(isopentyloxy)-4-methylbenzene (2b).**

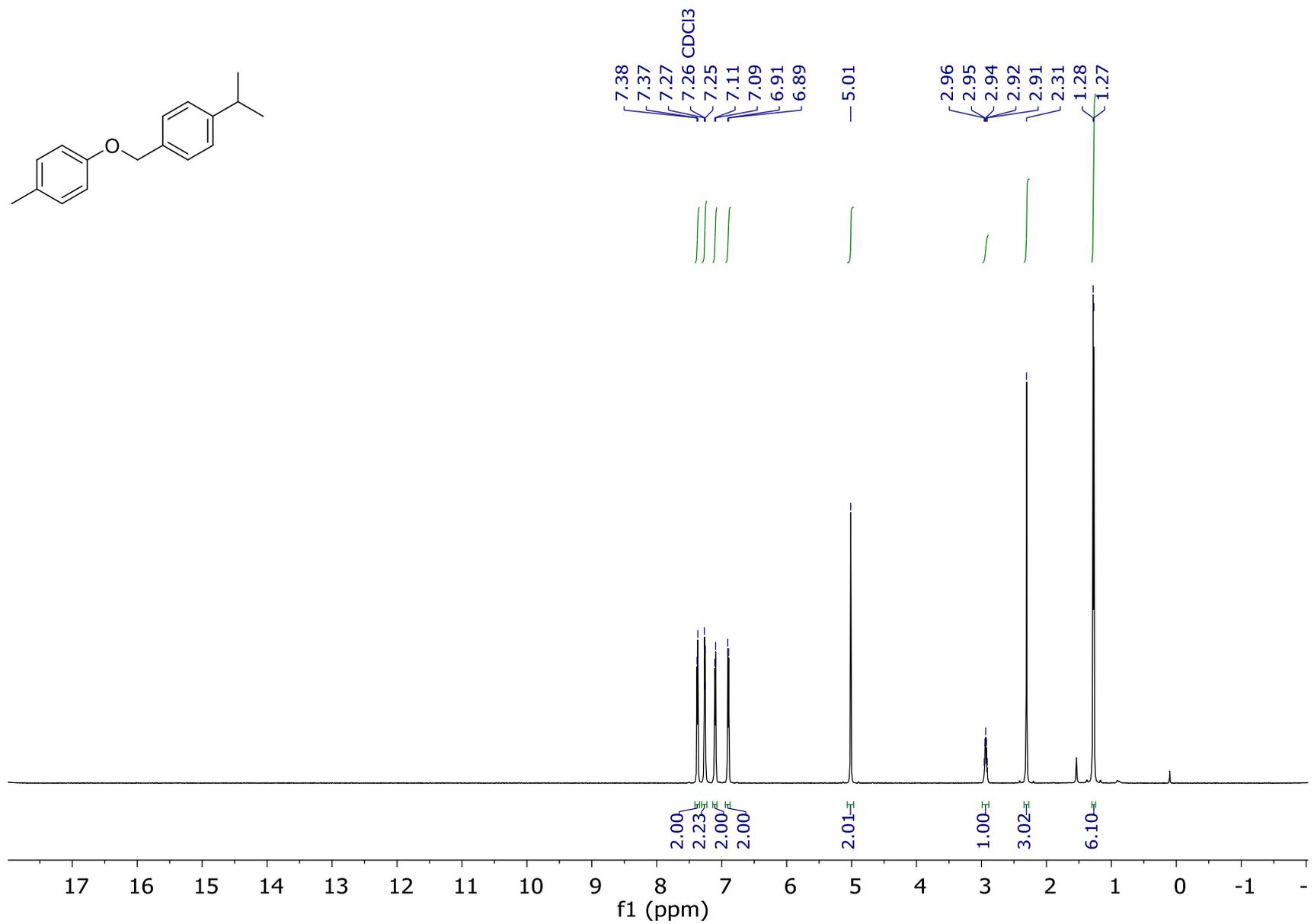


Figure S20.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*) of 1-isopropyl-4-(*p*-toloxymethyl)benzene (2c).

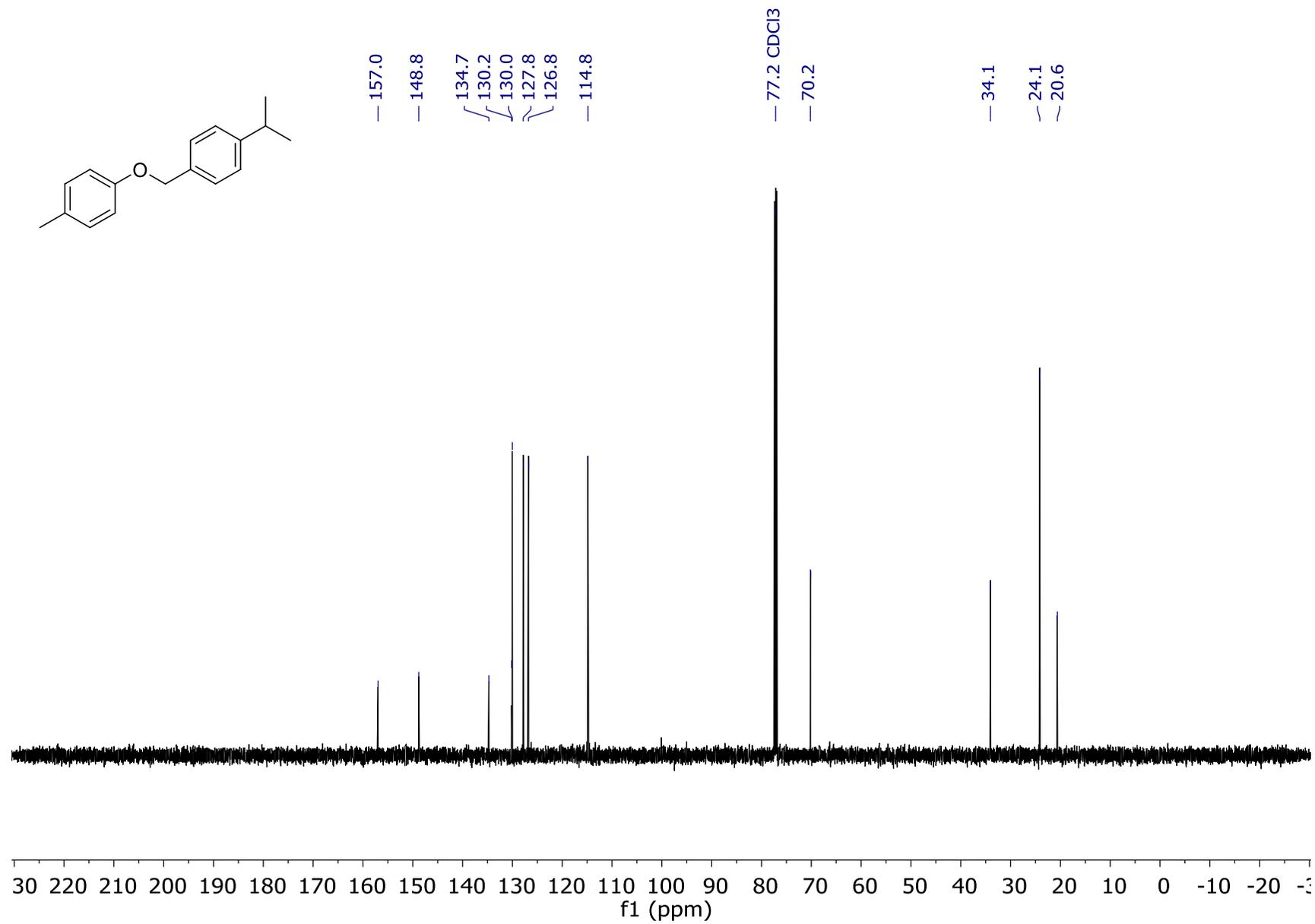
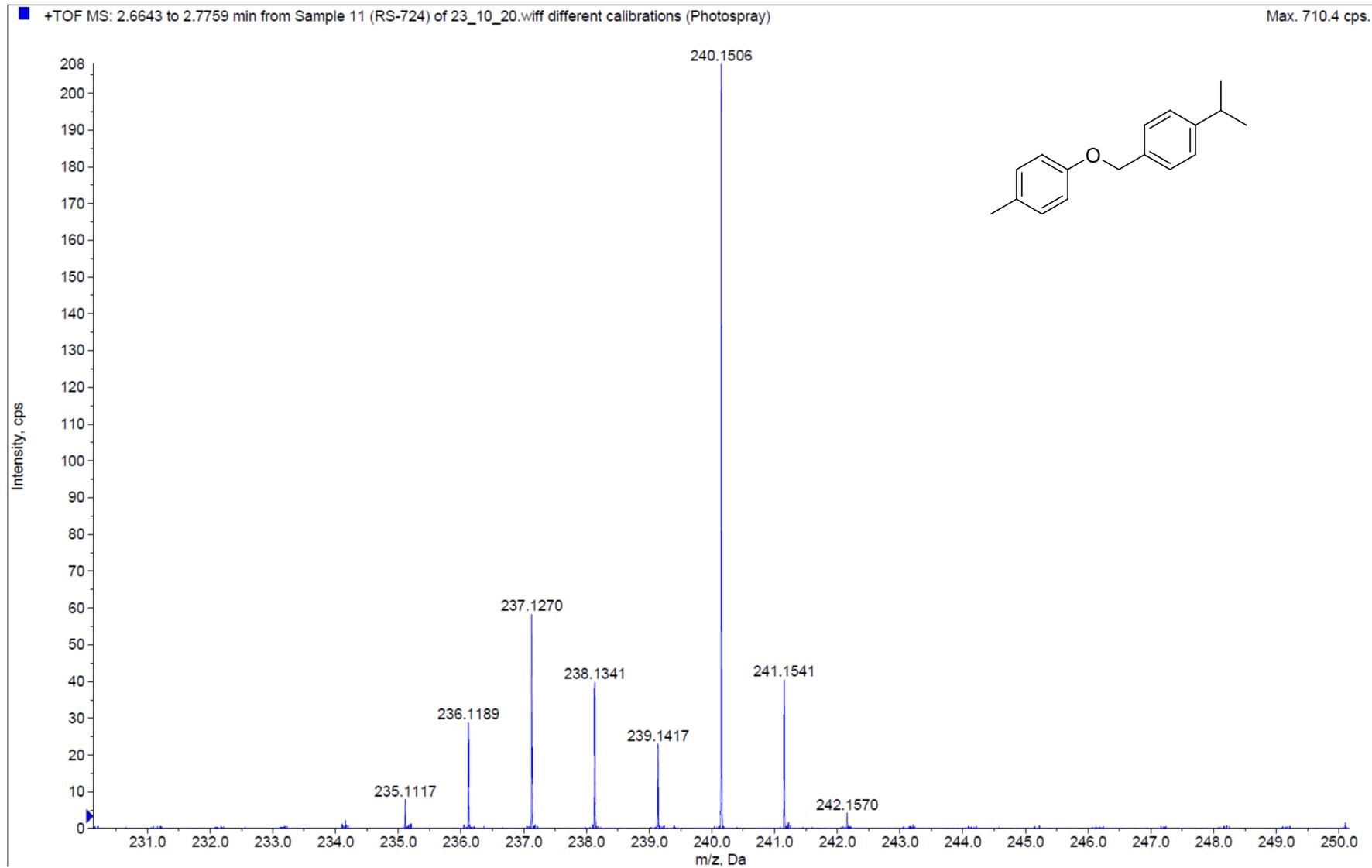


Figure S21.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform-*d*) of 1-isopropyl-4-(p-toloxymethyl)benzene (2c).



**Figure S22. HRMS Spectra of of 1-isopropyl-4-(p-toloxymethyl)benzene (2c).**

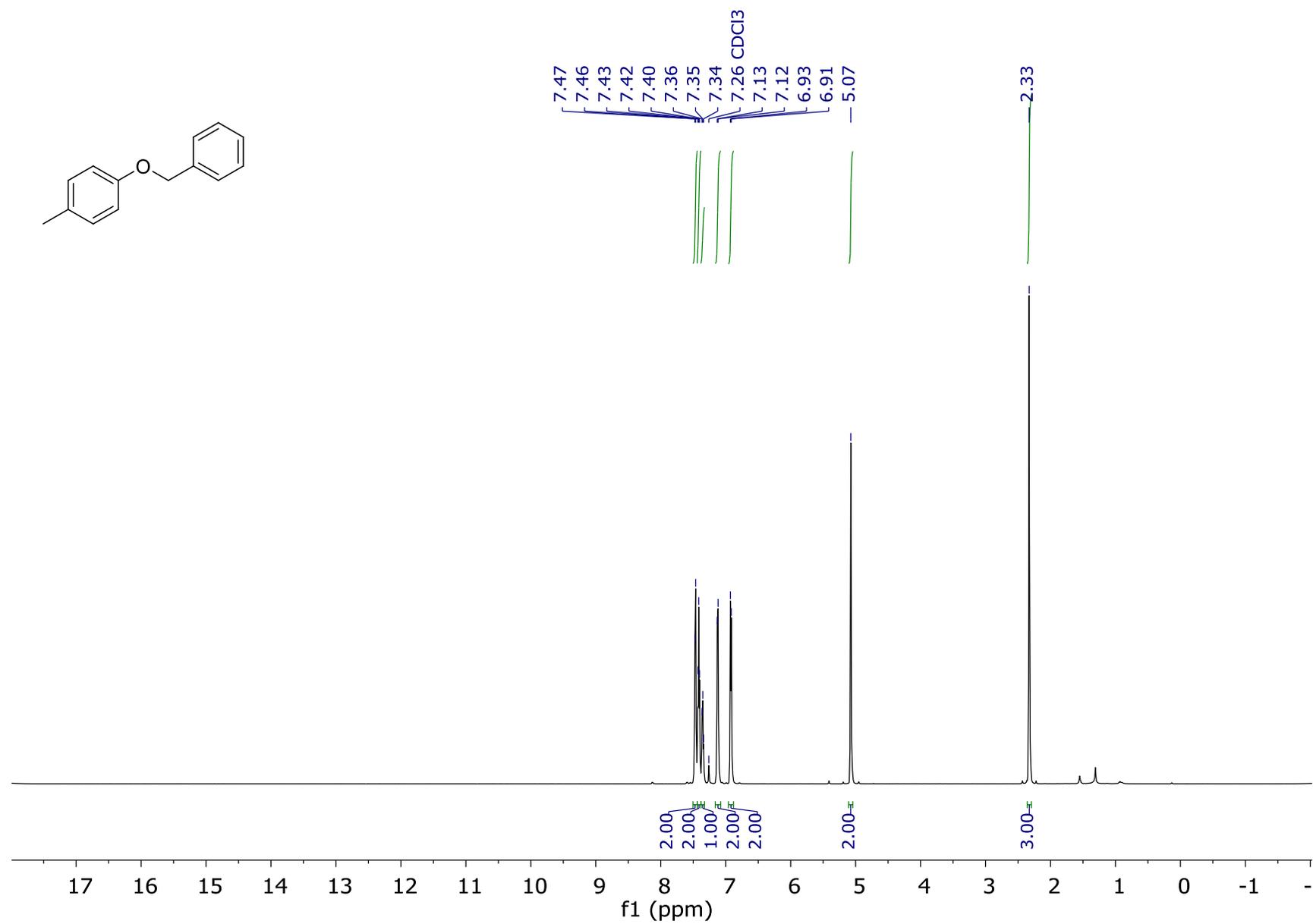


Figure S23. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) of 1-(benzyloxy)-4-methylbenzene (2d).

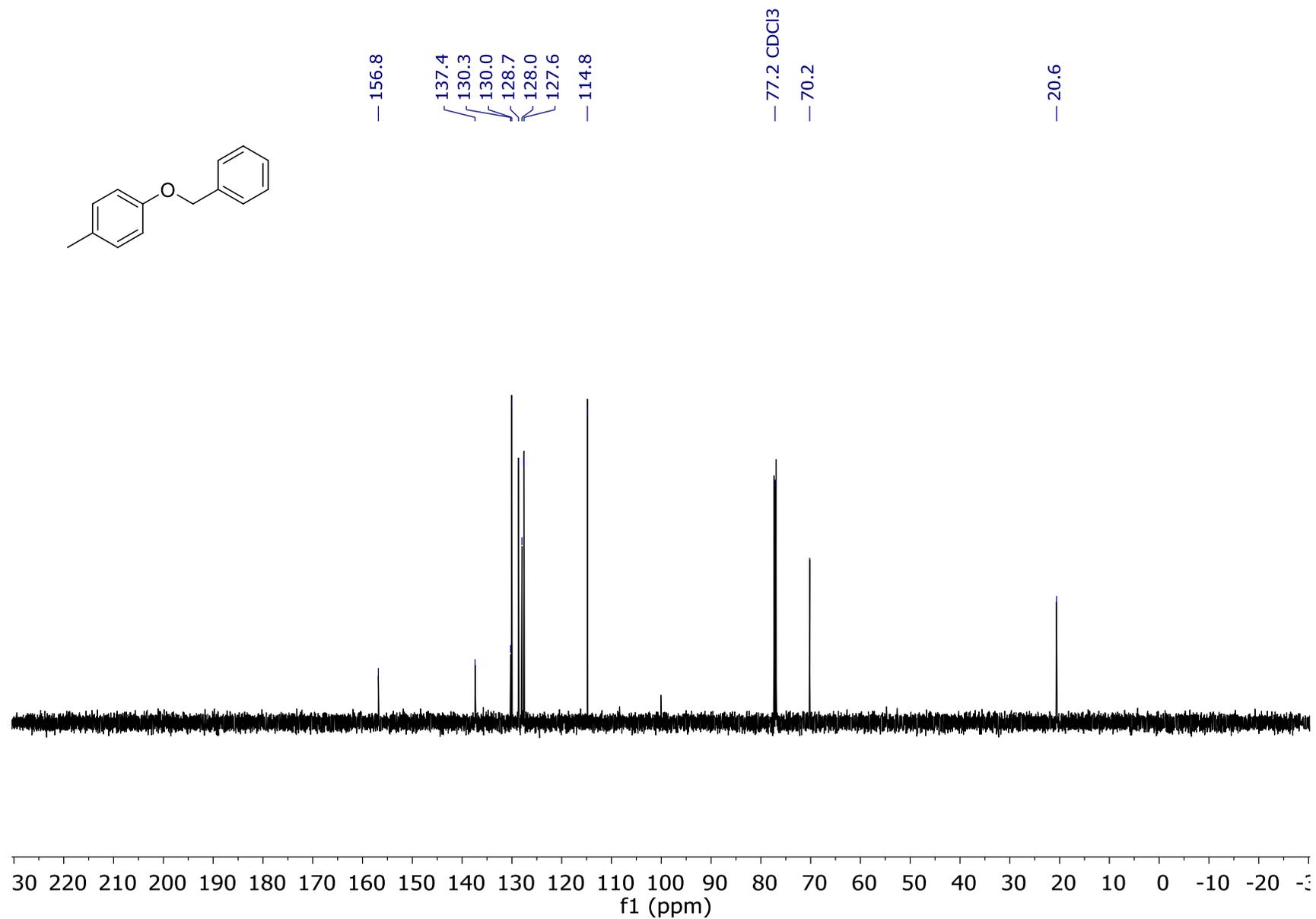


Figure S24.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform-*d*) of 1-(benzyloxy)-4-methylbenzene (2d).

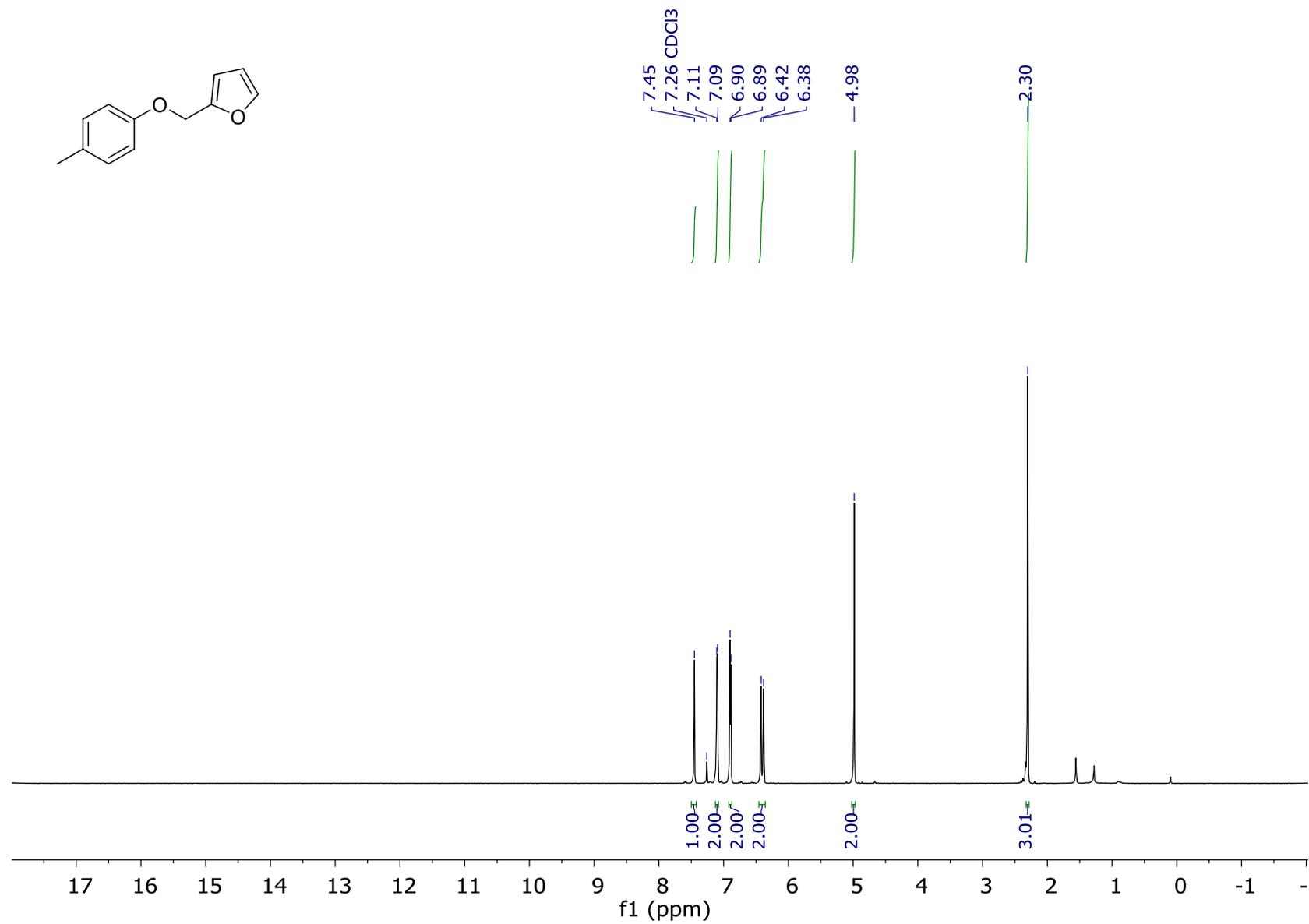


Figure S25. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) of 2-(p-toloxymethyl)furan (2e).

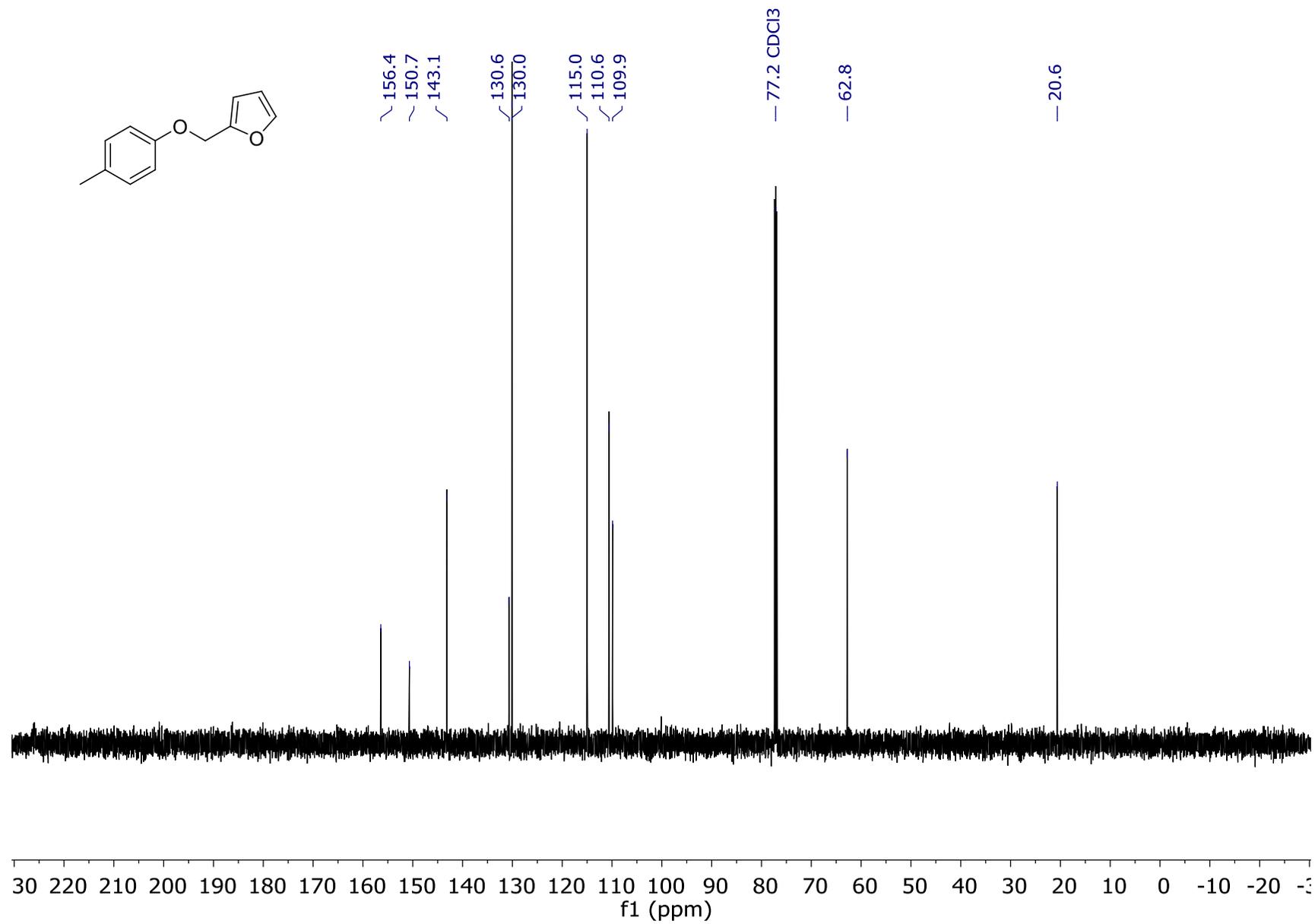
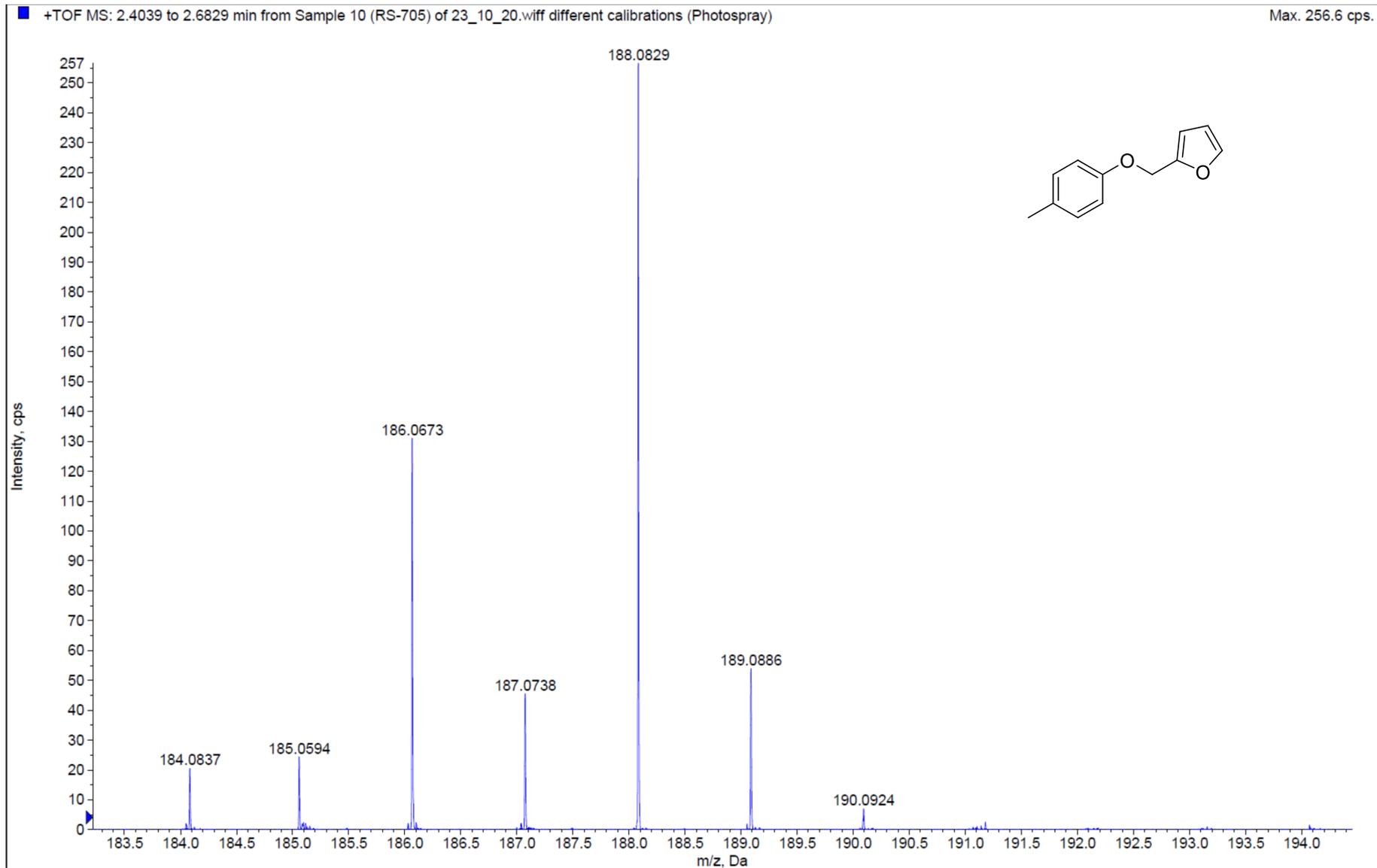


Figure S26.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform-*d*) of 2-(p-tolyloxymethyl)furan (2e).



**Figure S27. HRMS Spectra of of 2-(p-toloxymethyl)furan (2e).**

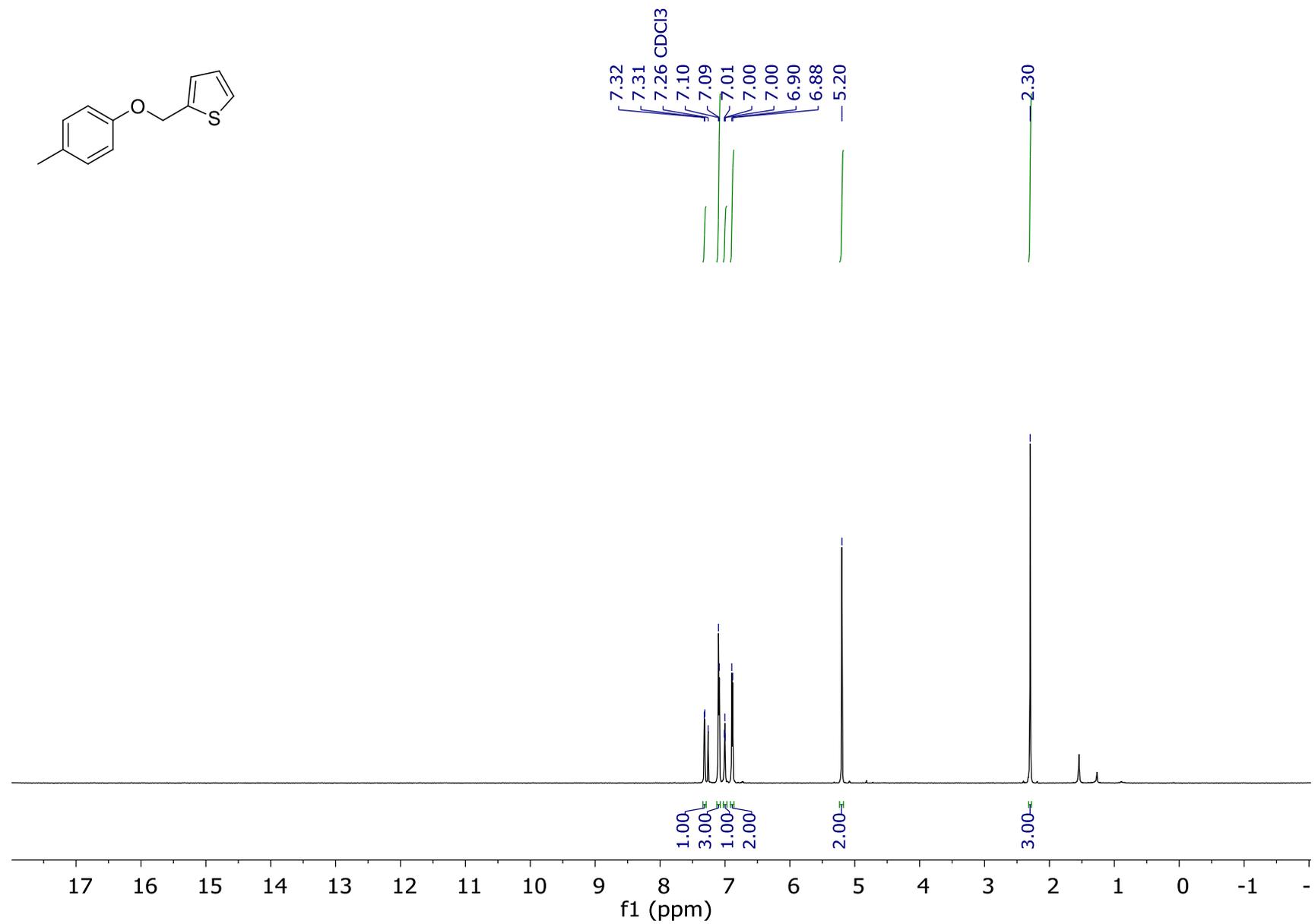


Figure S28. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) of 2-(p-toloxymethyl)thiophene (2f).

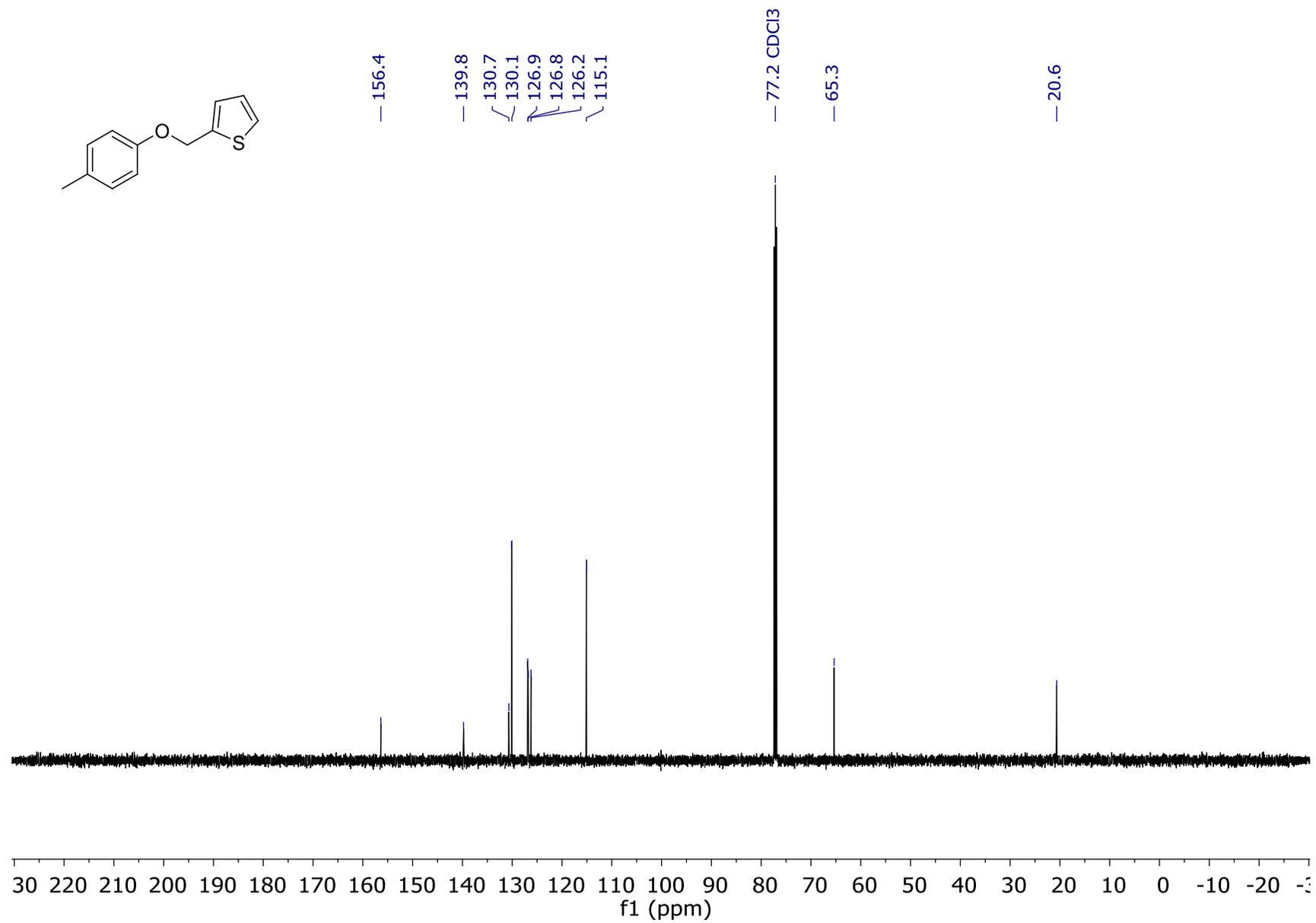


Figure S29.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform-*d*) of 2-(p-toloxymethyl)thiophene (2f).

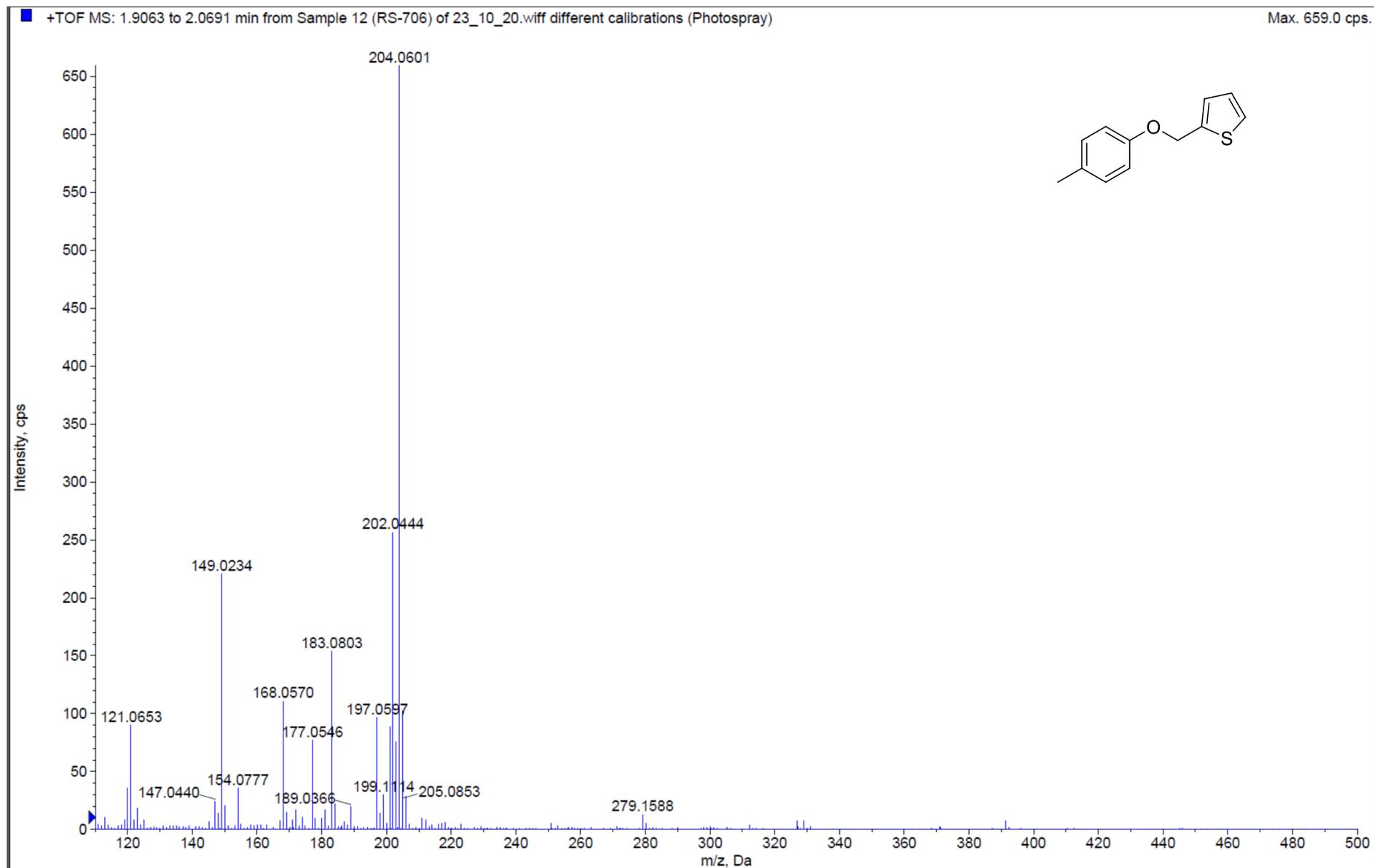


Figure S30. HRMS Spectra of of 2-(p-toloxymethyl)thiophene (2f).

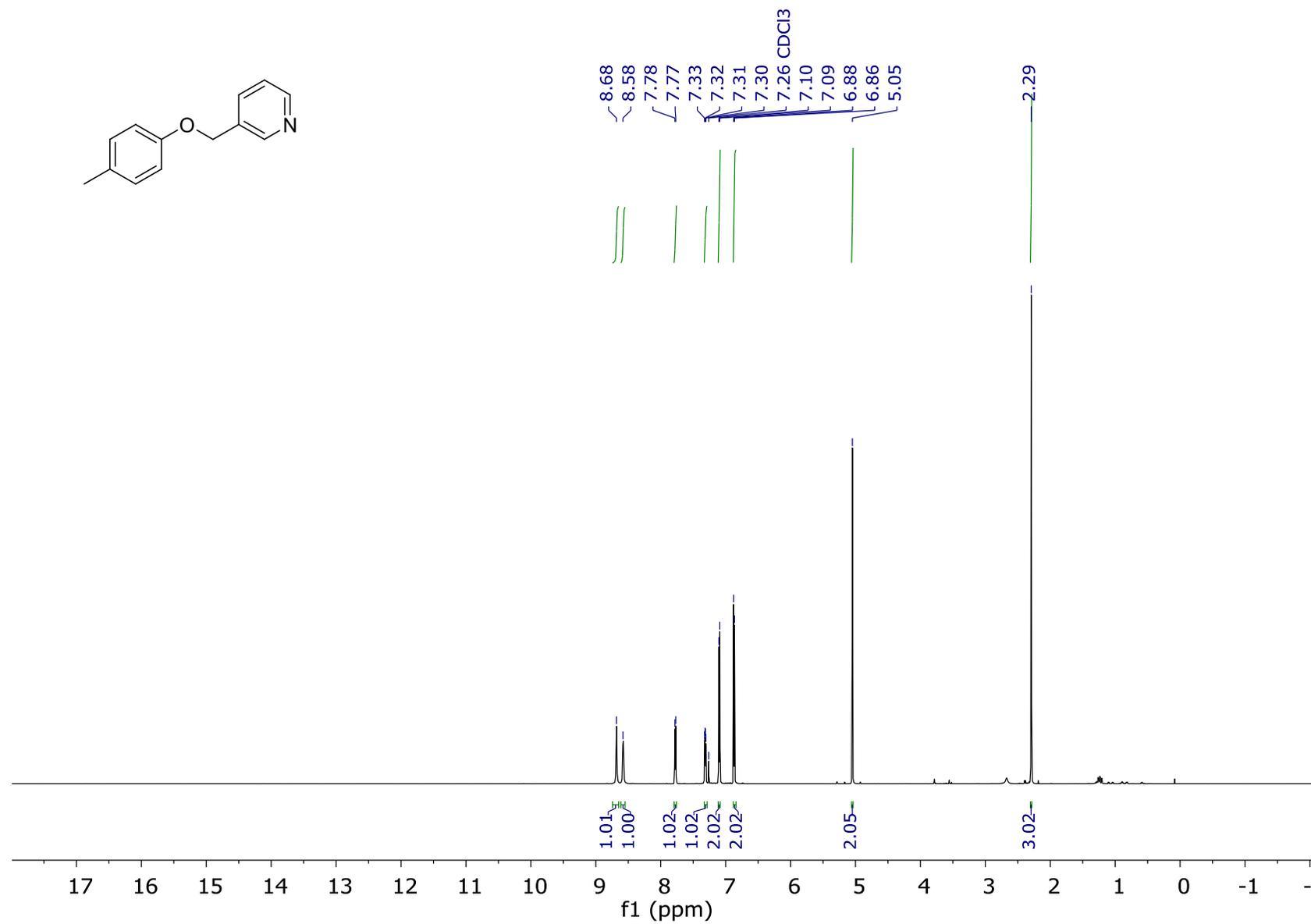


Figure S31. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) of 3-(p-toloxymethyl)pyridine (2g).

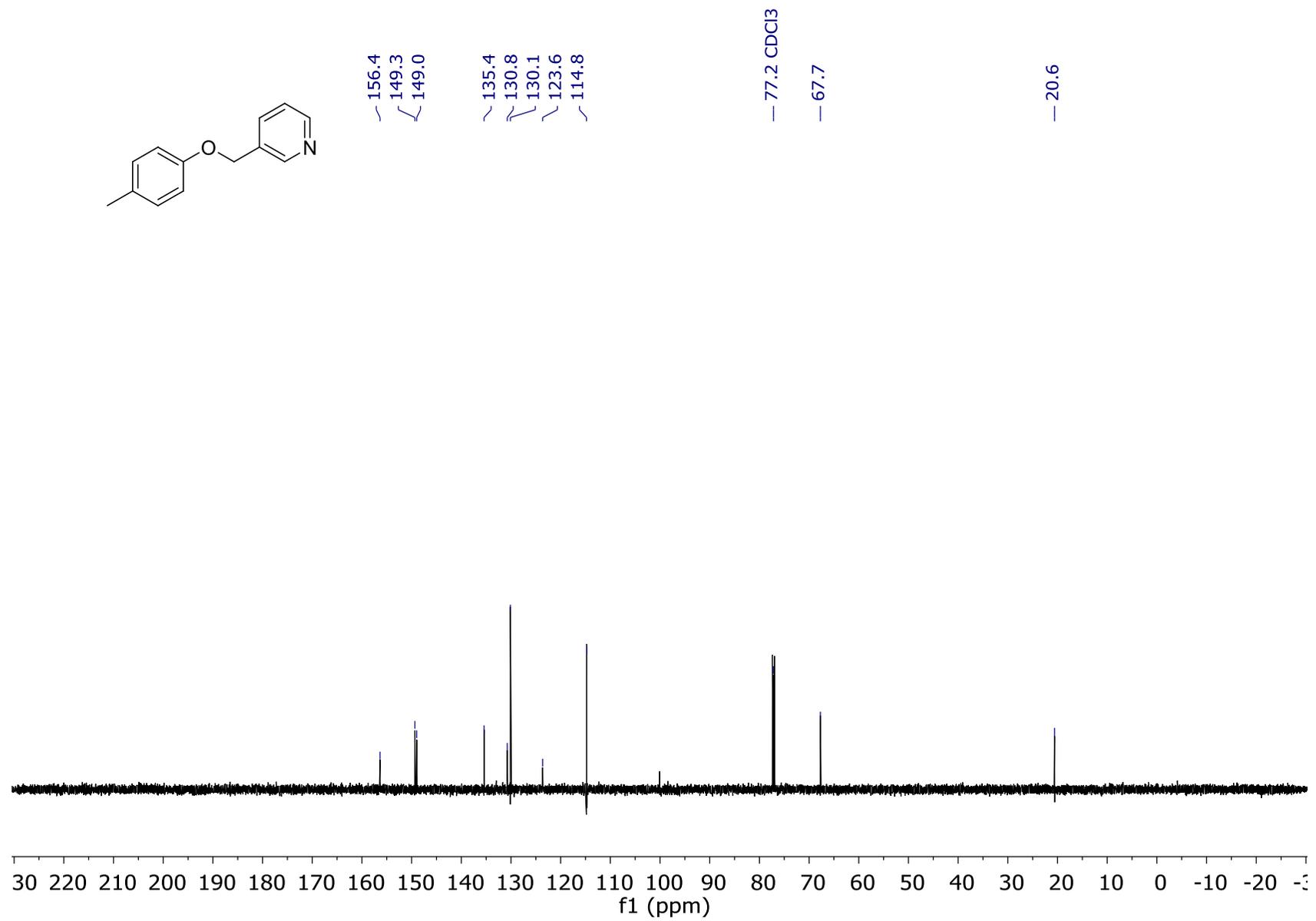


Figure S32.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform-*d*) of 3-(p-toloxymethyl)pyridine (2g).

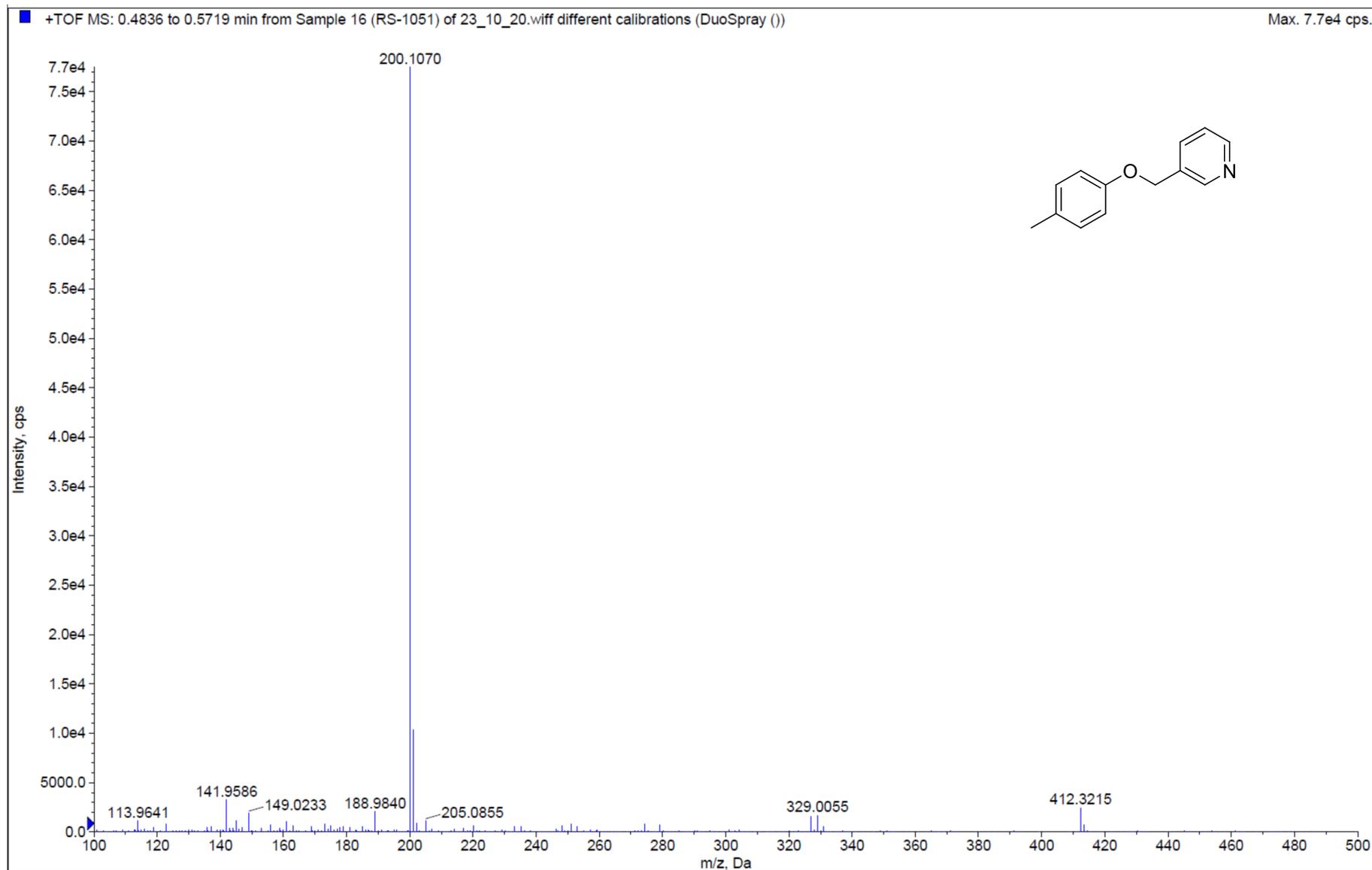


Figure S33. HRMS Spectra of of of 3-(p-toloxymethyl)pyridine (2g).

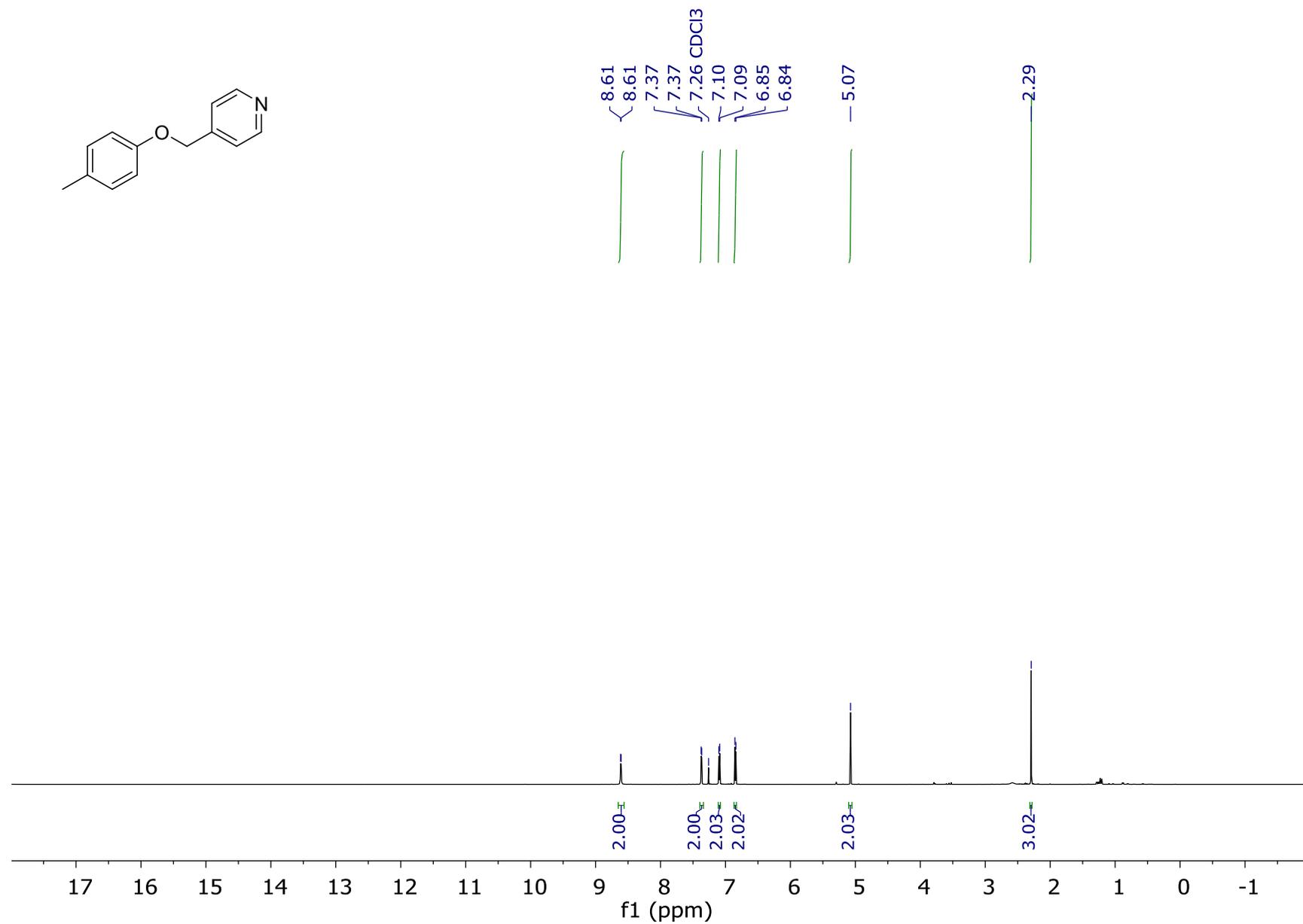


Figure S34. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) of 4-(p-toloxymethyl)pyridine (2h).

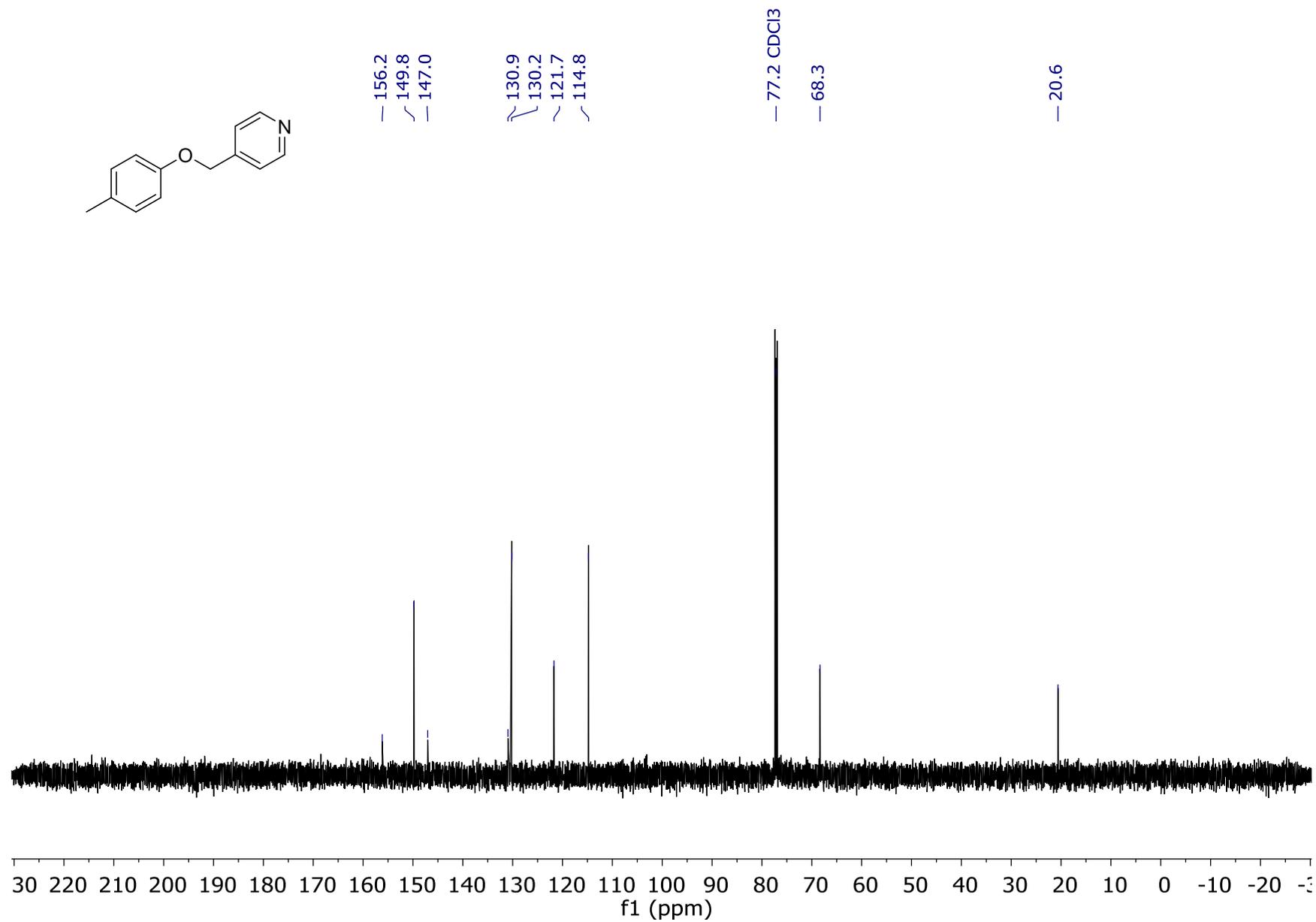


Figure S35.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform-*d*) of 4-(p-tolyloxymethyl)pyridine (2h).

+TOF MS: 0.9532 to 1.0880 min from Sample 15 (RS-1052) of 23\_10\_20.wiff different calibrations (DuoSpray ())

Max. 8.8e5 cps.

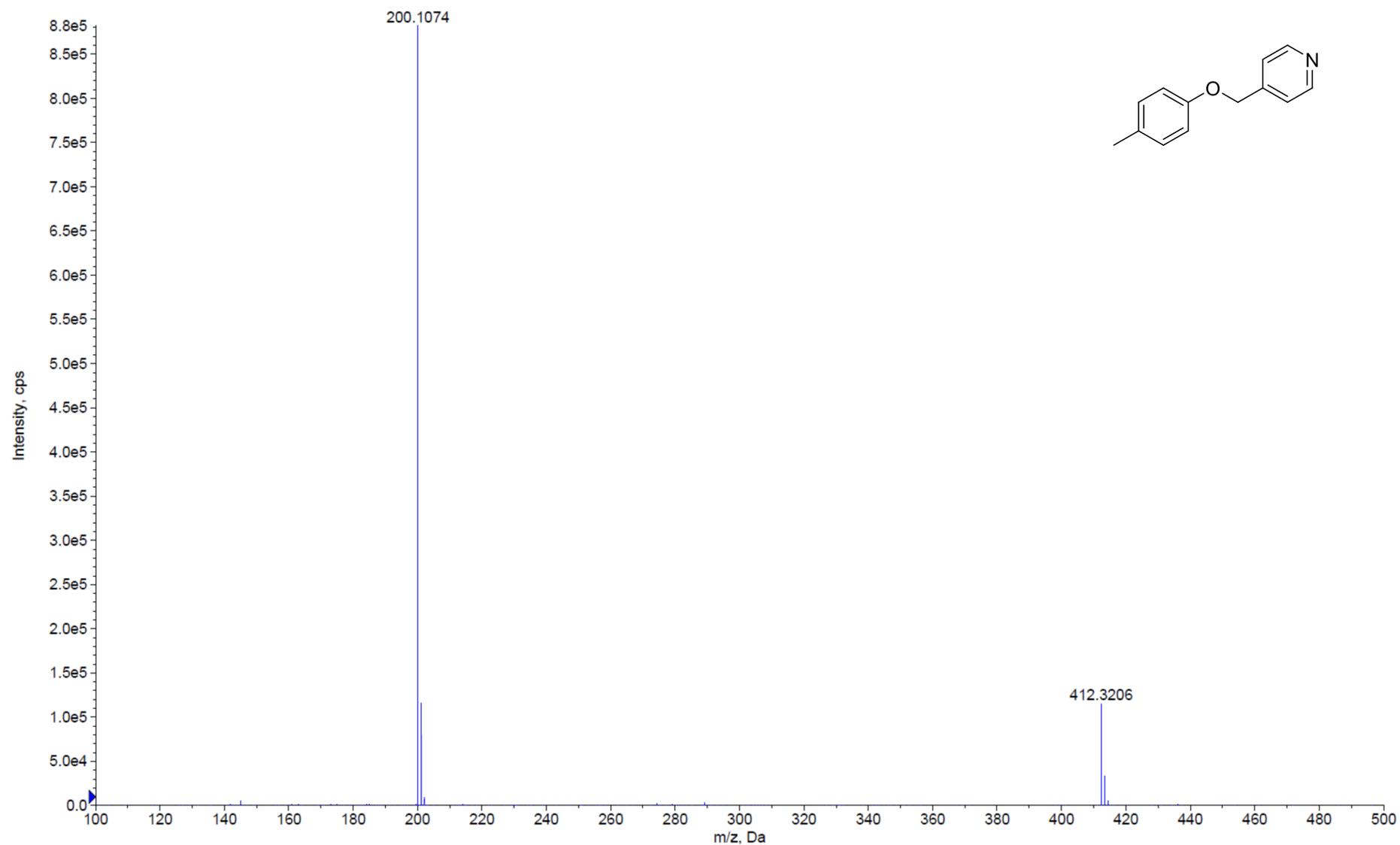


Figure S36. HRMS of of 4-(p-toloxymethyl)pyridine (2h).

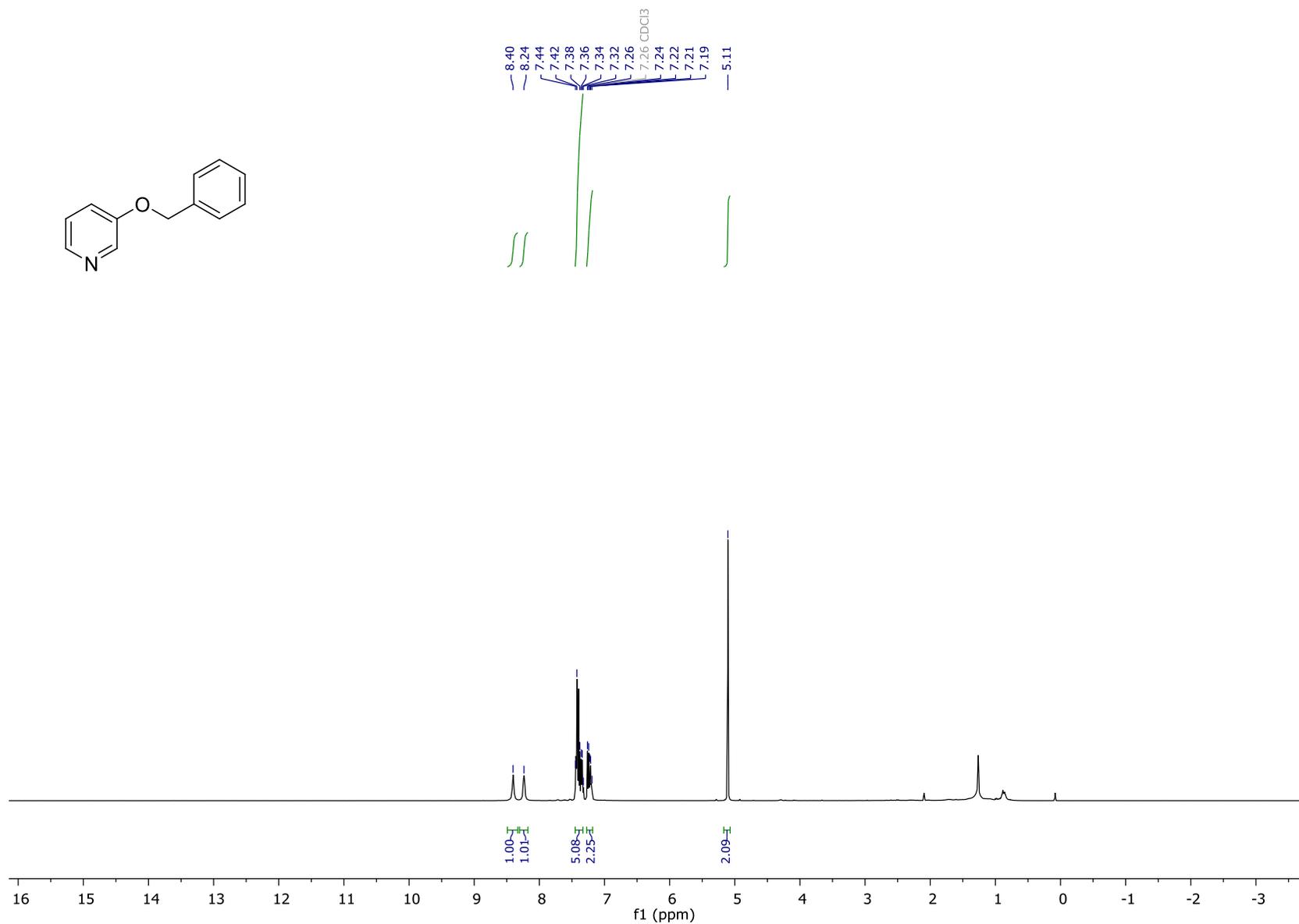


Figure S37. <sup>1</sup>H NMR (400 MHz, Chloroform-d) of 3-(benzyloxy)pyridine (2i)

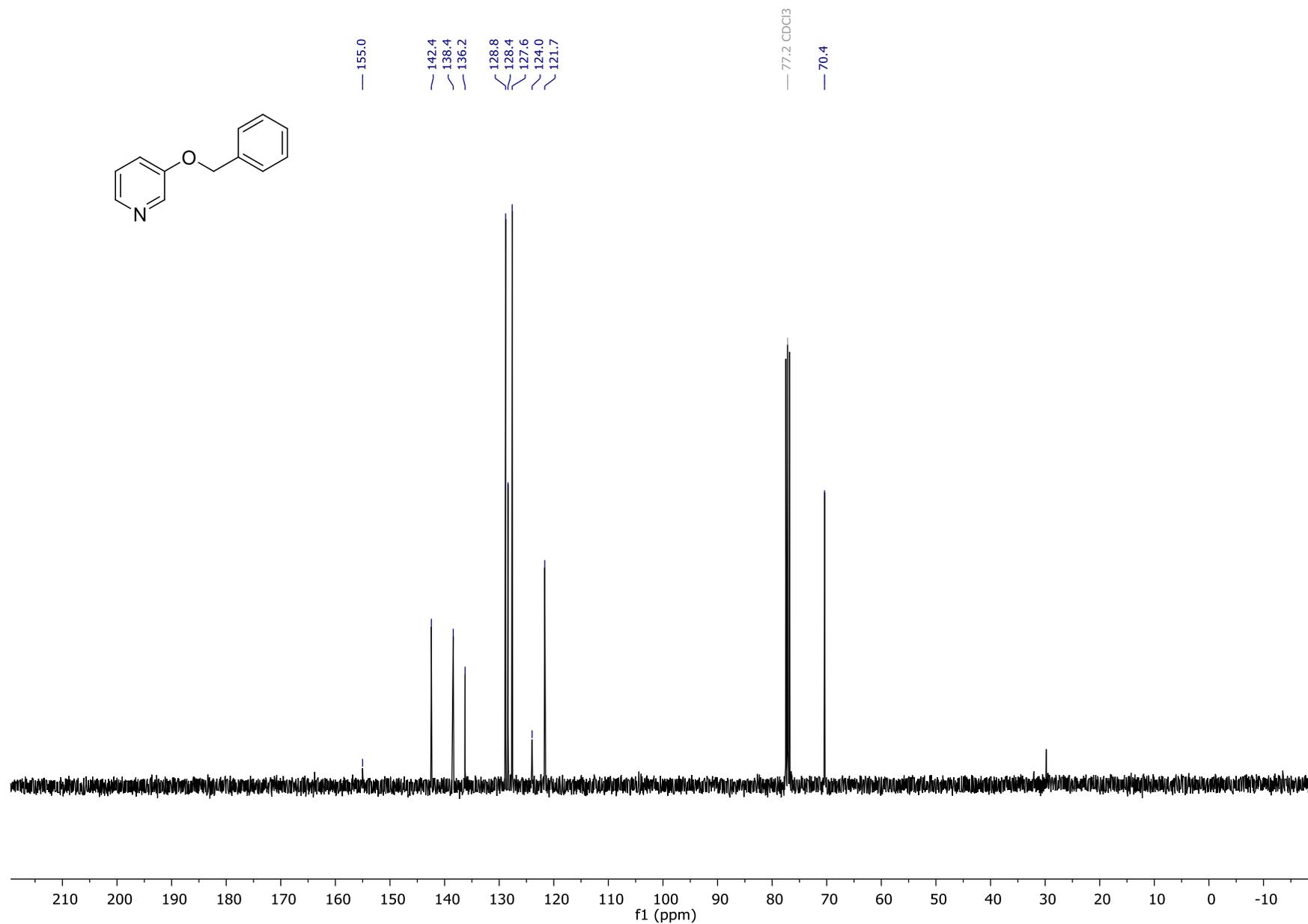


Figure S38.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform-d) of 3-(benzyloxy)pyridine (2i)

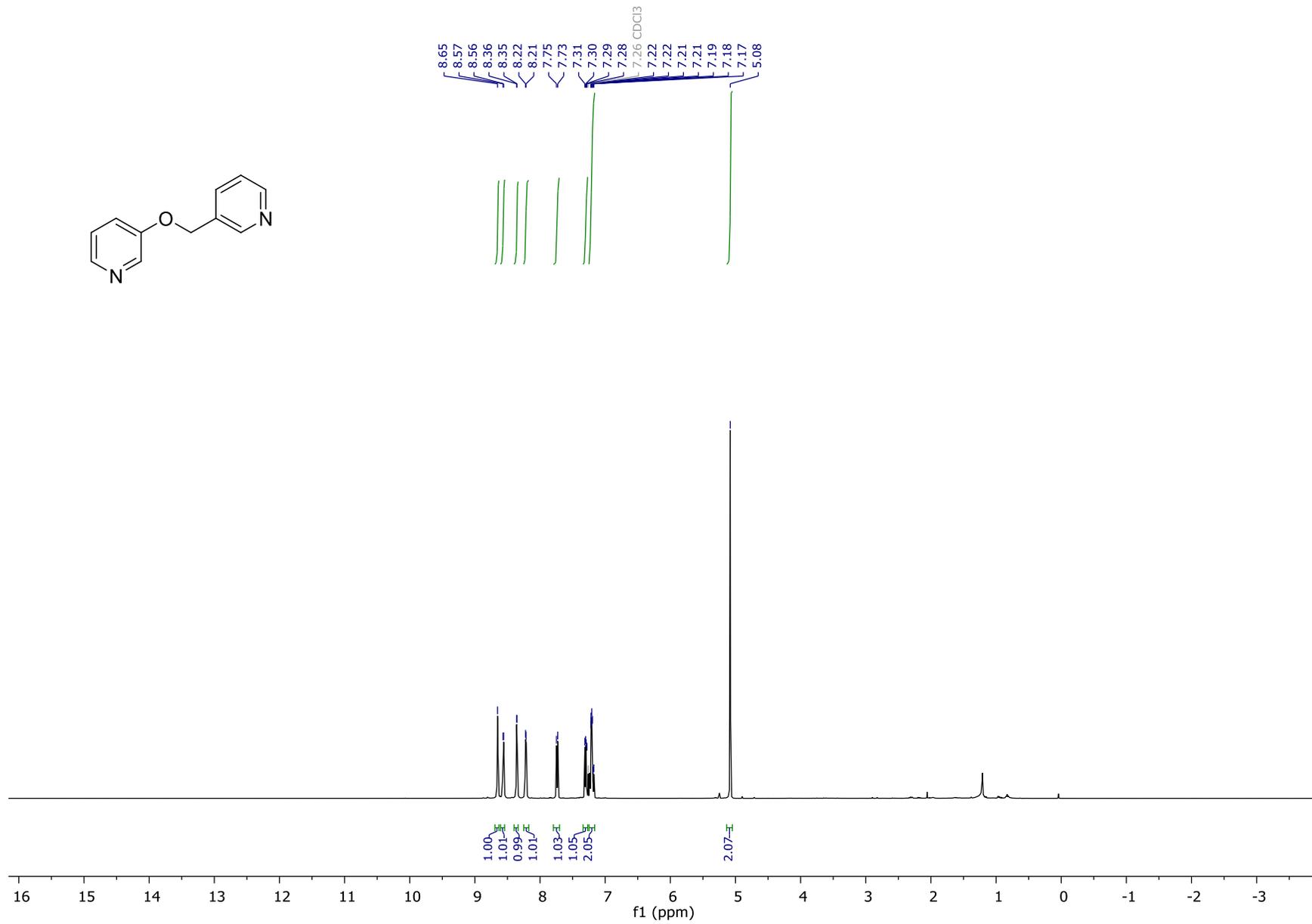


Figure S39. <sup>1</sup>H NMR (101 MHz, Chloroform-*d*) of 3-(pyridin-3-ylmethoxy)pyridine (2j).

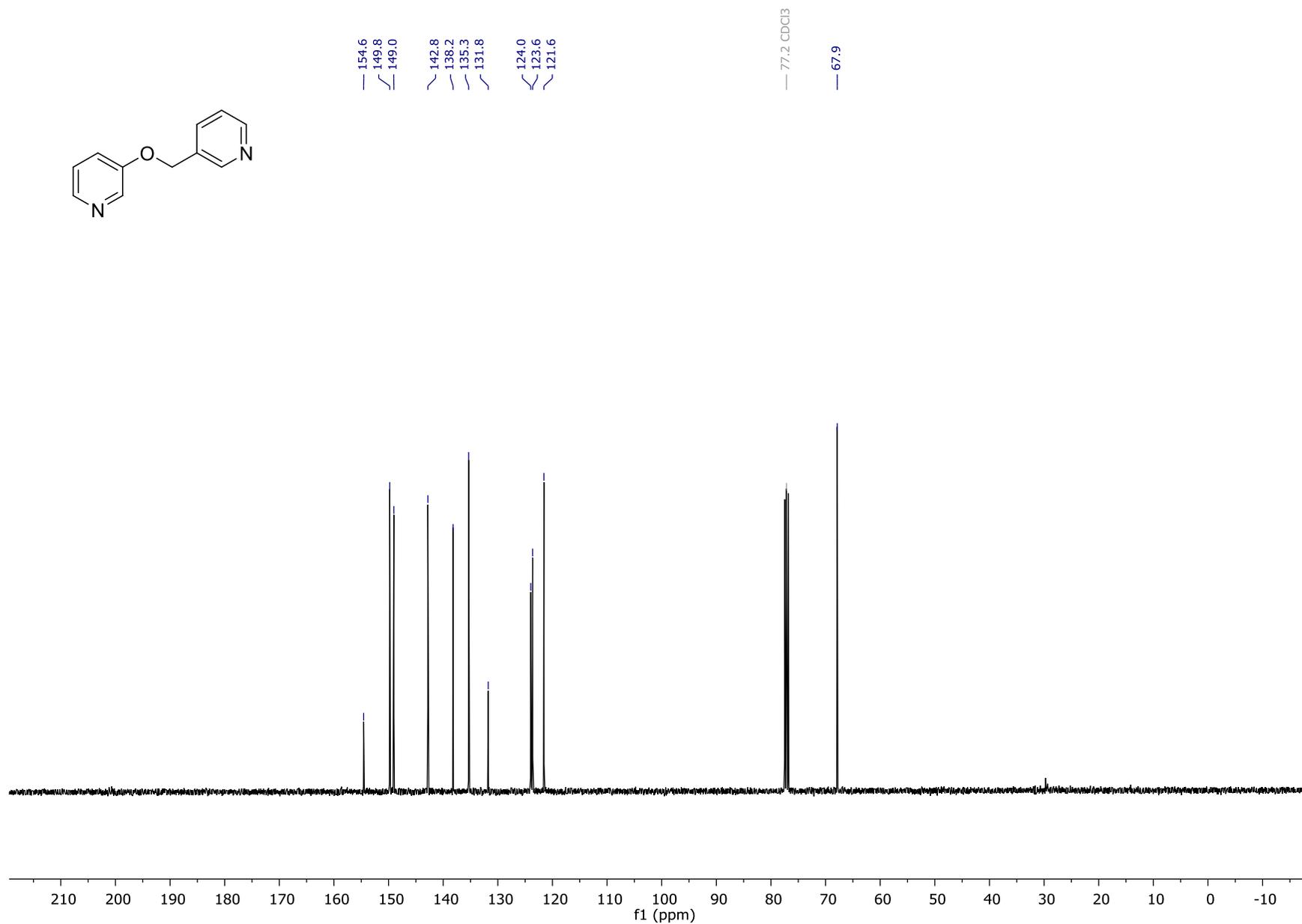


Figure S40.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform-*d*) of 3-(pyridin-3-ylmethoxy)pyridine (2j).

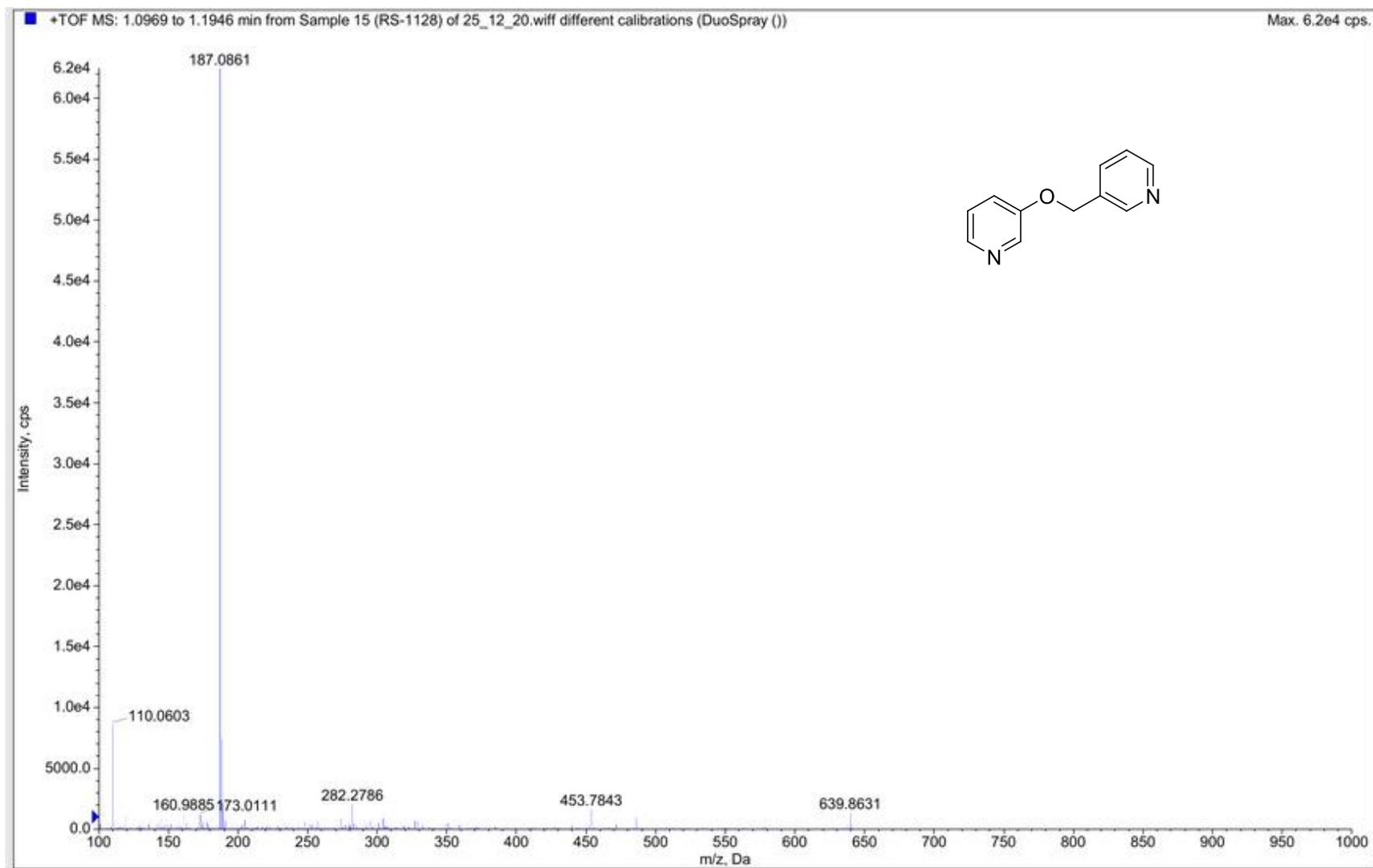


Figure S41. HRMS of 3-(pyridin-3-ylmethoxy)pyridine (2j).

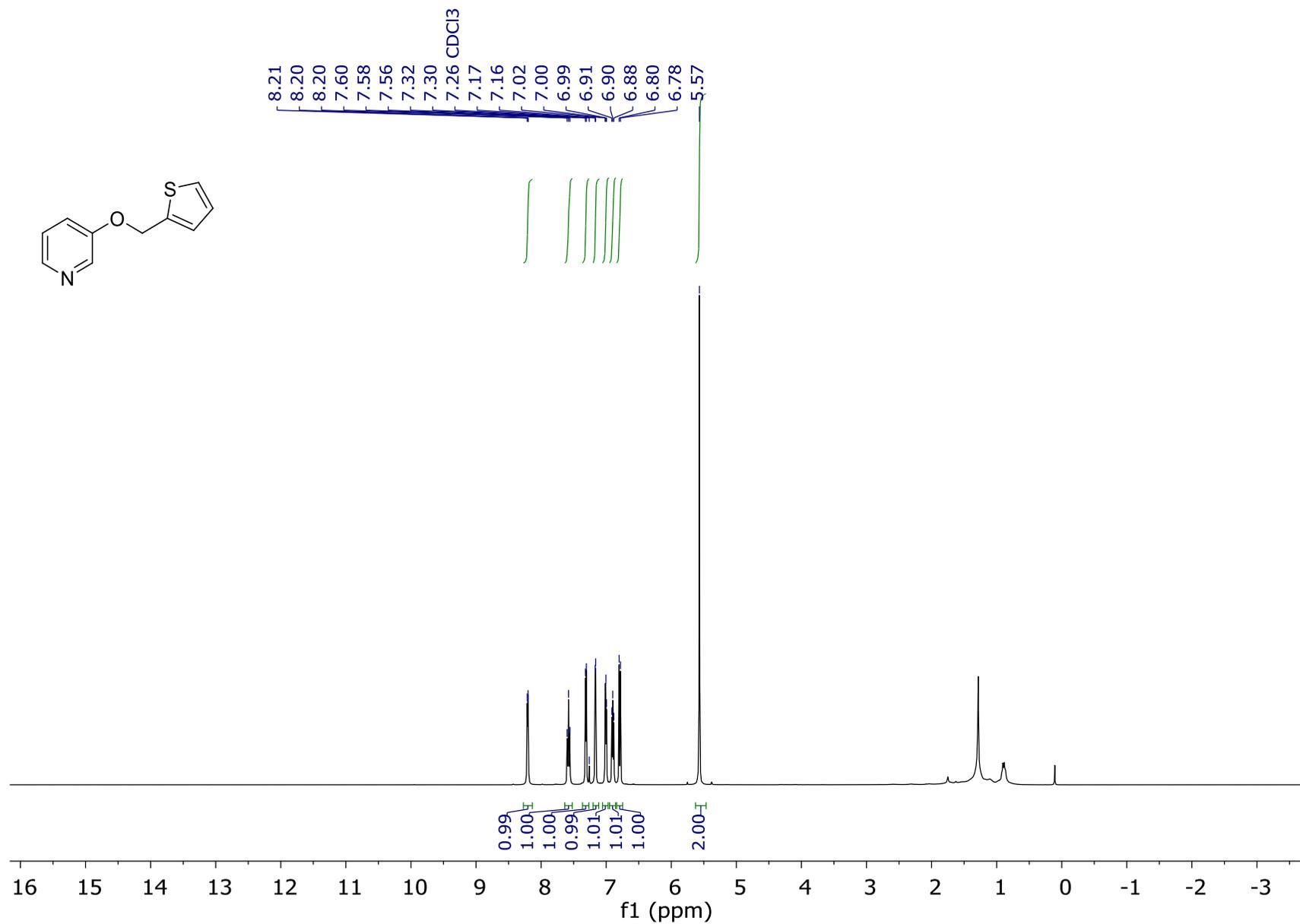


Figure S42. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) of 3-(thiophen-2-ylmethoxy)pyridine (2k).

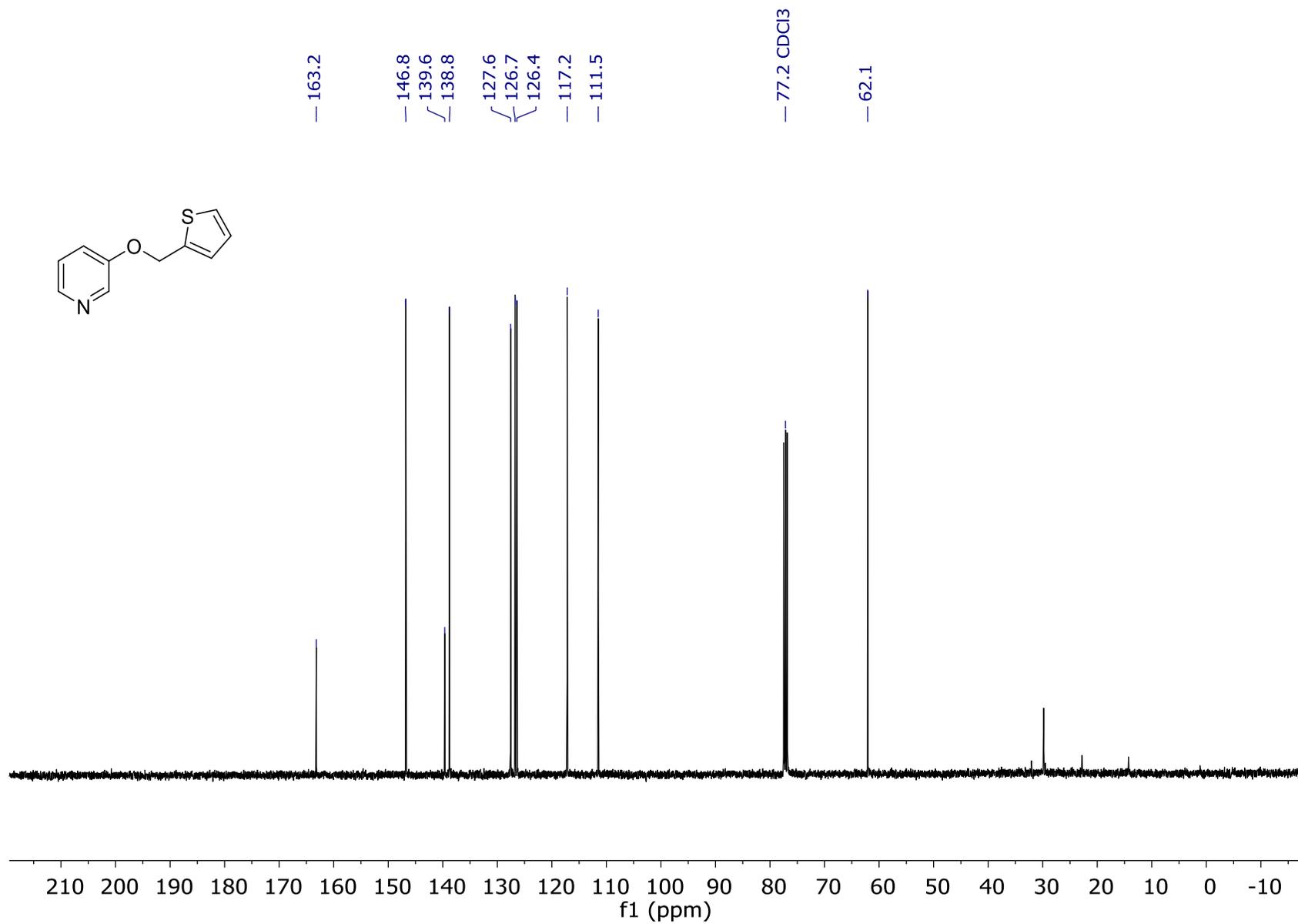


Figure S43.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform-*d*) of 3-(thiophen-2-ylmethoxy)pyridine (2k).

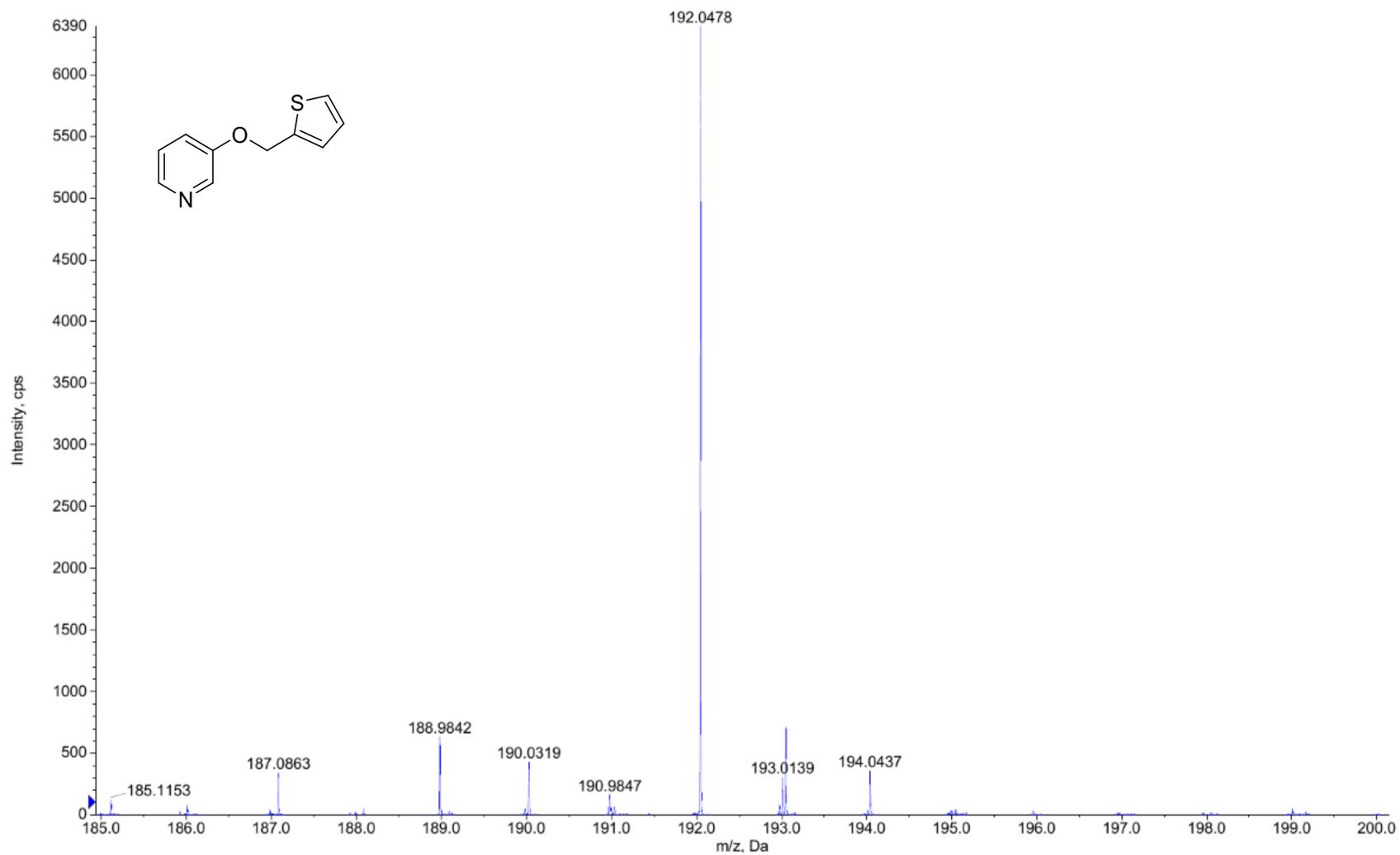


Figure S44. HRMS of 3-(thiophen-2-ylmethoxy)pyridine (2k)

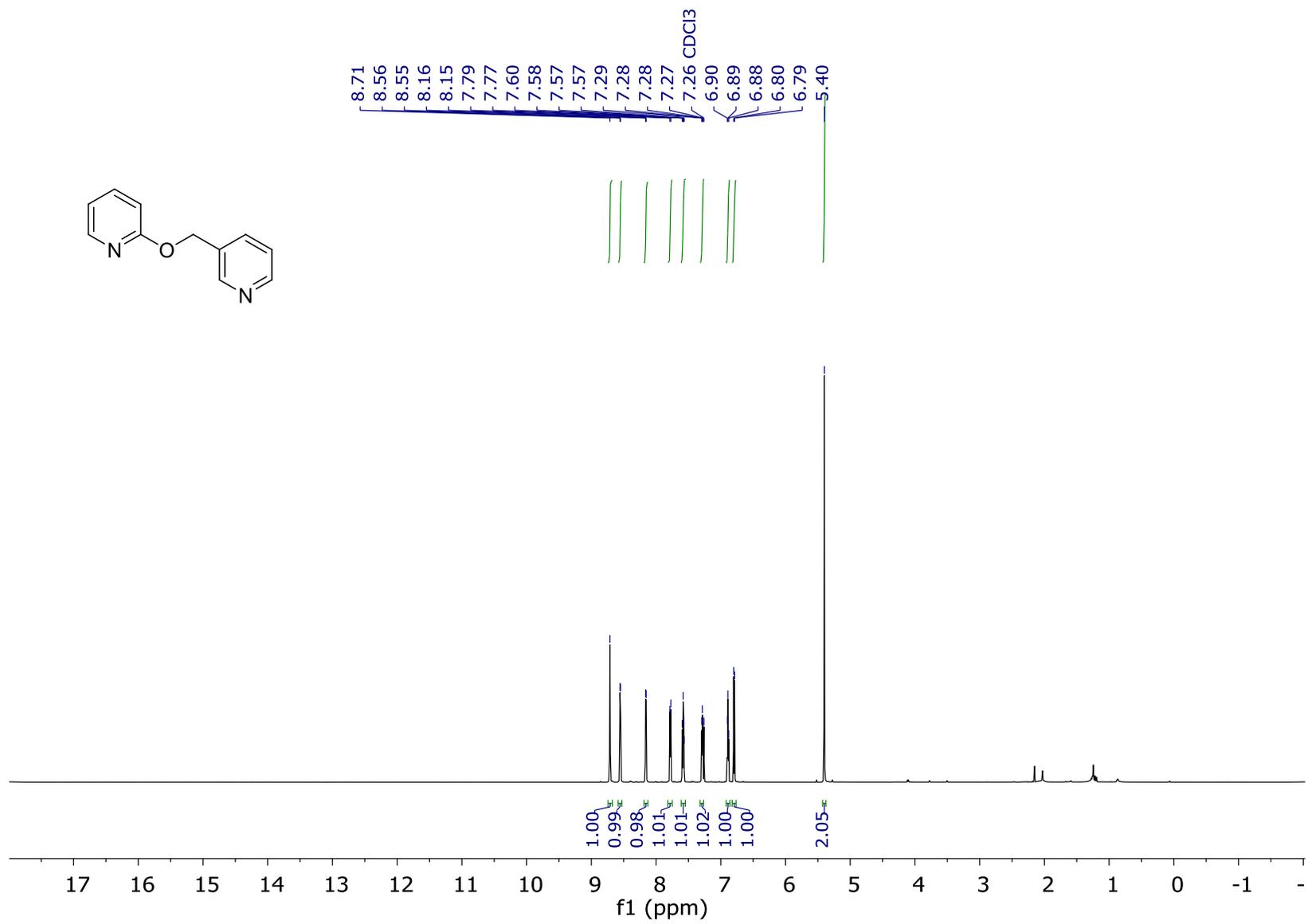


Figure S45. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) of 3-(pyridin-3-ylmethoxy)pyridine (2l).

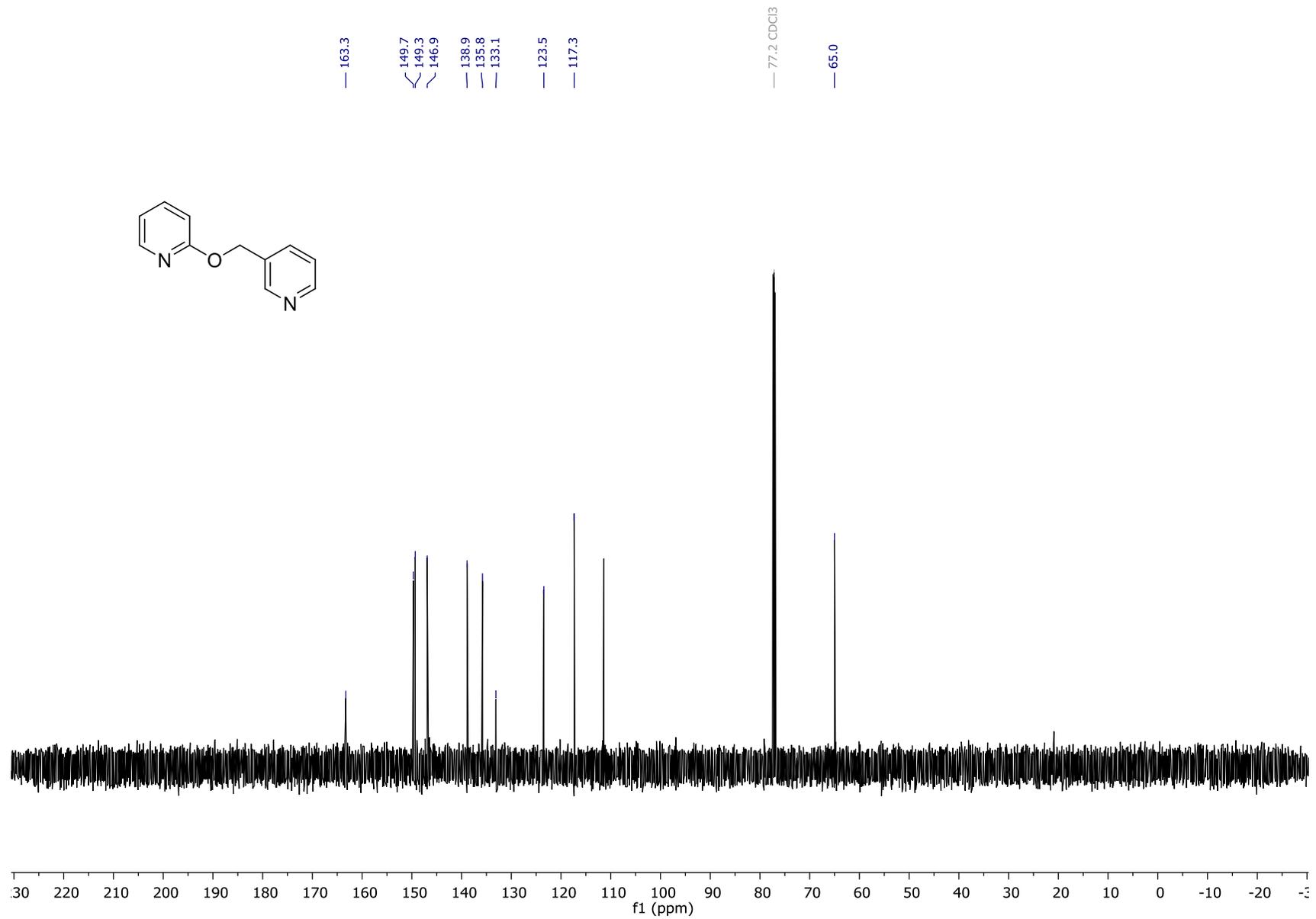


Figure S46.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform-*d*) of 3-(pyridin-3-ylmethoxy)pyridine (2l).

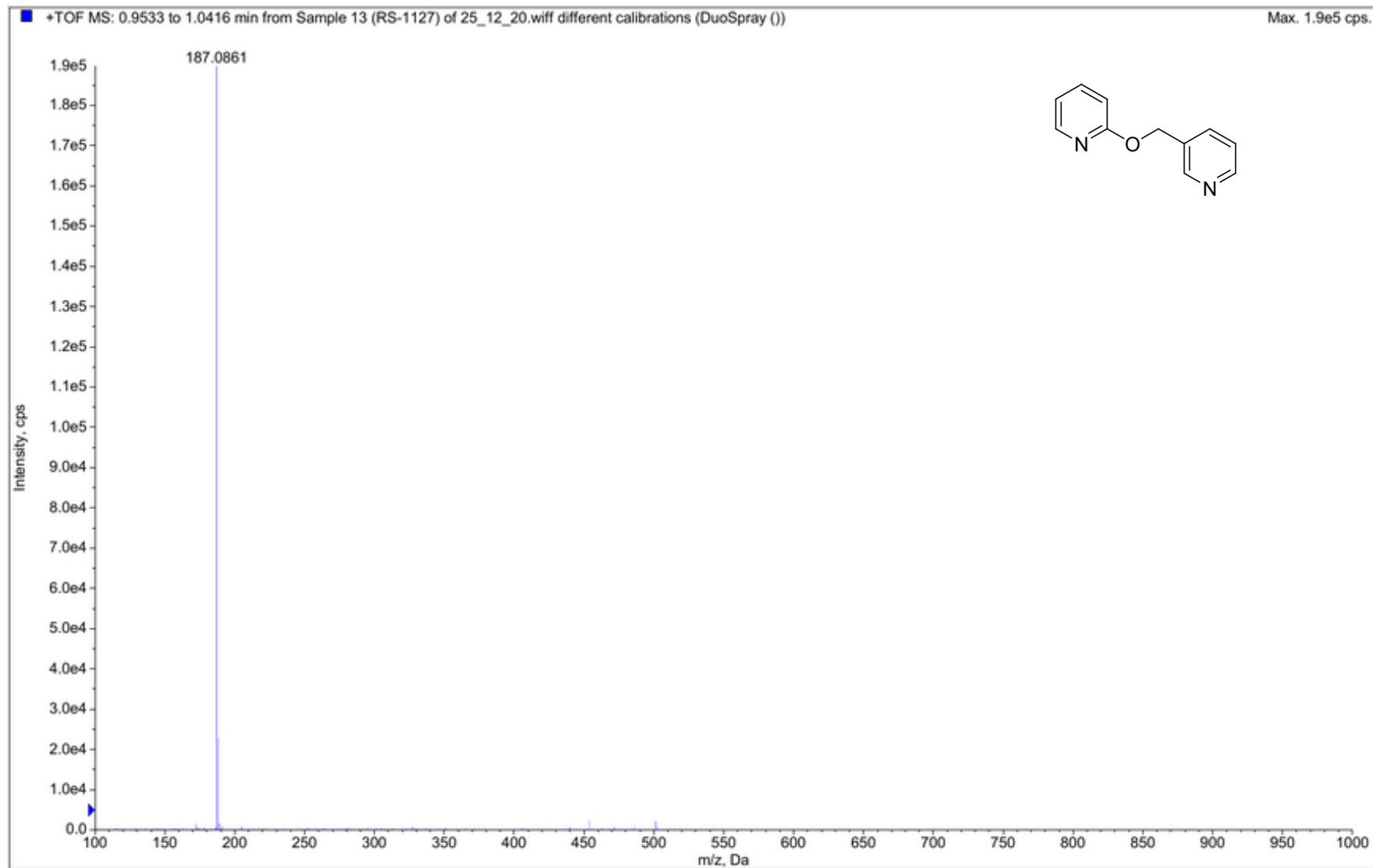


Figure S47. HRMS of 3-(pyridin-3-ylmethoxy)pyridine (21)

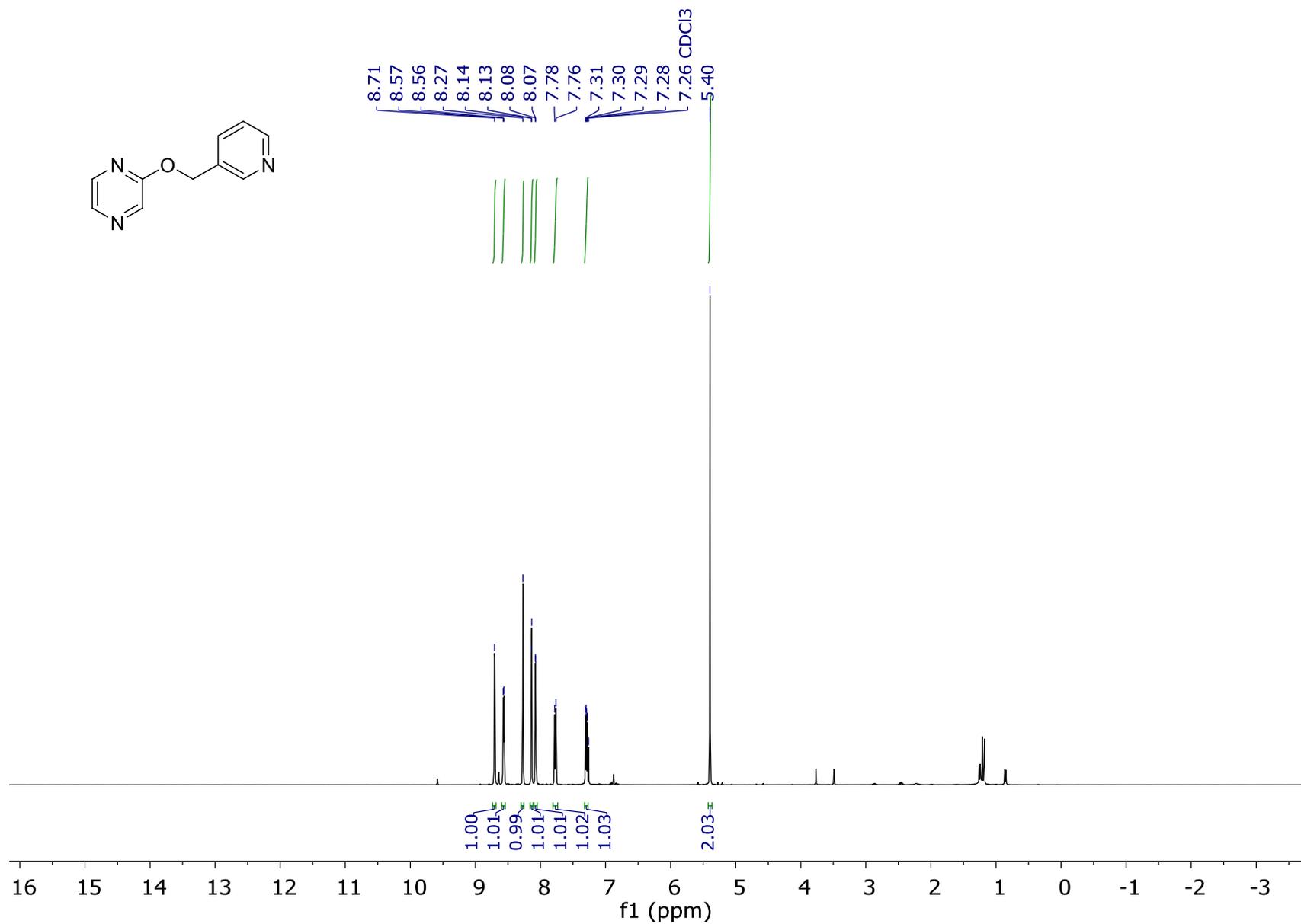


Figure S48. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) of 2-(pyridin-3-ylmethoxy)pyrazine (2m)

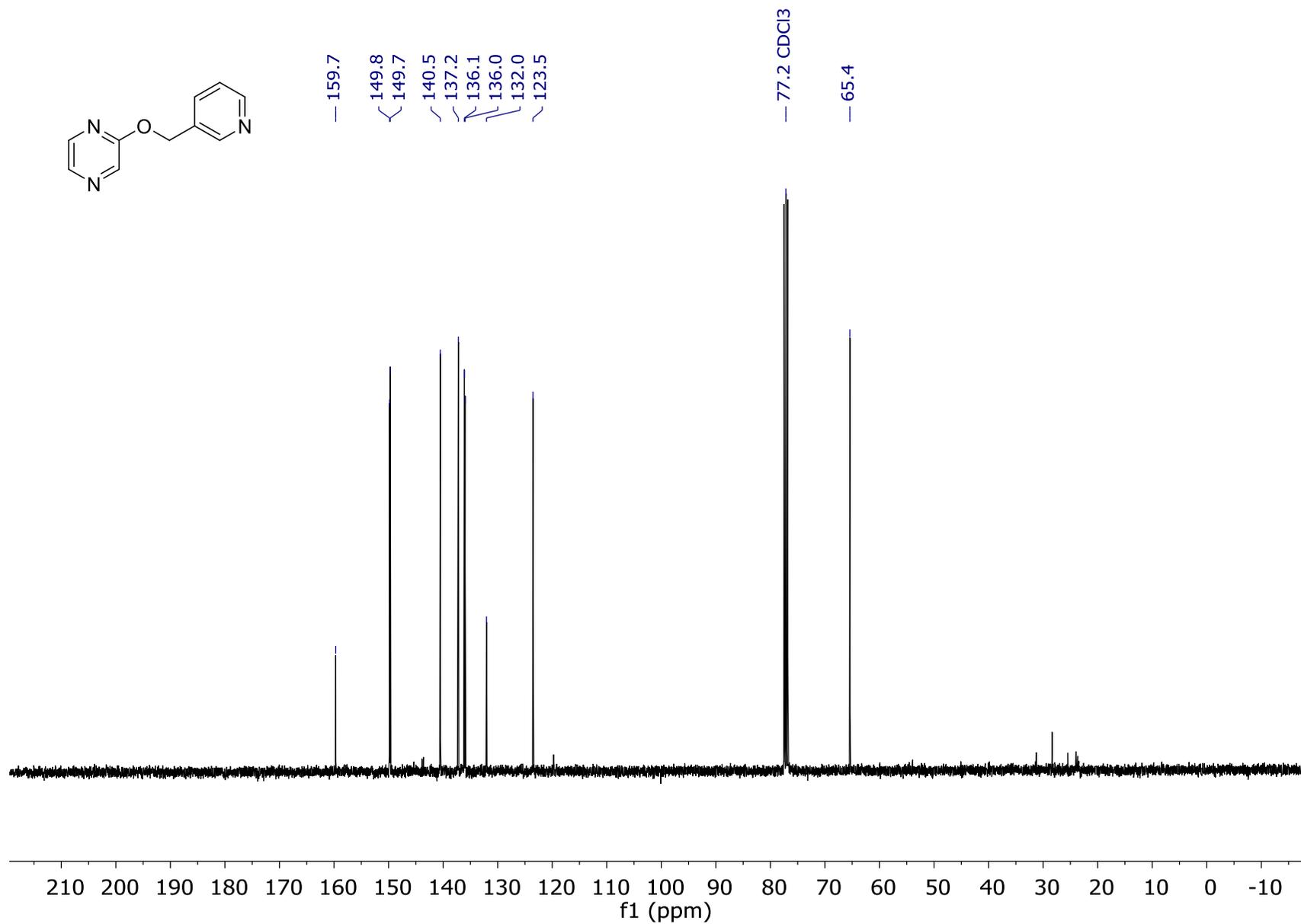


Figure S49.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform-*d*) of 2-(pyridin-3-ylmethoxy)pyrazine (2m)

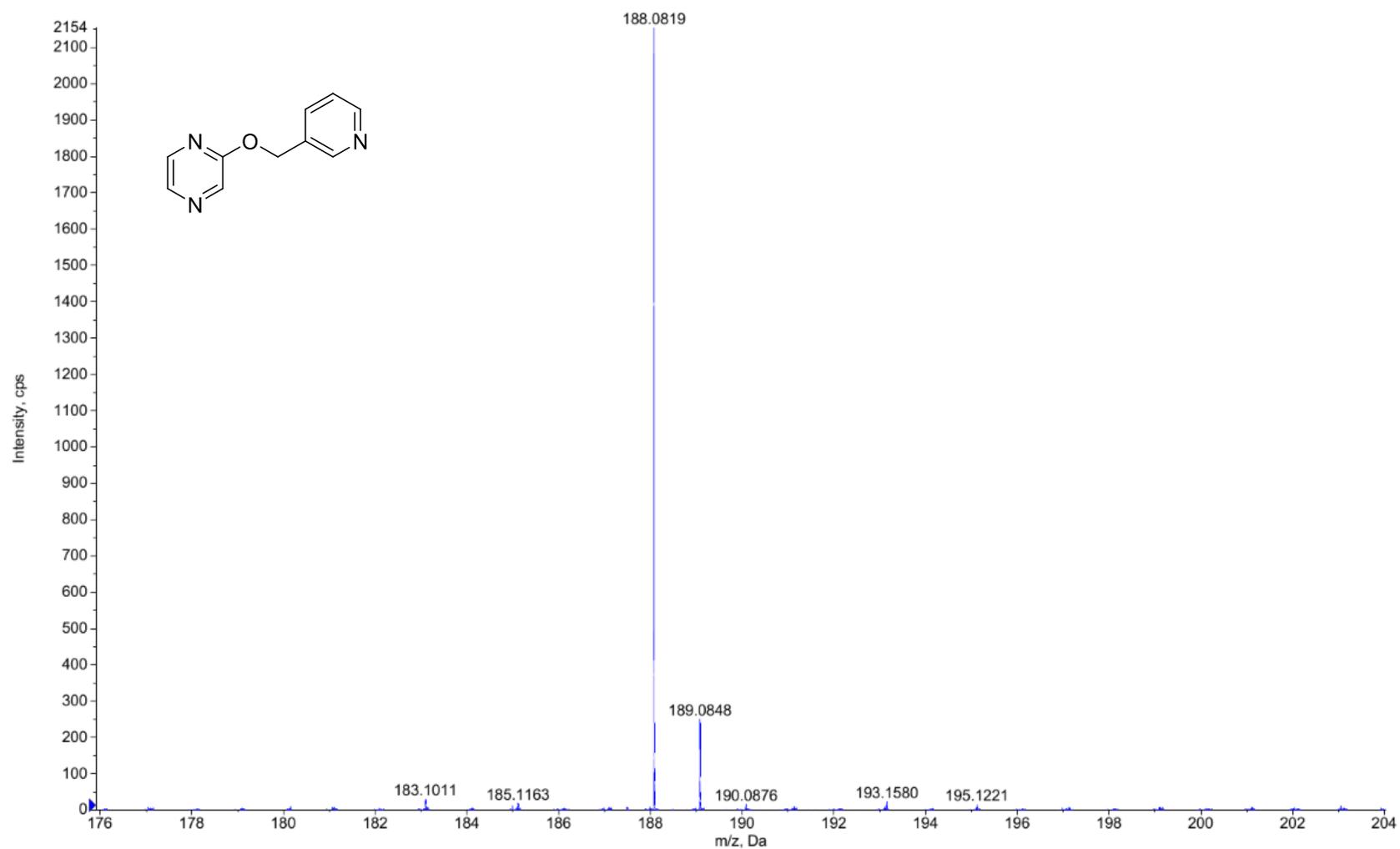


Figure S50. HRMS of 2-(pyridin-3-ylmethoxy)pyrazine (2m)

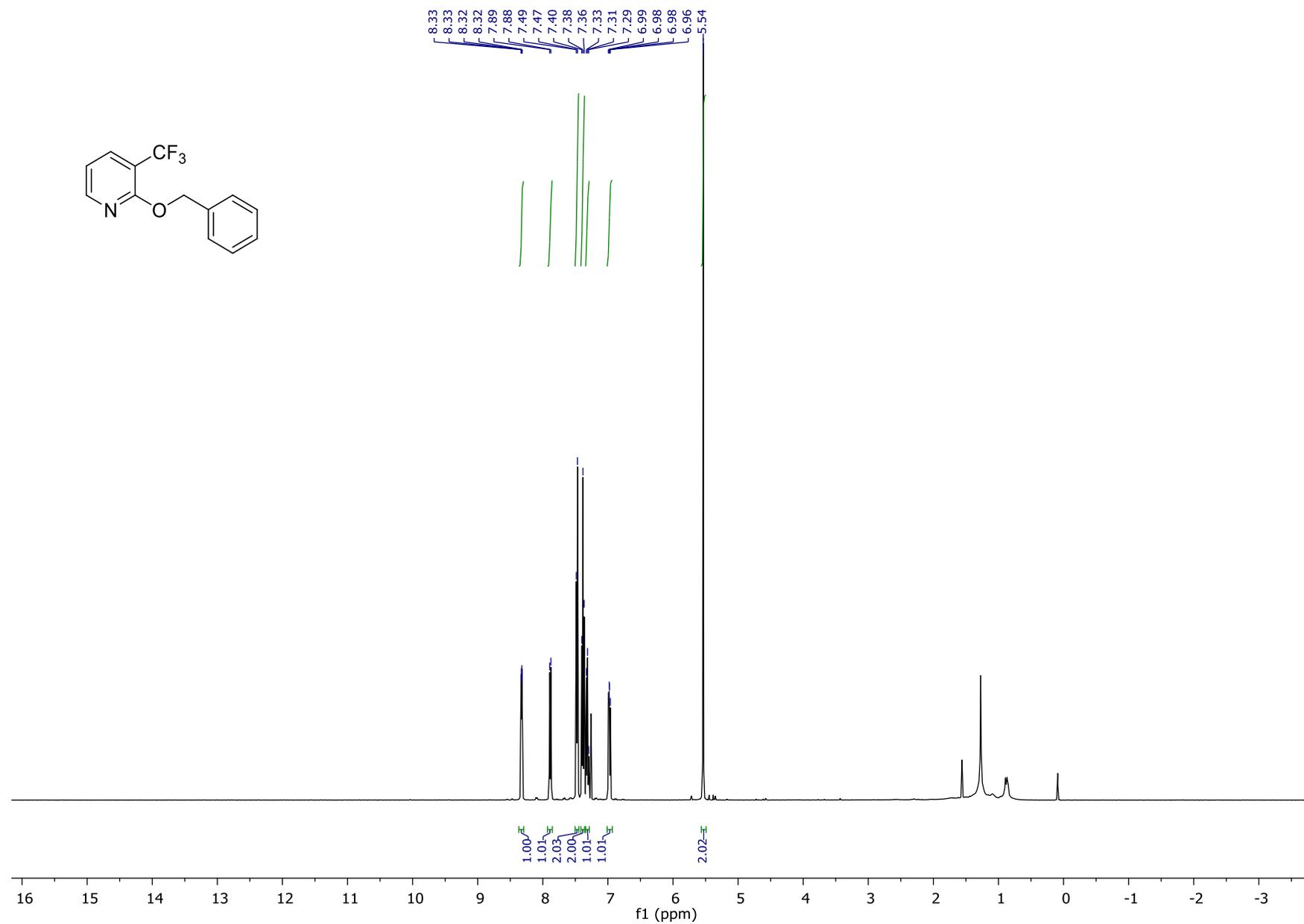


Figure S51. <sup>1</sup>H NMR (400 MHz, Chloroform-d) of 2-(benzyloxy)-3-(trifluoromethyl)pyridine (2n)

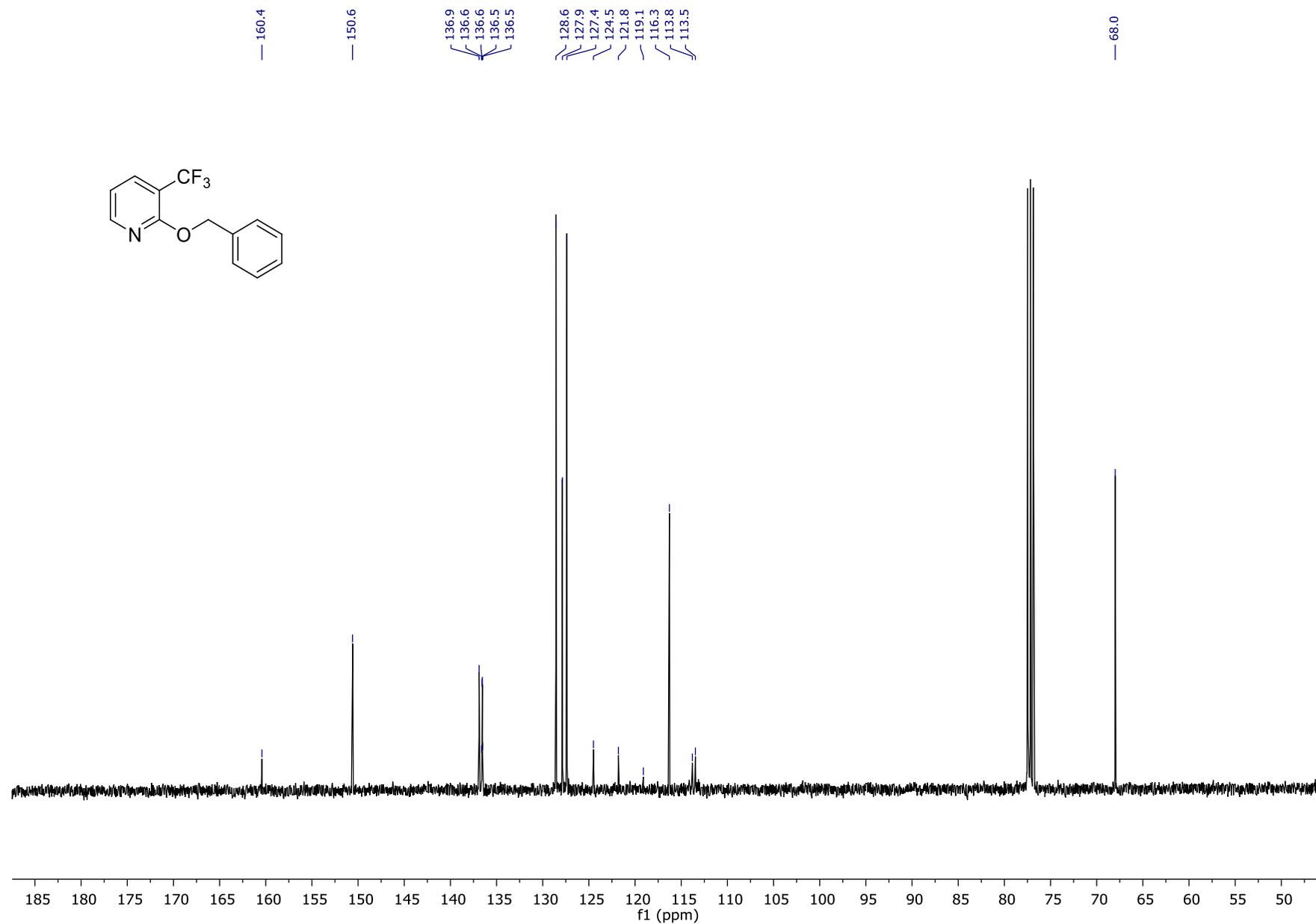


Figure S52.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform- $d$ ) of 2-(benzyloxy)-3-(trifluoromethyl)pyridine (2n)

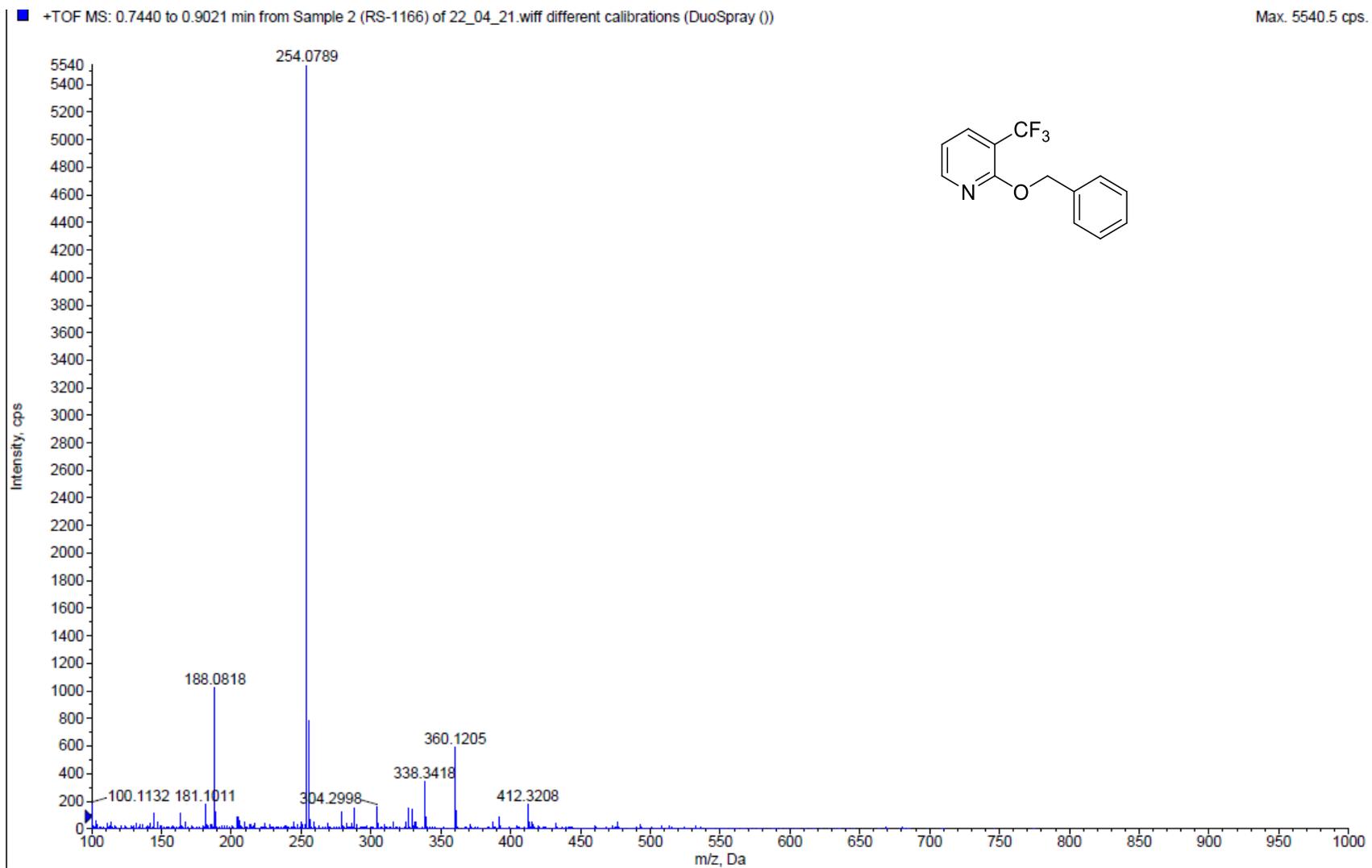


Figure S53. HRMS of 2-(benzyloxy)-3-(trifluoromethyl)pyridine (2n)

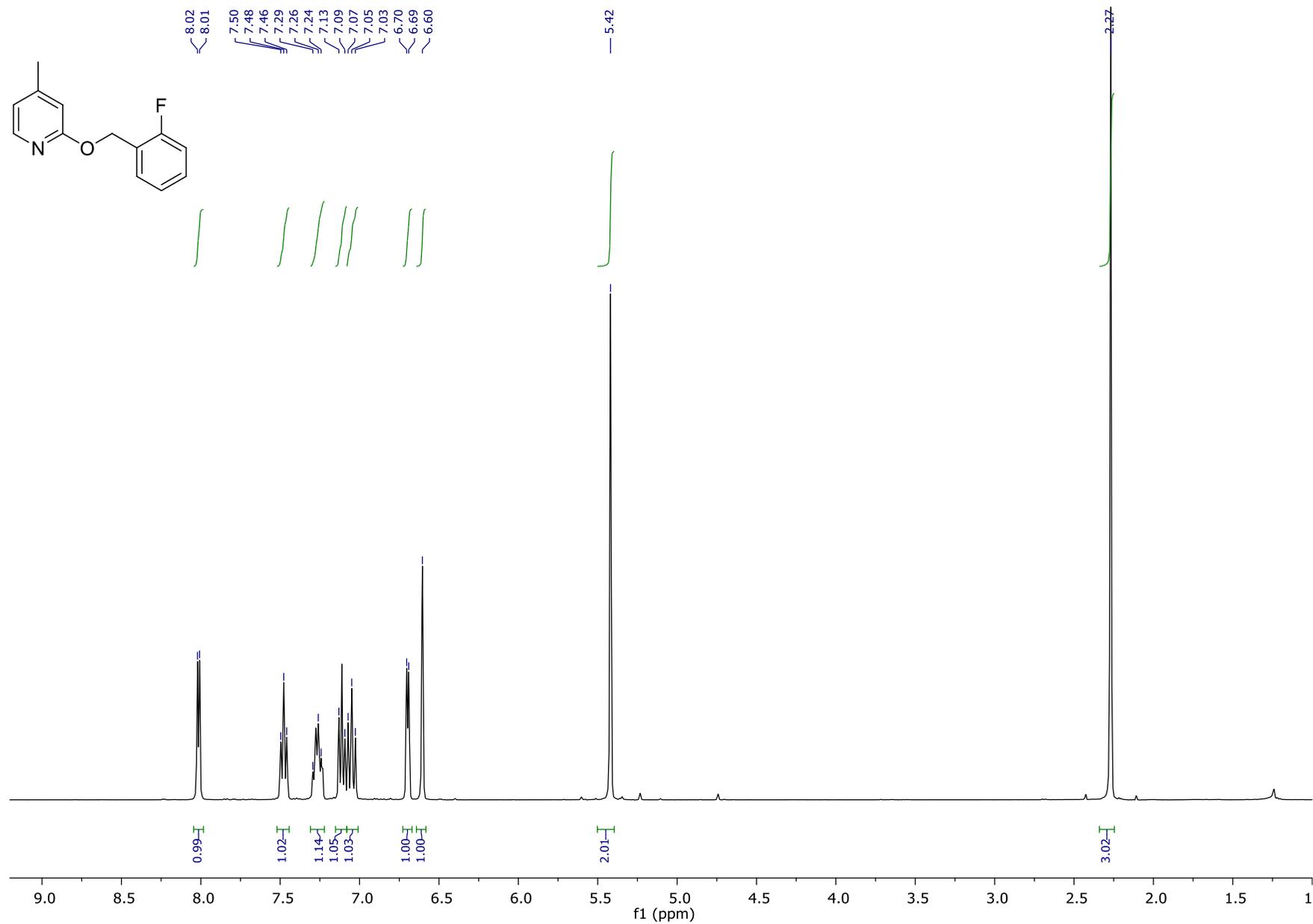


Figure S54. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) of 2-(2-fluorobenzoyloxy)-4-methylpyridine (2o)

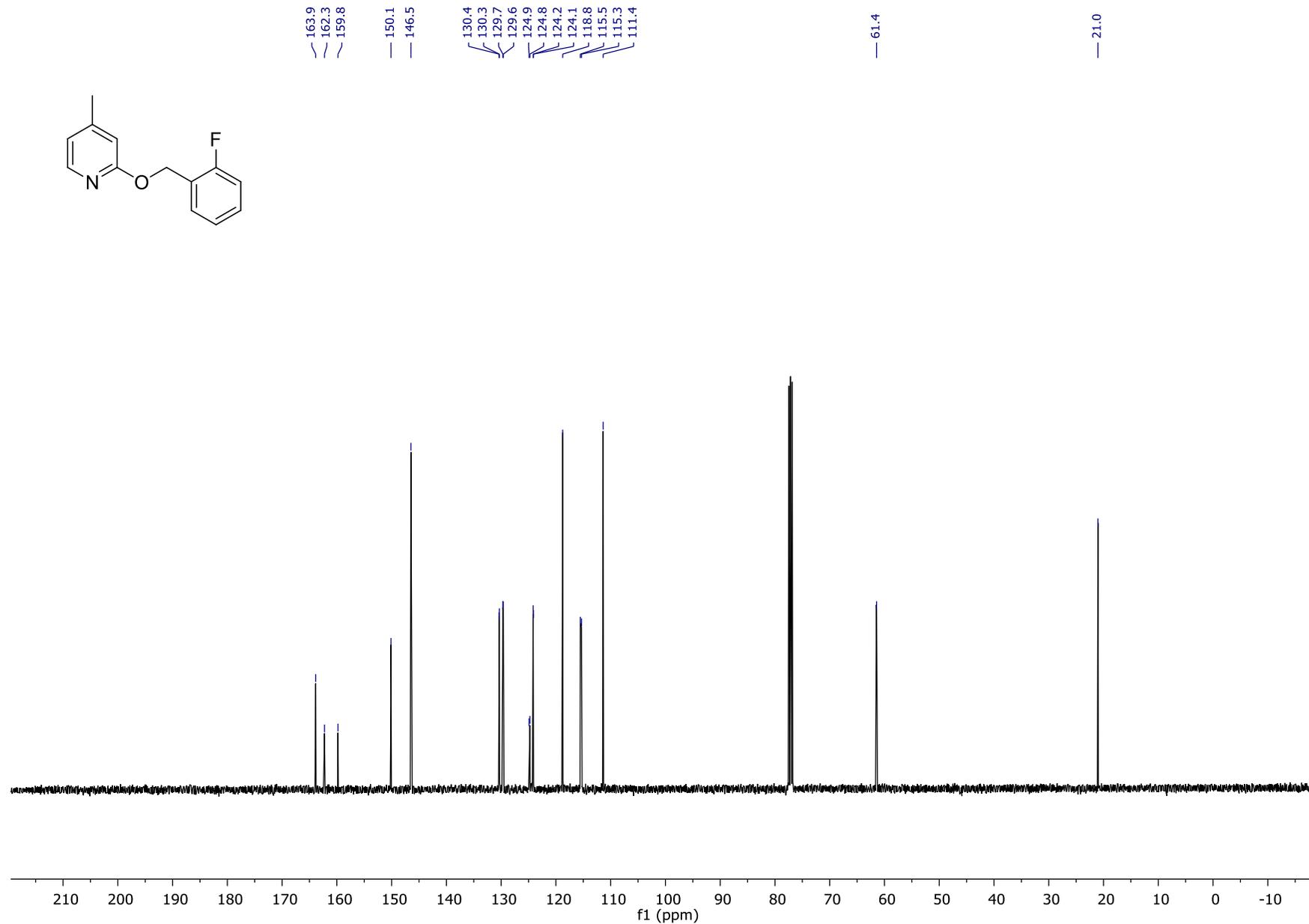
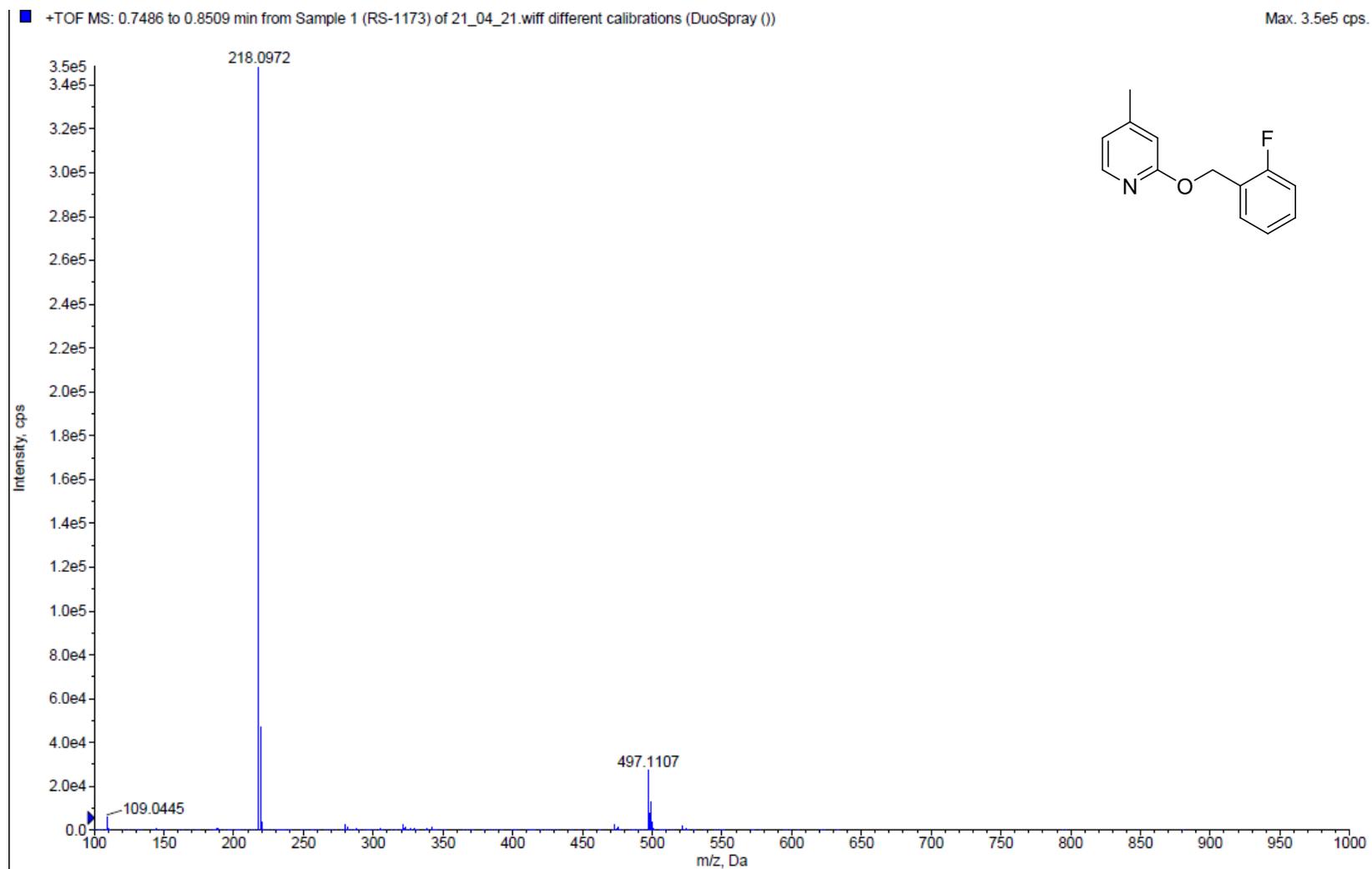


Figure S55.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, Chloroform-*d*) of 2-(2-fluorobenzoyloxy)-4-methylpyridine (2o)



**Figure S56. HRMS of 2-(2-fluorobenzoyloxy)-4-methylpyridine (2o)**