

## **Solvent-free palladium-catalyzed C–O cross-coupling of aryl bromides with phenols**

**Sergey A. Rzhavskiy, Maxim A. Topchiy, Vasilii N. Bogachev, Lidiya I. Minaeva, Iliia R. Cherkashchenko, Konstantin V. Lavrov, Grigorii K. Sterligov, Mikhail S. Nechaev and Andrey F. Asachenko**

*General information.* 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 were purchased from DalChem without further purification. Only freshly synthesized  $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$  was used.<sup>S1</sup> 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 “Avance 600” (600 MHz  $^1\text{H}$ , 151 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 and APCI) or Photospray (APPI) ionization sources.

### *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 (1.2 mmol) and the ligand (2 mol%),  $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$  (10 mg, 1 mol%) and mixture was mixed thoroughly followed by addition of  $\text{Cs}_2\text{CO}_3$  (650mg, 2.0 mmol). The tube was sealed and placed in a pre-heated oil bath at 110°C and stirred for 18h. Then the reaction mixture was allowed to cool to room temperature, and resulting dark heterogeneous mixture was dissolved in water (10 ml) and ethyl acetate (10 mL). 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.

The products **3a,b** were synthesized using another reagents proportion: dibromoarene (1eq.), 4-MeC<sub>6</sub>H<sub>4</sub>OH (2 eq.), Pd<sub>2</sub>(dba)<sub>3</sub>·CHCl<sub>3</sub> (2 mol%), *t*-BuBrettPhos **L1** (4 mol%), Cs<sub>2</sub>CO<sub>3</sub> (4 eq.), neat, 110°C, 18 h.

*4-(4-acetylphenoxy)benzonitrile (1a)*<sup>S2</sup>

Yield 114 mg (48%), white solid, m.p. 100-102°C (lit. data: m.p. 100–102°C).<sup>S2</sup>

<sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 8.04 – 7.98 (m, 2H), 7.67 (d, *J* = 8.8 Hz, 1H), 7.53 (d, *J* = 8.8 Hz, 1H), 7.11 – 7.08 (m, 3H), 6.92 (d, *J* = 8.8 Hz, 1H), 2.61 (d, *J* = 2.8 Hz, 3H).

<sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, Chloroform-*d*) δ 197.1 (C=O), 160.2, 159.6, 134.5, 133.7, 131.0, 119.41, 118.9 (C≡N), 116.5, 107.4, 26.7 (CH<sub>3</sub>).

*1-nitro-2-phenoxybenzene (1b)*<sup>S3</sup>

Yield 153 mg (71%), colorless oil.

<sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 8.1 Hz, 1H), 7.49 (t, *J* = 7.9 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.22 – 7.16 (m, 2H), 7.05 (d, *J* = 8.4 Hz, 2H), 7.01 (d, *J* = 8.4 Hz, 1H).

<sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, Chloroform-*d*) δ 155.9, 150.8, 141.5, 134.2, 130.2, 125.8, 124.7, 123.2, 120.6, 119.3.

*1-nitro-3-phenoxybenzene (1c)*<sup>S4</sup>

Yield 146 mg (68%), colorless oil.

<sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 7.96 – 7.90 (m, 1H), 7.79 (t, *J* = 2.2 Hz, 1H), 7.48 (t, *J* = 8.2 Hz, 1H), 7.41 (t, *J* = 8.0 Hz, 2H), 7.32 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.07 (d, *J* = 7.7 Hz, 2H).

<sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, Chloroform-*d*) δ 158.7, 155.6, 149.4, 130.4, 130.4, 125.0, 124.28, 119.9, 117.7, 112.9.

*1-nitro-4-phenoxybenzene (1d)*<sup>S4</sup>

Yield 140 mg (65%), white solid, m.p. 58-59°C (lit. data: m.p. 58-59°C).<sup>S5</sup>

<sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 8.20 (d, *J* = 8.9 Hz, 2H), 7.44 (t, *J* = 7.3 Hz, 2H), 7.30 – 7.23 (m, 1H), 7.09 (d, *J* = 7.7 Hz, 2H), 7.01 (d, *J* = 8.9 Hz, 2H).

<sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, Chloroform-*d*) δ 163.5, 154.8, 142.7, 130.4, 126.1, 125.5, 120.7, 117.2.

*4-phenoxybenzonitrile (1e)*<sup>S2</sup>

Yield 115 mg (59%), white solid, m.p. 43-45°C (lit. data: m.p. 44-45°C).<sup>S6</sup>

<sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 8.6 Hz, 2H), 7.41 (t, *J* = 7.8 Hz, 2H), 7.23 (t, *J* = 7.2 Hz, 1H), 7.06 (d, *J* = 8.0 Hz, 2H), 7.00 (d, *J* = 8.6 Hz, 2H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  161.7, 154.9, 134.2, 130.3, 125.2, 120.4, 118.9 (C $\equiv$ N), 118.0, 105.9.

*4-(4-chlorophenoxy)benzotrile (If)*<sup>S2</sup>

Yield 126 mg (55%), white solid, m.p. 79-81°C (lit. data: m.p. 74-76°C).<sup>S2</sup>

$^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.61 (d,  $J$  = 8.8 Hz, 2H), 7.37 (d,  $J$  = 8.8 Hz, 2H), 7.03 – 6.99 (m, 4H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  161.3, 153.6, 134.4, 130.4, 121.8, 118.8 (C $\equiv$ N), 118.1, 106.5.

*2-(o-tolyloxy)benzotrile (Ig)*<sup>S2</sup>

Yield 111 mg (53%), white solid, m.p. 64-66°C (lit. data: m.p. 61-63°C).<sup>S2</sup>

$^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.68 – 7.63 (m, 1H), 7.44 – 7.40 (m, 1H), 7.29 (d,  $J$  = 7.5 Hz, 1H), 7.23 (t,  $J$  = 7.1 Hz, 1H), 7.16 (t,  $J$  = 7.1 Hz, 1H), 7.09 (t,  $J$  = 7.6 Hz, 1H), 6.99 (d,  $J$  = 7.9 Hz, 1H), 2.22 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  160.1, 152.7, 134.3, 134.0, 132.0, 130.5, 127.6, 125.7, 122.3, 120.8, 116.2 (C $\equiv$ N), 115.5, 102.8, 16.1 (CH<sub>3</sub>).

*4-(2-isopropylphenoxy)benzotrile (Ih)*<sup>S2</sup>

Yield 126 mg (53%), white solid, m.p. 49-52°C (lit. data: m.p. 52-54°C).<sup>S2</sup>

$^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.58 (d,  $J$  = 8.9 Hz, 2H), 7.41 – 7.37 (m, 1H), 7.25 – 7.21 (m, 2H), 6.94 (d,  $J$  = 8.8 Hz, 3H), 3.17 – 3.08 (m, 1H), 1.19 (d,  $J$  = 6.9 Hz, 6H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  162.4, 151.6, 141.0, 134.3, 127.7, 127.4, 126.0, 121.2, 119.1 (C $\equiv$ N), 117.1, 105.4, 27.2 (CH), 23.1 (CH<sub>3</sub>).

*1-phenoxy-4-(trifluoromethyl)benzene (Ii)*<sup>S7</sup>

Yield 188 mg (79%), colorless oil.

$^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.58 (d,  $J$  = 8.5 Hz, 2H), 7.40 (t,  $J$  = 8.0 Hz, 2H), 7.20 (t,  $J$  = 7.4 Hz, 1H), 7.06 (t,  $J$  = 8.7 Hz, 4H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  160.67, 155.87, 130.22, 127.3 (q,  $J$  = 3.8 Hz), , 125.0 (q,  $J$  = 32.7 Hz), 125.6, 124.4, 123.45 (q,  $J$  = 271.2 Hz, CF<sub>3</sub>), 120.1, 119.2, 118.0.

*1-phenoxy-2-(trifluoromethyl)benzene (Ij)*<sup>S8</sup>

Yield 186 mg (78%), colorless oil.

$^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.68 (d,  $J$  = 7.7 Hz, 1H), 7.45 (t,  $J$  = 7.8 Hz, 1H), 7.37 (t,  $J$  = 7.7 Hz, 2H), 7.17 (t,  $J$  = 7.4 Hz, 2H), 7.05 (d,  $J$  = 8.0 Hz, 2H), 6.94 (d,  $J$  = 8.3 Hz, 1H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  156.6, 155.7, 133.3, 130.0, 127.5 (q,  $J = 5.1$  Hz), 124.3, 123.6 (q,  $J = 272.2$  Hz,  $\text{CF}_3$ ), 122.8, 121.64, 121.5 (q,  $J = 31.2$  Hz), 119.6, 119.3.

*1-methyl-2-(4-(trifluoromethyl)phenoxy)benzene (1k)*<sup>S2</sup>

Yield 207 mg (82%), colorless oil.

$^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.55 (d,  $J = 8.4$  Hz, 2H), 7.30 (d,  $J = 7.4$  Hz, 1H), 7.23 (t,  $J = 7.6$  Hz, 1H), 7.15 (t,  $J = 7.4$  Hz, 1H), 7.04 – 6.89 (m, 3H), 2.21 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  161.0, 153.3, 131.9, 130.6, 127.6, 127.2 (q,  $J = 3.5$  Hz), 125.3, 124.3 (q,  $J = 32.9$  Hz), 122.63 (q,  $J = 271.2$  Hz,  $\text{CF}_3$ ), 120.9, 119.2, 116.6, 16.2 ( $\text{CH}_3$ ).

*1-methyl-2-(2-(trifluoromethyl)phenoxy)benzene (1l)*<sup>S2</sup>

Yield 187 mg (74%), colorless oil.

$^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.68 (d,  $J = 7.7$  Hz, 1H), 7.39 (t,  $J = 7.8$  Hz, 1H), 7.29 (d,  $J = 7.4$  Hz, 1H), 7.22 (t,  $J = 7.6$  Hz, 1H), 7.17 – 7.08 (m, 2H), 6.96 (d,  $J = 7.9$  Hz, 1H), 6.72 (d,  $J = 8.3$  Hz, 1H), 2.24 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  156.0, 153.5, 133.3, 131.8, 130.5, 127.5, 127.4 (q,  $J = 5.0$  Hz), 125.1, 123.7 (q,  $J = 272.4$  Hz,  $\text{CF}_3$ ), 121.7, 120.5, 120.0 (q,  $J = 31.4$  Hz) 116.6, 16.1 ( $\text{CH}_3$ ).

*1-phenoxy-3,5-bis(trifluoromethyl)benzene (1m)*

Yield 220 mg (72%), colorless oil.

$^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.57 (s, 1H), 7.43 (t,  $J = 8.0$  Hz, 2H), 7.38 (s, 2H), 7.27 – 7.23 (m, 1H), 7.07 (d,  $J = 7.7$  Hz, 2H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  157.0, 155.2, 133.3 (q,  $J = 33.6$  Hz), 130.6, 125.4, 123.1 (q,  $J = 273.0$  Hz,  $\text{CF}_3$ ), 120.1, 118.04, 116.32.

HRMS calc. for  $\text{C}_{14}\text{H}_8\text{F}_6\text{O}$   $[\text{M}]^+$  306.0479; found 306.0475.

*1-methyl-4-phenoxybenzene (2a)*<sup>S4</sup>

Yield 162 mg (88%), colorless oil.

$^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.33 (t,  $J = 8.0$  Hz, 2H), 7.16 (d,  $J = 8.3$  Hz, 2H), 7.09 (t,  $J = 7.4$  Hz, 1H), 7.01 (d,  $J = 7.8$  Hz, 2H), 6.95 (d,  $J = 8.4$  Hz, 2H), 2.36 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  157.9, 154.8, 133.0, 130.4, 129.8, 122.9, 119.3, 118.5, 20.8 ( $\text{CH}_3$ ).

*1,3-dimethyl-5-phenoxybenzene (2b)*<sup>S7</sup>

Yield 170 mg (86%), colorless oil.

$^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.34 (t,  $J$  = 8.0 Hz, 2H), 7.10 (t,  $J$  = 7.4 Hz, 1H), 7.01 (d,  $J$  = 8.6 Hz, 2H), 6.76 (s, 1H), 6.65 (s, 2H), 2.30 (s, 6H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  157.6, 157.3, 139.7, 129.8, 125.1, 123.1, 119.0, 116.7, 21.5 ( $\text{CH}_3$ ).

*1,3-dimethyl-5-(p-tolyloxy)benzene (2c)*<sup>S9</sup>

Yield 185 mg (87%), colorless oil.

$^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.16 (d,  $J$  = 8.3 Hz, 2H), 6.95 (d,  $J$  = 8.4 Hz, 2H), 6.75 (s, 1H), 6.65 (s, 2H), 2.37 (s, 3H), 2.31 (s, 6H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  157.8, 154.9, 139.5, 132.6, 130.2, 124.6, 119.1, 116.1, 21.3 ( $\text{CH}_3$ ), 20.7 ( $\text{CH}_3$ ).

*1-methyl-2-(p-tolyloxy)benzene (2d)*<sup>S9</sup>

Yield 170 mg (86%) obtained from *p*-TolBr and *o*-Me-phenol, and yield 140 mg (71%) obtained from *o*-TolBr and *p*-Me-phenol, colorless oil.

$^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.31 – 7.24 (m, 1H), 7.19 – 7.11 (m, 3H), 7.07 (t,  $J$  = 7.4 Hz, 1H), 6.90 (d,  $J$  = 8.0 Hz, 1H), 6.85 (d,  $J$  = 7.9 Hz, 2H), 2.35 (s, 3H), 2.29 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  155.7, 155.1, 132.0, 131.5, 130.3, 129.8, 127.2, 123.7, 119.3, 117.6, 20.7 ( $\text{CH}_3$ ), 16.3 ( $\text{CH}_3$ ).

*1-(4-tert-butylphenoxy)-2-methylbenzene (2e)*<sup>S2</sup>

Yield 197 mg (82%), colorless oil.

$^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.37 – 7.32 (m, 2H), 7.28 – 7.25 (m, 1H), 7.17 (t,  $J$  = 7.1 Hz, 1H), 7.07 (t,  $J$  = 6.9 Hz, 1H), 6.93 (d,  $J$  = 8.0 Hz, 1H), 6.90 – 6.85 (m, 2H), 2.29 (s, 3H), 1.34 (s, 9H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  155.6, 155.0, 145.3, 131.5, 129.9, 127.2, 126.6, 123.8, 119.5, 117.1, 34.4 (C), 31.7 ( $\text{CH}_3$ ), 16.4 ( $\text{CH}_3$ ).

*1-butyl-2-(p-tolyloxy)benzene (2f)*

Yield 204 mg (85%), colorless oil.

$^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.33 – 7.28 (m, 1H), 7.18 – 7.08 (m, 4H), 6.93 – 6.80 (m, 3H), 3.18 – 2.98 (m, 1H), 2.34 (s, 3H), 1.72 – 1.58 (m, 2H), 1.23 (d,  $J$  = 7.0 Hz, 3H), 0.86 (t,  $J$  = 7.4 Hz, 3H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  156.2, 154.6, 139.0, 131.9, 130.2, 127.6, 126.8, 123.9, 119.5, 117.8, 34.1 ( $\text{CH}_2$ ), 30.2 ( $\text{CH}_2$ ), 21.1 ( $\text{CH}_2$ ), 20.8 ( $\text{CH}_3$ ), 12.4 ( $\text{CH}_3$ ).

HRMS calc. for  $\text{C}_{17}\text{H}_{20}\text{O}$   $[\text{M}]^+$  240.1514; found 240.1506.

*1-methoxy-4-phenoxybenzene (2g)*<sup>S4</sup>

Yield 130 mg (65%), colorless oil.

<sup>1</sup>H NMR (600 MHz, Chloroform-*d*)  $\delta$  7.34 – 7.30 (m, 2H), 7.06 (t, *J* = 7.4 Hz, 1H), 7.01 (d, *J* = 9.1 Hz, 2H), 6.97 (d, *J* = 8.7 Hz, 2H), 6.91 (d, *J* = 9.1 Hz, 2H), 3.82 (s, 3H).

<sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, Chloroform-*d*)  $\delta$  158.6, 156.0, 150.2, 129.7, 122.5, 120.9, 117.7, 115.0, 55.8 (OCH<sub>3</sub>).

*1-methoxy-2-(o-tolyloxy)benzene (2h)*<sup>S2</sup>

Yield 48% colorless oil.

<sup>1</sup>H NMR (600 MHz, Chloroform-*d*)  $\delta$  7.23 (d, *J* = 7.40 Hz, 1H), 7.11 (t, *J* = 7.68 Hz, 1H), 7.06 (t, *J* = 8.46 Hz, 1H), 7.03 – 6.99 (m, 2H), 6.86 (t, *J* = 8.35 Hz, 1H), 6.81 – 6.71 (m, 2H), 3.88 (d, *J* = 1.05 Hz, 3H), 2.30 (s, 3H).

<sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, Chloroform-*d*)  $\delta$  155.3, 153.0, 146.5, 131.3, 129.1, 127.1, 123.7, 123.4, 121.1, 119.0, 118.1, 112.8, 56.2 (OCH<sub>3</sub>), 16.3 (CH<sub>3</sub>).

*1-methoxy-3-phenoxybenzene (2i)*<sup>S2</sup>

Yield 160 mg (80%), colorless oil.

<sup>1</sup>H NMR (600 MHz, Chloroform-*d*)  $\delta$  7.34 (t, *J* = 7.9 Hz, 2H), 7.22 (t, *J* = 8.3 Hz, 1H), 7.11 (t, *J* = 7.3 Hz, 1H), 7.03 (d, *J* = 8.3 Hz, 2H), 6.66 (d, *J* = 8.8 Hz, 1H), 6.59 (m, 2H), 3.78 (s, 3H)

<sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, Chloroform-*d*)  $\delta$  161.1, 158.6, 157.1, 130.2, 129.9, 123.5, 119.2, 111.1, 109.0, 105.0, 55.5 (OCH<sub>3</sub>).

*1-isopropyl-2-(4-methoxyphenoxy)benzene (2j)*<sup>S2</sup>

Yield 131 mg (54%), colorless oil.

<sup>1</sup>H NMR (600 MHz, Chloroform-*d*)  $\delta$  7.36 – 7.33 (m, 1H), 7.16 – 7.12 (m, 1H), 7.12 – 7.08 (m, 1H), 6.94 (d, *J* = 9.1 Hz, 2H), 6.89 (d, *J* = 9.2 Hz, 2H), 6.84 – 6.79 (m, 1H), 3.82 (s, 3H), 3.39 (p, *J* = 6.9 Hz, 1H), 1.29 (d, *J* = 7.0 Hz, 6H).

<sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, Chloroform-*d*)  $\delta$  155.4, 155.0, 151.6, 139.5, 126.9, 126.8, 123.4, 119.5, 118.4, 114.9, 55.8 (OCH<sub>3</sub>), 27.2 (CH), 23.1 (CH<sub>3</sub>).

*1,4-bis(p-tolyloxy)benzene (3a)*<sup>S10</sup>

Yield 110 mg (38%), colorless oil.

<sup>1</sup>H NMR (600 MHz, Chloroform-*d*)  $\delta$  7.14 (d, *J* = 8.2 Hz, 4H), 6.97 (d, *J* = 1.0 Hz, 4H), 6.93 – 6.89 (m, 4H), 2.34 (s, 6H).

<sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, Chloroform-*d*)  $\delta$  155.5, 153.1, 132.0, 130.3, 120.4, 118.6, 20.1 (CH<sub>3</sub>).

4,4'-bis(*p*-tolylloxy)biphenyl (**3b**)<sup>S10</sup>

Yield 169 mg (46%), white solid, m.p. 180°C (lit. data: m.p. 179-180°C).<sup>S10</sup>

<sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 8.5 Hz, 4H), 7.17 (d, *J* = 8.2 Hz, 4H), 7.04 (d, *J* = 8.6 Hz, 4H), 6.97 (d, *J* = 8.3 Hz, 4H), 2.36 (s, 6H).

<sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, Chloroform-*d*) δ 157.3, 154.8, 135.4, 133.2, 130.4, 128.2, 119.32, 118.7, 20.9 (CH<sub>3</sub>).

## References

- S1. S. S. Zalesskiy and V. P. Ananikov, *Organometallics*, 2012, **31**, 2302-2309.
- S2. C. H. Burgos, T. E. Barder, X. Huang and S. L. Buchwald, *Angew. Chem., Int. Ed.*, 2006, **45**, 4321-4326.
- S3. H. Xu and Y. Chen, *Synth. Commun.*, 2007, **37**, 2411-2420.
- S4. S. Jammi, S. Sakthivel, L. Rout, T. Mukherjee, S. Mandal, R. Mitra, P. Saha and T. Punniyamurthy, *J. Org. Chem.*, 2009, **74**, 1971-1976.
- S5. C. Paradisi, U. Quintily and G. Scorrano, *J. Org. Chem.*, 1983, **48**, 3022-3026.
- S6. F. Li, Q. Meng, H. Chen, Z. Li, Q. Wang and F. Tao, *Synthesis*, 2005, **2005**, 1305-1313.
- S7. Q. Zhang, D. Wang, X. Wang and K. Ding, *J. Org. Chem.*, 2009, **74**, 7187-7190.
- S8. T. D. Senecal, A. T. Parsons and S. L. Buchwald, *J. Org. Chem.*, 2011, **76**, 1174-1176.
- S9. A. B. Naidu, E. A. Jaseer and G. Sekar, *J. Org. Chem.*, 2009, **74**, 3675-3679.
- S10. X. Qu, T. Li, Y. Zhu, P. Sun, H. Yang and J. Mao, *Org. Biomol. Chem.*, 2011, **9**, 5043-5046.

# NMR and HRMS spectra pictures

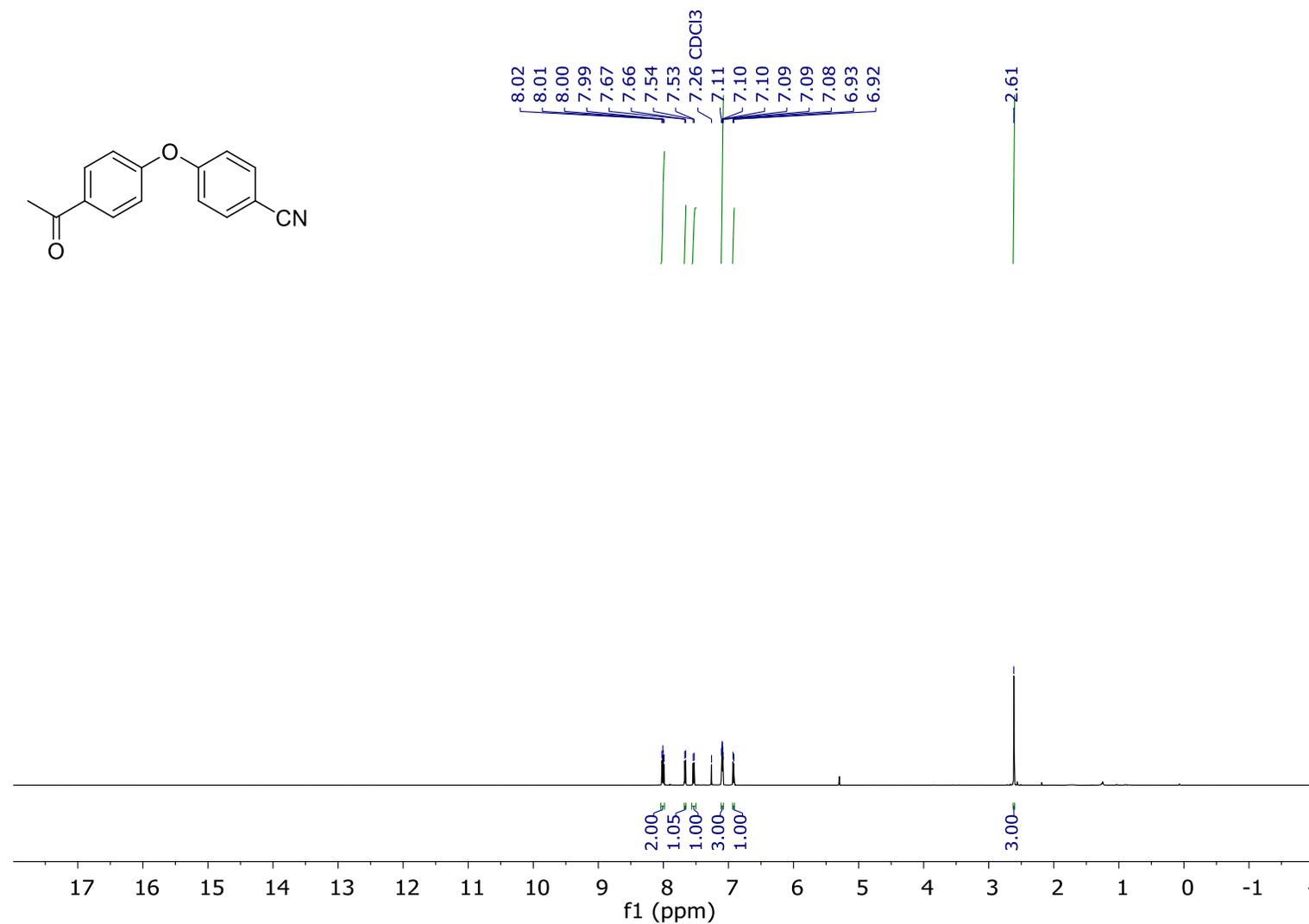


Figure S1. <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) of 4-(4-acetylphenoxy)benzonitrile (1a).

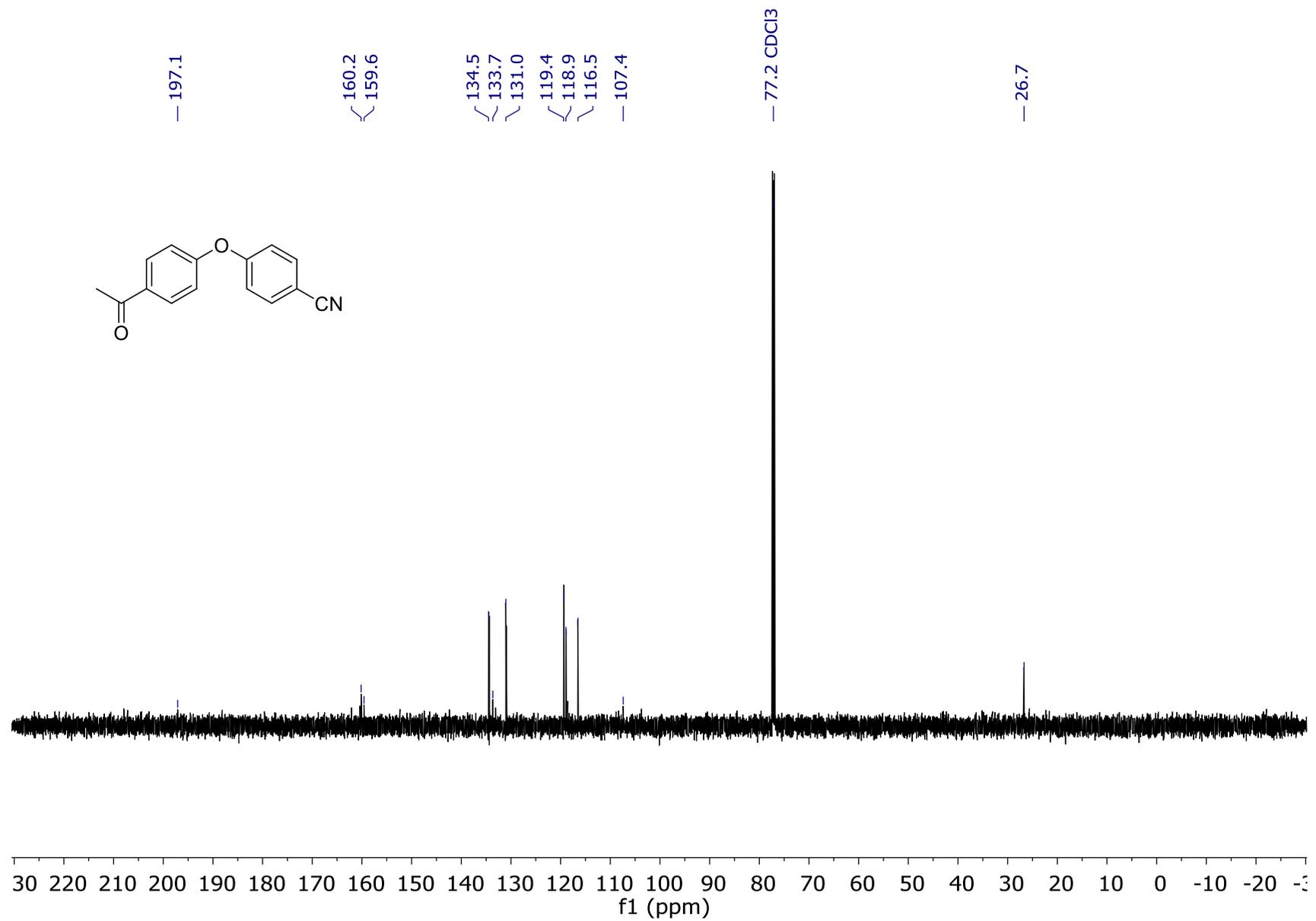


Figure S2.  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz, Chloroform-*d*) of 4-(4-acetylphenoxy)benzonitrile (1a).

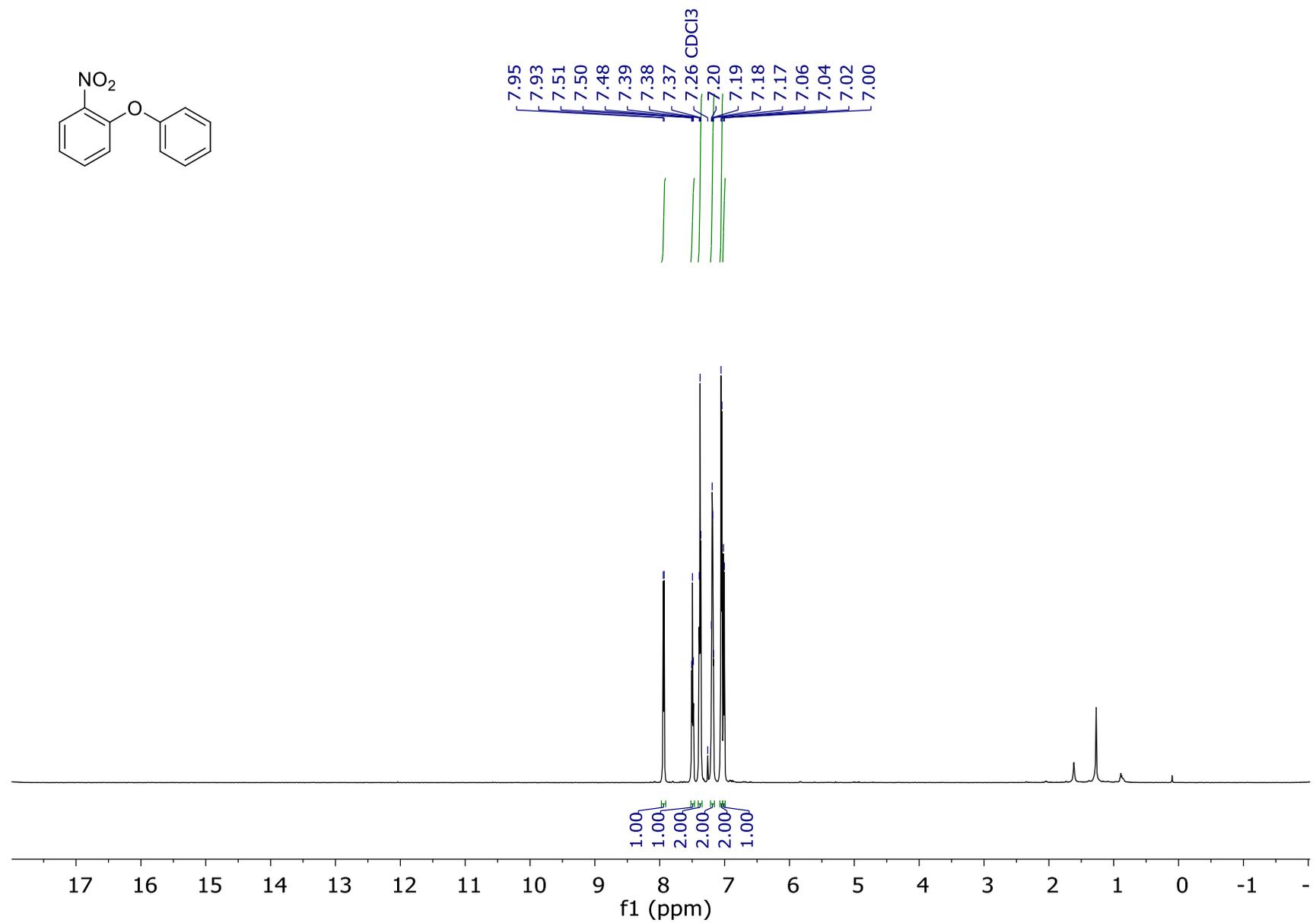


Figure S3. <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) of 1-nitro-2-phenoxybenzene (1b).

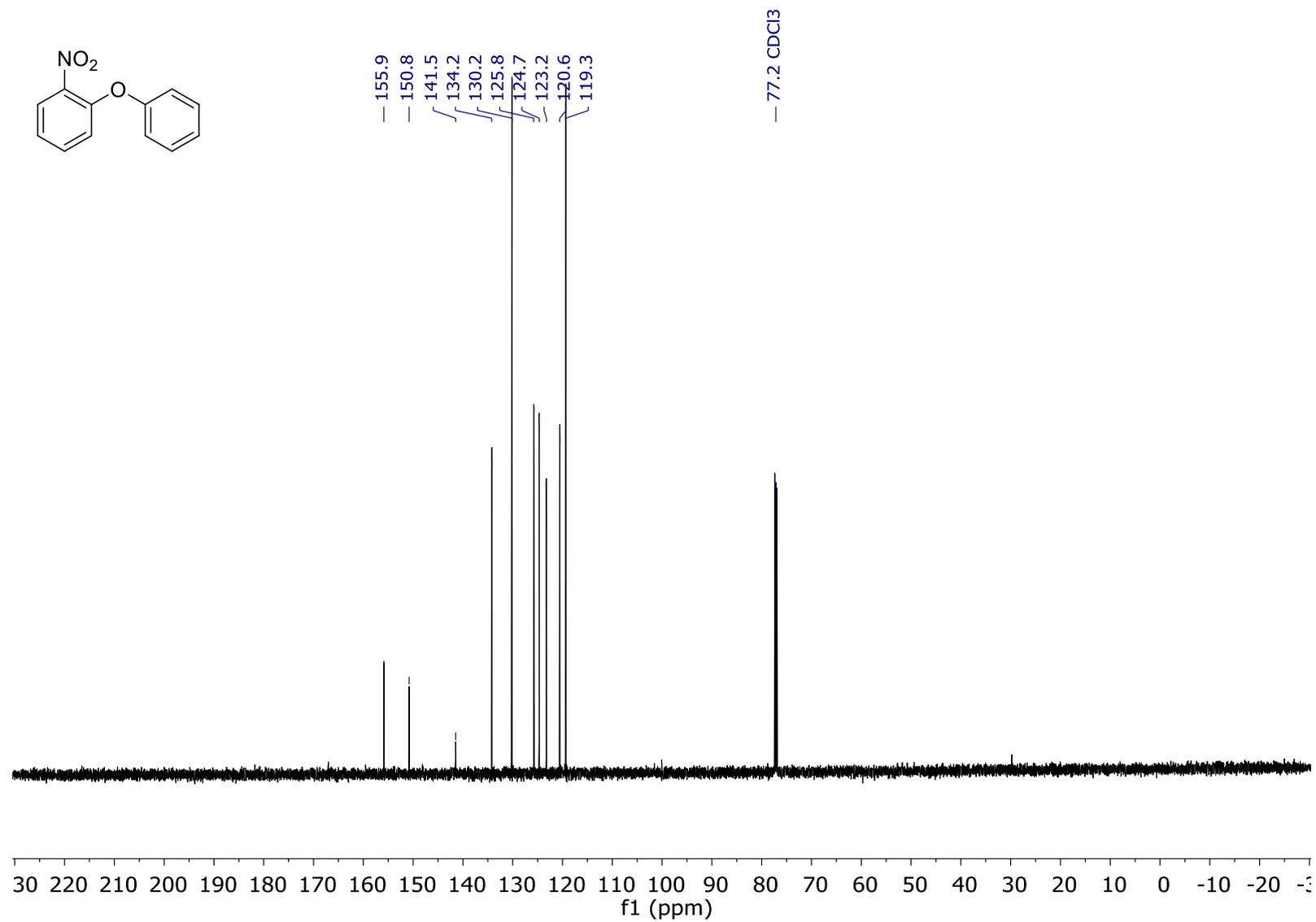


Figure S4.  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz, Chloroform-*d*) of 1-nitro-2-phenoxybenzene (1b).

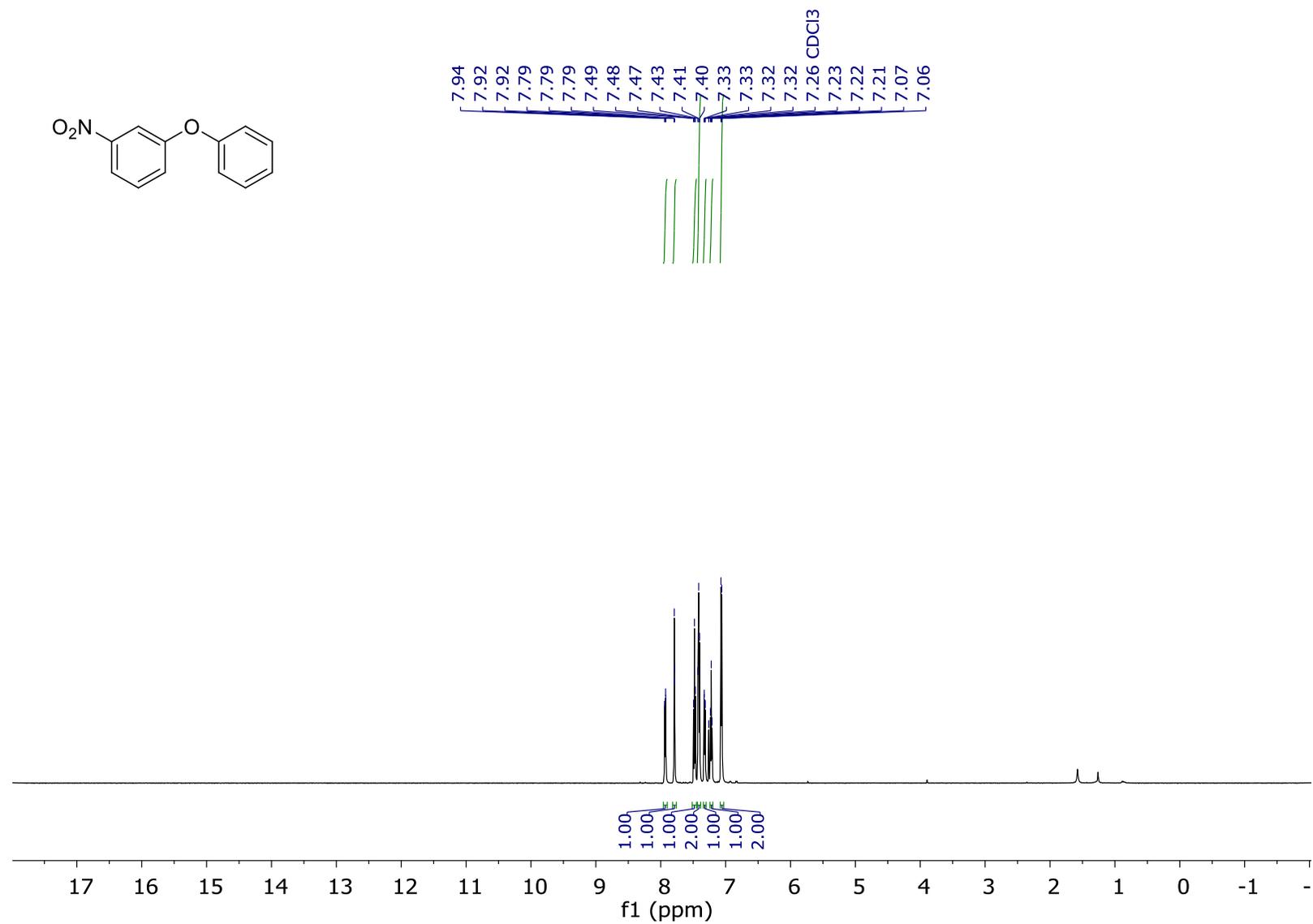


Figure S5. <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) of 1-nitro-3-phenoxybenzene (1c).

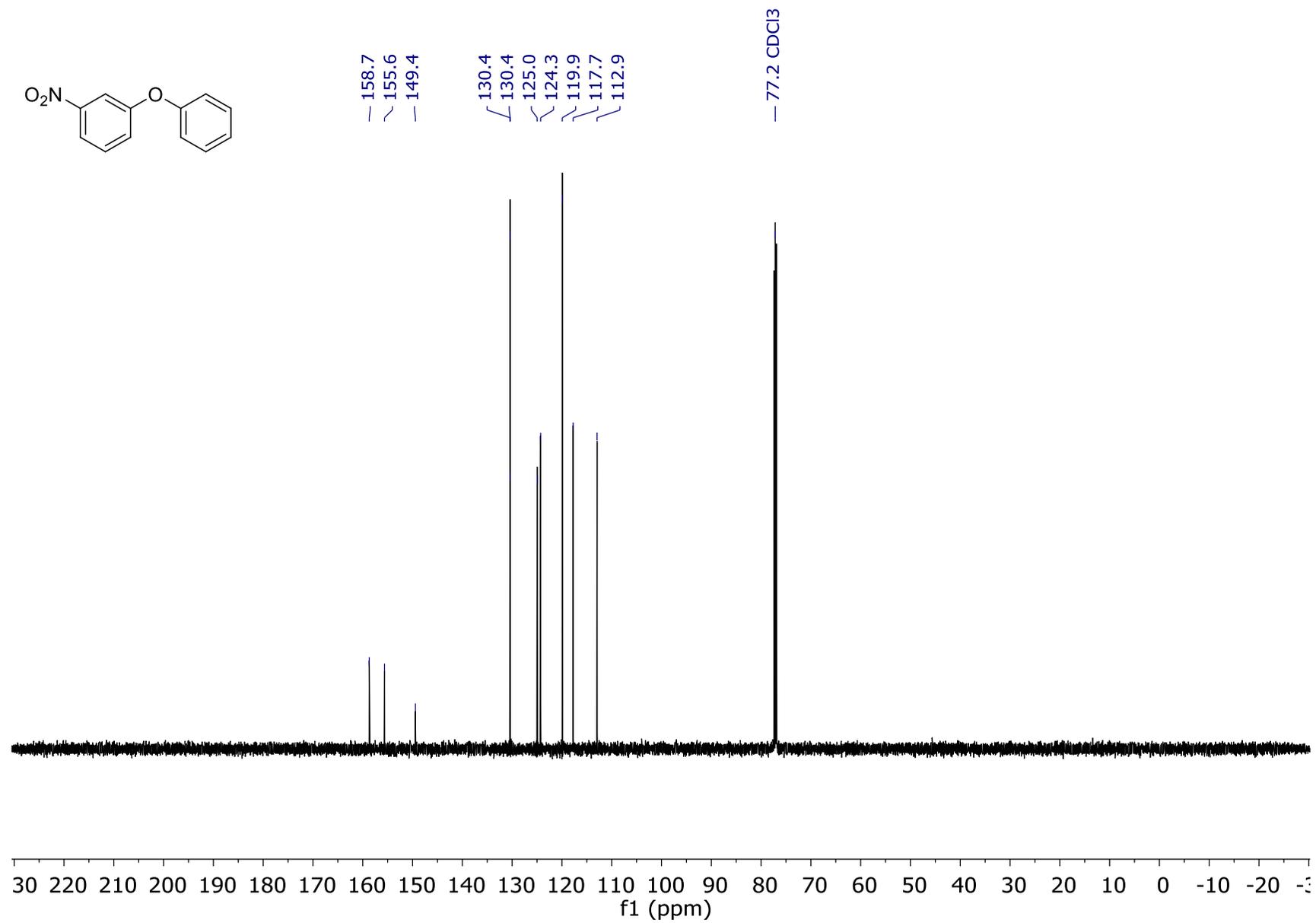


Figure S6.  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz, Chloroform-*d*) of 1-nitro-3-phenoxybenzene (1c).

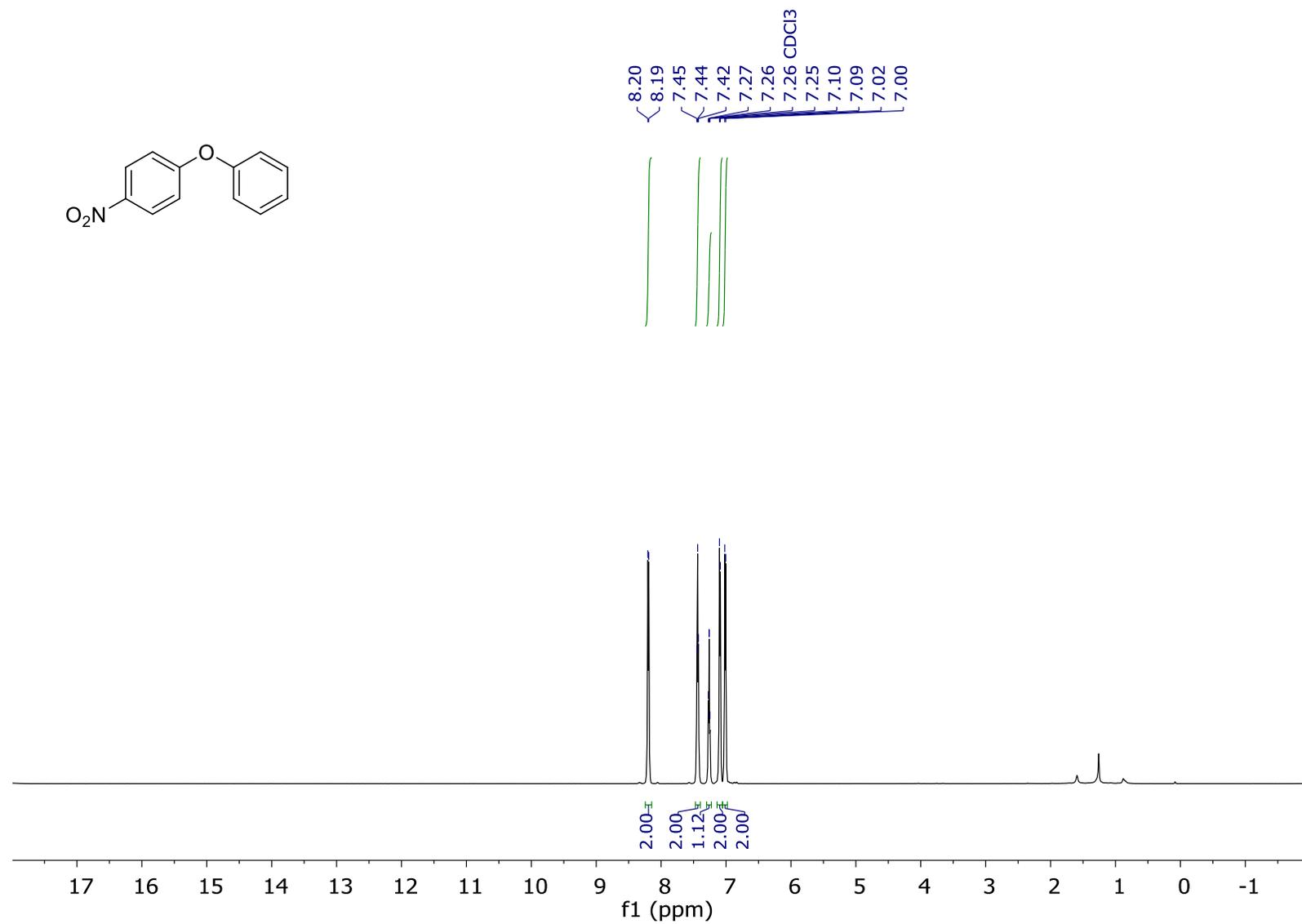


Figure S7. <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) of 1-nitro-4-phenoxybenzene (1d).

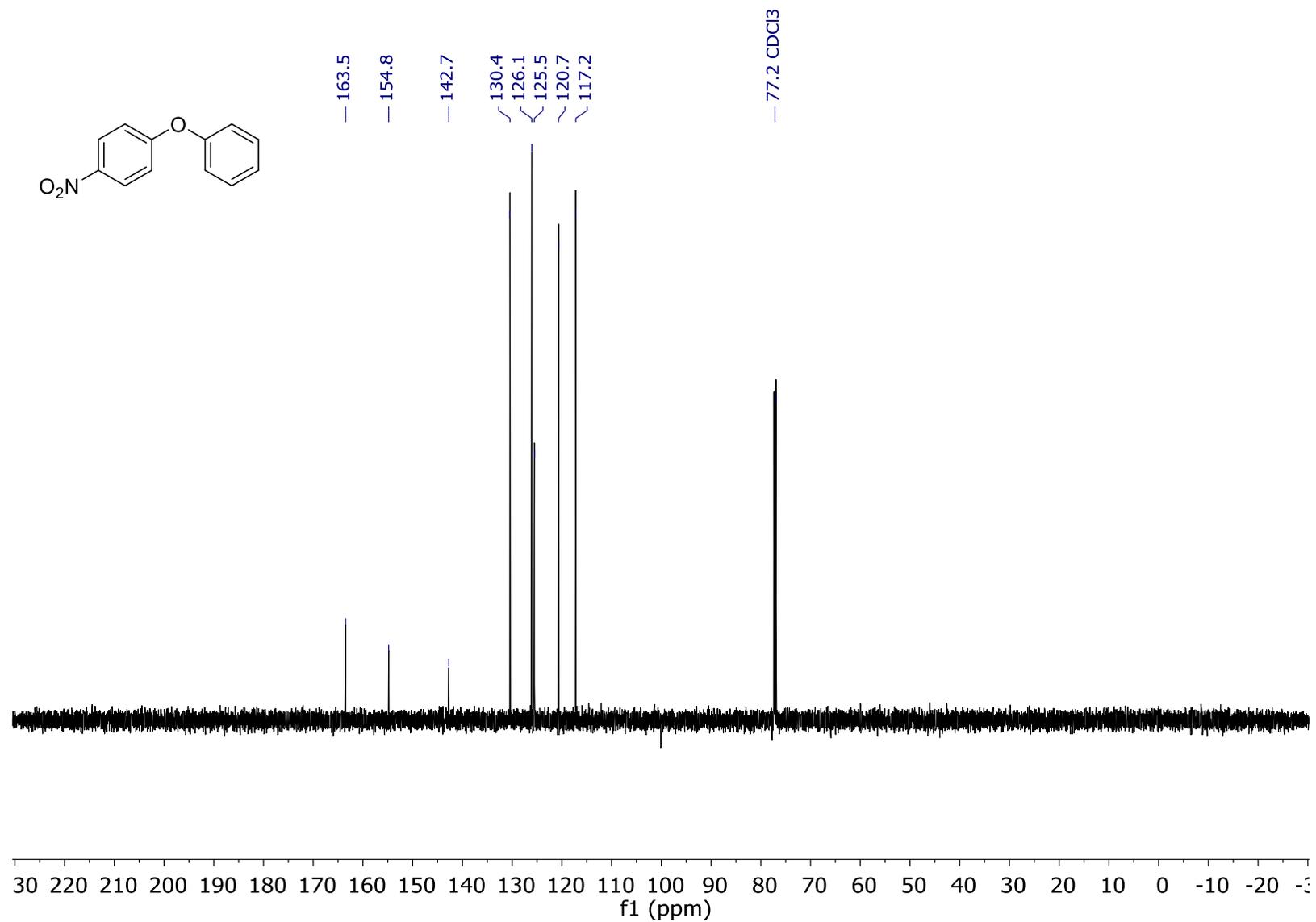


Figure S8.  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz, Chloroform-*d*) of 1-nitro-4-phenoxybenzene (1d).

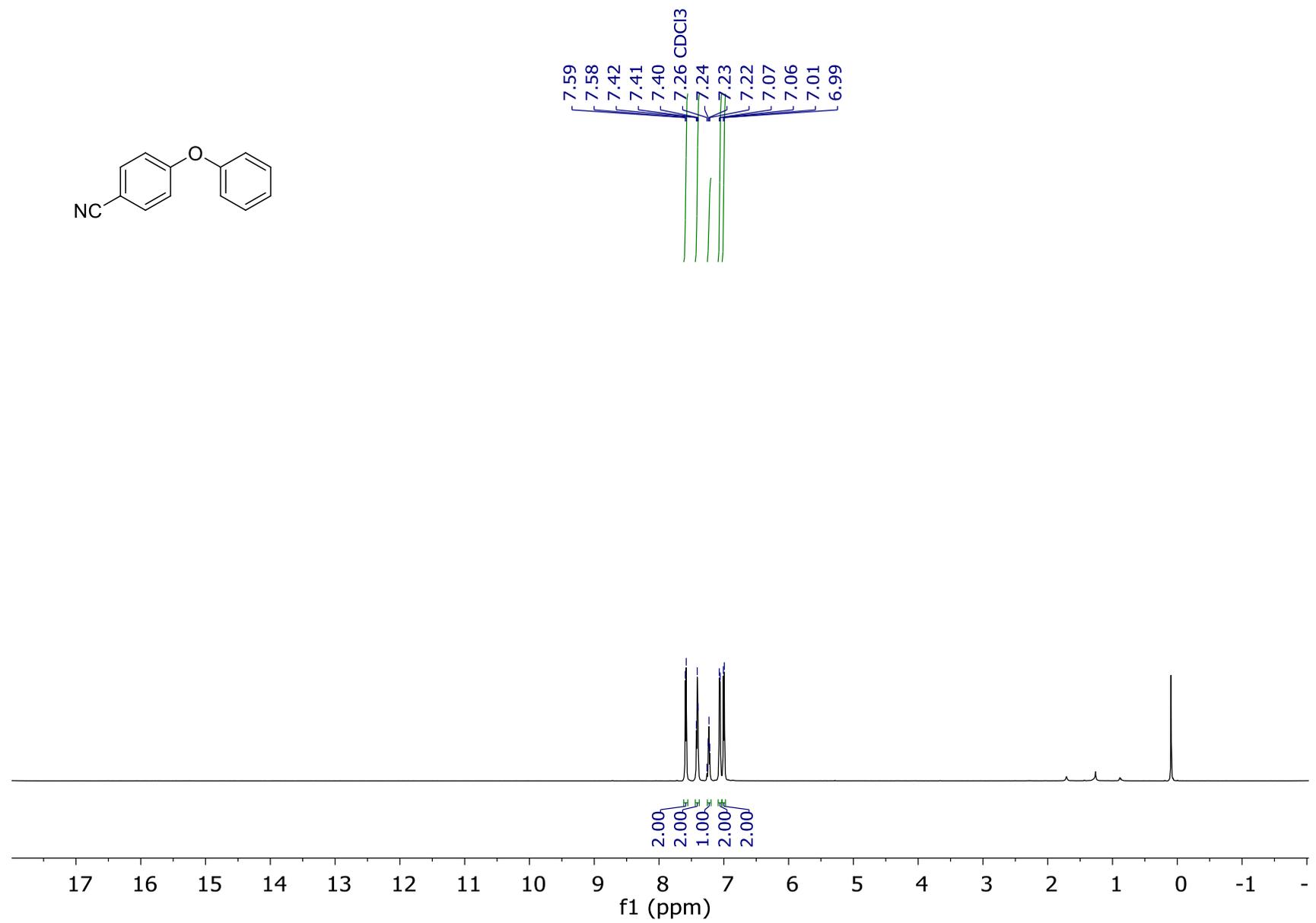


Figure S9. <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) of 4-phenoxybenzonitrile (1e).

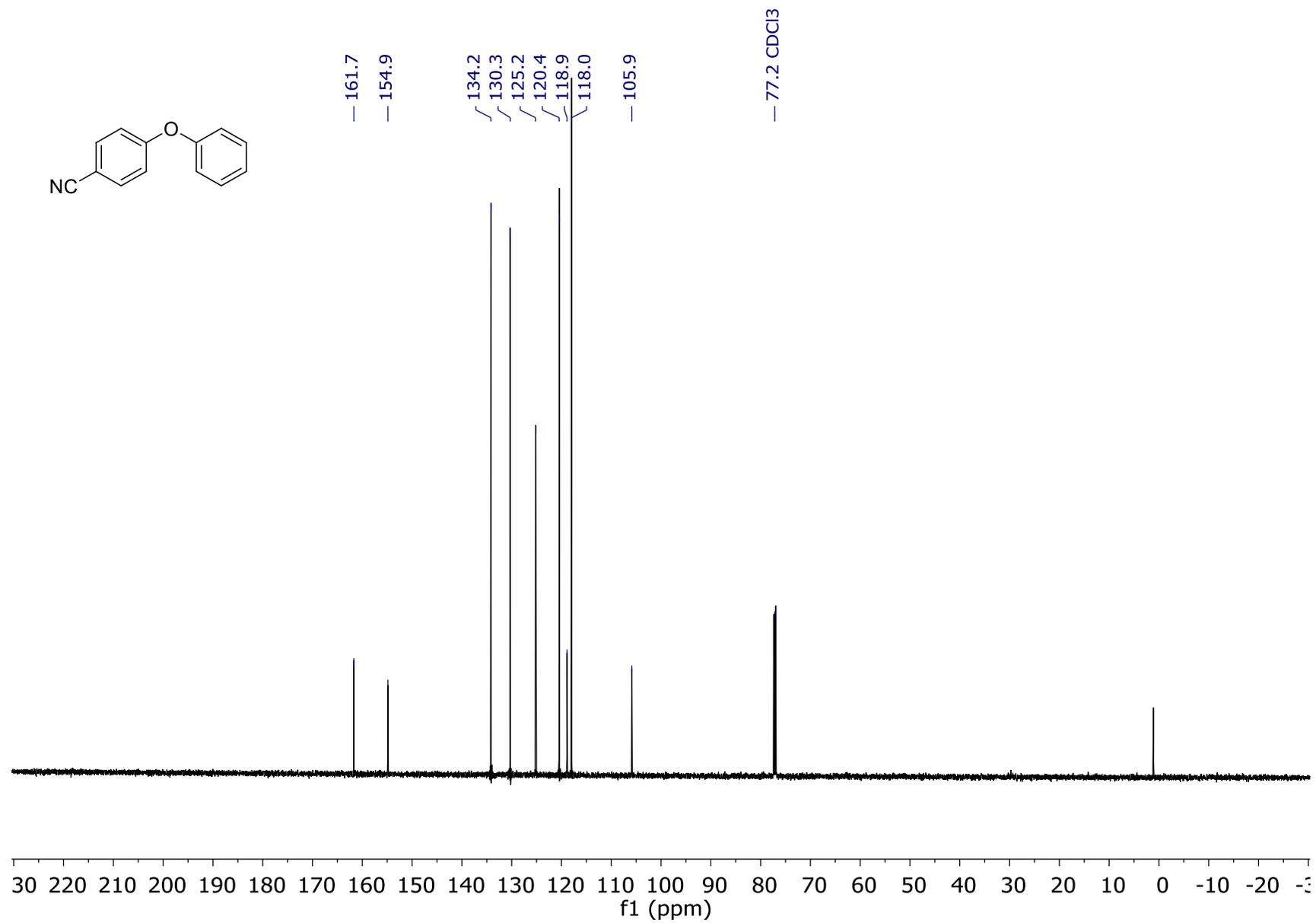


Figure S10.  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz, Chloroform-*d*) of 4-phenoxybenzotrile (1e).

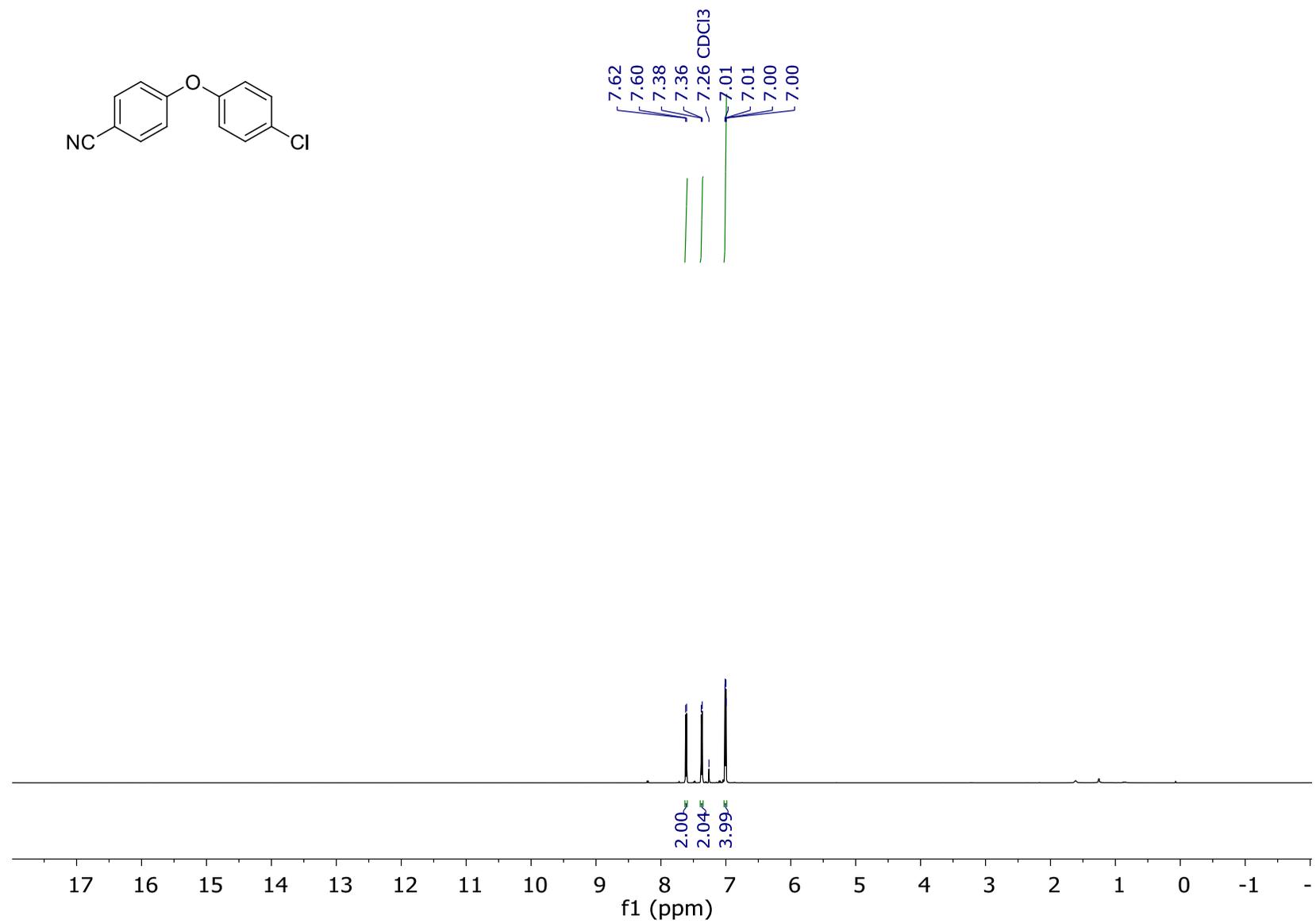


Figure S11. <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) of 4-(4-chlorophenoxy)benzonitrile (1f).

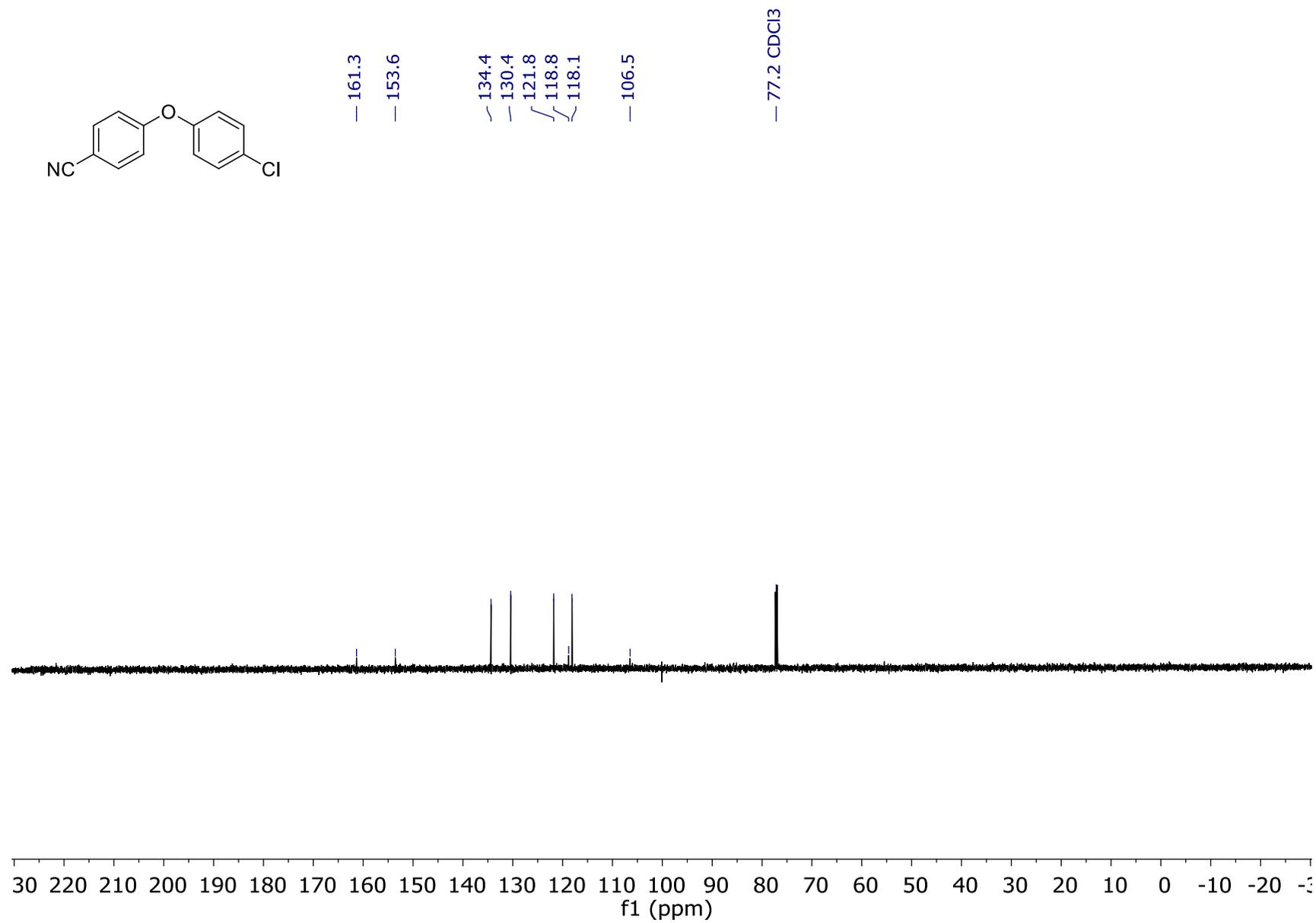


Figure S12.  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz, Chloroform-*d*) of 4-(4-chlorophenoxy)benzonitrile (1f).

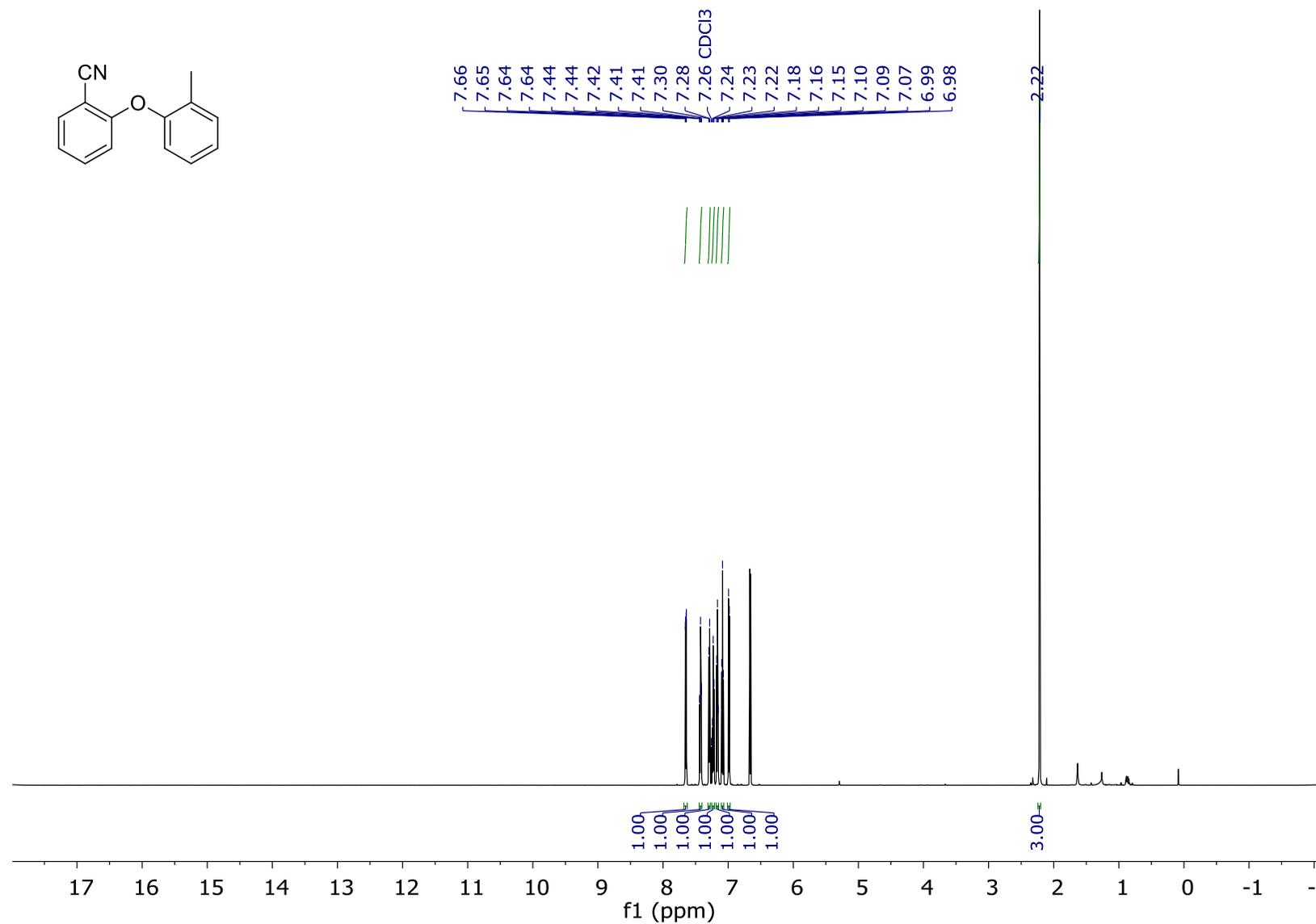


Figure S13. <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) of 2-(*o*-tolylloxy)benzonitrile (1g).

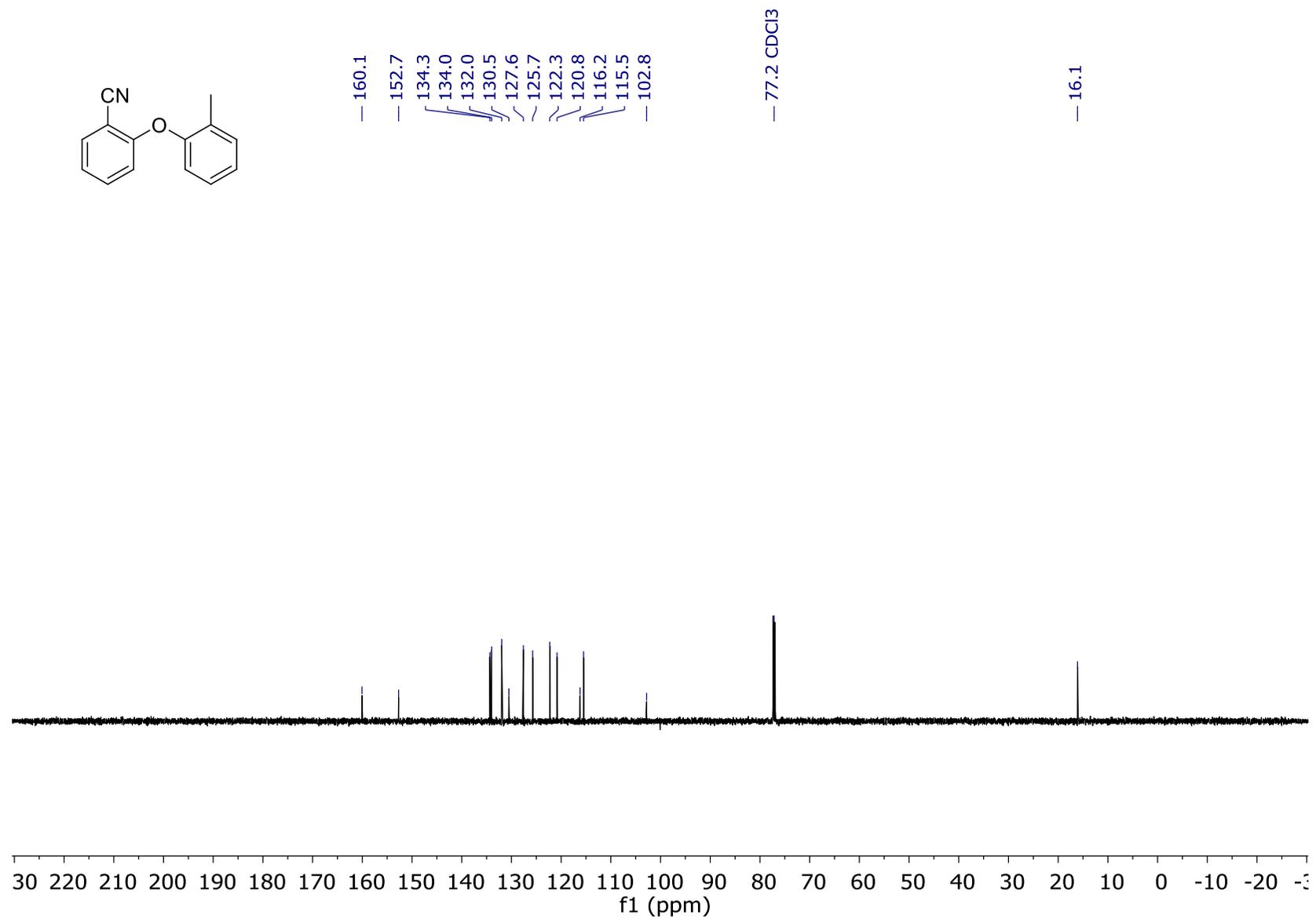


Figure S14.  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz, Chloroform-*d*) of 2-(*o*-tolylloxy)benzonitrile (1g).

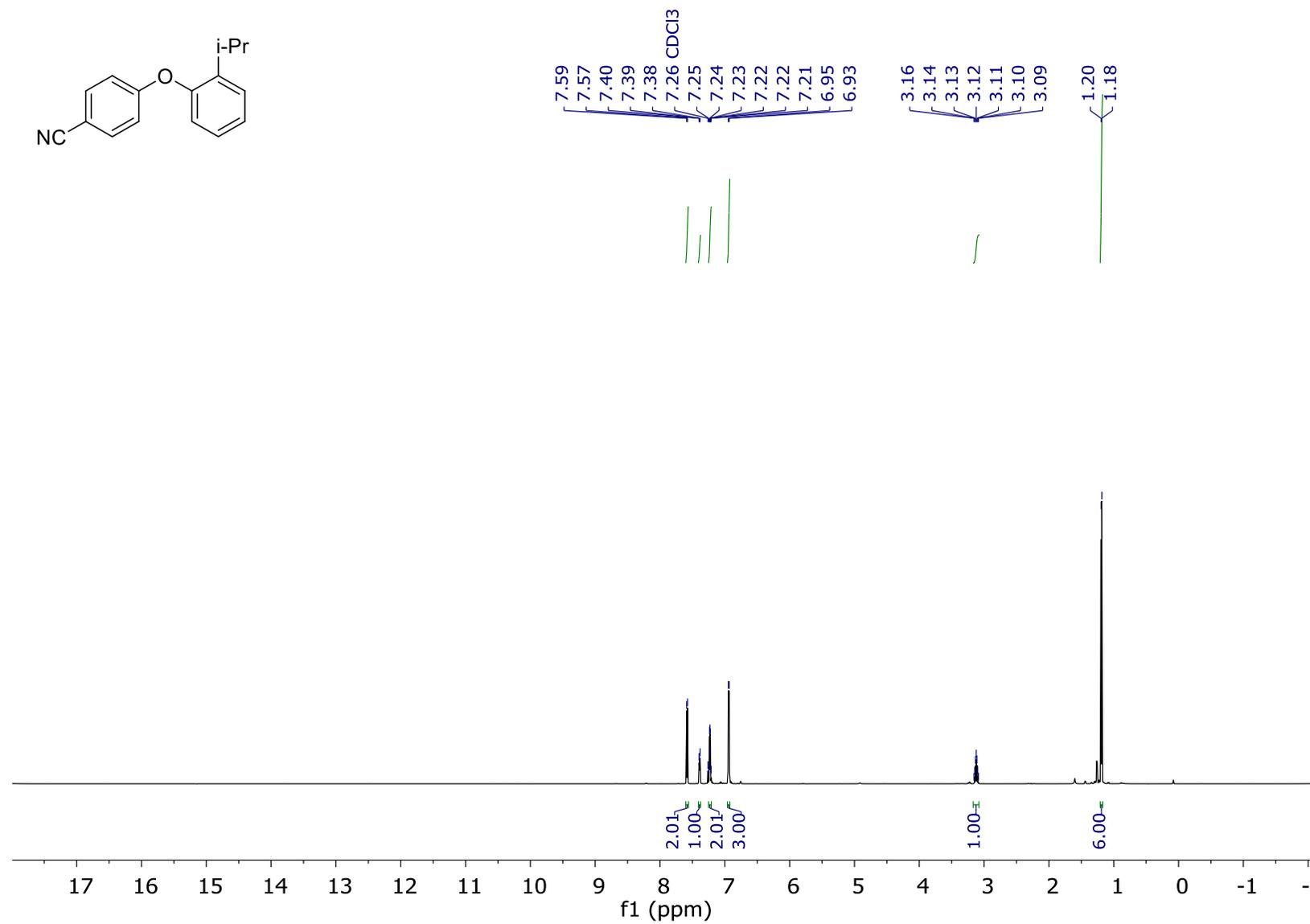


Figure S15. <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) of 4-(2-isopropylphenoxy)benzonitrile (1h).

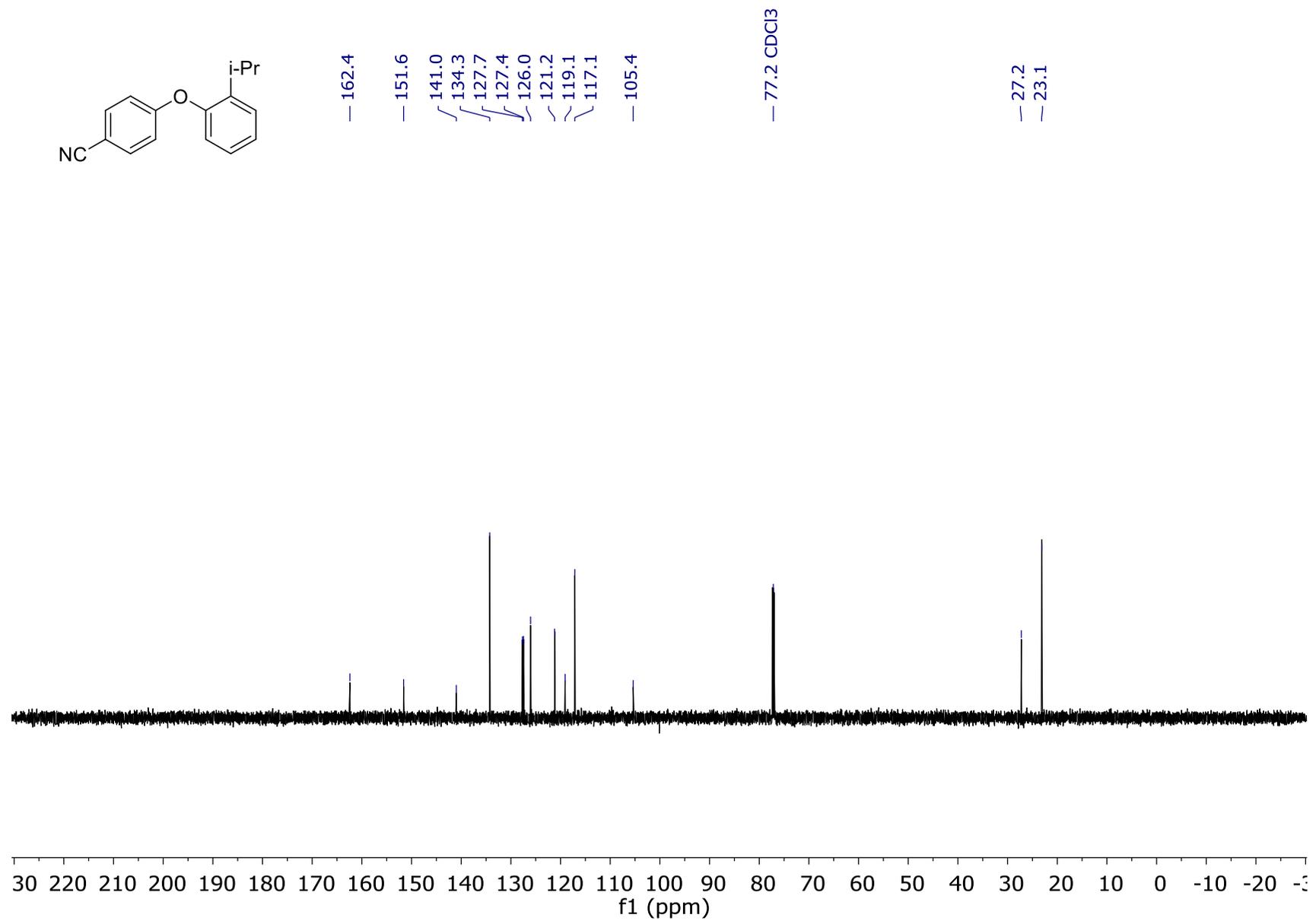


Figure S16.  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz, Chloroform-*d*) of 4-(2-isopropylphenoxy)benzonitrile (1h).

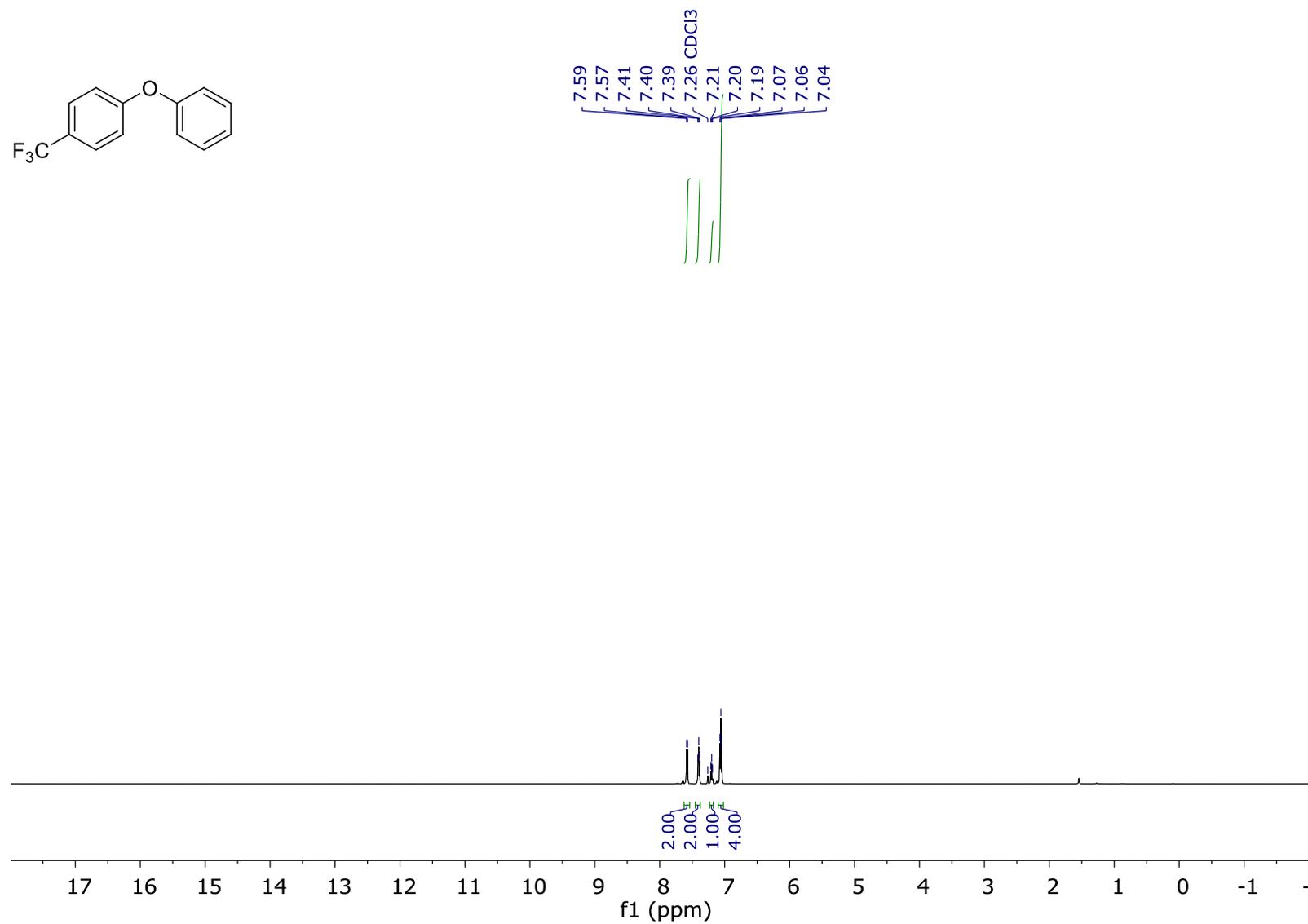
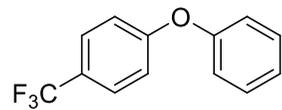


Figure S17. <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) of 1-phenoxy-4-(trifluoromethyl)benzene (1i).

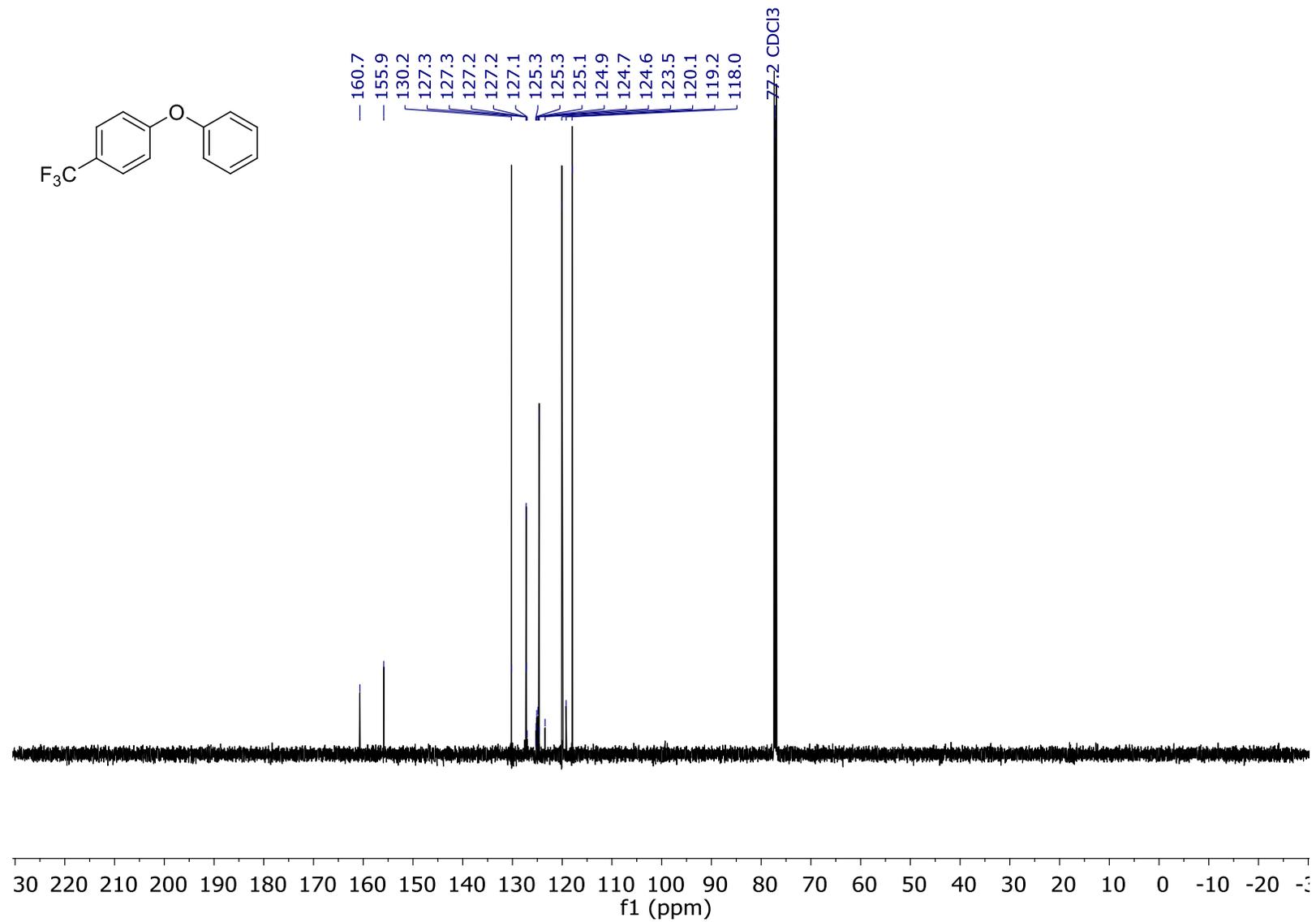


Figure S18.  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz, Chloroform-*d*) of 1-phenoxy-4-(trifluoromethyl)benzene (1i).

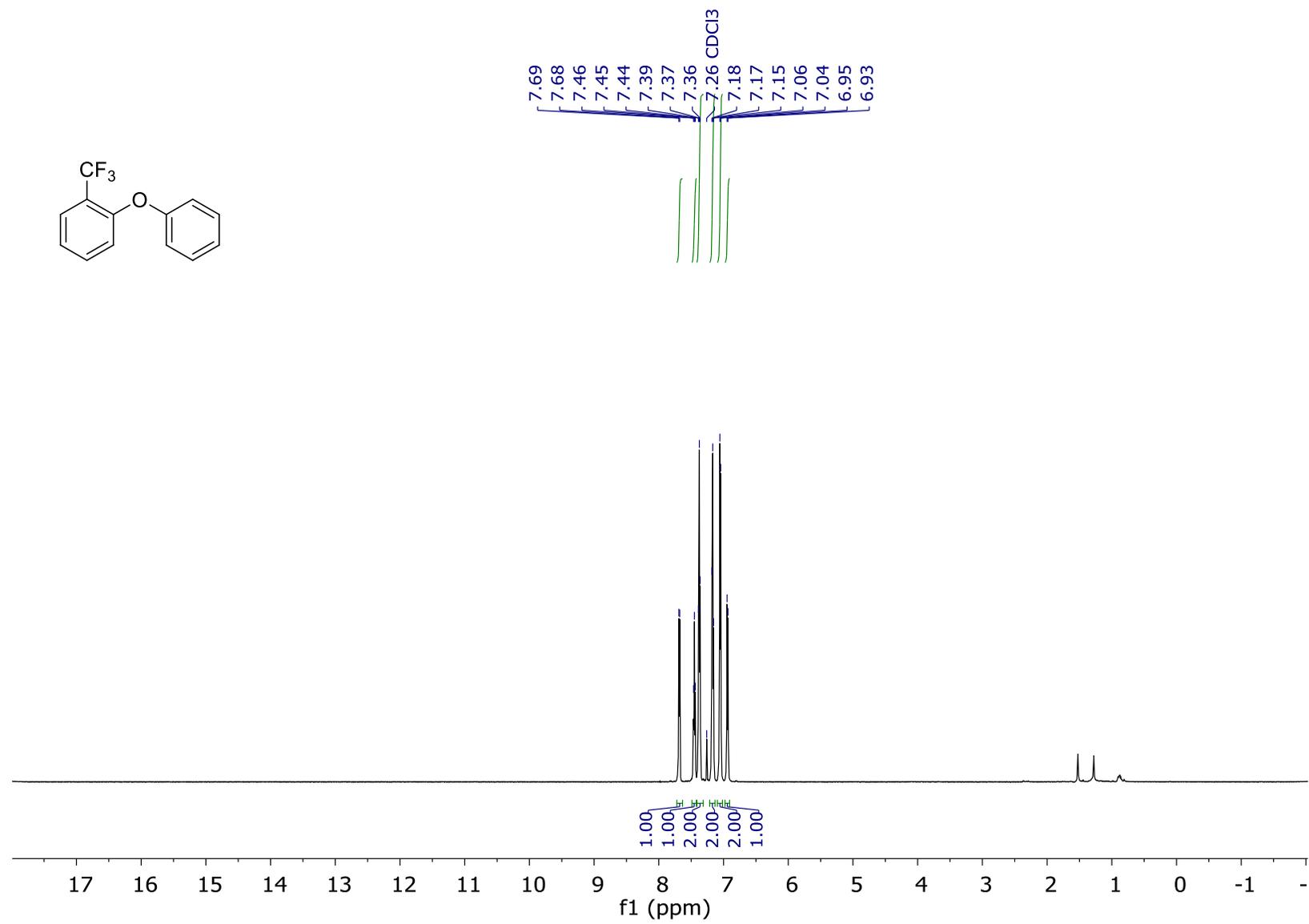


Figure S19. <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) of 1-phenoxy-2-(trifluoromethyl)benzene (1j).

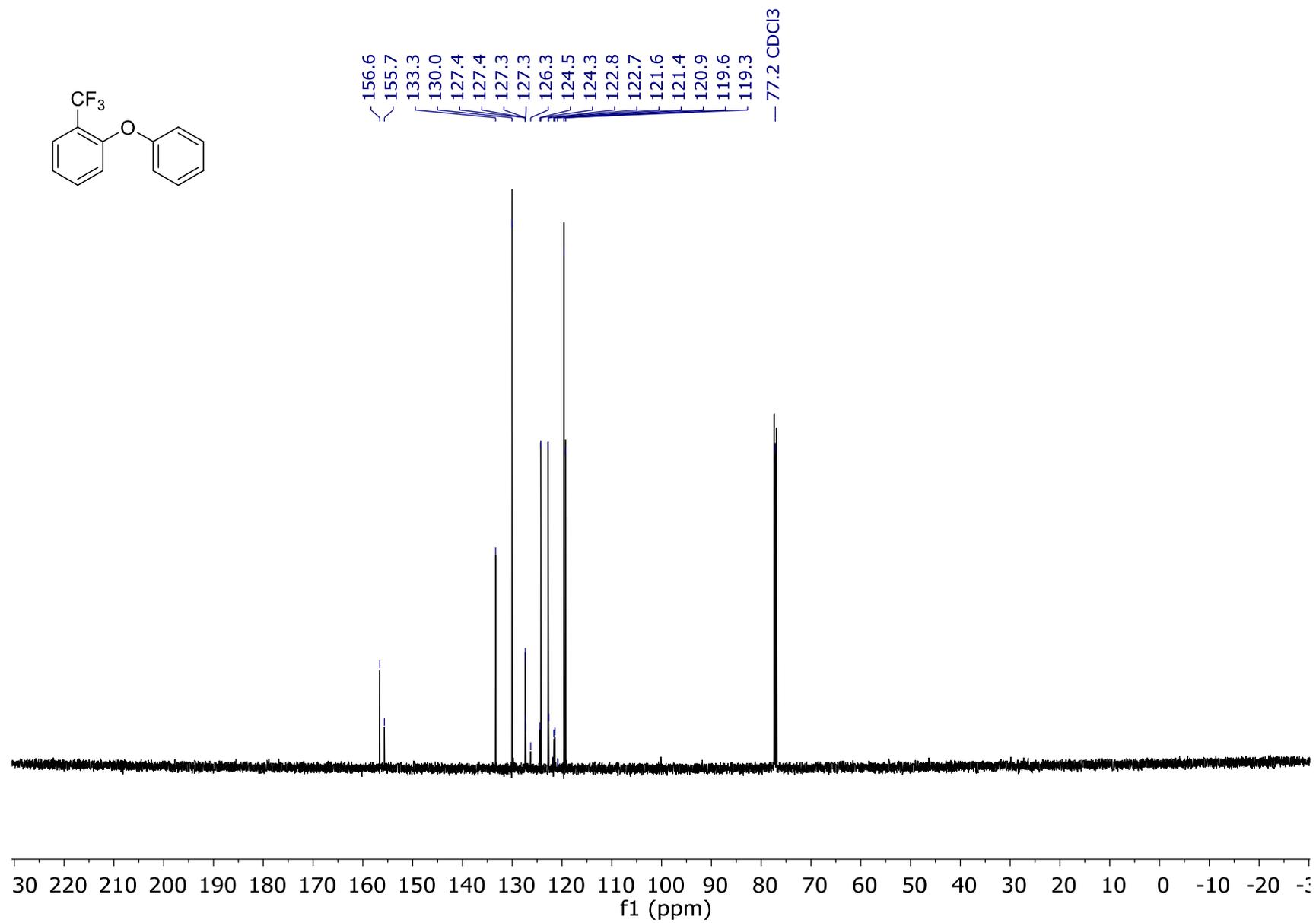


Figure S20.  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz, Chloroform-*d*) of 1-phenoxy-2-(trifluoromethyl)benzene (1j).

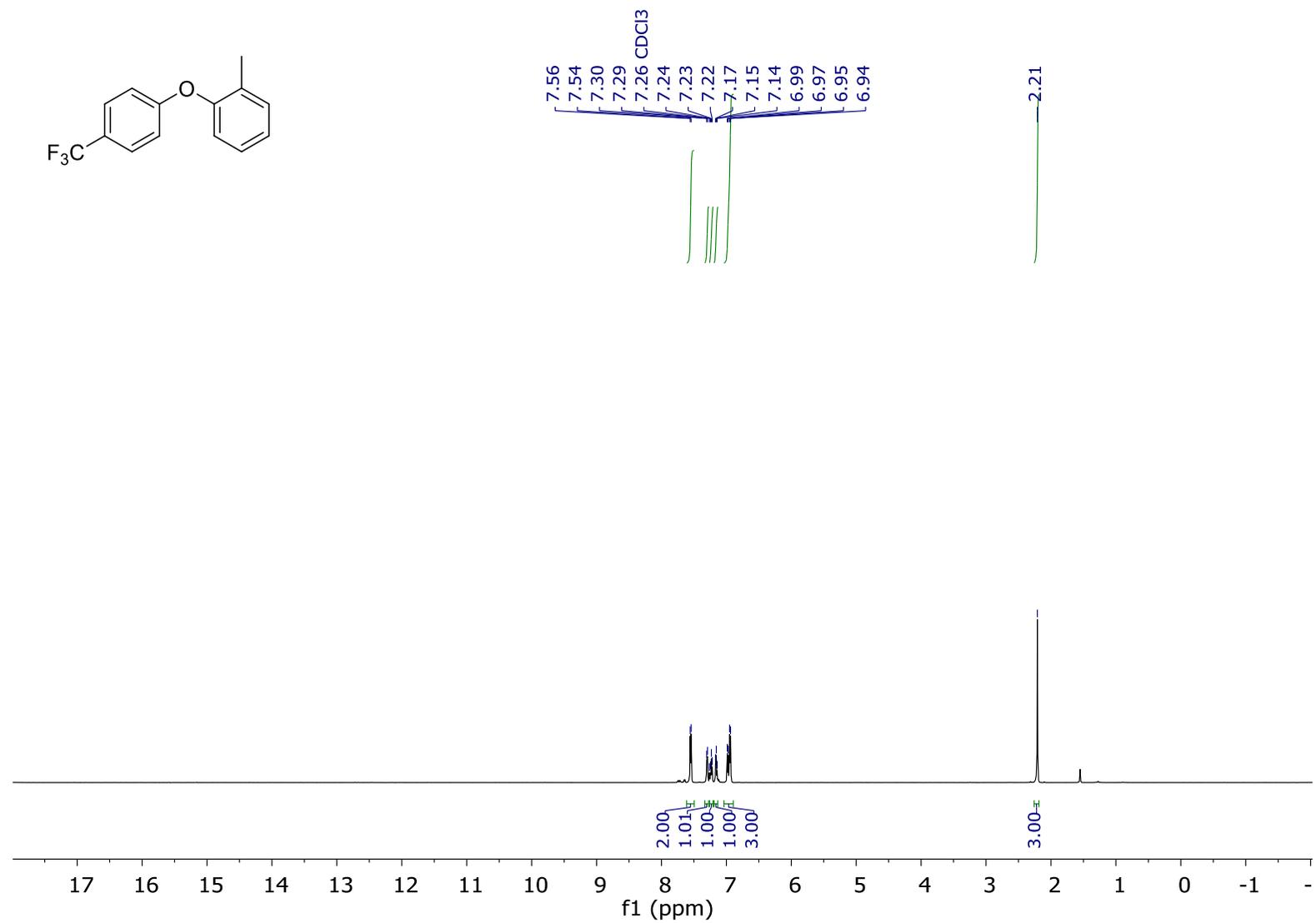


Figure S21. <sup>1</sup>H NMR (600 MHz, Chloroform-d) of 1-methyl-2-(4-(trifluoromethyl)phenoxy)benzene (1k).

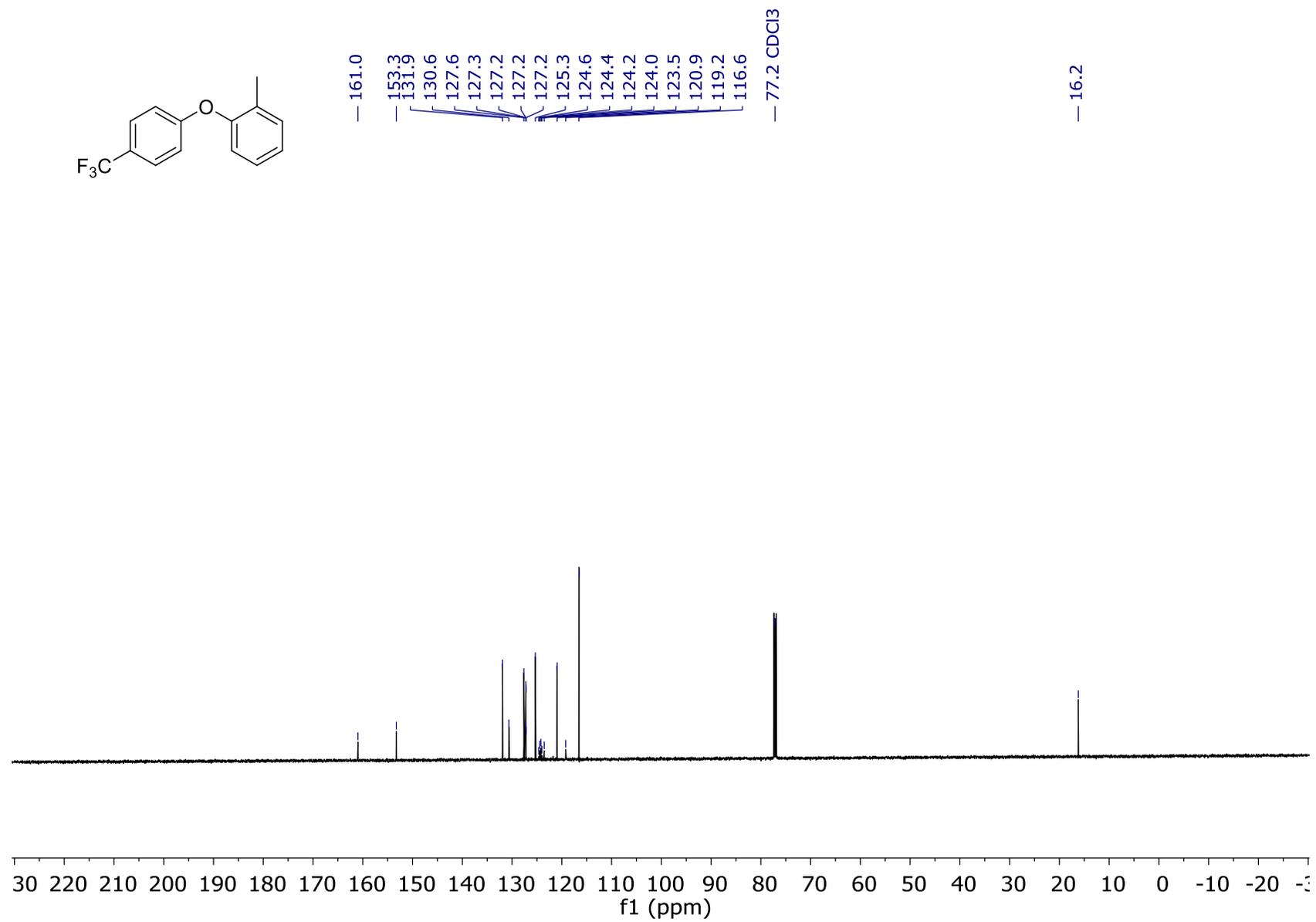


Figure S22.  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz, Chloroform-*d*) of 1-methyl-2-(4-(trifluoromethyl)phenoxy)benzene (1k).

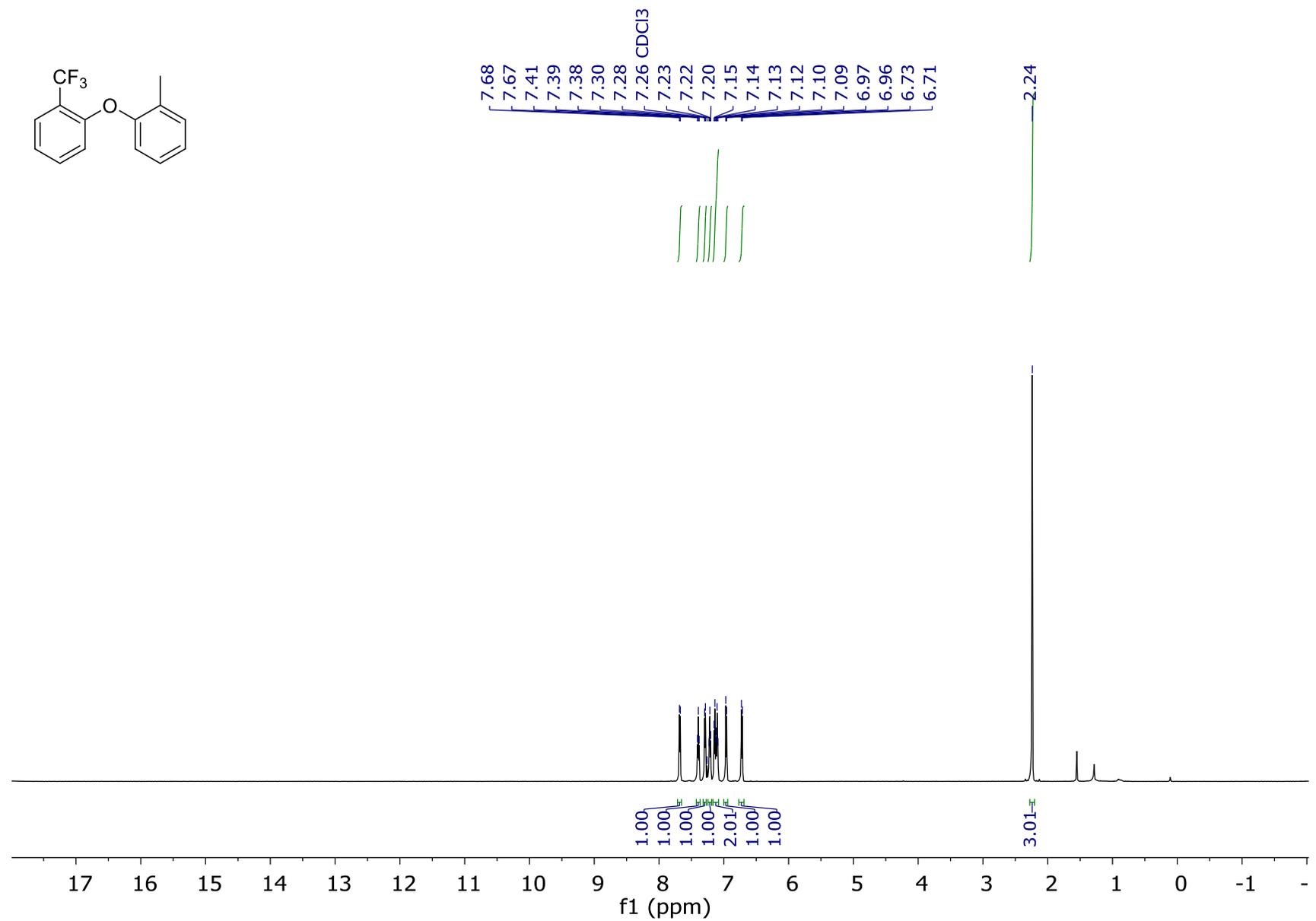


Figure S23. <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) of 1-methyl-2-(2-(trifluoromethyl)phenoxy)benzene (11).

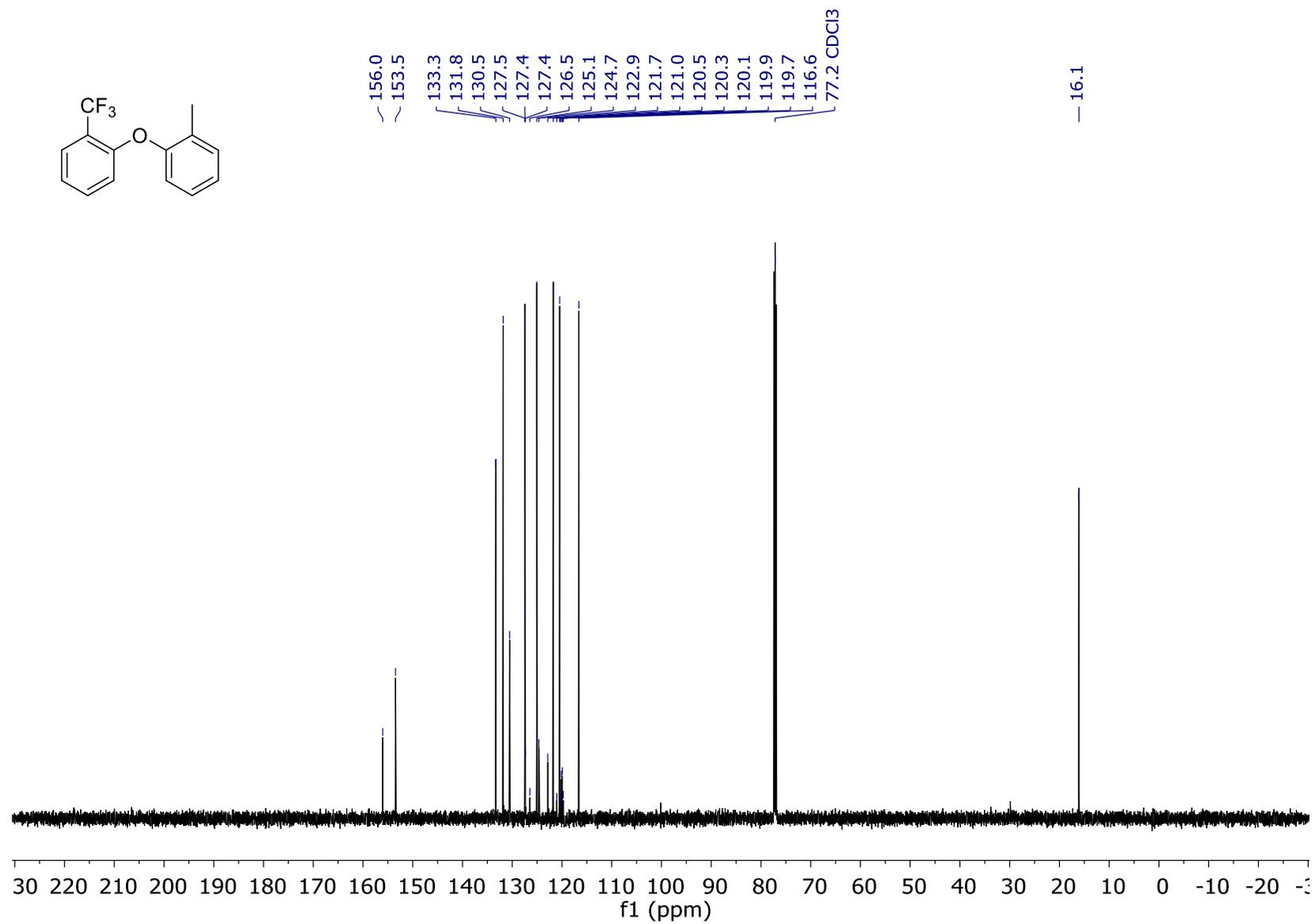


Figure S24.  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz, Chloroform-*d*) of 1-methyl-2-(2-(trifluoromethyl)phenoxy)benzene (11).

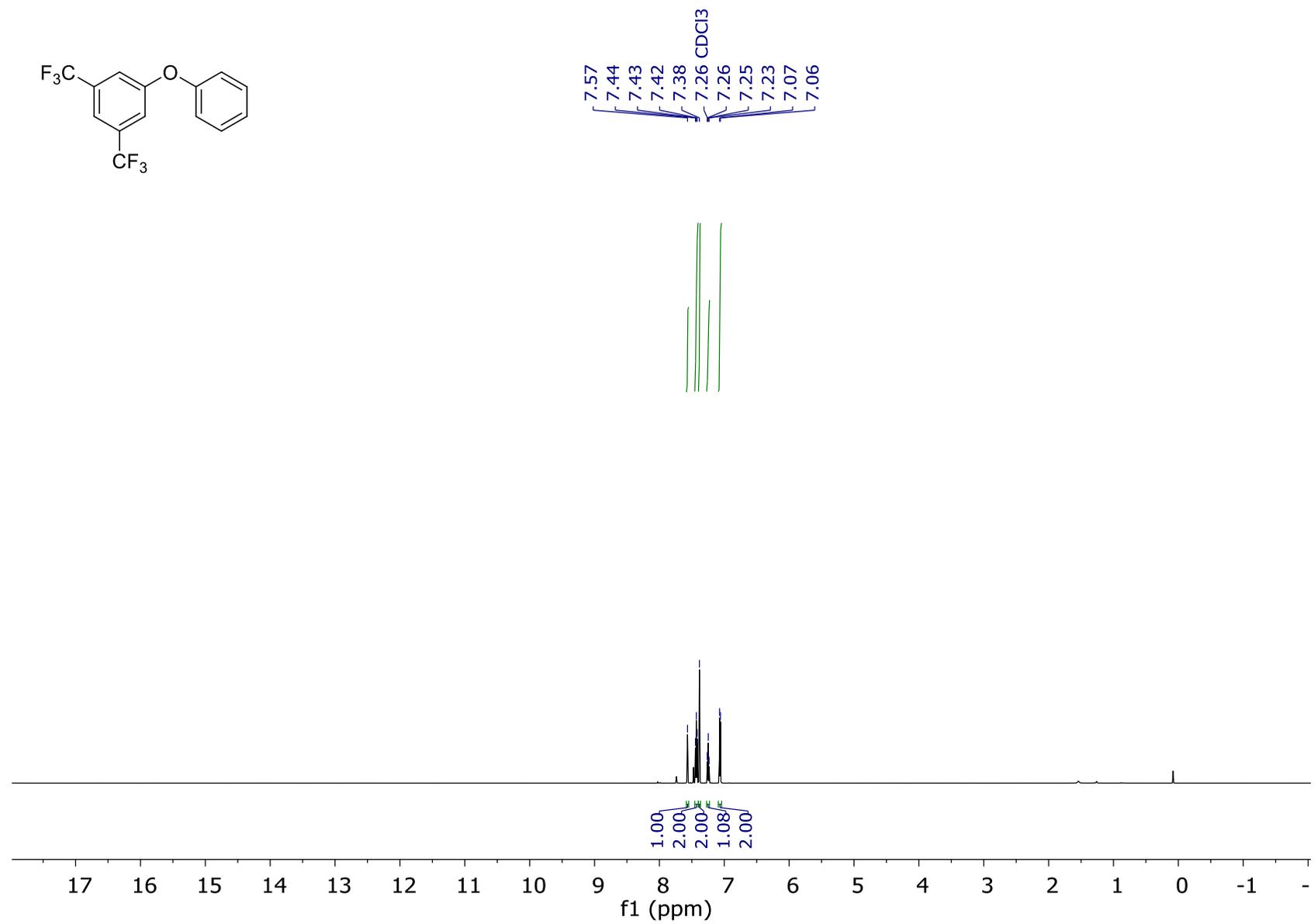


Figure S25. <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) of 1-phenoxy-3,5-bis(trifluoromethyl)benzene (1m).

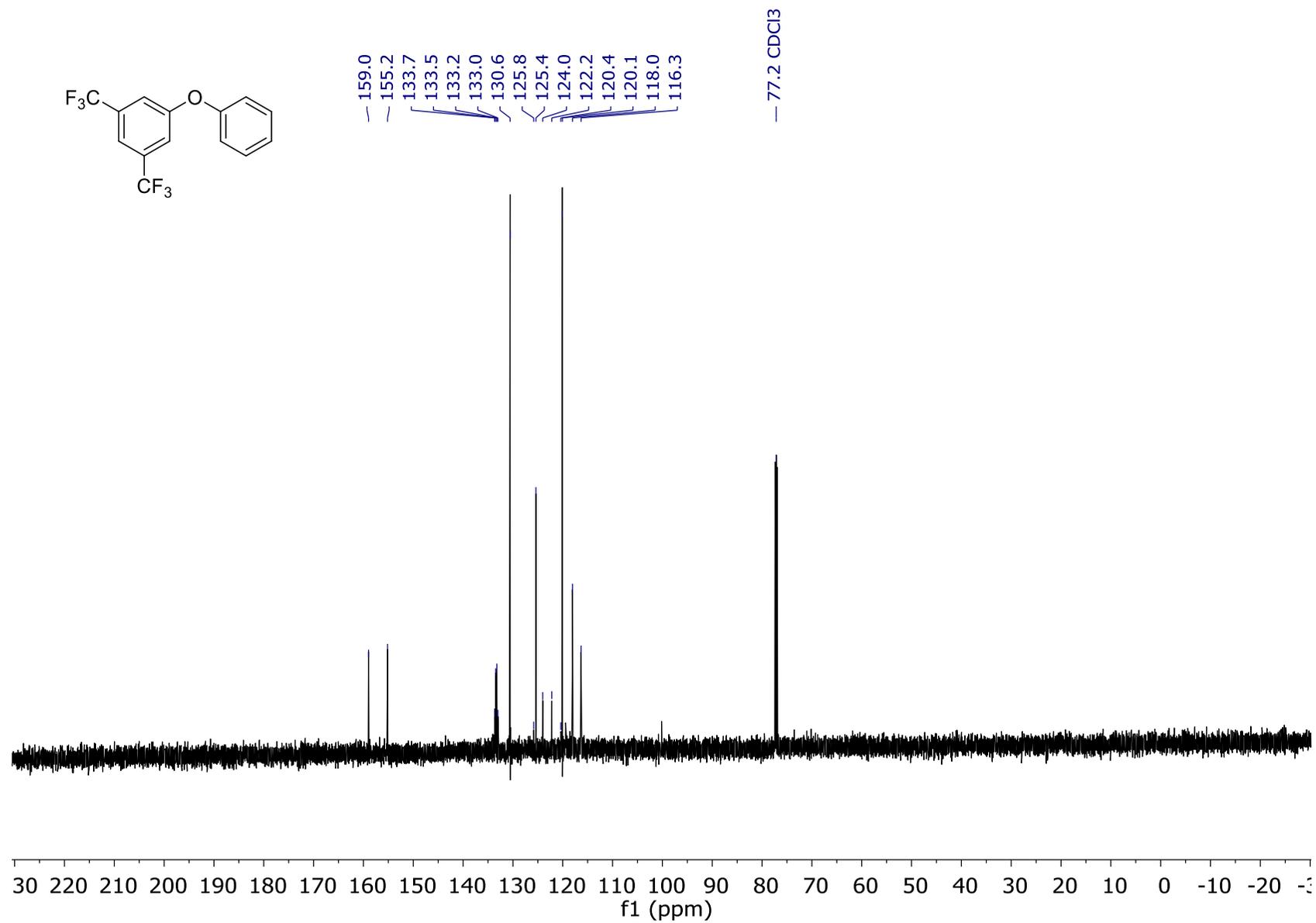


Figure S26.  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz, Chloroform-*d*) of 1-phenoxy-3,5-bis(trifluoromethyl)benzene (1m).

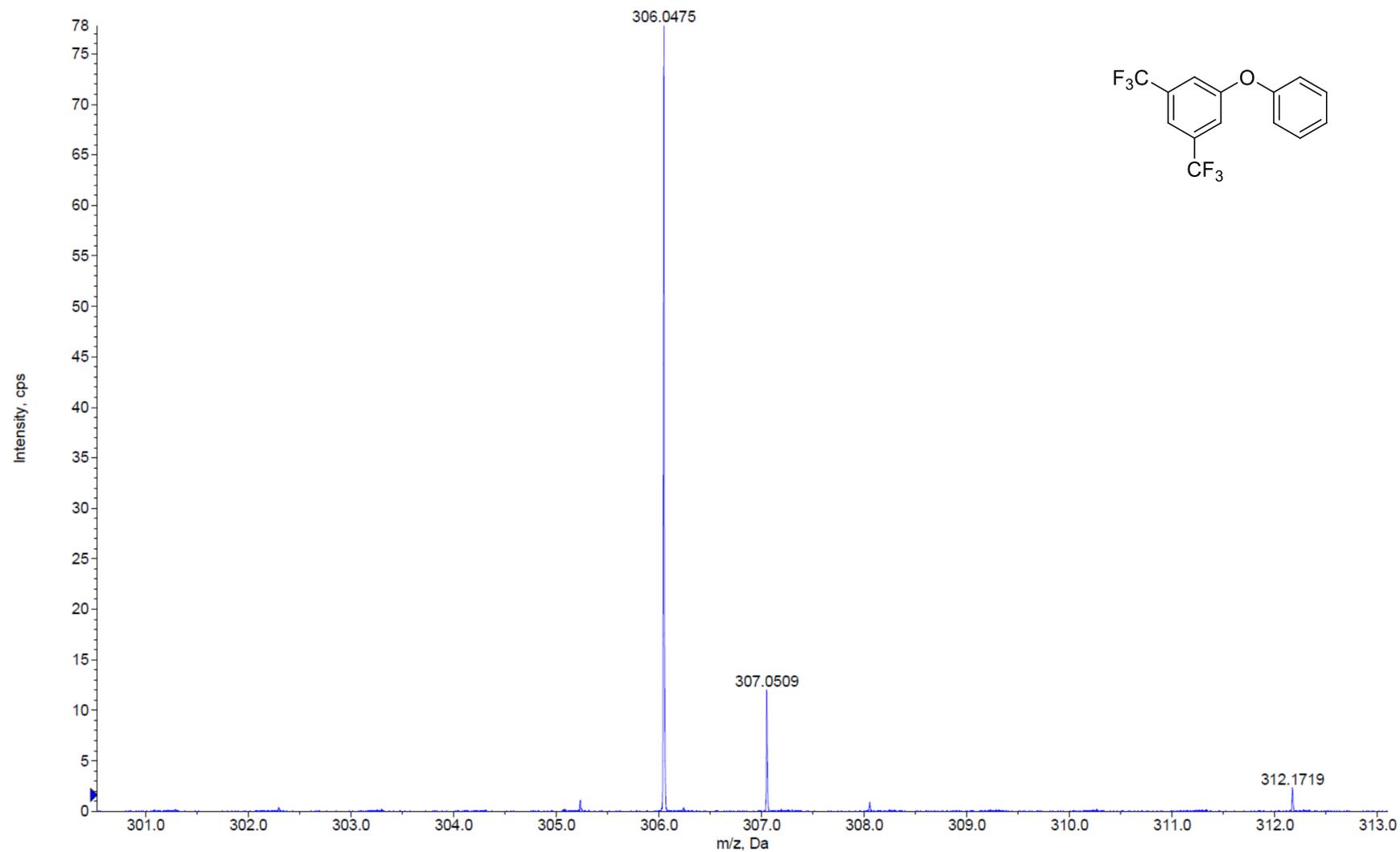


Figure S27. HRMS spectra of 1-phenoxy-3,5-bis(trifluoromethyl)benzene (1m).

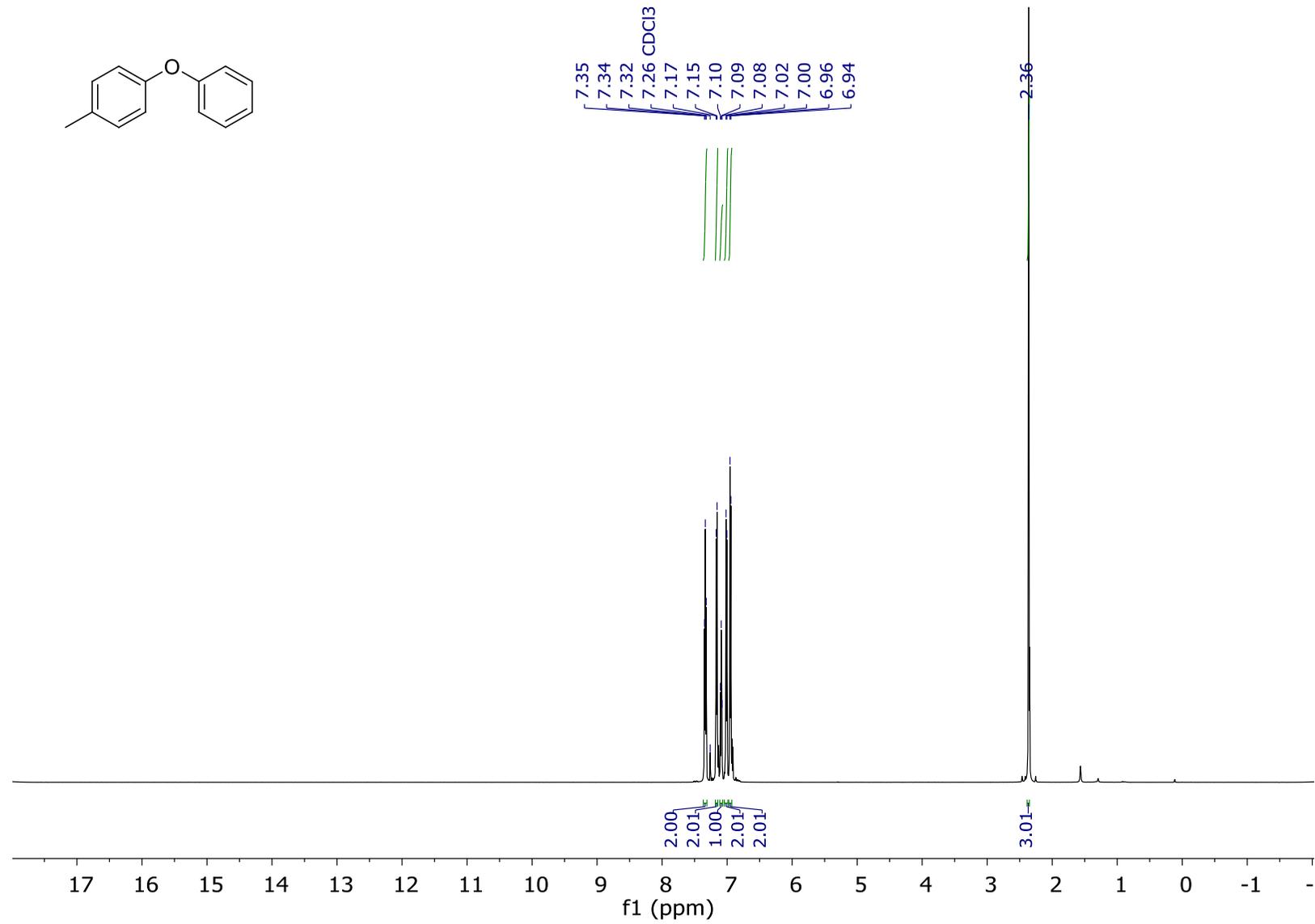


Figure S36. <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) of 1-methyl-4-phenoxybenzene (2a).

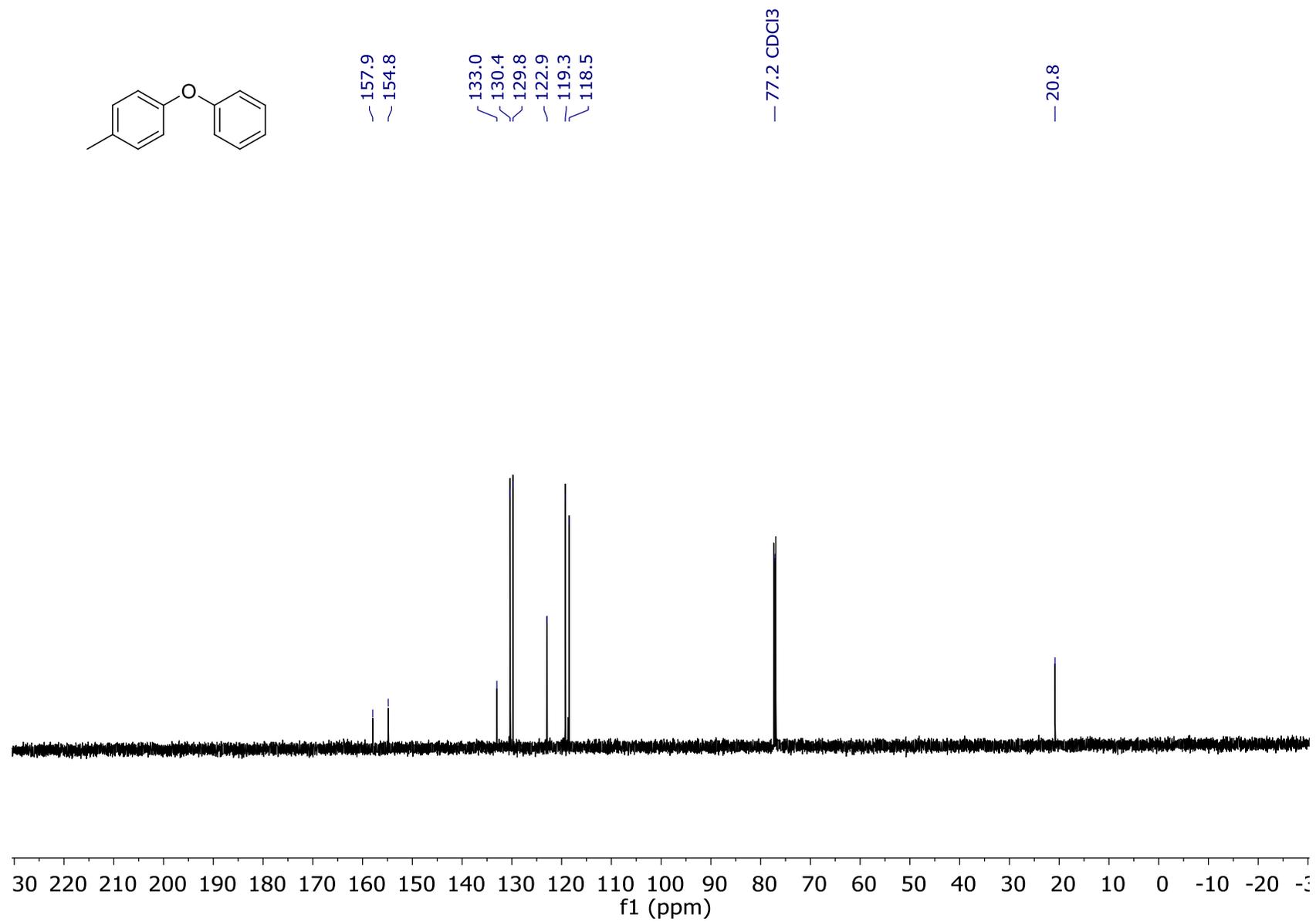


Figure S37.  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz, Chloroform-*d*) of 1-methyl-4-phenoxybenzene (2a).

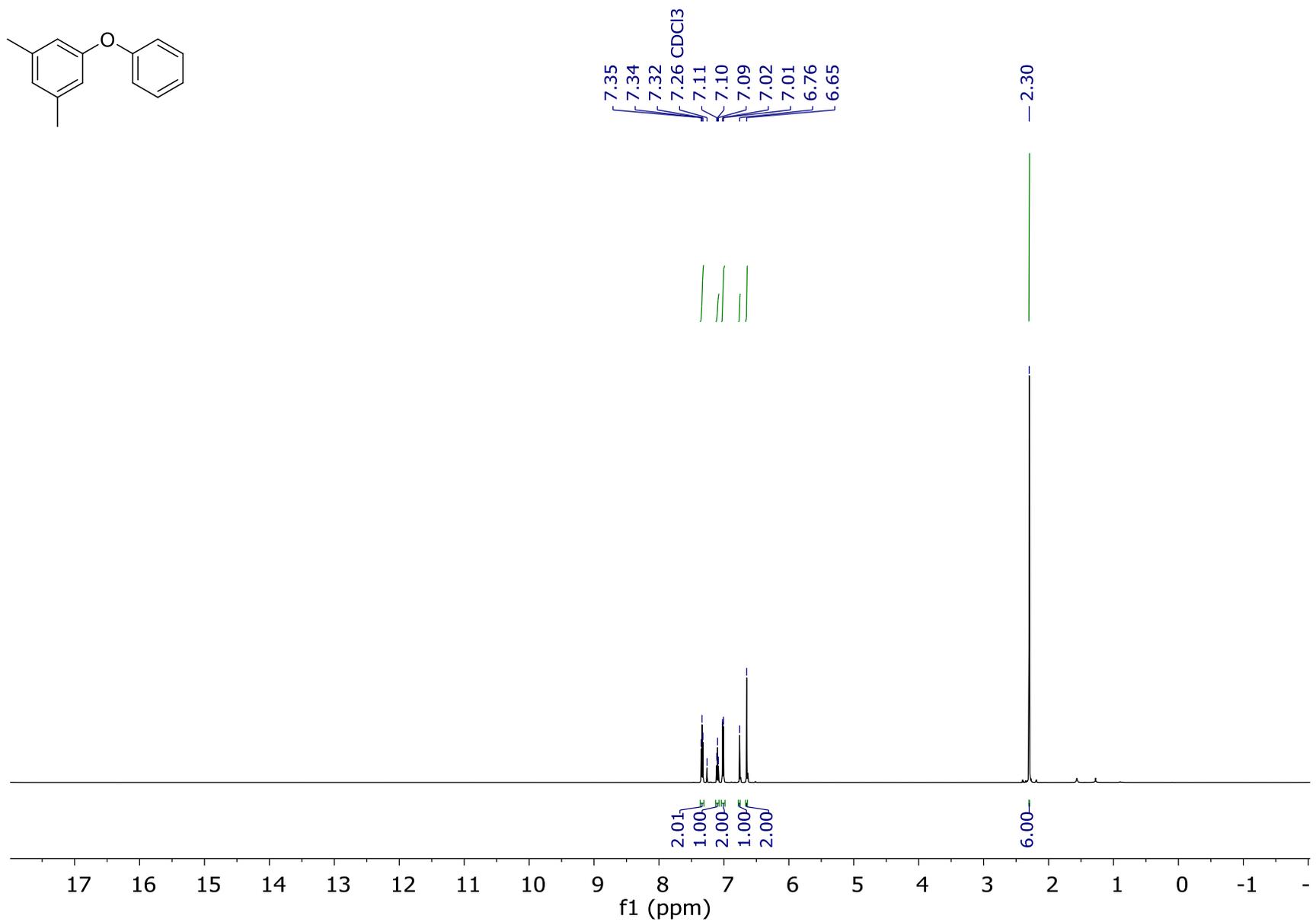
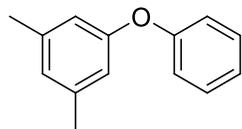


Figure S38.  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*) of 1,3-dimethyl-5-phenoxybenzene (2b).

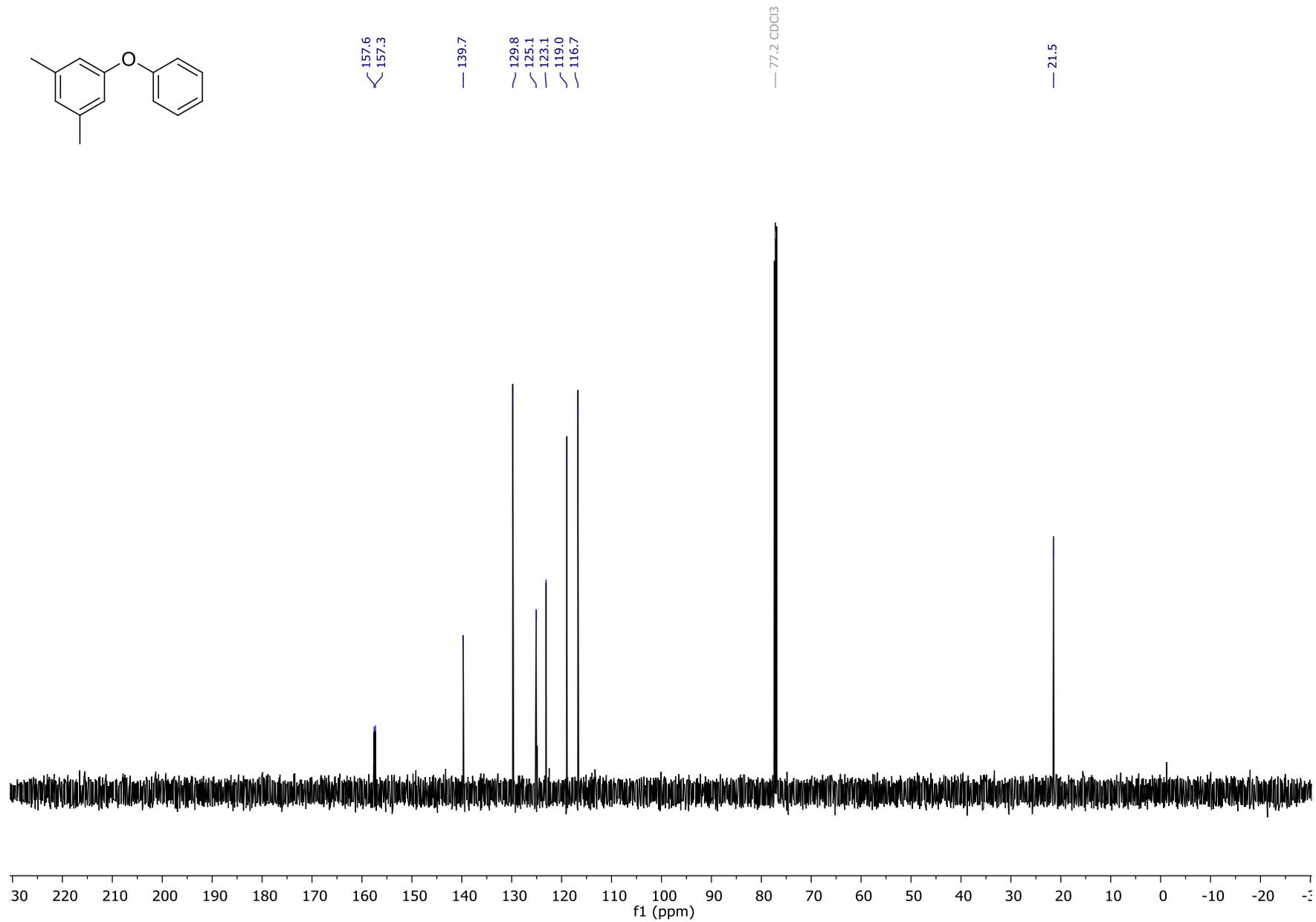
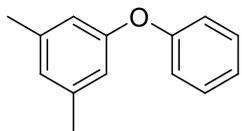


Figure S39.  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz, Chloroform-*d*) of 1,3-dimethyl-5-phenoxybenzene (2b).

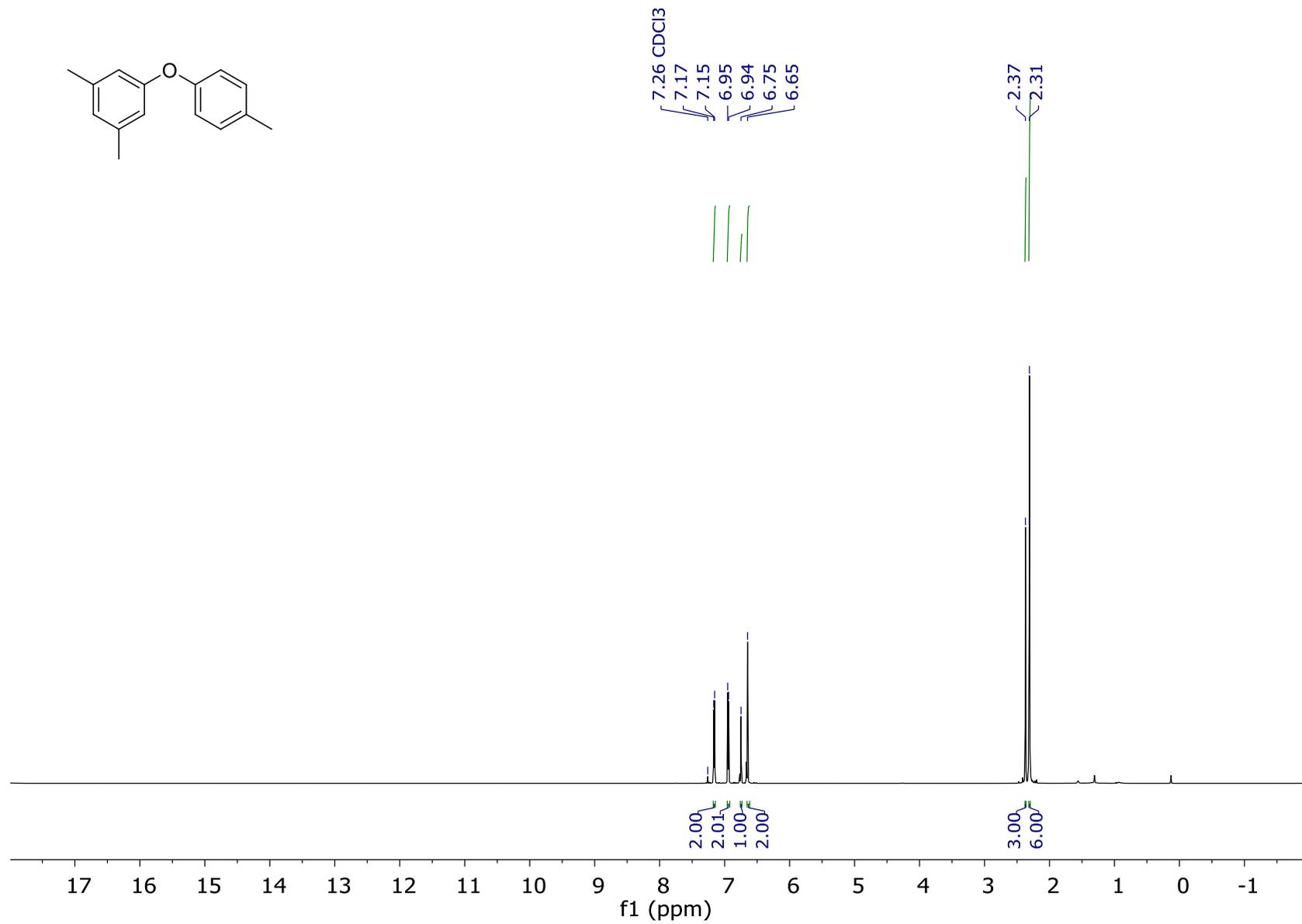


Figure S40.  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*) of 1,3-dimethyl-5-(*p*-toloxy)benzene (2c).

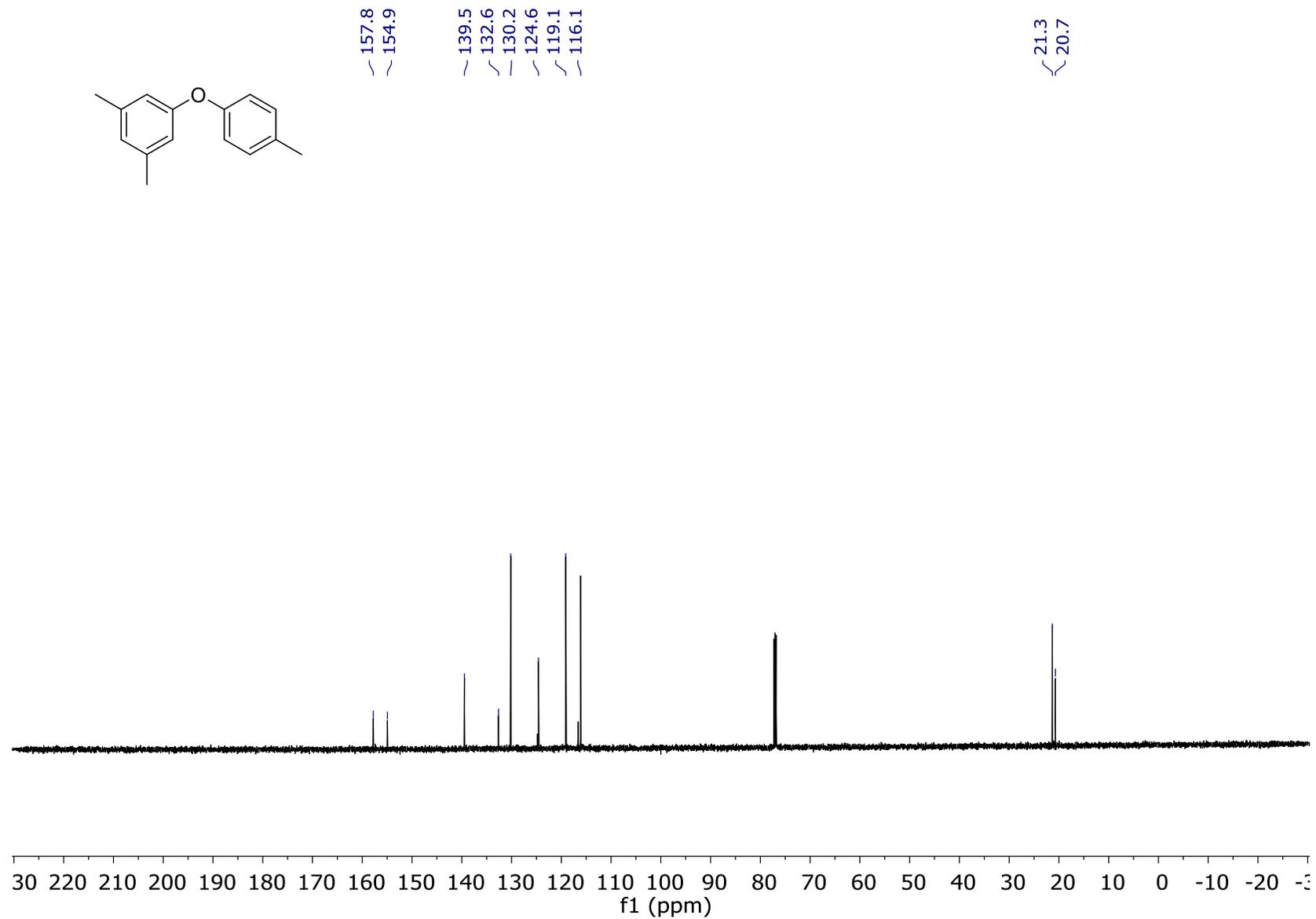


Figure S41.  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz, Chloroform-*d*) of 1,3-dimethyl-5-(*p*-toloxy)benzene (2c).

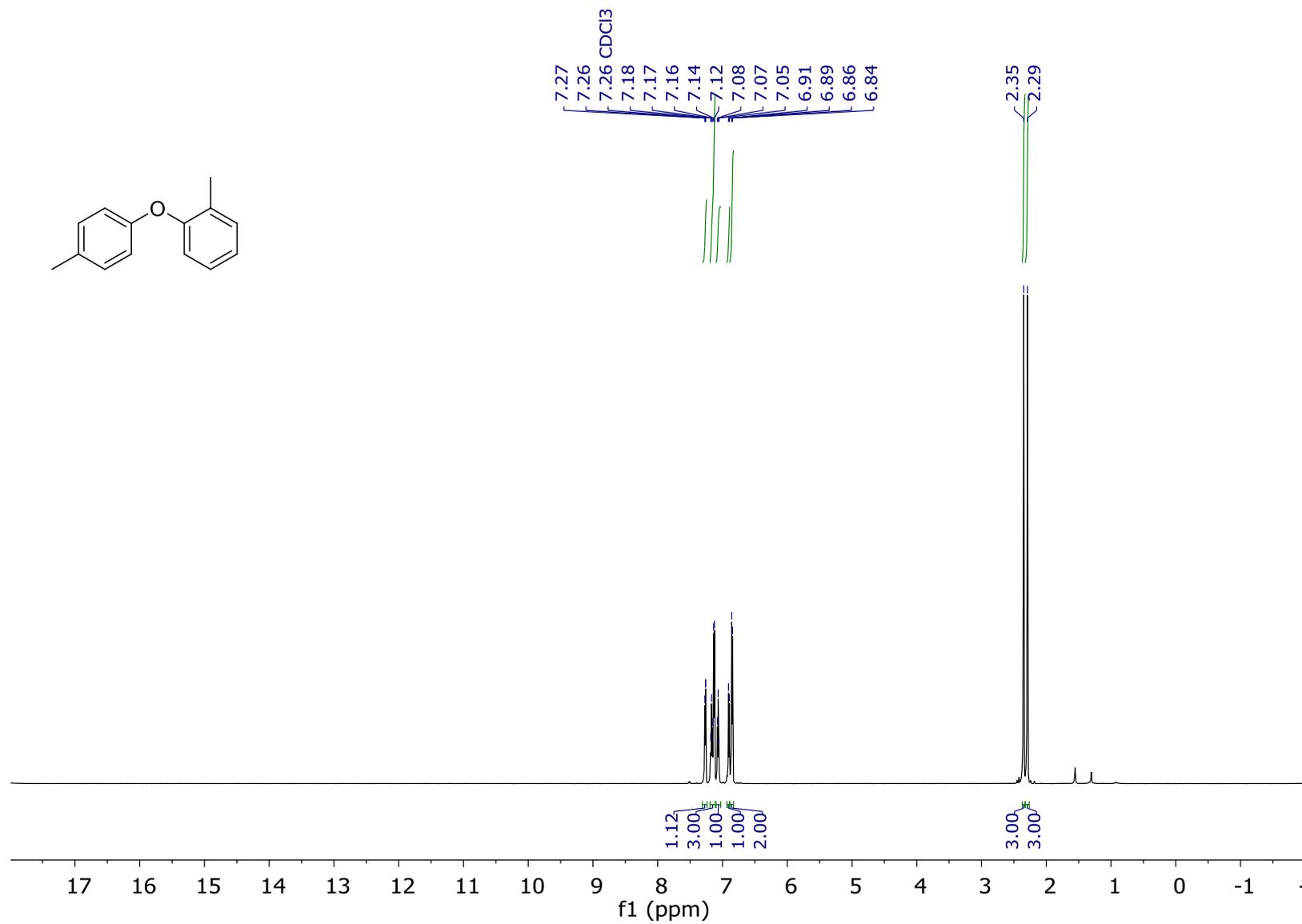


Figure S42. <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) of 1-methyl-2-(*p*-toloxy)benzene (2d).

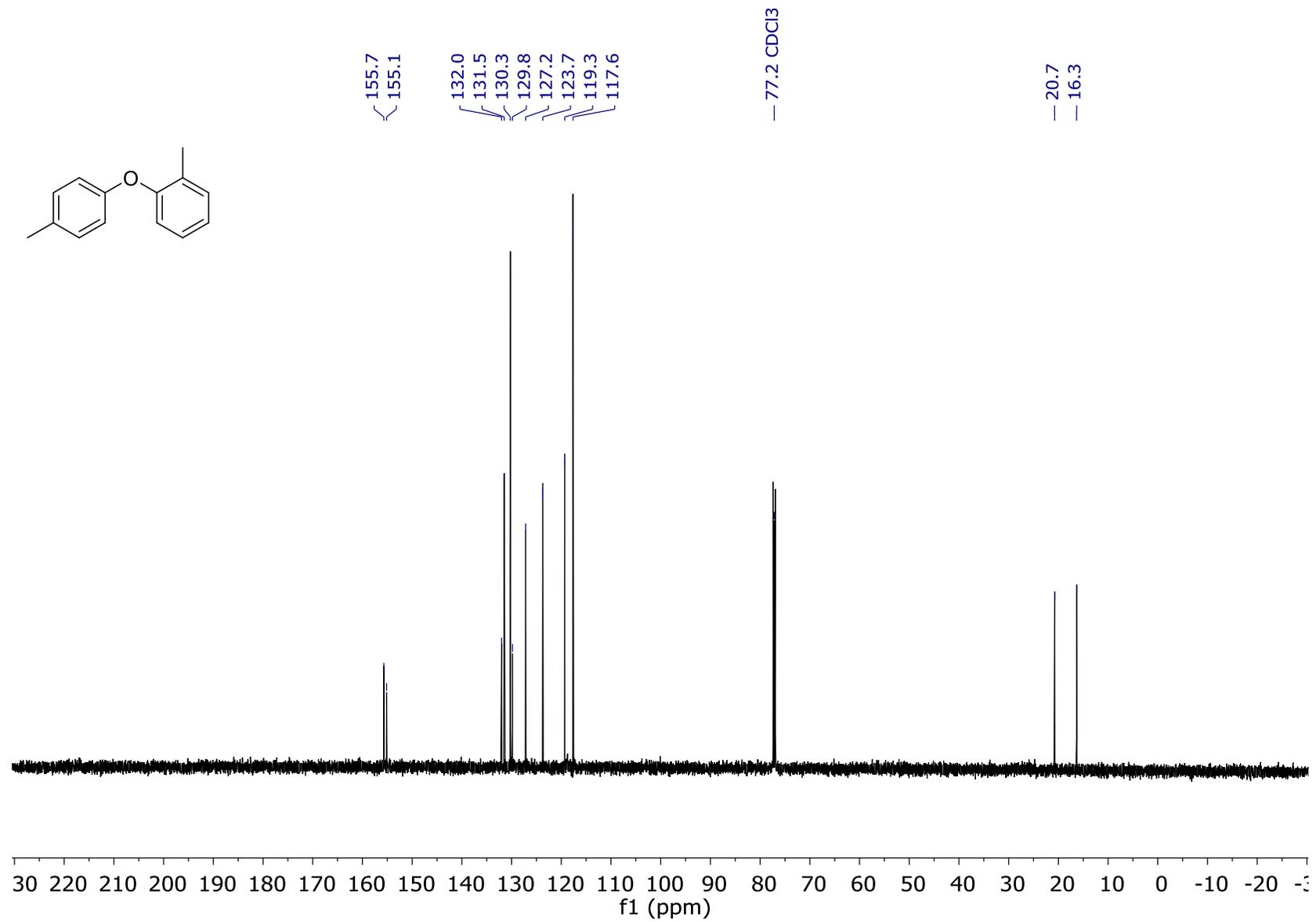


Figure S43.  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz, Chloroform-*d*) of 1-methyl-2-(*p*-toloxy)benzene (2d).

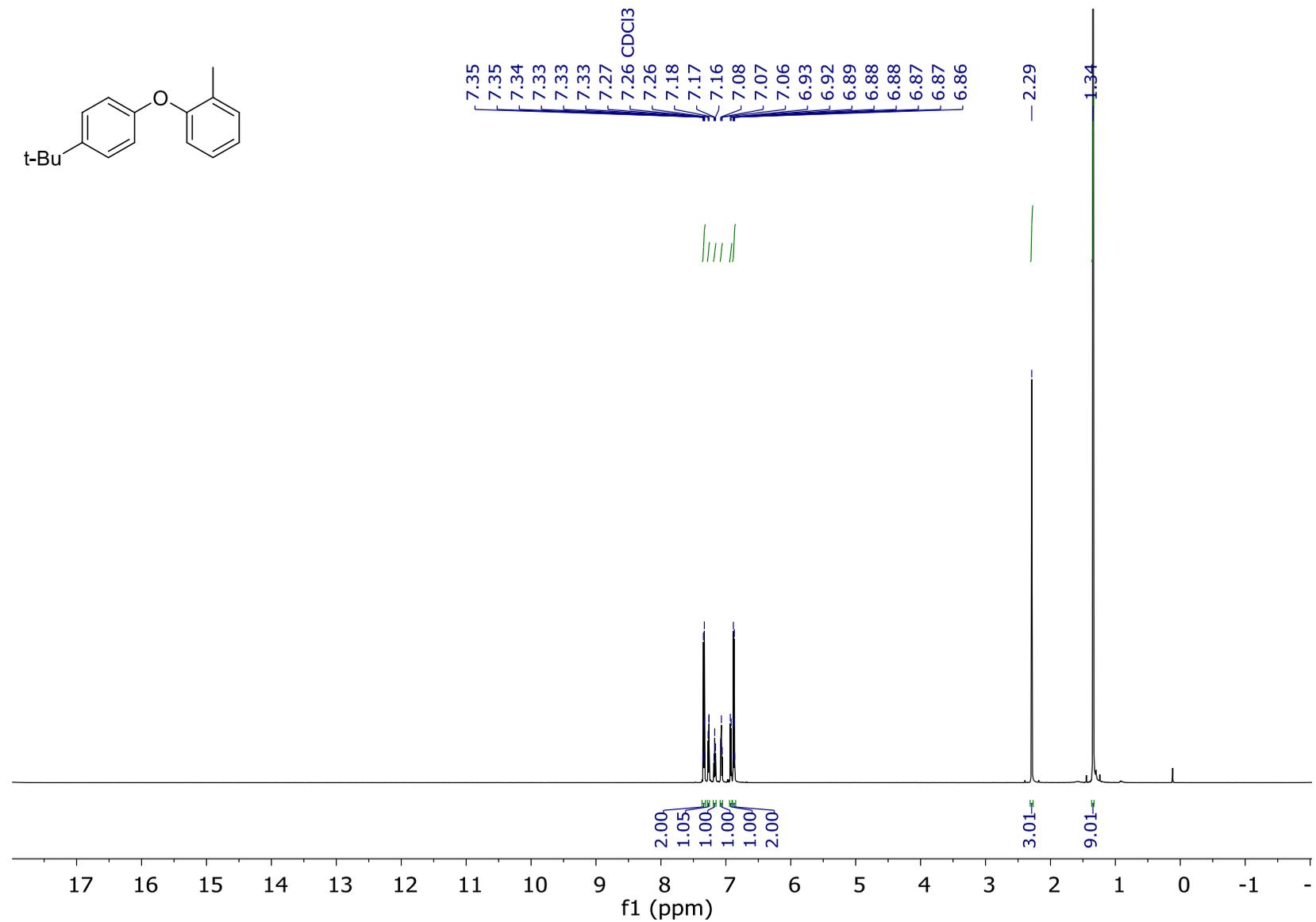


Figure S44. <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) of 1-(4-tert-butylphenoxy)-2-methylbenzene (2e).

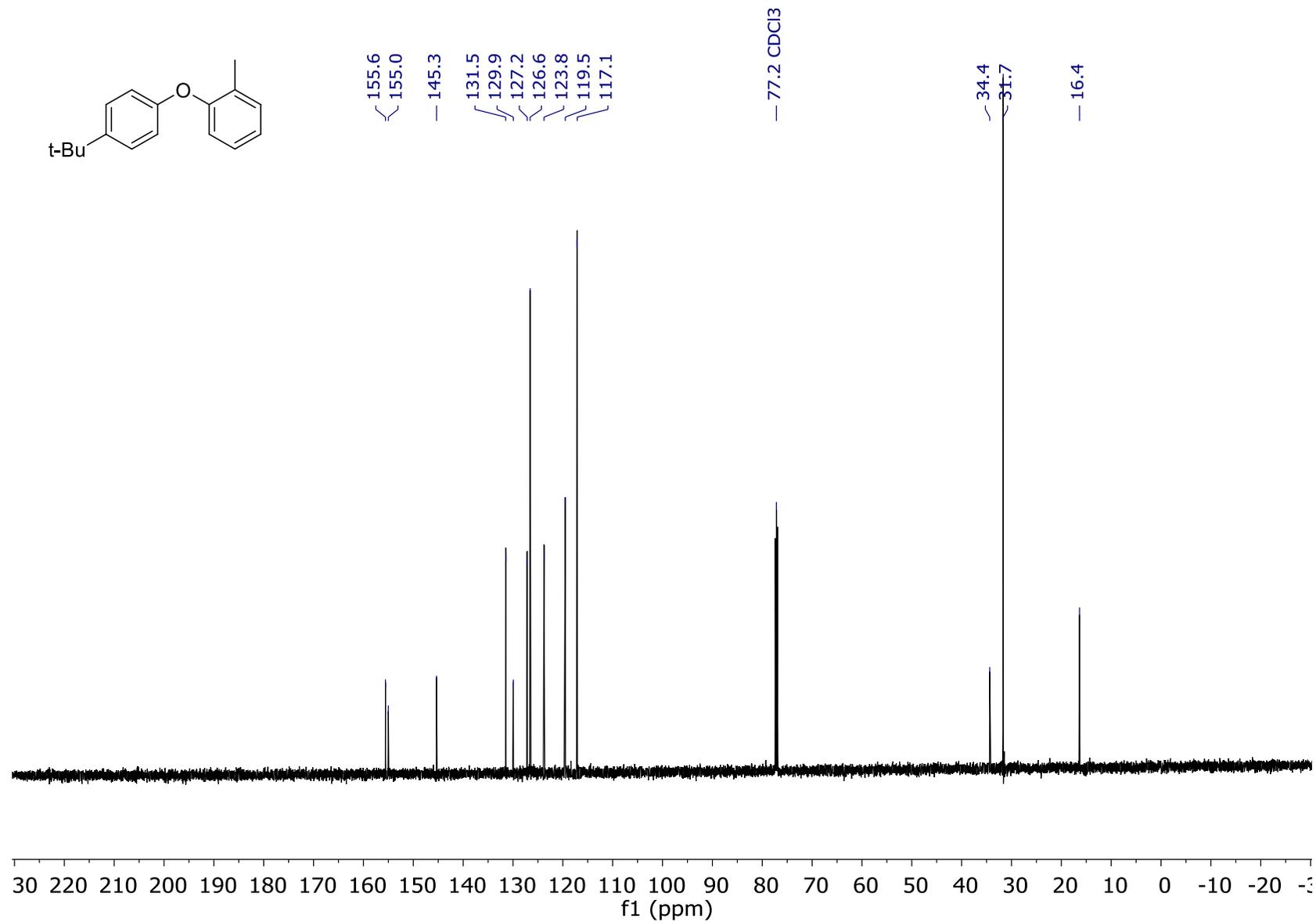


Figure S45.  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz, Chloroform-*d*) of 1-(4-*tert*-butylphenoxy)-2-methylbenzene (2e).

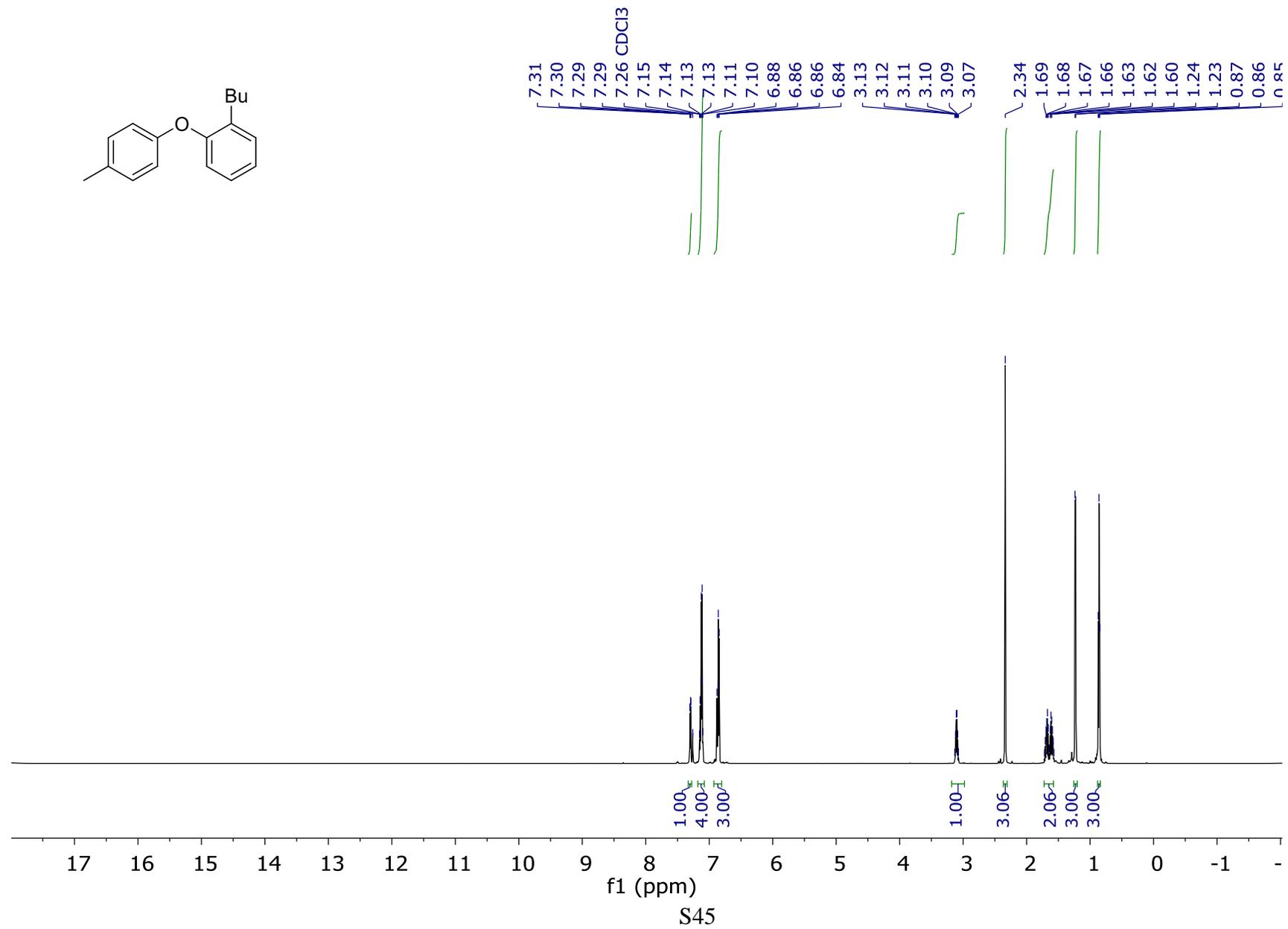


Figure S46. <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) of 1-butyl-2-(p-tolyloxy)benzene (2f).

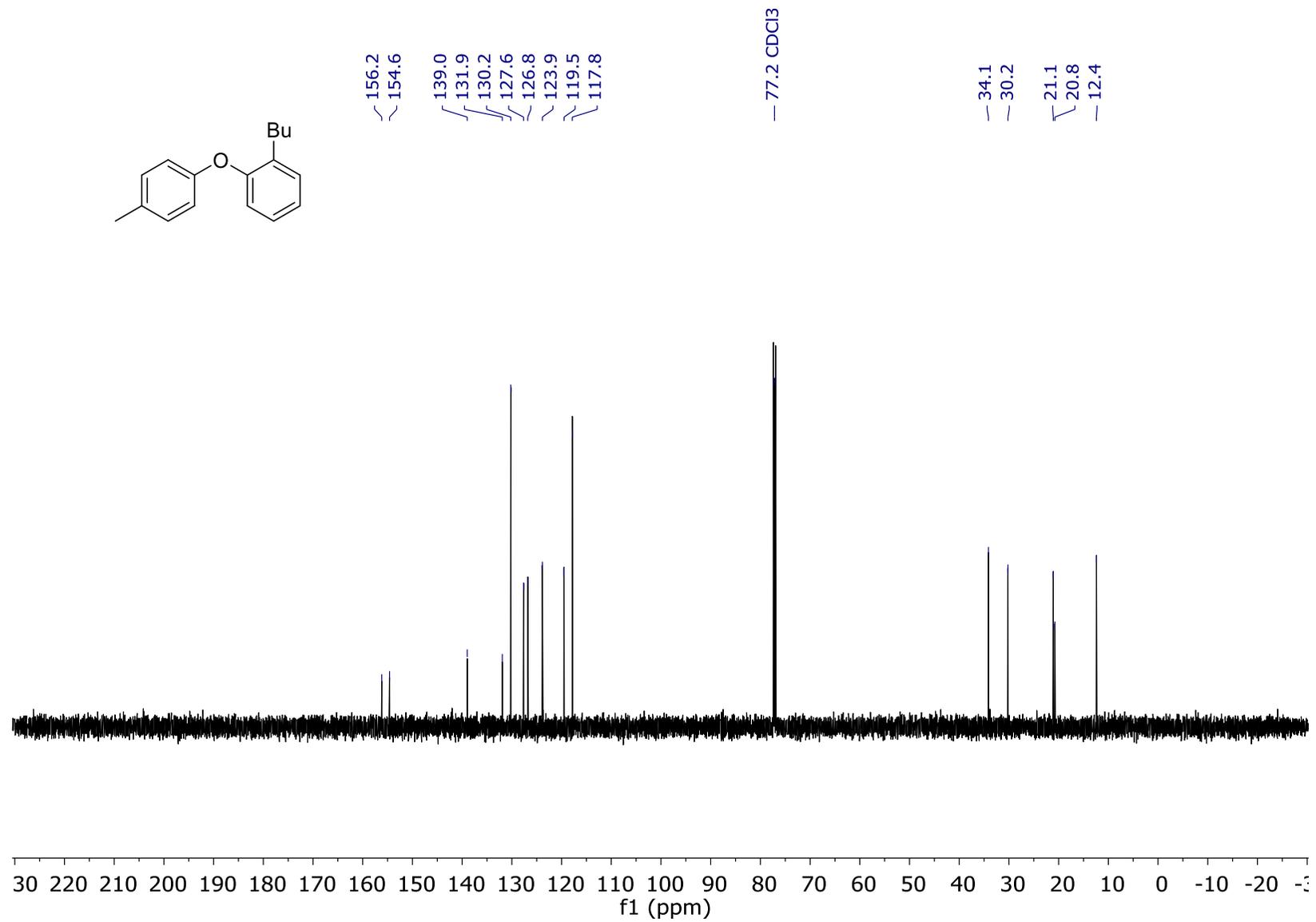


Figure S47.  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz, Chloroform-*d*) of 1-butyl-2-(p-tolyloxy)benzene (2f).

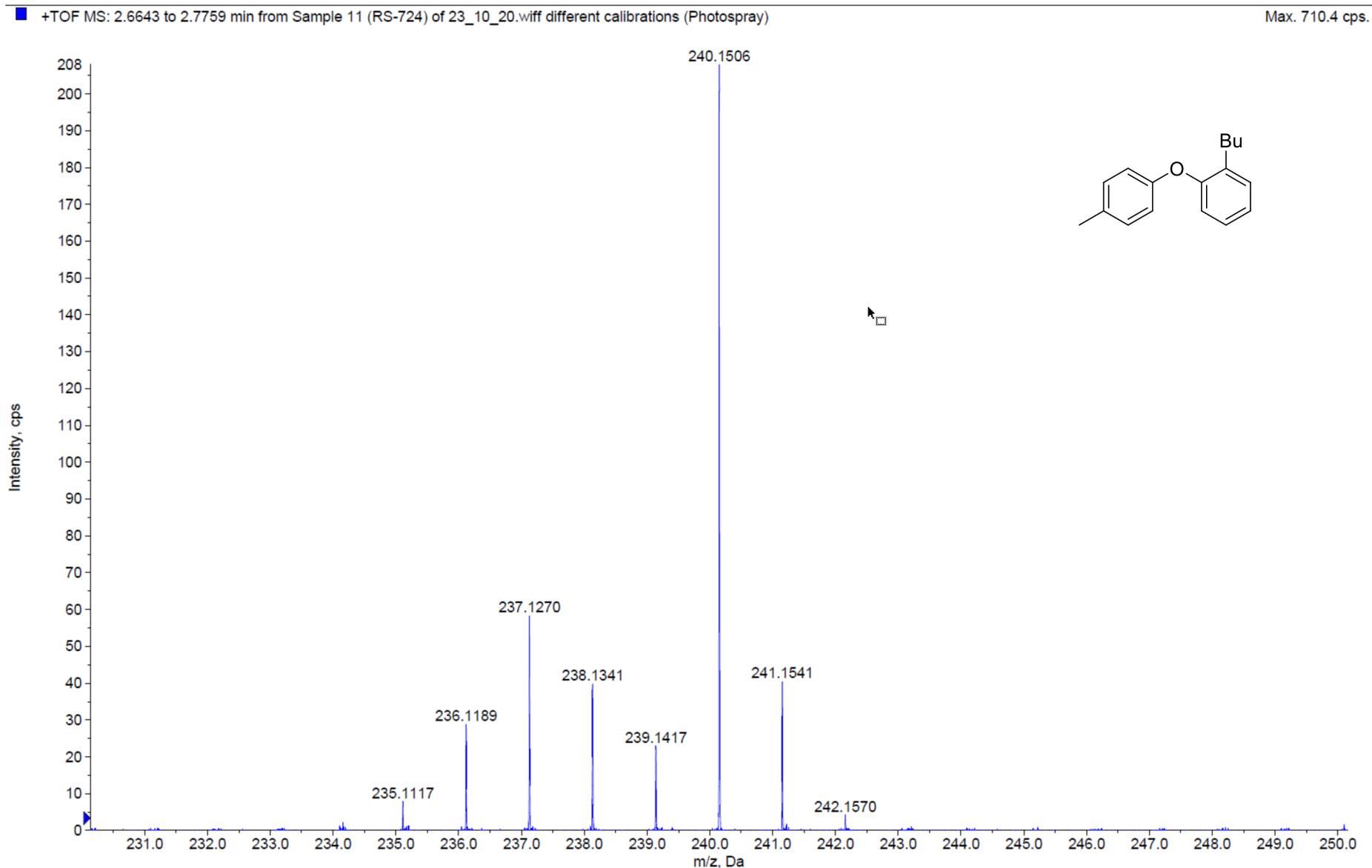


Figure S48. HRMS Spectra of 1-butyl-2-(p-tolyloxy)benzene (2f).

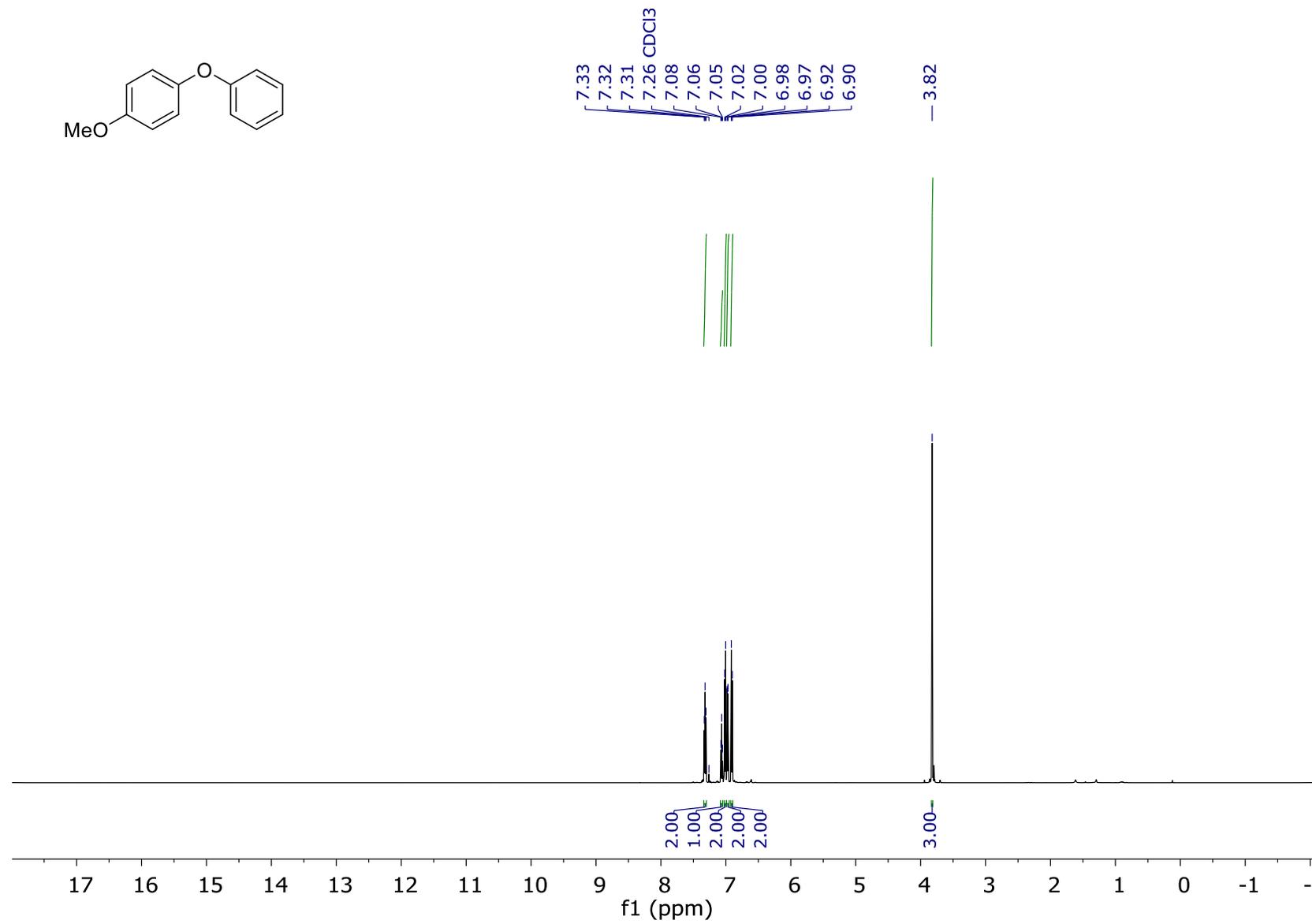


Figure S49. <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) of 1-methoxy-4-phenoxybenzene (2g).

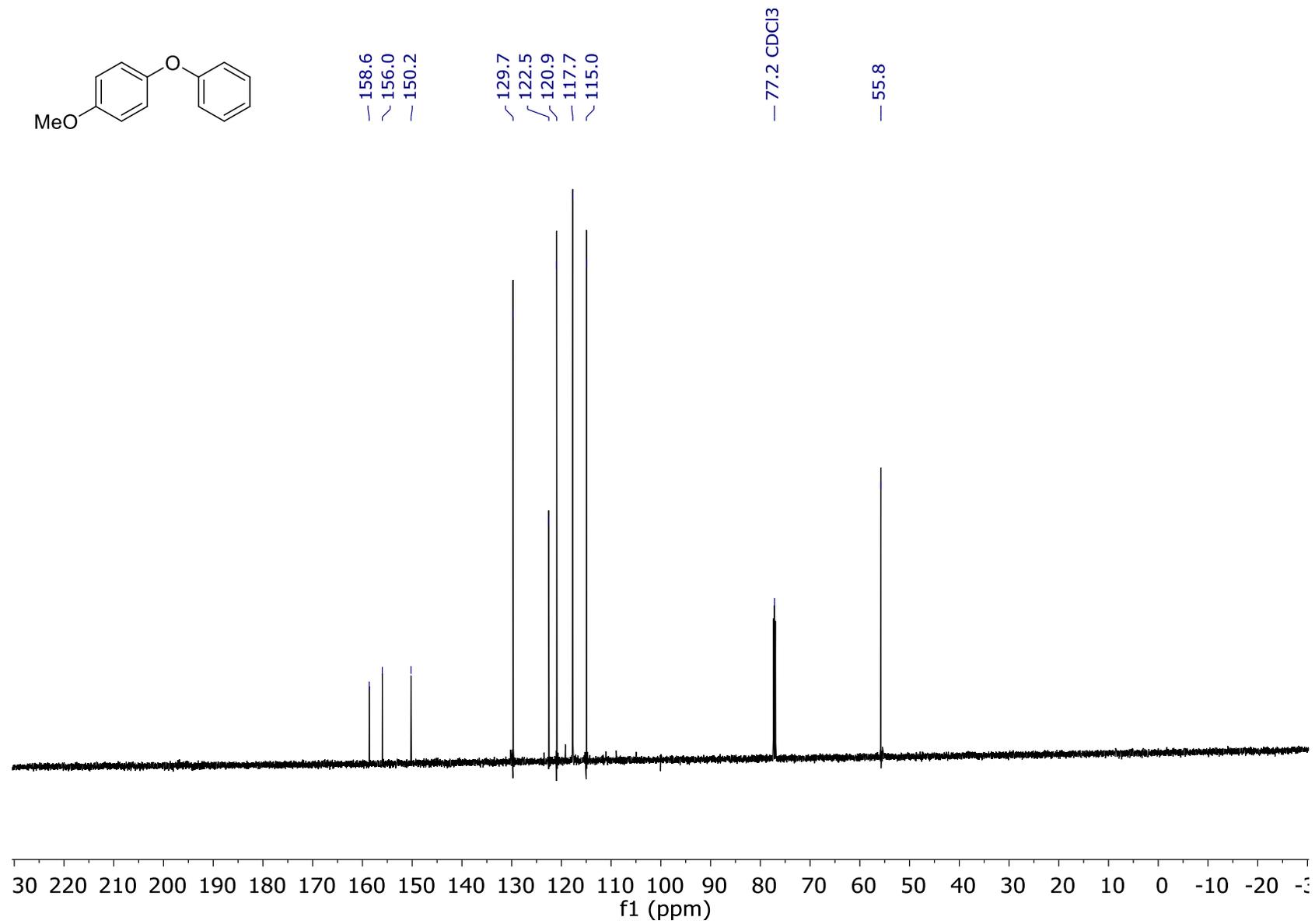
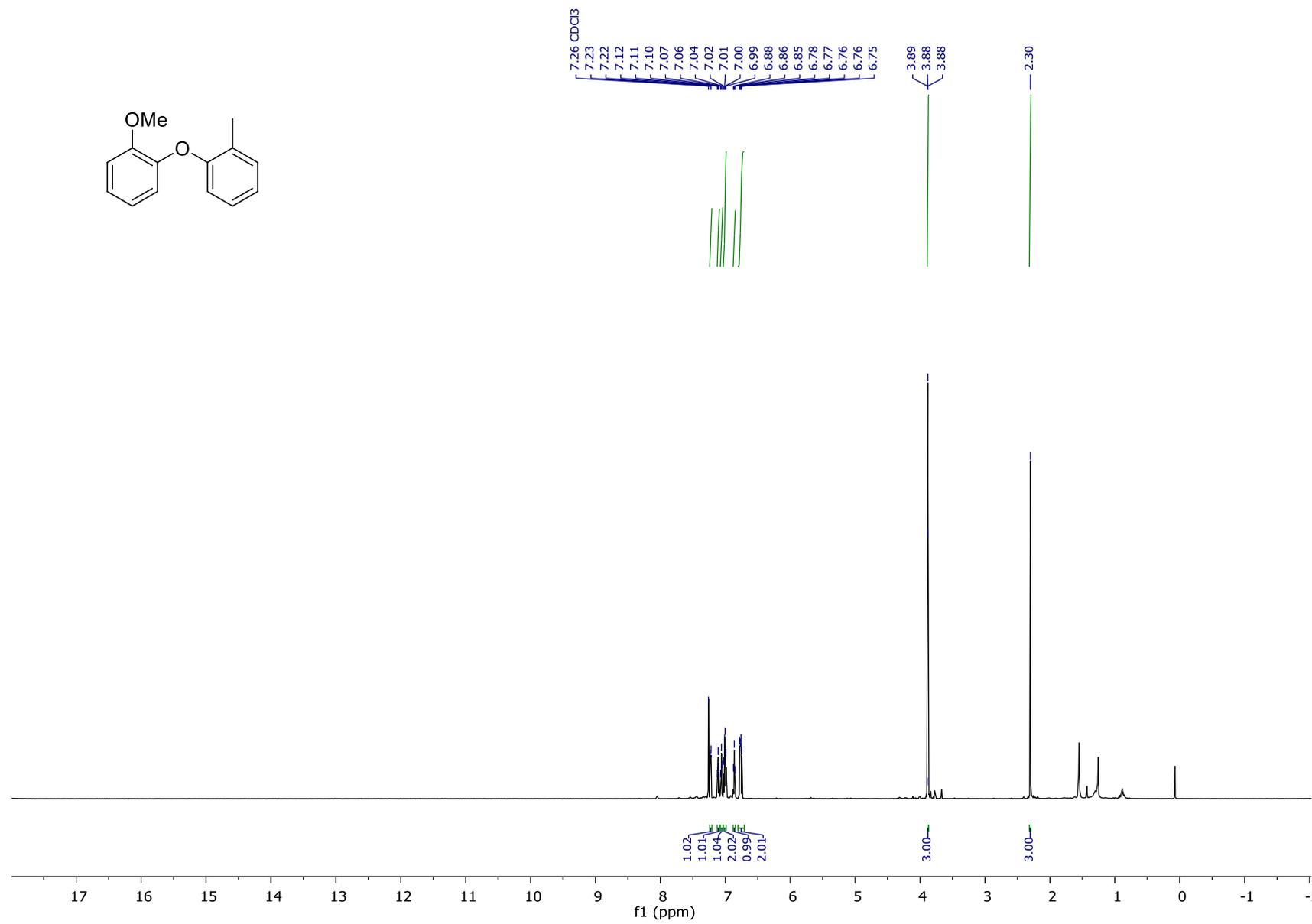


Figure S50.  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz, Chloroform-*d*) of 1-methoxy-4-phenoxybenzene (2g).



S50

Figure S51. <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) of 1-methoxy-2-(*o*-tolyl)oxybenzene (2h).

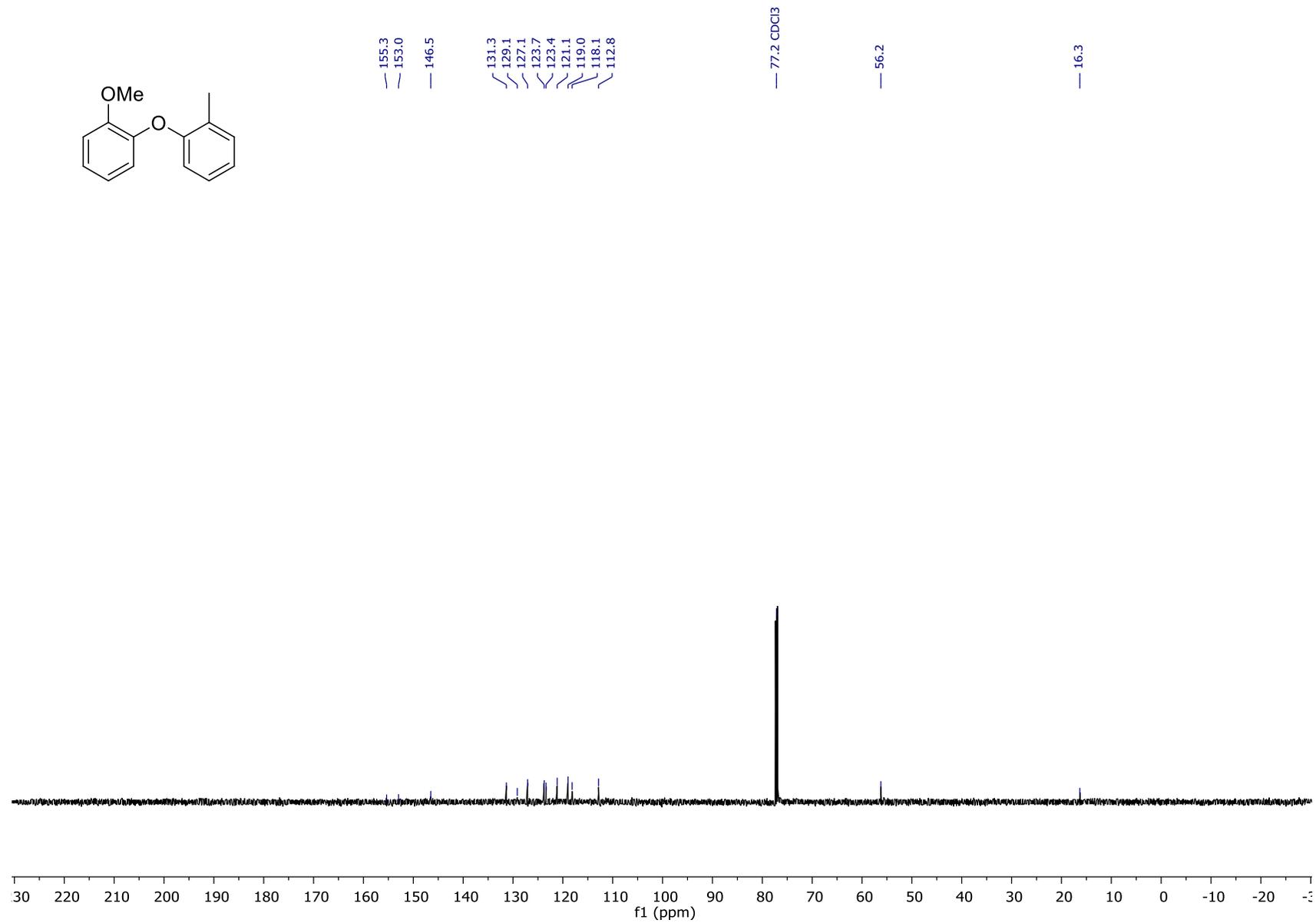


Figure S52.  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz, Chloroform-*d*) of 1-methoxy-2-(*o*-tolylloxy)benzene (2h).

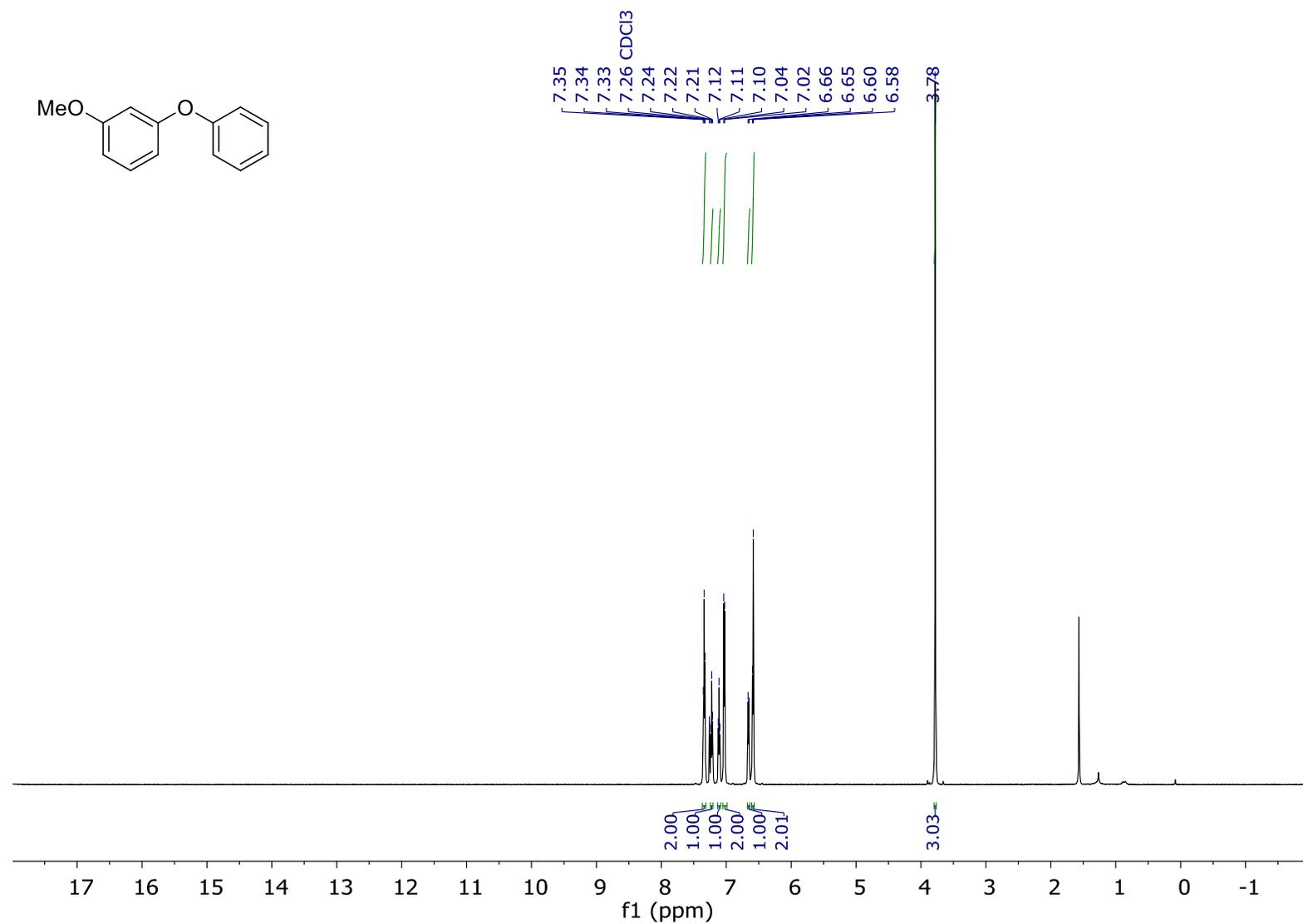


Figure S53. <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) of 1-methoxy-3-phenoxybenzene (2i).

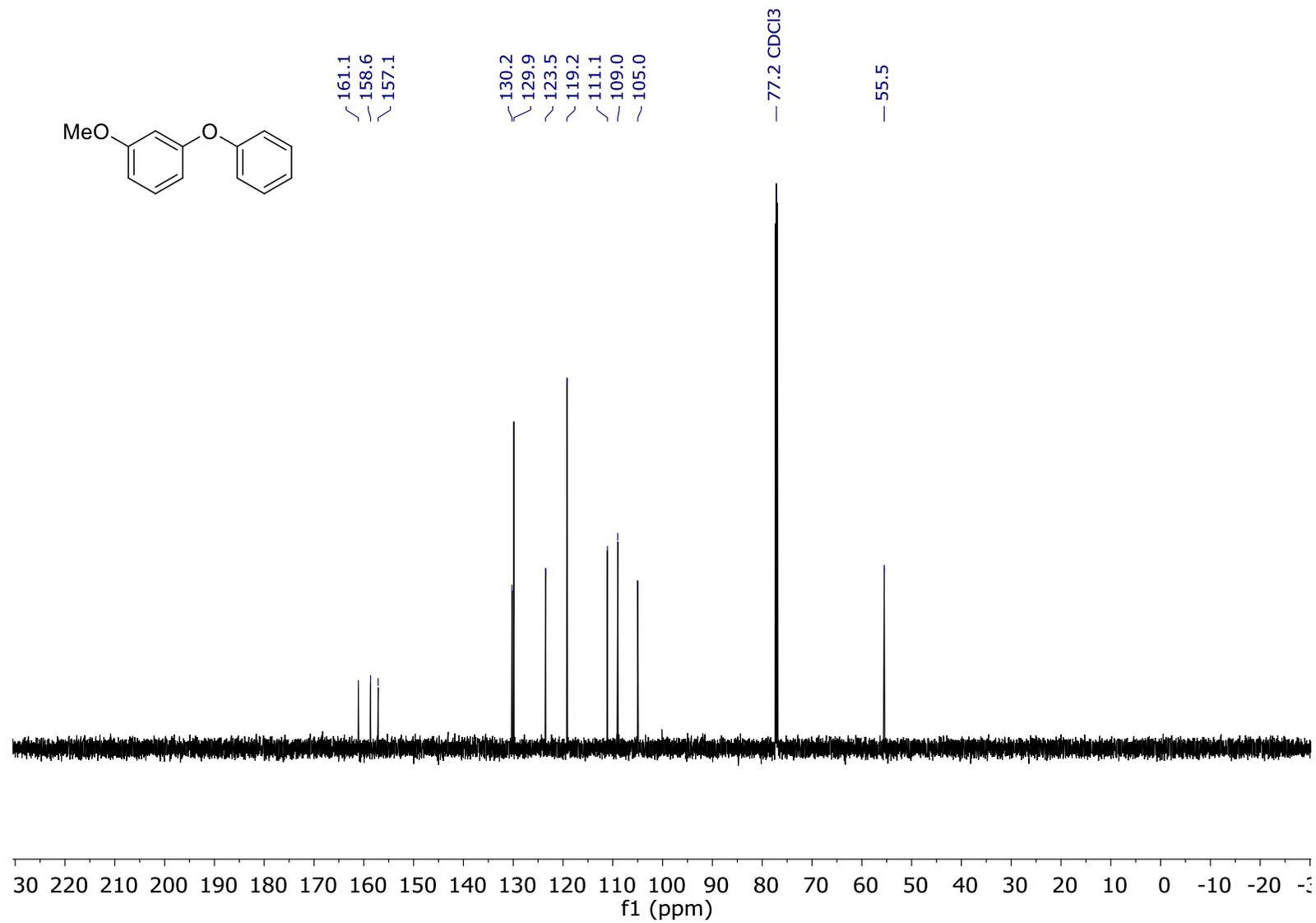


Figure S54.  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz, Chloroform-*d*) of 1-methoxy-3-phenoxybenzene (2i).

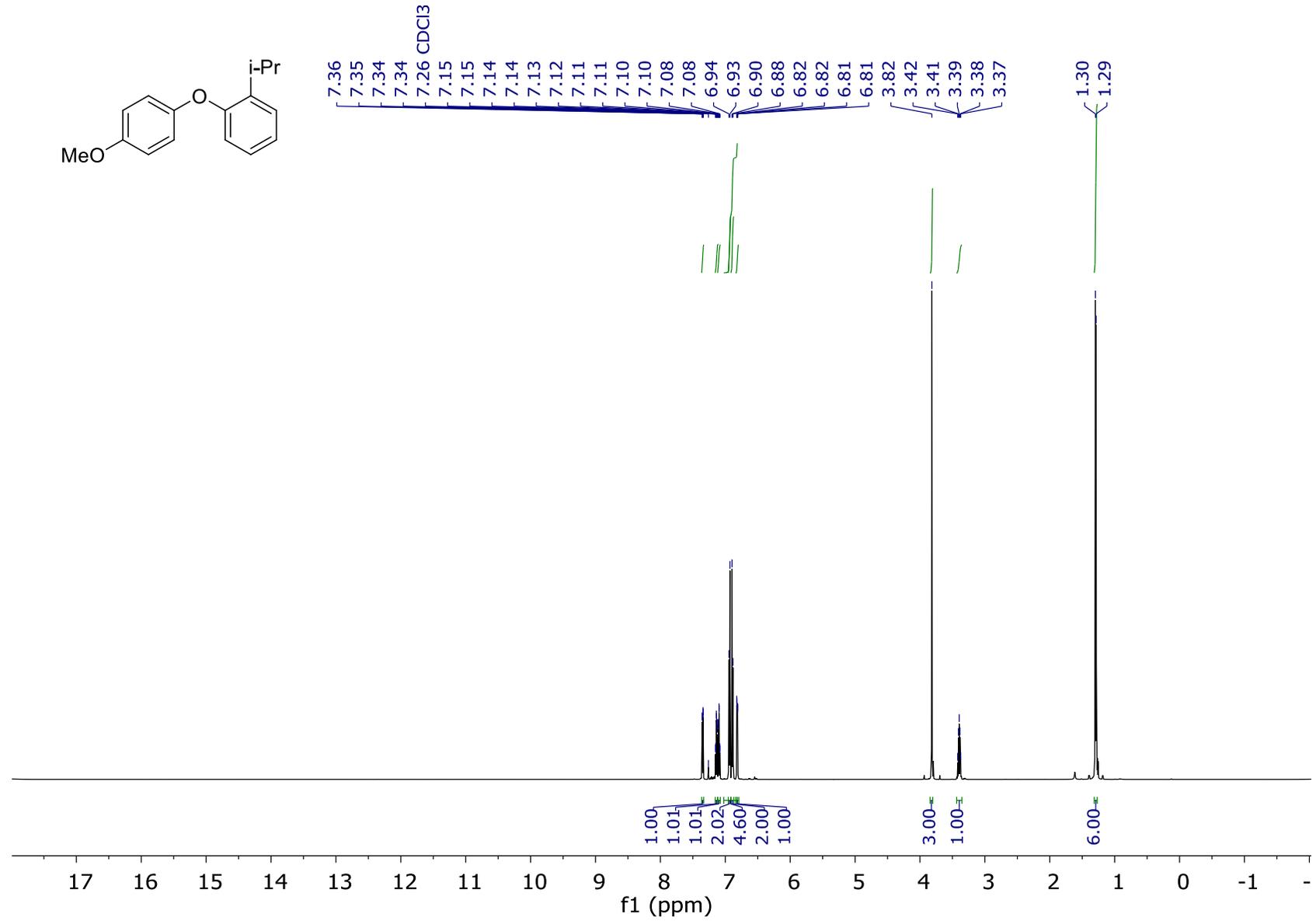


Figure S55. <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) of 1-isopropyl-2-(4-methoxyphenoxy)benzene(2j).

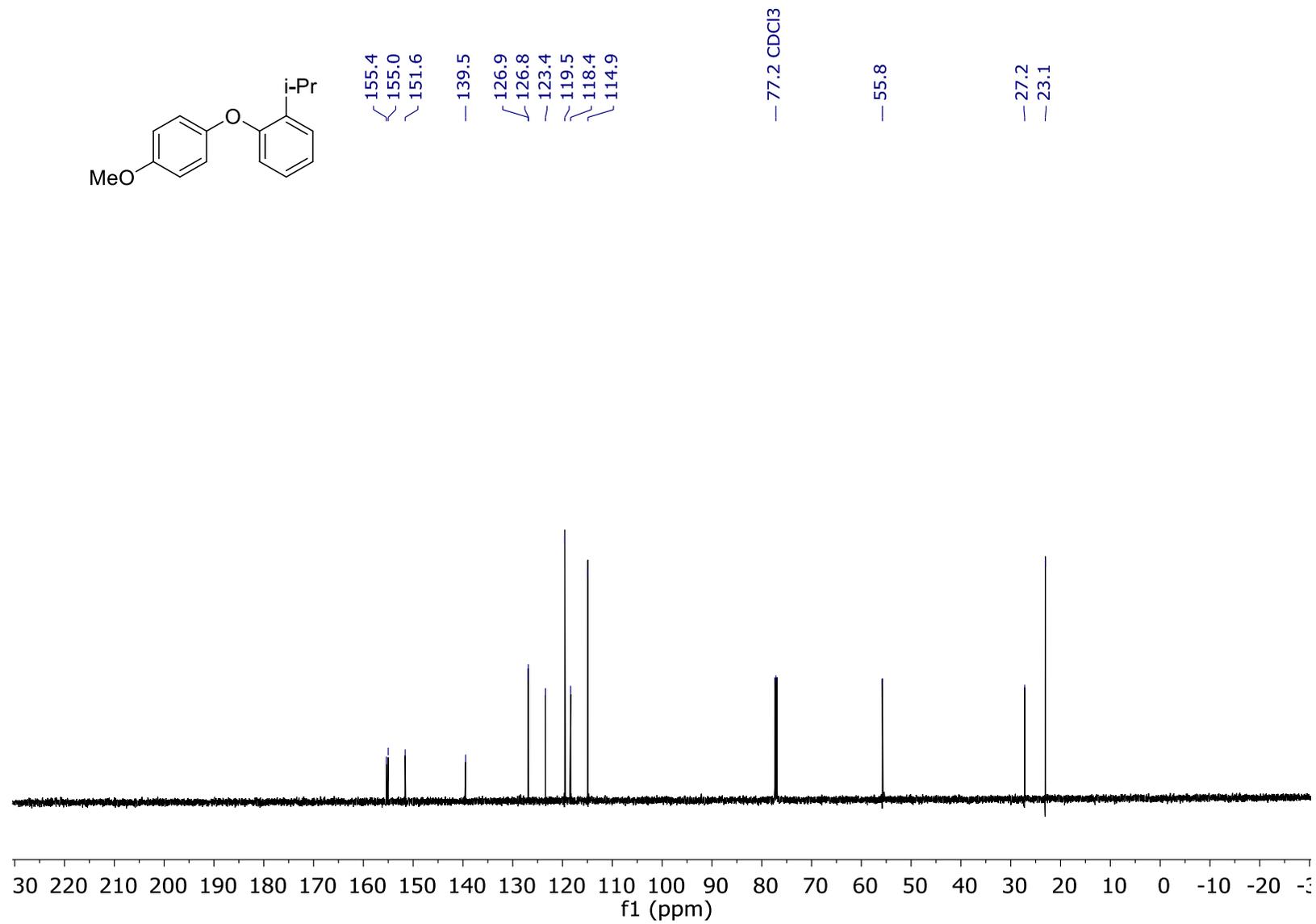


Figure S56.  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz, Chloroform-*d*) of 1-isopropyl-2-(4-methoxyphenoxy)benzene(2j).

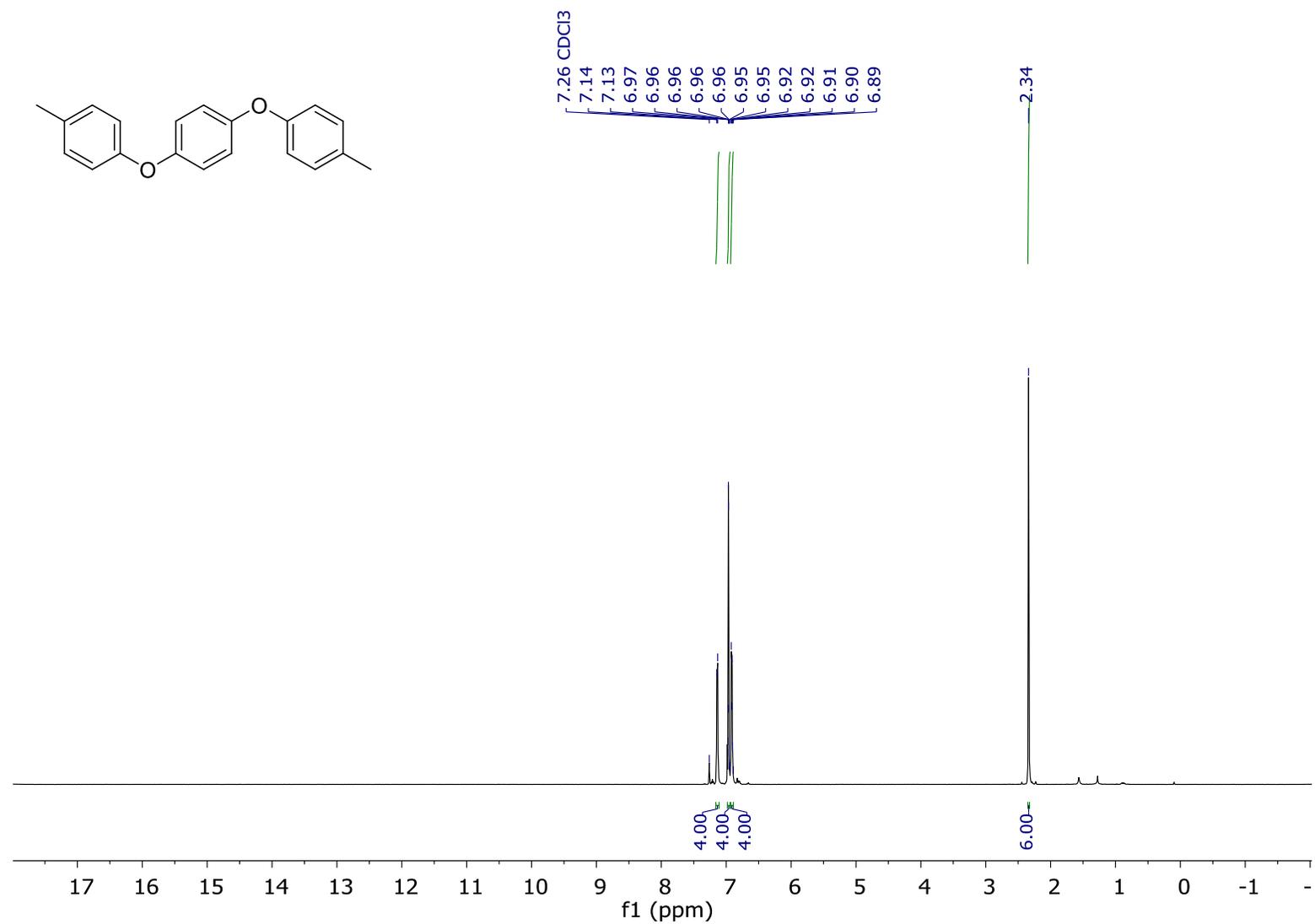


Figure S57.  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*) of 1,4-bis(p-tolyloxy)benzene (3a).

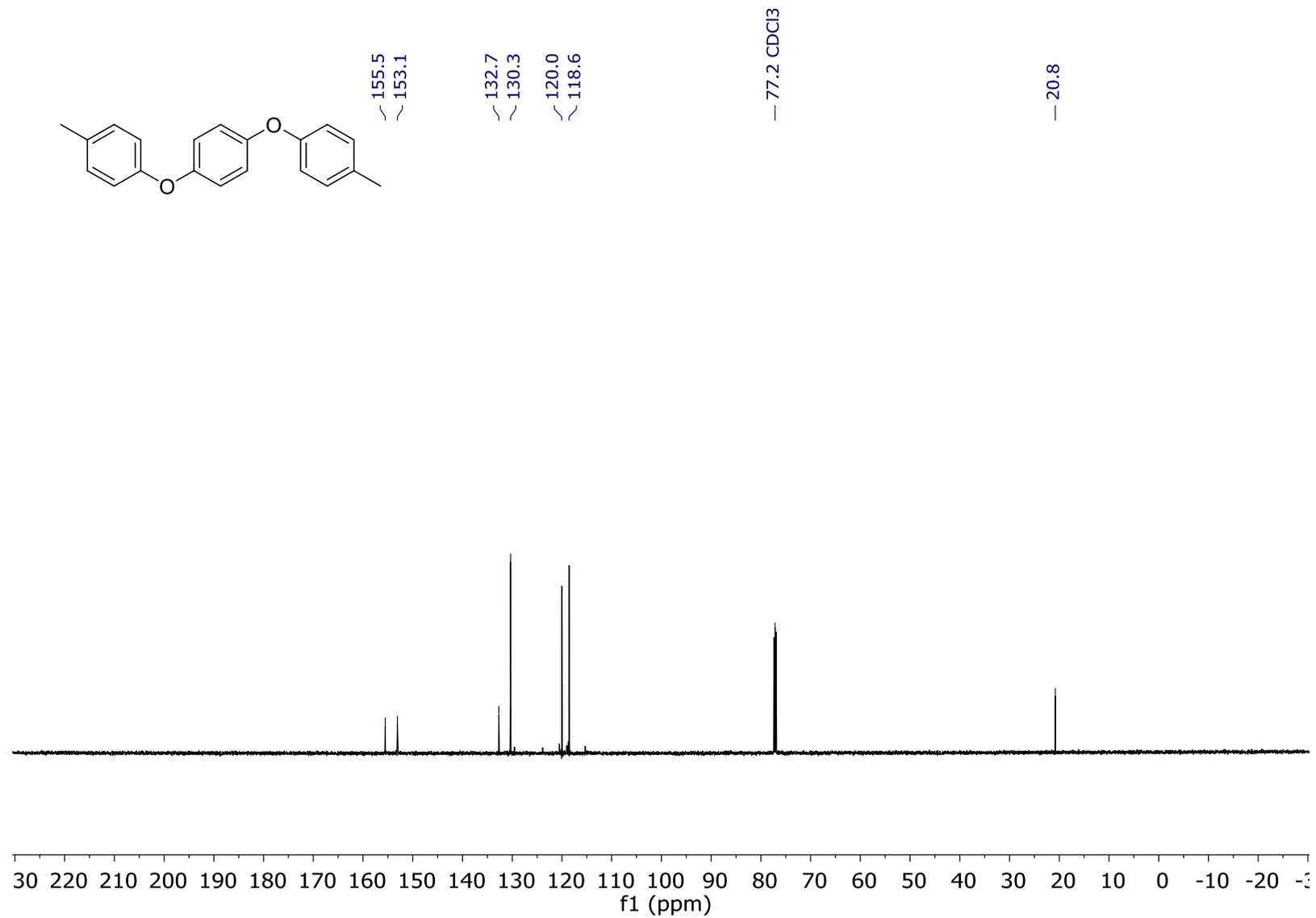


Figure S58.  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz, Chloroform-*d*) of 1,4-bis(p-tolyloxy)benzene (3a).

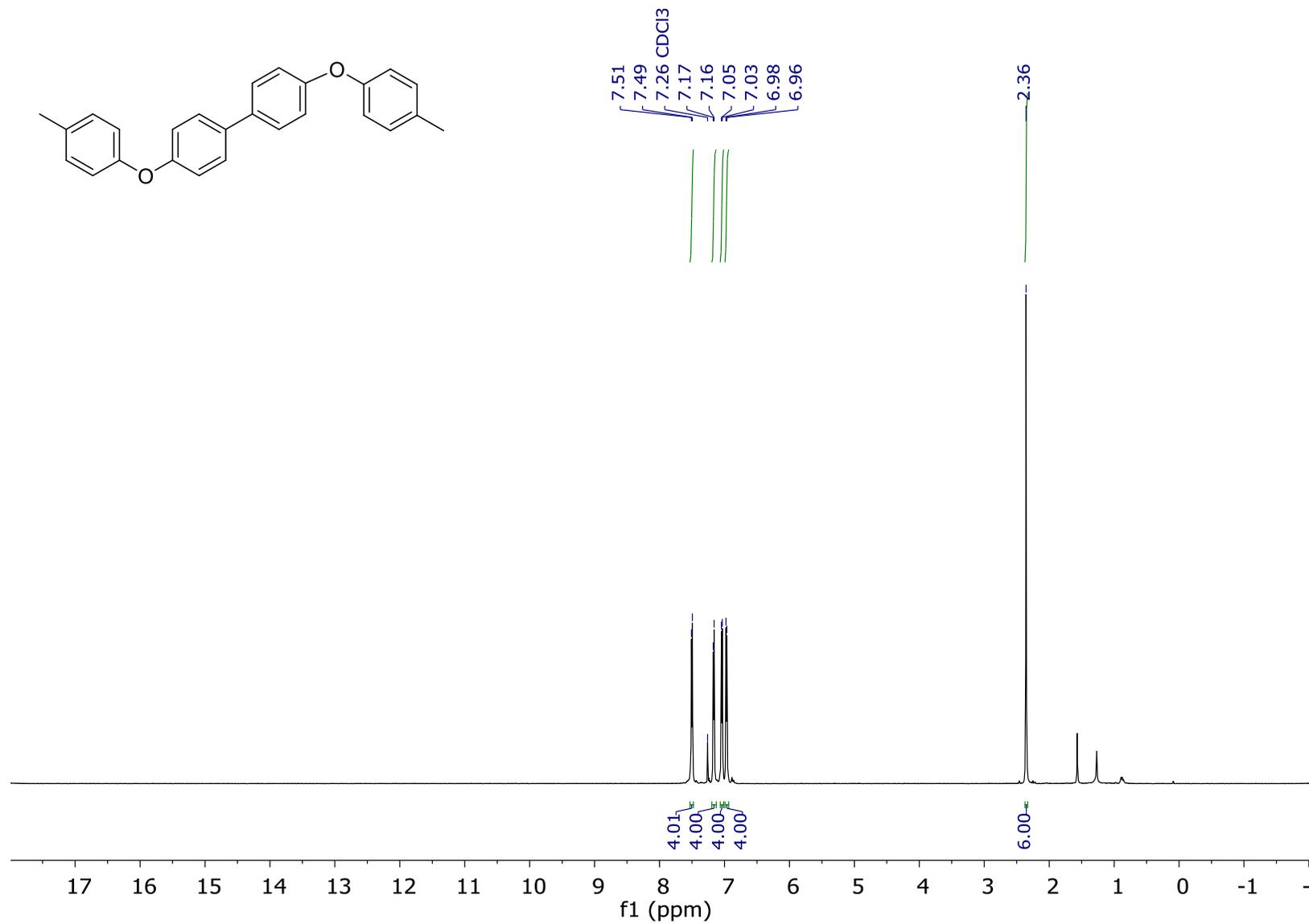
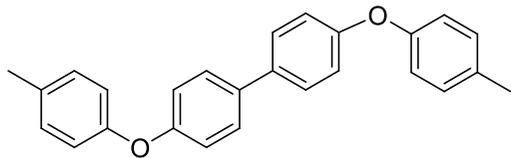


Figure S59.  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*) of 4,4'-bis(p-tolyloxy)biphenyl (3b).

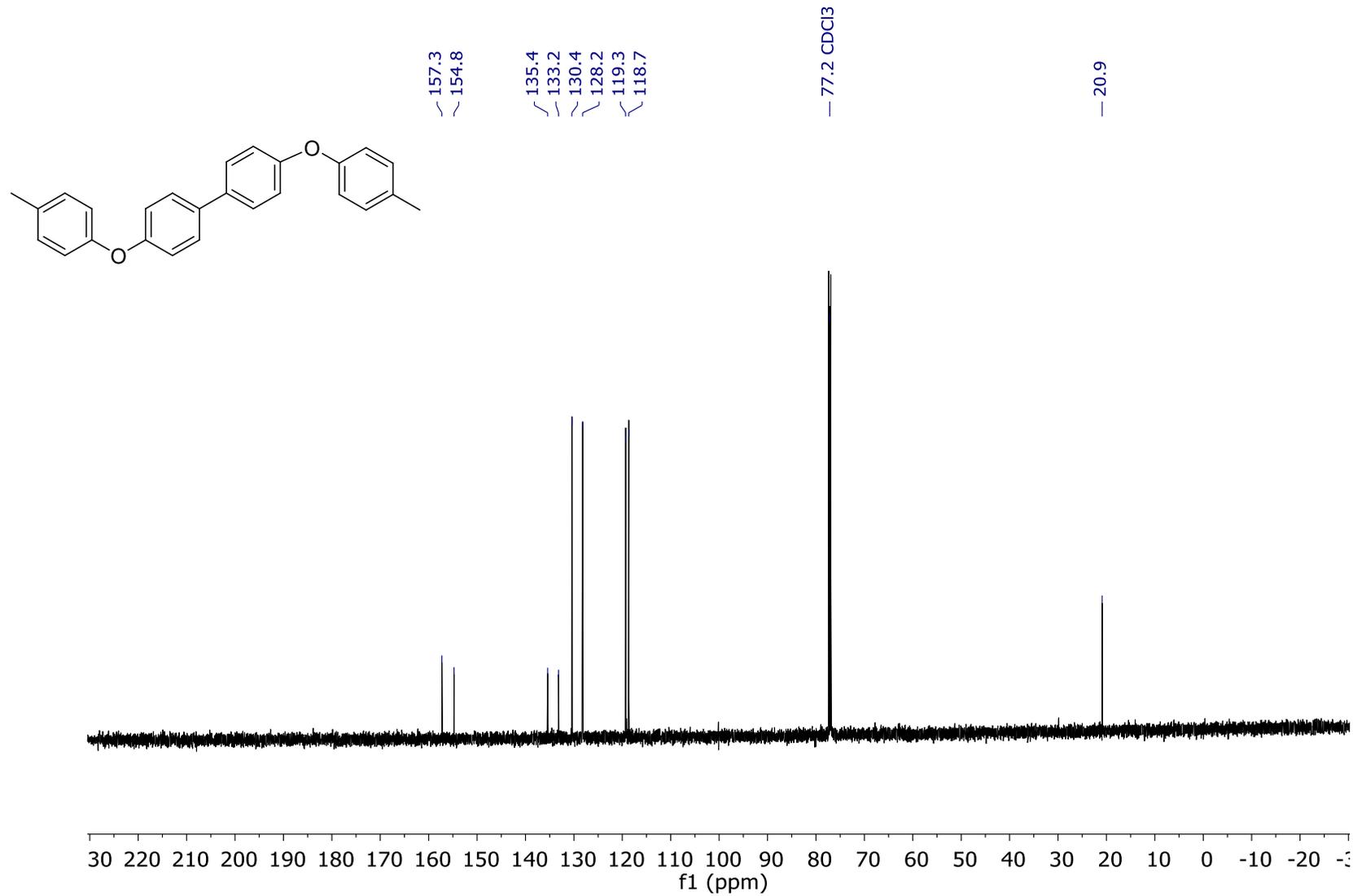


Figure S60.  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz, Chloroform-*d*) of 4,4'-bis(p-tolyloxy)biphenyl (3b).