

## Supporting Information

### Direct Synthesis of 2-Substituted Benzonitriles via Alkylcyanation of Arynes with *N,N*-Disubstituted Aminomalononitriles

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## 1. General Information

All reactions under standard conditions were carried out under argon atmosphere and monitored by thin-layer chromatography (TLC) on gel F254 plates. All products were purified through silica gel chromatography (200~300 mesh). Column chromatography was carried out with light petroleum ether (bp. 60~90 °C), ethyl acetate and dichloromethane as eluent. <sup>1</sup>H and <sup>13</sup>C spectra were recorded in CDCl<sub>3</sub> on 400 MHz instruments. Chemical shifts (δ) are reported in ppm, and coupling constants (J) are in hertz (Hz). High-resolution mass spectral analysis (HRMS) data were measured on the Apex II by means of the ESI technique. Melting point was measured with SGW-X4B instrument.

All the chemicals were used as obtained from vendors. The substrates 2-(Trimethylsilyl)phenyl trifluoromethanesulfonate (**2a**), 4-Methyl-2-(trimethylsilyl)phenyl Trifluoromethanesulfonate (**2b**), 2-Methyl-6-(trimethylsilyl)phenyl Trifluoromethanesulfonate (**2c**), 4-Methoxy-2-(trimethylsilyl)phenyl Trifluoromethanesulfonate (**2d**), 4,5-Dimethoxy-2-(trimethylsilyl)phenyl Trifluoromethanesulfonate (**2e**) and 3-(Trimethylsilyl)-2-naphthyl Trifluoromethanesulfonate (**2f**) are commercially available.

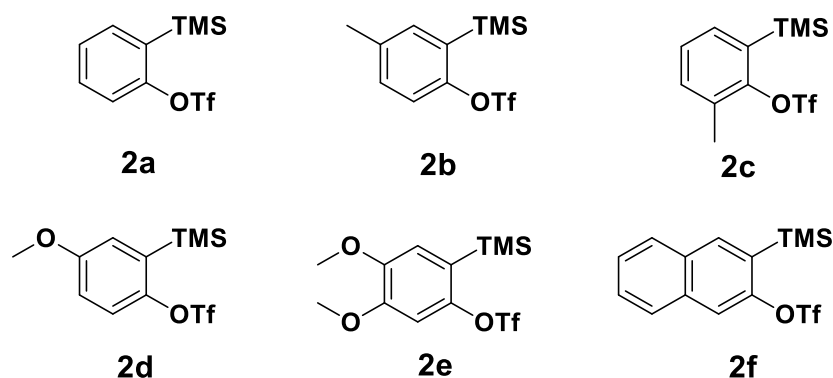
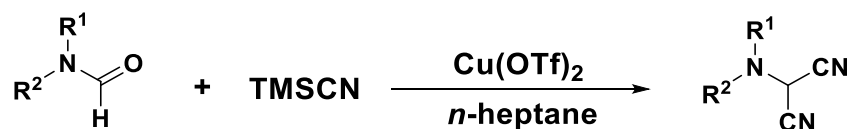


Figure 1. Commercially purchased aryne precursors 2a-2f

## 2. General experimental procedure

### 2.1 General procedure for the synthesis of *N,N*-disubstituted aminomalononitriles 1a-1w

Substrates **1** were prepared according to the procedure reported in literature.<sup>1</sup>



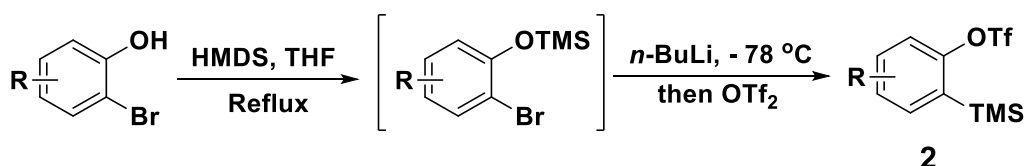
#### General Procedure A: using the preparation of 2-(methyl(phenyl)amino)malononitrile from *N*-methyl-*N*-phenylformamide as an example

To a stirred solution of *N*-methyl-*N*-phenylformamide (2.0 g, 14.80 mmol) in *n*-heptane (20.0 mL) were successively added Copper(II) trifluoromethanesulfonate (535 mg, 1.48 mmol) and Trimethylsilyl Cyanide (4.07 ml, 32.56 mmol) at 80 °C under argon atmosphere. The reaction mixture was continued stirring for 8 h. Upon completion of the reaction (monitored by TLC), the reaction mixture was quenched by slow addition of water. The aqueous layer was extracted three

times with EtOAc and the combined organic layers were washed with brine, dried over sodium sulfate, and evaporated to dryness and purified by column chromatography on silica gel (petroleum ether : EtOAc = 30:1 to 20:1) to afford 2-(methyl(phenyl)amino)malononitrile as a white solid (0.76 g, 30%).

## 2.2 General procedure for the synthesis of aryne precursors 2g and 2h

Substrates **2g** and **2h** were prepared according to the procedure reported in literature.<sup>2</sup>

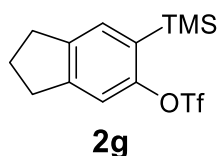


### General Procedure B: using the preparation of 6-(trimethylsilyl)benzo[d][1,3]dioxol-5-yl trifluoromethanesulfonate from sesamol as an example

To a cooled (0 °C) solution of sesamol (5.0 g, 36.2 mmol) in AcOH (11 mL) was added a solution of bromine (1.5 mL, 29.0 mmol) in AcOH (6.3 mL) dropwise over 15 minutes. The mixture was then rapidly poured onto ice. The resulting green solid was collected by filtration, washed copiously with water and extracted with ethyl acetate (3×35 mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure to afford the crude product as a dull green solid (3.99 g, 51 %), which was used without further purification.

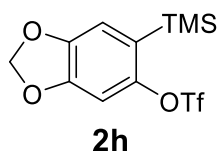
A mixture of the obtained crude product and HMDS (2.9 mL, 13.9 mmol) in THF (38 mL) was refluxed for 4 h. The solvent was evaporated under reduced pressure, and the residue was subjected to high vacuum to remove excess NH<sub>3</sub> and unreacted HMDS. The resulted crude product was used without further purification.

To a solution of the obtained crude product in THF (41 mL) was added *n*-BuLi (6.1 mL, 2.5 M, in THF, 15.3 mmol) dropwise at -78 °C. After stirring for 30 min, Tf<sub>2</sub>O (2.8 mL, 16.7mmol) was then added dropwise to the mixture. The mixture was then stirred for 30 min under the same temperature. Then the mixture was warmed to room temperature and stirred for 20 minutes. After that, NaHCO<sub>3</sub> (cold sat. aqueous solution) and H<sub>2</sub>O were sequentially added to the mixture. The aqueous layer was extracted with ethyl acetate (3×30 mL), the combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, filtrated and concentrated in vacuo. The crude material was purified by flash column chromatography on silica gel to afford the title compound **2h** as yellow oil, 4.35 g, 91% yield. (R<sub>f</sub> = 0.25, eluent: petroleum ether).



### 6-(trimethylsilyl)-2,3-dihydro-1H-inden-5-yl trifluoromethanesulfonate (**2g**):

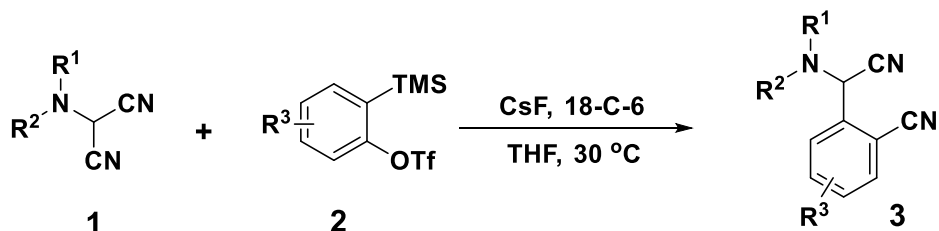
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.37 (s, 1H), 7.21 (s, 1H), 2.93-2.87 (m, 4H), 2.14-2.06 (m, 2H), 0.37 (s, 9H). The <sup>1</sup>H NMR of **2g** is consistent with the reported spectra.<sup>2</sup>



### 6-(trimethylsilyl) benzo[d] [1,3] dioxol-5-yl trifluoromethanesulfonate (2h):

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.89 (s, 1H), 6.86 (s, 1H), 6.02 (s, 2H), 0.35 (s, 9H). The  $^1\text{H NMR}$  of **2h** is consistent with the reported spectra.<sup>2</sup>

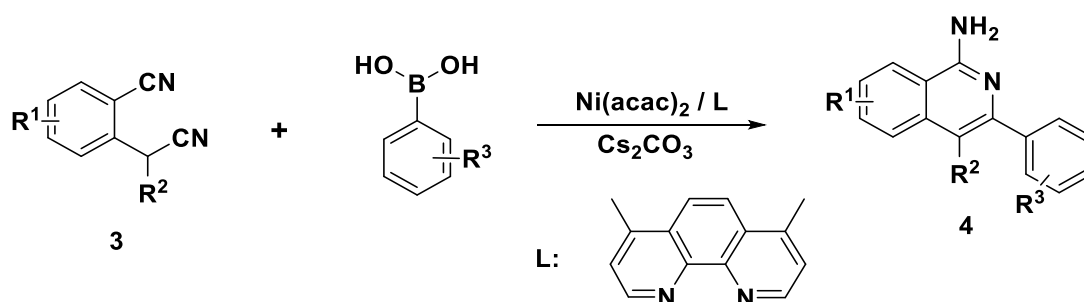
### 2.3 General experimental procedure C for products 3a-3ad.



#### Using the preparation of ethyl 1-aminoisoquinoline-3-carboxylate from 2-formylbenzonitrile and 2-isocyanoacetate as an example

To a reaction tube were added 2-(methyl(phenyl)amino)malononitrile **1b** (100 mg, 0.58 mmol) in  $\text{THF}$  (2.0 mL), 2-(Trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (213  $\mu\text{L}$ , 1.5 equiv),  $\text{CsF}$  (177 mg, 2.0 equiv) and **18-C-6** (309 mg, 2.0 equiv) under argon atmosphere. The mixture was stirred at  $30\text{ }^\circ\text{C}$  for 2 h. After completion of reaction as indicated by TLC, the mixture was concentrated *in vacuo*, and the residue was purified by flash column chromatograph (petroleum ether :  $\text{EtOAc}$  = 30:1 to 10:1) to give the desired product **3b**.

### 2.4 General experimental procedure D for products 4a and 4b.<sup>3</sup>

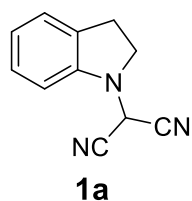


#### Using the preparation of $N^4$ -methyl- $N^4$ , 3-diphenylisoquinoline-1, 4-diamine from 2-(cyano(methyl(phenyl)amino)methyl)benzonitrile as an example

The aryl boronic acid (1.0 mmol),  $\text{Ni}(\text{acac})_2$  (0.025 mmol), ligand (0.025 mmol), and  $\text{Cs}_2\text{CO}_3$  (0.1 mmol) were added sequentially to a solution of the substituted 2-(cyanomethyl)benzonitrile (0.5 mmol) in toluene (2 mL). The reaction mixture was stirred at  $110\text{ }^\circ\text{C}$  for 6 h. After cooling, the mixture was diluted with  $\text{EtOAc}$  (20 mL) and  $\text{H}_2\text{O}$  (15 mL). After separation, the aqueous phase was washed with  $\text{EtOAc}$  (20 mL). The combined organic phase was washed with brine and then dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent was removed under reduced pressure, and the residue was purified under column chromatography to afford the desired product.

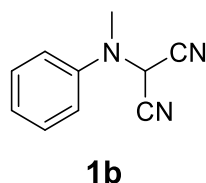
### 3. Characterization of substrates and products.

#### 3.1 Characterization of substrates 1a-1t.



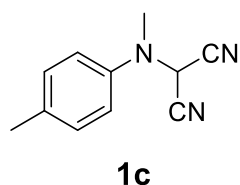
##### 2-(indolin-1-yl)malononitrile (**1a**):

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.24-7.19 (m, 2H), 6.98 (t,  $J = 7.6$  Hz, 1H), 6.70 (d,  $J = 8.0$  Hz, 1H), 5.42 (s, 1H), 3.57 (t,  $J = 8.0$  Hz, 2H), 3.10 (t,  $J = 8.0$  Hz, 2H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  145.91, 130.70, 127.64, 125.45, 122.30, 109.86, 108.88, 52.00, 41.28, 28.11. The  $^1\text{H NMR}$  and  $^{13}\text{C NMR}$  of **1a** are consistent with the reported spectra.<sup>1</sup>



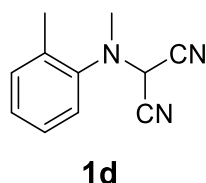
##### 2-(methyl(phenyl)amino)malononitrile (**1b**):

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38 (dd,  $J = 8.8, 7.6$  Hz, 2H), 7.13 (t,  $J = 7.2$  Hz, 1H), 7.05 (d,  $J = 8.0$  Hz, 2H), 5.43 (s, 1H), 3.09 (s, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  146.28, 129.78, 123.98, 118.59, 110.27, 46.75, 37.34. The  $^1\text{H NMR}$  and  $^{13}\text{C NMR}$  of **1b** are consistent with the reported spectra.<sup>1</sup>



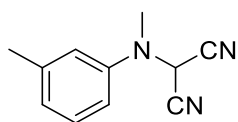
##### 2-(methyl(p-tolyl)amino)malononitrile (**1c**):

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.18 (d,  $J = 8.4$  Hz, 2H), 6.97 (d,  $J = 8.4$  Hz, 2H), 5.35 (s, 1H), 3.04 (s, 3H), 2.34 (s, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  144.01, 134.04, 130.25, 119.16, 110.33, 47.31, 37.58, 20.55; **HRMS** (ESI) calcd for  $\text{C}_{11}\text{H}_{11}\text{N}_3$  [ $\text{M-H}$ ] $^-$ : 184.0880, found 184.0886.



##### 2-(methyl(o-tolyl)amino)malononitrile (**1d**):

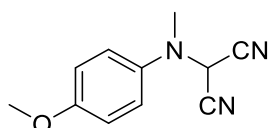
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.24-7.15 (m, 3H), 7.13-7.09 (m, 1H), 4.82 (s, 1H), 2.87 (s, 3H), 2.27 (s, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  145.66, 133.37, 131.29, 126.85, 126.43, 121.40, 110.34, 47.27, 37.92, 17.08; **HRMS** (ESI) calcd for  $\text{C}_{11}\text{H}_{11}\text{N}_3$  [ $\text{M-H}$ ] $^-$ : 184.0880, found 184.0886.



**1e**

**2-((methyl(*m*-tolyl)amino)malononitrile (1e):**

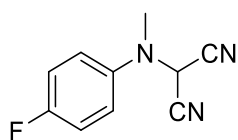
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.21 (t, *J* = 8.0 Hz, 1H), 6.90 (d, *J* = 7.2 Hz, 1H), 6.80-6.77 (m, 2H), 5.39 (s, 1H), 3.01 (s, 3H), 2.33 (s, 3H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 146.12, 139.61, 129.38, 124.47, 118.98, 115.26, 110.35, 46.55, 37.05, 21.37; **HRMS** (ESI) calcd for C<sub>11</sub>H<sub>11</sub>N<sub>3</sub> [M-H]<sup>-</sup>: 184.0880, found 184.0887.



**1f**

**2-((4-methoxyphenyl)(methyl)amino)malononitrile (1f):**

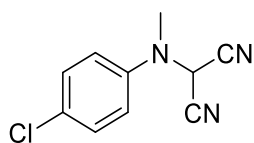
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.08 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 9.2 Hz, 2H), 5.21 (s, 1H), 3.79 (s, 3H), 2.98 (s, 3H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 156.94, 139.85, 122.07, 114.78, 110.38, 55.39, 48.30, 38.29; **HRMS** (ESI) calcd for C<sub>11</sub>H<sub>11</sub>N<sub>3</sub>O [M-H]<sup>-</sup>: 200.0829, found 200.0839.



**1g**

**2-((4-fluorophenyl)(methyl)amino)malononitrile (1g):**

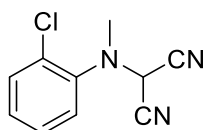
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.08 (s, 2H), 7.06 (d, *J* = 1.6 Hz, 2H), 5.31 (s, 1H), 3.02 (s, 3H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 159.49 (d, *J* = 243.3 Hz), 142.54 (d, *J* = 2.2 Hz), 121.58 (d, *J* = 8.1 Hz), 116.37 (d, *J* = 22.7 Hz), 110.19, 47.68, 38.00; **HRMS** (ESI) calcd for C<sub>10</sub>H<sub>8</sub>FN<sub>3</sub> [M-H]<sup>-</sup>: 188.0629, found 188.0639.



**1h**

**2-((4-chlorophenyl)(methyl)amino)malononitrile (1h):**

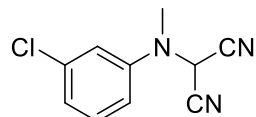
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.33 (d, *J* = 8.8 Hz, 2H), 6.98 (d, *J* = 9.2 Hz, 2H), 5.38 (s, 1H), 3.05 (s, 3H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 144.74, 129.74, 129.36, 120.03, 110.03, 46.71, 37.54; **HRMS** (ESI) calcd for C<sub>10</sub>H<sub>8</sub><sup>35</sup>ClN<sub>3</sub> [M-H]<sup>-</sup>: 204.0334, found 204.0341; **HRMS** (ESI) calcd for C<sub>10</sub>H<sub>8</sub><sup>37</sup>ClN<sub>3</sub> [M-H]<sup>-</sup>: 206.0305, found 206.0314.



**1i**

**2-((2-chlorophenyl)(methyl)amino)malononitrile (1i):**

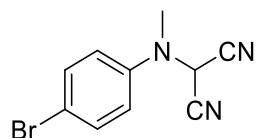
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.43 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.32 (td, *J* = 8.4, 1.2 Hz, 1H), 7.27 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.20-7.16 (m, 1H), 5.35 (s, 1H), 3.04 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 143.24, 130.82, 129.00, 128.10, 127.18, 122.85, 109.99, 46.65, 37.09; HRMS (ESI) calcd for C<sub>10</sub>H<sub>8</sub><sup>35</sup>ClN<sub>3</sub> [M-H]<sup>-</sup>: 204.0334, found 204.0326; HRMS (ESI) calcd for C<sub>10</sub>H<sub>8</sub><sup>37</sup>ClN<sub>3</sub> [M-H]<sup>-</sup>: 206.0305, found 206.0314.



**1j**

**2-((3-chlorophenyl)(methyl)amino)malononitrile (1j):**

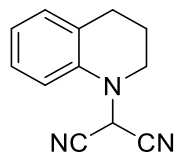
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.30 (t, *J* = 8.0 Hz, 1H), 7.10-7.08 (m, 1H), 7.00 (t, *J* = 2.0 Hz, 1H), 6.90 (dd, *J* = 8.4, 2.8 Hz, 1H), 5.44 (s, 1H), 3.09 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 147.27, 135.59, 130.79, 123.85, 118.53, 116.10, 109.94, 46.19, 37.17; HRMS (ESI) calcd for C<sub>10</sub>H<sub>8</sub><sup>35</sup>ClN<sub>3</sub> [M-H]<sup>-</sup>: 204.0334, found 204.0335; HRMS (ESI) calcd for C<sub>10</sub>H<sub>8</sub><sup>37</sup>ClN<sub>3</sub> [M-H]<sup>-</sup>: 206.0305, found 206.0311.



**1k**

**2-((4-bromophenyl)(methyl)amino)malononitrile (1k):**

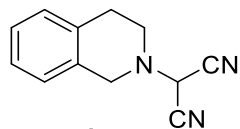
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.48 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 5.37 (s, 1H), 3.06 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 145.28, 132.74, 120.30, 116.95, 109.98, 46.53, 37.51; HRMS (ESI) calcd for C<sub>10</sub>H<sub>8</sub><sup>79</sup>BrN<sub>3</sub> [M-H]<sup>-</sup>: 247.9829, found 247.9840; HRMS (ESI) calcd for C<sub>10</sub>H<sub>8</sub><sup>81</sup>BrN<sub>3</sub> [M-H]<sup>-</sup>: 249.9809, found 249.9820.



**1l**

**2-(3,4-dihydroquinolin-1(2H)-yl)malononitrile (1l):**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.23-7.18 (m, 1H), 7.13 (dd, *J* = 7.6, 1.2 Hz, 1H), 6.94 (t, *J* = 7.2 Hz, 1H), 6.73 (d, *J* = 8.4 Hz, 1H), 5.67 (s, 1H), 3.44 (t, *J* = 6.0 Hz, 2H), 2.83 (t, *J* = 6.4 Hz, 2H), 2.14-2.08 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 140.45, 130.03, 127.27, 126.43, 121.27, 112.47, 110.48, 47.50, 42.94, 26.83, 21.70; HRMS (ESI) calcd for C<sub>12</sub>H<sub>11</sub>N<sub>3</sub> [M-H]<sup>-</sup>: 196.0880, found 196.0876.

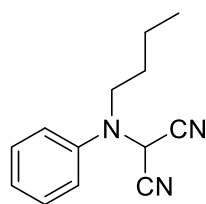


**1m**

**2-(3,4-dihydroisoquinolin-2(1H)-yl)malononitrile (1m):**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.22-7.14 (m, 3H), 7.09-7.07 (m, 1H), 4.85 (s, 1H), 3.93 (s, 2H), 3.04-2.98 (m, 4H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 132.35, 131.49, 128.71, 126.99, 126.45, 126.26, 109.67,

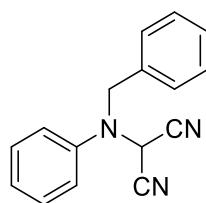
52.19, 48.15, 48.10, 28.69. The  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR of **1m** are consistent with the reported spectra.<sup>1</sup>



**1n**

**2-(butyl(phenyl)amino)malononitrile (1n):**

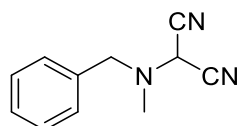
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40 (dd,  $J = 8.4, 7.6$  Hz, 2H), 7.19 (t,  $J = 7.2$  Hz, 1H), 7.15 (dd,  $J = 8.0, 1.2$  Hz, 2H), 5.29 (s, 1H), 3.37 (t,  $J = 7.2$  Hz, 2H), 1.61-1.54 (m, 2H), 1.46-1.36 (m, 2H), 0.95 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  144.73, 129.63, 124.75, 121.05, 110.89, 50.76, 46.48, 29.09, 19.79, 13.52; HRMS (ESI) calcd for  $\text{C}_{13}\text{H}_{15}\text{N}_3$  [M-H] $^-$ : 212.1193, found 212.1202.



**1o**

**2-(benzyl(phenyl)amino)malononitrile (1o)**

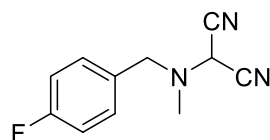
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37-7.36 (m, 2H), 7.35-7.32 (m, 4H), 7.31-7.29 (m, 1H), 7.21 (dd,  $J = 8.8, 1.2$  Hz, 2H), 7.15 (t,  $J = 7.2$  Hz, 1H), 5.13 (s, 1H), 4.43 (s, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  145.32, 134.98, 129.63, 128.97, 128.47, 128.26, 125.23, 121.39, 110.55, 56.39, 44.40; HRMS (ESI) calcd for  $\text{C}_{16}\text{H}_{13}\text{N}_3$  [M-H] $^-$ : 246.1037, found 246.1041.



**1p**

**2-(benzyl(methyl)amino)malononitrile (1p)**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43-7.35 (m, 5H), 4.62 (s, 1H), 3.70 (s, 2H), 2.56 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  134.80, 128.77, 128.36, 109.84, 58.71, 46.09, 39.24. The  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR of **1p** are consistent with the reported spectra.<sup>1</sup>

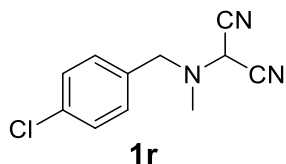


**1q**

**2-((4-fluorobenzyl)(methyl)amino)malononitrile (1q)**

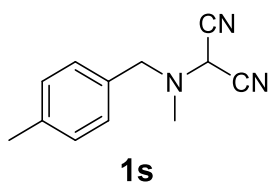
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31 (dd,  $J = 8.4, 5.2$  Hz, 2H), 7.07 (t,  $J = 8.4$  Hz, 2H), 4.63 (s, 1H), 3.66 (s, 2H), 2.53 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  162.51 (d,  $J = 245.8$  Hz), 130.70 (d,  $J = 2.5$  Hz), 130.54 (d,  $J = 8.1$  Hz), 115.68 (d,  $J = 21.3$  Hz), 109.82, 57.94, 46.23, 39.13; HRMS (ESI) calcd for  $\text{C}_{11}\text{H}_{10}\text{FN}_3$  [M-H] $^-$ : 202.0786, found 202.0789.





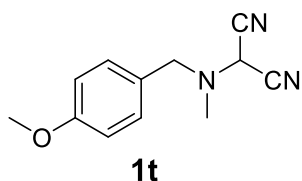
**2-((4-chlorobenzyl)(methyl)amino)malononitrile (1r)**

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35 (d,  $J = 8.4$  Hz, 2H), 7.27 (d,  $J = 8.4$  Hz, 2H), 4.61 (s, 1H), 3.66 (s, 2H), 2.52 (s, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  134.36, 133.39, 130.19, 129.09, 109.73, 58.12, 46.33, 39.37; **HRMS** (ESI) calcd for  $\text{C}_{11}\text{H}_{10}^{35}\text{ClN}_3$  [ $\text{M-H}$ ] $^-$ : 218.0490, found 218.0498; **HRMS** (ESI) calcd for  $\text{C}_{11}\text{H}_{10}^{37}\text{ClN}_3$  [ $\text{M-H}$ ] $^-$ : 220.0461, found 220.0470.



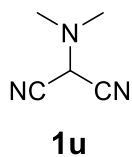
**2-(methyl(4-methylbenzyl)amino)malononitrile (1s)**

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.17 (dd,  $J = 12.4, 8.4$  Hz, 4H), 4.56 (s, 1H), 3.60 (s, 2H), 2.51 (s, 3H), 2.34 (s, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  138.26, 131.70, 129.49, 128.79, 109.88, 58.54, 45.88, 39.26, 20.93; **HRMS** (ESI) calcd for  $\text{C}_{12}\text{H}_{13}\text{N}_3$  [ $\text{M-H}$ ] $^-$ : 198.1037, found 198.1032.



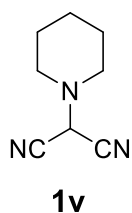
**2-((4-methoxybenzyl)(methyl)amino)malononitrile (1t)**

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.22 (d,  $J = 8.8$  Hz, 2H), 6.88 (d,  $J = 8.4$  Hz, 2H), 4.59 (s, 1H), 3.79 (s, 3H), 3.60 (s, 2H), 2.53 (s, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.68, 130.19, 126.65, 114.23, 109.92, 58.27, 55.14, 45.73, 39.30; **HRMS** (ESI) calcd for  $\text{C}_{12}\text{H}_{13}\text{N}_3\text{O}$  [ $\text{M-H}$ ] $^-$ : 214.0986, found 214.0987.



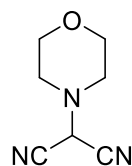
**2-(dimethylamino)malononitrile (1u)**

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.67 (s, 1H), 2.38 (s, 6H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  109.76, 48.74, 41.51; **HRMS** (ESI) calcd for  $\text{C}_5\text{H}_7\text{N}_3$  [ $\text{M+H}$ ] $^+$ : 110.0713, found 110.0715.



**2-(piperidin-1-yl)malononitrile (1v)**

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.64 (s, 1H), 2.61 (t,  $J = 5.2$  Hz, 4H), 1.69-1.63 (m, 4H), 1.50-1.44 (m, 2H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  109.90, 51.06, 48.79, 25.03, 22.78. The  $^1\text{H NMR}$  and  $^{13}\text{C NMR}$  of **1v** are consistent with the reported spectra.<sup>1</sup>

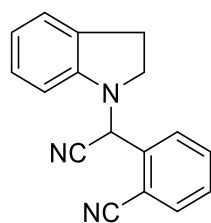


**1w**

### 2-morpholinomalononitrile (**1w**)

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.65 (s, 1H), 3.79 (t,  $J = 4.8$  Hz, 4H), 2.72 (t,  $J = 4.4$  Hz, 4H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  109.36, 65.91, 49.89, 48.24. The  $^1\text{H NMR}$  and  $^{13}\text{C NMR}$  of **1w** are consistent with the reported spectra.<sup>1</sup>

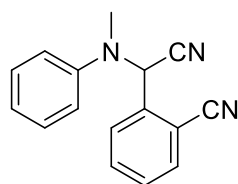
## 3.2 Characterization of products 3a-3y.



**3a**

### 2-(cyano(indolin-1-yl)methyl)benzonitrile (**3a**):

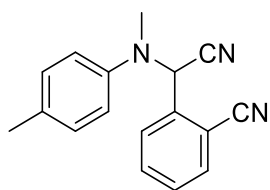
**3a** was obtained through the general procedure C in 75% yield as a white solid. IR (neat) 2928, 2226, 1618, 1485, 1251, 757  $\text{cm}^{-1}$ ; mp 195-197  $^{\circ}\text{C}$ ;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.91 (d,  $J = 7.6$  Hz, 1H), 7.79 (d,  $J = 7.6$  Hz, 1H), 7.73 (t,  $J = 7.6$  Hz, 1H), 7.57 (t,  $J = 7.6$  Hz, 1H), 7.17 (t,  $J = 7.2$  Hz, 2H), 6.87 (t,  $J = 7.2$  Hz, 1H), 6.78 (d,  $J = 8.0$  Hz, 1H), 5.97 (s, 1H), 3.44-3.37 (m, 1H), 3.17-3.12 (m, 1H), 3.09-3.02 (m, 1H), 3.00-2.91 (m, 1H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  148.29, 136.49, 134.18, 133.05, 130.40, 129.85, 128.54, 127.56, 125.01, 121.06, 116.26, 114.37, 112.71, 108.86, 53.50, 50.40, 28.03; HRMS (ESI) calcd for  $\text{C}_{17}\text{H}_{13}\text{N}_3$   $[\text{M}+\text{H}]^+$ : 260.1182, found 260.1190.



**3b**

### 2-(cyano(methyl(phenyl)amino)methyl)benzonitrile (**3b**):

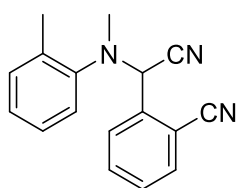
**3b** was obtained through the general procedure C in 68% yield as a white solid. IR (neat) 2924, 2225, 1619, 1496, 1262, 766  $\text{cm}^{-1}$ ; mp 167-169  $^{\circ}\text{C}$ ;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85-7.80 (m, 2H), 7.73-7.69 (m, 1H), 7.56 (t,  $J = 8.0$  Hz, 1H), 7.36 (t,  $J = 8.8$  Hz, 2H), 7.25 (d,  $J = 8.0$  Hz, 2H), 7.07 (t,  $J = 7.6$  Hz, 1H), 5.93 (s, 1H), 2.70 (s, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  148.72, 136.68, 134.48, 132.95, 129.84, 129.41, 129.35, 123.04, 119.05, 116.70, 114.54, 112.51, 59.31, 35.16; HRMS (ESI) calcd for  $\text{C}_{16}\text{H}_{13}\text{N}_3$   $[\text{M}+\text{H}]^+$ : 248.1182, found 248.1185.



**3c**

**2-(cyano(methyl(*p*-tolyl)amino)methyl)benzonitrile (3c):**

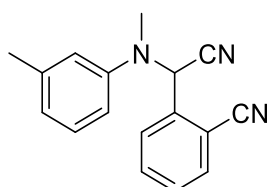
**3c** was obtained through the general procedure C in 61 % yield as a white solid. **IR** (neat) 2922, 2227, 1686, 1487, 1255, 773  $\text{cm}^{-1}$ ; **mp** 116-117  $^{\circ}\text{C}$ ;  **$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.83-7.80 (m, 2H), 7.72-7.68 (m, 1H), 7.58-7.54 (m, 1H), 7.17 (s, 4H), 5.85 (s, 1H), 2.67 (s, 3H), 2.32 (s, 3H);  **$^{13}\text{C NMR}$**  (100MHz,  $\text{CDCl}_3$ )  $\delta$  146.50, 136.83, 134.41, 132.94, 132.89, 129.94, 129.77, 129.36, 119.65, 116.77, 114.58, 112.62, 59.98, 35.51, 20.64; **HRMS** (ESI) calcd for  $\text{C}_{17}\text{H}_{15}\text{N}_3$   $[\text{M}+\text{H}]^+$ : 262.1339, found 262.1342.



**3d**

**2-(cyano(methyl(*o*-tolyl)amino)methyl)benzonitrile (3d):**

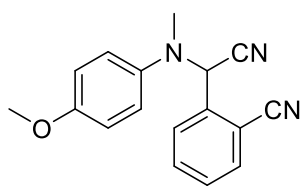
**3d** was obtained through the general procedure C in 72% yield as a white solid. **IR** (neat) 2925, 2223, 1619, 1494, 1255, 763  $\text{cm}^{-1}$ ; **mp** 94-96  $^{\circ}\text{C}$ ;  **$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.72 (d,  $J = 7.6$  Hz, 1H), 7.65-7.57 (m, 2H), 7.53-7.46 (m, 2H), 7.21 (t,  $J = 6.8$  Hz, 1H), 7.14-7.06 (m, 2H), 5.55 (s, 1H), 2.75 (s, 3H), 2.15 (s, 3H);  **$^{13}\text{C NMR}$**  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  147.43, 136.97, 134.94, 133.68, 132.63, 131.26, 129.48, 129.11, 126.70, 125.88, 122.30, 116.45, 116.24, 113.00, 58.78, 39.99, 17.63; **HRMS** (ESI) calcd for  $\text{C}_{17}\text{H}_{15}\text{N}_3$   $[\text{M}+\text{H}]^+$ : 262.1339, found 262.1343.



**3e**

**2-(cyano(methyl(*m*-tolyl)amino)methyl)benzonitrile (3e):**

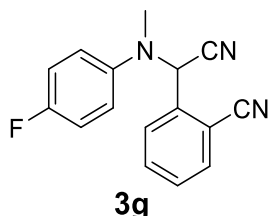
**3e** was obtained through the general procedure C in 62% yield as a white solid. **IR** (neat) 2920, 2224, 1603, 1494, 1280, 771  $\text{cm}^{-1}$ ; **mp** 89-91  $^{\circ}\text{C}$ ;  **$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85-7.79 (m, 2H), 7.70 (t,  $J = 7.6$  Hz, 1H), 7.55 (t,  $J = 7.6$  Hz, 1H), 7.26-7.22 (m, 1H), 7.05 (d,  $J = 6.4$  Hz, 2H), 6.88 (d,  $J = 7.6$  Hz, 1H), 5.93 (s, 1H), 2.67 (s, 3H), 2.36 (s, 3H);  **$^{13}\text{C NMR}$**  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  148.74, 139.17, 136.75, 134.46, 132.90, 129.78, 129.32, 129.17, 123.83, 119.61, 116.68, 116.02, 114.58, 112.49, 59.23, 35.11, 21.64; **HRMS** (ESI) calcd for  $\text{C}_{17}\text{H}_{15}\text{N}_3$   $[\text{M}+\text{H}]^+$ : 262.1339, found 262.1342.



**3f**

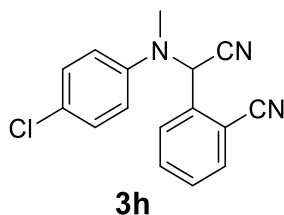
**2-(cyano((4-methoxyphenyl)(methyl)amino)methyl)benzonitrile (3f):**

**3f** was obtained through the general procedure C in 63% yield as a white solid. **IR** (neat) 2923, 2227, 1511, 1459, 1248, 763  $\text{cm}^{-1}$ ; **mp** 89-90 °C;  **$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.82 (d,  $J = 7.6$  Hz, 1H), 7.76 (d,  $J = 7.6$  Hz, 1H), 7.68 (t,  $J = 7.6$  Hz, 1H), 7.56 (t,  $J = 7.6$  Hz, 1H), 7.26 (d,  $J = 8.8$  Hz, 2H), 6.89 (d,  $J = 8.8$  Hz, 2H), 5.69 (s, 1H), 3.79 (s, 3H), 2.65 (s, 3H);  **$^{13}\text{C NMR}$**  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  156.41, 142.47, 136.83, 134.32, 132.87, 129.77, 129.43, 122.59, 116.92, 114.66, 114.53, 112.77, 61.27, 55.43, 36.43; **HRMS** (ESI) calcd for  $\text{C}_{17}\text{H}_{15}\text{N}_3\text{O}$   $[\text{M}+\text{H}]^+$ : 278.1288, found 278.1293.



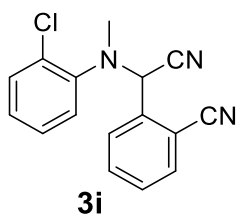
**2-(cyano((4-fluorophenyl)(methyl)amino)methyl)benzonitrile (3g):**

**3g** was obtained through the general procedure C in 61% yield as a white solid. **IR** (neat) 2924, 2227, 1509, 1488, 1232, 763  $\text{cm}^{-1}$ ; **mp** 92-93 °C;  **$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.84-7.79 (m, 2H), 7.71 (t,  $J = 7.6$  Hz, 1H), 7.58 (t,  $J = 7.6$  Hz, 1H), 7.29-7.26 (m, 2H), 7.05 (t,  $J = 8.8$  Hz, 2H), 5.76 (s, 1H), 2.66 (s, 3H);  **$^{13}\text{C NMR}$**  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.30 (d,  $J = 241.9$  Hz), 145.15 (d,  $J = 2.4$  Hz), 136.47, 134.42, 132.99, 129.95, 129.41, 122.16 (d,  $J = 8.2$  Hz), 116.84, 116.07 (d,  $J = 22.5$  Hz), 114.37, 112.62, 60.66, 35.98; **HRMS** (ESI) calcd for  $\text{C}_{16}\text{H}_{12}\text{FN}_3$   $[\text{M}+\text{H}]^+$ : 266.1088, found 266.1093.



**2-(((4-chlorophenyl)(methyl)amino)(cyano)methyl)benzonitrile (3h):**

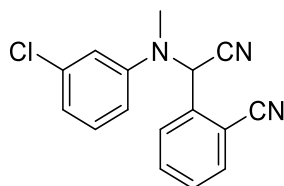
**3h** was obtained through the general procedure C in 55% yield as a white solid. **IR** (neat) 2920, 2228, 1647, 1496, 1265, 763  $\text{cm}^{-1}$ ; **mp** 108-109 °C;  **$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.82 (t,  $J = 7.2$  Hz, 2H), 7.72 (t,  $J = 7.6$  Hz, 1H), 7.58 (t,  $J = 7.2$  Hz, 1H), 7.31 (d,  $J = 8.8$  Hz, 2H), 7.18 (d,  $J = 8.8$  Hz, 2H), 5.87 (s, 1H), 2.67 (s, 3H);  **$^{13}\text{C NMR}$**  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  147.28, 136.33, 134.49, 133.05, 130.00, 129.40, 129.34, 128.31, 120.45, 116.67, 114.29, 112.47, 59.26, 35.33; **HRMS** (ESI) calcd for  $\text{C}_{16}\text{H}_{12}^{35}\text{ClN}_3$   $[\text{M}+\text{H}]^+$ : 282.0793, found 282.0802; **HRMS** (ESI) calcd for  $\text{C}_{16}\text{H}_{12}^{37}\text{ClN}_3$   $[\text{M}+\text{H}]^+$ : 284.0763, found 284.0771.



**2-(((2-chlorophenyl)(methyl)amino)(cyano)methyl)benzonitrile (3i):**

**3i** was obtained through the general procedure C in 71% yield as a white solid. **IR** (neat) 2921, 2228, 1648, 1481, 1267, 760  $\text{cm}^{-1}$ ; **mp** 79-80 °C;  **$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.76-7.73 (m, 2H), 7.65 (t,  $J = 7.6$  Hz, 1H), 7.52 (t,  $J = 7.6$  Hz, 1H), 7.45-7.37 (m, 2H), 7.29 (t,  $J = 7.6$  Hz, 1H), 7.12 (t,  $J = 7.6$  Hz,

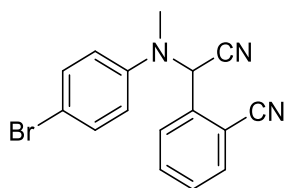
1H), 5.73 (s, 1H), 2.83 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 145.75, 136.09, 134.04, 132.72, 130.93, 130.82, 129.70, 129.03, 127.72, 126.58, 123.68, 116.29, 115.79, 113.03, 58.19, 38.46; HRMS (ESI) calcd for C<sub>16</sub>H<sub>12</sub><sup>35</sup>ClN<sub>3</sub> [M+H]<sup>+</sup>: 282.0793, found 282.0799; HRMS (ESI) calcd for C<sub>16</sub>H<sub>12</sub><sup>37</sup>ClN<sub>3</sub> [M+H]<sup>+</sup>: 284.0763, found 284.0768.



**3j**

**2-(((3-chlorophenyl)(methyl)amino)(cyano)methyl)benzonitrile (3j):**

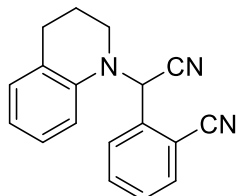
**3j** was obtained through the general procedure C in 56% yield as a white solid. IR (neat) 2921, 2228, 1594, 1488, 1277, 764 cm<sup>-1</sup>; mp 97-99 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.87-7.80 (m, 2H), 7.73 (t, *J* = 7.6 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.28 (t, *J* = 8.0 Hz, 1H), 7.16-7.12 (m, 2H), 7.04-7.02 (m, 1H), 5.94 (s, 1H), 2.70 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 149.70, 136.26, 135.12, 134.56, 133.09, 130.41, 130.04, 129.32, 122.68, 118.50, 116.54, 116.51, 114.30, 112.41, 58.39, 35.01; HRMS (ESI) calcd for C<sub>16</sub>H<sub>12</sub><sup>35</sup>ClN<sub>3</sub> [M+H]<sup>+</sup>: 282.0793, found 282.0801; HRMS (ESI) calcd for C<sub>16</sub>H<sub>12</sub><sup>37</sup>ClN<sub>3</sub> [M+H]<sup>+</sup>: 284.0763, found 284.0768.



**3k**

**2-(((4-bromophenyl)(methyl)amino)(cyano)methyl)benzonitrile (3k):**

**3k** was obtained through the general procedure C in 60% yield as a white solid. IR (neat) 2924, 2227, 1618, 1493, 1265, 763 cm<sup>-1</sup>; mp 90-91 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.82 (t, *J* = 8.8 Hz, 2H), 7.72 (t, *J* = 7.6 Hz, 1H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.45 (d, *J* = 8.8 Hz, 2H), 7.11 (d, *J* = 8.8 Hz, 2H), 5.88 (s, 1H), 2.67 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 147.70, 136.29, 134.49, 133.05, 132.31, 130.00, 129.31, 120.59, 116.63, 115.73, 114.26, 112.42, 58.94, 35.22; HRMS (ESI) calcd for C<sub>16</sub>H<sub>12</sub><sup>79</sup>BrN<sub>3</sub> [M+H]<sup>+</sup>: 326.0287, found 326.0298; HRMS (ESI) calcd for C<sub>16</sub>H<sub>12</sub><sup>81</sup>BrN<sub>3</sub> [M+H]<sup>+</sup>: 328.0267, found 328.0276.

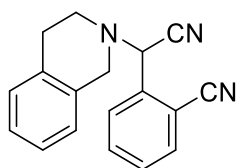


**3l**

**2-(cyano(3,4-dihydroquinolin-1(2H)-yl)methyl)benzonitrile (3l):**

**3l** was obtained through the general procedure C in 55% yield as a white solid. IR (neat) 2925, 2231, 1599, 1494, 1277, 764 cm<sup>-1</sup>; mp 177-179 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.94 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 7.6 Hz, 1H), 7.73 (t, *J* = 7.6 Hz, 1H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.15 (t, *J* = 7.2 Hz, 1H), 7.07 (d, *J* = 7.2 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 1H), 6.84 (t, *J* = 7.2 Hz, 1H), 6.14 (s, 1H), 3.20-3.14 (m, 1H),

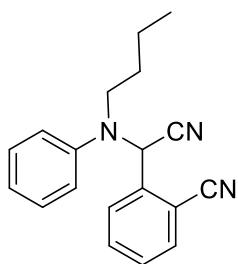
2.95-2.81 (m, 2H), 2.78-2.71 (m, 1H), 2.06-1.89 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  142.96, 137.03, 134.61, 132.98, 129.74, 129.63, 129.22, 127.14, 126.29, 120.22, 116.36, 115.21, 113.28, 112.19, 54.96, 45.78, 27.45, 21.98; HRMS (ESI) calcd for  $\text{C}_{18}\text{H}_{15}\text{N}_3$   $[\text{M}+\text{H}]^+$ : 274.1339, found 274.1348.



**3m**

**2-(cyano(3,4-dihydroisoquinolin-2(1H)-yl)methyl)benzonitrile (3m):**

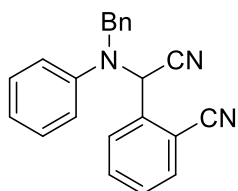
**3m** was obtained through the general procedure C in 80% yield as a white solid. IR (neat) 2922, 2227, 1618, 1449, 1267, 756  $\text{cm}^{-1}$ ; mp 110-112  $^{\circ}\text{C}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.84 (d,  $J = 7.6$  Hz, 1H), 7.77-7.69 (m, 2H), 7.54 (t,  $J = 7.2$  Hz, 1H), 7.16-7.09 (m, 3H), 6.97 (d,  $J = 8.0$  Hz, 1H), 5.29 (s, 1H), 3.91 (d,  $J = 14.4$  Hz, 1H), 3.63 (d,  $J = 14.4$  Hz, 1H), 3.11-3.00 (m, 2H), 2.92-2.81 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  136.78, 134.09, 133.51, 132.88, 132.61, 129.62, 128.71, 128.65, 126.44, 126.38, 125.79, 116.46, 113.88, 113.35, 60.77, 51.34, 48.09, 29.02; HRMS (ESI) calcd for  $\text{C}_{18}\text{H}_{15}\text{N}_3$   $[\text{M}+\text{H}]^+$ : 274.1339, found 274.1348.



**3n**

**2-((butyl(phenyl)amino)(cyano)methyl)benzonitrile (3n):**

**3n** was obtained through the general procedure C in 65% yield as a white solid. IR (neat) 2931, 2227, 1598, 1498, 1263, 763  $\text{cm}^{-1}$ ; mp 65-66  $^{\circ}\text{C}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.79 (d,  $J = 7.6$  Hz, 1H), 7.71 (d,  $J = 7.6$  Hz, 1H), 7.63 (t,  $J = 7.6$  Hz, 1H), 7.52 (t,  $J = 7.6$  Hz, 1H), 7.32 (t,  $J = 8.4$  Hz, 2H), 7.24 (d,  $J = 7.6$  Hz, 2H), 7.10 (t,  $J = 7.2$  Hz, 1H), 5.70 (s, 1H), 3.30-3.23 (m, 1H), 2.99-2.91 (m, 1H), 1.47-1.31 (m, 2H), 1.28-1.11 (m, 2H), 0.73 (t,  $J = 7.6$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  146.58, 137.19, 134.31, 132.77, 129.63, 129.51, 129.27, 124.33, 122.56, 116.88, 115.62, 112.80, 59.62, 49.14, 29.23, 19.91, 13.54; HRMS (ESI) calcd for  $\text{C}_{19}\text{H}_{19}\text{N}_3$   $[\text{M}+\text{H}]^+$ : 290.1652, found 290.1659.

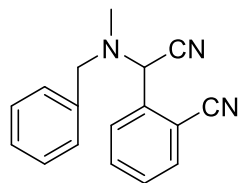


**3o**

**2-((benzyl(phenyl)amino)(cyano)methyl)benzonitrile (3o):**

**3o** was obtained through the general procedure C in 62% yield as a white solid. IR (neat) 2921, 2225, 1598, 1497, 1210, 764  $\text{cm}^{-1}$ ; mp 117-118  $^{\circ}\text{C}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.70 (t,  $J = 8.0$  Hz, 2H), 7.54 (t,  $J = 7.6$  Hz, 1H), 7.41 (t,  $J = 7.2$  Hz, 1H), 7.25-7.22 (m, 6H), 7.18 (t,  $J = 7.2$  Hz, 2H), 7.11 (t,  $J = 7.2$  Hz, 1H), 7.04-6.99 (m, 1H), 5.86 (s, 1H), 4.44 (d,  $J = 14.8$  Hz, 1H), 4.23 (d,  $J = 14.8$  Hz, 1H);

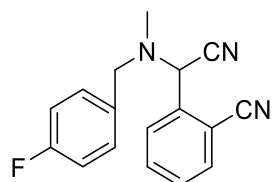
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  146.75, 136.60, 136.45, 134.25, 132.77, 129.67, 129.62, 129.15, 128.27, 127.93, 127.17, 124.10, 121.91, 116.91, 115.19, 112.65, 58.98, 53.82; **HRMS** (ESI) calcd for  $\text{C}_{22}\text{H}_{17}\text{N}_3$   $[\text{M}+\text{H}]^+$ : 324.1495, found 324.1504.



**3p**

**2-((benzyl(methyl)amino)(cyano)methyl)benzonitrile (3p):**

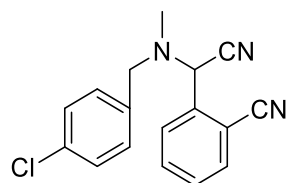
**3p** was obtained through the general procedure C in 65% yield as a white solid. **IR** (neat) 2921, 2228, 1601, 1454, 1267, 737  $\text{cm}^{-1}$ ; **mp** 82-84  $^{\circ}\text{C}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.79 (d,  $J = 8.0$  Hz, 2H), 7.65 (t,  $J = 7.6$  Hz, 1H), 7.51 (t,  $J = 7.6$  Hz, 1H), 7.40 (d,  $J = 6.8$  Hz, 2H), 7.32 (t,  $J = 7.2$  Hz, 2H), 7.27 (t,  $J = 6.8$  Hz, 1H), 5.23 (s, 1H), 3.75 (d,  $J = 12.8$  Hz, 1H), 3.66 (d,  $J = 12.8$  Hz, 1H), 2.17 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  137.12, 136.59, 134.20, 132.51, 129.41, 128.98, 128.82, 128.33, 127.57, 116.76, 113.66, 112.89, 60.44, 59.14, 37.30; **HRMS** (ESI) calcd for  $\text{C}_{17}\text{H}_{15}\text{N}_3$   $[\text{M}+\text{H}]^+$ : 262.1339, found 262.1342.



**3q**

**2-(cyano((4-fluorobenzyl)(methyl)amino)methyl)benzonitrile (3q):**

**3q** was obtained through the general procedure C in 70% yield as a yellow oil; **IR** (neat) 2924, 2228, 1603, 1510, 1223, 764  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.78 (d,  $J = 8.4$  Hz, 2H), 7.66 (t,  $J = 7.6$  Hz, 1H), 7.51 (t,  $J = 7.6$  Hz, 1H), 7.37 (t,  $J = 8.4$  Hz, 2H), 7.00 (t,  $J = 8.4$  Hz, 2H), 5.22 (s, 1H), 3.74 (d,  $J = 12.8$  Hz, 1H), 3.63 (d,  $J = 12.8$  Hz, 1H), 2.13 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  162.27 (d,  $J = 244.4$  Hz), 137.11, 134.28, 132.62, 132.38 (d,  $J = 2.9$  Hz), 130.69 (d,  $J = 8.2$  Hz), 129.53, 128.90, 116.83, 115.24 (d,  $J = 21.2$  Hz), 113.60, 112.93, 60.42, 58.65, 37.11; **HRMS** (ESI) calcd for  $\text{C}_{17}\text{H}_{14}\text{FN}_3$   $[\text{M}+\text{H}]^+$ : 280.1245, found 280.1251.

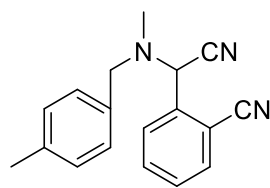


**3r**

**2-(((4-chlorobenzyl)(methyl)amino)(cyano)methyl)benzonitrile (3r):**

**3r** was obtained through the general procedure C in 70% yield as a yellow solid. **IR** (neat) 2923, 2228, 1619, 1492, 1321, 764  $\text{cm}^{-1}$ ; **mp** 101-103  $^{\circ}\text{C}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.80-7.77 (m, 2H), 7.66 (t,  $J = 7.6$  Hz, 1H), 7.52 (t,  $J = 7.6$  Hz, 1H), 7.36-7.27 (m, 4H), 5.23 (s, 1H), 3.74 (d,  $J = 12.8$  Hz, 1H), 3.62 (d,  $J = 12.8$  Hz, 1H), 2.14 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  137.02, 135.19, 134.28, 133.40, 132.63, 130.36, 129.56, 128.88, 128.55, 116.82, 113.56, 112.92, 60.51, 58.61 37.23; **HRMS** (ESI) calcd for  $\text{C}_{17}\text{H}_{14}^{35}\text{ClN}_3$   $[\text{M}+\text{H}]^+$ : 296.0949, found 296.0959; **HRMS** (ESI) calcd for  $\text{C}_{17}\text{H}_{14}^{37}\text{ClN}_3$

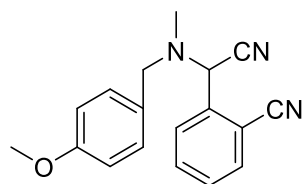
[M+H]<sup>+</sup>: 298.0920, found 298.0925.



**3s**

**2-(cyano(methyl(4-methylbenzyl)amino)methyl)benzonitrile (3s):**

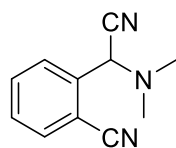
**3s** was obtained through the general procedure C in 71% yield as a yellow solid. **IR** (neat) 2923, 2228, 1600, 1450, 1267, 765 cm<sup>-1</sup>; **mp** 112-113 °C; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.78 (d, *J* = 7.6 Hz, 2H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 5.22 (s, 1H), 3.72 (d, *J* = 12.8 Hz, 1H), 3.65 (d, *J* = 12.8 Hz, 1H), 2.33 (s, 3H), 2.16 (s, 3H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 137.33, 137.32, 134.27, 133.56, 132.52, 129.41, 129.08, 129.07, 128.93, 116.79, 113.73, 113.04, 60.42, 59.05, 37.30, 21.03; **HRMS** (ESI) calcd for C<sub>18</sub>H<sub>17</sub>N<sub>3</sub> [M+H]<sup>+</sup>: 276.1495, found 276.1502.



**3t**

**2-(cyano((4-methoxybenzyl)(methyl)amino)methyl)benzonitrile (3t):**

**3t** was obtained through the general procedure C in 72% yield as a yellow solid. **IR** (neat) 2924, 2227, 1611, 1450, 1246, 763 cm<sup>-1</sup>; **mp** 91-93 °C; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.77 (d, *J* = 8.0 Hz, 2H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.33 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 5.21 (s, 1H), 3.78 (s, 3H), 3.70 (d, *J* = 12.8 Hz, 1H), 3.62 (d, *J* = 12.8 Hz, 1H), 2.13 (s, 3H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 159.15, 137.33, 134.30, 132.56, 130.37, 129.42, 128.93, 128.65, 116.86, 113.78, 113.73, 112.96, 60.31, 58.89, 55.16, 37.09; **HRMS** (ESI) calcd for C<sub>18</sub>H<sub>17</sub>N<sub>3</sub>O [M+H]<sup>+</sup>: 292.1444, found 292.1453.

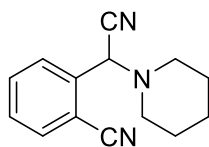


**3u**

**2-(cyano(dimethylamino)methyl)benzonitrile (3u):**

**3u** was obtained through the general procedure C in 28% yield as a yellow oil. **IR** (neat) 2953, 2228, 1605, 1487, 1223, 764 cm<sup>-1</sup>; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.74 (d, *J* = 7.6 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 5.06 (s, 1H), 2.33 (s, 6H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 137.31, 133.93, 132.56, 129.44, 128.51, 116.53, 113.52, 113.09, 61.38, 41.49; **HRMS** (ESI) calcd for C<sub>11</sub>H<sub>11</sub>N<sub>3</sub> [M+H]<sup>+</sup>: 186.1026, found 186.1023.

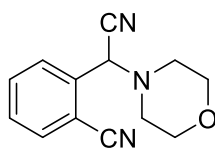




**3v**

**2-(cyano(dimethylamino)methyl)benzonitrile (3v):**

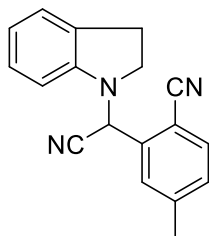
**3v** was obtained through the general procedure C in 45% yield as a yellow solid. **IR** (neat) 2938, 2228, 1628, 1451, 1278, 766  $\text{cm}^{-1}$ ; **mp** 65-67 °C;  **$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.72 (d,  $J = 7.6$  Hz, 1H), 7.69 (d,  $J = 8.0$  Hz, 1H), 7.62 (t,  $J = 7.6$  Hz, 1H), 7.48 (t,  $J = 7.6$  Hz, 1H), 5.00 (s, 1H), 2.60-2.57 (m, 2H), 2.46-2.40 (m, 2H), 1.65-1.57 (m, 2H), 1.55-1.40 (m, 4H);  **$^{13}\text{C NMR}$**  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  137.27, 133.96, 132.26, 129.17, 128.52, 116.47, 113.88, 113.02, 61.34, 50.59, 25.30, 23.61; **HRMS** (ESI) calcd for  $\text{C}_{14}\text{H}_{15}\text{N}_3$   $[\text{M}+\text{H}]^+$ : 226.1339, found 226.1335.



**3w**

**2-(cyano(morpholino)methyl)benzonitrile (3w):**

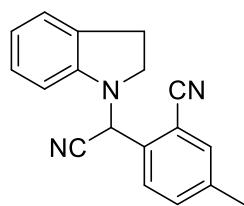
**3w** was obtained through the general procedure C in 64% yield as yellow solid. **IR** (neat) 2914, 2228, 1487, 1454, 1250, 766  $\text{cm}^{-1}$ ; **mp** 80-82 °C;  **$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.74 (d,  $J = 7.6$  Hz, 1H), 7.69 (d,  $J = 7.6$  Hz, 1H), 7.63 (t,  $J = 8.0$  Hz, 1H), 7.50 (t,  $J = 7.6$  Hz, 1H), 5.03 (s, 1H), 3.71-3.66 (m, 2H), 3.64-3.59 (m, 2H), 2.67-2.62 (m, 2H), 2.49-2.45 (m, 2H);  **$^{13}\text{C NMR}$**  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  136.13, 133.99, 132.45, 129.50, 128.60, 116.35, 113.44, 112.97, 66.10, 60.62, 49.47; **HRMS** (ESI) calcd for  $\text{C}_{13}\text{H}_{13}\text{N}_3\text{O}$   $[\text{M}+\text{H}]^+$ : 228.1131, found 228.1128.



**3x**

**2-(cyano(indolin-1-yl)methyl)-4-methylbenzonitrile (3x):**

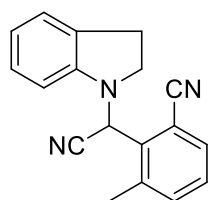
**3x** and **3x'** was obtained through the general procedure C in 72% yield ( $3x:3x' = 1:1.7$ ) as a white solid. **IR** (neat) 2925, 2227, 1608, 1485, 1266, 739  $\text{cm}^{-1}$ ; **mp** (**3x**) 161-163 °C;  **$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.69 (s, 1H), 7.67 (d,  $J = 7.6$  Hz, 1H), 7.35 (d,  $J = 7.6$  Hz, 1H), 7.18-7.14 (m, 2H), 6.86 (t,  $J = 7.2$  Hz, 1H), 6.77 (d,  $J = 7.6$  Hz, 1H), 5.93 (s, 1H), 3.43-3.36 (m, 1H), 3.18-3.12 (m, 1H), 3.09-3.02 (m, 1H), 3.00-2.91 (m, 1H), 2.52 (s, 3H);  **$^{13}\text{C NMR}$**  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  148.38, 144.42, 136.38, 134.06, 130.42, 129.35, 129.30, 127.56, 125.08, 121.01, 116.57, 114.55, 109.69, 108.89, 53.56, 50.39, 28.09, 22.02; **HRMS** (ESI) calcd for  $\text{C}_{18}\text{H}_{15}\text{N}_3$   $[\text{M}+\text{H}]^+$ : 274.1339, found 274.1335.



**3x'**

**2-(cyano(indolin-1-yl)methyl)-5-methylbenzonitrile (3x'):**

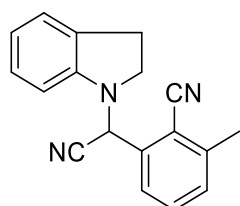
**3x** and **3x'** was obtained through the general procedure C in 72% yield ( $3x:3x' = 1:1.7$ ) as a white solid. IR (neat) 2923, 2229, 1607, 1485, 1251, 747  $\text{cm}^{-1}$ ; mp (**3x'**) 126-128  $^{\circ}\text{C}$ ;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.77 (d,  $J = 8.0$  Hz, 1H), 7.59 (s, 1H), 7.51 (d,  $J = 7.6$  Hz, 1H), 7.17-7.13 (m, 2H), 6.86 (t,  $J = 7.2$  Hz, 1H), 6.77 (d,  $J = 8.0$  Hz, 1H), 5.92 (s, 1H), 3.42-3.35 (m, 1H), 3.17-3.11 (m, 1H), 3.08-3.01 (m, 1H), 2.99-2.90 (m, 1H), 2.45 (s, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  148.38, 140.40, 134.61, 133.72, 133.59, 130.45, 128.52, 127.58, 125.01, 120.99, 116.45, 114.58, 112.54, 108.89, 53.22, 50.29, 28.07, 20.89; HRMS (ESI) calcd for  $\text{C}_{18}\text{H}_{15}\text{N}_3$   $[\text{M}+\text{H}]^+$ : 274.1339, found 274.1335.



**3y**

**2-(cyano(indolin-1-yl)methyl)-3-methylbenzonitrile (3y):**

**3y** and **3y'** was obtained through the general procedure C in 78% yield ( $3y:3y' = 1:2.1$ ) as a white solid. IR (neat) 2921, 2226, 1606, 1485, 1251, 749  $\text{cm}^{-1}$ ; mp (**3y**) 189-191  $^{\circ}\text{C}$ ;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.65 (d,  $J = 7.6$  Hz, 1H), 7.53 (d,  $J = 6.8$  Hz, 1H), 7.45 (t,  $J = 7.6$  Hz, 1H), 7.17-7.10 (m, 2H), 6.86 (t,  $J = 7.6$  Hz, 1H), 6.64 (d,  $J = 7.6$  Hz, 1H), 5.80 (s, 1H), 3.51-3.41 (m, 2H), 3.07-2.94 (m, 2H), 2.66 (s, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  149.08, 139.23, 136.30, 133.89, 132.52, 130.56, 129.78, 127.61, 124.99, 120.78, 117.04, 115.25, 113.48, 108.33, 51.98, 51.04, 28.21, 19.97; HRMS (ESI) calcd for  $\text{C}_{18}\text{H}_{15}\text{N}_3$   $[\text{M}+\text{H}]^+$ : 274.1339, found 274.1347.

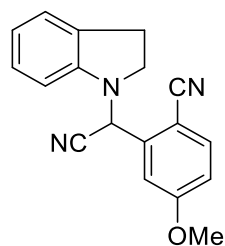


**3y'**

**2-(cyano(indolin-1-yl)methyl)-6-methylbenzonitrile (3y'):**

**3y** and **3y'** was obtained through the general procedure C in 78% yield ( $3y:3y' = 1:2.1$ ) as a white solid. IR (neat) 2920, 2221, 1602, 1484, 1247, 755  $\text{cm}^{-1}$ ; mp (**3y'**) 117-119  $^{\circ}\text{C}$ ;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.72 (d,  $J = 7.6$  Hz, 1H), 7.59 (t,  $J = 7.6$  Hz, 1H), 7.42 (t,  $J = 8.0$  Hz, 1H), 7.18-7.14 (m, 2H), 6.86 (t,  $J = 7.2$  Hz, 1H), 6.80 (d,  $J = 7.6$  Hz, 1H), 5.95 (s, 1H), 3.44-3.37 (m, 1H), 3.17-3.12 (m, 1H), 3.08-3.01 (m, 1H), 2.99-2.91 (m, 1H), 2.61 (s, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  148.42, 144.18, 136.69, 132.40, 131.10, 130.42, 127.56, 125.86, 124.96, 120.97, 115.41, 114.58, 112.95, 108.93,

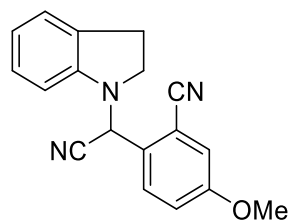
53.70, 50.43, 28.04, 20.79; **HRMS** (ESI) calcd for  $C_{18}H_{15}N_3$   $[M+H]^+$ : 274.1339, found 274.1347.



**3z**

**2-(cyano(indolin-1-yl)methyl)-4-methoxybenzonitrile (3z):**

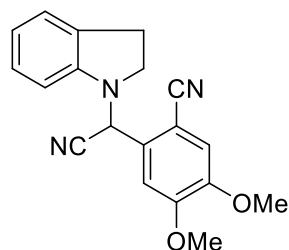
**3z** and **3z'** was obtained through the general procedure C in 70% yield ( $3z:3z' = 1:2.0$ ) as a white solid. **IR** (neat) 2929, 2229, 1606, 1486, 1257, 751  $cm^{-1}$ ; **mp** (**3z**) 168-169 °C;  **$^1H$  NMR** (400 MHz,  $CDCl_3$ )  $\delta$  7.71 (d,  $J = 8.8$  Hz, 1H), 7.39 (d,  $J = 2.4$  Hz, 1H), 7.18-7.14 (m, 2H), 7.00 (d,  $J = 8.4$  Hz, 1H), 6.86 (t,  $J = 7.6$  Hz, 1H), 6.77 (d,  $J = 8.0$  Hz, 1H), 5.92 (s, 1H), 3.93 (s, 3H), 3.43-3.36 (m, 1H), 3.21-3.16 (m, 1H), 3.09-2.92 (m, 2H);  **$^{13}C$  NMR** (100 MHz,  $CDCl_3$ )  $\delta$  162.91, 148.31, 138.50, 135.94, 130.39, 127.56, 124.99, 121.00, 116.66, 115.32, 114.39, 114.32, 108.86, 103.93, 55.89, 53.54, 50.42, 28.05; **HRMS** (ESI) calcd for  $C_{18}H_{15}N_3O$   $[M+H]^+$ : 290.1288, found 290.1299.



**3z'**

**2-(cyano(indolin-1-yl)methyl)-5-methoxybenzonitrile (3z'):**

**3z** and **3z'** was obtained through the general procedure C in 70% yield ( $3z:3z' = 1:2.0$ ) as a white solid. **IR** (neat) 2932, 2372, 1727, 1460, 1286, 745  $cm^{-1}$ ; **mp** (**3z'**) 134-136 °C;  **$^1H$  NMR** (400 MHz,  $CDCl_3$ )  $\delta$  7.77 (d,  $J = 8.4$  Hz, 1H), 7.26 (d,  $J = 2.8$  Hz, 1H), 7.20-7.13 (m, 3H), 6.85 (t,  $J = 7.6$  Hz, 1H), 6.76 (d,  $J = 8.4$  Hz, 1H), 5.90 (s, 1H), 3.86 (s, 3H), 3.40-3.33 (m, 1H), 3.16-3.11 (m, 1H), 3.07-2.89 (m, 2H);  **$^{13}C$  NMR** (100 MHz,  $CDCl_3$ )  $\delta$  160.03, 148.36, 130.43, 129.92, 128.18, 127.51, 124.95, 120.89, 119.43, 118.39, 116.14, 114.66, 113.56, 108.83, 55.80, 52.80, 50.25, 27.99; **HRMS** (ESI) calcd for  $C_{18}H_{15}N_3O$   $[M+H]^+$ : 290.1288, found 290.1299.

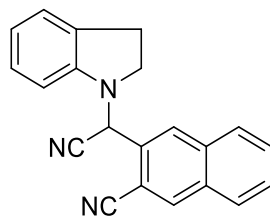


**3aa**

**2-(cyano(indolin-1-yl)methyl)-4,5-dimethoxybenzonitrile (3aa):**

**3aa** was obtained through the general procedure C in 64% yield as a yellow solid. **IR** (neat) 2937, 2223, 1601, 1460, 1224, 744  $cm^{-1}$ ; **mp** 183-185 °C;  **$^1H$  NMR** (400 MHz,  $CDCl_3$ )  $\delta$  7.27 (s, 1H), 7.17-7.13 (m, 3H), 6.85 (t,  $J = 7.2$  Hz, 1H), 6.76 (d,  $J = 8.0$  Hz, 1H), 5.91 (s, 1H), 4.00 (s, 3H), 3.91 (s, 3H), 3.41-3.34 (m, 1H), 3.21-3.16 (m, 1H), 3.08-2.91 (m, 2H);  **$^{13}C$  NMR** (100 MHz,  $CDCl_3$ )  $\delta$  152.50, 149.39, 148.30, 130.38, 130.32, 127.49, 124.92, 120.87, 116.58, 115.45, 114.76, 111.09, 108.78, 103.91,

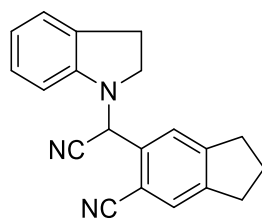
56.38, 56.31, 53.15, 50.36, 27.99; **HRMS** (ESI) calcd for  $C_{19}H_{17}N_3 O_2$   $[M+H]^+$ : 320.1394, found 320.1404.



**3ab**

**3-(cyano(indolin-1-yl)methyl)-2-naphthonitrile (3ab):**

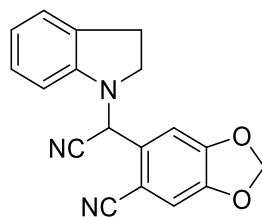
**3ab** was obtained through the general procedure C in 71% yield as a white solid. **IR** (neat) 2918, 2222, 1599, 1485, 1255, 754  $cm^{-1}$ ; **mp** 241-242 °C;  **$^1H$  NMR** (400 MHz,  $CDCl_3$ )  $\delta$  8.34 (d,  $J = 12.0$  Hz, 2H), 8.01 (d,  $J = 8.0$  Hz, 1H), 7.95 (d,  $J = 8.0$  Hz, 1H), 7.78-7.69 (m, 2H), 7.19-7.15 (m, 2H), 6.89-6.83 (m, 2H), 6.08 (s, 1H), 3.48-3.41 (m, 1H), 3.16-3.11 (m, 1H), 3.08-3.02 (m, 1H), 3.00-2.91 (m, 1H);  **$^{13}C$  NMR** (100 MHz,  $CDCl_3$ )  $\delta$  148.41, 136.66, 133.93, 132.14, 130.57, 130.47, 130.13, 128.81, 128.52, 128.43, 128.29, 127.62, 125.06, 121.10, 116.78, 114.65, 109.30, 109.03, 53.77, 50.36, 28.05; **HRMS** (ESI) calcd for  $C_{21}H_{15}N_3$   $[M+H]^+$ : 310.1339, found 310.1349.



**3ac**

**6-(cyano(indolin-1-yl)methyl)-2,3-dihydro-1H-indene-5-carbonitrile (3ac):**

**3ac** was obtained through the general procedure C in 76% yield as a yellow solid. **IR** (neat) 2930, 2228, 1605, 1485, 1250, 754  $cm^{-1}$ ; **mp** 156-158 °C;  **$^1H$  NMR** (400 MHz,  $CDCl_3$ )  $\delta$  7.74 (s, 1H), 7.59 (s, 1H), 7.18-7.14 (m, 2H), 6.87-6.81 (m, 2H), 5.97 (s, 1H), 3.43-3.36 (m, 1H), 3.20-3.14 (m, 1H), 3.08-2.90 (m, 6H), 2.21-2.14 (m, 2H);  **$^{13}C$  NMR** (100 MHz,  $CDCl_3$ )  $\delta$  150.62, 148.36, 146.28, 134.34, 130.26, 129.59, 127.36, 124.76, 124.56, 120.65, 116.90, 114.68, 109.93, 108.69, 53.20, 50.12, 33.10, 32.17, 27.86, 24.94; **HRMS** (ESI) calcd for  $C_{20}H_{17}N_3$   $[M+H]^+$ : 300.1495, found 300.1491.



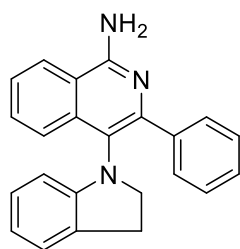
**3ad**

**6-(cyano(indolin-1-yl)methyl)benzo[d][1,3]dioxole-5-carbonitrile (3ad):**

**3ad** was obtained through the general procedure C in 70% yield as a yellow solid. **IR** (neat) 2909, 2218, 1618, 1487, 1252, 758  $cm^{-1}$ ; **mp** 169-171 °C;  **$^1H$  NMR** (400 MHz,  $CDCl_3$ )  $\delta$  7.32 (s, 1H), 7.18-7.12 (m, 3H), 6.86 (t,  $J = 7.2$  Hz, 1H), 6.78 (d,  $J = 8.4$  Hz, 1H), 6.13 (s, 2H), 5.90 (s, 1H), 3.42-3.35 (m, 1H), 3.25-3.19 (m, 1H), 3.09-2.91 (m, 2H);  **$^{13}C$  NMR** (100 MHz,  $CDCl_3$ )  $\delta$  151.66, 148.39, 148.25, 132.67, 130.29, 127.49, 124.92, 120.90, 116.29, 114.53, 112.68, 109.19, 108.77, 105.30, 103.06,

53.10, 50.31, 27.98; **HRMS** (ESI) calcd for  $C_{18}H_{13}N_3O_2$   $[M+H]^+$ : 304.1081, found 304.1077.

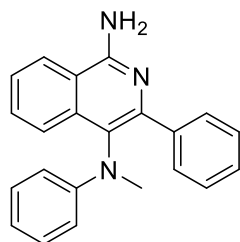
### 3.3 Characterization of products 4a and 4b



**4a**

#### 4-(indolin-1-yl)-3-phenylisoquinolin-1-amine (**4a**):

**4a** was obtained through the general procedure D in 61% yield as a yellow solid. **IR** (neat) 2925, 1721, 1605, 1434, 1273, 743  $cm^{-1}$ ; **mp** 191-192 °C;  **$^1H$  NMR** (400 MHz,  $CDCl_3$ )  $\delta$  7.86 (d,  $J = 8.4$  Hz, 1H), 7.70-7.63 (m, 3H), 7.57-7.48 (m, 2H), 7.36-7.29 (m, 3H), 7.13 (d,  $J = 7.2$  Hz, 1H), 6.95 (t,  $J = 8.0$  Hz, 1H), 6.63 (t,  $J = 7.2$  Hz, 1H), 6.05 (d,  $J = 7.6$  Hz, 1H), 5.29 (s, 2H), 3.70-3.63 (m, 1H), 3.46-3.40 (m, 1H), 3.21-3.13 (m, 1H), 3.03-2.94 (m, 1H);  **$^{13}C$  NMR** (100 MHz,  $CDCl_3$ )  $\delta$  154.45, 152.32, 150.47, 139.58, 136.11, 130.25, 128.64, 128.36, 128.08, 127.82, 127.58, 126.00, 124.60, 124.17, 123.37, 122.48, 118.33, 116.37, 106.18, 52.10, 28.67; **HRMS** (ESI) calcd for  $C_{23}H_{19}N_3$   $[M+H]^+$ : 338.1652, found 338.1645.

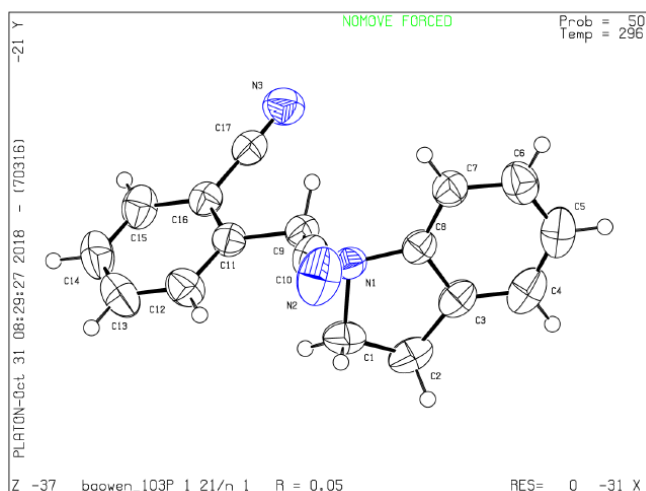


**4b**

#### $N^4$ -methyl- $N^4$ , 3-diphenylisoquinoline-1, 4-diamine (**4b**):

**4b** was obtained through the general procedure D in 63% yield as a yellow solid. **IR** (neat) 2928, 1720 1599, 1435, 1265, 739  $cm^{-1}$ ; **mp** 178-180 °C;  **$^1H$  NMR** (400 MHz,  $CDCl_3$ )  $\delta$  7.85 (d,  $J = 8.0$  Hz, 1H), 7.60-7.47 (m, 5H), 7.34-7.29 (m, 3H), 7.18 (t,  $J = 8.0$  Hz, 2H), 6.71 (t,  $J = 7.2$  Hz, 1H), 6.55 (d,  $J = 8.0$  Hz, 2H), 5.40 (s, 2H), 3.01 (s, 3H);  **$^{13}C$  NMR** (100 MHz,  $CDCl_3$ )  $\delta$  154.43, 149.78, 149.18, 139.30, 136.47, 130.67, 129.19, 128.37, 128.10, 127.88, 127.45, 126.14, 124.26, 123.22, 118.33, 116.35, 112.12, 38.72; **HRMS** (ESI) calcd for  $C_{22}H_{19}N_3$   $[M+H]^+$ : 326.1652, found 326.1646.

## 4. X-Ray ellipsoid plots of products



Bond precision: C-C = 0.0032 Å                      Wavelength=0.71073

Cell:                      a=8.4918 (5)                      b=10.0409 (5)                      c=16.7446 (7)  
                                 alpha=90                      beta=100.191 (5)                      gamma=90

Temperature:              296 K

	Calculated	Reported
Volume	1405.21 (13)	1405.22 (12)
Space group	P 21/n	P 1 21/n 1
Hall group	: -P 2yn	-P 2yn
Moiety formula	C17 H13 N3	C17 H13 N3
Sum formula	C17 H13 N3	C17 H13 N3
Mr	259.30	259.30
Dx, g cm <sup>-3</sup>	1.226	1.226
Z	4	4
Mu (mm <sup>-1</sup> )	0.075	0.075
F000	544.0	544.0
F000'	544.18	
h, k, lmax	10, 12, 20	10, 12, 20
Nref	2778	2772
Tmin, Tmax	0.987, 0.991	0.767, 1.000
Tmin'	0.987	

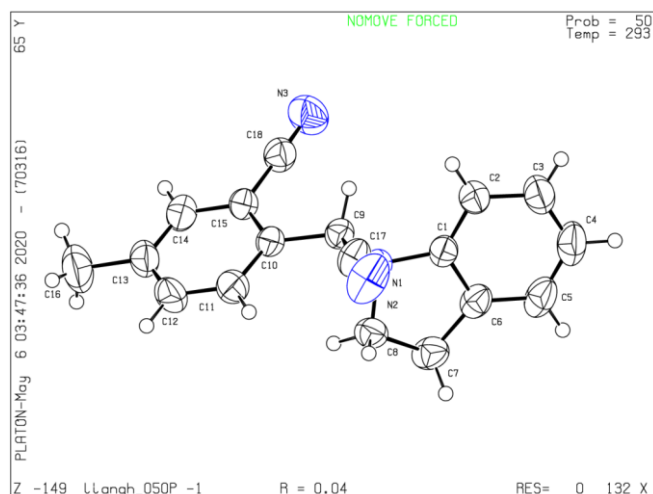
Correction method= # Reported T Limits: Tmin=0.767 Tmax=1.000  
AbsCorr = MULTI-SCAN

Data completeness= 0.998                      Theta(max)= 26.020

R(reflections)= 0.0543 ( 1855)                      wR2(reflections)= 0.1426 ( 2772)

S = 1.085                      Npar= 181

**Figure S1.** The single crystal analysis for 3a (CCDC number: 1876354)



Bond precision: C-C = 0.0020 Å      Wavelength=1.54184

Cell:            a=8.0685(11)      b=8.5074(8)      c=10.8878(13)  
                   alpha=93.111(9)      beta=96.047(10)      gamma=91.869(9)

Temperature: 293 K

	Calculated	Reported
Volume	741.55(15)	741.55(15)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C18 H15 N3	C18 H15 N3
Sum formula	C18 H15 N3	C18 H15 N3
Mr	273.33	273.33
Dx, g cm <sup>-3</sup>	1.224	1.224
Z	2	2
Mu (mm <sup>-1</sup> )	0.579	0.579
F000	288.0	288.0
F000'	288.78	
h, k, lmax	9, 10, 12	9, 10, 12
Nref	2616	2598
Tmin, Tmax	0.926, 0.960	0.541, 1.000
Tmin'	0.922	

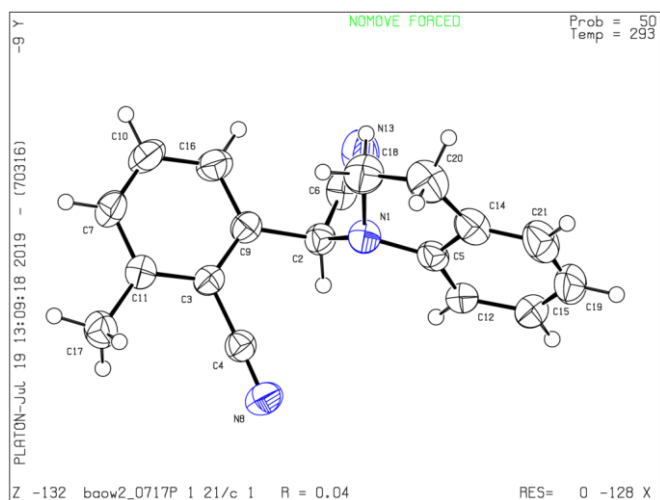
Correction method= # Reported T Limits: Tmin=0.541 Tmax=1.000  
 AbsCorr = MULTI-SCAN

Data completeness= 0.993      Theta(max)= 66.583

R(reflections)= 0.0410( 2232)      wR2(reflections)= 0.1220( 2598)

S = 1.064      Npar= 192

**Figure S2.** The single crystal analysis for 3x' (CCDC number: 2002471)



Bond precision: C-C = 0.0020 Å                      Wavelength=1.54184

Cell:                      a=8.2710(2)                      b=9.9844(2)                      c=18.3806(4)  
    alpha=90                      beta=102.740(2)                      gamma=90

Temperature:                      293 K

	Calculated	Reported
Volume	1480.52(6)	1480.52(6)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C18 H15 N3	C18 H15 N3
Sum formula	C18 H15 N3	C18 H15 N3
Mr	273.33	273.33
Dx, g cm <sup>-3</sup>	1.226	1.226
Z	4	4
Mu (mm <sup>-1</sup> )	0.580	0.580
F000	576.0	576.0
F000'	577.55	
h, k, lmax	9, 11, 21	9, 11, 21
Nref	2609	2566
Tmin, Tmax	0.901, 0.933	0.249, 1.000
Tmin'	0.896	

Correction method= # Reported T Limits: Tmin=0.249 Tmax=1.000  
 AbsCorr = MULTI-SCAN

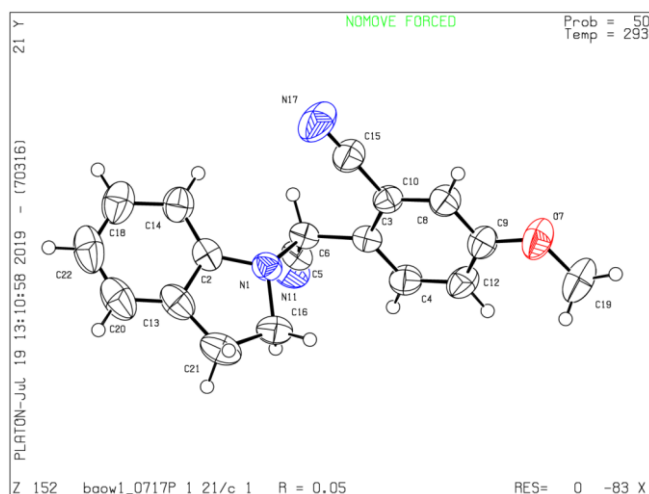
Data completeness= 0.984                      Theta(max)= 66.587

R(reflections)= 0.0433( 2341)                      wR2(reflections)= 0.1215( 2566)

S = 1.059                      Npar= 191

**Figure S3.** The single crystal analysis for 3y' (CCDC number: 1941766)





Bond precision:	C-C = 0.0025 Å	Wavelength=1.54184	
Cell:	a=9.2780 (4)	b=23.2807 (7)	c=7.4089 (3)
	alpha=90	beta=102.520 (4)	gamma=90
Temperature:	293 K		
	Calculated	Reported	
Volume	1562.26 (11)	1562.25 (10)	
Space group	P 21/c	P 1 21/c 1	
Hall group	-P 2ybc	-P 2ybc	
Moiety formula	C18 H15 N3 O	C18 H15 N3 O	
Sum formula	C18 H15 N3 O	C18 H15 N3 O	
Mr	289.33	289.33	
Dx, g cm <sup>-3</sup>	1.230	1.230	
Z	4	4	
Mu (mm <sup>-1</sup> )	0.628	0.628	
F000	608.0	608.0	
F000'	609.75		
h, k, lmax	11, 27, 8	11, 27, 8	
Nref	2764	2690	
Tmin, Tmax	0.900, 0.927	0.595, 1.000	
Tmin'	0.893		
Correction method=	# Reported T Limits: Tmin=0.595 Tmax=1.000		
AbsCorr =	MULTI-SCAN		
Data completeness=	0.973	Theta(max)= 66.592	
R(reflections)=	0.0454 ( 2277)	wR2(reflections)= 0.1337 ( 2690)	
S =	1.049	Npar= 200	

**Figure S4.** The single crystal analysis for 3z' (CCDC number: 1941767)

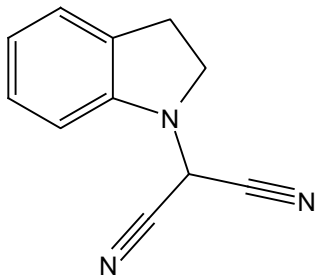
## 5. References

- (1) X.-Q. Mou, L. Xu, S.-H. Wang and C. Yang, *Tetrahedron Lett.*, 2015, 56, 2820-2822.
- (2) H. Jiang, Y. Zhang, W. Xiong, J. Cen, L. Wang, R. Cheng, C. Qi and W. Wu, *Org. Lett.*, 2019, 21, 345-349.
- (3) X. Yang, H. Yu, Y. Xu and L. Shao, *J. Org. Chem.*, 2018, 83, 9682-9695.

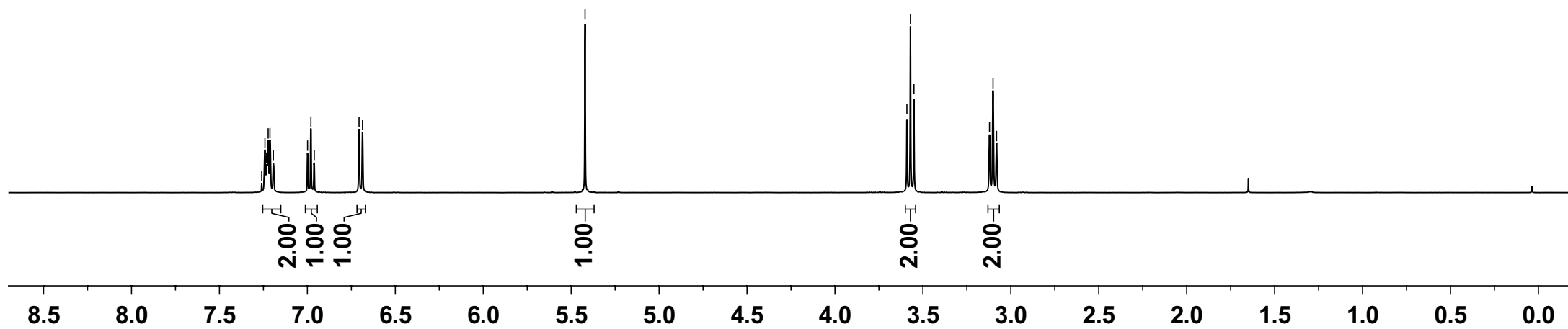
7.260  
7.241  
7.232  
7.230  
7.223  
7.213  
7.194  
6.999  
6.980  
6.961  
6.706  
6.686

— 5.421

3.591  
3.571  
3.551  
3.121  
3.101  
3.081



**1a**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



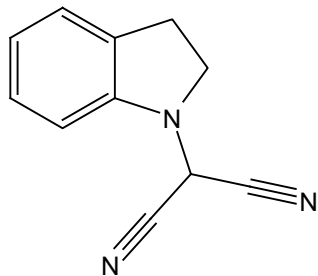
—145.913  
~130.695  
~127.640  
~125.449  
~122.297  
{109.862  
{108.883

{77.320  
{77.000  
{76.683

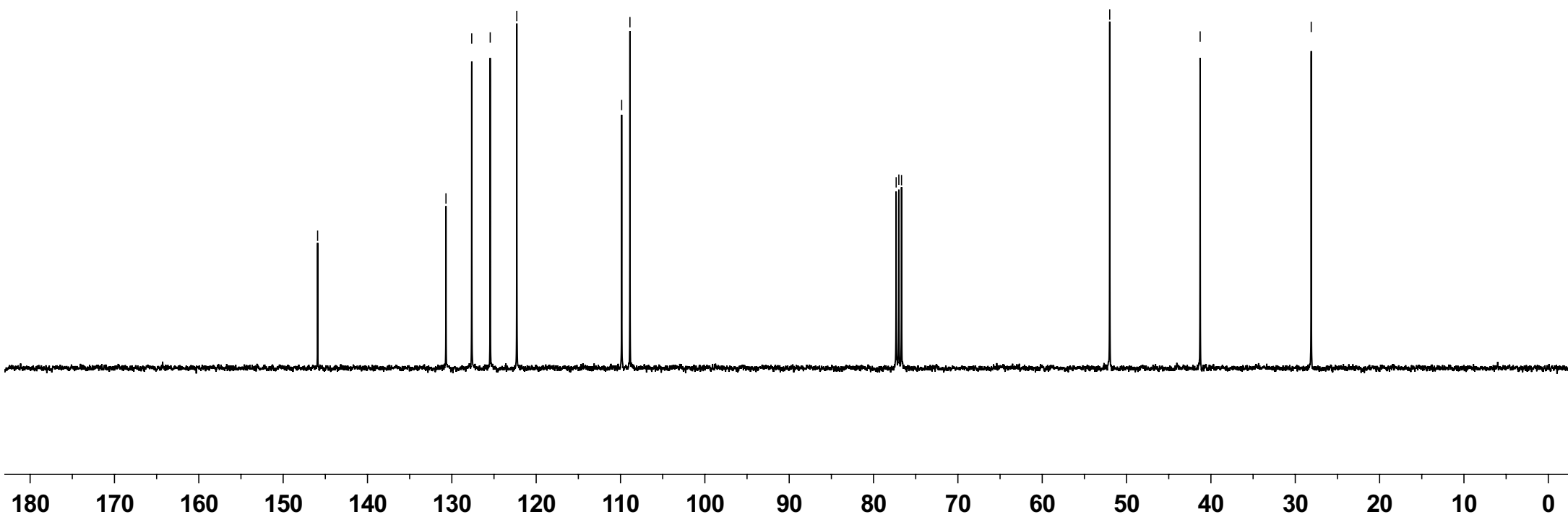
—51.998

—41.277

—28.109



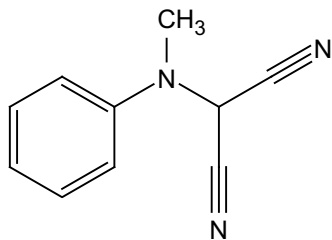
**1a**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )



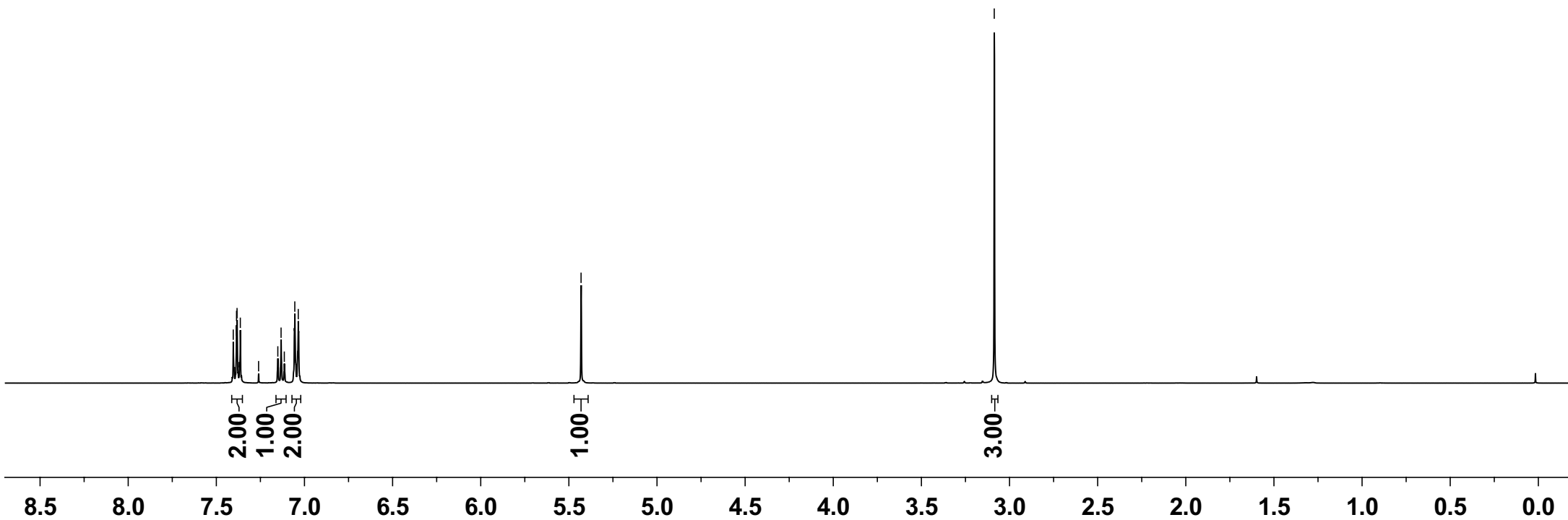
7.404  
7.385  
7.382  
7.364  
7.260  
7.151  
7.133  
7.114  
7.055  
7.035

5.431

3.087



**1b**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



—146.285

—129.781

—123.980

—118.585

—110.267

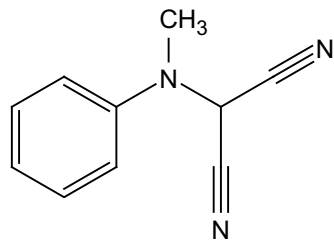
—77.317

—77.000

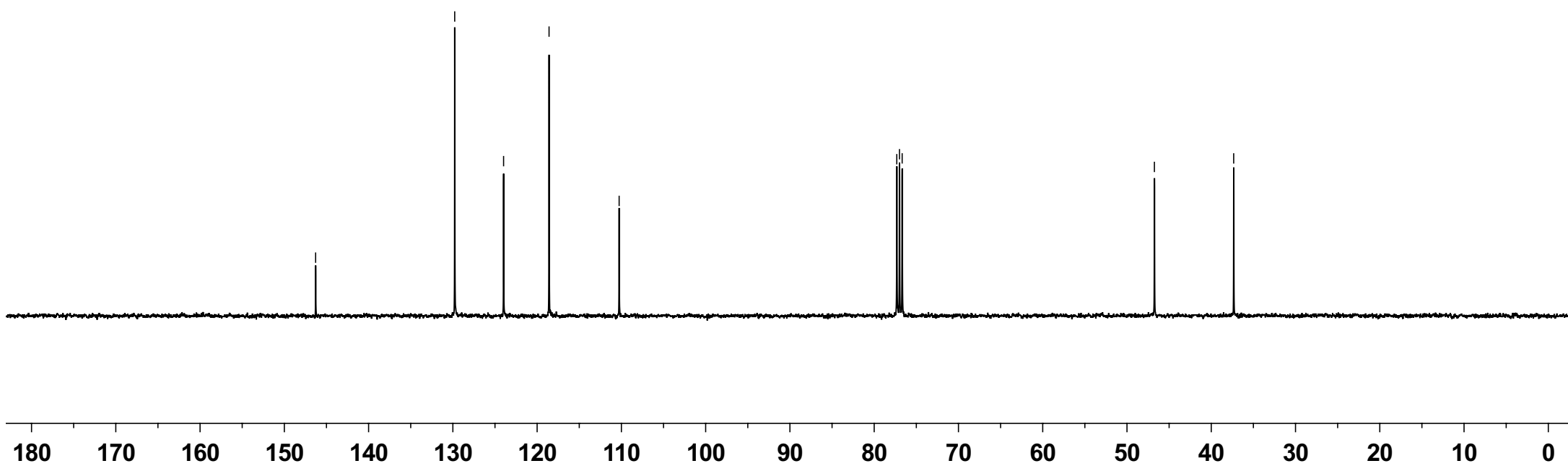
—76.681

—46.746

—37.337



**1b**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

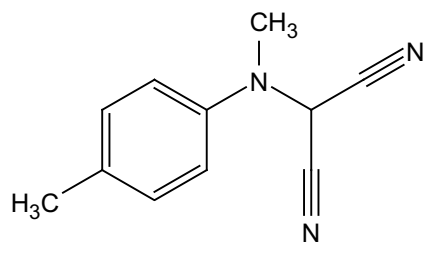


7.260  
7.195  
7.174  
6.984  
6.963

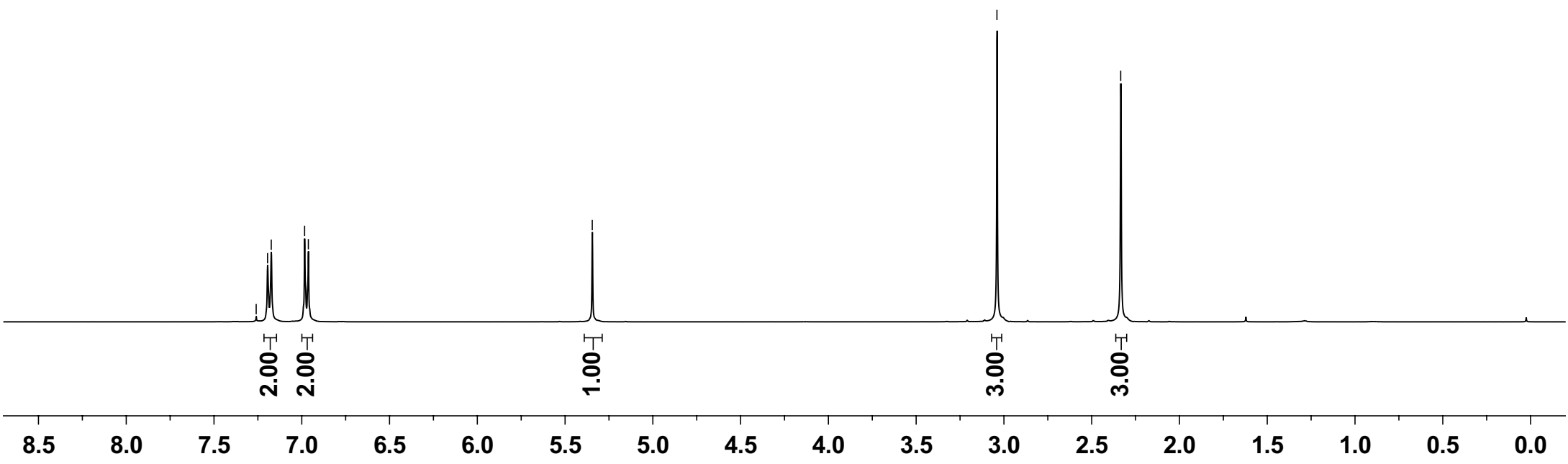
5.345

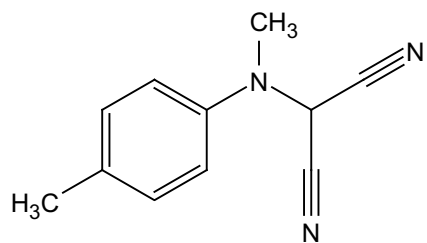
3.040

2.335

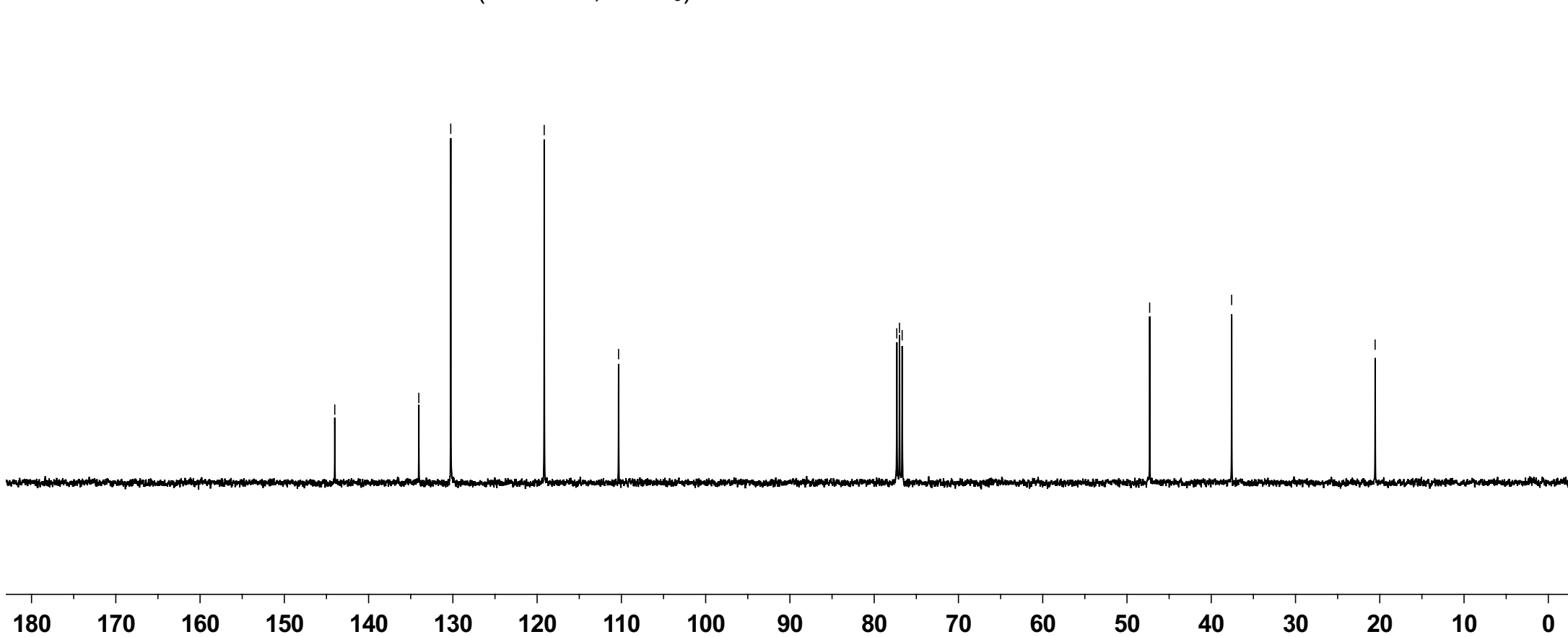


**1c** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)





**1c** <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)



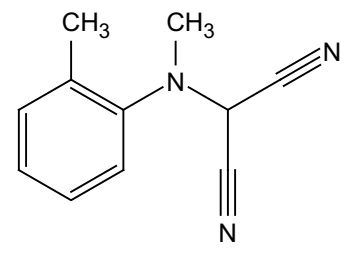
7.237  
7.234  
7.217  
7.214  
7.207  
7.187  
7.172  
7.168  
7.153  
7.149  
7.128  
7.125  
7.110  
7.107  
7.092  
7.088

—4.821

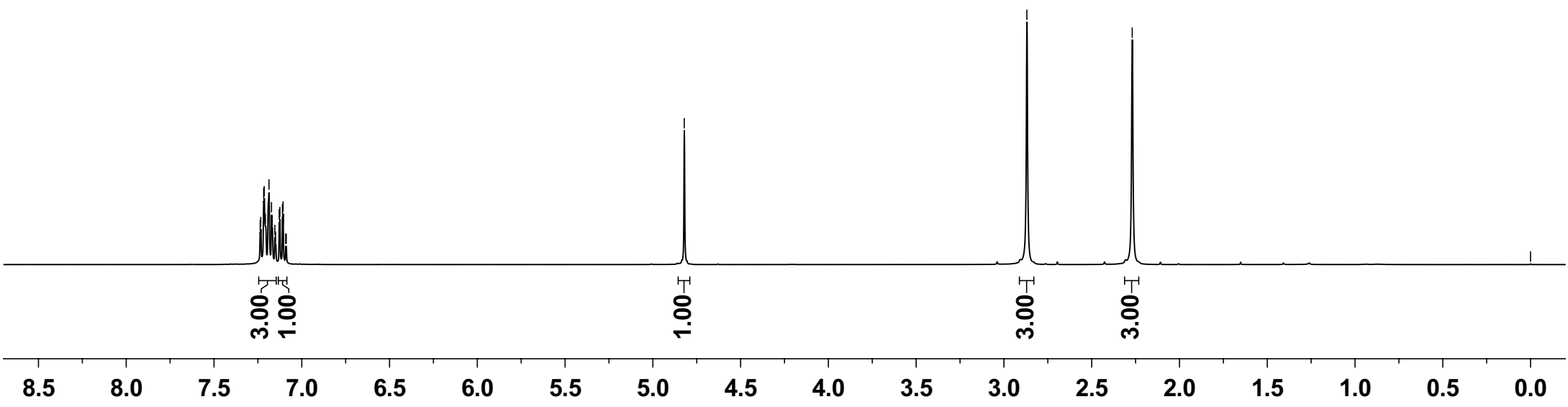
—2.869

—2.269

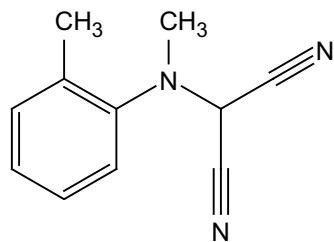
—0.000



**1d** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

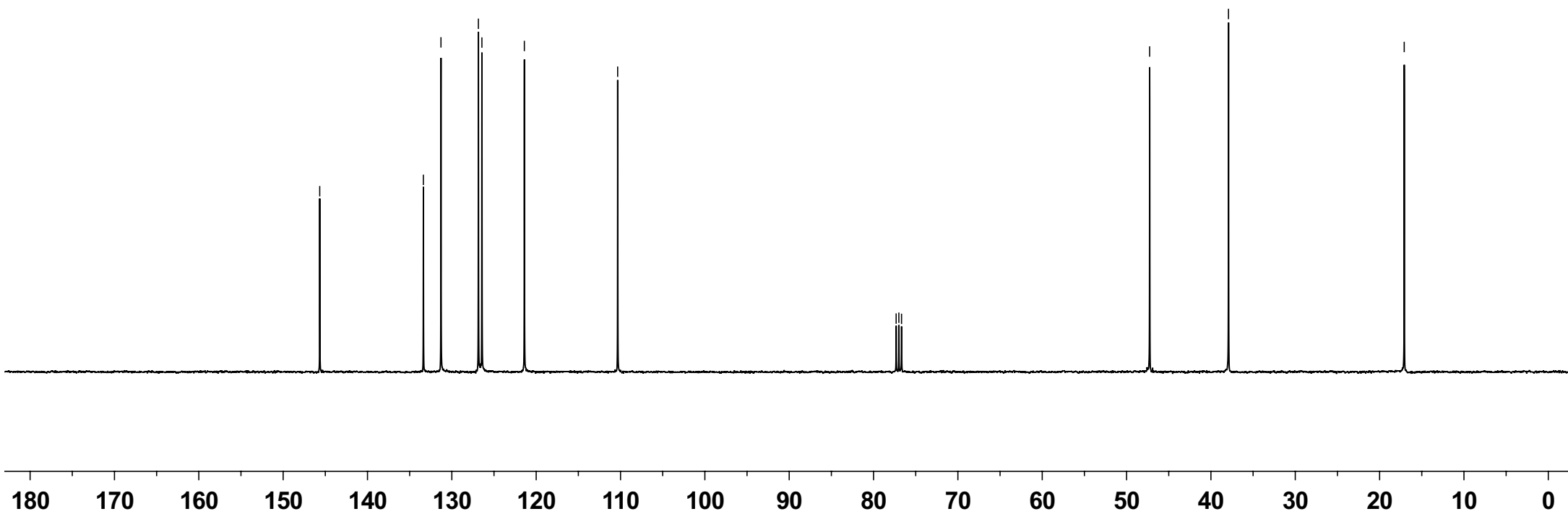






**1d**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

—145.663  
~133.374  
~131.289  
~126.852  
~126.435  
~121.401  
—110.338  
  
77.321  
77.000  
76.681  
  
—47.268  
—37.918  
  
—17.082



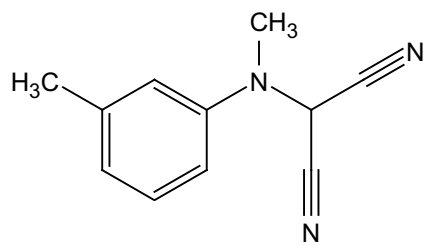
7.233  
7.214  
7.194  
6.905  
6.887  
6.799  
6.779  
6.774

5.392

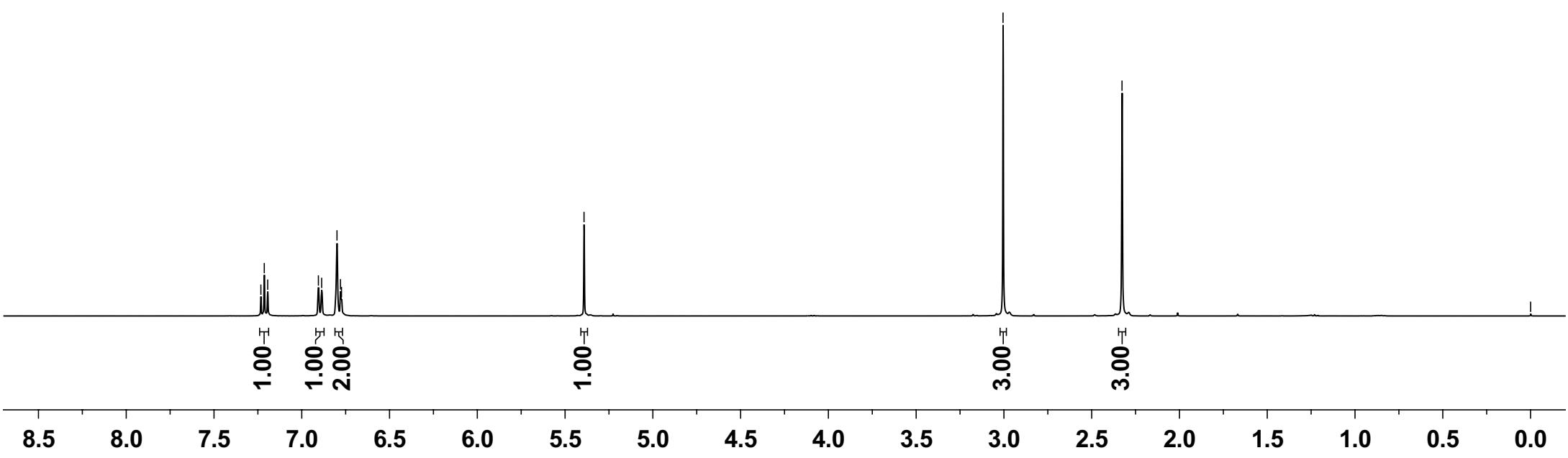
3.005

2.327

0.000



1e <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



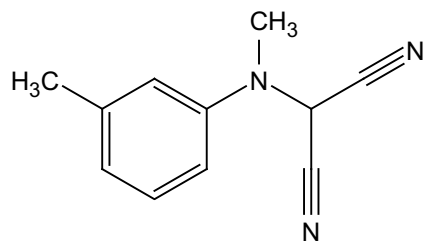
—146.123  
—139.611  
129.380  
124.475  
118.979  
115.258  
110.354

77.319  
77.000  
76.682

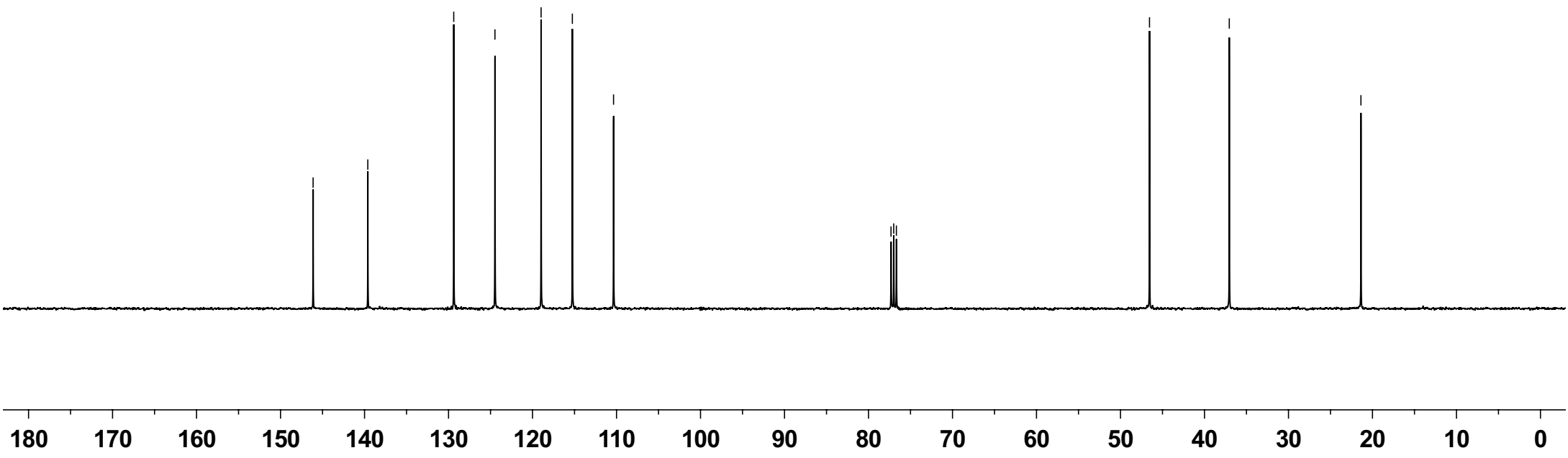
—46.546

—37.048

—21.374



**1e** <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

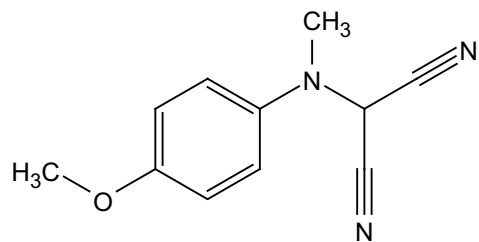


7.260  
7.091  
7.069  
6.908  
6.885

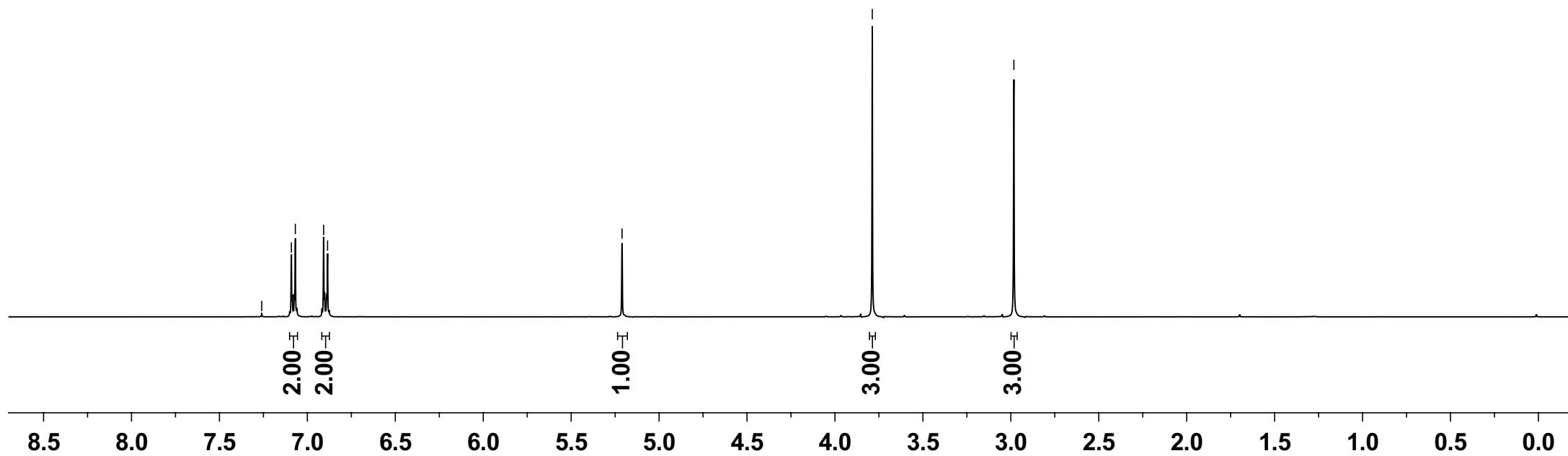
5.211

3.788

2.983



**1f** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



—156.937

—139.849

—122.068

—114.783

—110.383

77.319

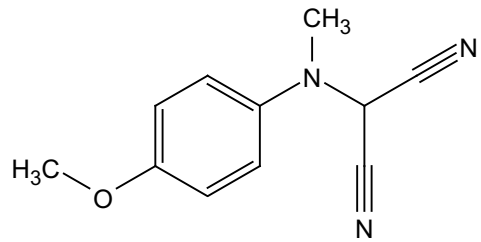
77.000

76.682

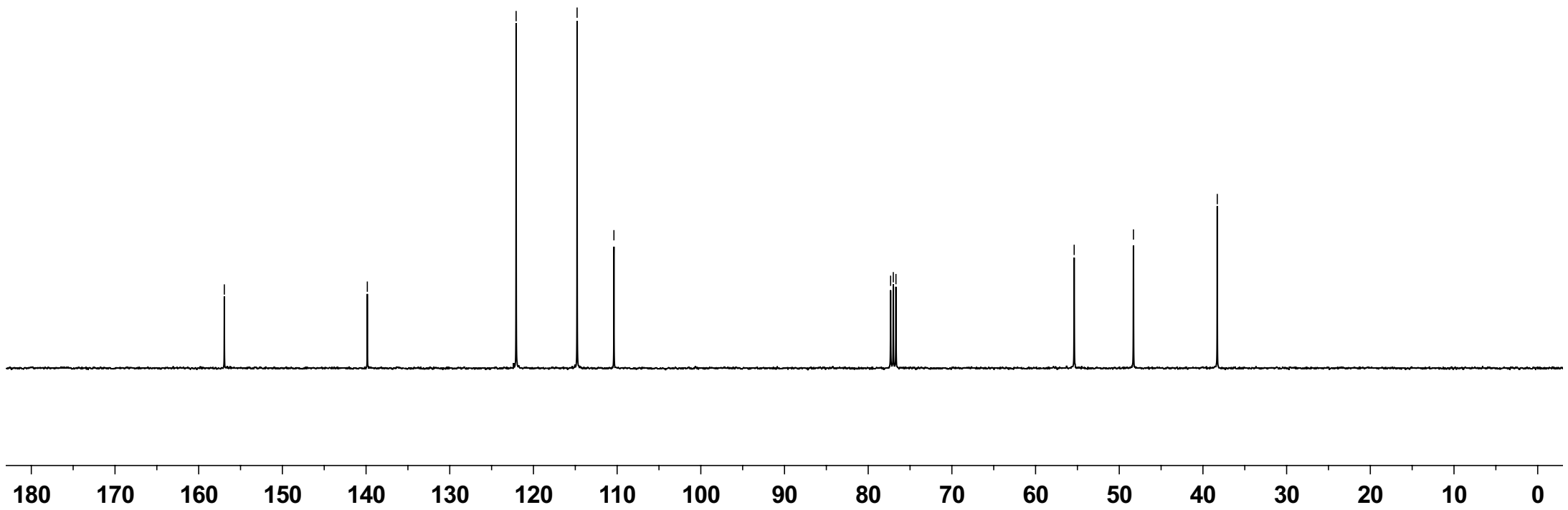
—55.386

—48.304

—38.289



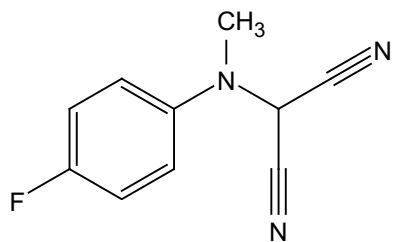
**1f** <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)



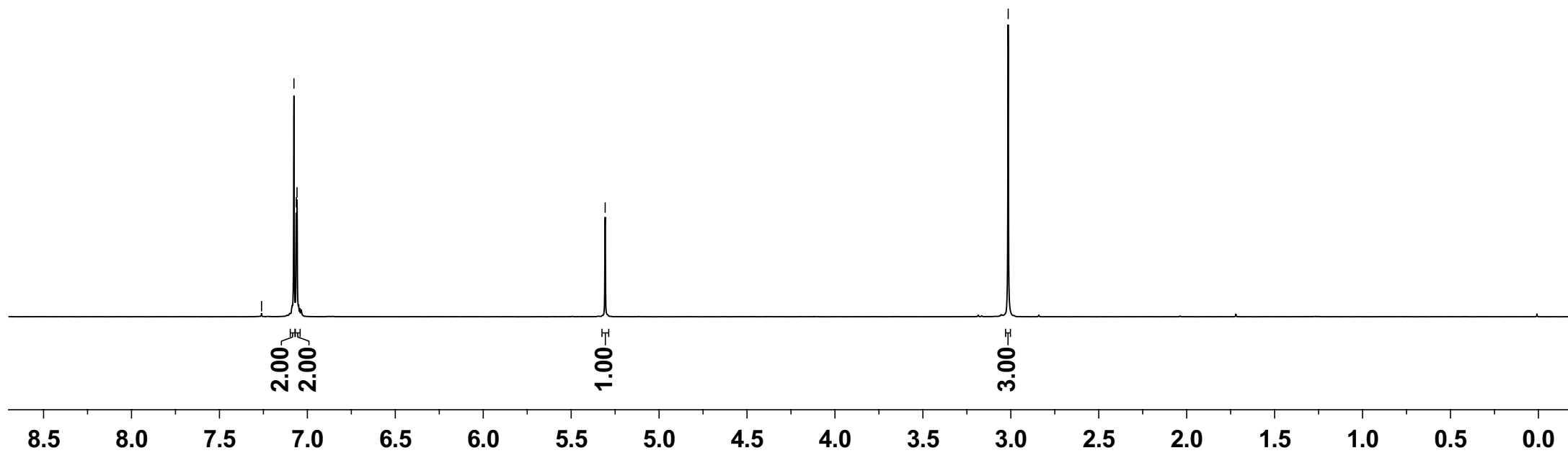
7.260  
7.076  
7.063  
7.059

5.307

3.015



**1g**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



160.705  
158.272

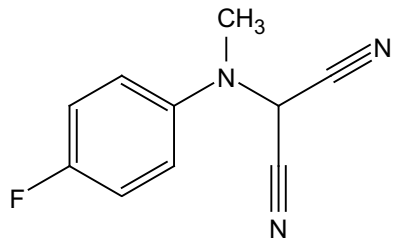
142.549  
142.527

121.622  
121.541  
116.479  
116.252  
110.187

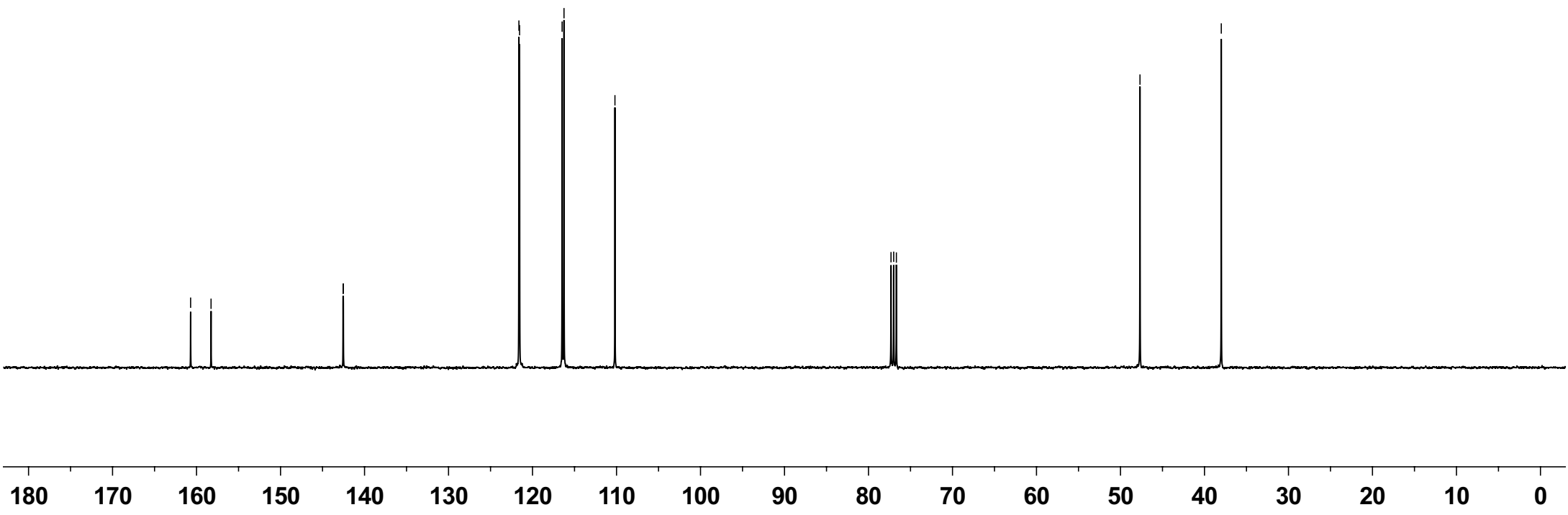
77.320  
77.000  
76.682

47.679

38.000



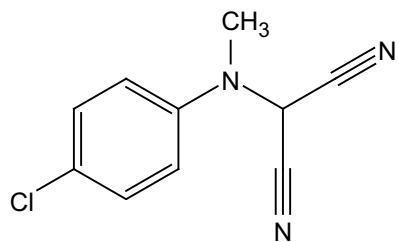
**1g**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )



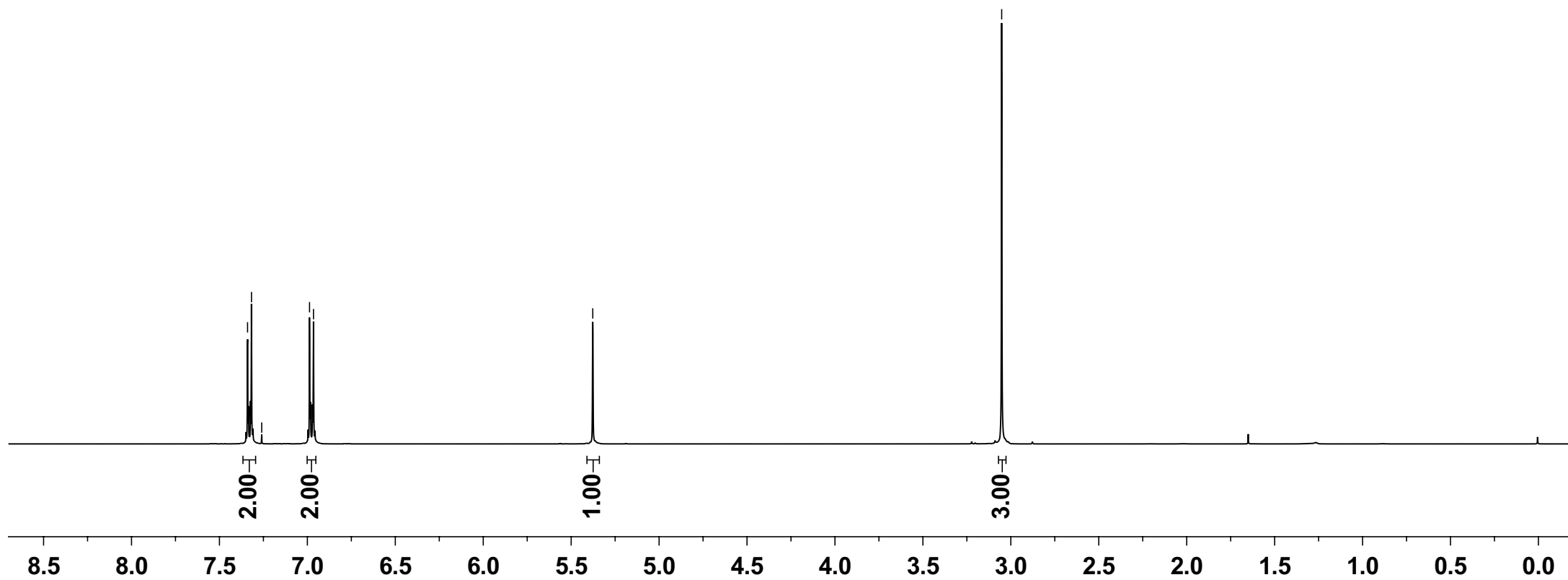
7.340  
7.318  
7.260  
6.988  
6.965

5.377

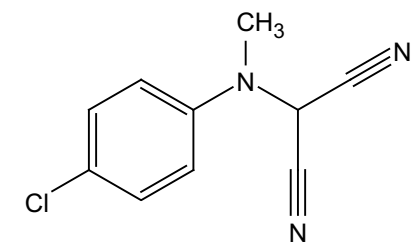
3.052



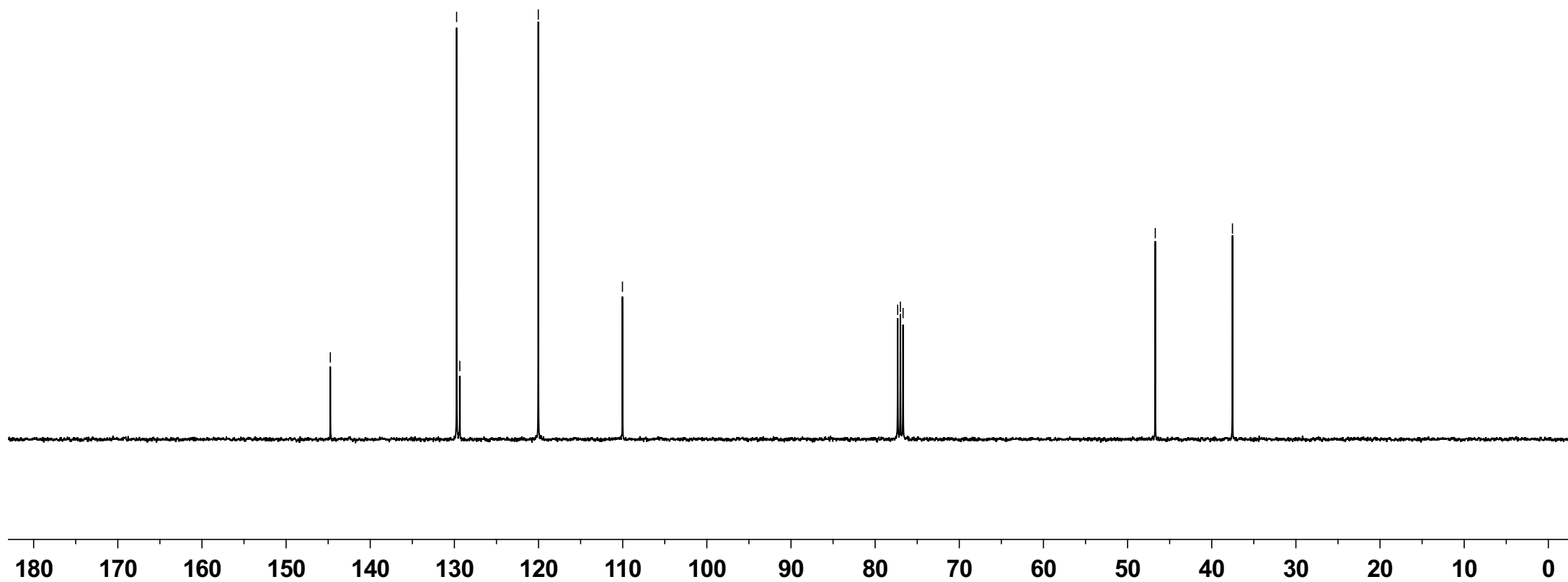
**1h**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



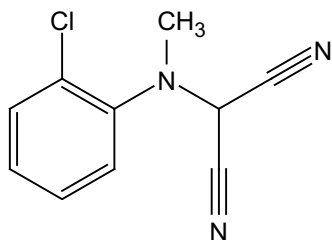




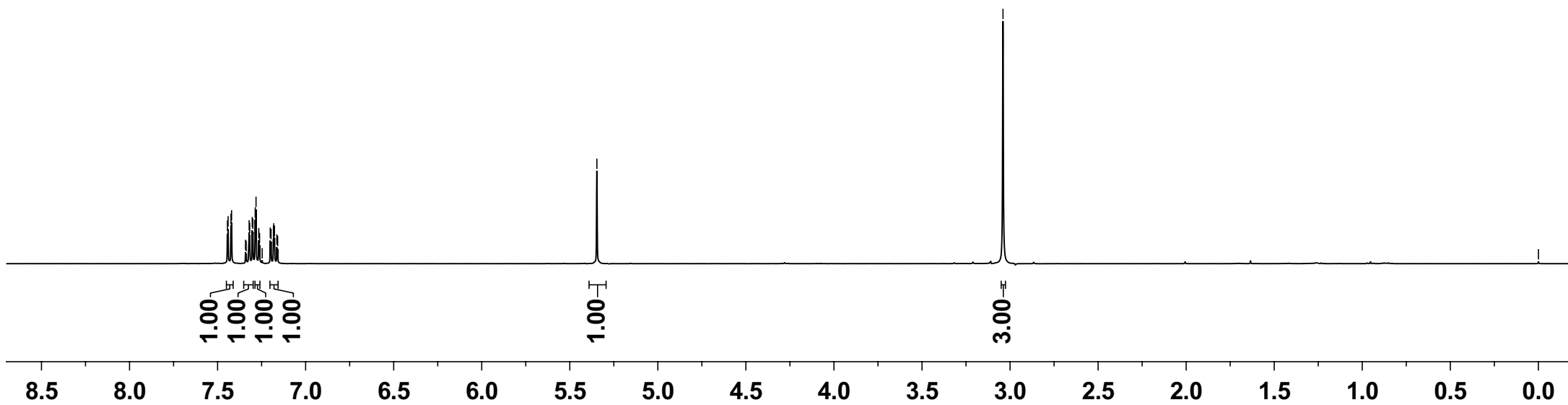
**1h** <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)



7.444  
7.440  
7.424  
7.421  
7.321  
7.318  
7.303  
7.300  
7.286  
7.282  
7.266  
7.262  
7.201  
7.196  
7.183  
7.181  
7.179  
7.177  
7.164  
7.159  
7.146  
3.040  
-0.000



1i <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

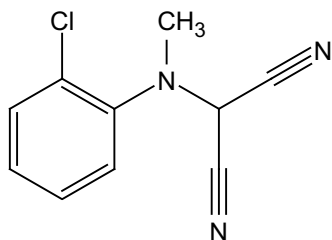


—143.241  
130.817  
128.997  
128.098  
127.181  
122.854  
—109.991

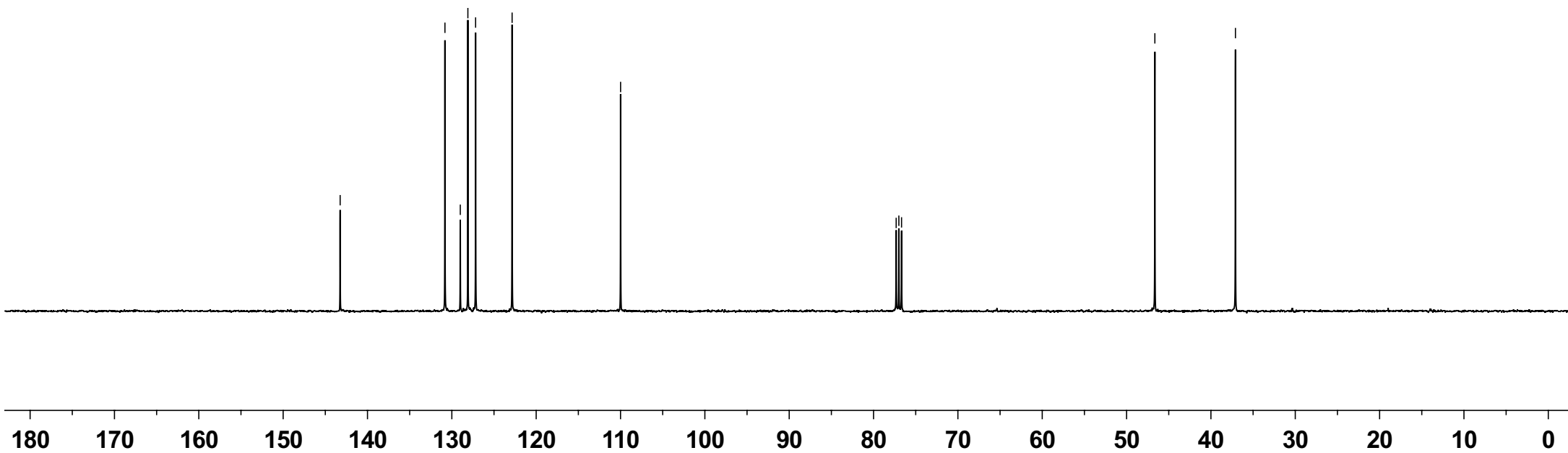
77.318  
77.000  
76.680

—46.646

—37.093



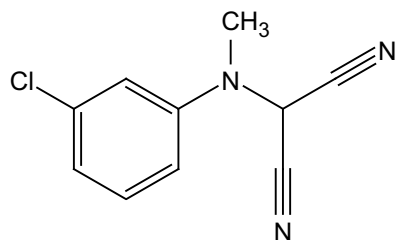
**1i**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )



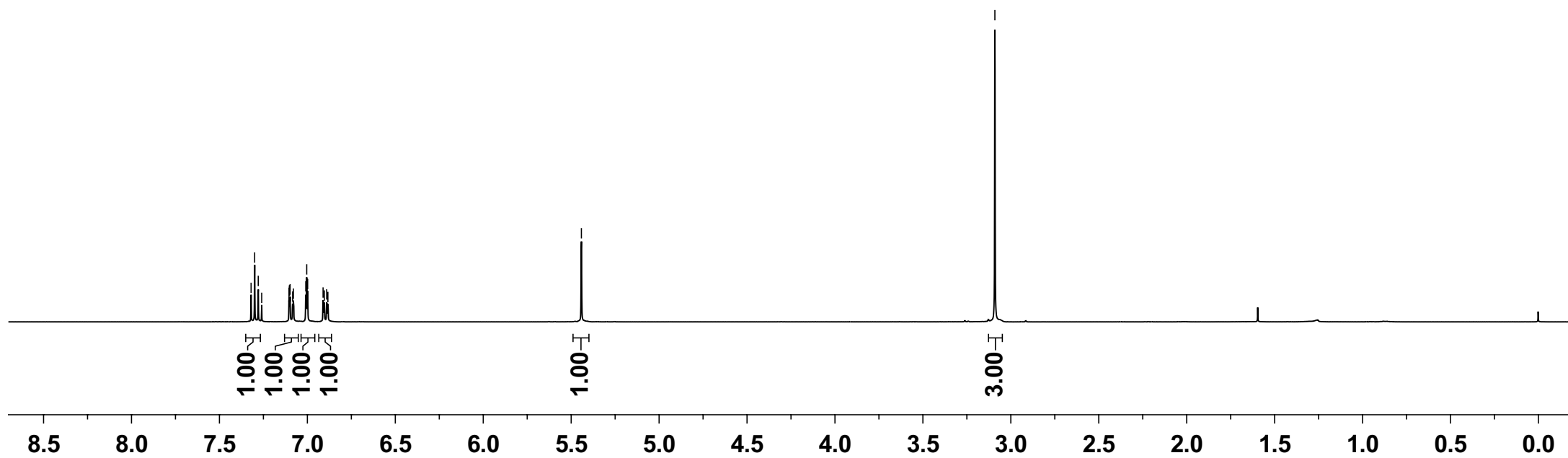
7.320  
7.300  
7.279  
7.260  
7.104  
7.103  
7.100  
7.098  
7.084  
7.079  
7.009  
7.004  
6.998  
6.911  
6.904  
6.890  
6.883

5.442

3.091



**1j**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

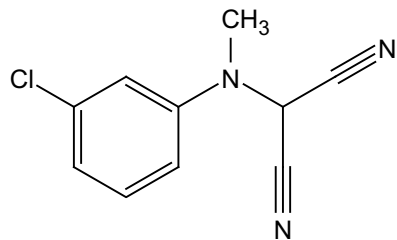


—147.273  
—135.592  
—130.794  
—123.849  
—118.531  
—116.097  
—109.936

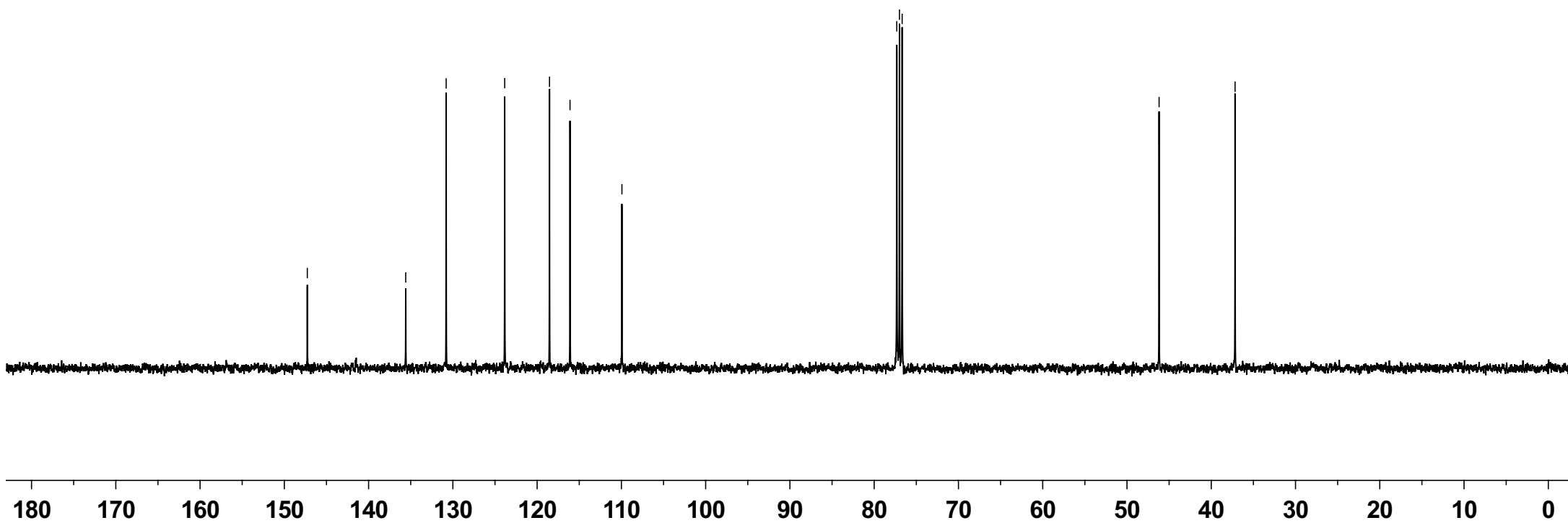
{77.318  
{77.000  
{76.682

—46.191

—37.173



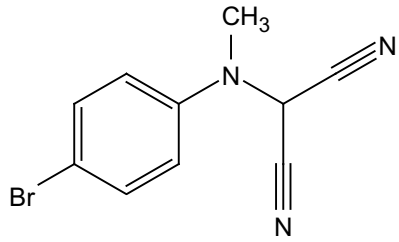
**1j**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )



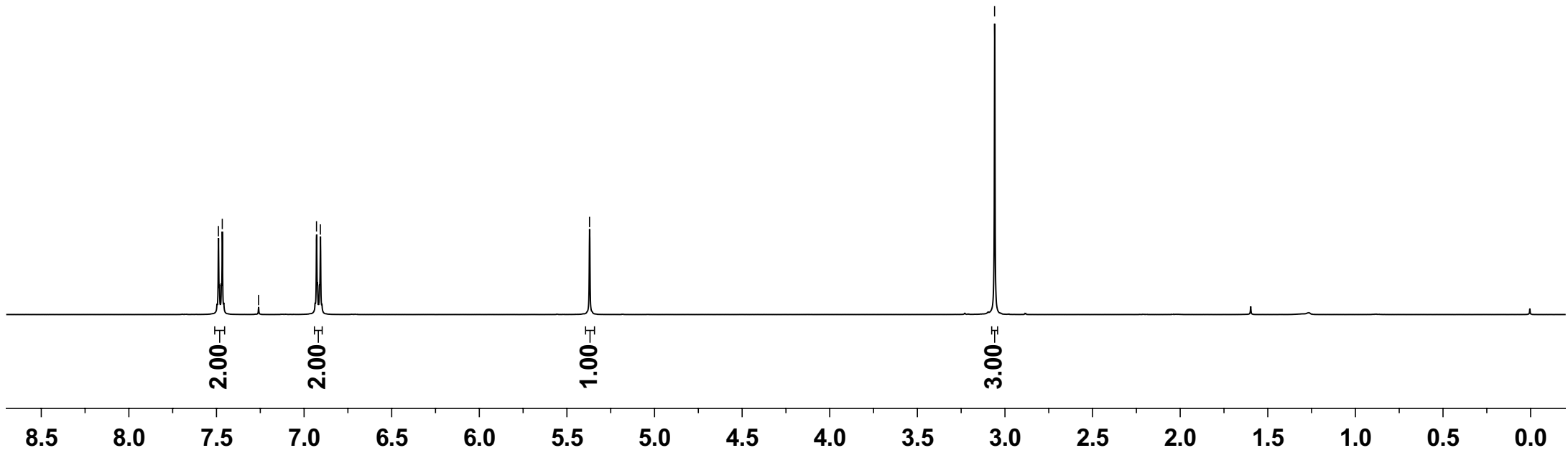
7.489  
7.467  
7.260  
6.929  
6.907

5.371

3.059



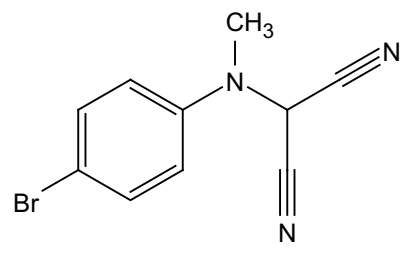
**1k**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



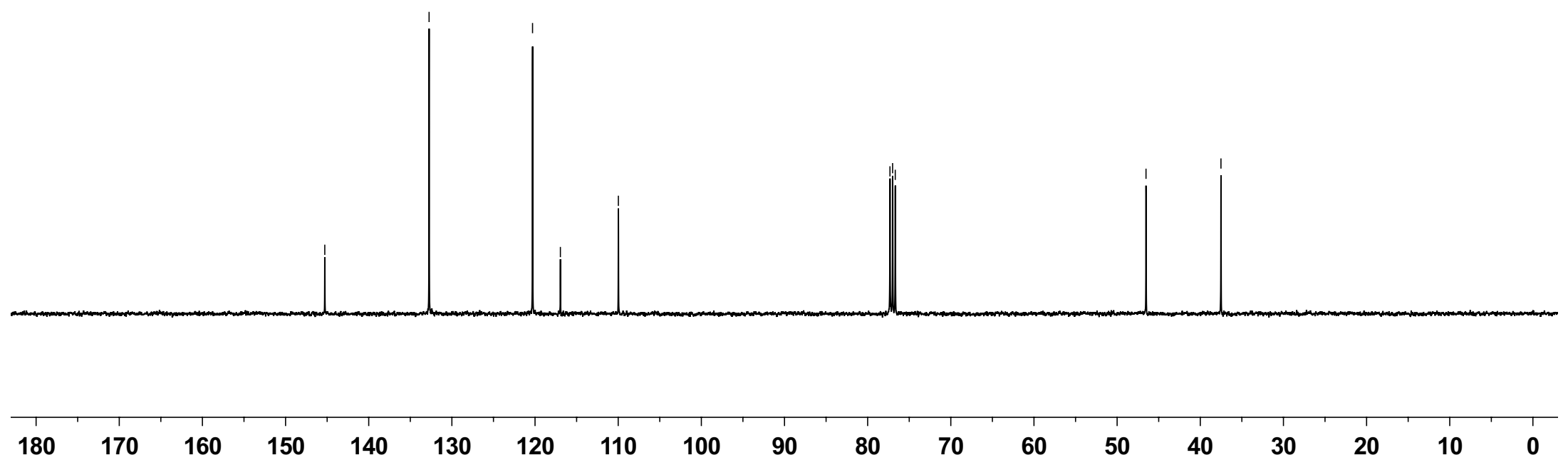
—145.284  
—132.741  
—120.300  
—116.951  
—109.979

77.317  
77.000  
76.681

—46.527  
—37.514

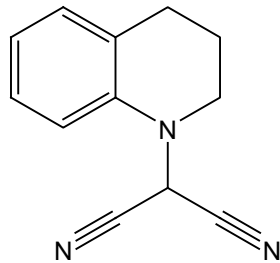


1k <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

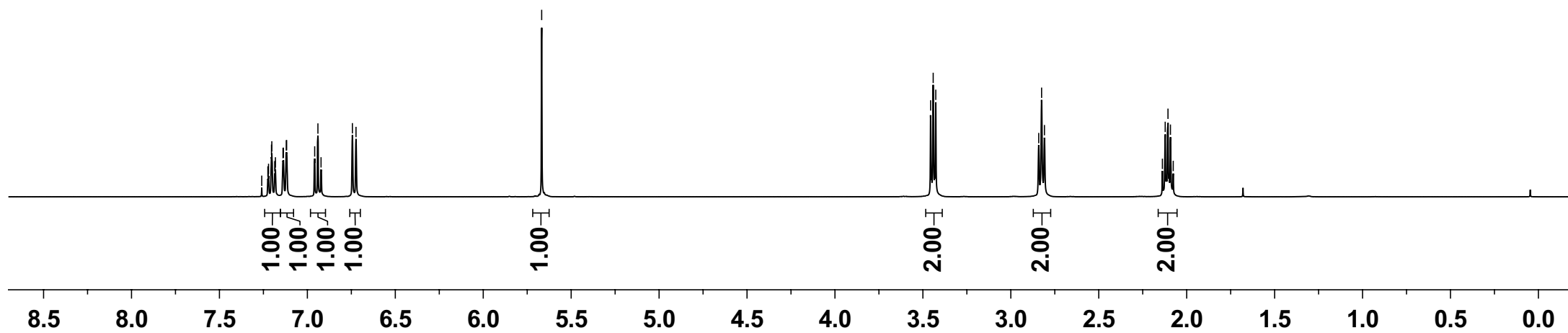


7.260  
7.225  
7.222  
7.221  
7.204  
7.202  
7.186  
7.184  
7.182  
7.139  
7.136  
7.120  
7.118  
6.958  
6.940  
6.922  
6.744  
6.723  
5.668

3.456  
3.441  
3.427  
2.841  
2.825  
2.809  
2.138  
2.122  
2.106  
2.092  
2.076



**11**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



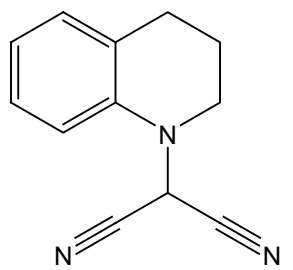


— 140.454  
~ 130.028  
— 127.267  
~ 126.429  
~ 121.268  
~ 112.470  
~ 110.478

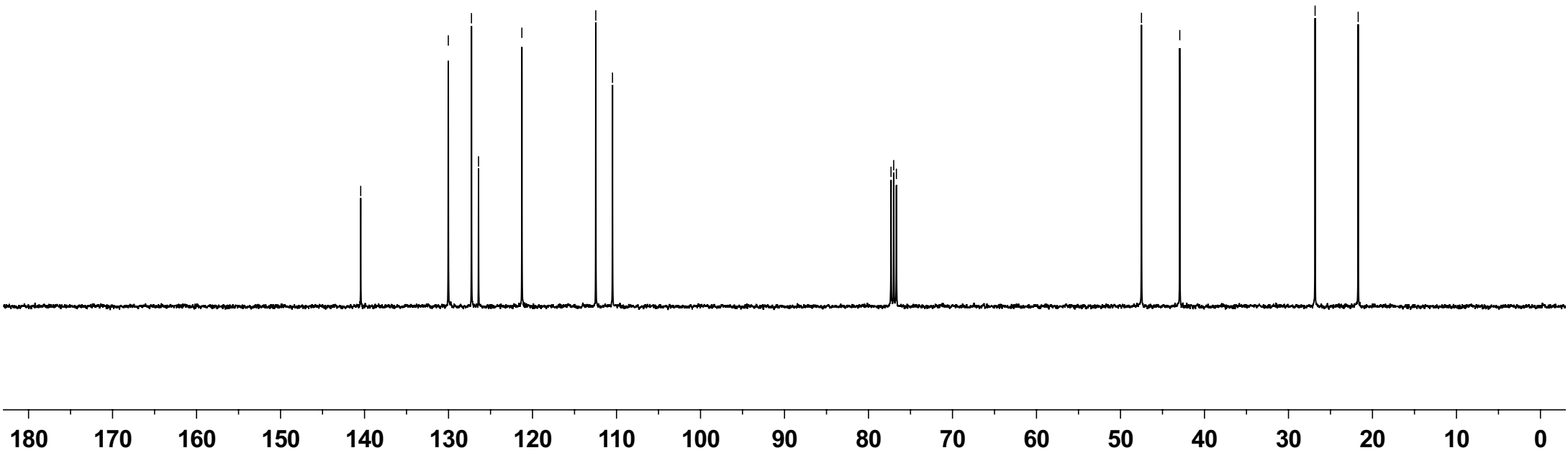
{ 77.318  
{ 77.000  
{ 76.681

— 47.501  
— 42.941

— 26.831  
— 21.700



1I <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

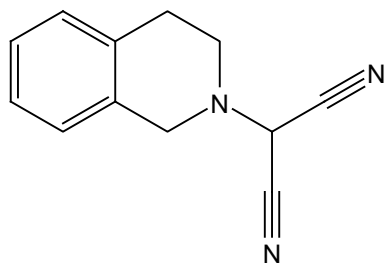


7.260  
7.218  
7.214  
7.205  
7.197  
7.191  
7.178  
7.172  
7.162  
7.155  
7.140  
7.087  
7.072  
7.065

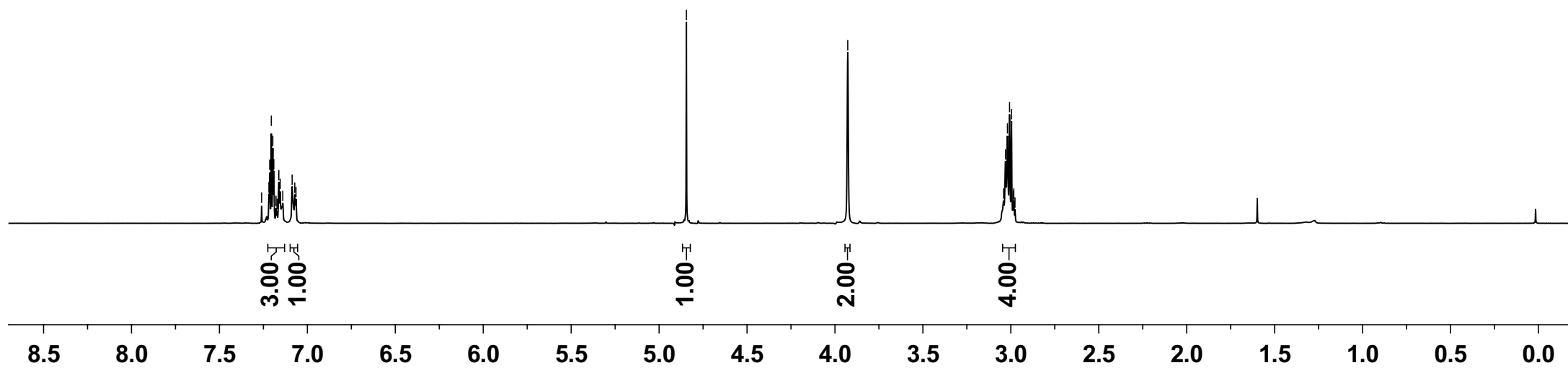
4.845

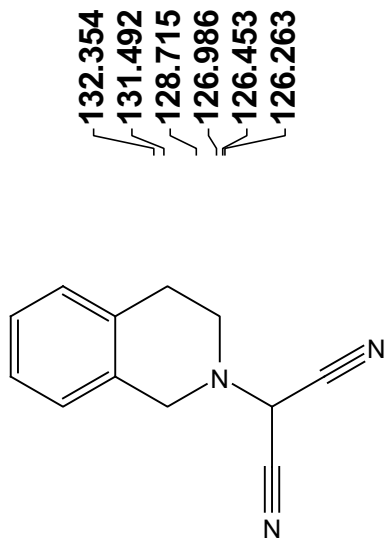
3.927

3.041  
3.030  
3.019  
3.007  
2.996  
2.986  
2.983  
2.976

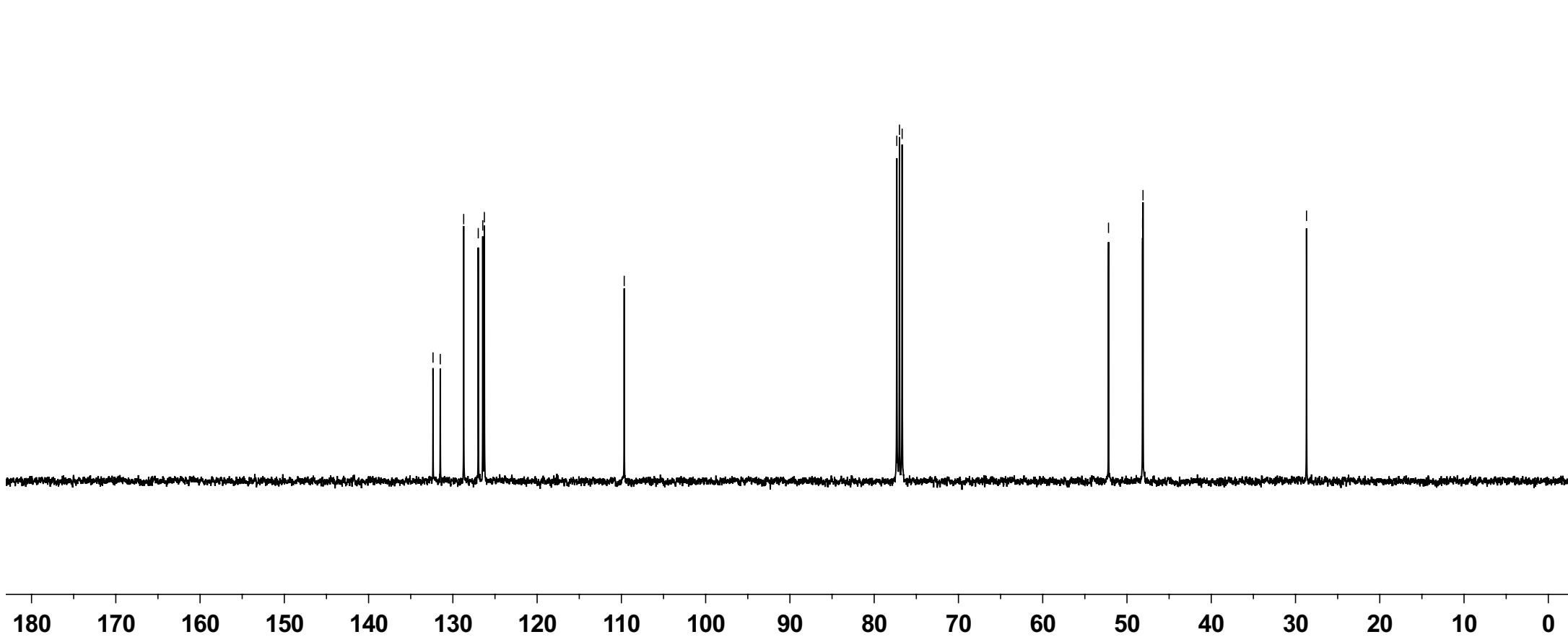


**1m**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )





**1m**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

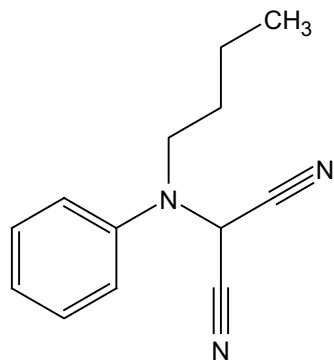


7.420  
7.401  
7.399  
7.380  
7.260  
7.204  
7.186  
7.167  
7.160  
7.157  
7.140  
7.138

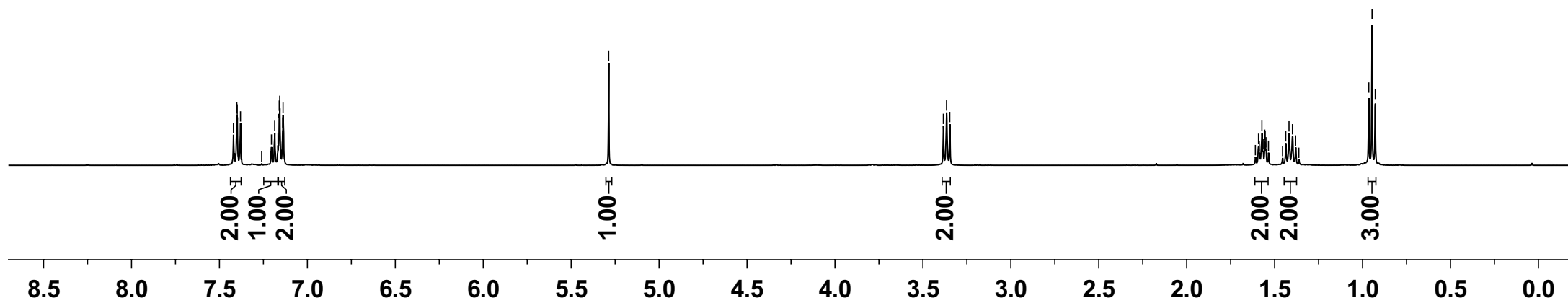
5.287

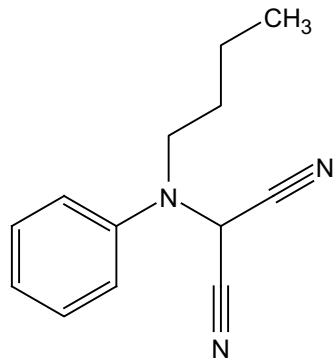
3.384  
3.366  
3.347

1.592  
1.587  
1.572  
1.565  
1.556  
1.554  
1.549  
1.535  
1.437  
1.418  
1.399  
1.381  
0.964  
0.928

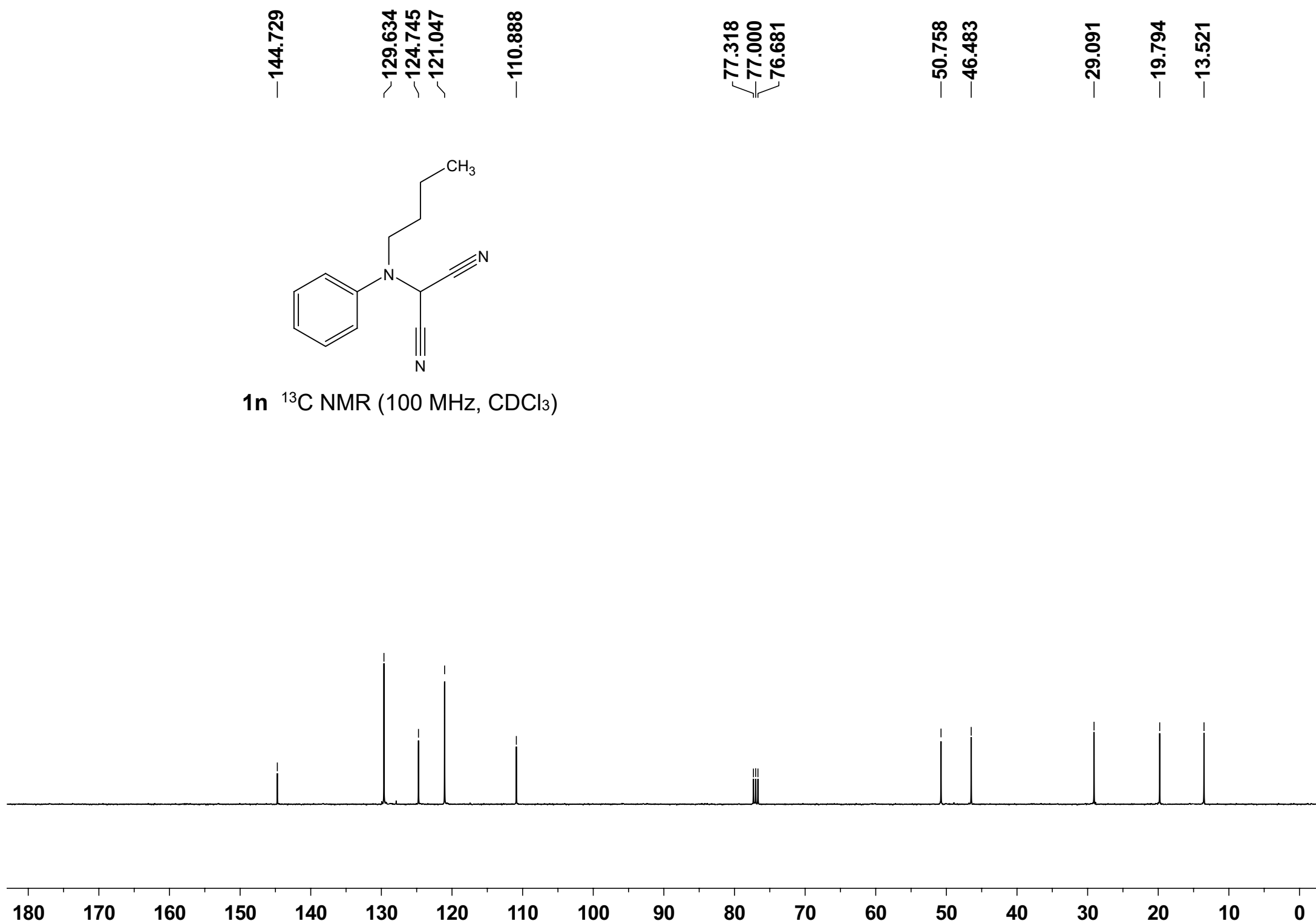


**1n**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )





**1n**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

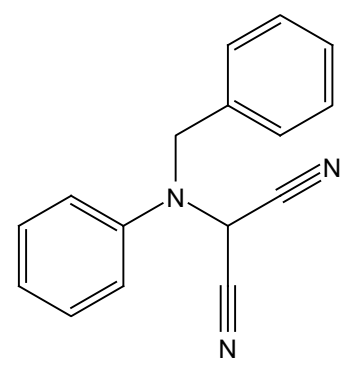


7.367  
7.356  
7.349  
7.345  
7.327  
7.323  
7.315  
7.311  
7.304  
7.301  
7.291  
7.227  
7.224  
7.205  
7.204  
7.169  
7.151  
7.133

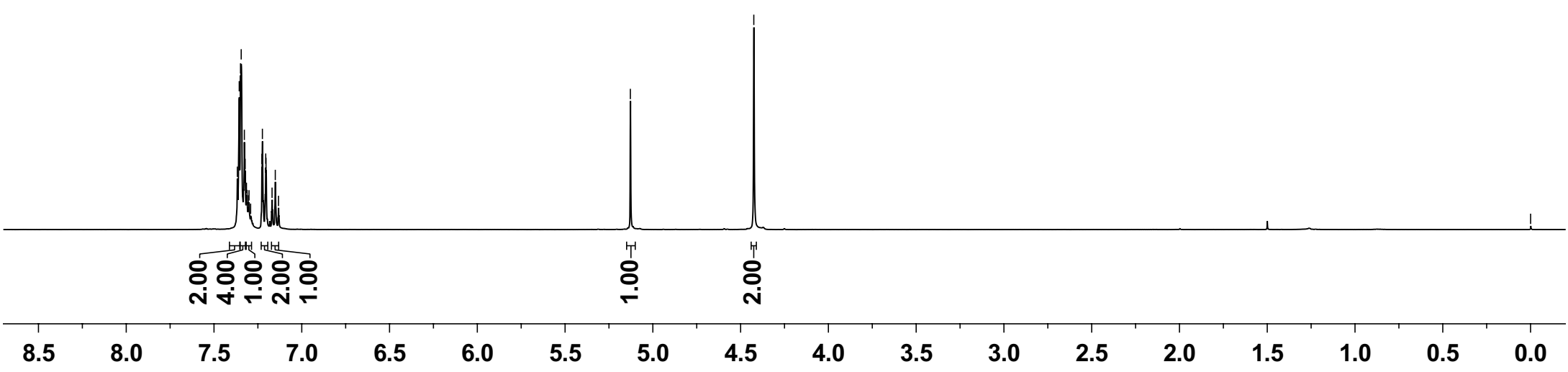
5.128

4.425

0.000



**1o** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

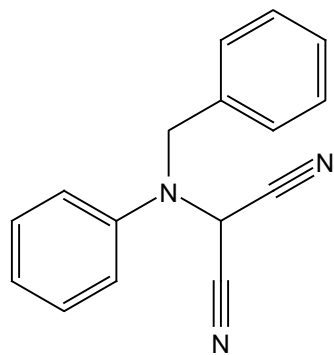


—145.324  
134.983  
129.634  
128.974  
128.471  
128.260  
125.228  
121.385  
—110.546

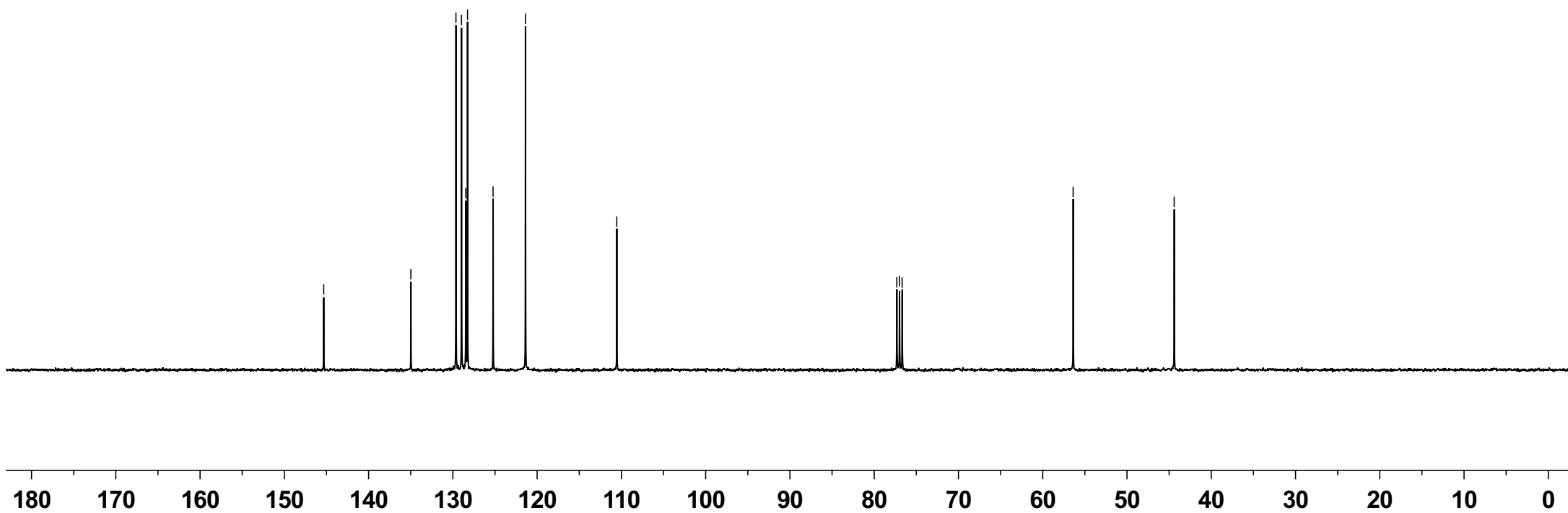
77.318  
77.000  
76.681

—56.391

—44.398



**1o**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

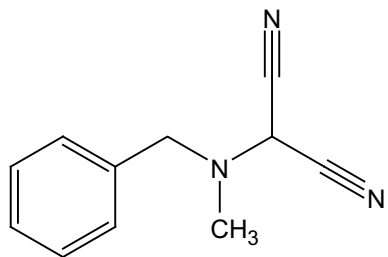


7.433  
7.427  
7.422  
7.411  
7.393  
7.384  
7.373  
7.367  
7.362  
7.353  
7.347  
7.260

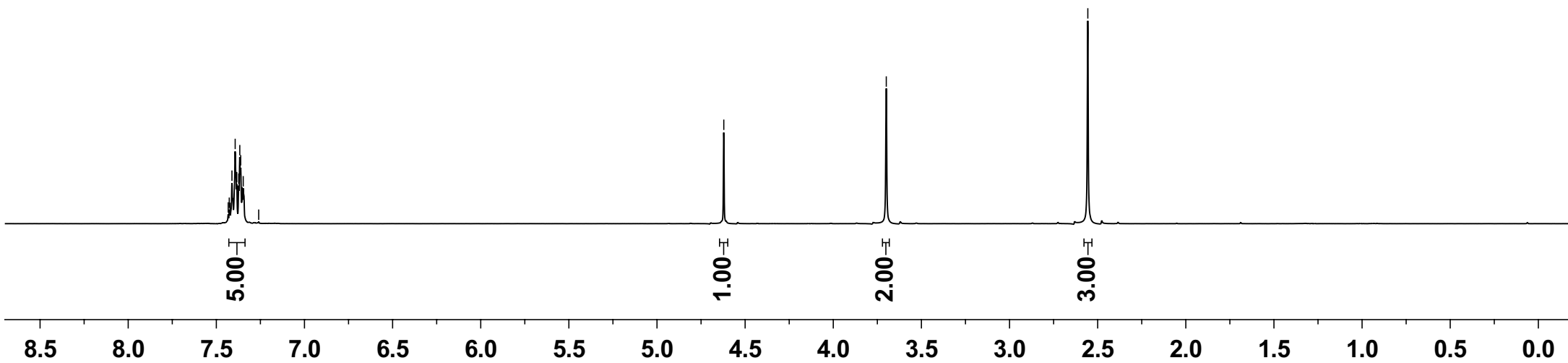
4.621

3.699

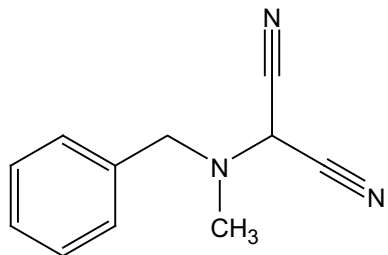
2.556



**1p**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )







**1p** <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

—134.796  
—128.769  
—128.361

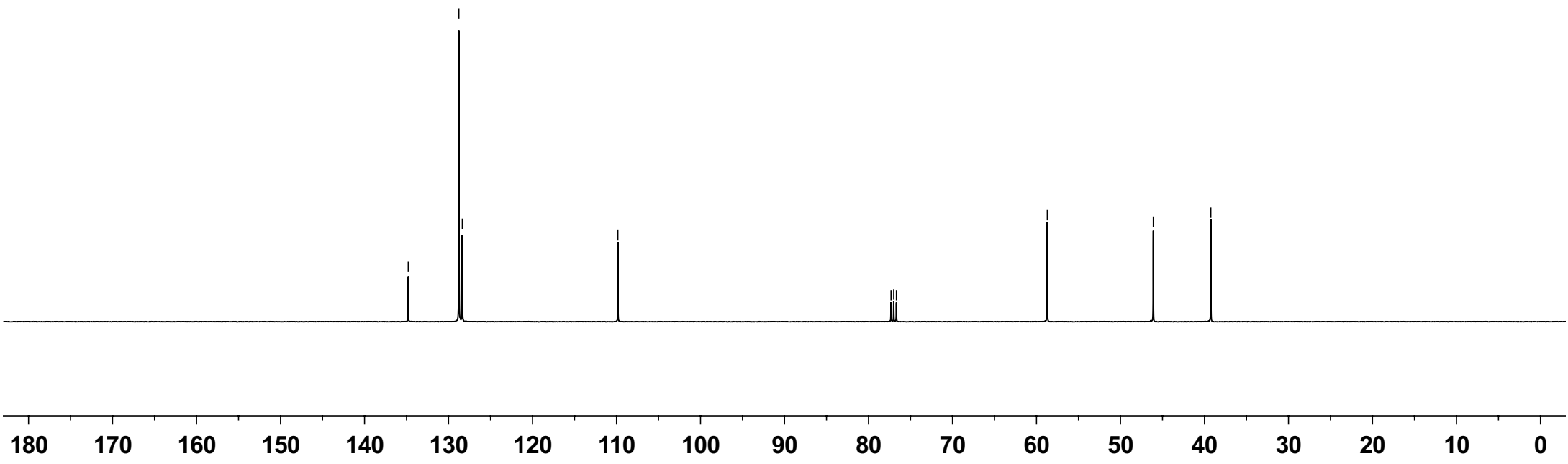
—109.840

77.319  
77.000  
76.680

—58.714

—46.093

—39.245

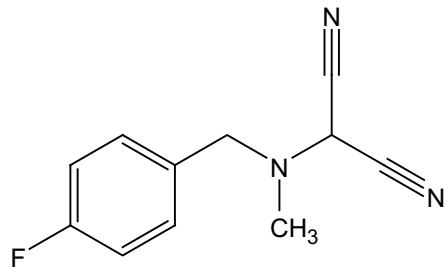


7.331  
7.318  
7.310  
7.296  
7.260  
7.086  
7.065  
7.043

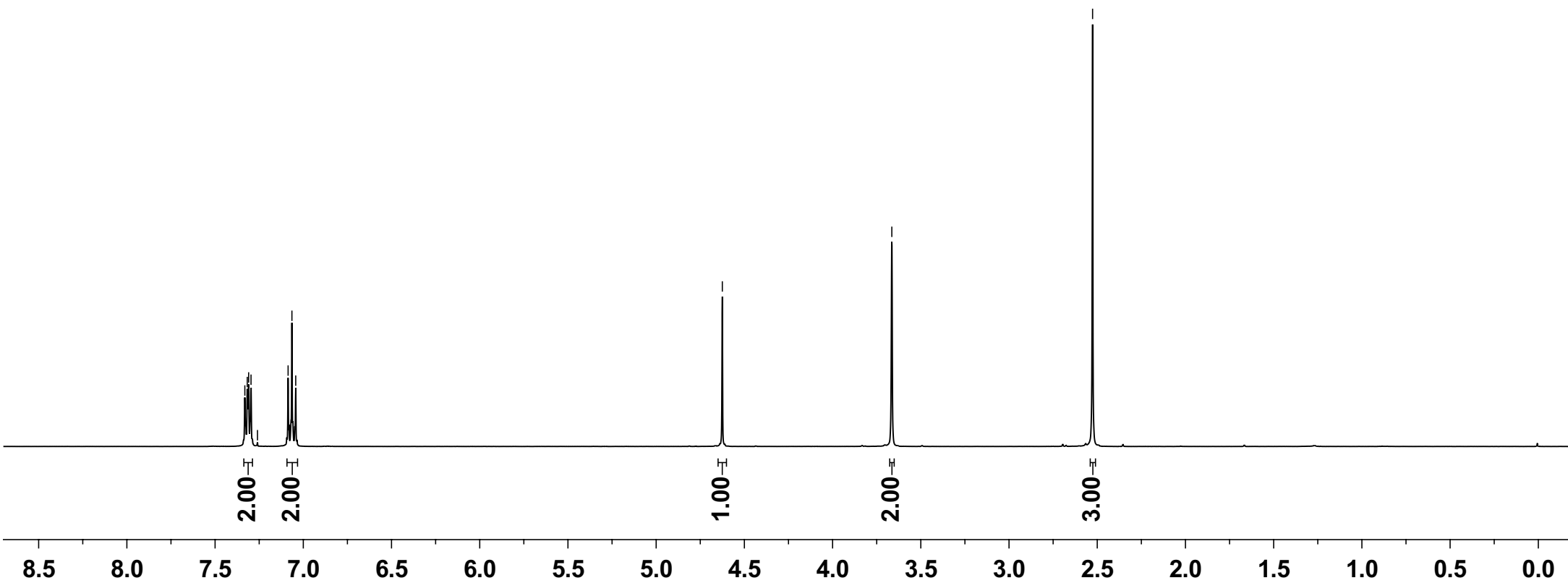
4.625

3.664

2.526



**1q** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



~163.742  
~161.284

130.710  
130.685  
130.585  
130.504

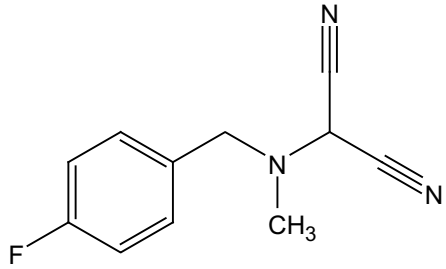
115.787  
115.574  
~109.816

77.318  
77.000  
76.680

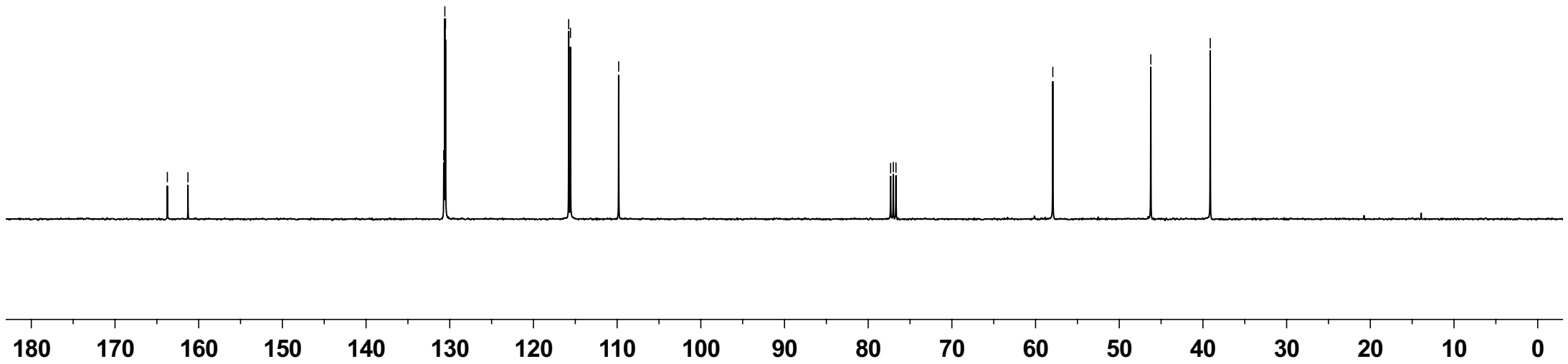
—57.937

—46.231

—39.129



**1q**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )



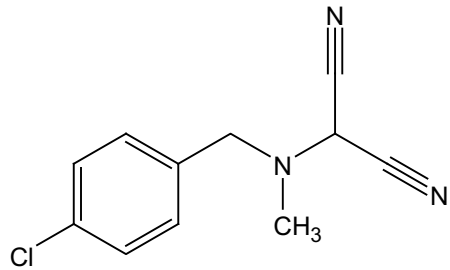
7.359  
7.337  
7.280  
7.259

4.605

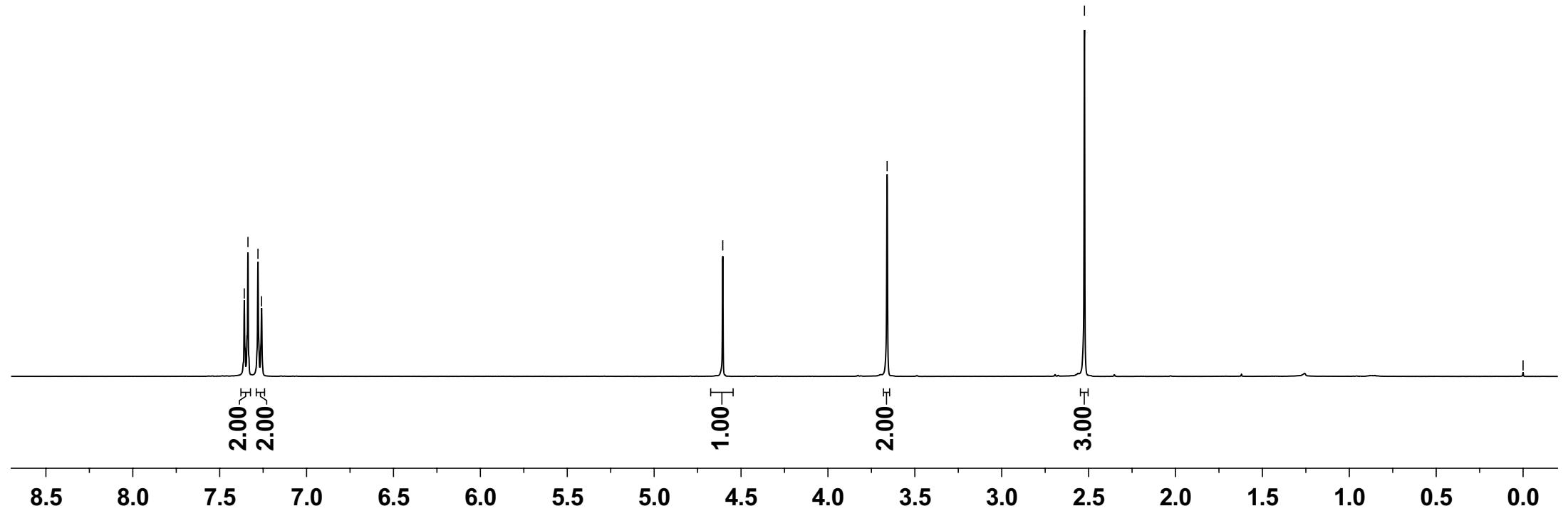
3.659

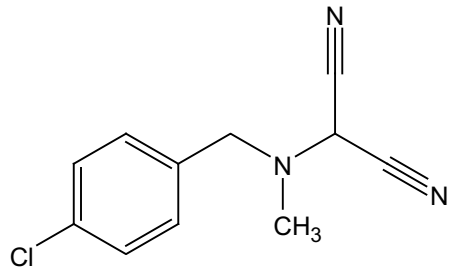
2.524

0.000



**1r** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)





**1r** <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

134.358  
133.386  
130.190  
129.089

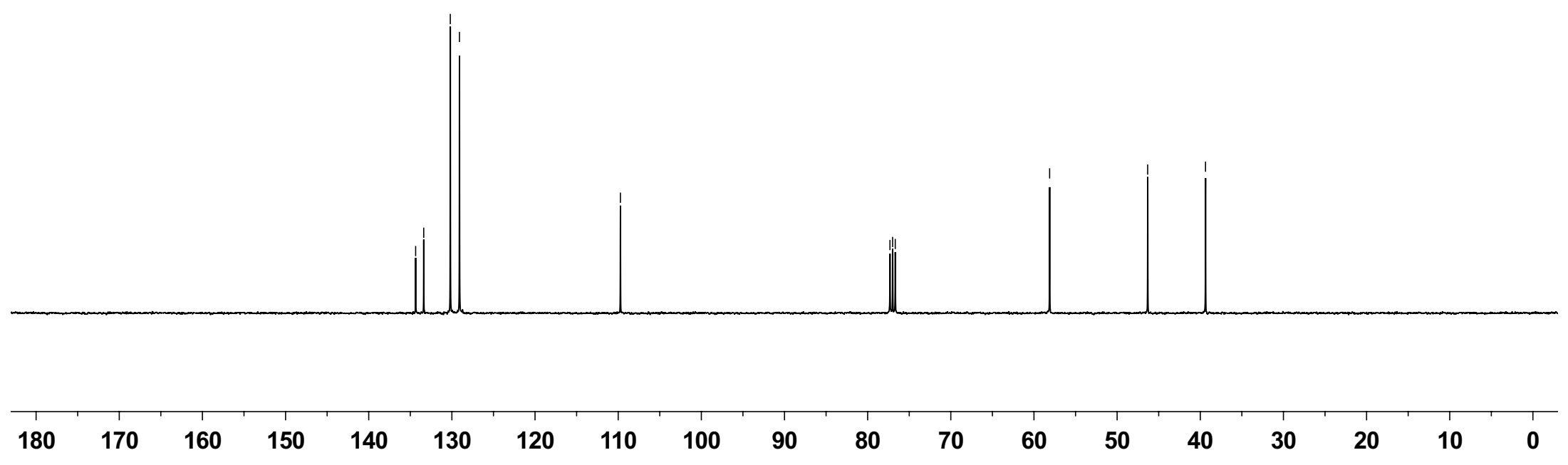
109.732

77.318  
77.000  
76.682

58.117

46.327

39.371



7.195  
7.174  
7.164  
7.143

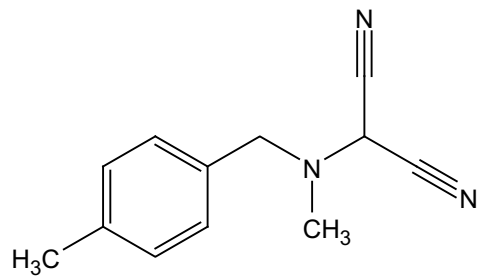
4.557

3.603

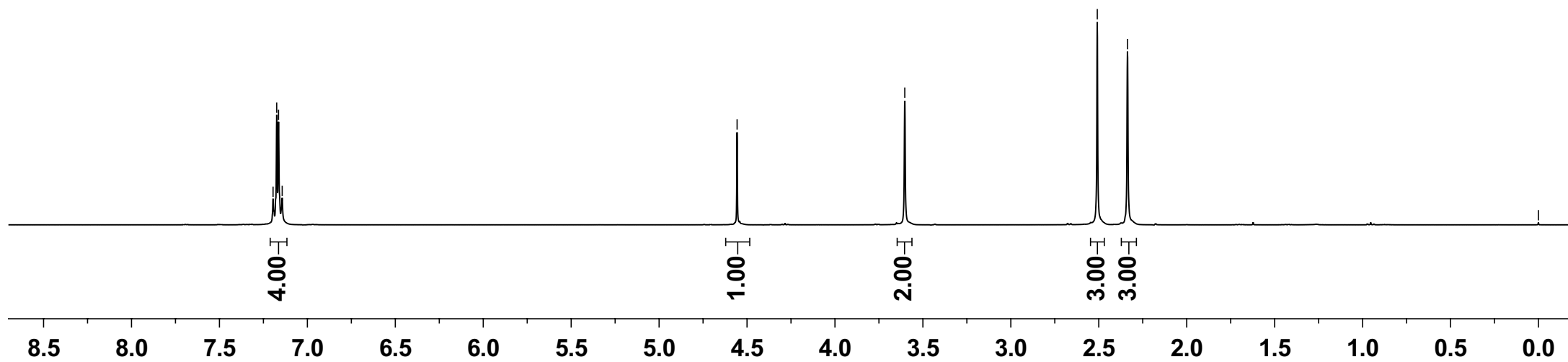
2.508

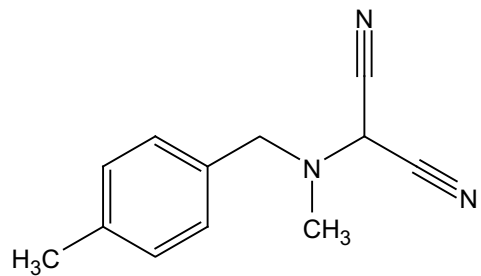
2.337

0.000

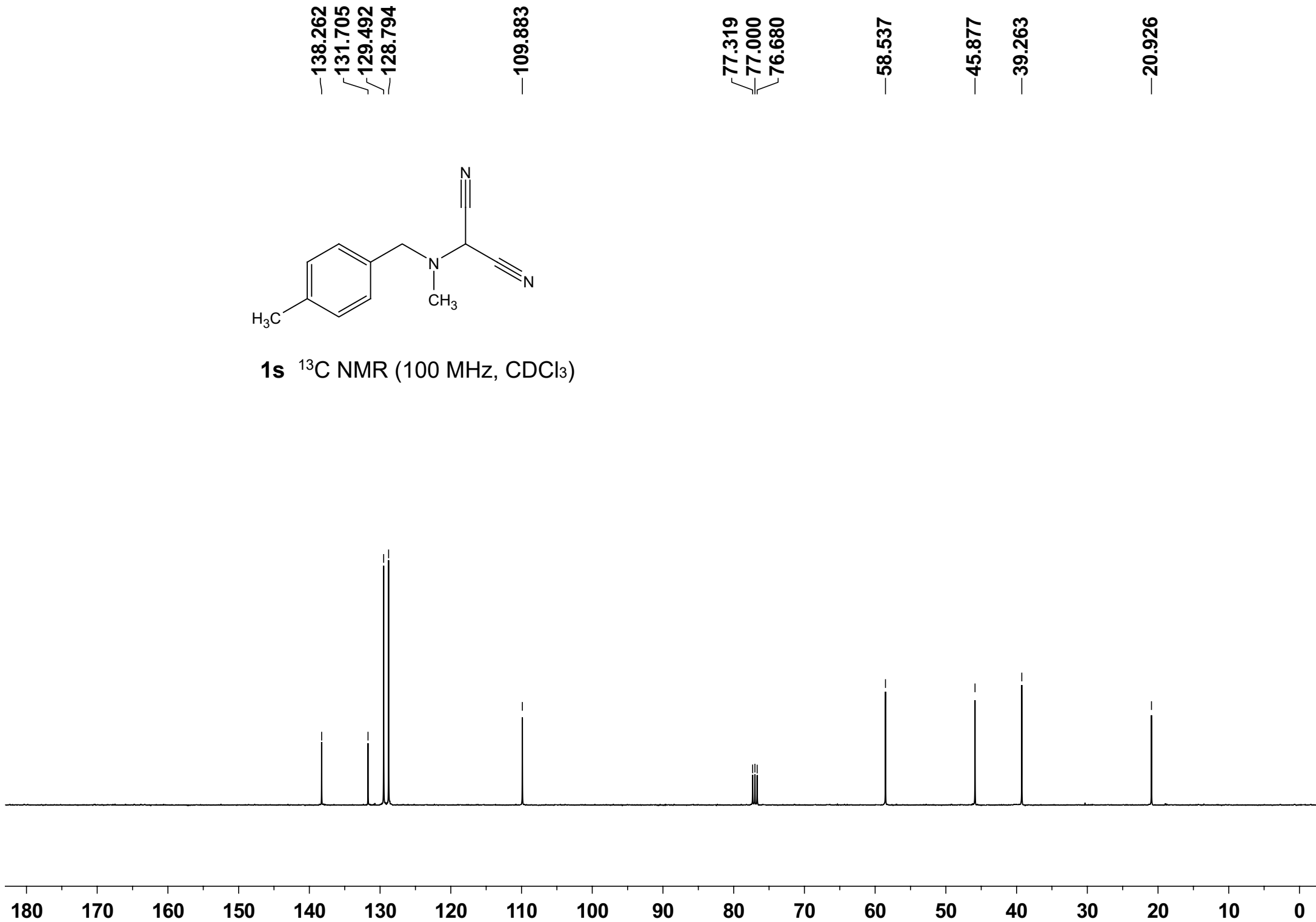


**1s** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)





**1s** <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)



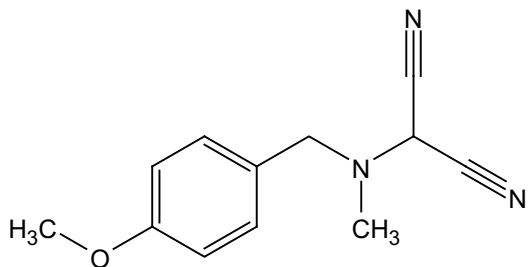
7.235  
7.213  
6.893  
6.872

4.589

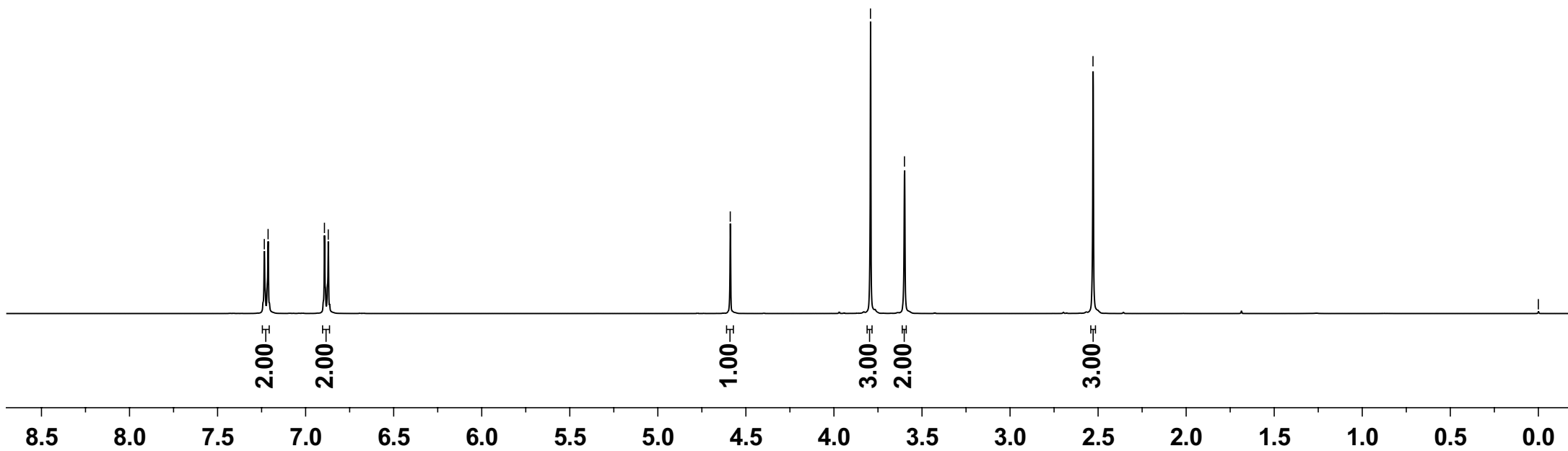
3.793  
3.600

2.529

0.000



**1t**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )





—159.678

—130.191  
—126.651

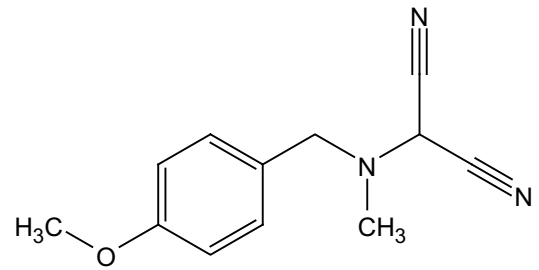
—114.227  
—109.920

77.320  
77.000  
76.682

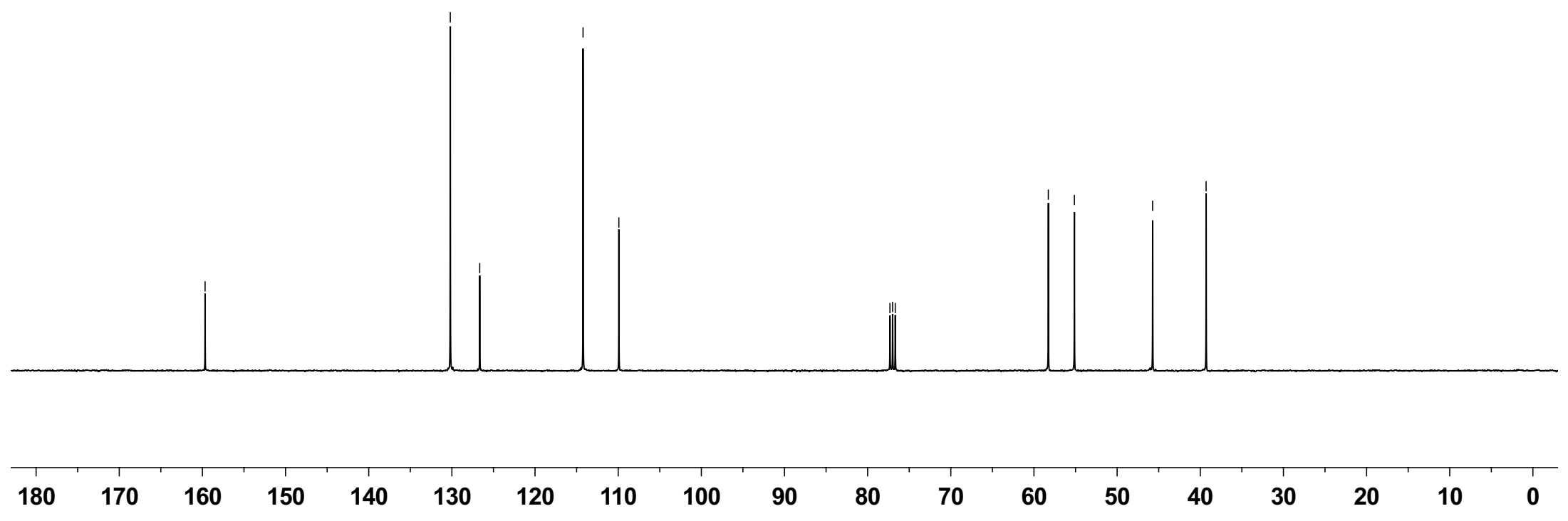
—58.275  
—55.140

—45.730

—39.299



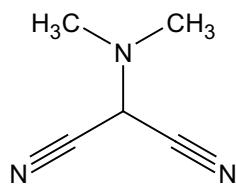
**1t** <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)



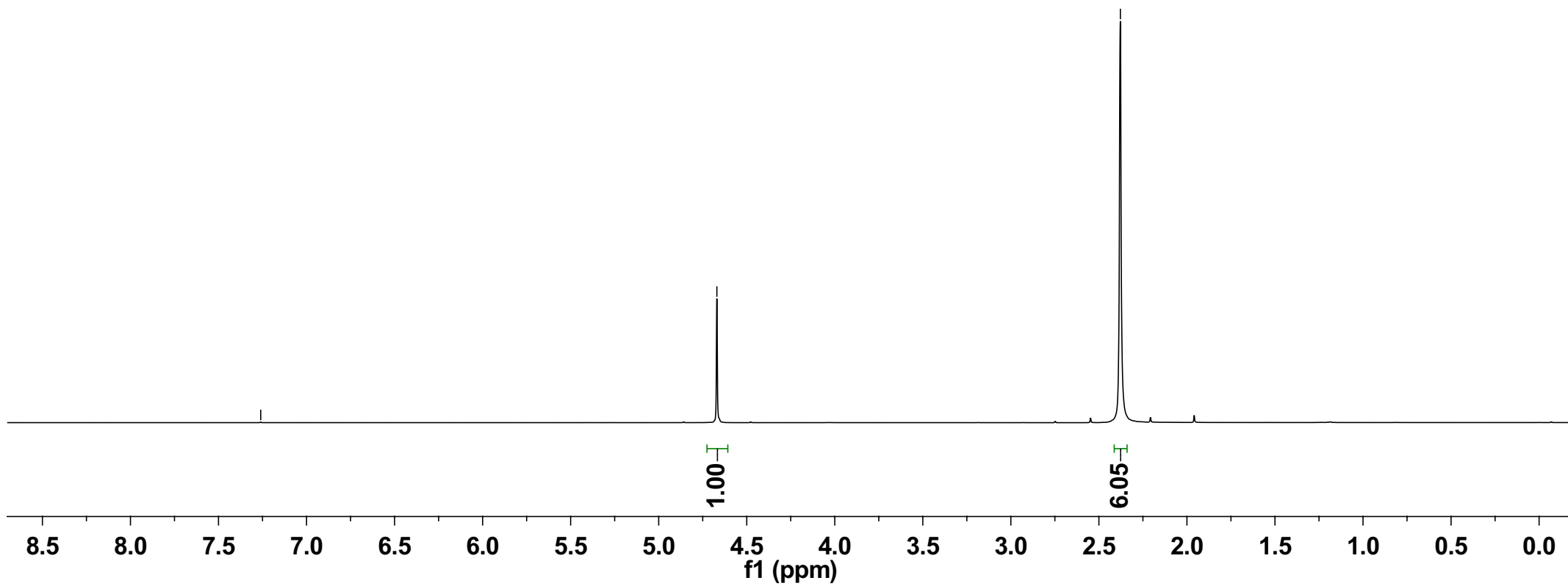
—7.26

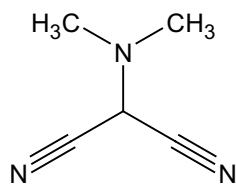
—4.67

—2.38

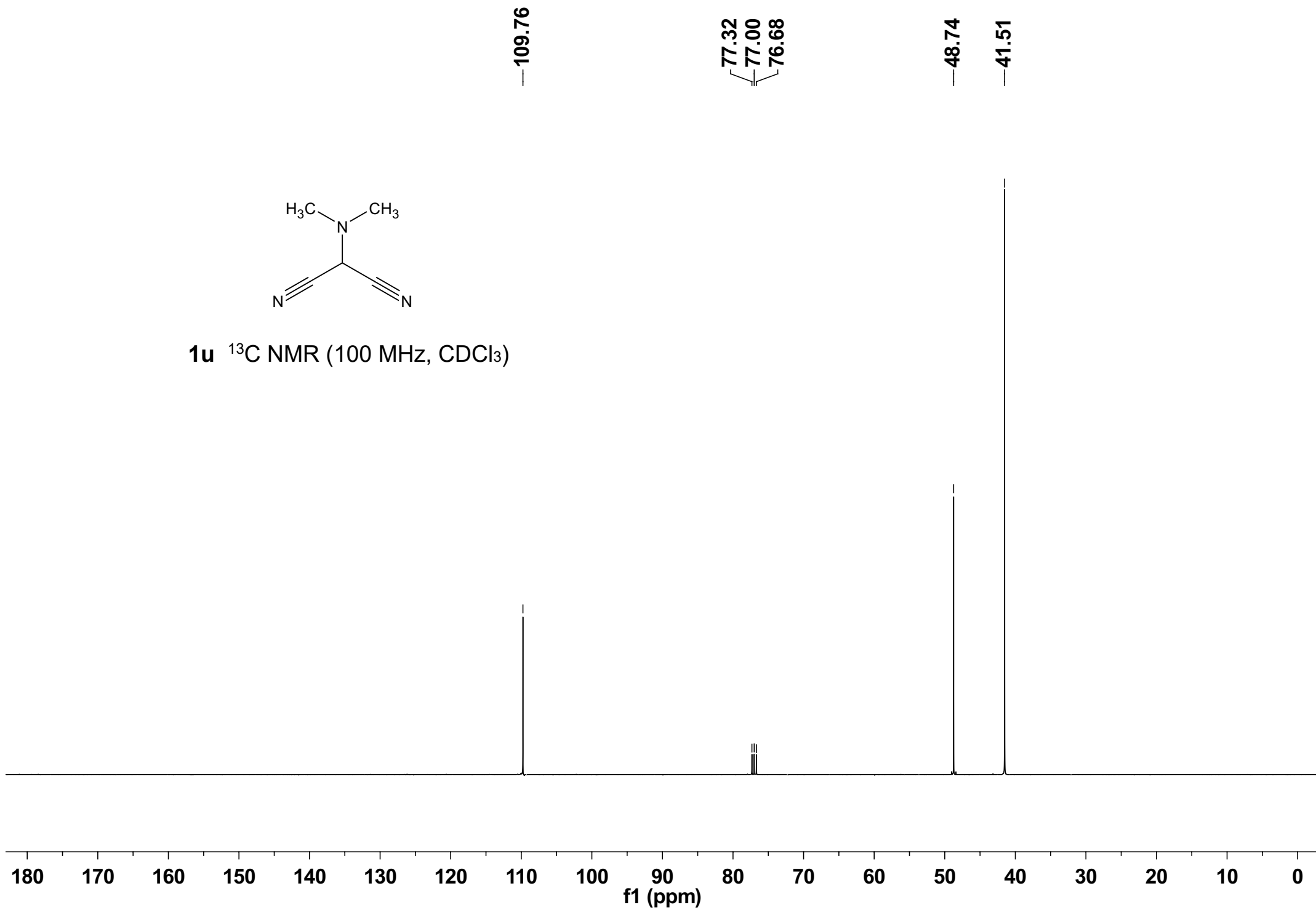


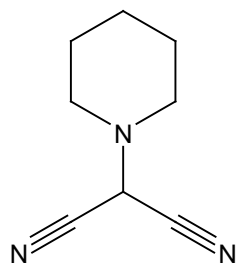
**1u**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )





**1u**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )



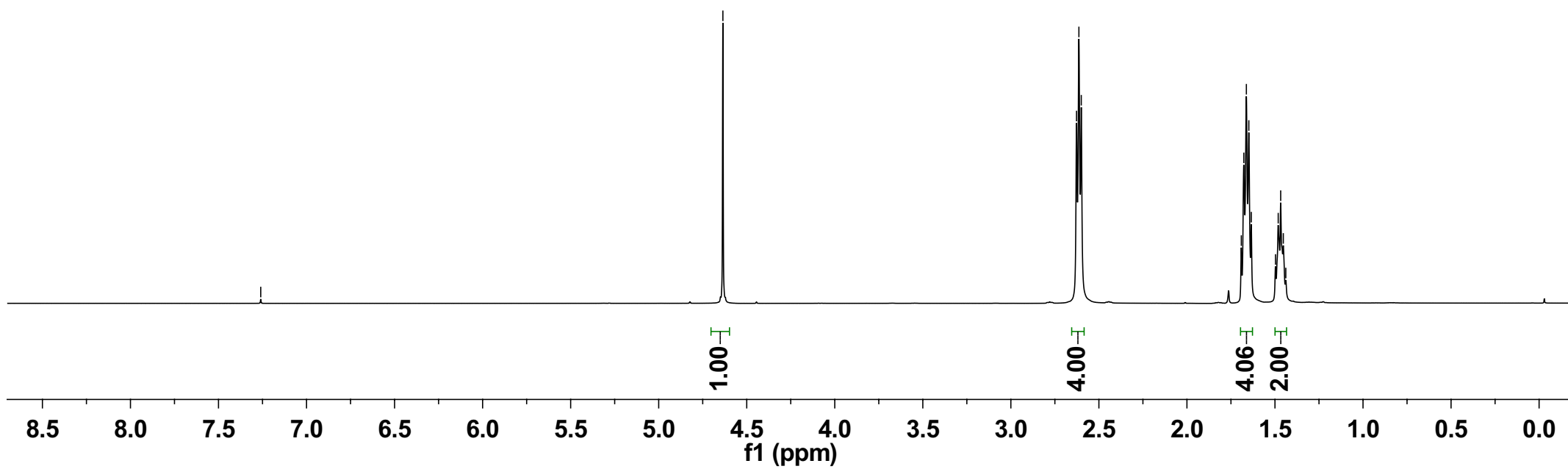


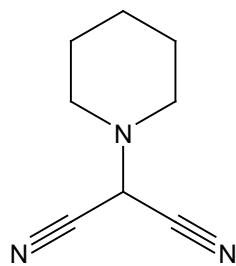
**1v**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

—7.26

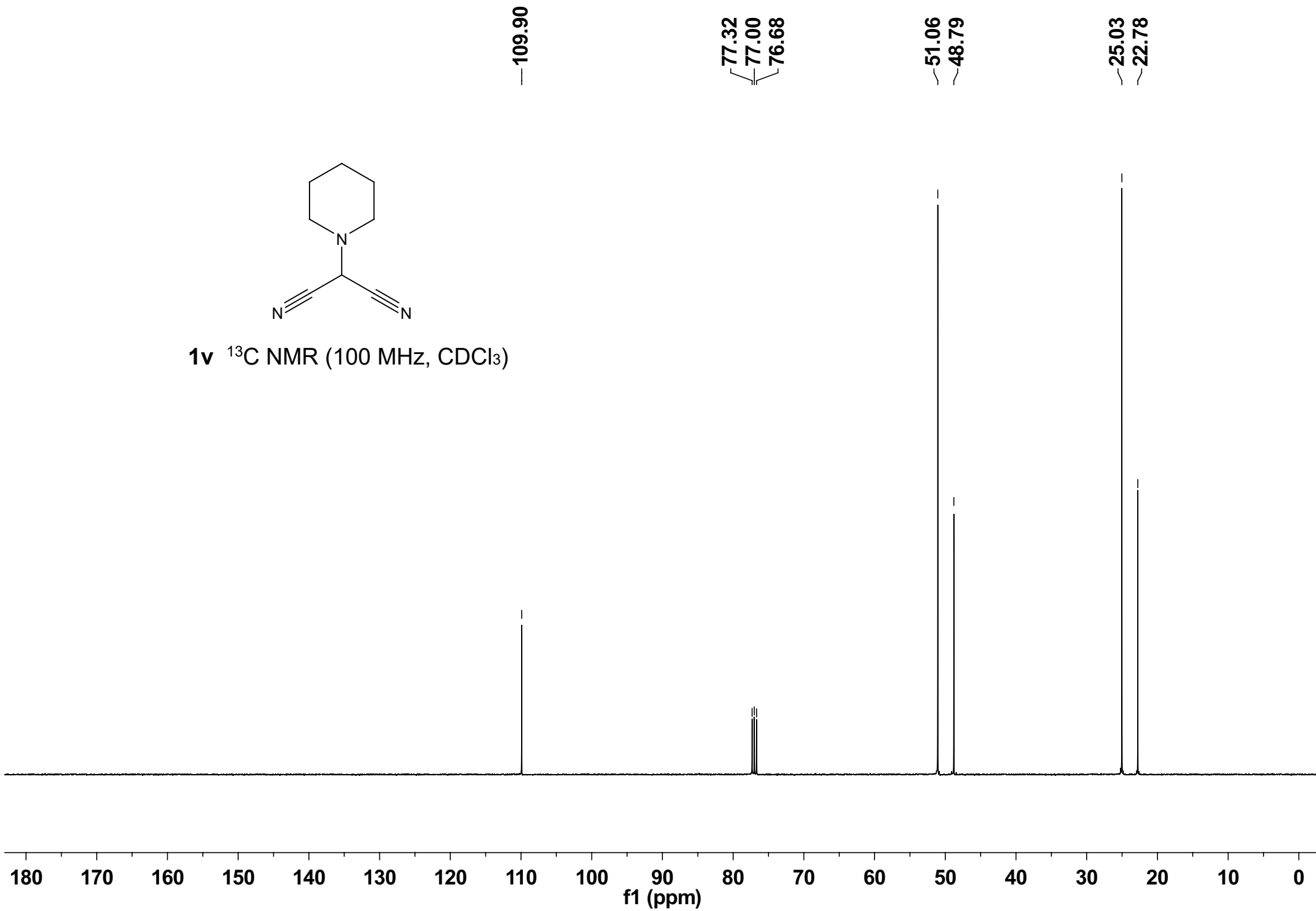
—4.64

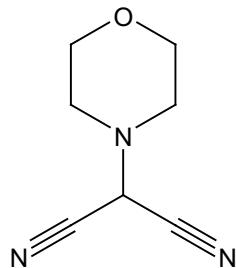
2.63  
2.61  
2.60  
1.69  
1.68  
1.66  
1.65  
1.63  
1.50  
1.48  
1.47  
1.45  
1.44





**1v**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )





**1w**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

—7.26

—4.65

3.80

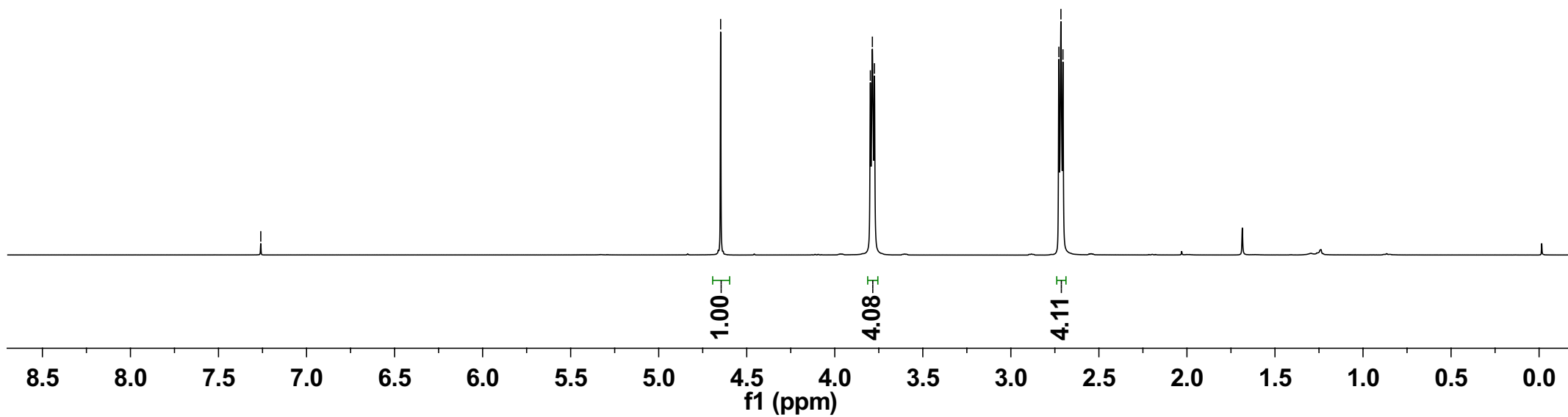
3.79

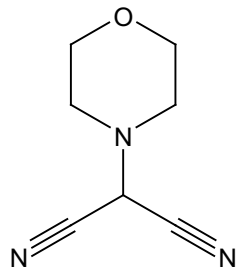
3.77

2.73

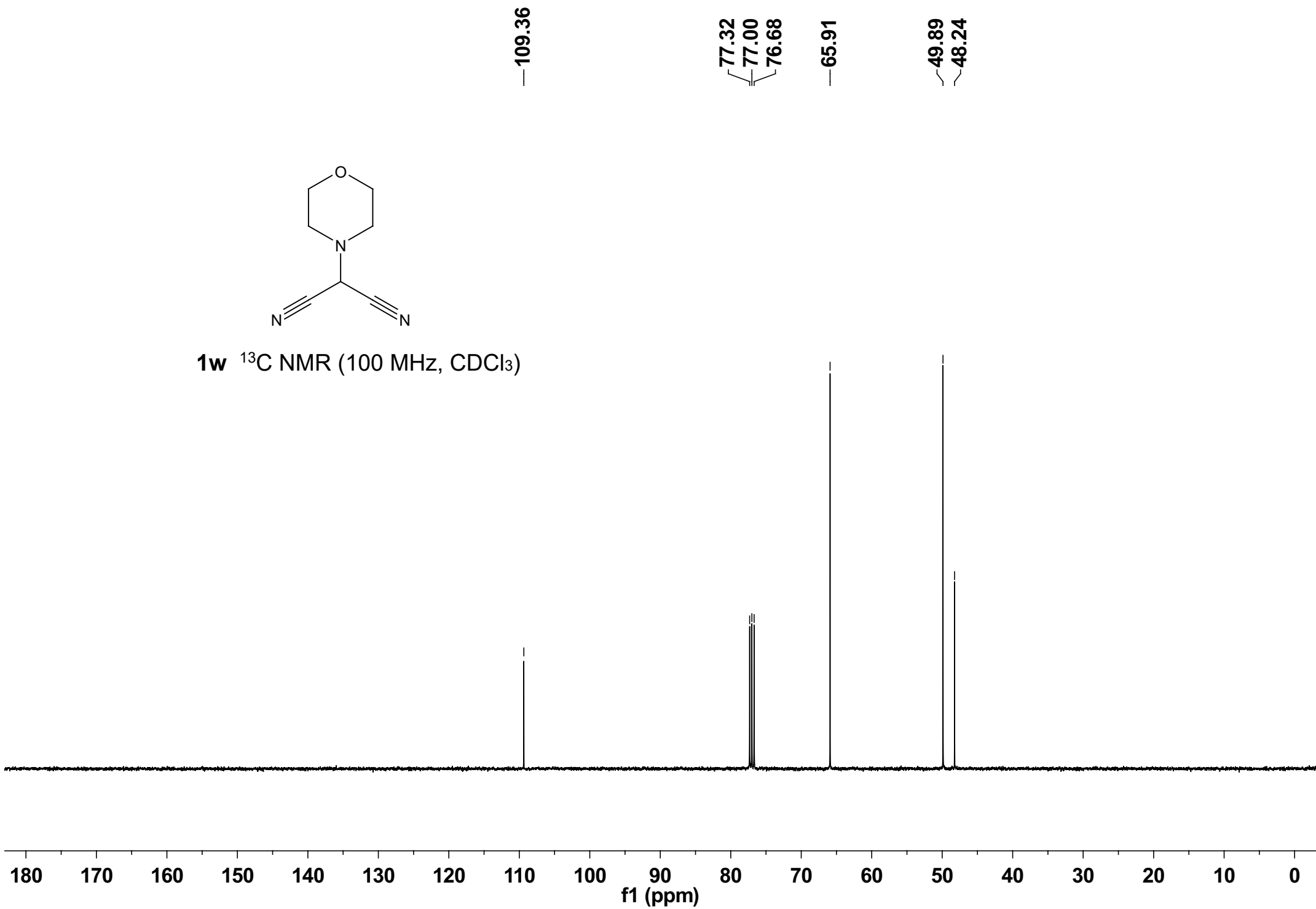
2.72

2.70





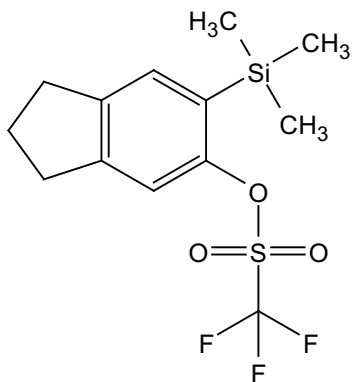
**1w**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )



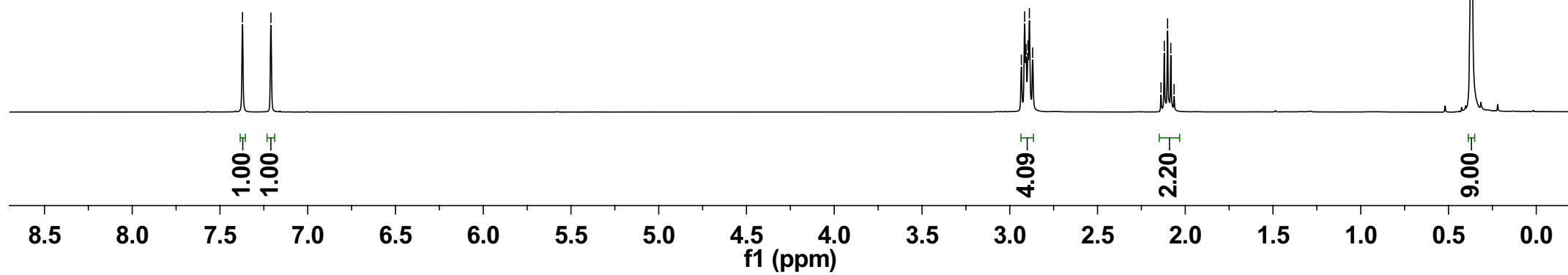
7.37  
7.21

2.93  
2.92  
2.91  
2.90  
2.89  
2.87  
2.14  
2.12  
2.10  
2.08  
2.06

0.37



**2g** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)





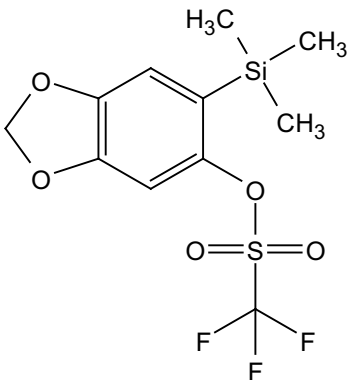
7.26

6.89

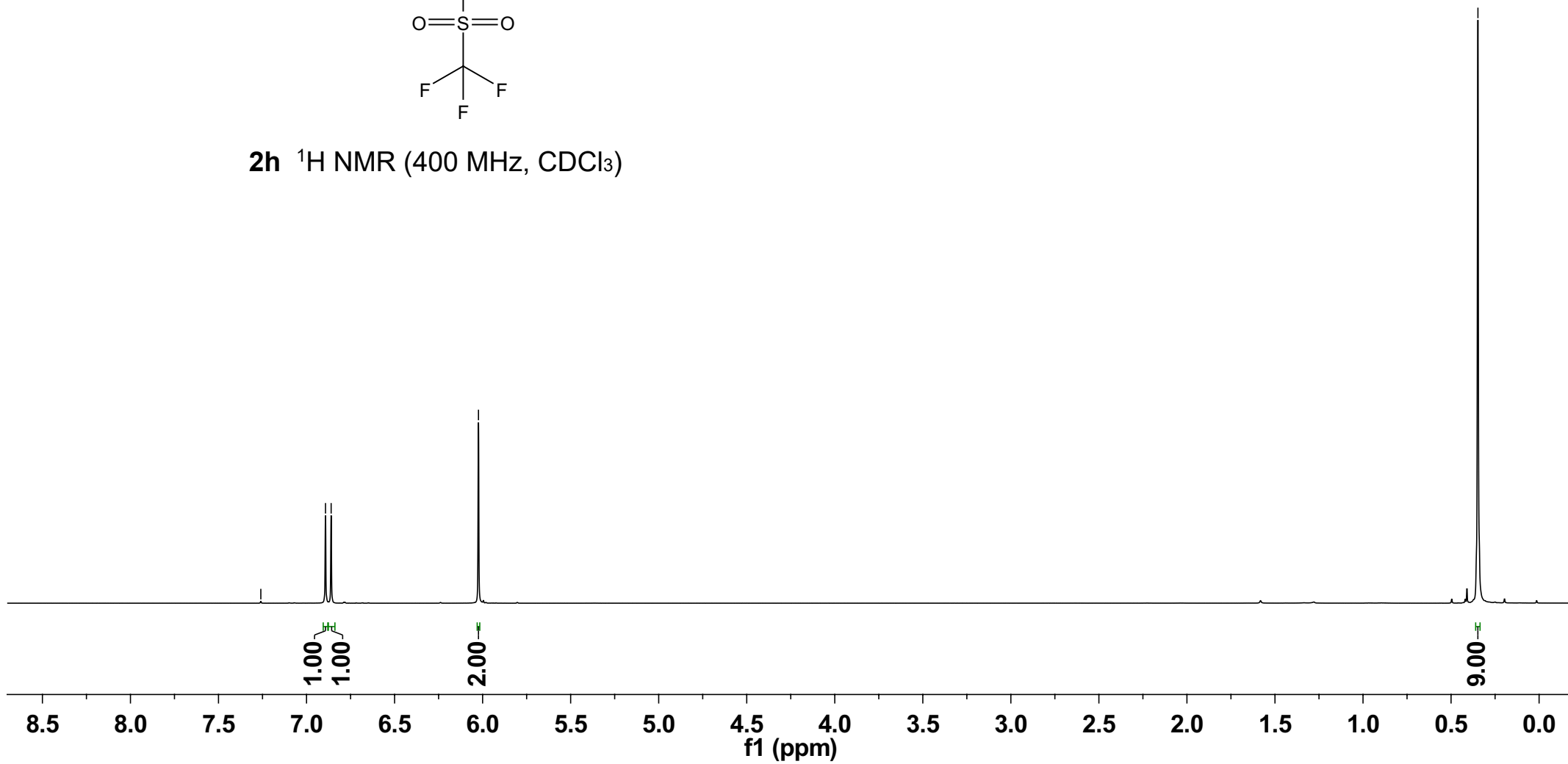
6.86

6.02

0.35



2h <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



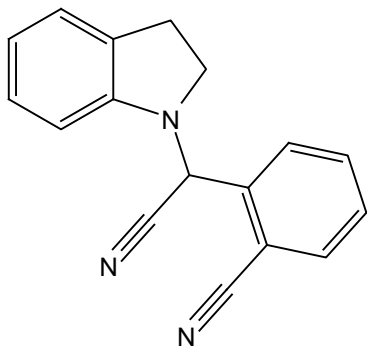


—148.290  
136.493  
134.179  
133.053  
130.400  
129.845  
128.545  
127.561  
125.013  
121.061  
116.264  
114.366  
112.709  
108.863

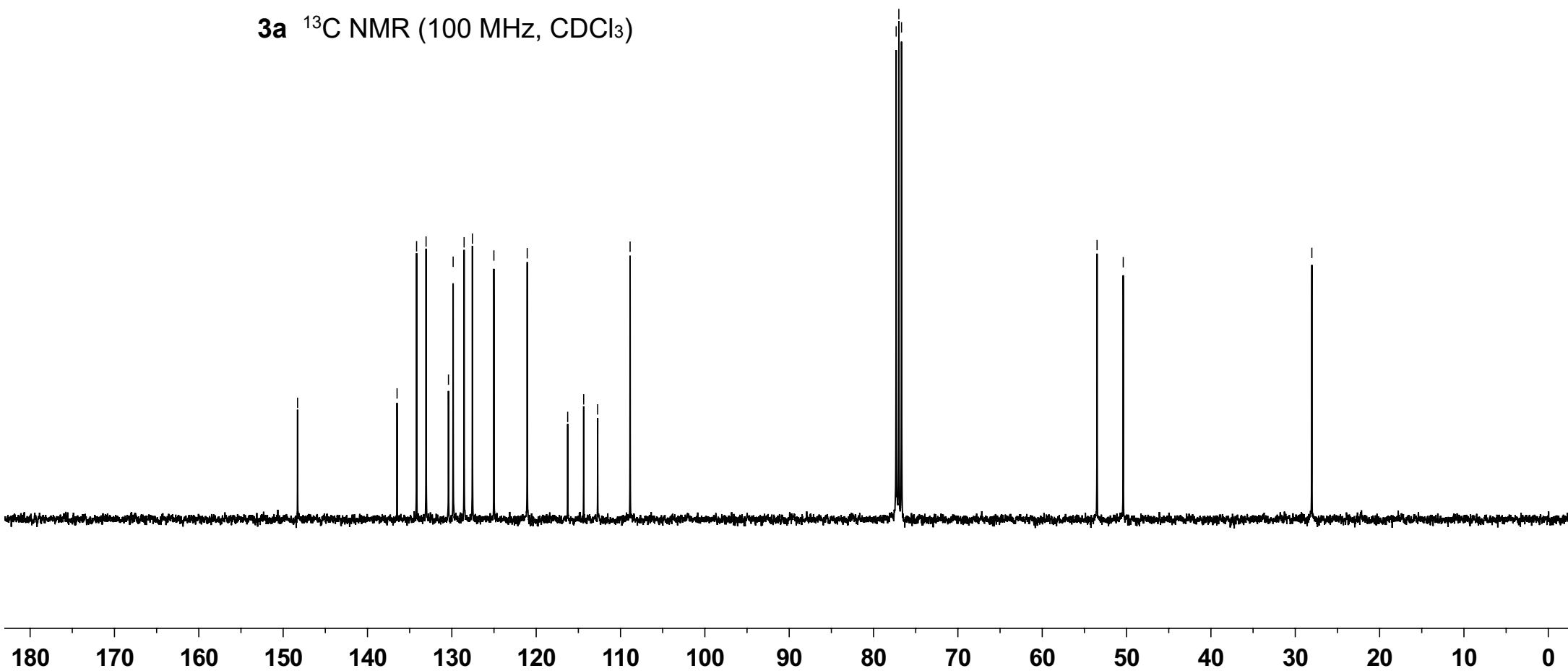
77.318  
77.000  
76.683

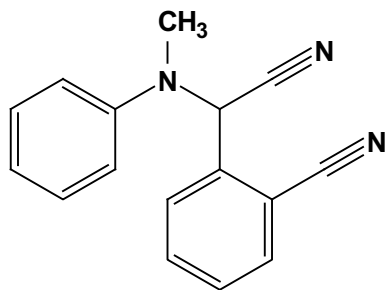
—53.498  
—50.396

—28.033

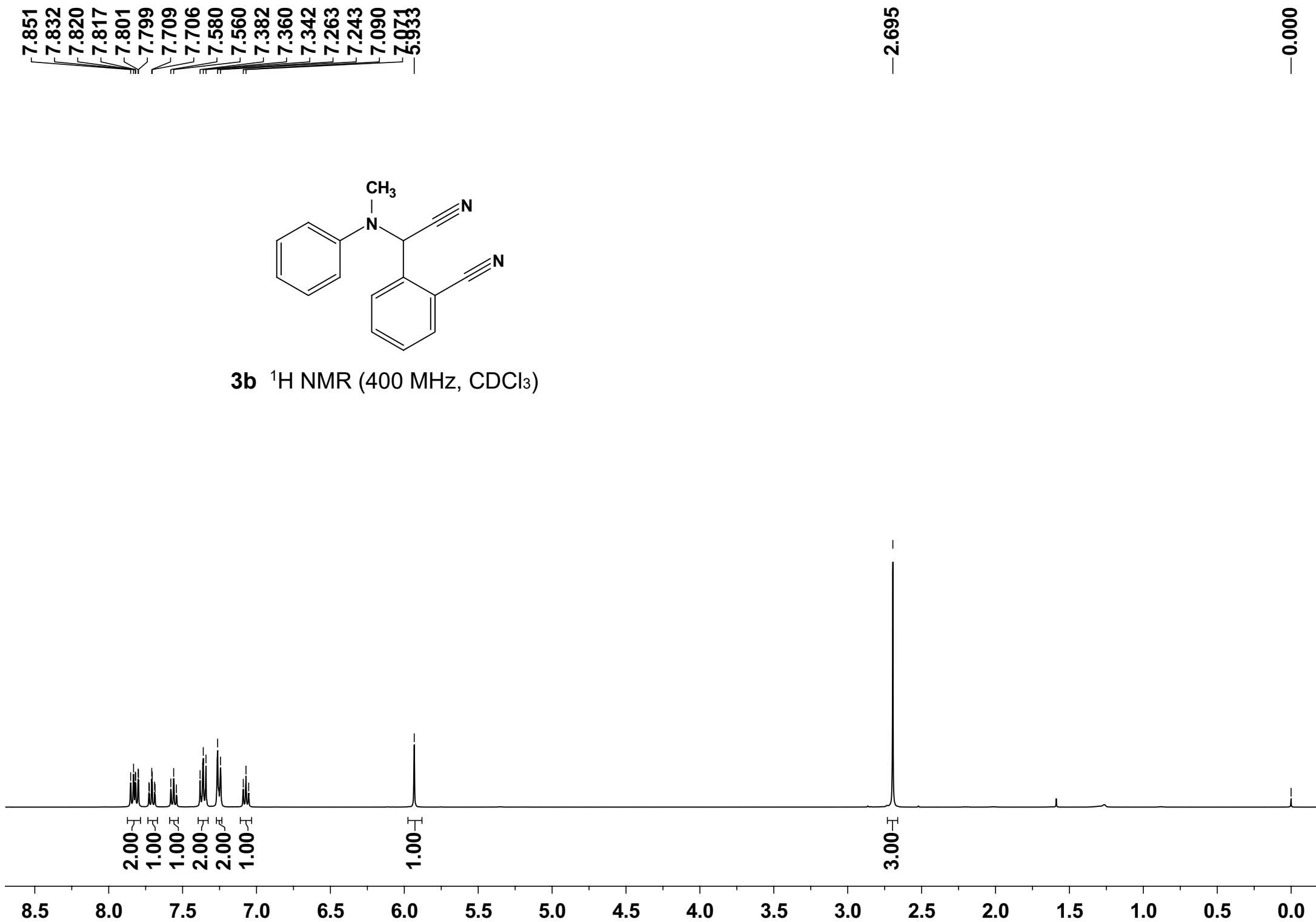


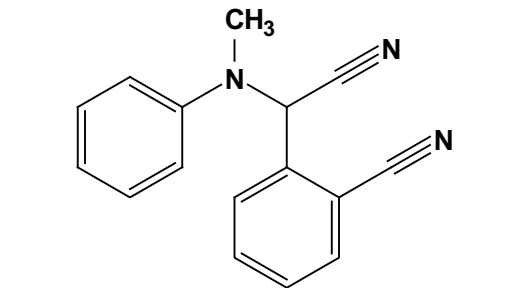
**3a**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )





**3b**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )





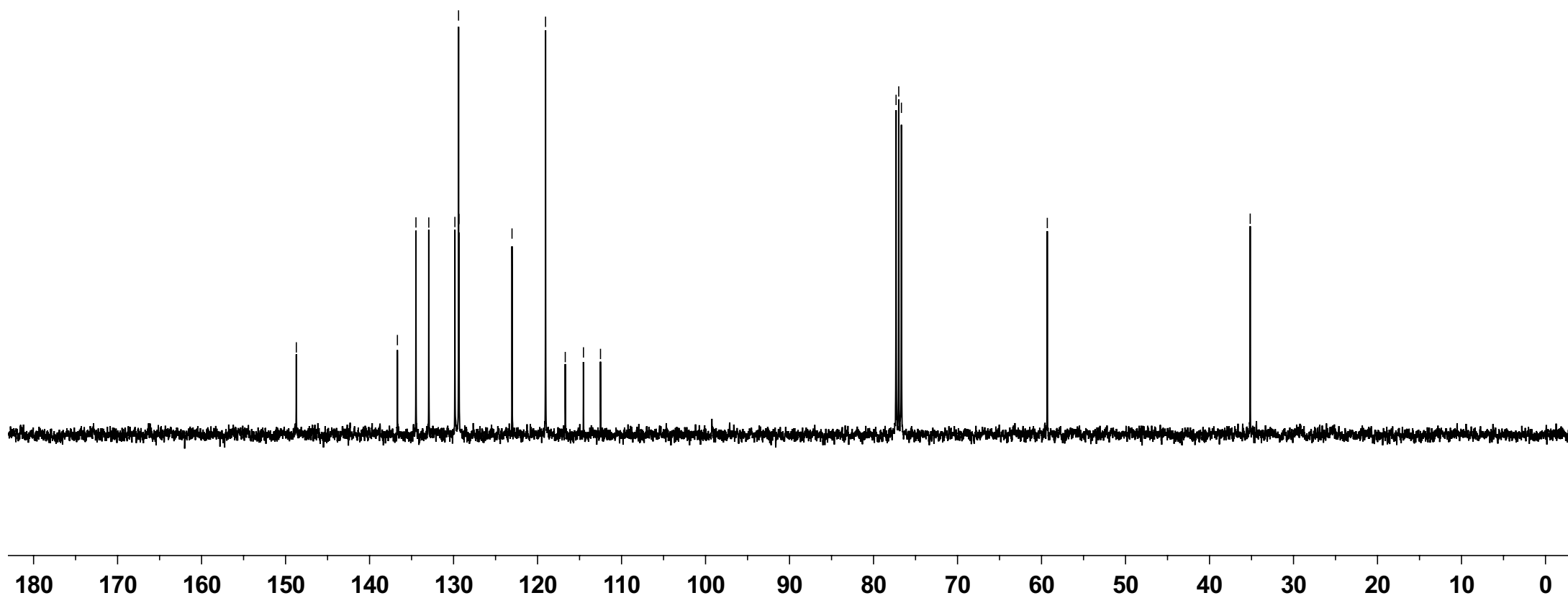
**3b**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

—148.721  
136.685  
134.477  
132.950  
129.841  
129.405  
129.352  
123.041  
119.048  
116.703  
114.536  
112.507

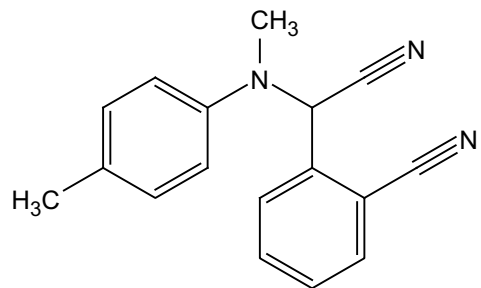
77.318  
77.000  
76.683

—59.313

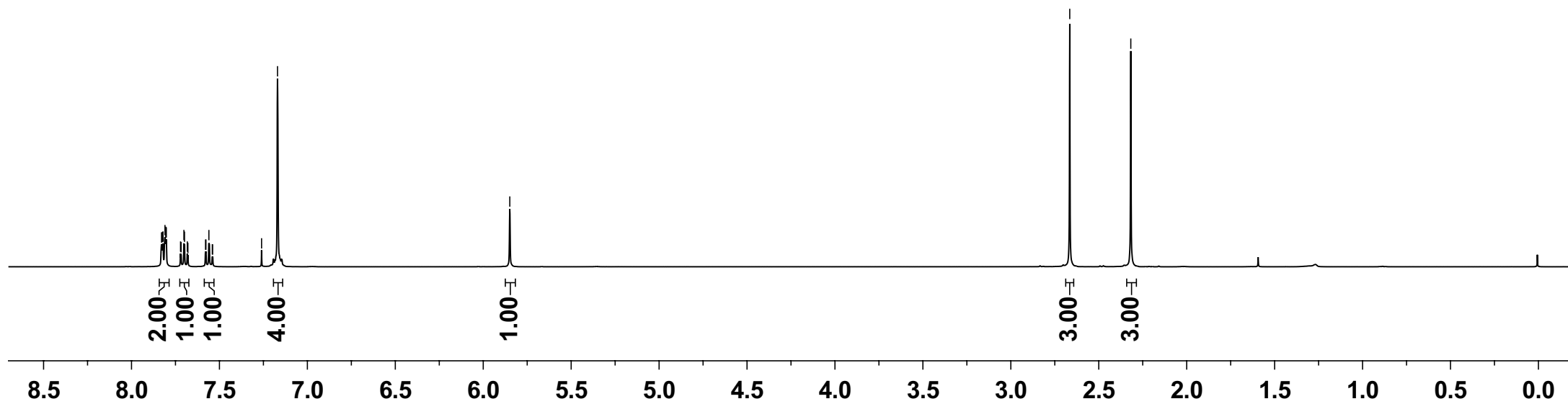
—35.155



7.829  
7.824  
7.821  
7.810  
7.805  
7.802  
7.721  
7.718  
7.702  
7.699  
7.683  
7.679  
7.579  
7.577  
7.560  
7.260  
7.179  
5.849

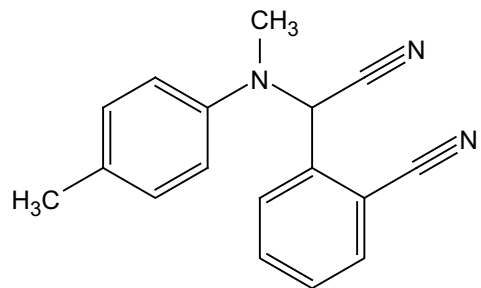


**3c**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



— 2.665

— 2.318



**3c** <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

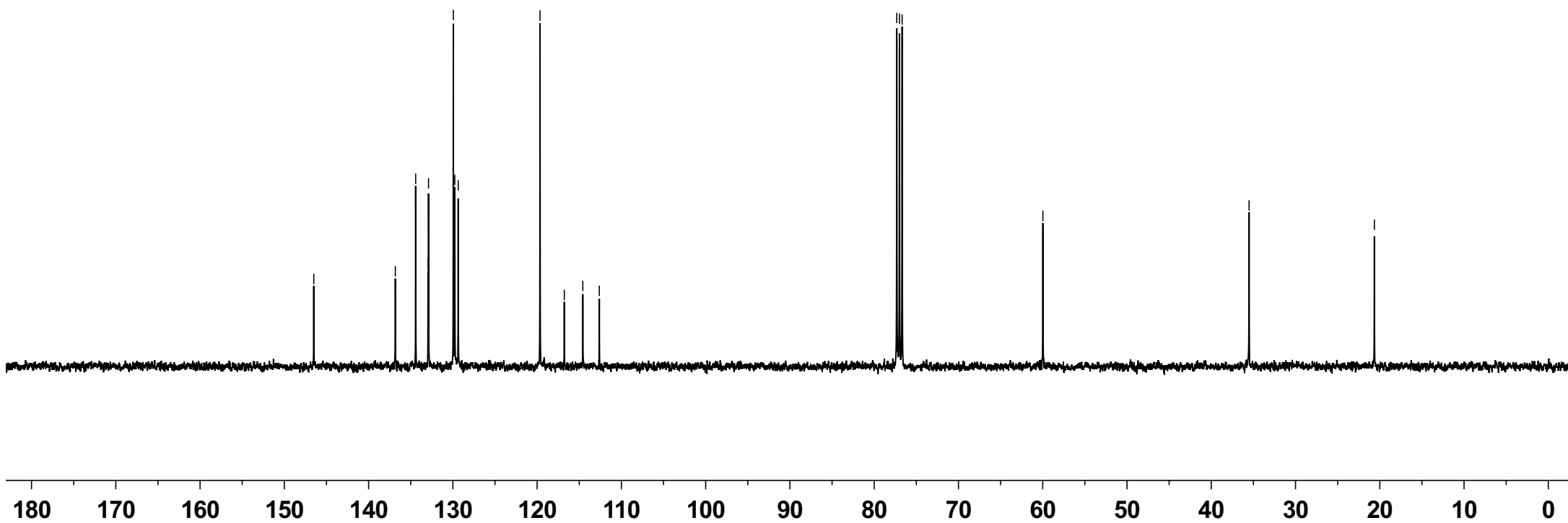
— 146.503  
— 134.413  
— 132.943  
— 132.886  
— 129.943  
— 129.771  
— 129.364  
— 119.655  
— 116.774  
— 114.580  
— 112.620

— 77.318  
— 77.000  
— 76.682

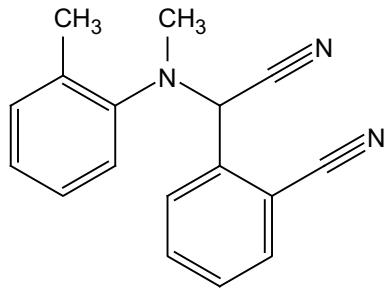
— 59.978

— 35.511

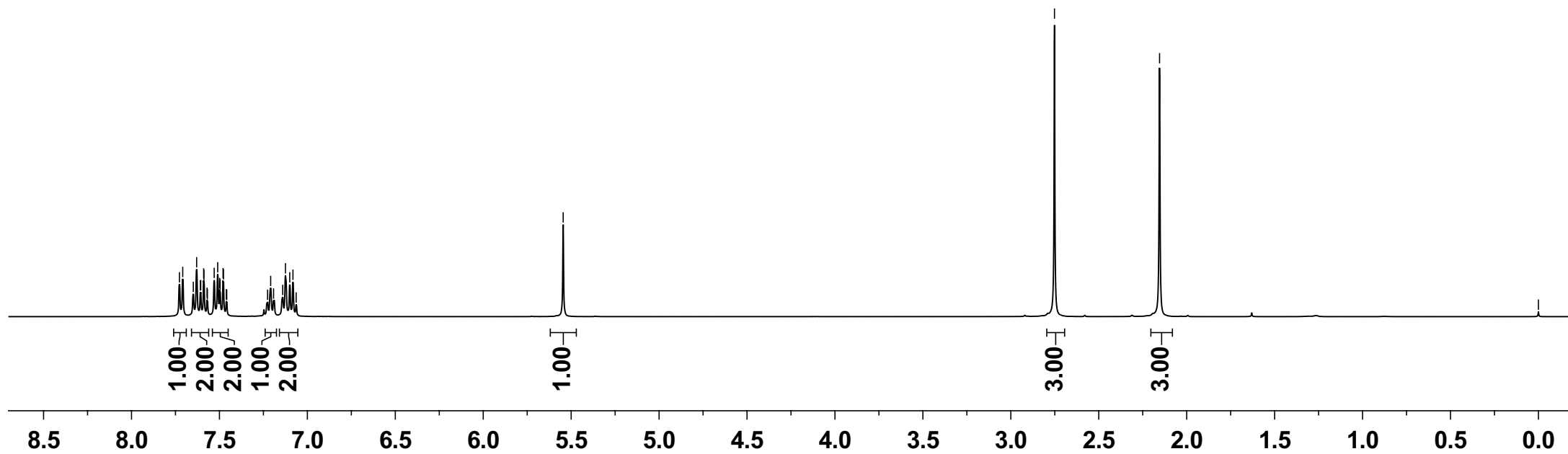
— 20.641



7.728  
7.709  
7.649  
7.630  
7.608  
7.606  
7.590  
7.588  
7.530  
7.510  
7.498  
7.496  
7.480  
7.477  
7.209  
7.140  
7.125  
7.100  
7.082  
7.045



3d <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



—2.752

—2.154

—0.000



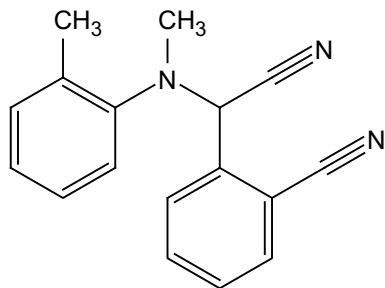
147.431  
136.969  
134.938  
133.683  
132.626  
131.262  
129.479  
129.105  
126.702  
125.885  
122.299  
116.451  
116.237  
113.003

77.318  
77.000  
76.682

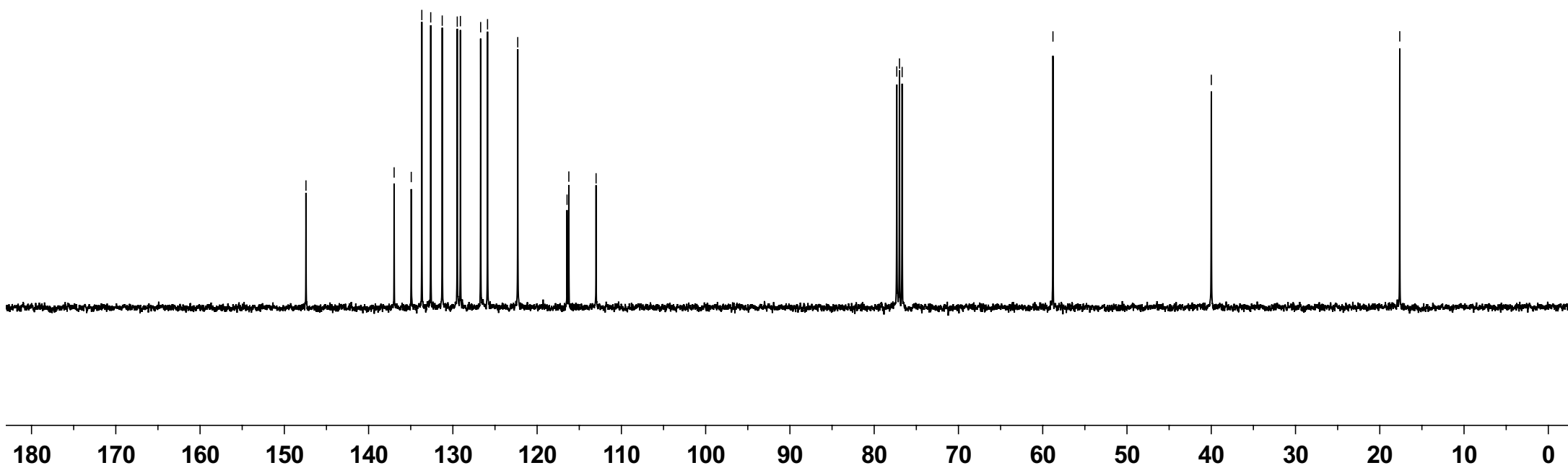
58.785

39.990

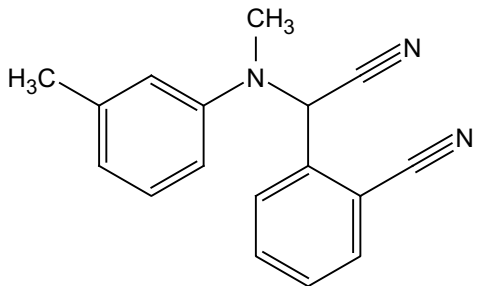
17.631



**3d**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )



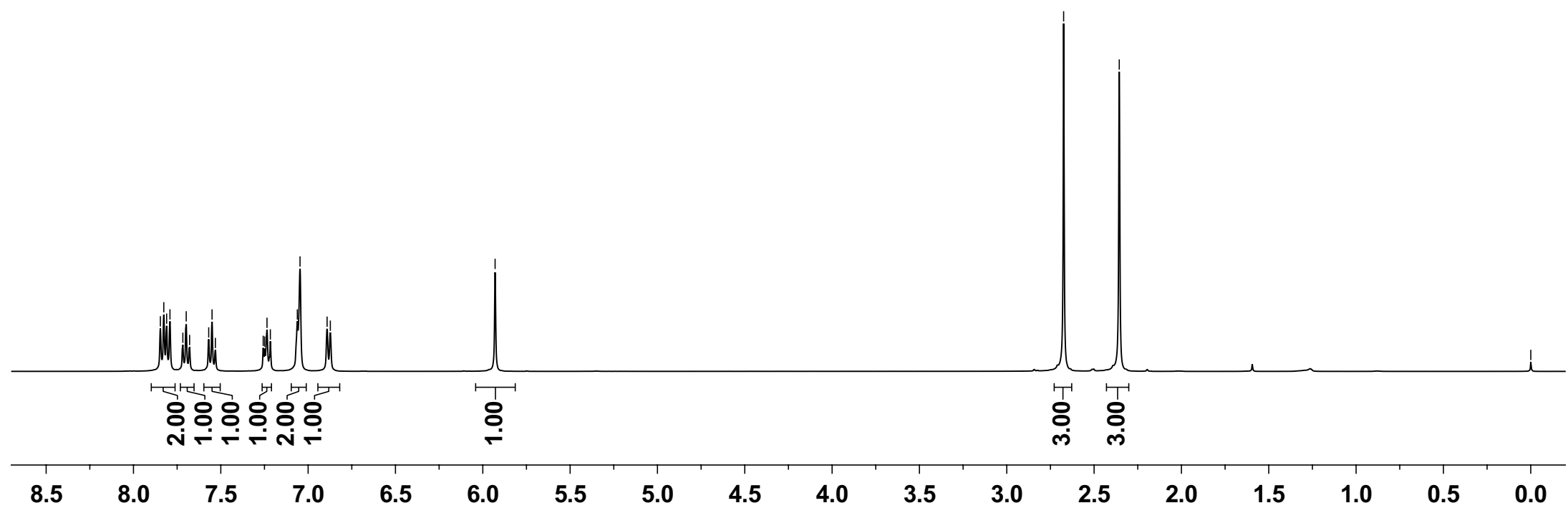
7.846  
7.826  
7.810  
7.791  
7.717  
7.698  
7.679  
7.569  
7.550  
7.257  
7.249  
7.236  
7.216  
7.062  
7.046  
6.892  
6.873



3e <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

2.674  
2.356

0.000



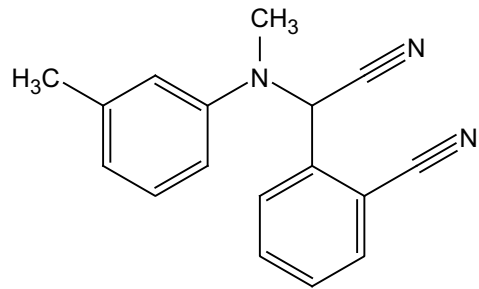
148.741  
139.168  
136.754  
134.461  
132.897  
129.779  
129.323  
129.167  
123.826  
119.614  
116.684  
116.020  
114.584  
112.490

77.318  
77.000  
76.681

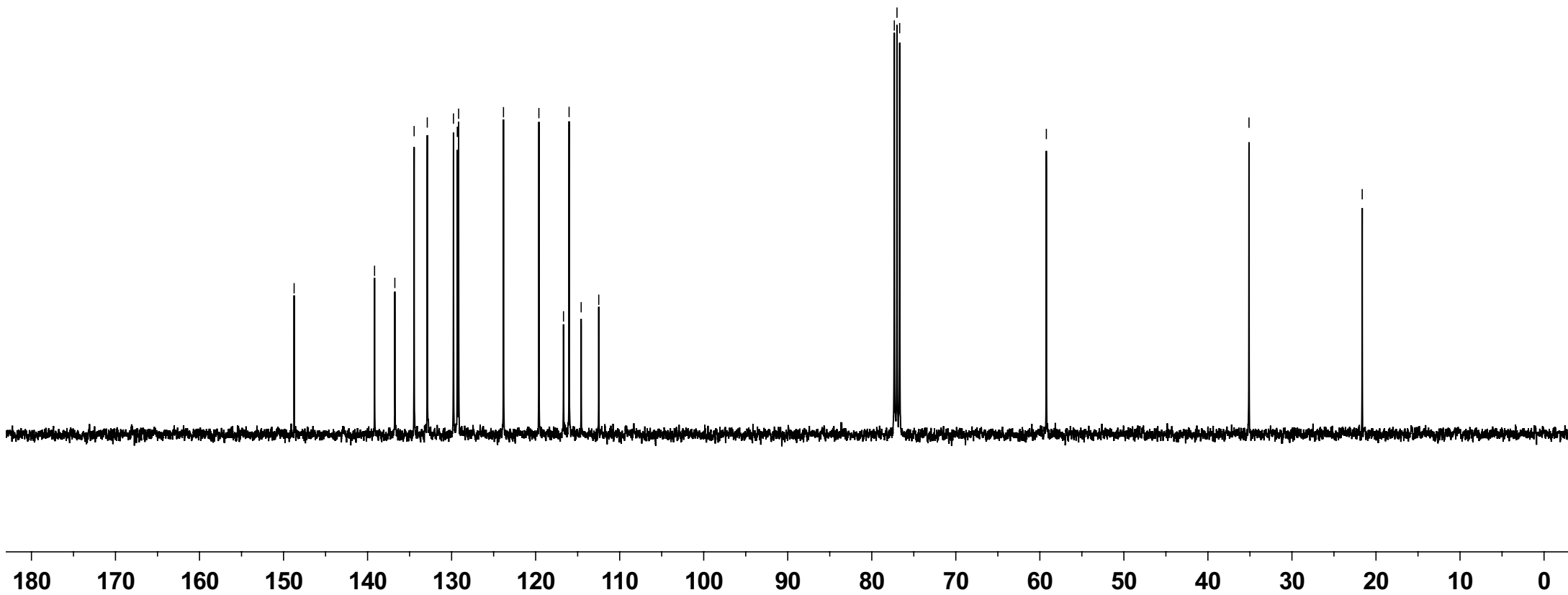
59.227

35.111

21.638



**3e** <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)



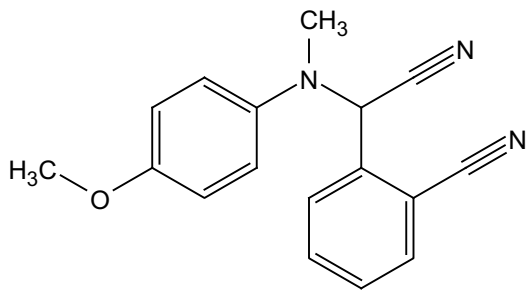
7.828  
7.809  
7.771  
7.752  
7.702  
7.683  
7.575  
7.556  
7.273  
7.251  
6.899  
6.877

5.694

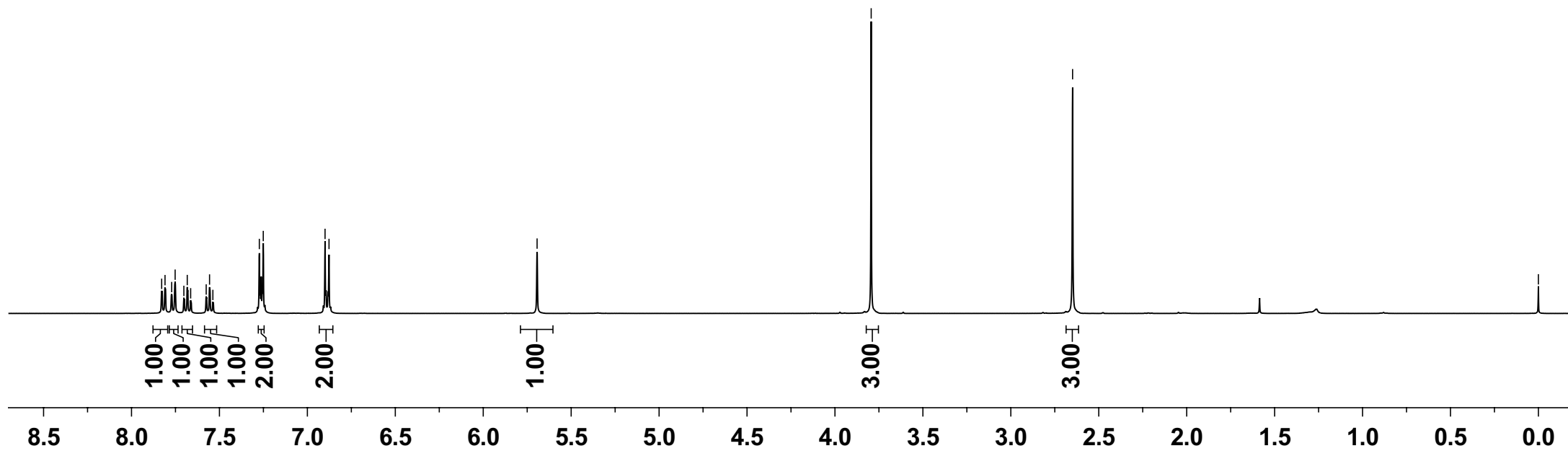
3.794

2.649

0.000



**3f** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



—156.413

142.472

136.833

134.321

132.865

129.768

129.433

122.593

116.924

114.663

114.531

112.773

77.318

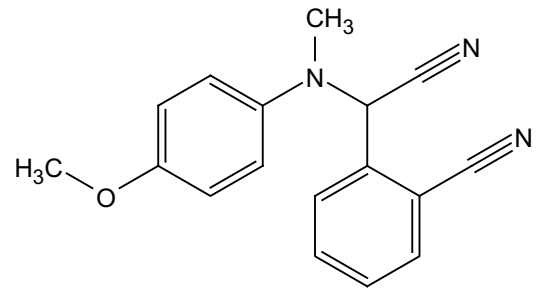
77.000

76.683

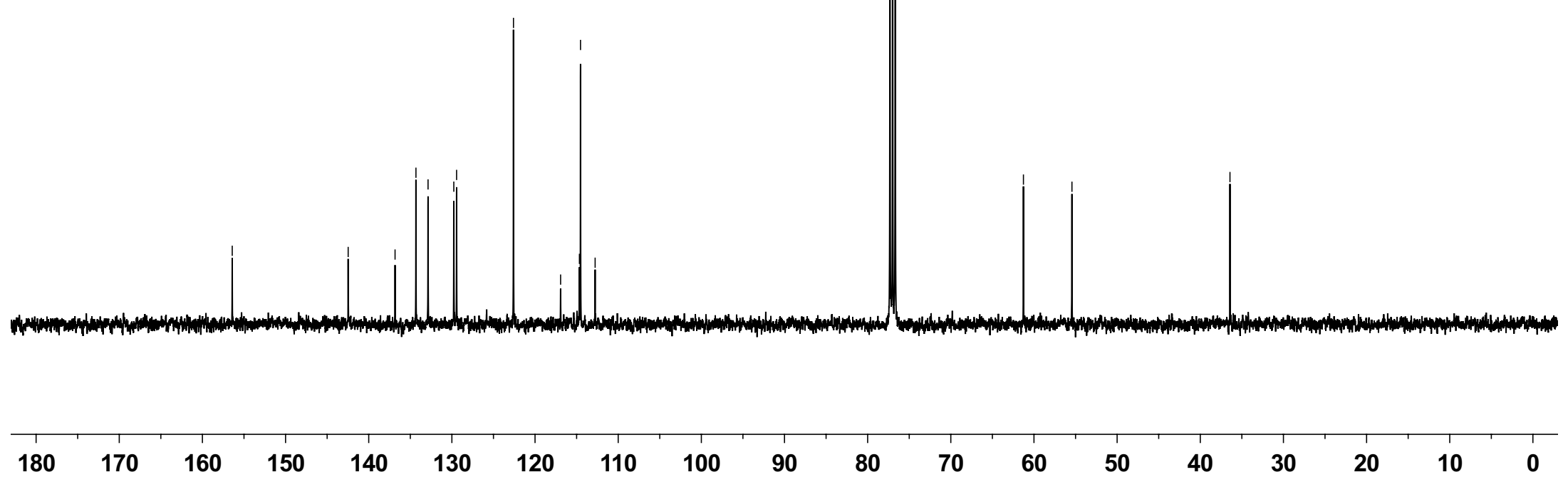
—61.267

—55.433

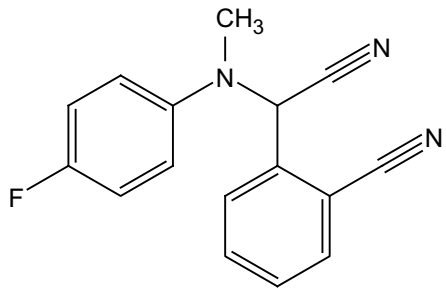
—36.429



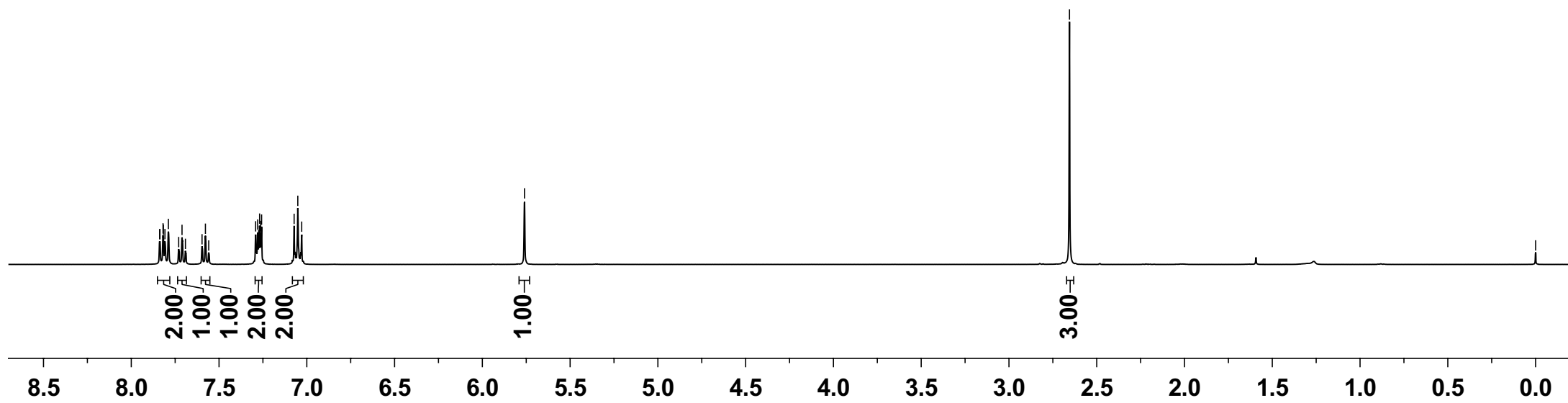
**3f** <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)



7.838  
7.837  
7.819  
7.817  
7.808  
7.789  
7.711  
7.597  
7.578  
7.291  
7.280  
7.274  
7.269  
7.263  
7.258  
7.072  
7.051  
5.928  
5.760



**3g** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



2.655

0.000

160.512  
158.093

145.163  
145.139

134.422  
132.992

129.946  
129.496

122.114

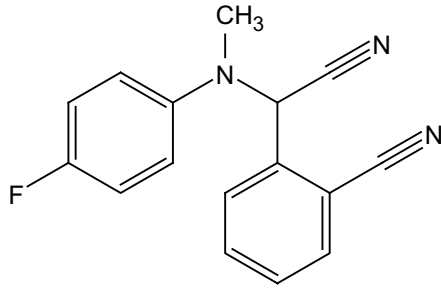
116.840  
116.180

115.955  
114.367  
112.618

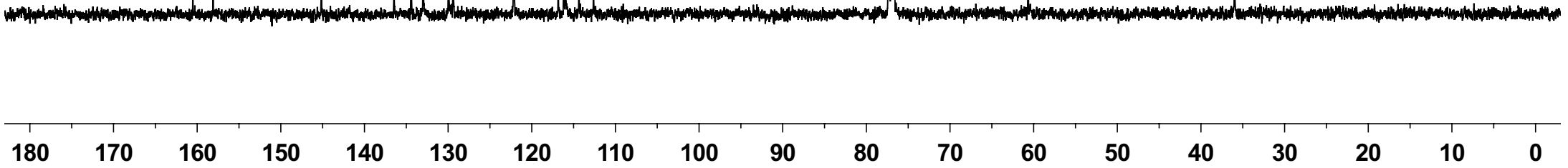
77.318  
77.000  
76.682

60.661

35.978



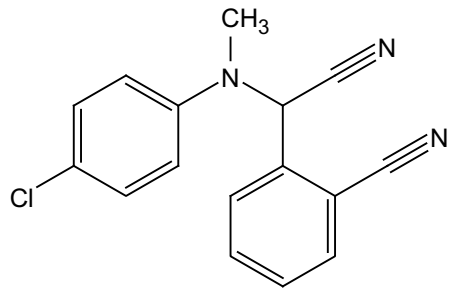
**3g**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )



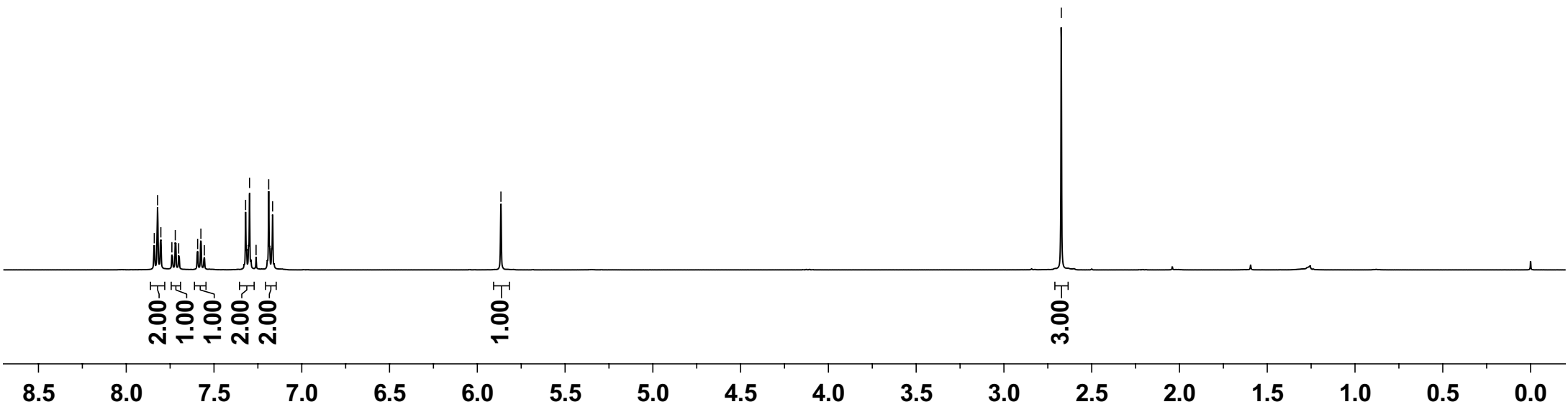
7.840  
7.822  
7.803  
7.740  
7.721  
7.701  
7.593  
7.575  
7.555  
7.320  
7.298  
7.260  
7.188  
7.166

5.865

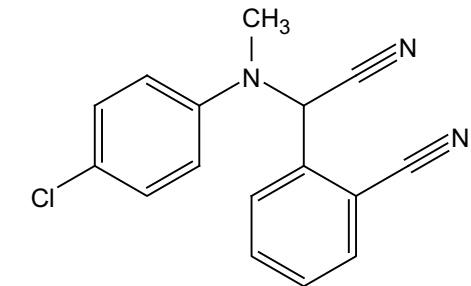
2.673



**3h** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)







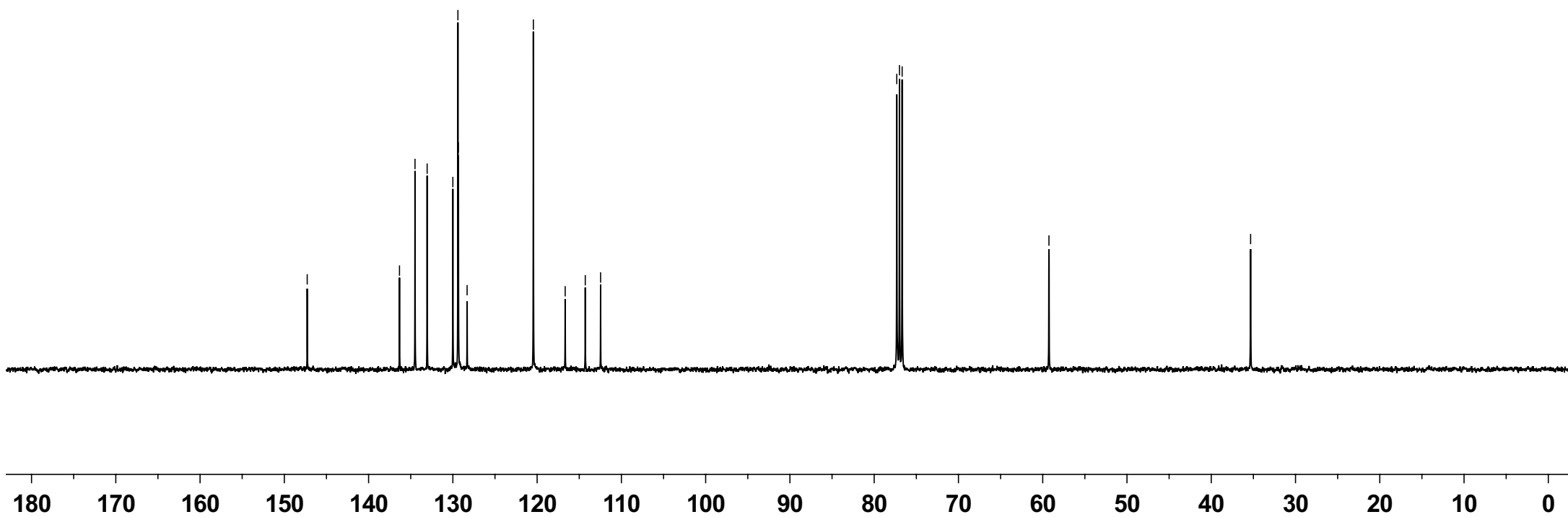
**3h**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

—147.285  
136.333  
134.492  
133.052  
130.001  
129.401  
129.342  
128.447  
116.670  
114.287  
112.467

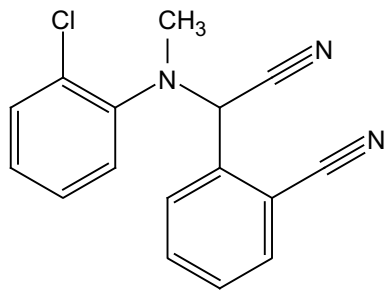
77.319  
77.000  
76.682

—59.261

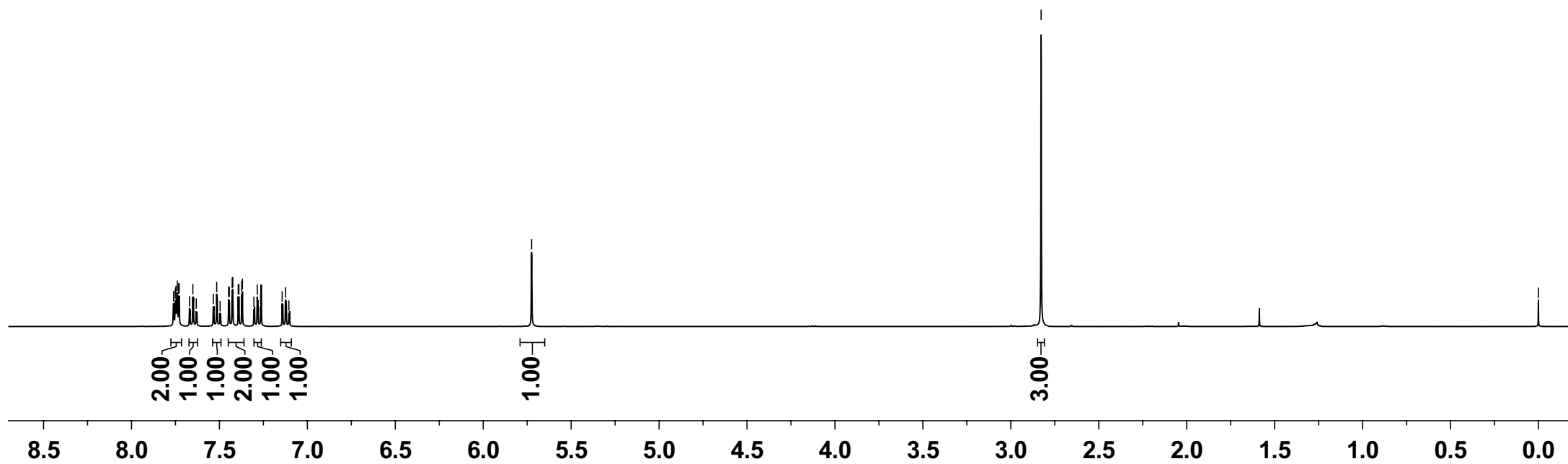
—35.328



7.761  
7.751  
7.748  
7.740  
7.732  
7.729  
7.651  
7.516  
7.448  
7.444  
7.428  
7.424  
7.393  
7.389  
7.373  
7.369  
7.285  
7.124  
7.125



3i <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



—2.828

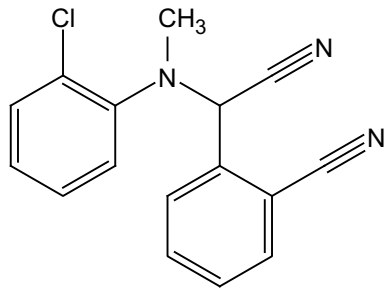
—0.000

—145.751  
134.037  
132.724  
130.935  
129.698  
129.034  
127.715  
123.981  
116.291  
115.794  
113.033

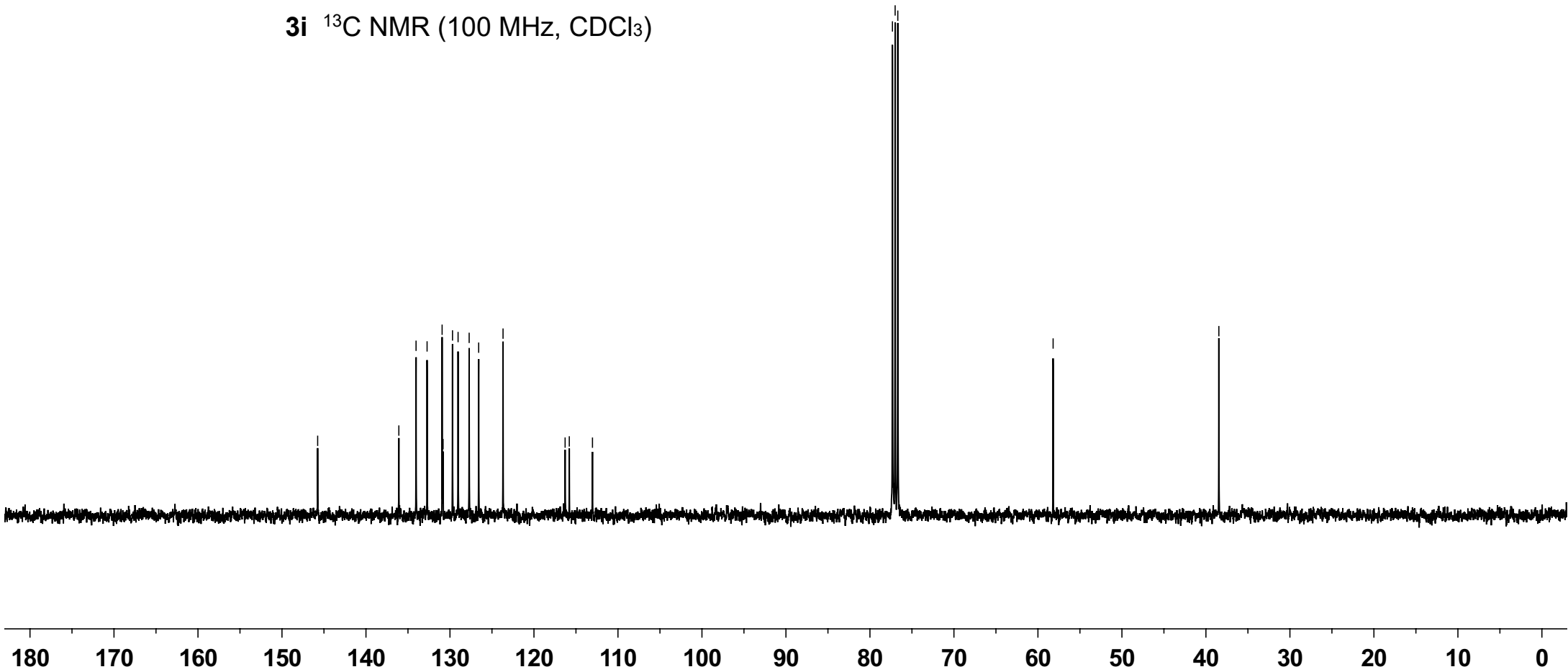
77.319  
77.000  
76.683

—58.192

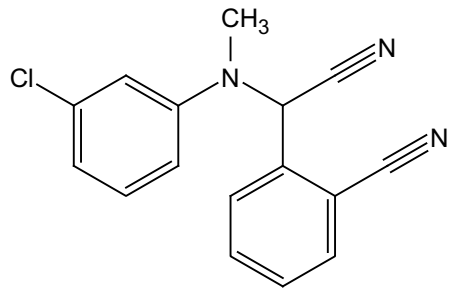
—38.459



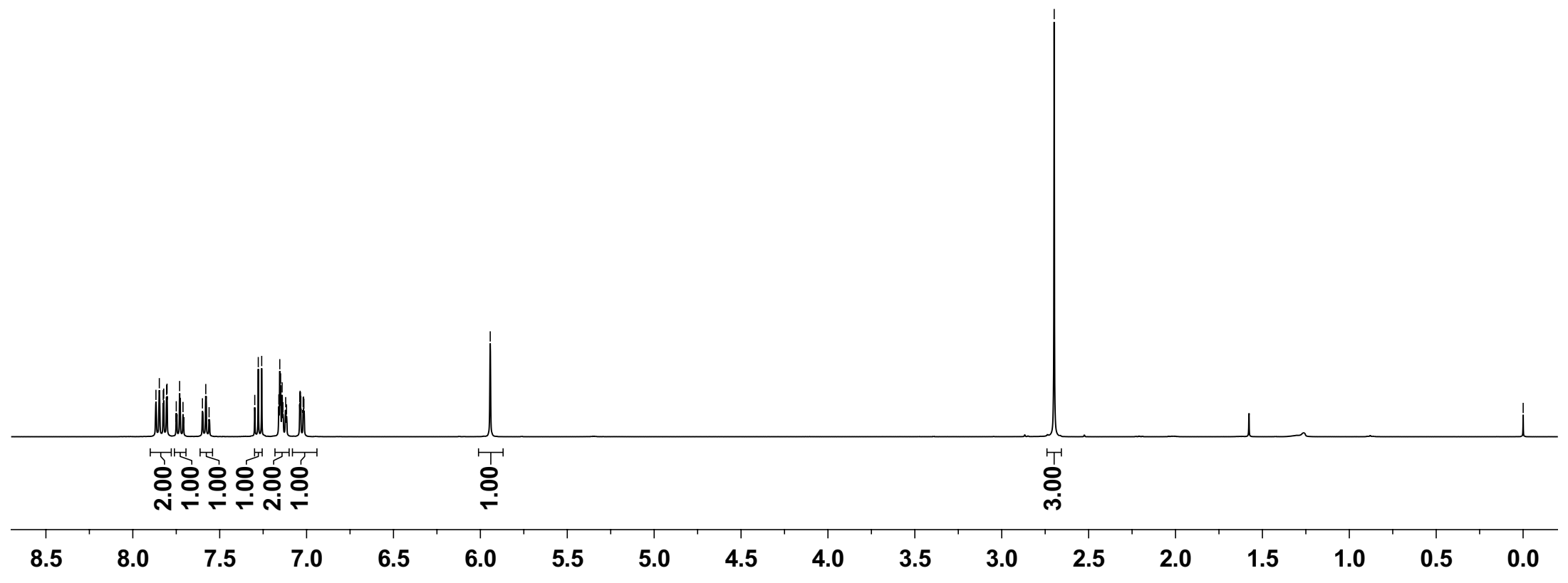
**3i**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )



7.867  
7.847  
7.825  
7.822  
7.806  
7.803  
7.731  
7.580  
7.278  
7.258  
7.160  
7.154  
7.149  
7.141  
7.039  
7.037  
5.943



3j <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



2.698

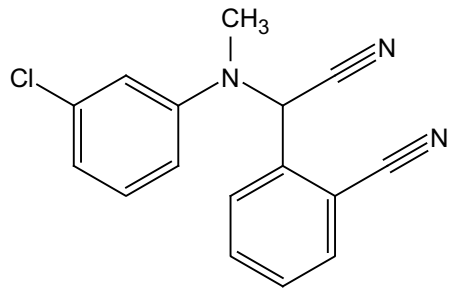
0.000

—149.701  
136.257  
134.558  
133.088  
130.406  
130.044  
129.323  
122.661  
118.505  
116.536  
116.509  
114.295  
112.412

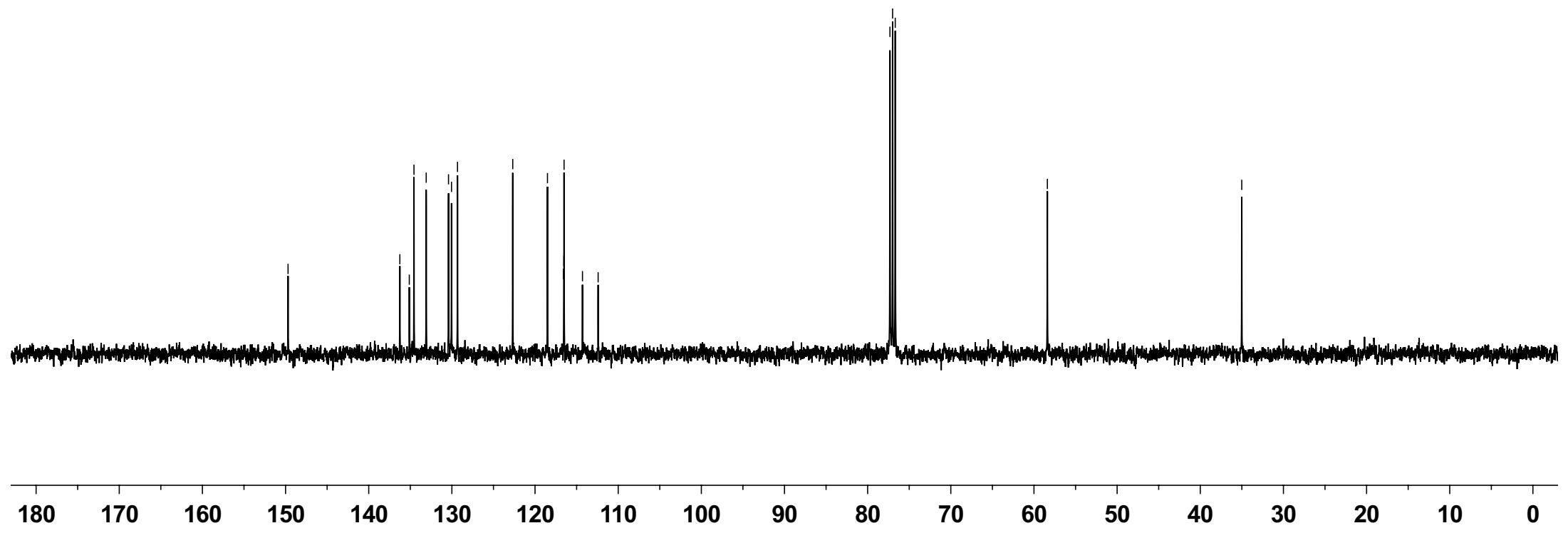
77.319  
77.000  
76.683

—58.388

—35.012



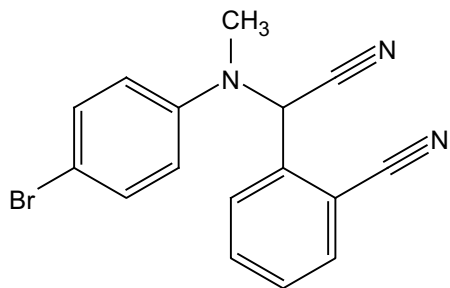
3j <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)



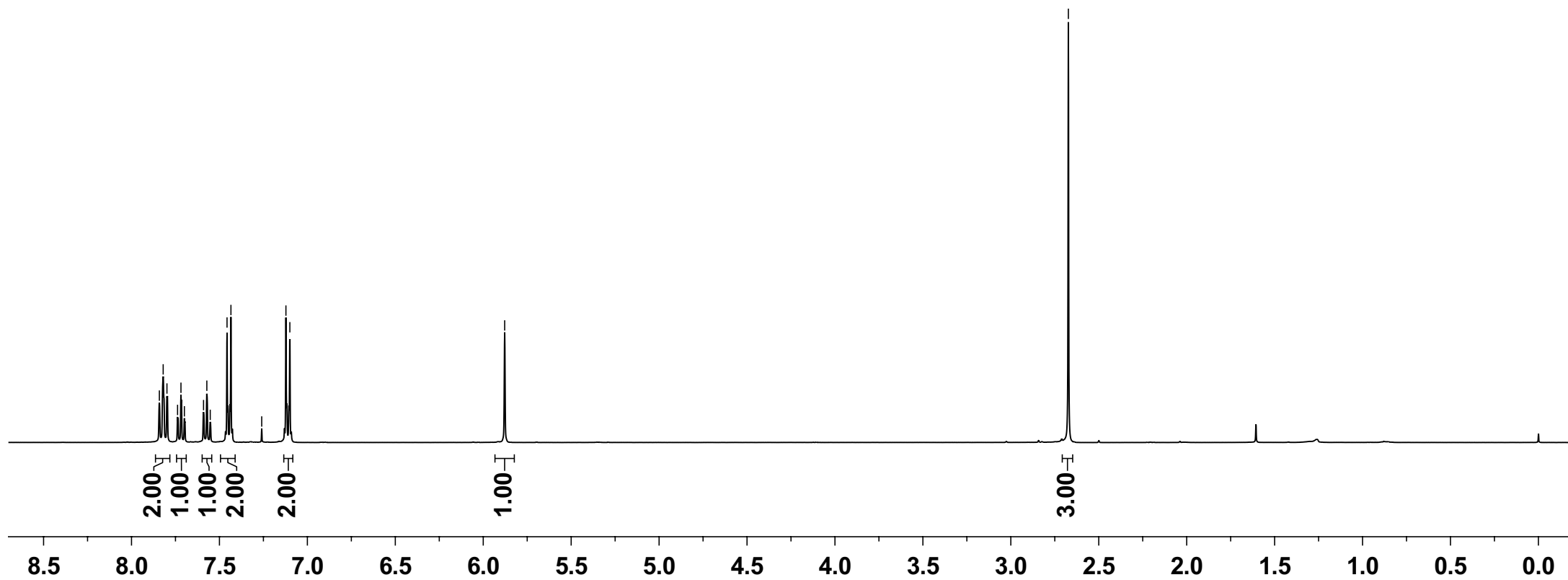
7.842  
7.820  
7.799  
7.738  
7.719  
7.699  
7.590  
7.572  
7.552  
7.457  
7.435  
7.260  
7.122  
7.100

5.878

2.673



**3k**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

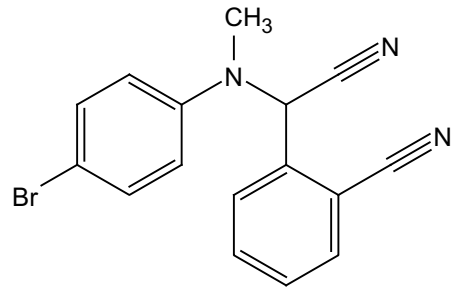


—147.698  
136.294  
134.493  
133.054  
132.313  
129.999  
129.308  
120.587  
116.626  
115.729  
114.263  
112.420

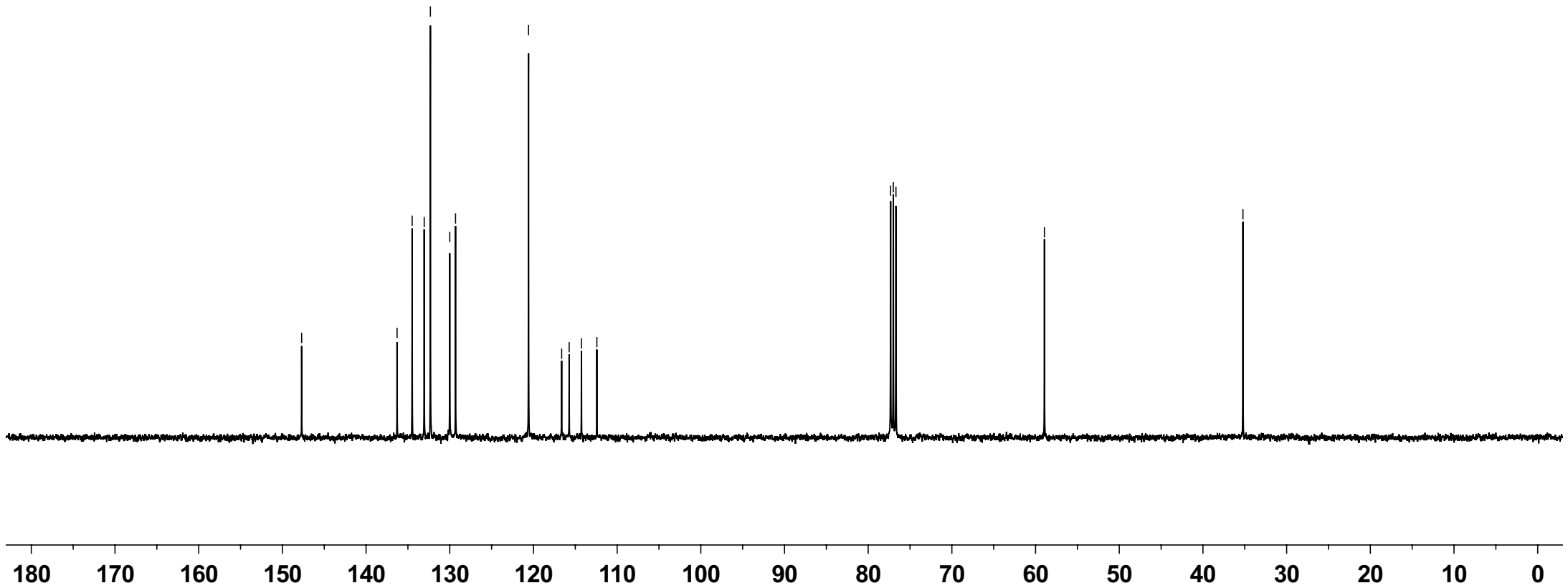
77.318  
77.000  
76.682

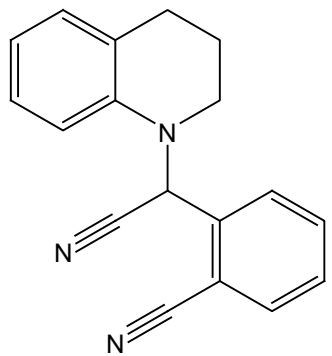
—58.942

—35.219

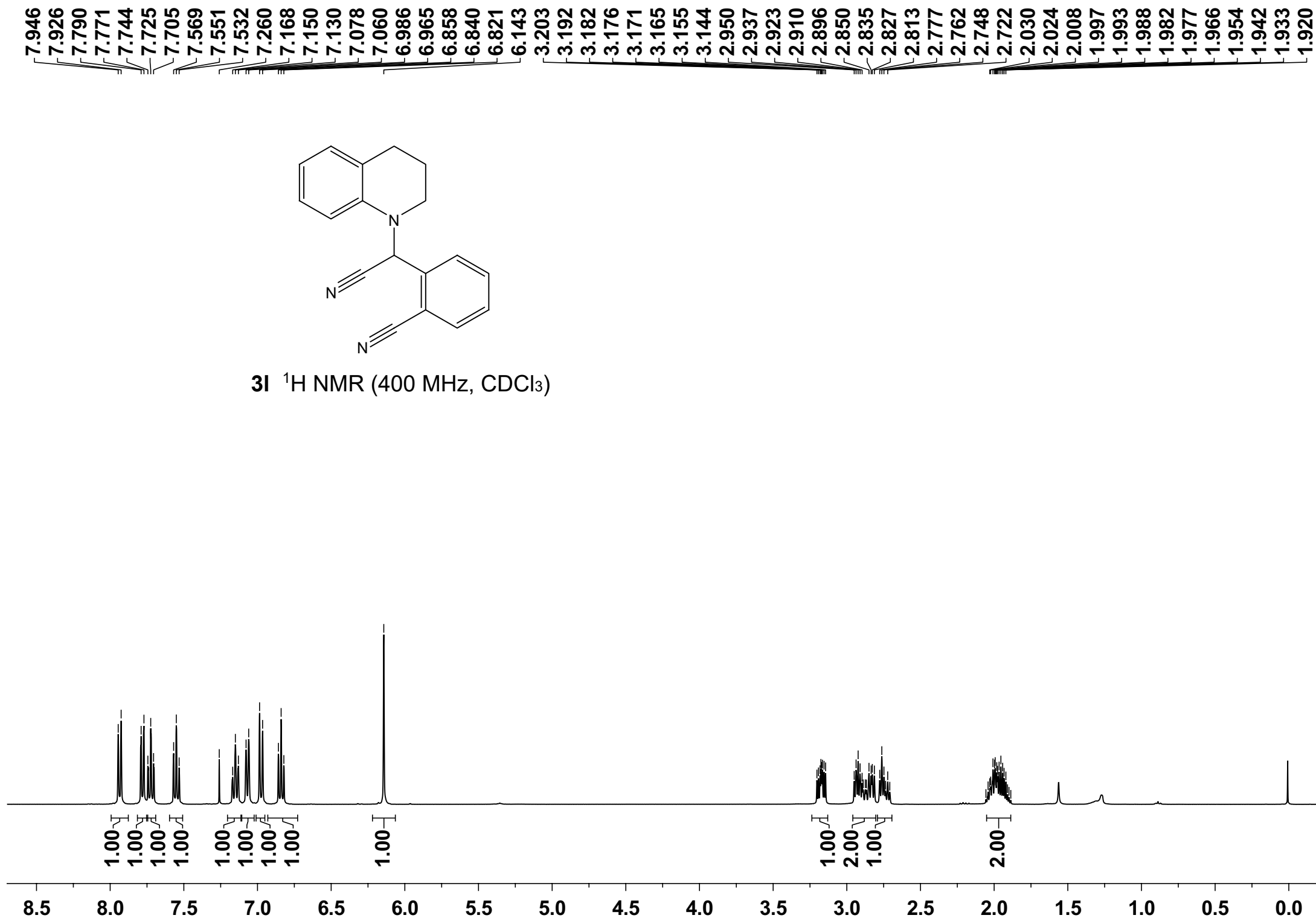


**3k** <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)





**3I**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )





142.957  
137.029  
134.607  
132.981  
129.741  
129.631  
129.221  
127.139  
126.287  
120.223  
116.358  
115.213  
113.281  
112.191

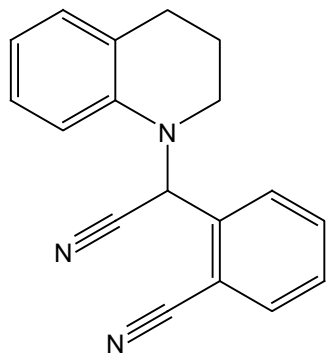
77.318  
77.000  
76.683

54.959

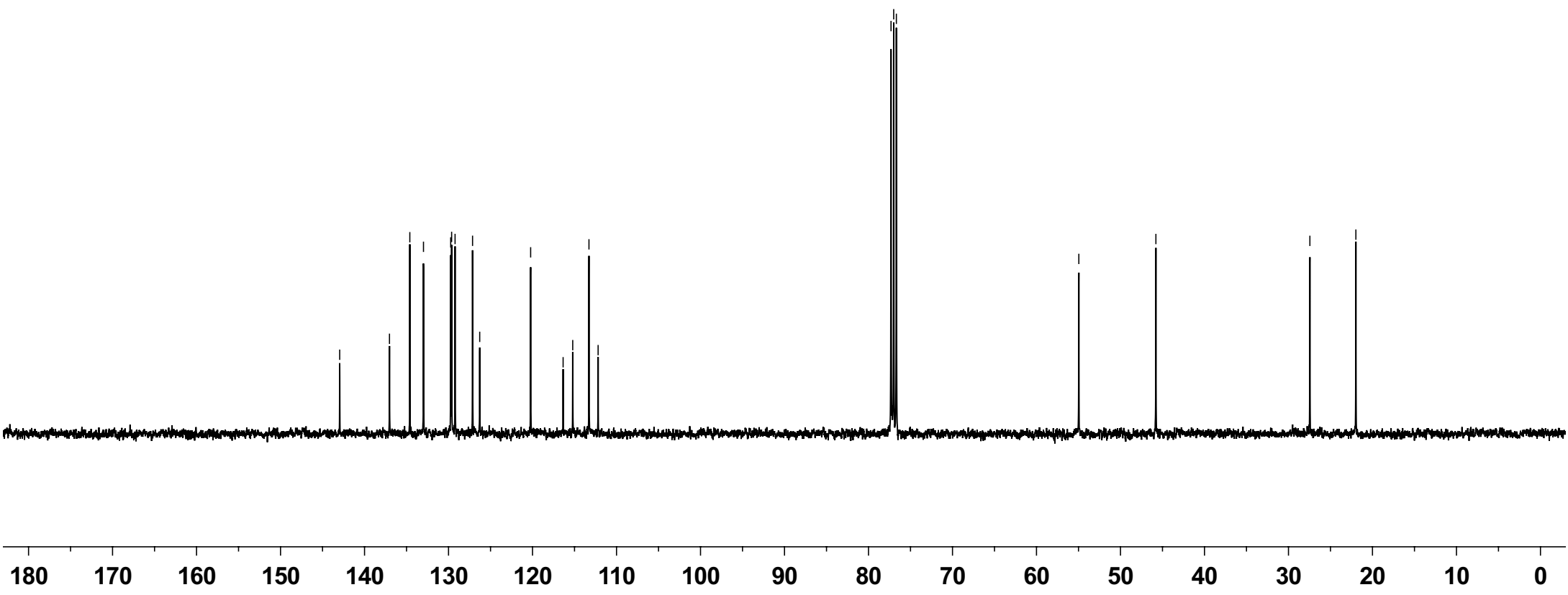
45.784

27.452

21.975

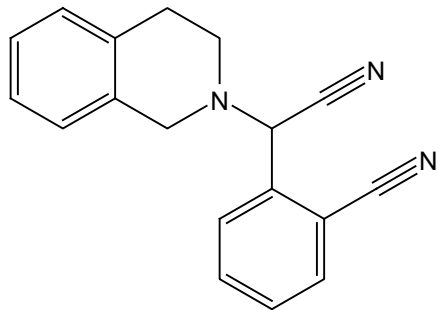


**3I** <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

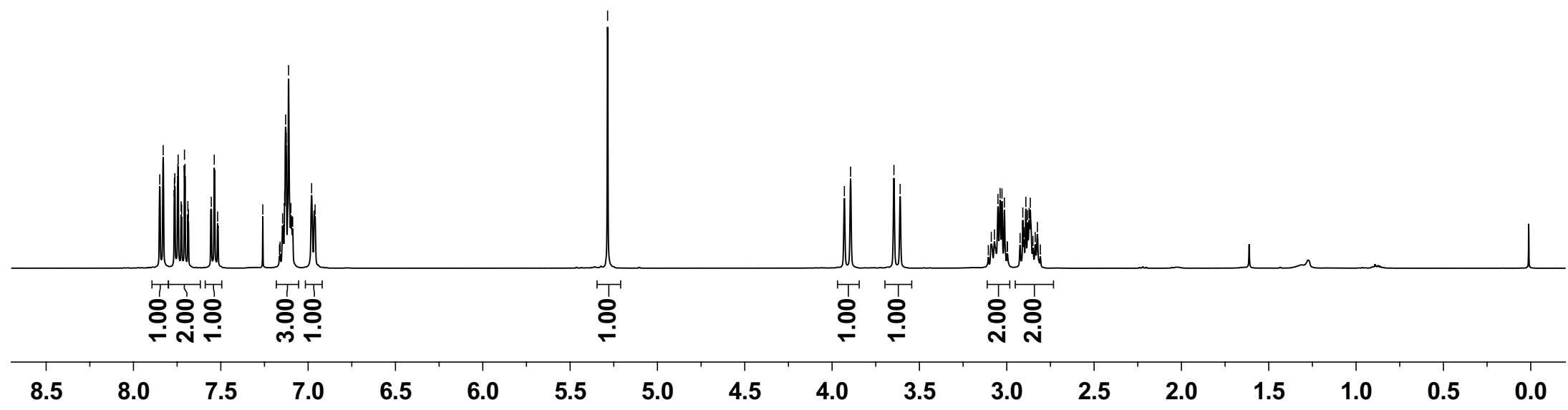


7.849  
7.830  
7.766  
7.763  
7.746  
7.744  
7.727  
7.724  
7.708  
7.705  
7.689  
7.555  
7.537  
7.260  
7.134  
7.129  
7.126  
7.112  
7.099  
6.980  
6.969

3.930  
3.894  
3.646  
3.610  
3.106  
3.089  
3.071  
3.050  
3.038  
3.027  
3.014  
2.998  
2.996  
2.924  
2.908  
2.901  
2.891  
2.881  
2.872  
2.865  
2.850  
2.837  
2.825  
2.808



**3m** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



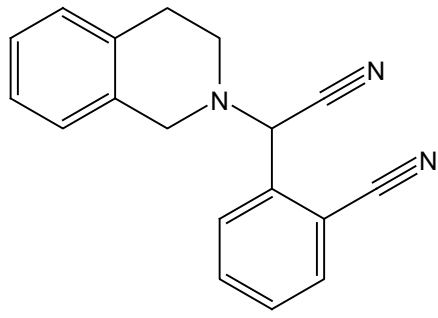
136.779  
134.090  
133.508  
132.881  
132.612  
129.624  
128.711  
128.654  
126.444  
126.385  
125.787  
116.465  
113.885  
113.351

77.318  
77.000  
76.681

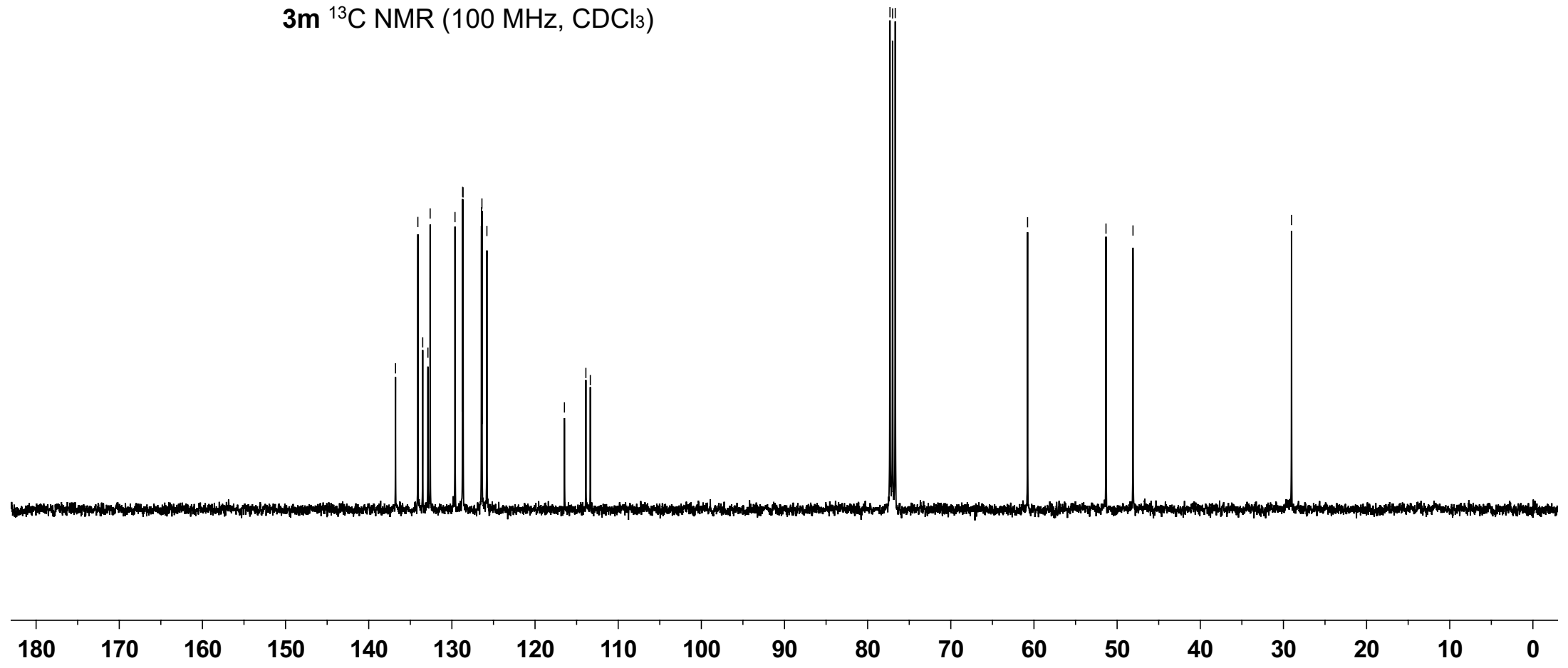
60.769

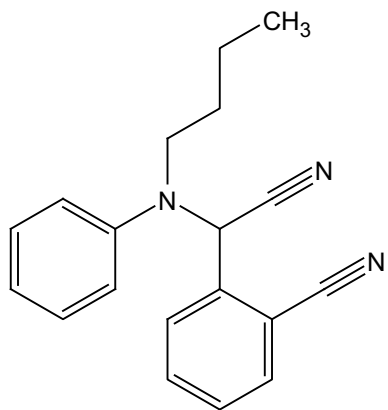
51.339  
48.092

29.024

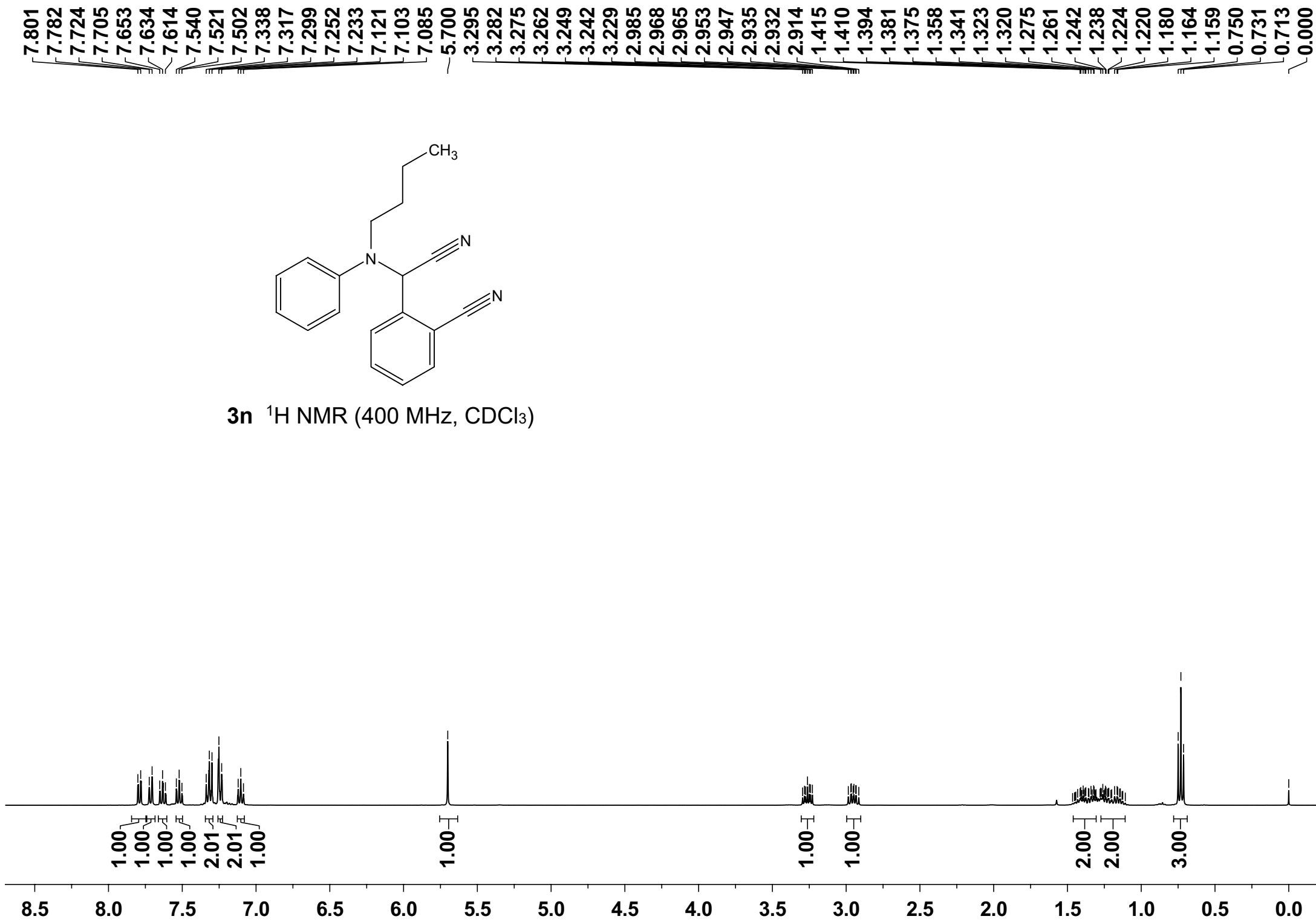


3m <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)





**3n**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



—146.581  
137.193  
134.311  
132.770  
129.627  
129.514  
129.270  
124.332  
122.560  
116.877  
115.622  
112.796

77.317  
77.000  
76.681

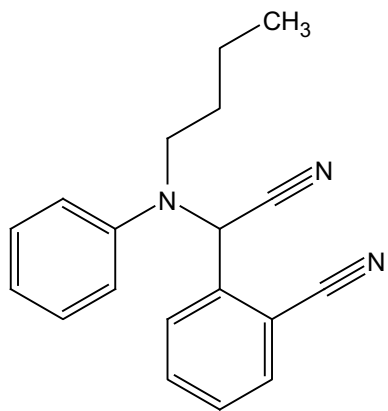
—59.624

—49.145

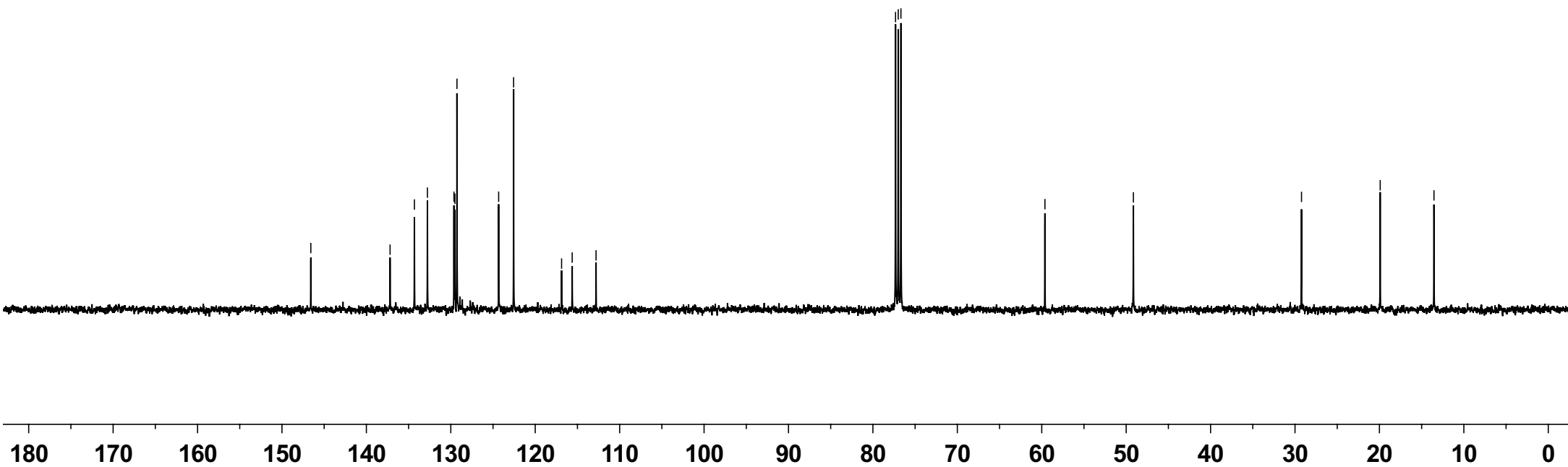
—29.231

—19.910

—13.539



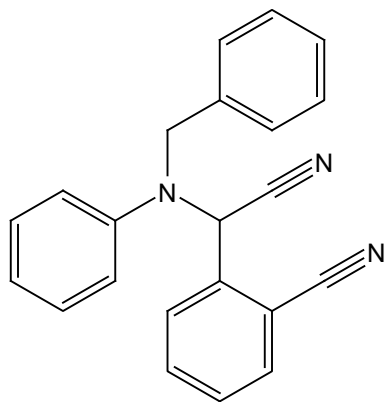
**3n**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )



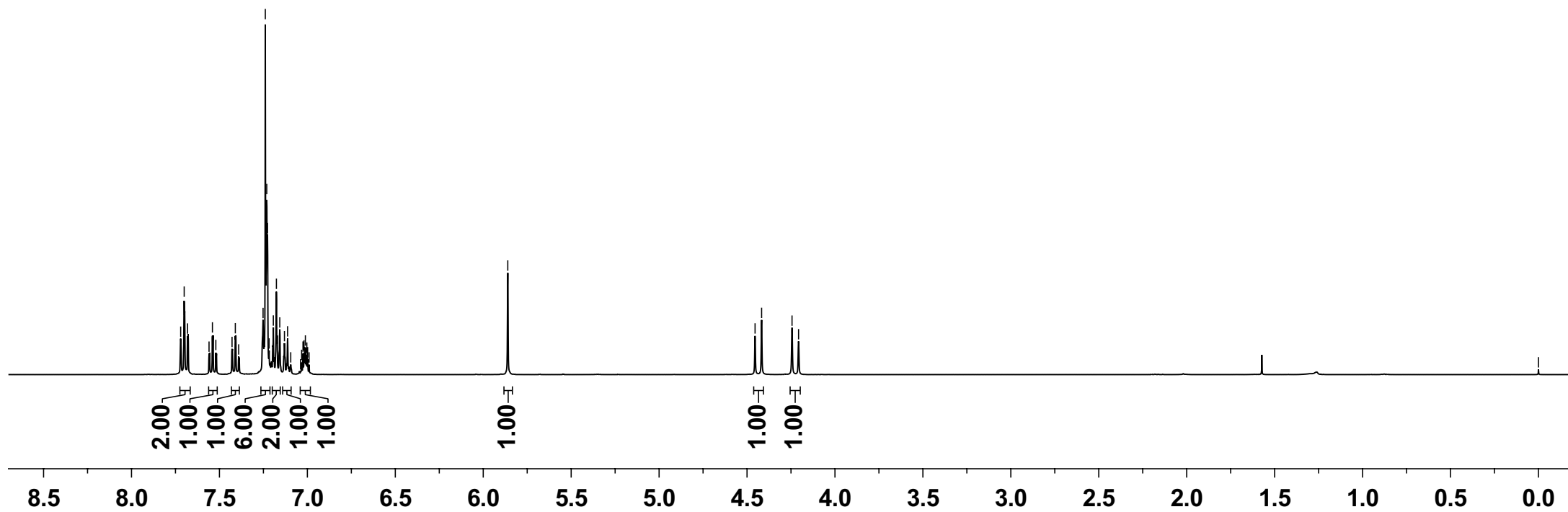
7.720  
7.700  
7.681  
7.540  
7.428  
7.410  
7.252  
7.245  
7.239  
7.231  
7.227  
7.194  
7.176  
7.157  
7.130  
7.112  
7.011  
5.860

4.454  
4.417  
4.244  
4.207

— 0.000



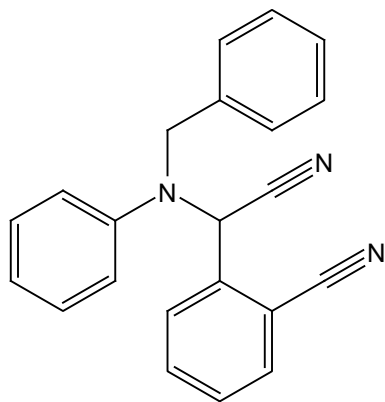
**3o** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



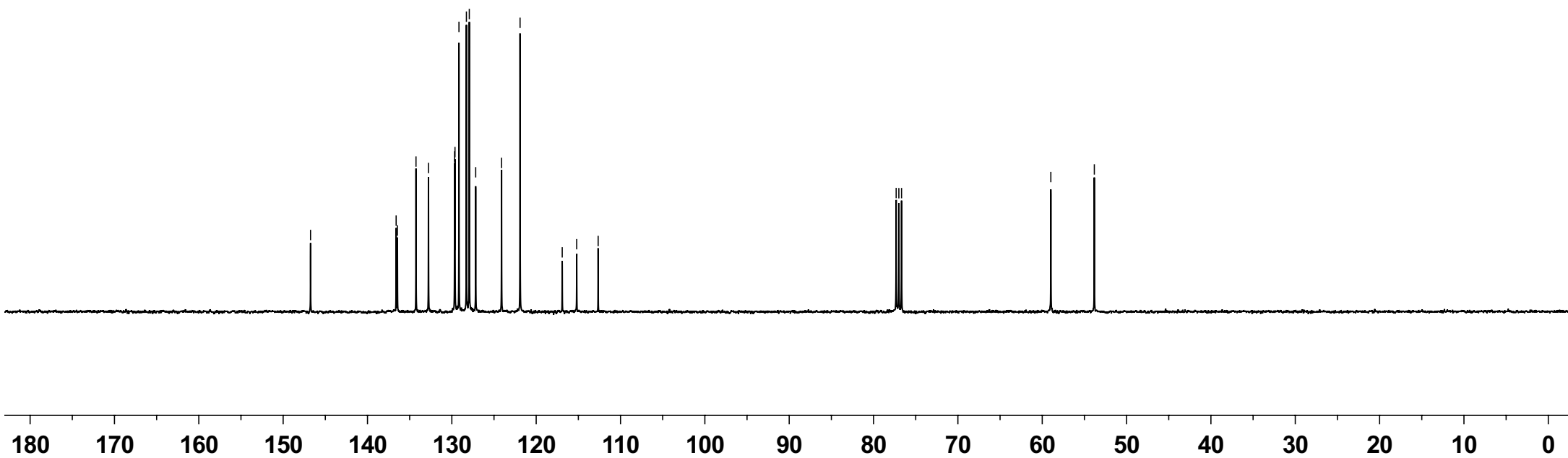
146.751  
136.603  
136.451  
134.249  
132.769  
129.672  
129.624  
129.155  
128.272  
127.929  
127.170  
124.105  
121.910  
116.912  
115.194  
112.652

77.318  
77.000  
76.681

58.979  
53.824



**3o**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )



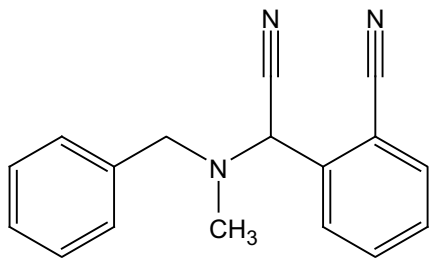
7.796  
7.776  
7.673  
7.654  
7.635  
7.530  
7.511  
7.492  
7.411  
7.394  
7.342  
7.324  
7.306  
7.285  
7.268  
7.256

5.234

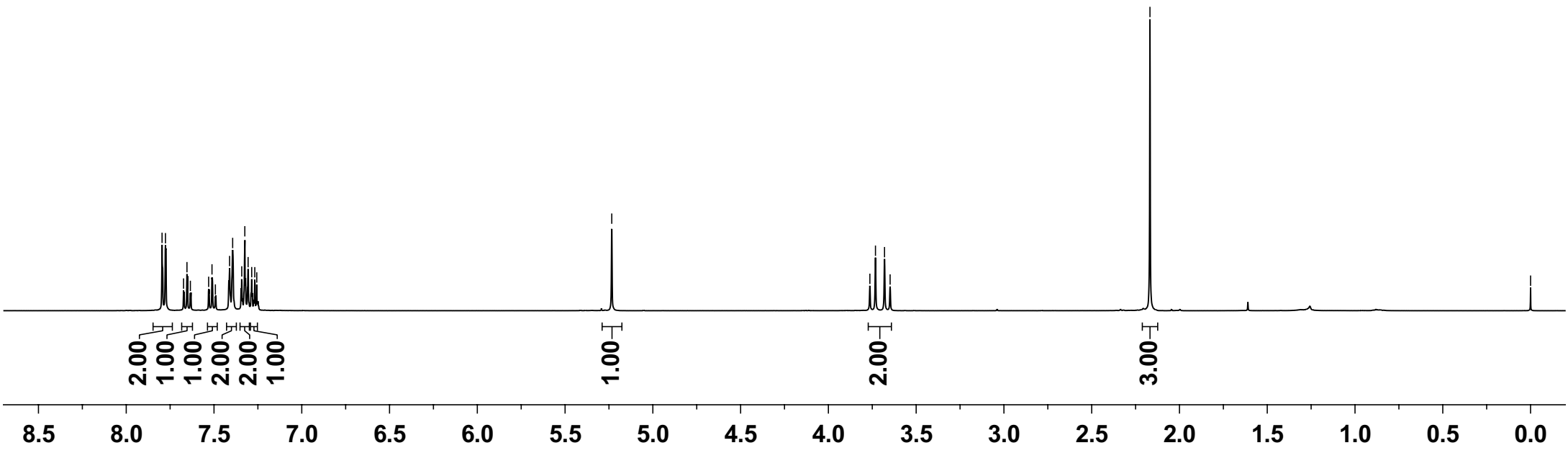
3.764  
3.732  
3.680  
3.648

2.168

0.000



3p <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



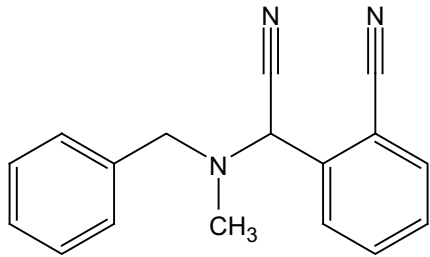


137.117  
136.587  
134.200  
132.508  
129.412  
128.981  
128.819  
128.328  
127.571  
116.756  
113.657  
112.888

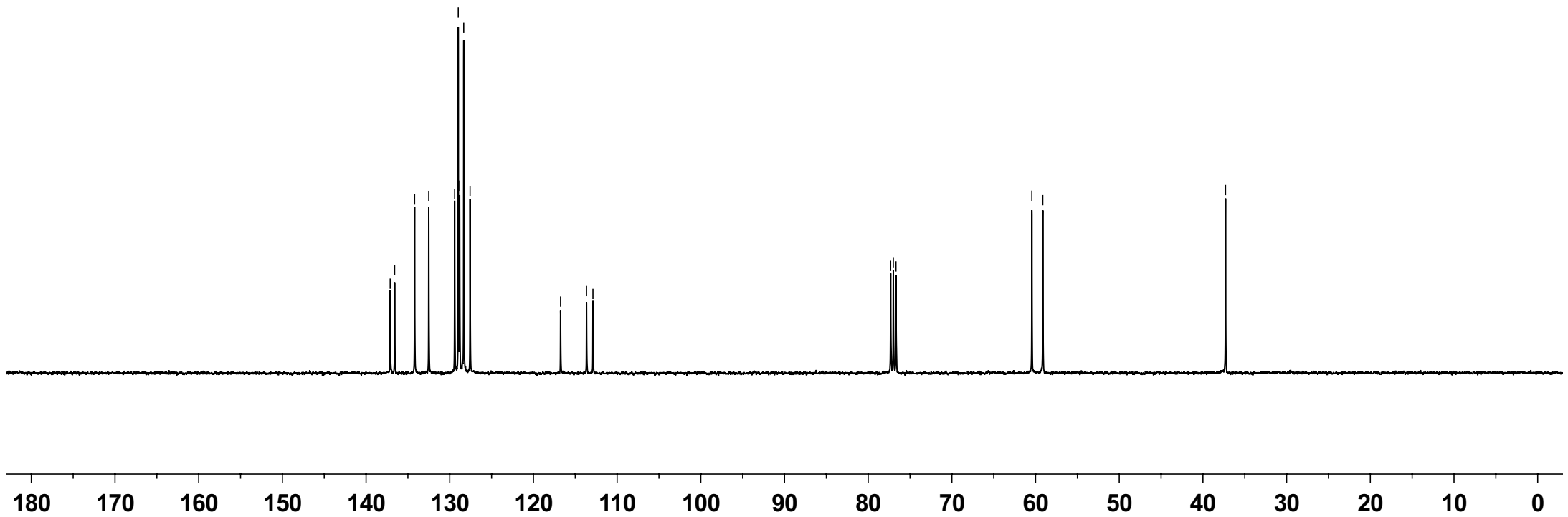
77.318  
77.000  
76.681

60.445  
59.137

37.301



**3p** <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

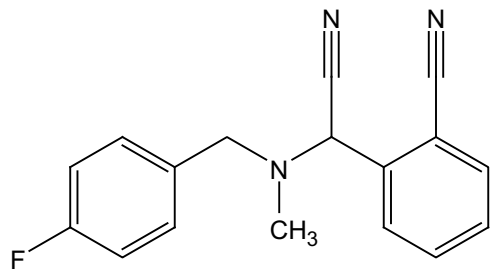


7.788  
7.767  
7.674  
7.655  
7.635  
7.533  
7.514  
7.495  
7.392  
7.371  
7.350  
7.260  
7.016  
6.995  
6.973

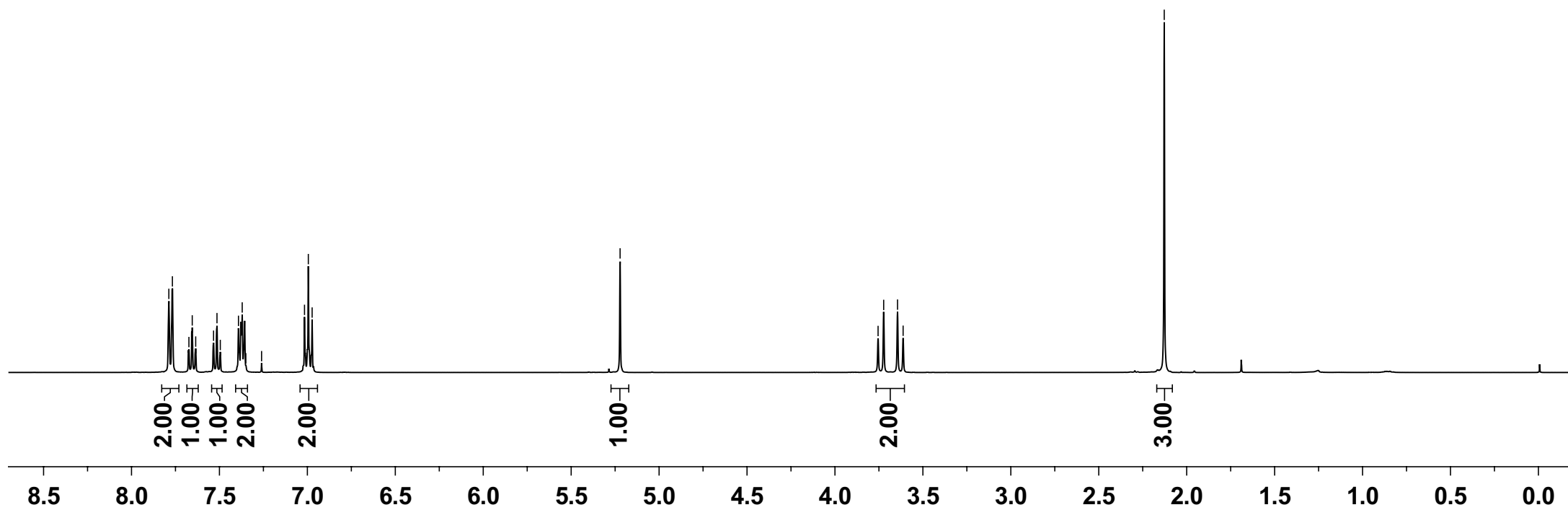
5.222

3.755  
3.723  
3.644  
3.612

2.128



**3q** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



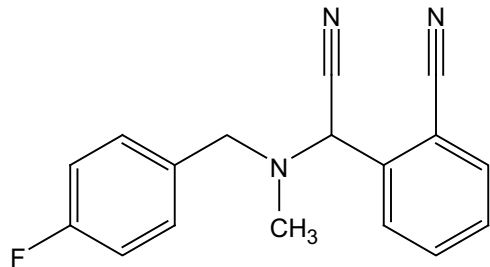
163.491  
161.047

137.105  
134.283  
132.620  
132.399  
132.370  
130.735  
130.653  
129.532  
128.899  
116.830  
115.350  
115.138  
113.603  
112.932

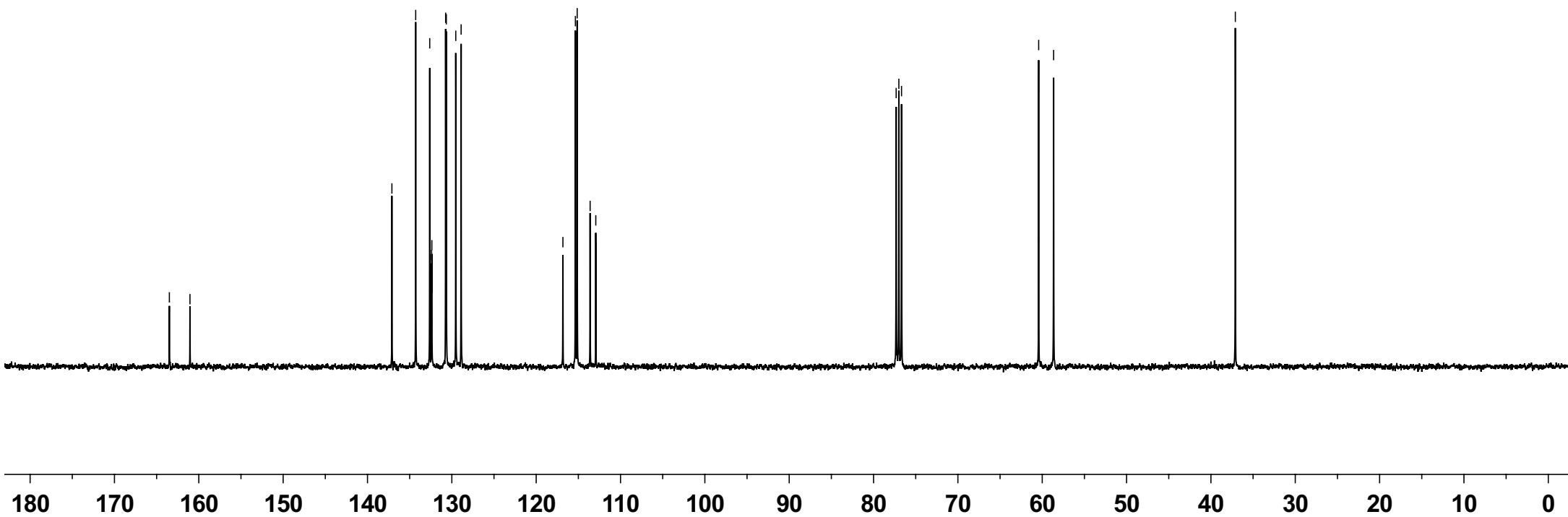
77.318  
77.000  
76.682

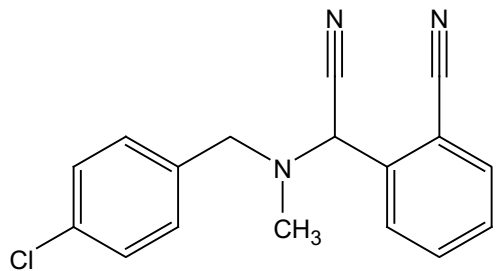
60.422  
58.651

37.105

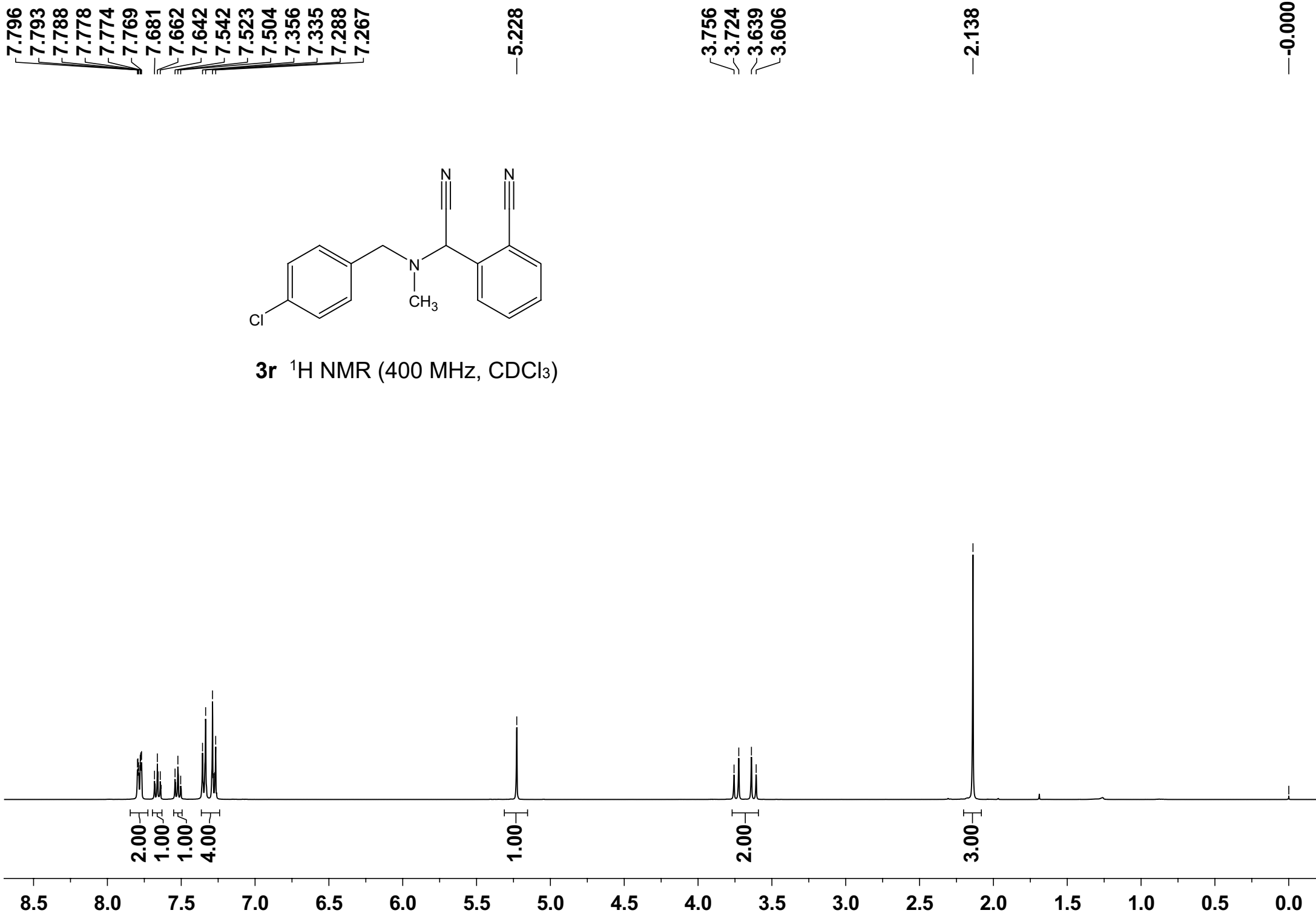


**3q**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )





3r <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

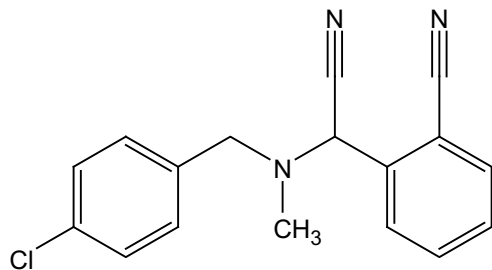


137.022  
135.189  
134.283  
133.397  
132.634  
130.363  
129.563  
128.877  
128.553  
116.818  
113.565  
112.924

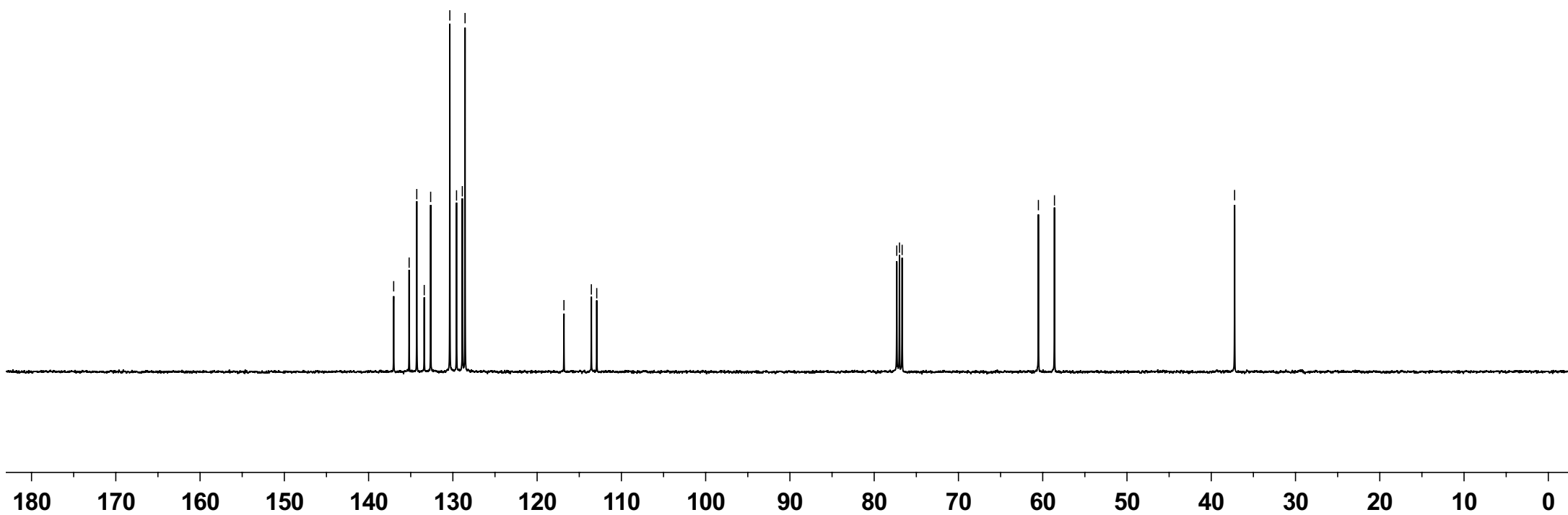
77.319  
77.000  
76.682

60.511  
58.607

37.228



**3r**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

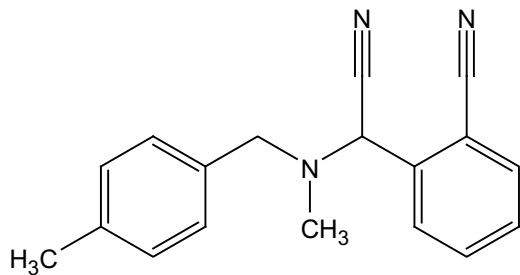


7.793  
7.774  
7.672  
7.653  
7.634  
7.529  
7.510  
7.490  
7.310  
7.290  
7.260  
7.149  
7.129

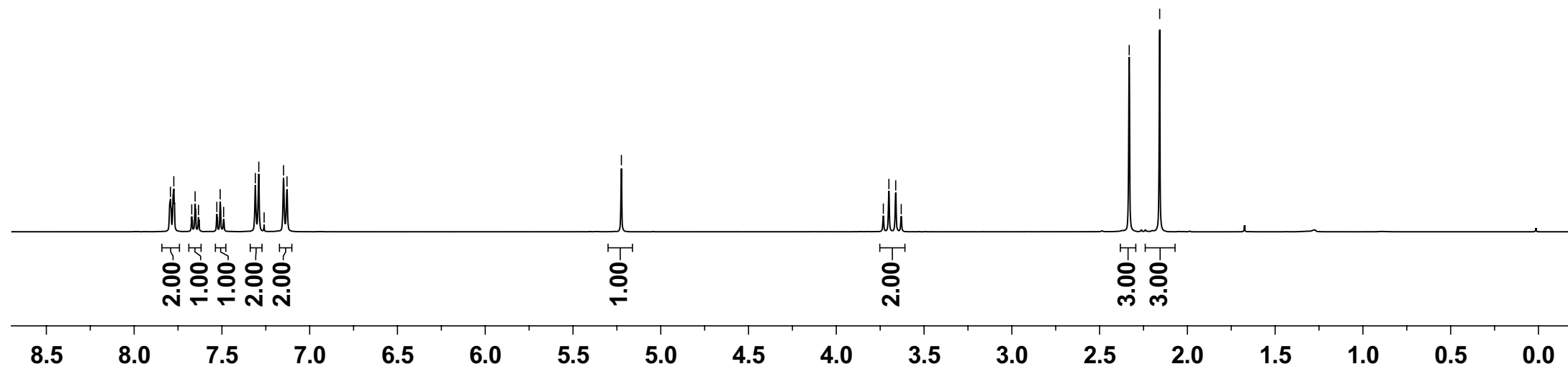
5.224

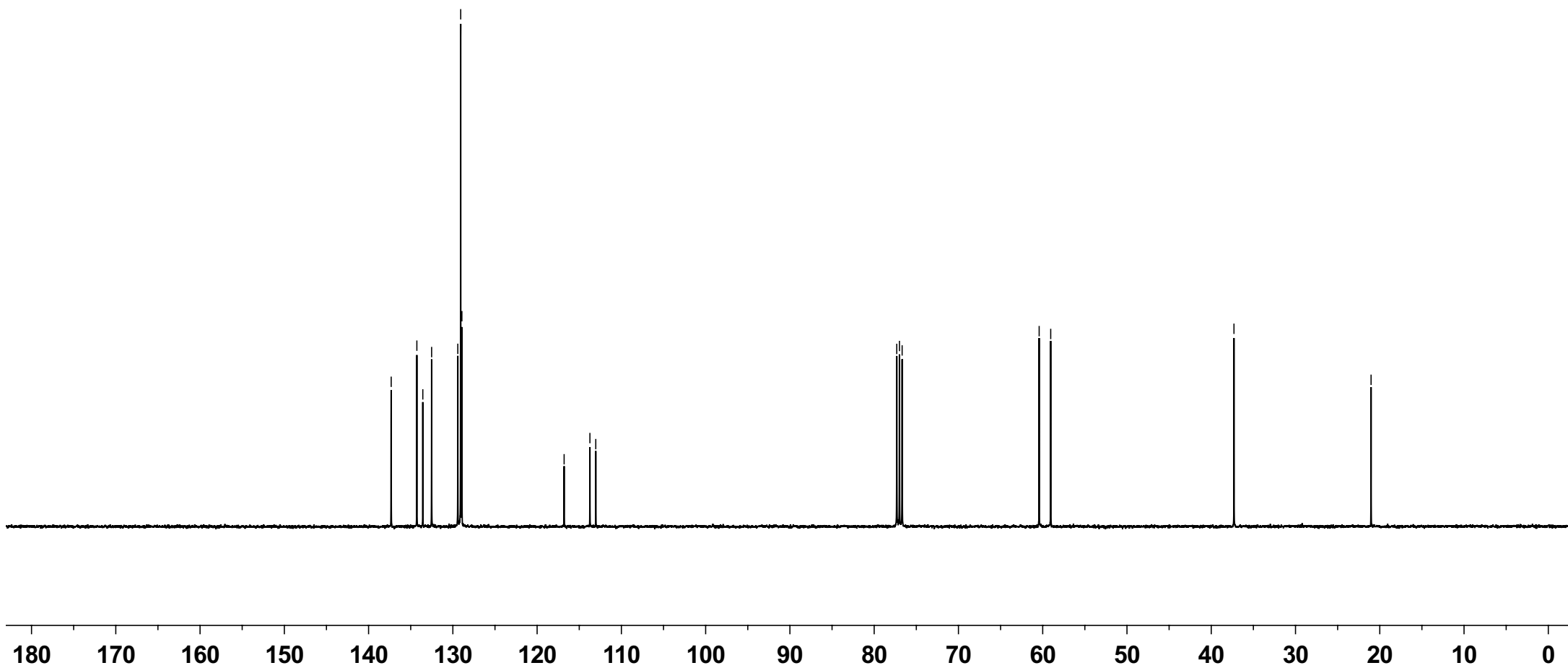
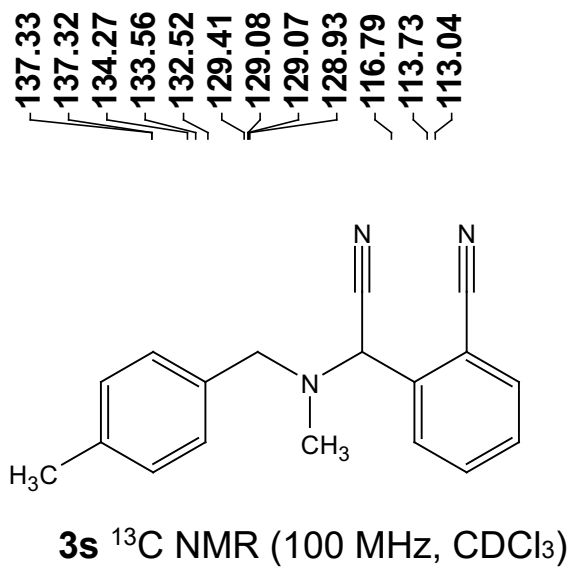
3.732  
3.700  
3.662  
3.630

2.331  
2.158



**3s**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



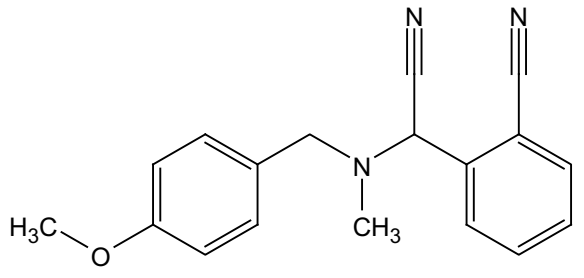


7.781  
7.761  
7.661  
7.642  
7.623  
7.518  
7.499  
7.480  
7.336  
7.314  
6.869  
6.847

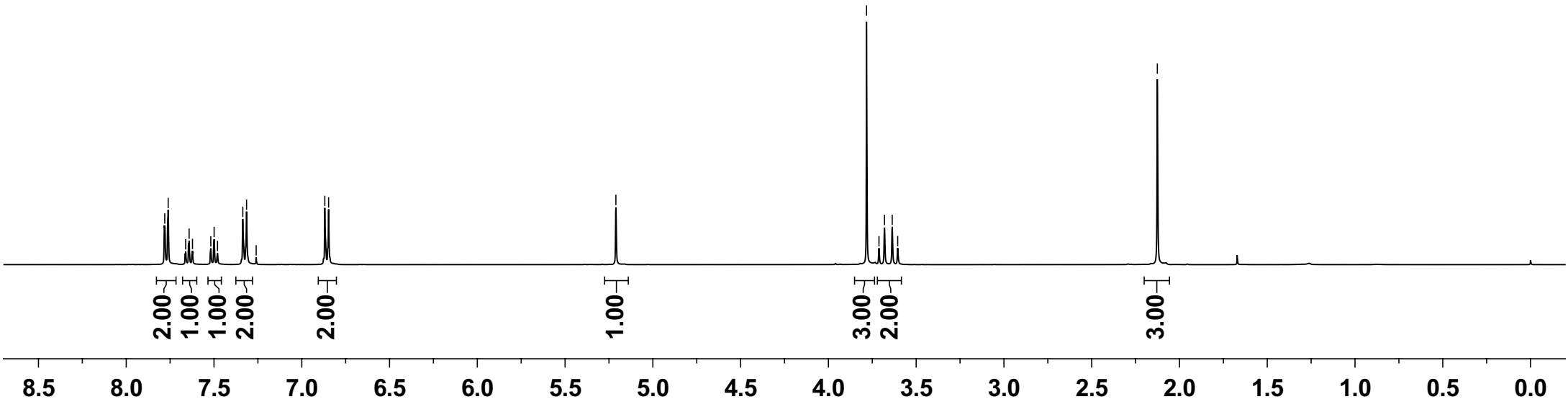
5.211

3.783  
3.712  
3.680  
3.636  
3.605

2.126



**3t** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)





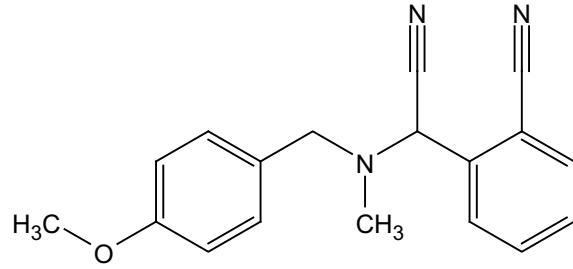
—159.148

137.326  
134.303  
132.556  
130.371  
129.424  
128.927  
128.651  
116.856  
113.783  
113.729  
112.964

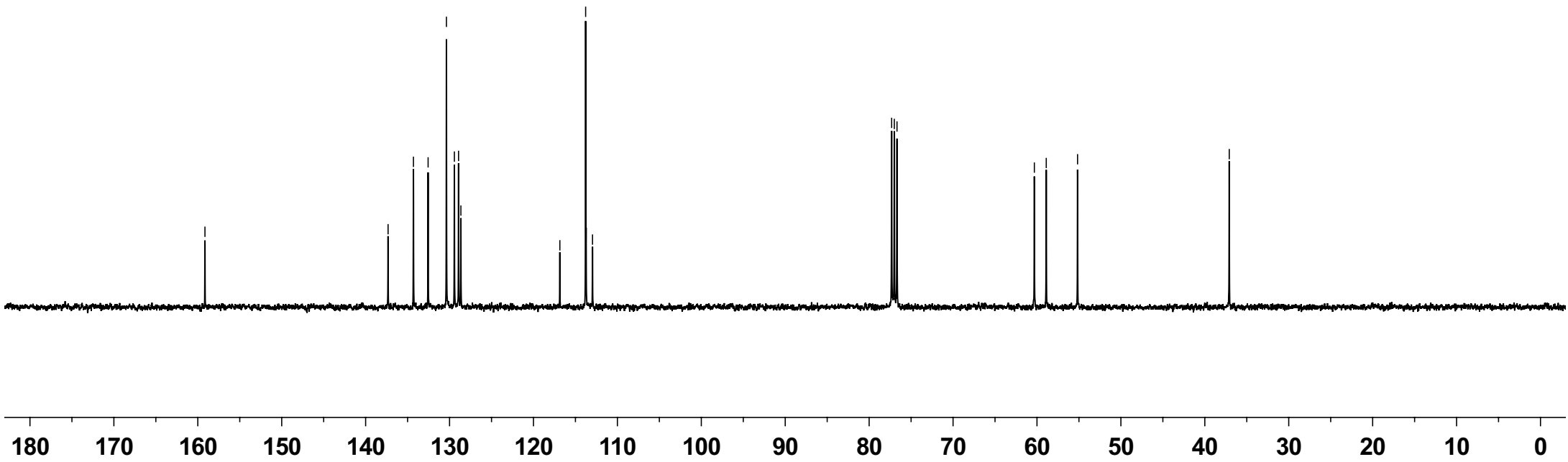
77.317  
77.000  
76.681

60.313  
58.895  
55.163

—37.088



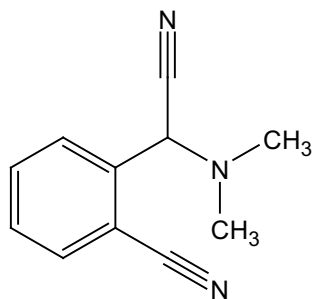
**3t** <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)



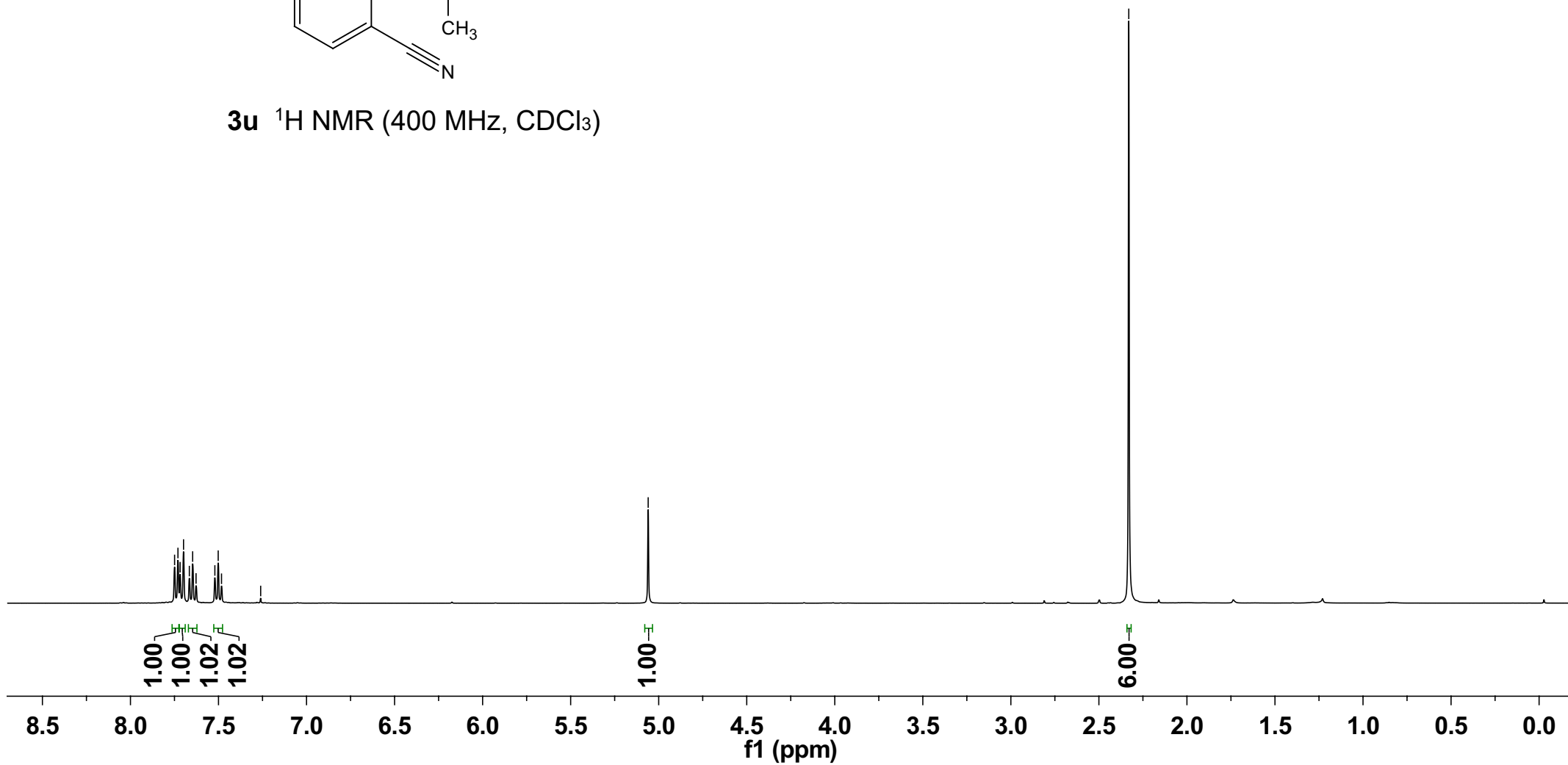
7.75  
7.73  
7.72  
7.70  
7.67  
7.65  
7.63  
7.52  
7.50  
7.48  
7.26

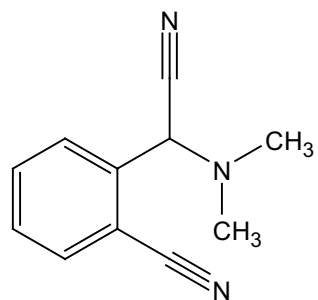
5.06

2.33

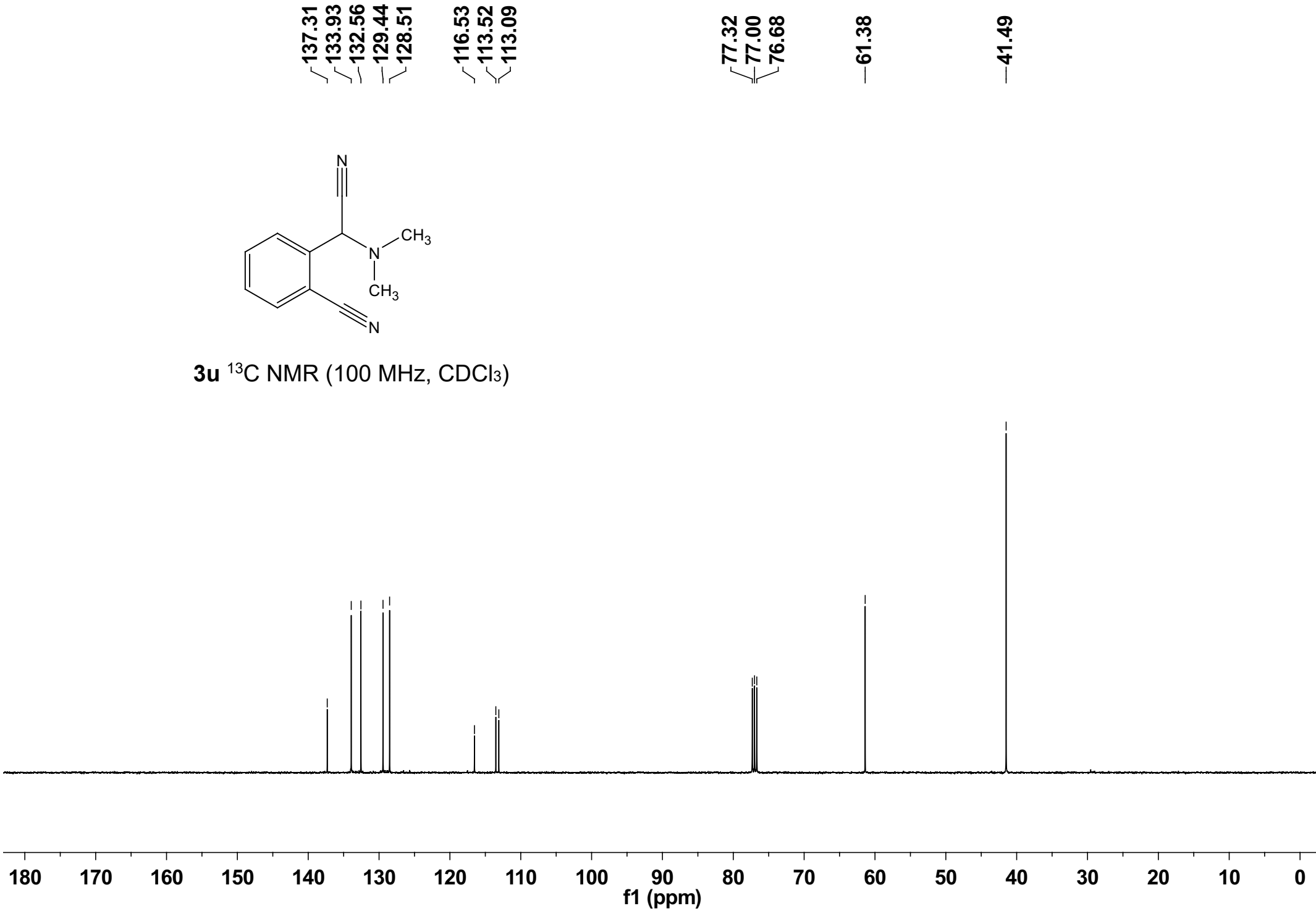


**3u**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )





**3u** <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

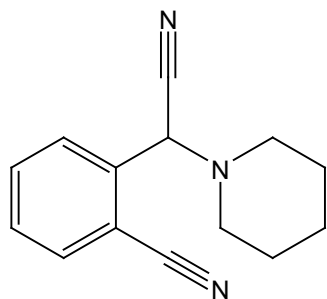


7.73  
7.71  
7.70  
7.68  
7.63  
7.62  
7.60  
7.50  
7.48  
7.46  
7.26

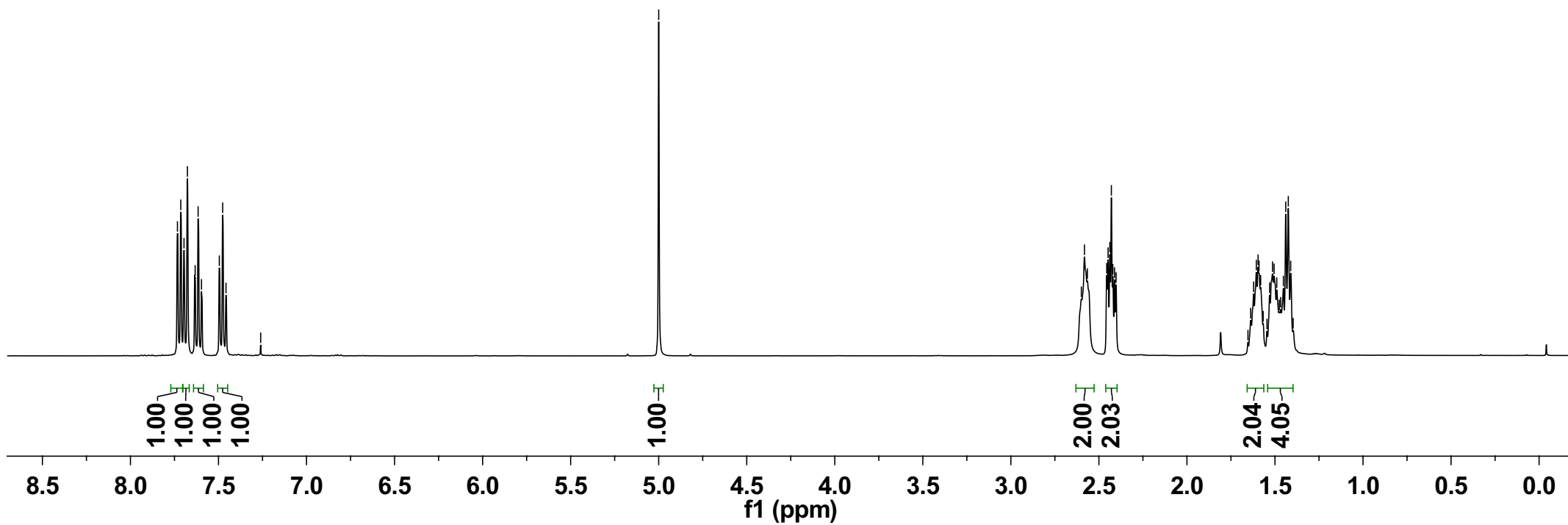
5.00

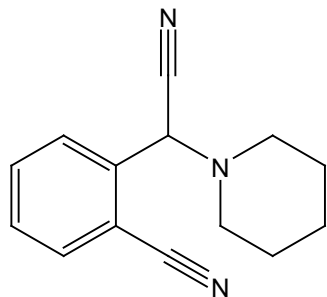
2.60  
2.58  
2.57  
2.46  
2.45  
2.44  
2.43  
2.42  
2.41  
2.40

1.62  
1.61  
1.60  
1.59  
1.58  
1.53  
1.51  
1.50  
1.49  
1.45  
1.44  
1.42  
1.41

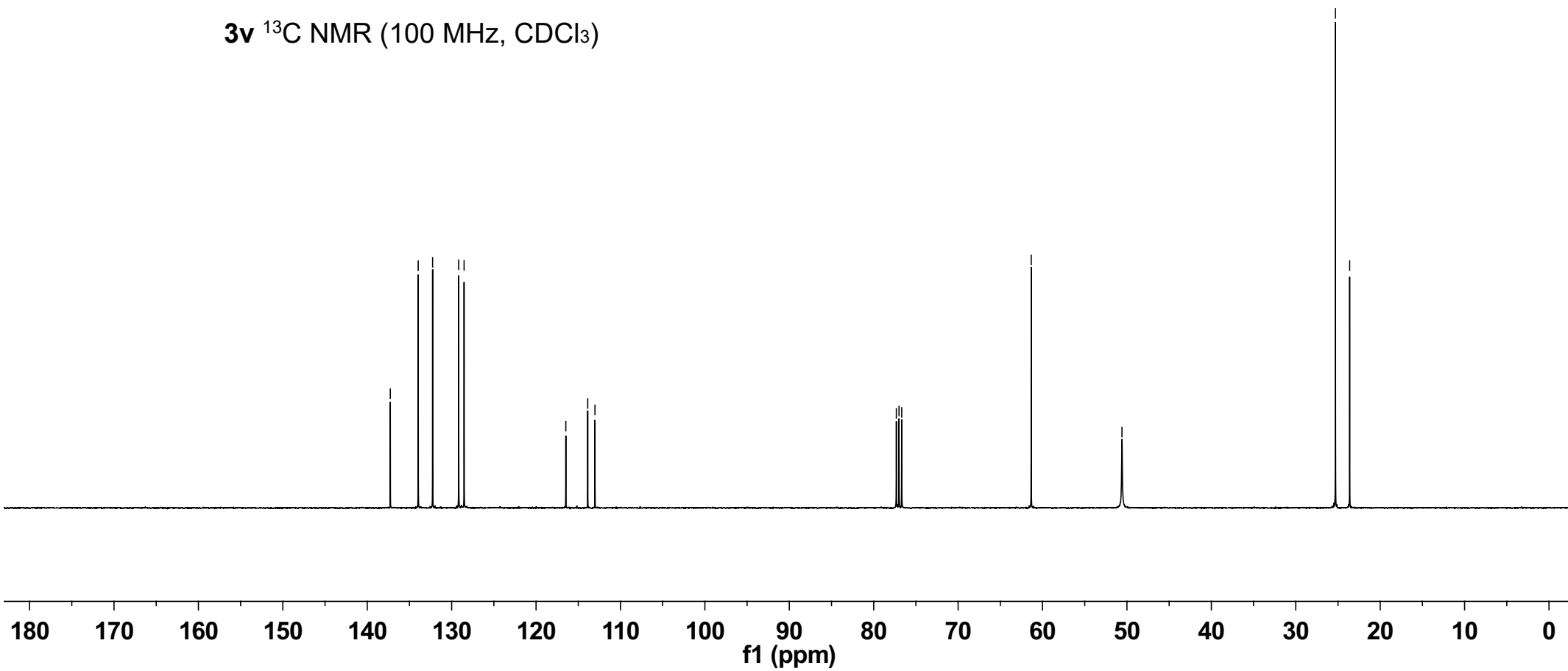


**3v**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )





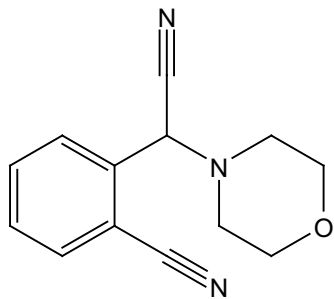
**3v**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )



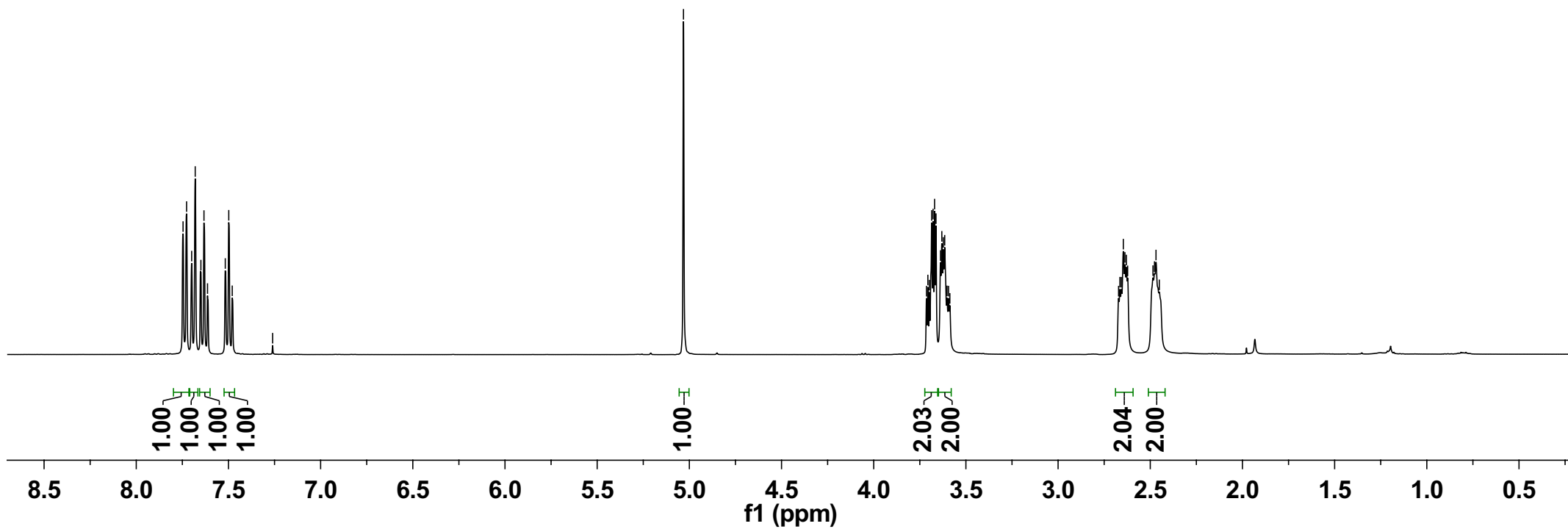
7.75  
7.73  
7.70  
7.68  
7.65  
7.63  
7.61  
7.52  
7.50  
7.48  
7.26

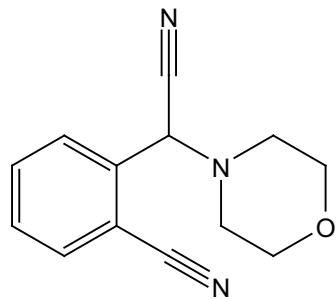
5.03

3.71  
3.70  
3.69  
3.68  
3.67  
3.66  
3.64  
3.63  
3.62  
3.61  
3.60  
2.67  
2.66  
2.66  
2.65  
2.64  
2.63  
2.62  
2.49  
2.48  
2.47  
2.45



**3w**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )





**3w**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

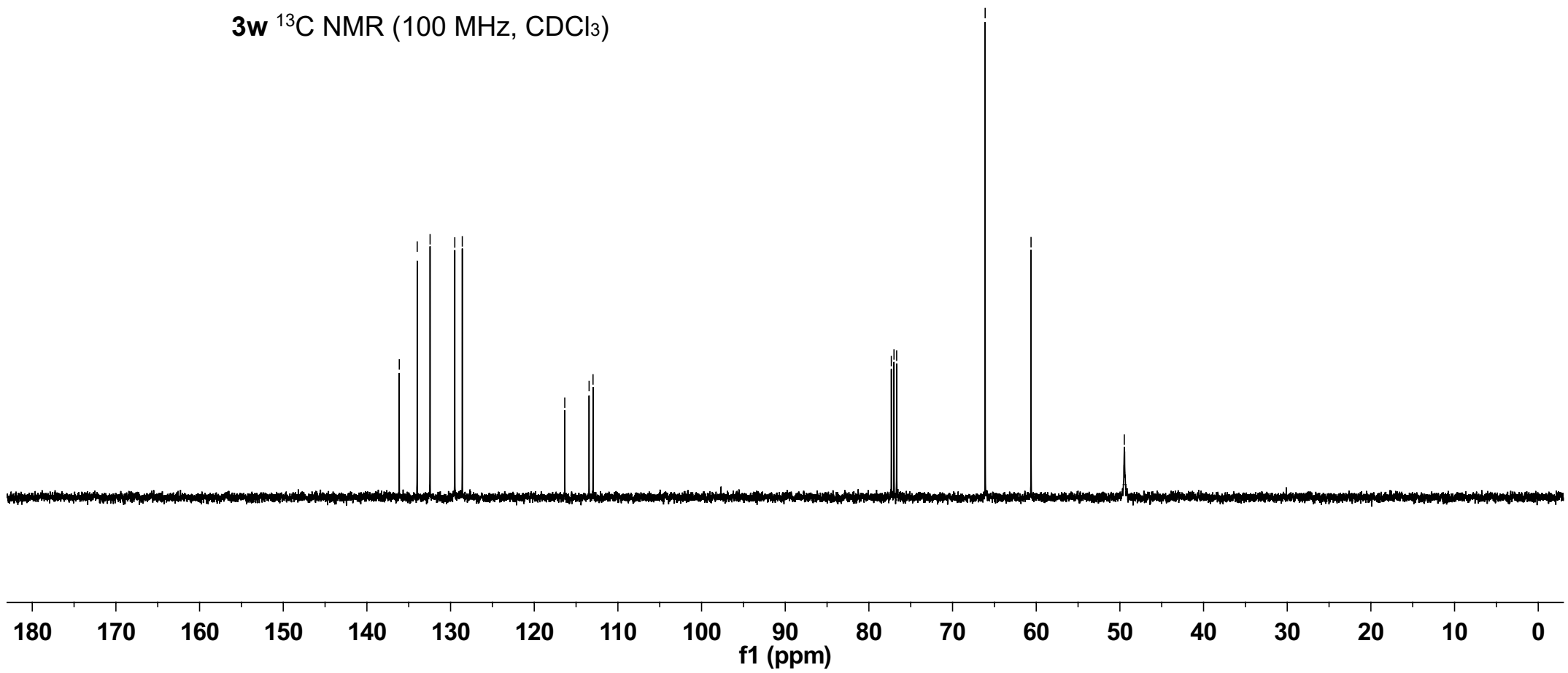
136.13  
133.99  
132.45  
129.50  
128.60

116.35  
113.44  
112.97

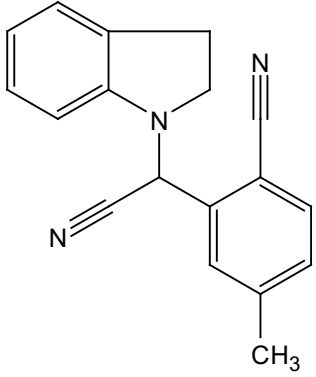
77.32  
77.00  
76.68

66.10  
60.62

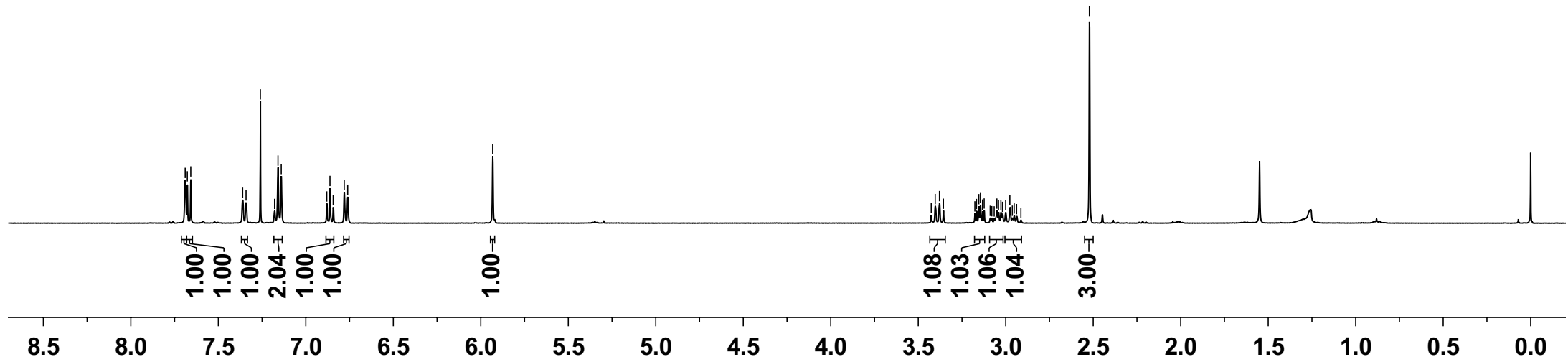
49.47



7.69 7.68 7.66 7.36 7.34 7.26 7.18 7.16 7.14 6.88 6.86 6.84 6.78 6.76 — 5.93 3.43 3.40 3.38 3.36 3.18 3.17 3.15 3.14 3.13 3.12 3.09 3.05 3.04 3.03 3.02 3.00 2.98 2.96 2.95 2.94



**3x** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



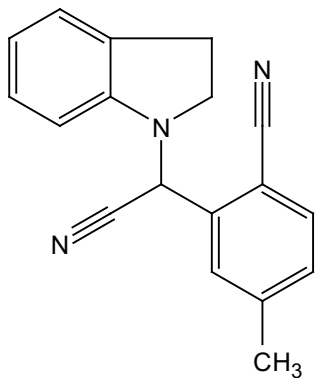


—148.38  
—144.42  
—136.38  
—134.06  
—130.42  
—129.35  
—129.30  
—127.56  
—125.08  
—121.01  
—116.57  
—114.55  
—109.69  
—108.89

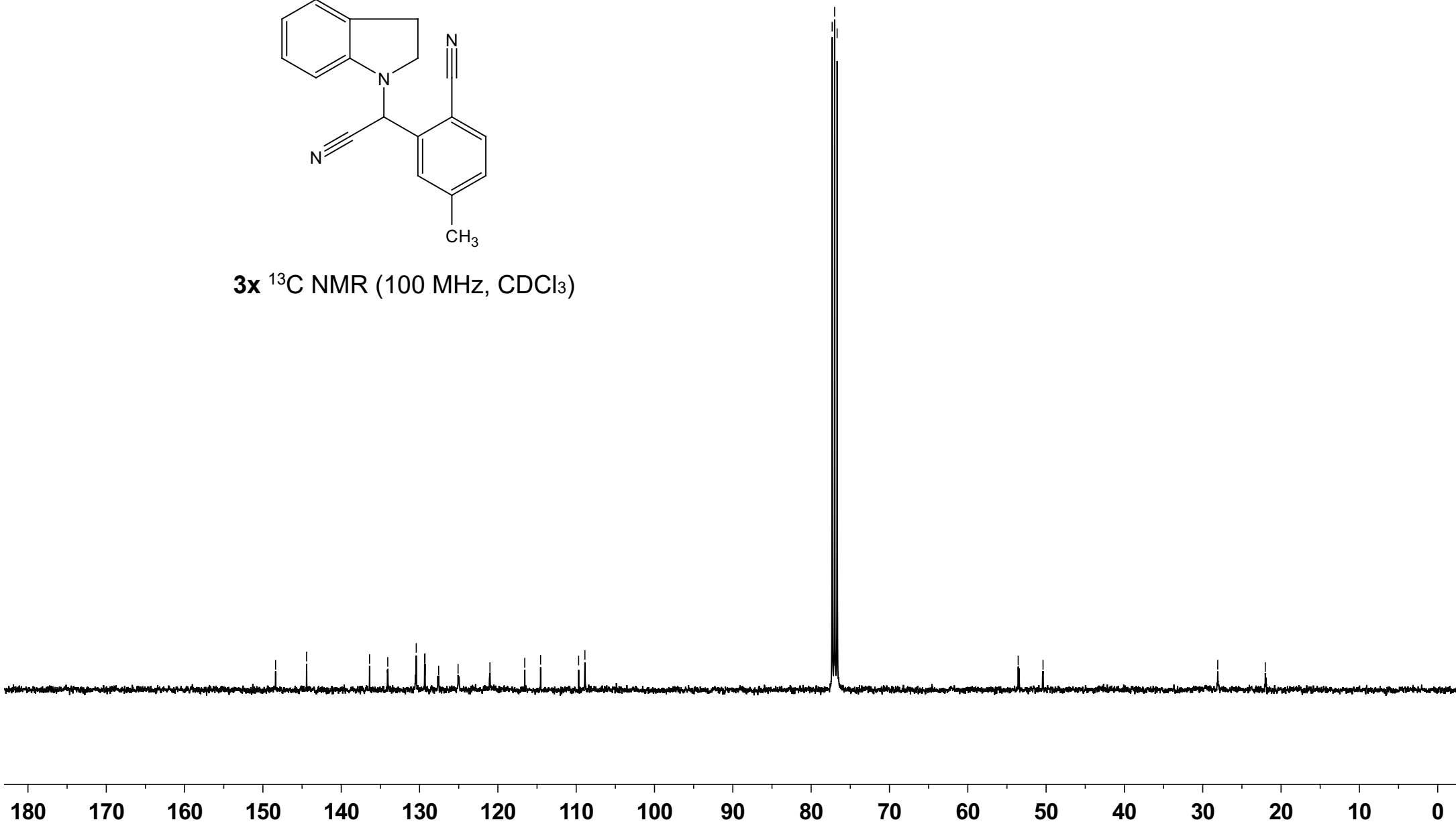
—77.32  
—77.00  
—76.68

—53.56  
—50.39

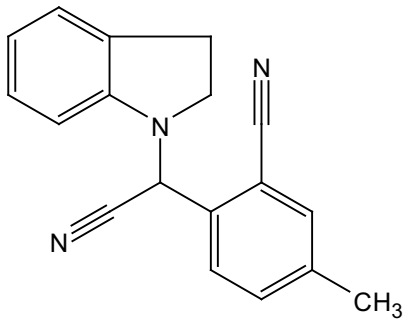
—28.09  
—22.02



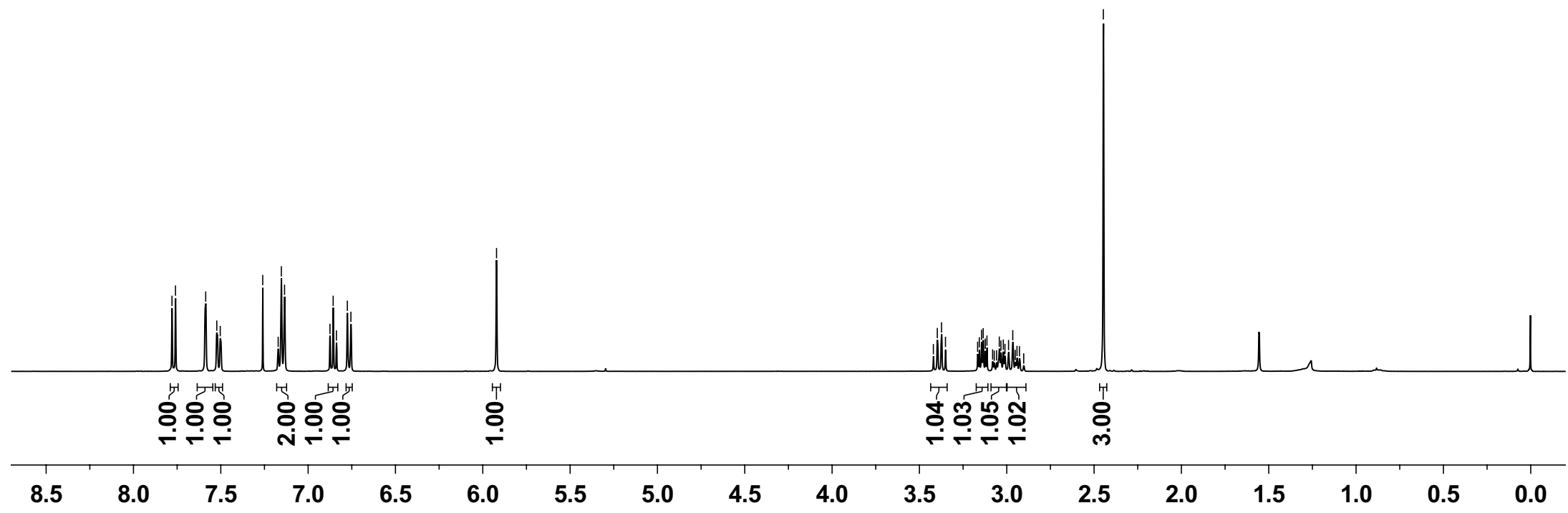
**3x** <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)



7.78  
7.76  
7.59  
7.52  
7.50  
7.26  
7.17  
7.15  
7.13  
6.87  
6.86  
6.84  
6.78  
6.76  
-5.92  
3.42  
3.40  
3.37  
3.35  
3.17  
3.16  
3.14  
3.13  
3.12  
3.11  
3.08  
3.06  
3.04  
3.03  
3.02  
3.01  
2.99  
2.97  
2.95  
2.94  
2.93  
2.93



3x' <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



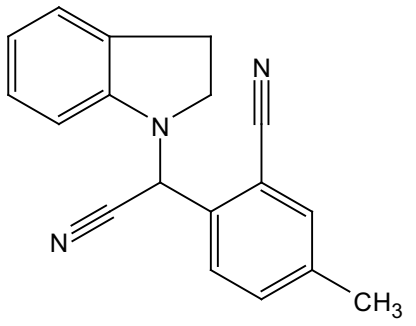
148.38  
140.40  
134.61  
133.72  
133.59  
130.45  
128.52  
127.58  
125.01  
120.99  
116.45  
114.58  
112.54  
108.89

77.32  
77.00  
76.68

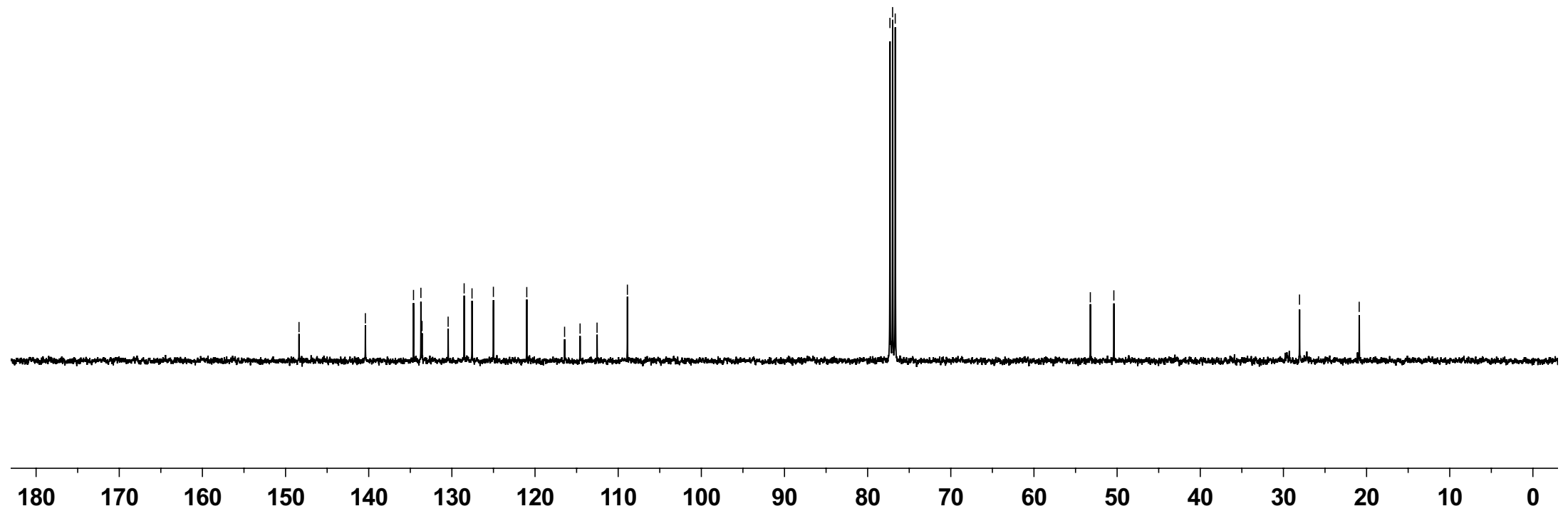
53.22  
50.39

28.07

20.89

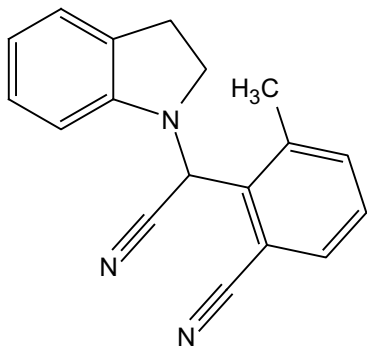


3x' <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

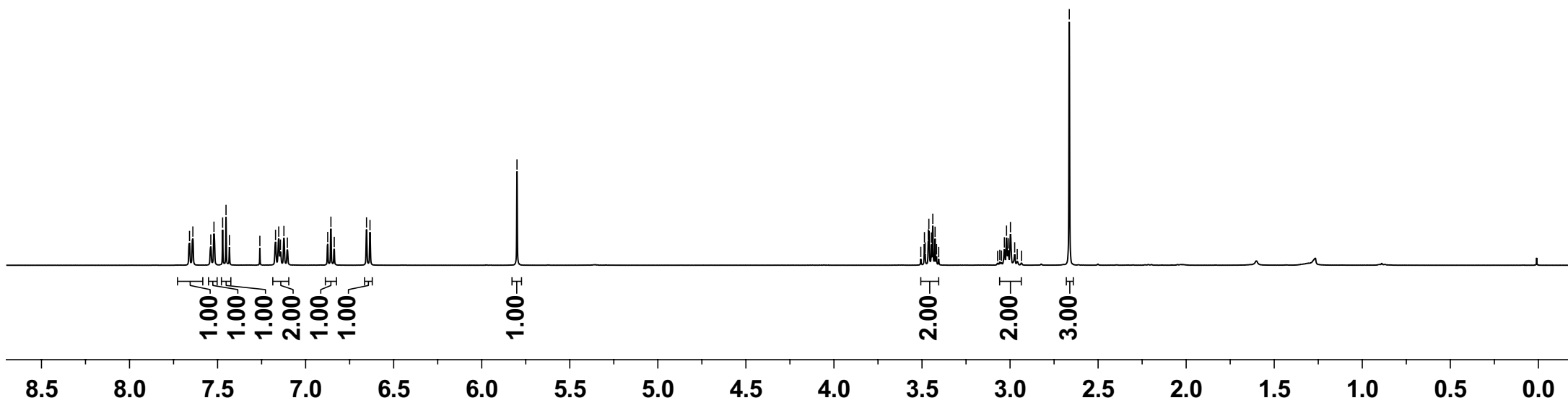


7.659  
7.640  
7.538  
7.521  
7.471  
7.452  
7.433  
7.260  
7.171  
7.153  
7.123  
7.104  
6.875  
6.856  
6.838  
6.654  
6.800

3.507  
3.486  
3.482  
3.464  
3.461  
3.447  
3.439  
3.426  
3.418  
3.405  
3.070  
3.058  
3.049  
3.032  
3.020  
3.010  
2.998  
2.974  
2.959  
2.935  
2.664



**3y** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



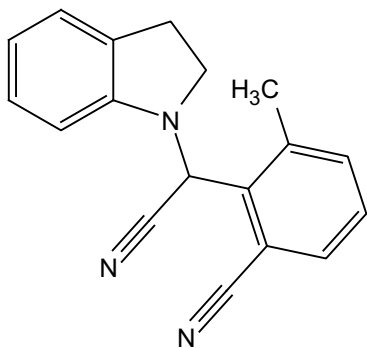
—149.080  
139.225  
136.296  
133.886  
132.521  
130.563  
129.778  
127.615  
124.991  
120.778  
117.038  
115.254  
113.484  
108.326

77.318  
77.000  
76.682

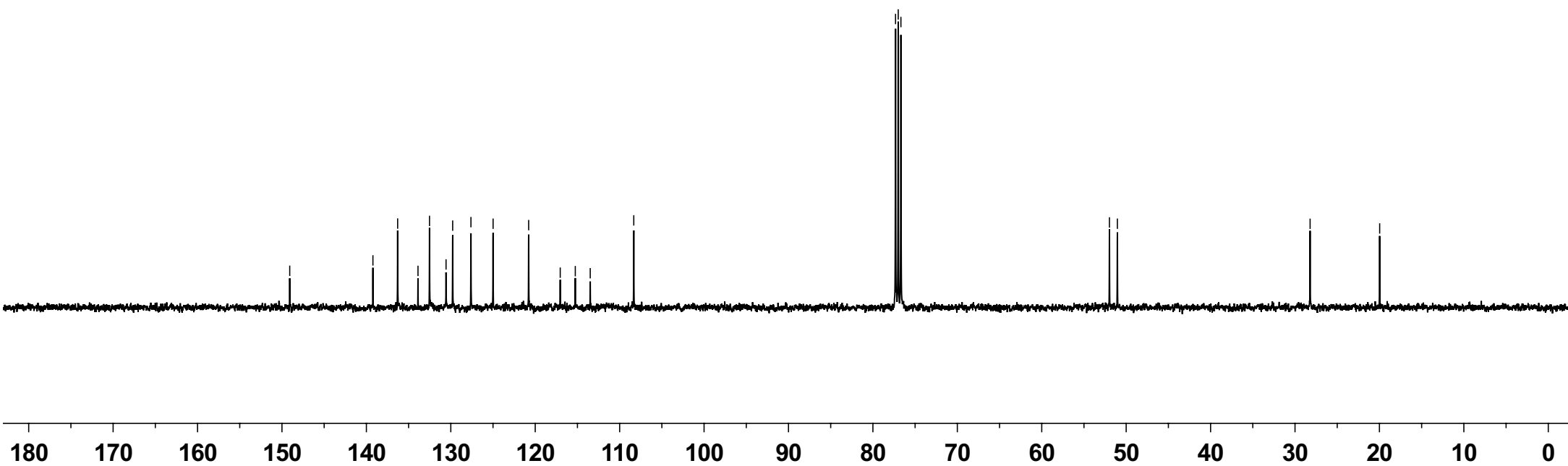
51.982  
51.041

—28.213

—19.973

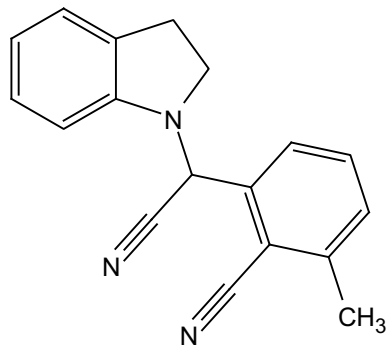


**3y** <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

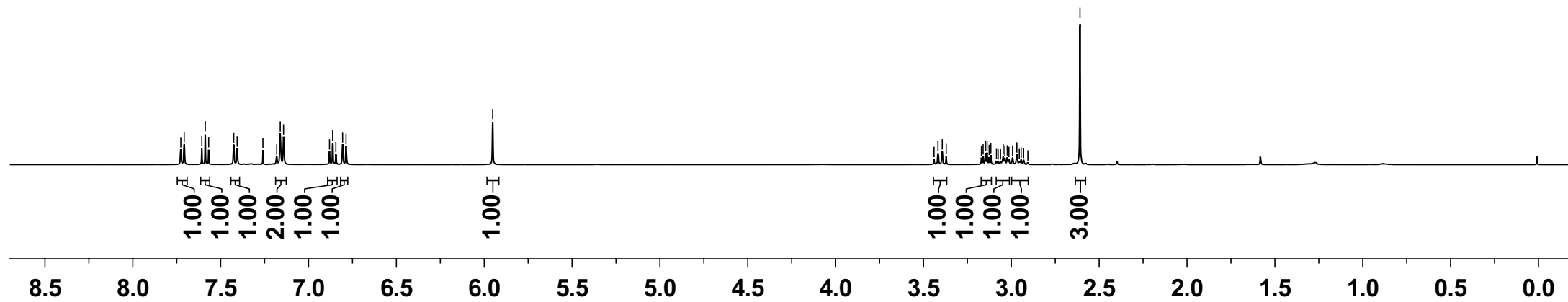


7.727  
7.708  
7.607  
7.588  
7.568  
7.426  
7.406  
7.260  
7.181  
7.161  
7.142  
6.881  
6.863  
6.844  
6.806  
6.787  
5.952

3.440  
3.417  
3.393  
3.371  
3.170  
3.161  
3.147  
3.138  
3.126  
3.117  
3.084  
3.075  
3.062  
3.046  
3.037  
3.023  
3.014  
2.993  
2.969  
2.955  
2.944  
2.930  
2.906  
2.609



**3y'** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



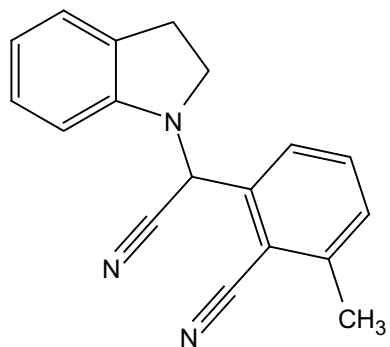
—148.416  
—144.179  
—136.692  
—132.398  
—131.101  
—130.422  
—127.565  
—125.860  
—124.963  
—120.967  
—115.408  
—114.582  
—112.955  
—108.933

—77.318  
—77.000  
—76.682

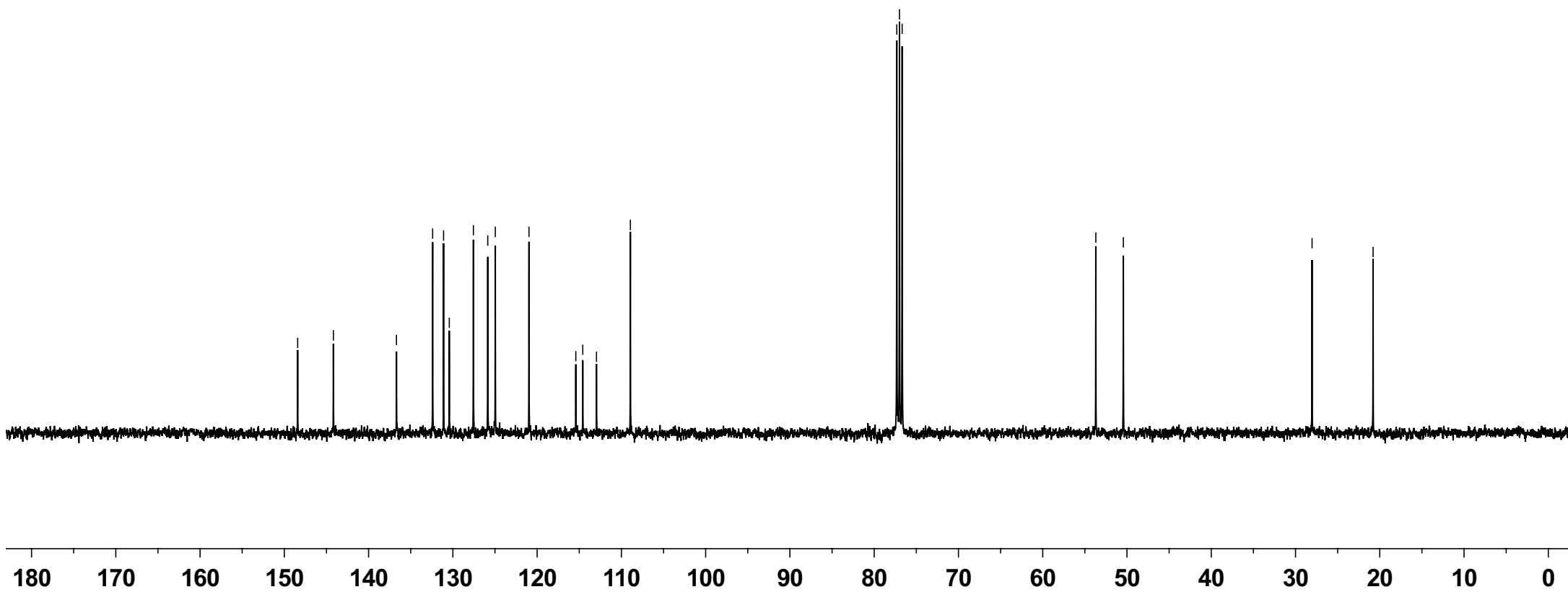
—53.700  
—50.431

—28.036

—20.795

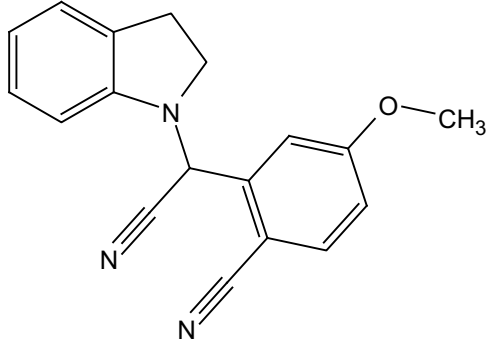


**3y'** <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

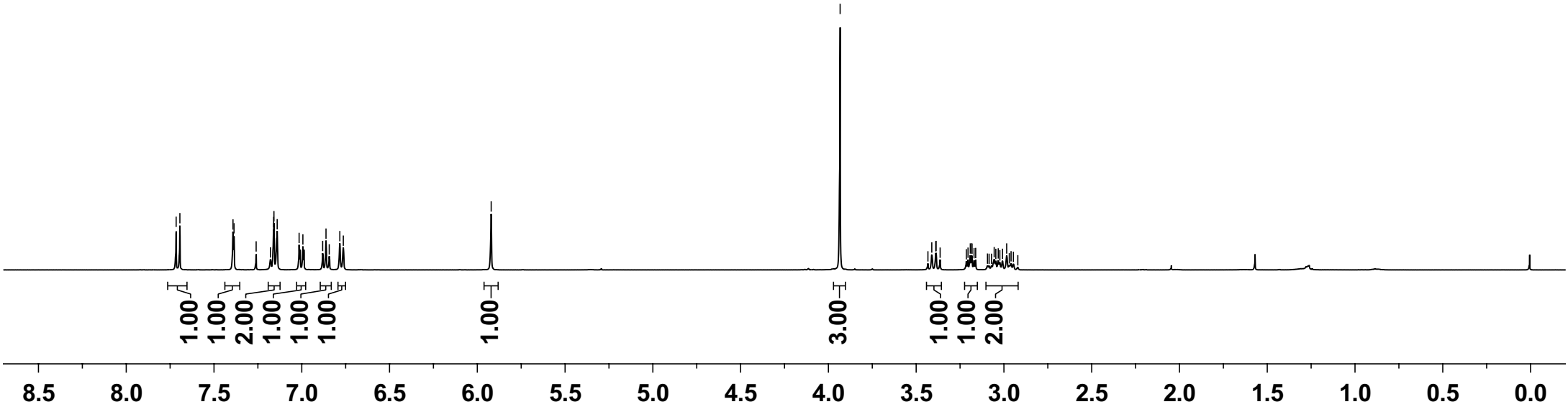


7.716  
7.694  
7.392  
7.386  
7.260  
7.178  
7.160  
7.159  
7.140  
7.015  
6.994  
6.881  
6.862  
6.843  
6.783  
6.763  
5.921

3.933  
3.433  
3.411  
3.388  
3.386  
3.363  
3.214  
3.205  
3.192  
3.183  
3.182  
3.170  
3.161  
3.094  
3.085  
3.071  
3.056  
3.046  
3.032  
3.023  
3.008  
2.984  
2.969  
2.959  
2.946  
2.921



**3z** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)





—162.911

—148.311

~138.503

—135.940

~130.385

~127.564

~124.989

~120.996

~116.656

~115.320

~114.391

~114.318

~108.860

~103.930

~77.318

~77.000

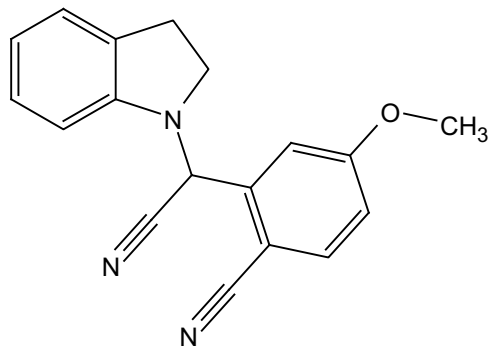
~76.682

~55.887

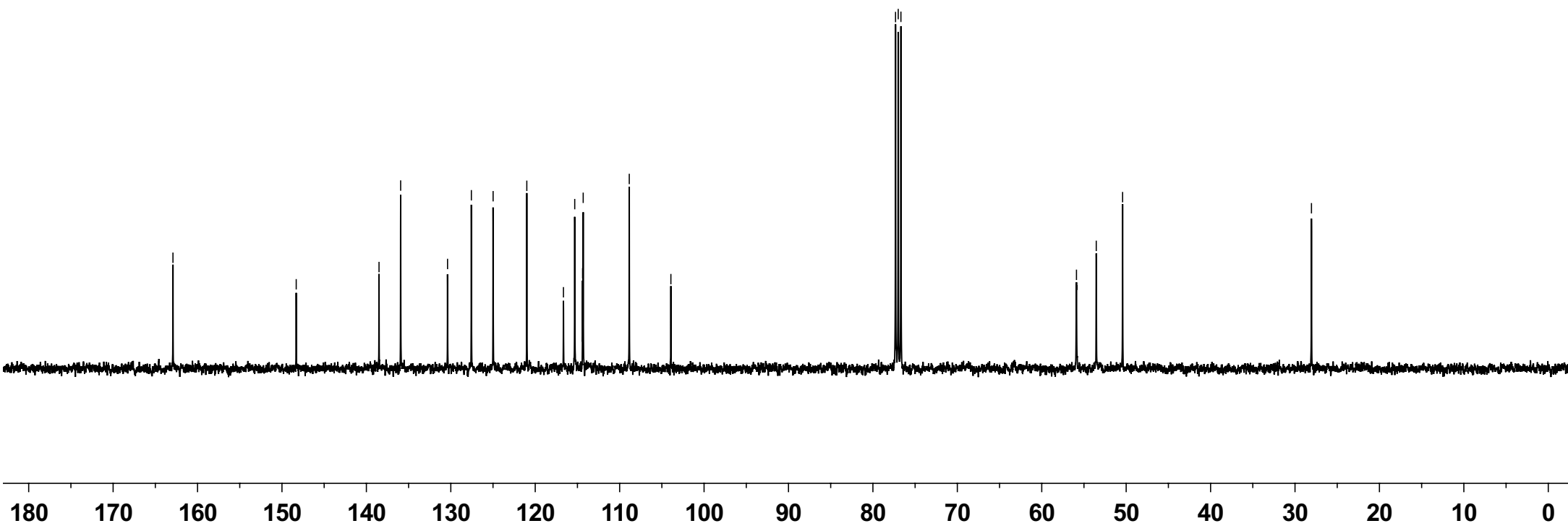
~53.544

~50.422

—28.051



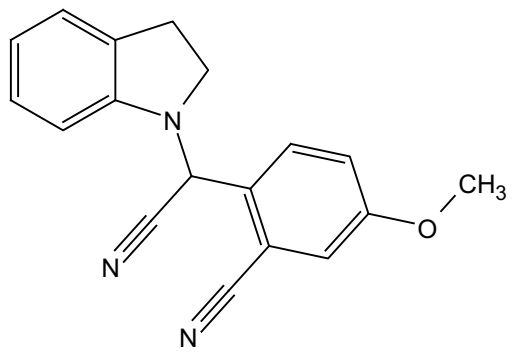
**3z** <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)



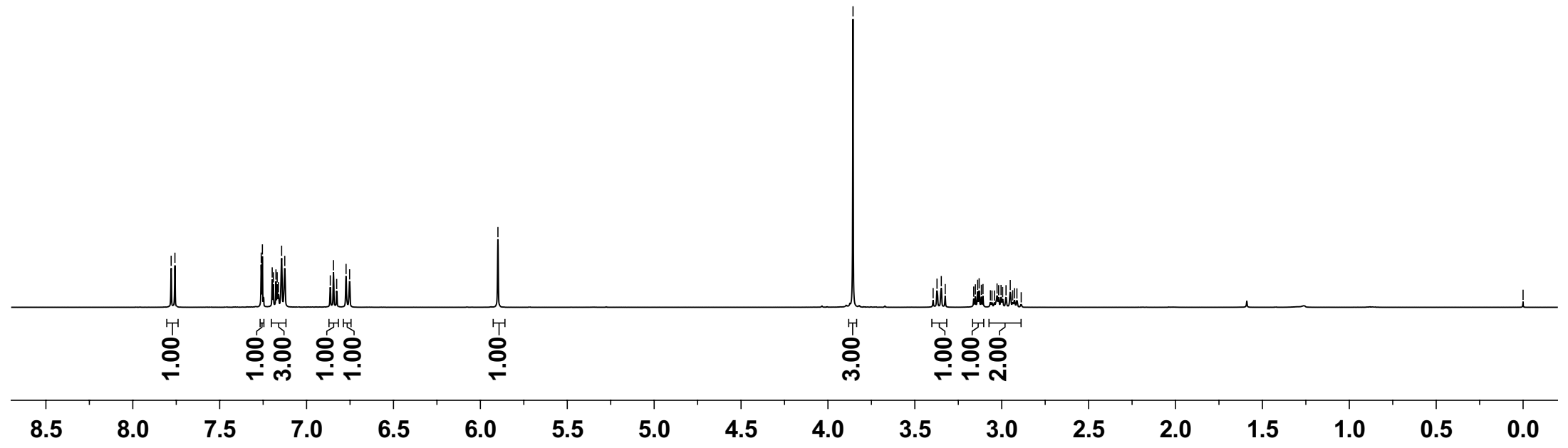
7.779  
7.758

7.261  
7.254  
7.198  
7.176  
7.169  
7.144  
7.126  
6.845  
6.773  
6.899

3.856  
3.395  
3.372  
3.348  
3.325  
3.161  
3.152  
3.139  
3.130  
3.117  
3.108  
3.065  
3.056  
3.042  
3.027  
3.018  
3.004  
2.995  
2.975  
2.951  
2.937  
2.926  
2.913  
2.888  
0.000



3z' <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



—160.029

—148.358

130.432

129.922

128.185

127.511

124.948

120.889

119.430

118.392

116.140

114.662

113.557

108.825

77.318

77.000

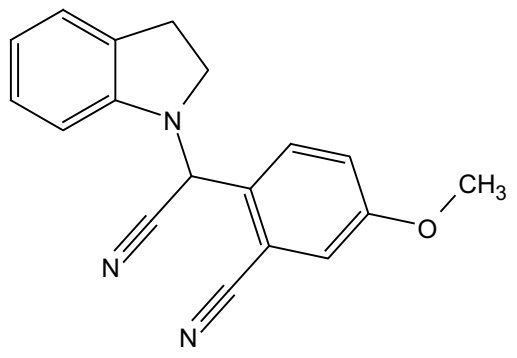
76.682

55.798

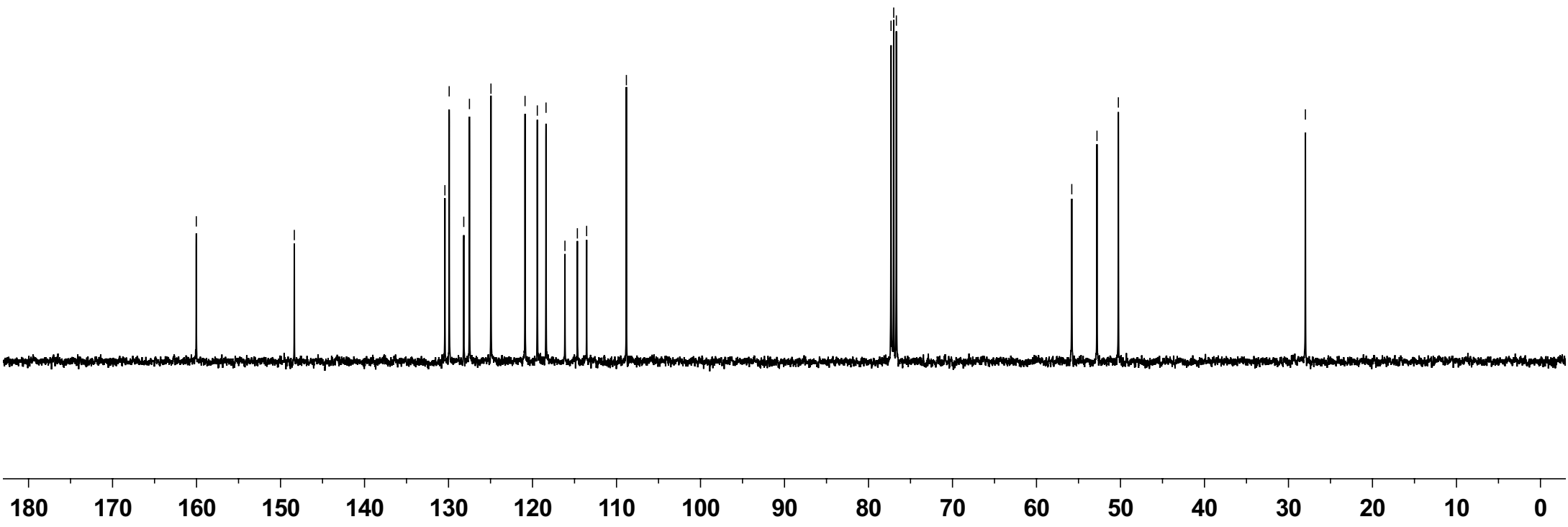
52.798

50.253

—27.986

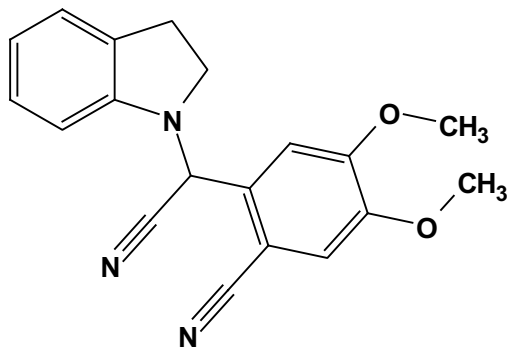


**3z'** <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

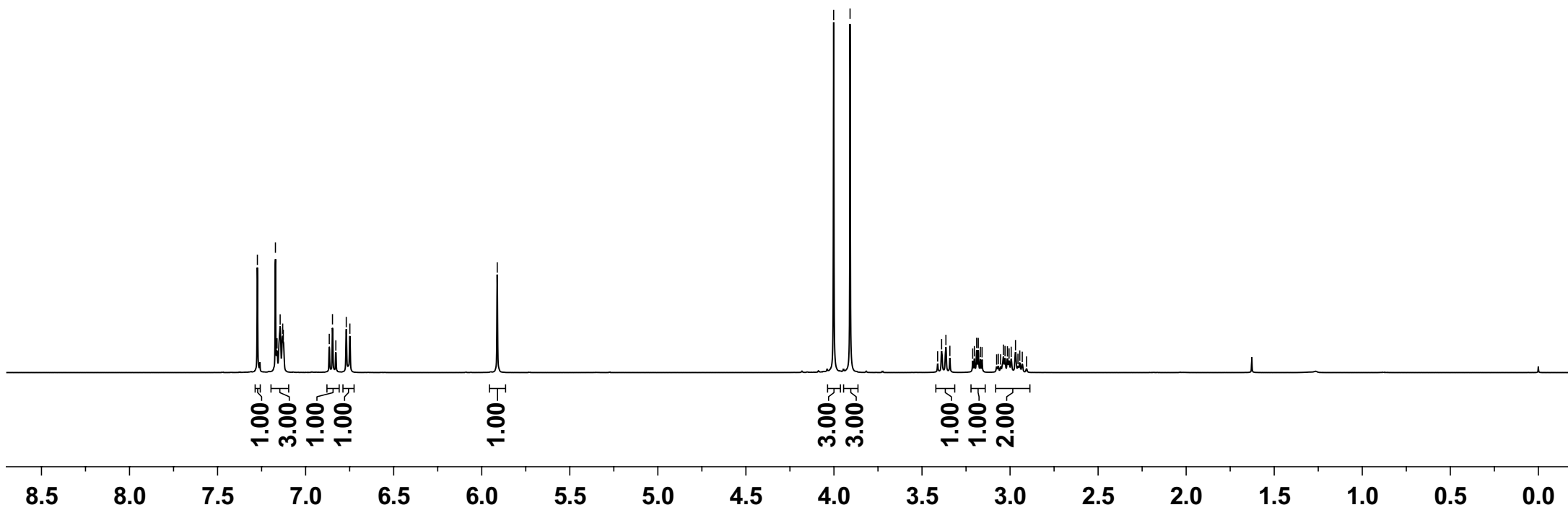


7.274  
7.172  
7.162  
7.145  
7.130  
7.127  
6.866  
6.848  
6.828  
6.769  
6.749  
— 5.912

4.002  
3.909  
3.411  
3.389  
3.364  
3.342  
3.212  
3.203  
3.190  
3.181  
3.168  
3.159  
3.076  
3.067  
3.053  
3.038  
3.029  
3.015  
3.006  
2.994  
2.969  
2.955  
2.945  
2.931  
2.906



**3aa** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



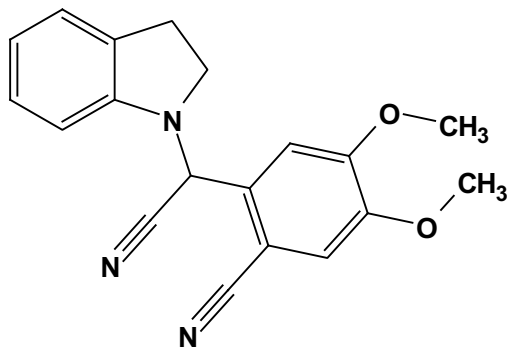
152.503  
149.391  
148.298

130.384  
130.323  
127.493  
124.920  
120.874  
116.577  
115.452  
114.764  
111.086  
108.778  
103.915

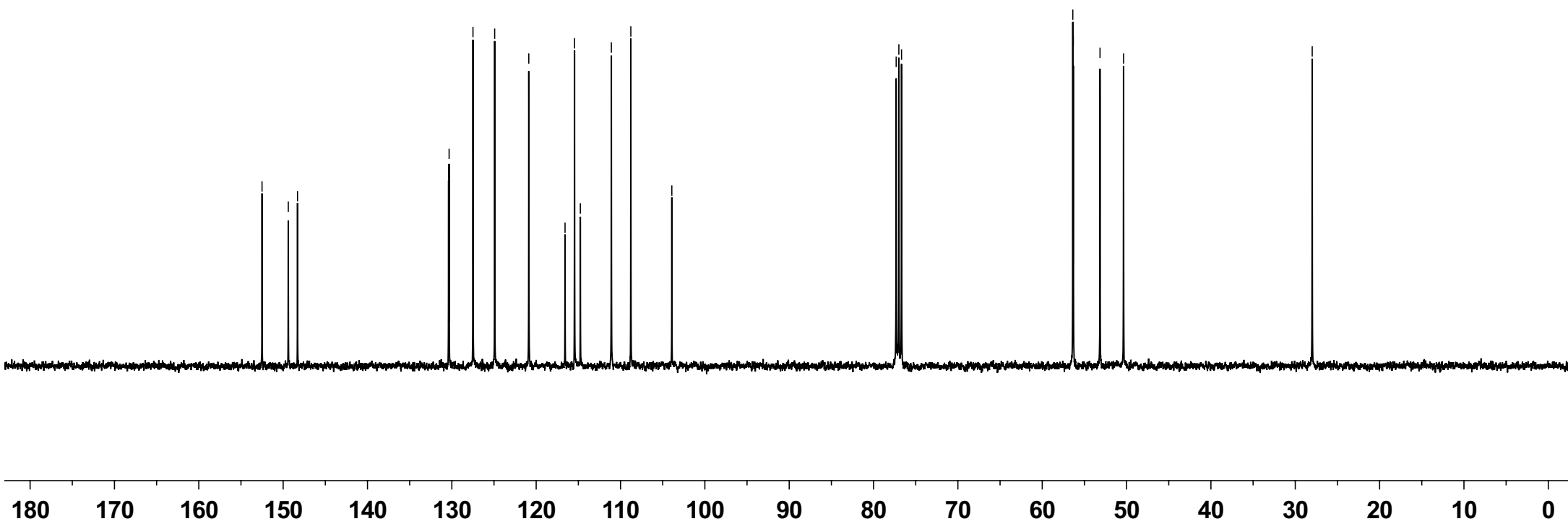
77.319  
77.000  
76.682

56.376  
56.313  
53.149  
50.360

27.992

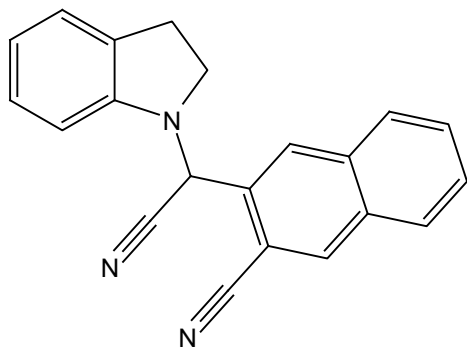


**3aa**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

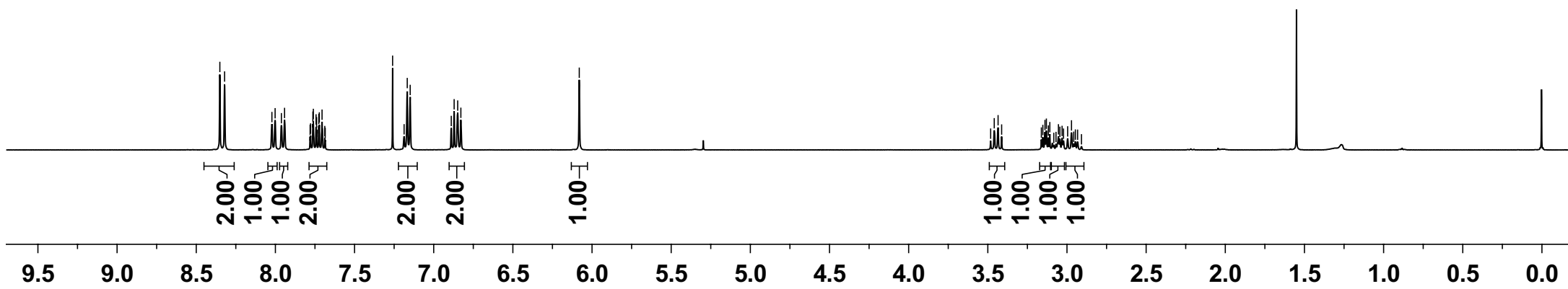


8.351  
8.321  
8.022  
8.002  
7.962  
7.942  
7.763  
7.760  
7.743  
7.726  
7.723  
7.705  
7.260  
7.167  
7.149  
6.889  
6.871  
6.848  
6.828

3.482  
3.459  
3.435  
3.413  
3.162  
3.152  
3.139  
3.130  
3.118  
3.108  
3.083  
3.069  
3.054  
3.045  
3.031  
3.022  
2.996  
2.971  
2.957  
2.947  
2.933  
2.908



**3ab**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

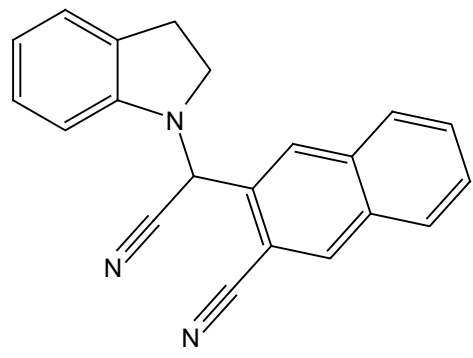


148.410  
136.657  
133.927  
132.138  
130.574  
130.468  
130.131  
128.812  
128.524  
128.426  
128.292  
127.625  
125.055  
121.100  
116.783  
114.648  
109.305  
109.030

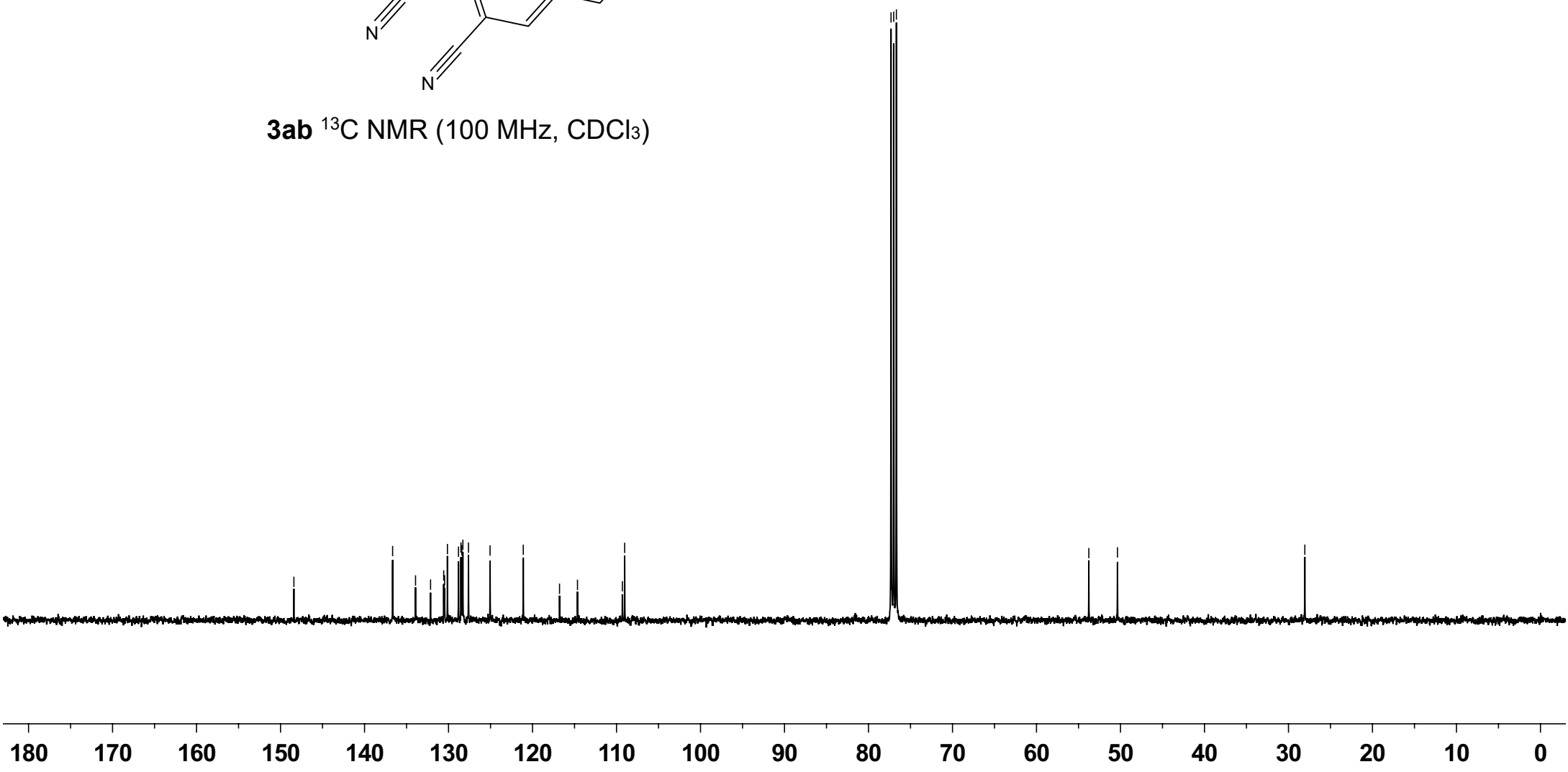
77.318  
77.000  
76.682

53.771  
50.360

28.054



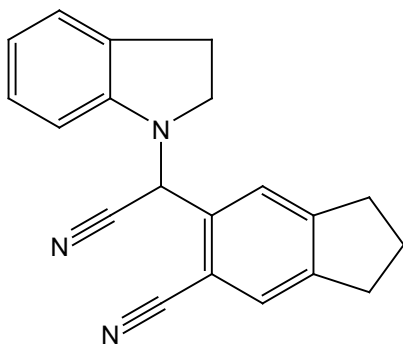
**3ab**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )



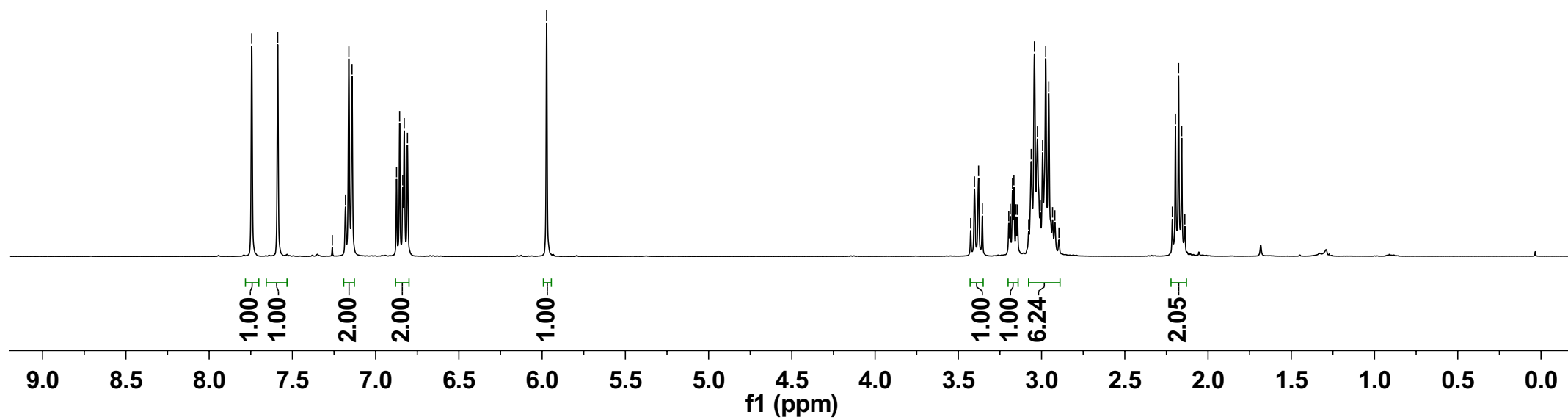
7.74  
7.59  
7.26  
7.18  
7.16  
7.14  
6.87  
6.86  
6.84  
6.83  
6.81

5.97

3.43  
3.40  
3.38  
3.36  
3.20  
3.19  
3.17  
3.17  
3.15  
3.14  
3.06  
3.04  
3.02  
3.01  
2.99  
2.97  
2.96  
2.93  
2.92  
2.91  
2.20  
2.18  
2.16  
2.14



**3ac**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



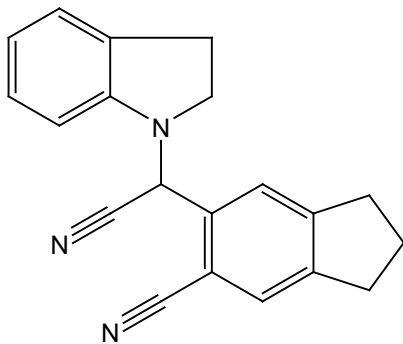


150.62  
148.36  
146.28  
134.34  
130.26  
129.59  
127.36  
124.76  
124.56  
120.65  
116.90  
114.68  
109.93  
108.69

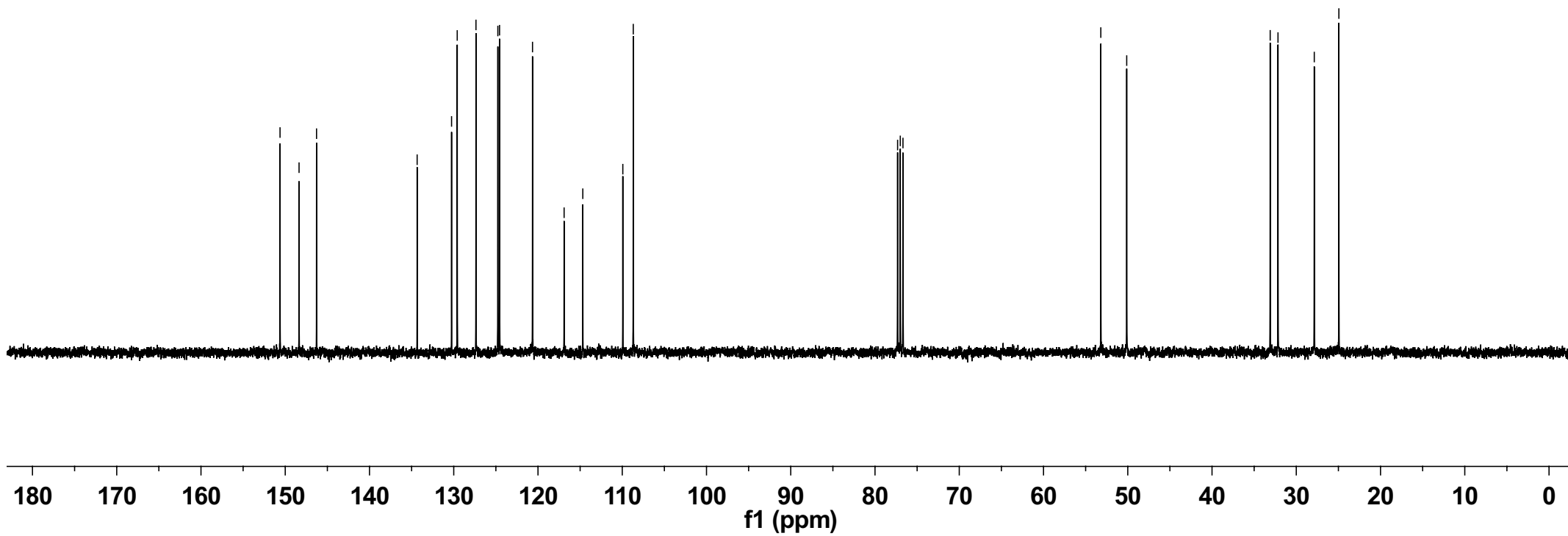
77.32  
77.00  
76.68

53.20  
50.12

33.10  
32.17  
27.86  
24.94

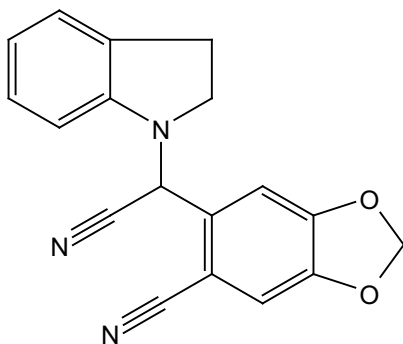


**3ac**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

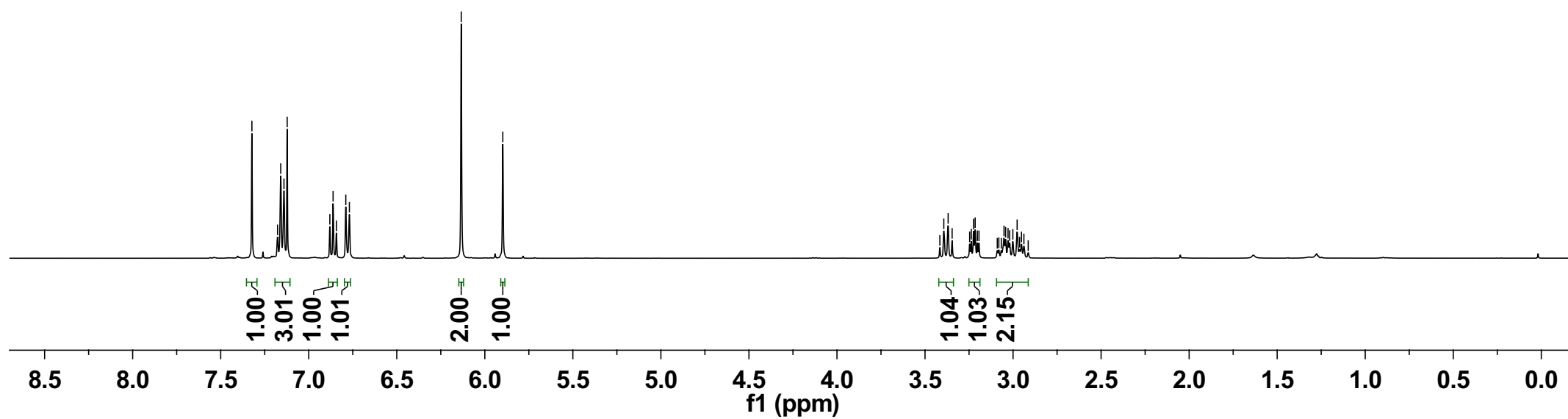


7.32  
7.18  
7.16  
7.14  
7.12  
6.88  
6.86  
6.84  
6.79  
6.77  
6.13  
5.90

3.42  
3.39  
3.37  
3.35  
3.25  
3.24  
3.22  
3.22  
3.20  
3.19  
3.09  
3.08  
3.07  
3.05  
3.04  
3.03  
3.02  
3.00  
2.98  
2.96  
2.95  
2.94  
2.91



**3ad**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



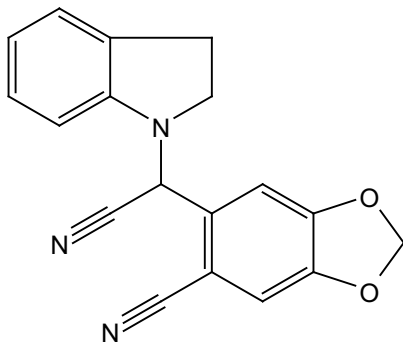
151.66  
148.39  
148.25

132.67  
130.29  
127.49  
124.92  
120.90  
116.29  
114.53  
112.68  
109.19  
108.77  
105.30  
103.06

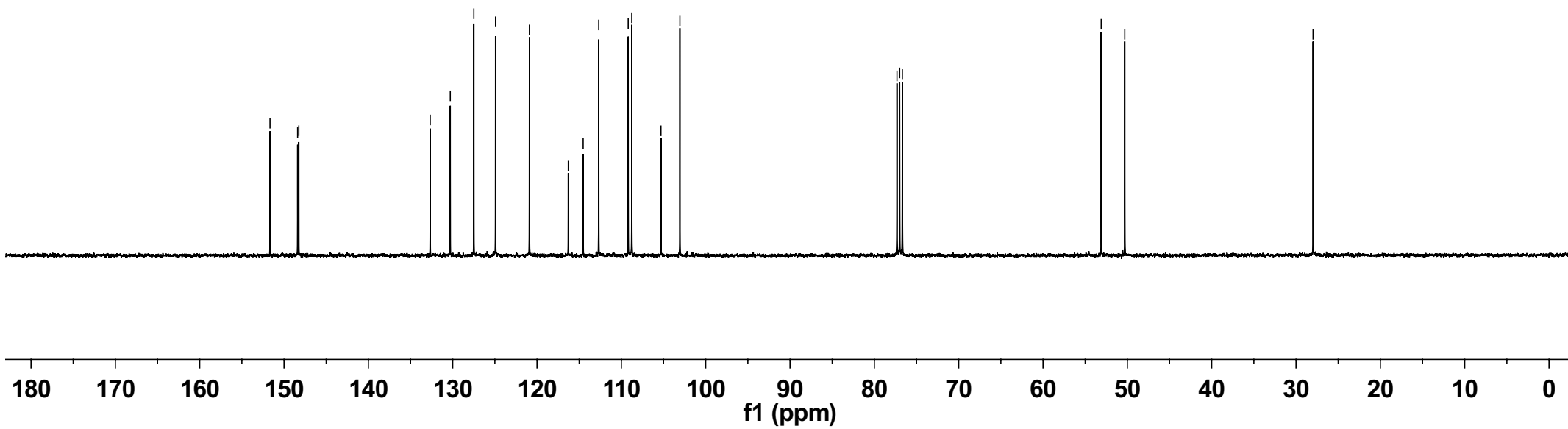
77.32  
77.00  
76.68

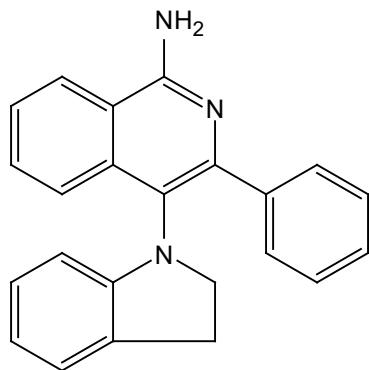
53.10  
50.31

27.98

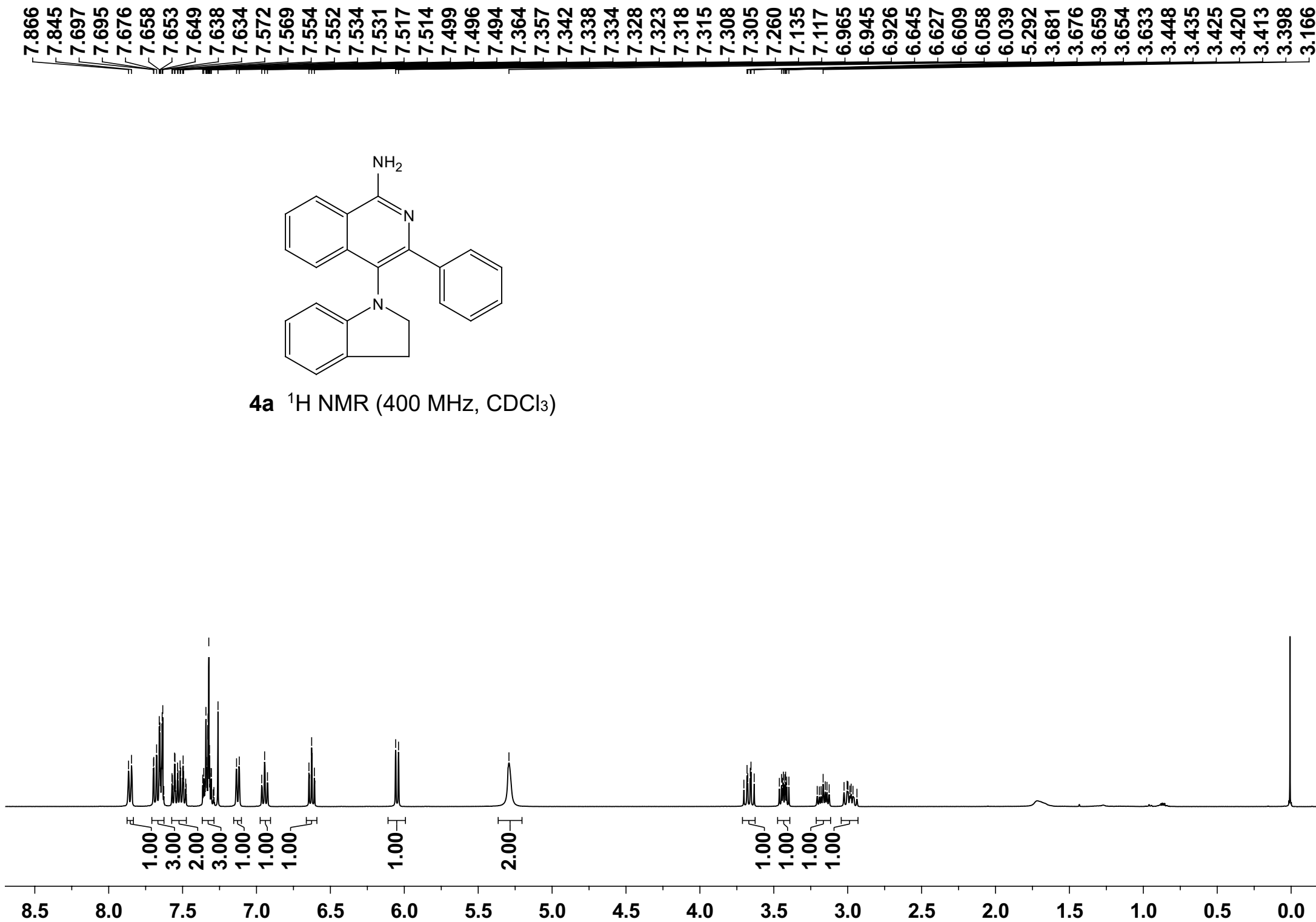


**3ad**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )





**4a** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

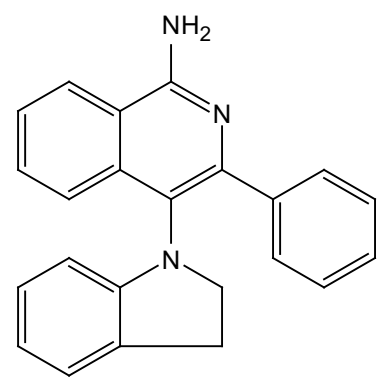


154.452  
152.324  
150.470  
139.582  
130.251  
128.645  
128.363  
128.075  
127.821  
127.579  
126.000  
124.595  
124.165  
123.371  
116.376

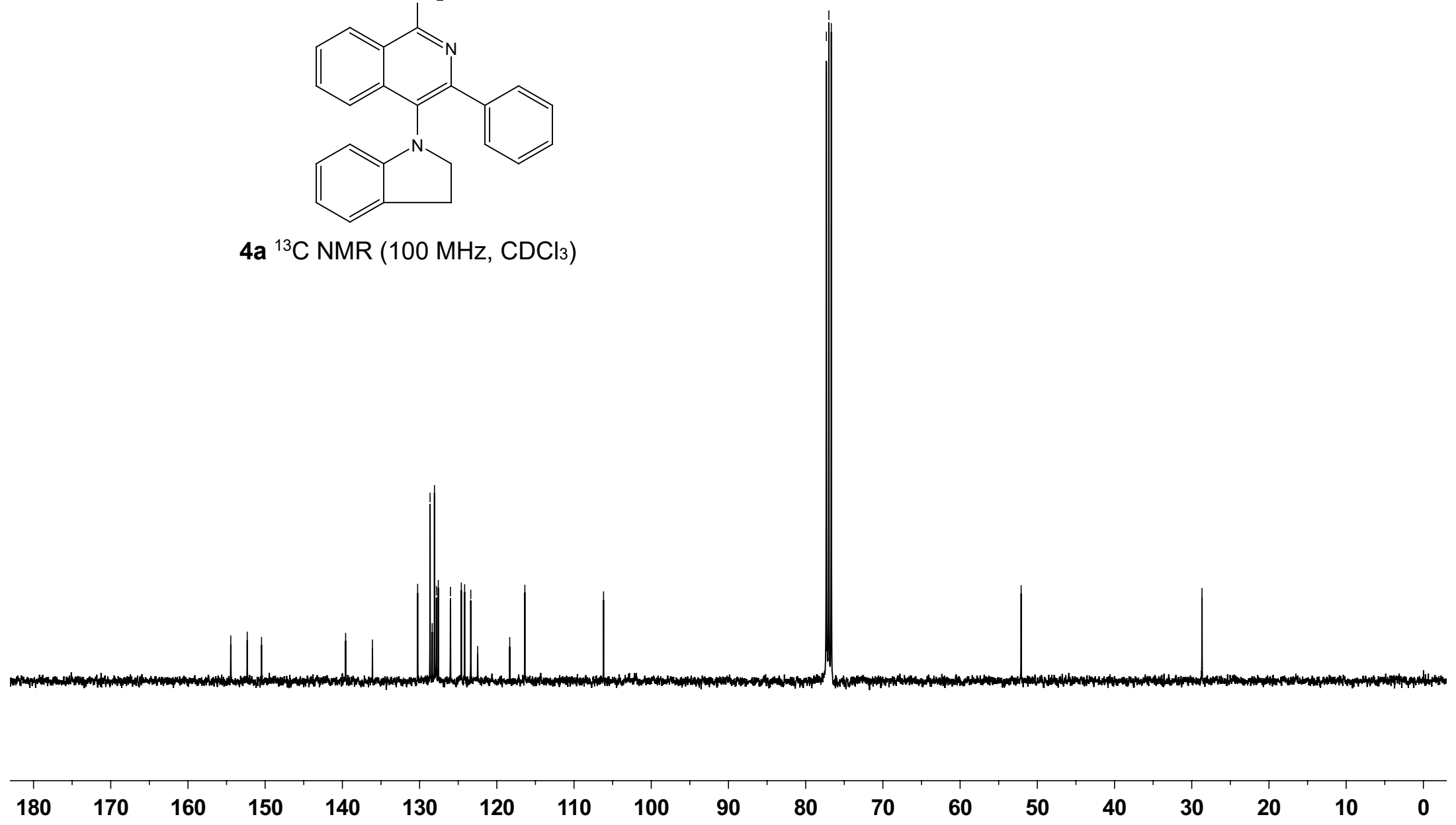
77.318  
77.000  
76.683

52.095

28.670



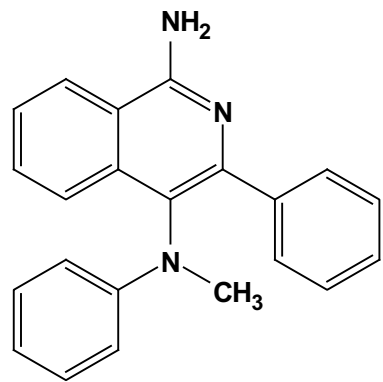
**4a** <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)



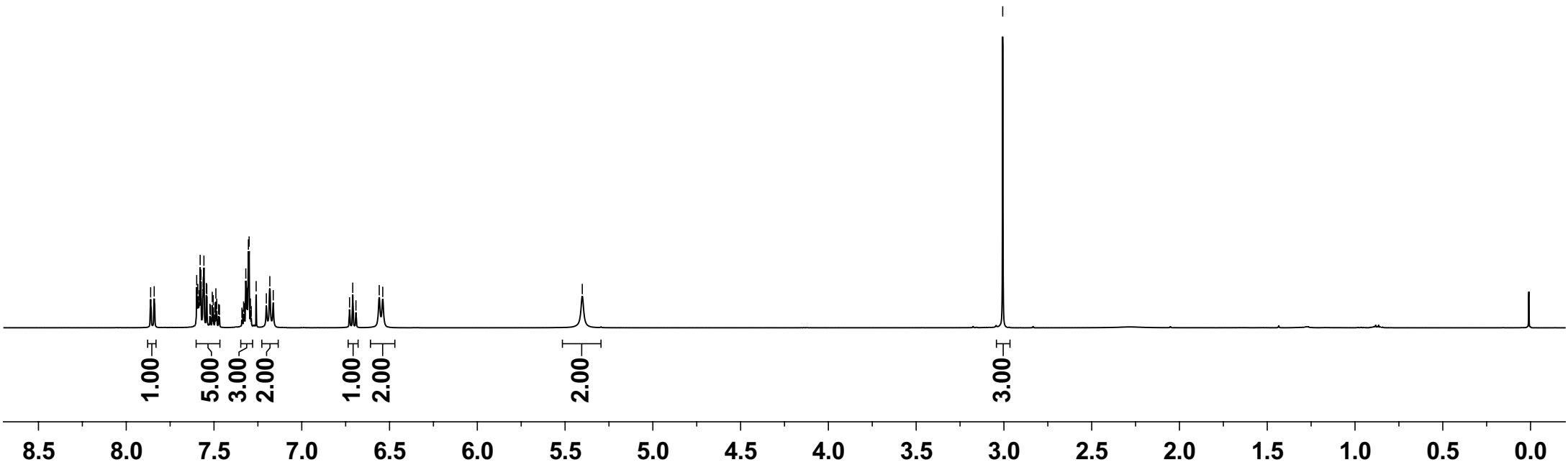
7.599  
7.579  
7.575  
7.561  
7.557  
7.544  
7.319  
7.304  
7.300  
7.260  
6.728  
6.710  
6.691  
6.559  
6.539

5.402

3.007



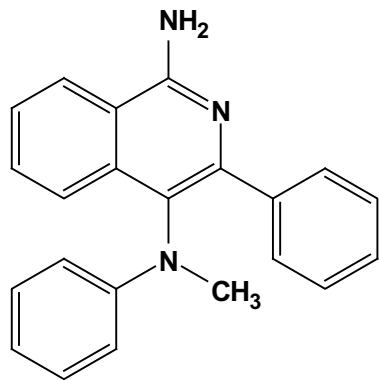
**4b** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



154.428  
149.779  
149.175  
139.295  
136.466  
130.667  
129.195  
128.370  
128.104  
127.875  
127.454  
126.137  
124.263  
123.224  
118.332  
116.348  
112.119

77.318  
77.000  
76.683

38.718



**4b**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

