

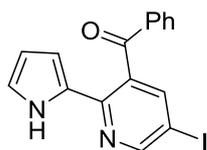
## Copper(I) halide-promoted formation of 3-acyl-5-halopyridine moiety from NH-2-(2-acylethynyl)pyrroles and propargylamine

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IR spectra were obtained on a “Bruker IFS-25” spectrometer (KBr pellets in 400-4000  $\text{cm}^{-1}$  region).  $^1\text{H}$  (400 MHz),  $^{13}\text{C}$  (101 MHz),  $^{19}\text{F}$  (377 MHz) and  $^{15}\text{N}$  (41 MHz) NMR spectra were recorded on a “Bruker Avance 400” instrument in  $\text{CDCl}_3$ . The assignment of signals in the  $^1\text{H}$  NMR spectra was made using COSY and NOESY experiments. Resonance signals of carbon atoms were assigned based on  $^1\text{H}$ - $^{13}\text{C}$  HSQC and  $^1\text{H}$ - $^{13}\text{C}$  HMBC experiments. The  $^1\text{H}$  chemical shifts ( $\delta$ ) were referenced to HMDS (0.05 ppm) in  $\text{CDCl}_3$  and the residual deuterated solvent (7.26 ppm), the  $^{13}\text{C}$  chemical shifts were expressed with respect to the deuterated solvent (77.10 ppm). The chemical shifts were recorded in ppm. The (C, H, N) microanalyses were performed on an Flash EA 1112 CHNS-O/MAS (CHN Analyzer) instrument. The chlorine, iodine and bromine content was determined by titrimetric method. Fluorine content was determined spectrophotometrically on a SPECOL 11 (Carl Zeiss Jena, Germany) spectrophotometer. Melting points (uncorrected) were determined with melting point SMP3 (Stuart Scientific).

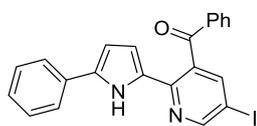
**General procedure for the synthesis of compounds 2,3.** 2-(2-Acylethynyl)pyrrole **1a-f** (1 mmol) and propargylamine (2 mmol) in DMSO (7-10 ml) were heated at 60-65 °C for 6-15 h until the signals of reactants **1a-f** disappeared. Then CuHal (1 mmol) was added and the mixture was heated at 60-65 °C for more 2.5 h. After cooling to room temperature, the mixture was diluted with brine (1:10). The precipitate formed was filtered off, washed with  $\text{H}_2\text{O}$  ( $5 \times 15$  ml), dried and fractionated by column chromatography ( $\text{Al}_2\text{O}_3$ , hexane-diethyl ether, 3 : 1) to elute first 5-halo-2-pyrrolylpyridines **2a-f**, **2'd**, **2''d**, **2'f**, **2''f**, then pyrrolylpyridines **3a-f**.

### [5-Iodo-2-(1H-pyrrol-2-yl)pyridin-3-yl](phenyl)methanone (**2a**).



Yield 0.034 g (9%), yellow crystals, mp 130-132 °C.  $^1\text{H}$  NMR (400.13 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 9.65 (br s, 1H, NH), 8.78 (d,  $J$  = 2.0 Hz, 1H, H-6 pyridine), 7.86-7.84 (m, 2H, H-2,6 CPh), 7.82 (d,  $J$  = 2.0 Hz, 1H, H-4 pyridine), 7.62-7.58 (m, 1H, H-4 CPh), 7.47-7.43 (m, 2H, H-3,5 CPh), 6.85-6.84 (m, 1H, H-5 pyrrole), 6.24-6.22 (m, 1H, H-3 pyrrole), 6.08-6.06 (m, 1H, H-4 pyrrole).  $^{13}\text{C}$  NMR (100.61 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 195.8 (C=O), 155.6 (C-6 pyridine), 145.9 (C-2 pyridine), 143.2 (C-4 pyridine), 136.0 (C-1 CPh), 134.4 (C-4 CPh), 132.5 (C-3 pyridine), 130.2 (C-2,6 CPh), 129.0 (C-3,5 CPh), 128.3 (C-2 pyrrole), 120.7 (C-5 pyrrole), 112.5 (C-3 pyrrole), 111.1 (C-4 pyrrole), 87.0 (C-5 pyridine). IR (KBr,  $\text{cm}^{-1}$ ): 3430, 3115, 3058, 2923, 2854, 2550, 1666, 1590, 1559, 1534, 1452, 1431, 1378, 1311, 1275, 1214, 1178, 1104, 1047, 945, 796, 733, 683, 644, 593, 457. Anal. Calcd for  $\text{C}_{16}\text{H}_{11}\text{IN}_2\text{O}$ : C, 51.36; H, 2.96; I, 33.92; N, 7.49; Found: C, 51.23; H, 2.88; I, 33.71; N, 7.54%.

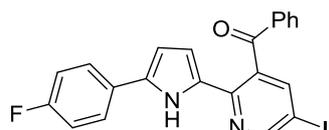
### [5-Iodo-2-(5-phenyl-1H-pyrrol-2-yl)pyridin-3-yl](phenyl)methanone (**2c**).



Yield 0.054 g (12%), yellow crystals, mp 181-182 °C.  $^1\text{H}$  NMR (400.13 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 9.87 (br s, 1H, NH), 8.79 (d,  $J$  = 2.0 Hz, 1H, H-6 pyridine), 7.89-7.87 (m, 2H, H-2,6 CPh), 7.83 (d,  $J$  = 2.0 Hz, 1H, H-4 pyridine), 7.63-7.59 (m, 1H, H-4 CPh), 7.54-7.52 (m, 2H, H-2,6 Ph), 7.49-7.45 (m, 2H, H-3,5 CPh), 7.39-7.35 (m, 2H, H-3,5 Ph), 7.26-7.23

(m, 1H, H-4 Ph), 6.38 (dd,  $J = 3.6, 2.9$  Hz, 1H, H-4 pyrrole), 6.29 (dd,  $J = 3.6, 2.4$  Hz, 1H, H-3 pyrrole).  $^{13}\text{C}$  NMR (100.61 MHz,  $\text{CDCl}_3$ ):  $\delta = 195.8$  (C=O), 155.7 (C-6 pyridine), 145.6 (C-2 pyridine), 143.3 (C-4 pyridine), 136.0 (C-1 COPh), 134.6 (C-5 pyrrole), 134.4 (C-4 CPh), 132.5 (C-3 pyridine), 131.8 (C-1 Ph), 130.3 (C-2,6 CPh), 129.1 (C-3,5 CPh), 129.0 (C-2,4,6 Ph), 127.2 (C-2 pyrrole), 124.4 (C-3,5 Ph), 114.4 (C-3 pyrrole), 108.8 (C-4 pyrrole), 86.9 (C-5 pyridine). IR (KBr,  $\text{cm}^{-1}$ ): 3434, 3110, 3061, 2923, 2853, 2735, 2251, 1962, 1666, 1597, 1561, 1533, 1466, 1418, 1373, 1276, 1178, 1059, 1005, 946, 906, 848, 756, 728, 687, 649, 596, 534. Anal.Calcd for  $\text{C}_{22}\text{H}_{15}\text{IN}_2\text{O}$ : C, 58.68; H, 3.36; I, 28.18; N, 6.22; Found: C, 58.33; H, 3.44; I, 28.12; N, 6.07%.

**{2-[5-(4-Fluorophenyl)-1H-pyrrol-2-yl]-5-iodopyridin-3-yl}(phenyl)methanone (2d).**

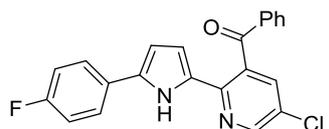


Yield 0.037 g (8%), yellow needles, mp 181-182 °C.

$^1\text{H}$  NMR (400.13 MHz,  $\text{CDCl}_3$ ):  $\delta = 9.81$  (br s, 1H, NH), 8.79 (d,  $J = 2.0$  Hz, 1H, H-6 pyridine), 7.88-7.86 (m, 2H, H-2,6 CPh), 7.83 (d,  $J = 2.0$  Hz, 1H, H-4 pyridine), 7.63-7.59 (m, 1H, H-4 CPh), 7.50-7.45 (m, 4H, H-2,6  $\text{C}_6\text{H}_4\text{F}$ , H-3,5 CPh), 7.09-7.04 (m, 2H, H-3,5  $\text{C}_6\text{H}_4\text{F}$ ), 6.31-6.28 (m, 2H, H-3,4 pyrrole).  $^{13}\text{C}$  NMR (100.61 MHz,  $\text{CDCl}_3$ ):  $\delta = 195.7$  (C=O), 162.1 (d,  $^1J_{\text{CF}} = 247.0$  Hz, C-4  $\text{C}_6\text{H}_4\text{F}$ ), 155.6 (C-6 pyridine), 145.5 (C-2 pyridine), 143.4 (C-4 pyridine), 136.0 (C-1 CPh), 134.5 (C-4 CPh), 133.8 (C-5 pyrrole), 132.5 (C-3 pyridine), 130.2 (C-2,6 CPh), 129.1 (C-2 pyrrole), 129.1 (C-3,5 CPh), 128.2 (d,  $^4J_{\text{CF}} = 3.2$  Hz, C-1  $\text{C}_6\text{H}_4\text{F}$ ), 126.1 (d,  $^3J_{\text{CF}} = 8.0$  Hz, C-2,6  $\text{C}_6\text{H}_4\text{F}$ ), 116.0 (d,  $^2J_{\text{CF}} = 21.8$  Hz, C-3,5  $\text{C}_6\text{H}_4\text{F}$ ), 114.3 (C-3 pyrrole), 108.7 (C-4 pyrrole), 87.0 (C-5 pyridine). IR (KBr,  $\text{cm}^{-1}$ ): 3436, 3109, 3059, 2922, 2854, 2738, 1741, 1666, 1564, 1524, 1473, 1419, 1371, 1276, 1232, 1159, 1058, 946, 906, 834, 771, 728, 683, 603, 514. Anal.Calcd for  $\text{C}_{22}\text{H}_{14}\text{FIN}_2\text{O}$ : C, 56.43; H, 3.01; F, 4.06; I, 27.10; N, 5.98; Found: C, 56.12; H, 2.88; F, 4.11; I, 27.11; N, 6.04%.

**{5-Bromo-2-[5-(4-fluorophenyl)-1H-pyrrol-2-yl]pyridin-3-yl}(phenyl)methanone (2'd),** yield 5%, was not isolated in pure state.

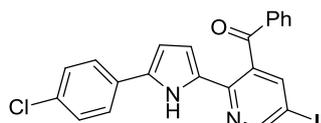
**{5-Chloro-2-[5-(4-fluorophenyl)-1H-pyrrol-2-yl]pyridin-3-yl}(phenyl)methanone (2''d).**



Yield 0.030 g (8%), yellow needles, mp 179-180 °C.

$^1\text{H}$  NMR (400.13 MHz,  $\text{CDCl}_3$ ):  $\delta = 9.81$  (br s, 1H, NH), 8.55 (d,  $J = 2.0$  Hz, 1H, H-6 pyridine), 7.88-7.86 (m, 2H, H-2,6 CPh), 7.63-7.60 (m, 1H, H-4 CPh), 7.54 (d,  $J = 2.0$  Hz, 1H, H-4 pyridine), 7.50-7.45 (m, 4H, H-2,6  $\text{C}_6\text{H}_4\text{F}$ , H-3,5 CPh), 7.08-7.04 (m, 2H, H-3,5  $\text{C}_6\text{H}_4\text{F}$ ), 6.31-6.30 (m, 1H, H-4 pyrrole), 6.29-6.27 (m, 1H, H-3 pyrrole).  $^{13}\text{C}$  NMR (100.61 MHz,  $\text{CDCl}_3$ ):  $\delta = 195.8$  (C=O), 162.1 (d,  $^1J_{\text{CF}} = 247.0$  Hz, C-4  $\text{C}_6\text{H}_4\text{F}$ ), 148.6 (C-6 pyridine), 145.0 (C-2 pyridine), 136.0 (C-1 CPh), 135.4 (C-4 pyridine), 134.5 (C-4 CPh), 133.7 (C-5 pyrrole), 131.7 (C-3 pyridine), 130.2 (C-2,6 CPh), 129.1 (C-2 pyrrole), 129.1 (C-3,5 CPh), 128.2 (d,  $^4J_{\text{CF}} = 3.3$  Hz, C-1  $\text{C}_6\text{H}_4\text{F}$ ), 127.6 (C-5 pyridine), 126.0 (d,  $^3J_{\text{CF}} = 8.0$  Hz, C-2,6  $\text{C}_6\text{H}_4\text{F}$ ), 116.0 (d,  $^2J_{\text{CF}} = 21.8$  Hz, C-3,5  $\text{C}_6\text{H}_4\text{F}$ ), 114.0 (C-3 pyrrole), 108.6 (C-4 pyrrole).  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ ):  $\delta = -115.1$ . IR (KBr,  $\text{cm}^{-1}$ ): 3435, 3385, 3059, 2923, 2854, 2625, 2373, 1666, 1590, 1571, 1521, 1473, 1418, 1276, 1230, 1153, 1133, 1061, 962, 911, 827, 746, 687, 609, 513. Anal.Calcd for  $\text{C}_{22}\text{H}_{14}\text{ClFN}_2\text{O}$ : C, 70.13; H, 3.75; Cl, 9.41; F, 5.04; N, 7.43; Found: C, 70.47; H, 3.40; Cl, 9.67; F, 5.19; N, 7.48%.

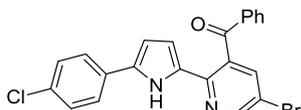
**{2-[5-(4-Chlorophenyl)-1*H*-pyrrol-2-yl]-5-iodopyridin-3-yl}(phenyl)methanone (2f).**



Yield 0.044 g (9%), yellow needles, mp 186-187 °C.

<sup>1</sup>H NMR (400.13 MHz, CDCl<sub>3</sub>): δ = 9.86 (br s, 1H, NH), 8.79 (d, *J* = 2.1 Hz, 1H, H-6 pyridine), 7.88-7.86 (m, 2H, H-2,6 C<sub>6</sub>H<sub>4</sub>Cl), 7.83 (d, *J* = 2.1 Hz, 1H, H-4 pyridine), 7.63-7.60 (m, 1H, H-4 C<sub>6</sub>H<sub>4</sub>Cl), 7.49-7.44 (m, 4H, H-2,6 C<sub>6</sub>H<sub>4</sub>Cl, H-3,5 C<sub>6</sub>H<sub>4</sub>Cl), 7.34-7.32 (m, 2H, H-3,5 C<sub>6</sub>H<sub>4</sub>Cl), 6.35 (dd, *J* = 3.6, 2.9 Hz, 1H, H-4 pyrrole), 6.29 (dd, *J* = 3.6, 2.4 Hz, 1H, H-3 pyrrole). <sup>13</sup>C NMR (100.61 MHz, CDCl<sub>3</sub>): δ = 195.7 (C=O), 155.7 (C-6 pyridine), 145.4 (C-2 pyridine), 143.4 (C-4 pyridine), 136.0 (C-1 C<sub>6</sub>H<sub>4</sub>Cl), 134.5 (C-4 C<sub>6</sub>H<sub>4</sub>Cl), 133.4 (C-5 pyrrole), 132.8 (C-4 C<sub>6</sub>H<sub>4</sub>Cl), 132.6 (C-3 pyridine), 130.3 (C-2,6 C<sub>6</sub>H<sub>4</sub>Cl), 129.5 (C-2 pyrrole), 129.4 (C-3,5 C<sub>6</sub>H<sub>4</sub>Cl), 129.2 (C-1 C<sub>6</sub>H<sub>4</sub>Cl), 129.1 (C-3,5 C<sub>6</sub>H<sub>4</sub>Cl), 125.5 (C-2,6 C<sub>6</sub>H<sub>4</sub>Cl), 114.4 (C-3 pyrrole), 109.2 (C-4 pyrrole), 87.2 (C-5 pyridine). <sup>15</sup>N NMR (40.55 MHz, CDCl<sub>3</sub>): δ = -237.6 (NH), -77.7 (N-1 pyridine). IR (KBr, cm<sup>-1</sup>): 3439, 3155, 3064, 2925, 2855, 2253, 1738, 1668, 1538, 1517, 1464, 1418, 1276, 1178, 1095, 1015, 945, 908, 828, 733, 650, 596, 513. Anal.Calcd for C<sub>22</sub>H<sub>14</sub>ClIN<sub>2</sub>O: C, 54.51; H, 2.91; Cl, 7.31; I, 26.18; N, 5.78; Found: C, 54.68; H, 3.11; Cl, 7.43; I, 26.01; N, 6.03%

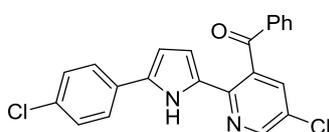
**{5-Bromo-2-[5-(4-chlorophenyl)-1*H*-pyrrol-2-yl]pyridin-3-yl}(phenyl)methanone (2'f).**



Yield 0.061 g (14%), yellow needles, mp 198-199 °C.

<sup>1</sup>H NMR (400.13 MHz, CDCl<sub>3</sub>): δ = 9.82 (br s, 1H, NH), 8.66 (d, *J* = 2.0 Hz, 1H, H-6 pyridine), 7.88-7.86 (m, 2H, H-2,6 C<sub>6</sub>H<sub>4</sub>Cl), 7.68 (d, *J* = 2.0 Hz, 1H, H-4 pyridine), 7.64-7.60 (m, 1H, H-4 C<sub>6</sub>H<sub>4</sub>Cl), 7.49-7.45 (m, 4H, H-2,6 C<sub>6</sub>H<sub>4</sub>Cl, H-3,5 C<sub>6</sub>H<sub>4</sub>Cl), 7.35-7.33 (m, 2H, H-3,5 C<sub>6</sub>H<sub>4</sub>Cl), 6.36 (dd, *J* = 3.6, 2.8 Hz, 1H, H-4 pyrrole), 6.29 (dd, *J* = 3.6, 2.4 Hz, 1H, H-3 pyrrole). <sup>13</sup>C NMR (100.61 MHz, CDCl<sub>3</sub>): δ = 195.6 (C=O), 150.8 (C-6 pyridine), 145.2 (C-2 pyridine), 138.1 (C-4 pyridine), 135.9 (C-1 C<sub>6</sub>H<sub>4</sub>Cl), 134.5 (C-4 C<sub>6</sub>H<sub>4</sub>Cl), 133.4 (C-5 pyrrole), 132.8 (C-3 pyridine), 132.2 (C-4 C<sub>6</sub>H<sub>4</sub>Cl), 130.3 (C-1 C<sub>6</sub>H<sub>4</sub>Cl), 130.2 (C-2,6 C<sub>6</sub>H<sub>4</sub>Cl), 129.4 (C-2 pyrrole), 129.2 (C-3,5 C<sub>6</sub>H<sub>4</sub>Cl), 129.1 (C-3,5 C<sub>6</sub>H<sub>4</sub>Cl), 125.5 (C-2,6 C<sub>6</sub>H<sub>4</sub>Cl), 115.9 (C-5 pyridine), 114.2 (C-3 pyrrole), 109.1 (C-4 pyrrole). IR (KBr, cm<sup>-1</sup>): 3432, 3369, 3060, 2921, 2853, 1830, 1741, 1667, 1540, 1518, 1465, 1419, 1275, 1212, 1180, 1092, 1016, 950, 907, 822, 766, 728, 685, 592, 511. Anal.Calcd for C<sub>22</sub>H<sub>14</sub>BrClN<sub>2</sub>O: C, 60.37; H, 3.22; Br, 18.25; Cl, 8.10; N, 6.40; Found: C, 60.18; H, 3.31; Br, 18.14; Cl, 8.12; N, 6.49%.

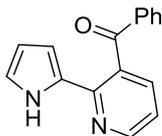
**{5-Chloro-2-[5-(4-chlorophenyl)-1*H*-pyrrol-2-yl]pyridin-3-yl}(phenyl)methanone (2''f).**



Yield 0.024 g (6%), yellow needles, mp 189-190 °C.

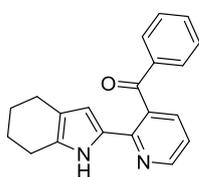
<sup>1</sup>H NMR (400.13 MHz, CDCl<sub>3</sub>): δ = 9.82 (br s, 1H, NH), 8.56 (d, *J* = 2.0 Hz, 1H, H-6 pyridine), 7.88-7.86 (m, 2H, H-2,6 C<sub>6</sub>H<sub>4</sub>Cl), 7.64-7.60 (m, 1H, H-4 C<sub>6</sub>H<sub>4</sub>Cl), 7.54 (d, *J* = 2.0 Hz, 1H, H-4 pyridine), 7.49-7.45 (m, 4H, H-2,6 C<sub>6</sub>H<sub>4</sub>Cl, H-3,5 C<sub>6</sub>H<sub>4</sub>Cl), 7.35-7.33 (m, 2H, H-3,5 C<sub>6</sub>H<sub>4</sub>Cl), 6.36 (dd, *J* = 3.6, 2.8 Hz, 1H, H-4 pyrrole), 6.28 (dd, *J* = 3.6, 2.4 Hz, 1H, H-3 pyrrole). <sup>13</sup>C NMR (100.61 MHz, CDCl<sub>3</sub>): δ = 195.7 (C=O), 148.6 (C-6 pyridine), 144.9 (C-2 pyridine), 136.0 (C-1 C<sub>6</sub>H<sub>4</sub>Cl), 135.4 (C-4 pyridine), 134.5 (C-4 C<sub>6</sub>H<sub>4</sub>Cl), 133.3 (C-5 pyrrole), 132.8 (C-4 C<sub>6</sub>H<sub>4</sub>Cl), 131.8 (C-3 pyridine), 130.3 (C-1 C<sub>6</sub>H<sub>4</sub>Cl), 130.2 (C-2,6 C<sub>6</sub>H<sub>4</sub>Cl), 129.4 (C-2 pyrrole), 129.2 (C-3,5 C<sub>6</sub>H<sub>4</sub>Cl), 129.1 (C-3,5 C<sub>6</sub>H<sub>4</sub>Cl), 127.8 (C-5 pyridine), 125.5 (C-2,6 C<sub>6</sub>H<sub>4</sub>Cl), 114.0 (C-3 pyrrole), 109.1 (C-4 pyrrole). IR (KBr, cm<sup>-1</sup>): 3440, 2923, 2853, 2367, 2253, 1669, 1574, 1547, 1466, 1418, 1276, 1206, 1097, 1058, 692, 908, 824, 734, 650. Anal.Calcd for C<sub>22</sub>H<sub>14</sub>Cl<sub>2</sub>N<sub>2</sub>O: C, 67.19; H, 3.59; Cl, 18.03; N, 7.12; Found: C, 67.14; H, 3.66; Cl, 18.11; N, 7.02%.

**[2-(1*H*-Pyrrol-2-yl)pyridin-3-yl](phenyl)methanone (3a).**



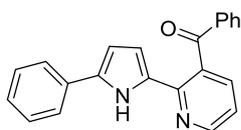
Yield 0.151 g (61%), yellow crystals, mp 111-112 °C. <sup>1</sup>H NMR (400.13 MHz, CDCl<sub>3</sub>): δ = 9.76 (br s, 1H, NH), 8.61 (dd, *J* = 4.7, 1.4 Hz, 1H, H-6 pyridine), 7.86-7.84 (m, 2H, H-2,6 C<sub>OPh</sub>), 7.59-7.54 (m, 2H, H-4 pyridine, H-4 C<sub>OPh</sub>), 7.45-7.41 (m, 2H, H-3,5 C<sub>OPh</sub>), 7.15 (dd, *J* = 7.6, 4.7 Hz, 1H, H-5 pyridine), 6.84-6.83 (m, 1H, H-5 pyrrole), 6.28-6.26 (m, 1H, H-3 pyrrole), 6.09-6.07 (m, 1H, H-4 pyrrole). <sup>13</sup>C NMR (100.61 MHz, CDCl<sub>3</sub>): δ = 197.5 (C=O), 149.8 (C-6 pyridine), 147.2 (C-2 pyridine), 136.5 (C-1 C<sub>OPh</sub>), 135.9 (C-4 pyridine), 134.0 (C-4 C<sub>OPh</sub>), 131.1 (C-3 pyridine), 130.2 (C-2,6 C<sub>OPh</sub>), 129.2 (C-2 pyrrole), 128.8 (C-3,5 C<sub>OPh</sub>), 120.2 (C-5 pyrrole), 119.5 (C-5 pyridine), 111.9 (C-4 pyrrole), 110.7 (C-3 pyrrole). IR (KBr, cm<sup>-1</sup>): 3435, 3249, 3068, 2923, 2855, 2158, 1740, 1666, 1569, 1445, 1313, 1277, 1227, 1151, 1129, 1095, 1045, 929, 878, 790, 742, 710, 639, 599, 425. Anal.Cald for C<sub>16</sub>H<sub>12</sub>N<sub>2</sub>O: C, 77.40; H, 4.87; N, 11.28; Found: C, 77.54; H, 4.77; N, 11.18%.

**(Phenyl)[2-(4,5,6,7-tetrahydro-1*H*-indol-2-yl)pyridin-3-yl]methanone (3b).**



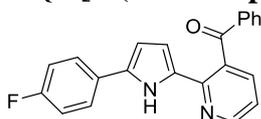
Yield 0.085 mg (28%), yellow crystals, mp 159-161 °C. <sup>1</sup>H NMR (400.13 MHz, CDCl<sub>3</sub>): δ = 9.27 (br s, 1H, NH), 8.54 (dd, *J* = 4.8, 1.4 Hz, 1H, H-6 pyridine), 7.88-7.86 (m, 2H, H-2,6 C<sub>OPh</sub>), 7.60-7.56 (m, 1H, H-4 C<sub>OPh</sub>), 7.47-7.42 (m, 3H, H-4 pyridine, H-3,5 C<sub>OPh</sub>), 7.04 (dd, *J* = 7.6, 4.8 Hz, 1H, H-5 pyridine), 6.01 (d, *J* = 2.0 Hz, 1H, H-3 pyrrole), 2.59-2.56 (m, 2H, CH<sub>2</sub>-4), 2.35-2.32 (m, 2H, CH<sub>2</sub>-7), 1.79-1.73 (m, 2H, CH<sub>2</sub>-5), 1.68-1.63 (m, 2H, CH<sub>2</sub>-6). <sup>13</sup>C NMR (100.61 MHz, CDCl<sub>3</sub>): δ = 197.8 (C=O), 149.6 (C-6 pyridine), 147.4 (C-2 pyridine), 136.7 (C-1 C<sub>OPh</sub>), 135.6 (C-4 pyridine), 133.9 (C-4 C<sub>OPh</sub>), 130.4 (C-3 pyridine), 130.3 (C-7a), 130.2 (C-2,6 C<sub>OPh</sub>), 128.8 (C-3,5 C<sub>OPh</sub>), 127.1 (C-2 pyrrole), 120.0 (C-5 pyridine), 118.5 (C-3a), 111.2 (C-3 pyrrole), 23.6, 23.2, 22.8, 22.8 (CH<sub>2</sub>-4,5,6,7). IR (KBr, cm<sup>-1</sup>): 3229, 3165, 3062, 2928, 2849, 2247, 1917, 1666, 1580, 1495, 1447, 1417, 1361, 1312, 1281, 1235, 1147, 1104, 1060, 1028, 951, 921, 803, 775, 726, 666, 642, 589. Anal.Cald for C<sub>20</sub>H<sub>18</sub>N<sub>2</sub>O: C, 79.44; H, 6.00; N, 9.26; Found: C, 79.37; H, 6.04; N, 8.87%.

**(Phenyl)[2-(5-phenyl-1*H*-pyrrol-2-yl)pyridin-3-yl]methanone (3c).**



Yield 0.156 mg (48%), yellow crystals, mp 108-110 °C. <sup>1</sup>H NMR (400.13 MHz, CDCl<sub>3</sub>): δ = 9.99 (br s, 1H, NH), 8.64 (dd, *J* = 4.7, 1.4 Hz, 1H, H-6 pyridine), 7.89-7.87 (m, 2H, H-2,6 C<sub>OPh</sub>), 7.60-7.54 (m, 4H, H-4 pyridine, H-2,6 Ph, H-4 C<sub>OPh</sub>), 7.47-7.43 (m, 2H, H-3,5 C<sub>OPh</sub>), 7.39-7.35 (m, 2H, H-3,5 Ph), 7.25-7.21 (m, 1H, H-4 Ph), 7.15 (dd, *J* = 7.6, 4.7 Hz, 1H, H-5 pyridine), 6.39 (dd, *J* = 3.7, 2.9 Hz, 1H, H-4 pyrrole), 6.32 (dd, *J* = 3.7, 2.3 Hz, 1H, H-3 pyrrole). <sup>13</sup>C NMR (100.61 MHz, CDCl<sub>3</sub>): δ = 197.5 (C=O), 149.8 (C-6 pyridine), 146.9 (C-2 pyridine), 136.6 (C-1 C<sub>OPh</sub>), 136.0 (C-4 pyridine), 134.1 (C-4 C<sub>OPh</sub>), 134.1 (C-5 pyrrole), 132.0 (C-1 Ph), 131.1 (C-3 pyridine), 130.2 (C-2,6 C<sub>OPh</sub>), 130.0 (C-2 pyrrole), 129.0 (C-3,5 C<sub>OPh</sub>), 128.9 (C-2,6 Ph), 126.9 (C-4 Ph), 124.3 (C-3,5 Ph), 119.5 (C-5 pyridine), 113.7 (C-3 pyrrole), 108.5 (C-4 pyrrole). <sup>15</sup>N NMR (40.55 MHz, CDCl<sub>3</sub>): δ = -236.8 (NH), -83.0 (N-1 pyridine). IR (KBr, cm<sup>-1</sup>): 3434, 3318, 3063, 2925, 2860, 2735, 2249, 1949, 1665, 1572, 1465, 1417, 1312, 1278, 1223, 1153, 1061, 996, 923, 846, 760, 717, 644, 591, 494. Anal.Cald for C<sub>22</sub>H<sub>16</sub>N<sub>2</sub>O: C, 81.46; H, 4.97; N, 8.64; Found: C, 81.64; H, 4.73; N, 8.42%.

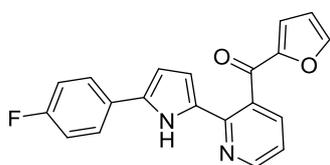
**{2-[5-(4-Fluorophenyl)-1*H*-pyrrol-2-yl]pyridin-3-yl}(phenyl)methanone (3d).**



Yield CuCl - 0.137 mg (40%); CuBr - 0.103 mg (30%); CuI - 0.106 mg (31%), yellow crystals, mp 125-127 °C.

<sup>1</sup>H NMR (400.13 MHz, CDCl<sub>3</sub>): δ = 9.95 (br s, 1H, NH), 8.62 (dd, *J* = 4.8, 1.6 Hz, 1H, H-6 pyridine), 7.88-7.86 (m, 2H, H-2,6 C<sub>6</sub>H<sub>4</sub>F), 7.61-7.56 (m, 2H, H-4 pyridine, H-4 C<sub>6</sub>H<sub>4</sub>F), 7.51-7.43 (m, 4H, H-3,5 C<sub>6</sub>H<sub>4</sub>F, H-2,6 C<sub>6</sub>H<sub>4</sub>F), 7.15 (dd, *J* = 7.4, 4.8 Hz, 1H, H-5 pyridine), 7.08-7.03 (m, 2H, H-3,5 C<sub>6</sub>H<sub>4</sub>F), 6.32-6.31 (m, 2H, H-3,4 pyrrole). <sup>13</sup>C NMR (100.61 MHz, CDCl<sub>3</sub>): δ = 197.5 (C=O), 161.9 (d, <sup>1</sup>*J*<sub>CF</sub> = 246.5 Hz, C-4 C<sub>6</sub>H<sub>4</sub>F), 149.8 (C-6 pyridine), 146.8 (C-2 pyridine), 136.4 (C-1 C<sub>6</sub>H<sub>4</sub>F), 136.0 (C-4 pyridine), 134.1 (C-4 C<sub>6</sub>H<sub>4</sub>F), 133.2 (C-5 pyrrole), 131.1 (C-3 pyridine), 130.2 (C-2,6 C<sub>6</sub>H<sub>4</sub>F), 129.9 (C-2 pyrrole), 128.9 (C-3,5 C<sub>6</sub>H<sub>4</sub>F), 128.3 (d, <sup>4</sup>*J*<sub>CF</sub> = 2.6 Hz, C-1 C<sub>6</sub>H<sub>4</sub>F), 125.9 (d, <sup>3</sup>*J*<sub>CF</sub> = 7.8 Hz, C-2,6 C<sub>6</sub>H<sub>4</sub>F), 119.6 (C-5 pyridine), 115.9 (d, <sup>2</sup>*J*<sub>CF</sub> = 21.7 Hz, C-3,5 C<sub>6</sub>H<sub>4</sub>F), 113.6 (C-3 pyrrole), 108.4 (C-4 pyrrole). <sup>15</sup>N NMR (40.55 MHz, CDCl<sub>3</sub>): δ = -237.7 (NH), -79.5 (N-1 pyridine). IR (KBr, cm<sup>-1</sup>): 3431, 3364, 3062, 2966, 2930, 2865, 2373, 2250, 1918, 1664, 1572, 1520, 1473, 1417, 1277, 1230, 1153, 1063, 1022, 922, 834, 767, 714, 680, 640, 605, 514. Anal.Calcd for C<sub>22</sub>H<sub>15</sub>FN<sub>2</sub>O: C, 77.18; H, 4.42; F, 5.55; N, 8.18; Found: C, 77.04; H, 4.33; F, 5.64; N, 8.14%.

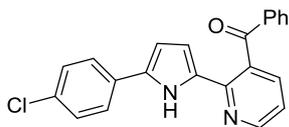
**{2-[5-(4-Fluorophenyl)-1H-pyrrol-2-yl]pyridin-3-yl}(furan-2-yl)methanone (3e).**



Yield 0.126 g (38%), yellow crystals, mp 55-56 °C.

<sup>1</sup>H NMR (400.13 MHz, CDCl<sub>3</sub>): δ = 10.05 (br s, 1H, NH), 8.60 (dd, *J* = 4.8, 1.6 Hz, 1H, H-6 pyridine), 7.67-7.65 (m, 2H, H-4 pyridine, H-5 furan), 7.51-7.48 (m, 2H, H-2,6 C<sub>6</sub>H<sub>4</sub>F), 7.14 (dd, *J* = 7.4, 4.8 Hz, 1H, H-5 pyridine), 7.07-7.03 (m, 3H, H-3 furan, H-3,5 C<sub>6</sub>H<sub>4</sub>F), 6.52 (dd, *J* = 3.5, 1.7 Hz, 1H, H-4 furan), 6.46 (dd, *J* = 3.7, 2.9 Hz, 1H, H-4 pyrrole), 6.38 (dd, *J* = 3.7, 2.3 Hz, 1H, H-3 pyrrole). <sup>13</sup>C NMR (100.61 MHz, CDCl<sub>3</sub>): δ = 184.3 (C=O), 161.9 (d, <sup>1</sup>*J*<sub>CF</sub> = 246.5 Hz, C-4 C<sub>6</sub>H<sub>4</sub>F), 152.4 (C-2 furan), 150.2 (C-6 pyridine), 148.3 (C-5 furan), 147.2 (C-2 pyridine), 136.3 (C-4 pyridine), 133.4 (C-5 pyrrole), 130.1 (C-3 pyridine), 129.8 (C-2 pyrrole), 128.4 (d, <sup>4</sup>*J*<sub>CF</sub> = 2.6 Hz, C-1 C<sub>6</sub>H<sub>4</sub>F), 125.9 (d, <sup>3</sup>*J*<sub>CF</sub> = 7.9 Hz, C-2,6 C<sub>6</sub>H<sub>4</sub>F), 121.6 (C-5 pyridine), 119.4 (C-3 furan), 115.9 (d, <sup>2</sup>*J*<sub>CF</sub> = 21.7 Hz, C-3,5 C<sub>6</sub>H<sub>4</sub>F), 113.5 (C-3 pyrrole), 112.8 (C-4 furan), 108.4 (C-4 pyrrole). IR (KBr, cm<sup>-1</sup>): 3433, 3349, 3131, 3044, 2967, 2853, 2748, 2251, 2040, 1886, 1653, 1569, 1521, 1469, 1418, 1393, 1305, 1230, 1157, 1061, 1020, 956, 910, 881, 835, 808, 767, 732, 647, 597, 519. Anal.Calcd for C<sub>20</sub>H<sub>13</sub>FN<sub>2</sub>O<sub>2</sub>: C, 72.28; H, 3.94; F, 5.72; N, 8.43; Found: C, 72.24; H, 4.03; F, 5.69; N, 8.36%.

**{2-[5-(4-Chlorophenyl)-1H-pyrrol-2-yl]pyridin-3-yl}(phenyl)methanone (3f).**

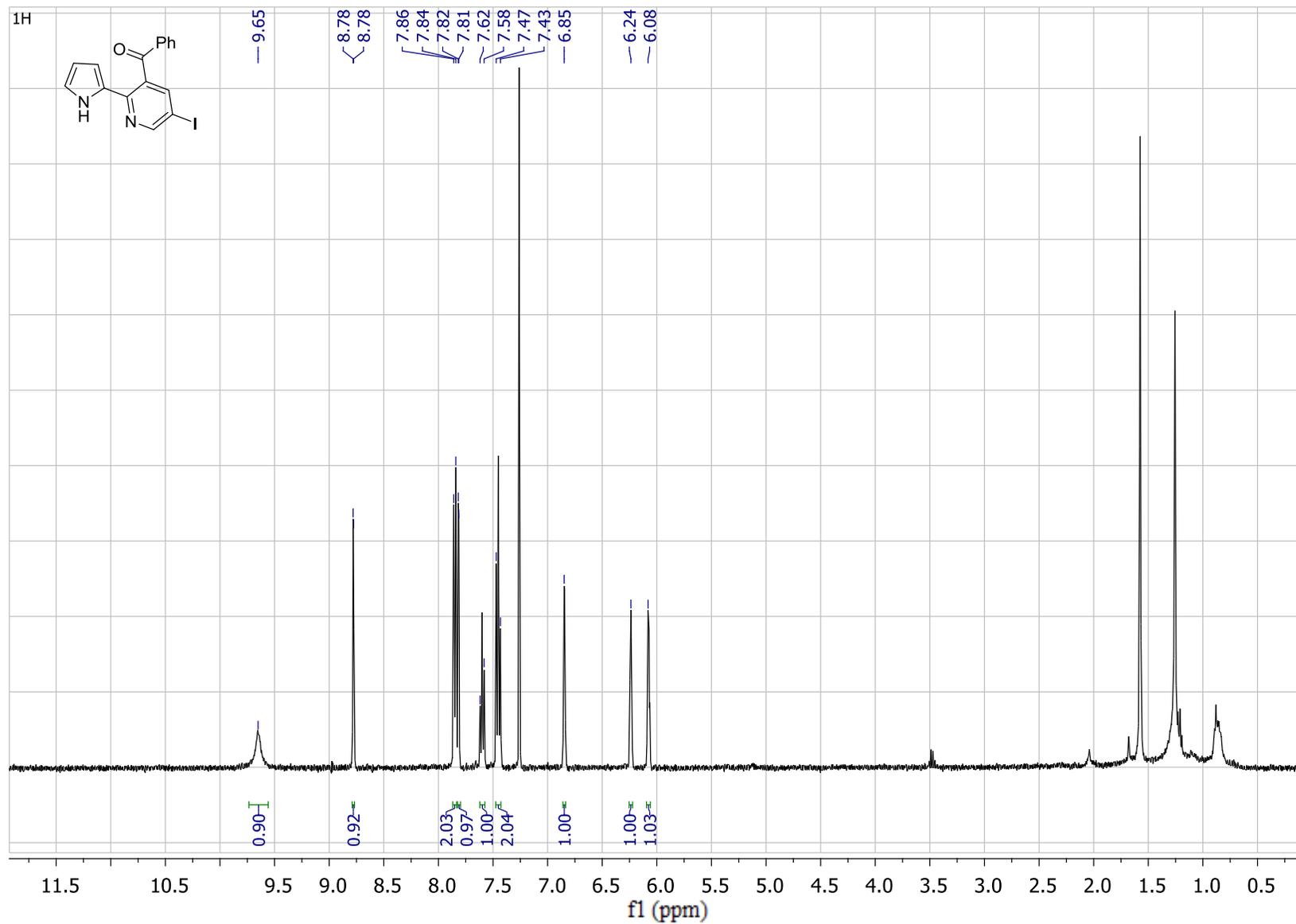


Yield CuCl - 0.151 mg (42%); CuBr - 0.100 mg (28%); CuI - 0.129 mg (36%), yellow crystals, mp 103-105 °C.

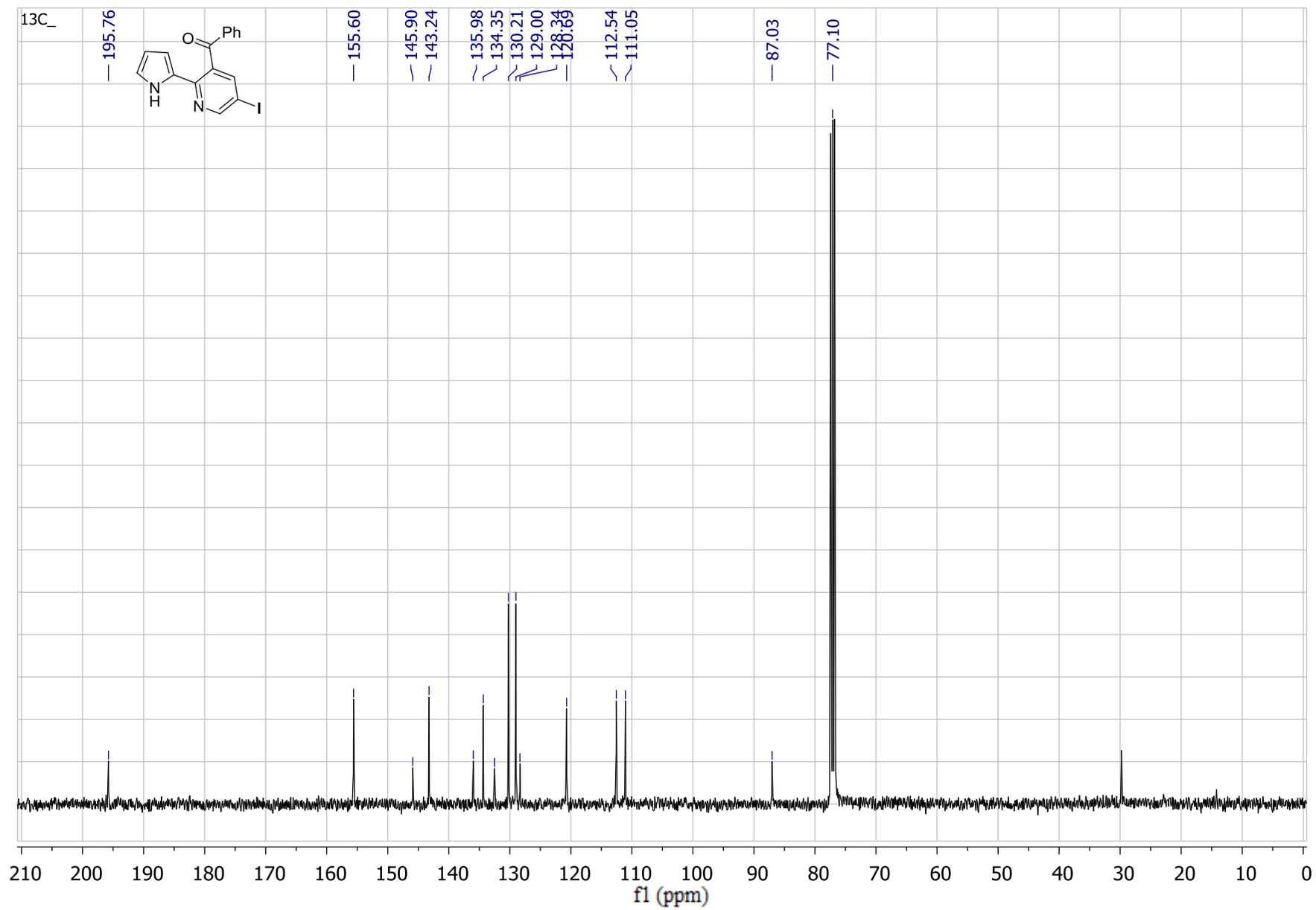
<sup>1</sup>H NMR (400.13 MHz, CDCl<sub>3</sub>): δ = 9.94 (br s, 1H, NH), 8.64 (dd, *J* = 4.8, 1.6 Hz, 1H, H-6 pyridine), 7.88-7.86 (m, 2H, H-2,6 C<sub>6</sub>H<sub>4</sub>Cl), 7.59-7.56 (m, 2H, H-4 pyridine, H-4 C<sub>6</sub>H<sub>4</sub>Cl), 7.47-7.43 (m, 4H, H-3,5 C<sub>6</sub>H<sub>4</sub>Cl, H-2,6 C<sub>6</sub>H<sub>4</sub>Cl), 7.34-7.32 (m, 2H, H-3,5 C<sub>6</sub>H<sub>4</sub>Cl), 7.17 (dd, *J* = 7.6, 4.8 Hz, 1H, H-5 pyridine), 6.36 (dd, *J* = 3.7, 2.9 Hz, 1H, H-4 pyrrole), 6.31 (dd, *J* = 3.7, 2.3 Hz, 1H, H-3 pyrrole). <sup>13</sup>C NMR (100.61 MHz, CDCl<sub>3</sub>): δ = 197.4 (C=O), 149.8 (C-6 pyridine), 146.7 (C-2 pyridine), 136.5 (C-1 C<sub>6</sub>H<sub>4</sub>Cl), 136.0 (C-4 pyridine), 134.1 (C-4 C<sub>6</sub>H<sub>4</sub>Cl), 132.9 (C-4 C<sub>6</sub>H<sub>4</sub>Cl), 132.4 (C-5 pyrrole), 131.2 (C-3 pyridine), 130.5 (C-1 C<sub>6</sub>H<sub>4</sub>Cl), 130.3 (C-2 pyrrole), 130.2 (C-2,6 C<sub>6</sub>H<sub>4</sub>Cl), 129.1 (C-3,5 C<sub>6</sub>H<sub>4</sub>Cl), 128.9 (C-3,5 C<sub>6</sub>H<sub>4</sub>Cl), 125.4 (C-2,6 C<sub>6</sub>H<sub>4</sub>Cl), 119.7 (C-5 pyridine), 113.7 (C-3 pyrrole), 108.9 (C-4 pyrrole). IR (KBr, cm<sup>-1</sup>): 3430, 3370, 3064, 2960, 2926, 2857, 2249, 1665, 1576, 1511, 1464, 1416, 1311, 1276, 1227, 1150, 1090, 1060, 1018, 923, 826, 767, 728, 680, 590. Anal.Calcd for C<sub>22</sub>H<sub>15</sub>ClN<sub>2</sub>O: C, 73.64; H, 4.21; Cl, 9.88; N, 7.81; Found: C, 73.54; H, 4.13; Cl, 10.09; N, 7.47%.

# Copies of $^1\text{H}$ and $^{13}\text{C}$ NMR spectra

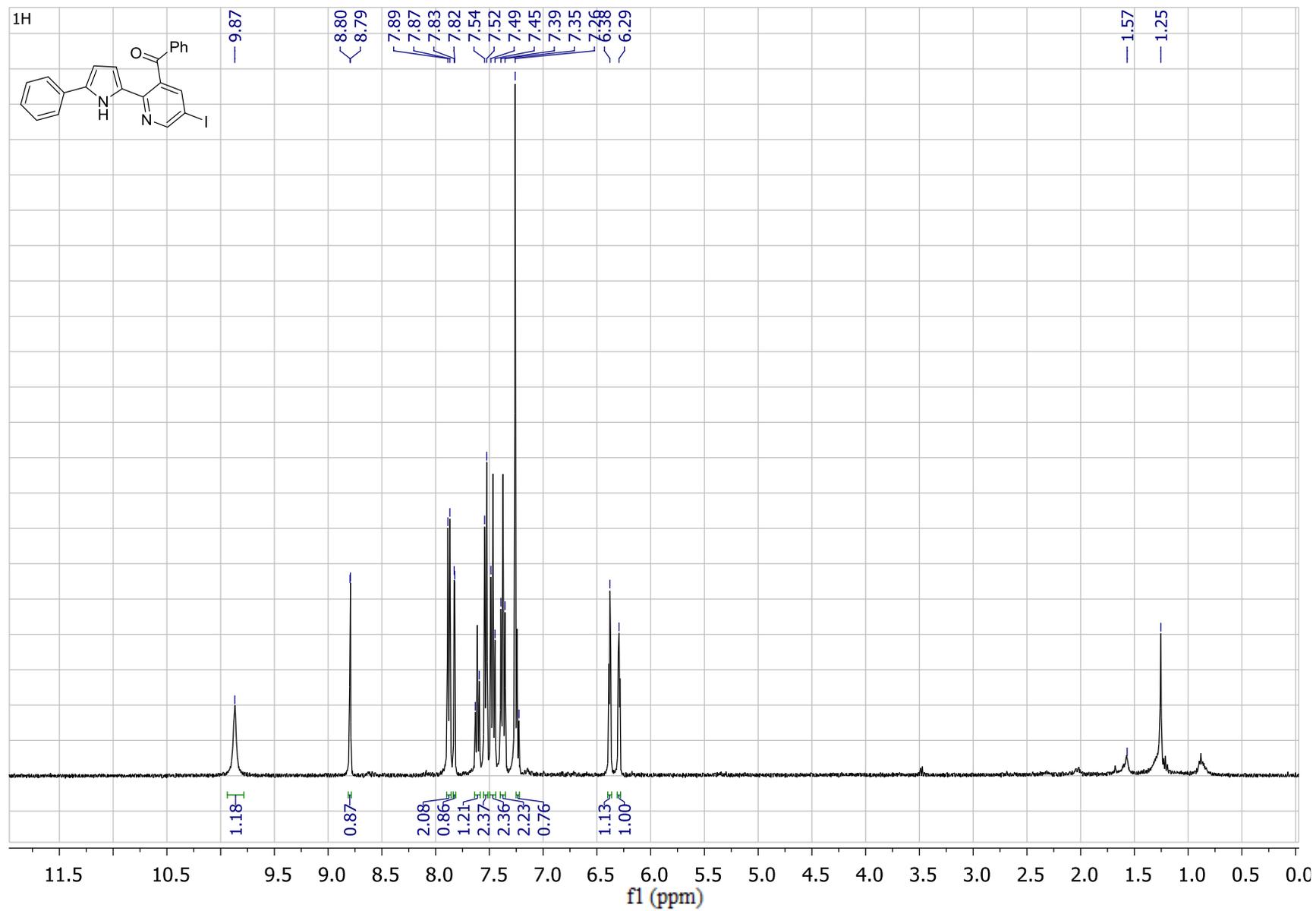
$^1\text{H}$  NMR spectrum of **2a** ( $\text{CDCl}_3$ ).



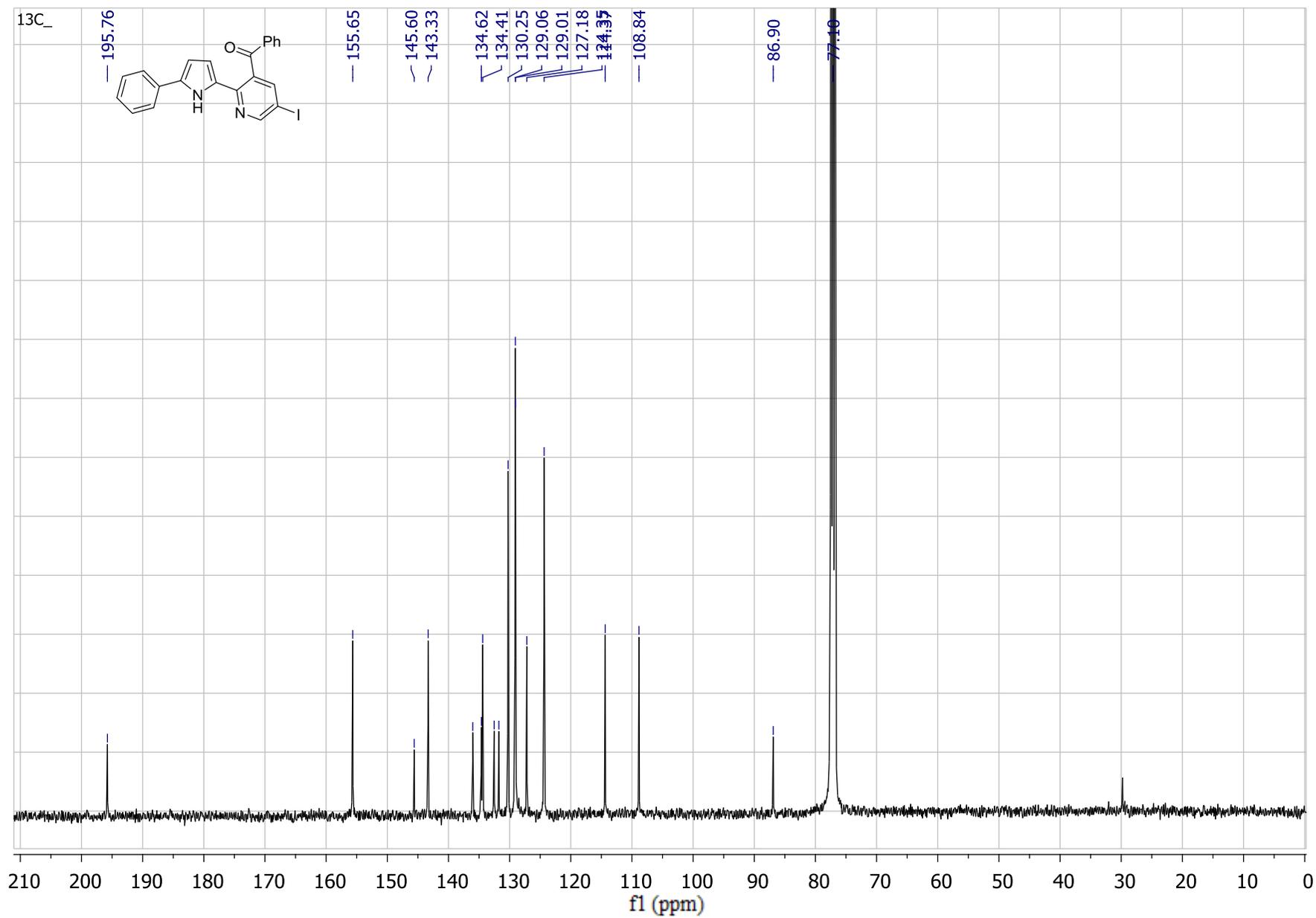
$^{13}\text{C}$  NMR spectrum of **2a** ( $\text{CDCl}_3$ ).



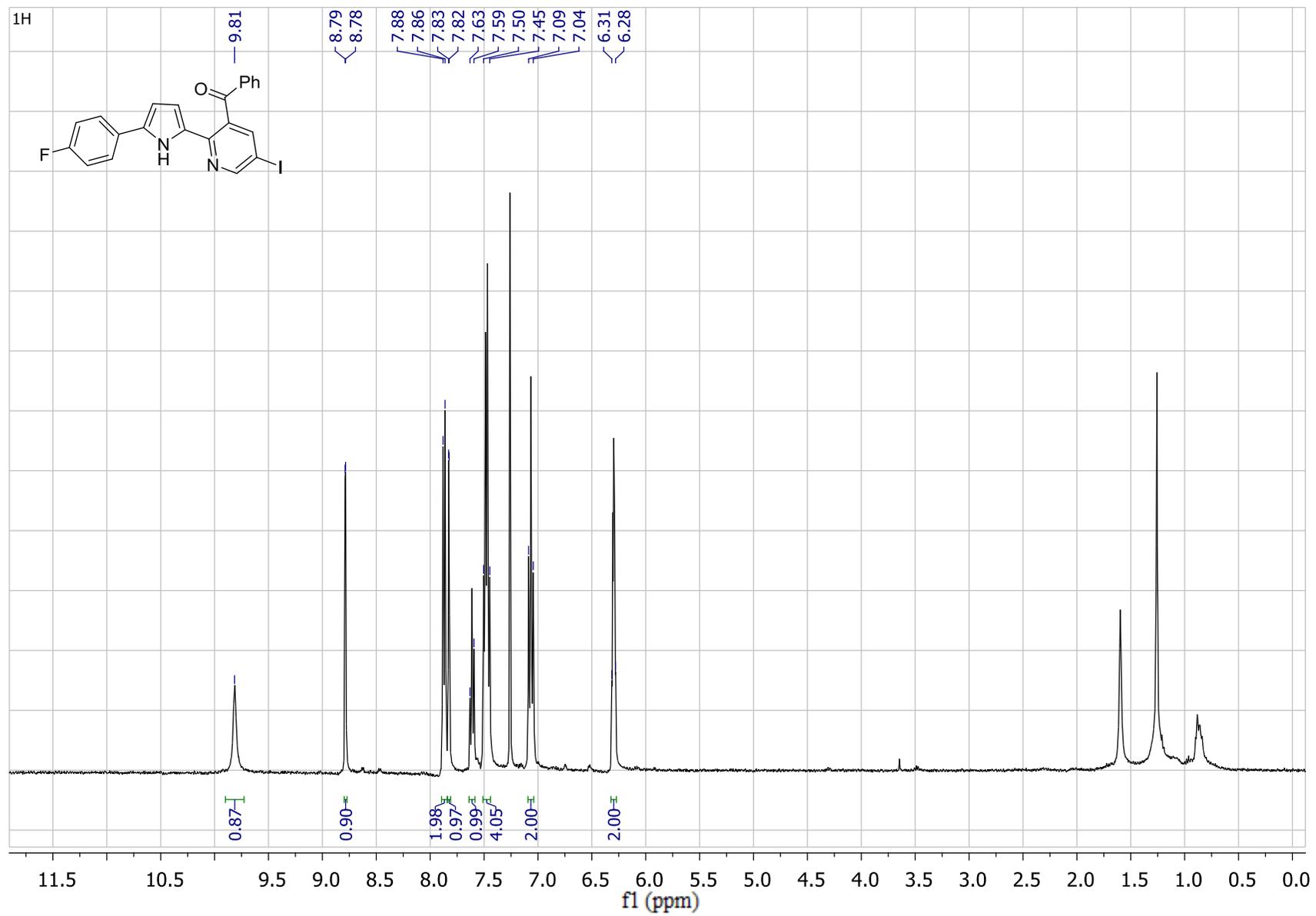
<sup>1</sup>H NMR spectrum of 2c (CDCl<sub>3</sub>).



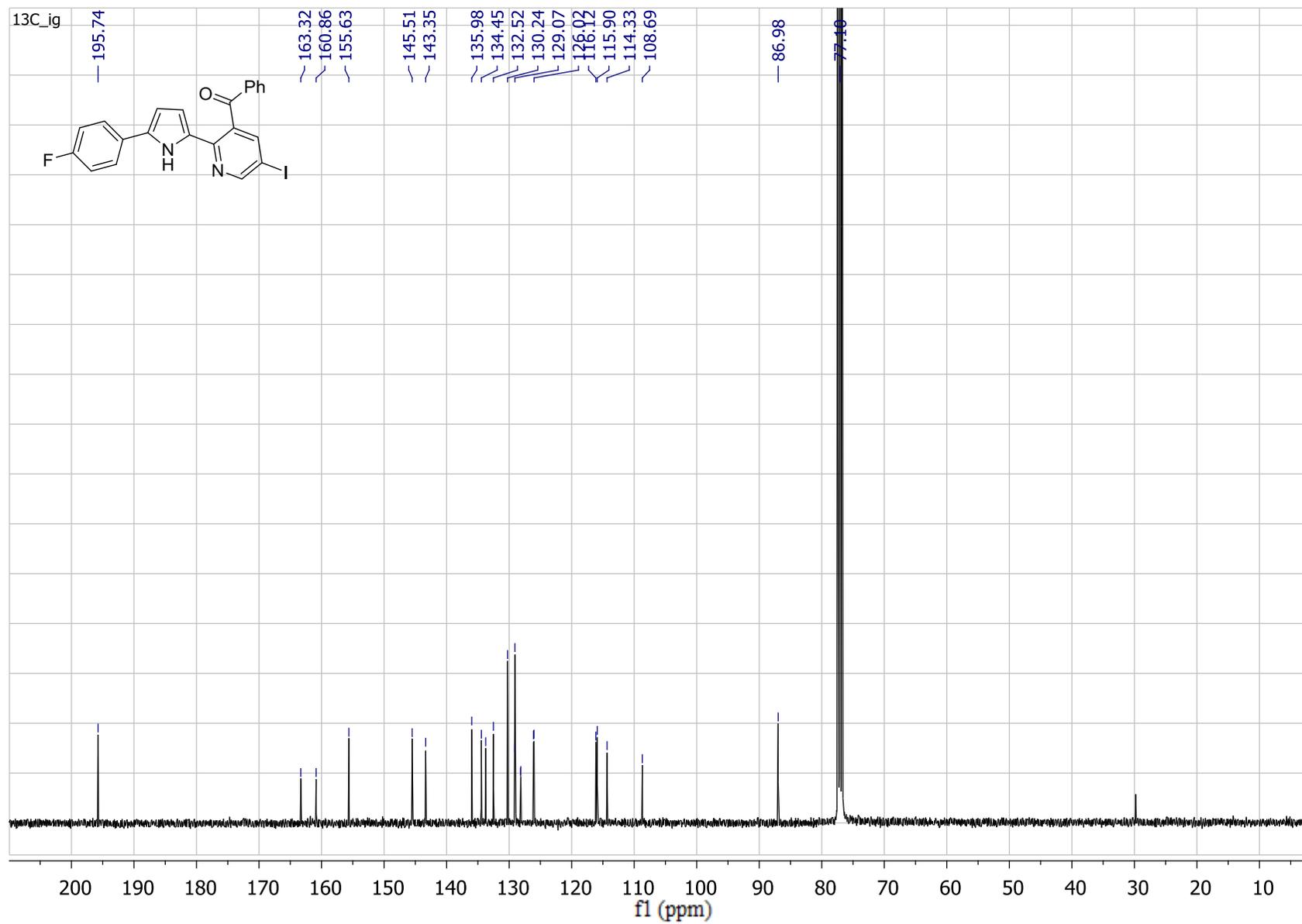
<sup>13</sup>C NMR spectrum of **2c** (CDCl<sub>3</sub>).



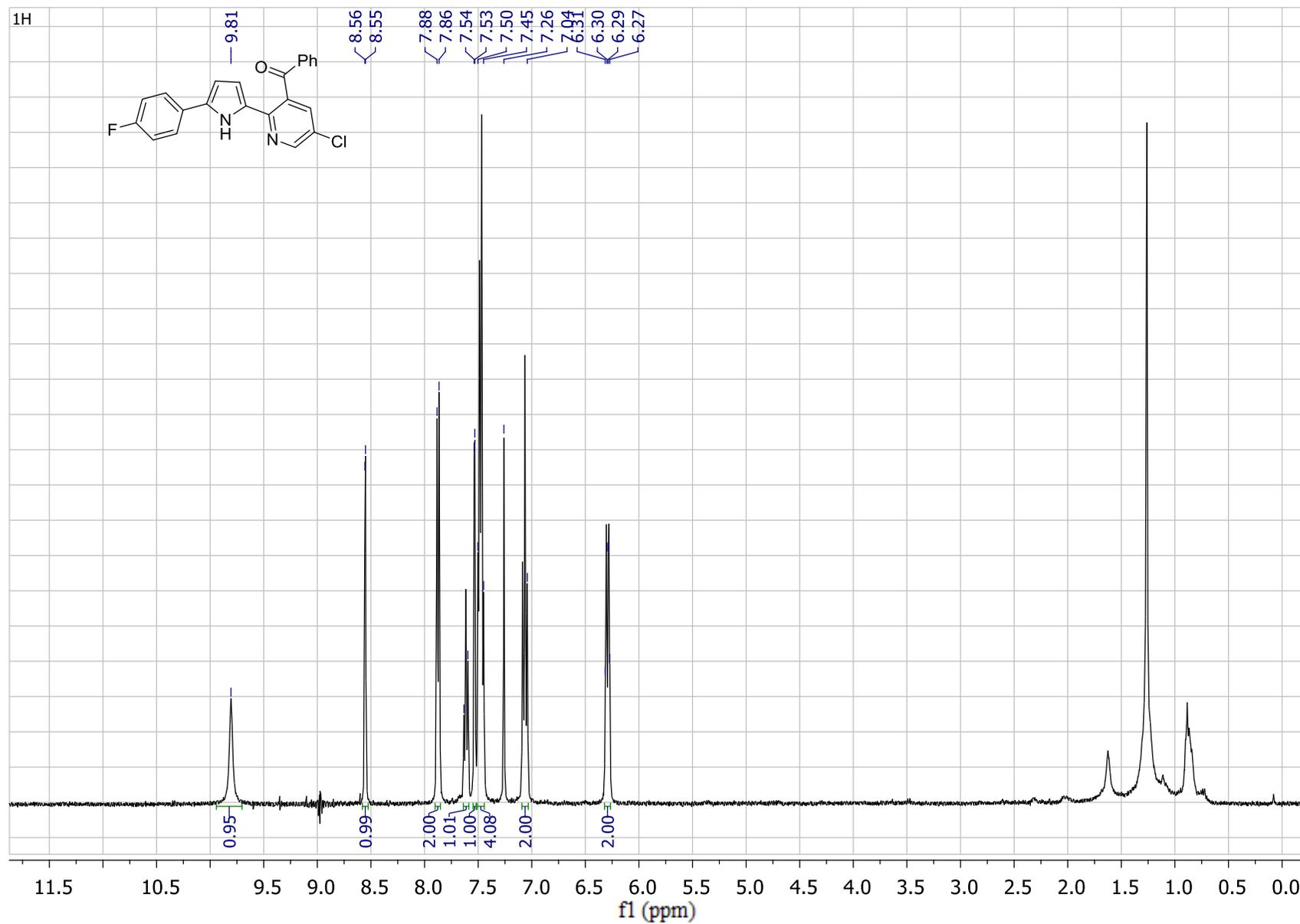
$^1\text{H}$  NMR spectrum of **2d** ( $\text{CDCl}_3$ ).



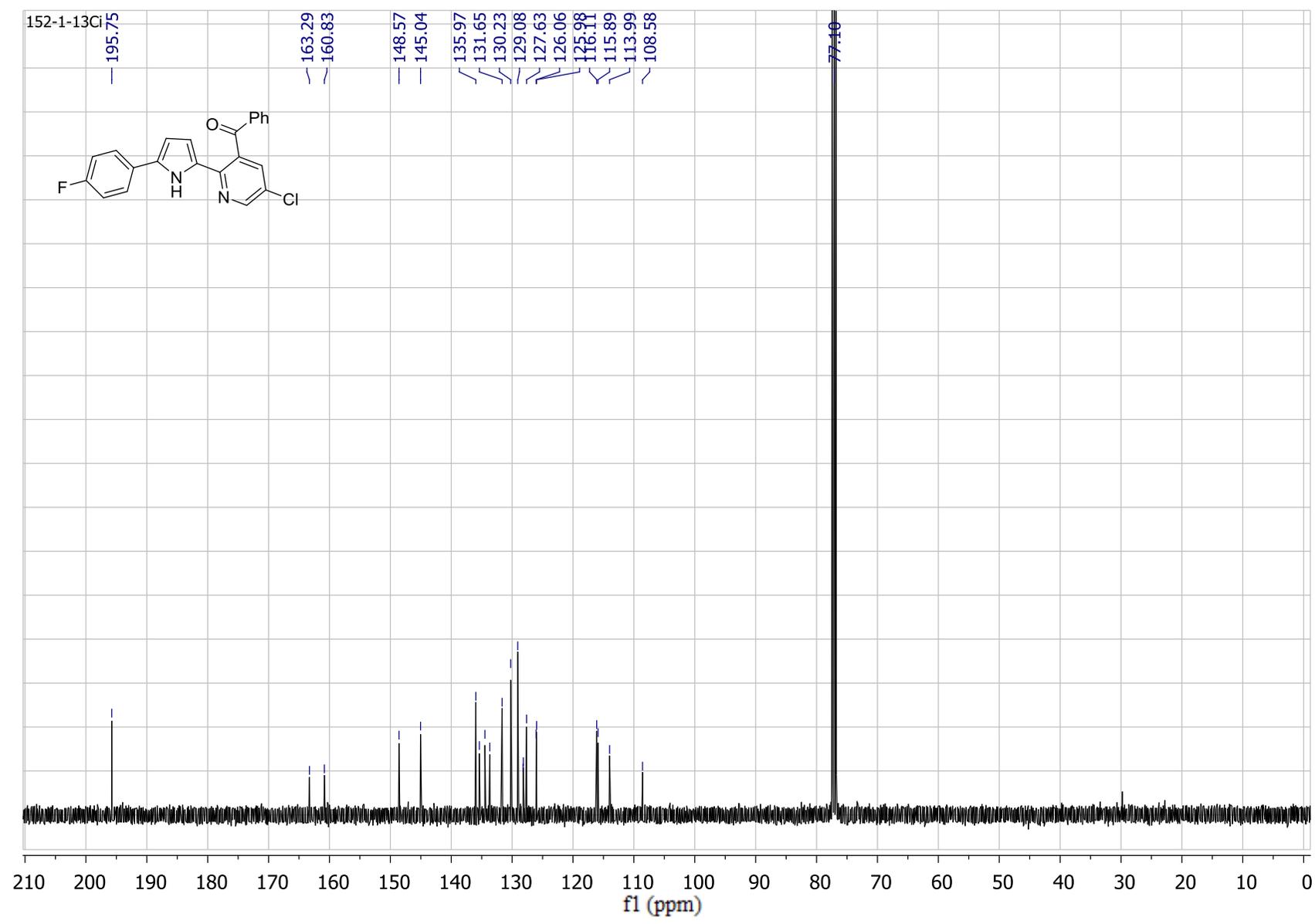
$^{13}\text{C}$  NMR spectrum of **2d** ( $\text{CDCl}_3$ ).



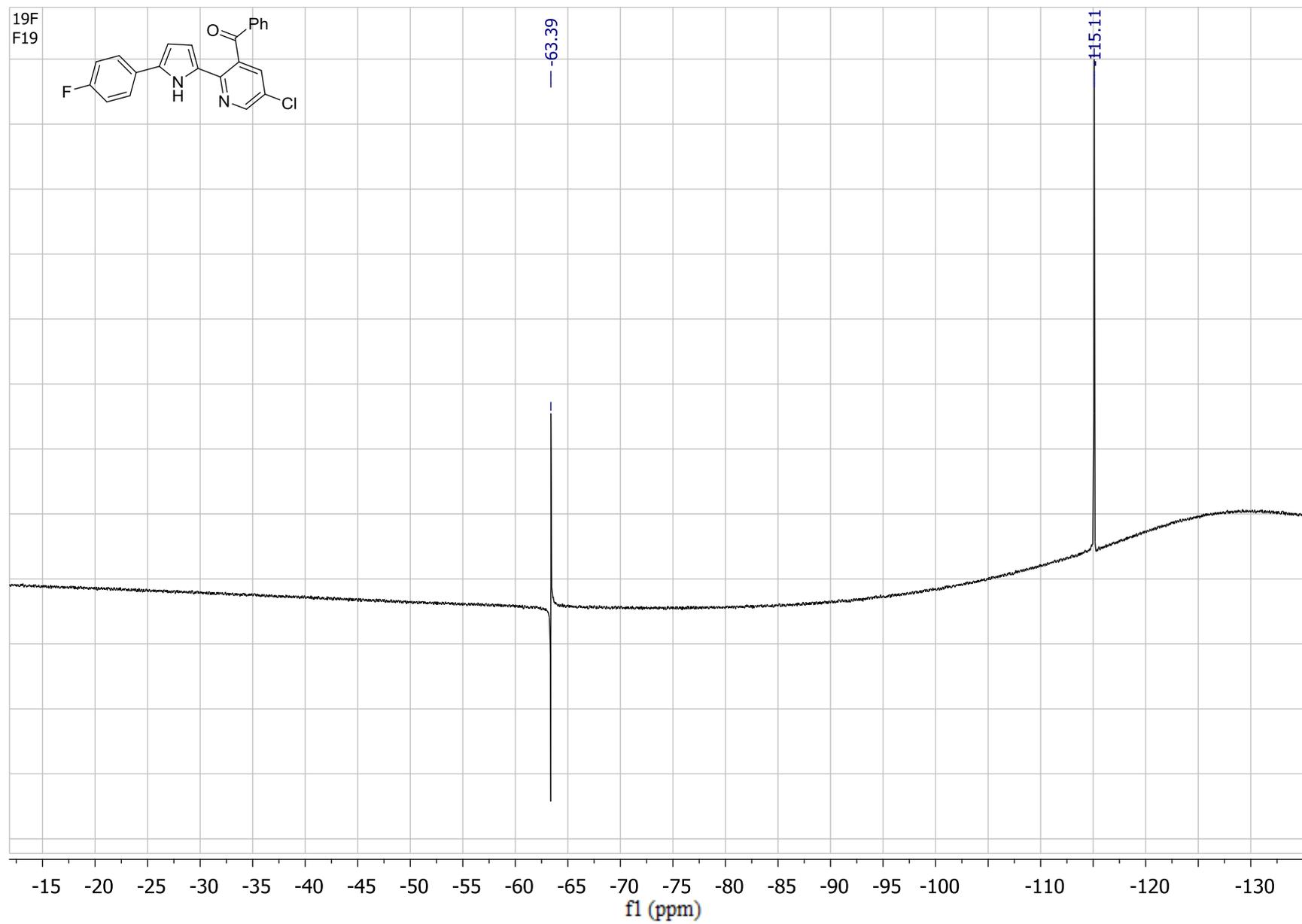
<sup>1</sup>H NMR spectrum of **2**<sup>d</sup> (CDCl<sub>3</sub>).



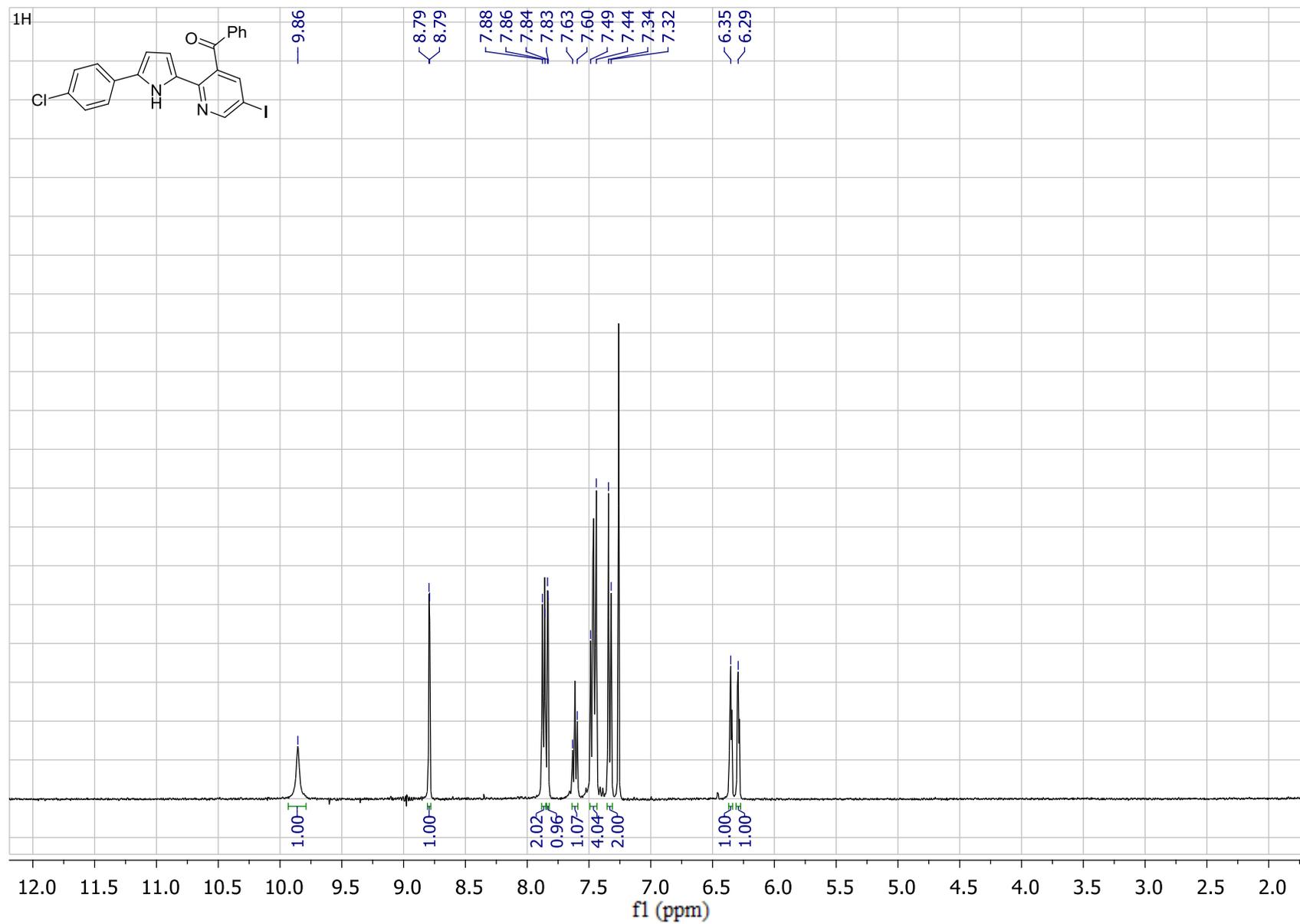
<sup>13</sup>C NMR spectrum of **2**<sup>d</sup> (CDCl<sub>3</sub>).



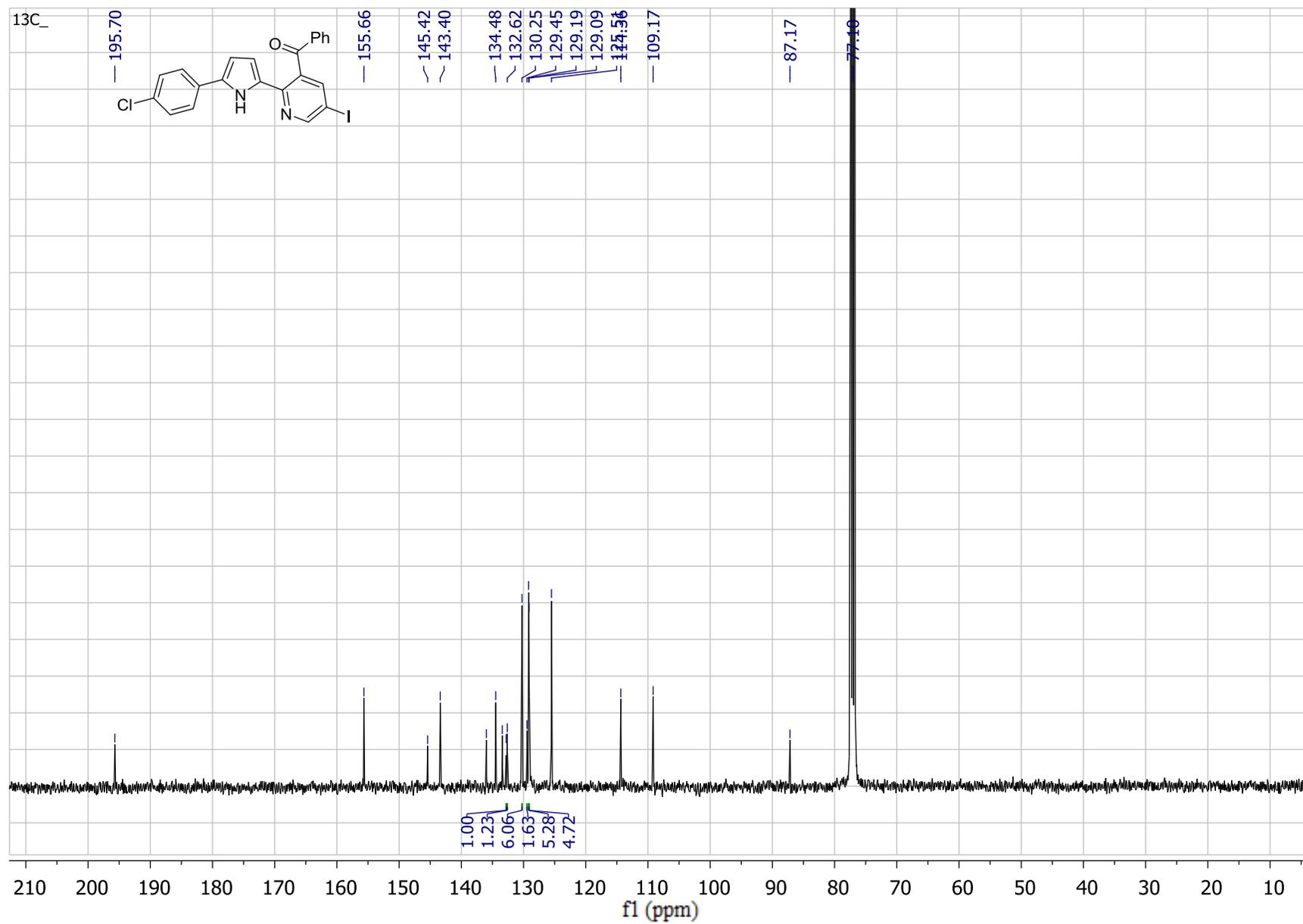
$^{19}\text{F}$  NMR spectrum of **2''d** ( $\text{CDCl}_3$ ).



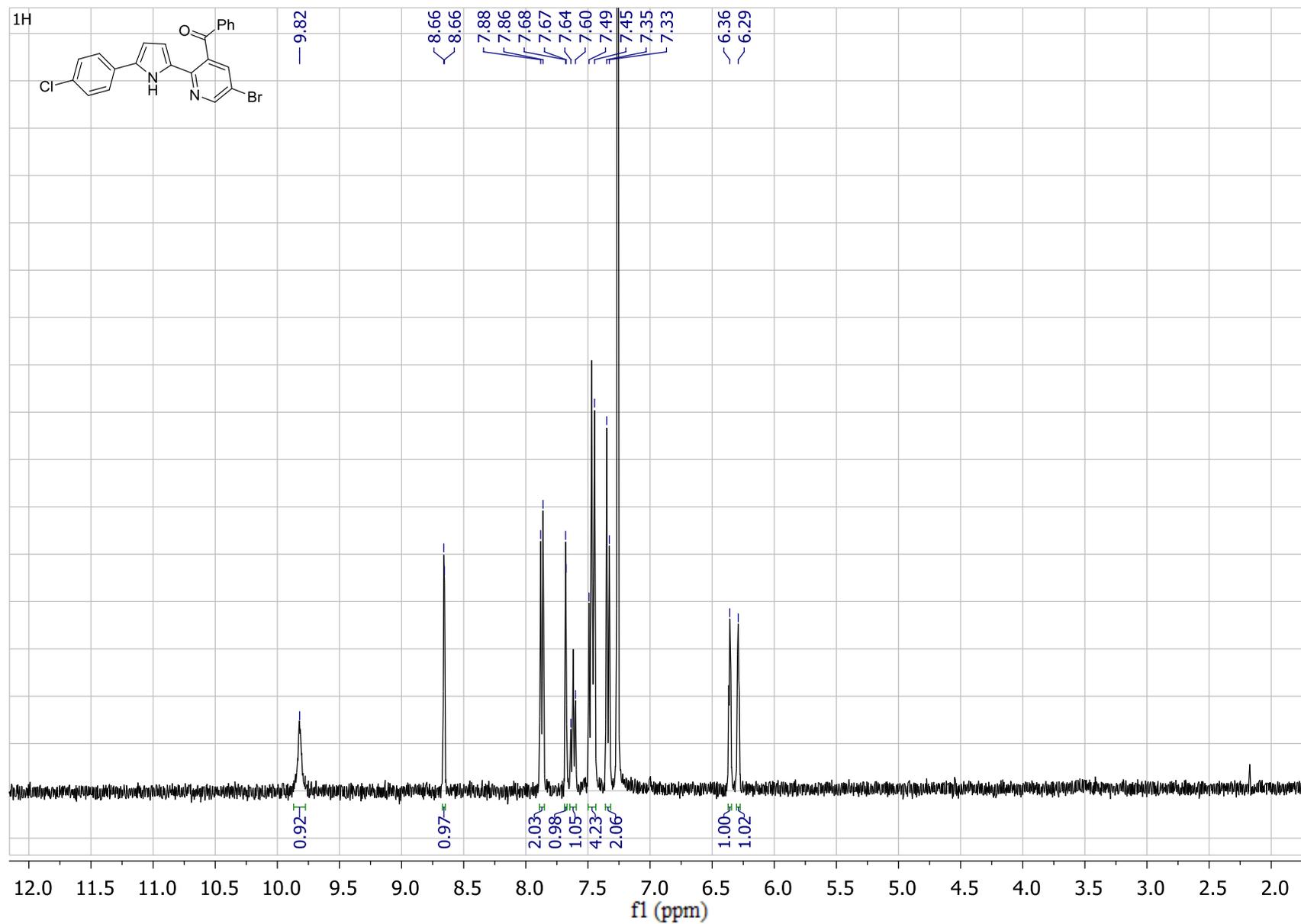
<sup>1</sup>H NMR spectrum of **2f** (CDCl<sub>3</sub>).



$^{13}\text{C}$  NMR spectrum of **2f** ( $\text{CDCl}_3$ ).

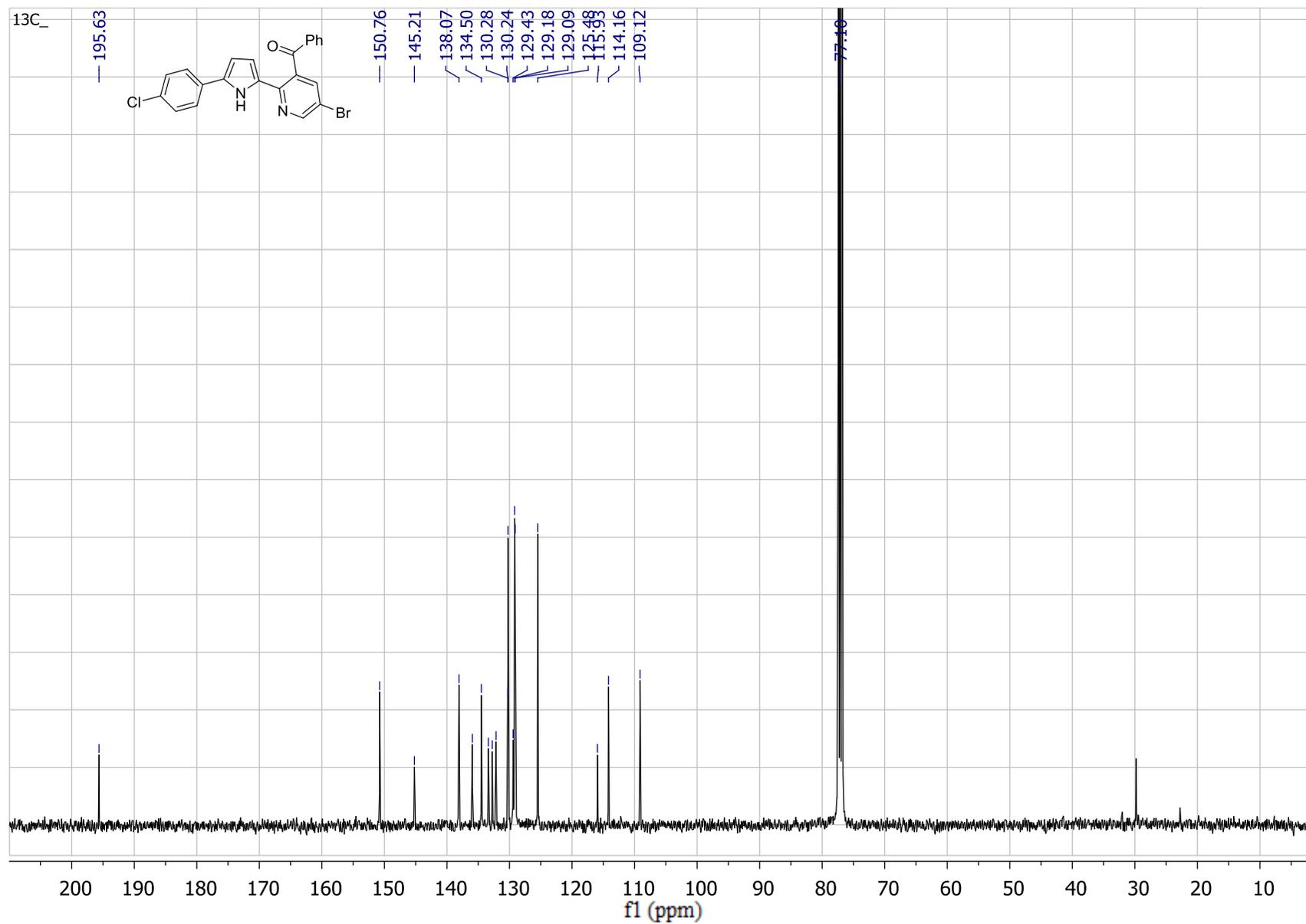


$^1\text{H}$  NMR spectrum of **2f** ( $\text{CDCl}_3$ ).

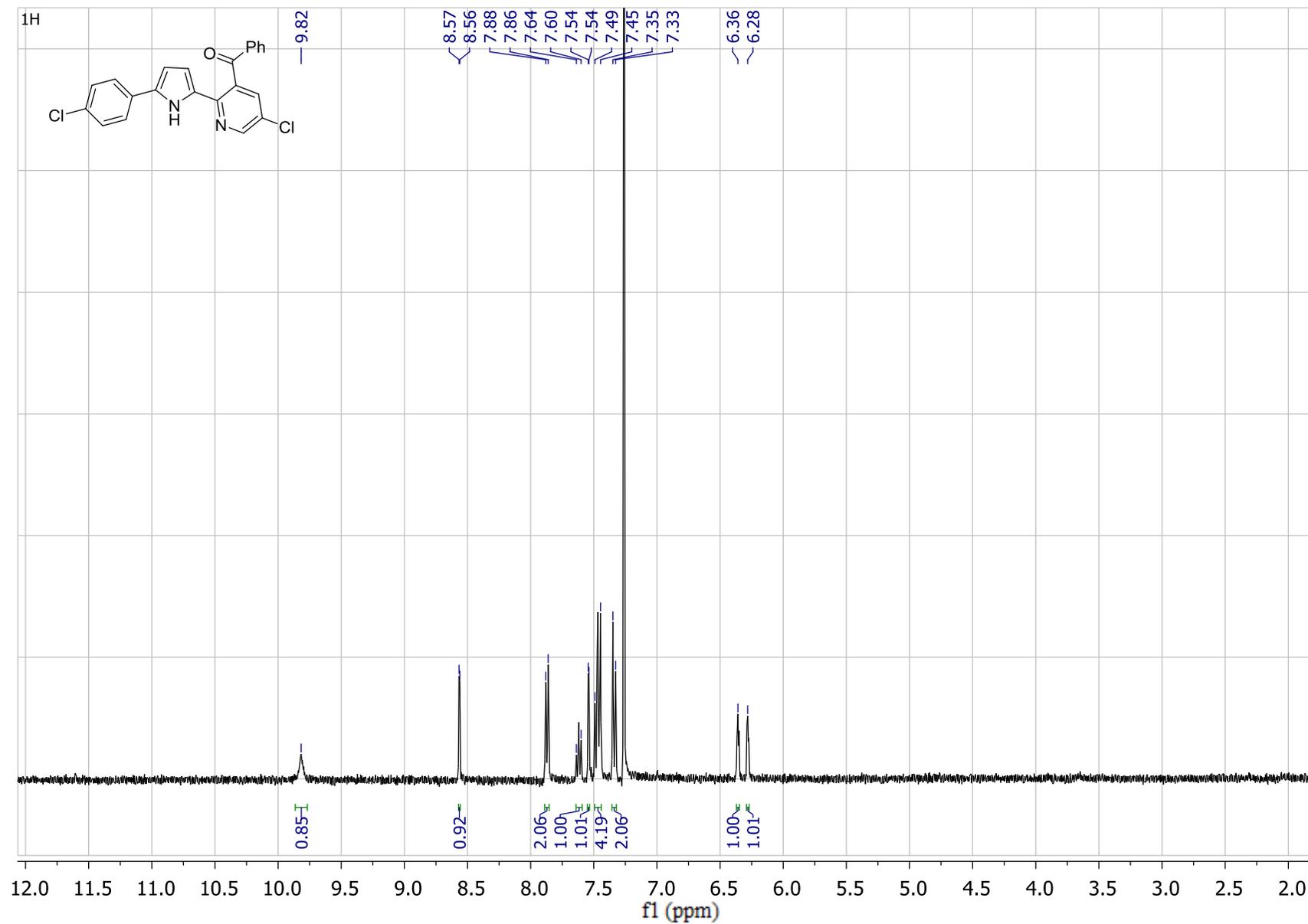


S17

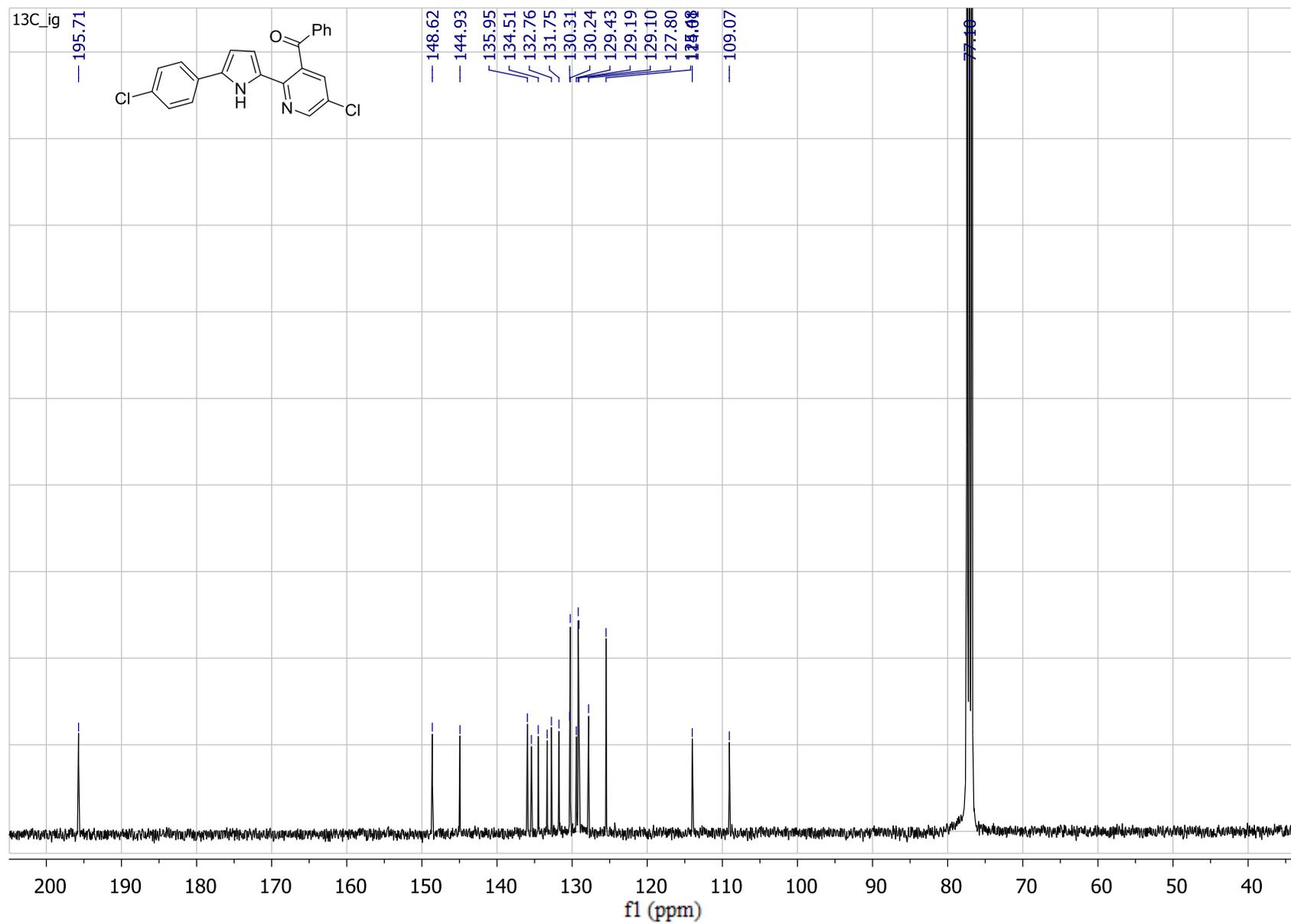
$^{13}\text{C}$  NMR spectrum of **2'f** ( $\text{CDCl}_3$ ).



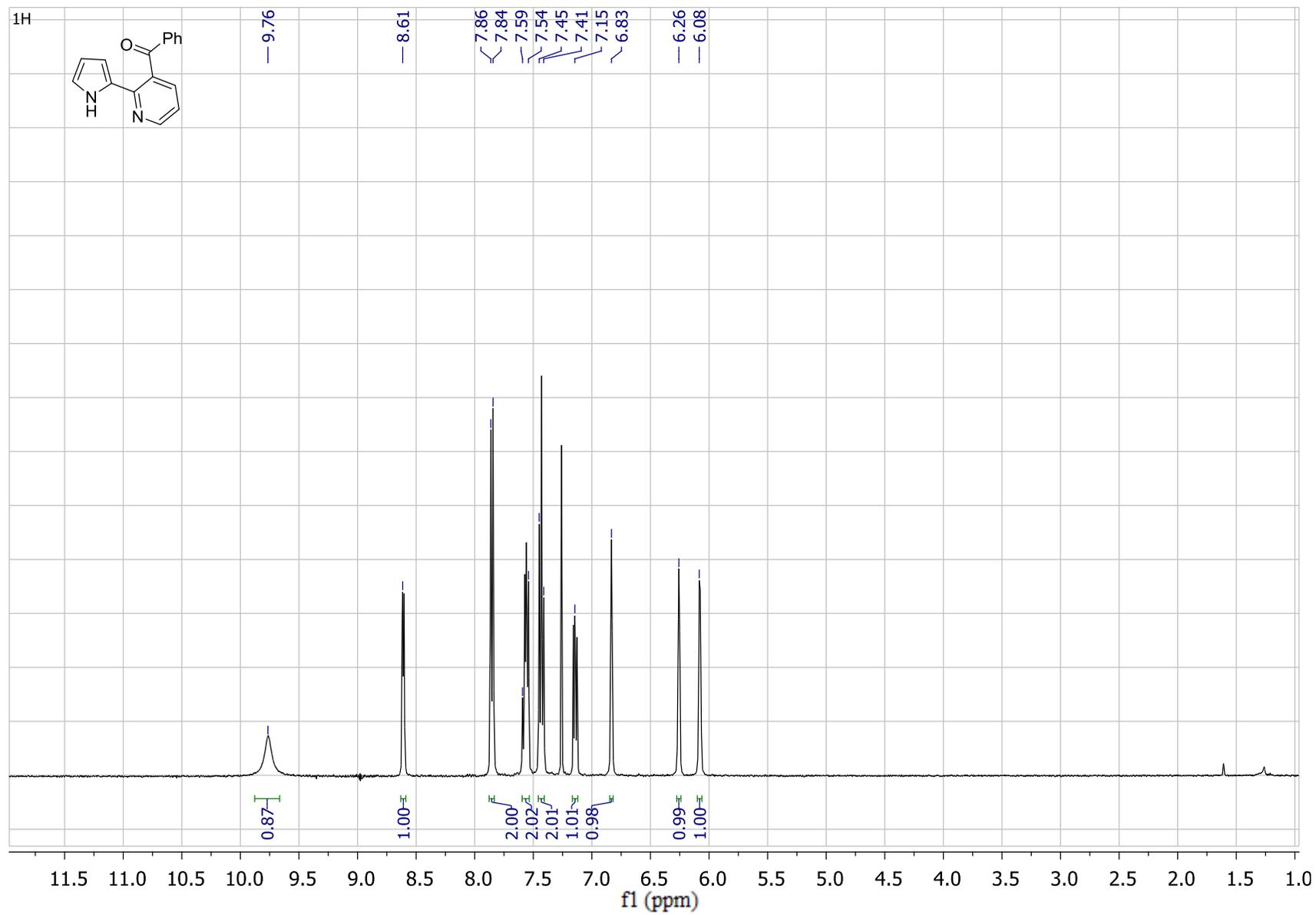
$^1\text{H}$  NMR spectrum of **2**<sup>f</sup> ( $\text{CDCl}_3$ ).



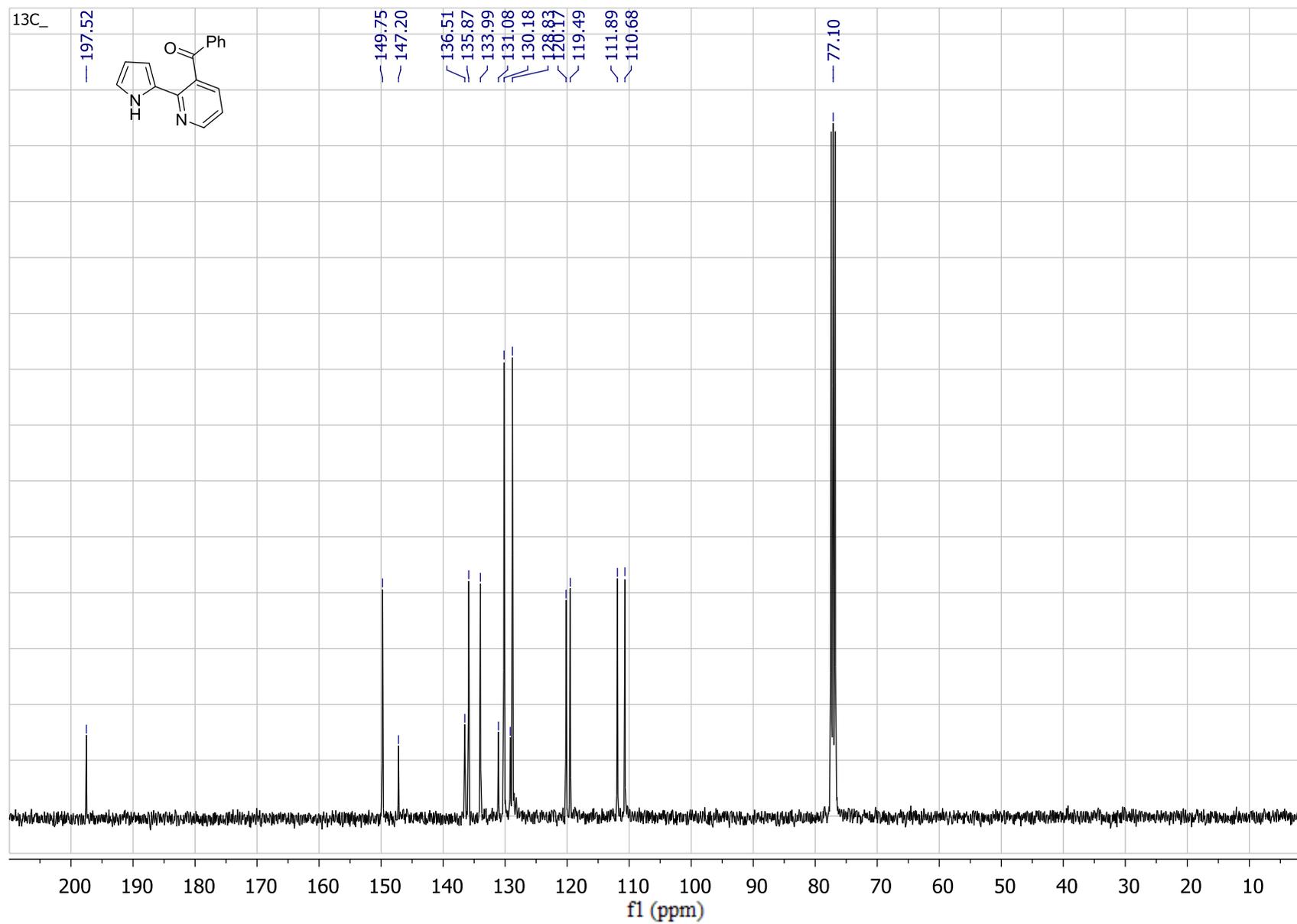
$^{13}\text{C}$  NMR spectrum of **2''f** ( $\text{CDCl}_3$ ).



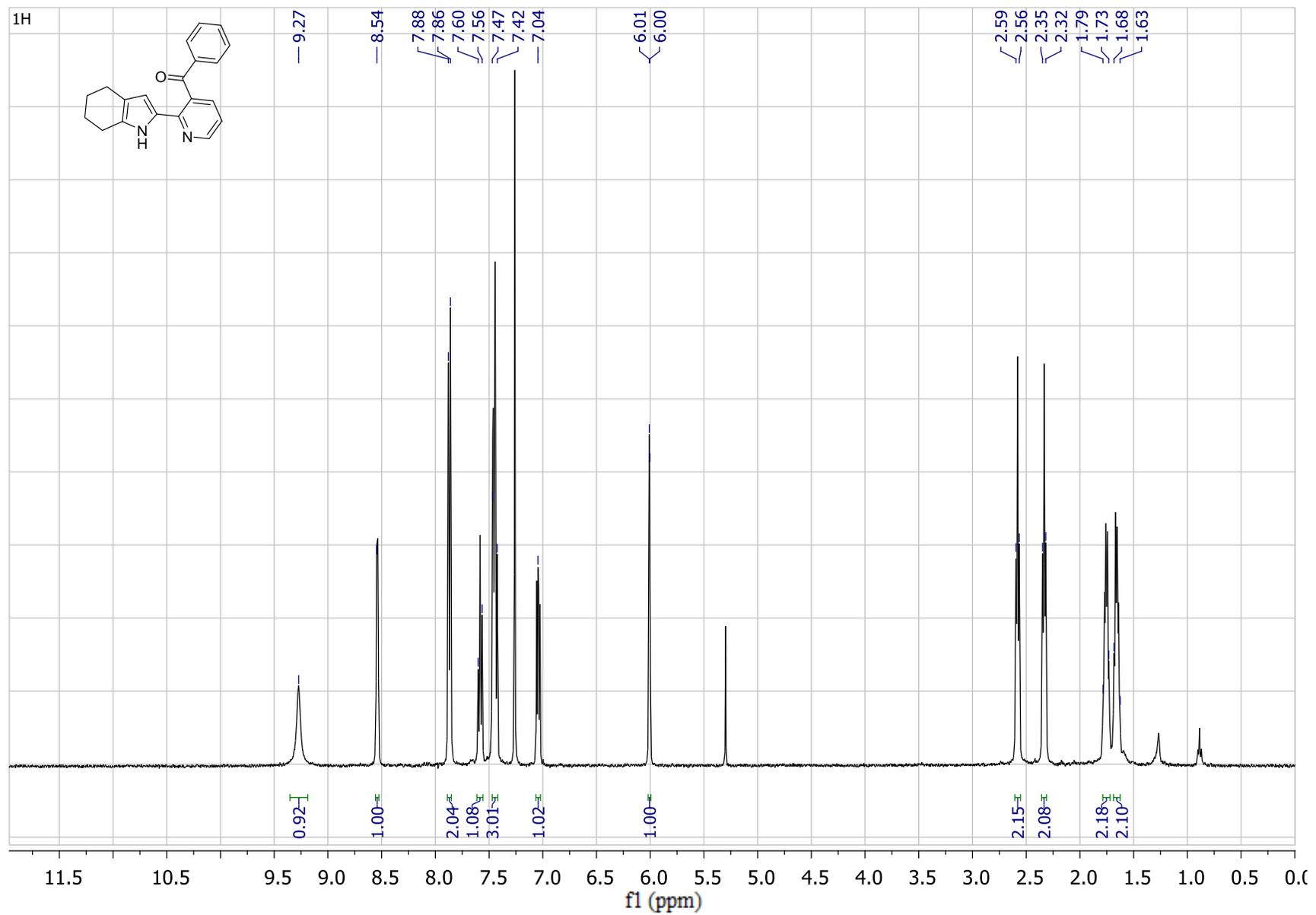
$^1\text{H}$  NMR spectrum of **3a** ( $\text{CDCl}_3$ ).



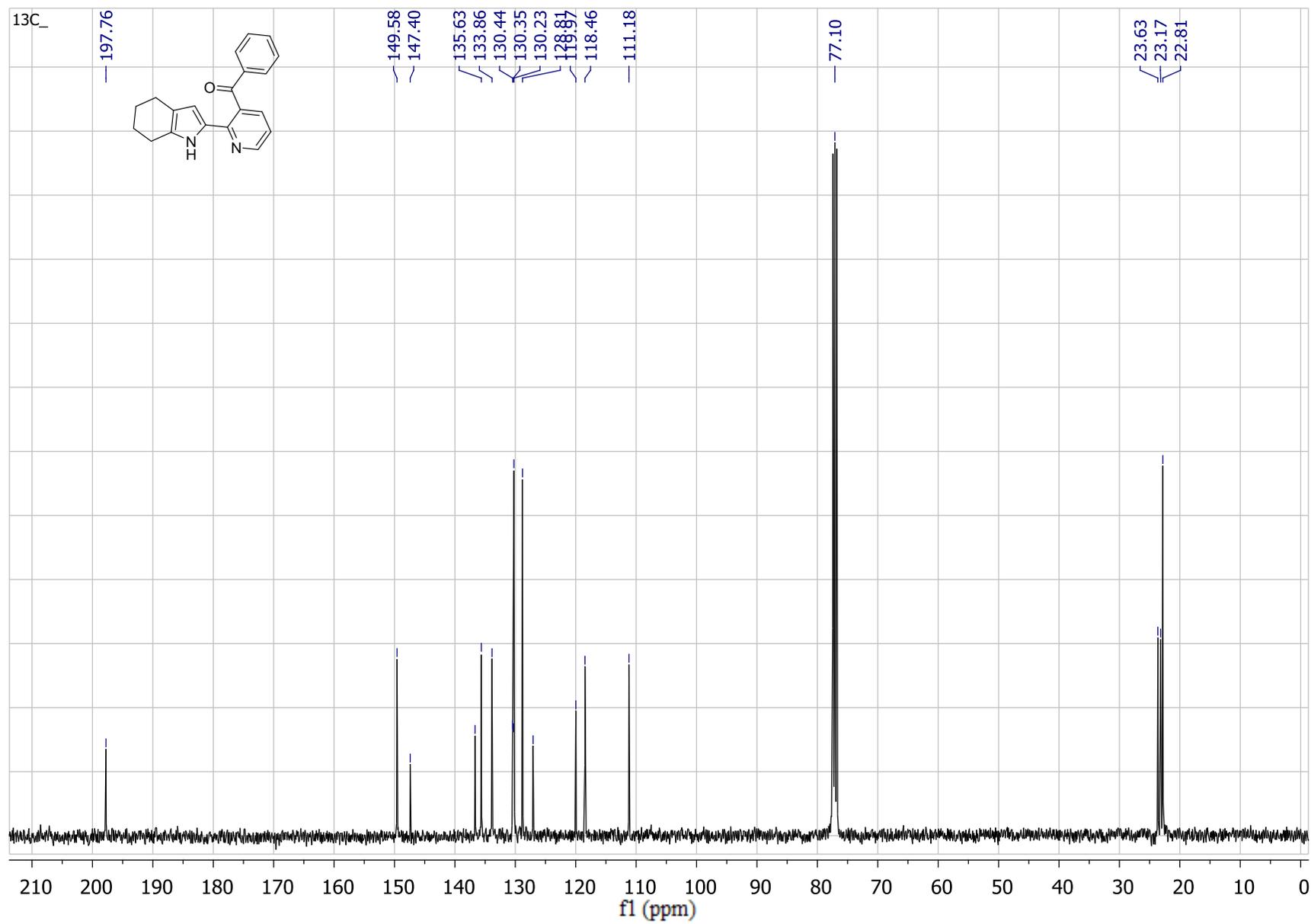
$^{13}\text{C}$  NMR spectrum of **3a** ( $\text{CDCl}_3$ ).



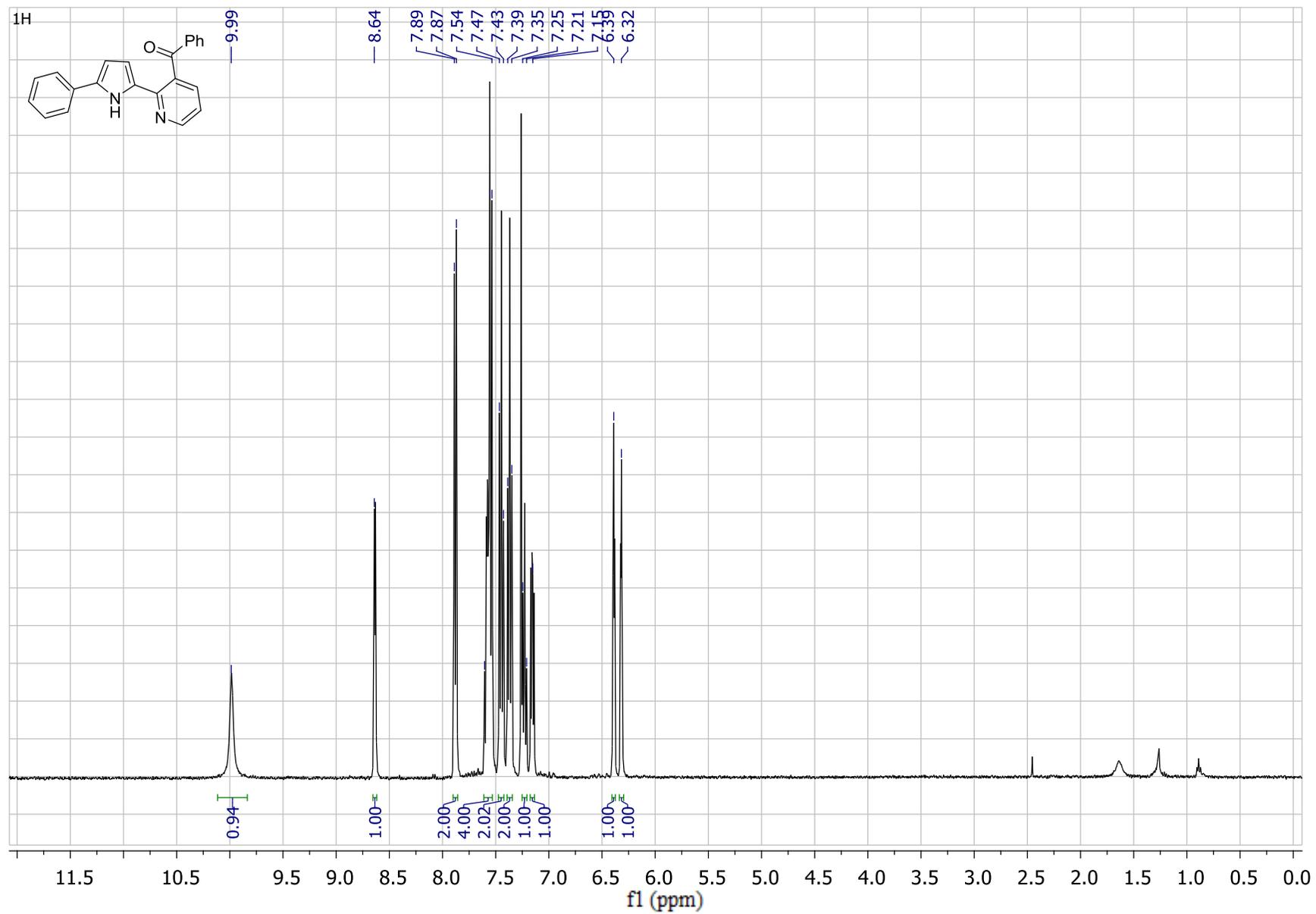
$^1\text{H}$  NMR spectrum of **3b** ( $\text{CDCl}_3$ ).



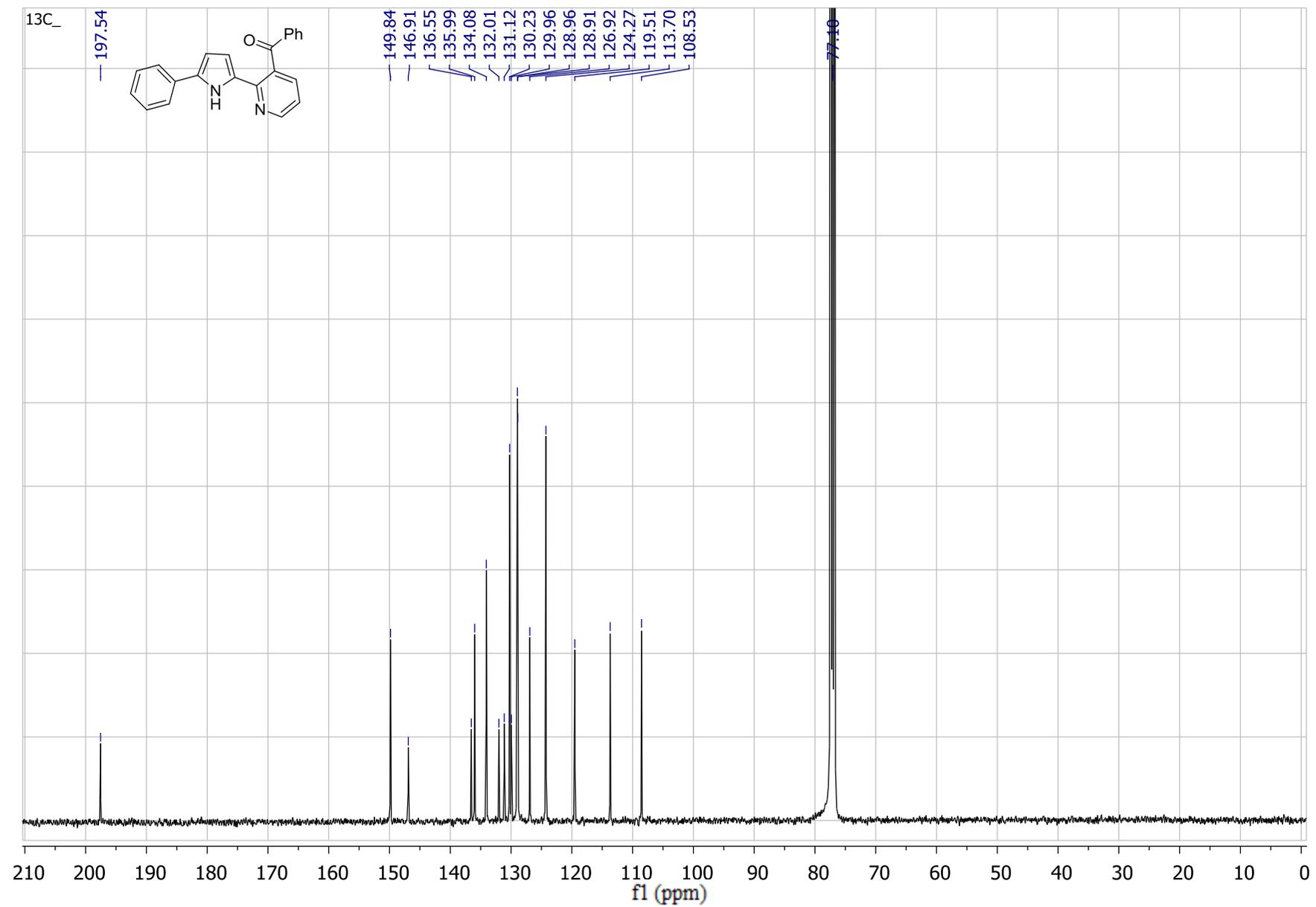
$^{13}\text{C}$  NMR spectrum of **3b** ( $\text{CDCl}_3$ ).



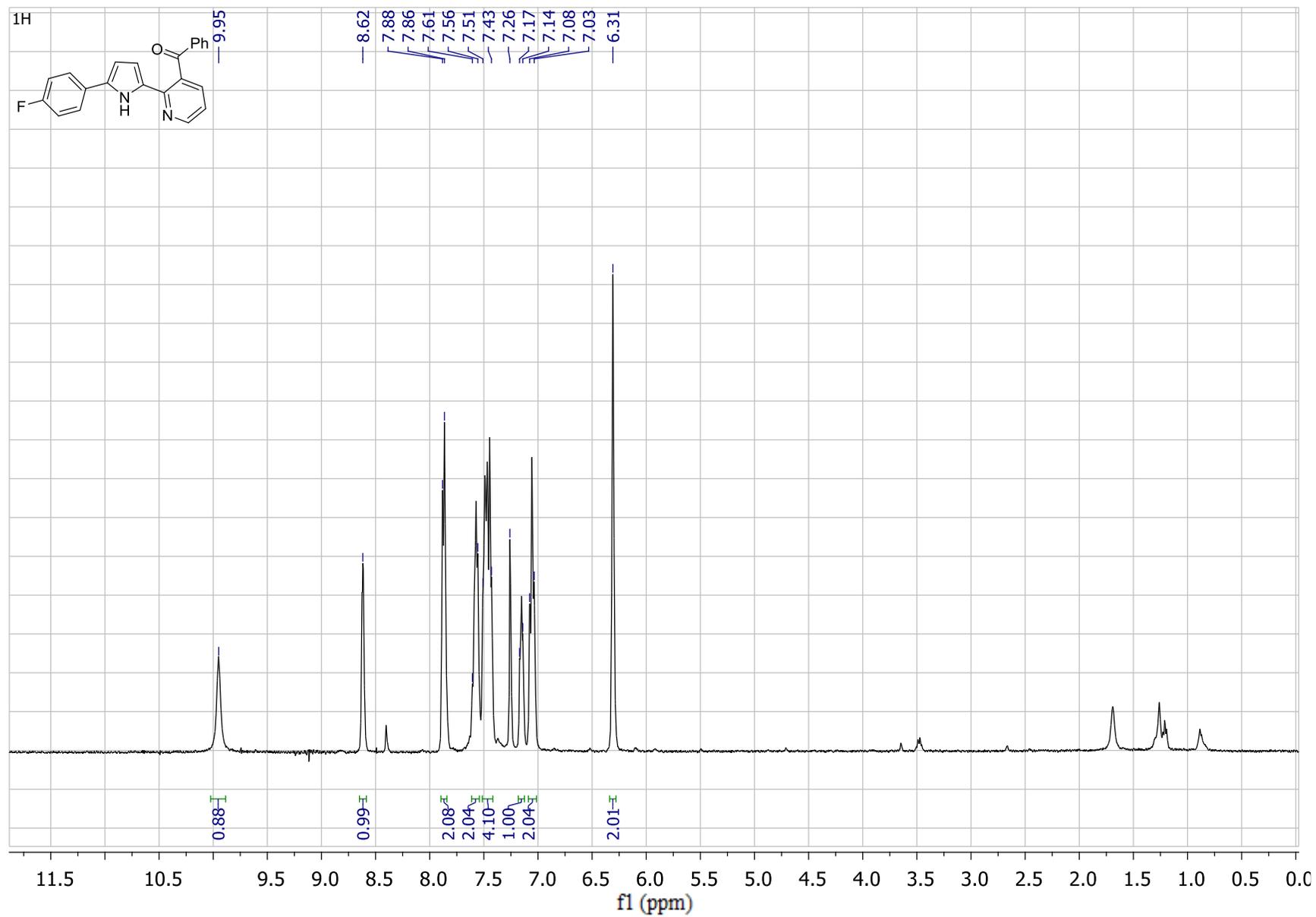
<sup>1</sup>H NMR spectrum of **3c** (CDCl<sub>3</sub>).



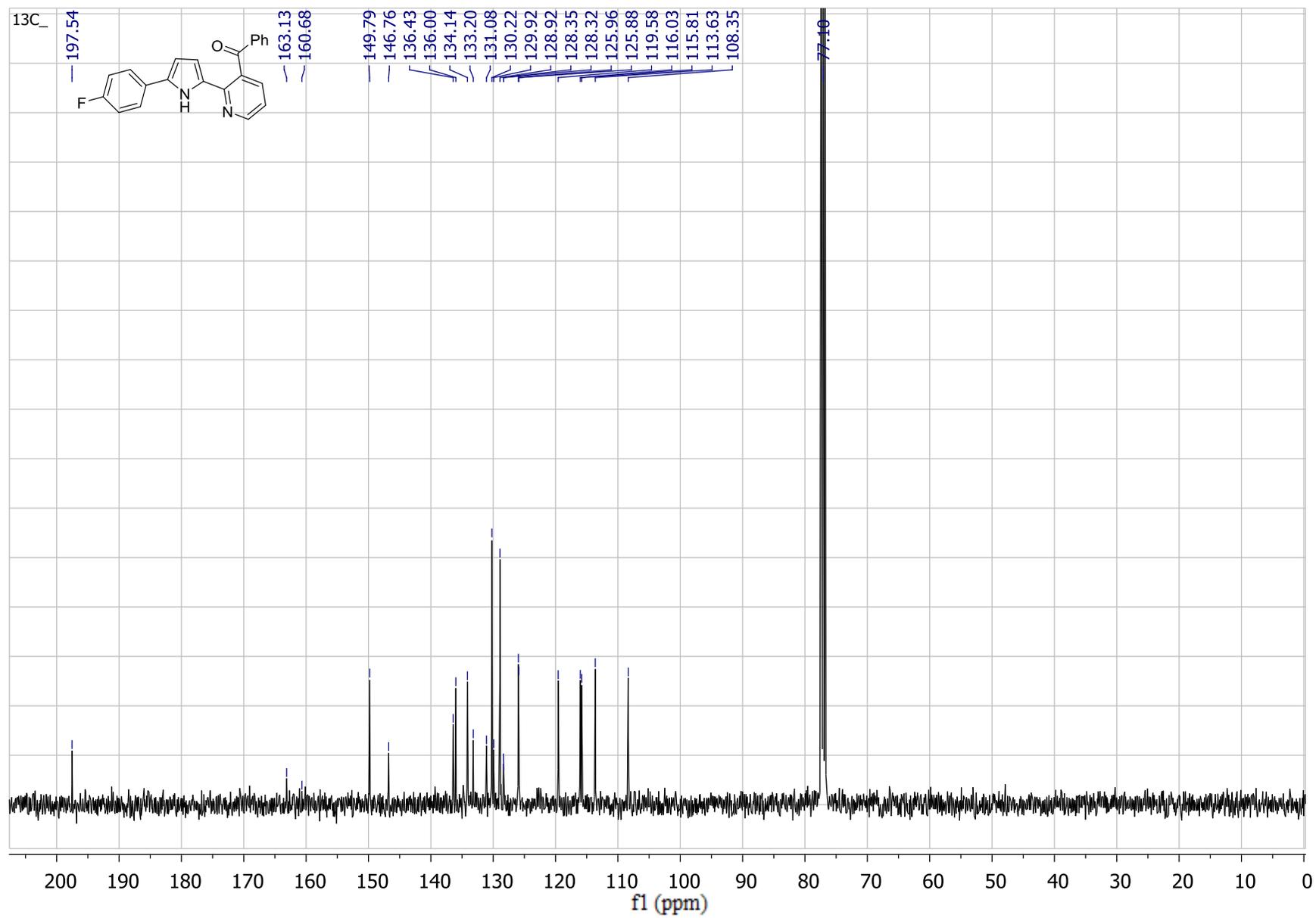
$^{13}\text{C}$  NMR spectrum of **3c** ( $\text{CDCl}_3$ ).



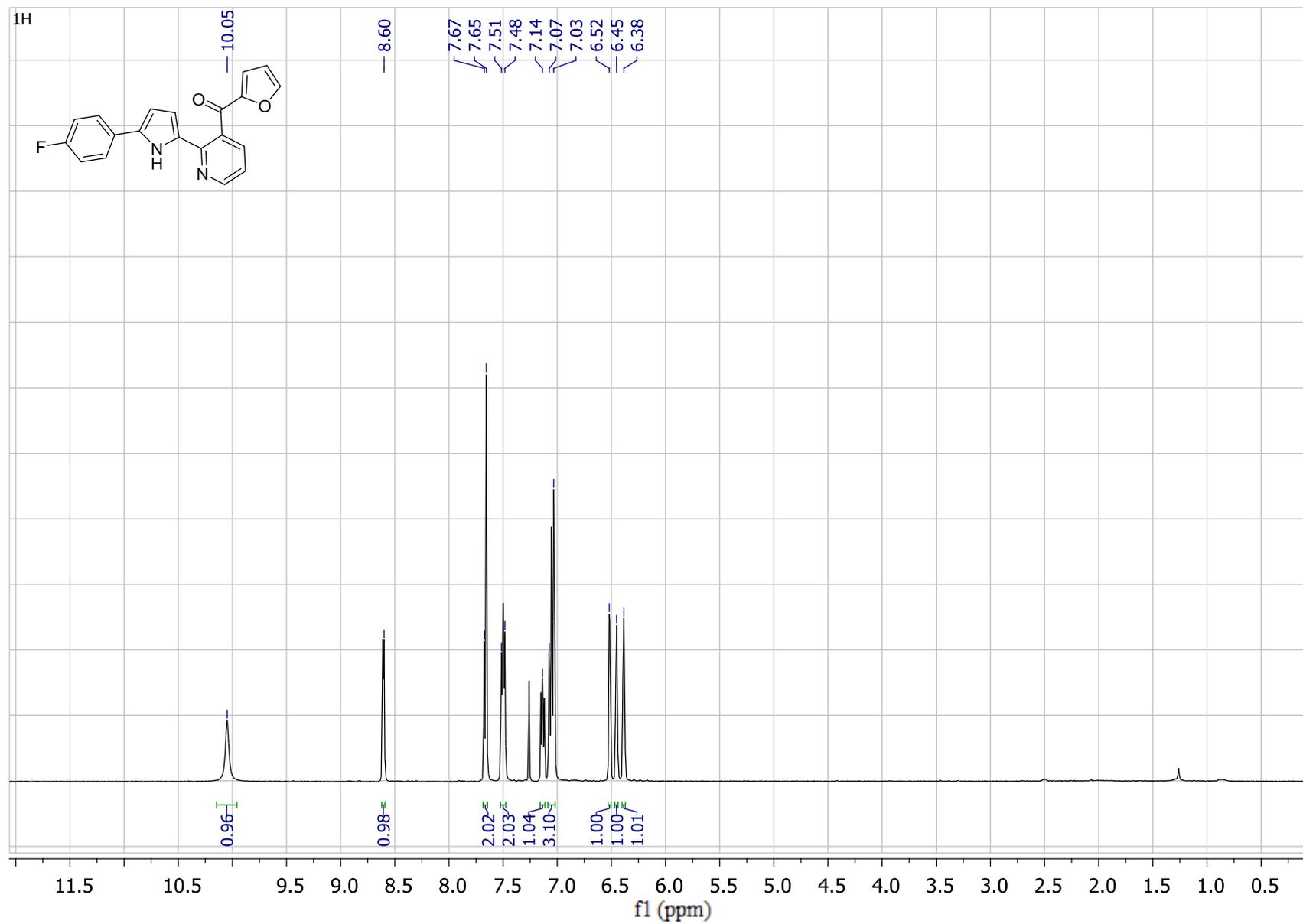
<sup>1</sup>H NMR spectrum of **3d** (CDCl<sub>3</sub>).



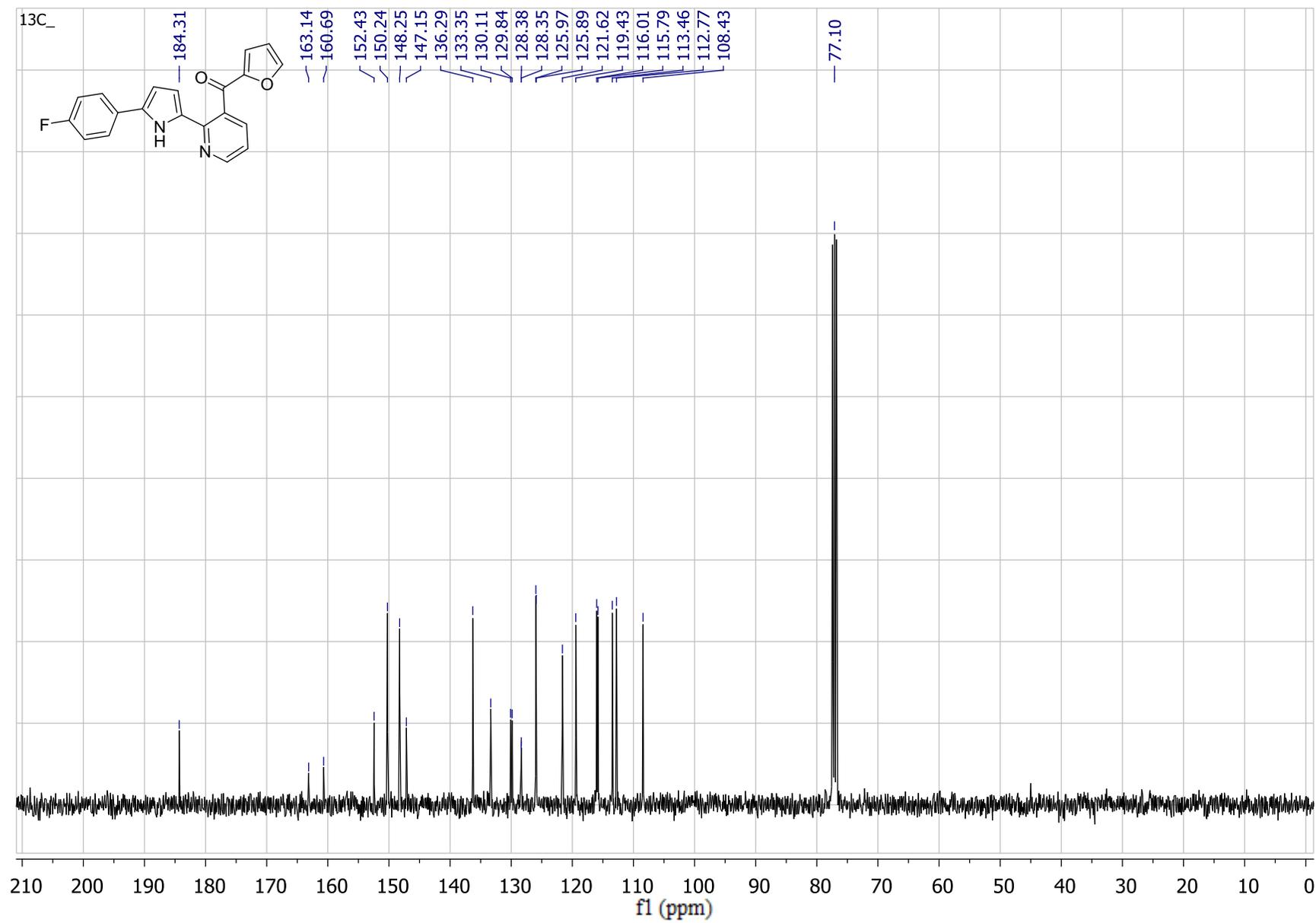
$^{13}\text{C}$  NMR spectrum of **3d** ( $\text{CDCl}_3$ ).



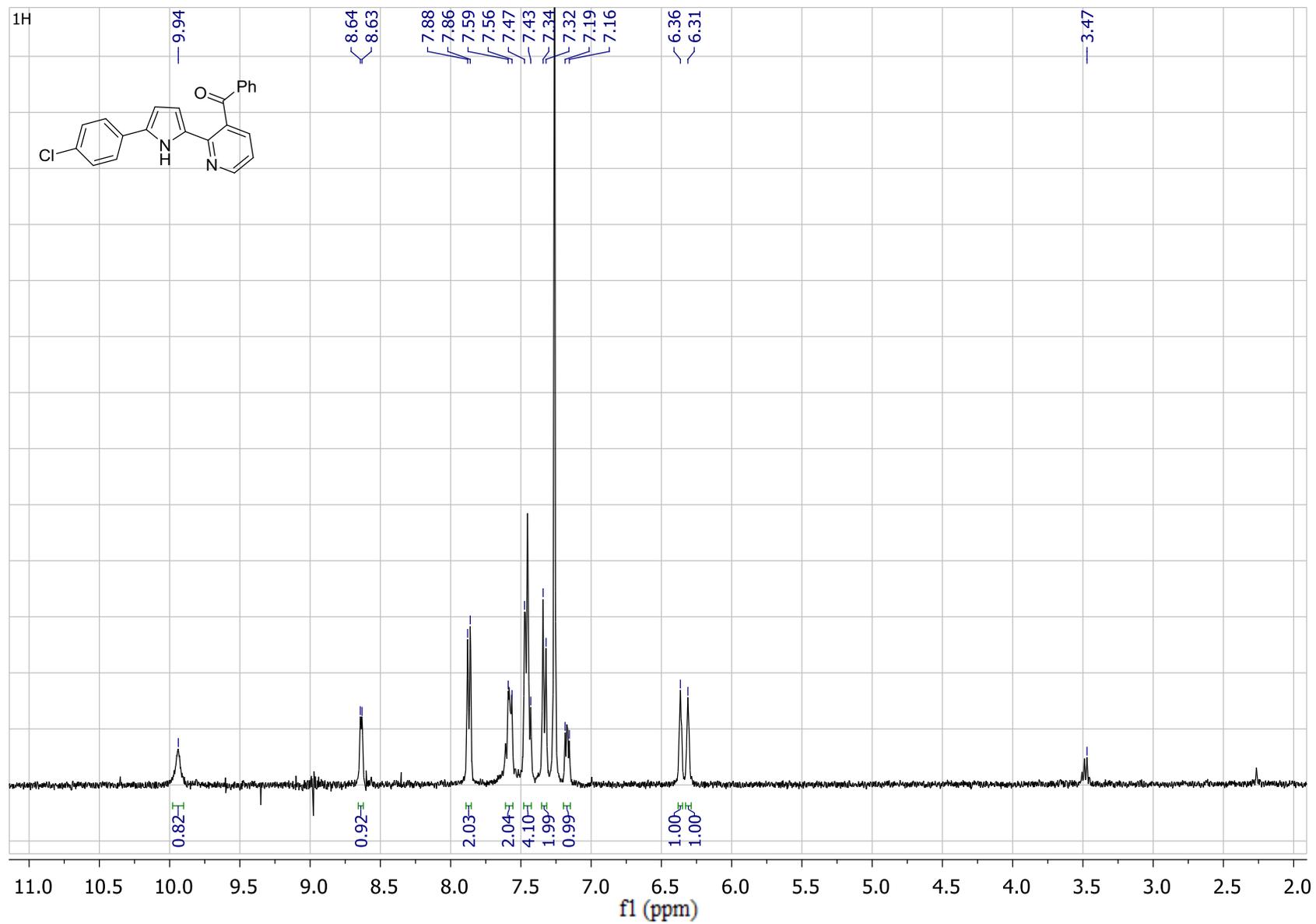
<sup>1</sup>H NMR spectrum of **3e** (CDCl<sub>3</sub>).



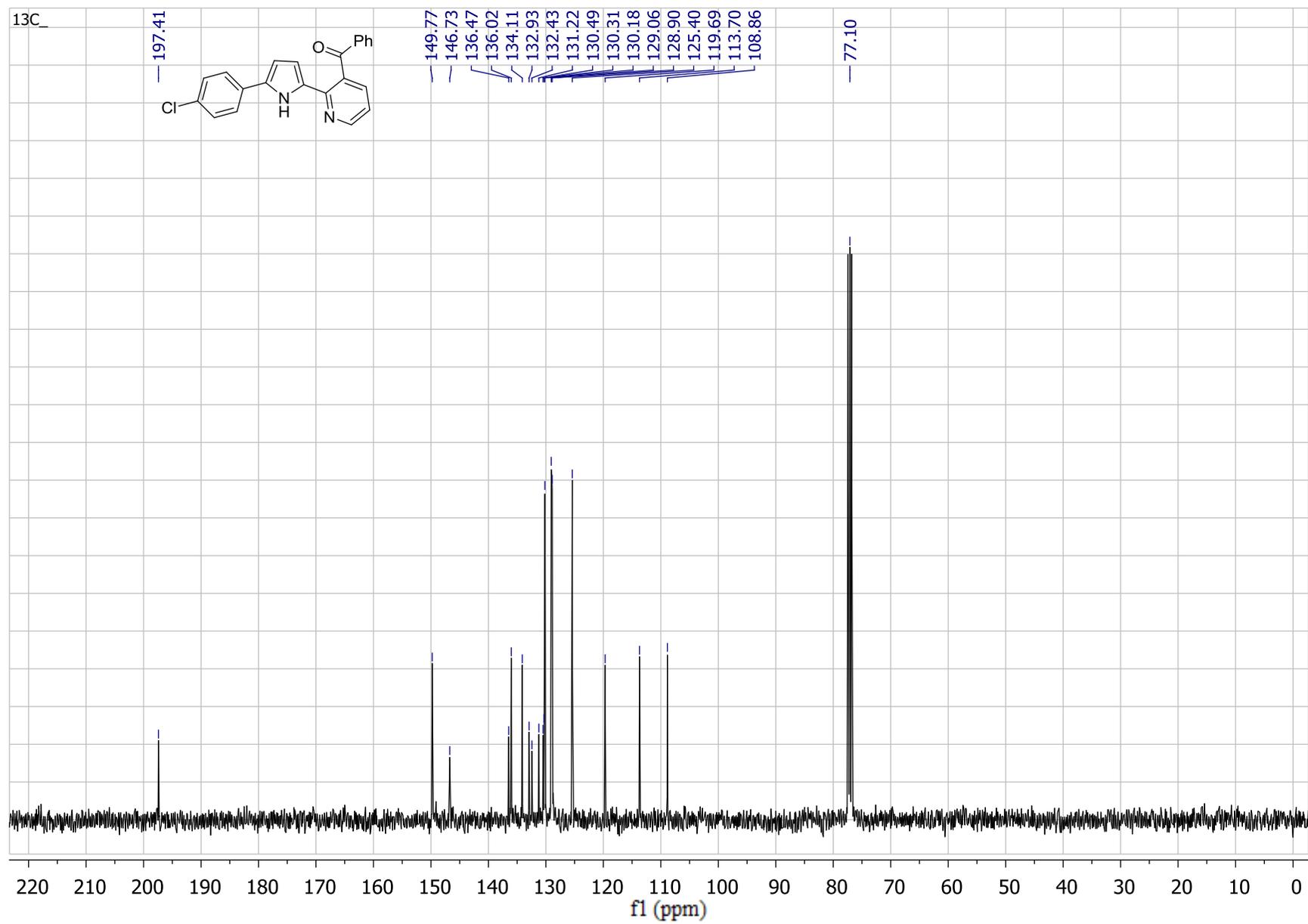
<sup>13</sup>C NMR spectrum of **3e** (CDCl<sub>3</sub>).



$^1\text{H}$  NMR spectrum of **3f** ( $\text{CDCl}_3$ ).

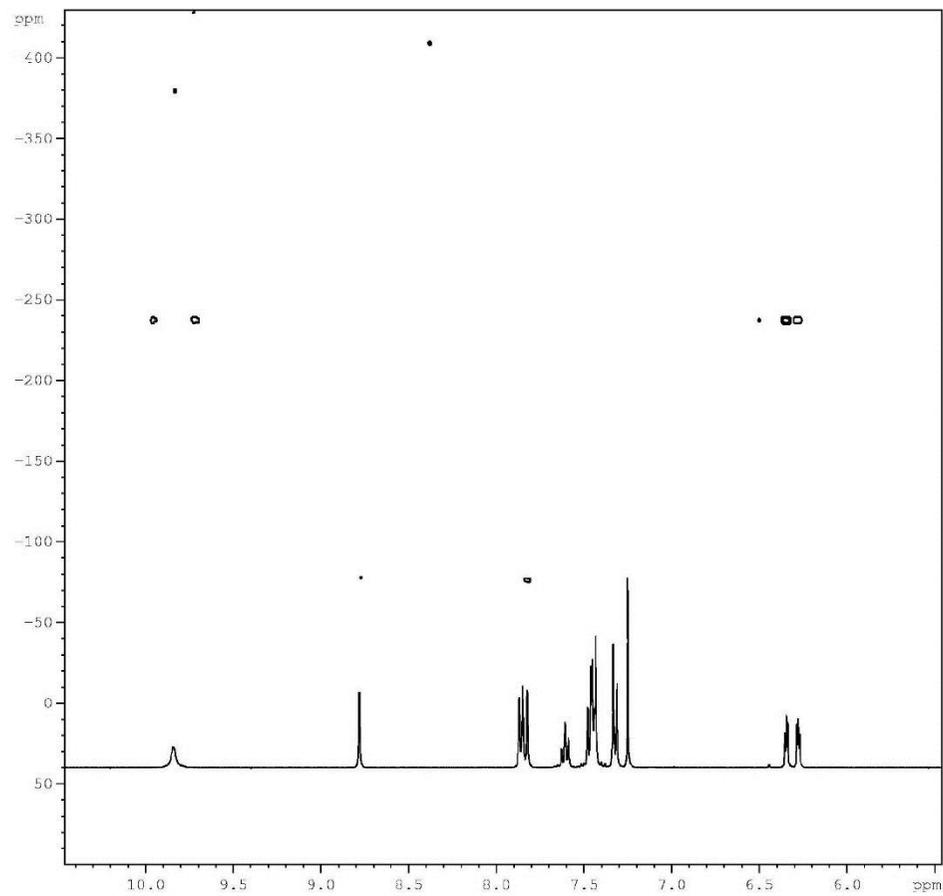


$^{13}\text{C}$  NMR spectrum of **3f** ( $\text{CDCl}_3$ ).

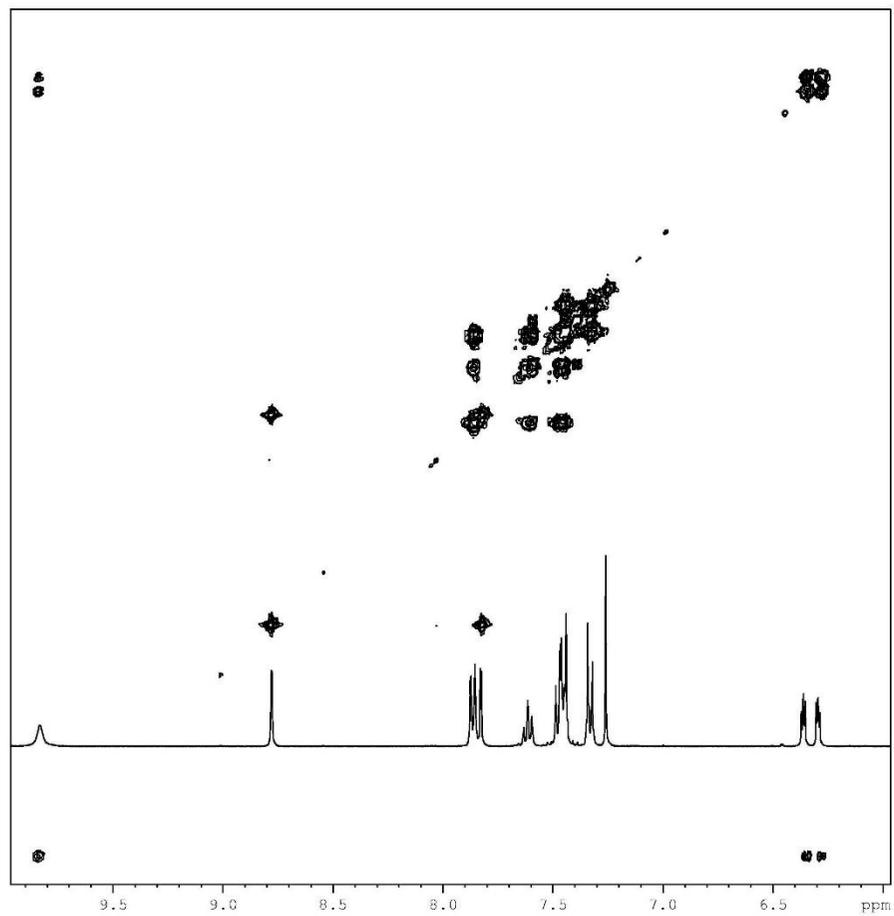


**Selected 2D NMR spectra.**

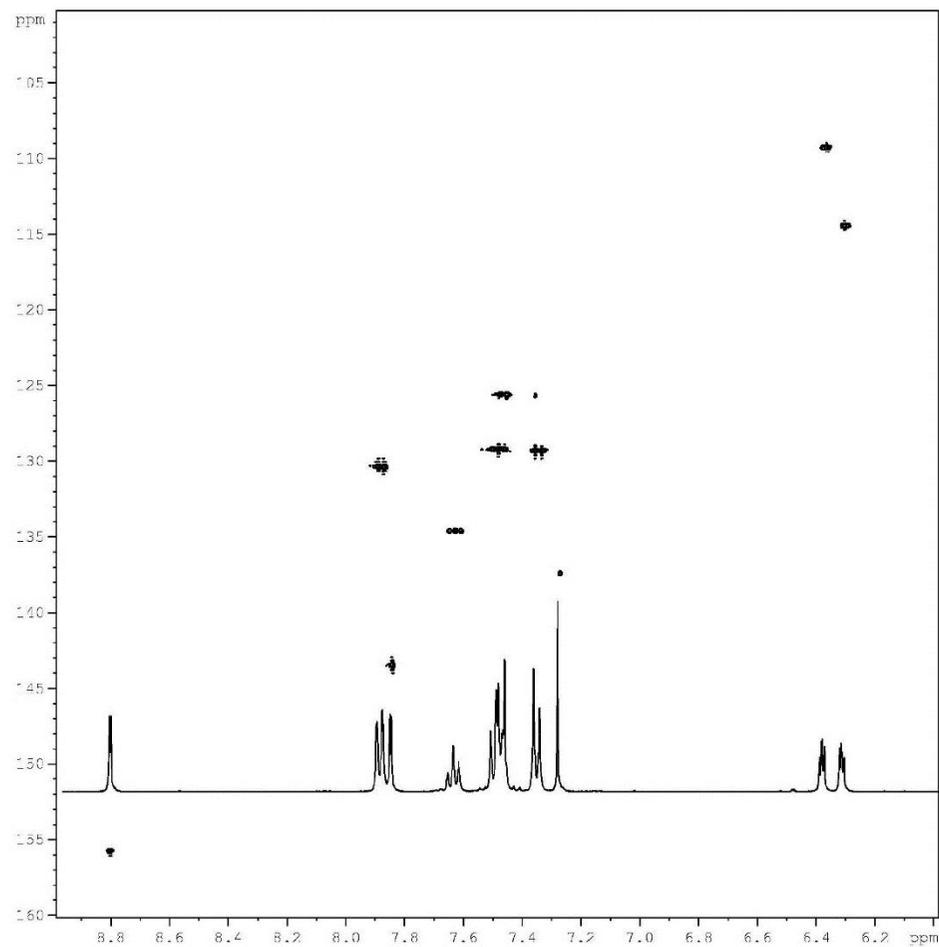
2D  $^1\text{H}$ - $^{15}\text{N}$  HMBC spectrum of **2f**.



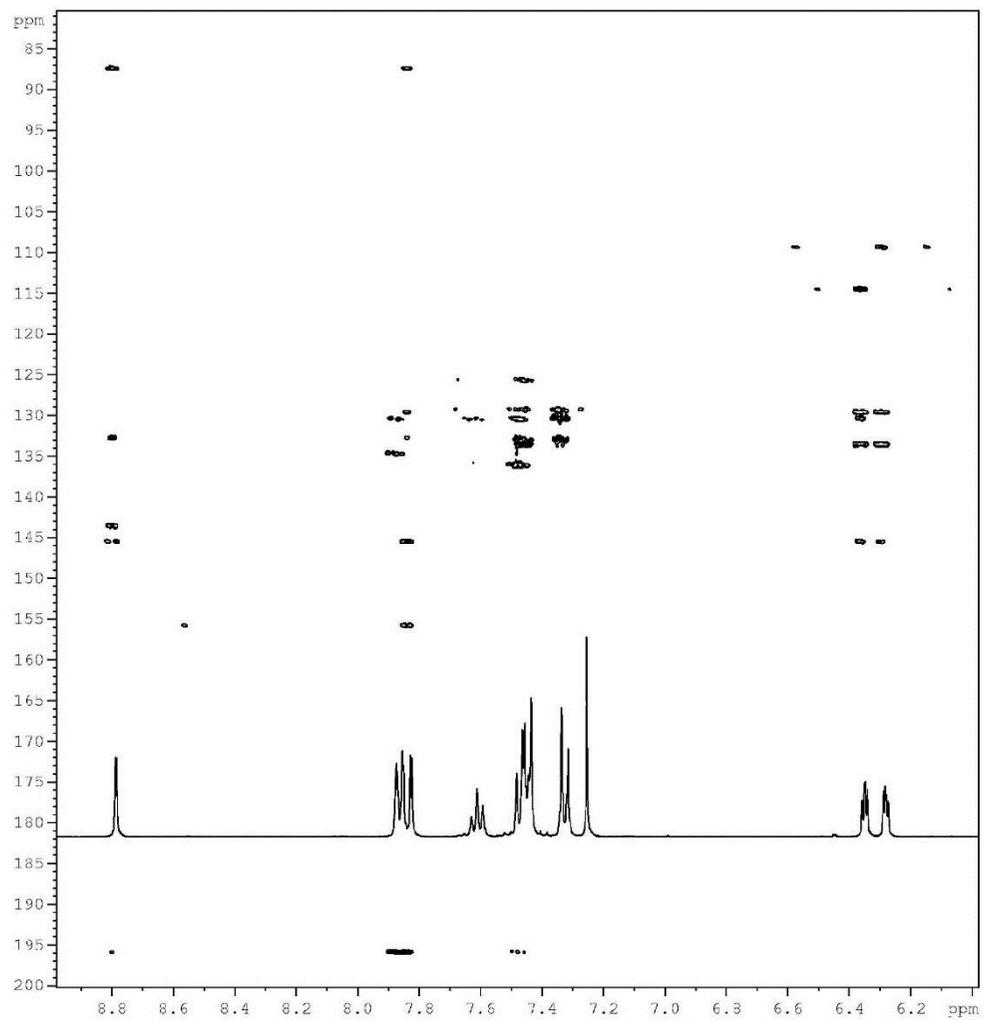
2D COSY spectrum of **2f** (400.1 MHz, CDCl<sub>3</sub>).



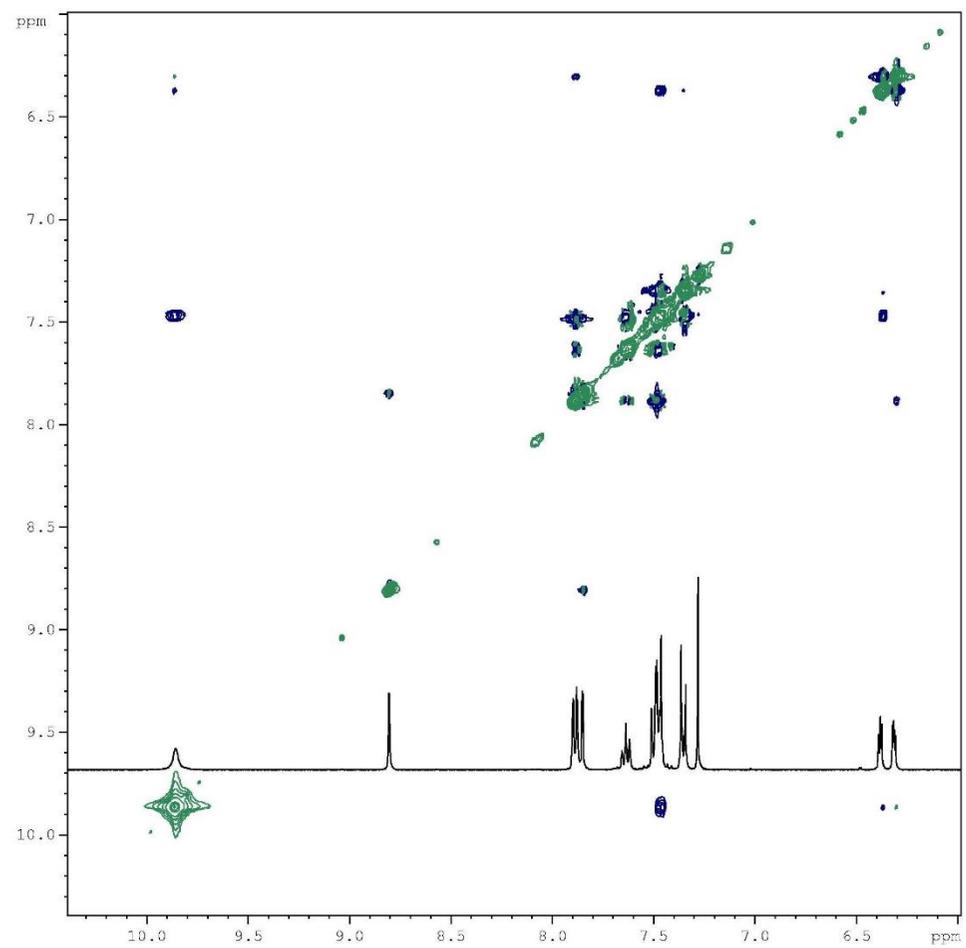
2D  $^1\text{H}$ - $^{13}\text{C}$  HSQC spectrum of **2f**.



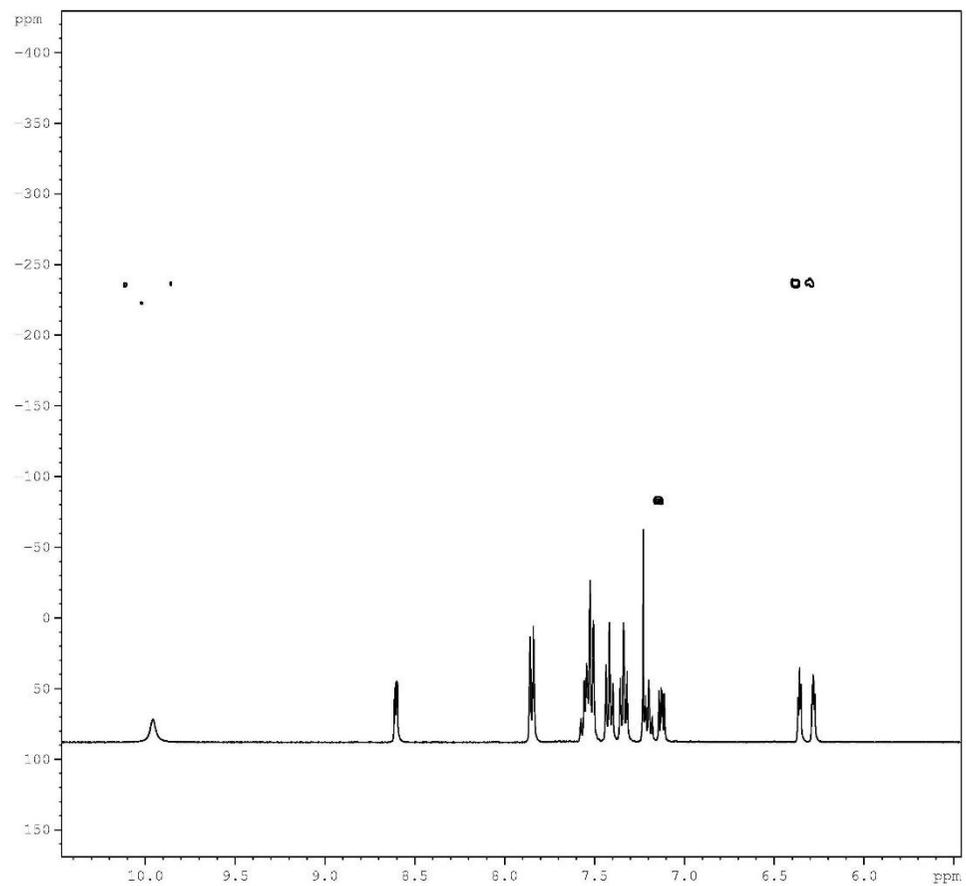
2D  $^1\text{H}$ - $^{13}\text{C}$  HMBC spectrum of **2f**.



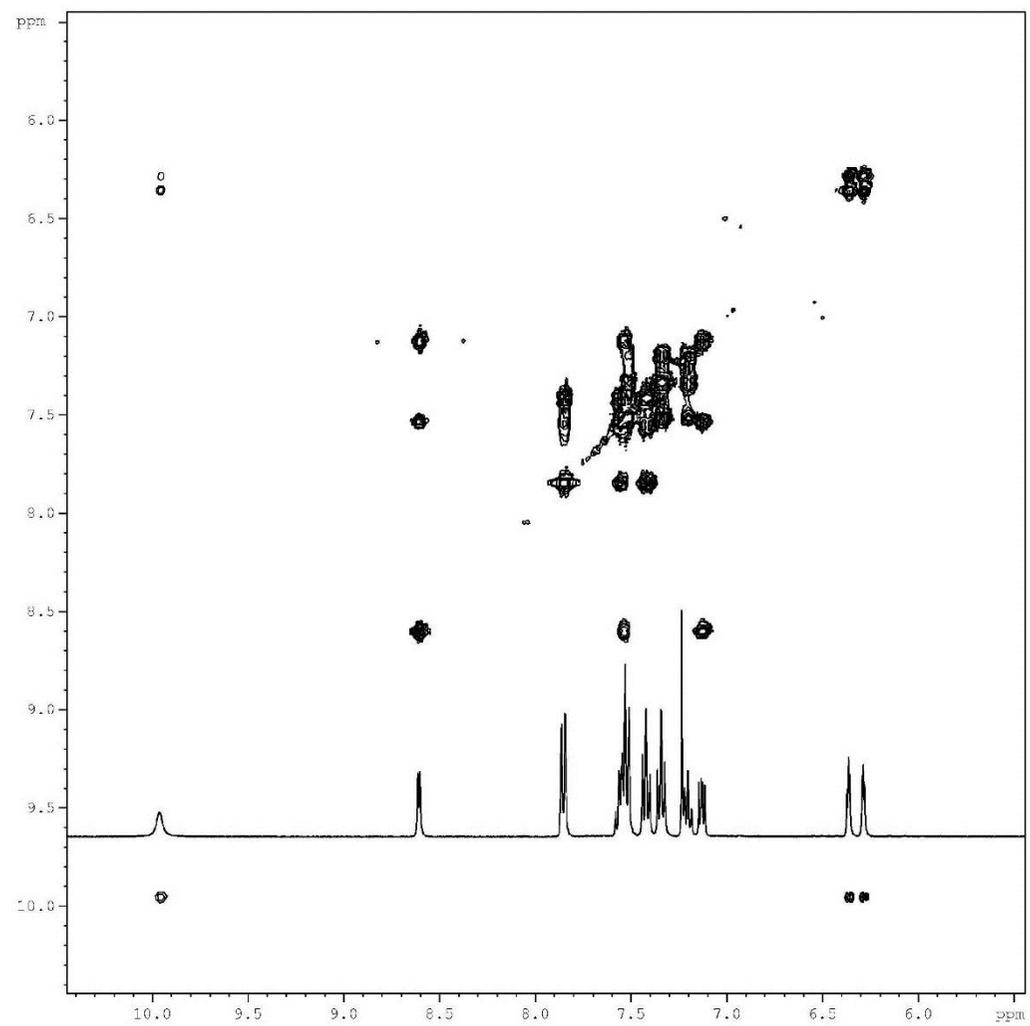
2D NOESY spectrum of **2f** (400.1 MHz, CDCl<sub>3</sub>).



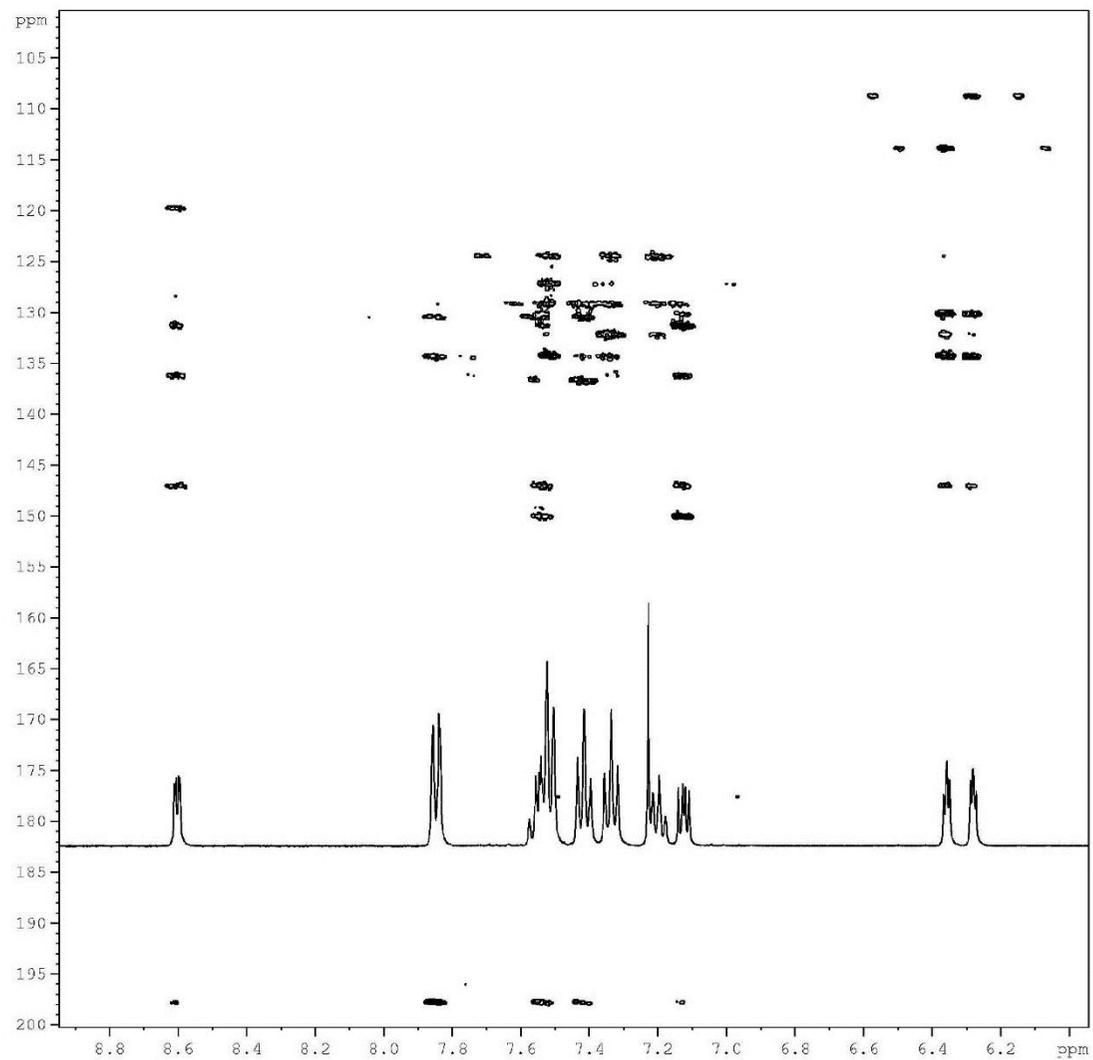
2D  $^1\text{H}$ - $^{15}\text{N}$  HMBC spectrum of **3c**.



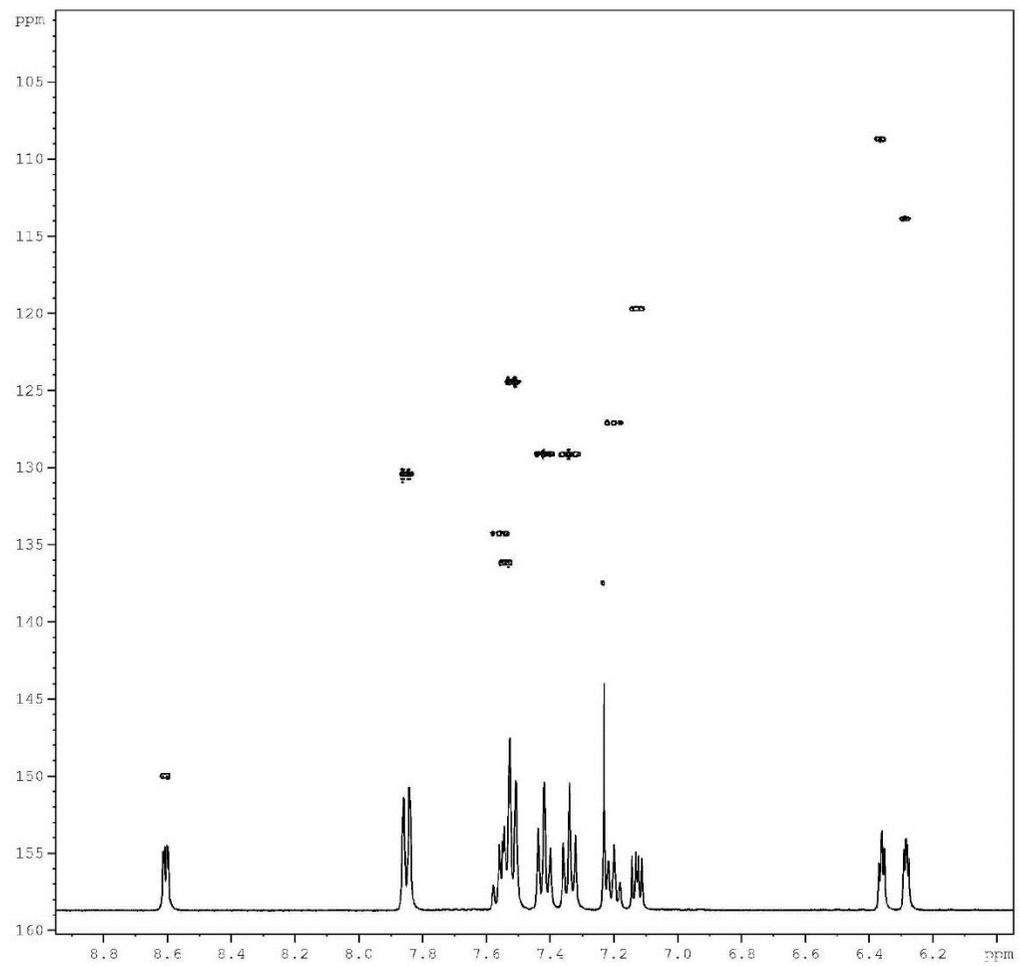
2D COSY spectrum of **3c** (400.1 MHz, CDCl<sub>3</sub>).



2D  $^1\text{H}$ - $^{13}\text{C}$  HMBC spectrum of **3c**.



2D  $^1\text{H}$ - $^{13}\text{C}$  HSQC spectrum of **3c**.



2D NOESY spectrum of **3c** (400.1 MHz, CDCl<sub>3</sub>).

