Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supplementary Information

Substituted pyrrolyl-cyanopyridines on the platform of acylethynylpyrroles via their 1:2 annulation with acetonitrile under the action of lithium metal

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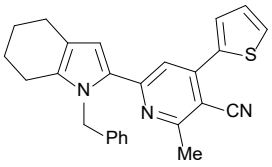
General Information

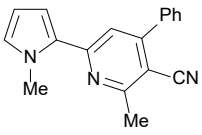
IR spectra were obtained on a “Bruker IFS-25” spectrometer (KBr pellets or films in 400-4000 cm^{-1} region). ^{1}H (400.13 MHz), ^{13}C (100.6 MHz) NMR spectra were recorded on a “Bruker Avance 400” instrument in $CDCl_3$. The assignment of signals in the ^{1}H NMR spectra was made using COSY and NOESY experiments. Resonance signals of carbon atoms were assigned based on ^{1}H-^{13}C HSQC and ^{1}H-^{13}C HMBC experiments. The ^{1}H chemical shifts (δ) were referenced to the residual solvent protons (7.26 ppm, $CDCl_3$), the ^{13}C chemical shifts were expressed with respect to the deuterated solvent (77.16 ppm). Coupling constants in hertz (Hz) were measured from one-dimensional spectra and multiplicities were abbreviated as following: br (broad), s (singlet), d (doublet), t (triplet), m (multiplet). The chemical shifts were recorded in ppm. The (C, H, N) microanalyses were performed on a Flash EA 1112 CHNS-O/MAS (CHN Analyzer) instrument. Sulfur was determined by complexometric titration with Chlorasenazo III. Fluorine content was determined on a SPECOL 11 (Carl Zeiss Jena, Germany) spectrophotometer. High-resolution mass spectra were recorded from acetonitrile solution with 0.1% HFBA on HPLC Agilent 1200/Agilent 6210 TOF instrument equipped with an electrospray ionization (ESI) source. Melting points (uncorrected) were determined with SMP50 Stuart Automatic melting point (Stuart Scientific). Acetonitrile was distilled over calcium hydride and degassed by freeze-pump-thaw method before use.

Synthesis of pyridines 2a-r. General procedure.

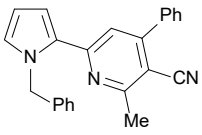
Ethynylpyrrole **1a-p** or acetylenic ketone **1q,r** (1 mmol) was dissolved in dry MeCN (5 ml), and then piece of lithium (14 mg, 2 mmol) was added to reaction mixture. Reaction vessel was sealed and stirred for 5 days at room temperature. Lithium slowly dissolves in solution, forming white to orange suspension. Then reaction mixture was diluted with water (30 ml) and extracted by diethyl ether (3x10 ml). Combined extracts were washed with water and dried over $CaCl_2$. The residue after removing solvent was fractionated by column chromatography (SiO_2, *n*-hexane : diethyl ether, 10 : 1) to afford pyridines **2a-r**.



6-(1-Benzyl-4,5,6,7-tetrahydro-1*H*-indol-2-yl)-2-methyl-4-(thiophen-2-yl)-nicotinonitrile (2a). Yield: 315 mg (77%), yellow crystals, mp 207-208 °C. IR (film) 3087, 2921, 2846, 2211, 1585, 1563, 1528, 1487, 1440, 1383, 1356, 1293, 1236, 1184, 1146, 1118, 1067, 1028, 1002, 876, 821, 796, 731, 714, 655, 458 cm^{-1}. ^1H NMR (400.13 MHz, $CDCl_3$): δ 7.40–7.32 (m, 4H, H*m,p* Ph, H-5, pyridine), 7.23-7.22 (m, 1H, H-5, thiophene), 7.12–7.05 (m, 1H, H-3, thiophene), 7.00–6.98 (m, 3H, H*o*, Ph, H-4, thiophene), 6.70 (s, 1H, H-3, pyrrole), 5.12 (s, 2H, CH_2Ph), 2.82 (s, 3H, CH_3, pyridine), 2.65–2.59 (m, 2H, CH_2-7), 2.51–2.46 (m, 2H, CH_2-4), 1.87–1.75 (m, 4H, CH_2-5,6). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 163.4, 153.3, 144.4, 143.5, 138.5, 134.6, 129.7, 129.2 (2C), 128.3, 127.5, 127.3, 126.5, 125.6 (2C), 119.7, 118.0, 114.6, 113.3, 104.4, 48.0, 24.4, 23.6, 23.2, 23.1, 22.5. Anal. Calcd for $C_{26}H_{23}N_3S$: C, 76.25; H, 5.66; N, 10.26; S, 7.83%. Found: C, 76.51; H, 5.81; N, 10.46; S, 7.51%.

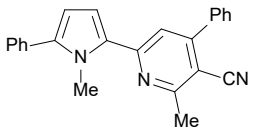


2-Methyl-6-(1-methyl-1*H*-pyrrol-2-yl)-4-phenylnicotinonitrile (2b). Yield: 175 mg (64%), yellow crystals, mp 117-118 °C. IR (film) 3128, 3095, 3040, 2923, 2220, 1581, 1542, 1473, 1282, 1093, 1059, 1031, 881, 781, 748, 717, 688, 597, 526 cm^{-1}. ^1H NMR (400.13 MHz, $CDCl_3$): δ 8.06–8.04 (m, 2H, H*o,* Ph), 7.57 (s, 1H, H-5, pyridine), 7.55–7.47 (m, 3H, H*m,p,* Ph), 6.89–6.87 (m, 1H, H-5, pyrrole), 6.65–6.64 (m, 1H, H-3, pyrrole), 6.32–6.30 (m, 1H, H-4, pyrrole), 3.73 (s, 3H, NCH_3), 2.91 (s, 3H, CH_3, pyridine). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 162.9, 158.7, 144.8, 137.8, 130.3, 129.0 (2C), 128.5, 127.4 (2C), 126.9, 117.7, 117.6, 113.4, 109.1, 106.0, 35.3, 24.5; Anal. Calcd for $C_{18}H_{15}N_3$: C, 79.10; H, 5.53; N, 15.37%. Found: C, 79.34; H, 5.77; N, 15.58%.

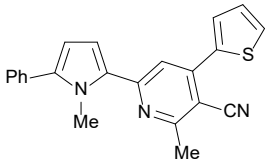


6-(1-Benzyl-1*H*-pyrrol-2-yl)-2-methyl-4-phenylnicotinonitrile (2c). Yield: 230 mg (66%), yellow crystals, mp 111-112 °C. IR (film) 3063, 3031, 2925, 2219, 1583, 1541, 1495, 1470, 1454, 1287, 1162, 1077, 1028, 912, 782, 729, 693, 526 cm^{-1}. IR (film) 3063, 3031, 2925, 2219, 1583, 1541, 1495, 1470, 1454, 1287, 1162, 1077, 1028, 912, 782, 729, 693, 526 cm^{-1}. ^1H NMR (400.13 MHz, $CDCl_3$): δ 7.75–7.73 (m, 2H, H*o*, Ph), 7.45–7.36 (m, 4H, H*m,p* Ph, H-5, pyridine),

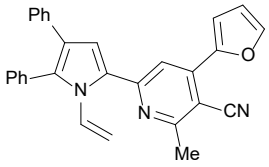
7.36–7.28 (m, 3H, H*m*,*p*, Bn), 7.01–6.99 (m, 2H, H*o*, Bn), 6.97–6.94 (m, 1H, H-5, pyrrole), 6.76–6.71 (m, 1H, H-4, pyrrole), 6.41–6.38 (m, 1H, H-3, pyrrole), 5.21 (s, 2H, CH_2-Ph), 2.85 (s, 3H, CH_3, pyridine). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 163.0, 158.5, 144.8, 138.3, 137.6, 130.3, 129.1 (2C), 128.9 (2C), 128.7, 127.8, 127.4 (2C), 126.7, 126.2 (2C), 117.5, 117.4, 113.9 (2C), 109.7, 51.6, 24.6. Anal. Calcd for $C_{24}H_{19}N_3$: C, 82.49; H, 5.48; N, 12.03%. Found: C, 82.22; H, 5.69; N, 12.29%.



2-Methyl-6-(1-methyl-5-phenyl-1*H*-pyrrol-2-yl)-4-phenylnicotinonitrile (2d). Yield: 255 mg (73%), yellow crystals, mp 145-146 °C. IR (film) 3048, 2211, 1576, 1533, 1455, 1302, 1241, 1192, 1072, 1059, 1032, 886, 810, 777, 752, 723, 687, 622, 523, 473 cm^{-1}. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 8.09–8.06 (m, 2H, H*o*, Ph), 7.65 (s, 1H, H-5, pyridine), 7.57–7.49 (m, 5H, Ph), 7.49–7.43 (m, 2H, Ph), 7.42–7.34 (m, 1H, H*p*, Ph), 6.76 (d, *J* = 3.8 Hz, 1H, H-3, pyrrole), 6.42 (d, *J* = 3.8 Hz, 1H, H-4, pyrrole), 3.66 (s, 3H, NCH_3), 2.92 (s, 3H, CH_3, pyridine). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 163.1, 158.8, 144.8, 140.5, 138.0, 132.6, 131.0, 130.3, 129.1 (2C), 129.0 (2C), 128.7 (2C), 127.8, 127.5 (2C), 117.9, 117.7, 113.7, 109.9, 105.6, 34.7, 24.6. Anal. Calcd for $C_{24}H_{19}N_3$: C, 82.49; H, 5.48; N, 12.03%. Found: C, 82.68; H, 5.66; N, 12.34%.

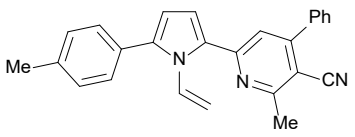


2-Methyl-6-(1-methyl-5-phenyl-1*H*-pyrrol-2-yl)-4-(thiophen-2-yl)nicotinonitrile (2e). Yield: 309 mg (87%), yellow crystals, mp 148-149 °C. IR (film) 3104, 3071, 2955, 2925, 2217, 1578, 1531, 1458, 1400, 1352, 1297, 1240, 1184, 1060, 1034, 910, 878, 853, 797, 759, 731, 701, 649 cm^{-1}.^{1}H NMR (400.13 MHz, $CDCl_3$): δ 7.86–7.85 (m, 1H, H-5, thiophene), 7.55–7.44 (m, 6H, H*o,m*, Ph, H-5, pyridine, H-3, thiophene), 7.42–7.35 (m, 1H, H*p*, Ph), 7.20–7.15 (m, 1H, H-4, thiophene), 6.77 (d, *J* = 3.8 Hz, 1H, H-3, pyrrole), 6.42 (d, *J* = 3.8 Hz, 1H, H-4, pyrrole), 3.64 (s, 3H, NCH_3), 2.90 (s, 3H, CH_3, pyridine). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 163.3, 153.9, 144.8, 143.6, 140.6, 132.6, 130.9, 130.0, 129.2 (2C), 128.7 (2C), 128.6, 127.8, 126.9, 117.9, 115.9, 113.7, 109.9, 105.2, 34.7, 24.4. Anal. Calcd for $C_{22}H_{17}N_3S$: C, 74.34; H, 4.82; N, 11.82; S, 9.02%. Found: C, 74.50; H, 4.98; N, 11.56; S, 8.81%.

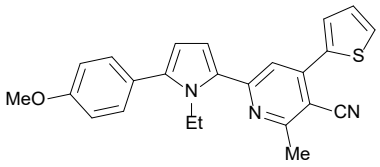


6-(4,5-Diphenyl-1-vinyl-1*H*-pyrrol-2-yl)-4-(furan-2-yl)-2-methylnicotinonitrile (2f). Yield: 307 mg (72%), yellow crystals, mp 156-157 °C. IR (film) 3142, 3060, 3032, 2220, 1640, 1598, 1570, 1486, 1407, 1297, 1193, 1096, 1072, 1012, 953, 910, 886, 828, 764, 733, 700, 648, 595, 508 cm^{-1}. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 7.67 (s, 1H, H-5, pyridine), 7.61–7.59 (m, 1H, H-5, furan), 7.43–7.35 (m, 5H, Ph), 7.25–7.23 (m, 1H, H*p*, Ph), 7.22–7.17 (m, 4H, H*o*,*m*, Ph), 7.17–7.12 (m, 1H, H-3, furan), 6.93 (s, 1H, H-3, pyrrole), 6.81 (dd, *J* = 15.7, 8.5 Hz, 1H, H_x), 6.60–6.58 (m, 1H, H-4, furan), 4.85 (d, *J* = 8.5 Hz, 1H, H_A), 4.57 (d, *J* = 15.7 Hz, 1H, H_B), 2.85 (s, 3H, CH_3, pyridine). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 163.1, 152.7, 150.2, 145.2, 144.9, 134.9, 134.8, 131.7 (2C), 131.4, 131.3, 128.7 (2C), 128.5, 128.3 (2C), 128.1 (2C), 127.9, 126.2, 124.8, 117.7,

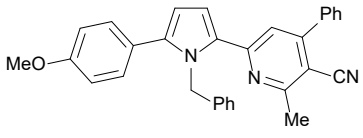
116.2, 116.0, 112.7, 112.0, 110.4, 105.2, 24.4. Anal. Calcd for $C_{29}H_{21}N_3O$: C, 81.48; H, 4.95; N, 9.83; O, 3.74%. Found: C, 81.62; H, 5.12; N, 10.03%.



2-Methyl-4-phenyl-6-(5-(*p*-tolyl)-1-vinyl-1*H*-pyrrol-2-yl)nicotinonitrile (2g). Yield: 263 mg (70%), yellow crystals, mp 118-119 °C. IR (film) 3063, 3028, 2919, 2850, 2219, 1640, 1580, 1537, 1537, 1476, 1423, 1286, 1238, 1074, 910, 822, 779, 733, 693 cm^{-1}. ^1H NMR (400.13 MHz, $CDCl_3$): δ 8.06–8.04 (m, 2H, H*o,* Ph), 7.65 (s, 1H, H-5, pyridine), 7.54–7.47 (m, 3H, H*m,p*, Ph), 7.38–7.36 (m, 2H, H*o*, *p*-tolyl), 7.26–7.23 (m, 2H, H*m*, *p*-tolyl), 6.95 (dd, J = 15.6, 8.6 Hz, 1H, H_X), 6.76 (d, J = 3.8 Hz, 1H, H-3, pyrrole), 6.38 (d, J = 3.8 Hz, 1H, H-4, pyrrole), 4.94 (d, J = 8.6 Hz, 1H, H_A), 4.64 (d, J = 15.6 Hz, 1H, H_B), 2.90 (s, 3H, CH_3, pyridine), 2.41 (s, 3H, CH_3, *p*-tolyl). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 162.7, 158.5, 145.4, 139.0, 137.9, 137.8, 131.5, 130.3, 129.4, 129.3 (2C), 129.2 (2C), 129.0 (2C), 128.5, 127.4 (2C), 118.4, 117.7, 115.8, 110.9, 110.6, 105.8, 24.5, 21.3. Anal. Calcd for $C_{26}H_{21}N_3$: C, 83.17; H, 5.64; N, 11.19%. Found: C, 83.38; H, 5.90; N, 11.35%.

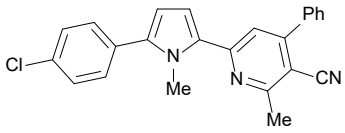


6-(1-Ethyl-5-(4-methoxyphenyl)-1*H*-pyrrol-2-yl)-2-methyl-4-(thiophen-2-yl)nicotinonitrile (2h). Yield: 283 mg (71%), yellow crystals, mp 141-142 °C. IR (film) 3140, 3058, 2976, 2934, 2836, 2218, 1611, 1580, 1531, 1471, 1442, 1287, 1249, 1177, 1060, 1032, 910, 836, 778, 731, 649, 548 cm^{-1}. ^1H NMR (400.13 MHz, $CDCl_3$): δ 7.88–7.85 (m, 1H, H-5, thiophene), 7.56–7.52 (m, 2H, H-5, pyridine, H-3, thiophene), 7.44–7.41 (m, 2H, H*o*, Ph), 7.19–7.16 (m, 1H, H-4, thiophene), 7.02–6.97 (m, 2H, H*m*, Ph), 6.68 (d, J = 3.7 Hz, 1H, H-3, pyrrole), 6.31 (d, J = 3.7 Hz, 1H, H-4, pyrrole), 4.10 (q, J = 7.2 Hz, 2H, NCH_2), 3.87 (s, 3H, OCH_3), 2.90 (s, 3H, CH_3, pyridine), 0.84 (t, J = 7.2 Hz, 3H, CH_3). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 163.2, 159.5, 153.9, 145.6, 143.6, 139.8, 130.6 (2C), 130.0, 129.3, 128.6, 126.9, 125.6, 117.6, 115.8, 114.4, 114.2 (2C), 110.6, 105.5, 55.4, 41.1, 24.4, 16.2. Anal. Calcd for $C_{24}H_{21}N_3OS$: C, 72.15; H, 5.30; N, 10.52; S, 8.02%. Found: C, 72.41; H, 5.48; N, 10.29; S, 7.83%. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{21}N_3OS$ 400.148359; Found 400.1484.

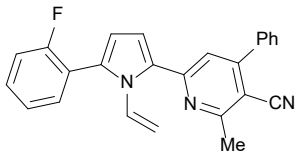


6-(1-Benzyl-5-(4-methoxyphenyl)-1*H*-pyrrol-2-yl)-2-methyl-4-phenylnicotinonitrile (2i). Yield: 337 mg (74%), yellow crystals, mp 135-136 °C. IR (film) 3105, 3063, 3031, 2932, 2848, 2218, 1580, 1536, 1473, 1251, 1178, 1031, 910, 836, 780, 732, 695, 544 cm^{-1}. ^1H NMR (400.13 MHz, $CDCl_3$): δ 7.77–7.75 (m, 2H, H*o*, Ph), 7.51 (s, 1H, H-5, pyridine), 7.43–7.40 (m, 3H, H*m,p*, Ph), 7.37–7.31 (m, 2H, H*o*, CH_3OPh), 7.22–7.16 (m, 3H, H*m,p,* Bn), 6.90–6.88 (m, 2H, H*m*, CH_3OPh), 6.78 (d, J = 3.8 Hz, 1H, H-3, pyrrole), 6.75–6.71 (m, 2H, H*o*, Bn), 6.42 (d, J = 3.8 Hz, 1H, H-4, pyrrole), 5.23 (s, 2H, CH_2-Ph), 3.82 (s, 3H, OCH_3), 2.83 (s, 3H, CH_3, pyridine). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 163.0, 159.5, 158.6, 145.2, 140.4, 138.9, 137.8, 130.7 (2C), 130.3, 130.1, 128.9 (2C), 128.8 (2C), 127.4 (3C), 125.9 (2C), 125.3, 117.7, 117.3, 114.6, 114.1 (2C),

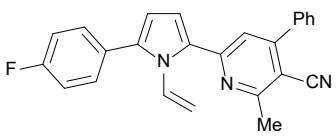
110.4, 106.1, 55.4, 49.6, 24.6. Anal. Calcd for $C_{31}H_{25}N_3O$: C, 81.73; H, 5.53; N, 9.22; O, 3.51%. Found: C, 81.97; H, 5.74; N, 9.41%.



6-(5-(4-Chlorophenyl)-1-methyl-1*H*-pyrrol-2-yl)-2-methyl-4-phenylnicotinonitrile (2j). Yield: 268 mg (70%), yellow crystals, mp 183-184 °C. IR (film) 3063, 2219, 1581, 1534, 1468, 1452, 1410, 1342, 1304, 1241, 1191, 1012, 909, 1053, 1012, 909, 833, 778, 733, 694, 650, 513 cm^{-1}. ^1H NMR (400.13 MHz, $CDCl_3$): δ 8.10–8.07 (m, 2H, H*o*, Ph), 7.64 (s, 1H, H-5, pyridine), 7.54–7.52 (m, 3H, Ph), 7.45–7.43 (m, 4H, Ph), 6.80 (d, *J* = 3.9 Hz, 1H, H-3, pyrrole), 6.42 (d, *J* = 3.9 Hz, 1H, H-4, pyrrole), 3.64 (s, 3H, NCH_3), 2.99 (s, 3H, CH_3, pyridine). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 163.2, 159.1, 144.9, 139.2, 138.0, 133.9, 131.5, 131.1, 130.5, 130.4 (2C), 129.1 (2C), 129.0 (2C), 127.5 (2C), 117.9, 117.8, 113.7, 110.2, 105.9, 34.7, 24.6. Anal. Calcd for $C_{24}H_{18}ClN_3$: C, 75.09; H, 4.73; Cl, 9.23; N, 10.95%. Found: C, 75.31; H, 4.96; Cl, 8.95; N, 10.72%.

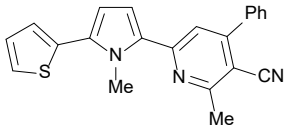


6-(5-(2-Fluorophenyl)-1-vinyl-1*H*-pyrrol-2-yl)-2-methyl-4-phenylnicotinonitrile (2k). Yield: 258 mg (68%), yellow crystals, mp 91-92 °C. IR (film) 3110, 3063, 3038, 2959, 2926, 2856, 2220, 1642, 1583, 1538, 1469, 1416, 1319, 1288, 1239, 1110, 1030, 961, 910, 816, 910, 816, 781, 758, 733, 694, 650, 542, 526 cm^{-1}. ^1H NMR (400.13 MHz, $CDCl_3$): δ 8.06–8.04 (m, 2H, H*o*, Ph), 7.68 (s, 1H, H-5, pyridine), 7.55–7.46 (m, 3H, H*m,p*, Ph), 7.46–7.37 (m, 2H, Ph), 7.25–7.14 (m, 2H, Ph), 6.90–6.81 (m, 2H, H-3, pyrrole, H_x), 6.45 (d, *J* = 3.7 Hz, 1H, H-4, pyrrole), 4.93 (d, *J* = 8.7 Hz, 1H, H_A), 4.67 (d, *J* = 15.7 Hz, 1H, H_B), 2.92 (s, 3H, CH_3, pyridine). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 162.8, 159.7 (d, *J* = 248.3 Hz, C-2, 2-FC_6H_4), 158.5, 144.8, 137.8, 132.2 (d, *J* = 4.0 Hz, C-6, 2-FC_6H_4), 132.1, 131.2, 130.3 (2C), 130.3, 130.2 (d, *J* = 6.5 Hz, C-4, 2-FC_6H_4), 128.9 (2C), 127.4 (2C), 124.2 (d, *J* = 3.3 Hz, C-5, 2-FC_6H_4), 120.4 (d, *J* = 14.7 Hz, C-1, 2-FC_6H_4), 118.3, 117.5, 116.1, 116.0 (d, *J* = 22.0 Hz, C-3, 2-FC_6H_4), 112.5, 110.7, 105.7, 24.4. Anal. Calcd for $C_{25}H_{18}FN_3$: C, 79.14; H, 4.78; N, 11.07; F, 5.01%. Found: C, 79.43; H, 5.01; N, 11.31; F, 4.79%.

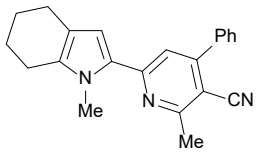


6-(5-(4-Fluorophenyl)-1-vinyl-1*H*-pyrrol-2-yl)-2-methyl-4-phenylnicotinonitrile (2l). Yield: 265 mg (70%), yellow crystals, mp 136-137 °C. IR (film) 3063, 2220, 1641, 1583, 1477, 1424, 1395, 1319, 1287, 1225, 1159, 1096, 1029, 965, 909, 39, 780, 732, 694, 648, 608, 527 cm^{-1}. ^1H NMR (400.13 MHz, $CDCl_3$): δ 8.06–8.04 (m, 2H, H*m,* Ph), 7.65 (s, 1H, H-5, pyridine), 7.51–7.49 (m, 3H, H*o,p,* Ph), 7.47–7.42 (m, 2H, H*o,* Ph), 7.15–7.10 (m, 2H, H*m*, Ph), 6.89 (dd, *J* = 15.7, 8.5 Hz, 1H, H_x), 6.75 (d, *J* = 3.8 Hz, 1H, H-3, pyrrole), 6.39 (d, *J* = 3.8 Hz, 1H, H-4, pyrrole), 4.97 (d, *J* = 8.5 Hz, 1H, H_A), 4.65 (d, *J* = 15.7 Hz, 1H, H_B), 2.90 (s, 3H, CH_3, pyridine). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 162.8, 162.6 (d, *J* = 248.3 Hz, C-4, 4-FC_6H_4), 158.7,

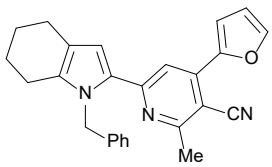
145.3, 137.9, 137.6, 131.3, 131.3 (d, J = 11.5 Hz, C-2,6, 4-FC_6H_4), 130.4, 129.1 (2C), 128.8, 128.5 (d, J = 2.6 Hz, C-1, 4-FC_6H_4), 127.5 (2C), 118.5, 117.6, 115.6 (d, J = 21.6 Hz, C-3,5, 4-FC_6H_4), 115.5, 111.3, 111.1, 106.0, 24.5. Anal. Calcd for $C_{25}H_{18}FN_3$: C, 79.14; H, 4.78; N, 11.07; F, 5.01%. Found: C, 79.38; H, 4.97; N, 11.38; F, 4.81%. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{25}H_{18}FN_3$ 380.1563; Found 380.1562.



2-Methyl-6-(1-methyl-5-(thiophen-2-yl)-*1H*-pyrrol-2-yl)-4-phenylnicotinonitrile (2m). Yield: 238 mg (67%), yellow crystals, mp 171-172 °C. IR (film) 3106, 3069, 3035, 2922, 2219, 1578, 1538, 1448, 1419, 1399, 1297, 1227, 1200, 1110, 1078, 1041, 910, 846, 778, 732, 695, cm^{-1}. ^1H NMR (400.13 MHz, $CDCl_3$): δ 8.07–8.06 (m, 2H, H*o*, Ph), 7.62 (s, 1H, H-5, pyridine), 7.52–7.50 (m, 3H, H*m,p* Ph,), 7.37–7.36 (m, 1H, H-5, thiophene), 7.18–7.17 (m, 1H, H-3, thiophene), 7.14–7.12 (m, 1H, H-4, thiophene), 6.72 (d, J = 3.9 Hz, 1H, H-3, pyrrole), 6.49 (d, J = 3.9 Hz, 1H, H-4, pyrrole), 3.73 (s, 3H, N-CH_3), 2.92 (s, 3H, CH_3, pyridine). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 163.2, 159.0, 144.8, 138.0, 134.2, 132.7, 131.0, 130.4, 129.1 (2C), 127.7, 127.5 (3C), 126.6, 126.0, 117.8, 113.7, 111.1, 105.9, 34.6, 24.6. Anal. Calcd for $C_{22}H_{17}N_3S$: C, 74.34; H, 4.82; N, 11.82; S, 9.02%. Found: C, 74.43; H, 4.60; N, 11.99; S, 8.78%.

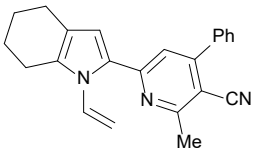


2-Methyl-6-(1-methyl-4,5,6,7-tetrahydro-1*H*-indol-2-yl)-4-phenylnicotinonitrile (2n). Yield: 235 mg (72%), yellow crystals, mp 186-187 °C. IR (film) 3062, 3036, 2930, 2851, 2217, 1639, 1586, 1563, 1538, 1496, 1457, 1444, 1368, 1298, 1240, 1189, 1147, 1057, 911, 782, 759, 732, 694 cm^{-1}. ^1H NMR (400.13 MHz, $CDCl_3$): δ 8.03–8.01 (m, 2H, H*o*, Ph), 7.51–7.48 (m, 4H, H*m,p*, Ph, H-5, pyridine), 6.48 (s, 1H, H-3, pyrrole), 3.54 (s, 3H, NCH_3), 2.88 (s, 3H, CH_3, pyridine), 2.64–2.61 (m, 2H, CH_2-7), 2.58–2.55 (m, 2H, CH_2-4), 1.94–1.86 (m, 2H, CH_2-5), 1.83–1.74 (m, 2H, CH_2-6). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 163.1, 158.6, 145.1, 138.2, 134.5, 130.2, 129.1 (2C), 127.4 (2C), 127.3, 119.1, 118.1, 117.3, 112.3, 105.1, 32.1, 24.6, 23.5, 23.2, 23.0, 22.6. Anal. Calcd for $C_{22}H_{21}N_3$: C, 80.70; H, 6.46; N, 12.83%. Found: C, 80.91; H, 6.64; N, 13.07%.

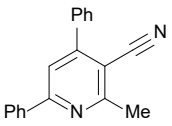


6-(1-Benzyl-4,5,6,7-tetrahydro-1*H*-indol-2-yl)-4-(furan-2-yl)-2-methylnicotinonitrile (2o). Yield: 263 mg (67%), yellow crystals, mp 193-194 °C. IR (film) 3137, 3115, 2922, 2850, 2211, 1595, 1559, 1530, 1490, 1441, 1381, 1356, 1296, 1236, 1157, 1011, 945, 882, 826, 765, 729, 660, 602, 458 cm^{-1}. ^1H NMR (400.13 MHz, $CDCl_3$): δ 7.44 (s, 1H, H-5, pyridine), 7.35–7.27 (m, 4H, H*m,p*, Ph, H-5, furan), 7.03–6.95 (m, 1H, H-3, furan), 6.91–6.90 (m, 2H, H*o*, Ph), 6.66 (s, 1H, H-3, pyrrole), 6.50–6.46 (m, 1H, H-4, furan), 5.14 (s, 2H, CH_2-Ph), 2.82 (s, 3H, CH_3, pyridine), 2.64–2.59 (m, 2H, CH_2-7), 2.50–2.45 (m, 2H, CH_2-4), 1.86–1.73 (m, 4H, CH_2-5,6). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 163.4, 152.6, 149.9, 144.6 (2C), 138.4, 134.6, 129.0 (2C), 127.4 (2C), 125.6 (2C), 119.7, 118.0, 114.7, 113.3, 112.4, 111.5, 104.5, 48.0, 24.5, 23.5,

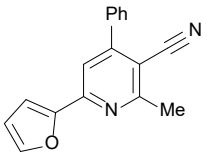
23.2, 23.1, 22.5. Anal. Calcd for $C_{26}H_{23}N_3O$: C, 79.36; H, 5.89; N, 10.68; O, 4.07%. Found: C, 79.52; H, 6.13; N, 10.96%.



2-Methyl-4-phenyl-6-(1-vinyl-4,5,6,7-tetrahydro-1*H*-indol-2-yl)nicotinonitrile (2p). Yield: 214 mg (63%), yellow crystals, mp 108-109 °C. IR (film) 3104, 3061, 3035, 2931, 2850, 2218, 1641, 1587, 1568, 1539, 1496, 1439, 1382, 1332, 1288, 119, 1146, 1028, 967, 910, 884, 781, 733, 694, 630, 590, 626 cm^{-1}. ^1H NMR (400.13 MHz, $CDCl_3$): δ 8.02–7.99 (m, 2H, H*o*, Ph), 7.60 (s, 1H, H-5, pyridine), 7.52–7.46 (m, 3H, H*m,p*, Ph), 6.76 (dd, *J* = 15.8, 8.8 Hz, 1H, H_x), 6.62 (s, 1H, H-3, pyrrole), 4.99 (d, *J* = 8.8 Hz, 1H, H_A), 4.90 (d, *J* = 15.8 Hz, 1H, H_B), 2.86 (s, 3H, CH_3 pyridine), 2.72–2.68 (m, 2H, CH_2-7), 2.59–2.56 (m, 2H, CH_2-4), 1.90–1.75 (m, 4H, CH_2-5,6). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 163.0, 158.3, 144.9, 138.2, 134.0, 130.9, 130.2, 129.0 (2C), 127.4 (2C), 126.4, 120.5, 118.0, 117.7, 115.1, 107.5, 104.8, 24.6, 23.8, 23.3, 23.2, 23.0. Anal. Calcd for $C_{23}H_{21}N_3$: C, 81.38; H, 6.24; N, 12.38%. Found: C, 81.65; H, 6.49; N, 12.71%.

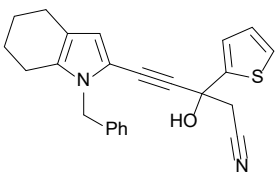


2-Methyl-4,6-diphenylnicotinonitrile (2q). Yield: 194 mg (72%), yellow crystals, mp 113-114 °C. IR (film) 3087, 3058, 3034, 2953, 2921, 2218, 1574, 1542, 1493, 1441, 1381, 1374, 1233, 1177, 1156, 1074, 1031, 999, 876, 776, 746, 698, 687 cm^{-1}. ^1H NMR (400.13 MHz, $CDCl_3$): δ 8.09–8.07 (m, 2H, Ph), 7.69 (s, 1H, H-5, pyridine), 7.66–7.62 (m, 2H, Ph), 7.55–7.54 (m, 3H, Ph), 7.51–7.49 (m, 3H, Ph), 2.93 (s, 3H, CH_3, pyridine). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 162.9, 159.3, 153.9, 137.9, 136.7, 130.4, 130.0, 129.1 (2C), 129.1 (2C), 128.5 (2C), 127.6 (2C), 118.0, 117.3, 105.9, 24.5. Anal. Calcd for $C_{19}H_{14}N_2$: C, 84.42; H, 5.22; N, 10.36%. Found: C, 84.72; H, 4.96; N, 10.67%.



4-(Furan-2-yl)-2-methyl-6-phenylnicotinonitrile (2r). Yield: 127 mg (49%), yellow crystals; mp 140-141 °C. IR (film) 3143, 3114, 2925, 2856, 2221, 1599, 1563, 1485, 1450, 1378, 1242, 1160, 1009, 945, 884, 828, 777, 754, 701 cm^{-1}. ^1H NMR (400.13 MHz, $CDCl_3$): δ 7.66-7.63 (m, 3H, Ph), 7.61 (s, 1H, H-5, pyridine), 7.55-7.54 (m, 3H, Ph, H-5, furan), 7.37-7.36 (m, 1H, H-3, furan), 6.61-6.60 (m, 1H, H-4, furan), 2.90 (s, 3H, CH_3, pyridine). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 163.1, 154.0, 152.5, 150.6, 145.1, 136.5, 130.1, 129.1 (2C), 128.5 (2C), 117.3, 115.9, 112.8, 112.4, 105.4, 24.4. Anal. Calcd for $C_{17}H_{12}N_2O$: C, 78.44; H, 4.65; N, 10.76%. Found: C, 78.71; H, 4.82; N, 10.45%.

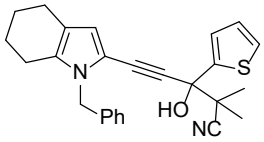
Synthesis of alcohols 3a-c



5-(1-Benzyl-4,5,6,7-tetrahydro-1*H*-indol-2-yl)-3-hydroxy-3-(thiophen-2-yl)pent-4-ynenitrile (3a)

Lithium (14 mg, 2 mmol) was added to solution of ethynylpyrrole **2a** (345 mg, 1 mmol) in dry MeCN (5 ml). Reaction was stirred at room temperature for 16 hours,

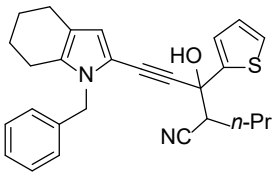
diluted with water (30 ml), and extracted by diethyl ether (3x10 ml). Extracts were washed with water and dried over $CaCl_2$. The residue after removing solvents was fractionated by column chromatography (SiO_2, *n*-hexane : diethyl ether, 10 : 1) to afford 120 mg (31%) of compound **3a** as yellow oil. IR (film) 3412, 3105, 3089, 3065, 3031, 2929, 2852, 2213, 1605, 1569, 1494, 1440, 1391, 1357, 1234, 1144, 1114, 1081, 1030, 910, 849, 804, 730, 704 649, 608, 458 cm^{-1}. ^1H NMR (400.13 MHz, $CDCl_3$): δ 7.33–7.27 (m, 2H, H*o*, Ph), 7.27–7.24 (m, 2H, H*p*, Ph, H-5, thiophene), 7.11–7.08 (m, 1H, H-3, thiophene), 7.05–7.01 (m, 2H, H*m*, Ph), 6.93–6.90 (m, 1H, H-4, thiophene), 6.39 (s, 1H, H-3, pyrrole), 5.15 (s, 2H, CH_2Ph), 3.06 (d, *J* = 16.3 Hz, 1H, CH_2CN), 2.97 (d, *J* = 16.3 Hz, 1H, CH_2CN), 2.91 (s, 1H, OH), 2.53–2.48 (m, 2H, CH_2-7), 2.46–2.41 (m, 2H, CH_2-4), 1.84–1.67 (m, 4H, CH_2-5,6). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 146.3, 138.2, 132.1, 128.7 (2C), 127.3, 127.1, 126.5 (2C), 126.1, 125.5, 118.4, 116.0, 115.1, 111.4, 91.8, 81.1, 68.4, 48.0, 35.8, 23.4, 23.1, 23.0, 22.4. Anal. Calcd for $C_{24}H_{22}N_2OS$: C, 74.58; H, 5.74; N, 7.25; O, 4.14; S, 8.29%. Found: C, 74.65; H, 5.87; N, 7.44; S, 8.27%.



5-(1-benzyl-4,5,6,7-tetrahydro-1H-indol-2-yl)-3-hydroxy-2,2-dimethyl-3-(thiophen-2-yl)pent-4-ynenitrile (3b)

Analogously, from of ethynylpyrrole **1a** (345 mg, 1 mmol), lithium (14 mg, 2 mmol) and Me_2CHCN (5 ml) 248 mg (60%) of compound **3b** as yellow oil was obtained.

IR (film) 3408, 2928, 2852, 2210, 1639, 1494, 1455, 1441, 1389, 1356, 1303, 1236, 1179, 1142, 1078, 1043, 1003, 973, 910, 799, 729, 699 cm^{-1}. ^1H NMR (400.13 MHz, $CDCl_3$): δ 7.31–7.23 (m, 4H, H*o*,*p* Ph, H-5, thiophene), 7.18–7.17 (m, 1H, H-3, thiophene), 7.00–6.98 (m, 2H, H*m*, Ph), 6.96–6.93 (m, 1H, H-4, thiophene), 6.39 (s, 1H, H-3, pyrrole), 5.15 (s, 2H, CH_2Ph), 2.86 (s, 1H, OH), 2.51–2.49 (m, 2H, CH_2-7), 2.44–2.42 (m, 2H, CH_2-4), 1.79–1.71 (m, 4H, CH_2-5,6), 1.41 (s, 3H, Me), 1.30 (s, 3H, Me). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 144.3, 138.2, 132.0, 128.8 (2C), 127.3, 127.1, 126.9, 126.3 (2C), 126.1, 123.4, 118.5, 115.1, 111.7, 91.8, 81.4, 75.1, 48.0, 44.4, 23.5, 23.2, 23.1, 23.1, 22.9, 22.4. Anal. Calcd for $C_{26}H_{26}N_2OS$: C, 75.33; H, 6.32; N, 6.76; O, 3.86; S, 7.73%. Found: C, 75.09; H, 6.51; N, 6.38; S, 7.90%.



5-(1-Benzyl-4,5,6,7-tetrahydro-1*H*-indol-2-yl)-3-hydroxy-2-propyl-3-(thiophen-2-yl)pent-4-ynnitrile (3c)

Analogously, from of ethynylpyrrole **1a** (345 mg, 1 mmol), lithium (14 mg, 2 mmol) and *n*-BuCN (5 ml) 111 mg (26%) of compound **3c** (two diasreoisomers) as yellow oil was obtained.

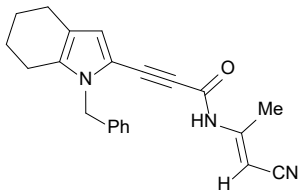
1 isomer:

IR (film) 3331, 3103, 3066, 3031, 2958, 2923, 2854, 2755, 2693, 2243, 2231, 1725, 1664, 1606, 1571, 1495, 1453, 1443, 1390, 1357, 1303, 1255, 1234, 1205, 1120, 1081, 1042, 911, 872, 803, 730, 700, 648, 641, 457 cm^{-1}. ^1H NMR (400.13 MHz, $CDCl_3$): δ 7.32–7.30 (m, 2H, H*m*, Ph), 7.28–7.24 (m, 2H, H*p*, Ph, H-5,

thiophene), 7.15–7.14 (m, 1H, H-3, thiophene), 7.01–7.00 (m, 2H, H*o*, Ph), 6.94–6.91 (m, 1H, H-4, thiophene), 6.39 (s, 1H, H-3, pyrrole), 5.15 (s, 2H, CH_2Ph), 3.05 (dd, *J* = 11.1, 4.03 Hz, 1H, CH), 2.87 (s, 1H, OH), 2.52–2.50 (m, 2H, CH_2-7), 2.44–2.42 (m, 2H, CH_2-4), 1.81–1.72 (m, 4H, CH_2-5,6), 1.53–1.49 (m, 1H, CH_2), 1.35–1.32 (m, 1H, CH_2), 0.98–0.96 (m, 2H, CH_2), 0.85 (t, *J* = 6.8 Hz, 3H, CH_3). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 145.8, 138.2, 132.0, 128.8 (2C), 127.3, 127.1, 126.3, 126.2, 126.1 (2C), 119.1, 118.5, 115.0, 111.7, 91.7, 81.2, 71.7, 48.0, 47.3, 30.2, 23.5, 23.1, 23.0, 22.4, 20.7, 13.6. Anal. Calcd for $C_{27}H_{28}N_2OS$: C, 75.67; H, 6.59; N, 6.54; O, 3.73; S, 7.48%. Found: C, 75.39; H, 6.31; N, 6.80; S, 7.64%.

2 isomer:

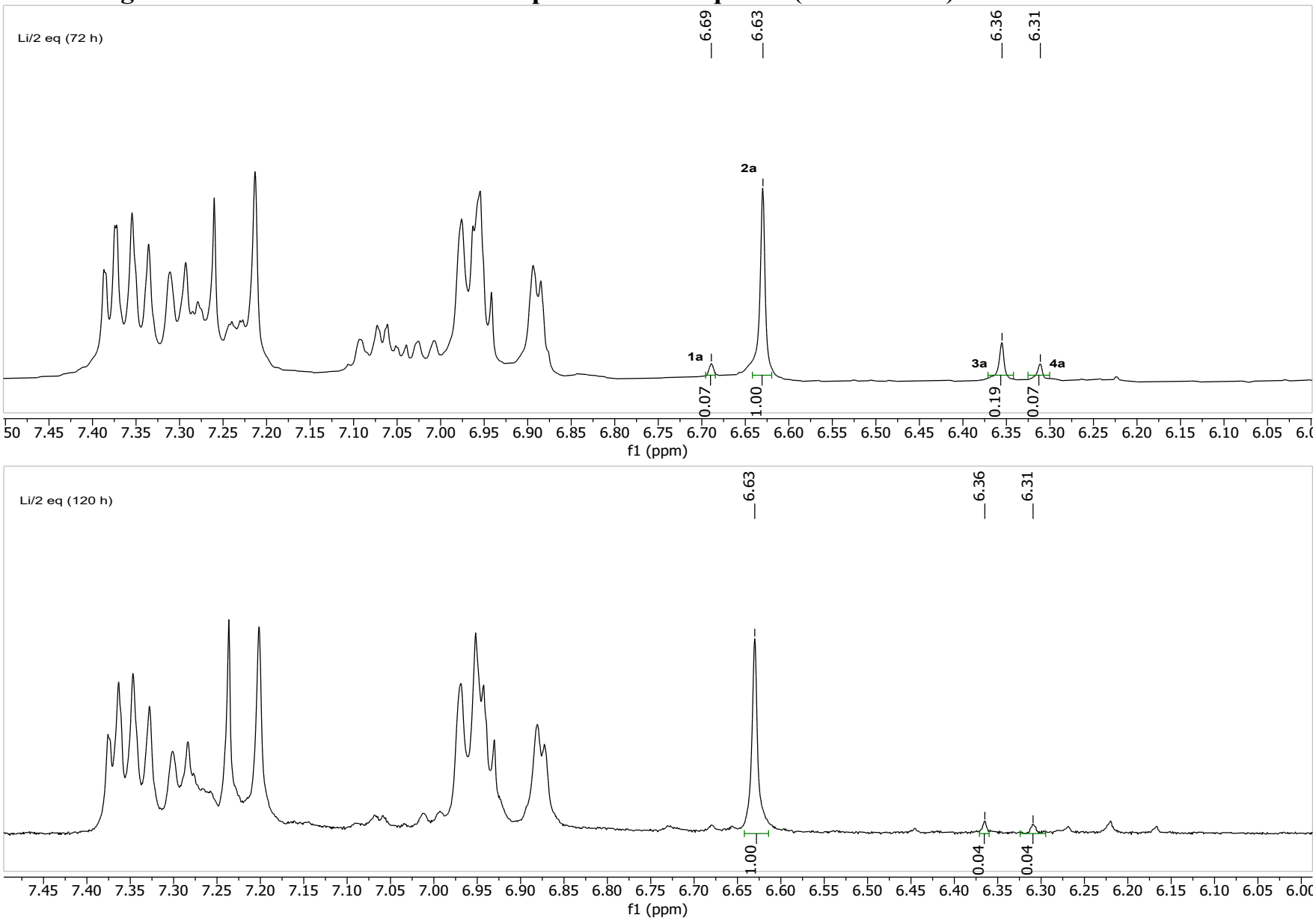
IR (film) 3401, 3065, 3031, 2958, 2932, 2873, 2855, 2245, 2212, 1722, 1605, 1495, 1453, 1441, 1390, 1357, 1303, 1234, 1144, 1116, 1079, 1032, 1005, 910, 849, 805, 732, 701, 648, 457 cm^{-1}. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 7.31–7.24 (m, 2H, H*m*, Ph), 7.30 (dd, *J* = 5.0, 1.0 Hz, 1H, H-5, thiophene), 7.23–7.21 (m, 1H, H*p*, Ph), 7.12 (dd, *J* = 3.8, 1.0 Hz, 1H, H-3, thiophene), 7.03–7.01 (m, 2H, H*o*, Ph), 6.92 (dd, *J* = 5.0, 3.8 Hz, 1H, H-4, thiophene), 6.42 (s, 1H, H-3, pyrrole), 5.23 (d, *J* = 16.5 Hz, 1H, CH_2Ph), 5.15 (d, *J* = 16.5 Hz, 1H, CH_2Ph), 3.06 (s, 1H, OH), 3.02 (dd, *J* = 11.2, 3.6 Hz, 1H, CH), 2.53–2.51 (m, 2H, CH_2-7), 2.44–2.42 (m, 2H, CH_2-4), 1.78–1.73 (m, 4H, CH_2-5,6), 1.50–1.48 (m, 1H, CH_2), 1.27–1.26 (m, 1H, CH_2), 1.00–0.89 (m, 2H, CH_2), 0.78 (m, *J* = 6.8 Hz, 3H, CH_3). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 145.6, 138.2, 132.0, 128.7 (2C), 127.3, 126.9, 126.5, 126.4, 126.3 (2C), 119.4, 118.5, 115.1, 111.7, 91.0, 81.8, 72.2, 48.0, 47.4, 30.5, 23.5, 23.1, 23.0, 22.4, 20.6, 13.4. Anal. Calcd for $C_{27}H_{28}N_2OS$: C, 75.67; H, 6.59; N, 6.54; O, 3.73; S, 7.48%. Found: C, 75.41; H, 6.72; N, 6.80; S, 7.22%.



Synthesis of (E)-3-(1-benzyl-4,5,6,7-tetrahydro-1*H*-indol-2-yl)-N-(1-cyanoprop-1-en-2-yl)propiolamide (7)

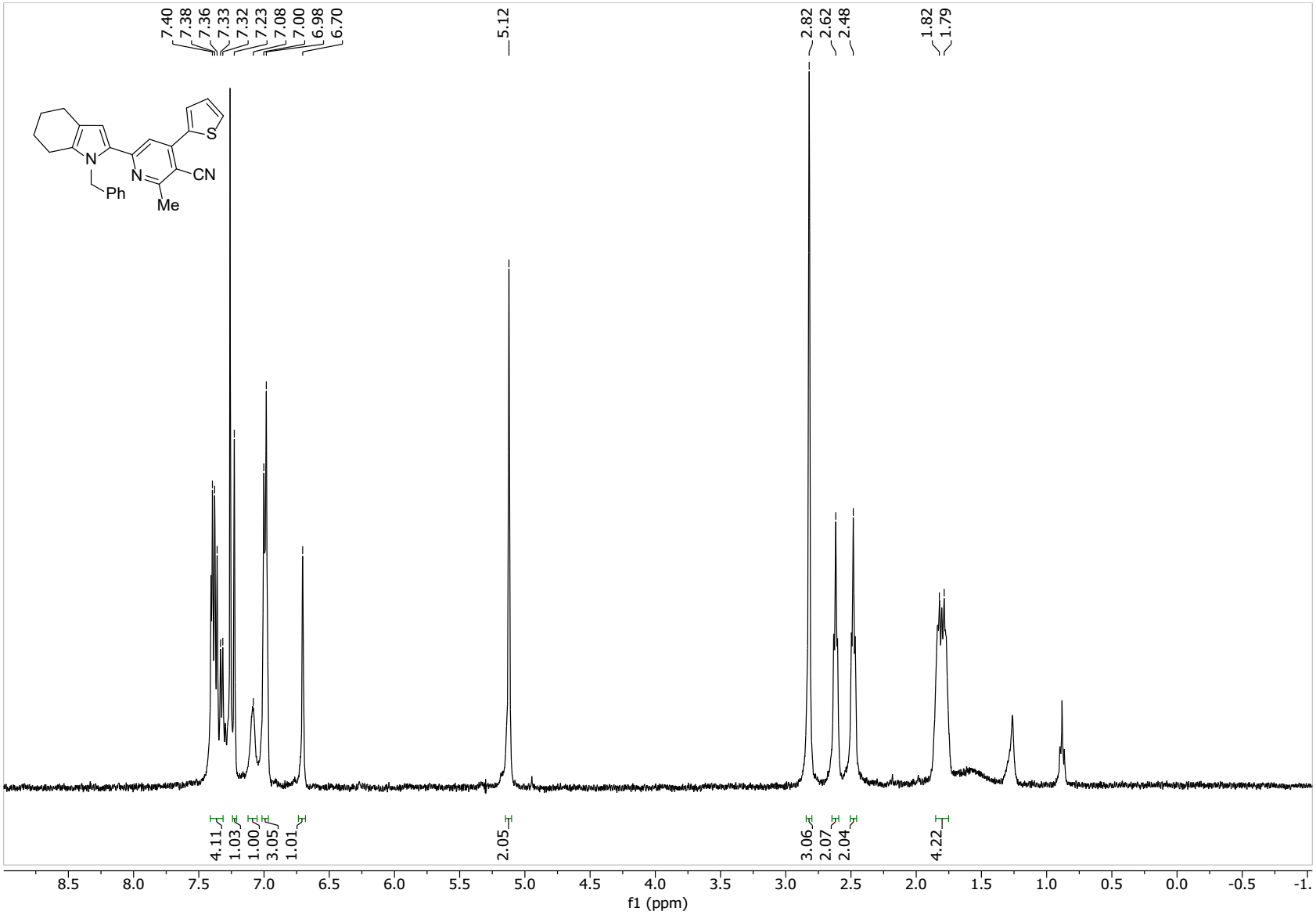
Lithium (14 mg, 2 mmol) was added to solution of ethynylpyrrole **6** (307 mg, 1 mmol) in dry MeCN (5 ml). Reaction mixture was stirred at room temperature for 24 h, diluted with water (30 ml), extracted with diethyl ether (3x10 ml). Extracts were washed with water and dried over $CaCl_2$. The residue after removing solvents was fractionated by column chromatography (SiO_2, *n*-hexane : diethyl ether, 5 : 1) to afford 223 mg (yield 65%) of amide **7** as white crystals, mp 168-169 °C. IR (KBr) 3272, 3181, 3137, 3093, 2925, 2209, 2171, 1667, 1631, 1520, 1434, 1397, 1377, 1309, 1251, 1208, 1133, 1109, 1072, 805, 754, 718, 698 cm^{-1}. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 7.35–7.24 (m, 3H, H*m,p*, Ph), 7.18–7.09 (m, 1H, NH), 7.04–7.03 (m, 2H, H*o,* Ph), 6.56 (s, 1H, H-3, pyrrole), 6.30 (s, 1H, HC=), 5.11 (s, 2H, CH_2Ph), 2.52–2.47 (m, 2H, CH_2-7), 2.45–2.40 (m, 2H, CH_2-4), 2.14 (s, 3H, CH_3), 1.81–1.67 (m, 4H, CH_2-5,6). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 152.1, 151.3, 137.4, 135.7, 128.9 (2C), 127.7, 126.6 (2C), 120.2, 119.4, 118.4, 110.1, 89.9, 84.6, 82.3, 48.4, 23.2, 23.0, 22.8, 22.7, 20.6. Anal. Calcd for $C_{22}H_{21}N_3O$: C, 76.94; H, 6.16; N, 12.24; O, 4.66%. Found: C, 76.97; H, 6.25; N, 12.26%.

^{1}H NMR monitoring of 1a with MeCN reaction in the presence of 2 eq of Li (72 and 120h)

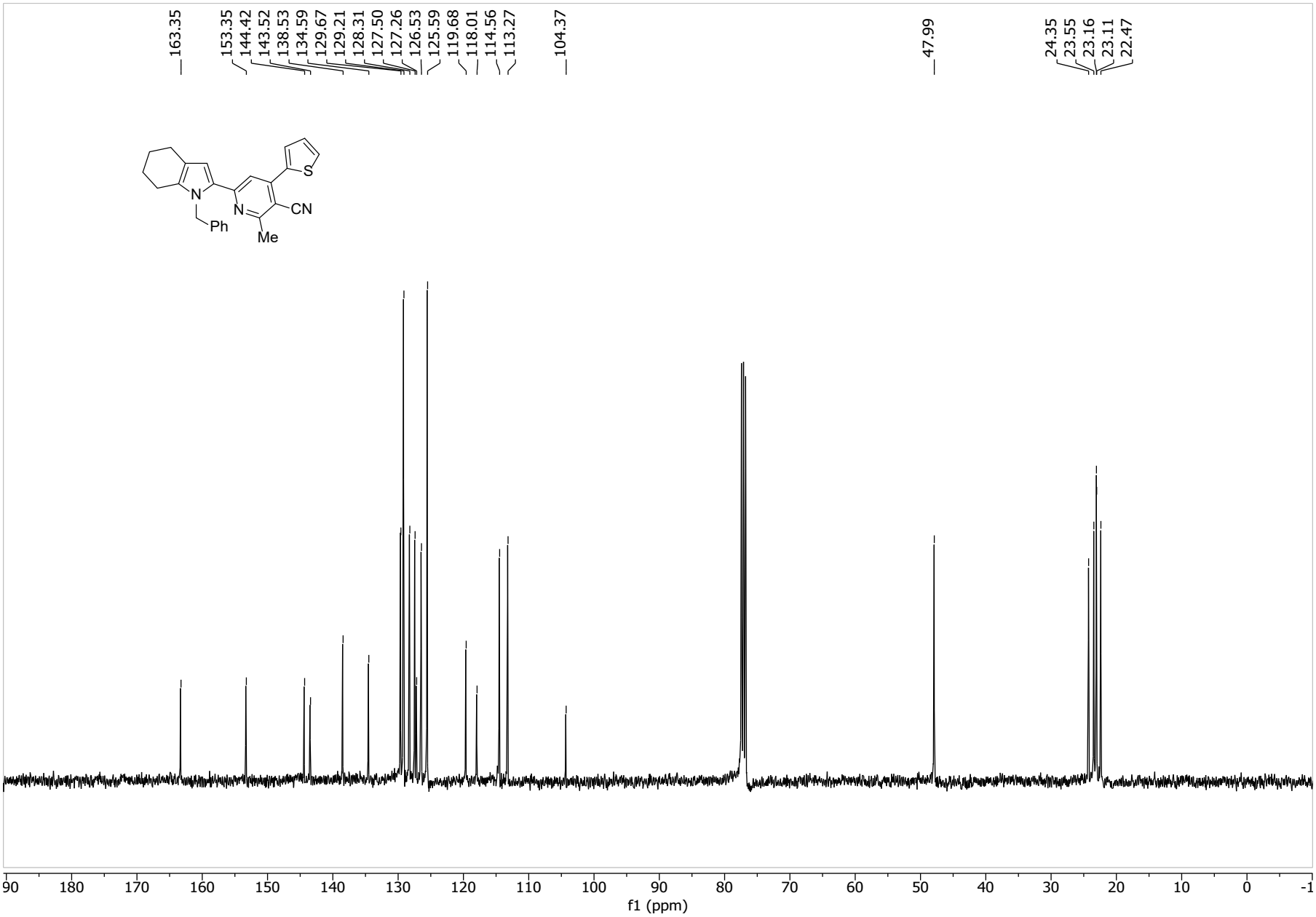


NMR Spectra of synthesized compounds

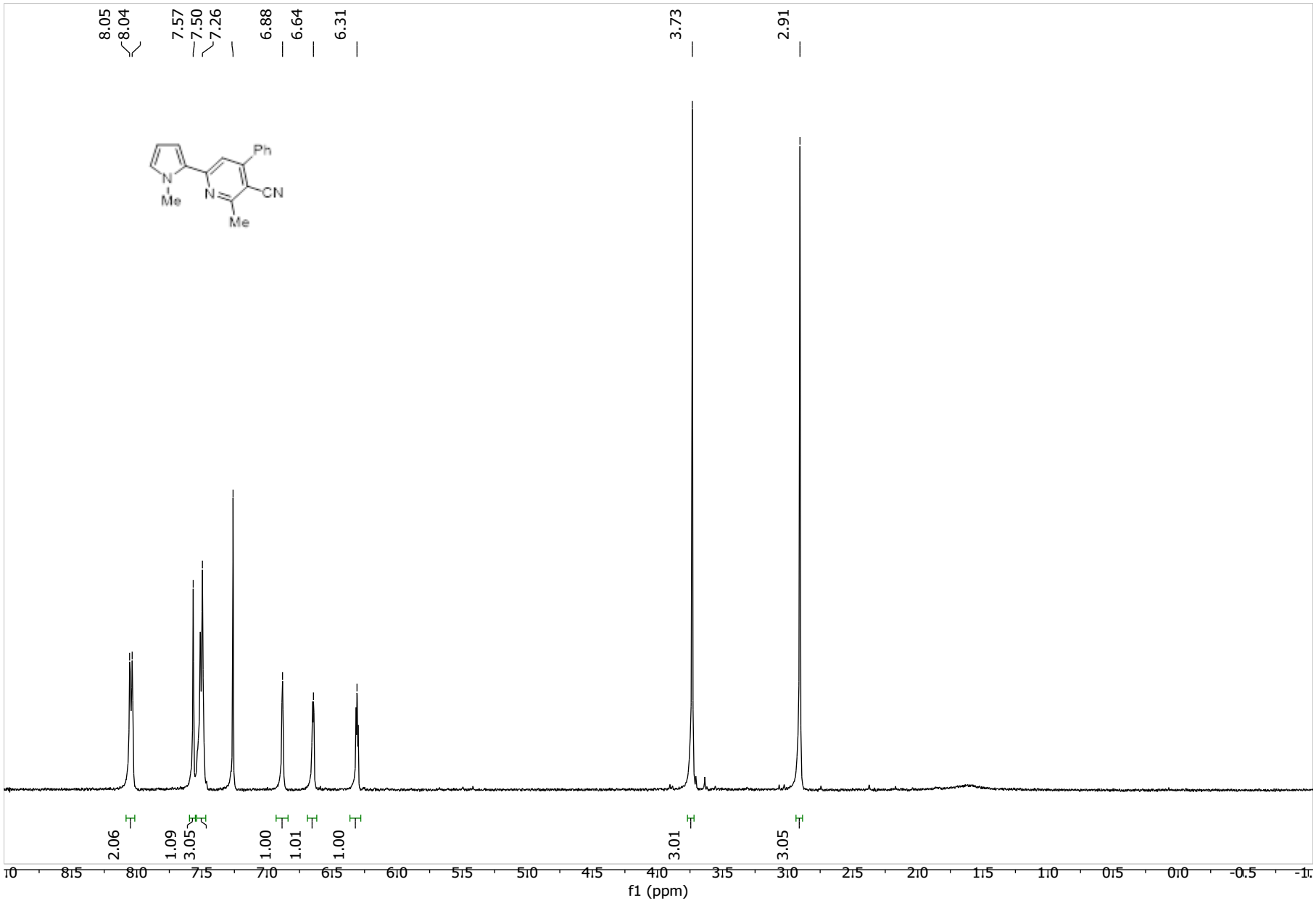
^{1}H NMR spectrum of 6-(1-benzyl-4,5,6,7-tetrahydro-1*H*-indol-2-yl)-2-methyl-4-(thiophen-2-yl)nicotinonitrile (**2a**) in $CDCl_3$



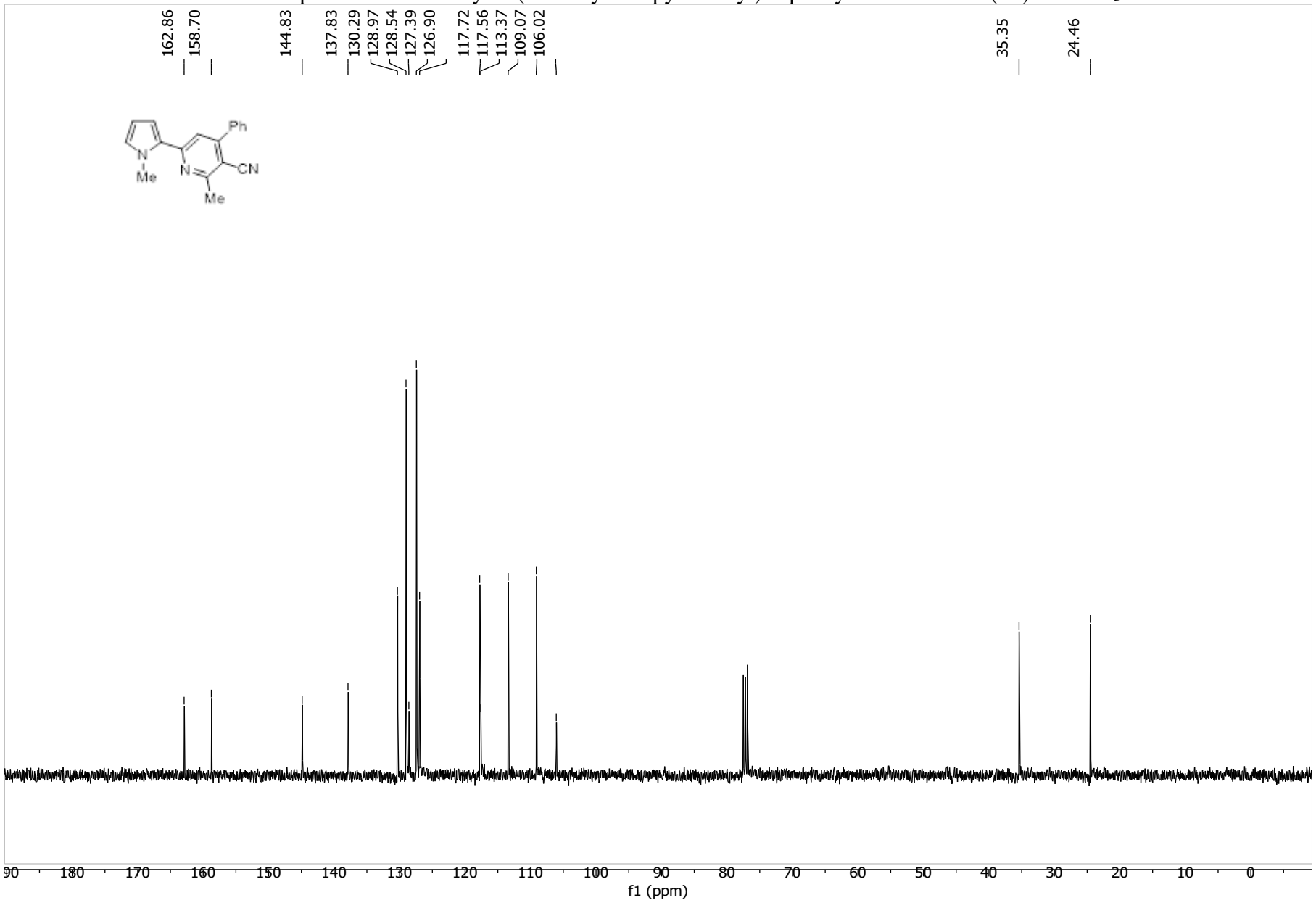
^{13}C NMR spectrum of 6-(1-benzyl-4,5,6,7-tetrahydro-1*H*-indol-2-yl)-2-methyl-4-(thiophen-2-yl)nicotinonitrile (**2a**) in $CDCl_3$



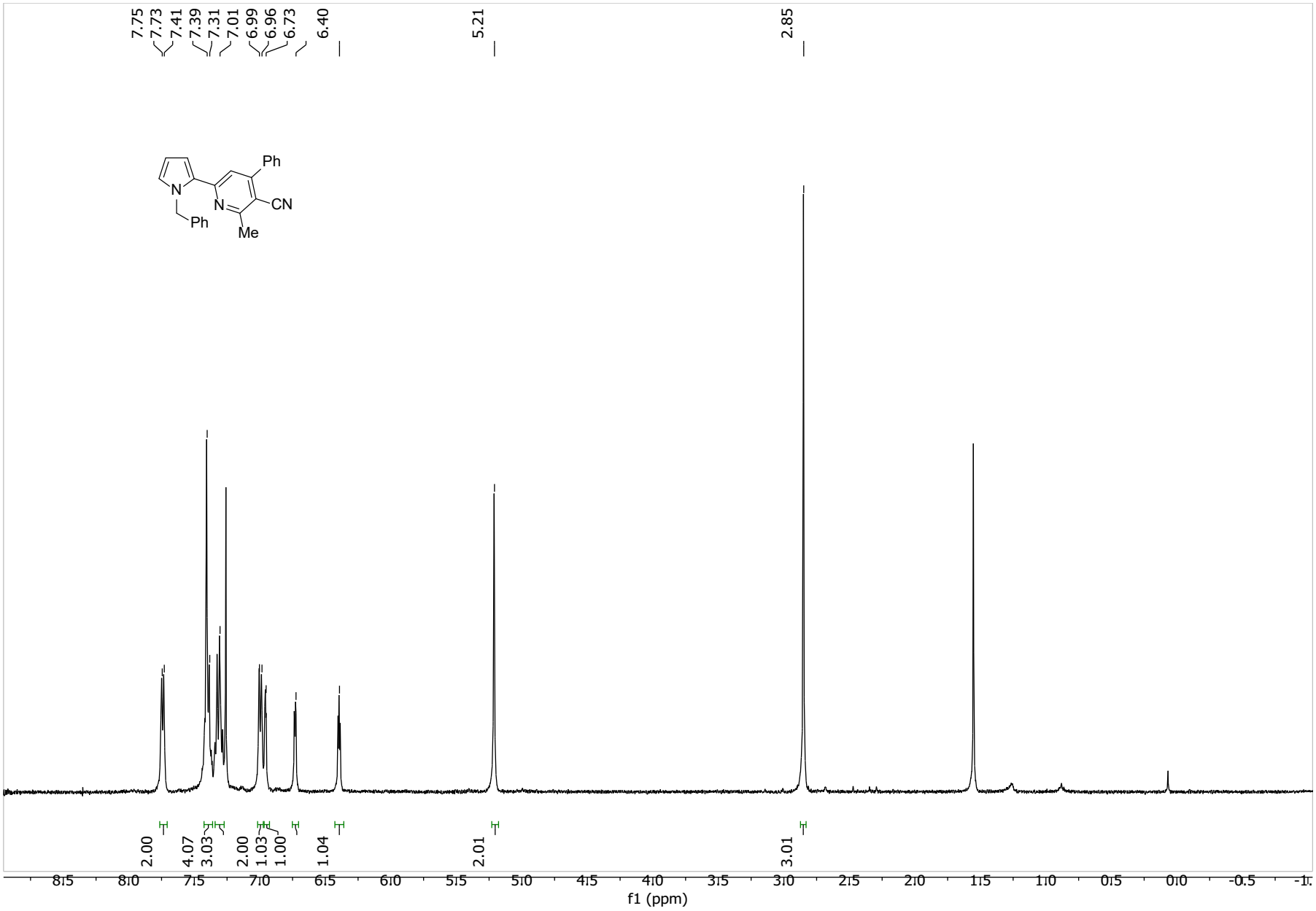
^{1}H NMR spectrum of 2-methyl-6-(1-methyl-1*H*-pyrrol-2-yl)-4-phenylnicotinonitrile (**2b**) in $CDCl_3$



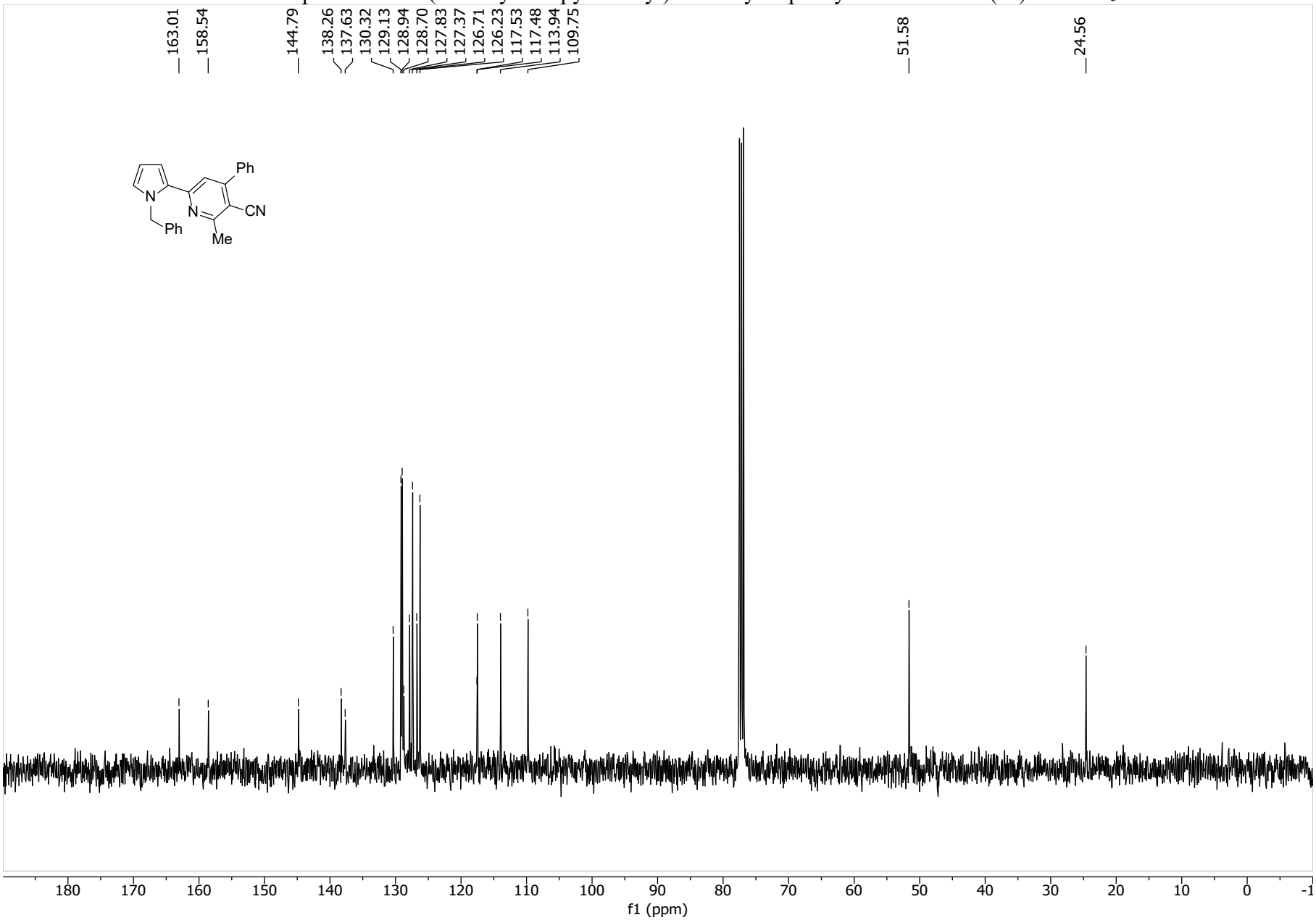
^{13}C NMR spectrum of 2-methyl-6-(1-methyl-1*H*-pyrrol-2-yl)-4-phenylnicotinonitrile (**2b**) in $CDCl_3$



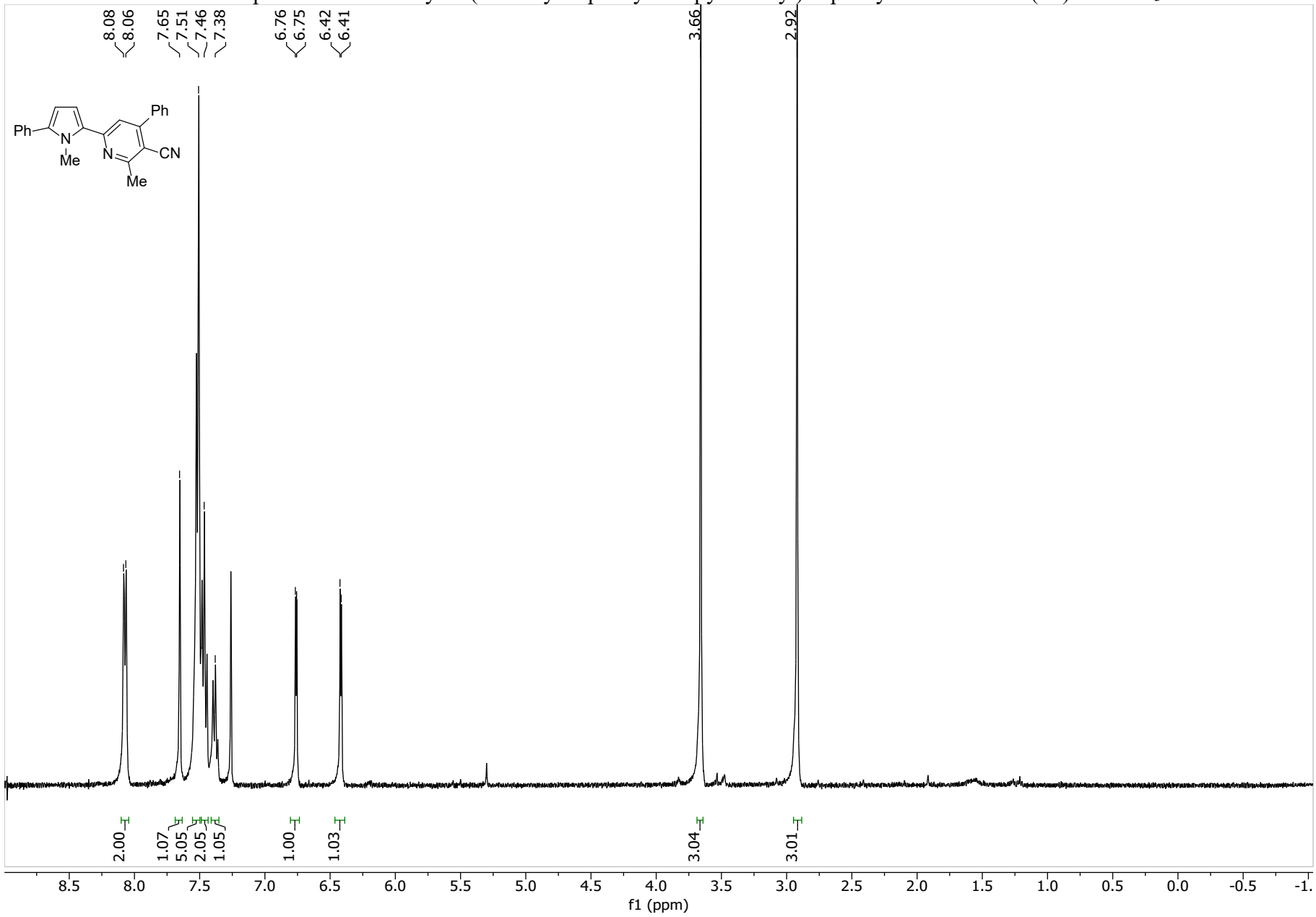
^{1}H NMR spectrum of 6-(1-benzyl-1*H*-pyrrol-2-yl)-2-methyl-4-phenylnicotinonitrile (**2c**) in $CDCl_3$



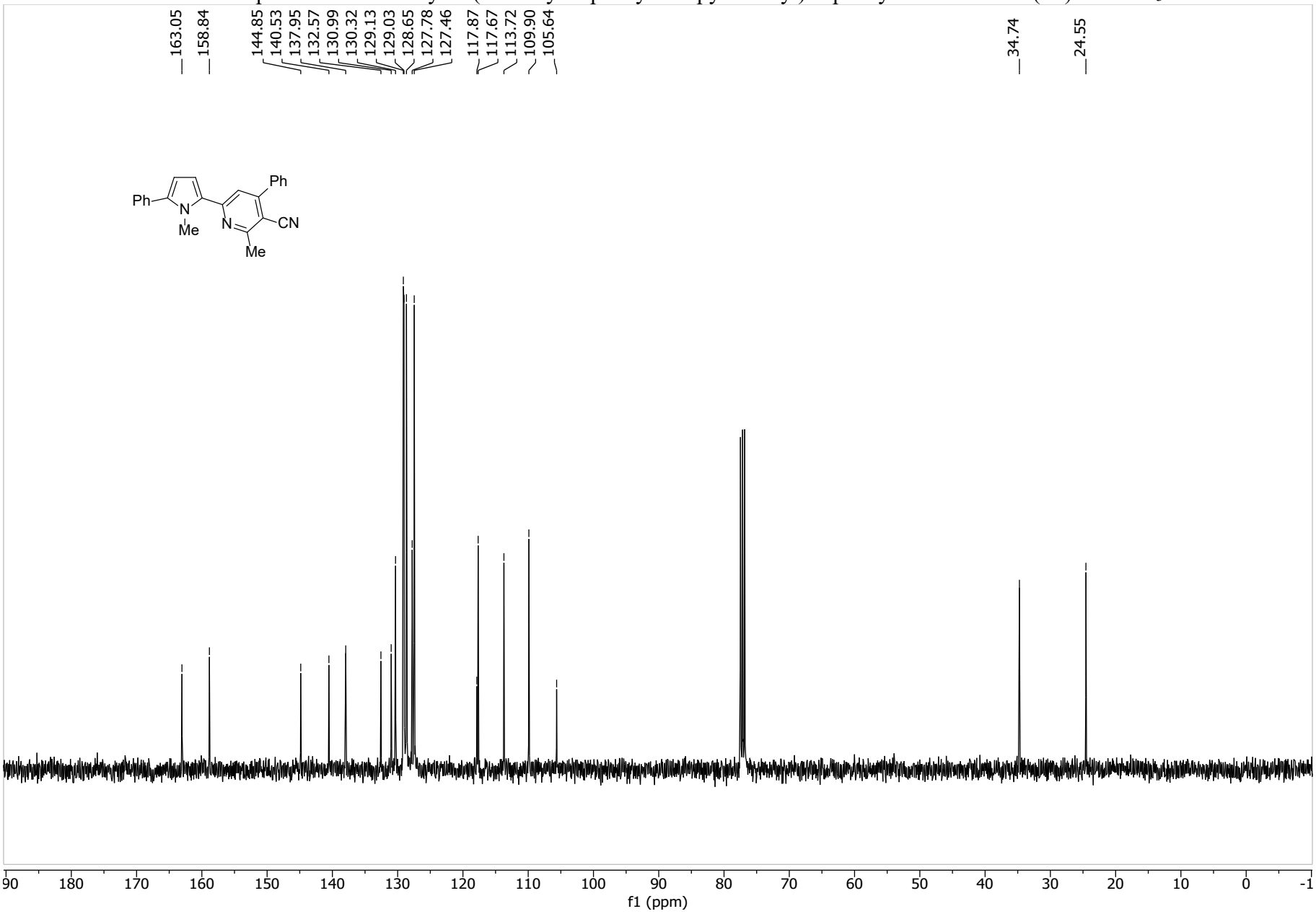
^{13}C NMR spectrum of 6-(1-benzyl-1*H*-pyrrol-2-yl)-2-methyl-4-phenylnicotinonitrile (**2c**) in $CDCl_3$



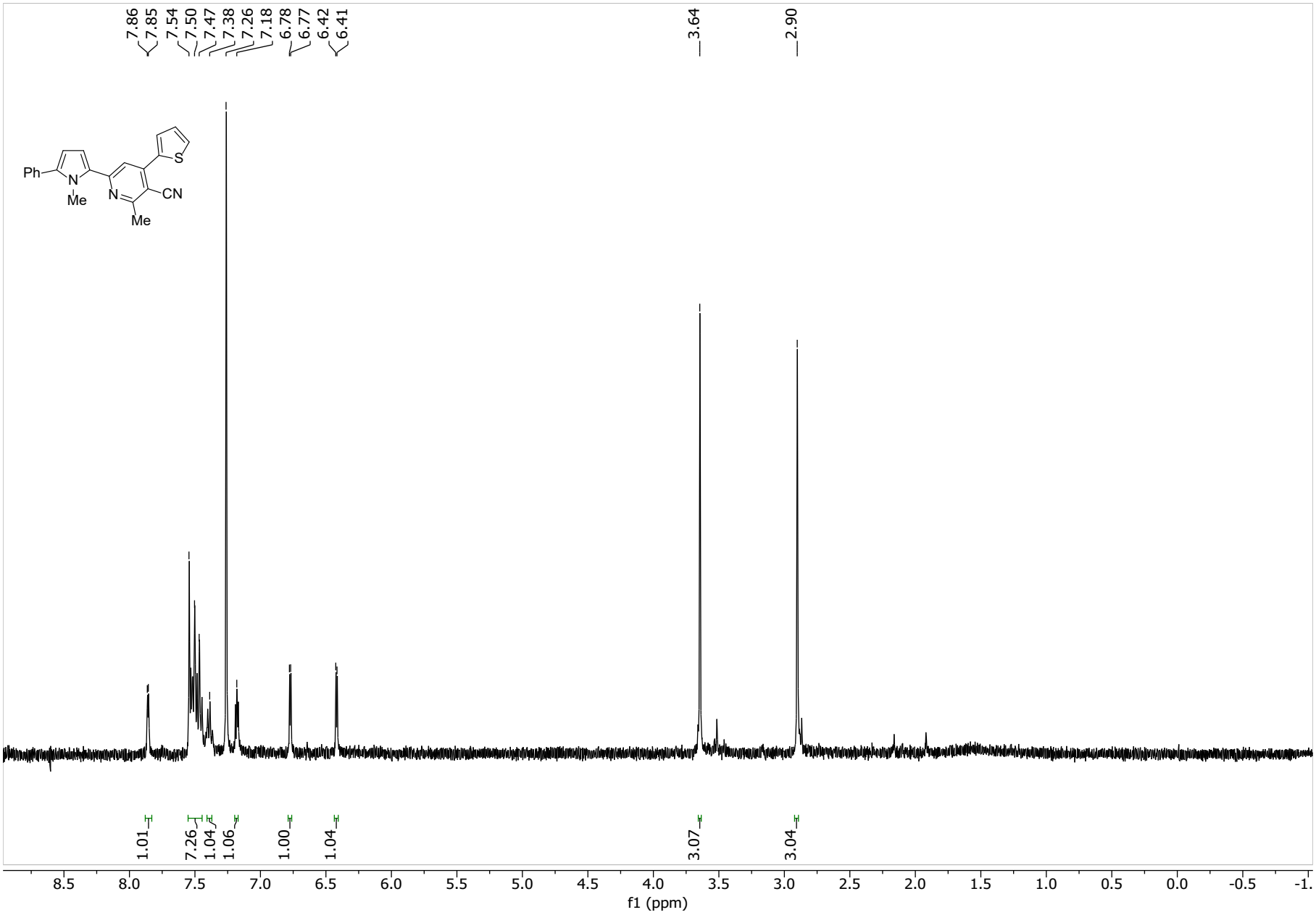
^{1}H NMR spectrum of 2-methyl-6-(1-methyl-5-phenyl-1*H*-pyrrol-2-yl)-4-phenylnicotinonitrile (**2d**) in $CDCl_3$



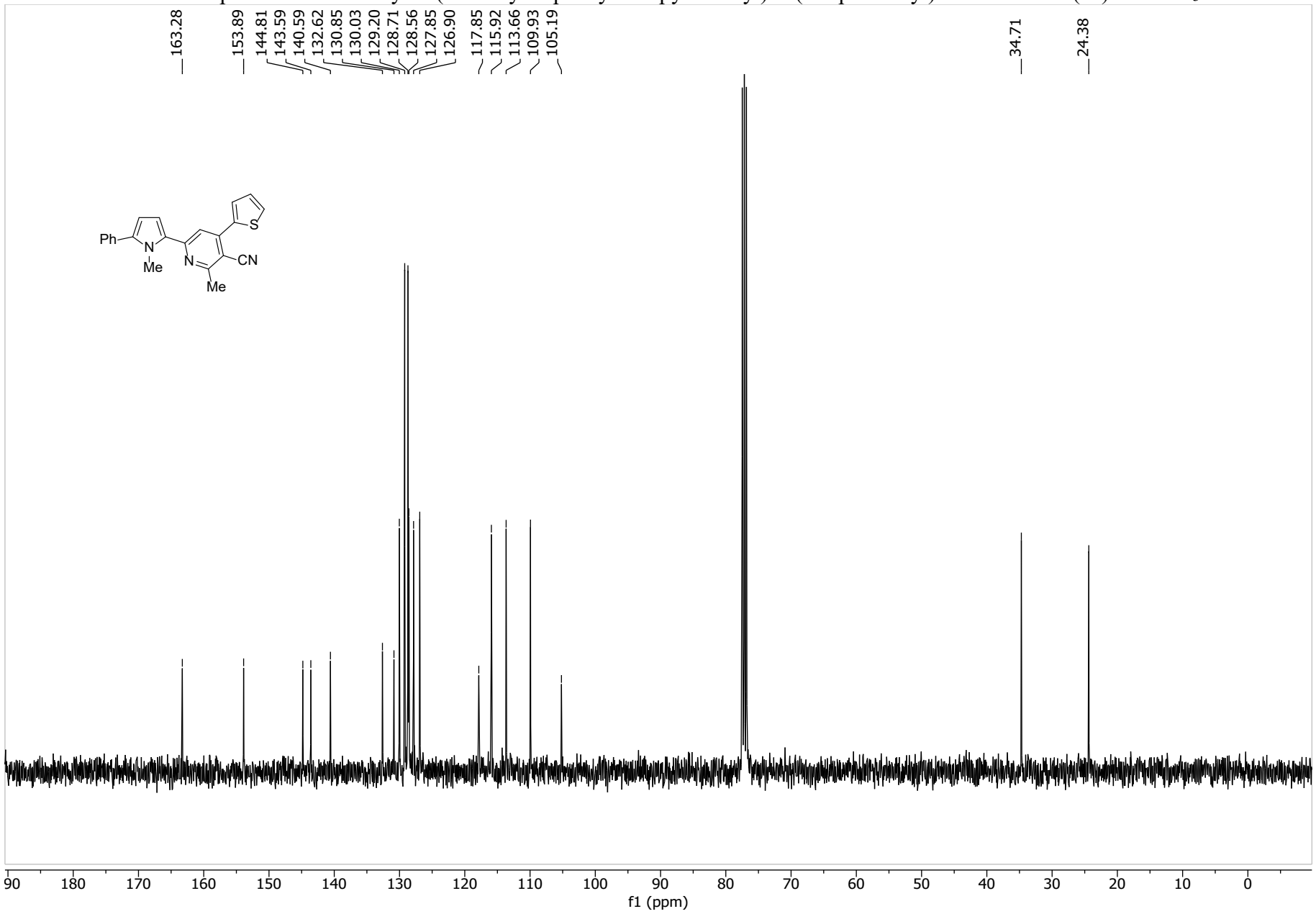
^{13}C NMR spectrum of 2-methyl-6-(1-methyl-5-phenyl-1*H*-pyrrol-2-yl)-4-phenylnicotinonitrile (**2d**) in $CDCl_3$



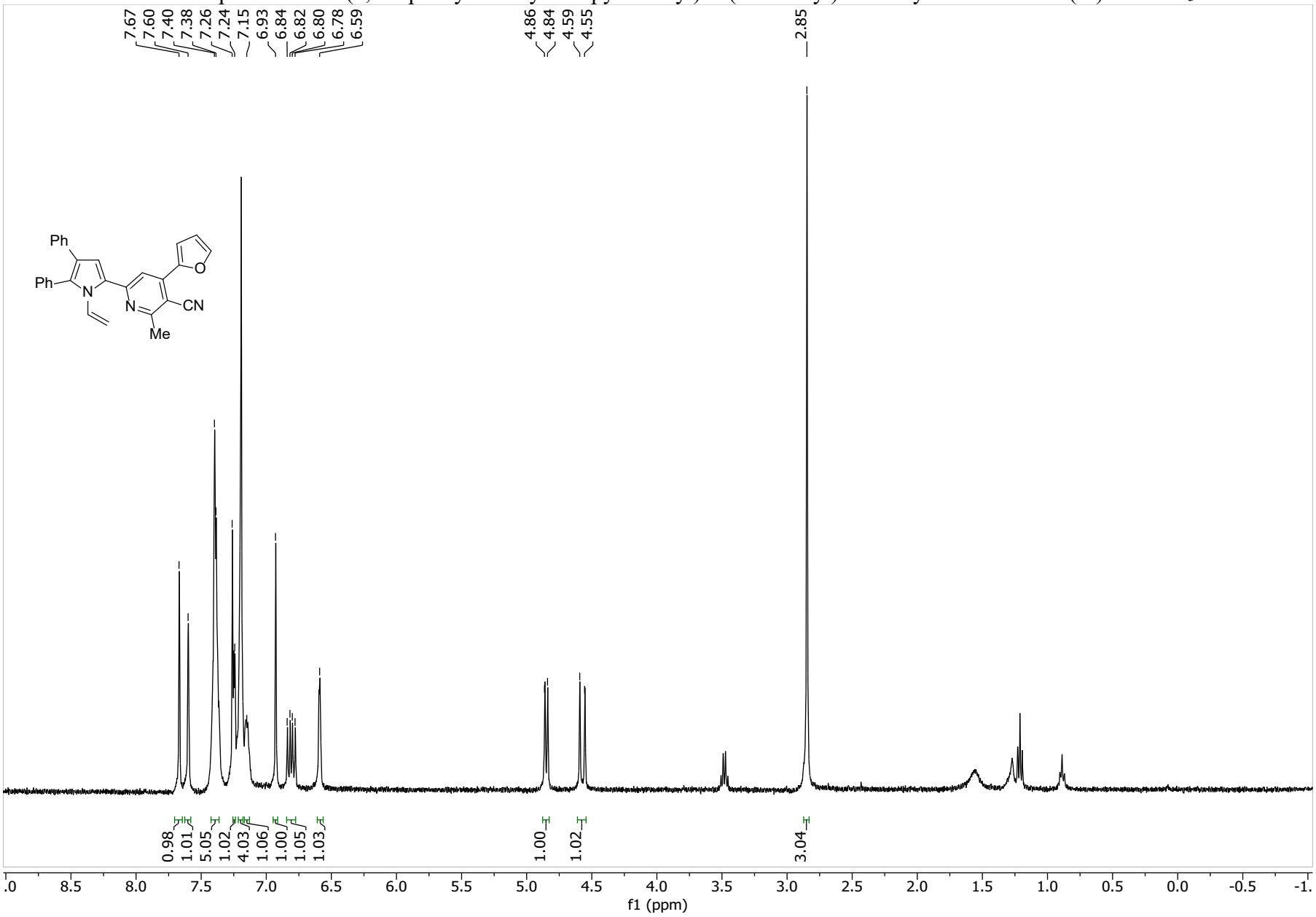
^{1}H NMR spectrum of 2-methyl-6-(1-methyl-5-phenyl-1*H*-pyrrol-2-yl)-4-(thiophen-2-yl)nicotinonitrile (**2e**) in $CDCl_3$



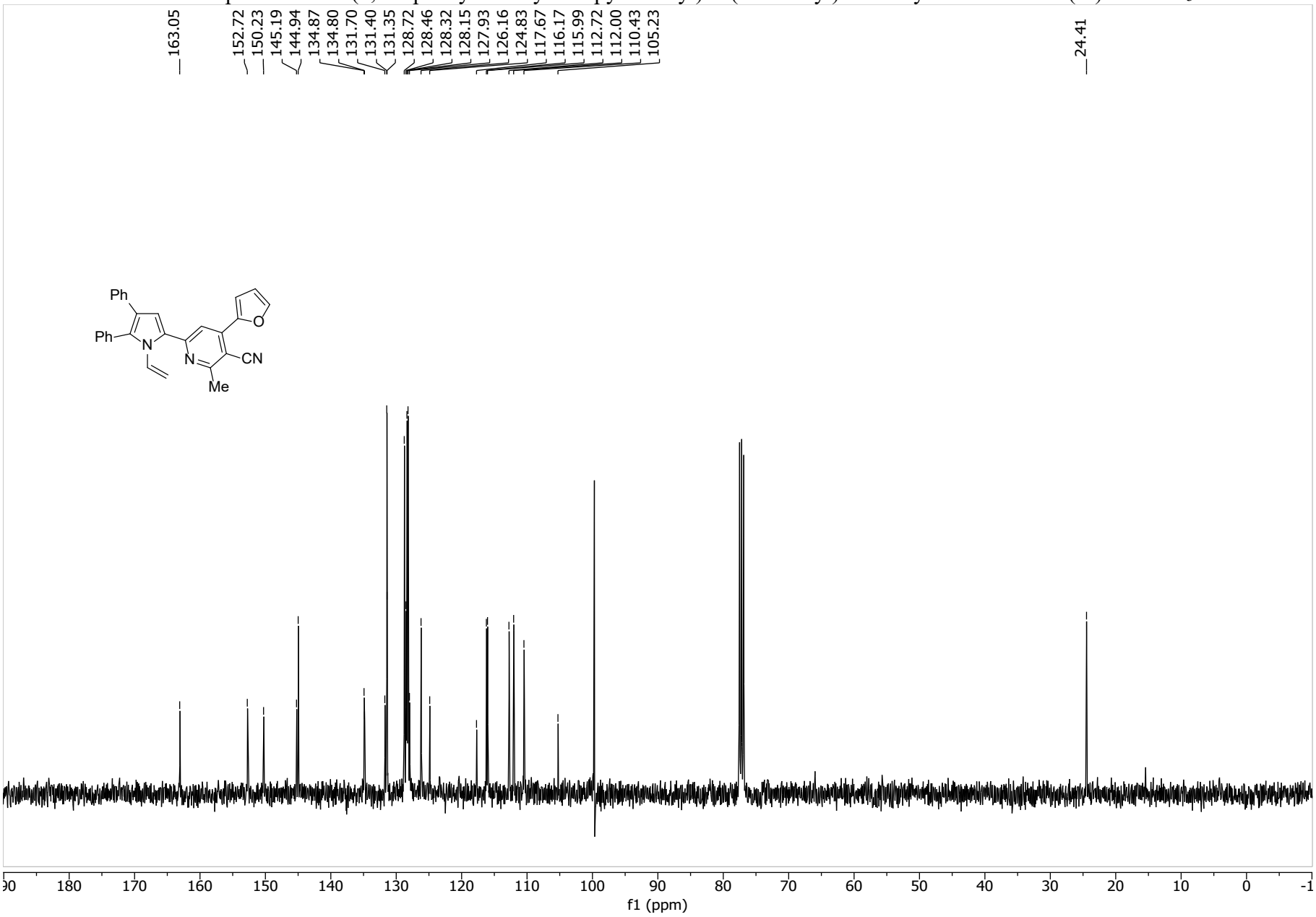
^{13}C NMR spectrum of 2-methyl-6-(1-methyl-5-phenyl-1*H*-pyrrol-2-yl)-4-(thiophen-2-yl)nicotinonitrile (**2e**) in $CDCl_3$



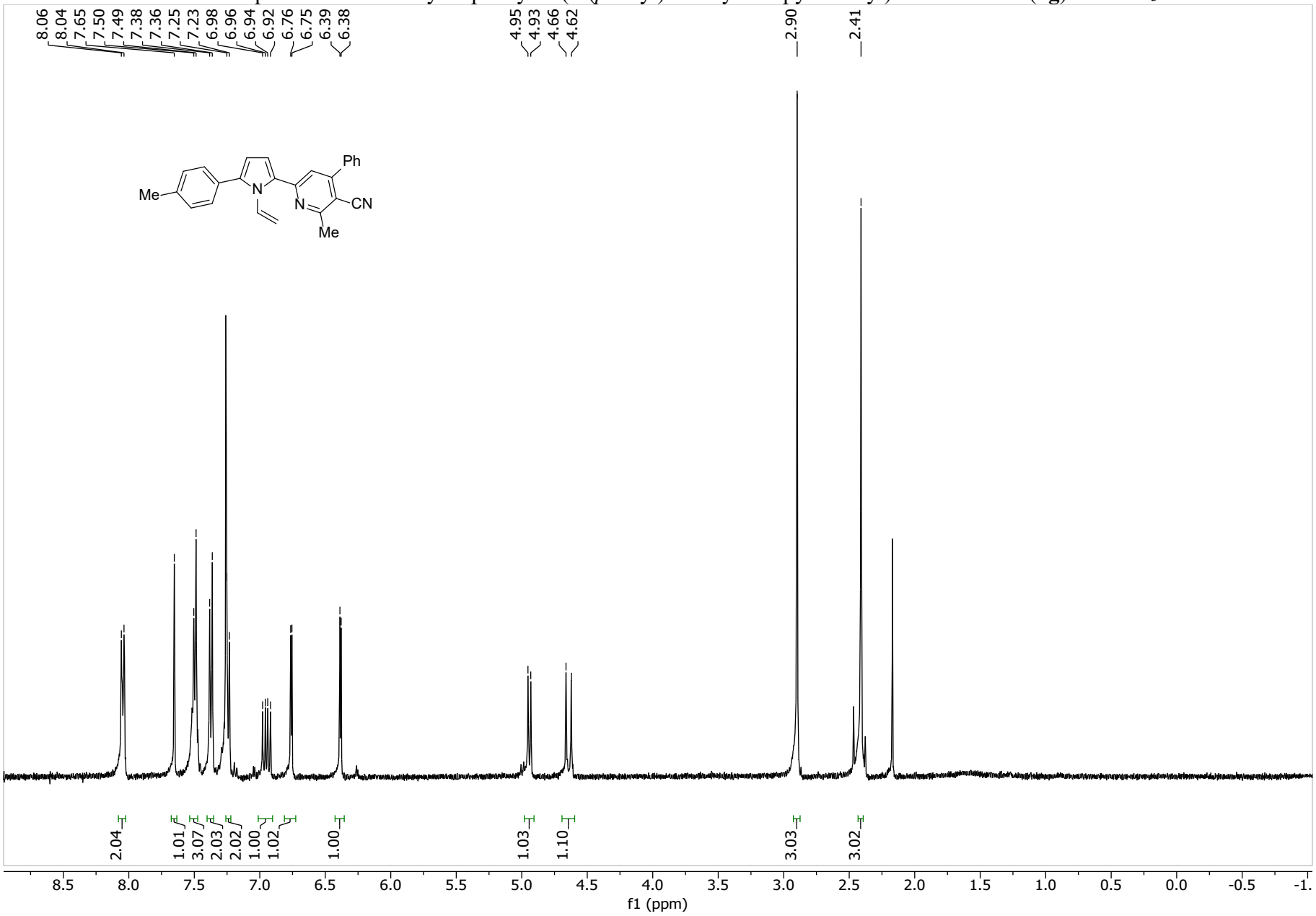
^{1}H NMR spectrum of 6-(4,5-diphenyl-1-vinyl-1*H*-pyrrol-2-yl)-4-(furan-2-yl)-2-methylnicotinonitrile (**2f**) in $CDCl_3$



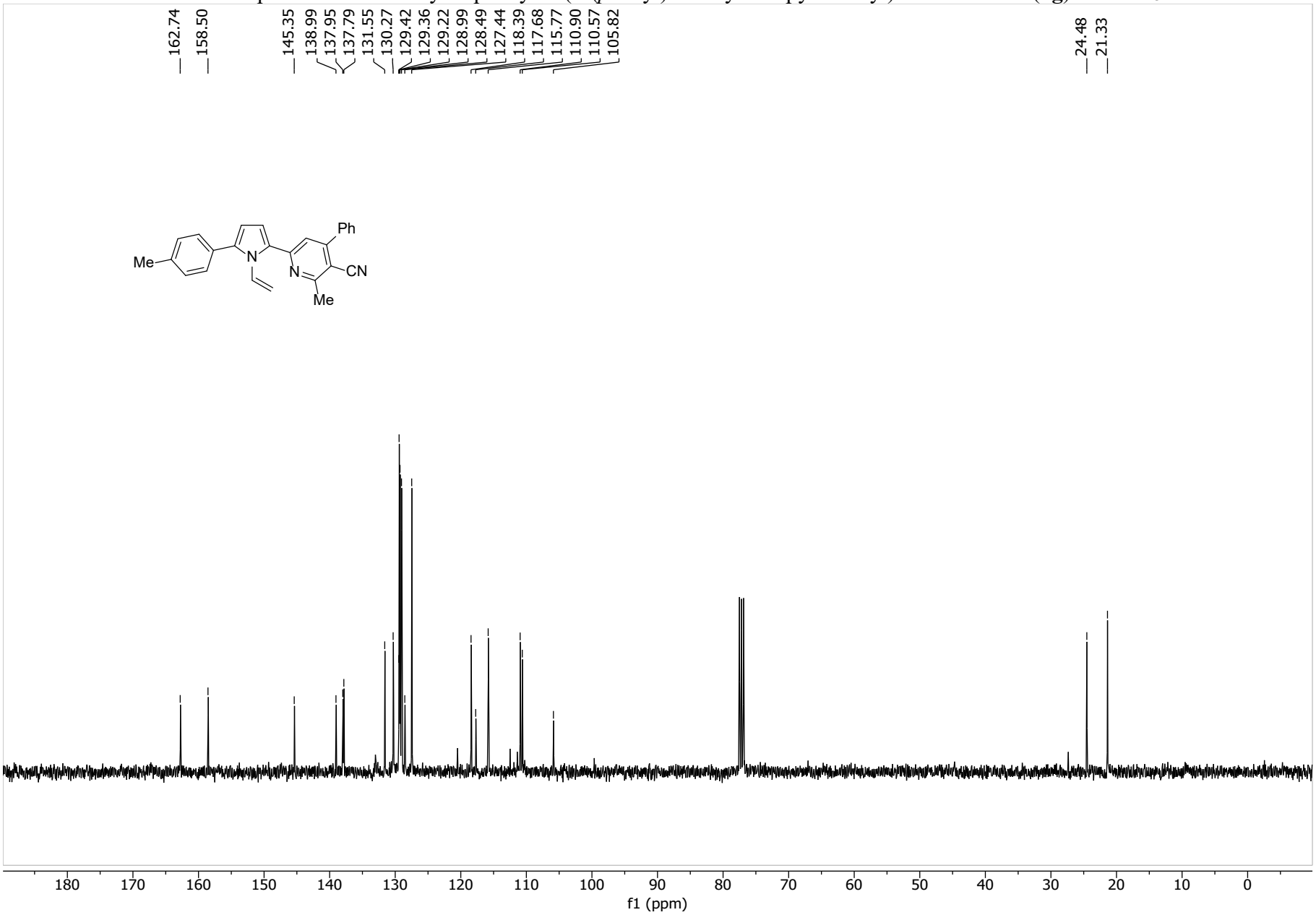
^{13}C NMR spectrum of 6-(4,5-diphenyl-1-vinyl-1*H*-pyrrol-2-yl)-4-(furan-2-yl)-2-methylnicotinonitrile (**2f**) in $CDCl_3$



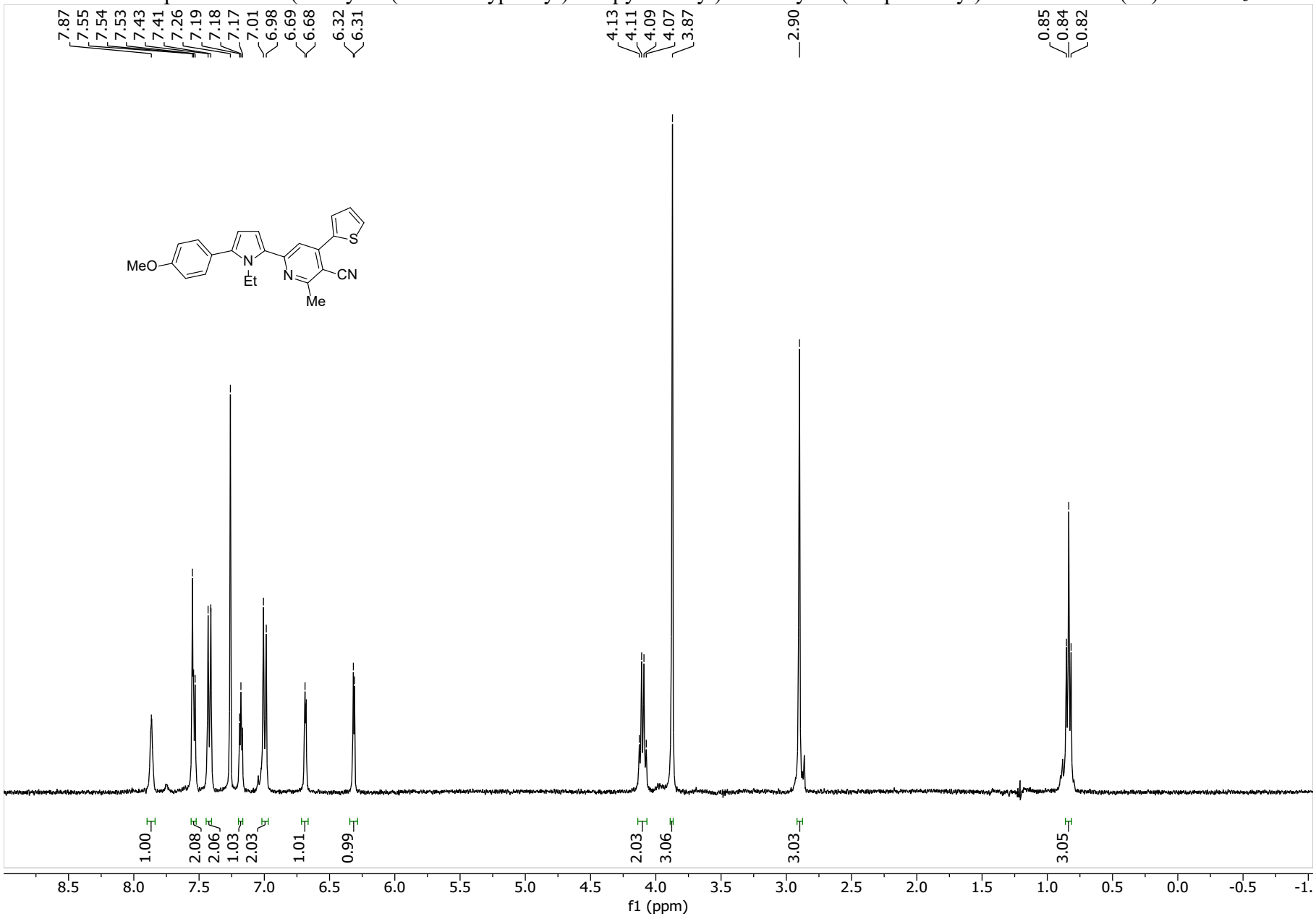
^{1}H NMR spectrum of 2-methyl-4-phenyl-6-(5-(*p*-tolyl)-1-vinyl-1*H*-pyrrol-2-yl)nicotinonitrile (**2g**) in $CDCl_3$



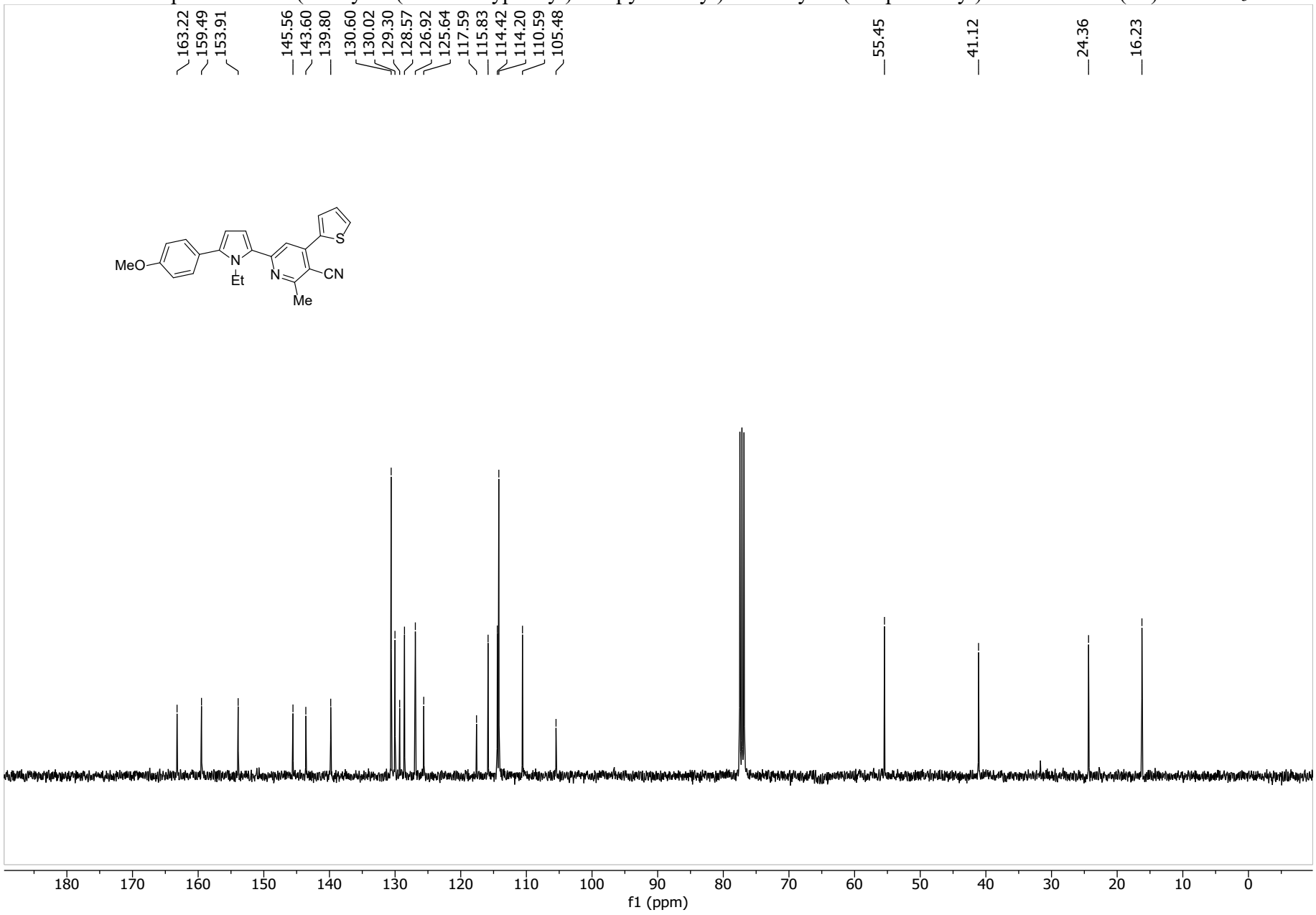
^{13}C NMR spectrum of 2-methyl-4-phenyl-6-(5-(*p*-tolyl)-1-vinyl-1*H*-pyrrol-2-yl)nicotinonitrile (**2g**) in $CDCl_3$



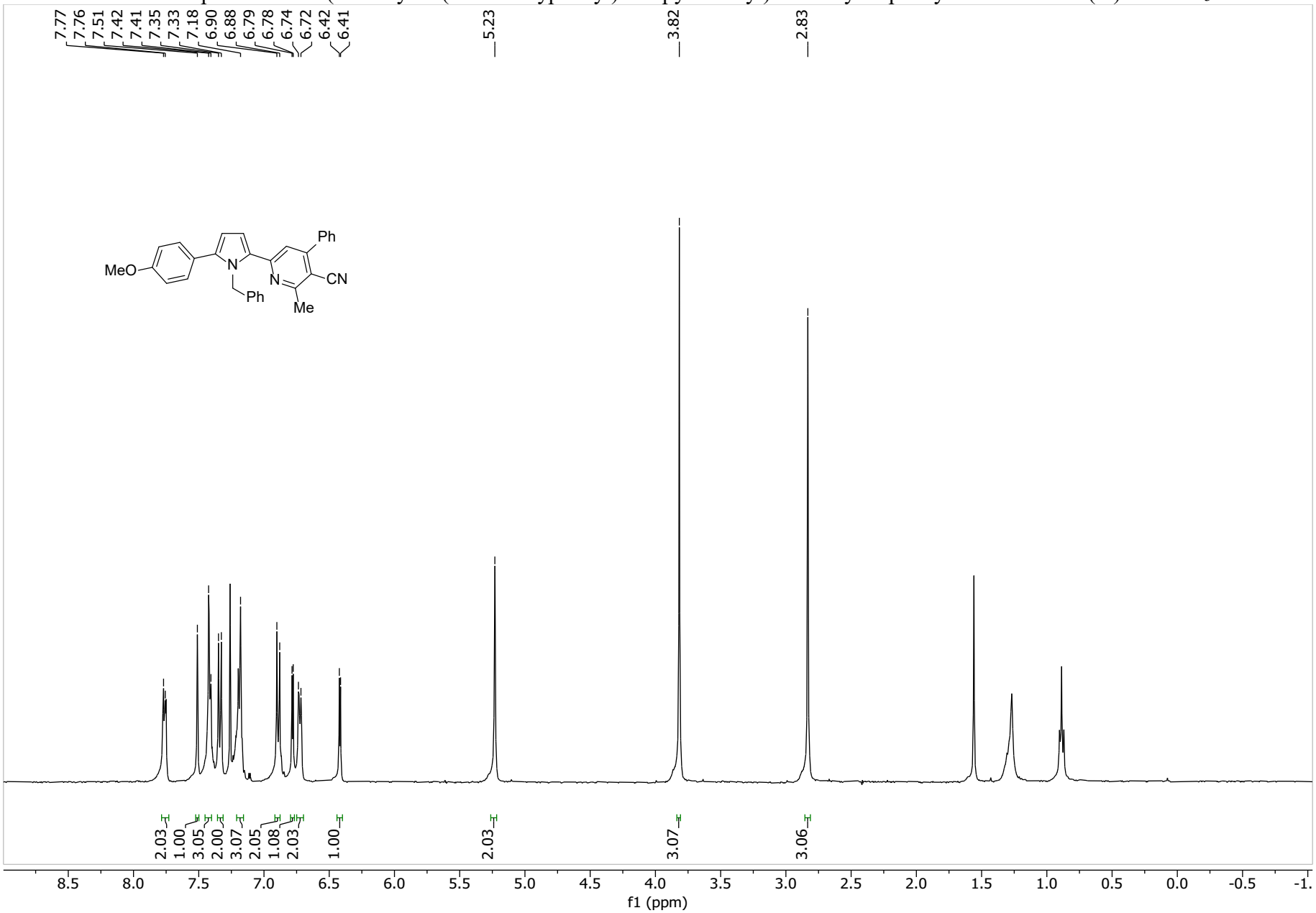
^{1}H NMR spectrum of 6-(1-ethyl-5-(4-methoxyphenyl)-1*H*-pyrrol-2-yl)-2-methyl-4-(thiophen-2-yl)nicotinonitrile (**2h**) in $CDCl_3$



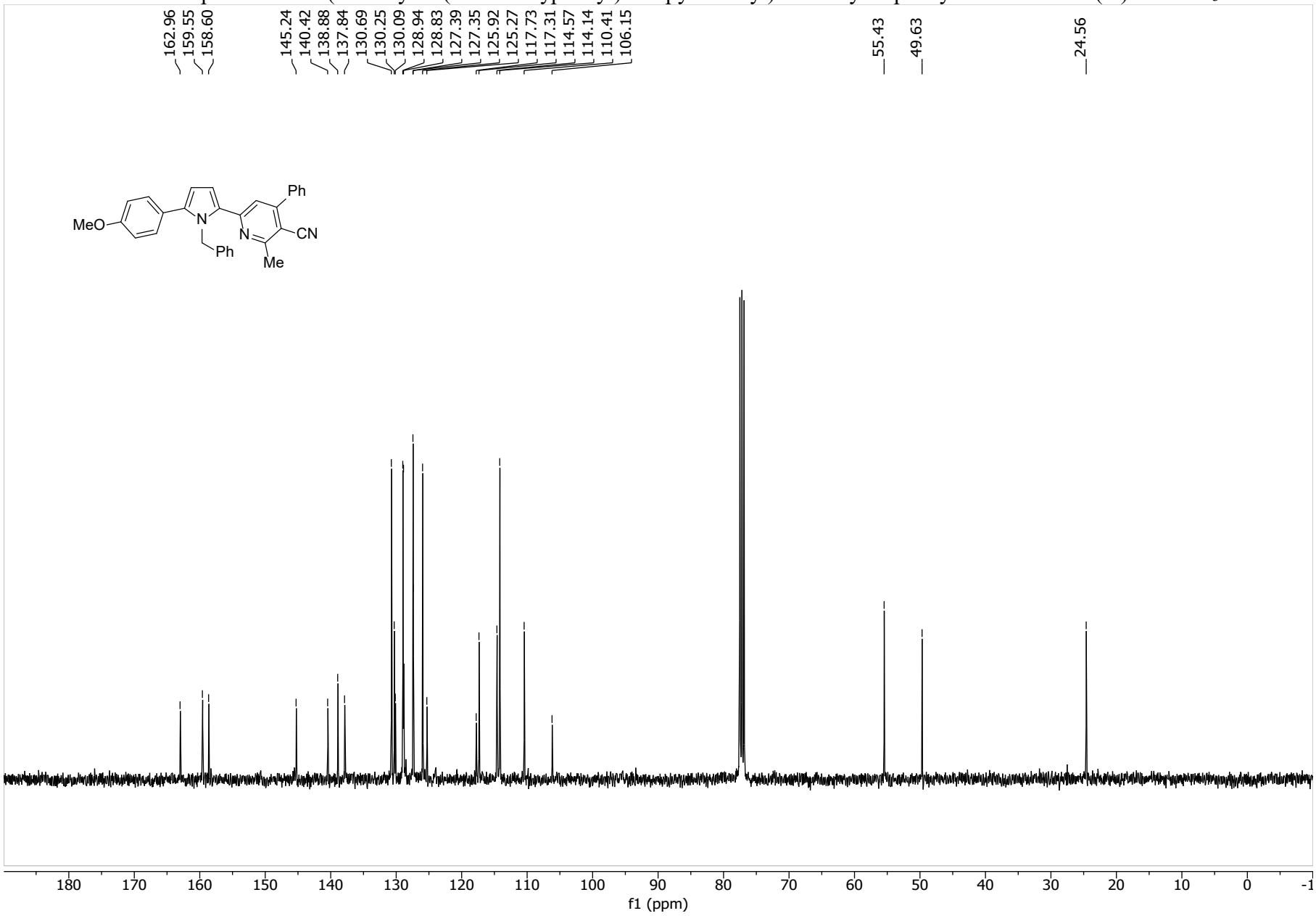
^{13}C NMR spectrum of 6-(1-ethyl-5-(4-methoxyphenyl)-1*H*-pyrrol-2-yl)-2-methyl-4-(thiophen-2-yl)nicotinonitrile (**2h**) in $CDCl_3$



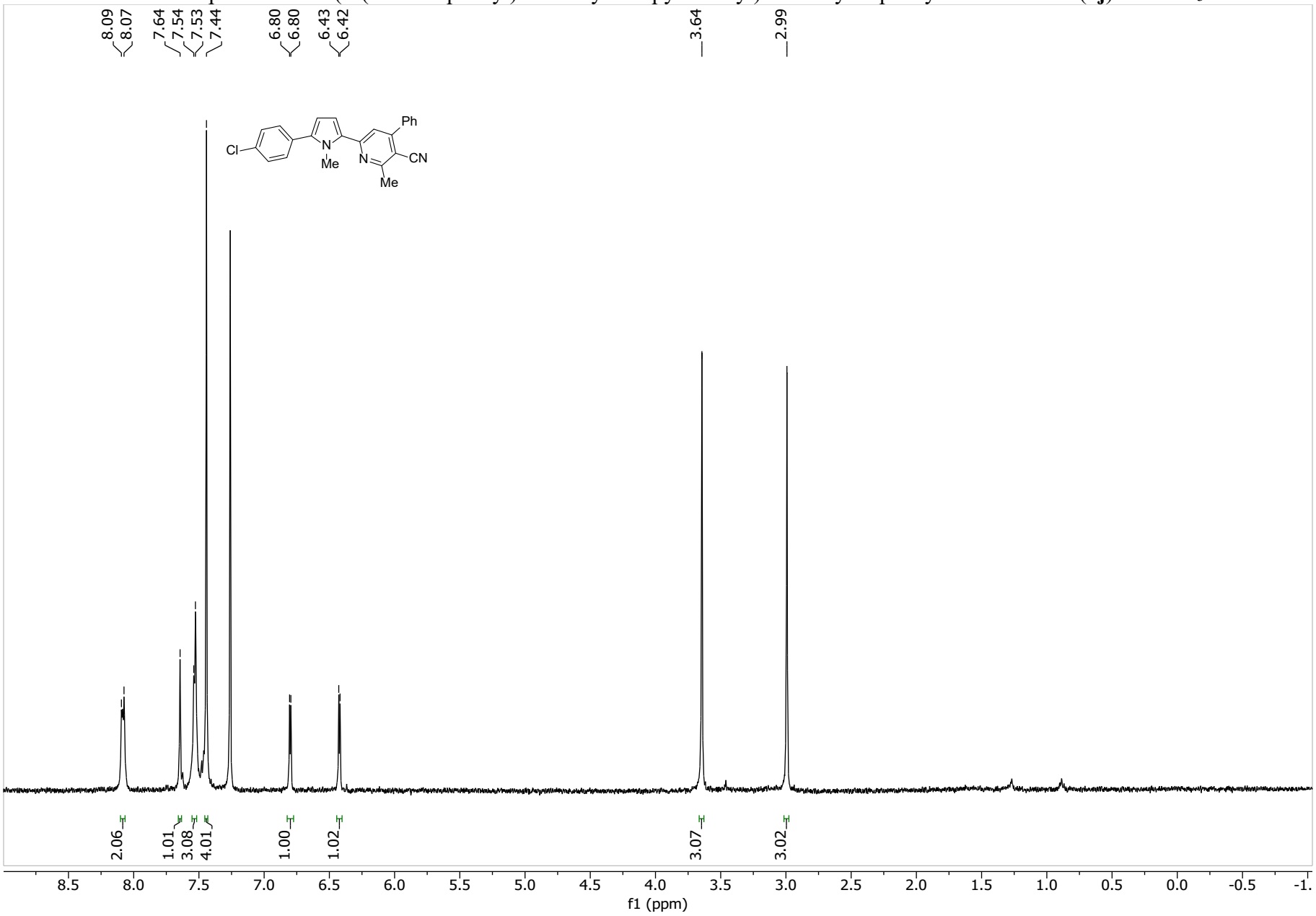
^{1}H NMR spectrum of 6-(1-benzyl-5-(4-methoxyphenyl)-1*H*-pyrrol-2-yl)-2-methyl-4-phenylnicotinonitrile (**2i**) in $CDCl_3$



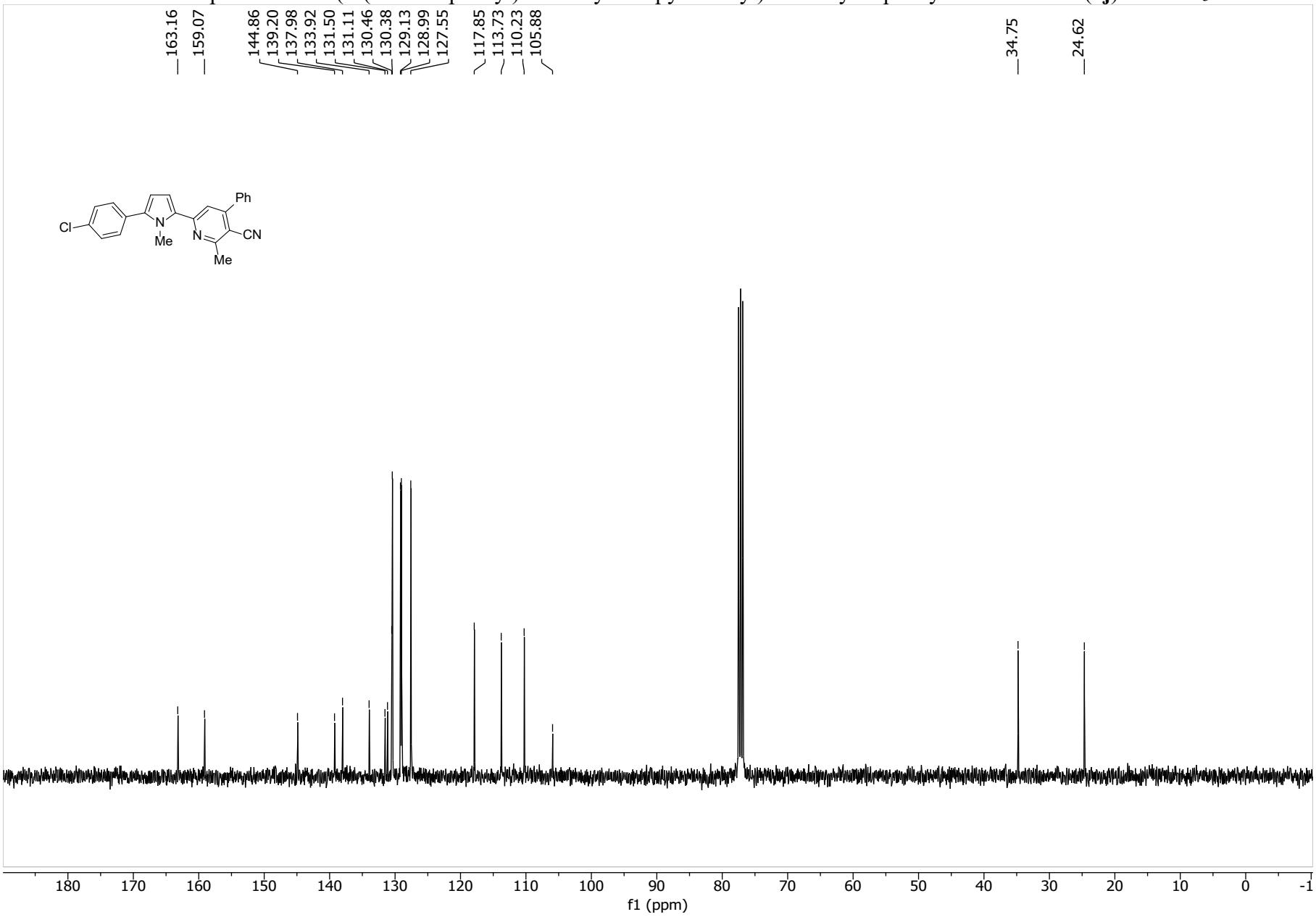
^{13}C NMR spectrum of 6-(1-benzyl-5-(4-methoxyphenyl)-1*H*-pyrrol-2-yl)-2-methyl-4-phenylnicotinonitrile (**2i**) in $CDCl_3$



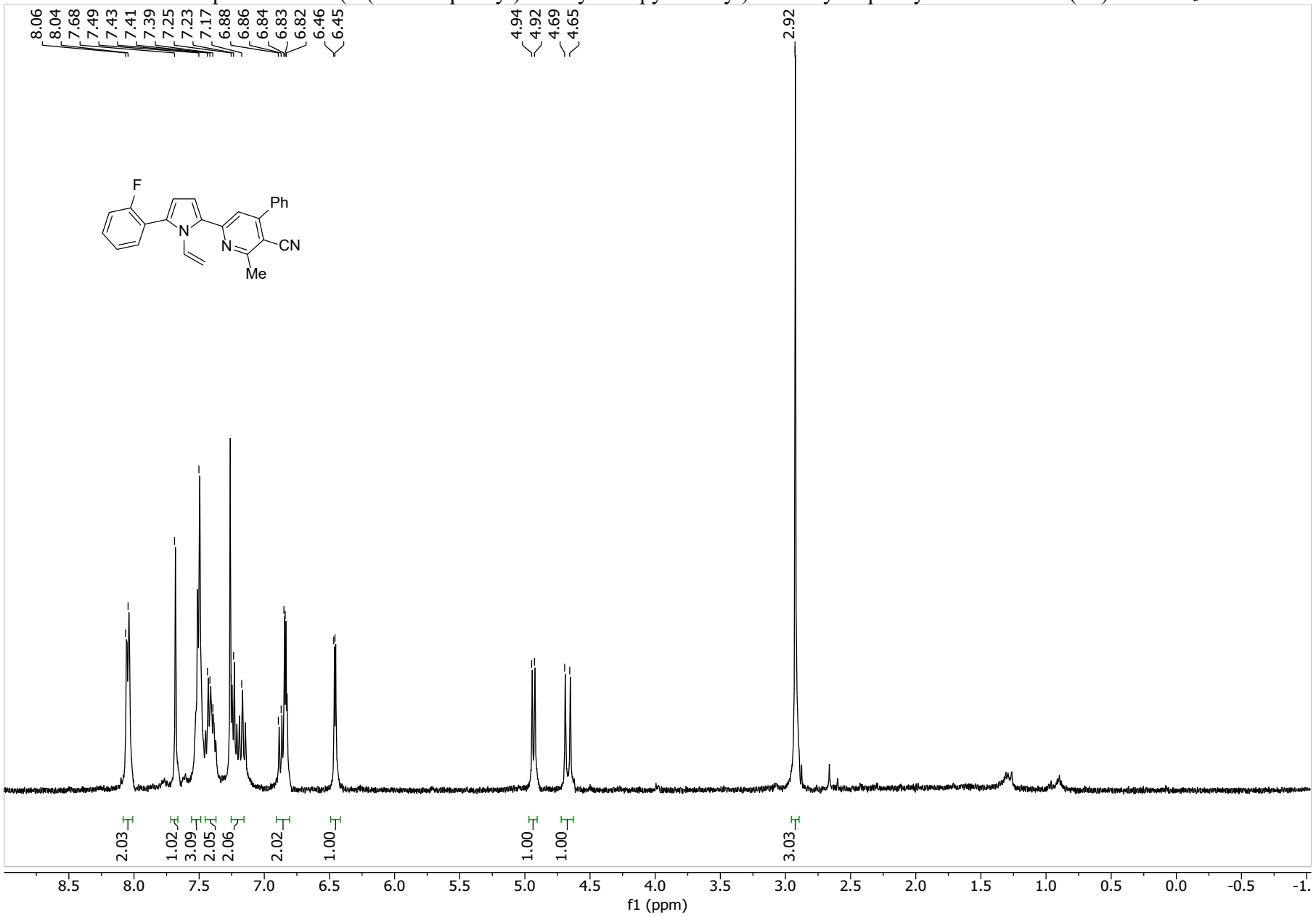
^{1}H NMR spectrum of 6-(5-(4-chlorophenyl)-1-methyl-1*H*-pyrrol-2-yl)-2-methyl-4-phenylnicotinonitrile (**2j**) in $CDCl_3$



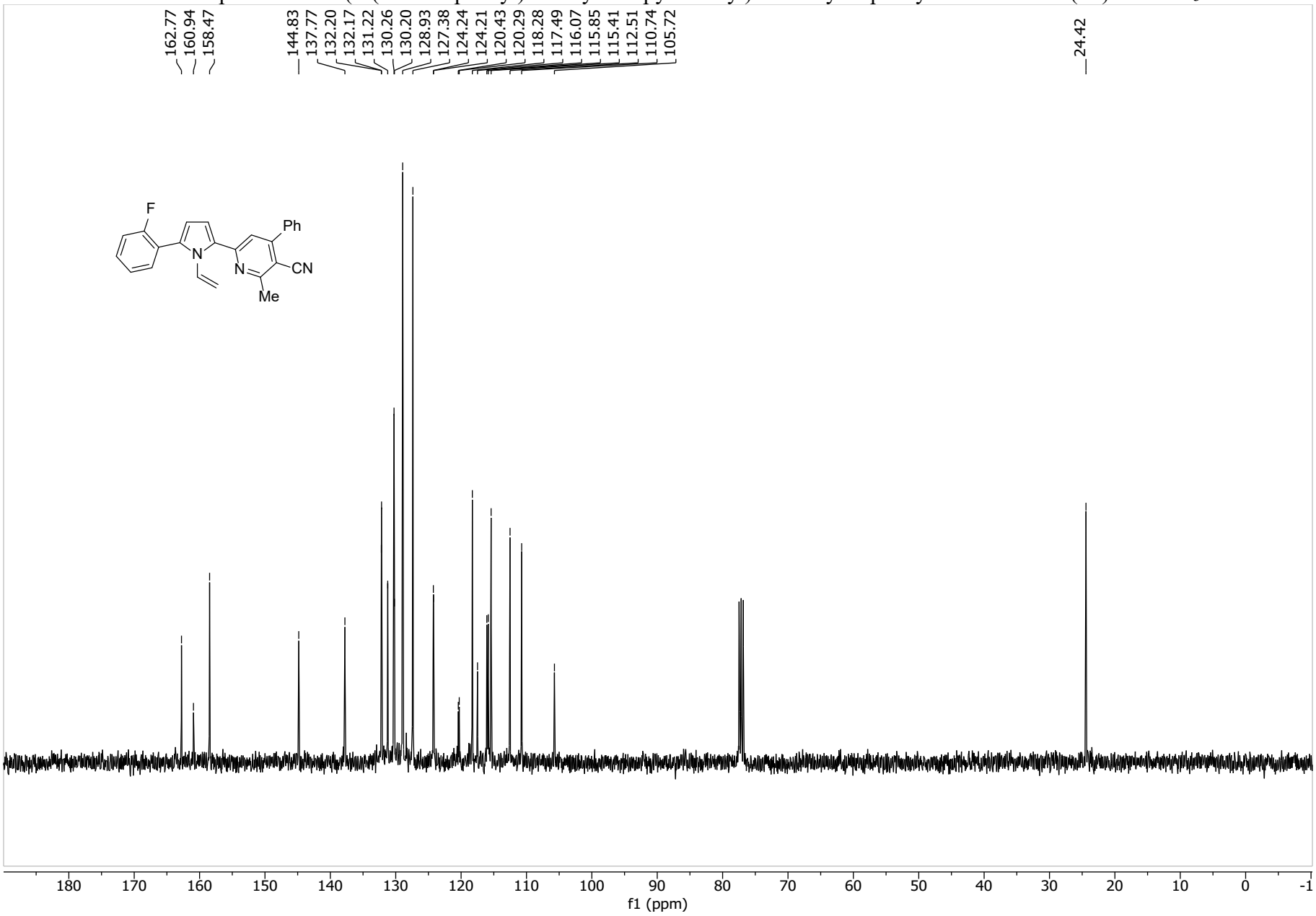
^{13}C NMR spectrum of 6-(5-(4-chlorophenyl)-1-methyl-1*H*-pyrrol-2-yl)-2-methyl-4-phenylnicotinonitrile (**2j**) in $CDCl_3$



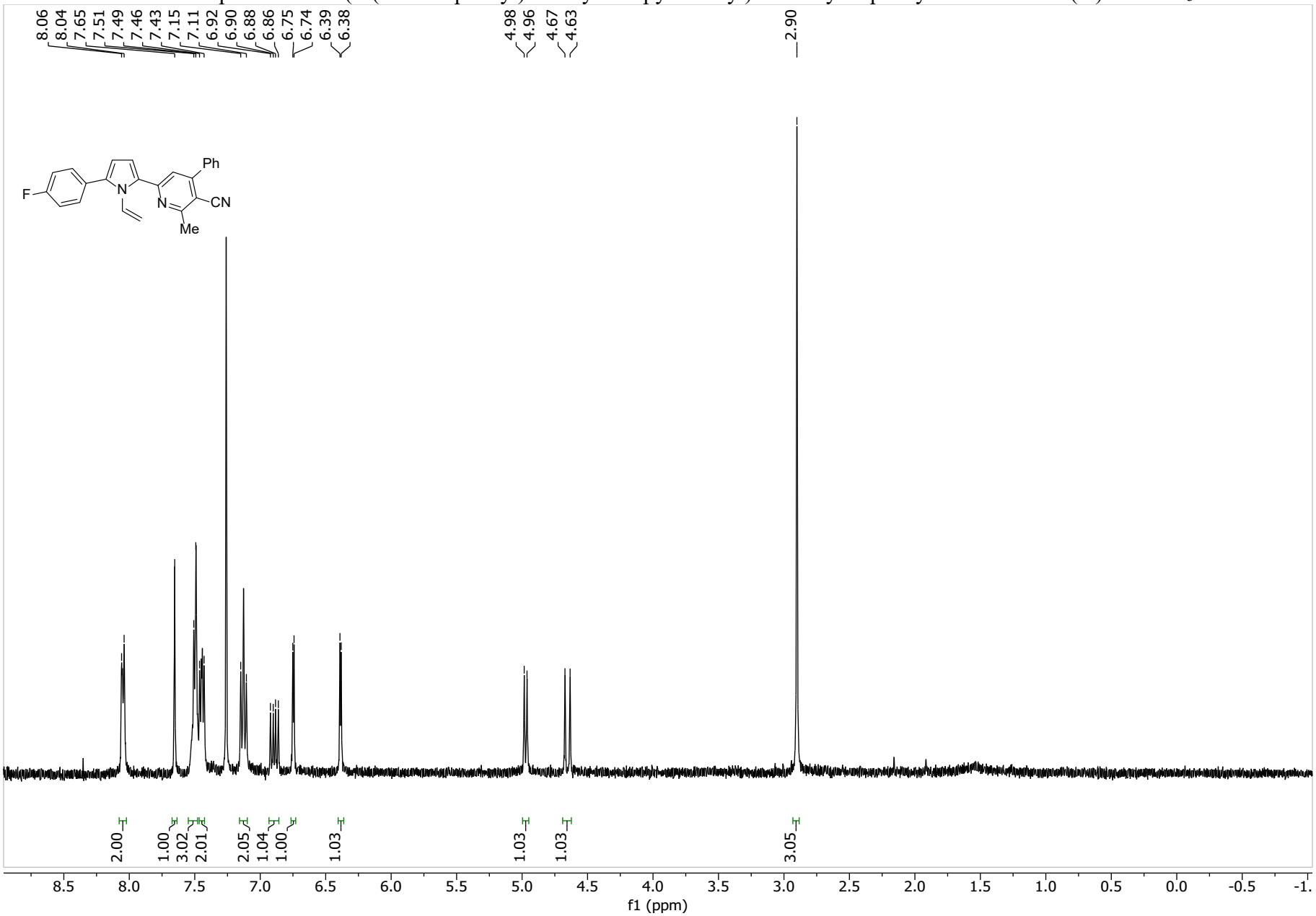
^{1}H NMR spectrum of 6-(5-(2-fluorophenyl)-1-vinyl-1*H*-pyrrol-2-yl)-2-methyl-4-phenylnicotinonitrile (**2k**) in $CDCl_3$



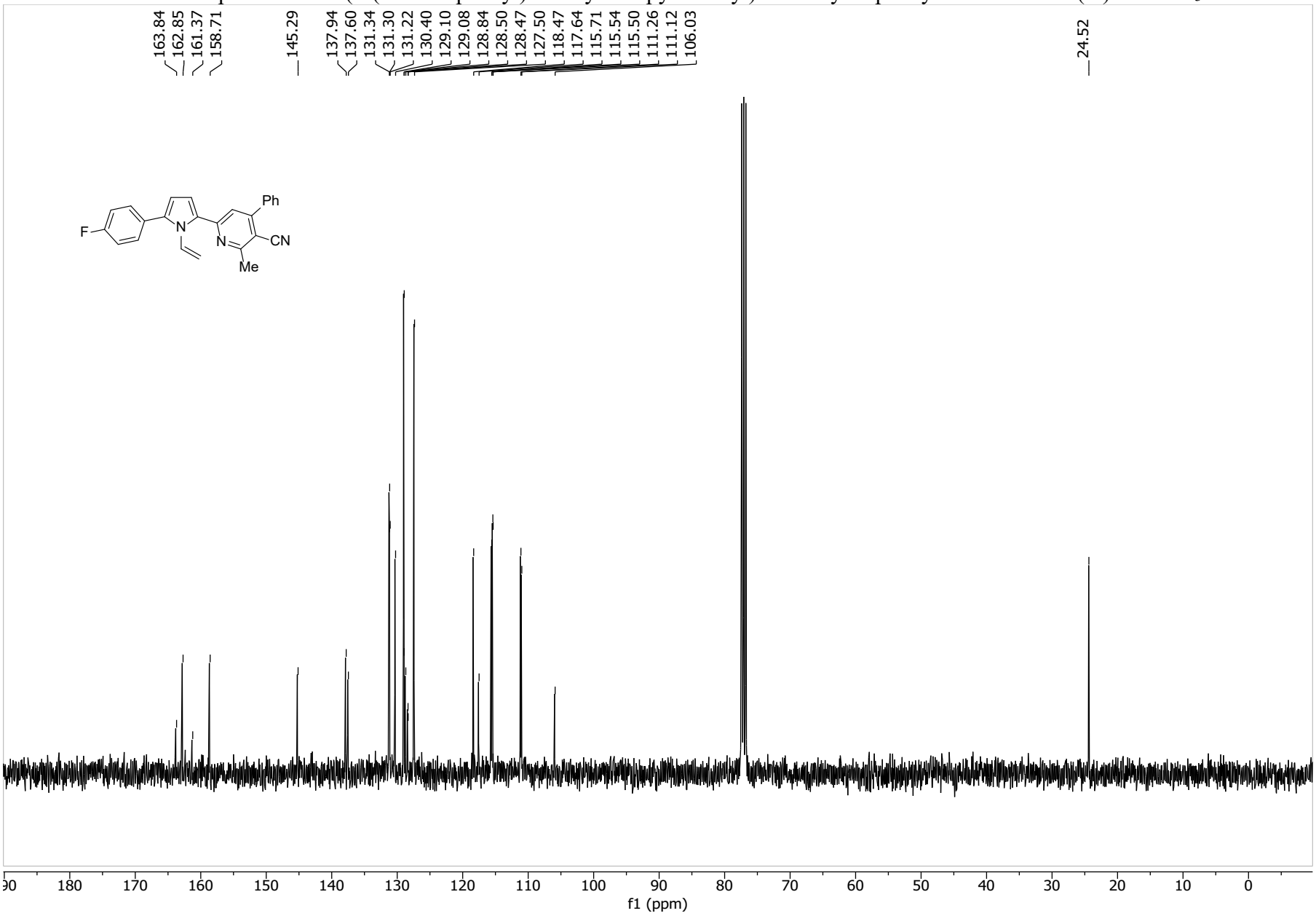
^{13}C NMR spectrum of 6-(5-(2-fluorophenyl)-1-vinyl-1*H*-pyrrol-2-yl)-2-methyl-4-phenylnicotinonitrile (**2k**) in $CDCl_3$



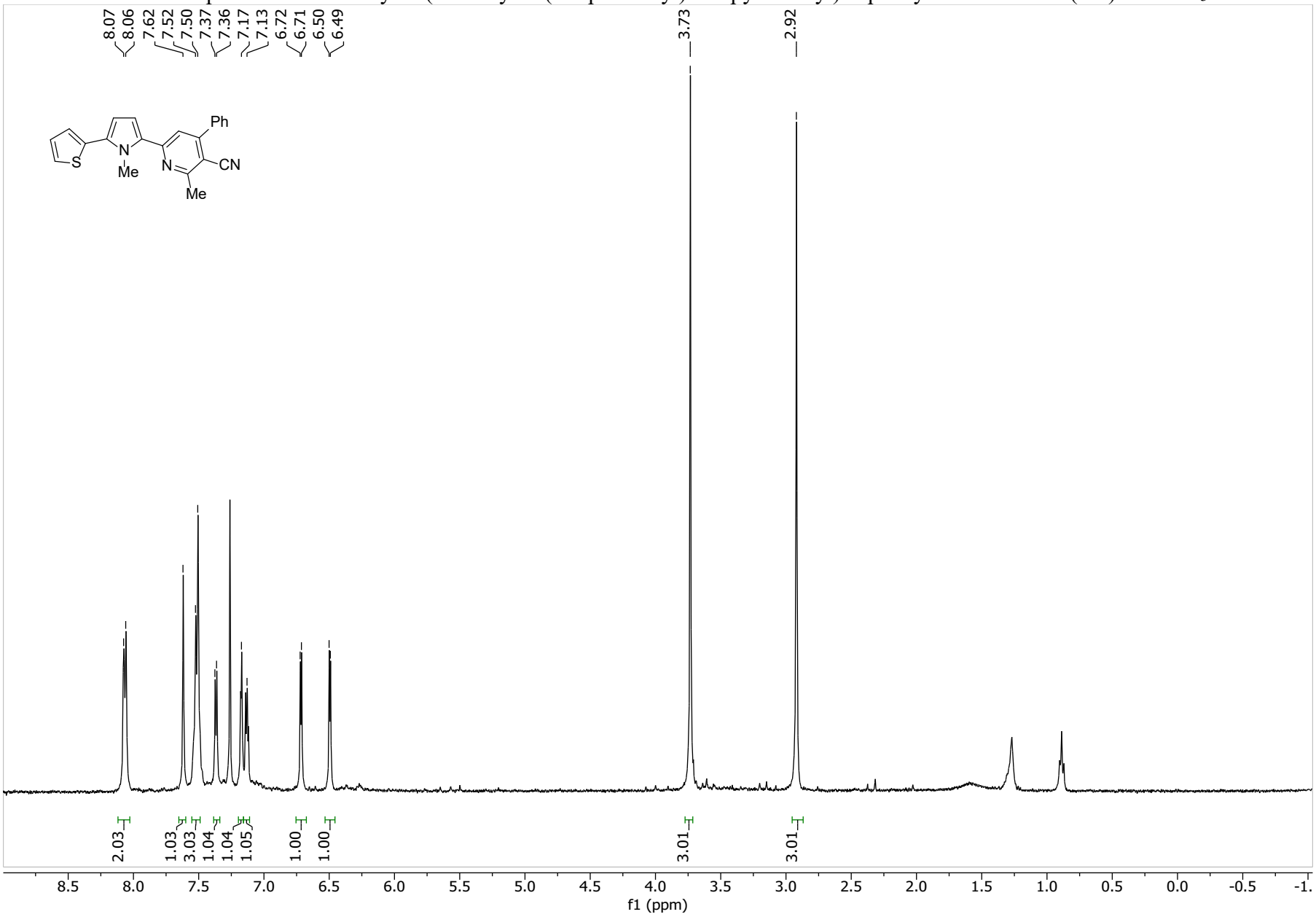
^{1}H NMR spectrum of 6-(5-(4-fluorophenyl)-1-vinyl-1*H*-pyrrol-2-yl)-2-methyl-4-phenylnicotinonitrile (**2l**) in $CDCl_3$



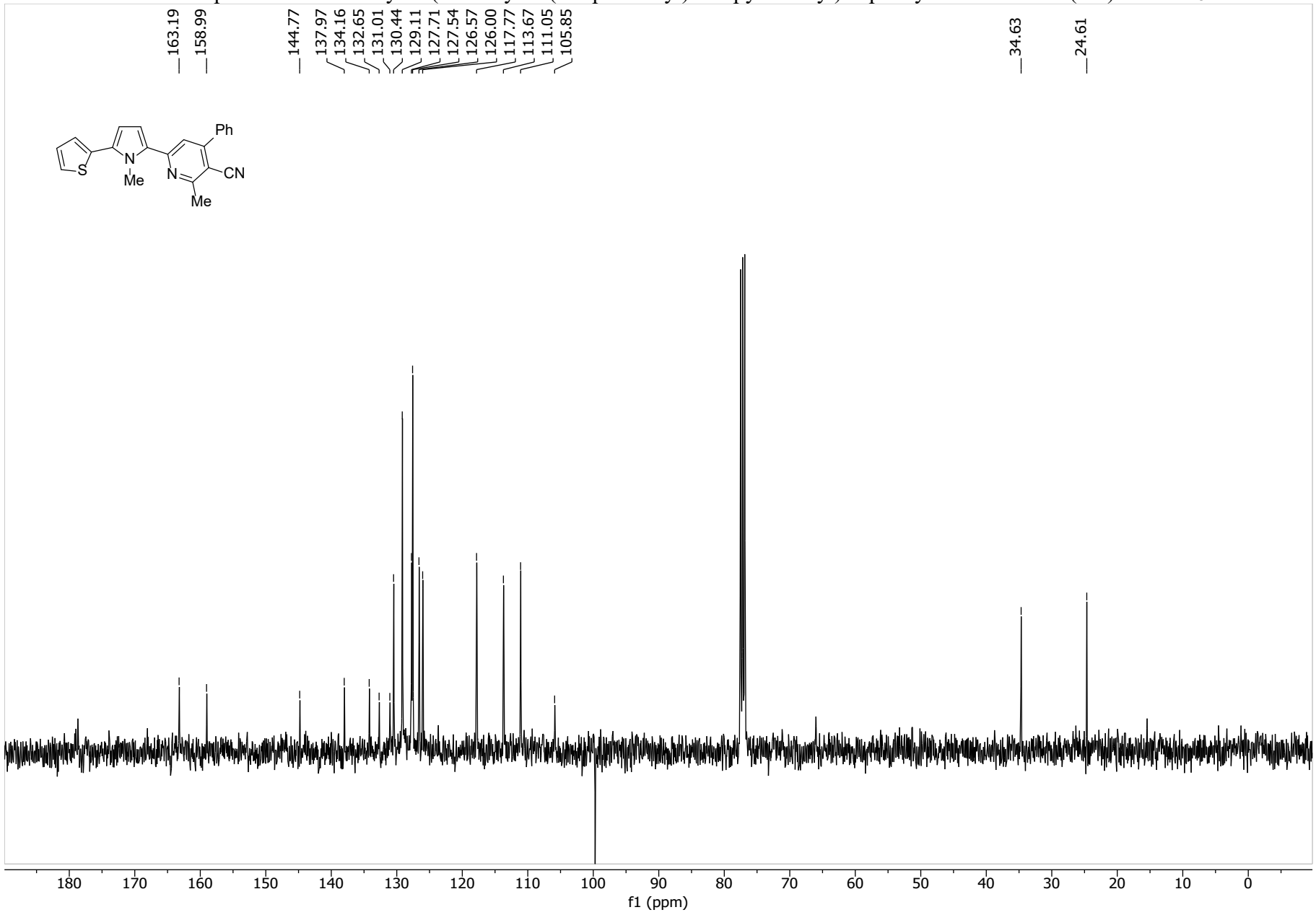
^{13}C NMR spectrum of 6-(5-(4-fluorophenyl)-1-vinyl-1*H*-pyrrol-2-yl)-2-methyl-4-phenylnicotinonitrile (**2l**) in $CDCl_3$



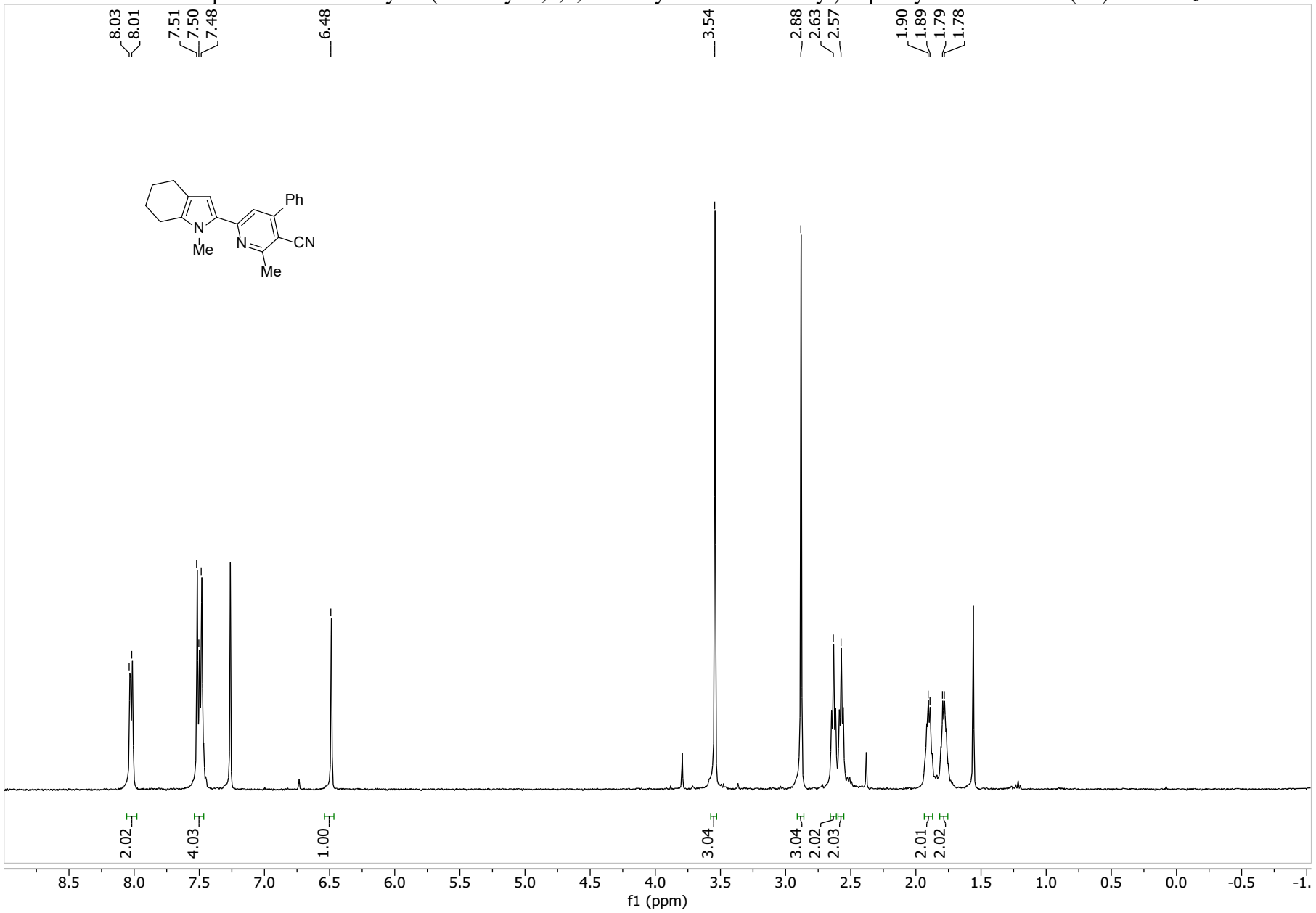
^{1}H NMR spectrum of 2-methyl-6-(1-methyl-5-(thiophen-2-yl)-*1H*-pyrrol-2-yl)-4-phenylnicotinonitrile (**2m**) in $CDCl_3$



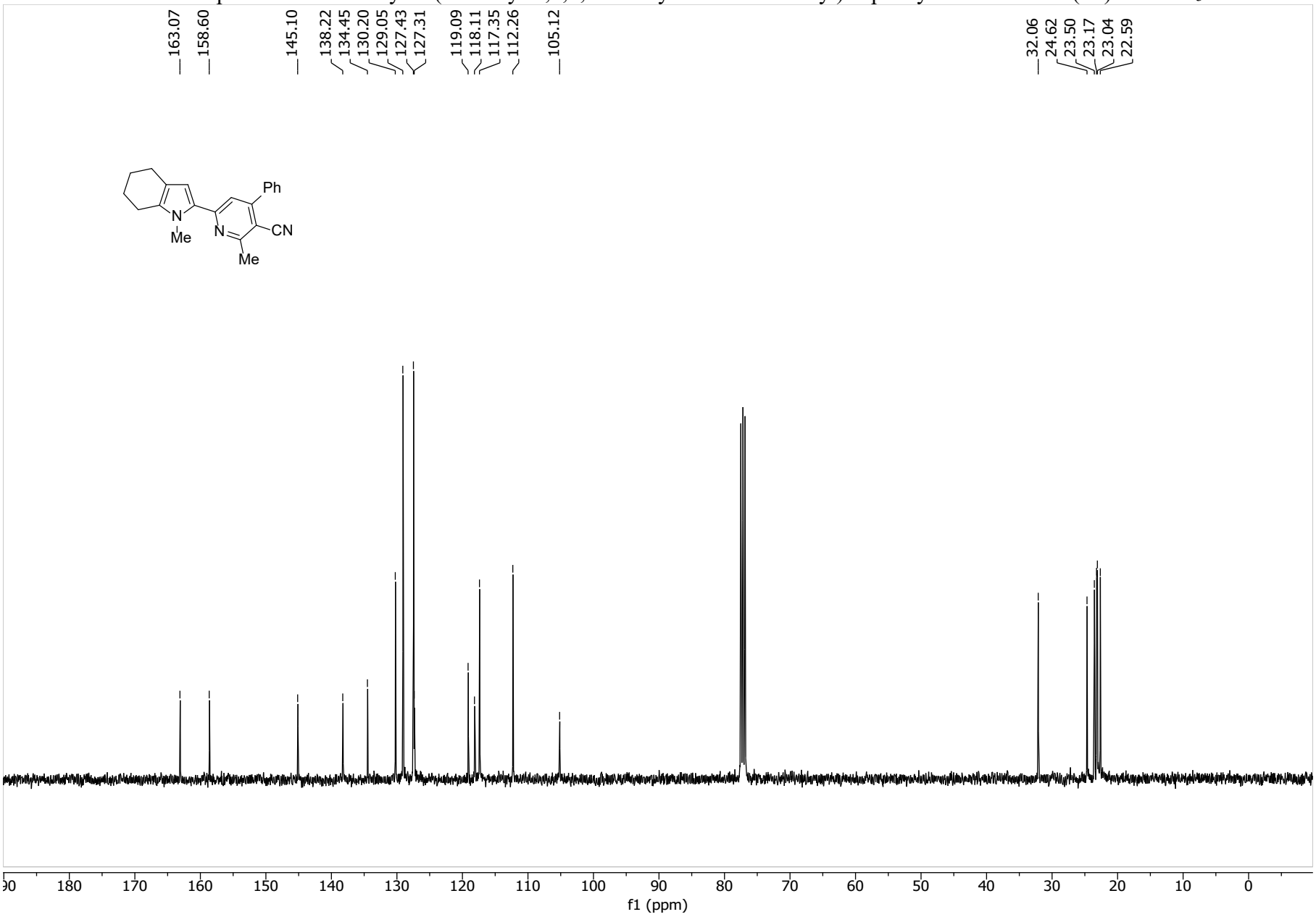
^{13}C NMR spectrum of 2-methyl-6-(1-methyl-5-(thiophen-2-yl)-*1H*-pyrrol-2-yl)-4-phenylnicotinonitrile (**2m**) in $CDCl_3$



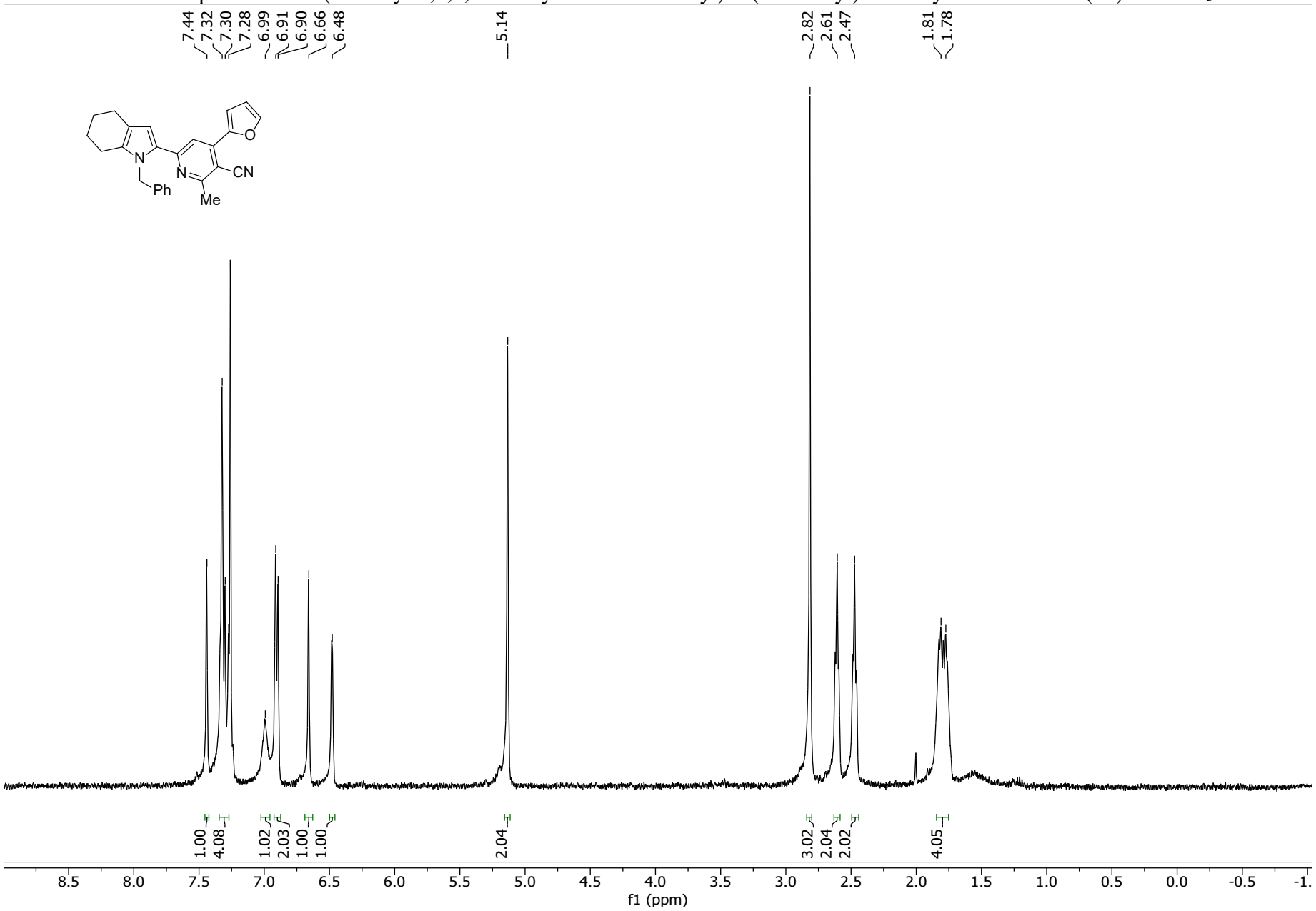
^{1}H NMR spectrum of 2-methyl-6-(1-methyl-4,5,6,7-tetrahydro-1*H*-indol-2-yl)-4-phenylnicotinonitrile (**2n**) in $CDCl_3$



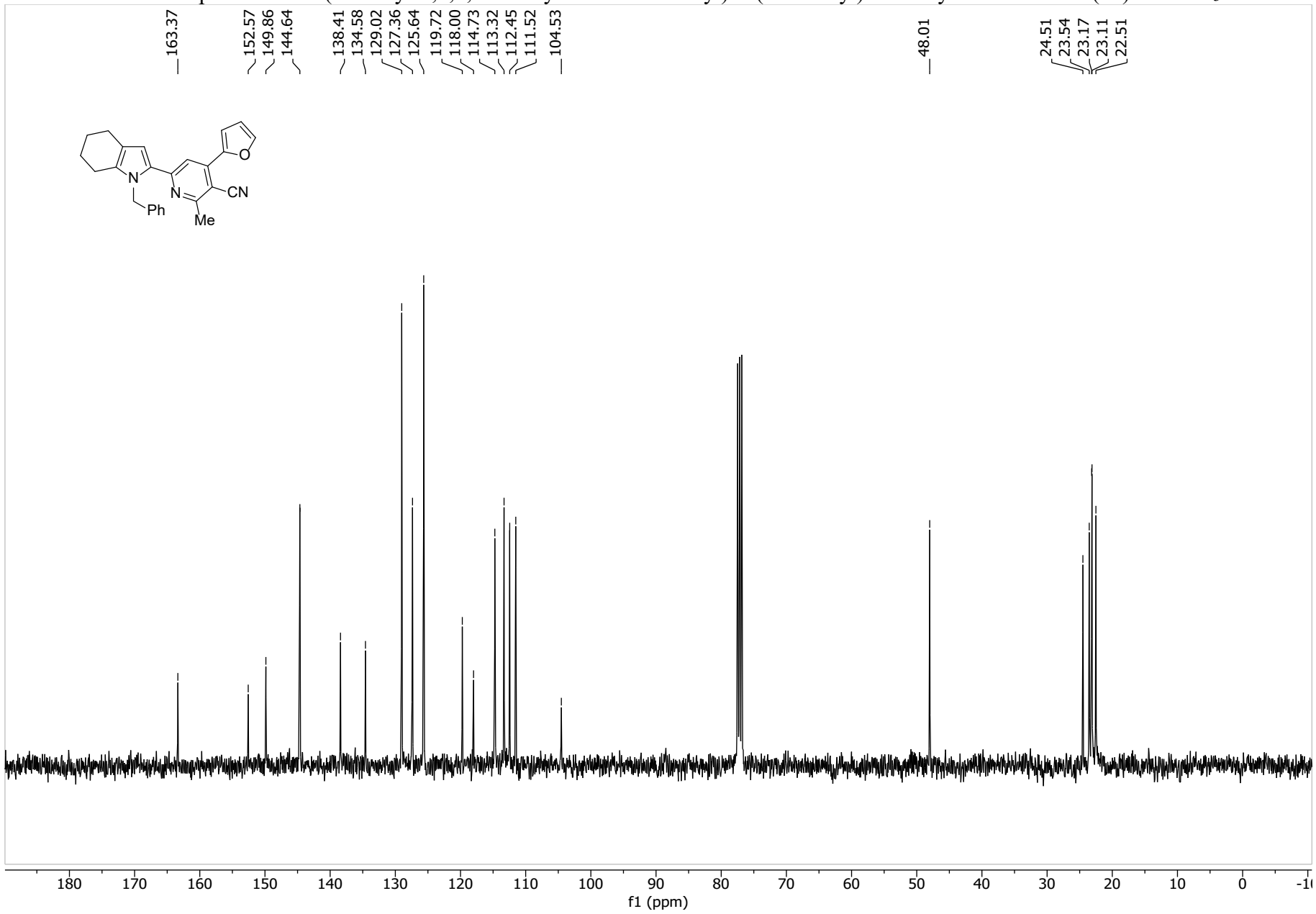
^{13}C NMR spectrum of 2-methyl-6-(1-methyl-4,5,6,7-tetrahydro-1*H*-indol-2-yl)-4-phenylnicotinonitrile (**2n**) in $CDCl_3$



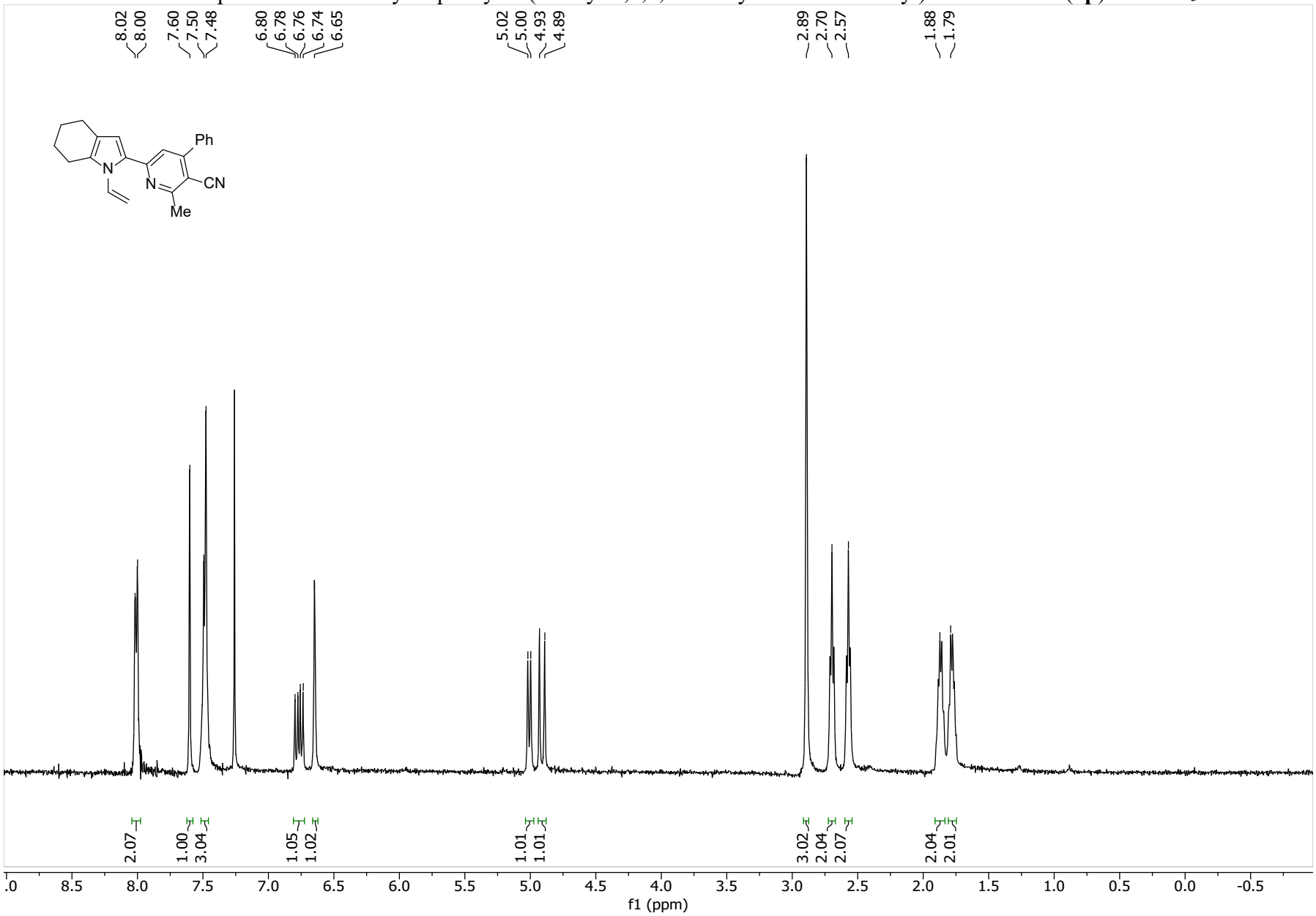
^{1}H NMR spectrum of 6-(1-benzyl-4,5,6,7-tetrahydro-1*H*-indol-2-yl)-4-(furan-2-yl)-2-methylnicotinonitrile (**2o**) in $CDCl_3$



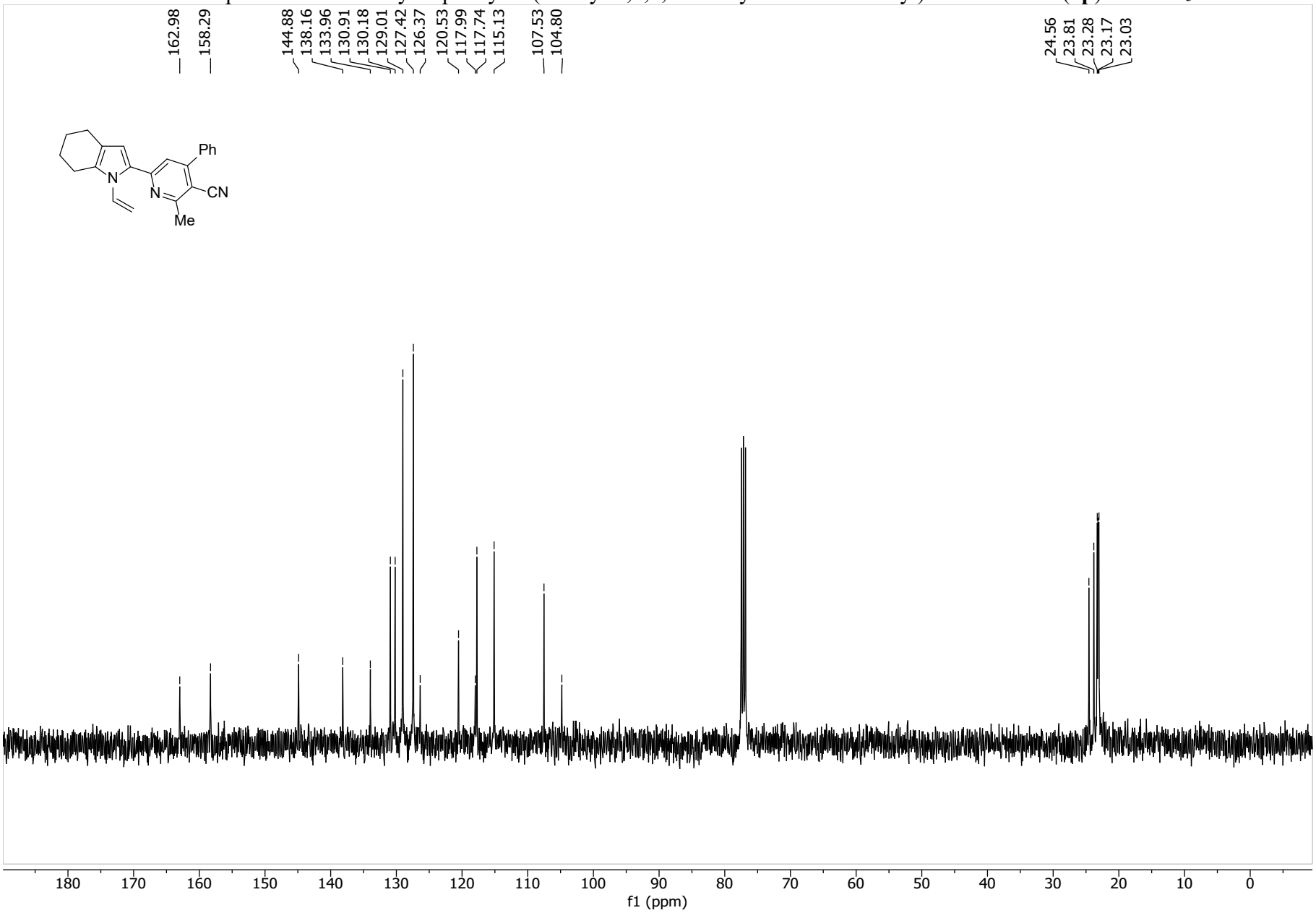
^{13}C NMR spectrum of 6-(1-benzyl-4,5,6,7-tetrahydro-1*H*-indol-2-yl)-4-(furan-2-yl)-2-methylnicotinonitrile (**2o**) in $CDCl_3$



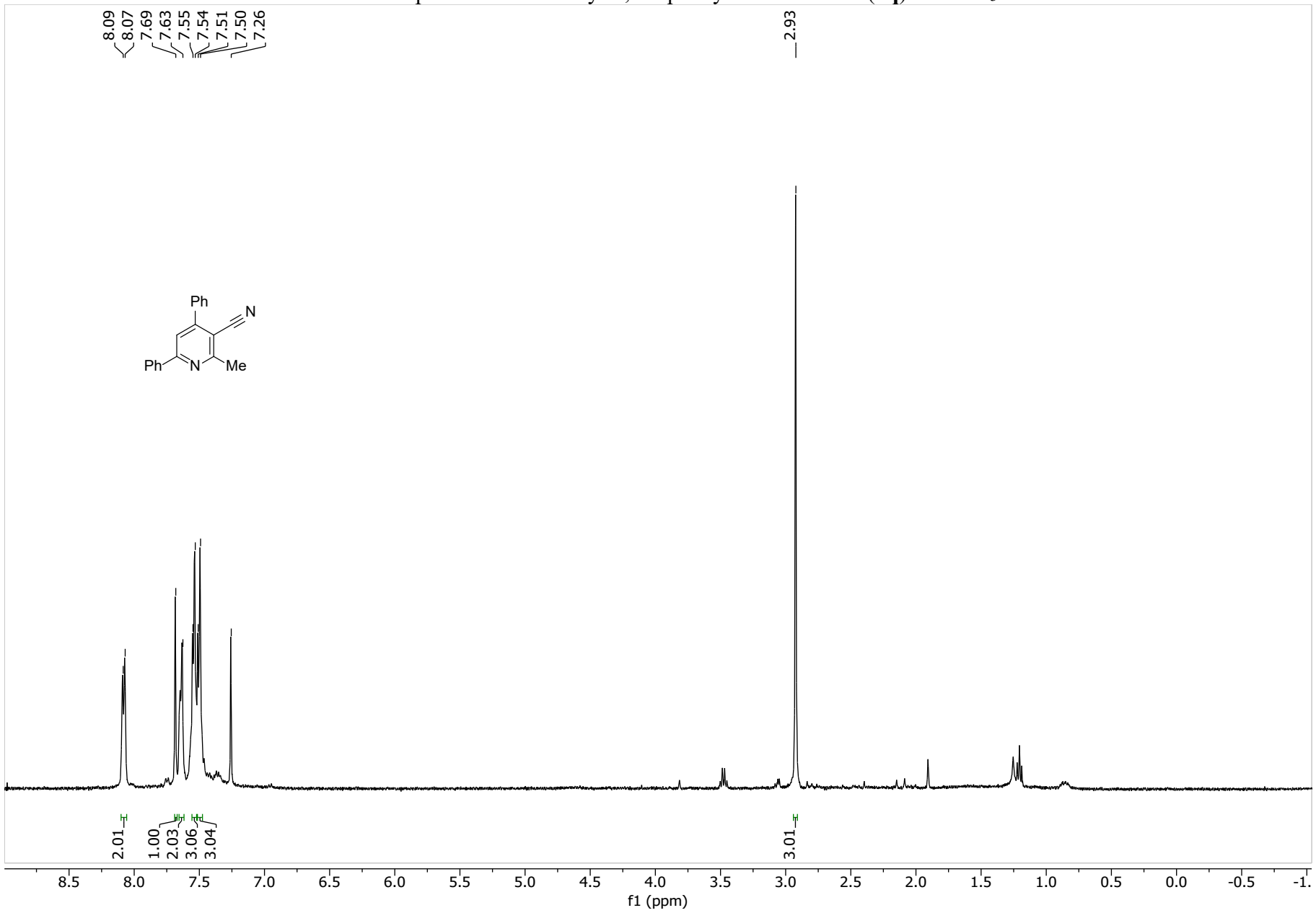
^{1}H NMR spectrum of 2-methyl-4-phenyl-6-(1-vinyl-4,5,6,7-tetrahydro-1*H*-indol-2-yl)nicotinonitrile (**2p**) in $CDCl_3$



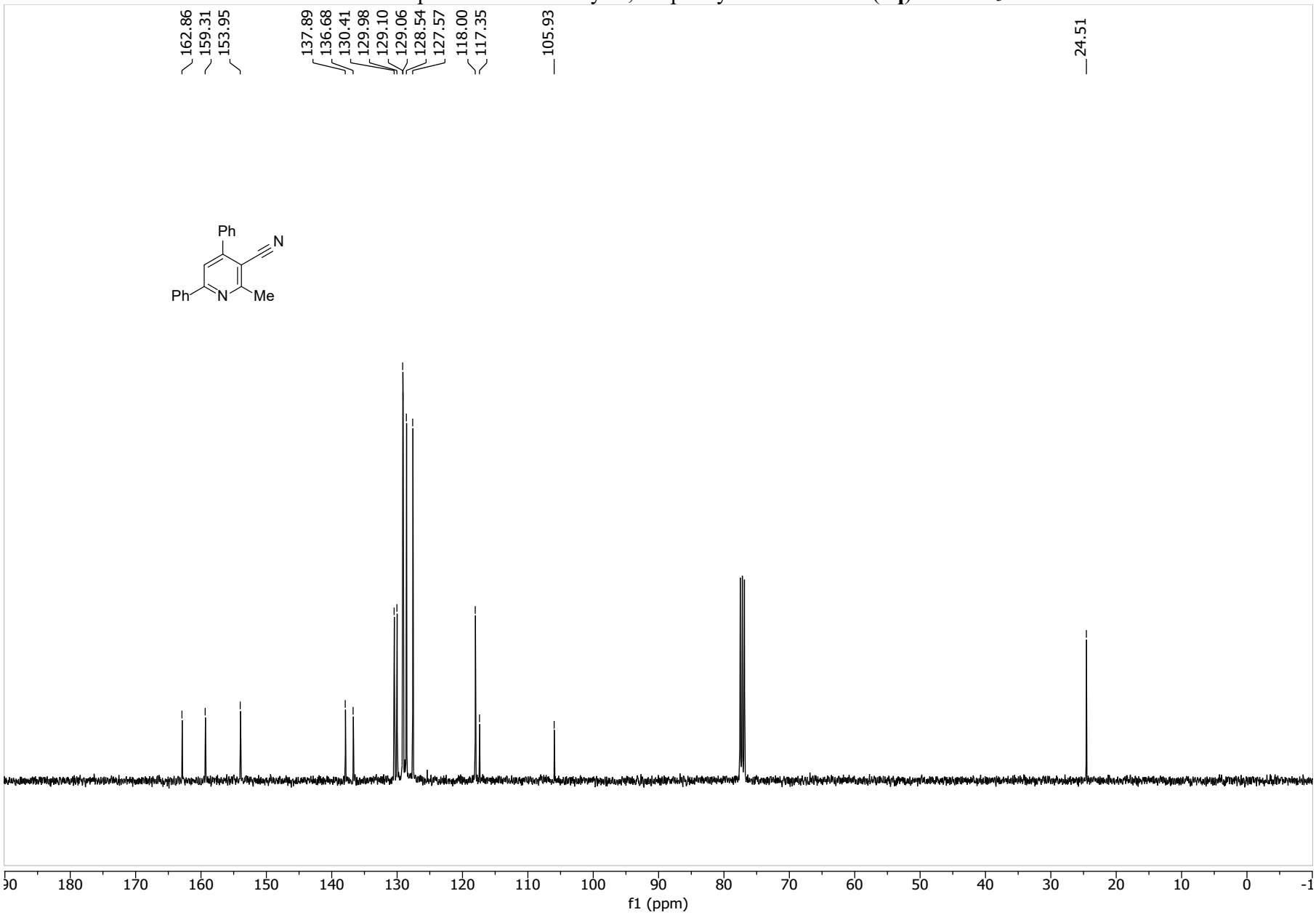
^{13}C NMR spectrum of 2-methyl-4-phenyl-6-(1-vinyl-4,5,6,7-tetrahydro-1*H*-indol-2-yl)nicotinonitrile (**2p**) in $CDCl_3$



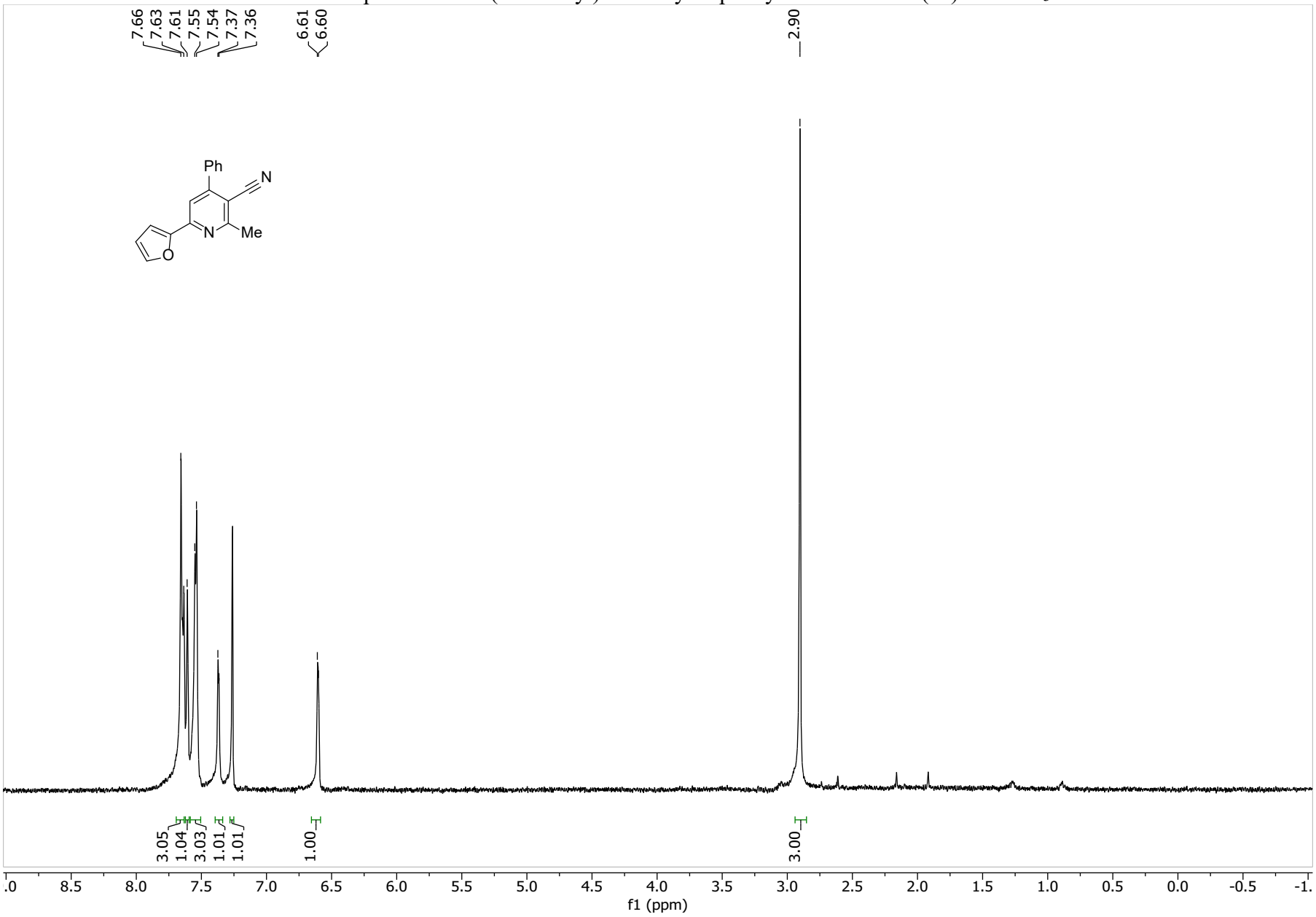
^{1}H NMR spectrum of 2-methyl-4,6-diphenylnicotinonitrile (**2q**) in $CDCl_3$



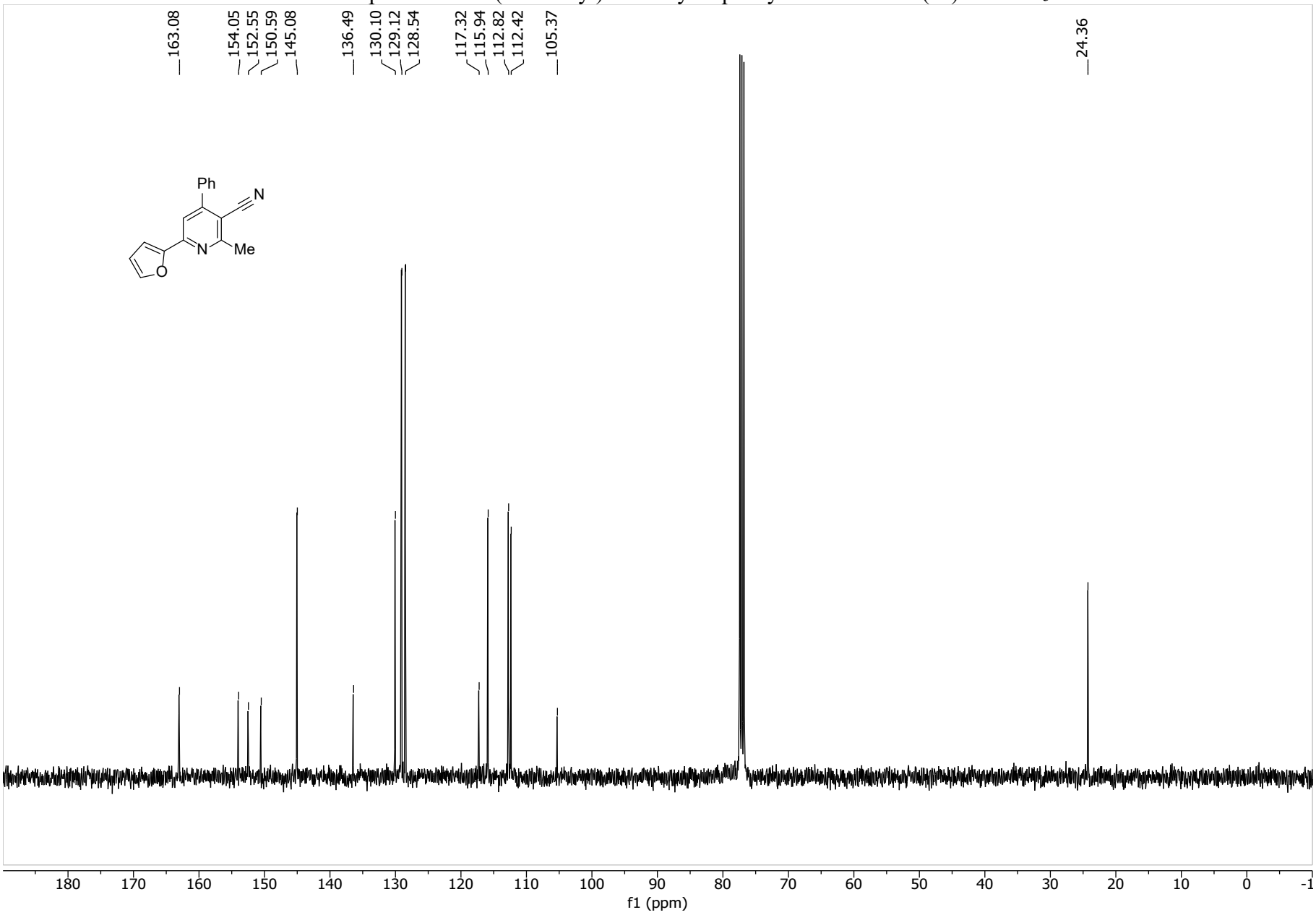
^{13}C NMR spectrum of 2-methyl-4,6-diphenylnicotinonitrile (**2q**) in $CDCl_3$



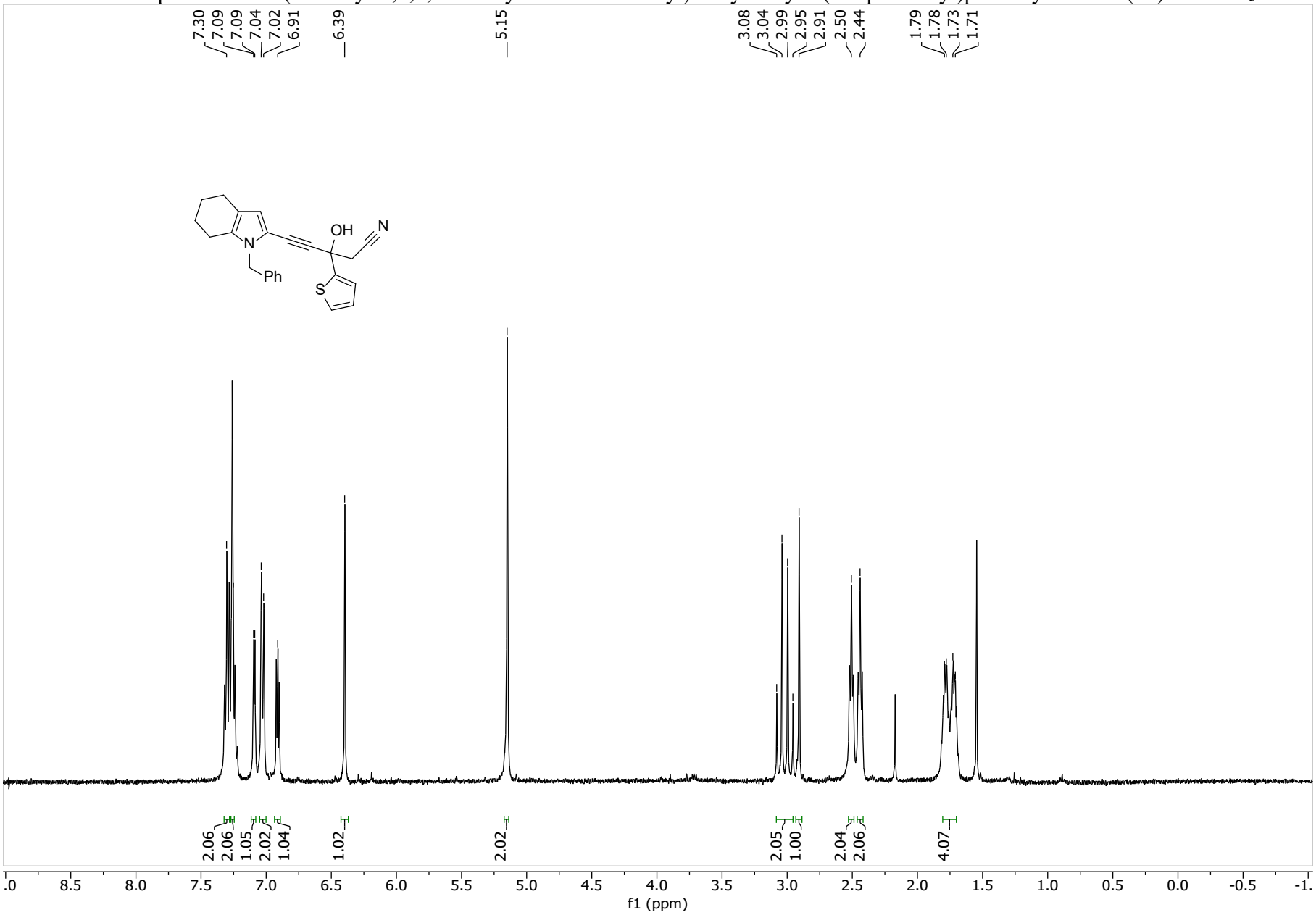
^{1}H NMR spectrum of 4-(furan-2-yl)-2-methyl-6-phenylnicotinonitrile (**2r**) in $CDCl_3$



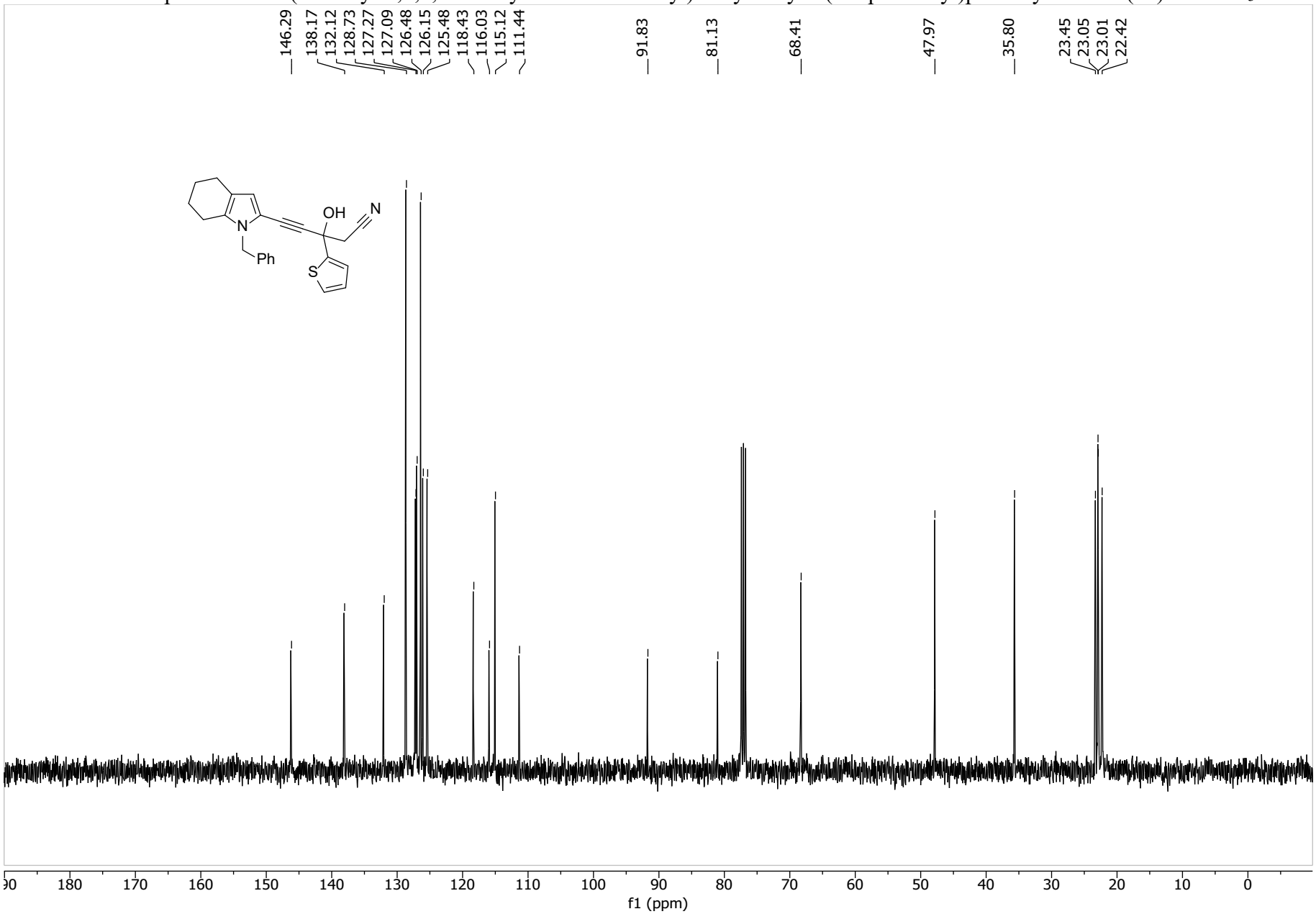
^{13}C NMR spectrum of 4-(furan-2-yl)-2-methyl-6-phenylnicotinonitrile (**2r**) in $CDCl_3$



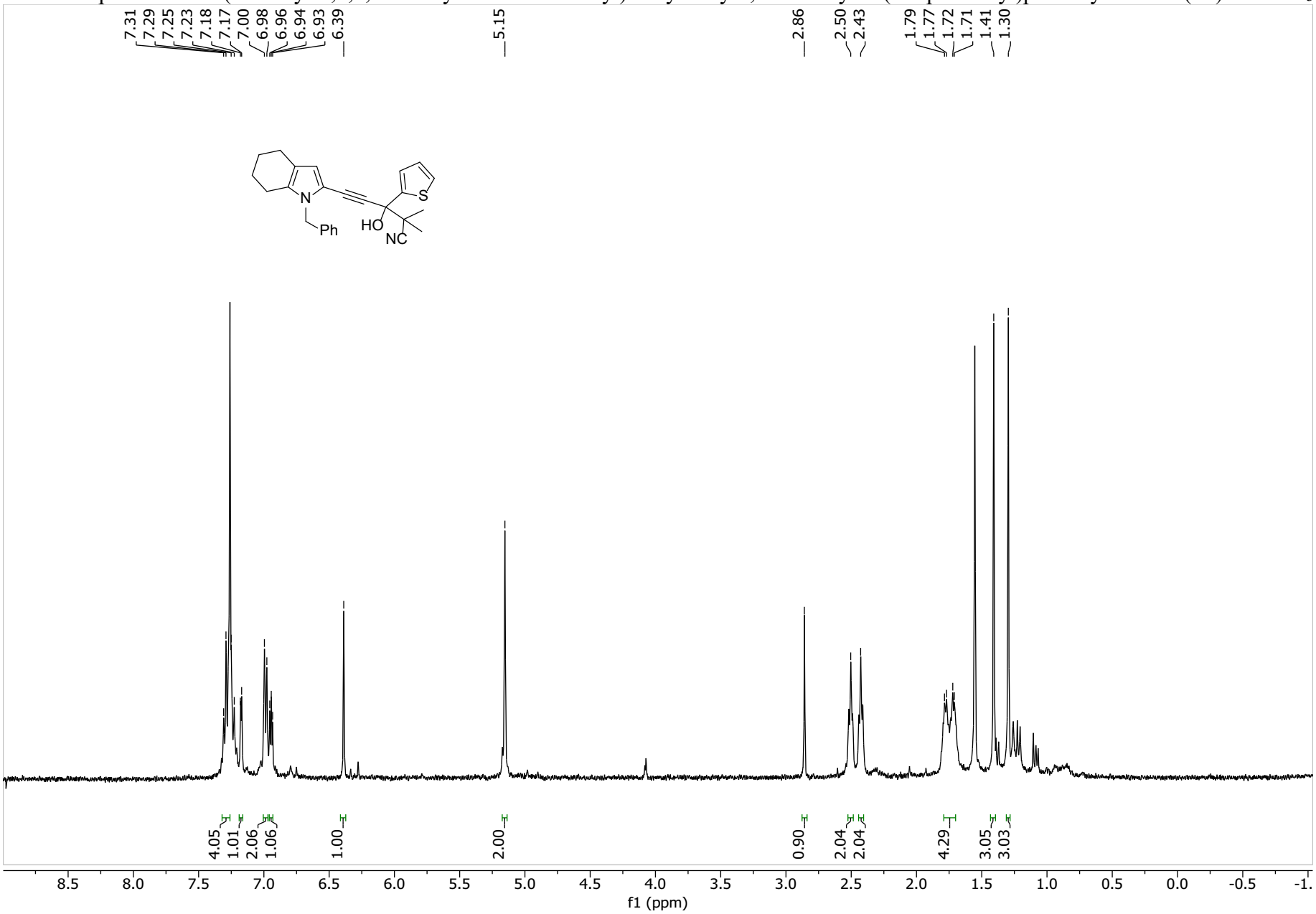
^{1}H NMR spectrum of 5-(1-benzyl-4,5,6,7-tetrahydro-1*H*-indol-2-yl)-3-hydroxy-3-(thiophen-2-yl)pent-4-ynenitrile (**3a**) in $CDCl_3$



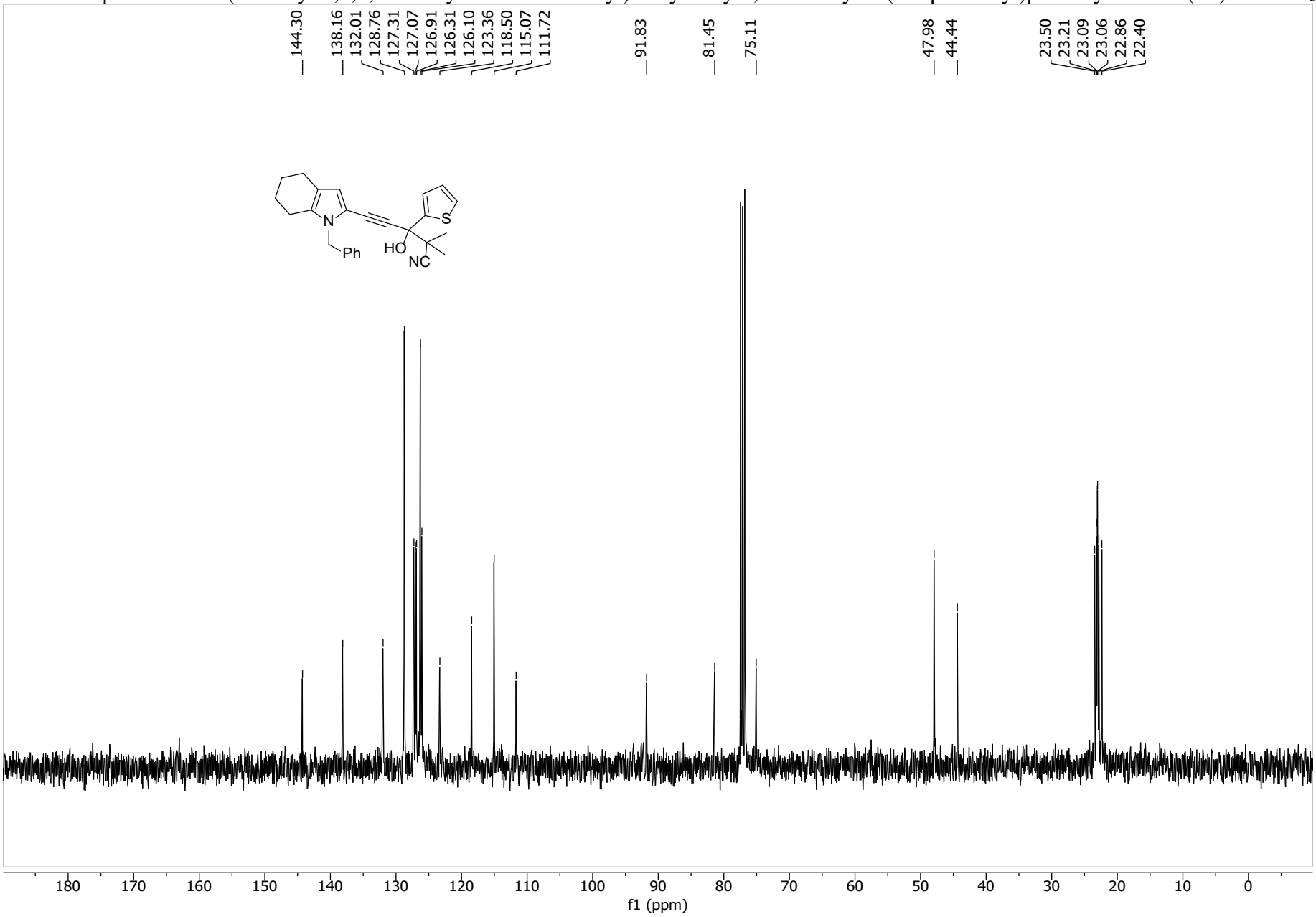
^{13}C NMR spectrum of 5-(1-benzyl-4,5,6,7-tetrahydro-1*H*-indol-2-yl)-3-hydroxy-3-(thiophen-2-yl)pent-4-ynenitrile (**3a**) in $CDCl_3$



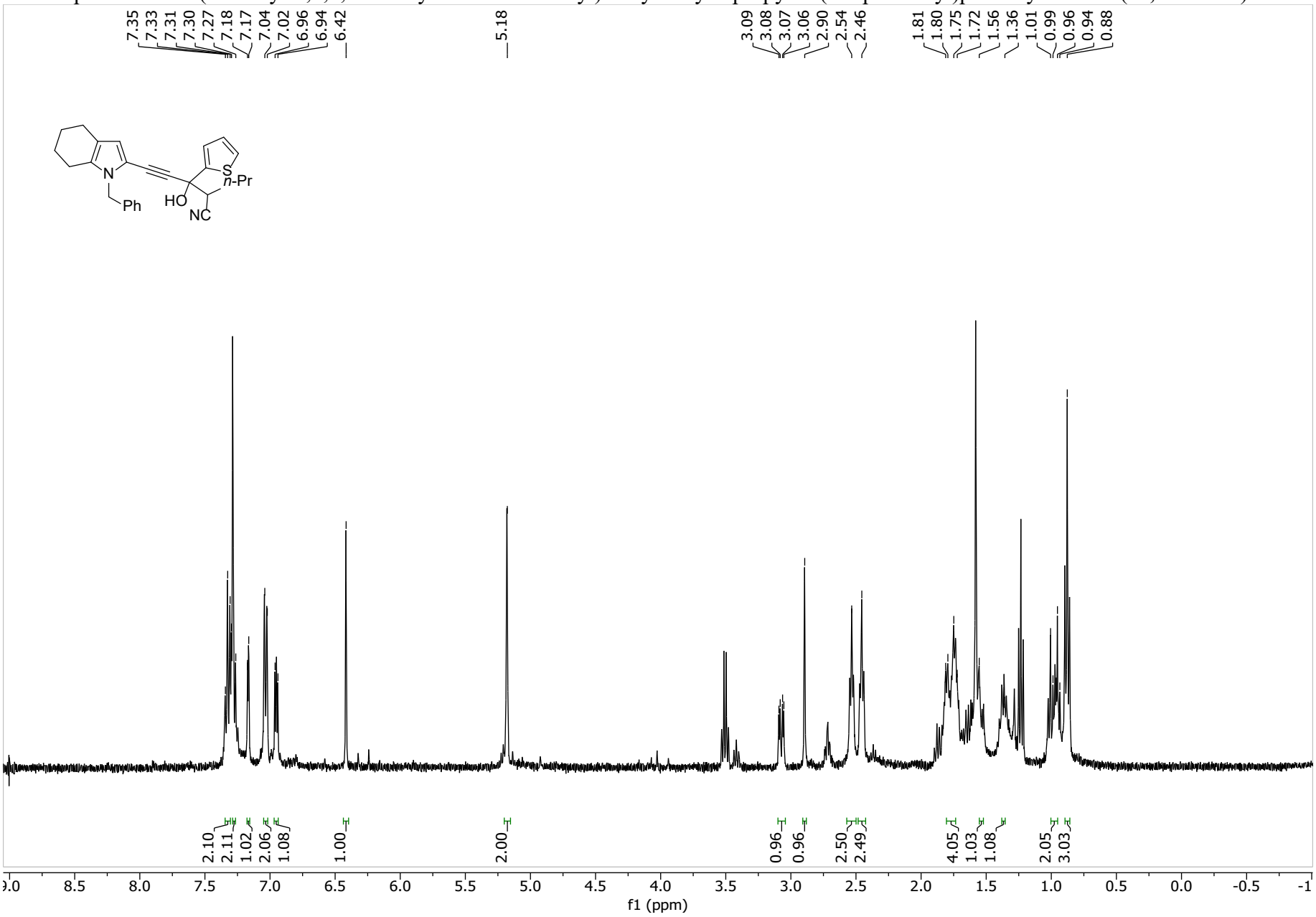
^{1}H NMR spectrum of 5-(1-benzyl-4,5,6,7-tetrahydro-1H-indol-2-yl)-3-hydroxy-2,2-dimethyl-3-(thiophen-2-yl)pent-4-ynenitrile (**3b**) in $CDCl_3$



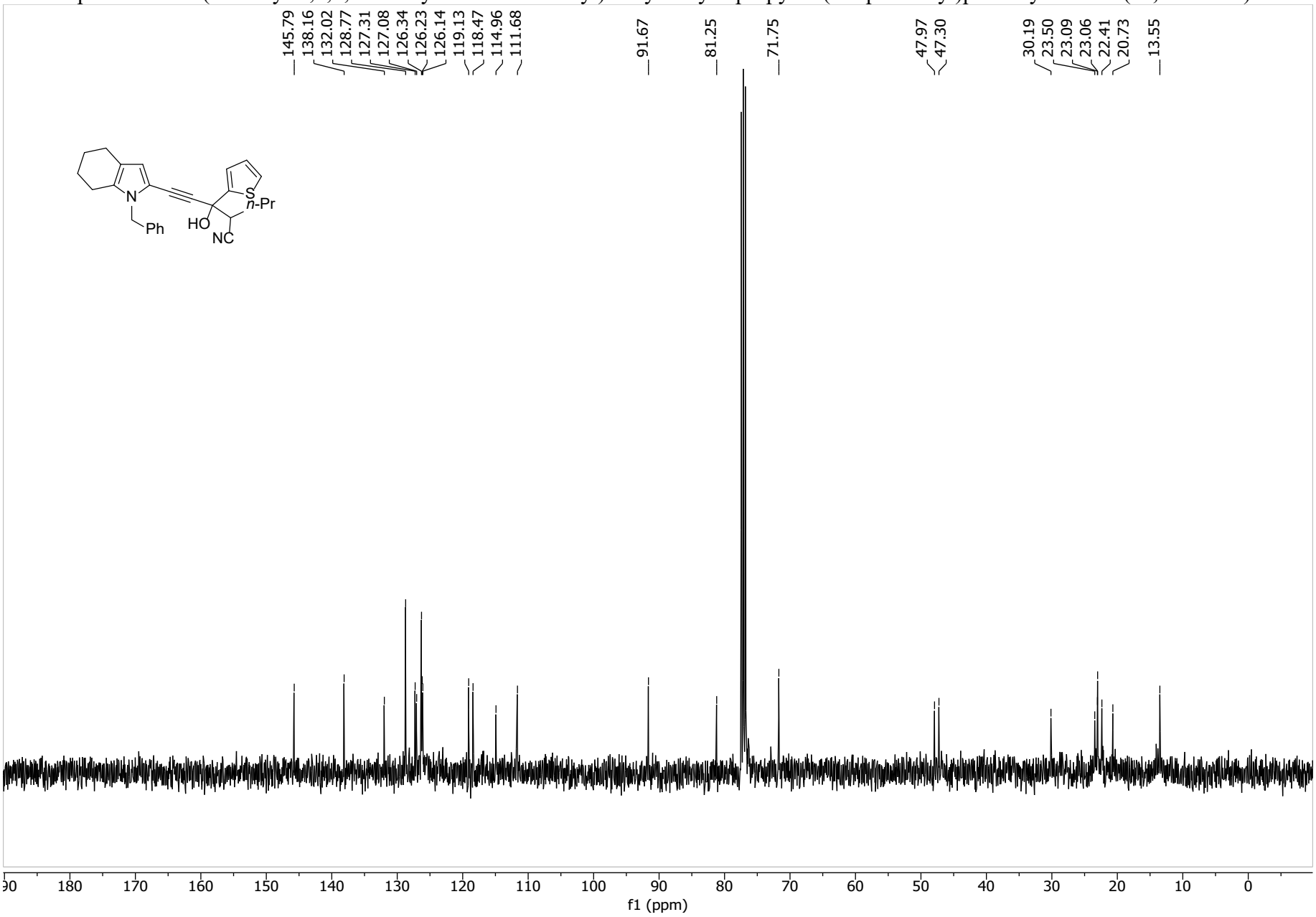
^{13}C NMR spectrum of 5-(1-benzyl-4,5,6,7-tetrahydro-1H-indol-2-yl)-3-hydroxy-2,2-dimethyl-3-(thiophen-2-yl)pent-4-ynenitrile (**3b**) in $CDCl_3$



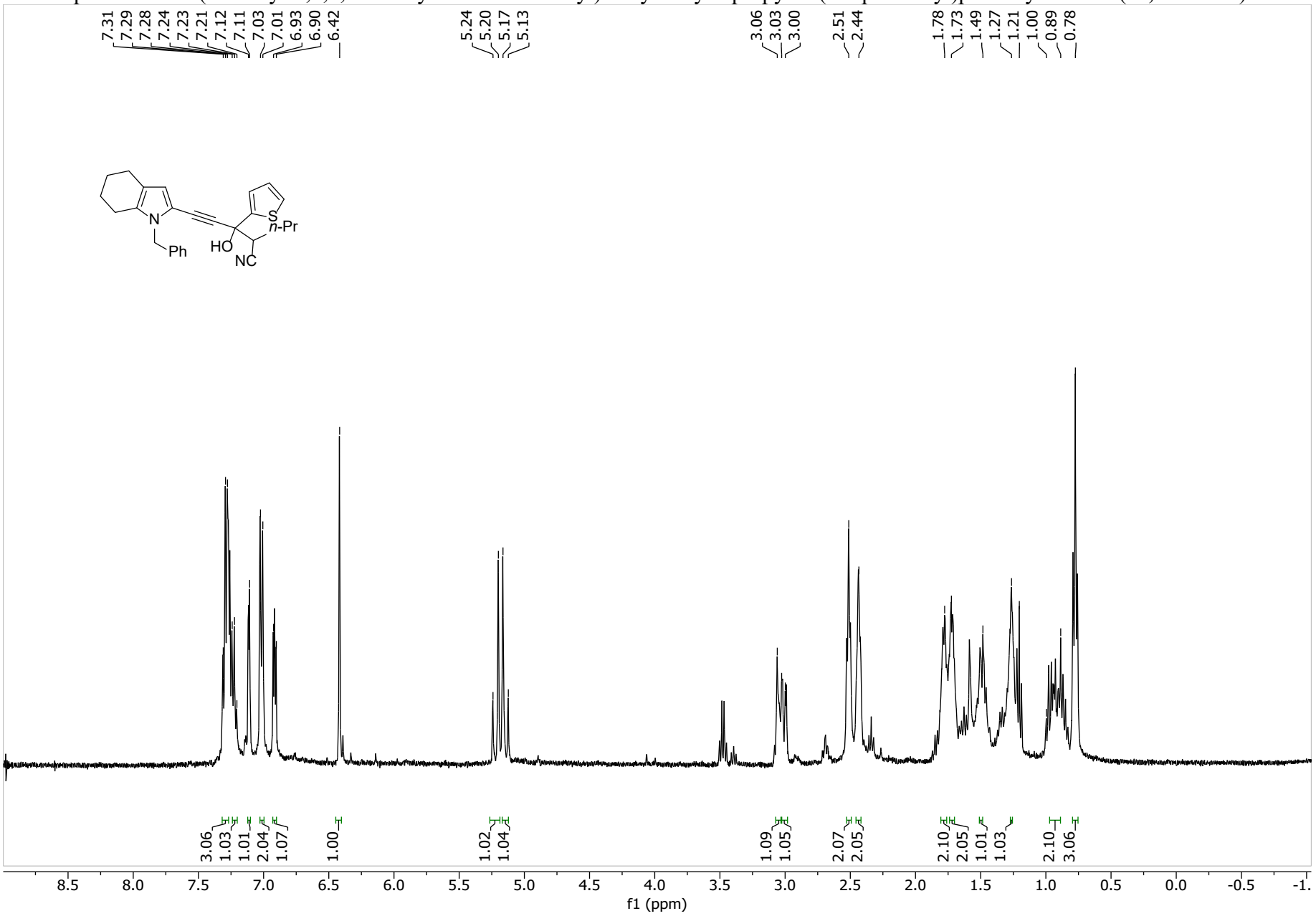
^{1}H NMR spectrum of 5-(1-benzyl-4,5,6,7-tetrahydro-1H-indol-2-yl)-3-hydroxy-2-propyl-3-(thiophen-2-yl)pent-4-ynenitrile (**3c,** isomer 1) in $CDCl_3$



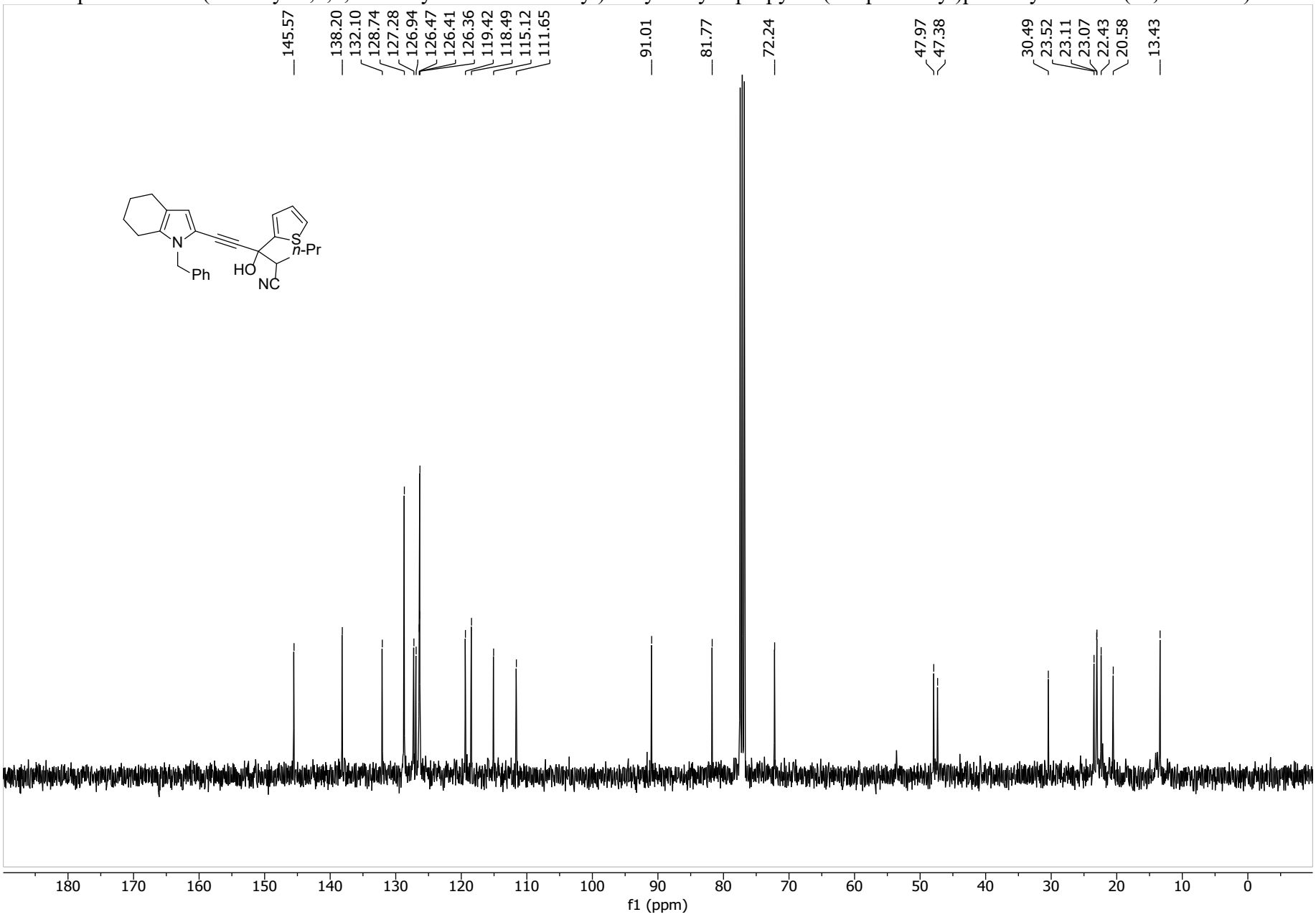
^{13}C NMR spectrum of 5-(1-benzyl-4,5,6,7-tetrahydro-1H-indol-2-yl)-3-hydroxy-2-propyl-3-(thiophen-2-yl)pent-4-ynenitrile (**3c,** isomer 1) in $CDCl_3$



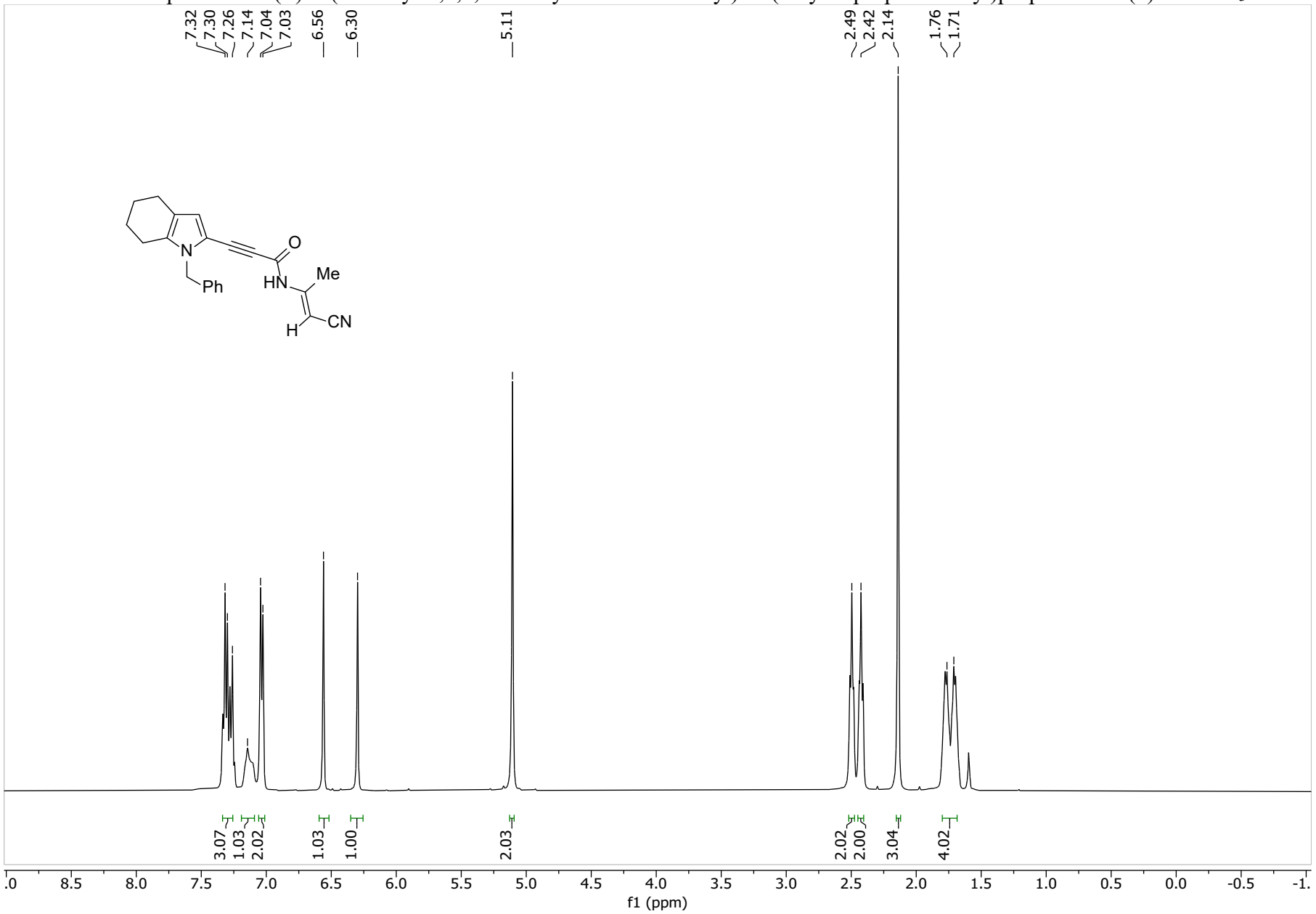
^{1}H NMR spectrum of 5-(1-benzyl-4,5,6,7-tetrahydro-1H-indol-2-yl)-3-hydroxy-2-propyl-3-(thiophen-2-yl)pent-4-ynenitrile (**3c,** isomer 2) in $CDCl_3$



^{13}C NMR spectrum of 5-(1-benzyl-4,5,6,7-tetrahydro-1H-indol-2-yl)-3-hydroxy-2-propyl-3-(thiophen-2-yl)pent-4-ynenitrile (**3c,** isomer 2) in $CDCl_3$



^{1}H NMR spectrum of (*E*)-3-(1-benzyl-4,5,6,7-tetrahydro-1*H*-indol-2-yl)-N-(1-cyanoprop-1-en-2-yl)propiolamide (**7**) in $CDCl_3$



^{13}C NMR spectrum of (*E*)-3-(1-benzyl-4,5,6,7-tetrahydro-1*H*-indol-2-yl)-N-(1-cyanoprop-1-en-2-yl)propiolamide (**7**) in $CDCl_3$