Redox-Neutral α-Arylation of Amines

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Supporting Information

General Information: Starting materials, reagents, and solvents were purchased from commercial sources and used as received unless stated otherwise. Pyrrolidine, piperidine, benzaldehyde, mesitaldehyde, 1-methylindole, 2,4-dimethylphenol, pyrroles and 2-ethylhexanoic acid (2-EHA) were distilled prior to use. 4-Chlorophenol and 2-methylindole were purified by Kugelrohr distillation. 2-Naphthol, 4-*t*-butylphenol, benzoic acid and 4-(dimethylamino)benzoic acid were recrystallized from toluene/ethanol. Purification of reaction products was carried out by flash column chromatography using Sorbent Technologies Standard Grade silica gel (60 Å, 230–400 mesh). Analytical thin layer chromatography was performed on EM Reagent 0.25 mm silica gel 60 F_{254} plates. Visualization was accomplished with UV light or Dragendorff-Munier stains, followed by heating. Melting points were recorded on a Thomas Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were recorded on an ATI Mattson Genesis Series FT-Infrared spectrophotometer. Proton nuclear magnetic resonance spectra (^{1}H-NMR) were recorded on a Varian VNMRS-500 MHz or Varian VNMRS-400 MHz and chemical shifts are reported in ppm using the solvent as an internal standard ($CDCl_3$ at 7.26 ppm). Data are reported as app = apparent, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, comp = complex, br = broad; coupling constant(s) in Hz. Proton-decoupled carbon nuclear magnetic resonance spectra (^{13}C-NMR) spectra were recorded on a Varian VNMRS-500 MHz or Varian VNMRS-400 MHz and chemical shifts are reported in ppm using the solvent as an internal standard ($CDCl_3$ at 77.0 ppm). Mass spectra were recorded on a Finnigan LCQ-DUO mass spectrometer. Arylation products **2c**, **2e**, **5c** and **5e** were previously reported and their published characterization data matched our own in all respects.[1–4] Ratios of regioisomeric products were determined by ^{1}H-NMR analysis of the crude reaction mixture.

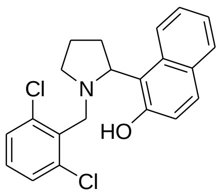
General Procedure for the Redox-Neutral α-Arylation of Amines with Naphthols or Phenols as Nucleophiles:

To a solution of the naphthol (1.5 mmol, 1.5 equiv) or phenol (5 mmol, 5 equiv) in toluene (4 mL) was added the amine (1.5 mmol, 1.5 equiv). The mixture was heated under reflux and aldehyde (1 mmol, 1 equiv, 1 M solution in toluene) was delivered through the top of the reflux condenser over 5 hours via syringe pump. Subsequently, the reaction mixture was allowed to cool to room temperature and the solvent was removed under reduced pressure. The residue was purified by silica gel chromatography.

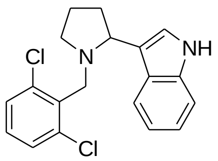
General Procedure for the Redox-Neutral α-Arylation of Amines with Indoles or Pyrroles as Nucleophiles:

To a solution of the indole (1.5 mmol, 1.5 equiv) or pyrrole (5 mmol, 5 equiv) in toluene (4 mL) was added the amine (1.5 mmol, 1.5 equiv) and 2-ethylhexanoic acid (1 mmol, 1 equiv).[5] The mixture was heated under reflux and aldehyde (1 mmol, 1 equiv, 1 M solution in toluene) was delivered through the top of the reflux condenser over 5 hours via syringe pump. Subsequently, the reaction mixture was allowed to cool to room temperature, diluted with EtOAc (10 mL) and washed with saturated aqueous $NaHCO_3$ (3 x 10 mL). The combined aqueous layer was extracted with EtOAc (3 x 10 mL) and the combined organic layer was washed with water (40 mL), brine (40 mL), and dried over anhydrous Na_2SO_4. Solvent was then removed under reduced pressure. The residue was purified by silica gel chromatography.

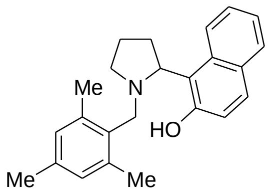
1-(1-(2,6-dichlorobenzyl)pyrrolidin-2-yl)naphthalen-2-ol (5a): Following the general procedure compound **5a** was obtained from 2-naphthol, pyrrolidine and 2,6-dichlorobenzaldehyde as a colorless oil in 96% yield (R_f = 0.37 in hexanes/EtOAc 90:10 v/v); IR (KBr) 3063, 2944, 2905, 2842, 1621, 1595, 1581, 1561, 1464, 1519, 1332, 1272, 1234, 1127, 1086, 959, 814, 776, 764, 750 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) 12.13 (br s, 1H), 7.93 (app d, J = 8.6 Hz, 1H), 7.74 (app d, J = 8.1 Hz, 1H), 7.58 (d, J = 8.8 Hz, 1H), 7.46 (ddd, J = 8.6, 6.8, 1.3 Hz, 1H), 7.29 (ddd, J = 8.1, 6.8, 1.0 Hz, 1H), 7.15 (d, J = 8.0 Hz, 2H), 7.01 (t, J = 8.0 Hz, 1H), 6.96 (d, J = 8.8 Hz, 1H), 4.71 (app t, J = 8.6 Hz, 1H), 4.18 (d, J = 12.7 Hz, 1H), 4.08 (d, J = 12.7 Hz, 1H), 3.36–3.29 (m, 1H), 2.83 (app td, J = 9.7, 7.5 Hz, 1H), 2.59–2.43 (m, 1H), 2.15–1.90 (comp, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.5, 136.7, 132.7, 132.5, 129.1, 128.6, 128.3, 128.1, 125.9, 122.1, 121.2, 119.4, 116.2, 65.4, 54.1, 53.5, 32.7, 23.5; m/z (ESI–MS) 372.1 ($^{35}Cl/^{35}Cl$) $[M + H]^+$, 374.1 ($^{35}Cl/^{37}Cl$) $[M + H]^+$.



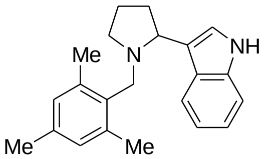
3-(1-(2,6-dichlorobenzyl)pyrrolidin-2-yl)-1H-indole (5b): Following the general procedure compound **5b** was obtained from indole, pyrrolidine and 2,6-dichlorobenzaldehyde as a colorless oil in 86% yield (R_f = 0.24 in hexanes/EtOAc 75:25 v/v); IR (KBr) 3446, 3123, 3059, 2971, 2833, 2794, 1616, 1576, 1559, 1456 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) 8.05 (br s, 1H), 7.89 (d, J = 7.8 Hz, 1H), 7.34–7.29 (m, 1H), 7.27–7.13 (comp, 5H), 7.01 (t, J = 8.0 Hz, 1H), 4.05 (d, J = 12.2 Hz, 1H), 3.87 (app t, J = 8.3 Hz, 1H), 3.74 (d, J = 12.2 Hz, 1H), 3.15–3.06 (m, 1H), 2.67 (app q, J = 8.8 Hz, 1H), 2.36–2.24 (m, 1H), 2.21–2.08 (m, 1H), 2.06–1.94 (m, 1H), 1.93–1.84 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.5, 136.4, 135.2, 128.2, 128.1, 126.9, 122.4, 121.6, 120.1, 118.8, 117.5, 110.9, 62.5, 53.7, 52.7, 32.9, 22.4; m/z (ESI–MS) 345.0 ($^{35}Cl/^{35}Cl$) $[M + H]^+$, 347.0 ($^{35}Cl/^{37}Cl$) $[M + H]^+$.



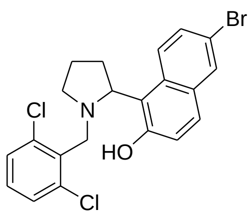
1-(1-(2,4,6-trimethylbenzyl)pyrrolidin-2-yl)naphthalen-2-ol (5d): Following the general procedure compound **5d** was obtained from 2-naphthol, pyrrolidine and mesitaldehyde as a colorless oil in 76% yield (R_f = 0.37 in hexanes/EtOAc 90:10 v/v); IR (KBr) 3059, 2967, 2915, 2873, 1622, 1599, 1521, 1467, 1414, 1360, 1270, 1240, 1134, 1090, 951, 854, 816, 745 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) 12.78 (br s, 1H), 8.02 (app d, J = 8.8 Hz, 1H), 7.84 (app d, J = 8.2 Hz, 1H), 7.74 (d, J = 8.8 Hz, 1H), 7.54 (ddd, J = 8.8, 6.8, 1.4 Hz, 1H), 7.38 (ddd, J = 8.2, 6.8, 1.0 Hz, 1H), 7.18 (d, J = 8.8 Hz, 1H), 6.88 (s, 2H), 4.64–4.58 (m, 1H), 4.03 (d, J = 12.9 Hz, 1H), 3.68 (d, J = 12.9 Hz, 1H), 3.17–3.10 (m, 1H), 2.66–2.58 (m, 1H), 2.58–2.50 (m, 1H), 2.40 (s, 6H), 2.31 (s, 3H), 2.09–1.95 (comp, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.5, 137.7, 136.8, 132.6, 130.8, 129.1, 128.8, 128.3, 126.2, 122.2, 120.8, 119.5, 116.1, 66.1, 52.8, 52.2, 32.3, 23.4, 20.7, 20.5; m/z (ESI–MS) 346.1 $[M + H]^+$.



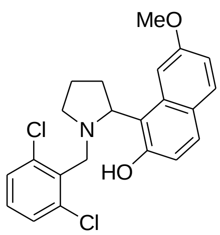
3-(1-(2,4,6-trimethylbenzyl)pyrrolidin-2-yl)-1H-indole (5f): Following the general procedure compound **5f** was obtained from indole, pyrrolidine and mesitaldehyde as a yellow oil in 60% yield (R_f = 0.25 in hexanes/EtOAc 75:25 v/v); IR (KBr) 3412, 3056, 2961, 2915, 1670, 1613, 1456, 1375, 1095, 1013, 887, 851, 805, 741 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) 8.14 (br s, 1H), 7.87 (d, *J* = 7.9 Hz, 1H), 7.45–7.35 (m, 1H), 7.32–7.19 (comp, 2H), 7.14 (ddd, *J* = 8.0, 7.1, 1.1 Hz, 1H), 6.79 (s, 2H), 3.78 (d, *J* = 12.4 Hz, 1H), 3.74–3.64 (m, 1H), 3.31 (d, *J* = 12.4 Hz, 1H), 3.06–2.94 (m, 1H), 2.46–2.31 (m, 1H), 2.25 (s, 3H), 2.21 (s, 6H), 2.03–1.90 (m, 1H), 1.88–1.76 (m, 1H), 1.51–1.26 (m, 1H), 1.02–0.87 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.6, 136.7, 135.7, 133.3, 128.7, 126.7, 122.6, 121.7, 120.3, 118.9, 117.8, 111.1, 63.0, 53.5, 51.8, 32.3, 22.6, 20.8, 20.2; *m/z* (ESI–MS) 319.1 $[M + H]^+$.



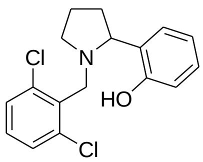
1-(1-(2,6-dichlorobenzyl)pyrrolidin-2-yl)-6-bromonaphthalen-2-ol (5g): Following the general procedure compound **5g** was obtained from 6-bromo-2-naphthol, pyrrolidine and 2,6-dichlorobenzaldehyde as a yellow oil in 85% yield (R_f = 0.37 in hexanes/EtOAc 90:10 v/v); IR (KBr) 3059, 2967, 2874, 1615, 1590, 1562, 1507, 1436, 1361, 1270, 1237, 1090, 901, 879, 814, 778, 765, 737 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) 12.19 (br s, 1H), 7.84 (d, *J* = 2.1 Hz, 1H), 7.76 (d, *J* = 9.1 Hz, 1H), 7.47 (dd, *J* = 9.1, 2.1 Hz, 1H), 7.42 (d, *J* = 8.8 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 2H), 7.00–6.94 (m, 1H), 6.89 (d, *J* = 8.8 Hz, 1H), 4.64 (app t, *J* = 8.6 Hz, 1H), 4.13 (d, *J* = 12.8 Hz, 1H), 4.08 (d, *J* = 12.8 Hz, 1H), 3.36 (ddd, *J* = 9.6, 7.2, 2.4 Hz, 1H), 2.81 (app td, *J* = 9.6, 7.7 Hz, 1H), 2.52–2.41 (m, 1H), 2.10–1.94 (comp, 2H), 1.94–1.85 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.7, 136.6, 132.4, 130.9, 130.3, 129.4, 129.1, 128.9, 128.0, 127.6, 123.1, 120.4, 116.5, 115.5, 65.1, 54.4, 53.5, 32.9, 23.5; *m/z* (ESI–MS) (^{35}Cl/^{35}Cl/^{79}Br) 450.0 $[M + H]^+$, (^{35}Cl/^{35}Cl/^{81}Br) or (^{35}Cl/^{37}Cl/^{79}Br) 452.0 $[M + H]^+$, (^{35}Cl/^{37}Cl/^{81}Br) 454.0 $[M + H]^+$.



1-(1-(2,6-dichlorobenzyl)pyrrolidin-2-yl)-7-methoxynaphthalen-2-ol (5h): Following the general procedure compound **5h** was obtained from 7-methoxy-2-naphthol, pyrrolidine and 2,6-dichlorobenzaldehyde as a yellow oil in 98% yield (R_f = 0.26 in hexanes/EtOAc 90:10 v/v); IR (KBr) 3055, 2955, 2874, 2836, 1622, 1583, 1562, 1519, 1467, 1436, 1267, 1225, 1135, 1091, 1035, 831, 778, 765, 737 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) 12.14 (br s, 1H), 7.63 (d, *J* = 8.9 Hz, 1H), 7.49 (d, *J* = 8.9 Hz, 1H), 7.24–7.21 (m, 1H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.04–6.96 (comp, 2H), 6.82 (d, *J* = 8.7 Hz, 1H), 4.62 (app t, *J* = 8.4 Hz, 1H), 4.19 (d, *J* = 12.7 Hz, 1H), 4.07 (d, *J* = 12.7 Hz, 1H), 3.96 (s, 3H), 3.32 (ddd, *J* = 9.7, 6.9, 2.1 Hz, 1H), 2.83 (app td, *J* = 9.7, 7.4 Hz, 1H), 2.57–2.46 (m, 1H), 2.10–1.90 (comp, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.3, 156.5, 137.1, 134.0, 133.0, 130.5, 129.5, 128.7, 128.5, 124.1, 117.4, 115.7, 113.9, 101.5, 65.8, 55.6, 54.5, 53.8, 32.8, 23.9; *m/z* (ESI–MS) (^{35}Cl/^{35}Cl) 402.1 $[M + H]^+$, (^{35}Cl/^{37}Cl) 404.1 $[M + H]^+$.

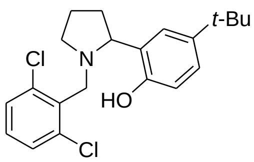


2-(1-(2,6-dichlorobenzyl)pyrrolidin-2-yl)phenol (5i): Following the general procedure



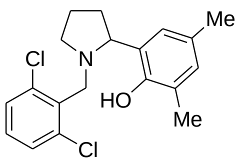
compound **5i** was obtained from phenol, pyrrolidine and 2,6-dichlorobenzaldehyde as a colorless oil in 49% yield (R_f = 0.43 in hexanes/EtOAc 90:10 v/v); IR (KBr) 3140, 3077, 2951, 2880, 2823, 1615, 1581, 1561, 1489, 1451, 1436, 1364, 1255, 1143, 1091, 896, 783, 751 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 10.46 (br s, 1H), 7.16 (d, J = 8.0 Hz, 2H), 7.06–6.98 (comp, 3H), 6.73–6.68 (m, 1H), 6.68–6.64 (m, 1H), 4.07 (d, J = 12.6 Hz, 1H), 3.97 (d, J = 12.6 Hz, 1H), 3.75–3.70 (m, 1H), 3.24–3.17 (m, 1H), 2.73–2.65 (m, 1H), 2.31–2.21 (m, 1H), 2.02–1.84 (comp, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.9, 136.5, 133.0, 129.1, 128.2(2), 128.1(9), 128.1(2), 125.8, 118.6, 116.2, 70.4, 54.3, 53.3, 33.2, 23.0; *m/z* (ESI–MS) 322.0 ($^{35}Cl/^{35}Cl$) $[M + H]^+$, 324.0 ($^{35}Cl/^{37}Cl$) $[M + H]^+$.

2-(1-(2,6-dichlorobenzyl)pyrrolidin-2-yl)-4-tert-butylphenol (5j): Following the general



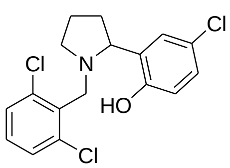
procedure compound **5j** was obtained from 4-*t*-butylphenol, pyrrolidine and 2,6-dichlorobenzaldehyde as a colorless oil in 90% yield (R_f = 0.46 in hexanes/EtOAc 90:10 v/v); IR (KBr) 3123, 3061, 2962, 2863, 2822, 1560, 1500, 1438, 1383, 1251, 1203, 1176, 1104, 949, 890, 788, 630 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 10.14 (br s, 1H), 7.10 (d, J = 8.0 Hz, 2H), 7.03–6.93 (comp, 3H), 6.52 (d, J = 8.3 Hz, 1H), 4.05 (d, J = 12.7 Hz, 1H), 4.02 (d, J = 12.7 Hz, 1H), 3.71 (app t, J = 8.2 Hz, 1H), 3.32–3.23 (m, 1H), 2.68 (app q, J = 9.0 Hz, 1H), 2.33–2.22 (m, 1H), 2.06–1.84 (comp, 3H), 1.29 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.2, 140.8, 136.4, 133.0, 128.9, 127.9, 125.0, 124.8, 124.7, 115.3, 70.7, 54.7, 53.5, 33.8, 33.4, 31.5, 22.9; *m/z* (ESI–MS) ($^{35}Cl/^{35}Cl$) 378.1 $[M + H]^+$, ($^{35}Cl/^{37}Cl$) 380.1 $[M + H]^+$.

2-(1-(2,6-dichlorobenzyl)pyrrolidin-2-yl)-4,6-dimethylphenol (5k): Following the



general procedure compound **5k** was obtained from 2,4-dimethylphenol, pyrrolidine and 2,6-dichlorobenzaldehyde as a colorless oil in 75% yield (R_f = 0.61 in hexanes/EtOAc 90:10 v/v); IR (KBr) 3013, 2971, 2853, 2814, 1581, 1560, 1485, 1462, 1381, 1330, 1245, 1200, 1129, 1107, 1086, 951, 856, 779, 745 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 10.25 (br s, 1H), 7.19 (d, J = 8.0 Hz, 2H), 7.02 (t, J = 8.0 Hz, 1H), 6.81–6.75 (m, 1H), 6.74–6.68 (m, 1H), 4.06 (d, J = 12.6 Hz, 1H), 3.93 (d, J = 12.6 Hz, 1H), 3.63 (app t, J = 8.4 Hz, 1H), 3.23–3.14 (m, 1H), 2.73–2.63 (m, 1H), 2.33–2.21 (comp, 4H), 2.13 (s, 3H), 2.07–1.93 (comp, 2H), 1.93–1.84 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.3, 136.5, 133.1, 130.0, 128.9, 128.0, 126.9, 126.7, 124.7(4), 124.6(8), 70.6, 54.0, 53.0, 32.7, 22.9, 20.3, 15.5; *m/z* (ESI–MS) ($^{35}Cl/^{35}Cl$) 350.1 $[M + H]^+$, ($^{35}Cl/^{37}Cl$) 352.1 $[M + H]^+$.

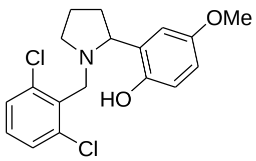
2-(1-(2,6-dichlorobenzyl)pyrrolidin-2-yl)-4-chlorophenol (5l): Following the general



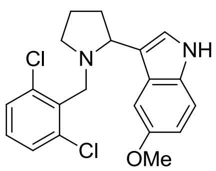
procedure compound **5l** was obtained from 4-chlorophenol, pyrrolidine and 2,6-dichlorobenzaldehyde as a yellow oil in 30% yield (R_f = 0.46 in hexanes/EtOAc 90:10 v/v); IR (KBr) 3051, 2946, 2841, 1580, 1483, 1435, 1383, 1260, 1178, 1084, 823, 782, 763, 685 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 10.51 (br s, 1H), 7.16 (d, J = 8.0 Hz, 2H), 7.01 (t, J = 8.0 Hz, 1H), 6.97 (d, J = 2.2 Hz, 1H), 6.96–6.91 (m, 1H), 6.55 (d, J = 8.5 Hz, 1H), 4.05 (d, J =

12.7 Hz, 1H), 4.01 (d, J = 12.7 Hz, 1H), 3.74–3.67 (m, 1H), 3.30–3.22 (m, 1H), 2.78–2.66 (m, 1H), 2.34–2.21 (m, 1H), 2.05–1.86 (comp, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.5, 136.6, 132.6, 129.3, 128.2, 127.9, 127.8, 127.4, 123.1, 117.5, 69.8, 54.6, 53.4, 33.2, 23.1; *m/z* (ESI–MS) (^{35}Cl/^{35}Cl/^{35}Cl) 356.1 $[M + H]^+$, (^{35}Cl/^{35}Cl/^{37}Cl) 358.1 $[M + H]^+$.

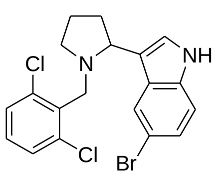
2-(1-(2,6-dichlorobenzyl)pyrrolidin-2-yl)-4-methoxyphenol (5m): Following the general procedure compound **5m** was obtained from 4-methoxyphenol, pyrrolidine and 2,6-dichlorobenzaldehyde as a colorless oil in 72% yield (R_f = 0.35 in hexanes/EtOAc 90:10 v/v); IR (KBr) 3079, 2972, 2831, 1623, 1581, 1560, 1498, 1470, 1436, 1383, 1331, 1304, 1250, 1206, 1157, 1036, 947, 849, 821, 778, 761, 657 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) 9.90 (br s, 1H), 7.17 (d, J = 8.0 Hz, 2H), 7.01 (t, J = 8.0 Hz, 1H), 6.61–6.55 (comp, 3H), 4.05 (d, J = 12.6 Hz, 1H), 3.96 (d, J = 12.6 Hz, 1H), 3.74 (s, 3H), 3.65 (app t, J = 8.3 Hz, 1H), 3.23–3.16 (m, 1H), 2.71–2.63 (m, 1H), 2.31–2.22 (m, 1H), 2.02–1.83 (comp, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.0, 150.6, 136.5, 133.0, 129.1, 128.1, 126.5, 116.5, 114.1, 113.2, 70.5, 55.7, 54.3, 53.3, 33.0, 23.0; *m/z* (ESI–MS) (^{35}Cl/^{35}Cl) 352.1 $[M + H]^+$, (^{35}Cl/^{37}Cl) 354.1 $[M + H]^+$.



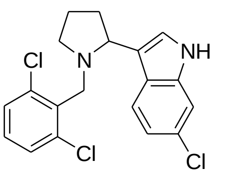
3-(1-(2,6-dichlorobenzyl)pyrrolidin-2-yl)-5-methoxy-1H-indole (5n): Following the general procedure compound **5n** was obtained from 5-methoxyindole, pyrrolidine and 2,6-dichlorobenzaldehyde as a yellow oil in 80% yield (R_f = 0.35 in hexanes/EtOAc 75:25 v/v); IR (KBr) 3413, 3051, 2953, 2831, 1672, 1625, 1582, 1561, 1485, 1436, 1364, 1288, 1212, 1171, 1091, 1029, 925, 797, 765, 737 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) 8.04 (br s, 1H), 7.34 (d, J = 2.3 Hz, 1H), 7.20 (d, J = 2.0 Hz, 1H), 7.19–7.13 (comp, 3H), 6.96 (t, J = 8.0 Hz, 1H), 6.86 (dd, J = 8.8, 2.3 Hz, 1H), 4.02 (d, J = 12.2 Hz, 1H), 3.93 (s, 3H), 3.79 (app t, J = 8.3 Hz, 1H), 3.73 (d, J = 12.2 Hz, 1H), 3.13–3.05 (m, 1H), 2.64 (app q, J = 8.8 Hz, 1H), 2.29–2.19 (m, 1H), 2.16–2.06 (m, 1H), 2.00–1.92 (m, 1H), 1.90–1.80 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.2, 136.5, 135.2, 131.7, 128.1, 128.0, 127.2, 123.4, 117.0, 111.8, 111.5, 102.3, 62.7, 55.9, 53.7, 52.7, 32.7, 22.4; *m/z* (ESI–MS) (^{35}Cl/^{35}Cl) 375.0 $[M + H]^+$, (^{35}Cl/^{37}Cl) 377.0 $[M + H]^+$.



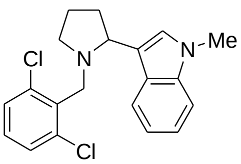
3-(1-(2,6-dichlorobenzyl)pyrrolidin-2-yl)-5-bromo-1H-indole (5o): Following the general procedure compound **5o** was obtained from 5-bromoindole, pyrrolidine and 2,6-dichlorobenzaldehyde as a yellow oil in 76% yield (R_f = 0.35 in hexanes/EtOAc 75:25 v/v); IR (KBr) 3445, 3197, 2966, 2875, 2841, 2799, 1581, 1561, 1459, 1435, 1264, 1196, 1091, 881, 794, 765, 738 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) 8.07 (br s, 1H), 7.97 (d, J = 1.7 Hz, 1H), 7.25–7.16 (comp, 2H), 7.15–7.07 (comp, 3H), 6.92 (t, J = 8.0 Hz, 1H), 3.93 (d, J = 12.3 Hz, 1H), 3.79–3.68 (comp, 2H), 3.17–3.05 (m, 1H), 2.61 (app q, J = 8.9 Hz, 1H), 2.26–2.15 (m, 1H), 2.10–1.90 (comp, 2H), 1.88–1.77 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.4, 135.1, 134.8, 128.3, 128.1, 128.0, 124.4, 123.7, 123.0, 117.3, 112.2, 112.1, 62.6, 53.9, 52.7, 33.0, 22.4; *m/z* (ESI–MS) (^{35}Cl/^{35}Cl/^{79}Br) 423.0 $[M + H]^+$, (^{35}Cl/^{35}Cl/^{81}Br) or (^{35}Cl/^{37}Cl/^{79}Br) 425.0 $[M + H]^+$, (^{35}Cl/^{37}Cl/^{81}Br) 427.0 $[M + H]^+$.



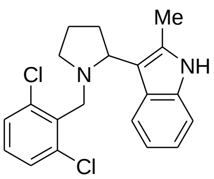
3-(1-(2,6-dichlorobenzyl)pyrrolidin-2-yl)-6-chloro-1H-indole (5p): Following the general procedure compound **5p** was obtained from 6-chloroindole, pyrrolidine and 2,6-dichlorobenzaldehyde as a yellow oil in 79% yield (R_f = 0.44 in hexanes/EtOAc 75:25 v/v); IR (KBr) 3451, 2965, 2876, 2842, 2802, 1620, 1561, 1455, 1435, 1371, 1334, 1196, 1090, 905, 804, 777, 765, 739 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) 8.01 (br s, 1H), 7.74 (d, J = 8.5 Hz, 1H), 7.25–7.23 (m, 1H), 7.18 (d, J = 2.2 Hz, 1H), 7.12 (d, J = 8.0 Hz, 2H), 7.08–7.03 (m, 1H), 6.99–6.93 (m, 1H), 3.95 (d, J = 12.2 Hz, 1H), 3.75 (app t, J = 8.2 Hz, 1H), 3.69 (d, J = 12.2 Hz, 1H), 3.11–3.04 (m, 1H), 2.61 (app q, J = 8.9 Hz, 1H), 2.26–2.17 (m, 1H), 2.09–2.00 (m, 1H), 1.99–1.88 (m, 1H), 1.87–1.78 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.8, 136.5, 135.0, 128.2, 128.1, 127.4, 125.3, 123.0, 121.3, 119.5, 117.8, 110.7, 62.5, 53.9, 52.7, 32.8, 22.5; *m/z* (ESI–MS) (^{35}Cl/^{35}Cl/^{35}Cl) 379.0 [M + H]$^+$, (^{35}Cl/^{35}Cl/^{37}Cl) 381.0 [M + H]$^+$.



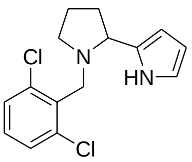
3-(1-(2,6-dichlorobenzyl)pyrrolidin-2-yl)-1-methyl-1H-indole (5q): Following the general procedure compound **5q** was obtained from 1-methylindole, pyrrolidine and 2,6-dichlorobenzaldehyde as a yellow oil in 46% yield (R_f = 0.58 in hexanes/EtOAc 75:25 v/v); IR (KBr) 3050, 2954, 2875, 2798, 1615, 1581, 1561, 1474, 1435, 1327, 1241, 1196, 1155, 1093, 1012, 887, 765, 739 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) 7.87 (d, J = 8.0 Hz, 1H), 7.30 (d, J = 8.1 Hz, 1H), 7.28–7.22 (m, 1H), 7.18 (d, J = 8.0 Hz, 2H), 7.16–7.11 (comp, 2H), 7.00 (t, J = 8.0 Hz, 1H), 4.03 (d, J = 12.2 Hz, 1H), 3.83 (app t, J = 8.3 Hz, 1H), 3.77 (s, 3H), 3.73 (d, J = 12.2 Hz, 1H), 3.12–3.06 (m, 1H), 2.65 (app q, J = 8.9 Hz, 1H), 2.32–2.23 (m, 1H), 2.19–2.08 (m, 1H), 2.05–1.94 (m, 1H), 1.93–1.82 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.2, 136.5, 135.4, 128.0(3), 128.0(1), 127.3, 127.2, 121.2, 120.3, 118.3, 116.1, 108.9, 62.5, 53.7, 52.7, 33.1, 32.5, 22.4; *m/z* (ESI–MS) (^{35}Cl/^{35}Cl) 359.1 [M + H]$^+$, (^{35}Cl/^{37}Cl) 361.1 [M + H]$^+$.



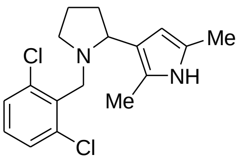
3-(1-(2,6-dichlorobenzyl)pyrrolidin-2-yl)-2-methyl-1H-indole (5r): Following the general procedure compound **5r** was obtained from 2-methylindole, pyrrolidine and 2,6-dichlorobenzaldehyde as a yellow oil in 97% yield (R_f = 0.53 in hexanes/EtOAc 75:25 v/v); IR (KBr) 3403, 3054, 2961, 2915, 2835, 2795, 1618, 1581, 1561, 1460, 1435, 1374, 1298, 1265, 1195, 1153, 1092, 889, 765, 742 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) 7.86 (d, J = 7.6 Hz, 1H), 7.66 (br s, 1H), 7.23 (d, J = 7.9 Hz, 1H), 7.19–7.10 (comp, 3H), 7.10–7.04 (m, 1H), 7.01–6.93 (m, 1H), 3.93 (d, J = 12.1 Hz, 1H), 3.74 (app t, J = 8.6 Hz, 1H), 3.62 (d, J = 12.1 Hz, 1H), 3.08 (app t, J = 8.1 Hz, 1H), 2.63–2.54 (m, 1H), 2.49 (s, 3H), 2.32–2.21 (m, 1H), 2.19–2.09 (m, 1H), 2.07–1.96 (m, 1H), 1.93–1.82 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.5, 135.3, 135.2, 132.5, 128.1, 128.0(0), 127.9(7), 120.6, 120.3, 118.5, 111.7, 109.8, 62.1, 53.9, 52.4, 31.0, 22.7, 12.1; *m/z* (ESI–MS) (^{35}Cl/^{35}Cl) 359.1 [M + H]$^+$, (^{35}Cl/^{37}Cl) 361.1 [M + H]$^+$.



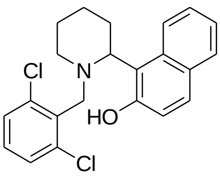
2-(1-(2,6-dichlorobenzyl)pyrrolidin-2-yl)-1H-pyrrole (5s): Following the general procedure compound **5s** was obtained from pyrrole, pyrrolidine and 2,6-dichlorobenzaldehyde as a brown solid in 48% yield (R_f = 0.39 in hexanes/EtOAc 75:25 v/v); mp: 88–90 ºC; IR (KBr) 3457, 3285, 3056, 2954, 2843, 1578, 1560, 1458, 1436, 1370, 1359, 1195, 1122, 1088, 1028, 885, 814, 779, 763, 730, 602 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 8.62 (br s, 1H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.10 (t, *J* = 8.0 Hz, 1H), 6.76–6.68 (m, 1H), 6.17–6.11 (m, 1H), 6.10–6.04 (m, 1H), 3.95 (d, *J* = 12.2 Hz, 1H), 3.72 (d, *J* = 12.2, 1H), 3.70–3.62 (m, 1H), 3.00–2.88 (m, 1H), 2.66–2.54 (m, 1H), 2.26–2.13 (m, 1H), 1.91–1.73 (comp, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.5, 134.8, 133.3, 128.5, 128.4, 116.6, 107.8, 105.9, 62.8, 53.1, 52.5, 33.2, 22.5; *m/z* (ESI–MS) ($^{35}Cl/^{35}Cl$) 295.0 $[M + H]^+$, ($^{35}Cl/^{37}Cl$) 297.0 $[M + H]^+$.



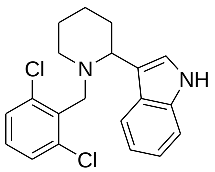
3-(1-(2,6-dichlorobenzyl)pyrrolidin-2-yl)-2,5-dimethyl-1H-pyrrole (5t): Following the general procedure compound **5t** was obtained from 2,5-dimethylpyrrole, pyrrolidine and 2,6-dichlorobenzaldehyde as a yellow oil in 57% yield (R_f = 0.31 in hexanes/EtOAc 75:25 v/v); IR (KBr) 3451, 3364, 3054, 2966, 2836, 1561, 1435, 1196, 1150, 1090, 890, 765, 736, 636 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 7.40 (br s, 1H), 7.24 (d, *J* = 8.1 Hz, 2H), 7.06 (t, *J* = 8.1 Hz, 1H), 5.91–5.87 (m, 1H), 3.92 (d, *J* = 12.0 Hz, 1H), 3.50 (d, *J* = 12.0 Hz, 1H), 3.37–3.30 (m, 1H), 2.98–2.91 (m, 1H), 2.50 (app q, *J* = 8.7 Hz, 1H), 2.26 (s, 3H), 2.22 (s, 3H), 2.10–2.02 (m, 1H), 1.91–1.79 (comp, 2H), 1.78–1.69 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.7, 135.8, 128.2, 128.1, 124.8, 123.6, 119.5, 105.9, 62.4, 53.4, 52.1, 32.6, 22.0, 13.0, 11.2; *m/z* (ESI–MS) ($^{35}Cl/^{35}Cl$) 323.0 $[M + H]^+$, ($^{35}Cl/^{37}Cl$) 325.0 $[M + H]^+$.



1-(1-(2,6-dichlorobenzyl)piperidin-2-yl)naphthalen-2-ol (5u): Following the general procedure compound **5u** was obtained from 2-naphthol, piperidine and 2,6-dichlorobenzaldehyde as a colorless oil in 16% yield (R_f = 0.47 in hexanes/EtOAc 90:10 v/v); IR (KBr) 3059, 2937, 2856, 1621, 1599, 1582, 1561, 1519, 1467, 1436, 1407, 1271, 1243, 1232, 1090, 931, 815, 779, 765, 743, 711 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 11.20 (br s, 1H), 8.02 (d, *J* = 8.7 Hz, 1H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.65 (d, *J* = 8.7 Hz, 1H), 7.51–7.44 (m, 1H), 7.34–7.27 (m, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.11–7.00 (comp, 2H), 4.30 (dd, *J* = 11.3, 3.1 Hz, 1H), 4.15 (d, *J* = 12.8 Hz, 1H), 3.71 (d, *J* = 12.8 Hz, 1H), 3.01–2.93 (m, 1H), 2.52–2.41 (m, 1H), 2.13–1.98 (m, 1H), 1.93–1.81 (comp, 2H), 1.81–1.72 (m, 1H), 1.65 (app qt, *J* = 13.0, 3.1 Hz, 1H), 1.49 (app qt, *J* = 13.0, 3.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.9, 137.2, 132.4, 132.0, 129.2, 129.0, 128.9, 128.7, 128.3, 126.2, 122.3, 120.8, 119.2, 117.9, 64.4, 55.8, 52.4, 30.9, 25.7, 24.3; *m/z* (ESI–MS) ($^{35}Cl/^{35}Cl$) 386.2 $[M + H]^+$, ($^{35}Cl/^{37}Cl$) 388.2 $[M + H]^+$.

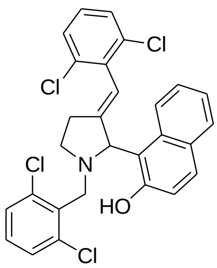


3-(1-(2,6-dichlorobenzyl)piperidin-2-yl)-1H-indole (5v): Following the general procedure compound **5v** was obtained from indole, piperidine and 2,6-dichlorobenzaldehyde as a yellow oil in 64% yield (R_f = 0.22 in hexanes/EtOAc 75:25 v/v); IR (KBr) 3412, 3184, 2931, 2846, 2796, 1579, 1560, 1457, 1435, 1229, 1190, 1087, 1040, 778, 762, 735, 718 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) 8.07 (br s, 1H), 7.89 (app d, *J* = 7.9 Hz, 1H), 7.39–7.32 (m, 1H), 7.32-7.27 (m, 1H), 7.23–7.15 (comp, 3H), 7.15–7.09 (m, 1H), 7.04–6.97 (m, 1H), 3.90 (d, *J* = 11.9 Hz, 1H), 3.55 (app d, *J* = 10.5 Hz, 1H), 3.45 (d, *J* = 11.9 Hz, 1H), 2.89–2.79 (m, 1H), 2.39–2.28 (m, 1H), 2.14–2.00 (m, 1H), 1.94–1.75 (comp, 2H), 1.70–1.54 (comp, 2H), 1.52–1.39 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.2, 136.0, 128.2, 128.1, 127.3, 122.6, 121.8, 120.2, 119.0, 111.0, 61.6, 54.7, 53.0, 34.6, 26.1, 25.2; *m/z* (ESI–MS) ($^{35}Cl/^{35}Cl$) 359.1 $[M + H]^+$, ($^{35}Cl/^{37}Cl$) 361.1 $[M + H]^+$.

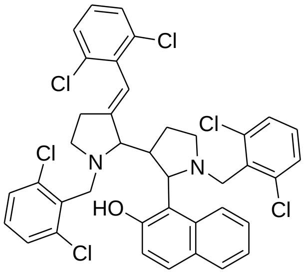


(E)-1-(1-(2,6-dichlorobenzyl)-3-(2,6-dichlorobenzylidene)pyrrolidin-2-yl)naphthalen-2-ol (6) and (E)-1-(1-(2,6-dichlorobenzyl)-3-(1-(2,6-dichlorobenzyl)-3-(2,6-dichlorobenzylidene)pyrrolidin-2-yl)pyrrolidin-2-yl)naphthalen-2-ol (7): To a solution of 2-naphthol (0.75 mmol, 1.5 equiv) in toluene (2 mL) were added benzoic acid (0.1 mmol, 0.2 equiv), pyrrolidine (0.75 mmol, 1.5 equiv) and 2,6-dichlorobenzaldehyde (0.5 mmol, 1 equiv). The mixture was heated under reflux for 15 min. Subsequently, the reaction mixture was allowed to cool to room temperature, diluted with EtOAc (10 ml) and washed with saturated aqueous $NaHCO_3$ (3 x 5 mL). The combined aqueous layer was extracted with EtOAc (3 x 5 mL) and the combined organic layer was washed with water (20 mL), brine (20 mL) and dried over anhydrous Na_2SO_4. Solvent was then removed under reduced pressure and the residue was purified by silica gel chromatography. Compound **5a** was obtained in 22% yield.

In addition, compound **6** was obtained as a colorless oil in 22% yield (R_f = 0.40 in hexanes/EtOAc 90:10 v/v); IR (KBr) 3060, 2966, 2834, 2248, 1932, 1675, 1621, 1598, 1581, 1560, 1517, 1467, 1436, 1406, 1361, 1271, 1235, 1199, 1141, 1091, 944, 816, 775, 744, 674, 645 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) 11.30 (br s, 1H), 8.16 (d, *J* = 8.7 Hz, 1H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.66 (d, *J* = 8.8 Hz, 1H), 7.53 (ddd, *J* = 8.7, 6.8, 1.2 Hz, 1H), 7.35–7.30 (m, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.05–6.99 (comp, 3H), 5.78–5.74 (m, 1H), 5.37–5.33 (m, 1H), 4.22 (d, *J* = 12.7 Hz, 1H), 4.08 (d, *J* = 12.7 Hz, 1H), 3.34 (app t, *J* = 8.6 Hz, 1H), 2.92 (ddd, *J* = 11.5, 9.3, 7.4 Hz, 1H), 2.75–2.64 (m, 1H), 2.54–2.45 (m, 1H); ^{13}C NMR (125 MHz, CDCl3) δ 156.1, 147.9, 136.8, 135.2, 134.5, 133.6, 132.4, 129.4, 129.2, 128.6, 128.3(2), 128.3(1), 128.1, 127.6, 126.4, 122.2, 121.4, 119.4, 118.2, 114.7, 68.9, 53.3, 52.5, 29.3; m/z (ESI–MS) ($^{35}Cl/^{35}Cl/^{35}Cl/^{35}Cl$) 527.9 $[M + H]^+$, ($^{35}Cl/^{35}Cl/^{35}Cl/^{37}Cl$) 529.9 $[M + H]^+$.

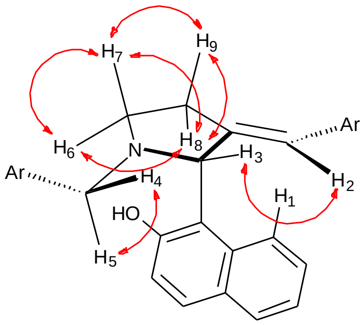


In addition, compound **7** was obtained as a yellow oil in 33% yield (mixture of diastereomers) (R_f = 0.33 in hexanes/EtOAc 90:10 v/v); IR (KBr) 3054, 2960, 2918, 2850, 2807, 1621, 1598, 1581, 1561, 1517, 1466, 1436, 1364, 1304, 1270, 1236, 1199, 1091, 909, 816, 776, 735 cm^{-1}; ^1H NMR (Note: Due to overlapping peaks, integration values of the diastereomers are reported together) (500 MHz, $CDCl_3$) 11.79 (br s, 1.2H), 8.39 (d, *J* = 8.6 Hz, 1.0H), 8.32 (d, *J* = 8.6 Hz, 0.3H), 7.88–7.73 (comp, 1.5H), 7.70–7.60 (comp, 1.4H), 7.52–7.35 (comp, 4.0H), 7.35–7.25 (comp, 4.0H), 7.23 (d, *J* = 8.0 Hz, 2.2H), 7.21–7.13 (comp, 4.2H), 7.13–6.97 (comp, 4.4H), 6.78 (s, 1.1H), 6.12–6.04 (m, 0.3H), 5.05 (d, *J* = 8.0 Hz, 0.3H), 4.96 (d, *J* = 8.1 Hz, 1.0H), 4.20–3.99 (comp, 2.6H), 3.95 (d, *J* = 12.7 Hz, 1.0H), 3.73 (d, *J* = 12.4 Hz, 1.1H), 3.69 (s, 0.3H), 3.51 (d, *J* = 12.4 Hz, 1.3H), 3.49–3.44 (comp, 0.9H), 3.33–3.19 (comp, 1.2H), 3.18–2.95 (comp, 3.2H), 2.89–2.71 (comp, 1.5H), 2.65–2.54 (comp, 0.4H), 2.55–2.44 (comp, 1.1H), 2.42–2.06 (comp, 6.0H); ^{13}C NMR of the diastereomers (125 MHz, CDCl3) δ 156.4, 156.3, 149.2, 137.1, 136.8, 136.7, 136.6, 135.8, 135.7, 135.0, 134.8, 134.6(4), 134.5(8), 133.5, 133.3(0), 133.2(8), 133.0, 129.1, 129.0(5), 129.0(0), 128.9, 128.8, 128.7(3), 128.7(1), 128.6, 128.5(4), 128.4(9), 128.4(2), 128.3, 128.2(5), 128.2(1), 127.9, 127.8, 125.9, 125.6, 122.3, 122.2, 122.1(4), 122.1(0), 119.9, 119.8, 117.8, 117.4, 117.2, 115.8, 70.2, 68.9, 67.5, 67.2, 54.6, 53.3(4), 53.3(2), 52.8, 52.7, 51.5, 51.1, 50.7, 48.3, 34.6, 34.5, 31.6, 30.7, 30.0, 29.7, 29.0, 26.6, 26.3, 25.3, 22.6, 20.7, 14.1, 11.4; m/z (ESI–MS) ($^{35}Cl/^{35}Cl/^{35}Cl/^{35}Cl/^{35}Cl/^{35}Cl$) 754.7 $[M + H]^+$, ($^{35}Cl/^{35}Cl/^{35}Cl/^{35}Cl/^{35}Cl/^{37}Cl$) 756.7 $[M + H]^+$, ($^{35}Cl/^{35}Cl/^{35}Cl/^{35}Cl/^{37}Cl/^{37}Cl$) 758.7 $[M + H]^+$.

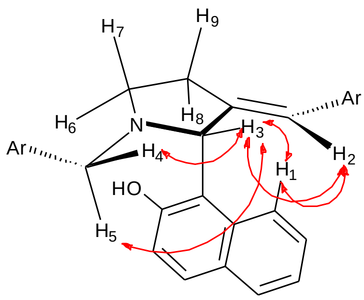


2D-NMR Analysis for Compound 6, Selected Interactions (Ar = 2,6-Dichlorophenyl):

GCOSY



NOESY



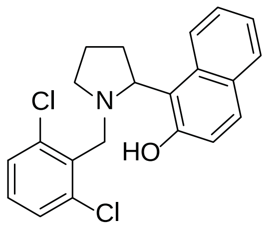
^{1}H NMR Shifts

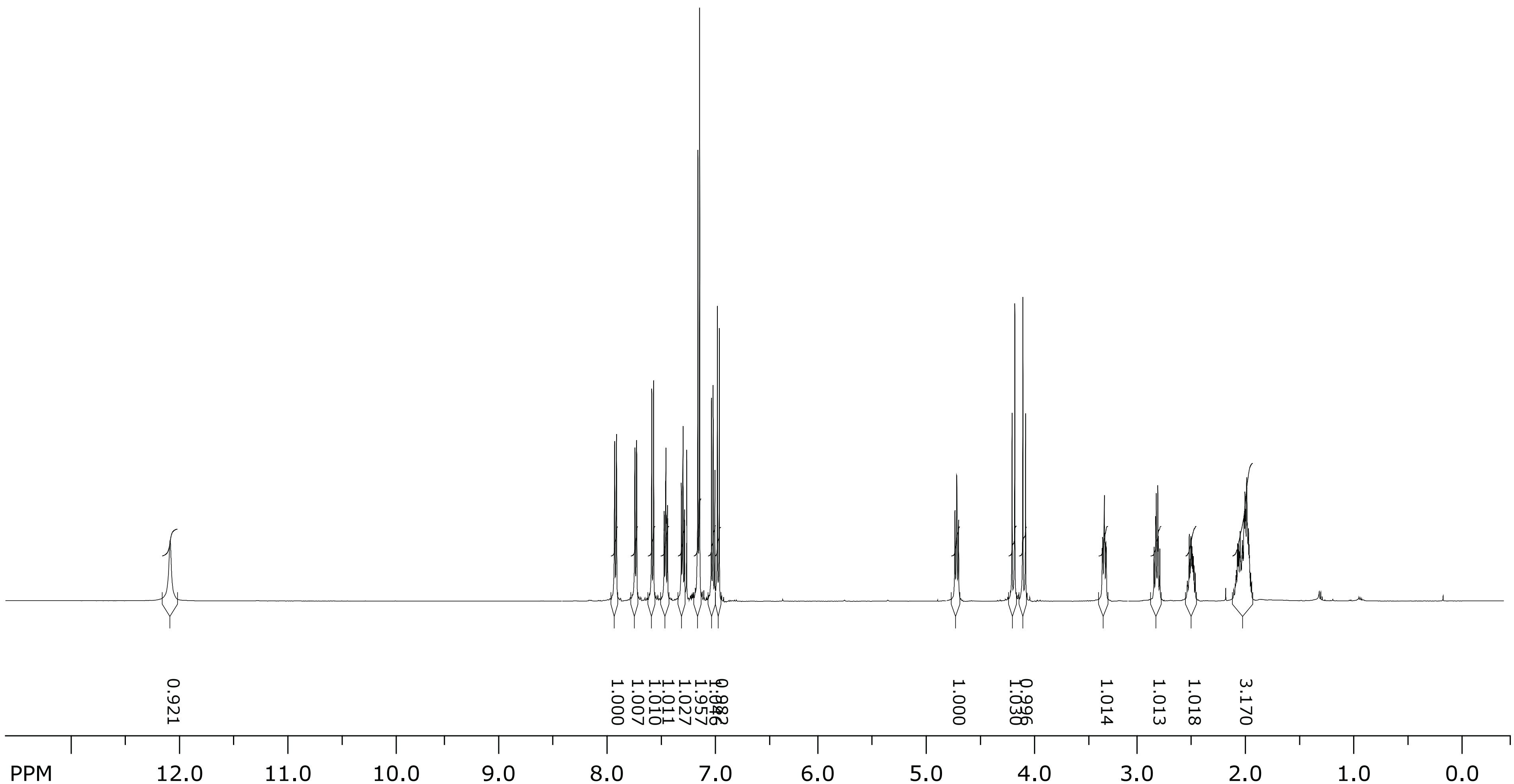
Protons	Chemical shifts (ppm)
H1	8.16
H2	5.78–5.74
H3	5.37–5.33
H4, H5	4.22, 4.08
H6	3.34
H7	2.92
H8	2.75–2.64
H9	2.54–2.45

References:

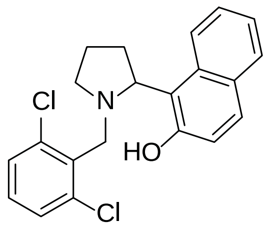
(1) Periasamy, M; Reddy, M. N.; Anwar, S. *Tetrahedron: Asymmetry* **2004**, *15*, 1809.
(2) Moriya, T.; Hagio, K.; Yoneda, N. *Synthesis*, **1980**, 728.
(3) Bi, H.-P.; Chen, W.-W.; Liang, Y.-M.; Li, C.-J. *Org. Lett.* **2009**, *11*, 3246.
(4) Zhang, C.; Seidel, D. *J. Am. Chem. Soc.* **2010**, *132*, 1798.
(5) For the reaction with 1-methylindole as the nucleophile, 2.5 equiv of 2-EHA was added.

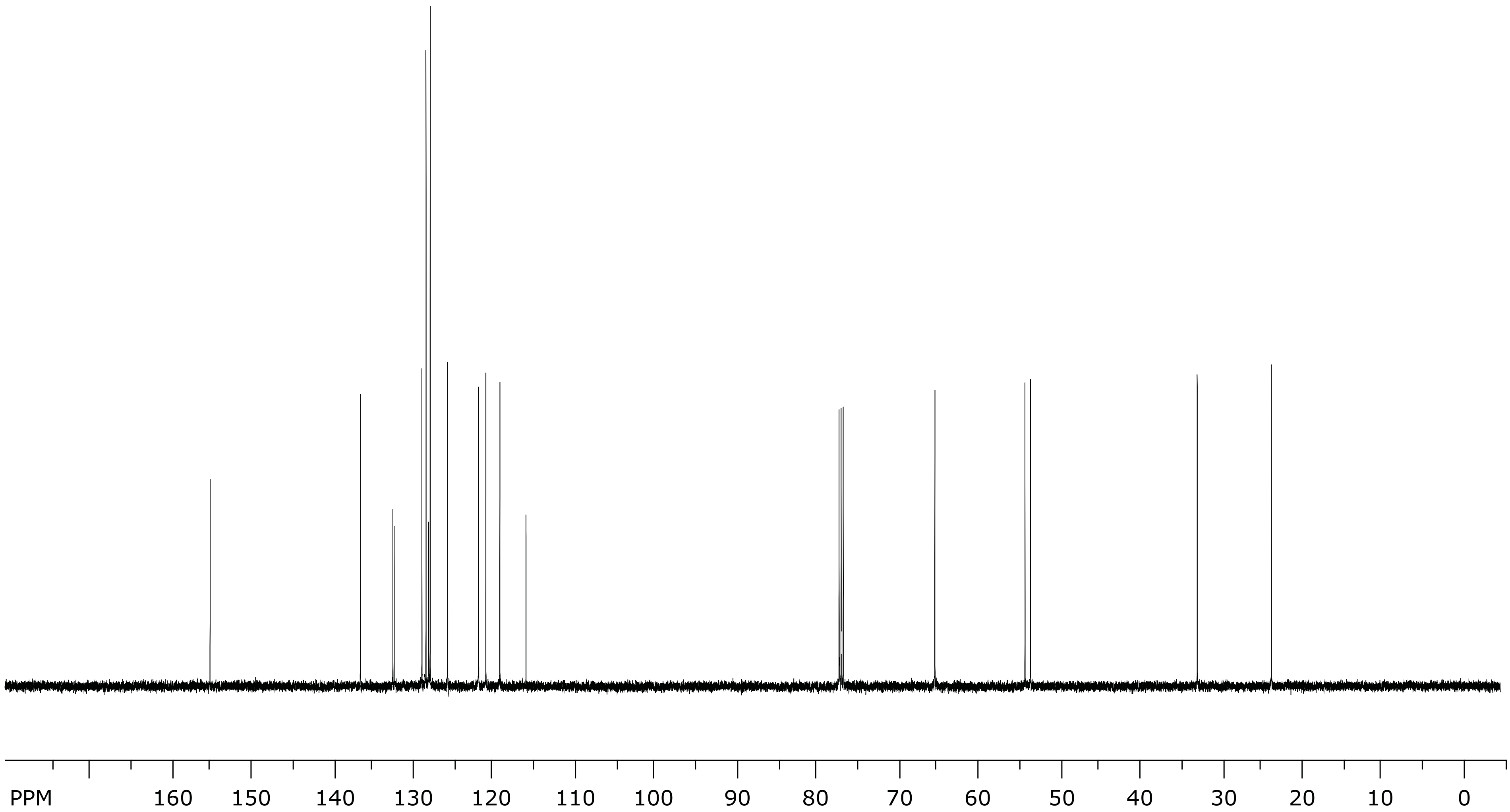
^{1}H NMR of **5a** in $CDCl_3$



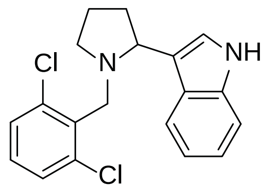


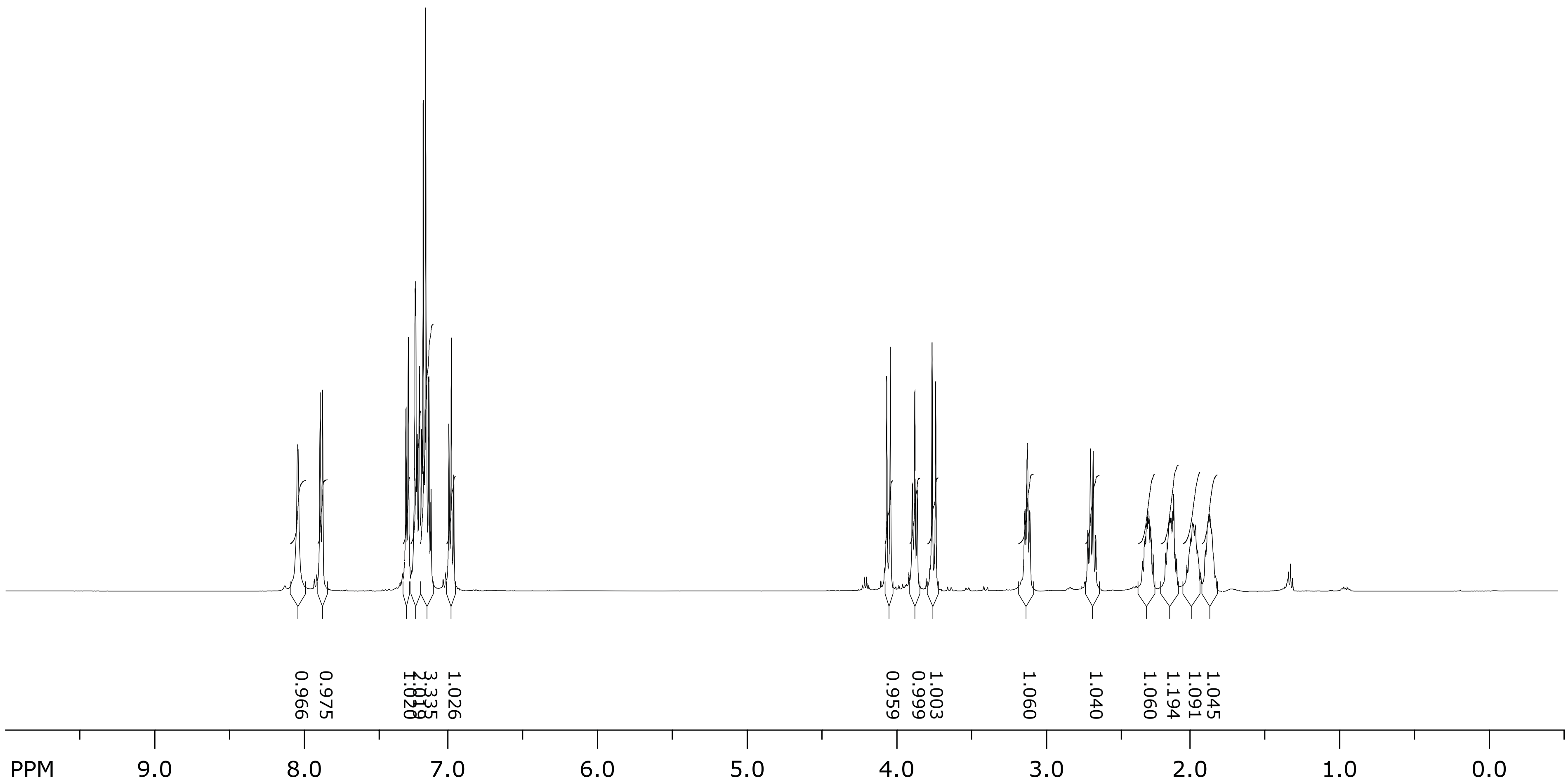
^{13}C NMR of **5a** in $CDCl_3$



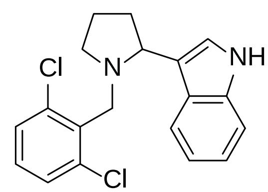


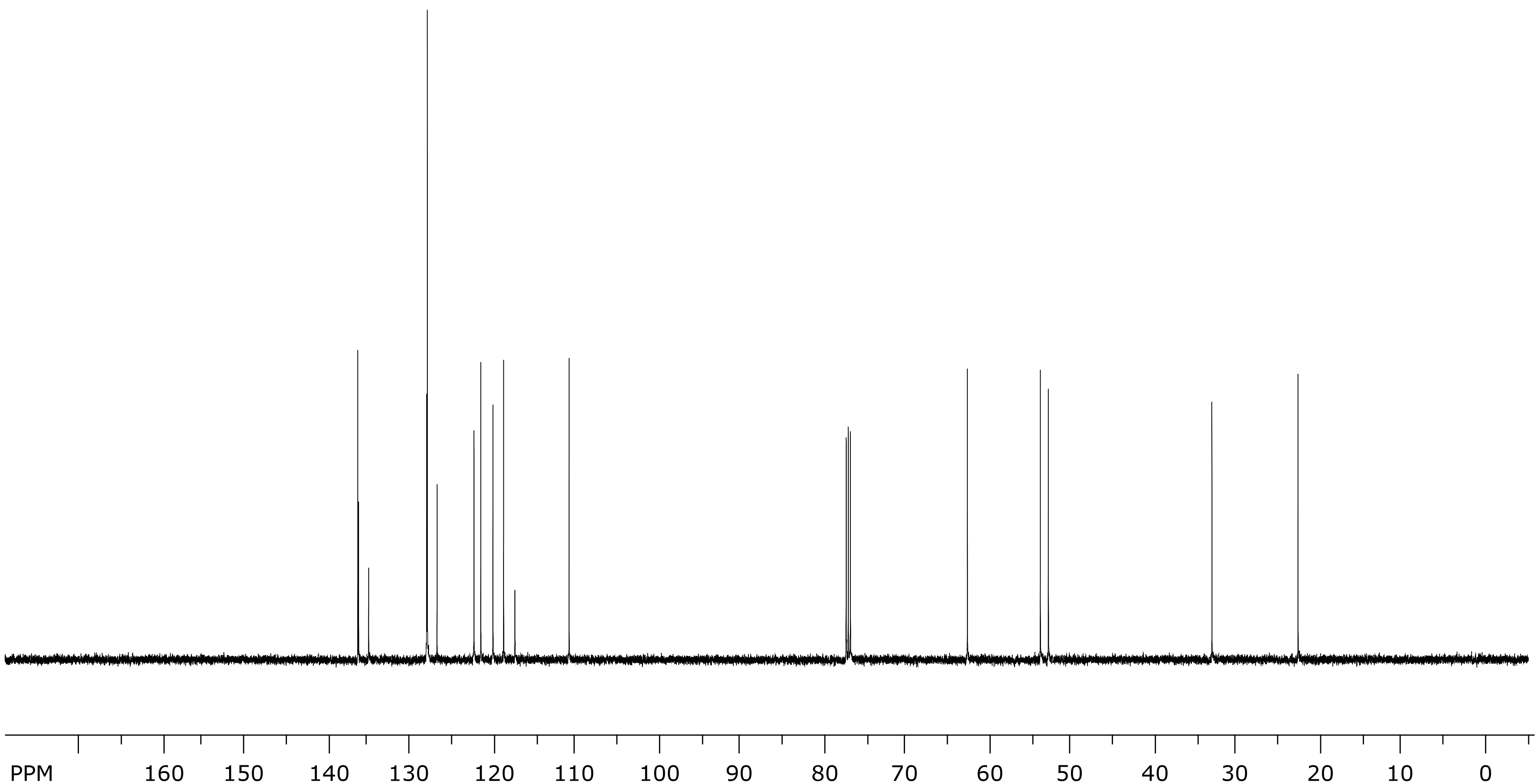
[1]H NMR of **5b** in $CDCl_3$



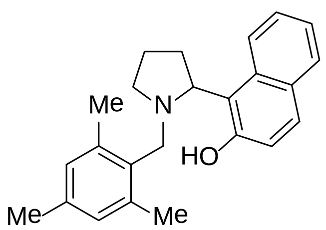


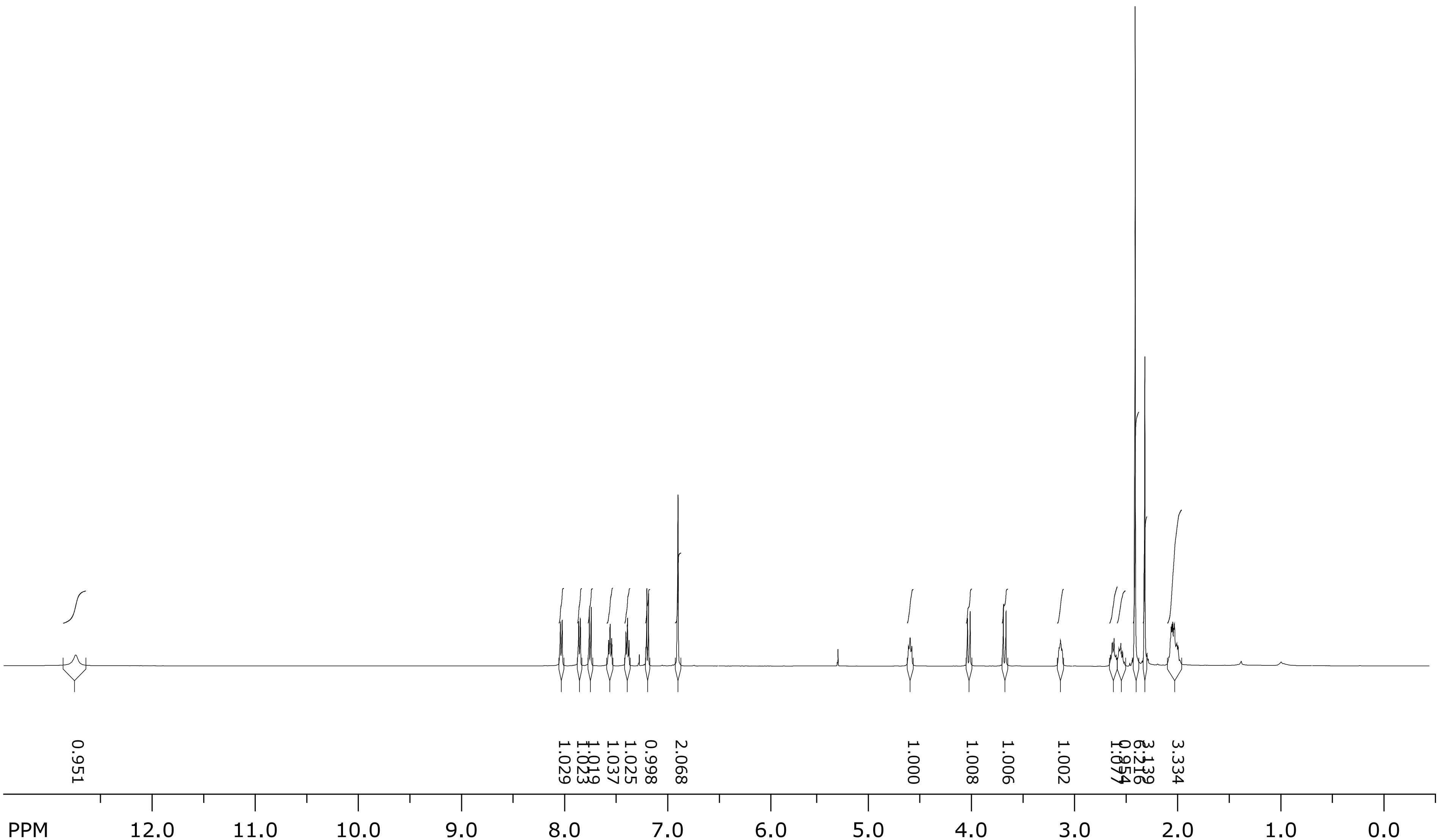
^{13}C NMR of **5b** in $CDCl_3$



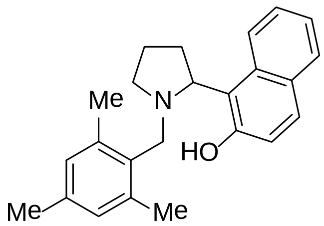


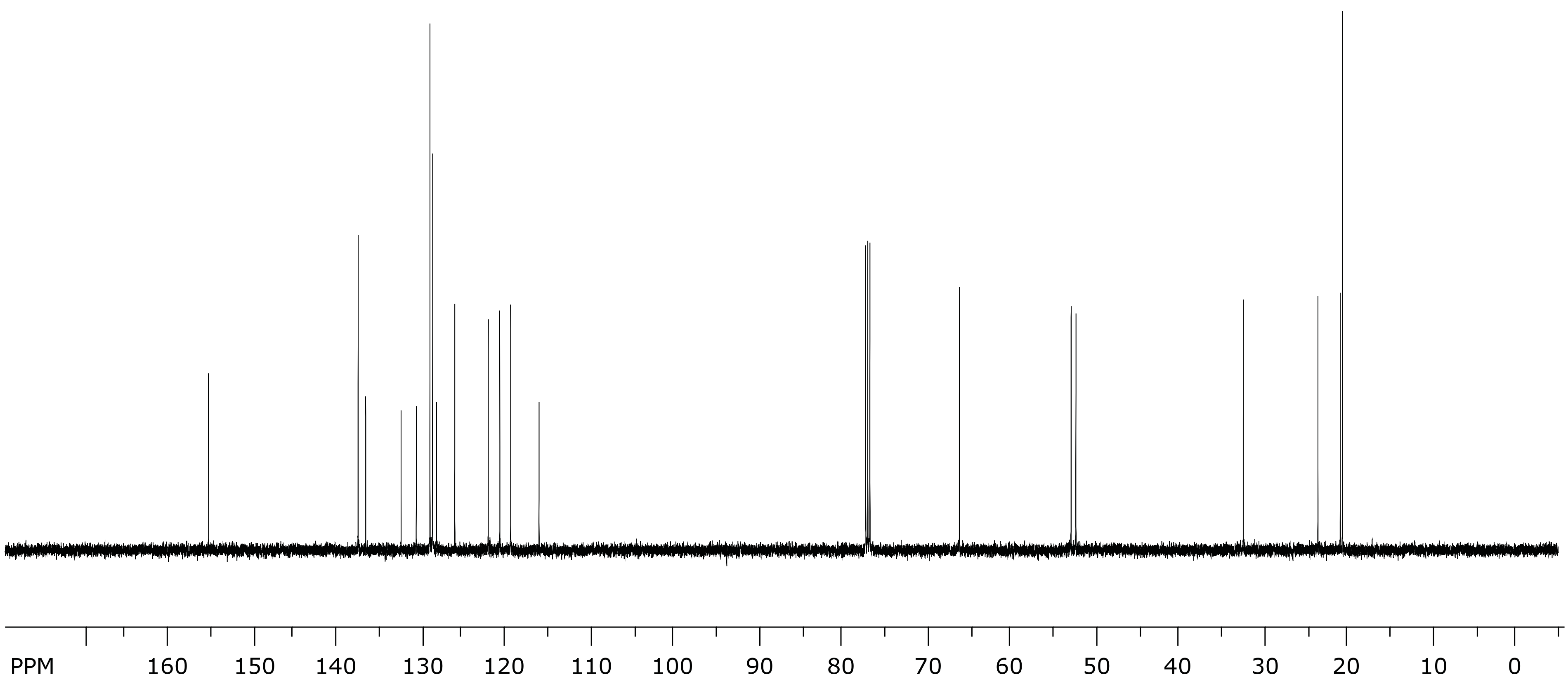
^{1}H NMR of **5d** in $CDCl_3$



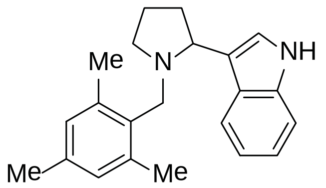


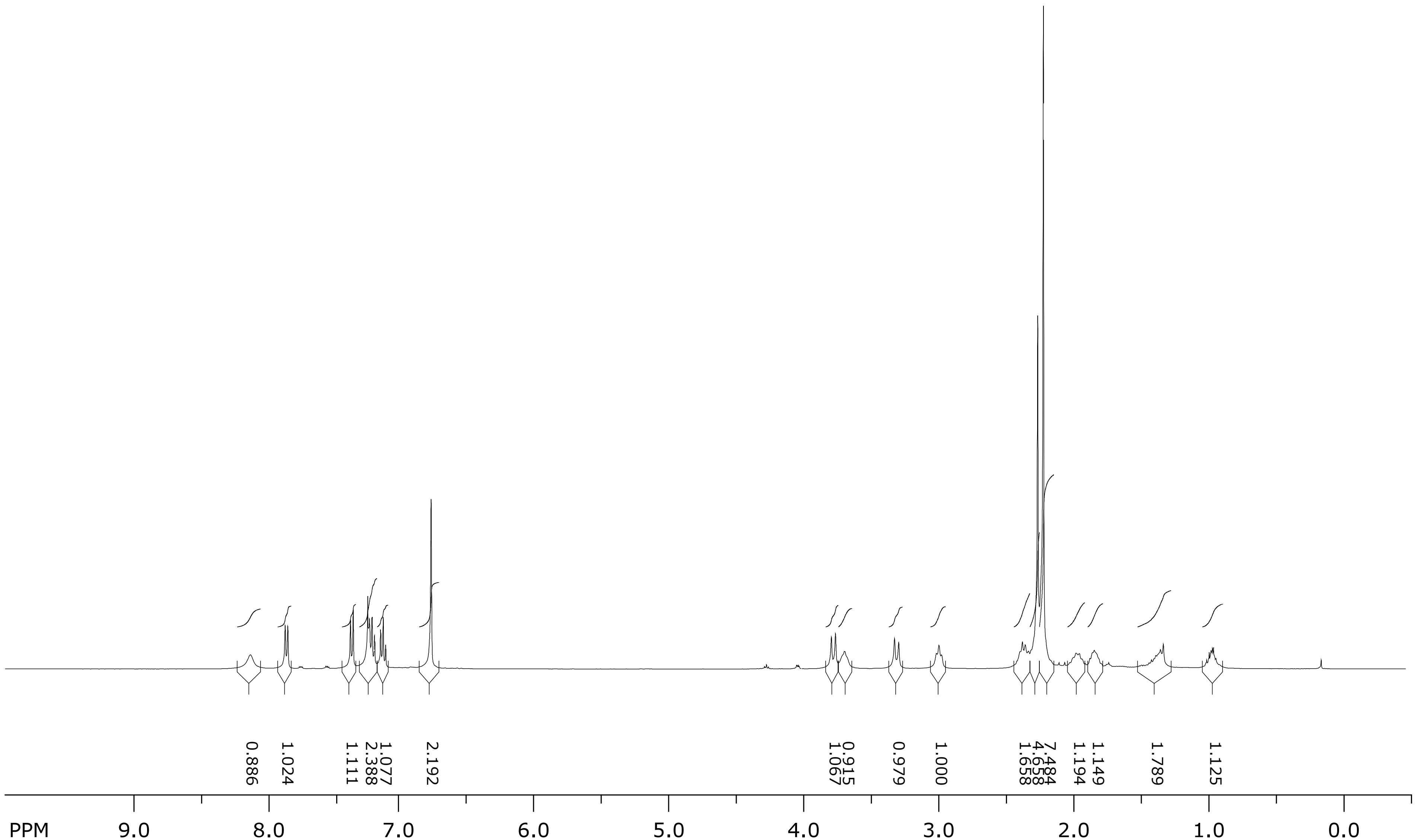
^{13}C NMR of **5d** in $CDCl_3$



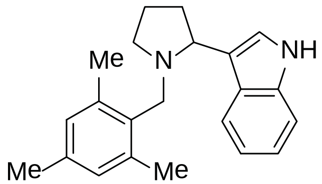


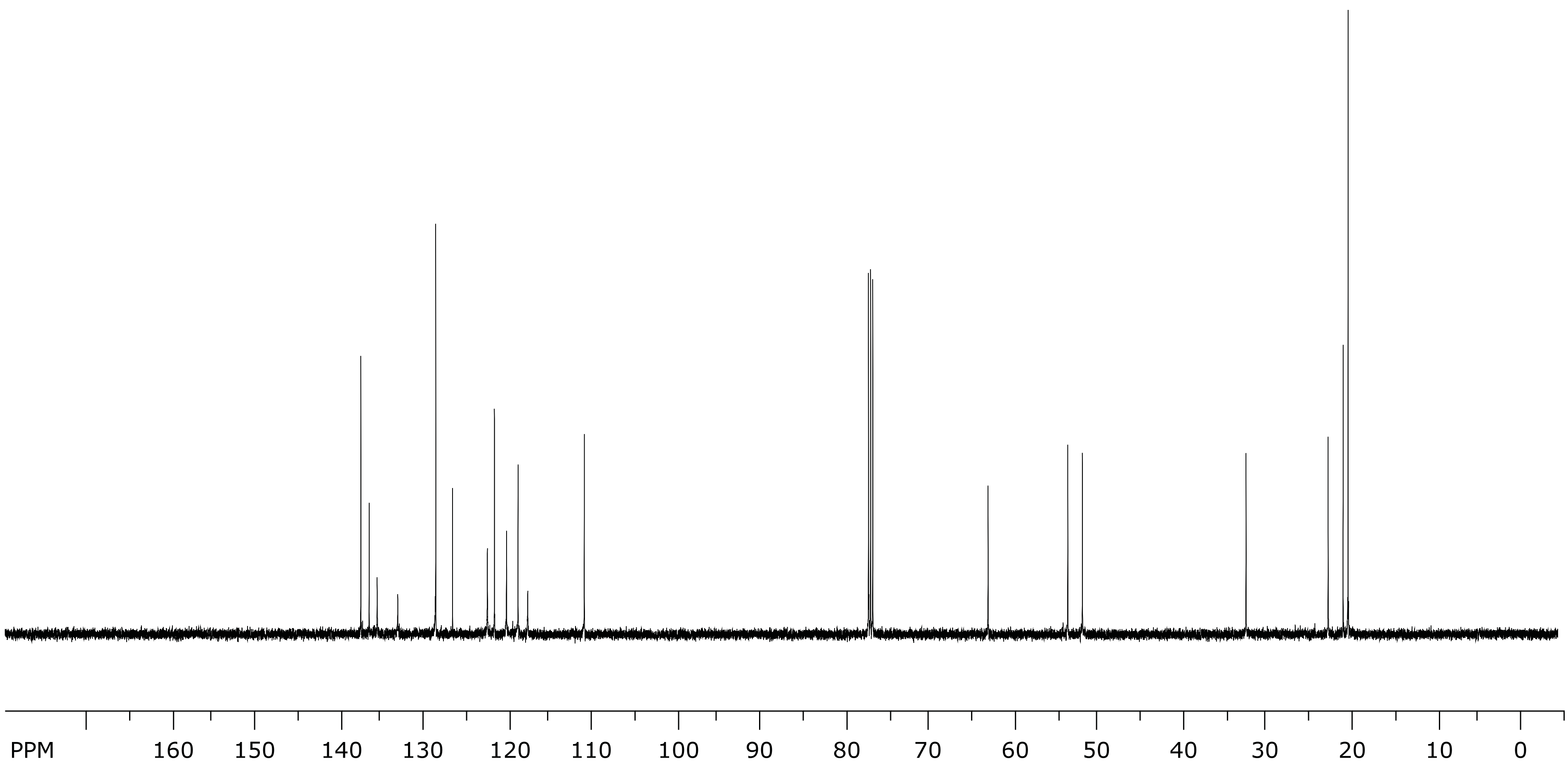
^{1}H NMR of **5f** in $CDCl_3$



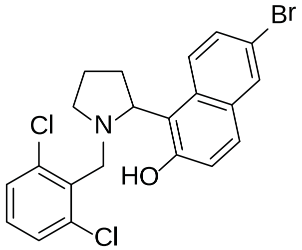


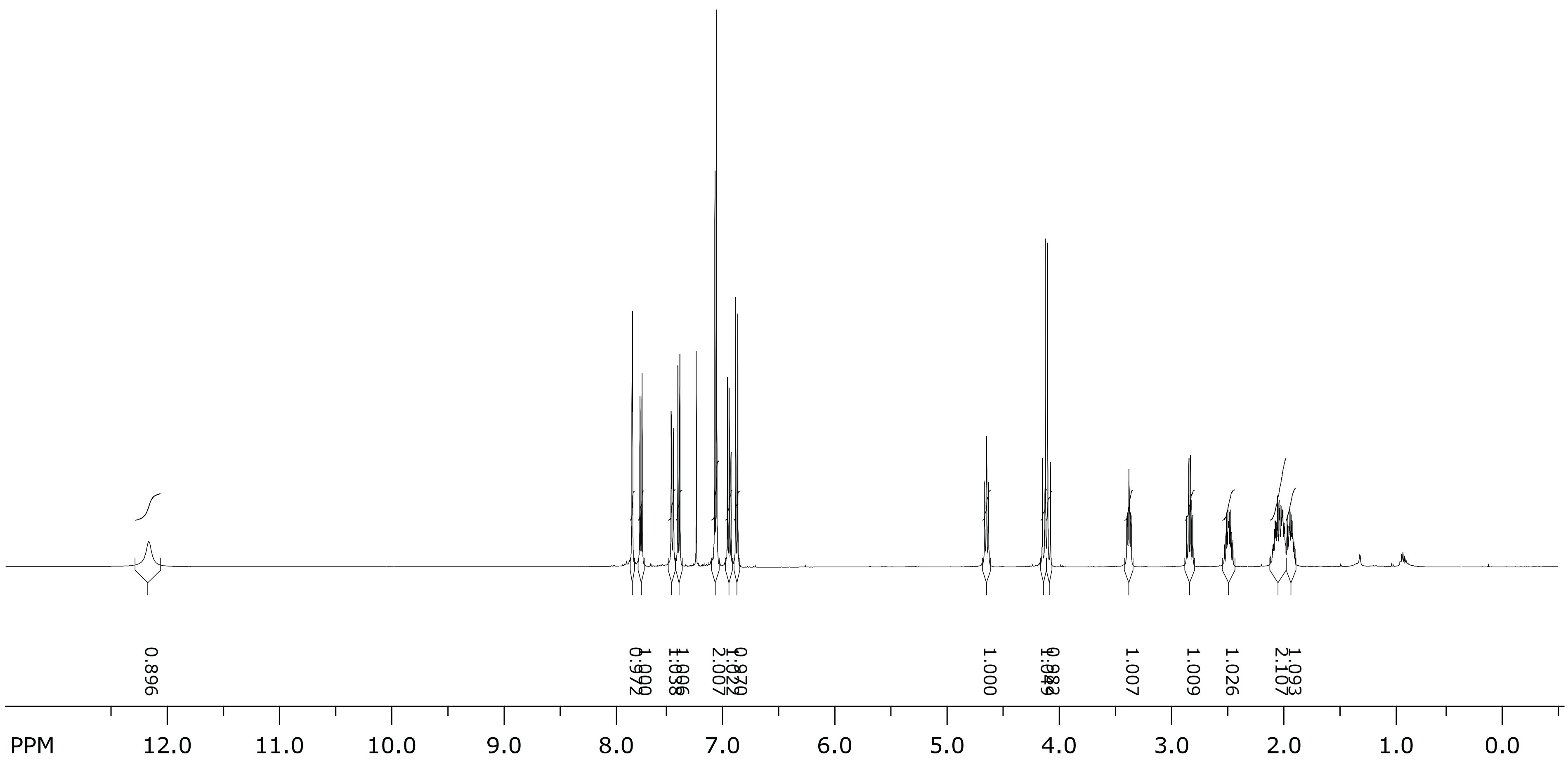
^{13}C NMR of **5f** in $CDCl_3$



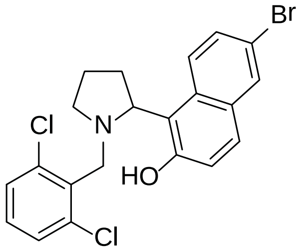


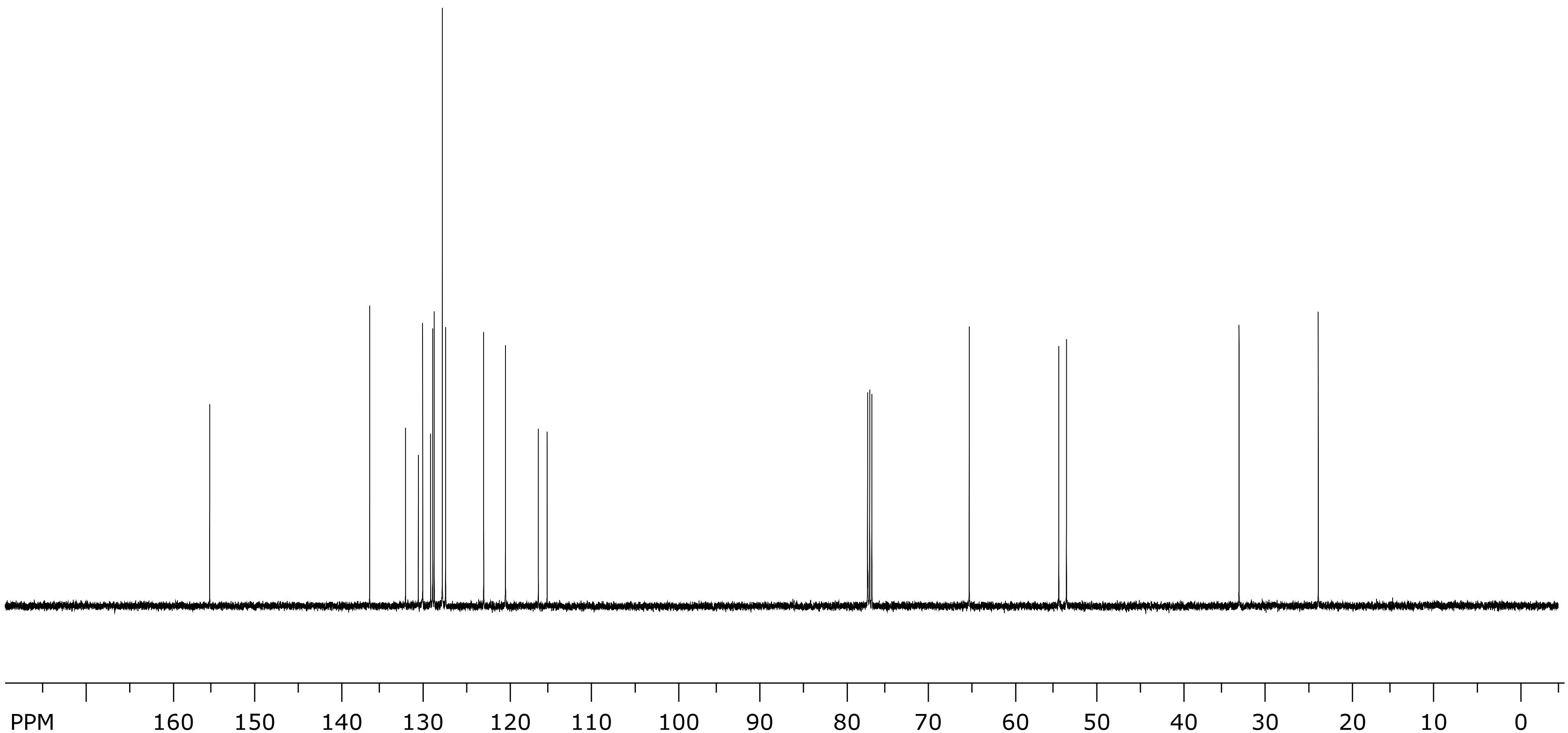
^{1}H NMR of **5g** in $CDCl_3$



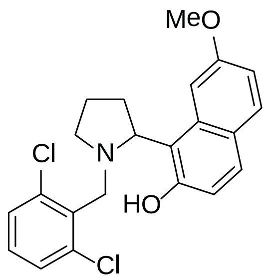


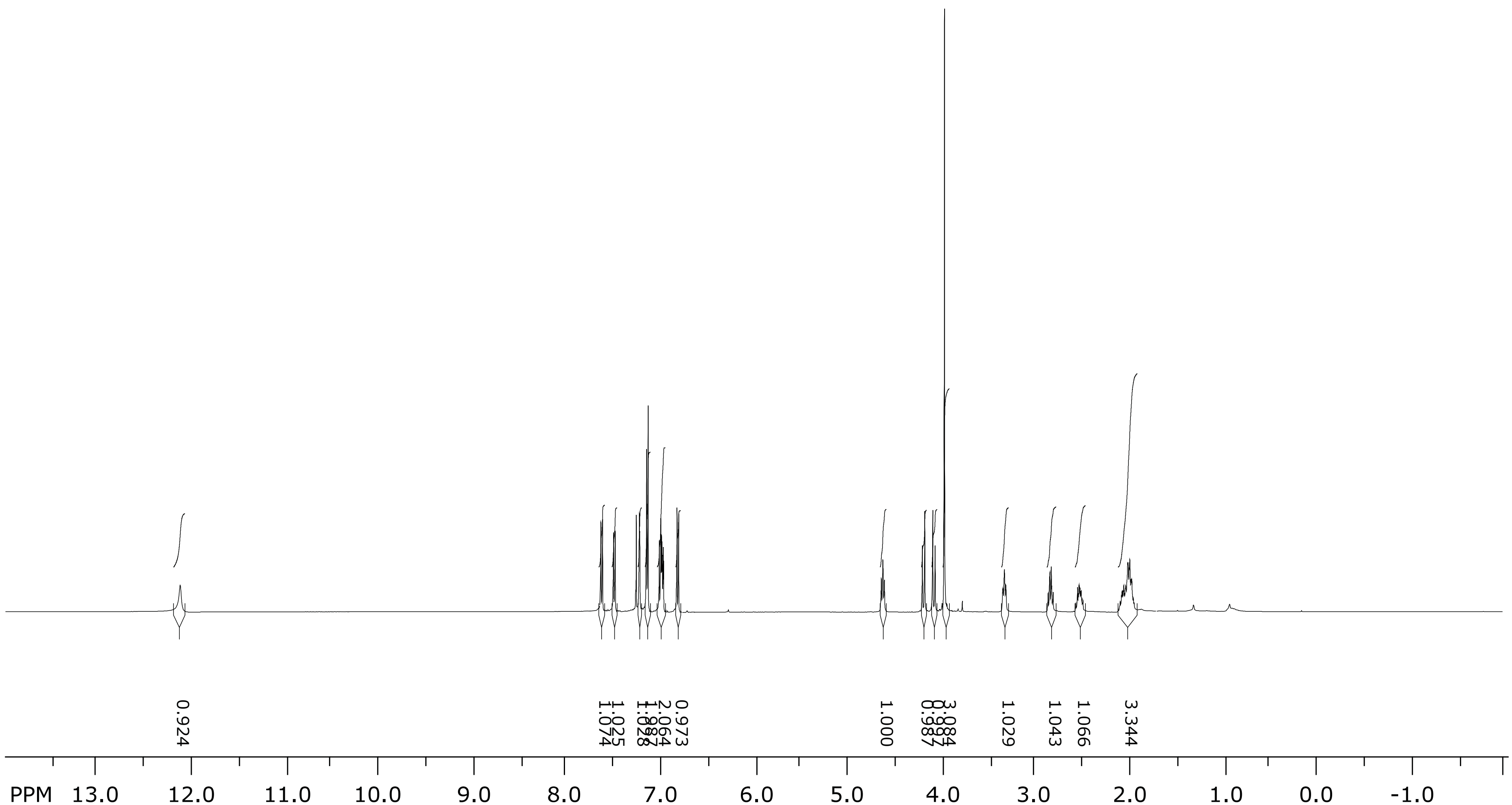
^{13}C NMR of **5g** in $CDCl_3$



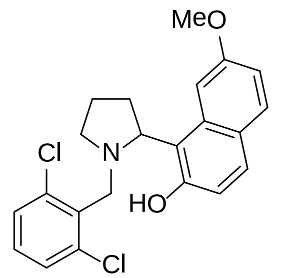


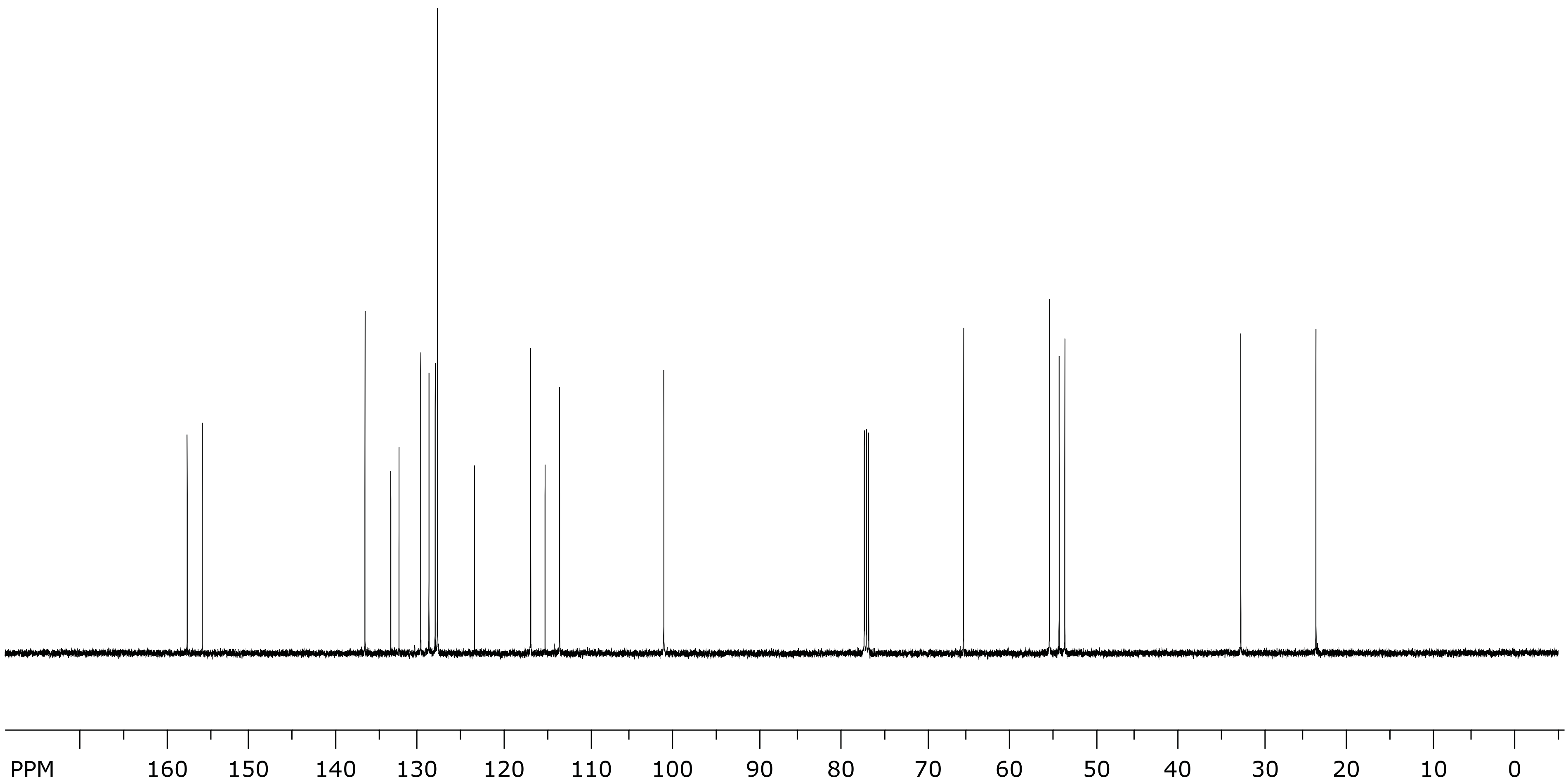
^{1}H NMR of **5h** in $CDCl_3$



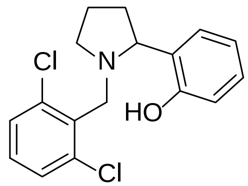


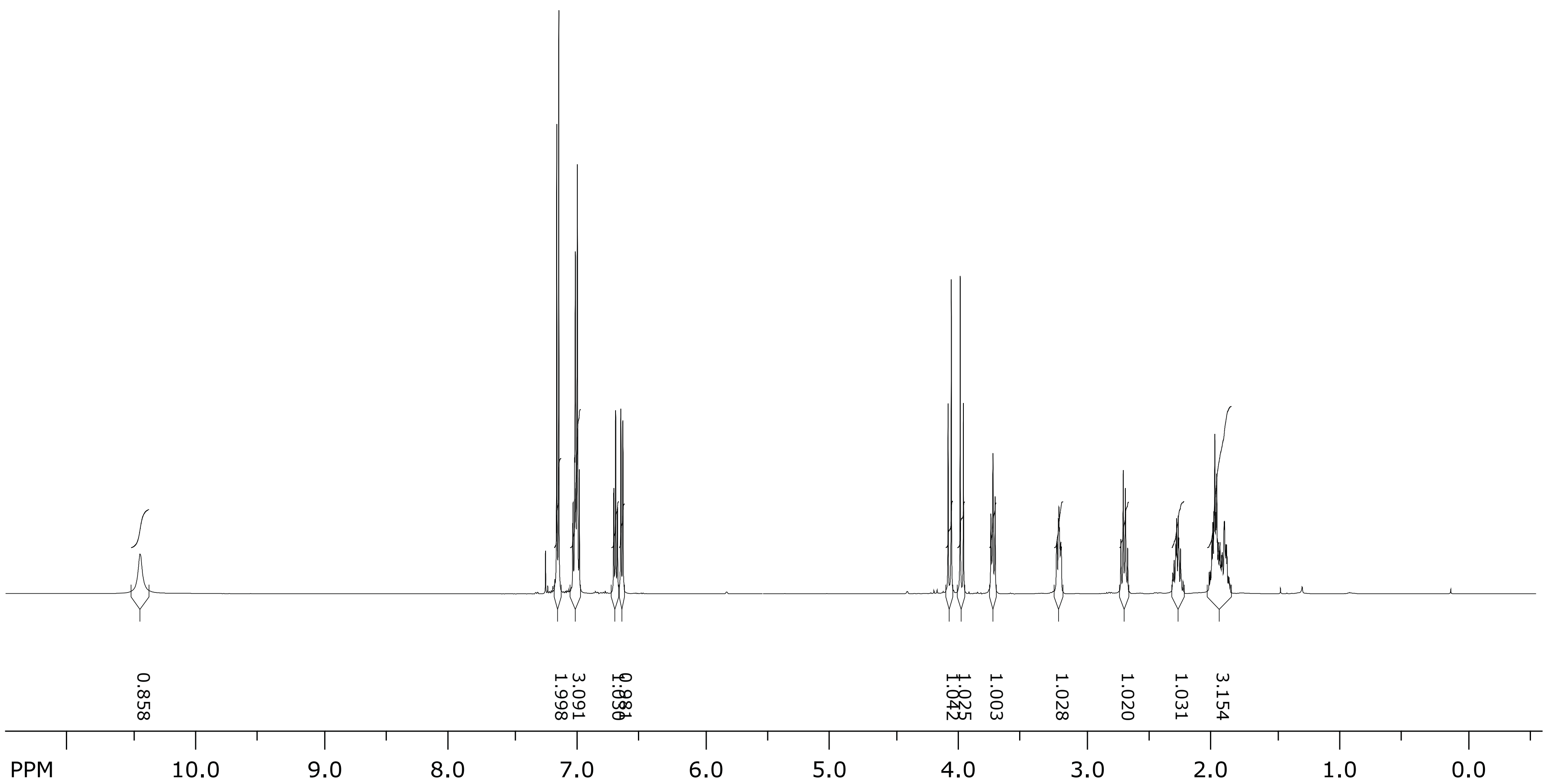
^{13}C NMR of **5h** in $CDCl_3$



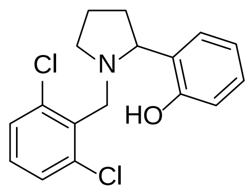


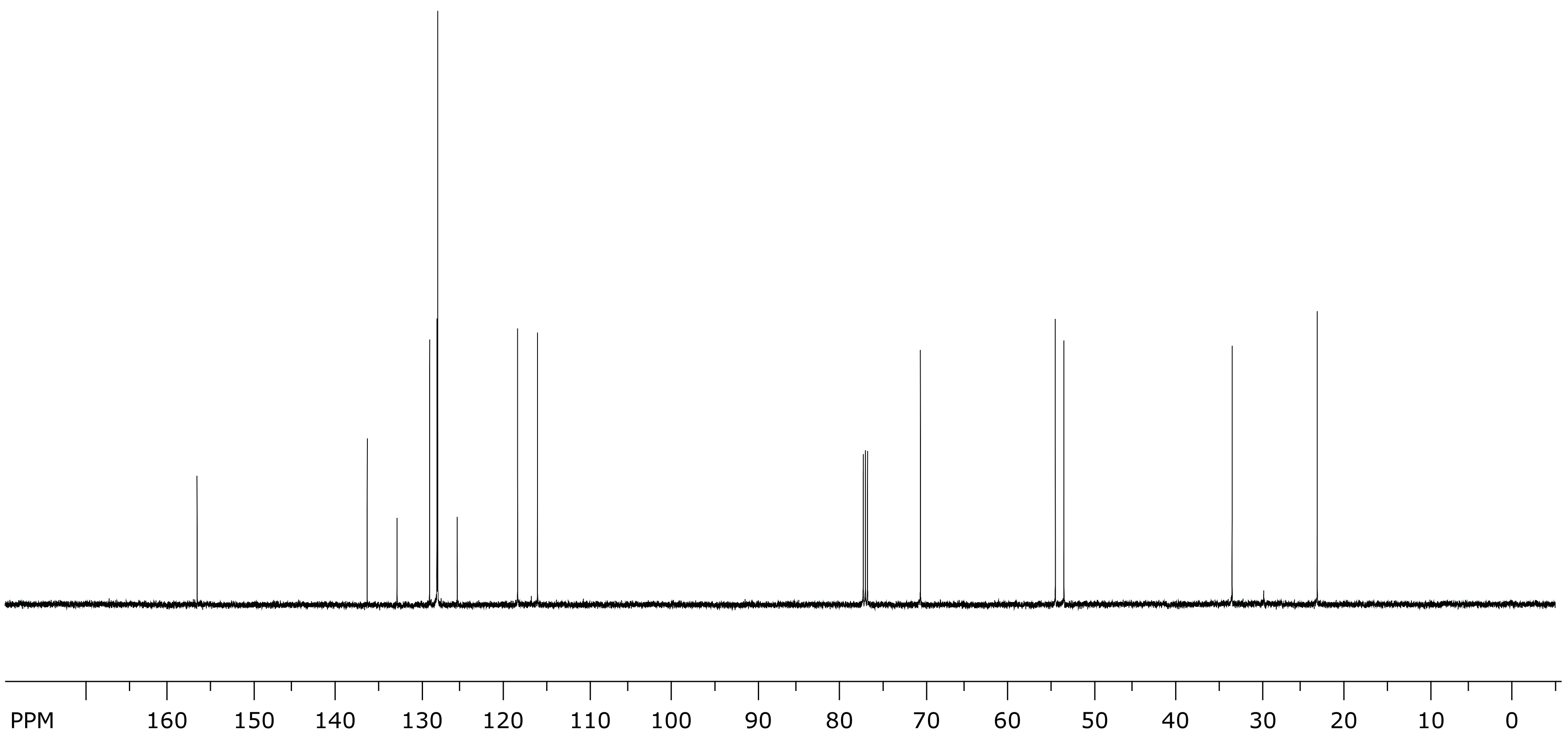
[1]H NMR of **5i** in $CDCl_3$



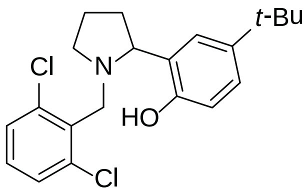


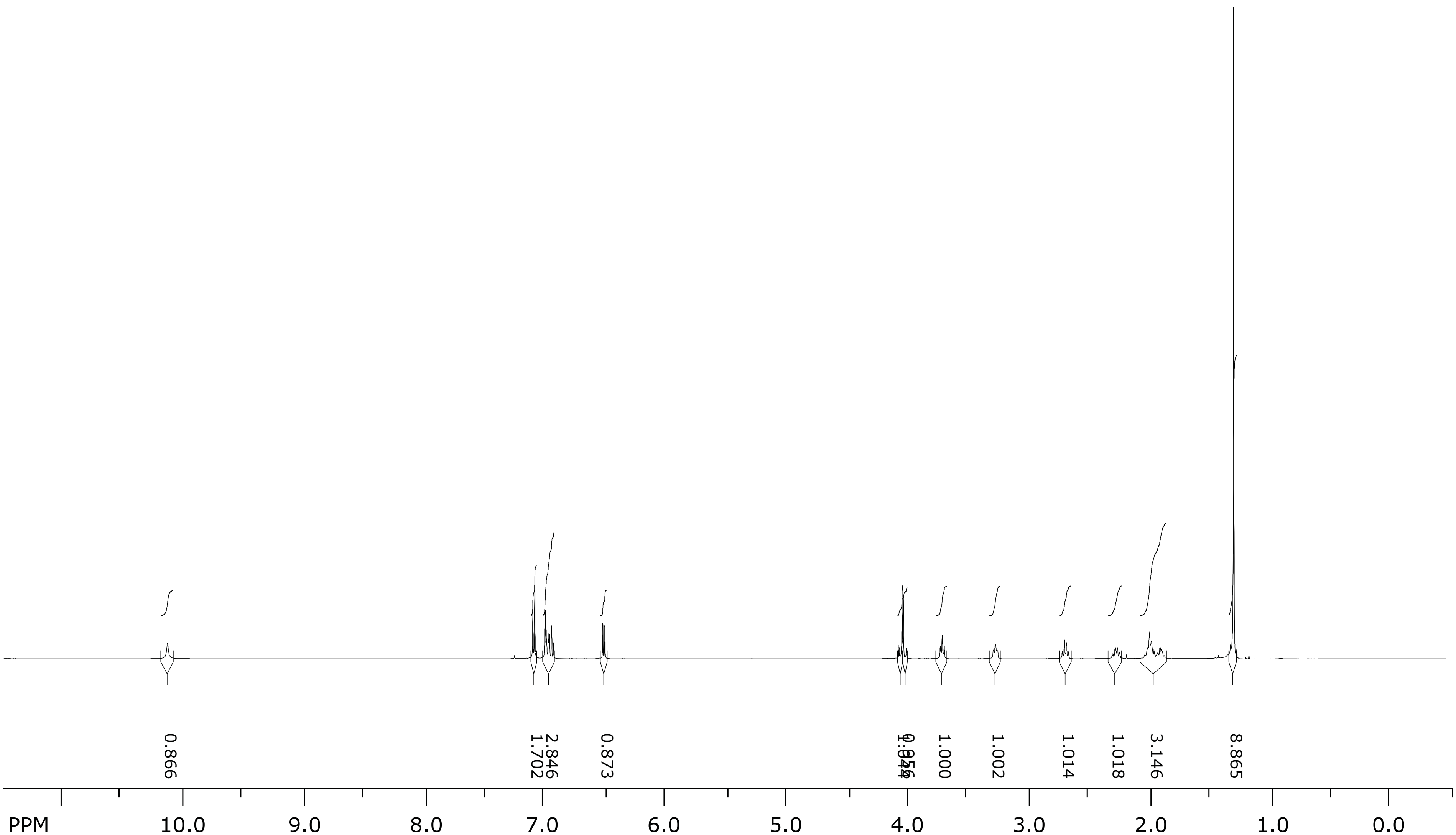
^{13}C NMR of **5i** in $CDCl_3$



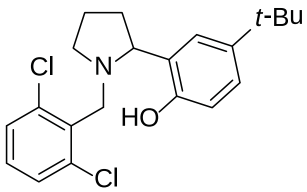


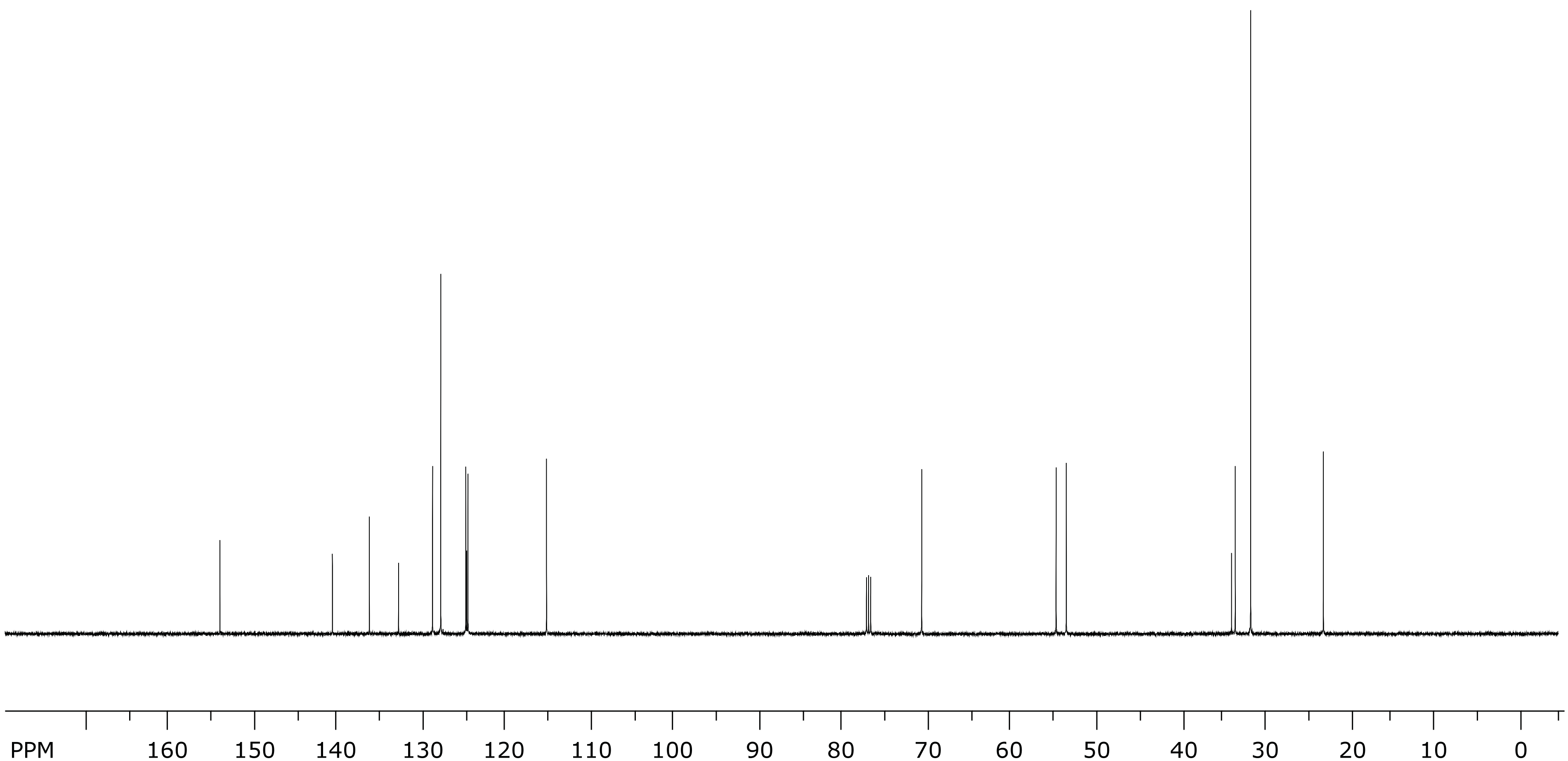
^{1}H NMR of **5j** in $CDCl_3$



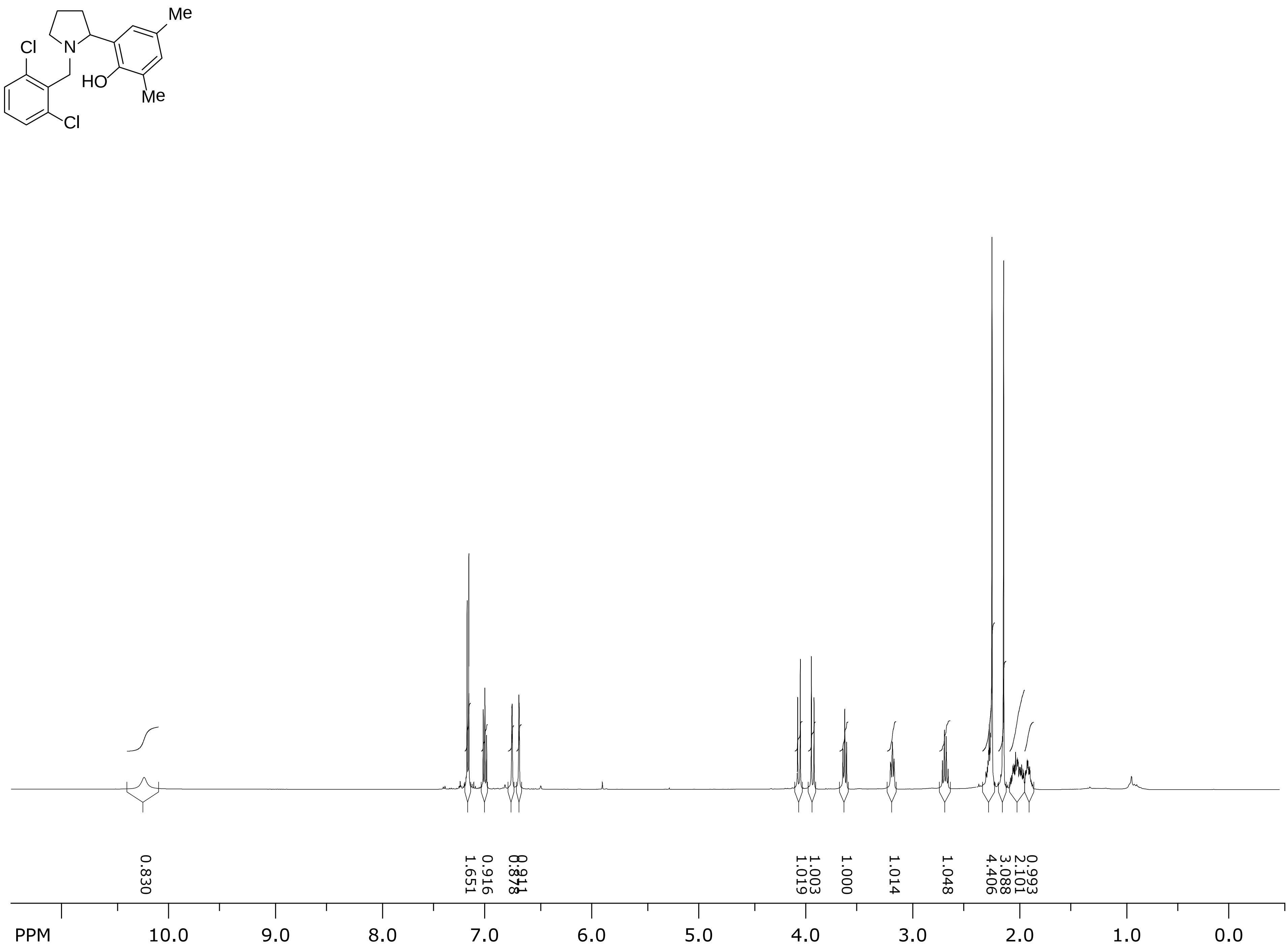


^{13}C NMR of **5j** in $CDCl_3$

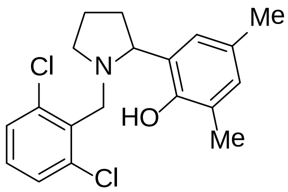


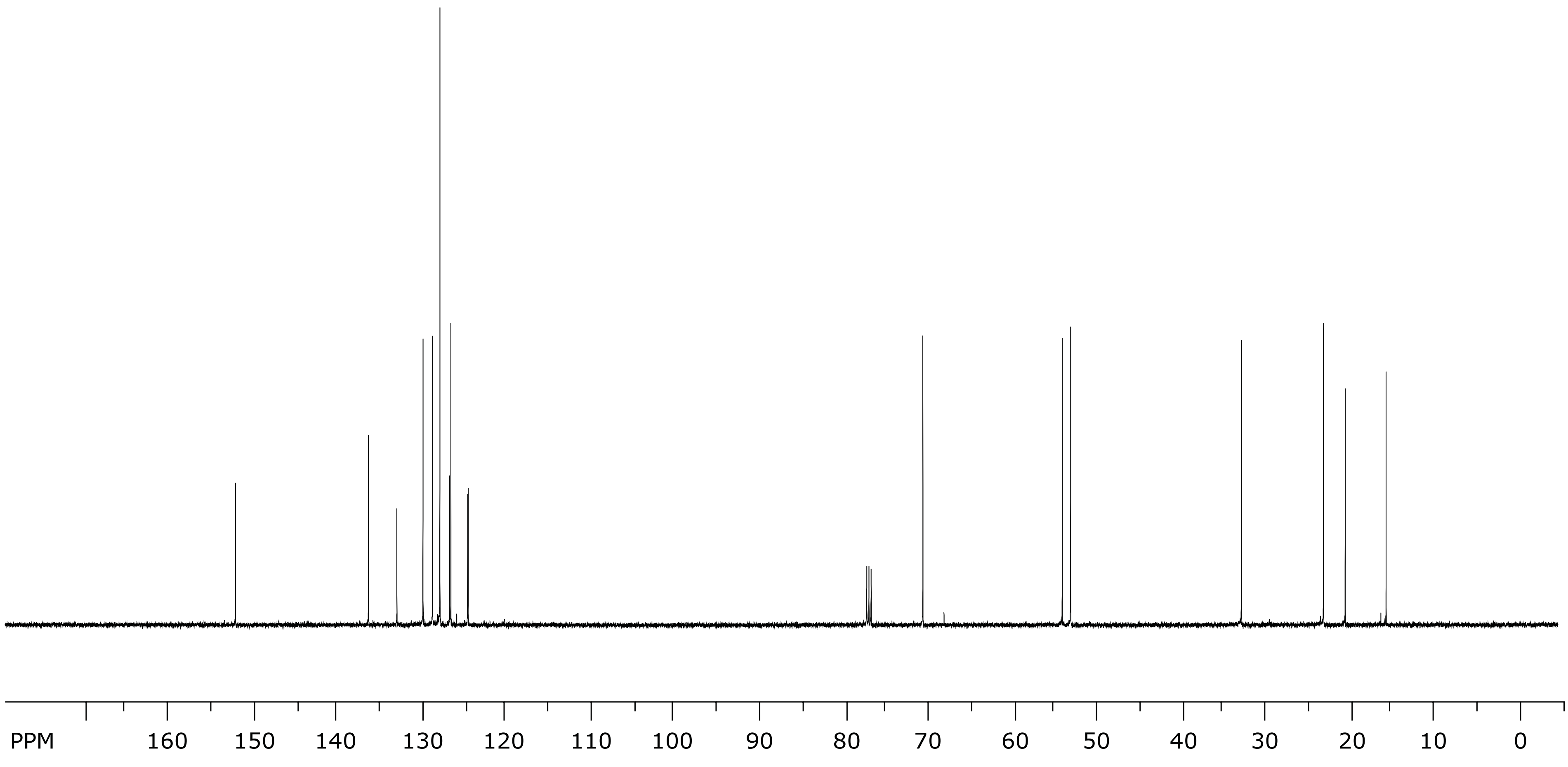


^{1}H NMR of **5k** in $CDCl_3$

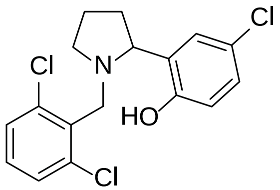


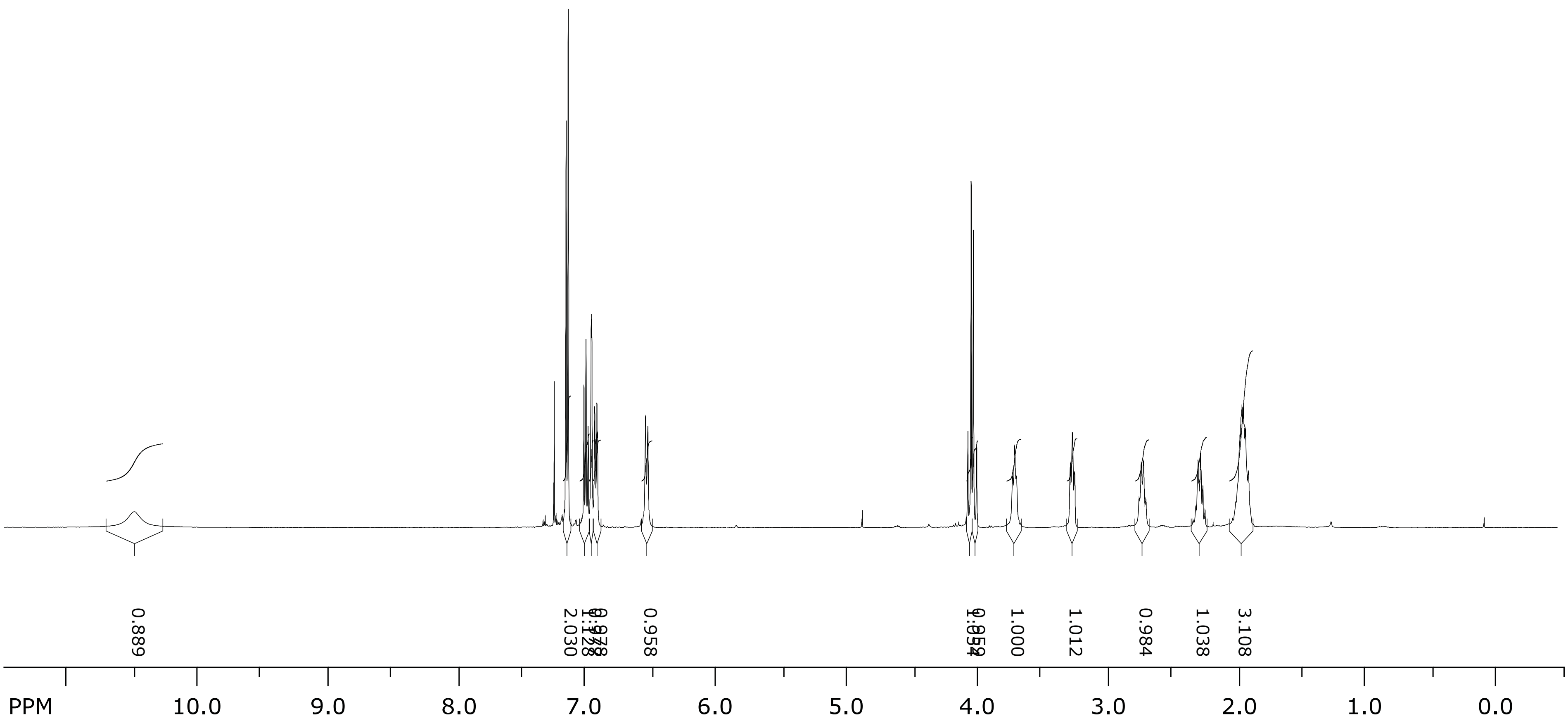
^{13}C NMR of **5k** in $CDCl_3$



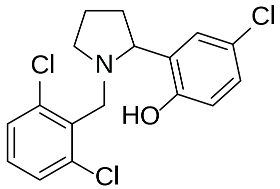


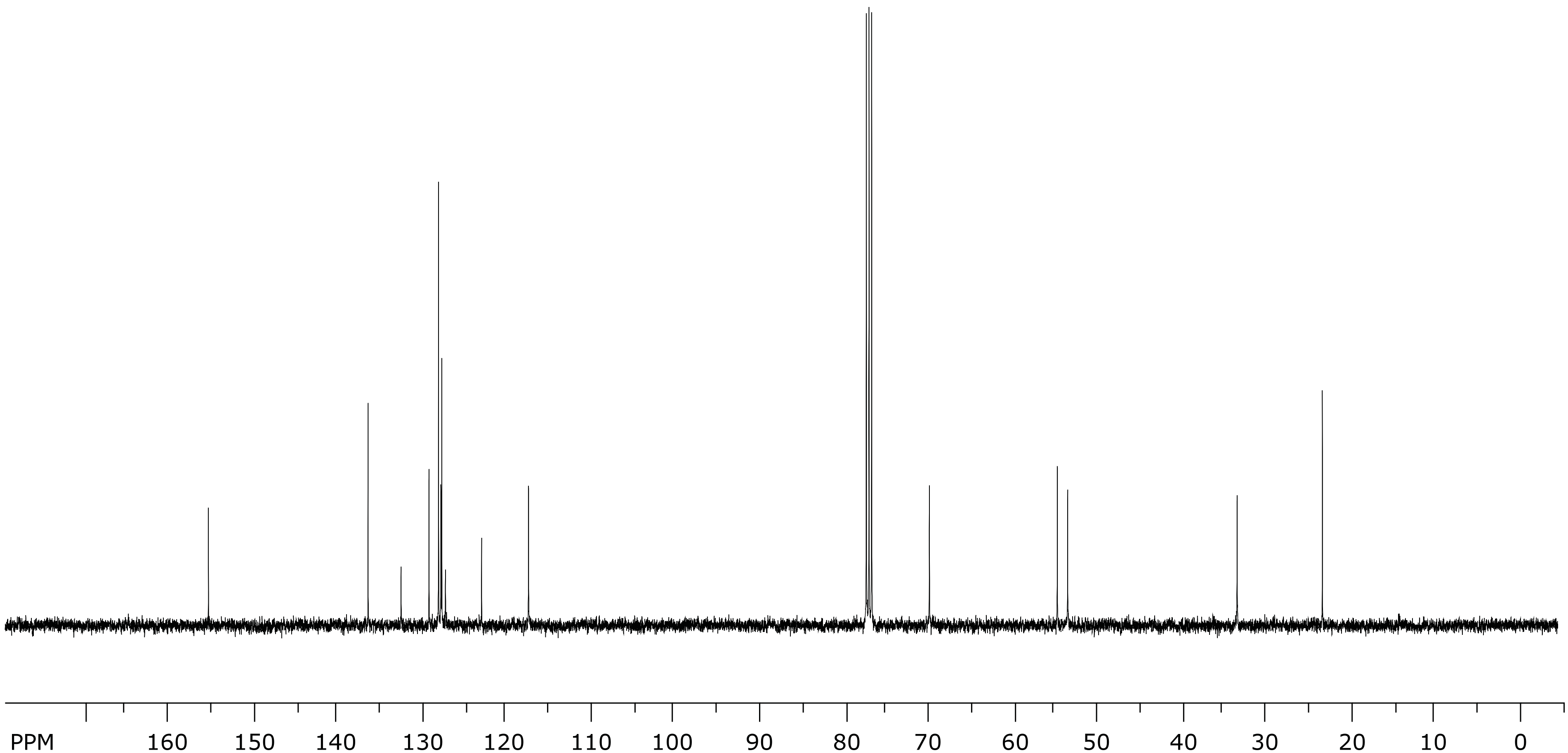
^{1}H NMR of **5l** in $CDCl_3$



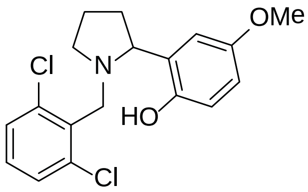


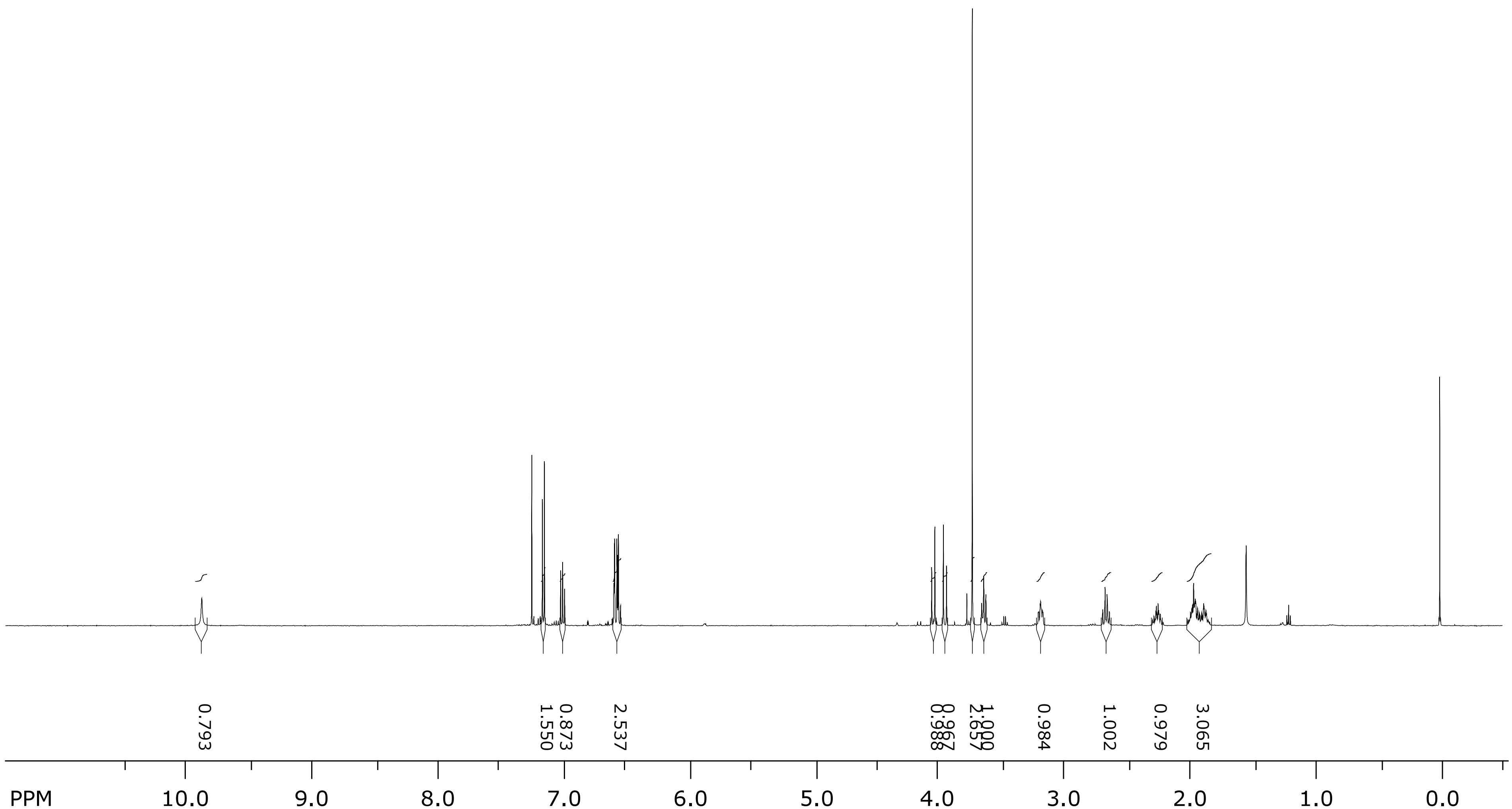
^{13}C NMR of **5l** in $CDCl_3$



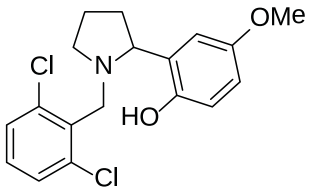


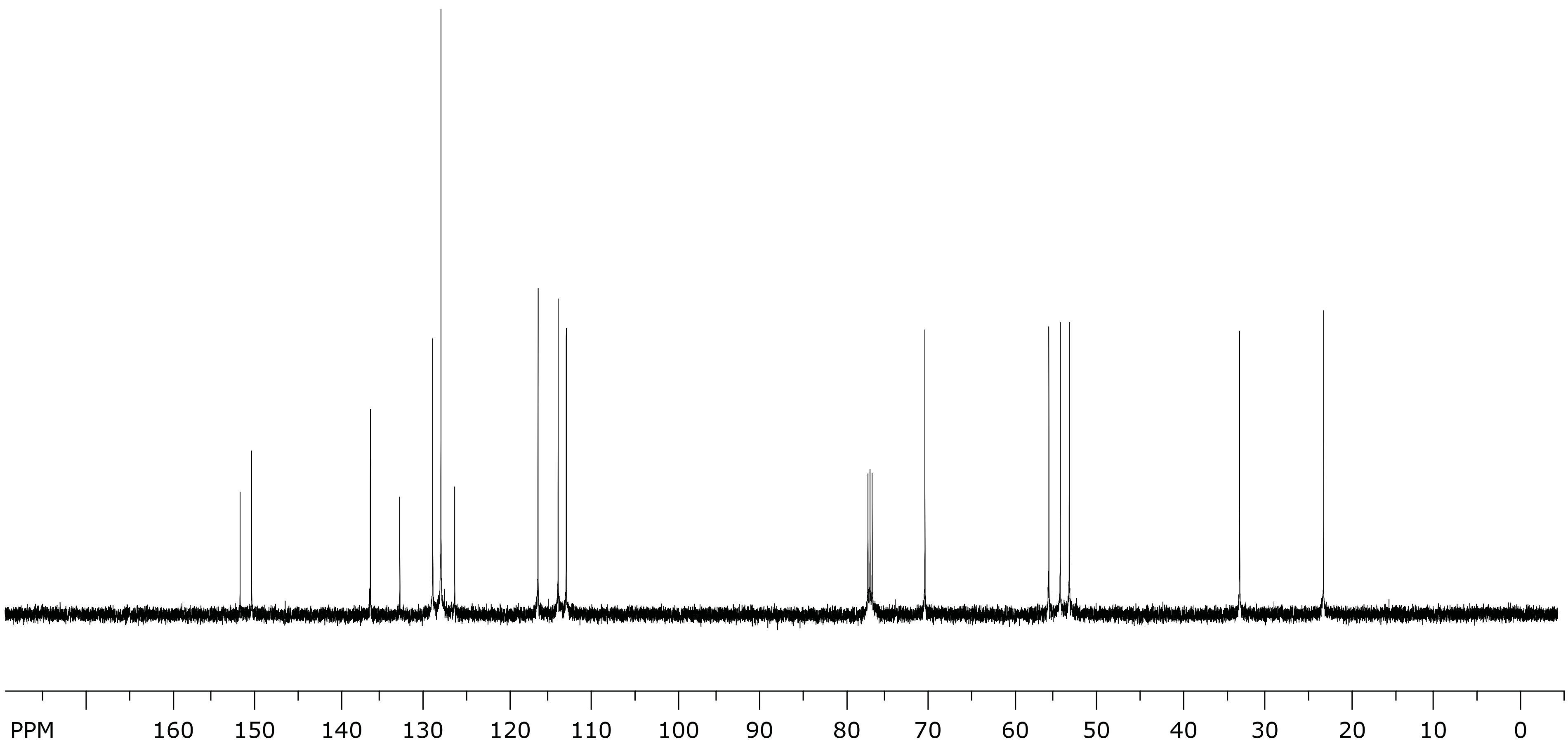
^{1}H NMR of **5m** in $CDCl_3$



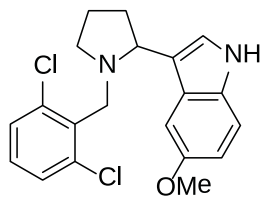


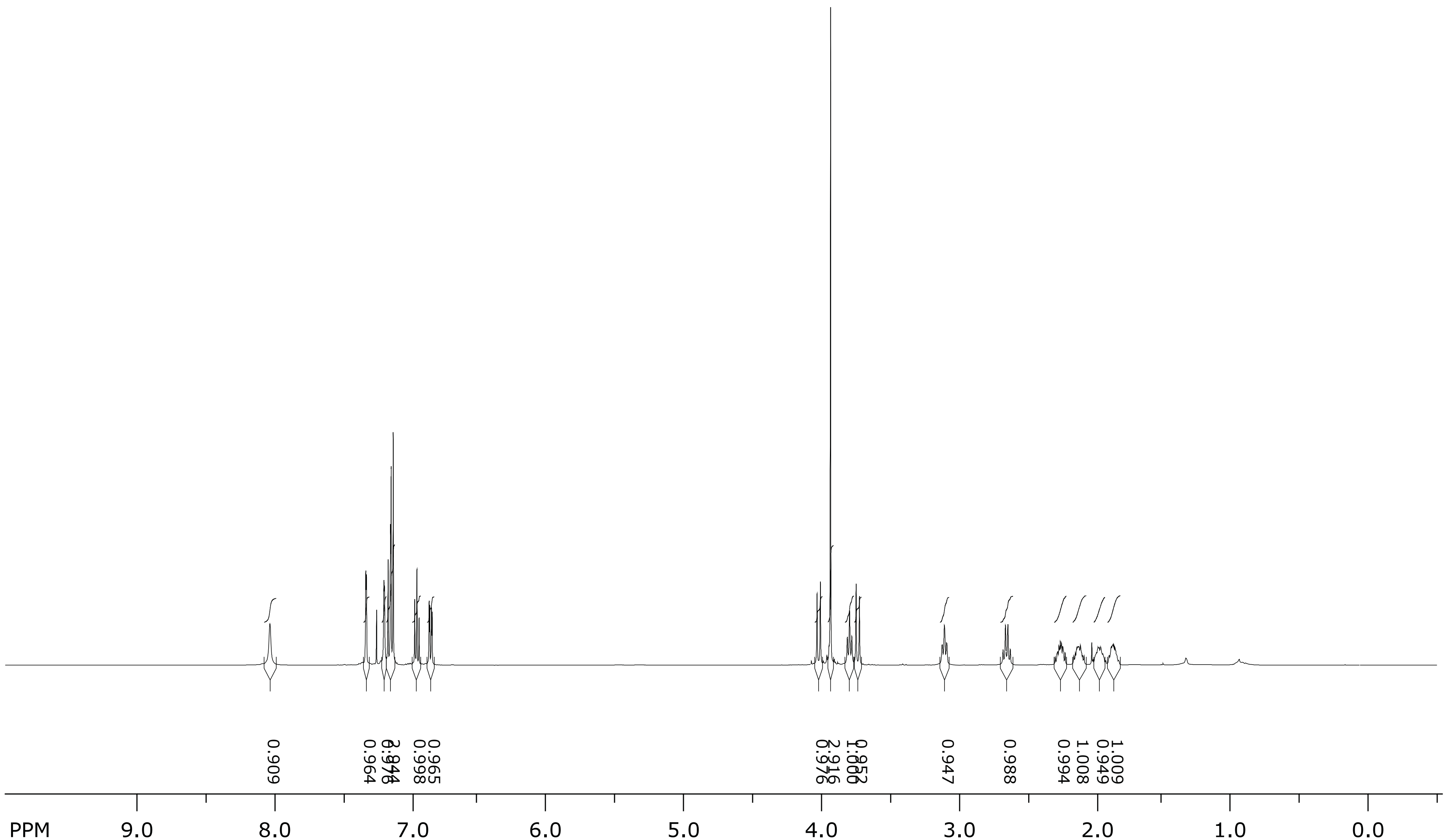
^{13}C NMR of **5m** in $CDCl_3$



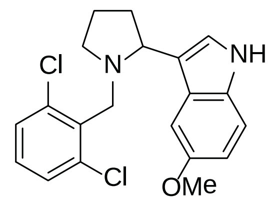


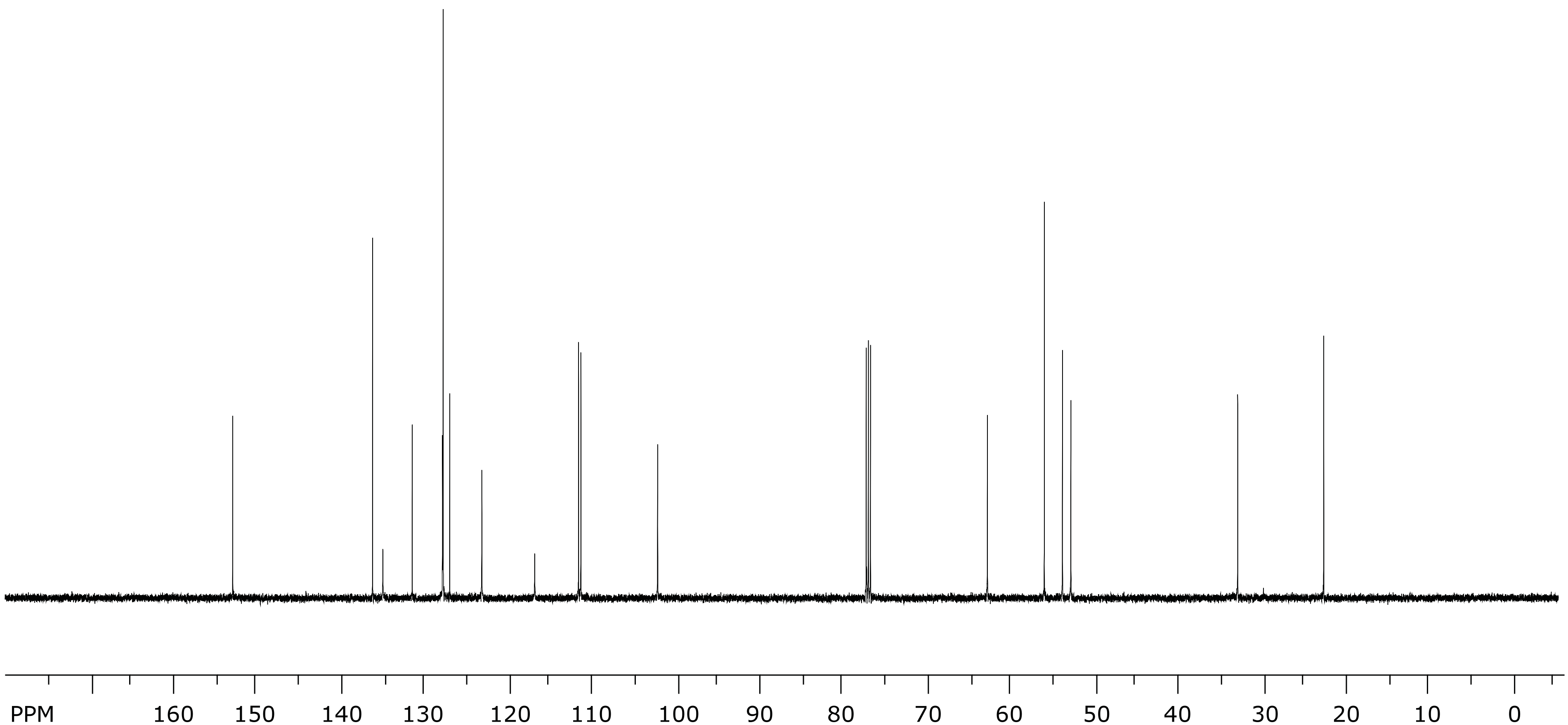
^1H NMR of **5n** in $CDCl_3$



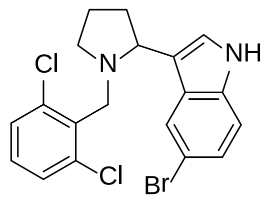


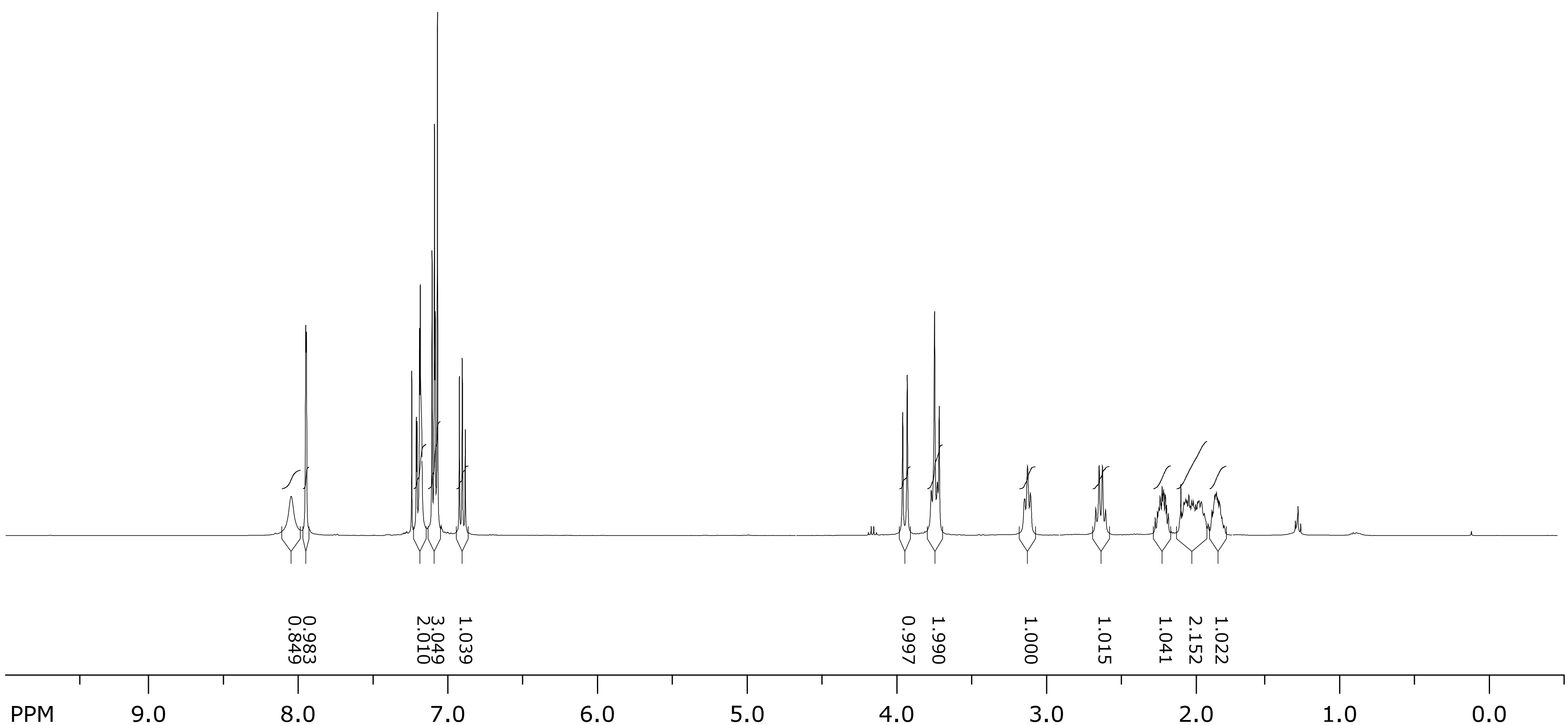
^{13}C NMR of **5n** in $CDCl_3$



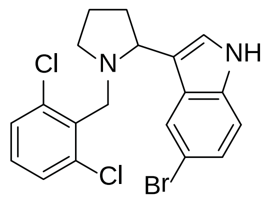


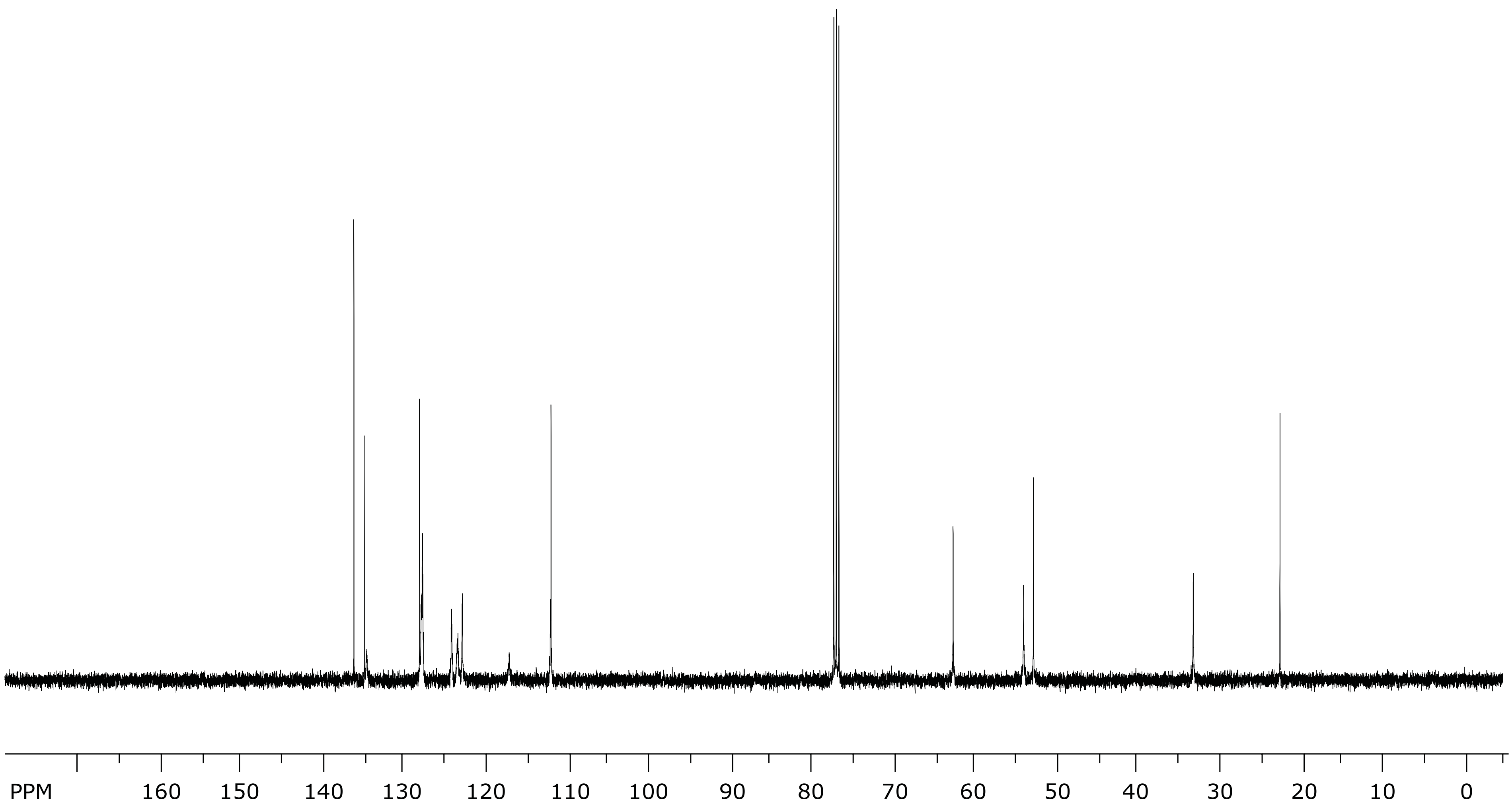
[1]H NMR of **5o** in $CDCl_3$



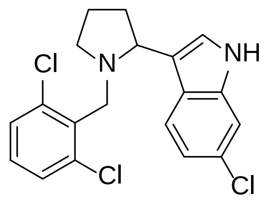


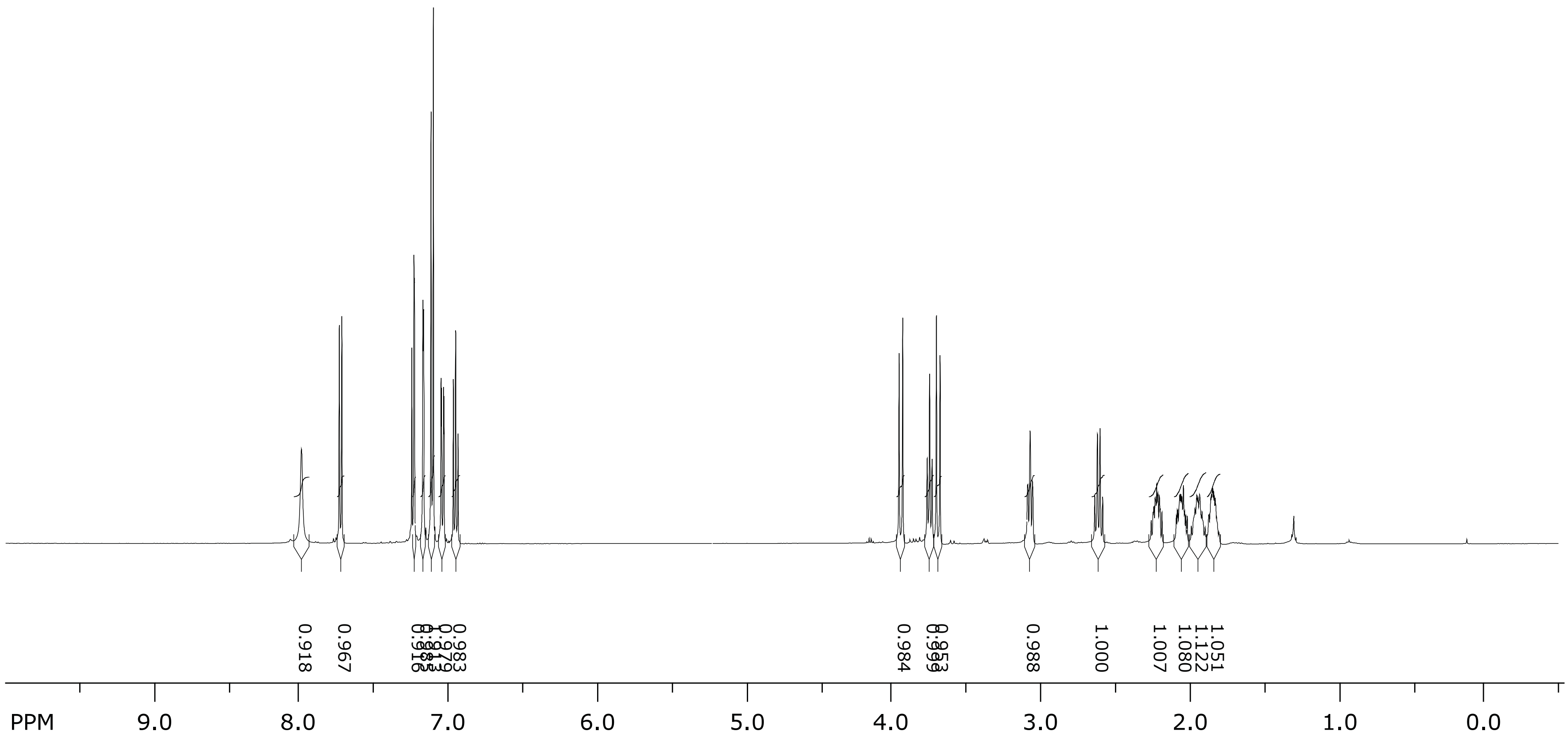
^{13}C NMR of **5o** in $CDCl_3$



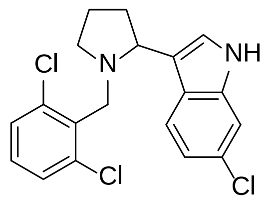


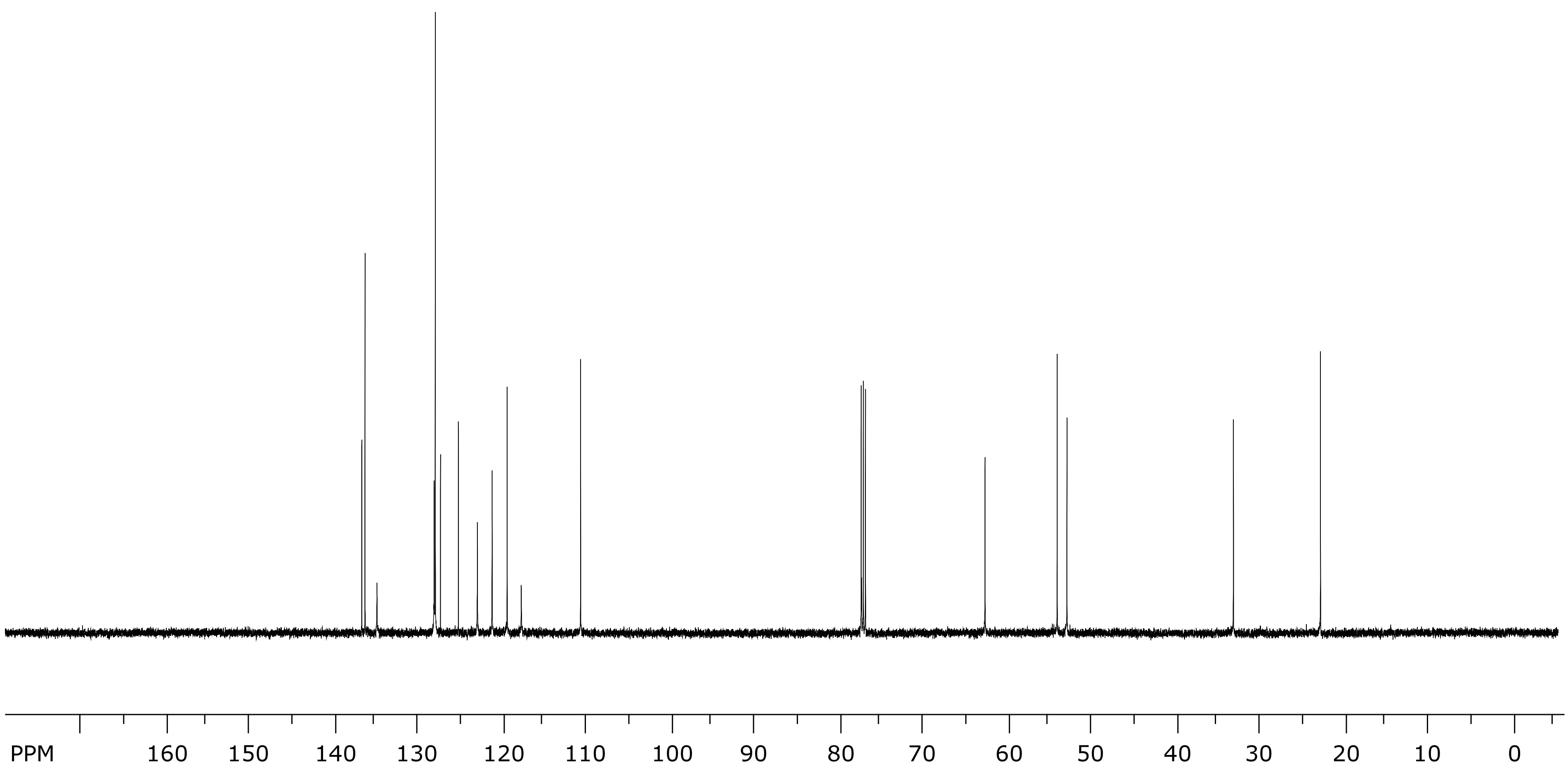
^{1}H NMR of **5p** in $CDCl_3$



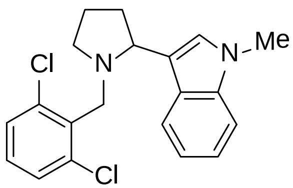


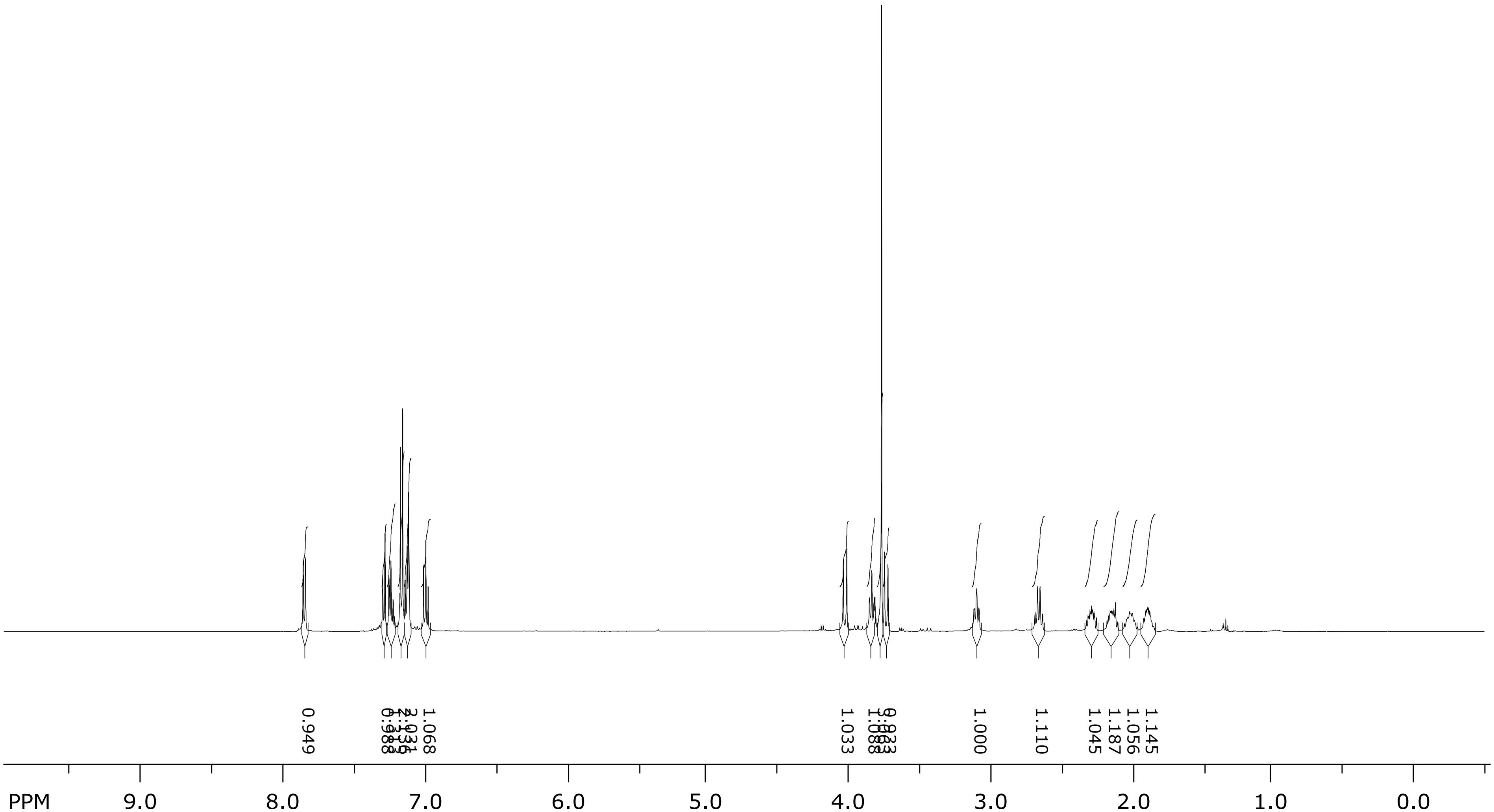
^{13}C NMR of **5p** in $CDCl_3$



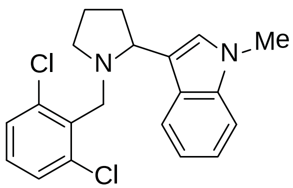


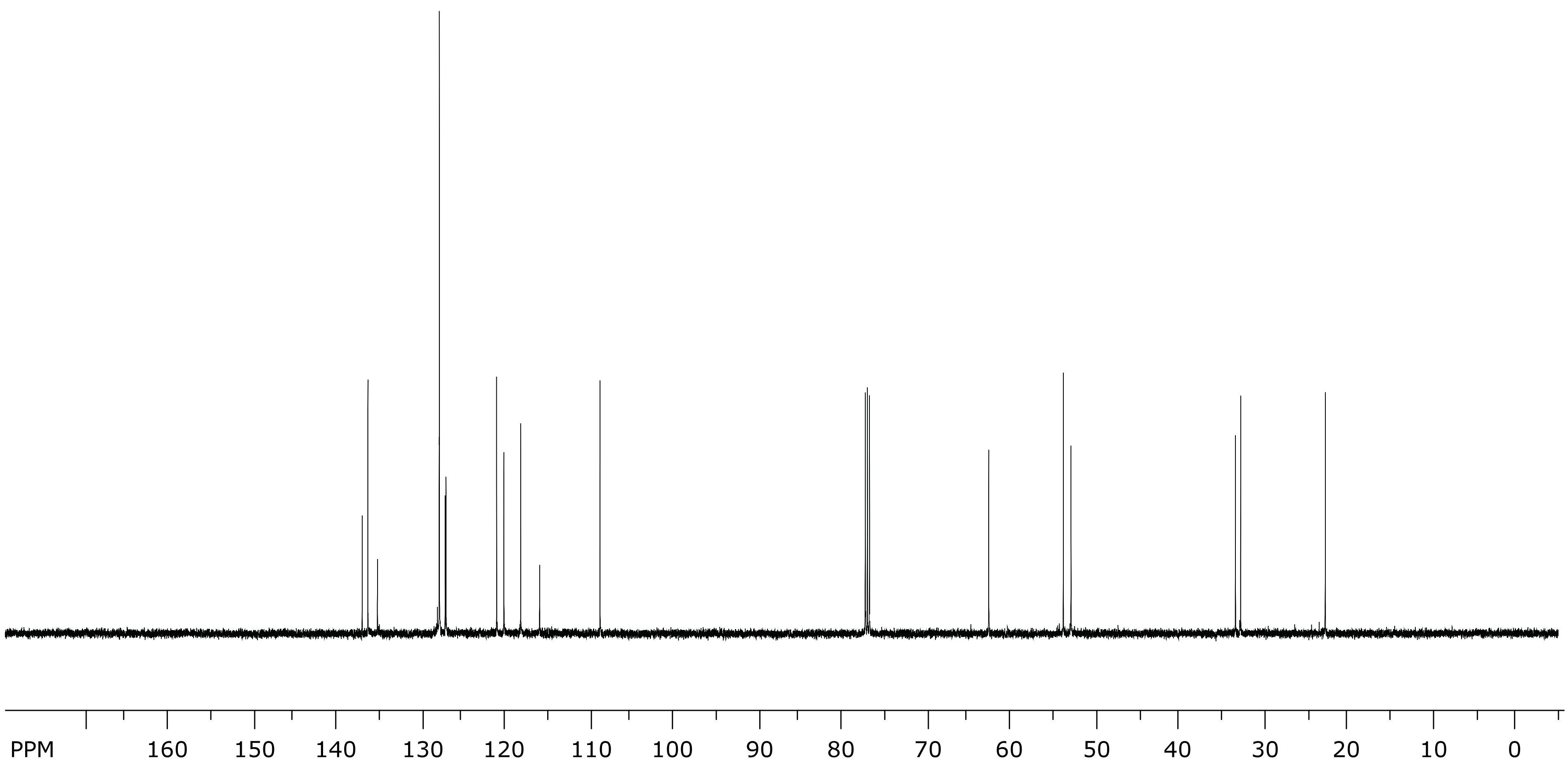
^{1}H NMR of **5q** in $CDCl_3$



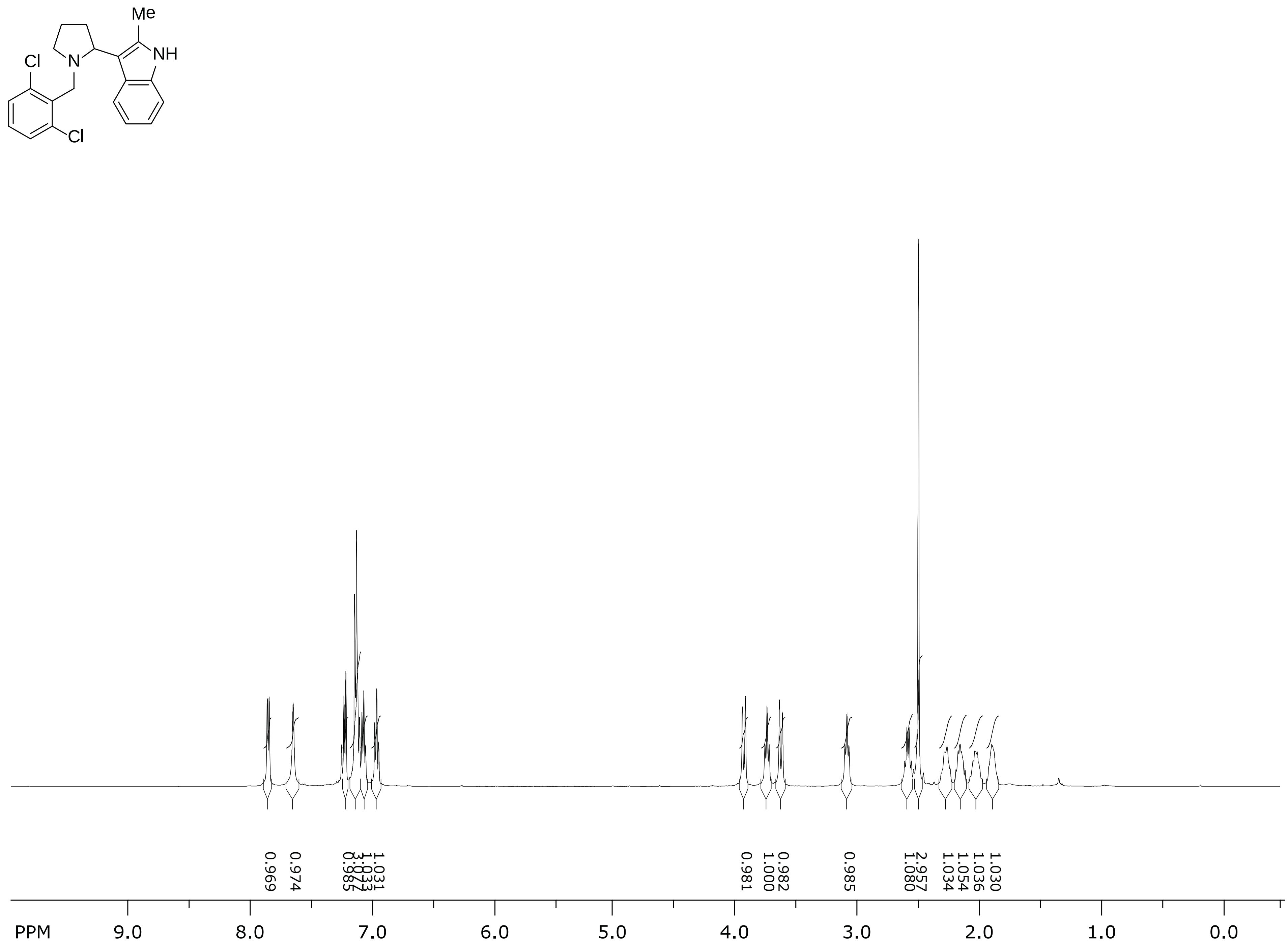


^{13}C NMR of **5q** in $CDCl_3$

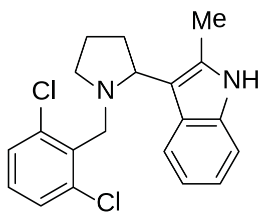


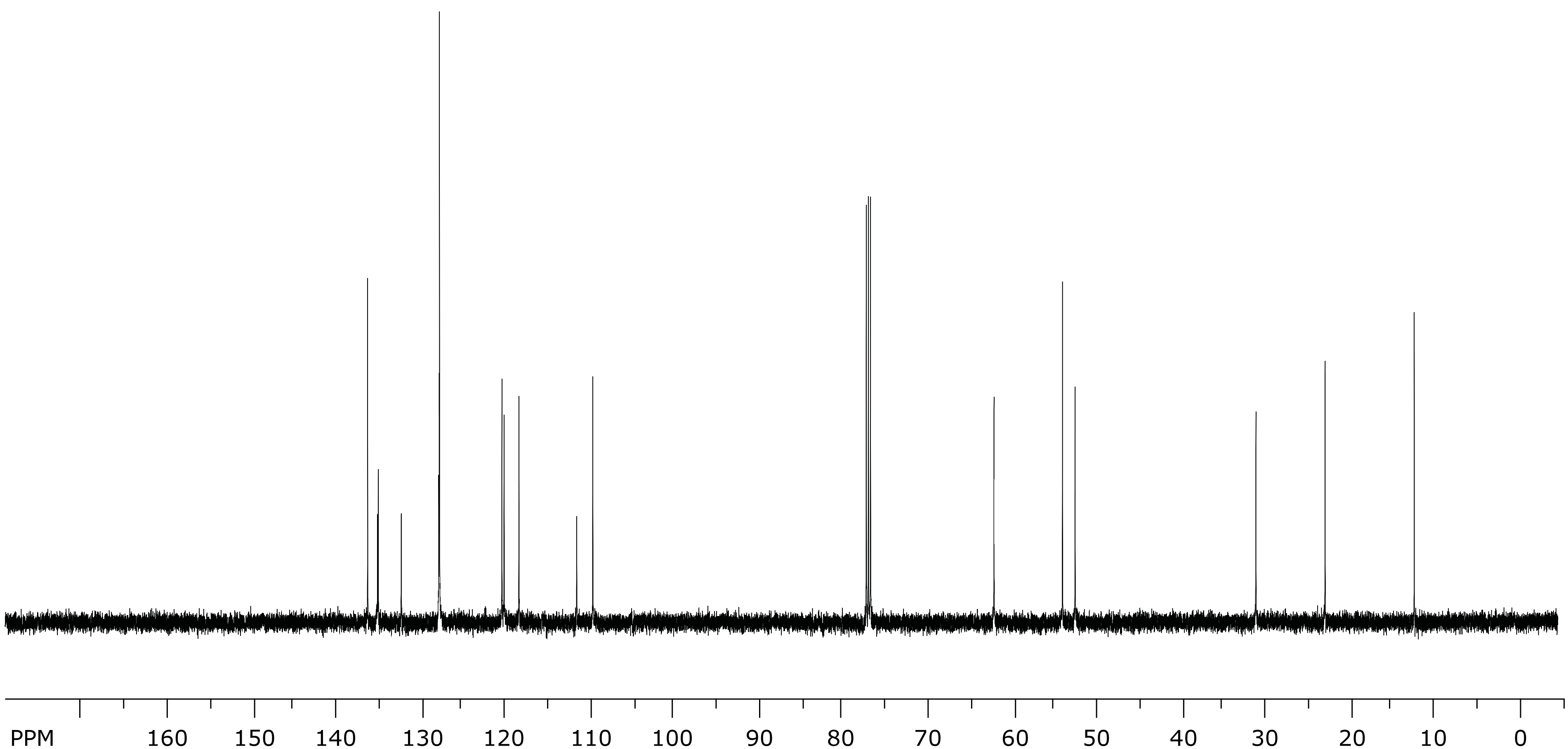


^{1}H NMR of **5r** in $CDCl_3$

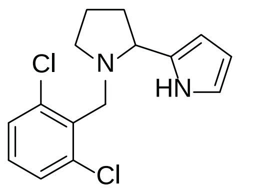


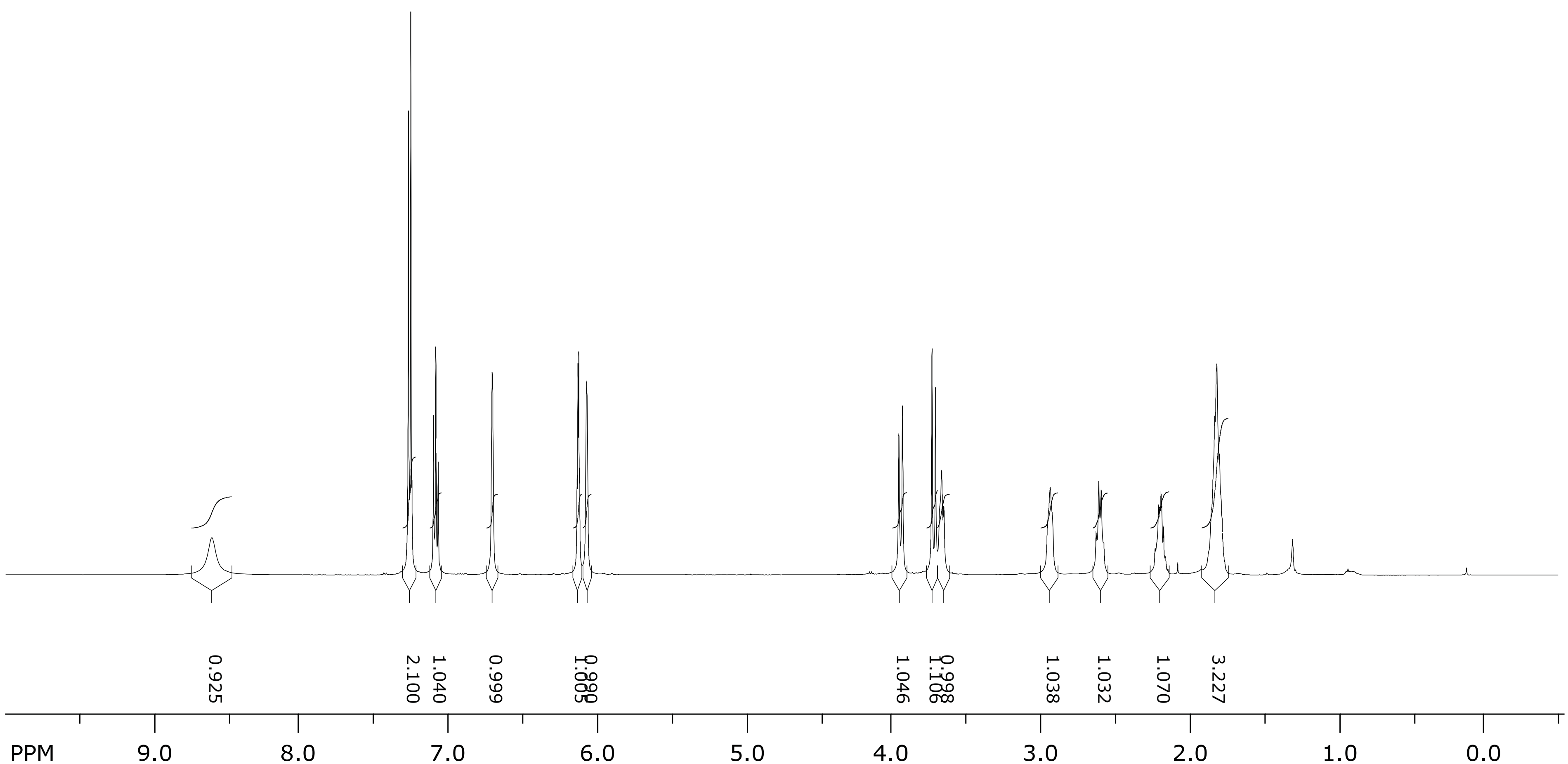
^{13}C NMR of **5r** in $CDCl_3$



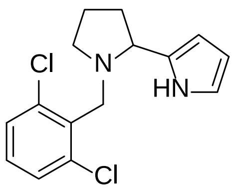


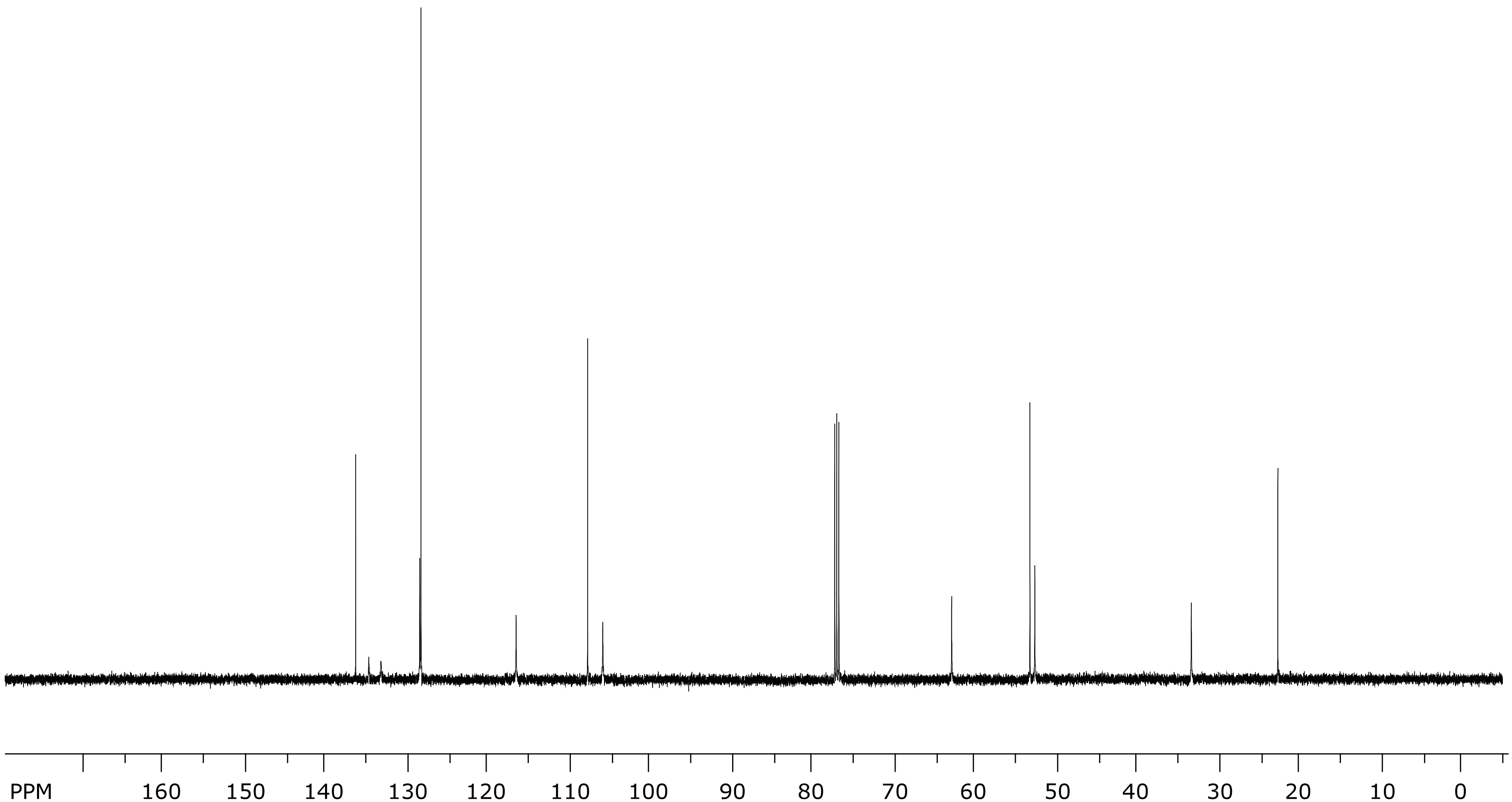
^{1}H NMR of **5s** in $CDCl_3$



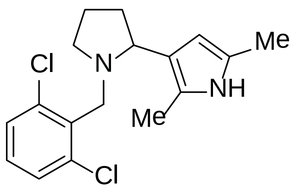


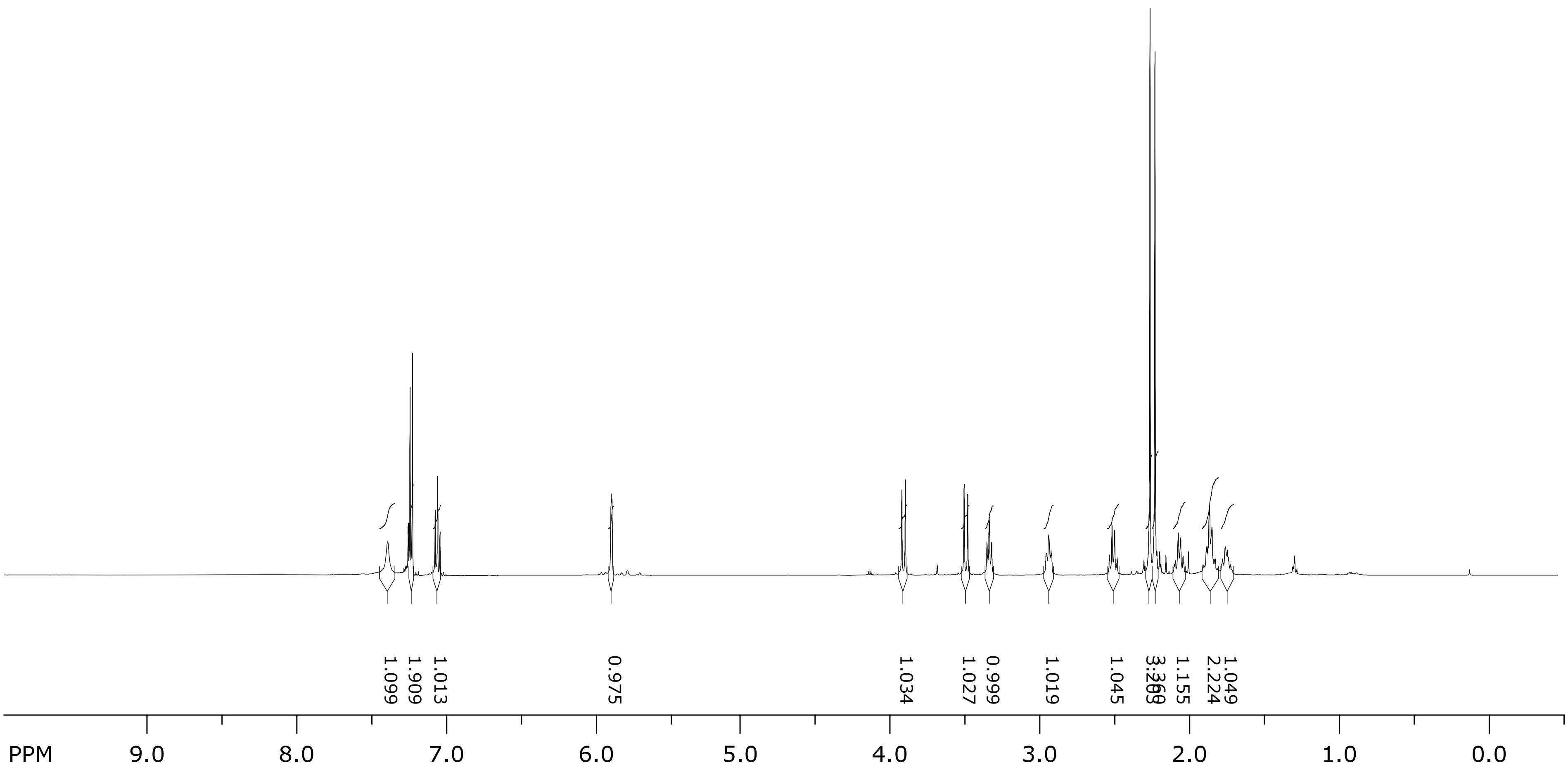
^{13}C NMR of **5s** in $CDCl_3$



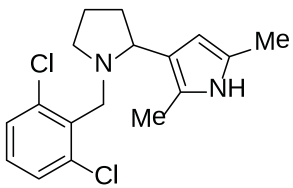


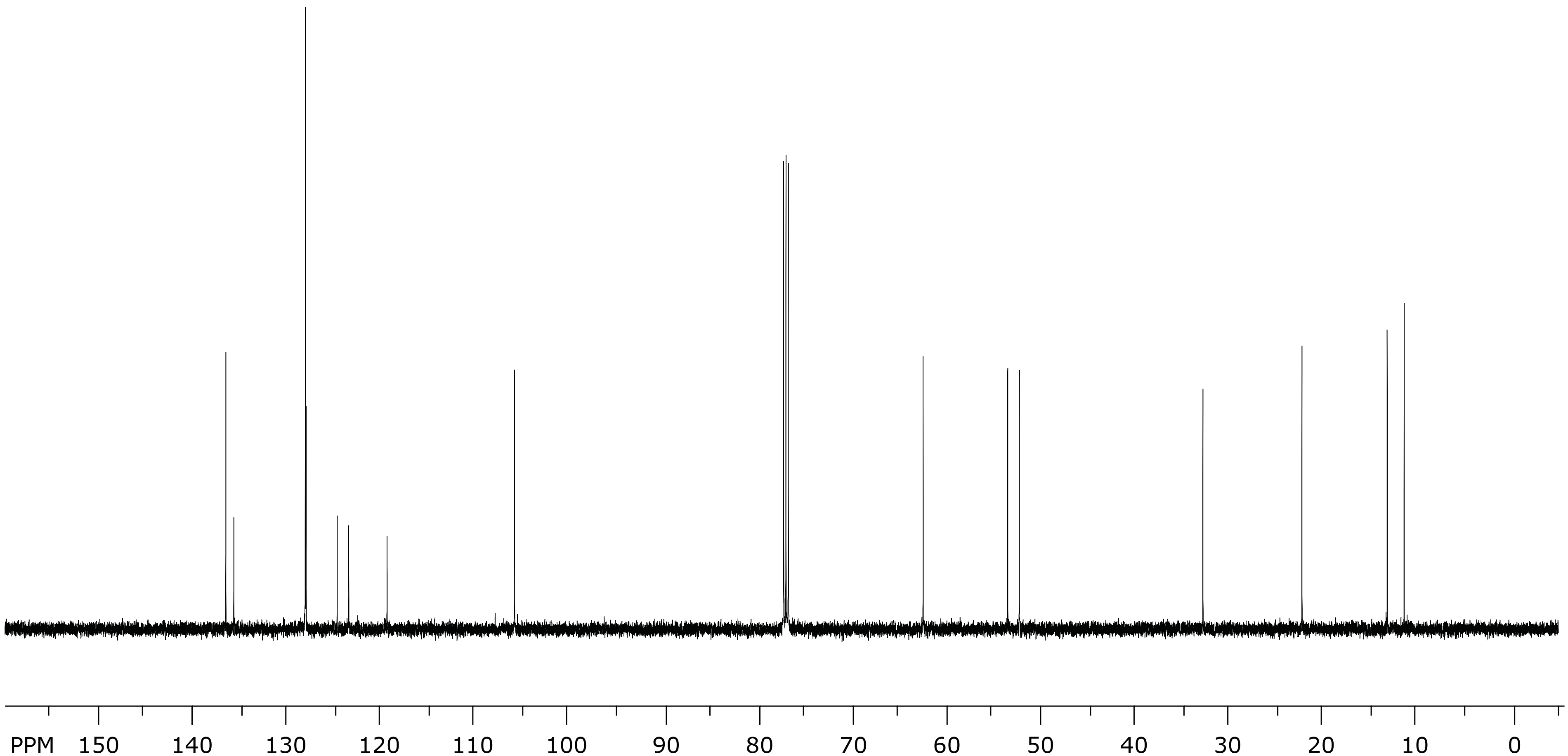
^{1}H NMR of **5t** in $CDCl_3$



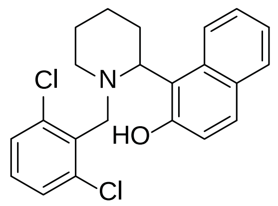


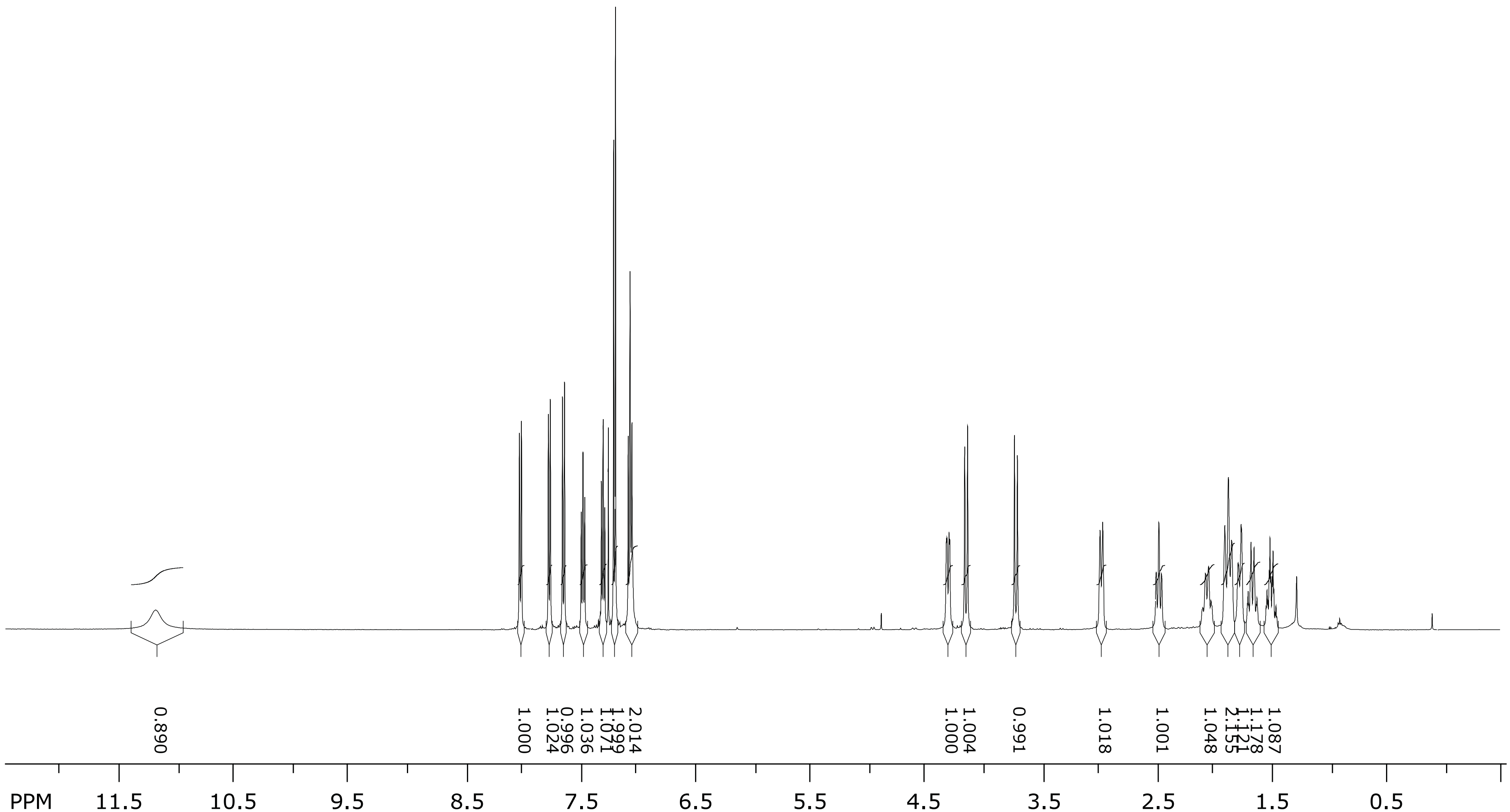
^{13}C NMR of **5t** in $CDCl_3$



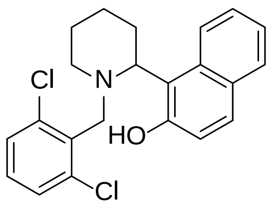


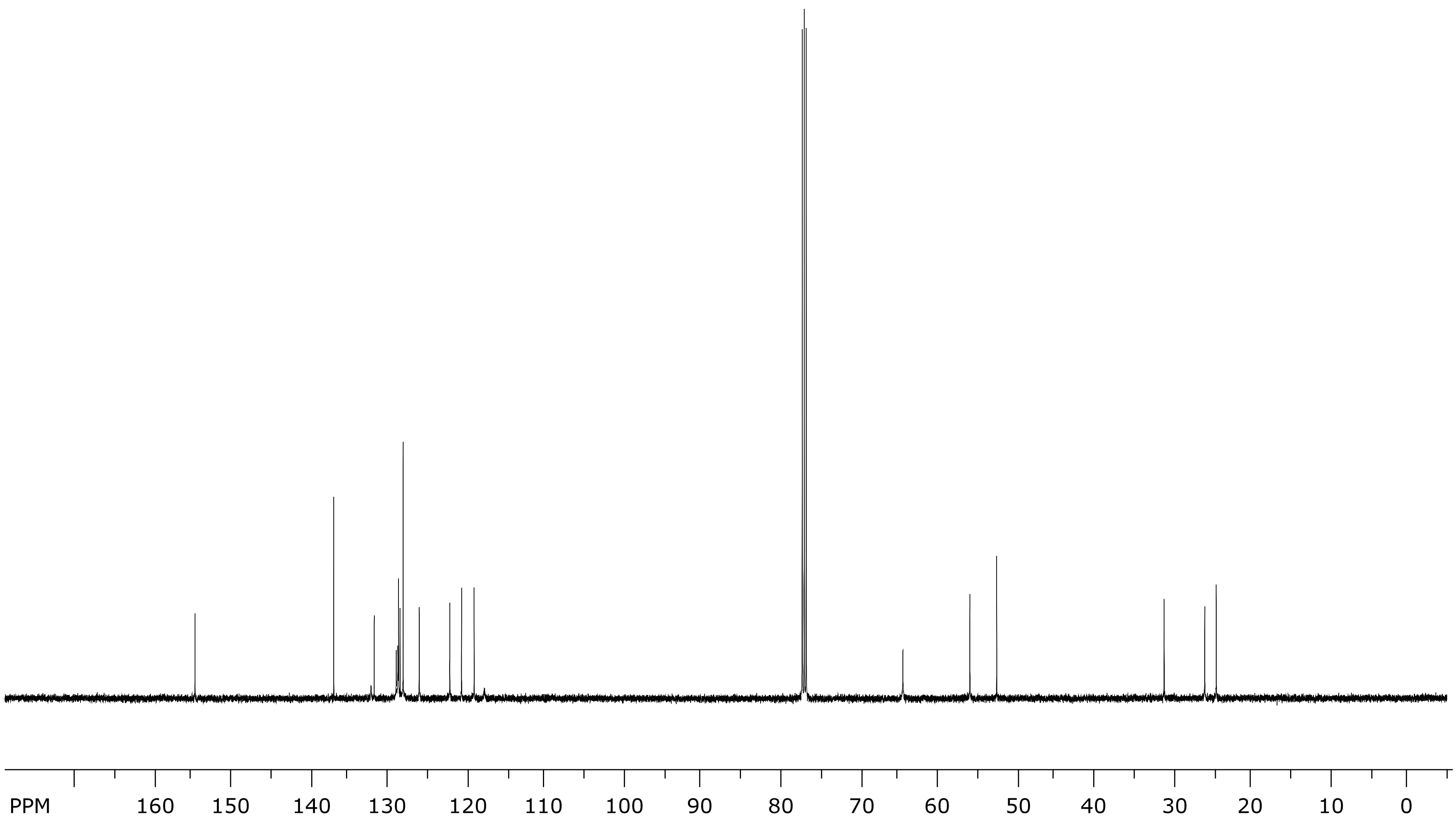
^{1}H NMR of **5u** in $CDCl_3$



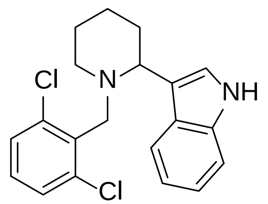


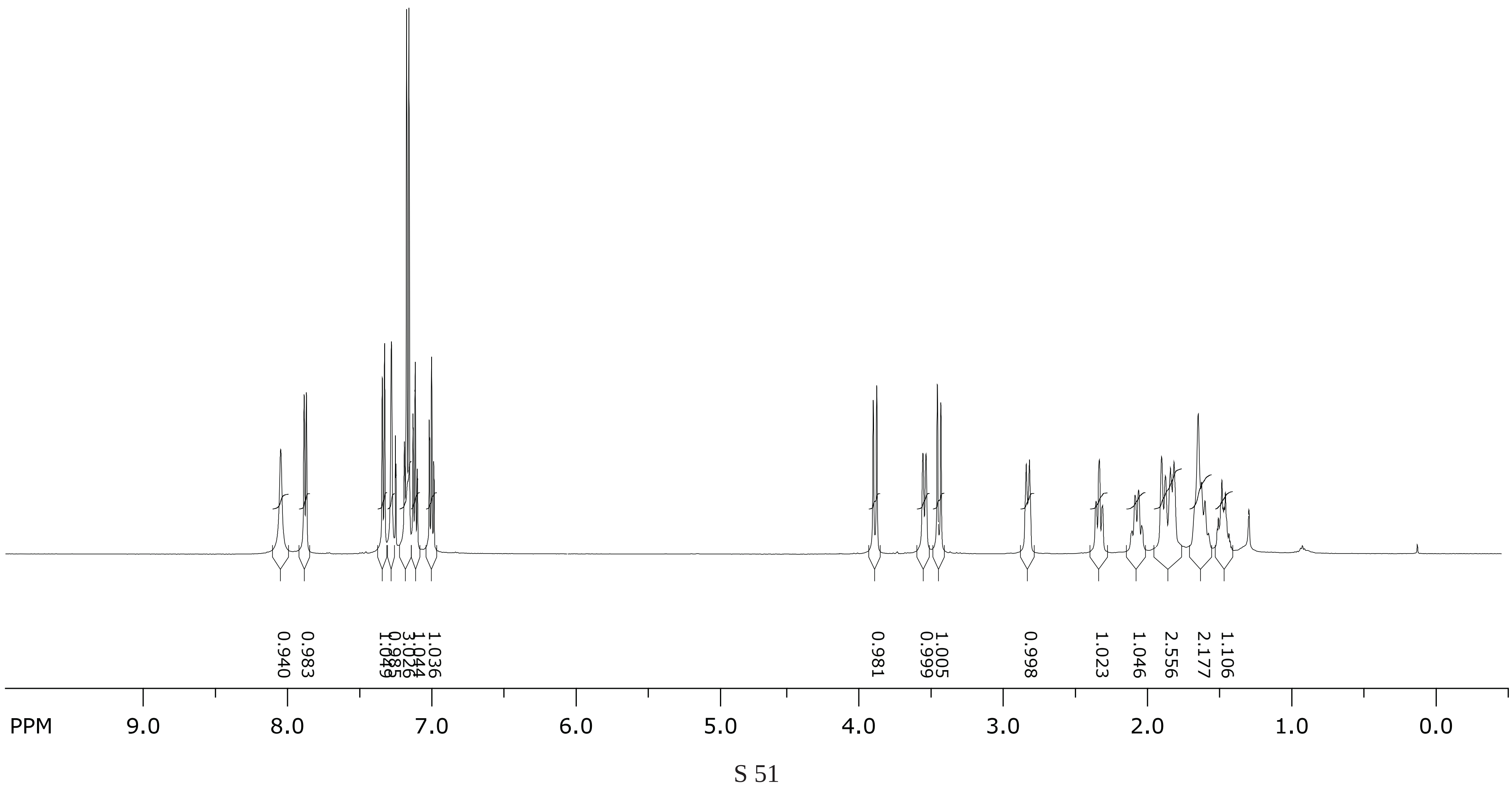
^{13}C NMR of **5u** in $CDCl_3$



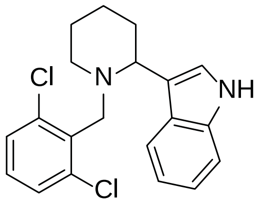


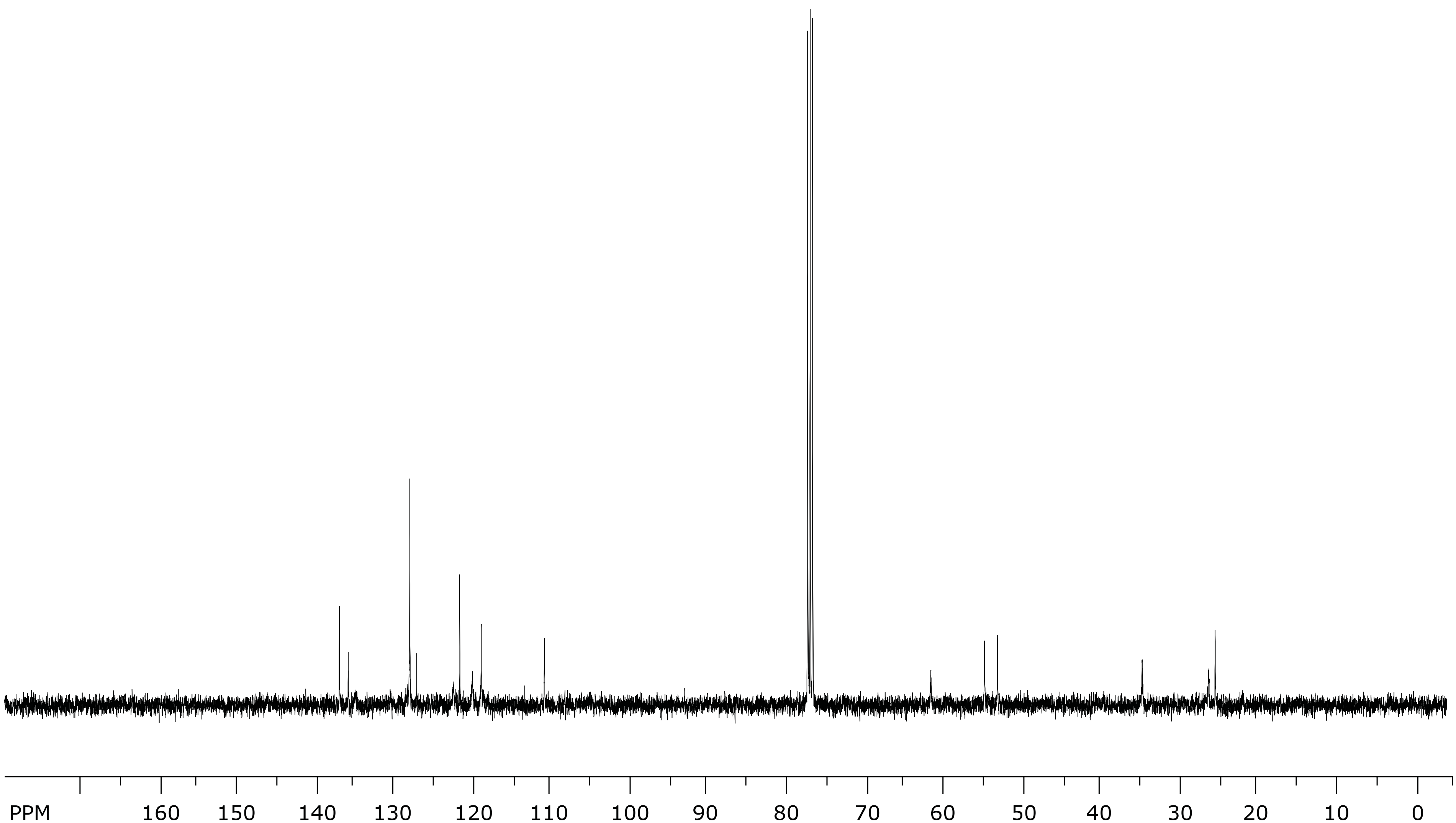
^{1}H NMR of **5v** in $CDCl_3$



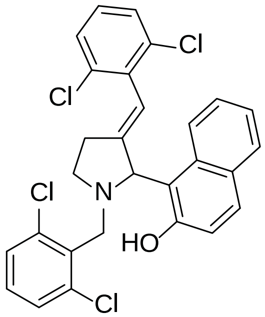


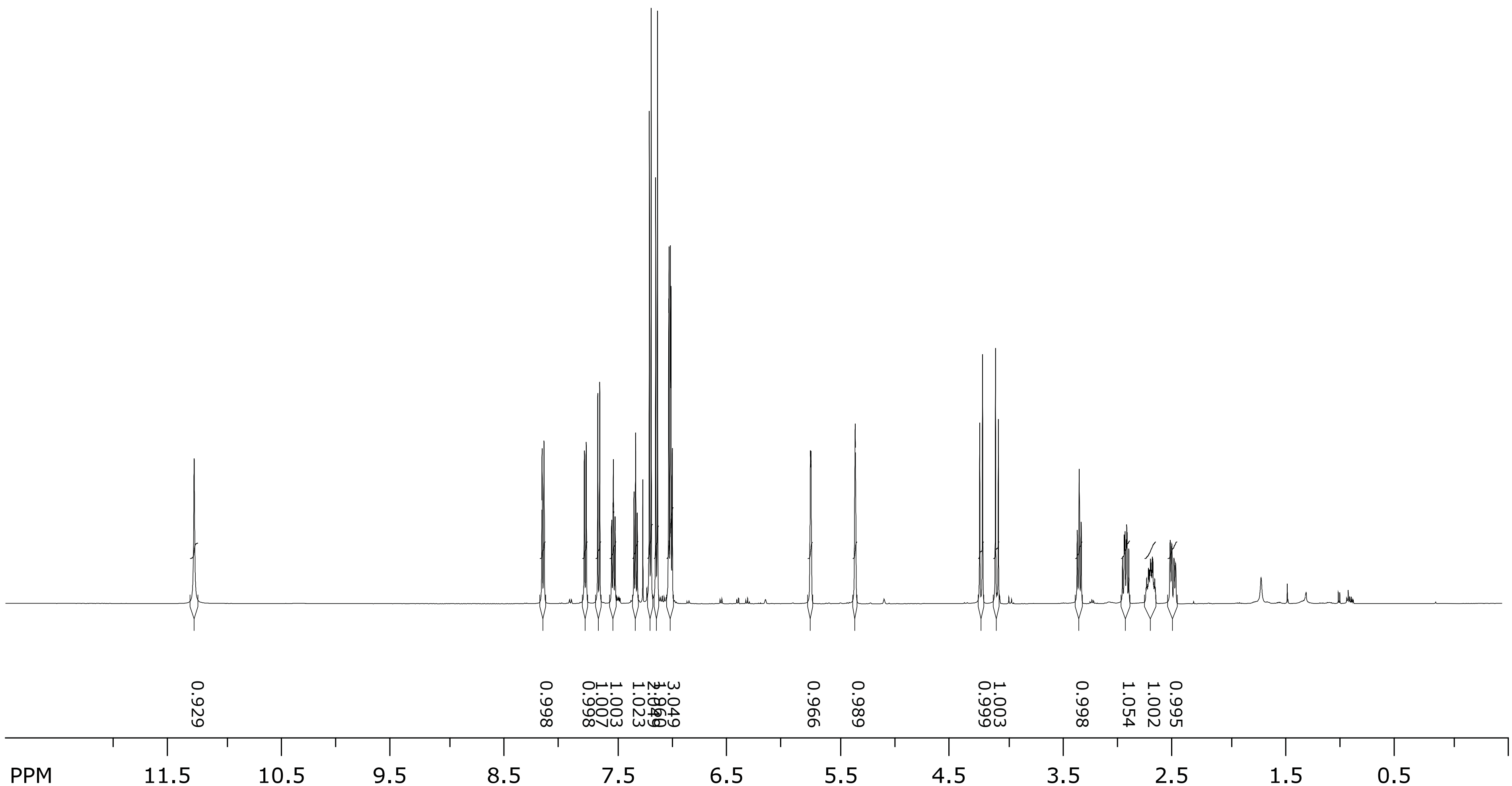
^{13}C NMR of **5v** in $CDCl_3$



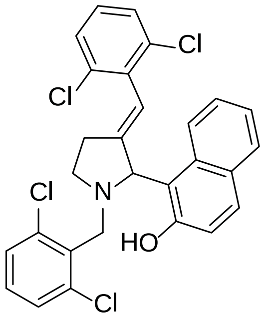


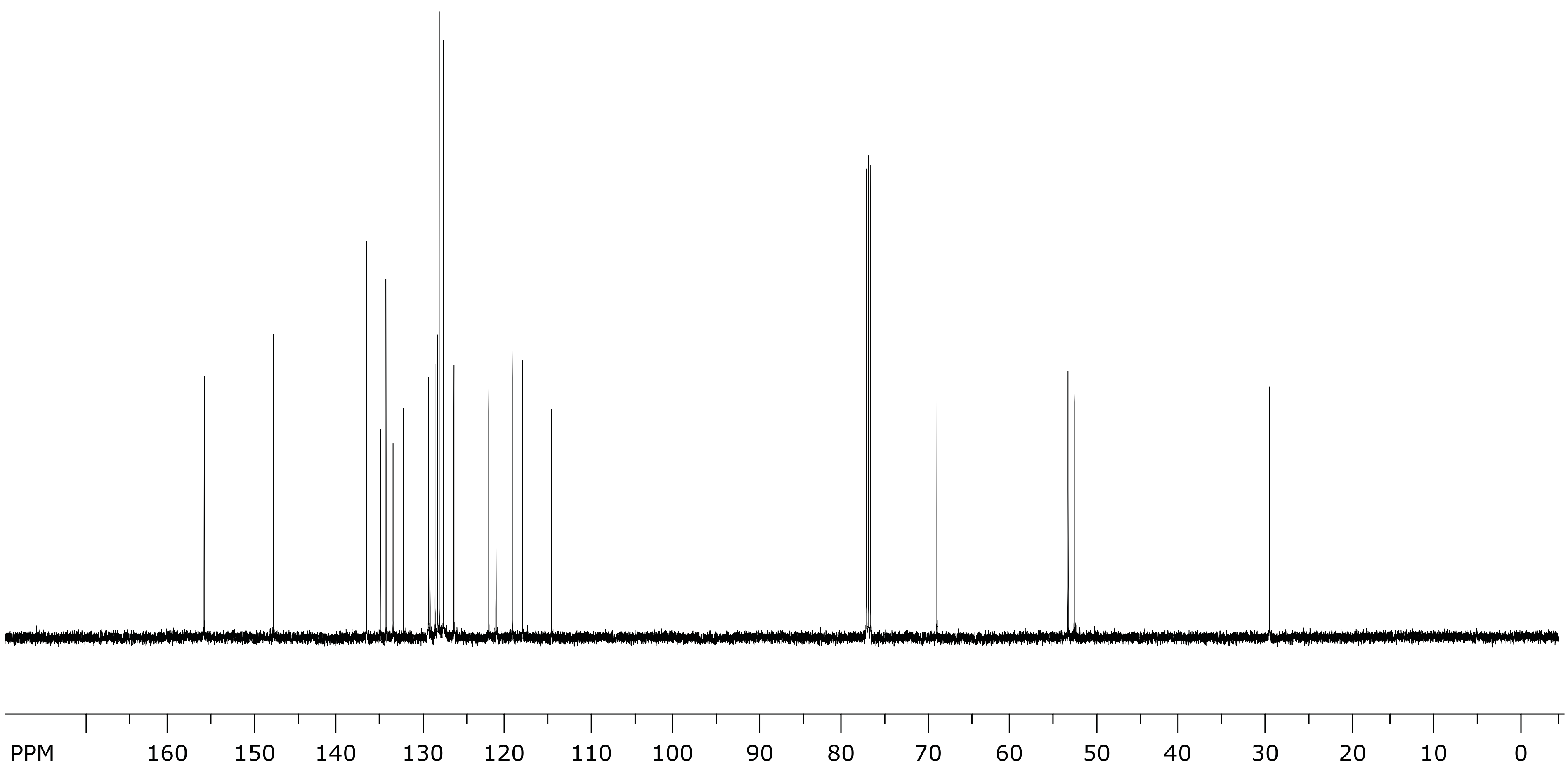
^1H NMR of **6** in $CDCl_3$



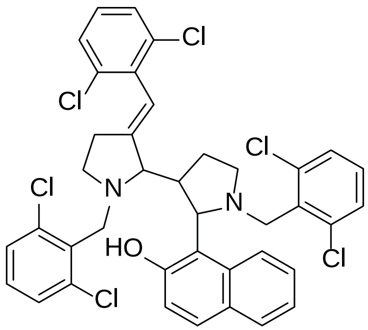


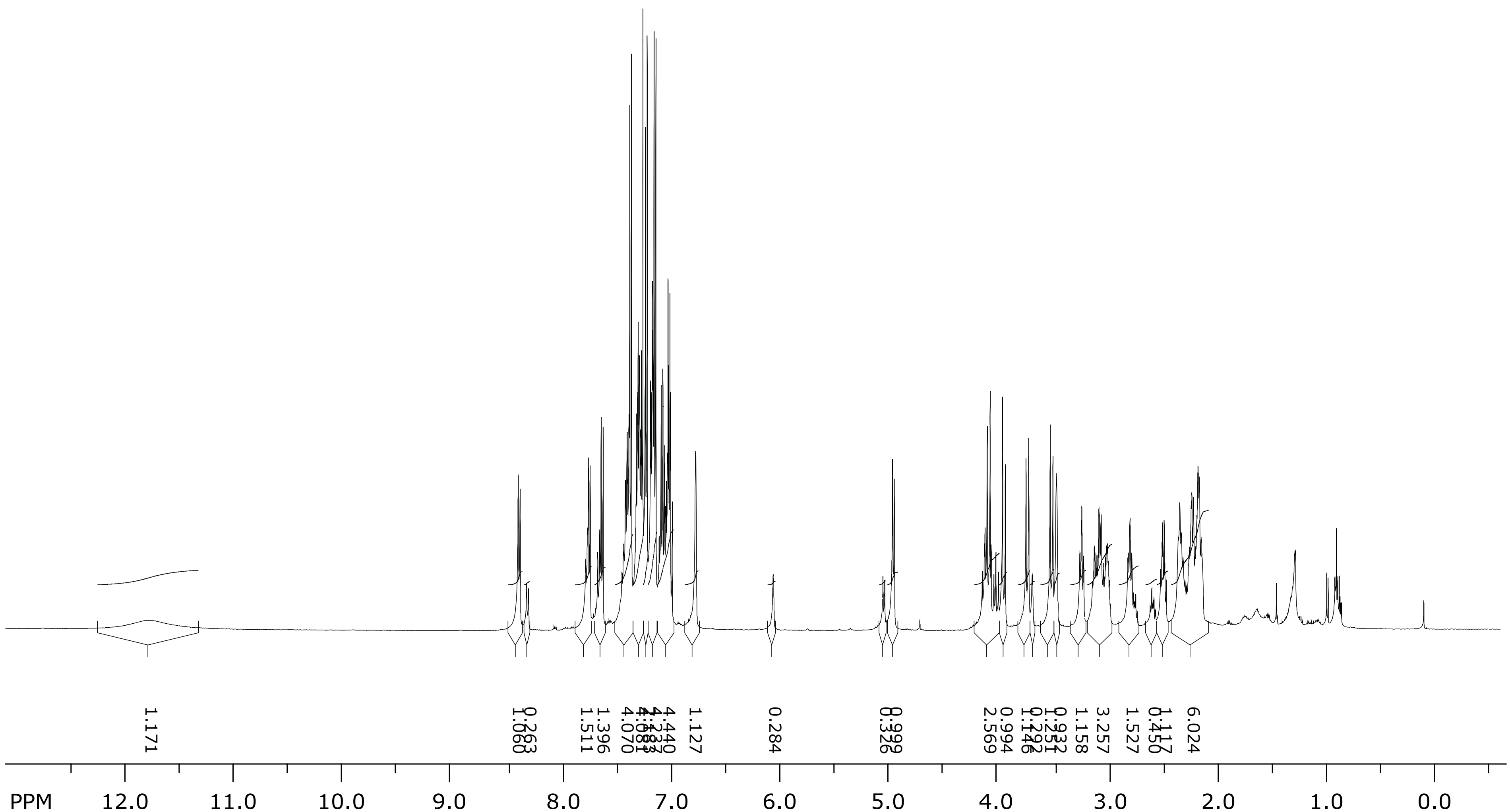
^{13}C NMR of **6** in $CDCl_3$



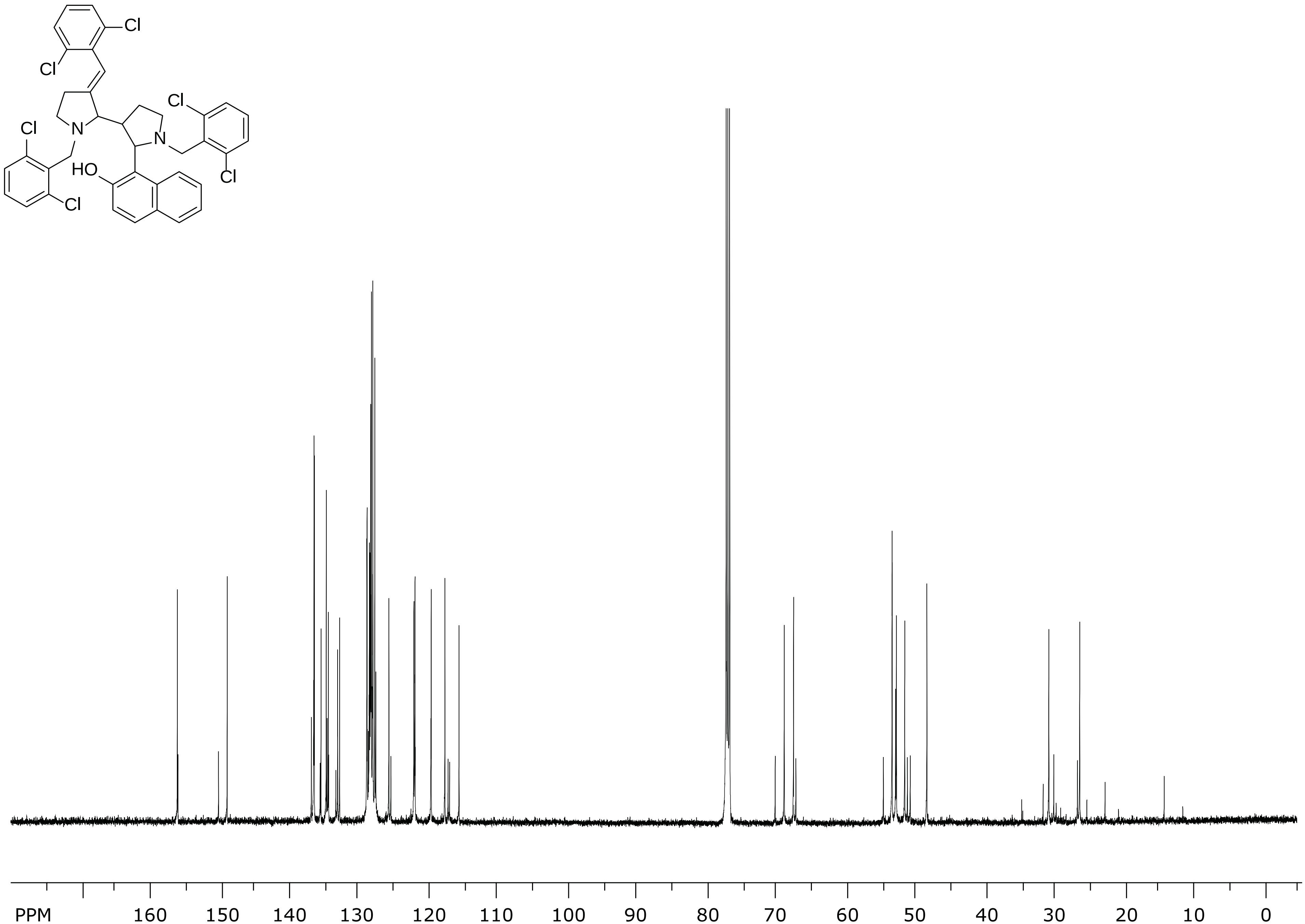


^{1}H NMR of **7** in $CDCl_3$
(mixture of diastereomers)

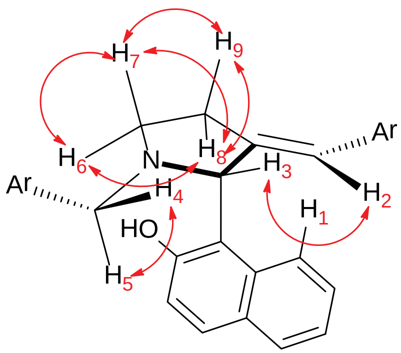


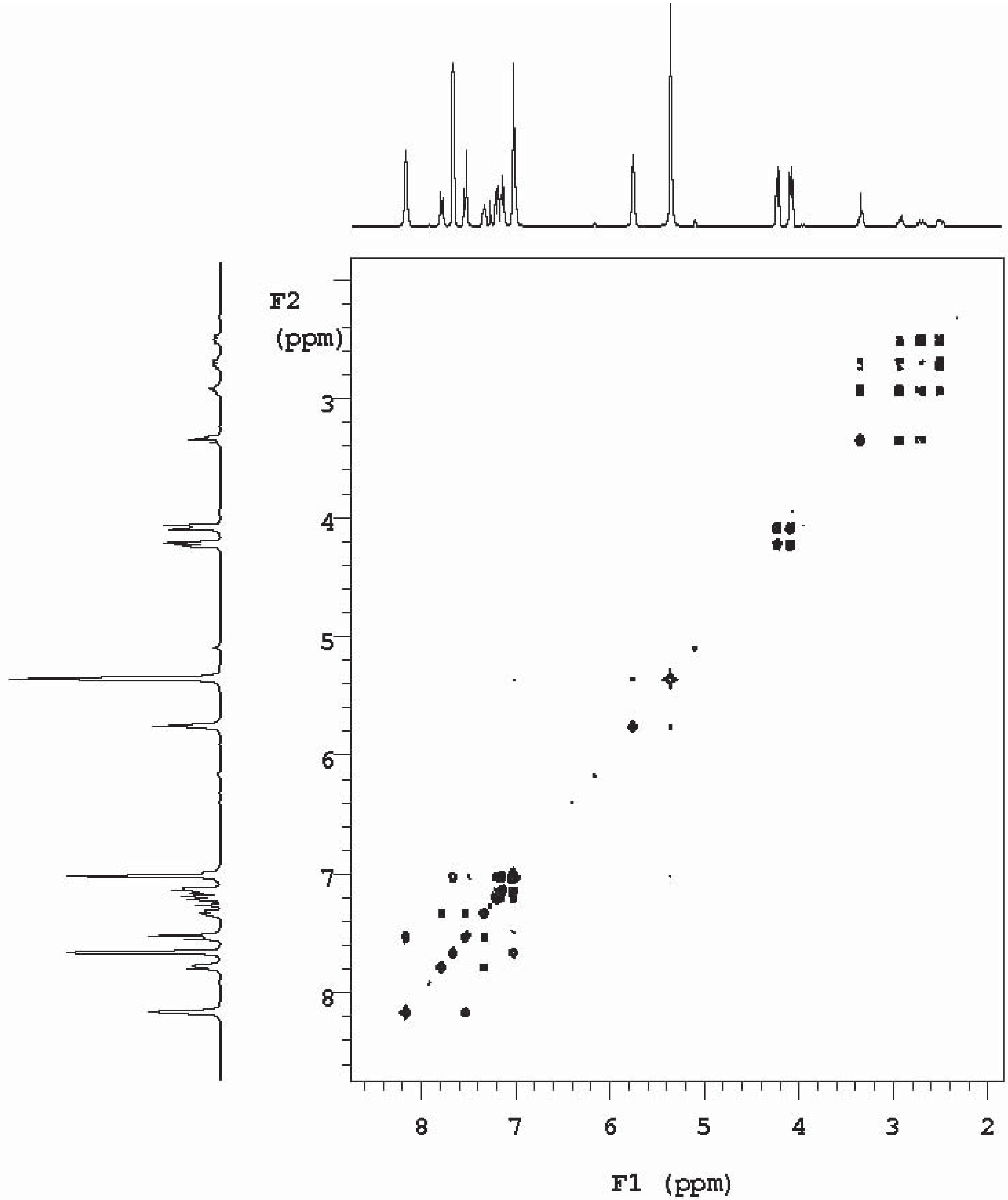


^{13}C NMR of **7** in $CDCl_3$
(mixture of diastereomers)



COSY of **6** in $CDCl_3$





NOESY of **6** in $CDCl_3$