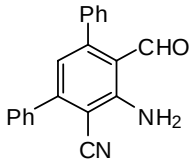
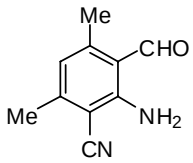
# Supporting Information

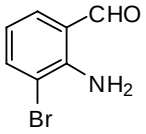
**General Information:** Starting materials, reagents and solvents were purchased from commercial sources and were used as received with the exception of pyrrolidine, piperidine, and hexamethyleneimine which were distilled prior to use. Reactions were run under an atmosphere of nitrogen unless mentioned otherwise. Purification of reaction products was carried out by flash chromatography using EM Reagent silica gel 60 (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 and permanganate stain, 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 instrument and are reported in ppm using 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; integration; coupling constant(s) in Hz. Proton-decoupled carbon nuclear magnetic resonance spectra ($^{13}$C-NMR) spectra were recorded on a Varian VNMRS-500 MHz instrument and are reported in ppm using solvent as an internal standard ($CDCl_3$ at 77.0 ppm). Mass spectra were recorded on a Finnigan LCQ-DUO mass spectrometer. The starting materials 2-amino-3,5-dichlorobenzaldehyde (**1d**),[1] 2-amino-4-chlorobenzaldehyde (**1e**),[1] 2-formyl-3-aminopyrazine (**1n**),[2] 2-aminobenzaldehyde (**1k**),[3] 2-amino-3-methoxybenzaldehyde (**1l**),[4] 2-(N-ethyl)-aminobenzaldehyde (**1o**),[5] 1-amino-2-naphthaldehyde (**1j**),[6] and 2,3-dihydro-1H-benzo[de]isoquinoline,[7] were prepared according to literature methods.



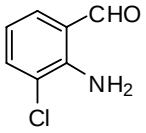

**2-amino-3-cyano-4,6-diphenylbenzaldehyde (1b):** To a solution of 2,6-dicyano-3,5-diphenylaniline[8] (0.6 g, 2.03 mmol) in 5 mL of anhydrous dichloromethane at 0 °C, was slowly added 3.04 mL of DIBAL-H (3.04 mmol, 1 M solution in toluene). The reaction mixture was allowed to warm up to room temperature and was stirred for an additional 24 h. The reaction mixture was diluted with ether and cooled to 0°C. Water (0.12 mL) was added slowly, followed by careful addition of 15 % aqueous NaOH (0.12 mL). Subsequently, water (0.3 mL) was added slowly and the reaction mixture was stirred rapidly at room temperature for 15 minutes. Anhydrous magnesium sulfate was then added, it was stirred for 15 minutes and the salts were removed by filtration. The volatile components were removed under reduced pressure and the crude product was purified by column chromatography to give the title compound as a solid in 30% yield (0.182 g). ($R_f$ = 0.17 in 40% DCM/Hex); mp: 220–222 °C; IR (KBr) 3474, 3316, 2923, 2877, 2209, 1650, 1593, 1570, 1499, 1400, 1296, 1226, 779, 763, 701 $cm^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$) 9.86 (s, 1H), 7.63–7.59 (m, 2H), 7.53–7.44 (comp, 6H), 7.42–7.37 (m, 2H), 6.75 (s, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) 193.4, 153.3, 153.2, 151.5, 138.0, 137.6, 130.0, 129.8, 129.1, 129.0, 128.8, 128.7, 120.1, 116.6, 115.1, 96.1; *m/z* (ESIMS) 299.2 $[M + H]^+$.



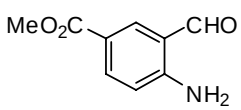

**2-amino-3-cyano-4,6-dimethylbenzaldehyde (1a)**: Starting from 2,6-dicyano-3,5-dimethylaniline,[9] the reaction was carried out in analogy to the preparation of **1b**. After purification by column chromatography, the title compound was obtained as a solid in 50% yield. ($R_f$ = 0.33 in DCM); mp: 175–181 °C; IR (KBr) 3440, 3321, 2208, 1658, 1651, 1607, 1585, 1548, 1505, 1441, 1405, 1375, 1309, 1225, 868, 592 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) 10.29 (s, 1H), 7.11 (br s, 2H), 6.39 (s, 1H), 2.57 (s, 3H), 2.44 (s, 3H); $^{13}C$ NMR (125 MHz, $CDCl_3$) 191.2, 152.5, 150.2, 148.3, 120.8, 115.8, 114.5, 96.9, 21.3, 19.3; *m/z* (ESIMS) 175.2 $[M + H]^+$.



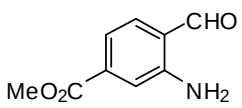

**2-amino-3-bromobenzaldehyde (1f):** Starting from 2-amino-3-bromobenzonitrile,[10] the reaction was carried out in analogy to the preparation of **1b**. After purification by column chromatography, the title compound was obtained as an oil in 32% yield. ($R_f$ = 0.19 in 20% DCM/Hex); IR (KBr) 3467, 3350, 2851, 2765, 1666, 1609, 1578, 1538, 1446, 1409, 1307, 1198, 1139, 1061, 882, 763, 726, 669 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) 9.80 (s, 1H), 7.59 (dd, 1H, *J* = 1.5 Hz, *J* = 7.7 Hz), 7.45 (dd, 1H, *J* = 1.5 Hz, *J* = 7.7 Hz), 6.69 (br s, 2H), 6.64 (app t, 1H, *J* = 7.7 Hz); $^{13}C$ NMR (125 MHz, $CDCl_3$) 193.1, 146.8, 137.9, 135.2, 119.5, 116.7, 110.0 ; *m/z* (ESIMS) 200.1 $[M]^+$.




**2-amino-3-chlorobenzaldehyde (1g):** Starting from 2-amino-3-chlorobenzonitrile,[11] the reaction was carried out in analogy to the preparation of **1b**. After purification by column chromatography, the title compound was obtained as a solid in 50% yield. ($R_f$ = 0.34 in 30% DCM/Hex); mp: 30–31 °C; IR (KBr) 3480, 3359, 2860, 2774, 1681, 1612, 1581, 1546, 1465, 1450, 1408, 1327, 1196, 1146, 1075, 884, 765, 726, 677 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) 9.85 (s, 1H), 7.42 (app ddd, 2H, *J* = 1.5 Hz, *J* = 5.6 Hz, *J* = 7.4 Hz), 6.70 (app t, 1H, *J* = 7.8 Hz), 6.62 (br s, 2H); $^{13}C$ NMR (125 MHz, $CDCl_3$) 193.1, 146.8, 137.9, 135.2, 119.5, 116.8, 110.0; *m/z* (ESIMS) 156.6 $[M + H]^+$.

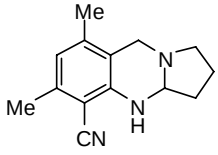



**methyl 4-amino-3-formyl benzoate (1h):** Methyl 3-formyl-4-nitro benzoate (0.5 g, 2.39 mmol), iron powder (1.02 g, 18.35 mmol), and conc. HCl (2 drops), were added to a mixture of EtOH, HOAc and $H_2O$ (2:2:1, 25 mL). The resulting suspension was heated at reflux for 15 min and then stirred at 25 °C for 30 min. Subsequently, it was filtered, diluted with water (100 mL) and extracted with EtOAc (3 x 100 mL). The organic layer was washed with saturated $NaHCO_3$ (2 x 100 mL) and $H_2O$ (2 x 100 mL), dried ($MgSO_4$), and concentrated under reduced pressure. The residue was purified by column chromatography to give the title compound 0.390 g as a solid in 91% yield. ($R_f$ = 0.41 in 20% EtOAc/Hex); mp: 122–124 °C; IR (KBr) 3451, 3334, 3200, 2961, 2803, 2728, 1683, 1613, 1549, 1485, 1444, 1391, 1368, 1275, 1164, 983, 901, 825, 767, 703, 592 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) 9.88 (s, 1H), 8.22 (d, 1H, *J* = 2.0 Hz), 7.93 (dd, 1H, *J* = 2.0 Hz, *J* = 8.7 Hz), 6.64 (d, 1H, *J* = 8.7 Hz), 6.56 (br s, 2H), 3.88 (s, 3H); $^{13}C$ NMR (125 MHz, $CDCl_3$) 193.9, 166.4, 153.2, 138.9, 136.1, 118.4, 118.1, 116.0, 52.1; *m/z* (ESIMS) 180.4 $[M + H]^+$.

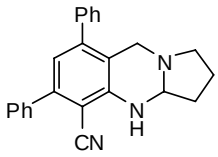



**methyl 3-amino-4-formyl benzoate (1i):** Starting with methyl 3-nitro-4-formyl benzoate, the reaction was carried out in analogy to the preparation of **1h**. After purification by column chromatography, the title compound was obtained as a solid in 70% yield. ($R_f$ = 0.48 in 20% EtOAc/Hex); mp: 119–121 °C; IR (KBr) 3463, 3360, 3066, 2961, 2827, 2745, 1712, 1666, 1626, 1598, 1545, 1492, 1435, 1310, 1262, 1186, 995, 812, 759, 522 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) 9.94 (s, 1H), 7.55 (d, 1H, *J* = 8.4 Hz), 7.36–7.32 (comp, 2H), 6.22 (br s, 2H), 3.91 (s, 3H); $^{13}C$ NMR (125 MHz, $CDCl_3$) 194.2, 166.6, 149.6, 135.9, 135.7, 121.1, 117.8, 116.8, 52.7; *m/z* (ESIMS) 180.2 $[M + H]^+$.

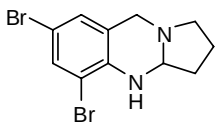
**General Procedure for the Reaction between Aminoaldehyde and Amines:**
To a stirred solution of aminoaldehyde (1 mmol) in 4 mL of EtOH was added the secondary amine (3 mmol), followed by heating at reflux. The reaction mixture was monitored by TLC. After the completion of the reaction, the solvent was evaporated off and the crude product was purified by column chromatography.




**(2a)** The reaction was carried out according to the general procedure (18 h). The product was obtained as a white solid in 95% yield. ($R_f$ = 0.47 in 2% MeOH/EtOAc); mp: 138–140 °C; IR (KBr) 3363, 2942, 2922, 2842, 2209, 1598, 1580, 1508, 1477, 1460, 1333, 1291, 1267, 1190, 1123, 1103 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) 6.38 (s, 1H), 4.53 (br s, 1H), 4.33 (dd, 1H, *J* = 3.0 Hz, *J* = 5.0 Hz), 3.87 (app d, 2H, *J* = 3.8 Hz), 2.88 (app dt, 1H, *J* = 6.5 Hz, *J* = 8.8 Hz), 2.81 (app dt, 1H, *J* = 4.8 Hz, *J* = 8.8 Hz), 2.36 (s, 3H), 2.14–2.27 (m, 1H), 2.14 (s, 3H), 1.89–2.07 (comp, 2H), 1.72–1.81 (m, 1H); $^{13}C$ NMR (125 MHz, $CDCl_3$) 145.9, 140.7, 139.5, 120.3, 117.2, 114.3, 93.9, 70.1, 50.1, 47.0, 32.0, 21.2, 20.3, 18.9; *m/z* (ESIMS) 228.1 $[M + H]^+$.



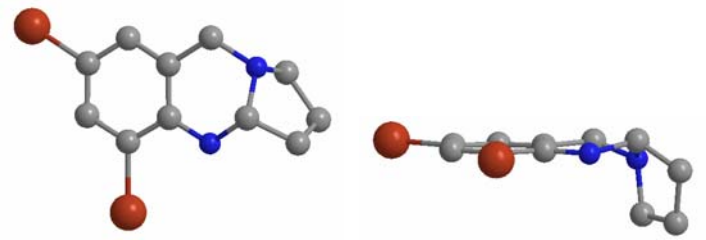

**(2b)** The reaction was carried out according to the general procedure (12 h). The product was obtained as a white solid in 92% yield. ($R_f$ = 0.28 in 40% EtOAc/Hex); mp: 154–158 °C; IR (KBr) 3333, 3055, 3026, 2957, 2908, 2831, 2211, 1735, 1586, 1509, 1460, 1441, 1429, 1379, 1336, 1309, 1279, 1189, 1134, 1008, 776, 765, 749 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) 7.58–7.54 (m, 2H), 7.47–7.36 (comp, 6H), 7.32–7.29 (m, 2H), 6.66 (s, 1H), 4.89 (br s, 1H), 4.52 (dd, 1H, *J* = 2.7 Hz, *J* = 5.1 Hz), 4.07 (d, 1H, *J* = 16.4 Hz), 3.74 (d, 1H, *J* = 16.4 Hz), 2.84–2.77 (m, 1H), 2.73 (app dt, 1H, *J* = 4.8 Hz, *J* = 8.8 Hz), 2.26–2.15 (m, 1H), 2.08–1.88 (comp, 2H), 1.82–1.74 (m, 1H); $^{13}C$ NMR (125 MHz, $CDCl_3$) 146.9, 145.7, 143.6, 139.6, 138.8, 128.52, 128.50, 128.47, 128.40, 128.37, 127.9, 119.6, 117.7, 114.5, 92.8, 70.8, 49.4, 47.9, 32.4, 21.4; *m/z* (ESIMS) 352.2 $[M + H]^+$



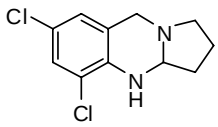

(**2c**) The reaction was carried out according to the general procedure (23 h). The product was obtained as a white solid in 92% yield. ($R_f$ = 0.19 in 40% EtOAc/Hex); mp: 122–124 °C; IR (KBr) 3403, 3052, 2971, 2938, 2907, 2839, 1768, 1692, 1575, 1438, 1349, 1258, 1119,

980, 927, 861, 747, 722, 637 $cm^{-1}$ $^1H$ NMR (500 MHz, $CDCl_3$) 7.37 (app d, 1H, *J* = 1.7 Hz), 6.99 (app d, 1H, *J* = 0.9 Hz), 4.37 (ddd, 1H, *J* = 5.2 Hz, *J* = 2.8 Hz, *J* = 0.8 Hz), 4.23 (br s, 1H), 4.09 (d, 1H, *J* = 16.2 Hz), 3.78 (d, 1H, *J* = 16.2 Hz), 2.82–2.75 (comp, 2H), 2.20–2.11 (m, 1H), 2.04–1.87 (comp, 2H), 1.73 (dddd, 1H, *J* = 2.8 Hz, *J* = 4.2 Hz, *J* = 9.9 Hz, *J* = 12.6 Hz); $^{13}C$ NMR (125 MHz, $CDCl_3$) 139.6, 132.5, 129.2, 121.7, 109.0, 108.3, 71.3, 49.9, 49.6, 32.7, 21.7; *m/z* (ESIMS) 333.0 $[M + H]^+$.

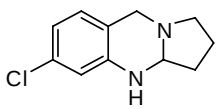
Product **2c** was further characterized by X-ray crystallography:



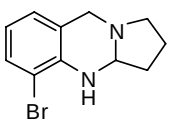
The requisite CIF file has been submitted to the journal.




**(2d)** The reaction was carried out according to the general procedure (12 h). The product was obtained as a white solid in 84% yield. ($R_f$ = 0.33 in 40% EtOAc/Hex); mp: 72–75 °C; IR (KBr) 3415, 3039, 2973, 2907, 2841, 1597, 1491, 1454, 1436, 1349, 1259, 1185, 1120, 981 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) 7.12 (app d, 1H, *J* = 2.2 Hz), 6.85 (app d, 1H, *J* = 1.2 Hz), 4.42–4.35 (m, 1H), 4.22 (br s, 1H), 4.11 (d, 1H, *J* = 16.2 Hz), 3.83 (d, 1H, *J* = 16.2 Hz), 2.91–2.75 (comp, 2H), 2.19 (app ddt, 1H, *J* = 5.3 Hz, *J* = 8.6 Hz, *J* = 12.6 Hz), 2.12–1.89 (m, 2H), 1.76 (dddd, 1H, *J* = 2.9 Hz, *J* = 4.3 Hz, *J* = 9.9 Hz, *J* = 12.6 Hz); $^{13}C$ NMR (125 MHz, $CDCl_3$) 138.2, 127.0, 125.8, 121.3, 121.1, 118.5, 71.1, 49.9, 49.6, 32.5, 21.6; *m/z* (ESIMS) 243.2 $[M]^+$.

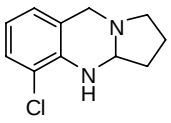



**(2e)** The reaction was carried out according to the general procedure (72 h). The product was obtained as a white solid in 57% yield. ($R_f$ = 0.22 in 40% EtOAc/Hex); mp: 83–84 °C; IR (KBr) 3213, 2970, 2941, 2827, 2793, 1858, 1603, 1579, 1491, 1382, 1351, 1249, 1143, 1083, 1001, 914, 848, 829, 600 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) 6.84 (d, 1H, *J* = 8.0 Hz), 6.63 (dd, 1H, *J* = 2.0 Hz, *J* = 8.0 Hz), 6.49 (d, 1H, *J* = 2.0 Hz), 4.22 (dd, 1H, *J* = 3.8 Hz, *J* = 5.1 Hz), 4.01 (d, 1H, *J* = 15.8 Hz), 3.90–3.74 (comp, 2H), 2.94 (app dt, 1H, *J* = 5.9 Hz, *J* = 8.9 Hz), 2.72 (app dt, 1H, *J* = 5.1 Hz, *J* = 8.8 Hz), 2.13 (app tdd, 1H, *J* = 5.6 Hz, *J* = 10.9 Hz, *J* = 12.4 Hz), 2.05–1.87 (comp, 2H), 1.69–1.61 (m, 1H); $^{13}C$ NMR (125 MHz, $CDCl_3$) 144.3, 132.6, 128.5, 117.9, 117.4, 114.3, 71.1, 50.2, 49.9, 32.2, 21.5; *m/z* (ESIMS) 209.1 $[M + H]^+$.

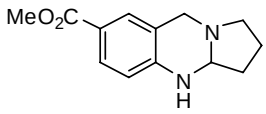



**(2f)** The reaction was carried out according to the general procedure (36 h). The product was obtained as an oil in 83% yield. ($R_f$ = 0.30 in 40% EtOAc/Hex); IR (film) 3398, 2970, 2838, 1600, 1485, 1443, 1346, 1379, 1292, 1265, 1146, 1118, 1069, 756, 721, 619 $cm^{-1}$ $^1H$ NMR (500 MHz,

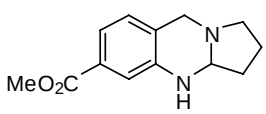
$CDCl_3$) 7.26 (app d, 1H, *J* = 7.9 Hz), 6.87 (app d, 1H, *J* = 7.4 Hz), 6.52 (app t, 1H, *J* = 7.7 Hz), 4.36–4.31 (m, 1H), 4.25 (br s, 1H), 4.09 (d, 1H, *J* = 15.9 Hz), 3.83 (d, 1H, *J* = 15.9 Hz), 2.88 (app dt, 1H, *J* = 6.4 Hz, *J* = 8.9 Hz), 2.75 (app dt, 1H, *J* = 4.8 Hz, *J* = 8.7 Hz), 2.16 (ddd, 1H, *J* = 5.6 Hz, *J* = 11.2 Hz, *J* = 17.4 Hz), 2.01 (dddd, 1H, *J* = 5.4 Hz, *J* = 9.9 Hz, *J* = 14.8 Hz, *J* = 15.4 Hz), 1.96–1.87 (m, 1H), 1.78–1.70 (m, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) 140.3, 130.4, 126.4, 120.3, 117.9, 108.9, 71.2, 50.0, 49.9, 32.4, 21.5; *m/z* (ESIMS) 253.3 $[M]^+$.




**(2g)** The reaction was carried out according to the general procedure (18 h). The product was obtained as an oil in 76% yield. ($R_f$ = 0.44 in 2% MeOH/EtOAc); IR (film) 3407, 2971, 2840, 1602, 1488, 1379, 1346, 1295, 1265, 1179, 1142, 1119, 1070, 758, 723 $cm^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$) 7.11 (app d, 1H, *J* = 7.9 Hz), 6.86 (app d, 1H, *J* = 7.4 Hz), 6.59 (app t, 1H, *J* = 7.7 Hz), 4.37–4.33 (m, 1H), 4.26 (br s, 1H), 4.12 (d, 1H, *J* = 16.0 Hz), 3.88 (d, 1H, *J* = 16.0 Hz), 2.92 (app dt, 1H, *J* = 6.3 Hz, *J* = 8.8 Hz), 2.78 (app dt, 1H, *J* = 4.9 Hz, *J* = 8.8 Hz), 2.19 (app dtd, 1H, *J* = 5.6 Hz, *J* = 11.0 Hz, *J* = 16.4 Hz), 2.04 (app ddt, 1H, *J* = 5.4 Hz, *J* = 10.1 Hz, *J* = 15.1 Hz), 1.98–1.89 (m, 1H), 1.79–1.72 (m, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) 139.3, 127.3, 125.7, 120.1, 118.4, 117.4, 71.1, 50.0, 49.9, 32.4, 21.5; *m/z* (ESIMS) 209.1 $[M + H]^+$.

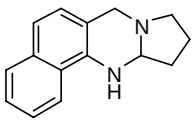



**(2h)** To a stirred solution of methyl 4-amino-3-formyl benzoate (1 mmol) in 4 mL of methanol was added pyrrolidine (3 mmol). The mixture was heated at 100°C in a sealed tube for 24 h. Following solvent removal and purification of the crude product by column chromatography, the product was obtained as a white solid in 76% yield. ($R_f$ = 0.43 in 5% MeOH/EtOAc); mp: 118–120 °C; IR (KBr) 3375, 2942, 2874, 2804, 1685, 1608, 1513, 1436, 1381, 1363, 1321, 1293, 1237, 1198, 1142, 1111, 1096, 1002, 989, 908, 832, 768, 443 $cm^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$) 7.66 (dd, 1H, *J* = 1.9 Hz, *J* = 8.4 Hz), 7.62 (app s, 1H), 6.40 (app d, 1H, *J* = 8.4 Hz), 4.38 (dd, 1H, *J* = 2.8 Hz, *J* = 5.1 Hz), 4.31 (br s, 1H), 4.10 (d, 1H, *J* = 16.0 Hz), 3.83 (d, 1H, *J* = 16.0 Hz), 3.81 (s, 3H), 2.82 (app dt, 1H, *J* = 6.6 Hz, *J* = 8.9 Hz), 2.76 (app dt, 1H, *J* = 4.9 Hz, *J* = 8.8 Hz), 2.15–2.07 (m, 1H), 2.01–1.85 (comp, 2H), 1.64 (dddd, 1H, *J* = 2.9 Hz, *J* = 4.3 Hz, *J* = 9.8 Hz, *J* = 12.6 Hz); $^{13}$C NMR (125 MHz, $CDCl_3$) 167.6, 147.5, 129.7, 129.6, 118.6, 117.2, 113.1, 70.9, 51.7, 49.8, 49.5, 32.5, 21.7; *m/z* (ESIMS) 233.1 $[M + H]^+$.

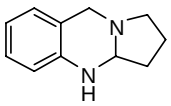



**(2i)** To a stirred solution of methyl 3-amino-4-formyl benzoate (1 mmol) in 4 mL of methanol was added pyrrolidine (3 mmol). The mixture was heated at 100°C in a sealed tube for 24 h. Following solvent removal and purification of the crude product by column chromatography, the product was obtained as a white solid in 60% yield. ($R_f$ = 0.43 in 5% MeOH/EtOAc); mp: 119–120 °C; IR (KBr) 3400, 2970, 2942, 2842, 1713, 1614, 1581, 1499, 1479, 1459, 1439, 1342, 1312, 1289, 1278, 1230, 1216, 1101, 1018, 854, 755, 440 $cm^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$) 7.32 (dd, 1H, *J* = 1.6 Hz, *J* = 7.8 Hz), 7.18 (app d, 1H, *J* = 1.6 Hz), 6.97 (app d, 1H, *J* = 7.8 Hz), 4.21 (dd, 1H, *J* = 4.0 Hz, *J* = 5.1 Hz), 4.06 (d, 1H, *J* = 16.3 Hz), 3.96–3.87 (comp, 2H), 3.86 (s, 3H), 2.94 (app dt, 1H, *J* = 5.8 Hz, *J* = 8.8 Hz), 2.71 (app dt, 1H, *J* = 5.3 Hz, *J* = 8.8 Hz), 2.13 (ddd, 1H, *J* = 5.6

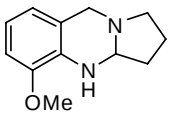
Hz, $J$ = 11.0 Hz, $J$ = 18.0 Hz), 2.04–1.85 (comp, 2H), 1.66 (app tdd, 1H, $J$ = 4.2 Hz, $J$ = 10.2 Hz, $J$ = 12.6 Hz); $^{13}$C NMR (125 MHz, $CDCl_3$) 167.6, 143.3, 129.3, 127.5, 124.5, 119.2, 115.8, 71.3, 52.1, 50.6, 50.4, 32.2, 21,5; *m/z* (ESIMS) 233.2 $[M + H]^+$.



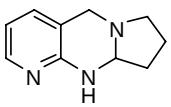
**(2j)** The reaction was carried out according to the general procedure (48 h). The product was obtained as a white solid in 58% yield. ($R_f$ = 0.27 in 5% MeOH/EtOAc); mp: 130–133 °C; IR (KBr) 3227, 3062, 2977, 2956, 2915, 2856, 1576, 1520, 1487, 1407, 1363, 1340, 1325, 1304, 1260, 1120, 1093, 775, 743 $cm^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$) 7.82–7.75 (comp, 2H), 7.47–7.40 (comp, 2H), 7.30 (d, 1H, $J$ = 8.3 Hz), 7.11 (d, 1H, $J$ = 8.3 Hz), 4.19–4.11 (comp, 3H), 4.06 (d, 1H, $J$ = 15.6 Hz), 3.14 (app dt, 1H, $J$ = 5.1 Hz, $J$ = 8.8 Hz), 2.69 (app dt, 1H, $J$ = 6.1 Hz, $J$ = 8.8 Hz), 2.30 (app dtd, 1H, $J$ = 5.5 Hz, $J$ = 10.8 Hz, $J$ = 16.1 Hz), 2.12–2.03 (m, 1H), 2.02–1.92 (m, 1H), 1.88–1.80 (m, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) 137.6, 133.3, 128.6, 126.0, 125.5, 125.2, 124.3, 120.0, 118.9, 115.2, 72.4, 51.9, 50.9, 31.9, 21.3; *m/z* (ESIMS) 225.1 $[M + H]^+$.



**(2k)** The reaction was carried out according to the general procedure (72 h). The product was obtained as a white solid in 73% yield. ($R_f$ = 0.25 in 5% MeOH/EtOAc); mp: 63–64 °C [lit. 69-70 °C][12]; IR (KBr) 3246, 2966, 2826, 1608, 1585, 1478, 1383, 1255, 749 $cm^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$) 7.02 (app t, 1H $J$ = 7.6 Hz), 6.95 (app d, 1H $J$ = 7.4 Hz), 6.70 (app dt, 1H, $J$ = 0.9 Hz, $J$ = 7.4 Hz), 6.54 (d, 1H, $J$ = 7.9 Hz), 4.17–4.13 (m, 1H), 4.04 (d, 1H, $J$ = 15.6 Hz), 3.90 (d, 1H, $J$ = 15.6 Hz), 3.67 (br s, 1H), 3.03 (app dt, 1H, $J$ = 5.5 Hz, $J$ = 8.8 Hz), 2.68 (app dt, 1H, $J$ = 5.5 Hz, $J$ = 8.8 Hz), 2.18–2.09 (m, 1H), 1.97–2.07 (m, 1H), 1.96–1.87 (m, 1H), 1.66 (app tdd, 1H, $J$ = 4.4 Hz, $J$ = 10.2 Hz $J$ = 12.3 Hz); $^{13}$C NMR (125 MHz, $CDCl_3$)142.9, 127.2, 127.0, 119.4, 118.1, 114.9, 71.2, 50.5, 50.3, 31.8, 21.1; *m/z* (ESIMS) 175.1 $[M + H]^+$.

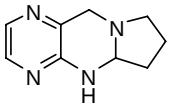


**(2l)** To a stirred solution of methyl 3-amino-4-formyl benzoate (0.151 g, 1 mmol) in 4 mL of ethanol was added pyrrolidine (0.25 ml, 3 mmol). The mixture was heated at 140°C in a sealed tube for 48 h. Following solvent removal and purification of the crude product by column chromatography, the product was obtained as a pale yellow solid in 81% yield (0.165 g). ($R_f$ = 0.20 in 70% EtOAc/Hex); mp: 84–86 °C; IR (KBr) 3398, 3031, 2970, 2934, 2909, 2851, 1609, 1587, 1496, 1478, 1457, 1354, 1313, 1247, 1184, 1139, 1119, 1082, 1037, 1008, 980, 898, 762, 728, 686 $cm^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$) 6.67–6.59 (comp, 3H), 4.21 (dd, 1H, $J$ = 4.0 Hz, $J$ = 4.9 Hz), 4.12–4.06 (comp, 2H), 3.90 (d, 1H, $J$ = 15.8 Hz), 3.83 (s, 3H), 3.01 (app dt, 1H, $J$ = 5.9 Hz, $J$ = 8.8 Hz), 2.72 (app dt, 1H, $J$ = 5.1 Hz, $J$ = 8.8 Hz), 2.14 (app tdd, 1H, $J$ = 5.5 Hz, $J$ = 10.9 Hz, $J$ = 12.2 Hz), 2.03 (dddd, 1H, $J$ = 5.4 Hz, $J$ = 9.0 Hz, $J$ = 10.7 Hz, $J$ = 14.8 Hz), 1.91 (app dddt, 1H, $J$ = 4.6 Hz, $J$ = 5.8 Hz, $J$ = 8.8 Hz, $J$ = 10.6 Hz), 1.78–1.71 (m, 1H)**;** $^{13}$C NMR (125 MHz, $CDCl_3$) 146.3, 132.7, 119.4, 119.1, 116.8, 107.8, 70.7, 55.4, 50.3, 50.0, 32.0, 21.3; *m/z* (ESIMS) 205.1 $[M + H]^+$.

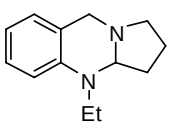


**(2m)** The reaction was carried out according to the general procedure (36 h). The product was obtained as a white solid in 94% yield. ($R_f$ = 0.28 in

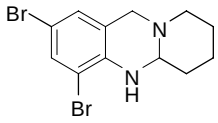
30% MeOH/EtOAc); mp: 123–126 °C; IR (KBr) 3225, 3093, 2912, 2842, 1584, 1523, 1458, 1444, 1357, 1339, 1303, 1268, 1179, 1120, 1092, 762 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) 7.91 (app d, 1H, *J* = 5.0 Hz), 7.17 (dd, 1H, *J* = 0.6 Hz, *J* = 7.2 Hz), 6.55 (dd, 1H, *J* = 5.0 Hz, *J* = 7.2 Hz), 4.85 (br s, 1H), 4.56 (dd, 1H, *J* = 2.3 Hz, *J* = 5.0 Hz), 4.13 (d, 1H, *J* = 16.2 Hz), 3.81 (d, 1H, *J* = 16.2 Hz) 2.79–2.87 (comp, 2H), 2.16 (dddd, 1H, *J* = 5.0 Hz, *J* = 6.4 Hz, *J* = 11.1 Hz, *J* = 12.5 Hz), 1.90–1.99 (comp, 2H), 1.73 (dddd, 1H, *J* = 2.3 Hz, *J* = 4.1 Hz, *J* = 9.8 Hz, *J* = 12.5 Hz); $^{13}C$ NMR (125 MHz, $CDCl_3$) 154.8, 146.7, 134.9, 113.5, 113.3, 71.2, 49.7, 48.9, 32.8, 21.8; *m/z* (ESIMS) 176.1 $[M + H]^+$.



**(2n)** The reaction was carried out according to the general procedure (13 h). The product was obtained as a white solid in 91% yield. ($R_f$ = 0.30 in 30% MeOH/EtOAc); mp: 92–95 °C; IR (KBr) 3227, 3116, 2978, 2917, 2840, 1579, 1557, 1487, 1455, 1442, 1335, 1311, 1263, 1187, 1144, 1110, 1093, 1005, 839 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) 7.81 (d, 1H, *J* = 2.7 Hz), 7.77 (d, 1H, *J* = 2.7 Hz), 4.88 (s, 1H), 4.62 (dd, 1H, *J* = 2.2 Hz, *J* = 5.0 Hz), 4.20 (d, 1H, *J* = 17.2 Hz), 3.96 (d, 1H, *J* = 17.2 Hz), 2.94 (app dt, 1H, *J* = 4.5 Hz, *J* = 9.0 Hz), 2.83 (app dt, 1H, *J* = 6.8 Hz, *J* = 9.0 Hz), 2.19 (app ddt, 1H, *J* = 5.2 Hz, *J* = 6.3 Hz, *J* = 11.4 Hz), 2.10–1.92 (comp, 2H), 1.80–1.72 (m, 1H); $^{13}C$ NMR (125 MHz, $CDCl_3$) 151.0, 140.6, 137.3, 132,9, 70.7, 51.2, 49.8, 32.3, 21.6; *m/z* (ESIMS) 177.1 $[M + H]^+$.

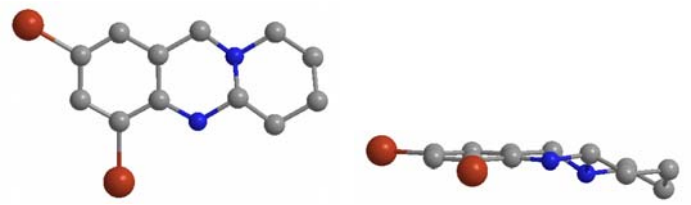


**(2o)** The reaction was carried out according to the general procedure (80 h). The product was obtained as an oil in 84% yield. ($R_f$ = 0.26 in 30% EtOAc/Hex); IR (film) 3354, 2969, 2876, 2842, 2786, 1650, 1605, 1494, 1457, 1373, 1325, 1255, 1168, 1134, 1045, 745 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) 7.11 (app t, 1H, *J* = 7.5 Hz), 6.94 (app d, 1H, *J* = 7.0 Hz), 6.71 (app d, 1H, *J* = 8.2 Hz), 6.67 (app t, 1H, *J* = 7.3 Hz), 3.87–3.92 (comp, 2H), 3.82 (d, 1H, *J* = 14.5 Hz), 3.46 (app qd, 1H, *J* = 7.1 Hz, *J* = 14.4 Hz), 3.14–3.24 (comp, 2H), 2.56 (ddd, 1H, *J* = 5.0 Hz, *J* = 7.8 Hz, *J* = 8.9 Hz), 2.08–2.16 (m, 1H), 1.82–2.03 (comp, 3H), 1.17 (t, 3H, *J* = 7.1 Hz); $^{13}C$ NMR (125 MHz, $CDCl_3$) 144.6, 127.5, 127.1, 121.2, 116.8, 112.1, 76.7, 52.5, 51.8, 41.7, 30.7, 20.7, 12.5; *m/z* (ESIMS) 203.1 $[M + H]^+$.

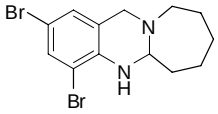


**(3)** To a stirred solution of 2-amino-3,5-dibromobenzaldehyde (1 mmol) in 4 mL of isopropanol was added piperidine (3 mmol). The mixture was heated at 140°C in a sealed tube for 48 h. Subsequent to solvent removal, the crude product was purified by column chromatography to give the product as a white solid in 67% yield. ($R_f$ = 0.28 in 30% EtOAc/Hex); mp: 89–92 °C; IR (KBr) 3405, 2936, 2853, 2771, 1596, 1561, 1486, 1442, 1370, 1351, 1294, 1272, 1190, 1119, 856, 713 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) 7.36 (app d, 1H, *J* = 2.1 Hz), 6.96 (app d, 1H, *J* = 1.4 Hz), 4.22 (s, 1H), 3.79 (br s, 1H), 3.72–3.59 (comp, 2H), 2.96–2.88 (m, 1H), 2.25–2.15 (m, 1H), 1.95–1.87 (m, 1H), 1.76 (app tt, 1H, *J* = 4.9 Hz, *J* = 10.1 Hz), 1.71–1.64 (comp, 2H), 1.63–1.54 (m, 1H), 1.50–1.41 (m, 1H); $^{13}C$ NMR (125 MHz, $CDCl_3$) 139.1, 132.5, 128.7, 122.3, 108.5, 108.3, 70.2, 56.0, 51.5, 31.9, 25.6. 21.3; *m/z* (ESIMS) 347.0 $[M + H]^+$.

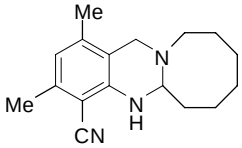
Product **3** was further characterized by X-ray crystallography:



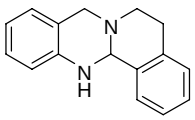
The requisite CIF file has been submitted to the journal.




**(4)** To a stirred solution of 2-amino-3,5-dibromobenzaldehyde (1 mmol) in 4 mL of isopropanol was added hexamethyleneimine (3 mmol). The mixture was heated at 140°C in a sealed tube for 24 h. Subsequent to solvent removal, the crude product was purified by column chromatography to give the product as an oil in 77% yield. ($R_f$ = 0.56 in 30% EtOAc/Hex); IR (film) 3400, 2924, 2850, 1724, 1593, 1479, 1357, 1318, 1279, 1235, 1136, 1001, 949, 857, 738, 687 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) 7.37 (app d, 1H, *J* = 2.1 Hz), 6.95 (app d, 1H, *J* = 1.0 Hz), 4.23 (app t, 1H, *J* = 5.2 Hz), 4.20 (br s, 1H), 4.07 (d, 1H, *J* = 15.6 Hz), 3.67 (d, 1H, *J* = 15.6 Hz), 2.86–2.79 (m, 1H), 2.46 (app td, 1H, *J* = 4.1 Hz, *J* = 9.4 Hz), 2.14–2.06 (m, 1H), 1.83–1.74 (m, 1H), 1.74–1.58 (comp, 5H), 1.57-1.47 (m, 1H); $^{13}C$ NMR (125 MHz, $CDCl_3$) 140.1, 132.4, 128.6, 123.3, 108.7, 108.2, 72.0, 57.6, 50.1, 35.5, 29.4, 29.2, 22.0; *m/z* (ESIMS) 361.1 $[M + H]^+$.

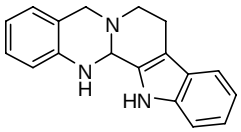



**(5)** The reaction was carried out according to the general procedure (48 h). The product was obtained as a white solid in 60% yield. ($R_f$ = 0.72 in 30% EtOAc/Hex); mp: 288–292 °C; IR (KBr) 3332, 2918, 2853, 2214, 1598, 1580, 1507, 1483, 1471, 1446, 1334, 1298, 1267, 1133, 1113, 1104, 1026, 888, 825 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) 6.33 (s, 1H), 4.52 (br s, 1H), 4.27 (dd, 1H, *J* = 4.3 Hz, *J* = 9.5 Hz), 3.93 (d, 1H, *J* = 16.3 Hz), 3.70 (d, 1H, *J* = 16.3 Hz), 2.90 (ddd, 1H, *J* = 3.5 Hz, *J* = 10.8 Hz, *J* = 14.5 Hz), 2.35 (s, 3H), 2.30 (app td, 1H, *J* = 4.6 Hz, *J* = 14.8 Hz), 2.11 (s, 3H), 1.96–1.86 (m, 1H), 1.83 (dddd, 1H, *J* = 2.7 Hz, *J* = 4.5 Hz, *J* = 7.2 Hz, *J* = 14.3 Hz), 1.79–1.50 (m, 7H), 1.46 (app dtd, 1H, *J* = 3.8 Hz, *J* = 7.7 Hz, *J* = 15.4 Hz); $^{13}C$ NMR (125 MHz, $CDCl_3$) 147.2, 140.7, 139.7, 120.0, 117.7, 116.1, 93.4, 70.9, 54.1, 47.2, 31.4, 29.7, 26.7, 25.2, 24.4, 20.6, 19.1; *m/z* (ESIMS) 270.1 $[M + H]^+$.

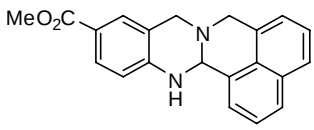



**(6)** The reaction was carried out according to the general procedure (48 h). The product was obtained as an oil in 95% yield. ($R_f$ = 0.33 in 30% EtOAc/Hex); IR (film) 3387, 3024, 2916, 2837, 2791, 2740, 1725, 1606, 1583, 1487, 1424, 1339, 1305, 1249, 1112, 1044, 1021, 936, 749 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) 7.36 (app dd, 1H, *J* = 1.7 Hz, *J* = 7.2 Hz), 7.30–7.23 (comp, 2H), 7.20 (app dd, 1H, *J* = 1.2 Hz, *J* = 7.2 Hz), 7.07 (app t, 1H, *J* = 7.6 Hz), 7.01 (app d, 1H, *J* = 7.5 Hz), 6.77 (app dt, 1H, *J* = 1.1 Hz, *J* = 7.4 Hz), 6.58 (d, 1H, *J* = 8.0 Hz), 5.16 (d, 1H, *J* = 3.2 Hz), 4.35 (d, 1H, *J* = 15.8 Hz), 3.87 (d, 1H, *J* = 15.8 Hz), 3.86 (br s, 1H), 3.21 (ddd, 1H, *J* = 4.8 Hz, *J* = 8.3 Hz, *J* = 11.4 Hz), 3.06 (ddd, 1H, *J* = 5.7 Hz, *J* = 8.3 Hz, *J* = 14.0 Hz), 2.98 (app td, 1H, *J* = 4.8 Hz, *J* = 16.4 Hz), 2.72 (app td, 1H, *J* =

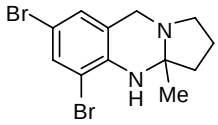
5.3 Hz, $J$ = 10.9 Hz); $^{13}$C NMR (125 MHz, $CDCl_3$) 142.3, 135.8, 134.9, 129.3, 128.1, 127.5, 127.3, 126.5, 126.4, 119.8, 118.7, 115.6, 69.7, 56.0, 45.5, 29.4; *m/z* (ESIMS) 237.1 $[M + H]^+$.



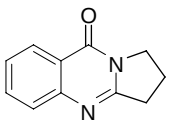
**(7)** The reaction was carried out according to the general procedure (72 h). The product was obtained as an oil in 66% yield. ($R_f$ = 0.25 in 40% EtOAc/Hex); IR (film) 3395, 3204, 3053, 2912, 2844, 2807, 1608, 1588, 1494, 1469, 1454, 1343, 1325, 1306, 1265, 1164, 1112, 741 cm$^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$) 8.53 (s, 1H), 7.51 (app d, 1H, $J$ = 7.8 Hz), 7.30–7.09 (comp, 4H), 7.05 (app d, 1H, $J$ = 7.5 Hz), 6.92 (app dt, 1H, $J$ = 1.1 Hz, $J$ = 7.5 Hz), 6.80 (app d, 1H, $J$ = 7.9 Hz), 4.72 (s, 1H), 4.01–3.90 (comp, 2H), 3.26 (app td, 1H, $J$ = 4.7 Hz, $J$ = 11.4 Hz), 3.00–2.79 (comp, 2H), 2.76 (ddd, 1H, $J$ = 4.7 Hz, $J$ = 8.7 Hz, $J$ = 11.5 Hz), 1.73 (br s, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) 141.6, 136.5, 131.8, 127.7, 127.6, 126.9. 123.9, 122.4, 121.3, 119.9, 119.4, 118.9, 111.4, 110.4, 68.5, 55.7, 49.1, 21.7; *m/z* (ESIMS) 276.2 $[M + H]^+$.



**(8)** The reaction was carried out according to the general procedure (48 h). The product was obtained as a white solid in 80% yield. ($R_f$ = 0.32 in 20% EtOAc/Hex); mp: 176–179 °C; IR (KBr) 3338, 3043, 2944, 2839, 1694, 1608, 1512, 1433, 1333, 1294, 1249, 1187, 1125, 1012, 780, 767 cm$^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$) 7.86 (app d, 1H, $J$ = 8.3 Hz), 7.77–7.70 (comp, 3H), 7.51–7.43 (comp, 2H), 7.40 (app d, 1H, $J$ = 6.9 Hz), 7.28 (app d, 1H, $J$ = 7.2 Hz), 6.40 (app d, 1H, $J$ = 8.3 Hz), 5.75 (s, 1H), 4.68 (d, 1H, $J$ = 16.5 Hz), 4.37–4.31 (comp, 2H), 3.99 (d, 1H, $J$ = 16.5 Hz), 3.94 (d, 1H, $J$ = 14.7 Hz), 3.87 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) 167.5, 146.6, 133.6, 133.0, 132.9, 129.9, 129.8, 128.8, 126.6, 126.4, 126.3, 125.7, 123.2, 123.1, 119.5, 117.1, 113.2, 69.3, 54.6, 51.9, 49.3; *m/z* (ESIMS) 331.1 $[M + H]^+$.

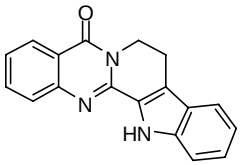


**(9)** The reaction was carried out according to the general procedure (24 h). Product **9a** was obtained as an oil in 60% yield. Additionally, **9b** was obtained as an oil in 25% yield (2:1 mixture of diastereomers). For **9a**: ($R_f$ = 0.22 in 30% EtOAc/Hex); IR (film) 3400, 2970, 2848, 1644, 1591, 1478, 1448, 1374, 1322, 1290, 1208, 1196, 1152, 1125, 1032, 857, 745, 711, 547 cm$^{-1}$ $^1$H NMR (500 MHz, $CDCl_3$) 7.40 (app d, 1H, $J$ = 1.7 Hz), 7.03 (app d, 1H, $J$ = 1.0 Hz), 4.22 (br s, 1H), 4.18 (d, 1H, $J$ = 17.1 Hz), 3.70 (d, 1H, $J$ = 17.1 Hz), 3.00 (ddd, 1H, $J$ = 5.2 Hz, $J$ = 7.2 Hz, $J$ = 8.8 Hz), 2.59 (app q, 1H, $J$ = 8.5 Hz), 2.03–1.95 (m, 1H), 1.93–1.81 (comp, 3H), 1.40 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) 138.7, 132.5, 129.3, 120.0, 108.7, 107.5, 74.4, 51.0, 45.6, 40.0, 26.2, 20.0; *m/z* (ESIMS) 347.0 $[M + H]^+$.



**Deoxyvasicinone:** To a solution of **2k** (0.042 g, 0.24 mmol) in acetone (2.4 mL), $KMnO_4$ (2.5eq. 0.603 mmol) was added. The reaction mixture was heated at reflux for 80 min, allowed to cool to room temperature and filtered. The filtrate was concentrated and purified by column chromatography to give the product as a white solid in 82% yield. ($R_f$ = 0.34 in 2% MeOH/EtOAc); mp: 99–102 °C [lit. 105-107 °C][13]; IR (KBr) 1666, 1622, 1560, 1466,

1425, 1385, 1337, 1322, 772, 694 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) 8.25 (app d, 1H, *J* = 7.9 Hz), 7.70 (app t, 1H, *J* = 7.6 Hz), 7.62 (app d, 1H, *J* = 8.1 Hz), 7.42 (app t, 1H, *J* = 7.5 Hz), 4.18 (t, 2H, *J* = 7.2 Hz), 3.16 (t, 2H, *J* = 7.9 Hz), 2.22-2.34 (m, 2H); $^{13}C$ NMR (125 MHz, $CDCl_3$) 161.1, 159.6, 149.3, 134.3, 126.9, 126.5, 126.4, 120.6, 46.6, 32.7, 19.7; *m/z* (ESIMS) 187.3 $[M + H]^+$.




**Rutaecarpine:** To a solution of **7** (0.048g, 0.174mmol) in acetone (1.75 mL), $KMnO_4$ (2.5eq. 0.436 mmol) was added. The reaction mixture was heated at reflux for 2 h, cooled to room temperature and filtered. The filtrate was concentrated and purified by column chromatography to give the product as a white solid in 61% yield. ($R_f$ = 0.28 in dichloromethane); mp: 256–260 °C [lit. 256–258 °C][14]; IR (KBr) 3342, 1669, 1600, 1577, 1559, 1541, 1522, 1507, 1458 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) 9.44 (br s, 1H), 8.33 (app dd, 1H, *J* = 1.2 Hz, *J* = 7.9 Hz), 7.71 (app ddd, 1H, *J* = 1.5 Hz, *J* = 7.0 Hz, *J* = 8.4 Hz), 7.65 (app dd, 2H, *J* = 4.4 Hz, *J* = 13.1 Hz), 7.46–7.29 (comp, 3H), 7.21–7.15 (m, 1H), 4.59 (t, 2H, *J* = 6.9 Hz), 3.24 (t, 2H, *J* = 6.9 Hz); $^{13}C$ NMR (125 MHz, $CDCl_3$) 161.8, 147.8, 145.2, 138.5, 134.6, 127.5, 127.4, 126.9, 126.4, 125.9, 125.8, 121.4, 120.9, 120.3, 118.6, 112.3, 41.4, 19.9; *m/z* (ESIMS) 288.4 $[M + H]^+$.

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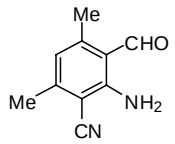
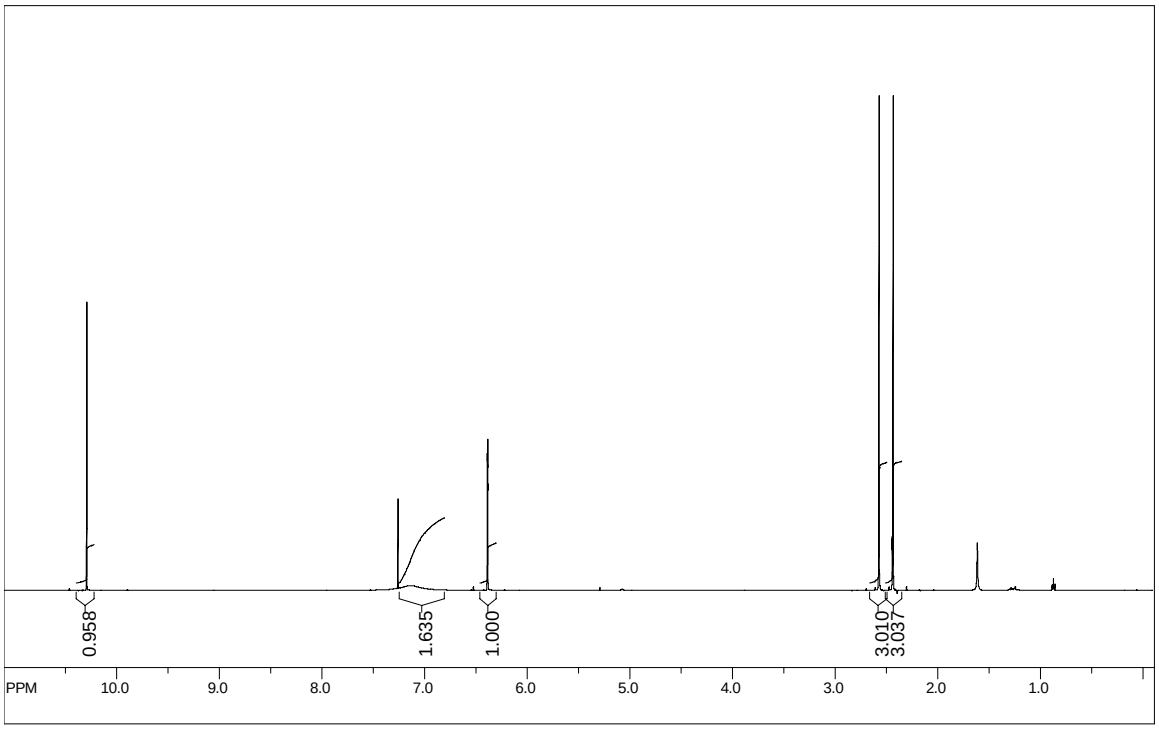
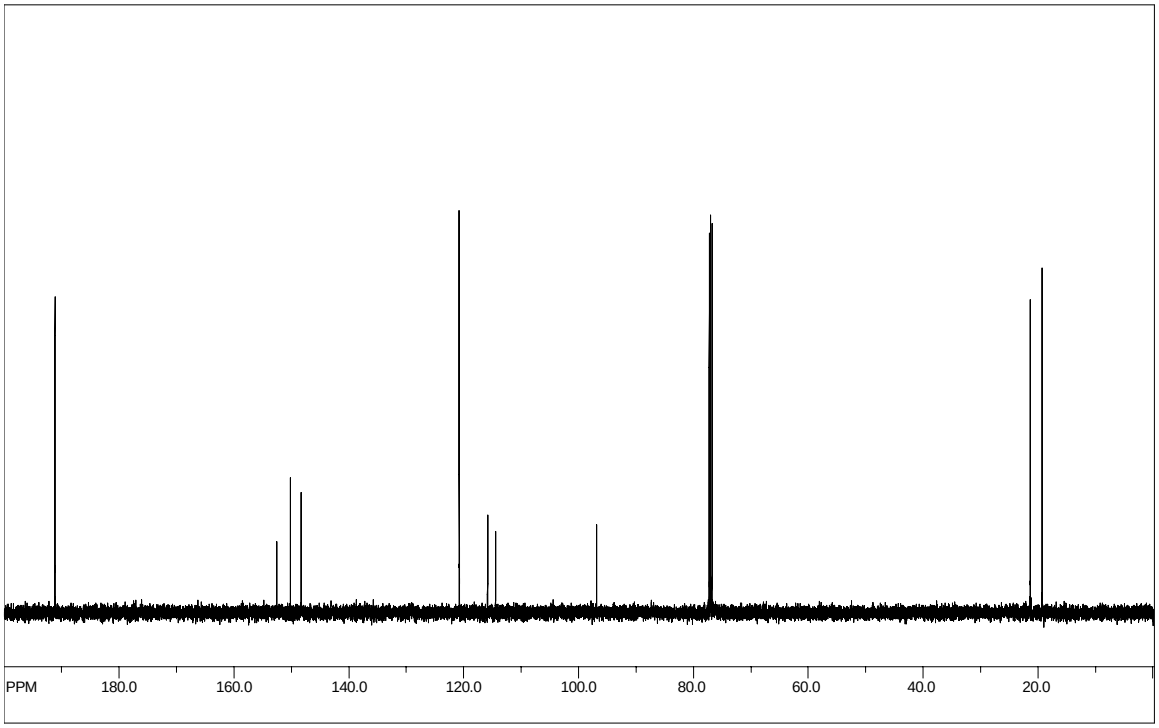
$^{1}$H-NMR and $^{13}$C-NMR of **1a**:



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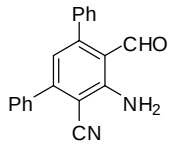


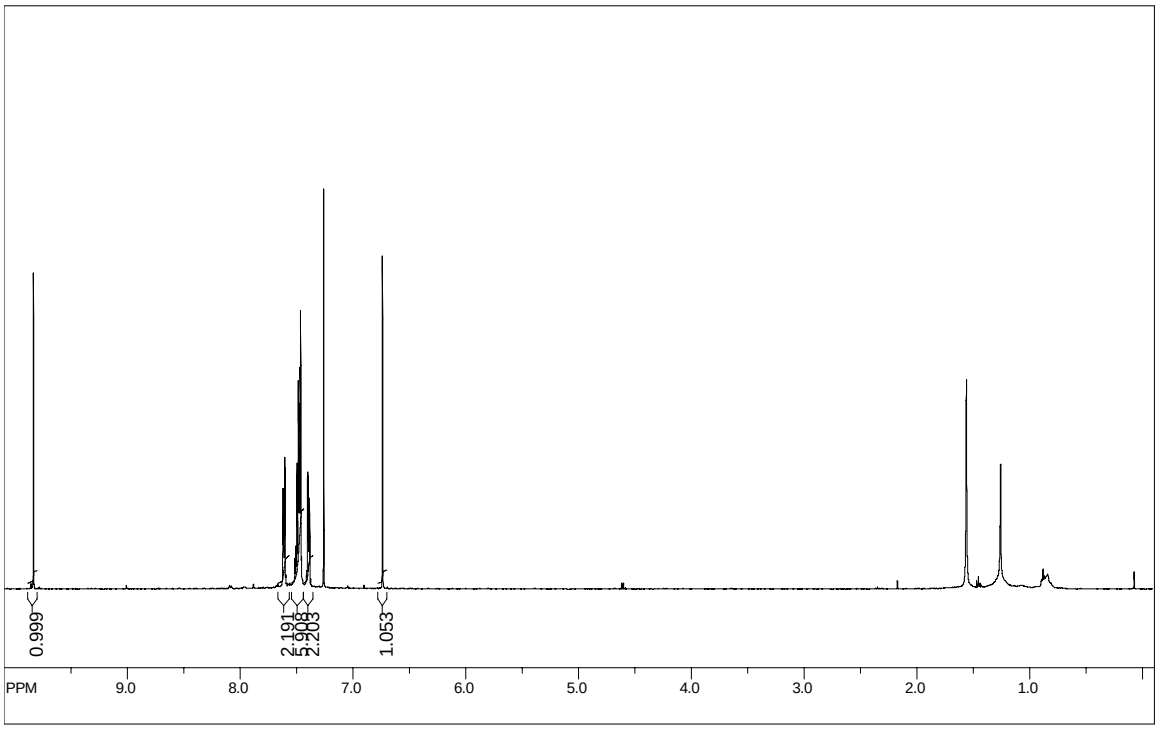


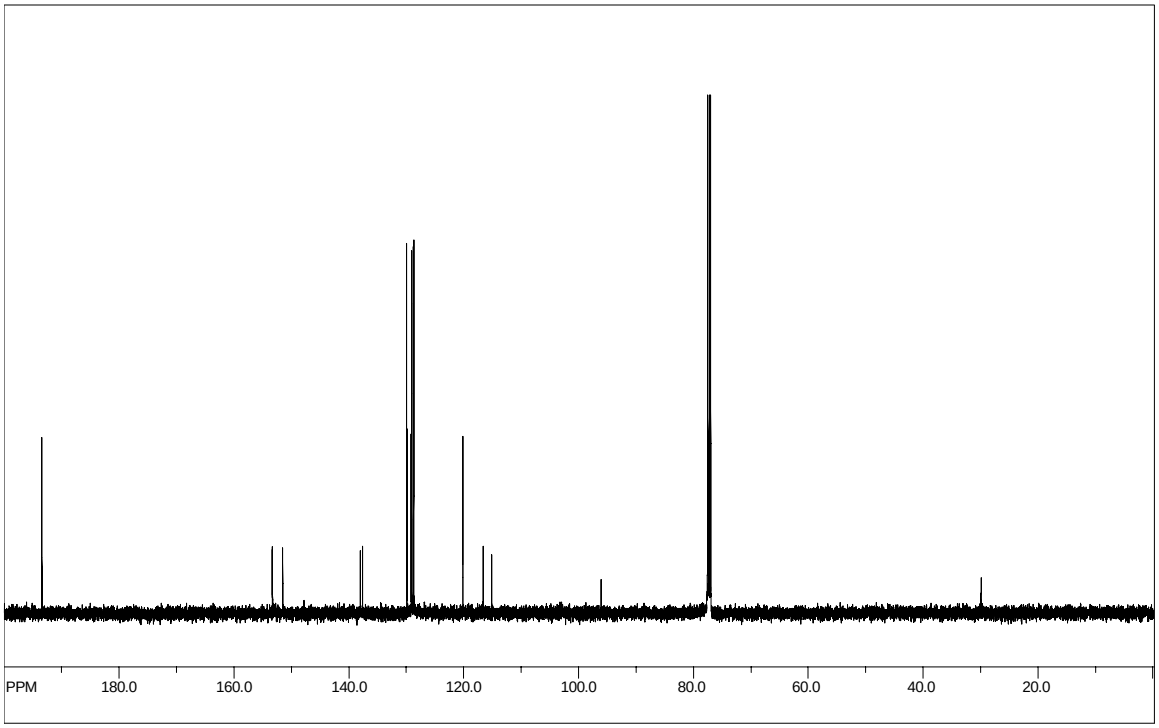

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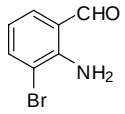


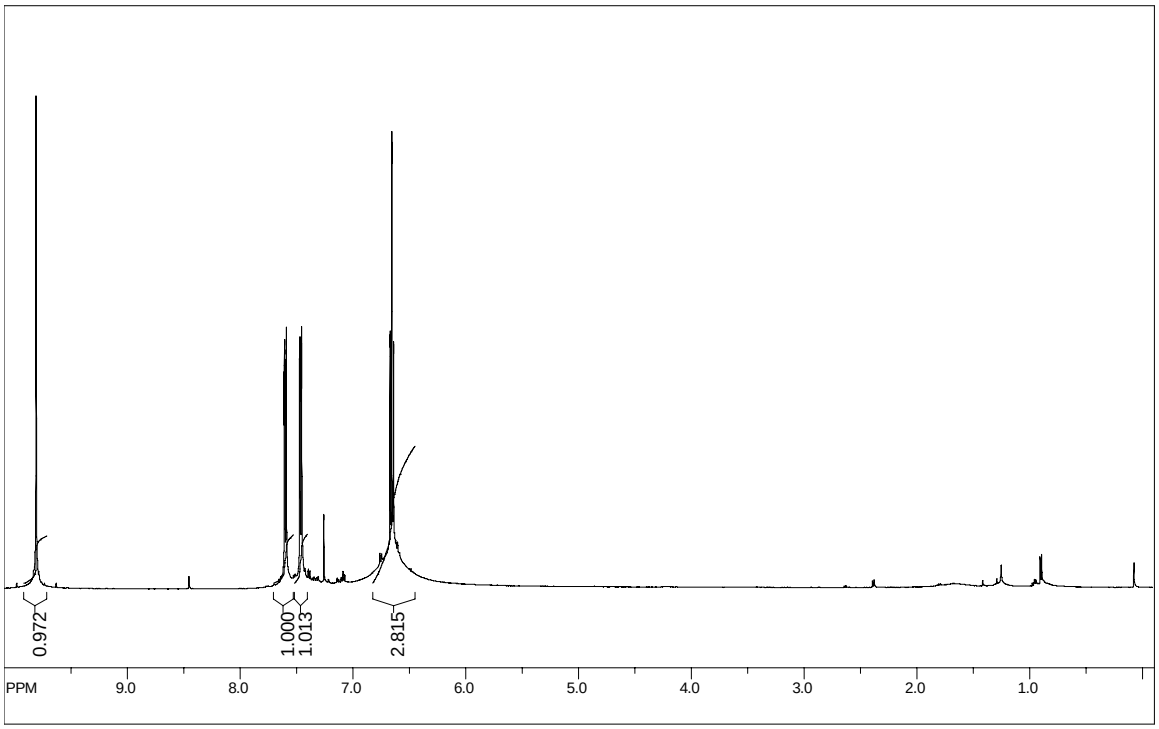


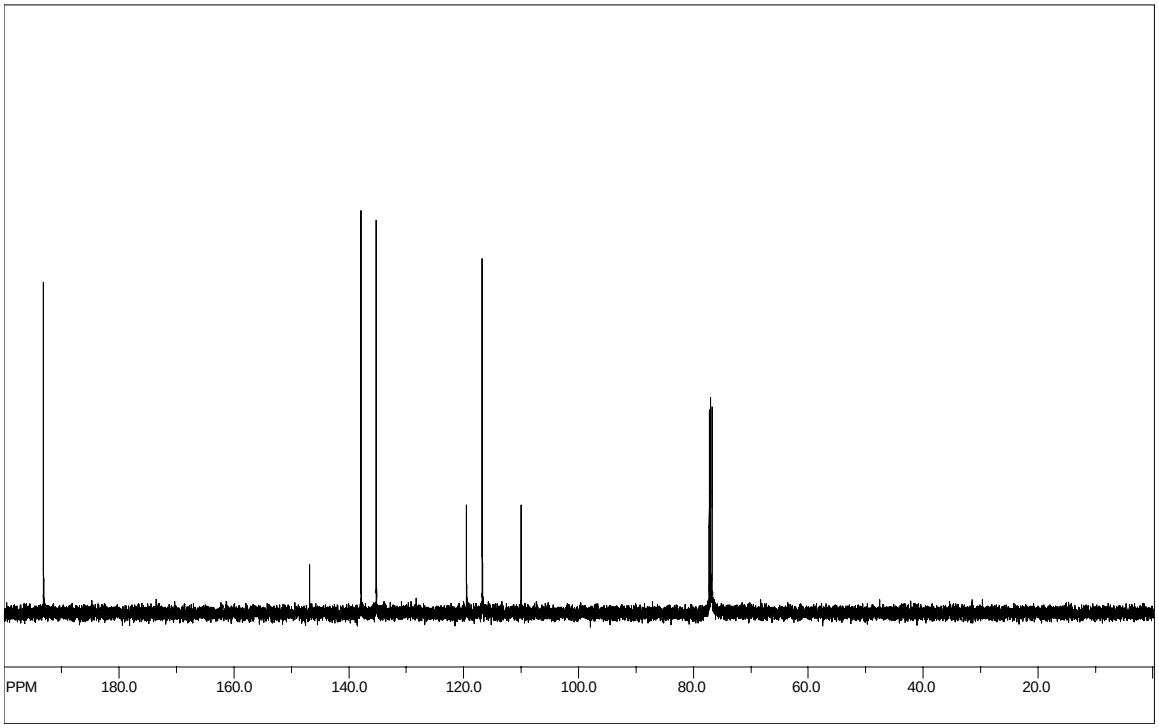

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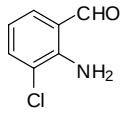
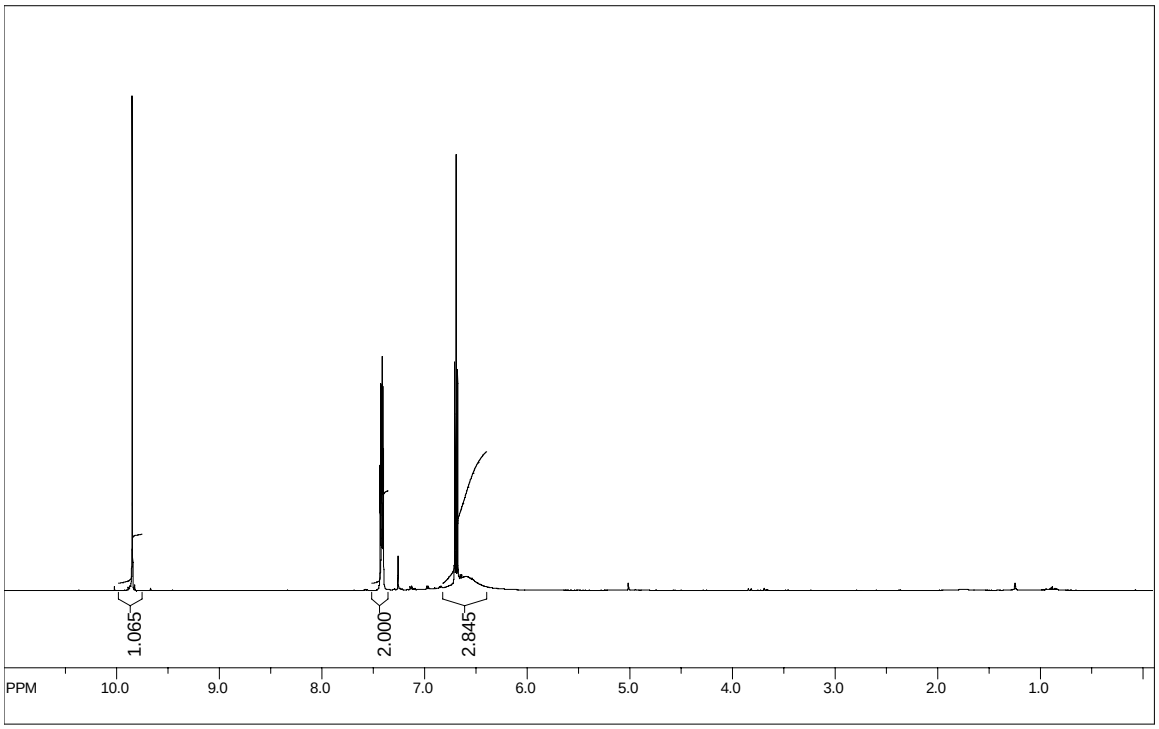
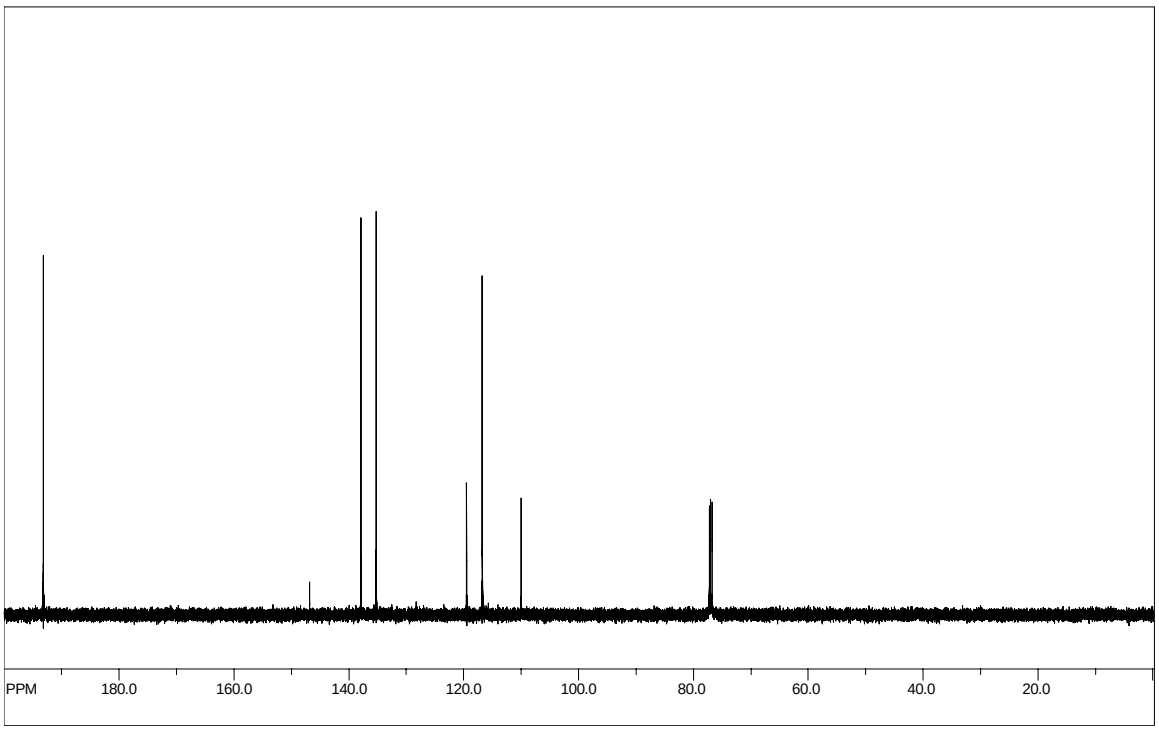
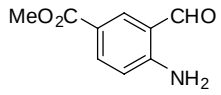
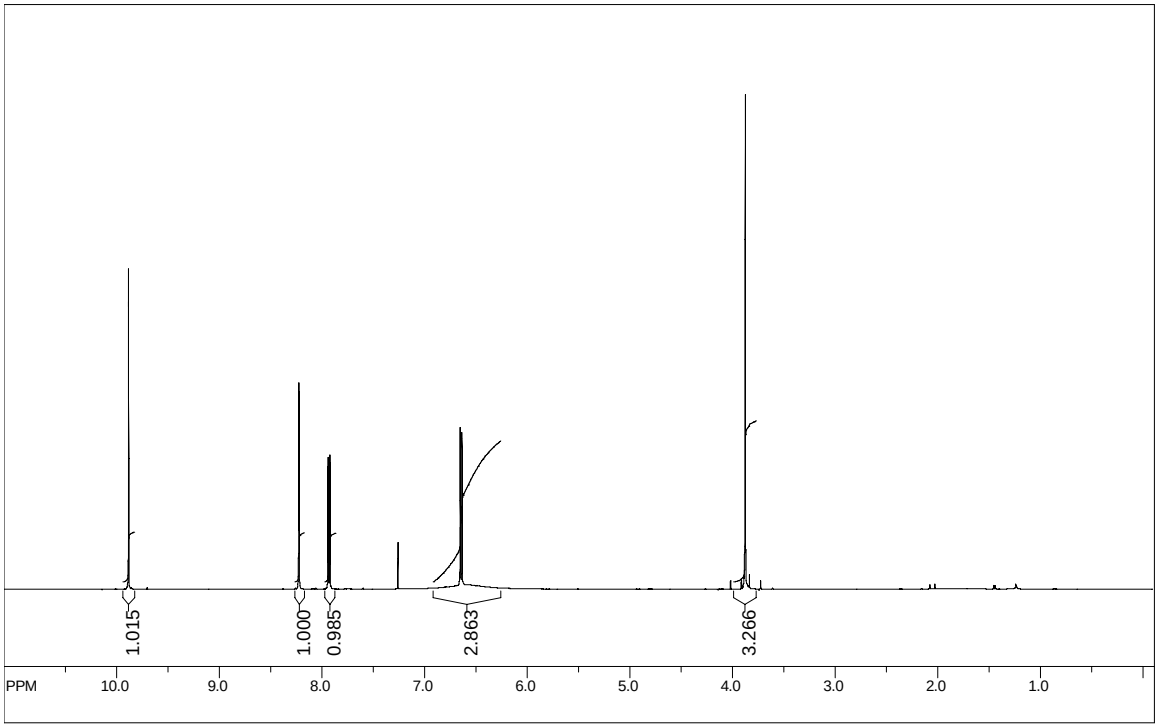


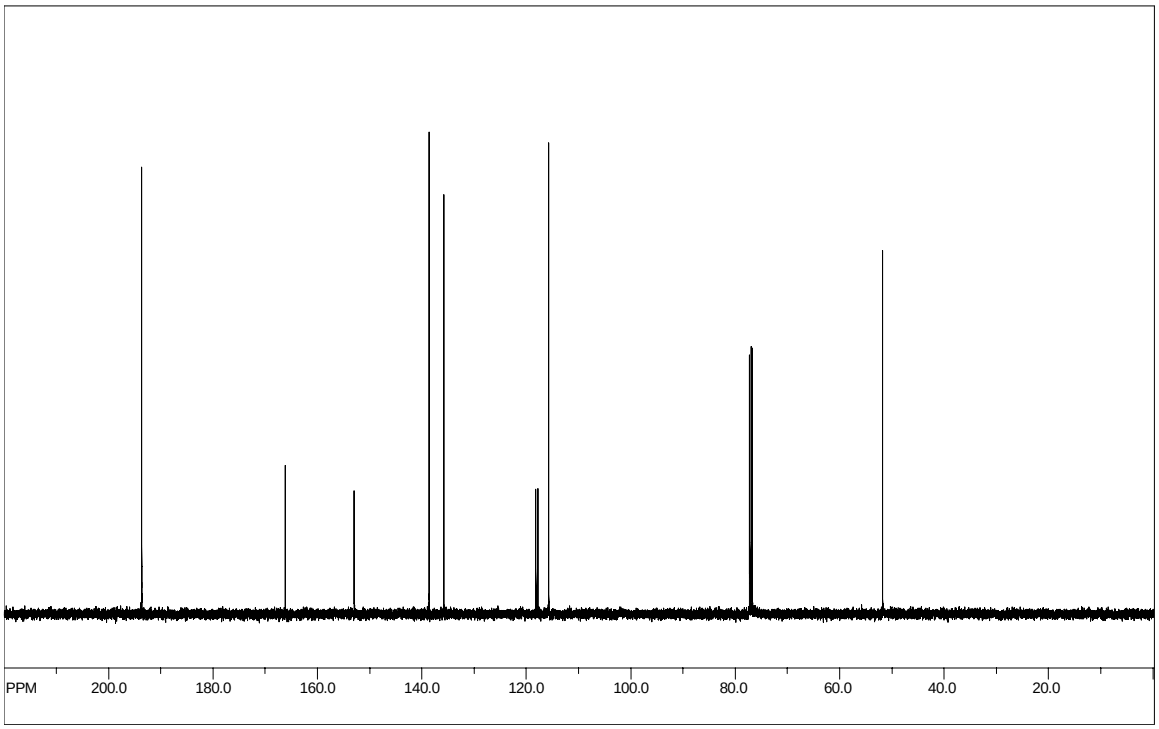



$^{1}$H-NMR and $^{13}$C-NMR of methyl 4-amino-3-formylbenzoate **1h**:



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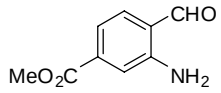
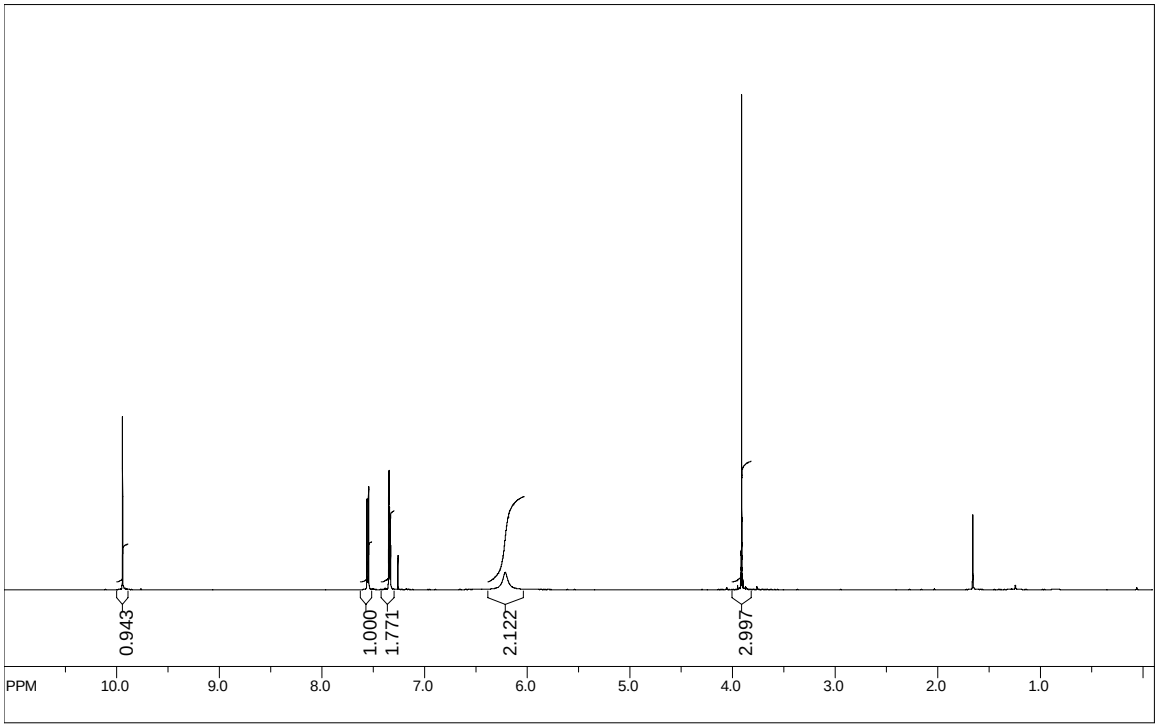
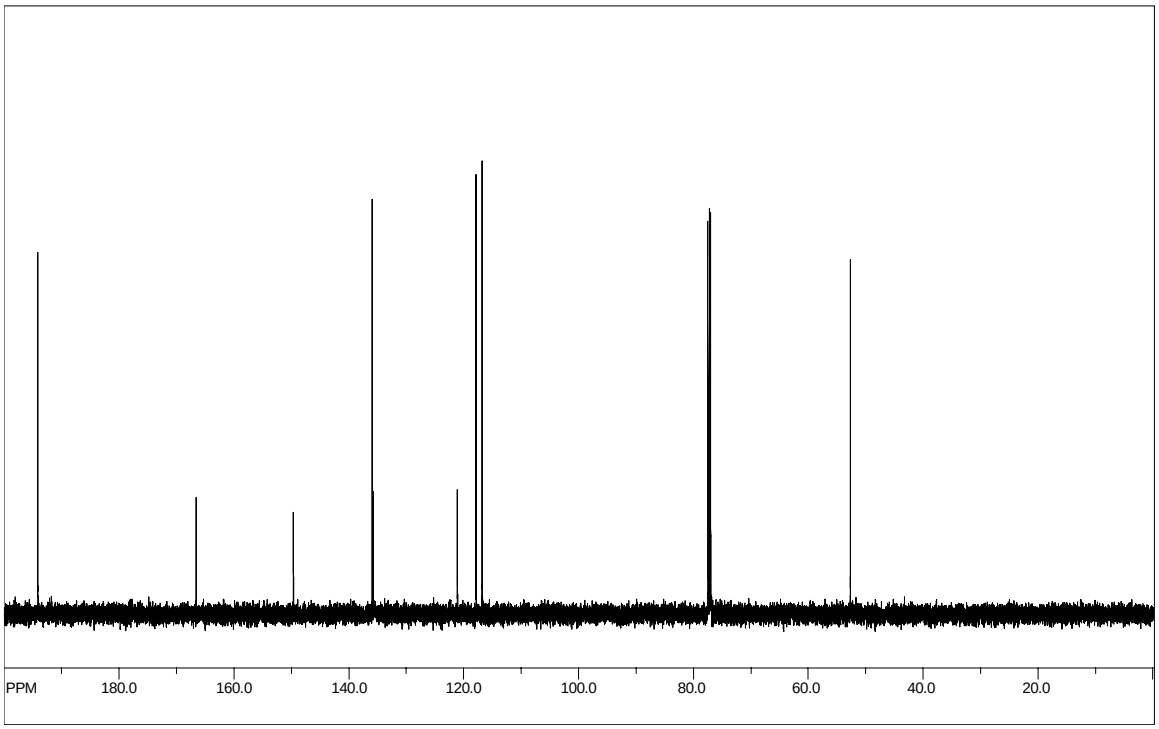
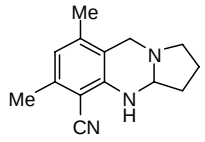
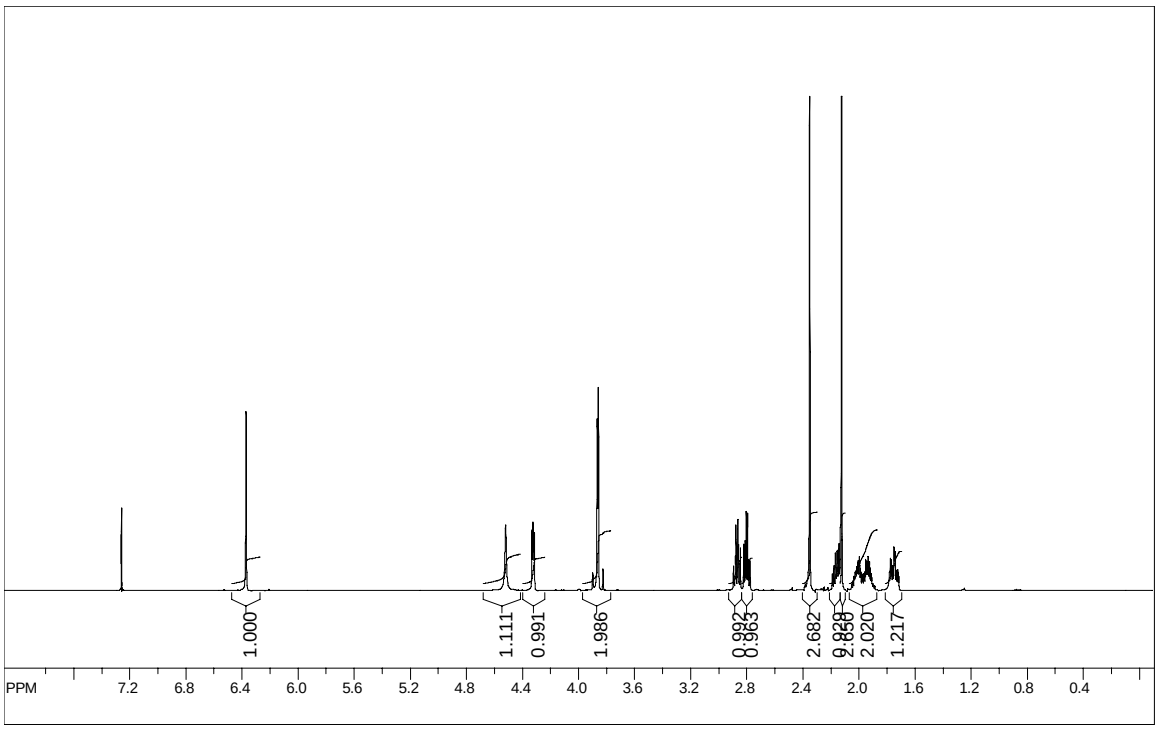


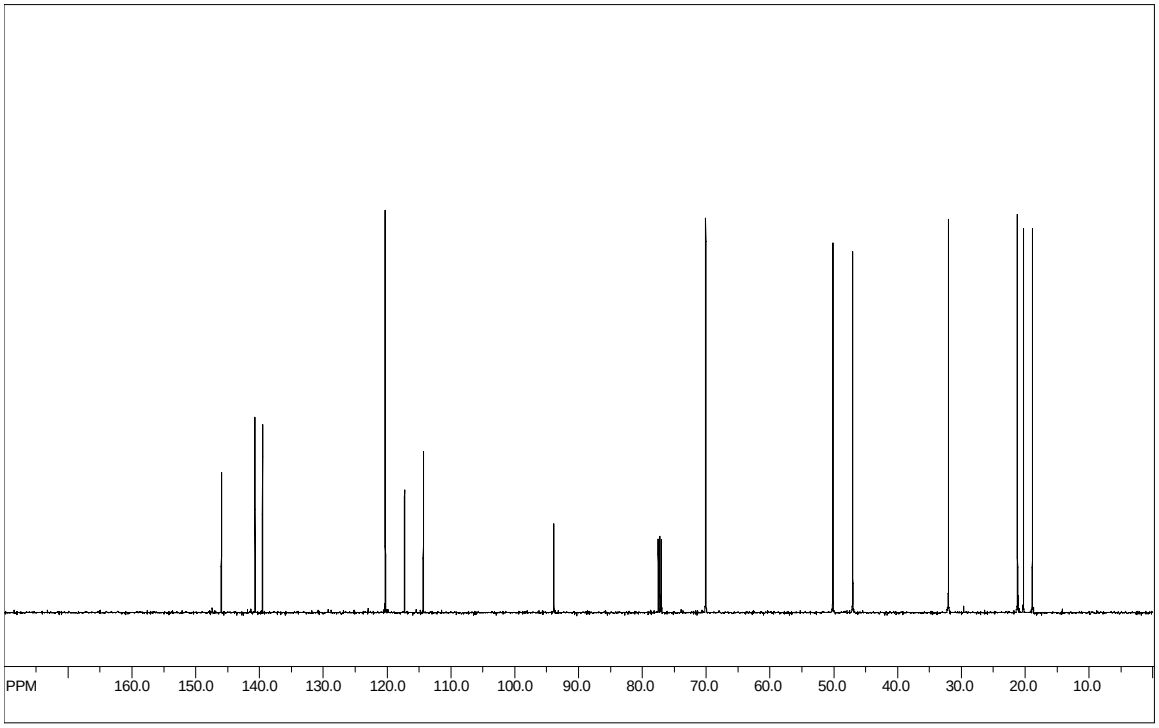



$^{1}$H-NMR and $^{13}$C-NMR of **2a**:



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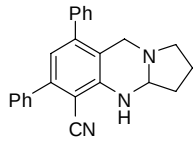


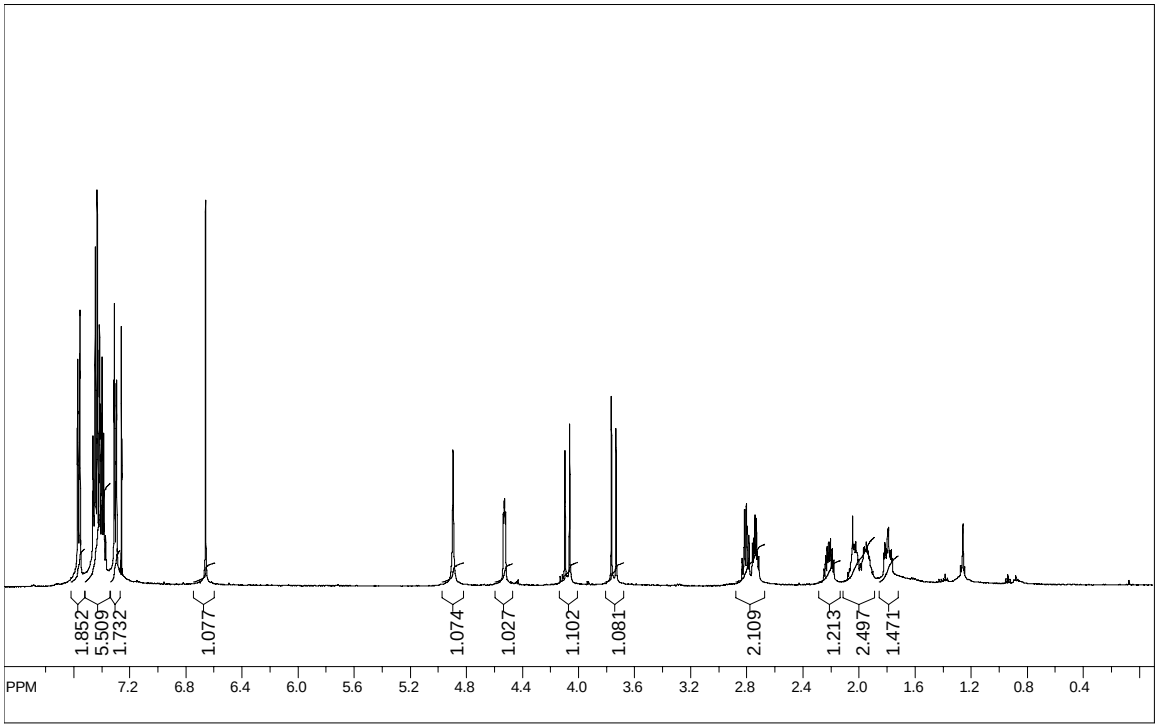


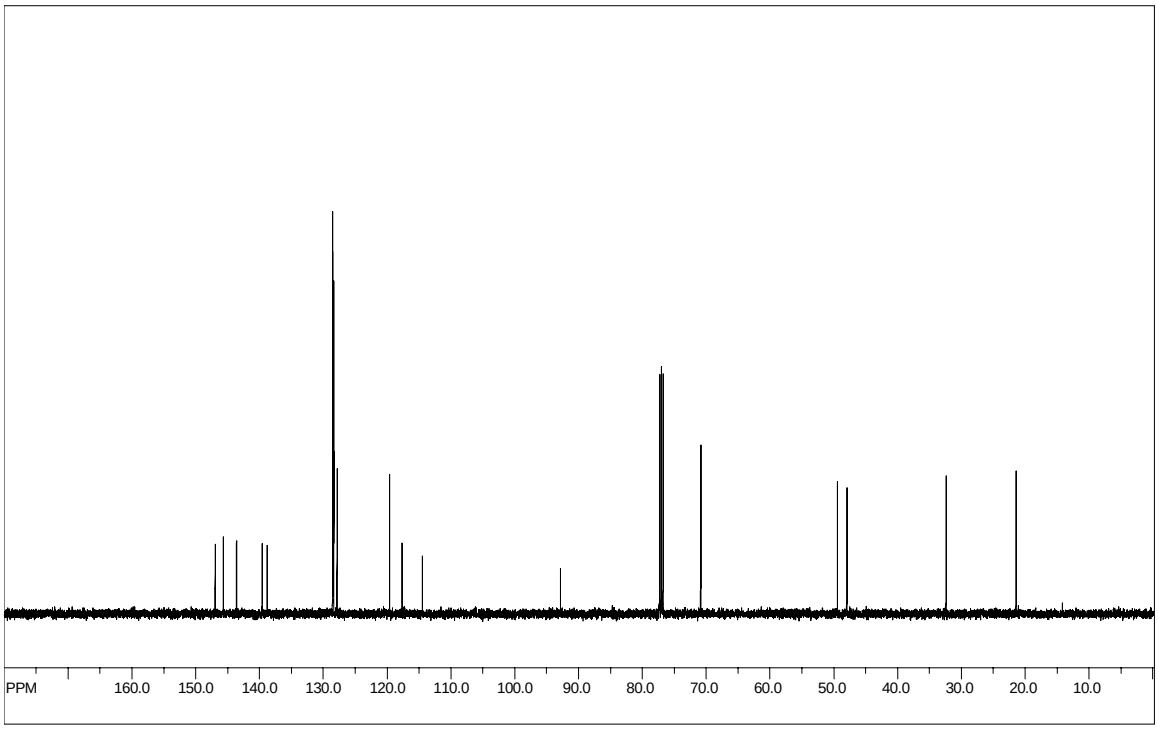

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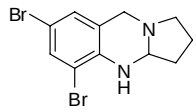
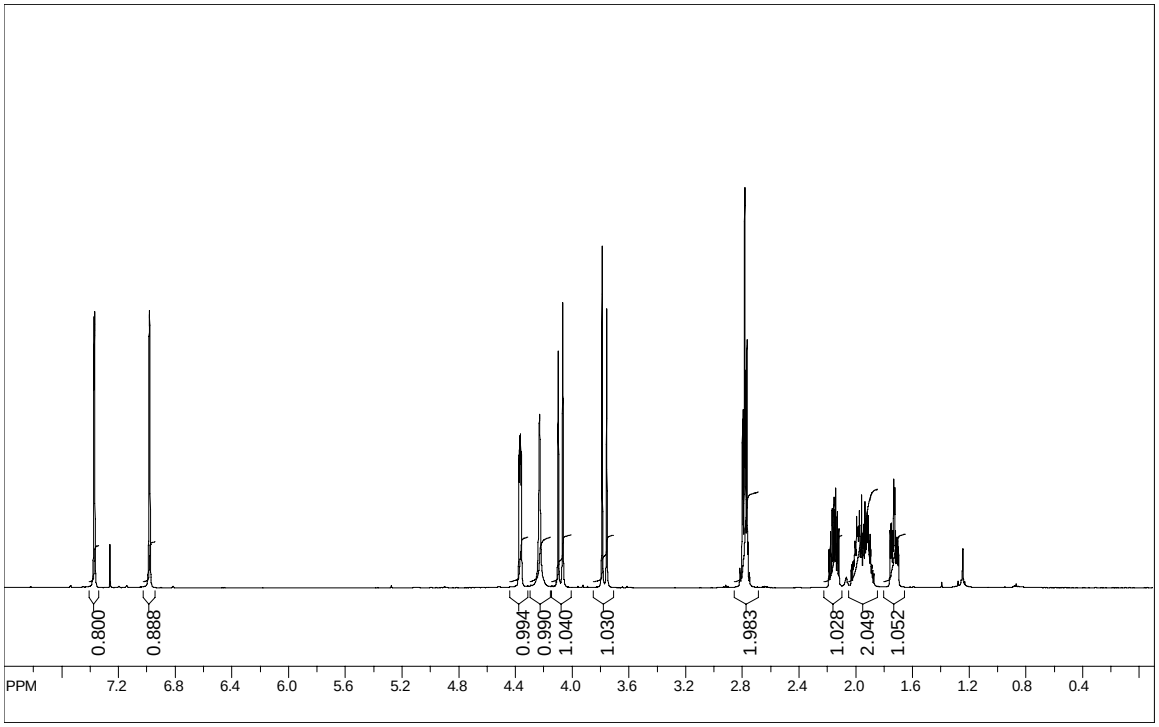
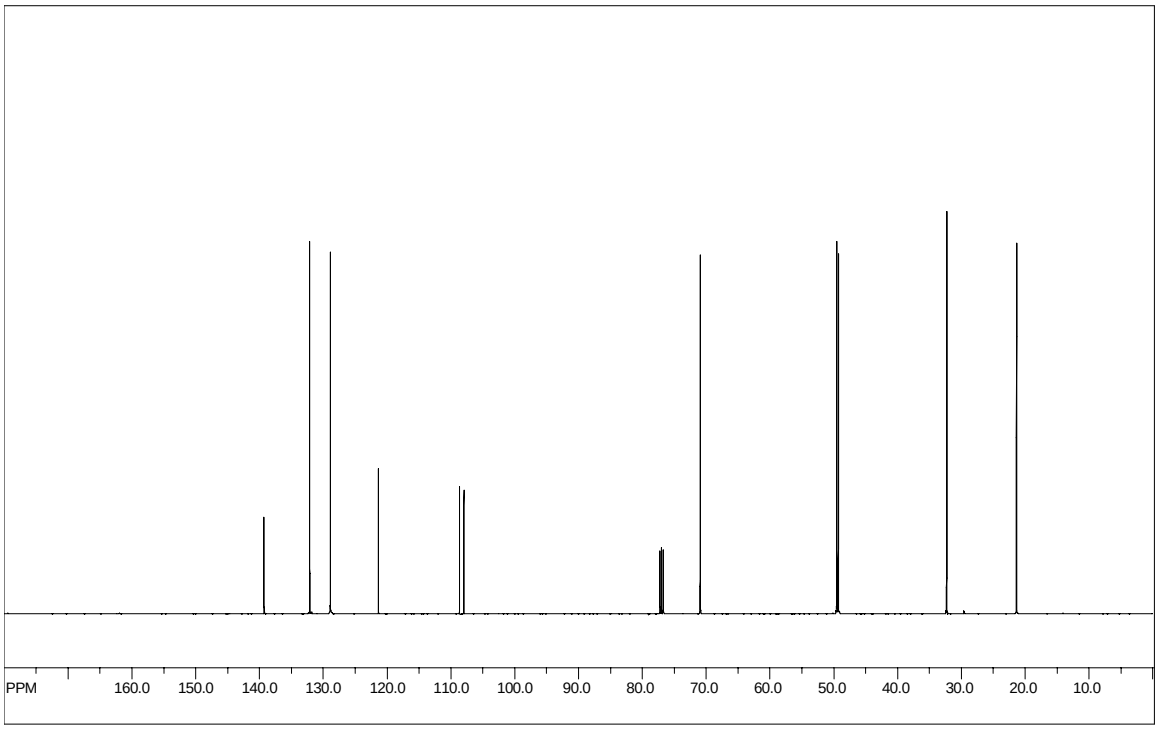
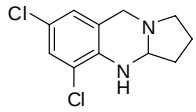
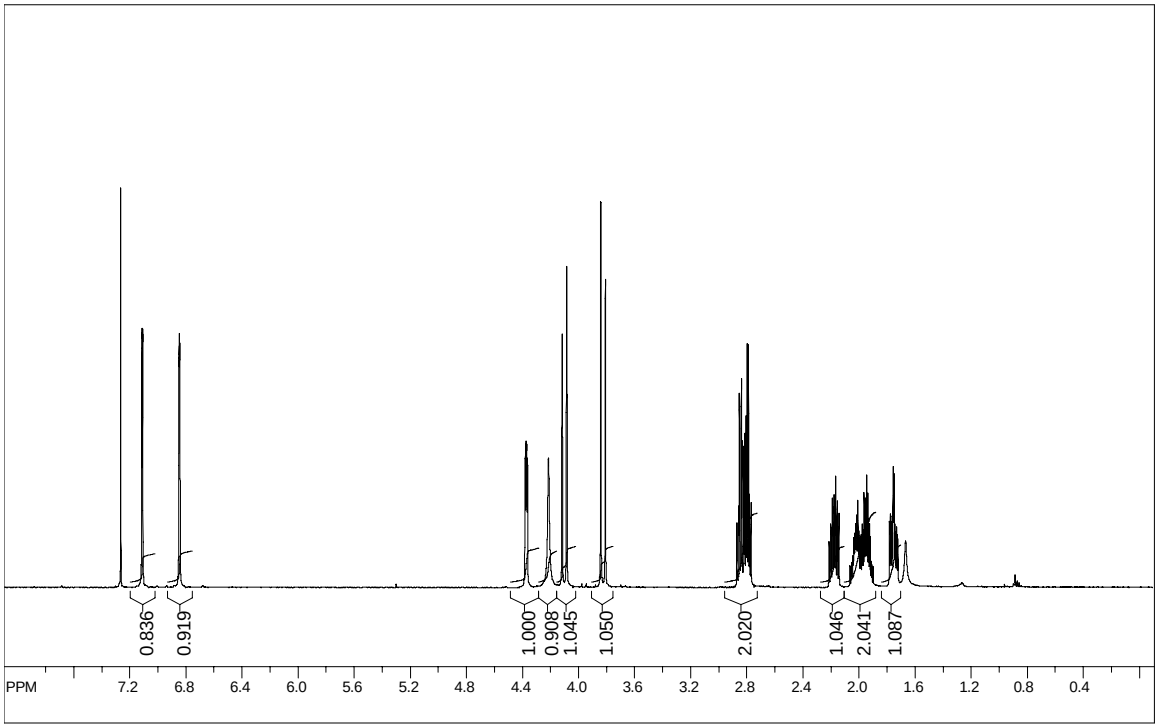


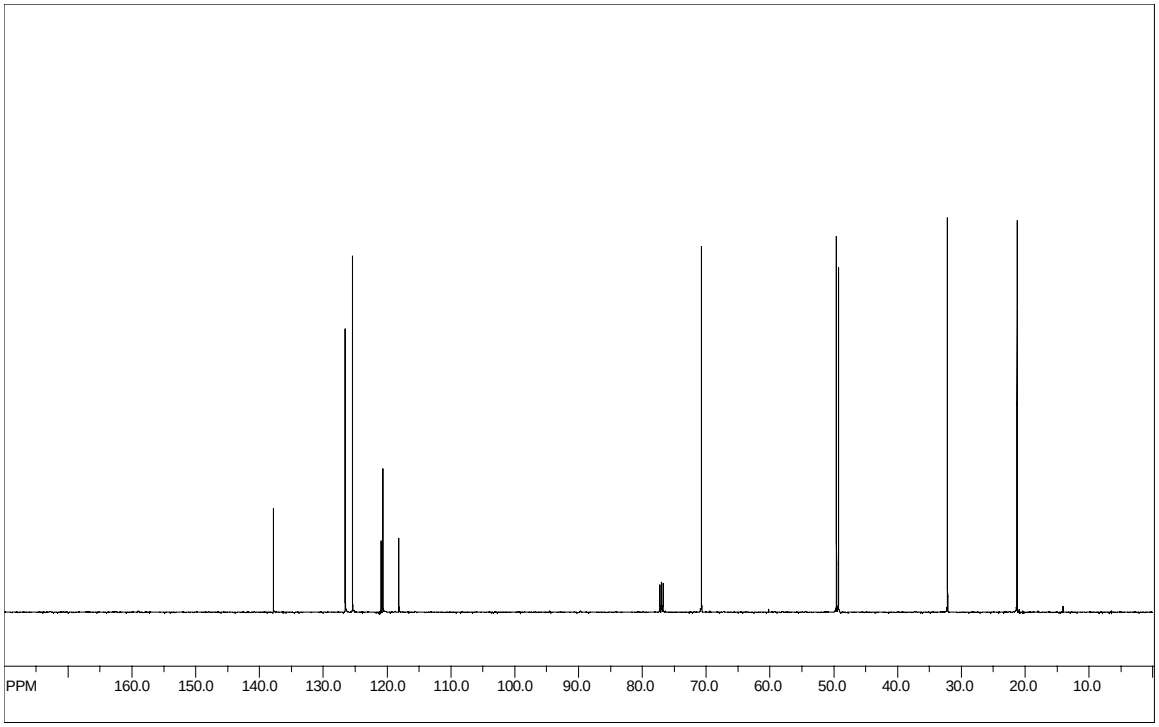



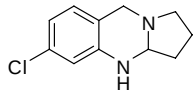
$^{1}$H-NMR and $^{13}$C-NMR of **2d**:

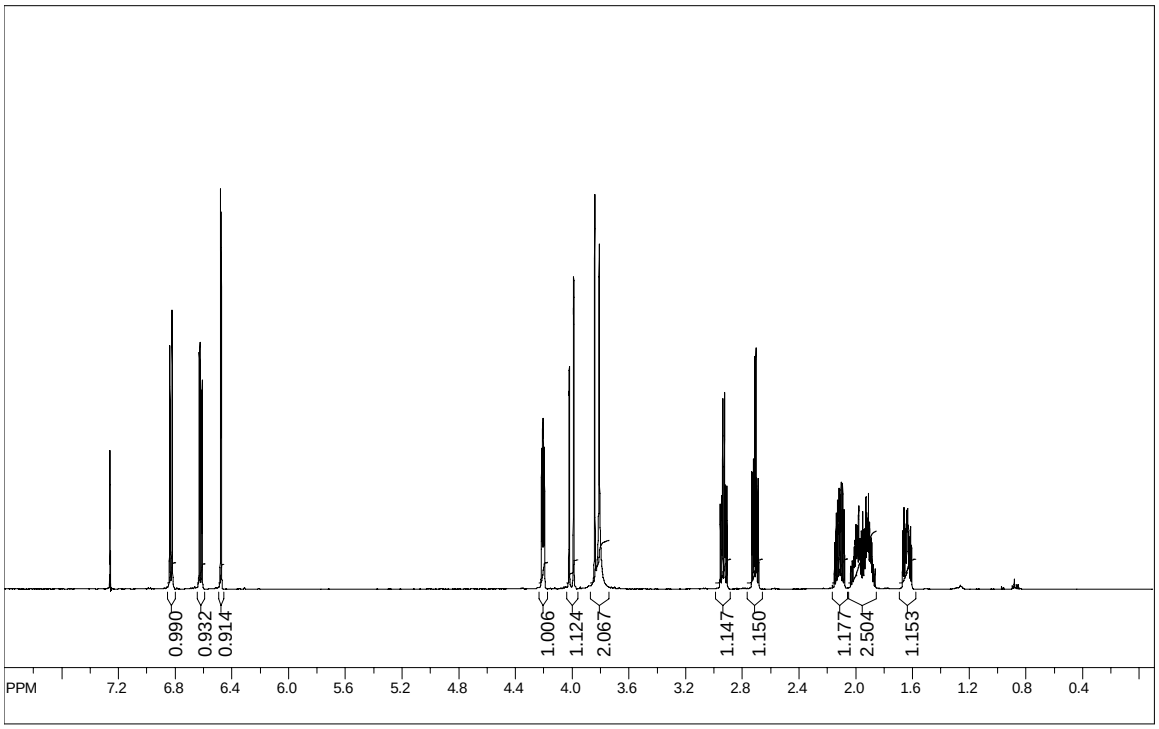


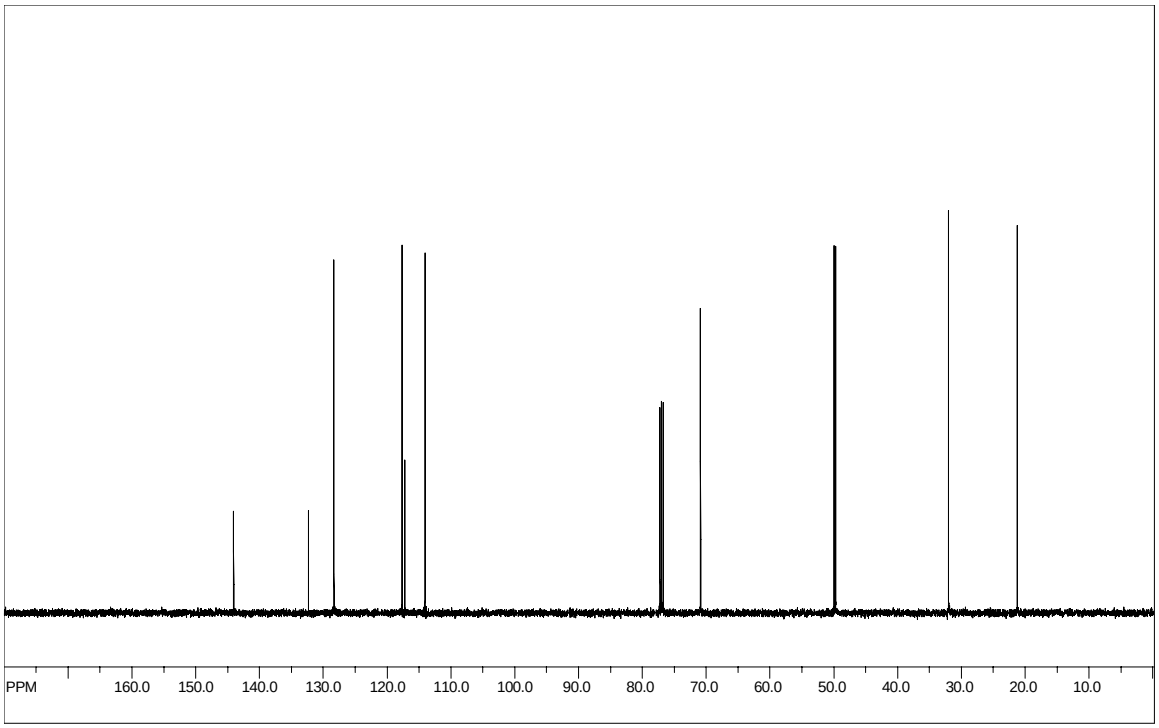



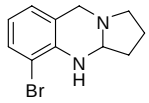
$^{1}$H-NMR and $^{13}$C-NMR of **2e**:

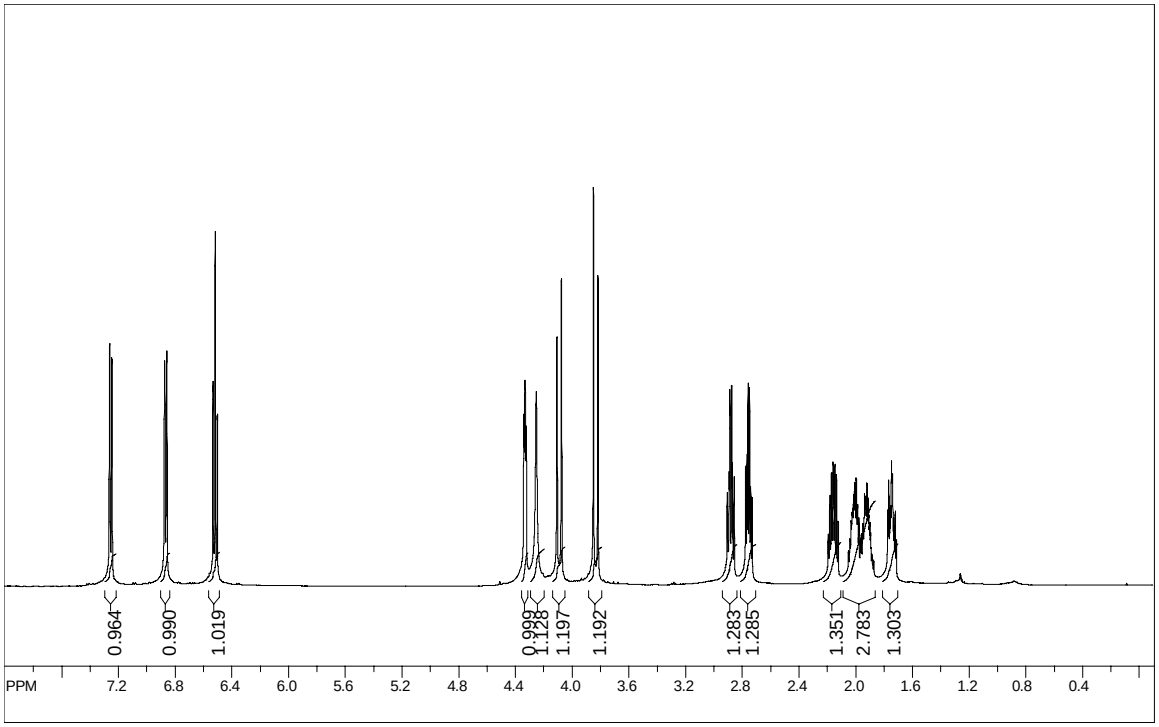


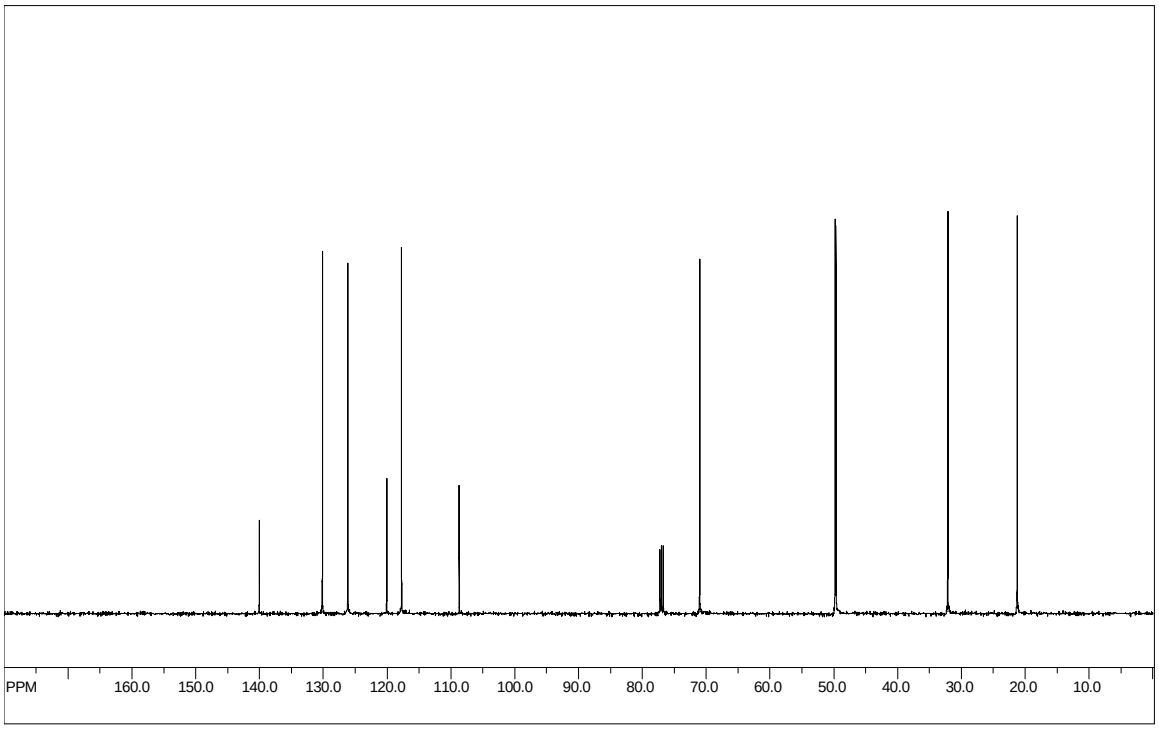



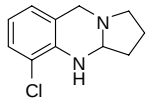
$^{1}$H-NMR and $^{13}$C-NMR of **2f**:

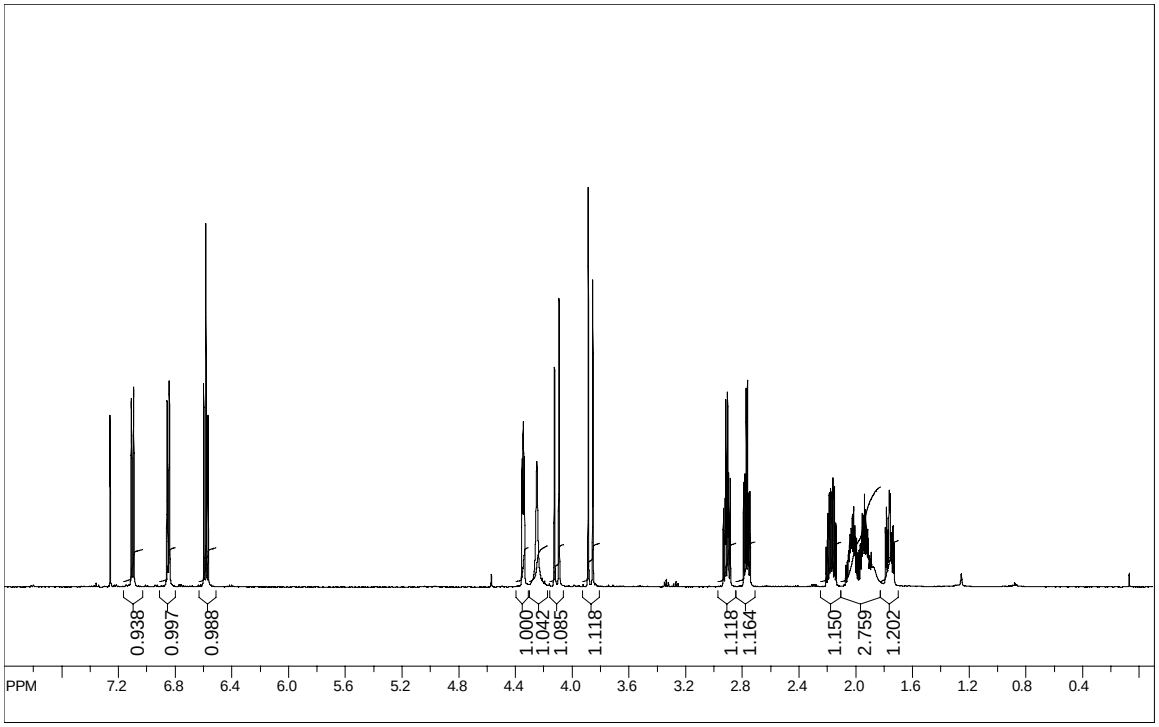


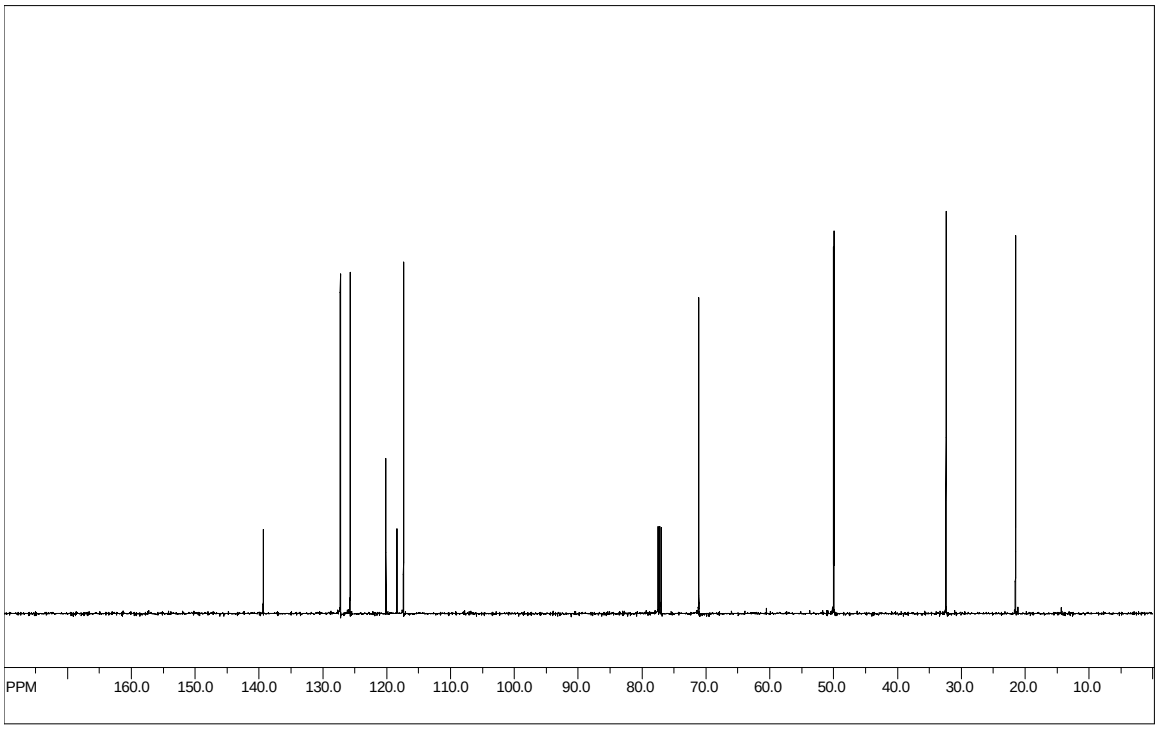



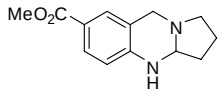
$^{1}$H-NMR and $^{13}$C-NMR of **2g**:

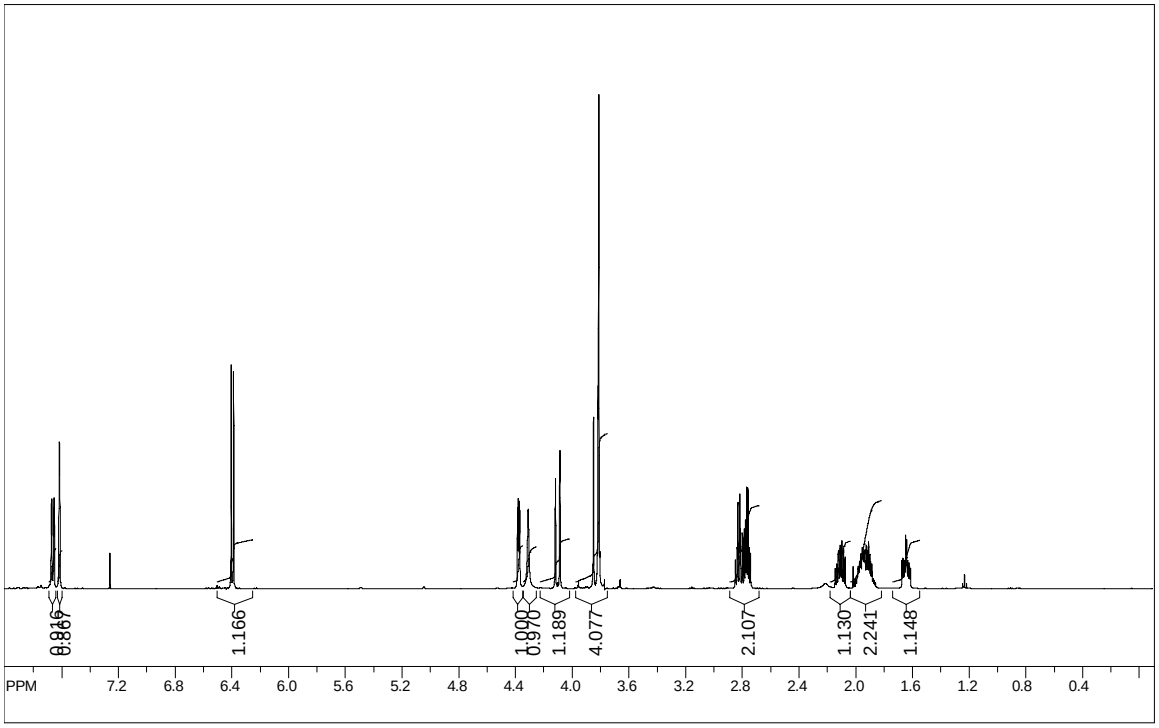


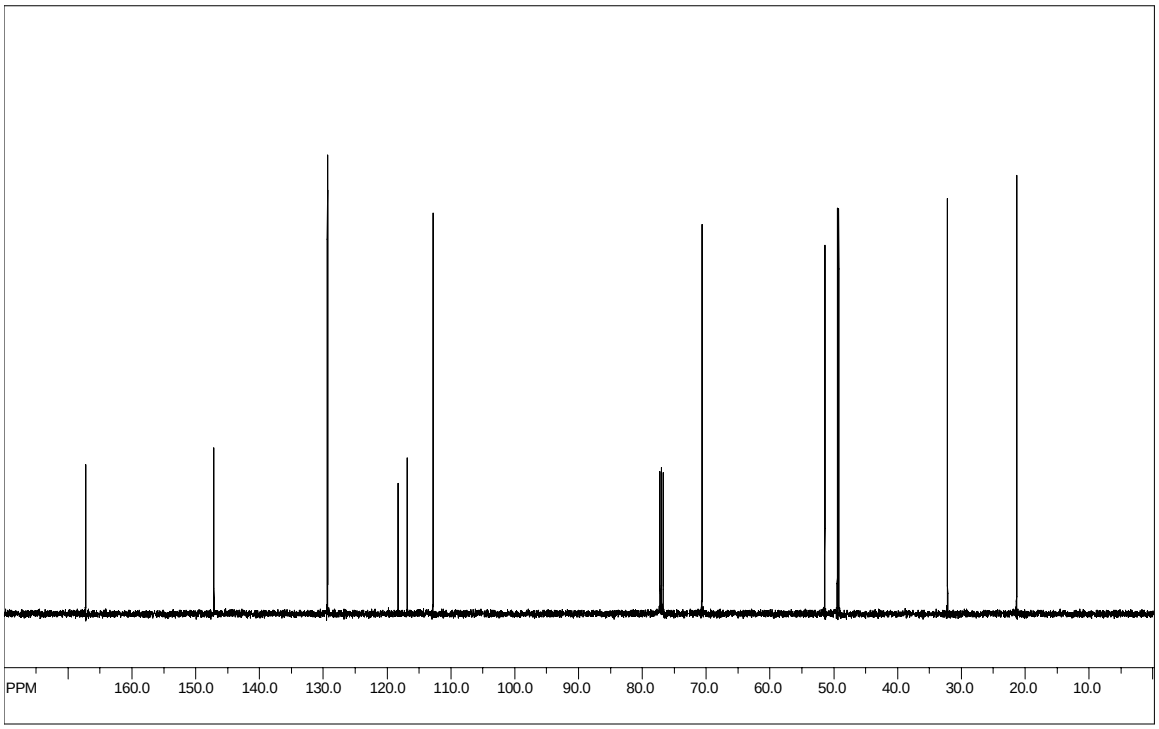



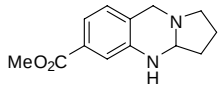
$^{1}$H-NMR and $^{13}$C-NMR of **2h**:

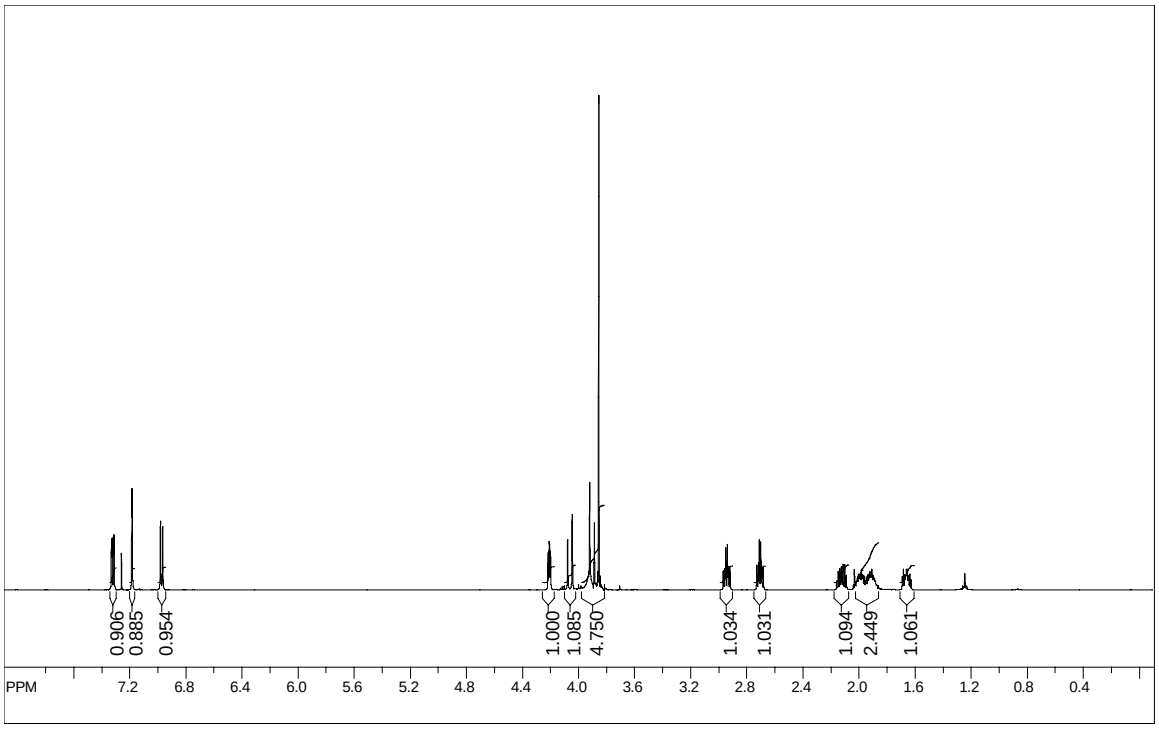


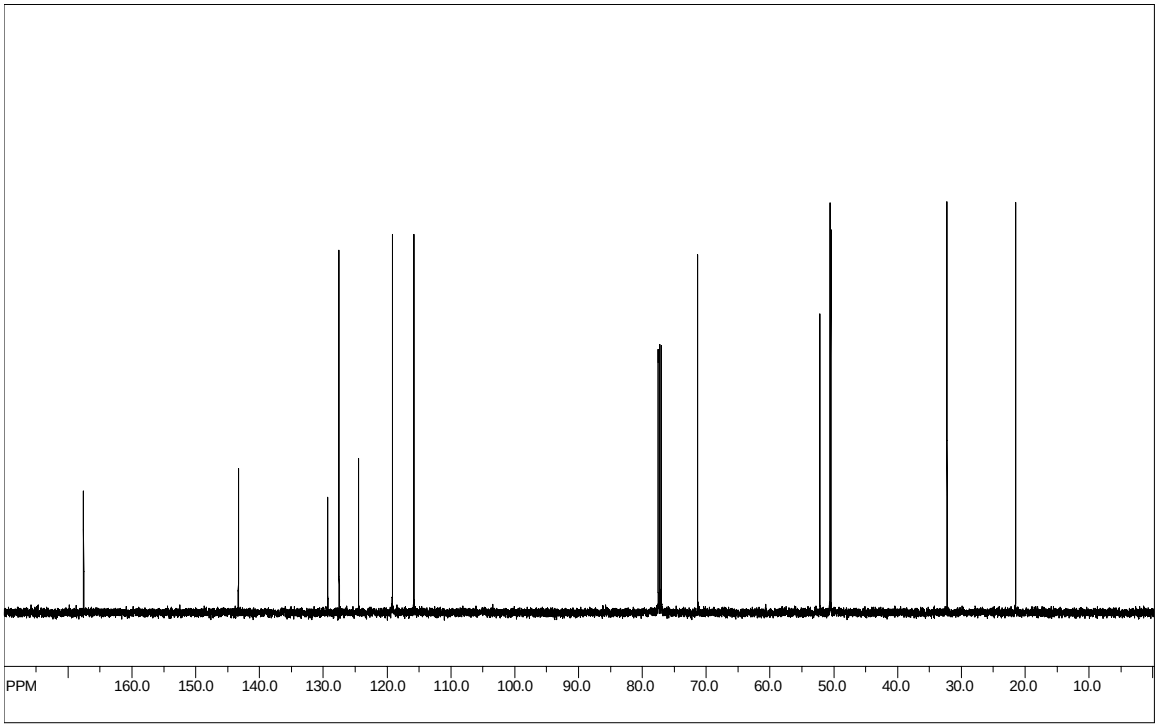



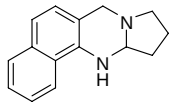
$^{1}$H-NMR and $^{13}$C-NMR of **2i**:

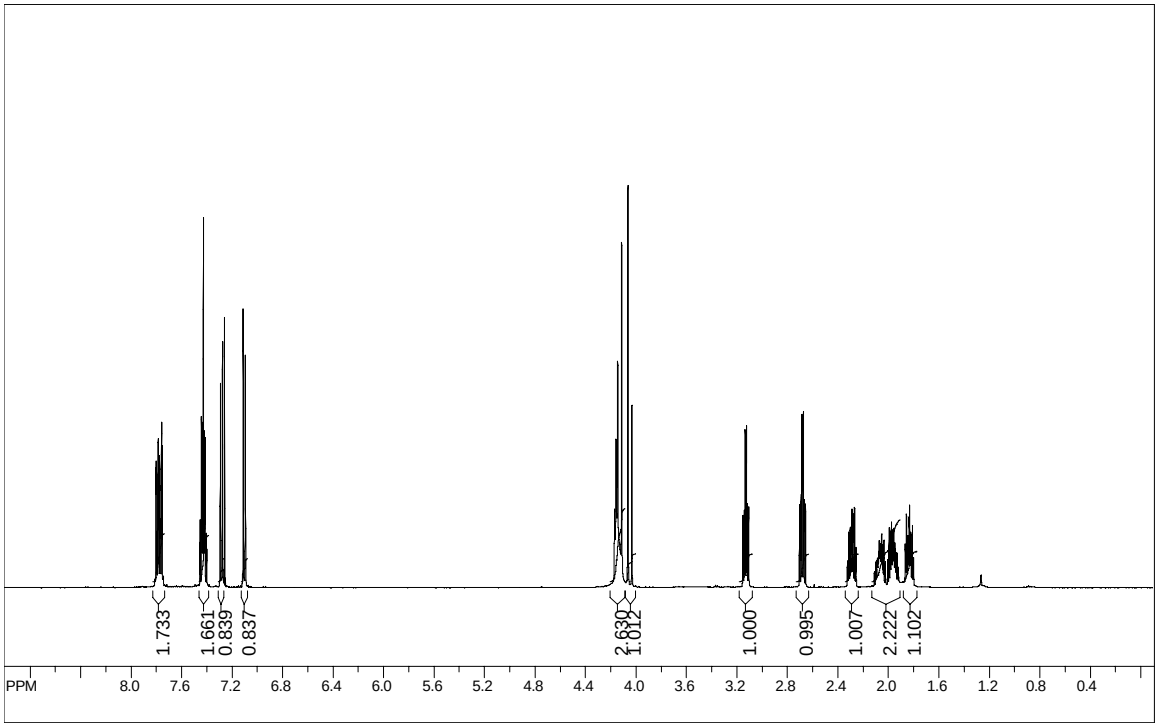


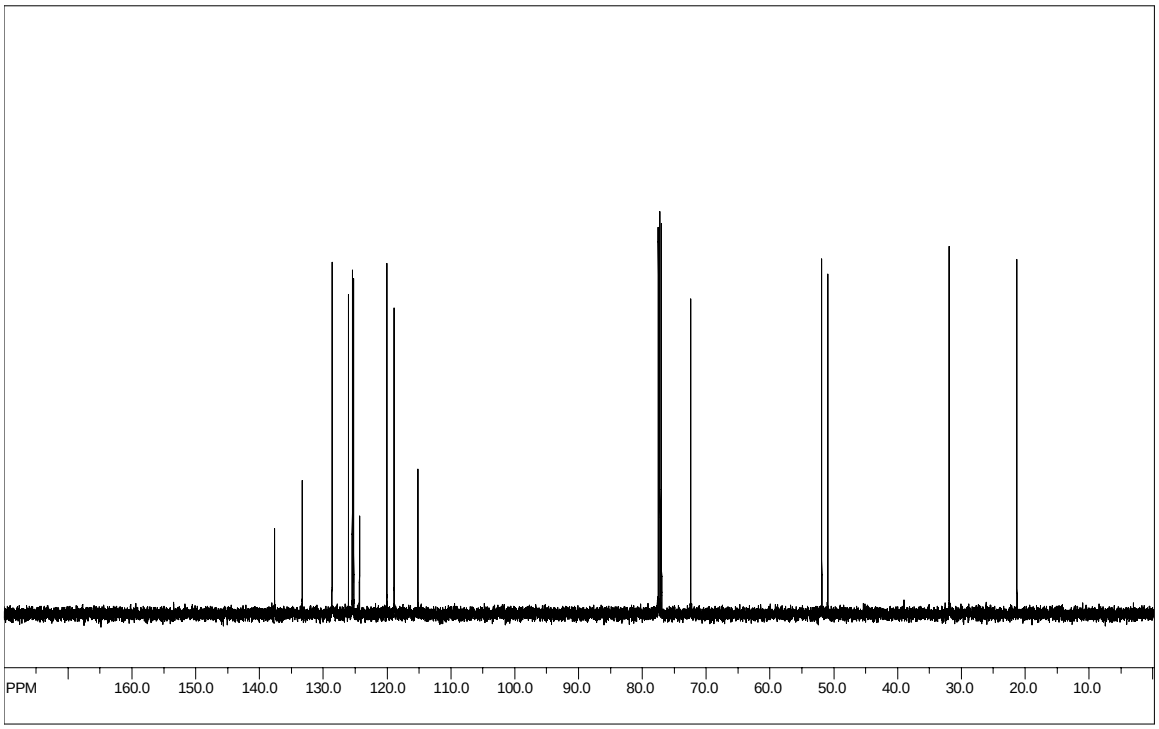



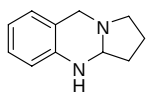
$^{1}$H-NMR and $^{13}$C-NMR of **2j**:

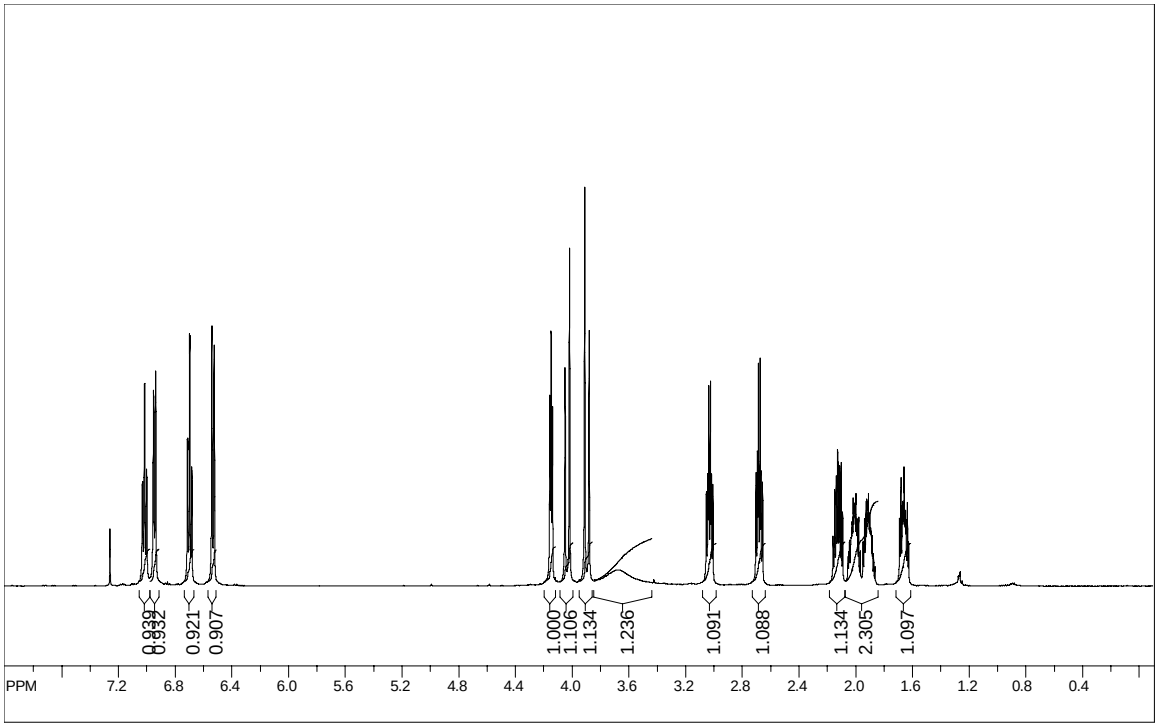


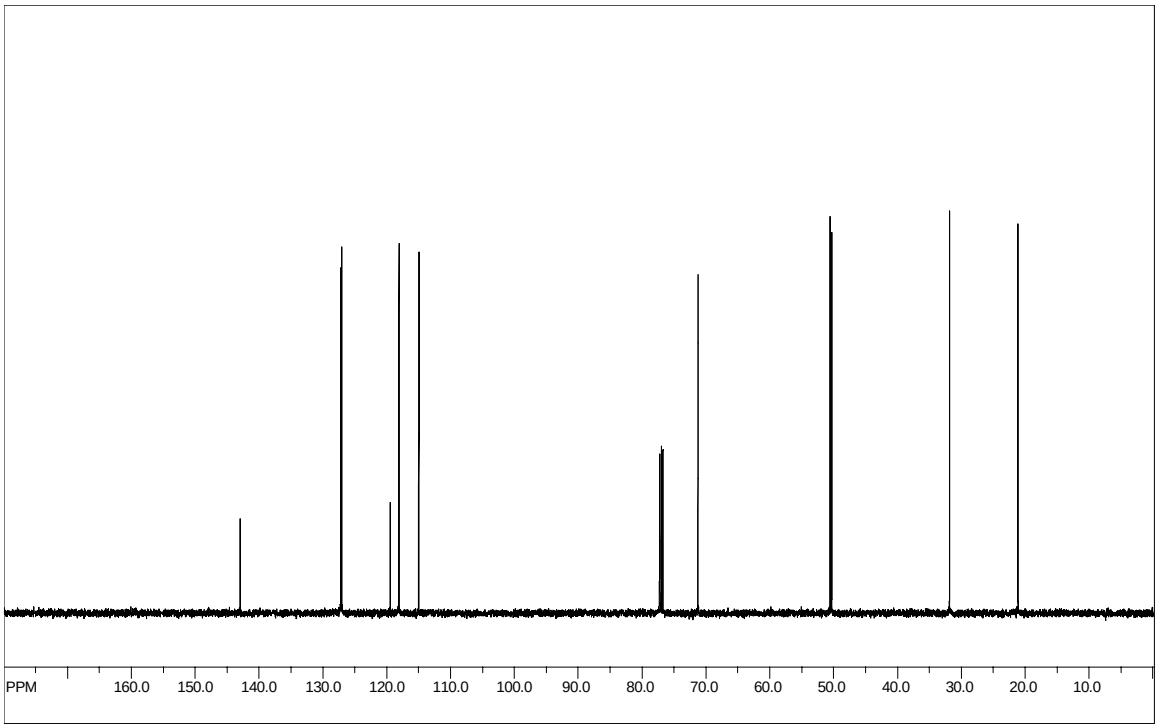



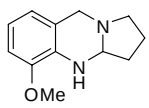
$^{1}$H-NMR and $^{13}$C-NMR of **2k**:

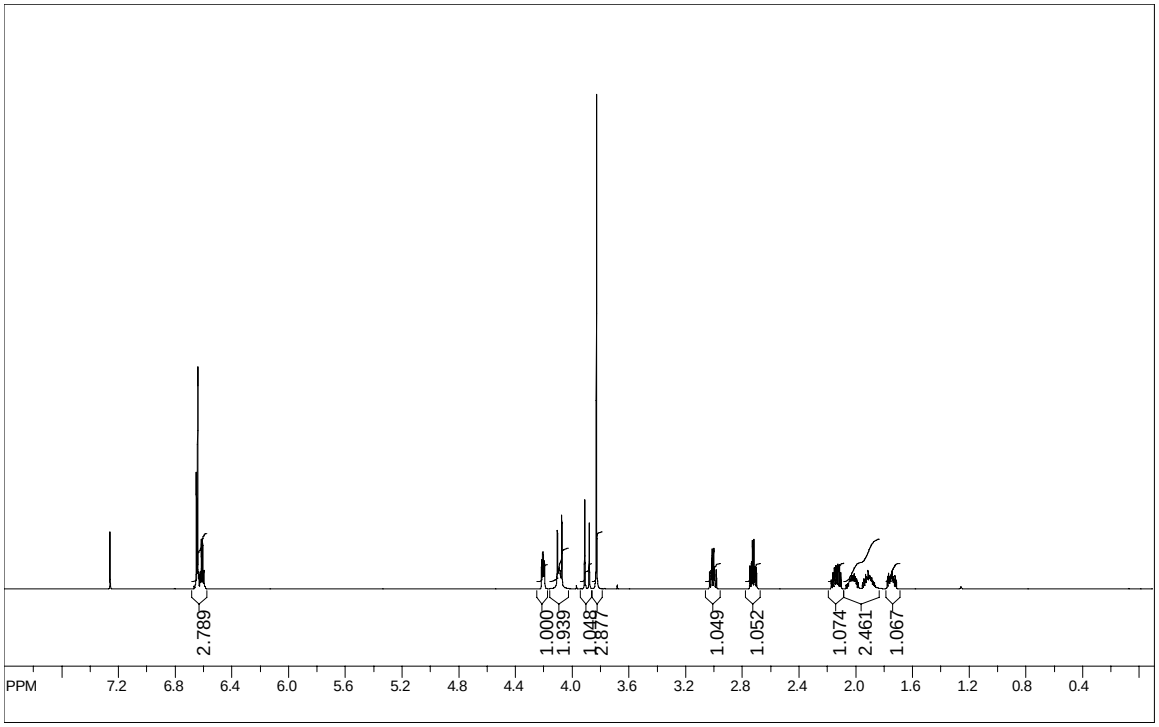


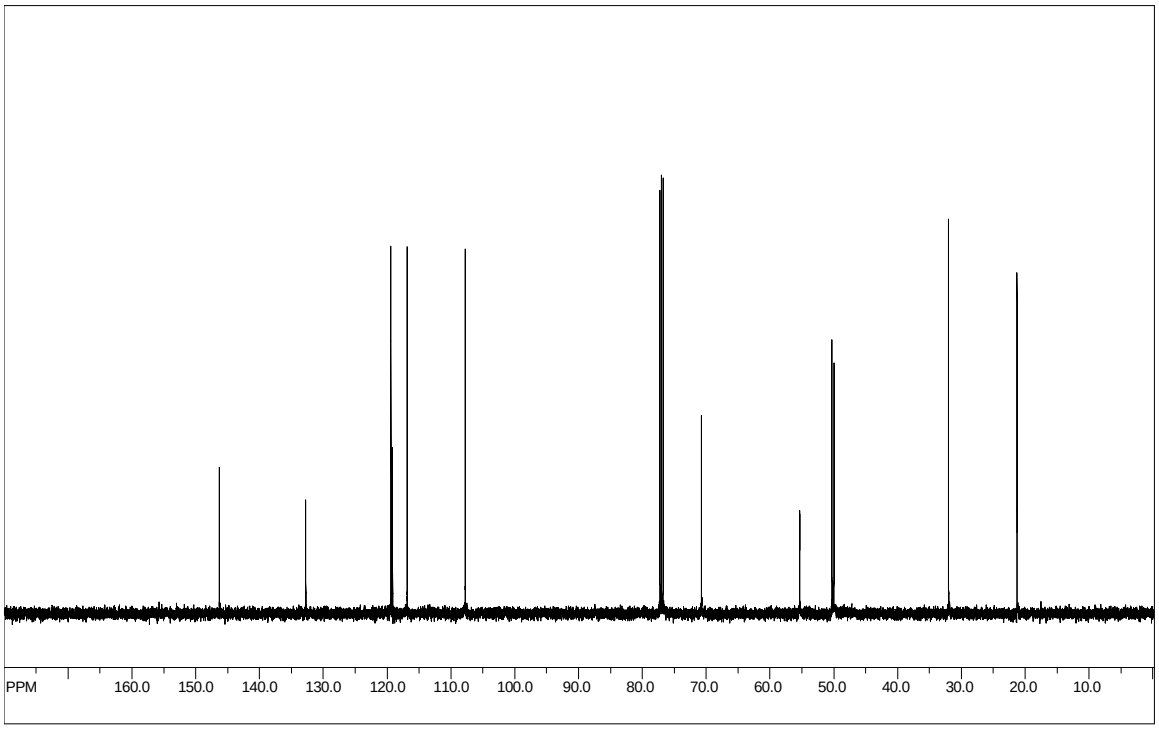



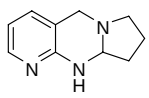
$^{1}$H-NMR and $^{13}$C-NMR of **2l**:

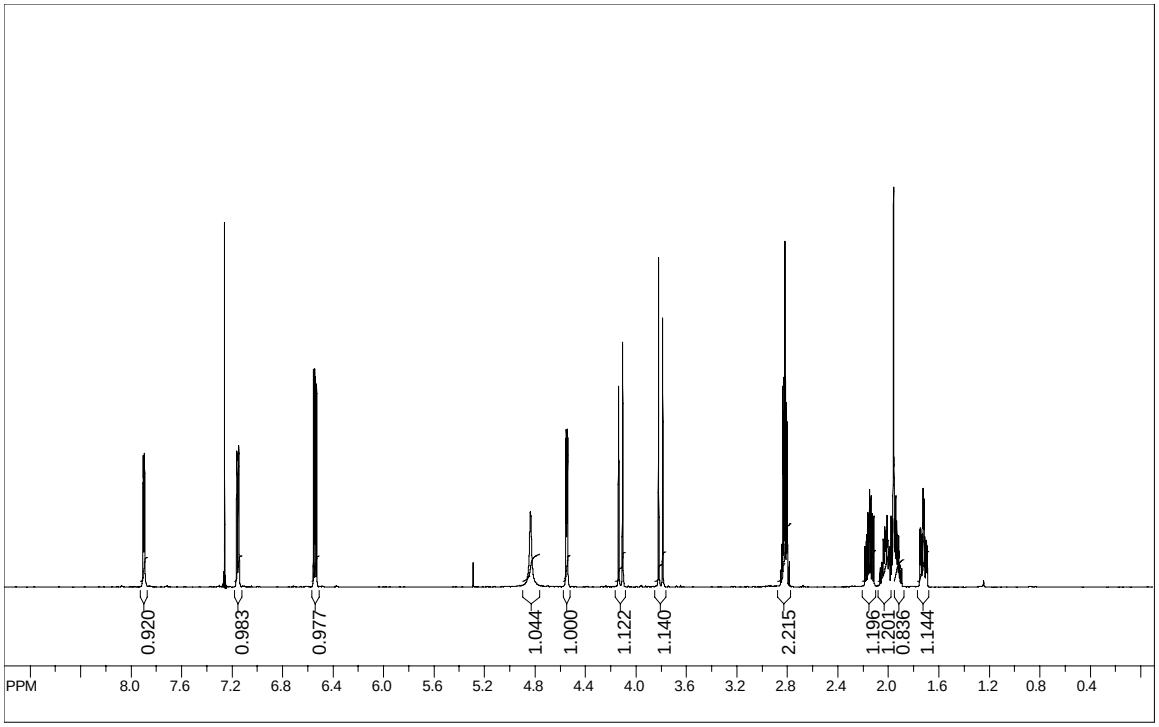


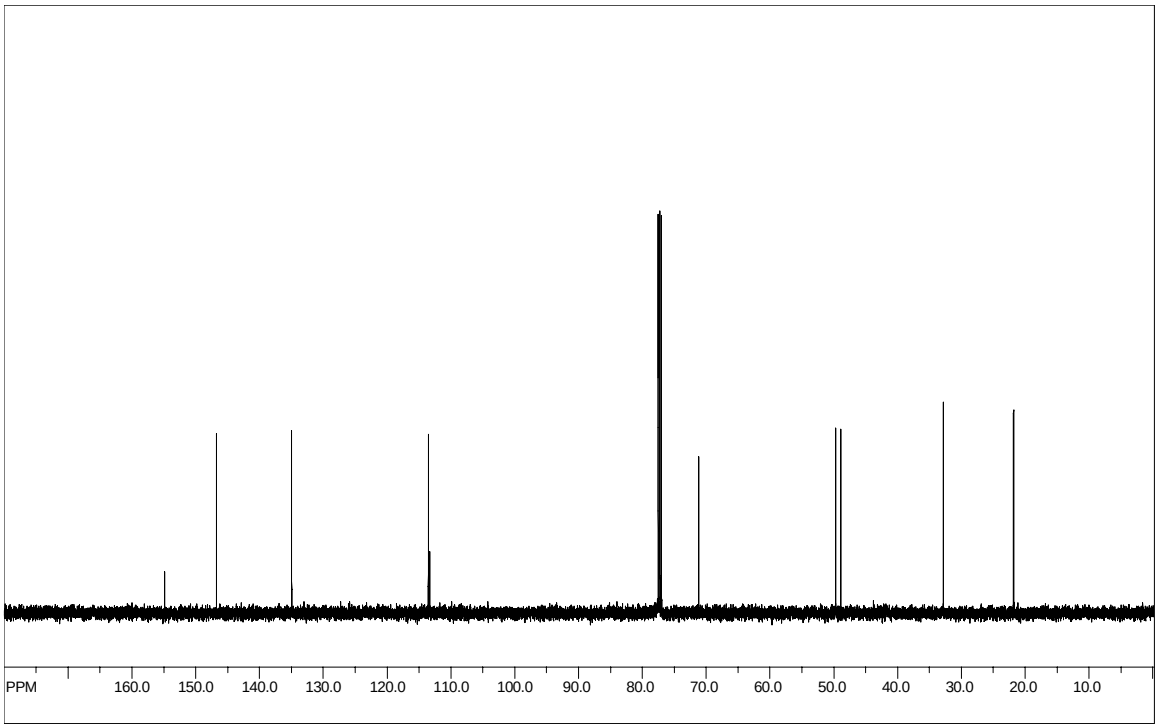



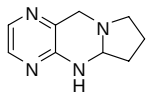
$^{1}$H-NMR and $^{13}$C-NMR of **2m**:

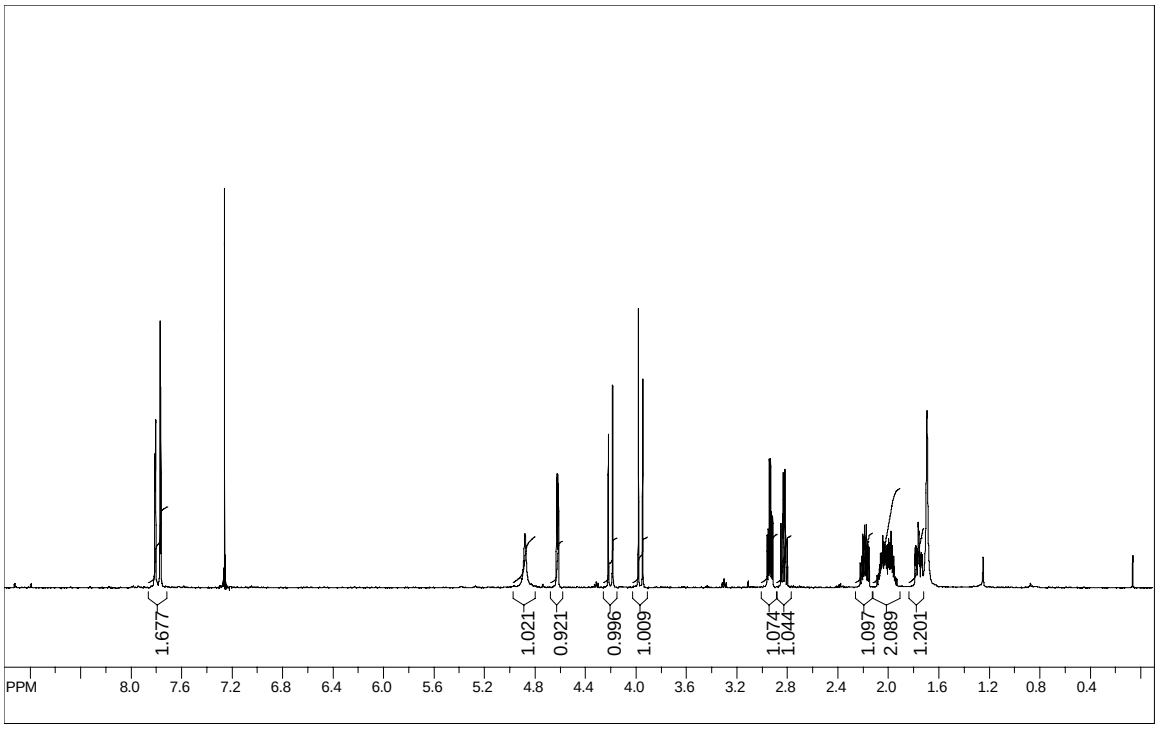


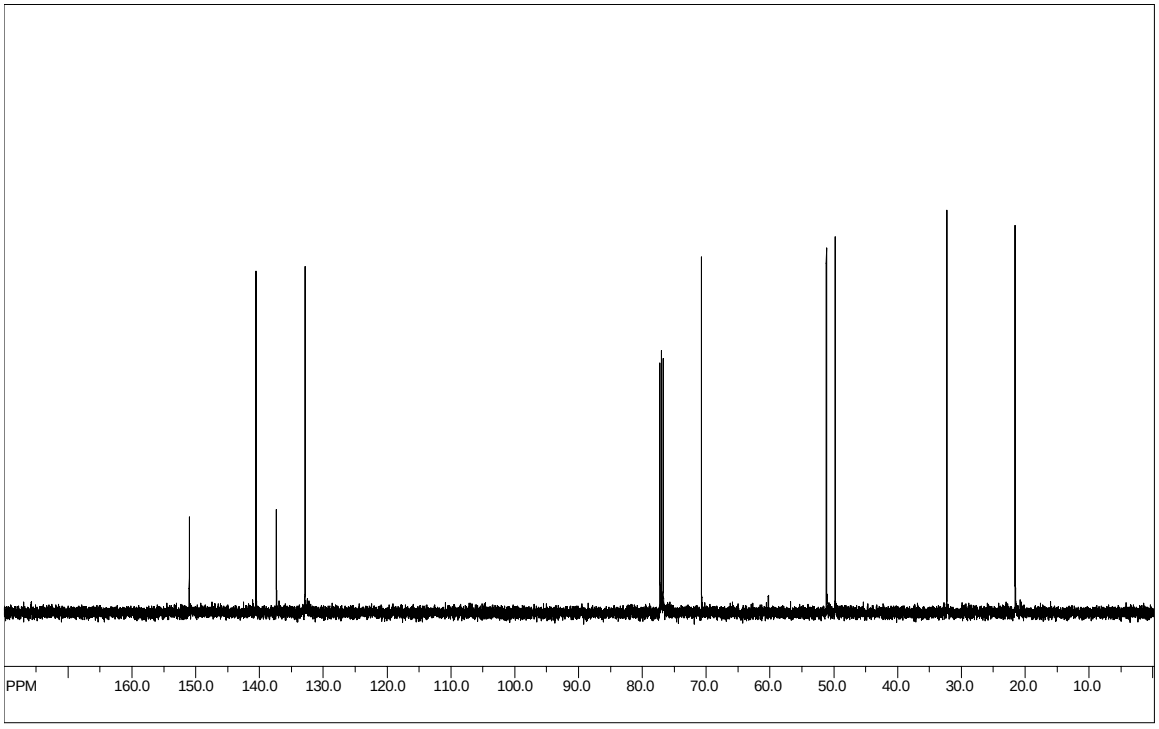



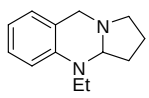
$^{1}$H-NMR and $^{13}$C-NMR of **2n**:

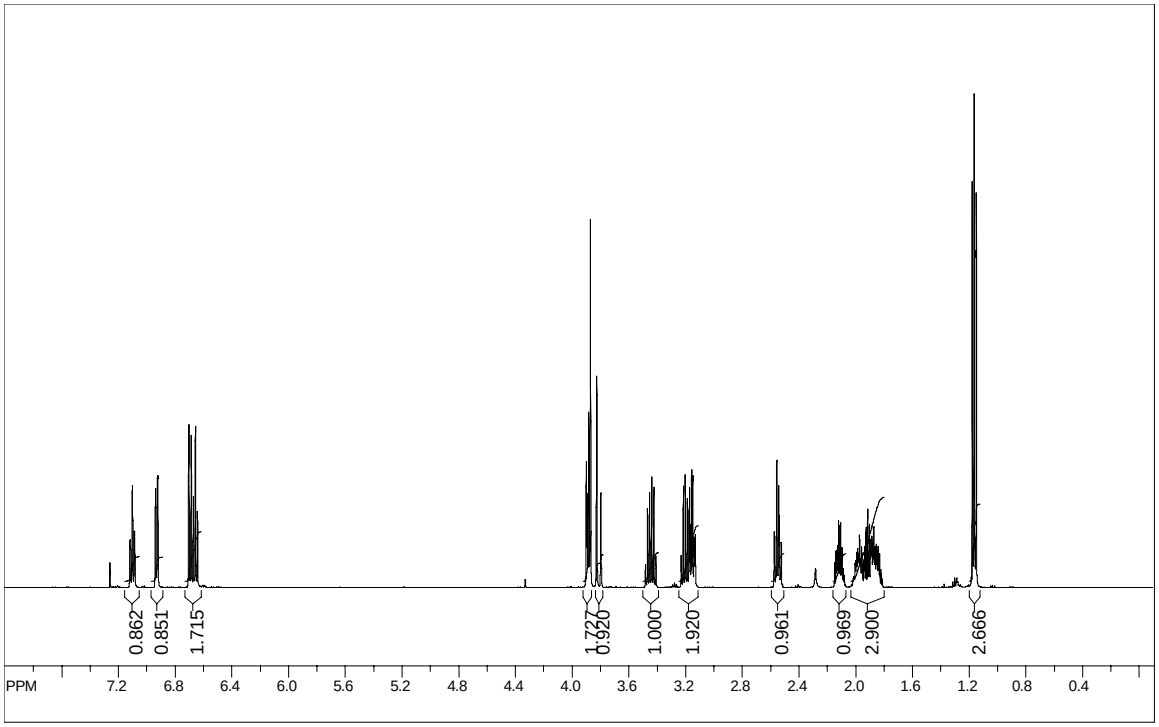


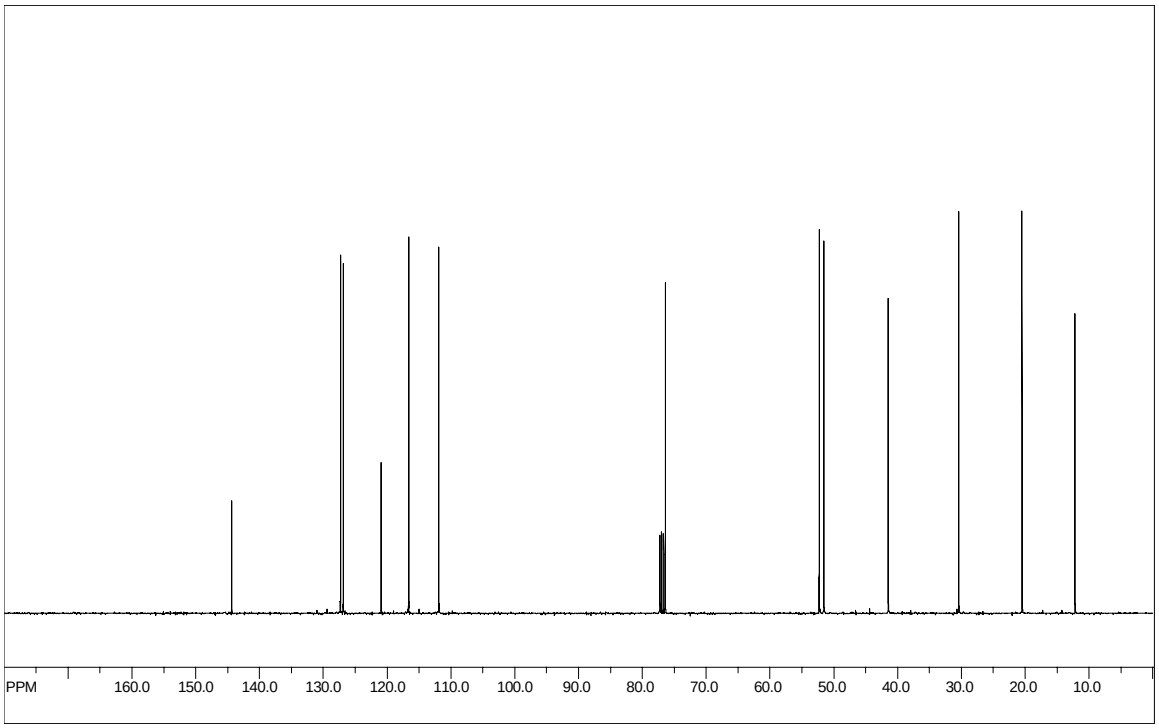



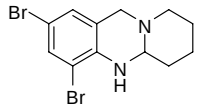
$^{1}$H-NMR and $^{13}$C-NMR of **2o**:

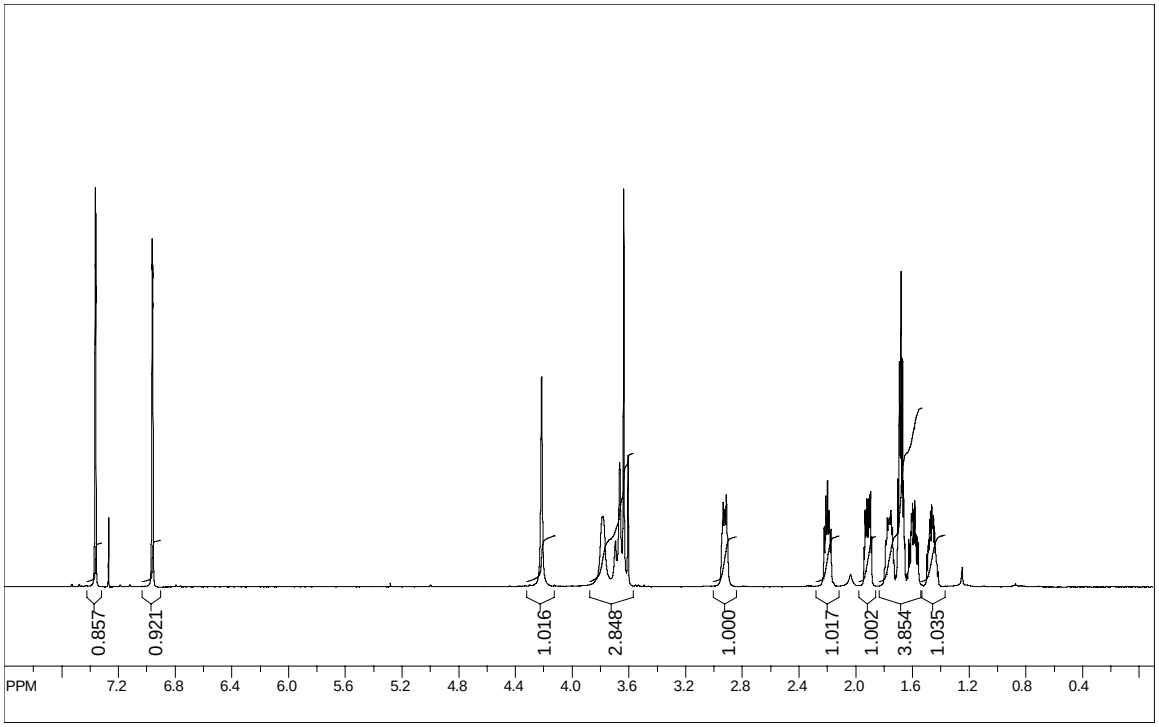


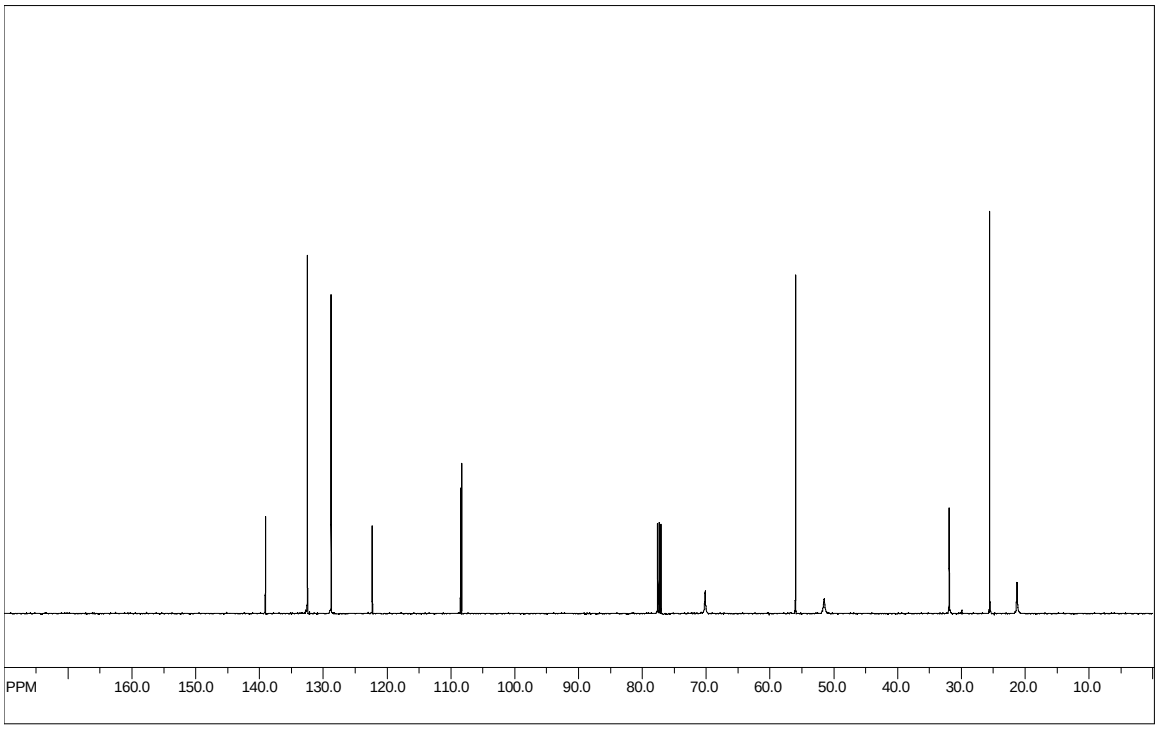



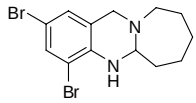
$^{1}$H-NMR and $^{13}$C-NMR of **3**:

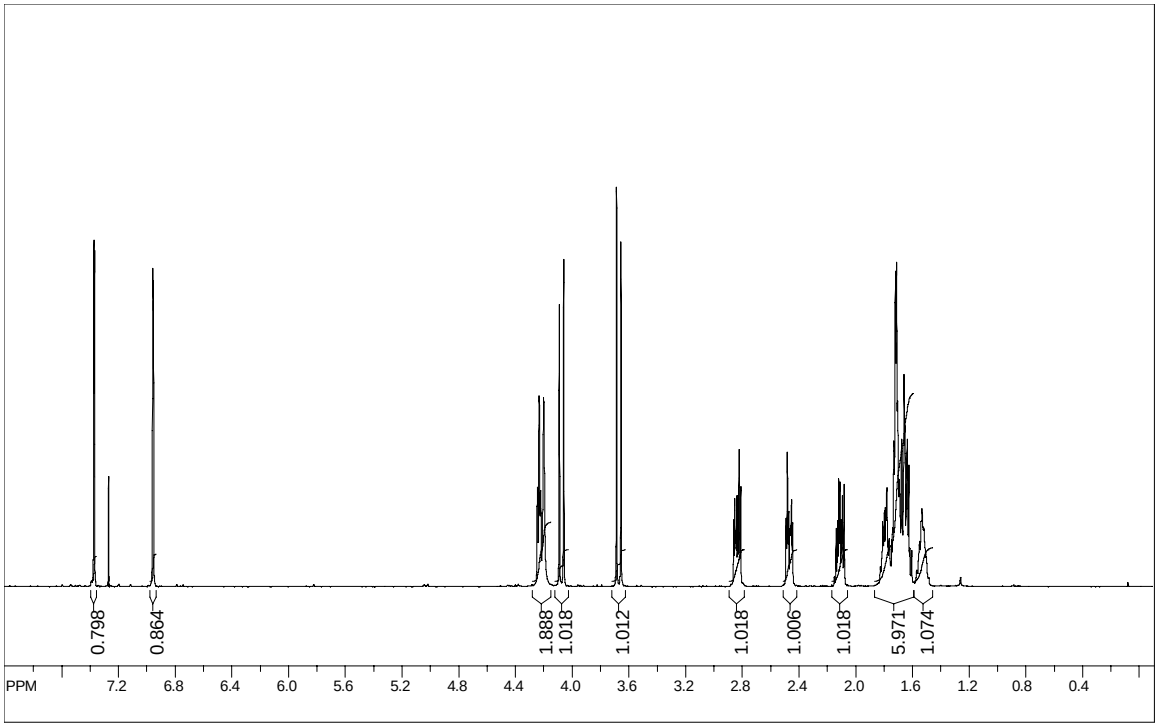


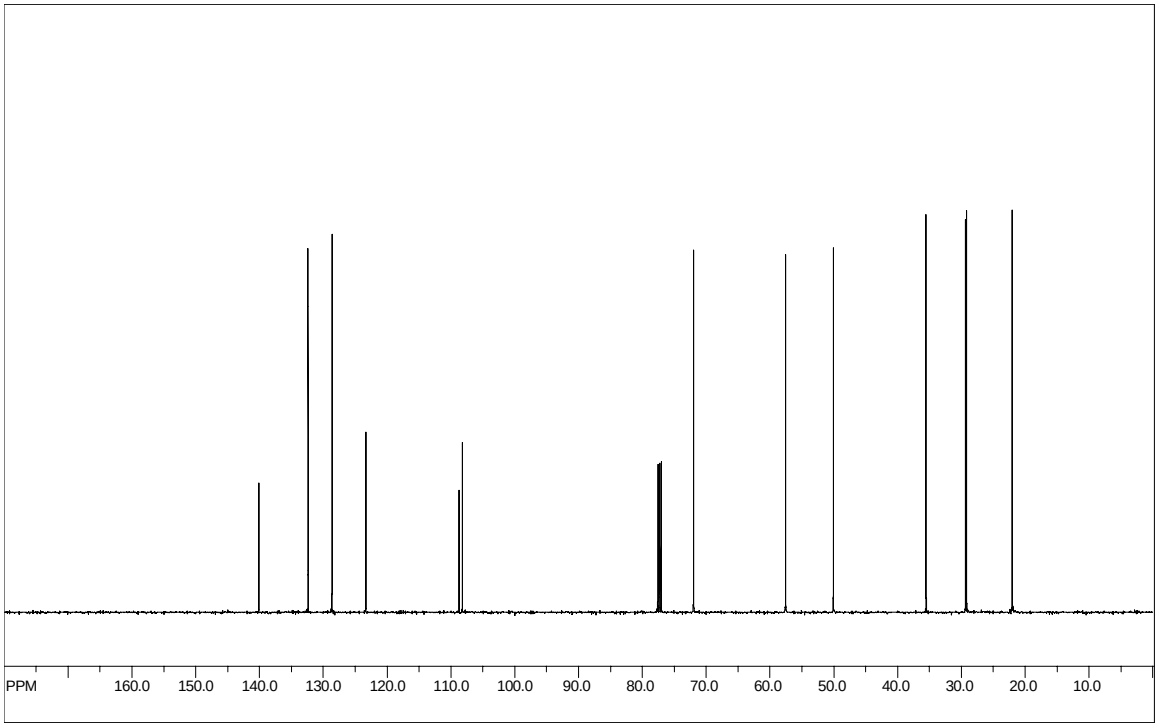



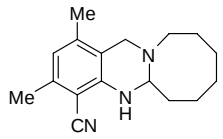
$^{1}$H-NMR and $^{13}$C-NMR of **4**:

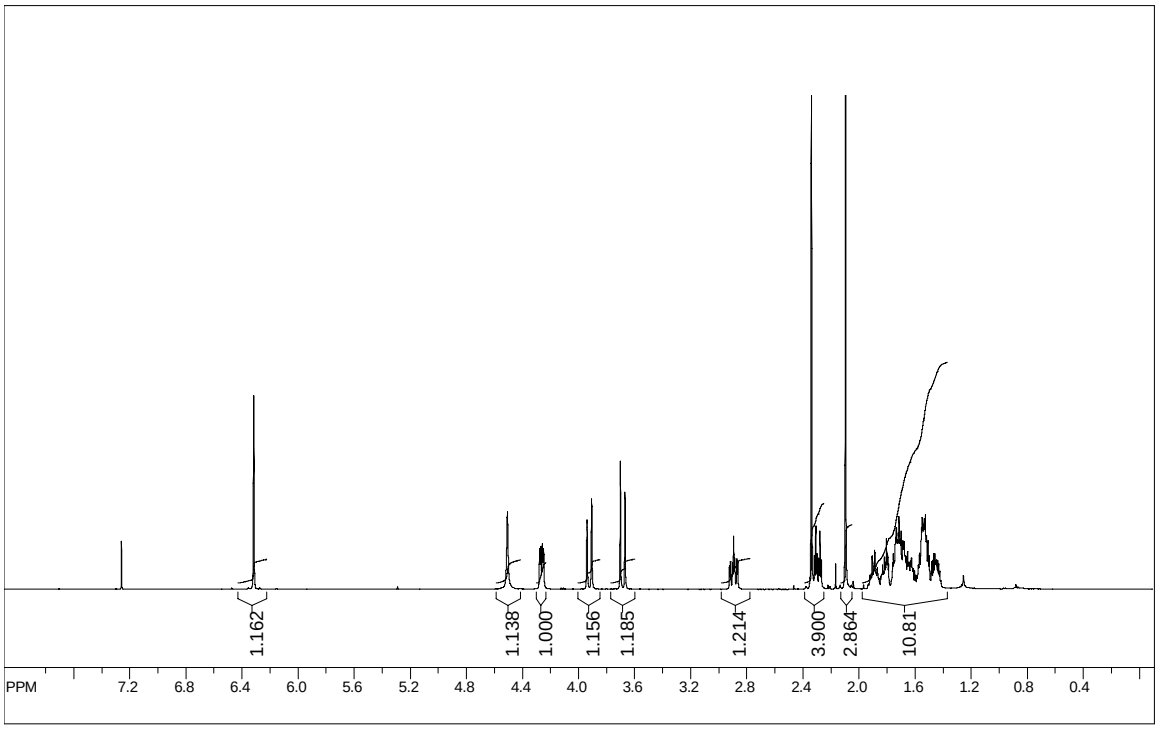


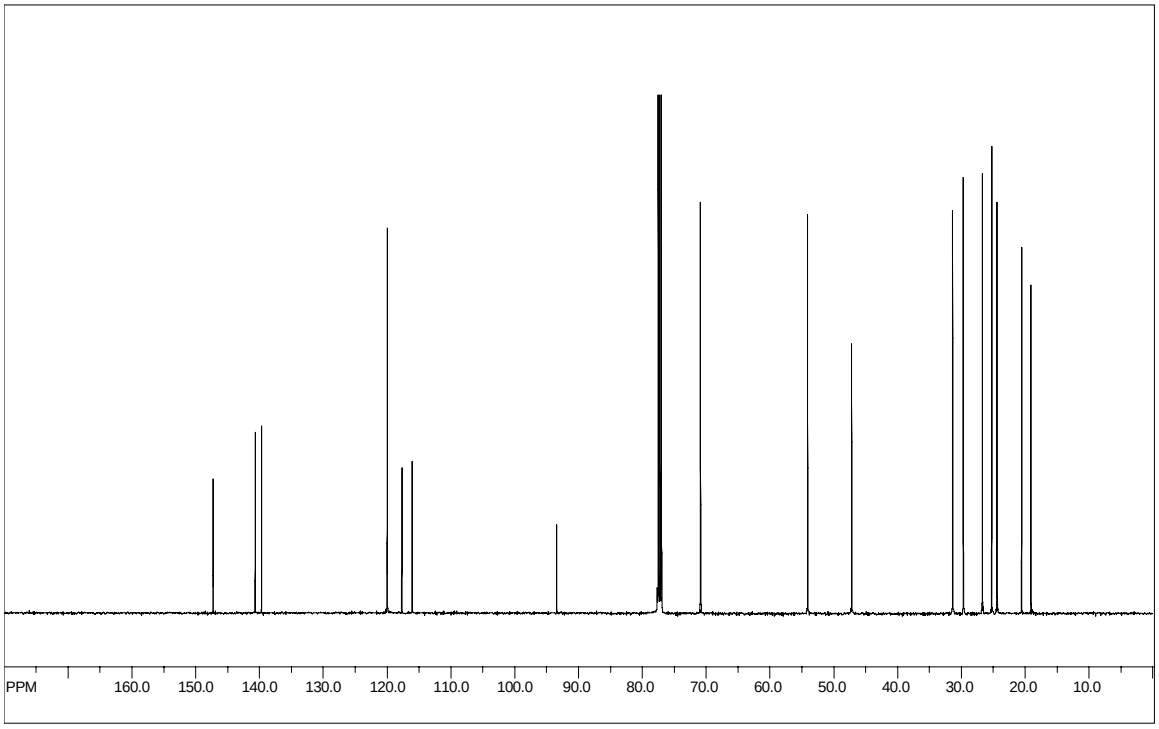



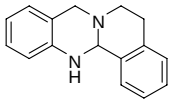
$^{1}$H-NMR and $^{13}$C-NMR of **5**:

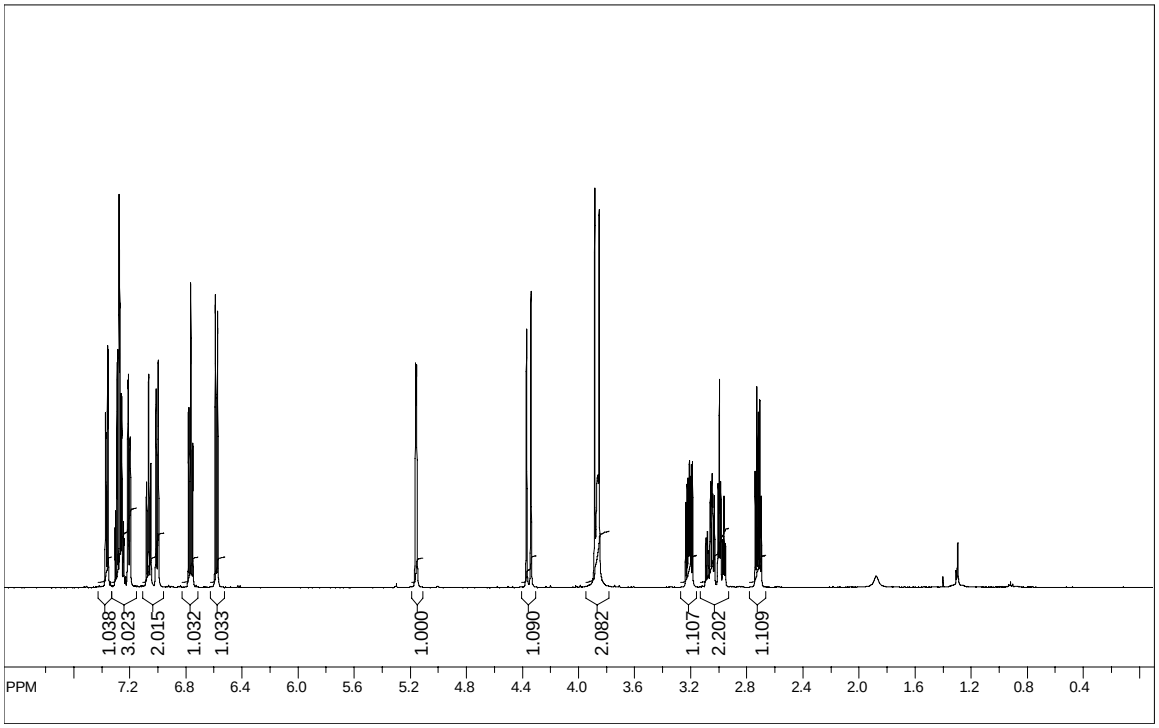


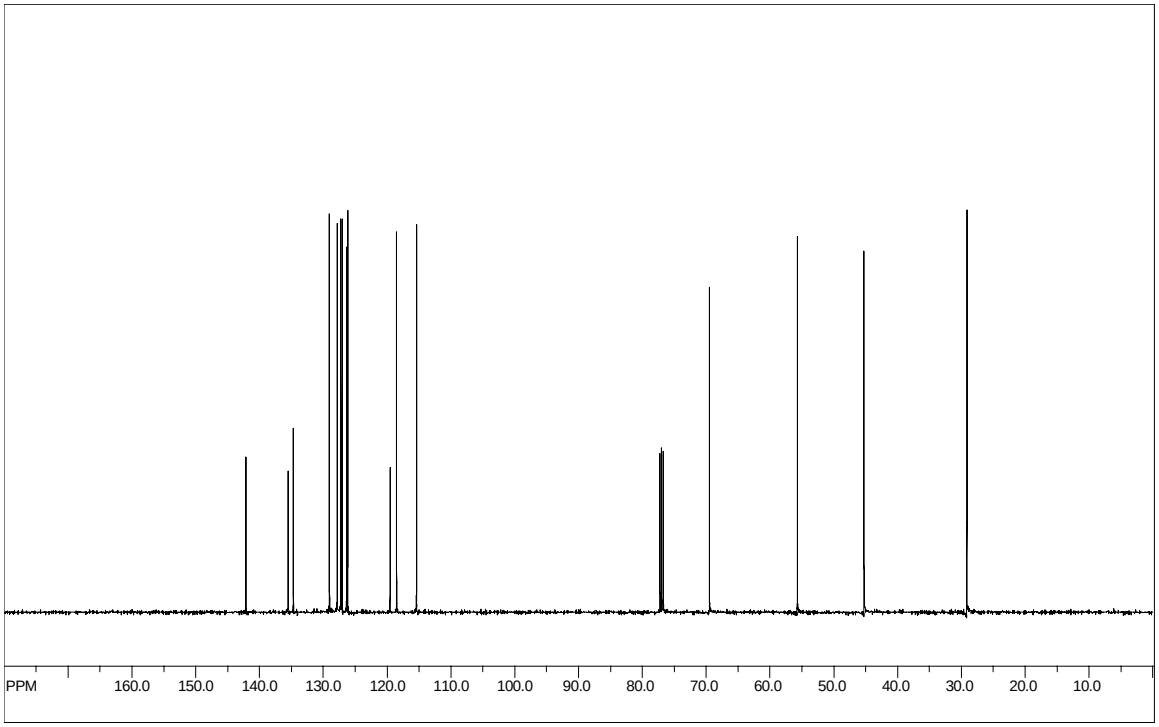



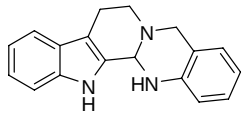
$^{1}$H-NMR and $^{13}$C-NMR of **6**:

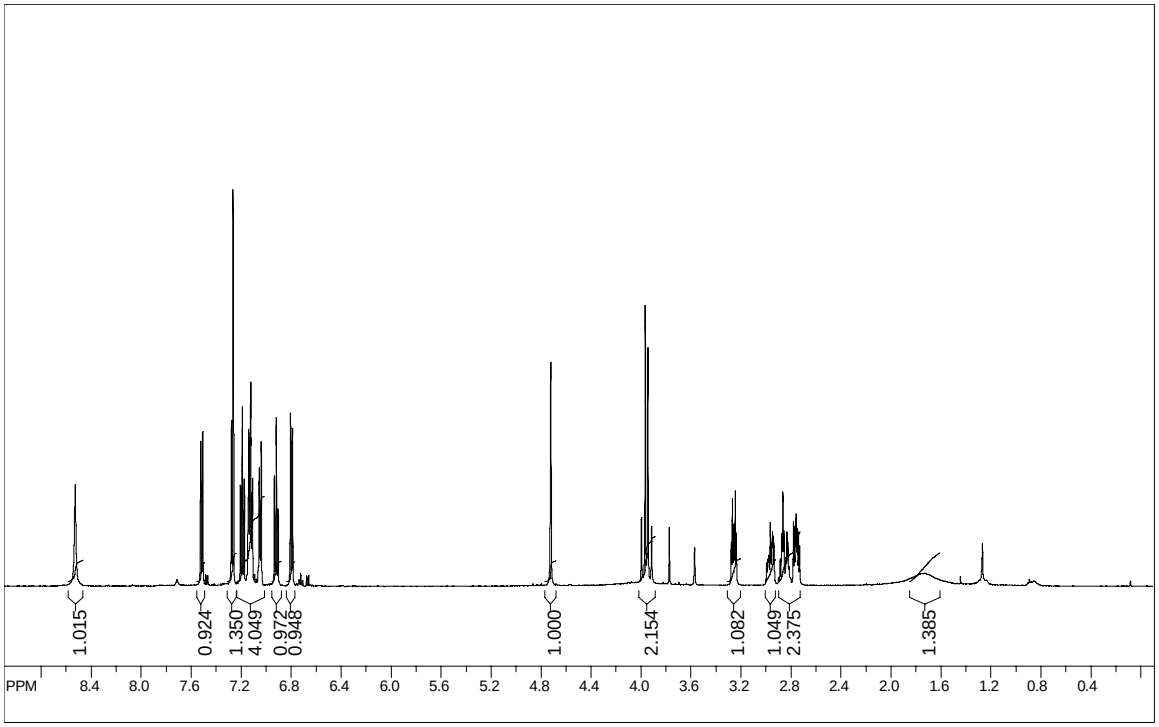


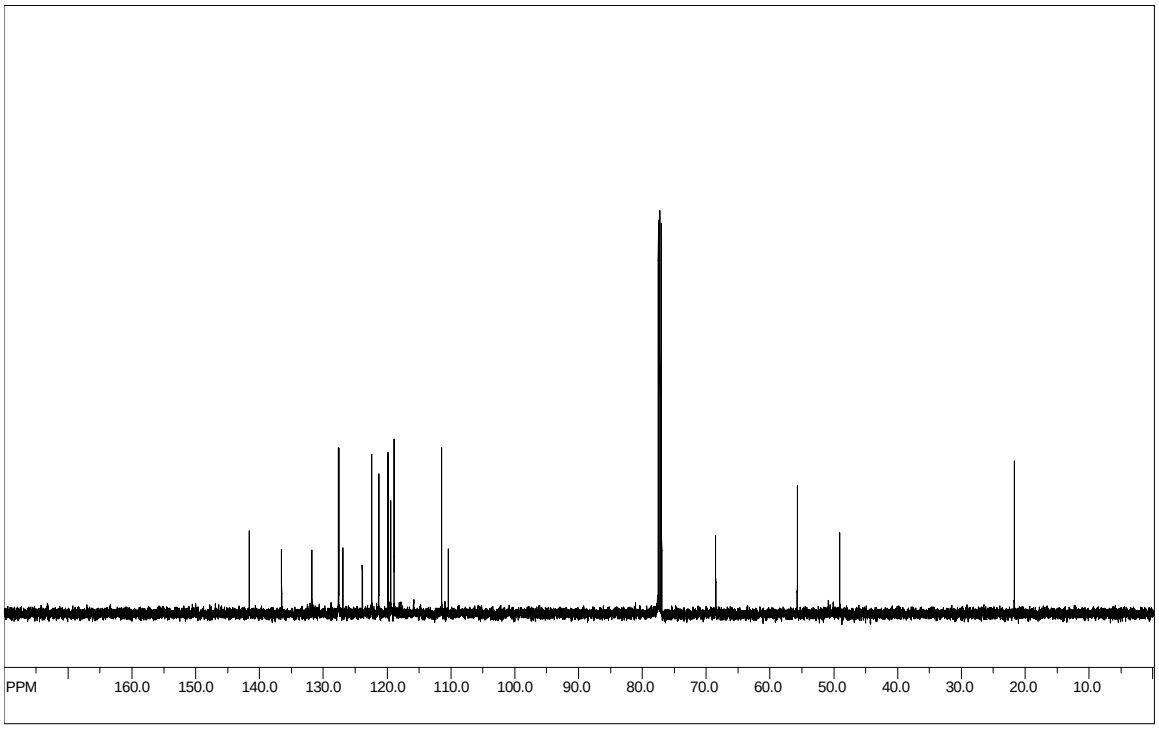



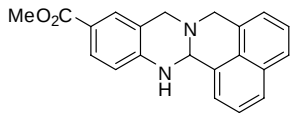
$^{1}$H-NMR and $^{13}$C-NMR of **7**:

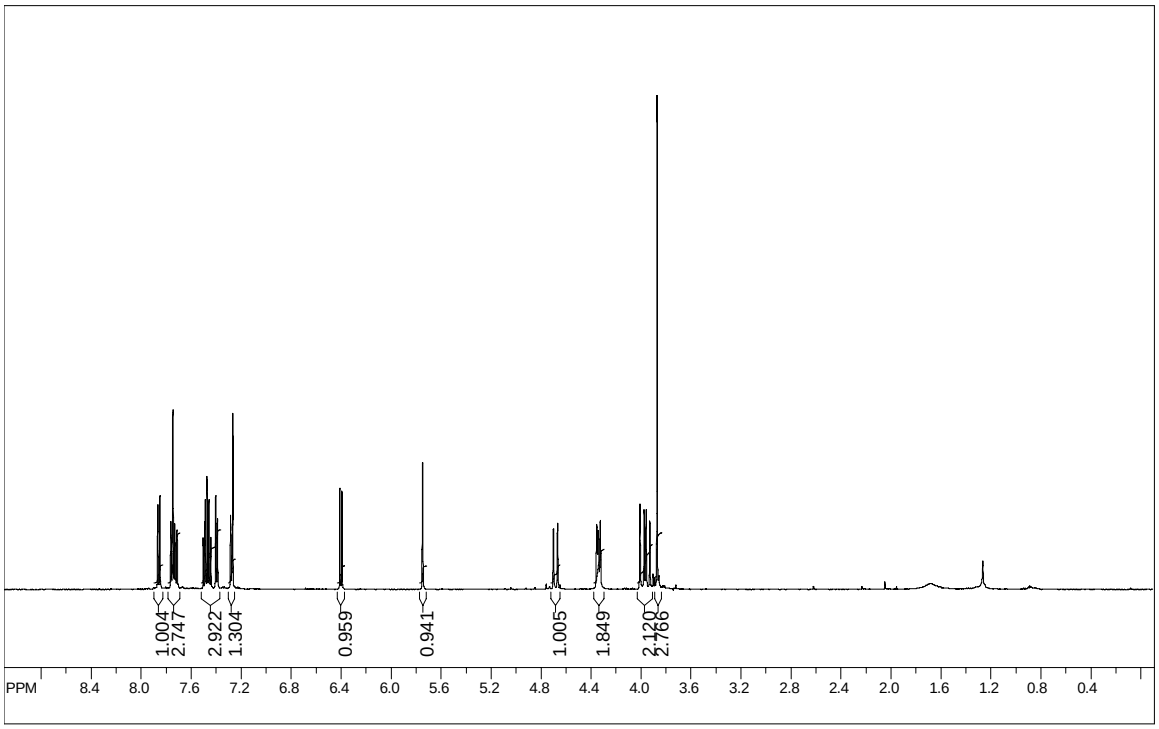


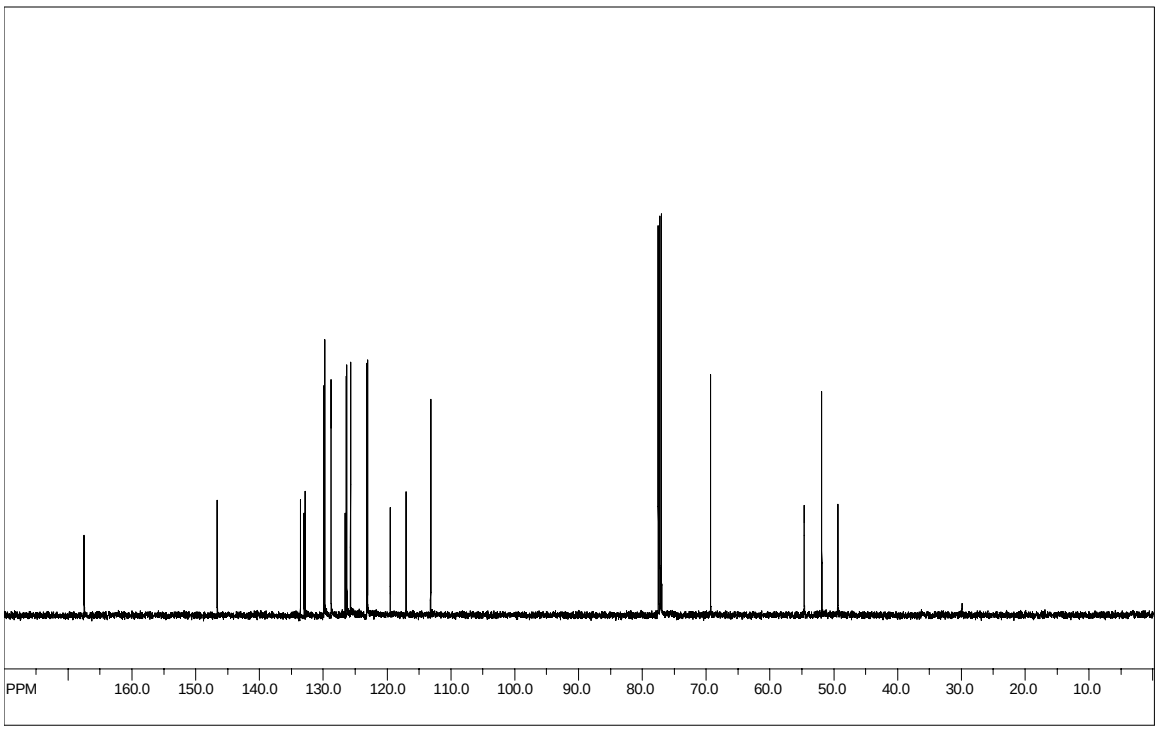



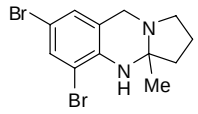
$^{1}$H-NMR and $^{13}$C-NMR of **8**:

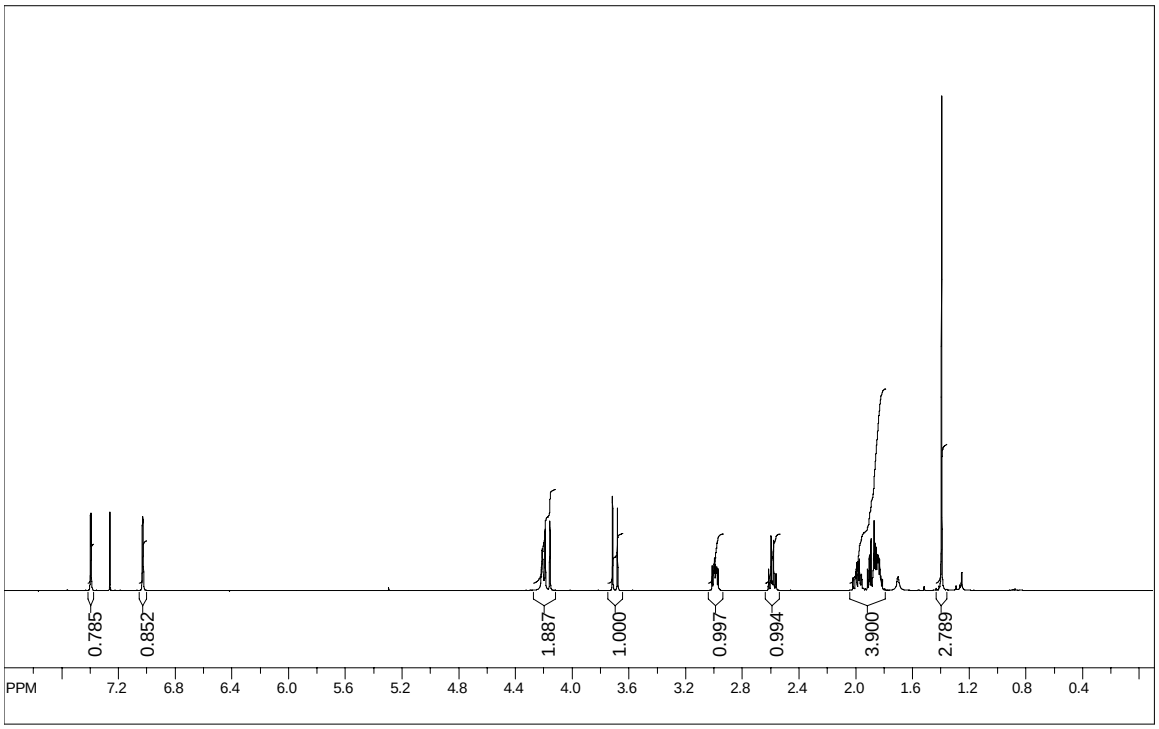


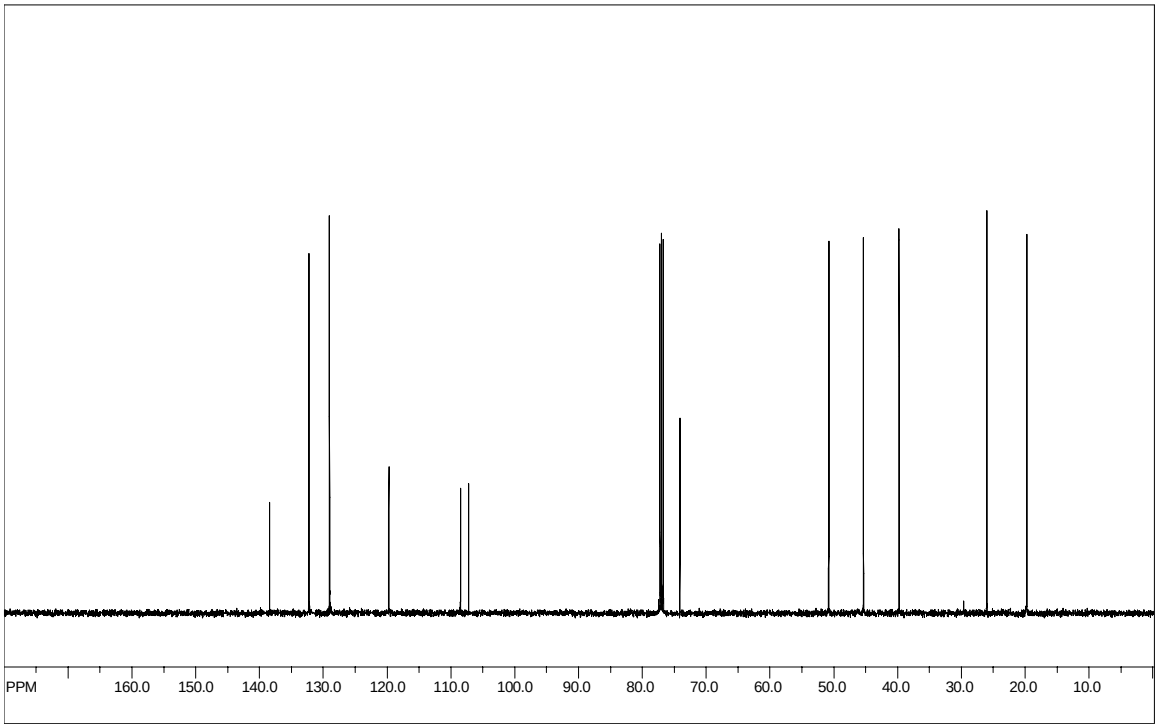



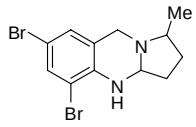
$^{1}$H-NMR and $^{13}$C-NMR of **9a**:

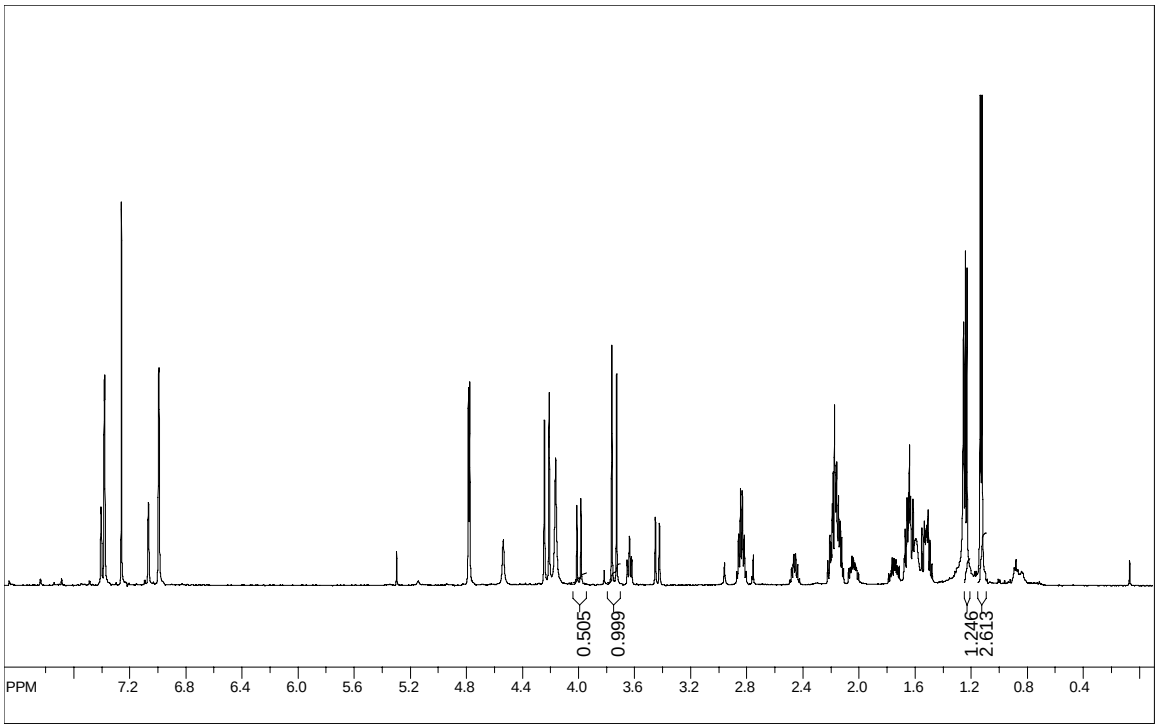


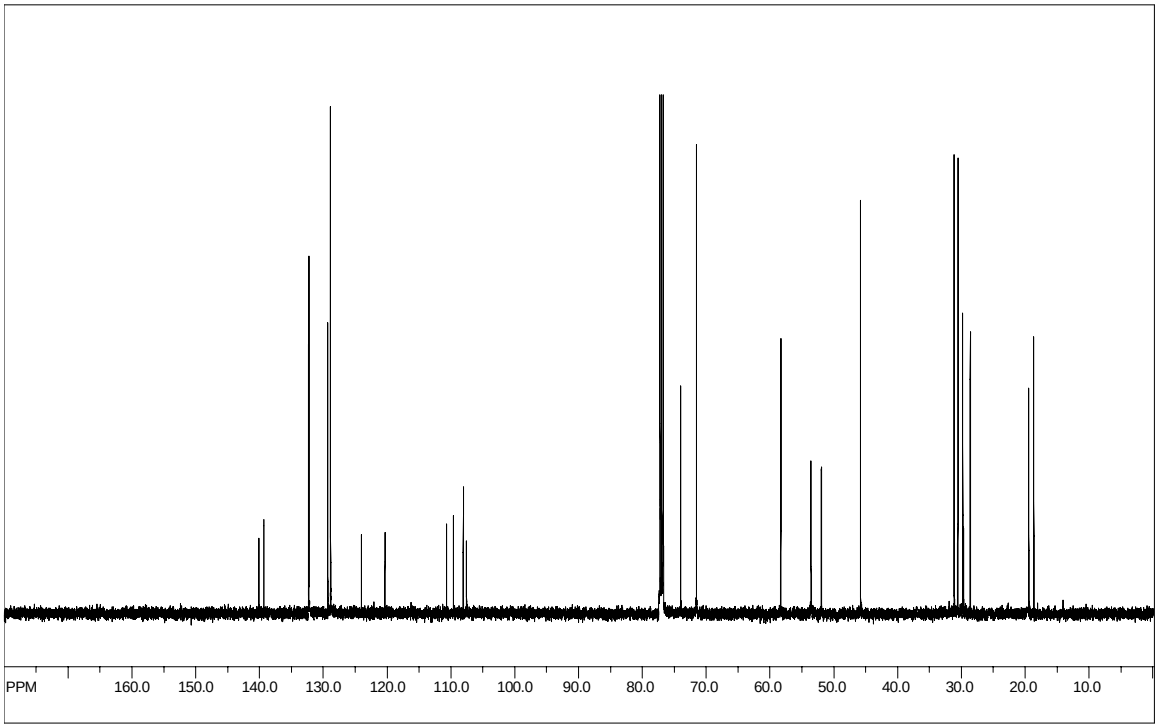



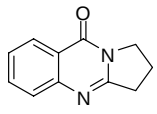
$^{1}$H-NMR of 2:1 mixture of diastereomers of **9b**:

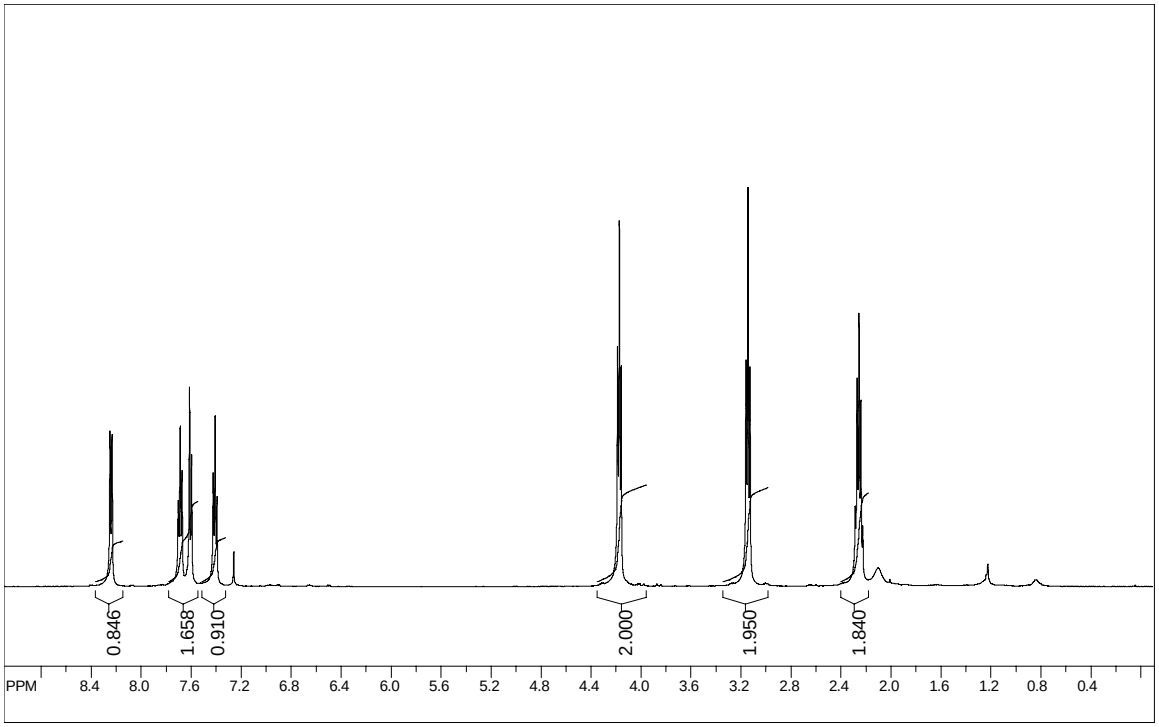


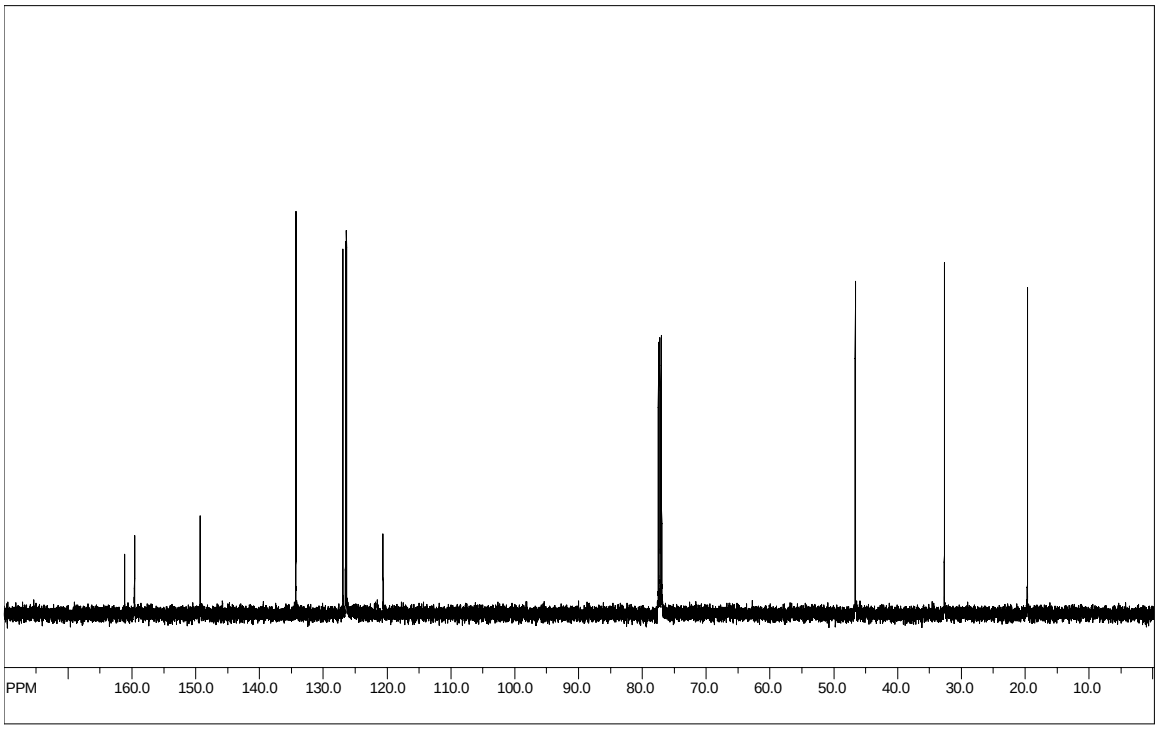



$^{1}$H-NMR and $^{13}$C-NMR of deoxyvasicinone:



$^{1}$H-NMR and $^{13}$C-NMR of rutaecarpine: