Facile Formation of Cyclic Aminals Through a Brønsted Acid Promoted Redox Process

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Supporting Information

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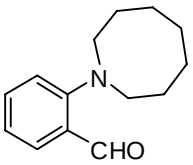
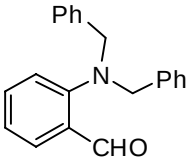
General Information: Starting materials, reagents and solvents were purchased from commercial sources and were used as received with the exception of aniline and benzylamine which were distilled prior to use. Reactions were run under an atmosphere of nitrogen unless mentioned otherwise. Purification 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. Proton nuclear magnetic resonance spectra (^{1}H–NMR) 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 are reported in ppm using solvent as an internal standard ($CDCl_3$ at 77.0 ppm). The starting materials 2-(pyrrolidin-1-yl)benzaldehyde (**6**),[1] 2-(piperidin-1-yl)benzaldehyde (**8a**),[1] 2-(azepan-1-yl)benzaldehyde (**8b**),[3] 2-(3,4-dihydroisoquinolin-2(1H)-yl)benzaldehyde (**8e**),[2] 2-(2-methylpyrrolidin-1-yl)benzaldehyde (**8h**),[1] 2-(3,4-dihydro-1H-pyrido[3,4-b]indol-2(9H)-yl)benzaldehyde (**8g**),[2] were prepared according to literature methods.

General procedure for the preparation of aminoaldehydes:
To a solution of 2-fluorobenzaldehyde (2.48 g, 20 mmol) and potassium carbonate (3.18 g, 23 mmol) in DMF (20 mL) was added the amine (23 mmol). The resulting reaction mixture was heated under reflux until complete consumption of 2-fluorobenzaldehyde, as judged by TLC analysis. The reaction mixture was subsequently allowed to cool to room temperature, diluted with water (100 mL), and extracted with ethyl acetate (3 x 75 mL). The combined organic layers were washed with a saturated NH_4C1 solution (3 x 75 mL) and subsequently dried (Na_2SO_4). The solvent was removed under reduced pressure, and the residue was purified by column chromatography.



2-(azocan-1-yl)benzaldehyde (8d): The title compound was prepared according to the general procedure and isolated as a liquid in 65% yield. (R_f = 0.50 in 80% DCM/Hex); IR (film) 2924, 2849, 1681, 1594, 1483, 1449, 1374, 1274, 1186, 1160, 756 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) 10.23 (app d, *J* = 4.6 Hz, 1H), 7.68 (d, *J* = 7.7 Hz, 1H), 7.49 – 7.26 (m, 1H), 7.07 (d, *J* = 8.4 Hz, 1H), 6.86 (app t, *J* = 7.4 Hz, 1H), 3.48 – 3.19 (comp, 4H), 1.87 – 1.46 (comp, 10H); ^{13}C NMR (125 MHz, $CDCl_3$) 191.3, 155.8, 134.6, 130.6, 127.7, 119.9, 119.5, 55.5, 27.8, 27.4, 25.2; *m/z* (ESIMS) 218.6 $[M + H]^+$.



2-(dibenzylamino)benzaldehyde (8k): The title compound was prepared according to the general procedure and isolated as a liquid in 25% yield (R_f = 0.61 in 80% DCM/Hex); IR (film) 3062, 3028, 2938, 2840, 2733, 1686, 1595, 1494, 1481, 1452, 1384, 1365, 1276, 1254, 1189, 1161, 1028, 833, 749 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) 10.57 (s, 1H), 7.91 – 7.81 (m, 1H), 7.51 – 7.41 (m, 1H), 7.39 – 7.24 (comp, 6H), 7.20 (d, *J* = 7.7 Hz, 4H), 7.09 (app dt, *J* = 9.7, 20.3Hz, 2H), 4.30 (s, 4H).; ^{13}C NMR (125 MHz, $CDCl_3$) 191.3, 154.4, 137.1, 134.4, 129.8, 129.5, 128.6, 128.4, 127.4, 122.9, 122.4, 58.7; *m/z* (ESIMS) 324.7 $[M + Na]^+$.

General procedure A for the reaction between aminoaldehydes and amines:

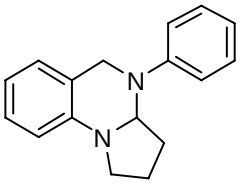
To a stirred solution of aminoaldehyde (1 mmol) in 10 mL of EtOH was added the primary amine (1.2 mmol) and triflic acid (0.2 mmol), followed by heating at reflux. The reaction mixture was monitored by TLC. After the completion of the reaction, 0.3 ml of triethylamine was added. The solution was concentrated in vacuo and the crude product was dissolved in ethyl acetate (20 ml) and washed with 25 ml of 1M NaOH. The aqueous layer was extracted with ethyl acetate (20 ml x 3). The combined organic layers were washed with brine (25 ml) and dried with sodium sulfate. The solvent was removed in vacuo and the crude product was purified by column chromatography.

General procedure B for the reaction between aminoaldehydes and amines:

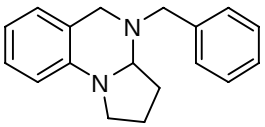
To a stirred solution of aminoaldehyde (1 mmol) in 10 mL of EtOH was added the primary amine (1.2 mmol) and trifluoroacetic acid (1.2 mmol), followed by heating at reflux. The reaction mixture was monitored by TLC. After the completion of the reaction, 1.0 ml of triethylamine was added. The solution was concentrated in vacuo and the crude product was dissolved in ethyl acetate (20 ml) and washed with 25 ml of 1M NaOH. The aqueous layer was extracted with ethyl acetate (20 ml x 3). The combined organic layers were washed with brine (25 ml) and dried with sodium sulfate. The solvent was removed in vacuo and the crude product was purified by column chromatography.

General procedure C for the reaction between aminoaldehydes and amines:

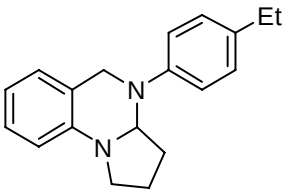
To a stirred solution of aminoaldehyde (1 mmol) in 10 mL of EtOH was added the primary amine (1.2 mmol) and triflic acid (0.2 mmol), followed by stirring at room temperature. The reaction mixture was monitored by TLC. After the completion of the reaction, 0.3 ml of triethylamine was added. The solution was concentrated in vacuo and the crude product was dissolved in ethyl acetate (20 ml) and washed with 25 ml of 1M NaOH. The aqueous layer was extracted with ethyl acetate (20 ml x 3). The combined organic layers were washed with brine (25 ml) and dried with sodium sulfate. The solvent was removed in vacuo and the crude product was purified by column chromatography.



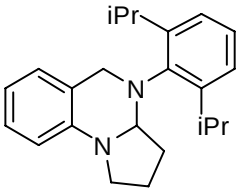
4-phenyl-1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinazoline (7a): The reaction was carried out according to the general procedure A (3 h). The product was obtained as a white solid in 71% yield. (R_f = 0.34 in 8% EtOAc/Hex); mp: 82 – 84 °C; IR (KBr) 3031, 2970, 2937, 2835, 1606, 1596, 1510, 1494, 1477, 1461, 1398, 1363, 1323, 1308, 1256, 1207, 1193, 774, 702 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 7.32 (app tt, *J* = 2.0, 3.9 Hz, 2H), 7.22 – 7.10 (comp, 4H), 6.97 (d, *J* = 7.4 Hz, 1H), 6.69 – 6.63 (m, 1H), 6.54 (d, *J* = 8.0 Hz, 1H), 4.65 (dd, *J* = 5.3, 8.3 Hz, 1H), 4.40 (d, *J* = 14.9 Hz, 1H), 4.12 (d, *J* = 14.9 Hz, 1H), 3.47 (app td, *J* = 3.1, 8.7 Hz, 1H), 3.39 (dd, *J* = 8.6, 16.2 Hz, 1H), 2.14 – 1.85 (comp, 3H), 1.80 – 1.68 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) 150.3, 143.5, 128.9, 127.8, 125.9, 125.2, 124.7, 120.8, 116.2, 111.3, 76.7, 57.3, 47.1, 31.9, 22.2; *m/z* (ESIMS) 251.2 $[M + H]^+$.



4-benzyl-1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinazoline (7b): The reaction was carried out according to the general procedure B (24 h). The product was obtained as a colorless oil in 75% yield. (R_f = 0.24 in 2% EtOAc/DCM); IR (film) 3066, 3025, 2968, 2834, 1606, 1578, 1509, 1483, 1462, 1395, 1369, 1321, 1304, 1160, 1130, 741, 698 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 7.45 – 7.26 (comp, 5H), 7.11 (app t, *J* = 7.5 Hz, 1H), 6.83 (d, *J* = 7.2 Hz, 1H), 6.59 (app td, *J* = 0.9, 7.4 Hz, 1H), 6.47 (d, *J* = 8.0 Hz, 1H), 4.17 (dd, *J* = 5.3, 8.3 Hz, 1H), 3.95 (d, *J* = 13.1 Hz, 1H), 3.69 (d, *J* = 14.8 Hz, 1H), 3.57 (d, *J* = 14.8 Hz, 1H), 3.50 – 3.30 (comp, 3H), 2.35 – 2.25 (m, 1H), 2.19 – 2.09 (m, 1H), 2.07 – 1.86 (comp, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) 143.2, 138.3, 129.0, 128.3, 127.6, 127.1, 126.4, 119.4, 115.7, 110.3, 78.4, 56.5, 54.4, 46.6, 31.8, 22.4; *m/z* (ESIMS) 265.2 $[M + H]^+$.

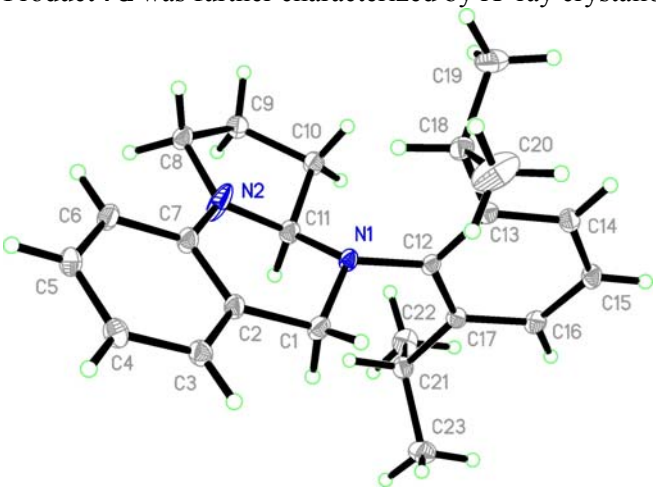


4-(4-ethylphenyl)-1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinazoline (7c): The reaction was carried out according to the general procedure A (12 h). The product was obtained as a white solid in 67% yield. (R_f = 0.34 in 15% Ether/Hex); mp: 67 – 69 °C; IR (KBr) 2959, 2851, 1605, 1509, 1457, 1359, 1345, 1194, 1178, 1104, 840, 741 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 7.20 – 7.07 (comp, 5H), 6.96 (d, *J* = 7.3 Hz, 1H), 6.65 (app t, *J* = 7.4 Hz, 1H), 6.54 (d, *J* = 8.1 Hz, 1H), 4.63 (dd, *J* = 5.3, 8.2 Hz, 1H), 4.38 (d, *J* = 14.9 Hz, 1H), 4.09 (d, *J* = 14.9 Hz, 1H), 3.53 – 3.34 (comp, 2H), 2.64 (app q, *J* = 7.6 Hz, 2H), 2.11 – 1.84 (comp, 3H), 1.74 (app tt, *J* = 8.2, 11.1 Hz, 1H), 1.32 – 1.19 (comp, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 148.0, 143.6, 140.9, 128.4, 127.8, 126.1, 125.3, 121.0, 116.2, 111.4, 76.9, 57.6, 47.2, 32.1, 28.4, 22.4, 15.6; *m/z* (ESIMS) 279.5 $[M + H]^+$.

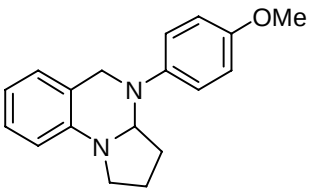


4-(2,6-diisopropylphenyl)-1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinazoline (7d): The reaction was carried out according to the general procedure A (5h). The product was obtained as a white solid in 71% yield. (R_f = 0.30 in 20% DCM/Hex); mp: 186 – 189 °C; IR (KBr) 3049, 3021, 2926, 2863, 2778, 1604, 1578, 1477, 1445, 1395, 1386, 1363, 1319, 1300, 1259, 1249, 1189, 1157, 1048, 763 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 7.25 (dd, *J* = 5.2, 10.0 Hz, 1H), 7.21 – 7.09 (comp, 3H), 6.97 (d, *J* = 7.3 Hz, 1H), 6.70 (app t, *J* = 7.3 Hz, 1H), 6.65 (d, *J* = 8.0 Hz, 1H), 4.96 (dd, *J* = 5.6, 7.9 Hz, 1H), 4.64 (d, *J* = 15.3 Hz, 1H), 3.98 (d, *J* = 15.3 Hz, 1H), 3.73 (app dt, *J* = 6.9, 13.9 Hz, 1H), 3.57 – 3.35 (comp, 2H), 3.11 (app dt, *J* = 6.8, 13.6 Hz, 1H), 2.09 – 1.85 (comp, 2H), 1.84 – 1.73 (m, 1H), 1.50 (app dt, *J* = 8.4, 12.1 Hz, 1H), 1.28 (dd, *J* = 3.3, 6.8 Hz, 6H), 1.15 (d, *J* = 7.0 Hz, 3H), 1.03 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 150.5, 149.3, 144.3, 141.9, 127.1, 127.0, 125.8, 124.4, 123.7, 121.8, 116.3, 112.7, 74.6, 54.0, 47.5, 31.3, 28.8, 27.3, 25.5, 25.3, 24.3, 23.6, 22.5; *m/z* (ESIMS) 335.2 $[M + H]^+$

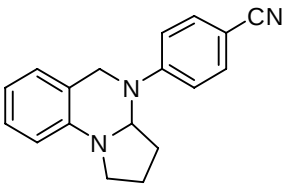
Product **7d** was further characterized by X–ray crystallography:



The requisite CIF file has been submitted to the journal.

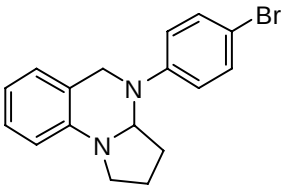


4-(4-methoxyphenyl)-1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinazoline (7e): The reaction was carried out according to the general procedure A (0.5 h). The product was obtained as a yellow solid in 57% yield. (R_f = 0.65 in DCM); mp: 73 – 75 °C; IR (KBr) 3040, 2931, 2833, 1606, 1579, 1509, 1482, 1461, 1392, 1362, 1322, 1288, 1244, 1204, 1180, 1134, 1121, 1104, 1037, 1016, 992, 835, 816, 772, 744, 713 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 7.17 – 7.09 (comp, 3H), 6.96 (d, *J* = 7.3 Hz, 1H), 6.89 – 6.83 (comp, 2H), 6.64 (app tt, *J* = 1.9, 3.8 Hz, 1H), 6.53 (d, *J* = 8.0 Hz, 1H), 4.58 (dd, *J* = 4.9, 8.2 Hz, 1H), 4.38 (d, *J* = 14.9 Hz, 1H), 4.02 (d, *J* = 14.9 Hz, 1H), 3.80 (s, 3H), 3.47 (app td, *J* = 2.8, 8.6 Hz, 1H), 3.42 – 3.32 (m, 1H), 2.02 – 1.83 (comp, 3H), 1.76 – 1.61 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) 157.1, 143.4, 143.1, 127.7, 126.7, 126.0, 120.8, 116.0, 114.1, 111.2, 77.2, 57.6, 55.4, 47.1, 31.9, 22.3; *m/z* (ESIMS) 281.2 $[M]^+$.

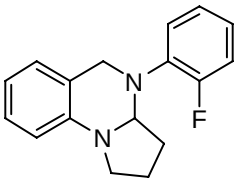


4-(1,2,3,3a-tetrahydropyrrolo[1,2-a]quinazolin-4(5H)-yl)benzonitrile (7f): The reaction was carried out according to the general procedure C (15 h). The product was obtained as a white solid in 50% yield. (R_f = 0.51 in DCM); mp: 116 – 118 °C; IR (KBr) 3048, 2949, 2838, 2213, 1602, 1513, 1461, 1383, 1175, 820, 755 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 7.58 – 7.50 (comp, 2H), 7.20 (app t, *J* = 7.7 Hz, 1H), 7.08 – 6.98 (comp, 3H), 6.77 (app t, *J* = 7.4 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 1H), 4.59 (dd, *J* = 5.5, 8.3 Hz, 1H), 4.46 (d, *J* = 14.8 Hz, 1H), 4.29 (d, *J* = 14.8 Hz, 1H), 3.52 – 3.40 (m, 1H), 3.34 (app td, *J* = 5.3,

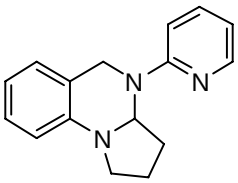
8.9 Hz, 1H), 2.43 – 2.30 (m, 1H), 2.14 – 1.91 (comp, 2H), 1.78 (app dq, *J* = 8.9, 12.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) 152.8, 144.2, 133.1, 128.2, 125.6, 122.1, 120.1, 119.6, 118.0, 112.2, 103.4, 75.0, 52.6, 46.2, 31.2, 21.5; *m/z* (ESIMS) 276.2 $[M + H]^+$.



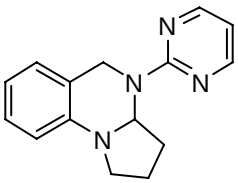
4-(4-bromophenyl)-1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinazoline (7g): The reaction was carried out according to the general procedure A (1.5 h). The product was obtained as a white solid in 65% yield. (R_f = 0.27 in 50% DCM/Hex); mp: 97 – 99 °C; IR (KBr) 2967, 2831, 1604, 1578, 1508, 1496, 1483, 1461, 1394, 1362, 1322, 1290, 1254, 1233, 1206, 1175, 1130, 1101, 1070, 1036, 1007, 992, 842, 823, 805, 744, 716, 680 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) 7.45 – 7.38 (comp, 2H), 7.15 (app t, *J* = 7.5 Hz, 1H), 7.07 – 7.00 (comp, 2H), 6.97 (d, *J* = 7.4 Hz, 1H), 6.67 (app td, *J* = 0.9, 7.4 Hz, 1H), 6.54 (d, *J* = 8.0 Hz, 1H), 4.62 (dd, *J* = 5.3, 8.3 Hz, 1H), 4.38 (d, *J* = 15.0 Hz, 1H), 4.09 (d, *J* = 15.0 Hz, 1H), 3.51 – 3.31 (comp, 2H), 2.14 – 1.85 (comp, 3H), 1.70 (app ddt, *J* = 8.3, 10.8, 12.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) 149.1, 143.4, 131.9, 127.9, 126.8, 125.9, 120.4, 117.7, 116.4, 111.4, 76.4, 57.0, 47.0, 31.7, 22.2; *m/z* (ESIMS) 329.2 $[M + H]^+$.



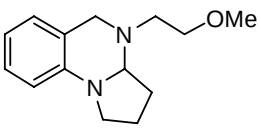
4-(2-fluorophenyl)-1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinazoline (7h): The reaction was carried out according to the general procedure A (6 h). The product was obtained as a white solid in 50% yield. (R_f = 0.37 in 10% Ether/Hex); mp: 80 – 82 °C; IR (KBr) 3064, 3047, 3023, 2978, 2962, 2937, 2847, 2790, 1604, 1576, 1497, 1483, 1461, 1366, 1327, 1262, 1222, 1196, 1172, 1033, 772, 746 cm^{-1} ^{1}H NMR (500 MHz, $CDCl_3$) 7.22 – 7.02 (comp, 5H), 6.96 (d, *J* = 7.3 Hz, 1H), 6.67 (app t, *J* = 7.4 Hz, 1H), 6.55 (d, *J* = 8.0 Hz, 1H), 4.92 – 4.76 (m, 1H), 4.52 (d, *J* = 15.2 Hz, 1H), 4.13 (d, *J* = 15.2 Hz, 1H), 3.55 – 3.31 (comp, 2H), 2.12 (ddd, *J* = 2.6, 7.6, 12.4 Hz, 1H), 2.05 – 1.86 (comp, 2H), 1.69 (ddd, *J* = 8.5, 11.0, 19.3 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) 160.05, 158.08, 143.62, 136.92, 136.84, 127.68, 127.04, 127.02, 126.17, 126.10, 125.85, 124.39, 124.36, 120.38, 116.25, 116.18, 116.02, 111.54, 75.80, 55.89, 46.88, 30.80, 22.18; *m/z* (ESIMS) 267.3 $[M - H]^+$.



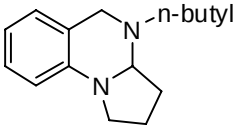
4-(pyridin-2-yl)-1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinazoline (7i): The reaction was carried out according to the general procedure A (24 h). The product was obtained as a yellow liquid in 35% yield. (R_f = 0.46 in 2% EtOAc/DCM); IR (film) 3043, 2967, 2815, 1591, 1561, 1497, 1479, 1460, 1436, 1379, 1320, 1213, 1158, 1047, 977, 768, 749 cm^{-1} ^{1}H NMR (500 MHz, $CDCl_3$) 8.31 – 8.22 (m, 1H), 7.51 (ddd, *J* = 2.0, 7.2, 8.5Hz, 1H), 7.24 – 7.16 (m, 1H), 7.11 (d, *J* = 7.3 Hz, 1H), 6.85 – 6.64 (comp, 4H), 4.85 (d, *J* = 14.7 Hz, 1H), 4.72 (dd, *J* = 5.4, 8.6 Hz, 1H), 4.33 (d, *J* = 14.7 Hz, 1H), 3.49 (app td, *J* = 5.7, 8.7 Hz, 1H), 3.33 (app td, *J* = 5.7, 9.0 Hz, 1H), 2.64 (app tdd, *J* = 3.1, 5.4, 12.1 Hz, 1H), 2.15 – 1.93 (comp, 2H), 1.81 (ddd, *J* = 9.2, 12.2, 18.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) 159.4, 147.8, 144.8, 137.1, 127.8, 125.6, 123.6, 117.9, 114.7, 112.3, 111.4, 73.8, 48.6, 46.0, 31.3, 21.3; *m/z* (ESIMS) 250.3 $[M - H]^+$.



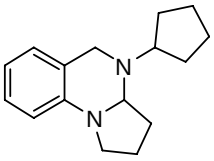
4-(pyrimidin-2-yl)-1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinazoline (7j): The reaction was carried out according to the general procedure A (48 h). The product was obtained as a white solid in 36% yield. (R_f = 0.17 in 5% EtOAc/DCM); mp: 105 – 107 °C; IR (film) 3024, 2960, 2825, 1585, 1547, 1486, 1459, 1371, 1350, 1316, 1280, 1227, 1175, 1156, 797, 751 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) 8.34 (d, *J* = 4.7 Hz, 2H), 7.22 (app t, *J* = 7.7 Hz, 1H), 7.18 (d, *J* = 7.3 Hz, 1H), 6.82 (dd, *J* = 4.2, 10.7 Hz, 1H), 6.73 (d, *J* = 7.9 Hz, 1H), 6.52 (t, *J* = 4.7 Hz, 1H), 5.47 (d, *J* = 14.8 Hz, 1H), 4.79 (dd, *J* = 5.4, 8.9 Hz, 1H), 4.22 (d, *J* = 14.8 Hz, 1H), 3.53 (app td, *J* = 4.0, 9.3 Hz, 1H), 3.23 (app td, *J* = 7.1, 9.3 Hz, 1H), 2.86 – 2.63 (m, 1H), 2.23 – 1.90 (comp, 2H), 1.89 – 1.70 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) 160.7, 157.4, 145.8, 128.0, 125.7, 125.5, 119.0, 112.9, 110.1, 72.8, 45.2, 43.6, 30.6, 20.5; *m/z* (ESIMS) 253.2 $[M + H]^+$.



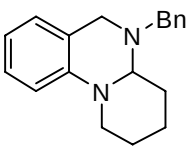
4-(2-methoxyethyl)-1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinazoline (7k): The reaction was carried out according to the general procedure B (15 h). The product was obtained as a liquid in 70% yield. (R_f = 0.27 in 60% EtOAc/Hex); IR (film) 2969, 2874, 1666, 1607, 1581, 1509, 1483, 1462, 1392, 1369, 1307, 1196, 1159, 1119, 960, 742, 716 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 7.08 (app t, *J* = 7.7 Hz, 1H), 6.92 (d, *J* = 7.3 Hz, 1H), 6.59 (app t, *J* = 7.4 Hz, 1H), 6.41 (d, *J* = 8.0 Hz, 1H), 4.14 (dd, *J* = 5.5, 8.5 Hz, 1H), 3.94 (d, *J* = 14.9 Hz, 1H), 3.80 (d, *J* = 14.9 Hz, 1H), 3.65 – 3.53 (comp, 2H), 3.43 – 3.35 (comp, 3H), 3.32 (dd, *J* = 8.8, 16.1 Hz, 1H), 2.83 (app dt, *J* = 5.9, 13.3 Hz, 1H), 2.55 (app dt, *J* = 5.9, 13.2 Hz, 1H), 2.21 (ddd, *J* = 1.9, 7.2, 12.3 Hz, 1H), 2.12 – 2.02 (m, 1H), 1.99 – 1.75 (comp, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 143.2, 127.6, 126.4, 119.0, 115.6, 110.3, 78.1, 71.0, 58.8, 55.4, 50.6, 46.4, 31.2, 22.2.; *m/z* (ESIMS) 233.4 $[M + H]^+$.



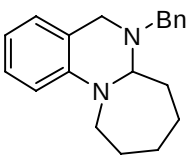
4-butyl-1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinazoline (7l): The reaction was carried out according to the general procedure B (24 h). The product was obtained as a colorless oil in 65% yield. (R_f = 0.20 in 5% EtOAc/DCM); IR (film) 2955, 2931, 2869, 2755, 1607, 1510, 1483, 1463, 1396, 1369, 1351, 1320, 1307, 1160, 1138, 741, 715 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 7.09 (app t, *J* = 7.7 Hz, 1H), 6.96 (d, *J* = 7.4 Hz, 1H), 6.61 (app td, *J* = 0.8, 7.4 Hz, 1H), 6.43 (d, *J* = 7.9 Hz, 1H), 4.06 – 3.87 (comp, 2H), 3.56 (d, *J* = 14.5 Hz, 1H), 3.40 (app td, *J* = 2.3, 8.7 Hz, 1H), 3.34 (app dt, *J* = 8.1, 16.2 Hz, 1H), 2.71 (ddd, *J* = 7.0, 8.9, 12.2 Hz, 1H), 2.23 (app tdd, *J* = 3.9, 7.7, 8.9 Hz, 2H), 2.14 – 2.02 (m, 1H), 1.94 (app qdd, *J* = 5.5, 7.9, 8.7 Hz, 1H), 1.80 (app tt, *J* = 8.3, 11.7 Hz, 1H), 1.68 – 1.53 (comp, 2H), 1.49 – 1.30 (comp, 2H), 0.97 (app t, *J* = 7.4 Hz, 3H)**;** ^{13}C NMR (125 MHz, $CDCl_3$) 143.1, 127.5, 126.2, 119.5, 115.5, 110.2, 78.4, 54.5, 52.0, 46.4, 31.7, 29.4, 22.3, 20.7, 13.9; *m/z* (ESIMS) 231.1 $[M + H]^+$.



4-cyclopentyl-1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinazoline (7m): The reaction was carried out according to the general procedure B (24 h). The product was obtained as an oil in 66% yield. (R_f = 0.26 in 10% EtOAc/DCM); IR (film) 3043, 2957, 2866, 1607, 1510, 1482, 1462, 1394, 1362, 1323, 1305, 1161, 1133, 739 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 7.06 (app t, *J* = 7.7 Hz, 1H), 6.93 (d, *J* = 7.3 Hz, 1H), 6.56 (app td, *J* = 0.8, 7.4 Hz, 1H), 6.39 (d, *J* = 7.9 Hz, 1H), 4.08 (dd, *J* = 4.8, 9.1 Hz, 1H), 3.81 (d, *J* = 14.2 Hz, 1H), 3.71 (d, *J* = 14.2 Hz, 1H), 3.44 (app p, *J* = 8.0 Hz, 1H), 3.40 – 3.26 (comp, 2H), 2.24 (app dt, *J* = 5.7, 11.4 Hz, 1H), 2.14 – 2.02 (m, 1H), 2.00 – 1.78 (comp, 3H), 1.77 – 1.46 (comp, 7H); ^{13}C NMR (125 MHz, $CDCl_3$) 143.0, 127.5, 126.1, 120.1, 115.4, 110.1, 77.6, 60.9, 47.9, 46.2, 32.2, 30.0, 24.6, 23.9, 23.2, 22.4; *m/z* (ESIMS) 243.2 $[M + H]^+$.

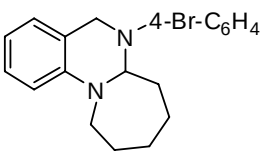


5-benzyl-2,3,4,4a,5,6-hexahydro-1H-pyrido[1,2-a]quinazoline (9a): The reaction was carried out according to the general procedure B (24 h). The product was obtained as a colorless oil in 65% yield. (R_f = 0.21 in 2% EtOAc/DCM); IR (film) 3060, 3019, 2936, 2853, 1601, 1493, 1453, 1441, 1341, 1236, 1125, 1007, 747, 731, 698 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 7.34 (app dt, *J* = 7.3, 12.7 Hz, 4H), 7.26 (dd, *J* = 5.5, 8.5 Hz, 1H), 7.15 (dd, *J* = 4.1, 11.4 Hz, 1H), 6.87 (app t, *J* = 9.0 Hz, 2H), 6.68 (app t, *J* = 7.3 Hz, 1H), 4.09 – 3.97 (comp, 2H), 3.90 (dd, *J* = 3.5, 10.2 Hz, 1H), 3.83 (d, *J* = 13.5 Hz, 1H), 3.71 (dd, *J* = 11.6, 15.0 Hz, 2H), 2.90 – 2.74 (m, 1H), 1.97 – 1.84 (m, 1H), 1.82 – 1.69 (comp, 2H), 1.62 – 1.48 (comp, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 144.54, 139.46, 128.91, 128.23, 127.54, 127.51, 126.88, 120.60, 117.05, 112.25, 75.37, 56.05, 49.27, 47.63, 29.19, 24.87, 23.59; *m/z* (ESIMS) 279.2 $[M + H]^+$.

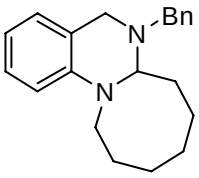


6-benzyl-5,6,6a,7,8,9,10,11-octahydroazepino[1,2-a]quinazoline (9b): The reaction was carried out according to the general procedure B (2 h). The product was obtained as an oil in 82% yield. (R_f = 0.33 in 10% EtOAc/Hex); IR (film) 3061, 3025, 2926, 2854, 1602, 1574, 1503, 1468, 1454, 1364, 1348, 1327, 1314, 1292, 1275, 1171, 1120, 1104, 1069, 1055, 910, 742 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 7.34 (app t, *J* = 6.1 Hz, 4H), 7.31 – 7.25 (m, 1H), 7.14 (app t, *J* = 7.6 Hz, 1H), 6.92 (d, *J* = 7.5 Hz, 1H), 6.62 (dd, *J* = 4.1, 7.7 Hz, 2H), 4.35 (d, *J* = 16.8 Hz, 1H), 3.95

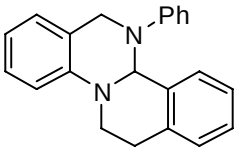
– 3.83 (comp, 2H), 3.69 – 3.63 (comp, 2H), 3.59 (d, *J* = 16.8 Hz, 1H), 3.09 – 2.99 (m, 1H), 2.11 (ddd, *J* = 5.5, 10.8, 21.2 Hz, 1H), 1.96 – 1.77 (comp, 2H), 1.70 – 1.51 (comp, 3H), 1.50 – 1.30 (comp, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) 142.65, 139.07, 129.09, 128.22, 127.53, 127.28, 126.95, 116.56, 114.92, 108.93, 76.32, 57.95, 47.59, 46.86, 35.65, 26.23, 26.21, 24.82; *m/z* (ESIMS) 293.2 $[M + H]^+$.



6-(4-bromophenyl)-5,6,6a,7,8,9,10,11-octahydroazepino[1,2-a]quinazoline (9c): The reaction was carried out according to the general procedure A (1.5 h). The product was obtained as a white solid in 90% yield. (R_f = 0.5 in 50% DCM/Hex); mp: 105 – 108 °C; IR (KBr) 3064, 2933, 2910, 2852, 1605, 1584, 1511, 1493, 1482, 1471, 1459, 1380, 1365, 1350, 1297, 1263, 1236, 1214, 1171, 1152, 1115, 1058, 1009, 968, 812, 739, 735, 711 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) 7.36 – 7.29 (comp, 2H), 7.11 (app t, *J* = 7.8 Hz, 1H), 7.01 (d, *J* = 7.4 Hz, 1H), 6.86 – 6.79 (comp, 2H), 6.69 – 6.58 (comp, 2H), 4.82 (dd, *J* = 4.3, 9.9 Hz, 1H), 4.57 (d, *J* = 16.2 Hz, 1H), 4.34 (d, *J* = 16.2 Hz, 1H), 3.89 (ddd, *J* = 3.3, 6.3, 15.0 Hz, 1H), 3.31 – 3.16 (m, 1H), 2.25 – 2.09 (m, 1H), 2.01 – 1.82 (comp, 2H), 1.69 (app tdt, *J* = 6.9, 13.6, 19.2 Hz, 3H), 1.60 – 1.45 (m, 1H), 1.44 – 1.32 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) 148.7, 142.3, 131.8, 127.8, 126.4, 118.9, 117.3, 115.7, 111.9, 110.1, 74.9, 47.0, 46.3, 33.0, 26.3, 25.9, 24.6; *m/z* (ESIMS) 357.3 $[M + 1]^+$.

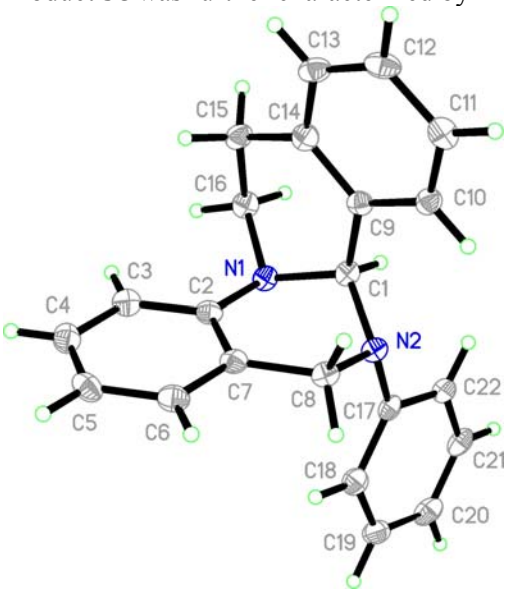


6-benzyl-6,6a,7,8,9,10,11,12-octahydro-5H-azocino[1,2-a]quinazoline (9d): The reaction was carried out according to the general procedure B (1.5 h). The product was obtained as an oil in 85% yield. (R_f = 0.38 in 10% EtOAc/Hex); IR (film) 3061, 3026, 2921, 2849, 1602, 1574, 1500, 1463, 1452, 1365, 1346, 1323, 1293, 1218, 1176, 1151, 1103, 1071, 1027, 1016, 995, 743 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) 7.40 – 7.34 (comp, 4H), 7.33 – 7.28 (m, 1H), 7.19 (dd, *J* = 4.2, 11.3 Hz, 1H), 6.95 (d, *J* = 7.2 Hz, 1H), 6.67 (dd, *J* = 5.0, 12.2 Hz, 2H), 4.34 (d, *J* = 16.8 Hz, 1H), 3.95 (app dt, *J* = 4.4, 15.0 Hz, 1H), 3.89 – 3.85 (m, 1H), 3.58 (comp, 3H), 3.19 – 3.08 (m, 1H), 2.02 – 1.58 (comp, 7H), 1.54 – 1.30 (comp, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 142.46, 139.00, 128.95, 128.20, 127.42, 127.36, 126.92, 116.78, 115.21, 110.06, 78.18, 57.44, 52.35, 47.71, 35.00, 28.26, 27.78, 26.92, 26.77; *m/z* (ESIMS) 307.2 $[M + H]^+$.

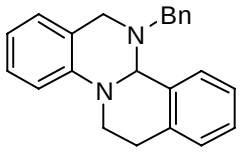


5-phenyl-5,6,12,13-tetrahydro-4bH-isoquinolino[2,1-a]quinazoline (9e): The reaction was carried out according to the general procedure C (12 h) at rt. The product was obtained as a white solid in 99% yield. (R_f = 0.58 in 10% EtOAc/Hex); mp: 139 – 141 °C; IR (KBr) 3059, 3032, 2963, 2911, 1599, 1581, 1492, 1470, 1450, 1427, 1362, 1342, 1288, 1253, 1221, 1200, 1137, 1061, 1035, 985, 972, 948, 873, 770, 757, 734 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) 7.63 (d, *J* = 7.4 Hz, 1H), 7.34 – 6.85 (comp, 11H), 6.70 (app t, *J* = 7.3 Hz, 1H), 6.07 (s, 1H), 4.40 (app dd, *J* = 16.6, 40.2 Hz, 2H), 4.28 (dd, *J* = 4.8, 14.5 Hz, 1H), 3.51 (ddd, *J* = 4.1, 12.7, 14.4 Hz, 1H), 3.23 – 3.10 (m, 1H), 2.58 (dd, *J* = 3.7, 16.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) 150.7, 143.8, 137.3, 136.5, 129.2, 128.9, 127.6, 127.4, 126.8, 126.3, 125.9, 122.1, 120.7, 118.4, 118.0, 113.6, 73.8, 46.5, 45.2, 24.9; *m/z* (ESIMS) 313.2 $[M + H]^+$.

Product **9e** was further characterized by X–ray crystallography:

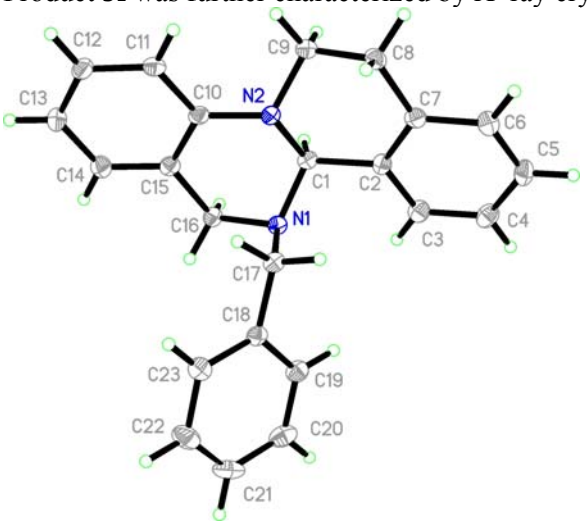


The requisite CIF file has been submitted to the journal.

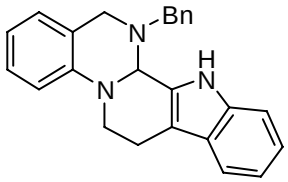


5-benzyl-5,6,12,13-tetrahydro-4bH-isoquinolino[2,1-a]quinazoline (9f): The reaction was carried out according to the general procedure B (0.5 h). The product was obtained as a white solid in 64% yield. (R_f = 0.30 in 60% DCM/Hex); IR (film) 3061, 3026, 2895, 2848, 1602, 1576, 1493, 1455, 1382, 1346, 1326, 1291, 1264, 1221, 1145, 1109, 996, 932 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 7.82 (d, *J* = 7.7 Hz, 1H), 7.47 – 7.23 (comp, 6H), 7.18 (dd, *J* = 7.6, 18.1 Hz, 2H), 7.09 (d, *J* = 7.5 Hz, 1H), 6.99 (d, *J* = 8.3 Hz, 1H), 6.86 (d, *J* = 7.3 Hz, 1H), 6.71 (app t, *J* = 7.3 Hz, 1H), 5.34 (s, 1H), 4.20 (dd, *J* = 4.1, 12.7 Hz, 1H), 3.90 (app t, *J* = 15.2 Hz, 2H), 3.76 (app s, 2H), 3.28 (app td, *J* = 3.4, 12.6 Hz, 1H), 3.21 – 3.06 (m, 1H), 2.69 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) 144.63, 139.81, 136.74, 136.40, 128.71, 128.38, 128.19, 127.73, 127.39, 127.13, 126.83, 126.75, 126.63, 121.01, 117.76, 112.21, 74.80, 53.37, 49.10, 43.57, 27.37; *m/z* (ESIMS) 327.2 $[M + H]^+$.

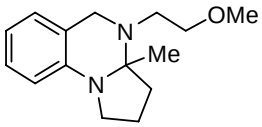
Product **9f** was further characterized by X–ray crystallography:



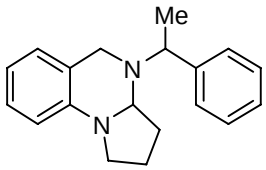
The requisite CIF file has been submitted to the journal.



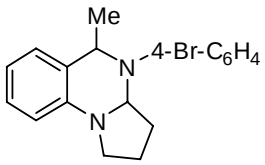
(9g): The reaction was carried out according to the general procedure B (1 h). The product was obtained as a solid in 74% yield. (R_f = 0.24 in 10% EtOAc/Hex); mp: 86 – 90 °C; IR (film) 3421, 3058, 3028, 2902, 2844, 1602, 1576, 1490, 1453, 1391, 1337, 1315, 1291, 1265, 1240, 1217, 1139, 1103, 980, 957, 943 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 8.29 (s, 1H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.39 (app dt, *J* = 6.7, 7.2 Hz, 5H), 7.31 (app t, *J* = 7.1 Hz, 1H), 7.21 (app t, *J* = 7.3 Hz, 2H), 7.12 (app t, *J* = 7.5 Hz, 2H), 6.85 (d, *J* = 7.2 Hz, 1H), 6.74 (app t, *J* = 7.3 Hz, 1H), 5.50 (s, 1H), 4.38 (dd, *J* = 4.4, 13.6 Hz, 1H), 4.00 – 3.74 (comp, 4H), 3.33 (ddd, *J* = 4.0, 11.8, 13.6 Hz, 1H), 3.12 – 2.98 (m, 1H), 2.72 (d, *J* = 15.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) 144.4, 139.1, 135.9, 132.7, 128.8, 128.3, 127.7, 127.6, 127.2, 127.1, 122.0, 120.5, 119.4, 118.4, 118.1, 113.2, 111.8, 111.1, 72.2, 54.3, 48.8, 45.0, 19.6; *m/z* (ESIMS) 364.4 $[M - H]^+$.



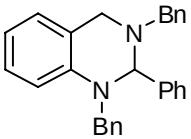
4-(2-methoxyethyl)-3a-methyl-1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinazoline (9h): The reaction was carried out according to the general procedure B (1 h). The product was obtained as an oil in 60% yield. (R_f = 0.25 in 30% EtOAc/DCM); IR (film) 2967, 2927, 2876, 2830, 2770, 1606, 1580, 1508, 1484, 1461, 1308, 1180, 1142, 1119, 1092, 998, 743, 715 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 7.08 (app t, *J* = 7.6 Hz, 1H), 6.97 (d, *J* = 7.3 Hz, 1H), 6.61 (app t, *J* = 7.3 Hz, 1H), 6.45 (d, *J* = 8.0 Hz, 1H), 3.96 (d, *J* = 15.3 Hz, 1H), 3.77 (d, *J* = 15.3 Hz, 1H), 3.56 (app t, *J* = 6.3 Hz, 2H), 3.52 – 3.43 (m, 1H), 3.43 – 3.32 (comp, 4H), 2.91 (app dt, *J* = 6.7, 13.2 Hz, 1H), 2.51 – 2.36 (m, 1H), 2.14 – 1.83 (comp, 4H), 1.07 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 142.0, 127.4, 126.3, 119.0, 115.4, 111.5, 77.6, 72.1, 58.9, 51.9, 50.6, 46.6, 39.4, 21.6, 15.7; *m/z* (ESIMS) 247.3 $[M + H]^+$.



4-(1-phenylethyl)-1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinazoline (9i): The reaction was carried out according to the general procedure B (15 h). The product was obtained as a mixture of diastereomers in 52% yield, dr = 59 : 41 determined by integration of one set of ^1H-NMR signals (δ_{major} 1.49 – 1.45 ppm, δ_{minor} 1.67 – 1.62 ppm). (R_f = 0.28 in 1% EtOAc/DCM); IR (film) 3026, 2970, 2936, 2875, 2828, 1606, 1581, 1509, 1483, 1460, 1395, 1373, 1321, 1304, 1159, 1132, 1106, 741, 714, 700 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) (major diastereomer) 7.54 (d, *J* = 7.7 Hz, 2H), 7.45 – 7.25 (comp, 4H), 6.83 (d, *J* = 7.3 Hz, 1H), 6.58 (app t, *J* = 7.4 Hz, 1H), 6.48 (d, *J* = 8.0 Hz, 1H), 4.38 (comp, 1H), 4.32 (dd, *J* = 4.7, 9.1 Hz, 1H), 3.76 (d, *J* = 14.2 Hz, 1H), 3.50 – 3.35 (comp, 3H), 2.32 (app dt, *J* = 5.7, 11.3 Hz, 1H), 2.23 – 1.83 (comp, 3H), 1.46 (app t, *J* = 12.1 Hz, 3H); ^{13}C NMR of the diastereomeric mixture (125 MHz, $CDCl_3$) 143.2, 143.1, 142.8, 138.9, 128.2, 128.0, 127.9, 127.7, 127.4, 127.3, 127.2, 126.6, 126.0, 125.9, 120.8, 120.2, 115.3(6), 115.3(3), 110.3, 110.0, 76.2, 76.0, 57.5, 56.3, 47.7, 46.5, 46.4, 32.4, 32.2, 22.3, 22.2, 19.1, 9.8; *m/z* (ESIMS) 279.1 $[M + H]^+$.

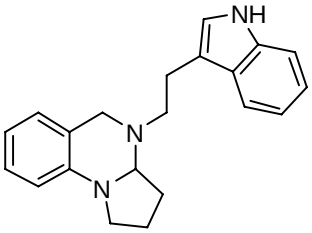


4-(4-bromophenyl)-5-methyl-1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinazoline (9j): The reaction was carried out according to the general procedure A (3 h). The product was obtained as a mixture of diastereomers in 65% yield dr = 66 : 34, determined by integration of one set of ^1H-NMR signals (δ_{major} 1.43 – 1.38 ppm, δ_{minor} 1.31 – 1.27 ppm). (R_f = 0.21 in 10% EtOAc/Hex); IR (film) 3064, 3035, 2969, 2921, 2864, 2839, 2676, 2602, 1604, 1503, 1486, 1461, 1358, 1327, 1239, 1192, 1066, 1043, 1007, 837, 744 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$)(major diastereomer) 7.42 – 7.33 (comp, 2H), 7.22 – 7.15 (m, 1H), 7.02 (dd, *J* = 1.1, 7.5 Hz, 1H), 6.96 – 6.91 (comp, 2H), 6.70 (app t, *J* = 7.4 Hz, 1H), 6.57 (app t, *J* = 8.3 Hz, 1H), 4.93 (dd, *J* = 5.4, 8.6 Hz, 1H), 4.36 (q, *J* = 6.9 Hz, 1H), 3.50 – 3.33 (comp, 2H), 2.29 – 2.19 (m, 1H), 2.06 – 1.75 (comp, 2H), 1.71 – 1.58 (m, 1H), 1.41 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR of the diastereomers (125 MHz, $CDCl_3$) 148.0, 147.4, 143.3, 142.9, 132.0, 131.5, 128.3, 128.0, 127.6, 127.5, 126.4, 126.0, 125.5, 124.6, 118.4, 116.9, 116.7, 115.8, 111.2, 111.0, 77.0(3), 68.8, 59.9, 58.3, 46.6(2), 46.5(9), 32.2, 31.0, 22.0, 21.6, 21.4, 19.8; *m/z* (ESIMS) 343.2 $[M + H]^+$.

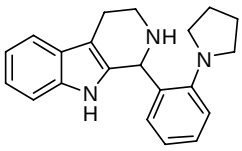


1,3-dibenzyl-2-phenyl-1,2,3,4-tetrahydroquinazoline (9k): The reaction was carried out according to the general procedure B (12 h). The product was obtained as a white solid in 27% yield. (R_f = 0.23 in 5% EtOAc/Hex); mp: 118 – 120 °C; IR (film) 3083, 3060, 3027,

2920, 2844, 1651, 1602, 1575, 1499, 1464, 1451, 1403, 1339, 1323, 1277, 1199, 1146, 1104, 1027, 951, 769, 742, 698, 645 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 7.41 – 7.21 (comp, 15H), 7.14 (app t, *J* = 7.8 Hz, 1H), 6.89 (d, *J* = 7.3 Hz, 1H), 6.74 (d, *J* = 8.2 Hz, 1H), 6.67 (app t, *J* = 7.3 Hz, 1H), 5.10 (s, 1H), 4.75 (d, *J* = 17.0 Hz, 1H), 4.13 (d, *J* = 17.0 Hz, 1H), 3.90 (comp, 3H), 3.45 (d, *J* = 16.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) 143.81, 141.11, 139.02, 138.97, 128.95, 128.58, 128.33, 128.26, 127.79, 127.64, 127.39, 127.25, 127.05, 127.04, 126.79, 118.26, 116.06, 109.61, 78.05, 57.94, 51.77, 46.97; *m/z* (ESIMS) 391.4 $[M + H]^+$.

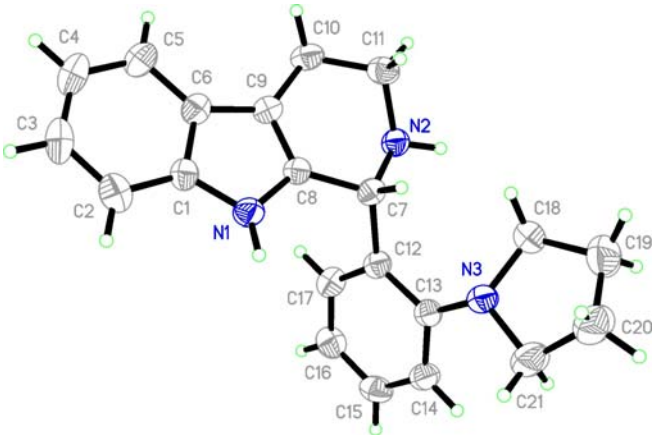


4-(2-(1H-indol-3-yl)ethyl)-1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinazoline (10): The reaction was carried out according to the general procedure B (12 h). The product was obtained as a white solid in 13% yield. (R_f = 0.31 in 50% EtOAc/Hex); mp: 75 – 78 °C; IR (film) 3409, 3043, 2968, 2856, 1660, 1606, 1572, 1509, 1482, 1458, 1368, 1269, 1228, 1152, 1129, 1101, 1047, 1000, 960, 925 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 8.03 (s, 1H), 7.74 – 7.50 (m, 1H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.23 – 7.16 (m, 1H), 7.16 – 7.07 (comp, 2H), 7.01 (dd, *J* = 4.7, 20.9 Hz, 2H), 6.62 (app t, *J* = 7.4 Hz, 1H), 6.44 (d, *J* = 8.0 Hz, 1H), 4.13 (d, *J* = 14.5 Hz, 1H), 4.06 (dd, *J* = 5.3, 8.5 Hz, 1H), 3.75 (d, *J* = 14.5 Hz, 1H), 3.47 – 3.38 (m, 1H), 3.33 (dd, *J* = 8.8, 16.0 Hz, 1H), 3.22 – 3.00 (comp, 3H), 2.70 – 2.55 (m, 1H), 2.23 (app dt, *J* = 6.1, 11.9 Hz, 1H), 2.15 – 2.02 (m, 1H), 2.01 – 1.79 (comp, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) 143.2, 136.2, 127.8, 127.4, 126.5, 122.0, 121.6, 119.4, 119.3, 118.7, 115.8, 114.3, 111.1, 110.4, 78.4, 54.7, 53.0, 46.6, 31.8, 23.6, 22.4; *m/z* (ESIMS) 318.2 $[M + H]^+$.



1-(2-(pyrrolidin-1-yl)phenyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (11): The reaction was carried out according to the general procedure B (12 h). The product was obtained as a yellow solid in 21% yield. (R_f = 0.20 in 10% MeOH/EtOAc); mp: 184 – 186 °C; IR (film) 3397, 3054, 2936, 2840, 1666, 1596, 1484, 1448, 1351, 1308, 1264, 1188, 1138, 1096, 1006, 954, 738 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 7.73 (s, 1H), 7.53 (dd, *J* = 2.4, 6.4 Hz, 1H), 7.25 – 7.17 (comp, 2H), 7.15 – 7.07 (comp, 4H), 6.90 (app td, *J* = 1.1, 7.5 Hz, 1H), 5.64 (s, 1H), 3.44 – 3.37 (m, 1H), 3.34 – 3.27 (comp, 2H), 3.26 – 3.19 (comp, 2H), 3.17 – 3.10 (m, 1H), 2.96 – 2.79 (comp, 2H), 2.05 (s, 1H), 2.00 – 1.90 (comp, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) 149.48, 135.74, 135.70, 134.25, 129.74, 128.47, 127.46, 122.09, 121.40, 119.20, 118.44, 118.03, 110.73, 109.99, 53.15, 52.94, 43.09, 24.81, 22.70; *m/z* (ESIMS) 318.2 $[M + H]^+$.

Product **11** was further characterized by X–ray crystallography:



The requisite CIF file has been submitted to the journal.

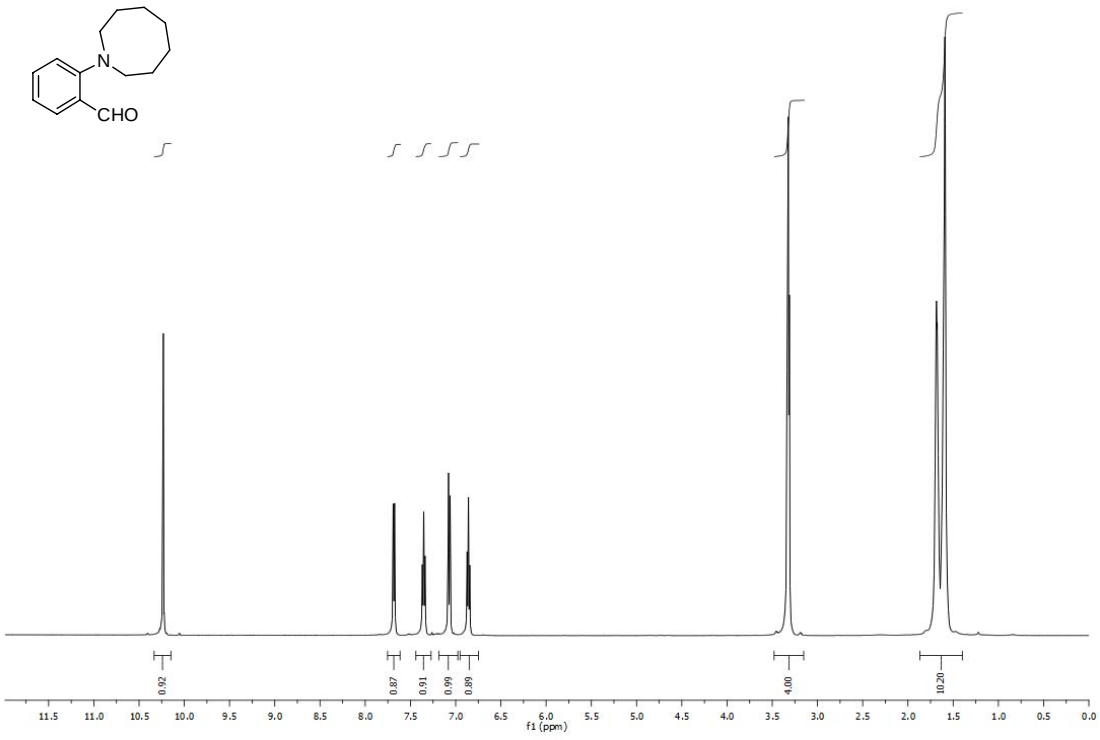
References:

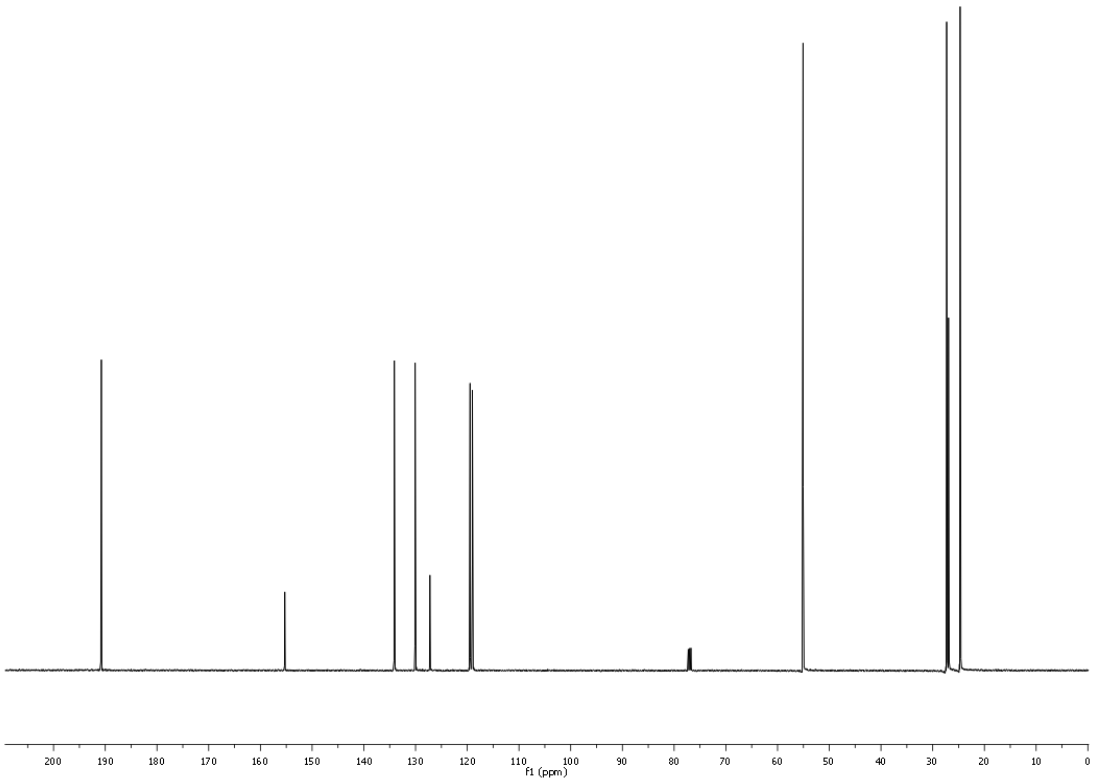
(1) Nijhuis, W. H. N.; Verboom, W.; Abuelfadl, A.; Harkema, S.; Reinhoudt, D. N. *J. Org. Chem.* **1989**, *54*, 199 – 209.

(2) Nijhuis, W. H. N.; Leus, G. R. B.; Egberink, R. J. M.; Verboom, W.; Reinhoudt, D. N. *Recl. Trav. Chim. Pays–Bas* **1989**, *108*, 172 – 178.

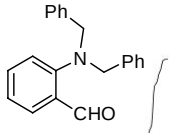
(3) D'yachenko, E. V.; Glukhareva, T. V.; Nikolaenko, E. F.; Tkachev, A. V.; Morzherin, Yu. Yu. *Russ. Chem. Bull.* **2004**, *53*, 1240 – 1247.

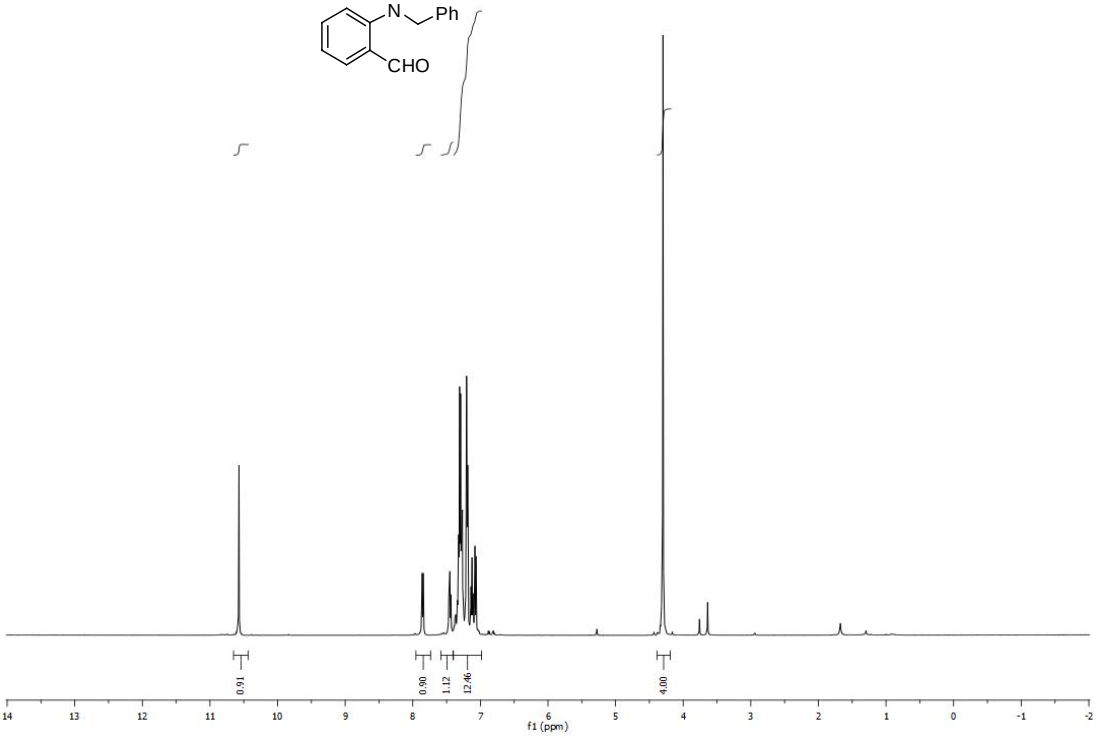
^{1}H–NMR and ^{13}C–NMR of **8d**:

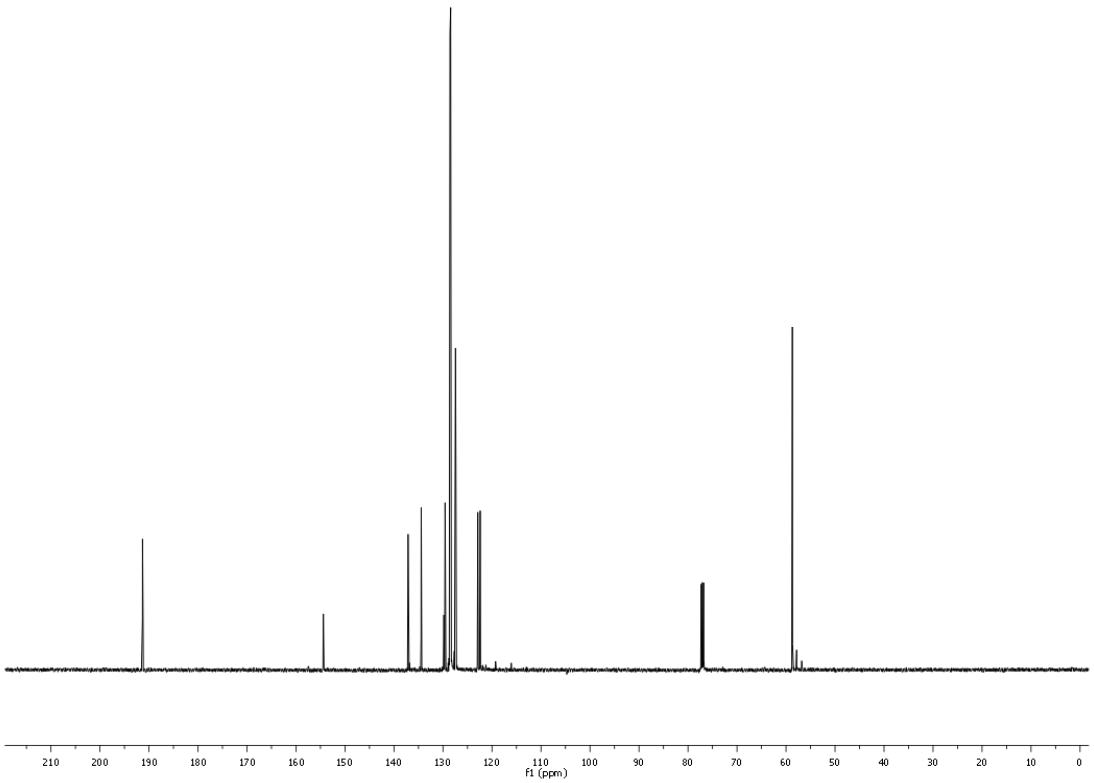




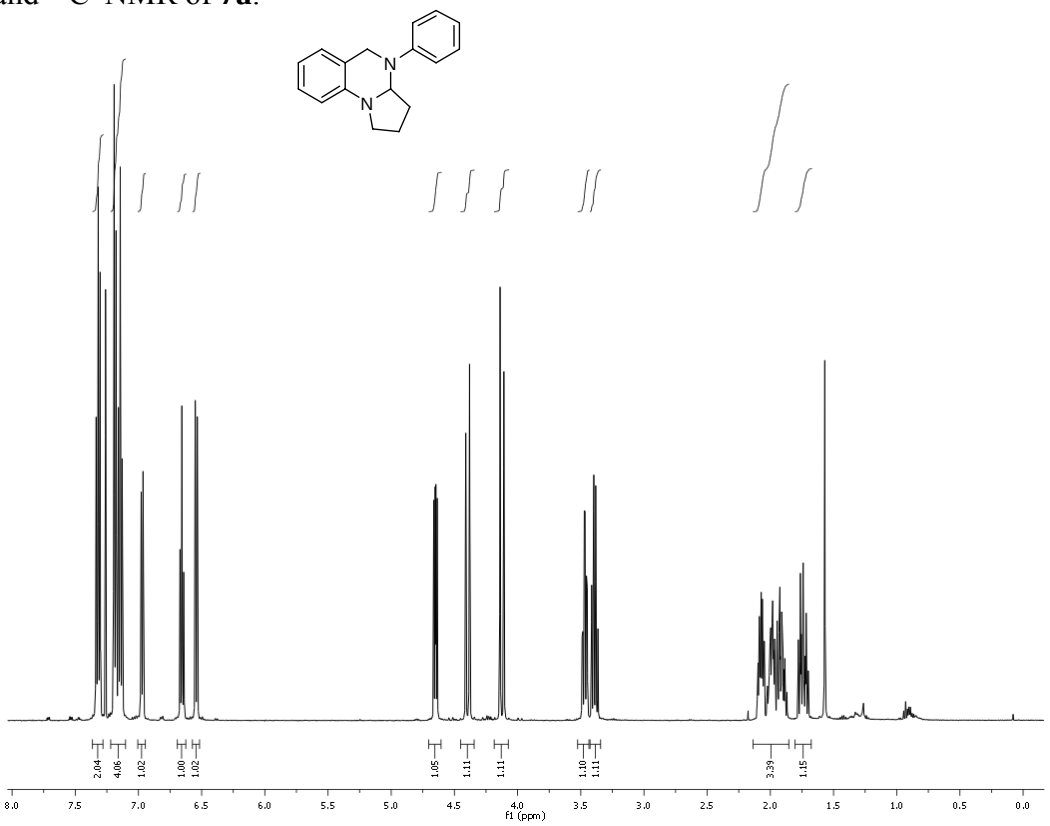
^{1}H–NMR and ^{13}C–NMR of **8k**:

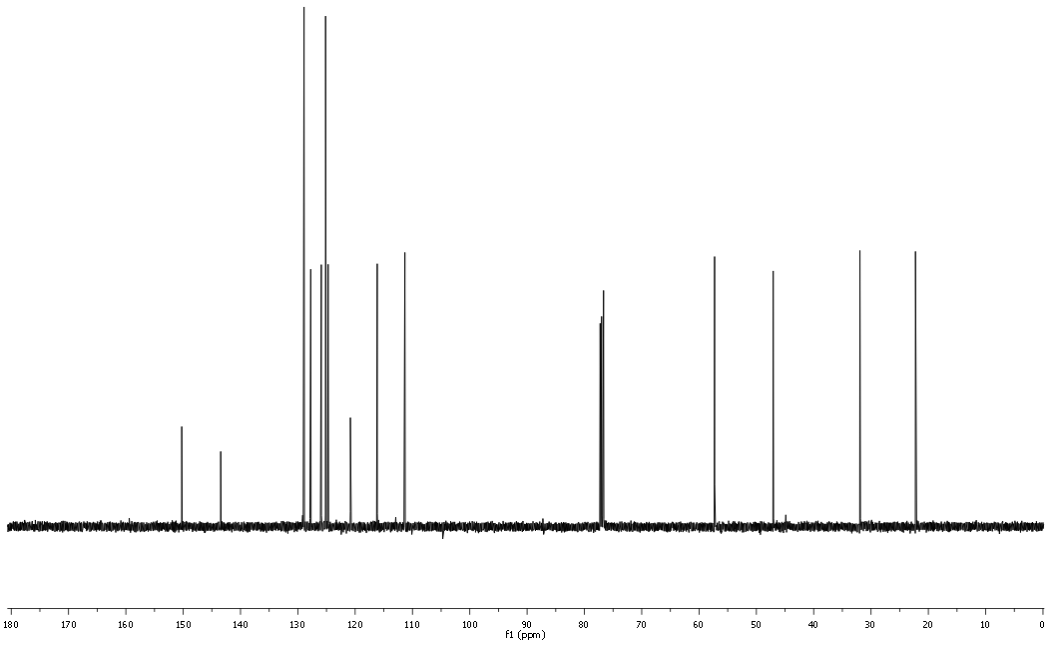




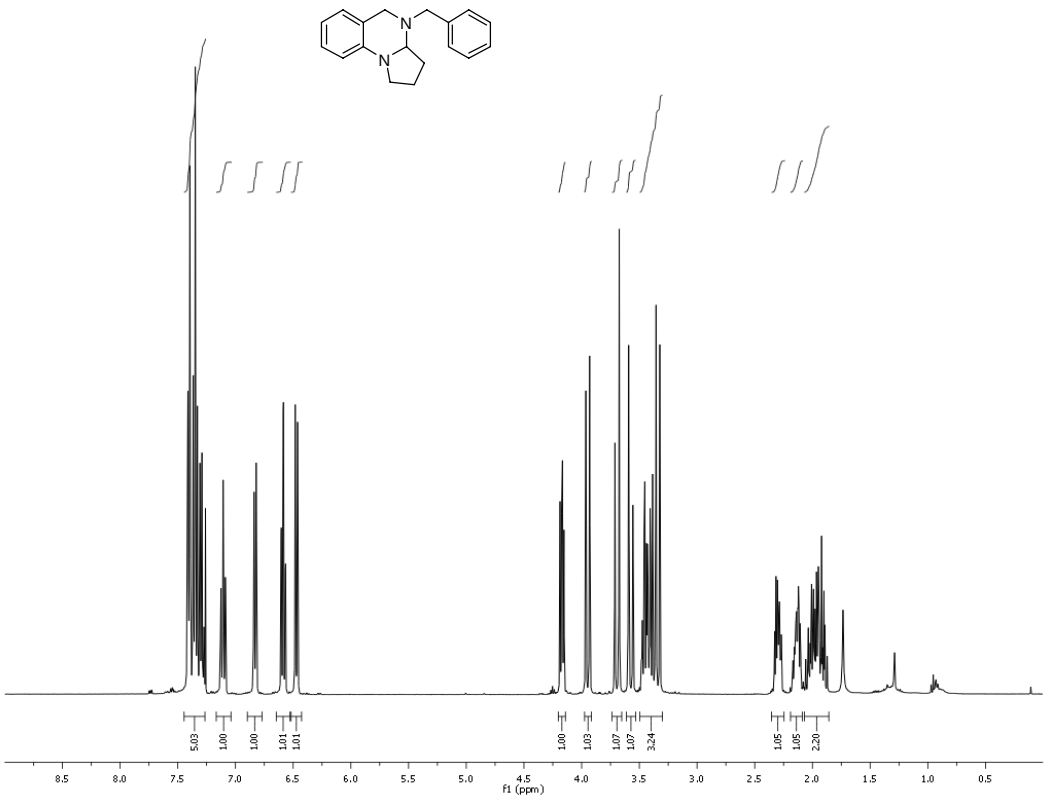


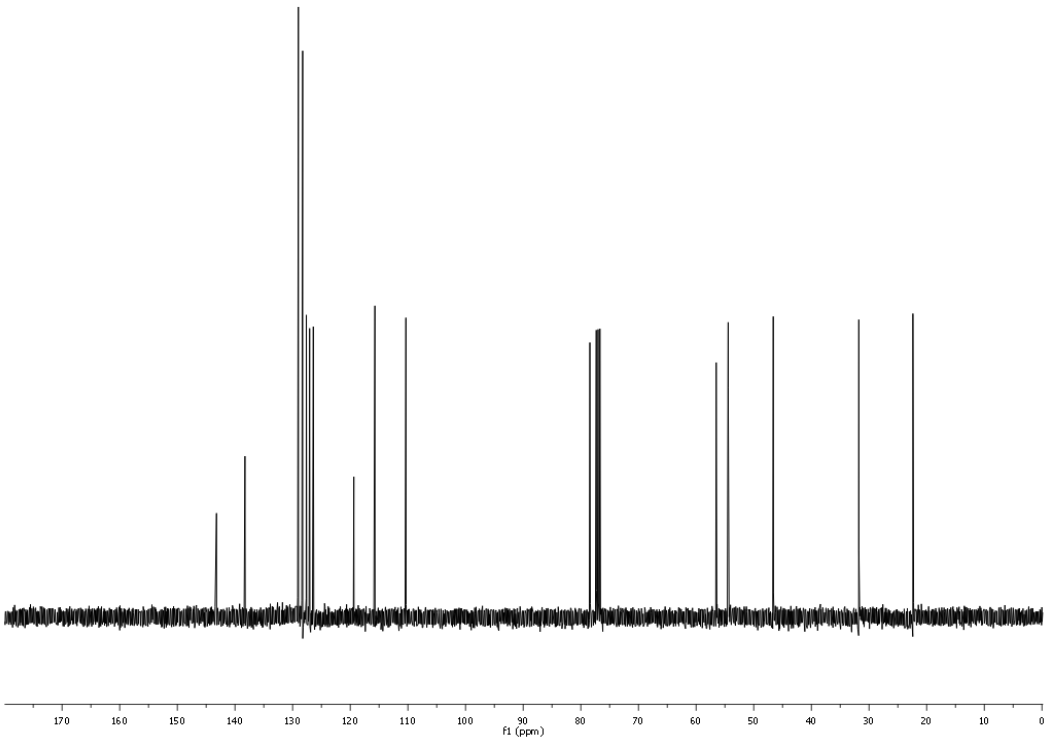
^{1}H–NMR and ^{13}C–NMR of **7a**:



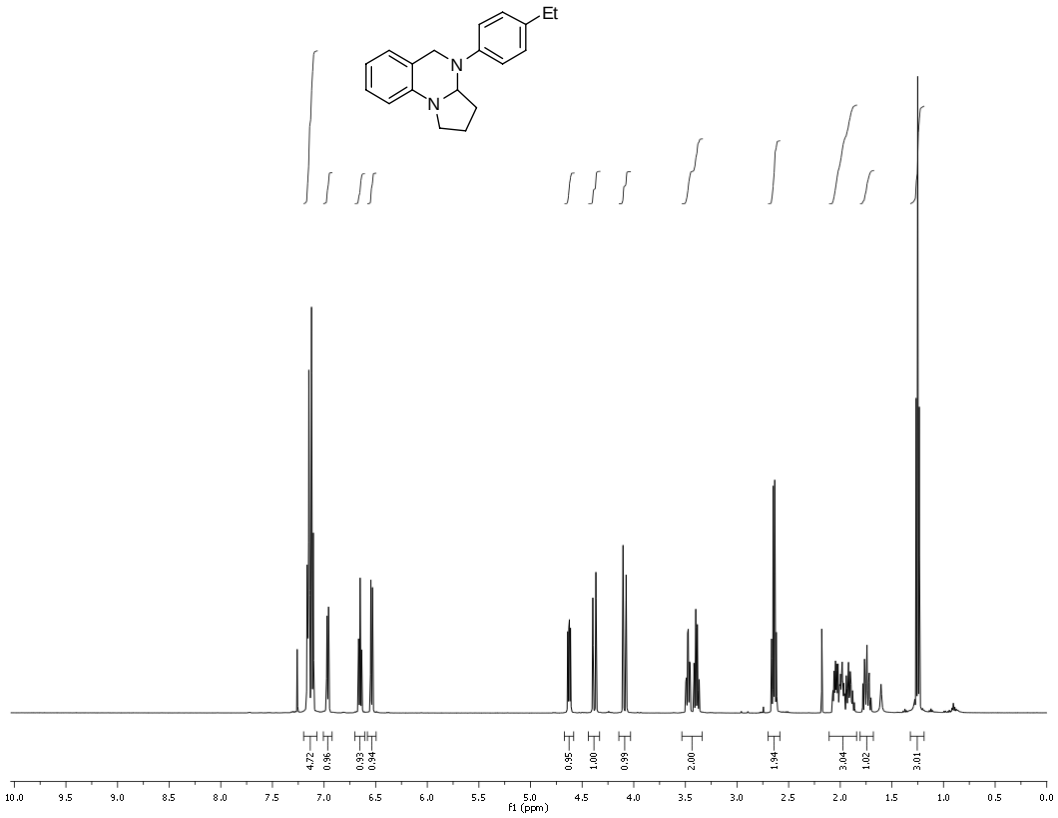


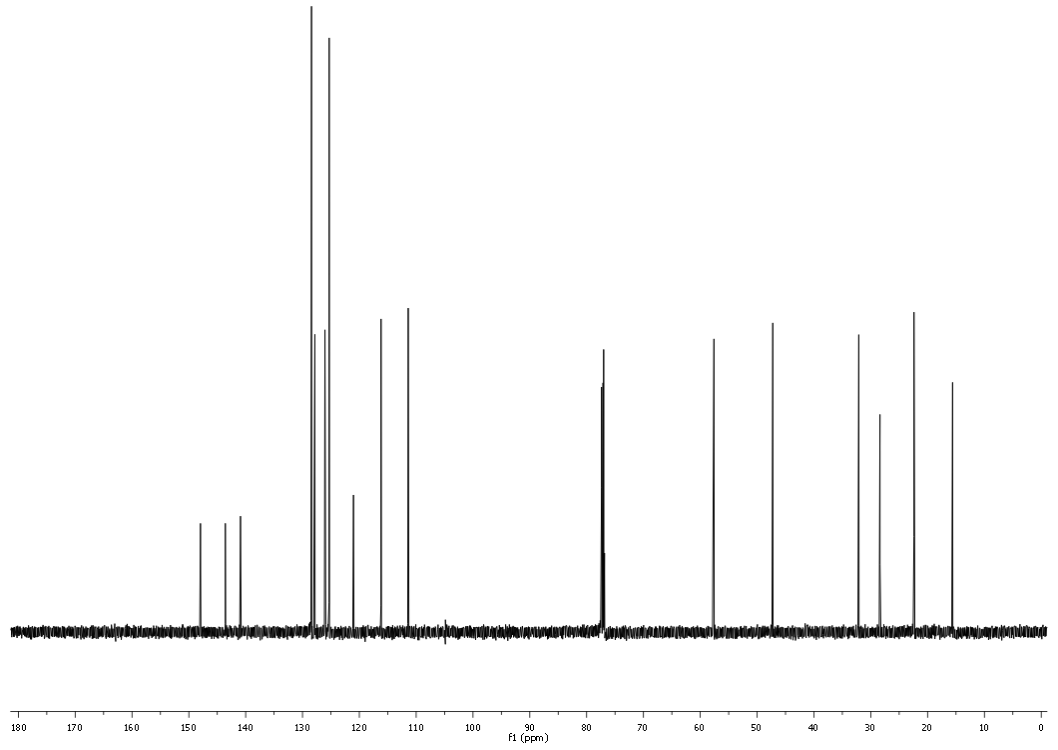
^{1}H–NMR and ^{13}C–NMR of **7b**:



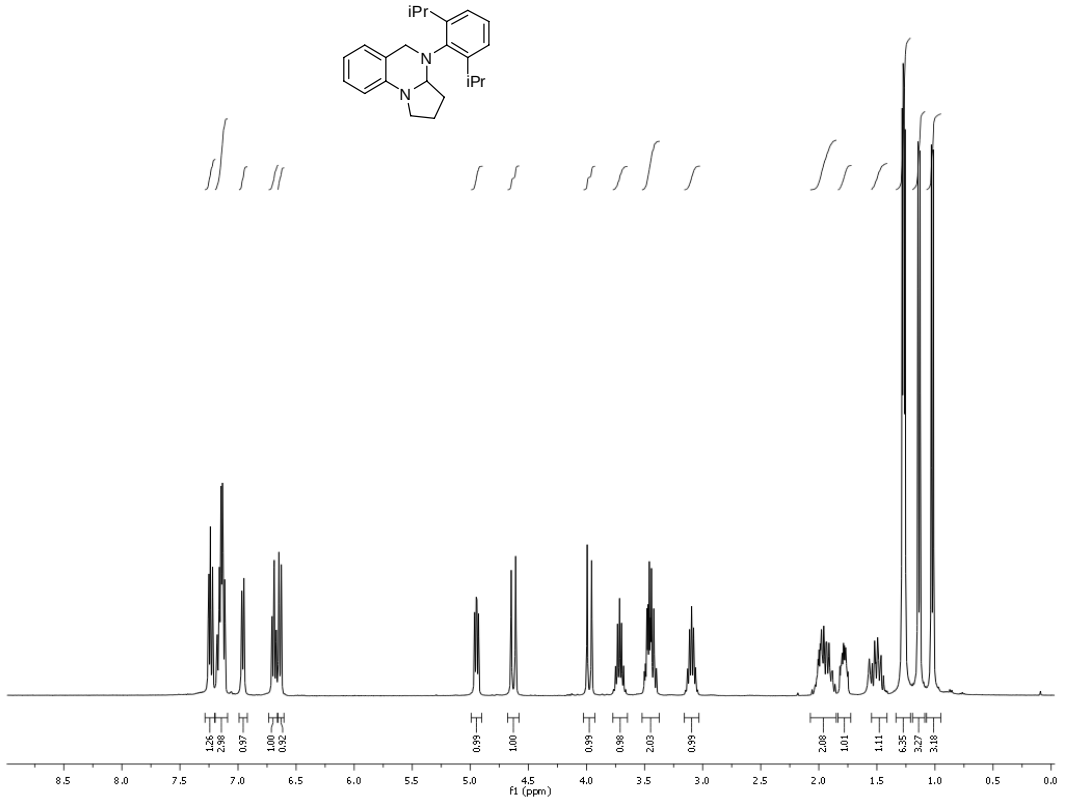


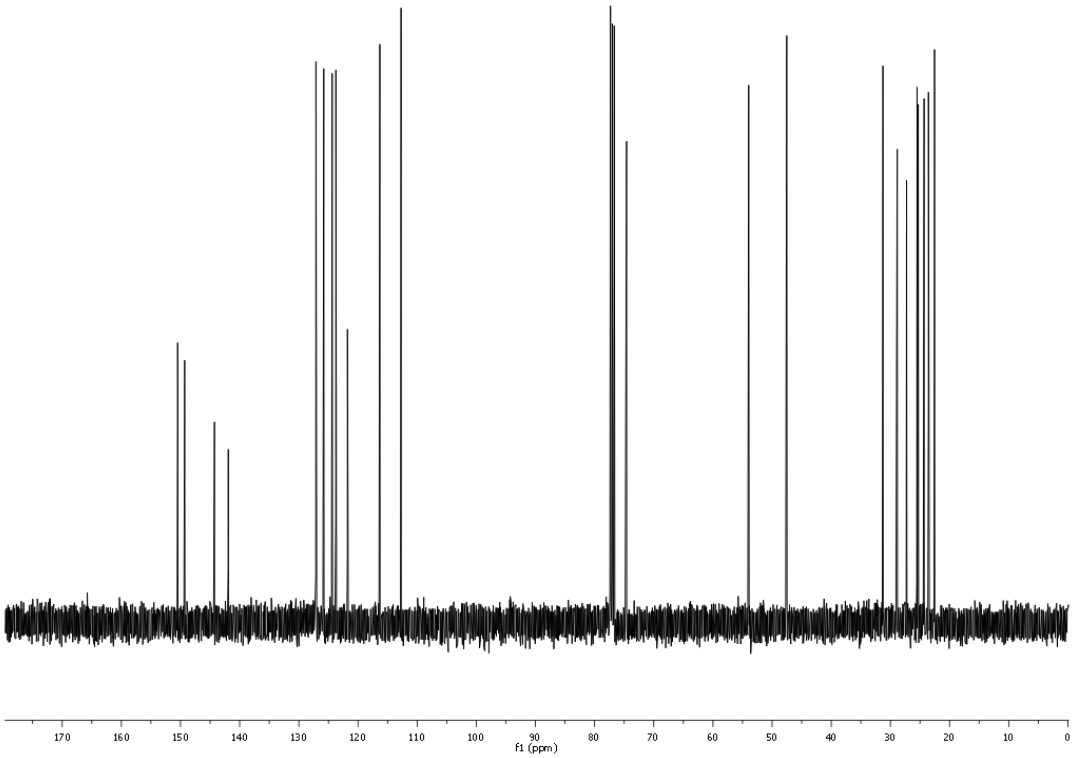
^{1}H–NMR and ^{13}C–NMR of **7c**:



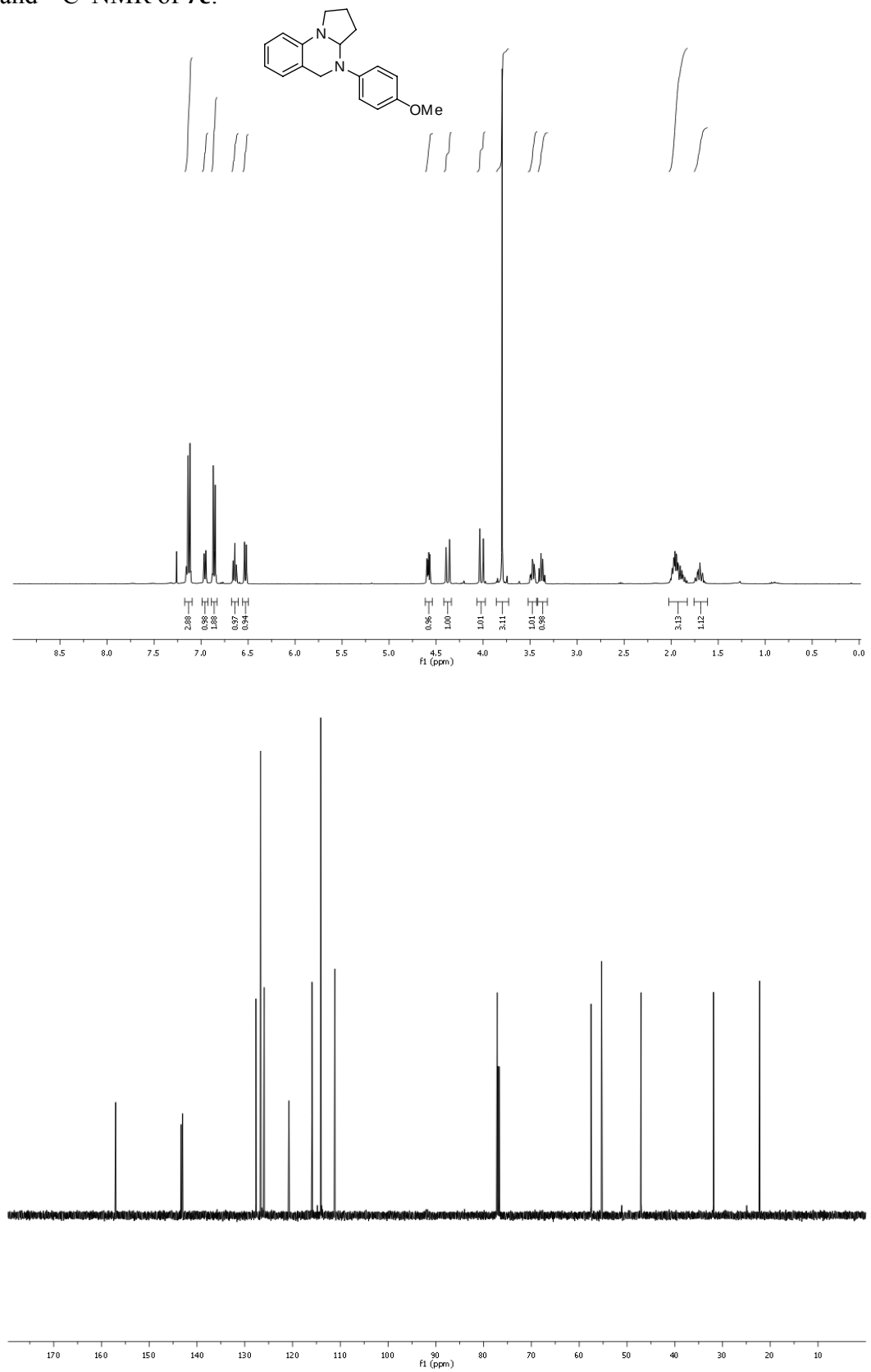


^{1}H–NMR and ^{13}C–NMR of **7d**:

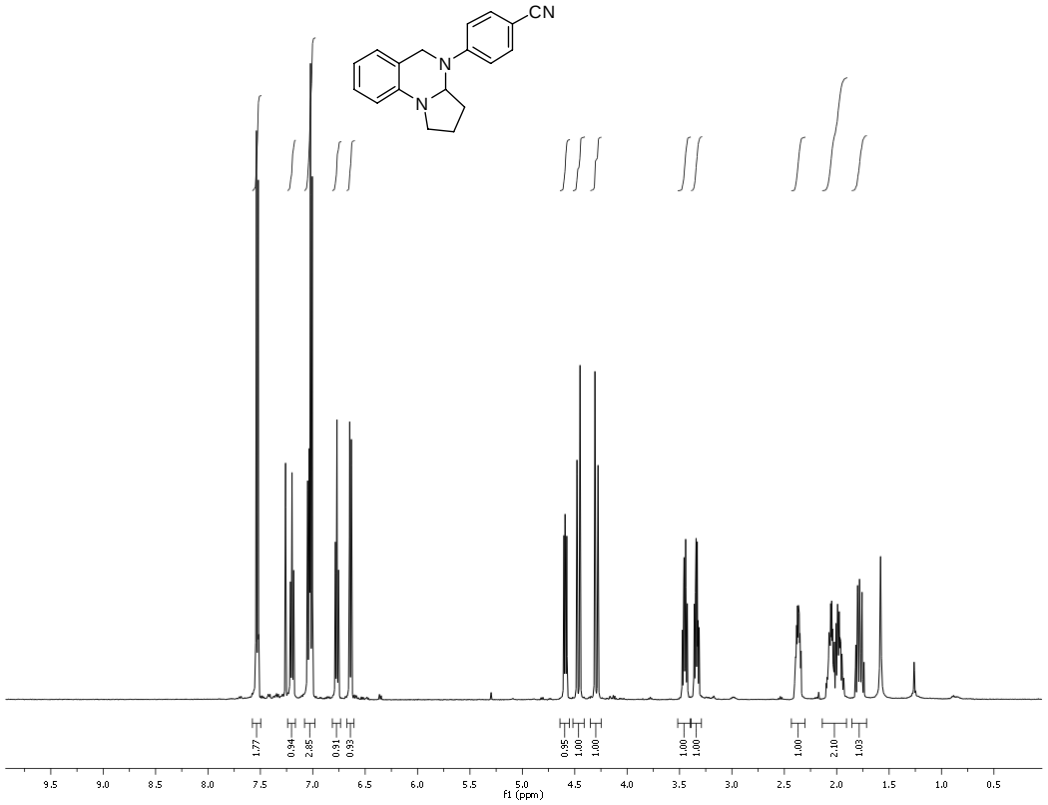


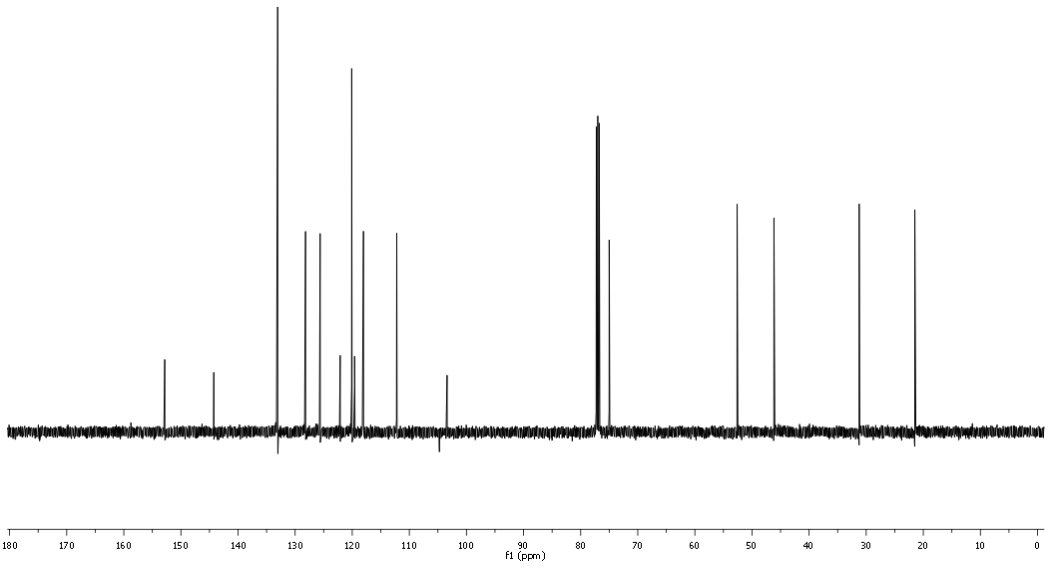


^{1}H–NMR and ^{13}C–NMR of **7e**:

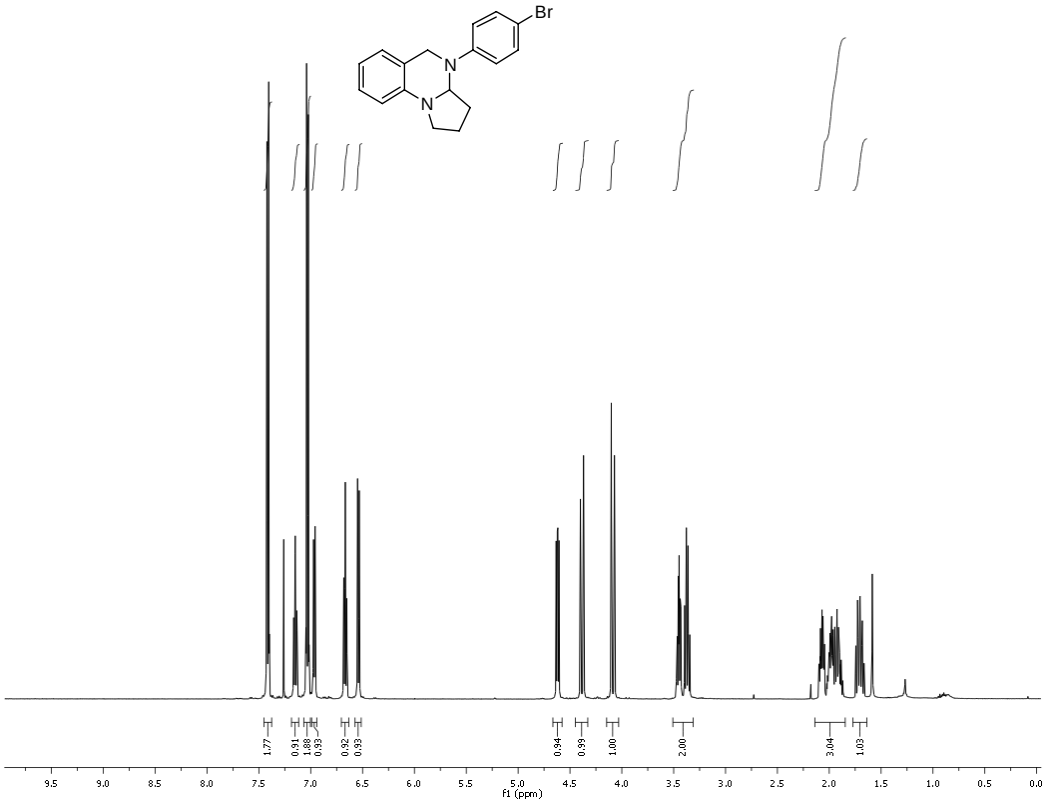


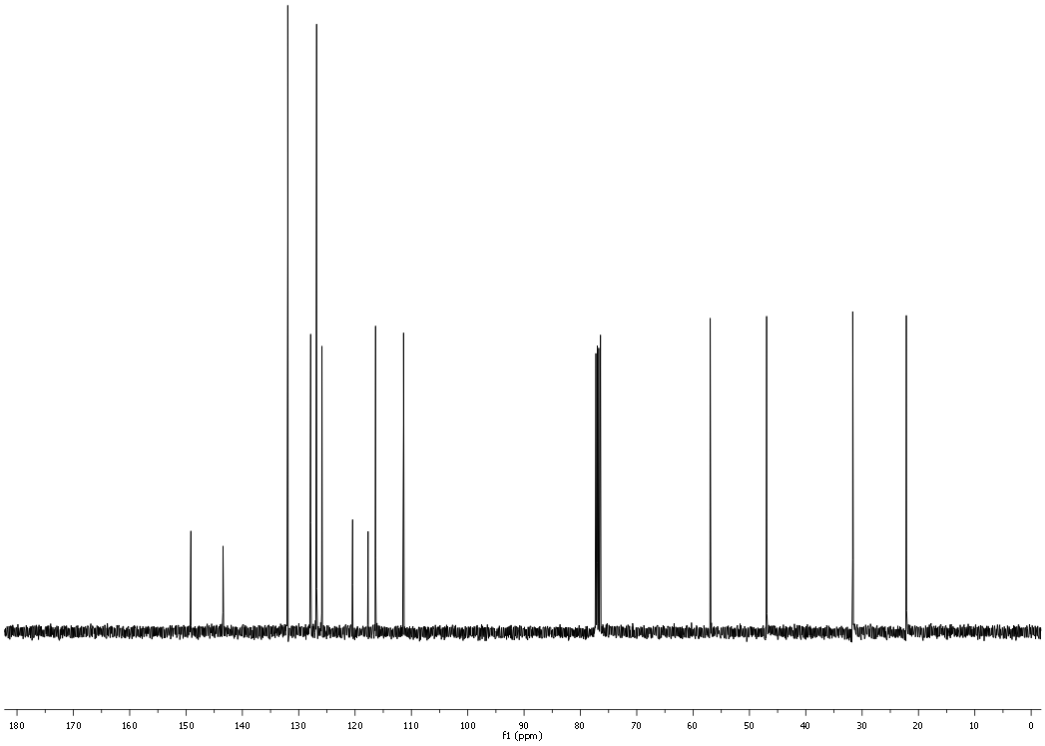
^{1}H–NMR and ^{13}C–NMR of **7f**:



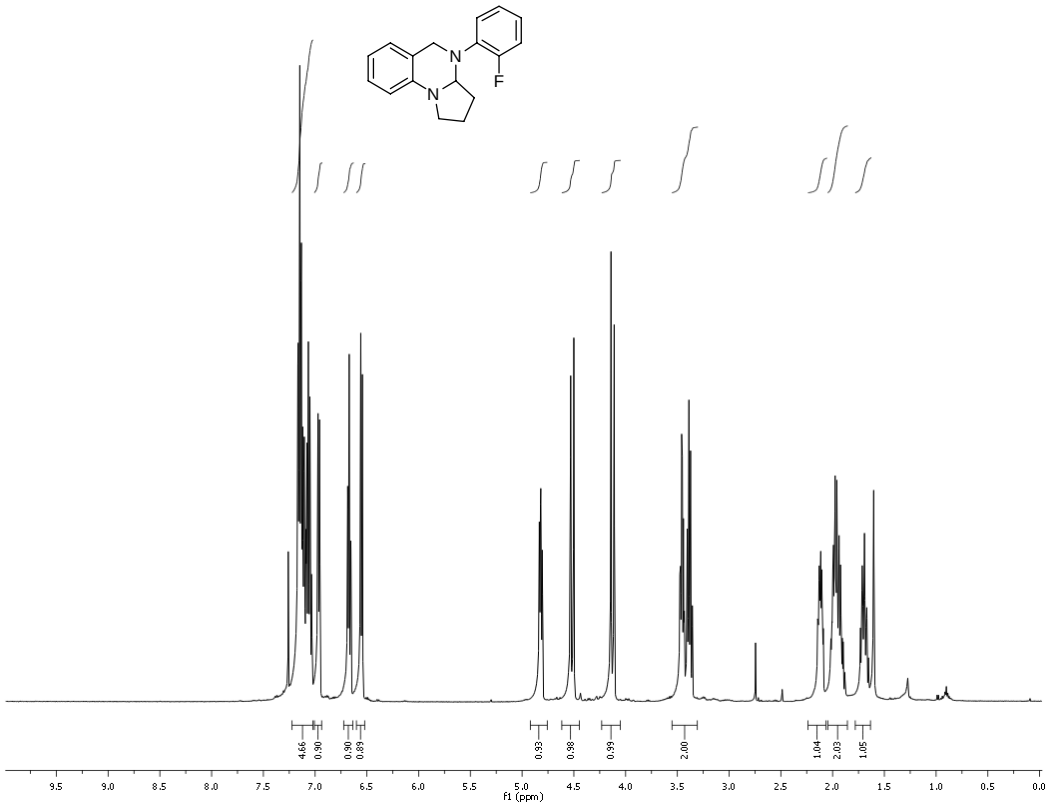


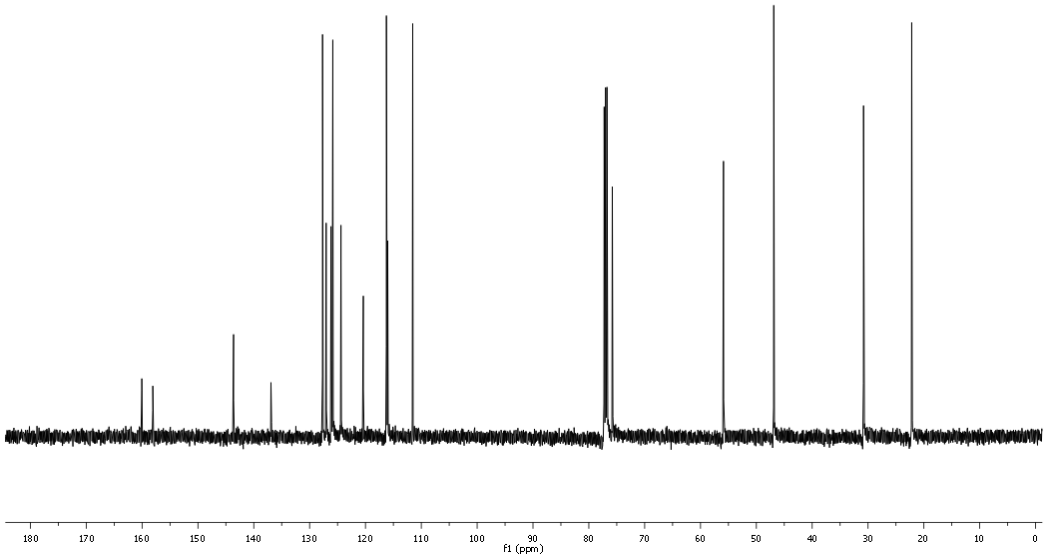
^{1}H–NMR and ^{13}C–NMR of **7g**:



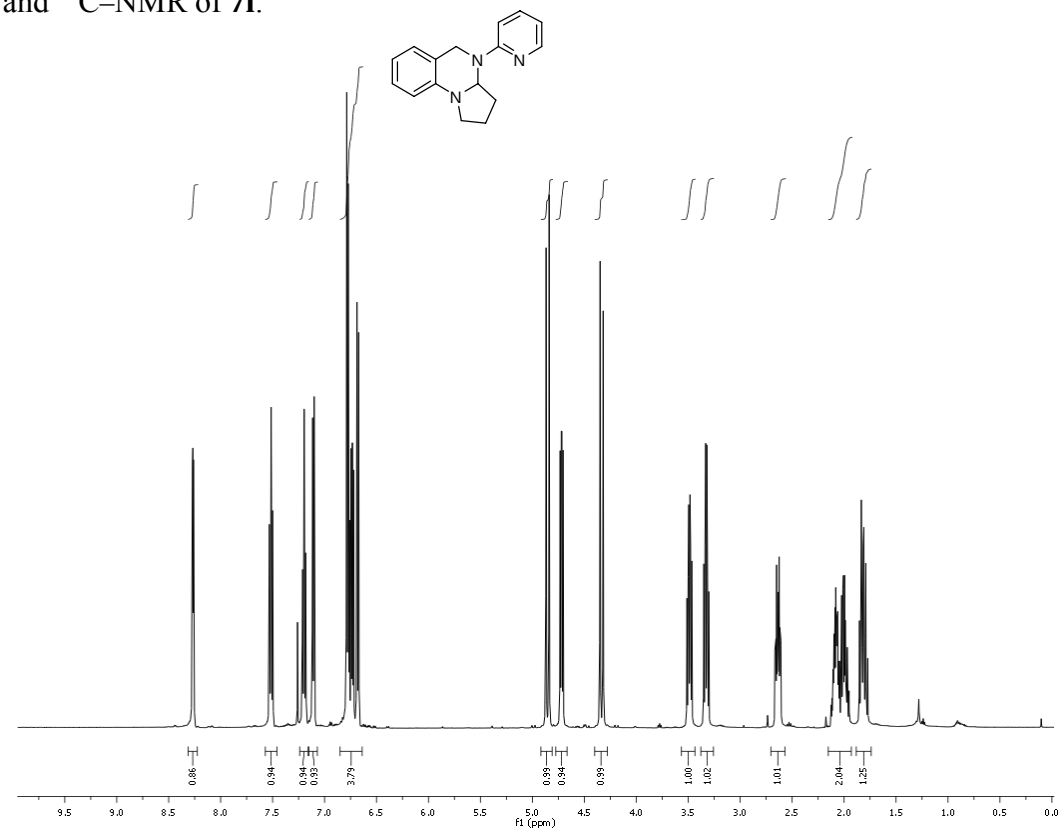


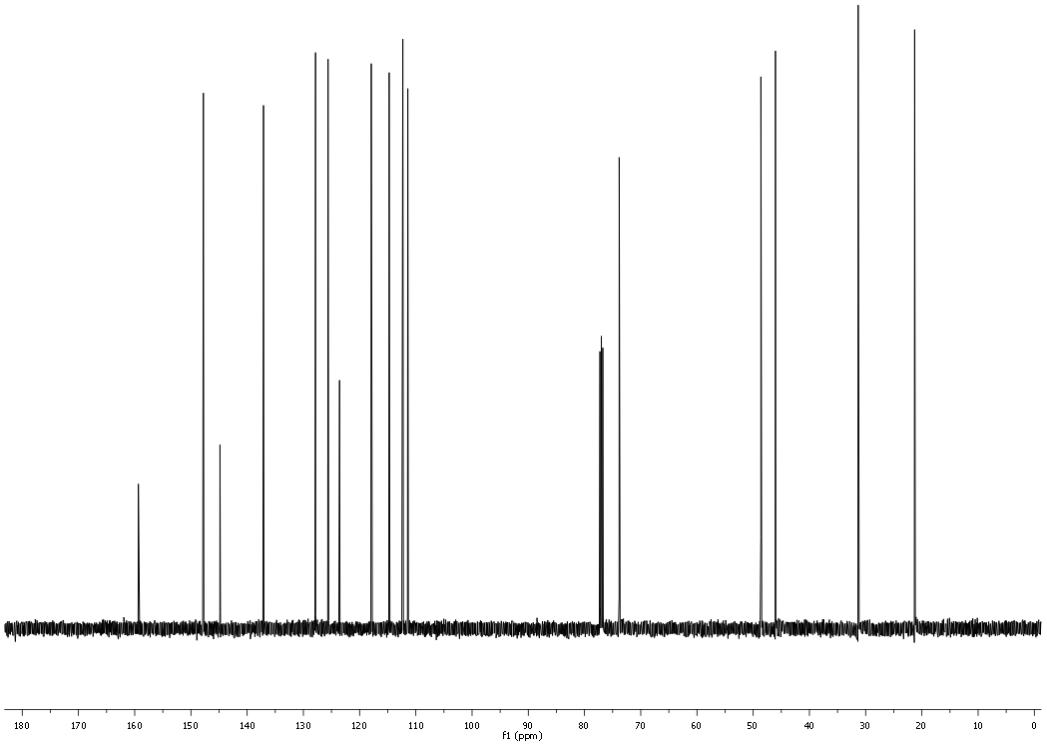
^{1}H–NMR and ^{13}C–NMR of **7h**:



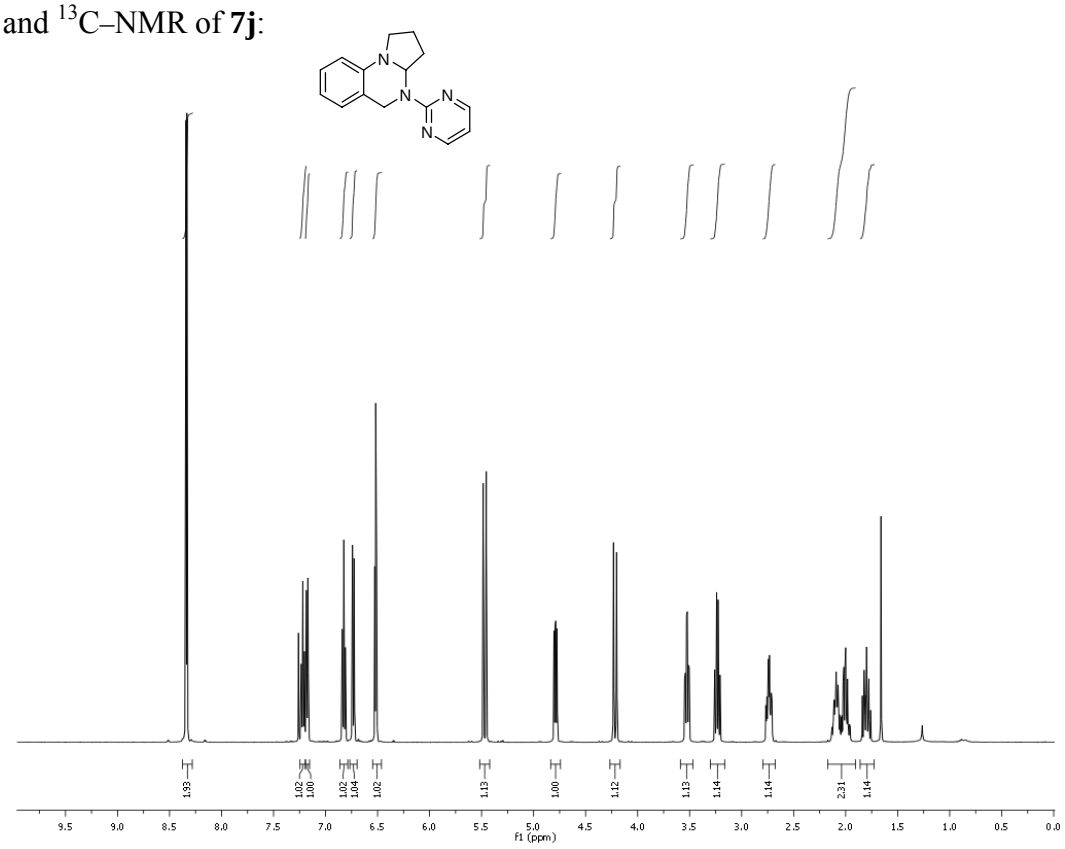


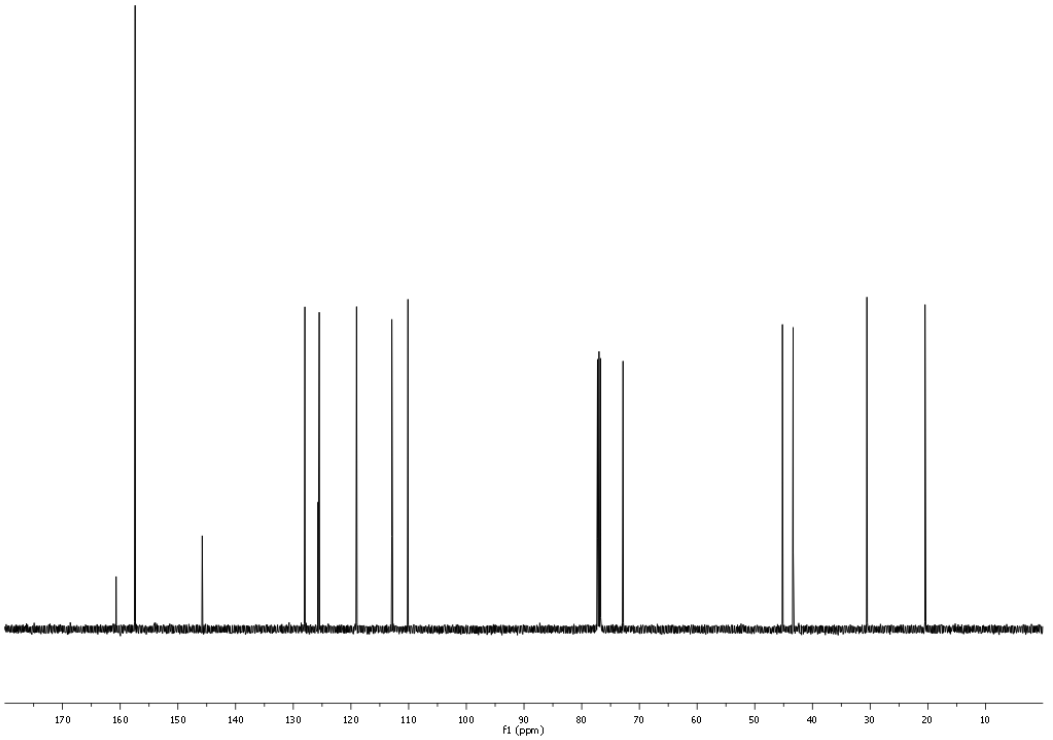
^{1}H–NMR and ^{13}C–NMR of **7i**:



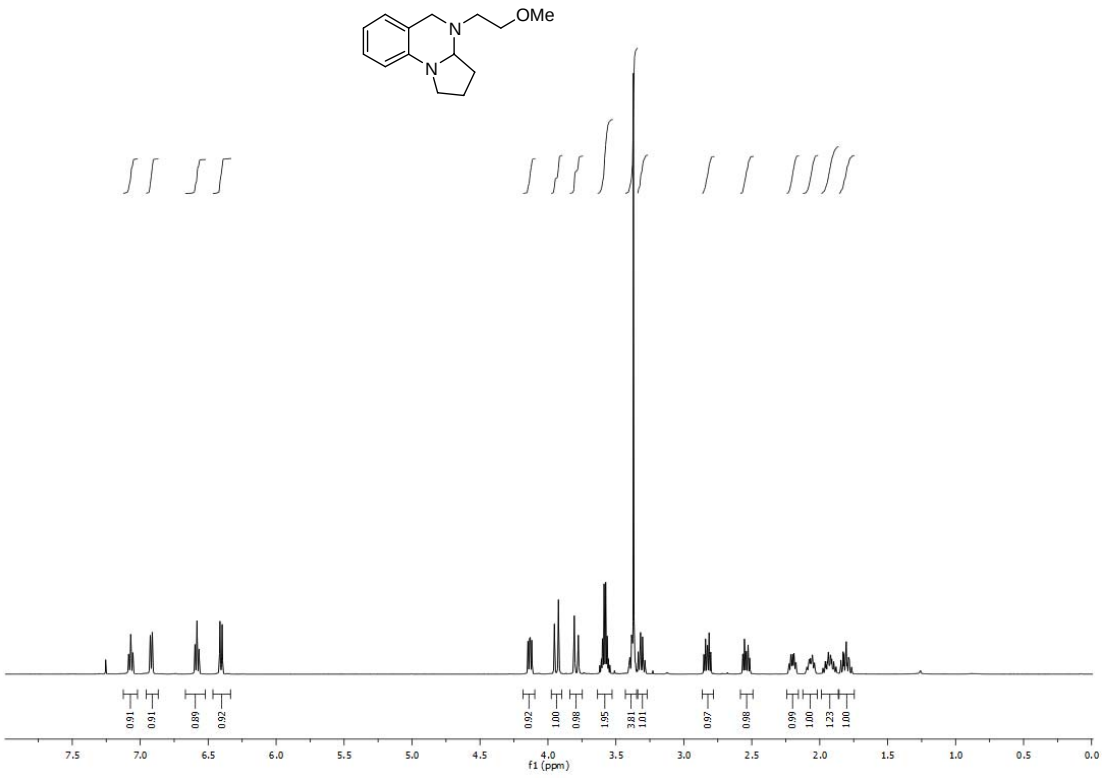


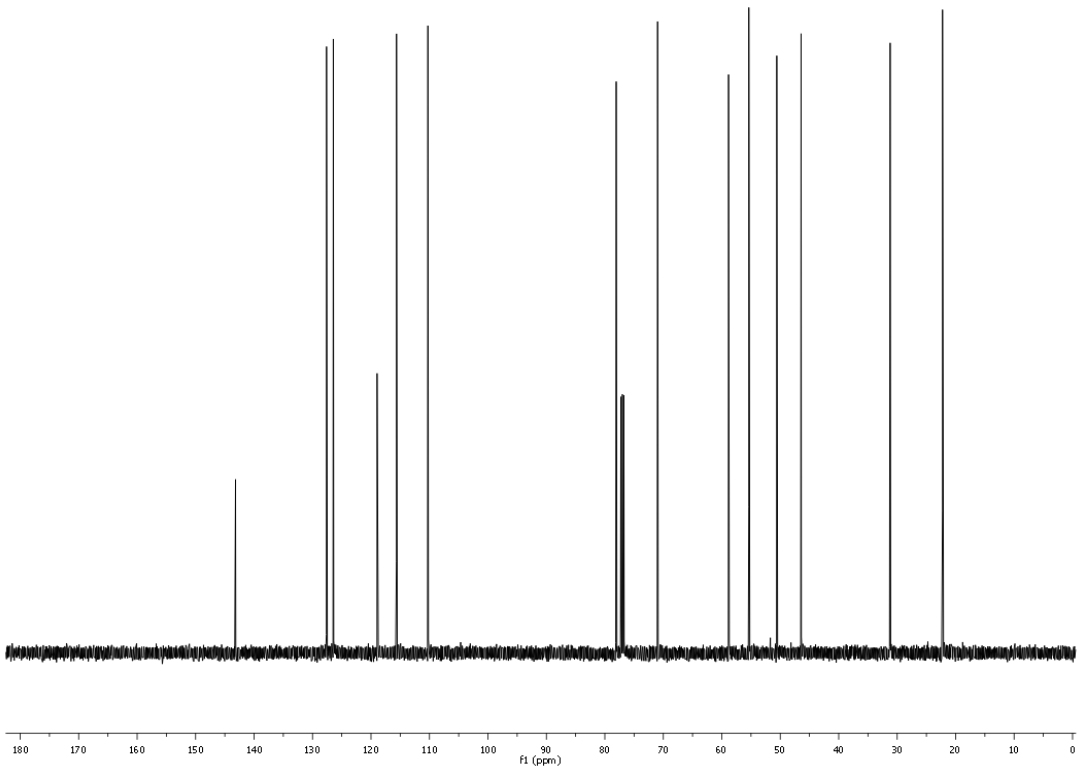
^{1}H–NMR and ^{13}C–NMR of **7j**:



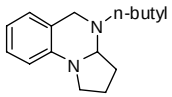


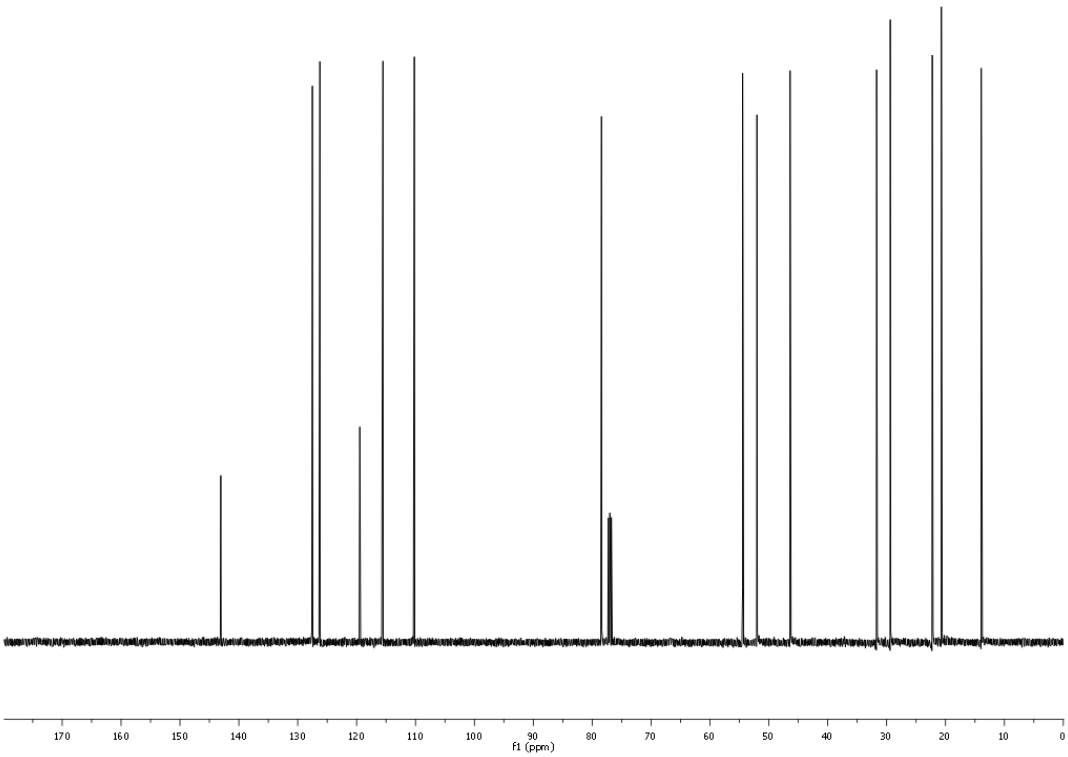
^{1}H–NMR and ^{13}C–NMR of **7k**:



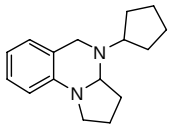


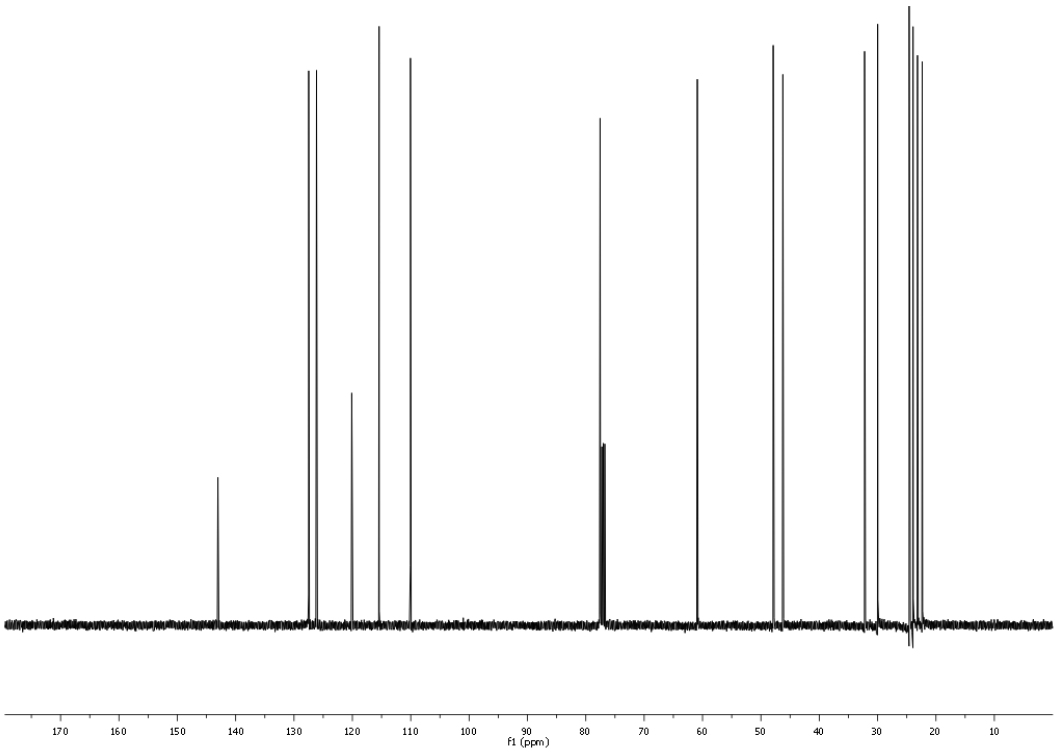
^{1}H–NMR and ^{13}C–NMR of **7l**:



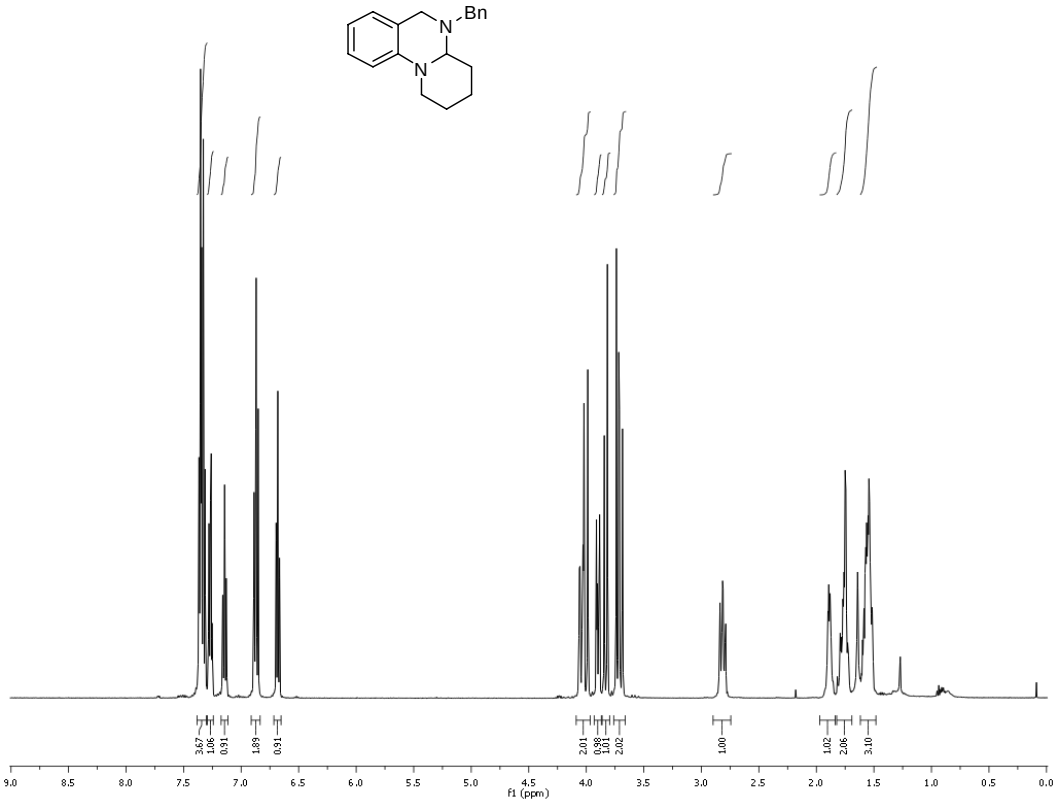


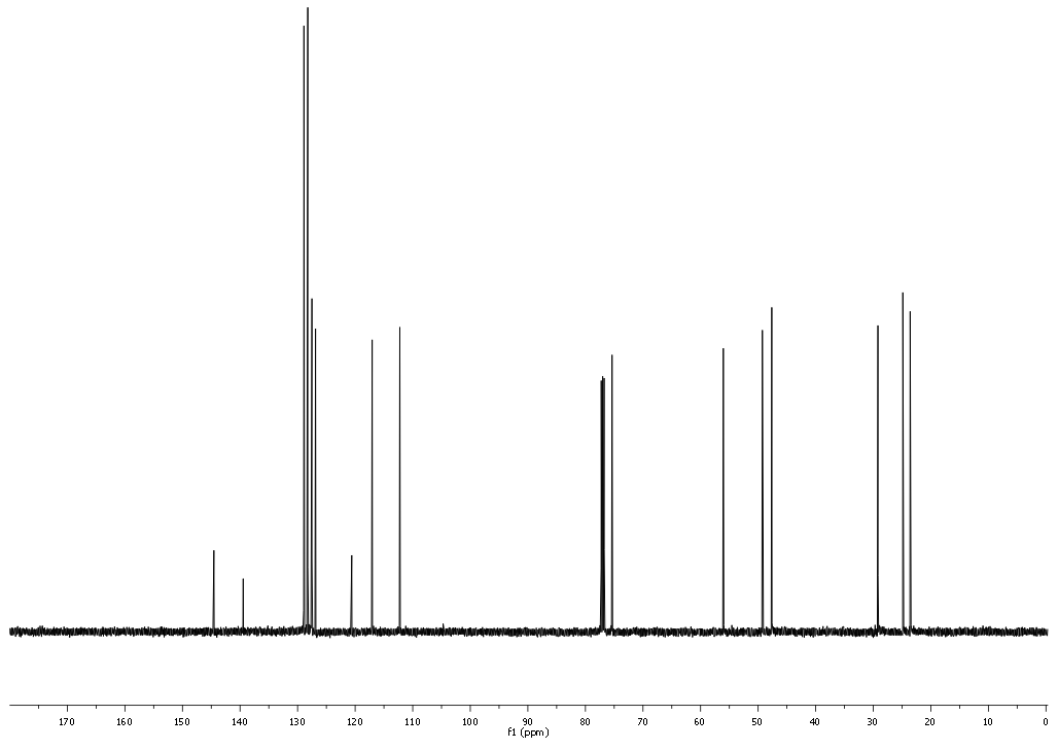
^{1}H–NMR and ^{13}C–NMR of **7m**:



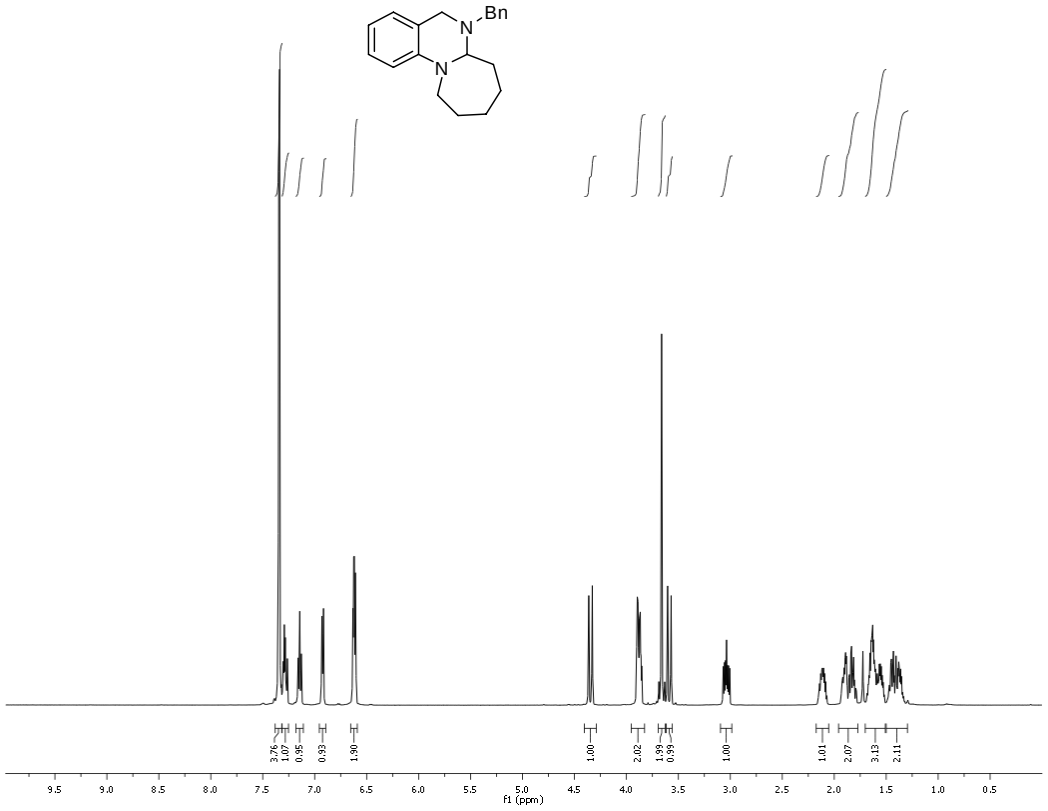


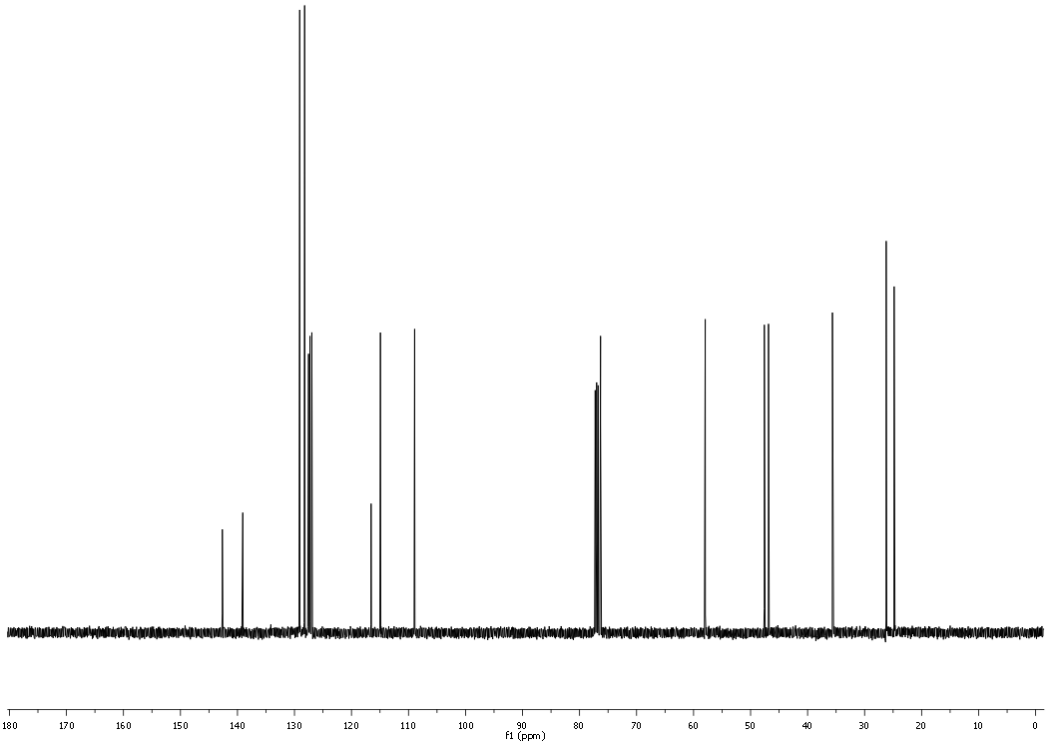
^{1}H–NMR and ^{13}C–NMR of **9a**:



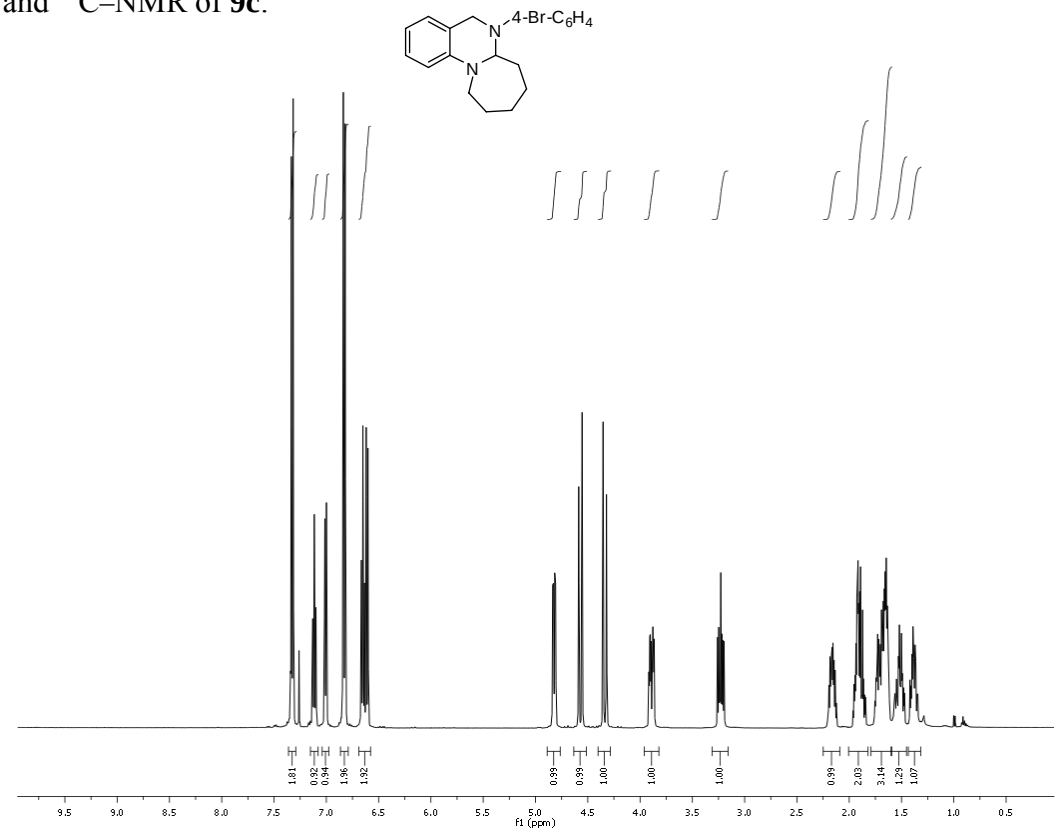


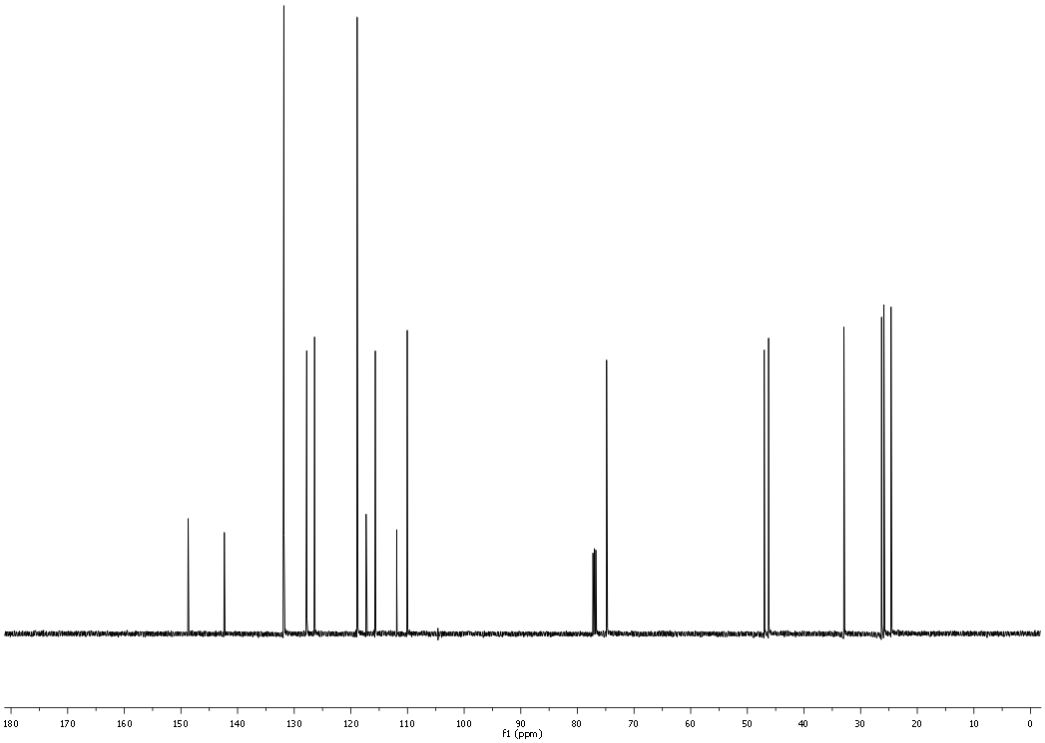
^{1}H–NMR and ^{13}C–NMR of **9b**:



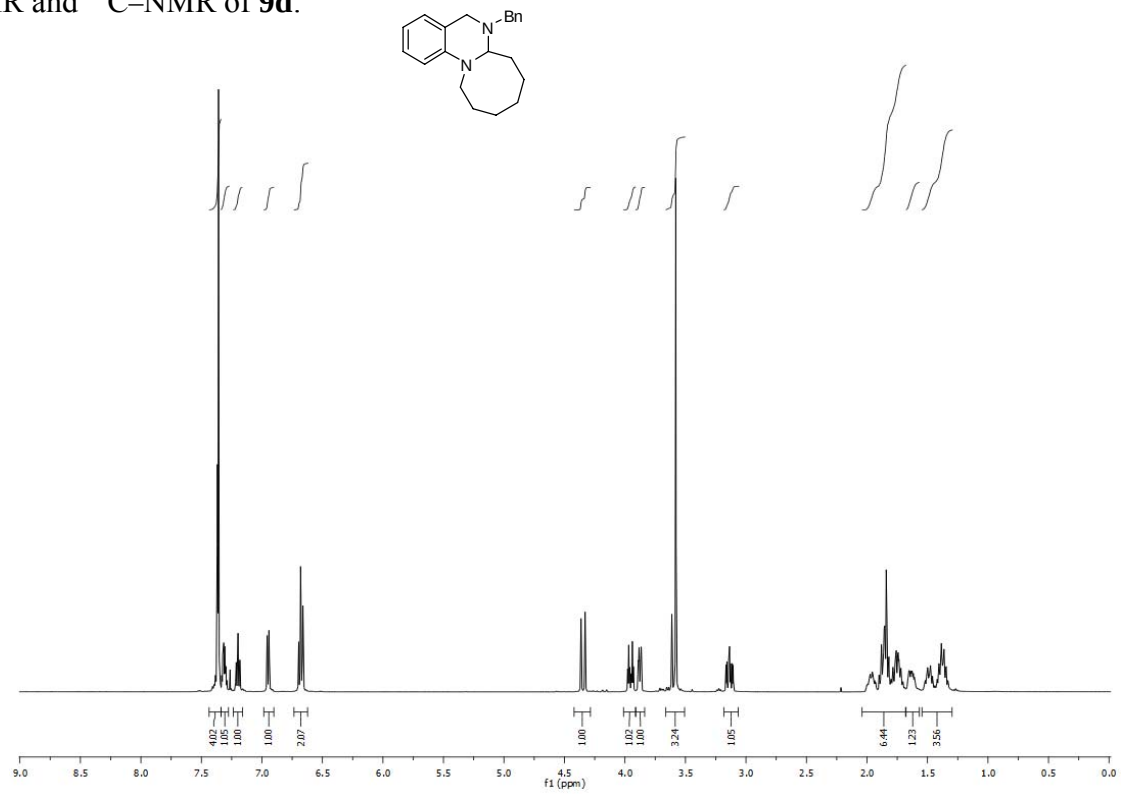


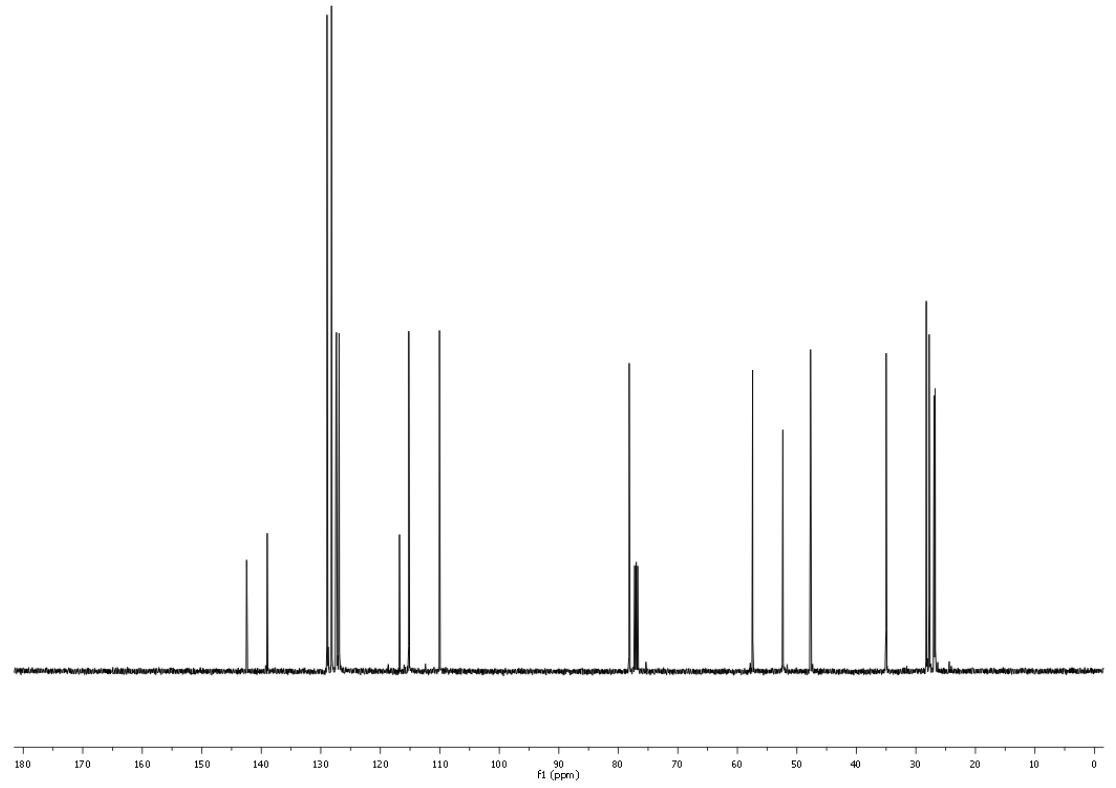
^{1}H–NMR and ^{13}C–NMR of **9c**:



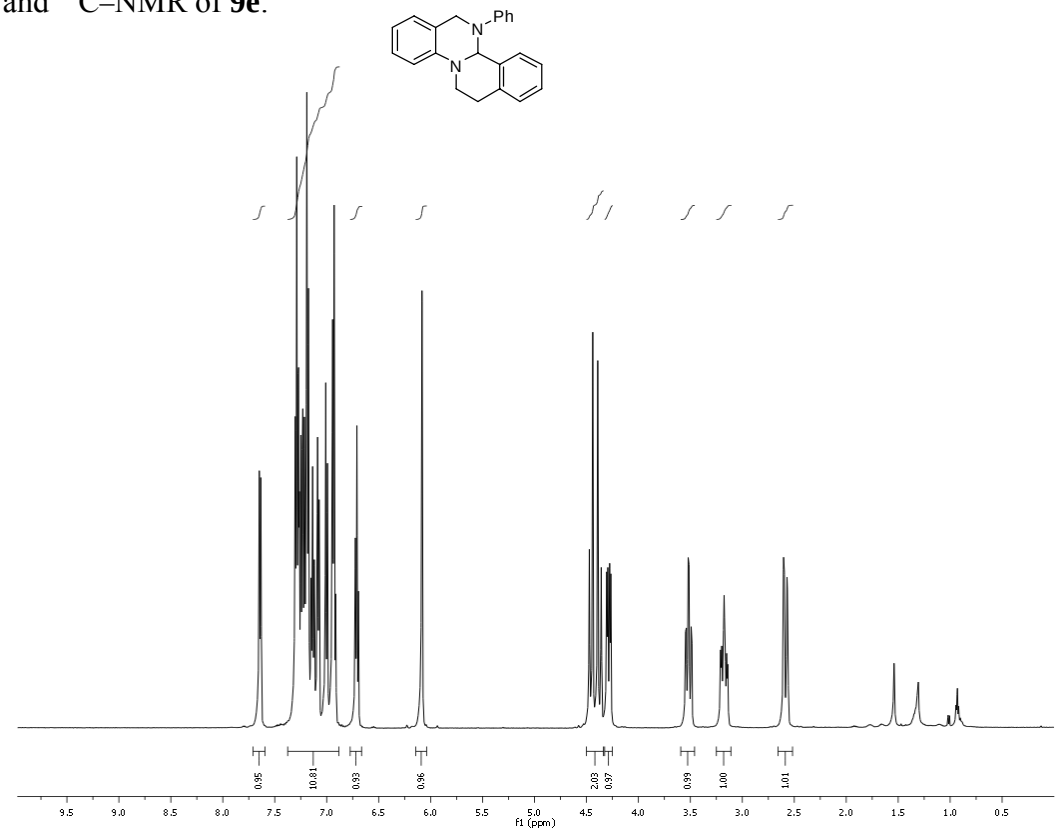


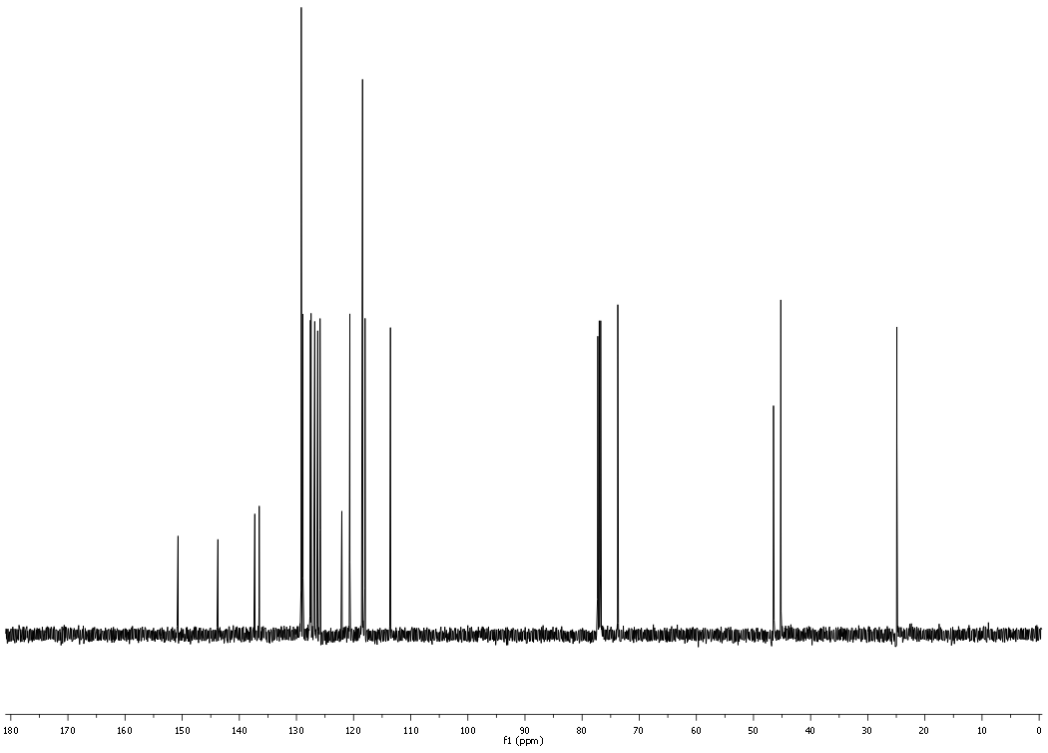
^{1}H–NMR and ^{13}C–NMR of **9d**:



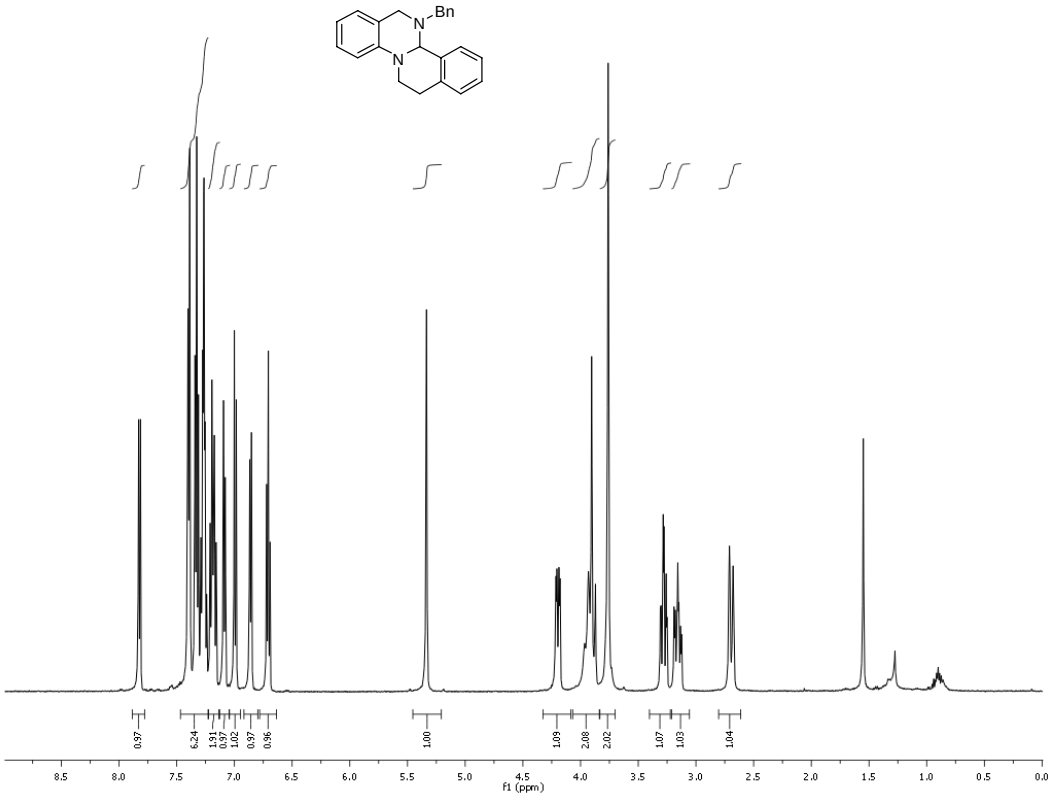


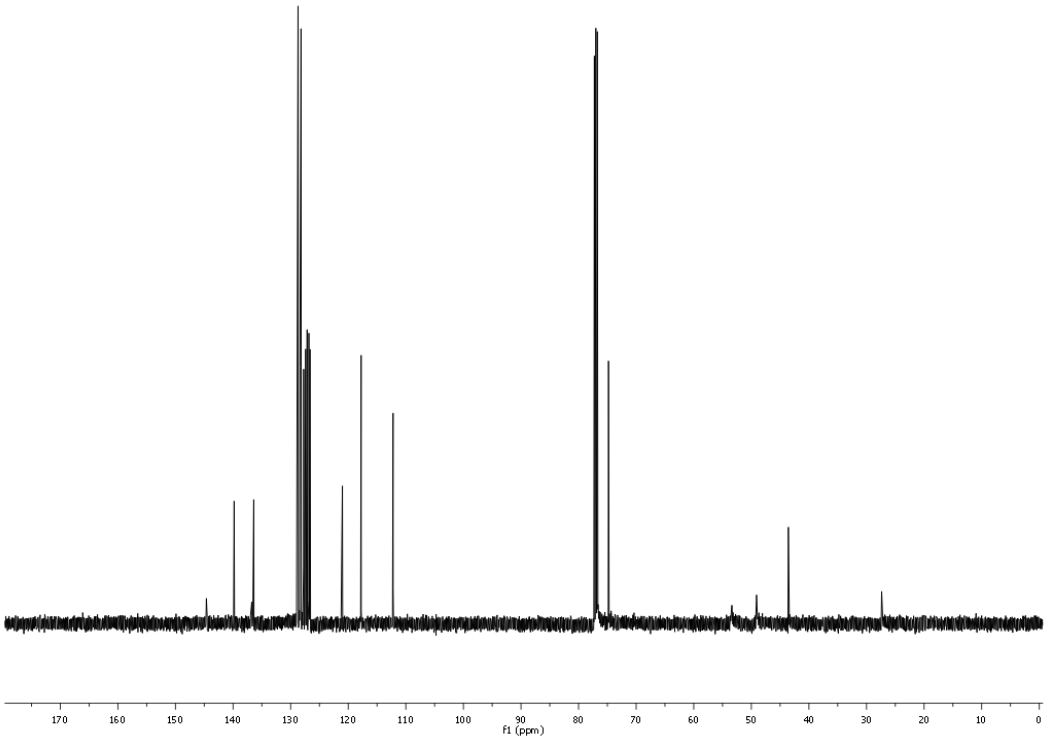
^{1}H–NMR and ^{13}C–NMR of **9e**:



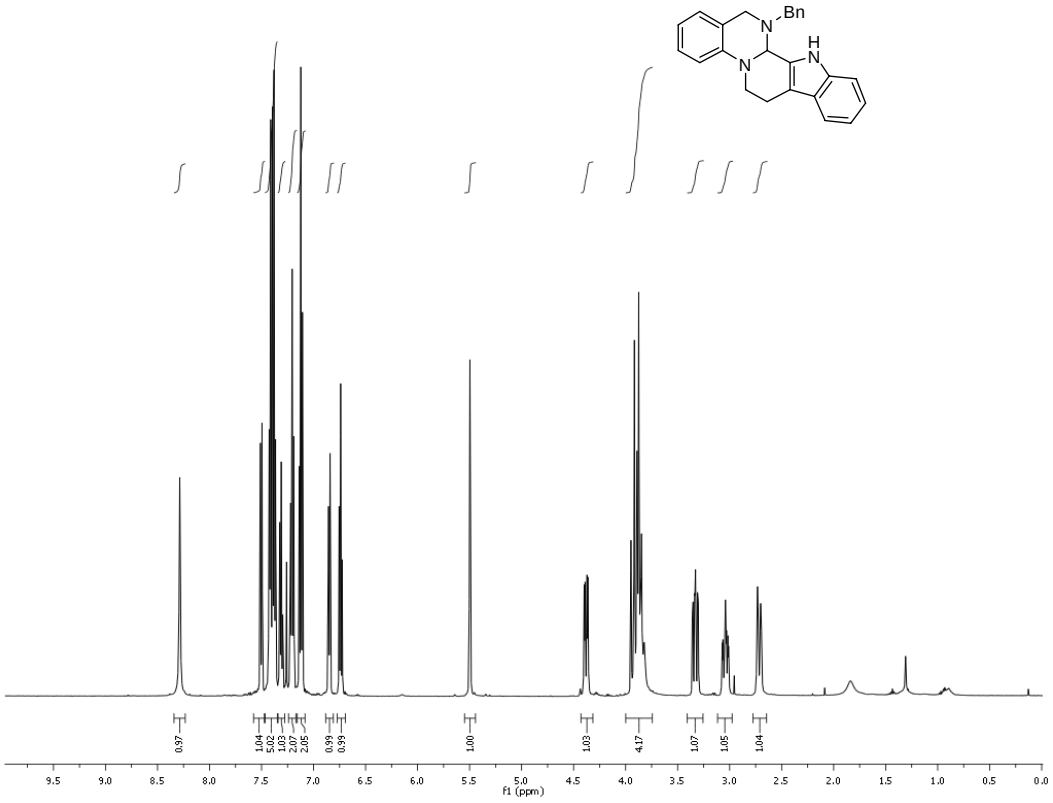


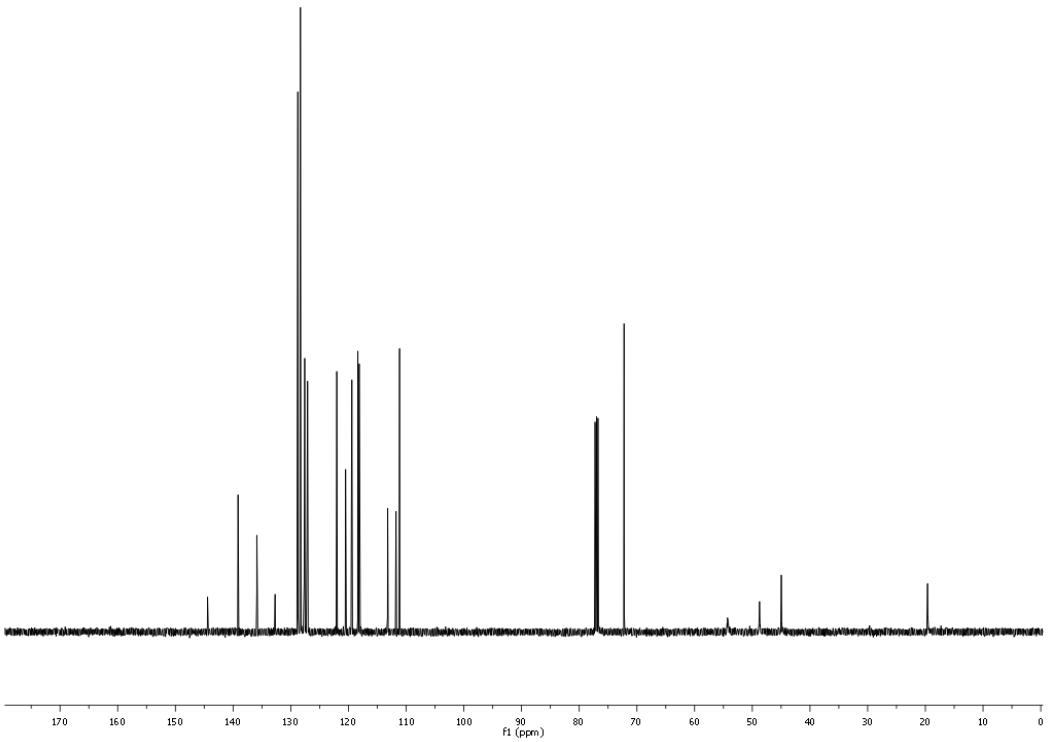
^{1}H–NMR and ^{13}C–NMR of **9f**:



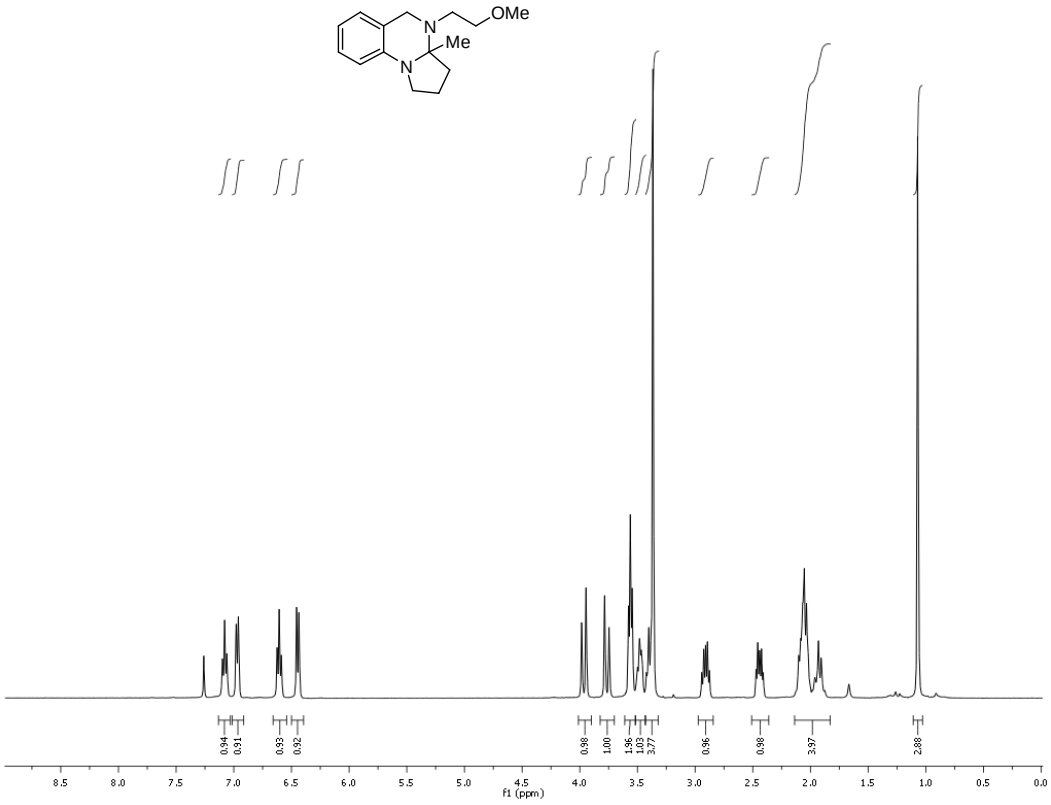


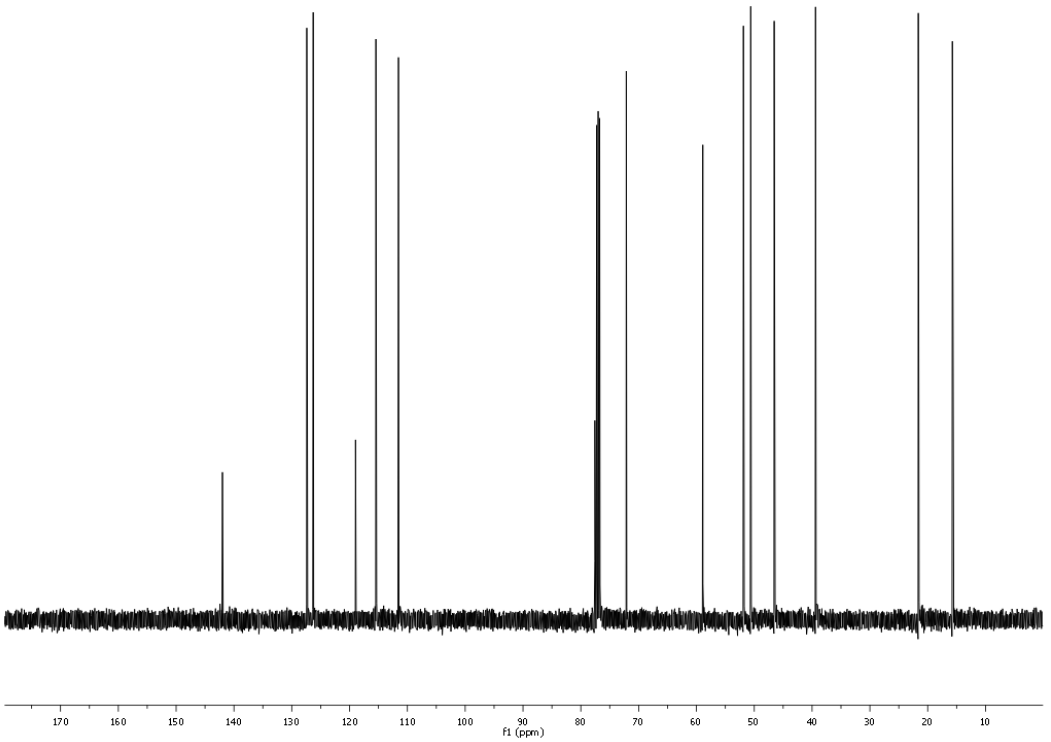
^{1}H–NMR and ^{13}C–NMR of **9g**:



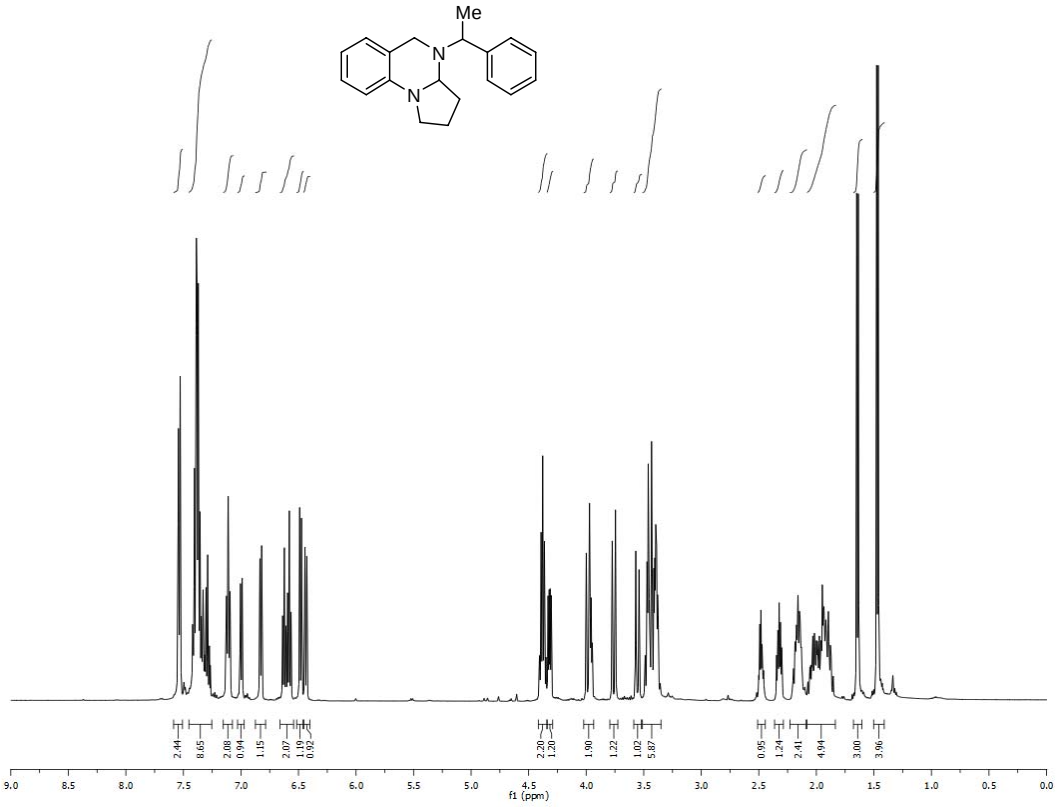


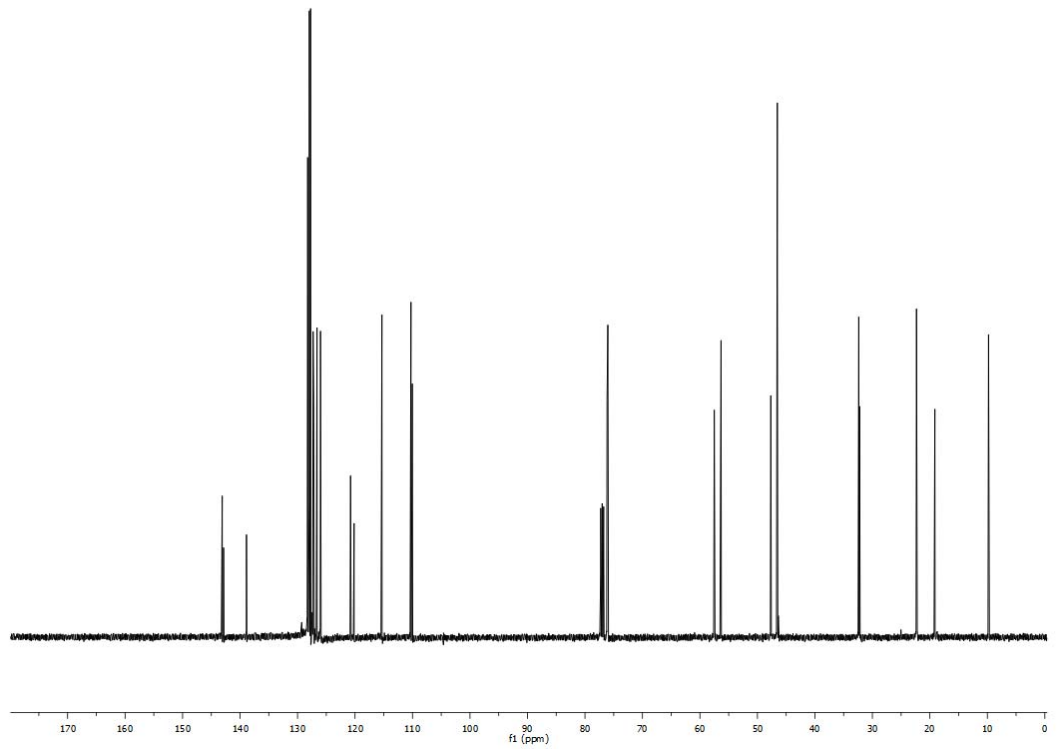
^{1}H–NMR and ^{13}C–NMR of **9h**:



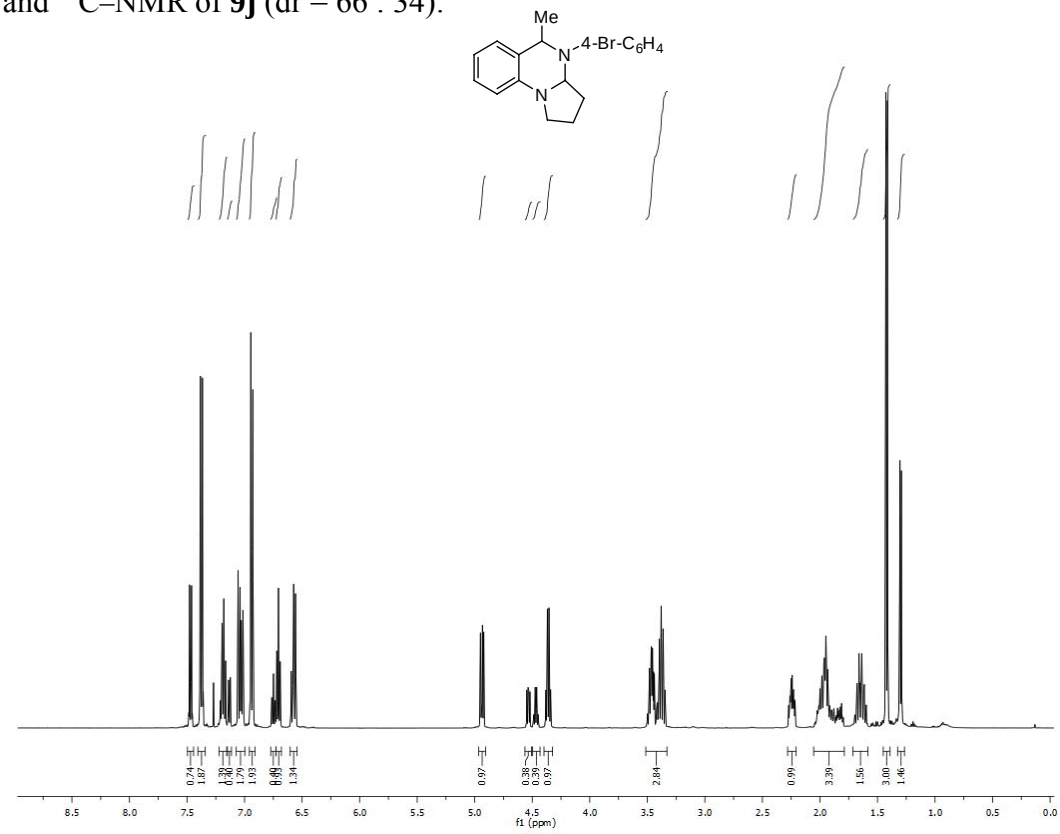


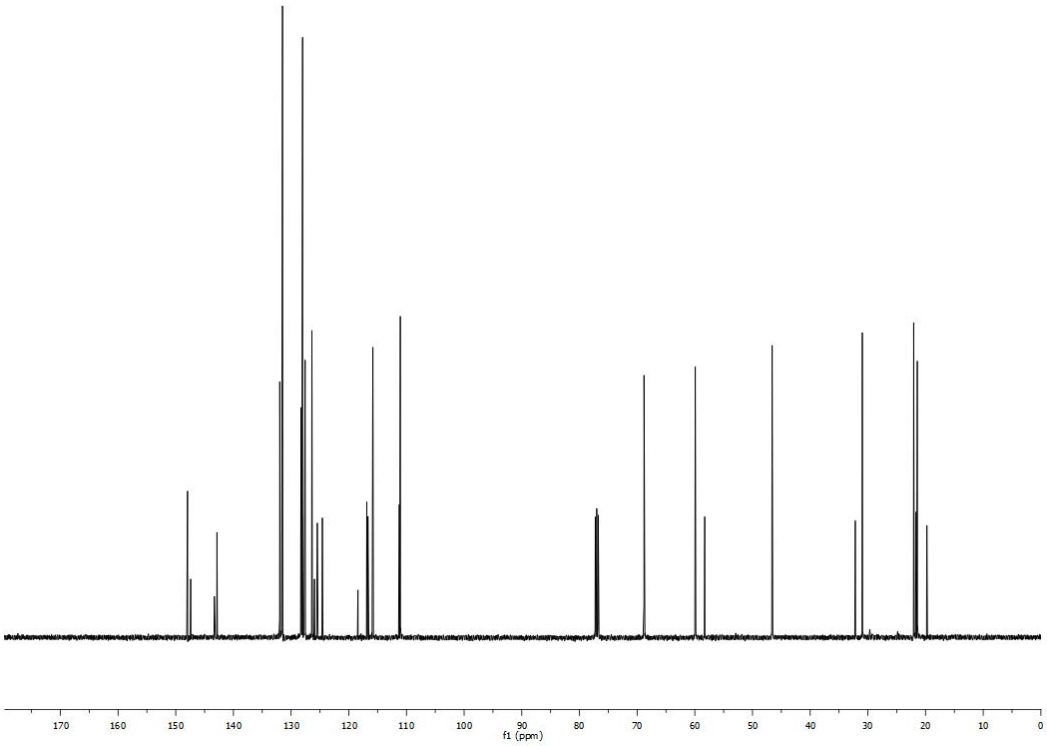
^{1}H–NMR and ^{13}C–NMR of **9i** (dr = 59 : 41):



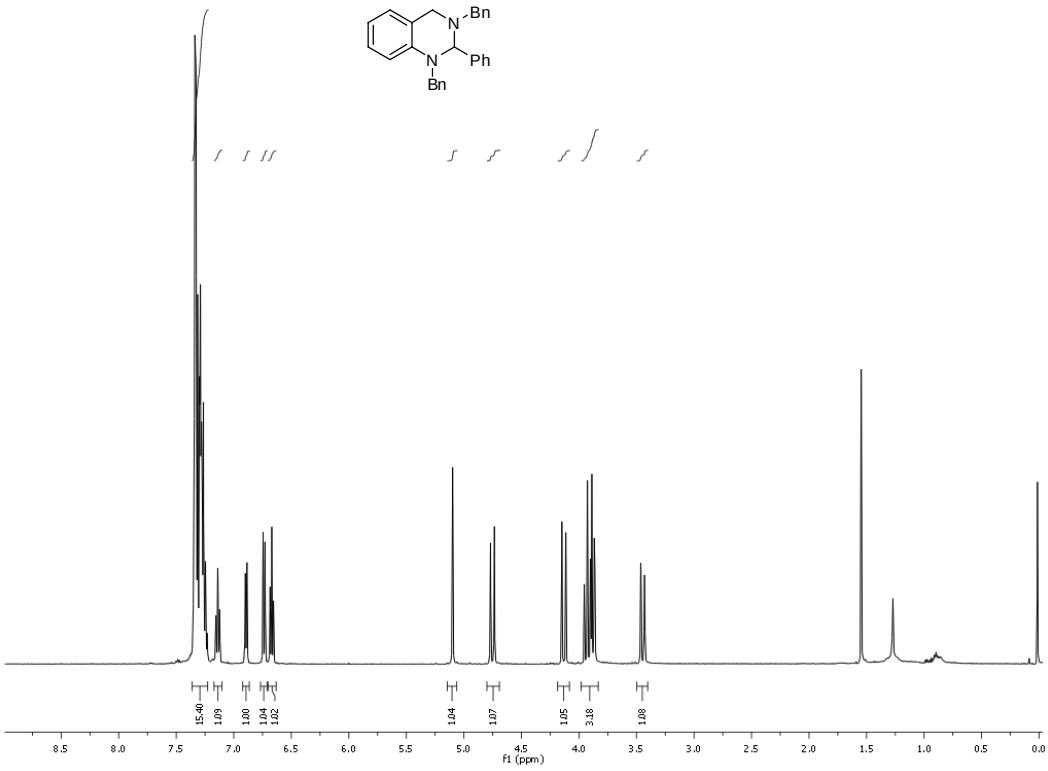


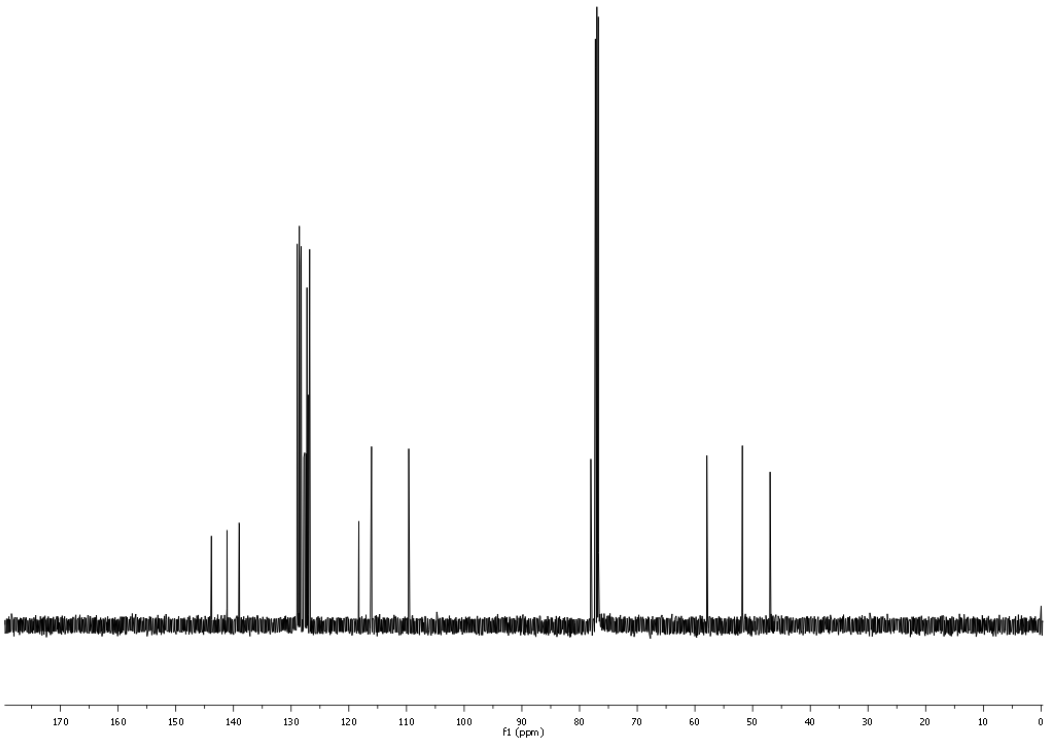
^{1}H–NMR and ^{13}C–NMR of **9j** (dr = 66 : 34):



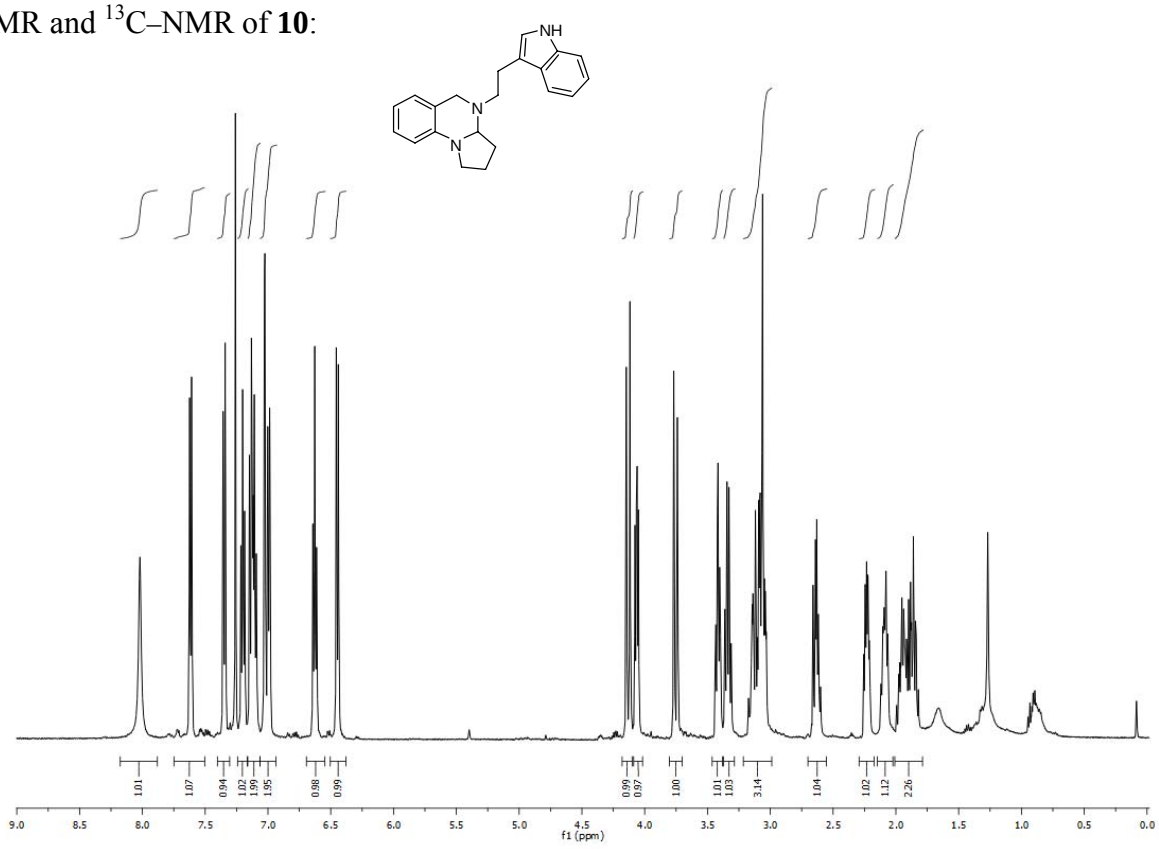


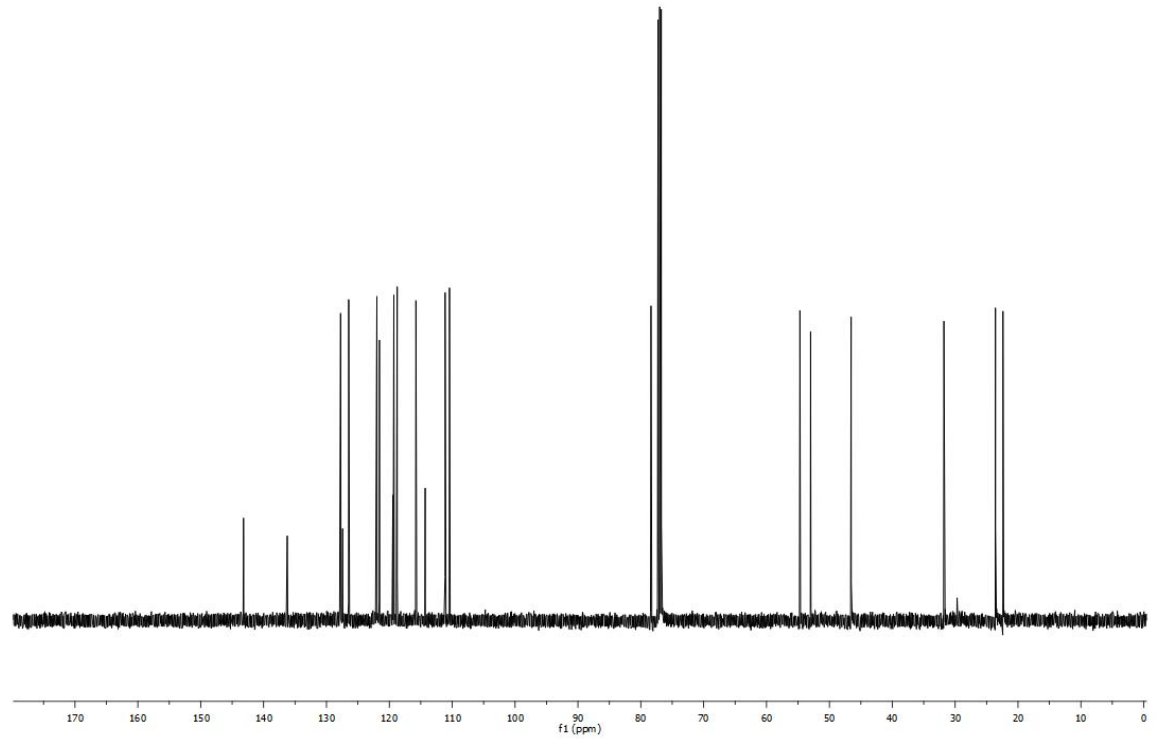
^{1}H–NMR and ^{13}C–NMR of **9k** (TMS containing $CDCl_3$ was used):





^{1}H–NMR and ^{13}C–NMR of **10**:





^{1}H–NMR and ^{13}C–NMR of **11** (TMS containing $CDCl_3$ was used):