One pot Synthesis of Cis-bispyrimidodiazepinone Derivatives via Low-valent Titanium Reagent ($TiCl_4$/Sm)

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5a: white solid, mp: >300 °C; IR (KBr): *v* 3202, 3129, 3059, 2905, 2757, 2698, 1672, 1603, 1468, 1420, 1374, 1336, 1321, 1295, 1265, 1221, 1157, 1109, 1049, 936, 864, 754, 701 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ 9.48 (s, 1H, NH), 8.94 (s, 1H, NH), 7.15 (t, J = 5.7 Hz, 1H, ArH), 6.89-6.84 (m, 2H, ArH), 6.71-6.69 (m, 1H, ArH), 6.58-6.49 (m, 2H, ArH), 6.46-6.43 (m, 1H, ArH), 5.84 (d, J = 5.7 Hz, 1H, ArH), 5.12 (s, 1H, CH), 4.36 (s, 1H, CH), 4.16-4.00 (m, 2H, CH_2), 2.99-2.86 (m, 2H, CH_2), 2.28-2.27 (m, 1H, CH), 1.63-1.57 (m, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6): δ 153.32, 152.36, 137.83, 137.44, 128.58, 128.51, 127.68, 127.43, 119.69, 119.45, 117.50, 117.29, 113.08, 112.66, 65.78, 64.48, 46.77, 45.59, 23.82; HRMS [Found: *m/z* 334.1432 (M^+), calcd for $C_{19}H_{18}N_4O_2$: M, 334.1430]

5b: white solid, mp: >300 °C; IR (KBr): *v* 3185, 3083, 3037, 2918, 2749, 1672, 1601, 1499, 1464, 1424, 1398, 1291, 1262, 1156, 1090, 1017, 822, 757 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ 9.67 (s, 2H, 2 × NH), 7.24-7.27 (m, 2H, ArH), 6.91-6.88 (m, 2H, ArH), 5.89 (s, 2H, ArH), 4.44 (s, 2H, 2 × CH), 4.04-3.99 (m, 2H, CH_2), 2.89-2.84 (m, 2H, CH_2), 2.26-2.24 (m, 2H, CH_2); HRMS [Found: *m/z* 402.0652 (M^+), calcd for $C_{19}H_{16}N_4O_2{}^{35}Cl_2$: M, 402.0650]

5c: white solid, mp: >300 °C; IR (KBr): *v* 3196, 3083, 2937, 2886, 1670, 1624, 1526, 1464, 1389, 1292, 1257, 1240, 1209, 1140, 1097, 1010, 969, 853, 774 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ 9.14 (s, 2H, 2 × NH), 6.48 (s, 2H, ArH), 5.44 (s, 2H, ArH), 4.13 (s, 2H, 2 × CH), 3.77-3.73 (m, 4H, 2 × CH_2), 3.65 (s, 6H, 2 × CH_3O), 3.22 (s, 6H, 2 × CH_3O), 2.19-2.16 (m, 2H, CH_2); HRMS [Found: *m/z* 454.1855 (M^+), calcd for $C_{23}H_{26}N_4O_6$: M, 454.1852]

5d: white solid, mp: >300 °C; IR (KBr): *v* 3210, 3123, 2905, 1718, 1661, 1502, 1462, 1340, 1264, 1229, 1039, 935, 846, 776, 758 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ 9.20 (s, 1H, NH), 8.05 (s, 1H, NH), 7.18-7.17 (m, 1H, ArH), 6.91-6.83 (m, 1H, ArH), 6.59-6.56 (m, 1H, ArH), 6.44 (s, 1H,

ArH), 6.07 (s, 2H, CH_2), 5.91 (s, 1H, CH), 5.87 (s, 1H, CH), 5.77 (s, 1H, CH), 5.51 (s, 1H, CH), 4.29-4.26 (m, 1H, CH), 4.17 (s, 1H, CH), 3.86-3.84 (m, 1H, CH), 2.78-2.74 (m, 1H, CH), 2.18-2.12 (m, 2H, CH_2); HRMS [Found: *m/z* 422.1226 (M^+), calcd for $C_{21}H_{18}N_4O_6$: M, 422.1226]

5e: white solid, mp: >300 °C; IR (KBr): *v* 3197, 3124, 3053, 2913, 1674, 1602, 1465, 1260, 1110, 1051, 814, 751 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ 9.98 (s, 1H, NH), 9.56 (s, 1H, NH), 7.21-7.13 (m, 2H, ArH), 6.94-6.86 (m, 2H, ArH), 6.65-6.54 (m, 21H, ArH), 5.89-5.84 (m, 2H, ArH), 5.38-5.35 (m, 1H, OH), 4.57-4.37 (m, 4H, 2 × CH_2), 4.13-4.03 (m, 3H, 3 × CH); HRMS [Found: *m/z* 350.1380 (M^+), calcd for $C_{19}H_{18}N_4O_3$: M, 350.1379]

5f: white solid, mp: >300 °C; IR (KBr): *v* 3185, 3083, 3037, 2918, 2749, 1672, 1601, 1499, 1464, 1398, 1336, 1291, 1262, 1156, 1090, 1017, 822, 757 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ 10.08 (s, 1H, NH), 9.69 (s, 1H, NH), 7.31-7.24 (m, 3H, ArH), 6.96-6.88 (m, 3H, ArH), 5.93-5.89 (m, 2H, CH_2), 4.64-4.61 (m, 1H, OH), 4.53-4.45 (m, 2H, 2 × CH), 4.17-4.13 (m, 3H, CH_2 + CH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 155.46, 152.59, 136.67, 136.04, 128.62, 128.52, 128.25, 124.20, 123.52, 118.86, 118.17, 115.20, 114.83, 109.37, 69.53, 65.21, 65.12, 54.66, 52.90; HRMS [Found: *m/z* 418.0595 (M^+), calcd for $C_{19}H_{16}N_4O_3{}^{35}Cl_2$: M, 418.0599]

8a: white solid, mp: >300 °C; IR (KBr): *v* 2926, 2834, 1736, 1492, 1458, 1430, 1412, 1373, 1274, 1212, 1102, 1044, 1082, 882, 829, 754 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 7.20-7.15 (m, 4H, ArH), 6.82 (d, *J* = 8.4 Hz, 2H, ArH), 5.35 (s, 2H, 2 × CH), 4.11-4.09 (m, 2H, CH_2), 3.29-3.17 (m, 4H, 2 × CH_2); ^{13}C NMR (100 MHz, DMSO-d_6): δ 148.67, 148.14, 129.04, 127.89, 127.42, 120.57, 117.07, 62.27, 49.67, 21.89; HRMS [Found: *m/z* 471.9554 (M^+), calcd for $C_{22}H_{18}N_2O_4{}^{35}Cl_2$: M, 471.9551]

8b: white solid, mp: >300 °C; IR (KBr): *v* 2947, 1730, 1485, 1428, 1407, 1273, 1233, 1209, 1129, 945, 884 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 7.63-7.59 (m, 1H, ArH), 7.34-7.29 (m, 2H, ArH), 7.20-7.17 (m, 1H, ArH), 6.79-6.76 (m, 1H, ArH), 6.32-6.31 (m, 1H, ArH), 5.36 (s, 1H, CH), 4.81 (s, 1H, CH), 4.12-4.01 (m, 2H, CH_2), 3.26-3.09 (m, 4H, 2 × CH_2); HRMS [Found: *m/z* 491.9317 (M^+), calcd for $C_{22}H_{18}N_2O_4{}^{35}Cl_2$: M, 491.9320]

8c: white solid, mp: >300 °C; IR (KBr): *v* 2936, 2836, 1719, 1613, 1504, 1459, 1431, 1376, 1321, 1287, 1219, 1162, 1127, 1033, 951, 897, 833, 817, 779, 747, 681 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 7.13-7.11 (m, 1H, ArH), 6.96-6.94 (m, 1H, ArH), 6.72-6.66 (m, 4H, ArH), 5.69 (s, 1H, CH), 5.29 (s, 1H, CH), 4.67 (s, 1H, CH), 4.11-3.99(m, 2H, CH_2), 3.59 (s, 3H, CH_3O), 3.47 (s,

3H, CH_3O), 3.25-3.15 (m, 2H, CH_2), 1.72-1.69 (m, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6): δ 154.78, 154.38, 150.11, 149.56, 144.00, 143.39, 119.38, 118.91, 116.76, 116.13, 115.98, 115.38, 113.17, 112.27, 65.67, 62.64, 55.47, 55.24, 49.05, 46.89, 22.12; HRMS [Found: *m/z* 396.1322 (M^+), calcd for $C_{21}H_{20}N_2O_6$: M, 396.1321]

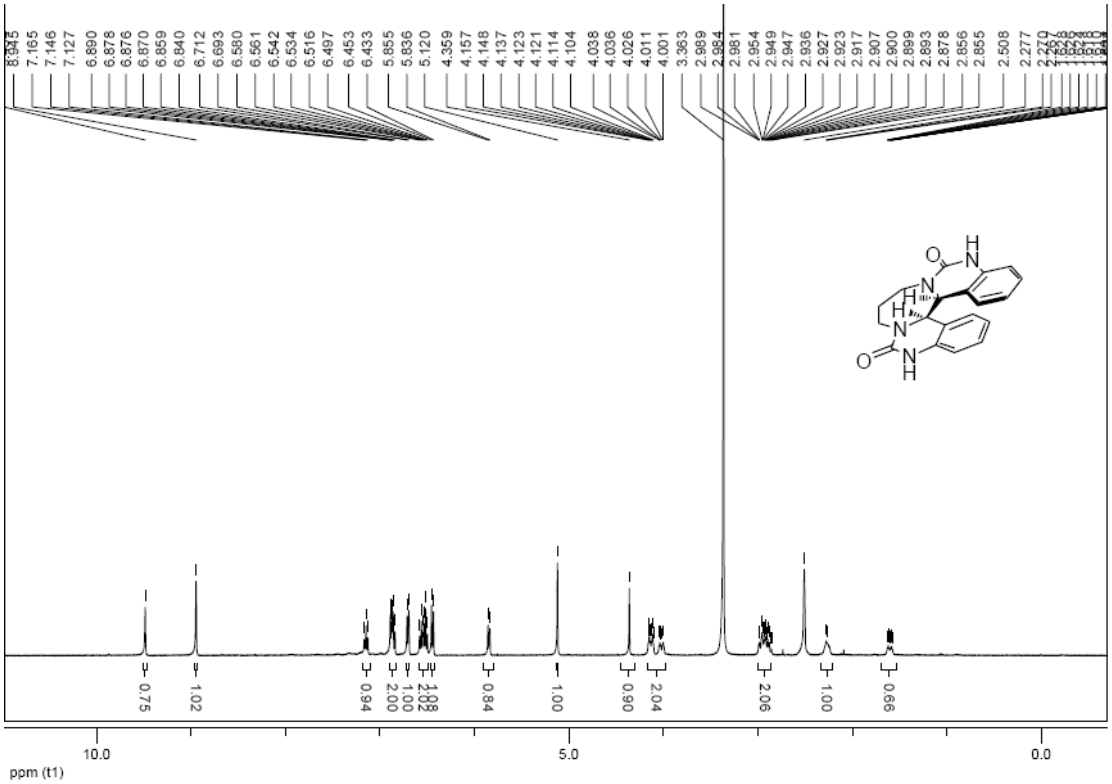
8d: white solid, mp: >300 °C; IR (KBr): *v* 3079, 2974, 1730, 1602, 1471, 1429, 1405, 1372, 1314, 1264, 1251, 1206, 1185, 1109, 1039, 977, 940, 895, 863, 846, 810, 753, 695 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 7.53-7.52 (m, 2H, ArH), 7.23-7.22 (m, 2H, ArH), 5.42 (s, 2H, 2 × CH), 4.13-4.09 (m, 2H, CH_2), 3.25-3.21 (m, 4H, 2 × CH_2); HRMS [Found: *m/z* 471.9554 (M^+), calcd for $C_{19}H_{12}N_2O_4{}^{35}Cl_4$: M, 471.9551]

8e: white solid, mp: >300 °C; IR (KBr): *v* 3072, 2946, 1734, 1461, 1427, 1399, 1371, 1248, 1207, 1175, 1104, 1038, 962, 865, 831, 776 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 7.73 (d, *J* = 2.0 Hz, 2H, ArH), 7.38 (d, *J* = 2.0 Hz, 2H, ArH), 5.39 (s, 2H, 2 × CH), 4.13-4.09 (m, 2H, CH_2), 3.28-3.22 (m, 3H, CH_2 + CH), 1.73-1.69 (m, 1H, CH); HRMS [Found: *m/z* 647.7533 (M^+), calcd for $C_{19}H_{12}N_2O_4{}^{79}Br_4$: M, 647.7531]

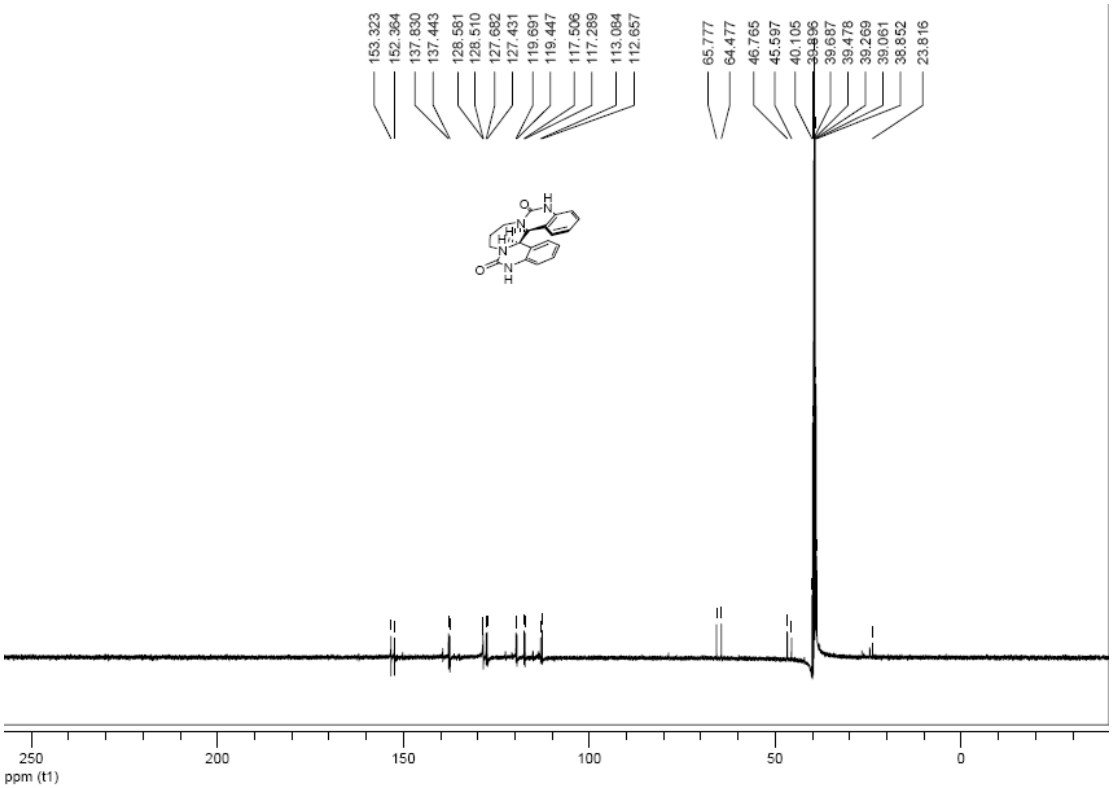
8f: white solid, mp: >300 °C; IR (KBr): *v* 2979, 2944, 1734, 1718, 1624, 1496, 1462, 1433, 1370, 1329, 1274, 1218, 1203, 1126, 1080, 1040, 950, 760, 728, 696 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 6.82 (d, *J* = 4.4 Hz, 4H, ArH), 6.53 (t, *J* = 5.2 Hz, 2H, ArH), 5.35 (s, 2H, 2 × CH), 4.11-4.08 (m, 2H, CH_2), 3.68 (s, 6H, 2 × CH_3O), 3.38-3.22 (m, 3H, CH_2 + CH), 1.76-1.72 (m, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6): δ 149.24, 146.19, 138.71, 123.34, 119.59, 119.32, 112.05, 62.40, 55.96, 48.90, 22.07; HRMS [Found: *m/z* 396.1322 (M^+), calcd for $C_{21}H_{20}N_2O_6$: M, 396.1321]

11: white solid, mp: >300 °C; IR (KBr): *v* 3031, 2941, 1725, 1631, 1518, 1457, 1374, 1339, 1220, 1076, 998, 816, 747 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ 7.73 (d, *J* = 8.8 Hz, 2H, ArH), 7.38 (d, *J* = 8.0 Hz, 2H, ArH), 7.33 (d, J = 8.8 Hz, 2H, ArH), 6.91 (t, *J* = 7.2 Hz, 2H, ArH), 6.73-6.65 (m, 4H, ArH), 5.67 (s, 2H, 2 × CH), 4.13-4.07 (m, 2H, CH_2), 3.62-3.54 (m, 2H, CH), 2.45-2.38 (m, 2H, CH_2); ^{13}C NMR (100 MHz, DMSO-d_6): δ 150.15, 148.63, 130.49, 129.56, 129.33, 127.30, 125.21, 124.04, 120.79, 115.43, 112.52, 62.23, 46.76, 22.87; HRMS [Found: *m/z* 476.1737 (M^+), calcd for $C_{30}H_{24}N_2O_4$: M, 476.1736]

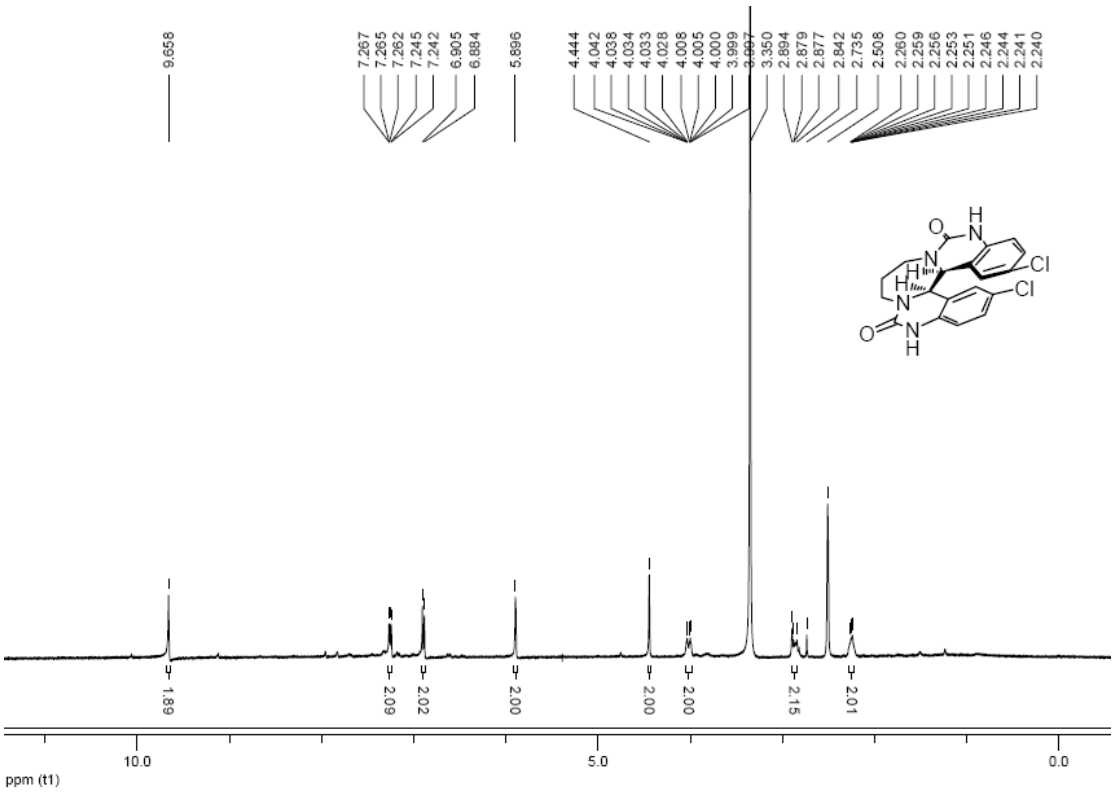
Copies of spectra for compounds 5, 8 and 11



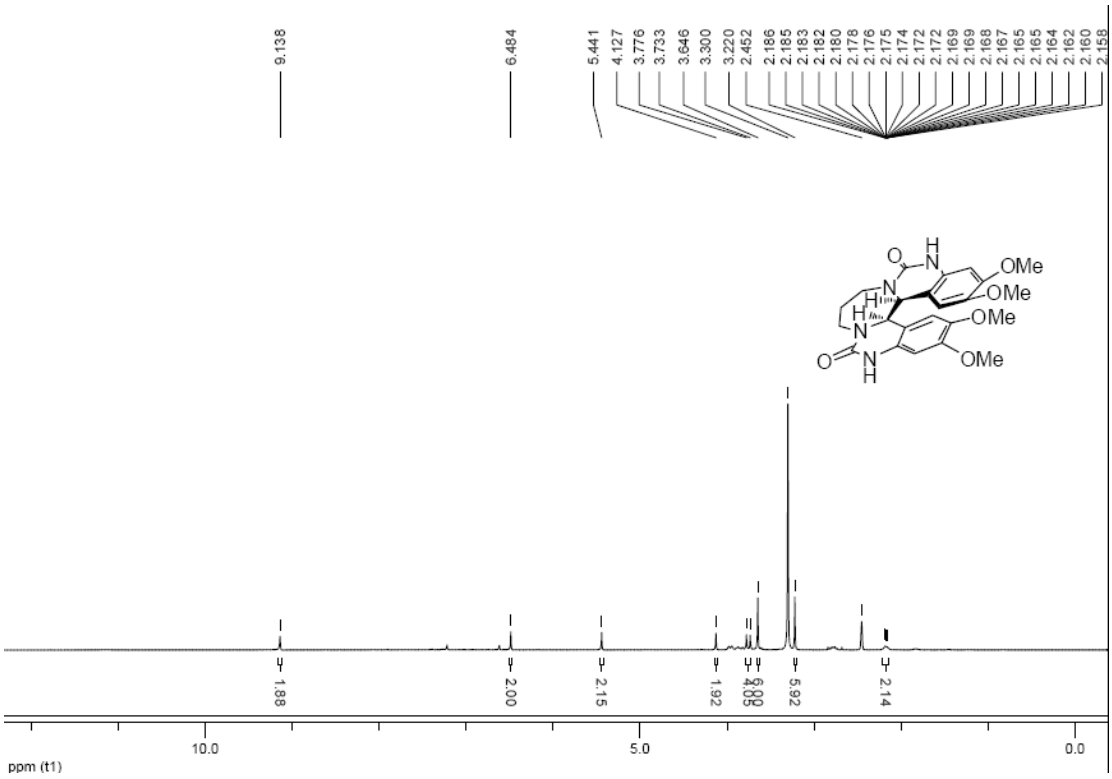
^{1}H NMR Spectrum of compound 5a



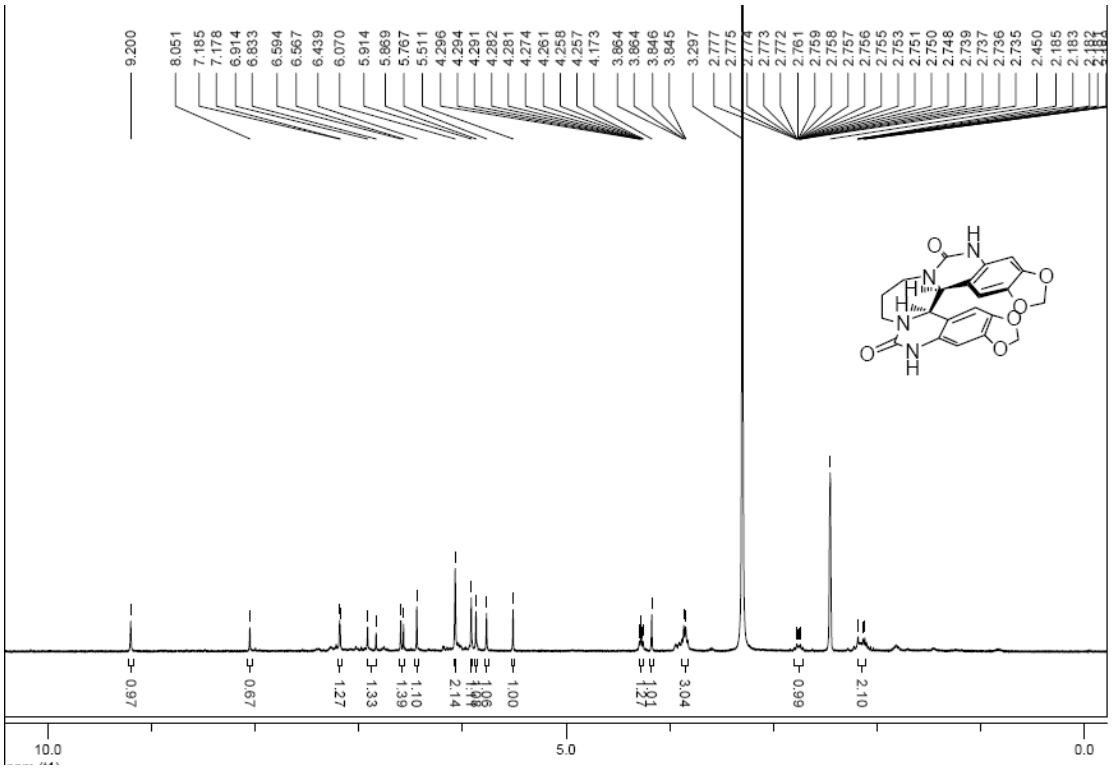
^{13}C NMR Spectrum of compound 5a



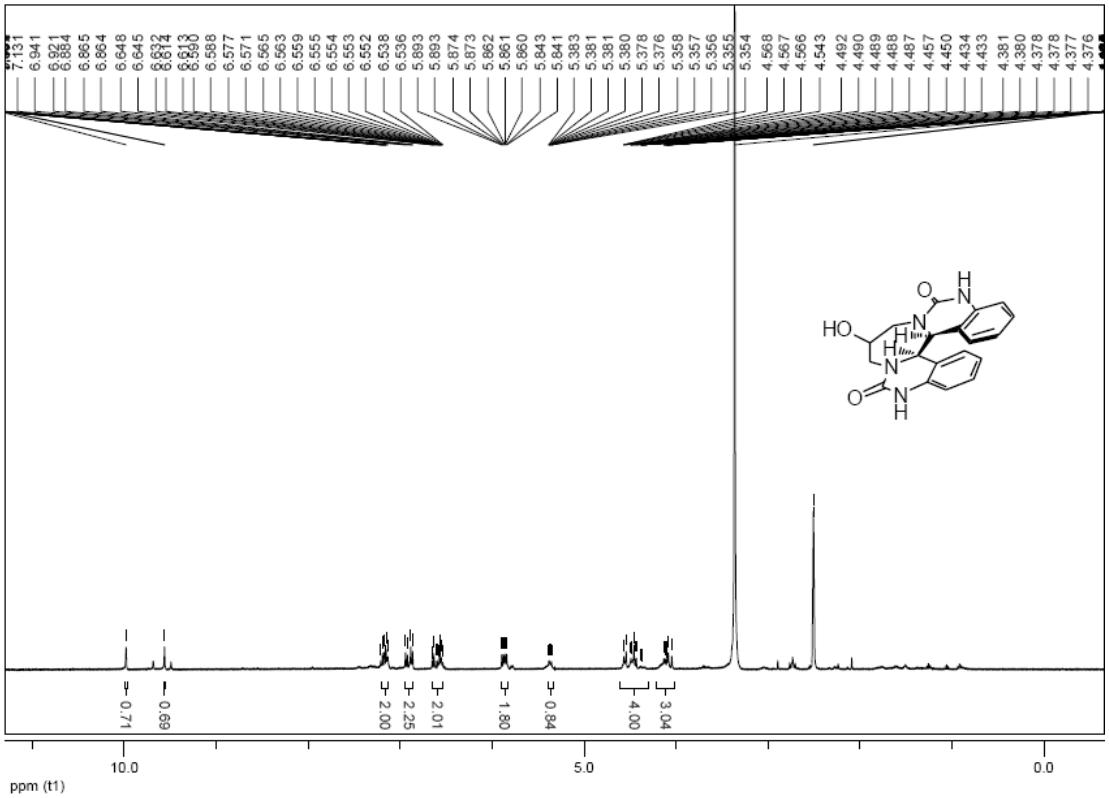
^{1}H NMR Spectrum of compound 5b



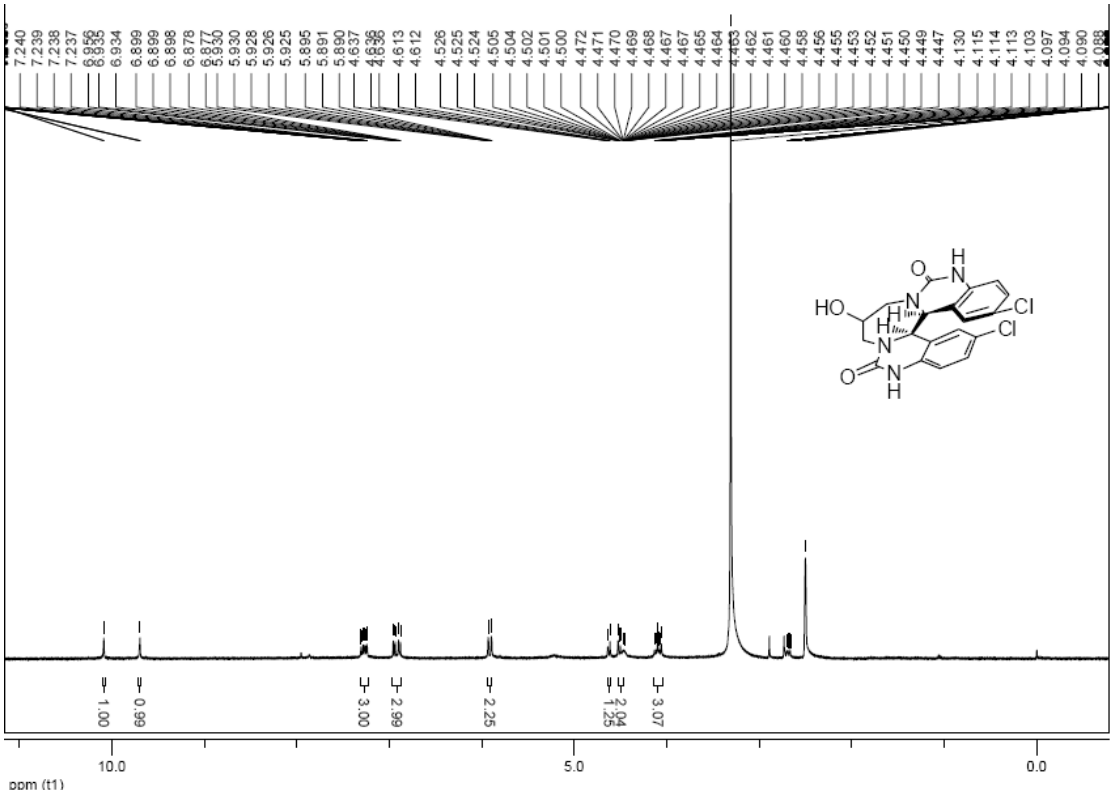
^{1}H NMR Spectrum of compound 5c



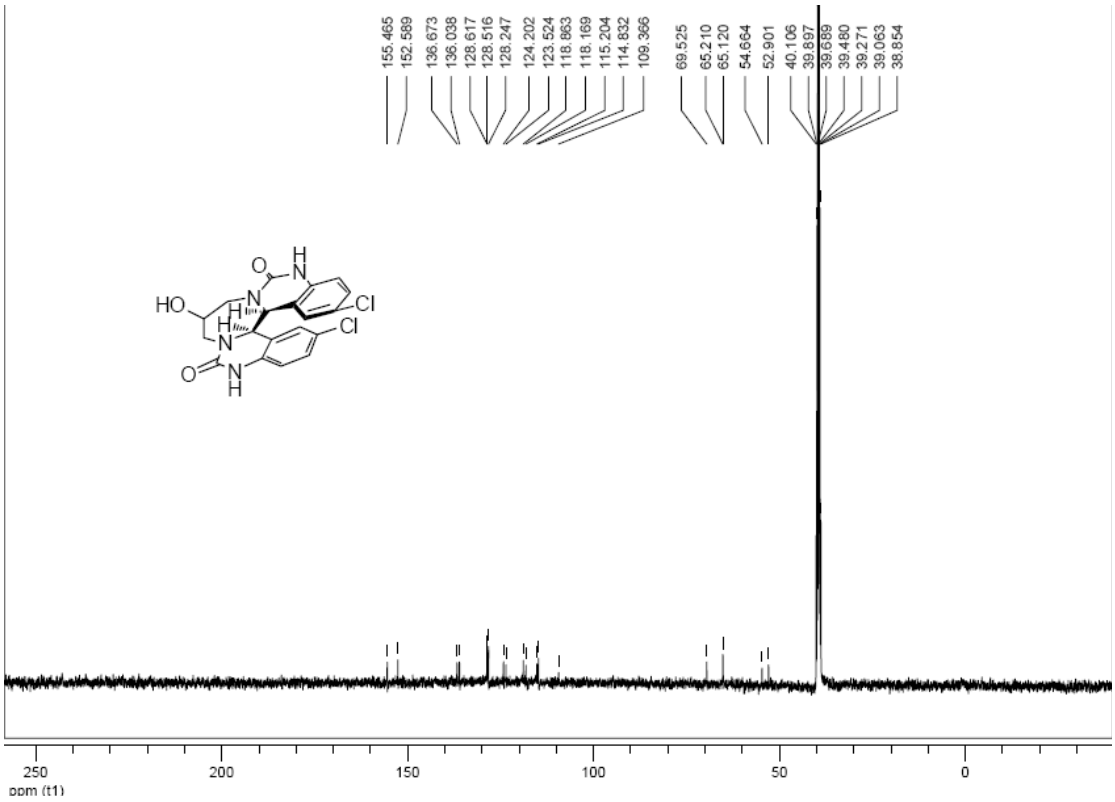
^{1}H NMR Spectrum of compound 5d



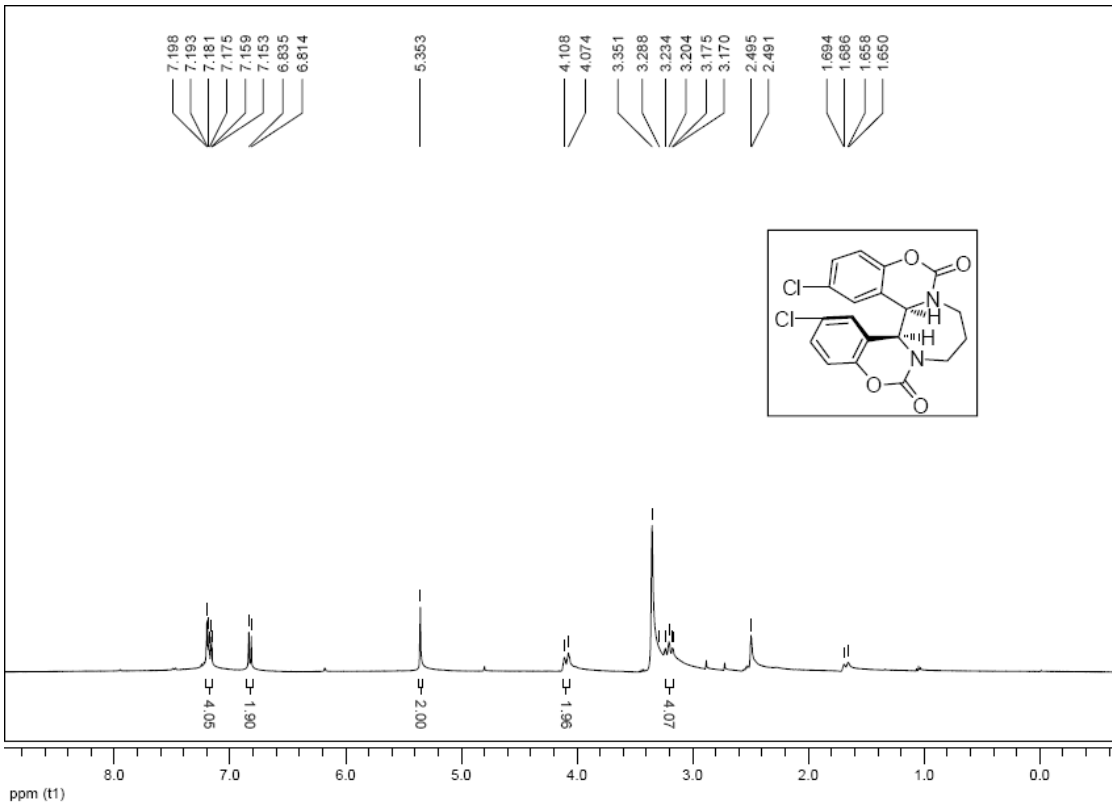
^{1}H NMR Spectrum of compound 5e



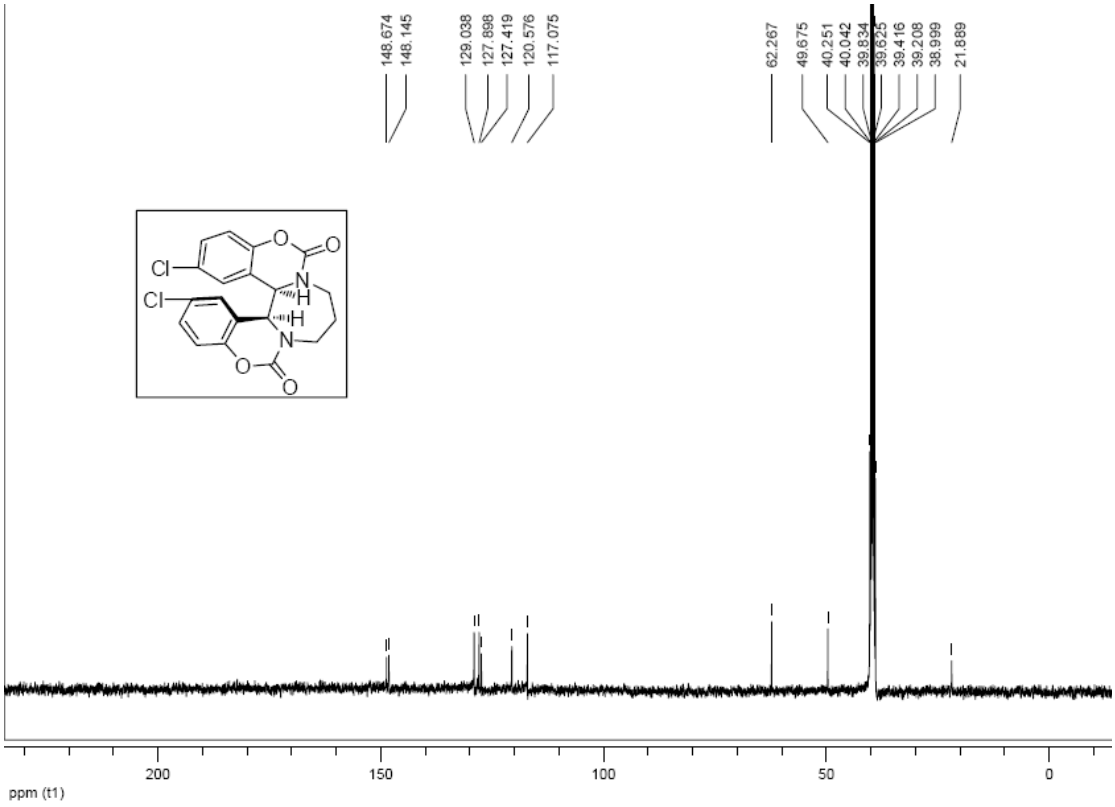
^{1}H NMR Spectrum of compound 5f



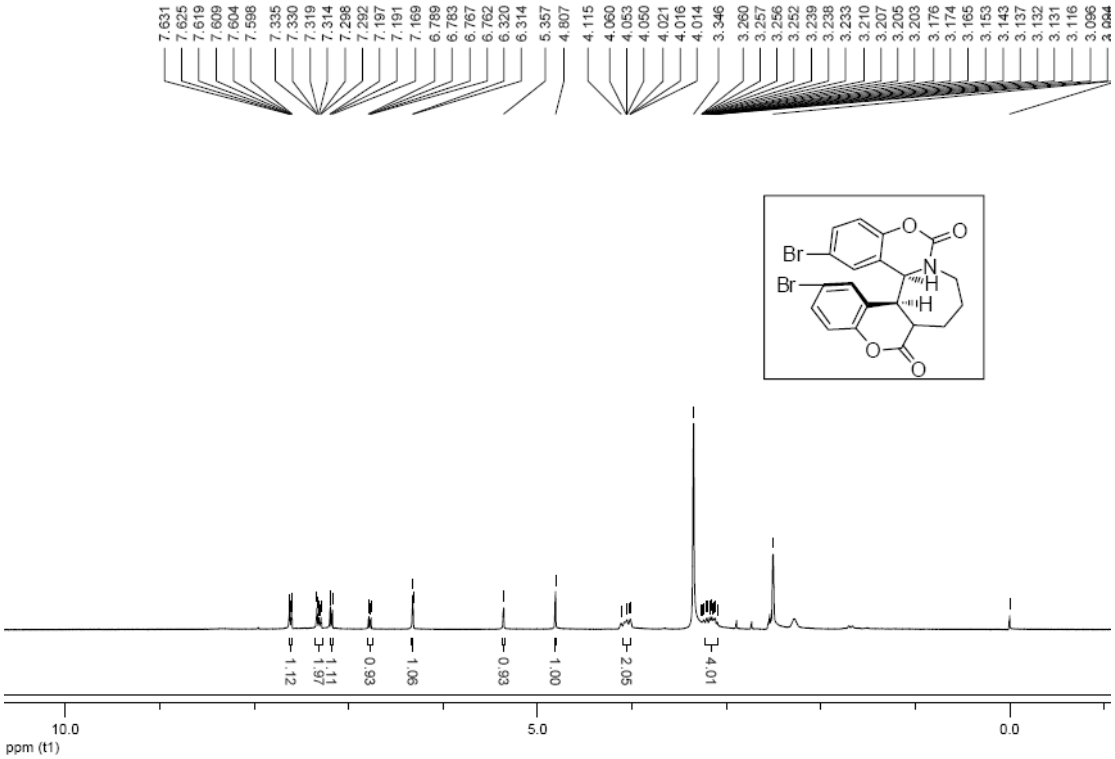
^{13}C NMR Spectrum of compound 5f



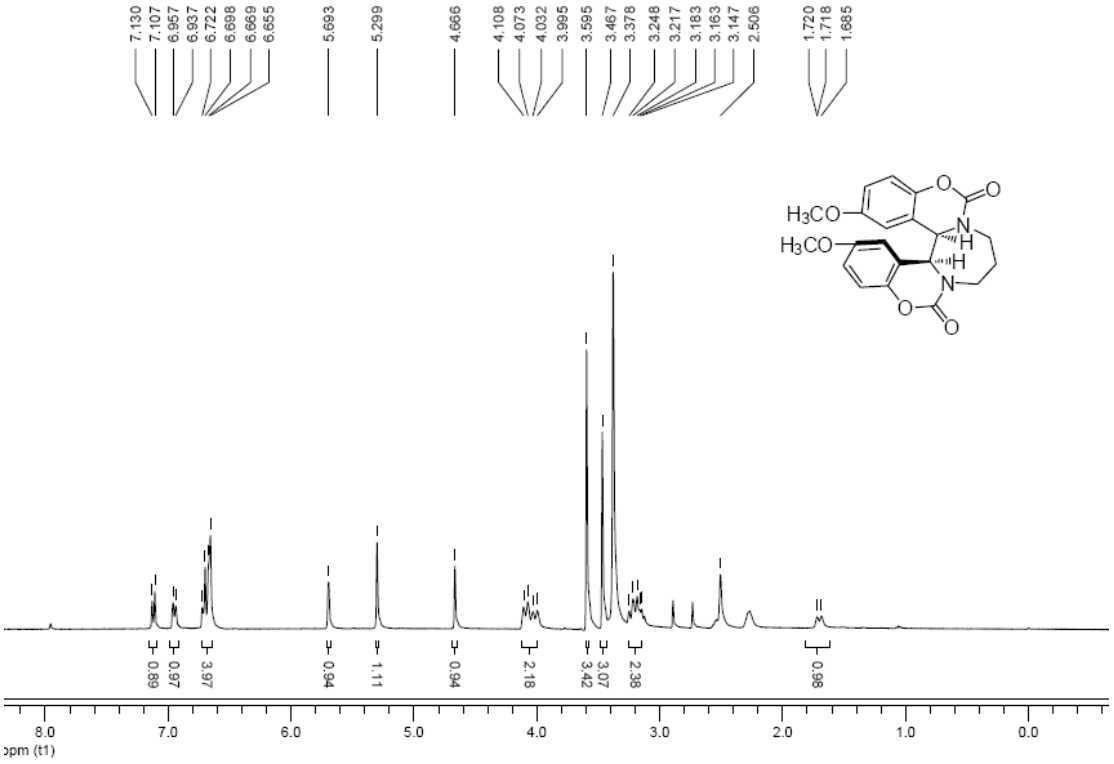
^{1}H NMR Spectrum of compound 8a



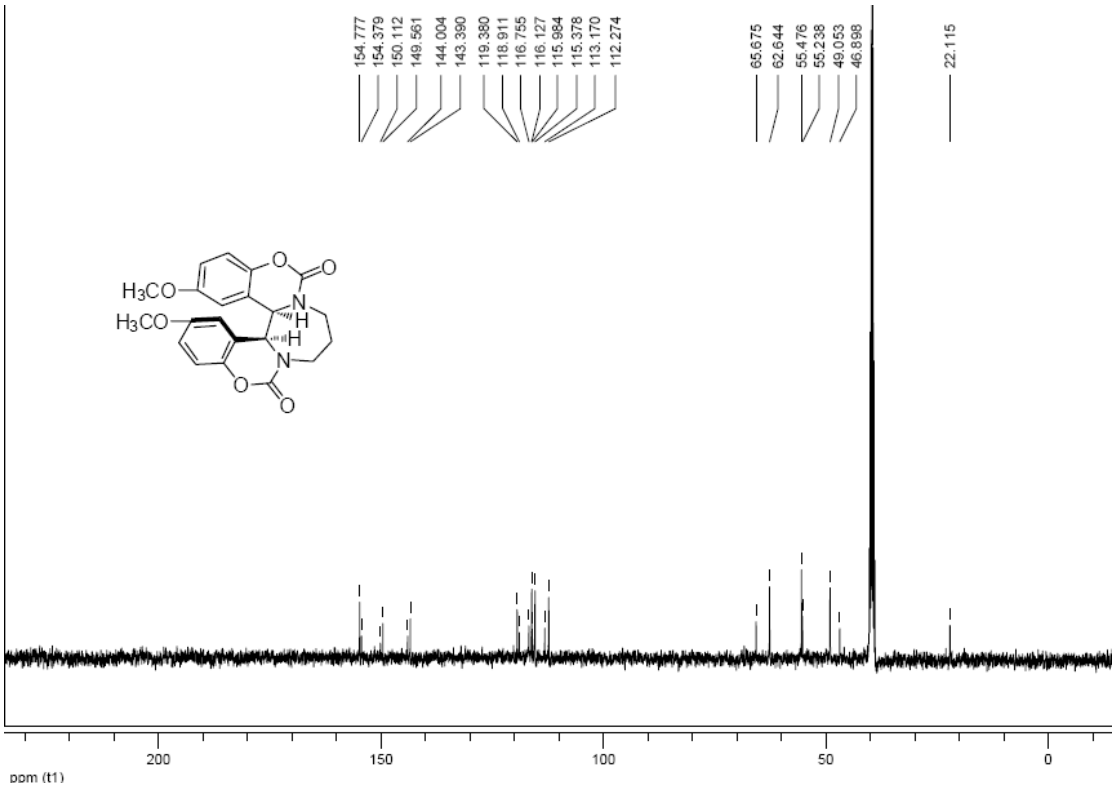
^{13}C NMR Spectrum of compound 8a



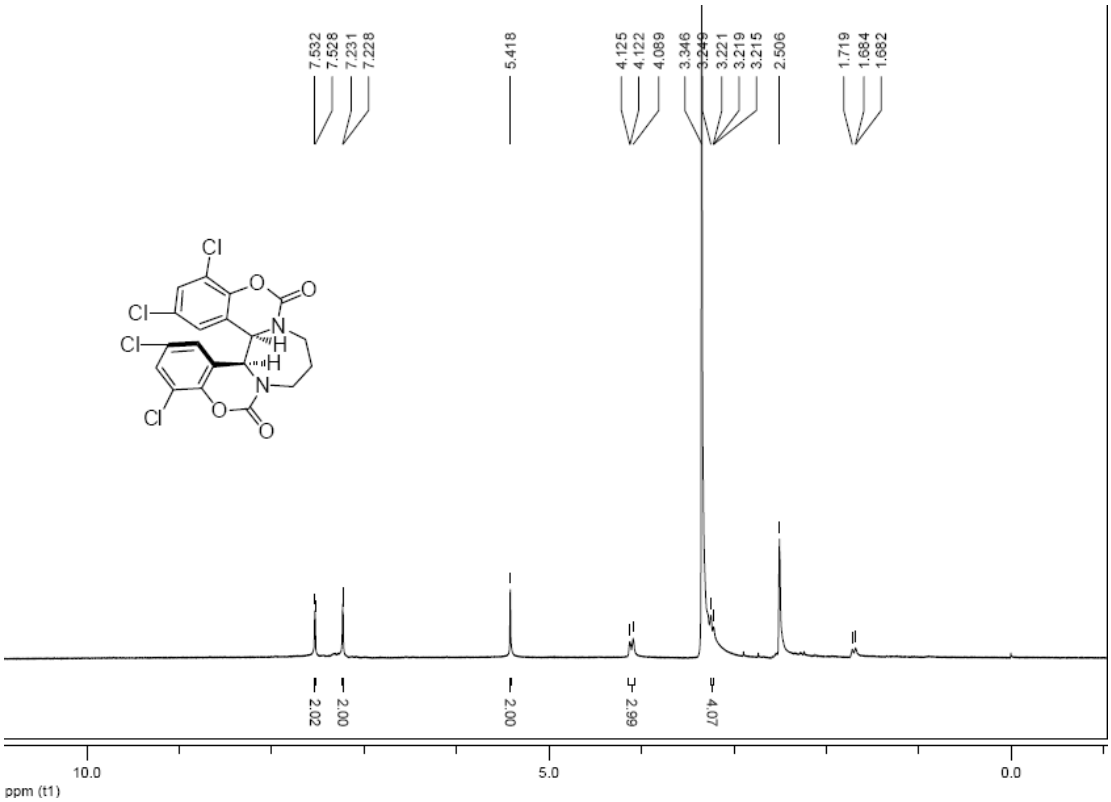
^{1}H NMR Spectrum of compound 8b



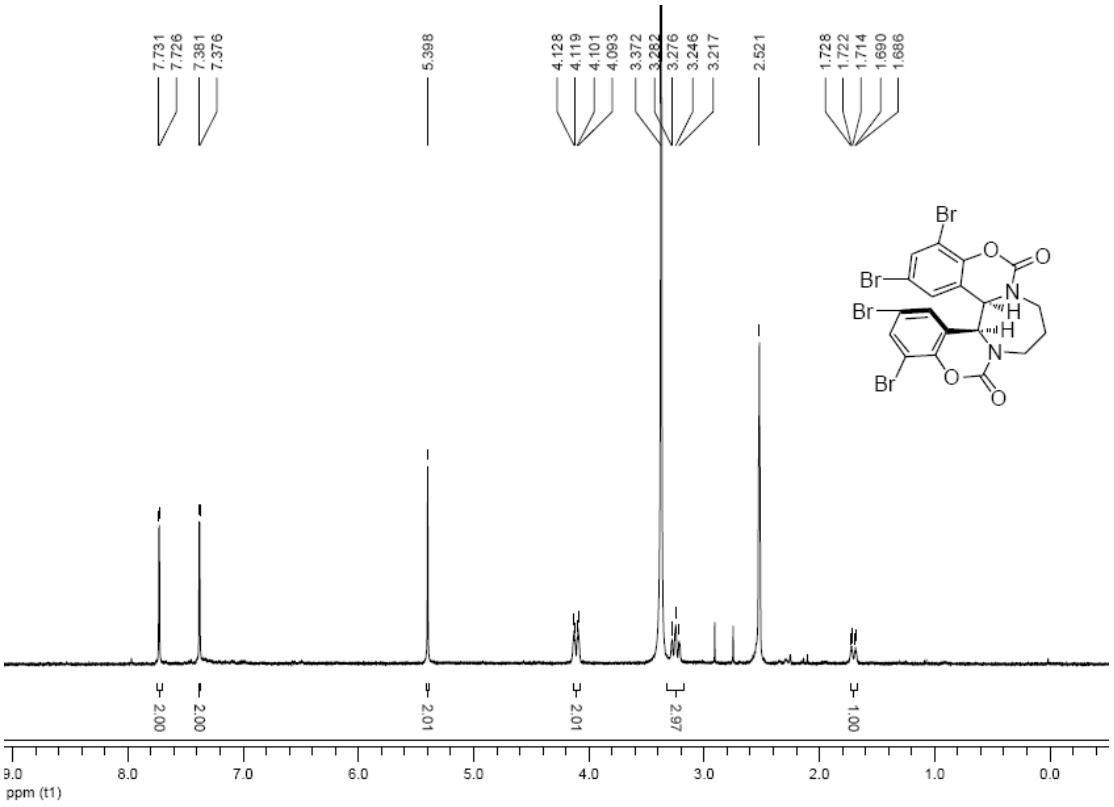
^{1}H NMR Spectrum of compound 8c



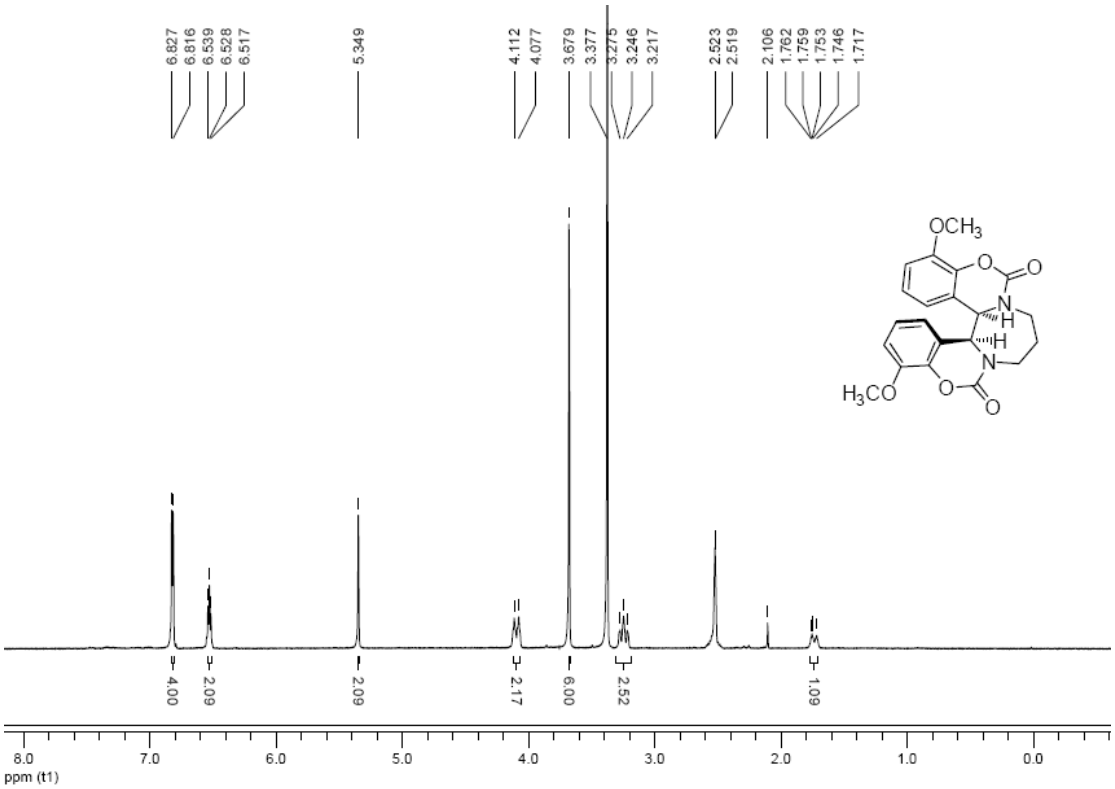
^{13}C NMR Spectrum of compound 8c



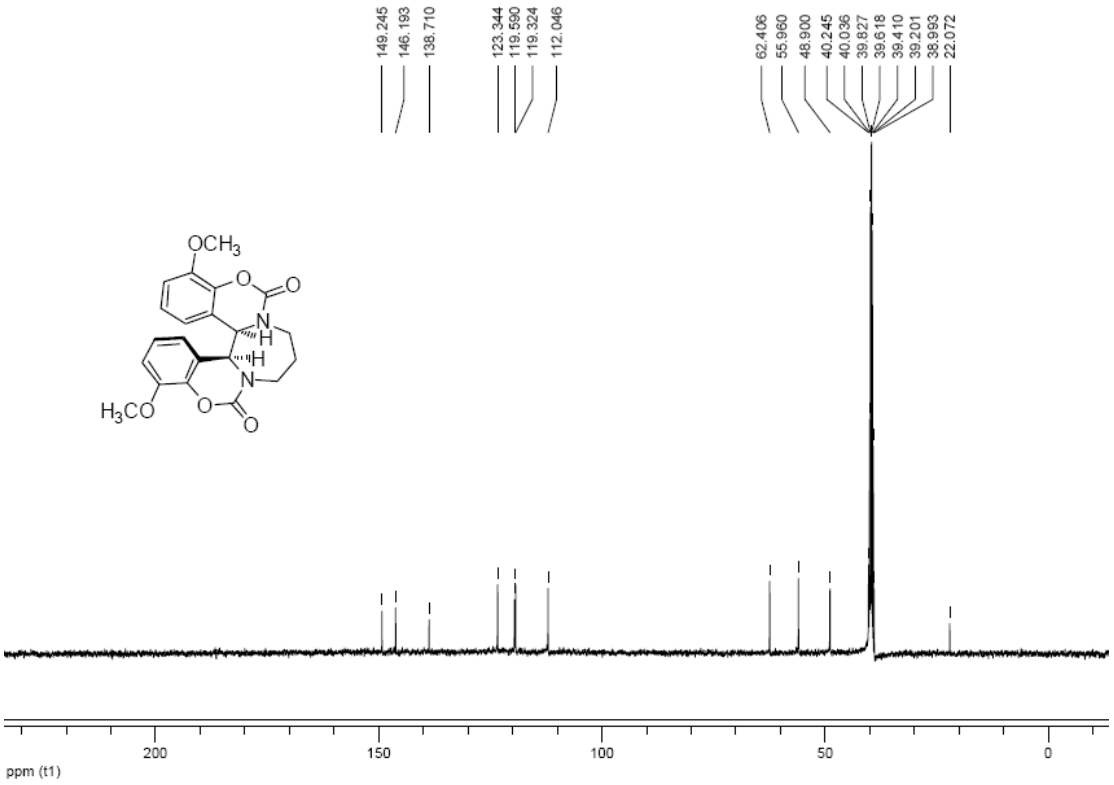
^{1}H NMR Spectrum of compound 8d



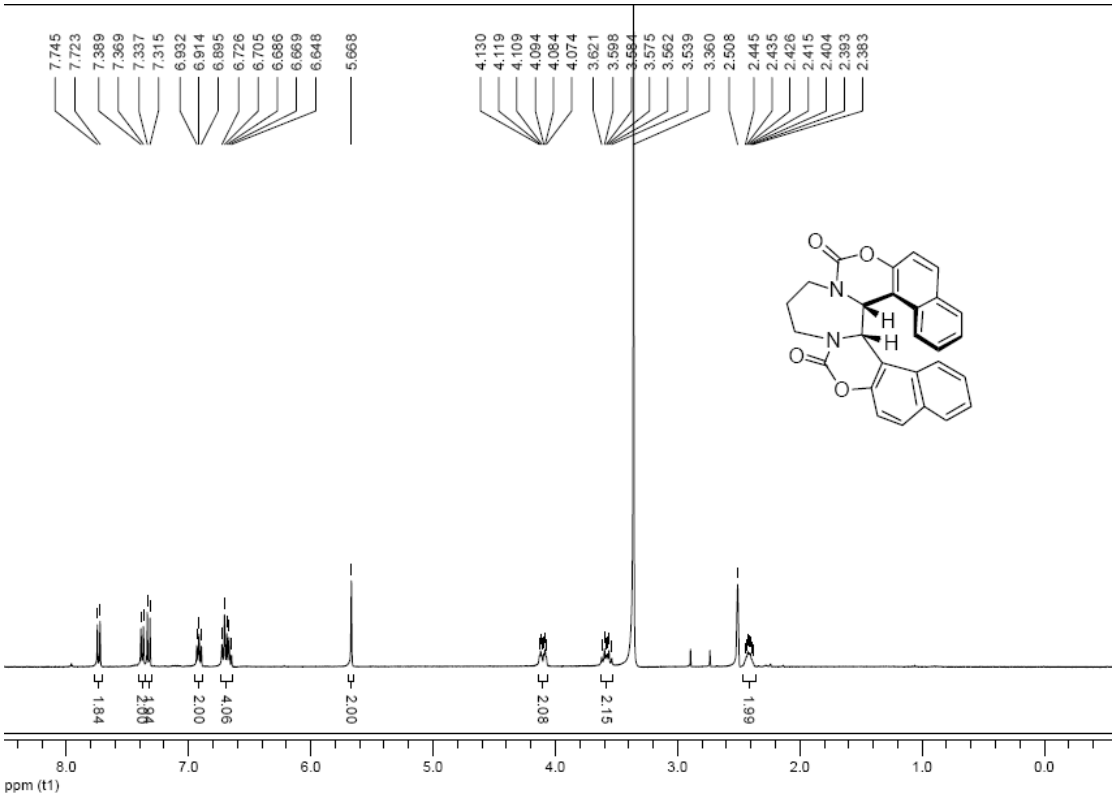
^{1}H NMR Spectrum of compound 8e



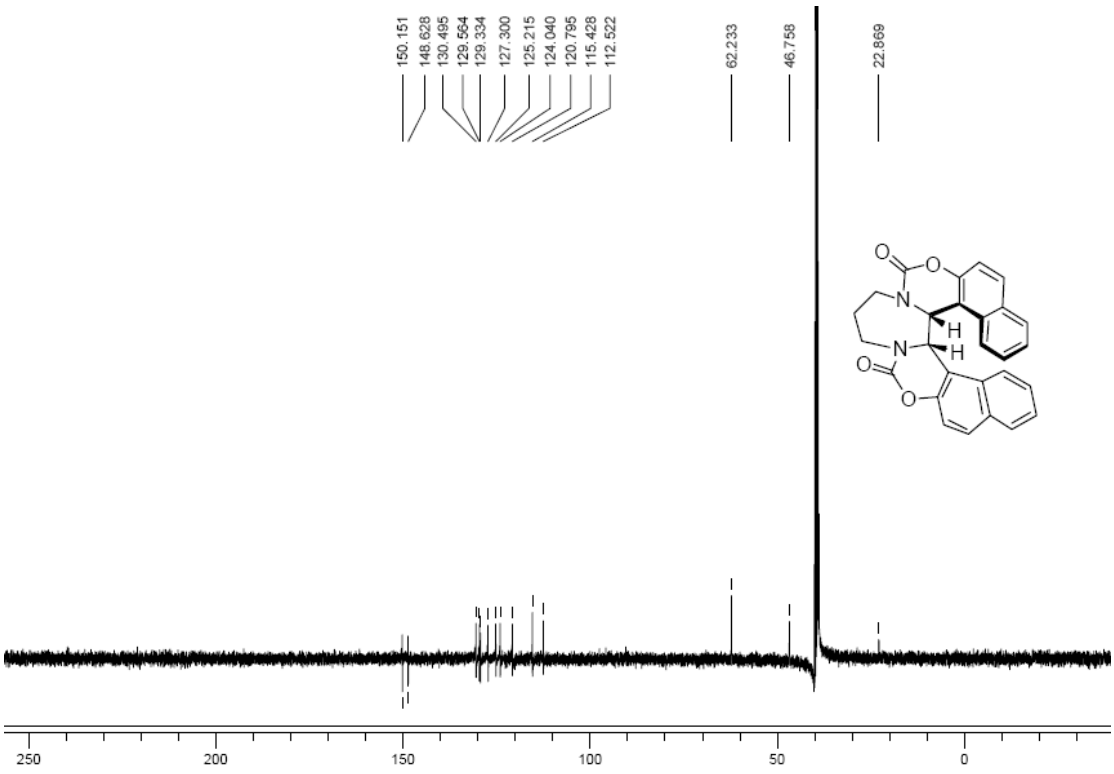
^{1}H NMR Spectrum of compound 8f



^{13}C NMR Spectrum of compound 8f



^{1}H NMR Spectrum of compound 11



^{13}C NMR Spectrum of compound 11