Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information for

Sequential oxonium-olefin-alkyne cyclization for the stereoselective synthesis of octahydro-1*H*-pyrano[3,4-c]pyridin-5-yl)methanone derivatives

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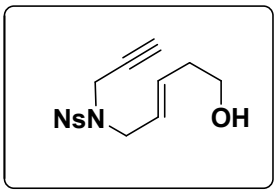
(*E*)-*N*-(5-Hydroxypent-2-enyl)-4-nitro-*N*-(prop-2-ynyl)benzenesulfonamide (6a)

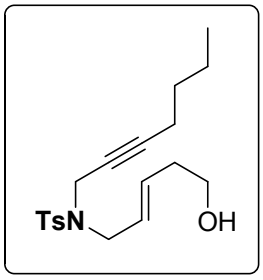


^{1}H NMR (500 MHz, $CDCl_3$) δ 8.36 (d, *J* = 7.3 Hz, 2H), 8.05 (d, *J* = 7.1 Hz, 2H), 5.81 – 5.71 (m, 1H), 5.55 – 5.47 (m, 1H), 4.15 (d, *J* = 6.3 Hz, 2H), 3.84 (d, *J* = 6.7 Hz, 2H), 3.68 (t, *J* = 6.3 Hz, 2H), 2.33 (q, *J* = 6.6 Hz, 2H), 2.04 – 2.01 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.10, 144.79, 133.66, 128.94, 125.39, 124.08, 75.89, 74.30, 61.59, 48.55, 35.78, 35.43.

(*E*)-*N*-(4-Hydroxybut-2-enyl)-4-nitro-*N*-(prop-2-ynyl)benzenesulfonamide (6b)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (d, *J* = 8.6 Hz, 2H), 8.09 (d, *J* = 7.8 Hz, 2H), 5.95-5.89 (m, 1H), 5.74 – 5.60 (m, 1H), 4.16 (d, *J* = 2.2 Hz, 4H), 3.88 (d, *J* = 6.6 Hz, 2H), 2.24 – 2.09 (m, 1H), 2.09 (t, *J* = 2.6 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.06, 144.57, 135.42, 128.89, 124.08, 123.49, 75.64, 74.46, 62.21, 47.95, 35.84.

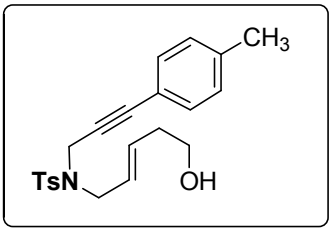
(*E*)-*N*-(Hept-2-ynyl)-*N*-(5-hydroxypent-2-enyl)-4-methylbenzenesulfonamide (6c)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 6.8 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 8H), 5.73 – 5.64 (m, 1H), 5.57 – 5.42 (m, 1H), 4.10 (s, 1H), 4.05 (t, *J* = 2.2 Hz, 2H), 3.76 (d, *J* = 6.2 Hz, 2H), 3.65 (t, *J* = 9.2 Hz, 2H), 2.42 (s, 3H), 2.33 – 2.25 (m, 2H),1.95 - 1.89 (m, 2H), 1.25 – 1.19 (m, 4H), 0.85

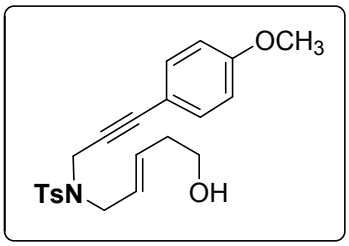
(t, *J* = 8.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.16, 136.15, 132.09, 129.26, 127.75, 126.67, 86.15, 72.42, 61.67, 48.18, 36.32, 35.51, 30.38, 21.78, 21.45, 18.06, 13.47.

(*E*)-*N*-(5-Hydroxypent-2-enyl)-4-methyl-*N*-(3-*p*-tolylprop-2-ynyl)benzenesulfonamide (6d)



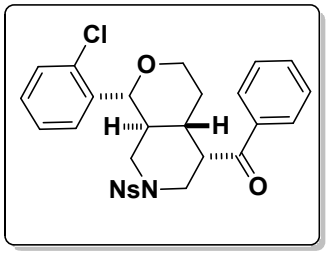
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 6.3 Hz, 1H), 7.77 (d, *J* = 6.8 Hz, 2H), 7.34 – 7.27 (m, 1H), 7.05 (d, *J* = 7.9 Hz, 2H), 6.96 (d, *J* = 8.1 Hz, 2H), 5.76 – 5.71 (m, 1H), 5.60 – 5.50 (m, 1H), 4.29 (s, 2H), 3.85 (d, *J* = 6.6 Hz, 2H), 3.66 (dd, *J* = 10.6, 4.2 Hz, 2H), 2.45 – 2.37 (m, 2H), 2.34 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.94, 144.83, 139.23, 133.47, 131.10, 129.09, 128.97, 125.68, 123.99, 118.32, 86.45, 80.36, 61.66, 48.84, 48.70, 36.83, 36.72, 35.50, 35.44, 21.50, 21.39.

(*E*)-*N*-(5-Hydroxypent-2-enyl)-*N*-(3-(4-methoxyphenyl)prop-2-ynyl)-4-methylbenzene sulfonamide (6e)



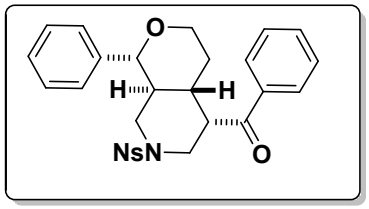
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.8 Hz, 2H), 7.25 (d, *J* = 7.0 Hz, 2H), 7.02 (d, *J* = 6.8 Hz, 2H), 6.76 (d, *J* = 7.2 Hz, 2H), 5.76 – 5.70 (, *J* = 15.2, 6.9 Hz, 1H), 5.55 – 5.50 (m, 1H), 4.27 (s, 2H), 3.84 (d, *J* = 6.6 Hz, 2H), 3.78 (s, 3H), 3.64 (t, *J* = 6.4 Hz, 2H), 2.34 (s, 3H), 2.33 – 2.28 (m, 2H), 2.00 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.50, 143.34, 135.82, 132.82, 132.44, 129.37, 127.67, 126.30, 114.13, 113.63, 85.46, 80.22, 61.59, 55.19, 48.45, 36.68, 35.46, 21.34.

(1-(2-Chlorophenyl)-7-((4-nitrophenyl)sulfonyl)octahydro-1*H*-pyrano[3,4-*c*]pyridin-5-yl)(Phenyl)methanone (8a):



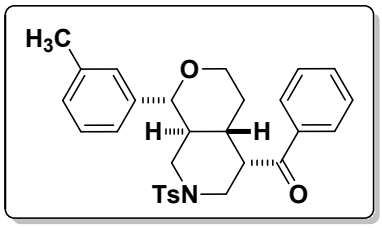
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81(d, *J* = 8.4 Hz, 2H), 7.73 – 7.64 (m, 2H), 7.62 – 7.51 (m, 3H), 7.51 – 7.41 (m, 3H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.28 (d, *J* = 8.9 Hz, 1H), 4.52 (d, *J* = 10.0 Hz, 1H), 4.19 – 4.10 (m, 2H), 3.73 – 3.62 (m, 1H), 3.49 – 3.42 (m, 1H), 3.27 (dd, *J* = 13.5, 4.4 Hz, 1H), 3.10 – 2.95 (m, 1H), 2.59 (t, *J* = 12.0 Hz, 1H), 2.06 – 1.91 (m, 2H), 1.52 – 1.40 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.7, 148.0, 137.0, 136.8, 133.4, 133.2, 132.8, 132.0, 131.4, 130.8, 129.4, 129.2, 128.9, 128.8, 128.0, 127.8, 124.0, 68.8, 48.7, 46.9, 43.2, 41.6, 41.0, 29.2; IR (KBr) υ 3062, 3010, 2935, 2841, 1753, 1648, 1583, 1512, 1419, 1365, 1298, 1218, 1173, 1136, 1069, 1016, 780 cm^{-1}; HRMS: *m/z* calcd for $C_{27}H_{25}ClN_2O_6S$ $(M+H)^+$ 541.1195; found 541.1187

(7-((4-Nitrophenyl)sulfonyl)-1-phenyloctahydro-1*H*-pyrano[3,4-*c*]pyridin-5-yl)(phenyl)methanone (8b):



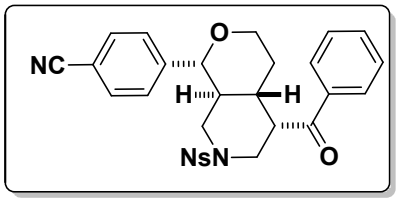
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.5 Hz, 2H), 7.70 (t, *J* = 6.3 Hz, 1H), 7.63 (t, *J* = 6.3 Hz, 3H), 7.56 (dt, *J* = 15.2, 4.4 Hz, 3H), 7.40 – 7.32 (m, 3H), 7.28 (dd, *J* = 8.7, 3.0 Hz, 2H), 4.14 – 3.96 (m, 3H), 3.66 (td, *J* = 14.7, 11.3 Hz, 2H), 3.23 (dd, *J* = 12.9, 2.3 Hz, 1H), 2.95 (t, *J* = 10.4 Hz, 1H), 2.52 (t, *J* = 12.3 Hz, 1H), 2.21 – 2.06 (m, 1H), 1.96 – 1.78 (m, 1H), 1.54 – 1.50 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.3, 147.9, 138.8, 136.6, 134.0, 133.6, 131.7, 131.6, 130.8, 130.1, 129.0, 128.7, 128.6, 128.4, 126.9, 124.2, 82.3, 68.1, 48.6, 48.1, 46.9, 44.8, 41.5, 30.1; IR (KBr) υ 3064, 3029, 2922, 2852, 1727, 1674, 1593, 1543, 1450, 1370, 1290, 1218, 1163, 1126, 1084, 1029 cm^{-1}; HRMS: *m/z* calcd for $C_{27}H_{26}N_2O_6S$ $(M+Na)^+$ 529.1404; found 529.1441

Phenyl(1-(*m*-tolyl)-7-tosyloctahydro-1*H*-pyrano[3,4-*c*]pyridin-5-yl)methanone (8c):



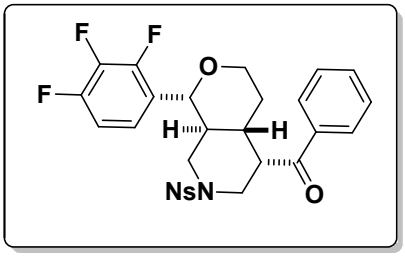
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 – 7.95 (m, 2H), 7.68 – 7.61 (m, 1H), 7.53 (t, *J* = 7.7 Hz, 2H), 7.48 (d, *J* = 8.2 Hz, 2H), 7.29 (dd, *J* = 11.6, 7.9 Hz, 3H), 7.19 – 7.11 (m, 2H), 7.04 (d, *J* = 7.5 Hz, 1H), 4.06 – 3.94 (m, 2H), 3.90 (d, *J* = 8.6 Hz, 1H), 3.59 (td, *J* = 14.9, 11.2 Hz, 2H), 3.30 (d, *J* = 10.2 Hz, 1H), 2.44 (s, 3H), 2.42 – 2.32 (m, 1H), 2.39 (s, 3H), 2.03 – 1.84 (m, 3H), 1.52 – 1.44 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.6, 143.7, 138.8, 138.56, 136.6, 134.3, 133.1, 129.7, 129.5, 129.0, 128.6, 128.3, 127.5, 124.1, 82.8, 68.1, 49.1, 47.7, 47.17, 44.2, 41.6, 30.1, 21.5; IR (KBr) υ 3025, 2921, 2856, 1730, 1678, 1590, 1478, 1450, 1385, 1285, 1261, 1218, 1165, 1129, 1083, 1045, 995, 971 cm^{-1}; HRMS: *m/z* calcd for $C_{29}H_{31}NO_4S(M+Na)^+$ 512.1866; found 512.1851

4-(5-Benzoyl-7-((4-nitrophenyl)sulfonyl)octahydro-1*H*-pyrano[3,4-*c*]pyridin-1-yl) benzonitrile (8d):



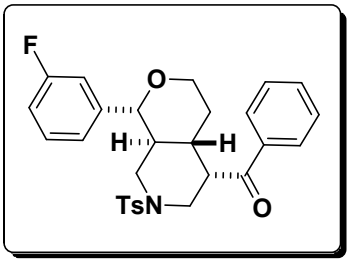
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (t, *J* = 10.2 Hz, 2H), 7.77 (d, *J* = 7.8 Hz, 1H), 7.71 – 7.66 (m, 3H), 7.62 (d, *J* = 8.6 Hz, 3H), 7.54 (t, *J* = 7.1 Hz, 2H), 7.43 (t, *J* = 10.7 Hz, 2H), 4.11 – 4.00 (m, 3H), 3.72 – 3.58 (m, 2H), 3.19 (d, *J* = 6.8 Hz, 1H), 2.90 (t, *J* = 10.5 Hz, 1H), 2.54 (t, *J* = 12.3 Hz, 1H), 2.12 (d, *J* = 9.2 Hz, 1H), 1.87 – 1.80 (m, 1H), 1.57 – 1.49 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.9, 148.0, 144.2, 136.4, 134.2, 133.9, 132.6, 131.7, 131.4, 130.8, 129.1, 128.4, 127.8, 124.3, 124.0, 118.58, 112.5, 81.5, 68.1, 48.7, 48.0, 46.7, 45.1, 41.3, 29.9; IR (KBr) υ 3029, 2951, 2891, 2240, 1751, 1675, 1514, 1469, 1380, 1340, 1220, 1168, 1078, 1029, 996, 971 cm^{-1}; HRMS: *m/z* calcd for $C_{28}H_{25}N_3O_6S$ $(M+Na)^+$ 554.1356; found 554.1402

(7-((4-Nitrophenyl)sulfonyl)-1-(2,3,4-trifluorophenyl)octahydro-1*H*-pyrano[3,4-*c*]pyridin-5-yl)(phenyl)methanone (8e):



^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07(d, *J* = 10.5 Hz, 2H), 7.83 – 7.78 (m, 1H), 7.75 – 7.69 (m, 1H), 7.68 – 7.60 (m, 3H), 7.54 (t, *J* = 7.8 Hz, 2H), 7.32 – 7.27 (m, 1H), 6.96 (t, *J* = 9.6 Hz, 1H), 4.37 (d, *J* = 7.8 Hz, 1H), 4.10 – 4.00 (m, 2H), 3.70 – 3.58 (m, 2H), 3.32 (d, *J* = 9.5 Hz, 1H), 2.92 (t, *J* = 10.2 Hz, 1H), 2.62 (t, *J* = 11.8 Hz, 1H), 2.12 (t, *J* = 11.0 Hz, 1H), 1.79 – 1.72 (m, 1H), 1.56 – 1.47 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.9, 148.0, 136.3, 134.1, 133.9, 131.6, 131.3, 130.7, 129.0, 128.4, 124.3, 73.5, 68.2, 48.7, 47.9, 46.3, 45.4, 41.2, 29.8; IR (KBr) υ 3068, 2922, 2852, 1731, 1675, 1630, 1593, 1545, 1515, 1449, 1428, 1372, 1290, 1246, 1218, 1165, 1089, 1028, 990, 967 cm^{-1}; HRMS: *m/z* calcd for $C_{27}H_{23}F_3N_2O_6S$ $(M+Na)^+$ 561.1302; found 561.1318

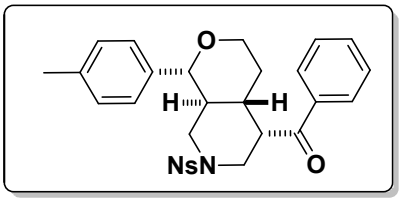
(1-(2-Fluorophenyl)-7-tosyloctahydro-1*H*-pyrano[3,4-*c*]pyridin-5-yl)(phenyl)methanone (8f):



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 11.2 Hz, 2H), 7.74 (d, *J* = 7.7 Hz, 1H), 7.65 (t, *J* = 7.0 Hz, 1H), 7.58 – 7.43 (m, 5H), 7.39 – 7.29 (m, 3H), 7.21 (d, *J* = 7.4 Hz, 1H), 4.01 (t, *J* = 9.0 Hz, 2H), 3.91 (d, *J* = 9.2 Hz, 1H), 3.65 – 3.57 (m, 2H), 3.28 (d, *J* = 10.6 Hz, 1H), 2.45 (s, 3H), 2.00 (t, *J* = 10.1 Hz, 2H), 1.95 – 1.78 (m, 2H), 1.54 – 1.47 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.5, 141.4, 136.7, 134.1, 133.2, 131.9, 130.4, 130.2, 129.9, 129.1, 128.4, 127.5, 125.6, 82.0, 68.2, 49.1, 47.7, 47.0, 44.4, 41.5, 30.0, 21.6; IR (KBr) υ 3065, 2928, 2854, 1732, 1668, 1589,

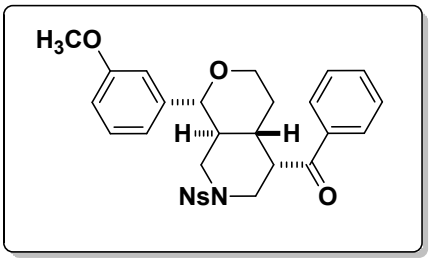
1518, 1450, 1375, 1290, 1251, 1217, 1168, 1089, 970 cm^{-1}; HRMS: *m/z* calcd for $C_{28}H_{28}FNO_4S$ $(M+Na)^+$ 516.1615; found 516.1620.

(7-((4-Nitrophenyl)sulfonyl)-1-(p-tolyl)octahydro-1H-pyrano[3,4-c]pyridin-5-yl)(phenyl)methanone (8g):



^{1}H NMR (500 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.4 Hz, 2H), 7.73 (d, *J* = 7.9 Hz, 1H), 7.67 (d, *J* = 7.1 Hz, 1H), 7.65 – 7.57 (m, 3H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.17 (s, 4H), 4.05 (t, *J* = 11.2 Hz, 2H), 3.96 (d, *J* = 9.8 Hz, 1H), 3.65 (td, *J* = 14.7, 11.3 Hz, 2H), 3.28 (d, *J* = 6.9 Hz, 1H), 2.95 (t, *J* = 11.4 Hz, 1H), 2.49 (t, *J* = 12.3 Hz, 1H), 2.36 (s, 3H), 2.13 – 2.03 (m, 1H), 1.88 – 1.80 (m, 1H), 1.53 – 1.46 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.4, 147.9, 138.3, 136.5, 135.8, 134.0, 133.6, 131.7, 131.6, 130.8, 129.4, 129.03, 128.4, 126.8, 124.2, 82.1, 68.0, 48.6, 48.0, 46.9, 44.7, 41.6, 30.1, 21.2; IR (KBr) υ 3025, 2921, 2851, 2312, 1736, 1675, 1593, 1545, 1450, 1371, 1218, 1165, 1085, 1029, 989, 966 cm^{-1}; HRMS: *m/z* calcd for $C_{28}H_{28}N_2O_6S$ $(M+Na)^+$ 543.1560; found 543.1573

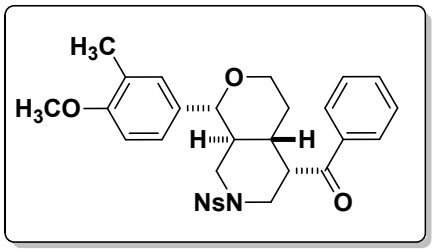
(1-(3-Methoxyphenyl)-7-((4-nitrophenyl)sulfonyl)octahydro-1H-pyrano[3,4-c]pyridin-5-yl)(phenyl)methanone (8h):



^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 9.5 Hz, 2H), 7.74 – 7.71 (m, 1H), 7.71 – 7.66 (m, 1H), 7.66 – 7.61 (m, 2H), 7.59 (t, *J* = 7.7 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 2H), 7.30 – 7.26 (m, 1H),

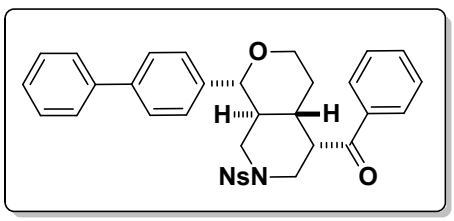
6.90 – 6.82 (m, 3H), 4.11 – 4.00 (m, 2H), 3.98 (d, *J* = 9.5 Hz, 1H), 3.83 (s, 3H), 3.72 – 3.59 (m, 2H), 3.31 – 3.23 (m, 1H), 2.96 (t, *J* = 13.0 Hz, 1H), 2.58 – 2.46 (m, 1H), 2.12 – 2.06 (m, 1H), 1.86 – 1.79 (m, 1H), 1.54 – 1.40 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.3, 159.9, 147.8, 140.3, 136.5, 134.0, 133.6, 131.7, 131.6, 130.8, 129.7, 129.0, 128.3, 124.20, 119.4, 114.5, 112.0, 82.2, 68.0, 55.2, 48.5, 48.0, 46.8, 44.7, 41.5, 30.0; IR (KBr) υ 3012, 2923, 2852, 1731, 1673, 1592, 1489, 1453, 1453, 1370, 1288, 1265, 1215, 1161, 1082, 1041, 990 cm^{-1}; HRMS: *m/z* calcd for $C_{28}H_{28}N_2O_7S$ $(M+Na)^+$ 559.1509; found 559.1521

(1-(4-Methoxy-3-methylphenyl)-7-((4-nitrophenyl)sulfonyl)octahydro-1*H*-pyrano[3,4-c]pyridin-5-yl)(phenyl)methanone (8i):



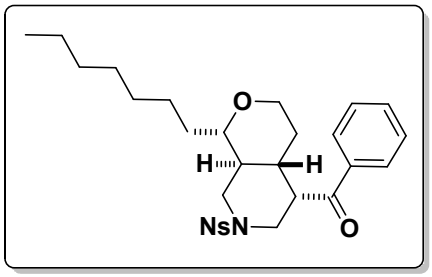
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (d, *J* = 11.8 Hz, 2H), 7.99 (d, *J* = 11.2 Hz, 2H), 7.80 (d, *J* =11.6 Hz, 2H), 7.67 (t , *J* = 7.4 Hz, 1H), 7.55 (t, *J* = 7.8 Hz, 2H), 7.07 (dd, *J* = 13.6, 5.4 Hz, 2H), 6.84 (t, *J* = 7.1 Hz, 1H), 4.01 (d, *J* = 8.6 Hz, 2H), 3.87 (s, 3H), 3.65 (td, *J* = 10.9, 3.9 Hz, 1H), 3.59 – 3.51 (m, 1H), 3.37 (d, *J* = 10.0 Hz, 1H), 2.55 (t, *J* = 11.6 Hz, 1H), 2.25 (s, 3H), 2.07 – 1.85 (m, 4H), 1.51 – 1.46 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.2, 158.0, 150.2, 142.4, 136.5, 134.2, 130.3, 129.1, 128.5, 128.3, 127.3, 125.5, 124.4, 109.9, 82.1, 68.0, 55.3, 49.0, 47.7, 47.2, 44.3, 41.8, 30.1, 16.4; IR (KBr) υ 3075, 3015, 2928, 2845, 1727, 1664, 1593, 1543, 1451, 1365, 1281, 1210, 1160, 1126, 1091, 1020, 975 cm^{-1}; HRMS: *m/z* calcd for $C_{29}H_{30}N_2O_7S$ $(M+H)^+$ 551.1846; found 551.1815

(1-([1,1'-Biphenyl]-4-yl)-7-((4-nitrophenyl)sulfonyl)octahydro-1*H*-pyrano[3,4-c]pyridin-5-yl)(phenyl)methanone (8j):



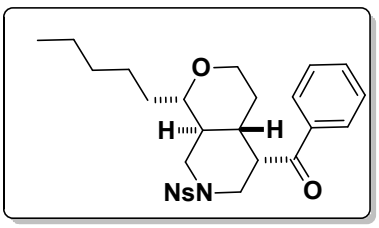
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (d, *J* = 11.8 Hz, 2H), 8.04 – 7.98 (m, 2H), 7.83 – 7.78 (m, 2H), 7.70 – 7.61 (m, 5H), 7.56 (t, *J* = 7.8 Hz, 2H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.38 (dd, *J* = 7.7, 5.3 Hz, 3H), 4.03 - 3.80 (m, 3H), 3.72 – 3.56 (m, 2H), 3.41 (d, *J* = 9.9 Hz, 1H), 2.57 (t, *J* = 11.6 Hz, 1H), 2.19 – 1.91 (m, 3H), 1.38 – 1.25 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.1, 150.2, 142.3, 141.7, 140.5, 137.6, 136.4, 134.2, 129.1, 128.8, 128.5, 128.3, 127.6, 127.5, 127.4, 127.5, 124.4, 82.2, 68.1, 49.0, 47.7, 47.1, 44.4, 41.7, 30.0; IR (KBr) υ 3085, 3026, 2945, 2872, 1787, 1692, 1583, 1503, 1465, 1370, 1290, 1210, 1175, 1106, 1091, 1014, 985 cm^{-1}; HRMS: *m/z* calcd for $C_{33}H_{30}N_2O_6S$ $(M+Na)^+$ 605.1680; found 605.1717

(1-Heptyl-7-((4-nitrophenyl)sulfonyl)octahydro-1*H*-pyrano[3,4-*c*]pyridin-5-yl)(phenyl) methanone (8k):



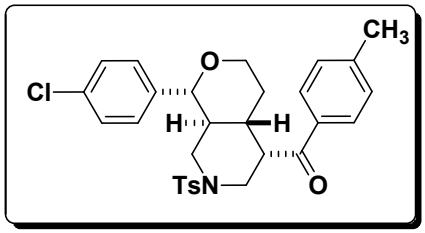
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 – 8.25 (m, 2H), 7.90 – 7.84 (m, 2H), 7.77 (d, *J* = 8.3 Hz, 2H), 7.60 – 7.53 (m, 1H), 7.44 (dd, *J* = 10.6, 4.8 Hz, 2H), 4.06 – 3.94 (m, 2H), 3.89 (d, *J* = 9.7 Hz, 1H), 3.64 (d, *J* = 4.1 Hz, 1H), 3.39 (t, *J* = 11.9 Hz, 1H), 3.02 – 2.81 (m, 2H), 2.54 - 2.40 (m, 1H), 2.20 (t, *J* = 11.6 Hz, 1H), 1.88 – 1.73 (m, 2H), 1.40 – 1.20 (m, 13H), 0.89 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.4, 150.0, 143.6, 136.5, 133.2, 128.7, 128.6, 127.9, 124.1, 79.9, 68.0, 48.2, 47.0, 42.9, 41.3, 38.3, 32.8, 31.8, 30.9, 29.3, 29.3, 25.0, 22.6, 14.0; IR (KBr) υ 3060, 3015, 2912, 2862, 1749, 1654, 1581, 1535, 1450, 1381, 1290, 1216, 1173, 1120, 1061, 1019, 973 960 cm^{-1}; HRMS: *m/z* calcd for $C_{28}H_{36}N_2O_6S$ $(M+H)^+$ 529.2367; found 529.2347

(7-((4-Nitrophenyl)sulfonyl)-1-pentyloctahydro-1*H*-pyrano[3,4-c]pyridin-5-yl)(phenyl) methanone (8l):



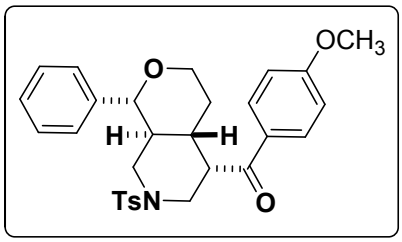
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 10.0 Hz, 2H), 7.85 (d, *J* = 11.4 Hz, 2H), 7.78 (d, *J* = 9.6 Hz, 2H), 7.61 – 7.50 (m, 1H), 7.44 (dd, *J* = 10.6, 4.8 Hz, 2H), 4.05 – 3.95 (m, 2H), 3.92 (d, *J* = 9.8 Hz, 1H), 3.64 (d, *J* = 4.2 Hz, 1H), 3.39 (t, *J* = 8.5 Hz, 1H), 2.97 (d, *J* = 8.8 Hz, 1H), 2.92 – 2.83 (m, 1H), 2.60 – 2.42 (m, 1H), 2.19 (t, *J* = 10.0 Hz, 1H), 1.85 – 1.70 (m, 1H), 1.52 – 1.46 (m, 2H), 1.37 – 1.25 (m, 8H), 0.90 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.4, 150.0, 143.6, 136.5, 133.2, 128.7, 128.6, 127.9, 124.1, 79.9, 68.0, 48.2, 47.0, 42.9, 41.3, 38.2, 32.7, 31.9, 29.3, 24.6, 22.6, 14.0; IR (KBr) υ 3055, 3016, 2938, 2352, 1748, 1684, 1595, 1519, 1460, 1386, 1295, 1209, 1175, 1106, 1086, 1016, 975, 962 cm^{-1}; HRMS: *m/z* calcd for $C_{26}H_{32}N_2O_6S$ $(M+H)^+$ 501.2054; found 501.2024

1-(4-Chlorophenyl)-7-tosyloctahydro-1H-pyrano[3,4-c]pyridin-5-yl)(p-tolyl)methanone (8m)



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.2 Hz, 2H), 7.48 (d, *J* = 9.4 Hz, 2H), 7.37 (d, *J* = 7.8 Hz, 2H), 7.34 – 7.27 (m, 4H), 7.25 – 7.22 (m, 2H), 4.04 – 3.98 (m, 1H), 3.97 – 3.90 (m, 2H), 3.63 – 3.51 (m, 2H), 3.25 (d, *J* = 10.5 Hz, 1H), 2.46 (s, 3H), 2.45 (s, 3H), 2.37 – 2.31 (m, 1H), 1.96 (t, *J* = 14.4 Hz, 1H), 1.91 – 1.84 (m, 2H), 1.50 – 1.43 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.06, 145.27, 143.92, 137.63, 134.46, 134.11, 133.04, 129.84, 129.78, 129.10, 128.54, 128.38, 127.54, 81.96, 68.18, 49.15, 47.57, 44.56, 41.53, 30.03, 29.73, 21.78, 21.59.

(4-Methoxyphenyl)-(1-phenyl-7-tosyloctahydro-1H-pyrano[3,4-c]pyridin-5-yl)methanone (8n)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.2 Hz, 1H), 7.63 (d, *J* = 7.5 Hz, 2H), 7.49 (d, *J* = 7.8 Hz, 3H), 7.39 (dd, *J* = 14.1, 7.1 Hz, 2H), 7.34 – 7.26 (m, 3H), 7.02 – 6.97 (m, 1H), 6.80 – 6.73 (m, 1H), 4.38 (d, *J* = 9.8 Hz, 1H), 4.31 – 4.23 (m, 2H), 4.19 (d, *J* = 11.2 Hz, 1H), 4.01 – 3.92 (m, 1H), 3.83 (d, *J* = 10.0 Hz, 1H), 3.77 – 3.70 (m, 3H), 3.45 (d, *J* = 6.5 Hz, 1H), 2.99 (d, *J* = 8.0 Hz, 1H), 2.53 (dd, *J* = 11.4, 3.0 Hz, 1H), 2.39 (d, *J* = 3.5 Hz, 3H), 2.12 – 2.08 (m, 2H), 1.54 (d, *J* = 11.6 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 207.27, 171.11, 158.19, 149.56, 143.63, 140.04, 138.57, 136.04, 134.61, 133.71, 130.16, 129.68, 128.47, 127.55, 126.09, 120.21, 111.87, 110.64, 101.21, 77.84, 67.03, 60.44, 55.82, 55.48, 45.10, 39.22, 30.97, 21.50, 14.18.

NMR spectroscopic data:

1D (^{1}H, ^{1}H-^{1}H Homo-nuclear Decoupling and ^{13}C) and 2D (DQCOSY, NOESY, TOCSY and HSQC) NMR spectra of 8a dissolved in $CDCl_3$, are recorded at 298 K on a Bruker Avance 700 MHz and 600 MHz (^{13}C at 150 MHz) spectrometers Chemical shifts (δ) are reported in ppm and tetra methyl silane (TMS) δ=0.00 ppm for ^{1}H ($CDCl_3$ δ=77.00 ppm for ^{13}C) is used as the internal standard. Coupling constants (*J*) are reported in hertz (Hz). The following abbreviations are used to designate the multiplicities: d=doublet, ddd= doublet of doublet of doublet, tdd= triplet of doublet of doublet, td=triplet of doublet, q=quartet, m=multiplet.

The structure of 8a is unambiguously conformed by the incisive NMR studies such as 2D-NOESY, and *J*-coupling analysis.

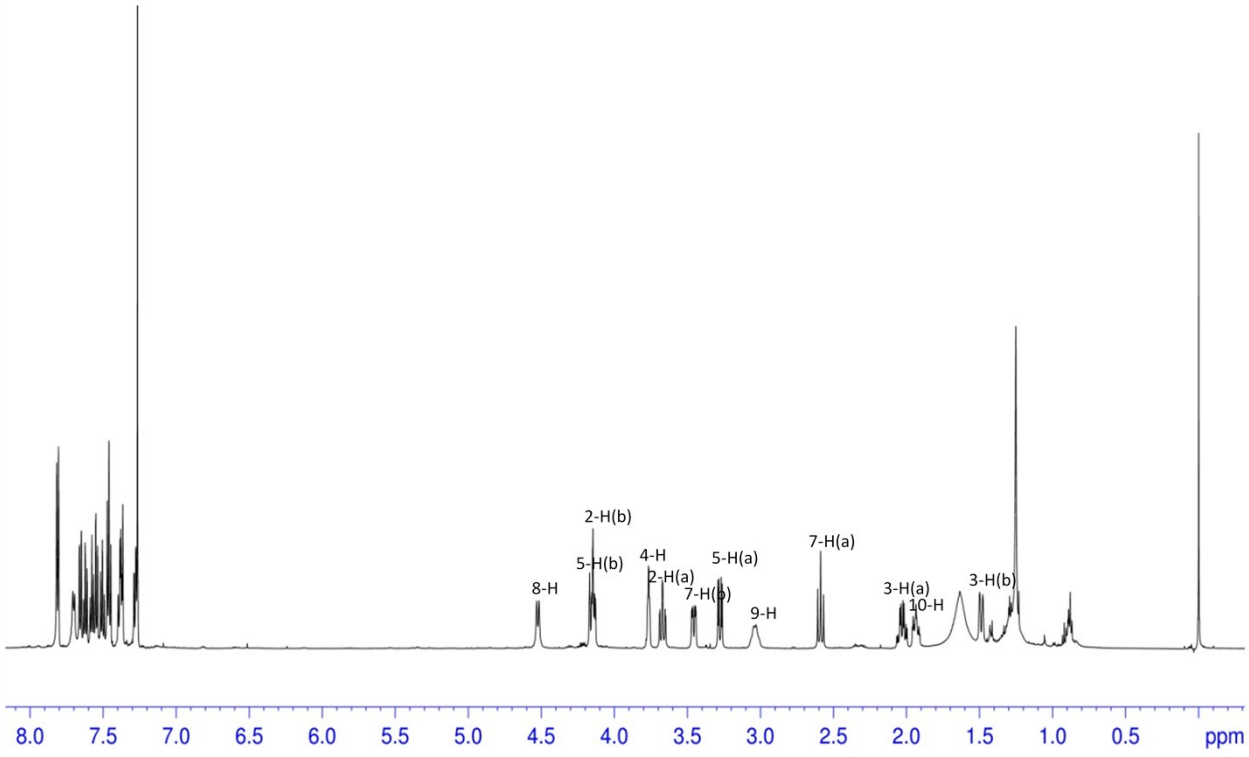
Table 1. ^{1}H NMR chemical shift (ppm) and coupling constant (Hz) values of compound-8a in $CDCl_3$ (298 K, 700 MHz):

Proton	(δ) ppm	multiplicity	Coupling constant *(J)* values (Hz)
2-H(a)	3.66	td	$^2J_{2\text{-H(a)}/2\text{-H(b)}}$ = 12.3 $^3J_{2\text{-H(a)}/3\text{-H(a)}}$ = 12.1 $^3J_{2\text{-H(a)}/3\text{-H(b)}}$ = 3.5
2-H(b)	4.13	ddd	$^2J_{2\text{-H(b)}/2\text{-H(a)}}$ = 12.3 $^3J_{2\text{-H(b)}/3\text{-H(a)}}$ = 4.8 $^3J_{2\text{-H(b)}/3\text{-H(b)}}$ = 1.9
3-H(a)	2.03	m	$^2J_{3\text{-H(a)}/3\text{-H(b)}}$ = 12.8 $^3J_{3\text{-H(a)}/2\text{-H(a)}}$ = 12.1

			$^{3}J_{\text{3-H(a)/10-H}} = 12.0$ $^{3}J_{\text{3-H(a)/2-H(b)}} = 4.8$
3-H(b)	1.48	m	$^{2}J_{\text{3-H(b)/3-H(a)}} = 12.8$ $^{3}J_{\text{3-H(b)/2-H(a)}} = 3.5$ $^{3}J_{\text{3-H(b)/2-H(b)}} = 1.9$ $^{3}J_{\text{3-H(b)/10-H}} = 1.5$
4-H	3.76	m	$^{3}J_{\text{4-H/5-H(a)}} = 4.4$ $^{3}J_{\text{4-H/10-H}} = 4.2$ $^{3}J_{\text{4-H/5-H(b)}} = 1.8$
5-H(a)	3.27	dd	$^{2}J_{\text{5-H(a)/5-H(b)}} = 12.8$ $^{3}J_{\text{5-H(a)/4-H}} = 4.4$
5-H(b)	4.15	dt	$^{2}J_{\text{5-H(b)/5-H(a)}} = 12.8$ $^{3}J_{\text{5-H(b)/4-H}} = 1.8$
7-H(a)	2.58	t	$^{2}J_{\text{7-H(a)/7-H(b)}} = 12.2$ $^{3}J_{\text{7-H(a)/9-H}} = 12.0$
7-H(b)	3.45	ddd	$^{2}J_{\text{7-H(b)/7-H(a)}} = 12.2$ $^{3}J_{\text{7-H(b)/9-H}} = 4.4$
8-H	4.52	d	$^{3}J_{\text{8-H/9-H}} = 9.9$

9-H	3.03	m	$^3J_{9\text{-H}/7\text{-H(a)}} = 12.0$ $^3J_{9\text{-H}/10\text{-H}} = 12.5$ $^3J_{9\text{-H}/8\text{-H}} = 9.9$ $^3J_{9\text{-H}/7\text{-H(b)}} = 4.4$
10-H	1.93	m	$^3J_{10\text{-H}/9\text{-H}} = 12.5$ $^3J_{10\text{-H}/3\text{-H(a)}} = 12.0$ $^3J_{10\text{-H}/4\text{-H}} = 4.2$ $^3J_{10\text{-H}/3\text{-H(b)}} = 1.5$

Figure 2. ^{1}H NMR spectrum of **8a** with chemical shift assignments ($CDCl_3$, 298 K, AVANCE 600 MHz)



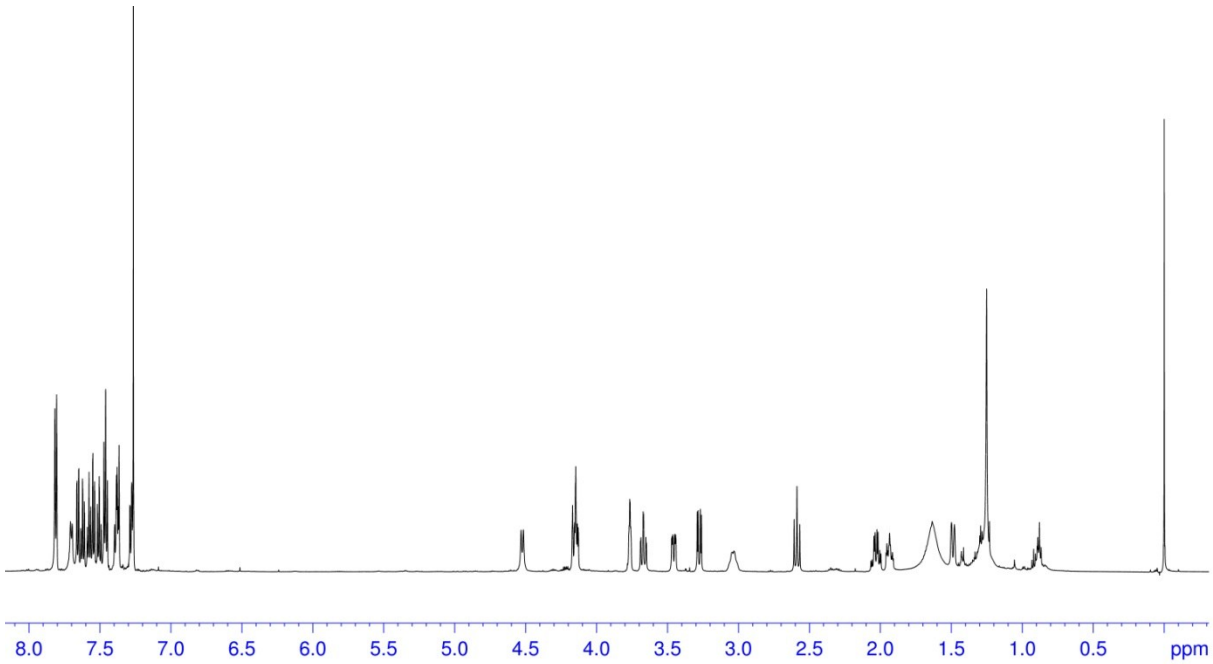


Figure 2. ^{1}H NMR spectrum of **8a** ($CDCl_3$, 298 K, AVANCE 600 MHz)

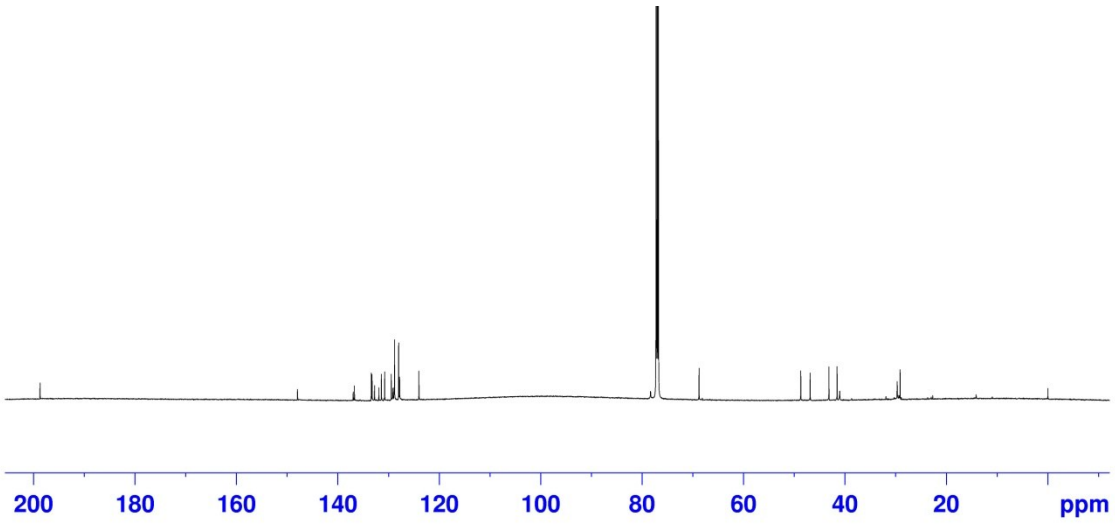


Figure 3. ^{13}C NMR spectrum of **8a** ($CDCl_3$, 298 K, AVANCE 150 MHz)

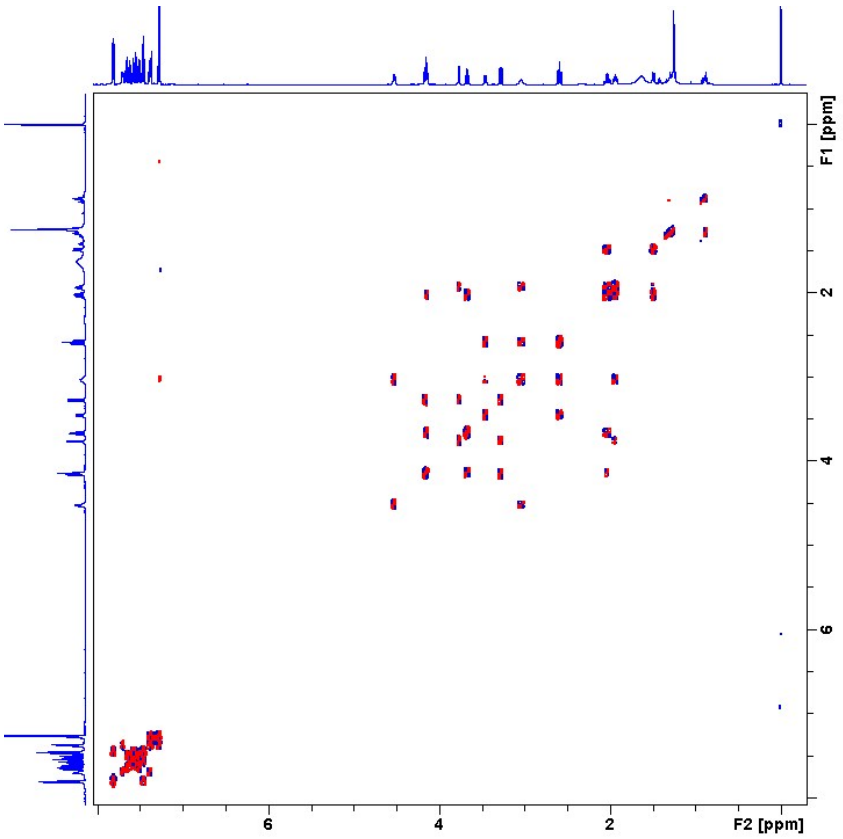


Figure 4. DQFCOSY spectrum of **8a** ($CDCl_3$, 298 K, AVANCE 600 MHz)

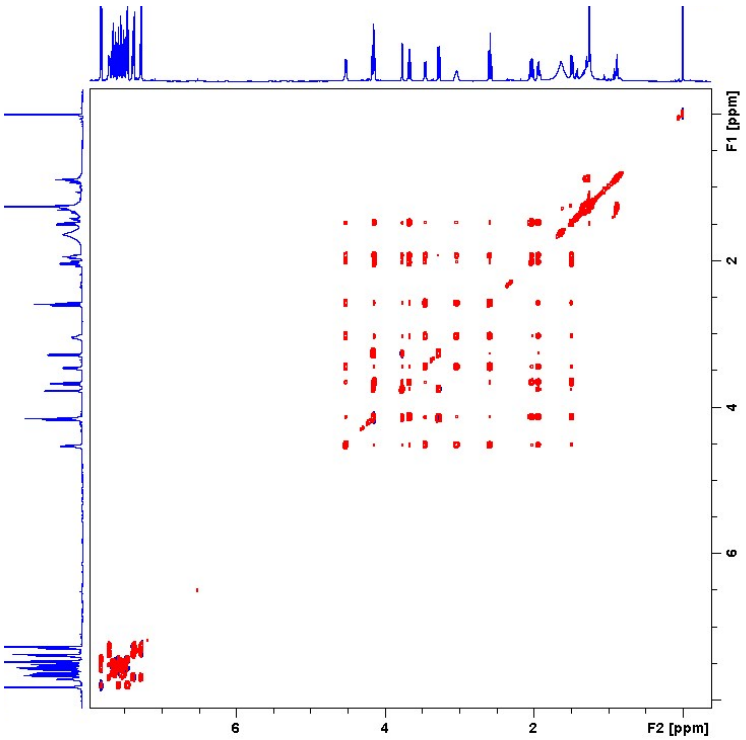


Figure 5. TOCSY spectrum of **8a** ($CDCl_3$, 298 K, AVANCE 600 MHz)

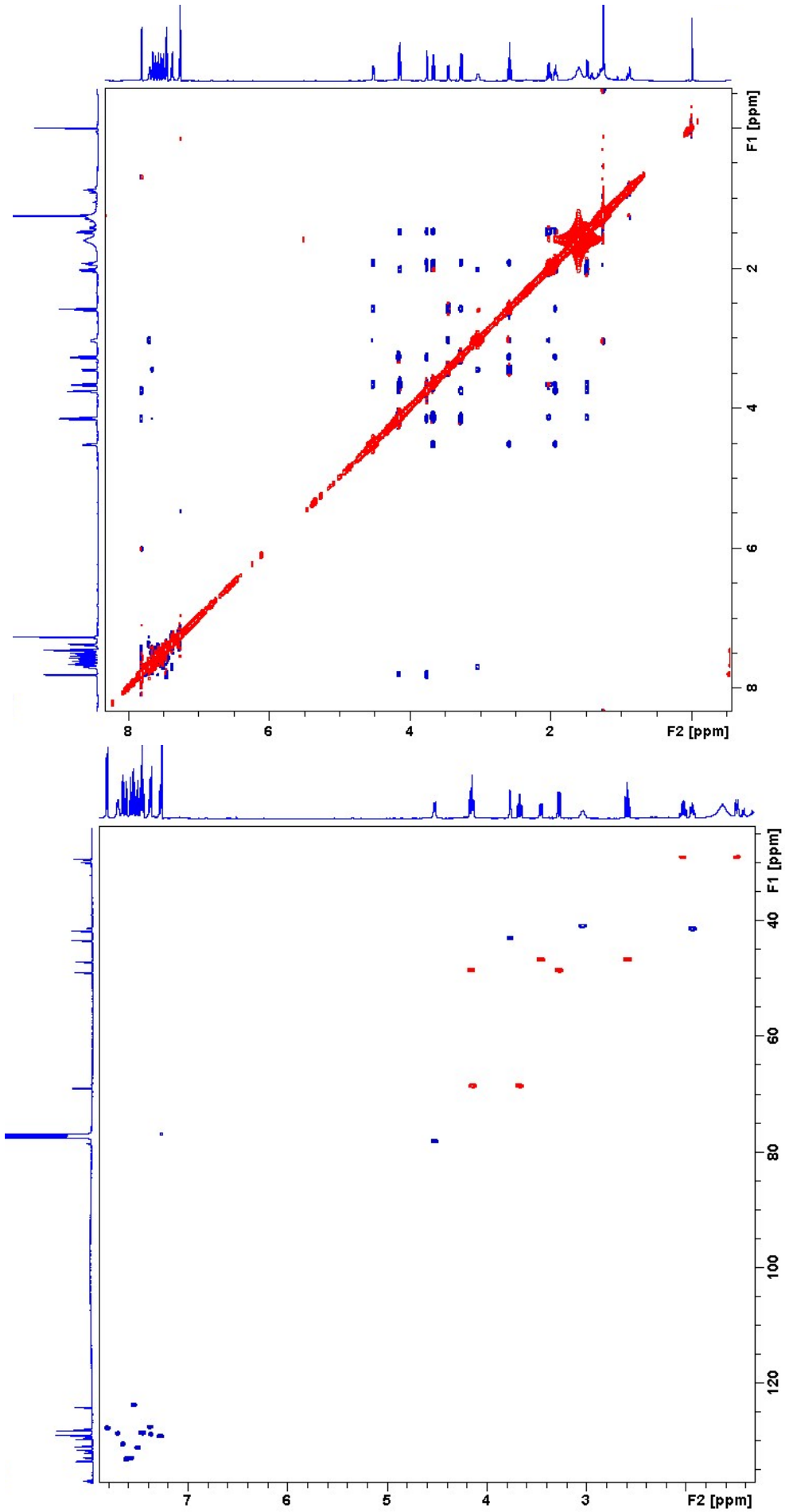


Figure 6. NOESY spectrum of **8a** ($CDCl_3$, 298 K, AVANCE 600 MHz)

Figure 7. HSQC spectrum of **8a** ($CDCl_3$, 298 K, AVANCE 600 MHz)

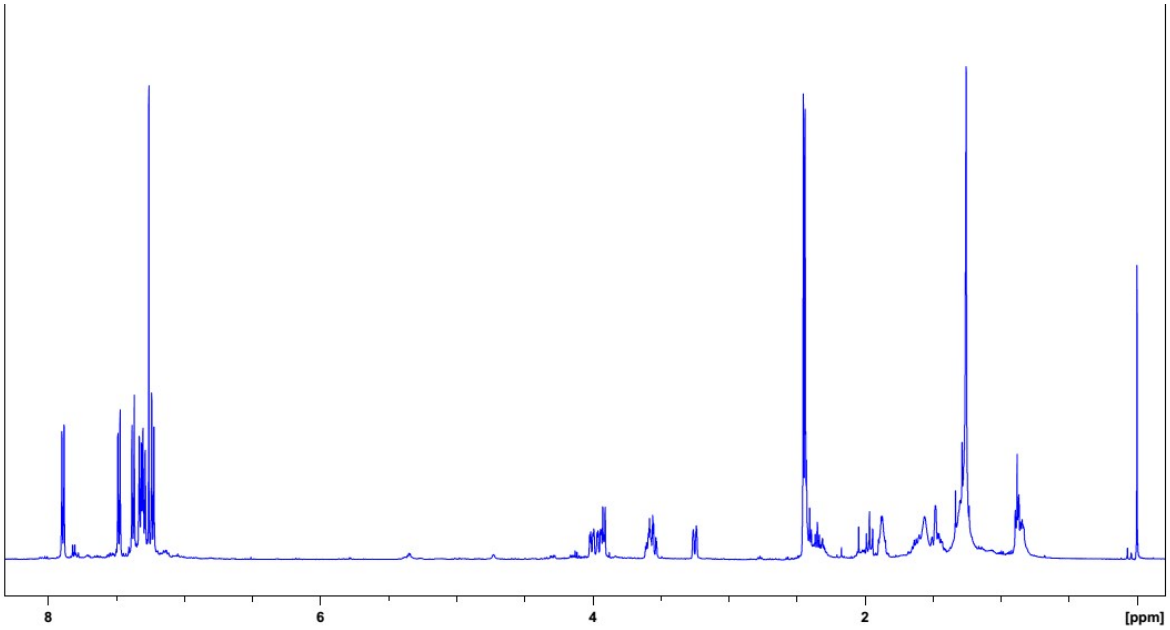


Figure 1. ^{1}H NMR spectrum of **8m** ($CDCl_3$, 298 K, AVANCE 500 MHz)

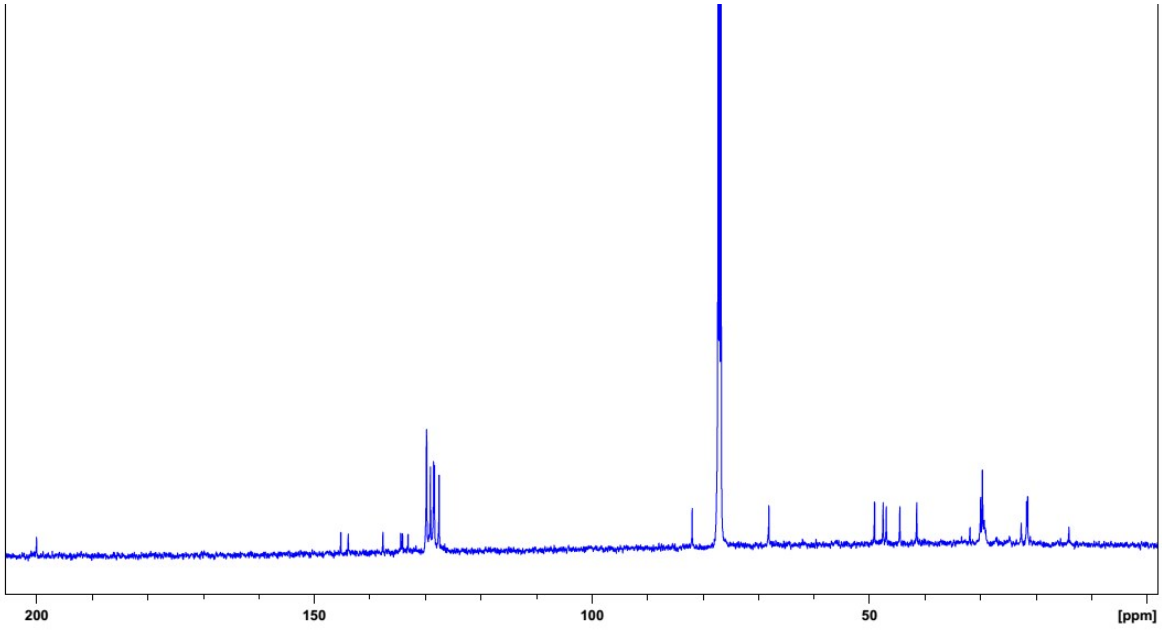


Figure 2. ^{13}C NMR spectrum of **8m** ($CDCl_3$, 298 K, AVANCE 125 MHz)

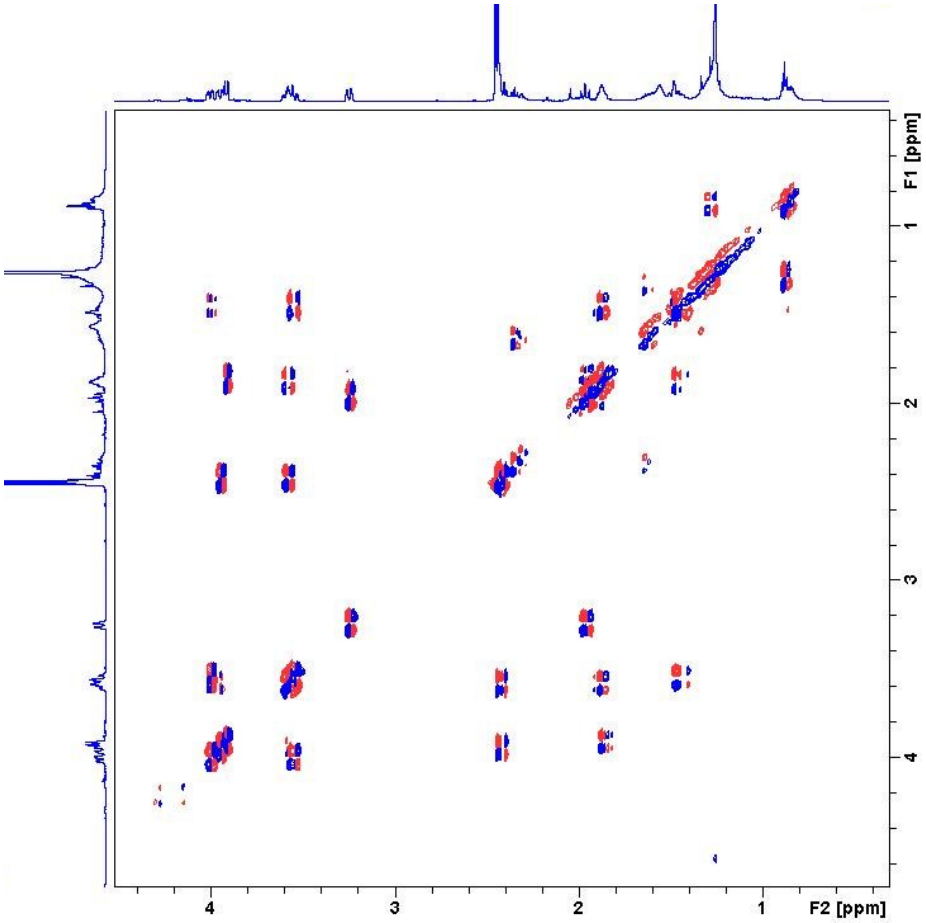


Figure 3. Expanded region of DQFCOSY spectrum of **8m** ($CDCl_3$, 298 K, AVANCE 500 MHz)

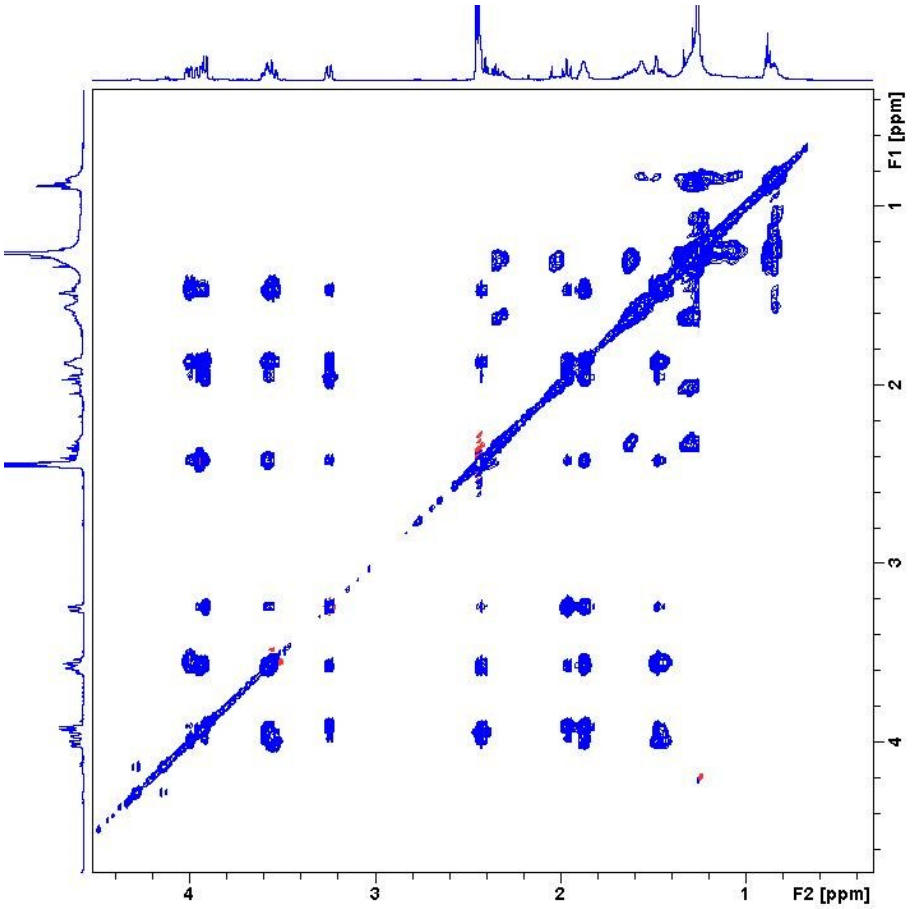


Figure 4. Expanded region of TOCSY spectrum of **8m** ($CDCl_3$, 298 K, AVANCE 500 MHz)

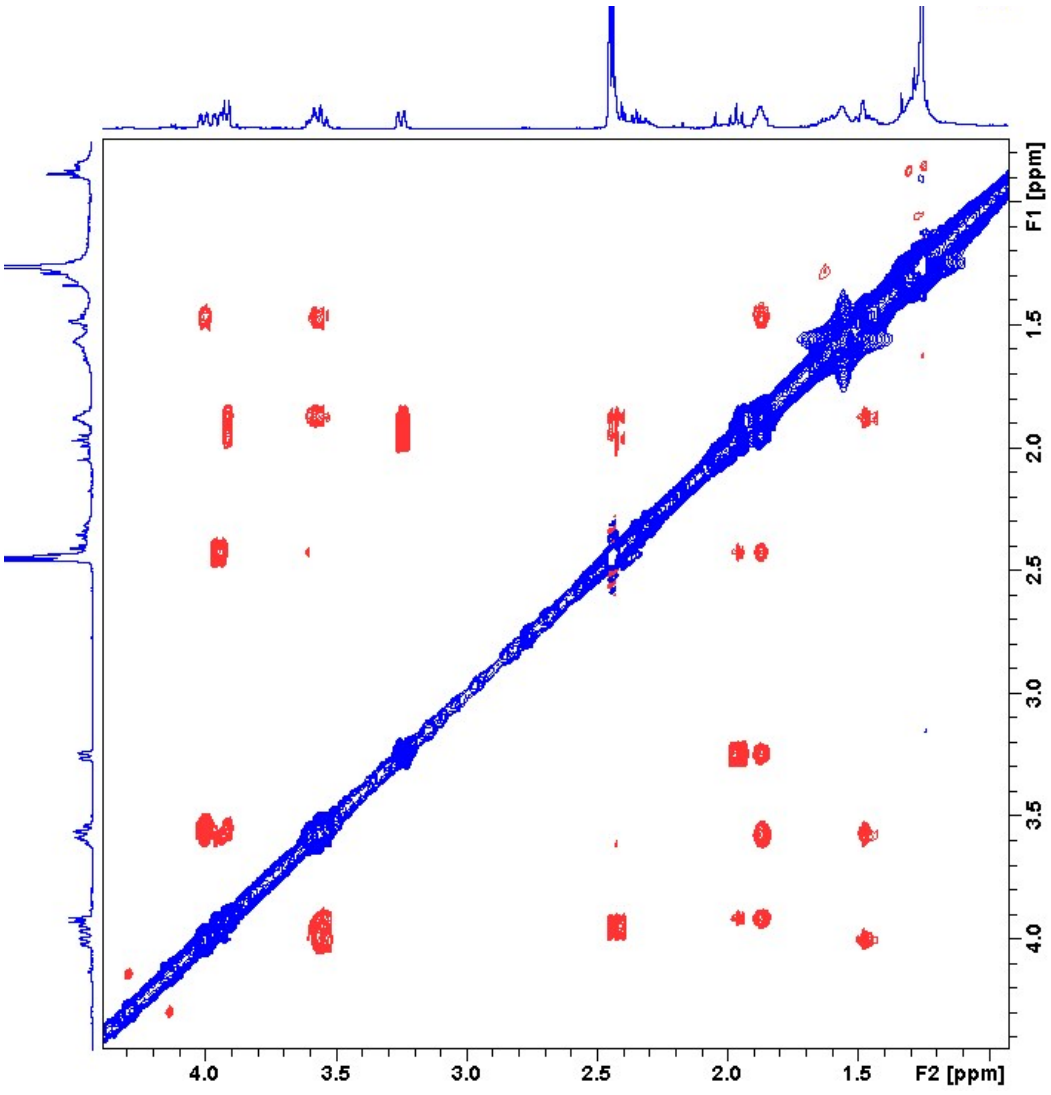


Figure 5. Expanded region of TOCSY spectrum of **8m** ($CDCl_3$, 298 K, AVANCE 500 MHz)

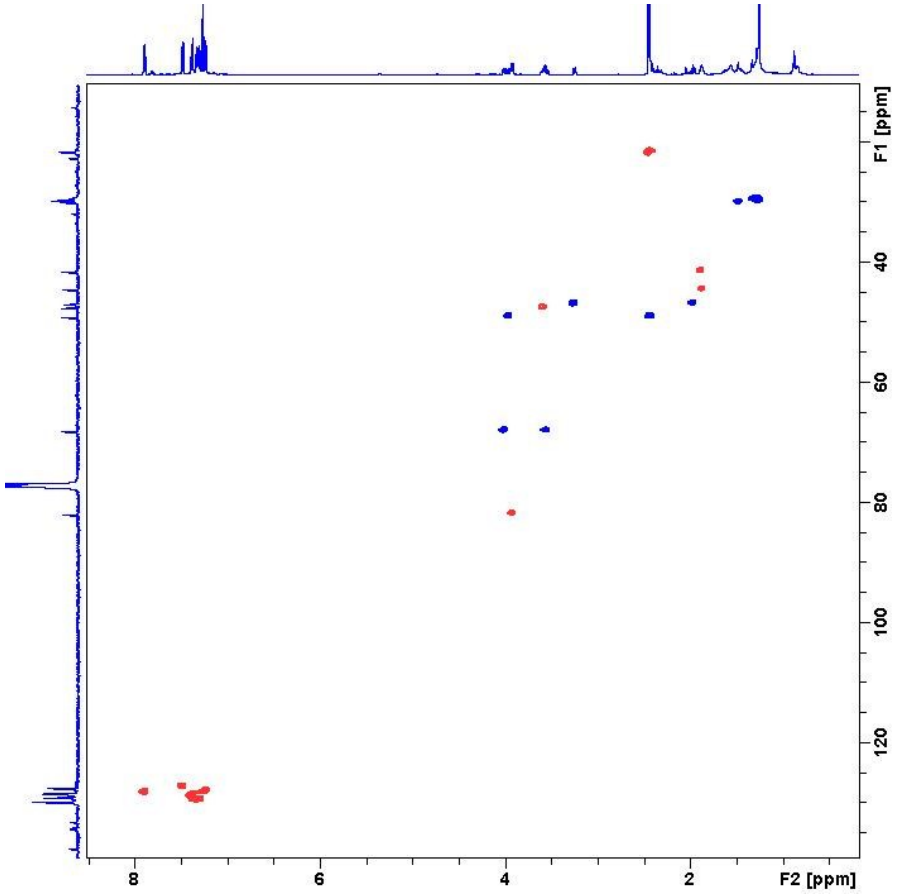
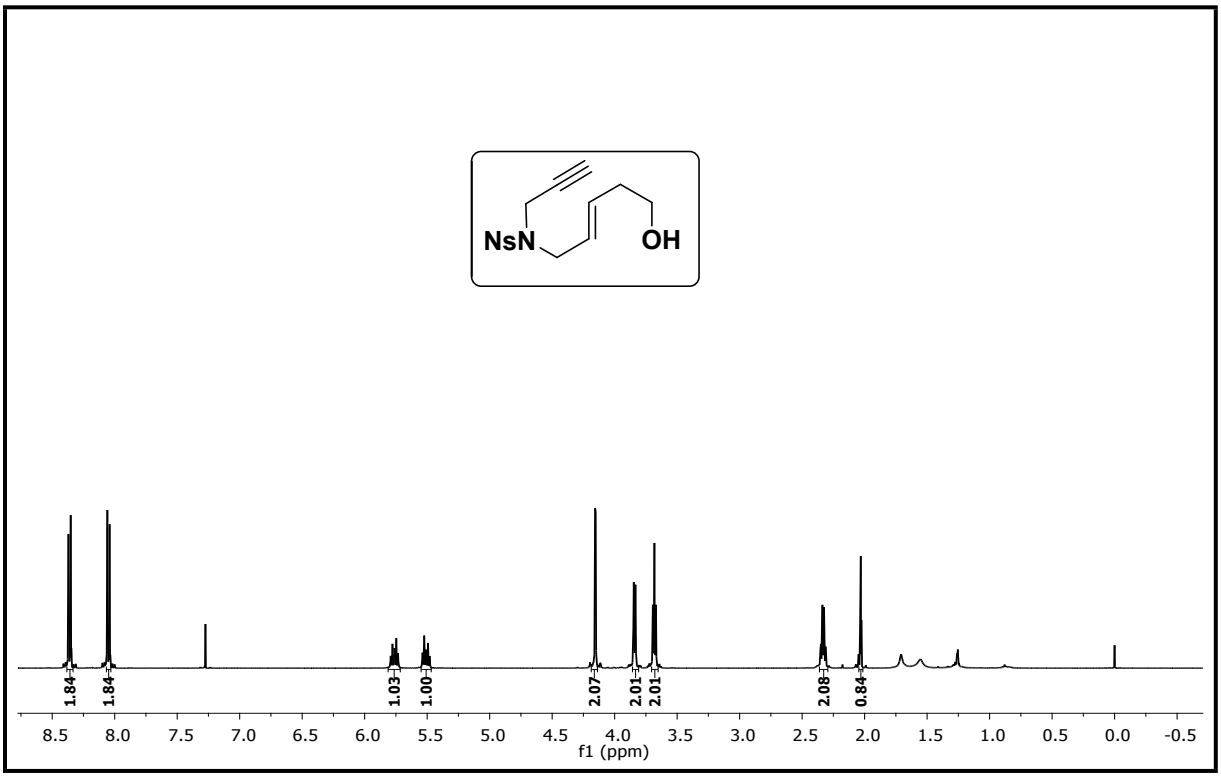
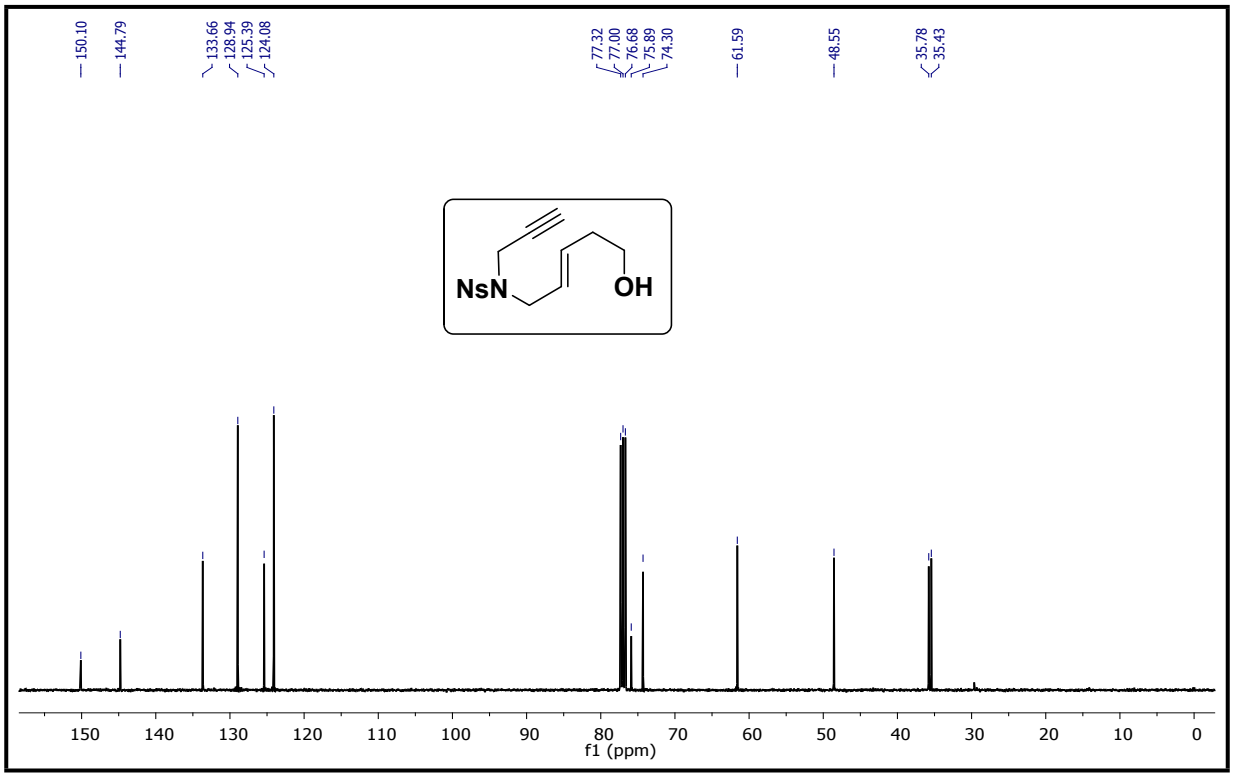


Figure 6. HSQC spectrum of **8m** ($CDCl_3$, 298 K, AVANCE 500 MHz)

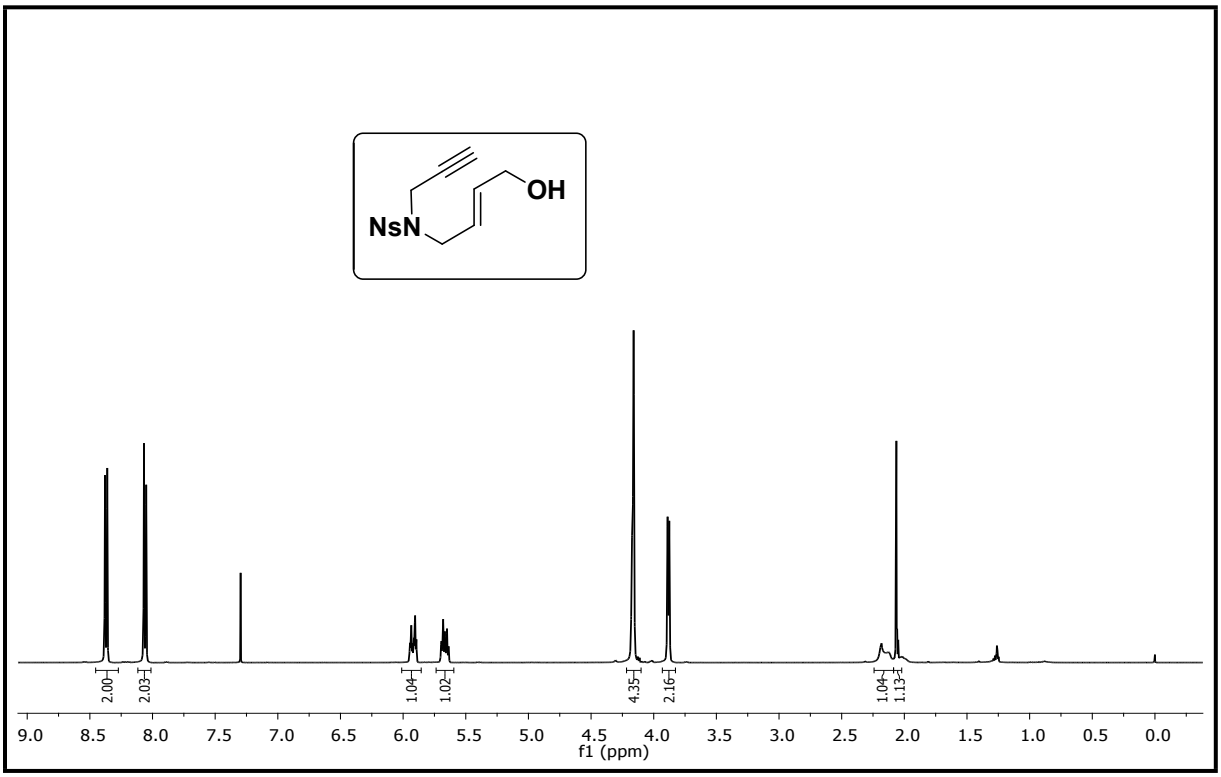
^{1}H NMR Spectra of compound 6a (500 MHz, $CDCl_3$)



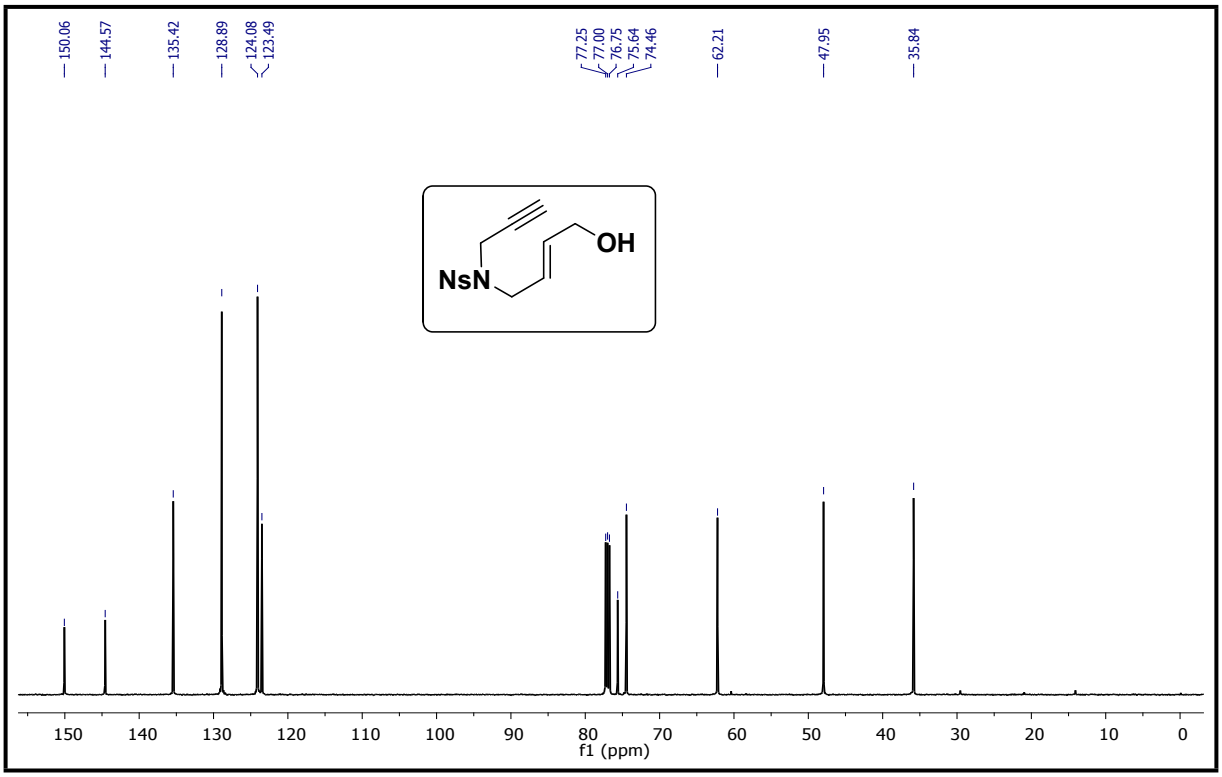
^{13}C NMR Spectra of compound 6a (100 MHz, $CDCl_3$)



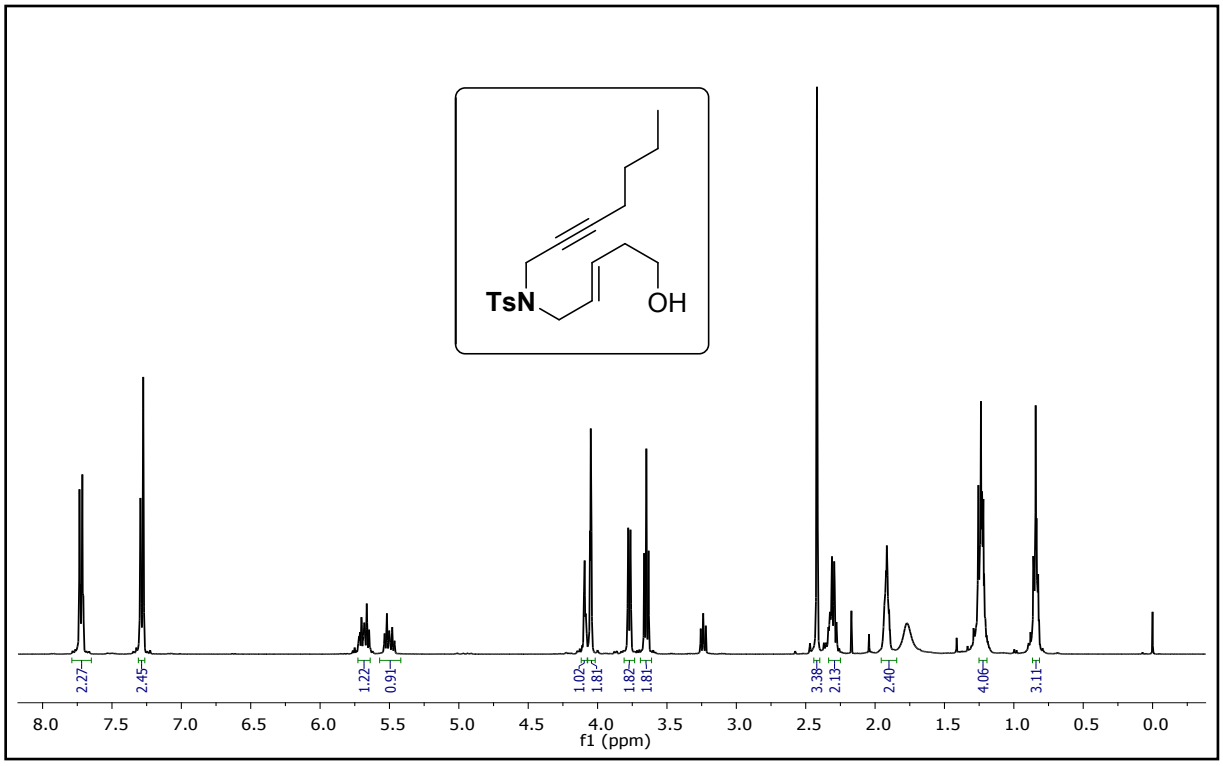
^{1}H NMR Spectra of compound 6b (500 MHz, $CDCl_3$)



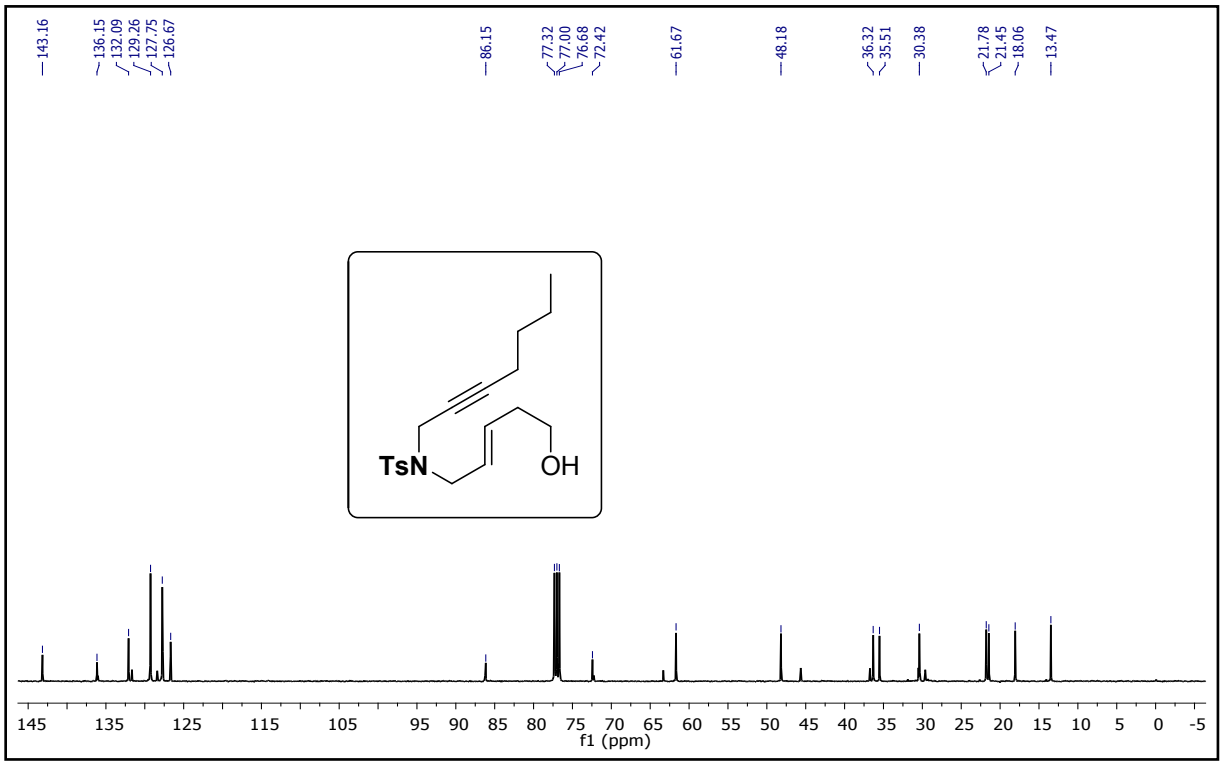
^{13}C NMR Spectra of compound 6b (125 MHz, $CDCl_3$)



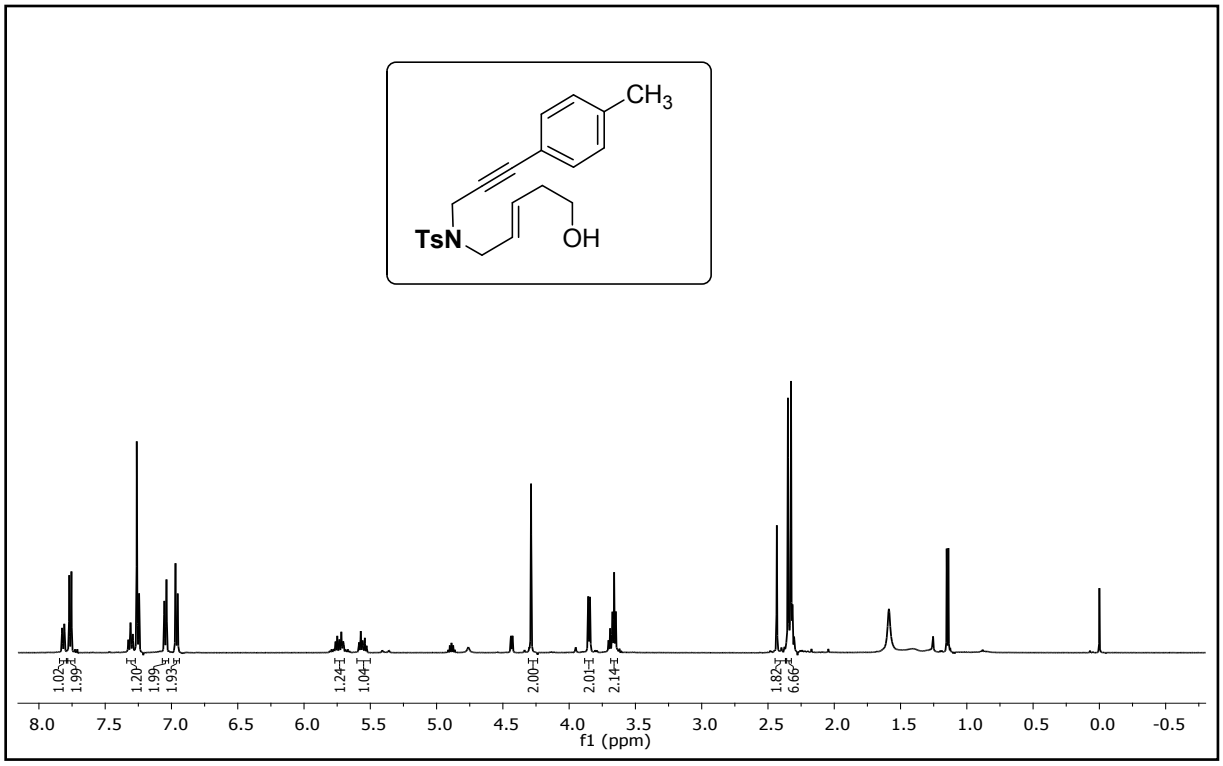
^{1}H NMR Spectra of compound 6c (400 MHz, $CDCl_3$)



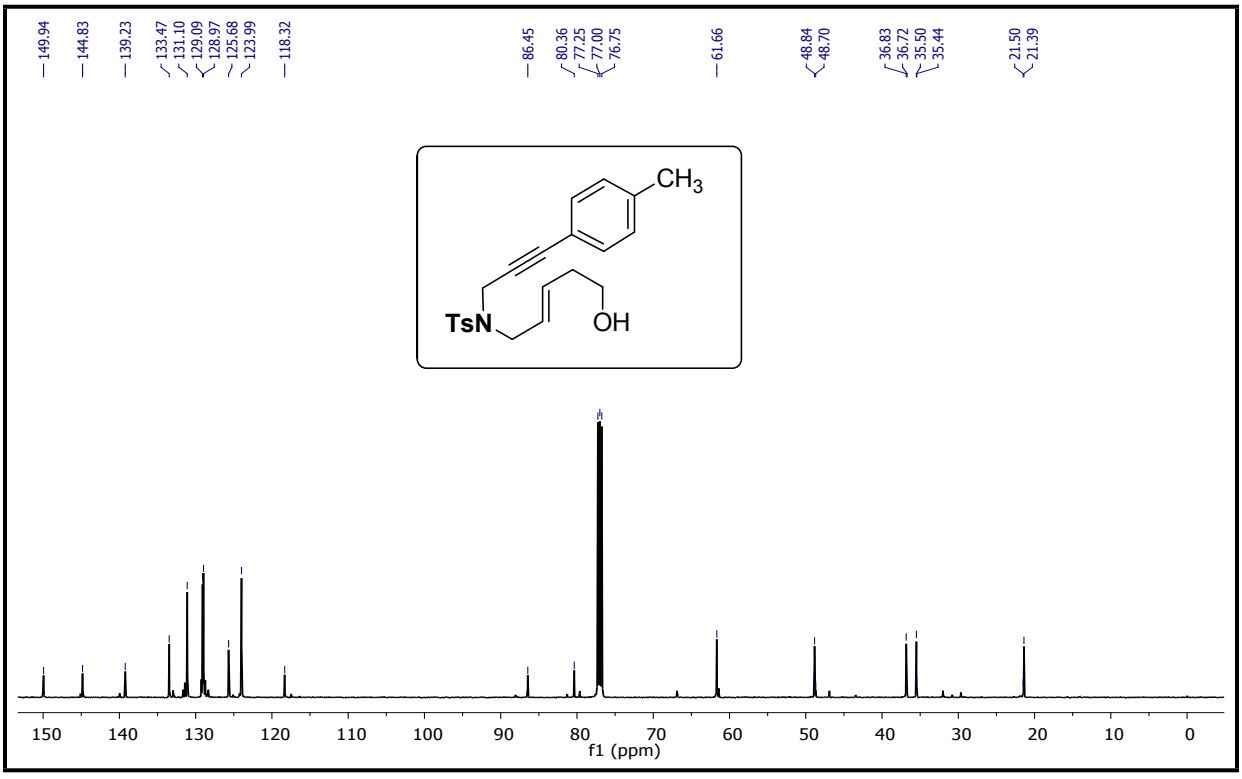
^{13}C NMR Spectra of compound 6c (100 MHz, $CDCl_3$)



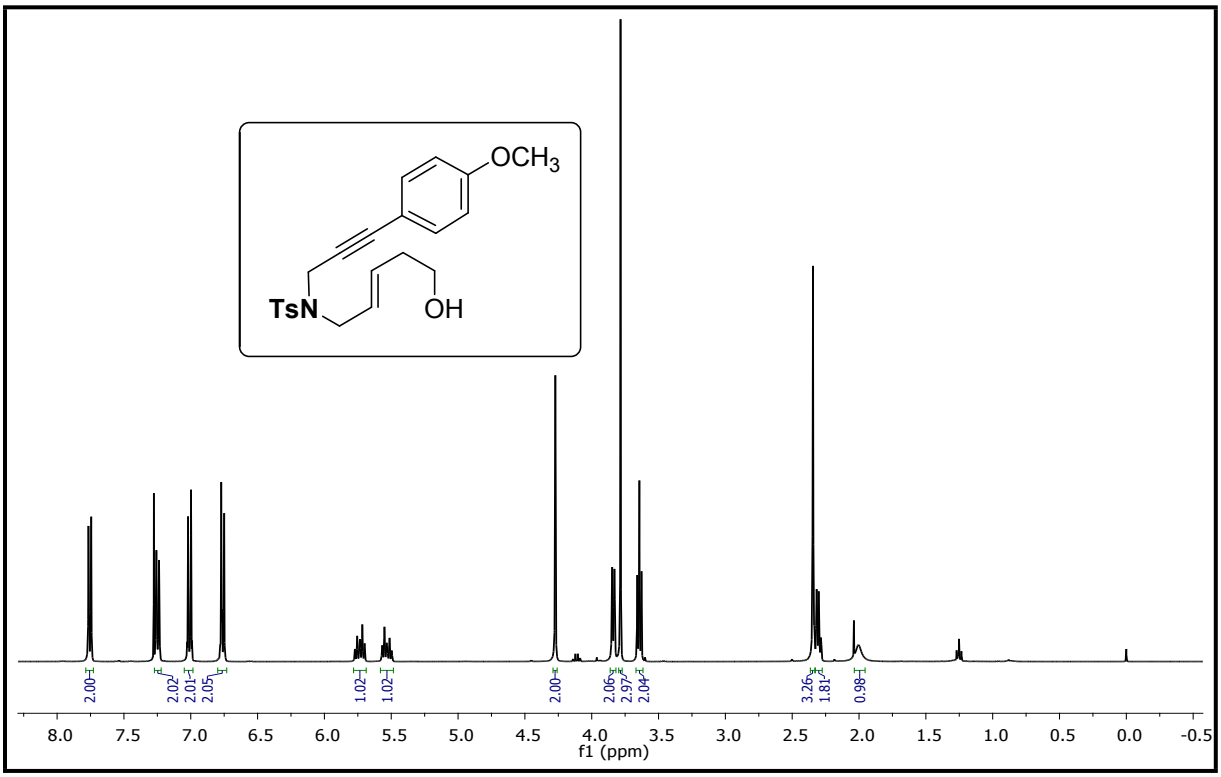
^{1}H NMR Spectra of compound 6d (500 MHz, $CDCl_3$)



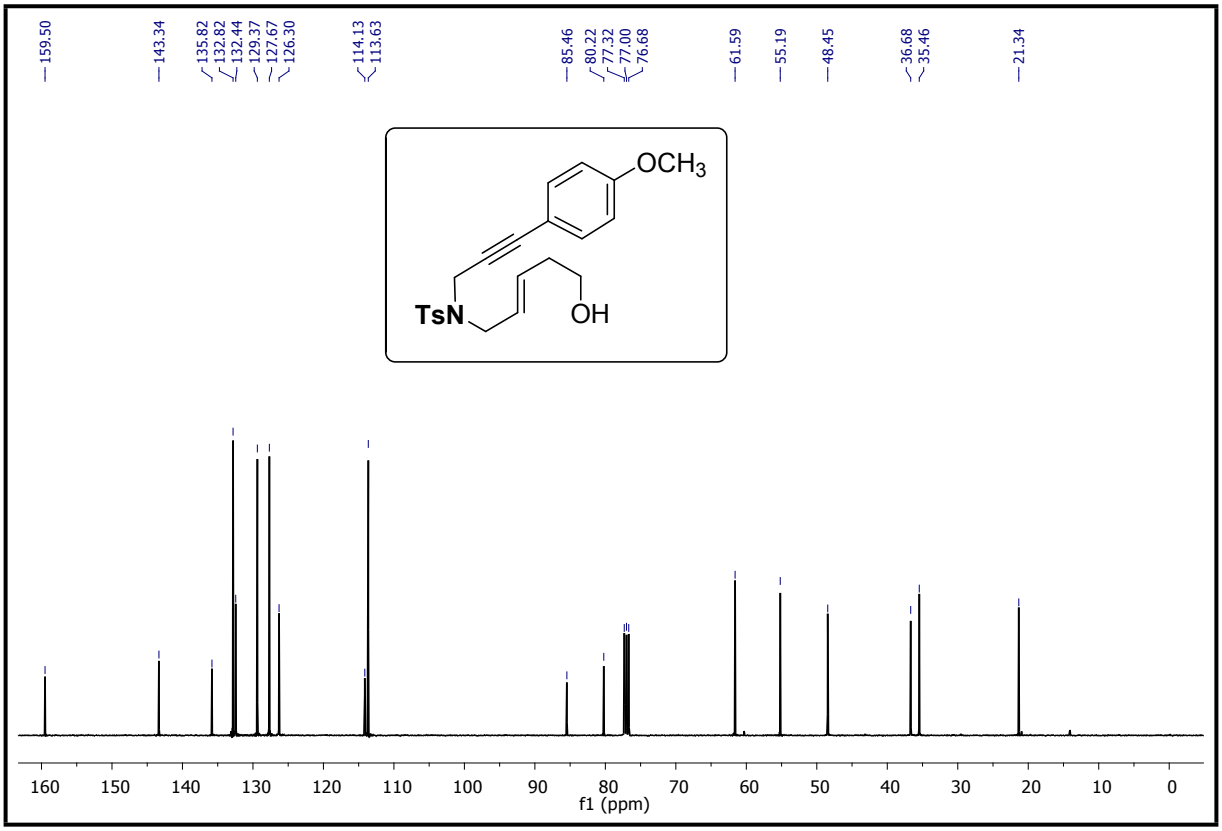
^{13}C NMR Spectra of compound 6d (125 MHz, $CDCl_3$)



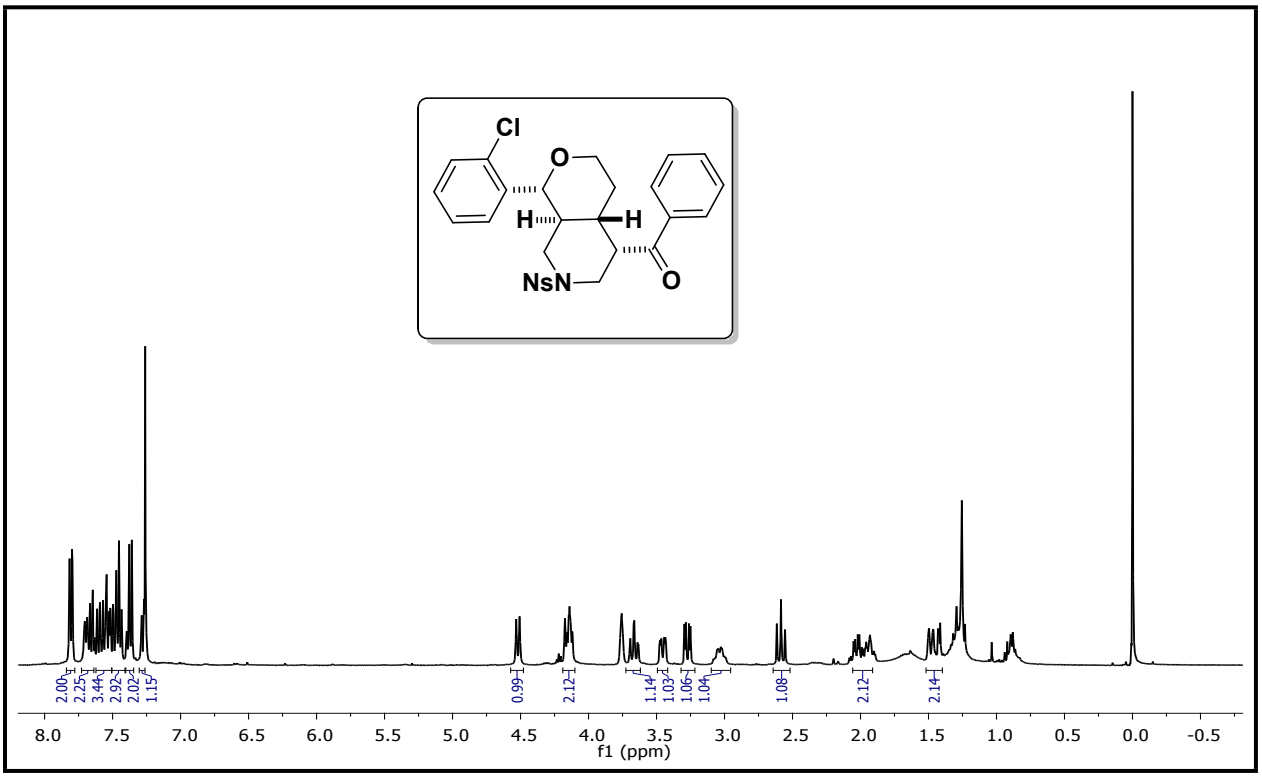
^{1}H NMR Spectra of compound 6e (400 MHz, $CDCl_3$)



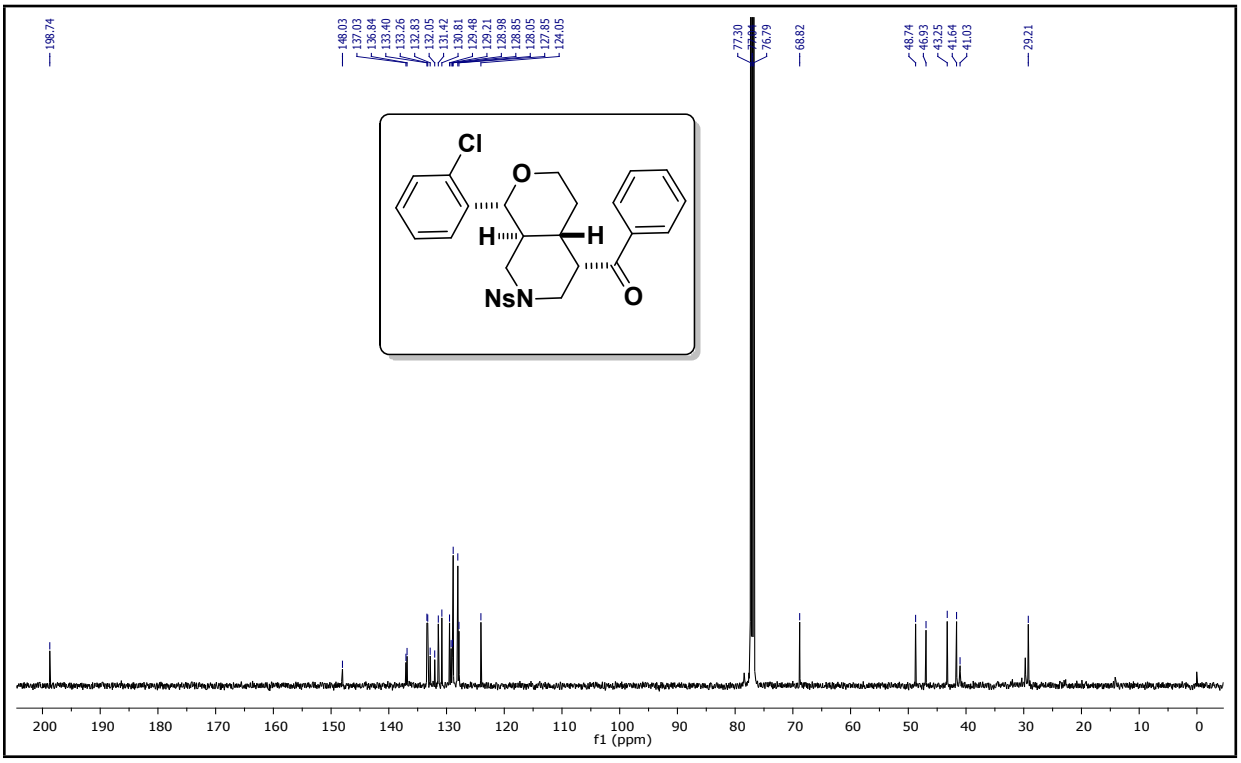
^{13}C NMR Spectra of compound 6e (100 MHz, $CDCl_3$)



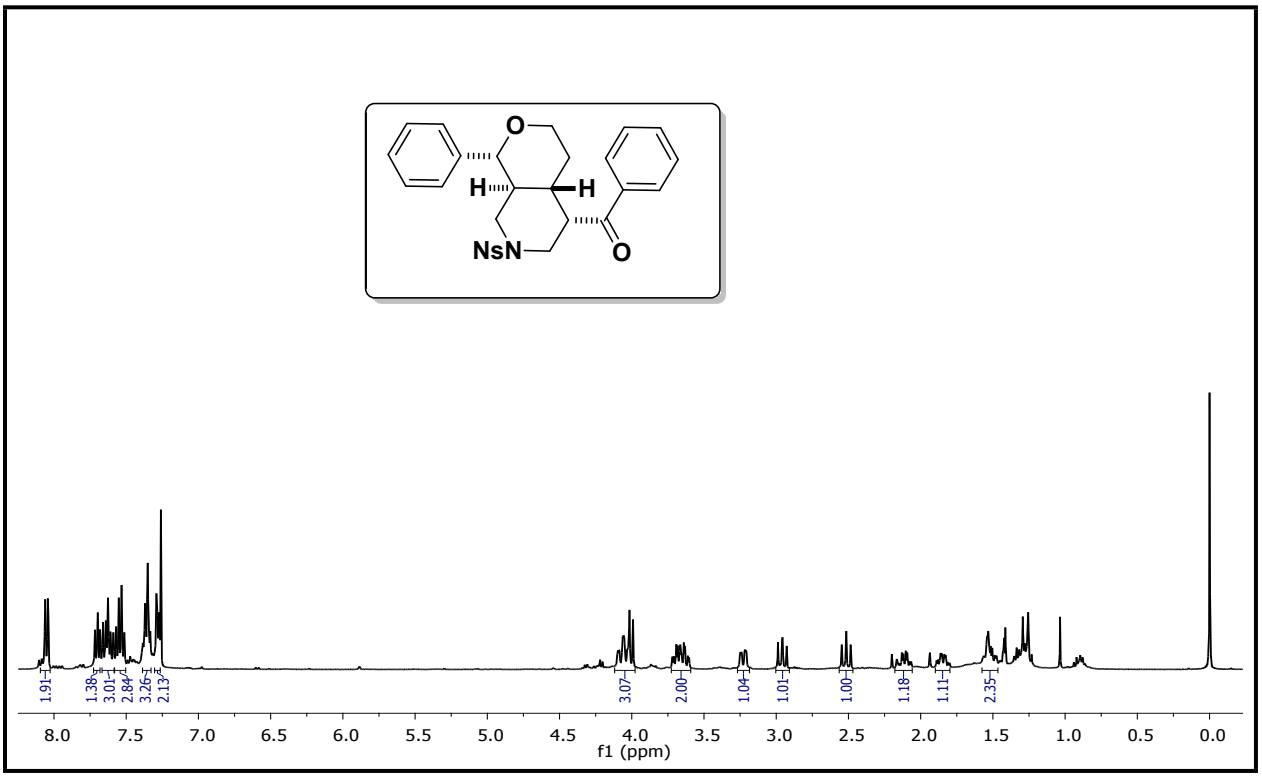
^{1}H NMR Spectra of compound 8a (500 MHz, $CDCl_3$)



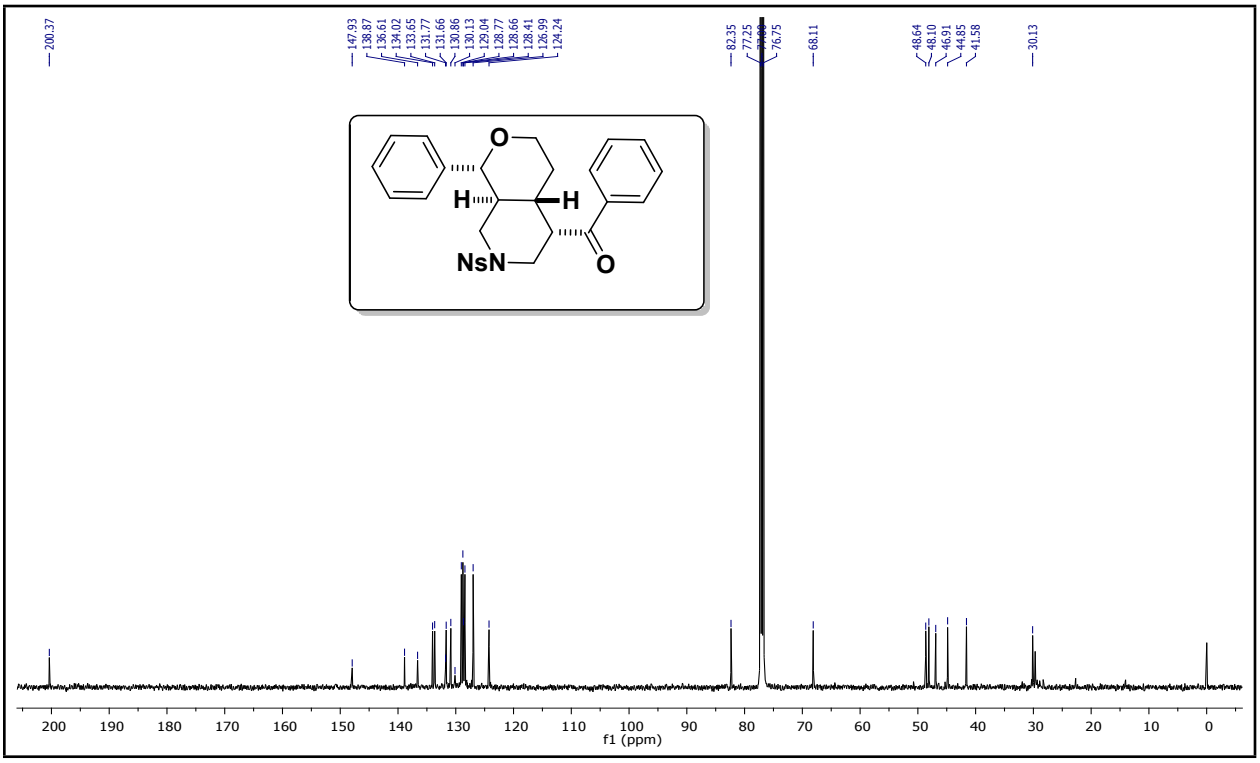
^{13}C NMR Spectra of compound 8a (125 MHz, $CDCl_3$)



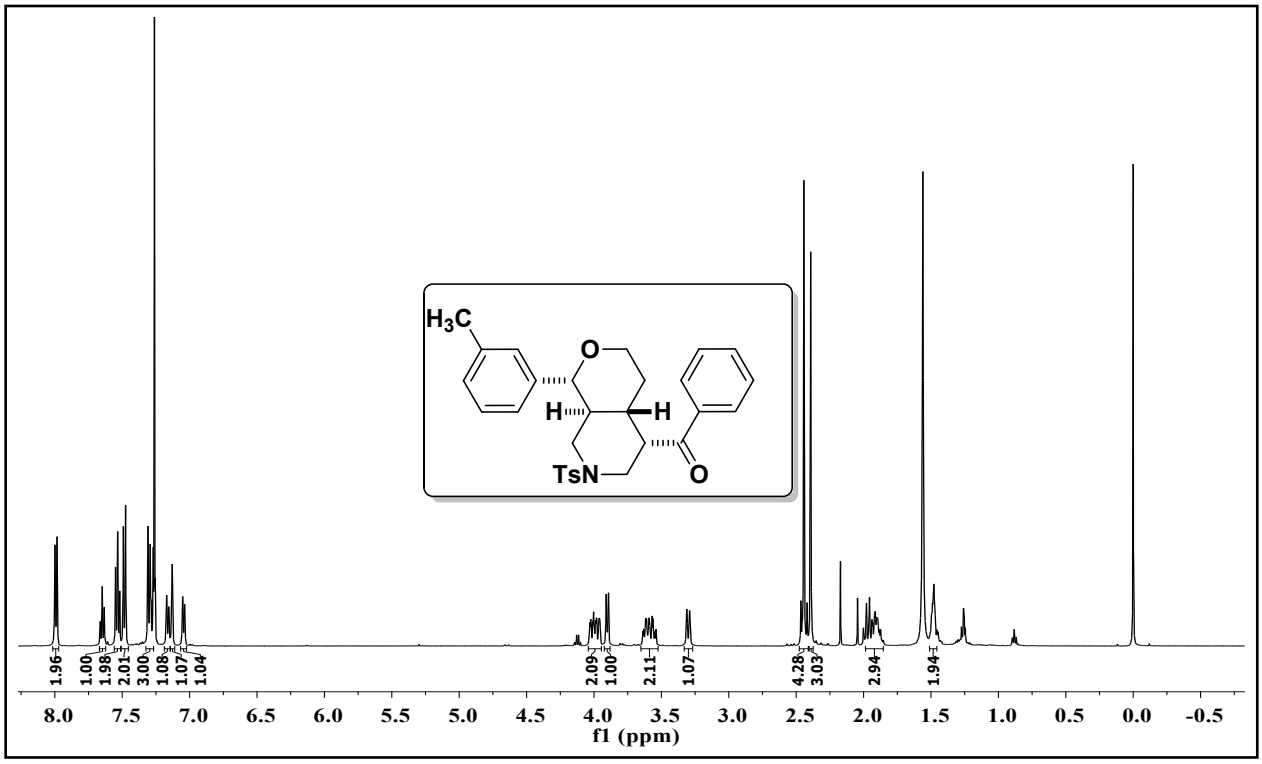
^{1}H NMR Spectra of compound 8b (400 MHz, $CDCl_3$)



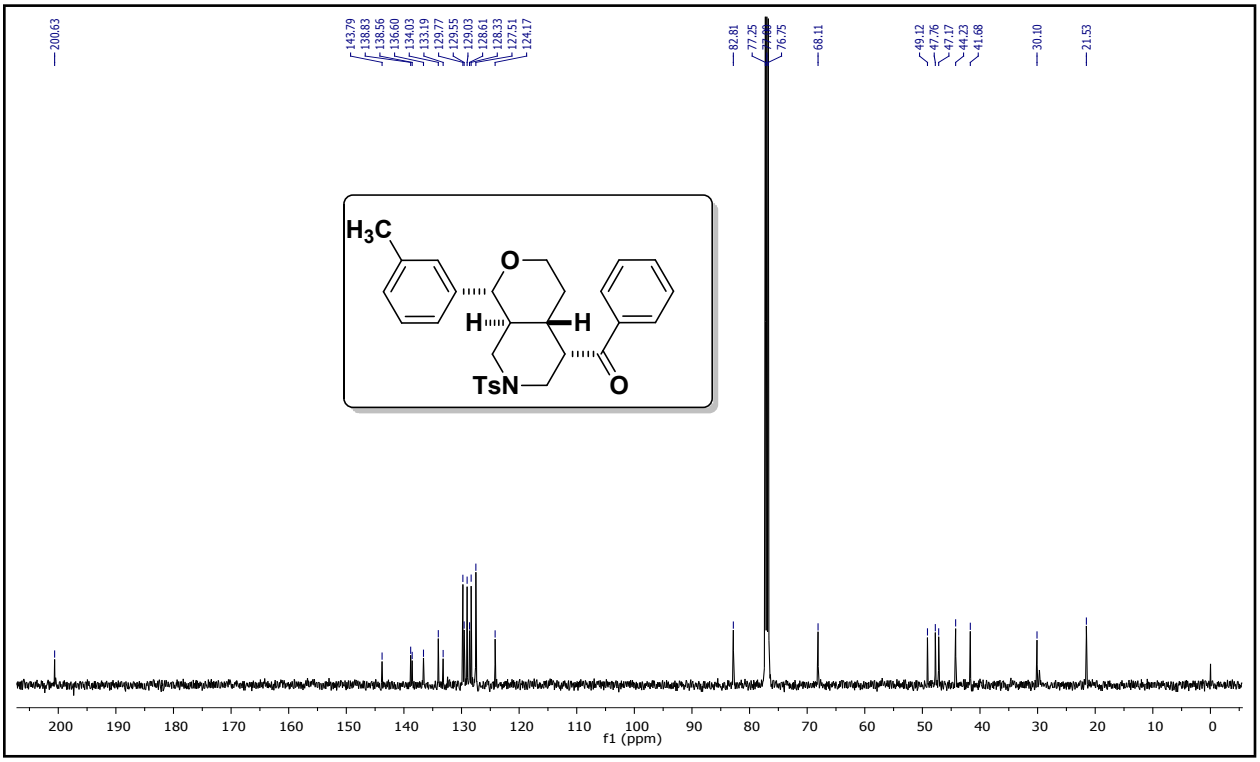
^{13}C NMR Spectra of compound 8b (125 MHz, $CDCl_3$)



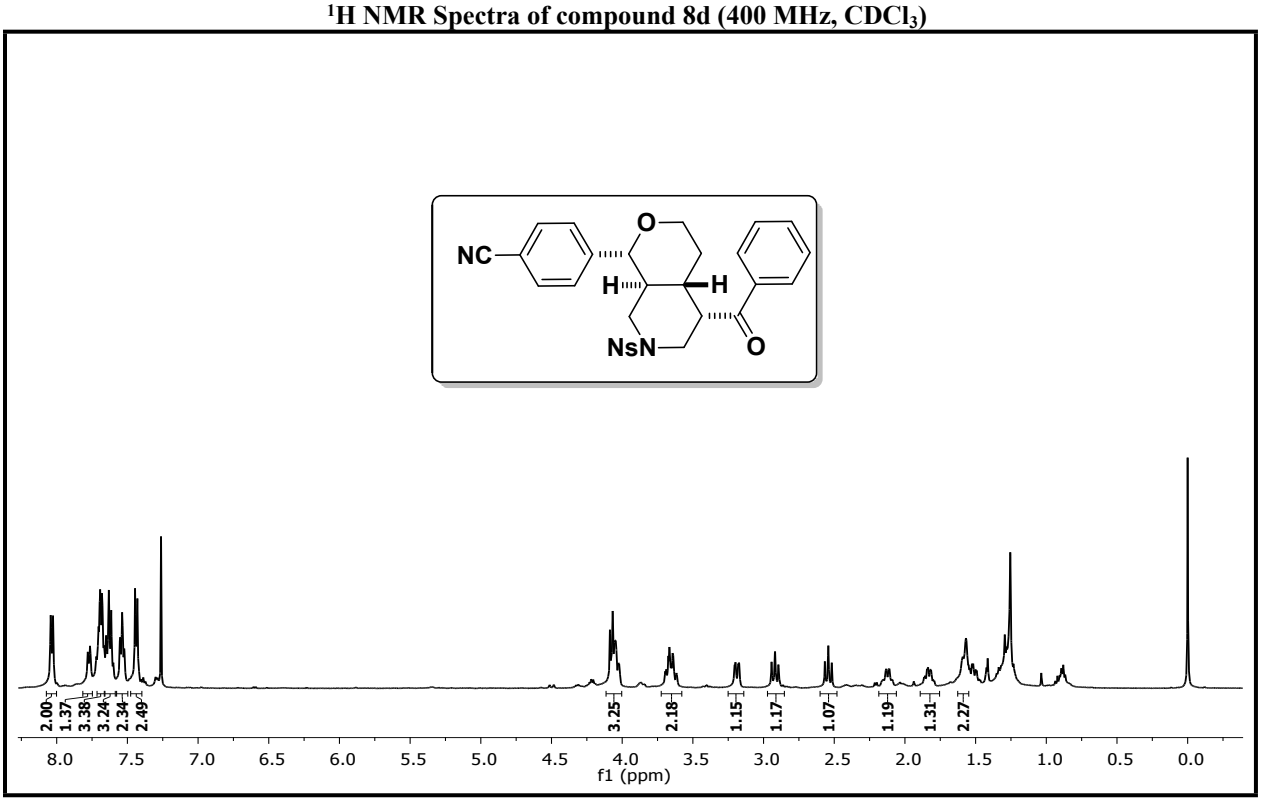
^{1}H NMR Spectra of compound 8c (500 MHz, $CDCl_3$)



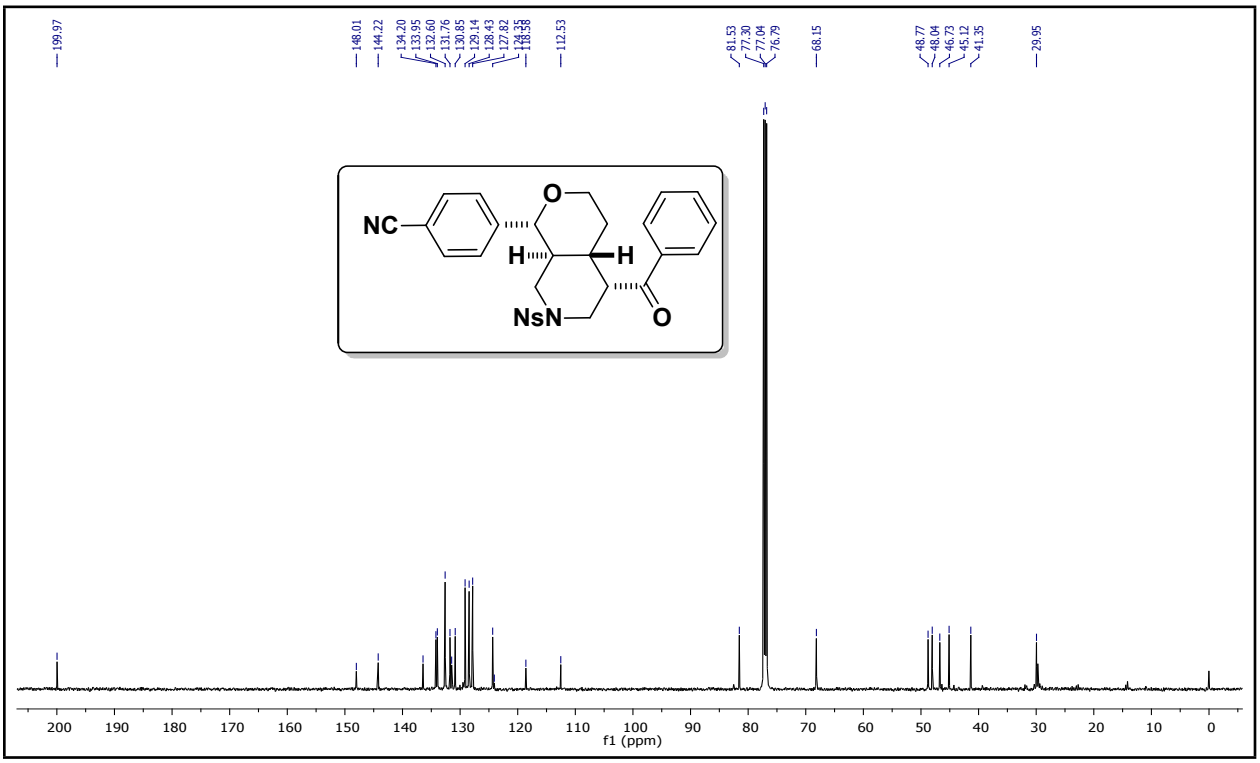
^{13}C NMR Spectra of compound 8c (125 MHz, $CDCl_3$)



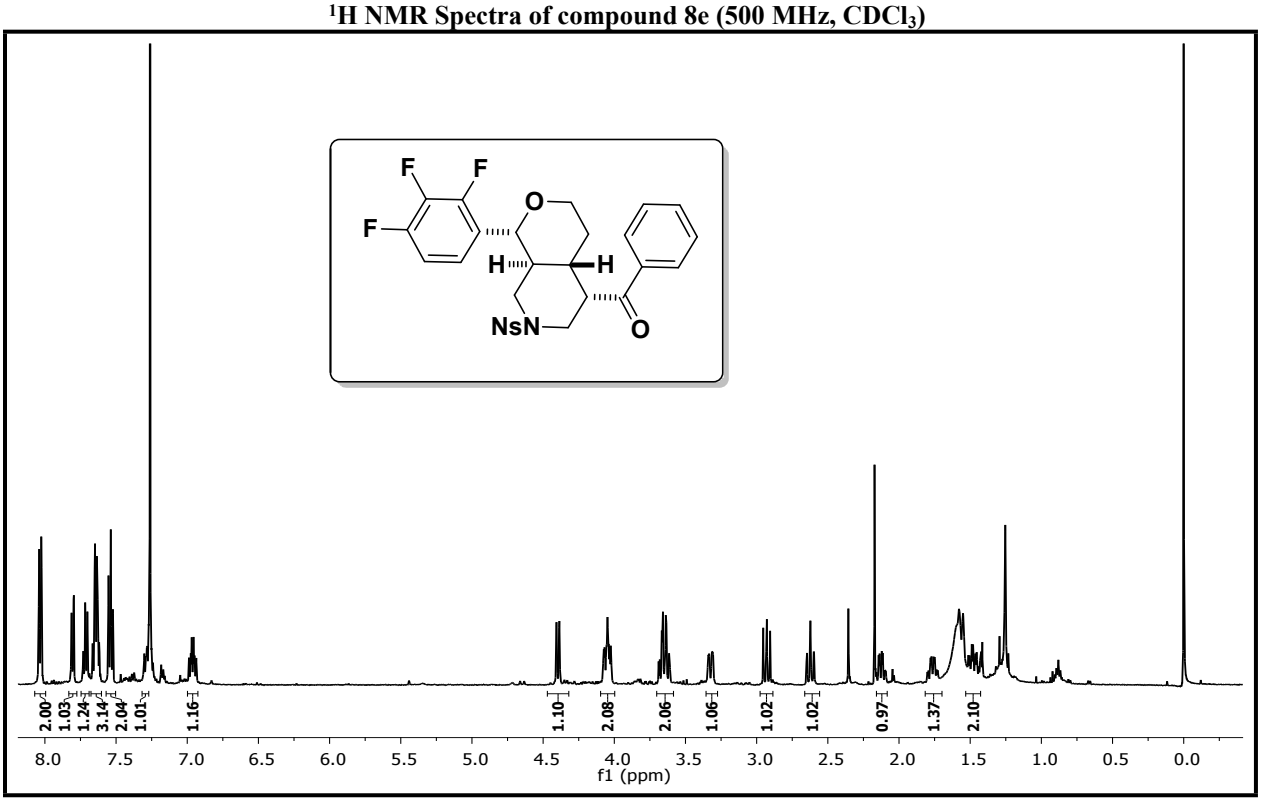
^{1}H NMR Spectra of compound 8d (400 MHz, $CDCl_3$)



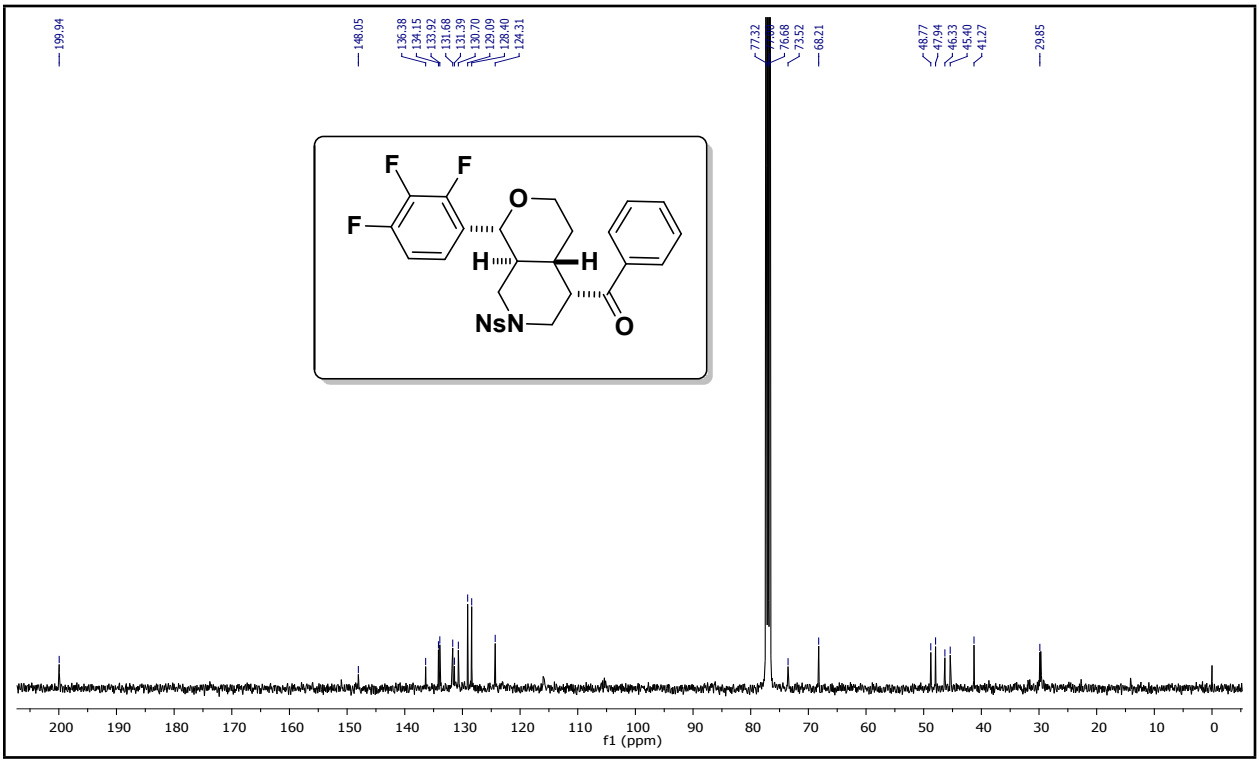
^{13}C NMR Spectra of compound 8d (125 MHz, $CDCl_3$)



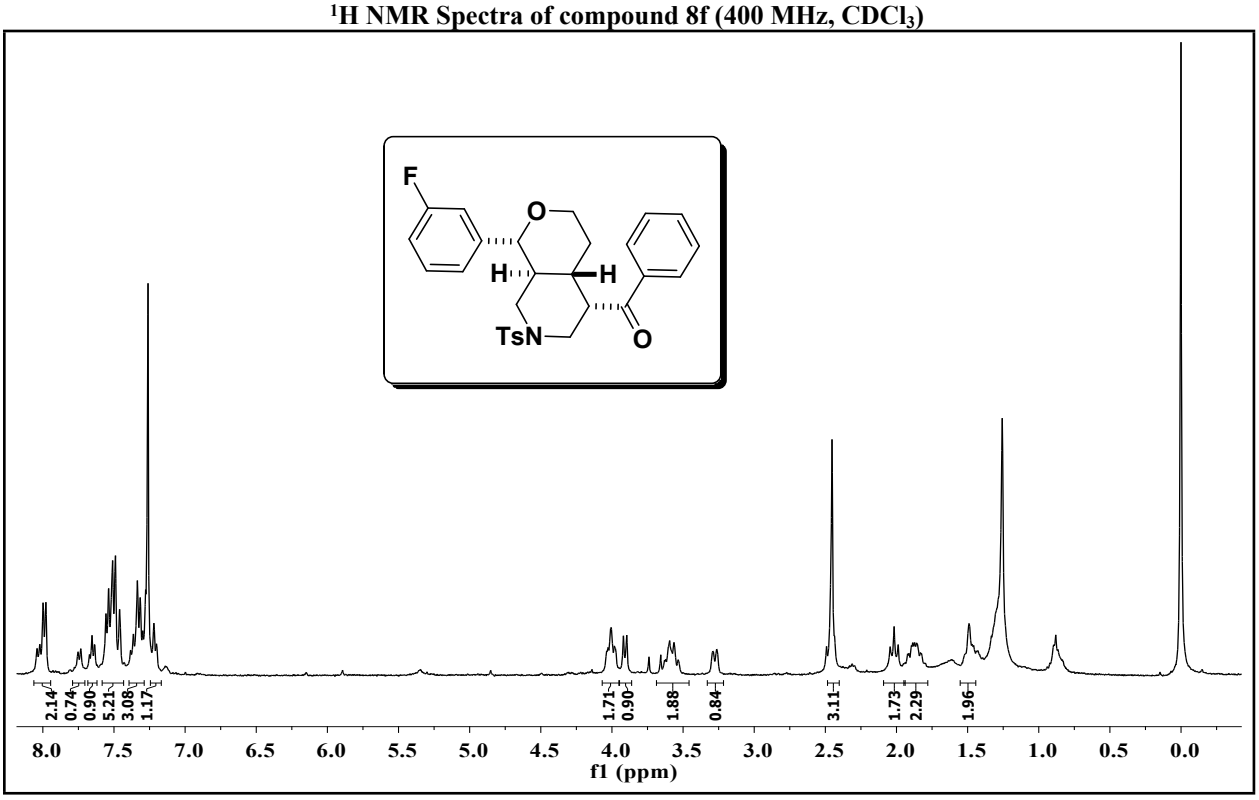
^{1}H NMR Spectra of compound 8e (500 MHz, $CDCl_3$)



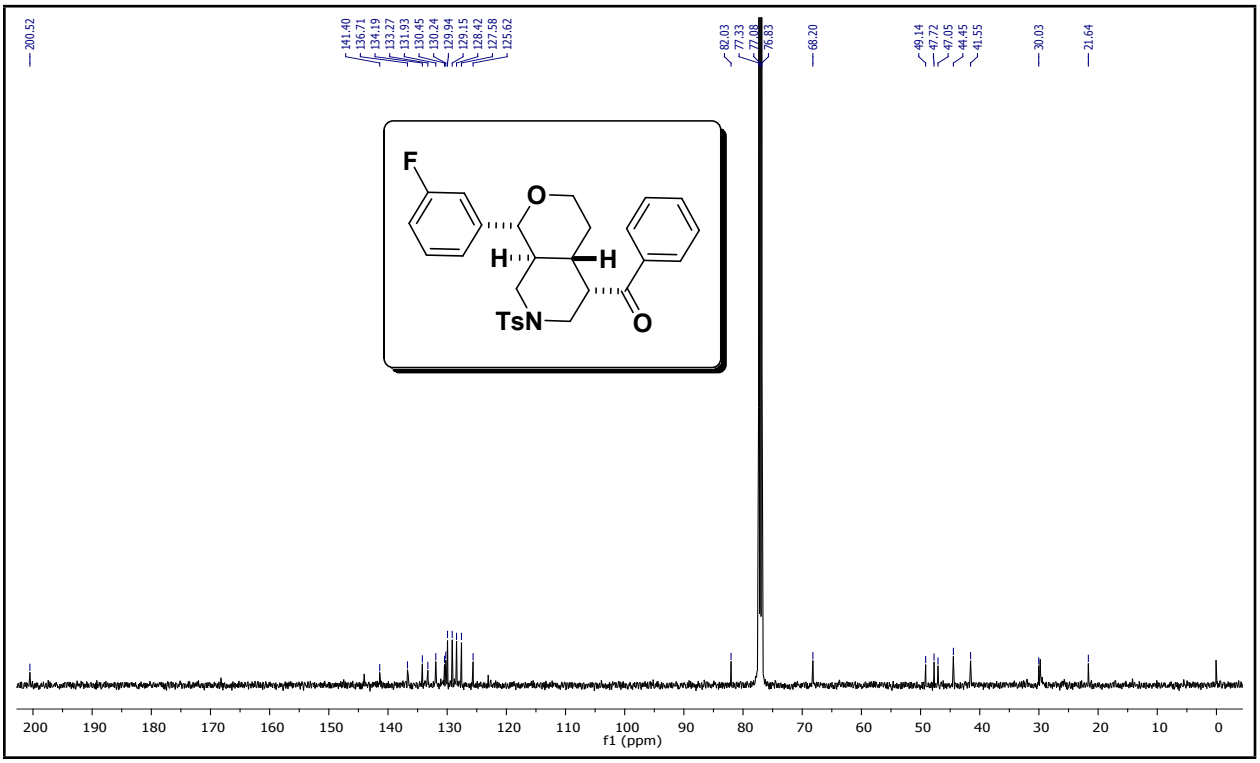
^{13}C NMR Spectra of compound 8e (100 MHz, $CDCl_3$)



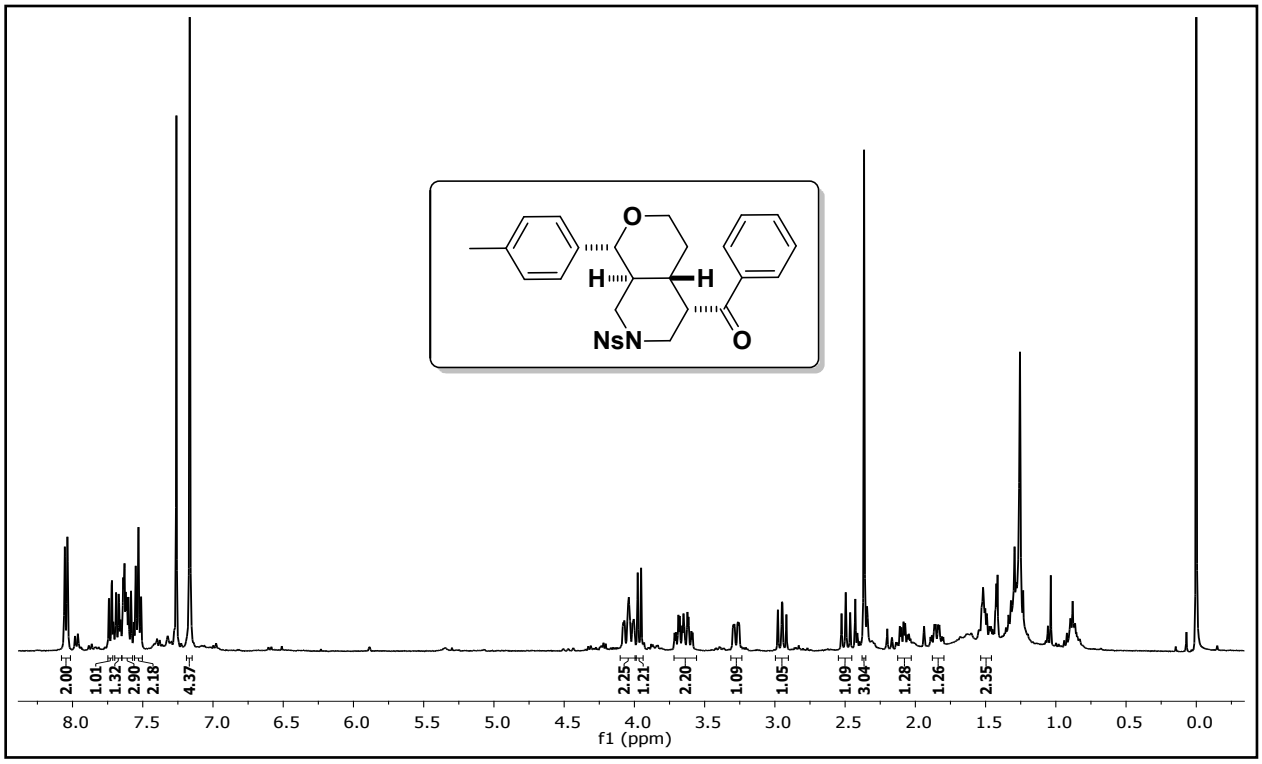
^{1}H NMR Spectra of compound 8f (400 MHz, $CDCl_3$)



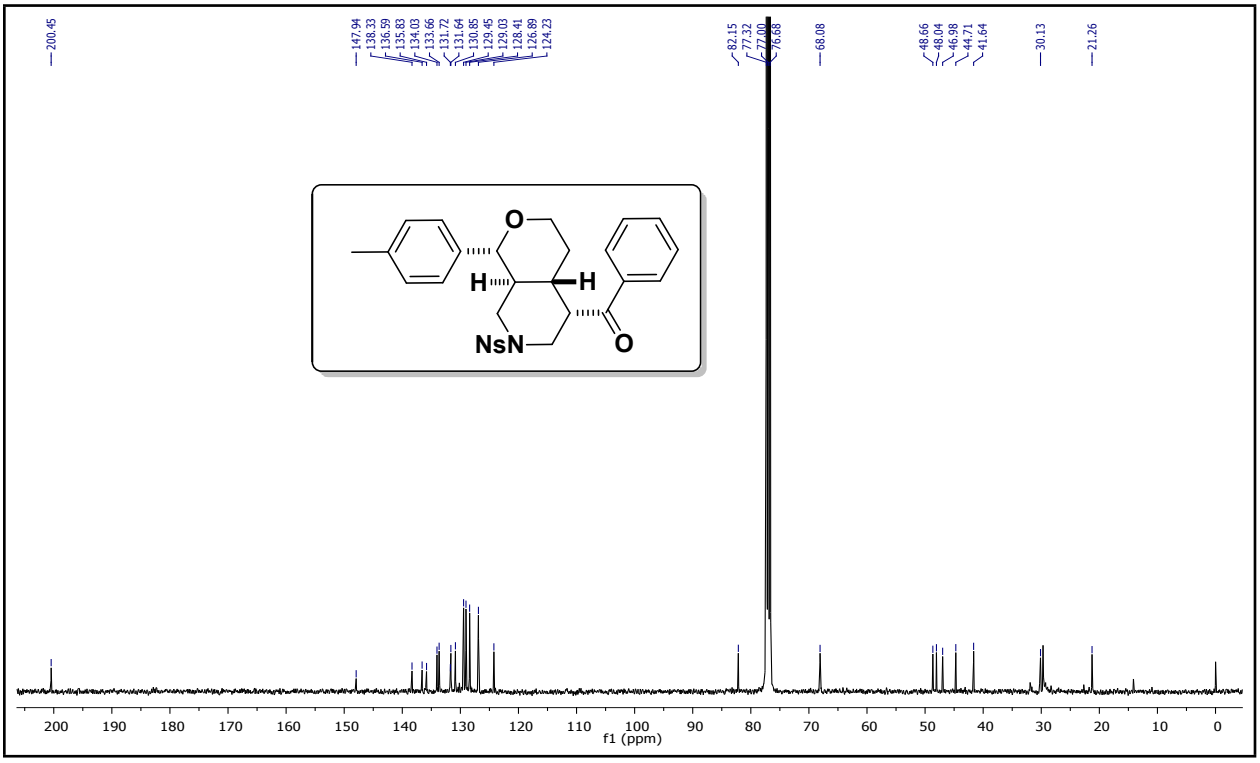
^{13}C NMR Spectra of compound 8f (125 MHz, $CDCl_3$)



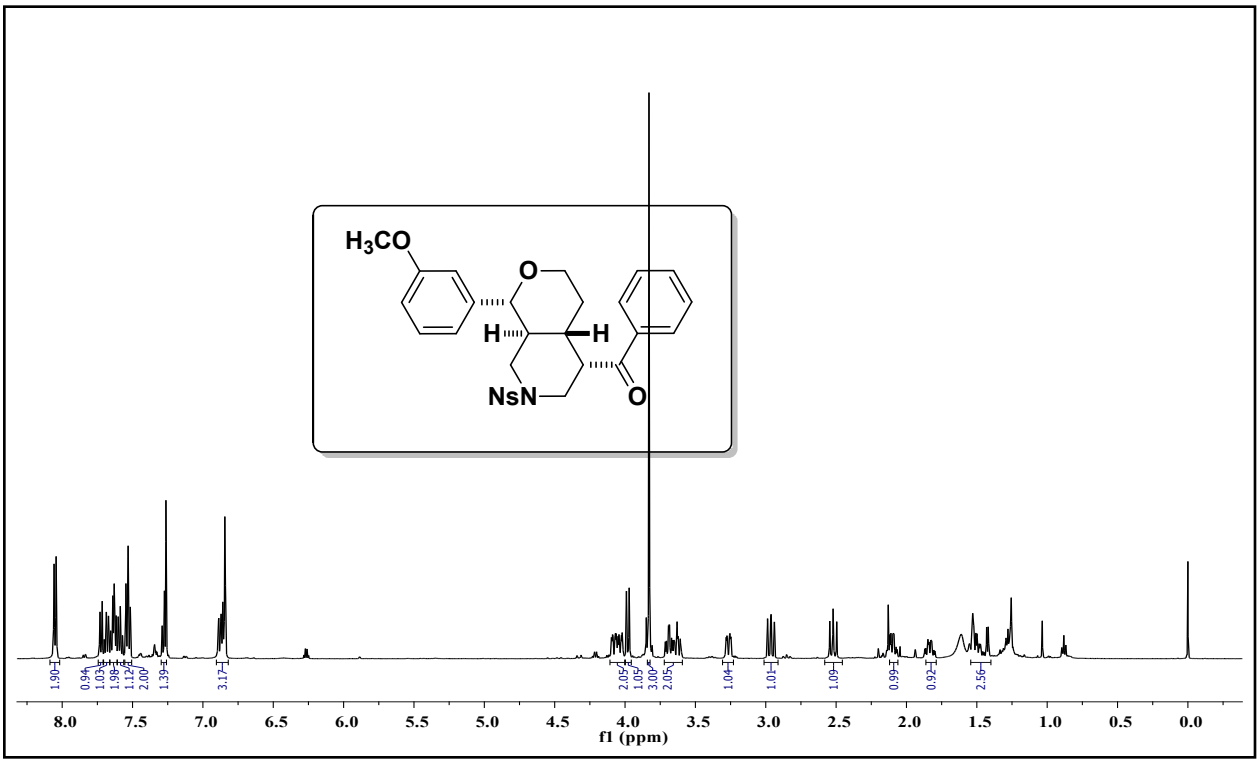
^{1}H NMR Spectra of compound 8g (500 MHz, $CDCl_3$)



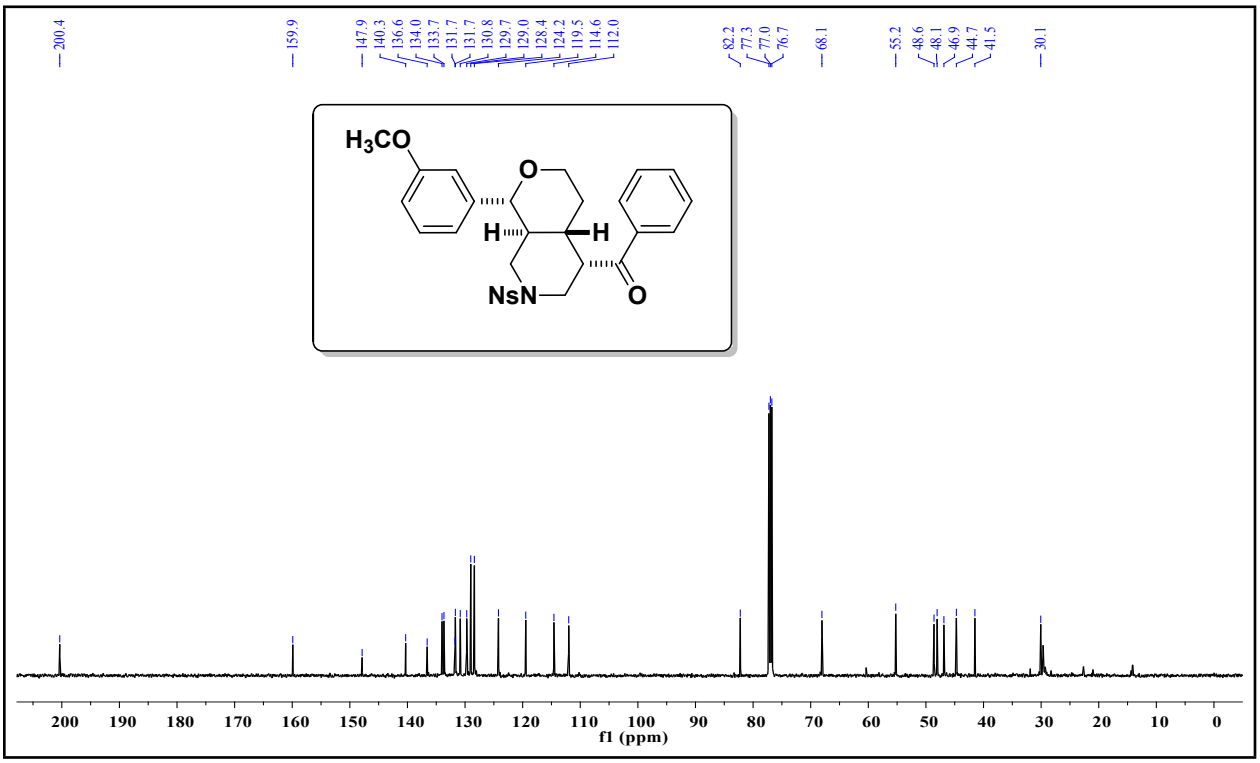
^{13}C NMR Spectra of compound 8g (100 MHz, $CDCl_3$)



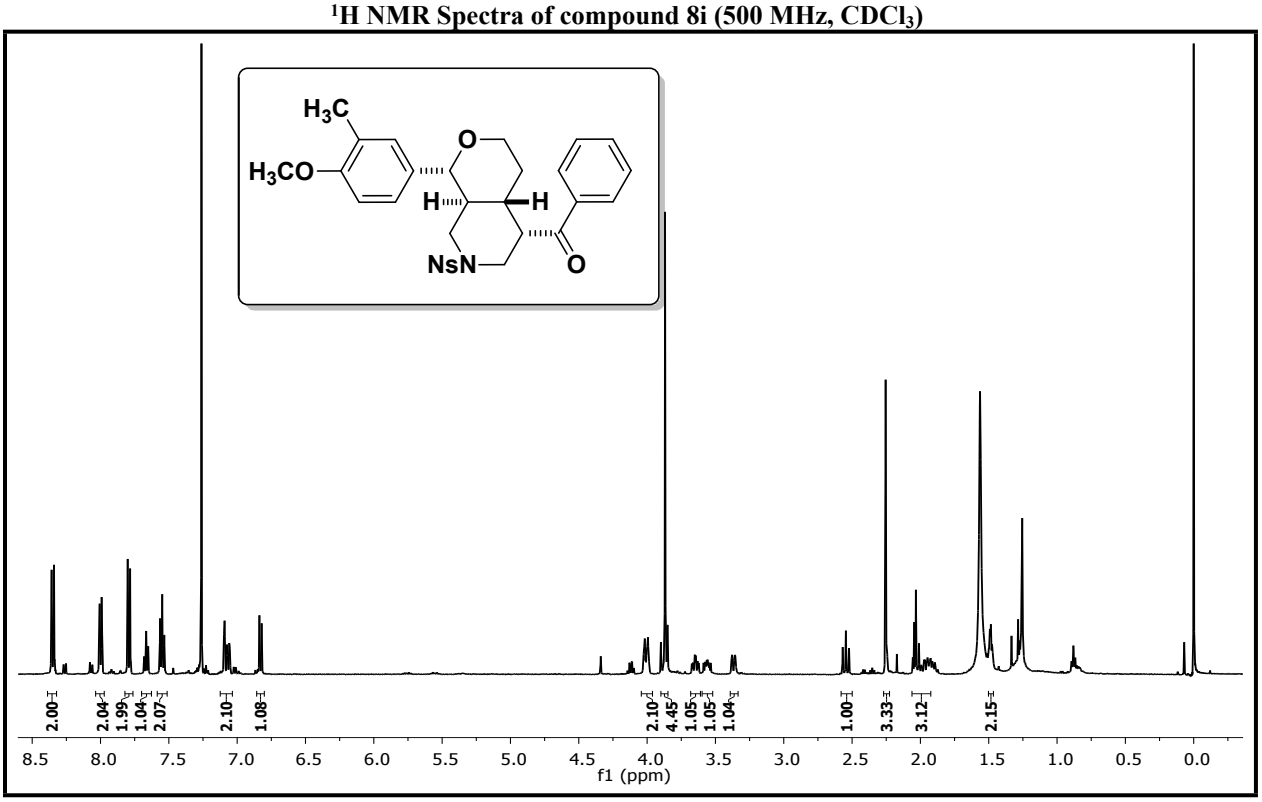
^{1}H NMR Spectra of compound 8h (500 MHz, $CDCl_3$)



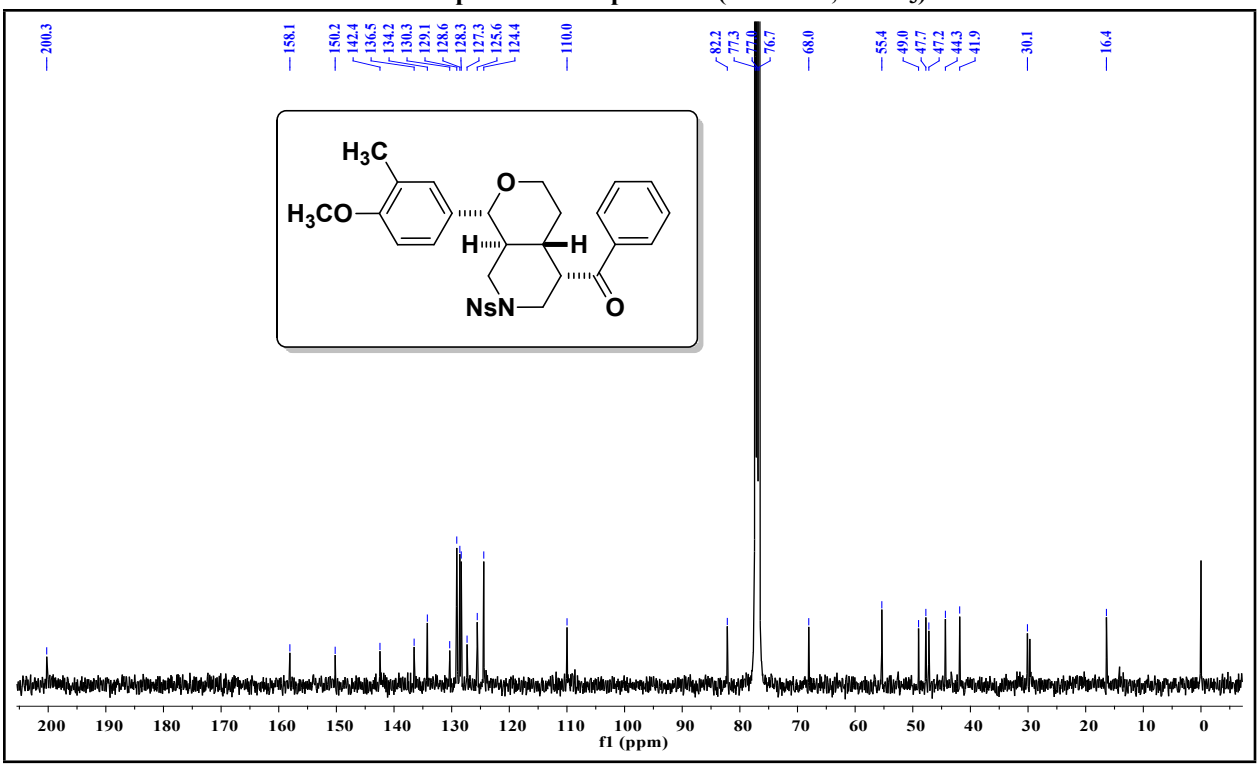
^{13}C NMR Spectra of compound 8h (125 MHz, $CDCl_3$)



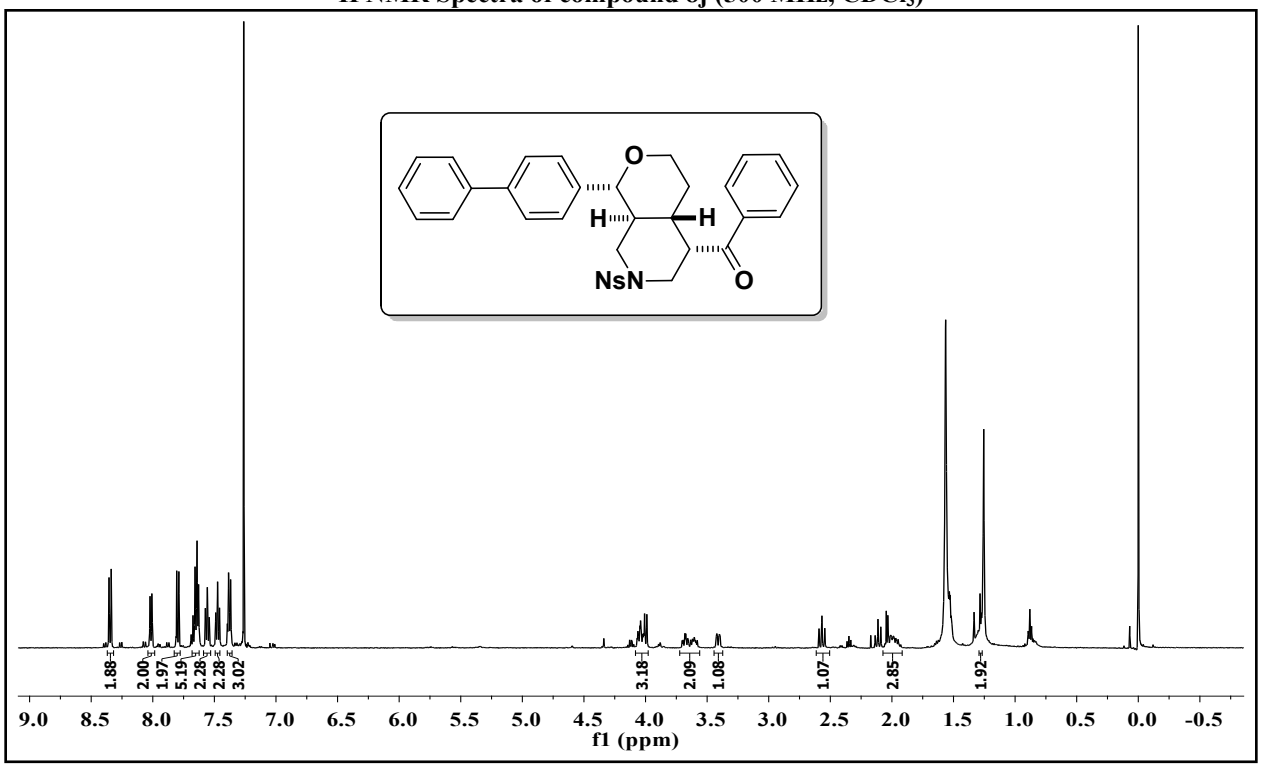
^{1}H NMR Spectra of compound 8i (500 MHz, $CDCl_3$)



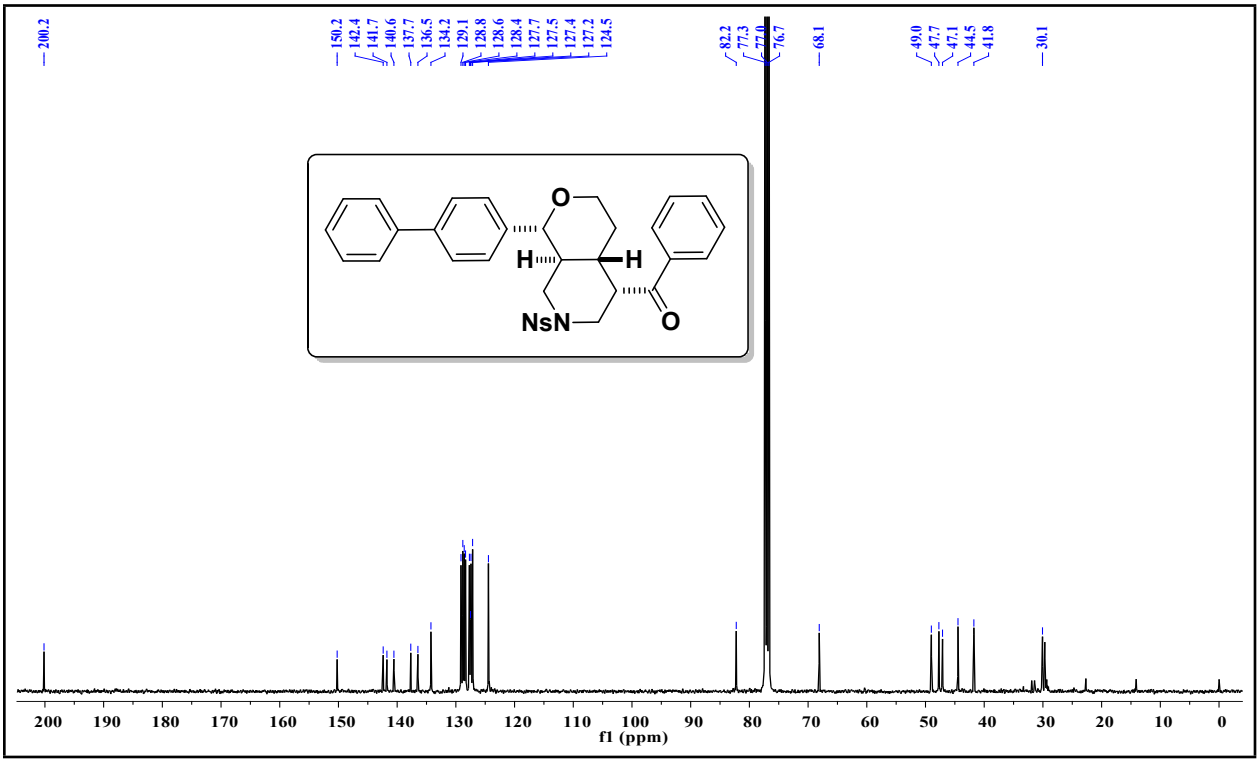
^{13}C NMR Spectra of compound 8i (100 MHz, $CDCl_3$)



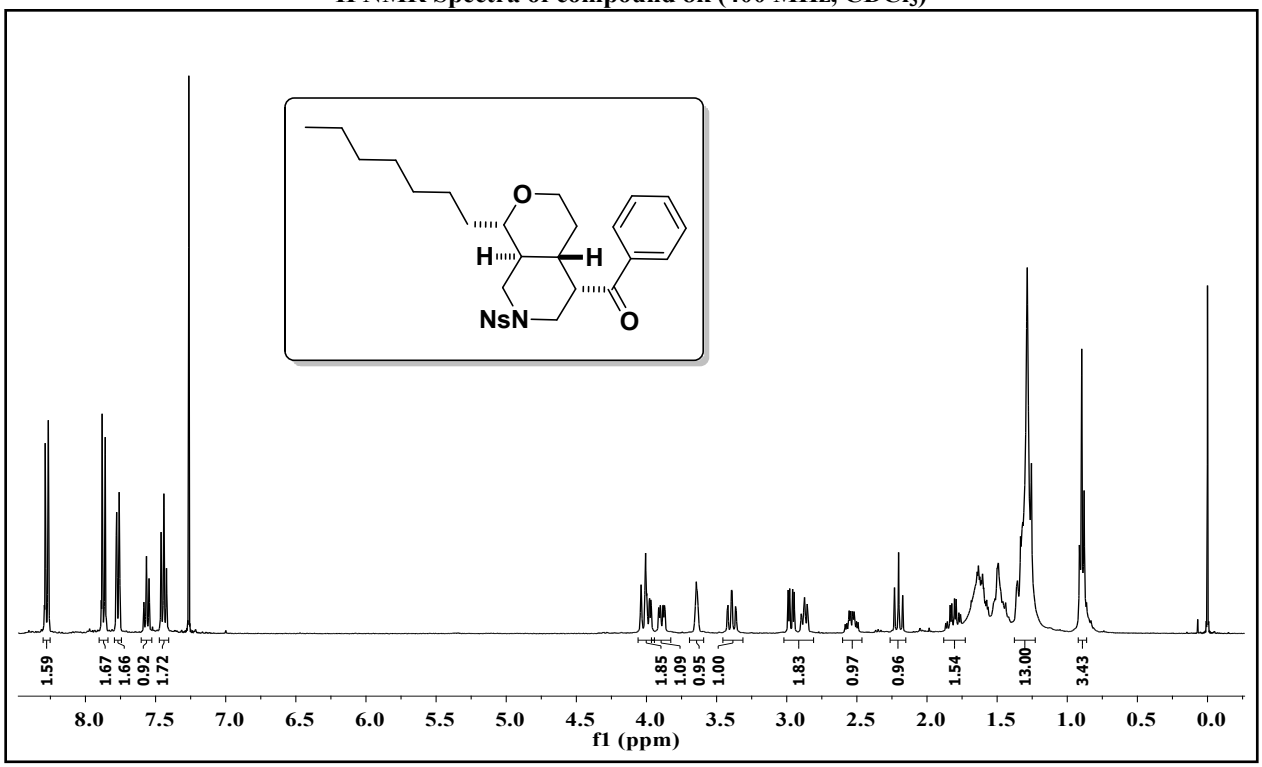
^{1}H NMR Spectra of compound 8j (500 MHz, $CDCl_3$)



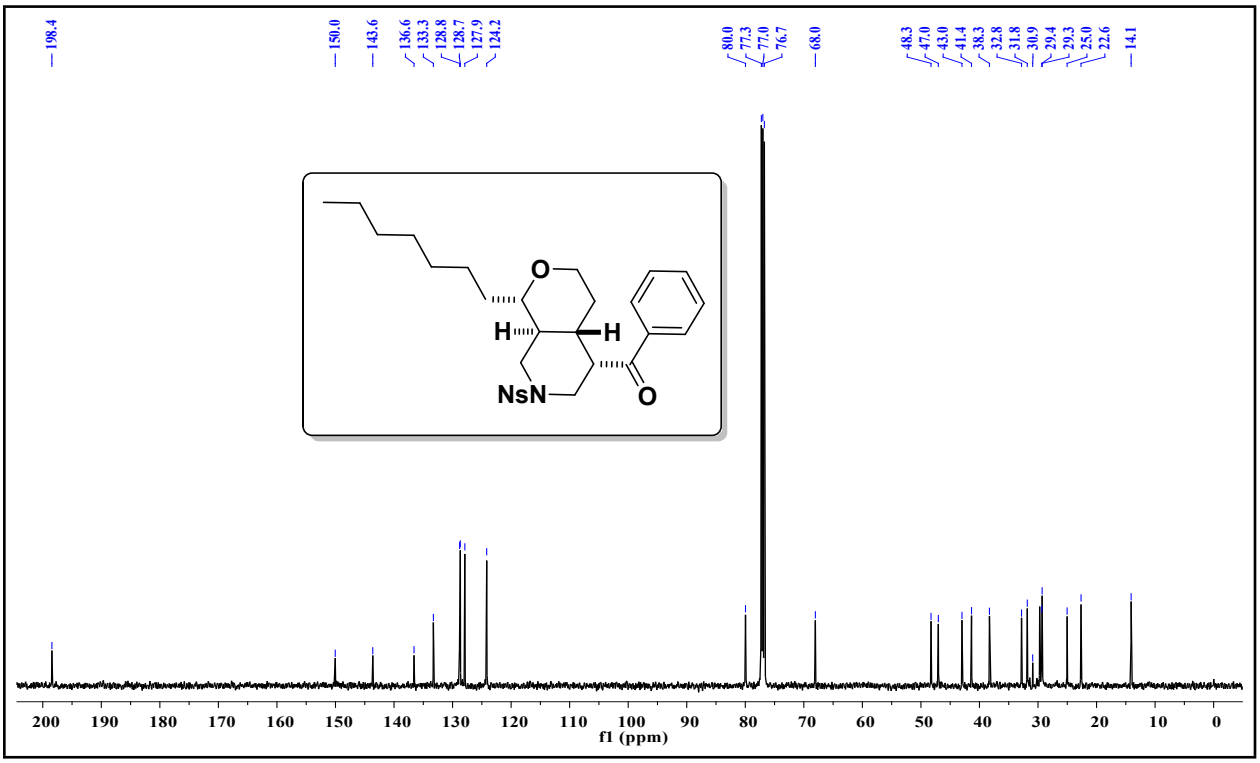
^{13}C NMR Spectra of compound 8j (100 MHz, $CDCl_3$)



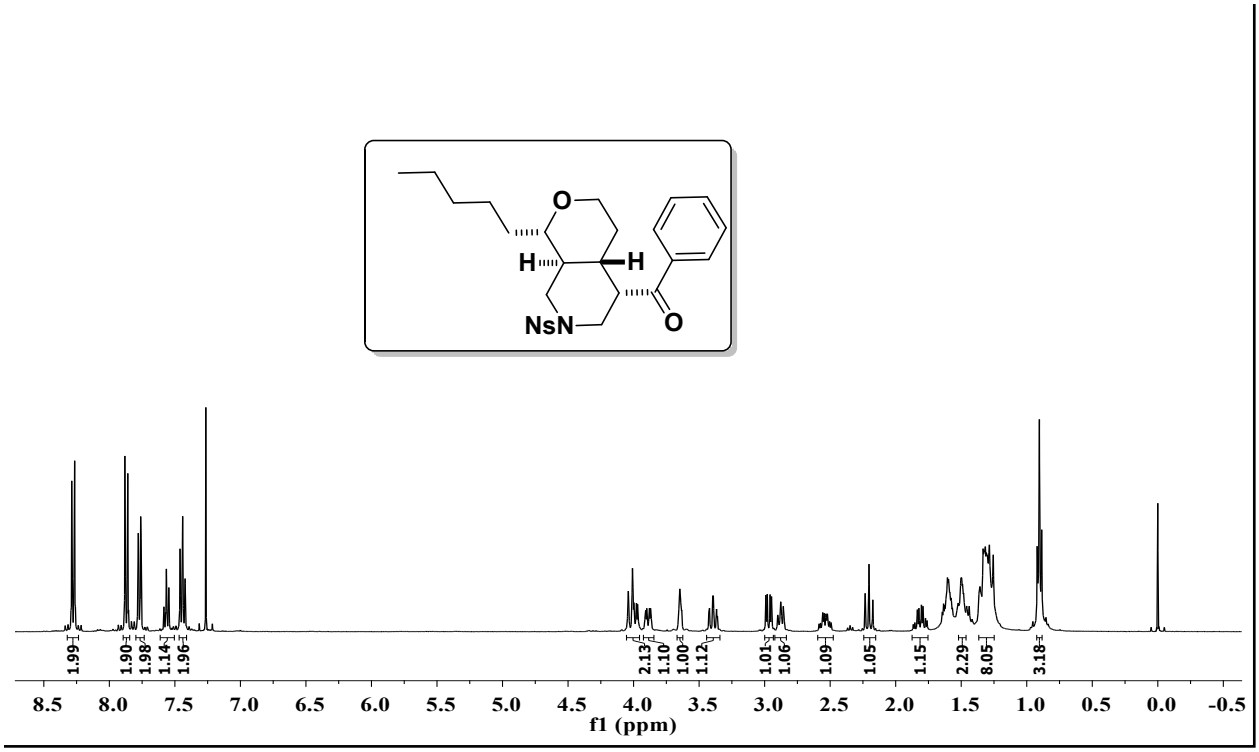
^{1}H NMR Spectra of compound 8k (400 MHz, $CDCl_3$)



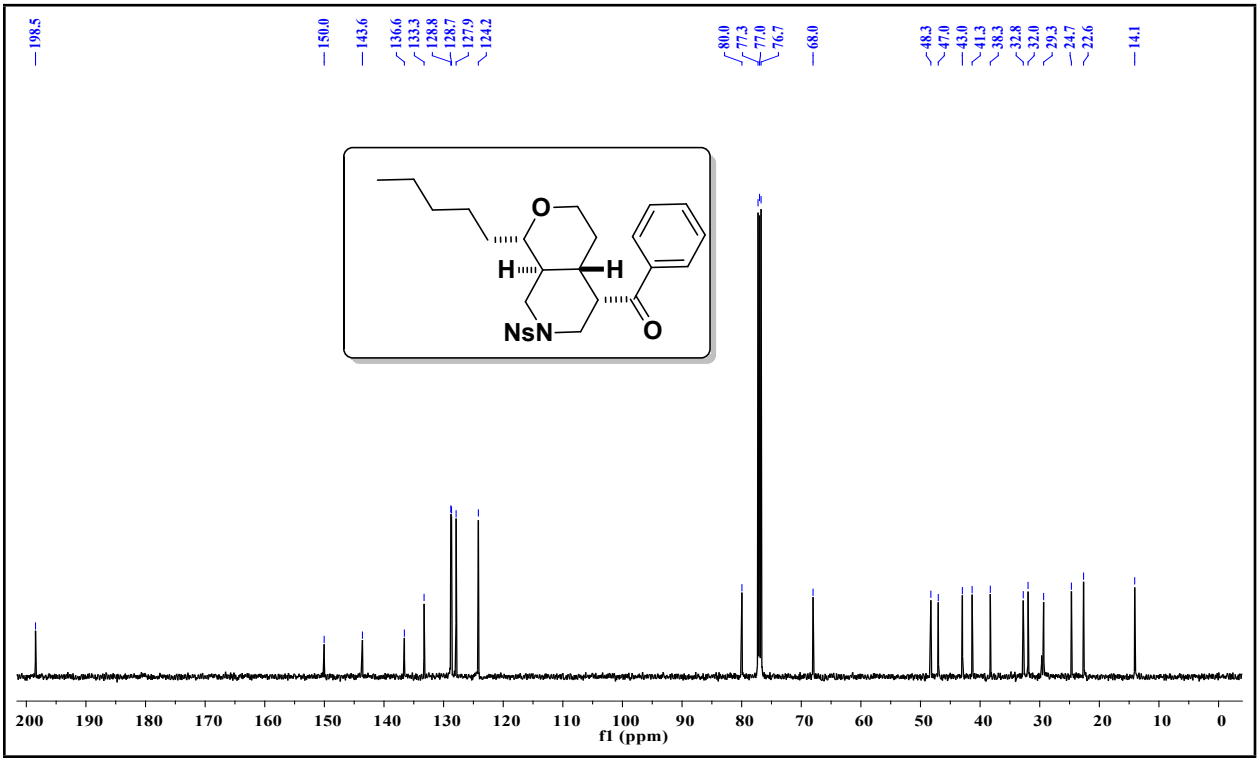
^{13}C NMR Spectra of compound 8k (125 MHz, $CDCl_3$)



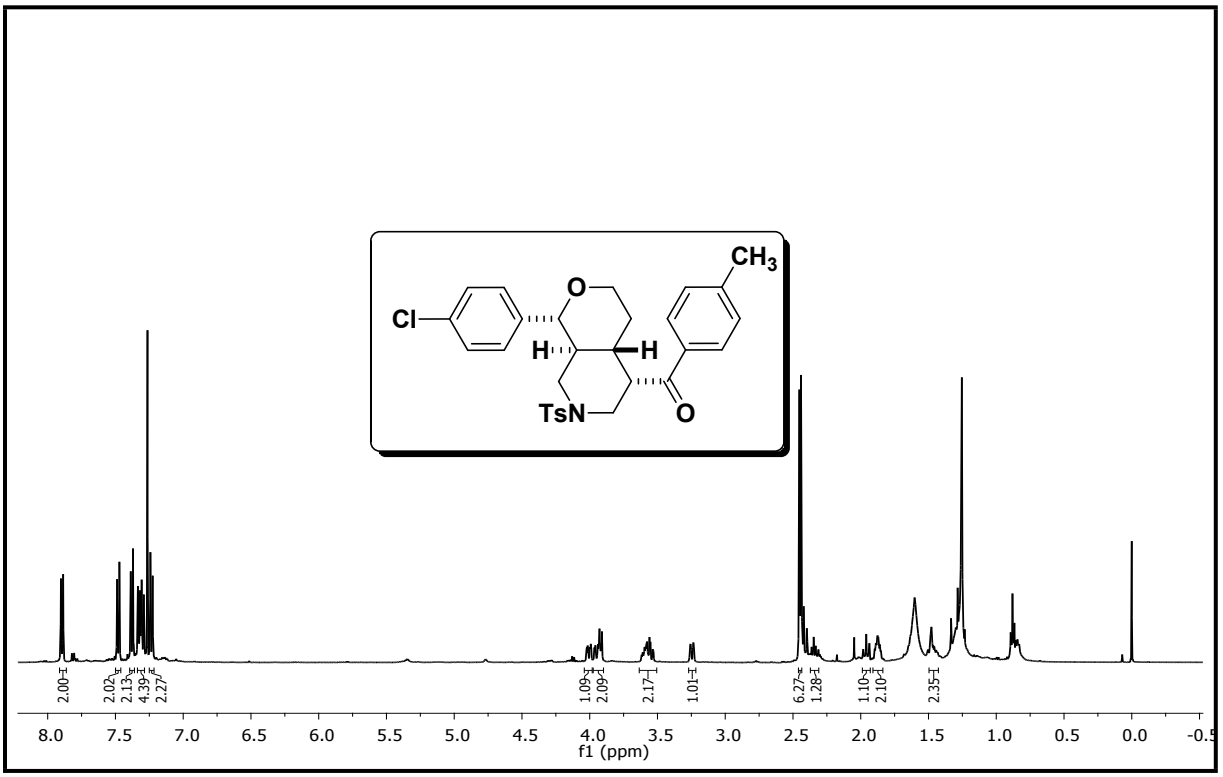
^{1}H NMR Spectra of compound 8l (400 MHz, $CDCl_3$)



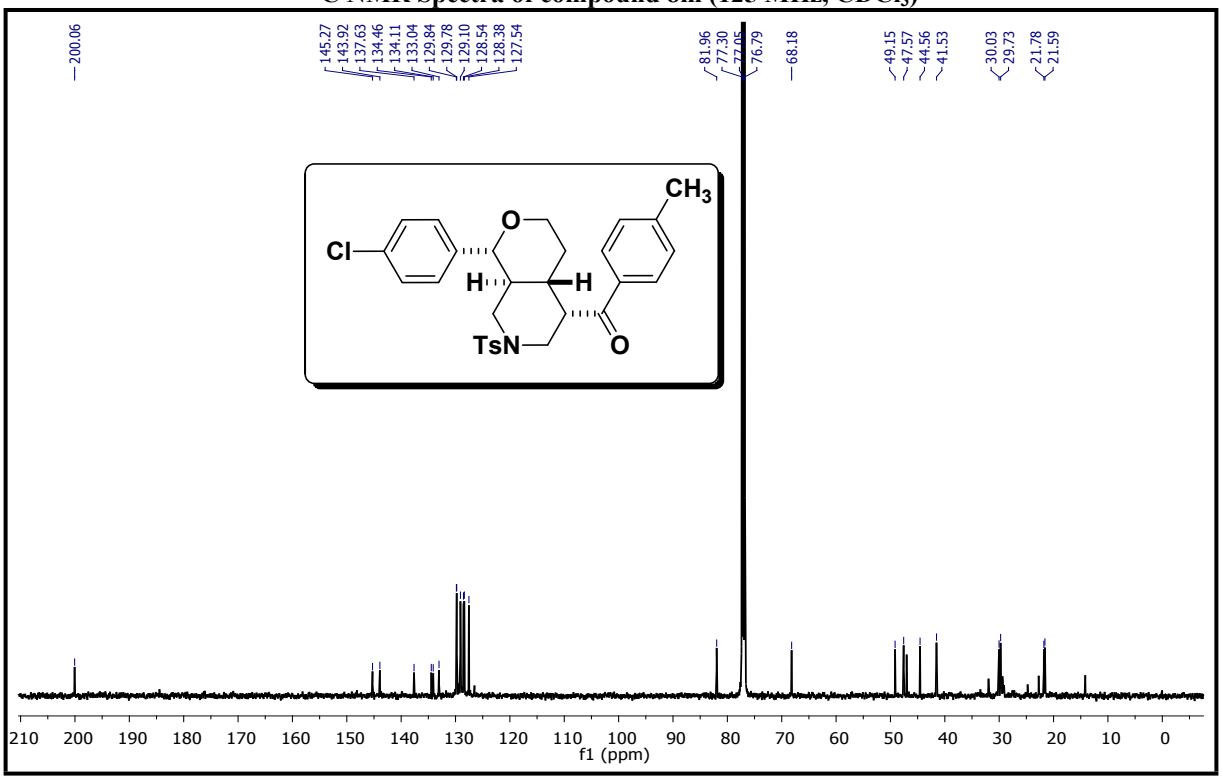
^{13}C NMR Spectra of compound 8l (125 MHz, $CDCl_3$)



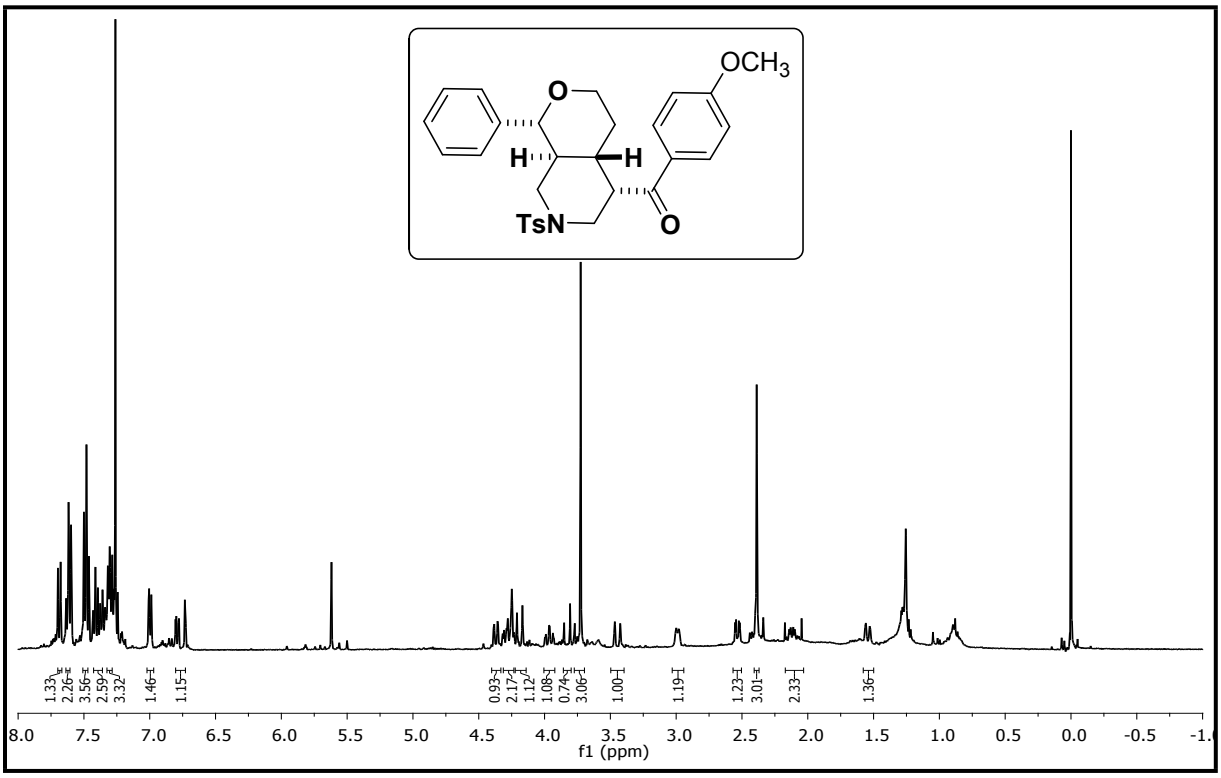
^{1}H NMR Spectra of compound 8m (500 MHz, $CDCl_3$)



^{13}C NMR Spectra of compound 8m (125 MHz, $CDCl_3$)



^{1}H NMR Spectra of compound 8n (400 MHz, $CDCl_3$)



^{13}C NMR Spectra of compound 8n (150 MHz, $CDCl_3$)