

Supporting Information

Tandem Prins spirocyclization for the stereoselective synthesis of tetrahydrospiro[chroman-2,4'-pyran] derivatives

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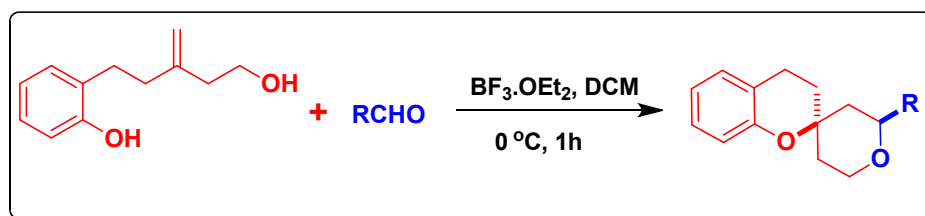
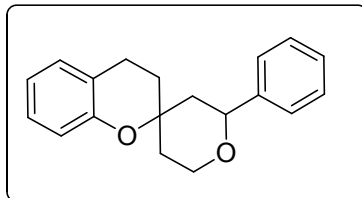


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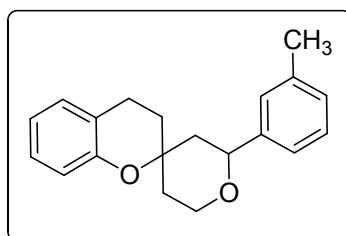
1. Characterization data of products (9a-r, 7x)

2'-Phenyl-2',3',5',6'-tetrahydrospiro[chroman-2,4'-pyran] (9a)



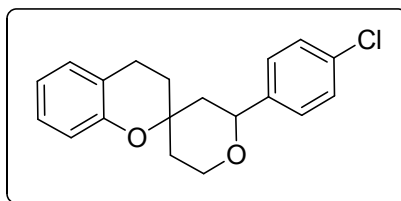
Viscous liquid; ^1H NMR (500 MHz, CDCl_3) δ 7.38 – 7.29 (m, 4H), 7.29 – 7.24 (m, 1H), 7.11 – 7.03 (m, 2H), 6.81 (dd, $J = 20.1, 13.3$ Hz, 2H), 4.47 (d, $J = 11.9$ Hz, 1H), 4.22 – 4.05 (m, 1H), 3.74 (tt, $J = 8.9, 4.4$ Hz, 1H), 2.88 – 2.77 (m, 2H), 2.26 – 2.11 (m, 2H), 2.10 – 1.99 (m, 2H), 1.94 – 1.83 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 153.1, 142.5, 129.5, 128.3, 127.4, 127.3, 125.9, 121.2, 120.1, 117.3, 74.77, 72.72, 63.7, 43.0, 34.3, 32.9, 30.9, 21.2; IR (KBr): ν 3120, 3090, 3019, 2924, 2853, 1598, 1504, 1482, 1417, 1215, 1074, 1041, 971 cm^{-1} ; HRMS: m/z calcd for $\text{C}_{19}\text{H}_{20}\text{O}_2$ ($\text{M}+\text{H}$) $^+$ 281.1458; found 281.1435.

2'-(*m*-Tolyl)-2',3',5',6'-tetrahydrospiro[chroman-2,4'-pyran] (9b)



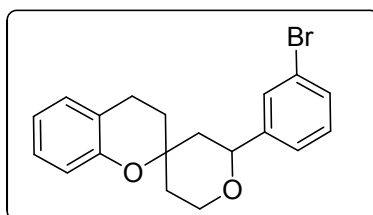
Pale yellow liquid; ^1H NMR (500 MHz, CDCl_3) δ 7.30 – 7.15 (m, 2H), 7.08 (ddd, $J = 17.5, 11.6, 8.4$ Hz, 4H), 7.01 – 6.73 (m, 2H), 4.47 (d, $J = 11.9$ Hz, 1H), 4.22 – 4.11 (m, 1H), 3.73 (td, $J = 13.0, 2.1$ Hz, 1H), 2.90 – 2.73 (m, 2H), 2.34 (d, $J = 12.1$ Hz, 3H), 2.25 – 2.10 (m, 2H), 2.03 (td, $J = 13.4, 3.8$ Hz, 2H), 1.94 – 1.81 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.5, 141.6, 138.0, 129.3, 128.4, 128.2, 127.4, 126.6, 123.0, 120.9, 120.0, 117.3, 76.6, 74.1, 64.9, 43.2, 36.1, 26.8, 21.4, 21.3; IR (KBr): ν 3012, 2950, 2925, 2851, 1725, 1604, 1582, 1489, 1465, 1359, 1309, 1239, 1153, 1098, 1072, 993, 959 cm^{-1} ; HRMS: m/z calcd for $\text{C}_{20}\text{H}_{22}\text{O}_2$ ($\text{M}+\text{H}$) $^+$ 295.1693; found 295.1684.

2'-(4-Chlorophenyl)-2',3',5',6'-tetrahydrospiro[chroman-2,4'-pyran] (9c)



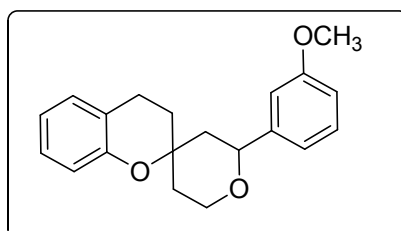
Pale yellow liquid; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.32 – 7.26 (m, 4H), 7.07 (dd, $J = 17.2$, 7.6 Hz, 2H), 6.83 (t, $J = 7.5$ Hz, 1H), 6.77 (d, $J = 8.1$ Hz, 1H), 4.45 (d, $J = 11.9$ Hz, 1H), 4.18 – 4.12 (m, 1H), 3.73 (td, $J = 12.6$, 2.2 Hz, 1H), 2.82 (t, $J = 6.8$ Hz, 2H), 2.20 – 2.13 (m, 2H), 2.08 – 1.96 (m, 2H), 1.90 – 1.78 (m, 2H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 171.1, 153.4, 140.4, 133.3, 129.4, 128.5, 127.5, 127.35, 120.8, 120.2, 117.4, 75.9, 73.9, 64.8, 60.4, 43.4, 36.0, 26.9, 21.5; IR (KBr): ν 3014, 2951, 2926, 2852, 1724, 1604, 1581, 1487, 1453, 1356, 1305, 1233, 1150, 1086, 1063, 1012, 991, 953 cm^{-1} ; HRMS: m/z calcd for $\text{C}_{19}\text{H}_{19}\text{ClO}_2$ ($\text{M}+\text{Na}$) $^+$ 337.0966; found 337.0967.

2'-(3-Bromophenyl)-2',3',5',6'-tetrahydrospiro[chroman-2,4'-pyran] (9d)



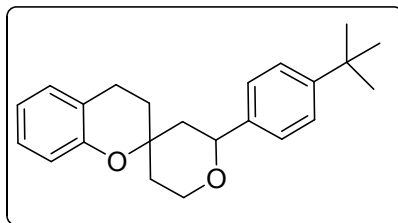
Pale yellow liquid; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.54 (s, 1H), 7.38 (d, $J = 6.1$ Hz, 1H), 7.26 (d, $J = 6.3$ Hz, 1H), 7.21 – 7.11 (m, 2H), 7.06 (t, $J = 7.8$ Hz, 1H), 6.93 – 6.84 (m, 2H), 4.83 (d, $J = 11.6$ Hz, 1H), 4.11 – 3.96 (m, 2H), 2.86 – 2.73 (m, 2H), 2.03 (dt, $J = 13.7$, 2.4 Hz, 1H), 1.87 – 1.80 (m, 3H), 1.77 – 1.68 (m, 1H), 1.62 – 1.58 (m, 1H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 153.0, 144.9, 130.4, 129.8, 129.6, 128.9, 127.4, 124.51, 122.5, 121.1, 120.2, 117.3, 74.03, 72.5, 63.7, 43.0, 34.2, 32.8, 30.1, 21.1, 14.1. IR (KBr) ν 3015, 2952, 2935, 2865, 1746, 1614, 1583, 1491, 1462, 1342, 1312, 1245, 1158, 1092, 1059, 1010, 991, 945 cm^{-1} ; HRMS: m/z calcd for $\text{C}_{19}\text{H}_{19}\text{BrO}_2$ ($\text{M}+\text{H}$) $^+$ 359.0641; found 359.0644.

2'-(3-Methoxyphenyl)-2',3',5',6'-tetrahydrospiro[chroman-2,4'-pyran] (9e)



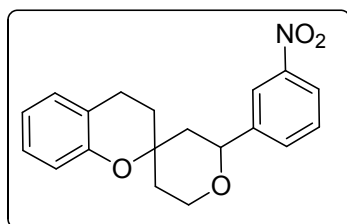
Pale yellow liquid; ^1H NMR (400 MHz, CDCl_3) δ 7.24 – 7.21 (d, $J = 14.2$, 1H), 7.07 (dd, $J = 14.2$, 6.9 Hz, 2H), 6.91 (dd, $J = 11.4$, 5.1 Hz, 2H), 6.85 – 6.75 (m, 3H), 4.45 (d, $J = 11.9$ Hz, 1H), 4.22 – 4.12 (m, 1H), 3.81 (s, 3H), 3.74 (t, $J = 12.8$ Hz, 1H), 2.82 (t, $J = 6.7$ Hz, 2H), 2.17 (dd, $J = 13.9$, 10.2 Hz, 2H), 2.10 – 1.98 (m, 2H), 1.94 – 1.81 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 158.93, 153.10, 134.70, 130.07, 129.52, 127.34, 127.21, 121.20, 120.06, 117.32, 113.90, 113.68, 74.34, 72.75, 63.74, 55.21, 42.81, 34.34, 32.91, 21.18; IR (KBr) ν 3016, 2968, 2946, 2854, 1610, 1573, 1481, 1459, 1458, 1246, 1165, 1091, 1047, 945 cm^{-1} ; HRMS: m/z calcd for $\text{C}_{20}\text{H}_{22}\text{O}_3$ ($\text{M}+\text{H}$) $^+$ 311.1642; found 311.1667.

2'-(4-(*tert*-Butyl)phenyl)-2',3',5',6'-tetrahydrospiro[chroman-2,4'-pyran] (9f)



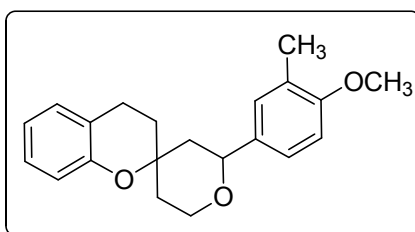
Viscous liquid; ^1H NMR (500 MHz, CDCl_3) δ 7.35 (d, $J = 8.1$ Hz, 2H), 7.28 (d, $J = 8.3$ Hz, 2H), 7.10 – 7.01 (m, 2H), 6.87 – 6.73 (m, 2H), 4.45 (d, $J = 11.9$ Hz, 1H), 4.22 – 4.04 (m, 1H), 3.80 (t, $J = 7.6$ Hz, 1H), 2.81 (t, $J = 6.7$ Hz, 2H), 2.29 – 2.09 (m, 2H), 2.11 – 1.97 (m, 2H), 1.99 – 1.77 (m, 2H), 1.29 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 153.5, 150.7, 138.6, 129.3, 127.3, 125.7, 125.3, 120.9, 120.0, 117.3, 76.5, 74.1, 64.9, 42.9, 36.2, 34.48, 31.3, 26.8, 21.5; IR (KBr) ν 3010, 2955, 2927, 2854, 1610, 1581, 1486, 1454, 1360, 1234, 1120, 1089, 1062, 991, 953, 905 cm^{-1} ; HRMS: m/z calcd for $\text{C}_{23}\text{H}_{28}\text{O}_2$ ($\text{M}+\text{Na}$) $^+$ 359.1982; found 359.2009.

2'-(3-Nitrophenyl)-2',3',5',6'-tetrahydrospiro[chroman-2,4'-pyran] (9g)



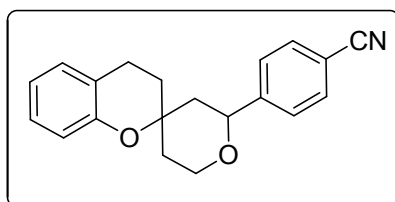
Pale yellow liquid; ^1H NMR (500 MHz, CDCl_3) δ 8.27 (s, 1H), 8.12 (d, $J = 8.2$ Hz, 1H), 7.68 (d, $J = 7.7$ Hz, 1H), 7.49 (dd, $J = 14.4, 6.5$ Hz, 1H), 7.18 – 7.11 (m, 1H), 7.08 (d, $J = 7.4$ Hz, 1H), 6.95 – 6.85 (m, 2H), 4.97 (d, $J = 11.6$ Hz, 1H), 4.14 – 4.00 (m, 2H), 2.88 – 2.73 (m, 2H), 2.09 (dt, $J = 13.7, 2.3$ Hz, 1H), 1.90 – 1.82 (m, 3H), 1.80 – 1.71 (m, 1H), 1.64 – 1.57 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 152.8, 148.3, 144.8, 132.0, 129.6, 129.2, 127.5, 122.3, 121.0, 120.9, 120.3, 117.3, 73.6, 72.4, 63.7, 43.1, 34.0, 32.8, 21.1; IR (KBr) ν 3015, 2950, 2923, 2855, 1730, 1706, 1581, 1529, 1486, 1453, 1348, 1307, 1229, 1141, 1085, 1045, 979, 926 cm^{-1} ; HRMS: m/z calcd for $\text{C}_{19}\text{H}_{19}\text{NO}_4$ ($\text{M}+\text{Na}$) $^+$ 348.1206; found 348.1212.

2'-(4-Methoxy-3-methylphenyl)-2',3',5',6'-tetrahydrospiro[chroman-2,4'-pyran] (9h)



Pale yellow liquid; ^1H NMR (400 MHz, CDCl_3) δ 7.19 – 7.00 (m, 4H), 6.88 – 6.72 (m, 3H), 4.39 (d, $J = 11.7$ Hz, 1H), 4.20 – 4.07 (m, 1H), 3.80 (s, 3H), 3.72 (t, $J = 12.9$ Hz, 1H), 2.81 (t, $J = 6.8$ Hz, 2H), 2.19 (s, 3H), 2.19 – 2.10 (m, 2H), 2.09 – 1.97 (m, 2H), 1.97 – 1.80 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 157.3, 153.6, 133.4, 129.3, 128.6, 127.4, 126.6, 124.5, 121.0, 120.0, 117.3, 109.7, 76.5, 74.2, 64.9, 55.4, 43.1, 36.18, 26.9, 21.5, 16.2; IR (KBr): ν 3120, 3093, 3010, 2945, 2865, 1596, 1514, 1484, 1427, 1235, 1064, 1051, 984 cm^{-1} ; HRMS: m/z calcd for $\text{C}_{21}\text{H}_{24}\text{O}_3$ ($\text{M}+\text{Na}$) $^+$ 347.1765; found 347.1748.

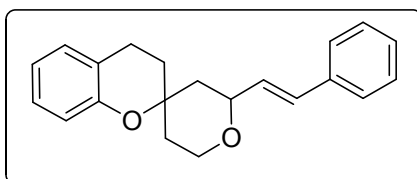
4-(2',3',5',6'-Tetrahydrospiro[chroman-2,4'-pyran]-2'-yl)benzotrile (9i)



^1H NMR (400 MHz, CDCl_3) δ 7.62 (d, $J = 8.3$ Hz, 6H), 7.48 (t, $J = 13.4$ Hz, 7H), 7.19 – 7.02 (m, 7H), 6.89 (dd, $J = 17.4, 7.8$ Hz, 6H), 4.91 (d, $J = 11.5$ Hz, 3H), 4.13 – 3.96 (m,

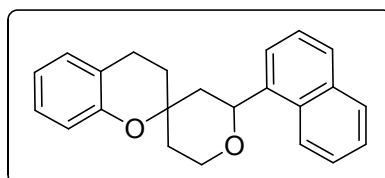
6H), 2.88 – 2.72 (m, 6H), 2.08 – 2.00 (m, 4H), 1.84 (dd, $J = 13.3, 6.9$ Hz, 9H), 1.79 – 1.67 (m, 5H); ^{13}C NMR (125 MHz, CDCl_3) δ 152.89, 148.12, 132.18, 129.63, 127.51, 126.43, 121.11, 120.35, 117.33, 111.07, 73.94, 72.45, 63.71, 43.14, 34.10, 30.19, 29.36, 22.69, 21.14, 14.11; IR (KBr) ν 3014, 2955, 2926, 2842, 1734, 1609, 1587, 1477, 1450, 1359, 1315, 1243, 1154, 1096, 1072, 1015, 996, 963 cm^{-1} ; HRMS: m/z calcd for $\text{C}_{20}\text{H}_{19}\text{NO}_4$ ($\text{M}+\text{Na}$) $^+$ 328.1308; found 328.1320.

2'-Styryl-2',3',5',6'-tetrahydrospiro[chroman-2,4'-pyran] (9j)



Viscous liquid; ^1H NMR (500 MHz, CDCl_3) δ 7.38 – 7.33 (m, 2H), 7.29 (dd, $J = 10.4, 4.8$ Hz, 2H), 7.24 – 7.18 (m, 1H), 7.15 – 7.10 (m, 1H), 7.07 (d, $J = 7.5$ Hz, 1H), 6.87 (ddd, $J = 9.0, 8.4, 4.6$ Hz, 2H), 6.62 (d, $J = 15.5$ Hz, 1H), 6.18 (d, $J = 16.0$ Hz, 1H), 4.52 – 4.46 (m, 1H), 4.02 (td, $J = 12.0, 2.4$ Hz, 1H), 3.94 (ddd, $J = 11.5, 5.2, 1.1$ Hz, 1H), 2.81 (t, $J = 6.8$ Hz, 2H), 1.96 (d, $J = 13.7$ Hz, 1H), 1.86 – 1.75 (m, 3H), 1.68 (dd, $J = 13.8, 12.5$ Hz, 1H), 1.51 (d, $J = 13.6$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 153.1, 136.9, 130.2, 130.1, 129.6, 128.5, 127.5, 127.4, 126.4, 121.2, 120.1, 117.4, 72.9, 72.5, 63.3, 41.1, 34.5, 32.9, 21.2; IR (KBr): ν 3023, 2947, 2920, 2859, 1726, 1580, 1486, 1452, 1368, 1303, 1269, 1227, 1188, 1139, 1082, 1041, 965 cm^{-1} ; HRMS: m/z calcd for $\text{C}_{21}\text{H}_{22}\text{O}_2$ ($\text{M}+\text{H}$) $^+$ 307.1693; found 307.1684.

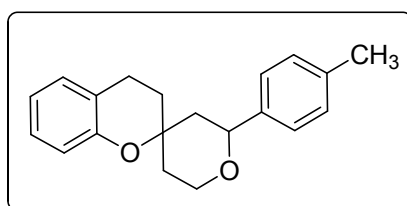
2'-(Naphthalen-1-yl)-2',3',5',6'-tetrahydrospiro[chroman-2,4'-pyran] (9k)



White Solid; M.P 185-187°C ^1H NMR (500 MHz, CDCl_3) δ 8.03 (d, $J = 8.4$ Hz, 1H), 7.85 (d, $J = 7.6$ Hz, 1H), 7.77 (d, $J = 8.2$ Hz, 1H), 7.66 (d, $J = 7.1$ Hz, 1H), 7.52 (dd, $J = 8.4, 6.9$ Hz, 1H), 7.46 (t, $J = 7.6$ Hz, 2H), 7.07 (t, $J = 8.2$ Hz, 2H), 6.86 – 6.74 (m, 2H), 5.22 (d, $J = 11.9, 1.5$ Hz, 1H), 4.27 (dd, $J = 12.0, 5.3$ Hz, 1H), 3.90 (t, $J = 13.0$ Hz, 1H), 2.94 – 2.83 (m, 2H),

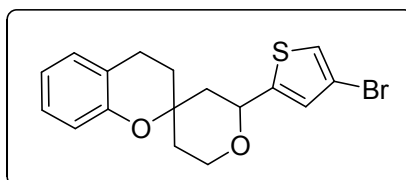
2.44 – 2.33 (m, 1H), 2.33 – 2.23 (m, 2H), 2.19 – 2.02 (m, 2H), 1.98 – 1.90 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 153.4, 137.2, 133.7, 130.1, 129.3, 128.9, 128.1, 127.4, 126.0, 125.5, 125.3, 123.1, 122.6, 120.8, 120.0, 117.3, 74.3, 73.5, 65.2, 42.4, 36.4, 26.9, 21.6; IR (KBr): ν 3021, 2951, 2928, 2860, 1731, 1581, 1476, 1441, 1372, 1313, 1272, 1237, 1178, 1149, 1062, 1053, 965 cm^{-1} ; HRMS: m/z calcd for $\text{C}_{23}\text{H}_{22}\text{O}_2$ ($\text{M}+\text{Na}$) $^+$ 353.1512; found 353.1534.

2'-(*p*-Tolyl)-2',3',5',6'-tetrahydrospiro[chroman-2,4'-pyran] (9l)



Pale yellow liquid; ^1H NMR (500 MHz, CDCl_3) δ 7.24 (d, $J = 8.1$ Hz, 2H), 7.13 (d, $J = 7.9$ Hz, 2H), 7.07 (dd, $J = 11.6, 9.1$ Hz, 2H), 6.82 (td, $J = 7.4, 1.1$ Hz, 1H), 6.78 (d, $J = 8.2$ Hz, 1H), 4.43 (d, $J = 11.9$ Hz, 1H), 4.18 – 4.10 (m, 1H), 3.78 – 3.68 (m, 1H), 2.88 – 2.77 (m, 2H), 2.32 (s, 3H), 2.23 – 2.13 (m, 2H), 2.03 (dd, $J = 16.1, 9.2$ Hz, 2H), 1.94 – 1.82 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 153.5, 138.7, 137.4, 129.1, 129.4, 127.9, 125.9, 120.9, 120.0, 117.3, 76.5, 74.1, 64.8, 43.3, 36.0, 26.8, 21.5, 21.0; IR (KBr): ν 3015, 2951, 2926, 2855, 1735, 1607, 1582, 1514, 1486, 1456, 1358, 1304, 1244, 1151, 1089, 1068, 995 cm^{-1} ; HRMS: m/z calcd for $\text{C}_{20}\text{H}_{22}\text{O}_2$ ($\text{M}+\text{H}$) $^+$ 295.1693; found 295.1684.

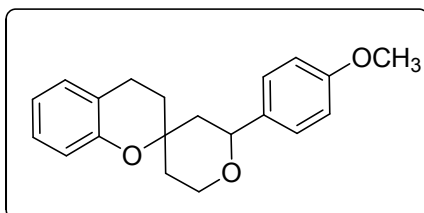
2'-(4-Bromothiophen-2-yl)-2',3',5',6'-tetrahydrospiro[chroman-2,4'-pyran] (9m)



Viscous liquid; ^1H NMR (400 MHz, CDCl_3) δ 7.16 – 7.13 (s, 1H), 7.13 – 7.03 (m, 2H), 6.85 (dd, $J = 10.1, 3.1$ Hz, 2H), 6.78 (dd, $J = 8.2, 1.0$ Hz, 1H), 4.70 (d, $J = 6.7$ Hz, 1H), 4.14 (td, $J = 7.5, 5.2$ Hz, 1H), 3.73 (td, $J = 12.2, 2.5$ Hz, 1H), 2.88 – 2.72 (m, 2H), 2.14 (dd, $J = 19.3, 7.8$ Hz, 3H), 2.04 – 1.94 (m, 2H), 1.84 (dq, $J = 13.4, 2.4$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.0, 153.3, 146.7, 129.3, 127.0, 126.8, 122.1, 120.6, 120.1, 117.6, 108.9, 76.4,

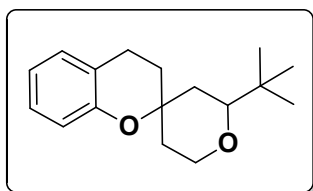
73.4, 71.8, 64.5, 60.3, 42.4, 35.7, 27.1, 21.3; IR (KBr): ν 3012, 2968, 2924, 2851, 1610, 1585, 1490, 1460, 1358, 1310, 1239, 1156, 1085, 1065, 1015, 998, 951 cm^{-1} ; HRMS: m/z calcd for $\text{C}_{17}\text{H}_{17}\text{BrO}_2\text{S}$ ($\text{M}+\text{Na}$)⁺ 387.0025; found 387.0017.

2'-(4-Methoxyphenyl)-2',3',5',6'-tetrahydrospiro[chroman-2,4'-pyran] (9n)



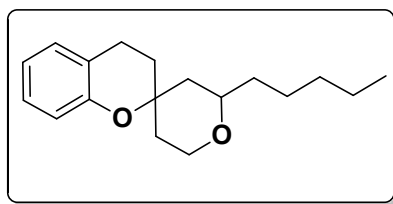
Pale yellow liquid; ^1H NMR (500 MHz, CDCl_3) δ 7.31 – 7.26 (m, 2H), 7.19 – 7.01 (m, 2H), 6.91 (t, J = 6.1 Hz, 1H), 6.88 – 6.83 (m, 3H), 4.80 (d, J = 11.6 Hz, 1H), 4.16 – 3.93 (m, 2H), 3.79 (s, 3H), 2.90 – 2.69 (m, 2H), 2.00 (dt, J = 13.8, 2.2 Hz, 1H), 1.89 – 1.78 (m, 3H), 1.77 – 1.70 (m, 1H), 1.65 (d, J = 13.7 Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 158.9, 153.1, 134.7, 129.56, 127.3, 127.2, 121.2, 120.1, 117.3, 113.7, 74.3, 72.80, 63.7, 55.2, 42.8, 34.3, 32.9, 21.2; IR (KBr): ν 3010, 2951, 2927, 2853, 1611, 1581, 1504, 1487, 1454, 1357, 1307, 1233, 1180, 1132, 1086, 1034 cm^{-1} ; HRMS: m/z calcd for $\text{C}_{20}\text{H}_{22}\text{O}_3$ ($\text{M}+\text{H}$)⁺ 311.1642; found 311.1667.

2'-(*tert*-Butyl)-2',3',5',6'-tetrahydrospiro[chromane-2,4'-pyran] (9o)



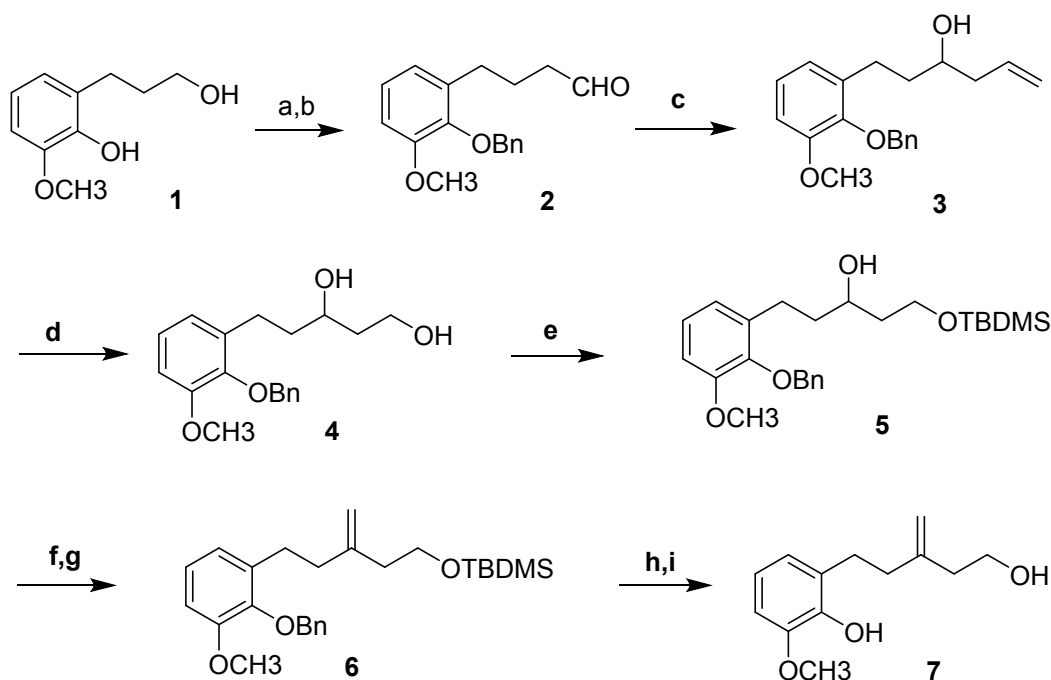
^1H NMR (500 MHz, CDCl_3) δ 7.12 – 7.02 (m, 9H), 6.86 – 6.78 (m, 9H), 4.00 (ddd, J = 11.9, 5.2, 1.4 Hz, 2H), 3.87 – 3.76 (m, 6H), 3.54 – 3.40 (m, 5H), 3.00 (dd, J = 11.9, 1.5 Hz, 2H), 2.84 – 2.69 (m, 10H), 2.09 – 2.00 (m, 4H), 1.86 – 1.70 (m, 17H), 1.58 – 1.48 (m, 5H), 1.38 – 1.23 (m, 6H), 0.89 (d, J = 4.3 Hz, 43H); ^{13}C NMR (126 MHz, CDCl_3) δ 153.64, 153.23, 129.44, 129.36, 127.38, 127.24, 121.28, 121.05, 119.87, 117.33, 117.27, 82.21, 79.94, 77.25, 77.00, 76.75, 74.75, 72.91, 64.65, 63.60, 36.35, 35.94, 35.74, 34.18, 33.92, 33.63, 33.36, 25.97, 21.46, 21.30;); HRMS: m/z calcd for $\text{C}_{17}\text{H}_{24}\text{O}_2$ ($\text{M}+\text{Na}$)⁺ 283.1669; found 283.1681.

2'-Pentyl-2',3',5',6'-tetrahydrospiro[chroman-2,4'-pyran] (9p)



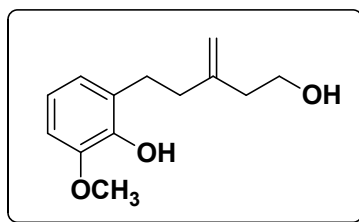
^1H NMR (400 MHz, CDCl_3) δ 7.16 – 6.98 (m, 2H), 6.92 – 6.74 (m, 2H), 4.02 – 3.87 (m, 1H), 3.83 (dd, $J = 11.5, 5.4$ Hz, 1H), 3.79 – 3.70 (m, 1H), 3.58 – 3.36 (m, 1H), 2.83 – 2.70 (m, 2H), 2.04 (t, $J = 6.8$ Hz, 1H), 1.83 – 1.70 (m, 3H), 1.65 – 1.52 (m, 2H), 1.34 – 1.25 (m, 8H), 0.89 (dd, $J = 6.8, 1.6$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 153.61, 153.21, 129.50, 129.32, 127.37, 127.29, 121.25, 121.00, 119.93, 117.32, 101.68, 77.32, 77.00, 76.68, 74.45, 73.99, 72.63, 72.51, 64.21, 63.28, 41.58, 41.17, 36.26, 36.21, 34.63, 34.37, 33.02, 31.96, 31.87, 27.09, 25.21, 25.18, 23.23, 22.97, 22.59, 21.48, 21.24, 14.04; HRMS: m/z calcd for $\text{C}_{18}\text{H}_{26}\text{O}_2$ ($\text{M}+\text{Na}$) $^+$ 297.1825; found 297.1808.

Preparation of starting material (7x)



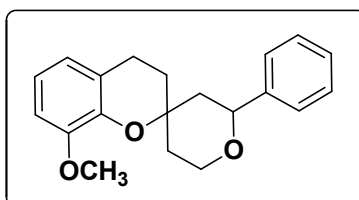
Reagents and conditions: a) Benzyl bromide, K_2CO_3 , DMF, 25 °C, 2h; b) PCC, DCM, 0-25 °C; c) Zn, allyl bromide, aq. NH_4Cl ; d) O_3 , TPP, NaBH_4 ; e) TBSCl, imidazole, DCM; f) PCC, DCM; g) Methyl triphenylphosphonium bromide salt, $n\text{-BuLi}$; h) TBAF, THF; i) Li, naphthalene, THF, 0 to 25 °C.

2-(5-Hydroxy-3-methylenepentyl)-6-methoxyphenol (7x)



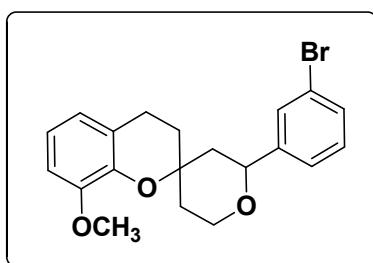
^1H NMR (400 MHz, CDCl_3) δ 6.81 – 6.70 (m, 3H), 5.74 (s, 1H), 4.94 – 4.84 (m, 2H), 3.88 (s, 3H), 3.74 (t, J = 6.3 Hz, 2H), 3.49 – 3.47 (m, 1H), 2.79 (dd, J = 9.1, 7.0 Hz, 2H), 2.35 (dd, J = 13.2, 6.5 Hz, 4H); ^{13}C NMR (101 MHz, CDCl_3) δ 146.30, 145.82, 143.43, 127.65, 122.14, 119.28, 111.92, 108.45, 77.32, 77.00, 76.68, 60.35, 55.96, 50.83, 39.40, 35.66, 28.35; HRMS: m/z calcd for $\text{C}_{13}\text{H}_{18}\text{O}_3$ ($\text{M}+\text{H}$) $^+$ 223.1389; found 223.1310.

8-Methoxy-2'-phenyl-2',3',5',6'-tetrahydrospiro[chroman-2,4'-pyran] (9q)



^1H NMR (400 MHz, CDCl_3) δ 7.57 – 7.53 (m, 2H), 7.37 – 7.29 (m, 3H), 6.77 (dd, J = 17.6, 6.6 Hz, 2H), 6.71 – 6.66 (m, 1H), 4.90 (dd, J = 11.6, 2.2 Hz, 1H), 4.14 (ddd, J = 12.4, 9.8, 2.4 Hz, 1H), 4.00 (dd, J = 11.5, 4.0 Hz, 1H), 3.89 (s, 3H), 2.85 – 2.75 (m, 2H), 2.16 – 2.06 (m, 1H), 1.93 – 1.70 (m, 4H), 1.69 – 1.61 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 149.25, 143.43, 142.61, 130.51, 128.97, 128.29, 128.25, 127.40, 127.17, 126.01, 122.18, 121.44, 119.58, 109.83, 77.32, 77.00, 76.68, 74.78, 73.01, 63.86, 56.16, 42.65, 34.34, 32.78, 27.53, 21.28; HRMS: m/z calcd for $\text{C}_{20}\text{H}_{22}\text{O}_3$ ($\text{M}+\text{Na}$) $^+$ 333.1461; found 333.1477.

2'-(3-Bromophenyl)-8-methoxy-2',3',5',6'-tetrahydrospiro[chroman-2,4'-pyran] (9r)

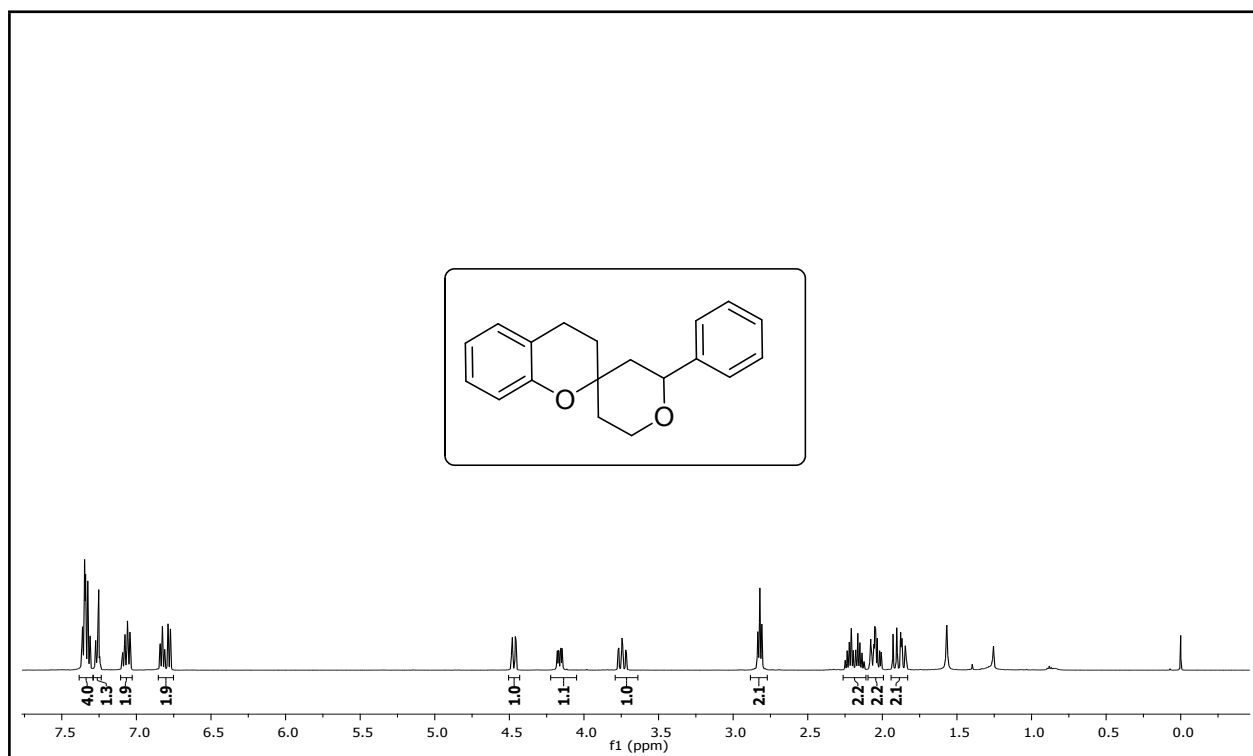


^1H NMR (400 MHz, CDCl_3) δ 7.51 (s, 1H), 7.38 (d, J = 7.9 Hz, 1H), 7.27 (d, J = 5.7 Hz, 1H), 7.18 (t, J = 7.8 Hz, 1H), 6.79 (t, J = 7.8 Hz, 1H), 6.69 (t, J = 8.2 Hz, 2H), 4.44 (dd, J = 11.8, 2.0 Hz, 1H), 4.21 – 4.13 (m, 1H), 3.83 (s, 3H), 3.78 – 3.68 (m, 1H), 2.83 (t, J = 6.8 Hz, 2H),

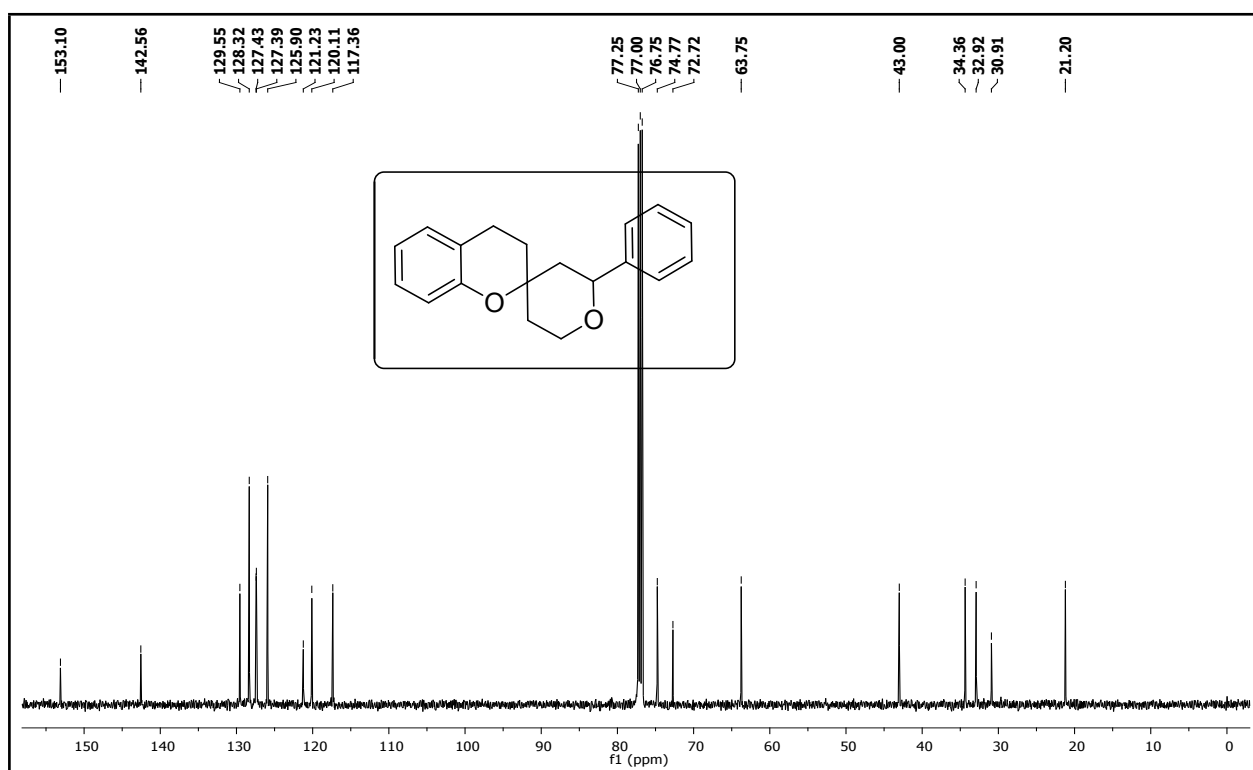
2.25 – 2.06 (m, 4H), 1.99 – 1.84 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 148.84, 144.08, 142.91, 130.69, 129.93, 129.19, 124.54, 122.46, 121.61, 121.27, 119.60, 109.54, 77.32, 77.00, 76.68, 76.04, 74.29, 64.92, 55.97, 43.03, 36.02, 26.71, 21.54; HRMS: m/z calcd for $\text{C}_{20}\text{H}_{21}\text{BrO}_3$ ($\text{M}+\text{Na}$) $^+$ 411.0566; found 411.0596.

2. ^1H , ^{13}C NMR spectra of 9a-r & 7x:

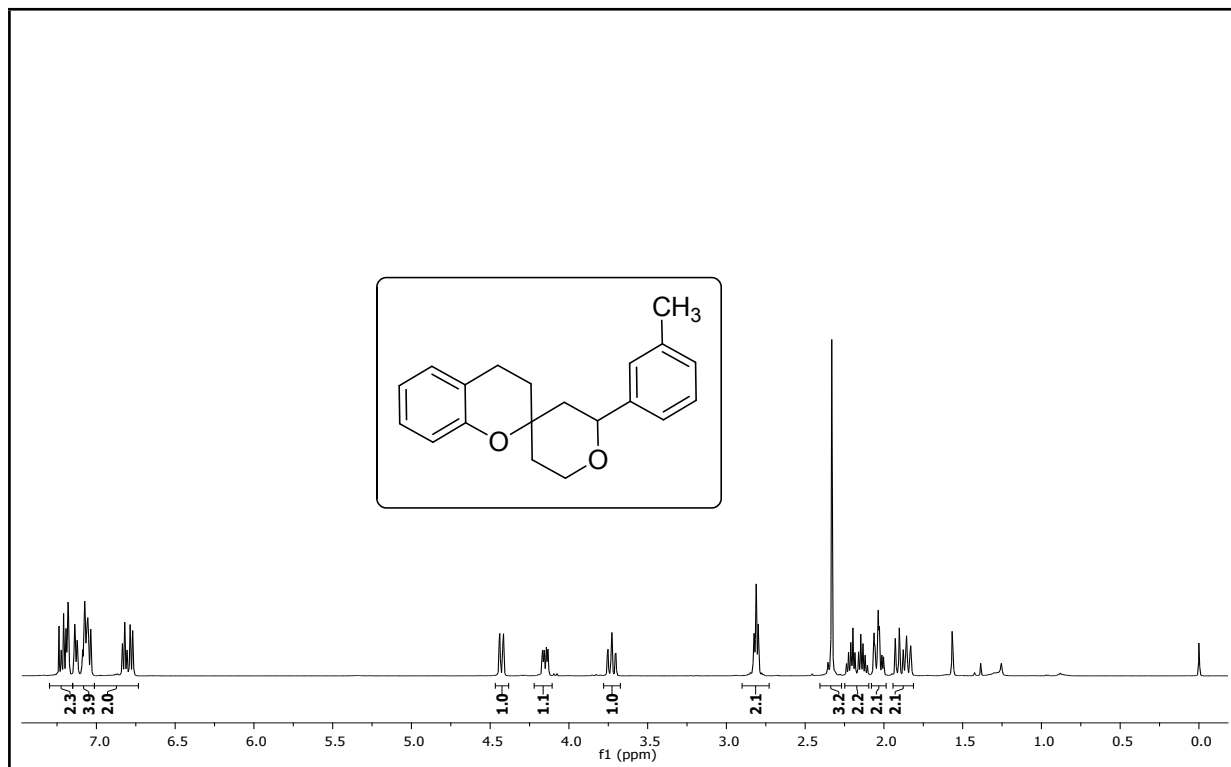
¹H NMR Spectra of compound 9a (500 MHz, CDCl₃)



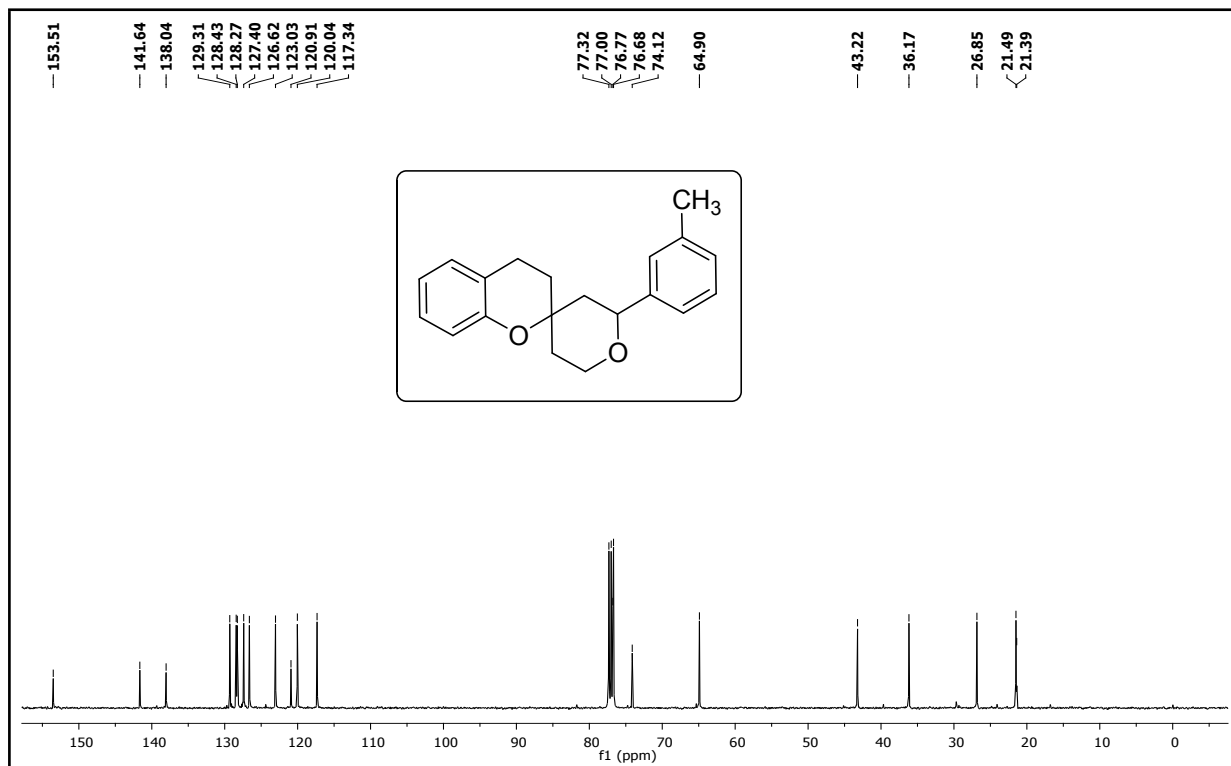
¹³C NMR Spectra of compound 9a (125 MHz, CDCl₃)



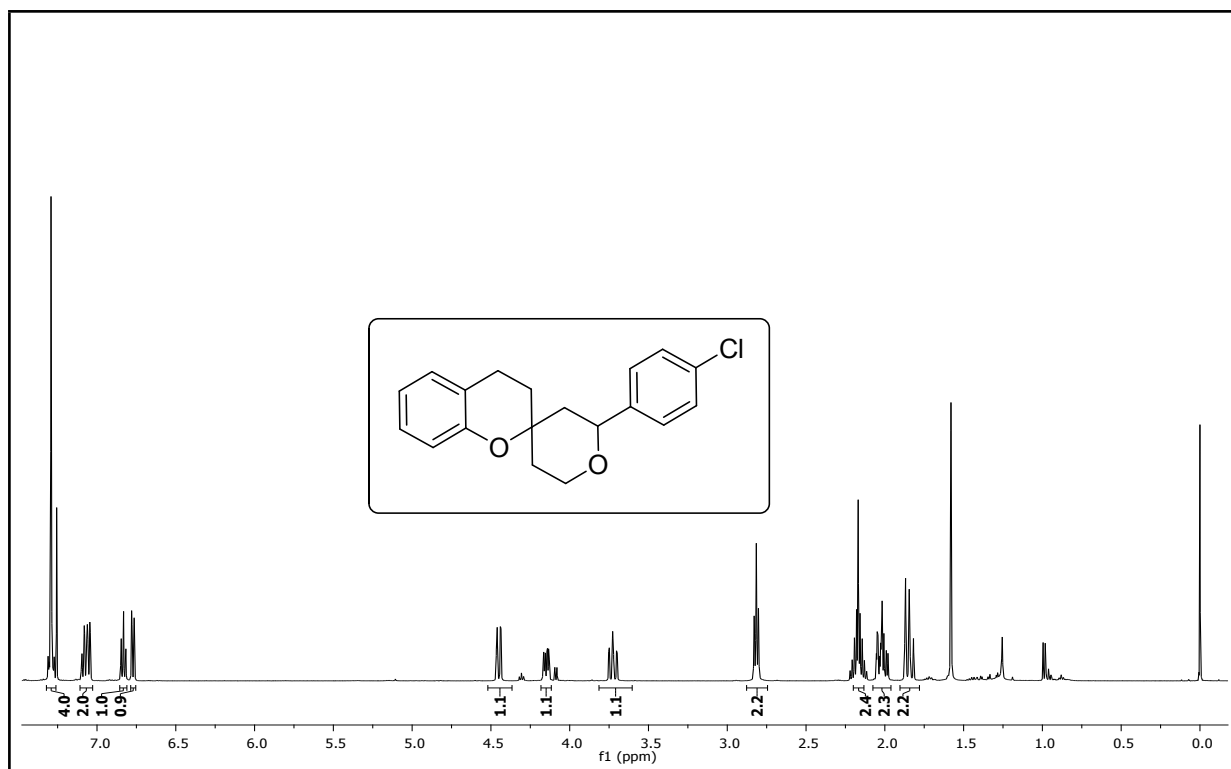
¹H NMR Spectra of compound 9b (500 MHz, CDCl₃)



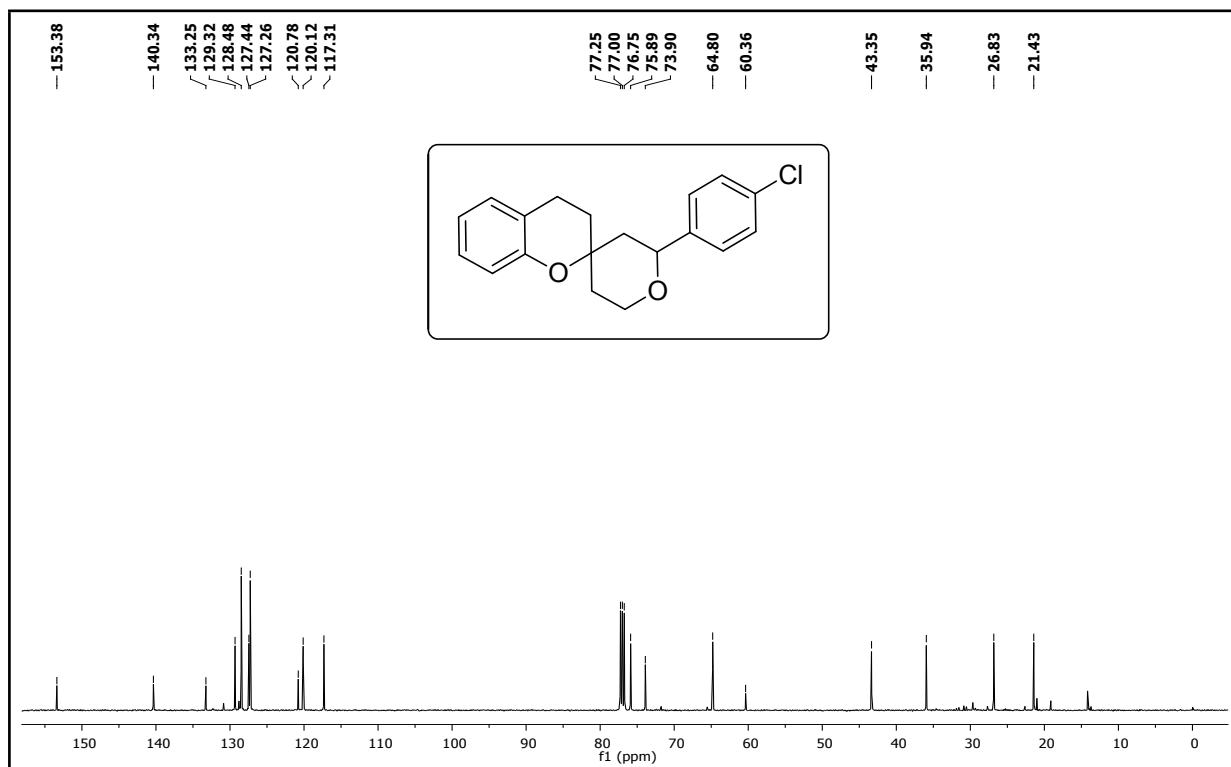
¹³C NMR Spectra of compound 9b (125 MHz, CDCl₃)



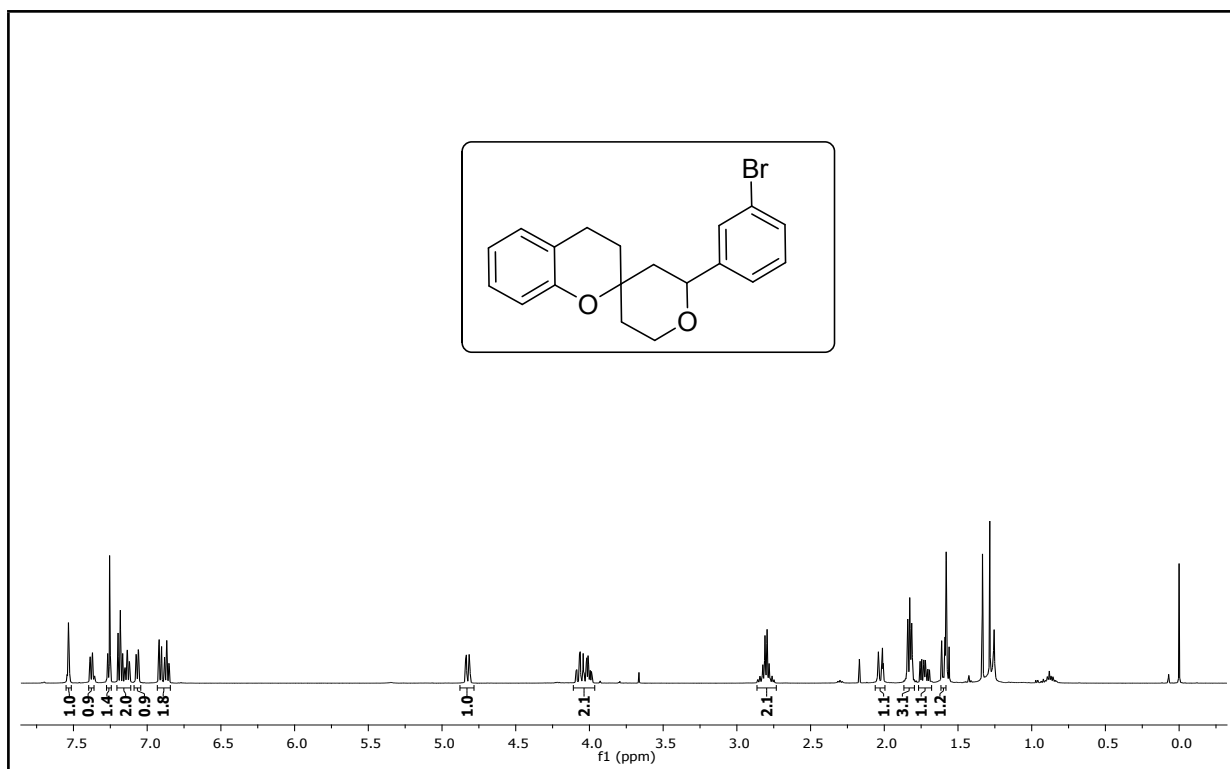
¹H NMR Spectra of compound 9c (500 MHz, CDCl₃)



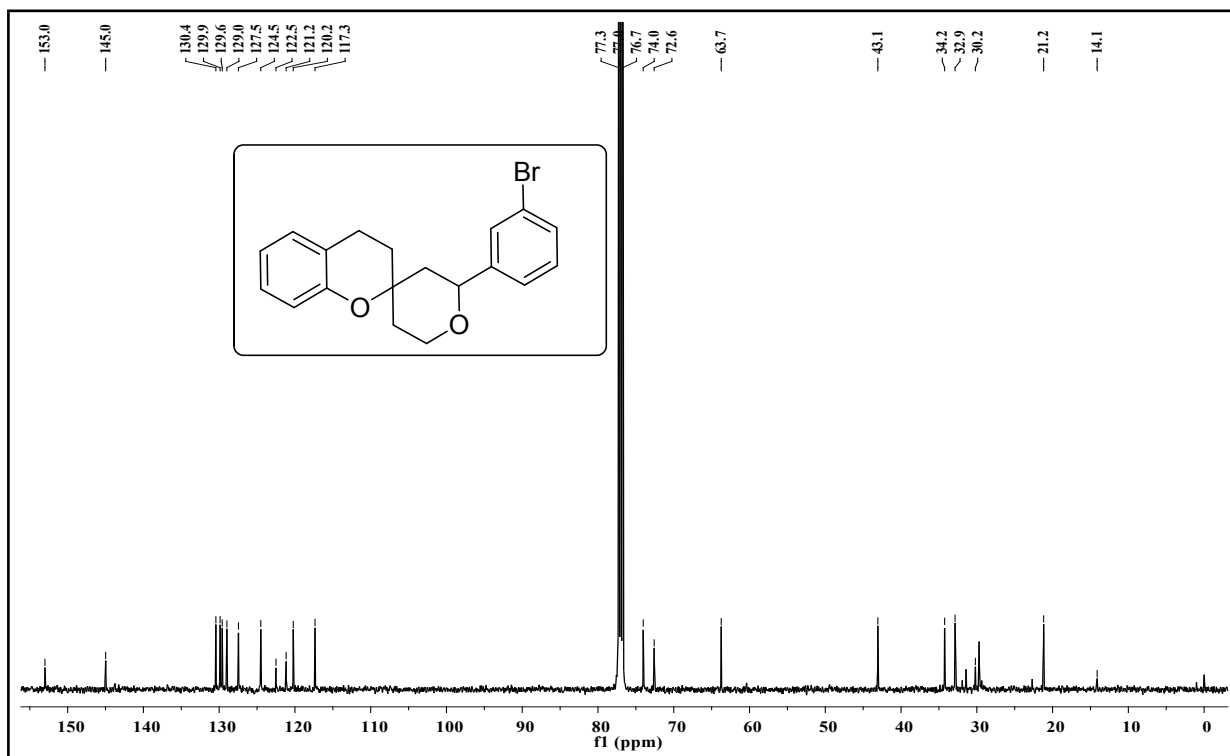
¹³C NMR Spectra of compound 9c (125 MHz, CDCl₃)



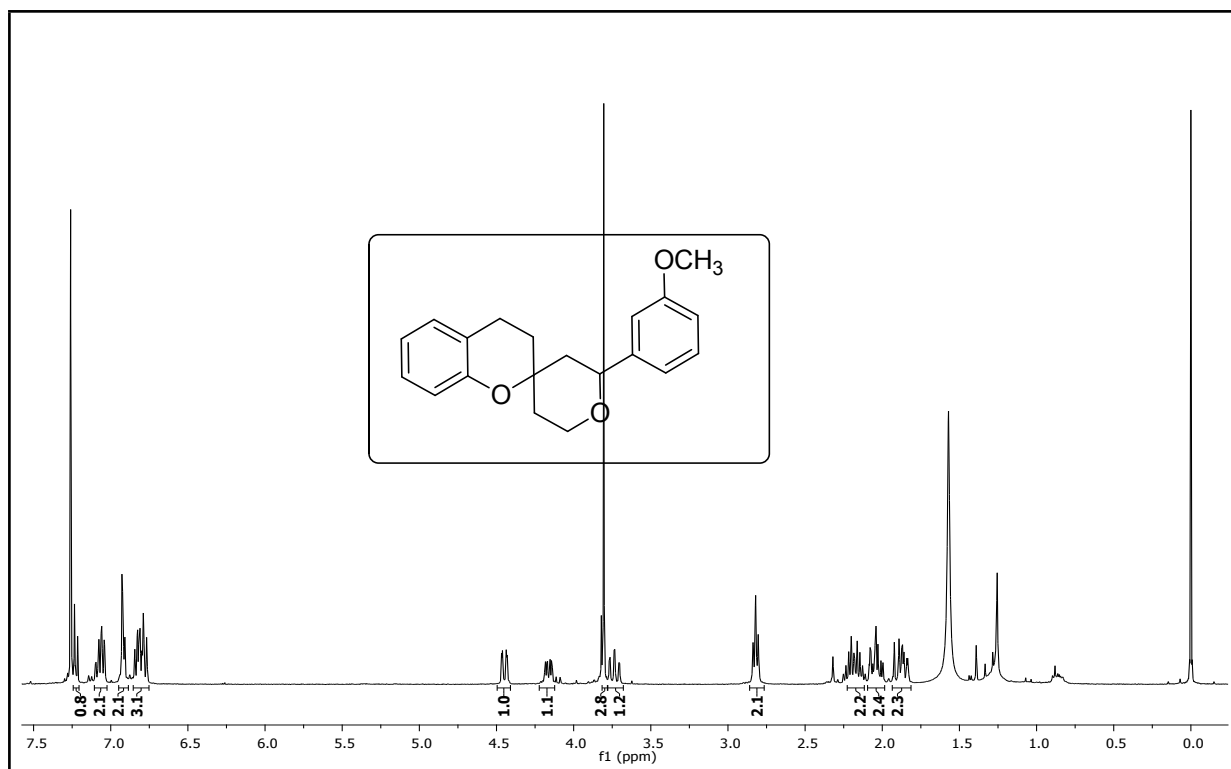
¹H NMR Spectra of compound 9d (500 MHz, CDCl₃)



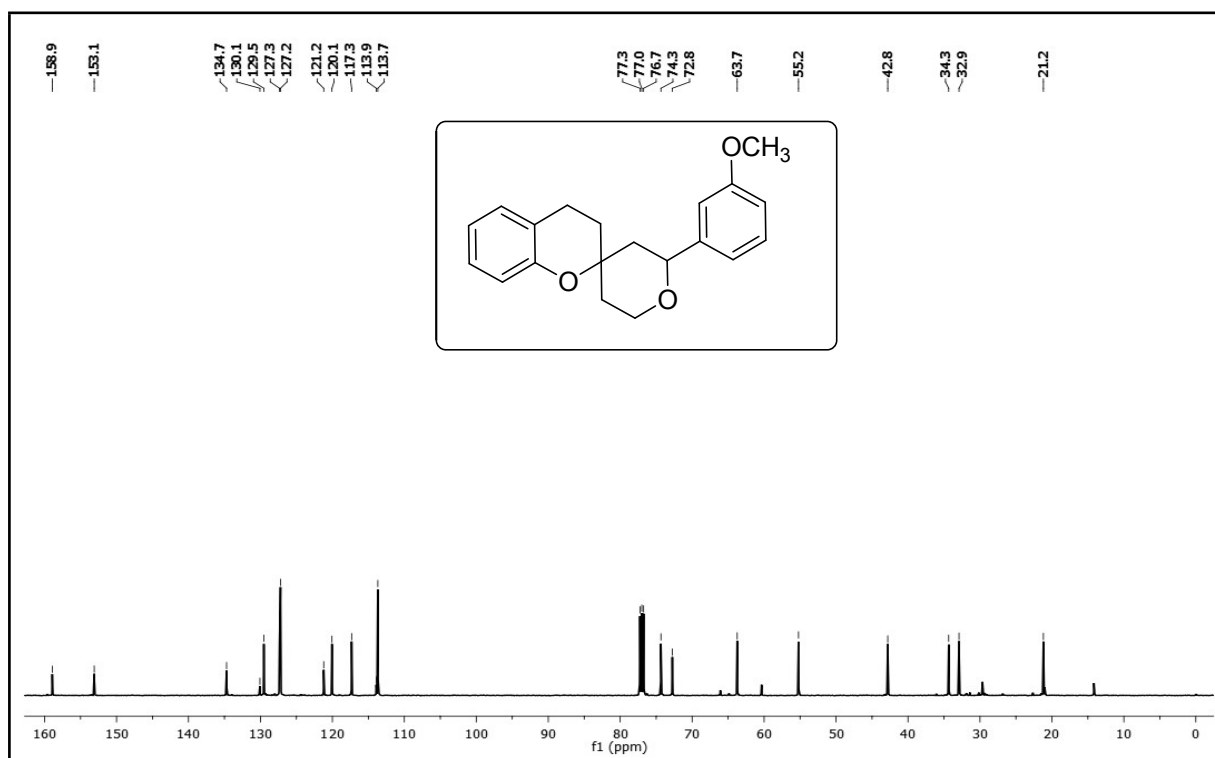
¹³C NMR Spectra of compound 9d (125 MHz, CDCl₃)



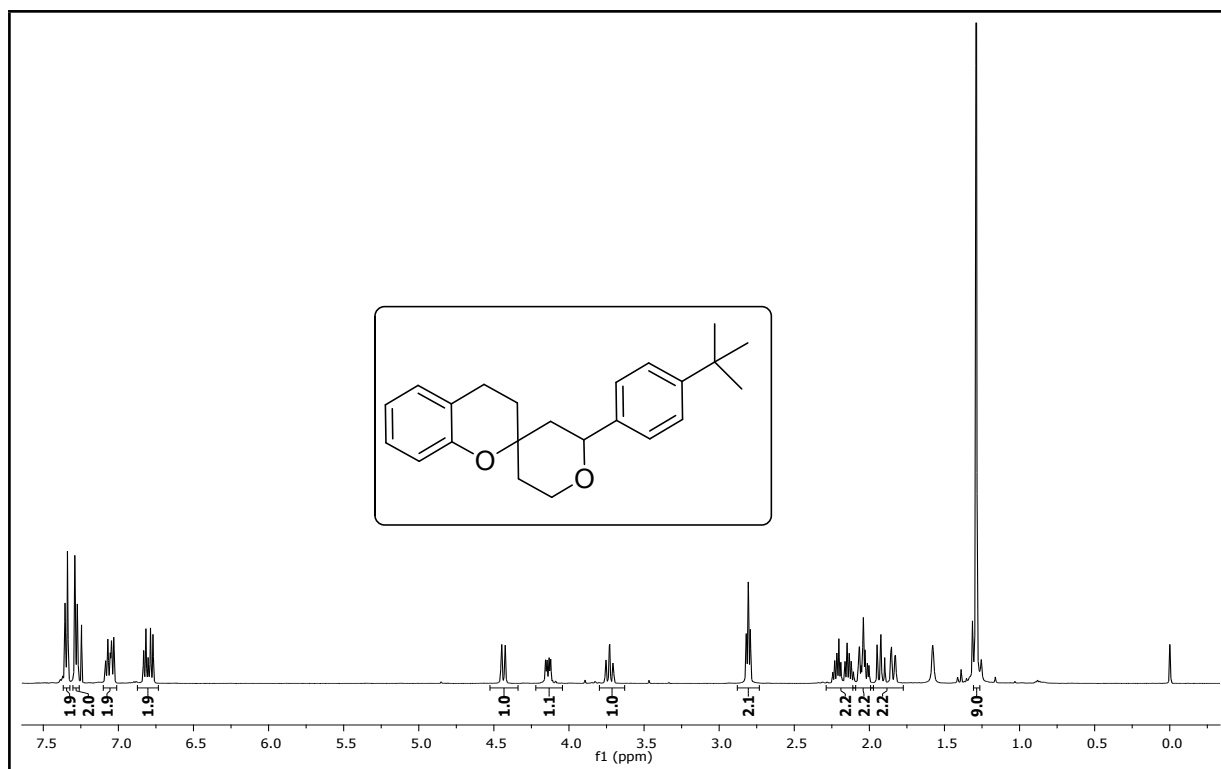
¹H NMR Spectra of compound 9e (500 MHz, CDCl₃)



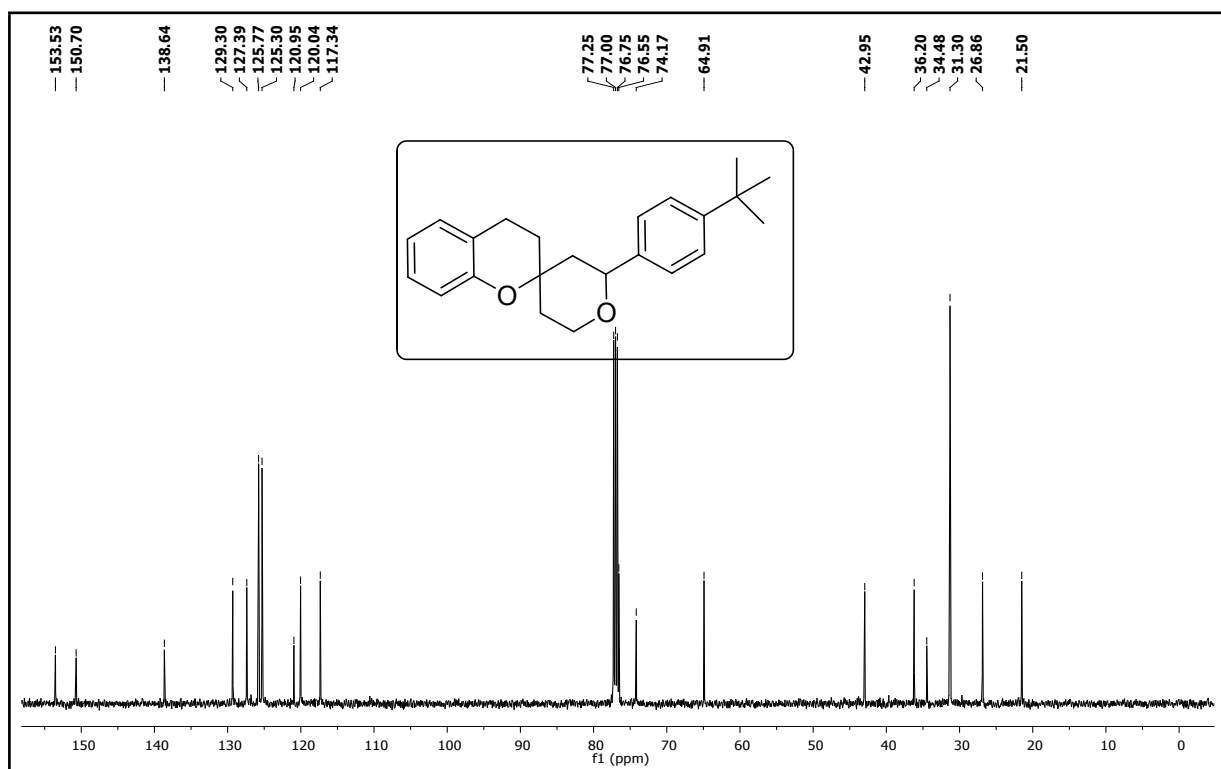
¹³C NMR Spectra of compound 9e (125 MHz, CDCl₃)



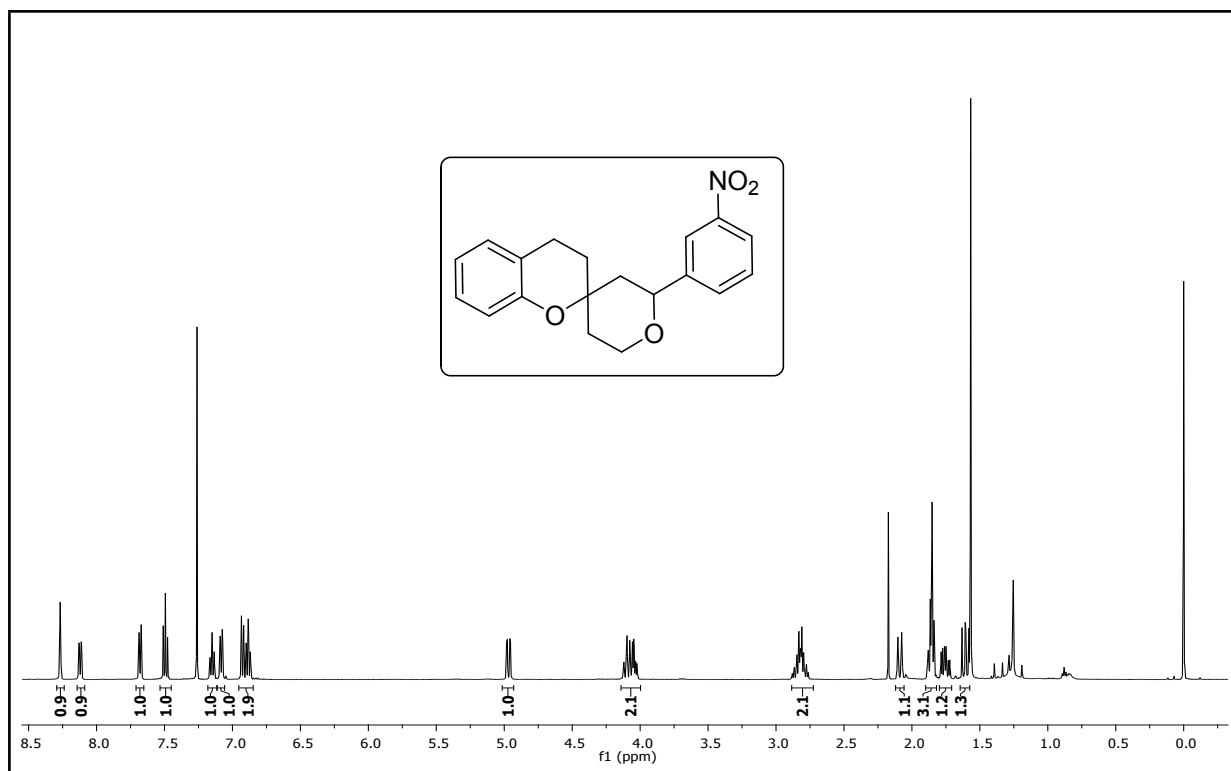
¹H NMR Spectra of compound 9f (500 MHz, CDCl₃)



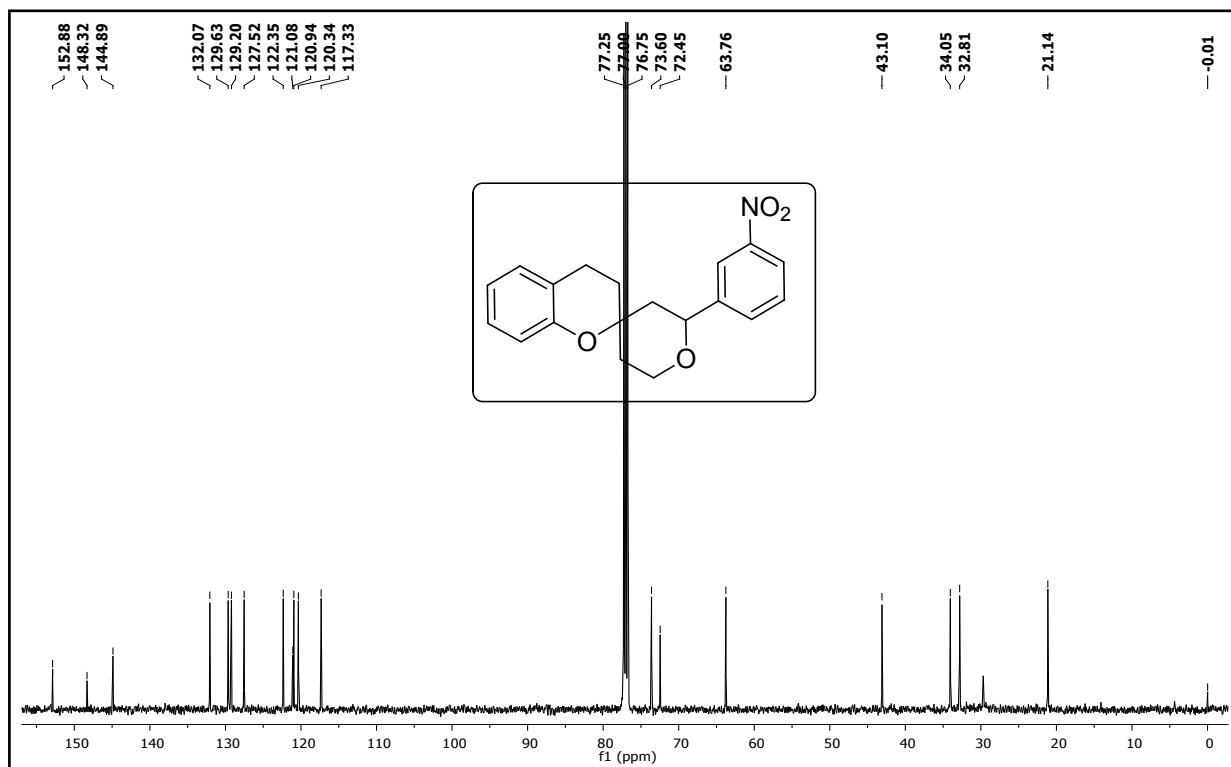
¹³C NMR Spectra of compound 9f (125 MHz, CDCl₃)



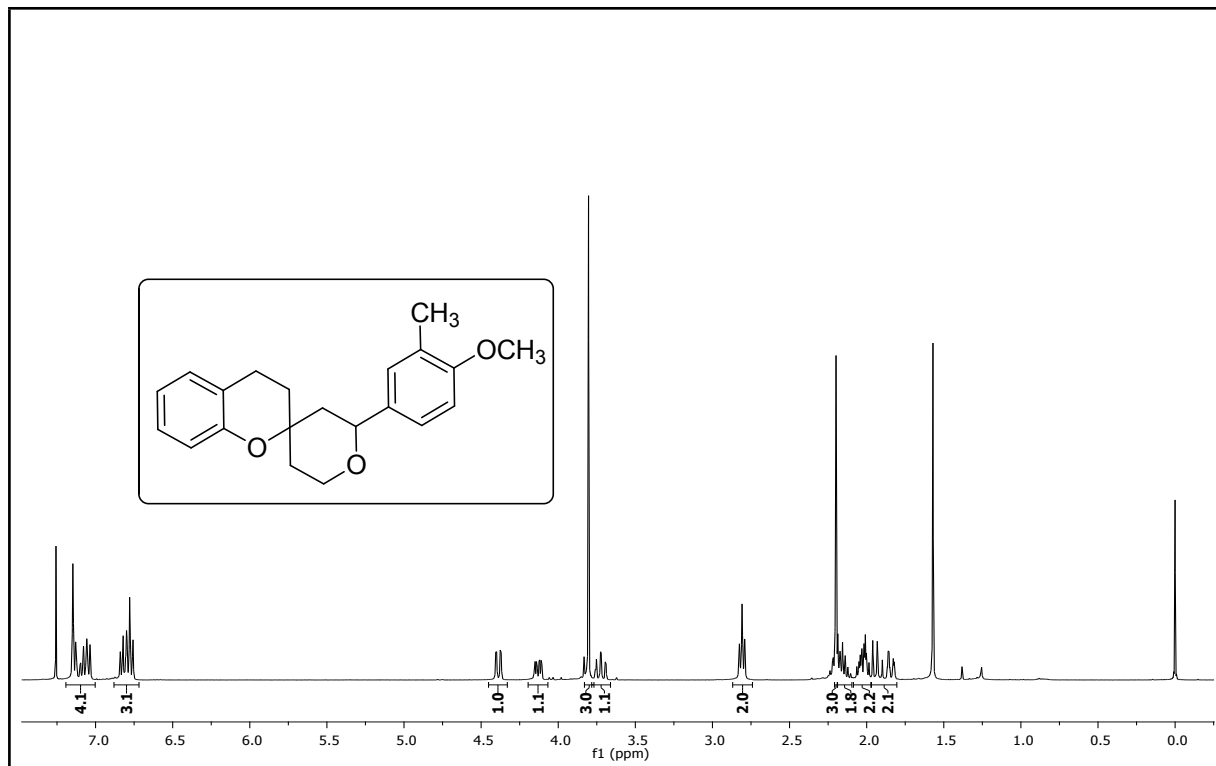
¹H NMR Spectra of compound 9g (500 MHz, CDCl₃)



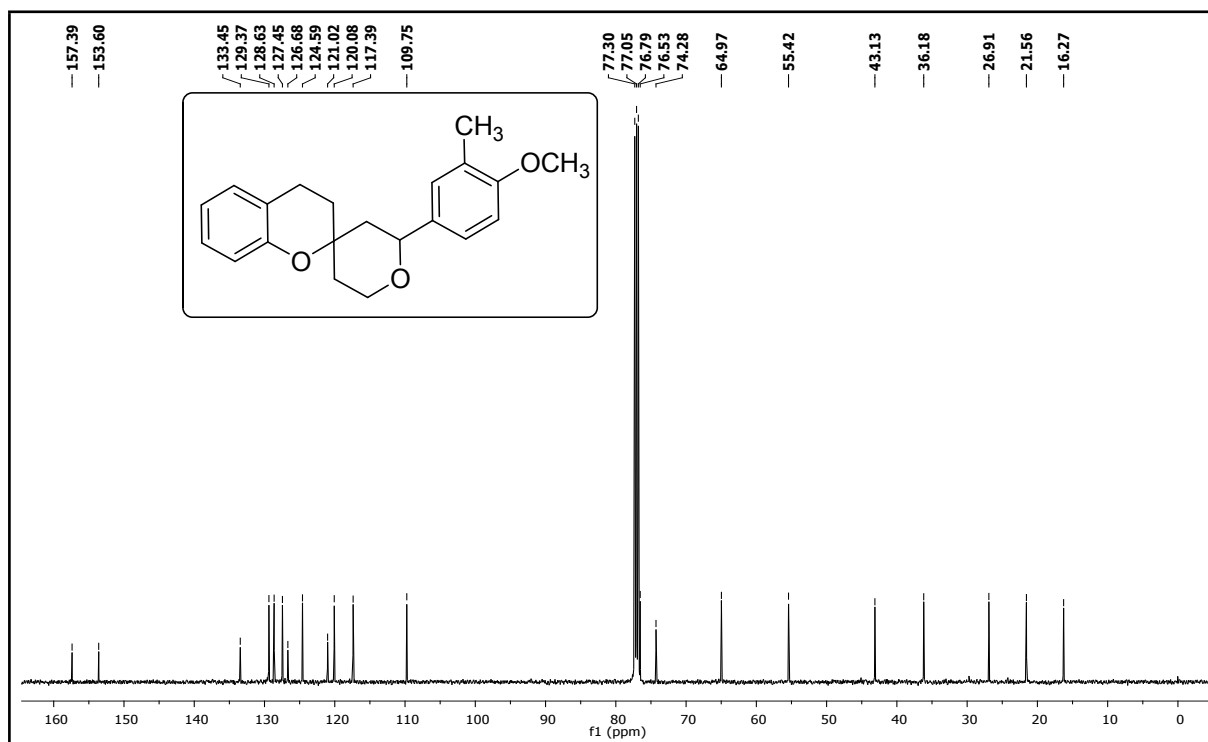
¹³C NMR Spectra of compound 9g (125 MHz, CDCl₃)



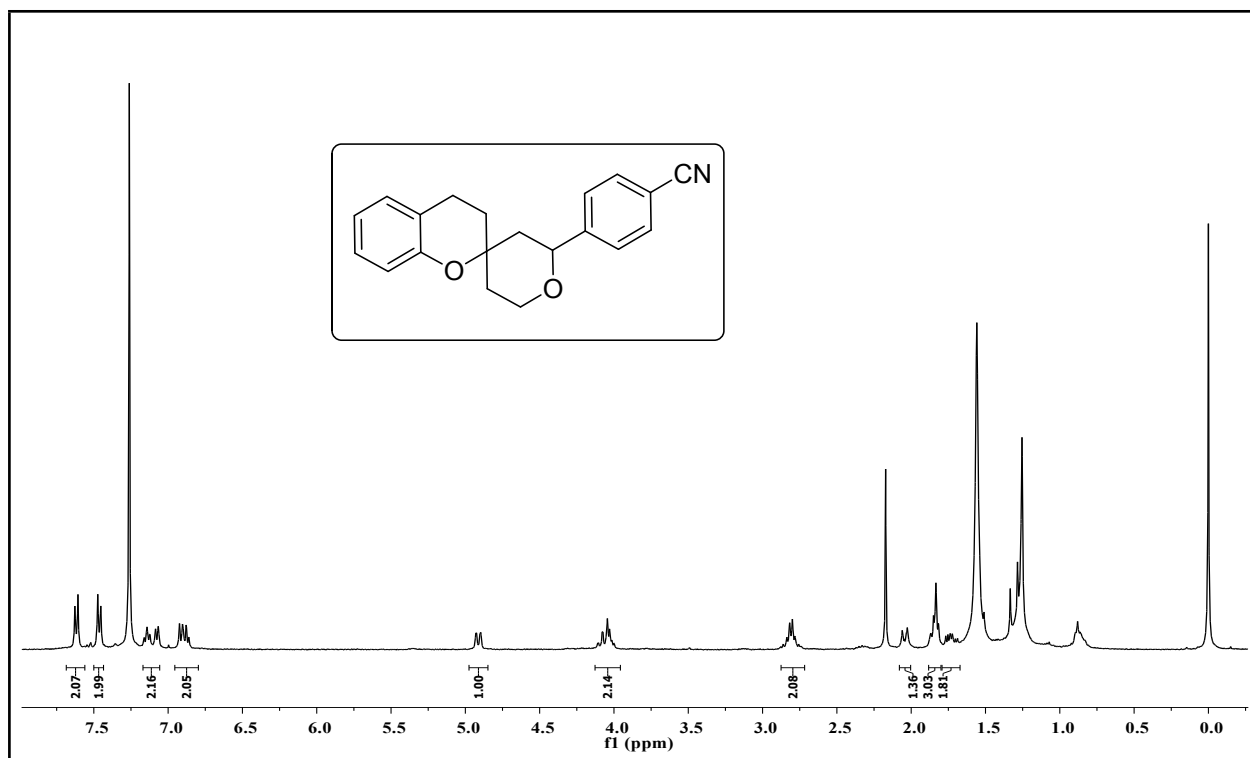
¹H NMR Spectra of compound 9h (500 MHz, CDCl₃)



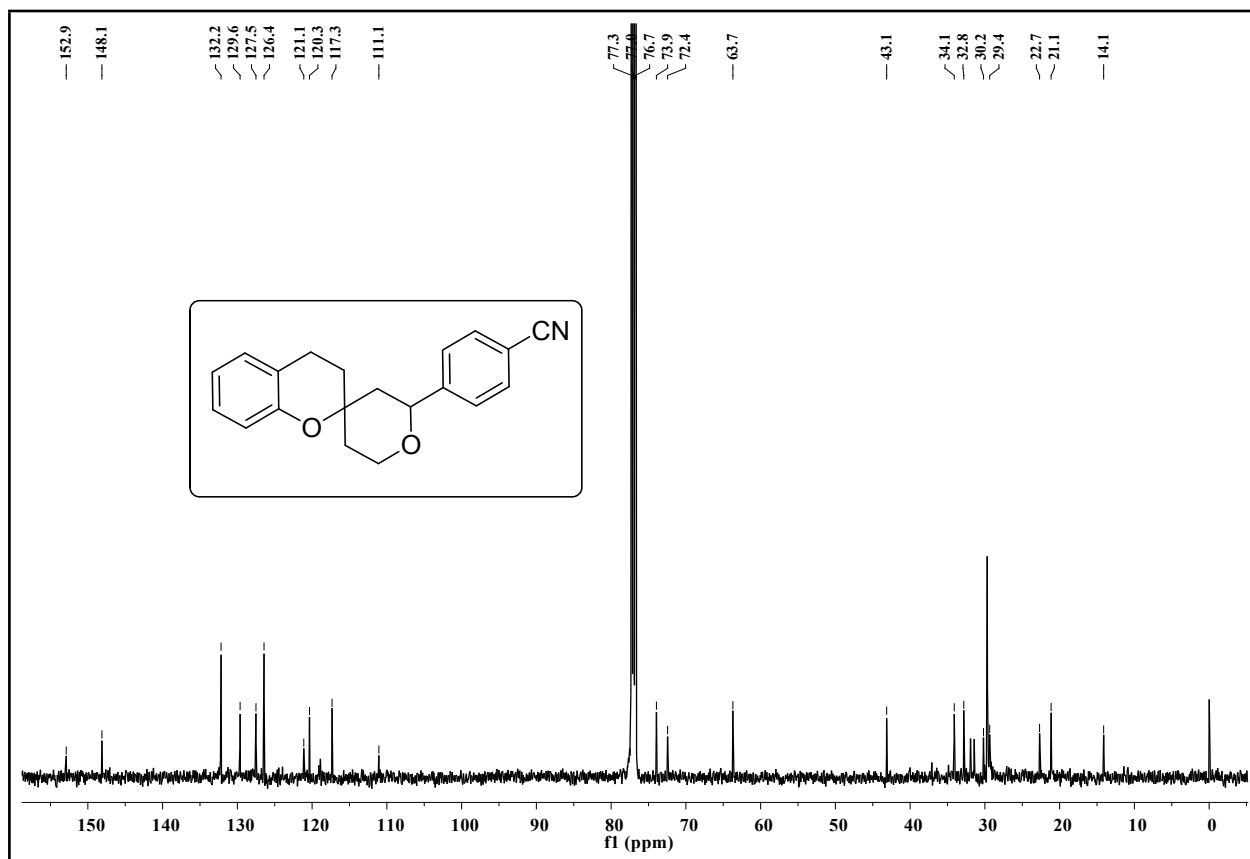
¹³C NMR Spectra of compound 9h (125 MHz, CDCl₃)



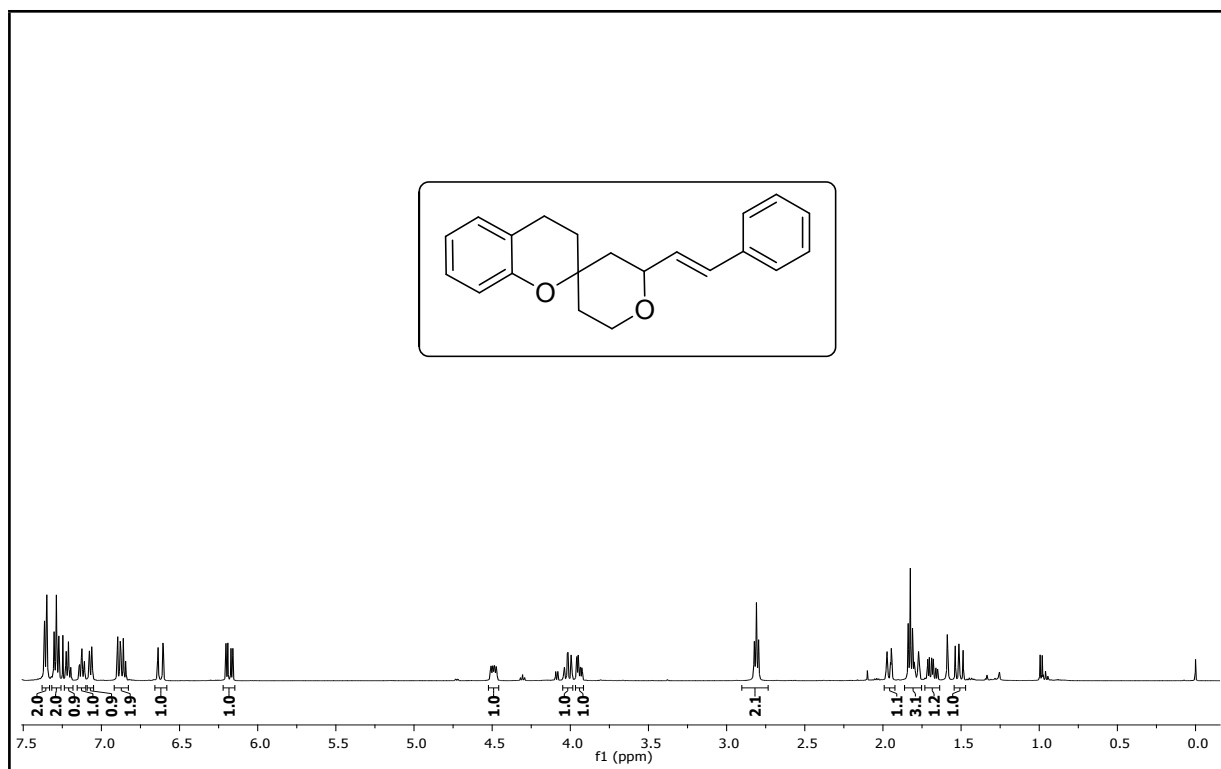
¹H NMR Spectra of compound 9i (500 MHz, CDCl₃)



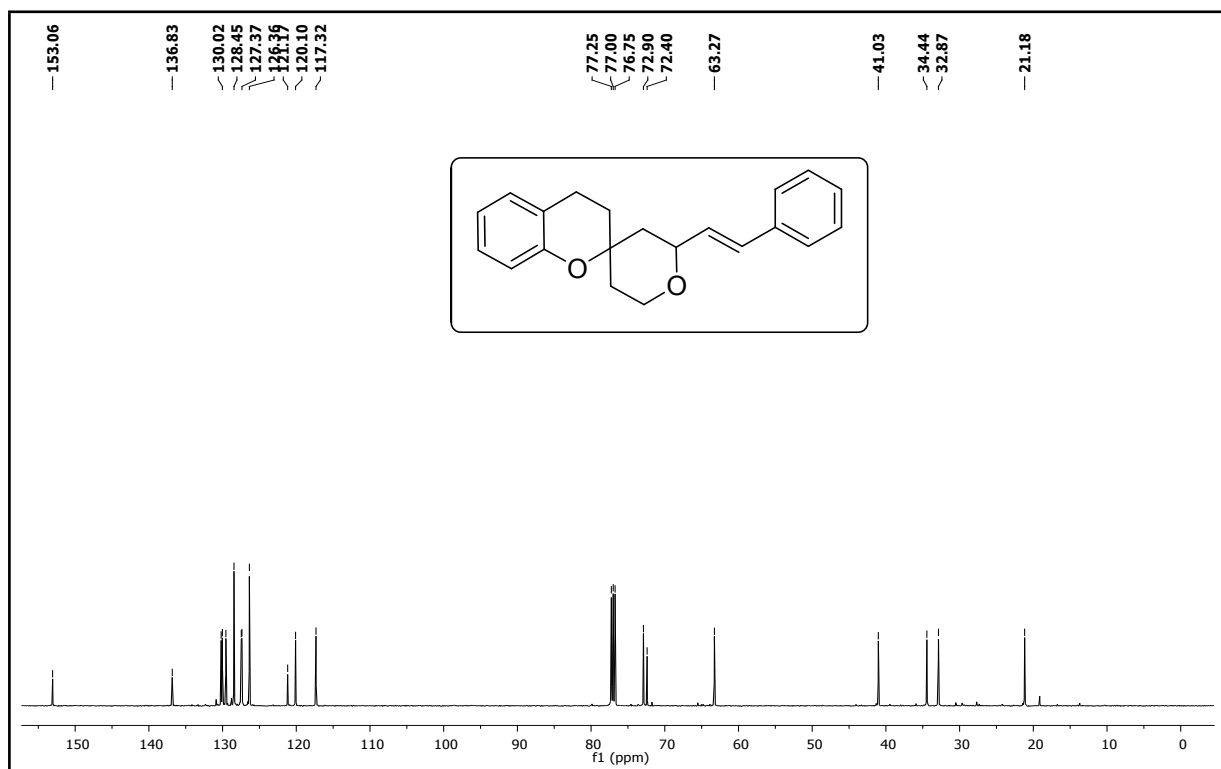
¹³C NMR Spectra of compound 9i (125 MHz, CDCl₃)



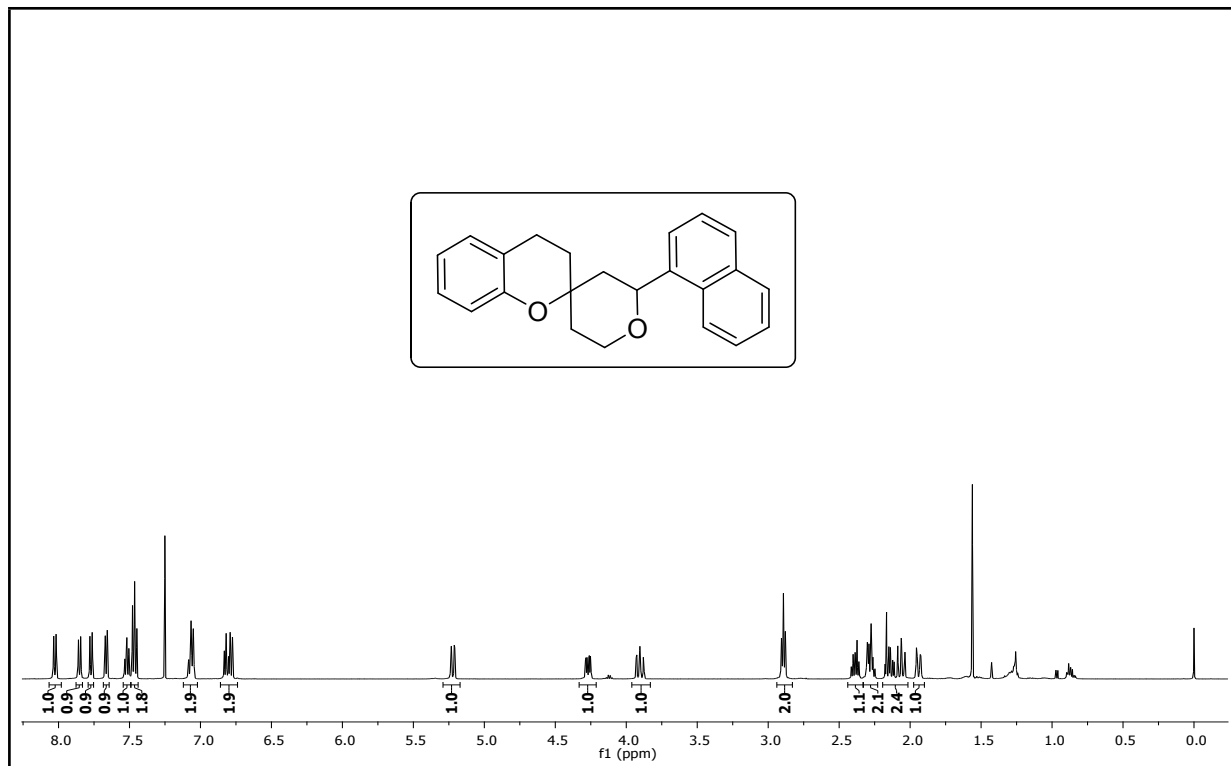
¹H NMR Spectra of compound 9j (500 MHz, CDCl₃)



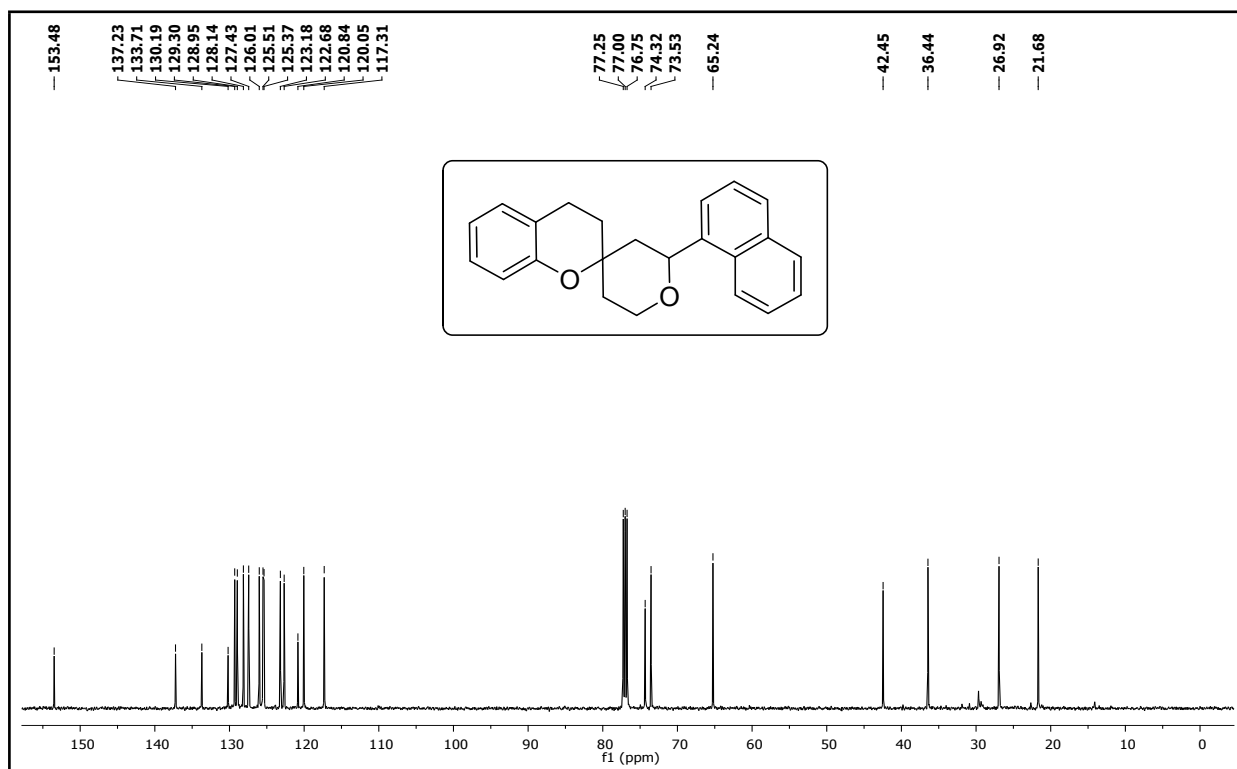
¹³C NMR Spectra of compound 9j (125 MHz, CDCl₃)



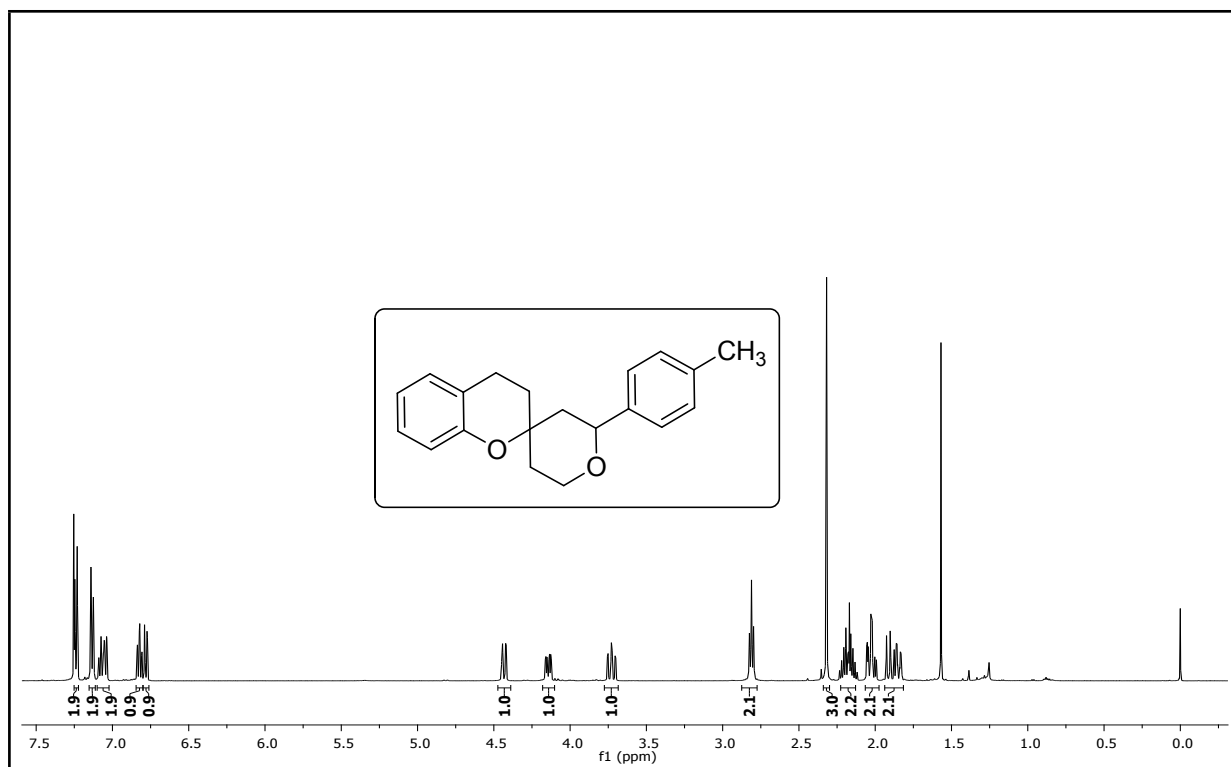
¹H NMR Spectra of compound 9k (500 MHz, CDCl₃)



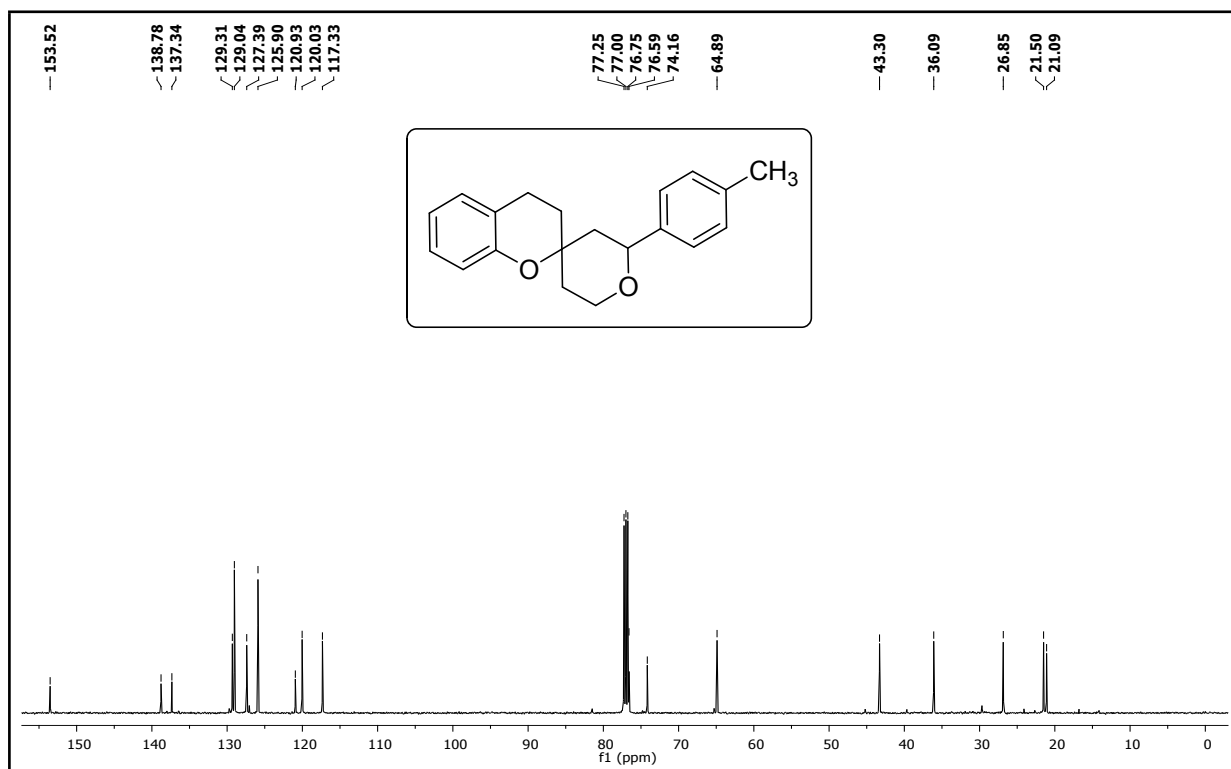
¹³C NMR Spectra of compound 9k (125 MHz, CDCl₃)



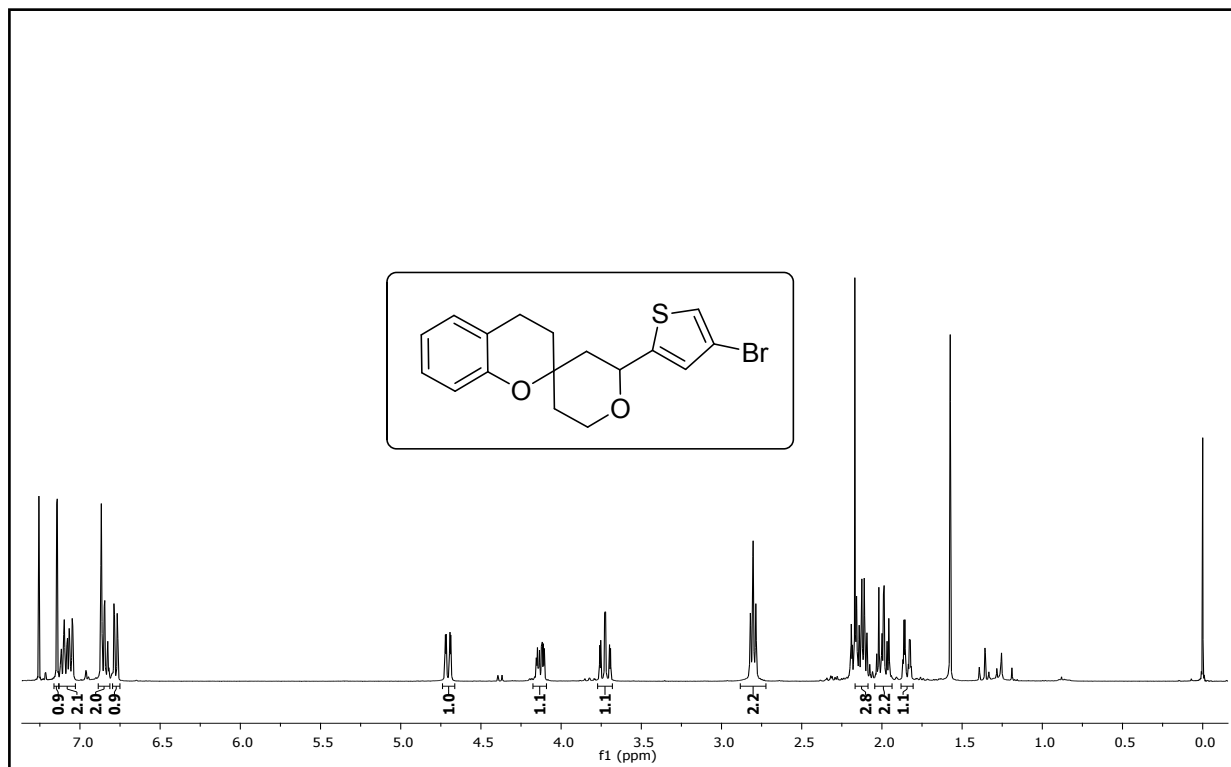
¹H NMR Spectra of compound 91 (500 MHz, CDCl₃)



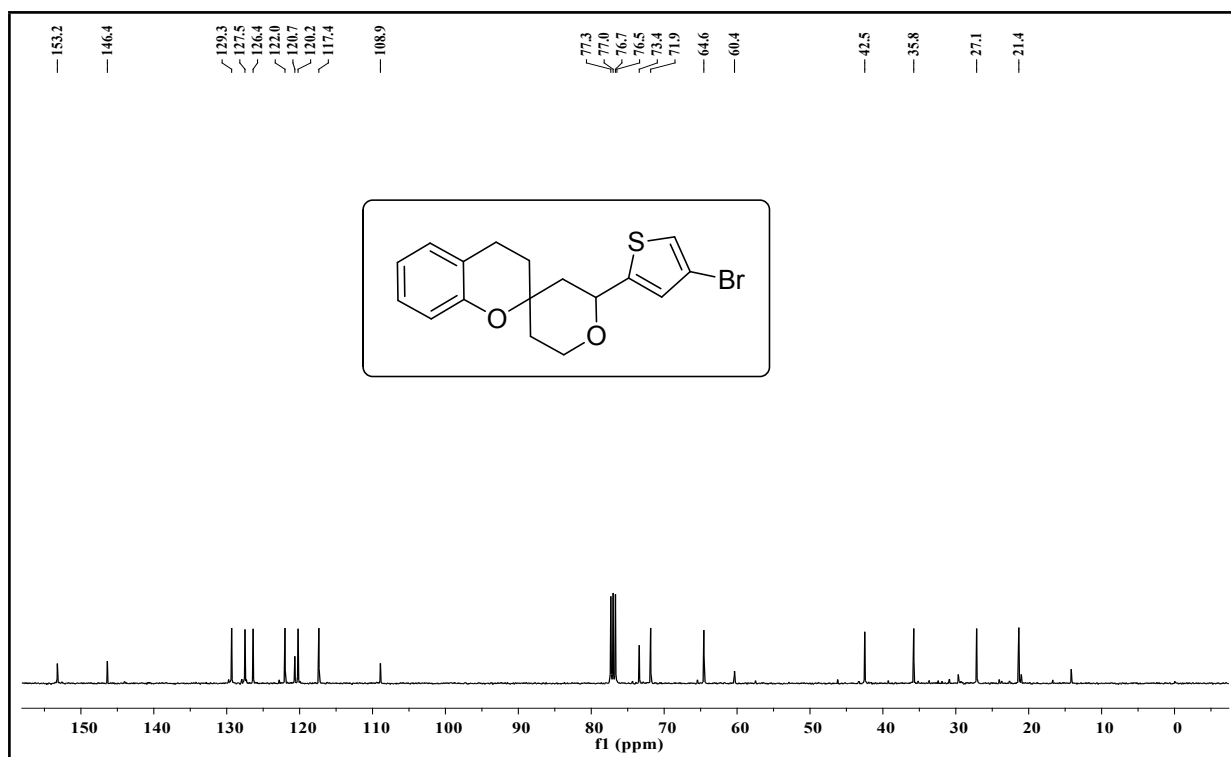
¹³C NMR Spectra of compound 91 (125 MHz, CDCl₃)



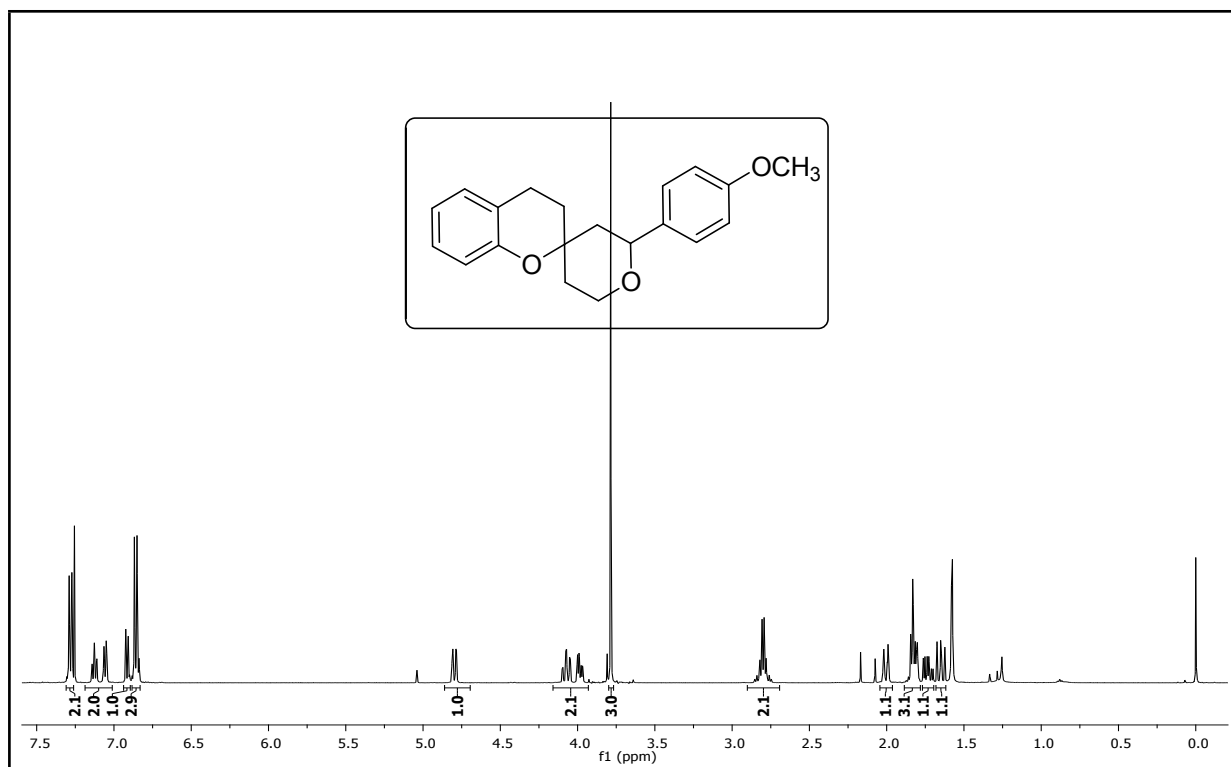
¹H NMR Spectra of compound 9m (500 MHz, CDCl₃)



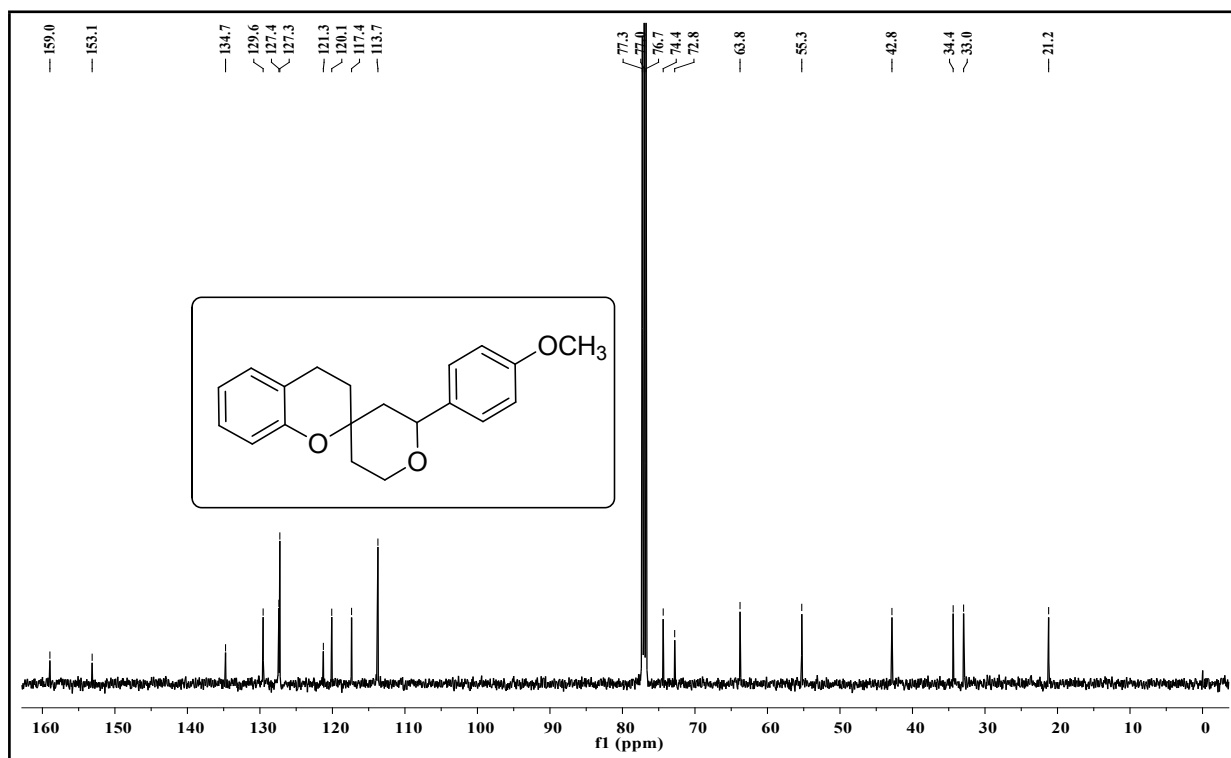
¹³C NMR Spectra of compound 9m (100 MHz, CDCl₃)



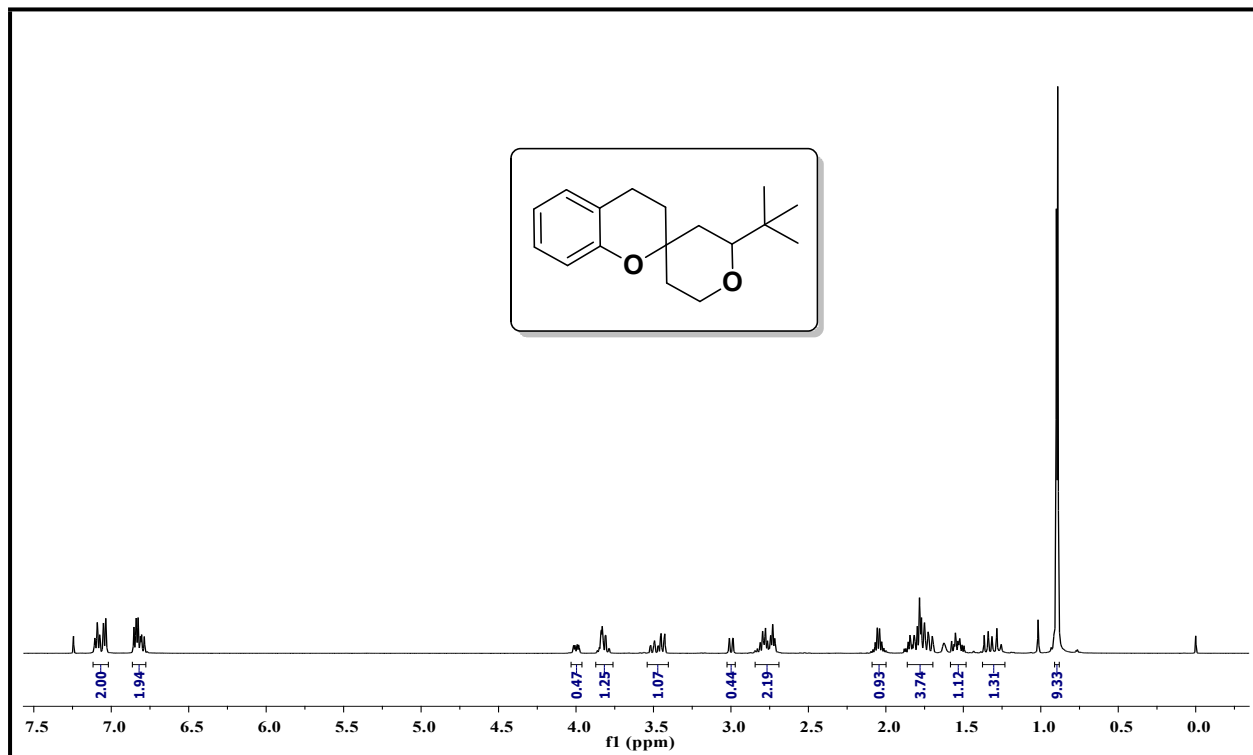
¹H NMR Spectra of compound 9n (500 MHz, CDCl₃)



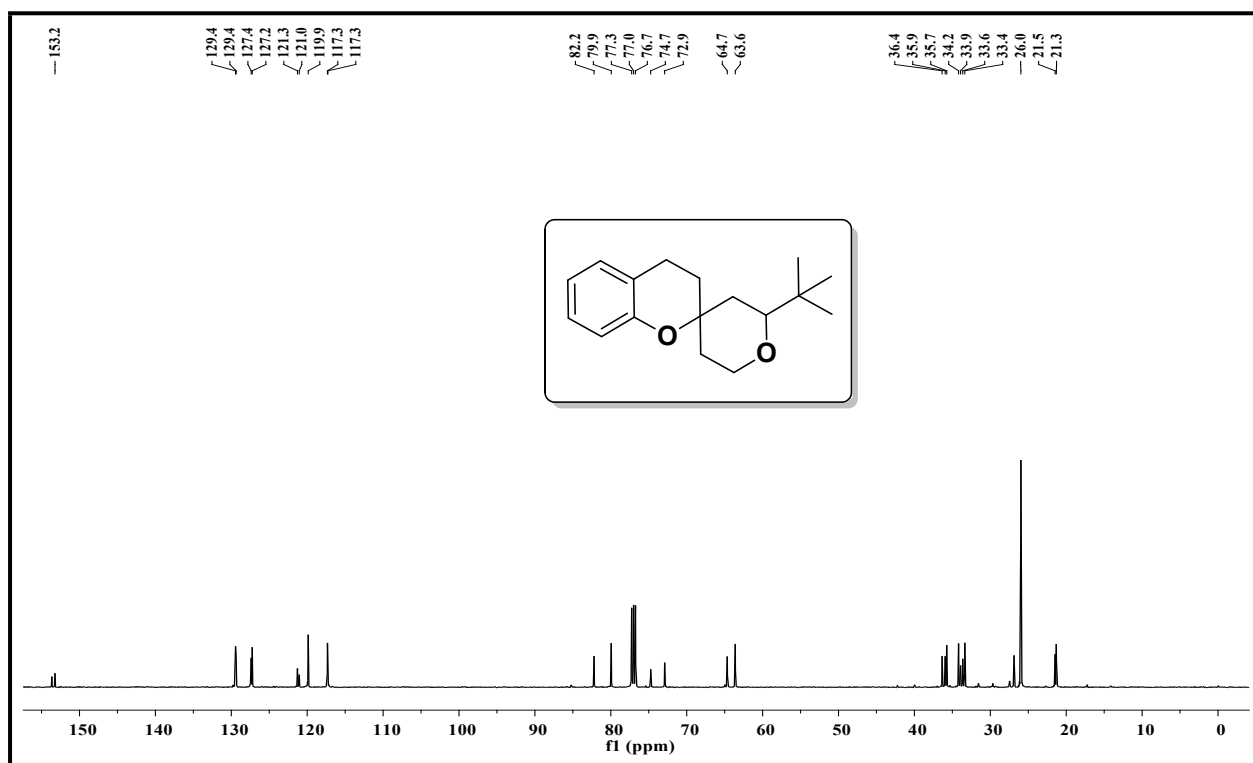
¹³C NMR Spectra of compound 9n (125 MHz, CDCl₃)



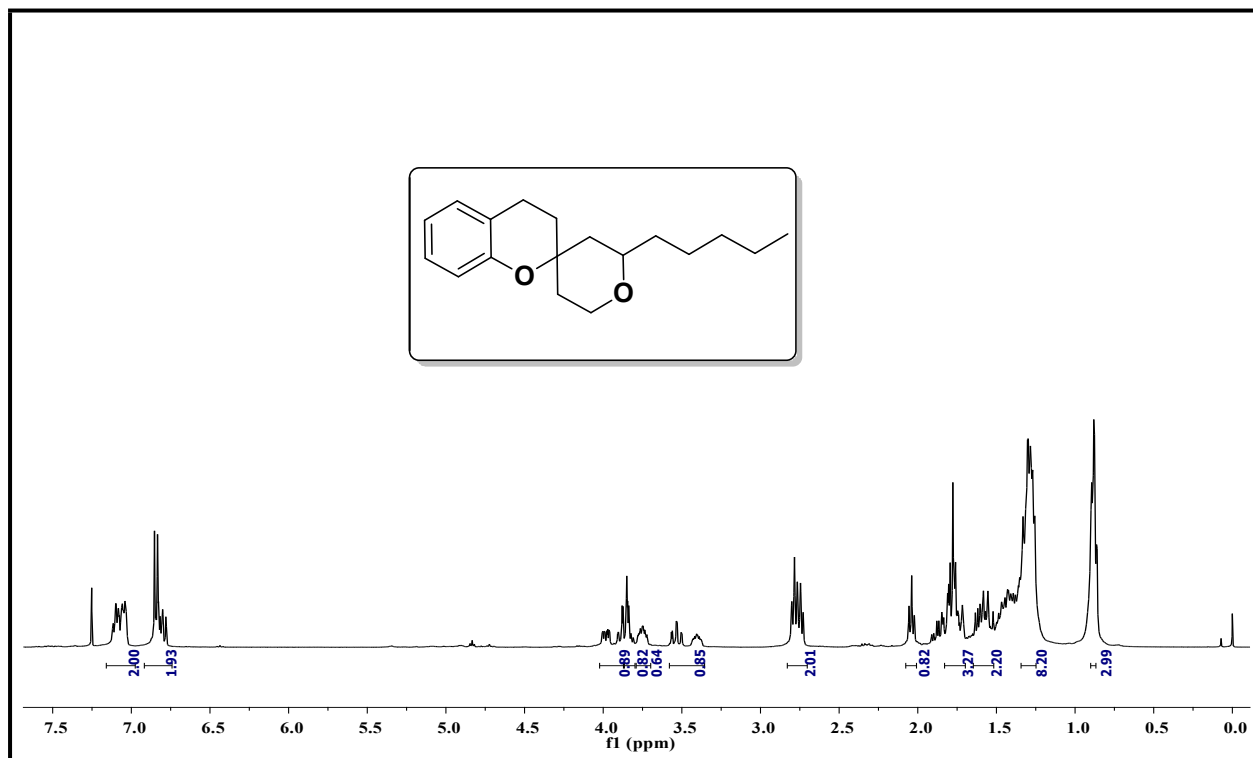
¹H NMR Spectra of compound 9o (400 MHz, CDCl₃)



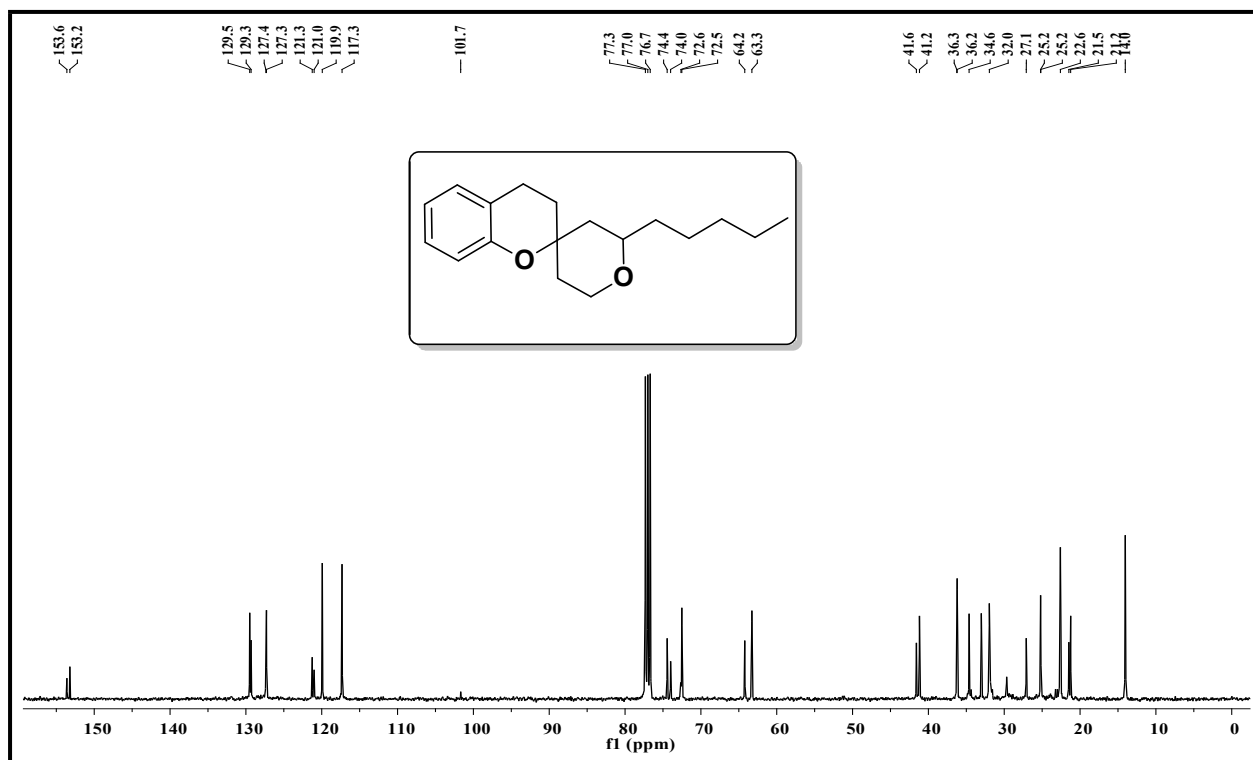
¹³C NMR Spectra of compound 9o (400 MHz, CDCl₃)



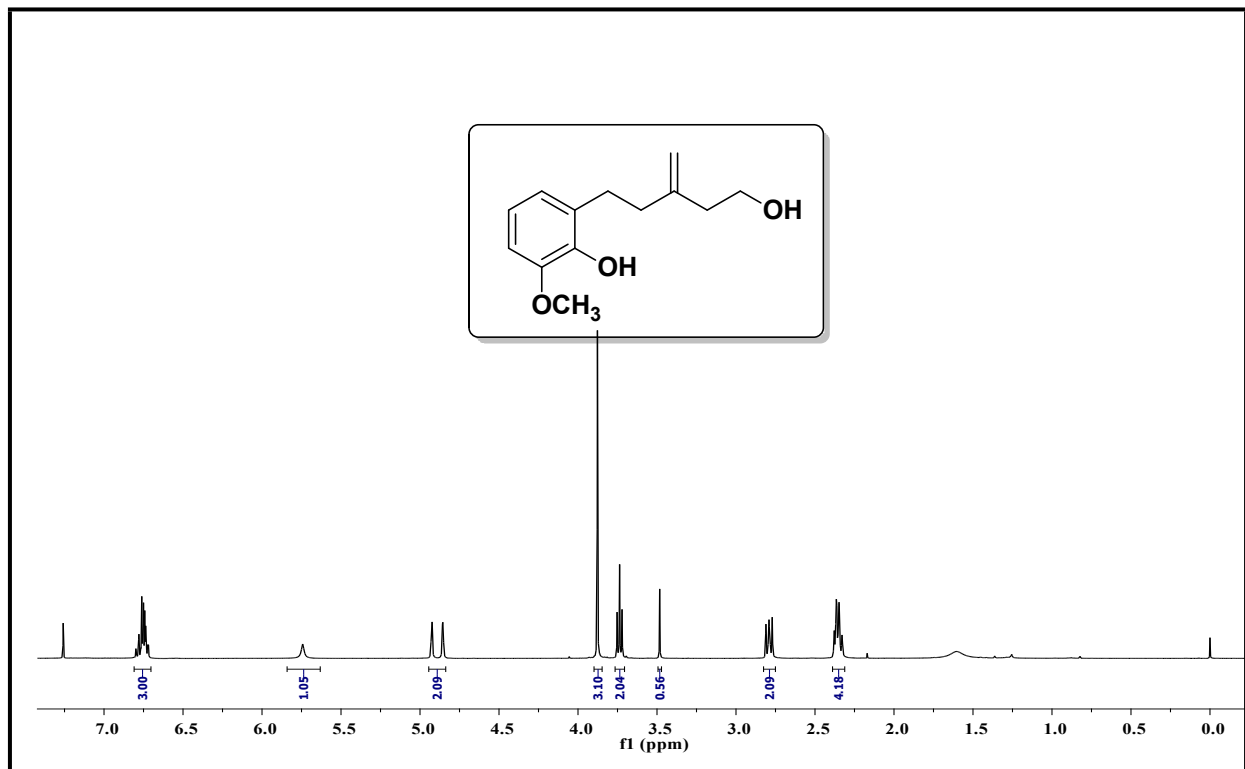
¹H NMR Spectra of compound 9p (400 MHz, CDCl₃)



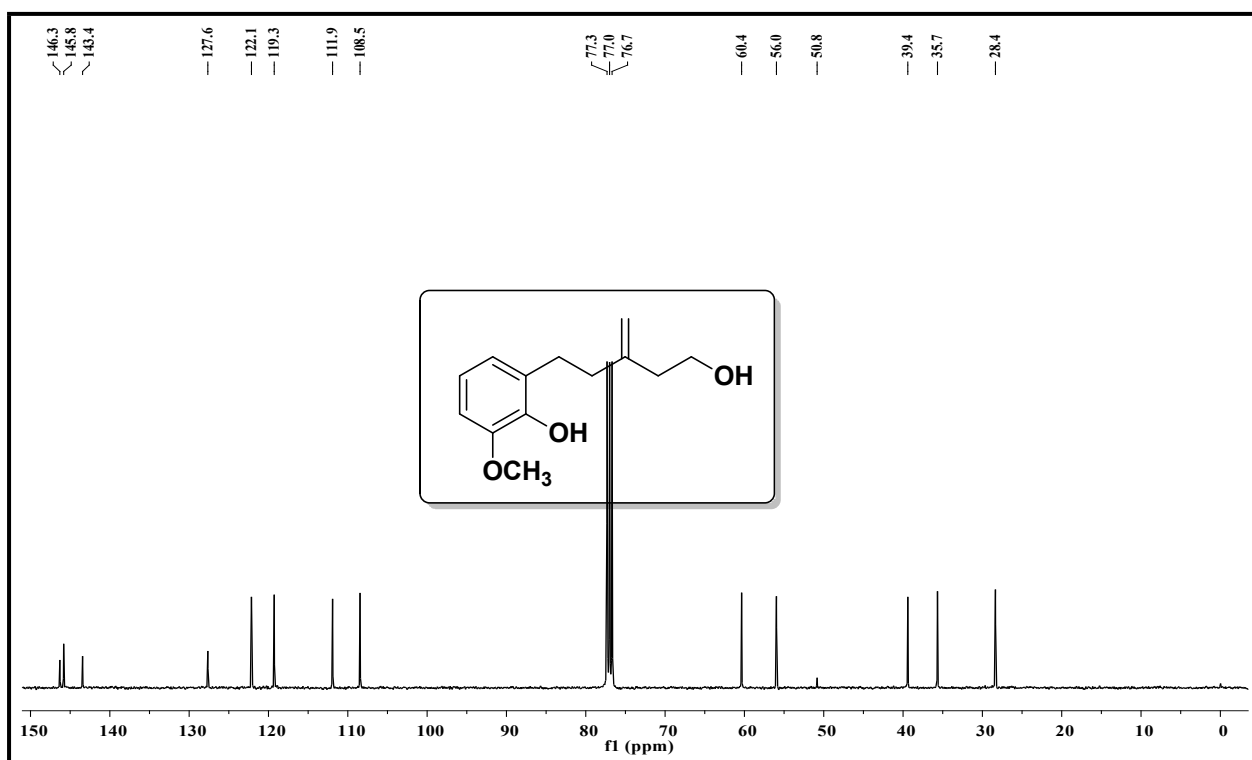
¹³C NMR Spectra of compound 9p (400 MHz, CDCl₃)



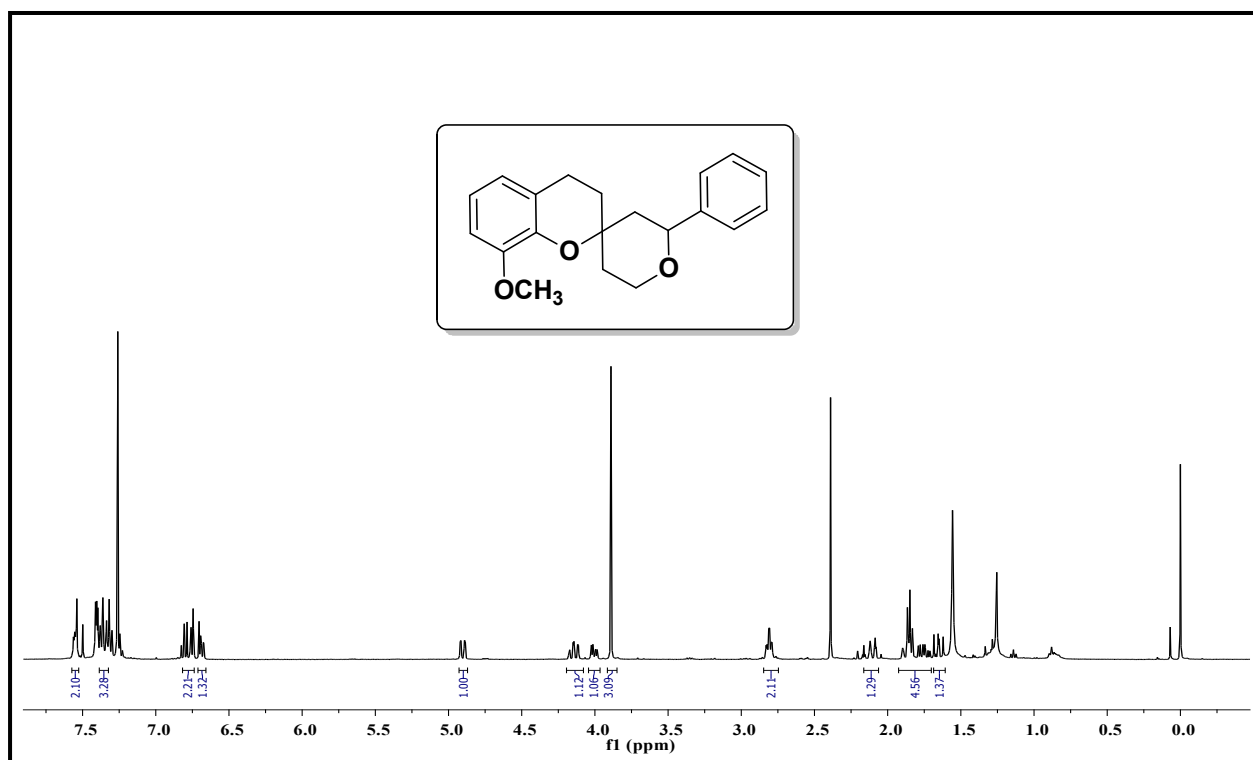
¹H NMR Spectra of compound 7x (400 MHz, CDCl₃)



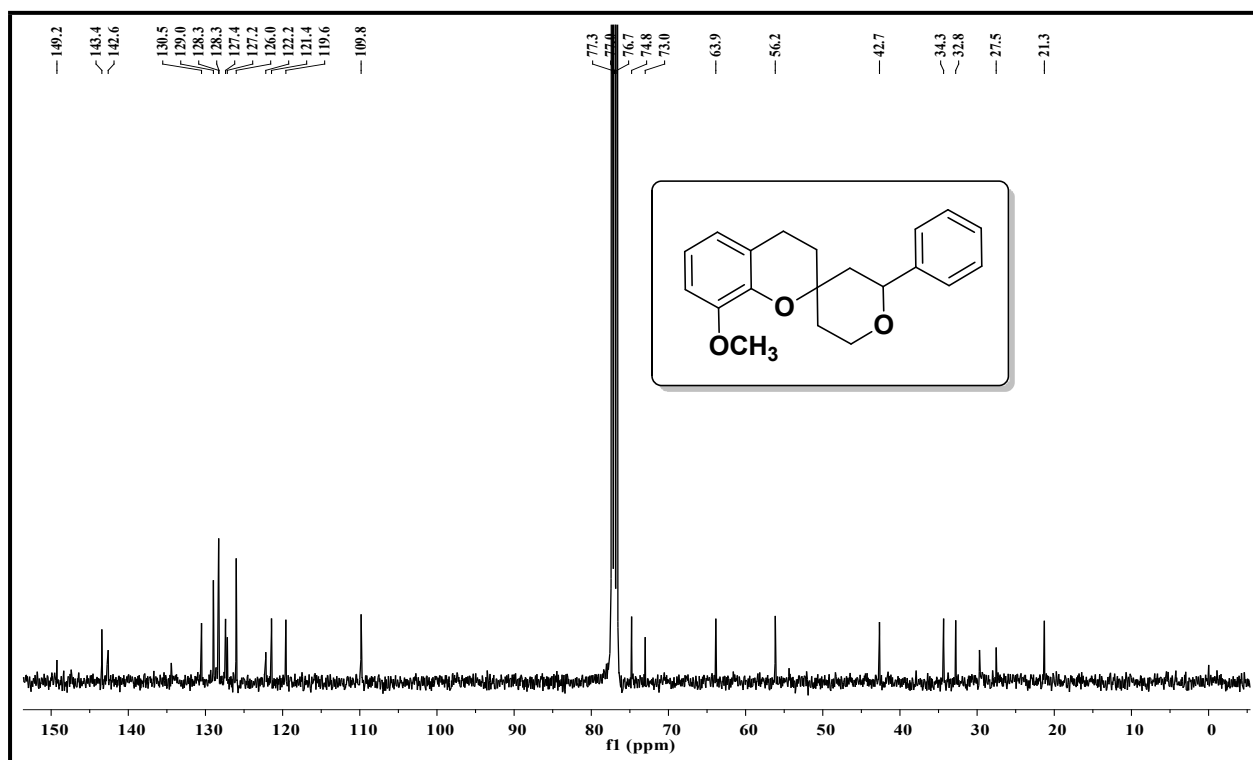
¹³C NMR Spectra of compound 7x (100 MHz, CDCl₃)



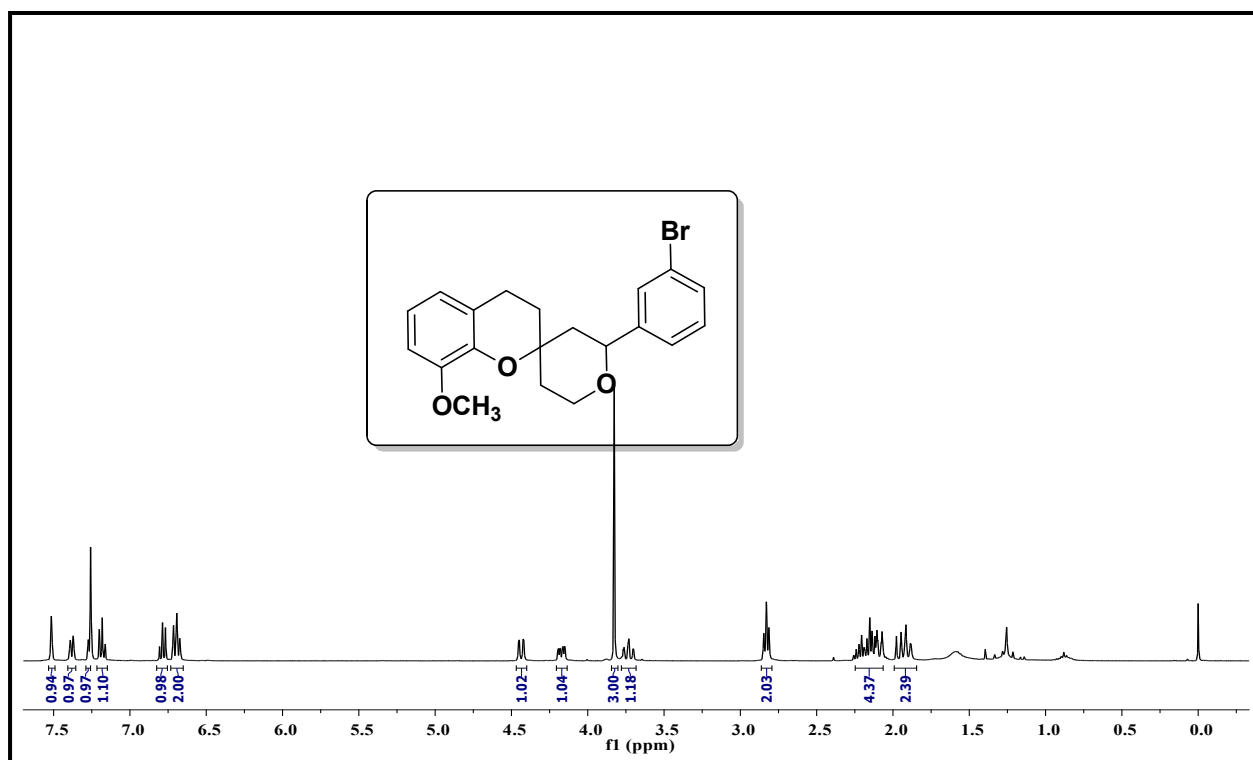
¹H NMR Spectra of compound 9q (400 MHz, CDCl₃)



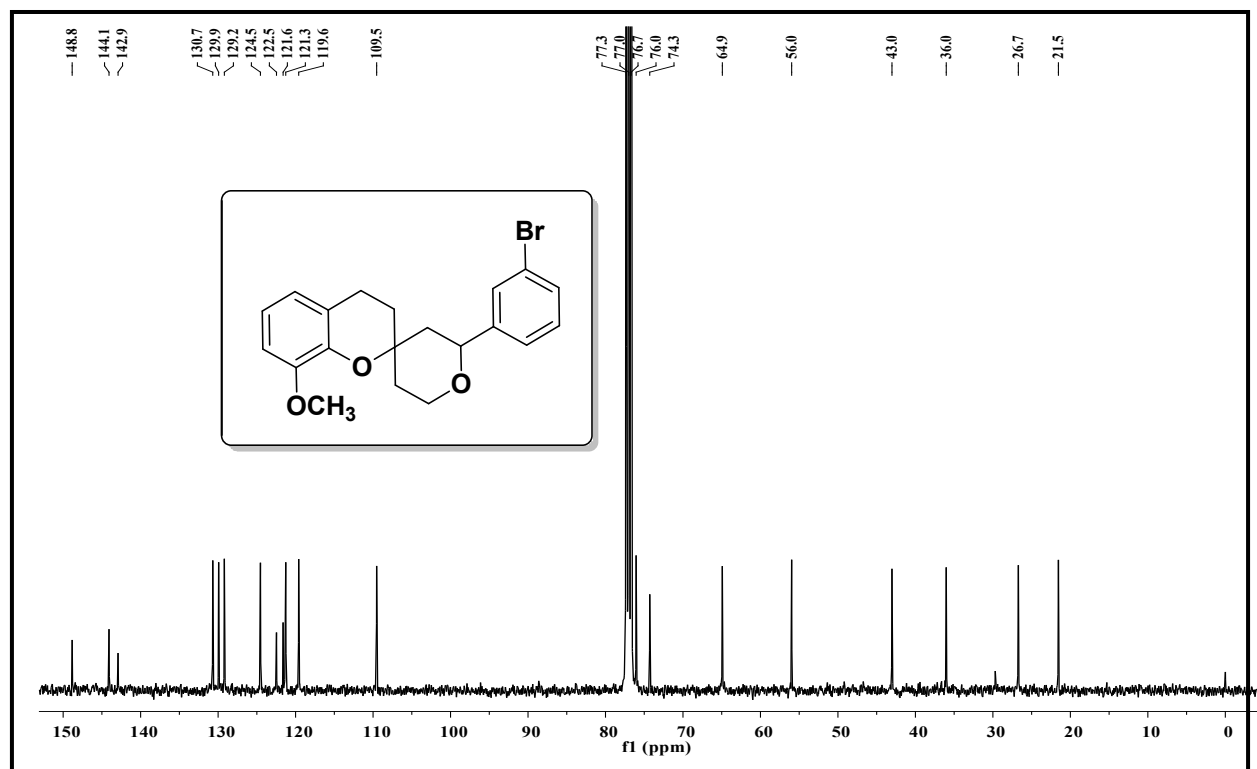
¹³C NMR Spectra of compound 9q (400 MHz, CDCl₃)



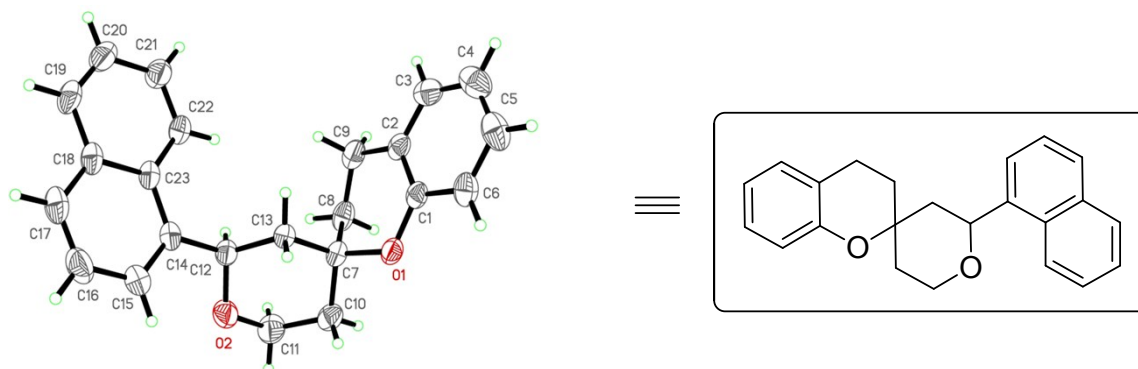
¹H NMR Spectra of compound 9r (400 MHz, CDCl₃)



¹³C NMR Spectra of compound 9r (400 MHz, CDCl₃)



3. X-ray Crystallography (9k)



X-ray data for the compounds were collected at room temperature using a Bruker Smart Apex CCD diffractometer with graphite monochromated MoK α radiation ($\lambda=0.71073\text{\AA}$) with ω -scan method [1]. Preliminary lattice parameters and orientation matrices were obtained from four sets of frames.

Integration and scaling of intensity data was accomplished using SAINT program [1]. The structure was solved by direct methods using SHELXS [2] and refinement was carried out by full-matrix least-squares technique using SHELXL [2]. Anisotropic displacement parameters were included for all non-hydrogen atoms. C-bound H atoms were located in a difference density map but were positioned geometrically and included as riding atoms, with C—H distance = 0.93 -0.97 \AA and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Crystal Data for 9k: C₂₃H₂₂O₂ ($M=330.40$): monoclinic, space group C2/c (no. 15), $a = 28.1542(16)\text{\AA}$, $b = 8.5012(5)\text{\AA}$, $c = 17.4613(10)\text{\AA}$, $\beta = 122.6090(10)^\circ$, $V = 3520.5(4)\text{\AA}^3$, $Z = 8$, $T = 294.15\text{ K}$, $\mu(\text{MoK}\alpha) = 0.078\text{ mm}^{-1}$, $D_{\text{calc}} = 1.247\text{ g/mm}^3$, 19985 reflections measured ($3.434 \leq 2\Theta \leq 56.536$), 4266 unique ($R_{\text{int}} = 0.0232$) which were used in all calculations. The final R_1 was 0.0471 ($I > 2\sigma(I)$) and wR_2 was 0.1348 (all data). CCDC 1440306 contains supplementary Crystallographic data for the structure. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0) 1223 336 033; email: deposit@ccdc.cam.ac.uk].

1. Bruker (2001). SAINT (Version 6.28a) & SMART (Version 5.625). Bruker AXS Inc., Madison, Wisconsin, USA.
2. Sheldrick G. M. (2015) *Acta Crystallogr* C71: 3-8.

Figure Caption

Fig.1. A view of **9k**, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are represented by circles of arbitrary radii.