## Supporting Information

# Iodine catalyzed metal free domino process for the stereoselective synthesis of oxygen bridged bicyclic ethers

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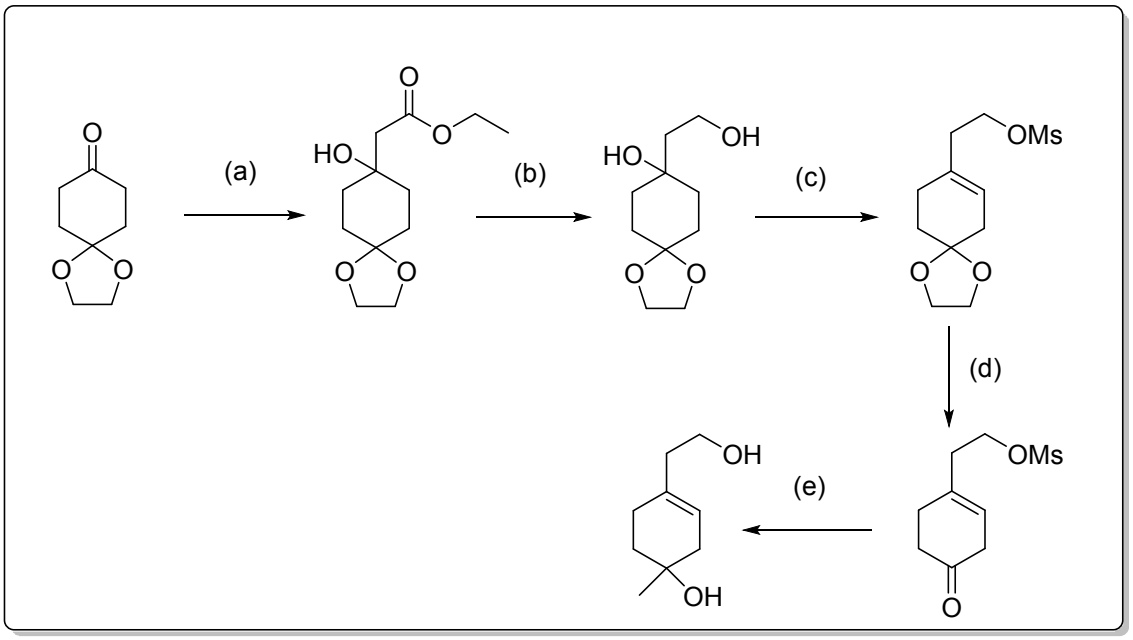
**General methods**: IR spectra were recorded on FT-IR spectrometer (KBr) and reported in reciprocal centimetres ($cm^{-1}$). $^{1}$HNMR spectra were recorded at 500 MHz and $^{13}$C NMR at 125 MHz. For 1H NMR, tetramethylsilane (TMS) was used as internal standard ($\delta = 0$) and the values are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t= triplet, q =quartet, m = multiplet), and the coupling constants in Hz. For $^{13}$C NMR, $CDCl_3$ ($\delta = 77.27$) was used as internal standard and spectra were obtained with complete proton decoupling. HRMS data were obtained using EI ionization.

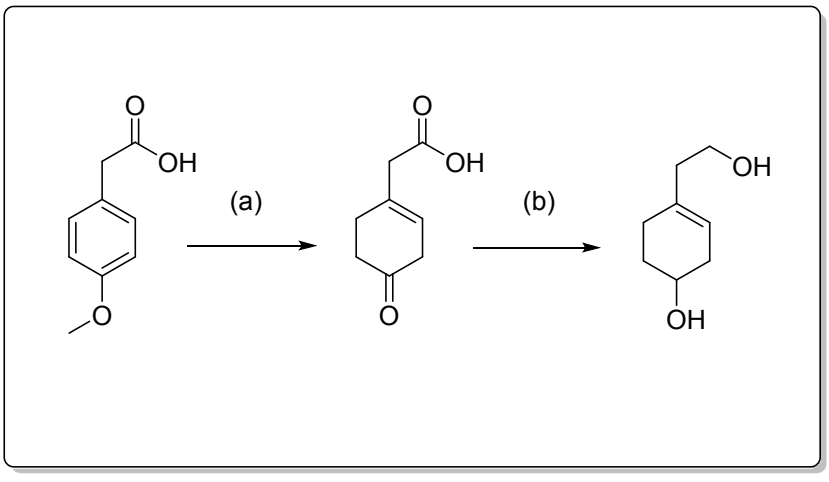
## (1) General procedure:

**Scheme 1.** Synthetic procedure of **1a**




**Reagents & conditions:** (a) Zn, $BrCH_2COOEt$, $C_6H_6$, reflux (b) LAH, THF,0 $^{o}$C- rt, (c) MsCl, TEA, DCM , -23 $^{o}$C to rt (d) PPTS, wet acetone, reflux, (e) $CH_3MgBr$, THF, 0 $^{o}$C to rt .

**Scheme 2.** Synthetic procedure of **1b**

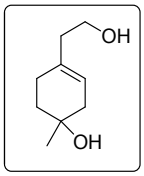


**Reagents & conditions:** (a) Li, $NH_3$, *t*-BuOH, -78 $^oC$ (b) LAH, THF,0 $^oC$ to rt.

**General Procedure for Products 3(a-n):**
To a stirred solution of aldehyde (1.1 mmol) and **1a** or **1b** (1.0mmol) in dichloromethane (5.0mL), was added 10 mol% of molecular iodine at 0 $^oC$. The resulting mixture was stirred at 25 °C for the specified time. The progress of the reaction was monitored by TLC using ethyl acetate and hexane as eluent. After completion, the mixture was quenched with water and the product was extracted with ethyl acetate. The organic layers were washed with aqueous sodium thiosulfate followed by brine solution and dried over anhydrous sodium sulfate. Removal of the solvent followed by purification on silica gel (Merck 100–200 mesh) using ethyl acetate/hexane (2:8) as eluent gave the pure tetrahydropyran.

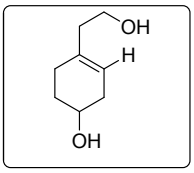
## (2) Characterization data of starting materials and products:

**Characterization data for 1a:**




Light yellow Liquid; $^1H$ NMR (500 MHz, $CDCl_3$): δ 5.42 (s, 1H), 3.74-3.64 (m, 2H), 2.31-1.91 (m, 8H), 1.71 (td, *J* = 13.1, 7.1 Hz, 1H), 1.64-1.54 (m, 1H), 1.24 (s, 3H) ppm; $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 133.5, 121.3, 68.3, 60.0, 40.5, 39.5, 35.2, 28.8, 25.6 ppm; IR(neat): ν 3353.7, 2925.4, 1648.8, 1431.0, 1044.8, 764.5 $cm^{-1}$; HRMS (*m/z*) calcd for $C_9H_{16}O_2$: 156.11503, found: 156.11510.

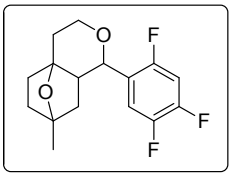
**Characterization data for 1b:**




Light yellow Liquid; $^1H$ NMR (500 MHz, $CDC_{13}$): δ 5.41 (s, 1H), 4.01-3.95 (m, 1H), 3.75-3.59 (m, 2H), 2.62-2.30 (m, 2H), 2.29-2.11 (m, 3H), 2.10-1.93 (m, 2H), 1.89-1.77 (m, 1H), 1.76-1.63 (m, 2H); $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 133.9, 120.7, 66.2, 60.0, 40.6, 33.9, 30.4, 25.5 ppm; IR (neat): ν 3377.5, 2927.1, 1714.6, 1648.6, 1439.2, 1049.9, 758.7 $cm^{-1}$; HRMS (*m/z*) calcd for $C_8H_{14}O_2$: 142.09938, found: 142.09942.

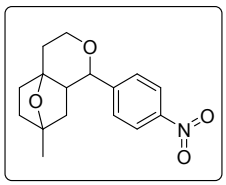
## Characterization data of products:

**7-Methyl-1-(2,4,5-trifluorophenyl)octahydro-4a,7-epoxyisochromene (3a):**



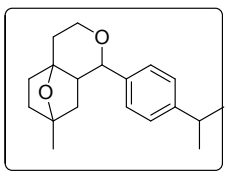
Light yellow Liquid; $^{1}$H NMR (500 MHz, $CDCl_3$): δ 7.29-7.22 (m, 1H, Ar-H), 6.93-6.85 (m, 1H, Ar-H), 4.34 (dd, *J* = 1.0, 10.5 Hz, 1H, H1), 4.01 (ddd, *J* = 1.2, 6.0, 11.5 Hz, 1H, H5), 3.83 (ddd, *J* = 3.0, 11.5, 12.7 Hz, 1H, H5'), 2.07 (ddd, *J* = 6.1, 12.8, 14.8 Hz, 1H, H4), 2.01-2.03 (m, 1H, H4'), 2.04-1.95 (m, 1H, H2), 1.74-1.54 (m, 5H, H8, H8', H9, H9', H6), 1.49 (s, 3H, Me10), 1.15-1.10 (m, 1H, H6'); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 156.1, 156.0, 154.2, 154.1, 150.4, 150.3, 150.2, 148.4, 148.3, 148.2, 148.1, 148.0, 146.2, 146.1, 124.5, 124.4, 116.7, 116.7, 116.6, 116.5, 105.5, 105.3, 105.2, 105.1, 84.5, 82.1, 75.7, 65.5, 48.8, 39.3, 37.4, 37.3, 30.0, 21.2 ppm; $^{19}$F NMR (470 MHz, $CDCl_3$): δ -118.98 (d, *J* = 15.5 Hz), -134.32 (s), -134.36 (s), -142.24 (dd, *J* = 21.4, 15.6 Hz); IR(neat): ν 2957.8, 2284.4, 1638.4,1514.6 1206.2, 767.9 cm$^{-1}$; HRMS (*m/z*) calcd for $C_{16}H_{17}F_3O_2$: 298.11806, found: 298.11750.

**7-Methyl-1-(4-nitrophenyl)octahydro-4a,7-epoxyisochromene (3b):**



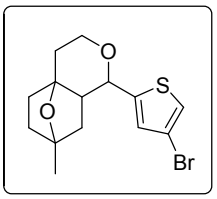
Light yellow Liquid; $^{1}$H NMR (500 MHz, $CDCl_3$): δ 8.19 (d, *J* = 8.7 Hz, 2H), 7.50 (d, *J* = 15.0 Hz, 2H), 4.19–4.00 (m, 2H), 3.97–3.77 (m, 1H), 2.22–1.85 (m, 3H), 1.75–1.56 (m, 5H), 1.52 (s, 3H), 1.20-1.12 (m, 1H) ppm; $^{13}$C NMR (125 MHz, $CDCl_3$): δ 148.2, 147.4, 128.0, 123.5, 84.6, 82.9, 82.1, 65.3, 49.1, 40.5, 37.5, 37.1, 30.1, 21.3 ppm; IR(neat): ν 2937.9, 2267.5, 1734.8, 1527.4, 1374.3, 1074.3, 819.6, 746.1 cm$^{-1}$; HRMS (*m/z*) calcd for $C_{16}H_{19}NO_4$: 289.13141, found: 289.13131.

**1-(4-Isopropylphenyl)-7-methyloctahydro-4a,7-epoxyisochromene (3c):**



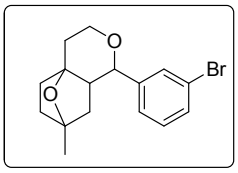
Light yellow Liquid; $^{1}$H NMR (500 MHz, $CDCl_3$): δ 7.26 (d, *J* = Hz, 2H), 7.18 (d, *J* = 8.1 Hz, 2H), 4.09-3.99 (m, 1H), 3.99 (dd, *J* = 24.1, 5.7 Hz, 1H), 3.84 (ddd, *J* = 12.9, 11.5, 2.8 Hz, 1H), 2.98-2.78 (m, 1H), 2.14–2.05 (m, 2H), 1.98 (dd, *J* = 14.7, 1.9 Hz, 1H), 1.73–1.54 (m, 4H), 1.49 (s, 3H), 1.22 (d, *J* = 7.0 Hz, 6H), 1.17–1.11 (m, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 148.5, 137.7, 127.4, 126.4, 84.4, 83.7, 82.3, 65.3, 48.5, 40.7, 37.6, 37.3, 33.8, 30.3, 23.9, 23.9, 21.4 ppm; IR(neat): ν 2960.4, 2864.9, 1731.8, 1457.4, 1084.8, 822.5 cm$^{-1}$; HRMS (*m/z*) calcd for $C_{19}H_{26}O_2$: 286.19328, found: 286.19402.

**1-(4-Bromothiophen-2-yl)-7-methyloctahydro-4a,7-epoxyisochromene (3d):**



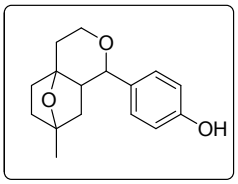

Light yellow Liquid; $^{1}$H NMR (500 MHz, $CDCl_3$): δ 7.16 (d, *J* = 1.4 Hz, 1H), 6.89 (d, *J* = 0.8 Hz, 1H), 4.21 (d, *J* = 10.3 Hz, 1H), 4.03 (ddd, *J* = 11.5, 6.0, 1.1 Hz, 1H), 3.83 (ddd, *J* = 12.9, 11.5, 2.9 Hz, 1H), 2.10–2.02 (m, 2H), 1.97 (dd, *J* = 14.8, 1.9 Hz, 1H), 1.80 (dd, *J* = 12.5, 8.1 Hz, 1H), 1.75–1.56 (m, 5H), 1.50 (s, 3H), 1.17 (dt, *J* = 12.5, 3.1 Hz, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 145.4, 127.2, 122.3, 108.9, 84.6, 82.1, 78.7, 65.4, 49.2, 41.1, 37.3, 37.2, 30.0, 21.3 ppm; IR(neat): ν 2925.0, 1721.1, 1362.2, 1091.4,765.6 cm$^{-1}$; HRMS (*m/z*) calcd for $C_{14}H_{17}BrO_2S$: 328.01326, found: 328.01320.

**1-(3-Bromophenyl)-7-methyloctahydro-4a,7-epoxyisochromene (3e):**



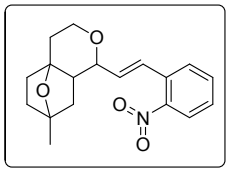

Light yellow Liquid; $^{1}$H NMR (500 MHz, $CDCl_3$): δ 7.51 (s, 1H), 7.41 (d, *J* = 7.8 Hz, 1H), 7.26 (d, *J* = 6.3 Hz, 1H), 7.19 (t, *J* = 7.8 Hz, 1H), 4.04 (dd, *J* = 11.4, 5.9 Hz, 1H), 3.96 (d, *J* = 10.3 Hz, 1H), 3.88–3.78 (m, 1H), 2.15–1.93 (m, 3H), 1.75–1.54 (m, 5H), 1.50 (s, 3H), 1.18-1.08 (m, 1H) . $^{13}$C NMR (125 MHz, $CDCl_3$): δ 142.9, 130.9, 130.4, 129.8, 126.1, 122.5, 84.5, 83.2, 82.1, 65.3, 48.8, 40.5, 37.5, 37.2, 30.2, 21.3 ppm; IR(neat): ν 2936.7, 2861.8, 2357.3, 1717.0, 1609.4, 1371.5,1262.7, 1020.2, 958.6, 770.9 cm$^{-1}$ ; HRMS (*m/z*) calcd for $C_{16}H_{19}BrO_2$: 323.00715, found: 323.00700.

**4-(7-Methyloctahydro-4a,7-epoxyisochromen-1-yl)phenol (3f):**



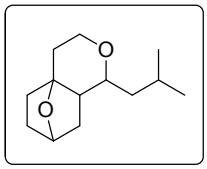

Light yellow Liquid; $^{1}$H NMR (500 MHz, $CDCl_3$): δ 7.21 (d, *J* = 8.4 Hz, 2H), 6.76 (d, *J* = 8.5 Hz, 2H), 4.06–3.99 (m, 1H), 3.93 (d, *J* = 10.4 Hz, 1H), 3.90-3.80 (m, 1H), 2.13–2.02 (m, 2H), 1.98 (dd, *J* = 14.8, 1.9 Hz, 1H), 1.77–1.54 (m, 5H), 1.49 (s, 3H), 1.10-1.00 (m, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$); δ 155.3, 132.5, 129.0, 115.2, 84.5, 83.4, 82.4, 65.4, 48.6, 40.6, 37.5, 37.3, 30.3, 21.3 ppm; IR(neat): ν 3419.8, 2931.9, 2265.6, 1716.8, 1451.3, 1202.7, 1077.2, 764.1 cm$^{-1}$; HRMS (*m/z*) calcd for $C_{16}H_{20}O_3$: 260.14124, found260.14023.

**(E)-7-Methyl-1-(2-nitrostyryl)octahydro-4a,7-epoxyisochromene (3g):**



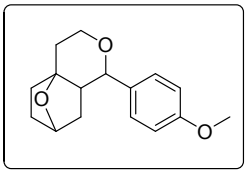
Light yellow Liquid; $^1$H NMR (500 MHz, $CDCl_3$): δ 7.93 (d, *J* = 8.0 Hz, 1H), 7.64–7.49 (m, 2H), 7.43–7.35 (m, 1H), 7.06 (d, *J* = 15.8 Hz, 1H), 6.07 (dd, *J* = 15.9, 6.2 Hz, 1H), 4.04-3.96 (m, 1H), 3.88–3.64 (m, 2H), 2.08–1.91 (m, 2H), 1.90–1.78 (m, 2H), 1.73–1.54 (m, 4H), 1.52 (s, 3H), 1.28–1.20 (m, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 133.3, 133.0, 132.7, 128.7, 128.1, 126.6, 124.4, 84.5, 81.8, 81.3, 64.7, 47.3, 40.5, 37.5, 37.2, 30.2, 29.7, 21.3 ppm; IR(neat): ν 2947.8, 2862.9, 2275.5, 1738.8, 1528.4, 1372.5, 1004.7, 809.8, 745.6 cm$^{-1}$; HRMS (*m/z*) calcd for $C_{18}H_{21}O_2N$: 315.14706, found: 315.14702.

**1-Isobutyloctahydro-4a,7-epoxyisochromene (3h):**



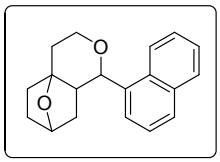
Light yellow Liquid; $^1$H NMR (500 MHz, $CDCl_3$): δ 4.52 (t, *J* = 5.3 Hz, 1H), 3.92 (ddd, *J* = 11.3, 5.8, 1.0 Hz, 1H), 3.60 (ddd, *J* = 12.7, 11.5, 2.9 Hz, 1H), 2.94 (td, *J* = 10.1, 1.9 Hz, 1H), 2.05–1.96 (m, 1H), 1.92 (dd, *J* = 14.6, 2.0 Hz, 1H), 1.87–1.73 (m, 1H), 1.63-1.57(m, 2H), 1.53–1.44 (m, 3H), 1.33–1.20 (m, 3H), 1.10-1.03(m, 1H), 0.89 (dd, *J* = 14.9, 6.0 Hz, 6H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 81.9, 79.0, 64.6, 46.6, 42.5, 35.8, 35.0, 31.4, 30.1, 29.6, 24.3, 23.9, 21.6; IR(neat): ν 2955.2, 2864.9, 1733.7, 1464.2, 1108.1, 759.3 cm $^{-1}$ ; HRMS (*m/z*) calcd for $C_{13}H_{22}O_2$: 210.16198, found: 210.16189.

**1-(4-Methoxyphenyl)octahydro-4a,7-epoxyisochromene (3i):**



Light yellow Liquid; $^1$H NMR (500 MHz, $CDCl_3$): δ 7.31–7.23 (m, 2H), 6.89–6.83 (m, 2H), 4.56 (t, *J* = 5.1 Hz, 1H), 4.07–4.01 (m, 1H), 3.90 (d, *J* = 10.3 Hz, 1H), 3.86-3.80 (m, 1H), 3.79 (s, 3H), 2.21–2.08 (m, 1H), 2.04–1.96 (m, 2H), 1.86–1.75 (m, 1H), 1.61–1.53 (m, 2H), 1.51–1.33 (m, 3H) ppm; $^{13}$C NMR (125 MHz, $CDCl_3$): δ 159.1, 132.4, 128.5, 113.6, 83.1, 82.0, 76.8, 65.2, 55.0, 46.9, 35.6, 34.4, 31.4, 29.8 ppm; IR(neat): ν 2929.3, 2860.3, 1730.4, 1614.7, 1513.6, 1247.5, 1083.8, 815.5 cm$^{-1}$ ; HRMS (*m/z*) calcd for $C_{16}H_{20}O_3$: 260.14124, found: 260.14223.

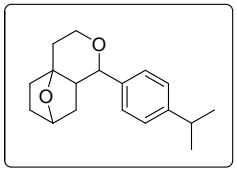
**1-(Naphthalen-1-yl) octahydro-4a,7-epoxyisochromene (3j):**



White solid; $^1$H NMR (500 MHz, $CDCl_3$): δ 8.31 (d, *J* = 8.5 Hz, 1H), 7.84 (d, J = 7.8 Hz, 1H), 7.79 (d, J = 8.1 Hz, 1H), 7.56–7.36 (m, 4H), 4.62 (d, *J* = 10.6 Hz, 1H), 4.57 (t, *J* = 5.2 Hz, 1H), 4.17–4.08 (m, 1H), 4.00 (ddd, *J* = 13.1, 11.5, 2.7 Hz, 1H), 2.50 – 2.40 (m, 1H), 2.33–2.22 (m, 1H), 2.11 (dd, *J* = 14.8, 1.9 Hz, 1H), 1.89–1.78 (m, 1H), 1.70–1.57 (m, 2H), 1.52–1.39 (m, 2H), 1.37–1.29 (m, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 134.9, 134.2, 132.1, 128.7, 128.6, 125.9, 125.4, 125.2, 124.9, 124.6, 82.2, 81.2, 65.7, 45.2, 35.9, 35.0, 31.6, 30.1,

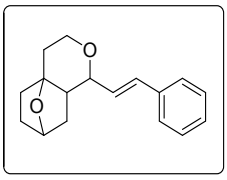
29.6; IR(neat): ν 2926.6, 2857.8, 2298.1, 1641.4, 1511.2, 1215.7, 1090.4, 771.0 $cm^{-1}$; HRMS (*m/z*) calcd for $C_{19}H_{26}O_2$: 280.14633, found: 280.14630.

**1-(4-Isopropylphenyl)octahydro-4a,7-epoxyisochromene (3k):**



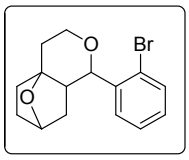
Light yellow Liquid; $^1$H NMR (500 MHz, $CDCl_3$): δ 7.28-7.24 (m, 2H), 7.18 (d, *J* = 8.1 Hz, 2H), 4.56 (t, *J* = 5.0 Hz, 1H), 4.07–3.99 (m, 1H), 3.92 (d, *J* = 10.4 Hz, 1H), 3.82 (ddd, *J* = 13.1, 11.6, 2.7 Hz, 1H), 2.94–2.79 (m, 2H), 2.21–2.12 (m, 1H), 2.04–1.97 (m, 2H), 1.85–1.76 (m, 1H), 1.62–1.55 (m, 1H), 1.51-1.35 (m, 3H), 1.21 (d, *J* = 6.7 Hz, 6H); $^{13}$C NMR (125 MHz, $CDCl_3$); δ 129.0, 128.4, 127.2, 126.2, 83.4, 82.0, 76.8, 65.2, 46.7, 35.6, 34.5, 33.6, 31.4, 29.8, 23.7 ppm ; IR(neat): ν 2960.4, 2863.9, 1727.6, 1638.3, 1084.7, 764.5 $cm^{-1}$; HRMS (*m/z*) calcd for $C_{18}H_{24}O_2$: 272.17763, found: 272.17642.

**(E)-1-Styryloctahydro-4a,7-epoxyisochromene (3l):**



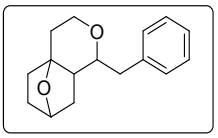
White solid; $^1$H NMR (500 MHz, $CDCl_3$): δ 7.37 (d, *J* = 7.5 Hz, 2H), 7.30 (t, *J* = 5.7 Hz, 2H), 7.23 (t, *J* = 7.3 Hz, 1H), 6.60 (d, *J* = 16.0 Hz, 1H), 6.09 (dd, *J* = 16.0, 6.6 Hz, 1H), 4.57 (t, *J* = 5.2 Hz, 1H), 4.02 (dd, *J* = 11.4, 5.8 Hz, 1H), 3.80–3.71 (m, 1H), 3.60 (dd, *J* = 10.1, 6.6 Hz, 1H), 2.09 (ddd, *J* = 19.9, 13.8, 6.5 Hz, 1H), 1.98 (dd, *J* = 14.7, 2.2 Hz, 1H), 1.87–1.71 (m, 2H), 1.64–1.47 (m, 4H), 1.47-1.40 (m, 1H. $^{13}$C NMR (125 MHz, $CDCl_3$): δ 136.7, 131.5, 128.4, 127.7, 127.6, 126.4, 81.7, 81.7, 77.1, 64.7, 45.9, 35.7, 34.6, 31.6, 29.9 ppm; IR(neat): ν 2929.2, 2860.9, 2271.1, 1728.7, 1645.9, 1454.7, 1100.1, 975.1, 747.7 $cm^{-1}$; HRMS (*m/z*) calcd for $C_{17}H_{20}O_2$: 256.14633, found: 256.14630.

**1-(2-Bromophenyl)octahydro-4a,7-epoxyisochromene (3m)**:



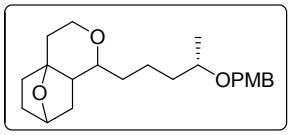
Light yellow Liquid; $^1$H NMR (500 MHz, $CDCl_3$): δ 7.55 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.44 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.34–7.29 (m, 1H), 7.14 (td, *J* = 7.9, 1.7 Hz, 1H), 4.59 (t, *J* = 5.2 Hz, 1H), 4.51 (d, *J* = 10.6 Hz, 1H), 4.07–4.00 (m, 1H), 3.88 (ddd, *J* = 12.9, 11.5, 2.8 Hz, 1H), 2.20–2.08 (m, 2H), 2.03 (dd, *J* = 14.7, 2.1 Hz, 1H), 1.88–1.78 (m, 1H), 1.64–1.55 (m, 2H), 1.54–1.44 (m, 2H), 1.44–1.36 (m, 1H) ppm; $^{13}$C NMR (125 MHz, $CDCl_3$): δ 139.4, 132.9, 129.3, 129.1, 127.6, 124.9, 82.1, 81.0, 77.1, 65.6, 46.8, 35.8, 33.5, 31.7, 29.9 ppm; IR(neat): ν 2925.5, 2860.5, 2361.9, 1708.1, 1611.9, 1465.4, 1204.5, 1076.9, 989.4, 753.4 $cm^{-1}$ ; HRMS (*m/z*) calcd for $C_{15}H_{17}BrO_2$: 308.04119, found: 308.04110.

**1-Benzyloctahydro-4a,7-epoxyisochromene (3n):**



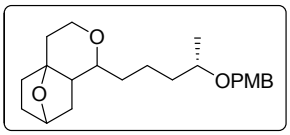
Light yellow Liquid; $^{1}$H NMR (500 MHz, $CDCl_3$): δ 7.31–7.25 (m, 2H), 7.24–7.17 (m, 3H), 4.52 (t, *J* = 5.2 Hz, 1H), 3.93–3.85 (m, 1H), 3.56 (ddd, *J* = 12.9, 11.5, 2.8 Hz, 1H), 3.24–3.17 (m, 1H), 2.73 (dd, *J* = 14.4, 3.2 Hz, 1H), 2.61 (dd, *J* = 14.4, 8.5 Hz, 1H), 2.06–1.96 (m, 1H), 1.90 (dd, *J* = 14.7, 1.8 Hz, 1H), 1.83–1.73 (m, 1H), 1.67–1.56 (m, 2H), 1.55–1.43 (m, 3H), 1.34–1.27 (m, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 139.0, 129.2, 128.1, 126.0, 81.9, 81.9, 77.0, 64.7, 46.0, 39.7, 35.8, 35.3, 31.4, 30.0; IR(neat): ν 2926.1, 2864.8, 1738.5, 1474.6, 1106.3, 757.8 cm$^{-1}$; HRMS (*m/z*) calcd for $C_{16}H_{20}O_2$: 244.14633, found: 244.14629.

**1-((*S*)-4-((4-methoxybenzyl)oxy)pentyl)octahydro-4a,7-epoxyisochromene (3o):**



Light yellow Liquid; $^{1}$H NMR (500 MHz, $CDCl_3$): δ 7.28-7.24 (m, 2H), 6.86(d, *J* = 8.6 Hz, 2H), 4.53-4.46 (m, 2H), 4.38 (d, *J* = 11.4 Hz, 1H), 3.95-3.89 (m, 1H), 3.80 (s, 3H), 3.64-3.57 (m, 1H), 3.52-3.44 (m,1H), 2.90-2.85 (m, 1H), 2.09-1.85 (m,2H), 1.81–1.74 (m, 1H), 1.62–1.49 (m, 6H), 1.47-1.22 (m, 6H), 1.17 (d, *J* = 1.5,4.7 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 158.9, 131.2, 129.1, 113.6, 81.9, 80.7, 74.4, 69.8, 69.6, 55.2, 46.3, 36.5, 35.8, 35.1, 33.2, 31.4, 30.1, 29.6, 21.7, 19.5; IR(neat): ν 2919.5, 2856.4, 1741.6, 1450.9, 750.8 cm$^{-1}$; HRMS (*m/z*) calcd for $C_{22}H_{32}O_4$:360.4870, found: 360.4859.

**1-((*S*)-4-((4-methoxybenzyl)oxy)pentyl)octahydro-4a,7-epoxyisochromene (3o'):**



Light yellow Liquid ;$^{1}$H NMR (500 MHz, $CDCl_3$): δ 7.28-7.24 (m, 2H), 6.86(d, *J* = 8.2 Hz, 2H), 4.53-4.46 (m, 2H), 4.38 (d, *J* = 11.4 Hz, 1H), 3.94-3.89 (m,1H), 3.80 (s, 3H), 3.63-3.57 (m,1H), 3.51-3.45 (m,1H), 2.91-2.85 (m, 1H), 2.05-1.96(m,1H),1.94-1.88 (m,1H) 1.81–1.73 (m, 1H), 1.62–1.48 (m, 6H), 1.46-1.27 (m, 6H), 1.17 (d, *J* = 1.5,4.5 Hz, 3H); IR(neat): ν 2927.6, 2869.5, 1725.4, 1439.4, 769.8, cm$^{-1}$; HRMS (*m/z*) calcd for $C_{22}H_{32}O_4$:360.4870, found: 360.4855.

**(3) X-Ray crystallography**

X-ray data for the compounds were collected at room temperature using a Bruker Smart Apex CCD diffractometer with graphite monochromated MoKα radiation (λ=0.71073Å) with ω-scan method [1]. Preliminary lattice parameters and orientation matrices were obtained from four sets of frames.

Integration and scaling of intensity data were 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. All H atoms were positioned geometrically and treated as riding on their parent C atoms [C-H = 0.93-0.98 Å and $U_{iso}(H) = 1.2U_{eq}(C)$]. Compound shows a meaningless Flack parameter (Flack & Bernardinelli, 2000) value of -0.5(5). This is due to the molecular structure having light atoms (<Si) with no significant anomalous scattering effects. In this case, the Flack parameter is indeterminate with Mo radiation and hence the absolute structure cannot be determined. However, the absolute configuration of the procured material was known in advance.

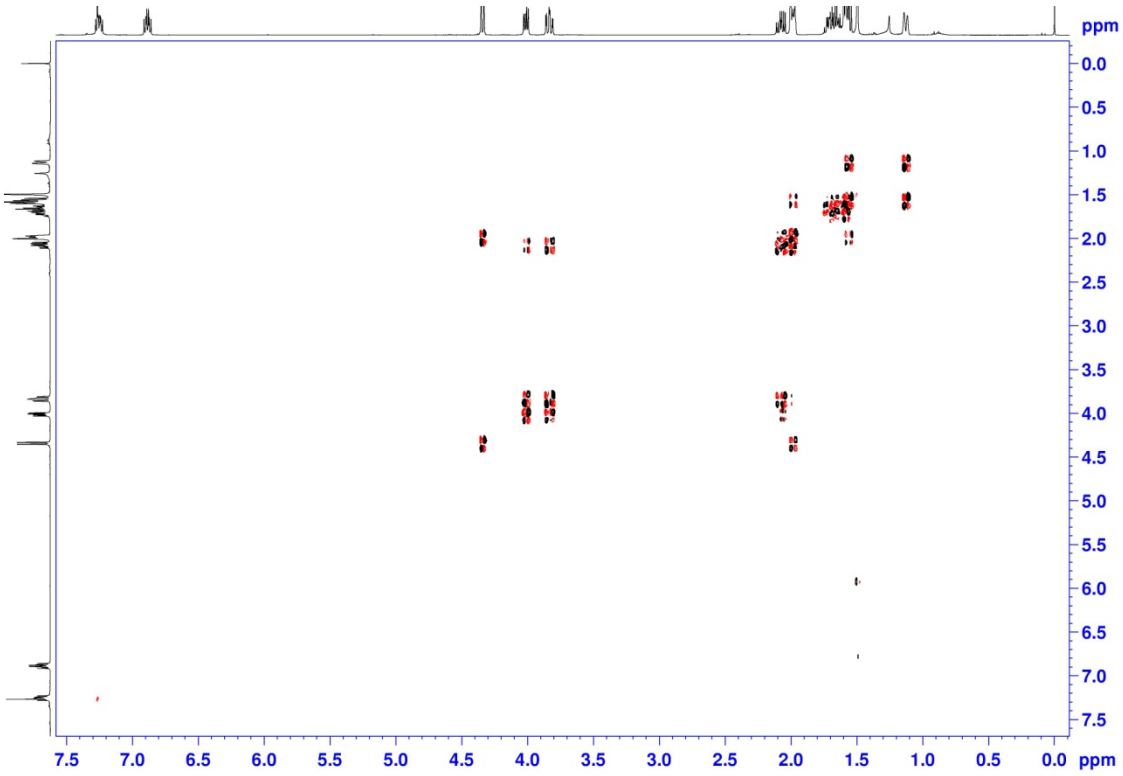
Crystal data for **3j**: $C_{19}H_{20}O_2$, *M* = 280.35, 0.18 x 0.16 x 0.07 $mm^3$, orthorhombic, space group $Pna2_1$ (No. 33), *a* = 8.6637(7), *b* = 15.5478(12), *c* = 11.0472(9) Å, *V* = 1488.1(2) $Å^3$, *Z* = 4, $D_c$ = 1.251 $g/cm^3$, $F_{000}$ = 600, MoKα radiation, λ = 0.71073 Å, *T* = 294(2)K, $2\theta_{max}$ = 50.0º, 13621 reflections collected, 2626 unique ($R_{int}$ = 0.0304). Final *GooF* = 1.269, *R1* = 0.0489, *wR2* = 0.1084, *R* indices based on 2542 reflections with I >2σ(I) (refinement on $F^2$), 190 parameters, 1 restraint. μ = 0.080 $mm^{-1}$. Absolute structure parameter = -0.5(5) (Flack & Bernardinelli, 2000). CCDC 1048635 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.
3. Flack, H. D. & Bernardinelli, G. (2000). J. Appl. Cryst. 33, 1143–1148.


Figure Caption

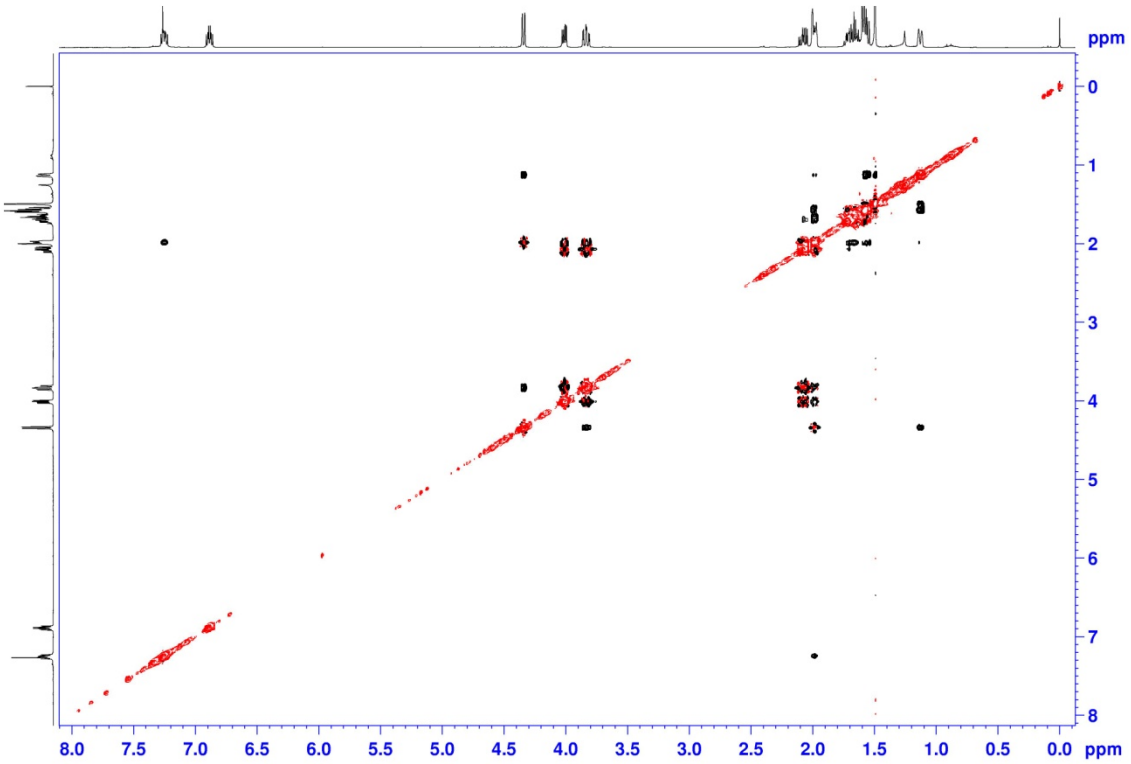
Fig.1. A view of **3j**, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are represented by circles of arbitrary radii.

## (4) 2D-NOESY and DQCOSY Spectra of product 3a




**2D DQCOSY (Double Quantum coherence spectroscopy) spectrum of compound 3a**

**( 500 MHz NMR spectrometer)**

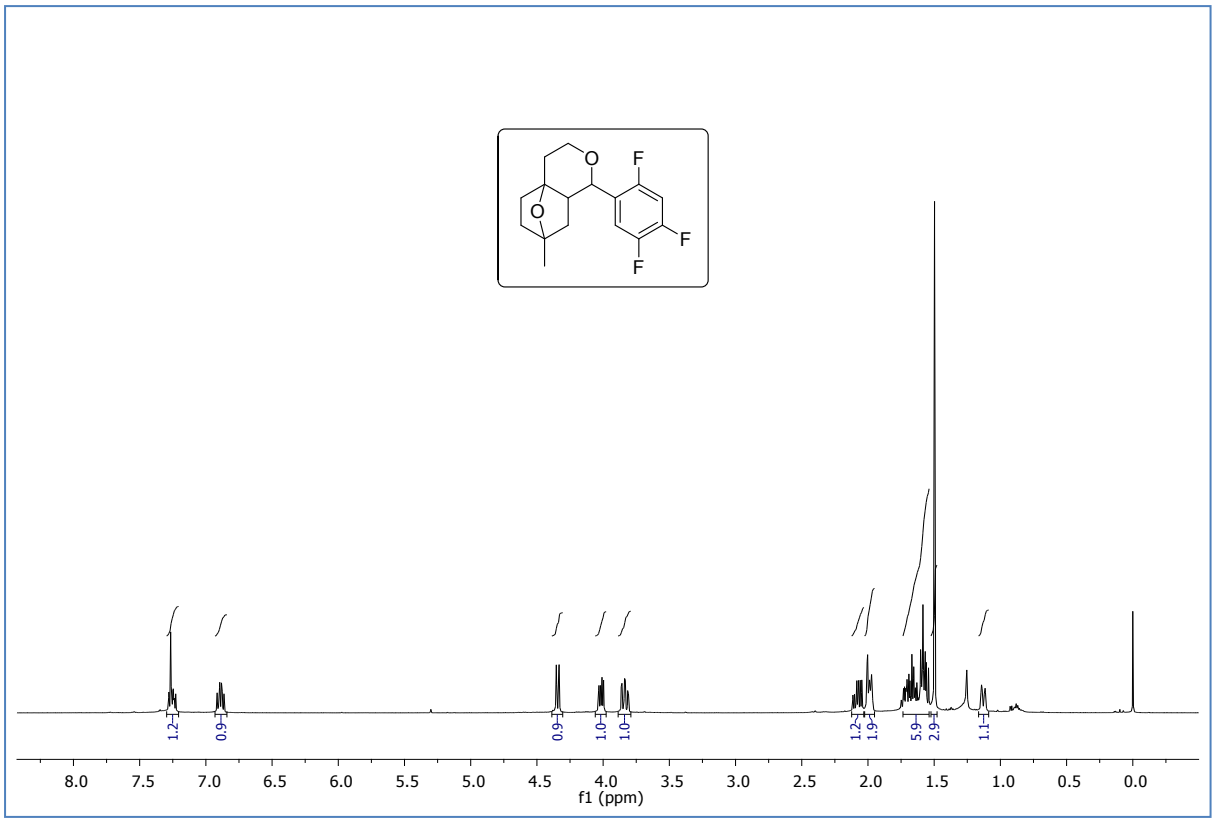



**2D NOESY (Nuclear Overhauser effect spectroscopy) spectrum of compound 3a**

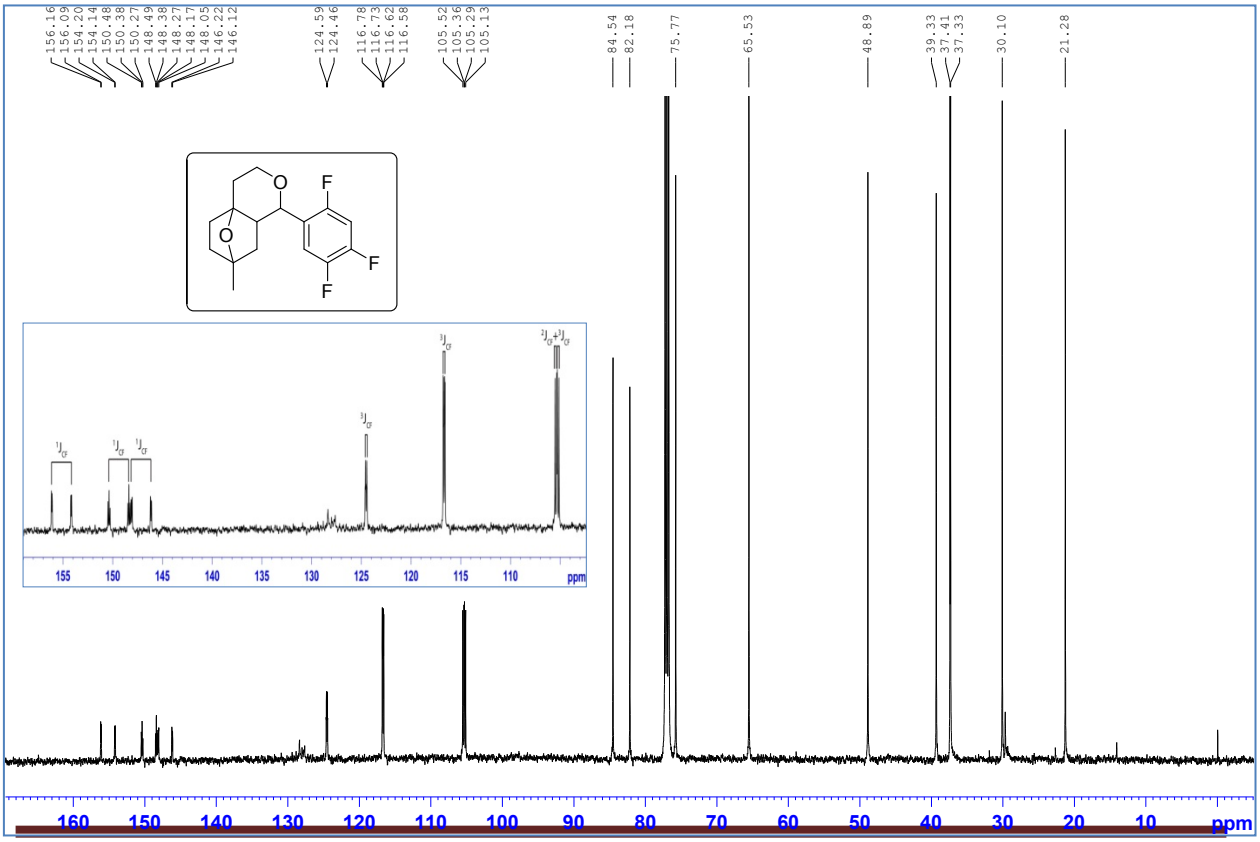
**( 500 MHz NMR spectrometer).**

## (5) Copies of $^{1}H$ and $^{13}C$ NMR spectra of products

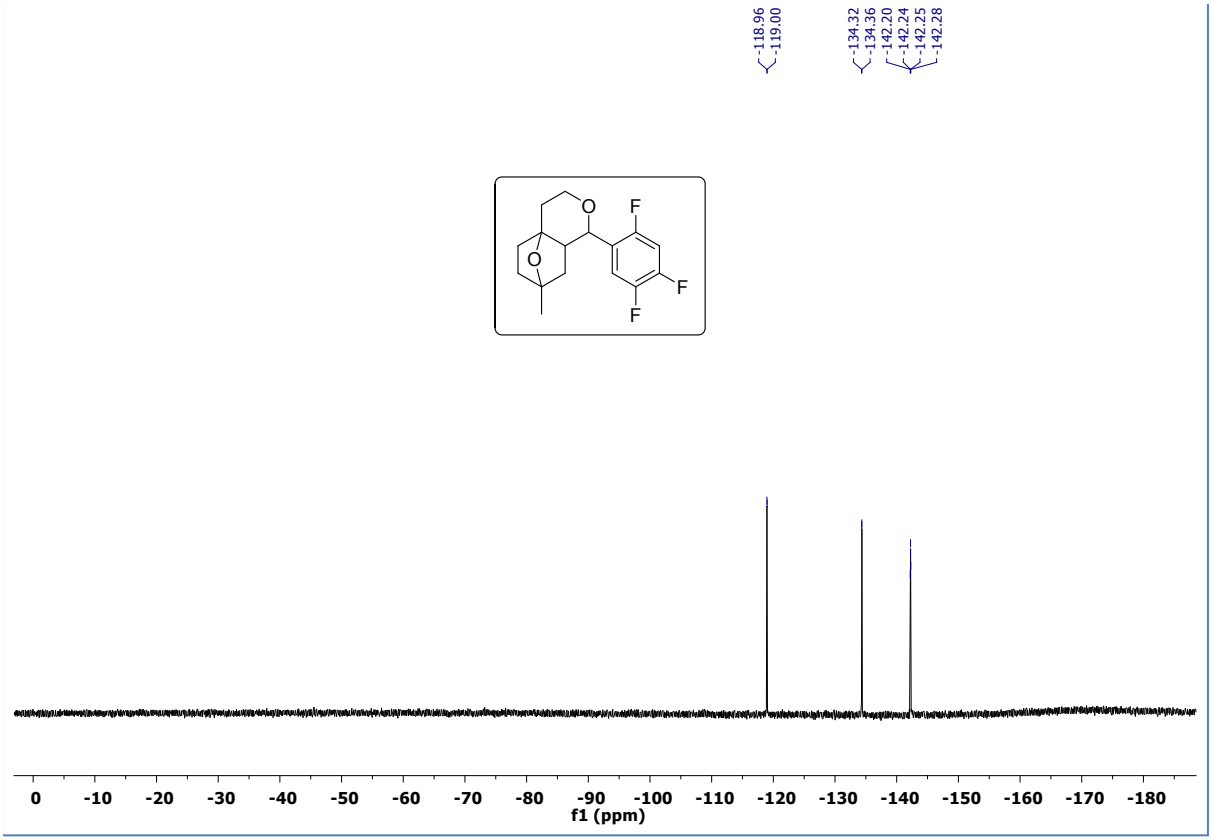
### $^{1}H$ NMR (500 MHz, $CDCl_3$) spectrum of compound 3a



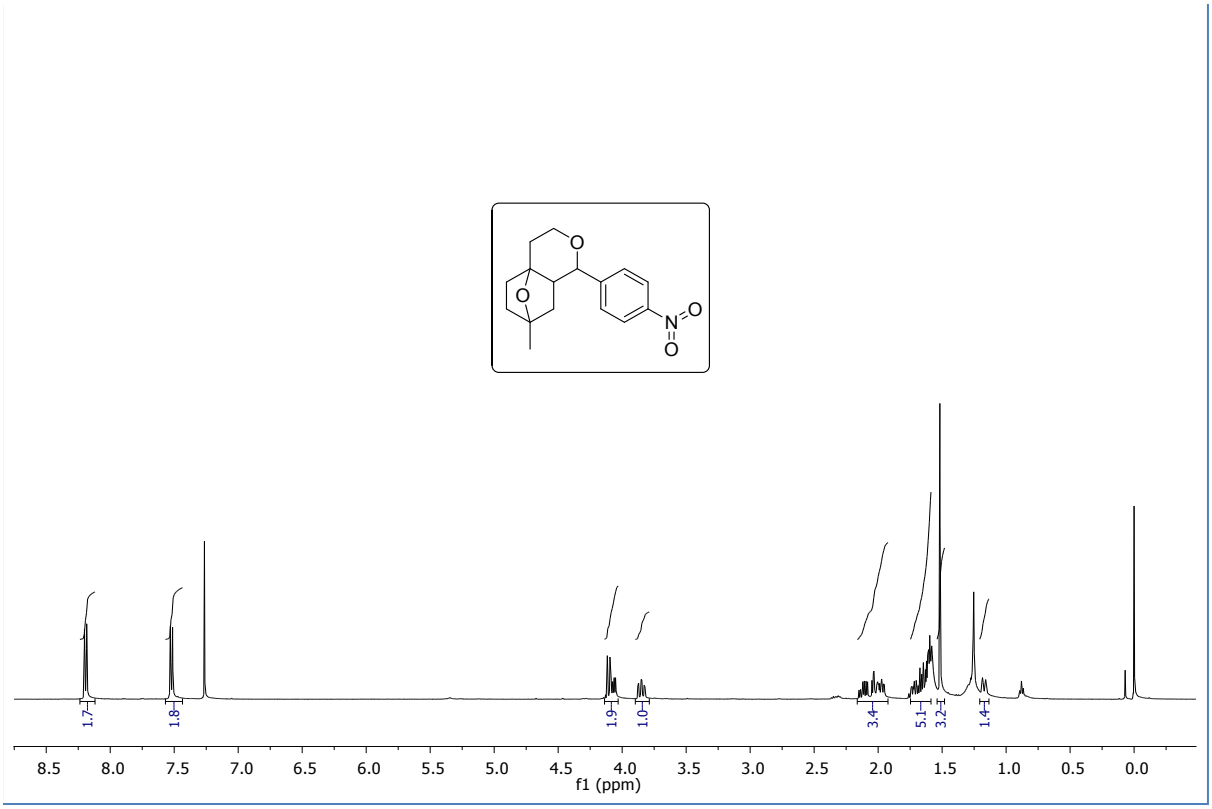

### $^{13}C$ NMR (125 MHz, $CDCl_3$) spectrum of compound 3a



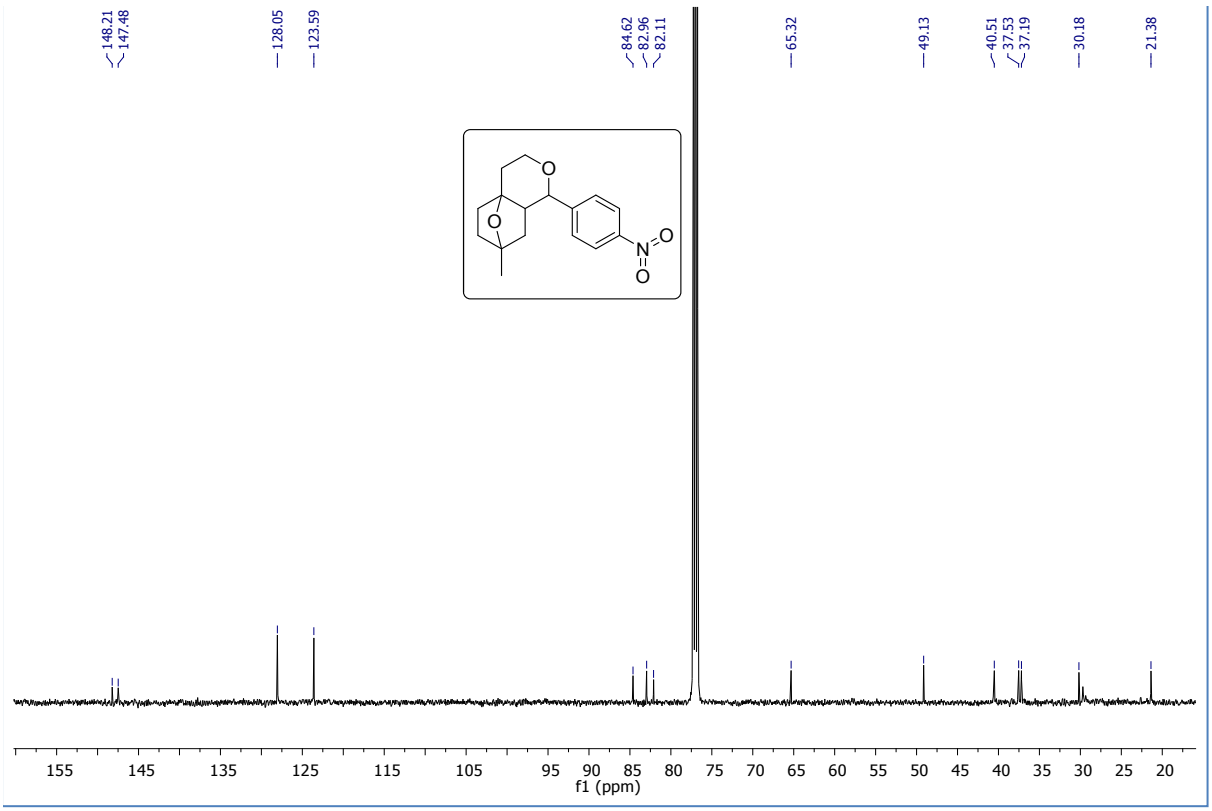
**$F^{19}$- NMR (470 MHz, $CDCl_3$) spectrum of compound 3a**



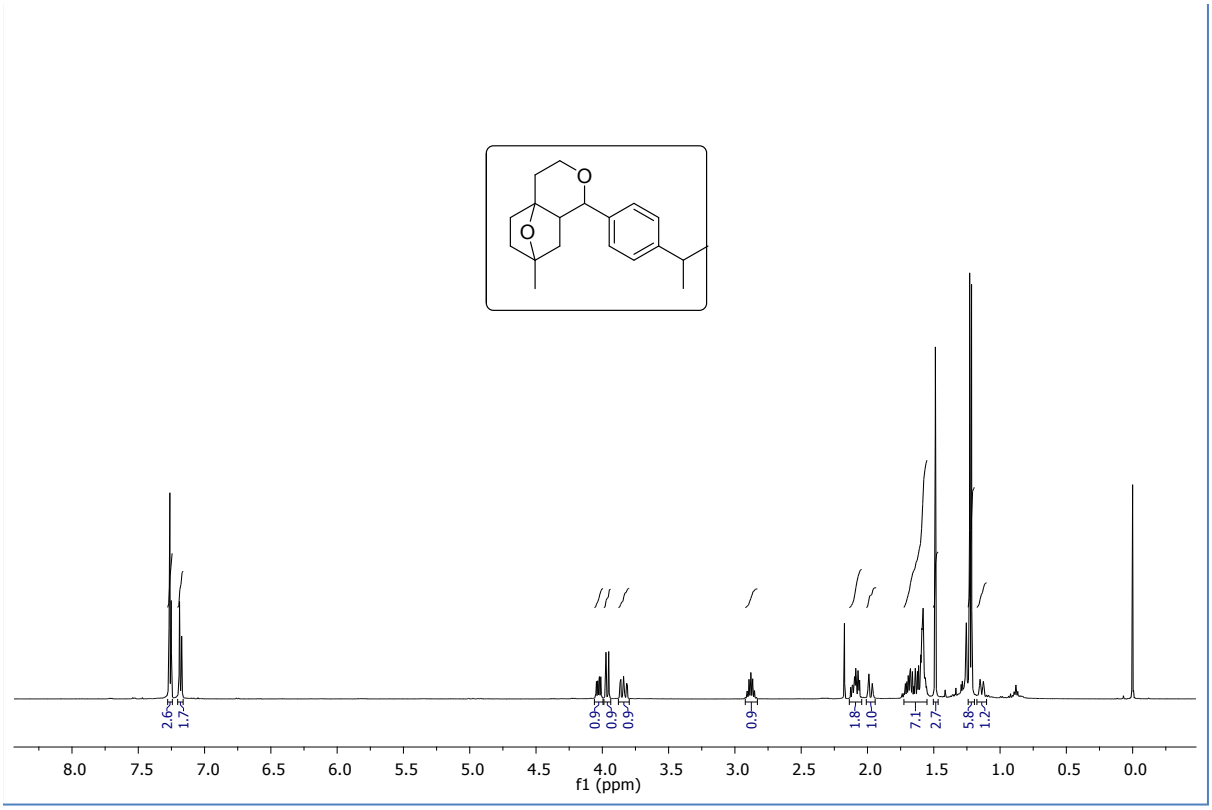
**$^{1}$H NMR (500 MHz, $CDCl_3$) spectrum of compound 3b**



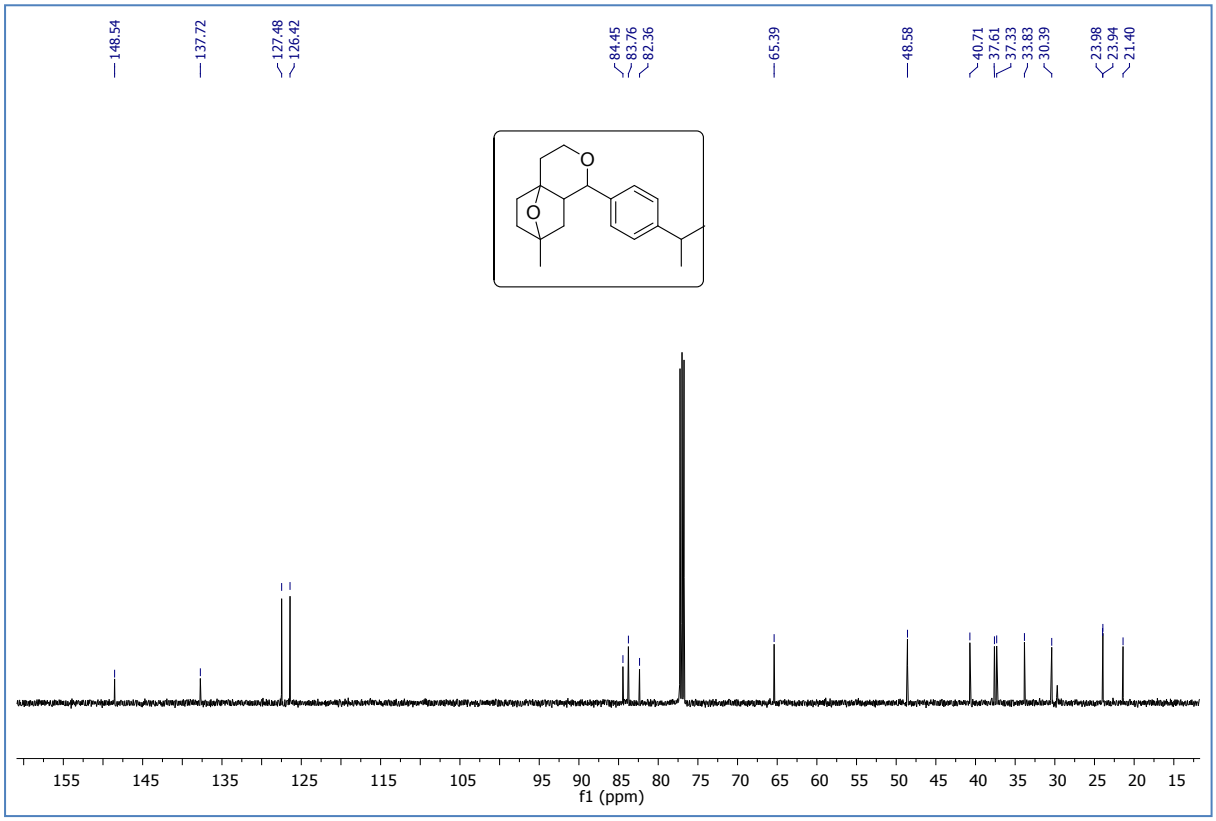

**$^{13}$C NMR (125 MHz, $CDCl_3$) spectrum of compound 3b**



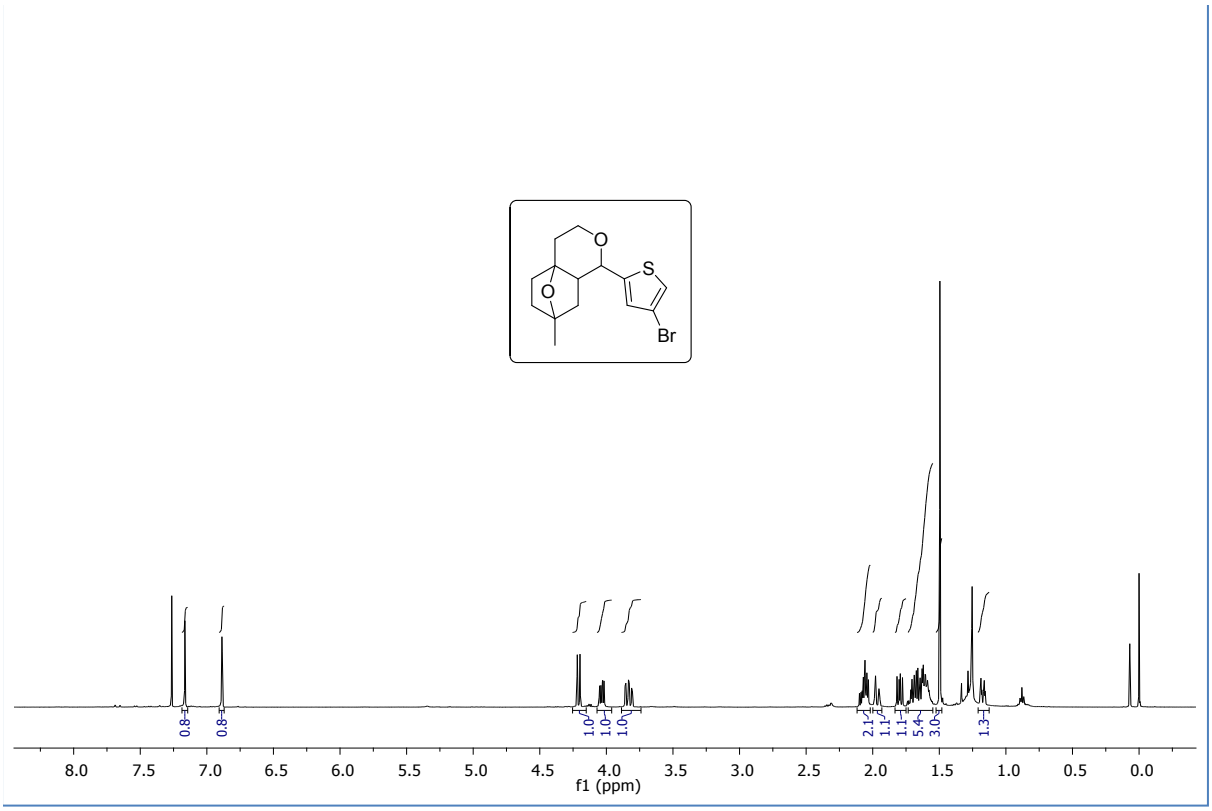

**$^{1}$H NMR (500 MHz, $CDCl_3$) spectrum of compound 3c**



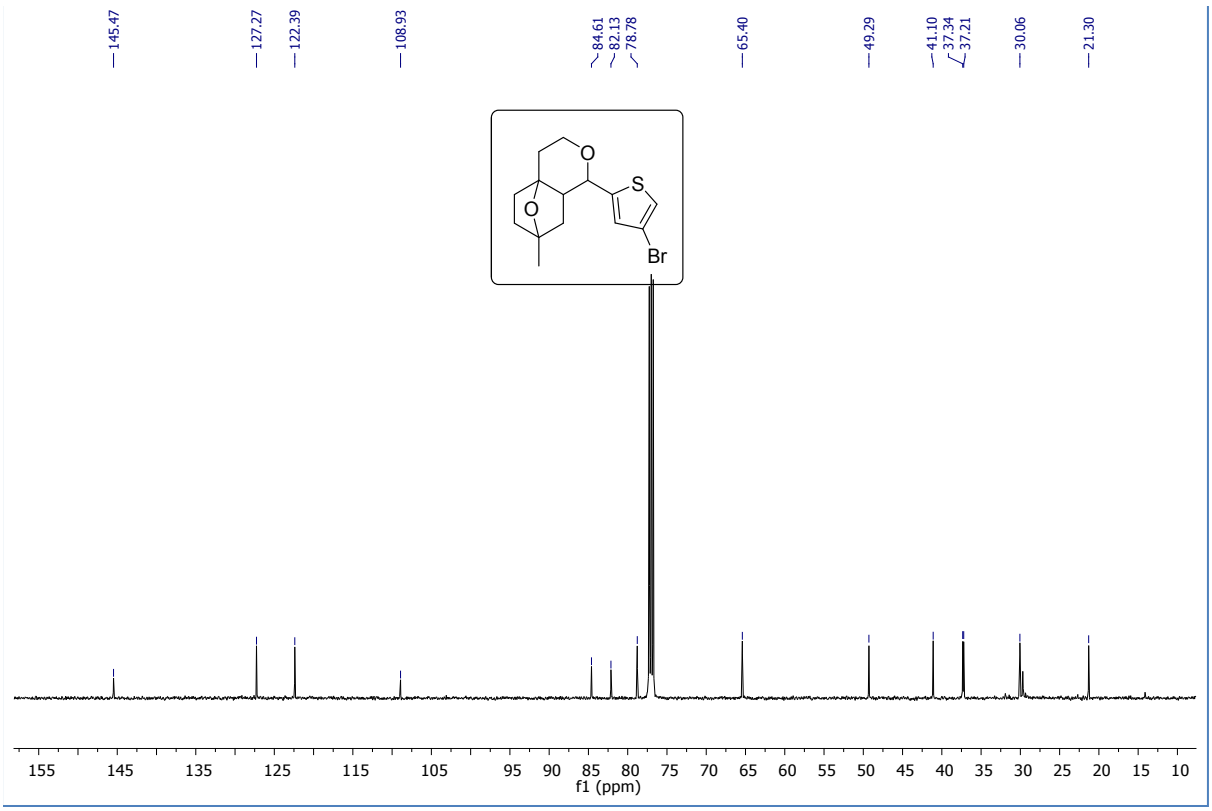

**$^{13}$C NMR (125 MHz, $CDCl_3$) spectrum of compound 3c**



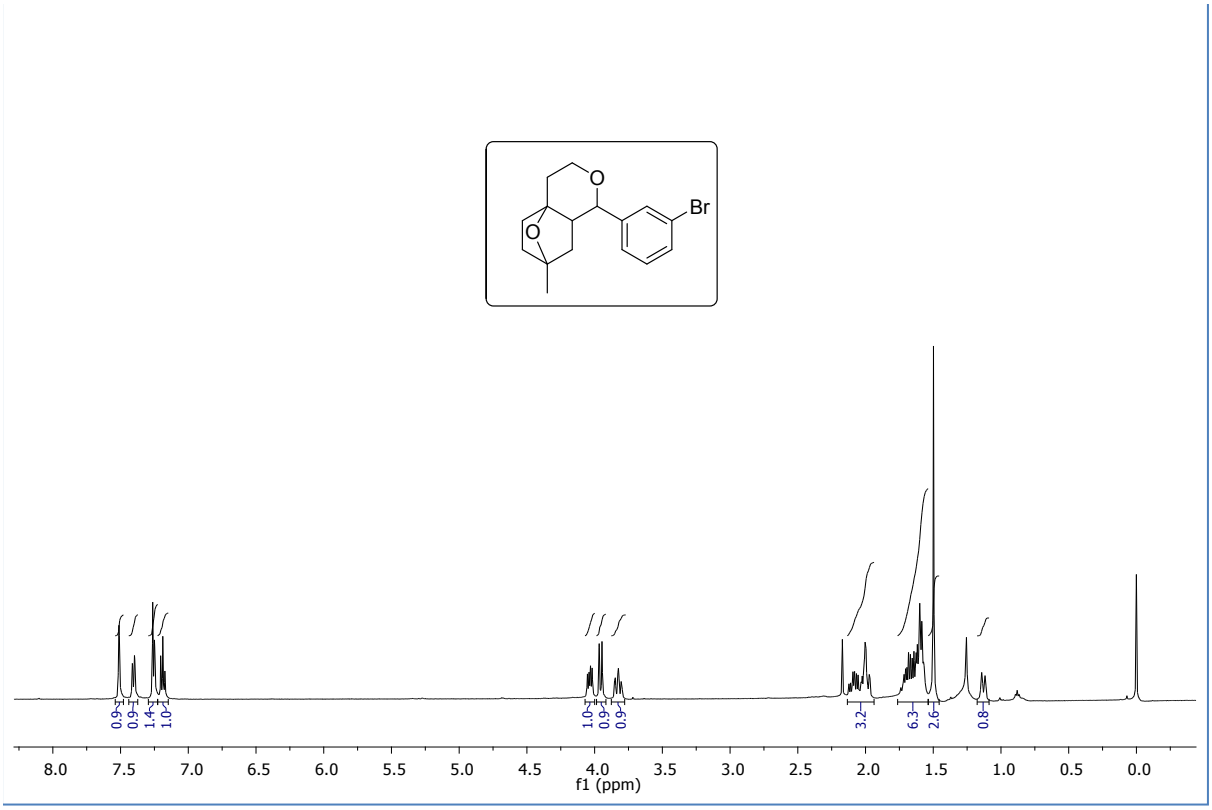

**$^{1}$H NMR (500 MHz, $CDCl_3$) spectrum of compound 3d**



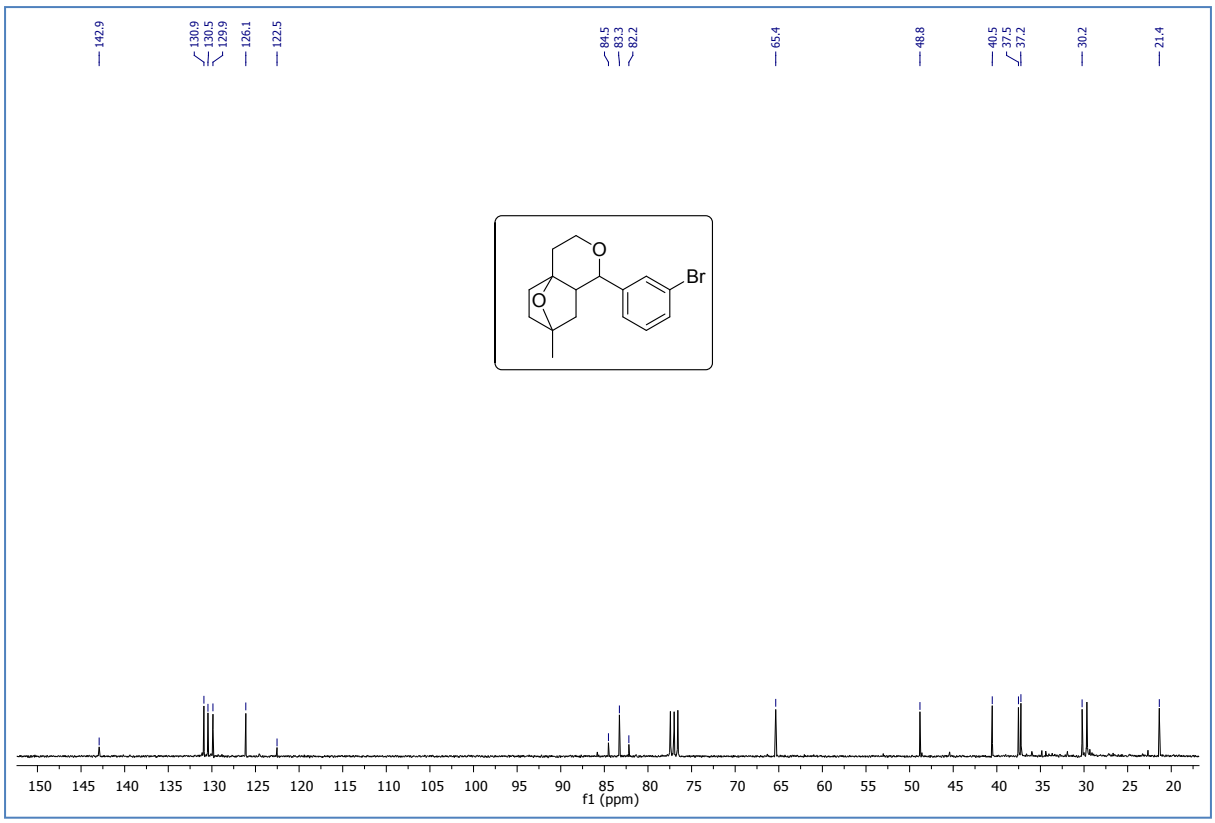

**$^{13}$C NMR (125 MHz, $CDCl_3$) spectrum of compound 3d**



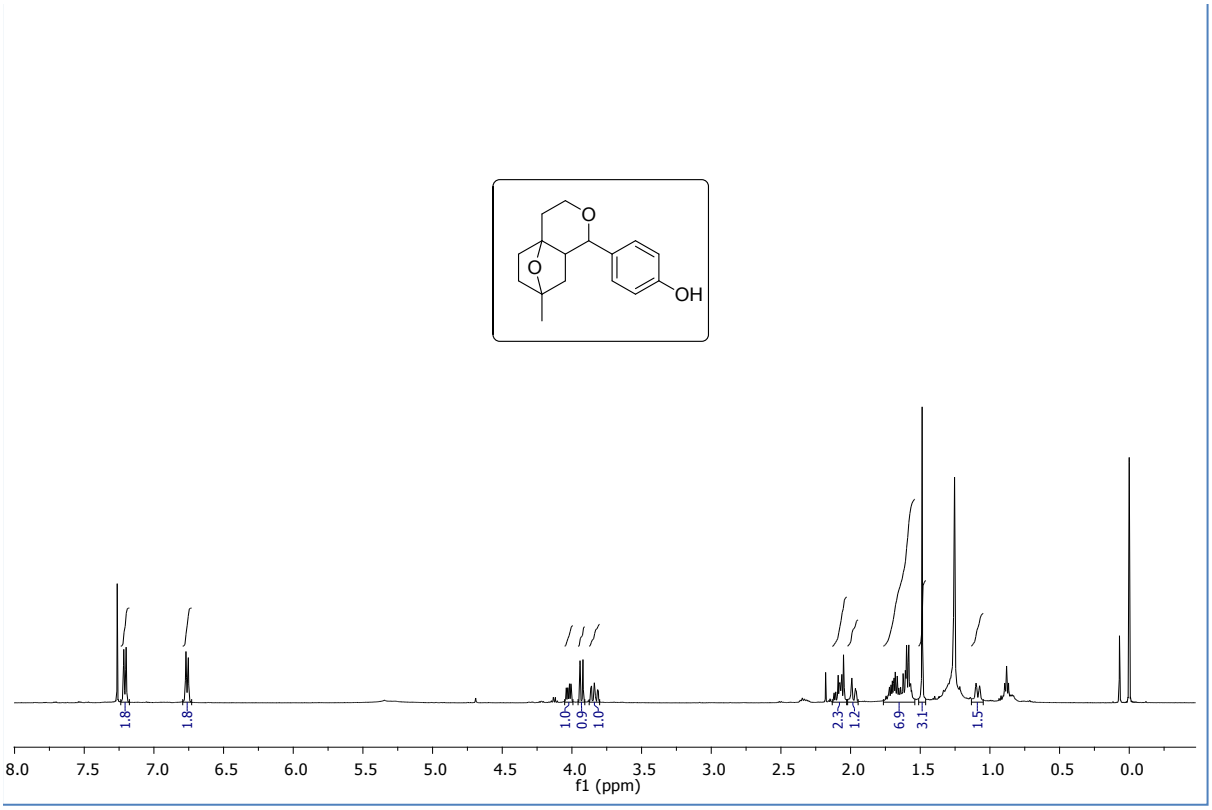

**$^{1}$H NMR (500 MHz, $CDCl_3$) spectrum of compound 3e**



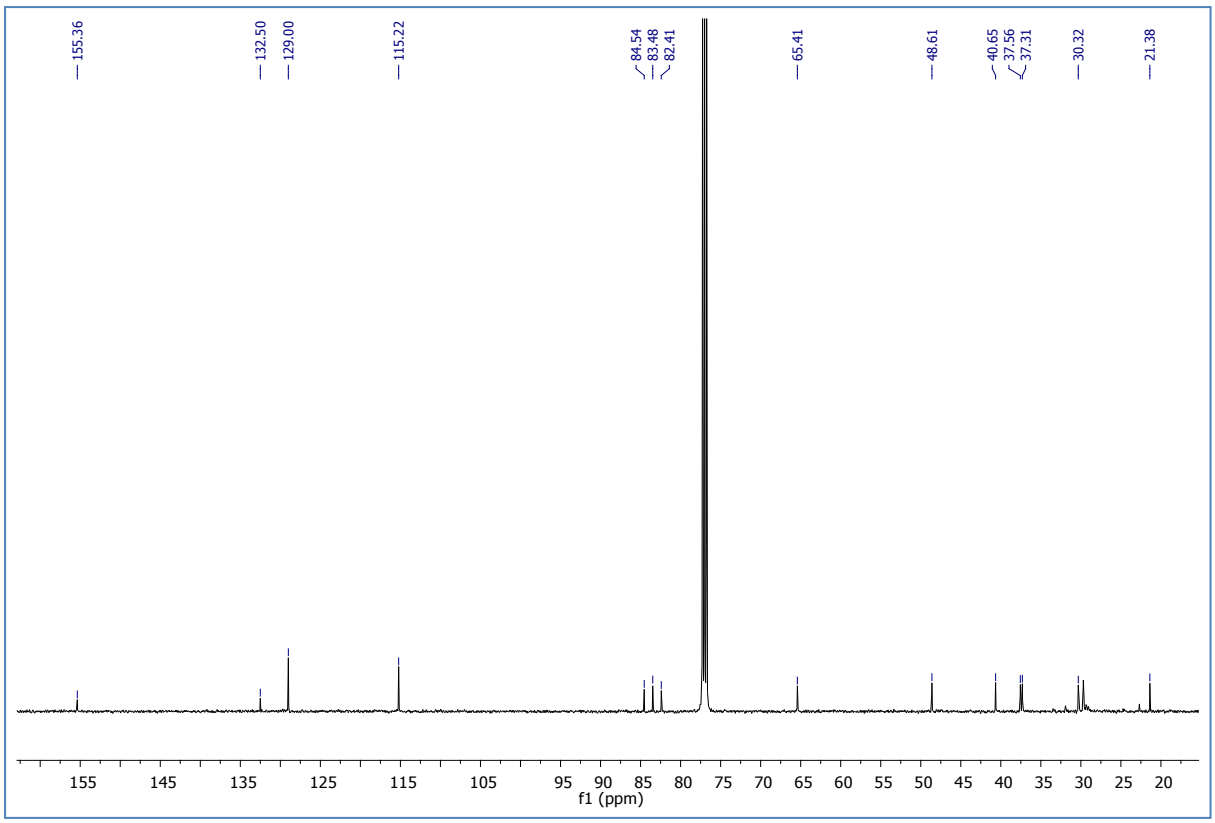

**$^{13}$C NMR (125 MHz, $CDCl_3$) spectrum of compound 3e**



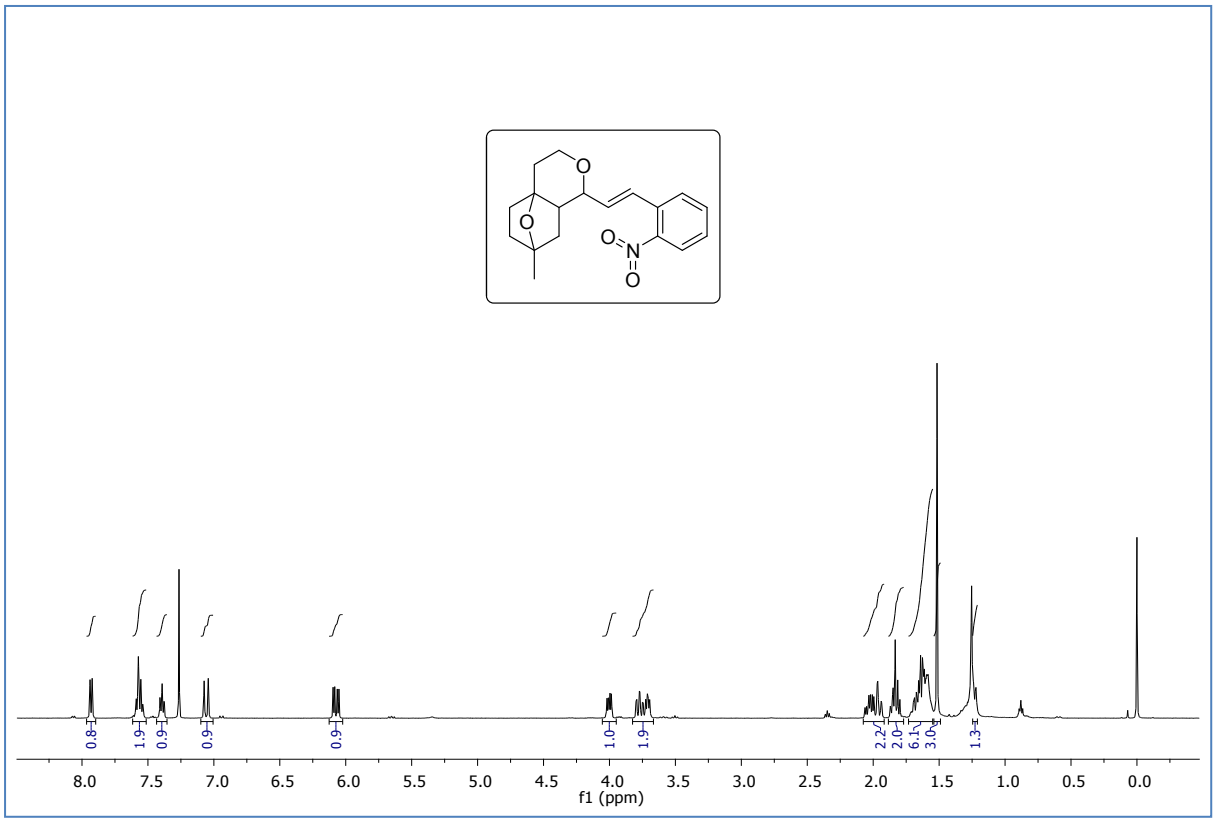

**$^{1}$H NMR (500 MHz, $CDCl_3$) spectrum of compound 3f**



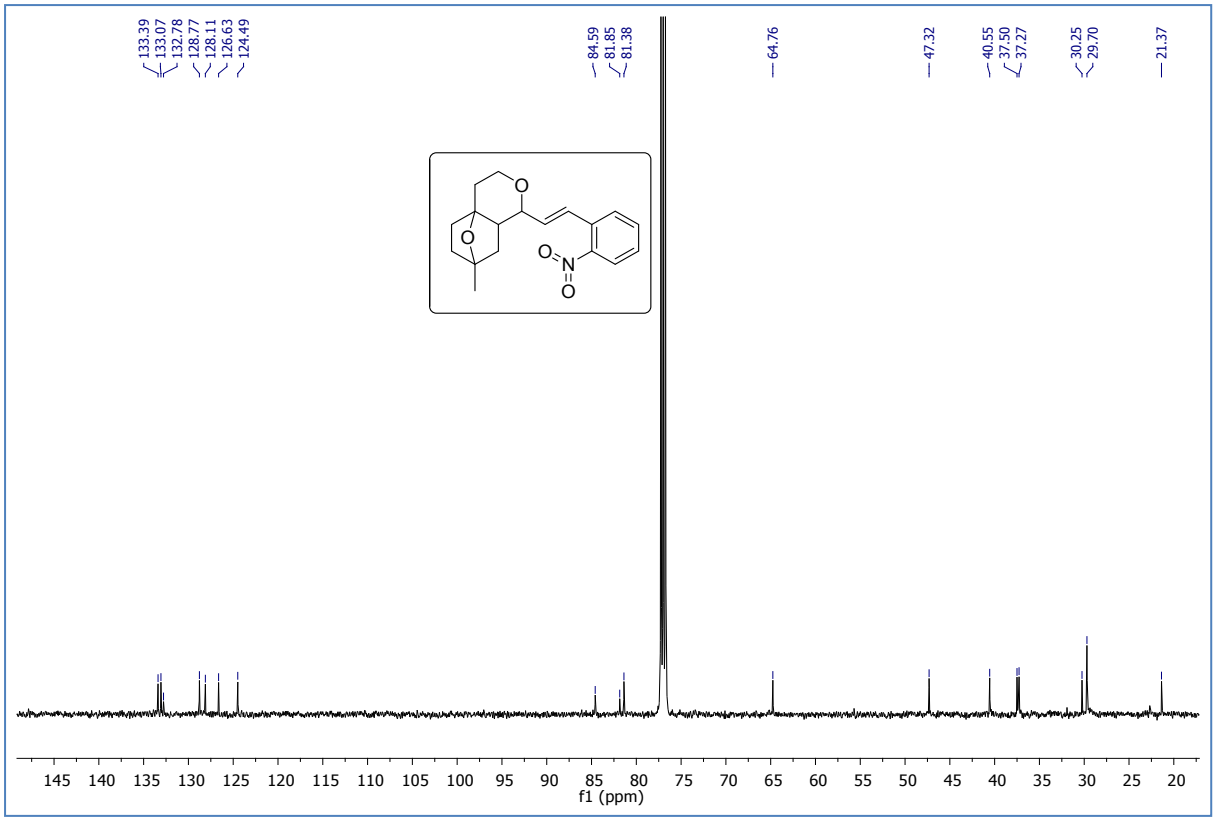

**$^{13}$C NMR (125 MHz, $CDCl_3$) spectrum of compound 3f**



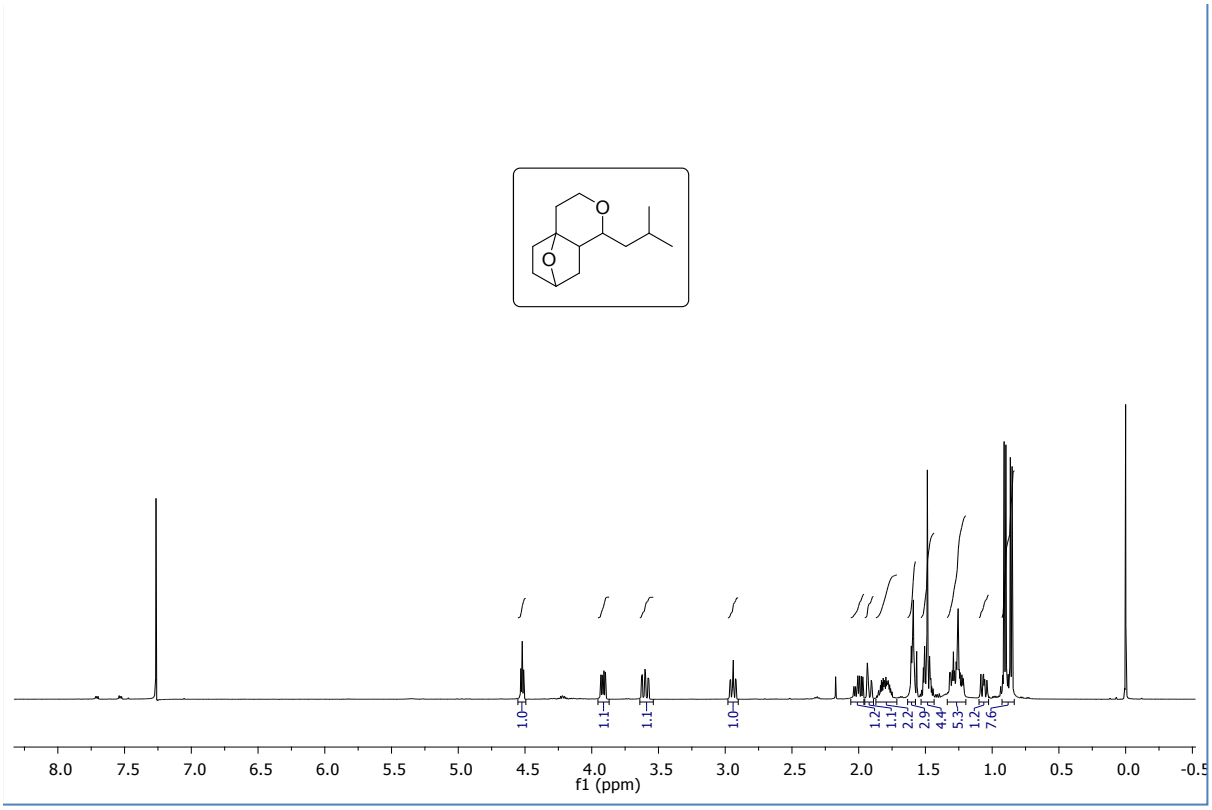

**$^{1}$H NMR (500 MHz, $CDCl_3$) spectrum of compound 3g**



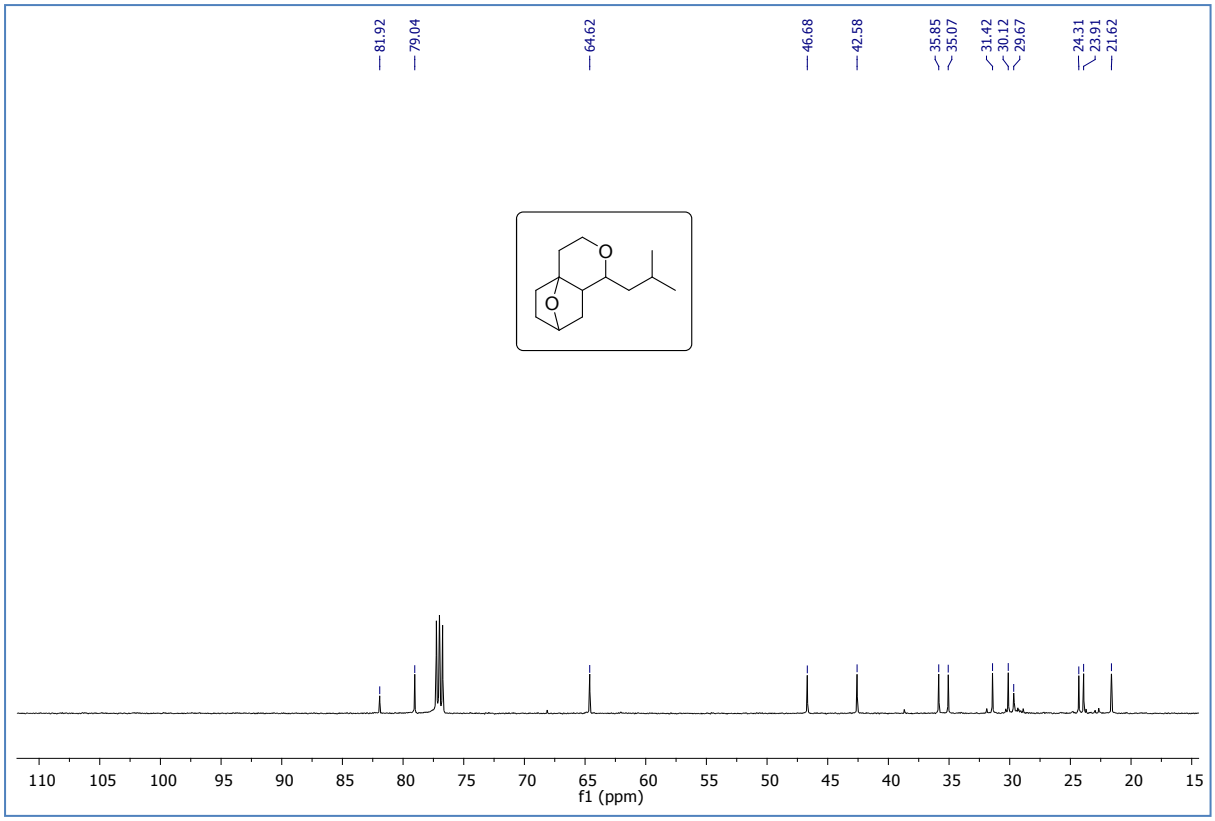

**$^{13}$C NMR (125 MHz, $CDCl_3$) spectrum of compound 3g**



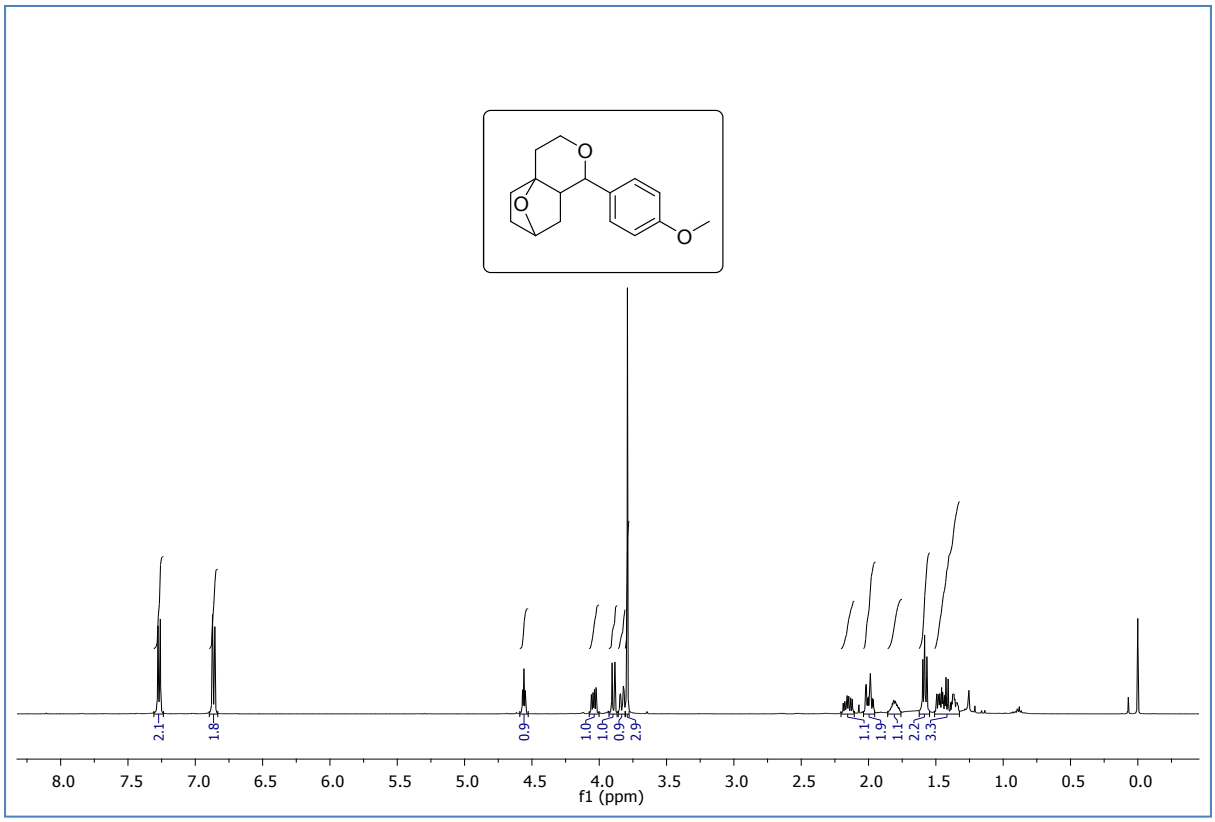

**$^{1}$H NMR (500 MHz, $CDCl_3$) spectrum of compound 3h**



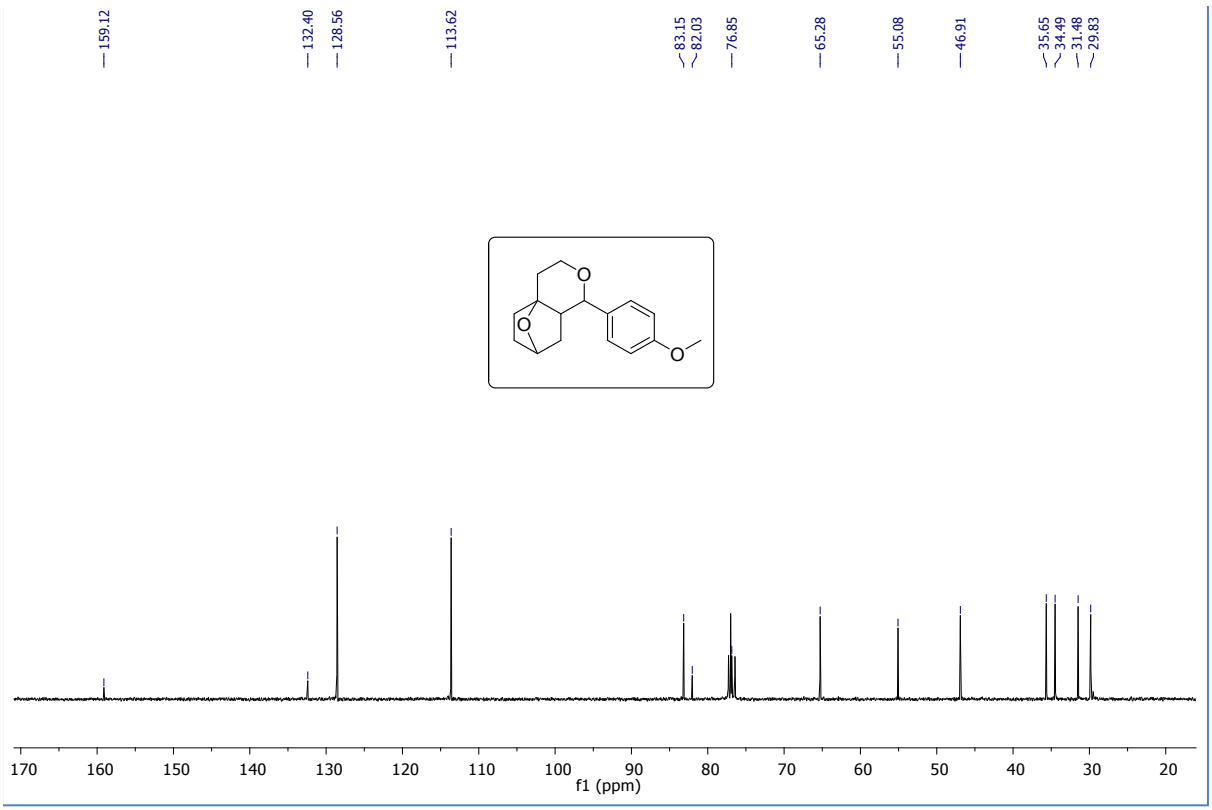

**$^{13}$C NMR (125 MHz, $CDCl_3$) spectrum of compound 3h**



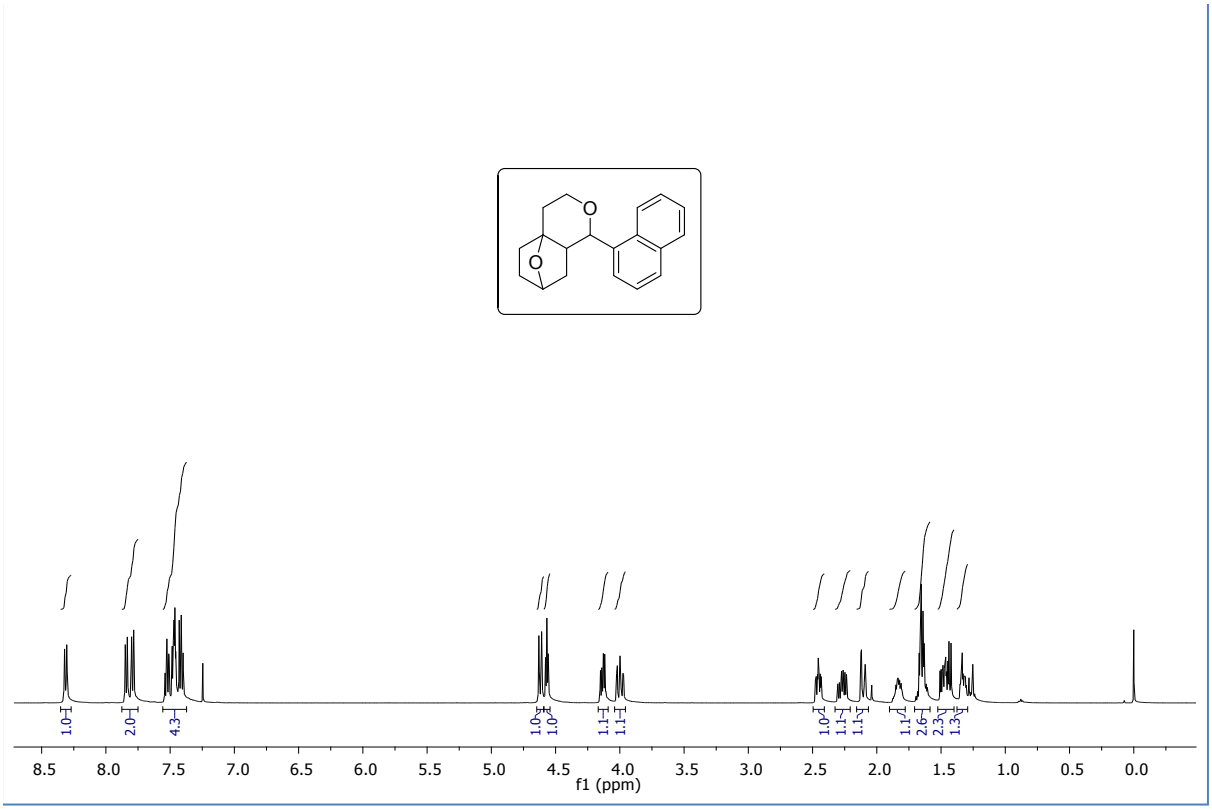

**$^{1}$H NMR (500 MHz, $CDCl_3$) spectrum of compound 3i**



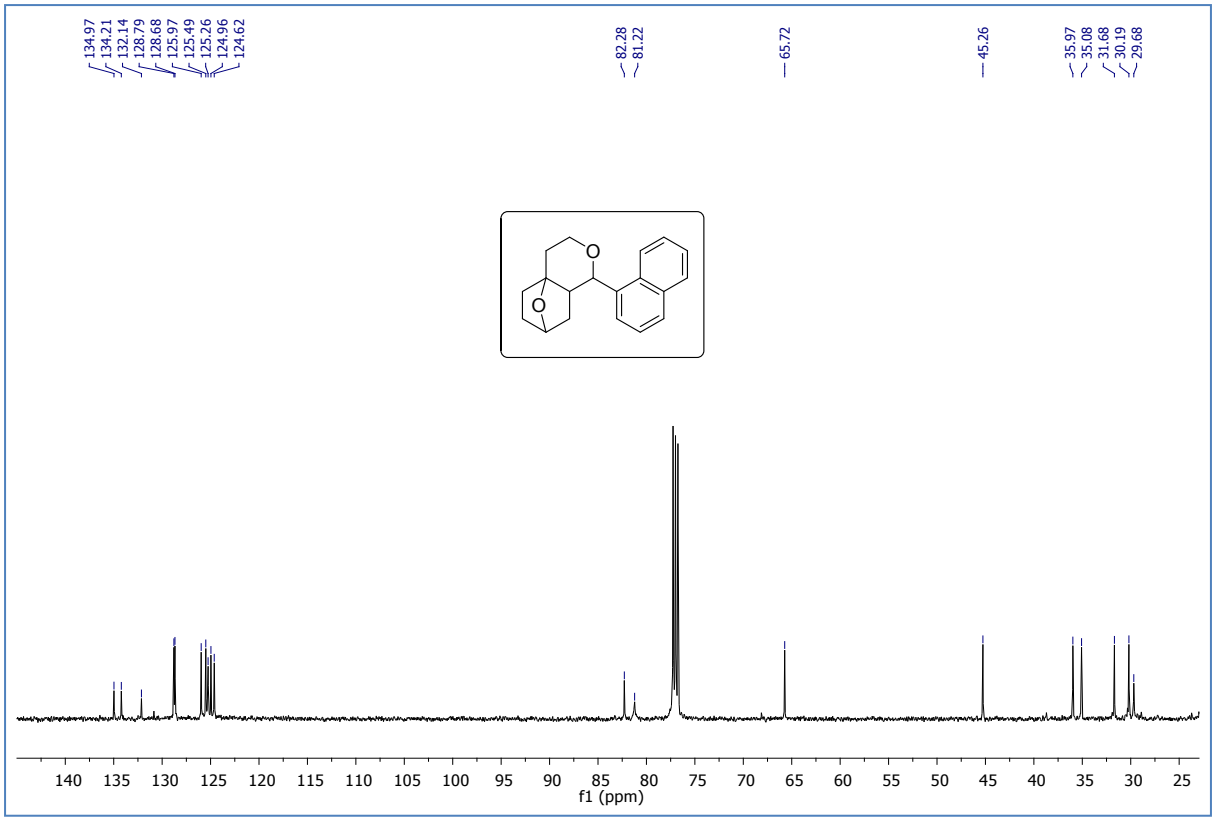

**$^{13}$C NMR (125 MHz, $CDCl_3$) spectrum of compound 3i**



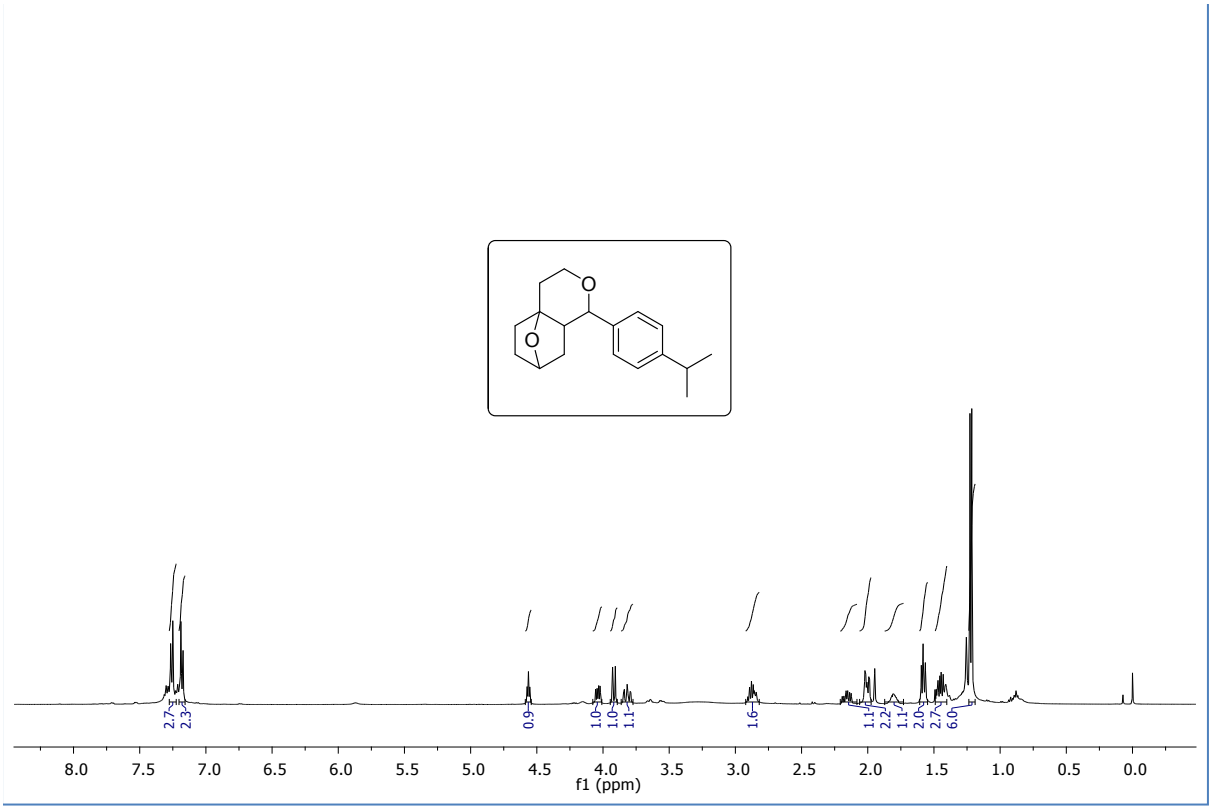

**$^{1}$H NMR (500 MHz, $CDCl_3$) spectrum of compound 3j**



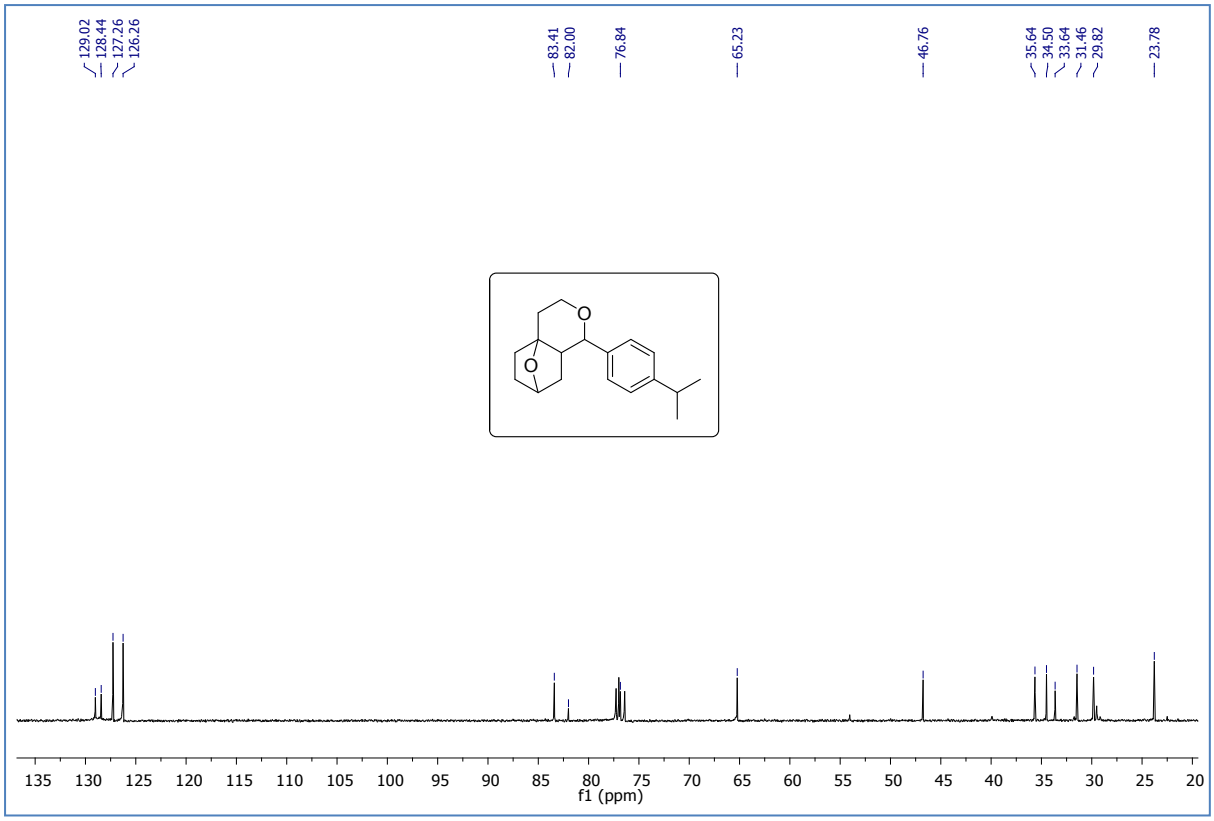

**$^{13}$C NMR (125 MHz, $CDCl_3$) spectrum of compound 3j**



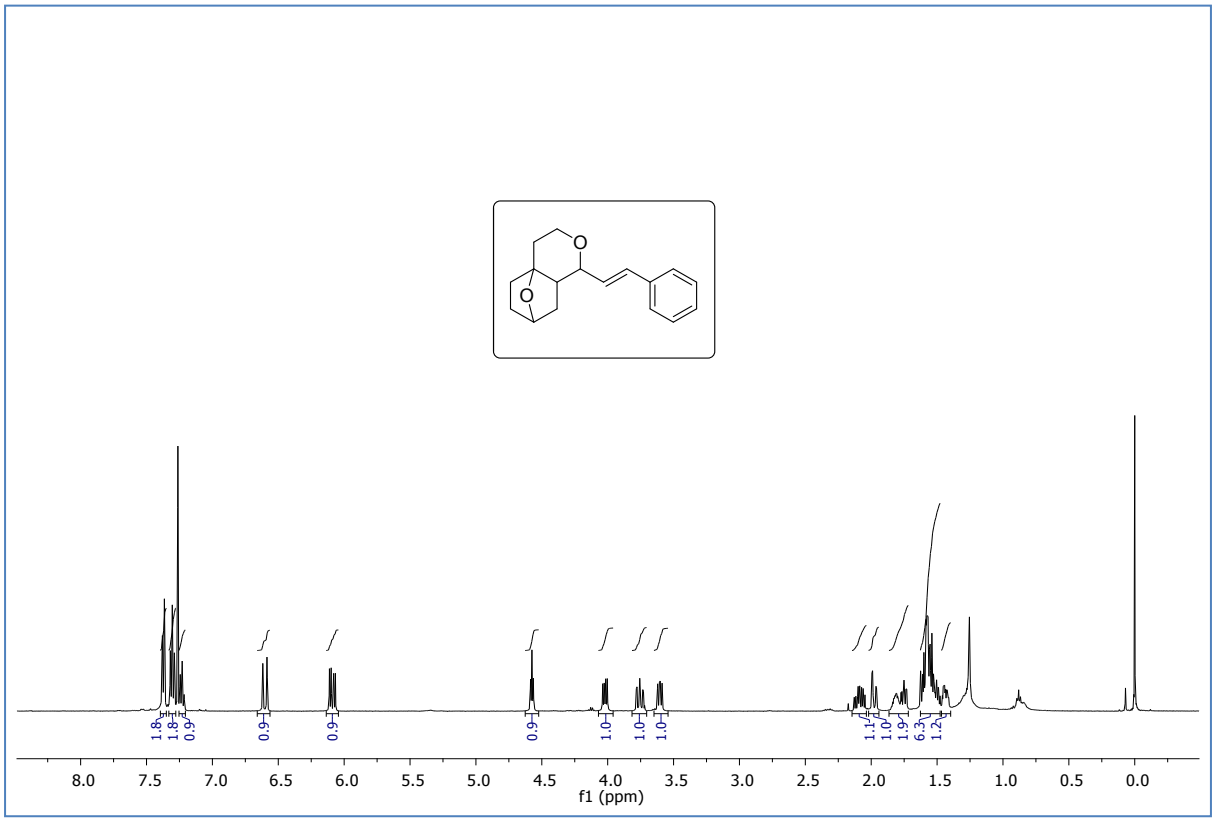

**$^{1}$H NMR (500 MHz, $CDCl_3$) spectrum of compound 3k**



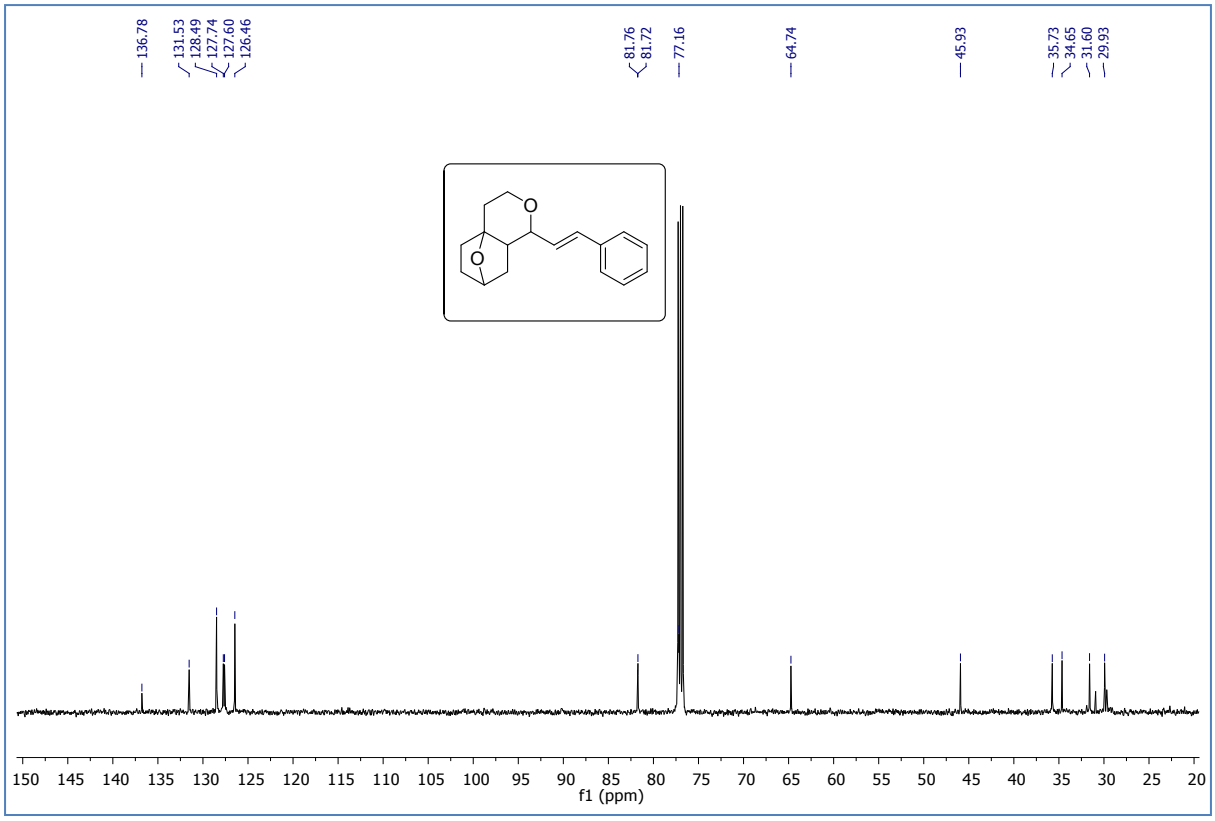

**$^{13}$C NMR (125 MHz, $CDCl_3$) spectrum of compound 3k**



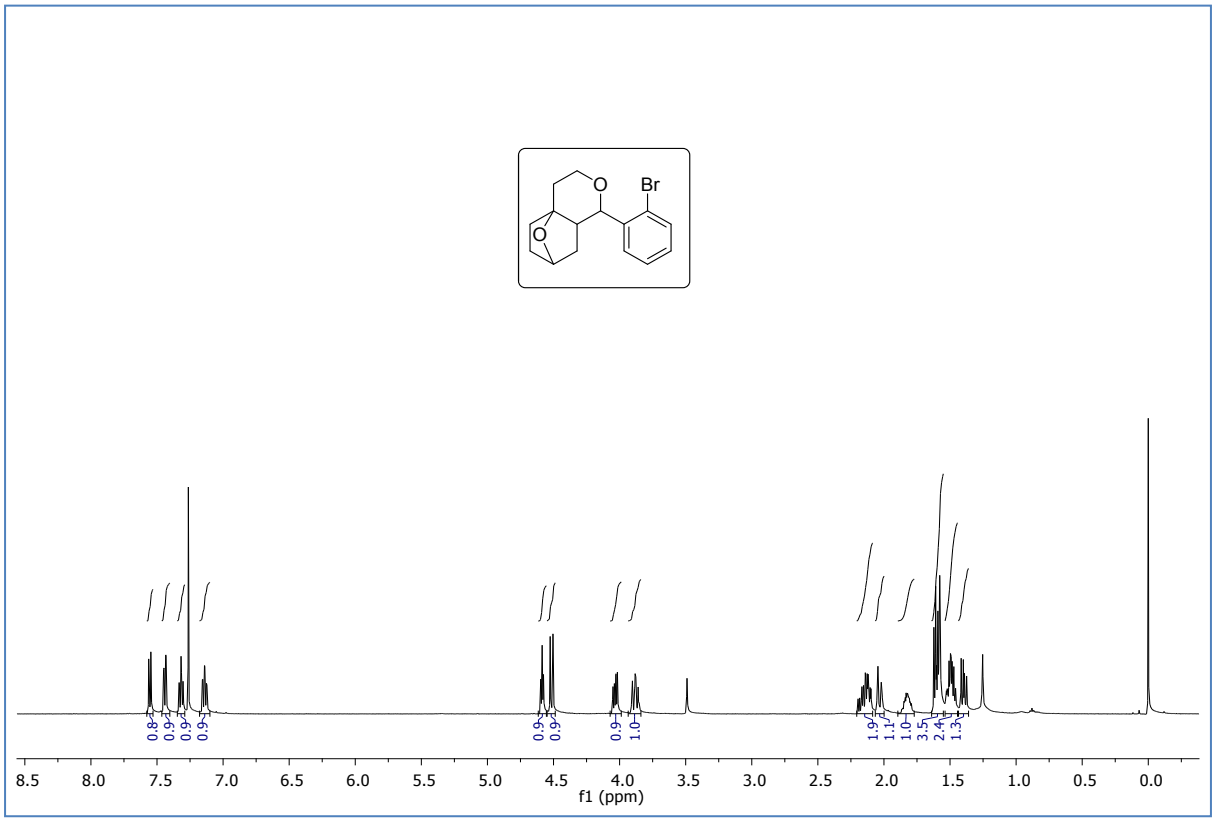

**$^{1}$H NMR (500 MHz, $CDCl_3$) spectrum of compound 3l**



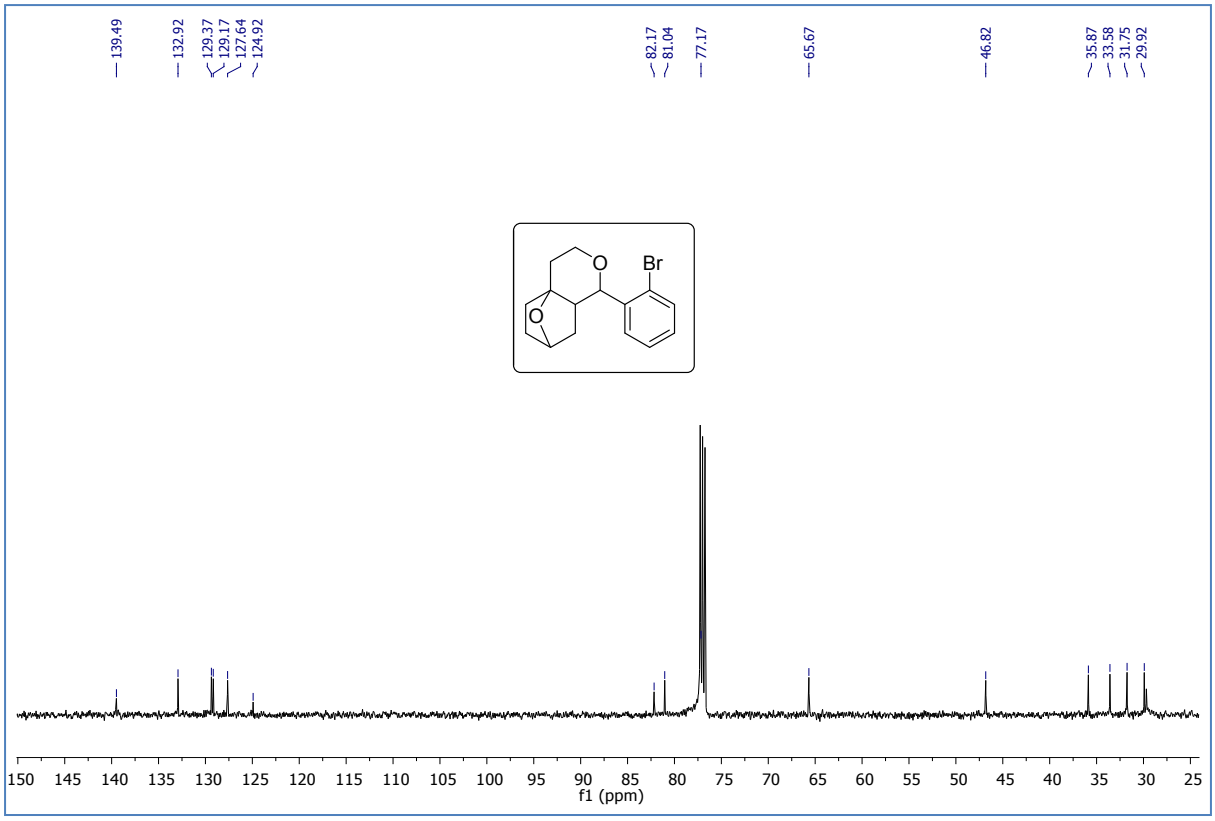

**$^{13}$C NMR (125 MHz, $CDCl_3$) spectrum of compound 3l**



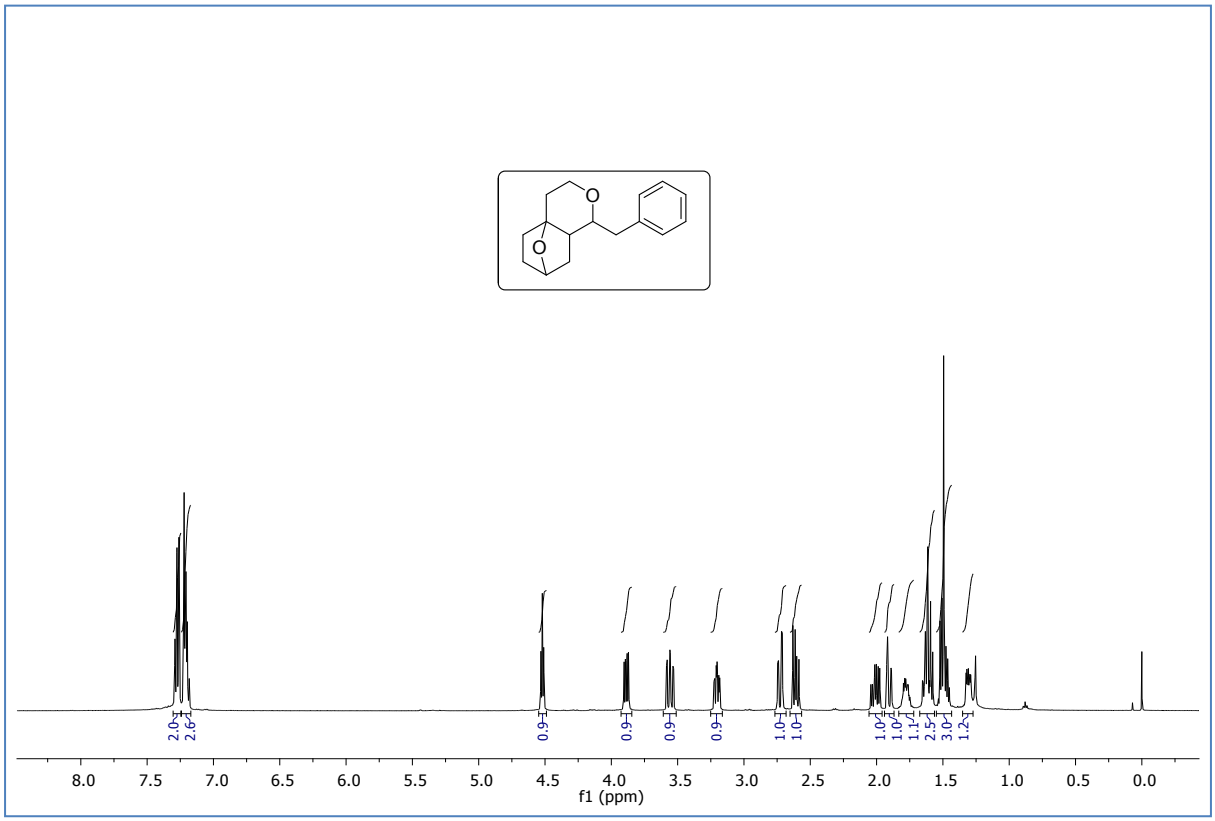

**$^{1}$H NMR (500 MHz, $CDCl_3$) spectrum of compound 3m**



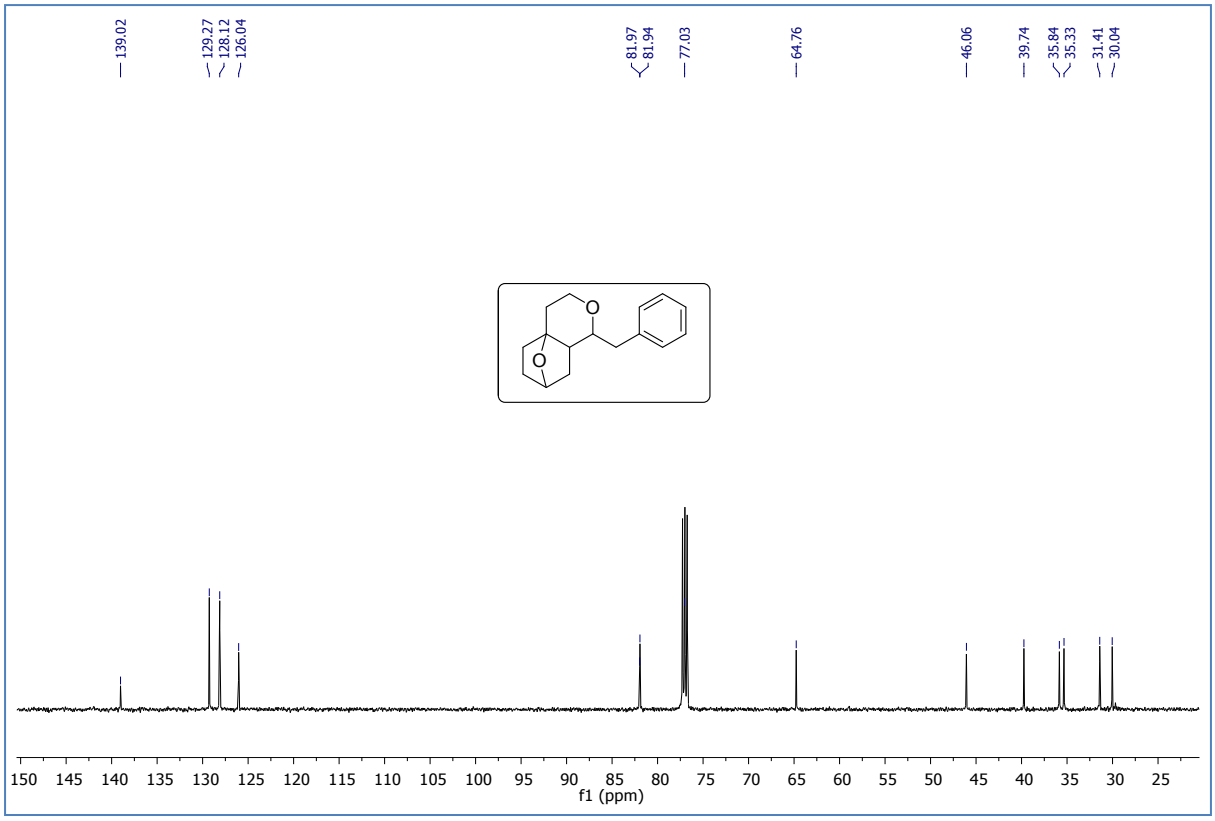

**$^{13}$C NMR (125 MHz, $CDCl_3$) spectrum of compound 3m**



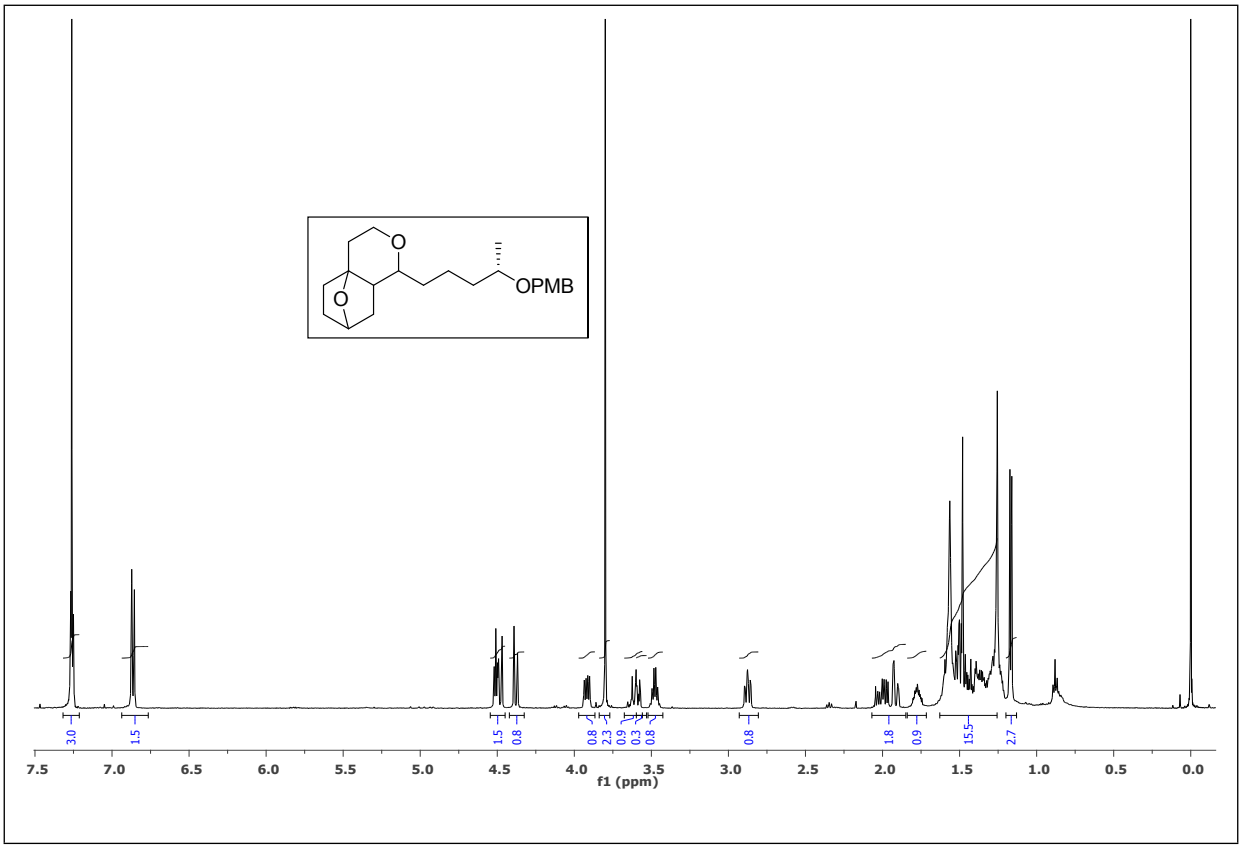

**$^{1}$H NMR (500 MHz, $CDCl_3$) spectrum of compound 3n**



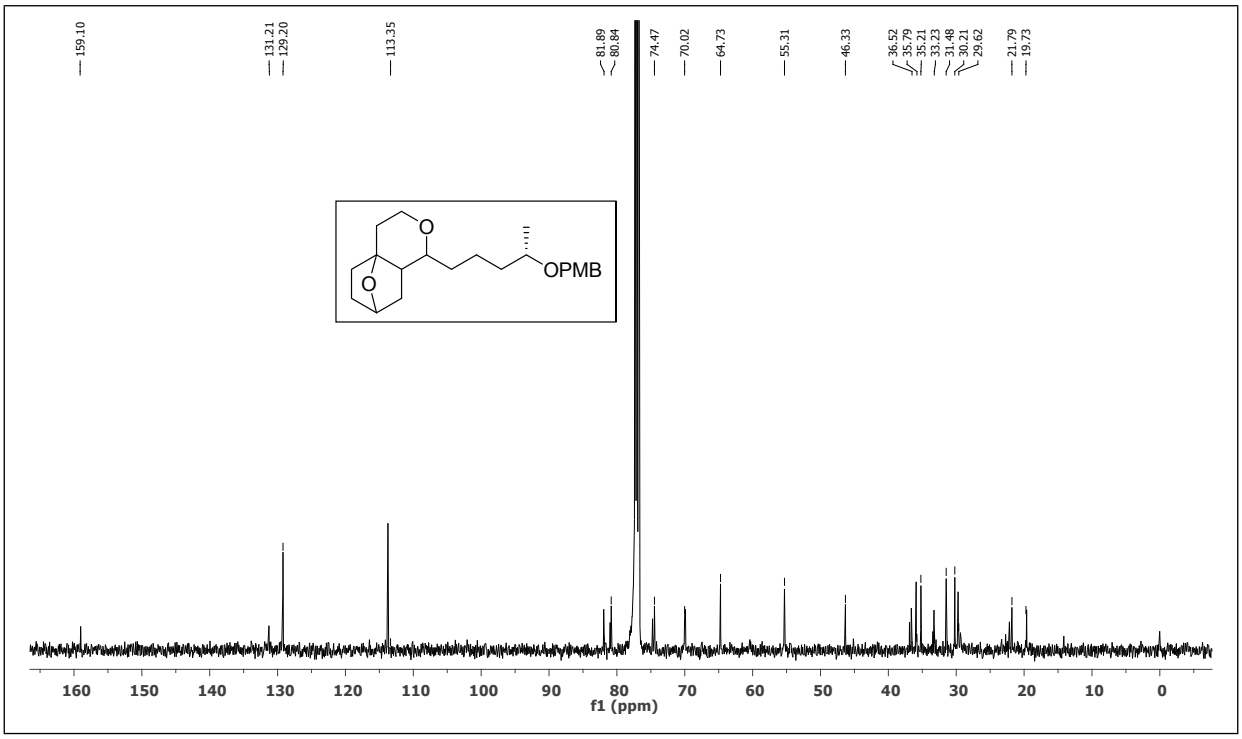

**$^{13}$C NMR (125 MHz, $CDCl_3$) spectrum of compound 3n**



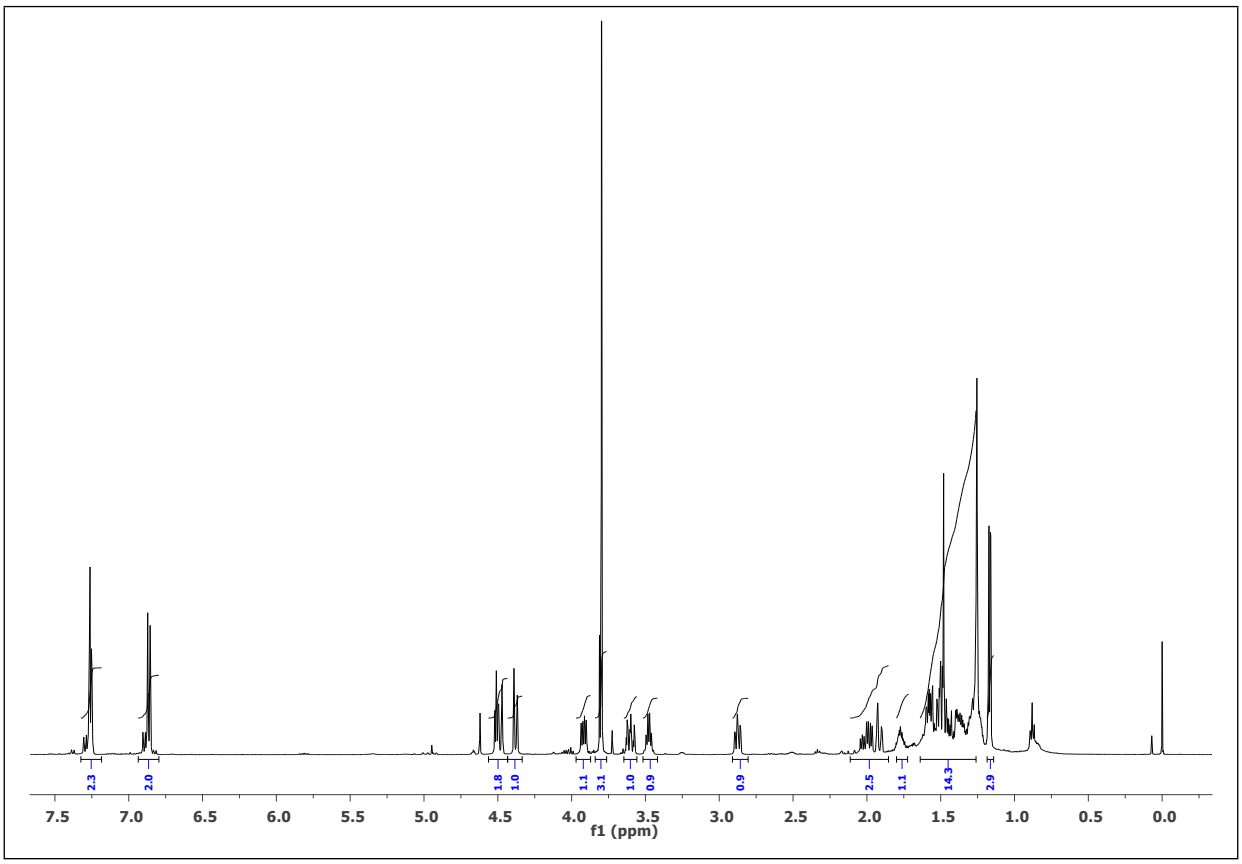

**$^1$H NMR (500 MHz, $CDCl_3$) spectrum of compound 3o**



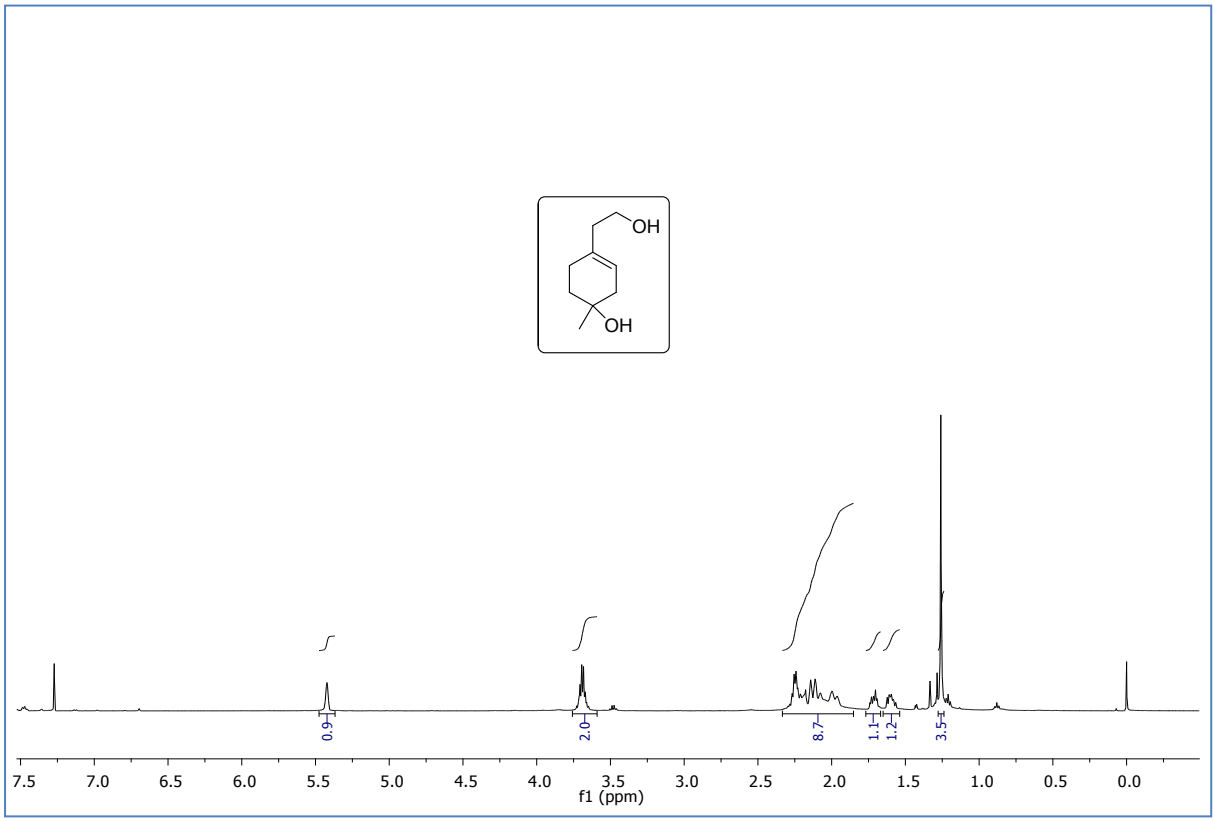
## $^{13}C$ NMR (125 MHz, $CDCl_3$) spectrum of compound 3o



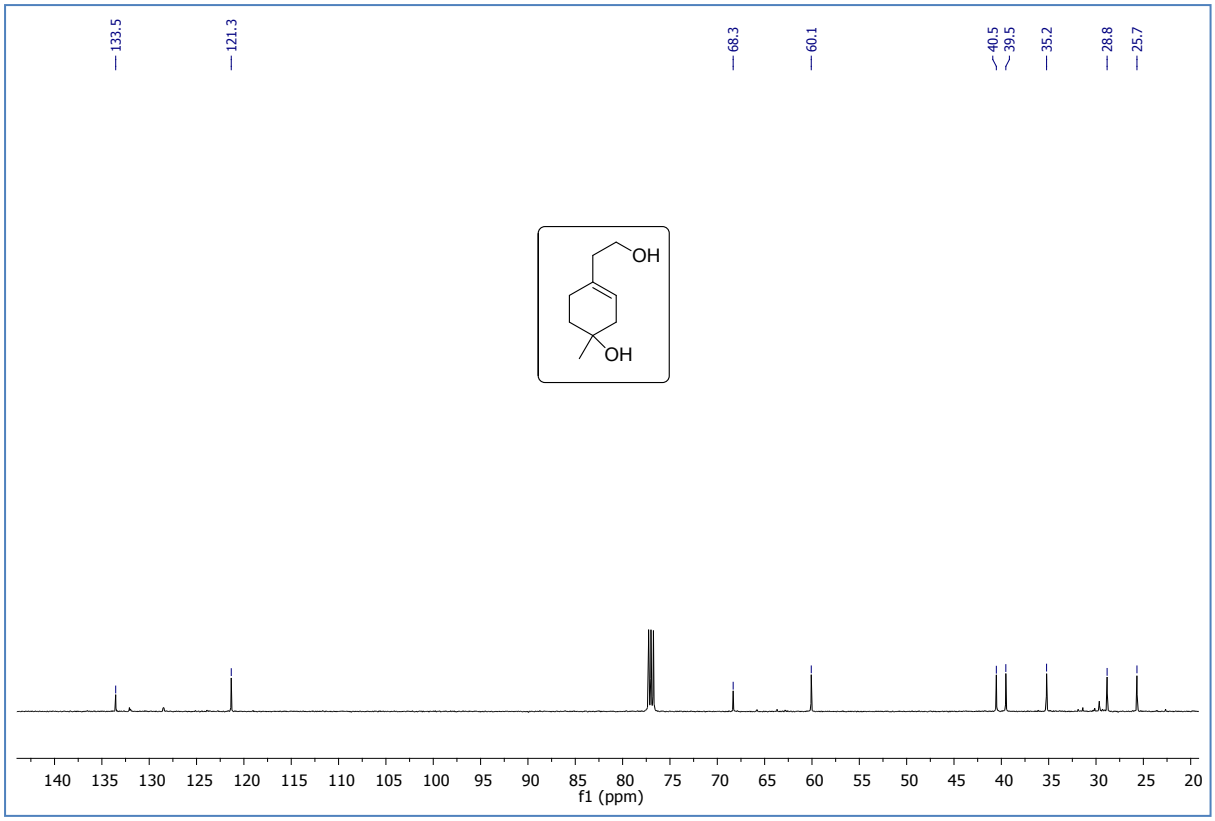

## $^{1}H$ NMR (500 MHz, $CDCl_3$) spectrum of compound 3o



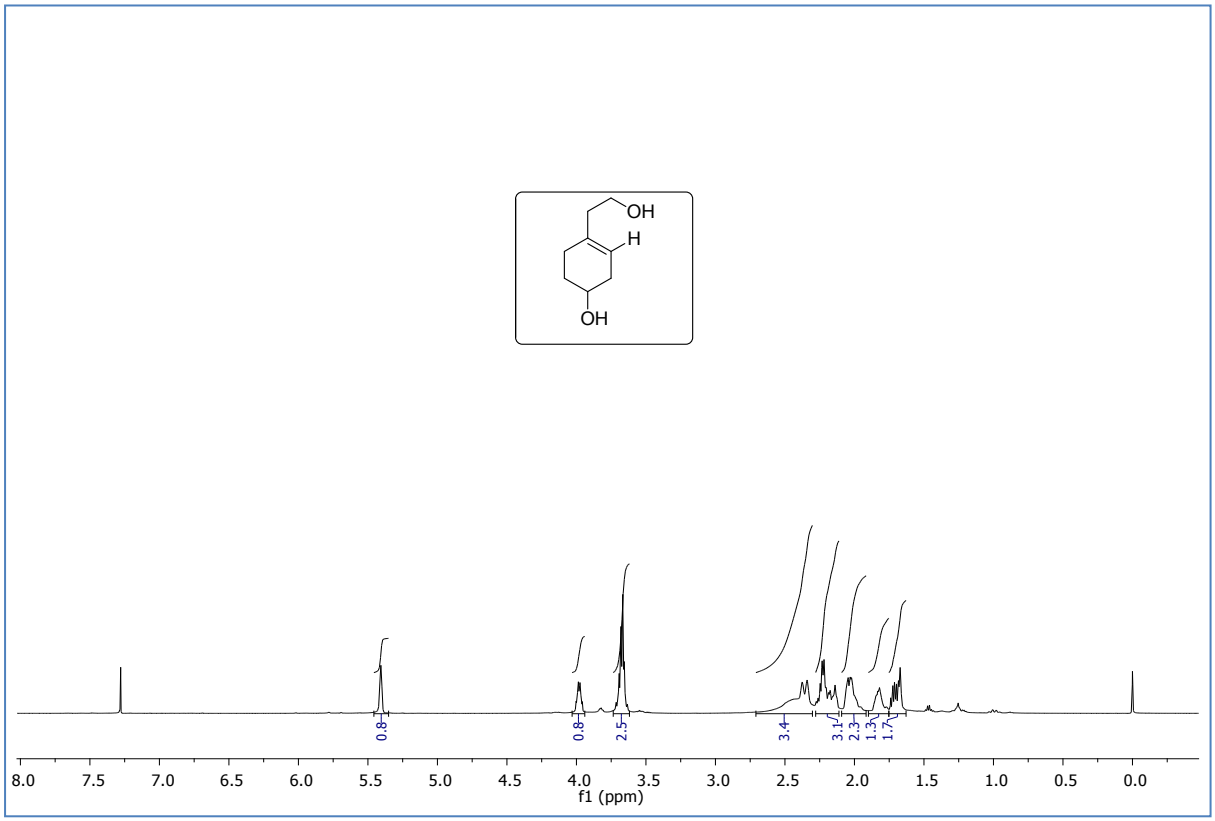
**$^{1}$H NMR (500 MHz, $CDCl_3$) spectrum of compound 1a**



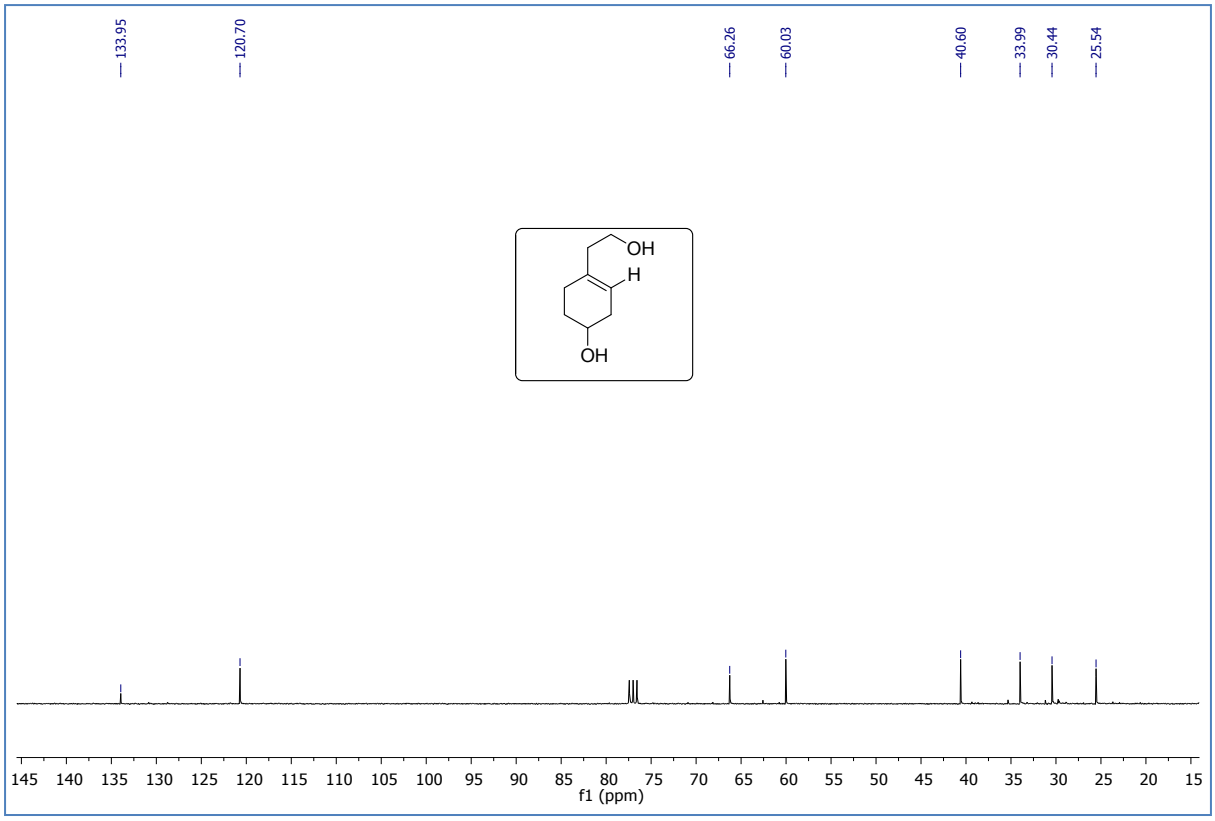

**$^{13}$C NMR (125 MHz, $CDCl_3$) spectrum of compound 1a**




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




**$^{13}$C NMR (125 MHz, $CDCl_3$) spectrum of compound 1b**


133.95
120.70
66.26
60.03
40.60
33.99
30.44
25.54
OH
H
OH
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15
f1 (ppm)