Supporting Information For:

Catalytic Hydroxylcyclopropanol Ring-Opening Carbonylative Lactonization to Fused Bicyclic Lactones

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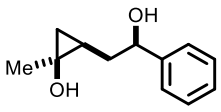
Part 1. Experimental procedures and spectra data.

General Methods: Reactions were performed using standard syringe techniques under argon unless stated otherwise. Starting materials and reagents were used as received from suppliers. Acetonitrile (CH_3CN), dichloromethane (CH_2Cl_2), methanol (MeOH), tetrahydrofuran (THF), and toluene were purified by passing the previously degassed solvents through activated alumina columns. 1,2-Dichloroethane (DCE) was purified by distillation over calcium hydride. Benzoquinone was purified by recrystallization from hexanes. Flash chromatography was performed using silica gel (230-400 mesh). Thin layer chromatography (TLC) was performed using glass-backed silica plates (Silicycle). NMR spectra were recorded on a Bruker ARX-400 spectrometer or AV-500 spectrometer at room temperature. Chemical shifts (in ppm) are given in reference to the solvent signal [^{1}H NMR: $CDCl_3$ (7.26); ^{13}C NMR: $CDCl_3$ (77.2)]. 1H NMR data are reported as follows: chemical shifts (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintuplet, m = multiplet, br = broad), coupling constant (Hz), and integration. ^{13}C NMR data are reported in terms of chemical shift and multiplicity. High-resolution mass measurements for compound characterization were carried out using a Waters SYNAPT G2-Si system with QuanTof analyzer or an Agilent 6550 QTOF system. IR data were recorded on a Thermo Nicolet Nexus 470 FTIR.

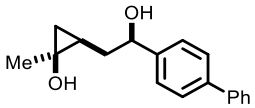
General procedure for the synthesis of cyclopropanols:[1]

A solution of titanium(IV) isopropoxide (1.1 equiv.) and the allyl alcohol (1.0 equiv.) in toluene (0.5 M) was stirred at room temperature for 1 h, then at 40 °C using an oil bath for 10 min. After volatile components were removed under vacuum, THF (0.1 M) and the corresponding ester (1.0 equiv.) were added at room temperature, followed by a solution of cyclopentylmagnesium chloride (2 M, 4.4 equiv.) in tetrahydrofuran, over a period of 1 h (with a syringe pump). The reaction mixture was then stirred for an additional 30 min before it was quenched by addition of water (1 ml/1 mmol alcohol). The resulting mixture was stirred for 1 h, dried over anhydrous sodium sulfate, and filtered. The filter cake was washed with CH_2Cl_2. The combined filtrates were concentrated under reduced pressure. The resulting residue was purified by flash chromatography.

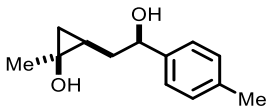


15a: 692 mg; 72%; pale yellow oil; purified by column chromatography (hexane/Et_2O = 2/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.40 – 7.34 (m, 4H), 7.28 – 7.25 (m, 1H), 4.91 (dd, J = 5.2, 4.1 Hz, 1H), 2.92 (s, 2H), 2.25 – 2.22 (m, 1H), 1.87 – 1.81 (m, 1H), 1.30 (s, 3H), 0.56 – 0.52 (m, 1H), 0.42 – 0.38 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 144.2, 128.3, 127.4, 125.9, 73.6, 54.5, 37.5, 25.8, 20.3, 20.0. **IR** (neat, cm^{-1}): v = 3308,

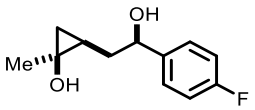
2952, 2916, 1451, 1377, 1270, 1045, 758, 699. **HRMS** (ESI): *m/z* 175.1117 calc. for $C_{12}H_{15}O^+$ [M+H-H_2O]$^+$, found 175.1119.



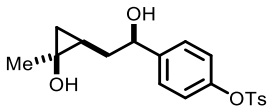
15b: 130 mg; 27% yield; white solid; purified by column chromatography (hexane/Et_2O = 2/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.67 – 7.55 (m, 4H), 7.47 – 7.40 (m, 4H), 7.39 – 7.31 (m, 1H), 5.00 (t, *J* = 4.6 Hz, 1H), 2.28 (dt, *J* = 14.6, 4.1 Hz, 1H), 1.92 (ddd, *J* = 14.5, 10.0, 5.4 Hz, 1H), 1.36 (s, 3H), 0.59 (dd, *J* = 9.0, 4.7 Hz, 1H), 0.54 – 0.39 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 143.1, 140.8, 140.2, 128.8, 127.3, 127.1, 127.0, 126.2, 73.4, 54.5, 37.3, 25.7, 20.2, 20.0. **IR** (neat, cm^{-1}): *v* = 3316, 3028, 2953, 2916, 1601, 1488, 1446, 1406, 1376, 1269, 1049, 1008, 971, 842, 765, 737, 697. **HRMS** (ESI): *m/z* 291.1356 calc. for $C_{18}H_{20}NaO_2^+$ [M+Na]$^+$, found 291.1355.



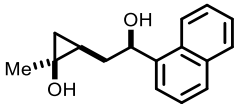
15c: 150 mg; 39%; colorless liquid; purified by column chromatography (hexane/Et_2O = 2/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.0 Hz, 2H), 7.18 – 7.13 (m, 2H), 4.90 – 4.81 (m, 1H), 3.08 (s, 2H), 2.35 (s, 3H), 2.20 (dt, *J* = 14.4, 4.0 Hz, 1H), 1.86 – 1.78 (m, 1H), 1.30 (s, 3H), 0.53 (q, *J* = 4.3 Hz, 1H), 0.46 – 0.35 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 141.0, 136.9, 128.9, 125.7, 73.4, 54.3, 37.4, 25.7, 21.1, 20.3, 19.8. **IR** (neat, cm^{-1}): *v* = 3358, 2922, 1717, 1445, 1409, 1376, 1270, 1179, 1047, 1020, 972, 815. **HRMS** (ESI): *m/z* 189.1274 calc. for $C_{13}H_{17}O^+$ [M+H-H_2O]$^+$, found 189.1275.



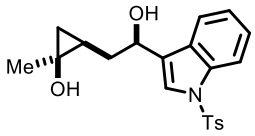
15d: 240 mg; 51%; colorless liquid; purified by column chromatography (hexane/Et_2O = 2/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.34 – 7.26 (m, 2H), 7.06 – 6.88 (m, 2H), 4.87 (t, *J* = 4.5 Hz, 1H), 3.80 – 3.68 (m, 1H), 3.68 – 3.53 (m, 1H), 2.16 (dt, *J* = 14.4, 4.1 Hz, 1H), 1.80 (ddd, *J* = 14.6, 9.9, 5.0 Hz, 1H), 1.30 (s, 3H), 0.53 (dd, *J* = 9.1, 4.9 Hz, 1H), 0.43 – 0.24 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 161.9 (d, *J* = 274 Hz), 139.8 (d, *J* = 3 Hz), 127.2 (d, *J* = 9 Hz), 114.9 (d, *J* = 21 Hz), 72.5, 54.3, 37.4, 25.6, 20.0, 19.9. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -116.8. **IR** (neat, cm^{-1}): *v* = 3330, 2951, 2868, 1603, 1508, 1270, 1220, 1156, 1049, 1014, 835. **HRMS** (ESI): *m/z* 193.1023 calc. for $C_{12}H_{14}FO^+$ [M+H-H_2O]$^+$, found 193.1025.



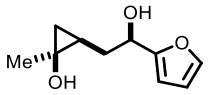
15e: 430 mg; 29%; colorless solid; purified by column chromatography (hexane/Et_2O = 2/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.73 – 7.54 (m, 2H), 7.34 – 7.23 (m, 4H), 7.02 – 6.91 (m, 2H), 4.89 (t, *J* = 4.5 Hz, 1H), 3.25 (s, 1H), 2.94 (s, 1H), 2.44 (s, 3H), 2.17 (dt, *J* = 14.6, 4.2 Hz, 1H), 1.81 (ddd, *J* = 14.9, 10.3, 5.0 Hz, 1H), 1.29 (s, 3H), 0.55 (dd, *J* = 9.3, 5.2 Hz, 1H), 0.38 (t, *J* = 5.8 Hz, 1H), 0.35 – 0.24 (m, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 148.5, 145.4, 143.2, 132.4, 129.8, 128.5, 126.9, 122.1, 72.6, 54.4, 37.3, 25.6, 21.7, 20.0, 19.9. **IR** (neat, cm^{-1}): *v* = 3324, 2922, 1597, 1500, 1370, 1197, 1174, 1152, 1093, 865, 815, 663, 552. **HRMS** (ESI): *m/z* 385.1080 calc. for $C_{19}H_{22}NaO_5S^+$ $[M+Na]^+$, found 385.1080.



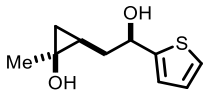
15f: 480 mg; 31%; white solid; purified by column chromatography (hexane/Et_2O = 2/1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.1 Hz, 1H), 7.89 (dd, *J* = 7.6, 2.1 Hz, 1H), 7.77 (dd, *J* = 20.1, 7.6 Hz, 2H), 7.51 (ddd, *J* = 9.7, 5.4, 2.9 Hz, 3H), 5.77 (t, *J* = 4.5 Hz, 1H), 3.00 (s, 1H), 2.77 (s, 1H), 2.49 (dt, *J* = 14.5, 4.1 Hz, 1H), 2.04 (ddd, *J* = 14.9, 10.5, 4.8 Hz, 1H), 1.32 (s, 3H), 0.52 (dd, *J* = 9.4, 5.1 Hz, 1H), 0.42 (t, *J* = 5.7 Hz, 1H), 0.35 (dd, *J* = 9.7, 6.2 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 139.4, 133.7, 130.0, 129.0, 127.8, 126.0, 125.6, 125.2, 123.2, 122.9, 70.1, 54.5, 36.0, 25.7, 20.5, 20.1. **IR** (neat, cm^{-1}): *v* = 3297, 2952, 2923, 1444, 1376, 1263, 1052, 1017, 963, 791, 776. **HRMS** (ESI): *m/z* 265.1199 calc. for $C_{16}H_{18}NaO_2^+$ $[M+Na]^+$, found 265.1202.



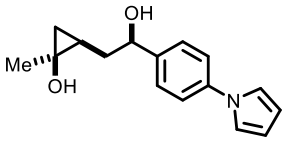
15g: 410 mg; 40%; white solid; purified by column chromatography (hexane/Et_2O = 2/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.3 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.61 – 7.51 (m, 2H), 7.36 – 7.29 (m, 1H), 7.27 – 7.15 (m, 3H), 5.18 (t, *J* = 4.3 Hz, 1H), 2.88 (s, 2H), 2.42 – 2.27 (m, 4H), 2.01 – 1.92 (m, 1H), 1.34 (s, 3H), 0.55 (dd, *J* = 9.2, 5.1 Hz, 1H), 0.47 – 0.33 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 145.1, 135.8, 135.4, 130.0, 128.7, 127.0, 126.1, 125.0, 123.3, 123.1, 120.1, 114.0, 67.8, 54.7, 35.3, 25.9, 21.7, 20.4, 20.2. **IR** (neat, cm^{-1}): *v* = 3320, 2968, 2922, 1447, 1367, 1271, 1173, 1121, 748, 665, 591, 572. **HRMS** (ESI): *m/z* 408.1240 calc. for $C_{21}H_{23}NO_4SNa^+$ $[M+Na]^+$, found 408.1240.



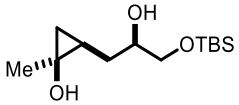
15h: 313 mg; 31%; colorless oil; purified by column chromatography (hexane/Et_2O = 2/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 1.8, 0.9 Hz, 1H), 6.35 (dd, *J* = 3.2, 1.8 Hz, 1H), 6.28 (dt, *J* = 3.3, 0.8 Hz, 1H), 4.88 (ddd, *J* = 5.3, 4.4, 0.8 Hz, 1H), 2.79 (s, 2H), 2.29 (dt, *J* = 14.3, 4.4 Hz, 1H), 1.98 – 1.79 (m, 1H), 1.33 (d, *J* = 0.7 Hz, 3H), 0.73 – 0.53 (m, 2H), 0.44 (ddd, *J* = 5.4, 4.5, 0.8 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 156.8, 141.8, 110.4, 106.0, 68.0, 54.7, 34.4, 25.8, 20.7, 20.1. **IR** (neat, cm^{-1}): *v* = 3319, 2955, 2923, 1445, 1376, 1266, 1149, 1055, 1008, 738. **HRMS** (ESI): *m/z* 205.0835 calc. for $C_{10}H_{14}O_3Na^+$ $[M+Na]^+$, found 205.0836.



15i: 345 mg; 40%; colorless oil; purified by column chromatography (hexane/Et_2O = 2/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.23 (dd, *J* = 4.8, 1.4 Hz, 1H), 7.00 – 6.98 (m, 2H), 5.17 (t, *J* = 4.4 Hz, 1H), 3.01 (s, 2H), 2.29 – 2.24 (m, 1H), 1.95 – 1.89 (m, 1H), 1.36 (s, 3H), 0.63 – 0.60 (m, 2H), 0.46 – 0.44 (m, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 148.5, 126.8, 124.2, 123.3, 70.3, 54.7, 37.8, 25.8, 20.4, 20.1. **IR** (neat, cm^{-1}): *v* = 3307, 2954, 2916, 1444, 1376, 1266, 1034, 963, 697. **HRMS** (ESI): *m/z* 181.0682 calc. for $C_{10}H_{13}OS^+$ $[M+H-H_2O]^+$, found 181.0679.

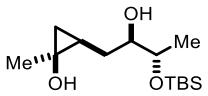


15j: 236 mg; 34%; white solid; purified by column chromatography (hexane/Et_2O = 2/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.46 – 7.35 (m, 4H), 7.09 (t, *J* = 2.2 Hz, 2H), 6.35 (t, *J* = 2.2 Hz, 2H), 4.96 (t, *J* = 4.5 Hz, 1H), 3.14 (s, 2H), 2.24 (dt, *J* = 14.6, 4.1 Hz, 1H), 1.89 (ddd, *J* = 14.6, 9.8, 5.1 Hz, 1H), 1.35 (s, 3H), 0.63 – 0.53 (m, 1H), 0.47 – 0.38 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 141.5, 139.8, 126.9, 120.2, 119.3, 110.4, 72.9, 54.4, 37.3, 25.7, 20.1. **IR** (neat, cm^{-1}): *v* = 3305, 2916, 1521, 1327, 1270, 1070, 1049, 1019, 723. **HRMS** (ESI): *m/z* 258.1489 calc. for $C_{16}H_{20}NO_2^+$ $[M+H]^+$, found 258.1490.

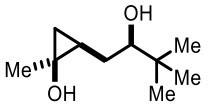


15k: 98 mg; 28%; colorless liquid; purified by column chromatography (hexane/Et_2O = 2/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 3.79 – 3.74 (m, 1H), 3.68 – 3.59 (m, 2H), 2.84 (s, 1H), 1.94 (dt, *J* = 14.7, 4.1 Hz, 1H), 1.60

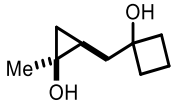
– 1.55 (m, 1H), 1.36 (d, J = 0.7 Hz, 3H), 0.89 (s, 9H), 0.59 (dd, J = 4.0, 2.2 Hz, 2H), 0.39 (dt, J = 4.2, 2.5 Hz, 1H), 0.08 (d, J = 2.1 Hz, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 71.5, 66.1, 54.0, 31.0, 25.9 (2C), 20.5, 20.3, 18.3, -5.3, -5.4. **IR** (neat, cm^{-1}): v = 3320, 2929, 2162, 2021, 2001, 1978, 1955, 837, 549, 469. **HRMS** (ESI): *m/z* 243.1775 calc. for $C_{13}H_{27}O_2Si^+$ $[M+H-H_2O]^+$, found 243.1774.



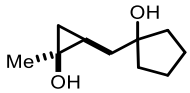
15l: 224 mg; 21%; colorless oil; purified by column chromatography (hexane/Et_2O = 2/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 3.86 – 3.82 (m, 1H), 3.61 – 3.58 (m, 1H), 1.86 (ddd, J = 14.6, 6.4, 5.1 Hz, 1H), 1.55 (ddd, J = 14.4, 9.1, 4.8 Hz, 1H), 1.41 (s, 3H), 1.15 (d, J = 6.3 Hz, 3H), 0.89 (s, 9H), 0.76 (tdd, J = 9.2, 6.2, 5.1 Hz, 1H), 0.62 (dd, J = 9.3, 5.3 Hz, 1H), 0.41 (t, J = 5.8 Hz, 1H), 0.08 (s, 3H), 0.08 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 75.4, 71.1, 54.8, 30.4, 26.1, 26.0, 21.3, 19.9, 18.2, -4.2, -4.7. **IR** (neat, cm^{-1}): v = 3318, 2955, 2929, 2858, 1463, 1374, 1256, 1086, 967, 834, 775. **HRMS** (ESI): *m/z* 297.1856 calc. for $C_{14}H_{30}O_3NaSi^+$ $[M+Na]^+$, found 297.1857.



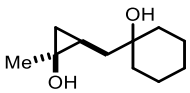
15m: 208 mg; 23%; white solid; purified by column chromatography (hexane/Et_2O = 2/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 3.36 (dd, J = 9.1, 2.6 Hz, 1H), 2.09 (s, 1H), 1.83 (s, 1H), 1.74 (ddd, J = 14.6, 8.1, 2.6 Hz, 1H), 1.62 (dd, J = 9.0, 5.7 Hz, 1H), 1.43 (d, J = 0.7 Hz, 3H), 0.93 (s, 9H), 0.85 – 0.77 (m, 1H), 0.66 (dd, J = 9.2, 5.2 Hz, 1H), 0.44 (t, J = 5.7 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 80.2, 54.5, 35.1, 30.4, 26.0, 25.9, 22.5, 19.9. **IR** (neat, cm^{-1}): v = 3340, 2954, 2869, 1363, 1259, 1238, 1091, 1075, 1028, 1018, 1007, 991, 957, 871. **HRMS** (ESI): *m/z* 155.1430 calc. for $C_{10}H_{19}O^+$ $[M+H-H_2O]^+$, found 155.1432.



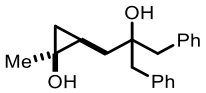
15n: 436 mg; 42%; colorless liquid; purified by column chromatography (hexane/Et_2O = 2/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 3.60 (s, 1H), 2.88 (s, 1H), 2.26 – 2.12 (m, 2H), 2.10 – 1.95 (m, 3H), 1.75 – 1.66 (m, 1H), 1.56 – 1.47 (m, 2H), 1.36 (d, J = 0.6 Hz, 3H), 0.75 – 0.67 (m, 1H), 0.64 (dd, J = 9.2, 5.0 Hz, 1H), 0.48 – 0.40 (m, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 75.1, 54.2, 37.8, 37.6, 35.5, 25.9, 20.4, 20.1, 12.0. **IR** (neat, cm^{-1}): v = 3346, 2933, 1371, 1272, 1244, 1165, 1111, 1020, 956. **HRMS** (ESI): *m/z* 139.1117 calc. for $C_9H_{15}O^+$ $[M+H-H_2O]^+$, found 139.1118.



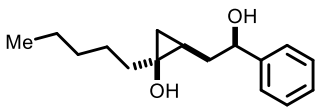
15o: 421 mg; 52%; colorless oil; purified by column chromatography (hexane/Et_2O = 2/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.70 (s, 2H), 1.92 (dd, *J* = 14.6, 4.3 Hz, 1H), 1.82 – 1.76 (m, 2H), 1.73 – 1.55 (m, 7H), 1.39 (s, 3H), 0.76 – 0.71 (m, 1H), 0.64 (dd, *J* = 9.2, 5.1 Hz, 1H), 0.41 (t, *J* = 5.6 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 83.0, 54.3, 41.2, 40.0, 38.8, 26.2, 23.8, 23.6, 21.7, 20.6. **IR** (neat, cm^{-1}): *v* = 3319, 2956, 2873, 1445, 1375, 1272, 1016, 958. **HRMS** (ESI): *m/z* 153.1274 calc. for $C_{10}H_{17}O^+$ $[M+H-H_2O]^+$, found 153.1273.



15p: 309 mg; 26%; colorless liquid; purified by column chromatography (hexane/Et_2O = 2/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.24 (s, 1H), 2.60 (s, 1H), 1.99 (dd, *J* = 14.8, 4.4 Hz, 1H), 1.65 – 1.57 (m, 1H), 1.57 – 1.38 (m, 8H), 1.38 – 1.24 (m, 5H), 0.68 (dddd, *J* = 10.6, 9.2, 6.1, 4.4 Hz, 1H), 0.59 (dd, *J* = 9.3, 5.0 Hz, 1H), 0.37 (t, *J* = 5.5 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 72.0, 54.0, 40.3, 39.4, 36.1, 26.0, 25.8, 22.7, 22.3, 20.6, 20.0. **IR** (neat, cm^{-1}): *v* = 3342, 2928, 2858, 1447, 1375, 1273, 1162, 1047, 966. **HRMS** (ESI): *m/z* 207.1356 calc. for $C_{11}H_{20}NaO_2^+$ $[M+Na]^+$, found 207.1357.

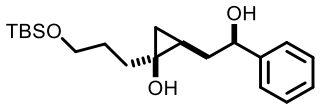


15q: 124 mg; 14%; white solid; purified by column chromatography (hexane/Et_2O = 2/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.39 – 7.10 (m, 10H), 3.03 (d, *J* = 13.6 Hz, 1H), 2.87 (d, *J* = 13.5 Hz, 1H), 2.74 (q, *J* = 13.7 Hz, 2H), 1.95 (dd, *J* = 14.8, 4.3 Hz, 1H), 1.43 (dd, *J* = 14.9, 10.5 Hz, 1H), 1.39 (d, *J* = 0.6 Hz, 3H), 0.77 (dddd, *J* = 10.5, 9.2, 6.1, 4.3 Hz, 1H), 0.63 (dd, *J* = 9.2, 5.1 Hz, 1H), 0.33 (t, *J* = 5.7 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 137.4, 137.1, 130.7, 128.4, 128.1, 126.7, 126.5, 74.5, 54.3, 46.7, 45.4, 38.1, 26.0, 20.6, 20.5. **IR** (neat, cm^{-1}): *v* = 3466, 3028, 2924, 1495, 1454, 1243, 1031, 753, 701. **HRMS** (ESI): *m/z* 319.1669 calc. for $C_{20}H_{24}NaO_2^+$ $[M+Na]^+$, found 319.1669.

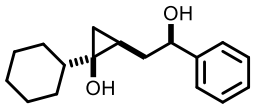


15r: 494 mg; 59%; colorless oil; purified by column chromatography (hexane/Et_2O = 2/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.40 – 7.34 (m, 4H), 7.28 – 7.25 (m, 1H), 4.92 (t, *J* = 4.7 Hz, 1H), 2.80 (s, 2H), 2.23 (dt, *J* = 14.5, 4.3 Hz, 1H), 1.89 (ddd, *J* = 14.5, 10.0, 5.3 Hz, 1H), 1.56 – 1.49 (m, 1H), 1.48 – 1.40 (m, 2H), 1.36 – 1.23 (m, 5H), 0.89 (t, *J* = 7.0 Hz, 3H), 0.55 (dd, *J* = 9.2, 5.0 Hz, 1H), 0.49 – 0.42 (m, 1H), 0.37 (t, *J* = 5.5

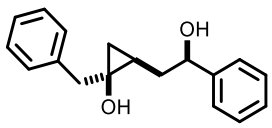
Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 144.2, 128.4, 127.3, 125.9, 73.6, 58.2, 39.5, 37.3, 32.1, 25.4, 22.8, 19.4, 19.1, 14.2. **IR** (neat, cm^{-1}): *v* = 3318, 2954, 2929, 1452, 1249, 1044, 700. **HRMS** (ESI): *m/z* 271.1669 calc. for $C_{16}H_{24}O_2Na^+$ $[M+Na]^+$, found 271.1670.



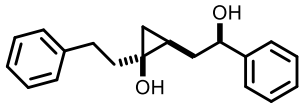
15s: 614 mg; 35%; colorless oil; purified by column chromatography (hexane/Et_2O = 2/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.43 – 7.31 (m, 4H), 7.26 – 7.21 (m, 1H), 4.92 (t, *J* = 4.6 Hz, 1H), 3.79 – 3.63 (m, 2H), 2.22 (dt, *J* = 14.6, 4.6 Hz, 1H), 2.02 – 1.88 (m, 1H), 1.84 – 1.76 (m, 1H), 1.76 – 1.69 (m, 2H), 1.39 – 1.31 (m, 1H), 0.91 (s, 9H), 0.55 (dd, *J* = 9.2, 4.9 Hz, 1H), 0.47 – 0.40 (m, 1H), 0.41 – 0.32 (m, 1H), 0.09 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 144.8, 128.2, 127.0, 125.9, 73.4, 64.0, 57.8, 37.5, 37.4, 29.7, 26.1, 19.7, 19.0, 18.5, -5.2, -5.3. **IR** (neat, cm^{-1}): *v* = 3325, 2952, 2928, 2856, 1471, 1451, 1255, 1096, 1043, 1004, 835, 776, 80. **HRMS** (ESI): *m/z* 351.2350 calc. for $C_{20}H_{35}O_3Si^+$ $[M+H]^+$, found 351.2351.



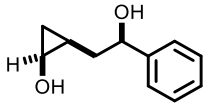
15t: 505 mg; 29%; colorless solid; purified by column chromatography (hexane/Et_2O = 2/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.43 – 7.31 (m, 4H), 7.29 – 7.23 (m, 1H), 4.91 (t, *J* = 4.9 Hz, 1H), 2.33 – 2.19 (m, 3H), 1.96 – 1.88 (m, 1H), 1.80 – 1.72 (m, 3H), 1.68 – 1.59 (m, 2H), 1.23 – 1.09 (m, 5H), 0.86 – 0.78 (m, 1H), 0.60 – 0.46 (m, 2H), 0.32 (d, *J* = 3.0 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 144.3, 128.4, 127.3, 125.8, 73.6, 62.0, 46.2, 37.3, 28.8, 28.7, 26.6, 26.5, 18.7, 18.3. **IR** (neat, cm^{-1}): *v* = 3332, 2925, 2852, 1450, 1260, 1046, 755, 701. **HRMS** (ESI): *m/z* 283.1669 calc. for $C_{17}H_{24}NaO_2^+$ $[M+Na]^+$, found 283.1668.



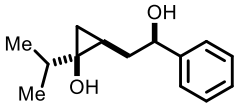
15u: 473 mg; 52%; colorless oil; purified by column chromatography (hexane/Et_2O = 2/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.38 – 7.22 (m, 10H), 4.87 (t, *J* = 4.8 Hz, 1H), 2.87 (d, *J* = 14.1 Hz, 1H), 2.76 (d, *J* = 14.0 Hz, 1H), 2.35 (s, 2H), 2.23 (dt, *J* = 14.6, 4.5 Hz, 1H), 1.90 (ddd, *J* = 14.8, 10.0, 5.1 Hz, 1H), 0.75 (dd, *J* = 9.4, 5.2 Hz, 1H), 0.68 – 0.61 (m, 1H), 0.46 (t, *J* = 5.3 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 144.1, 138.7, 129.7, 128.5, 128.4, 127.4, 126.6, 125.8, 73.5, 58.5, 45.1, 37.2, 19.0, 18.9. **IR** (neat, cm^{-1}): *v* = 3346, 2923, 1495, 1453, 1046, 1030, 755, 701. **HRMS** (ESI): *m/z* 291.1356 calc. for $C_{18}H_{20}O_2Na^+$ $[M+Na]^+$, found 291.1355.



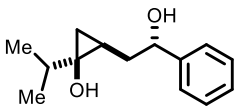
15v: 577 mg; 66%; colorless liquid; purified by column chromatography (hexane/Et_2O = 2/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.41 – 7.32 (m, 4H), 7.32 – 7.26 (m, 3H), 7.19 (d, *J* = 7.2 Hz, 3H), 4.95 (t, *J* = 4.7 Hz, 1H), 2.90 – 2.70 (m, 3H), 2.62 (d, *J* = 49.9 Hz, 1H), 2.27 – 2.15 (m, 1H), 1.94 – 1.80 (m, 2H), 1.65 – 1.61 (m, 1H), 0.58 (dd, *J* = 9.2, 5.0 Hz, 1H), 0.53 – 0.43 (m, 1H), 0.42 (ddd, *J* = 6.2, 4.9, 1.4 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 143.9, 142.6, 128.4, 128.4, 128.3, 127.3, 125.7, 125.7, 73.5, 57.8, 41.8, 37.1, 32.2, 19.6, 19.1. **IR** (neat, cm^{-1}): *v* = 3338, 3026, 2917, 1712, 1495, 1248, 1044, 749, 698. **HRMS** (ESI): *m/z* 305.1512 calc. for $C_{19}H_{22}NaO_2^+$ $[M+Na]^+$, found 305.1511.



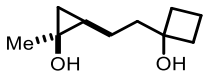
15w: 98 mg; 20%; colorless liquid; purified by column chromatography (hexane/Et_2O = 2/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.5 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.30 – 7.25 (m, 1H), 4.95 (t, *J* = 4.8 Hz, 1H), 3.39 (td, *J* = 6.5, 3.2 Hz, 1H), 2.96 (s, 2H), 2.23 (dt, *J* = 14.4, 4.4 Hz, 1H), 1.87 (ddd, *J* = 14.9, 10.2, 5.1 Hz, 1H), 0.65 (dt, *J* = 9.4, 5.9 Hz, 1H), 0.55 – 0.45 (m, 1H), 0.27 (td, *J* = 6.1, 3.2 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 143.9, 128.3, 127.4, 125.7, 73.7, 49.1, 36.0, 13.5, 13.2. **IR** (neat, cm^{-1}): *v* = 3317, 3027, 2920, 1452, 1324, 1215, 1040, 755, 701. **HRMS** (ESI): *m/z* 177.0910 calc. for $C_{11}H_{13}O_2^+$ $[M-H]^+$, found 177.0890.



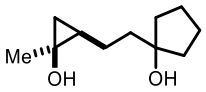
15x: 671 mg; 45%; colorless solid; purified by column chromatography (hexane/Et_2O = 2/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.2 Hz, 2H), 7.36 (dd, *J* = 8.4, 6.7 Hz, 2H), 7.30 – 7.23 (m, 1H), 4.93 (t, *J* = 4.8 Hz, 1H), 2.25 (dt, *J* = 14.6, 4.2 Hz, 1H), 2.01 – 1.86 (m, 1H), 1.17 (p, *J* = 6.8 Hz, 1H), 0.98 (d, *J* = 6.8 Hz, 3H), 0.95 (d, *J* = 6.8 Hz, 3H), 0.65 – 0.48 (m, 2H), 0.35 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 144.2, 128.4, 127.3, 125.8, 73.5, 62.4, 37.3, 36.2, 19.2, 18.6, 18.4, 18.3. **IR** (neat, cm^{-1}): *v* = 3331, 2961, 2872, 1451, 1269, 1045, 993, 702. **HRMS** (ESI): *m/z* 203.1430 calc. for $C_{14}H_{19}O^+$ $[M+H-H_2O]^+$, found 203.1431. (Note: **15x** and **15y** were produced from the same reaction.)



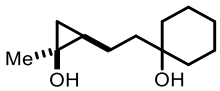
15y: 290 mg; 20%; colorless solid; purified by column chromatography (hexane/Et_2O = 2/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.38 – 7.31 (m, 4H), 7.30 – 7.26 (m, 1H), 4.78 (dd, *J* = 10.5, 2.3 Hz, 1H), 2.17 (ddd, *J* = 14.9, 4.2, 2.3 Hz, 1H), 1.69 (dt, *J* = 14.9, 10.5 Hz, 1H), 1.25 (s, 1H), 1.19 (h, *J* = 7.0 Hz, 1H), 1.06 (d, *J* = 6.8 Hz, 3H), 1.03 (d, *J* = 6.9 Hz, 3H), 0.84 (tdd, *J* = 10.1, 6.0, 4.1 Hz, 1H), 0.63 (dd, *J* = 9.3, 5.3 Hz, 1H), 0.40 (t, *J* = 5.7 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 145.2, 128.7, 127.7, 125.7, 75.5, 62.0, 39.0, 36.8, 22.9, 19.4, 18.3, 18.2. **IR** (neat, cm^{-1}): *v* = 3338, 2962, 2930, 1970, 1451, 1270, 1061, 1003, 754, 700. **HRMS** (ESI): *m/z* 203.1430 calc. for $C_{14}H_{19}O^+$ $[M+H-H_2O]^+$, found 203.1432.



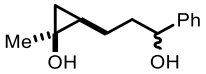
15za: 314 mg; 58%; white solid; purified by column chromatography (hexane/Et_2O = 2/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.08 – 1.95 (m, 5H), 1.74 – 1.65 (m, 4H), 1.52 (dt, *J* = 11.3, 8.8 Hz, 1H), 1.43 (m, 4H), 1.28 – 1.21 (m, 1H), 1.05 – 0.95 (m, 1H), 0.85 (dd, *J* = 10.0, 5.2 Hz, 1H), 0.09 (dd, *J* = 6.4, 5.2 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 75.2, 55.7, 39.3, 36.1, 36.0, 25.7, 24.0, 20.5, 20.3, 12.1. **IR** (neat, cm^{-1}): *v* = 3316, 2979, 2931, 1443, 1376, 1258, 1224, 1167, 1075, 1022, 955, 637. **HRMS** (ESI): *m/z* 153.1274 calc. for $C_{10}H_{17}O^+$ $[M+H-H_2O]^+$, found 153.1274.



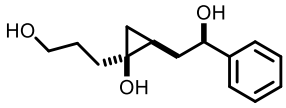
15zb: 327 mg; 53%; colorless oil; purified by column chromatography (hexane/Et_2O = 2/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 1.90 – 1.75 (m, 2H), 1.73 – 1.65 (m, 2H), 1.65 – 1.55 (m, 5H), 1.58 – 1.51 (m, 1H), 1.49 – 1.41 (m, 4H), 1.34 – 1.21 (m, 1H), 1.07 – 0.95 (m, 1H), 0.84 (dd, *J* = 10.0, 5.2 Hz, 1H), 0.08 (dd, *J* = 6.4, 5.2 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 82.6, 55.8, 41.5, 40.0, 39.8, 26.0, 25.4, 23.9, 23.9, 20.6, 20.4. **IR** (neat, cm^{-1}): *v* = 3346, 2955, 2869, 1440, 1375, 1230, 1213, 979. **HRMS** (ESI): *m/z* 207.1356 calc. for $C_{11}H_{20}O_2Na^+$ $[M+Na]^+$, found 207.1357.



15zc: 187 mg; 30%; white solid; purified by column chromatography (hexane/Et_2O = 2/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 1.61 – 1.57 (m, 1H), 1.50 – 1.16 (m, 16H), 1.00 – 0.91 (m, 1H), 0.83 (dd, *J* = 10.1, 5.2 Hz, 1H), 0.06 (dd, *J* = 6.4, 5.1 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 71.3, 55.6, 42.2, 37.6, 37.3, 25.9, 25.8, 23.4, 22.3, 20.5, 20.2. **IR** (neat, cm^{-1}): *v* = 3351, 2928, 2859, 1447, 1227, 1164, 967. **HRMS** (ESI): *m/z* 221.1512 calc. for $C_{12}H_{22}NaO_2^+$ $[M+Na]^+$, found 221.1527.

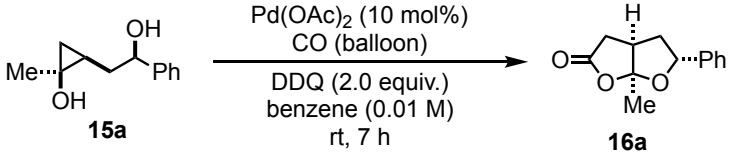


15zd: 612 mg as a 1:1 mixture of diastereomers; 45%; colorless liquid; purified by column chromatography (hexane/Et_2O = 2/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.38 – 7.26 (m, 5H), 4.70 (ddd, *J* = 12.1, 7.7, 5.7 Hz, 1H), 2.01 – 1.73 (m, 4H), 1.38 (d, *J* = 11.6 Hz, 3H), 1.34 – 1.13 (m, 2H), 0.99 (dt, *J* = 10.0, 6.7 Hz, 1H), 0.84 (ddd, *J* = 10.2, 5.2, 2.6 Hz, 1H), 0.07 (ddd, *J* = 8.2, 6.5, 5.1 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 144.8, 144.7, 128.5, 127.6, 127.6, 125.9, 125.9, 74.4, 74.3, 55.7, 55.6, 38.9, 38.9, 26.2, 26.1, 25.4, 25.3, 20.5, 20.3, 20.2. **IR** (neat, cm^{-1}): *ν* = 3342, 2930, 2861, 1453, 1378, 1220, 1064, 1027, 763, 701. **HRMS** (ESI): *m/z* 229.1199 calc. for $C_{13}H_{18}NaO_2^+$ $[M+Na]^+$, found 229.1199.



17: To a solution of **15s** (106 mg, 0.303 mmol, 1.0 equiv.) in THF at 0 °C was added 1.0 M TBAF (0.37 ml, 1.2 equiv.). The reaction was slowly warmed to room temperature. After 6 h, the reaction was quenched with water, extracted with EtOAc, washed with brine, dried with Na_2SO_4, then concentrate under reduced pressure. The residue was purified by flash column (hexane/EtOAc = 1/4 to pure EtOAc) to give triol **17** (65.0 mg, 91%) as colorless solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.40 – 7.26 (m, 5H), 4.97 (t, *J* = 4.5 Hz, 1H), 3.77 – 3.65 (m, 2H), 3.03 (s, 3H), 2.24 (dt, *J* = 14.6, 4.2 Hz, 1H), 1.92 (dt, *J* = 9.5, 4.8 Hz, 1H), 1.80 – 1.73 (m, 3H), 1.45 – 1.36 (m, 1H), 0.58 (dd, *J* = 9.2, 4.9 Hz, 1H), 0.52 – 0.44 (m, 1H), 0.42 (ddd, *J* = 6.1, 4.9, 1.3 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 144.1, 128.3, 127.2, 125.7, 73.4, 63.2, 57.8, 37.3, 37.0, 29.4, 19.7, 19.0. **IR** (neat, cm^{-1}): *ν* = 3316, 2939, 1450, 1305, 1256, 1042, 1003, 755, 701. **HRMS** (ESI): *m/z* 259.1305 calc. for $C_{14}H_{20}NaO_3^+$ $[M+Na]^+$, found 259.1306.

A representative procedure for the synthesis of bicyclic lactone.



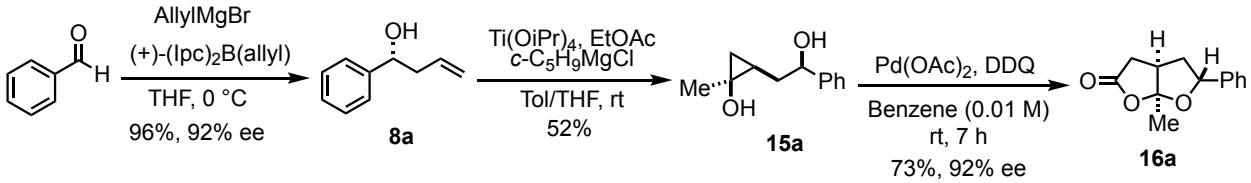
To a stirred solution of **15a** (38.4 mg, 0.2 mmol, 1.0 equiv.) and DDQ (90.8 mg, 0.4 mmol, 2.0 equiv.) in benzene (20 ml) under carbon monoxide (the reactor was evacuated and backfilled three times using a carbon monoxide balloon) was added $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 0.1 equiv.) in one portion. The resulting solution was stirred at room temperature for 7 h. The reaction mixture was quenched with water. The aqueous layer was extracted with ethyl acetate three times. The combined organic layers were washed

with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The resulting residue was purified by flash chromatography (hexane/ethyl acetate = 2/1) to obtain **16a** (32.3 mg, 74%) as colorless solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.39 – 7.29 (m, 5H), 5.16 (dd, *J* = 10.4, 5.6 Hz, 1H), 3.06 – 2.98 (m, 1H), 2.99 (t, *J* = 2.4 Hz, 1H), 2.66 – 2.57 (m, 1H), 2.25 – 2.10 (m, 2H), 1.78 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 174.8, 139.2, 128.6, 128.2, 126.0, 117.2, 80.3, 43.4, 41.9, 36.6, 24.4. **IR** (neat, cm^{-1}): *v* = 2987, 1771, 1256, 1130, 1091, 1007, 919, 760, 701. **HRMS** (ESI): *m/z* 219.1016 calc. for $C_{13}H_{15}O_3^+$ $[M+H]^+$, found 219.1016

Scale-up synthesis

To a stirred solution of **15a** (560 mg, 2.92 mmol, 1.0 equiv.) and DDQ (1.33 g, 5.83 mmol, 2.0 equiv.) in benzene (290 ml) under carbon monoxide (the reactor was evacuated and backfilled three times using a carbon monoxide balloon) was added $Pd(OAc)_2$ (65.6 mg, 0.292 mmol, 0.1 equiv.) in one portion. The resulting solution was stirred at room temperature for 7 h. The reaction mixture was quenched with water. The aqueous layer was extracted with ethyl acetate three times. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The resulting residue was purified by flash chromatography (hexane/ethyl acetate = 2/1) to obtain **16a** (414 mg, 65%) as colorless solid.

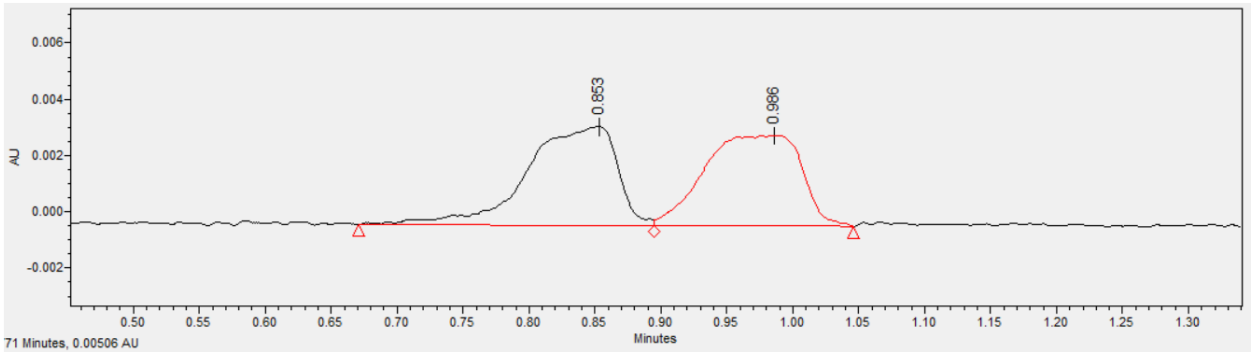
Asymmetric synthesis



Enantioenriched homoallylic alcohol was prepared according to a reported literature procedure.[2] Following the above cyclopropanol synthesis and carbonylative lactonization procedures, compound **16a** was produced in 73% yield and 92% ee.

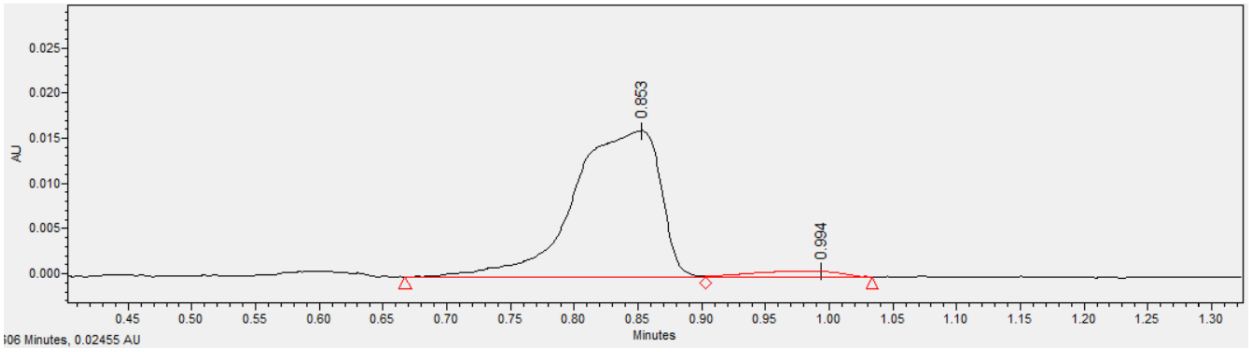
8a: SFC conditions: CEL-1, [97:3 to 50:50 CO2:(IPA/MeOH = 1:1)], 8 min, 1.5 mL/min

Racemic **8a** Peak Results			
	RT/min	Area/(μV*sec)	% Area
1	0.853	16718	50.46
2	0.986	16413	49.54



Racemic **8a**

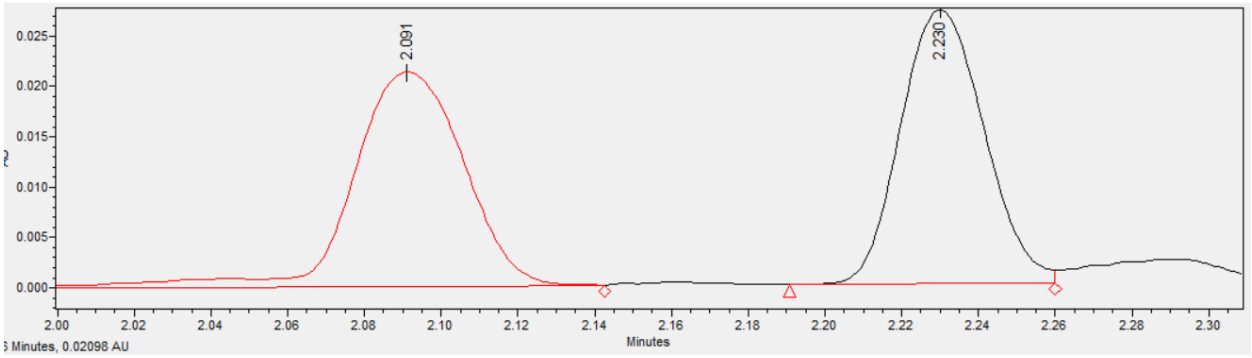
Enantioenriched **8a** Peak Results			
	RT/min	Area/(μV*sec)	% Area
1	0.853	76259	96.06
2	0.994	3128	3.94



Enantioenriched **8a**

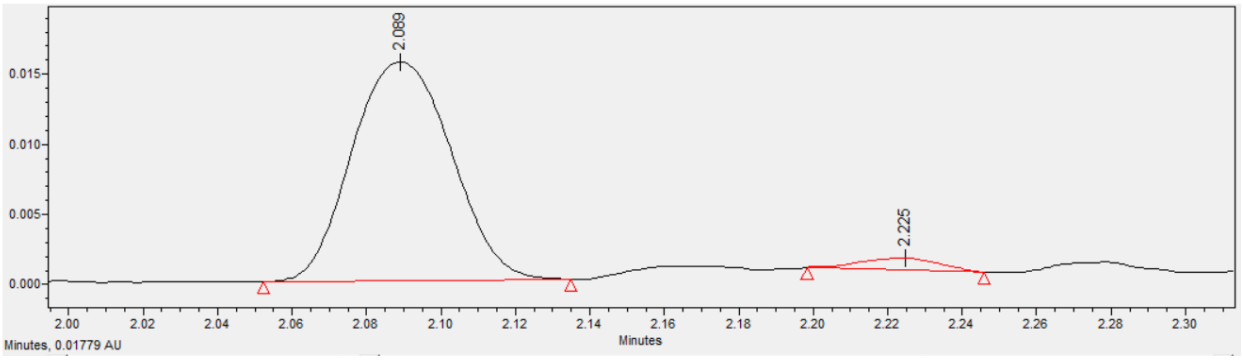
16a: SFC Conditions: CEL-1, [97:3 to 50:50 CO2:(IPA/MeOH = 1:1)], 8 min, 1.5 mL/min

Racemic **16a** Peak Results			
	RT/min	Area/(μV*sec)	% Area
1	2.091	43081	51.22
2	2.230	41028	48.78

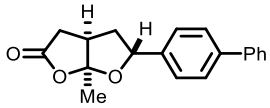


Racemic

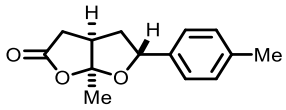
Enantioenriched **16a** Peak Results			
	RT/min	Area/(μV*sec)	% Area
1	2.089	29034	96.04
2	2.225	1196	3.96



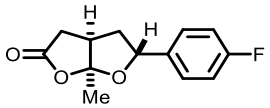
Enantioenriched **16a**



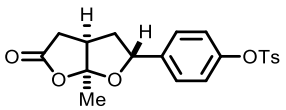
16b: 21.2 mg; 48% (7 h); white solid; purified by column chromatography (hexane/EtOAc = 2/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.62 – 7.54 (m, 4H), 7.47 – 7.39 (m, 4H), 7.39 – 7.31 (m, 1H), 5.22 (dd, *J* = 10.4, 5.6 Hz, 1H), 3.08 – 2.98 (m, 2H), 2.65 (dd, *J* = 15.4, 7.2 Hz, 1H), 2.33 – 2.22 (m, 1H), 2.19 (ddd, *J* = 13.4, 5.6, 1.8 Hz, 1H), 1.81 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 174.8, 141.3, 140.7, 138.1, 128.8, 127.5, 127.4, 127.1, 126.5, 117.1, 80.1, 43.5, 41.9, 36.6, 24.4. **IR** (neat, cm^{-1}): *v* = 3031,2986, 2166, 1974, 1770, 1388, 1256, 1088, 917, 766. **HRMS** (ESI): *m/z* 295.1329 calc. for $C_{19}H_{19}O_3^+$ $[M+H]^+$, found 295.1328.



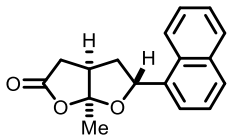
16c: 13.4 mg; 50% (10 h); colorless solid; purified by column chromatography (hexane/EtOAc = 2/1). Note: 12.8 mg product (65%, 0.085 mmol scale) was prepared according to the representative procedure with slow addition of DDQ for 1 h. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.24 – 7.15 (m, 4H), 5.13 (dd, *J* = 10.4, 5.5 Hz, 1H), 3.06 – 2.94 (m, 2H), 2.66 – 2.56 (m, 1H), 2.35 (s, 3H), 2.26 – 2.17 (m, 1H), 2.12 (ddd, *J* = 13.0, 5.5, 1.9 Hz, 1H), 1.77 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 174.8, 138.1, 136.1, 129.3, 126.0, 117.1, 80.2, 43.4, 41.9, 36.6, 24.4, 21.2. **IR** (neat, cm^{-1}): *v* = 2925, 2159, 1976, 1770, 1256, 1088, 919. **HRMS** (ESI): *m/z* 233.1172 calc. for $C_{14}H_{17}O_3^+$ $[M+H]^+$, found 233.1173.



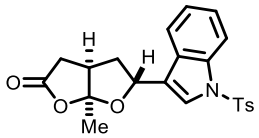
16d: 14.6 mg; 44% (10 h); colorless solid; purified by column chromatography (hexane/EtOAc = 2/1). Note: 14.0 mg product (62%, 0.0985 mmol scale) was prepared according to the representative procedure with slow addition of DDQ for 1 h. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.35 – 7.26 (m, 2H), 7.11 – 7.01 (m, 2H), 5.13 (dd, *J* = 10.3, 5.8 Hz, 1H), 3.08 – 2.91 (m, 2H), 2.61 (d, *J* = 15.4 Hz, 1H), 2.22 – 2.07 (m, 2H), 1.77 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 174.7, 162.6 (d, *J* = 246 Hz), 134.9 (d, *J* = 3 Hz), 127.7 (d, *J* = 9 Hz), 117.0, 115.5 (d, *J* = 21 Hz), 79.6, 43.4, 42.0, 36.6, 24.3. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -115.0. **IR** (neat, cm^{-1}): *v* = 2960, 1771, 1732, 1513, 1373, 1230, 1159, 1128, 1089, 919, 836. **HRMS** (ESI): *m/z* 237.0921 calc. for $C_{13}H_{14}FO_3^+$ $[M+H]^+$, found 237.0921.



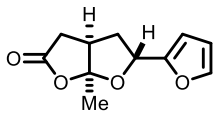
16e: 51.4 mg; 68% (7 h); 55% with toluene as solvent; colorless solid; purified by column chromatography (hexane/EtOAc = 2/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.75 – 7.56 (m, 2H), 7.33 – 7.28 (m, 2H), 7.26 – 7.23 (m, 2H), 7.03 – 6.93 (m, 2H), 5.10 (dd, *J* = 9.4, 6.7 Hz, 1H), 3.06 – 2.94 (m, 2H), 2.64 – 2.53 (m, 1H), 2.44 (s, 3H), 2.18 – 2.08 (m, 2H), 1.75 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 174.6, 149.3, 145.5, 138.2, 132.3, 129.8, 128.5, 127.2, 122.6, 117.0, 79.4, 43.4, 42.0, 36.5, 24.3, 21.7. **IR** (neat, cm^{-1}): *v* = 2987, 2196, 1772, 1505, 1371, 1198, 1176, 1154, 1092, 920, 866, 568, 552. **HRMS** (ESI): *m/z* 389.1053 calc. for $C_{20}H_{21}O_6S^+$ $[M+H]^+$, found 389.1054.



16f: 36.6 mg; 67% (7 h); white solid; purified by column chromatography (hexane/EtOAc = 2/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.02 – 7.72 (m, 3H), 7.69 – 7.37 (m, 4H), 5.89 (t, *J* = 7.8 Hz, 1H), 3.13 – 3.01 (m, 2H), 2.76 – 2.67 (m, 1H), 2.38 (ddd, *J* = 6.9, 5.2, 1.8 Hz, 2H), 1.86 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 174.7, 134.9, 133.7, 130.4, 128.9, 128.6, 126.4, 125.8, 125.4, 123.1, 122.3, 117.1, 77.6, 43.4, 40.7, 36.9, 24.2. **IR** (neat, cm^{-1}): *v* = 2935, 1770, 1258, 1089, 919, 836, 779. **HRMS** (ESI): *m/z* 269.1172 calc. for $C_{17}H_{17}O_3^+$ $[M+H]^+$, found 269.1172.

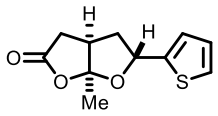


16g: 37.0 mg; 45% (7 h); white solid; purified by column chromatography (hexane/EtOAc = 2/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.97 (dt, *J* = 8.4, 0.9 Hz, 1H), 7.80 – 7.71 (m, 2H), 7.58 – 7.50 (m, 2H), 7.33 (ddd, *J* = 8.4, 7.2, 1.3 Hz, 1H), 7.26 – 7.19 (m, 3H), 5.36 (ddd, *J* = 10.5, 5.6, 1.0 Hz, 1H), 3.09 – 2.98 (m, 2H), 2.69 – 2.59 (m, 1H), 2.51 – 2.40 (m, 1H), 2.35 (s, 3H), 2.18 (ddd, *J* = 13.2, 5.7, 2.0 Hz, 1H), 1.78 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 174.5, 145.2, 135.4, 135.1, 130.0, 128.5, 126.9, 125.1, 123.4, 123.2, 120.4, 120.1, 116.9, 113.8, 74.2, 43.3, 39.5, 36.7, 24.3, 21.6. **IR** (neat, cm^{-1}): *v* = 2925, 1771, 1446, 1370, 1258, 1174, 1123, 1087, 990, 917, 582, 538. **HRMS** (ESI): *m/z* 412.1213 calc. for $C_{22}H_{22}NO_5S^+$ $[M+H]^+$, found 412.1209.

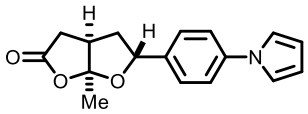


16h: 22.7 mg; 55% (7 h); colorless liquid; purified by column chromatography (hexane/EtOAc = 2/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 1.8, 1.0 Hz, 1H), 6.40 – 6.27 (m, 2H), 5.18 (dd, *J* = 9.6, 6.0 Hz,

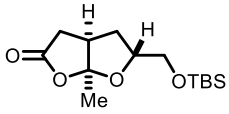
1H), 3.05 – 2.93 (m, 2H), 2.65 – 2.54 (m, 2H), 2.06 – 1.98 (m, 1H), 1.72 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 174.4, 151.0, 143.2, 116.9, 110.4, 109.1, 73.8, 43.2, 37.3, 36.5, 24.1. **IR** (neat, cm^{-1}): v = 2926, 1769, 1257, 1088, 999, 916, 745. **HRMS** (ESI): *m/z* 209.0808 calc. for $C_{11}H_{13}O_4^+$ $[M+H]^+$, found 209.0809.



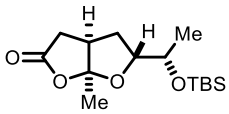
16i: 18.5 mg; 42% (4 h); colorless liquid; purified by column chromatography (hexane/EtOAc = 2/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.30 (dd, J = 5.1, 1.2 Hz, 1H), 7.07 – 6.94 (m, 2H), 5.42 (dd, J = 10.0, 5.6 Hz, 1H), 3.04 – 2.94 (m, 2H), 2.64 – 2.54 (m, 1H), 2.44 – 2.36 (m, 1H), 2.20 (ddd, J = 13.6, 5.6, 2.2 Hz, 1H), 1.75 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 174.5, 142.1, 126.8, 125.7, 116.8, 76.4, 43.4, 42.0, 36.5, 24.4. **IR** (neat, cm^{-1}): v = 2935, 1772, 1256, 1127, 1090, 919, 708. **HRMS** (ESI): *m/z* 225.0580 calc. for $C_{11}H_{13}O_3S^+$ $[M+H]^+$, found 225.0581.



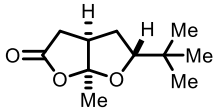
16j: 22.0 mg; 40% (7 h); colorless liquid; purified by column chromatography (hexane/EtOAc = 2/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.39 (s, 4H), 7.08 (t, J = 2.2 Hz, 2H), 6.35 (t, J = 2.2 Hz, 2H), 5.18 (dd, J = 10.4, 5.7 Hz, 1H), 3.08 – 2.98 (m, 2H), 2.68 – 2.59 (m, 1H), 2.27 – 2.14 (m, 2H), 1.80 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 174.6, 140.6, 136.4, 127.3, 120.6, 119.3, 117.0, 110.6, 79.7, 43.4, 41.9, 36.6, 24.4. **IR** (neat, cm^{-1}): v = 2935, 1769, 1524, 1328, 1256, 1124, 1088, 917, 731. **HRMS** (ESI): *m/z* 284.1281 calc. for $C_{17}H_{18}NO_3^+$ $[M+H]^+$, found 284.1281.



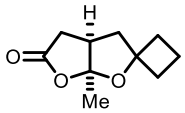
16k: 20.2 mg; 36% (4 h); colorless liquid; purified by column chromatography (hexane/EtOAc = 2/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.28 (ddt, J = 7.9, 6.5, 3.7 Hz, 1H), 3.74 (dd, J = 11.1, 3.8 Hz, 1H), 3.65 (dd, J = 11.1, 3.6 Hz, 1H), 2.92 – 2.78 (m, 2H), 2.51 (dd, J = 17.4, 1.8 Hz, 1H), 2.28 – 2.18 (m, 1H), 1.77 (ddd, J = 12.8, 6.6, 4.1 Hz, 1H), 1.64 (s, 3H), 0.89 (s, 9H), 0.06 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 174.6, 117.9, 80.1, 64.2, 43.3, 36.8, 34.6, 25.9, 23.8, 18.3, -5.3, -5.4. **IR** (neat, cm^{-1}): v = 2954, 2929, 2857, 1775, 1253, 1136, 1096, 921, 836, 778. **HRMS** (ESI): *m/z* 287.1673 calc. for $C_{14}H_{27}O_4Si^+$$[M+H]^+$, found 287.1674.



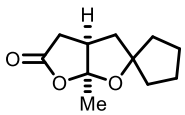
16l: 39.1 mg; 65% (6 h); colorless liquid; purified by column chromatography (hexane/EtOAc = 2/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.03 – 3.91 (m, 2H), 2.90 (dd, *J* = 18.2, 9.6 Hz, 1H), 2.78 (tt, *J* = 9.7, 2.9 Hz, 1H), 2.50 (dd, *J* = 18.3, 2.7 Hz, 1H), 2.29 (dt, *J* = 12.9, 9.5 Hz, 1H), 1.66 (ddd, *J* = 12.9, 6.0, 3.0 Hz, 1H), 1.62 (s, 3H), 1.09 (d, *J* = 6.3 Hz, 3H), 0.87 (s, 9H), 0.05 (d, *J* = 7.9 Hz, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 174.8, 117.6, 83.5, 68.2, 43.0, 37.0, 32.7, 25.8, 23.8, 20.8, 18.0, -4.5, -4.6. **IR** (neat, cm^{-1}): *v* = 2955, 2930, 2886, 2857, 1774, 1254, 1091, 1005, 939, 916, 835, 776. **HRMS** (ESI): *m/z* 301.1830 calc. for $C_{15}H_{29}O_4Si^+$ $[M+H]^+$, found 301.1829.



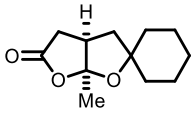
16m: 21.6 mg; 55% (3 h); white solid; purified by column chromatography (hexane/EtOAc = 2/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 3.87 (dd, *J* = 10.4, 5.8 Hz, 1H), 2.91 (dd, *J* = 18.4, 9.9 Hz, 1H), 2.77 (tt, *J* = 9.6, 2.7 Hz, 1H), 2.49 (dd, *J* = 18.4, 3.2 Hz, 1H), 2.01 (dt, *J* = 12.9, 9.9 Hz, 1H), 1.62 (s, 3H), 1.62 – 1.57 (m, 1H), 0.89 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 175.0, 117.4, 86.7, 43.1, 37.0, 33.8, 32.8, 25.6, 24.1. **IR** (neat, cm^{-1}): *v* = 2958, 2871, 1770, 1387, 1258, 1091, 1000, 917. **HRMS** (ESI): *m/z* 199.1329 calc. for $C_{11}H_{19}O_3^+$ $[M+H]^+$, found 199.1329.



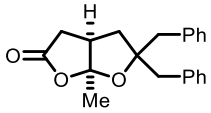
16n: 20.5 mg; 57% (5 h); 46% with toluene as solvent; colorless liquid; purified by column chromatography (hexane/EtOAc = 2/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.94 – 2.79 (m, 2H), 2.51 (dd, *J* = 17.8, 2.1 Hz, 1H), 2.44 – 2.33 (m, 2H), 2.28 (dd, *J* = 13.0, 9.2 Hz, 1H), 2.08 – 1.97 (m, 3H), 1.77 (tddd, *J* = 10.9, 6.4, 3.2, 0.9 Hz, 1H), 1.61 (d, *J* = 0.9 Hz, 3H), 1.59 – 1.52 (m, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 174.4, 117.3, 85.2, 43.4, 43.3, 37.0, 36.4, 34.7, 24.5, 13.0. **IR** (neat, cm^{-1}): *v* = 2935, 1771, 1387, 1272, 1140, 1080, 925. **HRMS** (ESI): *m/z* 183.1016 calc. for $C_{10}H_{15}O_3^+$ $[M+H]^+$, found 183.1016.



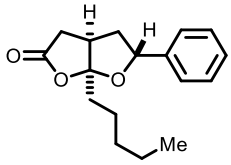
16o: 26.6 mg; 68% (3 h); colorless liquid; purified by column chromatography (hexane/EtOAc = 2/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.93 – 2.81 (m, 2H), 2.56 – 2.48 (m, 1H), 2.35 – 2.27 (m, 1H), 2.02 – 1.93 (m, 1H), 1.88 – 1.71 (m, 4H), 1.65 – 1.57 (m, 7H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 174.5, 117.7, 94.6, 44.0, 43.1, 39.6, 39.0, 37.1, 25.0, 24.3, 23.6. **IR** (neat, cm^{-1}): *v* = 2959, 2872, 1769, 1738, 1258, 1084, 906. **HRMS** (ESI): *m/z* 197.1172 calc. for $C_{11}H_{17}O_3^+$ $[M+H]^+$, found 197.1173.



16p: 30.1 mg; 72% (4 h); colorless liquid; purified by column chromatography (hexane/EtOAc = 2/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.91 – 2.70 (m, 2H), 2.53 – 2.43 (m, 1H), 2.27 – 2.16 (m, 1H), 1.71 – 1.51 (m, 9H), 1.47 – 1.30 (m, 5H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 174.2, 117.6, 87.2, 43.7, 42.8, 38.7, 38.1, 37.2, 25.1, 24.7, 23.4. **IR** (neat, cm^{-1}): *v* = 2933, 2859, 1767, 1449, 1385, 1273, 1250, 1148, 983, 902. **HRMS** (ESI): *m/z* 211.1329 calc. for $C_{12}H_{19}O_3^+$ $[M+H]^+$, found 211.1330.

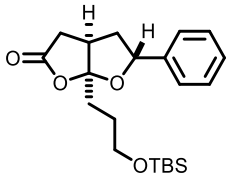


16q: 36.4 mg; 57% (17 h); colorless liquid; purified by column chromatography (hexane/EtOAc = 2/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.38 – 7.14 (m, 10H), 3.13 (d, *J* = 13.7 Hz, 1H), 2.94 (d, *J* = 13.7 Hz, 1H), 2.86 (d, *J* = 13.8 Hz, 1H), 2.62 – 2.49 (m, 2H), 2.44 – 2.36 (m, 1H), 2.33 (d, *J* = 17.7 Hz, 1H), 1.77 – 1.67 (m, 2H), 1.41 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 173.7, 136.9, 136.8, 131.0, 130.8, 128.1, 128.0, 126.7, 126.7, 118.6, 89.8, 48.9, 44.9, 44.2, 40.6, 36.9, 22.8. **IR** (neat, cm^{-1}): *v* = 3061, 3028, 2934, 1969, 1766, 1454, 1263, 1151, 1093, 895, 751, 702. **HRMS** (ESI): *m/z* 323.1642 calc. for $C_{21}H_{23}O_3^+$ $[M+H]^+$, found 323.1641.

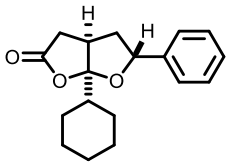


16r: 39.7 mg; 73% (6 h); colorless liquid; purified by column chromatography (hexane/EtOAc = 2/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.40 – 7.28 (m, 5H), 5.15 (dd, *J* = 9.6, 6.5 Hz, 1H), 3.08 – 2.94 (m, 2H), 2.60 (dd, *J* = 18.0, 2.7 Hz, 1H), 2.18 – 2.10 (m, 2H), 2.04 – 1.97 (m, 2H), 1.53 (pd, *J* = 5.8, 3.2 Hz, 2H), 1.39 – 1.31 (m, *J* = 3.4 Hz, 4H), 0.91 (td, *J* = 5.8, 4.6, 2.5 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 175.0, 139.2, 128.6, 128.2, 126.0, 119.2, 79.9, 42.3, 41.7, 37.5, 36.7, 31.7, 23.3, 22.5, 14.0. **IR** (neat, cm^{-1}): *v* = 2930,

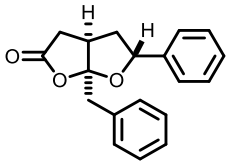
2870, 1768, 1251, 1126, 987, 921, 902, 756, 699. **HRMS** (ESI): *m/z* 275.1642 calc. for $C_{17}H_{23}O_3^+$ [M+H]$^+$, found 275.1642.



16s: 51.5 mg; 68% (6 h); colorless liquid; purified by column chromatography (hexane/EtOAc = 2/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 5H), 5.16 (dd, *J* = 9.9, 6.2 Hz, 1H), 3.74 – 3.63 (m, 2H), 3.08 – 2.92 (m, 2H), 2.61 (dd, *J* = 18.2, 2.9 Hz, 1H), 2.19 – 2.02 (m, 4H), 1.79 – 1.69 (m, 2H), 0.90 (s, 9H), 0.06 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 175.0, 139.2, 128.6, 128.2, 126.0, 119.1, 80.0, 62.6, 42.3, 41.8, 36.6, 34.0, 27.1, 26.0, 18.4, -5.3. **IR** (neat, cm^{-1}): *v* = 2955, 2929, 2856, 2032, 1974, 1776, 1257, 1099, 835, 777, 699. **HRMS** (ESI): *m/z* 377.2143 calc. for $C_{21}H_{33}O_4Si^+$ [M+H]$^+$, found 377.2142.

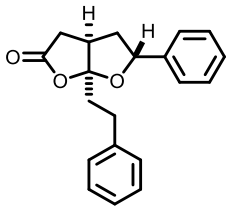


16t: 35.0 mg; 60% (5 h); colorless liquid; purified by column chromatography (hexane/EtOAc = 2/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.40 – 7.27 (m, 5H), 5.13 (dd, *J* = 10.6, 5.7 Hz, 1H), 3.11 (tdd, *J* = 10.7, 3.3, 1.9 Hz, 1H), 2.94 (dd, *J* = 18.8, 10.7 Hz, 1H), 2.58 (dd, *J* = 18.8, 3.4 Hz, 1H), 2.14 – 2.03 (m, 2H), 2.00 – 1.88 (m, 3H), 1.87 – 1.78 (m, 2H), 1.76 – 1.69 (m, 1H), 1.31 – 1.14 (m, 5H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 175.2, 139.2, 128.6, 128.2, 126.0, 121.0, 79.7, 44.4, 42.7, 39.6, 36.9, 26.9, 26.2, 25.8. **IR** (neat, cm^{-1}): *v* = 2929, 2854, 1772, 1450, 1257, 1217, 867, 918, 904, 760, 699. **HRMS** (ESI): *m/z* 287.1642 calc. for $C_{18}H_{23}O_3^+$ [M+H]$^+$, found 287.1641.

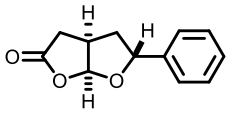


16u: 35.3 mg; 60% (21 h); colorless liquid; purified by column chromatography (hexane/EtOAc = 2/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.40 – 7.27 (m, 10H), 5.16 (dd, *J* = 10.3, 5.9 Hz, 1H), 3.37 (d, *J* = 13.9 Hz, 1H), 3.29 (d, *J* = 13.9 Hz, 1H), 3.08 (dddd, *J* = 9.2, 6.7, 4.2, 2.0 Hz, 1H), 2.52 – 2.38 (m, 2H), 2.05 – 1.93 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 174.8, 139.0, 134.3, 130.6, 128.6, 128.3, 127.4, 126.2, 118.2, 80.3,

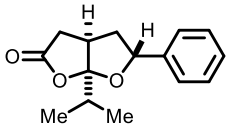
43.2, 41.8, 40.9, 36.7. **IR** (neat, cm^{-1}): v = 3031, 2927, 1772, 1455, 1262, 983, 906, 760, 700. **HRMS** (ESI): *m/z* 295.1329 calc. for $C_{19}H_{19}O_3^+$ $[M+H]^+$, found 295.1329.



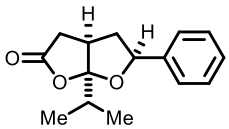
16v: 40.1 mg; 65% (17 h); colorless liquid; purified by column chromatography (hexane/EtOAc = 2/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.40 – 7.29 (m, 7H), 7.28 – 7.21 (m, 3H), 5.19 (dd, J = 9.6, 6.5 Hz, 1H), 3.05 – 2.87 (m, 4H), 2.68 – 2.55 (m, 1H), 2.35 (q, J = 8.0 Hz, 2H), 2.22 – 2.12 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 174.9, 140.8, 139.0, 128.6, 128.3, 128.3, 126.3, 126.0, 118.4, 80.0, 42.2, 41.9, 39.3, 36.5, 30.0. **IR** (neat, cm^{-1}): v = 3028, 2936, 1770, 1497, 1454, 1265, 1243, 1177, 1029, 922, 902, 754, 700. **HRMS** (ESI): *m/z* 309.1485 calc. for $C_{20}H_{21}O_3^+$ $[M+H]^+$, found 309.1482.



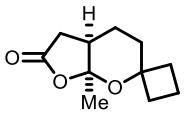
16w: 26.5 mg; 65% (10 h); colorless liquid; purified by column chromatography (hexane/EtOAc = 2/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.39 – 7.31 (m, 5H), 6.29 (d, J = 5.6 Hz, 1H), 5.18 (dd, J = 9.8, 6.0 Hz, 1H), 3.38 – 3.31 (m, 1H), 2.95 (dd, J = 18.8, 10.6 Hz, 1H), 2.56 (dd, J = 18.8, 4.0 Hz, 1H), 2.21 – 2.12 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 175.3, 138.9, 128.6, 128.3, 126.0, 108.1, 80.0, 41.2, 38.9, 35.1. **IR** (neat, cm^{-1}): v = 2924, 2160, 1782, 1177, 1103, 975, 897, 759, 701. **HRMS** (ESI): *m/z* 203.0703 calc. for $C_{12}H_{11}O_3^+$ $[M-H]^+$, found 203.0704.



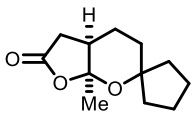
16x: 28.4 mg; 58% (4 h); colorless liquid; purified by column chromatography (hexane/EtOAc = 2/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.39 – 7.29 (m, 5H), 5.20 – 5.06 (m, 1H), 3.14 – 3.04 (m, 1H), 2.96 (dd, J = 18.8, 10.7 Hz, 1H), 2.60 (dd, J = 18.8, 3.4 Hz, 1H), 2.32 – 2.22 (m, 1H), 2.14 – 2.03 (m, 2H), 1.11 (dd, J = 11.0, 6.8 Hz, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 175.3, 139.1, 128.6, 128.2, 126.0, 121.5, 79.8, 42.8, 39.4, 37.0, 34.9, 16.9, 16.9. **IR** (neat, cm^{-1}): v = 2969, 1769, 1245, 1227, 1098, 973, 949, 923, 904, 700. **HRMS** (ESI): *m/z* 247.1329 calc. for $C_{15}H_{19}O_3^+$ $[M+H]^+$, found 247.1327.



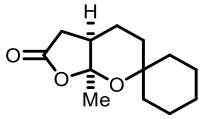
16y: 27.6 mg; 56% (30 h); colorless liquid; purified by column chromatography (hexane/EtOAc = 2/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.43 – 7.30 (m, 4H), 7.31 – 7.25 (m, 1H), 5.17 (dd, *J* = 9.0, 6.5 Hz, 1H), 3.02 (qd, *J* = 8.7, 1.8 Hz, 1H), 2.81 – 2.68 (m, 2H), 2.39 (dd, *J* = 18.2, 1.8 Hz, 1H), 2.19 (p, *J* = 6.8 Hz, 1H), 1.82 (dt, *J* = 13.0, 8.9 Hz, 1H), 1.08 (dd, *J* = 14.6, 6.8 Hz, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 174.2, 141.0, 128.6, 127.9, 125.6, 121.5, 83.2, 41.8, 40.3, 36.9, 35.3, 16.9, 16.6. **IR** (neat, cm^{-1}): *v* = 2970, 2159, 2022, 1972, 1775, 1061, 998, 945. **HRMS** (ESI): *m/z* 247.1329 calc. for $C_{15}H_{19}O_3^+$ $[M+H]^+$, found 247.1326.



16za: 19.4 mg; 50% (5 h); colorless liquid; purified by column chromatography (hexane/EtOAc = 2/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.73 (dd, *J* = 17.3, 7.4 Hz, 1H), 2.33 (dd, *J* = 17.3, 2.7 Hz, 1H), 2.30 – 2.16 (m, 3H), 2.02 – 1.90 (m, 2H), 1.89 – 1.72 (m, 3H), 1.64 – 1.57 (m, 2H), 1.54 – 1.49 (m, 4H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 174.2, 108.7, 76.0, 37.2, 37.1, 35.0, 34.0, 29.6, 26.4, 22.4, 13.2. **IR** (neat, cm^{-1}): *v* = 2988, 2938, 1770, 1277, 1244, 1111, 1065, 942, 897. **HRMS** (ESI): *m/z* 197.1172 calc. for $C_{11}H_{17}O_3^+$ $[M+H]^+$, found 197.1173.

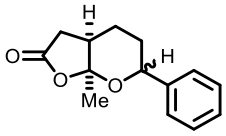


16zb: 20.2 mg; 48% (4 h); white solid; purified by column chromatography (hexane/EtOAc = 2/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.83 (dd, *J* = 17.4, 7.6 Hz, 1H), 2.31 (dd, *J* = 17.4, 1.4 Hz, 1H), 2.25 (dddd, *J* = 9.9, 7.8, 6.5, 1.4 Hz, 1H), 2.15 – 2.07 (m, 1H), 1.90 – 1.74 (m, 4H), 1.69 – 1.63 (m, 1H), 1.62 – 1.56 (m, 3H), 1.54 – 1.41 (m, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 174.1, 109.6, 84.9, 41.0, 37.9, 37.3, 36.7, 31.6, 27.6, 24.1, 24.0, 22.9. **IR** (neat, cm^{-1}): *v* = 2941, 2870, 1767, 1250, 1179, 1117, 1022, 896, 868. **HRMS** (ESI): *m/z* 211.1329 calc. for $C_{12}H_{19}O_3^+$ $[M+H]^+$, found 211.1328.

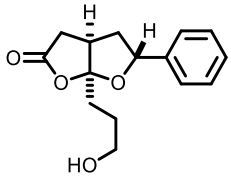


16zc: 23.8 mg; 53% (4 h); white solid; purified by column chromatography (hexane/EtOAc = 2/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.84 (dd, *J* = 17.6, 8.0 Hz, 1H), 2.35 – 2.23 (m, 2H), 1.92 – 1.84 (m, 1H), 1.82

– 1.76 (m, 1H), 1.74 – 1.64 (m, 2H), 1.64 – 1.57 (m, 3H), 1.53 – 1.46 (m, 5H), 1.44 – 1.27 (m, 5H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 174.4, 109.6, 74.9, 39.4, 37.8, 37.5, 35.6, 31.0, 28.0, 25.8, 22.4, 22.0. **IR** (neat, cm^{-1}): *v* = 2933, 2860, 1766, 1270, 1249, 1139, 1048. 896, 883. **HRMS** (ESI): *m/z* 225.1485 calc. for $C_{13}H_{21}O_3^+$ $[M+H]^+$, found 225.1485.

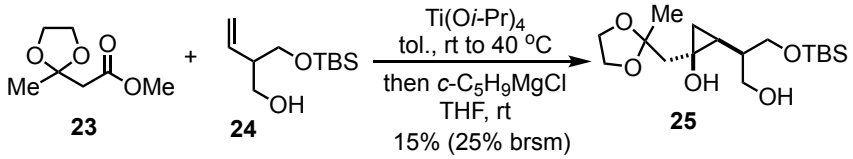


16zd: 35.0 mg as a mixture of 1:1.3 diastereomers from a 1:1 mixture of starting materials; 75% (4 h); colorless liquid; purified by column chromatography (hexane/EtOAc = 2/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.35 (t, *J* = 4.4 Hz, 9H), 7.29 (dddd, *J* = 7.1, 6.3, 3.4, 2.0 Hz, 2H), 4.76 (dd, *J* = 11.2, 2.3 Hz, 1H), 4.58 (dd, *J* = 11.0, 3.0 Hz, 1H), 2.90 (dd, *J* = 17.2, 6.9 Hz, 1H), 2.84 – 2.74 (m, 1H), 2.51 – 2.43 (m, 3H), 2.40 – 2.30 (m, 2H), 2.14 – 2.04 (m, 3H), 2.01 – 1.94 (m, 1H), 1.91 – 1.84 (m, 1H), 1.83 – 1.51 (m, 14H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 175.6, 173.9, 141.3, 141.1, 128.5, 127.9, 127.8, 126.1, 125.6, 109.2, 107.0, 75.6, 74.0, 38.6, 37.7, 36.7, 31.4, 30.4, 27.1, 26.8, 26.4, 22.4, 20.7. **IR** (neat, cm^{-1}): *v* = 2989, 2938, 2864, 1788, 1452, 1385, 1250, 1222, 1176, 1157, 1089, 1075, 1047, 943, 899, 701. **HRMS** (ESI): *m/z* 233.1172 calc. for $C_{14}H_{17}O_3^+$ $[M+H]^+$, found 233.1172.



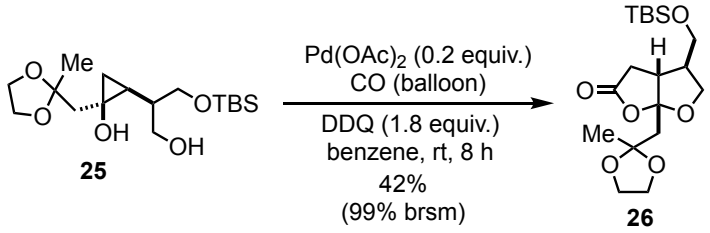
21: 14.0 mg; 47% (5 h); colorless solid; purified by column chromatography (hexane/EtOAc = 2/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.40 – 7.29 (m, 5H), 5.17 (dd, *J* = 10.1, 6.0 Hz, 1H), 3.75 (td, *J* = 6.3, 1.7 Hz, 2H), 3.09 – 2.95 (m, 2H), 2.62 (dd, *J* = 18.1, 2.7 Hz, 1H), 2.22 – 2.08 (m, 4H), 1.84 (tt, *J* = 8.2, 6.3 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 174.9, 139.0, 128.6, 128.3, 126.0, 118.7, 80.2, 62.4, 42.1, 42.1, 36.6, 34.1, 26.8. **IR** (neat, cm^{-1}): *v* = 3446, 2928, 2006, 1769, 1320, 1264, 1124, 1059, 964, 904, 701. **HRMS** (ESI): *m/z* 285.1097 calc. for $C_{15}H_{18}NaO_4^+$ $[M+Na]^+$, found 285.1096.

Total Synthesis of Paeonilide



A solution of titanium(IV) isopropoxide (0.04 ml, 0.13 mmol, 1.1 equiv.) and alcohol **24**[3] (26.4 mg, 0.12 mmol, 1.0 equiv.) in toluene (0.24 ml) was stirred at room temperature for 1 h and then at 40 °C (oil bath) for 10 min. After volatile components were removed under vacuum, THF (1.2 mL) and methyl ester **23**[4] (28.8 mg, 0.18 mmol, 1.5 equiv.) were added at room temperature, followed by a 2 M solution of cyclopentylmagnesium chloride (0.31 ml, 0.61 mmol, 5.0 equiv.) in tetrahydrofuran, over a period of 1 h (with a syringe pump). The reaction mixture was stirred for an additional 14 h and quenched by addition of water. The resulting mixture was stirred for 1 h, dried over anhydrous sodium sulfate, and filtered. The filter cake was washed with CH_2Cl_2, and the combined filtrates were concentrated under reduced pressure. The resulting residue was purified by flash chromatography (hexane/ether = 1/1) to give cyclopropanol **25** (4.1 mg, 15%, 25% brsm) as colorless oil.

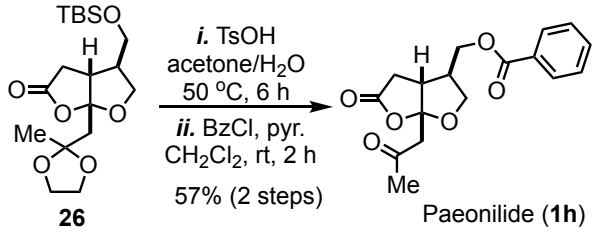
25: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.00 (qd, *J* = 3.3, 1.3 Hz, 4H), 3.91 – 3.80 (m, 3H), 3.78 – 3.72 (m, 2H), 2.75 (s, 1H), 1.91 (d, *J* = 2.5 Hz, 2H), 1.73 (dddt, *J* = 8.8, 5.3, 3.6, 1.8 Hz, 1H), 1.43 (s, 3H), 0.91 (s, 9H), 0.72 (dd, *J* = 9.5, 5.2 Hz, 1H), 0.64 (td, *J* = 9.8, 6.3 Hz, 1H), 0.51 – 0.45 (m, 1H), 0.09 (d, *J* = 1.9 Hz, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 110.9, 67.1, 66.5, 64.4, 55.6, 46.4, 42.0, 25.9, 24.4, 22.1, 18.2, 17.3, -5.5, -5.6. **IR** (neat, cm^{-1}): *v* = 3462, 2953, 2929, 2884, 2857, 1472, 1380, 1253, 1146, 1093, 1051, 948, 836, 778. **HRMS** (ESI): *m/z* 369.2068 calc. for $C_{17}H_{34}NaO_5Si^+$ $[M+Na]^+$, found 369.2067.



To a stirred solution of **25** (50.0 mg, 0.144 mmol, 1.0 equiv.) and DDQ (59.0 mg, 0.26 mmol, 1.8 equiv.) in benzene (14.4 ml, 0.01 M) under carbon monoxide (the reactor was evacuated and backfilled three times using a carbon monoxide balloon) was added $Pd(OAc)_2$ (6.5 mg, 0.029 mmol, 0.2 equiv.) in one portion. The resulting solution was stirred at room temperature for 7 h before the reaction was quenched with water. The aqueous layer was extracted with ethyl acetate three times. The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The resulting residue was purified by flash chromatography (hexane/ethyl acetate = 2/1) to obtain **26** as yellow oil (22.7 mg, 42%; 28.5 mg starting material was recovered; 99% yield brsm).

26: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.05 (dd, *J* = 9.0, 7.1 Hz, 1H), 3.97 – 3.91 (m, 4H), 3.71 – 3.58 (m, 3H), 3.23 (ddd, *J* = 10.4, 9.2, 3.9 Hz, 1H), 2.75 (dd, *J* = 18.8, 3.9 Hz, 1H), 2.70 – 2.57 (m, 2H), 2.40 (d, *J* = 15.1 Hz, 1H), 2.28 (d, *J* = 15.1 Hz, 1H), 1.40 (s, 3H), 0.88 (s, 9H), 0.05 (d, *J* = 0.7 Hz, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 175.3, 117.3, 108.0, 68.6, 64.4, 64.2, 60.2, 45.2, 43.4, 43.4, 29.9, 25.8, 25.3, 18.1, -5.5, -

5.6. **IR** (neat, cm^{-1}): ν = 2917, 2849, 1978, 1738, 1463, 1253, 1044, 778, 697. **HRMS** (ESI): *m/z* 395.1860 calc. for $C_{18}H_{32}NaO_6Si^+$ $[M+Na]^+$, found 395.1861.



To a solution of *cis*-fused lactone **26** (13.9 mg, 0.037 mmol, 1.0 equiv.) in acetone:H_2O = 15:1 (1.75 ml:0.12 ml) at room temperature was added $TsOH \cdot H_2O$ (3.5 mg, 0.019 mmol, 0.5 equiv.). The reaction was heated at 50 °C with an oil bath for 6 h. It was then cooled down, quenched with aqueous $NaHCO_3$ and extracted with EtOAc. The combined organic layer was washed with brine, dried with Na_2SO_4, and concentrated under reduced pressure. The resulting residue was used in the next step without purification.

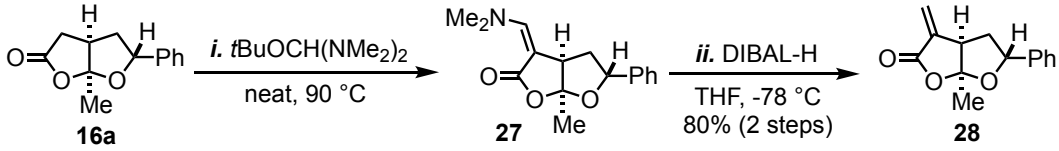
To a solution of alcohol (9.5 mg) in CH_2Cl_2 at room temperature was added pyridine (0.03 ml) and BzCl (6.9 µl, 0.06 mmol, 2.0 equiv.). After 2 h, the reaction was concentrated under reduced pressure. The resulting residue was purified by flash chromatography (hexane/ethyl acetate = 2/1) to obtain **1h** (6.7 mg, 57%, 2 steps) as colorless solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, 2H, *J*=7.8 Hz), 7.60 (t, 1H, *J*=7.6 Hz), 7.47 (t, 2H, *J*=7.6 Hz), 4.29 (dd, 1H, *J*=7.2 Hz, 11.0 Hz), 4.19 (dd, 1H, *J*=8.0 Hz, 11.0 Hz), 4.00-4.06 (m, 2H), 3.41 (d, 1H, *J*=17.8 Hz), 3.35 (dd, 1H, *J*=10.6 Hz, 18.6 Hz), 2.94-2.98 (m, 1H), 2.96 (d, 1H, *J*=17.6 Hz), 2.55 (dd, 1H, *J*=2.8 Hz, 18.4 Hz), 2.53 (m, 1H), 2.20 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 204.4, 174.5, 166.4, 133.5, 129.6, 129.5, 128.6, 115.0, 67.9, 64.9, 49.5, 46.8, 44.4, 36.6, 31.0. **IR** (neat, cm-1): ν = 2923, 2853, 1781, 1716, 1451, 1371, 1314, 1271, 1173, 1110, 1071, 1040, 1026, 950, 713. **HRMS** (ESI): *m/z* 319.1176 calc. for $C_{17}H_{19}O_6^+$ $[M+H]^+$, found 319.1177.

^{1}H NMR (500 MHz, $CDCl_3$)		**^{13}C NMR** (125 MHz, $CDCl_3$)	
Natural Product	Synthetic Sample	Natural Product	Synthetic Sample
2.20 (s, 3H)	2.20 (s, 3H)	30.9	31.0
2.54 (m, 1H)	2.53 (m, 1H)	36.6	36.6
2.55 (dd, 1H, *J*=2.8 Hz, 10.5 Hz)	2.55 (dd, 1H, *J*=2.8 Hz, 18.4 Hz)	44.4	44.4
2.96 (d, 1H, *J*=17.8 Hz)	2.96 (d, 1H, *J*=17.6 Hz)	46.7	46.8
2.97 (m, 1H)	2.94-2.98 (m, 1H)	49.5	49.5
3.34 (dd, 1H, *J*=8.0 Hz, 10.5 Hz)	3.35 (dd, 1H, *J*=10.6 Hz, 18.6 Hz)	64.9	64.9
3.40 (d, 1H, *J*=17.8 Hz)	3.41 (d, 1H, *J*=17.8 Hz)	67.9	67.9

4.03 (m, 2H)	4.00-4.06 (m, 2H)	114.9	115.0
4.19 (dd, 1H, *J*=8.0 Hz, 11.0 Hz)	4.19 (dd, 1H, *J*=8.0 Hz, 11.0 Hz)	128.5	128.6
4.30 (dd, 1H, *J*=7.3 Hz, 11.0 Hz)	4.29 (dd, 1H, *J*=7.2 Hz, 11.0 Hz)	129.6	129.5
7.47 (t, 2H, *J*=8.5 Hz)	7.47 (t, 2H, *J*=7.6 Hz)	129.6	129.6
7.60 (brt., 1H)	7.60 (t, 1H, *J*=7.6 Hz)	133.4	133.5
8.02 (dd, 2H, *J*=1.2 Hz, 8.5 Hz)	8.02 (d, 2H, *J*=7.8 Hz)	166.3	166.4
		174.4	174.5
		207.1	204.4

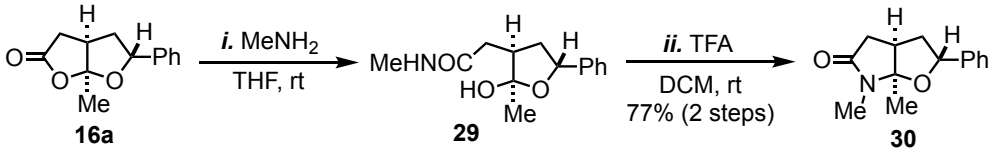
Diversification



To a solution of *cis*-fused lactone **16a** (55 mg, 0.252 mmol, 1.0 equiv.) was added Bredereck's reagent (219.6 mg, 1.26 mmol, 5.0 equiv.). The reaction was heated to 90 °C using an oil bath. After 4 h, the reaction was cooled to room temperature, the crude was purified by flash column (Hex/EA = 1/3) directly without work-up to give 66 mg crude product.

To a solution of the above crude enamine (61.5 mg, 0.225 mmol, 1.0 equiv.) in THF (4.5 ml, 0.05 M) at -78 °C was added DIBAL-H (2.4 equiv.) dropwise. After 1 h, the reaction was quenched with a saturated aqueous solution of NH_4Cl, extracted with EtOAc, washed with brine, dried with Na_2SO_4, and concentrated. The crude residue was purified by flash column (Hex/EA = 5/1) to give α-methylene γ-butyrolactone **28** (42.8 mg, 80%, over 2 steps) as white solid.

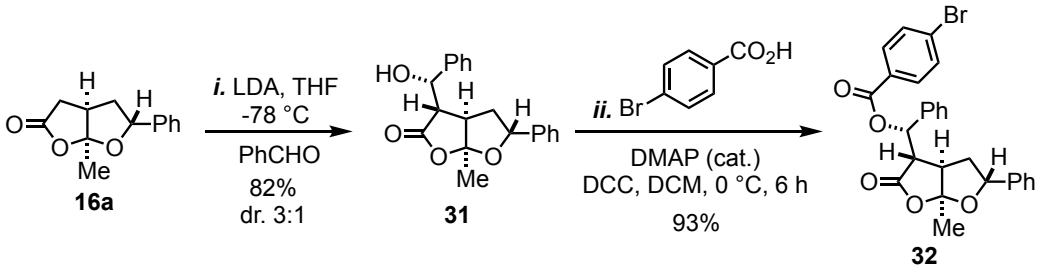
28: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.40 – 7.28 (m, 5H), 6.42 (d, *J* = 2.6 Hz, 1H), 5.78 (d, *J* = 2.2 Hz, 1H), 5.03 (dd, *J* = 11.1, 5.0 Hz, 1H), 3.49 (dd, *J* = 8.8, 1.8 Hz, 1H), 2.39 – 2.21 (m, 2H), 1.79 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 168.7, 139.6, 138.7, 128.6, 128.3, 126.0, 124.4, 113.9, 80.3, 48.7, 43.6, 24.6. **IR** (neat, cm^{-1}): *v* = 2937, 1762, 1276, 1125, 1067, 927, 913, 872, 759, 700. **HRMS** (ESI): *m/z* 231.1016 calc. for $C_{14}H_{15}O_3^+$ $[M+H]^+$, found 231.1014.



A solution of $MeNH_2$ (64.0 mg, 40 wt% in water, 2.06 mmol, 15.0 equiv) was added to *cis*-fused lactone **16a** (30.0 mg, 0.138 mmol, 1.0 equiv.) in THF (1.4 ml, 0.1 M) at room temperature. The reaction mixture was stirred at room temperature for 1 h. The resulting mixture was evaporated to dry under reduced pressure. The crude is proceeded to the next step without purification.

To a solution of the above crude (0.138 mmol, 1.0 equiv.) in DCM (1.4 ml, 0.1 M) was added TFA (21 µl, 0.275 mmol, 2.0 equiv.) in one portion at room temperature. After the reaction was stirred at room temperature for 30 min, it was quenched with a saturated aqueous solution of NH_4Cl, extracted with EtOAc, washed with brine, dried with Na_2SO_4, and concentrated. The crude was purified by flash column (Hex/EA = 6/1) to give lactam **30** (24.5 mg, 77%, over 2 steps) as colorless liquid.

30: ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.43 – 7.26 (m, 5H), 4.78 (dd, *J* = 10.9, 5.0 Hz, 1H), 2.84 (s, 3H), 2.80 (d, *J* = 6.5 Hz, 2H), 2.39 (d, *J* = 14.7 Hz, 1H), 2.21 – 2.11 (m, 1H), 2.03 (dd, *J* = 12.6, 5.0 Hz, 1H), 1.64 (s, 3H). ^{13}**C NMR** (125 MHz, $CDCl_3$) δ 139.7, 128.6, 128.1, 126.1, 100.6, 79.0, 43.3, 41.5, 37.4, 24.6, 23.4. **IR** (neat, cm^{-1}): *v* = 2939, 1674, 1602, 1423, 1204, 1149, 1131, 1066, 801, 756, 723, 699. **HRMS** (ESI): *m/z* 232.1332 calc. for $C_{14}H_{18}NO_2^+$ $[M+H]^+$, found 232.1331.



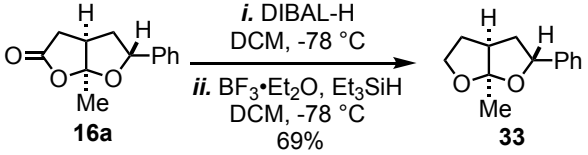
To a solution of *cis*-fused lactone **16a** (26.4 mg, 0.121 mmol, 1.0 equiv.) in THF (1.2 ml, 0.1 M) at -78 °C was added 1.0 M LDA (0.145 ml, 0.145mmol, 1.2 equiv.) dropwise. After 30 min, benzaldehyde (15 µl, 0.145 mmol, 1.2 equiv.) was added dropwise at -78 °C and the reaction was stirred at this temperature for 1.5 h. The reaction was quenched with a saturated aqueous solution of NH_4Cl and extracted with EtOAc. The combined organic layers were washed with brine and evaporated. The residue was purified via flash column (Hex:EA = 5:1) to give aldol product **31** (dr. 3:1, separable, total 32.0 mg, 82%) as white solid.

31, **major diastereomer**: ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.43 – 7.36 (m, 4H), 7.32 – 7.24 (m, 6H), 5.49 (dd, *J* = 4.8, 2.4 Hz, 1H), 5.03 (dd, *J* = 11.5, 4.5 Hz, 1H), 3.10 – 2.97 (m, 2H), 2.70 (d, *J* = 4.7 Hz, 1H), 2.00 – 1.87 (m, 1H), 1.73 (s, 3H), 1.61 (dd, *J* = 12.9, 4.6 Hz, 1H). ^{13}**C NMR** (125 MHz, $CDCl_3$) δ 176.3, 141.0, 138.8, 128.8, 128.5, 128.2, 128.0, 126.0, 125.3, 116.4, 80.4, 71.6, 56.9, 43.7, 42.1, 24.5. **IR** (neat, cm^{-1}): *v* = 3478, 3033, 2934, 1759, 1453, 1389, 1266, 1128, 1091, 905, 760, 700. **HRMS** (ESI): *m/z* 347.1254 calc. for $C_{20}H_{20}NaO_4^+$ $[M+Na]^+$, found 347.1250.

31a, **minor diastereomer**: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.47 – 7.36 (m, 4H), 7.36 – 7.26 (m, 5H), 7.25 (s, 1H), 5.07 (td, *J* = 10.0, 8.7, 2.9 Hz, 2H), 3.65 (d, *J* = 1.7 Hz, 1H), 3.10 (dd, *J* = 7.8, 5.6 Hz, 1H), 2.70 (dd, *J* = 8.4, 5.5 Hz, 1H), 1.96 (ddd, *J* = 13.0, 11.4, 8.3 Hz, 1H), 1.77 (dd, *J* = 13.0, 4.6 Hz, 1H), 1.45 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 176.6, 139.6, 138.6, 128.9, 128.8, 128.6, 128.3, 126.7, 126.0, 116.0, 80.6, 74.4, 55.3, 46.3, 41.7, 24.8. **IR** (neat, cm^{-1}): *v* = 3478, 3033, 2934, 1759, 1453, 1389, 1266, 1128, 1091, 905, 760, 700. **HRMS** (ESI): *m/z* 347.1254 calc. for $C_{20}H_{20}NaO_4^+$ $[M+Na]^+$, found 347.1250.

To a mixture of the major diastereomer of aldol product **31** (30.0 mg, 0.093 mmol, 1.0 equiv.), DMAP (1.0 mg), 4-bromo benzoic acid (20.5 mg, 0.102 mmol, 1.1 equiv.) was added CH_2Cl_2 (0.93 ml, 0.1 M). DCC (22.0 mg, 0.107 mmol, 1.15 equiv.) were sequentially added to the solution at 0 °C. The resulting mixture was stirred at 0 °C for 6 h before it was quenched with water. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were dried with Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column (Hex/EA = 8/1) to give **32** (43.5 mg, 93%) as white solid.

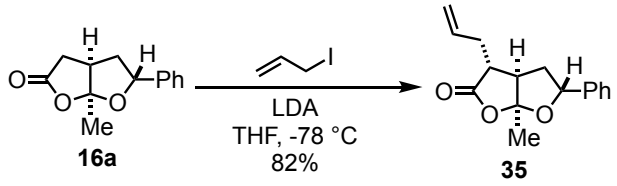
32: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.99 – 7.87 (m, 2H), 7.68 – 7.59 (m, 2H), 7.42 – 7.26 (m, 10H), 6.55 (d, *J* = 3.5 Hz, 1H), 5.07 (dd, *J* = 11.4, 4.4 Hz, 1H), 3.29 (dd, *J* = 5.7, 3.5 Hz, 1H), 3.17 (dd, *J* = 8.2, 5.8 Hz, 1H), 2.05 (ddd, *J* = 12.9, 11.4, 8.3 Hz, 1H), 1.77 (dd, *J* = 13.0, 4.5 Hz, 1H), 1.66 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 173.6, 164.3, 138.4, 137.0, 132.0, 131.1, 129.1, 128.8, 128.6, 128.4, 128.4, 126.0, 125.7, 115.4, 80.4, 74.2, 54.6, 45.2, 42.1, 25.1. **IR** (neat, cm^{-1}): *v* = 2243, 2072, 1974, 1771, 1728, 1590, 1300, 1266, 1092, 1012, 755, 699. **HRMS** (ESI): *m/z* 529.0621/531.0601 calc. for C27H23BrNaO5$^+$ $[M+Na]^+$, found 529.0620/531.0603.



To a solution of *cis*-fused lactone **16a** (41.5 mg, 0.19 mmol, 1.0 equiv.) in anhydrous CH_2Cl_2 (1.9 ml, 0.1 M) was added 1.0 M DIBAL-H solution in toluene (0.21 mL, 0.21 mmol, 1.1 equiv.) at -78 °C. The reaction mixture was stirred for 30 min and the progress of the reaction was monitored by TLC. After the reaction was over, a saturated solution of sodium potassium tartrate was added. The reaction was allowed to stir for 4-6 h till a clear separation of organic and aqueous layers resulted. The organic layer was separated and aqueous layer was further extracted with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4 and evaporated under vacuum. The residue obtained was purified by column chromatography (Hex/EA = 1/1) to yield a hemiacetal (43.3 mg, quant.) as colorless oil.

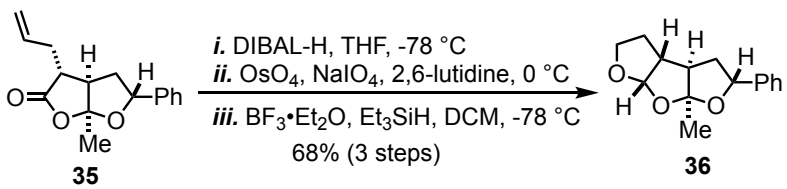
To a solution of the above hemiacetal (15.9 mg, 0.723 mmol, 1.0 equiv.) in anhydrous CH_2Cl_2 (5 mL) at 0 °C, triethylsilane (35 µl, 0.217 mmol, 3.0 equiv.) was added and the reaction mixture was cooled to -78 °C. A solution of BF_3 etherate (18 µl, 0.145 mmol, 2.0 equiv.) was added slowly to the reaction mixture and the reaction was allowed to raise to room temperature. After completion, a saturated solution of sodium bicarbonate was added. The mixture was extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over Na_2SO_4. The organic solvent was removed by rotatory evaporation. The residue was purified by column chromatography on silica gel with (Hex/EA = 2:1) to yield **33** (10.1 mg, 69%) as colorless oil.

33: ^{1}H NMR ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.26 (m, 5H), 5.16 (dd, *J* = 10.6, 5.6 Hz, 1H), 4.09 (td, *J* = 8.6, 6.7 Hz, 1H), 3.94 (ddd, *J* = 9.0, 7.9, 4.4 Hz, 1H), 2.69 (d, *J* = 4.1 Hz, 1H), 2.34 – 2.25 (m, 1H), 2.16 (ddd, *J* = 12.8, 5.6, 1.7 Hz, 1H), 2.12 – 2.05 (m, 1H), 1.91 – 1.85 (m, 1H), 1.63 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 141.8, 128.4, 127.5, 125.8, 116.7, 81.0, 68.2, 47.1, 42.4, 33.1, 24.5. **IR** (neat, cm^{-1}): *v* = 2926, 2854, 1452, 1380, 1108, 1016, 755, 699. **HRMS** (ESI): *m/z* 203.1068 calc. for $C_{13}H_{15}O_2^+$ $[M-H]^+$, found 203.1067.



To a solution of *cis*-fused lactone **16a** (24.0 mg, 0.11 mmol, 1.0 equiv.) in THF (0.1 M) at -78 °C was added 1.0 M LDA (0.22 mmol, 2.0 equiv.) dropwise. After 1 h, allyl iodide (25 µl, 0.275 mmol, 2.5 equiv.) was added over 5 min at -78 °C and the reaction was stirred at this temperature for 1 h before it was quenched with a saturated solution of NH_4Cl and extracted with EtOAc. The combined organic layer was washed with brine and evaporated. The residue was purified via flash column (Hex/EA = 3/1) to give **35** (23.4 mg, 82%) as colorless liquid.

35: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.29 (m, 5H), 5.85 – 5.71 (m, 1H), 5.24 – 5.14 (m, 2H), 5.12 (dd, *J* = 10.6, 5.3 Hz, 1H), 2.84 – 2.70 (m, 2H), 2.70 – 2.59 (m, 1H), 2.48 – 2.39 (m, 1H), 2.24 – 2.09 (m, 2H), 1.76 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 176.9, 139.0, 133.8, 128.6, 128.3, 126.0, 118.9, 115.4, 80.5, 48.7, 48.0, 42.0, 36.0, 25.4. **IR** (neat, cm^{-1}): *v* = 2936, 2040, 2025, 1769, 1388, 1289, 1264, 1134, 1093, 998, 920, 700. **HRMS** (ESI): *m/z* 259.1329 calc. for $C_{16}H_{19}O_3^+$ $[M+H]^+$, found 259.1328.

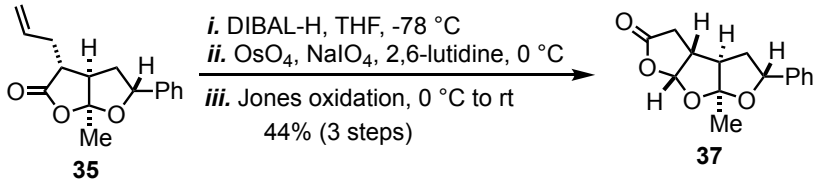


To a solution of **35** (55.3 mg, 0.214 mmol, 1.0 equiv.) in DCM (2.1 ml) was added 1.0 M DIBAL-H (1.15 equiv.) in toluene at -78 °C. The reaction mixture was stirred for 1 h followed by quenching with a saturated solution of sodium potassium tartrate. After stirring another 2 h, the organic layer was separated and the aqueous layer was further extracted with DCM. The combined organic layer was washed with brine and dried over Na_2SO_4, and evaporated. The crude was used in the next step without purification.

To a solution of the above crude product in dioxane: water mixture (3:1, v/v; 3 mL) at 0 °C was added 2,6-lutidine (25 µl, 0.214 mmol, 1.0 equiv.) and an OsO_4 solution in water (5 mg/ml, 0.00214 mmol, 0.01 equiv.) followed by $NaIO_4$ (137 mg, 0.214 mmol, 3.0 equiv.) at room temperature. After 5 h, the reaction was completed and quenched with aqueous sodium thiosulfate solution. The reaction mixture was exhaustively extracted with EtOAc. The combined organic layer was dried over Na_2SO_4, filtered through a celite-pad, and evaporated under vacuum to yield a crude diastereomeric tricyclic hemiacetal, which was subjected to next reaction without purification.

To a solution of the above crude (21 mg, 1.0 equiv.) in anhydrous DCM (0.8 ml) at -78 °C, triethylsilane (39 µl, 0.24 mmol, 3.0 equiv.) and BF_3 etherate (20 µl, 0.16 mmol, 2.0 equiv.) was added slowly. After 2 h, a saturated solution of sodium bicarbonate was added to it followed by extraction with DCM. The combined organic layer was washed with brine and dried over Na_2SO_4. The solvent was removed by rotatory evaporation. The residue was purified via flash column (Hex:EA = 4:1) to give **36** (13.4 mg, 68%, 3 steps) as colorless oil.

36: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.36 – 7.32 (m, 5H), 5.97 (d, J = 5.1 Hz, 1H), 5.00 (dd, J = 11.2, 4.8 Hz, 1H), 3.99 (td, J = 8.4, 2.5 Hz, 1H), 3.92 (ddd, J = 10.4, 8.8, 5.9 Hz, 1H), 2.78 (ddt, J = 8.8, 5.3, 2.7 Hz, 1H), 2.53 (dd, J = 8.1, 3.4 Hz, 1H), 2.19 – 2.13 (m, 2H), 2.07 (ddd, J = 12.6, 11.1, 8.3 Hz, 2H), 1.71 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 140.5, 128.4, 127.8, 126.0, 117.0, 109.4, 79.5, 66.7, 53.9, 50.5, 43.0, 33.2, 25.3. **IR** (neat, cm^{-1}): ν =2935, 2871, 1449, 1380, 1134, 1026, 989, 945, 895, 759, 700. **HRMS** (ESI): *m/z* 247.1329 calc. for $C_{15}H_{19}O_3^+$ $[M+H]^+$, found 247.1327.



To a solution of **35** (55.3 mg, 0.214 mmol, 1.0 equiv.) in DCM (2.1 ml) was added 1.0 M DIBAL-H (1.15 equiv.) in toluene at -78 °C. The reaction mixture was stirred for 1 h followed by quenching with a saturated solution of sodium potassium tartrate. After stirring another 2 h, the organic layer was separated and the

aqueous layer was further extracted with DCM. The combined organic layer was washed with brine and dried over Na_2SO_4 and evaporated. The crude was used to the next step without purification.

To a solution of the above crude product in dioxane/water mixture (3:1, v/v; 3 mL) at 0 °C was added 2,6-lutidine (25 µl, 0.214 mmol, 1.0 equiv.) and 5 mg/ml OsO_4 solution in water (0.00214 mmol, 0.01 equiv.) followed by $NaIO_4$ (137 mg, 0.214 mmol, 3.0 equiv.) at room temperature. After 5 h, the reaction was quenched with an aqueous sodium thiosulfate solution and exhaustively extracted with EtOAc. The combined organic layer was dried over Na_2SO_4, filtered through a celite-pad, and evaporated under vacuum to yield a crude diastereomeric tricyclic hemiacetal, which was subjected to next reaction without purification.

To a solution of the above crude product (23.0 mg, 0.088 mmol, 1.0 equiv.) in acetone (1 mL) was added dropwise 2.5 M Jones reagent (35 µl, 0.088 mmol, 1.0 equiv.) at 0 °C and the reaction mixture was gradually allowed to warm to room temperature. After 10 h, the reaction was quenched with a sat. $NaHCO_3$ solution and extracted with EtOAc. The combined organic layer was washed with brine and dried over Na_2SO_4, evaporated and subjected to column chromatography (Hex:EA = 3:1 to pure EtOAc) to yield tricyclic lactone **37** (9.9 mg, 44%, 3 steps) as colorless oil.

37: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.38 – 7.29 (m, 5H), 6.21 (d, J = 5.4 Hz, 1H), 5.06 (dd, J = 9.1, 6.8 Hz, 1H), 3.05 (tdd, J = 6.9, 3.4, 1.8 Hz, 1H), 2.93 (dd, J = 18.1, 9.3 Hz, 1H), 2.63 (dd, J = 18.1, 2.5 Hz, 1H), 2.54 (q, J = 4.5 Hz, 1H), 2.19 – 2.13 (m, 2H), 1.74 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.0, 139.3, 128.6, 128.1, 126.0, 119.6, 107.4, 79.9, 53.6, 46.6, 42.2, 36.3, 26.1. **IR** (neat, cm^{-1}): ν = 2918, 2026, 2010, 1782, 1174, 1102, 1005, 944, 886, 701. **HRMS** (ESI): *m/z* 261.1121 calc. for $C_{15}H_{17}O_4^+$ $[M+H]^+$, found 261.1119.

Part 2. X-Ray structure and analysis data.

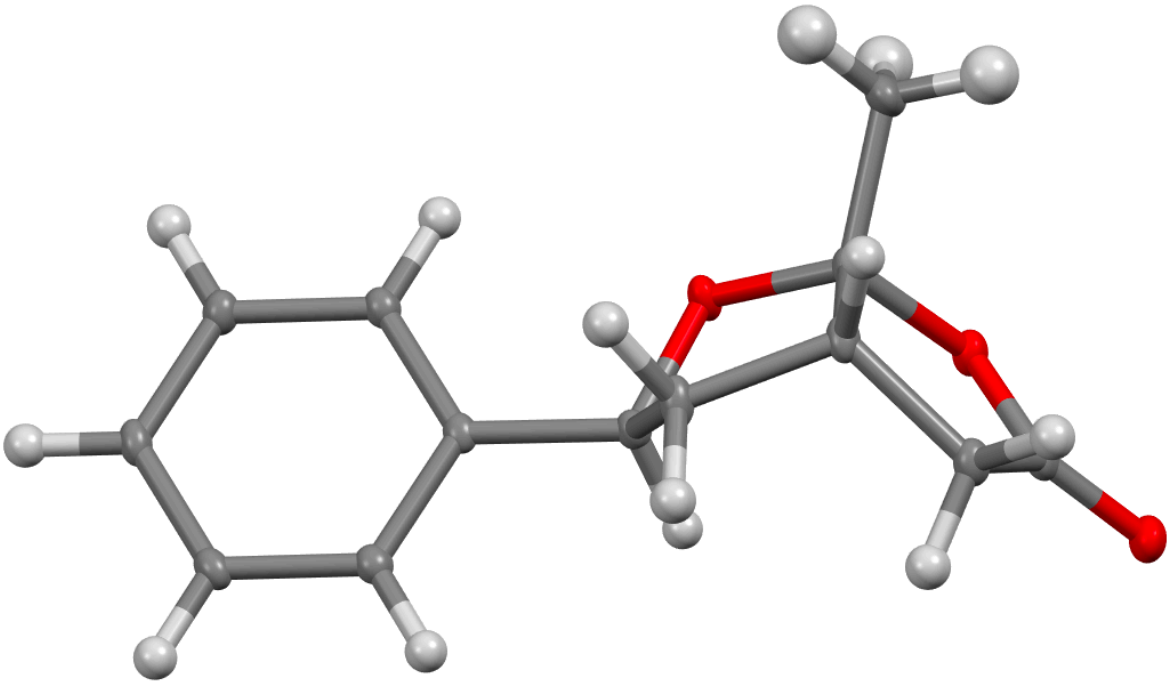


Figure S1. X-ray Structure of **16a**

A colorless plate shaped crystal of **16a** for X-ray diffraction was obtained by slow evaporation of a Hexanes/EtOAc solution of **16a**. The data were collected at 150(2) K on a Bruker AXS D8 Quest CMOS diffractometer with Mo sealed tube and curved triumph monochromator with a 10 cm x 10 cm Photon-100 detector and fixed chi angle. The supplementary crystallographic data was deposited in The Cambridge Crystallographic Data Centre. CCDC1997763.

X-ray analysis data:

Bond precision: C-C = 0.0022 A Wavelength=1.54178
Cell: a=11.8558(4) b=13.1276(4) c=7.1585(2)
alpha=90 beta=101.6907(10) gamma=90
Temperature: 150 K Calculated Reported
Volume 1091.02(6) 1091.02(6)
Space group P 21/c P 21/c
Hall group -P 2ybc -P 2ybc
Moiety formula C13 H14 O3 ?
Sum formula C13 H14 O3 C13 H14 O3
Mr 218.24 218.24

Dx,g cm-3 1.329 1.329
Z 4 4
Mu (mm-1) 0.766 0.766
F000 464.0 464.0
F000' 465.48
h,k,lmax 14,16,8 14,16,8
Nref 2154 2113
Tmin,Tmax 0.752,0.948 0.510,0.754
Tmin' 0.708
Correction method= # Reported T Limits: Tmin=0.510
Tmax=0.754 AbsCorr = MULTI-SCAN
Data completeness= 0.981 Theta(max)= 72.204
R(reflections)= 0.0516(1968) wR2(reflections)= 0.1600(2113)
S = 1.107 Npar= 147

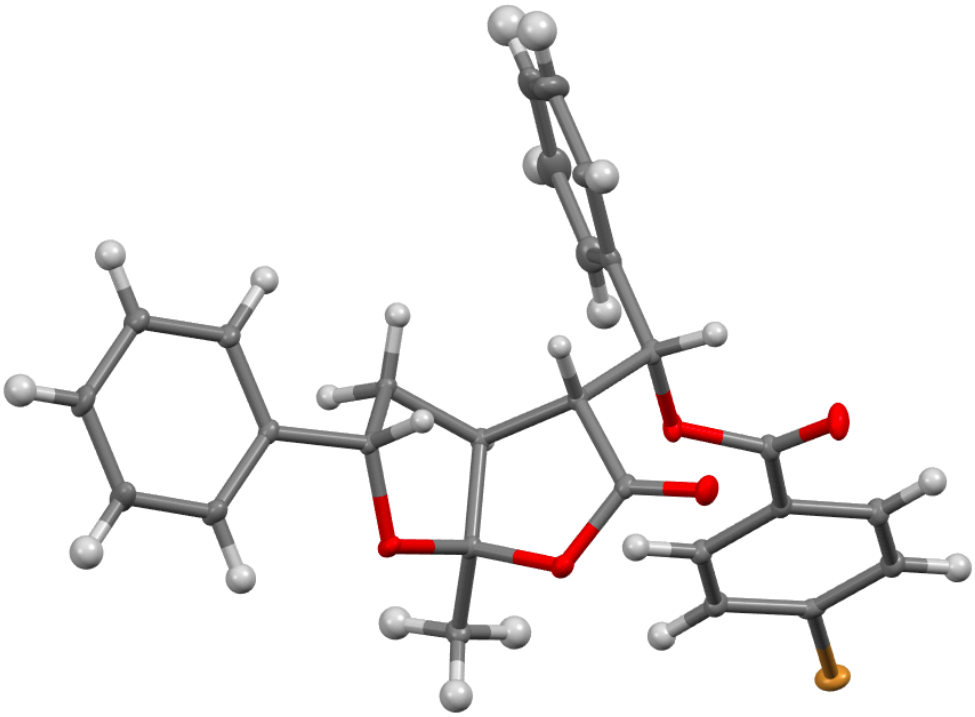


Figure S2. X-ray Structure of **32**

A colorless plate shaped crystal of **32** for X-ray diffraction was obtained by slow evaporation of a isopropyl alcohol/EtOAc solution of **32**. The data were collected at 150(2) K on a Bruker AXS D8 Quest CMOS diffractometer with Mo sealed tube and curved triumph monochromator with a 10 cm x 10 cm Photon-100 detector and fixed chi angle. The supplementary crystallographic data was deposited in The Cambridge Crystallographic Data Centre. CCDC 2016932.

Bond precision: C-C = 0.0048 A Wavelength=1.54178
Cell: a=10.1739(3) b=10.3086(3) c=11.0993(3)
alpha=90 beta=95.0877(14) gamma=90
Temperature: 150 K

	Calculated	Reported
Volume	1159.49(6)	1159.49(11)
Space group	P 21	P 21
Hall group	P 2yb	P 2yb
Moiety formula	C27 H23 Br O5	?
Sum formula	C27 H23 Br O5	C27 H23 Br O5
Mr	507.35	507.36
Dx,g cm-3	1.453	1.453
Z	2	2

Mu (mm-1)	2.719	2.719
F000	520.0	520.0
F000'	520.06	
h,k,lmax	12,13,14	12,13,14
Nref	5037[2662]	4768
Tmin,Tmax	0.710, 0.897	0.624, 0.754
Tmin'	0.568	

Correction method= # Reported T Limits: Tmin=0.624 Tmax=0.754
AbsCorr = MULTI-SCAN
Data completeness= 1.79/0.95 Theta(max)= 79.688
R(reflections)= 0.0268(4561) wR2(reflections)= 0.0627(4768)
S = 1.062 Npar= 299

Reference:

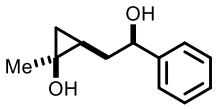
1. Quan, L. G.; Kim, S.-H.; Lee, J. C.; Cha, J. K. Diastereoselective Synthesis of trans-1,2-Dialkylcyclopropanols by the Kulinkovich Hydroxycyclopropanation of Homoallylic Alcohols. *Angew. Chem. Int. Ed.* **2002**, *41*, 2160-2162.

2. Sun, H.; Roush, W. S.; Hughes, D. Synthesis of (+)-B-Allyldiisopinocampheylborane and its Reaction with Aldehydes. *Org. Synth.* **2011**, *88*, 87-101.

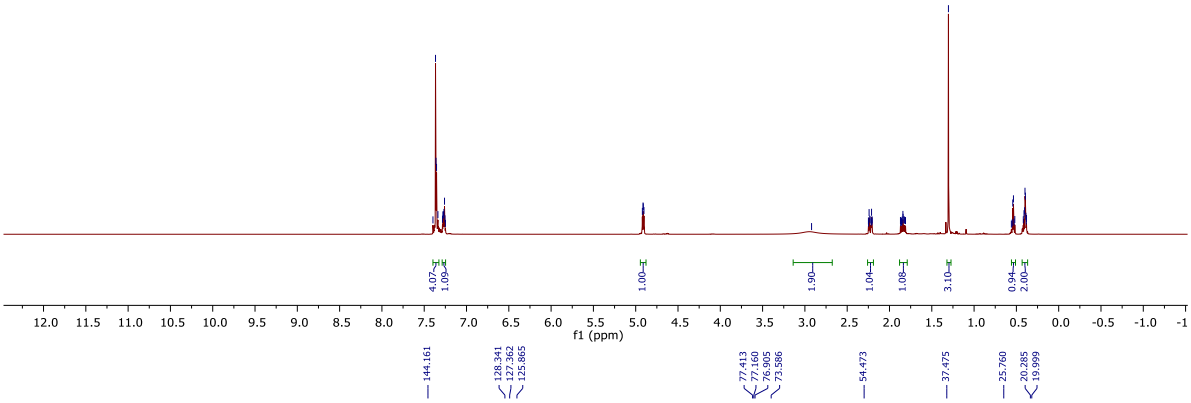
3. Lohse-Fraefel, N.; Carreira, E. M. Polyketide Building Blocks via Diastereoselective Nitrile Oxide Cycloadditions with Homoallylic Alcohols and Monoprotected Homoallylic Diols. *Chem. Eur. J.* **2009**, *15*, 12065-12081.

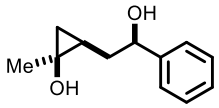
4. Ueda, Y.; Abe, H.; Iguchi, K.; Ito, H. Synthetic Study of Yonarolide: Stereoselective Construction of the Tricyclic Core. *Tetrahedron Lett.* **2011**, *52*, 3379-3381.

Part 3. ^{1}H, ^{13}C, and ^{19}F NMR spectra

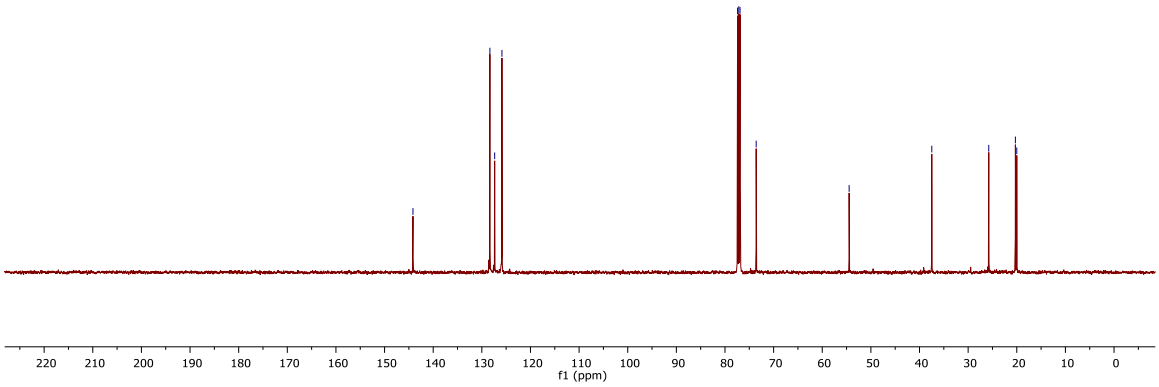


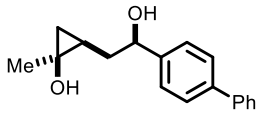
^{1}H NMR (500 MHz, $CDCl_3$)



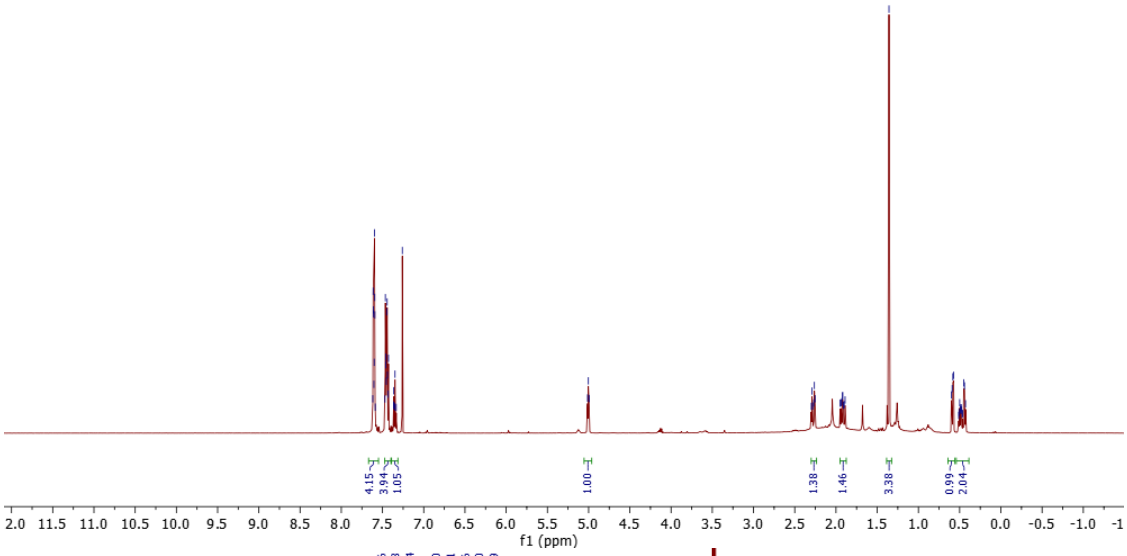


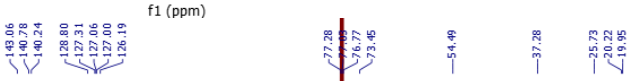
^{13}C NMR (125 MHz, $CDCl_3$)

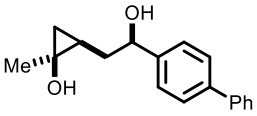




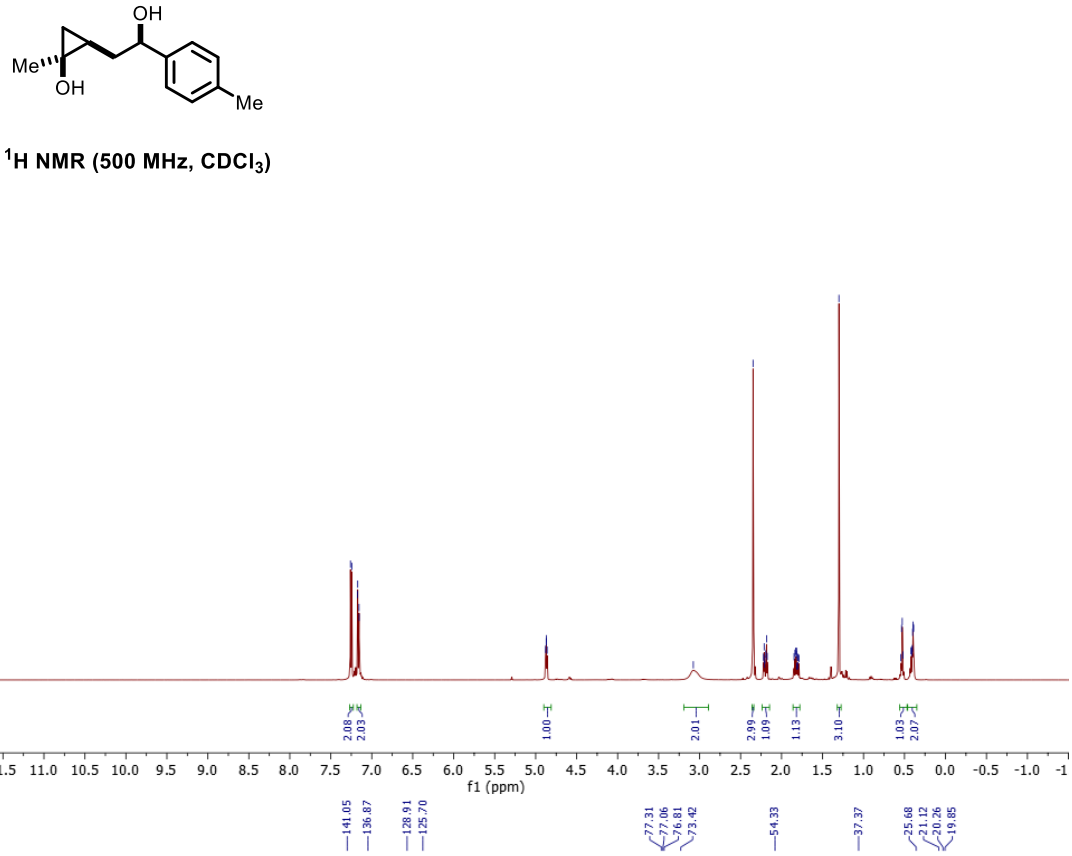
^{1}H NMR (500 MHz, $CDCl_3$)







^{13}C NMR (125 MHz, $CDCl_3$)



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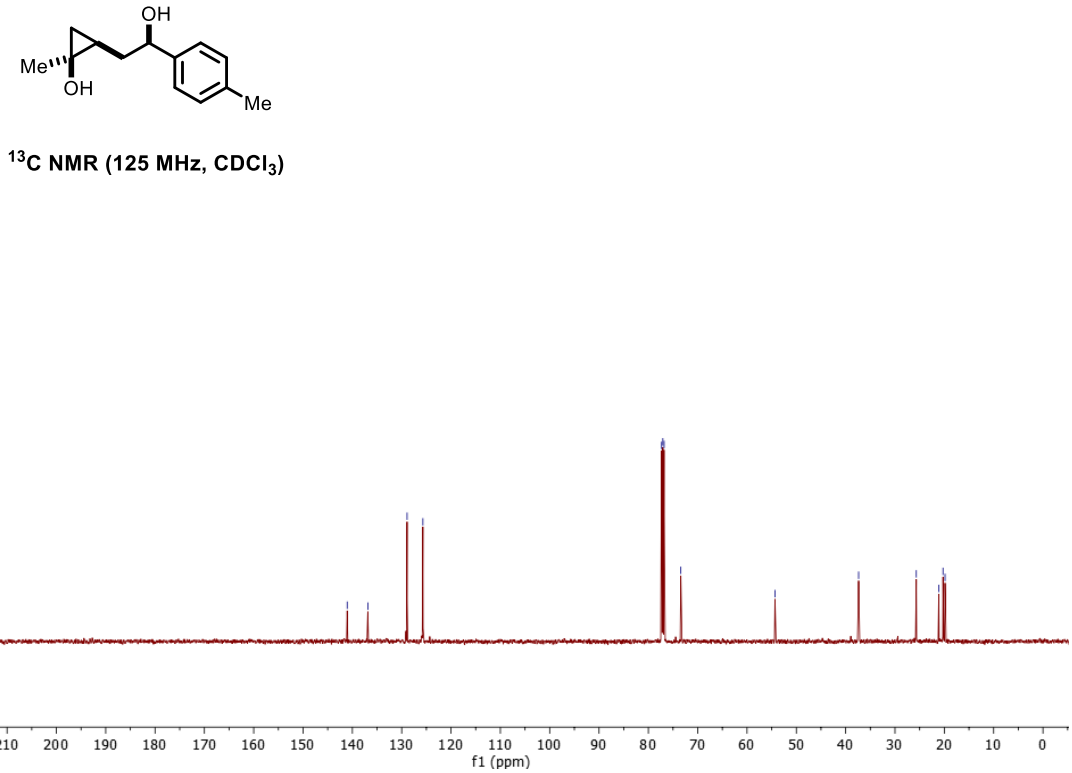
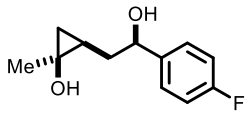


^{13}C NMR (125 MHz, $CDCl_3$)



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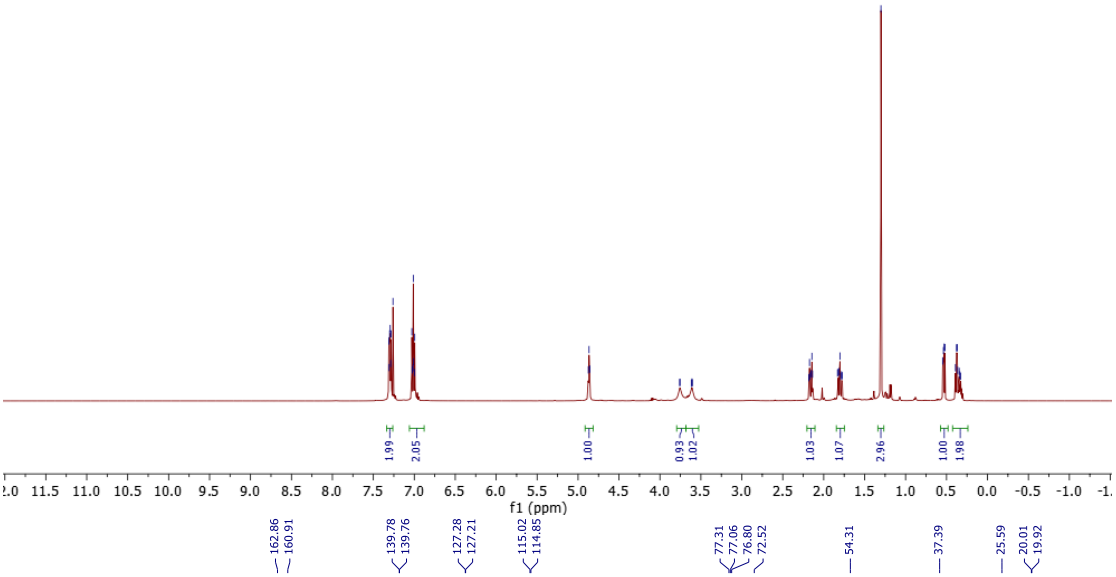
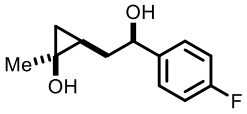
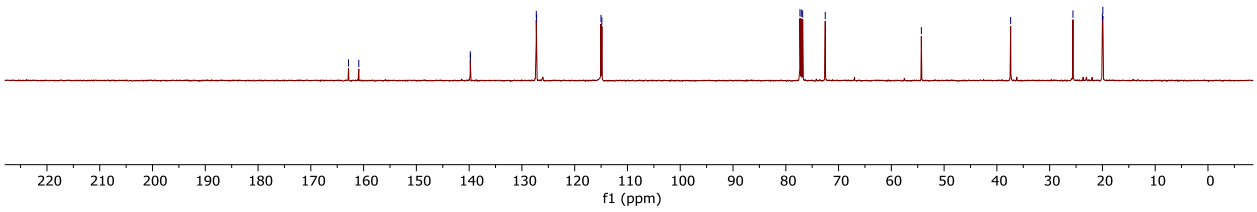
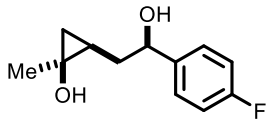


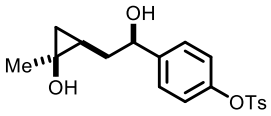


^{13}C NMR (125 MHz, $CDCl_3$)

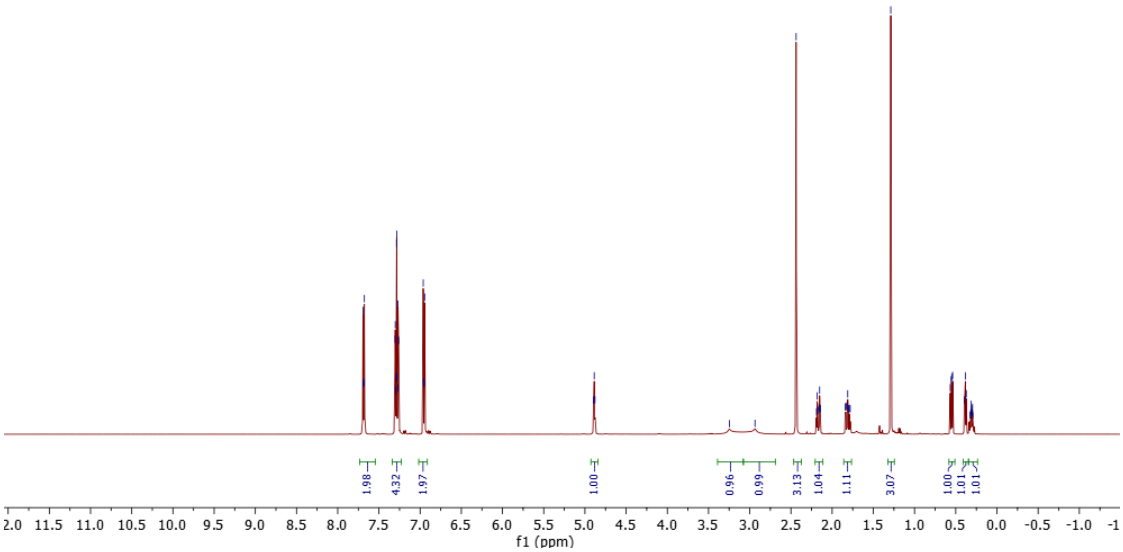


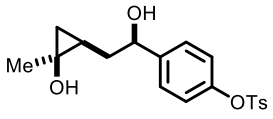


^{19}F NMR (471 MHz, $CDCl_3$)

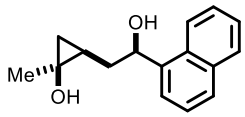


^{1}H NMR (500 MHz, $CDCl_3$)

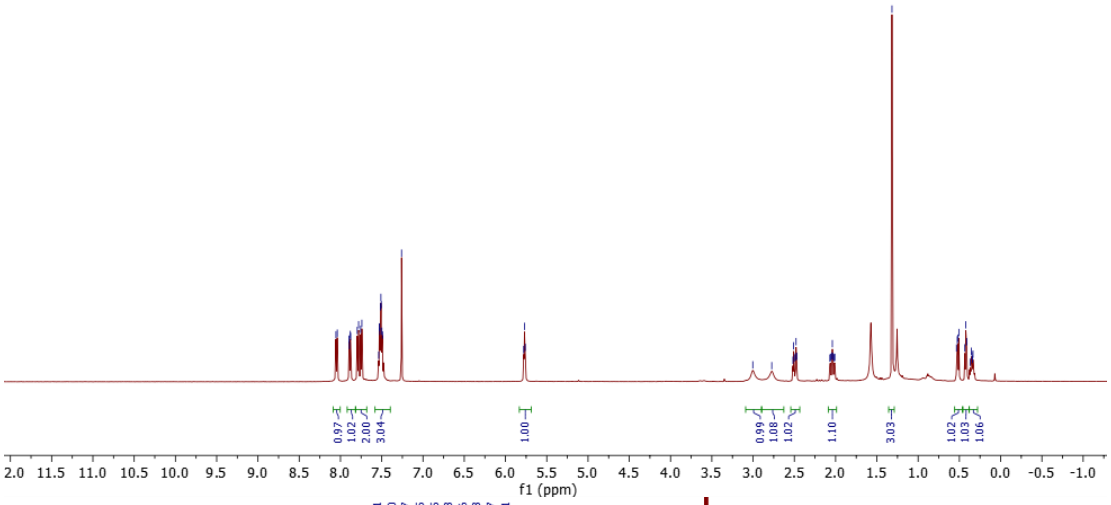


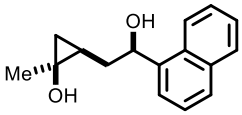


^{13}C NMR (125 MHz, $CDCl_3$)



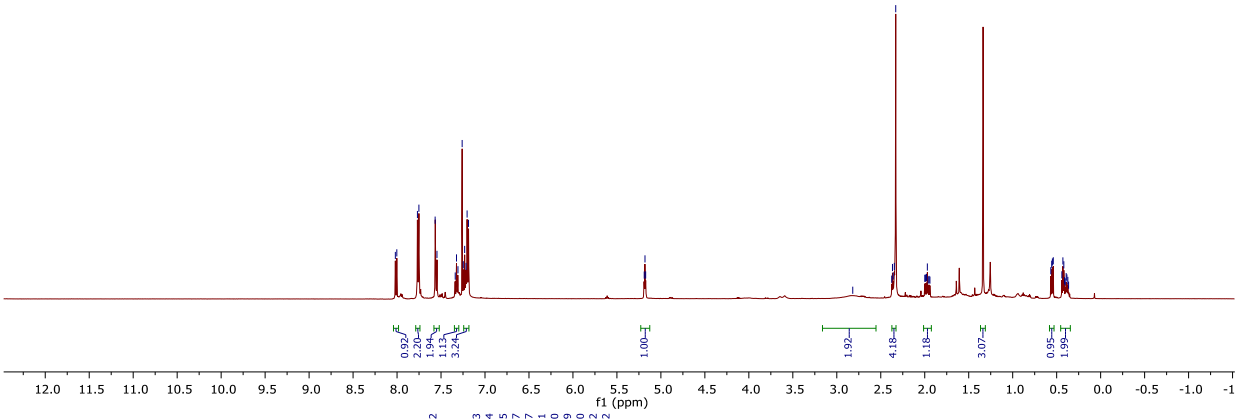
^{1}H NMR (500 MHz, $CDCl_3$)

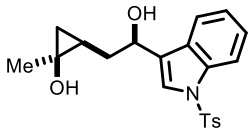




^{13}C NMR (125 MHz, $CDCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$)





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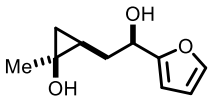

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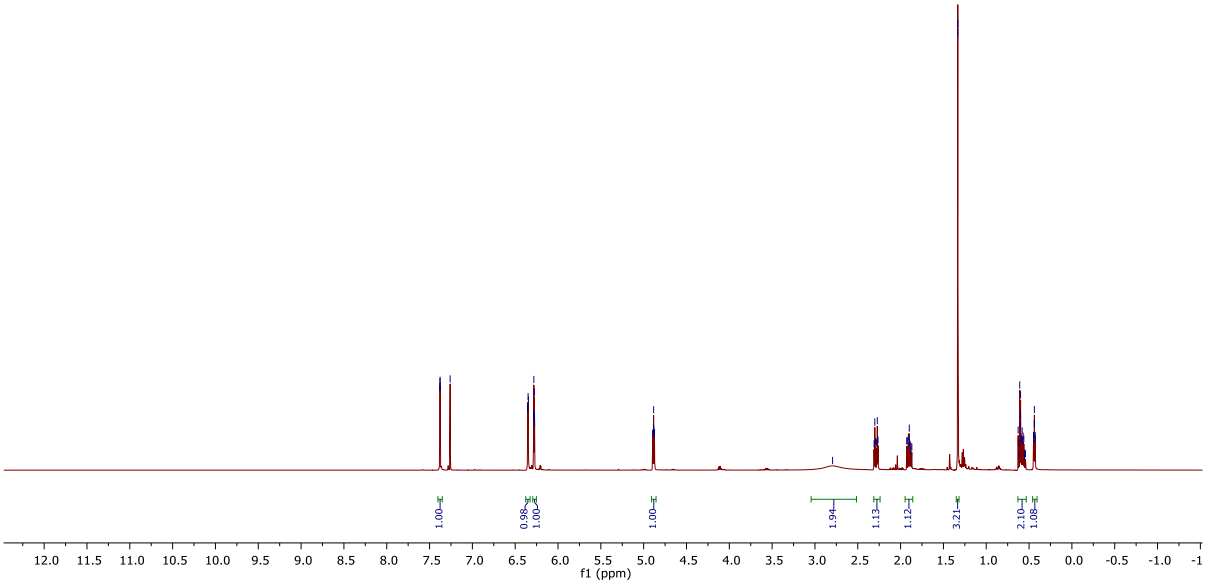

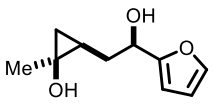

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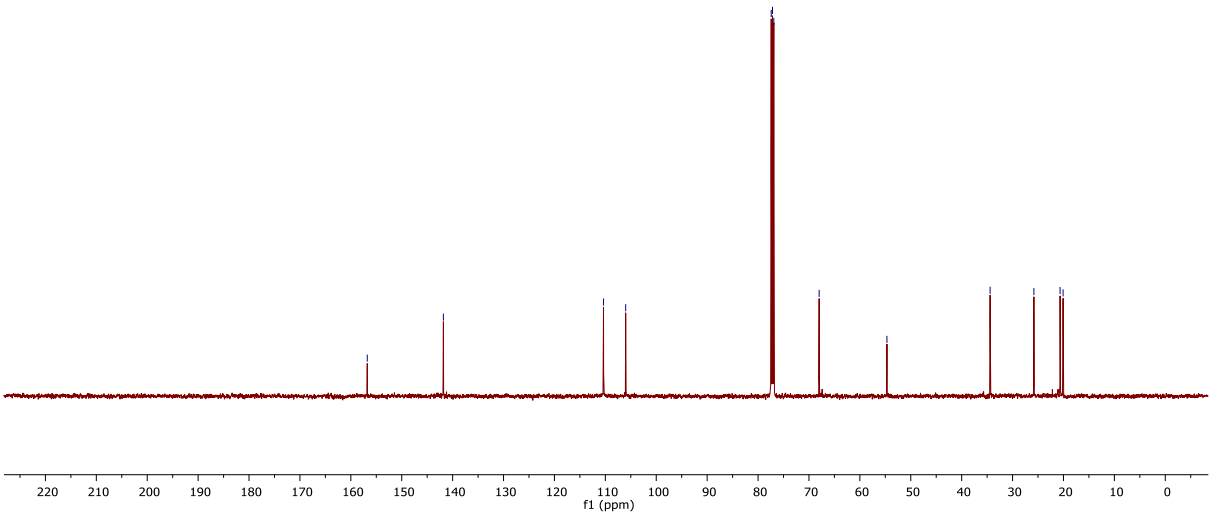

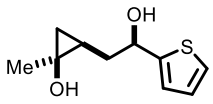

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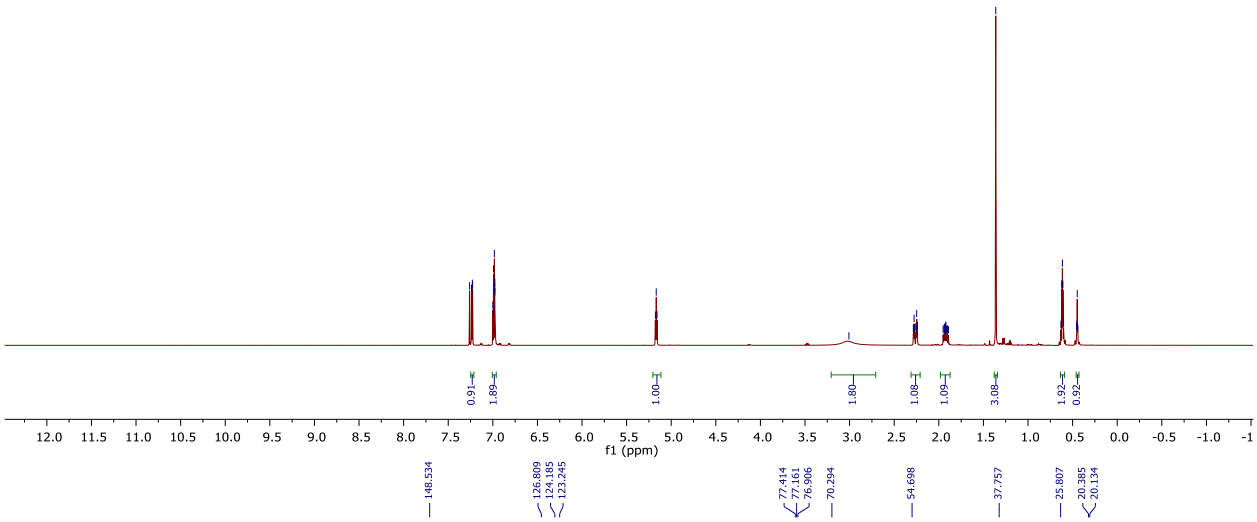

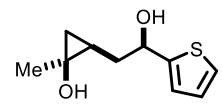

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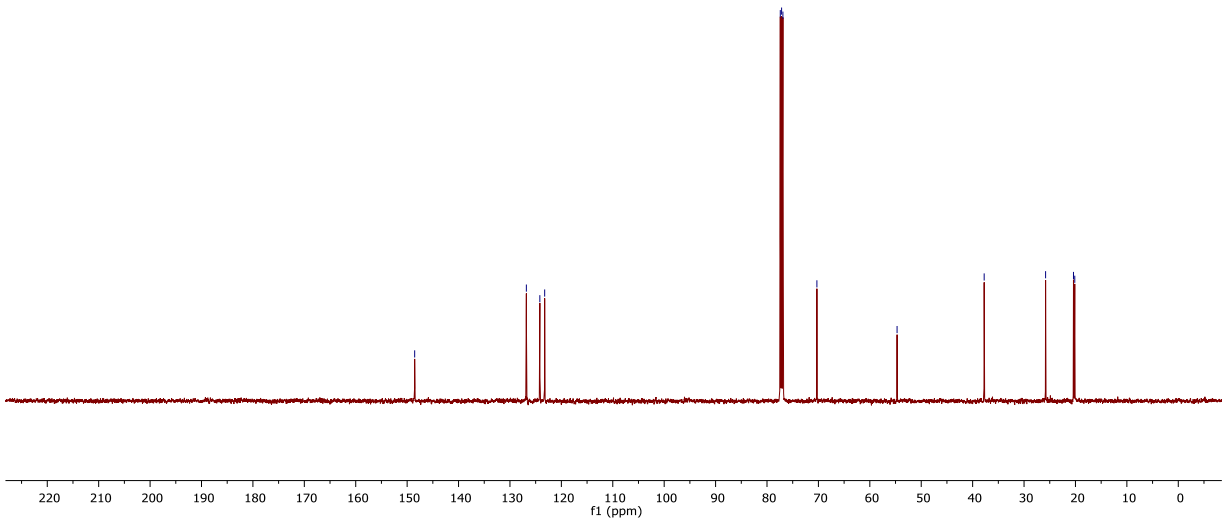

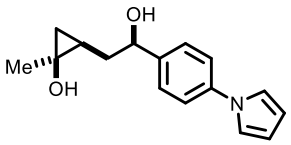

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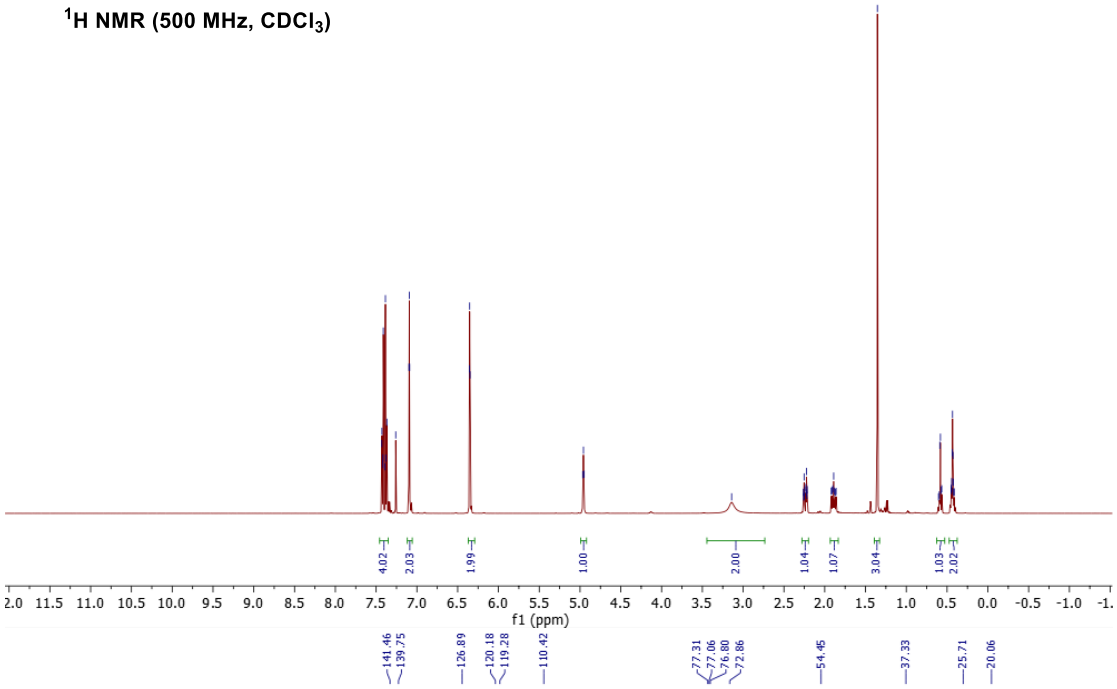

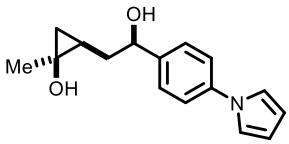

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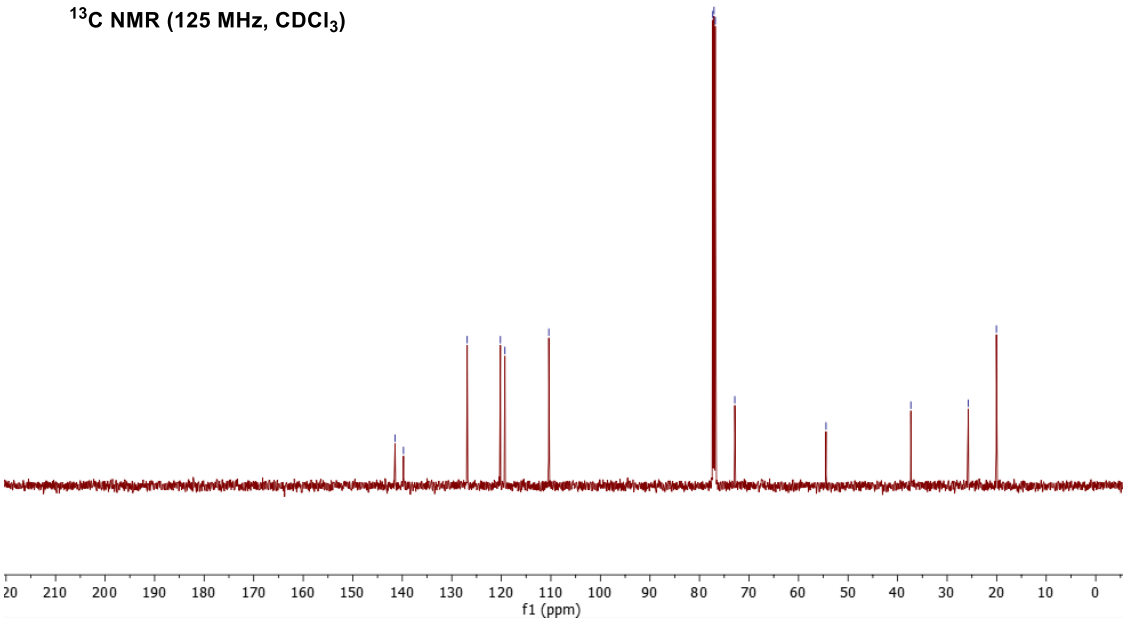

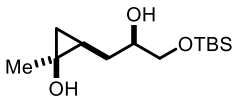

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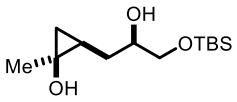

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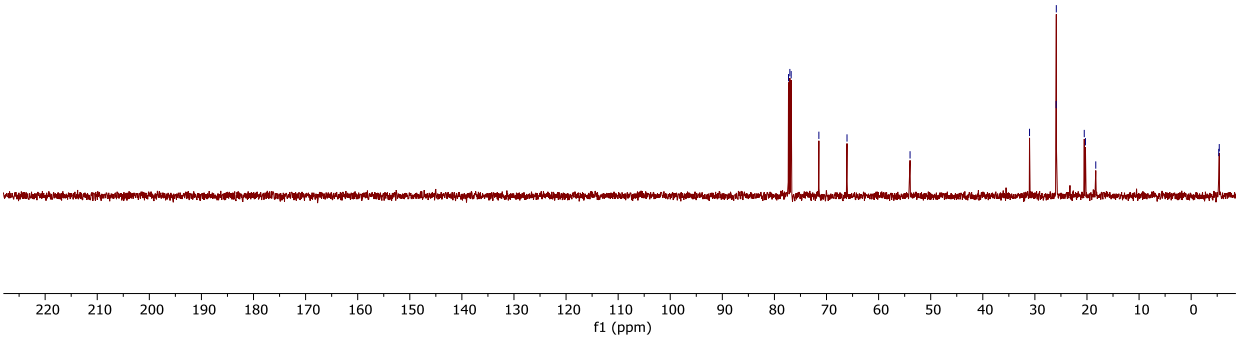

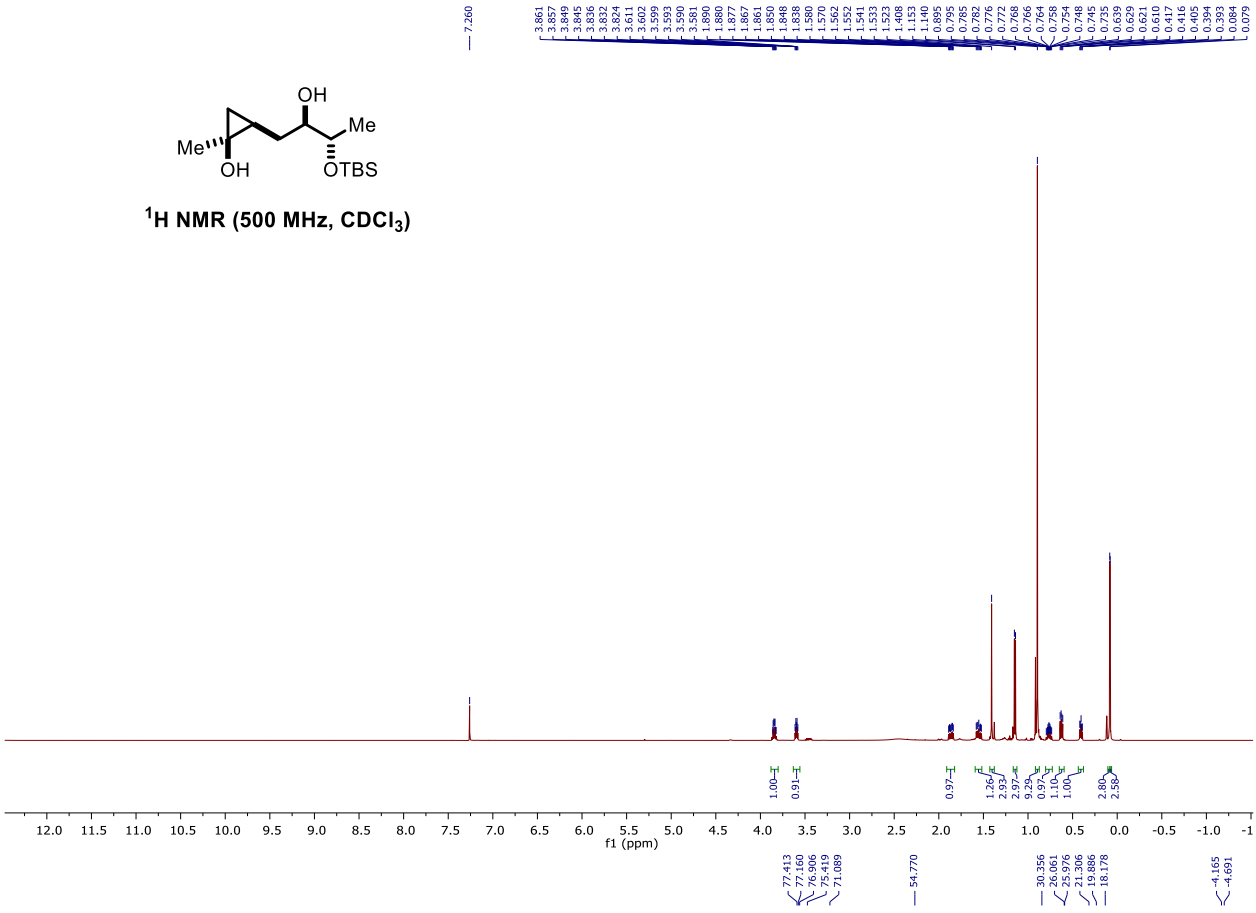

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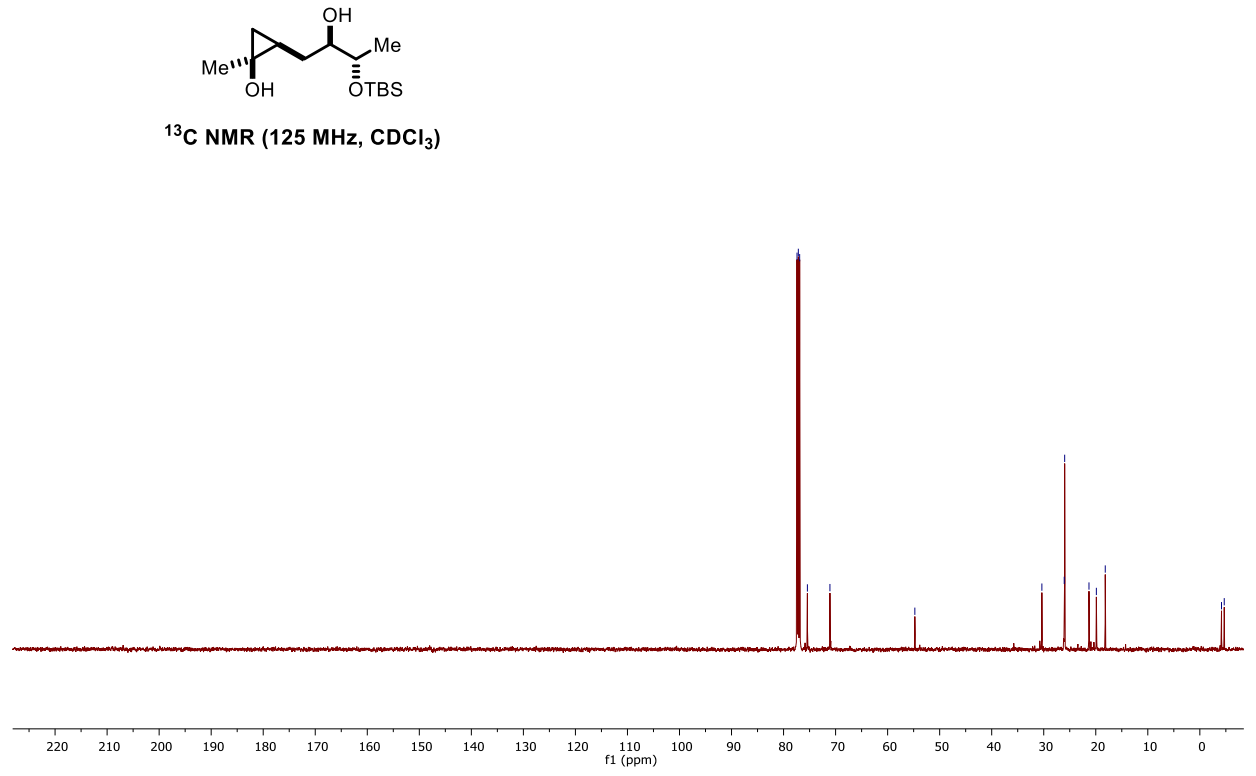

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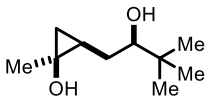
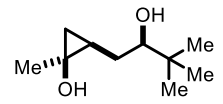


^{1}H NMR (500 MHz, $CDCl_3$)



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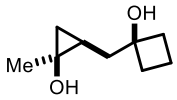

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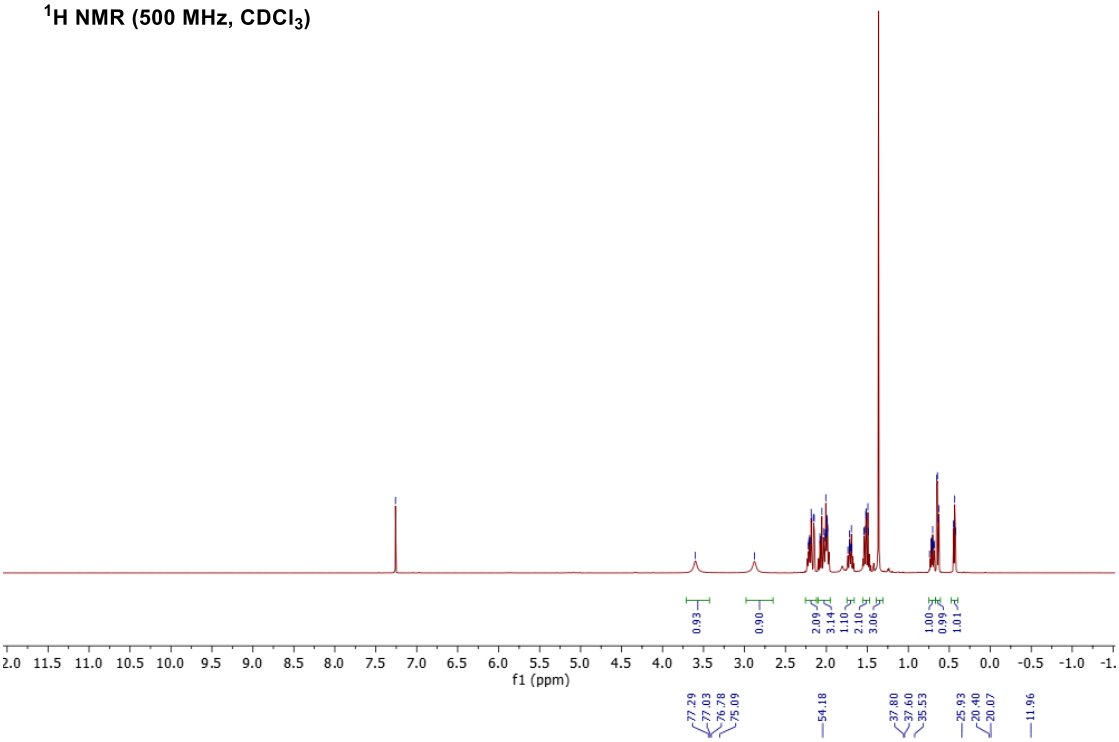

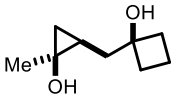

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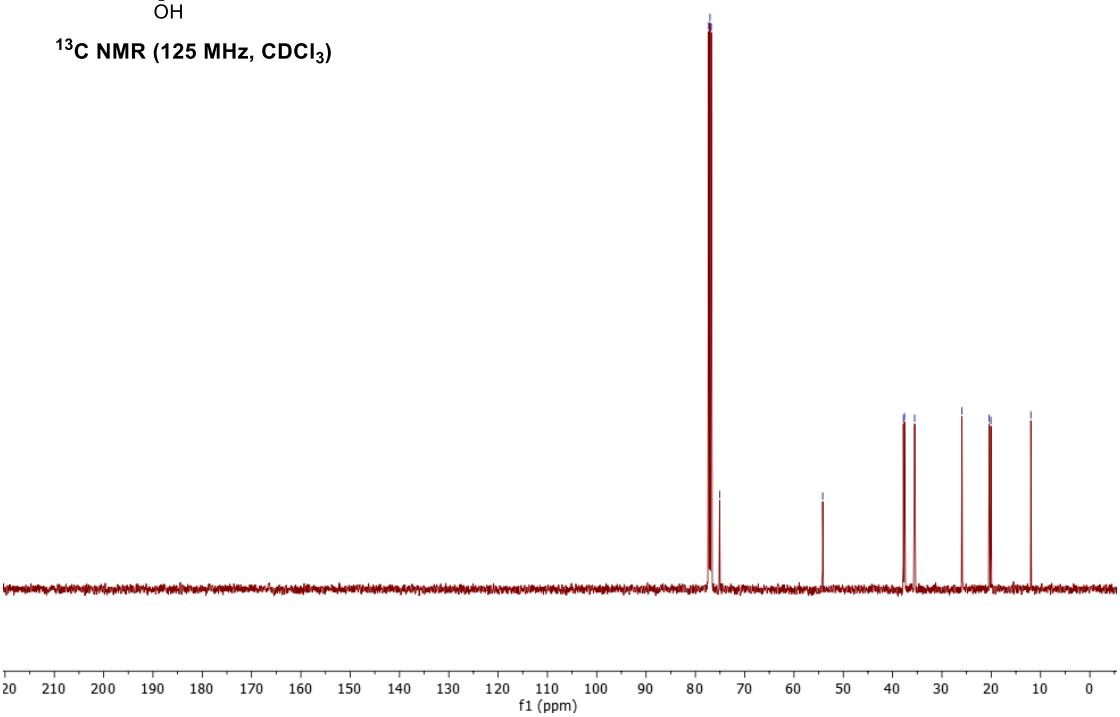

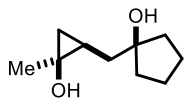

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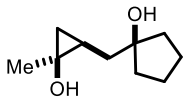

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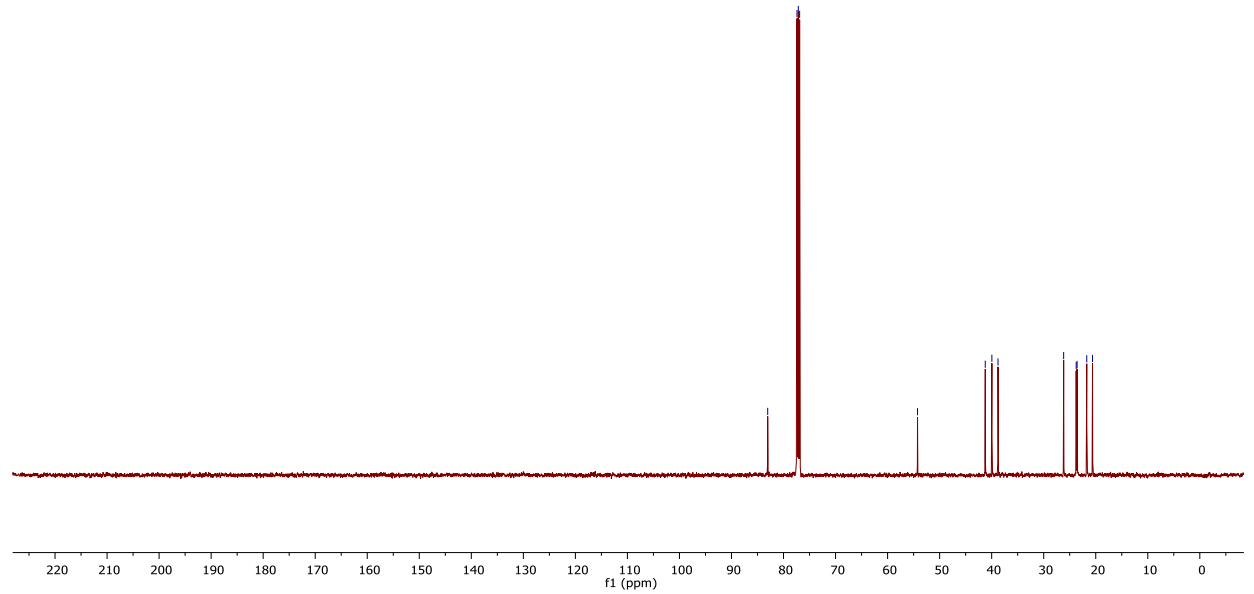

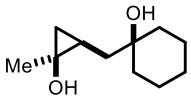

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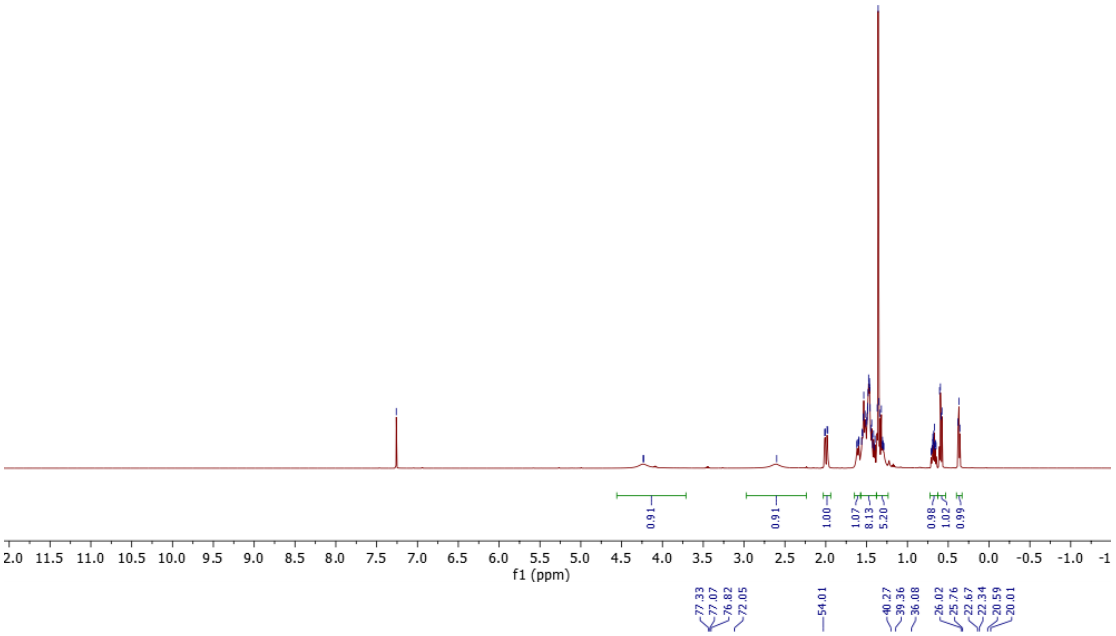
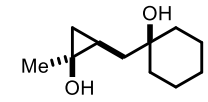
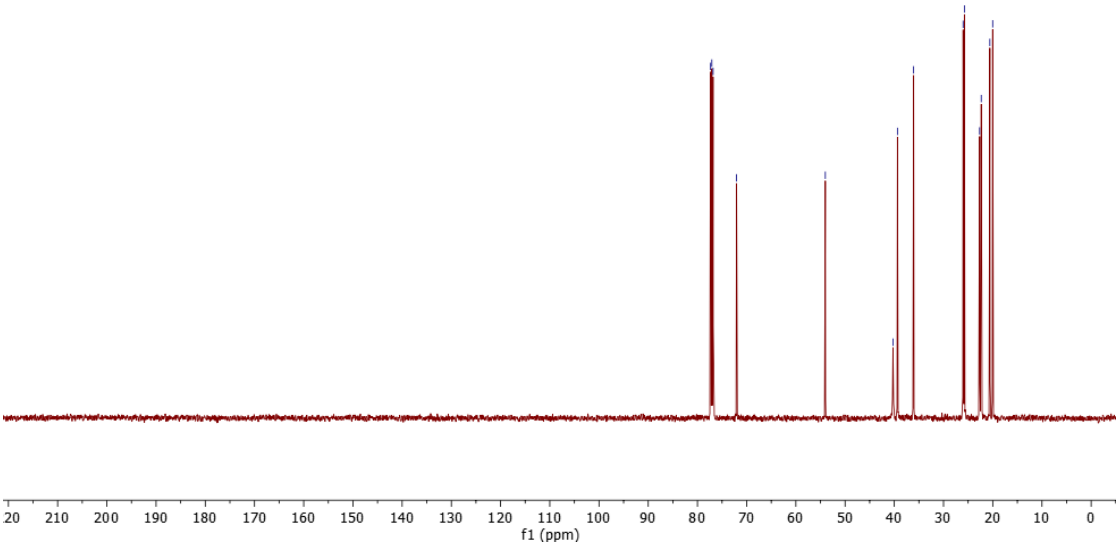
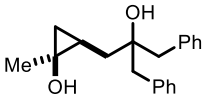




^{13}C NMR (125 MHz, $CDCl_3$)





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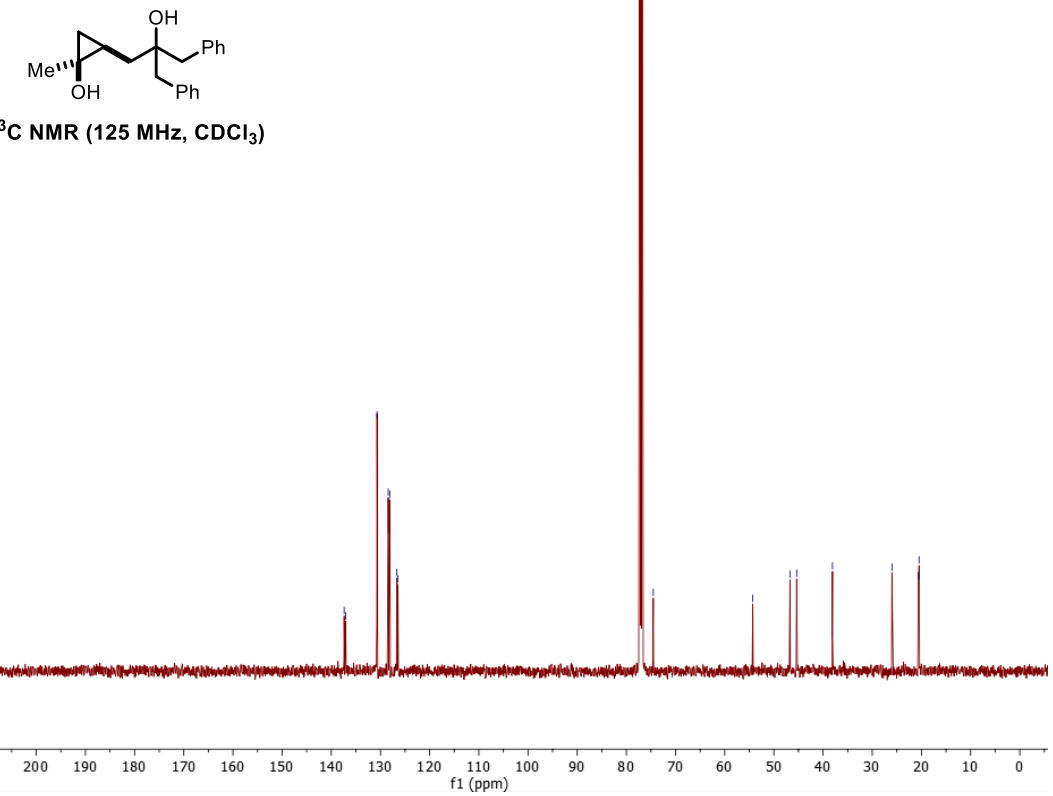

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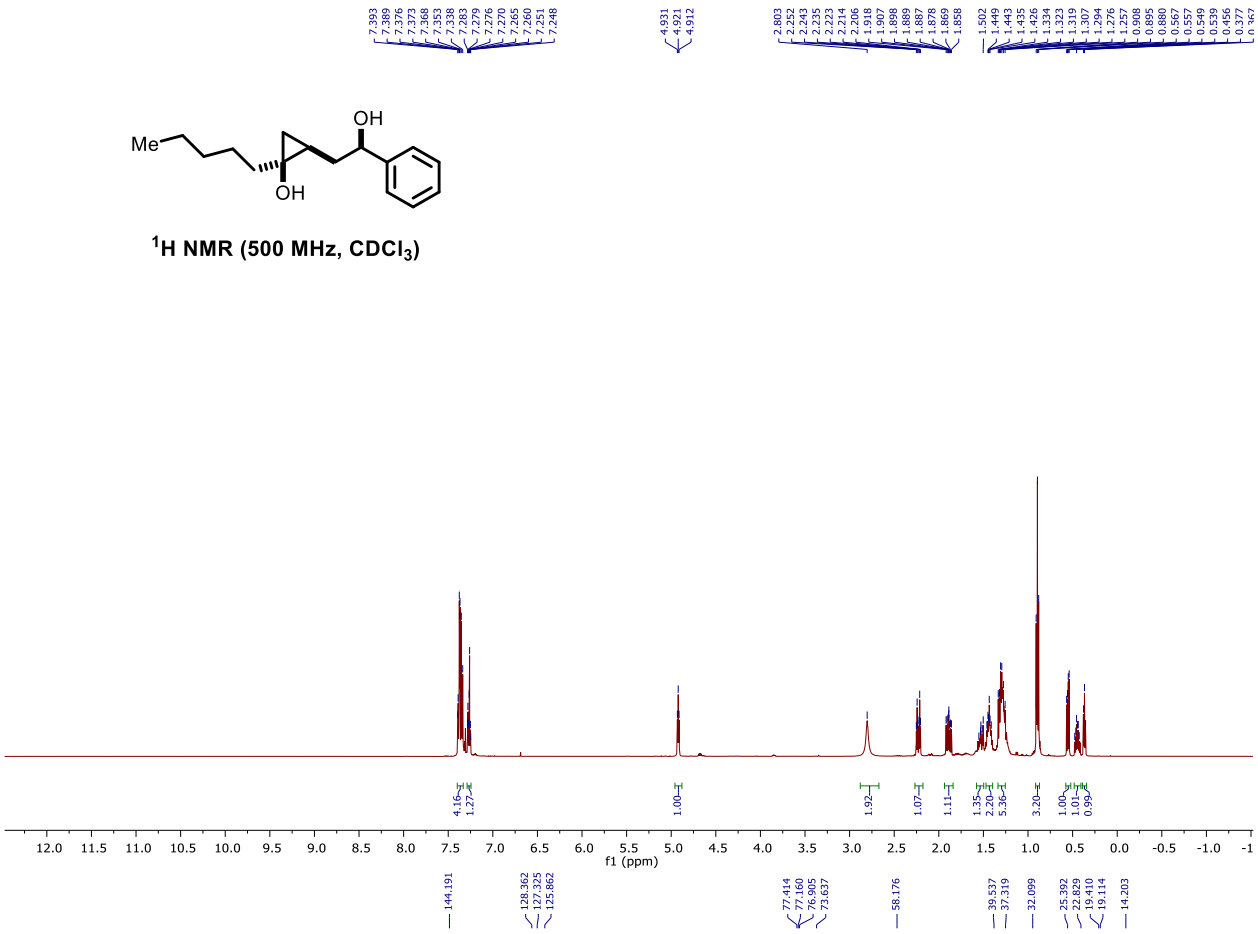

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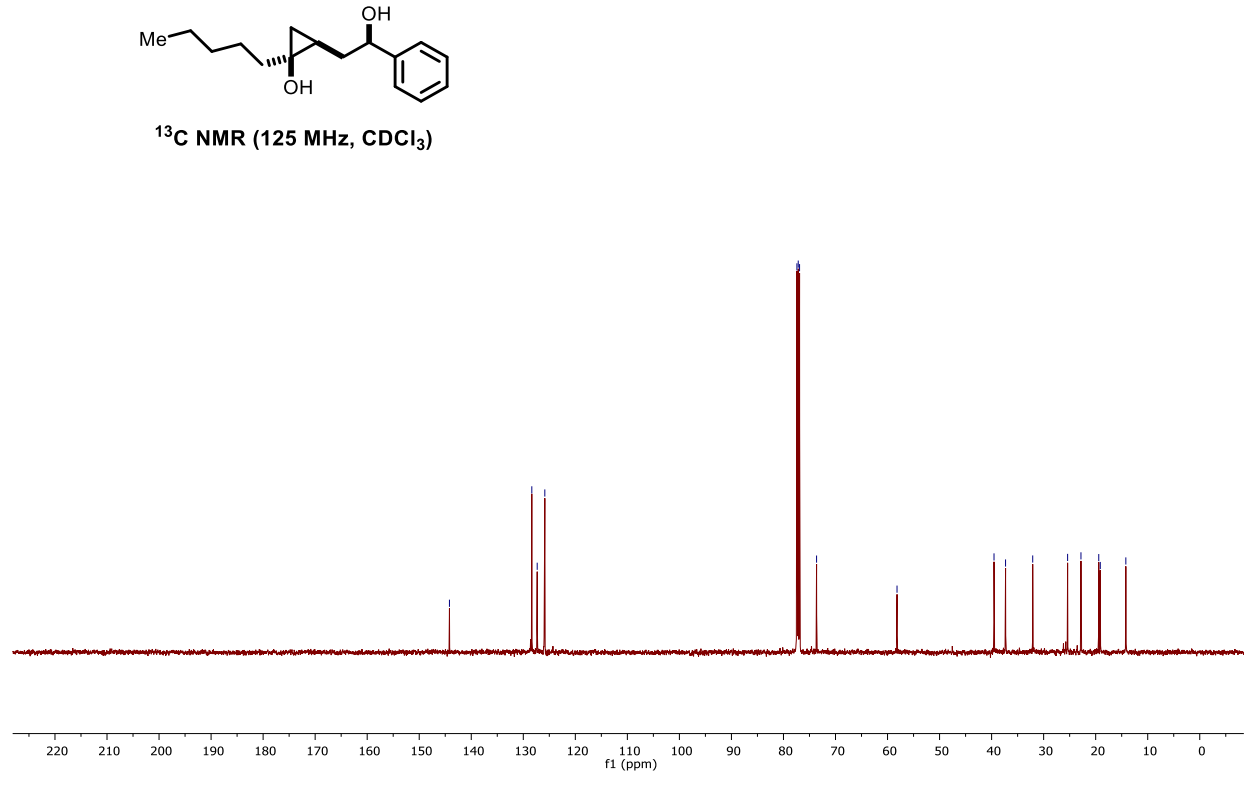

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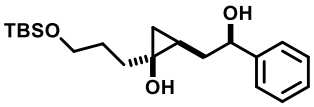
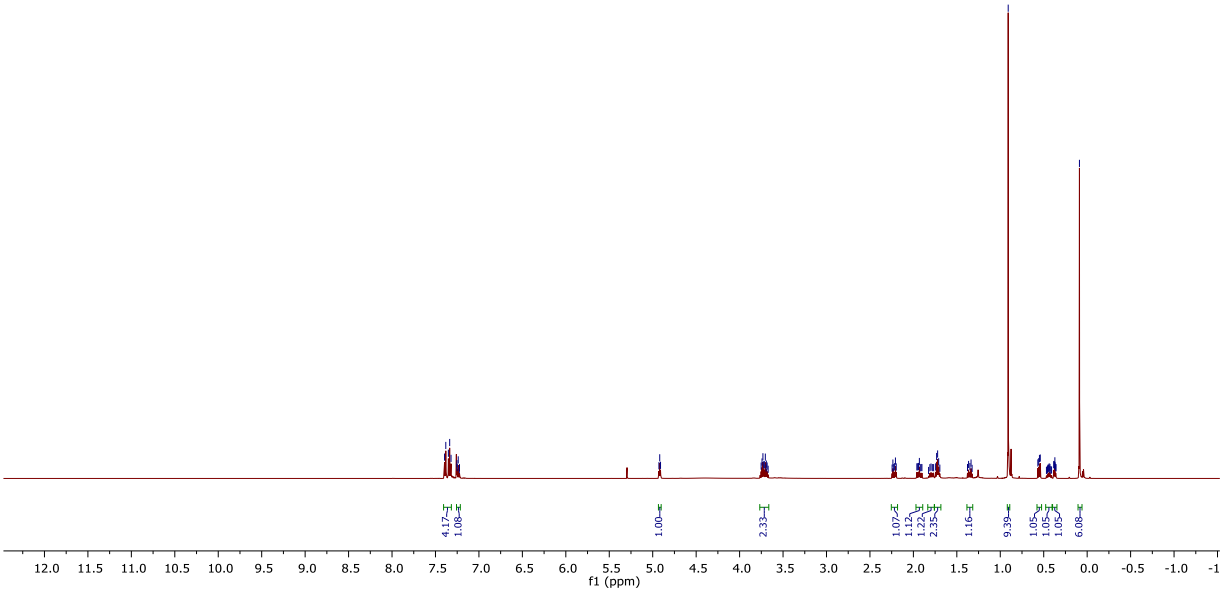
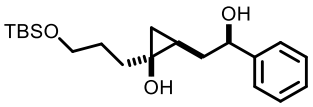
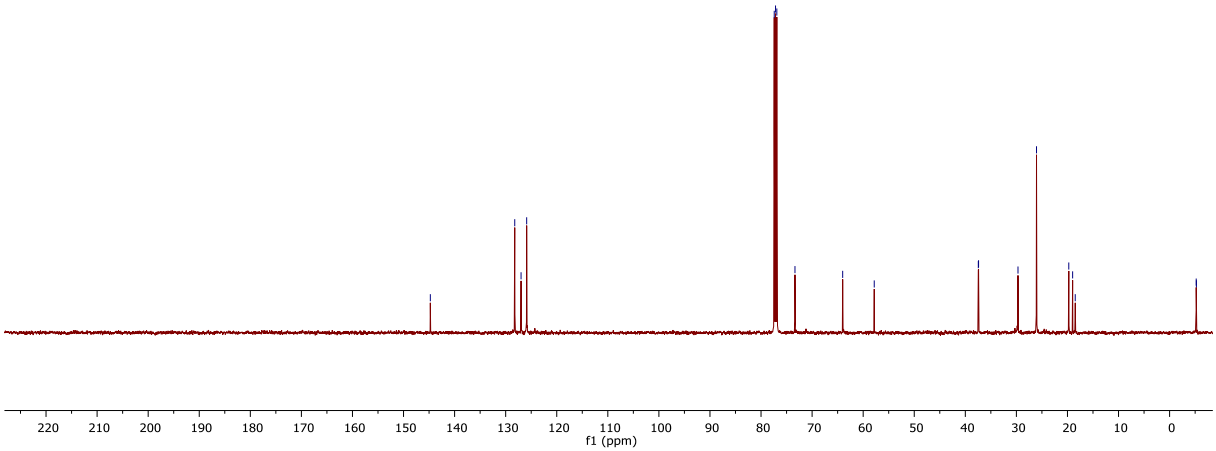


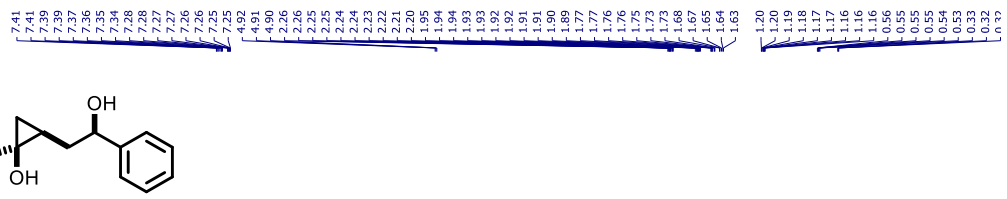
^{1}H NMR (500 MHz, $CDCl_3$)





^{13}C NMR (125 MHz, $CDCl_3$)





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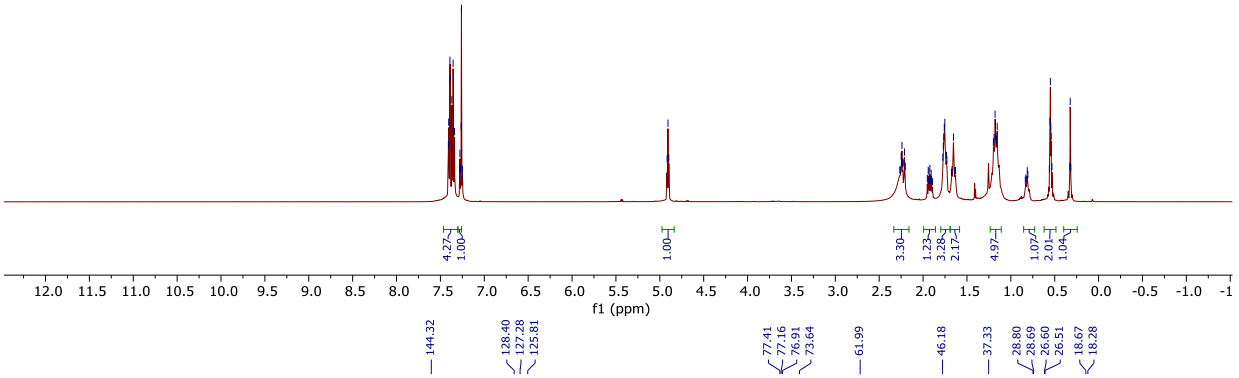

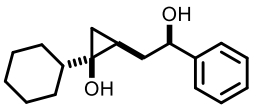

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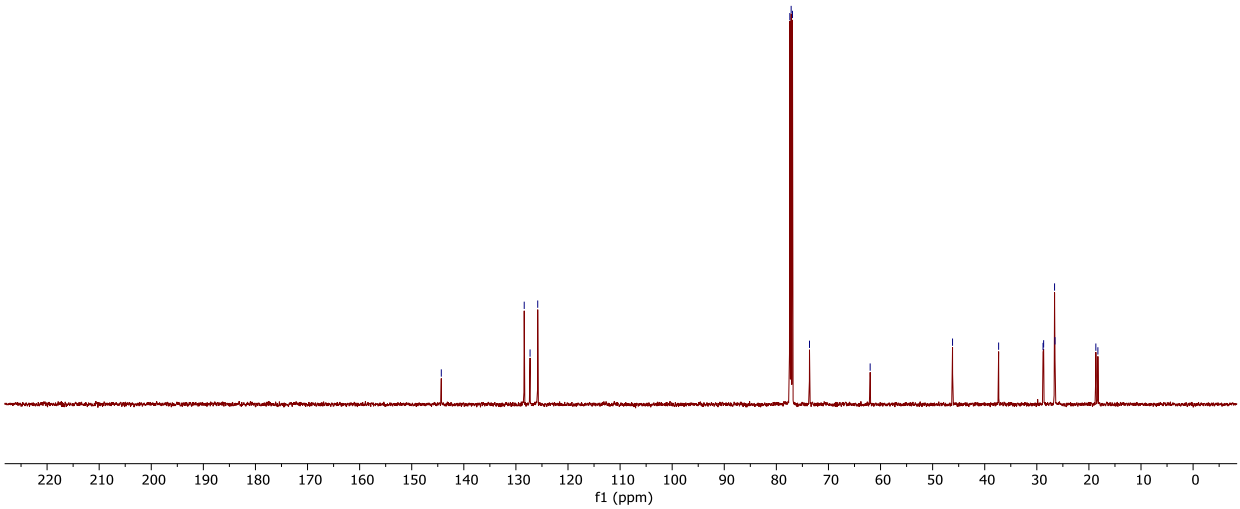
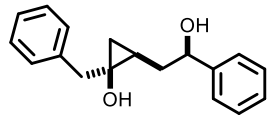
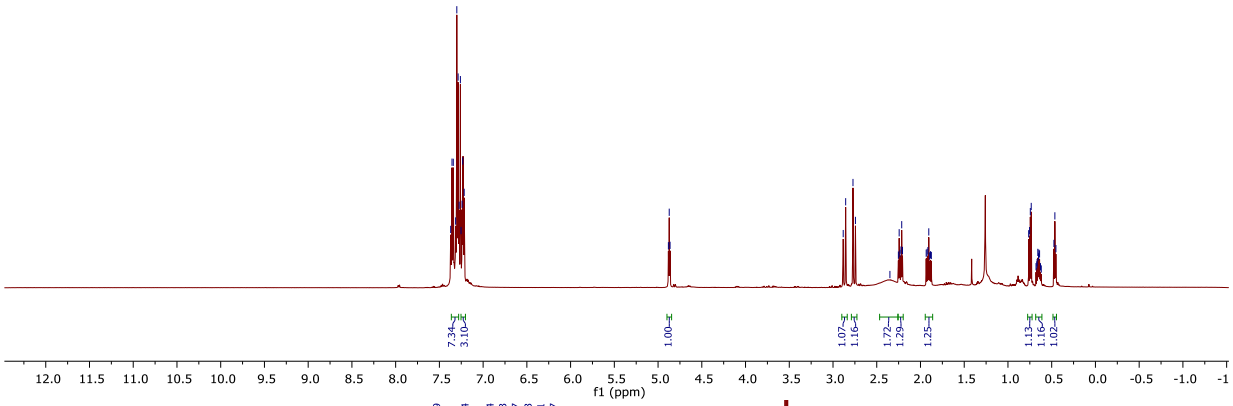
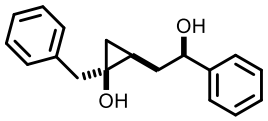


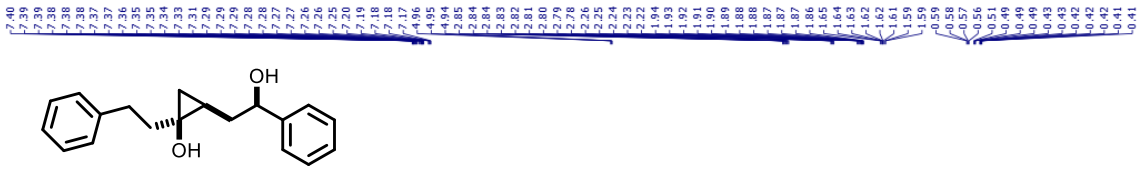


^{1}H NMR (500 MHz, $CDCl_3$)





^{13}C NMR (125 MHz, $CDCl_3$)



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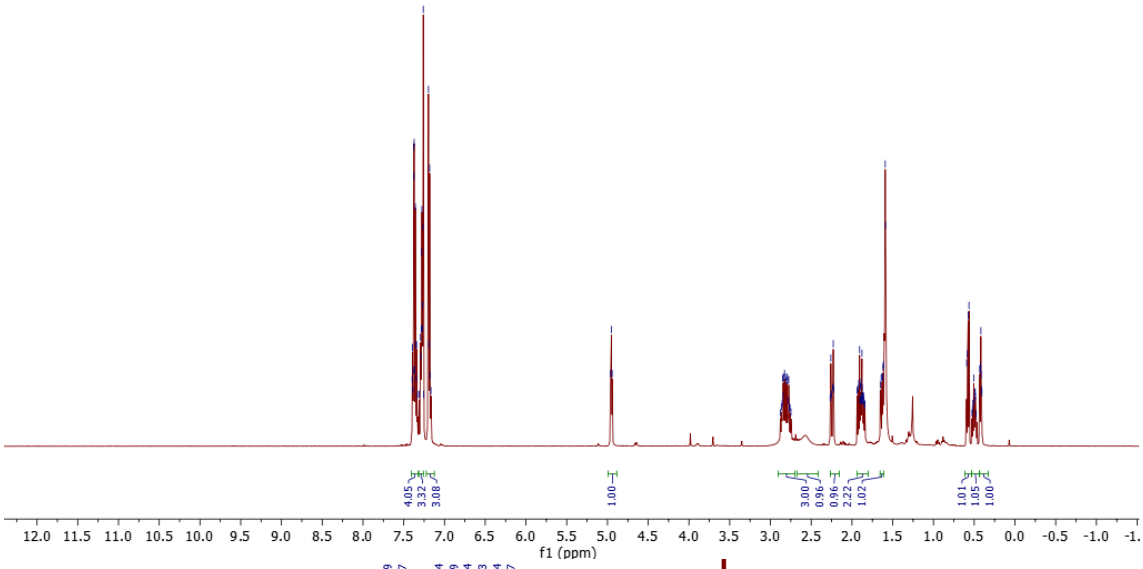

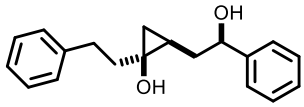

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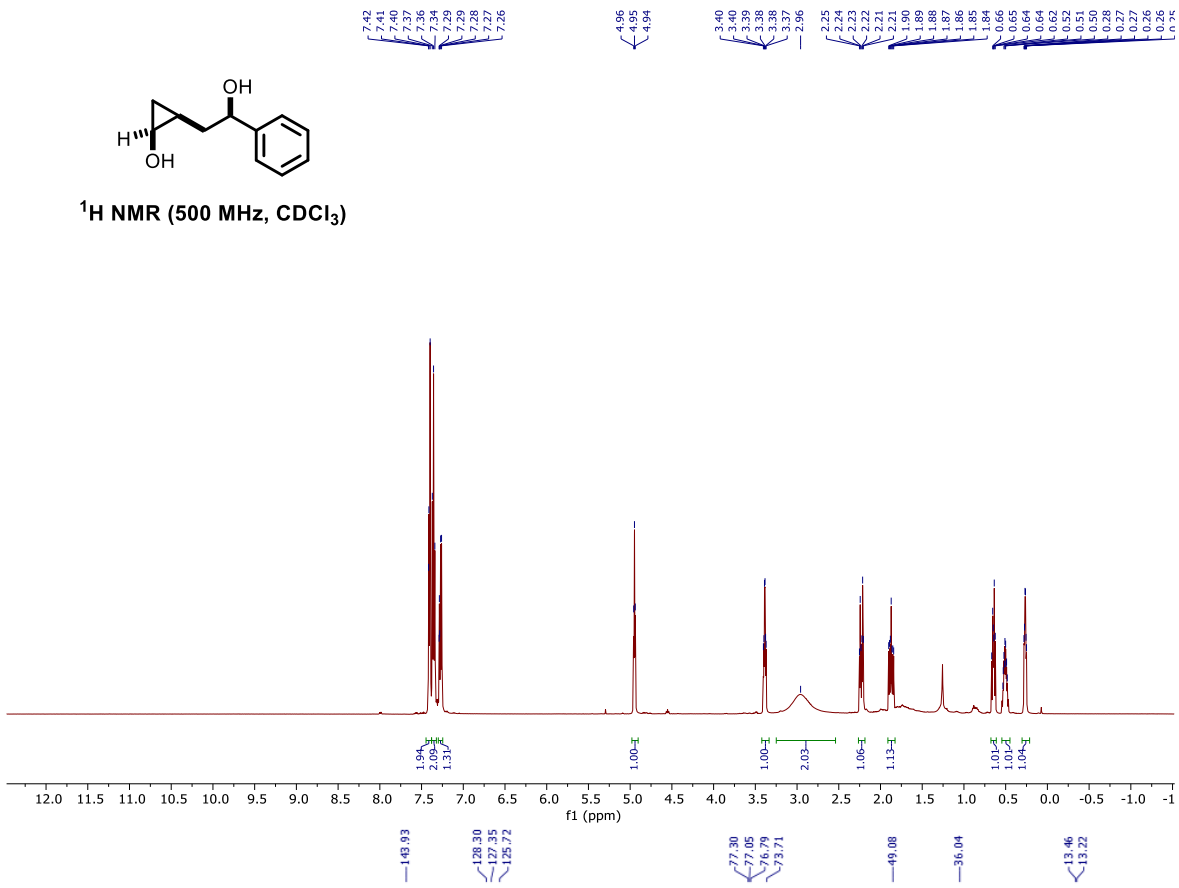

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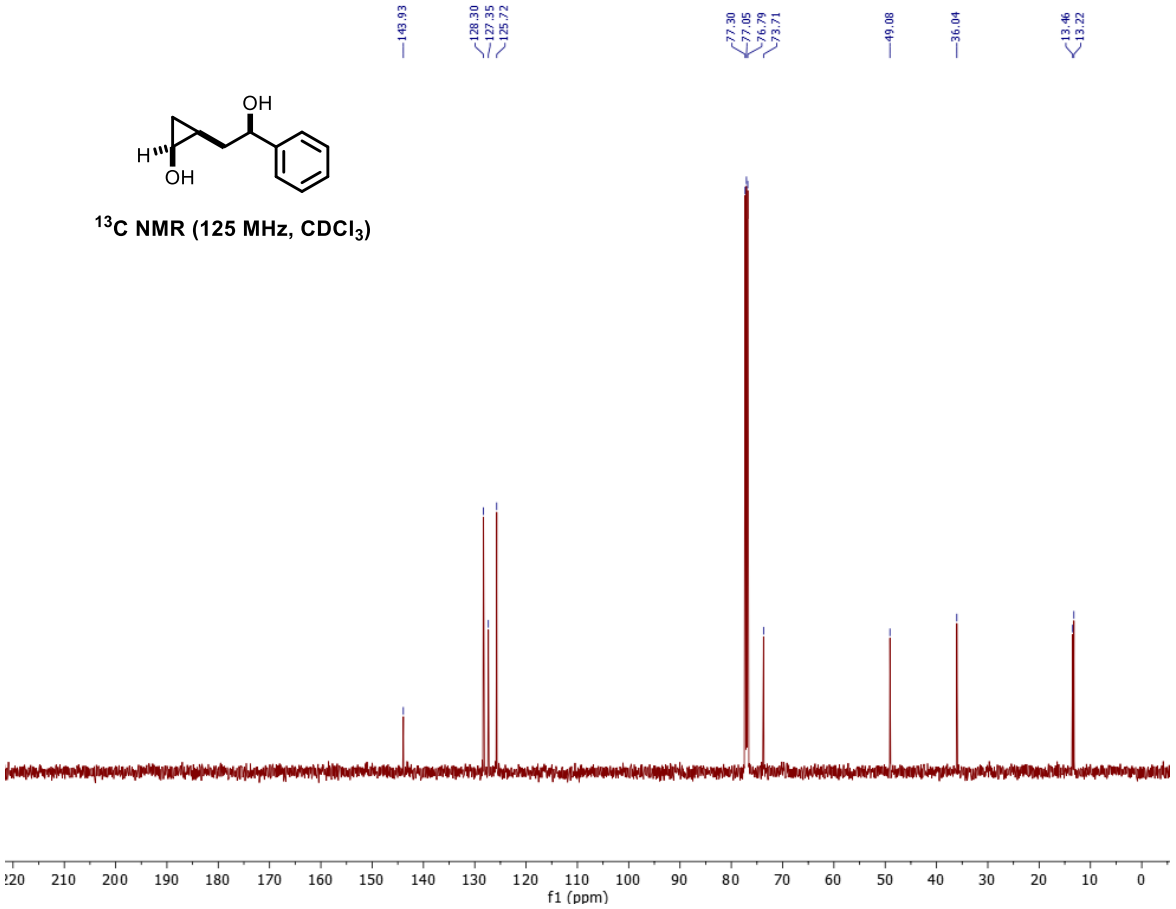

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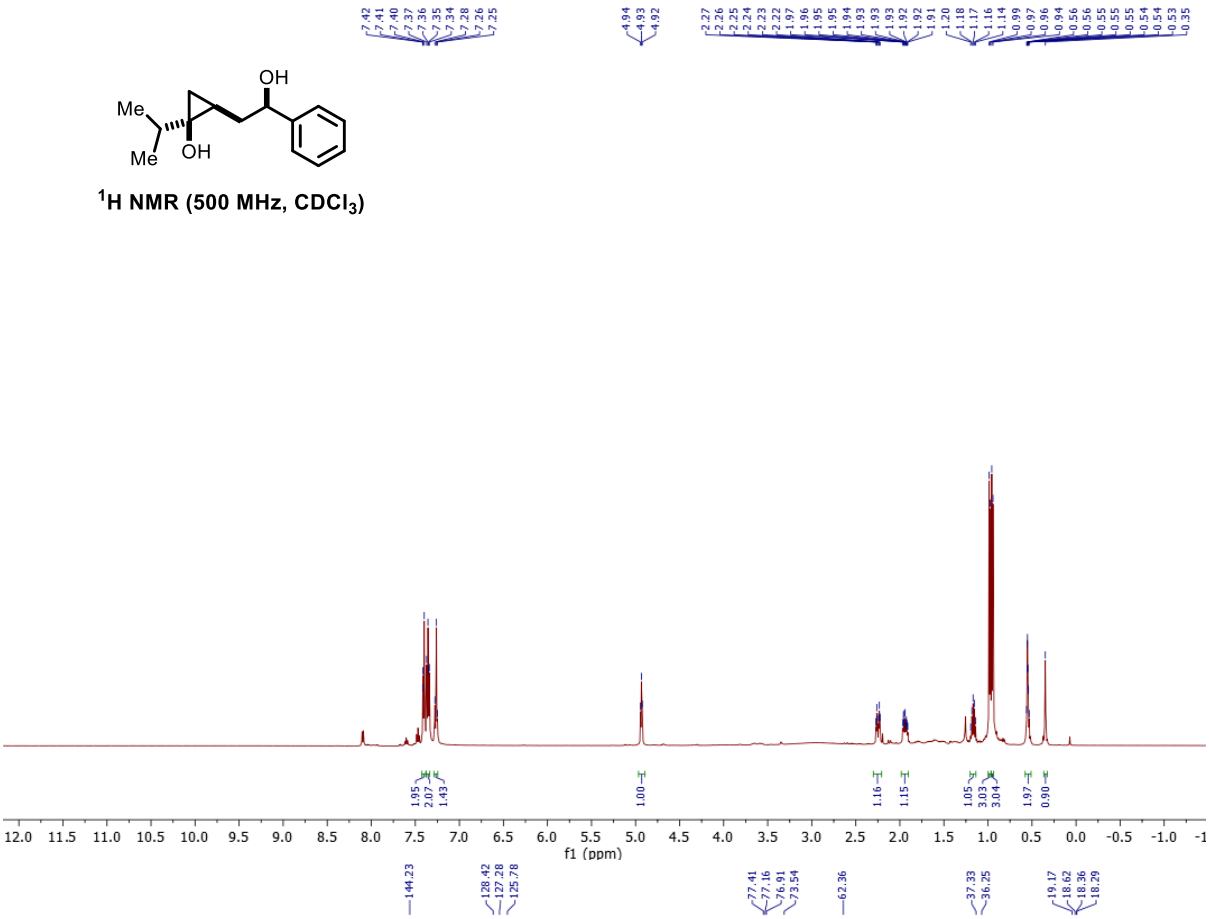
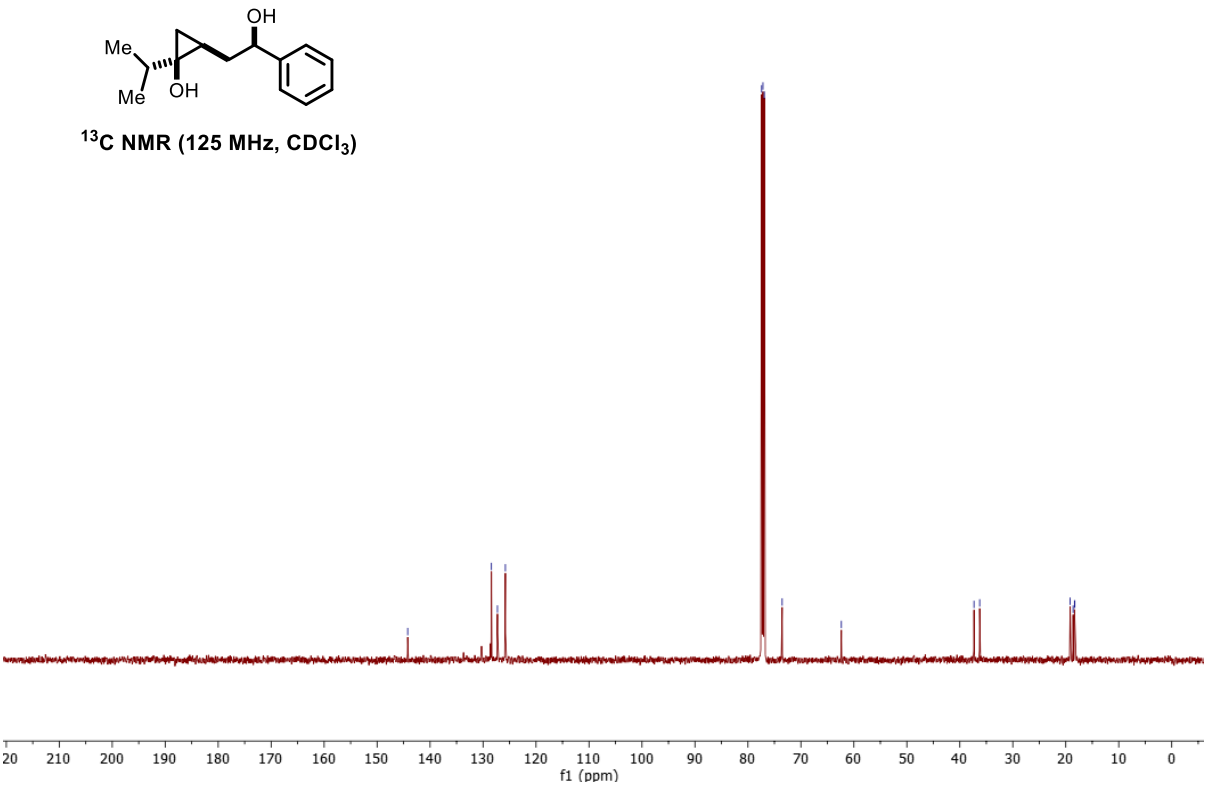
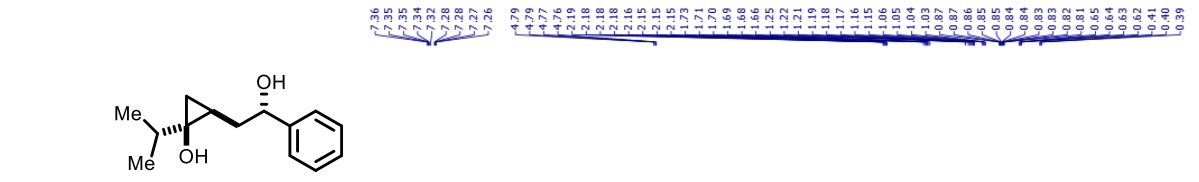


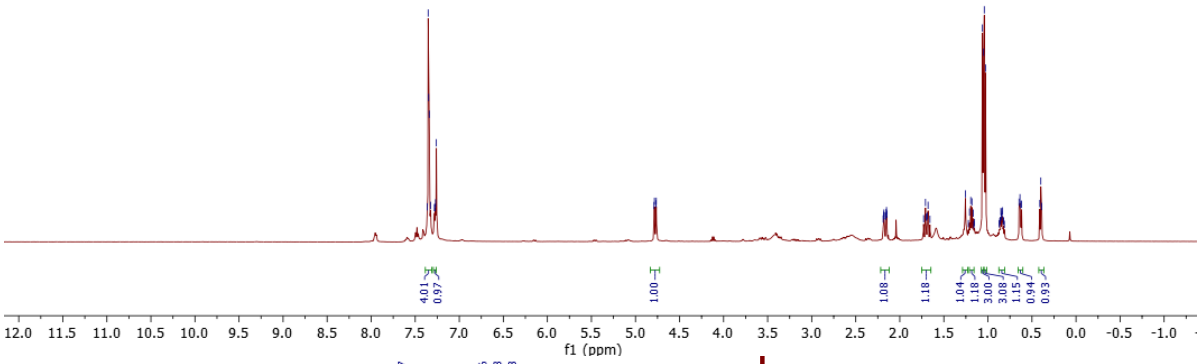
^{1}H NMR (500 MHz, $CDCl_3$)

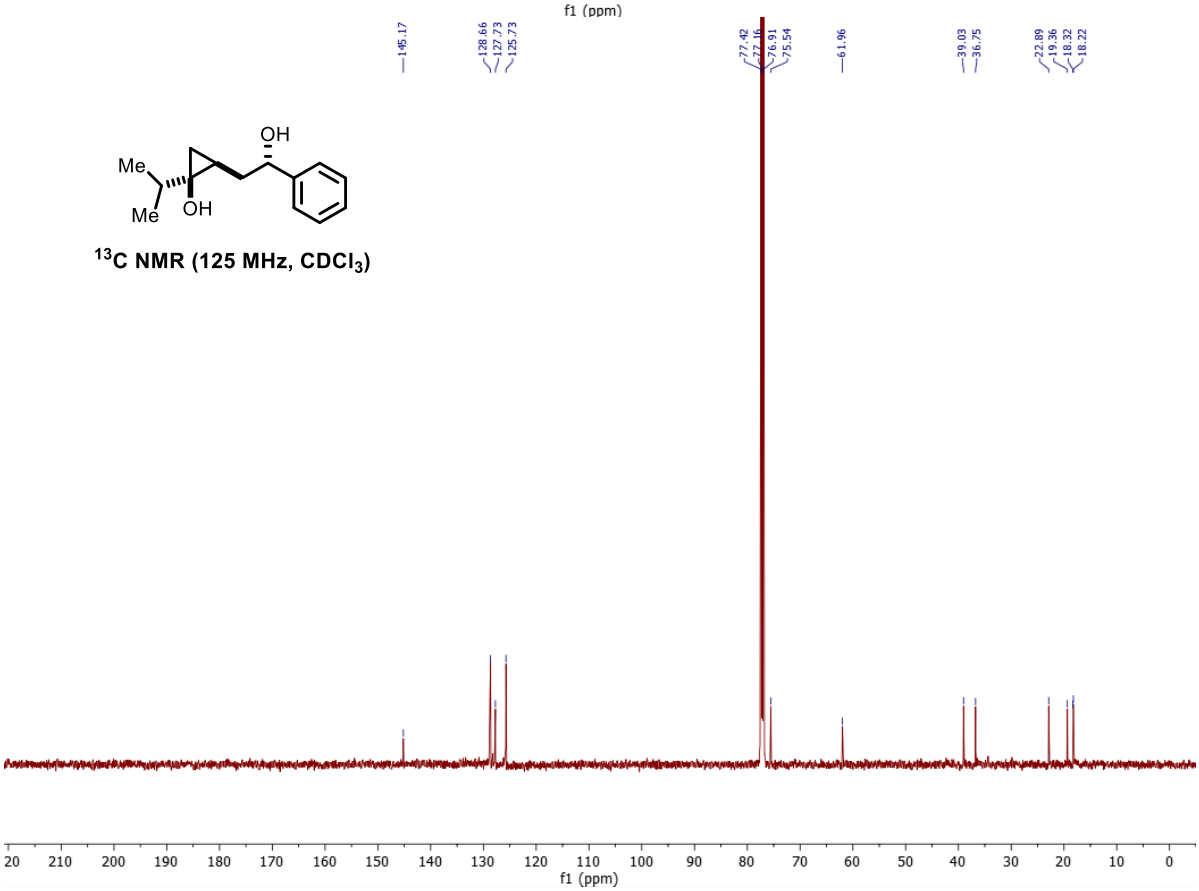


^{13}C NMR (125 MHz, $CDCl_3$)

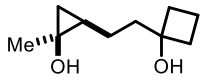


^{1}H NMR (500 MHz, $CDCl_3$)

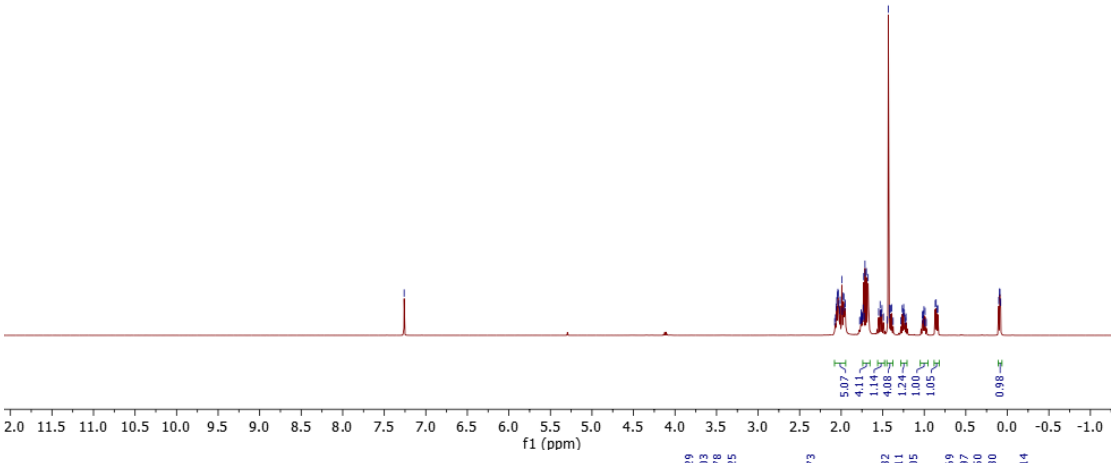


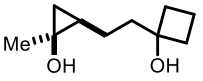


^{13}C NMR (125 MHz, $CDCl_3$)

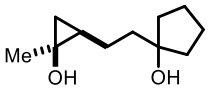


^{1}H NMR (500 MHz, $CDCl_3$)

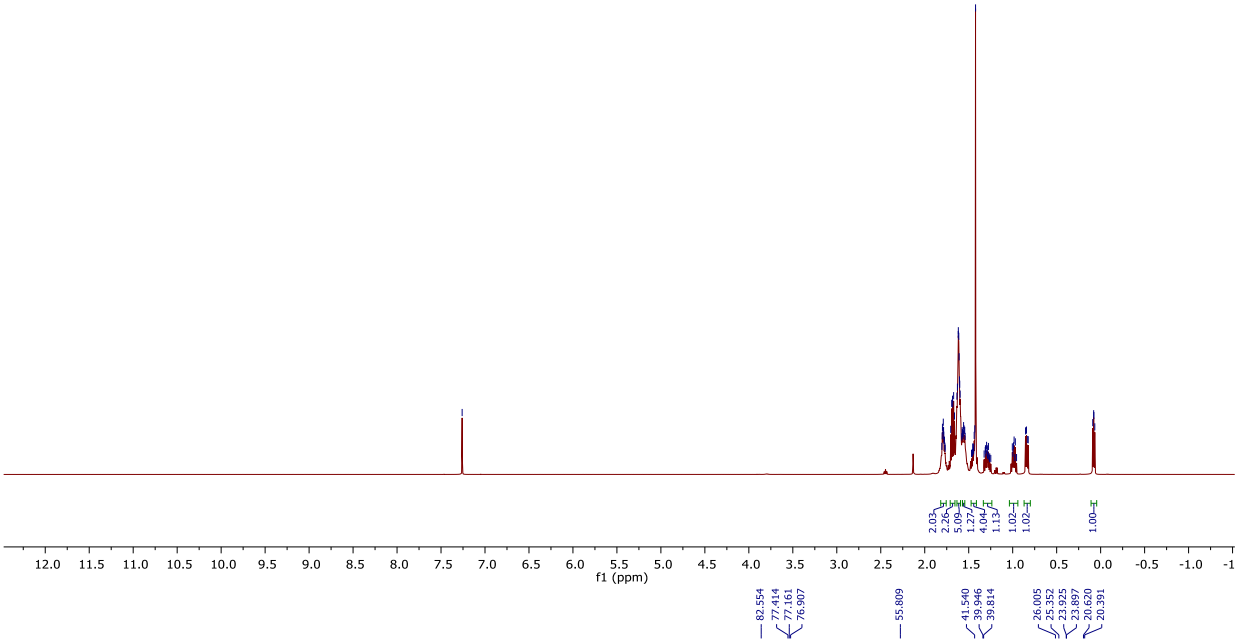


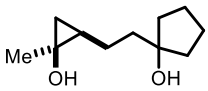


^{13}C NMR (125 MHz, $CDCl_3$)

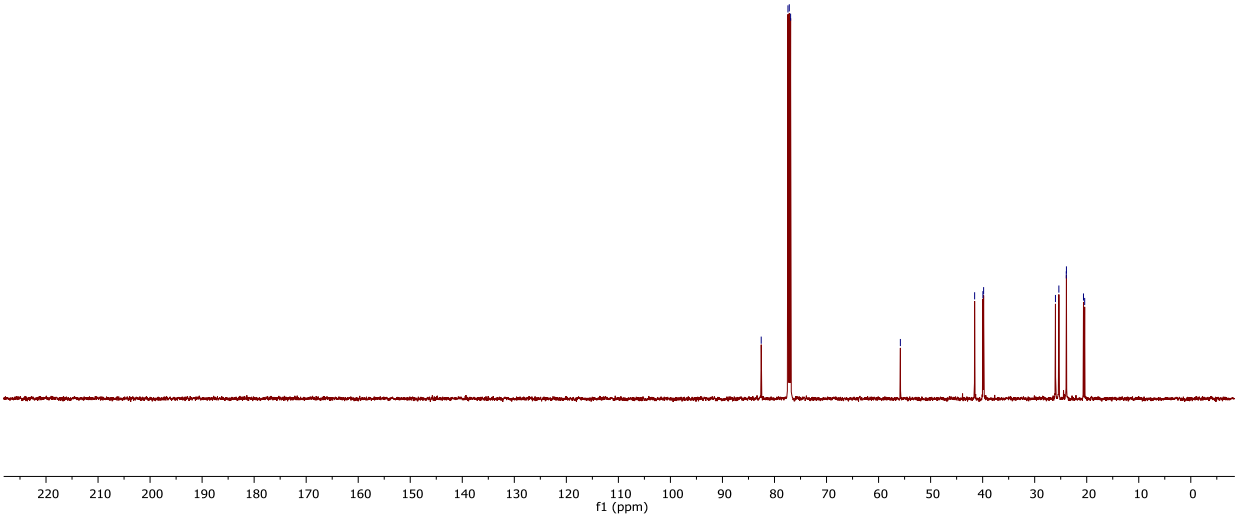


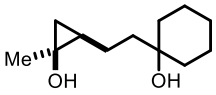
^{1}H NMR (500 MHz, $CDCl_3$)



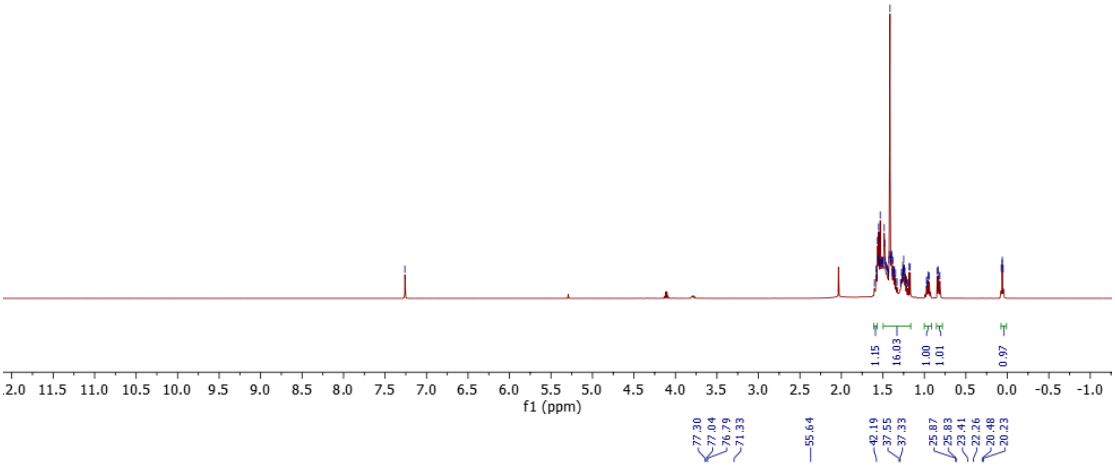


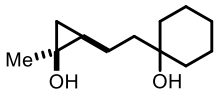
^{1}H NMR (500 MHz, $CDCl_3$)



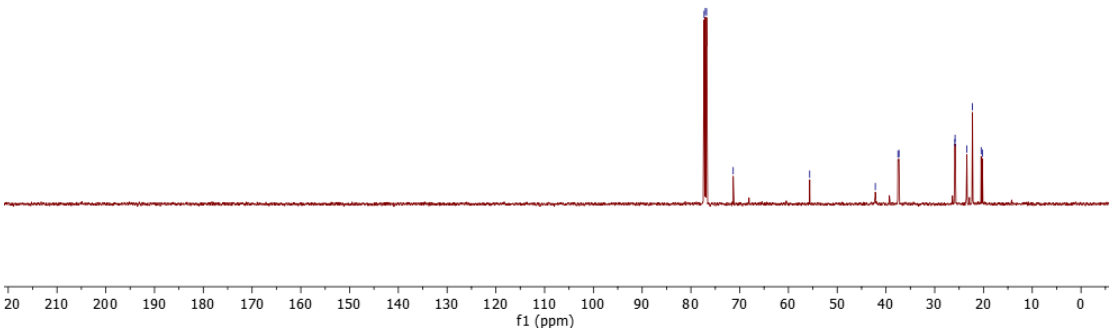


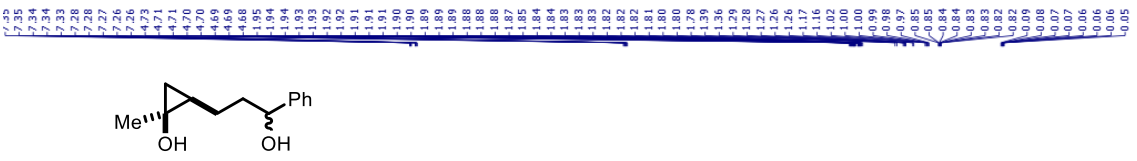
^{1}H NMR (500 MHz, $CDCl_3$)



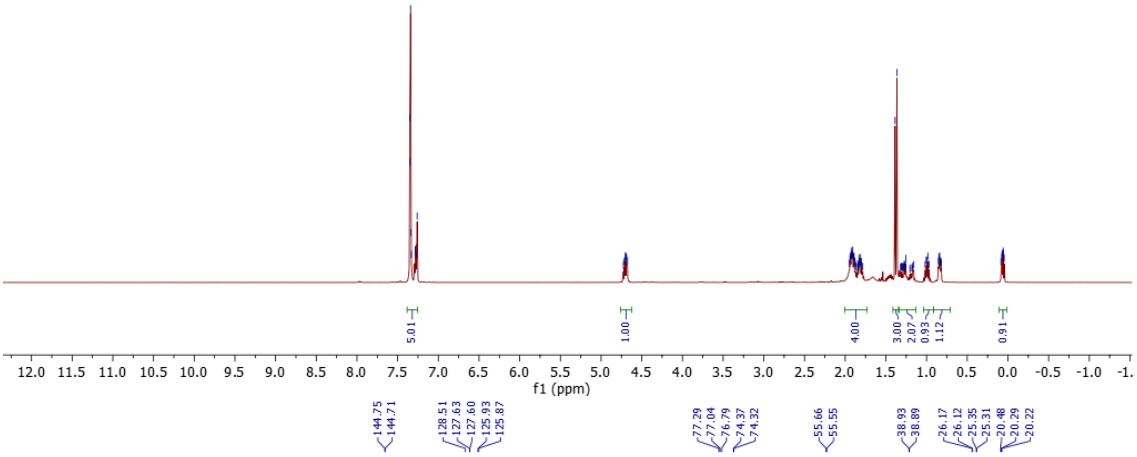


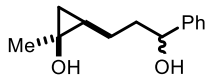
^{13}C NMR (125 MHz, $CDCl_3$)



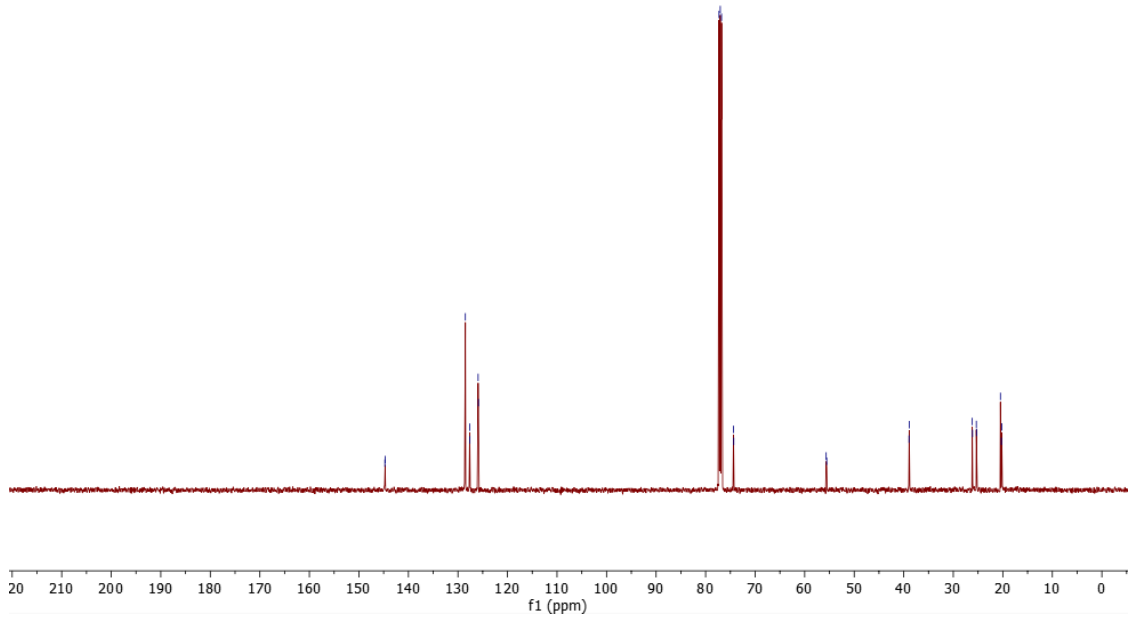


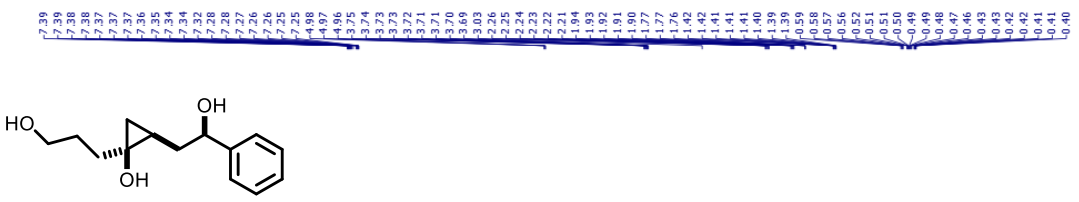
^{1}H NMR (500 MHz, $CDCl_3$)



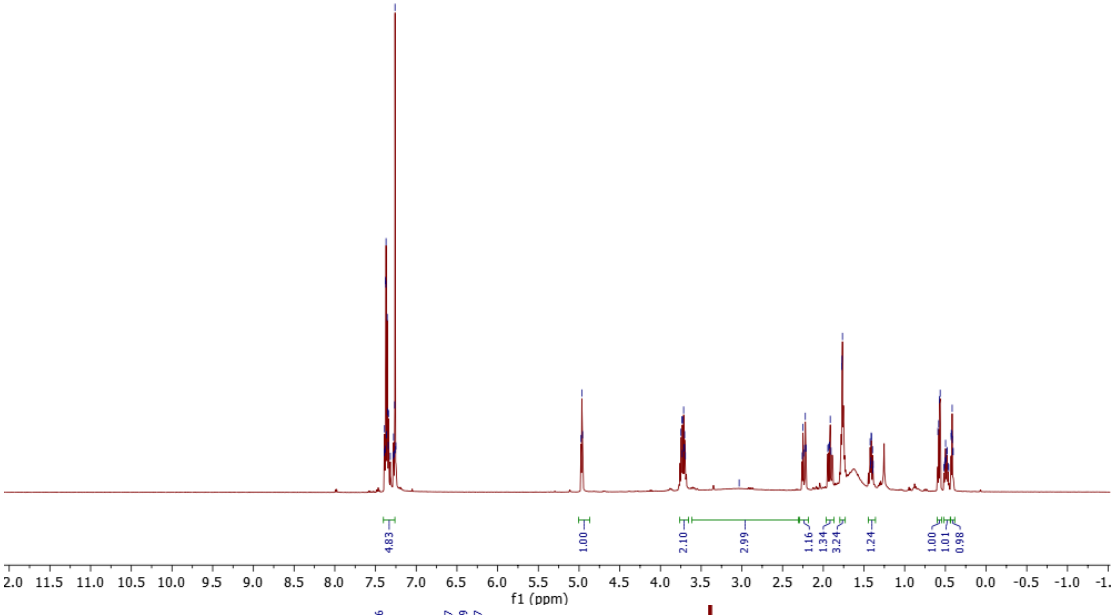


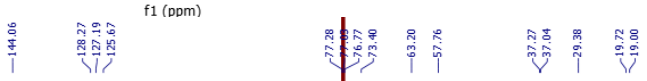
^{13}C NMR (125 MHz, $CDCl_3$)

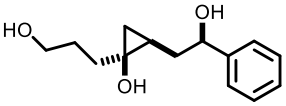




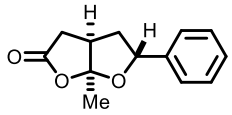
^{1}H NMR (500 MHz, $CDCl_3$)



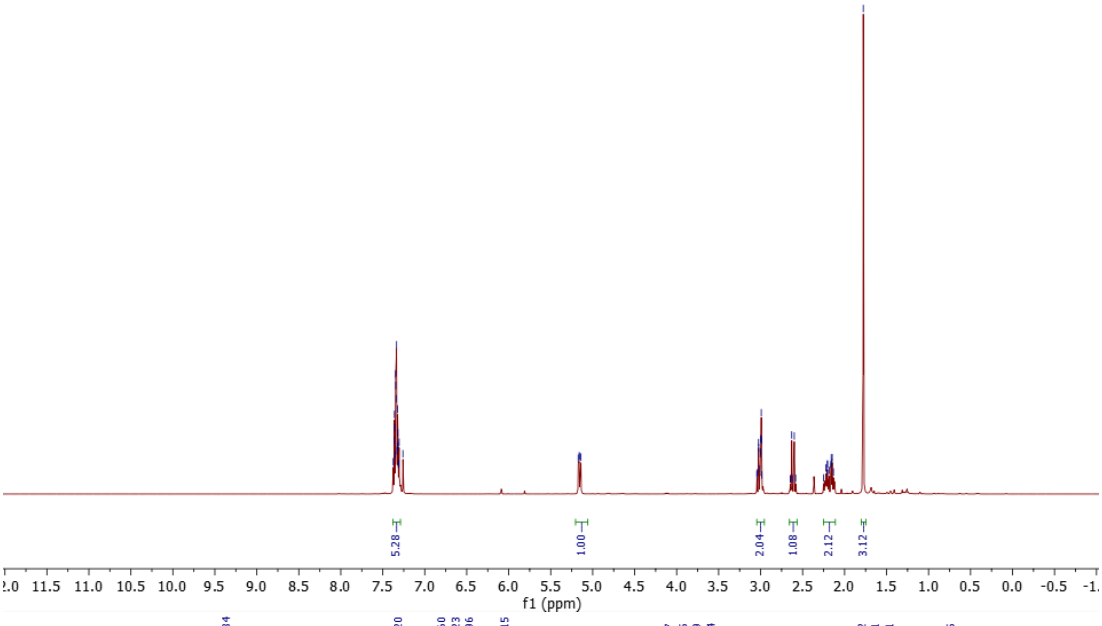


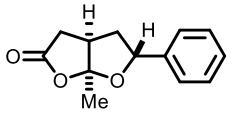


^{13}C NMR (125 MHz, $CDCl_3$)

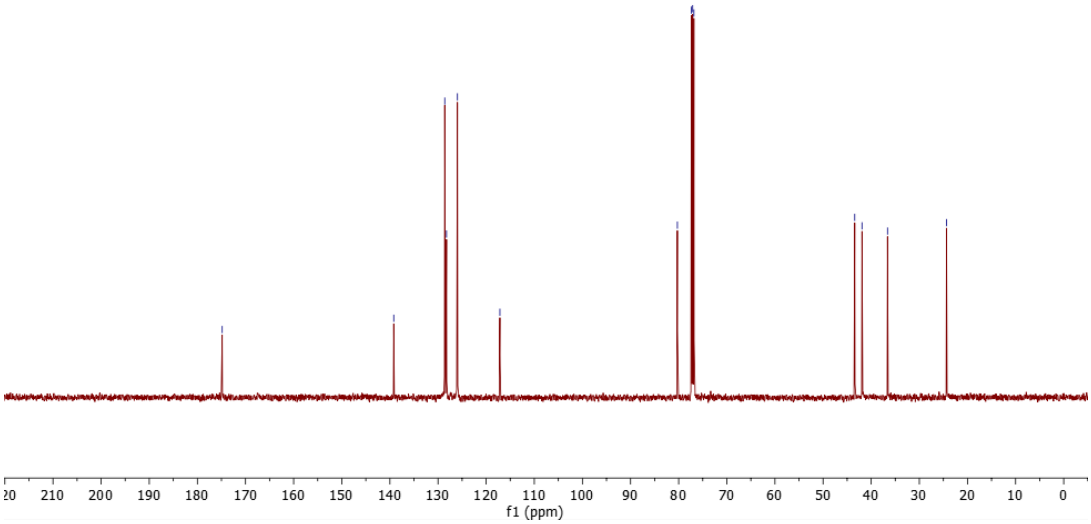


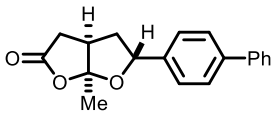
^{1}H NMR (500 MHz, $CDCl_3$)



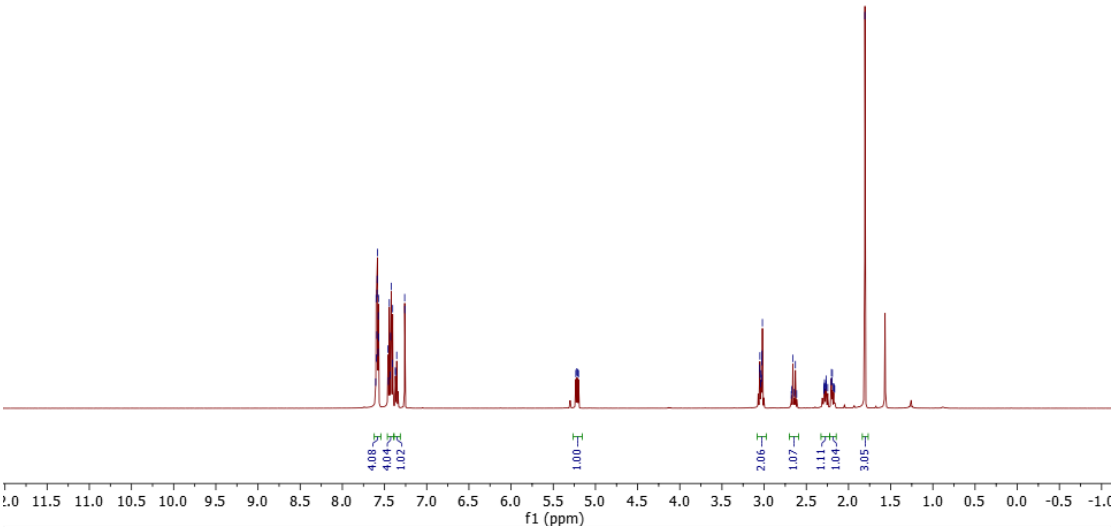


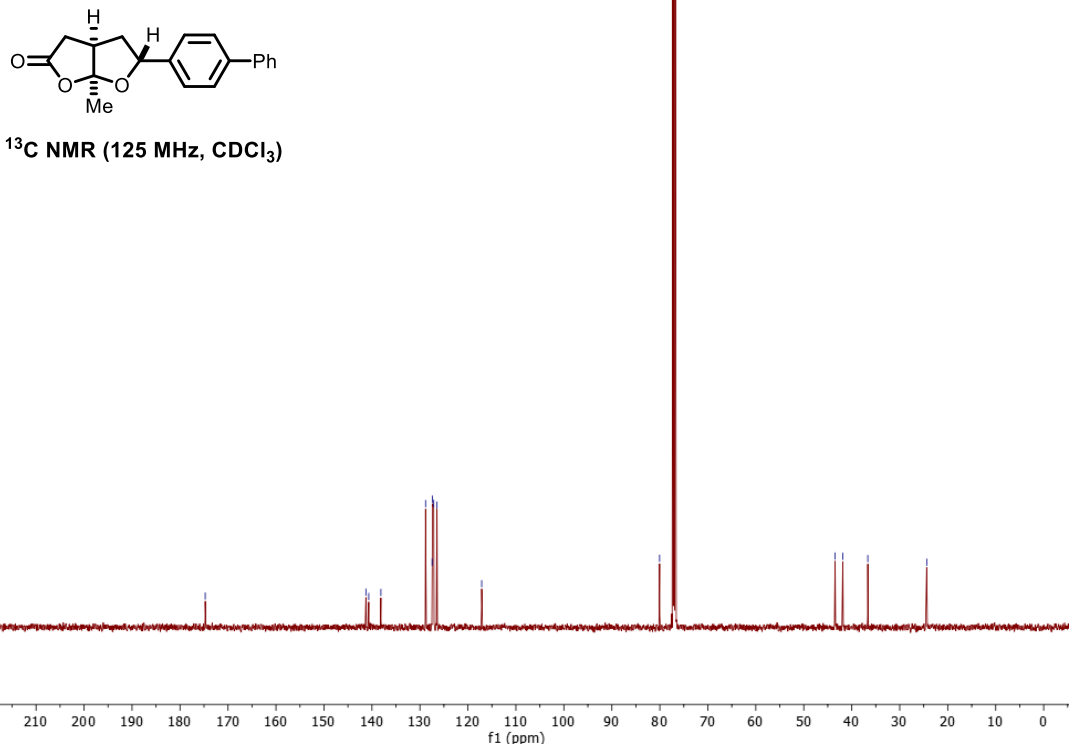
^{13}C NMR (125 MHz, $CDCl_3$)



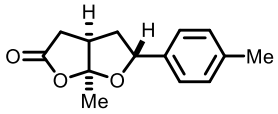


^{1}H NMR (500 MHz, $CDCl_3$)

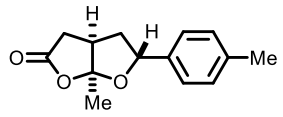




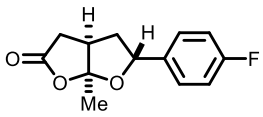
^{13}C NMR (125 MHz, $CDCl_3$)



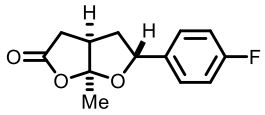
^{1}H NMR (500 MHz, $CDCl_3$)



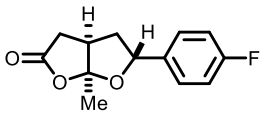
^{13}C NMR (125 MHz, $CDCl_3$)



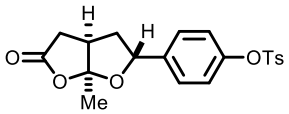
^{1}H NMR (500 MHz, $CDCl_3$)



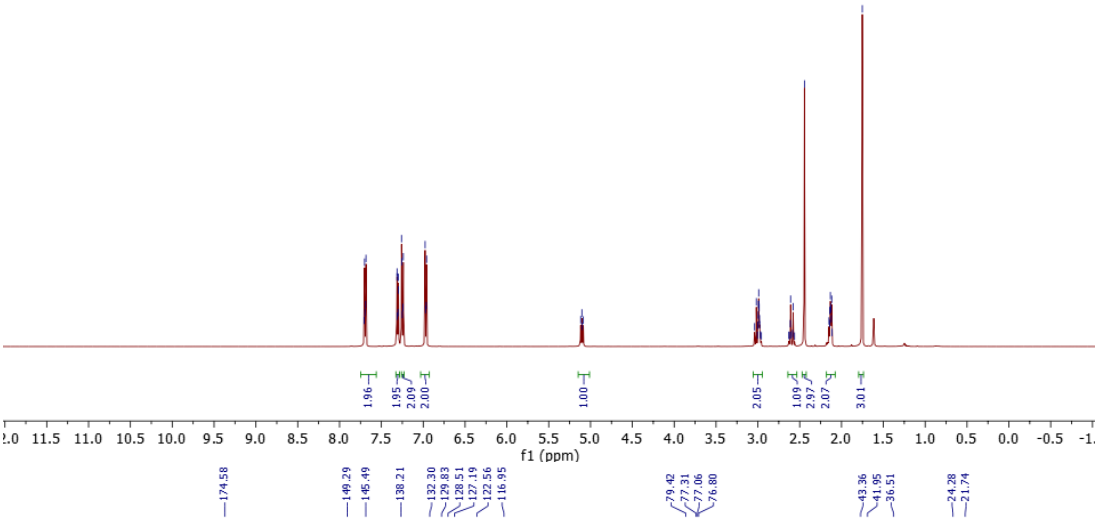
^{13}C NMR (125 MHz, $CDCl_3$)

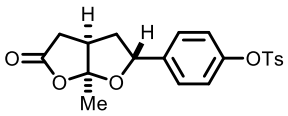


^{19}F NMR (471 MHz, $CDCl_3$)

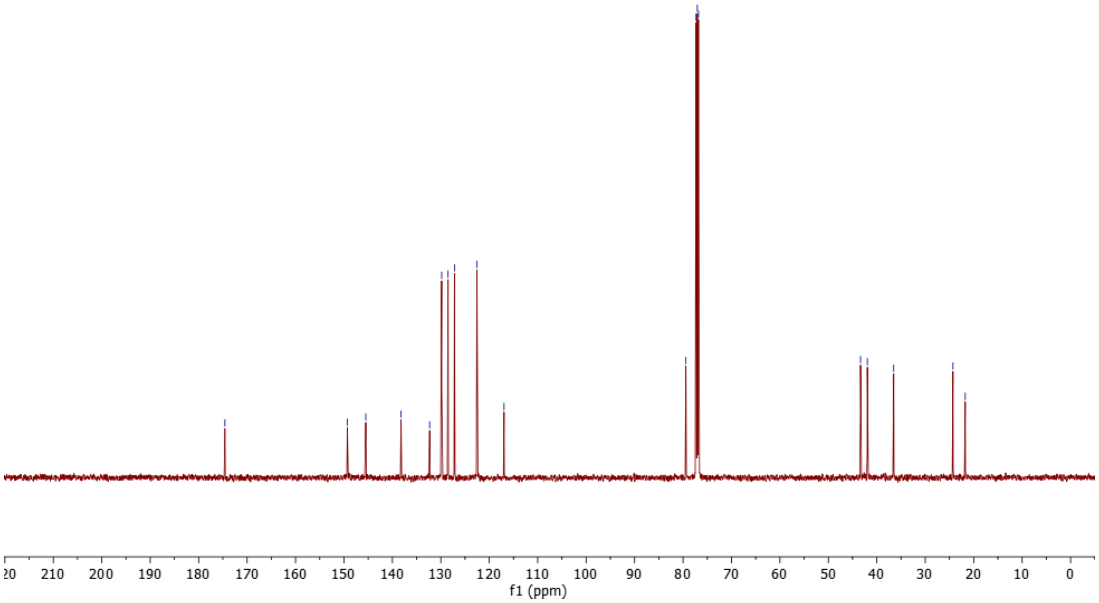


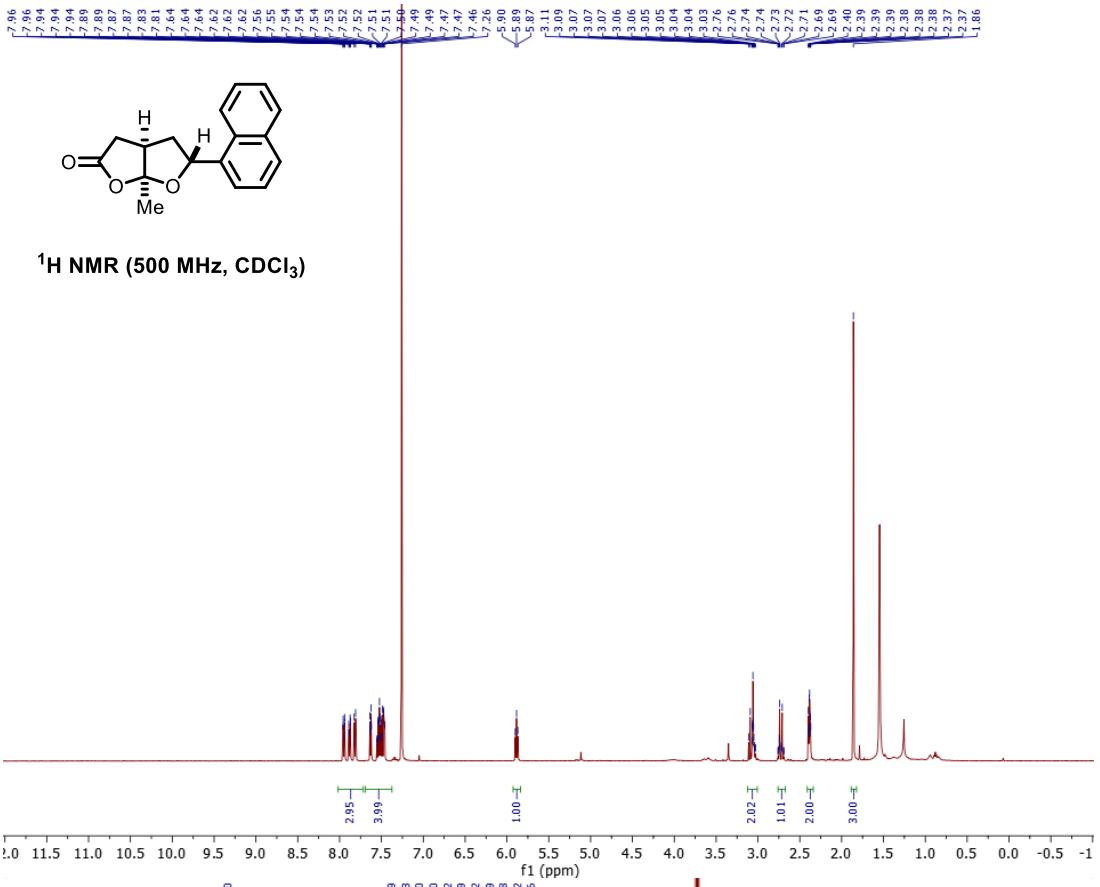
^{1}H NMR (500 MHz, $CDCl_3$)



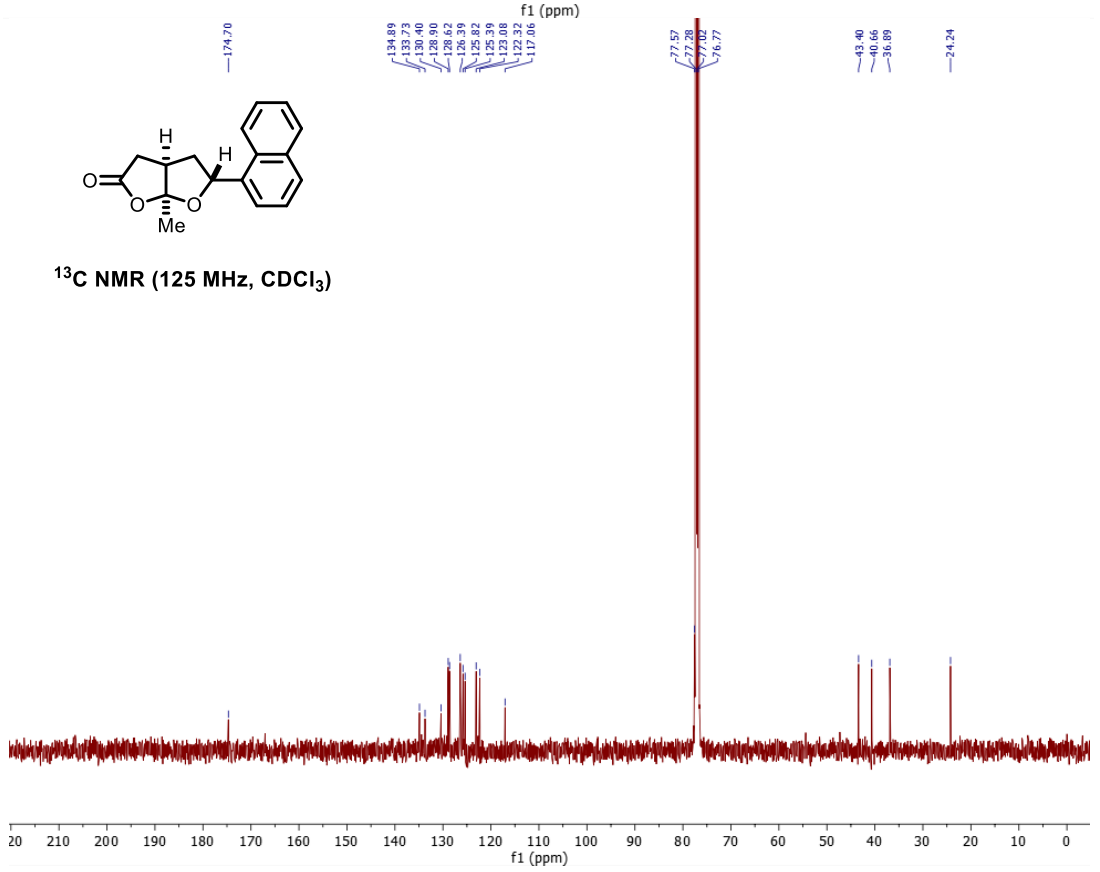


^{13}C NMR (125 MHz, $CDCl_3$)

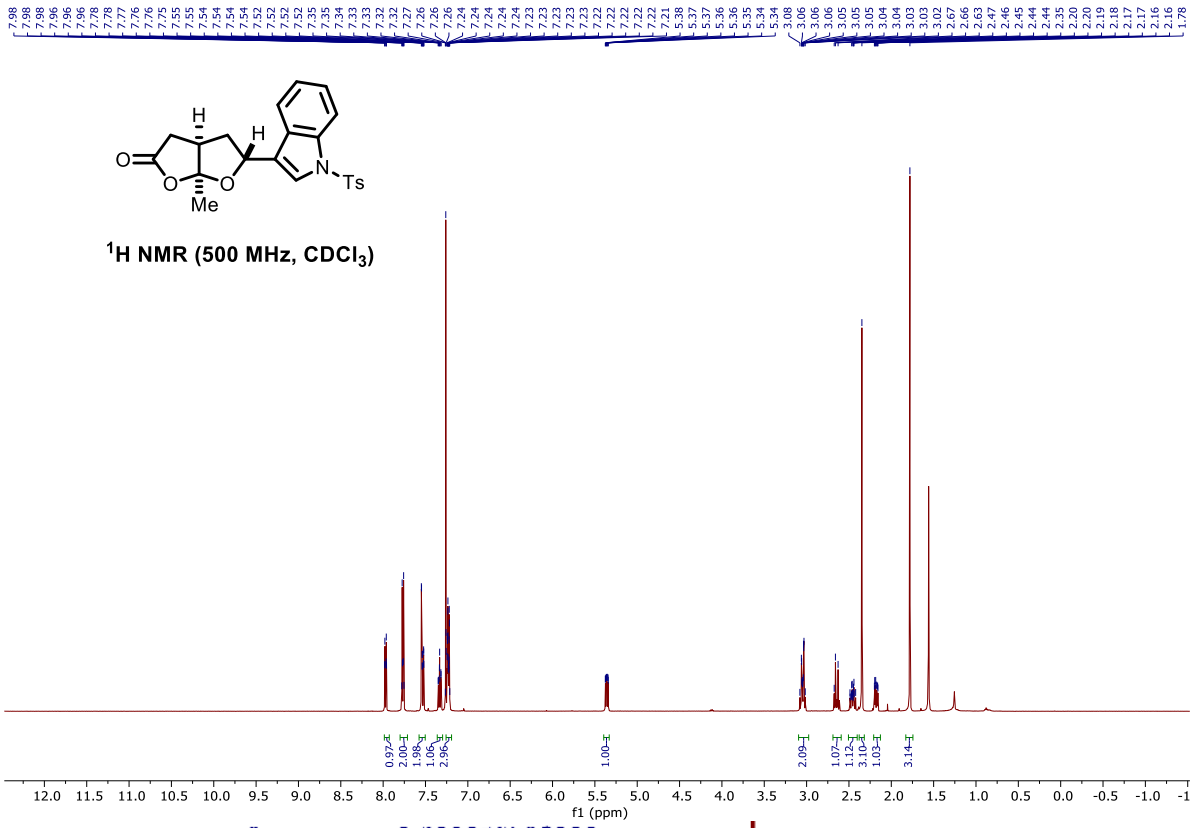




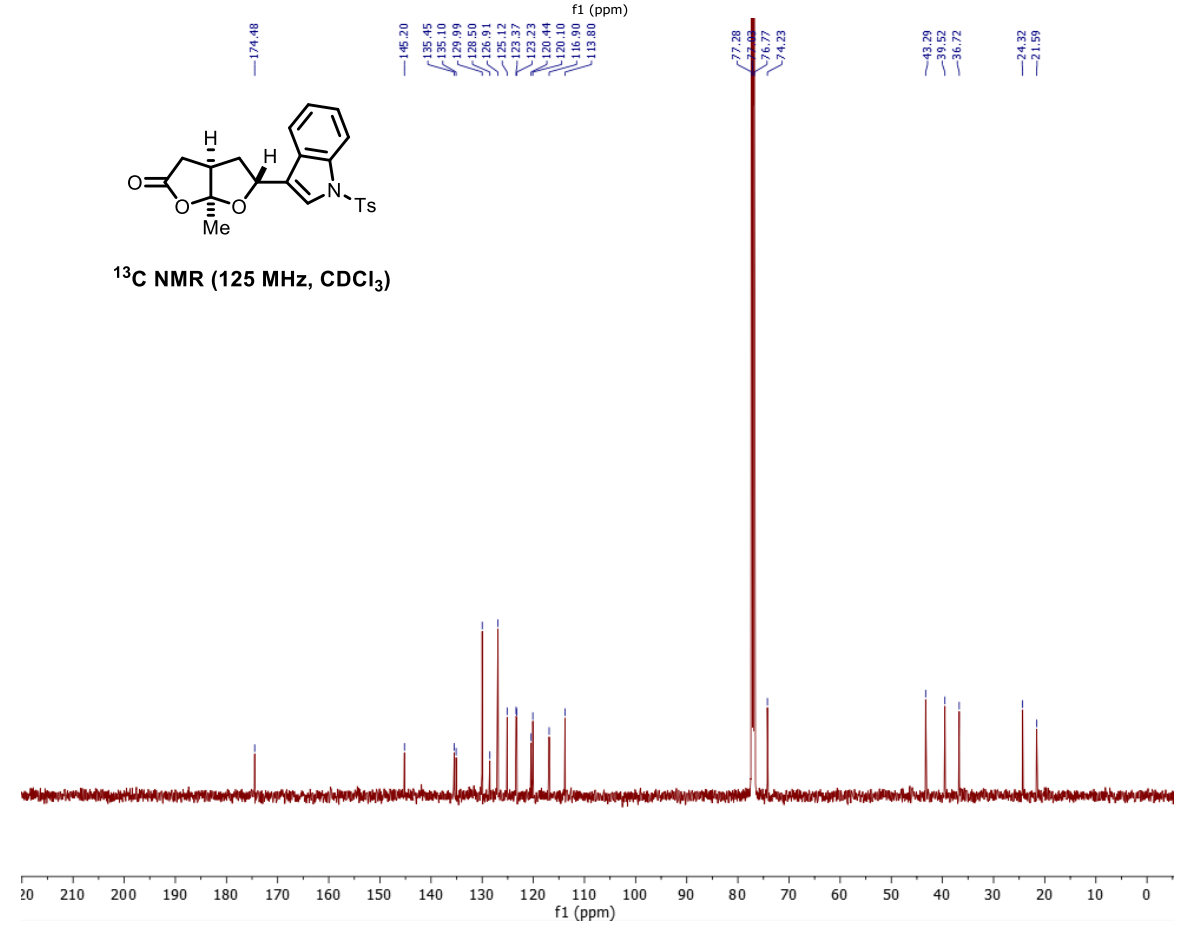
^{1}H NMR (500 MHz, $CDCl_3$)



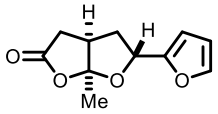
^{13}C NMR (125 MHz, $CDCl_3$)



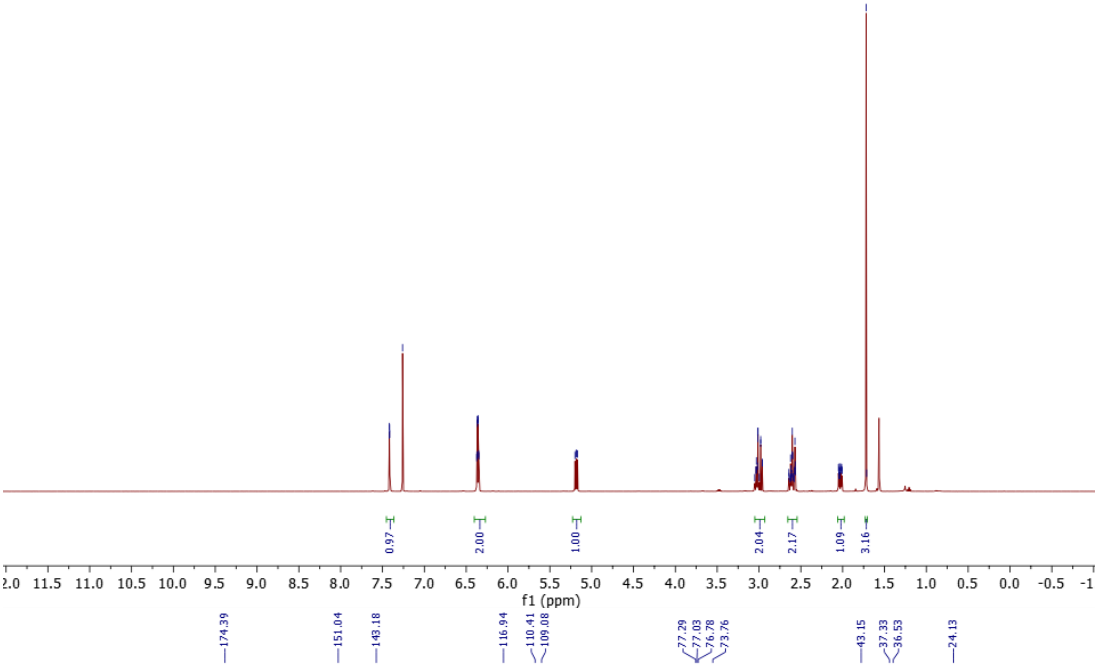
^{1}H NMR (500 MHz, $CDCl_3$)

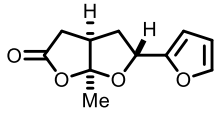


^{13}C NMR (125 MHz, $CDCl_3$)

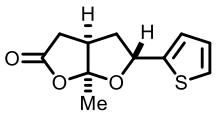


^{1}H NMR (500 MHz, $CDCl_3$)

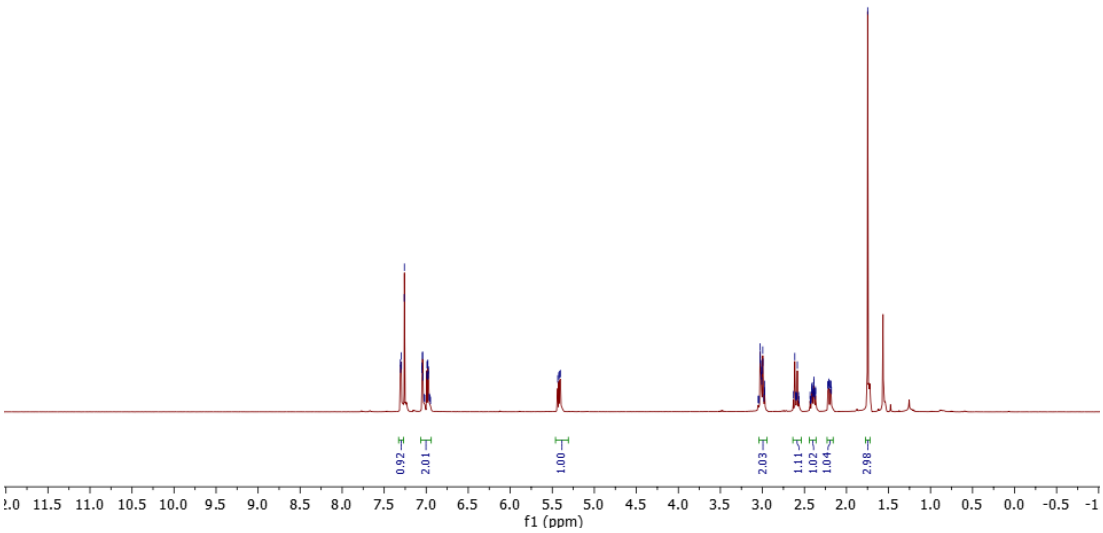


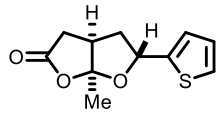


^{13}C NMR (125 MHz, $CDCl_3$)

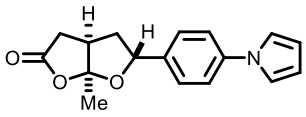


^{1}H NMR (500 MHz, $CDCl_3$)

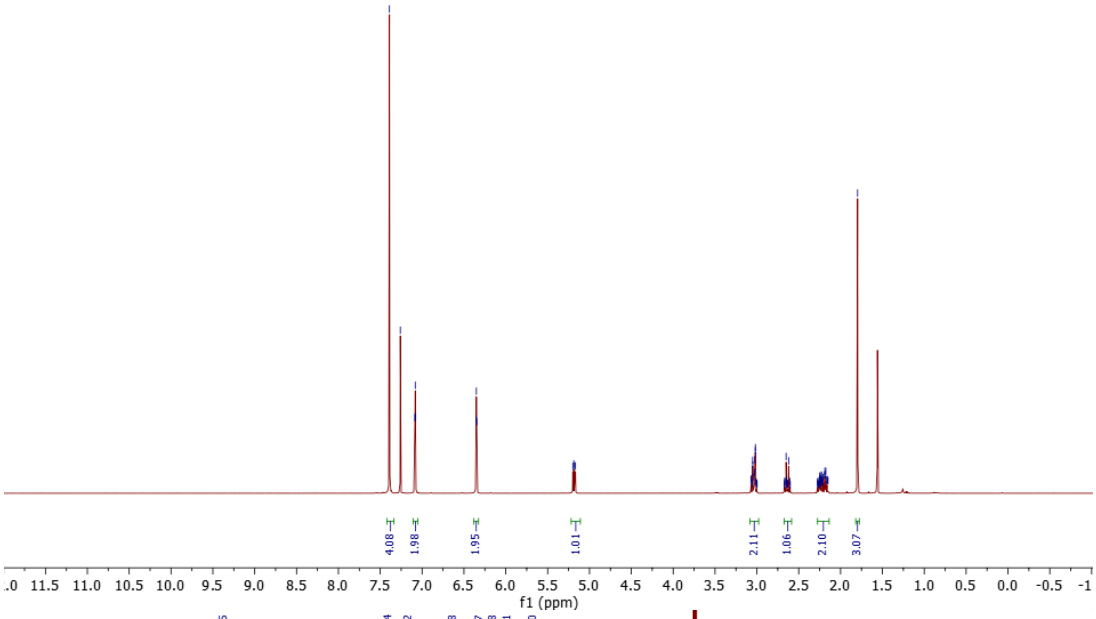


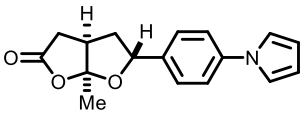


^{13}C NMR (125 MHz, $CDCl_3$)

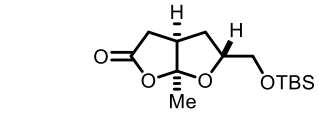


^{1}H NMR (500 MHz, $CDCl_3$)

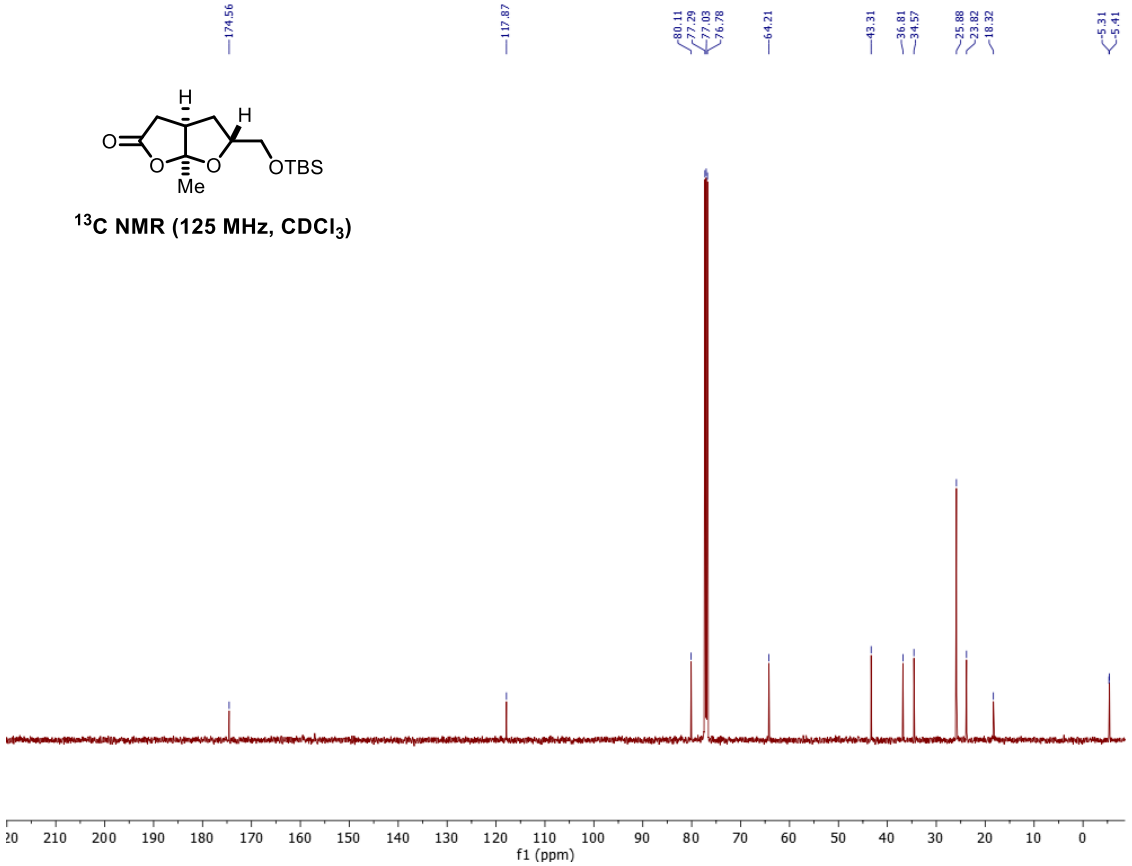




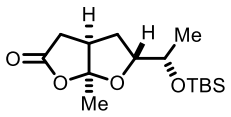
^{13}C NMR (125 MHz, $CDCl_3$)



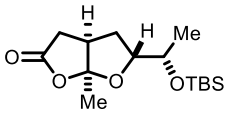
^{1}H NMR (500 MHz, $CDCl_3$)



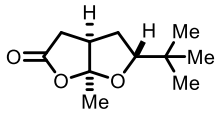
^{13}C NMR (125 MHz, $CDCl_3$)



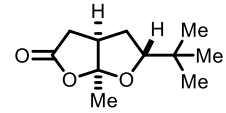
^{1}H NMR (500 MHz, $CDCl_3$)



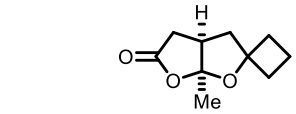
^{13}C NMR (125 MHz, $CDCl_3$)



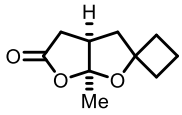
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)



^{1}H NMR (500 MHz, $CDCl_3$)



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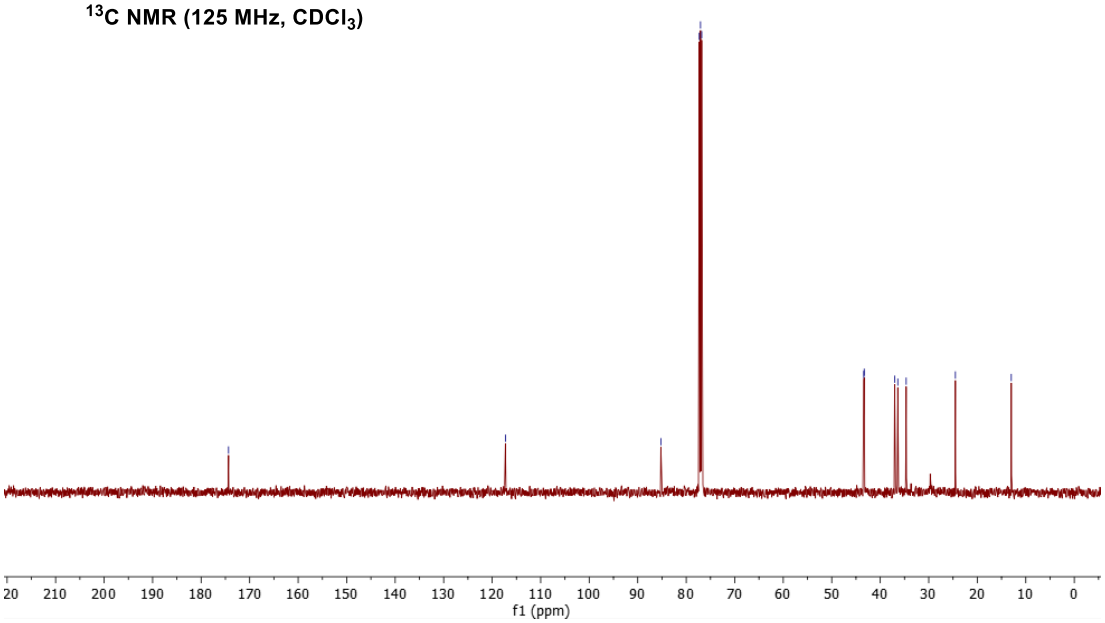

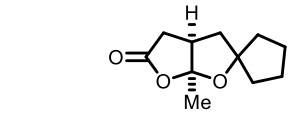

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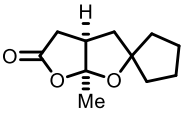

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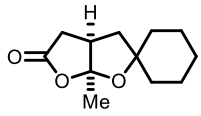

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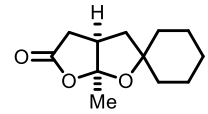

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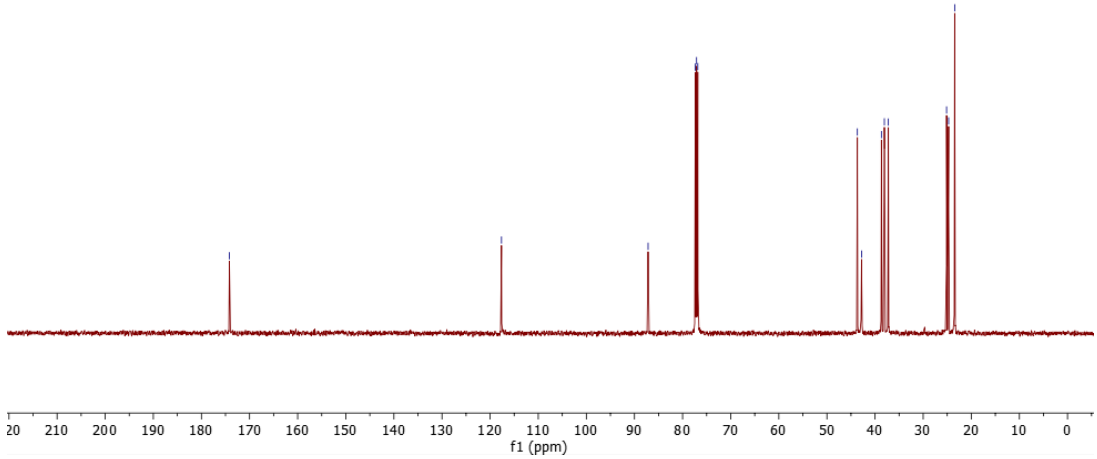

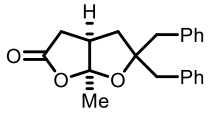

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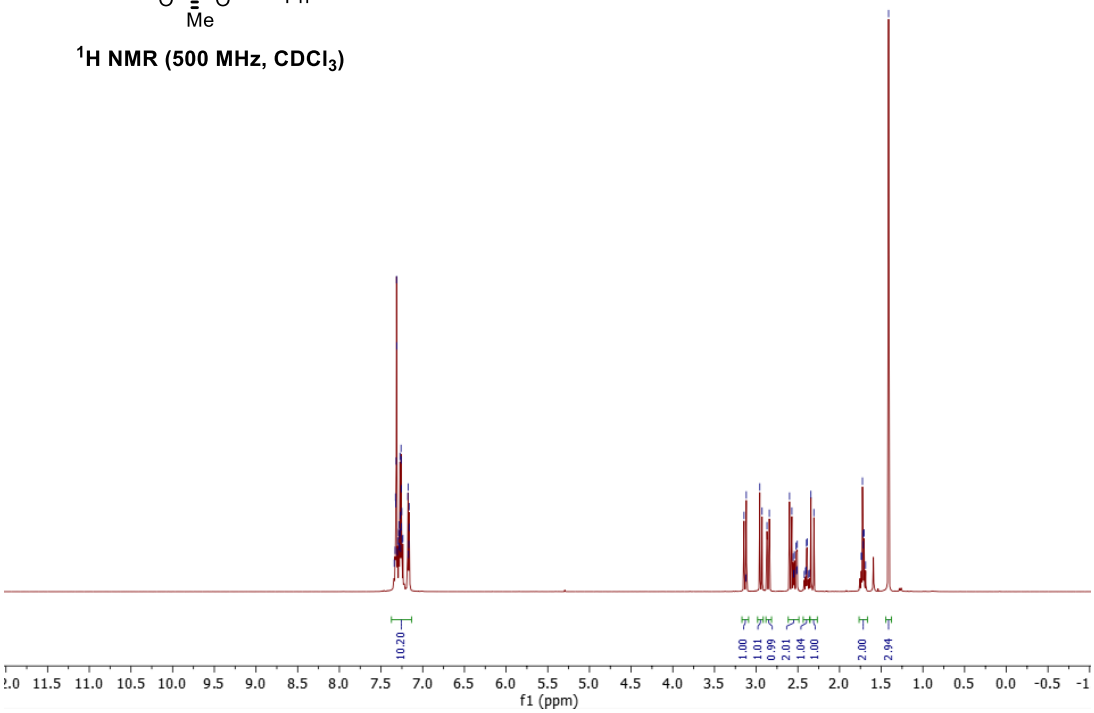

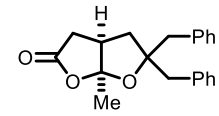

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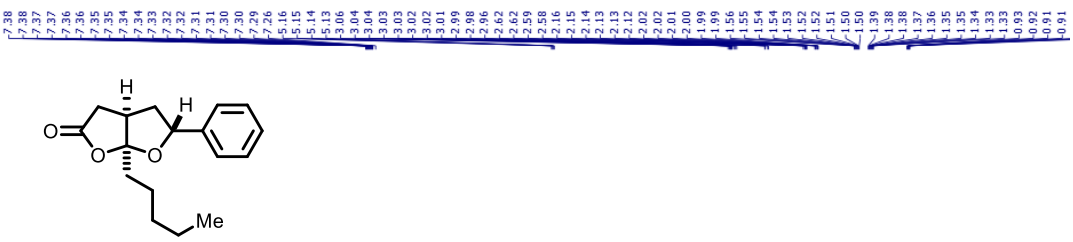

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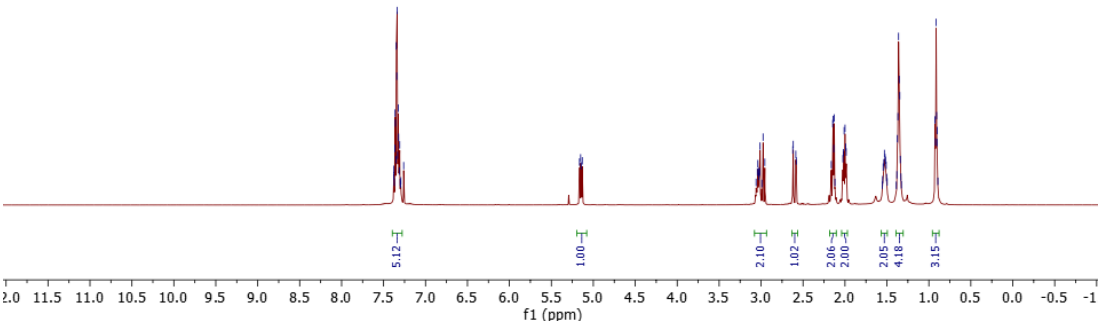

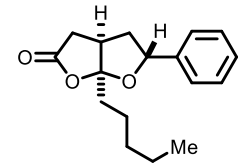

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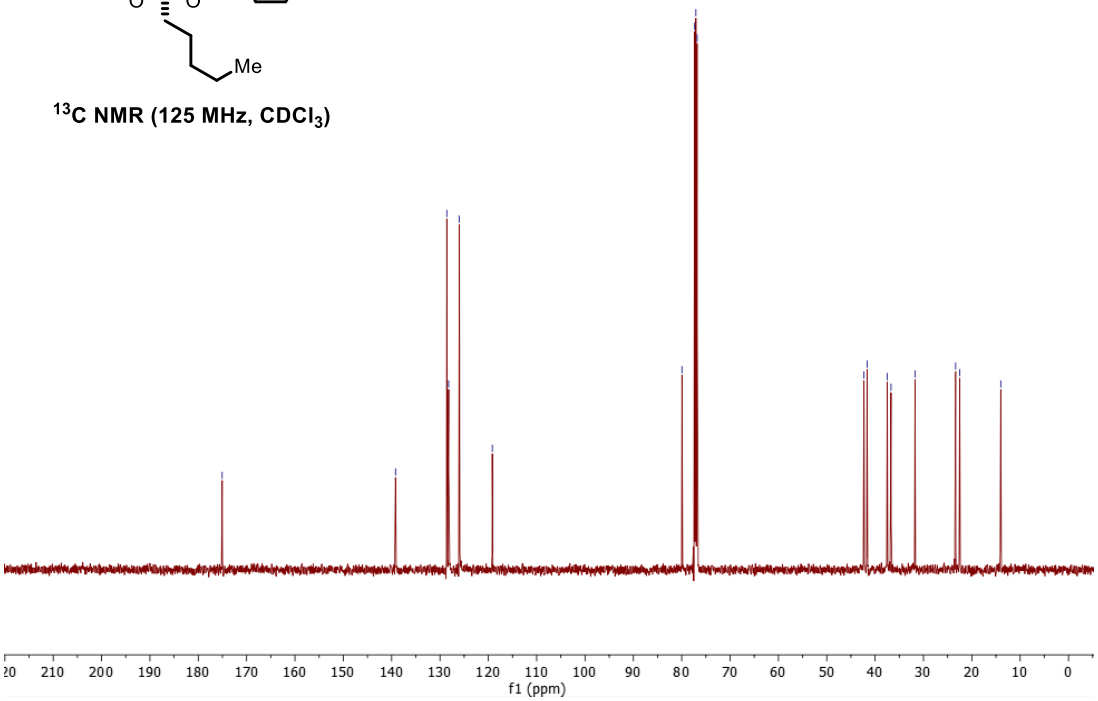

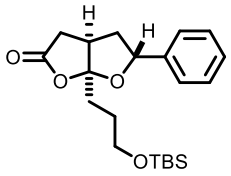

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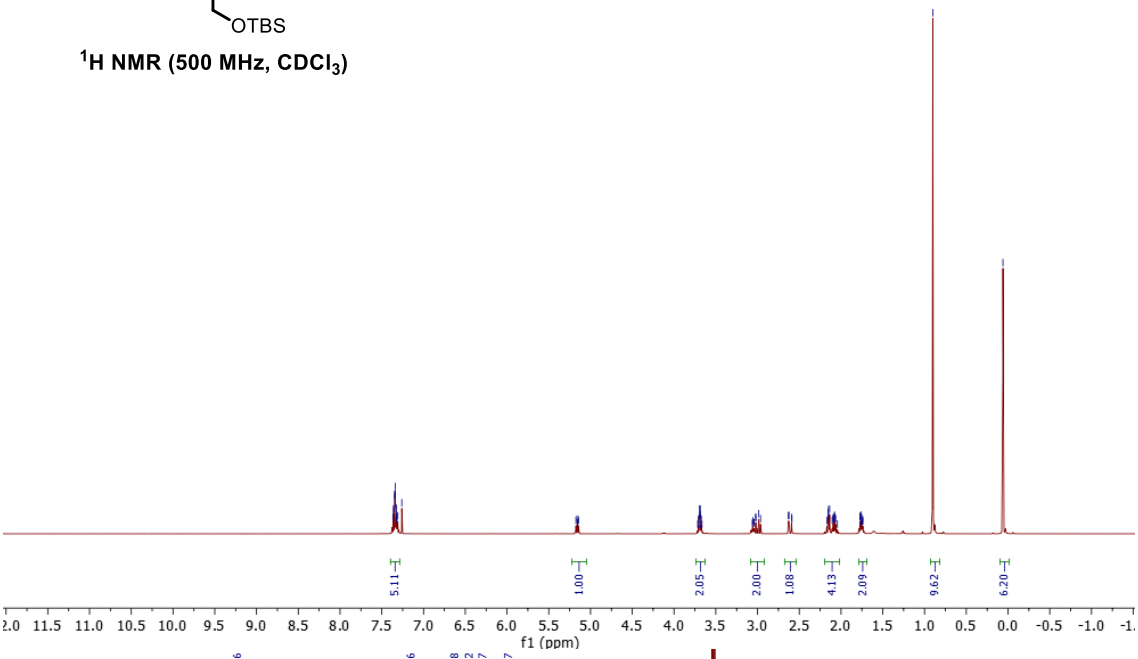
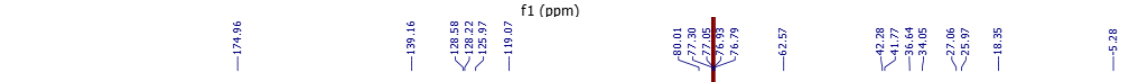
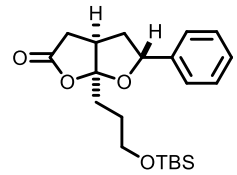
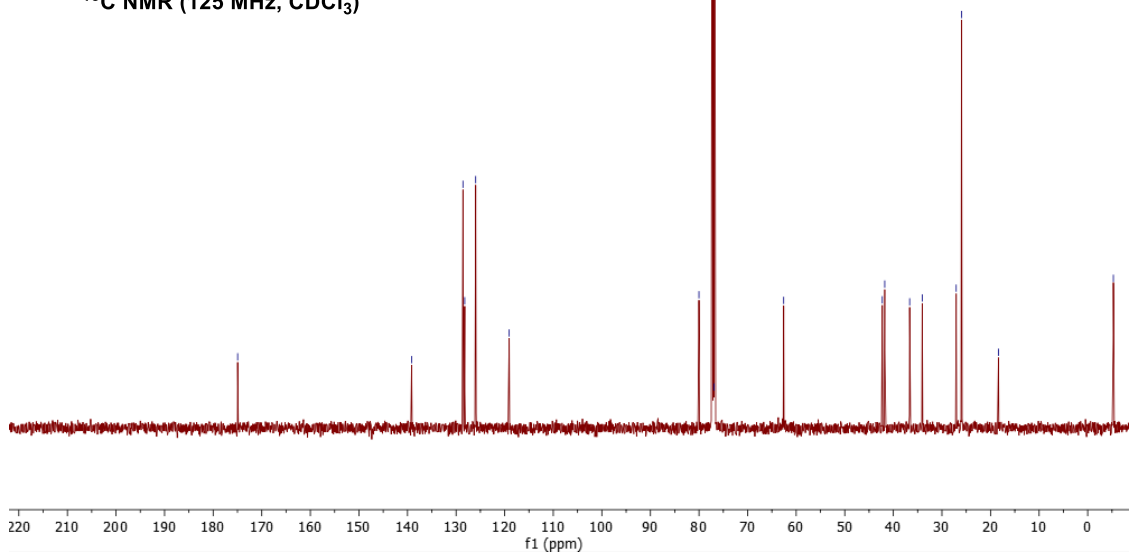
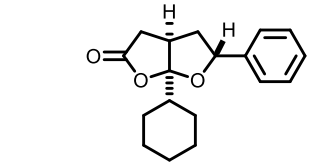




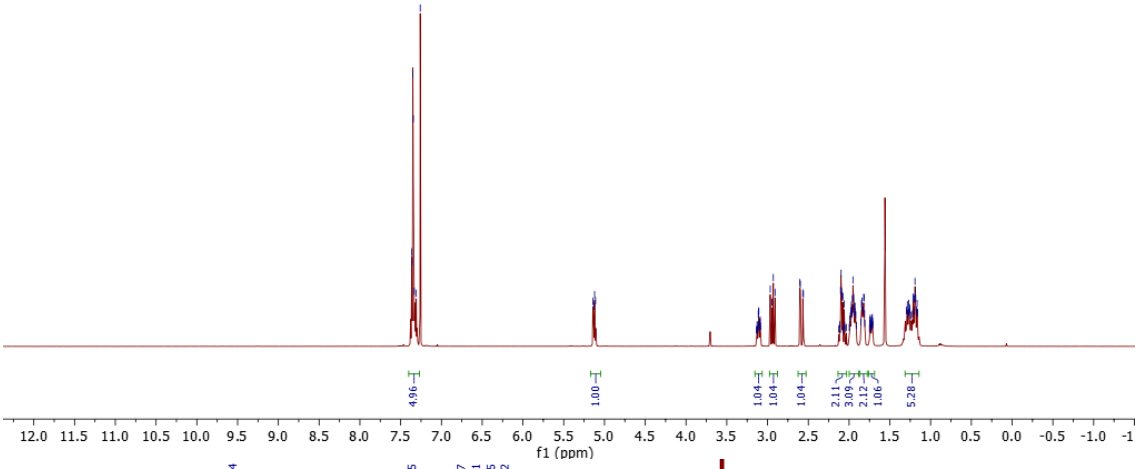


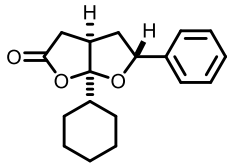
^{13}C NMR (125 MHz, $CDCl_3$)





^{1}H NMR (500 MHz, $CDCl_3$)





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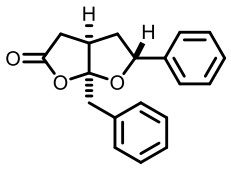
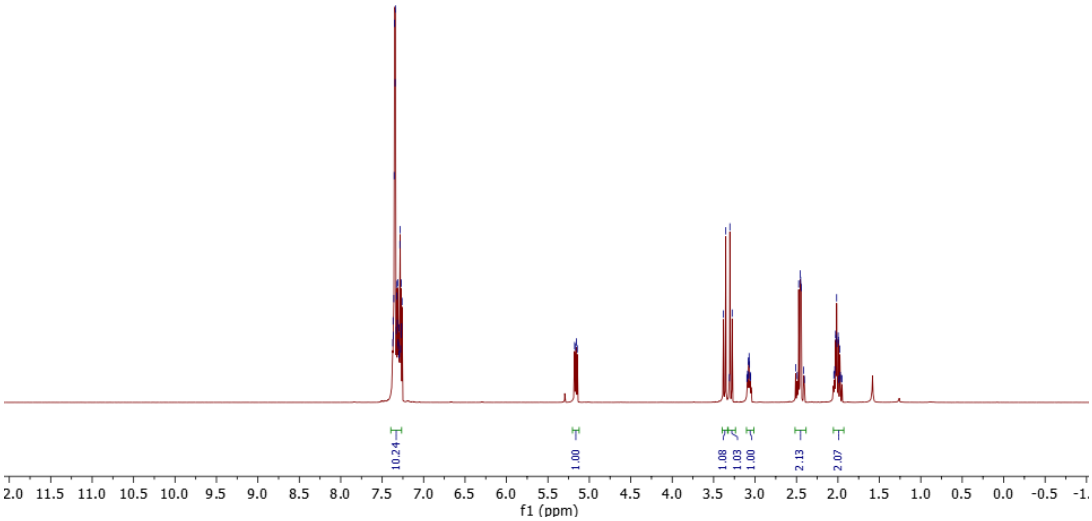
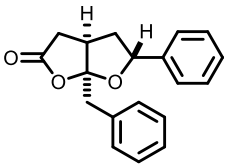


^{1}H NMR (500 MHz, $CDCl_3$)





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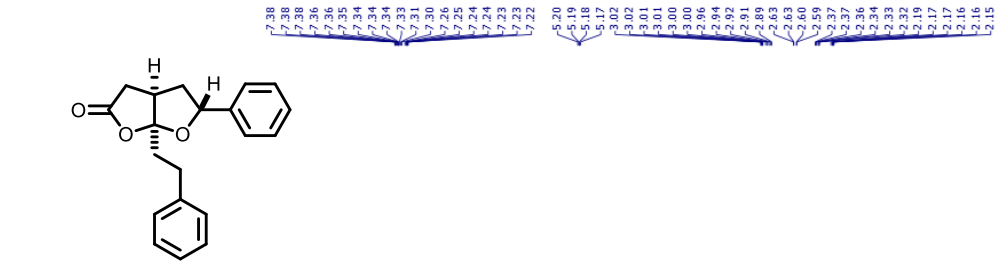

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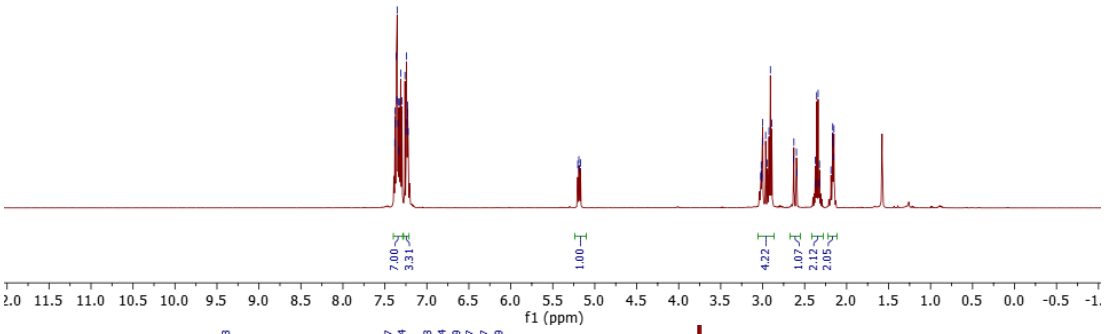

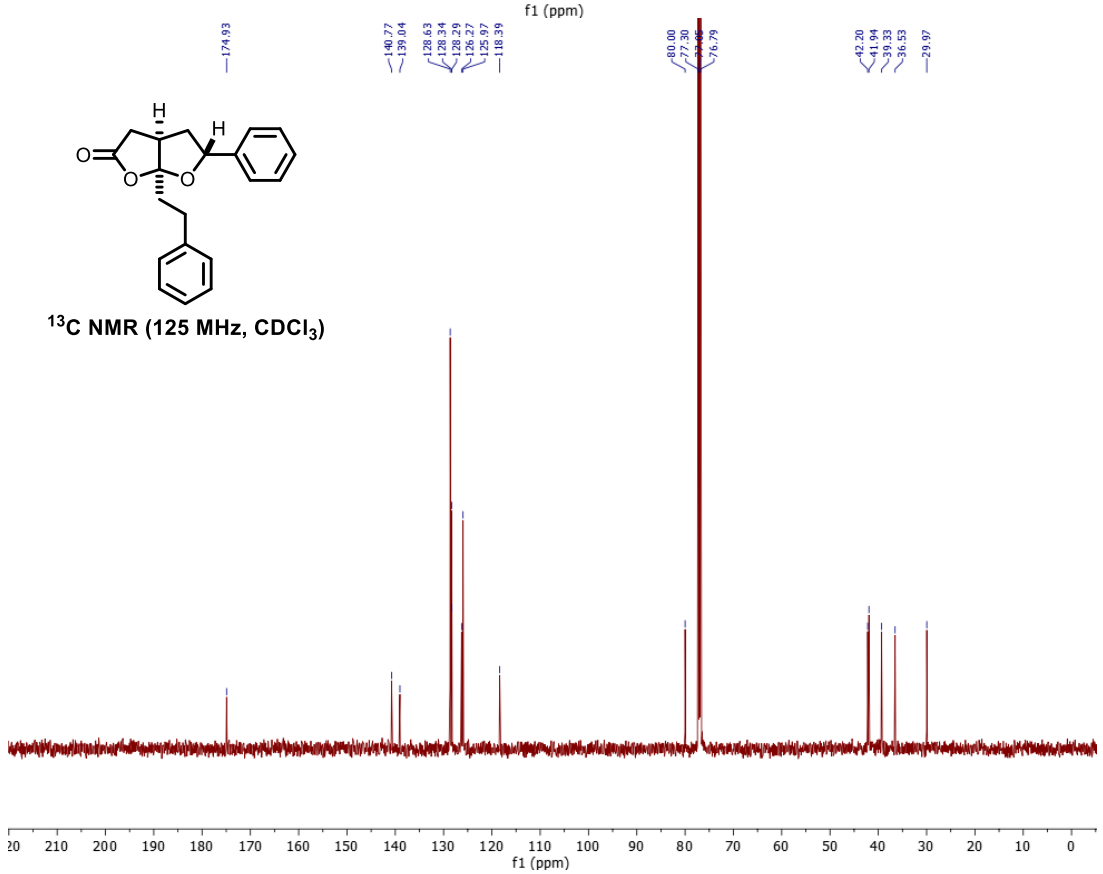

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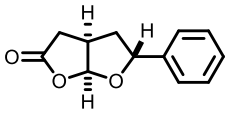

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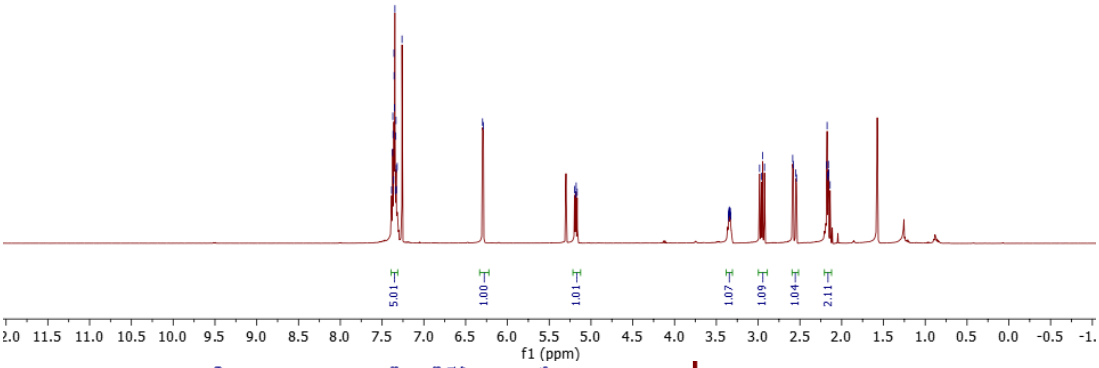

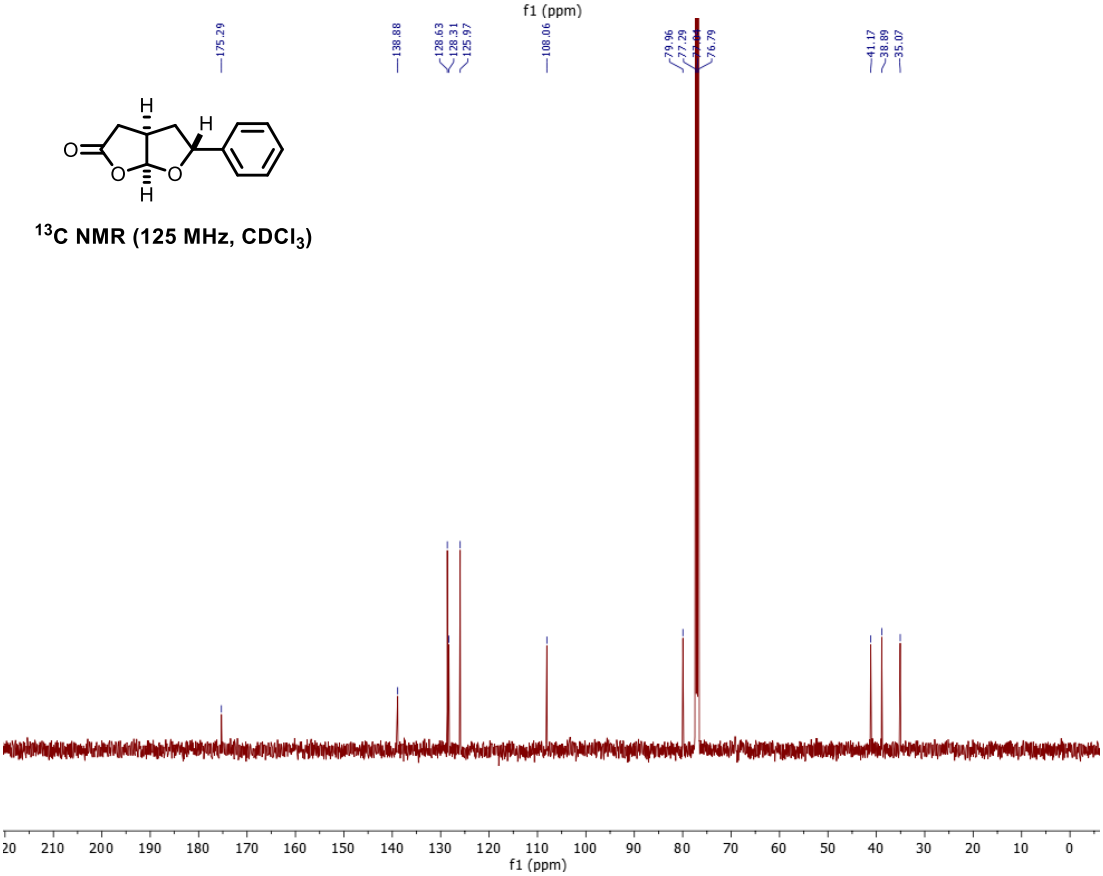

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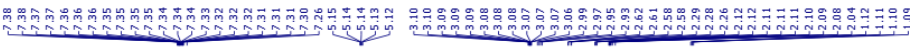

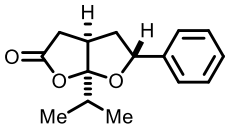

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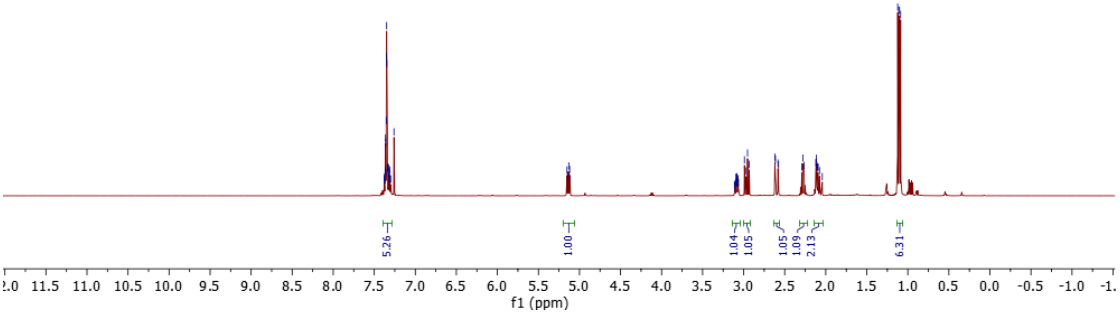

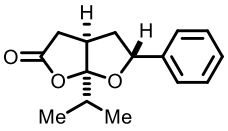

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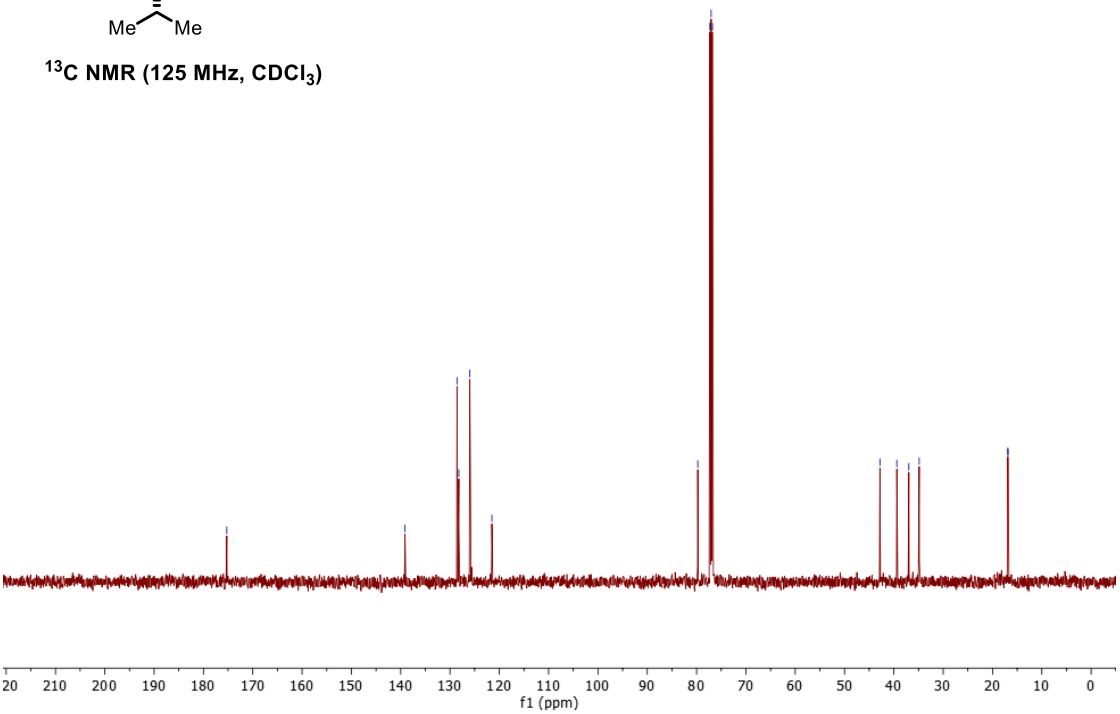

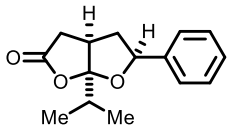

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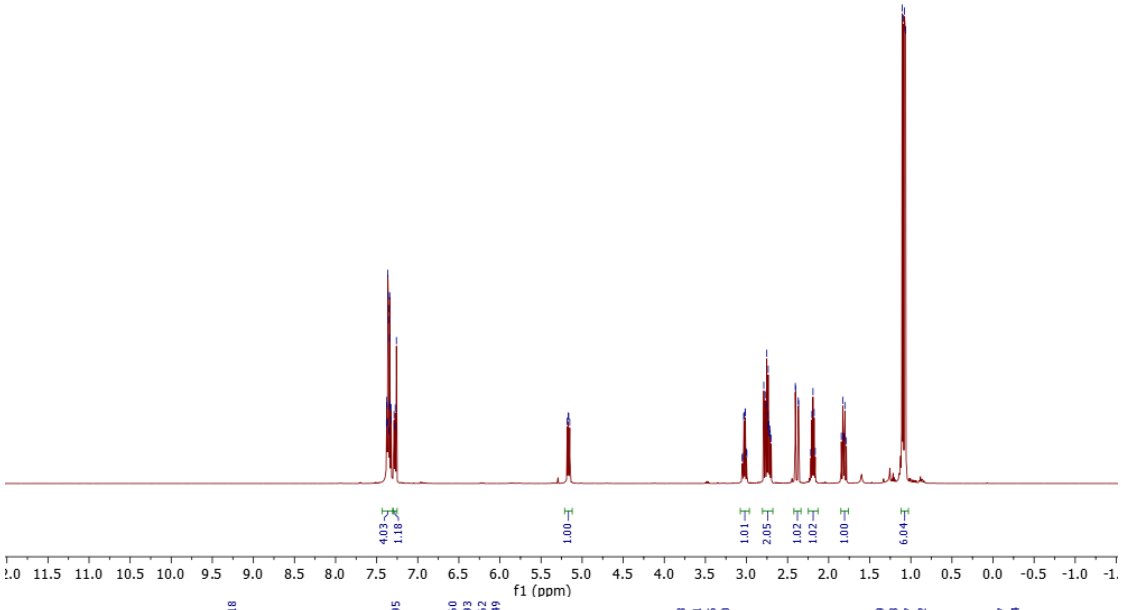

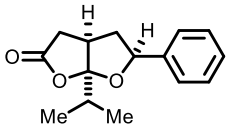

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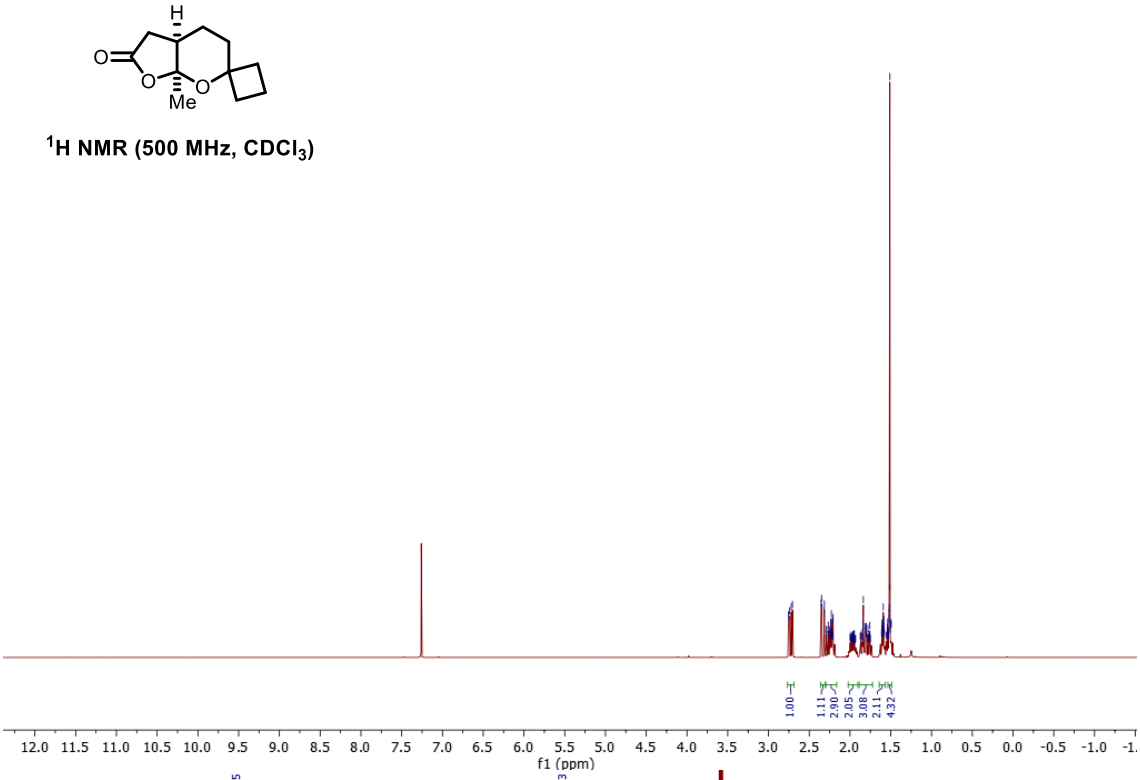

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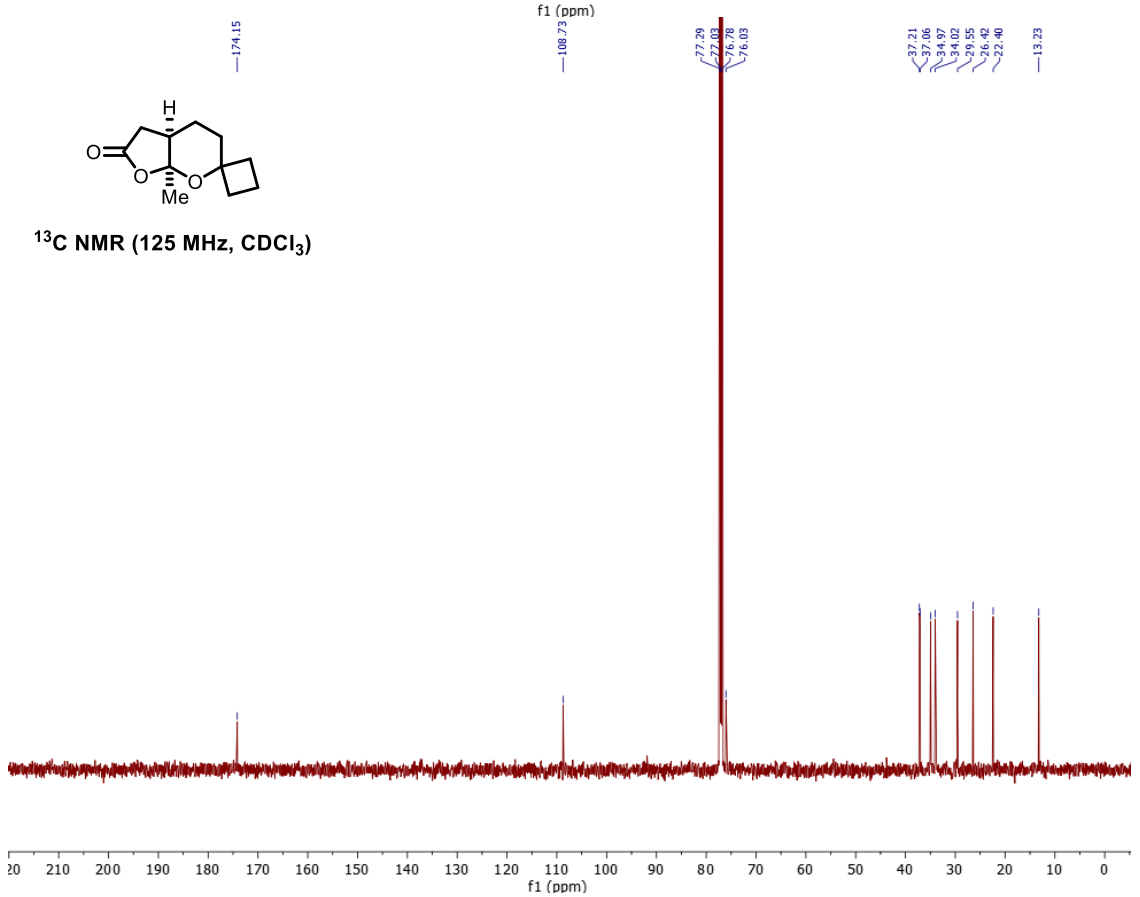

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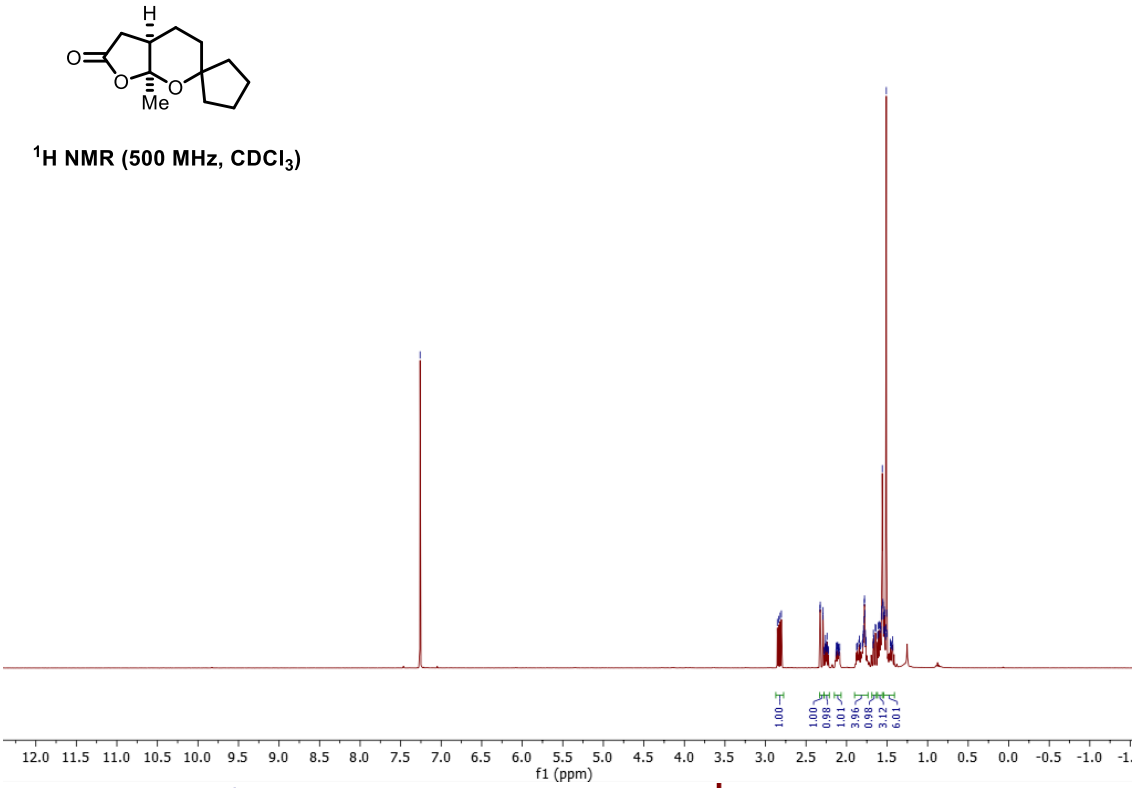
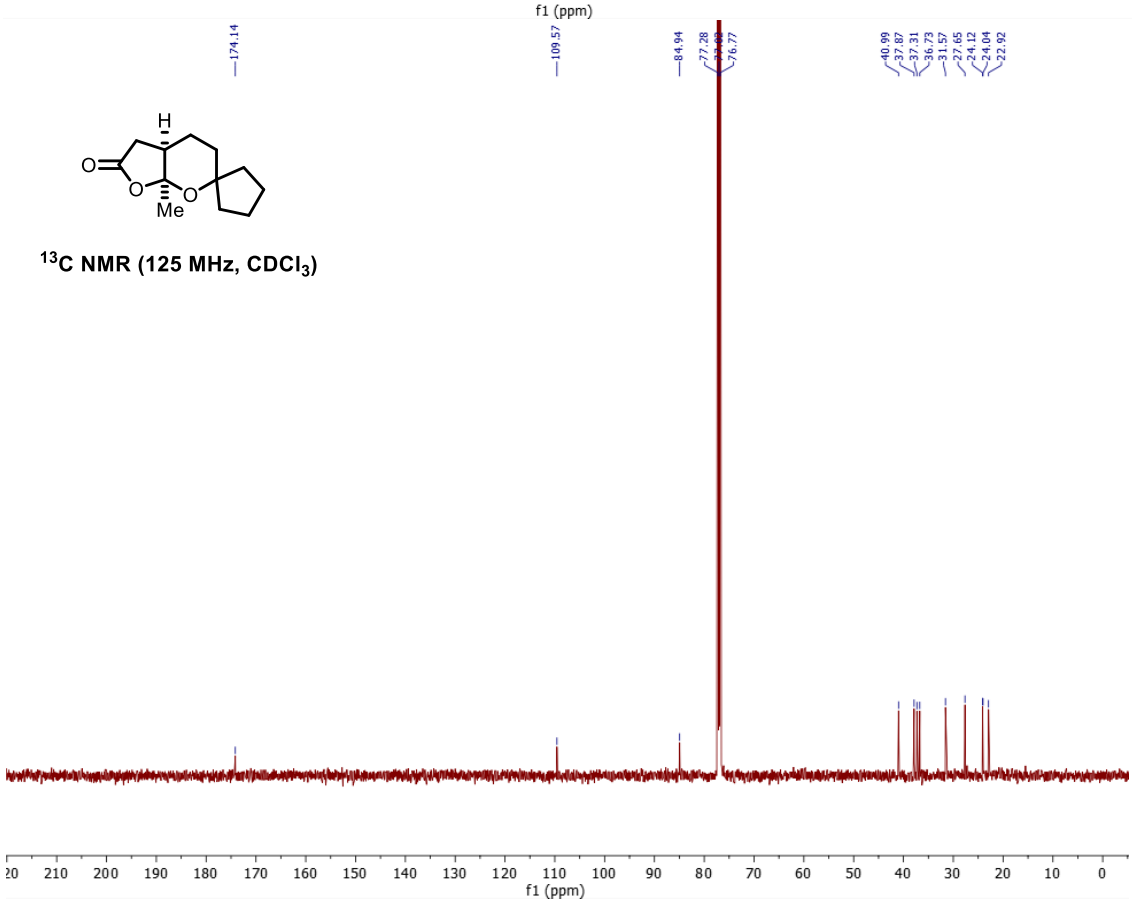


^{1}H NMR (500 MHz, $CDCl_3$)



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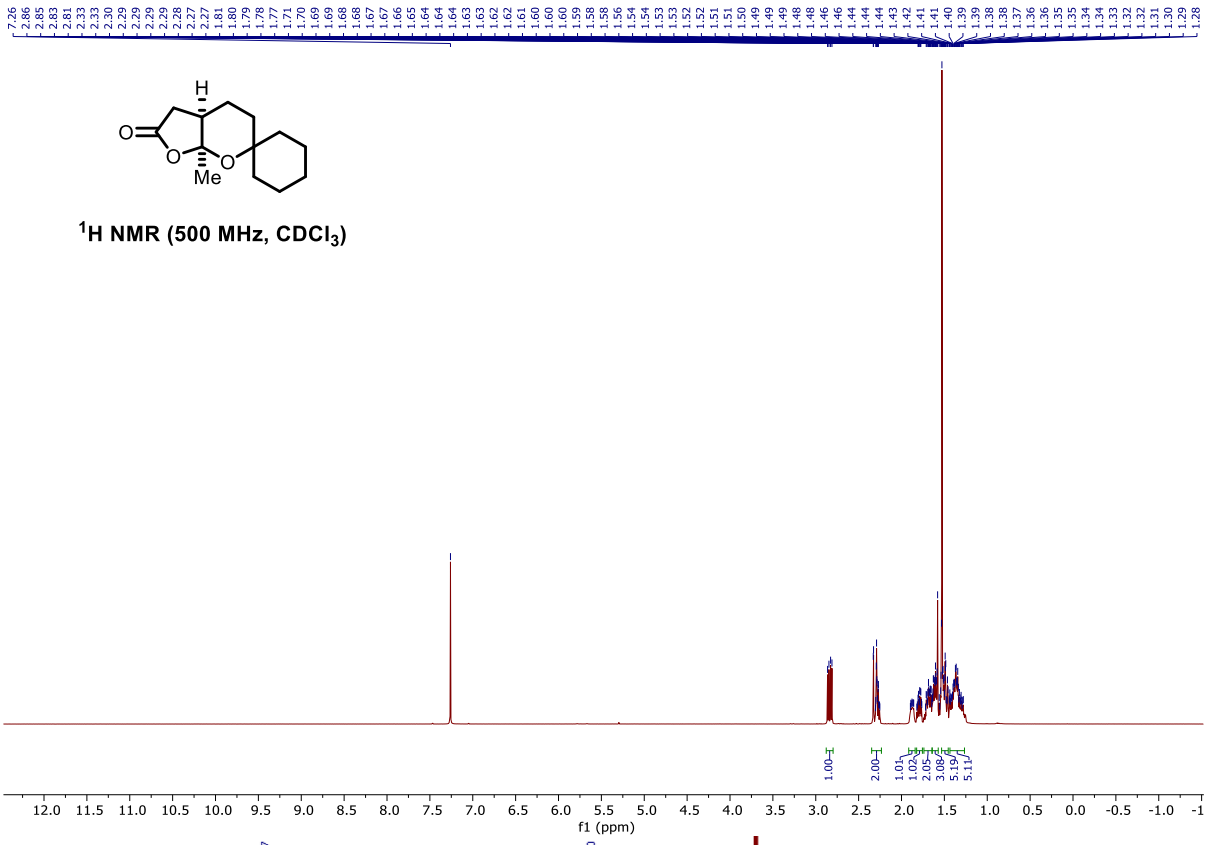

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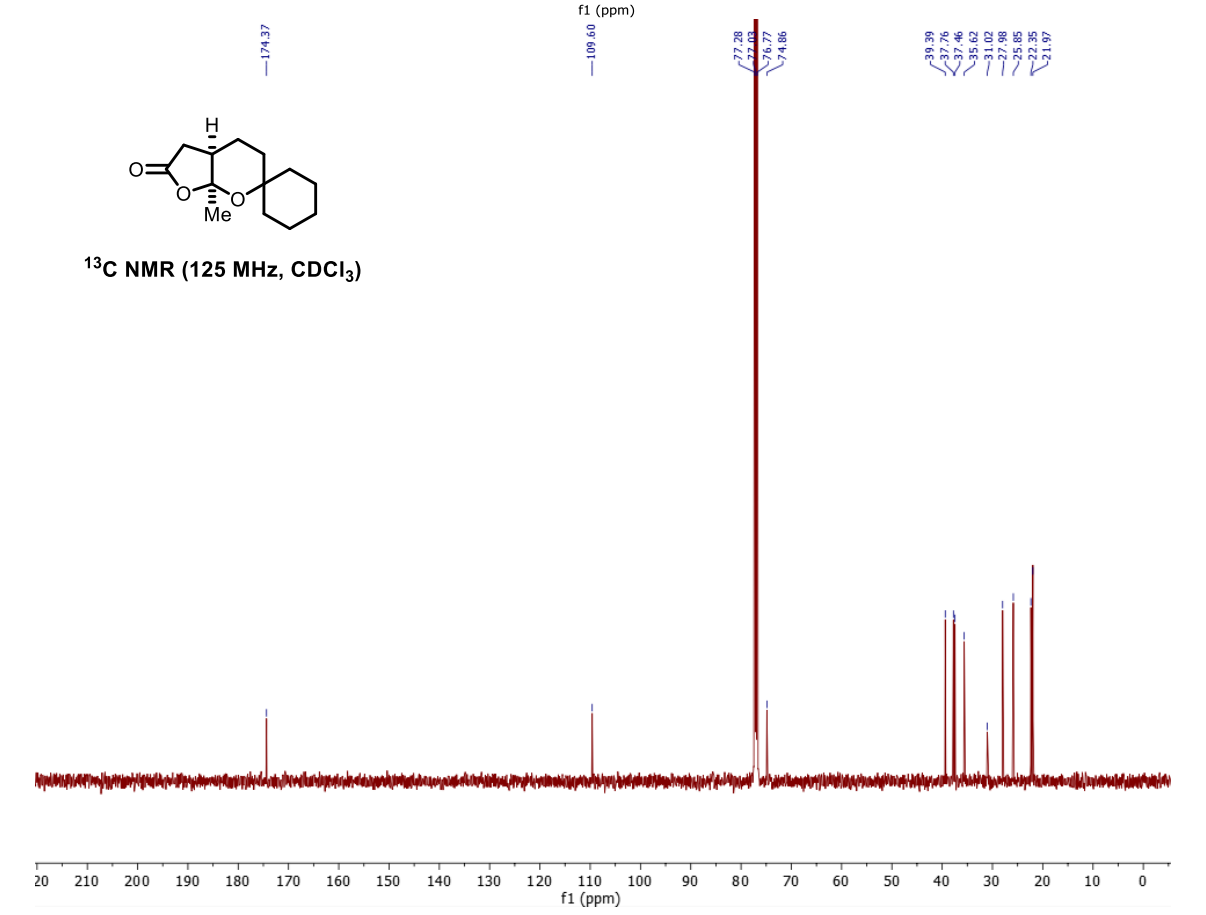
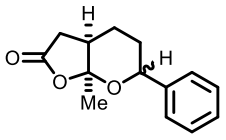


^{13}C NMR (125 MHz, $CDCl_3$)



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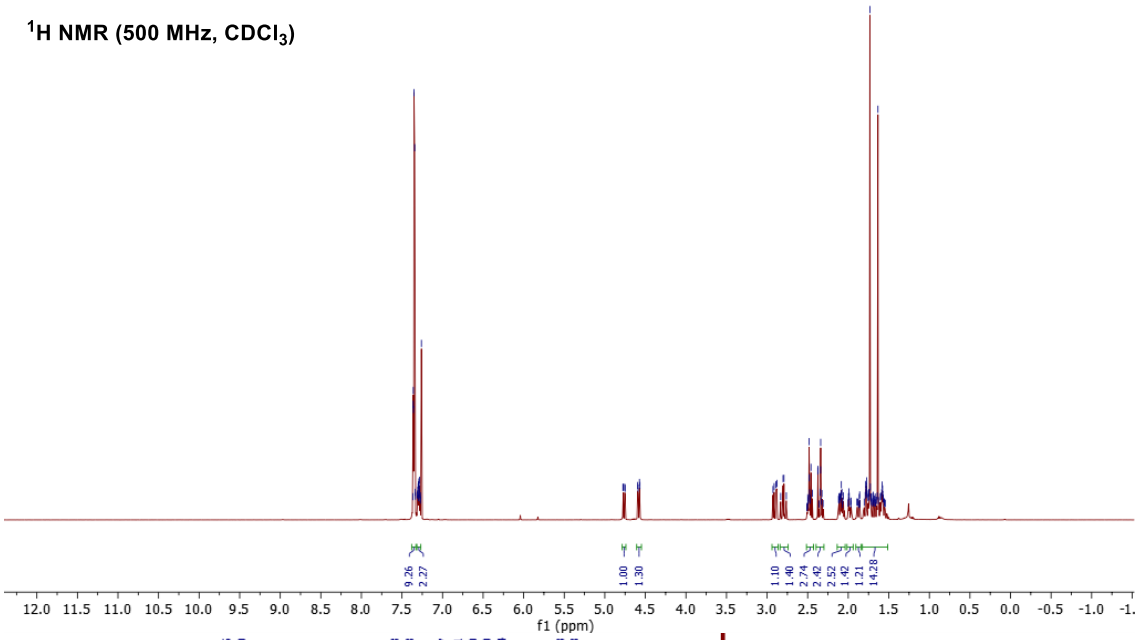

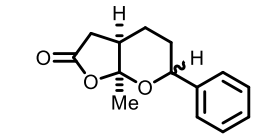

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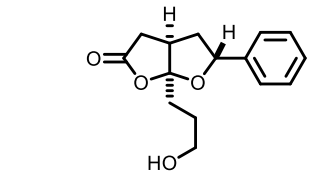
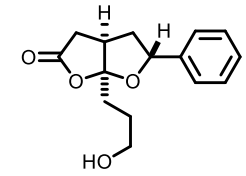


^{1}H NMR (500 MHz, $CDCl_3$)

V



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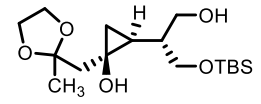

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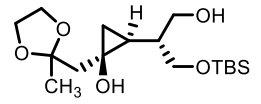
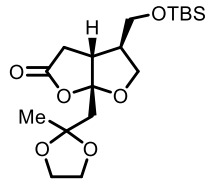
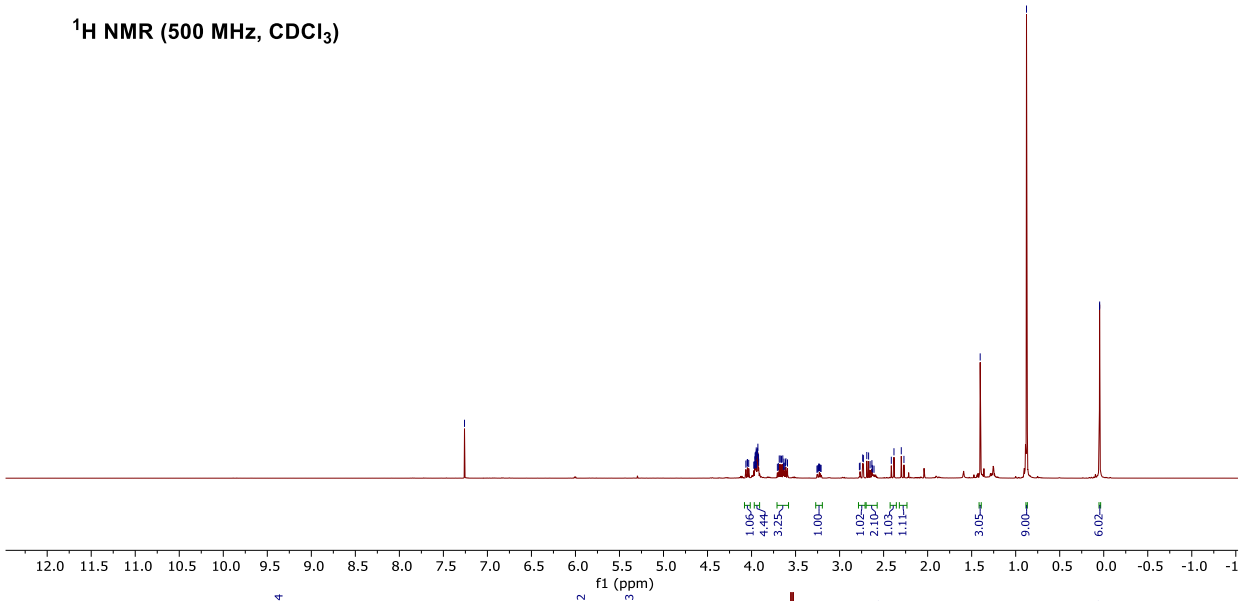


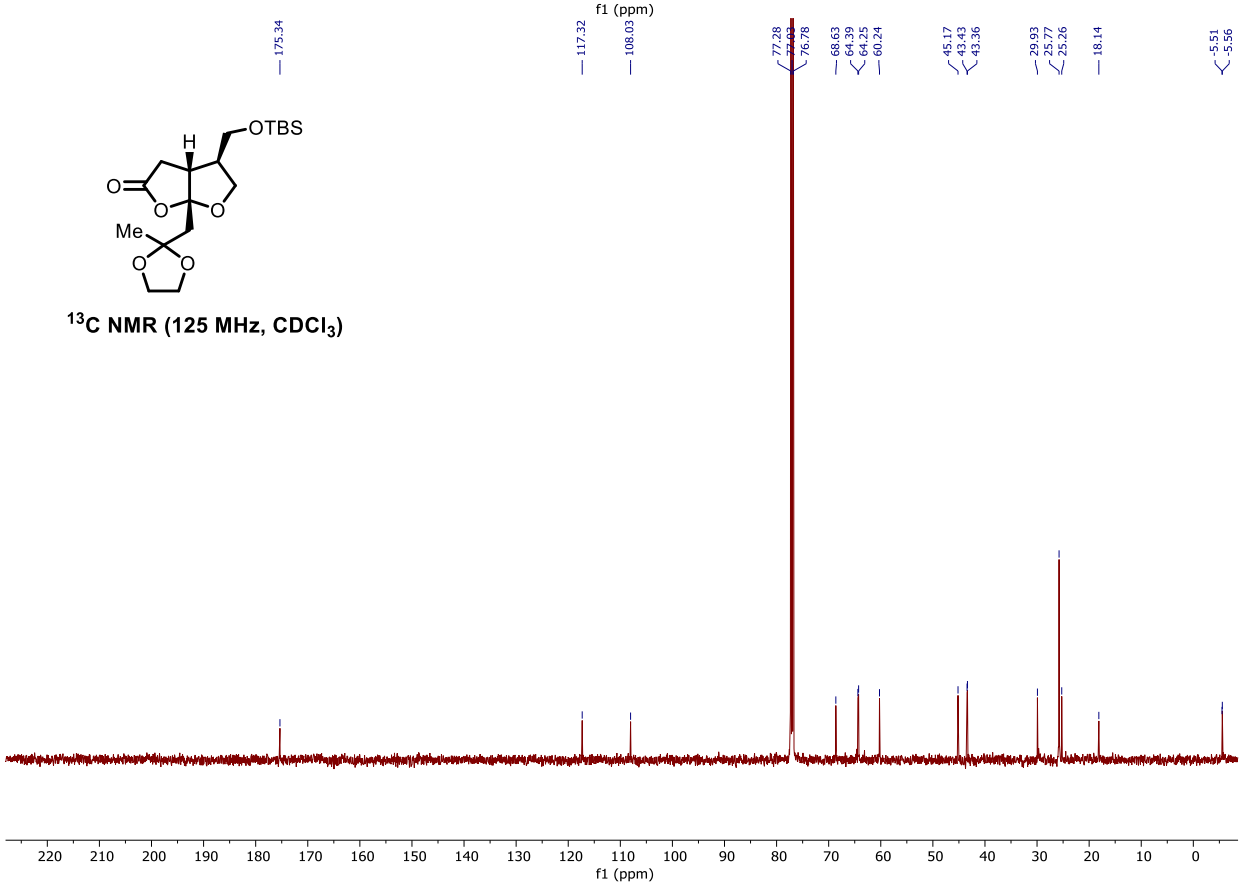
^{13}C NMR (125 MHz, $CDCl_3$)

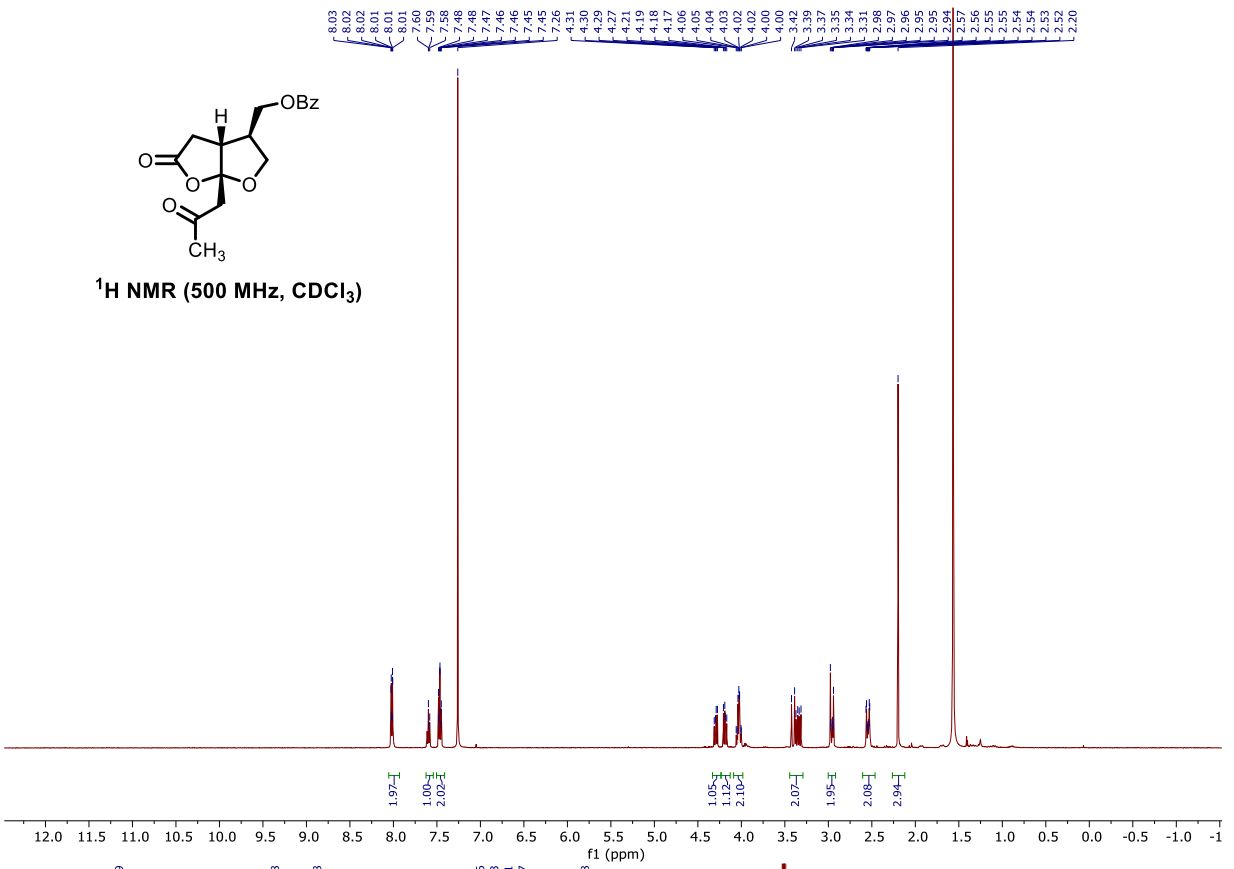


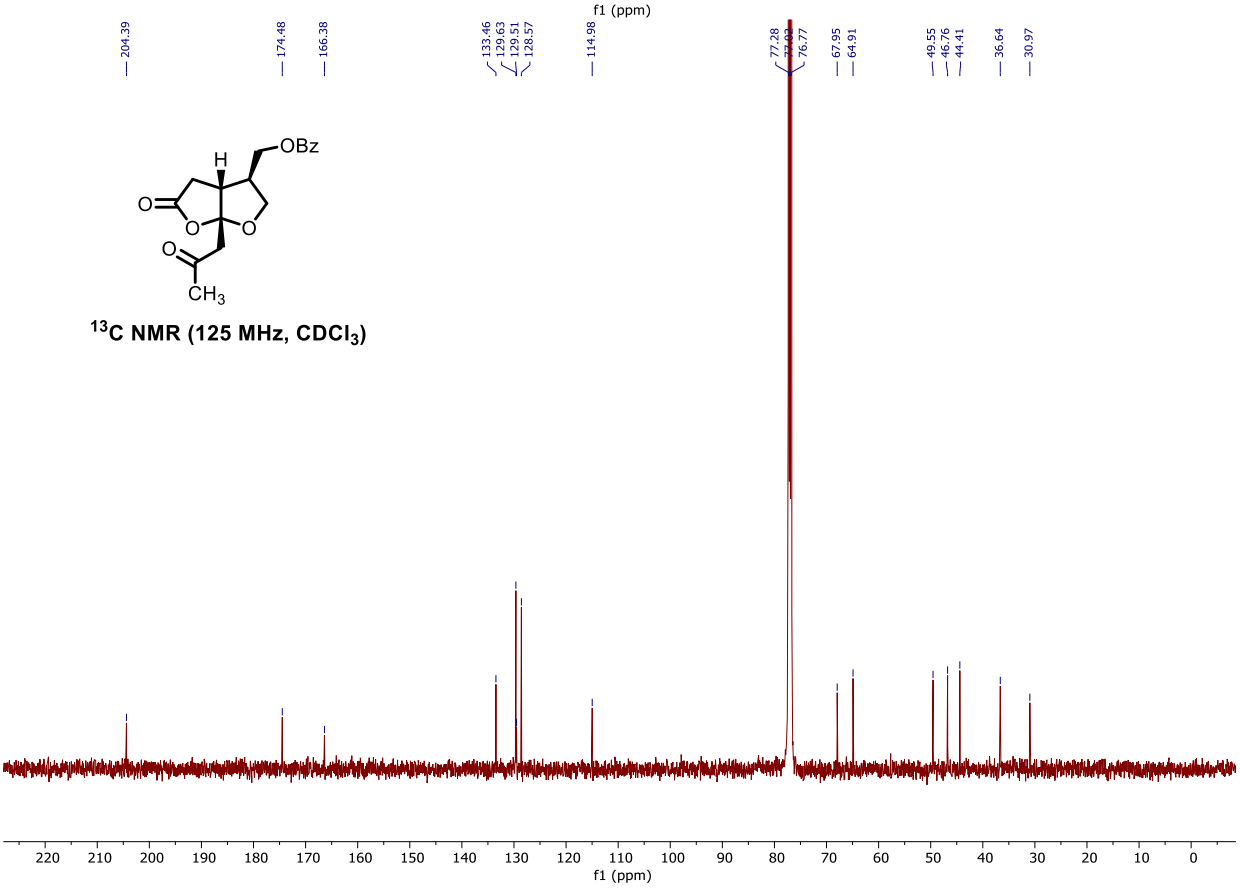
^{1}H NMR (500 MHz, $CDCl_3$)

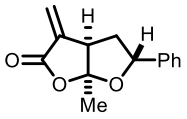


^{13}C NMR (125 MHz, $CDCl_3$)



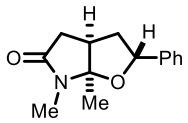

OBz
H
O
O
O
CH3
1H NMR (500 MHz, CDCl3)
f1 (ppm)


OBz
H
O
O
O
CH3
13C NMR (125 MHz, CDCl3)
f1 (ppm)

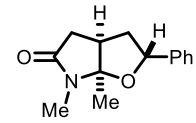


^{1}H NMR (500 MHz, $CDCl_3$)

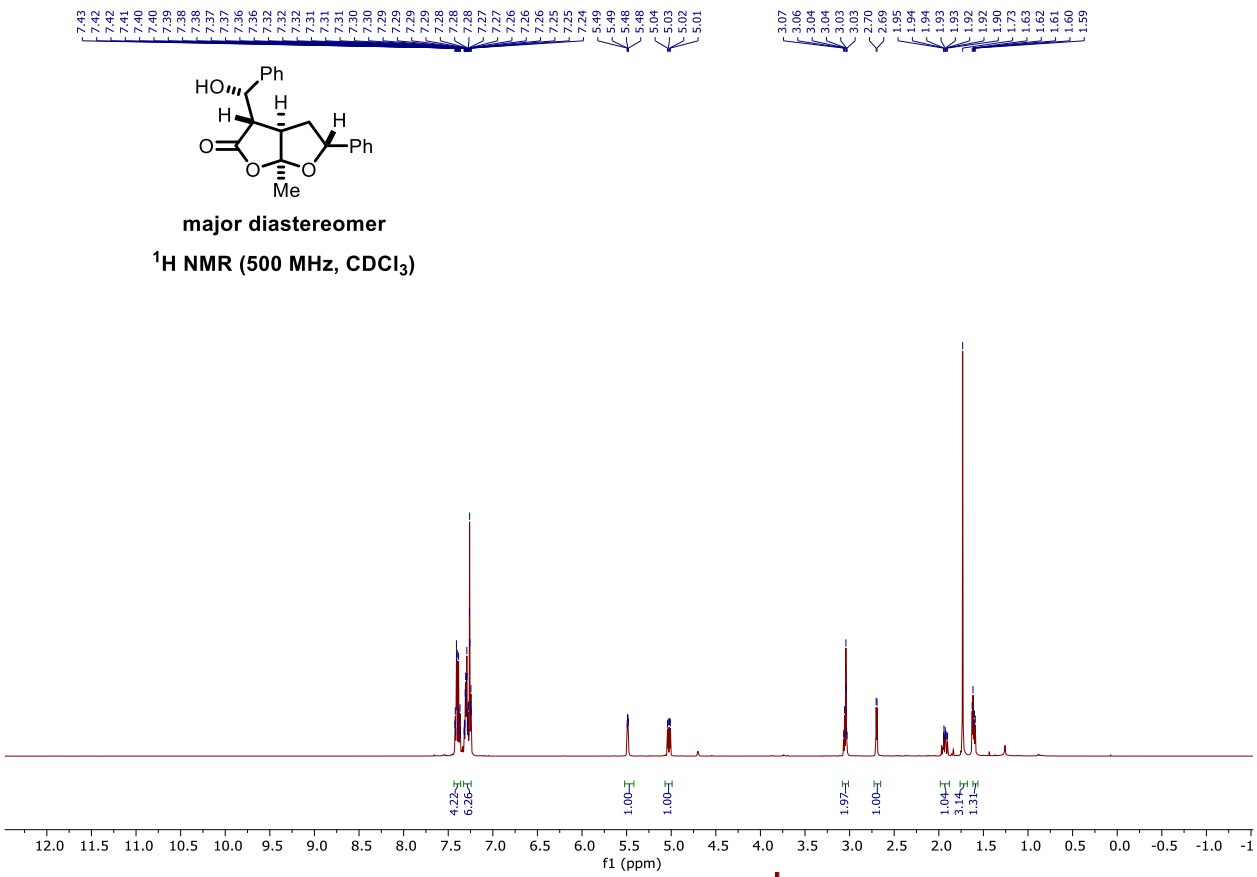
^{13}C NMR (125 MHz, $CDCl_3$)

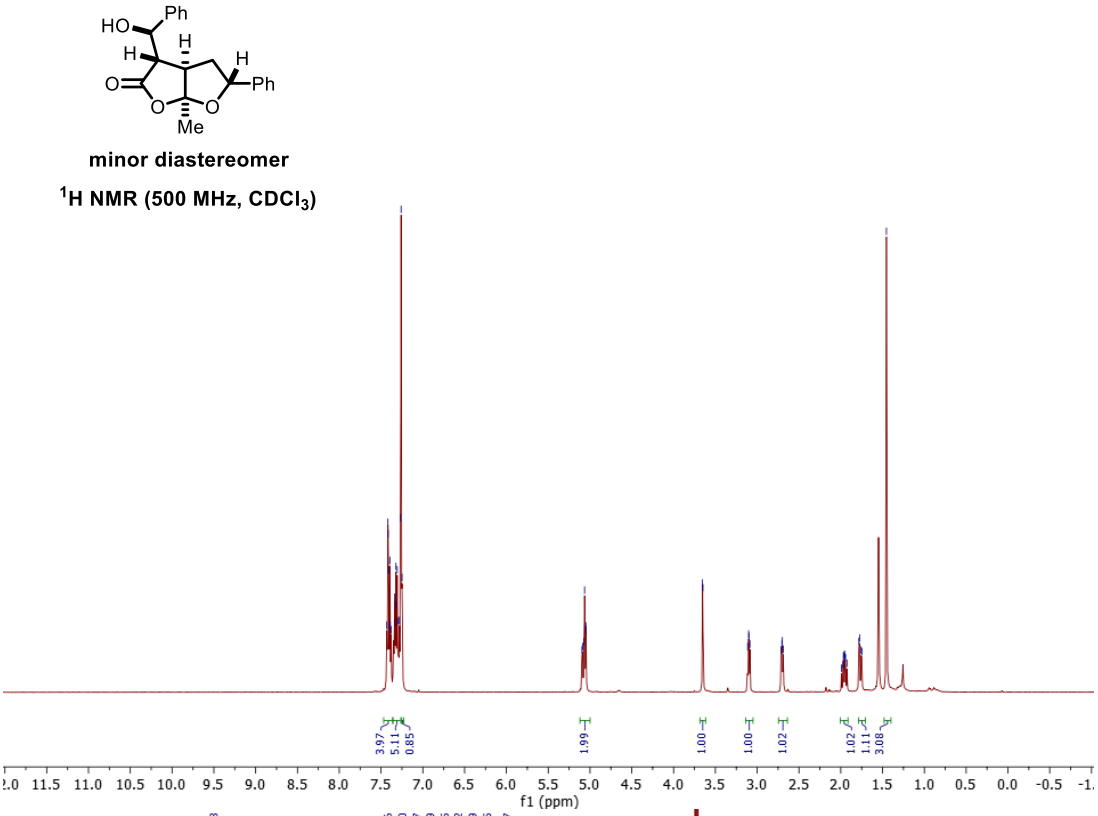


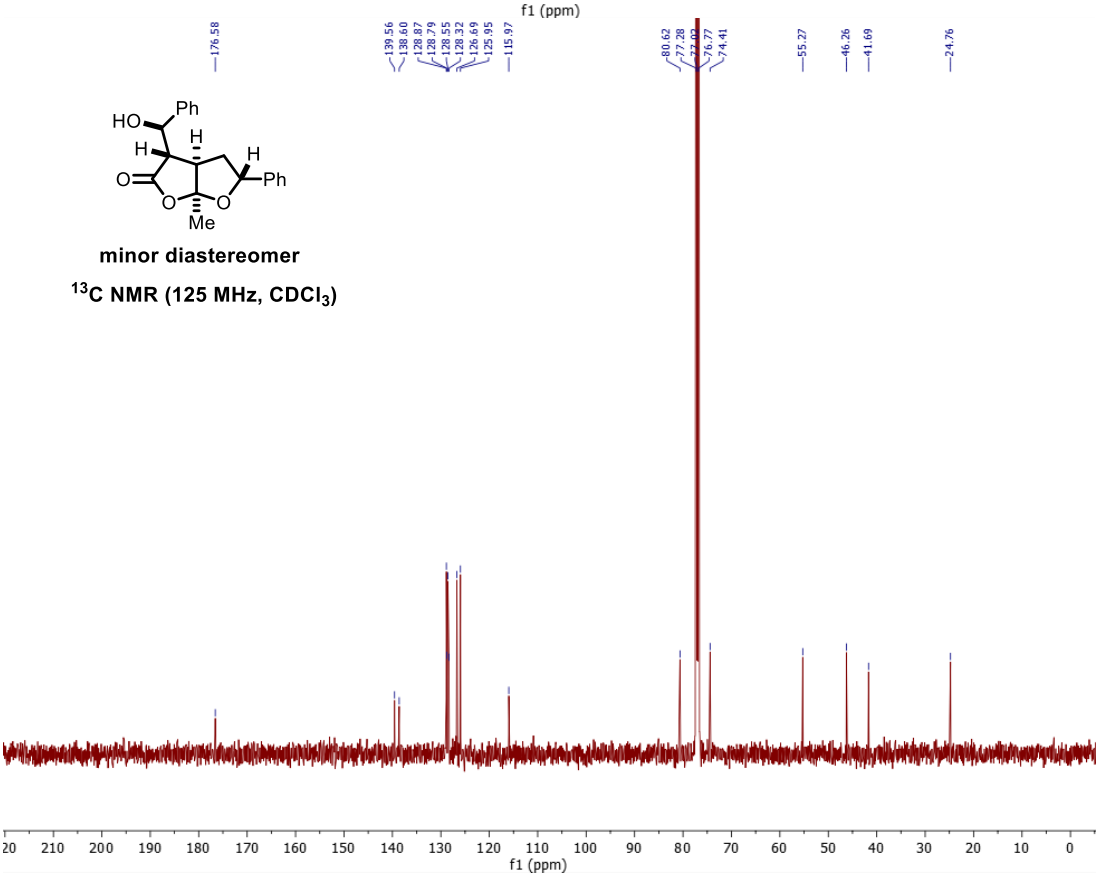
^{1}H NMR (500 MHz, $CDCl_3$)

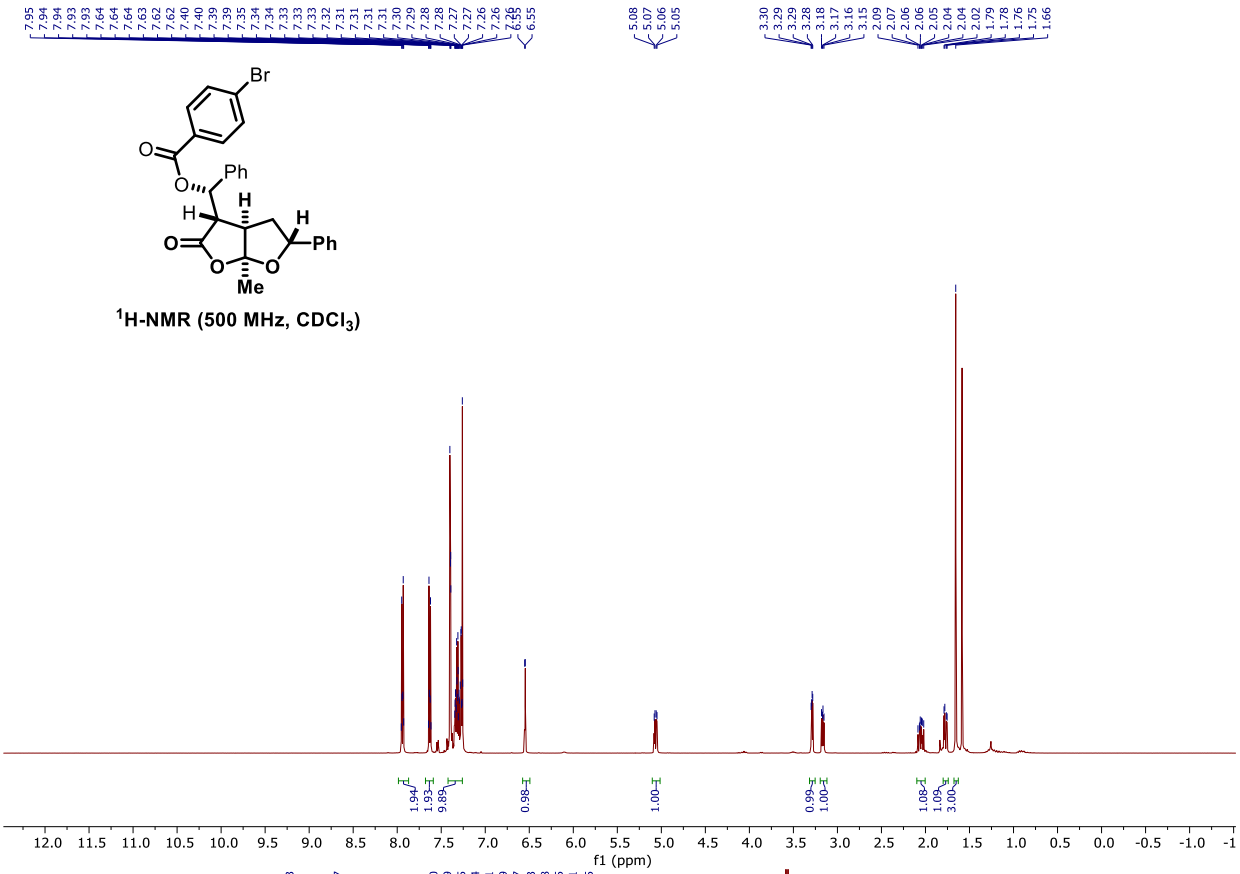


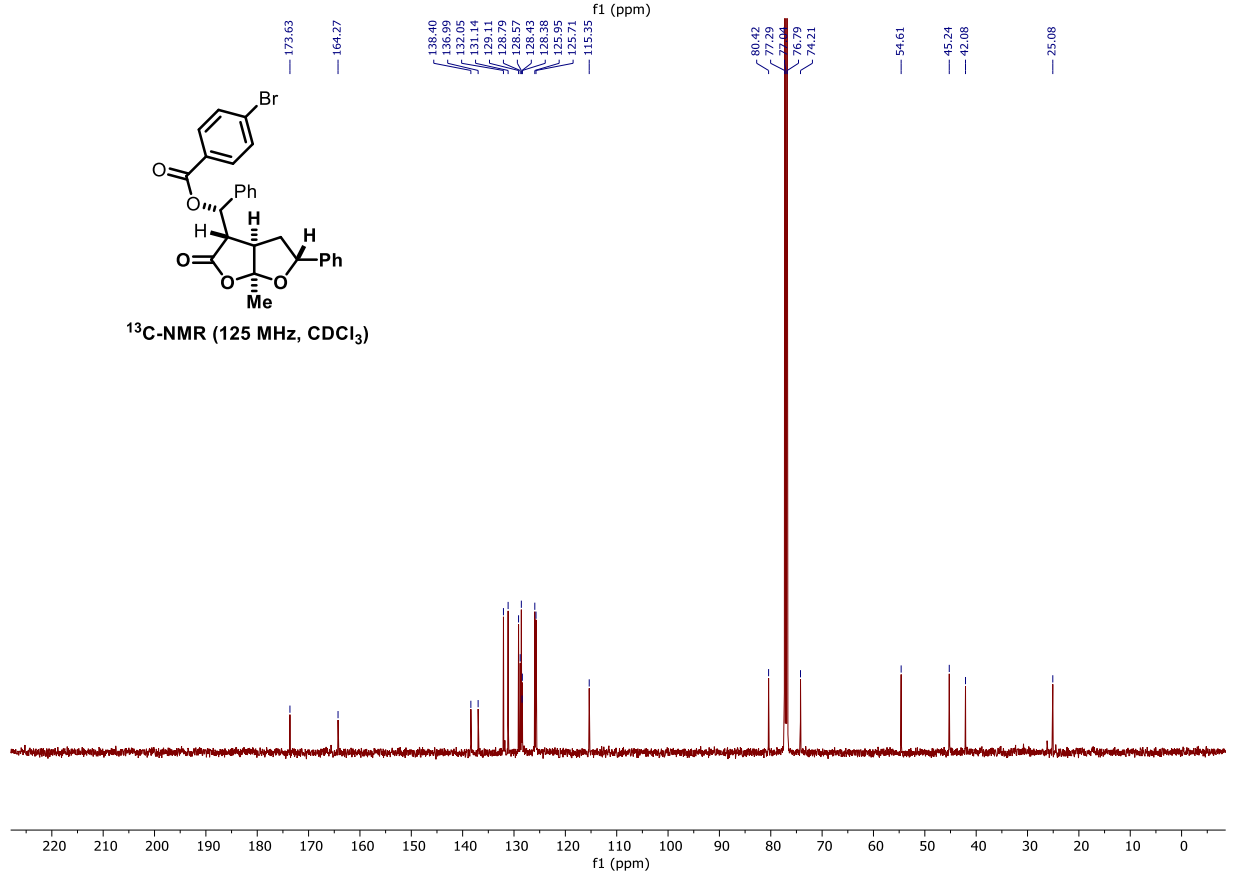
^{13}C NMR (125 MHz, $CDCl_3$)

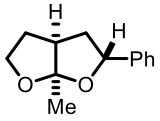

HO
Ph
H
H
H
O
O
O
Ph
Me
major diastereomer
1H NMR (500 MHz, CDCl3)
f1 (ppm)
major diastereomer
13C NMR (125 MHz, CDCl3)
f1 (ppm)


HO
Ph
H
H
H
O
O
O
Ph
Me
minor diastereomer
1H NMR (500 MHz, CDCl3)
f1 (ppm)

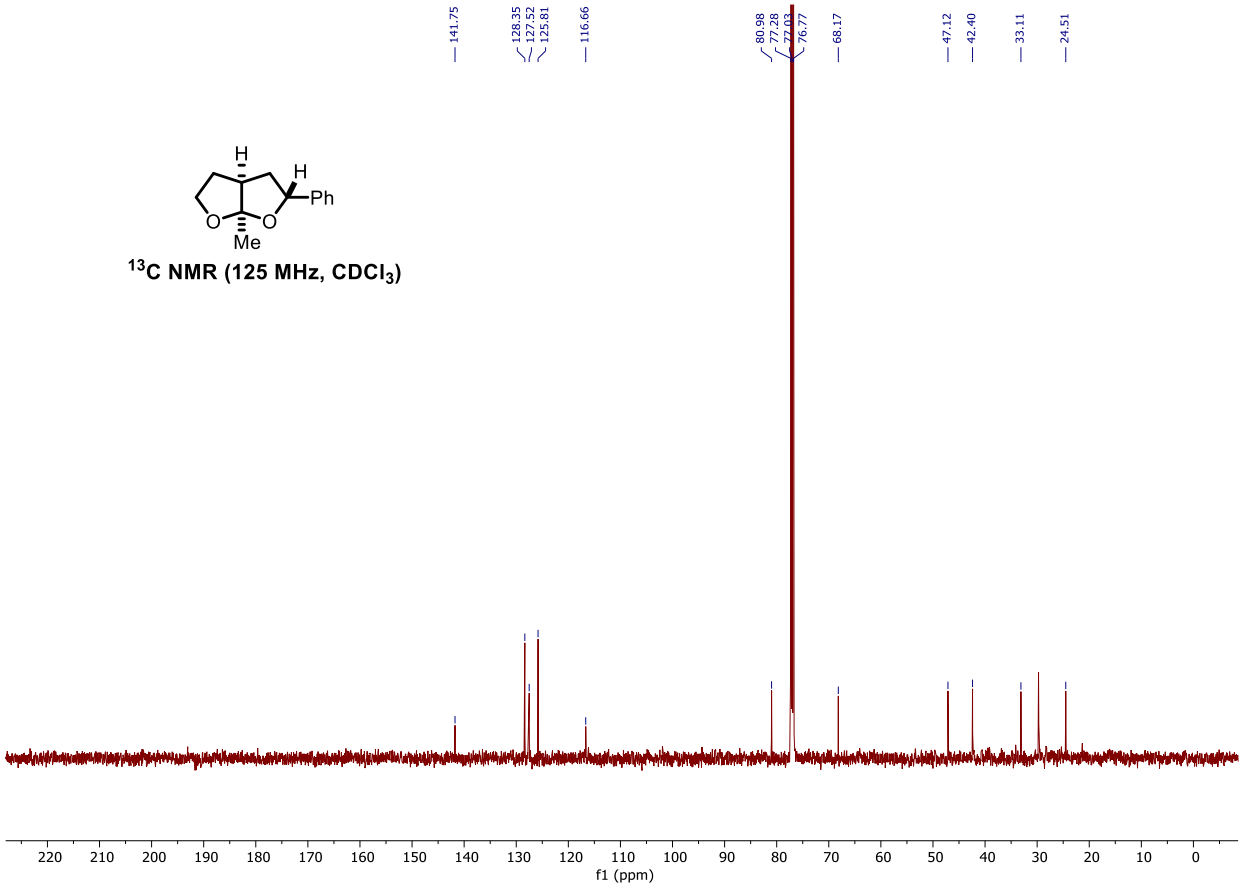

HO
Ph
H
H
H
O
O
O
Ph
Me
minor diastereomer
13C NMR (125 MHz, CDCl3)
f1 (ppm)


Br
O
O
Ph
H
H
H
O
Ph
O
O
Me
1H-NMR (500 MHz, CDCl3)
f1 (ppm)

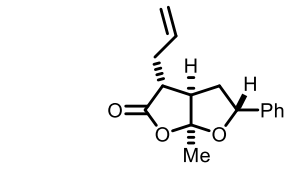

Br
O
O
Ph
H
H
H
O
Ph
O
O
Me
13C-NMR (125 MHz, CDCl3)
f1 (ppm)



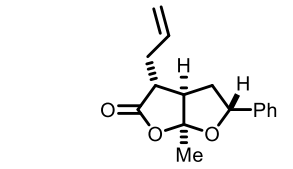
^{1}H NMR (500 MHz, $CDCl_3$)



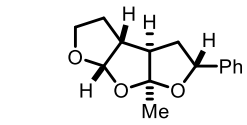
^{13}C NMR (125 MHz, $CDCl_3$)



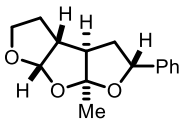
^{1}H NMR (500 MHz, $CDCl_3$)



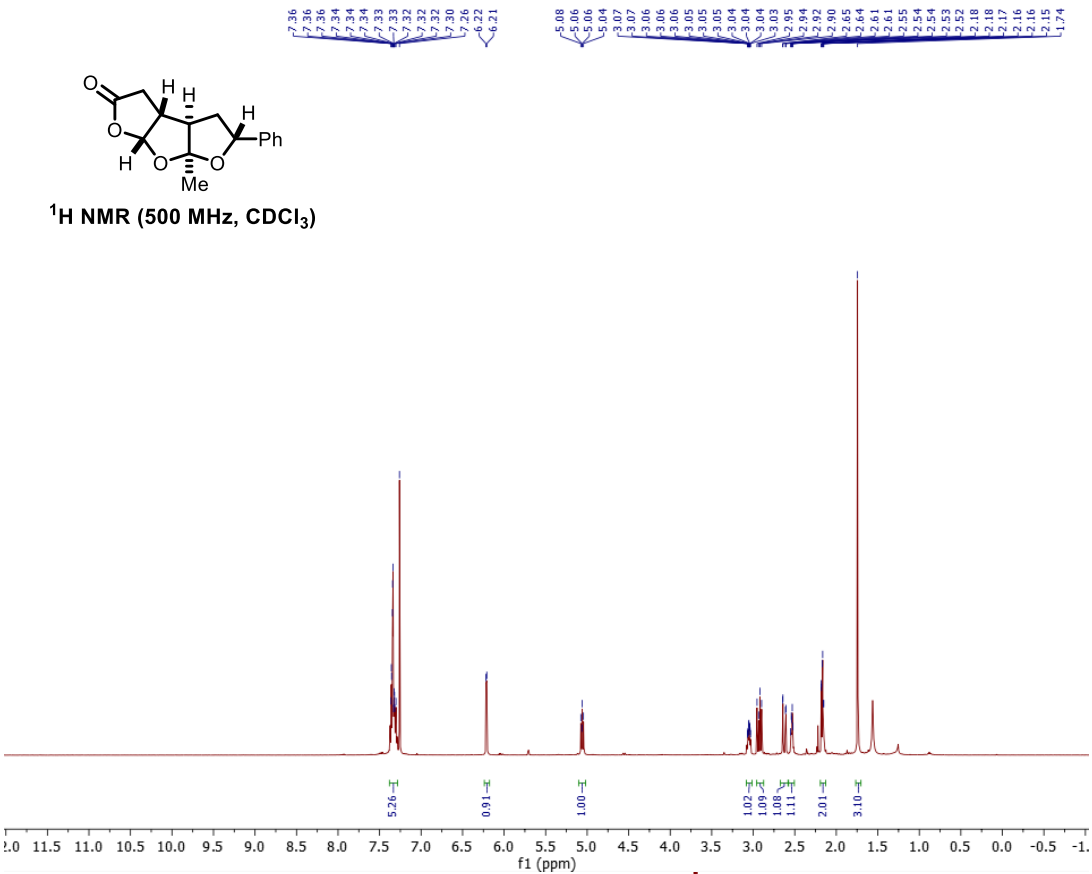
^{13}C NMR (125 MHz, $CDCl_3$)



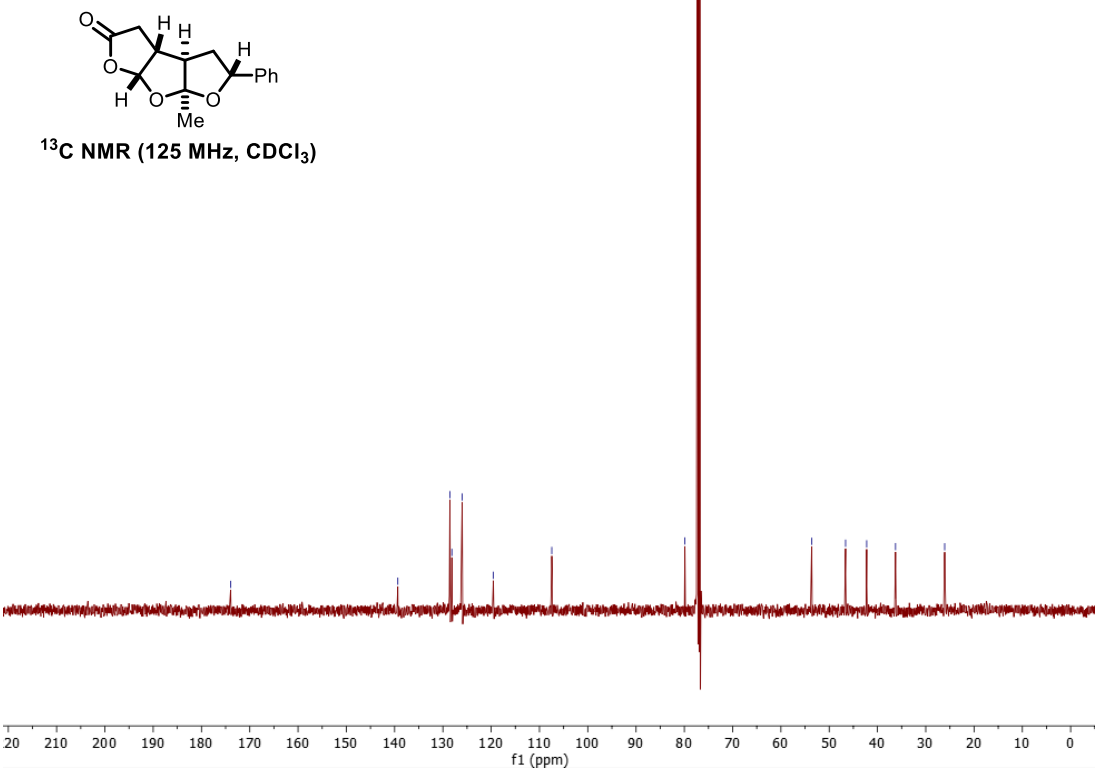
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)



^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)