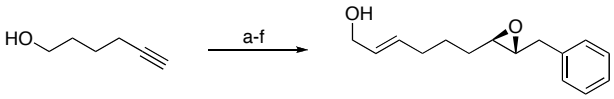
General

^{1}H NMR and ^{13}C NMR spectra were taken on a Bruker Avance 300 spectrometer at 300 MHz and 75 MHz respectively, a Bruker Avance 400 spectrometer at 400 MHz and 100 MHz, or a Bruker Avance 500 spectrometer at 500 MHz and 125 MHz, as specified. The chemical shifts are reported in parts per million (ppm) on the delta (δ) scale. The solvent peak was used as a reference value, for ^{1}H NMR: $CDCl_3$ = 7.27 ppm, CD_2Cl_2 = 5.31 ppm, C_6D_6 = 7.16 ppm, for ^{13}C NMR: $CDCl_3$ = 77.23, $CDCl_3$ = 53.52, C_6D_6 = 128.37 . Data are reported as follows: m = multiplet, s = singlet; d = doublet; t = triplet; q = quartet; p = pentet; dd = doublet of doublets; dt = doublet of triplets; br = broad. High resolution and low resolution mass spectra were collected on a VG 7070 spectrometer. Infrared (IR) spectra were taken on a Mattson Cygnus 100 spectrometer. Samples for IR were prepared as thin films on a NaCl plates by dissolving the corresponding compounds in CH_2Cl_2 followed by evaporation of the CH_2Cl_2. Methylene chloride was distilled under N_2 from CaH_2. Analytical TLC was performed on E. Merck pre-coated (25 mm) silica gel 60F-254 plates. Visualization was done under UV (254 nm). Flash chromatography was done using ICN SiliTech 32-63 60 Å silica gel. Reagent grade ethyl acetate, diethyl ether, pentane and hexanes (commercial mixture) were purchased from EM Science and used as is for chromatography. All reactions were performed in oven or flame-dried glassware under a positive pressure of N_2 with magnetic stirring unless otherwise noted.

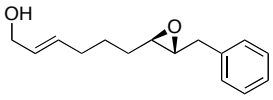
General procedure for rearrangement cyclization catalyzed by Re_2O_7

To a solution (~10 mM) of corresponding substrate in CH_2Cl_2 was added 0.05 equivalent of Re_2O_7, the reaction mixture was stirred at RT (unless otherwise mentioned in the substrate tables) and monitored by TLC until complete consumption of the starting chemicals, then the reaction was quenched with a few drops of pyridine or triethylamine and the solvent was removed under vacuum, follwed by purification by flash chromatography or preparation TLC to give the product.



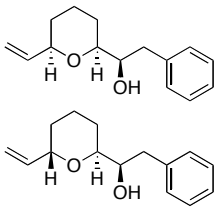
Reagents and conditions
a) DIBAL-H, hexanes, –78 °C, then I_2, THF, 51%. b) BnMgCl, $(dppf)_2PdCl_2$, THF, 95%. c) PCC, Celite, CH_2Cl_2. d) $(EtO)_2P(O)CH_2CO_2Et$, NaH, THF, 0 °C, 77% (two steps). e) D-Fructose-derived Shi ketone, Oxone, $Na_2B_4O_7$, $Na_2(EDTA)$, K_2CO_3, Bu_4NHSO_4, CH_3CN, H_2O, 0 °C, 39%. f) DIBAL-H, CH_2Cl_2, –78 °C, 91%.

Scheme 1. Synthesis of 1.



(*E*)-6-((2*R*,3*R*)-3-Benzyloxiran-2-yl)hex-2-en-1-ol (1)

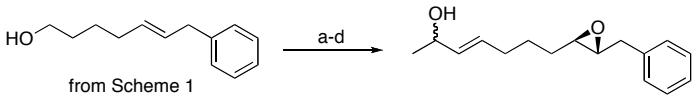
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.38 (m, 2H), 7.23-7.30 (m, 3H), 5.57-5.72 (m, 2H), 4.08 (d, *J* = 5.2, 2H), 2.90-2.98 (m, 2H), 2.77-2.86 (m, 2H), 2.03-2.13 (m, 2H), 1.83 (br, 1H), 1.45-1.65 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) 137.4, 132.3, 129.6, 128.9, 128.6, 126.6, 63.5, 58.8, 58.6, 38.5, 31.8, 31.3; IR (neat) 3407, 3027, 2973, 2929, 2857, 1669, 1604, 1494, 1370, 1088, 1001, 971, 932, 743 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{20}O_2Na$ $[M + Na]^+$ 255.1361, found 255.1387.



(*R*)-2-Phenyl-1-((2*S*,6*R*)-6-vinyltetrahydro-2H-pyran-2-yl)ethanol (2) and (*R*)-2-Phenyl-1-((2*S*,6*S*)-6-vinyltetrahydro-2H-pyran-2-yl)ethanol (3)

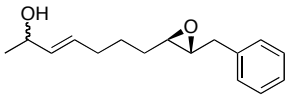
The general rearrangement procedure was followed with **1** (28 mg, 0.12 mmol), Re_2O_7 (3 mg, 0.006 mmol), and CH_2Cl_2 (12 mL). The reaction was stirred at rt for 4 h, then was quenched with five drops of pyridine. After evaporation of the solvent, the crude mixture was purified by flash chromatography (10%-20% ethyl acetate in hexanes) to give the product (25 mg, 89%, dr = 1.3:1). The mixture was further purified for analysis. Major

product (**2**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.35 (m, 2H), 7.21-7.28 (m, 3H), 5.89 (ddd, *J* = 5.2, 10.8, 17.2, 1H), 5.26 (dt, *J* = 1.6, 17.2, 1H), 5.12 (dt, *J* = 1.6, 10.8, 1H), 3.94 (h, *J* = 4.0, 1H), 3.88 (ddddd, *J* = 1.2, 1.6, 2.8, 5.2, 10.8, 1H), 3.35 (ddd, *J* = 2.0, 4.4, 10.8, 1H), 2.89 (dd, *J* = 4.8, 13.6, 1H), 2.80 (dd, *J* = 8.4, 13.2, 1H), 2.04 (d, *J* = 4.0, 1H), 1.92-1.99 (m, 1H), 1.62-1.77 (m, 2H), 1.41-1.62 (m, 2H), 1.28-1.39 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 139.4, 138.5, 129.4, 128.5, 126.3, 114.4, 79.5, 78.4, 74.7, 38.7, 31.6, 25.1, 23.0; IR (neat) 3446, 3027, 2934, 2855, 1646, 1603, 1495, 1453, 1306, 1201, 1077, 1046, 915, 748; HRMS (ESI) calcd for $C_{15}H_{20}O_2Na$ $[M + Na]^+$ 255.1361, found 255.1378. Minor product (**3**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.34 (m, 2H), 7.21-7.28 (m, 3H), 5.92-6.02 (m, 1H), 5.25-5.27 (m, 1H), 5.21-5.24 (m, 1H), 4.45-4.51 (m, 1H), 3.89 (h, *J* = 4.4, 1H), 3.63 (ddd, *J* = 2.0, 5.2, 9.2, 1H), 2.93 (dd, *J* = 4.0, 14.0, 1H), 2.69 (dd, *J* = 8.8, 14.0, 1H), 1.91 (d, *J* = 3.6, 1H), 1.77-1.88 (m, 1H), 1.63-1.75 (m, 4H), 1.52-1.63 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) 138.6, 138.1, 129.4, 128.5, 126.4, 116.4, 74.1, 73.3, 73.0, 39.0, 28.6, 25.5, 18.3; IR (neat) 3439, 3027, 2930, 2858, 1669, 1603, 1494, 1453, 1407, 1338, 1203, 1121, 1048, 1039, 921, 891, 748 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{20}O_2Na$ $[M + Na]^+$ 255.1361, found 255.1376.

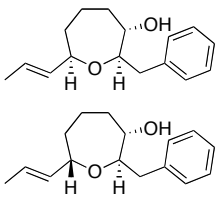


Reagents and conditions
a) PCC, Celite, CH_2Cl_2. b) $(EtO)_2P(O)CH_2COMe$, NaH, THF, 0 °C, 66% (two steps). c) D-Fructose -derived Shi ketone, Oxone, $Na_2B_4O_7$, $Na_2(EDTA)$, K_2CO_3, Bu_4NHSO_4,CH_3CN, H_2O, 0 °C, 58%. d) DIBAL-H, CH_2Cl_2, –78 °C, 91%.

Scheme 2. Synthesis of **4**.

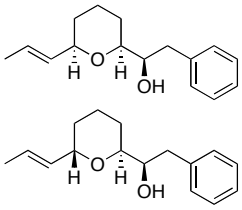


(*E*)-7-((2*R*, 3*R*)-3-Benzylloxiran-2-yl)hept-3-en-2-ol (4)
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30-7.38 (m, *2*H), 7.23-7.30 (m, 3H), 5.46-5.66 (m, 2H), 4.26 (p, *J* = 6.3, 1H), 2.90-2.98 (m, 2H), 2.77-2.85 (m, 2H), 2.05 (q, *J* = 6.6, 2H), 1.78 (br, 1H), 1.46-1.62 (m, 4H), 1.26 (d, *J* = 6.3, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.4, 134.8, 130.0, 128.9, 128.5, 126.6, 68.7, 58.8, 58.6, 38.5, 31.7, 31.3, 25.5, 23.5; IR (neat) 3412, 3027, 2971, 2925, 2857, 1604, 1494, 1453, 1367,1145, 1063, 969, 798, 743 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{22}O_2Na$ $[M + Na]^+$ 269.1517, found 269.1529.



(2*R*,3*S*,7*R*)-2-Benzyl-7-((*E*)-prop-1-en-1-yl)oxepan-3-ol (5) and (2*R*,3*S*,7*S*)-2-Benzyl-7-((*E*)-prop-1-en-1-yl)oxepan-3-ol (6)
The general rearrangement procedure was followed with **4** (25 mg, 0.10 mmol), Re_2O_7 (2 mg, 0.005 mmol), and CH_2Cl_2 (10 mL). The reaction was stirred at rt for 45 min, then was quenched with five drops of pyridine. After evaporation of the solvent, the crude mixture was purified by flash chromatography (20%-30% ethyl acetate in hexanes) to give the product (22 mg, 89%, dr = 1:1.2). The isomers were further purified for characterization. Minor product (**5**): ^{1}H NMR (400 MHz, $C6D_6$) δ 7.35-7.37 (m, 2H), 7.18-7.22 (m, 2H), 7.08-7.12 (m, 1H), 5.39-5.51 (m, 2H), 3.62-3.67 (m, 1H), 3.42-3.45 (m, 1H), 3.38 (dt, *J* = 3.2, 8.4, 1H), 3.04 (dd, *J* = 3.0, 13.8, 1H), 2.78 (dd, *J* = 8.6, 13.8, 1H), 1.70-1.79 (m, 1H), 1.49-1.58 (m, 2H), 1.53 (d, *J* = 5.2, 3H), 1.35-1.48 (m, 3H). 0.78 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 139.5, 132.3, 129.5, 128.1, 126.0, 125.8, 86.2, 82.4, 75.3, 40.7, 36.2, 35.8, 19.4, 17.8; IR (neat) 3415, 3027, 2926, 2857, 1672, 1604, 1495, 1452, 1133, 1101, 1037, 999, 966, 750 cm^{-1}; HRMS (EI) calcd for $C_{16}H_{22}O_2$ $[M]^+$ 246.1620, found 246.1629. Major product (**6**): ^{1}H NMR (400 MHz, C_6D_6) δ 7.29-7.33 (m, 2H), 7.17-7.22 (m, 2H), 7.07-7.12 (m, 1H), 5.24 (ddq, *J* = 1.2, 6.4, 15.6, 1H), 4.91 (ddq, *J*= 1.6, 5.6, 15.6, 1H), 3.92 (p, *J* = 5.2, 1H), 3.46 (dt, *J* = 2.8, 9.2, 1H), 3.12 (dt, *J* = 4.4, 9.2, 1H), 3.17 (dd, *J* = 2.8, 13.6, 1H), 2.64 (dd, *J* = 9.2, 13.6, 1H), 1.79-1.87 (m, 1H), 1.48-1.56 (m, 1H), 1.35-1.47 (m, 2H), 1.39 (d, *J* = 6.4, 3H), 1.18-1.35 (m, 3H), 0.90 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 139.4, 132.3, 130.0, 128.0, 125.9, 125.7, 78.3, 75.6, 75.3, 39.4, 38.4, 33.9, 21.5, 17.8; IR (neat) 3307, 3034, 2926, 2855, 1605,

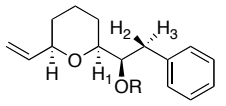
1495, 1451, 1354, 1123, 1091, 1036, 970, 744 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{22}O_2Na$ $[M + Na]^+$ 269.1517, found 269.1509.



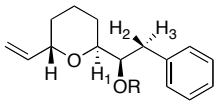
(*R*)-2-Phenyl-1-((2*S*,6*R*)-6-((*E*)-prop-1-en-1-yl)tetrahydro-2H-pyran-2-yl)ethanol (7) and (*R*)-2-phenyl-1-((2*S*,6*S*)-6-((*E*)-prop-1-en-1-yl)tetrahydro-2H-pyran-2-yl)ethanol (8)

The general rearrangement procedure was followed with **4** (30 mg, 0.12 mmol), Re_2O_7 (3 mg, 0.006 mmol), and CH_2Cl_2 (12 mL). The reaction was stirred at rt for 36 h (5% more catalyst added at 12 hr and 24 hr respectively), then was quenched with five drops of pyridine. After evaporation of the solvent, the crude mixture was purified by flash chromatography (10%-20% ethyl acetate in hexanes) to give the product (27 mg, 93%, dr = 1:1.1). These isomers were further purified for characterization. Minor product (**7**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.37 (m, 2H), 7.23-7.30 (m, 3H), 5.72 (ddt, *J* = 0.8, 6.4, 15.6, 1H), 5.55 (ddt, *J* = 1.6, 6.0, 15.6, 1H), 3.96 (h, *J* = 4.0, 1H), 3.84 (dd, *J* = 6.2, 10.2, 1H), 3.34 (ddd, *J* = 1.8, 4.2, 10.6, 1H), 2.88 (dd, *J* = 5.0, 13.8, 1H), 2.81 (dd, *J* = 8.2, 13.8), 2.01-2.04 (m, 1H), 1.92-1.98 (m, 1H), 1.73 (d, *J* = 6.4, 3H), 1.72 (br, 1H), 1.58-1.67 (m, 1H), 1.41-1.58 (m, 2H), 1.36 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 138.5, 132.4, 129.4, 128.5, 126.5, 126.3, 79.4, 78.5, 74.6, 38.7, 31.9, 24.9, 23.0, 17.9; IR (neat) 3360, 3029, 2960, 2928, 2912, 2839, 1677, 1495, 1453, 1379, 1293, 1196, 1078, 1037, 748 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{22}O_2Na$ $[M + Na]^+$ 269.1517, found 269.1535. Major product (**8**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.38 (m, 2H), 7.23-7.31 (m, 3H), 5.64-5.75 (m, 2H), 4.40-4.46 (m, 1H), 3.87-3.93 (m, 1H), 3.64 (ddd, *J* = 2.2, 5.2, 9.0, 1H), 3.95 (dd, *J* = 3.6, 14.0, 1H), 2.72 (dd, *J* = 9.0, 14.0, 1H), 1.92 (br, 1H), 1.78-1.86 (m, 1H), 1.76 (d, *J* = 4.8, 3H), 1.68-1.74 (m, 3H), 1.56-1.67 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) 138.7, 130.6, 129.5, 128.5, 127.9, 126.4, 73.9, 73.2, 72.8, 39.0, 29.2, 25.5, 18.4, 18.0; IR (neat) 3434, 3026, 2934, 2859, 1668, 1603, 1494, 1452, 1202, 1077, 1035, 966, 890, 748 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{22}O_2Na$ $[M + Na]^+$ 269.1517, found 269.1496.

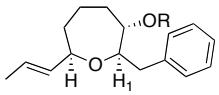
The absolute configurations of the secondary alcohols in structures **5-8** were determined by Mosher ester analysis. Typically, 5-6 mg of each alcohol was divided into two parts, these two parts were treated with R and S Mosher acid (5 equiv), DCC (5.5 equiv), and DMAP (5.5 equiv) in 1 mL CH_2Cl_2. The reactions were stirred at rt and were monitored by TLC. When the starting alcohol was completely consumed, the reaction mixtures were filtered through a short column of silica gel to remove the insoluble salts. After the removal of the solvents under reduced pressure, ^{1}H NMR and ^{19}F NMR were taken to determine the confituration and enantiopurity of the conrresponding alcohols.



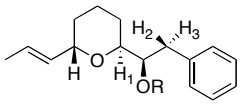
2



3



5

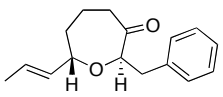


8

	R-Mosher ester			*S*-Mosher ester			
Structure	δ H1	δ H2	δ H3	δ H1	δ H2	δ H3	Solvent
2	5.79	2.88	2.88	5.75	2.91	3.01	$CDCl_3$
3	5.83	2.81	2.97	5.81	2.96	3.16	$CDCl_3$
5	3.51			3.65			C_6D_6
8	3.83	2.88	3.04	3.78	2.94	3.14	$CDCl_3$

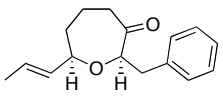
Structures **5** and **7**, **6** and **8** were difficult to differentiate by ^{1}H NMR, ^{13}C NMR, COSY and NOESY experiments, but could be differentiated oxidizing to the corresponding ketones. The ketone products were obained by submitting the corresponding alcohols to the PCC oxidation conditions: typically, 2-7 mg of alcohol was treated with 5-10 eq PCC and Celite in CH_2Cl_2 until complete consumption of the alcohol, then

thre reaction mixture was filtered through a short column of silica gel to give the pure ketones. (yield: 92%-97%) The sturctures **6** and **7** were also confirmed by X-ray crystallography.



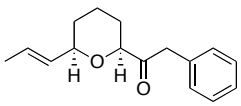
(2*R*,7*S*)-2-Benzyl-7-((*E*)-prop-1-en-1-yl)oxepan-3-one

^{1}H NMR (400 MHz, C_6D_6) δ 7.19-7.23 (m, 2H), 7.12-7.15 (m, 2H), 7.04-7.09 (m, 1H), 5.11-5.27 (m, 2H), 4.08 (dd, *J* = 3.6, 8.8, 1H), 3.91 (m, 1H), 3.23 (dd, *J* = 3.6, 14.4, 1H), 2.79 (dd, *J* = 8.8, 14.4, 1H), 2.46-2.54 (m, 1H), 2.27-2.36 (m, 1H), 1.41 (d, *J* = 5.6, 3H), 1.32-1.37 (m, 3H), 1.22-1.32 (m, 1H); ^{13}C NMR (100 MHz, C_6D_6) 212.9, 138.5, 130.9, 129.8, 127.6, 126.5, 126.1, 81.3, 76.4, 40.2, 37.0, 33.1, 21.3, 17.4; IR (neat) 3061, 3028, 2933, 2863, 1711, 1604, 1459, 1452, 1324, 1180, 1093, 968, 785 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{20}O_2Na$ $[M + Na]^+$ 267.1361, found 267.1379.



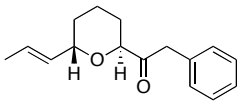
(2*R*,7*R*)-2-benzyl-7-((*E*)-prop-1-en-1-yl)oxepan-3-one

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20-7.32 (m, 5H), 5.40-5.56 (m, 2H), 4.03 (dd, *J* = 4.0, 8.4, 1H), 3.66 (d, *J* = 9.4, 1H), 3.06 (dd, *J* = 3.6, 14.0, 1H), 2.89 (dd, *J* = 9.0, 14.0, 1H), 2.69 (dt, *J* = 2.4, 12.4, 1H), 2.32 (dd, *J* = 6.4, 12.0, 1H), 1.90-1.99 (m, 1H), 1.80-1.88 (m, 1H), 1.64 (d, *J* = 6.0, 3H), 1.58-1.69 (m, 1H), 1.41-1.54 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 216.3, 137.6, 131.8, 129.6, 128.1, 126.4, 125.7, 87.1, 83.2, 41.6, 39.2, 36.2, 23.3, 17.4; IR (neat) 3061, 3029, 2931,2859, 1711, 1603, 1495, 1452, 1434, 1319, 1173, 1107, 966, 735 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{20}O_2Na$ $[M + Na]^+$ 267.1361, found 267.1350.



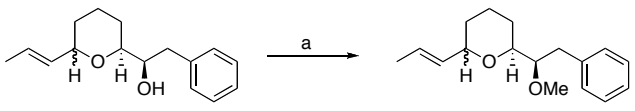
2-Phenyl-1-((2*S*,6*R*)-6-((*E*)-prop-1-en-1-yl)tetrahydro-2H-pyran-2-yl)ethanone

^{1}H NMR (400 MHz, C_6D_6) δ 7.22-7.28 (m, 2H), 7.12-7.17 (m, 2H), 7.03-7.09 (m, 1H), 5.65 (ddq, *J* = 0.8, 6.4, 15.2, 1H), 5.53 (ddq, *J* = 1.6, 5.6, 15.2, 1H), 3.92 (d, *J* = 15.2, 1H), 3.84 (d, *J* = 15.2, 1H), (3.61 (dd, *J* = 2.4, 11.2, 1H), 3.51 (ddt, *J* =1.2, 5.6, 10.2, 1H), 1.70-1.76 (m, 1H), 1.60 (dt, *J* = 1.2, 6.4, 3H), 1.43-1.49 (m, 1H), 1.25-1.30 (m, 1H), 1.02-1.21 (m, 3H); ^{13}C NMR (100 MHz, C_6D_6) 206.7, 134.7, 132.5, 130.0, 128.3, 126.5, 125.5, 82.0, 78.0, 44.7, 31.4, 27.5, 22.9, 17.6; IR (neat) 3061, 3029, 2936, 2855, 1722, 1601, 1495, 1452, 1299, 1199, 1095, 1034, 965, 742, 702 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{20}O_2Na$ $[M + Na]^+$ 267.1361, found 267.1406.



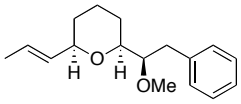
2-Phenyl-1-((2*S*,6*S*)-6-((*E*)-prop-1-en-1-yl)tetrahydro-2H-pyran-2-yl)ethanone

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.35 (m, 2H), 7.22-7.28 (m, 3H), 5.72 (ddt, *J* = 1.2, 6.4, 15.2, 1H), 5.56 (ddt, *J* = 1.6, 5.6, 15.2, 1H), 4.30 (t, *J* = 5.0, 1H), 4.11 (t, *J* = 5.6, 1H), 3.95 (d, *J* = 15.2, 1H), 3.85 (d, *J* = 15.2, 1H), 1.83-1.91 (m, 1H), 1.74 (dt, *J* = 1.2, 6.4, 3H), 1.64-1.72 (m, 3H), 1.44-1.62 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) 209.6, 134.2, 131.0, 128.5, 128.0, 126.8, 77.3, 74.4, 45.3, 30.2, 25.2, 19.3, 17.9; IR (neat) 3029, 2936, 2854, 1717, 1601, 1495, 1453, 1260, 1202, 1084, 1028, 965, 797 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{20}O_2Na$ $[M + Na]^+$ 267.1361, found 267.1359.



Reagents and conditions
a) NaH, THF, then MeI, 88%.

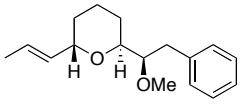
Scheme 3. Synthesis of **13**.



(2*S*,6*R*)-2-((*R*)-1-Methoxy-2-phenylethyl)-6-((*E*)-prop-1-en-1-yl) tetrahydro-2H-pyran (13-*cis*)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20-7.35 (m, 5H), 5.73 (dt, *J* = 6.4, 15.6, 1H), 5.56 (dd,

J = 4.4, 15.6, 1H), 3.74 (dd, J = 5.6, 10.4, 1H), 3.41 (q, J = 6.0, 1H), 3.36 (s, 3H), 3.23 (ddd, J = 1.8, 5.8, 11.0, 1H), 2.95 (dd, J = 4.4, 14.0, 1H), 2.85 (dd, J = 6.8, 14.0, 1H), 1.86-1.94 (m, 1H), 1.76-1.82 (m, 1H), 1.74 (d, J = 6.4, 3H), 1.59-1.66 (m, 1H), 1.44-1.56 (m, 1H), 1.28-1.41 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) 139.0, 132.7, 129.7, 128.1, 126.0, 125.9, 84.8, 78.7, 78.2, 58.8, 36.7, 31.9, 26.7, 23.3, 17.9; IR (neat) 3061, 3027, 2932, 2855, 1603, 1495, 1453, 1352, 1301, 1196, 1103, 1037, 964, 749 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{24}O_2Na$ $[M + Na]^+$ 283.1674, found 283.1684.

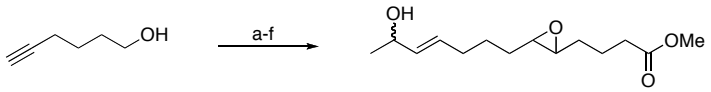


(2*S*,6*S*)-2-((*R*)-1-Methoxy-2-phenylethyl)-6-((*E*)-prop-1-en-1-yl) tetrahydro-2H-pyran (13-*trans*)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24-7.33 (m, 4H), 7.18-7.24 (m, 1H), 5.55-5.69 (m, 2H), 3.58 (ddd, J = 2.4, 6.0, 9.6, 1H), 3.41 (ddd, J = 4.0, 6.8, 7.2, 1H), 3.27 (s, 3H), 3.98 (dd, J = 3.6, 14.0, 1H), 3.75 (dd, J = 7.2, 14.0, 1H), 1.62-1.82 (m, 4H), 1.71 (d, J = 5.2, 3H), 1.46-1.60 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) 139.3, 130.9, 129.7, 128.1, 127.6, 125.9, 83.8, 72.9, 71.9, 58.7, 36.8, 29.5, 26.5, 18.8, 18.0; IR (neat) 3061, 3027, 2932, 2824, 1603, 1494, 1453, 1378, 1352, 1200, 1105, 1036, 966, 887, 749 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{24}O_2Na$ $[M + Na]^+$ 283.1674, found 283.1678.

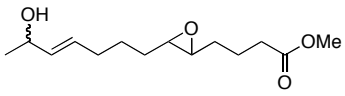
Isomerization of 13-*cis* and 13-*trans*

To a mixture of **13-*cis*** and **13-*trans*** (12 mg, 0.048 mmol, dr = 1:1) in CH_2Cl_2 (2 ml) was added Re_2O_7 (1 mg, 0.002 mmol). The reaction was stirred rt for 5 h, then was quenched with 5 drops of pyridine. After evaporation of the solvent, the crude mixture was purified by flash chromatography (5%-10% ethyl acetate in hexanes) to give the product (11 mg, 90%, dr > 30:1).



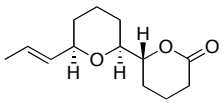
Reagents and conditions
a) DIBAL-H, hexanes, then I_2, THF, –78 °C, 51%. b) Pent-4-en-1-ylmagnesium bromide, $(dppf)PdCl_2$, Et_2O, 65%. c) Jones reagent, 0 °C, 64%. d) K_2CO_3, MeI, DMF, 99%. e) *m*-CPBA, $NaHCO_3$, CH_2Cl_2, 0 °C, 67%. f) (*Z*)-Hex-3-ene-2,5-diol, Grubbs-Hoveyda 2nd generation metathesis catalyst, CH_2Cl_2, 57%.

Scheme 4. Synthesis of **14**.



(*E*)-Methyl 4-(3-(6-hydroxyhept-4-en-1-yl)oxiran-2-yl) butanoate (14)

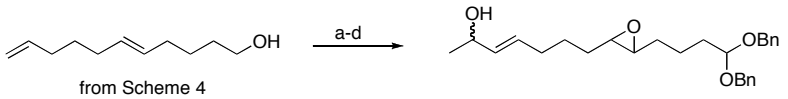
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.58 (dt, J = 6.4, 15.2, 1H), 5.49 (dd, J = 6.4, 15.2, 1H), 4.22 (p, J = 6.0, 1H), 3.64 (s, 3H), 2.62-2.67 (m, 2H), 2.34 (dt, J = 1.4, 7.2, 2H), 2.01-2.08 (m, 2H), 1.82 (br, 1H), 1.68-1.80 (m, 2H), 1.42-1.62 (m, 6H), 1.22 (d, J = 6.4, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 173.7, 134.8, 130.0, 68.7, 58.4, 58.2, 51.6, 33.6, 31.8, 31.40, 31.37, 25.5, 23.4, 21.5; IR (neat) 3433, 2928, 2860, 1737, 1438, 1367, 1248, 1169, 1117, 1061, 970, 893 cm^{-1}; HRMS (ESI) calcd for $C_{14}H_{24}O_4Na$ $[M + Na]^+$ 279.1572, found 279.1552.



(2*R*,2'*S*,6'*R*)-6'-((*E*)-Prop-1-en-1-yl)hexahydro-2H,2'H-[2,2'-bipyran]-6(3H)-one (15)

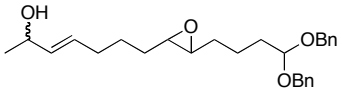
The general rearrangement procedure was followed with **14** (32 mg, 0.125 mmol), Re_2O_7 (3 mg, 0.006 mmol), and CH_2Cl_2 (12.5 mL). The reaction was stirred at rt for 12 h. The solvent was then removed under reduced pressure and the reaction mixture was kept at high vaccum for 1hr, after which the reaction mixture was redispersed in CH_2Cl_2 (12.5 mL) and 5% more catalyst was added. The reaction mixture was stirred at rt for another 12 h, then was quenched with 5 drops of pyridine. After the removal of solvent under reduced pressure, the crude mixture was purified by flash chromatography (20%-30% ethyl acetate in hexanes) to give the product (23 mg, purity: 87%, 71% with respect to the desired product). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.66 (ddq, J = 0.8, 6.4, 15.2, 1H), 5.46 (ddq, J = 1.2, 6.0, 15.2, 1H), 4.17 (ddd, J = 3.6, 6.4, 10.4, 1H), 3.79 (dd, J = 6.0, 10.4, 1H), 3.42 (ddd, J = 2.0, 6.0, 11.2, 1H), 2.52-2.62 (m, 1H), 2.41-2.51 (m, 1H), 2.06-2.14 (m, 1H), 1.75-1.98 (m, 4H), 1.68 (d, J = 6.4, 3H),

1.57-1.72 (m, 2H), 1.46-1.56 (m, 1H), 1.20-1.37 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) 171.5, 132.2, 126.4, 82.5, 78.8, 78.3, 31.6, 29.8, 27.2, 24.0, 22.9, 18.1, 17.9; IR (neat) 2935, 2855, 1738, 1440, 1346, 1240, 1203, 1169, 1089, 1049, 965, 933 cm^{-1}; HRMS (ESI) calcd for $C_{13}H_{21}O_3$ $[M + H]^+$ 225.1491, found 225.1481.



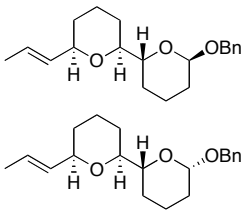
Reagents and conditions
a) PCC, Celite, CH_2Cl_2. b) BnOH, *p*-TsOH, Na_2SO_4, CH_2Cl_2, 67% (two steps). c) *m*-CPBA, $NaHCO_3$, CH_2Cl_2, 0 °C, 57%. d) (*Z*)-Hex-3-ene-2,5-diol, Grubbs-Hoveyda 2nd generation metathesis catalyst, CH_2Cl_2, 73%.

Scheme 5. Synthesis of **16**.



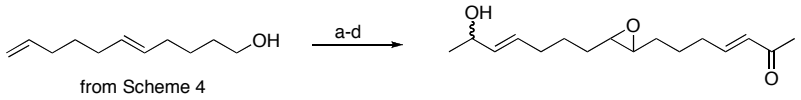
(*E*)-7-(3-(4,4-Bis(benzyloxy)butyl)oxiran-2-yl)hept-3-en-2-ol (16)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.40 (m,8H), 7.28-7.34 (m, 2H), 5.63 (dt, *J* = 6.4, 15.2, 1H), 5.54 (dd, *J* = 6.4, 15.2, 1H), 4.76 (t, *J* = 6.0, 1H), 4.68 (dd, *J* = 0.8, 12.0, 2H), 4.58 (d, *J* = 12.0, 2H), 4.26 (p, *J* = 6.4, 1H), 2.62-2.70 (m, 2H), 2.03-2.13 (m, 2H), 1.76-1.86 (m, 2H), 1.64 (br, 1H), 1.45-1.62 (m, 8H), 1.26 (d, *J* = 6.4, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 138.2, 134.8, 130.2, 128.5, 127.8, 127.7, 101.9, 68.8, 67.33, 67.28, 58.6, 33.1, 31.9, 31.8, 31.5, 25.6, 23.5, 21.4; IR (neat) 3444, 3030, 2929, 2863, 1605, 1496, 1454, 1366, 1307, 1207, 1123, 1046, 970, 737 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{36}O_4Na$ $[M + Na]^+$ 447.2511, found 447.2531.



(2*R*,2'*S*,6*R*,6'*R*)-6-(Benzyloxy)-6'-((*E*)-prop-1-en-1-yl)octahydro-2H,2'H-2,2'-bipyran (17a) and (2*R*,2'*S*,6*S*,6'*R*)-6-(benzyloxy)-6'-((*E*)-prop-1-en-1-yl) octahydro -2H,2'H-2,2'-bipyran (17b)

The general rearrangement procedure was followed with **16** (30 mg, 0.071 mmol), $Ph_3SiOReO_3$ (1.8 mg, 0.0036 mmol), and CH_2Cl_2 (7 mL). The reaction was stirred at –25 °C for 8 h (when all starting materials was consumed), and then at 20 °C for another 12 h before being quenched with five drops of pyridine. After evaporation of the solvent, the crude mixture was purified by flash chromatography (2%-5% ethyl acetate in hexanes) to give the product (12.6 mg, 56%, dr = 5:2). ^{1}H NMR (400 MHz, C_6D_6) δ 7.35-7.39 (m, 2H), 7.16-7.21 (m, 2H), 7.07-7.13 (m, 1H), 5.69 (ddq, *J* = 0.8, 6.4, 15.2, 1H), 5.59 (ddq, *J* = 1.2, 5.2, 15.2, 1H), 4.88 (d, *J* = 2.8, 1H), 4.80 (d, *J* = 12.0, 1H), 4.39 (d, *J* = 12.0, 1H), 3.91 (ddd, *J* = 2.0, 6.8, 10.8, 1H), 3.74 (dd, *J* = 5.2, 9.6, 1H), 3.33 (ddd, *J* = 2.0, 6.8, 10.4, 1H), 2.00-2.07 (m, 1H), 1.88-1.99 (m, 2H), 1.61-1.75 (m, 2H), 1.58 (dt, *J* = 1.2, 6.4, 3H), 1.27-1.54 (m, 7H); ^{13}C NMR (100 MHz, C_6D_6) 138.8, 133.3, 128.2, 127.9, 127.3, 124.6, 96.2, 80.3, 77.9, 71.8, 68.8, 32.2, 30.0, 27.9, 27.8, 23.3, 18.0, 17.6; IR (neat) 3029, 2932, 2854, 1496, 1453, 1440, 1360, 1302, 1195, 1126, 1079, 1036, 964, 734 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{28}O_3Na$ $[M + Na]^+$ 339.1936, found 339.1923. Second compound: ^{1}H NMR (400 MHz, C_6D_6) δ 7.36-7.40 (m, 2H), 7.17-7.21 (m, 2H), 7.08-7.12 (m, 1H), 5.55-5.70 (m, 2H), 4.95 (d, *J* = 12.0, 1H), 4.55 (d, *J* = 12.0, 1H), 4.33 (dd, *J* = 2.0, 9.2, 1H), 3.72 (dd, *J* = 4.8, 10.0, 1H), 3.38 (ddd, *J* = 2.0, 7.2, 10.4, 1H), 5.25 (ddd, *J* = 2.0, 7.2,10.4, 1H), 1.96-2.02 (m, 1H), 1.88-1.94 (m, 1H), 1.64-1.76 (m, 2H), 1.58 (d, *J* = 6.0, 3H), 1.50-1.61 (m, 2H), 1.41-1.49 (m, 1H), 1.14-1.40 (m, 5H); ^{13}C NMR (100 MHz, C_6D_6) 138.7, 133.2, 128.2, 127.6, 127.3, 124.8, 101.3, 80.2, 78.9, 77.9, 69.4, 32.3, 31.5, 28.2, 27.8, 23.2, 21.8, 17.6; IR (neat) 3030, 2933, 2854, 1496, 1453, 1439, 1360, 1305, 1261, 1199, 1123, 1086, 1024, 964, 732 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{28}O_3Na$ $[M + Na]^+$ 339.1936, found 339.1945.

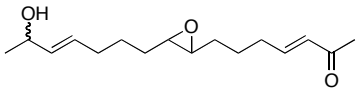


from Scheme 4

Reagents and conditions

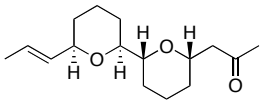
a) PCC, Celite, CH_2Cl_2. b) NaH, $(EtO)_2P(O)CH_2C(O)CH_3$, THF, 0 °C, 78% (two steps). c) *m*-CPBA, $NaHCO_3$, CH_2Cl_2, 0 °C, 66%. d) (*Z*)-Hex-3-ene-2,5-diol, Grubbs-Hoveyda 2nd generation metathesis catalyst, CH_2Cl_2, 56%.

Scheme 6. Synthesis of **18**.



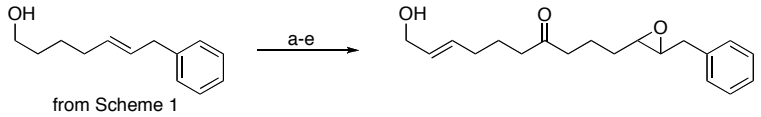
(*E*)-7-(3-((*E*)-6-Hydroxyhept-4-en-1-yl)oxiran-2-yl)hept-3-en-2-one (18)

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.78 (dt, *J* = 6.8, 16.0, 1H), 6.08 (d, *J* = 16.0, 1H), 5.62 (dt, *J* = 6.4, 15.2, 1H), 5.52 (dd, *J* = 6.4, 15.2, 1H), 5.26 (p, *J* = 6.4, 1H), 2.64-2.69 (m, 2H), 2.28 (q, *J* = 6.8, 2H), 2.24 (s, 3H), 2.03-2.10 (m, 2H), 1.57-1.70 (m, 4H), 1.45-1.57 (m, 5H), 1.25 (d, *J* = 6.4, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 198.7, 147.6, 134.8, 131.6, 130.1, 68.8, 58.5, 58.3, 32.1, 31.8, 31.5, 31.4, 27.0, 25.5, 24.6, 23.5; IR (neat) 3446, 2969, 2930, 2859, 1673, 1626, 1454, 1363, 1255, 1145, 1062, 974, 894 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{26}O_3Na$ $[M + Na]^+$ 289.1780, found 289.1795.



1-((2*R*,2'*S*,6*S*,6'*R*)-6'-((*E*)-Prop-1-en-1-yl)octahydro-2H,2'H-[2,2'-bipyran]-6-yl)propan-2-one (19)

The general rearrangement procedure was followed with **18** (22 mg, 0.083 mmol), Re_2O_7 (2 mg, 0.004 mmol), and CH_2Cl_2 (8.3 mL). The reaction was stirred at rt for 3.5 days, then was quenched with five drops of pyridine. $Me_2(Bn)SiH$ (5 µl) was added as an internal standard and crude NMR was used to determine the yield of 59% (dr >20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.66 (ddq, *J* = 0.8, 6.4, 15.2, 1H), 5.49 (ddq, *J* = 1.6, 6.0, 15.2, 1H), 3.72-3.81 (m, 2H), 3.15-3.25 (m, 2H), 2.64 (dd, *J* = 8.2, 15.0, 1H), 2.42 (dd, *J* = 4.6, 15.0, 1H), 2.18 (s, 3H), 1.76-1.95 (m, 2H), 1.68 (d, *J* = 6.4, 3H), 1.55-1.64 (m, 2H), 1.42-1.55 (m, 2H), 1.11-1.34 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) 207.9, 132.6, 126.2, 80.8, 80.3, 78.1, 74.7, 50.5, 31.9, 31.7, 30.8, 28.0, 27.9, 23.1, 23.0, 17.9; IR (neat) 2928, 2846, 1707, 1439, 1405, 1379, 1360, 1319, 1305, 1194, 1170, 1091, 1042, 963 cm^{-1}; HRMS (EI) calcd for $C_{16}H_{26}O_3$ $[M]^+$ 289.1780, found 289.1766.

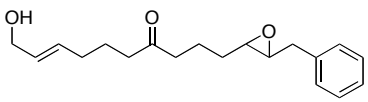


from Scheme 1

Reagents and conditions

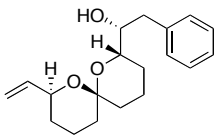
a) PCC, Celite, CH_2Cl_2. b) Pent-4-en-1-ylmagnesium bromide, Et_2O, 70% (two steps). c) PCC, Celite, CH_2Cl_2, 93%. d) *m*-CPBA, $NaHCO_3$, CH_2Cl_2, 0 °C, 52%. e) But-2-ene-1,4-diol, Grubbs-Hoveyda 2nd generation metathesis catalyst, CH_2Cl_2, 59%.

Scheme 7. Synthesis of **20**.

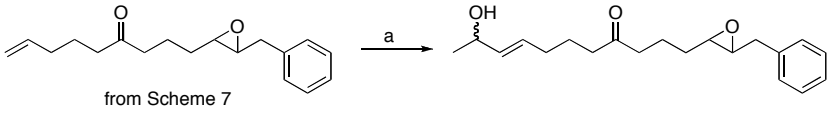


(*E*)-1-(3-Benzyloxiran-2-yl)-10-hydroxydec-8-en-4-one (20)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.35 (m, 2H), 7.22-7.27 (m, 3H), 5.59-5.69 (m, 2H), 4.08 (d, *J* = 2.0, 2H), 2.88-2.96 (m, 2H), 2.75-2.83 (m, 2H), 2.41 (d, *J* = 7.2, 2H), 2.37 (d, *J* = 7.2, 2H), 2.01-2.11 (m, 2H), 1.92 (br, 1H), 1.56-1.77 (m, 5H), 1.49 (p, *J* = 7.2, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 210.6, 137.3, 131.8, 130.0, 128.9, 128.6, 126.6, 63.5, 58.6, 58.4, 42.0, 41.9, 38.4, 31.6, 31.2, 23.0, 20.2; IR (neat) 3443, 3027, 2934, 2863, 1709, 1604, 1494, 1453, 1410, 1089, 1001, 972, 744 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{27}O_3$ $[M + H]^+$ 303.1960, found 303.1942.

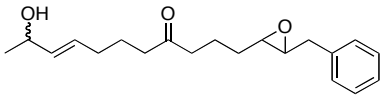


(*R*)-2-Phenyl-1-((2*S*,6*S*,8*S*)-8-vinyl-1,7-dioxaspiro[5.5]undecan-2-yl) ethanol (21)
The general rearrangement procedure was followed with **20** (34 mg, 0.11 mmol), Re_2O_7 (3 mg, 0.006 mmol), and CH_2Cl_2 (11.2 mL). The reaction was stirred at rt for 20 h, then was quenched with five drops of pyridine. After evaporation of the solvent, the crude mixture was purified by flash chromatography (10%-15% ethyl acetate in hexanes) to give the product (32 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23-7.37 (m, 5H), 5.85 (ddd, *J* = 5.6, 10.4, 17.2, 1H), 5.20 (dt, *J* = 1.6, 17.2, 1H), 5.09 (dt, *J* = 1.6, 10.4, 1H), 4.04 (ddddd, *J* = 0.8, 1.2, 2.6, 5.6, 11.2, 1H), 3.86 (p, *J* = 4.4, 1H), 3.00 (dd, *J* = 4.0, 14.0, 1H), 2.68 (dd, *J* = 9.2, 14.0, 1H), 1.86-2.04 (m, 3H), 1.74-1.82 (m, 1H), 1.57-1.73 (m, 5H), 1.41-1.51 (m, 2H), 1.27-1.41 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) 139.4, 138.9 129.3, 128.5, 126.4, 114.5, 96.6, 75.1, 71.7, 70.0, 39.3, 35.5, 35.0, 30.6, 24.9, 18.7, 18.2; IR (neat) 3470, 3062, 2938, 2868, 1646, 1603, 1495, 1453, 1438, 1373, 1279, 1222, 1142, 1059, 980, 915, 747 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{27}O_3$ $[M + H]^+$ 303.1960, found 303.1979.

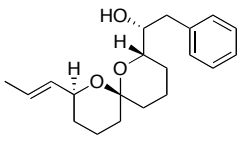


Reagents and conditions
a) (*Z*)-Hex-3-ene-2,5-diol, Grubbs-Hoveyda 2nd generation metathesis catalyst, CH_2Cl_2, 75%.

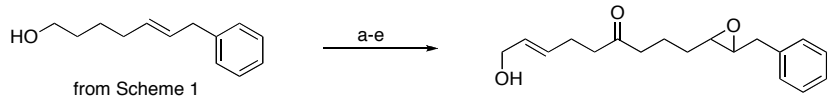
Scheme 8. Synthesis of **25**.



(*E*)-1-(3-Benzyloxiran-2-yl)-10-hydroxyundec-8-en-4-one (25)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.33 (m, 2H), 7.20-7.26 (m, 3H), 5.48-5.61 (m, 2H), 4.24 (p, *J* = 6.4, 1H), 2.87-2.93 (m, 2H), 2.73-2.82 (m, 2H), 2.39 (t, *J* = 7.6, 2H), 2.35 (t, *J* = 7.6, 2H), 2.06 (br, 1H), 2.00 (q, *J* = 6.8, 2H), 1.54-1.74 (m, 5H), 1.48 (p, *J* = 7.2, 1H), 1.24 (d, *J* = 6.4, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 210.5, 137.3, 135.2, 129.6, 128.9, 128.6, 126.6, 68.6, 58.6, 58.4, 42.0, 41.9, 38.4, 31.5, 31.2, 23.5, 23.1, 20.2; IR (neat) 3450, 3061, 2968, 2930, 1709, 1604, 1494, 1452, 1409, 1370, 1138, 1063, 970, 743 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{29}O_3$ $[M + H]^+$ 317.2117, found 317.2095.

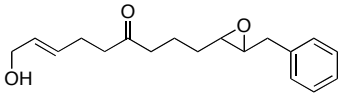


(*R*)-2-Phenyl-1-((2*S*,6*S*,8*S*)-8-((*E*)-prop-1-en-1-yl)-1,7-dioxaspiro [5.5]undecan-2-yl)ethanol (26)
The general rearrangement procedure was followed with **25** (12 mg, 0.038 mmol), $O_3ReOSiPh_3$ (1 mg, 0.002 mmol), and CH_2Cl_2 (3.8 mL). The reaction was initiated at –78 °C followed by warming to –30 °C, stirring at –30 °C for 90 min (complete consumption of starting material), then warming to 0 °C and strring for 4 h. The reaction was quenched immediately with five drops of pyridine when TLC indicated that one major product was present. After evaporation of the solvent, the crude mixture was purified by flash chromatography (10%-15% ethyl acetate in hexanes) to give the product (8.5 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21-7.35 (m, 5H), 5.55 (ddq, *J* = 0.8, 6.4, 15.6, 1H), 5.46 (ddq, *J* = 1.2, 6.4, 15.6, 1H), 3.94 (dd, *J* = 6.0, 11.6, 1H), 3.85 (p, *J* = 4.4, 1H), 3.58 (ddd, *J* = 2.4, 4.8, 11.6, 1H), 2.98 (dd, *J* = 4.4, 13.6, 1H), 2.68 (dd, *J* = 9.2, 13.6, 1H), 1.97 (br, 1H), 1.88 (tq, *J* = 4.0, 12.8, 2H), 1.72-1.80 (m, 1H), 1.69 (d, *J* = 6.4, 3H), 1.54-1.66 (m, 5H), 1.35-1.48 (m, 3H), 1.25-1.34 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 138.8, 132.3, 129.3, 128.5, 126.9, 126.3, 96.6, 75.1, 71.5, 70.0, 39.3, 35.5, 35.0,30.8, 24.8, 18.8, 18.3, 17.9; IR (neat) 3464, 3060, 2937, 2868, 1603, 1495, 1453, 1439, 1377, 1279, 1221, 1203, 1142, 1042, 979, 746 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{29}O_3$ $[M + H]^+$ 317.2117, found 317.2141.

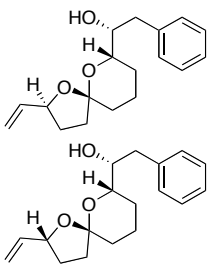


Reagents and conditions
a) PCC, Celite, CH_2Cl_2. b) But-3-en-1ylmagnesium bromide Et_2O, 0 °C, 77% (two steps). c) PCC, Celite, CH_2Cl_2, 86%. d) m-CPBA, $NaHCO_3$, CH_2Cl_2, 0 °C, 49%. e) But-2-ene-1,4-diol, Grubbs-Hoveyda 2nd generation metathesis catalyst, CH_2Cl_2, 71%.

Scheme 9. Synthesis of **27**.



(*E*)-1-(3-Benzyloxiran-2-yl)-9-hydroxynon-7-en-4-one (27)
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.27-7.33 (m, 2H), 7.19-7.26 (m, 3H), 5.57-5.68 (m, 2H), 4.01 (br, 2H), 2.76-2.89 (m, 3H), 2.73 (t, J = 5.6, 1H), 2.43 (t, J = 7.2, 2H), 2.39 (t, J = 7.2, 2H), 2.22-2.30 (m, 2H), 1.60-1.73 (m, 3H), 1.41-1.59 (m, 2H); ^{13}C NMR (100 MHz, CD_2Cl_2) 209.9, 138.1, 131.1, 130.5, 129.3, 128.8, 126.9, 63.6, 58.8, 58.6, 42.4, 42.3, 38.8, 31.6, 26.6, 20.5; IR (neat) 3433,3027, 2929, 2862, 1710, 1494, 1453, 1410, 1373, 1089, 1007, 972, 745 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{25}O_3$ $[M + H]^+$ 289.1804, found 289.1829.



(*R*)-2-Phenyl-1-((2*S*,5*R*,7*S*)-2-vinyl-1,6-dioxaspiro[4.5]decan-7-yl) ethanol (28) and (*R*)-2-phenyl-1-((2*R*,5*R*,7*S*)-2-vinyl-1,6-dioxaspiro[4.5]decan-7-yl) ethanol (29)
The general rearrangement procedure was followed with **27** (29 mg, 0.10 mmol), Re_2O_7 (2 mg, 0.005 mmol), and CH_2Cl_2 (10 mL). The reaction was stirred for 3 h, then was quenched with five drops of pyridine. After evaporation of the solvent, the crude mixture was purified by flash chromatography (10%-15% ethyl acetate in hexanes) to give the product (27.5 mg, 95%, **28**:**29** = 50:49). The mixture was further purified for characterization. **28**: ^{1}H NMR (400 MHz, C_6D_6) δ 7.19-7.23 (m, 2H), 7.13-7.19 (m, 2H), 7.05-7.10 (m, 1H), 5.82 (ddd, J = 6.4, 10.4, 16.8, 1H), 5.22 (dt, J = 1.6, 16.8, 1H), 4.98 (dt, J = 1.6, 10.4, 1H), 4.49 (q, J = 6.4, 1H), 3.85 (ddd, J = 2.4, 5.2, 11.6, 1H), 3.75-3.83 (m, 1H), 2.83 (dd, J = 3.6, 14.0, 1H), 2.66 (dd, J = 9.2, 14.0, 1H), 1.87-2.19 (m, 2H), 1.77-1.87 (m, 1H), 1.59-1.67 (m, 3H), 1.47-1.59 (m, 3H), 1.31-1.47 (m, 2H); ^{13}C NMR (100 MHz, C_6D_6) 135.4, 129.5, 128.3, 127.6, 126.1, 114.0, 106.4, 78.7, 74.9, 73.3, 39.3, 37.5, 33.6, 30.3, 25.0, 19.8; IR (neat) 3463, 3027, 2945, 2872, 1644, 1603, 1495, 1454, 1439, 1370, 1271, 1222, 1071,1036, 988, 874, 748 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{25}O_3$ $[M + H]^+$ 289.1804, found 289.1828. **29**: ^{1}H NMR (300 MHz, C_6D_6) δ 7.12-7.23 (m, 4H), 7.04-7.11 (m, 1H), 5.91 (ddd, *J* = 7.2, 10.2, 17.4, 1H), 5.10 (ddd, *J* = 1.2, 1.8, 17.2, 1H), 4.95 (ddd, *J* = 0.9, 1.8, 10.4, 1H), 4.35 (q, *J* = 7.2, 1H), 3.96 (ddd, *J* = 2.4, 5.1, 11.4, 1H), 3.74-3.83 (m, 1H), 2.88 (dd, *J* = 3.9, 13.8, 1H), 2.69 (dd, *J* = 9.3, 13.8, 1H), 1.78-2.05 (m, 3H), 1.56-1.76 (m, 4H), 1.30-1.55 (m, 5H); ^{13}C NMR (100 MHz, C_6D_6) 141.1, 139.4, 129.4, 128.3, 126.0, 114.4, 106.2, 81.6, 75.1, 73.0, 39.5, 38.9, 33.6, 30.6, 25.1, 19.8; IR (neat) 3463, 3026, 2943, 2870, 1643, 1603, 1495, 1454, 1370, 1296, 1220, 1034, 988, 875, 747 cm^{-1}; HRMS (ESI) calcd for for $C_{18}H_{25}O_3$ $[M + H]^+$ 289.1804, found 289.1832.

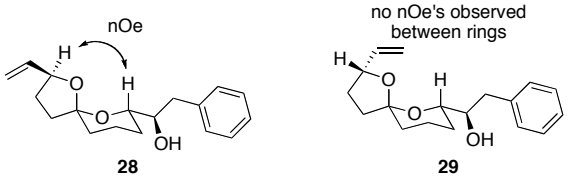
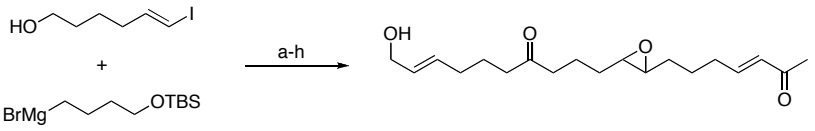


Figure 1. Spectral assignment for stereoisomers.

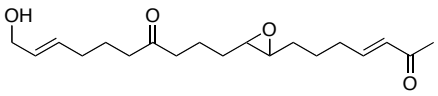
Equlibration experiments
Each stereoisomers was resubmitted to the following isomerization conditions: ~20mM solution, 5% Re_2O_7, stirring at rt for 18 h (no obvious change after 12 h) then quenching with 5 drops of pyridine. After evaporation of the solvent, the crude mixture was purified by flash chromatography (10%-15% ethyl acetate

in hexanes) to give the product (yield for each isomerization: ~90%-95%, dr = 11:9). Isomerization of **28** gave additional 19% of **29** while isomerization of **29** gave additional 22% of **28**. Thus after one recycling of isomerization: a total yield of 69% could be obtained for **28** and a total yield of 63% could be obtained for **29**. A second recycling gave a total yield of 78% for **28** and a total yield of 75% for **29**.

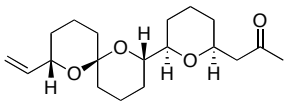


Reagents and conditions
a) $(dppf)_2PdCl_2$, Et_2O, 79%. b) Py•SO_3, DMSO, Et_3N, CH_2Cl_2, 0 °C, 86%. c) Pent-4-en-1-ylmagnesium bromide, Et_2O, 85%. d) Bu_4NF, THF, 69%. e) PCC, Celite, CH_2Cl_2, 66%. f) NaH, THF, then $(EtO)_2P(O)CH_2C(O)CH_3$, 0 °C, 87%. g) *m*-CPBA, $NaHCO_3$, CH_2Cl_2, 70%. h) But-2-ene-1,4-diol, Grubbs-Hoveyda 2nd generation metathesis catalyst, CH_2Cl_2, 69%.

Scheme 10. Synthesis of **30**.



(*E*)-10-Hydroxy-1-(3-((*E*)-6-oxohept-4-en-1-yl) oxiran-2-yl)dec-8-en-4-one (30)
^{1}H NMR (400 MHz, CD_2Cl_2) δ 6.76 (dt, *J* = 6.8, 16.0, 1H), 6.03 (dt, *J* = 1.6, 16.0, 1H), 5.56-5.67 (m, 2H), 4.02 (br, 2H), 2.60-2.65 (m, 2H), 2.43 (t, *J* = 7.2, 2H), 2.38 (t, *J* = 7.2, 2H), 2.26 (dq, *J* = 1.6, 7.2, 2H), 2.19 (s, 3H), 1.99-2.07 (m, 2H), 1.39-1.70 (m, 11H); ^{13}C NMR (100 MHz, CD_2Cl_2) 210.1, 198.2, 147.5, 131.6, 131.5, 130.1, 63.3, 58.1, 57.9, 42.1, 41.8, 32.1, 31.53, 31.46, 31.4, 26.6, 24.6, 23.1, 20.2; IR (neat) 3451, 2934, 2862, 11708, 1672, 1626, 1431, 1364, 1256, 1089, 976, 893 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{30}O_4Na$ $[M + Na]^+$ 345.2042, found 345.2071.



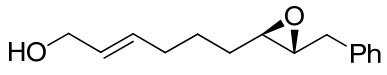
1-((2*S*,6*R*)-6-((2*S*,6*S*,8*S*)-8-vinyl-1,7-dioxaspiro[5.5] undecan-2-yl) tetrahydro-2H-pyran-2-yl)propan-2-one (31)
The general rearrangement procedure was followed with **30** (25 mg, 0.078 mmol), Re_2O_7 (2 mg, 0.004 mmol), and CH_2Cl_2 (7.8 mL). The reaction was stirred at 20 °C for 8 h, then was quenched with five drops of pyridine. After evaporation of the solvent, the crude mixture was purified by flash chromatography (10%-15% ethyl acetate in hexanes) to give the product (21 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.84 (ddd, *J* = 5.2, 10.4, 17.2, 1H), 5.23 (dt, *J* = 1.6, 17.2, 1H), 5.07 (dt, *J* = 1.6, 10.4, 1H), 4.04 (ddddd, *J* = 1.2, 1.6, 2.8, 5.2, 11.6, 1H), 3.77 (dddd, *J* = 1.2, 4.4, 8.8, 10.4, 1H), 3.42 (ddd, *J* = 2.0, 8.0, 10.4, 1H), 3.18 (ddd, *J* = 2.0, 8.0, 10.4, 1H), 2.64 (dd, *J* = 8.8, 14.8, 1H), 2.41 (dd, *J* = 4.4, 14.8, 1H), 2.18 (s, 3H), 1.95-2.03 (m, 1H), 1.78-1.94 (m, 4H), 1.49-1.69 (m, 7H), 1.33-1.44 (m, 2H), 1.21-1.32 (m, 2H), 1.05-1.21 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) 207.8, 139.5, 114.3, 96.1, 80.9, 74.8, 71.8, 69.7, 50.4, 35.6, 35.2, 31.7, 30.9, 30.7, 28.3, 27.8, 23.0, 18.8, 18.3; IR (neat) 3078, 2936, 2861, 1716, 1646, 1438, 1371, 1279, 1224, 1202, 1134, 1089, 1040, 981, 914, 861 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{30}O_4Na$ $[M + Na]^+$ 345.2042, found 345.2007.

Preparation of Re_2O_7 supported on SiO_2
A slurry of 1.8 g of SiO_2 and 200mg of Re_2O_7 in Et_2O was stirred at room temperature for 3 hours, followed by removal of Et_2O under reduced pressure, the obtained powder was dired under vaccum overnight .The catalyst was stored in dessicator and shielded from light.

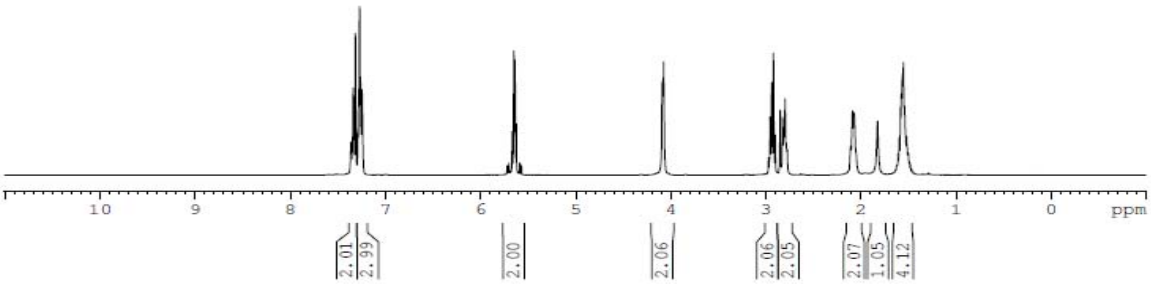
Representative cyclization with Re_2O_7 supported on SiO_2
The general rearrangement procedure was followed with **16** (25 mg, 0.059 mmol), 10% Re_2O_7 on SiO_2 (14 mg, 0.003 mmol), and CH_2Cl_2 (12.0 mL). The reaction was stirred at –25 °C for 8 h (starting material was consumed) and then at rt for 10 h. The reaction was quenched with five drops of pyridine. After evaporation

of the solvent, the crude mixture was purified by flash chromatography (2%-5% ethyl acetate in hexanes) to provide **17** (11.5 mg, 60%, dr = 5:2).

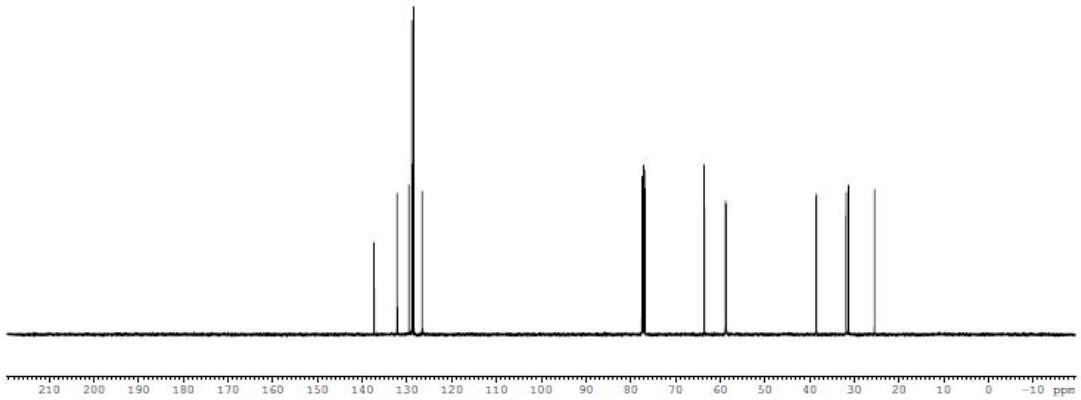
300 1H CDCl3 Reduction 042712

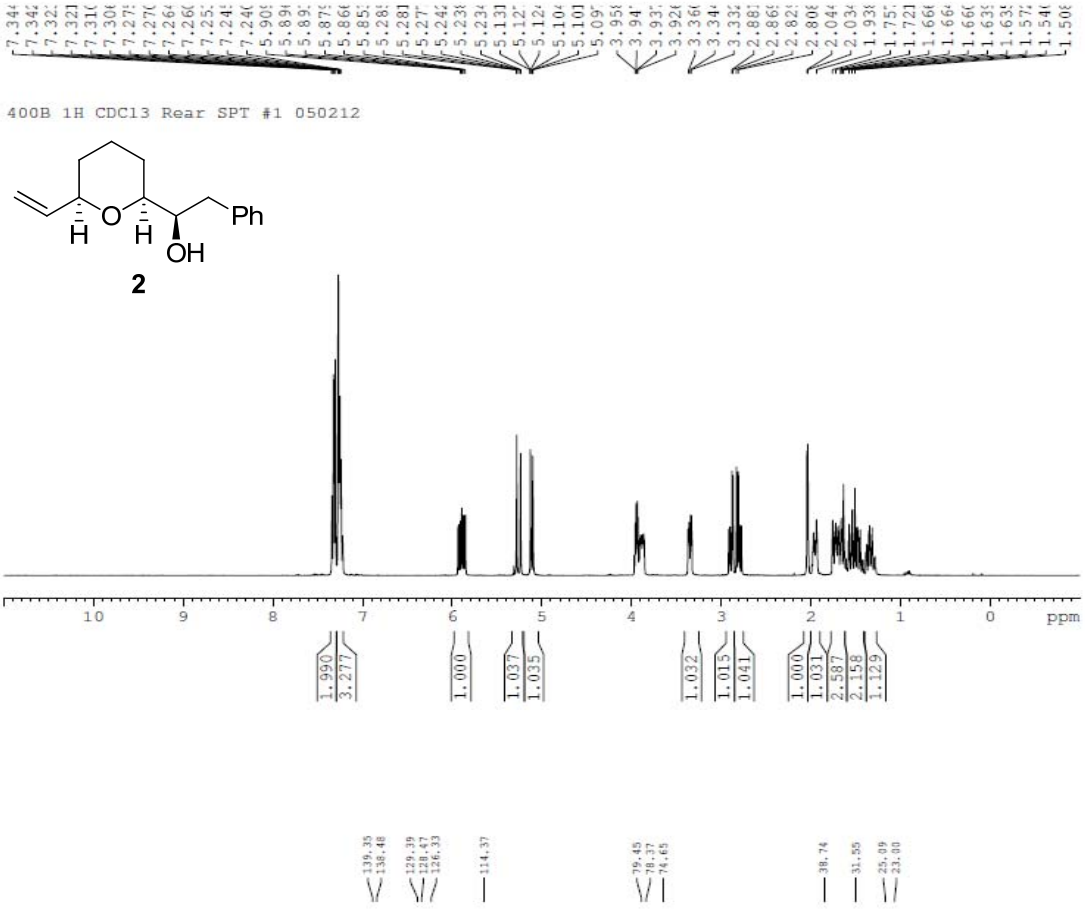


1



400A 1H CDCl3 Reduction 042712

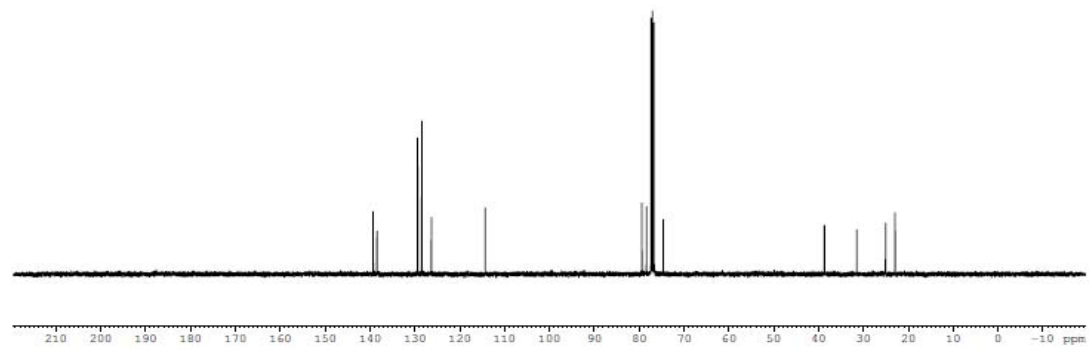




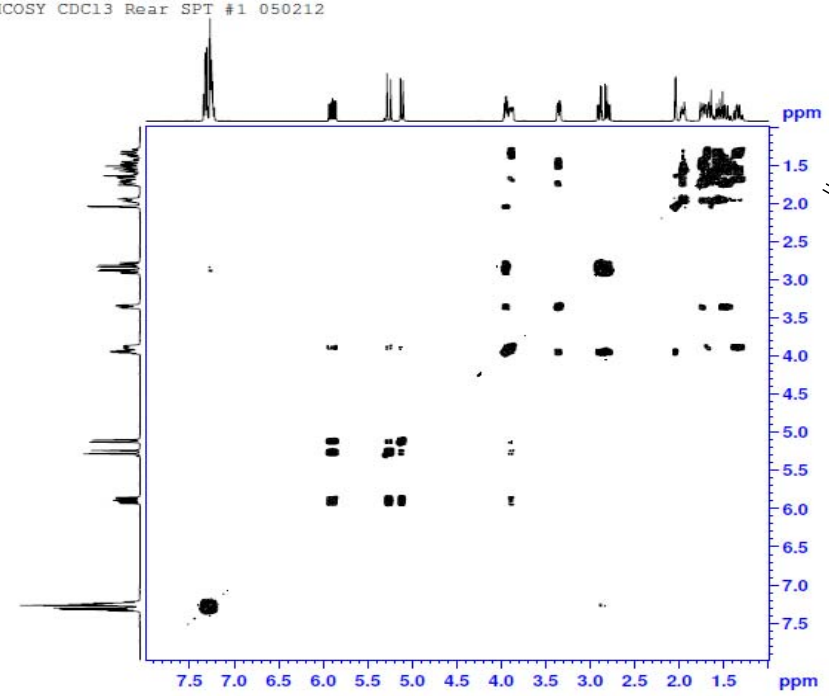
400B 1H CDCl3 Rear SPT #1 050212

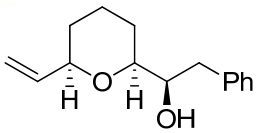
2

400A 13C CDCl3 Rear SPT #1-1 0502



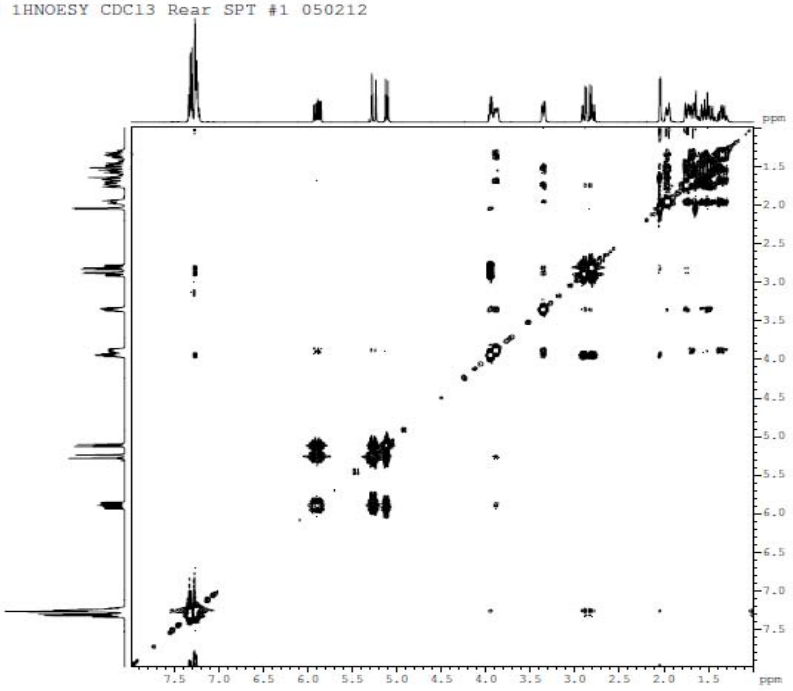
400B 1HCOSY CDCl3 Rear SPT #1 050212

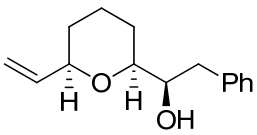




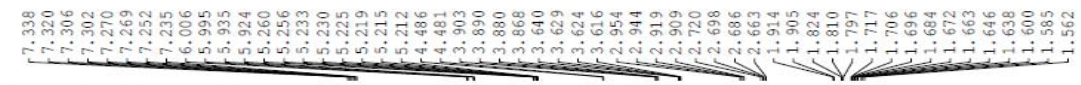
2

400B 1HNOESY CDCl3 Rear SPT #1 050212

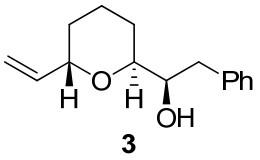




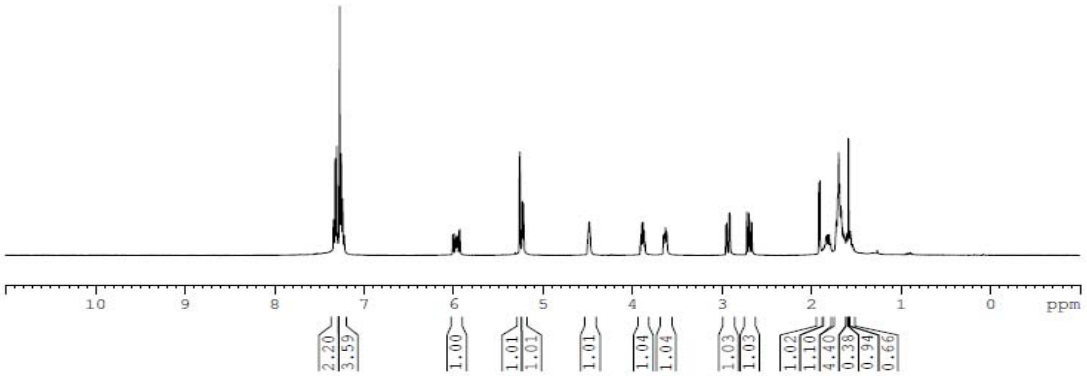
2

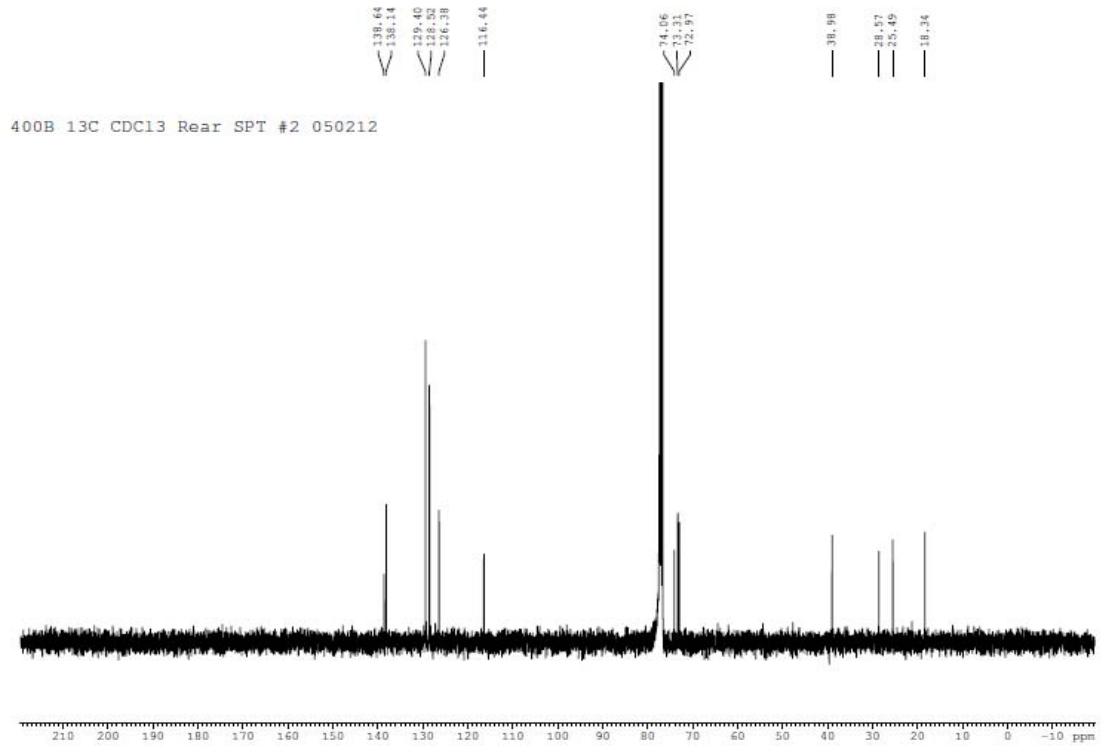


400B 1H CDCl3 Rear SPT #2 050212

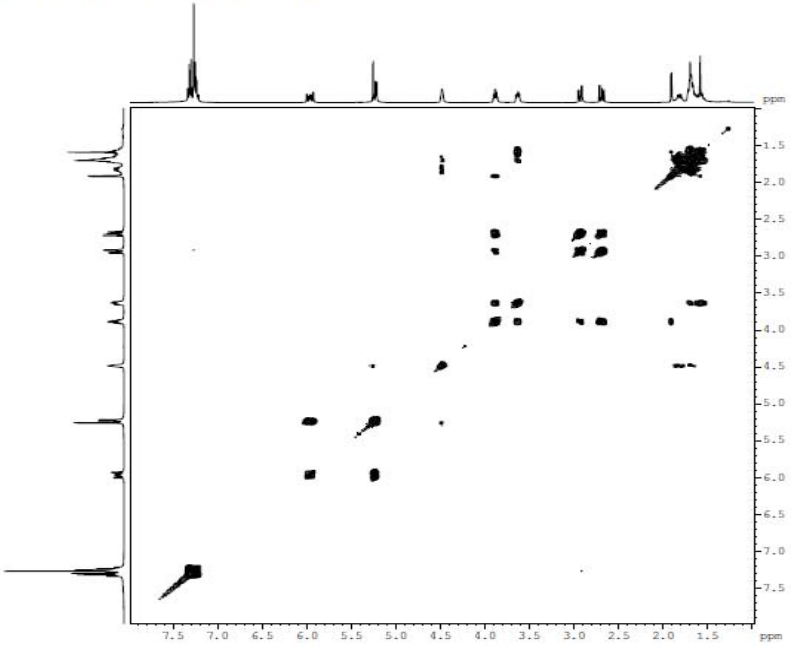


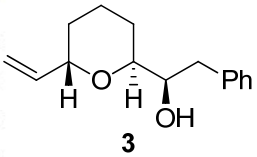
3





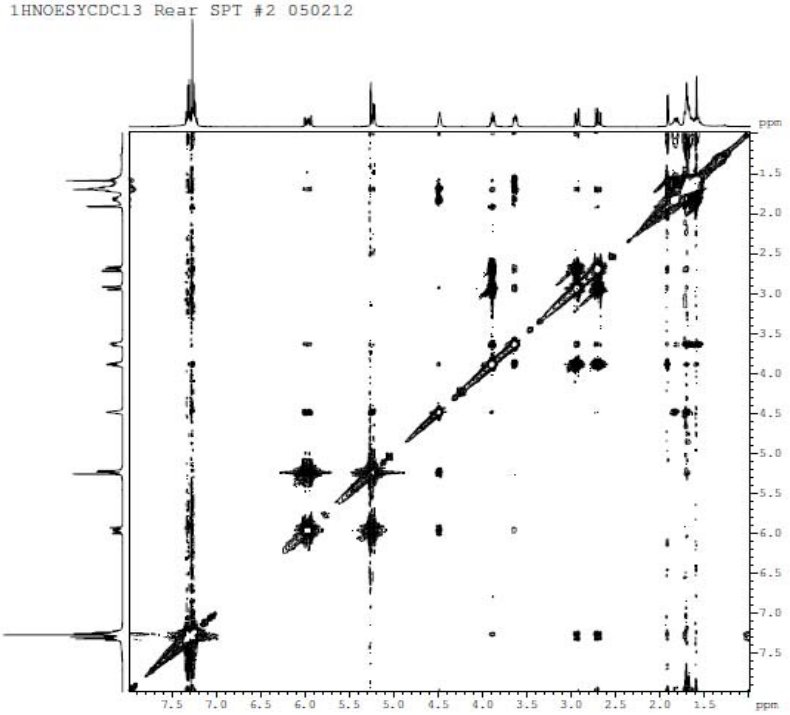
400B 1HCOSY CDC13 Rear SPT #2 050212

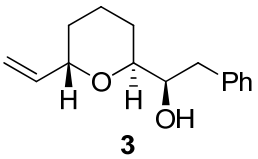




3

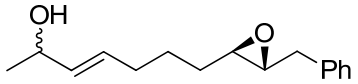
400B 1HNOESYCDC13 Rear SPT #2 050212



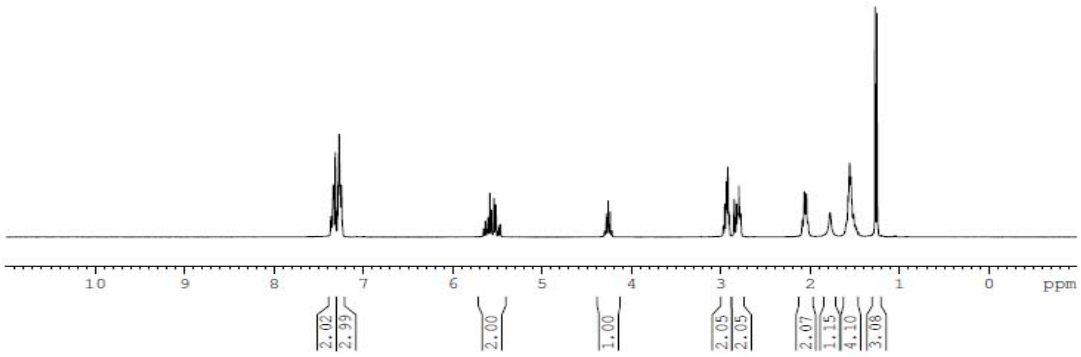


3

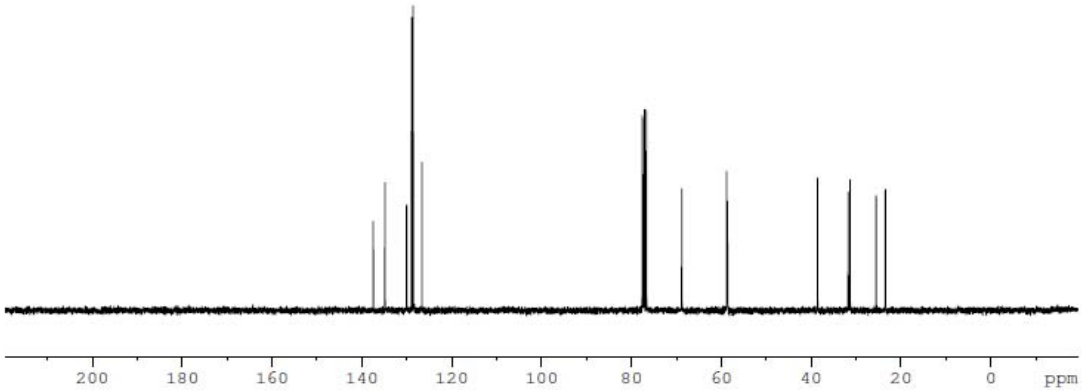
300 1H CDCl3 Reduction 032212

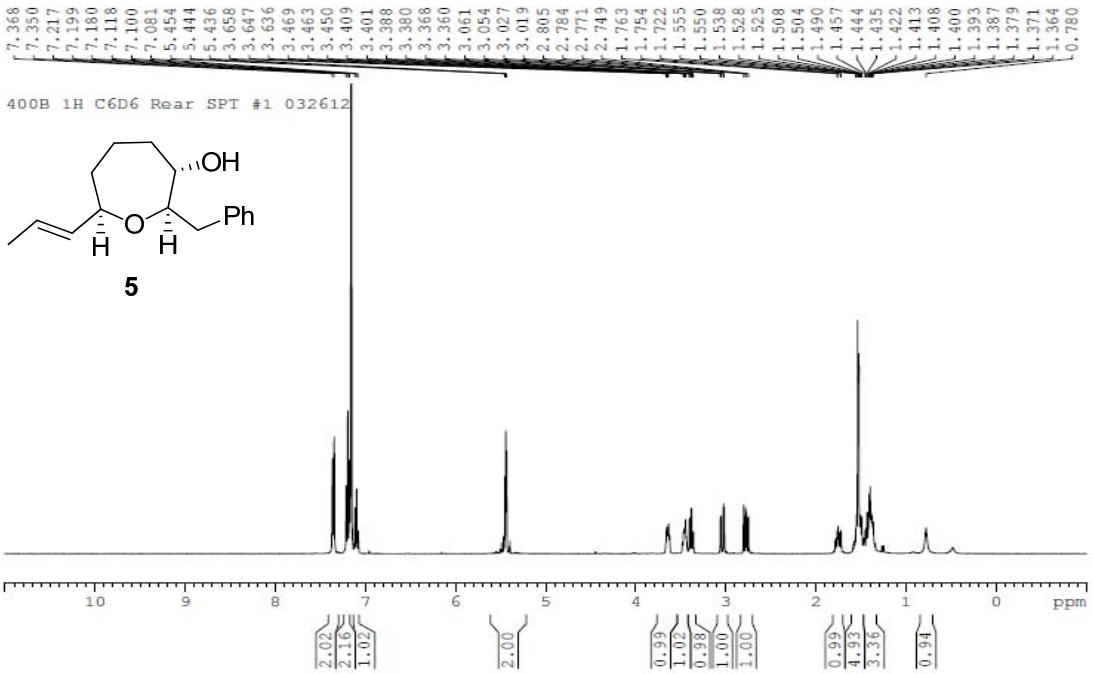


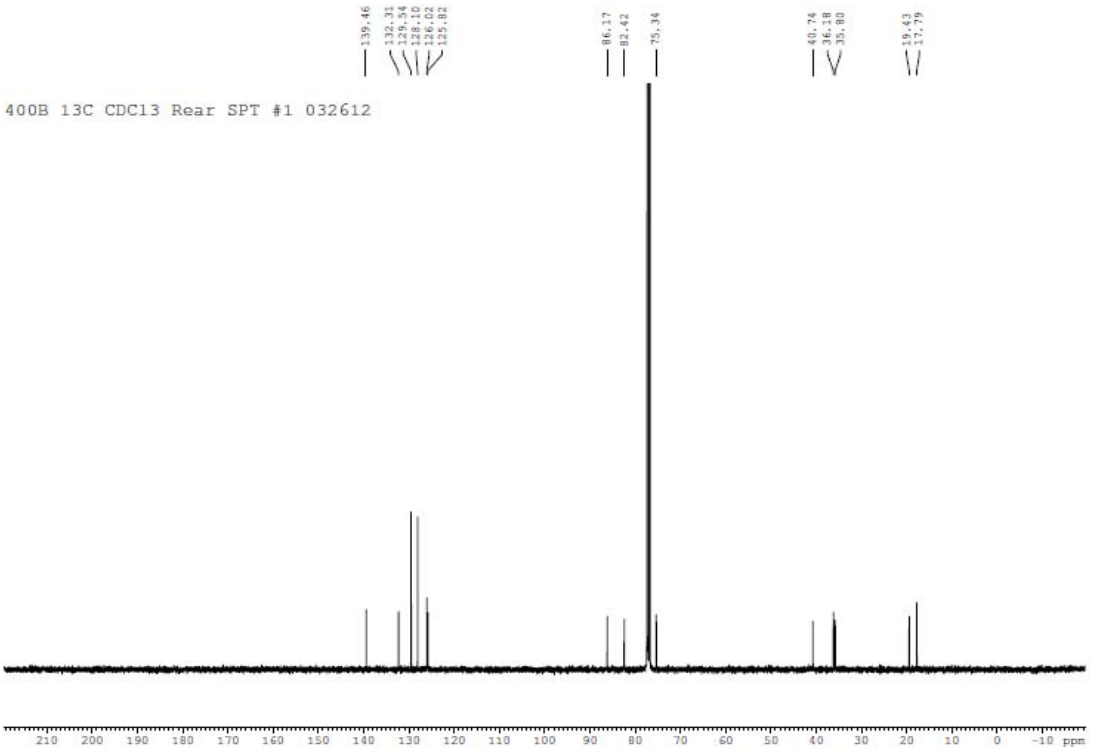
4

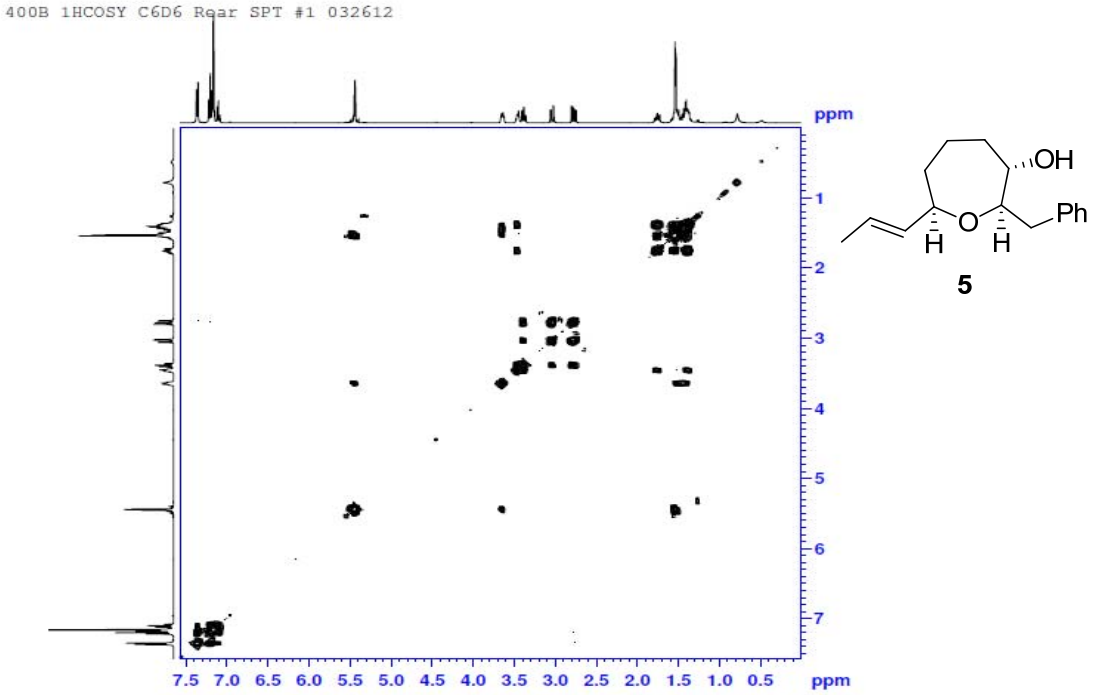


300 13C CDCl3 Reduction 032212

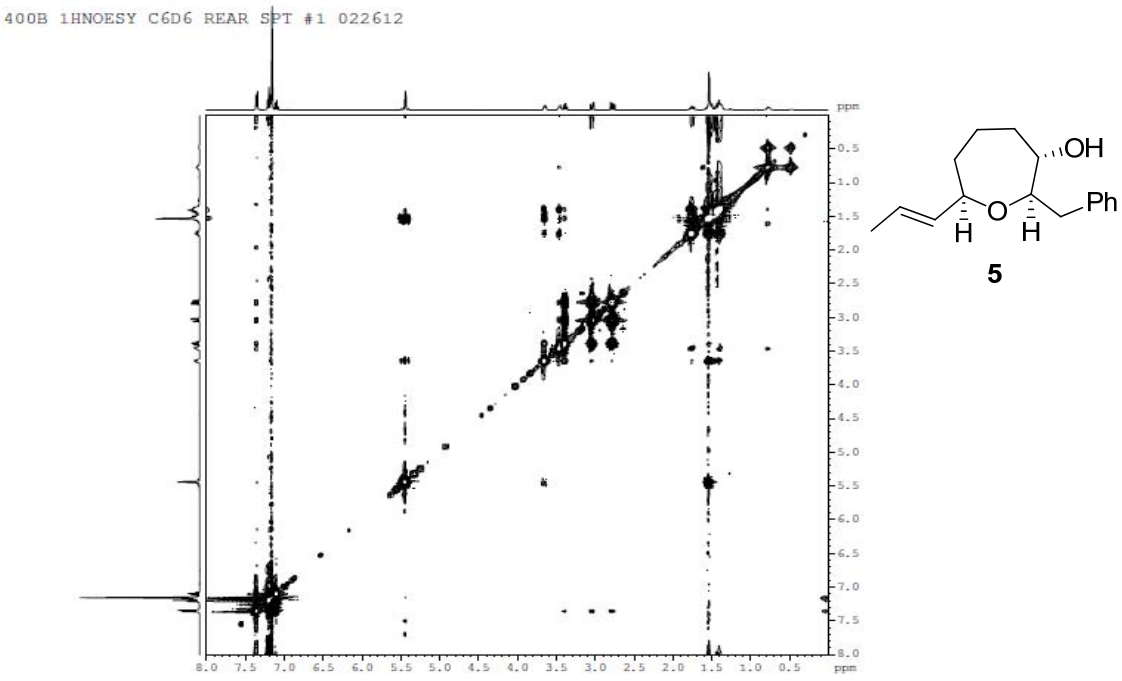



400B 1H C6D6 Rear SPT #1 032612
OH
Ph
O
H
H
5
ppm

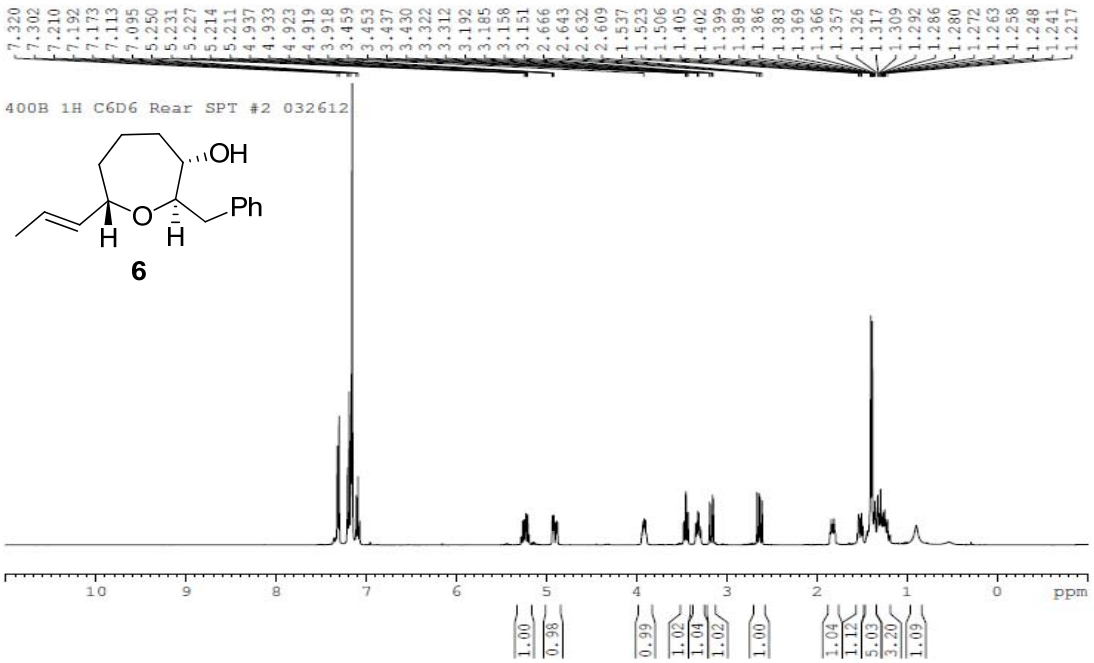

400B 13C CDCl3 Rear SPT #1 032612
ppm

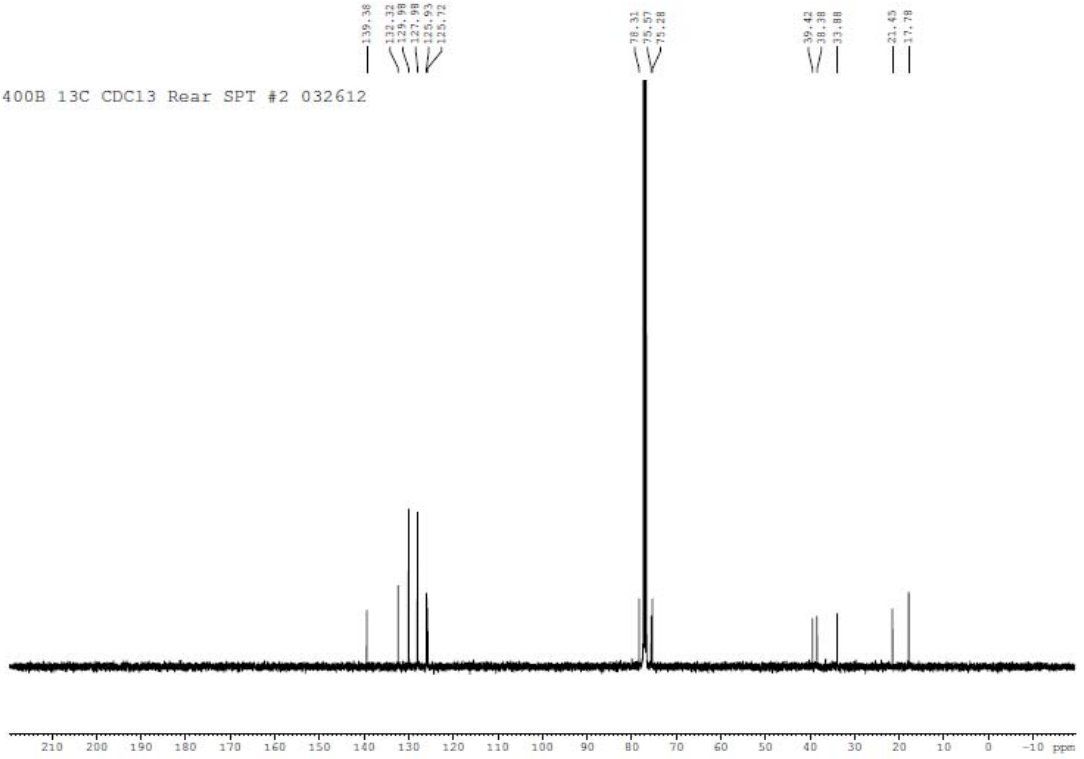

400B 1HCOSY C6D6 Rear SPT #1 032612
ppm
1
2
3
4
5
6
7
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm
OH
Ph
O
H
H

5

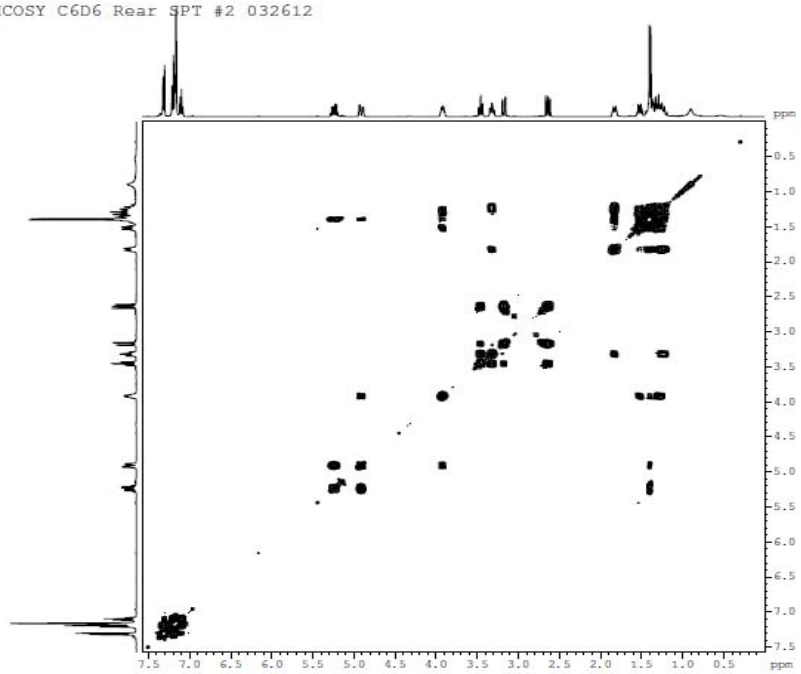

400B 1HNOESY C6D6 REAR SPT #1 022612
ppm
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm
OH
Ph
O
H
H

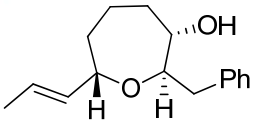
5


400B 1H C6D6 Rear SPT #2 032612
OH
Ph
O
H
H
6
ppm


400B 13C CDC13 Rear SPT #2 032612
ppm

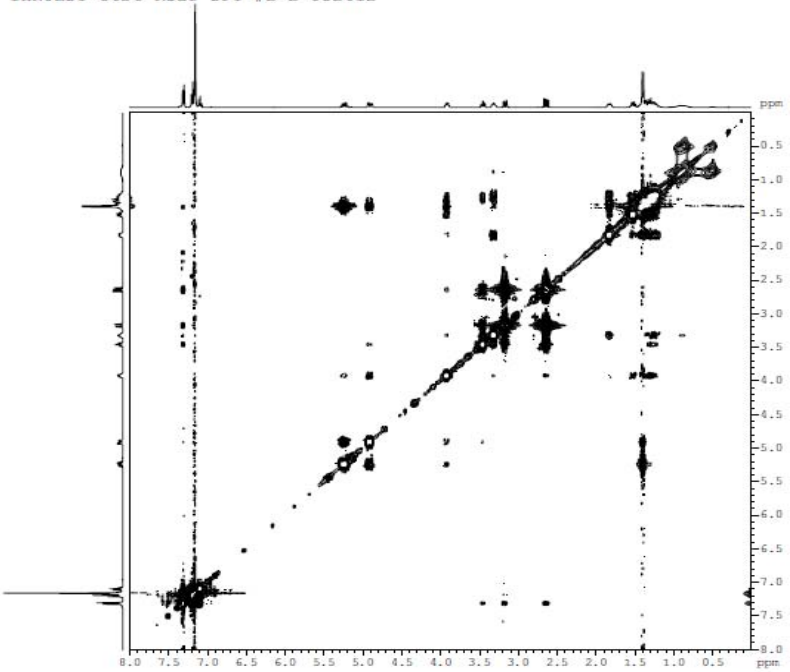
400B 1HCOSY C6D6 Rear SPT #2 032612

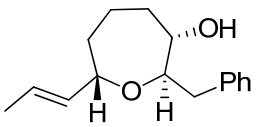




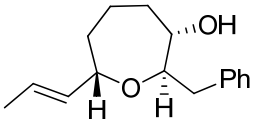
6

400B 1HNOESY C6D6 Rear SPT #2-2 032612

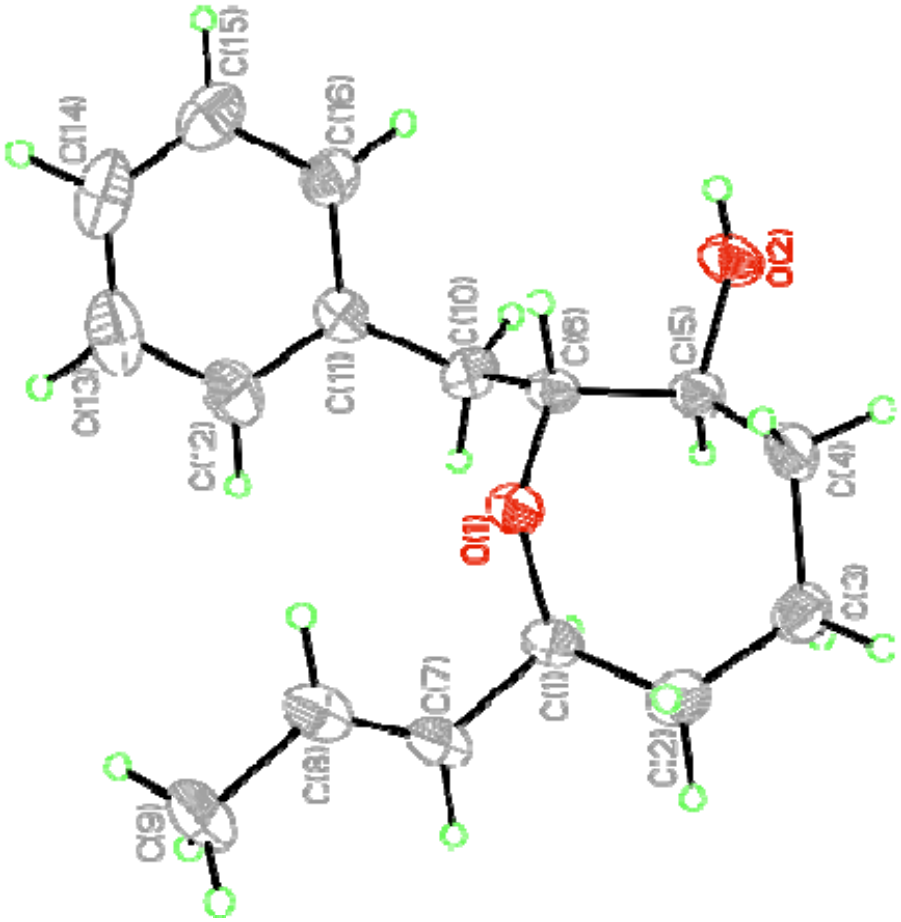




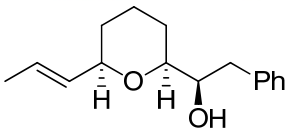
6



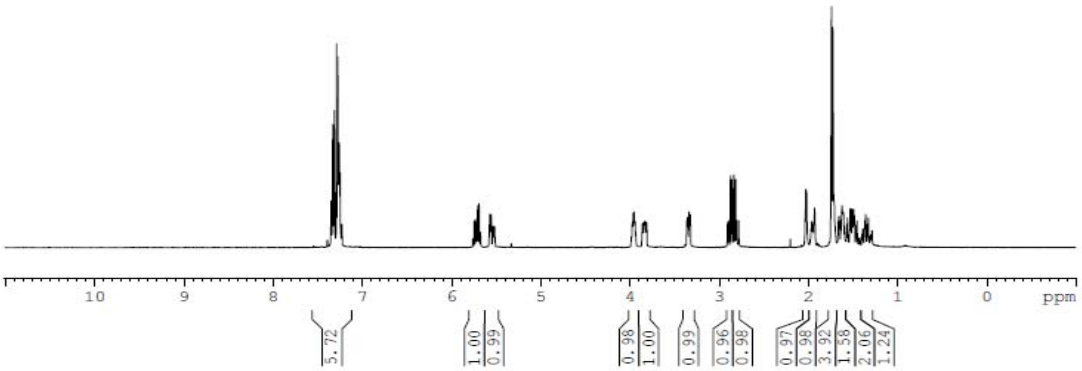
6



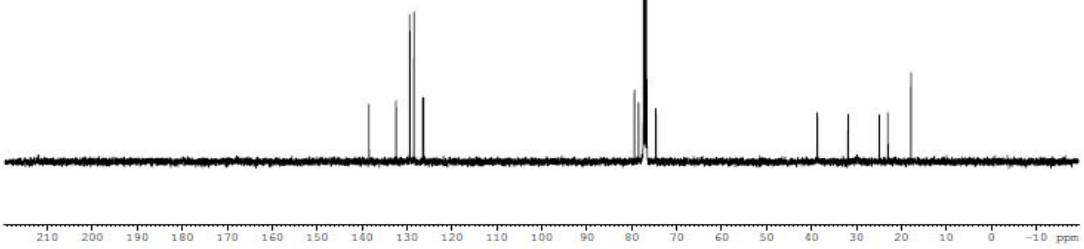
400B 1H Rear SPT #3 032412

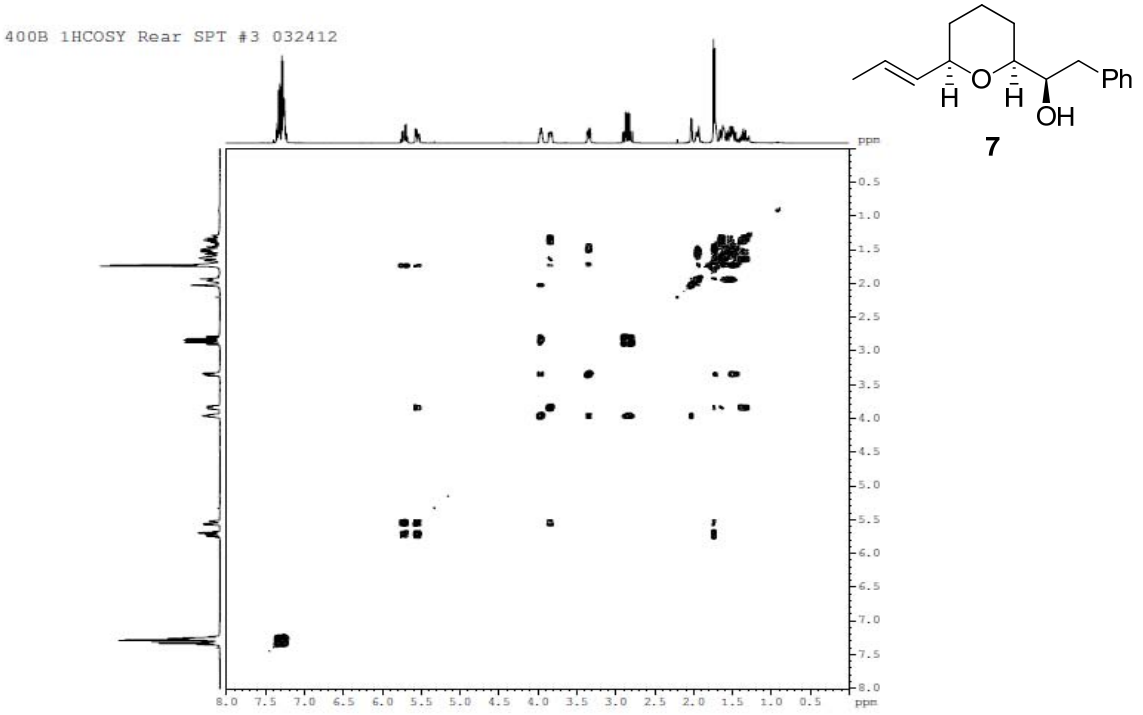


7

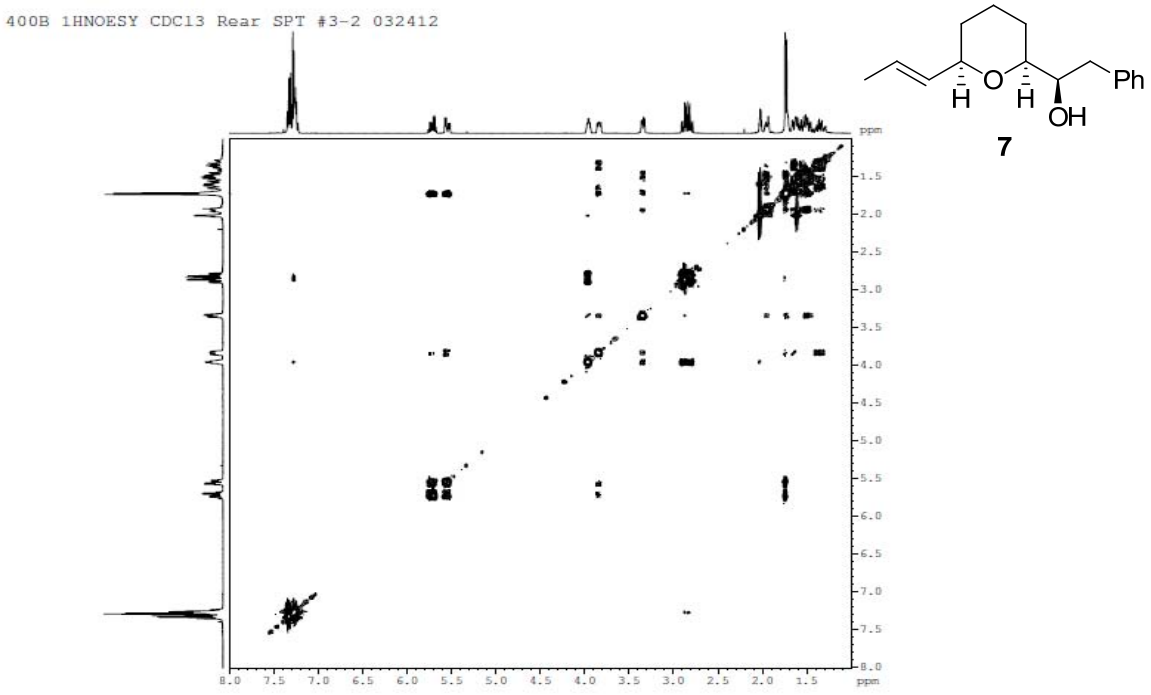


400B 13C Rear SPT #3 032412

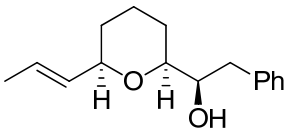



400B 1HCOSY Rear SPT #3 032412
ppm
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm
O
H
H
OH
Ph

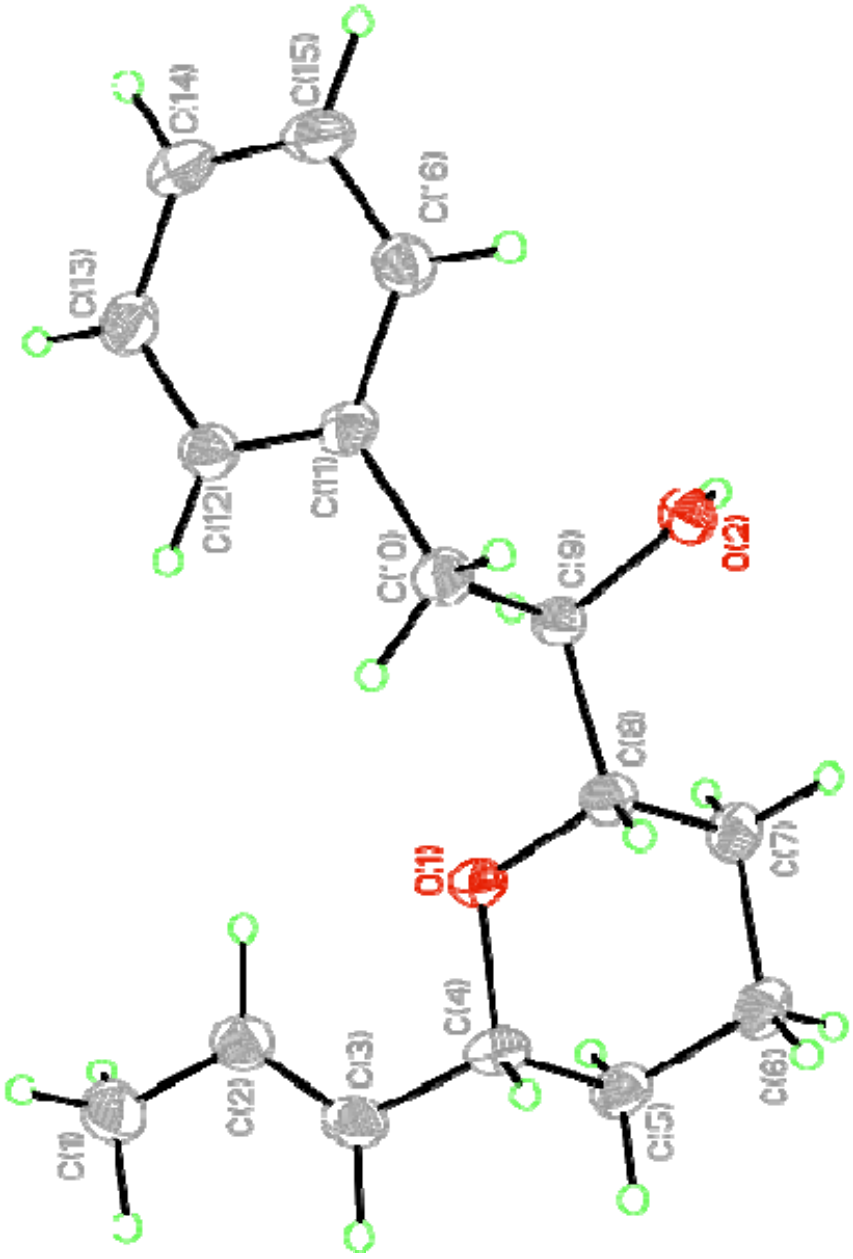
7

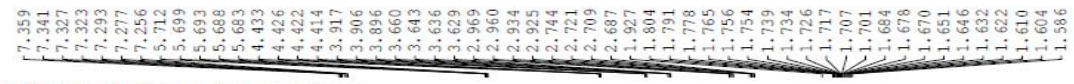

400B 1HNOESY CDC13 Rear SPT #3-2 032412
ppm
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5
ppm
O
H
H
OH
Ph

7

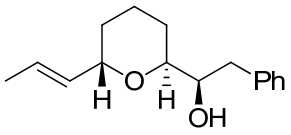


7

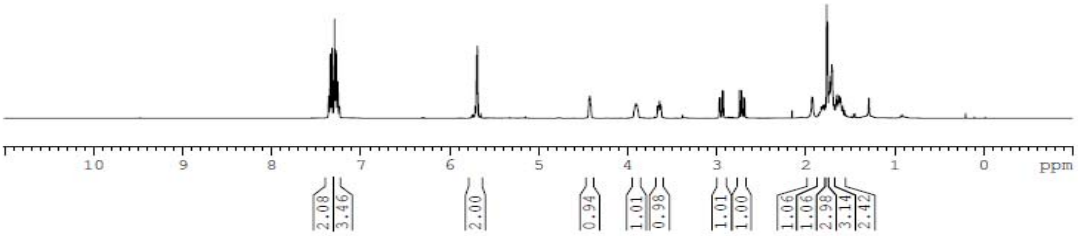




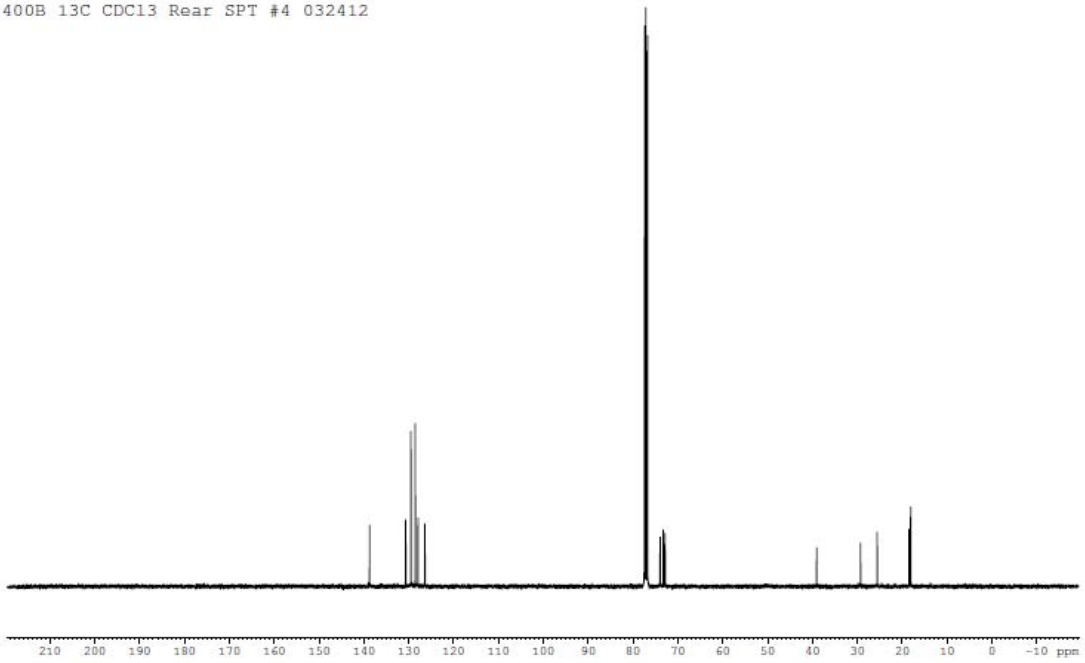
400B 1H CDCl3 Rear SPT #4 032412

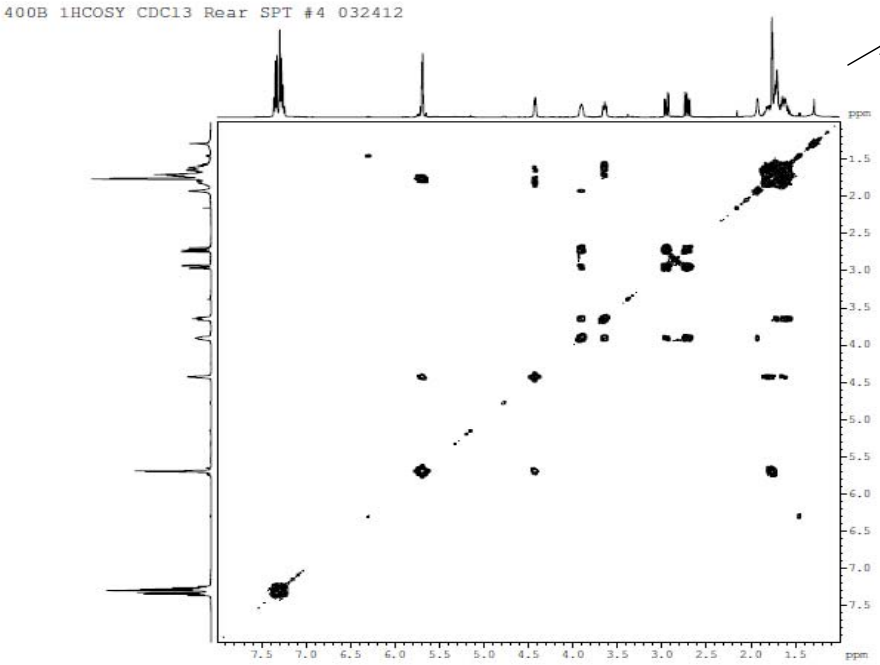


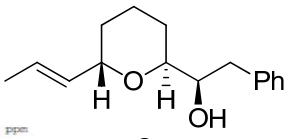
8



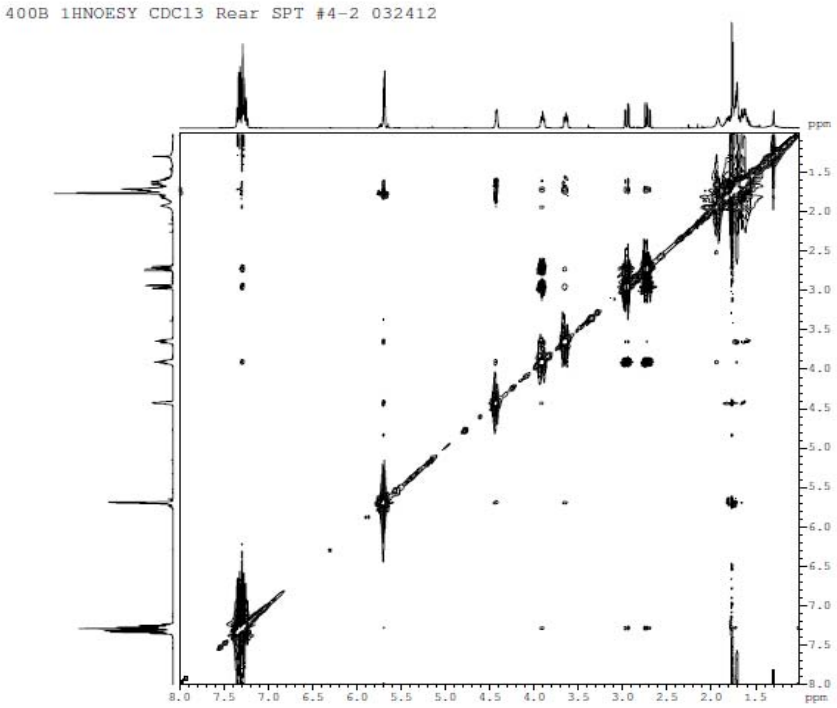
400B 13C CDCl3 Rear SPT #4 032412

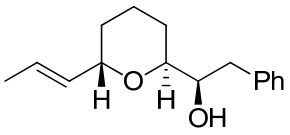



400B 1HCOSY CDCl3 Rear SPT #4 032412
ppm
ppm

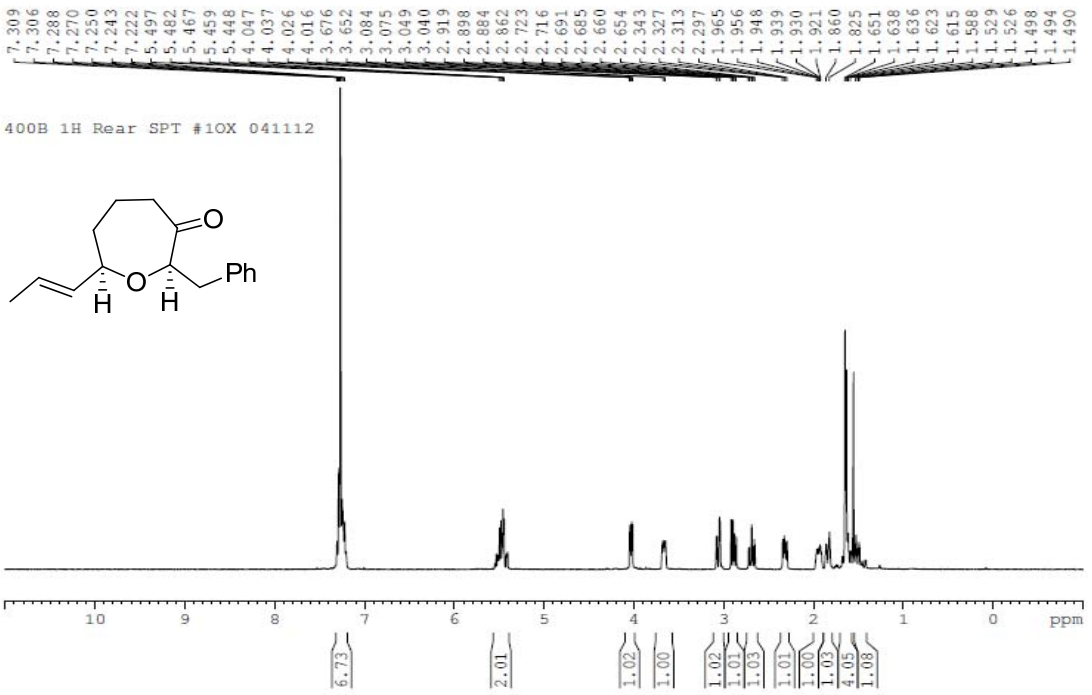

O
H
H
OH
Ph

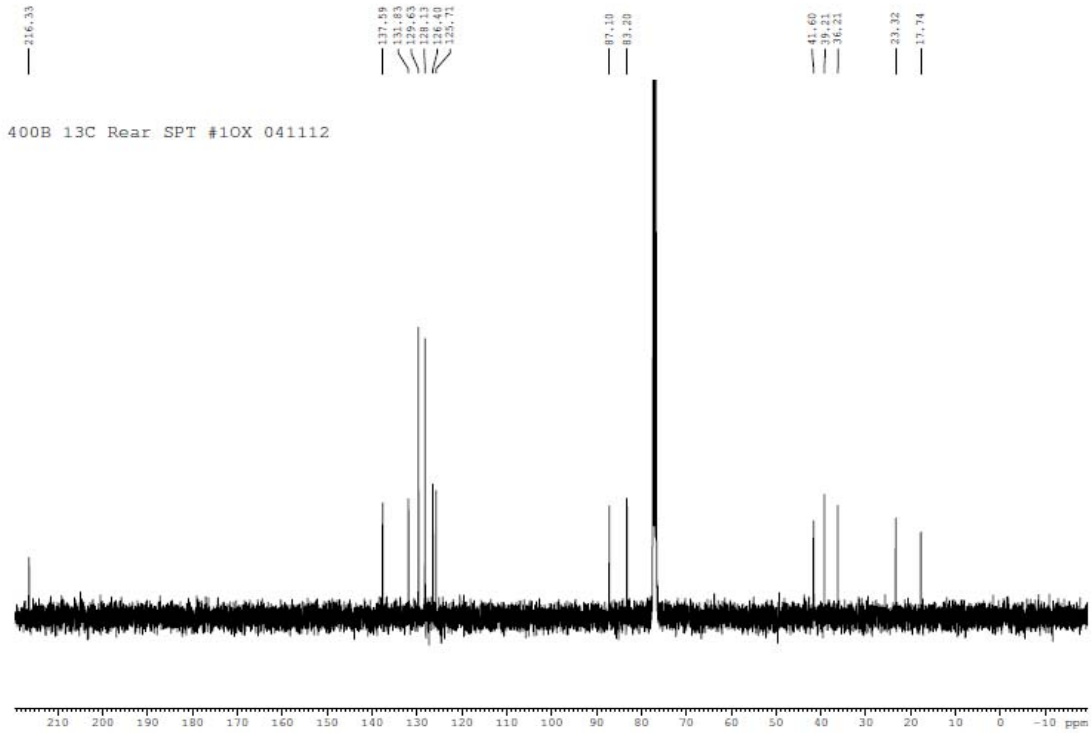
8


400B 1HNOESY CDCl3 Rear SPT #4-2 032412
ppm
ppm

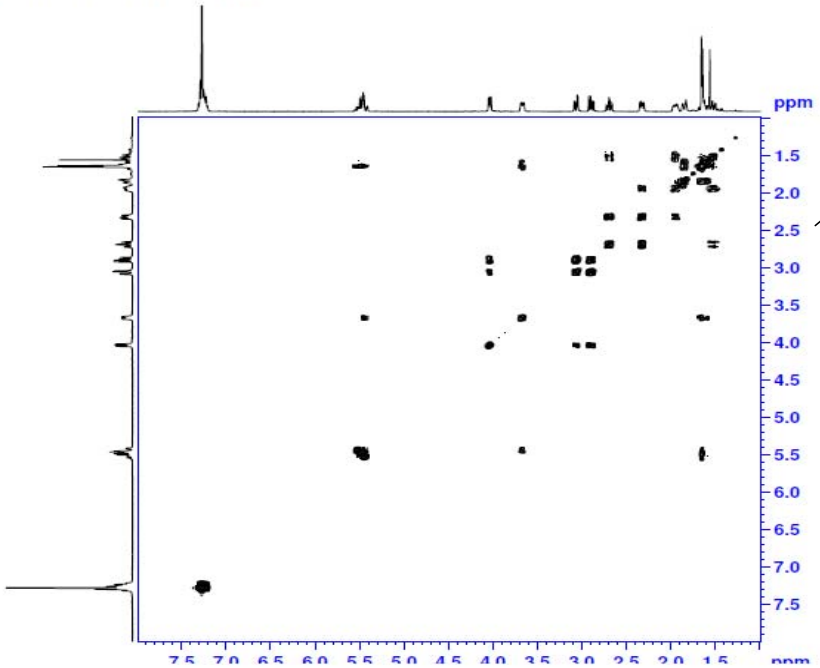

O
H
H
OH
Ph

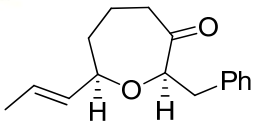
8


7.309
7.306
7.288
7.270
7.250
7.243
7.222
5.497
5.482
5.467
5.459
5.448
4.047
4.037
4.026
4.016
3.676
3.652
3.084
3.075
3.049
3.040
2.919
2.898
2.884
2.862
2.723
2.716
2.691
2.685
2.660
2.654
2.343
2.327
2.313
2.297
1.965
1.956
1.948
1.939
1.930
1.921
1.860
1.825
1.651
1.638
1.636
1.623
1.615
1.588
1.529
1.526
1.498
1.494
1.490
400B 1H Rear SPT #1OX 041112
O
Ph
O
H
H
10
9
8
7
6
5
4
3
2
1
0
ppm
6.73
2.01
1.02
1.00
1.02
1.01
1.03
1.01
1.00
1.03
4.05
1.08

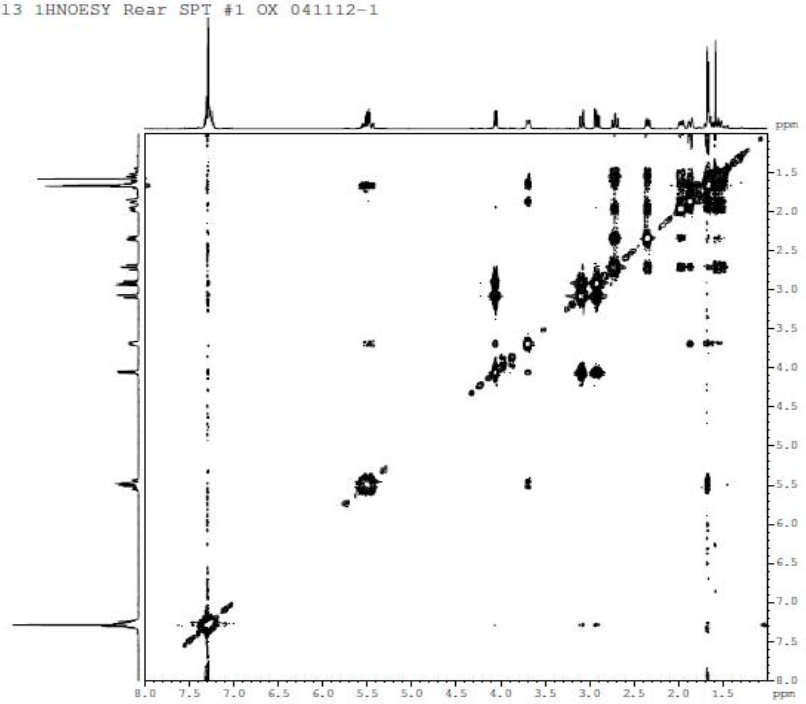

216.33
137.59
131.83
129.63
128.13
126.40
125.71
87.10
83.20
41.60
39.21
36.21
23.32
17.74
400B 13C Rear SPT #1OX 041112
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10 ppm

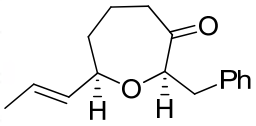
400B 1HCOSY Rear SPT #1OX 041112

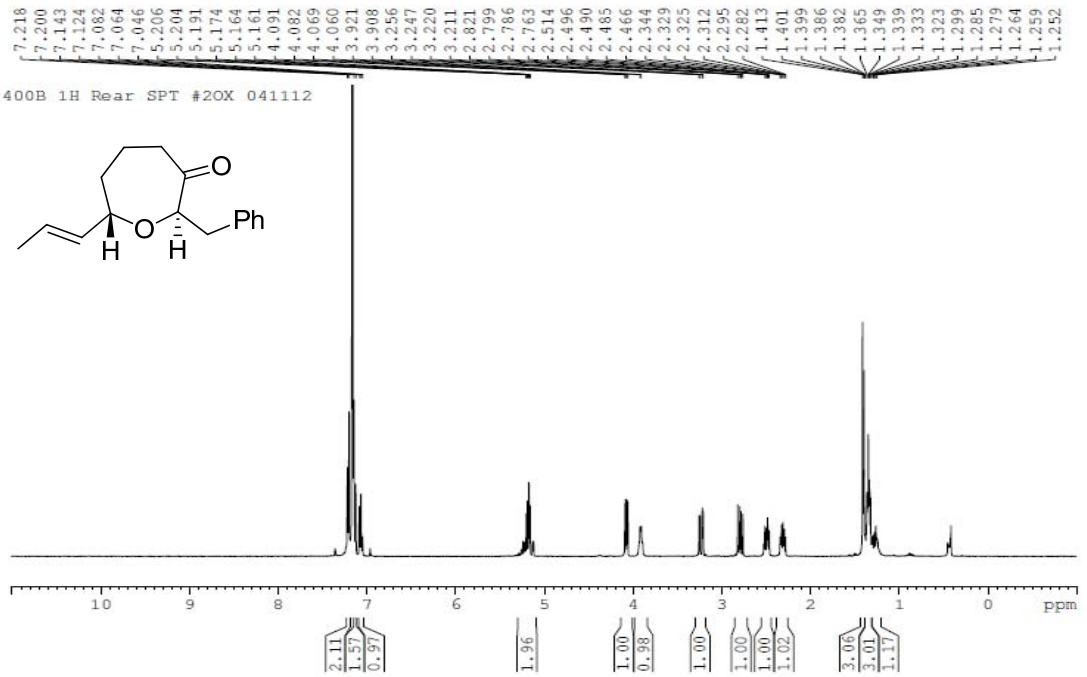


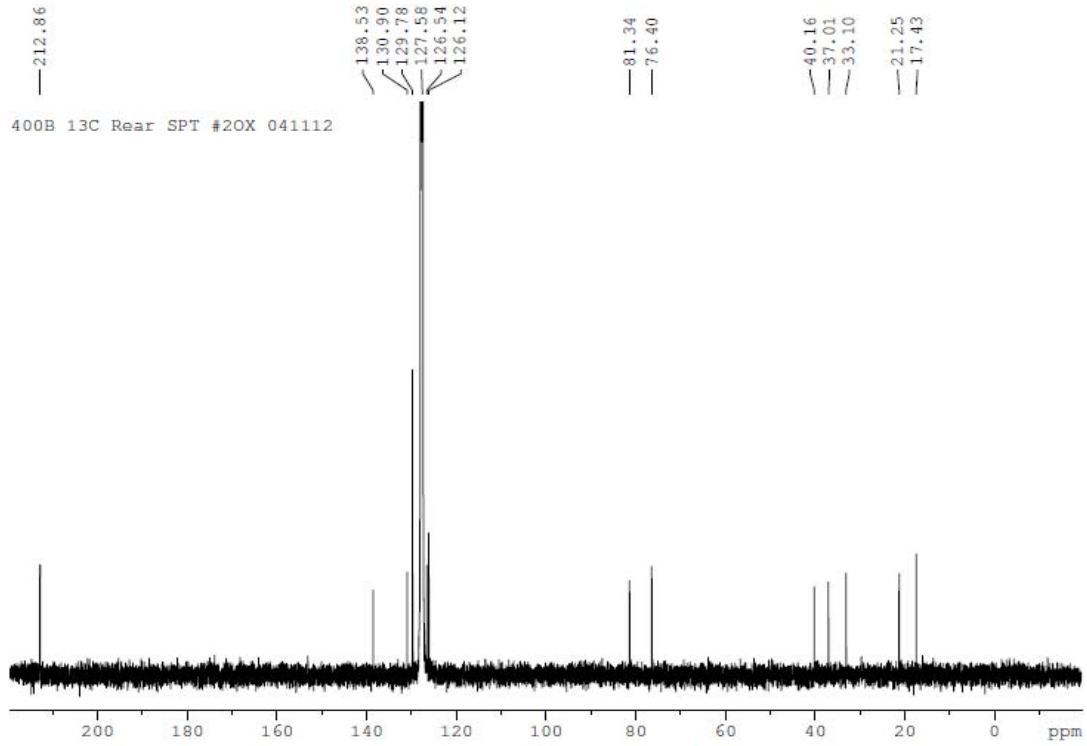


400B CDCl3 1HNOESY Rear SPT #1 OX 041112-1

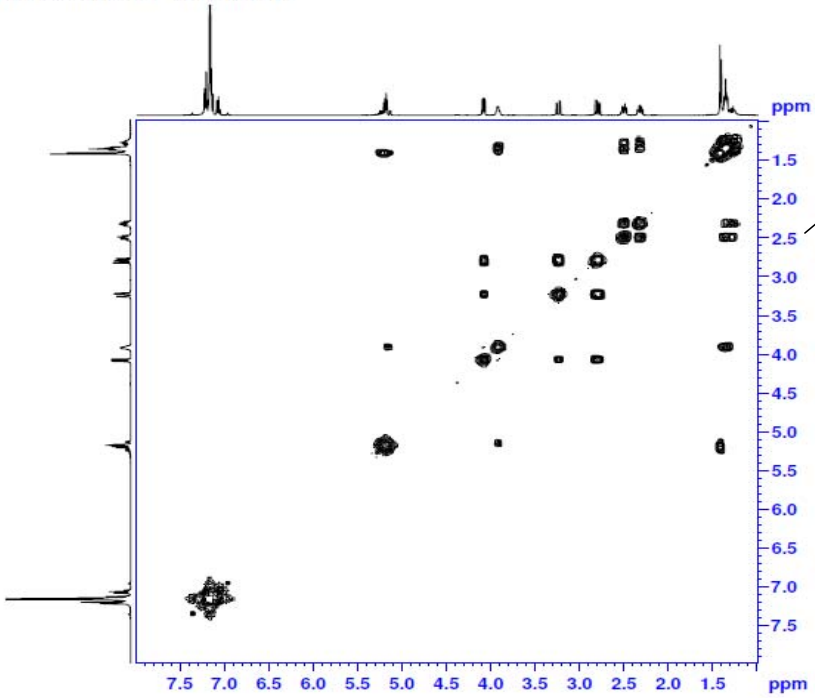


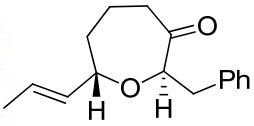



400B 1H Rear SPT #20X 041112
O
Ph
O
H
H
ppm

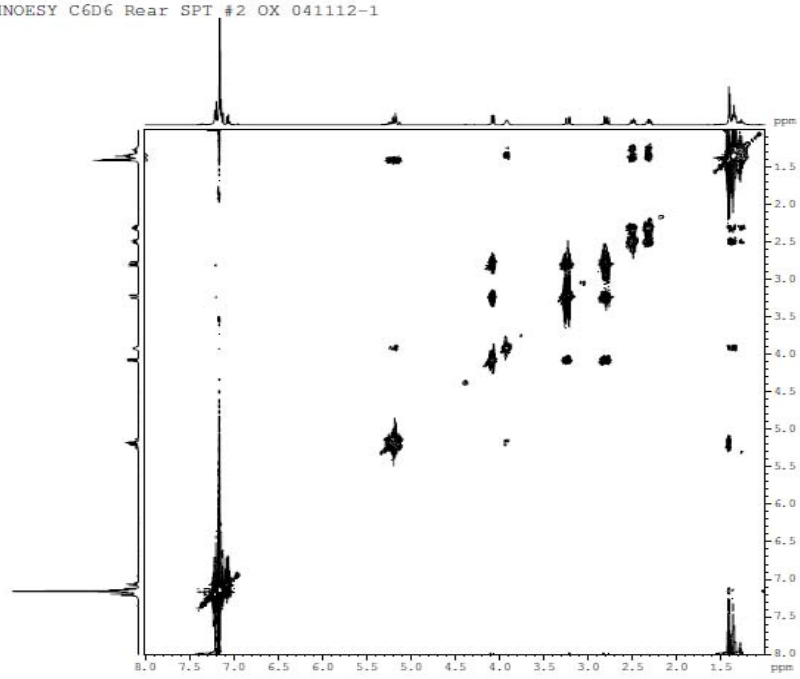

400B 13C Rear SPT #20X 041112
212.86
138.53
130.90
129.78
127.58
126.54
126.12
81.34
76.40
40.16
37.01
33.10
21.25
17.43
ppm

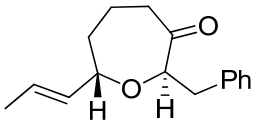
400B 1HCOSY Rear SPT #2OX 041112



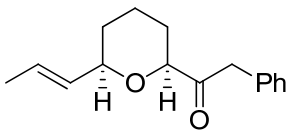


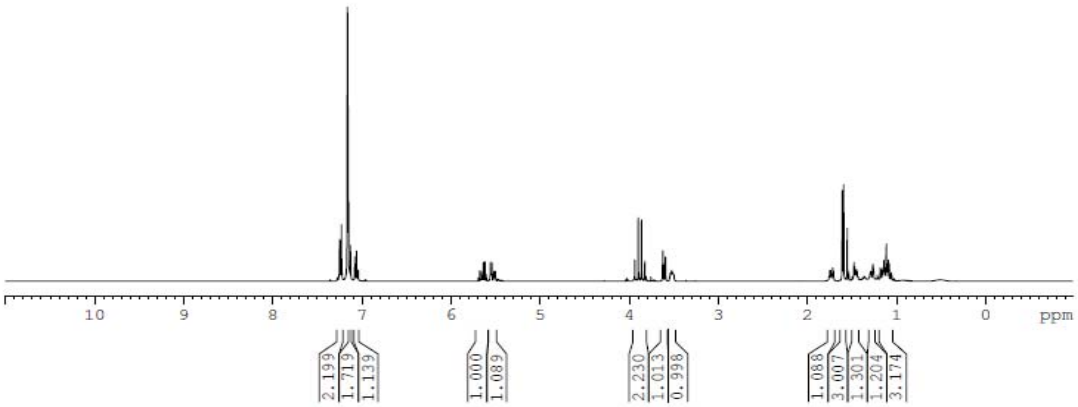
400B 1HNOESY C6D6 Rear SPT #2 OX 041112-1

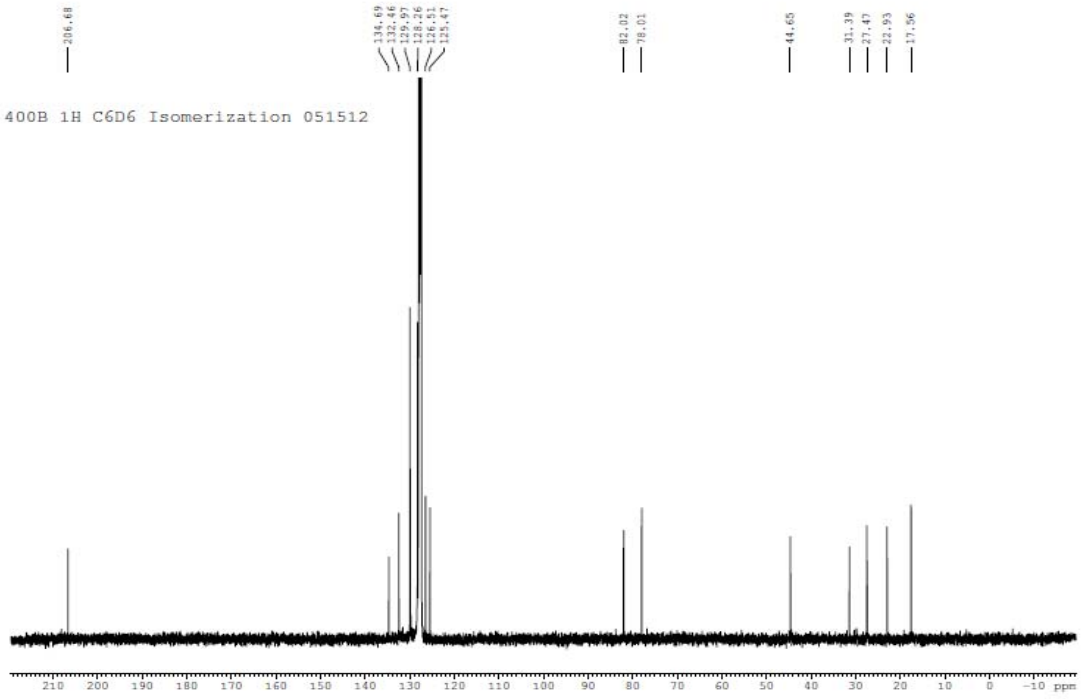


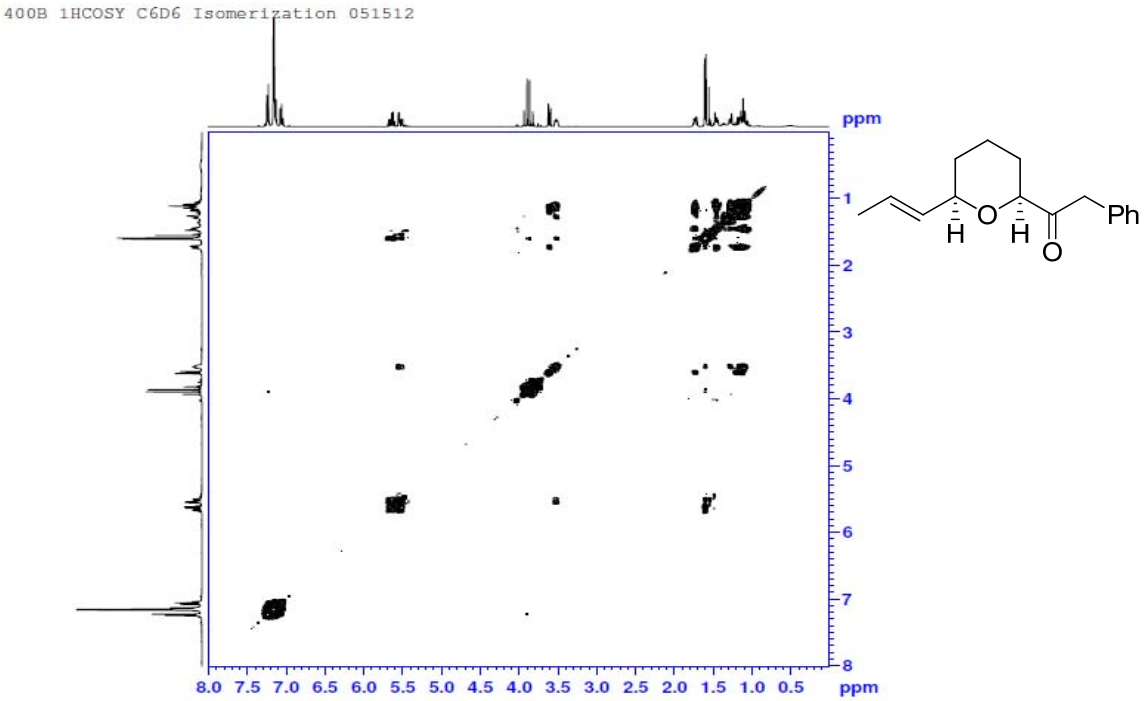


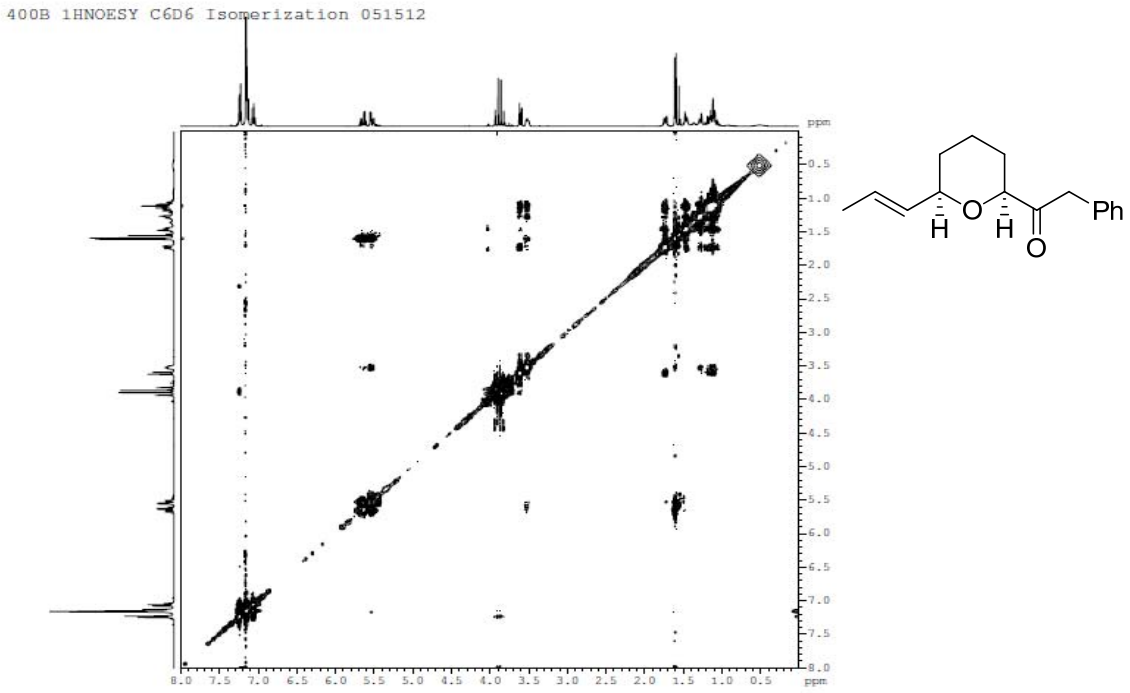
400B 1H-1 C6D6 Isomerization 051512



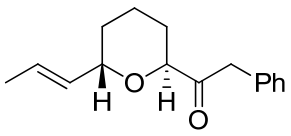


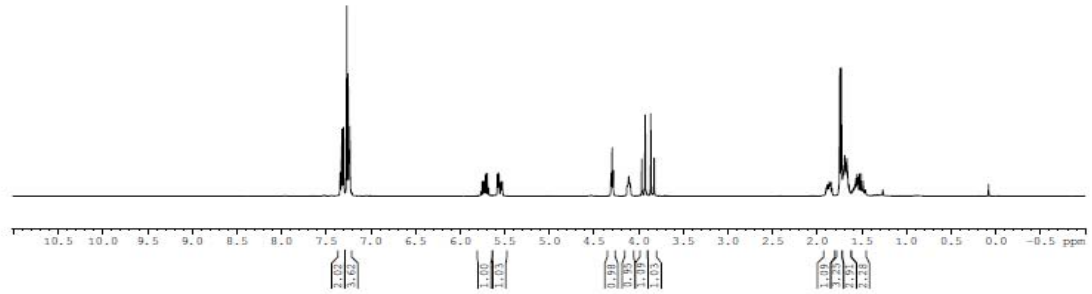


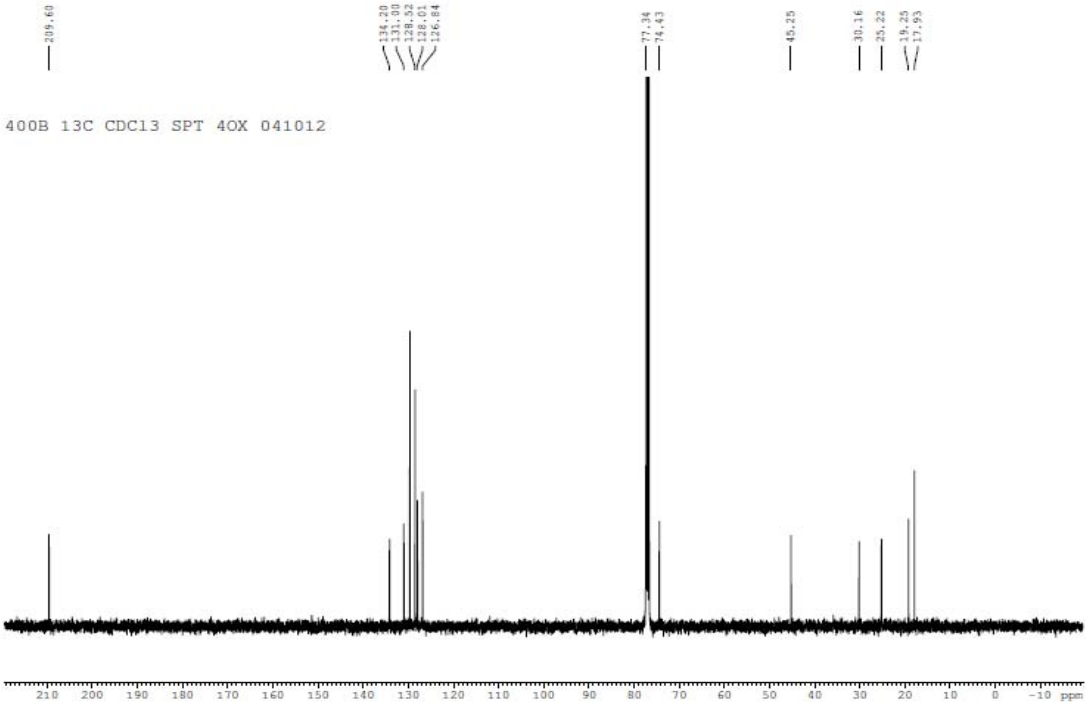

400B 1HCOSY C6D6 Isomerization 051512
ppm
1
2
3
4
5
6
7
8
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm
O
H
H
O
Ph

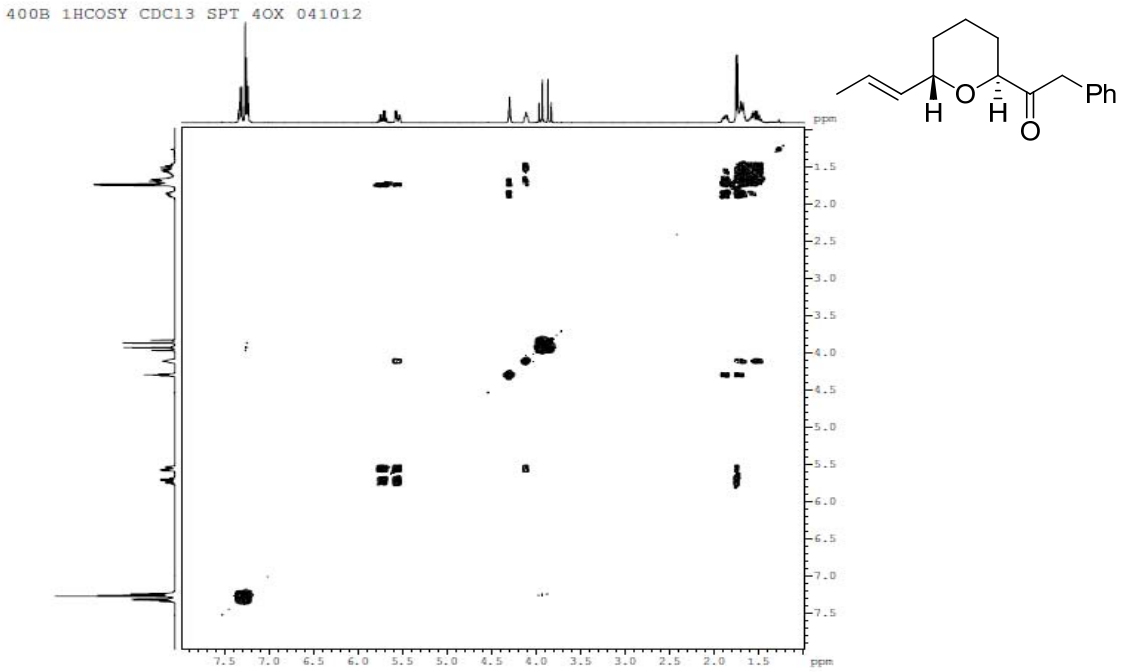

400B 1HNOESY C6D6 Isomerization 051512
O
H
H
O
Ph

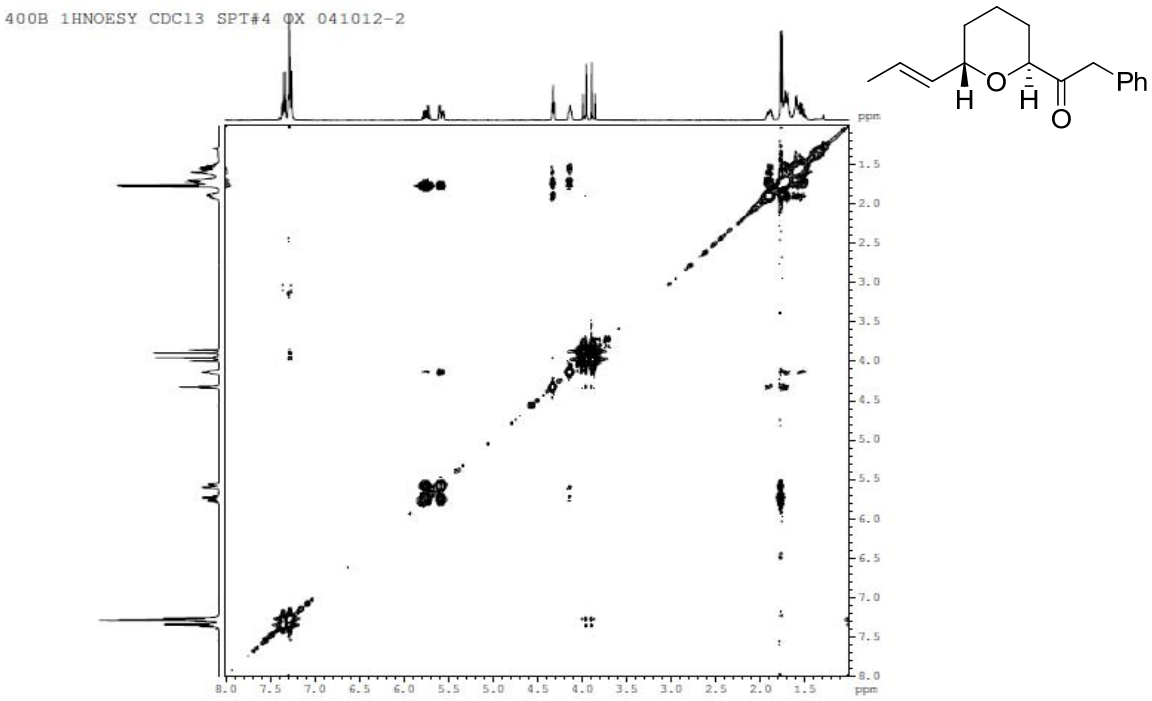
400B 1H CDC13 SPT 4OX 041012

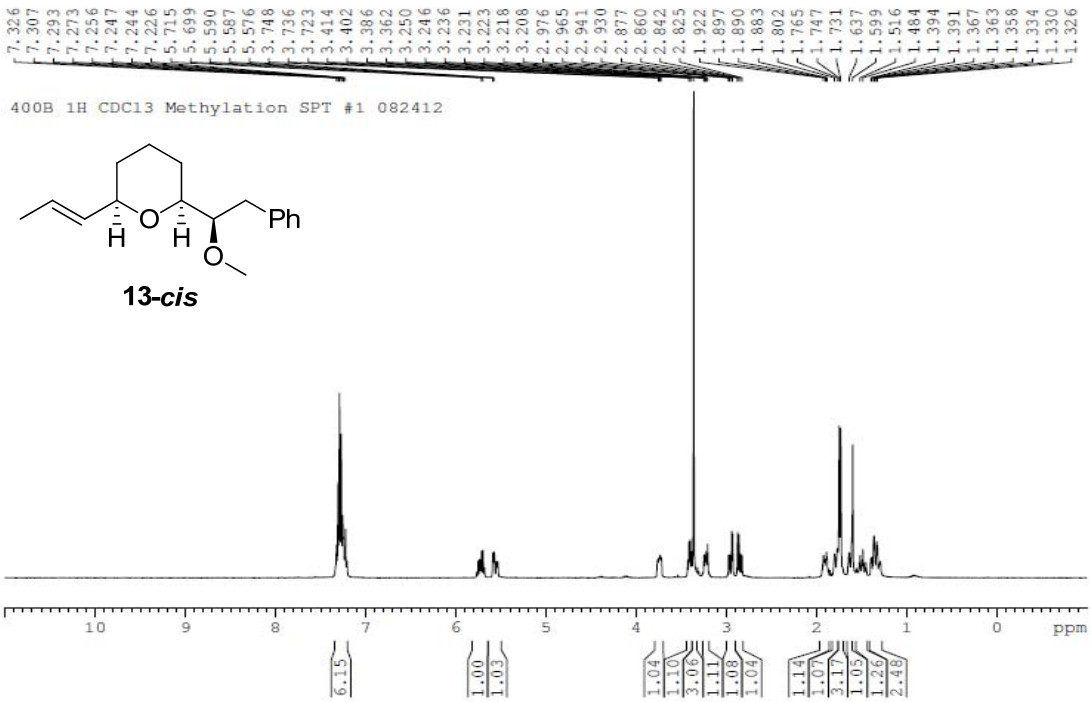


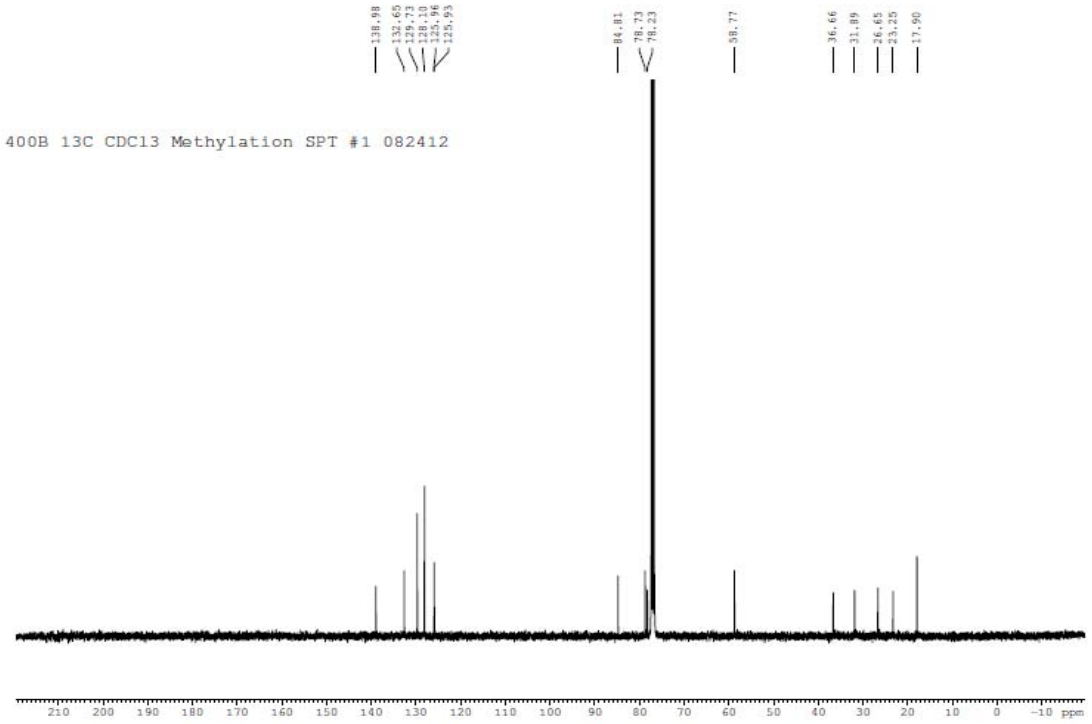


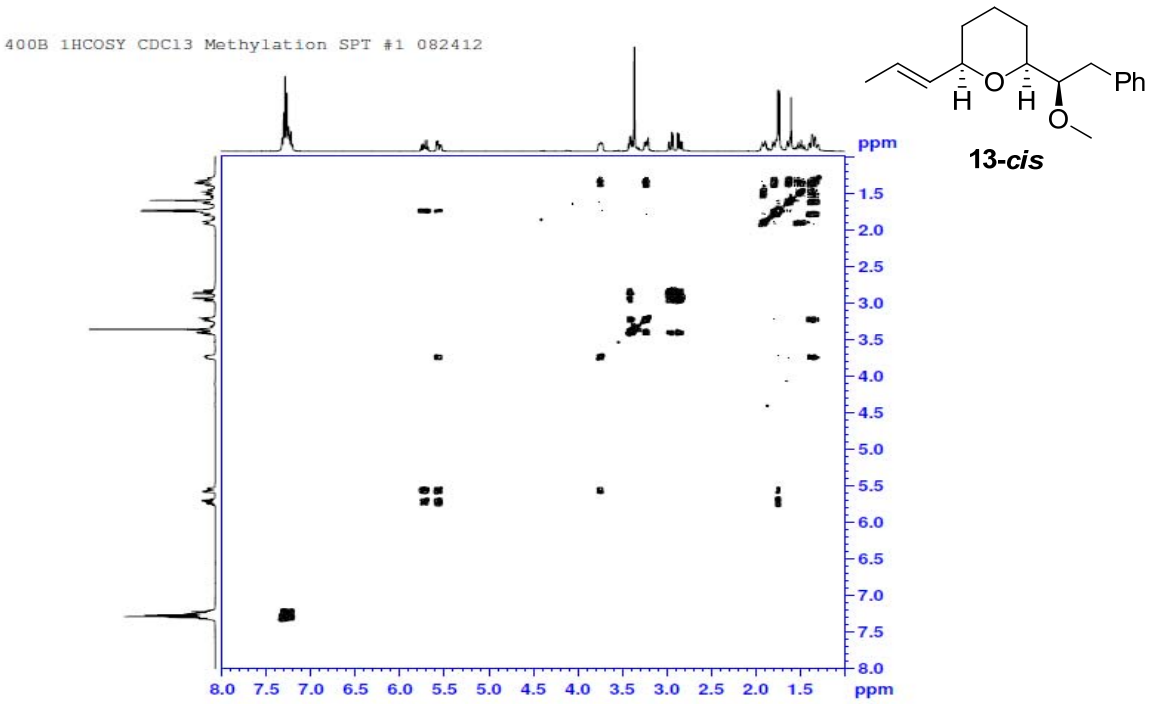



400B 1HCOSY CDC13 SPT 4OX 041012
O
H
H
O
Ph

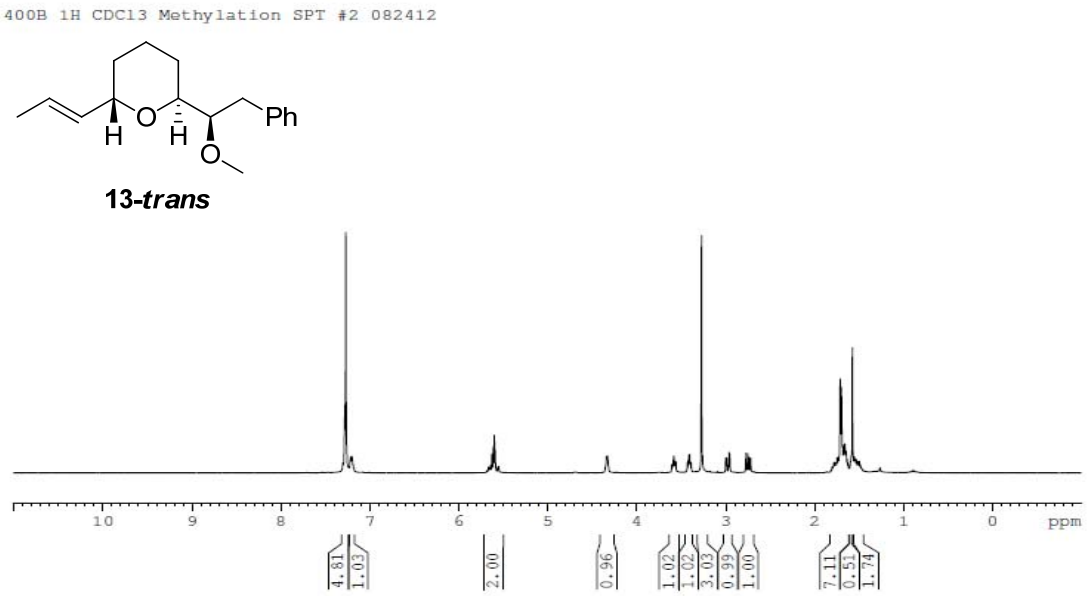

400B 1HNOESY CDC13 SPT#4 OX 041012-2
O
H
H
O
Ph


7.326
7.307
7.293
7.273
7.256
7.247
7.244
7.226
5.715
5.699
5.590
5.587
5.576
3.748
3.736
3.723
3.414
3.402
3.386
3.362
3.250
3.246
3.236
3.231
3.223
3.218
3.208
2.976
2.965
2.941
2.930
2.877
2.860
2.842
2.825
1.922
1.897
1.890
1.883
1.802
1.765
1.747
1.731
1.637
1.599
1.516
1.484
1.394
1.391
1.367
1.363
1.358
1.334
1.330
1.326
400B 1H CDC13 Methylation SPT #1 082412
O
H
H
O
Ph
13-cis
10
9
8
7
6
5
4
3
2
1
0
ppm
6.15
1.00
1.03
1.04
1.10
3.06
1.11
1.08
1.04
1.14
1.07
3.17
1.05
1.26
2.48

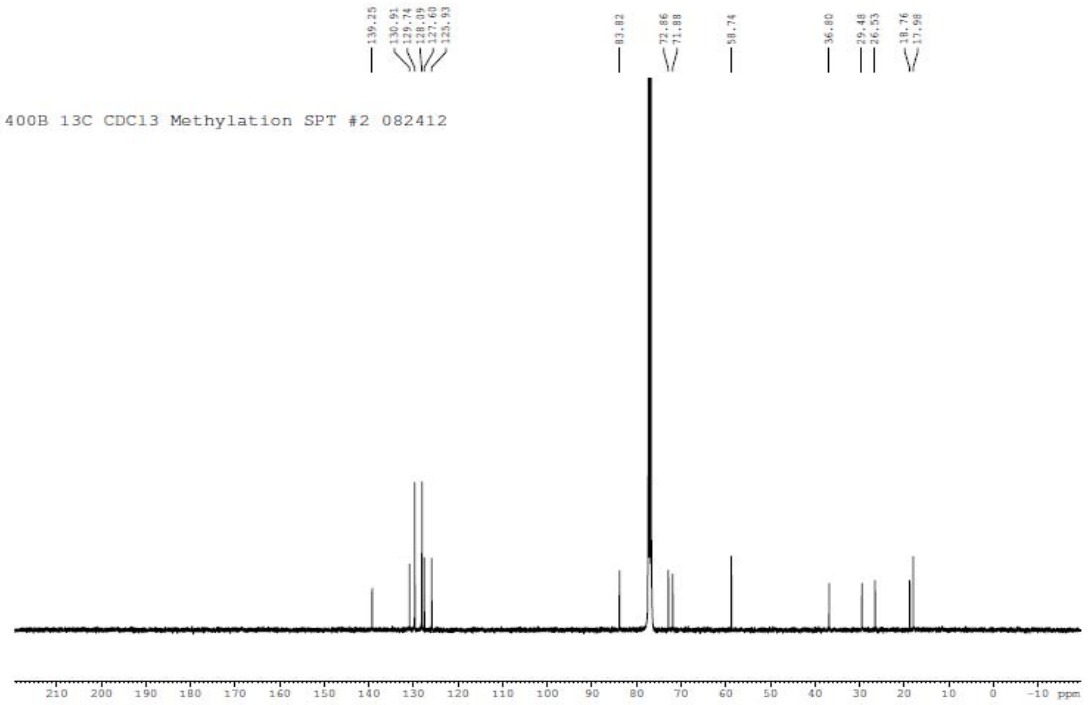

138.98
132.65
129.73
128.10
125.96
125.93
84.81
78.73
78.23
58.77
36.66
31.89
26.65
23.25
17.90
400B 13C CDC13 Methylation SPT #1 082412
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

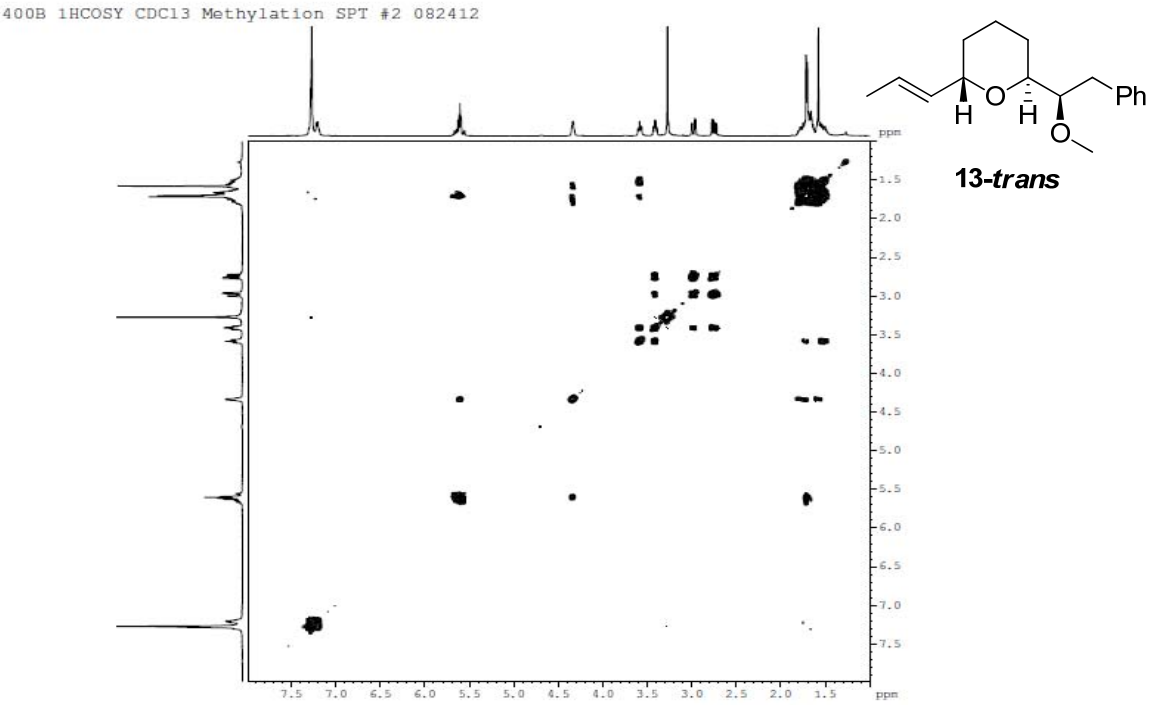


13-*cis*



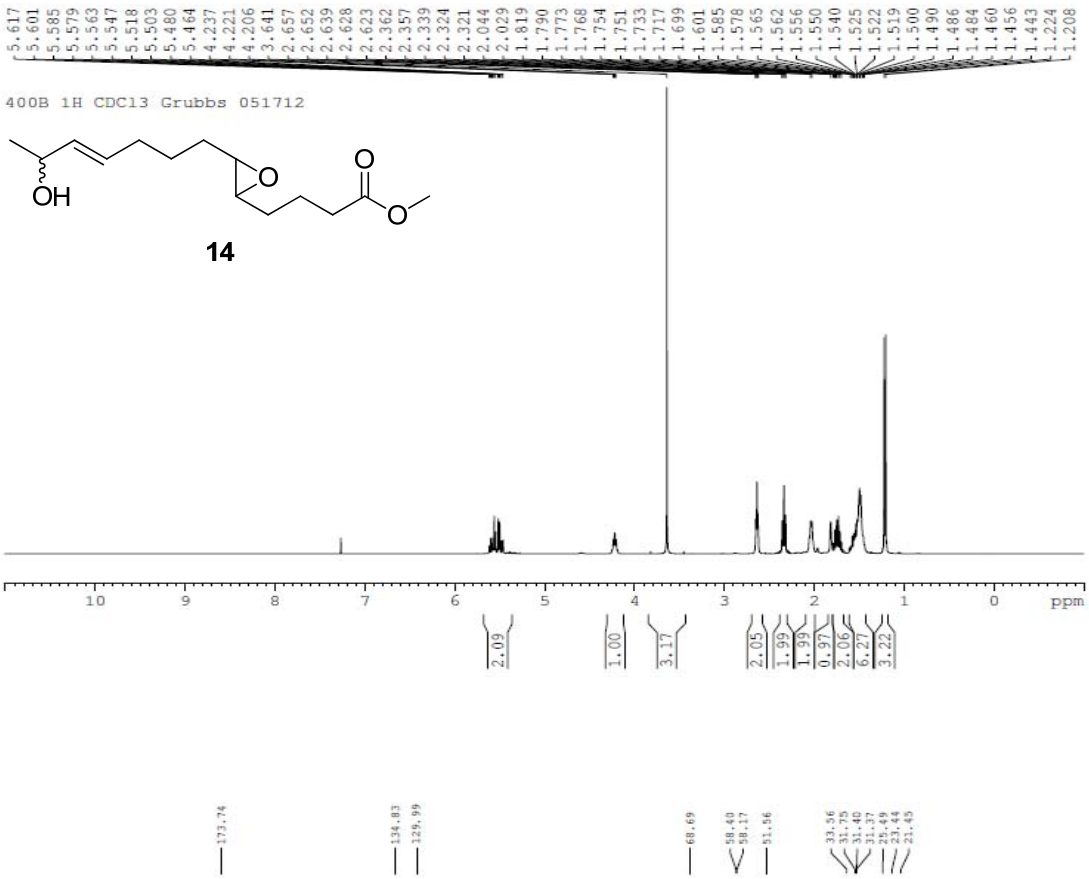
13-*trans*

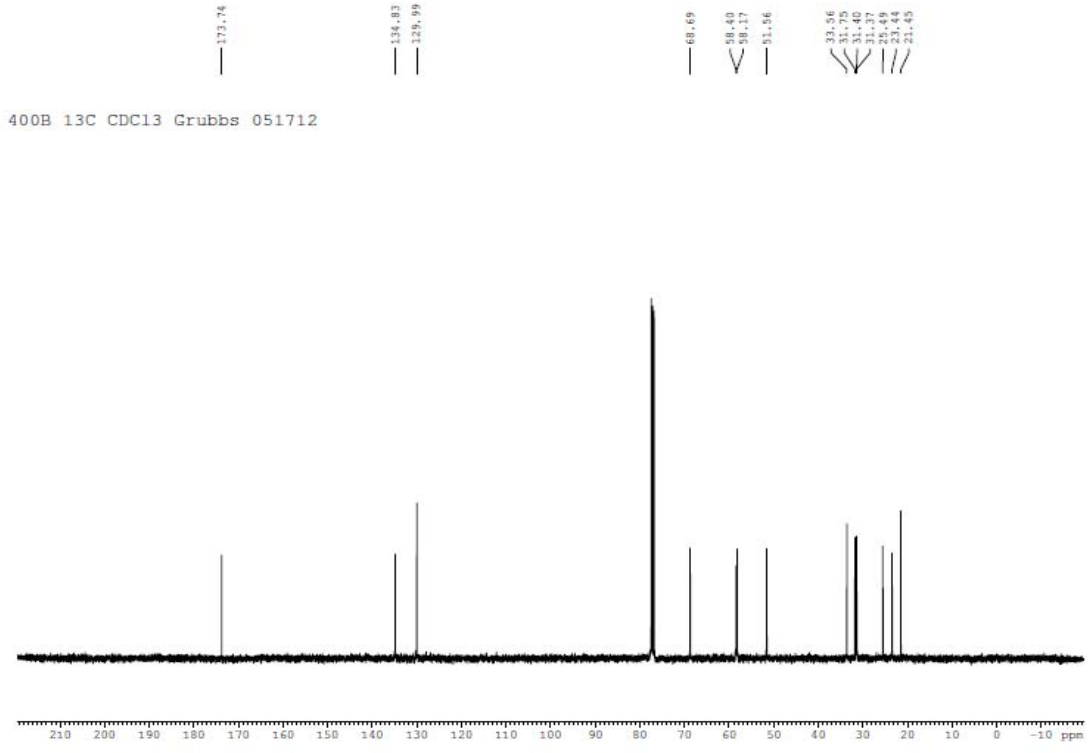

400B 13C CDCl3 Methylation SPT #2 082412
139.25
130.91
129.74
128.09
127.60
125.93
83.82
72.86
71.88
58.74
36.80
29.48
26.53
18.76
17.98
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm


400B 1HCOSY CDCl3 Methylation SPT #2 082412
ppm
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 ppm

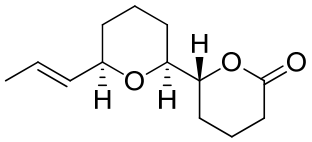
Ph
O
H
H
O

13-*trans*

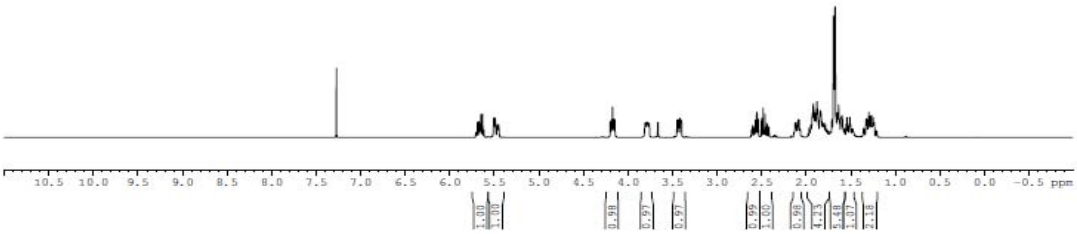

400B 1H CDCl3 Grubbs 051712
OH
O
O
O
14
ppm

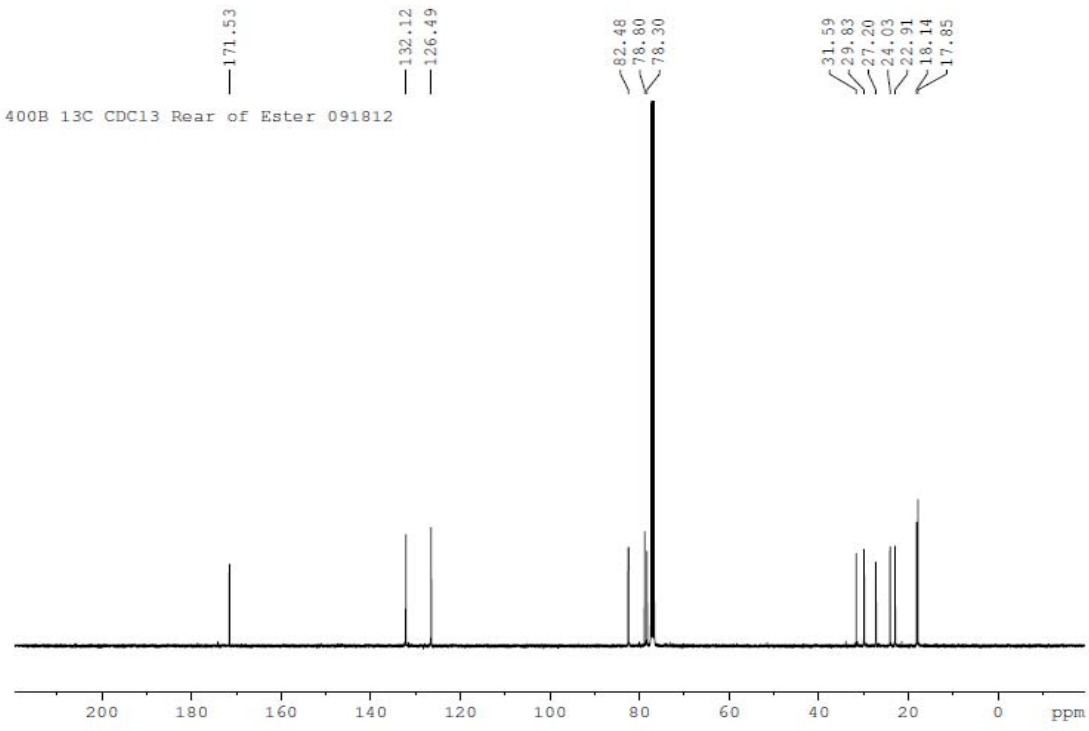

400B 13C CDCl3 Grubbs 051712
ppm

400B 1H CDCl3 Rear 091812

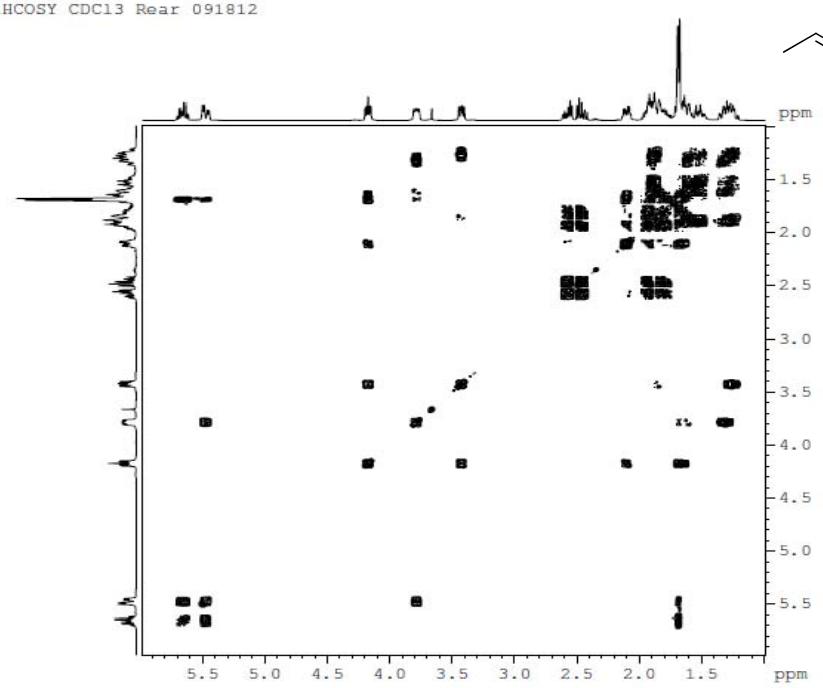


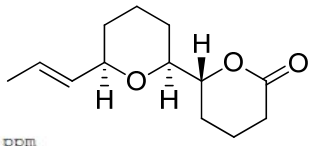
15





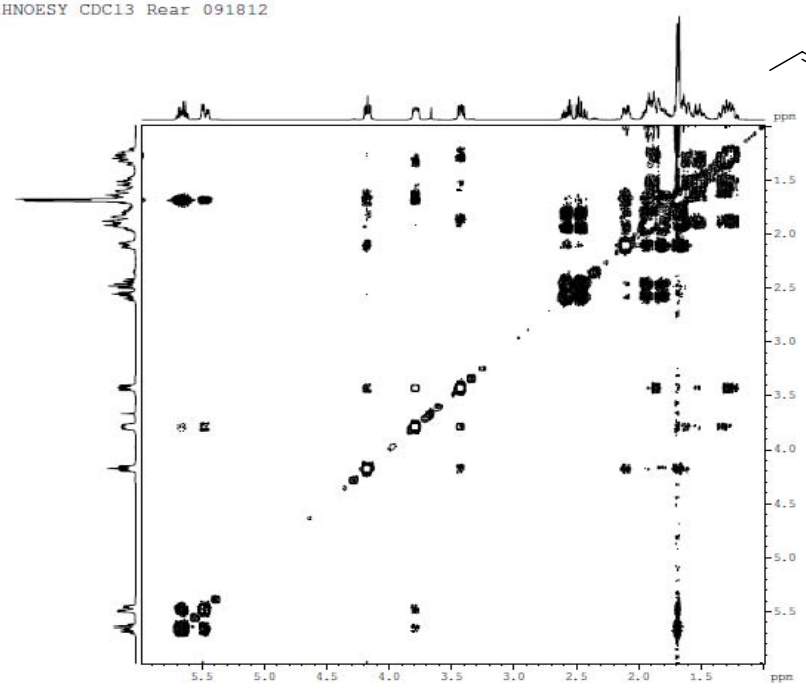
400B 1HCOSY CDCl3 Rear 091812

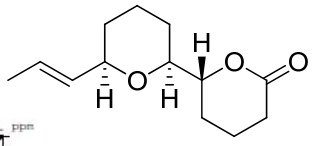




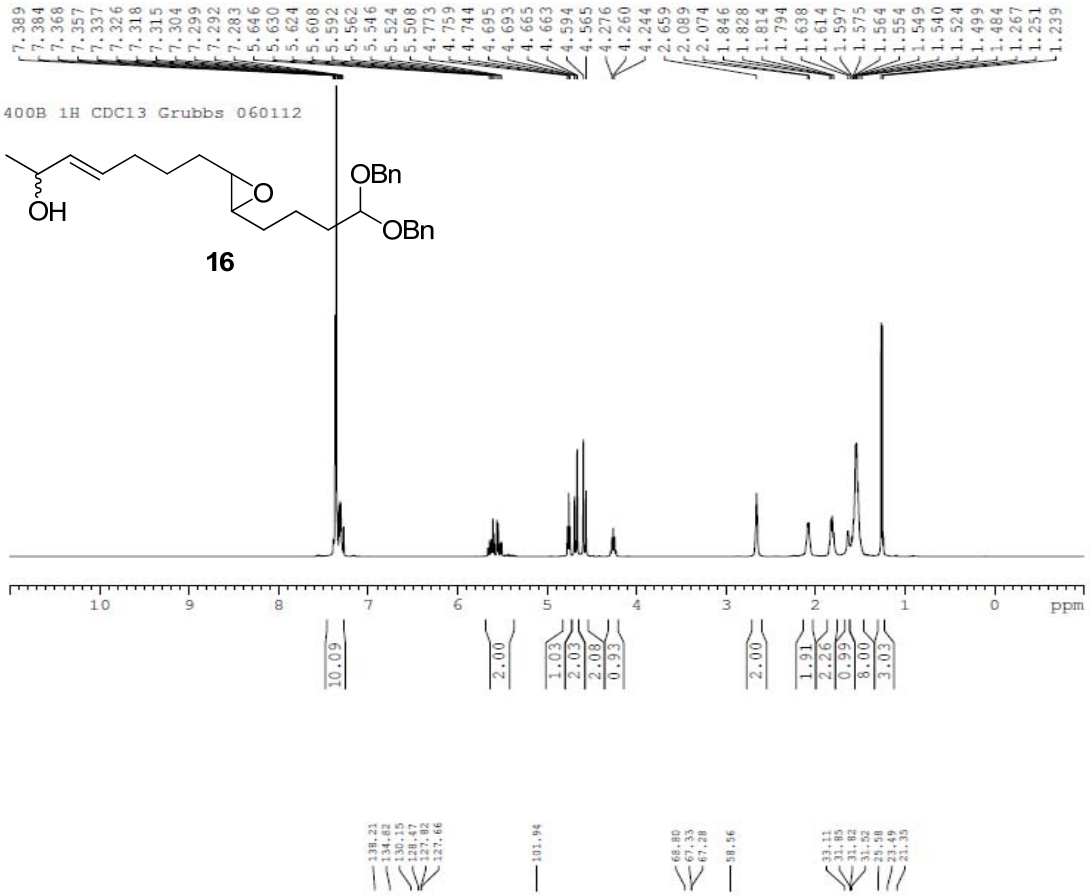
15

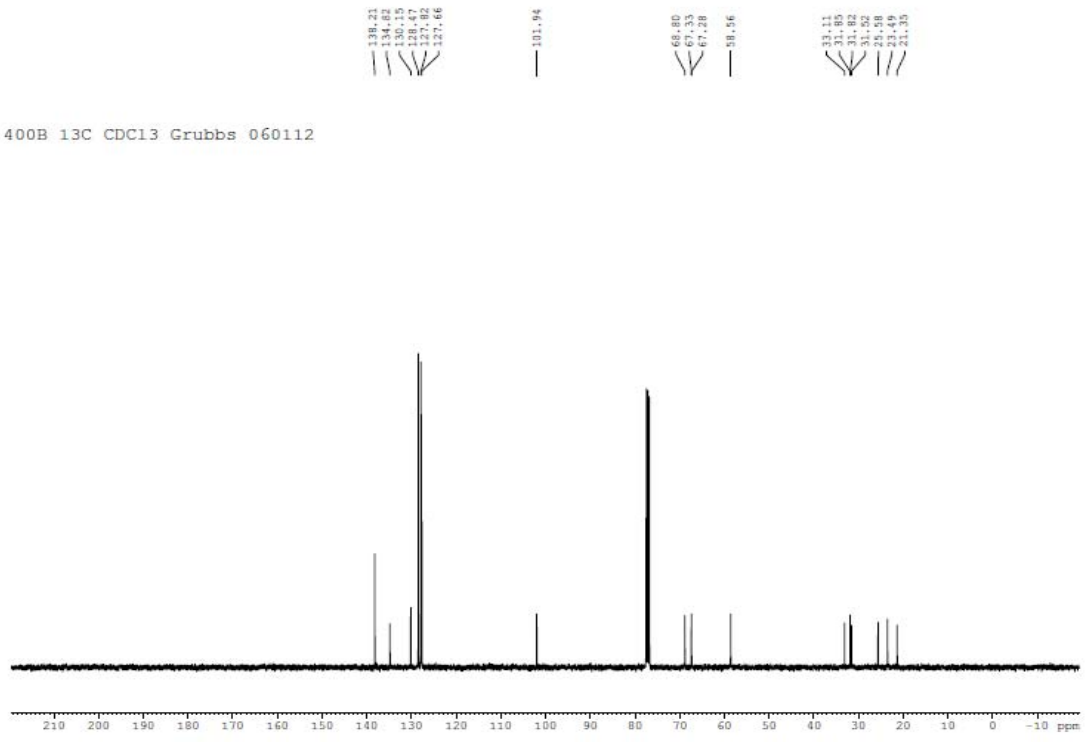
400B 1HNOESY CDCl3 Rear 091812

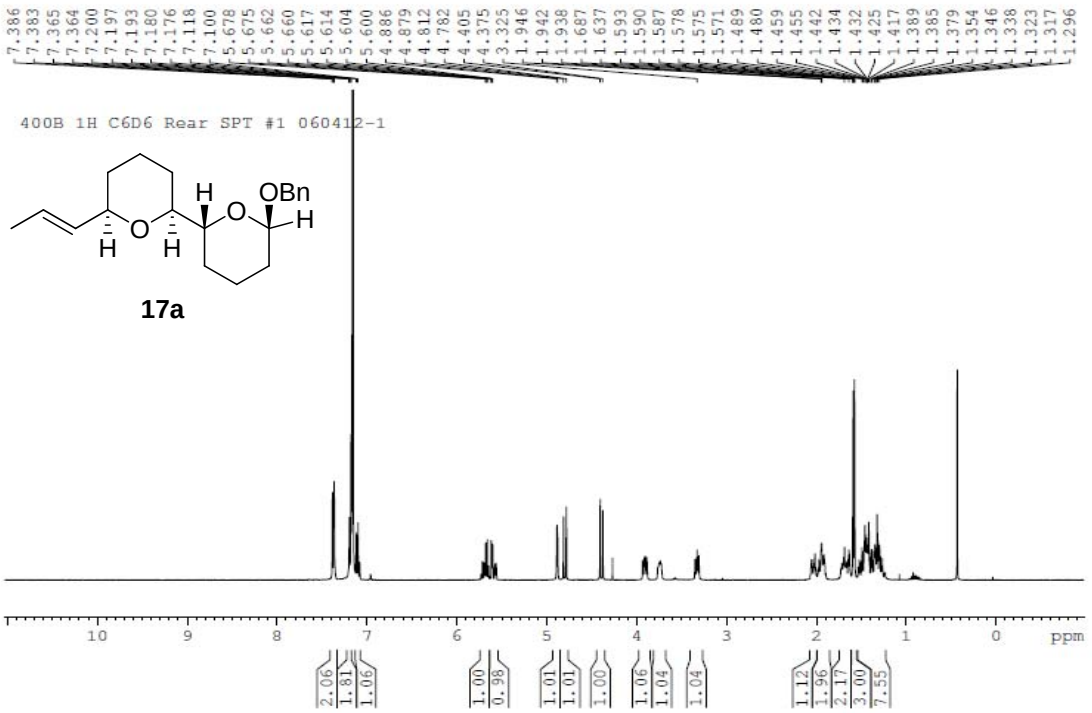


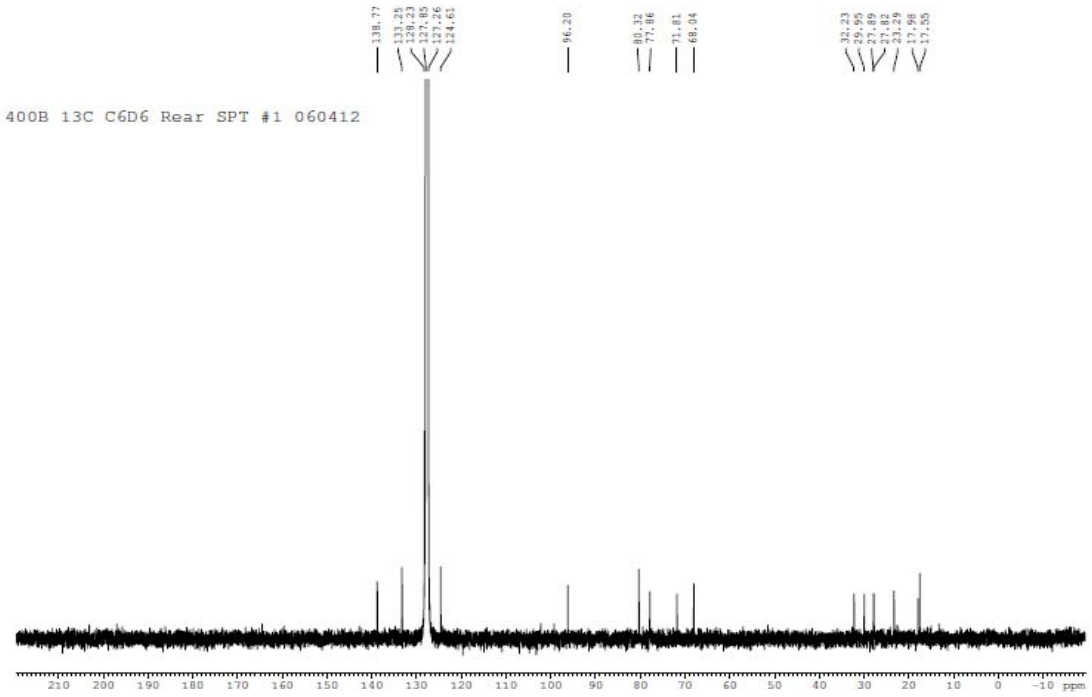


15

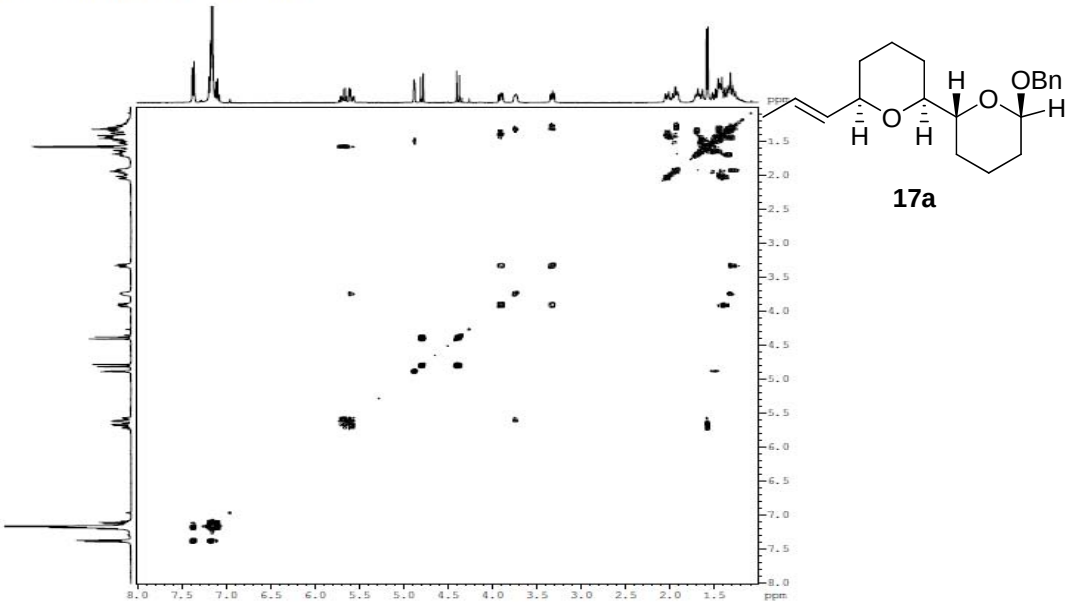

400B 1H CDC13 Grubbs 060112
OH
O
OBn
OBn
16
ppm


400B 13C CDC13 Grubbs 060112
ppm

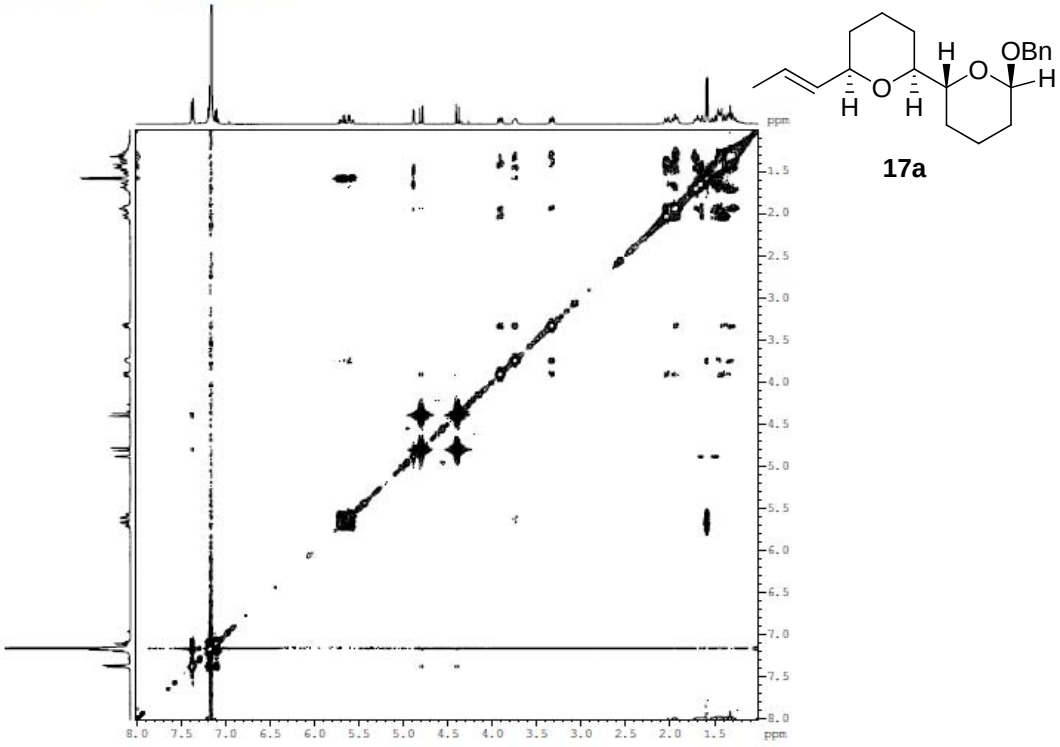

400B 1H C6D6 Rear SPT #1 060412-1
H
OBn
O
O
H
H
H
17a
ppm

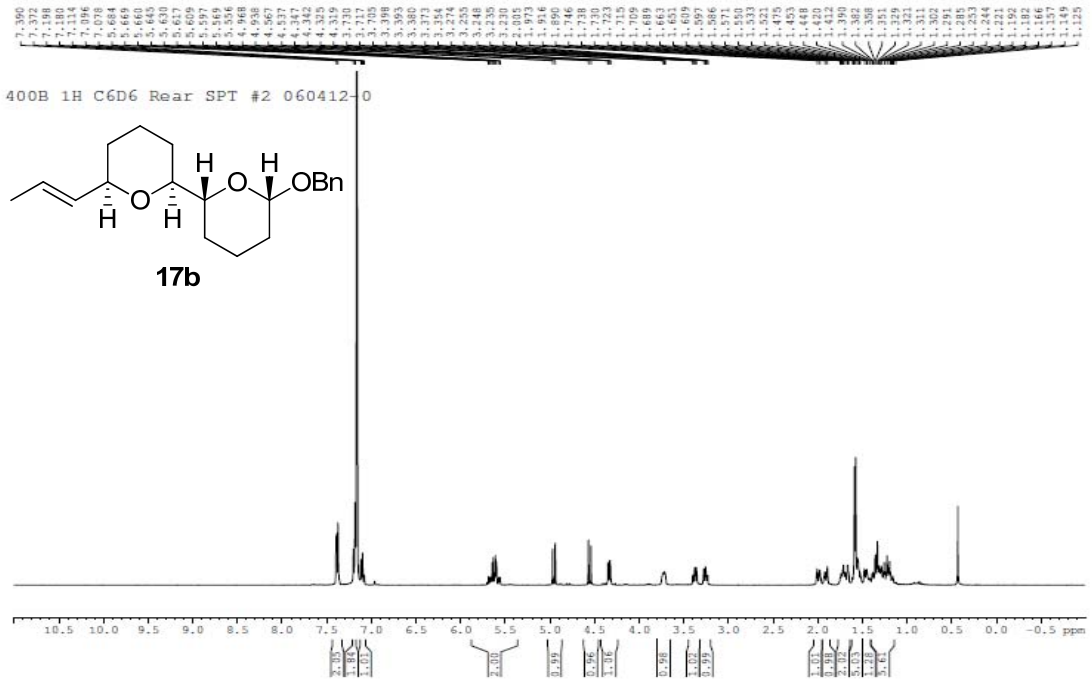

400B 13C C6D6 Rear SPT #1 060412
ppm

400B 1HCOSY C6D6 Rear SPT #1 060412

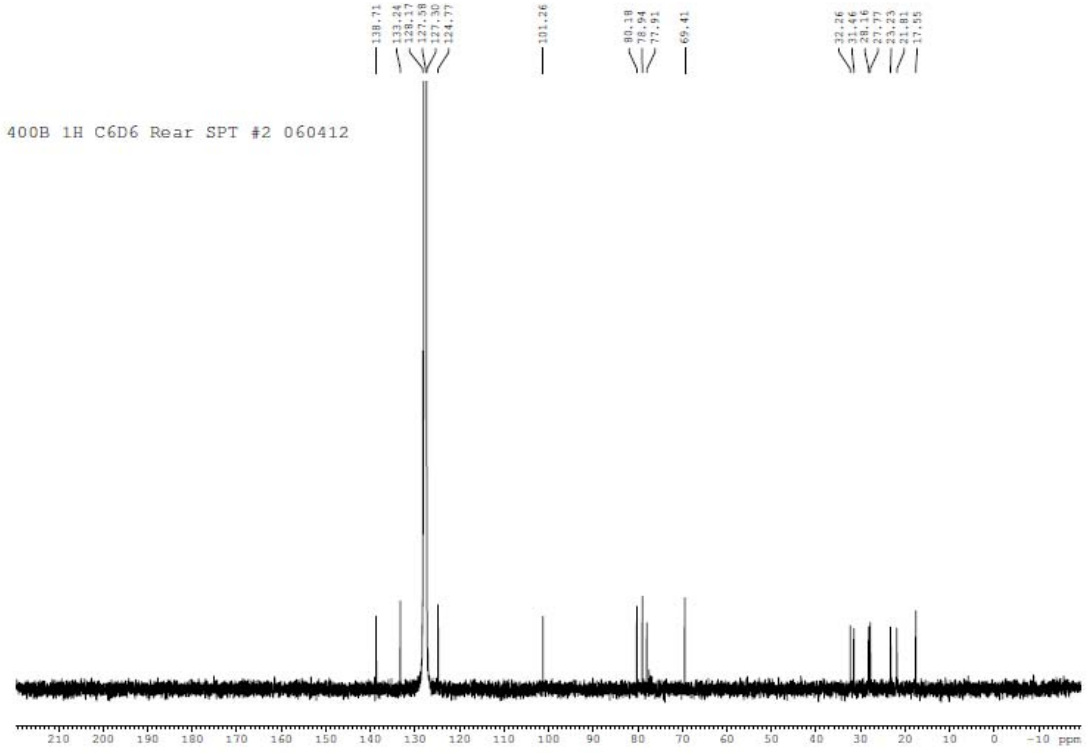


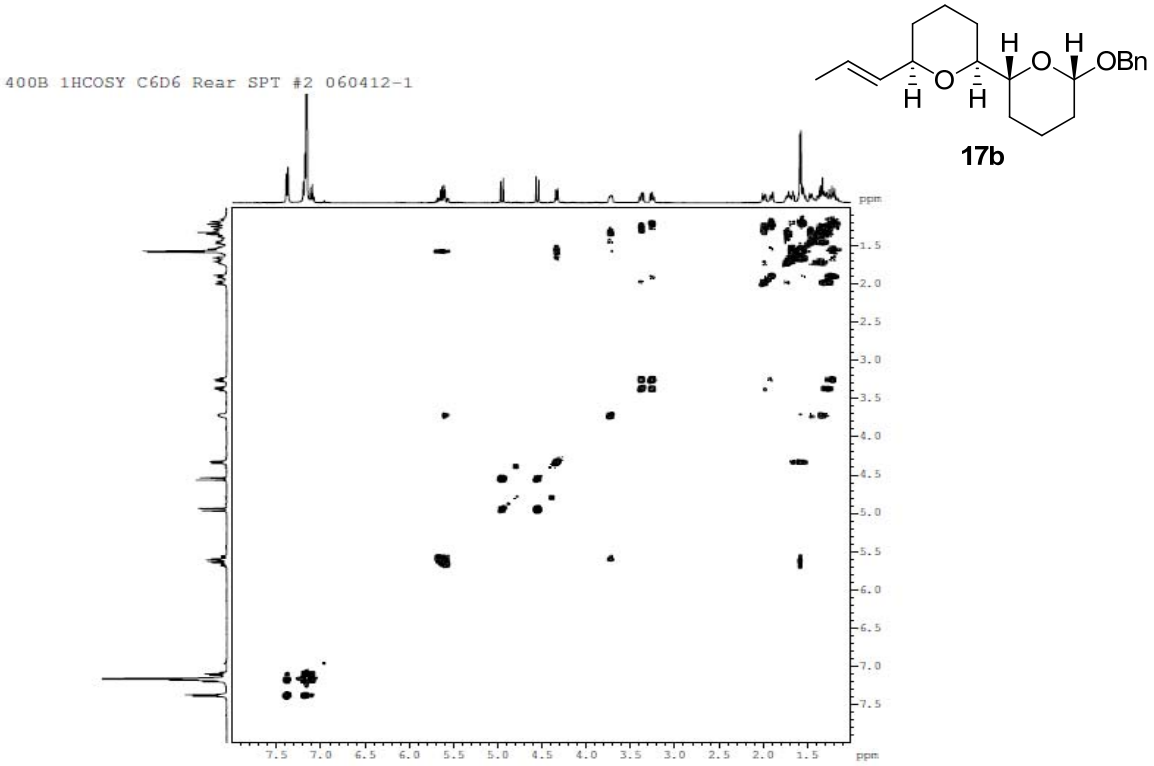
400B 1HNOESY C6D6 Rear SPT #1 060412



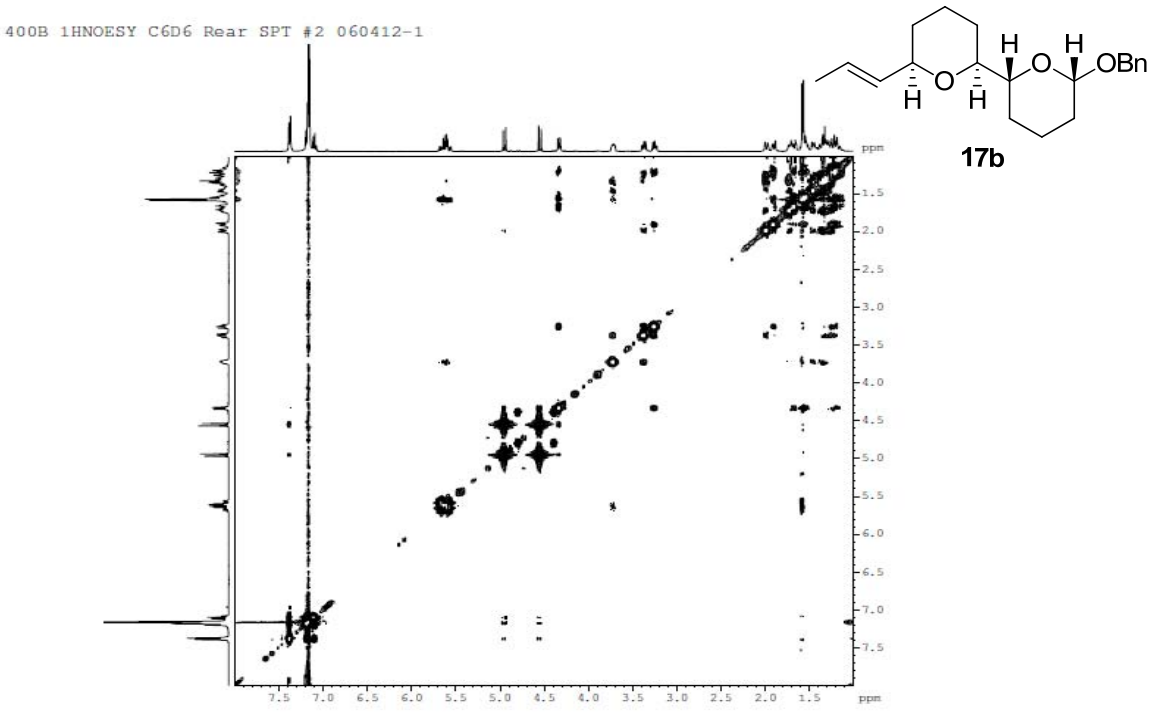

400B 1H C6D6 Rear SPT #2 060412-0
H
O
H
OBn
O
H
H

17b


400B 1H C6D6 Rear SPT #2 060412

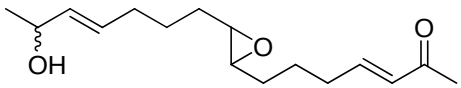

400B 1HCOSY C6D6 Rear SPT #2 060412-1
H
H
O
OBn
H
O
H

17b

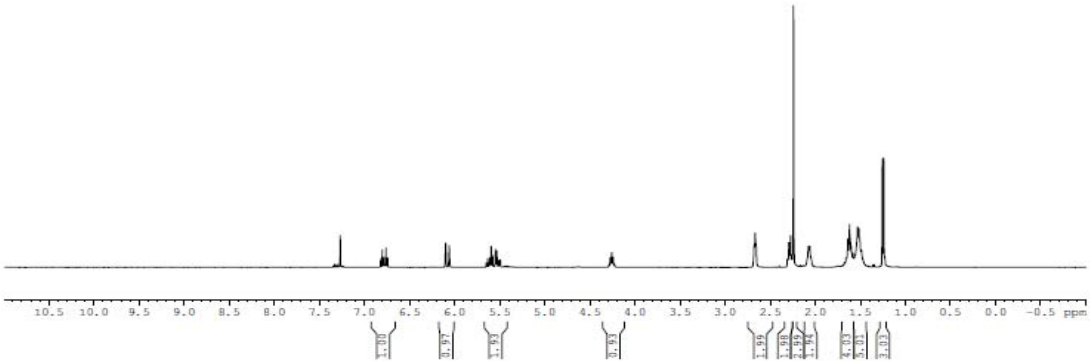

400B 1HNOESY C6D6 Rear SPT #2 060412-1
H
H
O
OBn
H
O
H

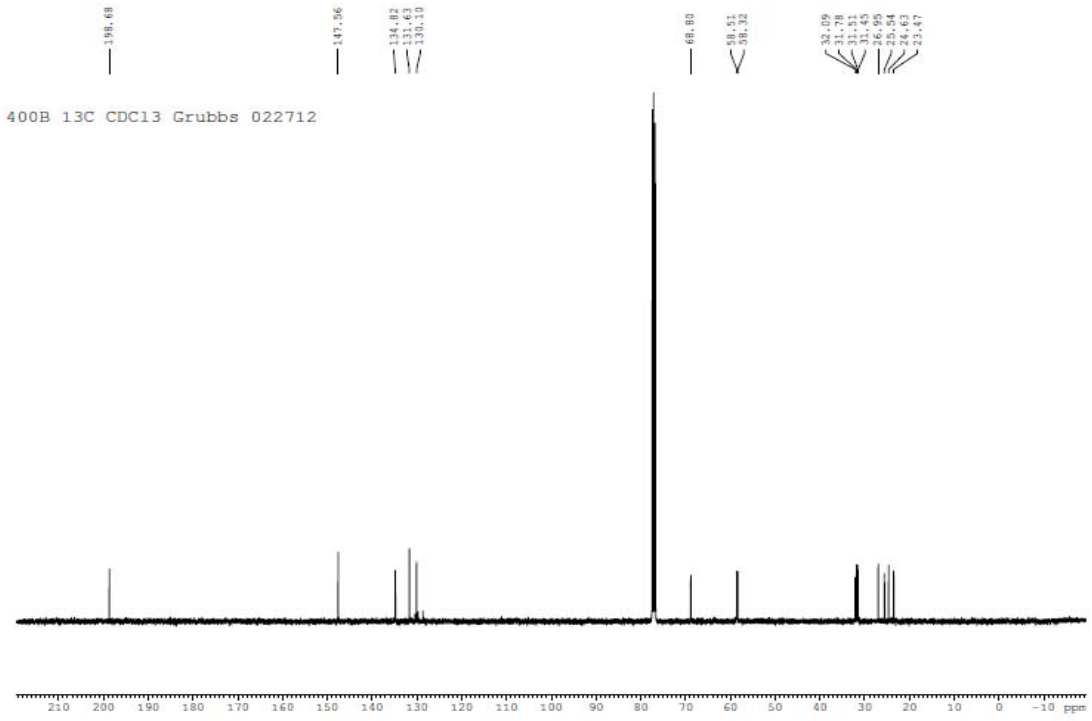
17b

400B 1H CDCl3 Grubbs 022712

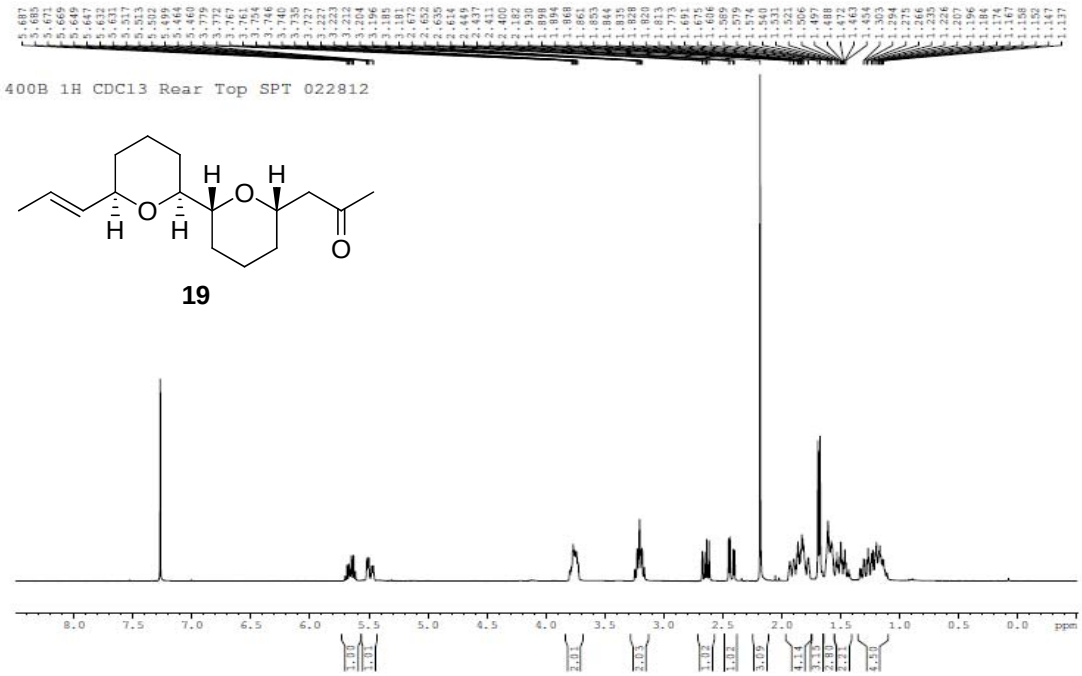


18

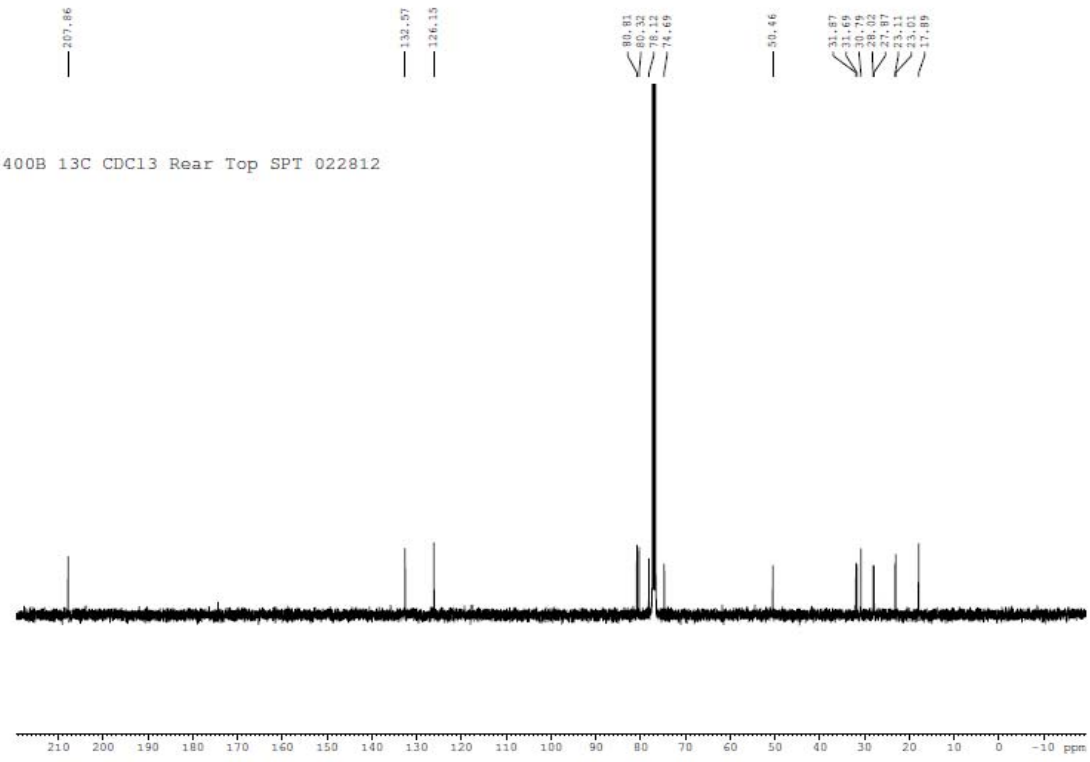


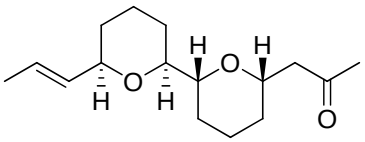


400B 13C CDCl3 Grubbs 022712

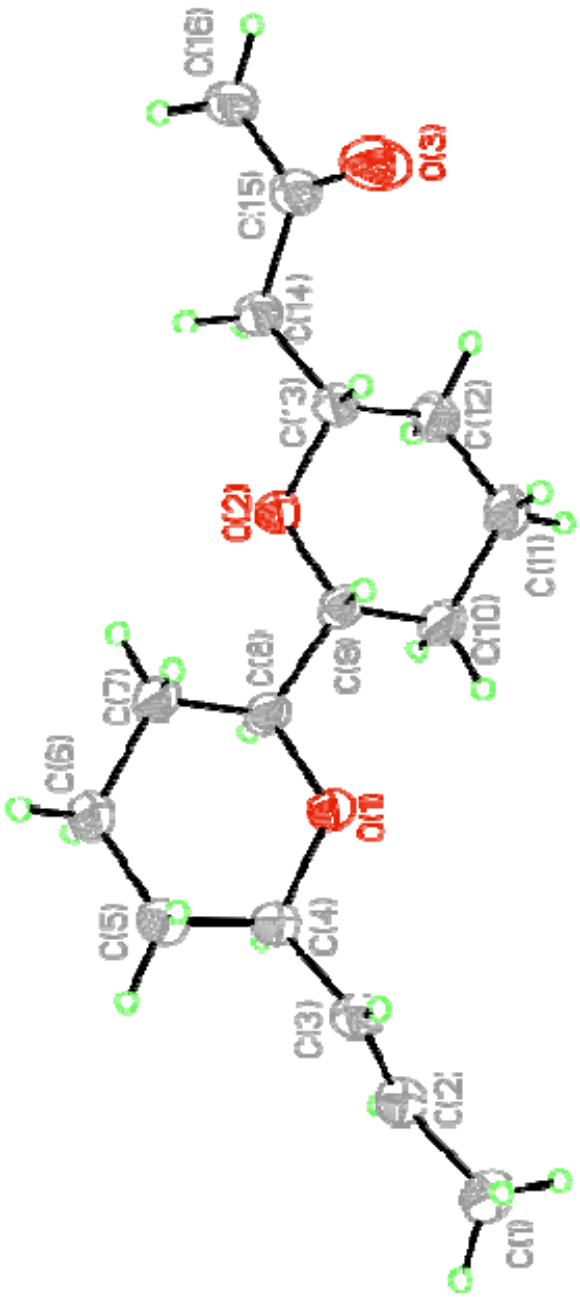

400B 1H CDC13 Rear Top SPT 022812
H
O
H
H
O
H
O

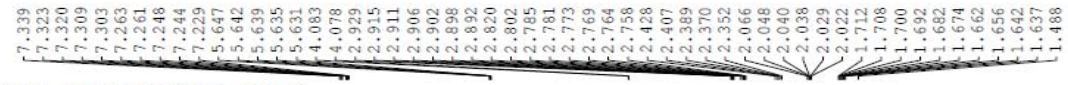
19


207.86
132.57
126.15
80.81
80.32
78.12
74.69
50.46
31.87
31.69
30.99
30.02
27.87
23.11
23.01
17.89
400B 13C CDC13 Rear Top SPT 022812

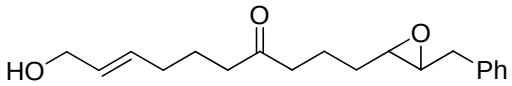


19

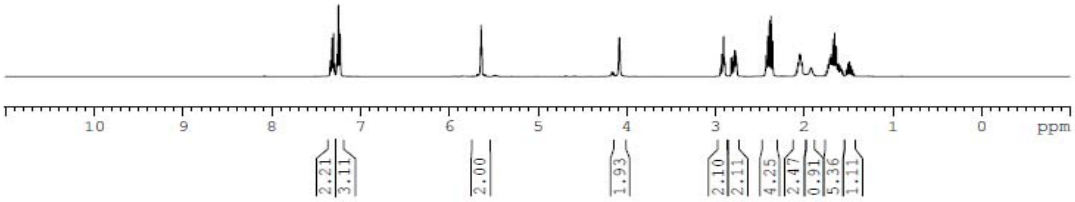




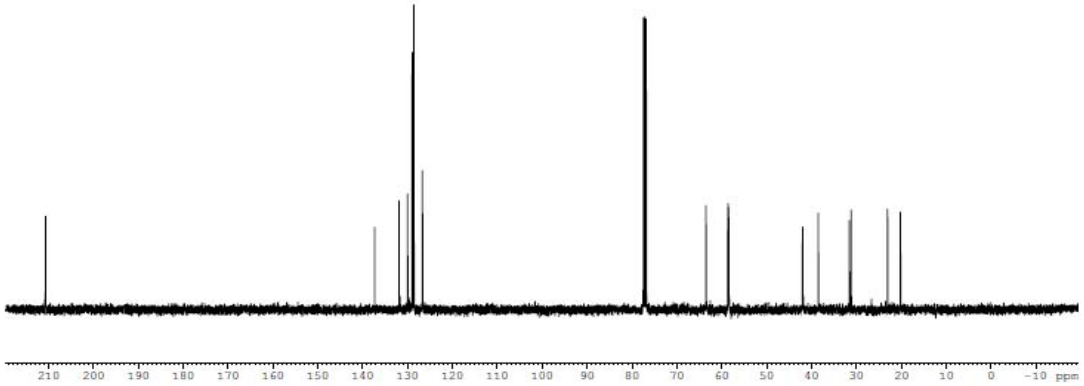
400B 1H CDC13 Grubbs 060612



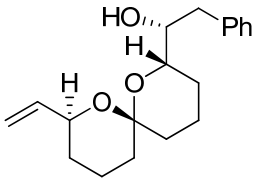
20



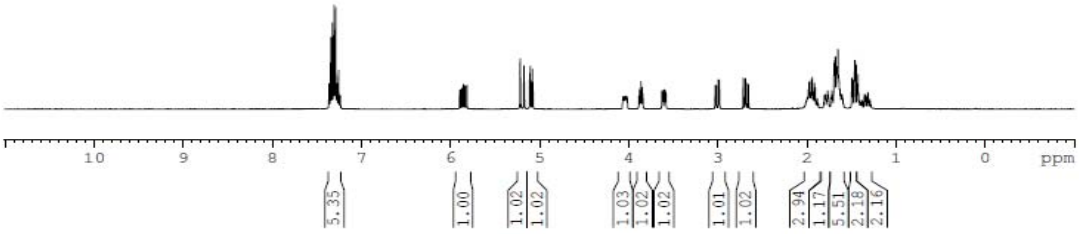
400B 13C CDC13 Grubbs 060612

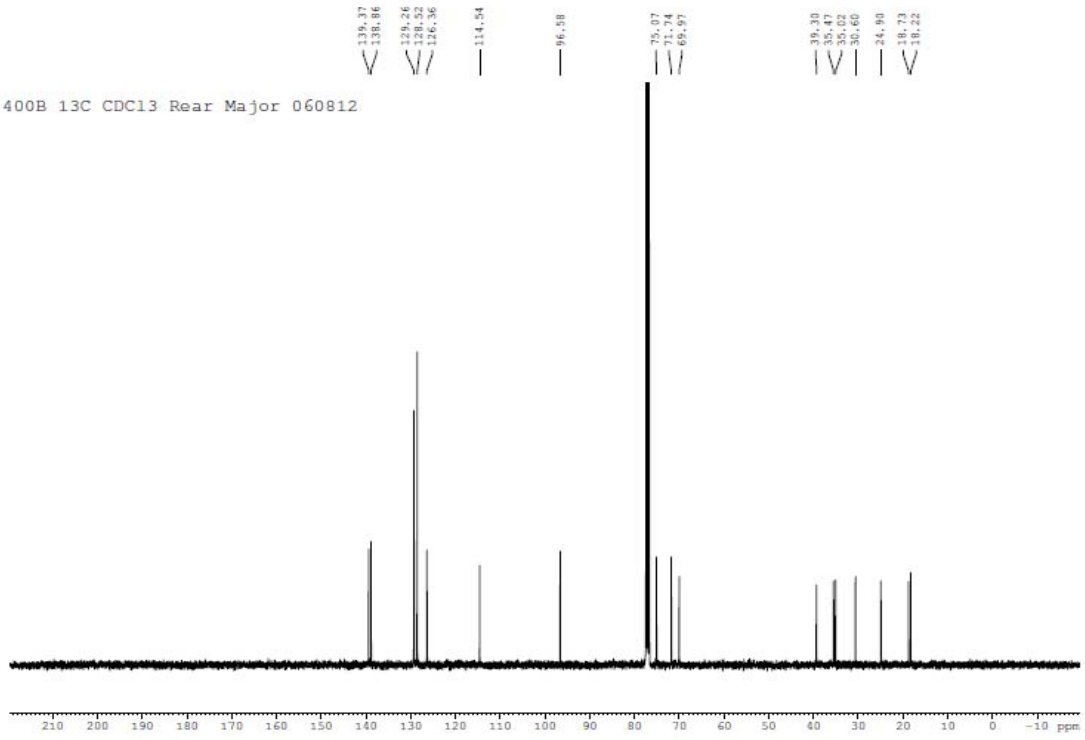


400B 1H CDCl3 Rear Major 060812

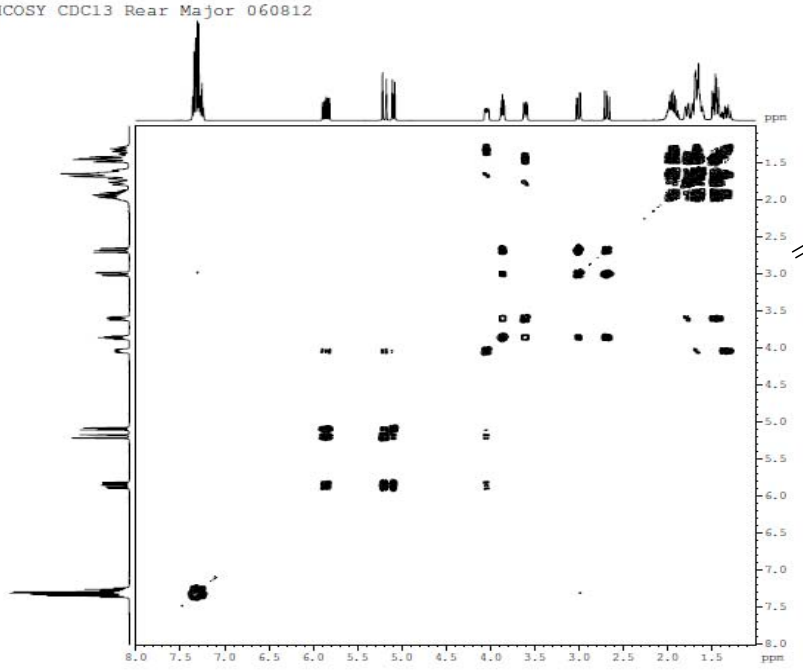


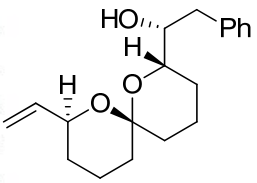
21





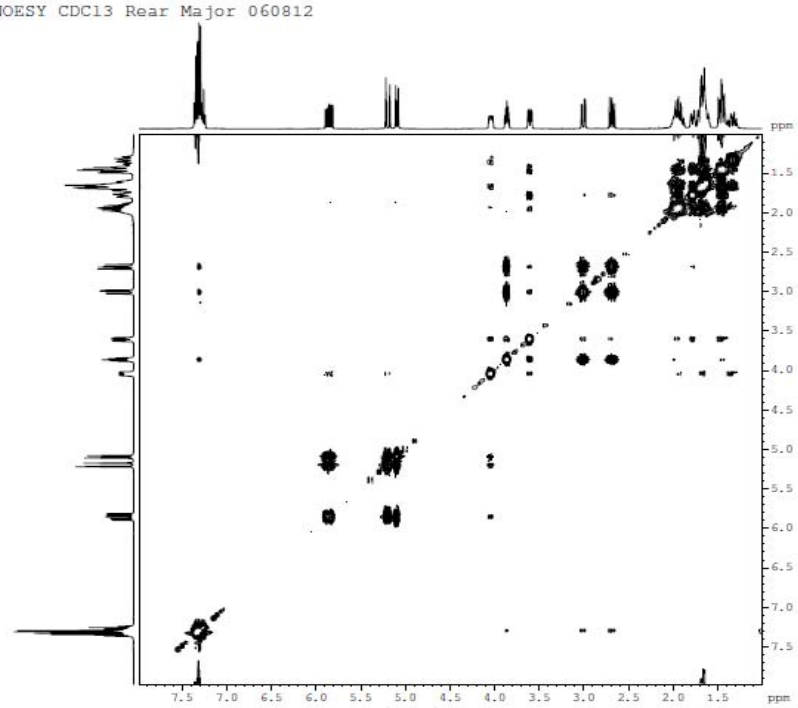
400B 1HCOSY CDCl3 Rear Major 060812

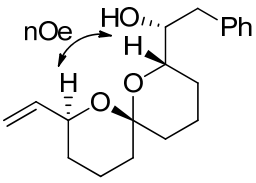




21

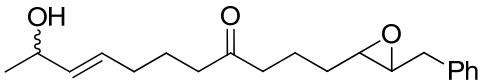
400B 1HNOESY CDCl3 Rear Major 060812



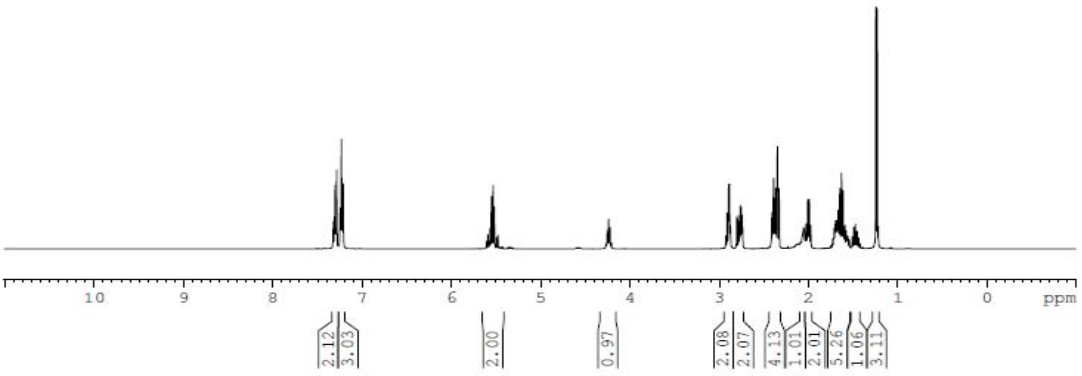


21

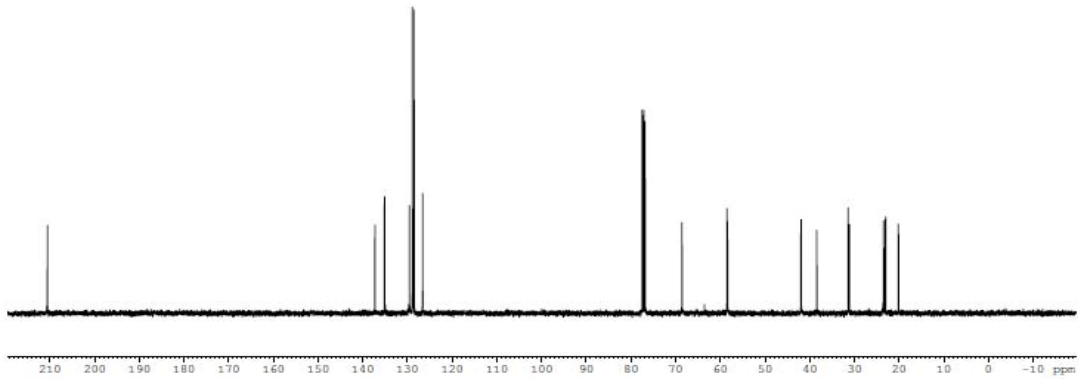
400B 1H CDCl3 Grubbs 052812



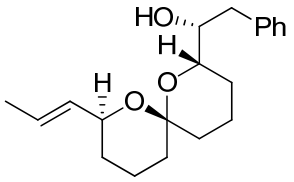
25



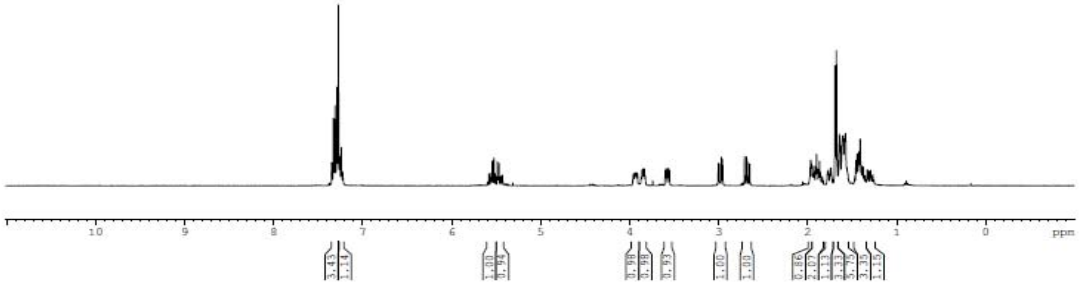
400B 13C CDCl3 Grubbs 052812

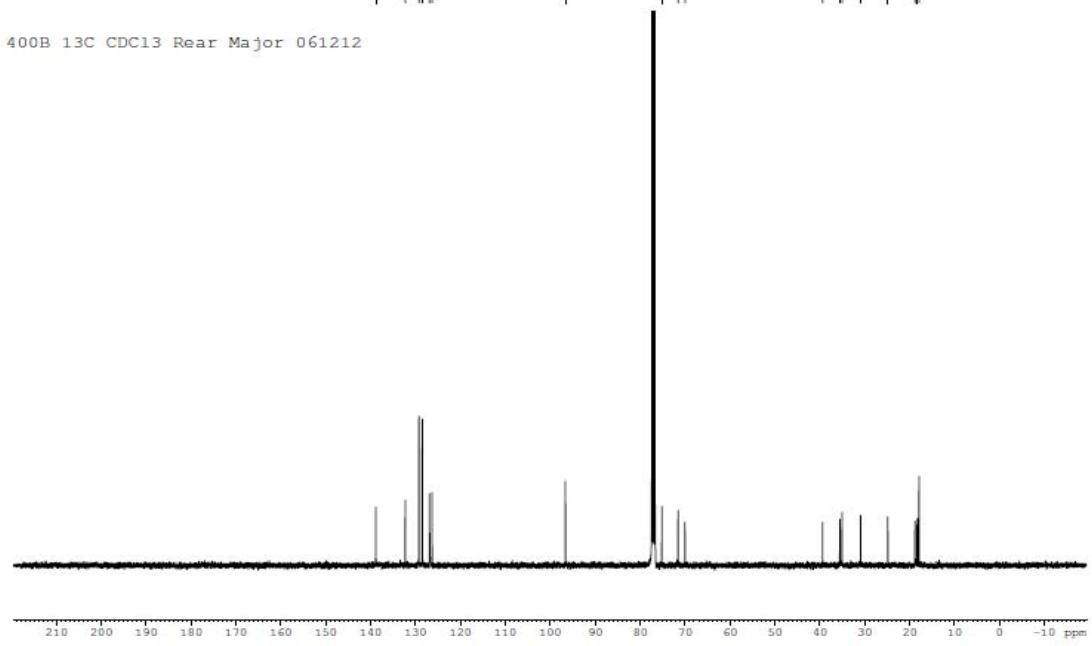


400B 1H CDC13 Rear Major 061212



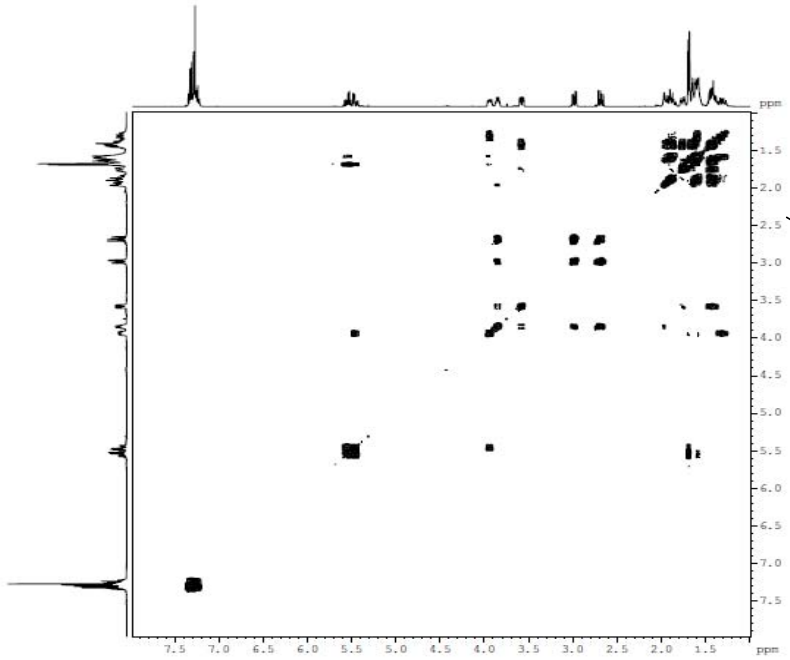
26

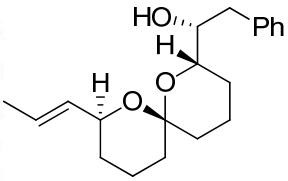




400B 13C CDC13 Rear Major 061212

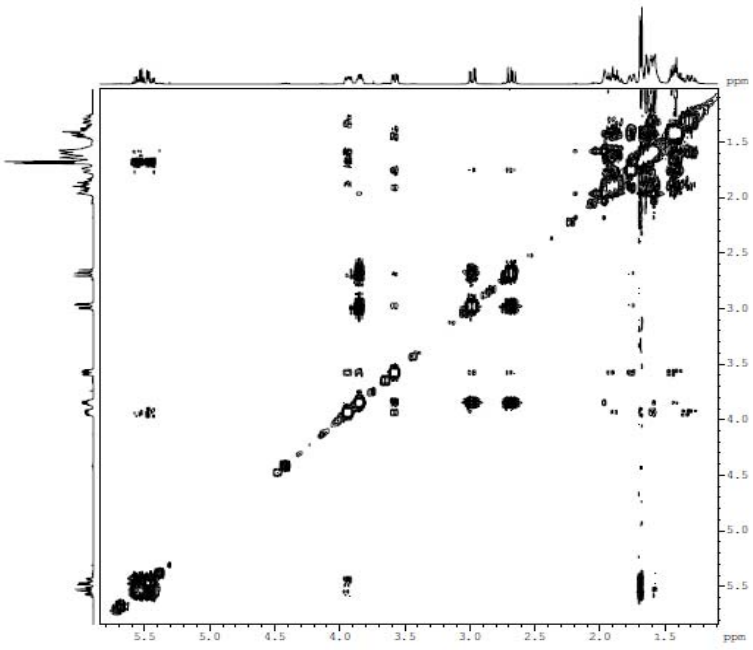
400B 1HCOSY CDCl3 Rear Major 061212

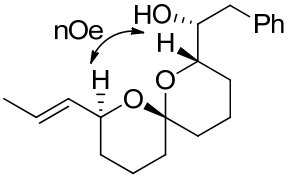




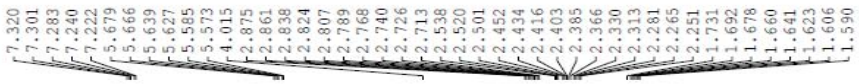
26

400B 1HNOESY CDCl3 Rear Major 061212

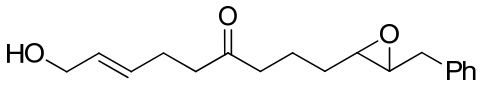




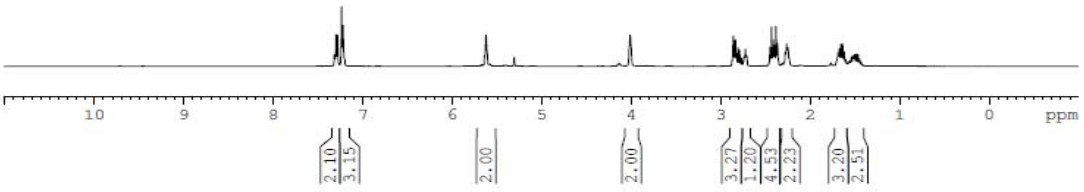
26



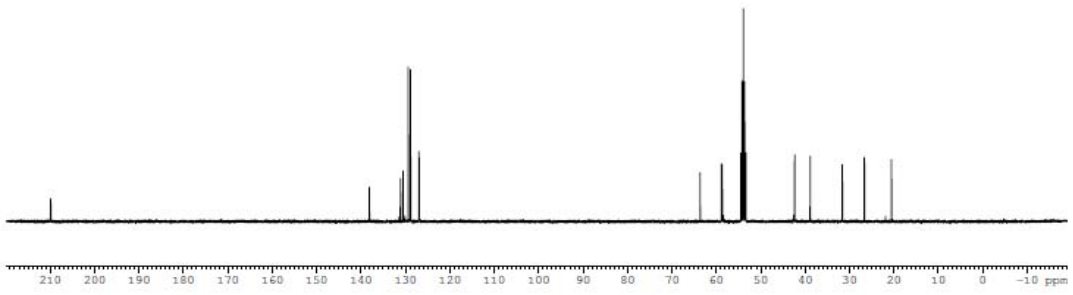
400A 1H CD2Cl2 Grubbs 062912

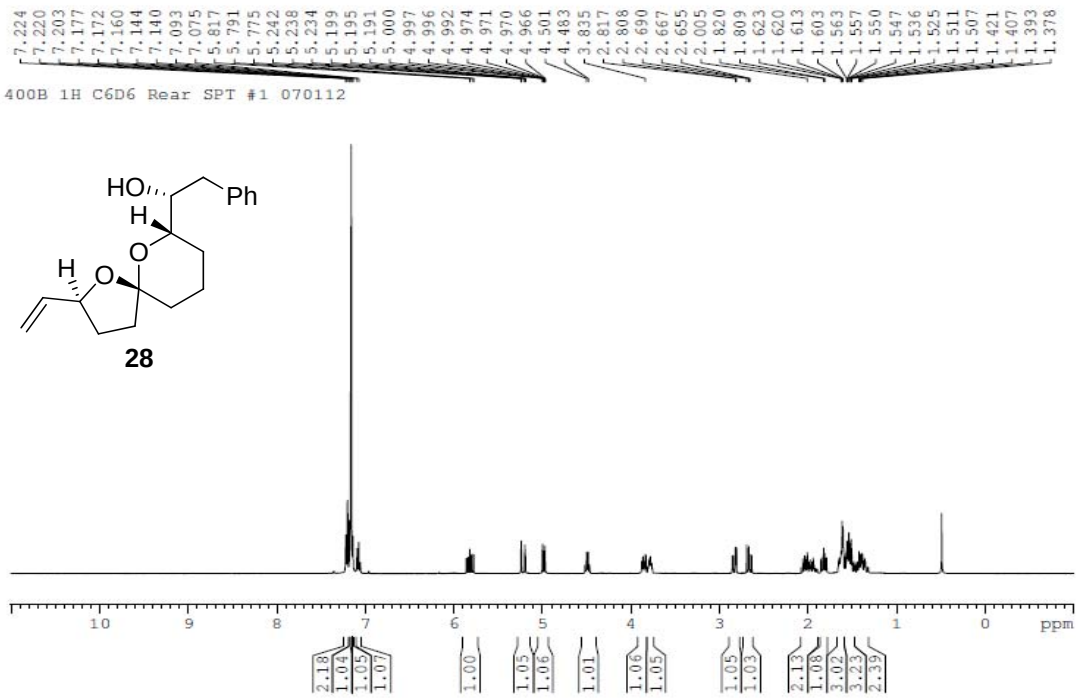


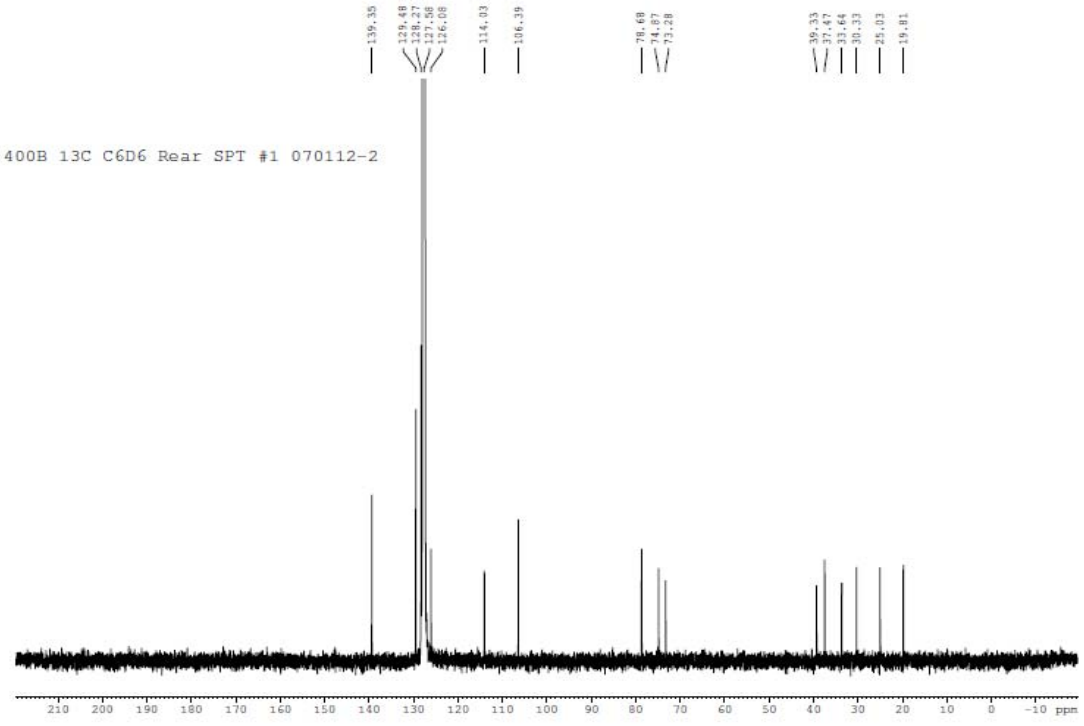
27



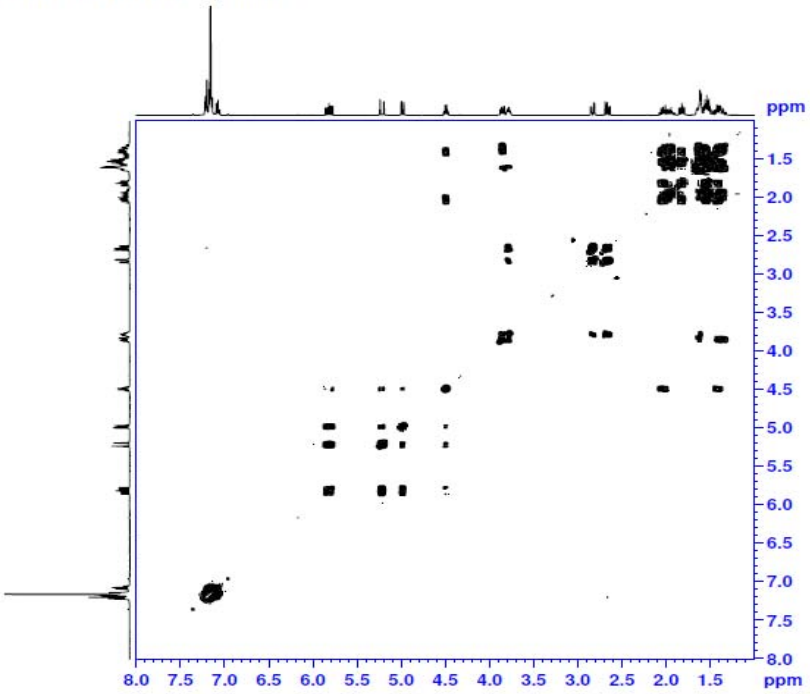
400A 13C CD2Cl2 Grubbs 062912

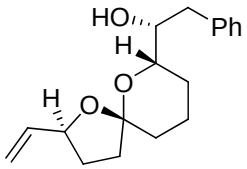



7.224
7.220
7.203
7.177
7.172
7.160
7.144
7.140
7.093
7.075
5.817
5.791
5.775
5.242
5.238
5.234
5.199
5.195
5.191
5.000
4.997
4.996
4.992
4.974
4.971
4.970
4.966
4.501
4.483
3.835
2.817
2.808
2.690
2.667
2.655
2.005
1.820
1.809
1.623
1.620
1.613
1.603
1.563
1.557
1.550
1.547
1.536
1.525
1.511
1.507
1.421
1.407
1.393
1.378
400B 1H C6D6 Rear SPT #1 070112
HO
Ph
H
O
H
O
28
10
9
8
7
6
5
4
3
2
1
0
ppm
2.18
1.04
1.05
1.07
1.00
1.05
1.06
1.01
1.06
1.05
1.05
1.03
2.13
1.08
3.02
3.23
2.39


139.35
129.48
128.27
127.56
126.08
114.03
106.39
78.68
74.87
73.28
39.33
37.47
33.64
30.33
25.03
19.81
400B 13C C6D6 Rear SPT #1 070112-2
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

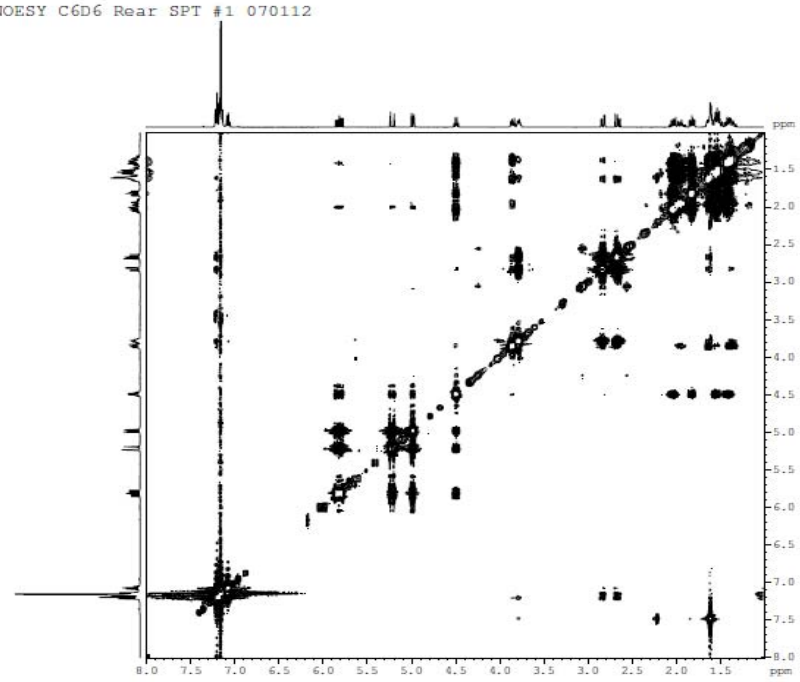
400B 1HCOSY C6D6 Rear SPT #1 070112

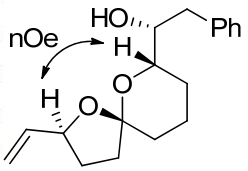




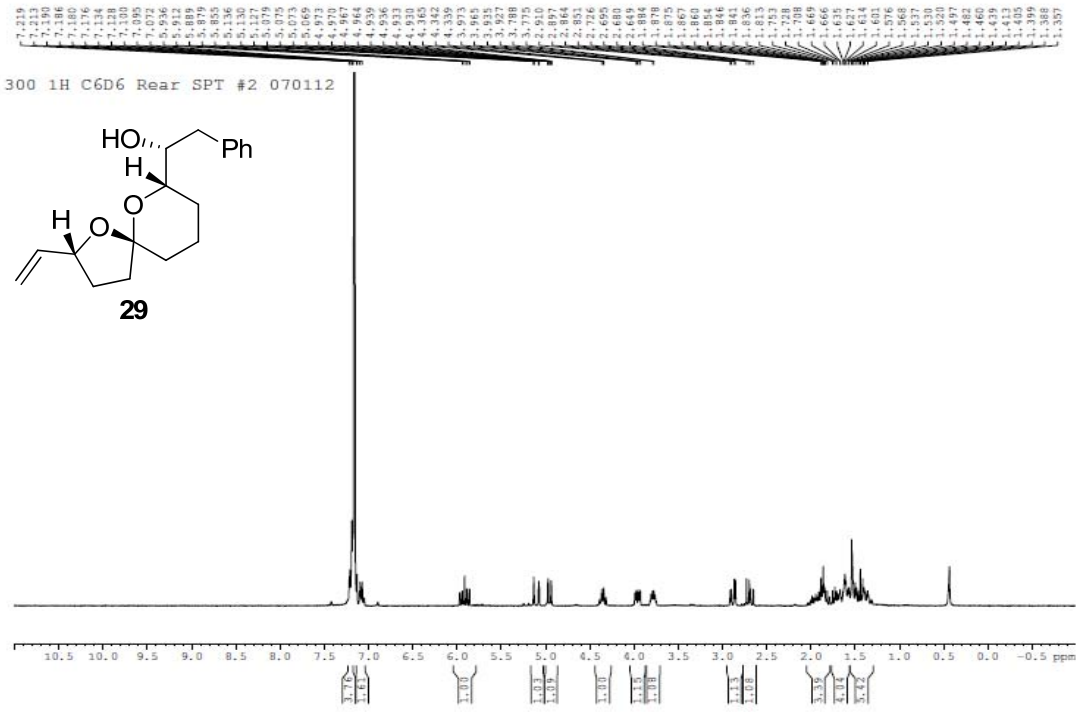
28

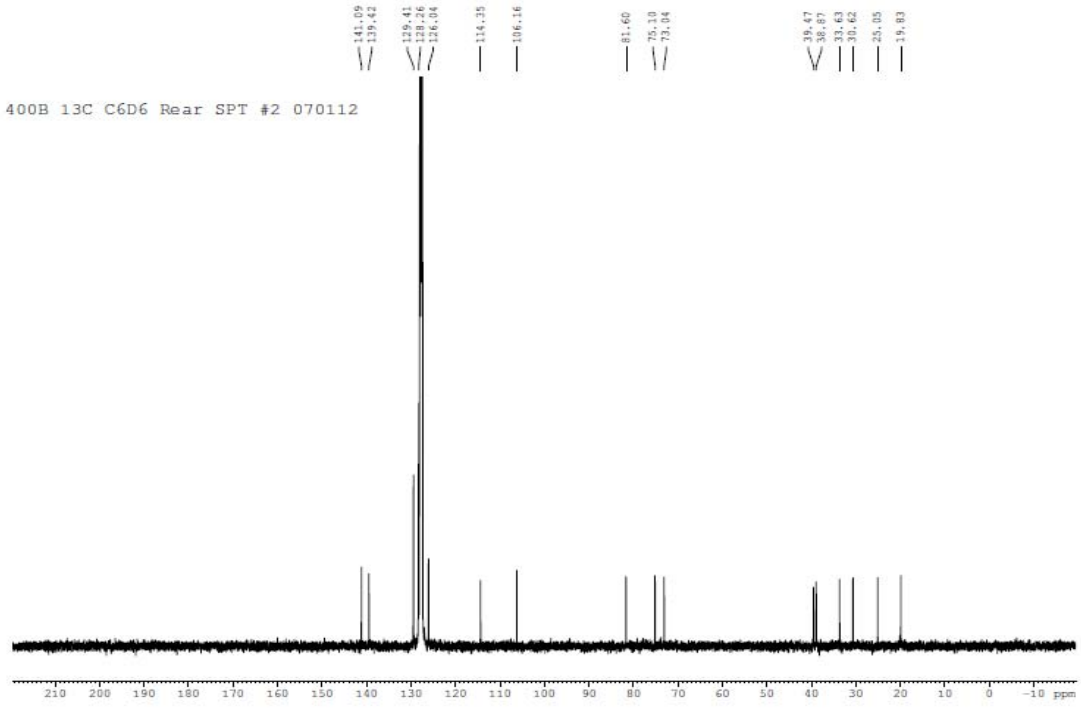
400B 1HNOESY C6D6 Rear SPT #1 070112



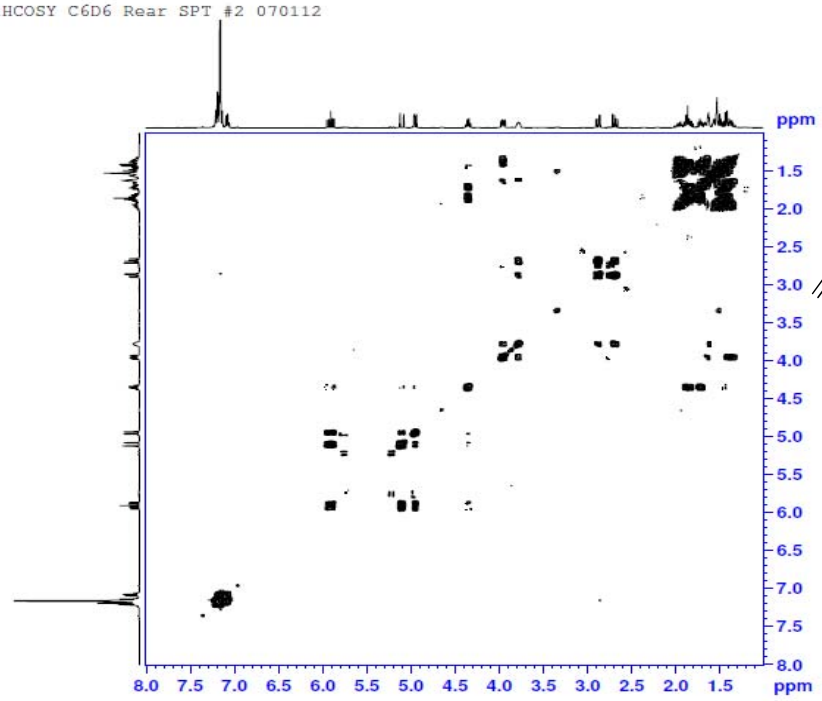


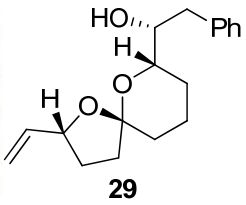
28


300 1H C6D6 Rear SPT #2 070112
HO
H
Ph
O
H
O
29


400B 13C C6D6 Rear SPT #2 070112

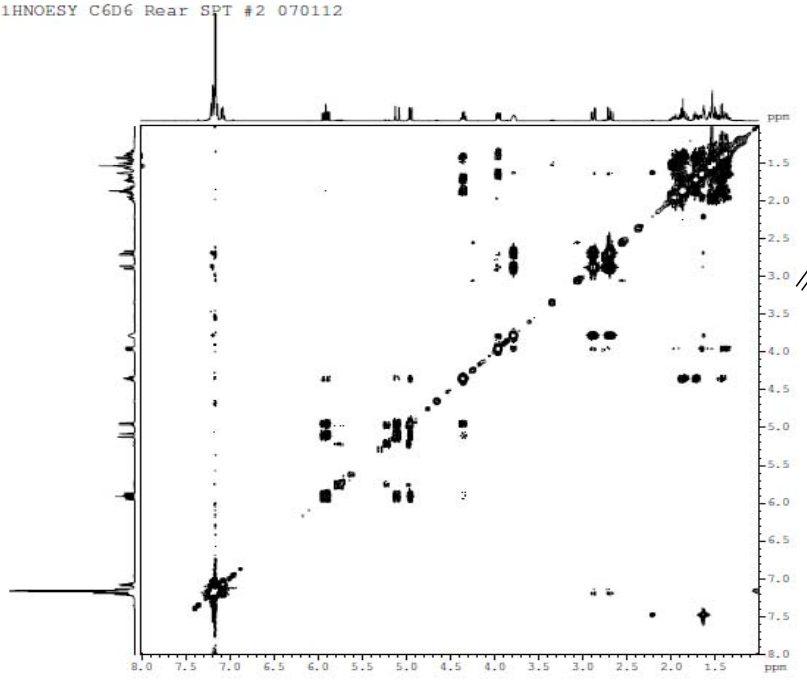
400B 1HCOSY C6D6 Rear SPT #2 070112

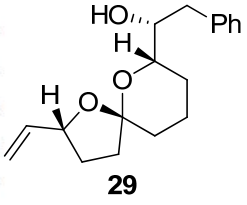




29

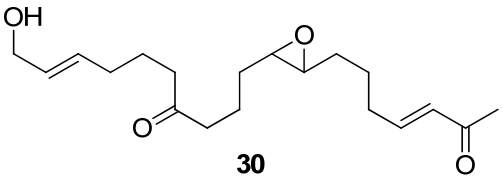
400B 1HNOESY C6D6 Rear SPT #2 070112



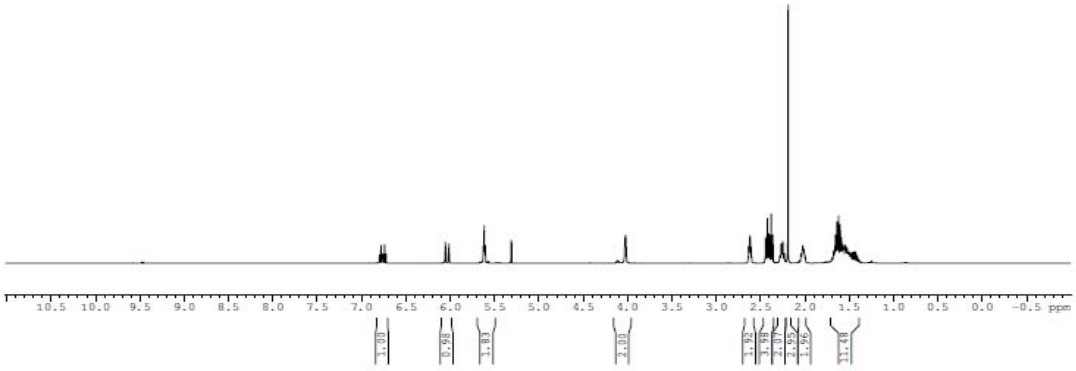


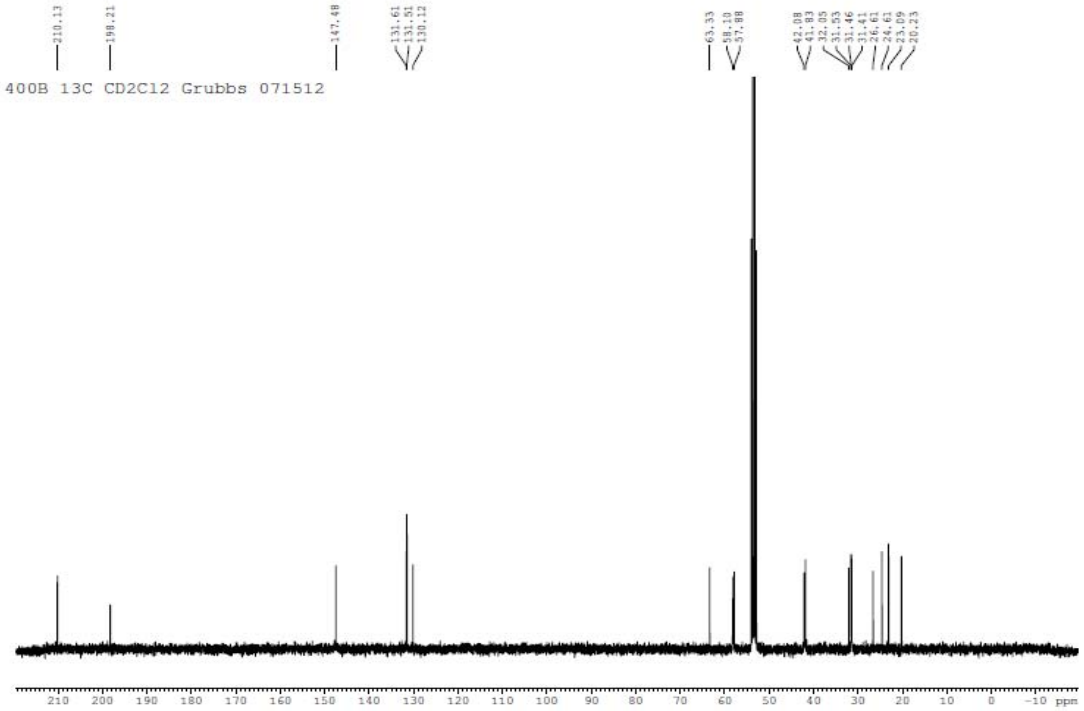
29

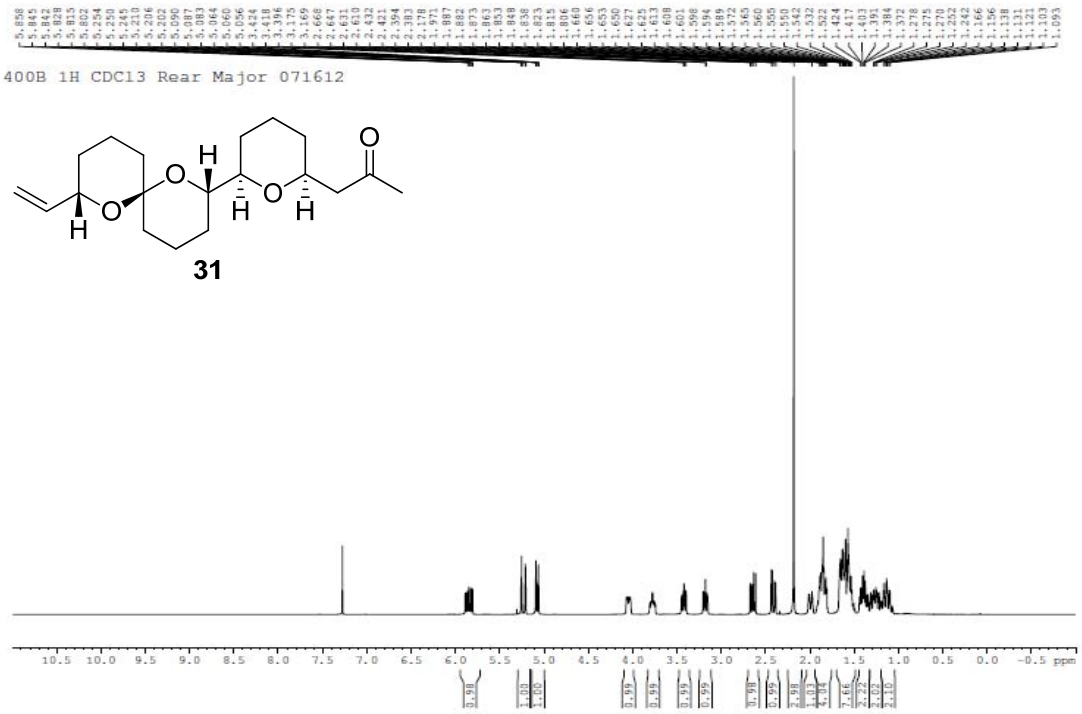

400B 1H CD2Cl2 Grubbs 071512

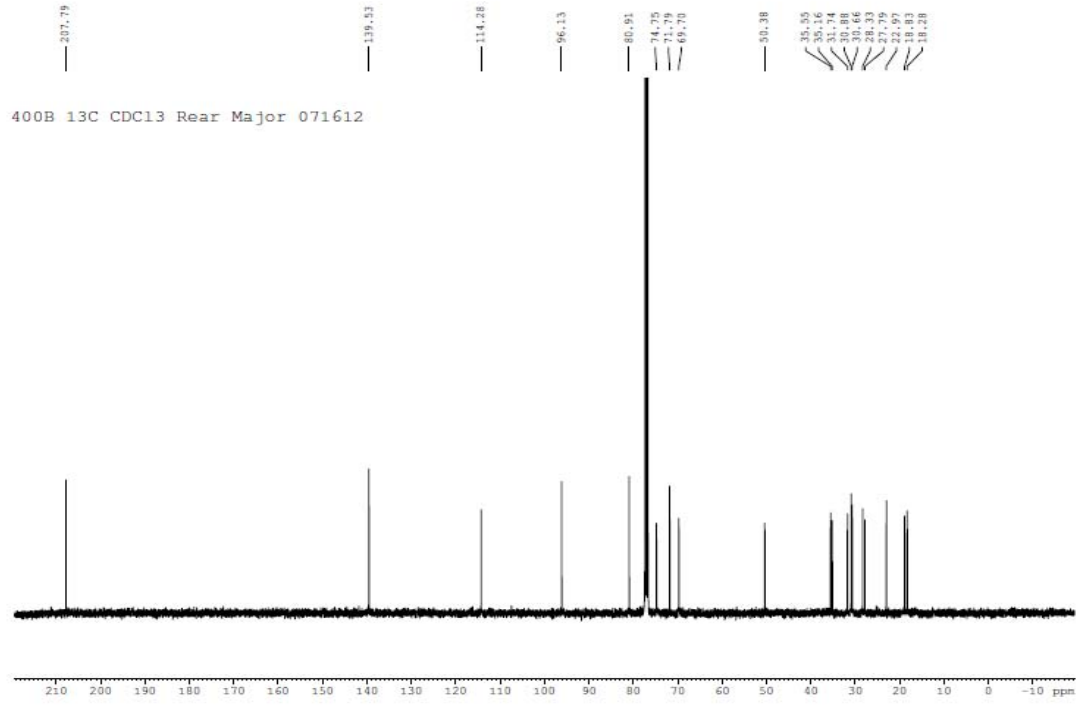

OH
O
O
O

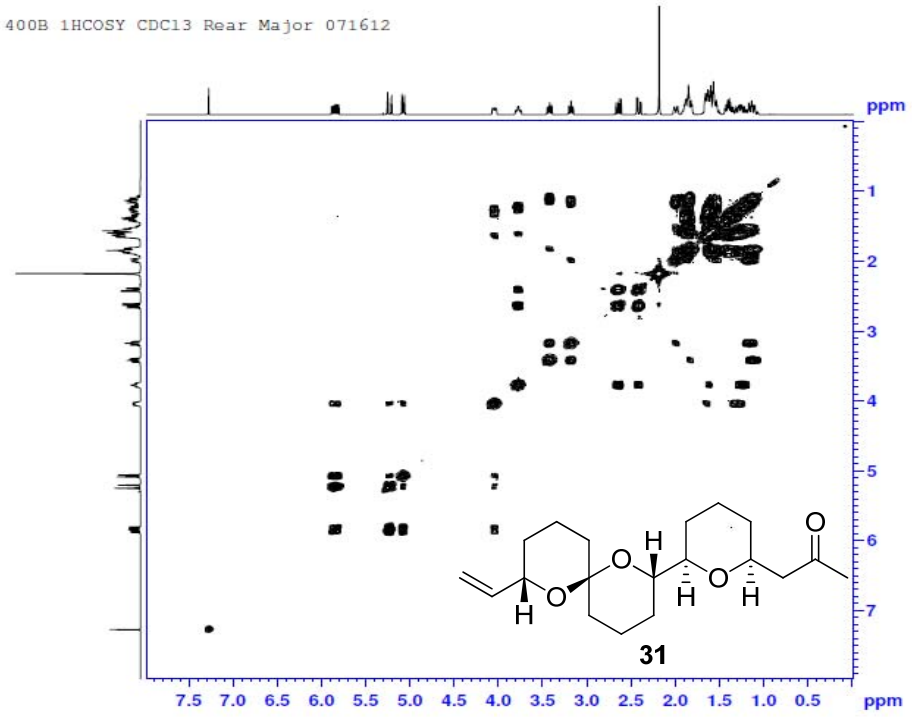
30

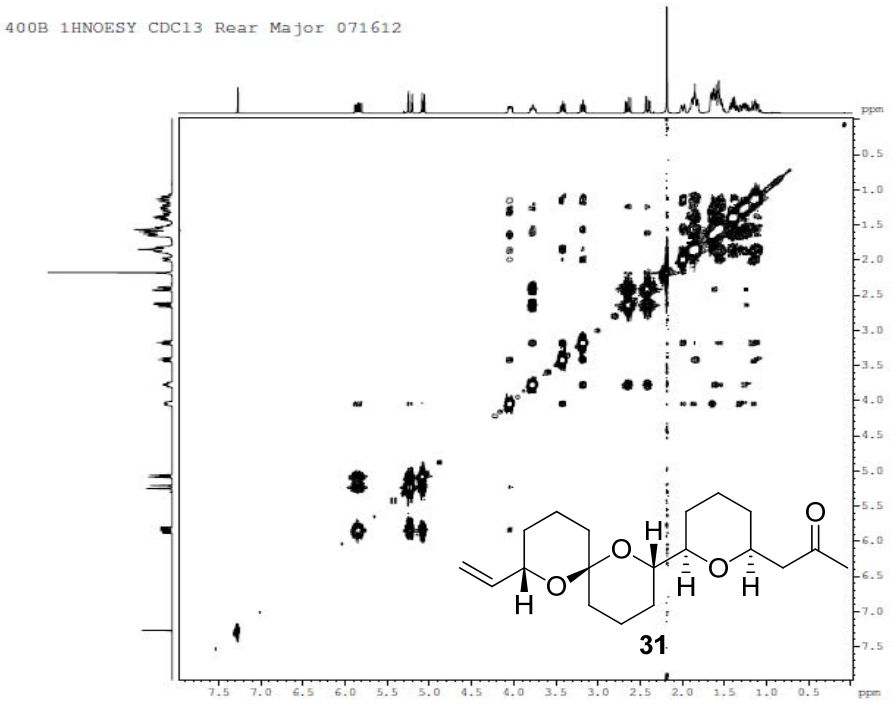

10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 ppm
1.00
0.98
1.03
2.00
1.92
3.08
2.07
2.05
1.96
11.48


210.13
198.21
147.48
131.61
131.51
130.12
63.33
58.10
57.88
42.08
41.83
32.05
31.53
31.46
31.41
26.61
24.61
23.99
20.23
400B 13C CD2Cl2 Grubbs 071512
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm


400B 1H CDC13 Rear Major 071612
O
H
O
O
H
H
O
H
31


207.79
139.53
114.28
96.13
80.91
74.75
71.79
69.70
50.38
35.55
35.16
31.74
30.88
30.66
30.33
29.79
27.97
22.97
18.83
18.28
400B 13C CDC13 Rear Major 071612


400B 1HCOSY CDC13 Rear Major 071612
ppm
1
2
3
4
5
6
7
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm
O
H
O
H
O
H
H
O
31


400B 1HNOESY CDC13 Rear Major 071612
ppm
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm
O
H
O
H
O
H
H
O
31