Supporting Information

Re_2O_7-Catalyzed Approach to Spirocyclic Ether Formation from Acyclic Precursors: Observation of Remote Stereoinduction

Cephas Afeke, Youwei Xie, and Paul E. Floreancig*

Department of Chemistry
University of Pittsburgh
Pittsburgh, Pennsylvania 15260

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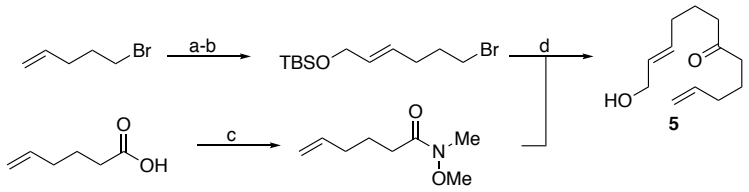
General Information

All reactions were performed in dry solvents under argon atmosphere using dried glassware unless otherwise specified. Dichloromethane was distilled over CaH_2 whereas diethyl ether and tetrahydrofuran solvents were distilled over sodium and benzophenone before use. Flash column chromatography with 60 Å silica gel and reagent grade ethyl acetate, hexanes, diethyl ether or pentanes as eluent was performed to purify all synthetic compounds. Analytical TLC was performed on E. Merck pre-coated (25 mm) silica gel 60 F_{-254} plates and visualized under UV (254 nm). High resolution and low-resolution mass spectra were collected on a VG 7070 spectrometer. IR spectra were obtained on a PerkinElmer FT-IR UATR spectrometer. ^{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 and a Bruker Avance 600 MHz and 150 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: $CDCl_3$ = 7.26 ppm, CD_2Cl_2 = 5.31 ppm, C_6D_6 = 7.16 ppm, for ^{13}C NMR: $CDCl_3$ = 77.2 ppm. Data are reported as follows: m = multiplet, s = singlet, d = doublet, t = triplet, q = quartet, pent = pentet, dd = doublet of doublets, dt = doublet of triplets, sext = sextet, sept = septet, oct = octet, dq = doublet of quartet, dp = doublet of pentet, ddd = doublet of doublet of doublets, ddt = doublet of doublet of triplets, tt = triplet of triplets, br = broad.

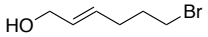
General Procedure for Re_2O_7-catalyzed spirocycle formation

To a solution of substrate (0.1 - 0.2 mmol) in DCM (0.5 – 1.5 mL), stirring at rt (unless otherwise noted), was added Re_2O_7 (3-6 mol %). The mixture was stirred until the substrate was consumed. The reaction mixture was quenched with a few drops of pyridine, concentrated *in vacuo* and purified via flash column chromatography with 0 – 10% ethyl acetate in hexanes as eluent in gradient elution.



Reagents and conditions
a) *cis*-2-Butene-1,4-diol, Grubbs-Hoveyda second generation catalyst, CH_2Cl_2, 38%.
b) TBSCl, imidazole, DMAP, CH_2Cl_2, 89%. c) MeON(Me)•HCl, DCC, Et_3N, DMAP, CH_2Cl_2, 87%. d) *t*BuLi, Et_2O, –78 °C, then Weinreb amide, then 2N aqueous HCl, 40%.

Scheme 1. Preparation of **5**.



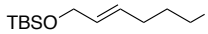
(*E*)-6-Bromohex-2-en-1-ol

To a solution of *cis*-2-butene-1,4-diol (3.54 g, 40.2 mmol) and 5-bromo-1-pentene (3.0 g, 20.1 mmol) in DCM (10.0 mL), was added Hoveyda-Grubbs II catalyst (40 mg, 0.064 mmol). The reaction was stirred at rt for 16 h. The reaction mixture was concentrated *in vacuo* and purified via flash column chromatography with 40% hexanes in ethyl acetate to yield the desired compound as a brown oil (1.38 g, 38.4%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 5.60-5.75 (m, 2H), 4.09 (d, J = 4.3 Hz, 2H), 3.41 (t, J = 6.7 Hz, 2H), 2.18-2.30 (m, 2H), 1.90-1.99 (m, 2H)

^{13}C NMR (75 MHz, $CDCl_3$): δ 130.7, 130.5, 63.5, 33.1, 32.0, 30.5

HRMS (ESI): *m/z* calcd for $C_6H_{10}BrO$ $[M–H]^-$ 176.9915, found 176.9816.



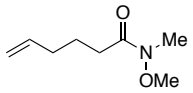
(*E*)-((6-Bromohex-2-en-1-yl)oxy)(*tert*-butyl)dimethylsilane

To a solution of the allylic alcohol (1.68 g, 9.38 mmol) and *tert*-butyldimethylsilyl chloride (2.83 g, 18.8 mmol) in DCM (50 mL) was added imidazole (1.92 g, 28.1 mmol) and DMAP (0.12 g, 0.94 mmol). The reaction was stirred at rt for 3 h. The reaction was quenched with water and extracted with DCM, concentrated *in vacuo* and purified via flash column chromatograpy with 10% ethyl acetate in hexanes to yield 2.46 g (89%) of the product as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 5.54-5.66 (m, 2H), 4.12 (d, J = 1.1 Hz, 2H), 3.40 (t, J = 6.7 Hz, 2H), 2.12-2.22 (m, 2H), 1.93 (pent, J = 6.8 Hz, 2H), 0.90 (s, 9H), 0.06 (s, 6H)

^{13}C NMR (75 MHz, $CDCl_3$): δ 130.8, 128.7, 63.7, 33.1, 32.1, 30.5, 26.0, 18.4, –5.1

HRMS (ESI): *m/z* calcd for $C_{12}H_{24}OSiBr$ $[M–H]^-$ 291.0780, found 291.0827.



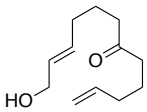
_N_-Methoxy-_N_-methylhex-5-enamide

To a solution of 5-hexenoic acid (1.8 g, 14.1 mmol) in DCM (45 mL) at 0 °C was added *N,O*-dimethylhydroxylamine hydrochloride (1.65 g, 16.9 mmol), DCC (3.48 g, 16.9 mmol), DMAP (0.21 g, 1.69 mmol) and triethylamine (1.71 g, 16.9 mmol). The reaction was stirred until starting material was fully consumed. The reaction mixture was filtered through Celite, washed with 0.5 N HCl and extracted with DCM after which the crude product was purified via flash column chromatography with 20% ethyl acetate in hexanes and concentrated *in vacuo* to yield the product as a pale-yellow oil (2.09 g, 87.3%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 5.70 (ddt, *J* = 17.1, 10.2, 7.1 Hz, 1H), 4.94 (dd, *J* = 17.2, 1.69 Hz), 4.88 (dd, *J* = 10.2, 1.5 Hz), 3.59 (s, 3H), 3.08 (s, 3H), 2.33 (t, *J* = 7.4 Hz, 2H), 2.02 (dt, *J* = 7.3, 7.0 Hz, 2H), 1.64 (pent, *J* = 7.7 Hz, 2H)

^{13}C NMR (75 MHz, $CDCl_3$): δ 174.3, 138.0, 114.9, 61.1, 33.2, 32.1, 31.0, 23.6

HRMS (ESI) *m/z* calcd for $C_8H_{16}O_2N$ $[M+H]^+$ 158.1181, found 158.1175.



(10*E*)-12-Hydroxydodeca-1,10-dien-6-one (5)

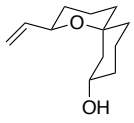
To an oven dried round bottom flask was added the alkyl bromide (1.86 g, 6.4 mmol) and diethyl ether (20 mL), and the solution was stirred at –78 °C. After 1 h of stirring, *tert*-butyllithium solution (1.7 M, 7.50 mL, 12.8 mmol) was added slowly and stirred for 0.25 h after which the Weinreb amide (1.0 g, 6.4 mmol) was added dropwise and stirred for an additional 0.5 h while maintaining the reaction at –78 °C. The reaction mixture was quenched with excess 2N HCl, extracted with diethyl ether, and the crude product purified via chromatography with 20% ethyl acetate in hexanes to yield 0.5 g (40% yield) of the product as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 5.75 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.60-5.68 (m, 2H), 5.00 (dd, *J* = 17.2, 1.2 Hz, 1H), 4.97 (dd, *J* = 10.2, 1.0 Hz, 1H), 4.08 (d, *J* = 3.1 Hz, 2H), 2.39 (t, *J* = 7.4 Hz, 4H), 2.04 (dt, *J* = 6.8, 6.3 Hz, 4H), 1.66 (pent, *J* = 7.4 Hz, 4H)

^{13}C NMR (125 MHz, $CDCl_3$): δ 210.8, 138.0, 132.1, 129.8, 115.2, 63.6, 42.0, 41.9, 33.1, 31.6, 23.1, 22.8

HRMS (ESI): *m/z* calcd for $C_{12}H_{21}O_2$ $[M+H]^+$ 197.1536, found 197.1532

IR (thin film): 3408, 3114, 2930, 1708 1410, 1216, 1088, 970, 912 cm^{-1}



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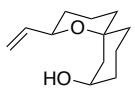

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(2*R*,6*R*,8*R*)-2-Vinyl-1-oxaspiro [5.5]undecan-8-ol (6) and (2*R*,6*R*,8*S*)-2-vinyl-1-oxaspiro[5.5] undecane-8-ol (7)

The general procedure for spirocycle synthesis was followed with **5** (20.0 mg, 0.1 mmol) and Re_2O_7 (3.0 mg, 0.006 mmol) in DCM (1.0 mL) for 25 min at rt after which the crude mixture was purified via flash column chromatography with 10% ethyl acetate in hexanes to give a mixture of **6** and **7** (18.6 mg, 93% yield) with a diastereomeric ratio (d.r.) of 4:1 respectively.

Major (slower-eluting) isomer (6)

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.80 (ddd, *J* = 17.2, 10.5, 5.1 Hz, 1H), 5.20 (dt, *J* = 17.2, 1.6 Hz, 1H), 5.03, (dt, *J* = 10.5, 1.5 Hz, 1H), 4.04 (dt, *J* = 11.0, 5.4 Hz, 1H), 3.74 (tt, *J* = 11.0, 4.2 Hz, 1H), 2.68 (ddt, *J* = 13.5, 4.0, 2.6 Hz, 1H), 1.95 (d, *J* = 13.0 Hz, 1H), 1.71-1.84, (m, 2H), 1.64-1.67 (m, 2H), 1.52-1.58 (m, 2H), 1.36-1.44, (m, 2H), 1.15-1.28 (m, 3H), 0.87 (dd, *J* = 13.2, 10.9 Hz, 1H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 140.1, 114.0, 74.1, 70.1, 67.0, 39.1, 38.3, 36.1, 35.9, 31.4, 19.5, 19.2

HRMS (ESI): *m/z* calcd for $C_{12}H_{21}O_2$ $[M+H]^+$ 197.1536, found 197.1533

IR (thin film): 3399, 2946, 2861 1458 1265, 1020, 735 cm^{-1}

Minor (faster-eluting) isomer (7)

^{1}H NMR (500 MHz, $CDCl_3$): δ 5.79 (ddd, *J* = 17.2, 10.5, 5.8 Hz, 1H), 5.25 (dt, *J* = 17.2, 1.4 Hz, 1H), 5.07, (dt, *J* = 10.5, 1.4 Hz, 1H), 4.22 (ddd, *J* = 12.0, 5.7, 1.0 Hz, 1H), 3.95 (dp, *J* = 10.3, 3.5 Hz, 1H), 3.55 (d, *J* = 10.0 Hz, 1H), 2.48 (d, *J* = 14.0 Hz, 1H), 1.94-2.02, (m, 1H), 1.75-1.78 (m, 1H), 1.64-1.74 (m, 4H), 1.38-1.45, (m, 4H), 1.22-1.33 (m, 3H)

^{13}C NMR (125 MHz, $CDCl_3$): δ 139.3, 115.0, 74.2, 71.6, 67.7, 39.8, 36.4, 33.3, 31.5, 19.4, 19.0, 15.9

HRMS (ESI): *m/z* calcd for $C_{12}H_{21}O_2$ $[M+H]^+$ 197.1536, found 197.1533

IR (thin film): 3402, 2927, 2872, 1463, 1263, 1077, 703 cm^{-1}

Mmol Scale Reactions

5 mol% catalyst

The general procedure for spirocycle synthesis was followed with **5** (220 mg, 1.12 mmol) and Re_2O_7 (26 mg, 0.056 mmol) in DCM (8.0 mL), except that the reaction was stirred at 0 °C prior to warming to rt and stirring for 25 min. The crude mixture was purified via flash column

chromatography with 10% ethyl acetate in hexanes to give a mixture of **6** and **7** (194 mg, 88% yield) with a diastereomeric ratio (d.r.) of 3.9:1 respectively.

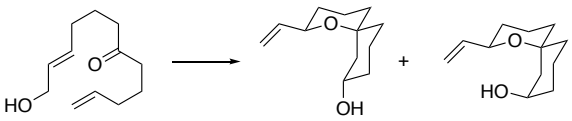
1.7 mol% catalyst

The general procedure for spirocycle synthesis was followed with **5** (203 mg, 1.03 mmol) and Re_2O_7 (8 mg, 0.017 mmol) in DCM (6.0 mL), except that the reaction was stirred at 0 °C prior to warming to rt and stirring for 70 min. The crude mixture was purified via flash column chromatography with 10% ethyl acetate in hexanes to give a mixture of **6** and **7** (172 mg, 85% yield) with a diastereomeric ratio (d.r.) of 3.9:1 respectively.

Reaction Optimization

General procedure for optimization studies.

The general protocol for spirocycle formation was followed with 10 mg (0.05 mmol) of **5** and catalyst (3 mol%) in 0.5 mL of each solvent listed and stirred at the respective temperature in a sealed 1-dram vial. The reaction mixture was quenched with a drop of pyridine, filtered through a plug of silica in a Fisherbrand 9-inch borosilicate Pasteur pipet column with 20% ethyl acetate in hexanes, and concentrated under reduced pressure to obtain total product yield. The concentrated mixture was then dissolved in $CDCl_3$ and analyzed with NMR spectroscopy for the diastereomeric ratio.



5 **6** **7**

No	Catalyst	Solvent	Temp (°C)	Time (h)	Yield (%)	d.r (6:7)
1	Re_2O_7•SiO_2	DCM	rt	0.25	0	n/a
2	Re_2O_7•SiO_2	DCM	0	1	0	n/a
3	Re_2O_7	DCM	rt	0.4	93	4:1
4	Re_2O_7	DCM	rt	1.75	89	2:1
5	Re_2O_7	MeCN	rt	1	91	4:1
6	Re_2O_7	Hexanes	rt	1.5	32	4:1
7	Re_2O_7	Nitromethane	rt	2	53	4:1
8	Re_2O_7	Diethyl ether	rt	1	0	n/a

9	Re_2O_7	Water	rt	1	0	n/a
10	Re_2O_7	Ethyl acetate	rt	1	0	n/a

Table 1. Optimization studies for Spirocycle formation.

Kinetic Studies

Procedure for kinetic studies

To a solution of **5** (10 mg, 0.05 mmol) in CD_2Cl_2 (0.2 mL) in a Wilmad 5 mm diameter, 7-inch borosilicate NMR tube was added 50 µL of 0.25 M solution of 1,4-difluorobenzene [(5.7 mg, 0.05 mmol) in CD_2Cl_2 (0.2 mL)] as internal standard. ^{1}H NMR spectrum was obtained on the sample with a Bruker Avance 600 MHz spectrometer at t = 0, after which the sample was removed from the spectrometer, loaded with Re_2O_7 (2 mg, 0.004 mmol), shaken and inserted back into the spectrometer for analysis after 5 min. The removal of sample from spectrometer, vigorous shaking of the reaction mixture and re-insertion of the sample into the spectrometer and analysis for product yield and d.r. was repeated every 5 min for the first 25 mins and then at 10 min intervals afterwards.

Time (min)	Yield (%)	d.r
5	34	11.2
10	45	8.7
15	50	6.8
25	65	4
35	71	2.8
45	73	2.5
60	81	2.4
90	88	2.4
120	91	2.4
130	94	2.3

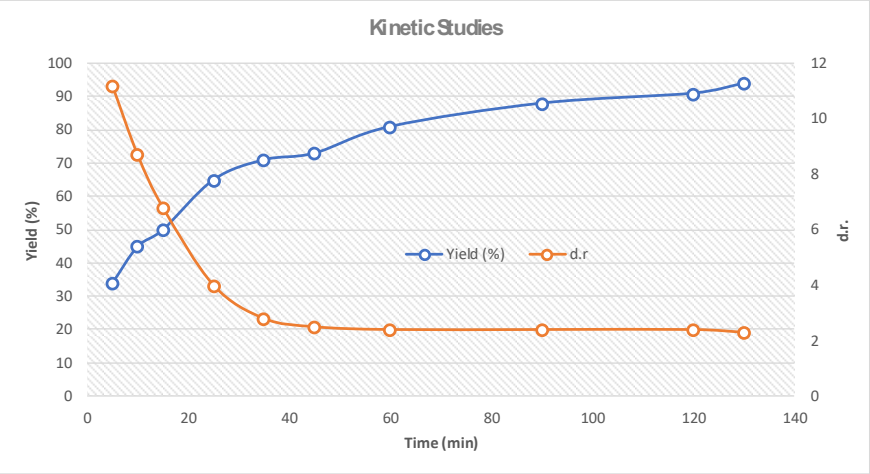
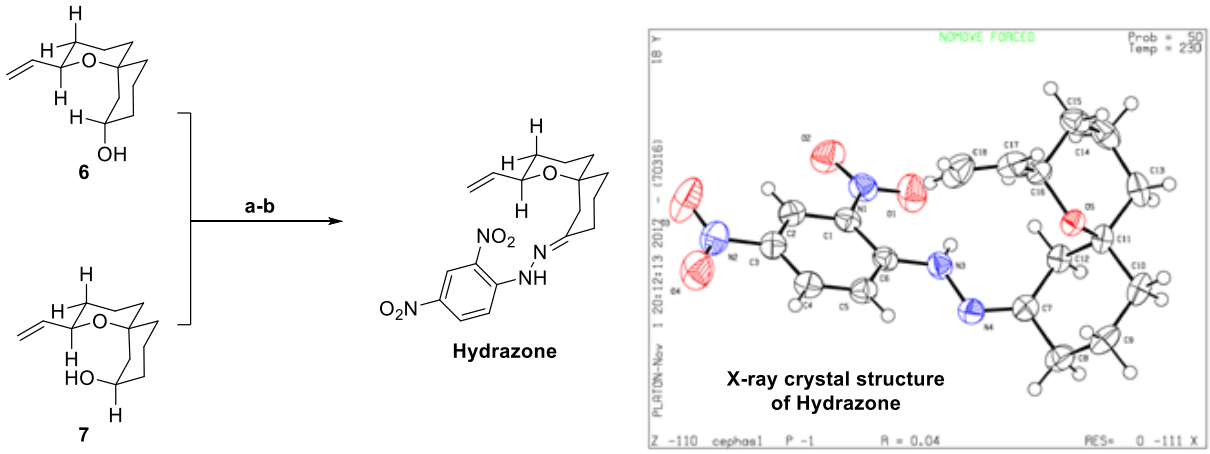


Table 2. Kinetic studies in CD_2Cl_2.

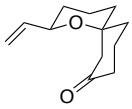
Determination of the stereochemistry at the Quaternary Stereocenter



Reagents and condition

a) PCC, Celite, DCM, rt, 88%(with **6**). b) 2,4-DNPH, MeOH, reflux, 91%.

Scheme 2. Derivatization of to the corresponding 2,4-dinitrophenylhydrazone.



(2*R*,6*S*)-2-Vinyl-1-oxaspiro[5.5]undecan-8-one (11)

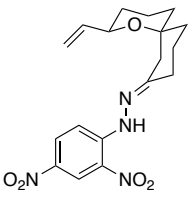
To a solution of a 1:1 mixture of **6** and **7** (40 mg, 0.2 mmol) in dichloromethane (2 mL) was added PCC (86 mg, 0.4 mmol) and Celite (0.1 g). The reaction stirred at rt for 15 min, then the mixture was purified via flash column chromatography with 20% ethyl acetate in hexanes as eluent and the eluted fractions concentrated under reduced pressure to yield a colorless oil (35 mg, 88%) identified by NMR spectroscopy as a single ketone product.

^{1}H NMR (500 MHz, $CDCl_3$): δ 5.77 (ddd, J = 17.5, 10.6, 5.3 Hz, 1H), 5.17 (dt, J = 17.3, 1.6 Hz, 1H), 5.04 (dt, J = 10.6, 1.5 Hz, 1H), 4.04 (ddt, J = 11.2, 2.6, 1.1Hz, 1H), 2.96 (dt, J = 13.9, 1.6 Hz, 1H), 2.31-2.38 (m, 2H), 2.25-2.31 (m, 1H), 2.10-2.19 (m, 1H), 1.85-1.89 (m, 1H), 1.75-1.83 (m 2H), 1.63-1.70 (m, 3H), 1.56-1.59 (m, 1H), 1.39-1.45 (m, 1H), 1.20-1.42 (m, 1H)

^{13}C NMR (125 MHz, $CDCl_3$): δ 210.0, 139.5, 114.6, 70.6, 46.4, 40.9, 38.9, 34.7, 31.1, 29.7, 20.5, 18.9

HRMS (ESI): *m/z* calcd for $C_{12}H_{19}O_2$ $[M+H]^+$ 195.1380, found 195.1376

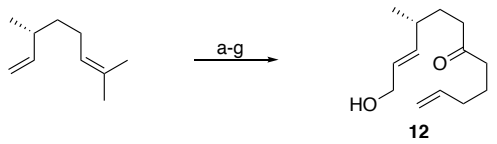
IR (thin film): 2933, 2870, 1711, 1440, 1227, 1048, 984, 710 cm^{-1}



2,4-Dinitrophenylhydrazone synthesis

To a solution of **11** (30 mg, 0.15 mmol) in methanol (3 mL) was added 2,4-dinitrophenylhydrazine (61 mg, 0.31 mmol). The mixture was stirred at reflux under argon until starting material **11** was fully consumed. The reaction mixture was concentrated and purified via flash column chromatography with 10% ethyl acetate in hexanes

after which the eluted fractions were concentrated to yield a yellow-orange powdery precipitate (51 mg, 91%). The precipitate was then recrystallized via vapor diffusion by dissolving it in approximately 80 µL of ether in a 1-dram borosilicate glass vial and placing the vial in a larger 4-dram glass vial containing approximately 5 mL of pentane. The bigger vial containing the smaller 1-dram vial was capped tightly and allowed to sit for 96 h at room temperature for the recrystallized hydrazone to form. The regenerated crystals were dried under vacuum and analyzed with X-ray crystallography for the crystal structure of the derived hydrazone.



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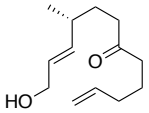
Reagents and conditions
a) *m*CPBA, CH_2Cl_2, 0 °C, 93%. b) *cis*-2-Butene-1,4-diol, Grubbs-Hoveyda second generation catalyst, CH_2Cl_2, 26%. c) TBSCl, imidazole, DMAP, CH_2Cl_2, 88%. d) H_5IO_6, CH_2Cl_2, 0 °C, 86%. e) Mg, 5-bromo-1-pentene, THF, 73%. f) PCC, Celite, CH_2Cl_2, 81%. g) HOAc, THF, H_2O, 67%.

Scheme 3. Synthesis of **12**.



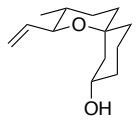
(9*R*,10*E*)-12-Hydroxy-9-methyldodeca-1,10-dien-6-one (12)

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.77 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.60 (dt, *J* = 15.4, 5.4 Hz, 1H), 5.50 (dd, *J* = 15.1, 7.7 Hz, 1H), 4.95-5.03 (m, 2H), 4.09 (t, *J* = 4.6 Hz, 2H), 2.39 (t, *J* = 7.8 Hz, 2H), 2.37 (t, *J* = 7.8 Hz, 2H), 2.12 (sept, *J* = 7.0 Hz, 1H) 2.04 (qt, *J* = 7.0, 1.6 Hz, 2H), 1.66 (pent, *J* = 7.3 Hz, 2H), 1.48-1.59 (m, 2H), 1.32 (t, *J* = 5.6 Hz, 1H), 1.00 (d, *J* = 6.8 Hz, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 211.1, 138.0, 137.9, 128.1, 115.2, 63.7, 42.0, 40.7, 36.2, 33.1, 30.4, 22.8, 20.5

HRMS (ESI): *m/z* calcd for $C_{13}H_{23}O_2$ $[M+H]^+$ 211.1693, found 211.1689

IR (thin film): 3406, 3107, 2927, 1709 1454, 1087, 971, 632 cm^{-1}



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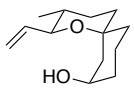


16

(2*S*,3*R*,6*R*,8*S*)-3-Methyl-2-vinyl-1-oxaspiro[5.5]undecan-8-ol (15) and (2*S*,3*R*,6*R*,8*R*)-3-methyl-2-vinyl-1-oxaspiro[5.5]undecan-8-ol (16)

The general procedure for spirocycle synthesis was followed with **12** (15.0 mg, 0.1 mmol) and Re_2O_7 (2.0 mg, 0.004 mmol) in DCM (0.7 mL) for 10 min at 0 °C. The reaction mixture was purified via flash chromatography (10% ethyl acetate in hexane) and the eluted fractions were

concentrated *in vacuo* to give products **15** and **16** (11.6 mg, 77% yield) with diastereomeric ratio of 4:1 respectively.

Major (slower-eluting) isomer (15)

^{1}H NMR (500 MHz, $CDCl_3$): δ 5.77 (ddd, *J* = 17.2, 10.3, 6.8 Hz, 1H), 5.22 (d, *J* = 17.1, 1H), 5.12 (d, *J* = 10.4 Hz, 1H), 3.74 (tt, *J* = 10.9, 4.8Hz, 1H), 3.58 (dd, *J* = 10.1, 7.0 Hz, 1H), 2.66 (dd, *J* = 13.2, 1.8 Hz, 1H), 1.97 (d, *J* = 11.6 Hz, 1H) 1.72-1.81 (m, 1H), 1.52-1.63 (m, 4H), 1.38-1.50 (m, 3H), 1.24-1.33 (m, 4H), 0.82 (d, *J* = 6.6 Hz, 3H)

^{13}C NMR (125 MHz, $CDCl_3$): δ 138.6, 116.5, 73.7, 67.1, 39.0, 38.3, 36.7, 36.0, 35.3, 28.1, 22.7, 19.6, 17.8

HRMS (ESI): *m/z* calcd for $C_{13}H_{23}O_2$ $[M+H]^+$ 211.1698, found 211.1691

IR (thin film): 3343, 2929, 2859, 1451, 1274, 1025, 920 cm^{-1}

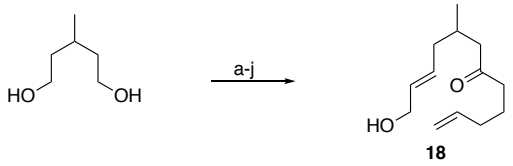
Minor (faster-eluting) isomer (16)

^{1}H NMR (500 MHz, $CDCl_3$): δ 5.75 (ddd, *J* = 17.4, 10.3, 7.3 Hz, 1H), 5.28 (dd, *J* = 17.2, 1.0 Hz, 1H), 5.16 (dd, *J* = 10.4, 1.2 Hz, 1H), 3.95 (dp, *J* = 10.4, 3.7 Hz, 1H), 3.78 (dd, *J* = 9.7, 7.3 Hz, 1H), 3.53 (d, *J* = 9.0 Hz, 1H), 2.48 (d, *J* = 14.2 Hz, 1H), 1.88-2.06 (m, 2H), 1.63-1.78 (m, 2H), 1.41-1.51 (m, 3H), 1.38-1.42 (m, 3H), 1.30-1.37 (m, 2H), 0.83 (d, *J* = 6.4 Hz, 3H)

^{13}C NMR (125 MHz, $CDCl_3$): δ 137.9, 117.6, 78.6, 73.8, 67.7, 39.7, 37.0, 35.3, 34.0, 33.3, 27.9, 17.7, 16.0

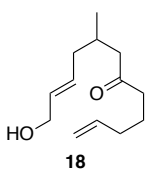
HRMS (ESI): *m/z* calcd for $C_{13}H_{23}O_2$ $[M+H]^+$ 211.1698, found 211.1692

IR (thin film): 3336, 2925, 2853, 1453, 1025, 920 cm^{-1}



Reagents and conditions
a) NaH, THF, then TBSCl, 0 °C, 58%. b) SO_3•Py, DMSO, Et_3N, CH_2Cl_2, 0 °C, 97%. c) NaH, THF, $(MeO)_2P(O)CH_2C(O)OMe$, 0 °C, 80%. d) DIBAL-H, THF, 0 °C, 98%. e) TBDPSCl, imidazole, CH_2Cl_2, 0 °C, 92%. f) 1N HCl, THF, 55%. g) PCC, Celite, CH_2Cl_2, 83%. h) Mg, I_2, pentenyl bromide, THF, 0 °C, 97%. i) PCC, Celite, CH_2Cl_2, 98%. j) Bu_4NF, THF, 91%.

Scheme 4. Synthesis of **18**.



(*E*)-12-Hydroxy-8-methyldodeca-1,10-dien-6-one (18)

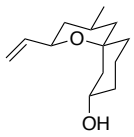
^{1}H NMR (500 MHz, $CDCl_3$): δ 5.76 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.63 (m, 2H), 5.00 (dq, *J* = 17.2, 1.7 Hz, 1H), 4.97 (ddt, *J* = 10.3, 2.0, 1.2 Hz, 1H), 4.09 (d, *J* =

3.6 Hz, 2H), 2.36-2.41 (m, 3H), 2.20 (dd, *J* = 16.0, 7.8 Hz, 1H), 2.10 (sept, *J* = 6.7 Hz, 1H), 2.01-2.07 (m, 2H), 1.92-2.00 (m, 2H), 1.66 (pent, *J* = 7.4 Hz, 2H), 0.89 (d, *J* = 6.6 Hz, 3H)

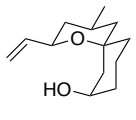
^{13}C NMR (125 MHz, $CDCl_3$): δ 210.7, 138.0, 131.1, 130.7, 115.2, 63.6, 49.5, 42.5, 39.5, 33.1, 29.1, 22.7, 19.8

HRMS (ESI): *m/z* calcd for $C_{13}H_{22}O_2Na$ $[M+Na]^+$ 233.1512, found 233.1505

IR (thin film): 3413, 2929, 1708, 1371, 912, 736 cm^{-1}



19



19a

(2*R*,4*R*,6*R*,8*S*)-4-Methyl-2-vinyl-1-oxaspiro[5.5]undecan-8-ol (19) and (2*R*,4*R*,6*R*,8*R*)-4-methyl-2-vinyl-1-oxaspiro[5.5]undecan-8-ol (19a)

The general procedure for spirocycle synthesis was followed with **18** (42 mg, 0.2 mmol) and Re_2O_7 (3 mg, 0.006 mmol) in DCM (1.0 mL) for 15 min at rt. The resultant mixture was purified via flash column chromatography using 0-20% ethyl acetate in hexanes as eluent in gradient elution and the eluted fractions concentrated *in vacuo* to give **19** and **19a** (32 mg, 76% yield) with a d.r. of 3.6:1 and **19** as the major isomer.

Major (slower-eluting) isomer (**19**)

^{1}H NMR (500 MHz, $CDCl_3$): δ 5.81 (ddd, *J* = 17.3, 10.6, 5.2 Hz, 1H), 5.21 (dt, *J* = 17.5, 1.6 Hz, 1H), 5.04 (dt, *J* = 10.5, 1.6 Hz, 1H), 4.03 (dd, *J* = 11.5, 3.4 Hz, 1H), 3.75 (tt, *J* = 11.1, 4.2 Hz, 1H), 2.61 (d, *J* = 13.3 Hz, 1H), 1.98 (d, *J* = 13.5 Hz, 1H), 1.85-1.90 (m. 1H), 1.80 (qt, *J* = 13.3, 3.7Hz, 1H), 1.66 (d, *J* = 13.1 Hz, 1H), 1.52-1.56 (m, 2H), 1.44 (ddd, *J* = 13.5, 3.8, 1.7 Hz, 1H), 1.25 (td, *J* = 13.0, 4.1 Hz, 1H), 1.17 (qd, *J* = 13.2, 4.0 Hz, 1H), 0.98 (t, *J* = 12.8 Hz, 1H), 0.91 (dd, *J* = 13.2, 11.3 Hz, 1H), 0.89 (d, *J* = 6.1 Hz, 3H), 0.86 (t, *J* = 12.4 Hz, 1H), 0.84 (t, *J* = 12.4 Hz, 1H)

^{13}C NMR (125 MHz, $CDCl_3$): δ 140.0, 114.1, 74.4, 70.2, 67.1, 45.1, 40.1, 39.1, 39.0, 36.0, 25.4, 22.5, 19.6

HRMS (ESI): *m/z* calcd for $C_{13}H_{23}O_2$ $[M+H]^+$ 211.1693, found 211.1690

IR (thin film): 3338, 2928 1480, 1263, 1020, 735 cm^{-1}

Minor (faster-eluting) isomer (**19a**)

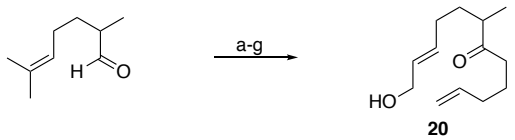
^{1}H NMR (500 MHz, $CDCl_3$): δ 5.80 (ddd, *J* = 17.2, 10.5, 5.8 Hz, 1H), 5.26 (dt, *J* = 17.3, 1.5 Hz, 1H), 5.08 (dt, *J* = 10.5, 1.3 Hz, 1H), 4.22 (dd, *J* = 11.4, 5.7, Hz, 1H), 3.94 (pent, *J* = 3.1 Hz, 1H), 2.43 (d, *J* = 14.3 Hz, 1H), 1.95-2.02 (m, 1H), 1.83-1.89 (m, 1H), 1.77(dd, *J* = 13.6, 3.5 Hz, 1H),

1.62-1.72 (m, 2H), 1.38-1.55 (m, 4H), 1.29 (d, J = 14.1 Hz, 1H), 1.18-1.26 (m, 1H), 0.90 (d, J = 6.6 Hz, 3H), 0.86-0.93 (m, 2H)

^{13}C NMR (125 MHz, $CDCl_3$): δ 139.1, 115.1, 74.6, 71.7, 67.7, 45.4, 40.1, 39.8, 34.7, 33.3, 25.3, 22.3, 16.0

HRMS (ESI): *m/z* calcd for $C_{13}H_{23}O_2$ $[M+H]^+$ 211.1693, found 211.1695

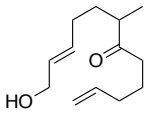
IR (thin film): 3420, 2927, 2868 1465, 1025, 920 cm^{-1}



20

Reagents and conditions
a) *cis*-2-Butene-1,4-diol, Grubbs-Hoveyda second generation catalyst, CH_2Cl_2, 21%. b) $(MeO)_3CH$, *p*-TsOH, MeOH, 0 °C, 88%. c) NaH, THF, then PMBCl, Bu_4NI, 62%. d) *p*-TsOH, acetone, 92%. e) Mg, 5-bromo-1-pentene, Et_2O, 73%. f) PCC, Celite, CH_2Cl_2, 81%. g) TFA, CH_2Cl_2, 65%.

Scheme 5. Synthesis of **20**.



20

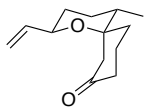
(10*E*)-12-Hydroxy-7-methyldodeca-1,10-dien-6-one (20)

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.76 (ddt, J = 17.0, 10.2, 6.7 Hz, 1H), 5.63-5.65 (m, 2H), 4.96-5.04 (m, 2H), 4.08 (t, J = 3.2 Hz, 2H), 2.52 (sept, J = 6.7 Hz, 1H), 2.47 (dt, J = 17.2, 7.3 Hz, 1H), 2.41 (dt, J = 17.2, 7.3 Hz, 1H), 1.99-2.08 (m, 4H), 1.76 (dp, J = 8.8, 4.0 Hz, 1H), 1.66 (pent, J = 7.4 Hz, 2H), 1.35-1.44 (m, 1H), 1.31 (t, J = 5.3 Hz, 1H), 1.06 (d, J = 7.0 Hz, 3H)

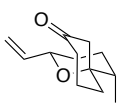
^{13}C NMR (100 MHz, $CDCl_3$): δ 214.4, 138.1, 132.2, 129.6, 115.2, 63.6, 45.7, 40.3, 33.1, 32.1, 29.9, 22.6, 16.5

HRMS (ESI): *m/z* calcd for $C_{13}H_{23}O_2$ $[M+H]^+$ 211.1698, found 211.1694

IR (thin film): 3400, 2934, 1706, 1425, 1268, 1078, 923 cm^{-1}



21



21a

(2*R*,5*S*,6*S*)-5-Methyl-2-vinyl-1-oxaspiro[5.5]undecan-8-one (21) and (2*S*,5*S*,6*R*)-5-methyl-2-vinyl-1-oxaspiro[5.5]undecan-8-one (21a)

The general procedure for spirocycle synthesis was followed with **20** (20.2 mg, 0.1 mmol) and Re_2O_7 (3.0 mg, 0.006 mmol) in DCM (1.2 mL) at rt for 10 min and the crude product mixture was purified via flash column chromatography with 20% ethyl acetate in hexane. The concentrated mixture was immediately subjected to PCC (40.0 mg, 0.19 mmol) and Celite (40.0 mg) in DCM

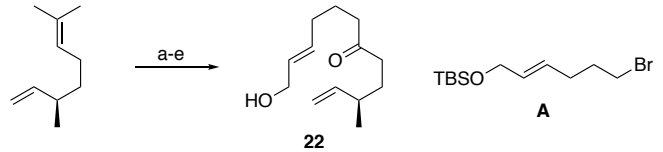
(1.0 mL) at rt for 15 min. The resultant crude mixture was then purified via flash column chromatography using 10% ethyl acetate in hexanes to give **21** and **21a** (18 mg, 88% yield over 2 steps) with a d.r. of 2.2:1 and **21** as the major diastereomer.

Mixture of diastereomers 21 and **21a**

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.77 (ddd, *J* = 17.2, 10.5, 5.4 Hz, 0.3H), 5.74 (ddd, *J* = 17.3, 10.6, 5.0 Hz, 0.7H), 5.16 (dt, *J* = 17.3, 1.4 Hz, 0.3H), 5.15 (dt, *J* = 17.3, 1.6 Hz, 0.7H), 5.00-5.04 (m, 1H), 4.05-4.08 (m, 0.3H), 4.00-4.03 (m, 0.7H), 2.98 (dt, *J* = 13.8, 1.9 Hz, 0.3H), 2.85 (dt, *J* = 13.9, 2.4 Hz, 0.7H), 2.48 (d, *J* = 13.8 Hz, 0.3H), 2.23 (d, *J* = 13.9 Hz, 0.7H), 2.16-2.35 (m, 3H), 1.97-2.06 (m, 1H), 1.74-1.95 (m, 1H), 1.63-1.73 (m, 2H), 1.54-1.60 (m, 2H), 1.41-1.50 (m, 1H), 1.28-1.40 (m, 1H), 1.03 (d, *J* = 7.0 Hz, 0.9H), 0.89 (d, *J* = 6.7 Hz, 2.1H)

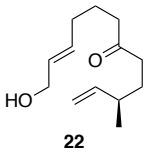
^{13}C NMR (100 MHz, $CDCl_3$): δ 210.7, 210.3, 139.6, 139.3, 114.6, 114.4, 80.7, 78.9, 70.6, 70.1, 48.4, 41.3, 40.83, 40.78, 39.0, 35.7, 34.4, 32.8, 31.6, 27.7, 26.0, 25.6, 20.7, 20.5, 17.3, 14.2

HRMS (ESI) *m/z* calcd for $C_{13}H_{21}O_2$ $[M+H]^+$ 209.1542, found 209.1567.



Reagents and conditions
a) *m*-CPBA, CH_2Cl_2, 0 °C, 93%%. b) PCC, H_5IO_6, CH_2Cl_2, 0 °C, 75%. c) MeON(H)OMe•HCl, DCC, DMAP, Et_3N, 71%. d) *t*-BuLi, **A**, Et_2O, –78 °C, 52%. e) HOAc, H_2O, 67%.

Scheme 6. Synthesis of **22**.



22

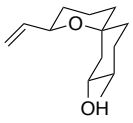
(3*R*,10*E*)-12-Hydroxy-3-methyldodeca-1,10-dien-6-one (22)

^{1}H NMR (500 MHz, $CDCl_3$): δ 5.63-5.66 (m, 2H), 5.62 (ddd, *J* = 17.0, 10.3, 7.9 Hz, 1H), 4.96 (d, *J* = 17.0 Hz, 1H), 4.93 (d, *J* = 10.3 Hz, 1H), 4.09 (dd, *J* = 5.0, 4.7 Hz, 2H), 2.36-2.41 (m, 4H), 2.09 (sept, *J* = 7.4 Hz, 1H), 2.02-2.07 (m, 2H), 1.66 (pent, *J* = 7.4 Hz, 2H), 1.58-1.64 (m, 1H), 1.48-1.55 (m, 1H), 1.24-1.27 (m, 1H), 1.00 (d, *J* = 6.8 Hz, 3H)

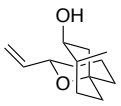
^{13}C NMR (125 MHz, $CDCl_3$): δ 210.9, 143.8, 132.2, 129.8, 113.4, 63.7, 42.0, 40.6, 37.6, 31.6, 30.2, 23.1, 20.3

HRMS (ESI): *m/z* calcd for $C_{13}H_{23}O_2$ $[M+H]^+$ 211.1693, found 211.1694

IR (thin film): 3408, 2937, 1720, 1338, 1210, 1062, 941, 716 cm^{-1}



23



23a

(2*R*,6*S*,8*R*,9*R*)-9-Methyl-2-vinyl-1-oxaspiro[5.5]undecan-8-ol (23) and (2*R*,6*S*,8*S*,9*R*)-9-methyl-2-vinyl-1-oxaspiro[5.5]undecan-8-ol (23a)

The general procedure for spirocycle synthesis was followed with **22** (15.3 mg, 0.1 mmol) and Re_2O_7 (2.0 mg, 0.004 mmol) in DCM (1.0 mL) at rt for 15 min after which the resultant mixture was purified via flash column chromatography with 0-5% ethyl acetate in hexanes (gradient elution) and concentrated in vacuo to give **23** and **23a** (11.0 mg, 73% yield) with a diastereomeric ratio of 3:1 respectively.

Major (faster-eluting) isomer (23)

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.82 (ddd, *J* = 17.5, 10.6, 5.1 Hz, 1H), 5.21 (dt, *J* = 17.3, 1.7 Hz, 1H), 5.05 (dt, *J* = 10.6, 1.6 Hz, 1H), 4.04 (ddt, *J* = 12.0, 5.4, 1.6 Hz, 1H), 3.32 (dd, *J* = 11.3, 3.0 Hz, 1H), 2.70 (ddd, *J* = 13.5, 3.7, 2.7 Hz, 1H), 1.70-1.79 (m, 1H), 1.61-1.68 (m, 2H), 1.46-1.57 (m, 2H), 1.36-1.42 (m, 3H), 1.18-1.35 (m, 4H), 1.02 (d, *J* = 6.4 Hz, 3H), 0.92 (dd, *J* = 13.6, 11.0 Hz, 1H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 140.2, 114.1, 74.3, 72.4, 70.1, 40.6, 39.5, 38.1, 36.1, 31.5, 28.3, 19.4, 18.2

HRMS (ESI): *m/z* calcd for $C_{13}H_{23}O_2$ $[M+H]^+$ 211.1693, found 211.1704

IR (thin film): 3401, 3028, 2929, 1442, 1054, 916, 776 cm^{-1}

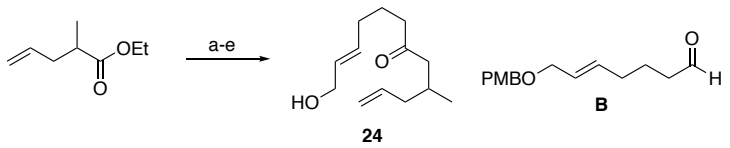
Minor (slower-eluting) isomer (23a)

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.81 (ddd, *J* = 16.6, 10.6, 5.9 Hz, 1H), 5.23 (dt, *J* = 17.2, 5.4 Hz, 1H), 5.08 (dt, *J* = 10.5, 1.3 Hz, 1H), 4.19 (dd, *J* = 11.1, 6.0 Hz, 1H), 3.36 (td, *J* = 7.4, 3.4 Hz, 1H), 2.62 (br, 1H), 1.96-2.05 (m, 1H), 1.88-1.95 (m, 1H), 1.77-1.83 (m, 1H), 1.60-1.76 (m, 5H), 1.22-1.32 (m, 4H), 1.05-1.16 (m, 1H), 0.98 (d, *J* = 6.9 Hz, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 139.7, 114.9, 74.4, 73.4, 71.3, 31.6, 26.6, 19.1, 17.3 (Note: some peaks did not emerge above the baseline and hence could not reported)

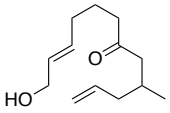
HRMS (ESI): *m/z* calcd for $C_{13}H_{23}O_2$ $[M+H]^+$ 211.1693, found 211.1698

IR (thin film): 3371, 2978, 1472, 1050, 946, 718 cm^{-1}



Reagents and conditions
a) DIBAL-H, THF, °C, 96%. b) I_2, Ph_3P, imidazole, CH_2Cl_2, 94%. c) Mg, I_2, THF, then **B**, 76%.
d) PCC, Celite, CH_2Cl_2, 89%. e) 10% TFA, CH_2Cl_2, 89%.

Scheme 7. Synthesis of **24**.



24

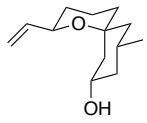
(*E*)-12-Hydroxy-4-methyldodeca-1,10-dien-6-one (24)

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.74 (ddt, *J* = 14.4, 11.2, 7.2 Hz, 1H), 5.61-5.69 (m, 2H), 4.99-5.02 (m, 2H), 4.09 (d, *J* = 3.7 Hz, 2H), 2.41 (dd, J = 15.9, 5.4 Hz, 1H) 1H), 2.38 (t, *J* = 6.3 Hz, 2H), 2.19 (dd, *J* = 16.0, 7.9 Hz, 1H), 2.11 (oct, *J* = 6.6 Hz, 1H), 2.03-2.07 (m, 3H), 1.95-2.01 (m, 2H), 1.66 (pent, *J* = 7.4 Hz, 2H), 0.90 (d, 3H, *J* = 6.9 Hz)

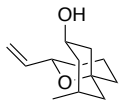
^{13}C NMR (125 MHz, $CDCl_3$) δ 210.6, 136.7, 132.2, 129.8, 116.4, 63.7, 49.4, 42.6, 41.2, 31.6, 28.9, 23.0, 19.8

HRMS (ESI): *m/z* calcd for $C_{13}H_{22}O_2Na$ $[M+Na]^+$ 233.1512, found 233.1507

IR (thin film): 3391, 3107, 2927, 1706, 1370, 1088, 998, 703 cm^{-1}



25



28

(2*R*,6*S*,8*S*,10*R*)-10-Methyl-2-vinyl-1-oxaspiro[5.5]undecan-8-ol (25) and (2*R*,6*S*,8*S*,10*S*)-10-methyl-2-vinyl-1-oxaspiro[5.5]undecan-8-ol (28)

The general procedure for spirocycle synthesis was followed with **24** (30 mg, 0.14 mmol) and Re_2O_7 (2 mg, 0.004 mmol) in DCM (1.0 mL) for 2 h with slow warming of the reaction from 0 °C to rt. The resultant crude mixture was purified via flash column chromatography with 10% ethyl acetate in hexanes as eluent to give **25** and **28** (21 mg, 70% yield) with a d.r. of 3.8:1 and **25** as the major diastereomer.

Major (faster-eluting) isomer (**25**)

^{1}H NMR (500 MHz, $CDCl_3$): δ 5.81 (ddd, *J* = 17.3, 10.6, 5.2 Hz, 1H), 5.20 (dt, *J* = 17.3, 1.7 Hz, 1H), 5.05 (dt, *J* = 10.5, 1.5 Hz, 1H), 4.04 (ddt, *J* = 11.4, 3.1, 1.4 Hz, 1H), 3.80 (tt, *J* = 11.3, 4.2 Hz, 1H), 2.71 (ddt, *J* = 13.2, 4.2, 2.2 Hz, 1H), 1.95-2.04 (m, 2H), 1.71-1.78 (m, 1H), 1.63-1.68 (m, 2H), 1.58 (ddt, *J* = 13.4, 4.1, 2.4 Hz, 1H), 1.36-1.41 (m, 3H), 1.24 (qd, *J* = 11.7, 4.2 Hz, 1H), 0.94 (dd, *J* = 13.3, 12.2 Hz, 1H), 0.90 (d, *J* = 6.6 Hz, 3H), 0.86 (t, *J* = 11.2 Hz, 1H), 0.80 (dd, *J* = 13.3, 11.4 Hz, 1H)

^{13}C NMR (125 MHz, $CDCl_3$) δ 140.1, 114.2, 74.3, 70.2, 66.9, 47.9, 47.8, 38.0, 36.1, 31.4, 25.7, 21.9, 19.3

HRMS (ESI): *m/z* calcd for $C_{13}H_{23}O_2$ $[M+H]^+$ 211.1693, found 211.1689

IR (thin film): 3370, 2930, 2868, 1457, 1366, 1024, 735 cm^{-1}

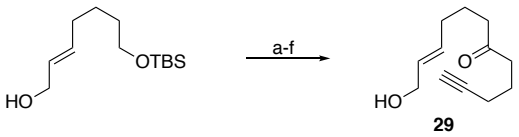
Minor (slower-eluting) isomer (28)

^{1}H NMR (600 MHz, $CDCl_3$): δ 5.81 (ddd, *J* = 17.0, 10.4, 5.9 Hz, 1H), 5.20 (d, *J* = 17.3 Hz, 1H), 5.05 (d, *J* = 10.4 Hz, 1H), 4.14 (dd, *J* = 10.9, 5.5 Hz, 1H), 3.61 (tt, *J* = 9.0, 4.4 Hz, 1H), 2.69 (dt, *J* = 11.8, 1.8 Hz, 1H), 1.96 (d, *J* = 12.1 Hz, 1H), 1.67-1.72 (m, 3H), 1.64 (d, *J* = 12.9 Hz, 1H), 1.57 (d, *J* =12.3 Hz, 1H), 1.50-1.54 (m, 1H), 1.39-1.47 (m, 1H), 1.19-1.31 (m, 4H), 1.07 (t, *J* = 11.7 Hz, 1H), 0.94 (d, *J* = 6.3 Hz, 3H)

^{13}C NMR (125 MHz, $CDCl_3$): δ 140.1, 114.8, 74.2, 71.1, 68.4, 49.0, 44.7, 39.9, 32.3, 31.7, 26.4, 22.2, 19.3

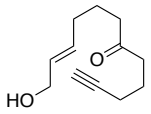
HRMS (ESI): *m/z* calcd for $C_{13}H_{23}O_2$ $[M+H]^+$ 211.1693, found 211.1687

IR (thin film): 3375, 2927, 2869, 1411, 1365, 1019, 720 cm^{-1}



Reagents and conditions
a) TBDPSCl, imidazole, CH_2Cl_2, 98%. b) PPTs, MeOH, 55 °C, 73%. c) PCC, Celite, CH_2Cl_2, 79%. d) $Me_3Si(CH_2)_3MgBr$, THF, 96%. e) PCC, Celite, CH_2Cl_2, 77%. f) Bu_4NF, THF, 83%.

Scheme 8. Synthesis of **29**.



29

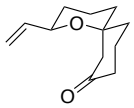
(*E*)-12-Hydroxydodec-10-en-1-yn-6-one (29)

^{1}H NMR (500 MHz, $CDCl_3$): δ 5.60-5.68 (m, 2H), 4.09 (d, *J* = 0.9 Hz, 2H), 2.54 (t, *J* = 7.2 Hz, 2H), 2.42 (t, *J* = 7.4 Hz, 2H), 2.22 (dt, *J* = 6.8, 2.6 Hz, 2H), 2.04-2.07 (m, 2H), 1.95 (t, *J* = 2.6 Hz, 1H), 1.78 (pent, *J* = 7.1 Hz, 2H), 1.68 (pent, *J* = 7.4 Hz, 2H)

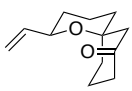
^{13}C NMR (125 MHz, $CDCl_3$): δ 210.2, 132.0, 129.9, 83.6, 69.0, 63.6, 42.1, 41.1, 31.5, 23.1, 22.2, 17.8

HRMS (ESI): *m/z* calcd for $C_{12}H_{18}O_2Na$ $[M+Na]^+$ 217.1199, found 217.1192

IR (thin film): 3414, 3288, 2934, 1706, 1372, 1091, 973, 639 cm^{-1}



11



30

(2*R*,6*S*)-2-Vinyl-1-oxaspiro[5.5]undecan-8-one (11) and (2*R*,6*R*)-2-vinyl-1-oxaspiro[5.5]undecan-8-one (30)

The general procedure for spirocycle synthesis was followed with **29** (25 mg, 0.13 mmol) and Re_2O_7 (3 mg, 0.006 mmol) in DCM (0.8 mL) at rt for 10 min. The crude reaction mixture was then quenched with a drop of pyridine and purified via gradient-elution flash column chromatography with 0-5% ethyl acetate in hexanes as eluent to yield **11** and **30** (20.2 mg, 81%) in a 1:1 ratio.

Faster-eluting product (11)

^{1}H NMR (500 MHz, $CDCl_3$): δ 5.77 (ddd, *J* = 17.5, 10.6, 5.3 Hz, 1H), 5.17 (dt, *J* = 17.3, 1.6 Hz, 1H), 5.04 (dt, *J* = 10.6, 1.5 Hz, 1H), 4.04 (ddt, *J* = 11.2, 2.6, 1.1Hz, 1H), 2.96 (dt, *J* = 13.9, 1.6 Hz, 1H), 2.31-2.38 (m, 2H), 2.25-2.31 (m, 1H), 2.10-2.19 (m, 1H), 1.85-1.89 (m, 1H), 1.75-1.83 (m 2H), 1.63-1.70 (m, 3H), 1.56-1.59 (m, 1H), 1.39-1.45 (m, 1H), 1.20-1.42 (m, 1H)

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 210.0, 139.5, 114.6, 70.6, 46.4, 40.9, 38.9, 34.7, 31.1, 29.7, 20.5, 18.9

HRMS (ESI): *m/z* calcd for $C_{12}H_{19}O_2$ $[M+H]^+$ 195.1380, found 195.1376

IR (thin film): 2933, 2870, 1711, 1440, 1227, 1048, 984, 710 cm^{-1}

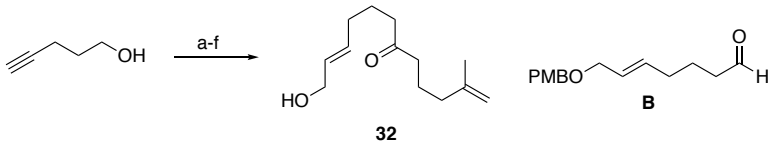
Slower-eluting product (30)

^{1}H NMR (500 MHz, $CDCl_3$): δ 5.77 (ddd, *J* = 17.2, 10.6, 5.2 Hz, 1H), 5.16 (dt, *J* = 17.3, 1.4 Hz, 1H), 5.02 (dt, *J* = 10.5, 1.2 Hz, 1H), 3.92 (dd, *J* = 11.6, 3.3 Hz, 1H), 2.37-2.45 (m, 3H), 2.28-2.36 (m, 1H), 2.19-2.26 (m, 1H), 1.74-1.87 (m, 3H), 1.68-1.74 (m, 2H), 1.56-1.67 (m, 2H), 1.48-1.53 (m, 1H), 1.38 (td, *J* = 13.1, 5.8 Hz, 1H)

^{13}C NMR (125 MHz, $CDCl_3$): δ 209.9, 139.6, 114.1, 70.6, 55.5, 40.9, 34.6, 30.9, 29.7, 28.4, 20.0, 19.4

HRMS (ESI): *m/z* calcd for $C_{12}H_{19}O_2$ $[M+H]^+$ 195.1380, found 195.1376

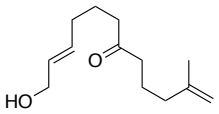
IR (thin film): 2932, 2850, 1715, 1442, 1225, 1019, 982 cm^{-1}



32 **B**

Reagents and conditions
a) Me_3Al, Cp_2ZrCl_2, CH_2Cl_2, 77%. b) MsCl, Et_3N, CH_2Cl_2, 0 °C, 64%. c) LiBr, acetone, reflux, 80%. d) Mg, I_2, THF, then **B**, 71%. e) PCC, Celite, CH_2Cl_2, 98%. f) TFA, CH_2Cl_2, 48%.

Scheme 9. Synthesis of **32**.



32

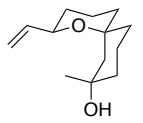
(*E*)-12-Hydroxy-2-methyldodeca-1,10-dien-6-one (32)

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.60-5.70 (m, 2H), 4.72 (dt, *J* = 1.3, 0.7 Hz, 1H), 4.66 (dt, *J* = 1.9, 1.0 Hz, 1H), 4.09 (d, *J* = 3.6 Hz, 2H), 2.39 (t, *J* = 7.6 Hz, 2H), 2.38 (t, *J* = 7.6 Hz, 2H), 2.02-2.10 (m, 2H), 2.00 (t, J = 7.7 Hz, 2H), 1.71 (pent, *J* = 7.8 Hz, 2H), 1.69 (s, 3H), 1.67 (pent, *J* = 7.4 Hz, 2H)

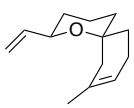
^{13}C NMR (100 MHz, $CDCl_3$): δ 211.0, 145.1, 132.2, 129.8, 110.6, 63.7, 42.1, 42.0, 37.1, 31.6, 23.1, 22.2, 21.4

HRMS (ESI): *m/z* calcd for $C_{13}H_{22}O_2Na$ $[M+Na]^+$ 233.1512, found 233.1504

IR (thin film): 3401, 3110, 2932, 1707, 1338, 1065, 921, 703 cm^{-1}



33



34

(2*R*,6*S*,8*S*)-8-Methyl-2-vinyl-1-oxaspiro[5.5]undecan-8-ol (33) and (2*R*)-8-methyl-2-vinyl-1-oxaspiro[5.5]undec-7-ene (34)

The general procedure for spirocycle synthesis was followed with **32** (43.7 mg, 0.21 mmol) and Re_2O_7 (3 mg, 0.006 mmol) in DCM (1.3 mL) at –10 °C. The reaction was slowly warmed to 0 °C over 2 h, after which time the crude mixture was purified with gradient-elution flash column chromatography using 0-10% ethyl acetate in hexanes as eluent and concentrated *in vacuo* to give **33** and **34** (37.6 mg, 86% yield) in a ratio of 2.6:1 with **33** as the major product.

Major (slower-eluting) product (33)

^{1}H NMR (500 MHz, $CDCl_3$): δ 5.80 (ddd, *J* = 17.1, 10.6, 5.3 Hz, 1H), 5.20 (d, *J* = 17.2 Hz, 1H), 5.05 (d, *J* = 10.5 Hz, 1H), 4.03 (dd, *J* = 11.3, 4.4 Hz, 1H), 2.26 (d, *J* = 13.9 Hz, 1H), 1.67-1.77 (m, 2H), 1.61-1.67 (m, 3H), 1.53-1.61 (m, 3H), 1.42 (dt, *J* = 12.4, 4.1 Hz, 1H), 1.33-1.38 (m, 3H), 1.32 (s, 3H), 1.22-1.28 (m, 2H)

^{13}C NMR (125 MHz, $CDCl_3$): δ 140.0, 114.1, 73.8, 71.2, 70.6, 42.0, 40.9, 40.01, 36.3, 31.6, 28.1, 19.4, 19.3

HRMS (ESI): *m/z* calcd for $C_{13}H_{21}O_2H$ $[M-H]^-$ 209.1536, found 209.1533

IR (thin film): 3377, 2927, 2851, 1439, 1022, 916, 776 cm^{-1}

Minor (faster-eluting) product (34)

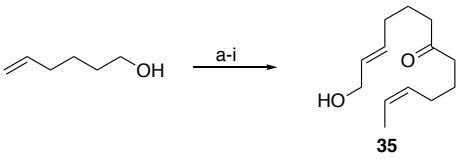
^{1}H NMR (500 MHz, $CDCl_3$): δ 5.84 (ddd, *J* = 16.8, 10.5, 5.8 Hz, 1H), 5.35 (s, 1H), 5.21 (d, *J* = 16.8 Hz, 1H), 5.06 (d, *J* = 10.5 Hz, 1H), 4.10 (dd, *J* = 11.2, 5.2 Hz, 1H), 2.30 (d, *J* = 16.7 Hz, 1H),

2.10-2.15 (m, 1H), 2.08 (d, J = 17.1 Hz, 1H), 1.96-2.05 (m, 1H), 1.67-1.75 (m, 3H), 1.62-1.67 (m, 4H), 1.52-1.56 (m, 1H), 1.25 (s, 3H)

^{13}C NMR (125 MHz, $CDCl_3$): δ 140.4, 131.5, 120.3, 114.4, 72.6, 70.9, 36.6, 36.3, 31.9, 31.7, 23.8, 23.0, 19.3

HRMS (ESI): *m/z* calcd for $C_{13}H_{21}O$ $[M+H]^+$ 193.1587, found 193.1583;

IR (thin film): 2931, 2844, 1438, 1043, 918, 737 cm^{-1}

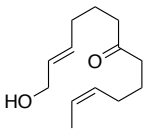


35

Reagents and conditions

a) TBSCl, imidazole, CH_2Cl_2, 99%. b) Methyl acrylate, Grubbs-Hoveyda II catalyst, CH_2Cl_2, 57%. c) DIBAL-H, CH_2Cl_2, –78 °C, 89%. d) NaH, THF, then PMBCl, 0 °C, 77%. e) Bu_4NF, THF, 0 °C, 39%. f) PCC, Celite, CH_2Cl_2, 80%. g) (*Z*)-CH_3CH=$CH(CH_2)_3MgBr$, THF, 80%. h) PCC, Celite, CH_2Cl_2, 94%. i) TFA, CH_2Cl_2, 91%.

Scheme 10. Synthesis of **35**.



35

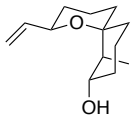
(2*E*,11*Z*)-1-Hydroxytrideca-2,11-dien-7-one (35)

^{1}H NMR (500 MHz, $CDCl_3$): δ 5.61-5.69 (m, 2H), 5.47 (dqt, *J* = 12.9, 7.3, 1.7 Hz, 1H), 5.34 (dtq, *J* = 12.4, 7.2, 1.6 Hz, 1H), 4.09 (d, *J* = 3.0 Hz, 2H), 2.40 (t, *J* = 7.2 Hz, 2H), 2.39 (t, *J* = 7.2 Hz, 2H), 2.02-2.10 (m, 4H), 1.67, (pent, *J* = 7.6 Hz, 2H), 1.64 (pent, *J* = 7.5 Hz, 2H), 1.59 (ddt, *J* = 6.9, 1.8, 0.8 Hz, 3H), 1.51-1.58 (m, 1H)

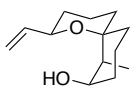
^{13}C NMR (125 MHz, $CDCl_3$): δ 210.9, 132.2, 129.8, 129.6, 124.8, 63.7, 42.2, 42.0, 31.6, 26.2, 23.6, 23.1, 12.8

HRMS (ESI): *m/z* calcd for $C_{13}H_{22}O_2Na$ $[M+Na]^+$ 233.1512, found 233.1508

IR (thin film): 3404, 3115, 2929, 1707, 1408, 1371, 1266, 1087, 971, 736 cm^{-1}



36



37

(2*R*,6*R*,7*S*,8*S*)-7-Methyl-2-vinyl-1-oxaspiro[5.5]undecan-8-ol (36) and (2*R*,6*R*,7*S*,8*R*)-7-methyl-2-vinyl-1-oxaspiro[5.5]undecan-8-ol (37)

The general procedure for spirocycle synthesis was followed with **35** (10 mg, 0.05 mmol) and Re_2O_7 (3 mg, 0.006 mmol) in DCM (0.6 mL) for 1 h at 0 °C. The crude reaction mixture was then purified via gradient-elution flash column chromatography with 0-10% ethyl acetate in hexanes as

eluent to give **36** and **37** (8.1 mg, 81%) with a diastereomeric ratio of 4:1 and **36** as the major isomer.

Major (slower-eluting) isomer (36)

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.83 (ddd, *J* = 16.9, 10.4, 5.8 Hz, 1H), 5.22 (dt, *J* = 16.9, 1.6 Hz, 1H), 5.07 (dt, *J* = 10.5, 1.6 Hz, 1H), 4.00 (dd, *J* = 9.2, 6.2 Hz, 1H), 3.79 (td, *J* = 9.9, 4.4 Hz, 1H), 2.39-2.46 (m, 1H), 1.96 (dt, *J* = 13.7, 4.0 Hz, 1H), 1.68-1.76 (m, 3H), 1.61-1.66 (m, 4H), 1.46-1.54 (m, 1H), 1.28-1.38 (m, 2H), 1.18-1.25 (m, 2H), 0.98 (d, *J* = 7.0 Hz, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 139.9, 114.7, 76.1, 70.7, 70.5, 53.4, 36.4, 34.8, 30.8, 29.7, 26.2, 23.6, 18.7

HRMS (ESI): *m/z* calcd for $C_{13}H_{23}O_2$ $[M+H]^+$ 211.1693, found 211.1687

IR (thin film): 3402, 2956, 2869, 1467, 1284, 1042, 917, 735 cm^{-1}

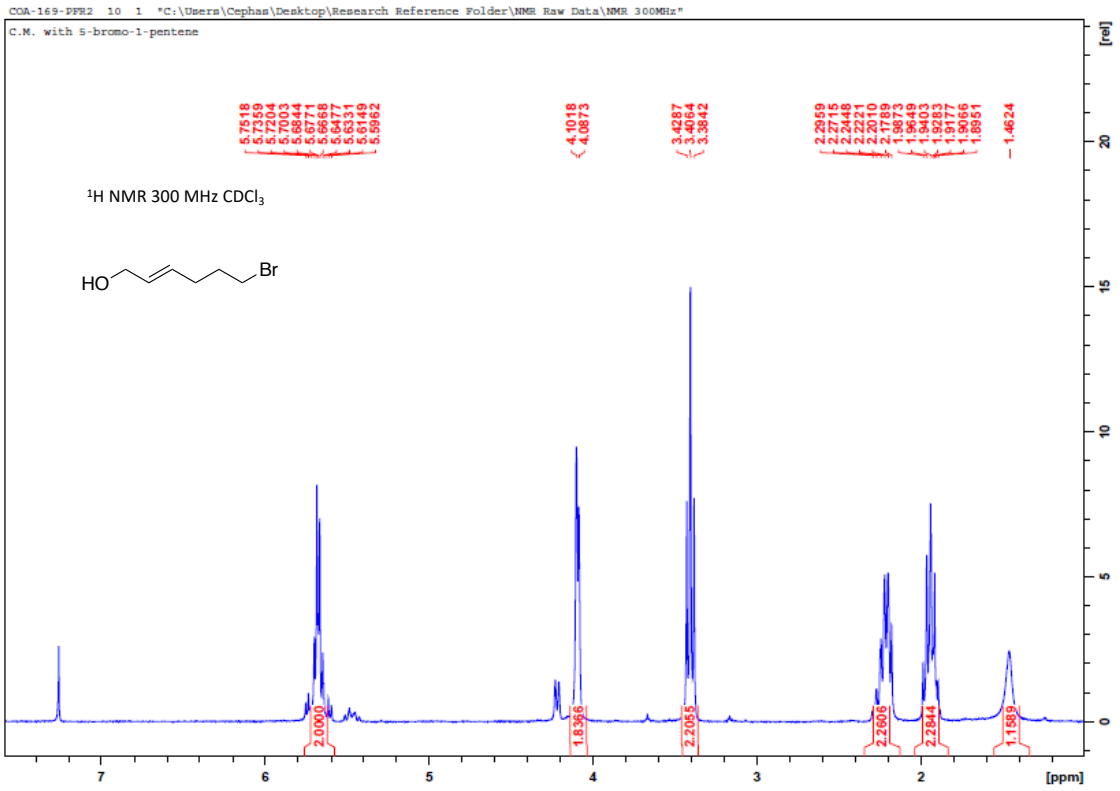
Minor (faster-eluting) isomer (37)

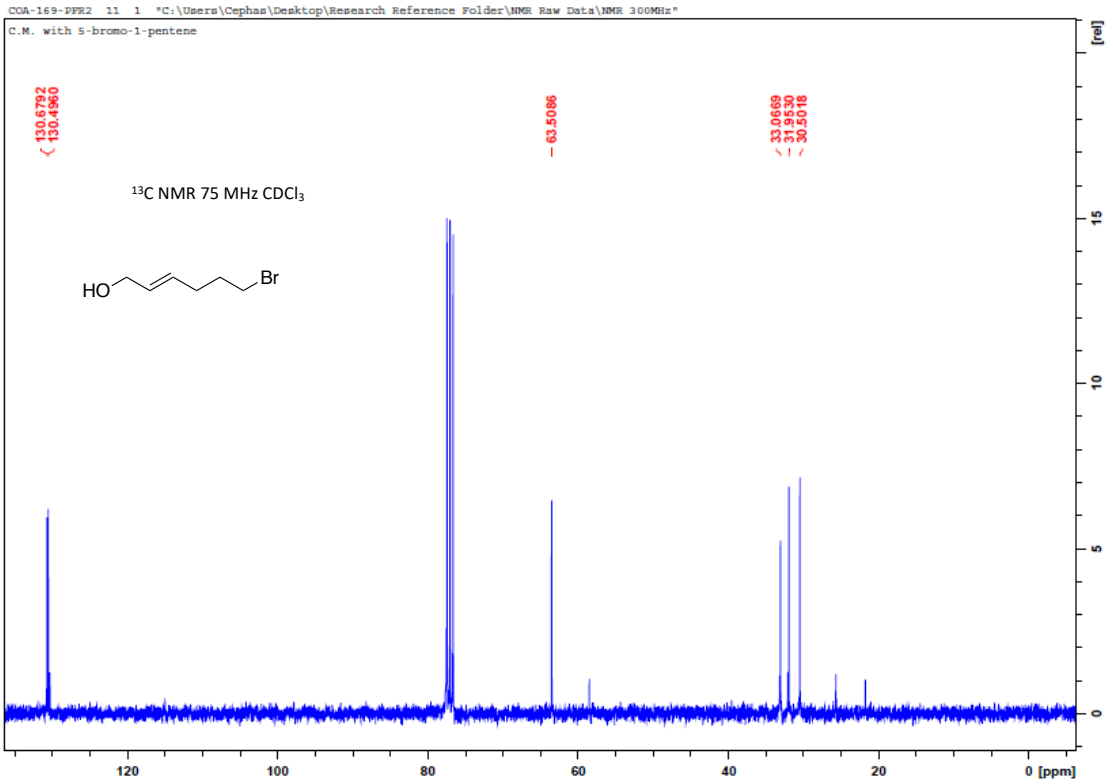
^{1}H NMR (400 MHz, $CDCl_3$): δ 5.82 (ddd, *J* = 17.3, 10.6, 5.9 Hz, 1H), 5.22 (dt, *J* = 17.3, 1.6 Hz, 1H), 5.05 (dt, *J* = 10.6, 1.6 Hz, 1H), 4.16 (dd, *J* = 11.4, 3.4 Hz, 1H), 4.02 (dq, *J* = 11.6, 4.4 Hz, 1H), 3.78 (d, *J* = 11.6 Hz, 1H), 2.63 (pent, *J* = 6.8 Hz, 1H), 2.34-2.43 (m, 1H), 2.00-2.08 (m, 1H), 1.79 (dt, *J* = 11.4, 4.5 Hz, 1H), 1.71 (ddt, *J* = 13.5, 3.4, 1.5 Hz, 1H), 1.62-1.65 (m, 2H), 1.47-1.52 (m, 2H), 1.37-1.45 (m, 2H), 1.27-1.30 (m, 2H), 0.86 (d, *J* = 6.9 Hz, 3H)

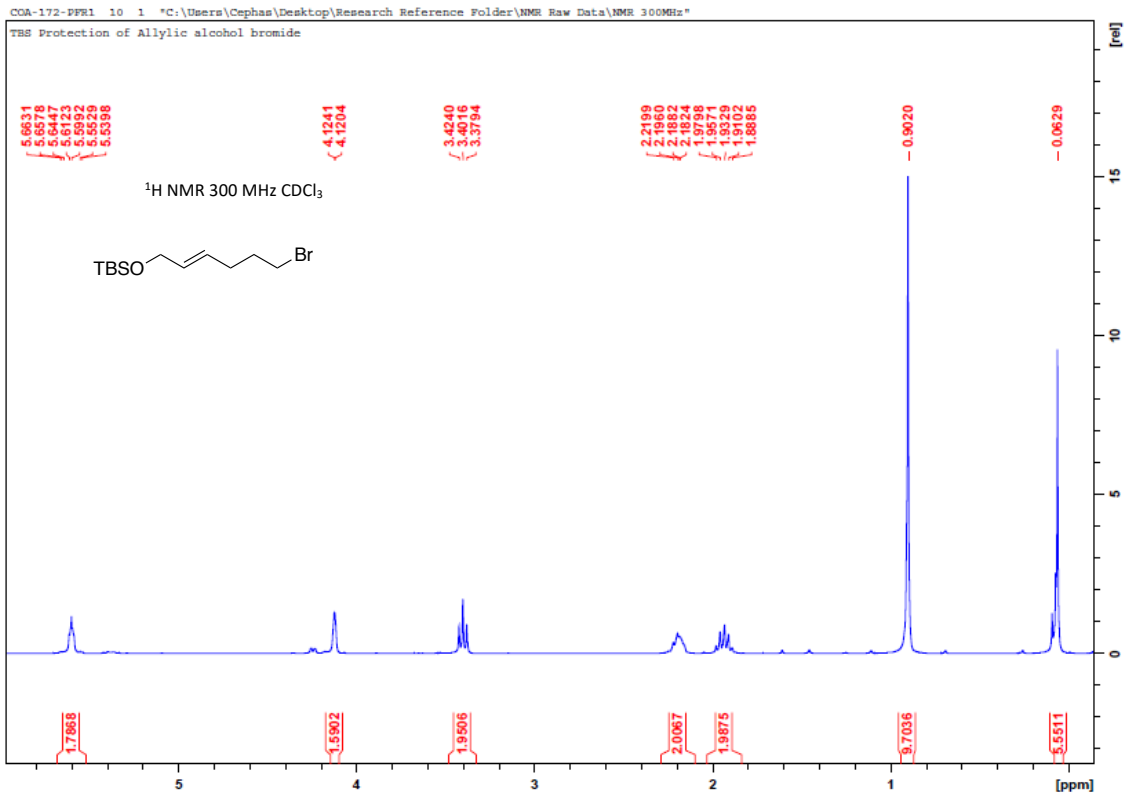
^{13}C NMR (100 MHz, $CDCl_3$): δ 140.4, 113.9, 75.32, 70.2, 69.1, 68.5, 34.3, 33.4, 33.0, 31.4, 28.8, 19.2, 18.4

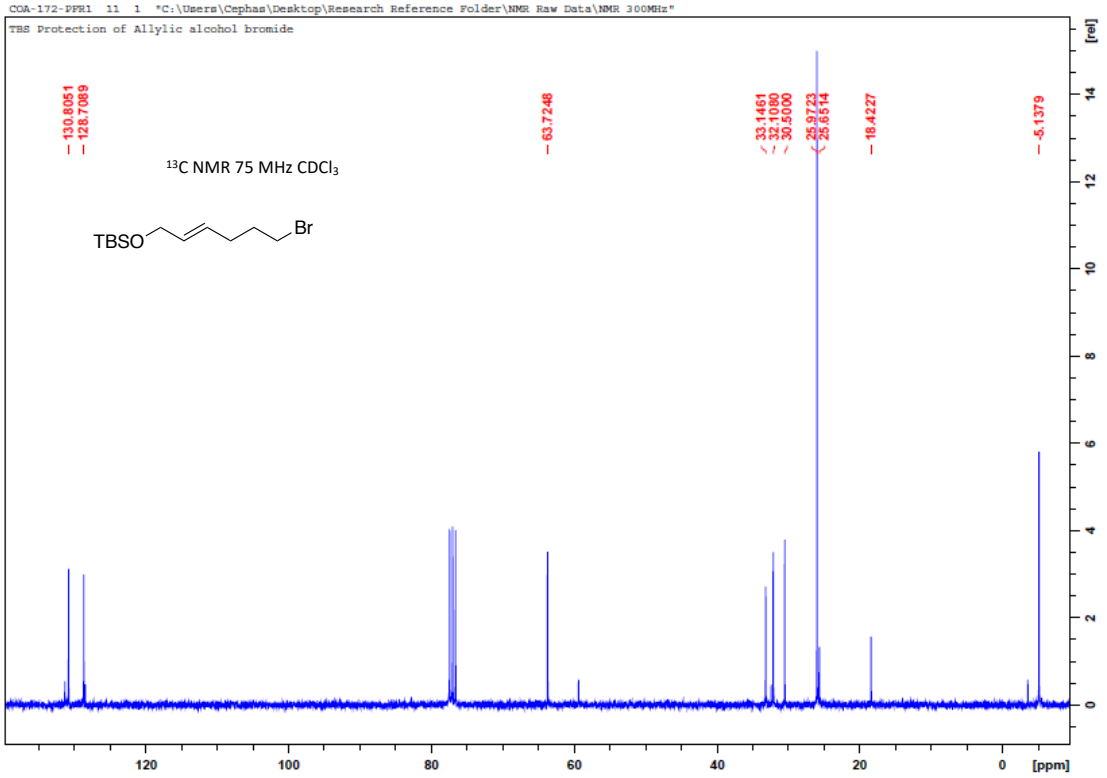
HRMS (ESI): *m/z* calcd for $C_{13}H_{23}O_2$ $[M+H]^+$ 211.1693, found 211.1687

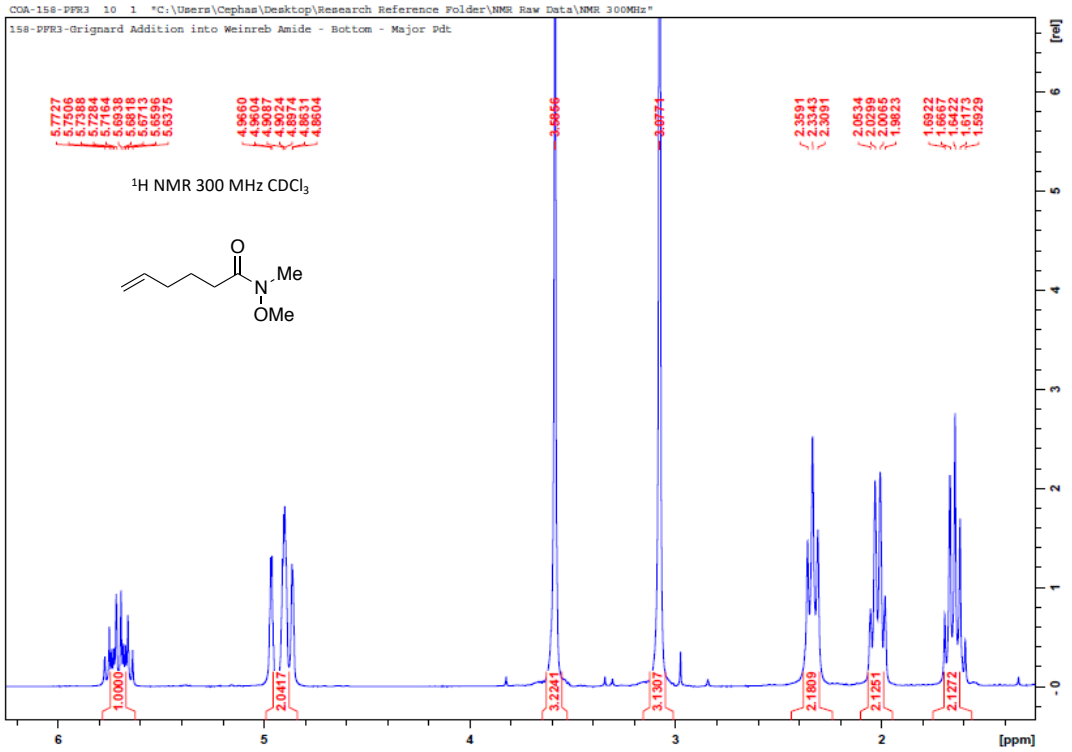
IR (thin film): 3403, 2981, 2876, 1414, 1254, 1012, 937, 731 cm^{-1}

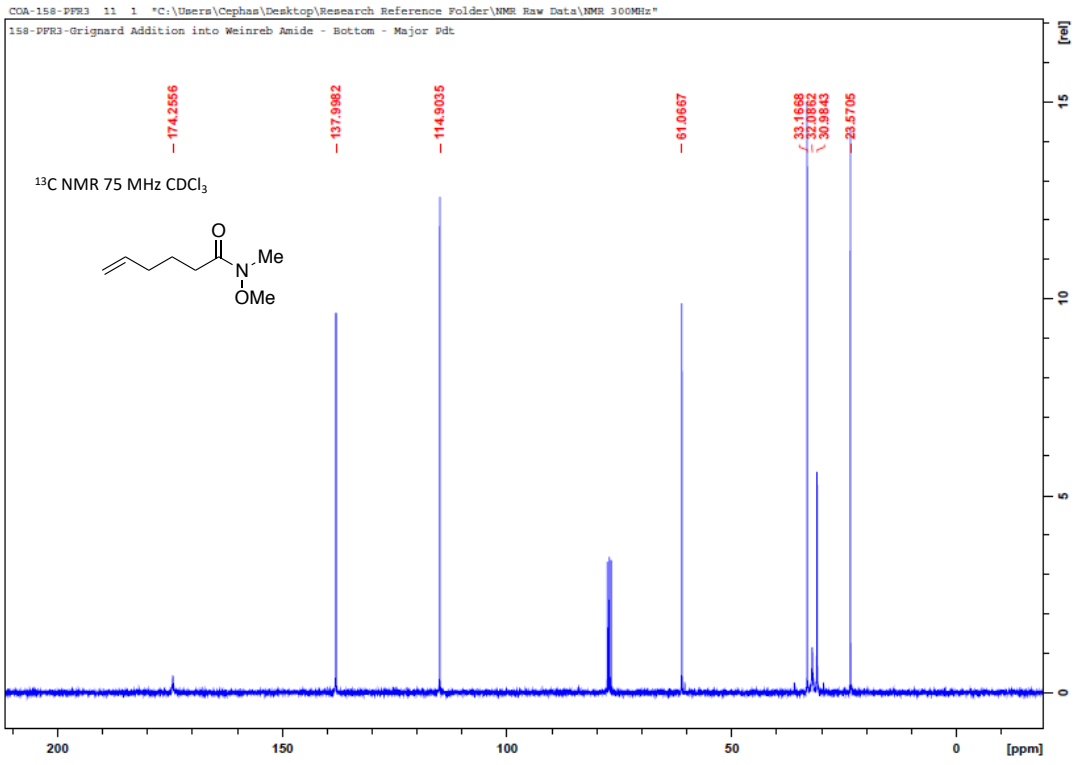

COA-169-PFR2 10 1 "C:\Users\Cephas\Desktop\Research Reference Folder\NMR Raw Data\NMR 300MHz"
C.M. with 5-bromo-1-pentene
5.7518
5.7359
5.7204
5.7003
5.6844
5.6774
5.6668
5.6477
5.6331
5.6149
5.5962
4.1018
4.0873
3.4287
3.4064
3.3842
2.2959
2.2715
2.2448
2.2221
2.2010
2.1789
1.9873
1.9649
1.9403
1.9283
1.9177
1.9066
1.8951
1.4624
[rel]
^{1}H NMR 300 MHz $CDCl_3$
HO
Br
2.0000
1.8366
2.2055
2.2605
2.2844
1.1589
[ppm]

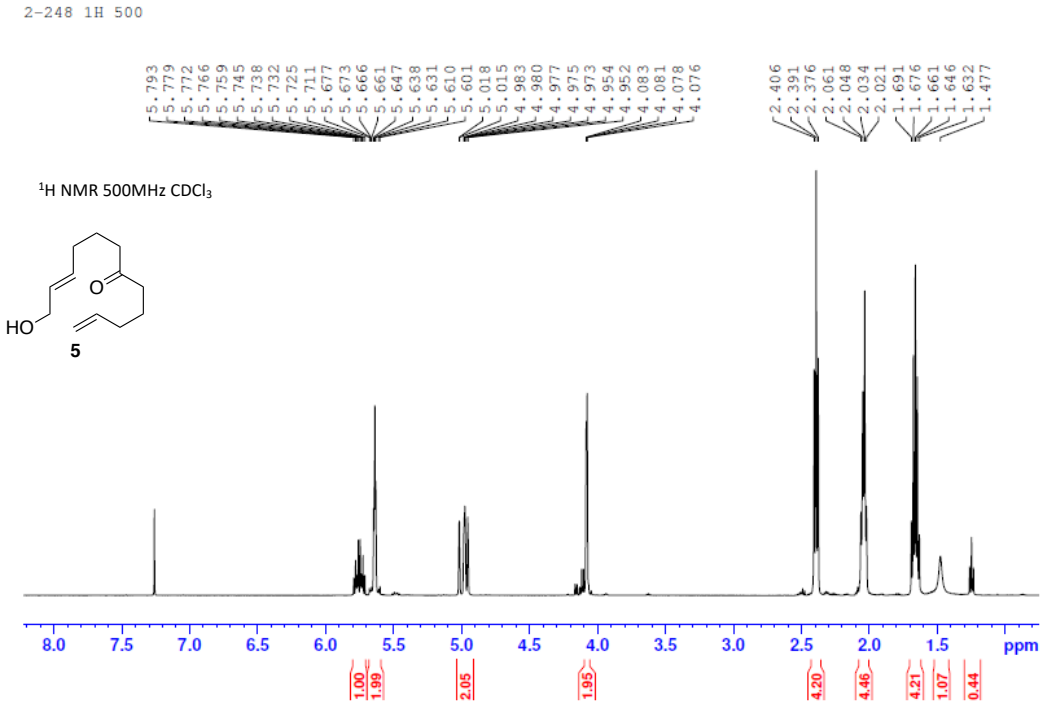

COA-169-PFR2 11 1 "C:\Users\Cephas\Desktop\Research Reference Folder\NMR Raw Data\NMR 300MHz"
C.M. with 5-bromo-1-pentene
130.6792
130.4960
63.5086
33.0669
31.9530
30.5018
[rel]
^{13}C NMR 75 MHz $CDCl_3$
HO
Br
[ppm]

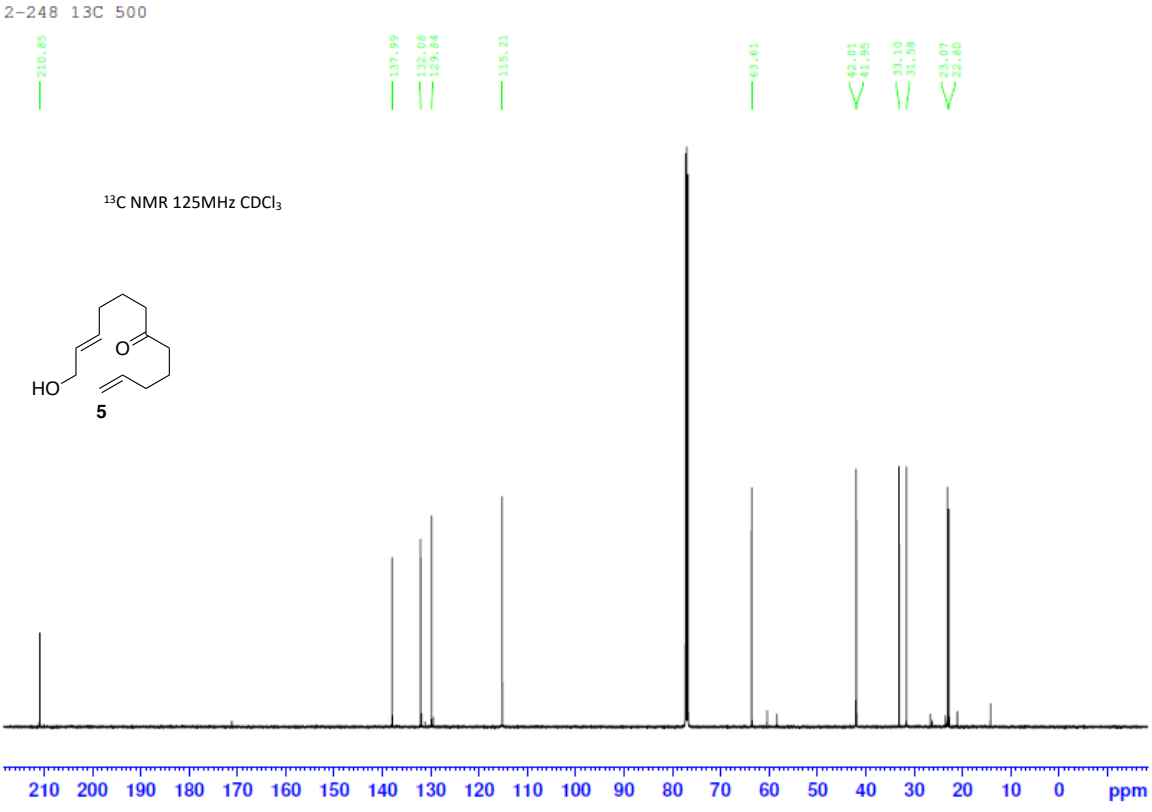

COA-172-PFR1 10 1 "C:\Users\Cephas\Desktop\Research Reference Folder\NMR Raw Data\NMR 300MHz"
TBS Protection of Allylic alcohol bromide
5.6631
5.6578
5.6447
5.6123
5.5992
5.5859
5.5398
4.1241
4.1204
3.4240
3.4016
3.3794
2.2199
2.1960
2.1882
2.1824
1.9798
1.9571
1.9329
1.9102
1.8885
0.9020
0.0629
1H NMR 300 MHz CDCl3
TBSO
Br
1.7868
1.5902
1.9506
2.0067
1.9875
9.7036
5.5511
[rel]
[ppm]

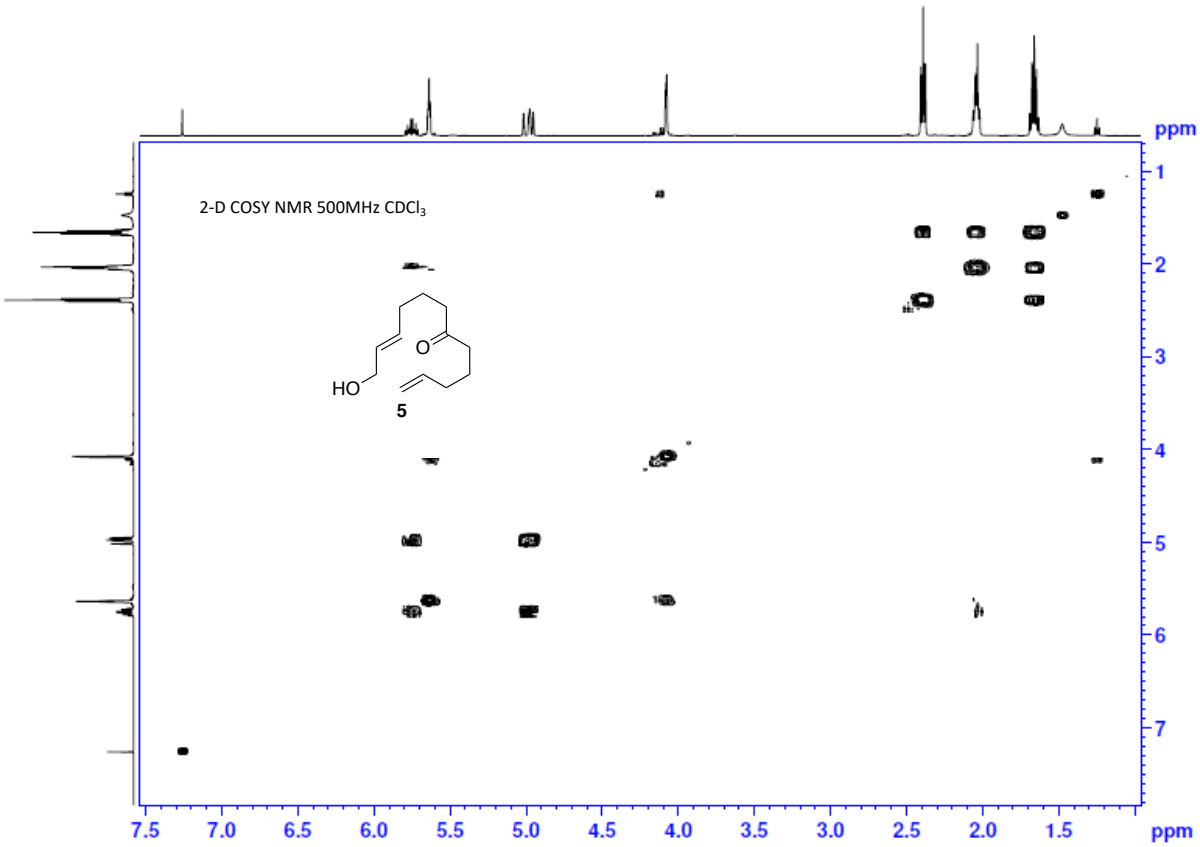

COA-172-PFR1 11 1 "C:\Users\Cephas\Desktop\Research Reference Folder\NMR Raw Data\NMR 300MHz"
TBS Protection of Allylic alcohol bromide
130.8051
126.7089
63.7248
33.1461
32.1080
30.5000
25.9723
25.8514
18.4227
-5.1379
13C NMR 75 MHz CDCl3
TBSO
Br
[rel]
[ppm]

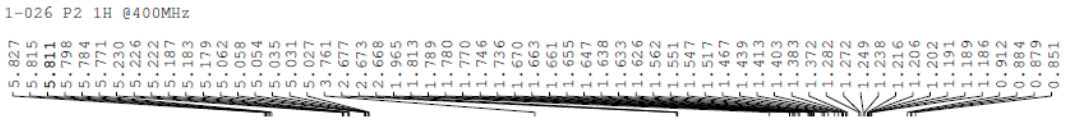

COA-158-PPR3 10 1 "C:\Users\Cephas\Desktop\Research Reference Folder\NMR Raw Data\NMR 300MHz"
158-PPR3-Grignard Addition into Weinreb Amide - Bottom - Major Pdt
5.7727
5.7506
5.7388
5.7284
5.7154
5.6938
5.6818
5.6713
5.6596
5.6375
4.9660
4.9604
4.9087
4.9024
4.8974
4.8631
4.8604
3.6856
3.6771
2.3591
2.3343
2.3091
2.0534
2.0299
2.0065
1.9823
1.6922
1.6667
1.6422
1.6173
1.5929
1.0000
2.0417
3.2241
3.1307
2.1809
2.1251
2.1272
[rel]
[ppm]
1H NMR 300 MHz CDCl3
O
N
Me
OMe


COA-158-PPR3 11 1 "C:\Users\Cephas\Desktop\Research Reference Folder\NMR Raw Data\NMR 300MHz"
158-PPR3-Grignard Addition into Weinreb Amide - Bottom - Major Pdt
174.2556
137.9862
114.9035
61.0667
33.1668
27.0062
30.9843
23.5705
[rel]
[ppm]
13C NMR 75 MHz CDCl3
O
N
Me
OMe

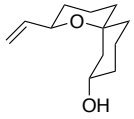

2-248 1H 500
5.793
5.779
5.772
5.766
5.759
5.745
5.738
5.732
5.725
5.711
5.677
5.673
5.666
5.661
5.647
5.638
5.631
5.610
5.601
5.018
5.015
4.983
4.980
4.977
4.975
4.973
4.954
4.952
4.083
4.081
4.078
4.076
2.406
2.391
2.376
2.061
2.048
2.034
2.021
1.691
1.676
1.661
1.646
1.632
1.477
^{1}H NMR 500MHz $CDCl_3$
HO
O
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
ppm
1.00
1.99
2.05
1.95
4.20
4.46
4.21
1.07
0.44


2-248 13C 500
210.85
137.99
132.08
129.84
115.21
63.61
42.01
41.95
33.10
31.58
23.07
22.80
^{13}C NMR 125MHz $CDCl_3$
HO
O
5
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


2-D COSY NMR 500MHz CDCl3
HO
O
5
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
ppm

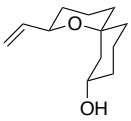


^{1}H NMR 400MHz $CDCl_3$

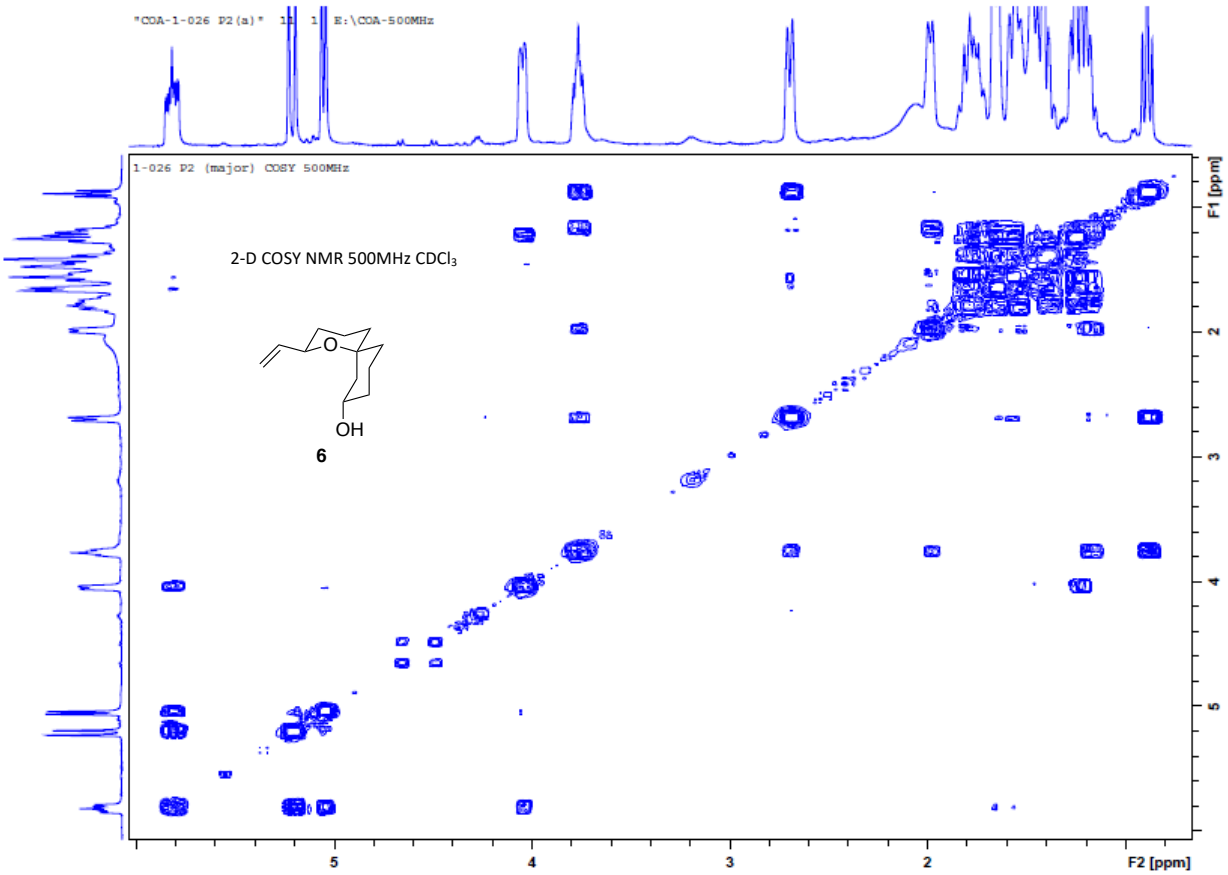


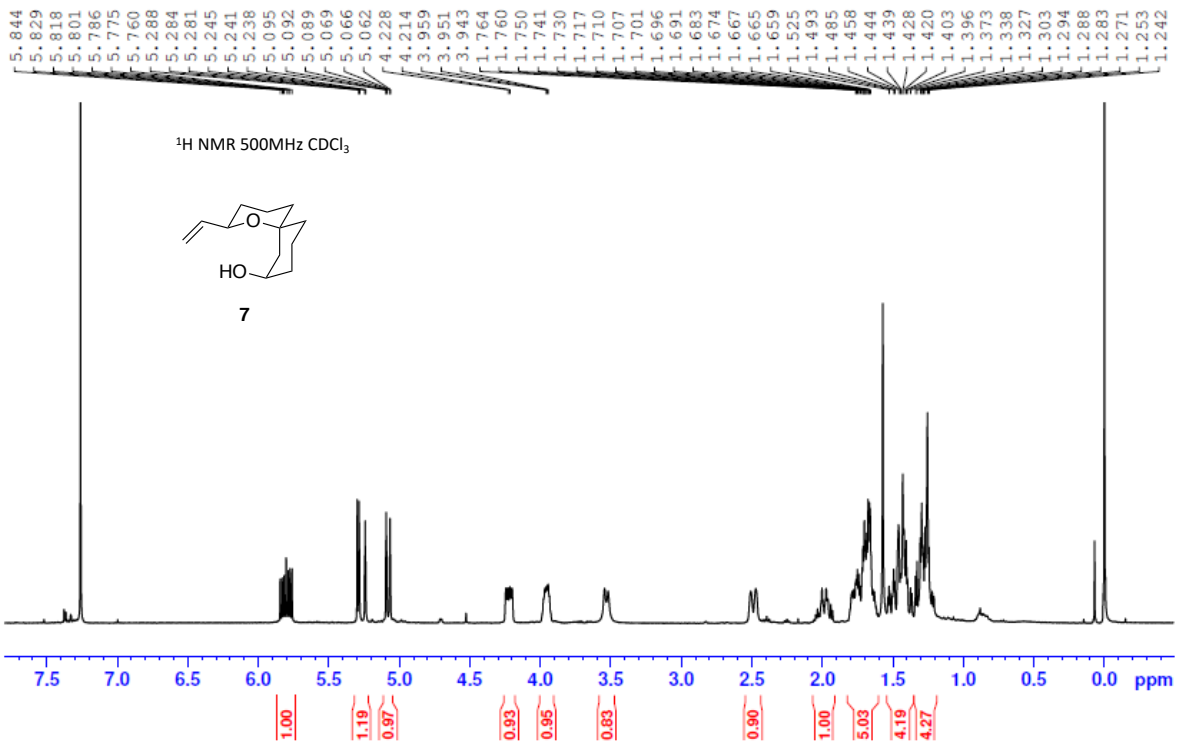
6

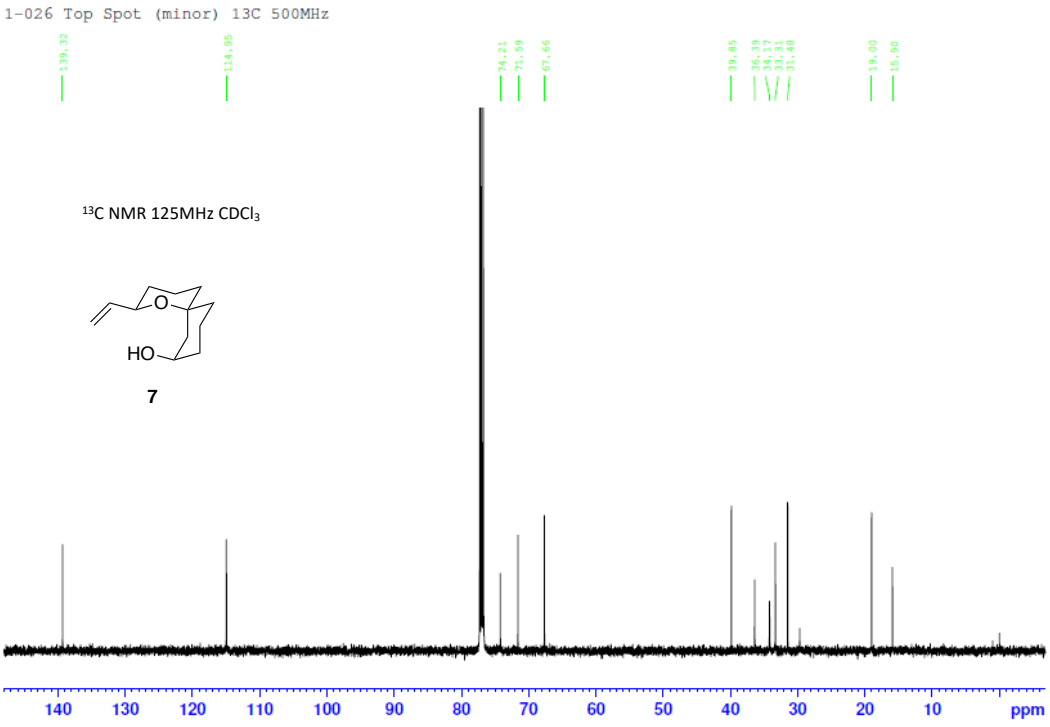
^{13}C NMR 125MHz $CDCl_3$

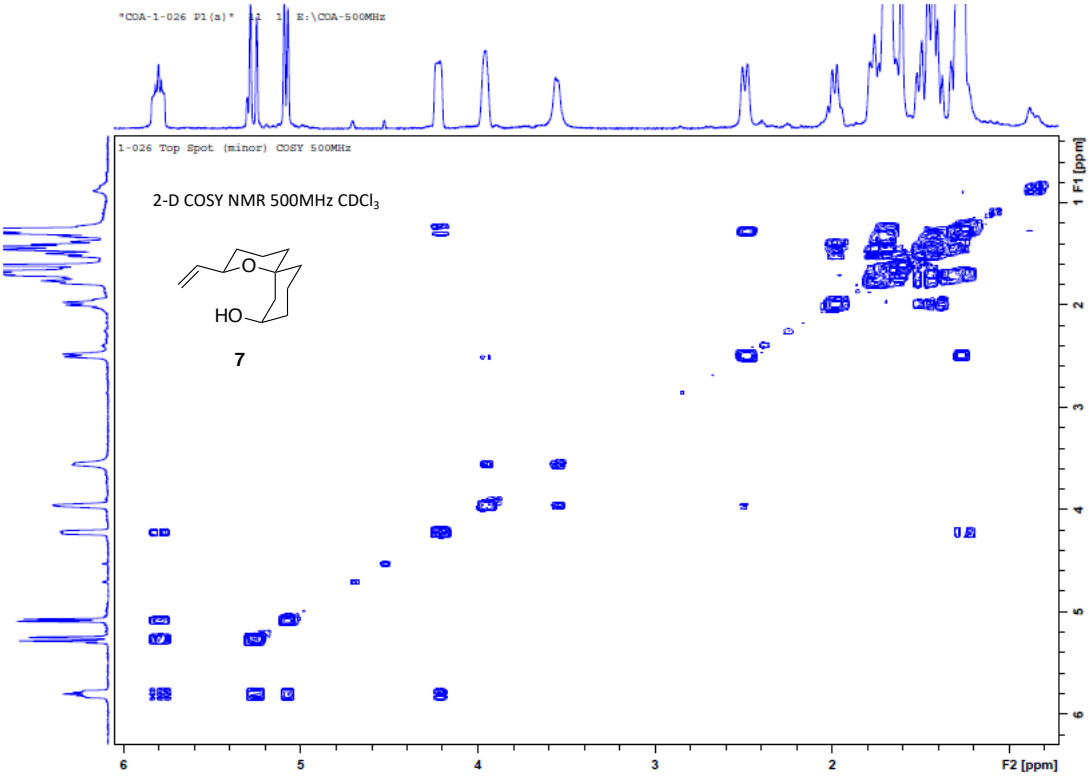


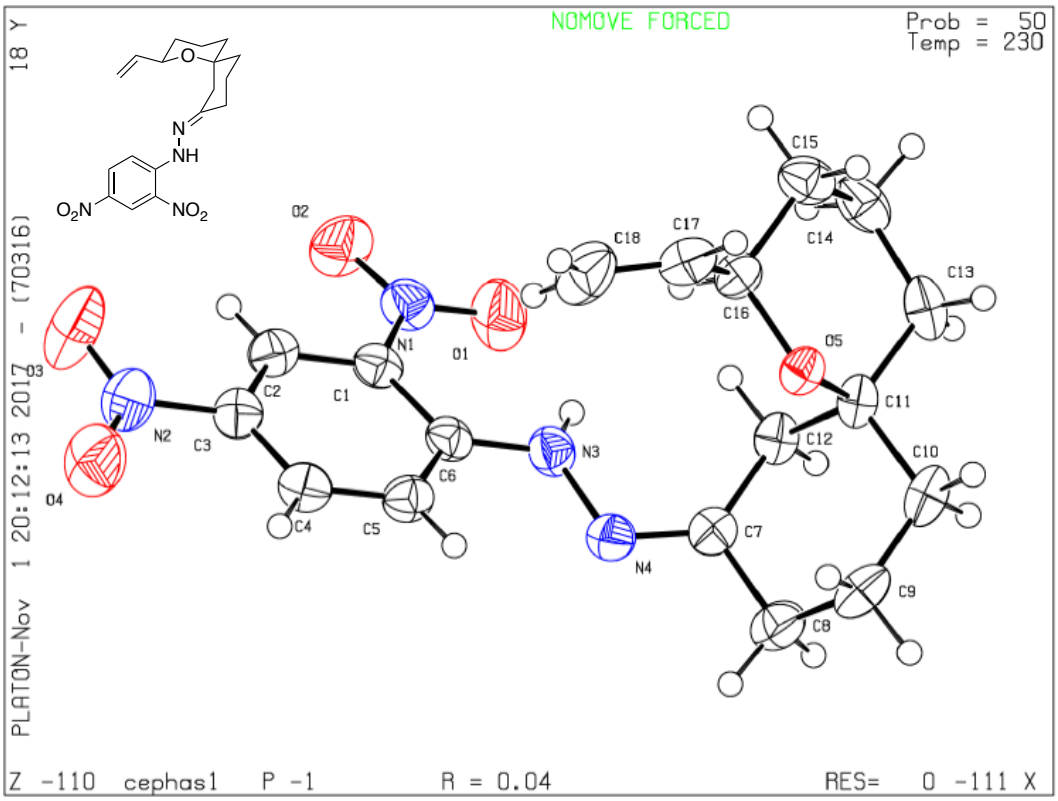
6


"COA-1-026 P2(a)* 1 1 E:\COA-500MHz
1-026 P2 (major) COSY 500MHz
2-D COSY NMR 500MHz CDCl3
O
OH
6
F1 [ppm]
F2 [ppm]
5
4
3
2


5.844
5.829
5.818
5.801
5.786
5.775
5.760
5.288
5.284
5.281
5.245
5.241
5.238
5.095
5.092
5.089
5.069
5.066
5.062
4.228
4.214
3.959
3.951
3.943
1.764
1.760
1.750
1.741
1.730
1.717
1.710
1.707
1.701
1.696
1.691
1.683
1.674
1.667
1.665
1.659
1.525
1.493
1.485
1.458
1.444
1.439
1.428
1.420
1.403
1.396
1.373
1.338
1.327
1.303
1.294
1.288
1.283
1.271
1.253
1.242
1H NMR 500MHz CDCl3
O
HO
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
0.0
ppm
1.00
1.19
0.97
0.93
0.95
0.83
0.90
1.00
5.03
4.19
4.27


1-026 Top Spot (minor) 13C 500MHz
139.32
114.95
74.21
71.59
67.66
39.85
36.39
34.17
33.31
31.48
19.00
15.90
^{13}C NMR 125MHz $CDCl_3$
O
HO
7
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


"COA-1-026 P1(a)" 11 1 E:\COA-500MHz
1-026 Top Spot (minor) COSY 500MHz
2-D COSY NMR 500MHz $CDCl_3$
O
HO
7
1 F1 [ppm]
2
3
4
5
6
6
5
4
3
2
F2 [ppm]



```
Bond precision:  C-C = 0.0019 A          Wavelength=1.54178

Cell:         a=8.9124(3)        b=9.5638(3)       c=11.5721(4)
              alpha=78.2389(17)  beta=76.9753(19)  gamma=72.7914(19)
Temperature:  230 K

                 Calculated                Reported
Volume           907.95(5)                 907.94(5)
Space group      P -1                      P -1
Hall group       -P 1                      -P 1
Moiety formula   C18 H22 N4 O5             ?
Sum formula      C18 H22 N4 O5             C18 H22 N4 O5
Mr               374.40                    374.39
Dx,g cm-3        1.370                     1.369
Z                2                         2
Mu (mm-1)        0.847                     0.847
F000             396.0                     396.0
F000'            397.31
h,k,lmax         10,11,13                  10,11,13
Nref             3335                      3244
Tmin,Tmax        0.850,0.903               0.750,0.910
Tmin'            0.844

Correction method= # Reported T Limits: Tmin=0.750 Tmax=0.910
AbsCorr = MULTI-SCAN

Data completeness= 0.973          Theta(max)= 68.440

R(reflections)= 0.0355( 2931)     wR2(reflections)= 0.1248( 3244)

S = 1.488                 Npar= 332
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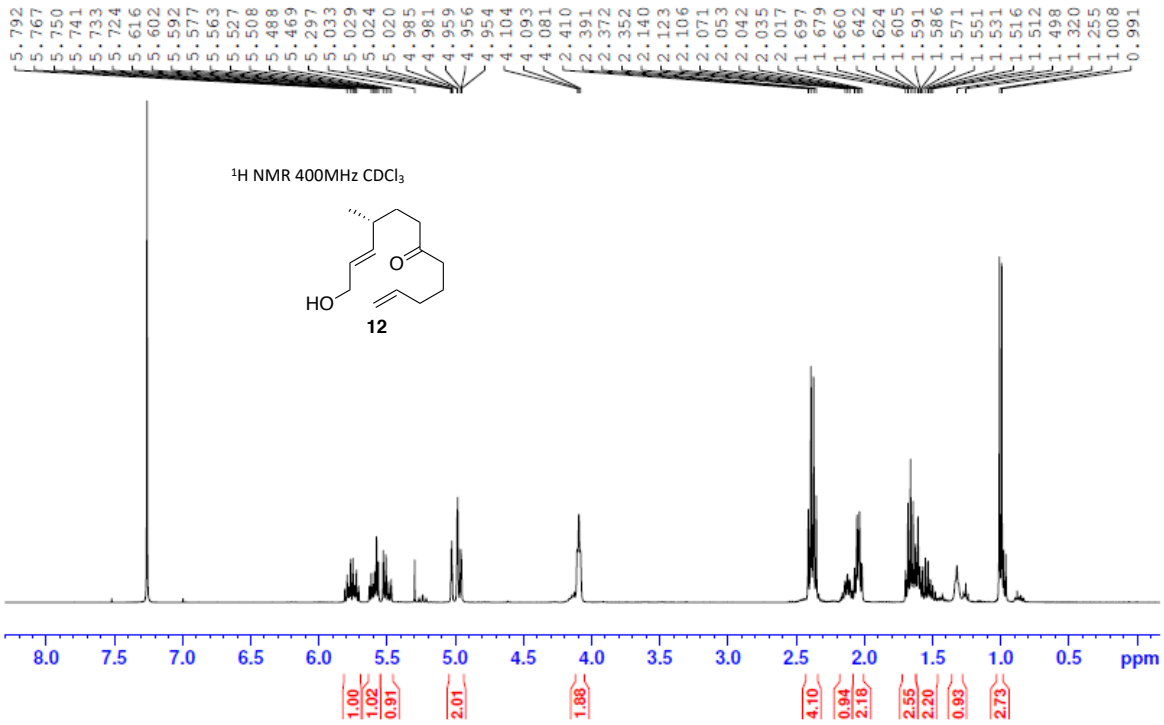
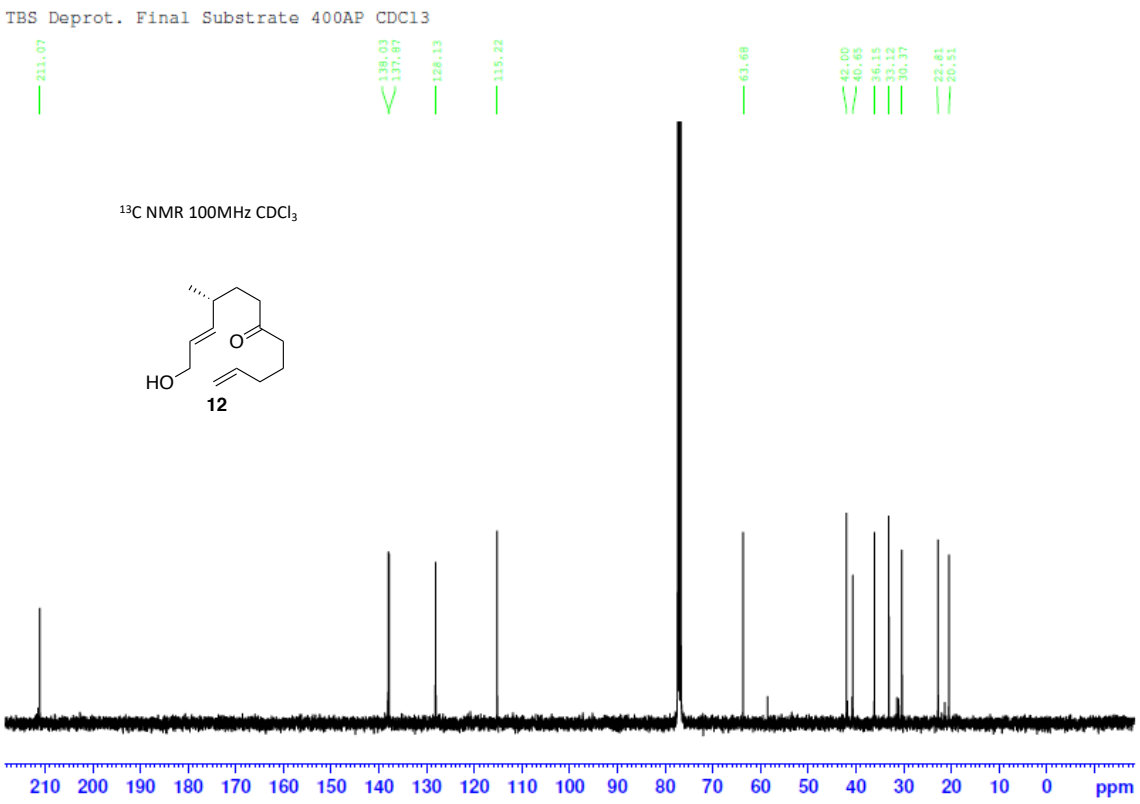
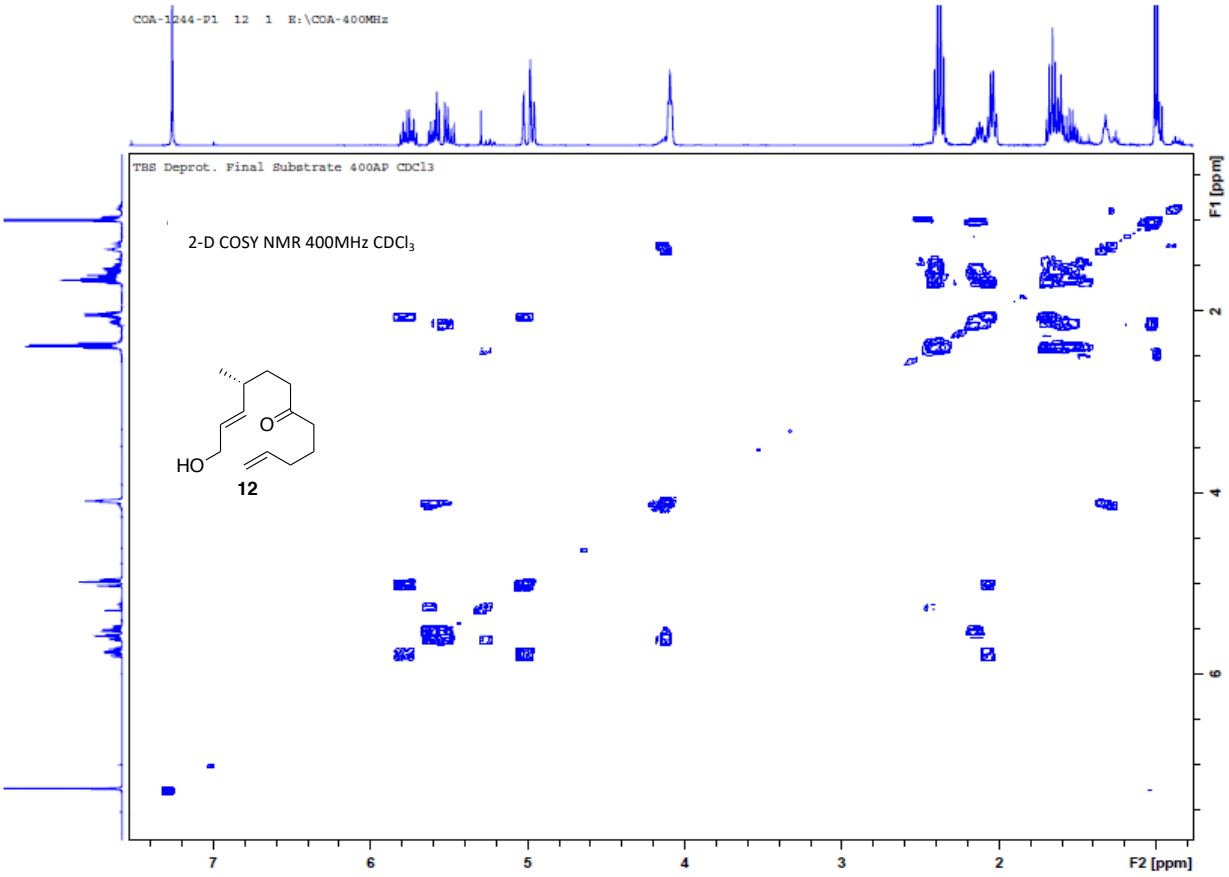
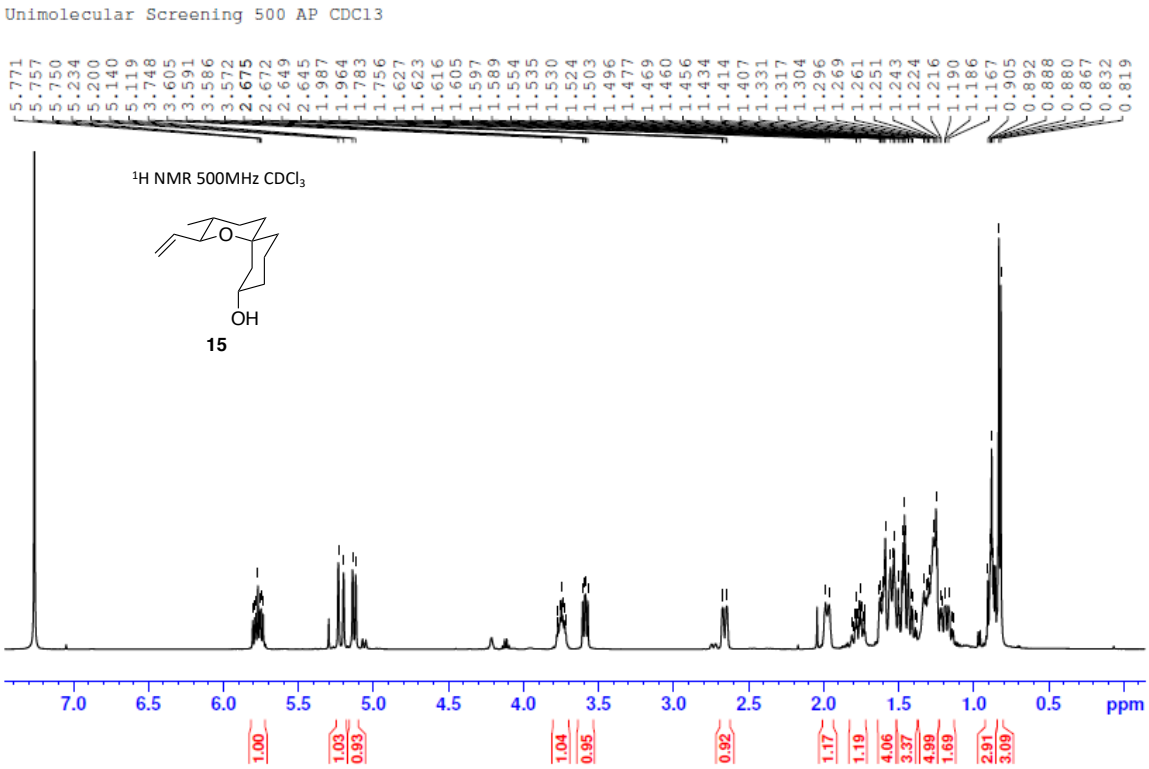
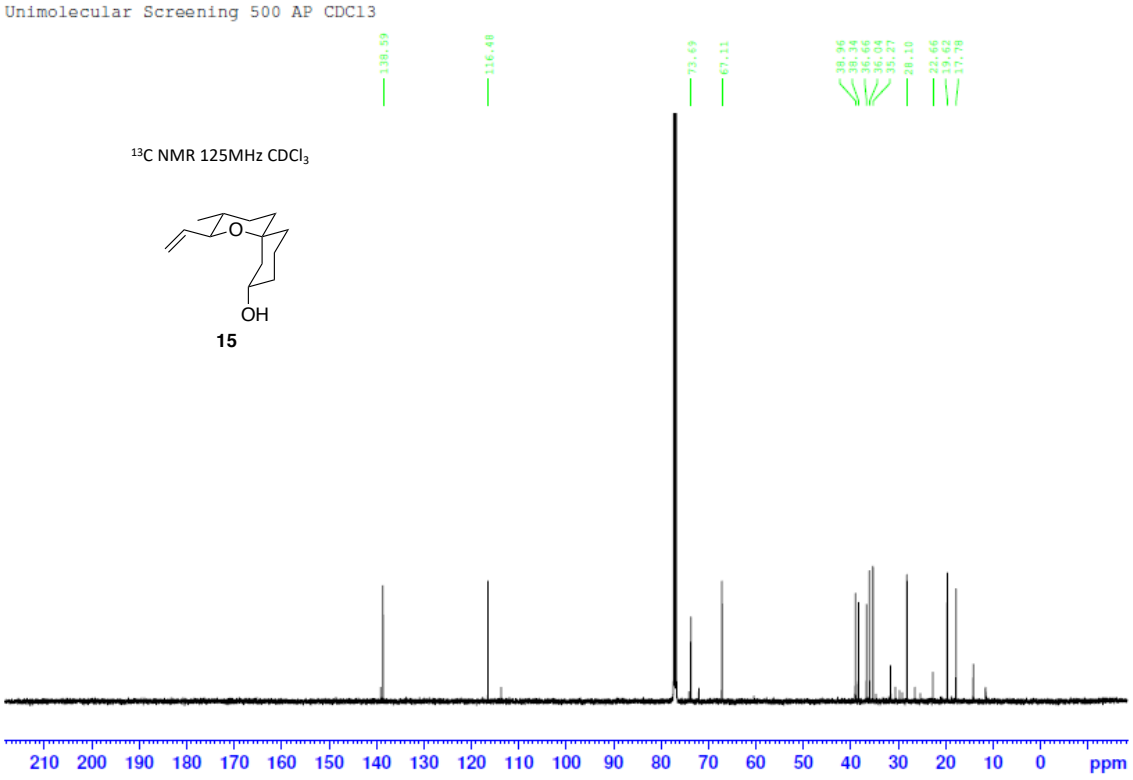
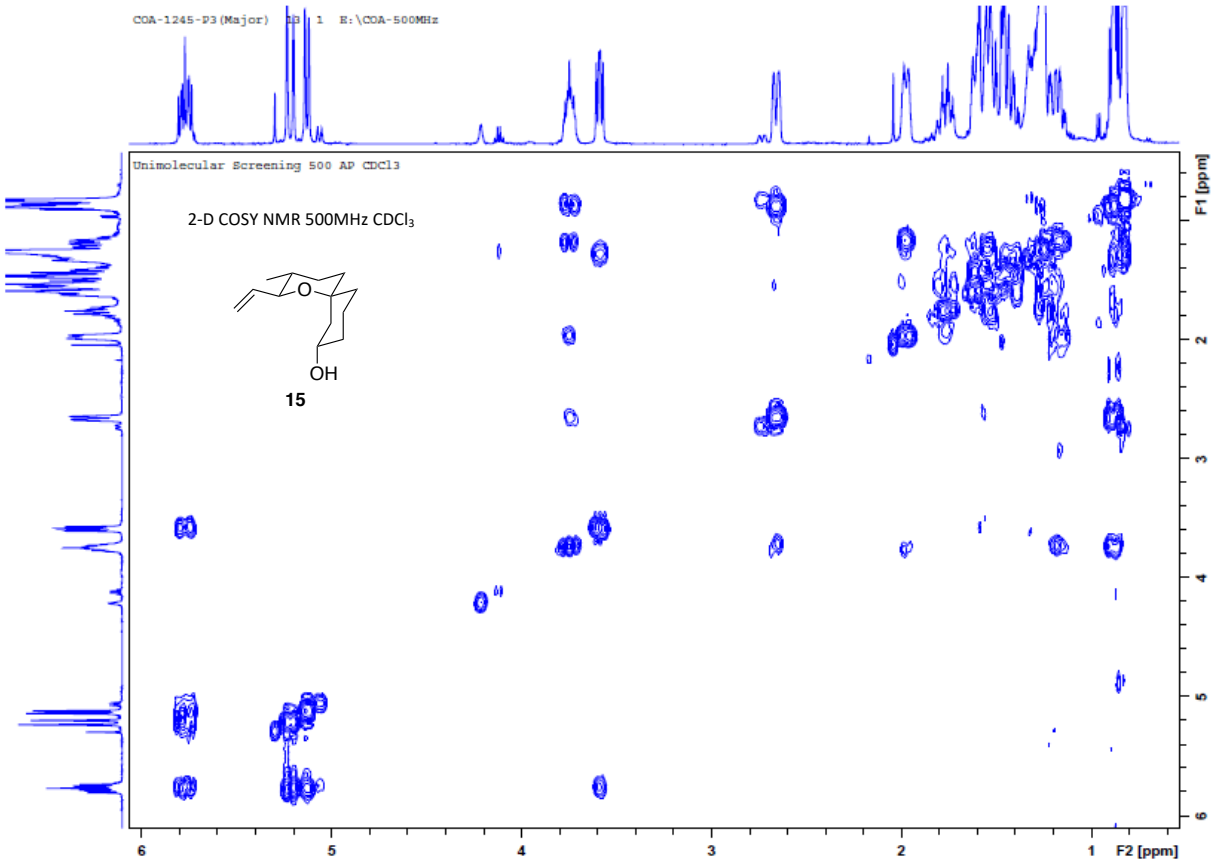

5.792
5.767
5.750
5.741
5.733
5.724
5.616
5.602
5.592
5.577
5.563
5.527
5.508
5.488
5.469
5.297
5.033
5.029
5.024
5.020
4.985
4.981
4.959
4.956
4.954
4.104
4.093
4.081
2.410
2.391
2.372
2.352
2.140
2.123
2.106
2.071
2.053
2.042
2.035
2.017
1.697
1.679
1.660
1.642
1.624
1.605
1.591
1.586
1.571
1.551
1.531
1.516
1.512
1.498
1.320
1.255
1.008
0.991
1H NMR 400MHz CDCl3
HO
O
12
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
1.00
1.02
0.91
2.01
1.88
4.10
0.94
2.18
2.55
2.20
0.93
2.73

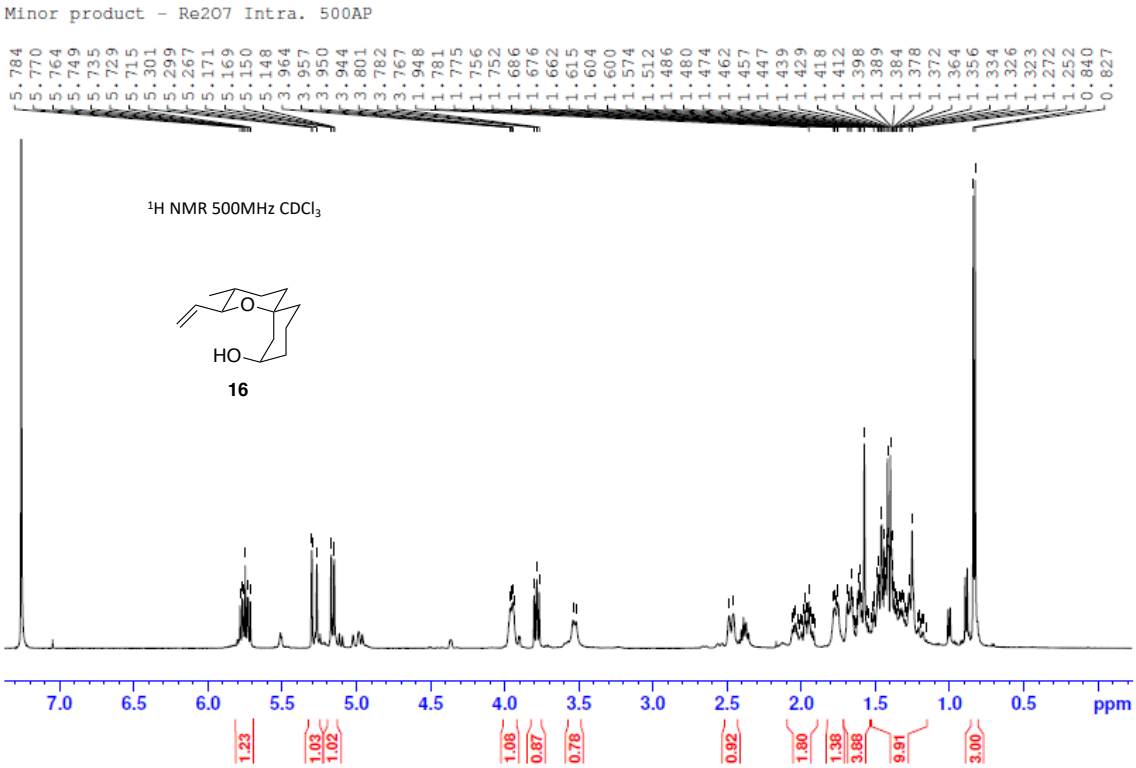

TBS Deprot. Final Substrate 400AP CDCl3
211.07
138.03
137.87
128.13
115.22
63.68
42.60
40.65
36.15
33.12
30.37
22.81
20.51
13C NMR 100MHz CDCl3
HO
O
12
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

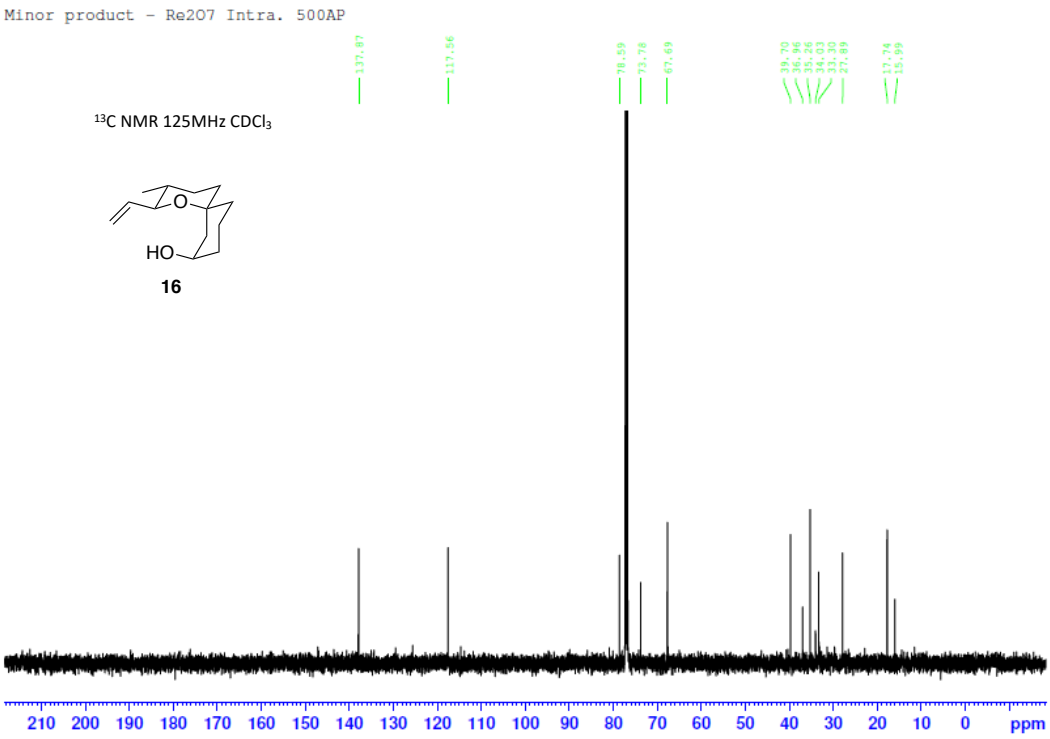

COA-1244-P1 12 1 E:\COA-400MHz
TBS Deprot. Final Substrate 400AP CDCl3
2-D COSY NMR 400MHz CDCl3
HO
O
12
F1 [ppm]
F2 [ppm]
7
6
5
4
3
2
2
4
6

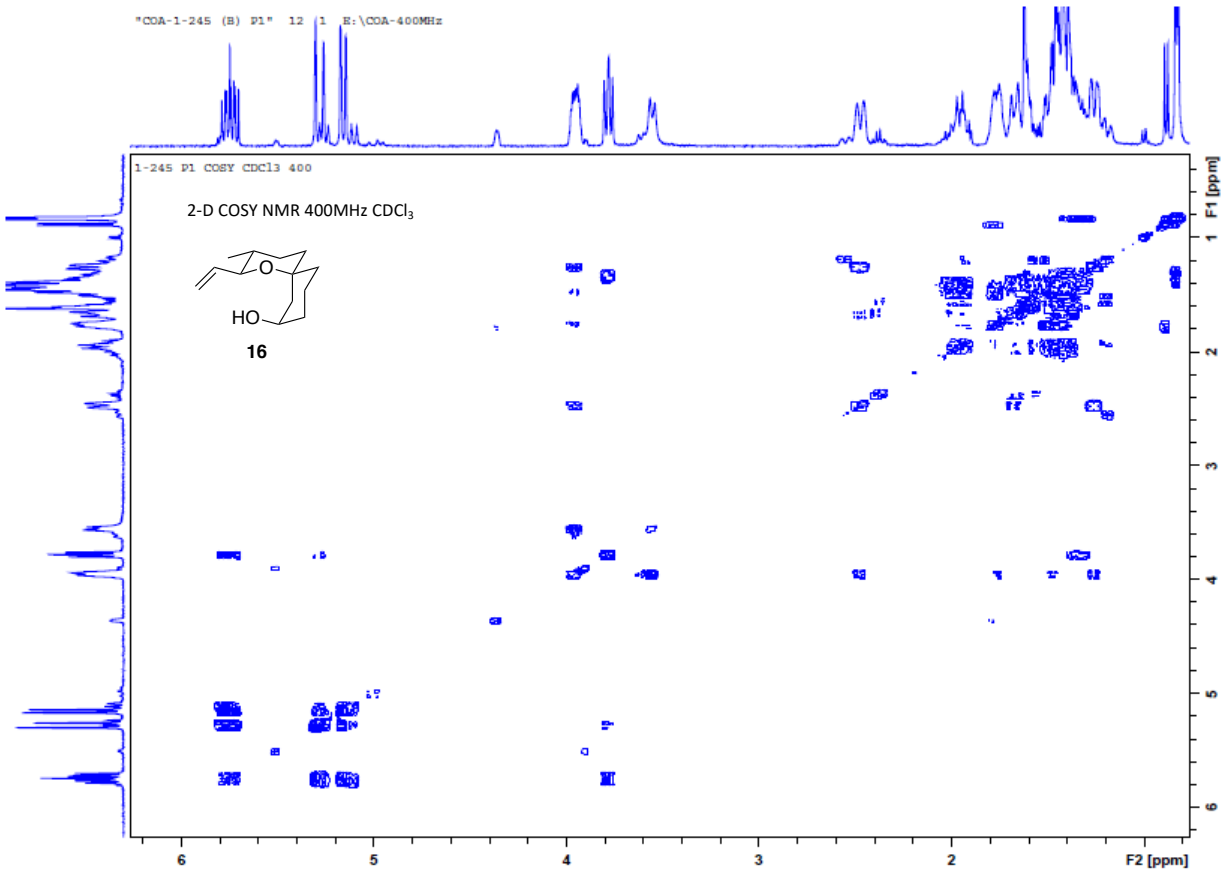

Unimolecular Screening 500 AP CDC13
5.771 5.757 5.750 5.234 5.200 5.140 5.119 3.748 3.605 3.591 3.586 3.572 2.675 2.672 2.649 2.645 1.987 1.964 1.783 1.756 1.627 1.623 1.616 1.605 1.597 1.589 1.554 1.535 1.530 1.524 1.503 1.496 1.477 1.469 1.460 1.456 1.434 1.414 1.407 1.331 1.317 1.304 1.296 1.269 1.261 1.251 1.243 1.224 1.216 1.190 1.186 1.167 0.905 0.892 0.888 0.880 0.867 0.832 0.819
1H NMR 500MHz CDCl3
OH
15
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
1.00 1.03 0.93 1.04 0.95 0.92 1.17 1.19 4.06 3.37 4.99 1.69 2.91 3.09

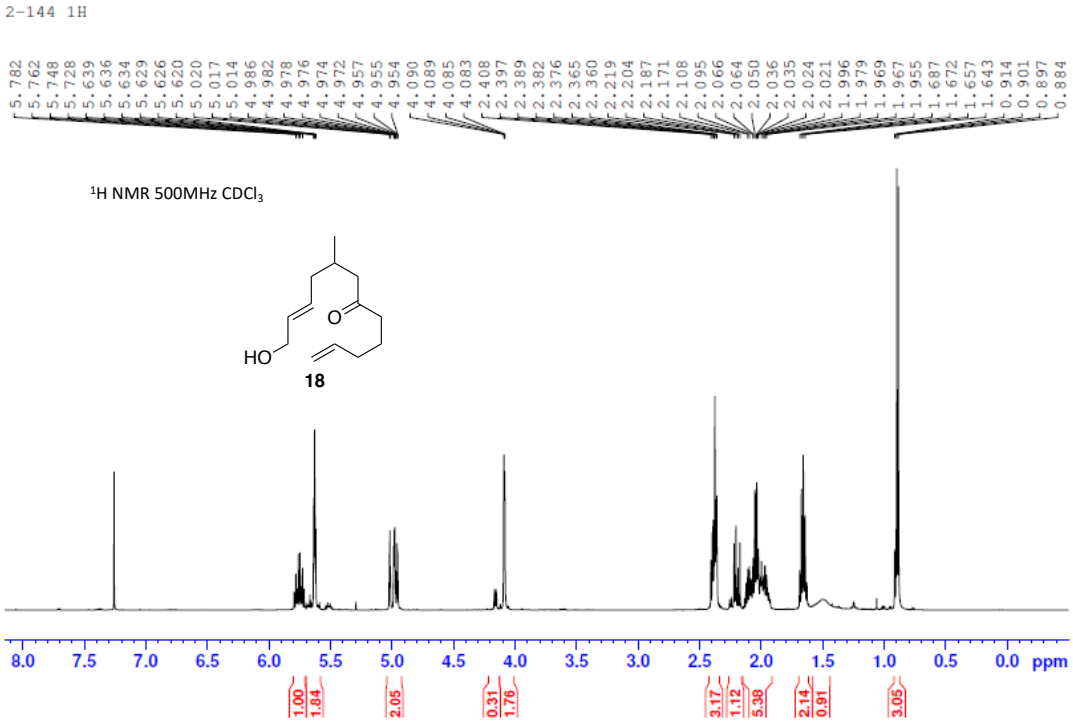

Unimolecular Screening 500 AP CDC13
138.59 116.48 73.69 67.11 38.96 38.34 36.66 36.04 35.27 28.10 22.66 19.62 17.78
13C NMR 125MHz CDCl3
OH
15
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

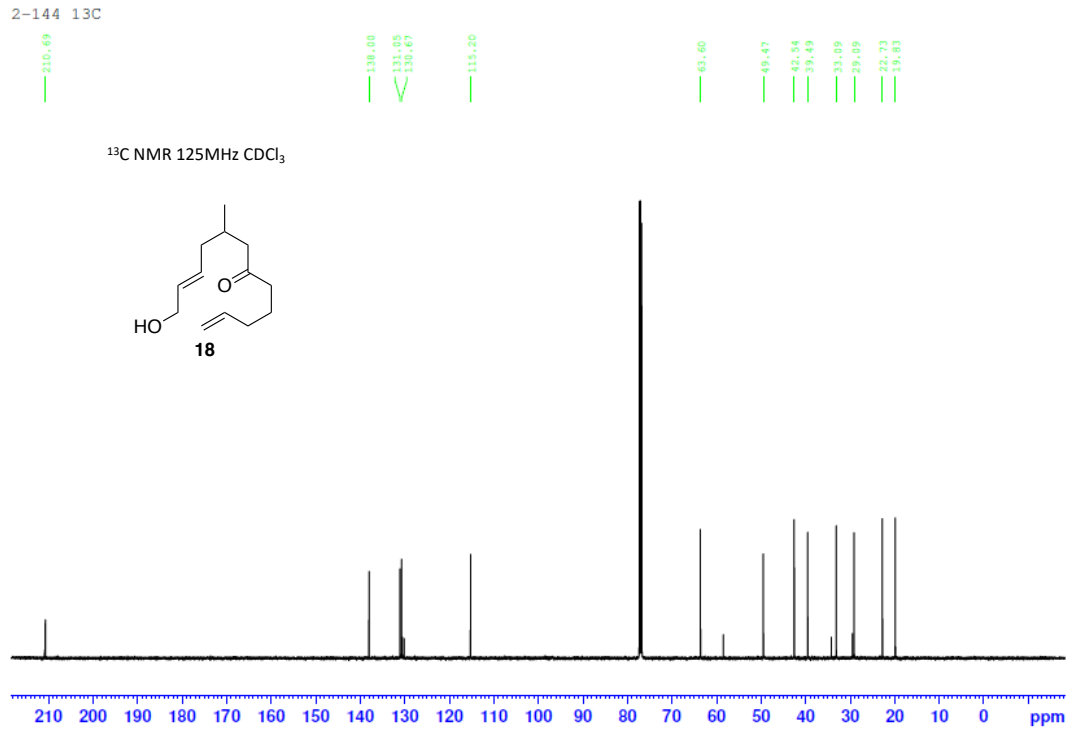

COA-1245-P3(Major) 1H 1 E:\COA-500MHz
Unimolecular Screening 500 AP CDCl3
2-D COSY NMR 500MHz CDCl3
O
OH
15
F1 [ppm]
F2 [ppm]
1
2
3
4
5
6

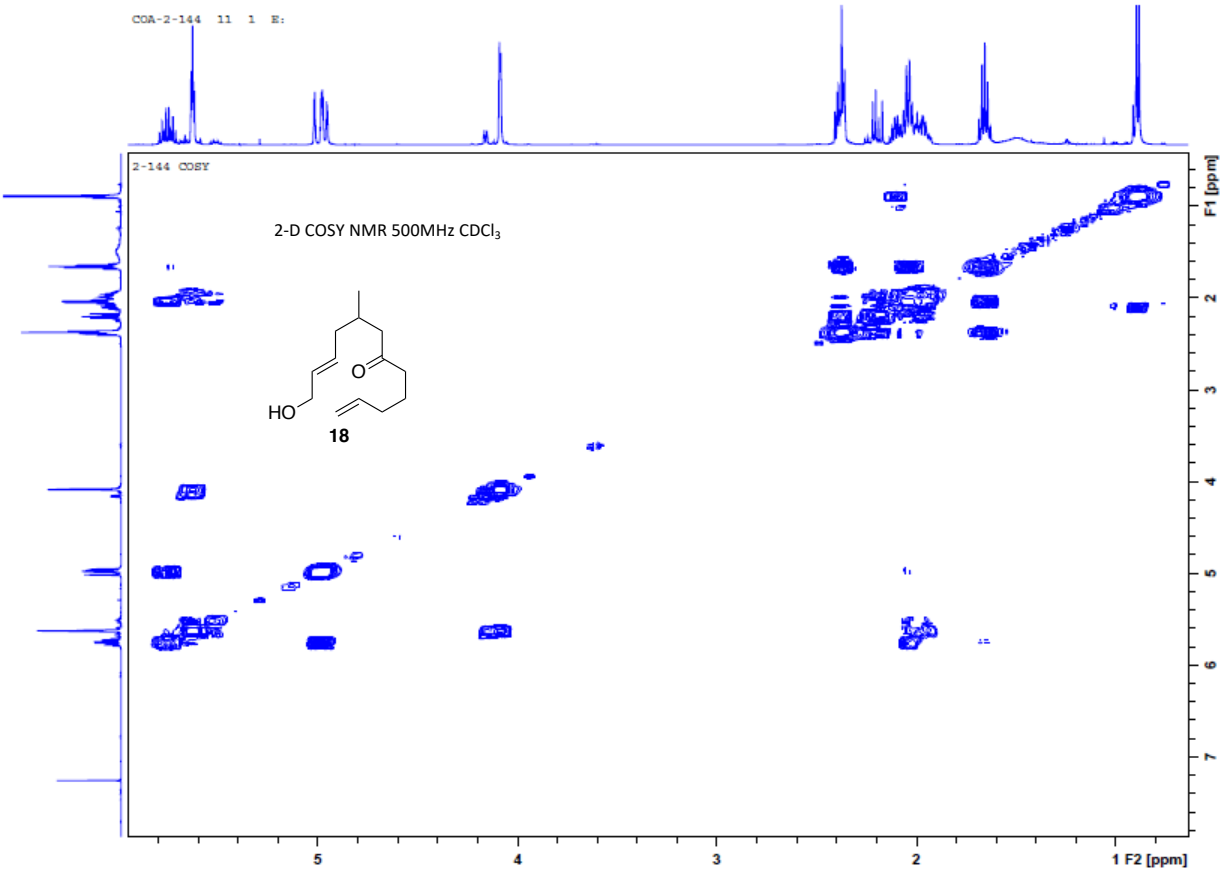

Minor product - Re2O7 Intra. 500AP
5.784
5.770
5.764
5.749
5.735
5.729
5.715
5.301
5.299
5.267
5.171
5.169
5.150
5.148
3.964
3.957
3.950
3.944
3.801
3.782
3.767
1.948
1.781
1.775
1.756
1.752
1.686
1.676
1.662
1.615
1.604
1.600
1.574
1.512
1.486
1.480
1.474
1.462
1.457
1.447
1.439
1.429
1.418
1.412
1.398
1.389
1.384
1.378
1.372
1.364
1.356
1.334
1.326
1.323
1.272
1.252
0.840
0.827
1H NMR 500MHz CDCl3
O
HO
16
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
1.23
1.03
1.02
1.06
0.87
0.78
0.92
1.80
1.38
3.88
9.91
3.00

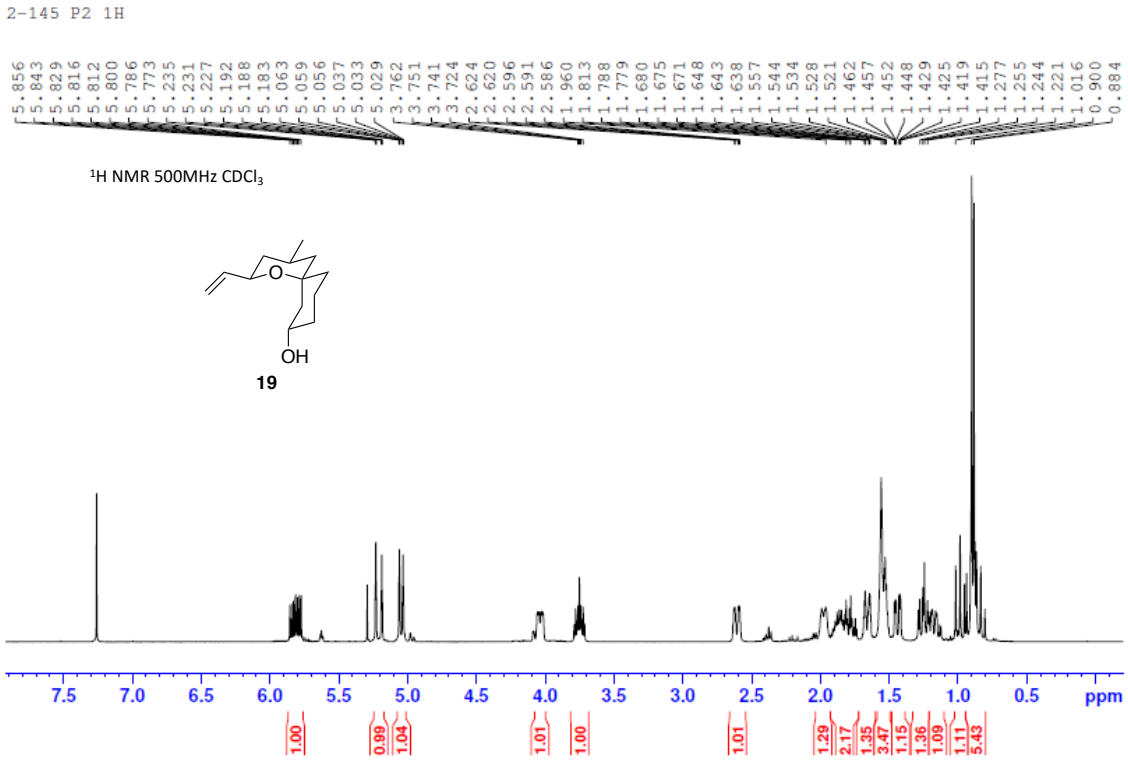

Minor product - Re2O7 Intra. 500AP
137.87
117.56
78.59
73.78
67.69
39.70
36.96
35.26
34.03
33.30
27.89
17.74
15.99
13C NMR 125MHz CDCl3
O
HO
16
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

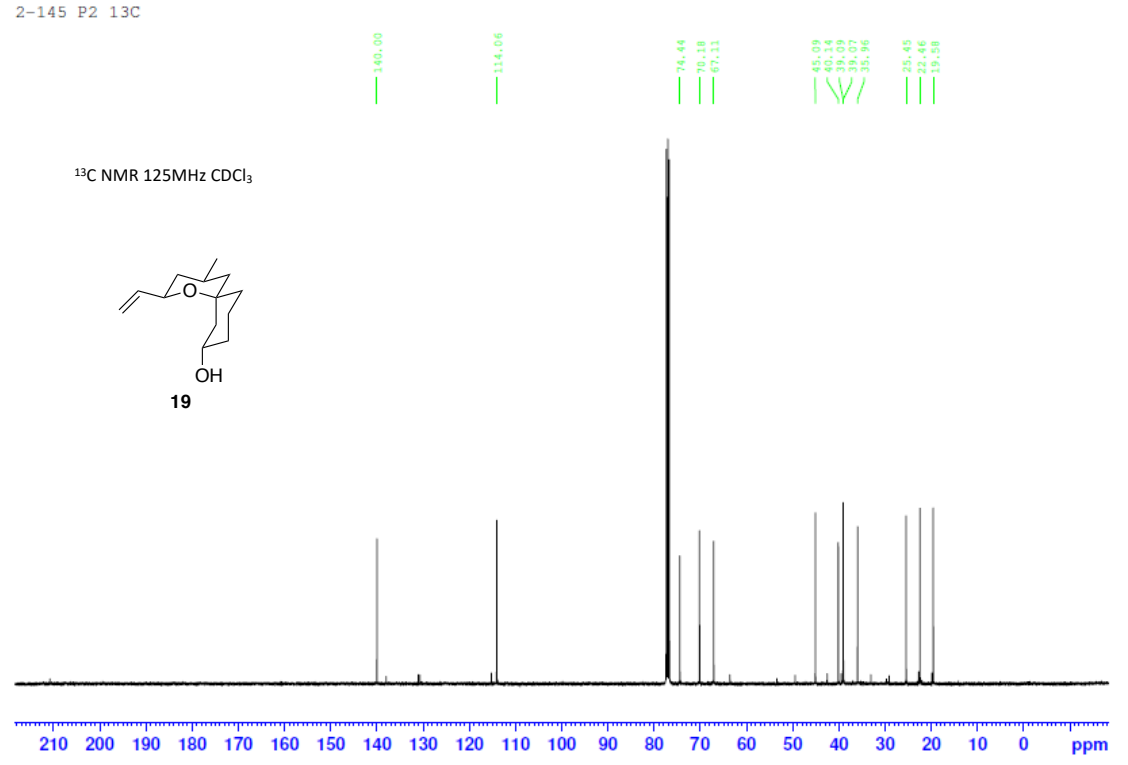

"COA-1-245 (B) P1" 12 1 E:\COA-400MHz
1-245 P1 COSY CDCl3 400
2-D COSY NMR 400MHz $CDCl_3$
O
HO
16
F1 [ppm]
F2 [ppm]
1
2
3
4
5
6

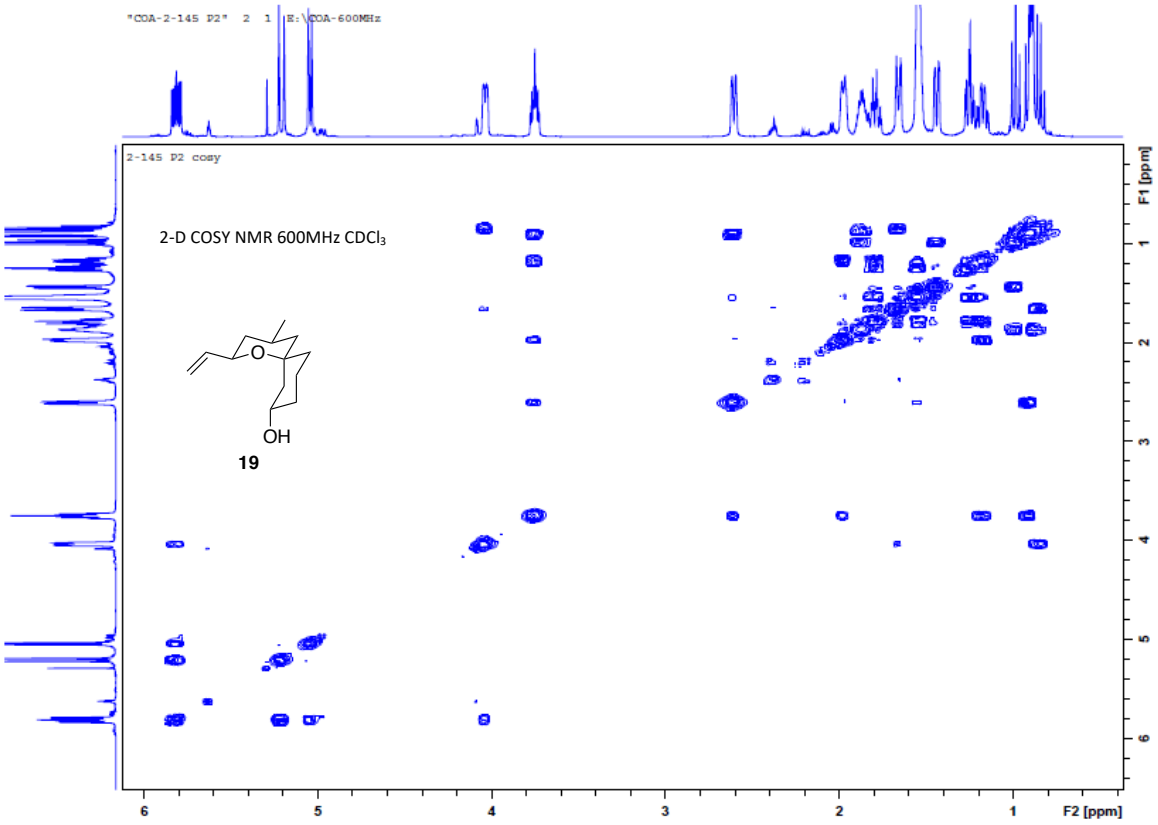

2-144 1H
5.782 5.762 5.748 5.728 5.639 5.636 5.634 5.629 5.626 5.620 5.020 5.017 5.014 4.986 4.982 4.978 4.976 4.974 4.972 4.957 4.955 4.954 4.090 4.089 4.085 4.083 4.008 2.397 2.389 2.382 2.376 2.365 2.360 2.219 2.204 2.187 2.171 2.108 2.095 2.066 2.064 2.050 2.036 2.035 2.024 2.021 1.996 1.979 1.969 1.967 1.955 1.687 1.672 1.657 1.643 0.914 0.901 0.897 0.884
1H NMR 500MHz CDCl3
HO
O
18
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 ppm
1.00 1.84 2.05 0.31 1.76 3.17 1.12 5.38 2.14 0.91 3.05

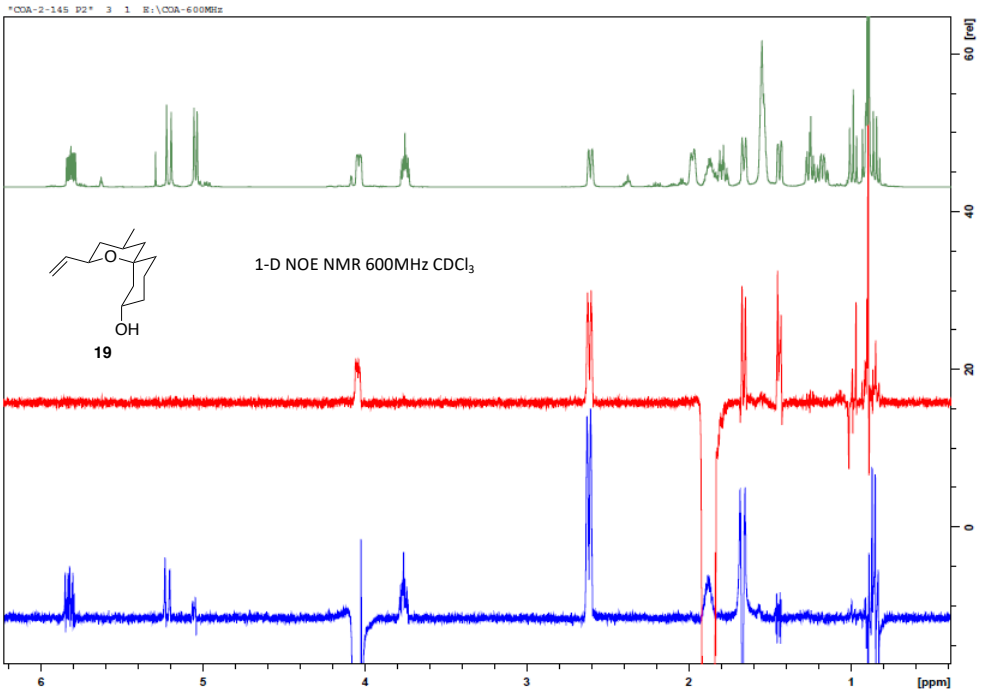

2-144 13C
210.69 138.00 131.05 130.67 115.20 63.60 49.47 42.54 39.49 33.09 29.09 22.73 19.83
13C NMR 125MHz CDCl3
HO
O
18
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

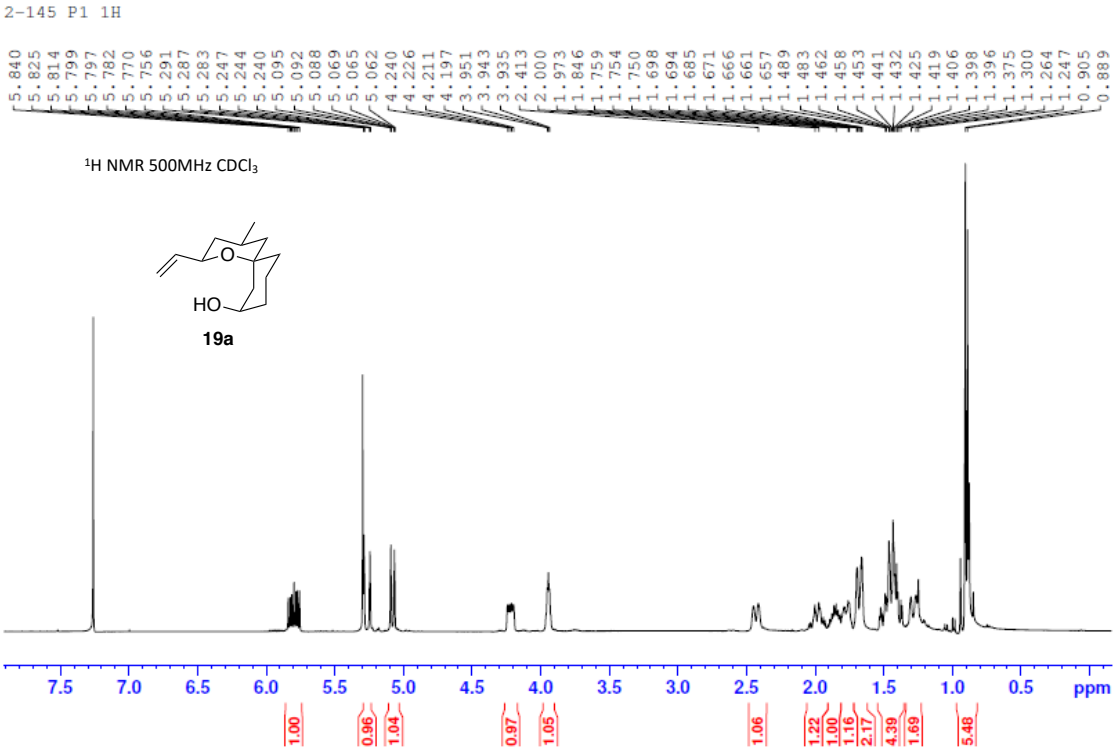

COA-2-144 11 1 E:
2-144 COSY
2-D COSY NMR 500MHz $CDCl_3$
HO
O
18
F1 [ppm]
1 F2 [ppm]

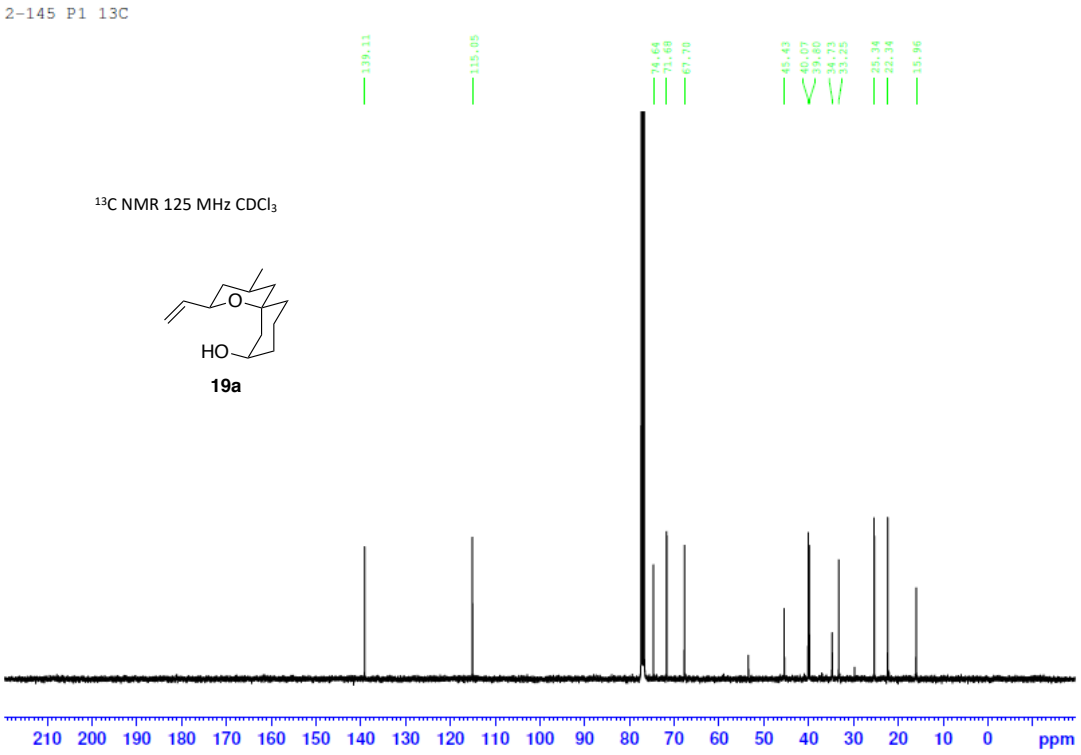

2-145 P2 1H
5.856
5.843
5.829
5.816
5.812
5.800
5.786
5.773
5.235
5.231
5.227
5.192
5.188
5.183
5.063
5.059
5.056
5.037
5.033
5.029
3.762
3.751
3.741
3.724
2.624
2.620
2.596
2.591
2.586
1.960
1.813
1.788
1.779
1.680
1.675
1.671
1.648
1.643
1.638
1.557
1.544
1.534
1.528
1.521
1.462
1.457
1.452
1.448
1.429
1.425
1.419
1.415
1.277
1.255
1.244
1.221
1.016
0.900
0.884
1H NMR 500MHz CDCl3
O
OH
19
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
1.00
0.99
1.04
1.01
1.00
1.01
1.29
2.17
1.35
3.47
1.15
1.36
1.09
1.11
5.43

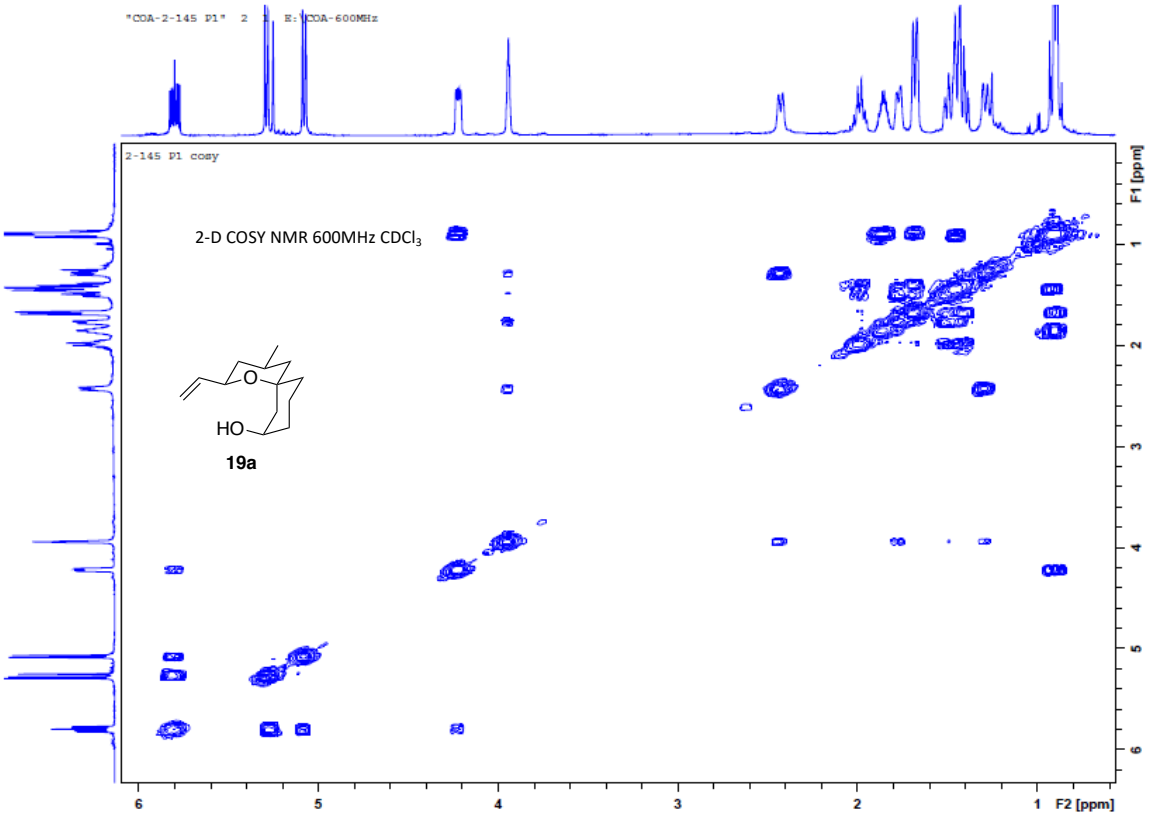

2-145 P2 13C
140.00
114.06
74.44
70.18
67.11
45.09
40.14
39.09
39.07
35.96
25.45
22.46
19.58
13C NMR 125MHz CDCl3
O
OH
19
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

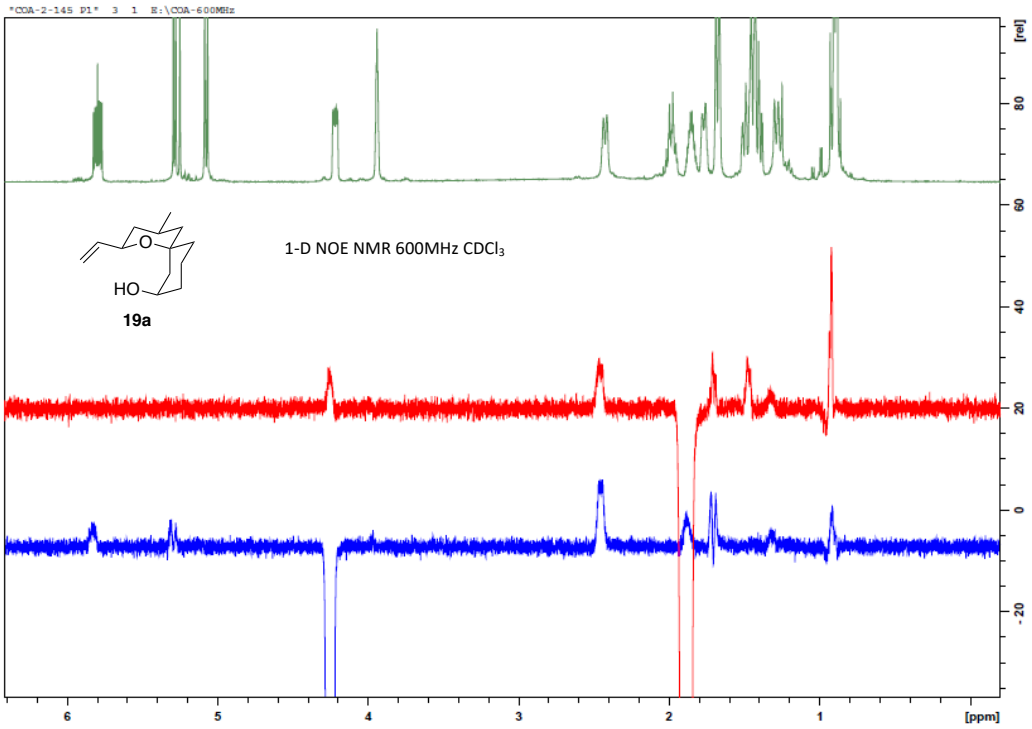

"COA-2-145 P2" 2 1 E:\COA-600MHz
2-145 P2 cosy
2-D COSY NMR 600MHz CDCl3
O
OH
19
F1 [ppm]
F2 [ppm]

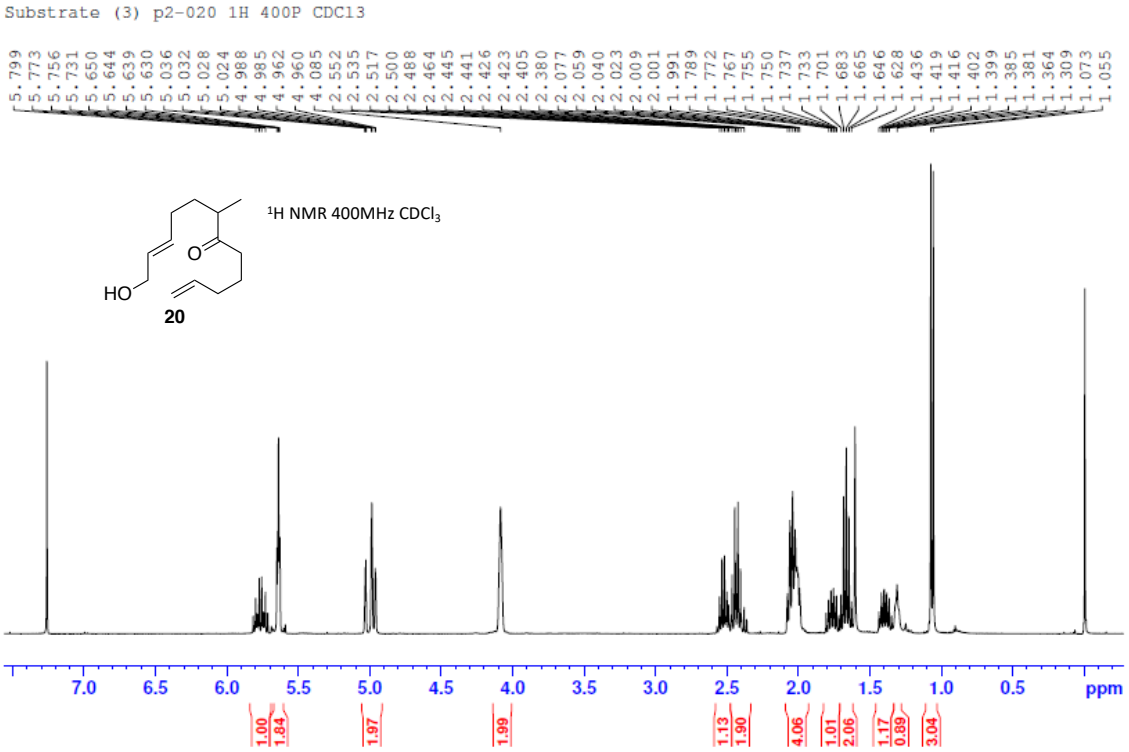

"COA-2-145 P2" 3 1 E:\COA-600MHz
1-D NOE NMR 600MHz CDCl3
O
OH
19
60 [rel]
[ppm]

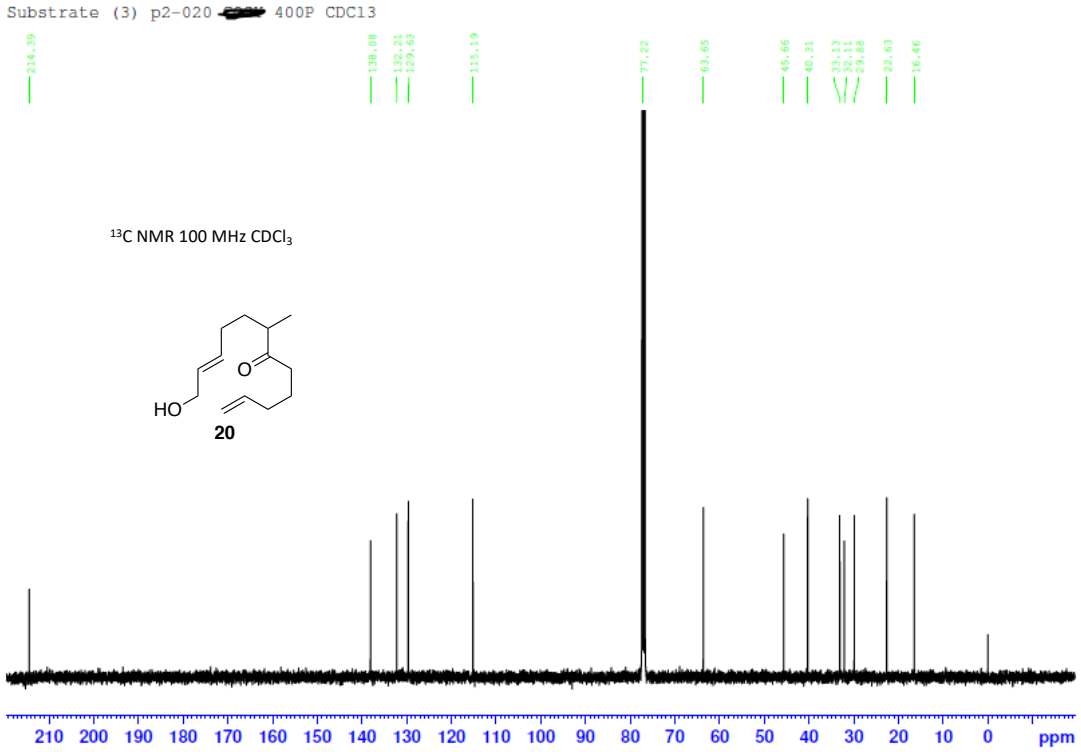

2-145 P1 1H
5.840
5.825
5.814
5.799
5.797
5.782
5.770
5.756
5.291
5.287
5.283
5.247
5.244
5.240
5.095
5.092
5.088
5.069
5.065
5.062
4.240
4.226
4.211
4.197
3.951
3.943
3.935
2.413
2.000
1.973
1.846
1.759
1.754
1.750
1.698
1.694
1.685
1.671
1.666
1.661
1.657
1.489
1.483
1.462
1.458
1.453
1.441
1.432
1.425
1.419
1.406
1.398
1.396
1.375
1.300
1.264
1.247
0.905
0.889
1H NMR 500MHz CDCl3
O
HO
19a
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
1.00
0.96
1.04
0.97
1.05
1.06
1.22
1.00
1.16
2.17
4.39
1.69
5.48

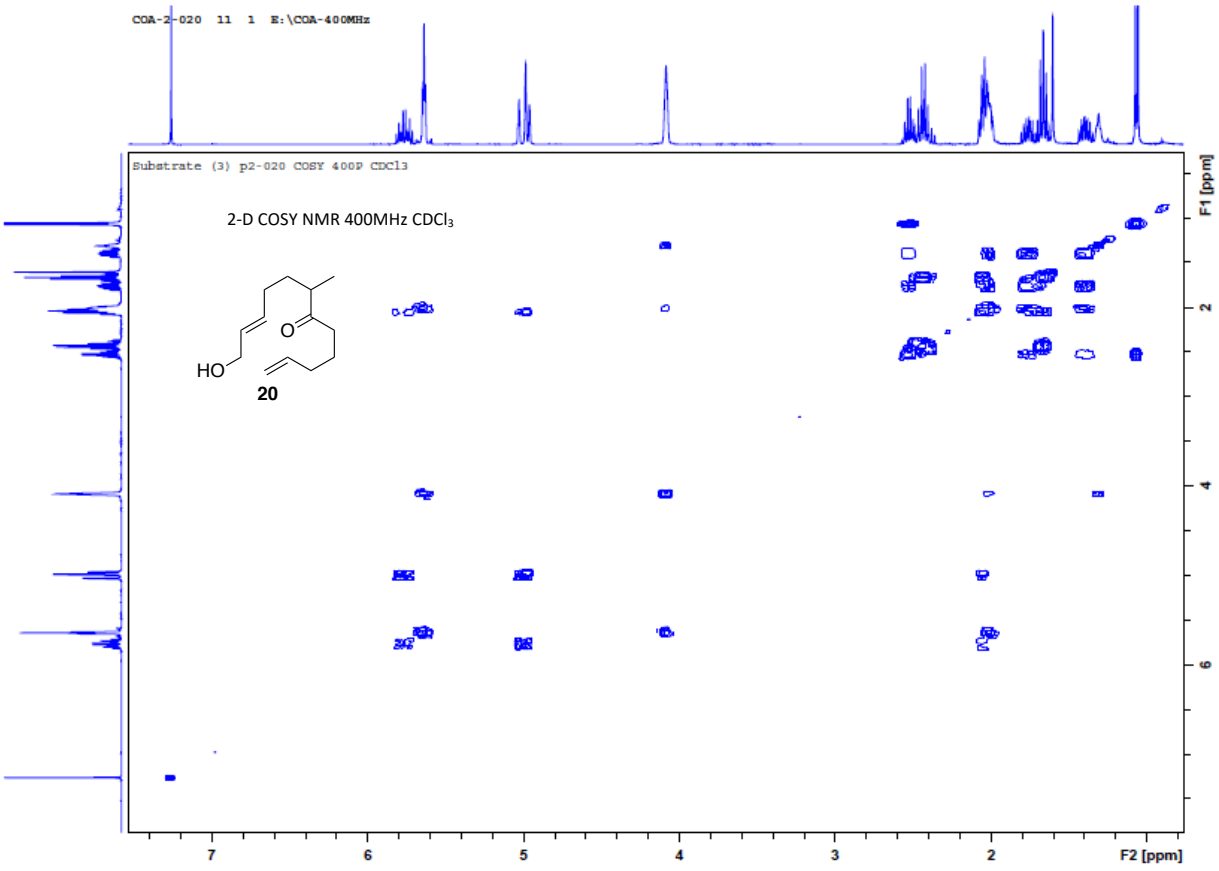

2-145 P1 13C
139.11
115.05
74.64
71.68
67.70
45.43
40.07
39.80
34.73
33.25
25.34
22.34
15.96
13C NMR 125 MHz CDCl3
O
HO
19a
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

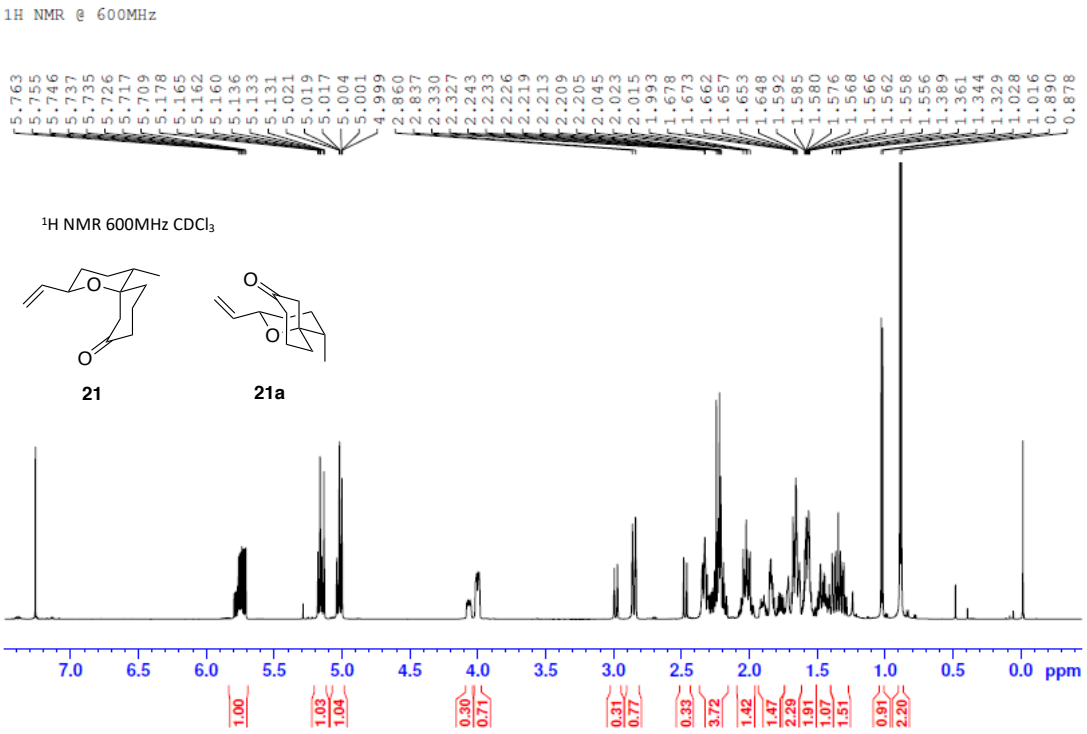

2-145 P1 cosy
2-D COSY NMR 600MHz CDCl3
O
HO
19a
F1 [ppm]
F2 [ppm]

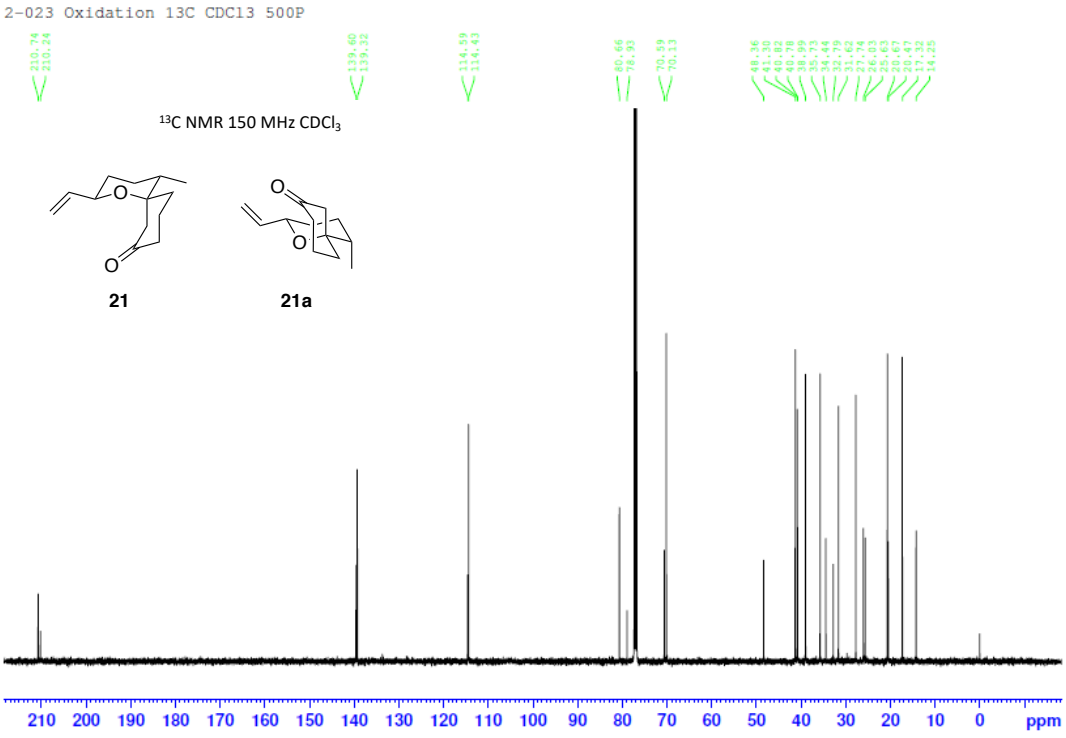

1-D NOE NMR 600MHz CDCl3
O
HO
19a
[rel]
[ppm]

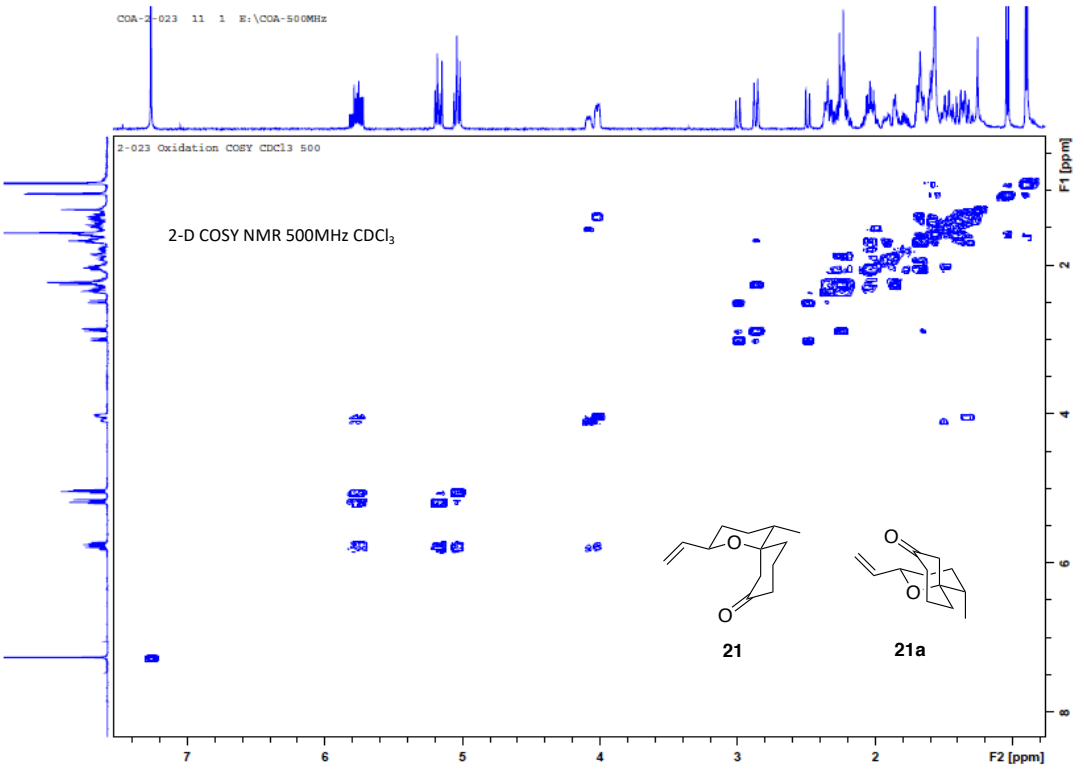

Substrate (3) p2-020 1H 400P CDCl3
5.799 5.773 5.756 5.731 5.650 5.644 5.639 5.630 5.036 5.032 5.028 5.024 4.988 4.985 4.962 4.960 4.085 2.552 2.535 2.517 2.500 2.488 2.464 2.445 2.441 2.426 2.423 2.405 2.380 2.077 2.059 2.040 2.023 2.009 2.001 1.991 1.789 1.772 1.767 1.755 1.750 1.737 1.733 1.701 1.683 1.665 1.646 1.628 1.436 1.419 1.416 1.402 1.399 1.385 1.381 1.364 1.309 1.073 1.055
1H NMR 400MHz CDCl3
HO
O
20
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
1.00 1.84 1.97 1.99 1.13 1.90 4.06 1.01 2.06 1.17 0.89 3.04

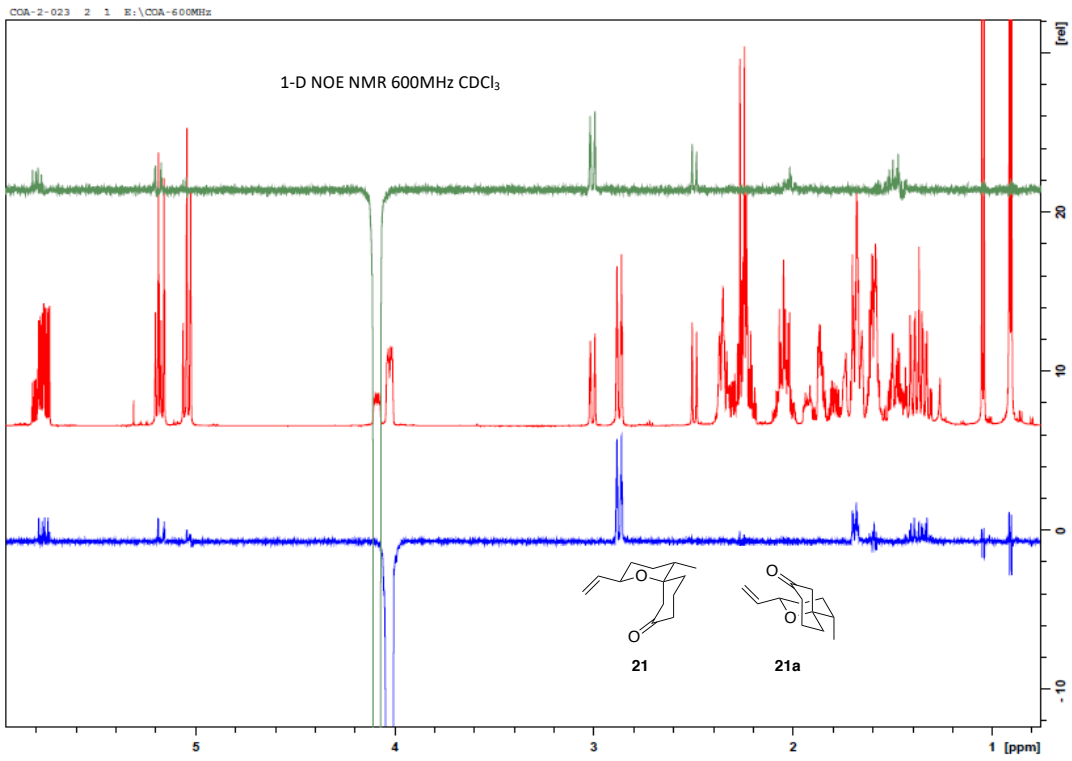

Substrate (3) p2-020 [redacted] 400P CDCl3
214.39 138.08 132.21 129.63 115.19 77.22 63.65 45.66 40.31 33.13 32.11 29.88 22.63 16.46
13C NMR 100 MHz CDCl3
HO
O
20
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

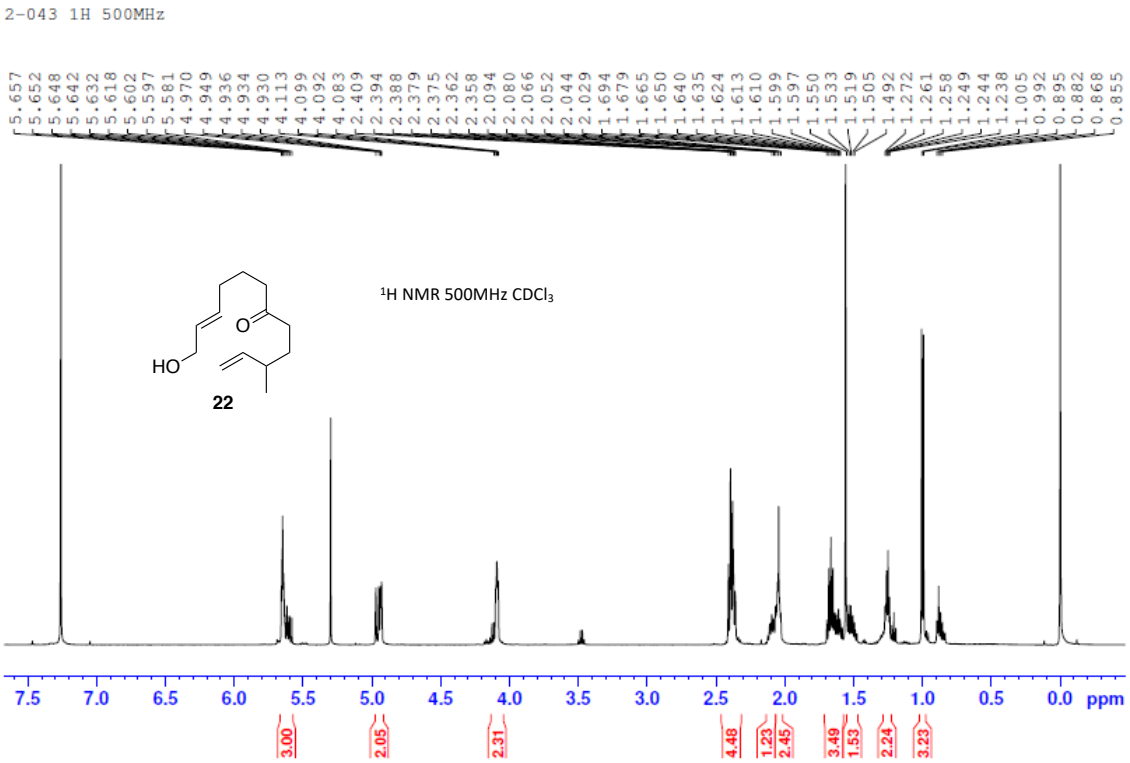

COA-2-020 11 1 E:\COA-400MHz
Substrate (3) p2-020 COSY 400P CDCl3
2-D COSY NMR 400MHz CDCl3
HO
O
20
F1 [ppm]
F2 [ppm]
2
4
6
7
5
3

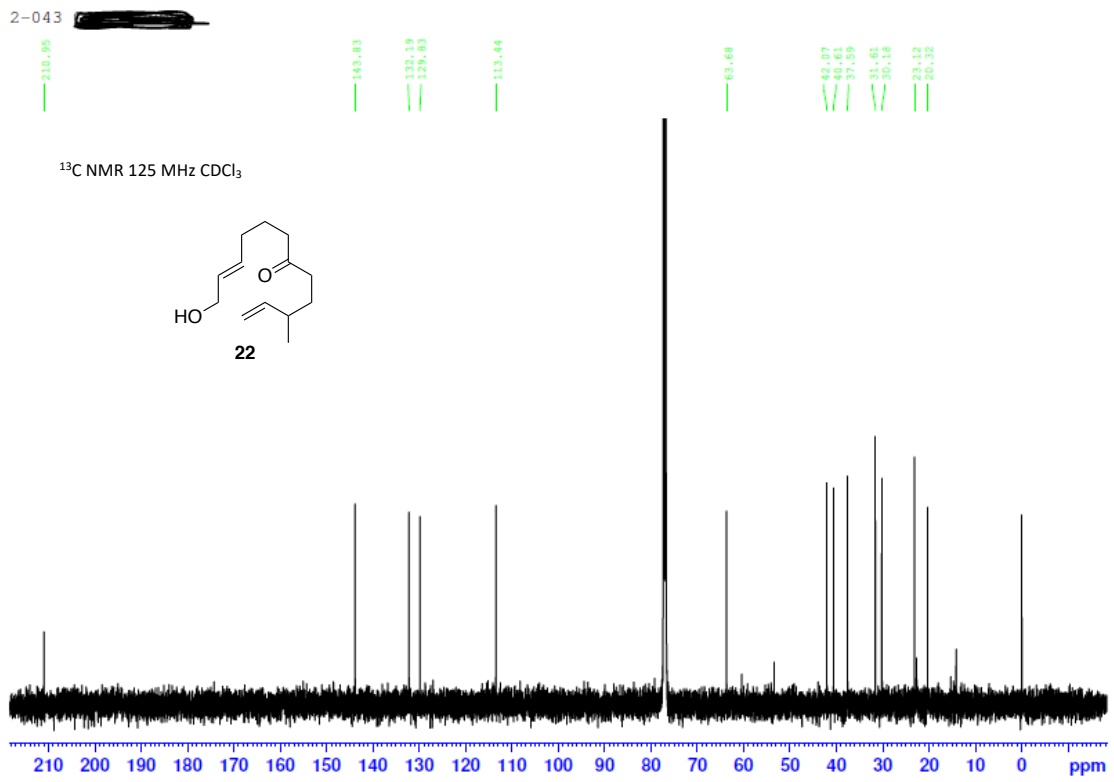

1H NMR @ 600MHz
5.763 5.755 5.746 5.737 5.735 5.726 5.717 5.709 5.178 5.165 5.162 5.160 5.136 5.133 5.131 5.021 5.019 5.017 5.004 5.001 4.999 2.860 2.837 2.330 2.327 2.243 2.233 2.226 2.219 2.213 2.209 2.205 2.045 2.023 2.015 1.993 1.678 1.673 1.662 1.657 1.653 1.648 1.592 1.585 1.580 1.576 1.568 1.566 1.562 1.558 1.556 1.389 1.361 1.344 1.329 1.028 1.016 0.890 0.878
1H NMR 600MHz CDCl3
21
21a
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 ppm
1.00 1.03 1.04 0.30 0.71 0.31 0.77 0.33 3.72 1.42 1.47 2.29 1.91 1.07 1.51 0.91 2.20

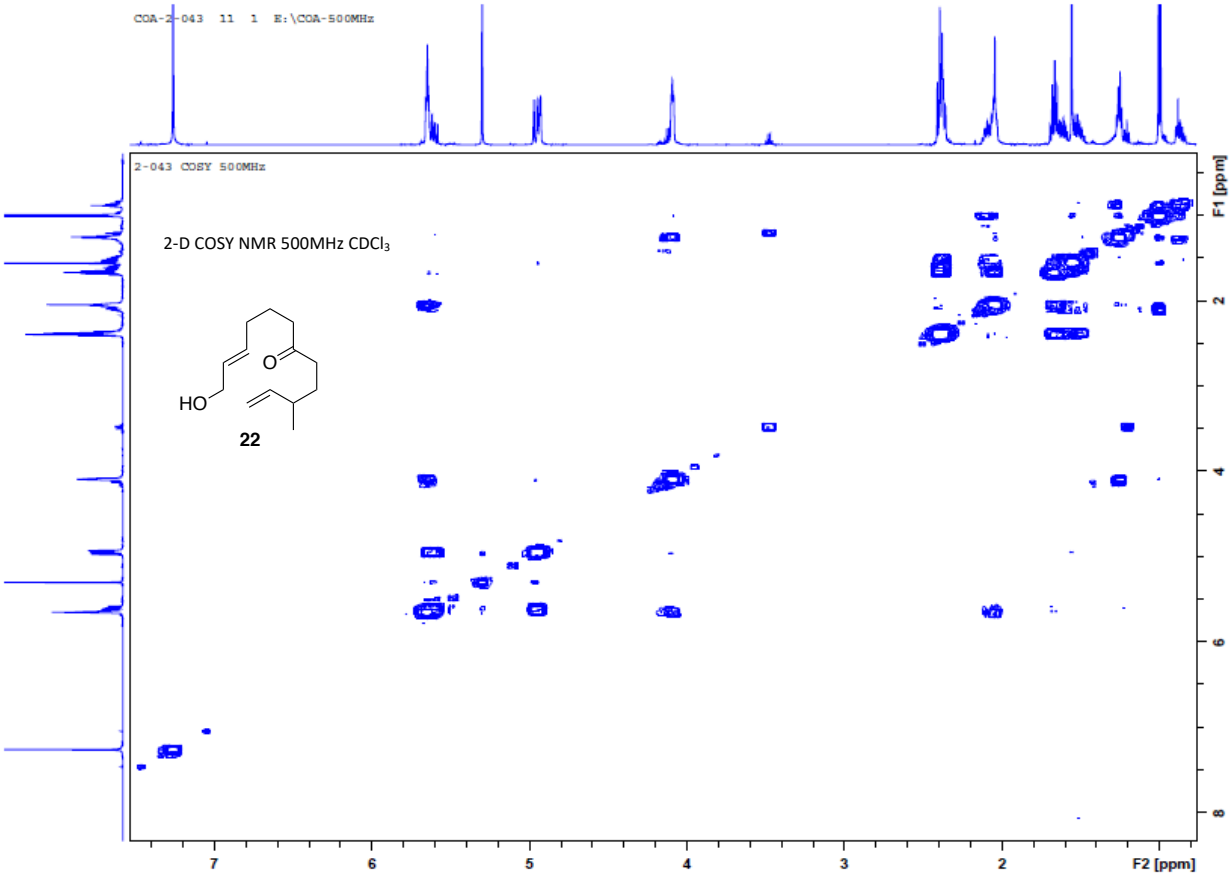

2-023 Oxidation 13C CDCl3 500P
210.74 210.24 139.60 139.32 114.59 114.43 80.66 78.93 70.59 70.13 48.36 41.30 40.88 40.78 38.99 35.73 34.44 32.79 31.62 27.74 26.03 25.63 20.67 20.47 17.32 14.28
13C NMR 150 MHz CDCl3
21
21a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

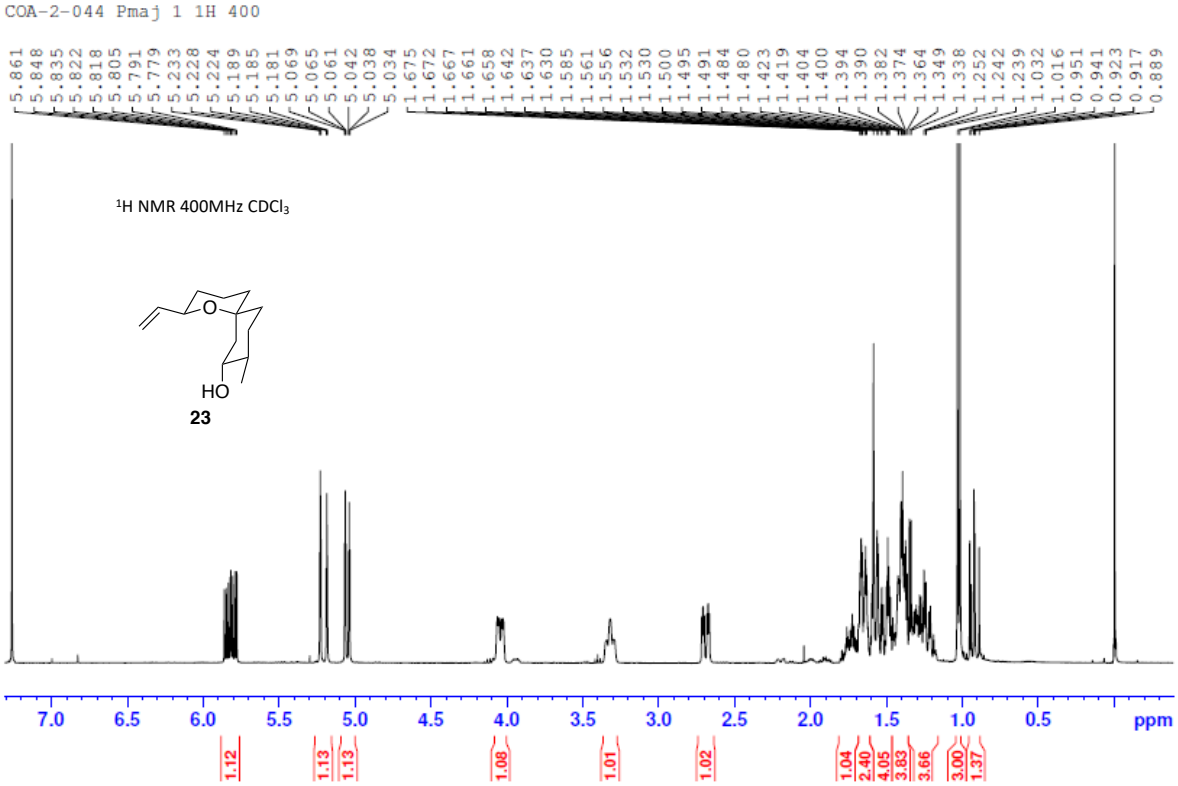

COA-2-023 11 1 E:\COA-500MHz
2-023 Oxidation COSY CDCl3 500
2-D COSY NMR 500MHz $CDCl_3$
F1 [ppm]
F2 [ppm]
21
21a

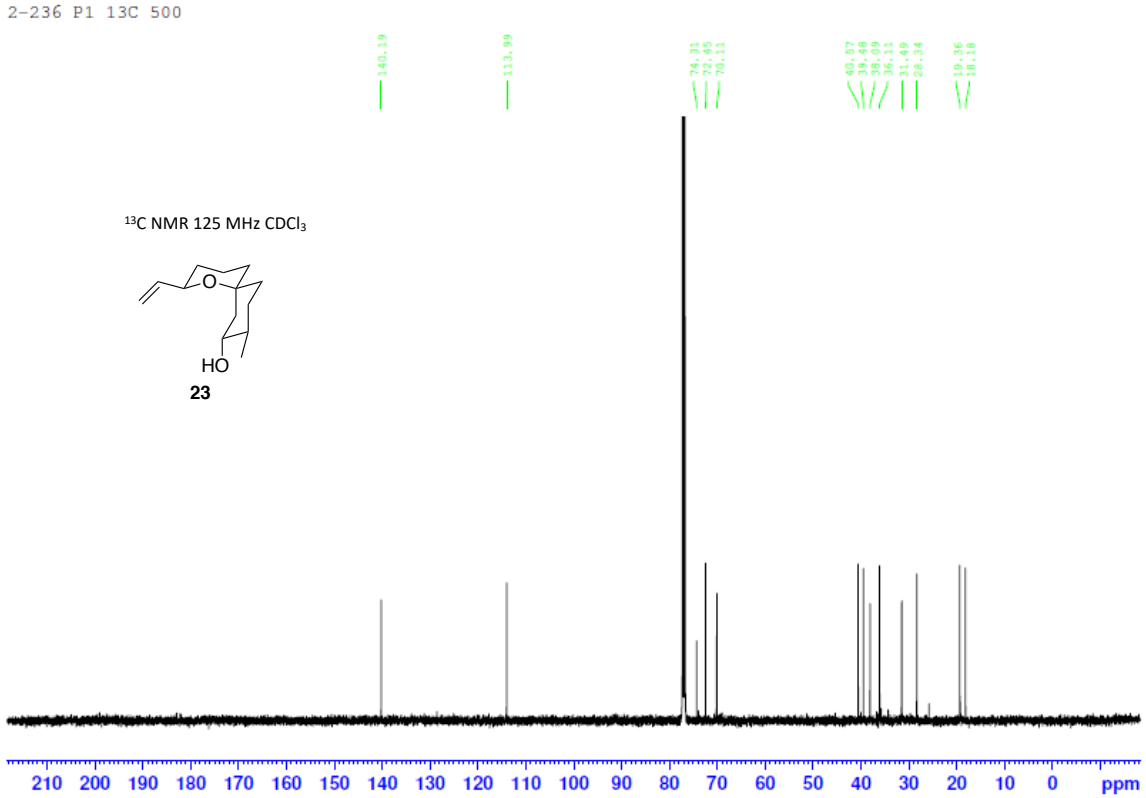

COA-2-023 2 1 E:\COA-600MHz
1-D NOE NMR 600MHz $CDCl_3$
[rel]
[ppm]
21
21a

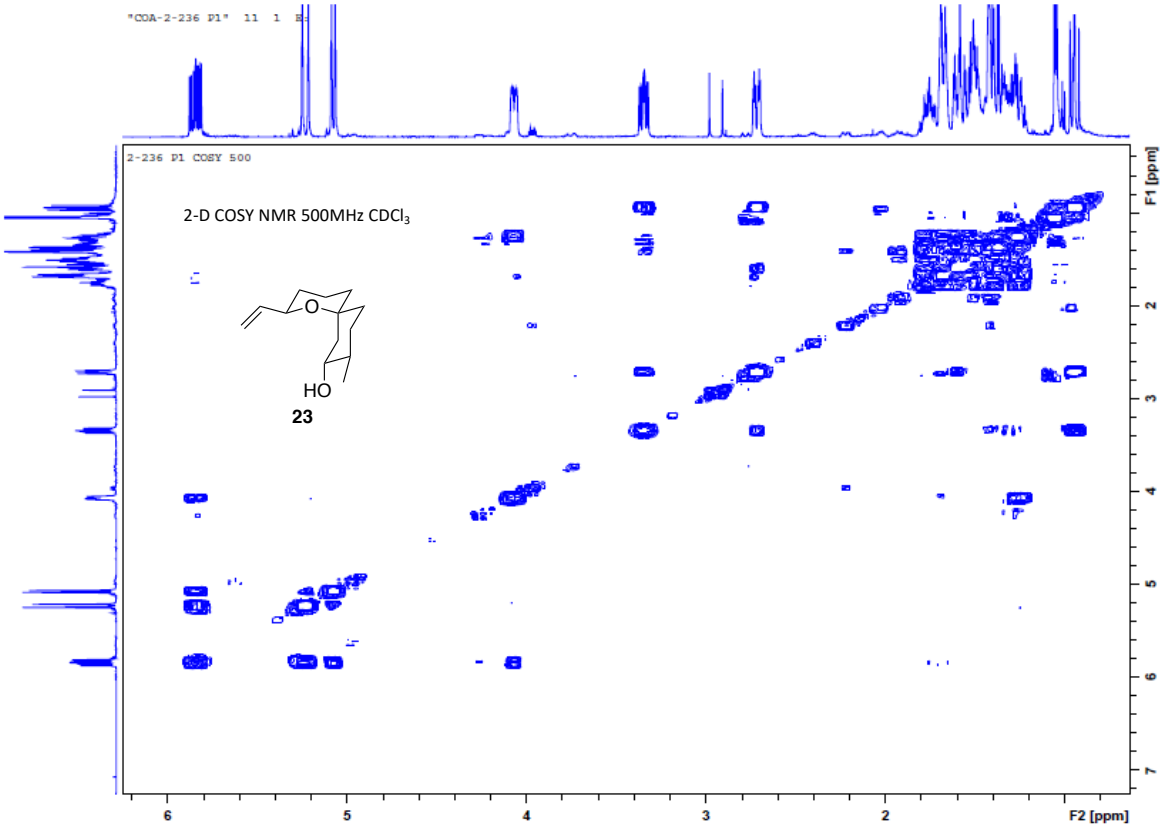

2-043 1H 500MHz
5.657 5.652 5.648 5.642 5.632 5.618 5.602 5.597 5.581 4.970 4.949 4.936 4.934 4.930 4.113 4.099 4.092 4.083 2.409 2.394 2.388 2.379 2.375 2.362 2.358 2.094 2.080 2.066 2.052 2.044 2.029 1.694 1.679 1.665 1.650 1.640 1.635 1.624 1.613 1.610 1.599 1.597 1.550 1.533 1.519 1.505 1.492 1.272 1.261 1.258 1.249 1.244 1.238 1.005 0.992 0.895 0.882 0.868 0.855
HO
O
22
1H NMR 500MHz CDCl3
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 ppm
3.00 2.05 2.31 4.46 1.23 2.45 3.49 1.53 2.24 3.23

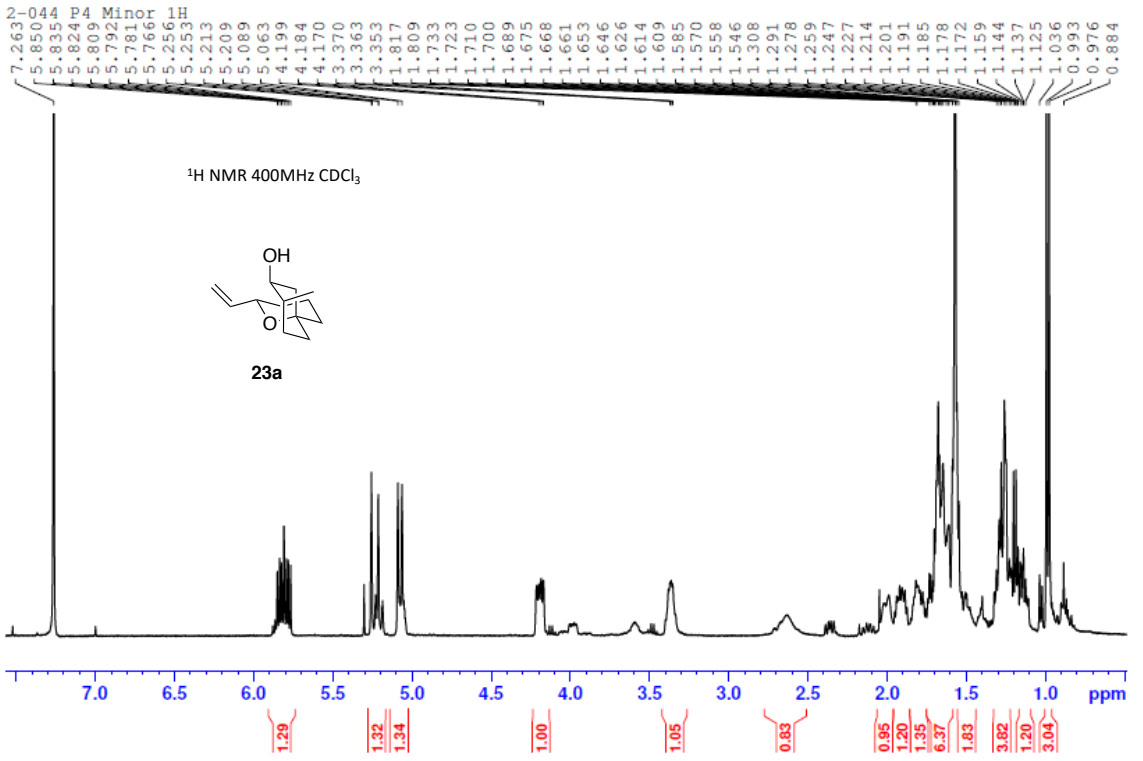

2-043
210.95 143.83 132.19 129.83 113.44 63.68 42.07 40.61 37.59 31.61 30.18 23.12 20.32
HO
O
22
13C NMR 125 MHz CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

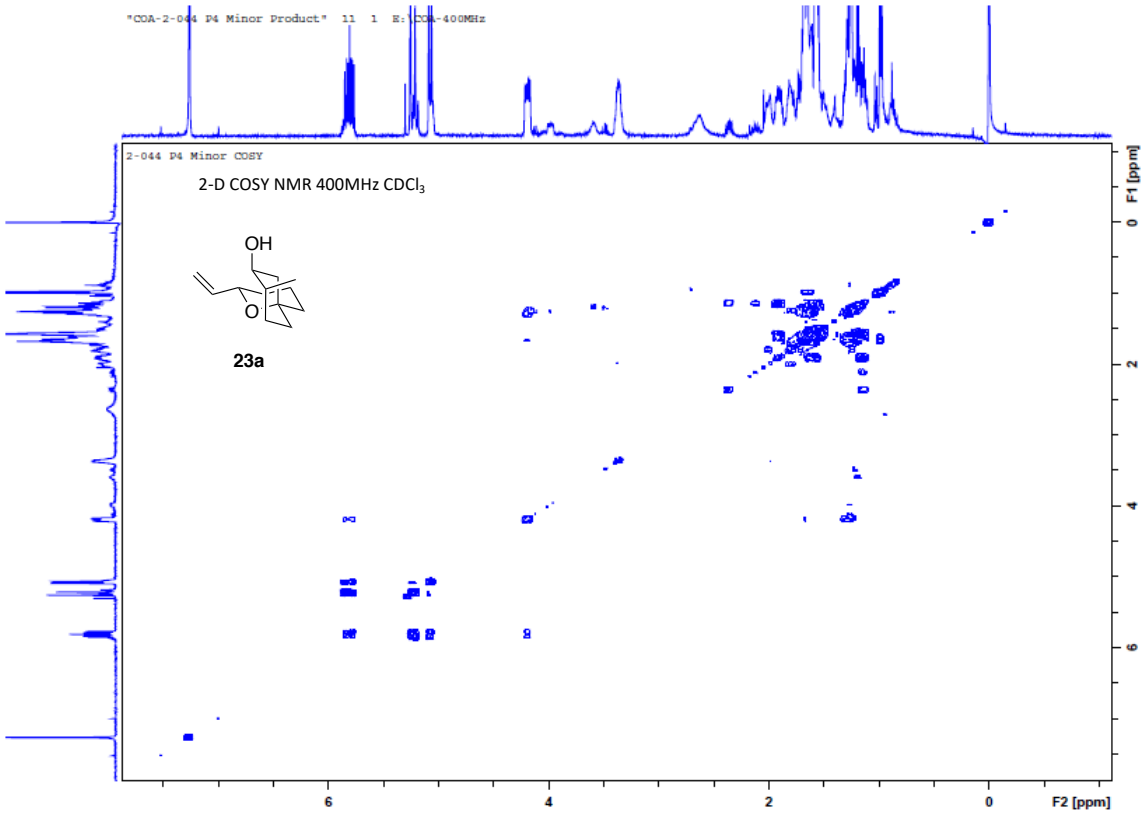

COA-2-043 11 1 E:\COA-500MHz
2-043 COSY 500MHz
2-D COSY NMR 500MHz $CDCl_3$
HO
O
22
F1 [ppm]
F2 [ppm]
2
4
6
8
7
6
5
4
3
2

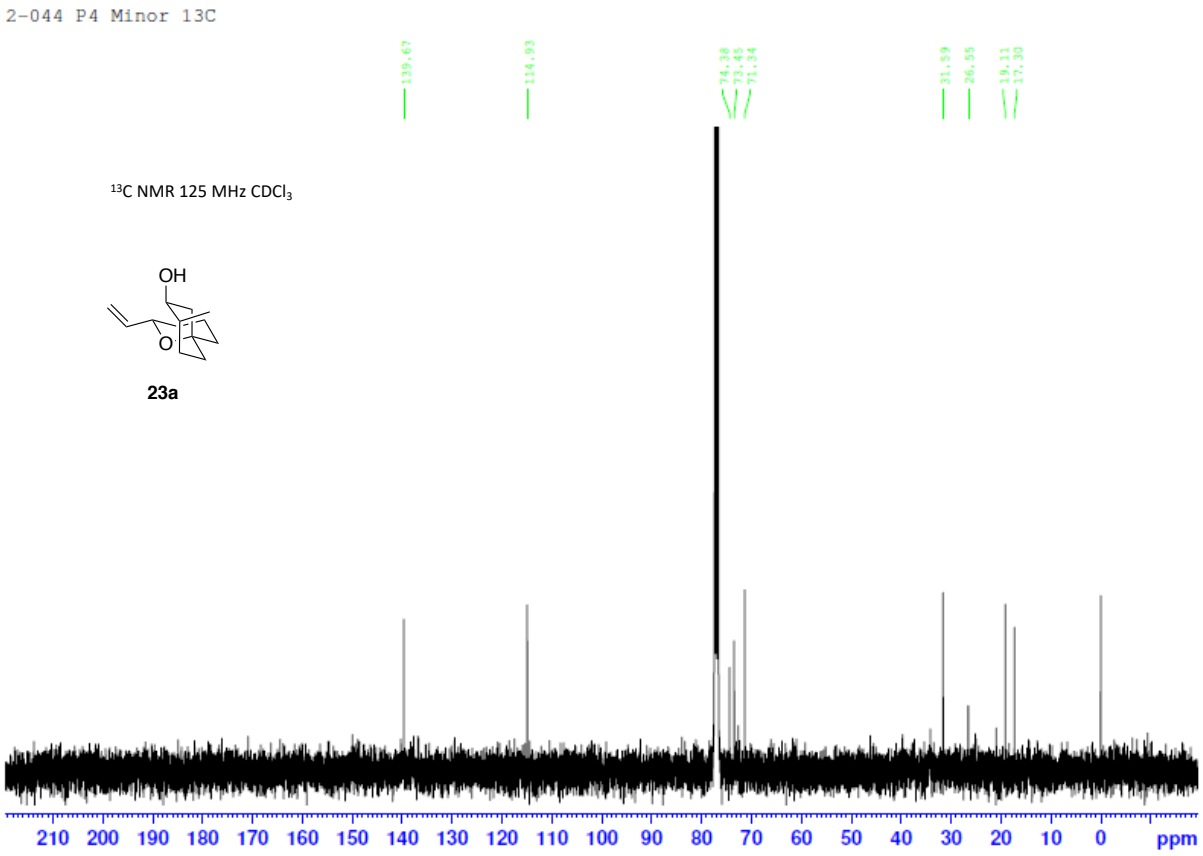

COA-2-044 Pmaj 1 1H 400
5.861 5.848 5.835 5.822 5.818 5.805 5.791 5.779 5.233 5.228 5.224 5.189 5.185 5.181 5.069 5.065 5.061 5.042 5.038 5.034 1.675 1.672 1.667 1.661 1.658 1.642 1.637 1.630 1.585 1.561 1.556 1.532 1.530 1.500 1.495 1.491 1.484 1.480 1.423 1.419 1.404 1.400 1.394 1.390 1.382 1.374 1.364 1.349 1.338 1.252 1.242 1.239 1.032 1.016 0.951 0.941 0.923 0.917 0.889
1H NMR 400MHz CDCl3
O
HO
23
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
1.12 1.13 1.13 1.08 1.01 1.02 1.04 2.40 4.05 3.83 3.66 3.00 1.37

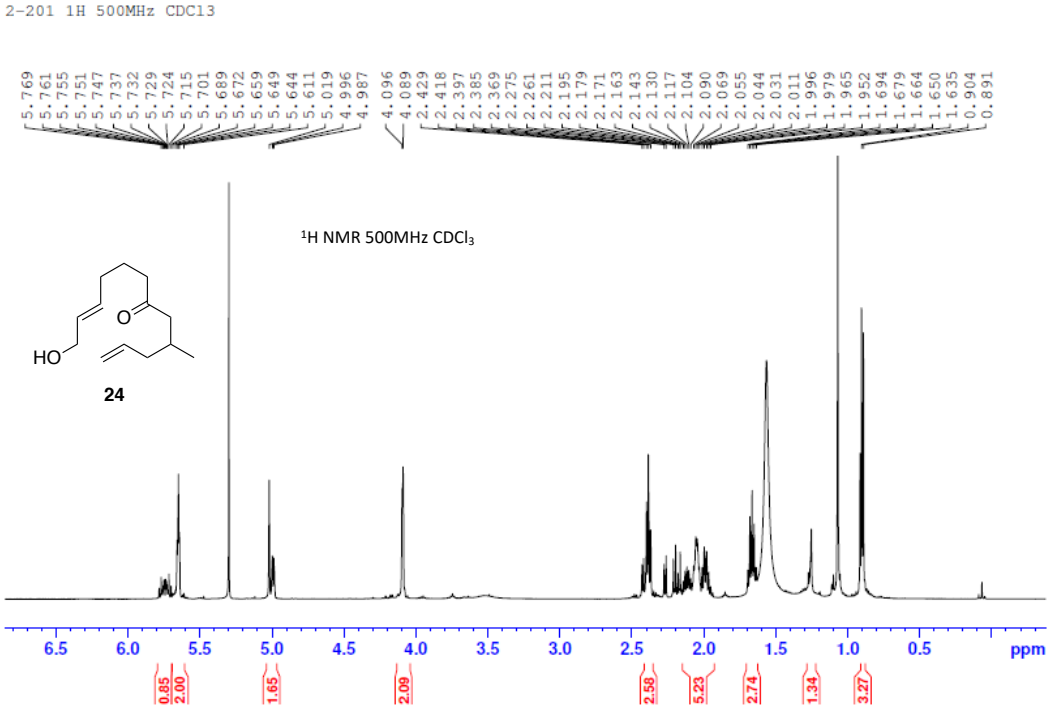

2-236 P1 13C 500
140.19 133.99 74.31 72.45 70.11 40.67 39.68 38.39 36.11 31.49 28.34 19.36 18.18
13C NMR 125 MHz CDCl3
O
HO
23
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

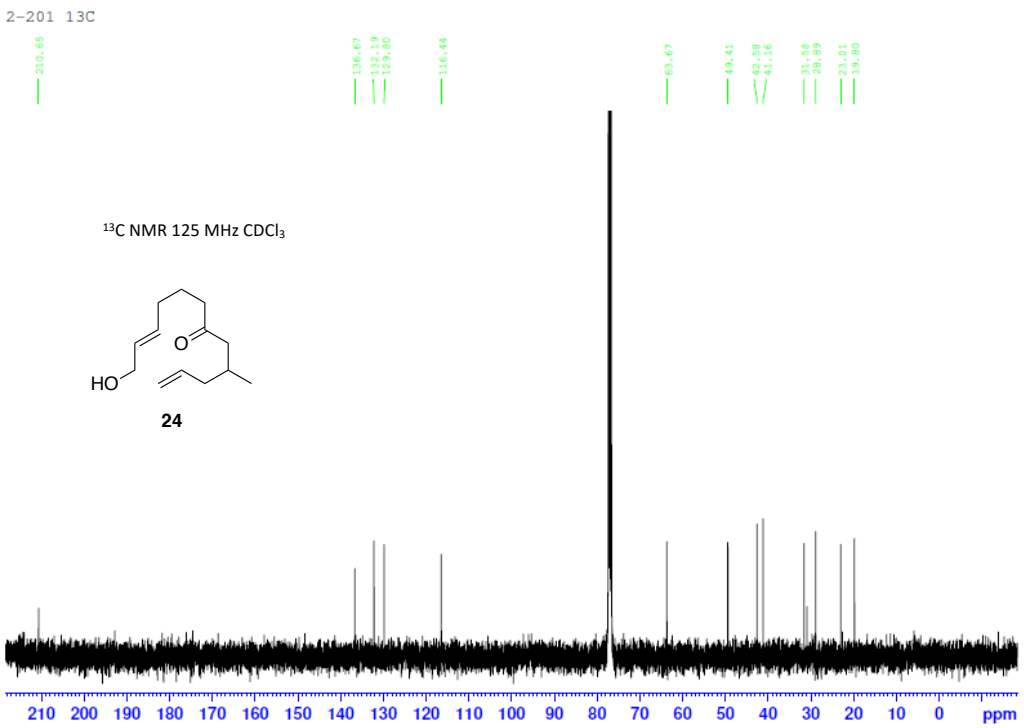

"COA-2-236 P1" 11 1
2-236 P1 COSY 500
2-D COSY NMR 500MHz $CDCl_3$
O
HO
23
F1 [ppm]
F2 [ppm]
6
5
4
3
2
1
2
3
4
5
6
7

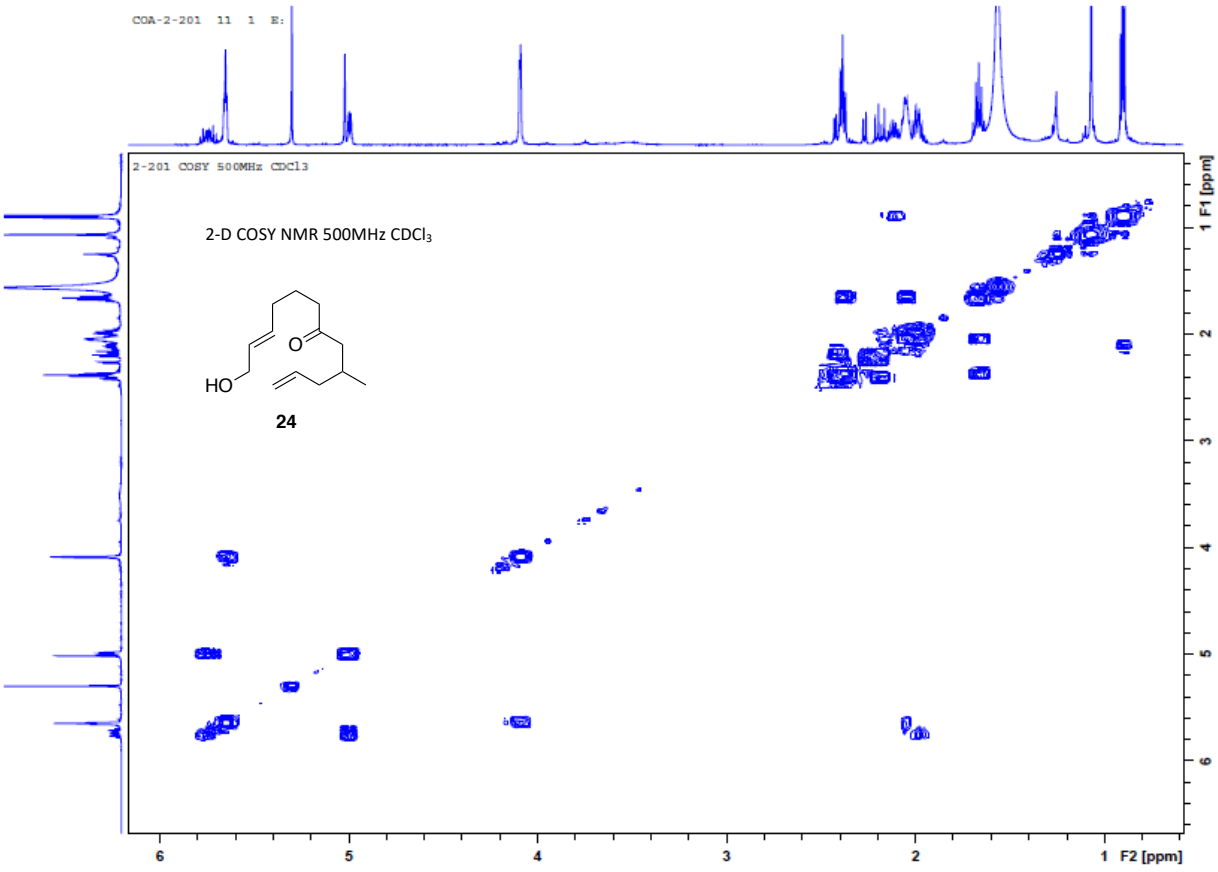

2-044 P4 Minor 1H
7.263 5.850 5.835 5.824 5.809 5.792 5.781 5.766 5.256 5.253 5.213 5.209 5.089 5.063 4.199 4.184 4.170 3.370 3.363 3.353 1.817 1.809 1.733 1.723 1.710 1.700 1.689 1.675 1.668 1.661 1.653 1.646 1.626 1.614 1.609 1.585 1.570 1.558 1.546 1.308 1.291 1.278 1.259 1.247 1.227 1.214 1.201 1.191 1.185 1.178 1.172 1.159 1.144 1.137 1.125 1.036 0.993 0.976 0.884
1H NMR 400MHz CDCl3
OH
O
23a
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 ppm
1.29 1.32 1.34 1.00 1.05 0.83 0.95 1.20 1.35 6.37 1.83 3.82 1.20 3.04

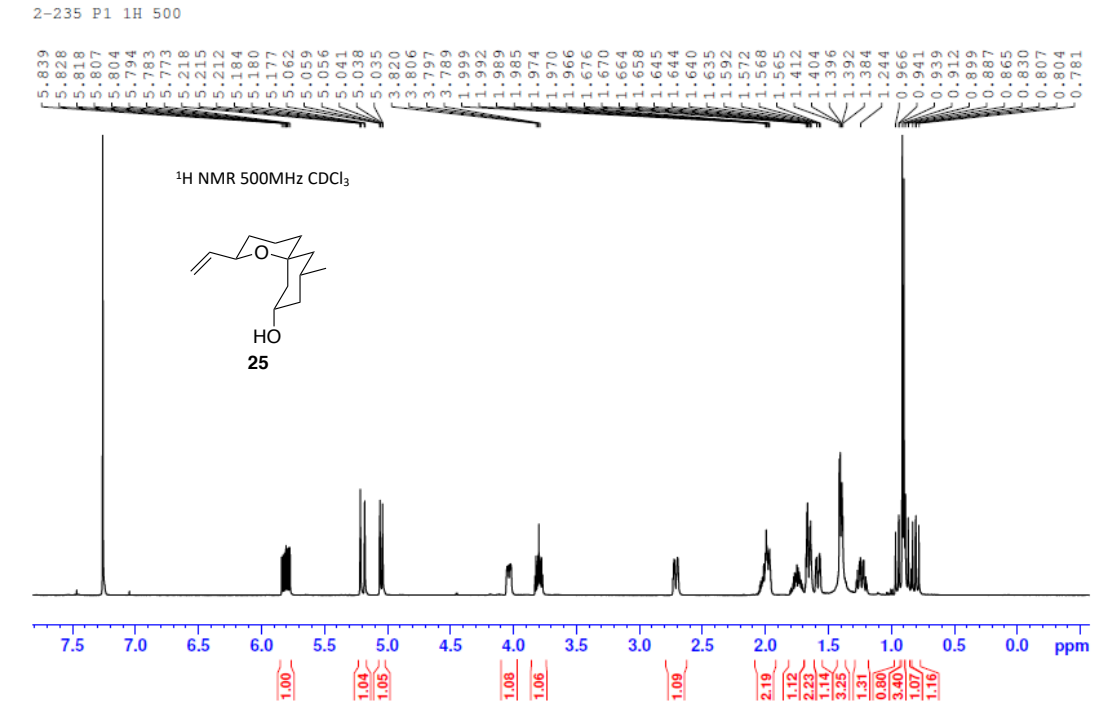

"COA-2-044 P4 Minor Product" 11 1 E:\COA-400MHz
2-044 P4 Minor COSY
2-D COSY NMR 400MHz CDCl3
OH
O
23a
F1 [ppm]
F2 [ppm]
6 4 2 0

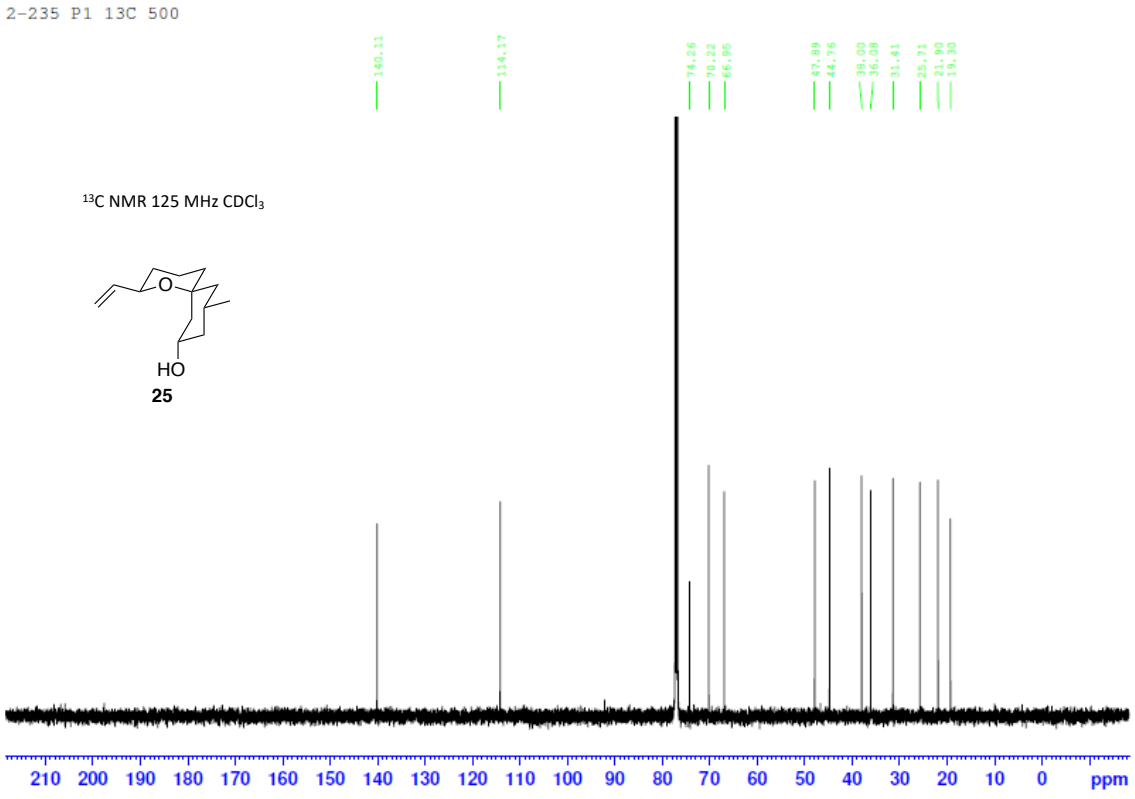

2-044 P4 Minor 13C
139.67
114.93
74.38
73.45
71.34
31.59
26.55
19.11
17.30
^{13}C NMR 125 MHz $CDCl_3$
OH
O
23a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

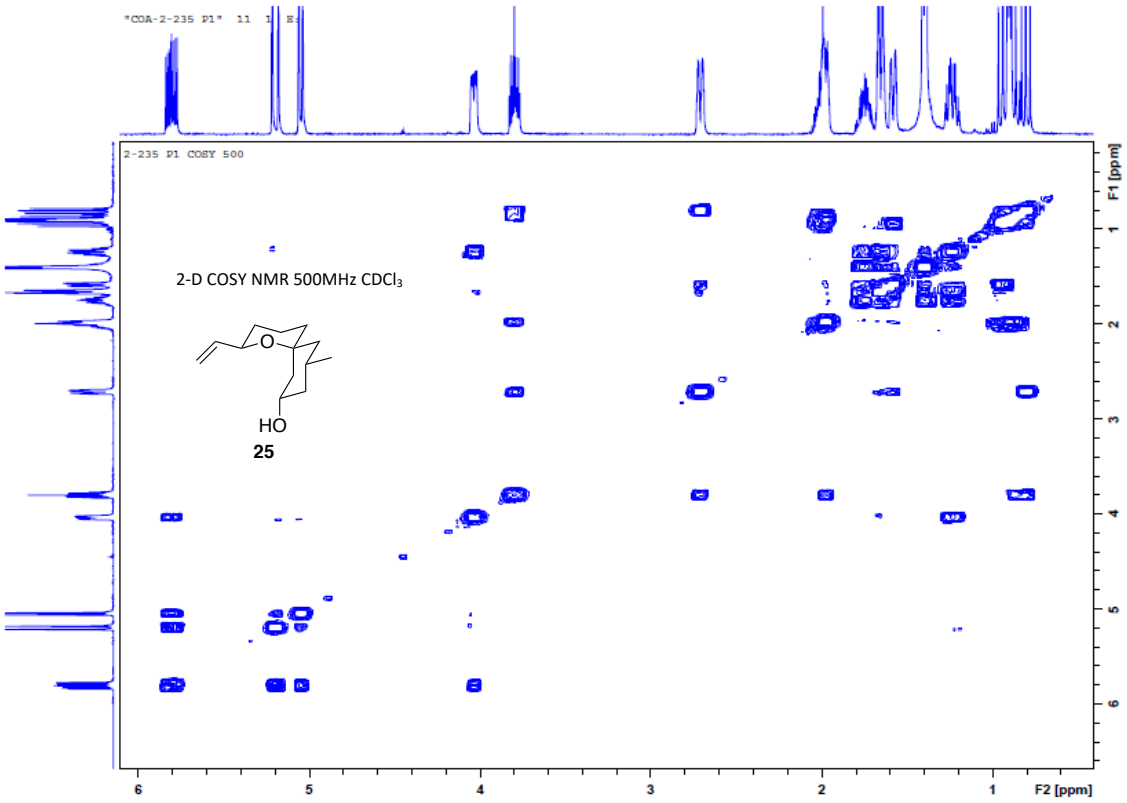

2-201 1H 500MHz CDCl3
5.769
5.761
5.755
5.751
5.747
5.737
5.732
5.729
5.724
5.715
5.701
5.689
5.672
5.659
5.649
5.644
5.611
5.019
4.996
4.987
4.096
4.089
4.429
2.418
2.397
2.385
2.369
2.275
2.261
2.211
2.195
2.179
2.171
2.163
2.143
2.130
2.117
2.104
2.090
2.069
2.055
2.044
2.031
2.011
1.996
1.979
1.965
1.952
1.694
1.679
1.664
1.650
1.635
0.904
0.891
1H NMR 500MHz CDCl3
HO
O
24
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
0.85
2.00
1.65
2.09
2.58
5.23
2.74
1.34
3.27

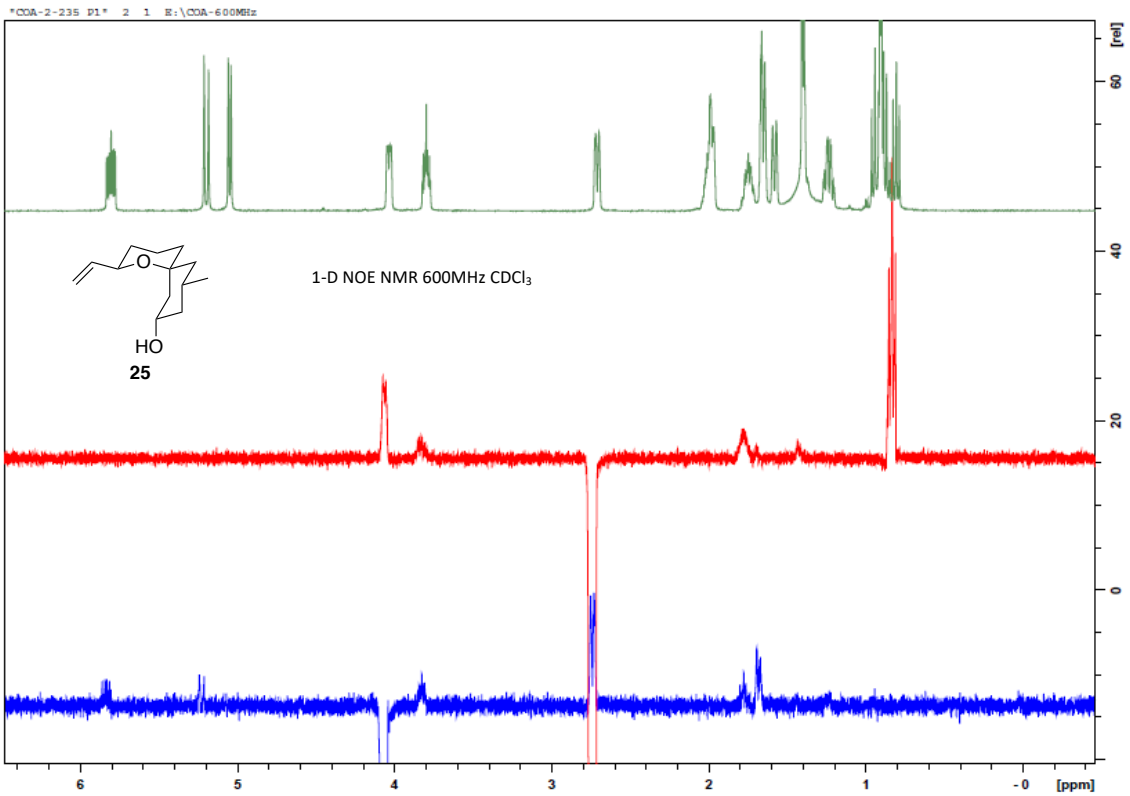

2-201 13C
210.65
136.67
132.19
129.80
116.44
63.67
49.41
42.58
41.16
31.58
28.89
23.01
19.80
13C NMR 125 MHz CDCl3
HO
O
24
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

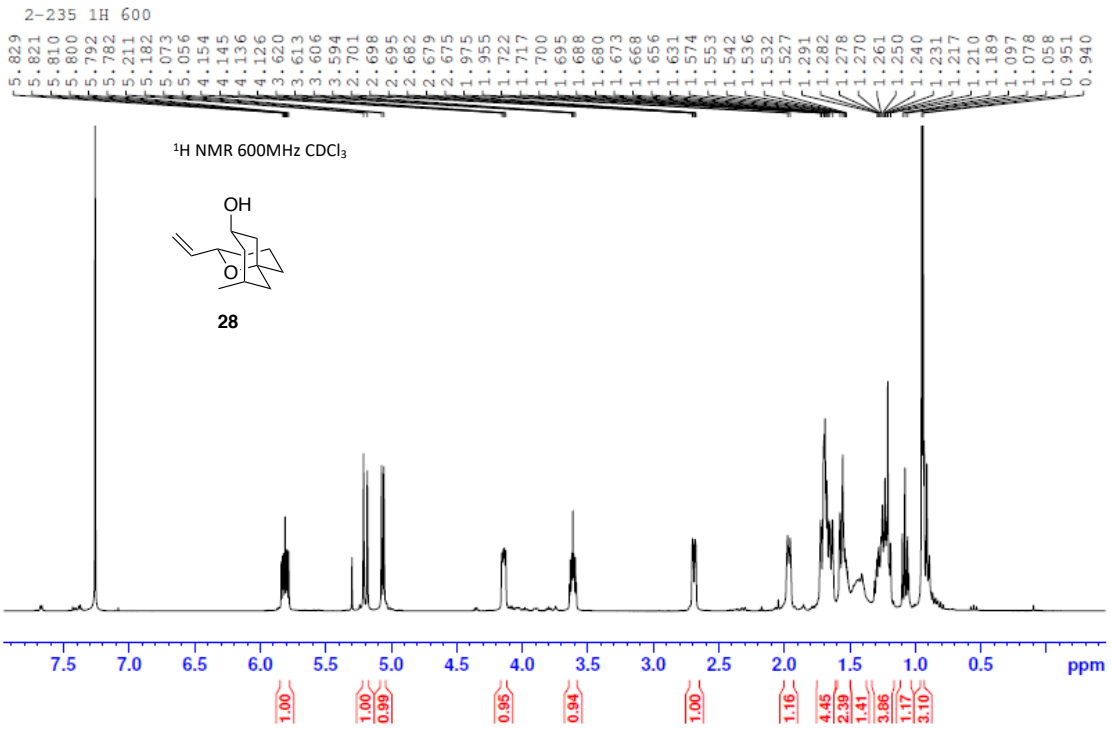

COA-2-201 11 1 E:
2-201 COSY 500MHz CDCl3
2-D COSY NMR 500MHz CDCl3
O
HO
24
F1 [ppm]
F2 [ppm]

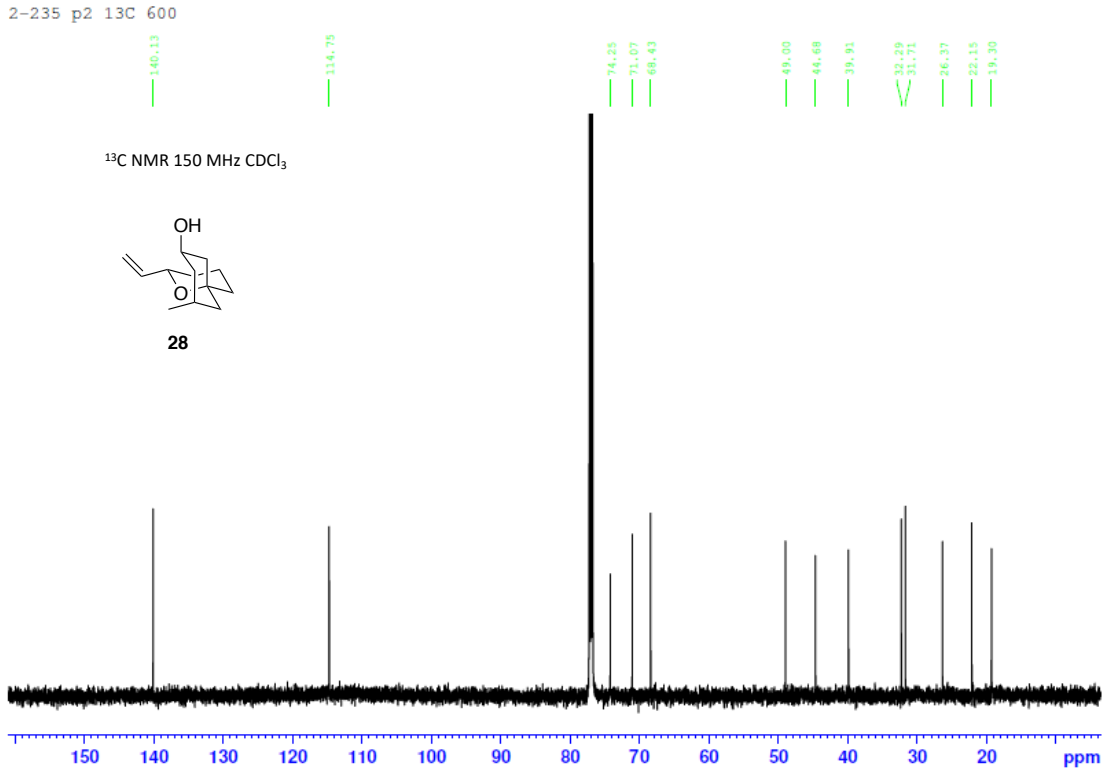

2-235 P1 1H 500
5.839 5.828 5.818 5.807 5.804 5.794 5.783 5.773 5.218 5.215 5.212 5.184 5.180 5.177 5.062 5.059 5.056 5.041 5.038 5.035 3.820 3.806 3.797 3.789 1.999 1.992 1.989 1.985 1.974 1.970 1.966 1.676 1.670 1.664 1.658 1.645 1.644 1.640 1.635 1.592 1.572 1.568 1.565 1.412 1.404 1.396 1.392 1.384 1.244 0.966 0.941 0.939 0.912 0.899 0.887 0.865 0.830 0.807 0.804 0.781
1H NMR 500MHz CDCl3
O
HO
25
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 ppm
1.00 1.04 1.05 1.08 1.06 1.09 2.19 1.12 2.23 1.14 3.25 1.31 0.80 3.40 1.07 1.16

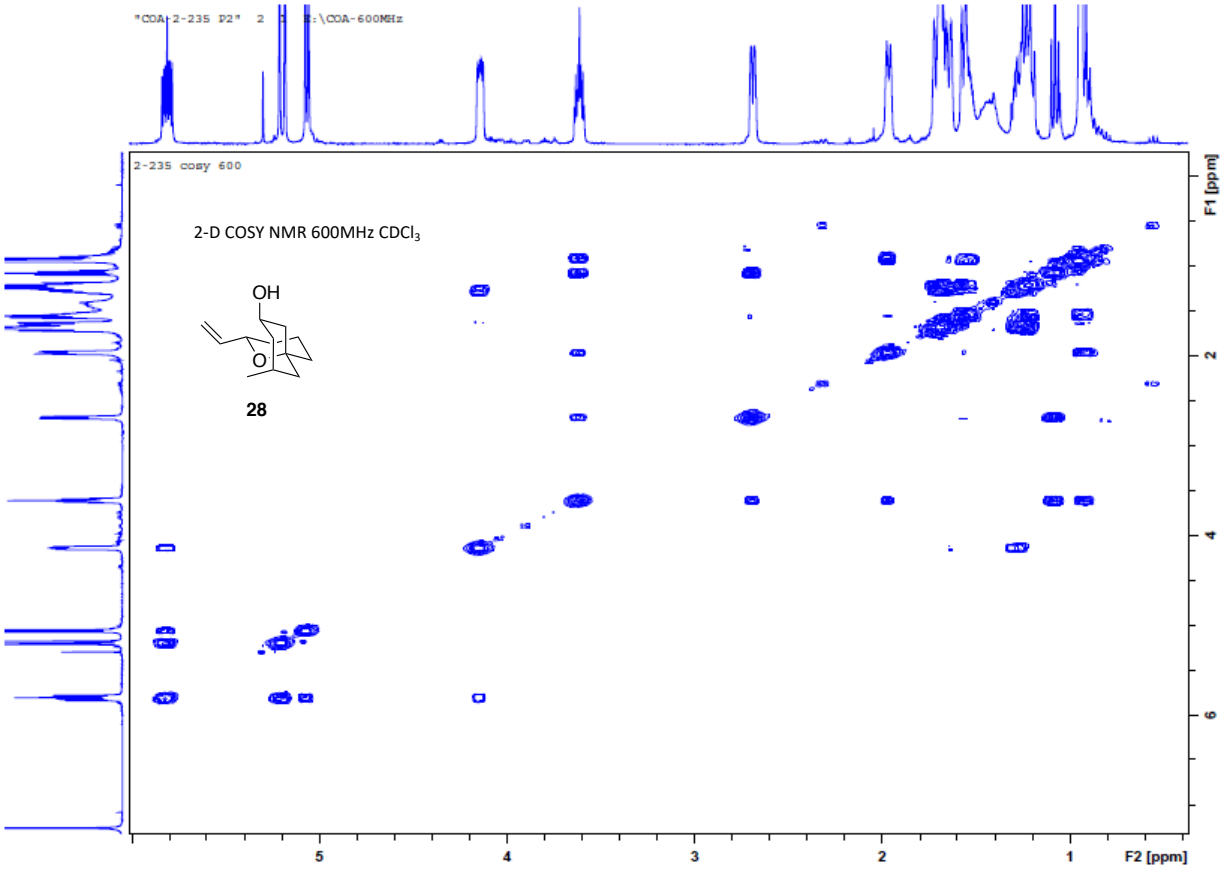

2-235 P1 13C 500
140.11 114.17 74.26 70.22 66.95 47.89 44.76 38.00 36.08 31.41 25.71 21.90 19.30
13C NMR 125 MHz CDCl3
O
HO
25
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


"COA-2-235 P1" 11 1
2-235 P1 COSY 500
2-D COSY NMR 500MHz $CDCl_3$
O
HO
25
F1 [ppm]
F2 [ppm]

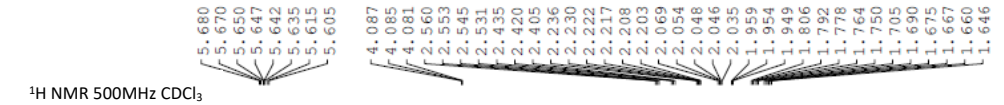

"COA-2-235 P1" 2 1 E:\COA-600MHz
1-D NOE NMR 600MHz $CDCl_3$
O
HO
25
[rel]
[ppm]


2-235 1H 600
5.829 5.821 5.810 5.800 5.792 5.782 5.211 5.182 5.073 5.056 4.154 4.145 4.136 4.126 3.620 3.613 3.606 3.594 2.701 2.698 2.695 2.682 2.679 2.675 1.975 1.955 1.722 1.717 1.700 1.695 1.688 1.680 1.673 1.668 1.656 1.631 1.574 1.553 1.542 1.536 1.532 1.527 1.291 1.282 1.278 1.270 1.261 1.250 1.240 1.231 1.217 1.210 1.189 1.097 1.078 1.058 0.951 0.940
1H NMR 600MHz CDCl3
OH
O
28
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
1.00 1.00 0.99 0.95 0.94 1.00 1.16 4.45 2.39 1.41 3.86 1.17 3.10

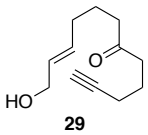

2-235 p2 13C 600
140.13 114.75 74.25 71.07 68.43 49.00 44.68 39.91 32.29 31.71 26.37 22.15 19.30
13C NMR 150 MHz CDCl3
OH
O
28
150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


"COA-2-235 P2" 2 E:\COA-600MHz
2-235 cosy 600
2-D COSY NMR 600MHz $CDCl_3$
OH
O
28
F1 [ppm]
F2 [ppm]
1
2
3
4
5
6

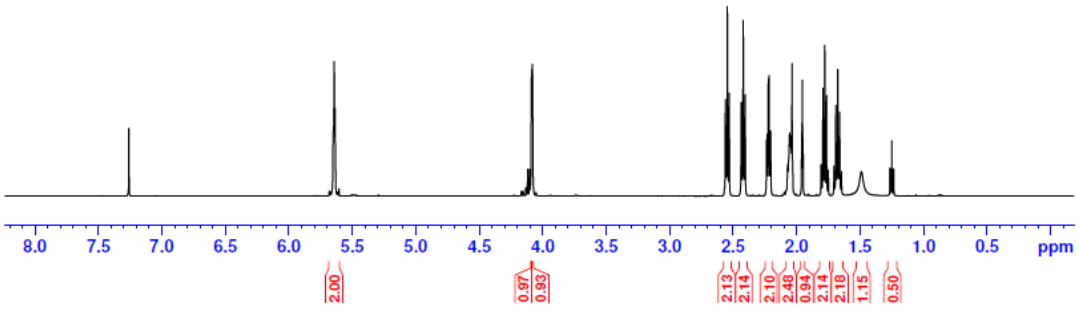
2-192 1H 500



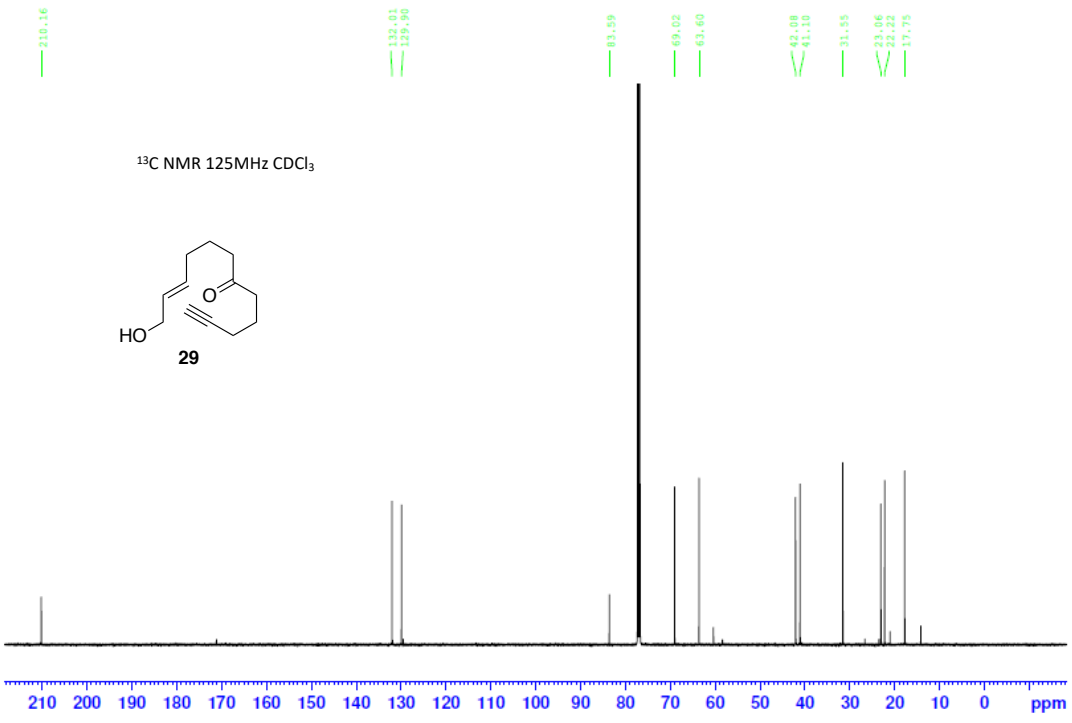
^{1}H NMR 500MHz $CDCl_3$



29

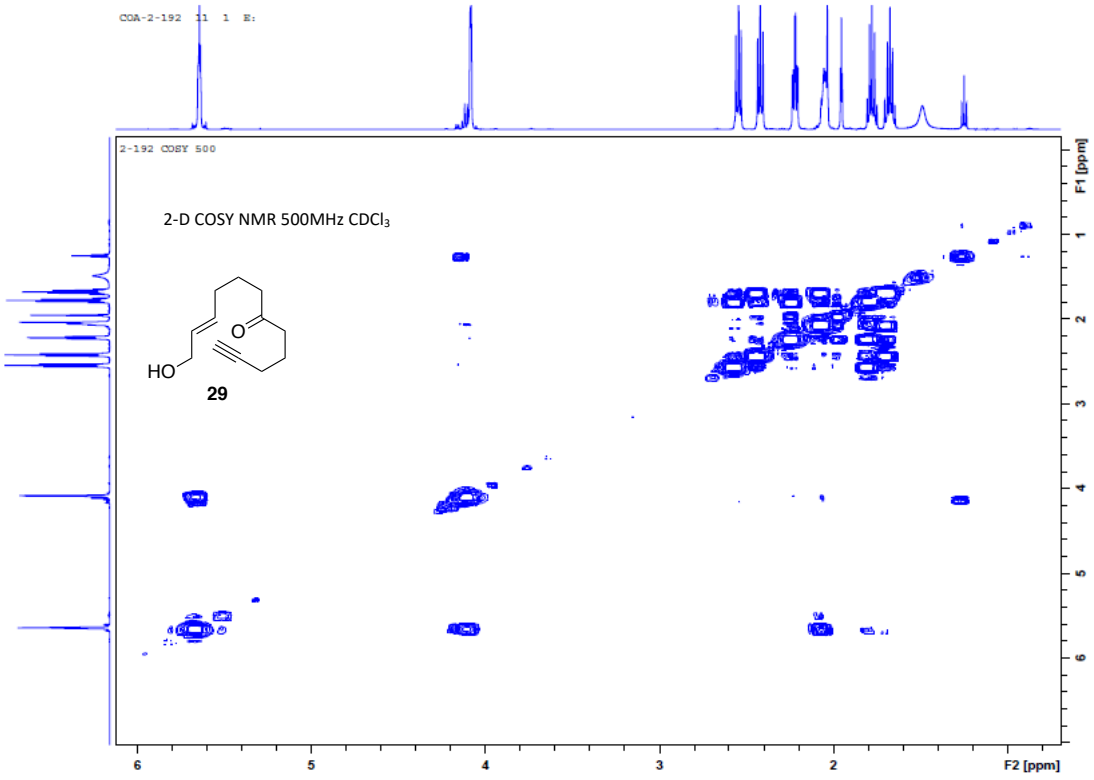


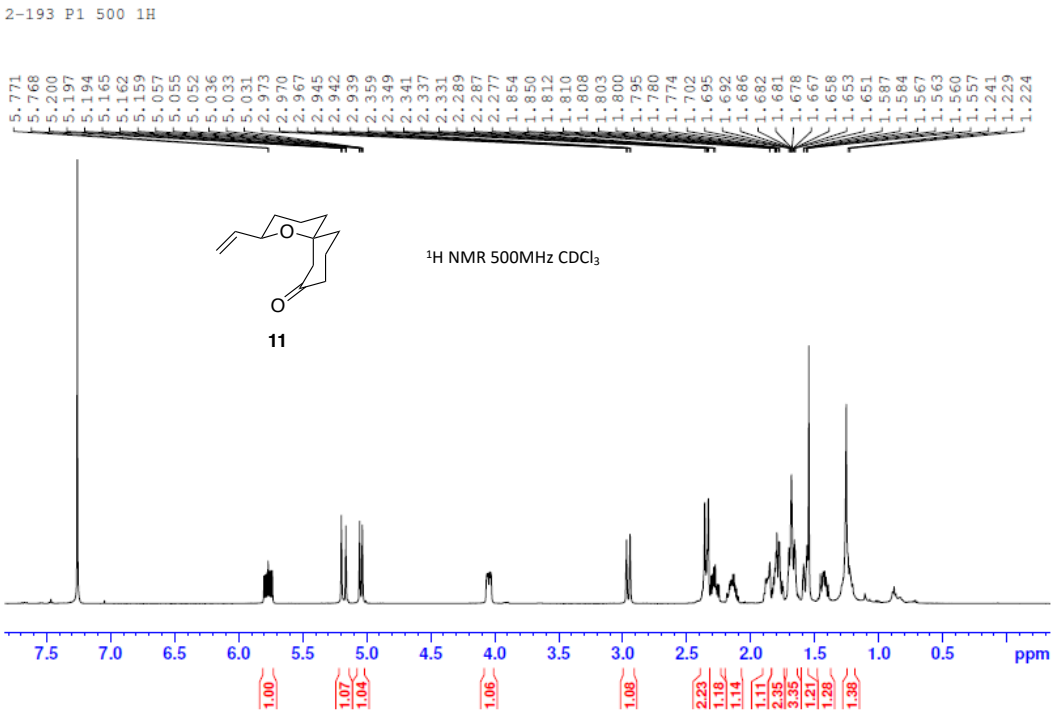
2-192 13C 500

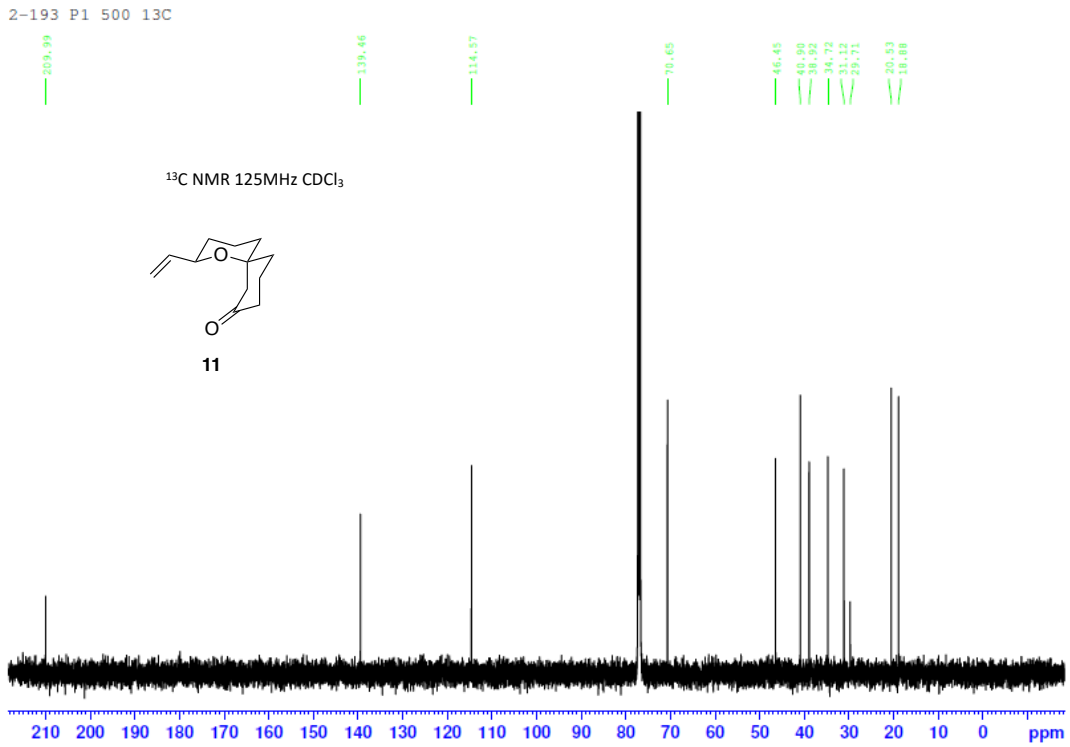


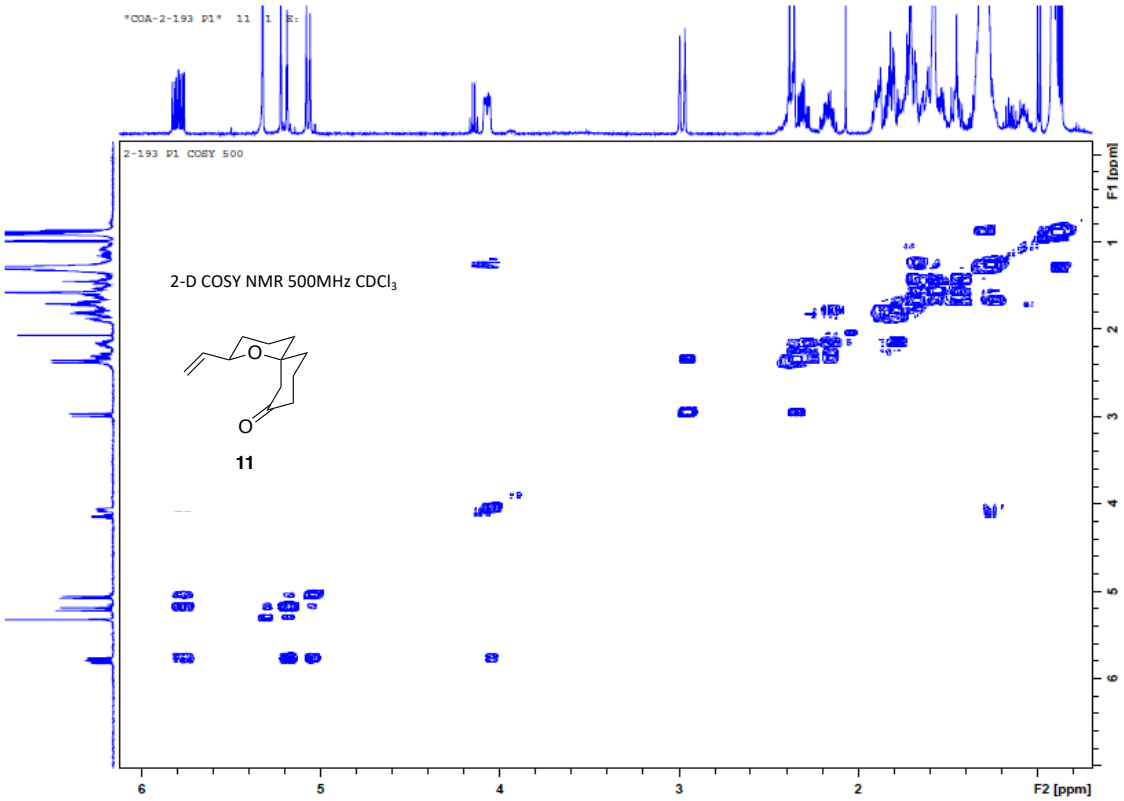
^{13}C NMR 125MHz $CDCl_3$

29


COA-2-192 11 1 E:
2-192 COSY 500
2-D COSY NMR 500MHz $CDCl_3$
HO
O
29
F1 [ppm]
F2 [ppm]
6
5
4
3
2
1

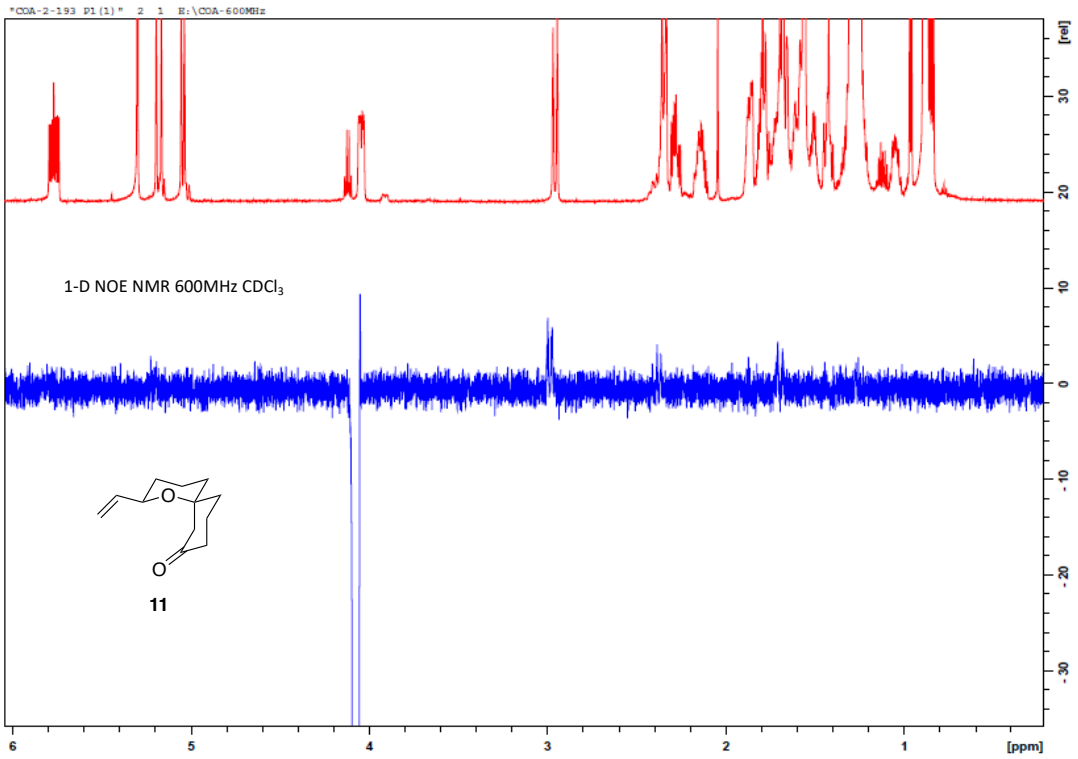

2-193 P1 500 1H
5.771
5.768
5.200
5.197
5.194
5.165
5.162
5.159
5.057
5.055
5.052
5.036
5.033
5.031
2.973
2.970
2.967
2.945
2.942
2.939
2.359
2.349
2.341
2.337
2.331
2.289
2.287
2.277
1.854
1.850
1.812
1.810
1.808
1.803
1.800
1.795
1.780
1.774
1.702
1.695
1.692
1.686
1.682
1.681
1.678
1.667
1.658
1.653
1.651
1.587
1.584
1.567
1.563
1.560
1.557
1.241
1.229
1.224
O
O
11
1H NMR 500MHz CDCl3
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
1.00
1.07
1.04
1.06
1.08
2.23
1.18
1.14
1.11
2.35
3.35
1.21
1.28
1.38


2-193 P1 500 13C
209.99
139.46
114.57
70.65
46.45
40.90
38.92
34.72
31.12
29.71
20.93
18.68
13C NMR 125MHz CDCl3
O
O
11
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



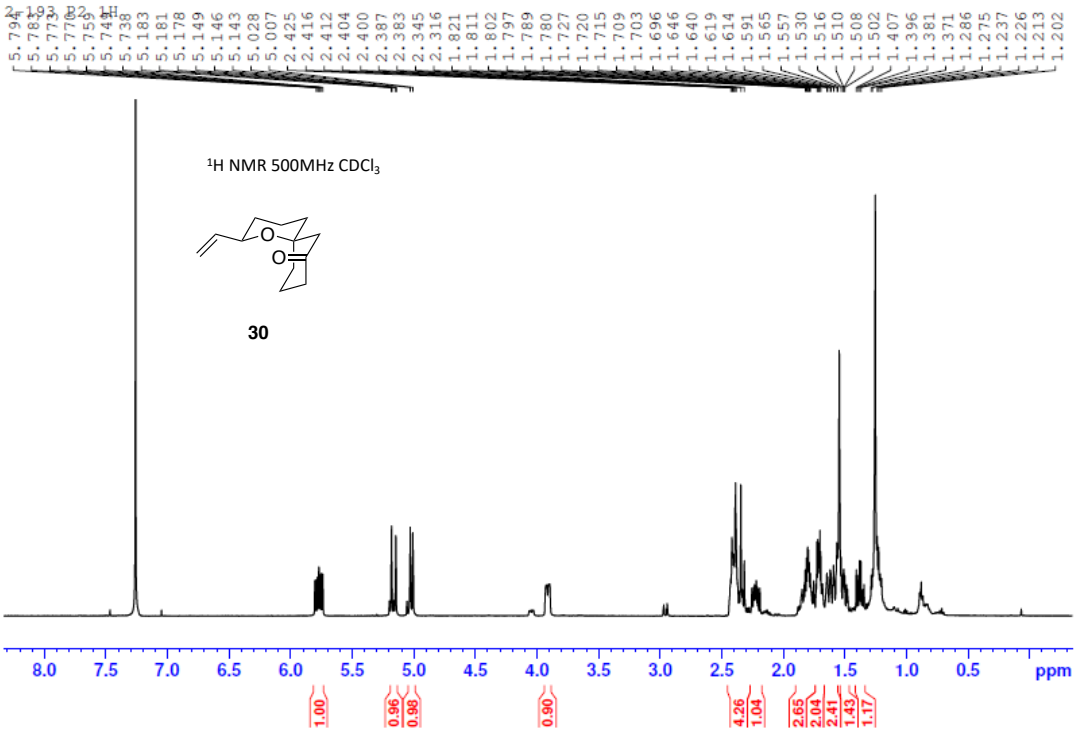
2-D COSY NMR 500MHz $CDCl_3$

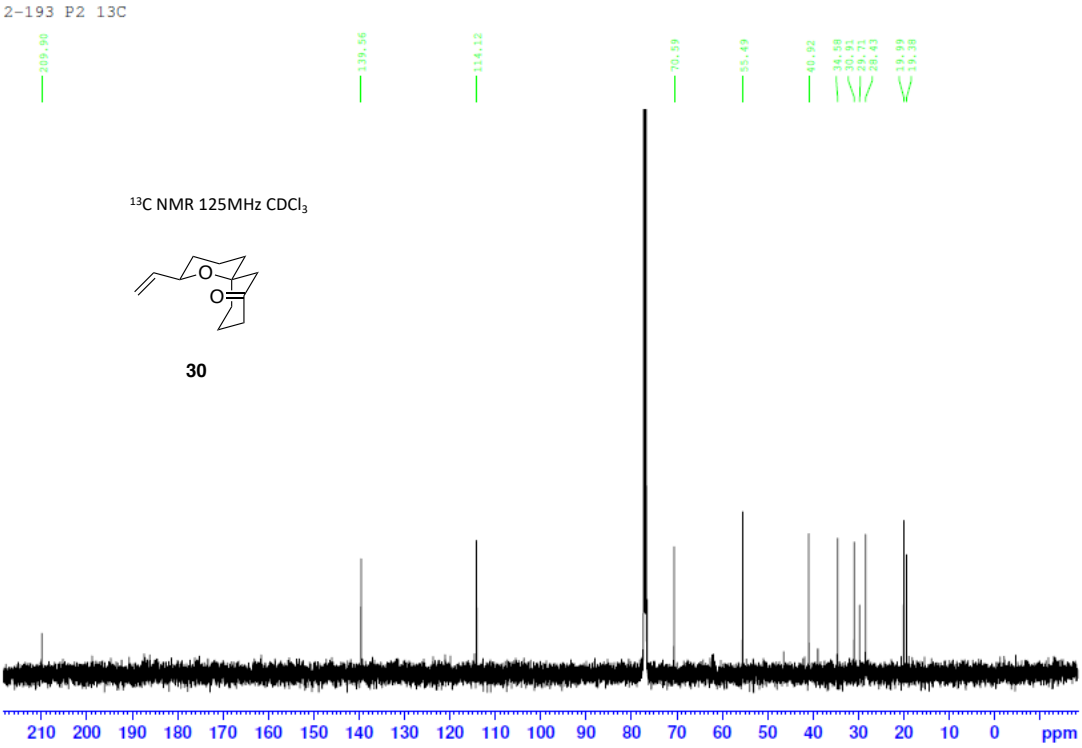
11

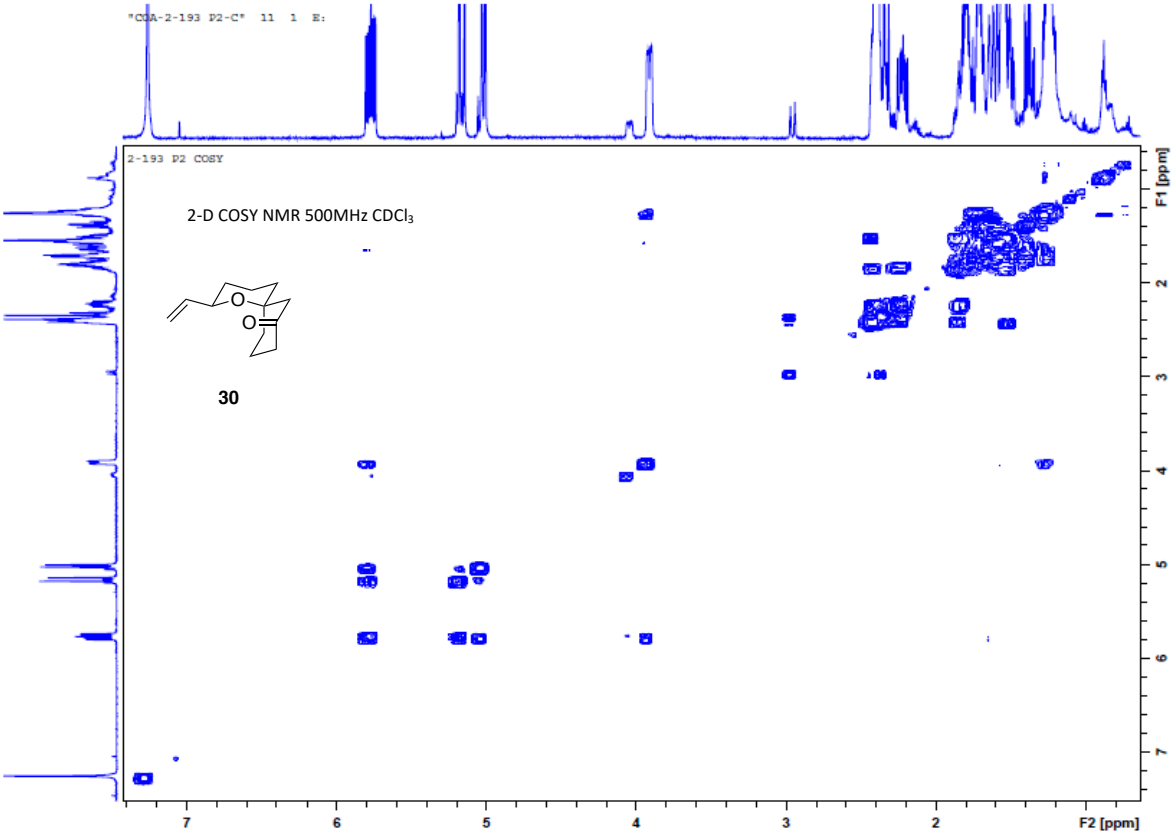


1-D NOE NMR 600MHz $CDCl_3$

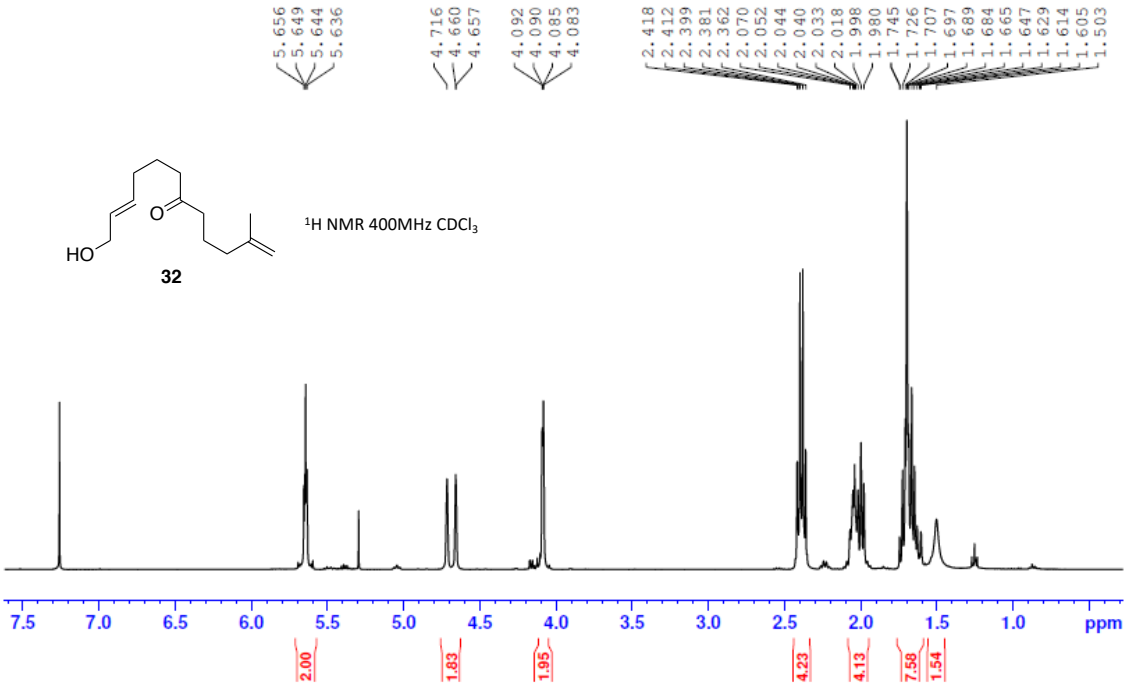
11


2-193 P2 1H
5.794 5.783 5.773 5.770 5.759 5.747 5.738 5.183 5.181 5.178 5.149 5.146 5.143 5.028 5.007 2.425 2.416 2.412 2.404 2.400 2.387 2.383 2.345 2.316 1.821 1.811 1.802 1.797 1.789 1.780 1.727 1.720 1.715 1.709 1.703 1.696 1.646 1.640 1.619 1.614 1.591 1.565 1.557 1.530 1.516 1.510 1.508 1.502 1.407 1.396 1.381 1.371 1.286 1.275 1.237 1.226 1.213 1.202
1H NMR 500MHz CDCl3
O
O
30
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
1.00 0.96 0.98 0.90 4.26 1.04 2.65 2.04 2.41 1.43 1.17

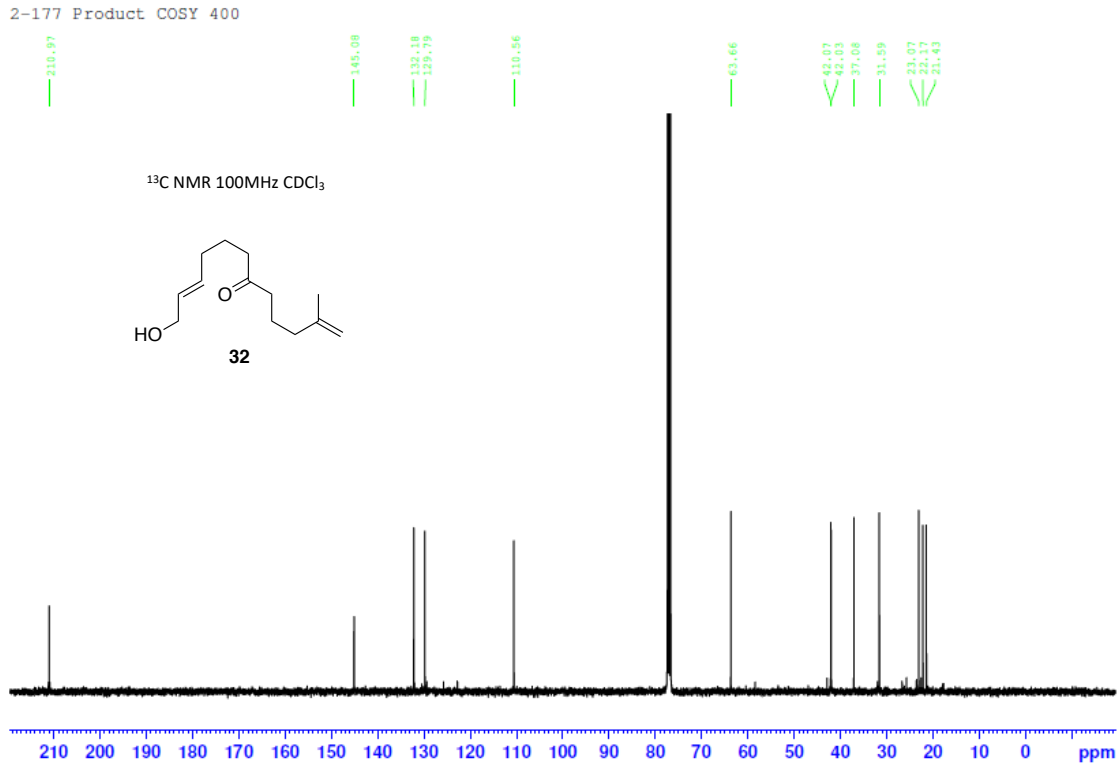

2-193 P2 13C
209.90 139.56 114.12 70.59 55.49 40.92 34.58 30.91 29.71 28.43 19.99 19.38
13C NMR 125MHz CDCl3
O
O
30
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

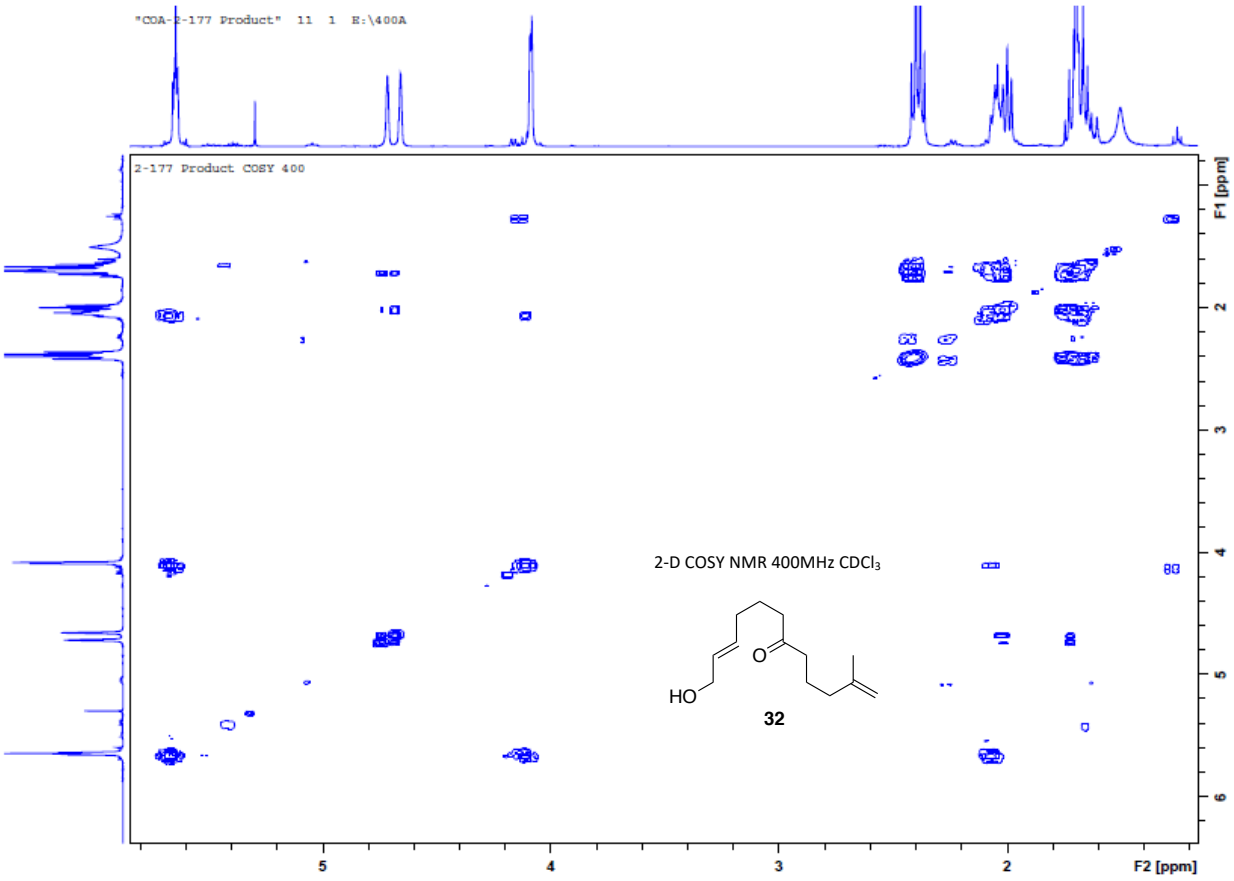

"CDA-2-193 P2-C" 11 1 E:
2-193 P2 COSY
2-D COSY NMR 500MHz $CDCl_3$
O
O
30
F1 [ppm]
F2 [ppm]
7
6
5
4
3
2

2-177 Product 1H 400

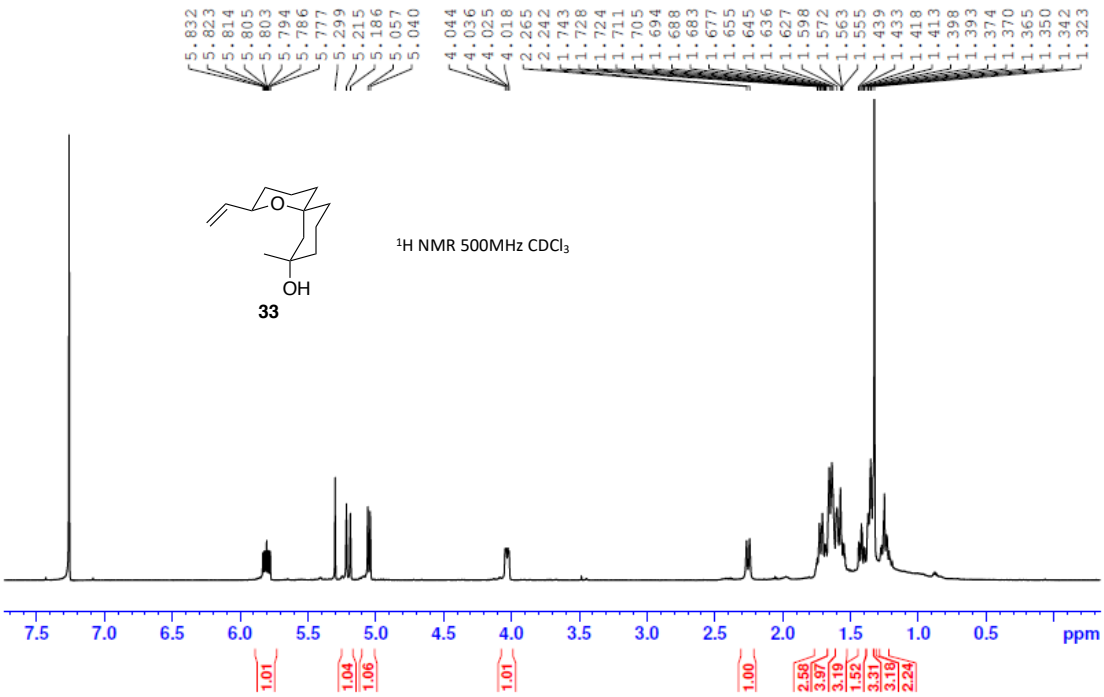


2-177 Product COSY 400

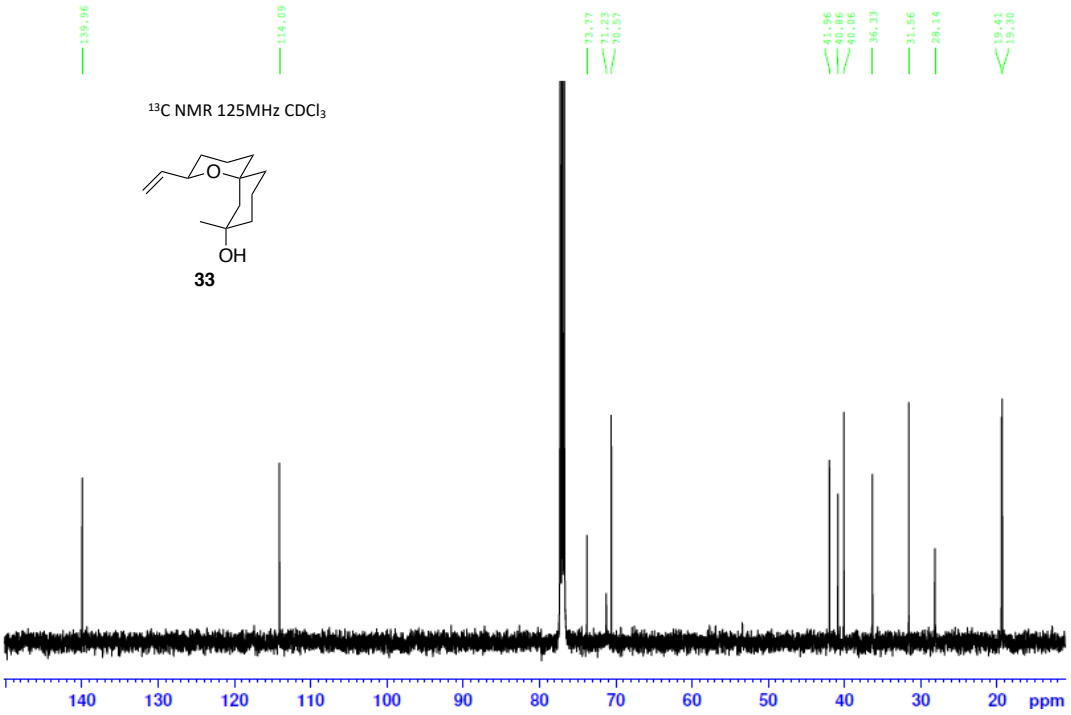


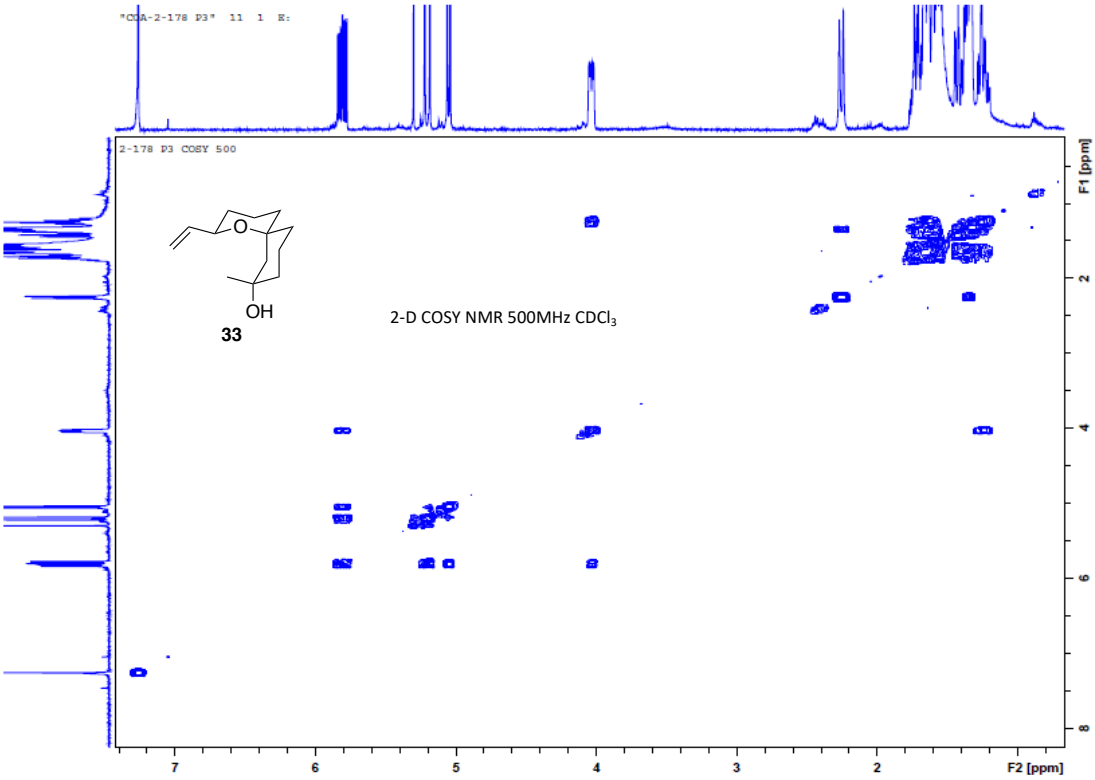

"COA-2-177 Product" 11 1 E:\400A
2-177 Product COSY 400
F1 [ppm]
F2 [ppm]
2-D COSY NMR 400MHz $CDCl_3$
HO
O
32

2-178 P3 1H



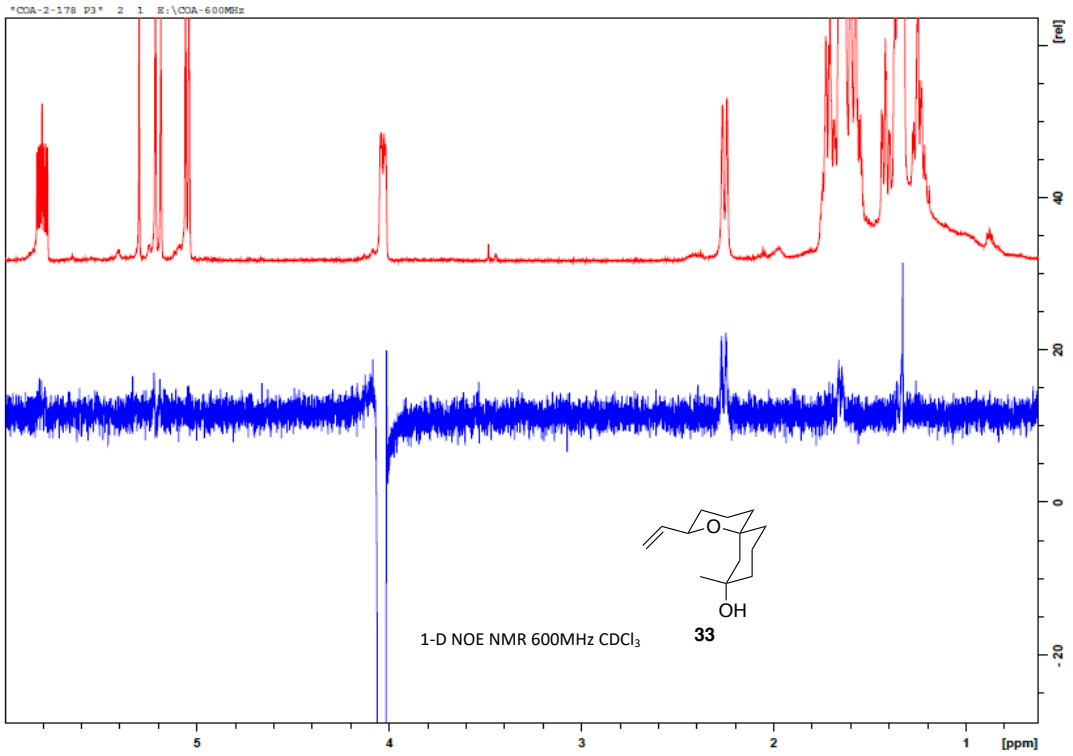
2-178 P3 COSY 500





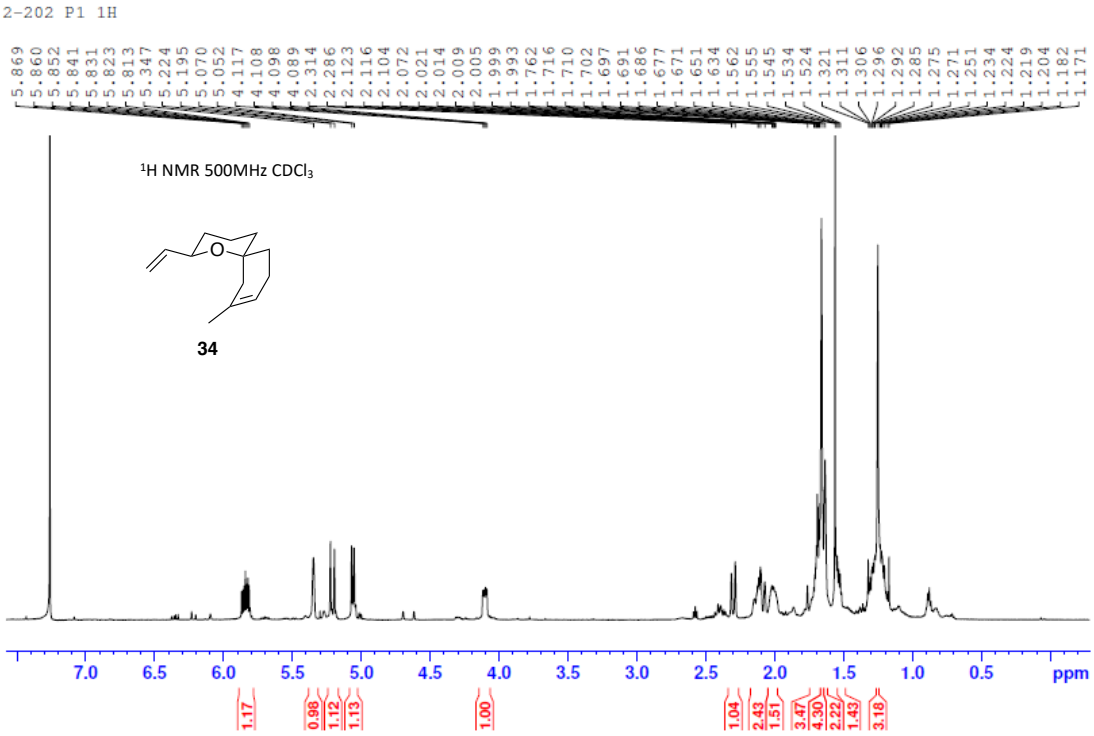
33

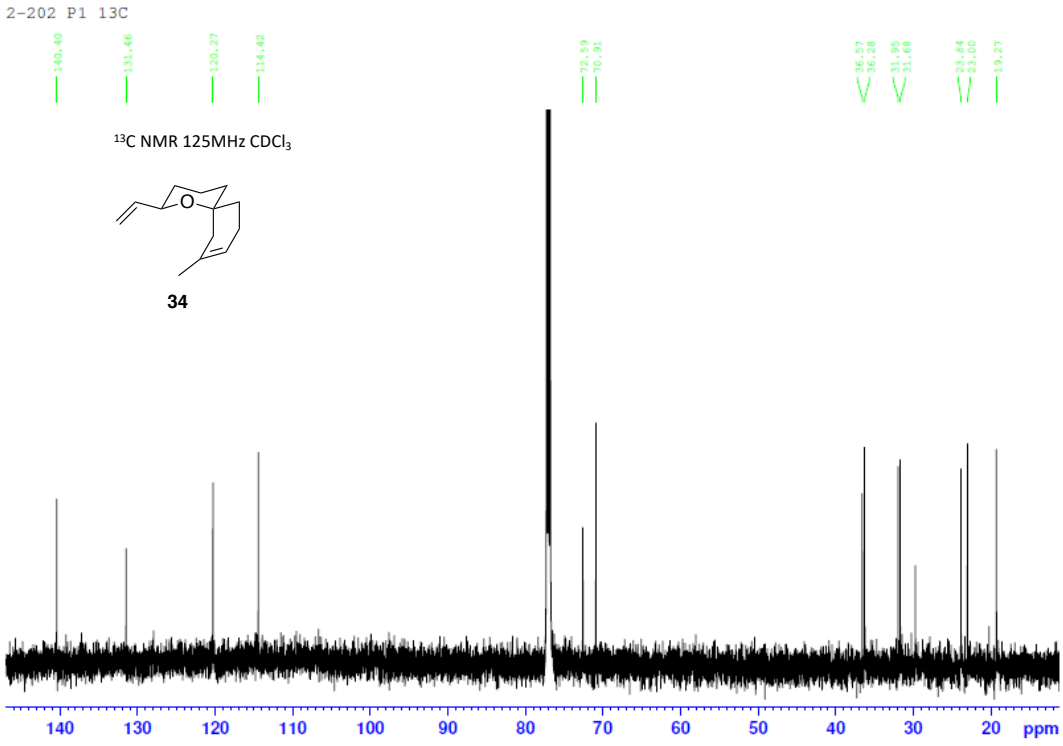
2-D COSY NMR 500MHz $CDCl_3$

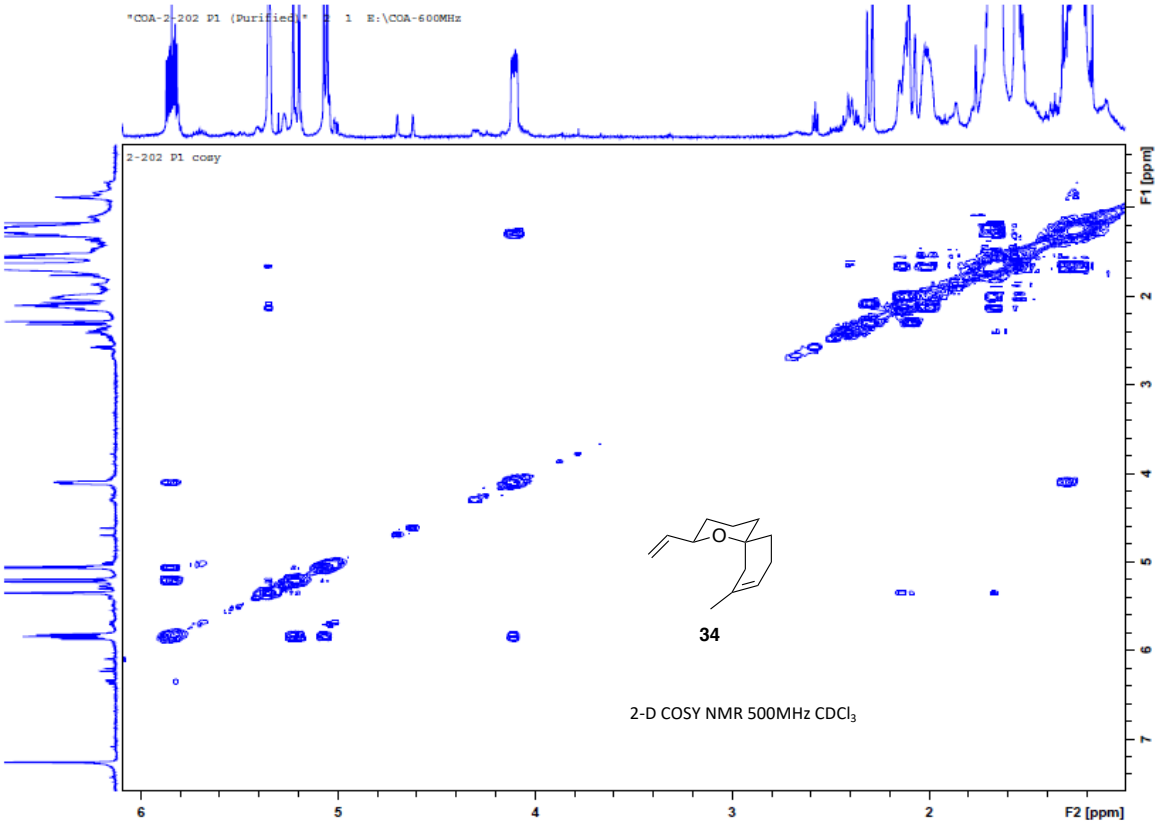


1-D NOE NMR 600MHz $CDCl_3$

33

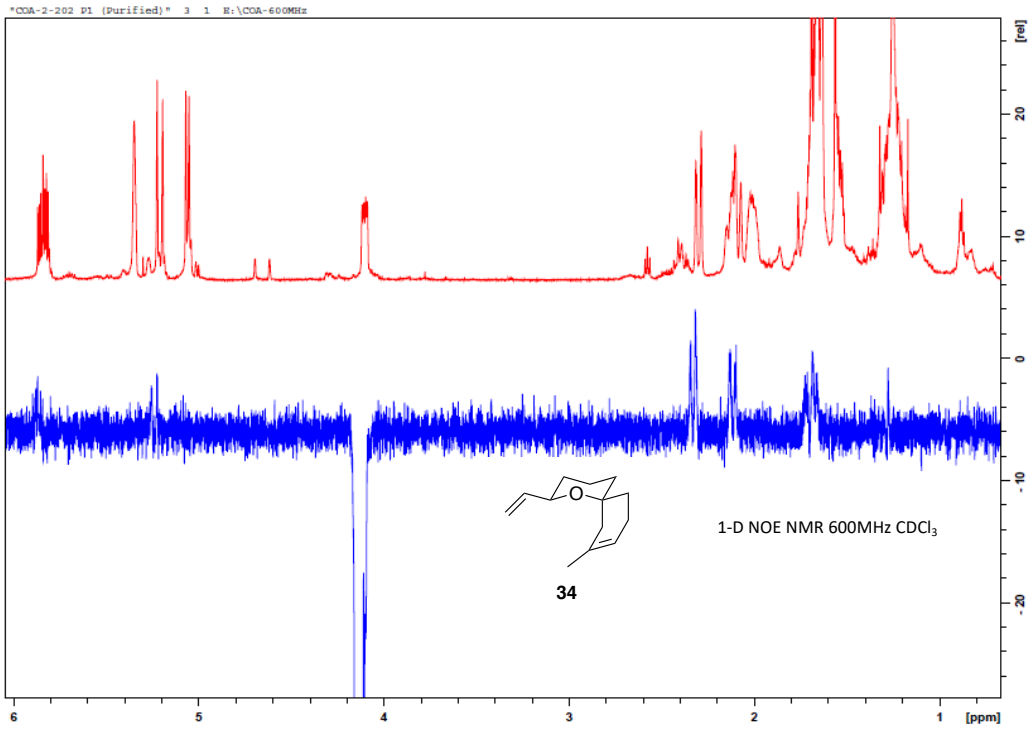

2-202 P1 1H
5.869 5.860 5.852 5.841 5.831 5.823 5.813 5.347 5.224 5.195 5.070 5.052 4.117 4.108 4.098 4.089 2.314 2.286 2.123 2.116 2.104 2.072 2.021 2.014 2.009 2.005 1.999 1.993 1.762 1.716 1.710 1.702 1.697 1.691 1.686 1.677 1.671 1.651 1.634 1.562 1.555 1.545 1.534 1.524 1.321 1.311 1.306 1.296 1.292 1.285 1.275 1.271 1.251 1.234 1.224 1.219 1.204 1.182 1.171
^{1}H NMR 500MHz $CDCl_3$
O
34
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
1.17 0.98 1.12 1.13 1.00 1.04 2.43 1.51 3.47 4.30 2.22 1.43 3.18


2-202 P1 13C
140.40 131.46 120.27 114.42 72.59 70.91 36.57 36.28 31.95 31.68 23.84 23.00 19.27
^{13}C NMR 125MHz $CDCl_3$
O
34
140 130 120 110 100 90 80 70 60 50 40 30 20 ppm



34

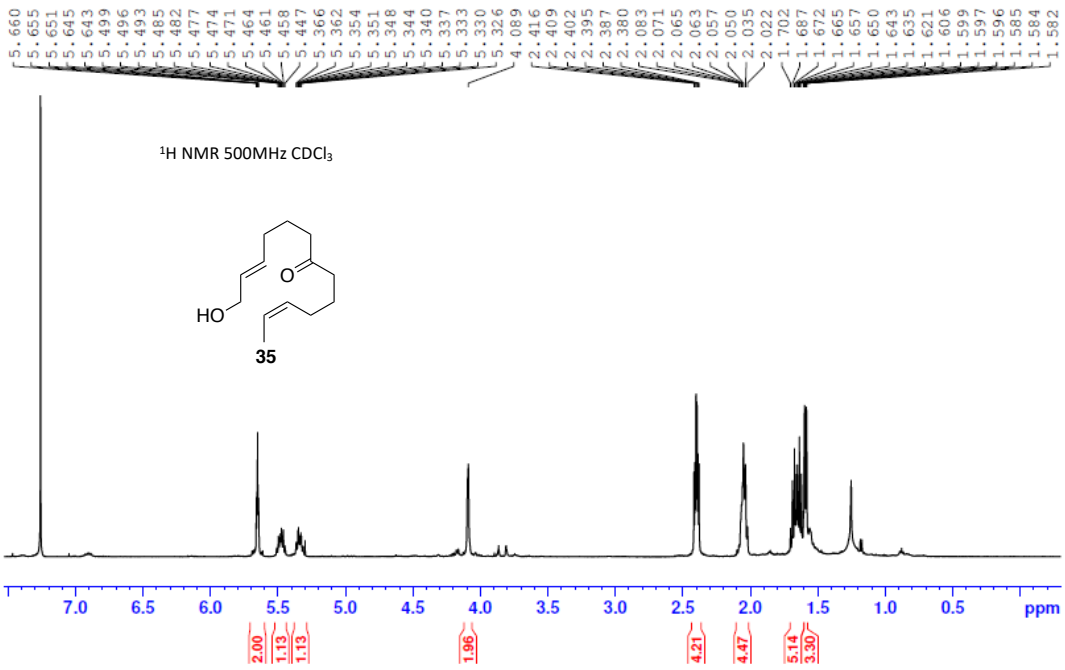
2-D COSY NMR 500MHz $CDCl_3$



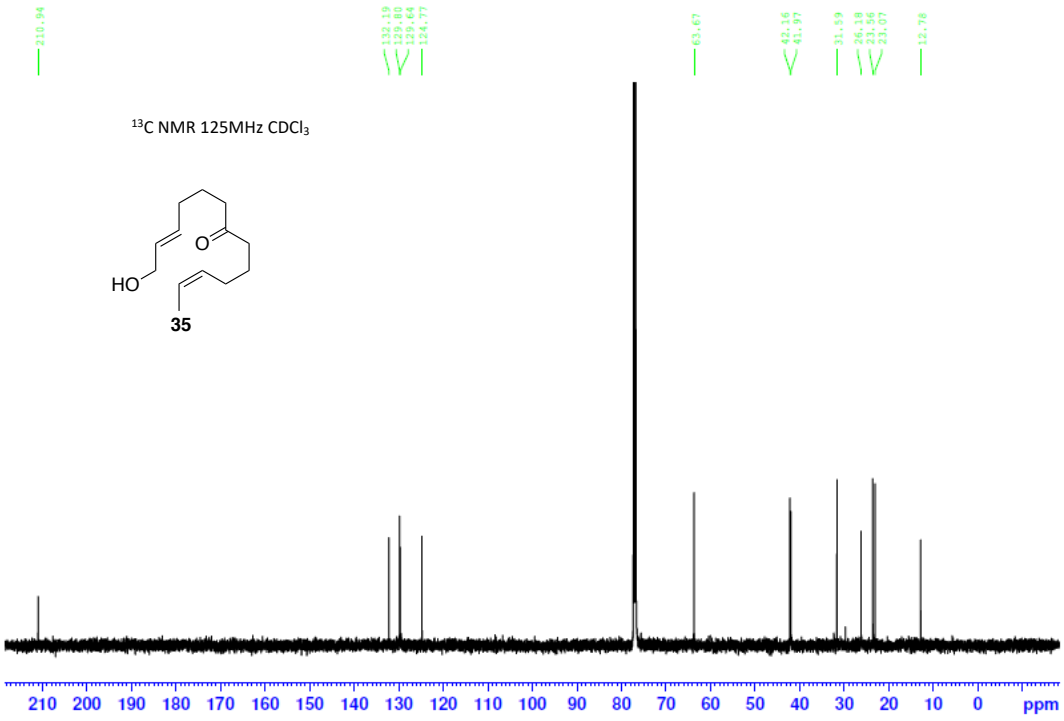
34

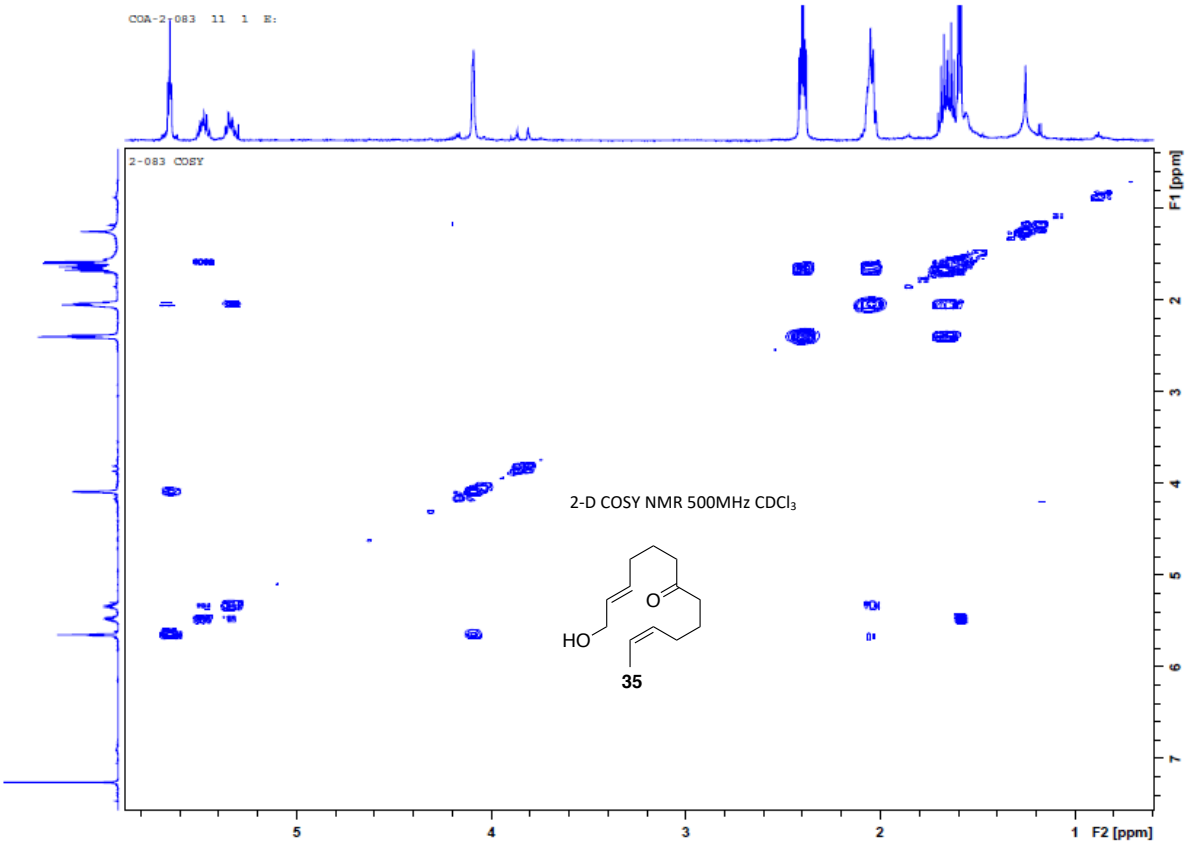
1-D NOE NMR 600MHz $CDCl_3$

2-083 1H

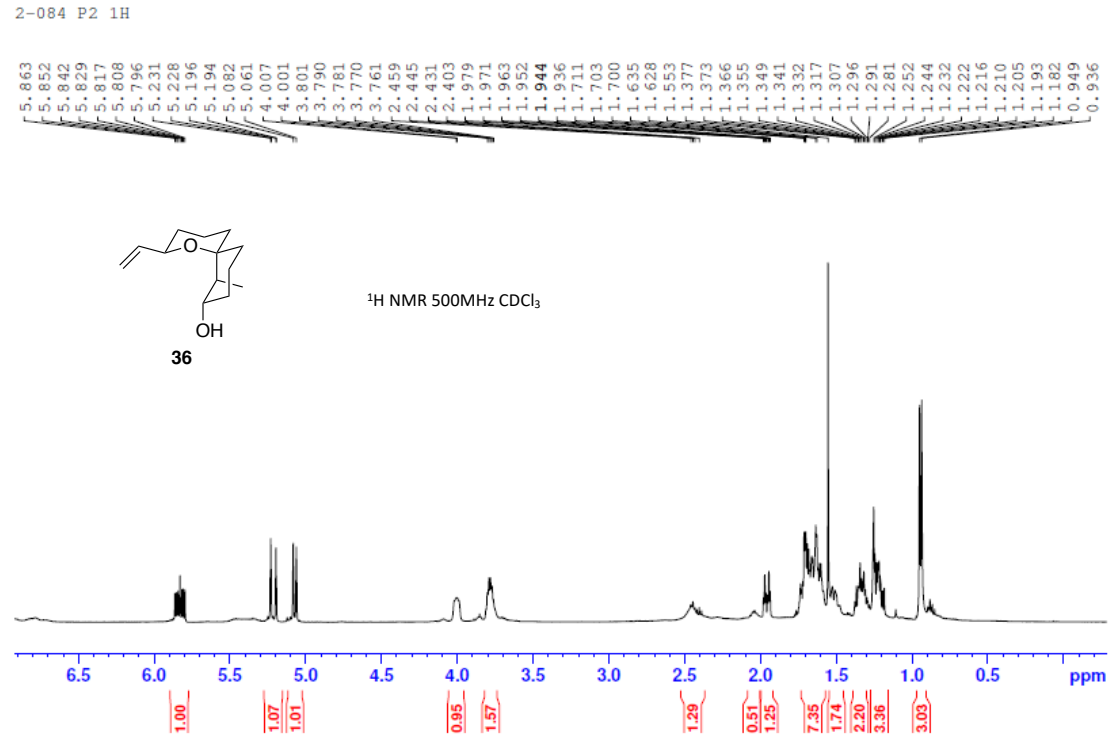


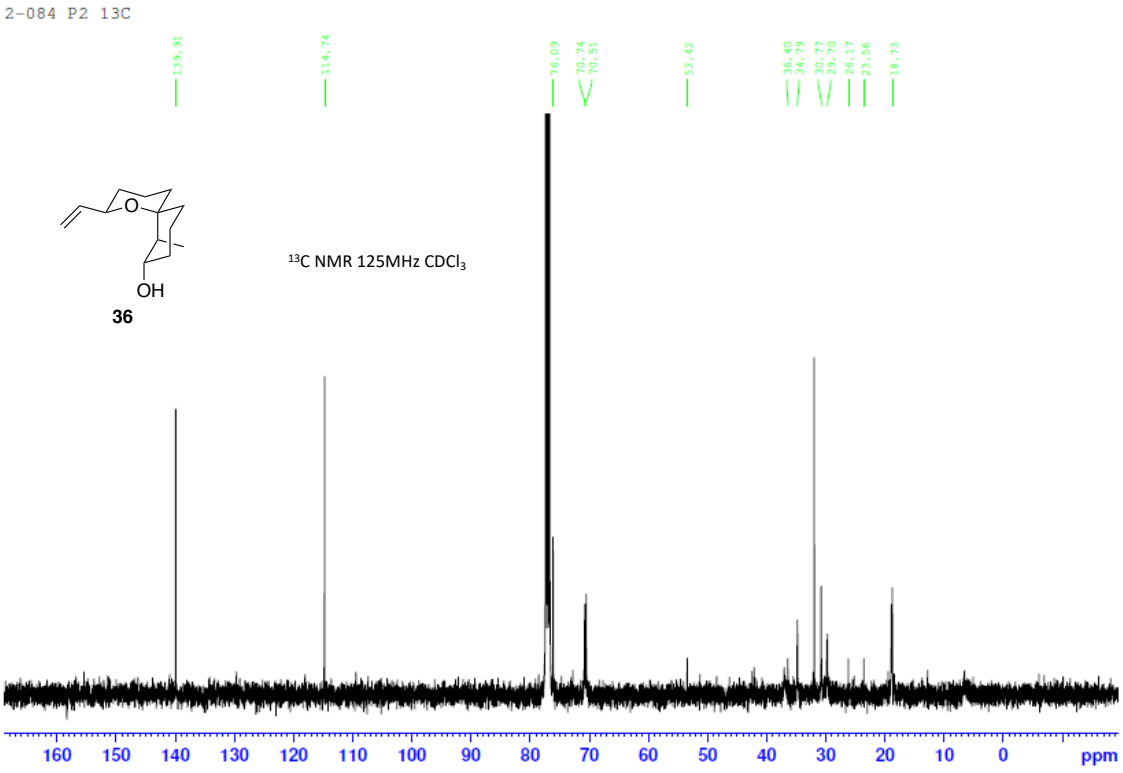
2-083 13C

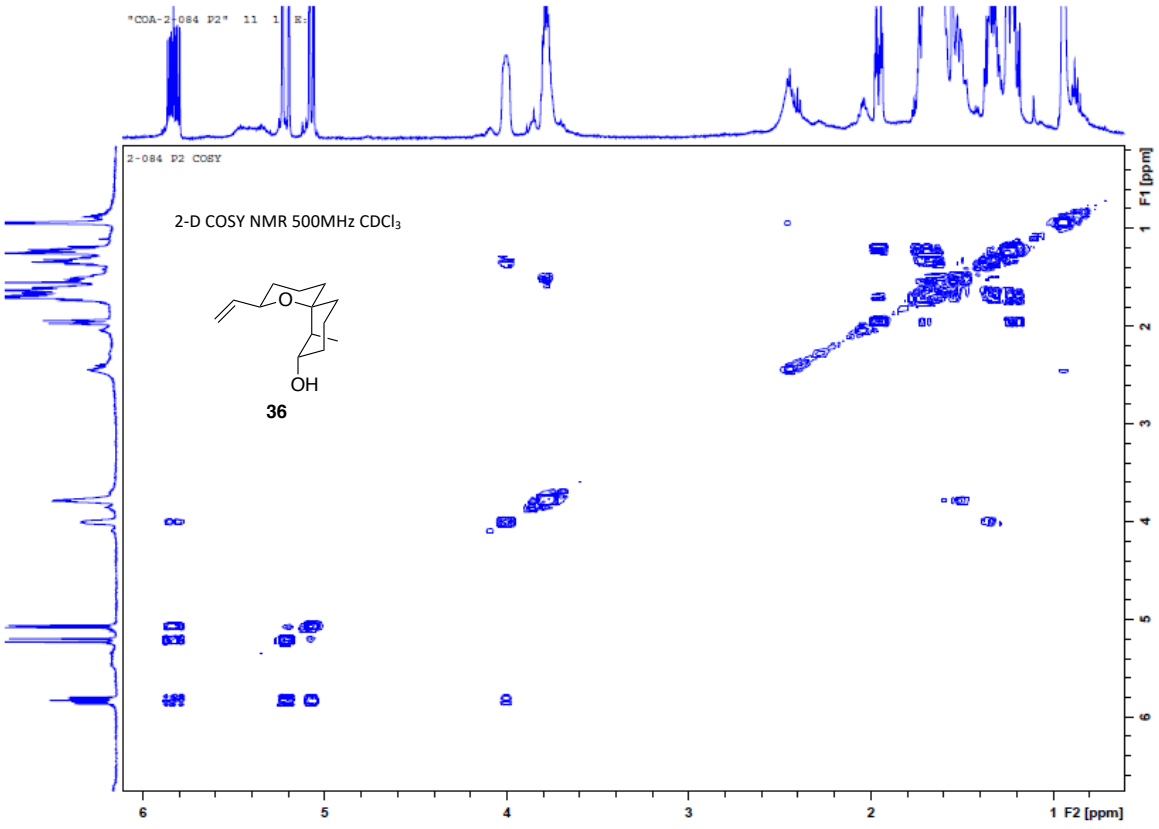


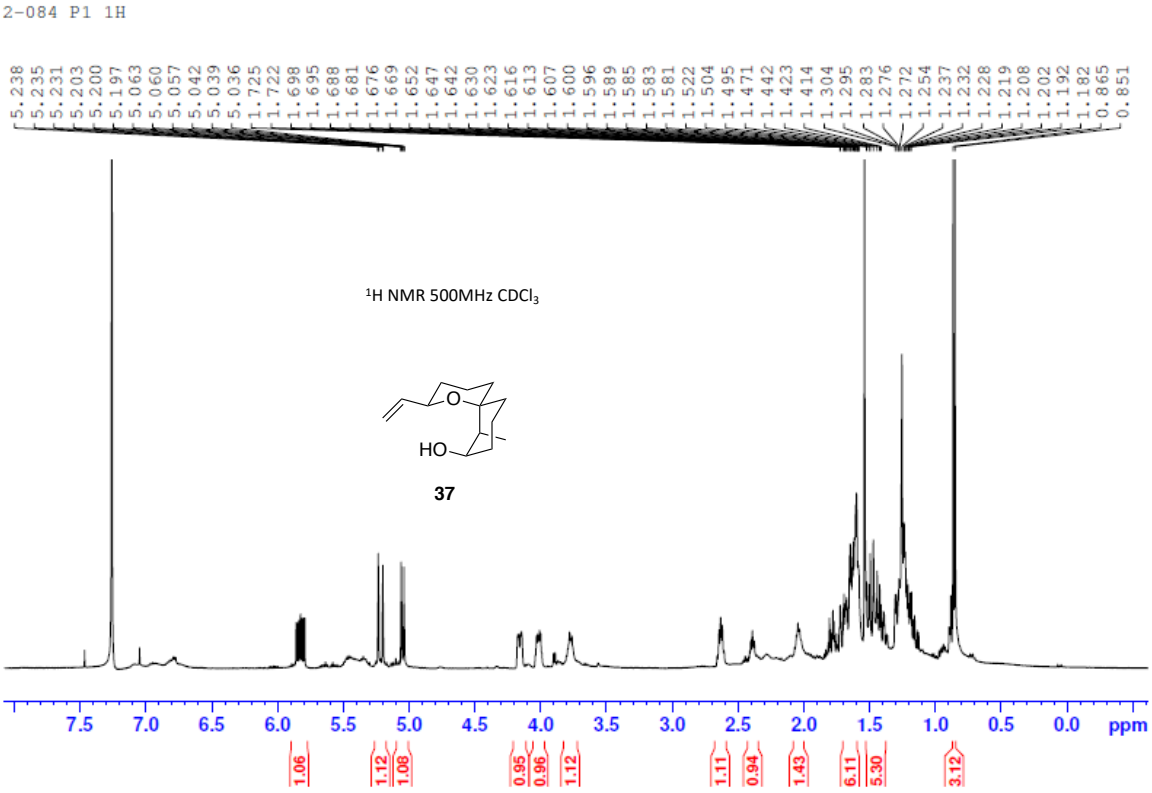


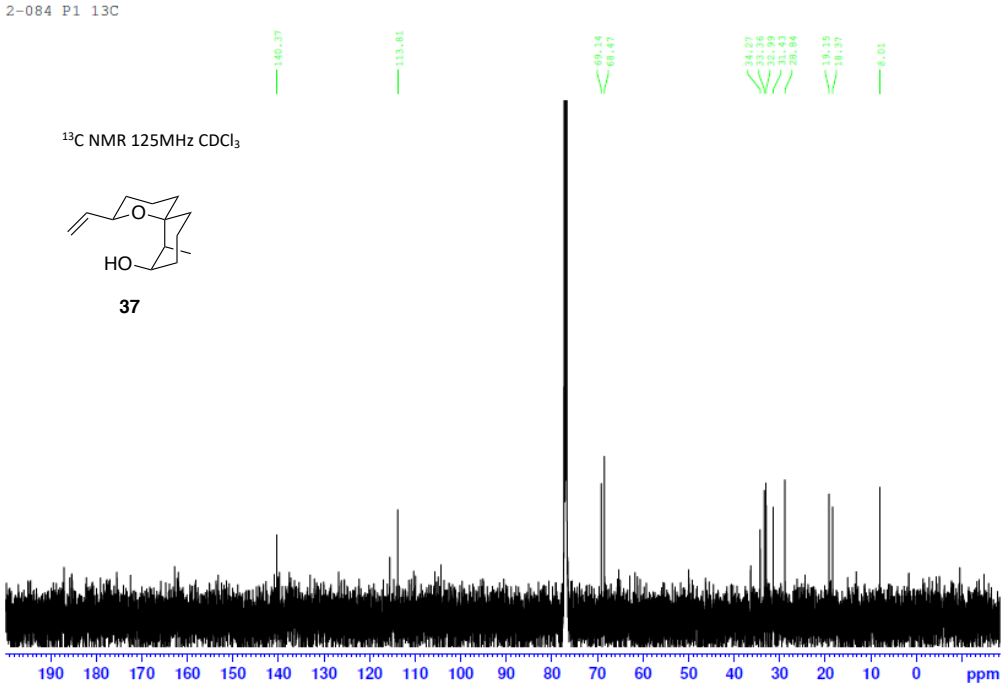
2-D COSY NMR 500MHz $CDCl_3$

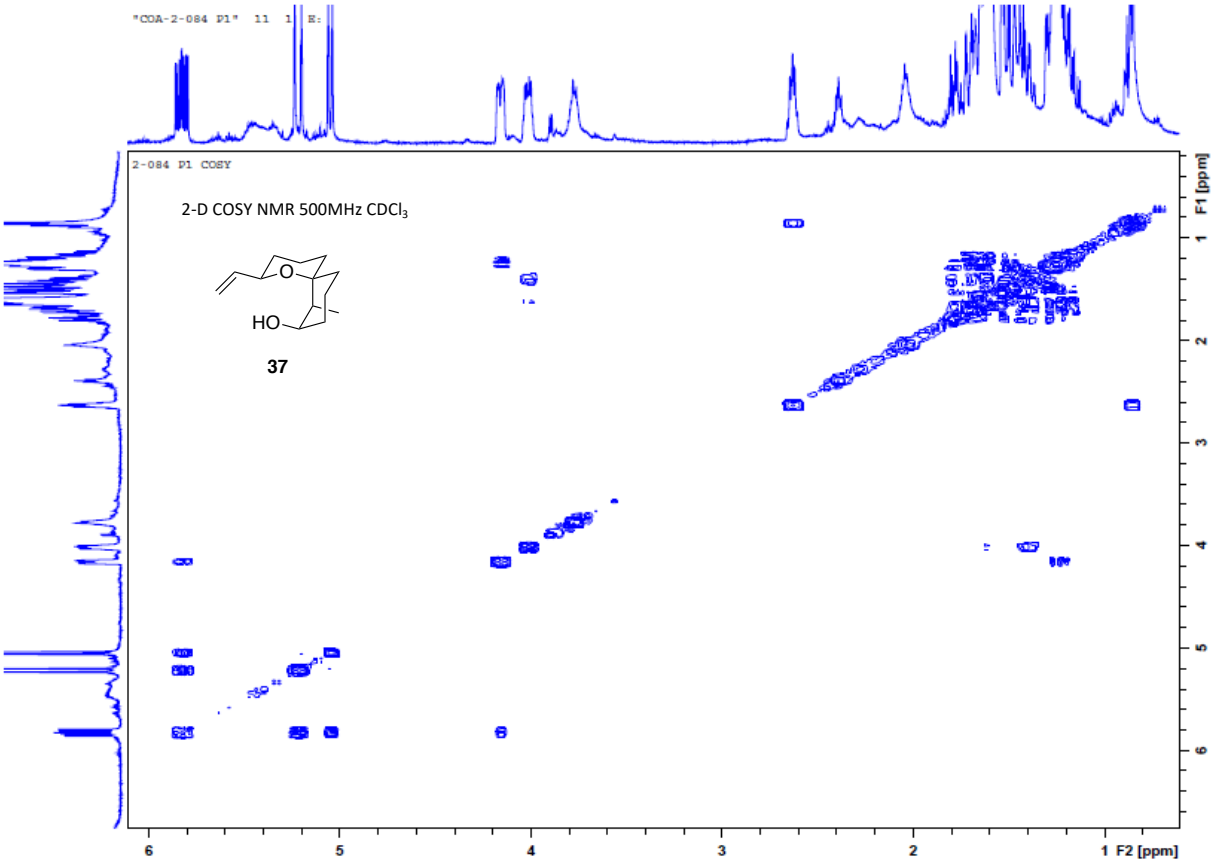

2-084 P2 1H
5.863
5.852
5.842
5.829
5.817
5.808
5.796
5.231
5.228
5.196
5.194
5.082
5.061
4.007
4.001
3.801
3.790
3.781
3.770
3.761
2.459
2.445
2.431
2.403
1.979
1.971
1.963
1.952
1.944
1.936
1.711
1.703
1.700
1.635
1.628
1.553
1.377
1.373
1.366
1.355
1.349
1.341
1.332
1.317
1.307
1.296
1.291
1.281
1.252
1.244
1.232
1.222
1.216
1.210
1.205
1.193
1.182
0.949
0.936
O
OH
36
1H NMR 500MHz CDCl3
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
1.00
1.07
1.01
0.95
1.57
1.29
0.51
1.25
7.35
1.74
2.20
3.36
3.03


2-084 P2 13C
139.91
114.74
76.09
70.74
70.51
53.42
36.40
34.79
30.77
29.70
26.17
23.56
18.73
O
OH
36
13C NMR 125MHz CDCl3
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


"COA-2-084 P2" 11 1 E:
2-084 P2 COSY
2-D COSY NMR 500MHz $CDCl_3$
O
OH
36
F1 [ppm]
F2 [ppm]
1
2
3
4
5
6


2-084 P1 1H
5.238
5.235
5.231
5.203
5.200
5.197
5.063
5.060
5.057
5.042
5.039
5.036
1.725
1.722
1.698
1.695
1.688
1.681
1.676
1.669
1.652
1.647
1.642
1.630
1.623
1.616
1.613
1.607
1.600
1.596
1.589
1.585
1.583
1.581
1.522
1.504
1.495
1.471
1.442
1.423
1.414
1.304
1.295
1.283
1.276
1.272
1.254
1.237
1.232
1.228
1.219
1.208
1.202
1.192
1.182
0.865
0.851
1H NMR 500MHz CDCl3
O
HO
37
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
ppm
1.06
1.12
1.08
0.95
0.96
1.12
1.11
0.94
1.43
6.11
5.30
3.12


2-084 P1 13C
140.37
133.81
69.14
68.47
34.27
33.36
32.99
31.43
28.84
19.15
18.37
8.01
13C NMR 125MHz CDCl3
O
HO
37
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


"COA-2-084 P1" 11 1 E:
2-084 P1 COSY
2-D COSY NMR 500MHz $CDCl_3$
O
HO
37
F1 [ppm]
F2 [ppm]
1
2
3
4
5
6