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Supporting Information

Sustainable Catalytic Protocols for the Solvent Free Epoxidation and (*anti*)-Dihydroxylation of the Alkene Bonds of Biorenewable Terpene Feedstocks Using H_2O_2 as Oxidant

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1 General Information

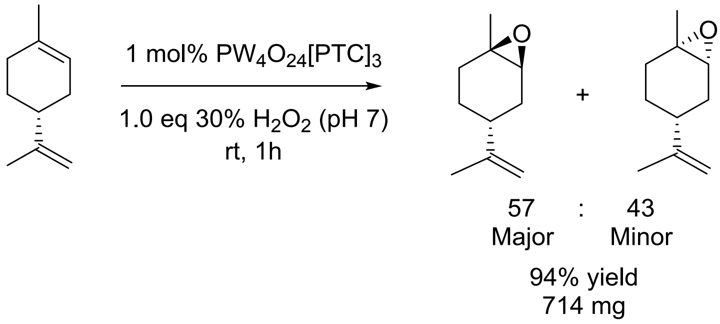
Reagents were used as received from commercial suppliers or prepared in our laboratory. All reactions were performed under air in oven-dried apparatus, with anhydrous solvents obtained from an Innovative Technology Inc. PS-400-7 solvent purification system. Flash chromatography was performed using chromatography grade silica and alumina, 60 Å particle size 35-70 microns from Fisher Scientific. ^{1}H NMR spectra were recorded at 500 MHz, 400 MHz, 300 MHz or 250 MHz and ^{13}C{^{1}H} spectra were recorded at 125 MHz, 100 MHz or 75 MHz on Brüker Avance 500, 400 or 300 spectrometers respectively. Chemical shifts (δ) are quoted in parts per million (ppm) and are referenced to the residual solvent peak. High resolution mass spectra were recorded on a Brüker Daltonics microTOF spectrometer with an electrospray source and external calibration. Long spin lattice relaxation times and quadrupolar broadening effects resulted in low intensity (or missing) resonances for the isocyanide and alkene carbon atoms in a some of the ^{13}C NMR spectra of the vinyl isocyanides.[1] Masses were recorded in positive electrospray ionisation mode with samples introduced by flow injection. Masses are accurate to 5 ppm with data processed using Data Analysis software from Brüker Daltonics. Infrared spectra were recorded on a Perkin Elmer Spectrum 100 FT-IR spectrometer using a Universal ATR accessory for sampling, with only selected absorbances reported as ν in cm^{-1}. Optical rotations were recorded on an Optical Activity Ltd AA-10 automatic polarimeter with a path length of 1 dm; with concentrations (*c*) quoted in g/100 mL.

2 Synthesis and characterization data for products

2.1 Epoxidation conditions used to prepare terpene epoxides and their corresponding spectroscopic data

***(R)*-(+)-1,2-Limonene oxides (1a/b)** – mixture of Major- and Minor- epoxides

(1*R*,4*R*,6*S*)-1-methyl-4-(prop-1-en-2-yl)-7-oxabicyclo[4.1.0]heptane and (1*S*,4*R*,6*R*)-1-methyl-4-(prop-1-en-2-yl)-7-oxabicyclo[4.1.0]heptane



(1*R*,4*R*,6*S*)-1-methyl-4-(prop-1-en-2-yl)-7-oxabicyclo[4.1.0]heptane (major)

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 1.14 – 1.22 (m, 1 H), 1.26 (s, 3H, CHC**H**$_3$) 1.47 – 1.53 (m, 1 H), 1.61 – 1.70 (m, 4 H), 1.75 – 1.86 (m, 2H), 2.00 – 2.15 (m, 2H), 3.05 (s, 1H, C(O)C**H**CH$_2$), 4.65 (m, 2H, CC**H**$_2$).

^{13}C NMR (300 MHz, $CDCl_3$) δ (ppm) 21.2, 24.4, 26.1, 28.8, 30.9, 36.4, 57.5, 60.7, 109.2, 149.2. ^{1}H and ^{13}C NMR spectra match data reported previously for these epoxides.[1]

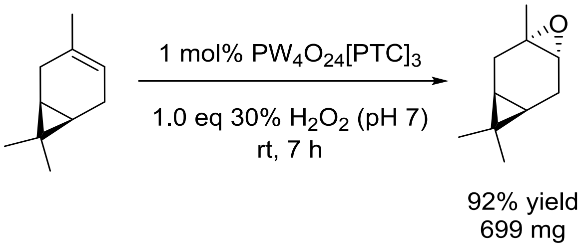
(1*S*,4*R*,6*R*)-1-methyl-4-(prop-1-en-2-yl)-7-oxabicyclo[4.1.0]heptane (minor)

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 1.32 (s, 3H, CHC**H**$_3$) 1.35 – 1.41 (m, 2 H), 1.66 – 1.74 (m, 5 H), 1.82 – 1.92 (m, 1H), 1.99 – 2.07 (m, 2H), 2.98 – 3.00 (m, 1H, C(O)C**H**CH$_2$), 4.67 (m, 2H, CC**H**$_2$).

^{13}C NMR (300 MHz, $CDCl_3$) δ (ppm) 20.4, 23.3, 24.5, 30.0, 30.9, 40.9, 57.7, 59.4, 109.2, 149.4. ^{1}H and ^{13}C NMR spectra match data reported previously for these epoxides.[1]

3-Carene oxide (2)

(1*S*,3*S*,5*R*,7*R*)-3,8,8-trimethyl-4-oxatricyclo[5.1.0.03,5]octane

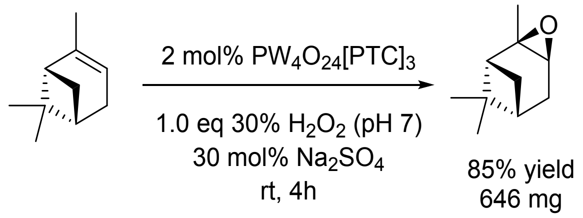


^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm) 0.44 (m, 1 H), 0.52 (m, 1 H), 0.72 (s, 3 H, C**H**$_3$), 1.00 (s, 3 H, C**H**$_3$), 1.25 (s, 3 H, C**H**$_3$), 1.50 (m, 1 H), 1.64 (m, 1 H), 2.12 (m, 1 H), 2.26 (m, 1 H), 2.82 (s, 1 H, C(O)C**H**).

^{13}C NMR (300 MHz, CDCl$_3$) δ (ppm) 13.8, 14.6, 16.0, 19.2, 19.1, 23.1, 23.3, 27.7, 55.8, 58.2. ^{1}H and ^{13}C NMR spectra match data reported previously for this epoxide.[1]

α-Pinene oxide (3)

(1*R*,2*R*,4*S*,6*R*)-2,7,7-trimethyl-3-oxatricyclo[4.1.1.02,4]octane

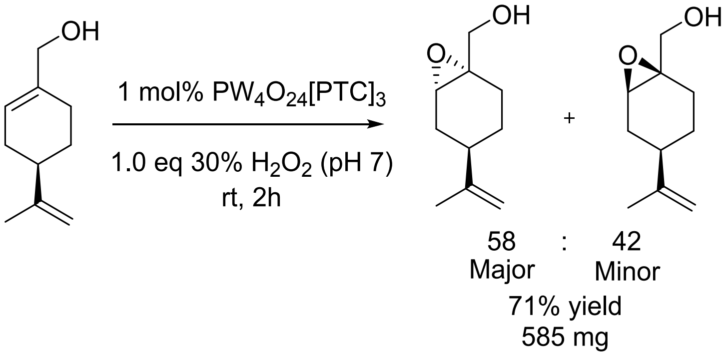


^{1}H NMR (500 MHz, CDCl$_3$) δ (ppm) 0.92 (s, 3 H, C**H**$_3$), 1.27 (s, 3 H, C**H**$_3$), 1.34 (s, 3 H, C**H**$_3$), 1.61 (m, 1 H), 1.71 – 1.76 (m, 1 H), 1.86 – 2.05 (m, 4 H), 3.06 (s, 1 H, C(O)C**H**).

^{13}C NMR (500 MHz, CDCl$_3$) δ (ppm) 20.1, 22.5, 25.8, 26.7, 27.6, 39.7, 40.5, 45.2, 56.9, 60.4. ^{1}H and ^{13}C NMR spectra match data reported previously for this epoxide.[1]

2,3-Epoxyperillyl alcohol (4a/b) – mixture of Major and Minor epoxides

(1*S*,4*R*,6*S*)-(4-(prop-1-en-2-yl)-7-oxabicyclo[4.1.0]heptan-1-yl)methanol and (1*R*,4*R*, 6*R*)-(4-(prop-1-en-2-yl)-7-oxabicyclo[4.1.0]heptan-1-yl)methanol

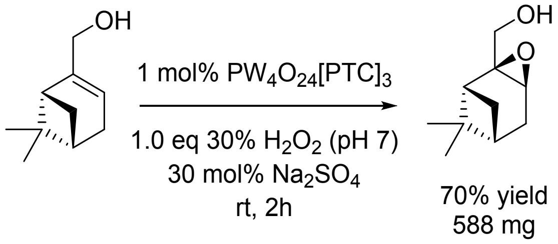


^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 1.15 - 1.27 (m, 1 H), 1.34 - 1.51 (m, 1 H), 1.54 - 1.95 (m, 6 H), 2.01 - 2.25 (m, 3 H), 3.27 (0.41 H, d, *J* = 3.27 Hz, Minor-epoxide C(O)C**H**), 3.34 (s, 0.59 H, Major-epoxide C(O)C**H**), 3.53 - 3.72 (m, 2 H, CC**H**$_2$OH), 4.66 (s, 1.36 H, Major-epoxide CC**H**$_2$), 4.71 (s, 0.64 H, Minor-epoxide CC**H**$_2$).

^{13}C NMR (300 MHz, $CDCl_3$) δ (ppm) 20.4, 21.1, 24.0, 24.9, 26.0, 26.1, 29.5, 30.4, 37.0, 41.0, 55.9, 56.9, 60.1, 60.4, 64.4, 64.6, 109.3, 109.4, 148.8, 149.0. ^1H and ^{13}C NMR spectra match data reported previously for these epoxides.[2]

Myrtenol oxide (5)

(1*R*,2*S*,4*S*,6*R*)-(7,7-dimethyl-3-oxatricyclo[4.1.1.0^{2,4}]octan-2-yl)methanol

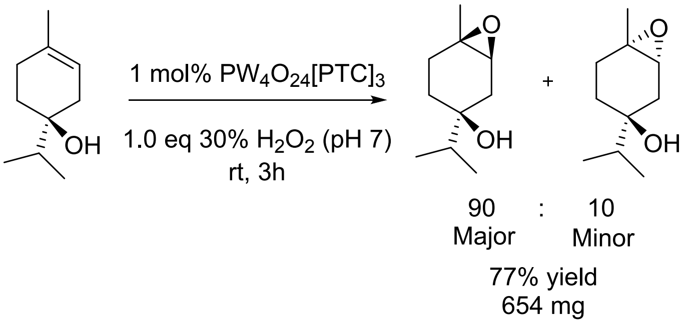


^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 0.89 (s, 3 H, C**H**$_3$), 1.27 (s, 3 H, C**H**$_3$), 1.63 (m, 1 H), 1.71 - 1.79 (m, 1 H), 1.84 - 2.09 (m, 4 H), 2.37 (m , 1 H), 3.37 (dd, *J* = 4.14, 1.32 Hz, 1 H, C(O)C**H**), 3.57 (m, 1 H, C**H**$_2$OH), 3.75 m, 1 H, C**H**$_2$OH).

^{13}C NMR (300 MHz, $CDCl_3$) δ (ppm) 20.0, 25.5, 26.4, 27.1, 40.1, 40.5, 40.5, 53.2, 62.9, 63.9. ^{1}H and ^{13}C NMR spectra match data reported previously for this epoxide.[3]

4-Carvomenthenol epoxides (6a/b) - mixture of Major and Minor epoxides

(1*S*,3*S*,6*R*)-3-isopropyl-6-methyl-7-oxabicyclo[4.1.0]heptan-3-ol and (1*R*,3*S*,6*S*)-3-isopropyl-6-methyl-7-oxabicyclo[4.1.0]heptan-3-ol



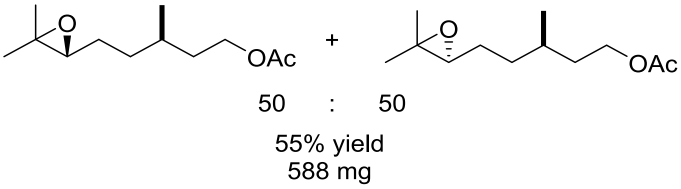
Major diastereomer data.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 0.90 (t, *J* = 6.69 Hz, 6 H, C**H**$_3$), 1.28 – 1.42 (m, 4 H), 1.47 - 1.65 (m, 2 H), 1.70 - 2.24 (m, 4 H), 3.21 (s, 1 H, Major-epoxide C(O)C**H**), 3.54 (s, 1 H, O**H**).

^{13}C NMR (300 MHz, $CDCl_3$) δ (ppm) 16.6, 16.9, 24.0, 25.8, 29.4, 31.9, 37.1, 58.8, 62.3, 72.0. ^{1}H and ^{13}C NMR spectra match data reported previously for this epoxide.[4]

(*rac*)-*O*-Acetyl-β-citronellol epoxides (7a/b)

6,7-Epoxy-3,7-dimethyloctylacetate – mixture of *syn*- and *anti*- diastereoisomers

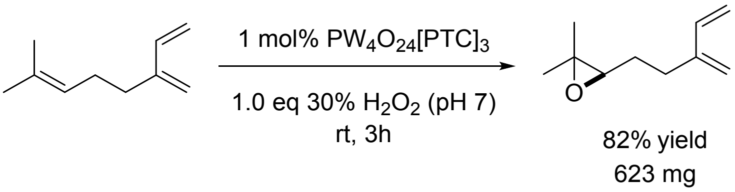


^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 0.90 - 0.96 (m, 3 H, C**H**$_3$), 1.25 - 1.32 (m, 6 H, C**H**$_3$), 1.39 - 1.72 (m, 7 H), 1.97 - 2.08 (m, 3 H, C**H**$_3$), 2.65 - 2.74 (m, 1 H, C**H**(O)C), 4.02 - 4.17 (m, 2 H, C**H**$_2$OAc).

^{13}C NMR (500 MHz, $CDCl_3$) δ (ppm) 19.2, 19.3, 21.0, 24.9, 26.3, 29.7, 29.7, 35.4, 62.9, 64.4, 64.5, 171.4. ^{1}H and ^{13}C NMR spectra match data reported previously for these epoxides.[5]

6,7-Myrcene oxide (8)

(*rac*)-2,2-dimethyl-3-(3-methylenepent-4-en-1-yl)oxirane

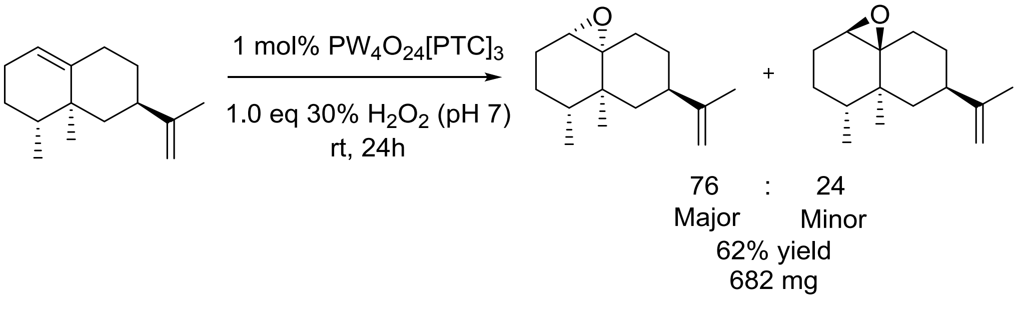


^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 1.25 (s, 3 H, C**H**$_3$), 1.30 (s, 3 H, C**H**$_3$), 1.65 - 1.79 (m, 2 H), 2.24 – 2.45 (m, 2 H), 2.76 (t, *J* = 6.3 Hz, 1 H, C(O)**H**), 5.01 - 5.11 (m, 3 H), 5.24 (d, *J* = 17.7, 1 H), 6.38 (m, 1 H).

^{13}C NMR (500 MHz, $CDCl_3$) δ (ppm) 18.3, 24.4, 27.1, 27.6, 58.0, 63.6, 113.0, 115.7, 138.1, 144.9. ^{1}H and ^{13}C NMR spectra match data reported previously for this epoxide.[1]

Valencene epoxides (9a/b) - mixture of Major- and Minor- epoxides

(1a*S*,4*R*,4a*S*,6*R*,8a*R*)-4,4a-dimethyl-6-(prop-1-en-2-yl)octahydro-1aH-naphtho[1,8a-b]oxirene and (1a*R*,4*R*,4a*S*,6*R*,8a*S*)-4,4a-dimethyl-6-(prop-1-en-2-yl)octahydro-1aH-naphtho[1,8a-b]oxirene.

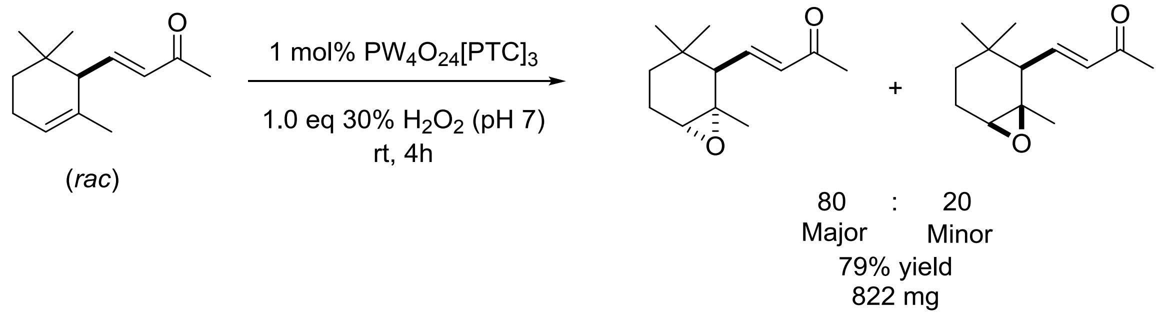


^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 0.81 – 0.92 (m, 3 H), 0.96 - 1.07 (m, 3 H), 1.44 – 1.10 (m, 6 H), 1.71 - 2.18 (m, 9 H), 2.93 (d, 0.28 H, *J* = 4.0 Hz, Minor-epoxide CH_2C**H**(O)C), 3.03 (s, 0.72 H, Major-epoxide CH_2C**H**(O)C), 4.72 (m, 1.44 H, Major-epoxide C=C**H**$_2$), 4.73 (s, 0.56 H, Minor-epoxide C=C**H**$_2$).

^{13}C NMR (300 MHz, $CDCl_3$) δ (ppm) 15.03, 15.22, 16.17, 16.94, 20.87, 21.21, 22.59, 24.63, 24.68, 25.82, 27.27, 28.68, 30.83, 30.90, 33.31, 33.57, 36.08, 40.22, 40.39, 40.64, 41.66, 46.01, 60.62, 63.78, 64.22, 108.68, 108.90, 111.32, 120.62, 150.11. ^{1}H and ^{13}C NMR spectra match data reported previously for these epoxides.[6]

(*rac*)-α-Ionone epoxides (10a/b) – mixture of Major and Minor epoxides

(*rac*)-4-(2,3-epoxy-2,6,6-trimethylcyclohexyl)-3-buten-2-one – mixture of *cis* and *trans* isomers

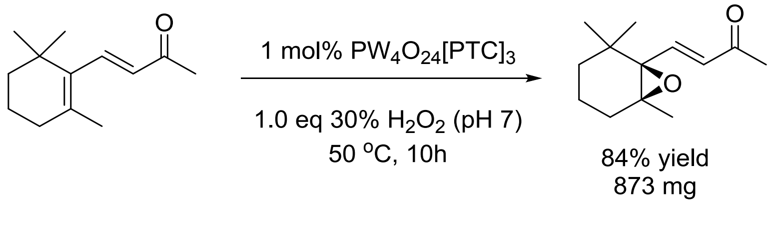


^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 0.68 – 1.07 (m, 7 H), 1.10 – 1.26 (m, 3 H), 1.29 – 1.47 (m, 1 H), 1.70 – 2.13 (m, 3 H), 2.20 – 2.35 (m, 3 H), 2.98 (m, 0.26 H, β-epoxide, C(O)C**H**), 3.08 (t, 0.74 H, *J* = 2.52 Hz, α-epoxide C(O)C**H**), 6.10 (m, 1 H), 6.69 (m, 1 H).

^{13}C NMR (300 MHz, $CDCl_3$) δ (ppm) 21.52, 21.77, 23.55, 23.64, 24.09, 26.49, 27.56, 27.76, 27.90, 28.49, 29.55, 31.24, 31.76, 32.57, 52.47, 54.11, 57.85, 58.82, 59.51, 59.83, 134.03, 134.17, 145.22, 146.45, 197.73, 198.82. ^{1}H and ^{13}C NMR spectra match data reported previously for these epoxides.[7]

(*rac*)-β-Ionone epoxide (11)

(*rac*)-4-(1,2-epoxy-2,6,6-trimethylcyclohexyl)-3-buten-2-one

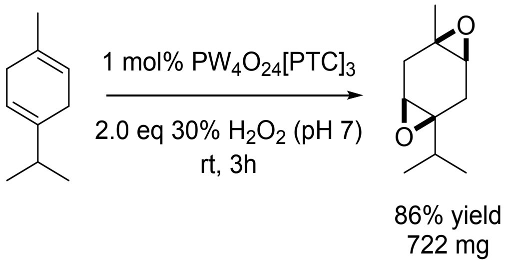


^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 0.89 (s, 3 H, CH_3), 1.10-1.30 (m, 6 H), 1.40 (m, 2 H), 1.75 (m, 4 H), 2.24 (s, 3 H, CH_3), 6.23 (d, *J* = 15.7 Hz, 1 H, CC**H**=CH), 6.98 (d, *J* = 15.7 Hz, 1 H, CCH=C**H**).

^{13}C NMR (500 MHz, $CDCl_3$) δ (ppm) 16.7, 20.6, 25.7, 27.3, 29.6, 33.4, 33.5, 35.3, 65.7, 70.4, 132.37, 142.5, 197.4. ^1H and ^{13}C NMR spectra match data reported previously for this epoxide.[8]

(*rac*)-γ-Terpinene *bis*-epoxide (12)

(*rac*)-(*syn*)-1-isopropyl-5-methyl-4,8-dioxatricyclo[5.1.0.03,5]octane

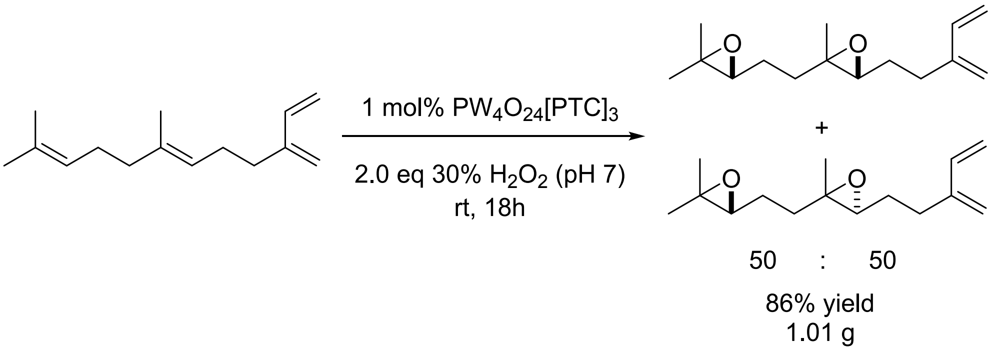


^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 0.91 (d, *J* = 7.0 Hz, 3H), 0.96 (d, *J* = 6.8 Hz, 3H), 1.31 (s, 3H), 1.47 (m, 1H), 2.10 – 2.32 (m, 4H), 2.85 (dt, *J* = 4.1, 0.9 Hz, 1H, C(O)**H**), 2.93 (dt, *J* = 3.4, 1.2 Hz, 1H, C(O)**H**).

^{13}C NMR (500 MHz, $CDCl_3$) δ (ppm) 17.2, 18.17, 23.4, 24.8, 30.1, 34.9, 55.2, 56.1, 57.3, 61.1. ^1H and ^{13}C NMR spectra match data reported previously for this epoxide.[9]

(*rac*)-Farnesene *bis*-epoxides (13a/b) - mixture of *syn*- and *anti*-epoxides

(*rac*)-2-(2-(3,3-dimethyloxiran-2-yl)ethyl)-2-methyl-3-(3-methylenepent-4-en-1-yl)oxirane - mixture of *syn*- and *anti*-epoxides

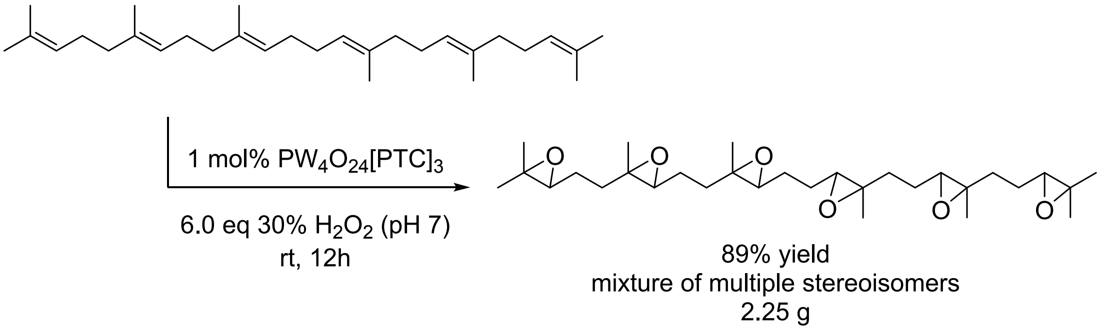


^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 1.23 - 1.28 (m, 9 H), 1.51 - 1.73 (m, 6 H), 2.22 - 2.48 (m, 2 H), 2.68 (m, 1 H, C(O)C**H**), 2.75 (t, *J* = 6.2 Hz, 1 H, C(O)C**H**), 5.02 (m, 3 H), 5.21 (d, *J* = 17.6 Hz, 1 H), 6.33 (m, 1 H).

^{13}C NMR (500 MHz, $CDCl_3$) δ (ppm) 16.2, 18.3, 24.2, 24.4, 26.95, 27.8, 35.3, 57.9, 60.2, 63.0, 63.6, 113.1, 115.8, 138.2, 145.0. I.R (thin film) $_{v}$max (cm^{-1}): C-H (2962), C=C (1595), C-O (1249). HRMS (ESI): m/z calculated. $C_{15}H_{24}O_2$: requires 259.1674 for $[M+Na]^+$; found: 259.1692.

(*rac*)-Squalene epoxides (14) – mixture of all possible stereoisomeric epoxides

(*rac*)-Hexaepoxysqualene

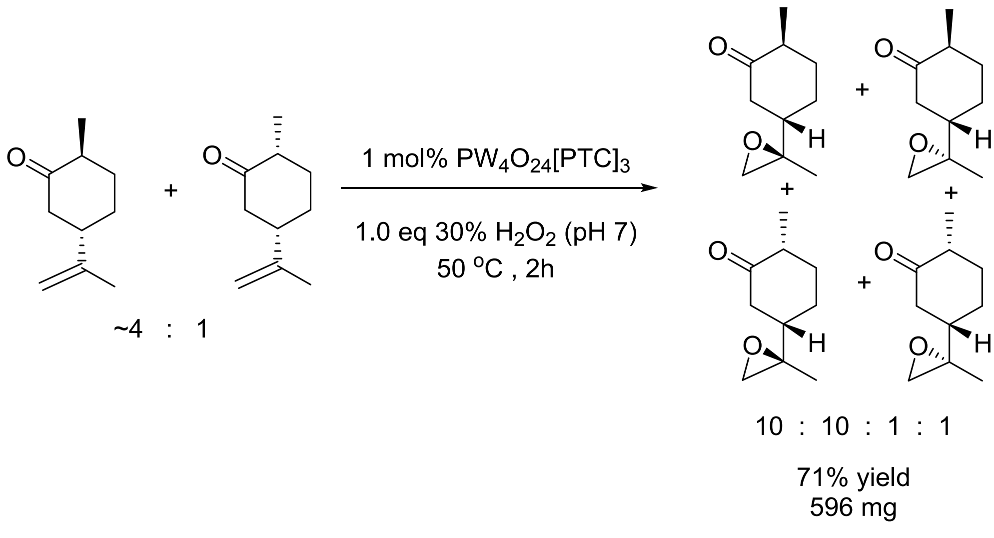


^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 1.22 - 1.26 (m, 24 H), 1.34 -1.68 (m, 20 H), 2.65 - 2.76 (m, 6 H, C(O)**H**).

^{13}C NMR (500 MHz, $CDCl_3$) δ (ppm) 16.3, 16.3, 16.3, 16.5, 18.5, 18.6, 24.2, 24.4, 24.5, 24.6, 24.7, 25.6, 25.8, 25.9, 35.1, 35.4, 35.4, 35.5, 58.3, 58.3, 60.2, 60.3, 60.4, 60.4, 62.5, 62.7, 63.0, 63.2, 63.7, 63.9. ^{1}H and ^{13}C NMR spectra match data reported previously for these epoxides.[10]

Dihydrocarvone epoxides (15a-d) - mixture of 4 diastereomeric epoxides

(2*S*,5*S*)-2-methyl-5-((*R*)-2-methyloxiran-2-yl)cyclohexan-1-one, (2*S*,5*S*)-2-methyl-5-((*S*)-2-methyloxiran-2-yl)cyclohexan-1-one, (2*R*,5*S*)-2-methyl-5-((*R*)-2-methyloxiran-2-yl)cyclohex-an-1-one and (2*R*,5*S*)-2-methyl-5-((*S*)-2-methyloxiran-2-yl)cyclohexan-1-one

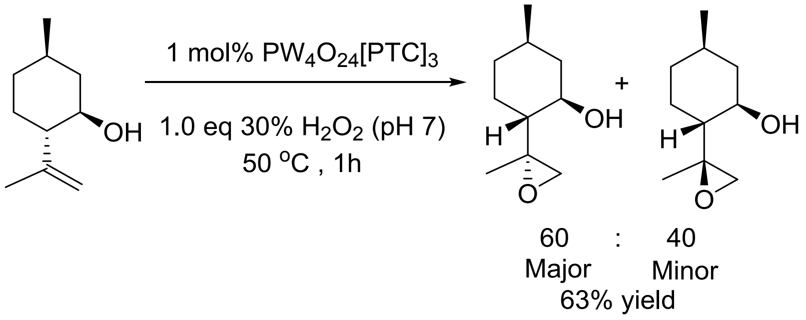


^{1}H NMR (500 MHz, CDCl$_3$) δ (ppm) 1.01 (d, *J* = 6.5 Hz, 3 H, C**H**$_3$), 1.27 - 1.32 (m, 3 H), 1.49 - 1.81 (m, 3 H), 1.90 – 1.97 (m, 1 H), 2.08 - 2.20 (m, 2 H), 2.28 - 2.38 (m, 1 H), 2.41 - 2.45 (m, 1 H), 2.54 (dd, *J* = 10.4, 4.6 Hz, 1 H, C(O)C**H**$_2$), 2.66 (d, *J* = 4.7Hz, 1 H, C(O)C**H**$_2$).

^{13}C NMR (500 MHz, CDCl$_3$) δ (ppm) 14.40, 14.41, 16.38, 18.07, 18.77, 18.77, 19.00, 23.03, 27.38, 27.65, 30.99, 34.51, 34.57, 40.56, 43.47, 43.61, 44.04, 44.30, 44.90, 45.04, 45.37, 46.06, 52.80, 53.00, 53.44, 58.39, 58.51, 58.56, 211.81, 211.89, 214.13. ^{1}H and ^{13}C NMR spectra match data reported previously for these epoxides.[11]

(-)-Isopulegol epoxides (16a/b) – mixture of two diastereomeric epoxides

(1*R*,2*R*,5*R*)-5-methyl-2-((*R*)-2-methyloxiran-2-yl)cyclohexanol and (1*R*,2*R*,5*R*)-5-methyl-2-((*S*)-2-methyloxiran-2-yl)cyclohexanol



Major Diastereomer data (~96% purity with 4% Minor diastereomer).

^{1}H NMR (500 MHz, CDCl$_3$) δ (ppm) 0.81 – 0.97 (m, 5 H), 1.02 – 1.16 (m, 1 H), 1.36 (s, 3 H, C**H**$_3$), 1.39 – 1.53 (m, 2 H), 1.63 – 1.76 (m, 1 H), 1.81 – 1.96 (m, 2H), 2.65 (d, *J* = 4.1 Hz, 1 H, C(O)C**H**$_2$), 2.92 (d, *J* = 4.1 Hz, 1 H, C(O)C**H**$_2$), 3.27 (td, *J* = 10.5, 4.4 Hz, 1 H, C**H**(OH)), 3.36 (br s, 1 H, O**H**).

^{13}C NMR (500 MHz, CDCl$_3$) □ (ppm) 21.1, 22.2, 27.8, 31.3, 34.0, 42.9, 49.0, 52.3, 60.5, 70.6.

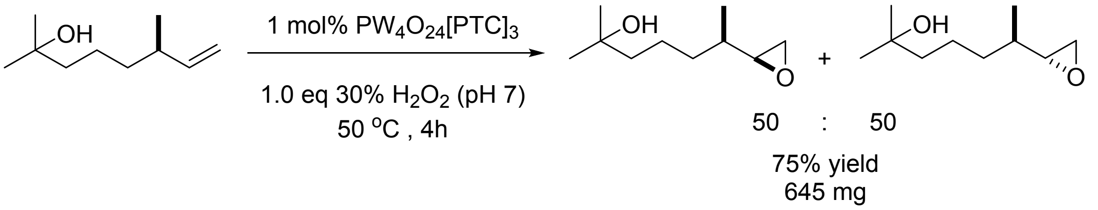
Minor Diastereomer data.

^{1}H NMR (500 MHz, CDCl$_3$) δ (ppm) 0.82 – 0.97 (m, 6 H), 1.20 (m, 1 H), 1.29 (s, 3 H, C**H**$_3$), 1.42 (m, 1 H), 1.62 – 1.72 (m, 2 H), 2.00 (m, 1 H), 2.51 (d, *J* = 4.7 Hz, 1 H, C(O)C**H**$_2$), 2.56 (d, *J* = 4.7 Hz, 1 H, C(O)C**H**$_2$), 2.60 – 2.76 (br s, 1 H, O**H**), 3.68 (td, *J* = 10.5, 4.5 Hz, 1 H, C**H**(OH)).

^{13}C NMR (500 MHz, CDCl$_3$) δ (ppm) 16.9, 22.0, 27.6, 30.9, 33.9, 43.5, 51.1, 52.7, 59.1, 71.2. ^{1}H and ^{13}C NMR spectra match data reported previously for these epoxides.[4]

(*rac*)-Dihydromyrcenol epoxides (17a/b) – mixture of two diastereomeric epoxides

(*rac*)-(*syn*)-2-methyl-6-(oxiran-2-yl)heptan-2-ol and (*rac*)-(*anti*)-2-methyl-6-(oxiran-2-yl)heptan-2-ol

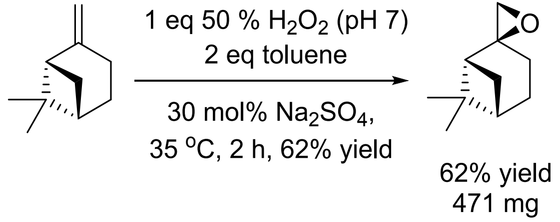


^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm) 0.89 - 1.04 (m, 3 H, C**H**$_3$), 1.19 (s, 6 H, C**H**$_3$), 1.23 - 1.61 (m, 8 H), 2.42 - 2.56 (m, 1 H, CH$_2$(O)C**H**), 2.64 - 2.77 (m, 2 H, C**H**$_2$(O)CH).

^{13}C NMR (300 MHz, CDCl$_3$) δ (ppm) 15.7, 21.7, 29.0, 29.2, 35.0, 44.0, 46.9, 57.0, 57.0, 70.8. ^{1}H and ^{13}C NMR spectra match data reported previously for these epoxides.[12]

β-Pinene oxide (18)

(1*R*,2*S*,5*S*)-6,6-dimethylspiro[bicyclo[3.1.1]heptane-2,2'-oxirane]

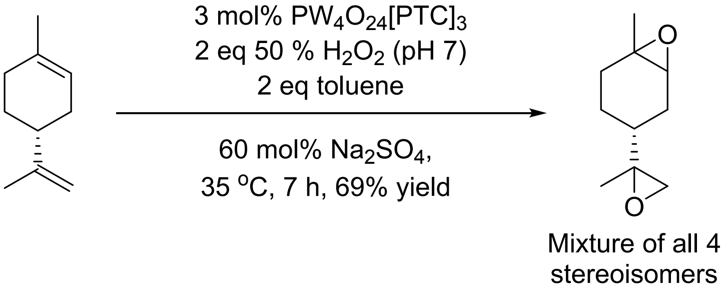


^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm) 0.90 (s, 3 H, C**H**$_3$), 1.23 (s, 3 H, C**H**$_3$), 1.50 (t, *J* = 5.3 Hz, 1 H), 1.64 – 2.00 (m, 5 H), 2.13 – 2.30 (m, 2 H), 2.59 (dt, *J* = 4.8, 0.7 Hz, 1 H, C(O)C**H**$_2$), 2.76 (d, *J* = 4.9 Hz, 1 H, C(O)C**H**$_2$).

^{13}C NMR (300 MHz, CDCl$_3$) δ (ppm) 21.1, 22.2, 23.5, 25.1, 26.0, 40.0, 40.7, 48.8, 56.5, 61.6. ^{1}H and ^{13}C NMR spectra match data reported previously for this epoxides.[13]

Limonene bis-epoxide (19) - mixture of four stereoisomers

(4R)-1-methyl-4-(2-methyloxiran-2-yl)-7-oxabicyclo[4.1.0]heptane



PTC = mixture of $MeN^+(C_8H_{17})_3$ and $MeN^+(C_{10}H_{21})_3$

^{1}H NMR (500 MHz, CDCl$_3$) δ (ppm) 1.22 (d, *J* = 5.3 Hz, 3H, C**H**$_3$), 1.30 (s, 3H, C**H**$_3$), 1.30 – 1.39 (m, 1H), 1.41 – 1.67 (m, 3H), 1.69 – 2.20 (m, 3H), 2.46 – 2.64 (m, 2H, C(O)C**H**$_2$), 2.93 – 3.07 (m, 1H, C(O)C**H**)

^{13}C NMR (126 MHz, CDCl$_3$) δ (ppm) 60.6, 60.2, 59.2, 58.9, 58.9, 58.8, 57.9, 57.8, 57.5, 57.4, 53.4, 53.3, 53.0, 52.8, 40.1, 39.5, 35.5, 35.0, 30.4, 30.3, 28.9, 28.6, 27.9, 27.9, 26.8, 26.7, 24.5, 24.4, 23.7, 23.5, 23.5, 23.1, 23.1, 21.6, 21.6, 21.5, 19.0, 18.4, 18.3, 17.7.

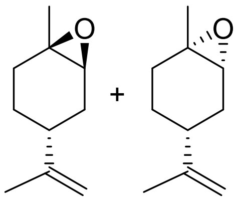
HRMS (ESI): m/z calculated. $C_{10}H_{16}O_2$: requires 169.1223 for $[M+H]^+$; found: 169.1226.

I.R. (thin film) *v* max (cm^{-1}): 2930, 1436, 1380, 1106, 941

R$_f$ = 0.30 (Petroleum ether : Ethyl Acetate (9:1))

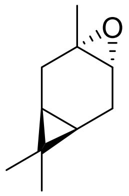
2.1.1 Large scale solvent free epoxidation of limonene, α-pinene and 3-carene using a modified Ishii-Venturello tungsten catalyst and H_2O_2 as oxidant

A terpene substrate (15g or 100g) and $PW_4O_{24}[PTC]_3$ (1 mol%) was added to an open 1 L three necked round bottom flask immersed in a water bath fitted with a condenser and thermometer, with the resultant suspension then stirred for 10 minutes to fully dissolve the catalyst. The terpene/catalyst mixture was then stirred at ~100 rpm, with 30% aqueous hydrogen peroxide solution [1 equivalent, buffered to pH 7 with 0.5 M NaOH, (with or without Na_2SO_4)] added in a dropwise manner (5 mL portions). The rate of addition of hydrogen peroxide was adjusted to ensure that the temperature of the reaction mixture remained between 35-50 ^{o}C to prevent thermal runaway. **Caution – too rapid addition of the H_2O_2 solution can result in a vigorous exotherm which can lead to the reaction mixture exiting the reaction flask in an uncontrolled manner.** The reaction mixture was then stirred at room temperature (2 - 8 h) until the epoxidation reaction was judged to be complete by tlc analysis. The top yellow organic layer of the resultant biphasic mixture was then separated off and purified *via* distillation to produce the desired epoxides as clear yellow oils.

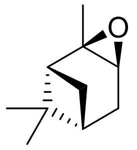


55 : 45

100 g of limonene
1 mol% catalyst, 2 h
1 eq H_2O_2
85g, 85% yield of
limonene oxide **1**

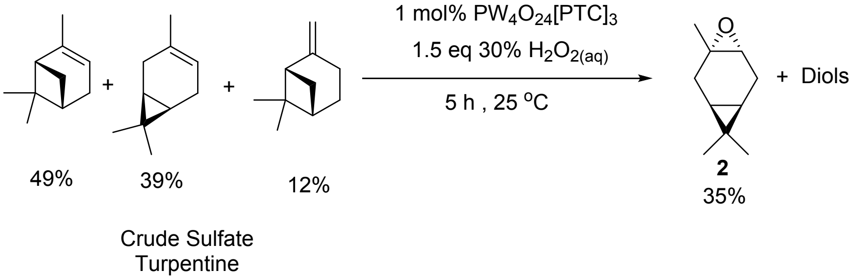


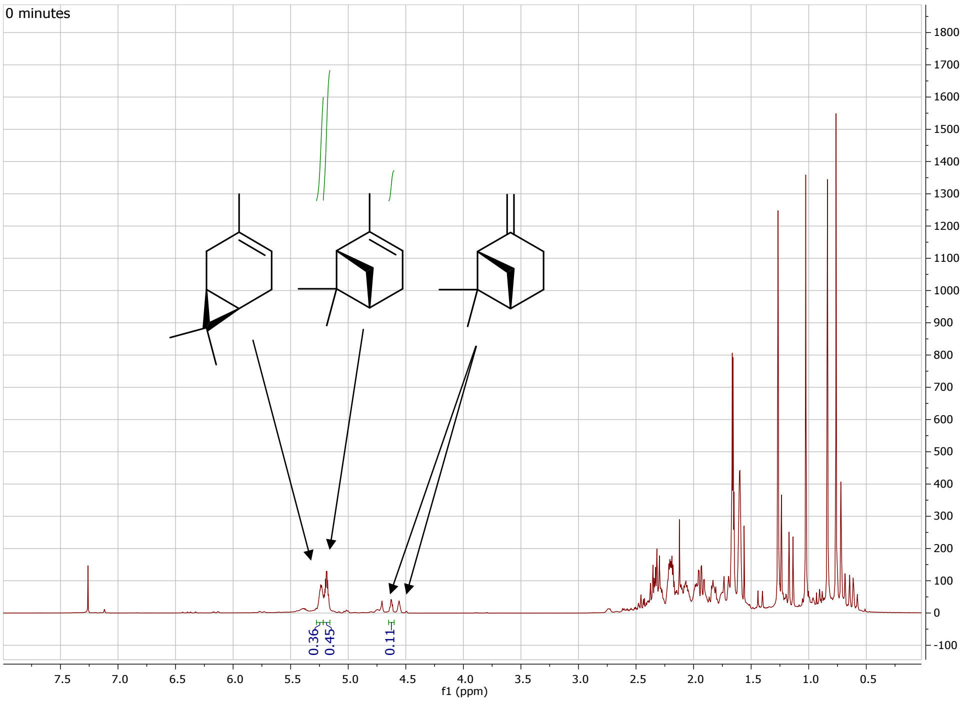
15g of 3-carene
1 mol% catalyst, 8 h
1 eq H_2O_2
11.4g, 76% yield of
3-carene oxide **2**

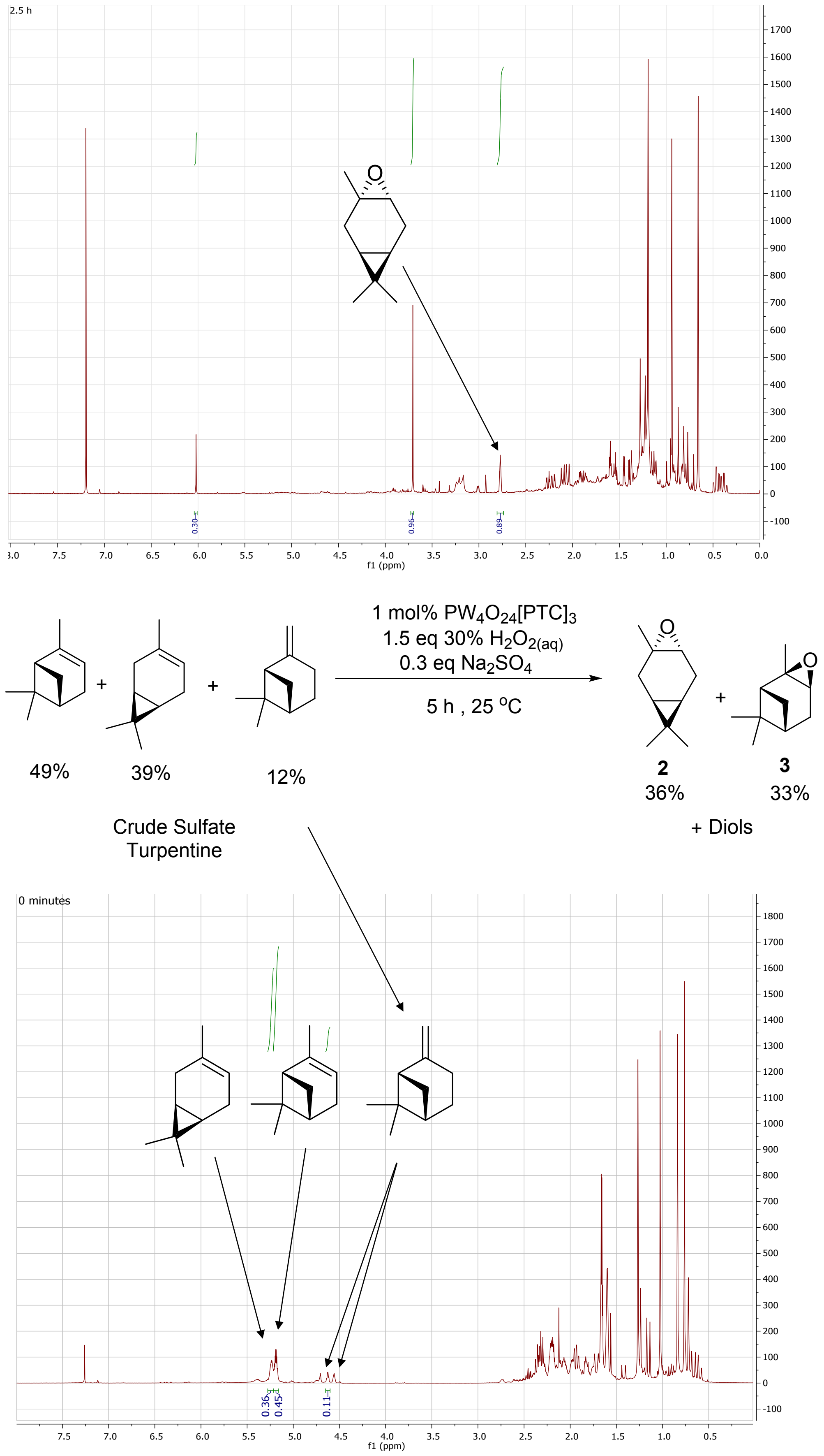


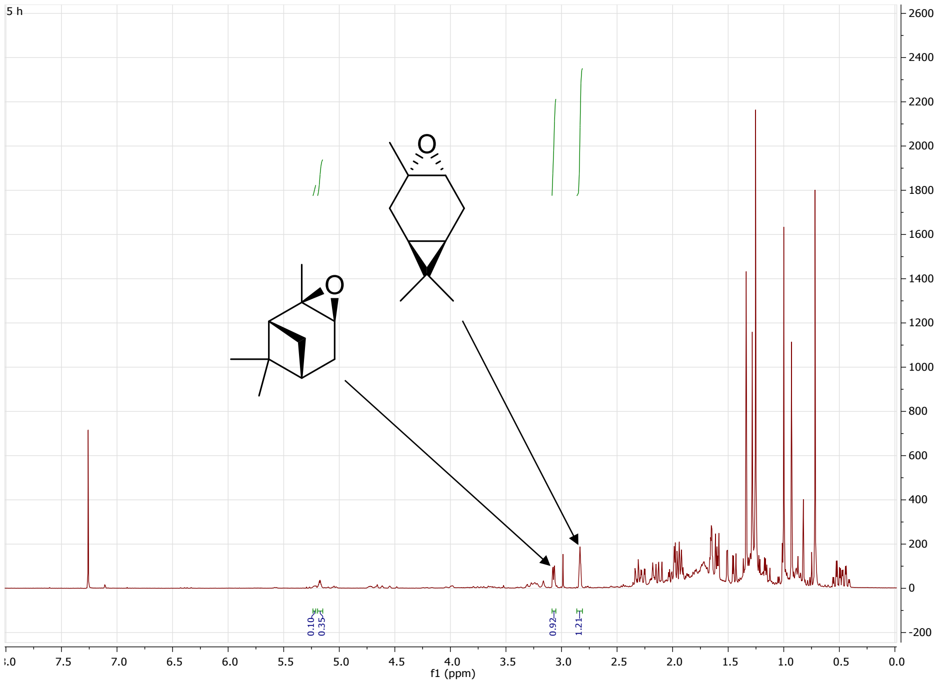
15 g of α-pinene
2 mol% catalyst, 5 h,
1 eq H_2O_2 (0.3 eq Na_2SO_4)
12.8g, 85% yield of
α-pinene oxide **3**

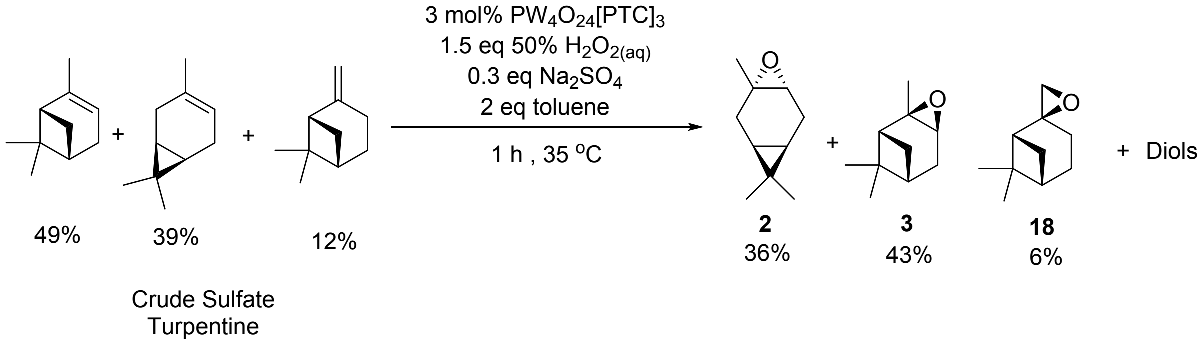
2.1.2 Epoxidation conditions used to prepare epoxides of 3-carene, α-pinene and β-pinene from crude sulfate turpentine

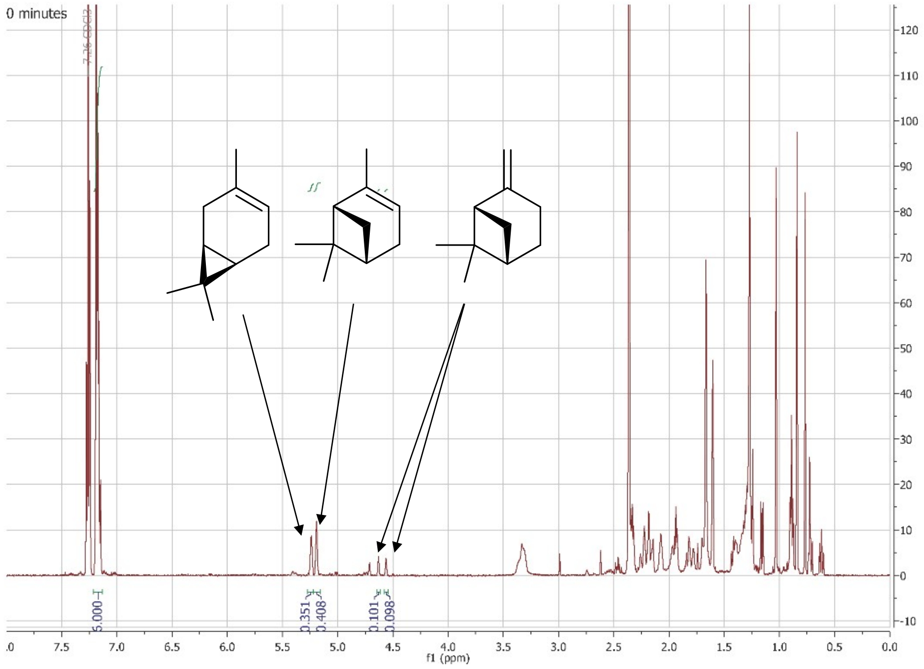


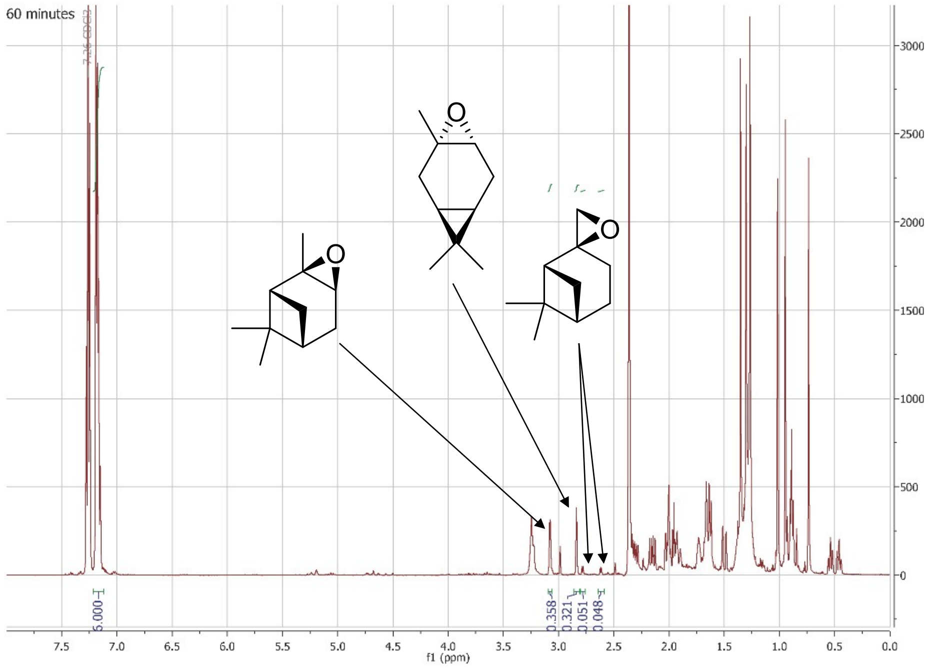



2.5 h
0.30
0.96
0.89
f1 (ppm)
1 mol% $PW_4O_{24}[PTC]_3$
1.5 eq 30% $H_2O_{2(aq)}$
0.3 eq Na_2SO_4
5 h , 25 °C
49%
39%
12%
Crude Sulfate Turpentine
2
36%
3
33%
+ Diols
0 minutes
0.36
0.45
0.11
f1 (ppm)


5 h
0.10
0.35
0.92
1.21
f1 (ppm)
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200


3 mol% $PW_4O_{24}[PTC]_3$
1.5 eq 50% $H_2O_{2(aq)}$
0.3 eq Na_2SO_4
2 eq toluene
1 h , 35 ^oC
+
49%
39%
12%
Crude Sulfate Turpentine
2
36%
3
43%
18
6%
+ Diols

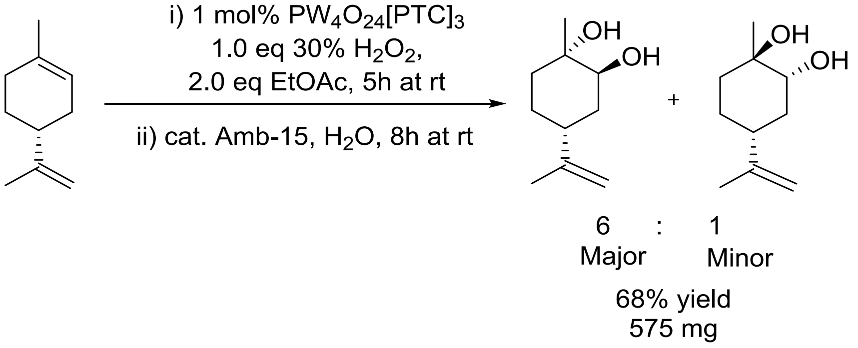

0 minutes
7.26 CDCl3
5.000
0.351
0.408
0.101
0.098
f1 (ppm)
120
110
100
90
80
70
60
50
40
30
20
10
0
-10



2.1.3 Epoxidation conditions used to prepare terpene-(*anti*)-diols and their corresponding spectroscopic data

Limonene 1,2-*anti*-diols (20a/b)

(1*S*,2*S*,4*R*)-1-methyl-4-(prop-1-en-2-yl)cyclohexane-1,2-diol and (1*R*,2*R*,4*R*)-1-methyl-4-(prop-1-en-2-yl)cyclohexane-1,2-diol



Major diastereomer data.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 1.26 (s, 3 H, C**H**$_3$), 1.46 - 1.68 (m, 4 H), 1.72 (m, 3 H), 1.92 (m, 2 H), 2.20 - 2.33 (m, 1 H), 3.63 (t, *J* = 3.49 Hz, 1 H, C**H**OH), 4.64 - 4.77 (m, 2 H, C=C**H**$_2$).

^{13}C NMR (300 MHz, $CDCl_3$) δ (ppm) 21.1, 26.1, 26.5, 33.6, 33.9, 37.4, 71.4, 73.8, 109.0, 149.2.

Minor diastereomer data.

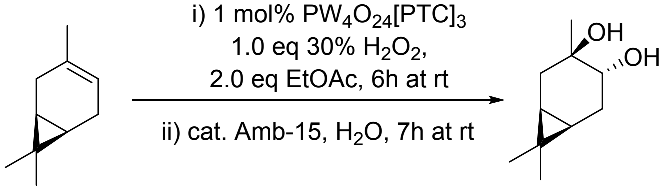
^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm) 1.21 (s, 3 H, C**H**$_3$), 1.25 - 1.35 (m, 3 H), 1.46 – 1.52 (m, 1 H), 1.66 – 1.75 (m, 4H) 1.77 – 1.82 (m, 1H) 1.88 - 1.95 (m, 1 H), 1.98 – 2.12 (m, 2 H), 3.58 (dd, *J* = 4.4, 11.5 Hz, 1 H, C**H**OH), 4.71 (m, 2 H, C=C**H**$_2$).

^{13}C NMR (300 MHz, CDCl$_3$) δ (ppm) 19.1, 28.8, 36.2, 38.7, 43.8, 148.6, 74.1, 77.4, 109.2, 148.6.

^{1}H and ^{13}C NMR spectra match data reported previously for these diols.[14]

Carene-3,4-*anti*-diol (21)

(1*S*,3*R*,4*R*,6*R*)-3,7,7-trimethylbicyclo[4.1.0]heptane-3,4-diol



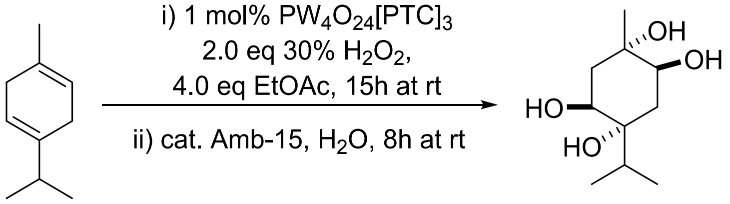
73% yield
620 mg

^{1}H NMR (500 MHz, CDCl$_3$) δ (ppm) 0.61 - 0.75 (m, 2 H), 0.95 (s, 3 H, C**H**$_3$), 0.97 (s, 3 H, C**H**$_3$), 1.18 (s, 3 H, C**H**$_3$), 1.24 (m, 1 H), 1.63 (m, 1 H), 1.94 (m, 1 H), 2.06 (m, 1 H), 2.72 – 3.14 (br s,. 2 H, O**H**), 3.32 (m, 1 H, C**H**OH).

^{13}C NMR (500 MHz, CDCl$_3$) δ (ppm) 15.7, 17.6, 18.9, 19.9, 20.9, 27.8, 28.6, 33.6, 73.3, 74.3. ^{1}H and ^{13}C NMR spectra match data reported previously for this diol.[15]

(*rac*)-γ-Terpinene-*anti*-tetrol (22)

(*rac*)-1-isopropyl-4-methylcyclohexane-1,2-(*anti*)-4,5-(*anti*)-tetrol



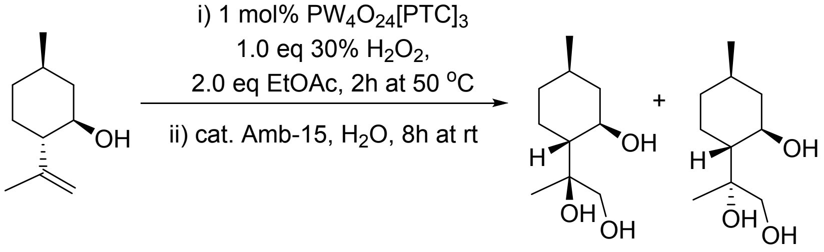
(*rac*)
62% yield

^1H NMR (500 MHz, DMSO-d_6) δ (ppm) 0.80 (d, *J* = 6.85 Hz, 3 H, C**H**$_3$), 0.85 (d, *J* = 6.85 Hz, 3 H, C**H**$_3$), 1.10 (s, 3 H, C**H**$_3$), 1.42 - 1.50 (m, 1 H), 1.67 (m, 1 H), 1.79 - 1.88 (m, 2 H), 2.00 (m, 1 H), 3.42 - 3.50 (m, 1 H, C**H**OH), 3.63 - 3.70 (m, 1 H, C**H**OH), 4.57 (s, 1 H, O**H**), 5.03 (d, *J* = 7.34 Hz, 1 H, O**H**), 5.12 (s, 1 H, O**H**), 5.38 (d, *J* = 6.36 Hz, 1 H, O**H**).

^{13}C NMR (500 MHz, DMSO-d_6) δ (ppm) 15.6, 16.2, 26.8, 31.1, 31.9, 34.2, 70.4, 71.9, 73.7, 74.2. ^1H and ^{13}C NMR spectra match data reported previously for this tetrol.[16]

(-)-Isopulegol-8,9-*anti*-diols (23a/b) mixture of two diastereomeric diols

(*S*)-2-((1*R*,2*R*,4*R*)-2-hydroxy-4-methylcyclohexyl)propane-1,2-diol and (*R*)-2-((1*R*,2*R*,4*R*)-2-hydroxy-4-methylcyclohexyl)propane-1,2-diol



68 : 32
Major Minor
65% yield
611 mg

Major diastereomer data. 80% pure (20% minor diastereomer).

^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 0.83 – 0.94 (m, 4 H), 0.97 – 1.05 (m, 2 H), 1.18 (s, 3 H, C**H**$_3$), 1.40 – 1.49 (m, 1 H), 1.49 – 1.57 (m, 1 H), 1.67 (m, 1 H), 1.77 (m, 1 H), 1.91 (m, 1 H), 3.13 (br s, 3 H, O**H**), 3.44 (d, *J* = 11.0 Hz, 1 H, C**H**$_2$OH), 3.75 (d, *J* = 11.0 Hz, 1 H, C**H**$_2$OH), 3.81 (dt, *J* = 10.7, 4.2 Hz, 1 H, C**H**(OH)).

^{13}C NMR (500 MHz, CDCl$_3$) δ (ppm) 22.0, 24.5, 26.5, 31.6, 34.7, 45.3, 52.2, 67.0, 72.9, 76.4.

Minor diastereomer data. 82% pure (18% Major diastereomer).

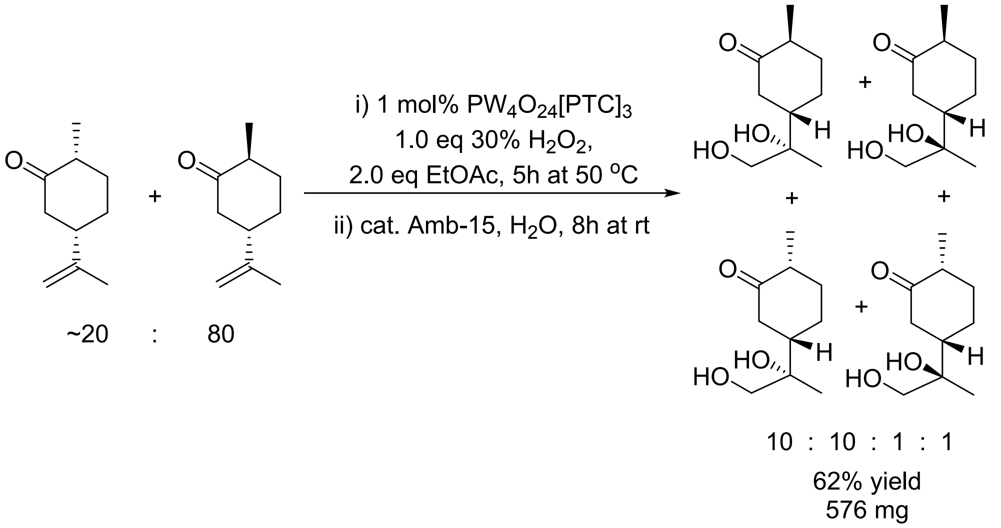
^{1}H NMR (500 MHz, CDCl$_3$) δ (ppm) 0.89 – 0.97 (m, 5 H), 1.06 (td, *J* = 12.2, 10.9 Hz, 1 H), 1.14 (s, 3 H, C**H**$_3$), 1.44 (m, 1 H), 1.59 – 1.70 (m, 3 H), 1.95 (m, 1 H), 3.31 (br s, 3 H, O**H**), 3.36 (d, *J* = 11.2 Hz, 1 H, C**H**$_2$OH), 3.52 (d, *J* = 11.2 Hz, 1 H, C**H**$_2$OH), 3.78 (td, *J* = 10.5, 4.3 Hz, 1 H, C**H**(OH)).

^{13}C NMR (500 MHz, CDCl$_3$) δ (ppm) 19.5, 22.1, 26.4, 31.4, 34.3, 44.9, 47.9, 68.8, 72.4, 76.7.

^{1}H and ^{13}C NMR spectra match data reported previously for these diols.[17]

Dihydrocarvone-8,9-*anti*-diols (24a-d)

(2*S*,5*S*)-5-((*S*)-1,2-dihydroxypropan-2-yl)-2-methylcyclohexanone, (2*S*,5*S*)-5-((*R*)-1,2-dihyd-roxypropan-2-yl)-2-methylcyclohexanone, (2*R*,5*S*)-5-((*S*)-1,2-dihydroxy propan-2-yl)-2-methylcyclohexanone and (2*R*,5*S*)-5-((*R*)-1,2-dihydroxypropan-2-yl)-2-methylcyclohexanone



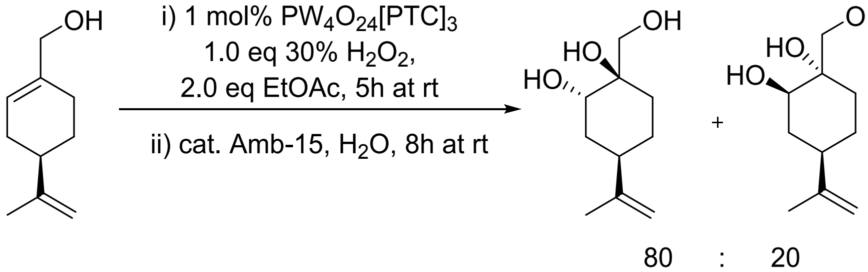
^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm) 0.94 (d, *J* = 1.51 Hz, 3 H, C**H**$_3$), 1.01 - 1.09 (s, 3 H, C**H**$_3$), 1.15 - 1.32 (m, 1 H), 1.39 – 1.57 (m, 1 H,), 1.72 - 1.99 (m, 2 H), 2.00 - 2.23

(m, 2 H), 2.23 - 2.41 (m, 2 H), 3.34 (m, 1 H, C(OH)C**H**$_2$OH), 3.43 - 3.53 (m, 1 H, C(OH)C**H**$_2$OH), 3.56 - 3.70 (br s, 2 H, O**H**).

^{13}C NMR (300 MHz, CDCl$_3$) δ (ppm) 14.1, 19.7, 25.5, 34.6, 43.3, 44.7, 46.2, 67.7, 73.8, 213.8. ^{1}H and ^{13}C NMR spectra match data reported previously for these diols.[18]

Perillyl alcohol 1,2-*anti*-diols (25a/b)

(1*R*,2*S*,4*R*)-1-(hydroxymethyl)-4-(prop-1-en-2-yl)cyclohexane-1,2-diol and (1S,2R,4R)-1-(hydroxymethyl)-4-(prop-1-en-2-yl)cyclohexane-1,2-diol



80 : 20
Major Minor
56% yield
520 mg

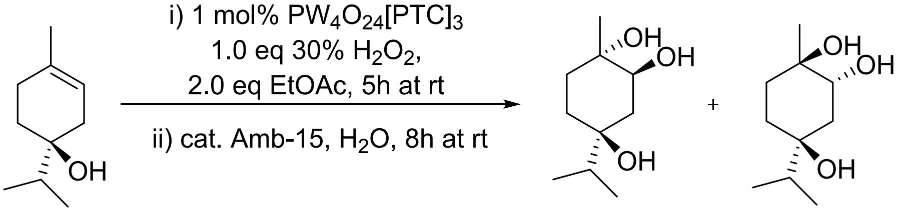
Major diastereomer data.

^{1}H NMR (300 MHz, DMSO-d$_6$) δ (ppm) 1.09 - 1.39 (m, 2 H), 1.39 - 1.54 (m, 3 H), 1.64 (s, 3 H, C**H**$_3$), 1.73 (m, 1 H), 2.15 - 2.30 (m, 1 H), 3.20 (d, *J* = 10.8 Hz, 1 H, C**H**$_2$OH), 3.38 (d, *J* = 10.8 Hz, 1 H, C**H**$_2$OH), 3.56 (s, 1 H, C**H**OH), 4.00 (br. s., 1 H, O**H**), 4.50 (br. s., 2 H, O**H**), 4.59 - 4.67 (s, 2 H, C=C**H**$_2$).

^{13}C NMR (300 MHz, DMSO-d$_6$) δ (ppm) 20.9, 25.5, 28.4, 33.8, 37.6, 67.7, 68.8, 71.3, 108.3, 150.4. ^{1}H and ^{13}C NMR spectra match data reported previously for these diols.[19]

4-Carvomenthenol-*anti*-diols (26a/b)

(1*S*,2*S*,4*S*)-4-isopropyl-1-methylcyclohexane-1,2,4-triol and (1*R*,2*R*,4*S*)-4-isopropyl-1-methylcyclohexane-1,2,4-triol



90 : 10

77% yield
723 mg

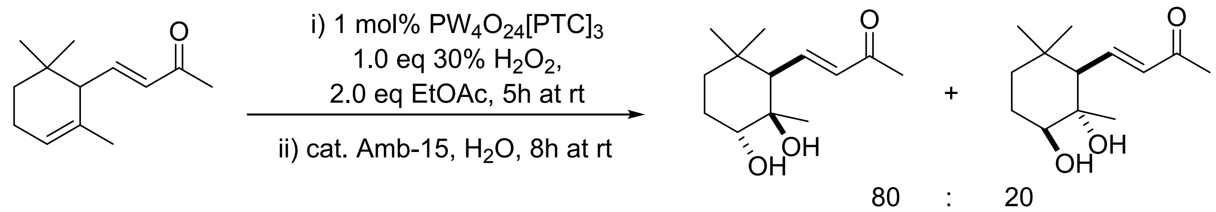
Major diastereomer data.

^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm) 0.93 (dd, *J* = 6.9, 1.4 Hz, 6 H, C**H**$_3$), 1.34 (s, 3 H, C**H**$_3$), 1.39 - 1.53 (m, 3 H), 1.58 - 1.62 (m, 2 H), 1.79 - 1.83 (d, *J* = 3.91 Hz, 2 H), 1.92 - 1.97 (m, 2 H), 2.03 (s, 1 H), 3.51 - 3.56 (m, 1 H, C**H**OH).

^{13}C NMR (300 MHz, CDCl$_3$) δ (ppm) 16.6, 16.7, 27.7, 29.2, 29.6, 33.8, 38.5, 71.6, 74.8, 75.3. ^{1}H and ^{13}C NMR spectra match data reported previously for these diols.[20]

(*rac*)-α-Ionone-*anti*-diols (27a/b)

(*rac*)-(*E*)-4-(*syn*,*anti*)-2,3-dihydroxy-2,6,6-trimethylcyclohexyl)but-3-en-2-one and (*rac*)-(*E*)-4-(*anti*,*anti*)-2,3-dihydroxy-2,6,6-trimethylcyclohexyl)but-3-en-2-one



80 : 20

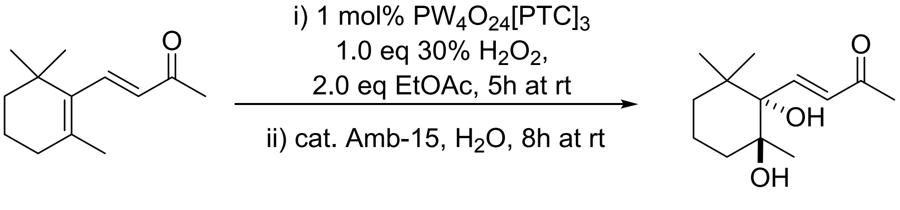
70% yield
791 mg

^{1}H NMR (500 MHz, CDCl$_3$) δ (ppm) 0.83 (s, 3 H, C**H**$_3$), 1.06 (s, 3 H, C**H**$_3$), 1.16 (s, 3 H, C**H**$_3$), 1.25 (m, 2 H), 1.58 (s, 1 H), 1.66 (m, 2 H), 2.10 (s, 1 H), 2.21 (s, 1 H), 2.30 (s, 3 H, C**H**$_3$), 3.58 (s, 1 H, C**H**OH), 6.09 (d, *J* = 16.14 Hz, 1 H, C=C**H**), 6.96 (m, 1 H, C=C**H**).

^{13}C NMR (500 MHz, $CDCl_3$) δ (ppm) 22.2, 25.2, 27.0, 28.0, 32.2, 33.6, 33.9, 53.2, 73.4, 74.4, 134.8, 146.6, 198.6. ^{1}H and ^{13}C NMR spectra match data reported previously for these diols.[21]

(*rac*)-β-Ionone-*anti*-diols (28)

(*rac*)-(*E*)-4-(1,2-dihydroxy-2,6,6-trimethylcyclohexyl)but-3-en-2-one

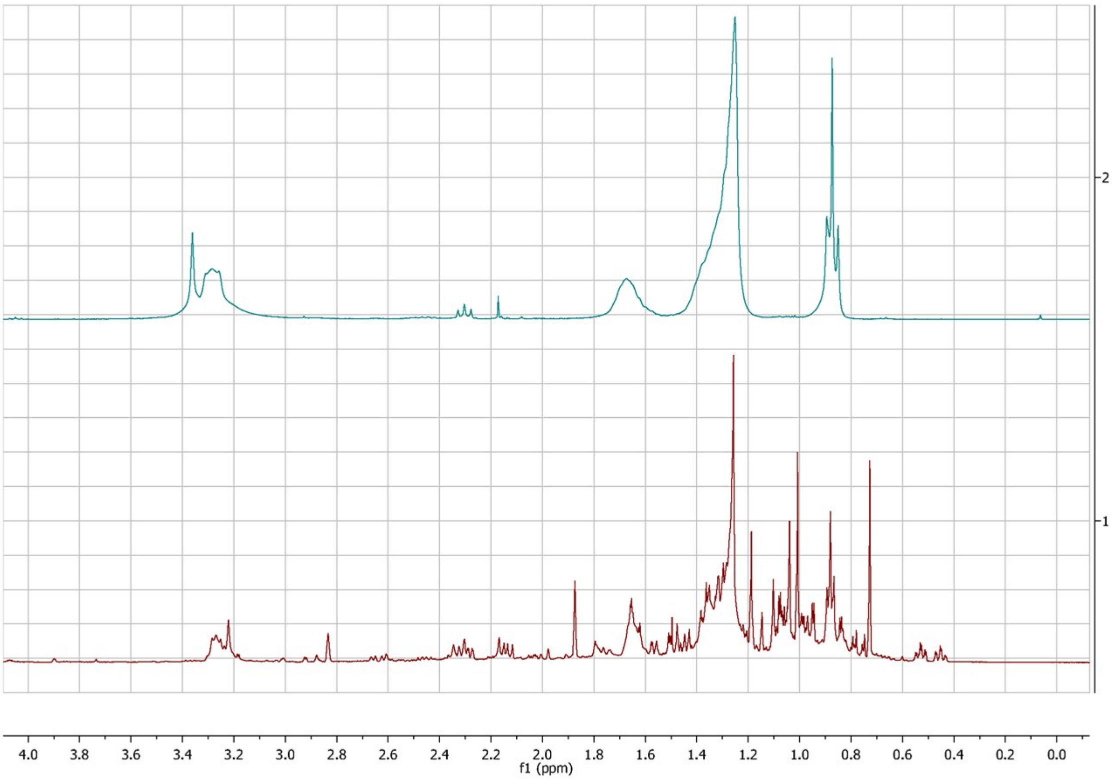


55% yield
625 mg

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 0.73 (s, 3 H, C**H**$_3$), 1.03 (s, 3 H, C**H**$_3$), 1.13 (s, 3 H, C**H**$_3$), 1.40 (s, 3 H), 1.49 (m, 3 H), 1.73 (m, 2 H), 2.21 (s, 3 H, C**H**$_3$), 6.24 (d, *J* = 6.14 Hz, 1 H, C**H**=CH), 7.22 (m, 1 H, CH=C**H**).

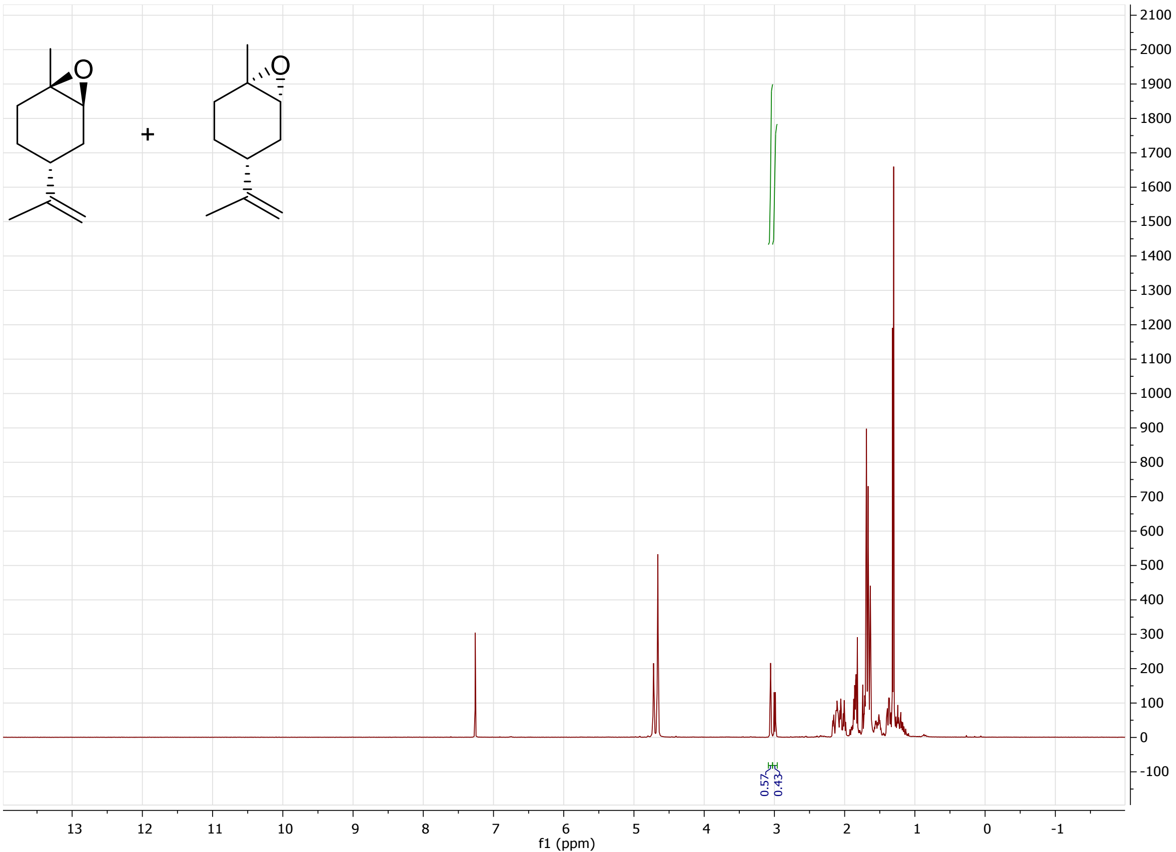
^{13}C NMR (500 MHz, $CDCl_3$) δ (ppm) 17.4, 24.7, 26.2, 27.1, 27.3, 36.0, 38.2, 53.2, 74.6, 79.2, 130.5, 149.0, 198.0. ^{1}H and ^{13}C NMR spectra match data reported previously for this diol.[22]

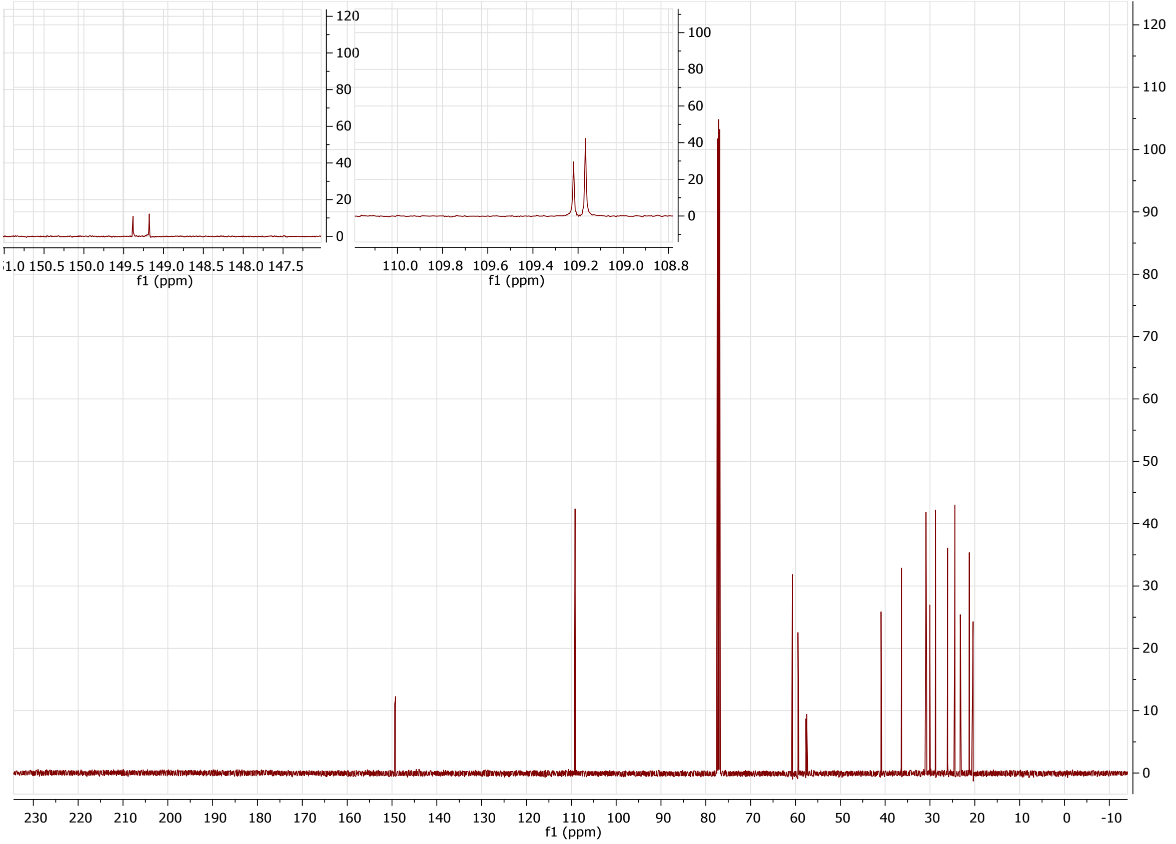
2.1.4 ^{1}H NMR spectra of fresh VPTC (top) and recycled VPTC recovered after 3 epoxidation runs (3-carene) (bottom)

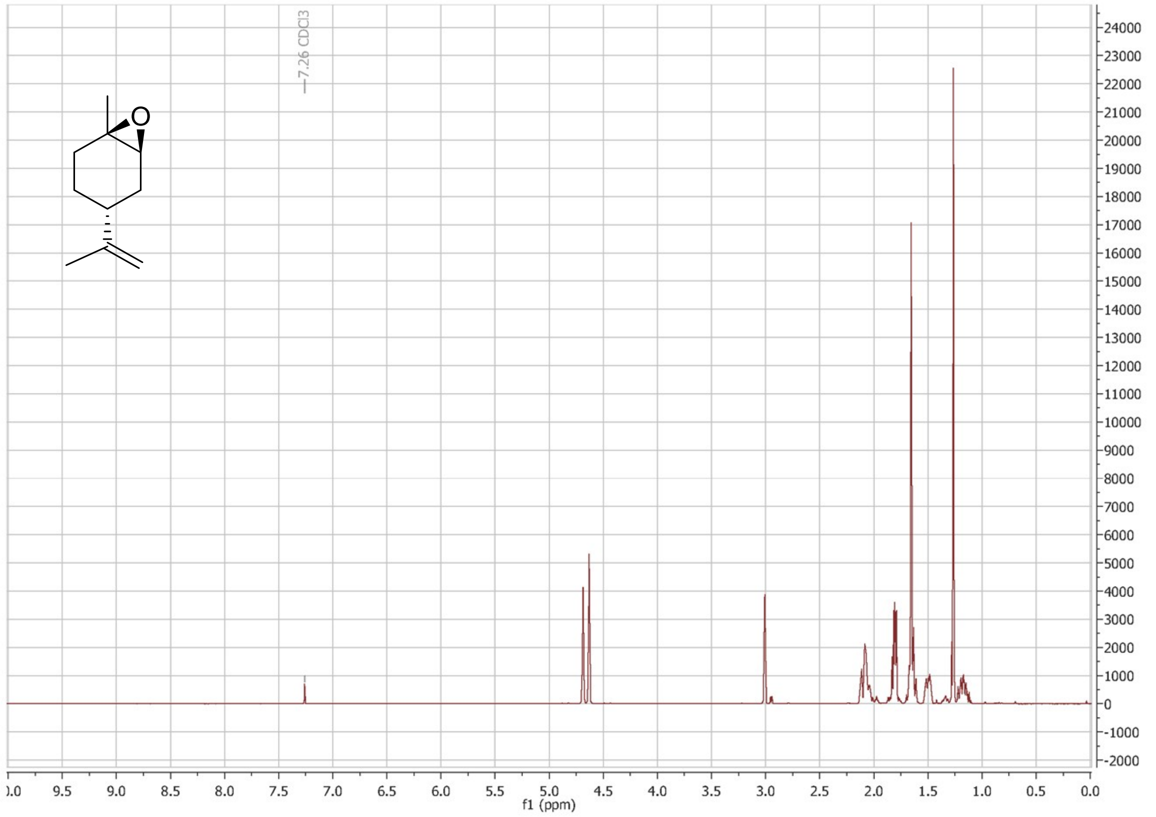

2
1
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
f1 (ppm)

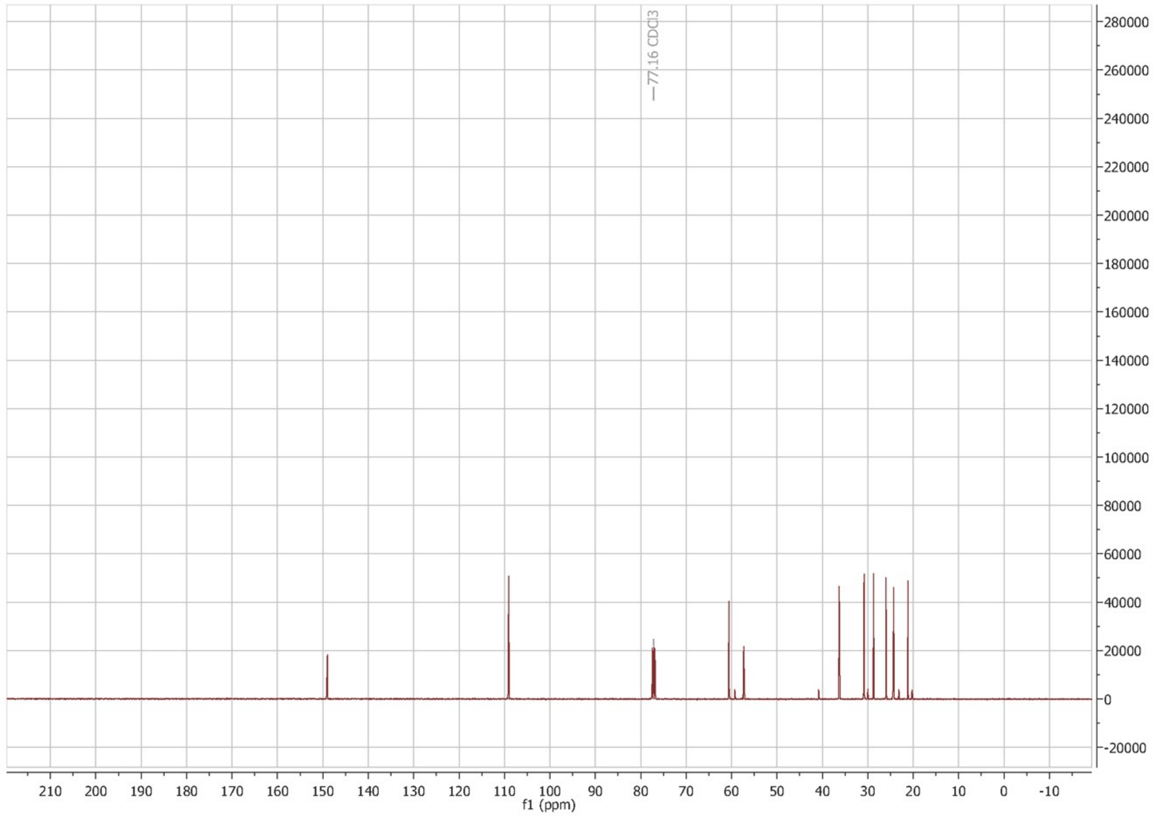
3 ^{1}H and ^{13}C NMR spectra of terpene epoxides and terpene-*anti*-diols

(*R*)-(+)-1,2-Limonene oxides (1a/b)


+
O
O
0.57
0.43
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100


1.0 150.5 150.0 149.5 149.0 148.5 148.0 147.5
f1 (ppm)
120
100
80
60
40
20
0
110.0 109.8 109.6 109.4 109.2 109.0 108.8
f1 (ppm)
100
80
60
40
20
0
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
120
110
100
90
80
70
60
50
40
30
20
10
0


O
—7.26 CDCl3
24000
23000
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


—77.16 CDCl3
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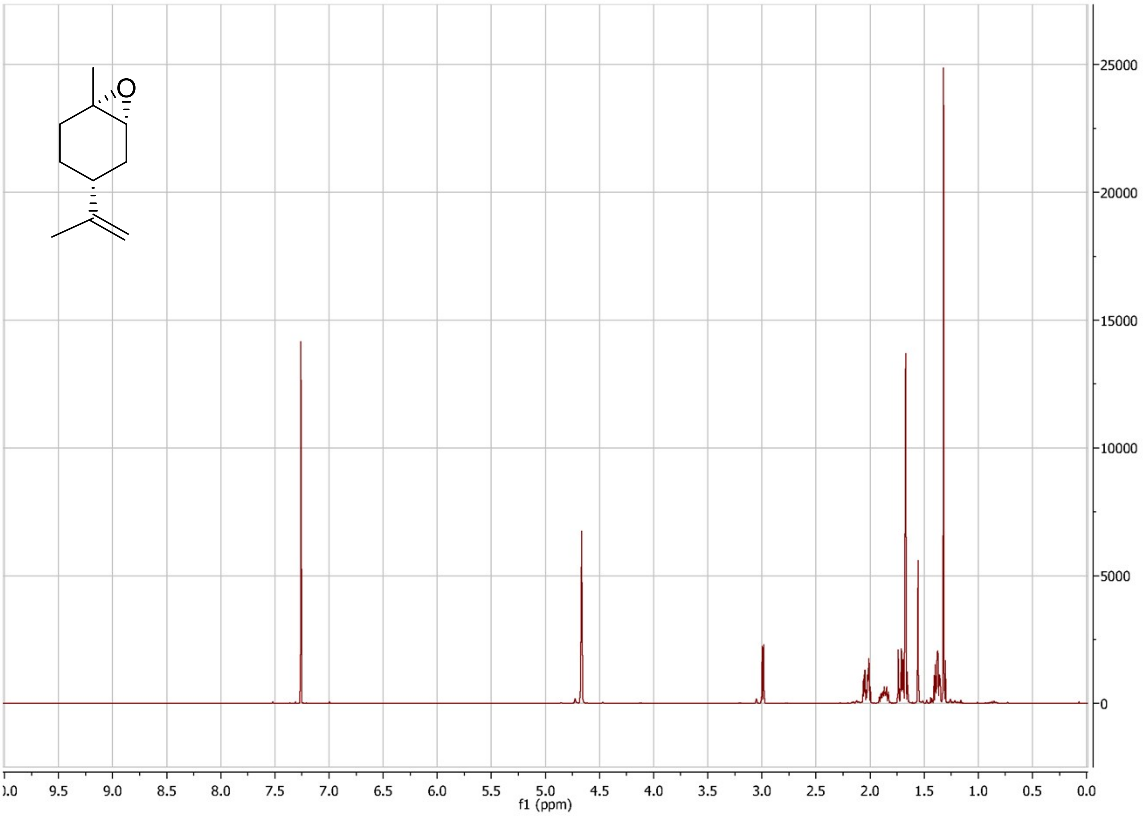
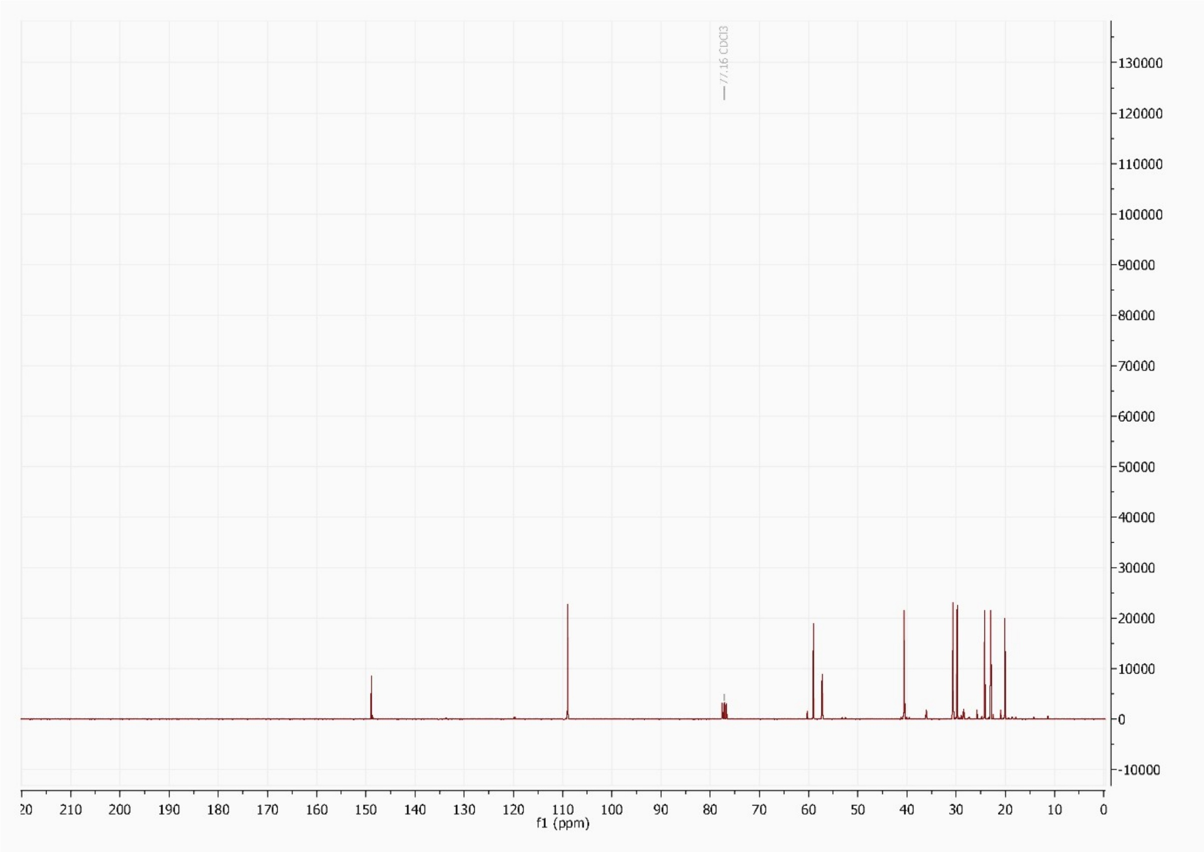
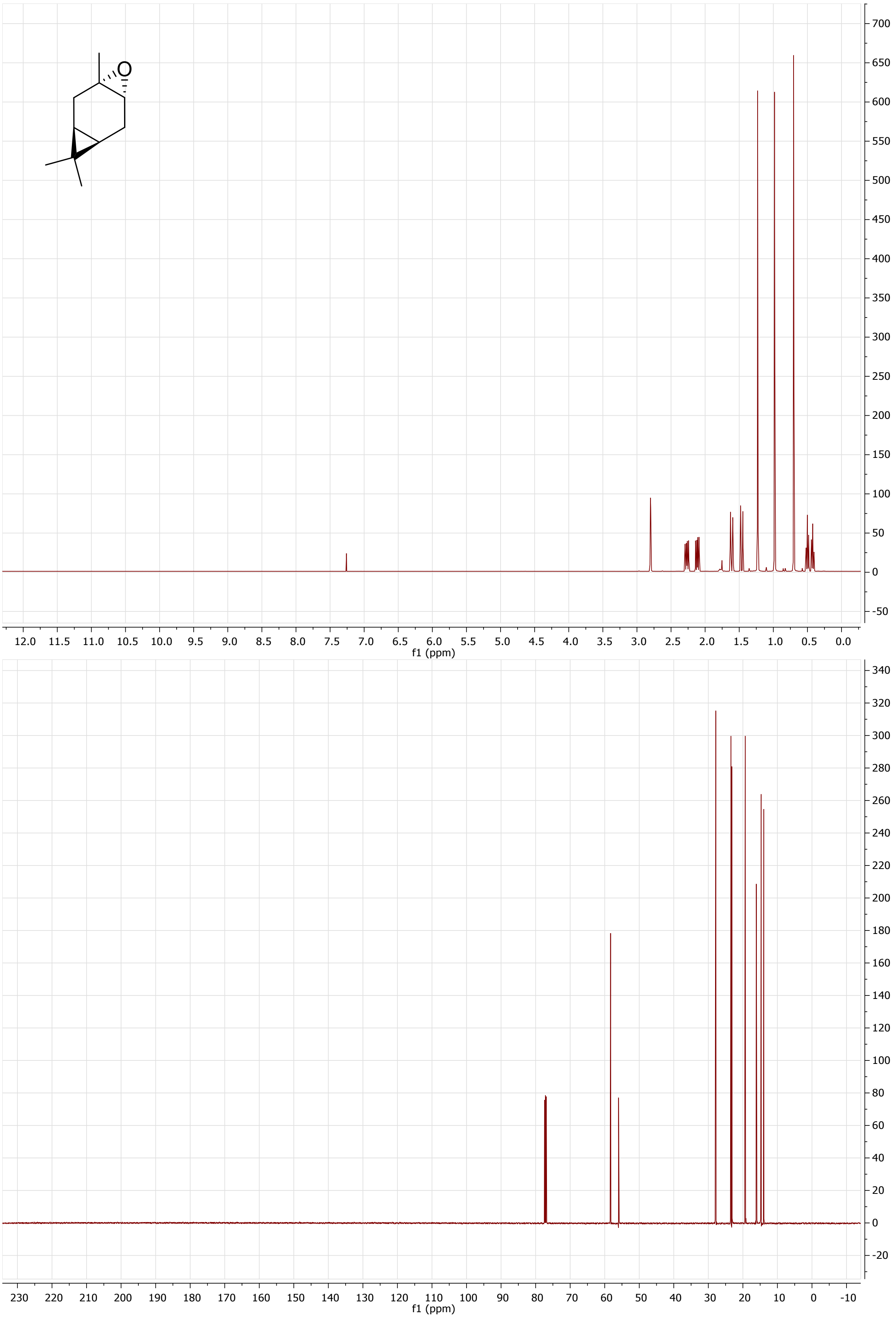
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
-20000
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

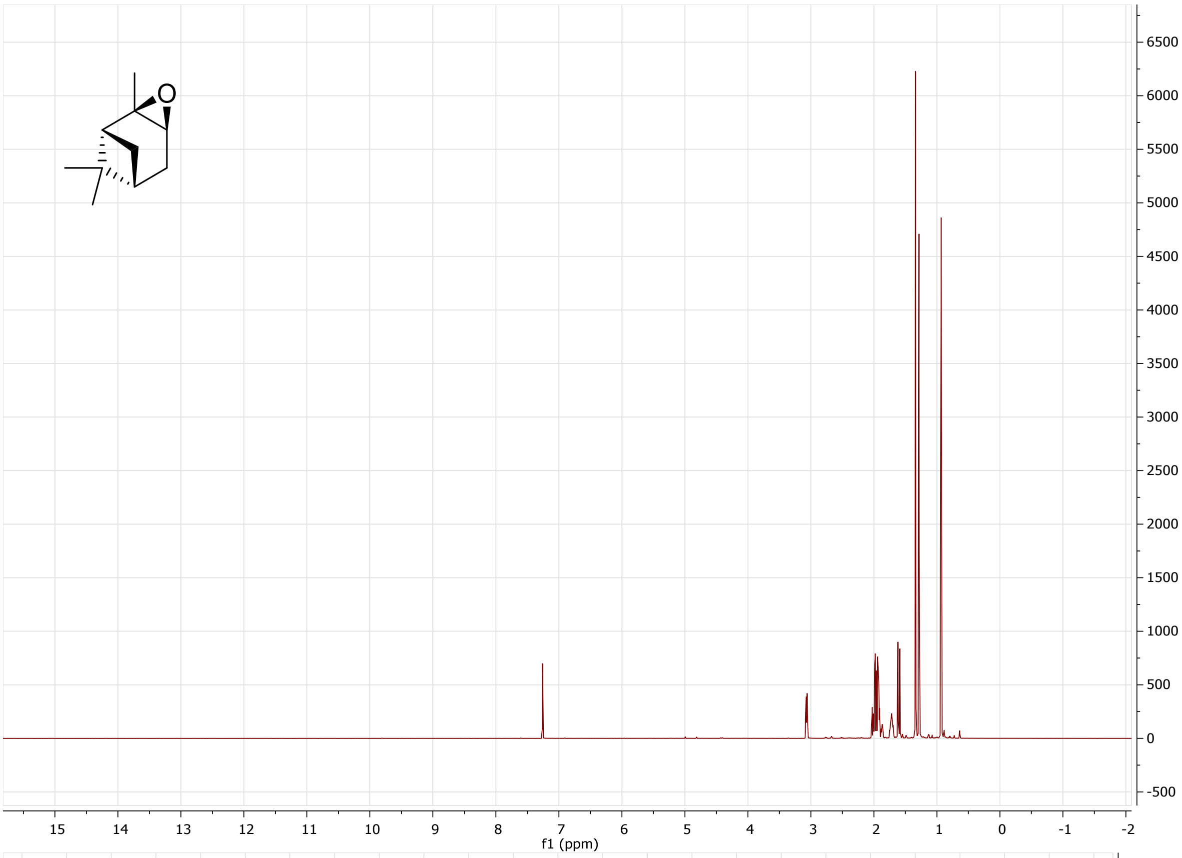

O
25000
20000
15000
10000
5000
0
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

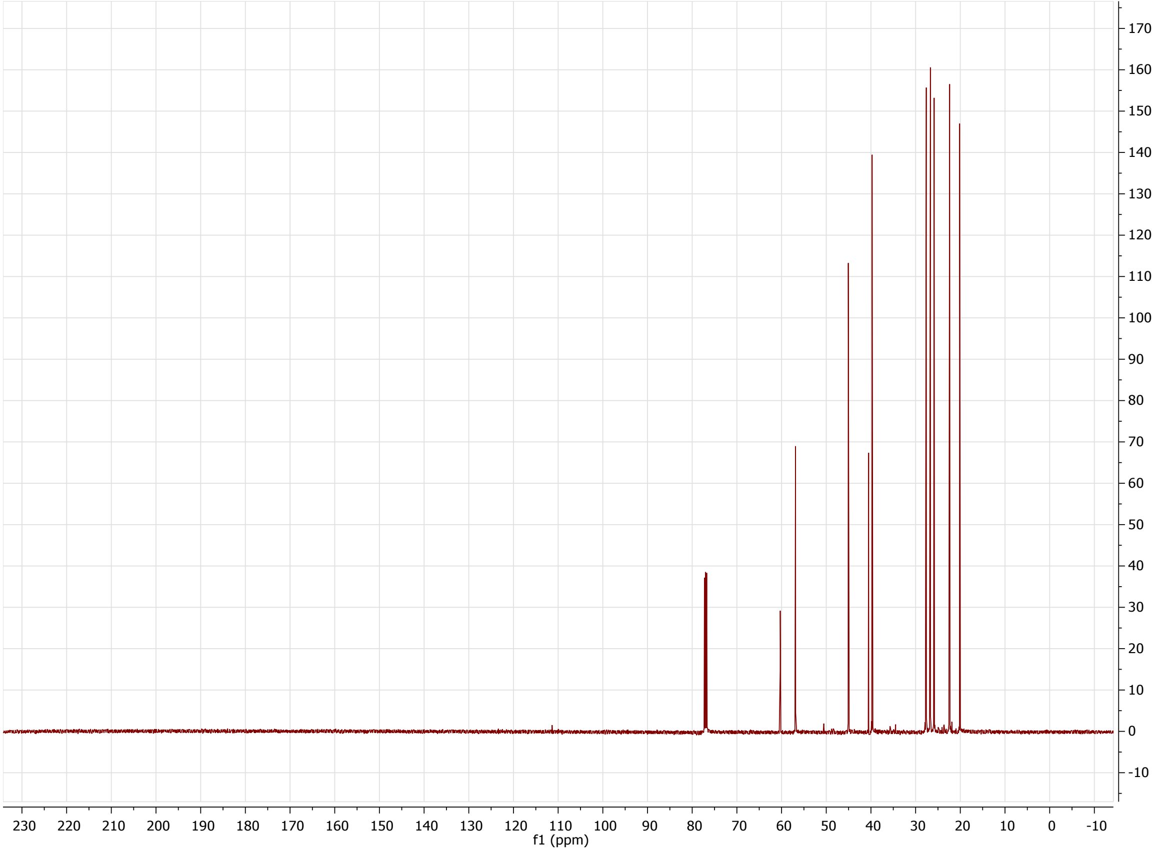

77.16 CDCl3
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3-Carene oxide (2)

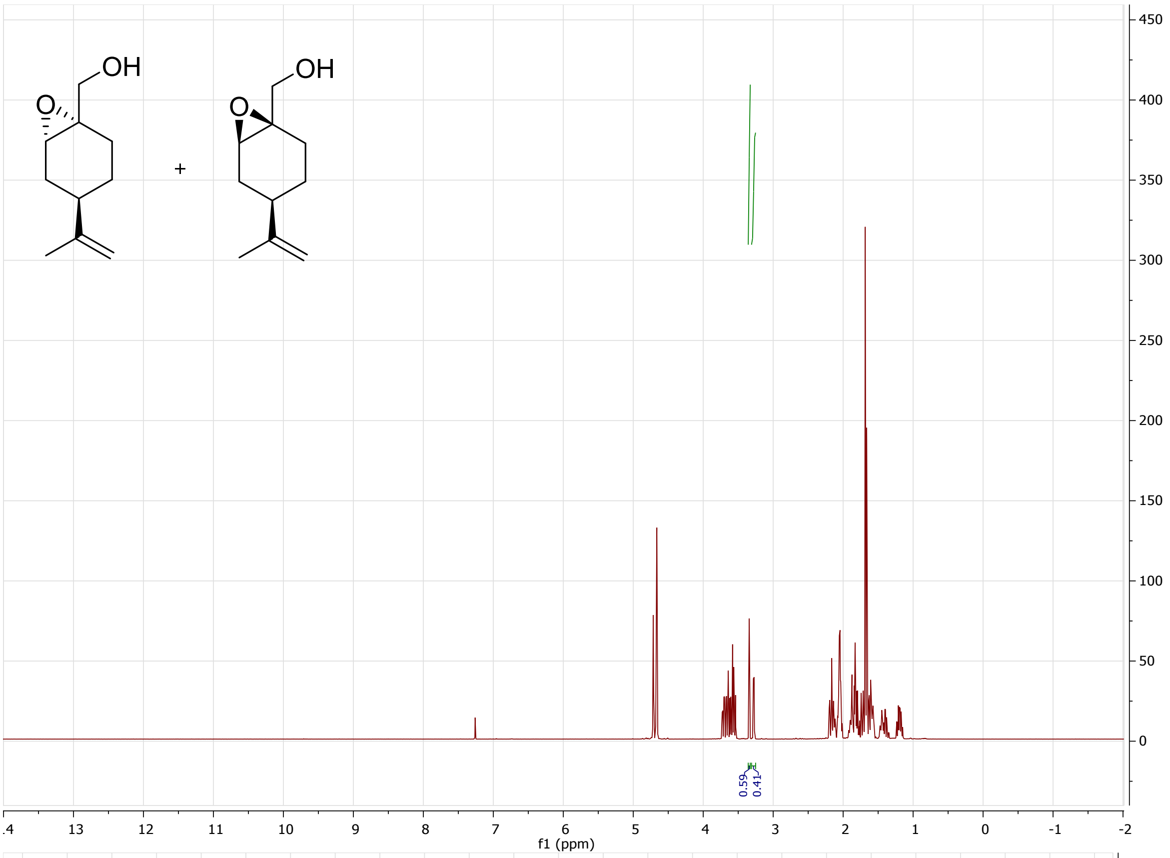


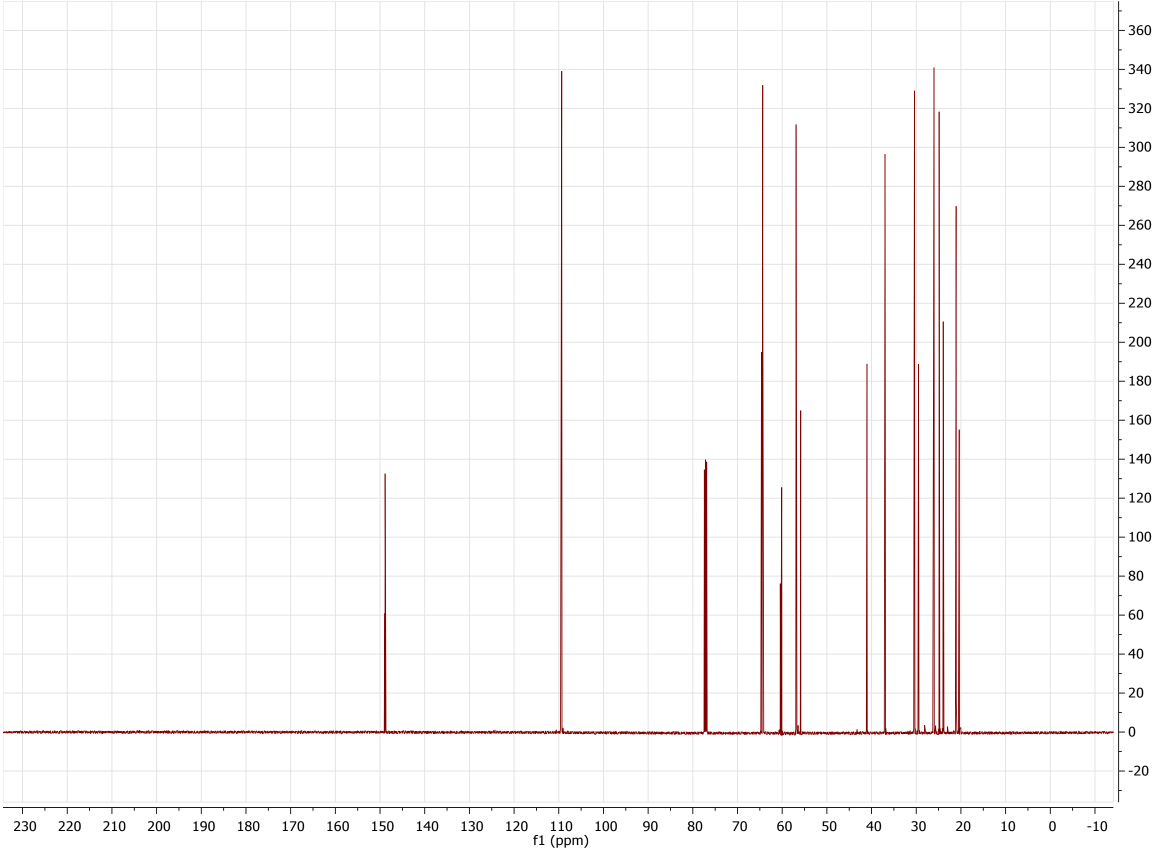
α-Pinene oxide (3)



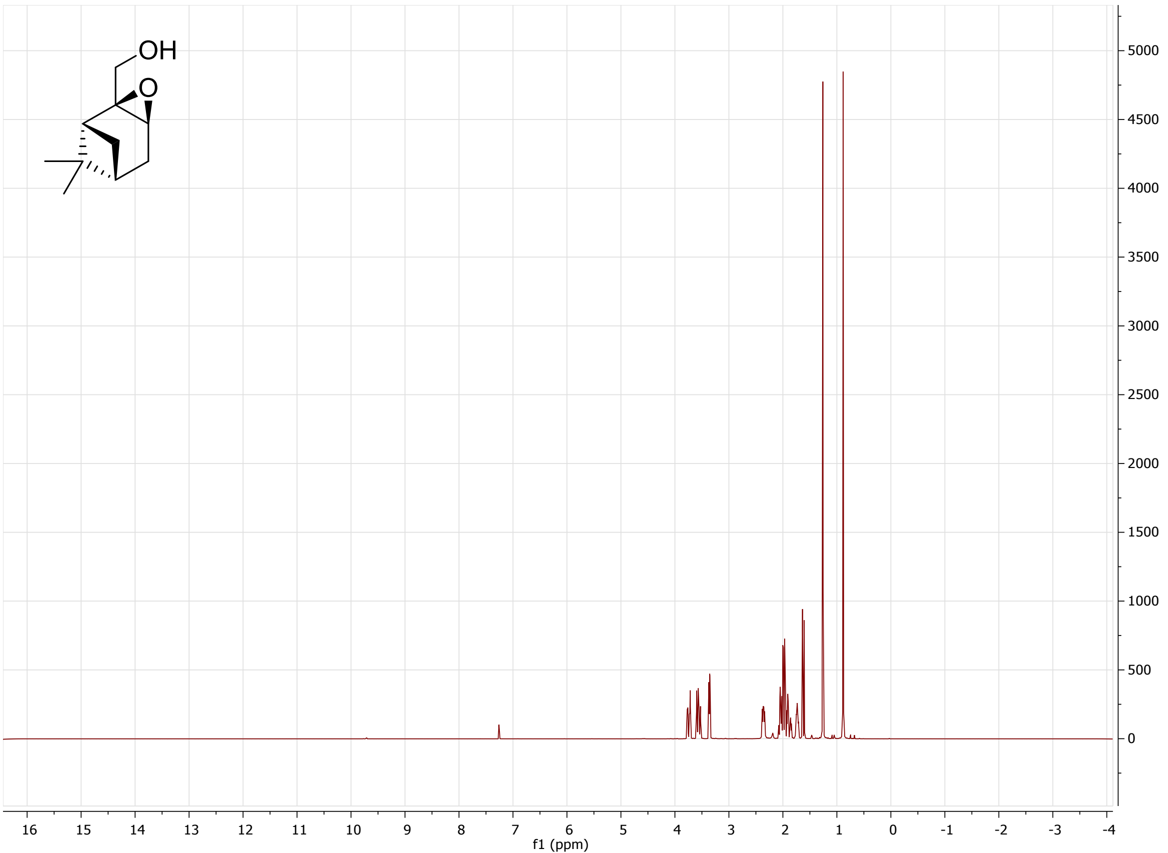


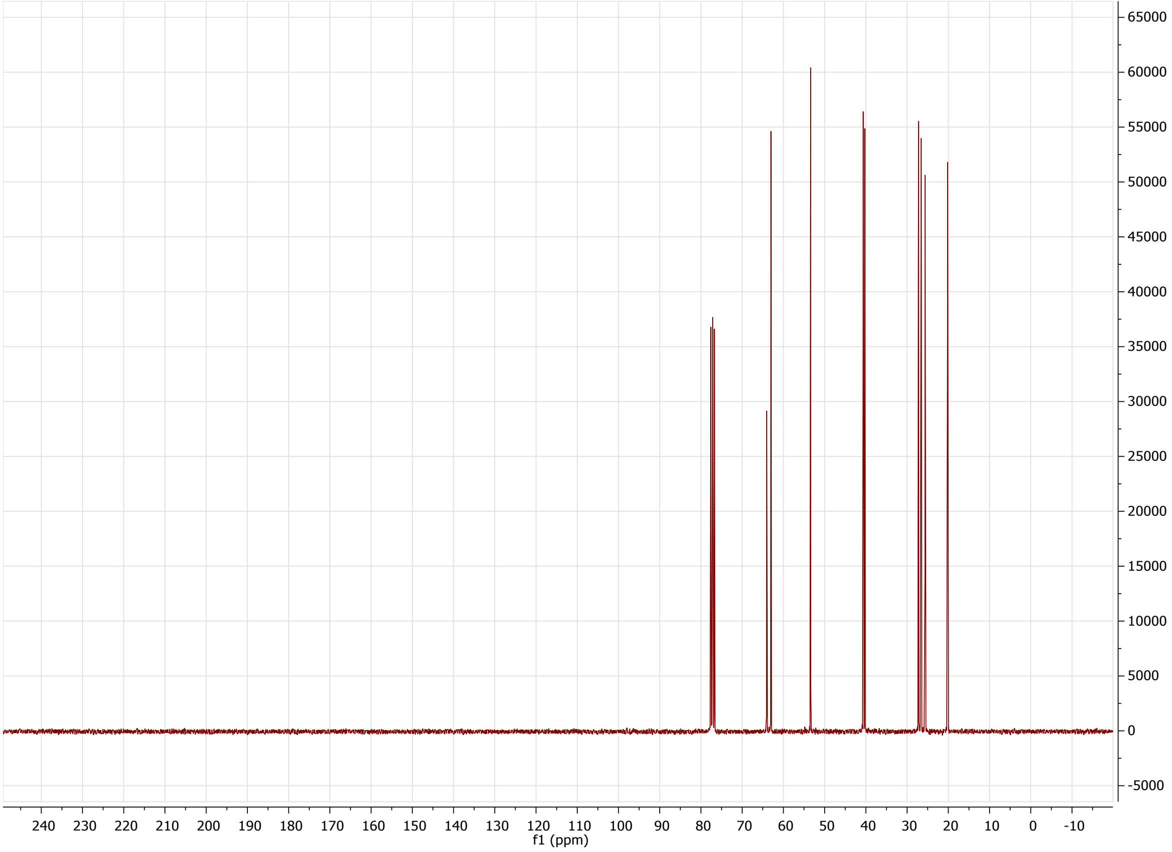
2,3-Epoxyperillyl alcohol (4a/b)



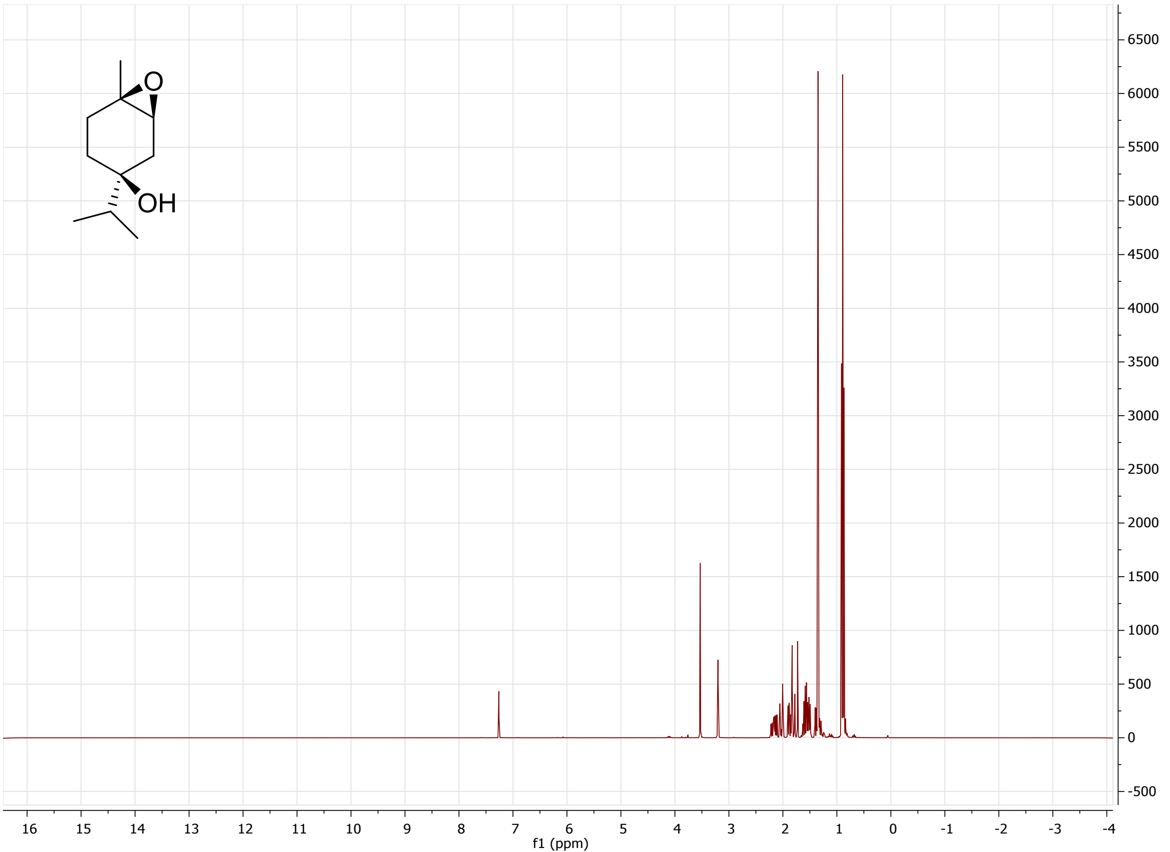


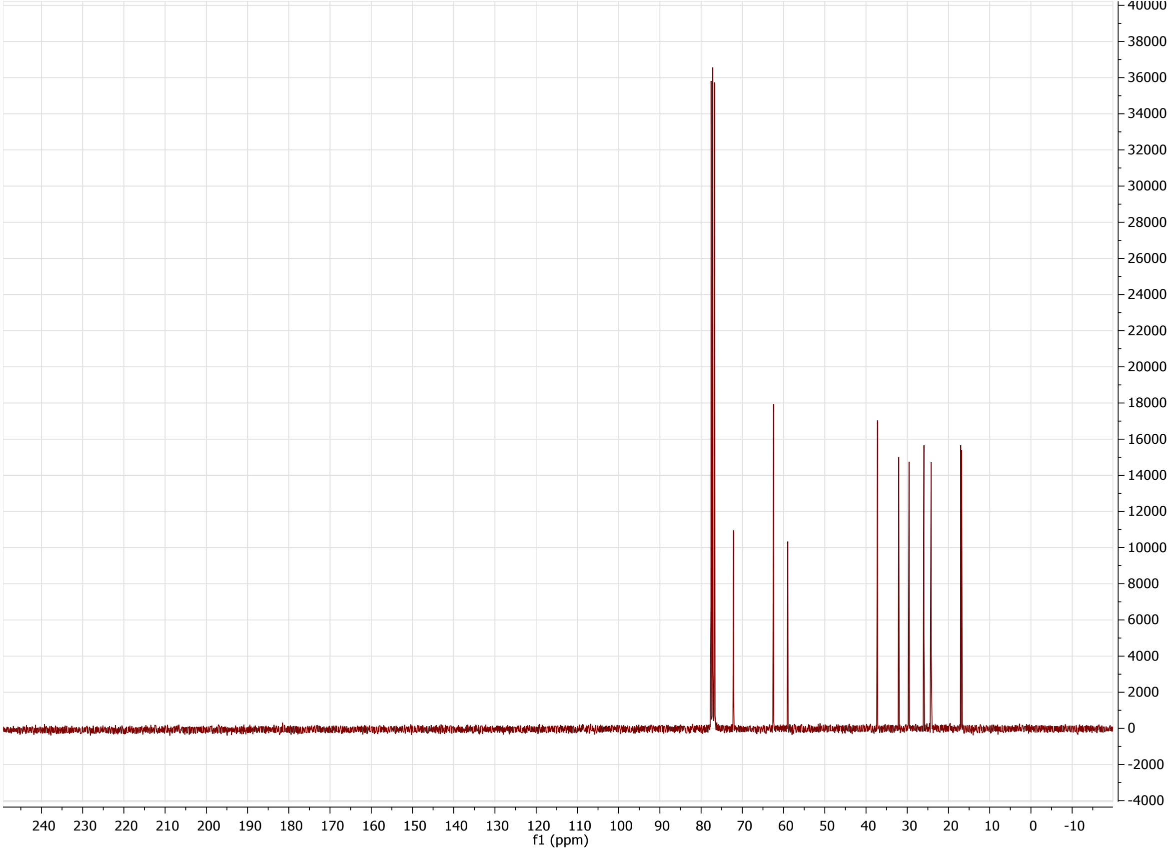
Myrtenol oxide (5)



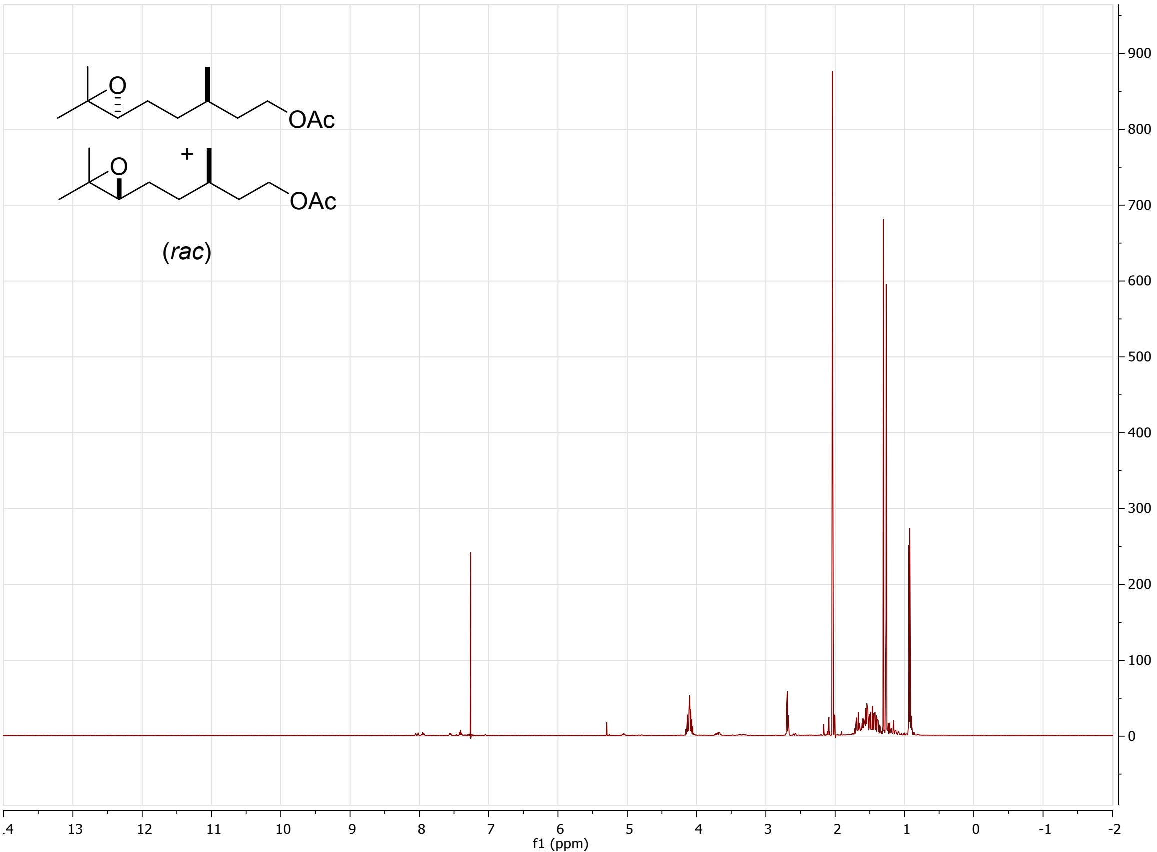


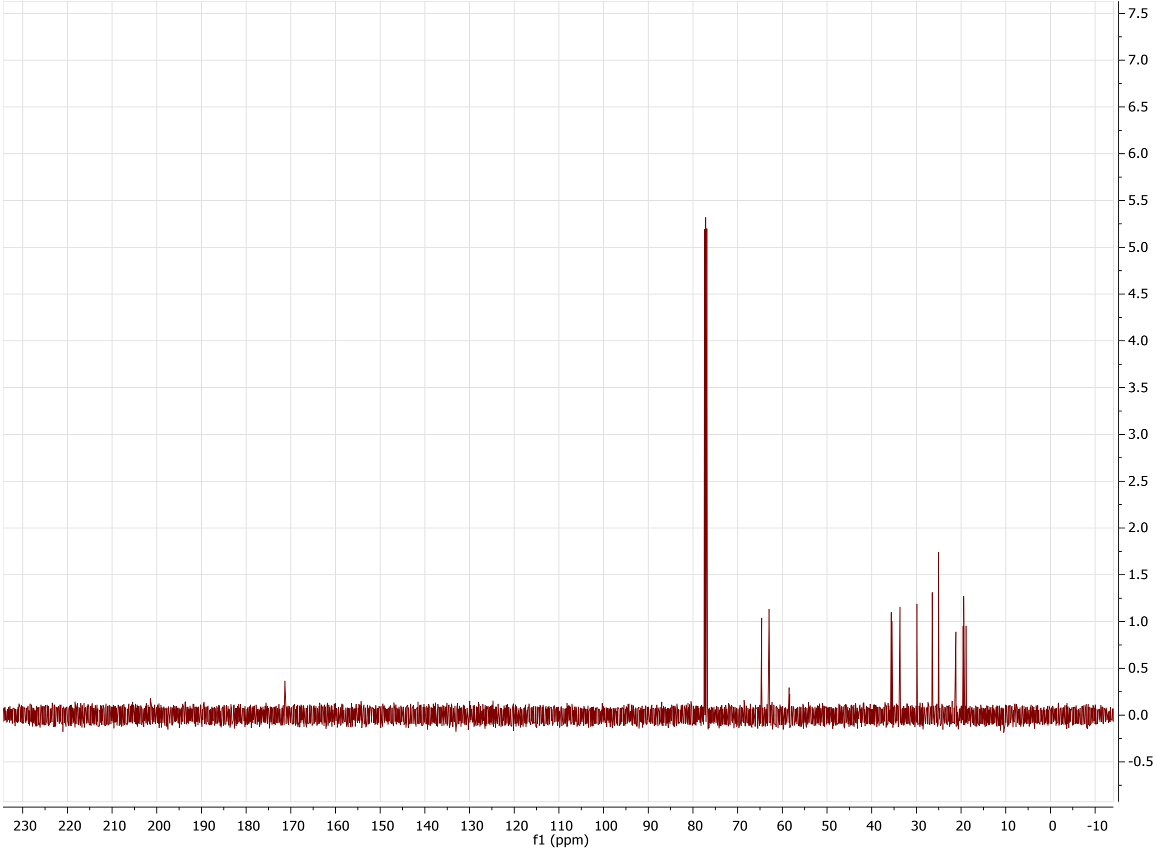
4-Carvomenthenol epoxides (6a/b)



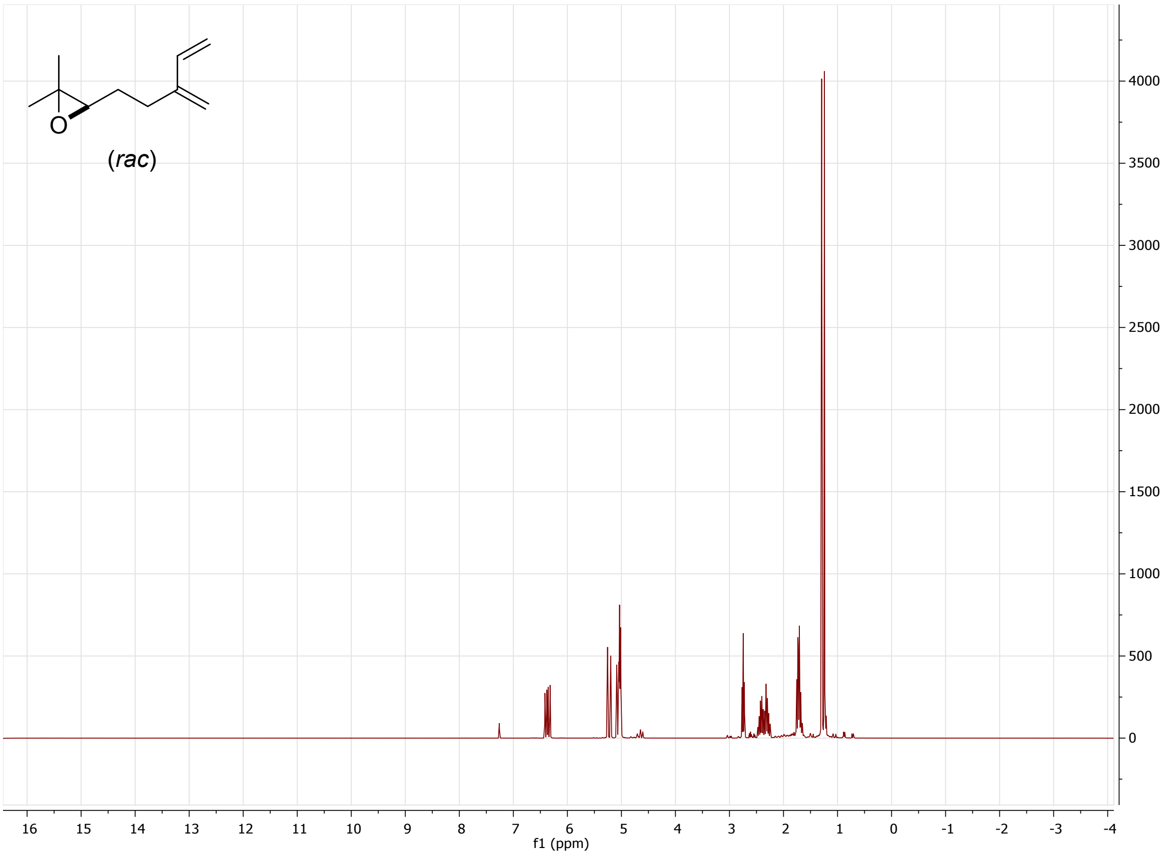


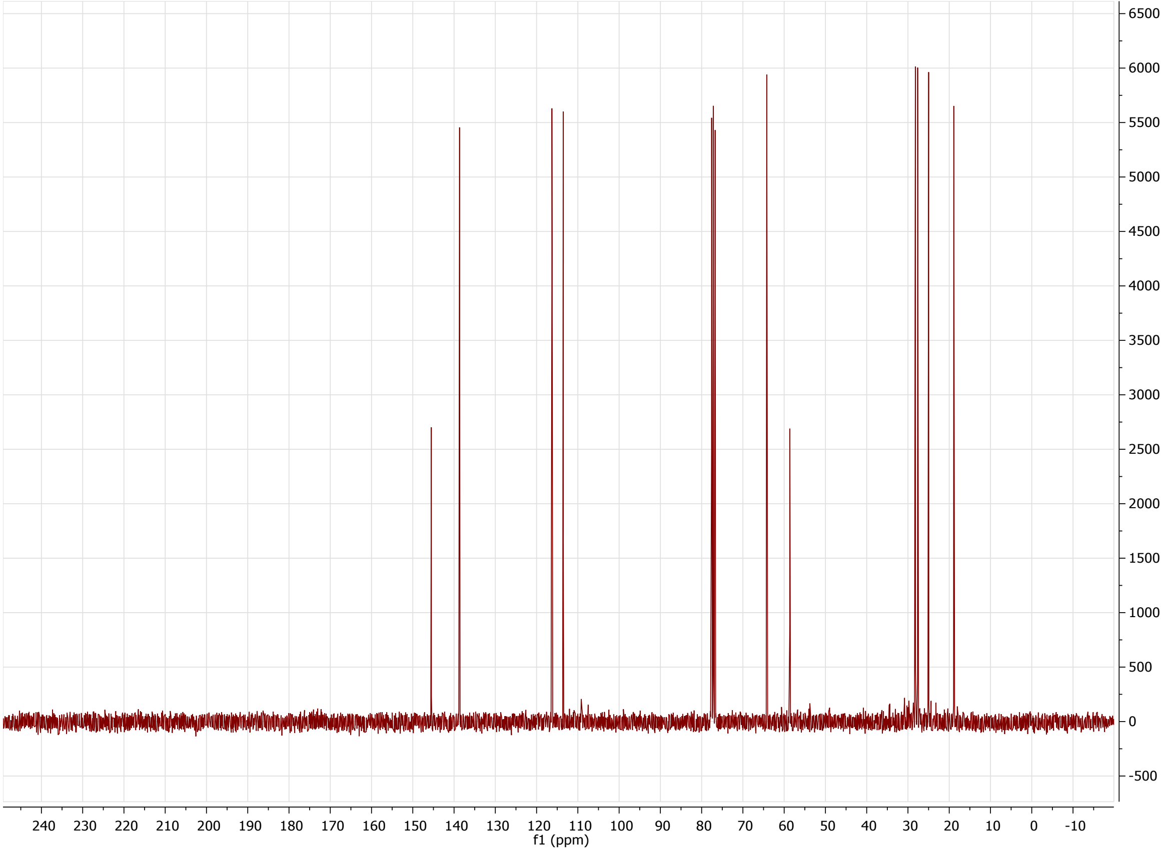
(*rac*)-*O*-Acetyl-β-citronellol epoxides (7a/b)



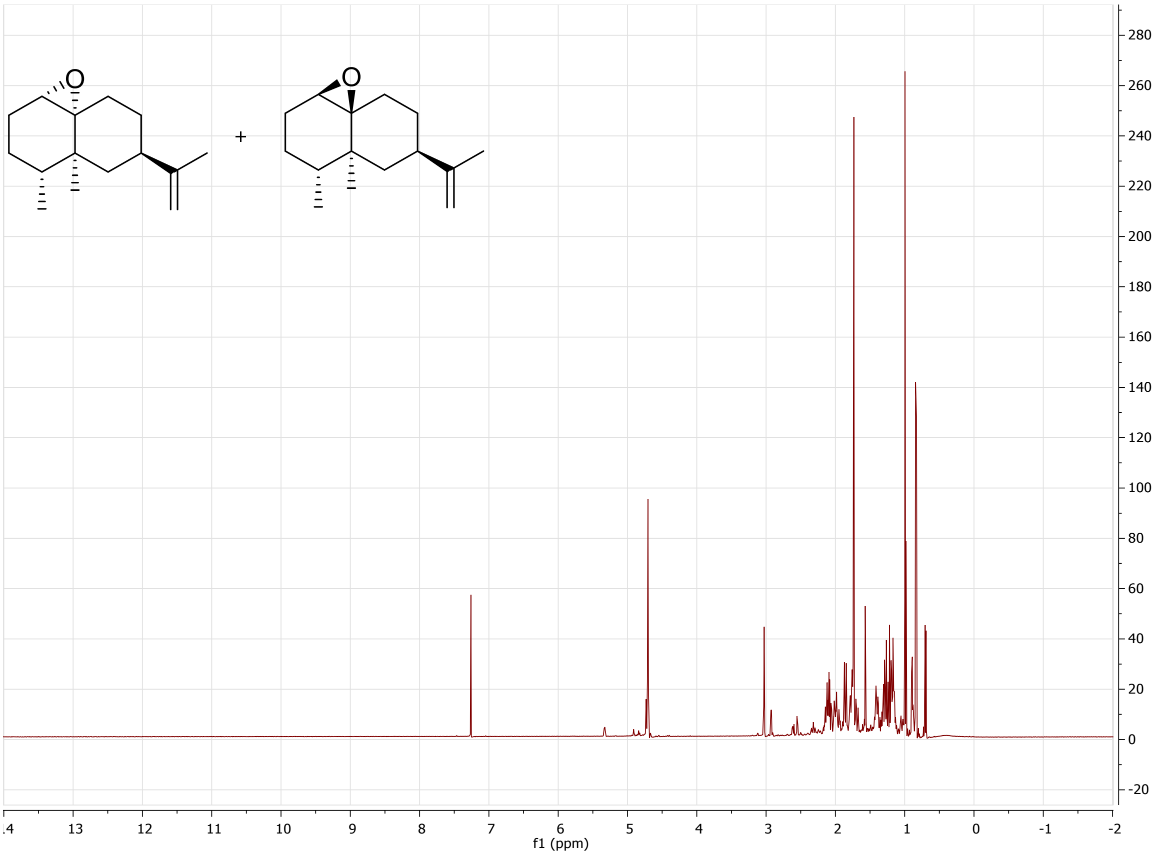


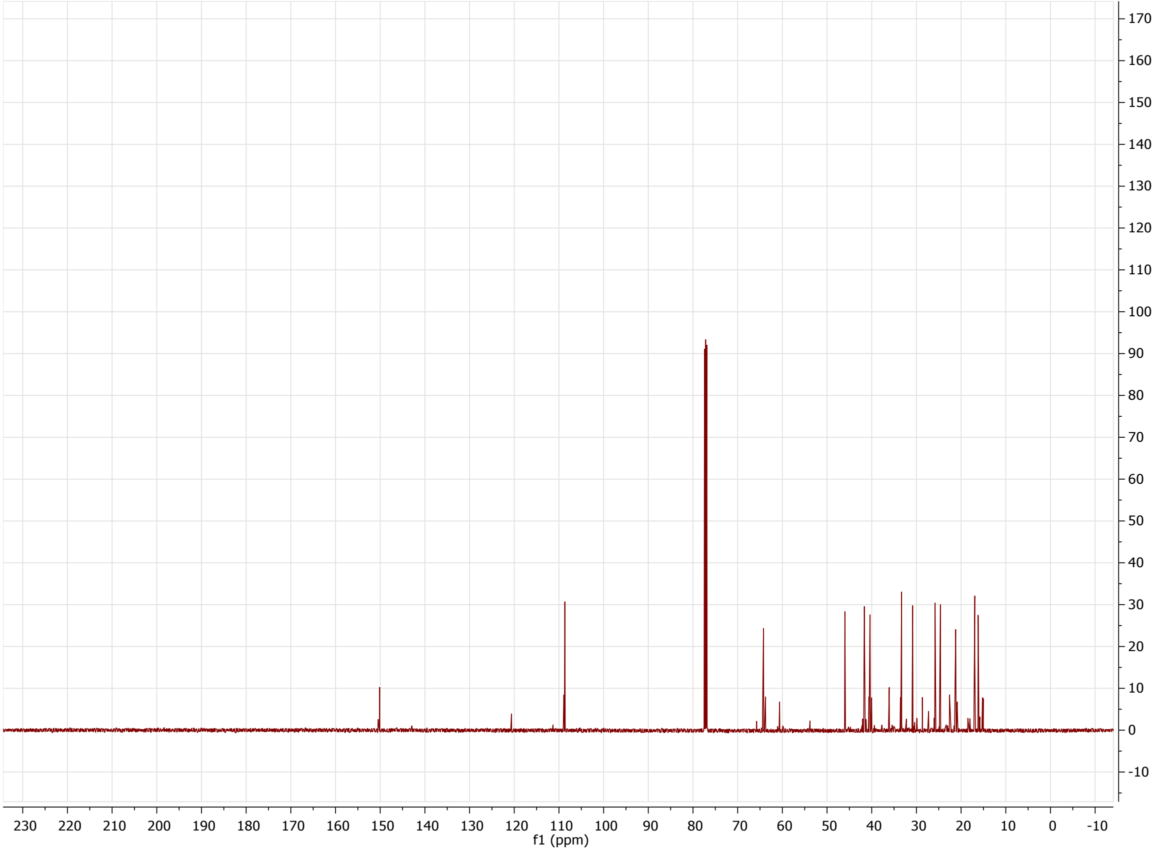
(*rac*)-6,7-Myrcene oxide (8)



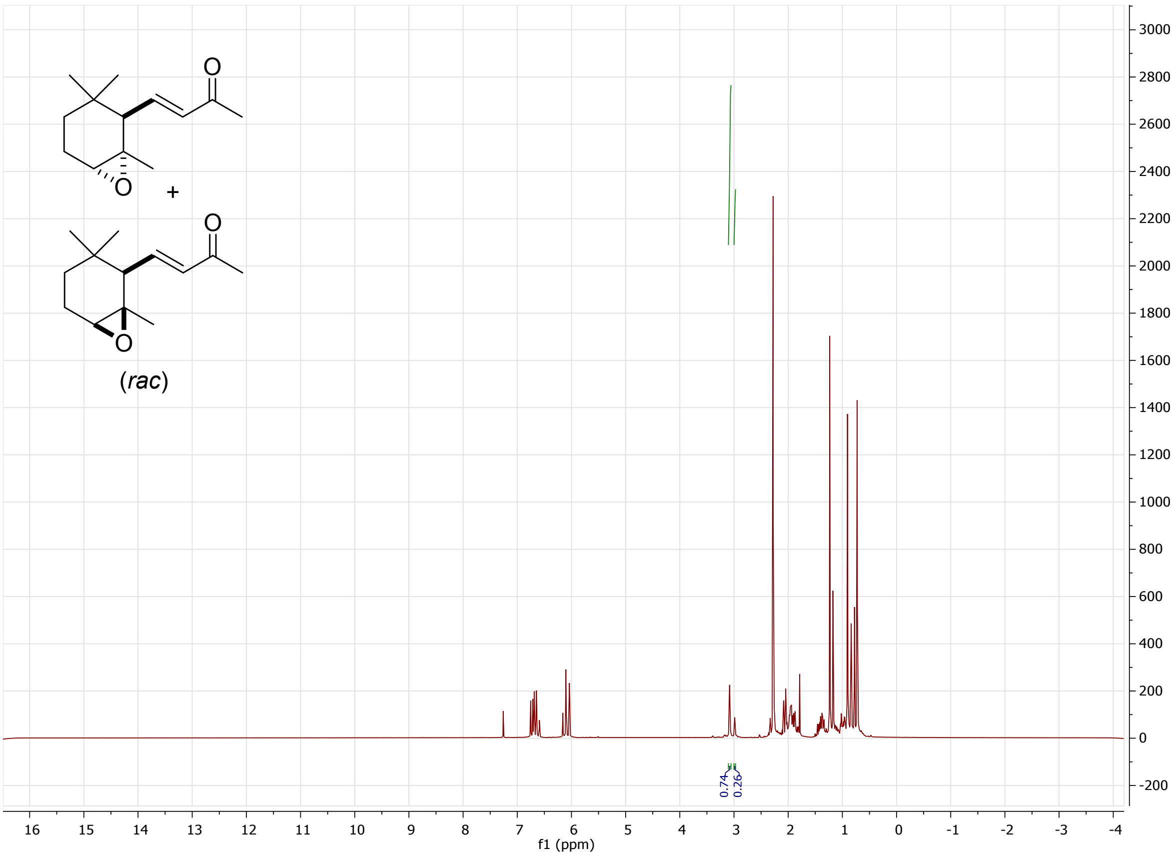


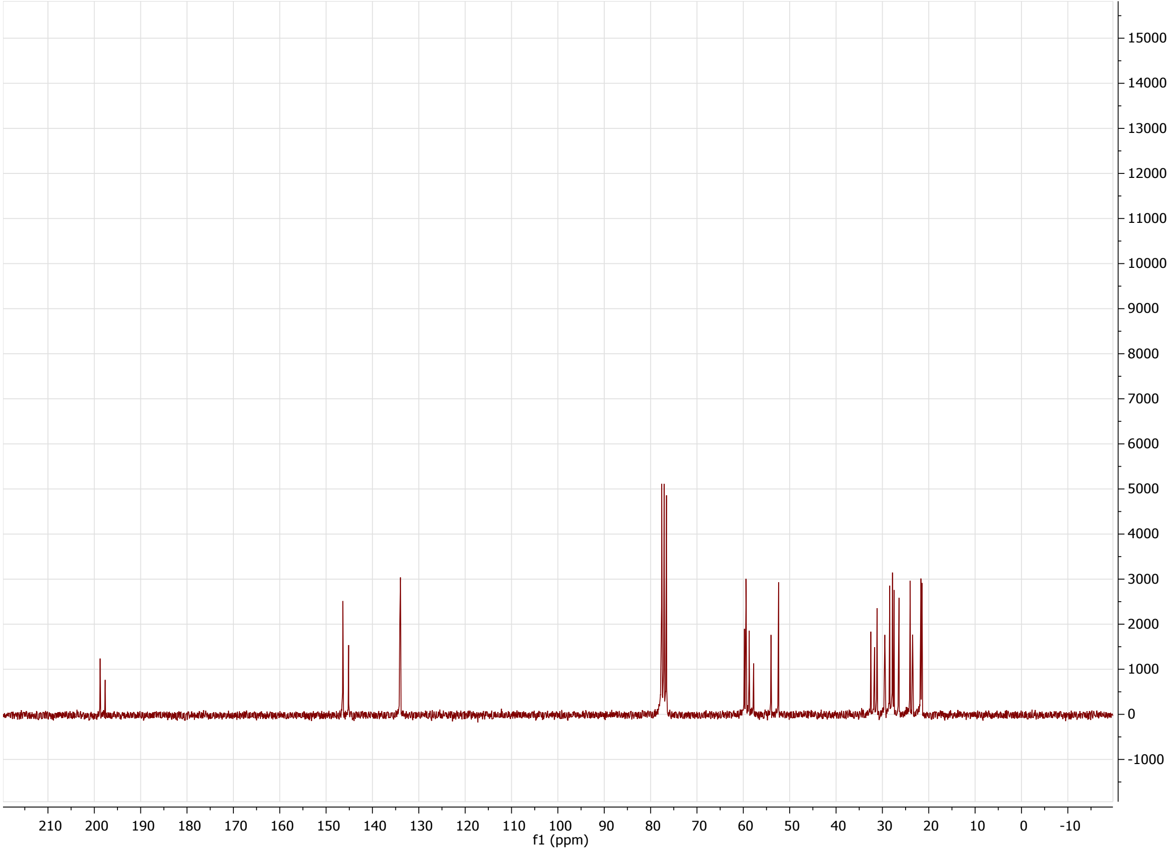
Valencene epoxides (9a/b)



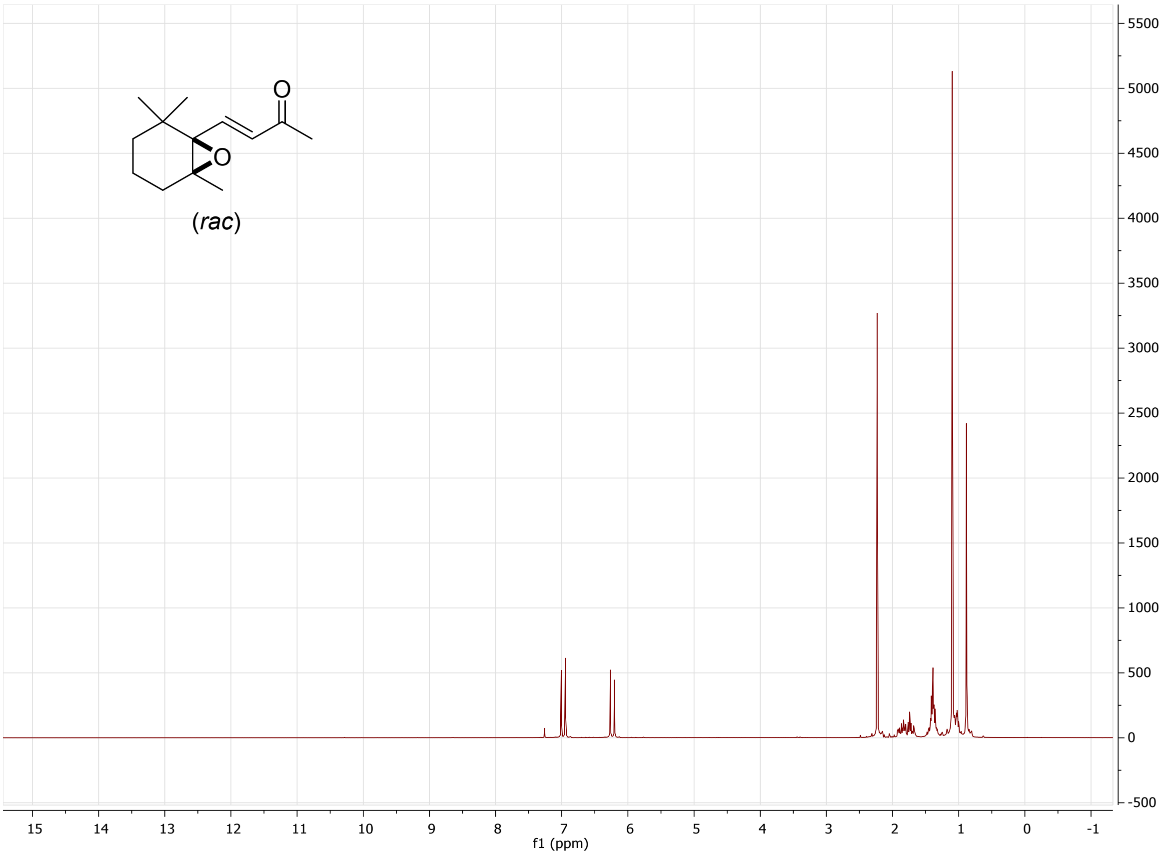


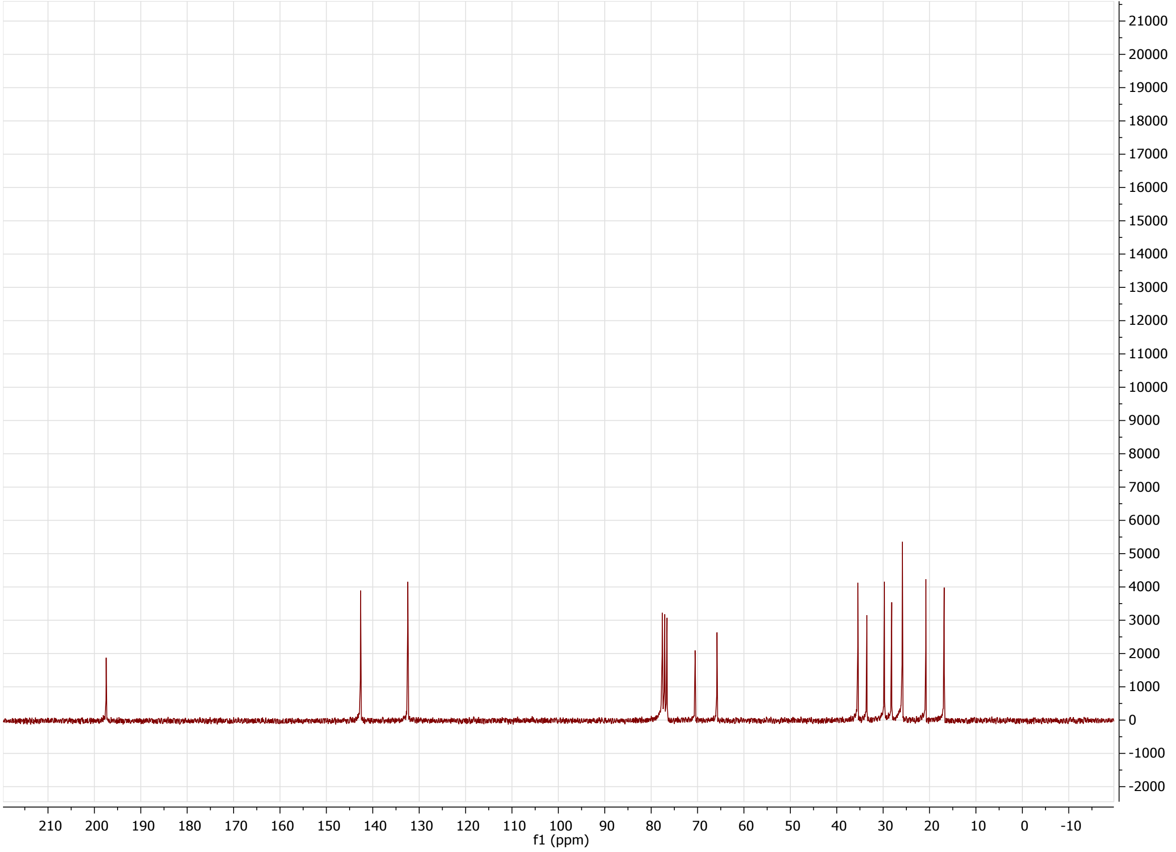
(*rac*)-α-Ionone epoxides (10a/b)



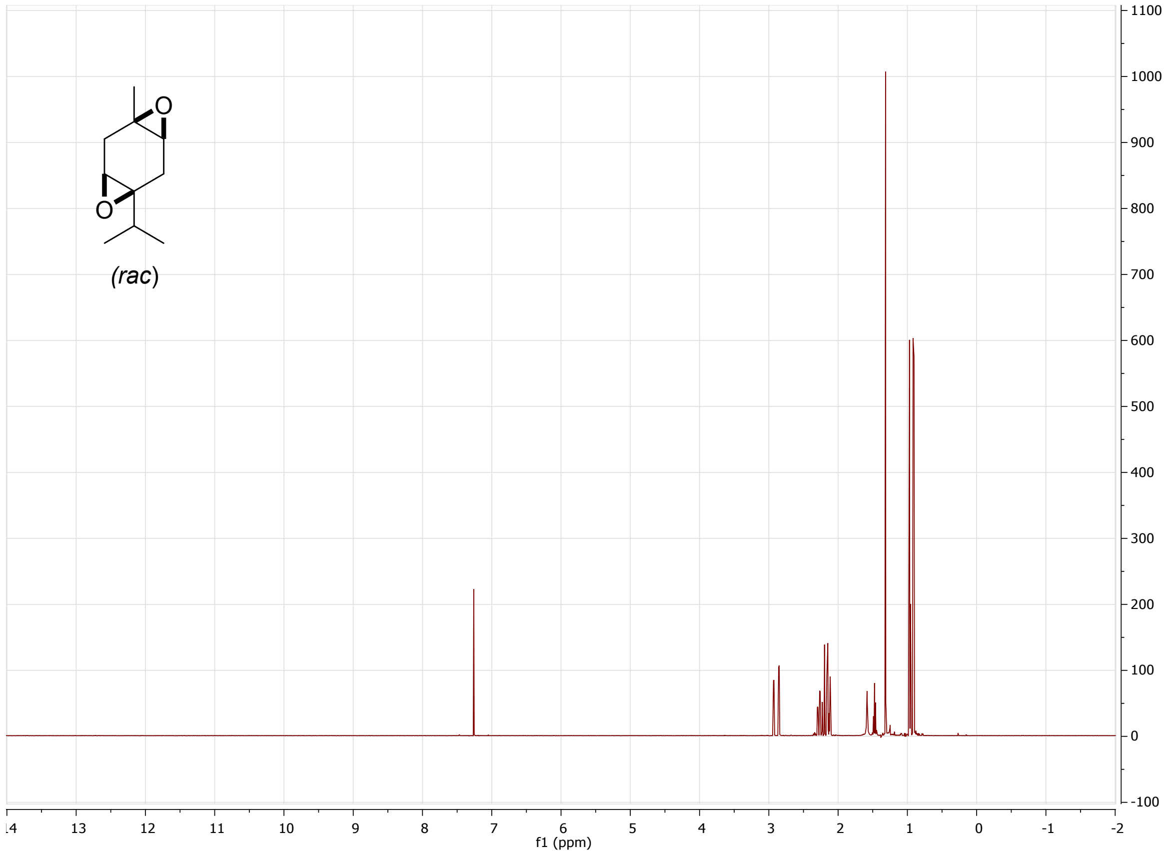


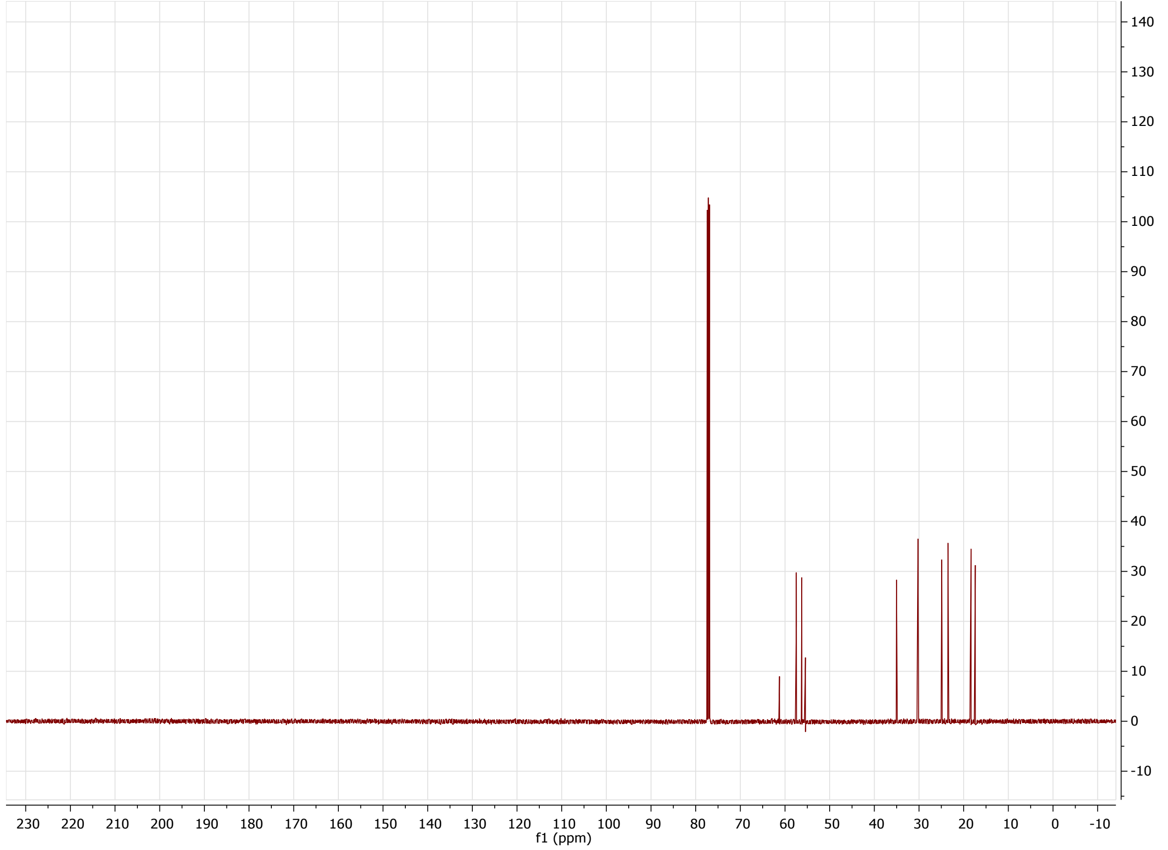
(*rac*)-β-Ionone epoxide (11)



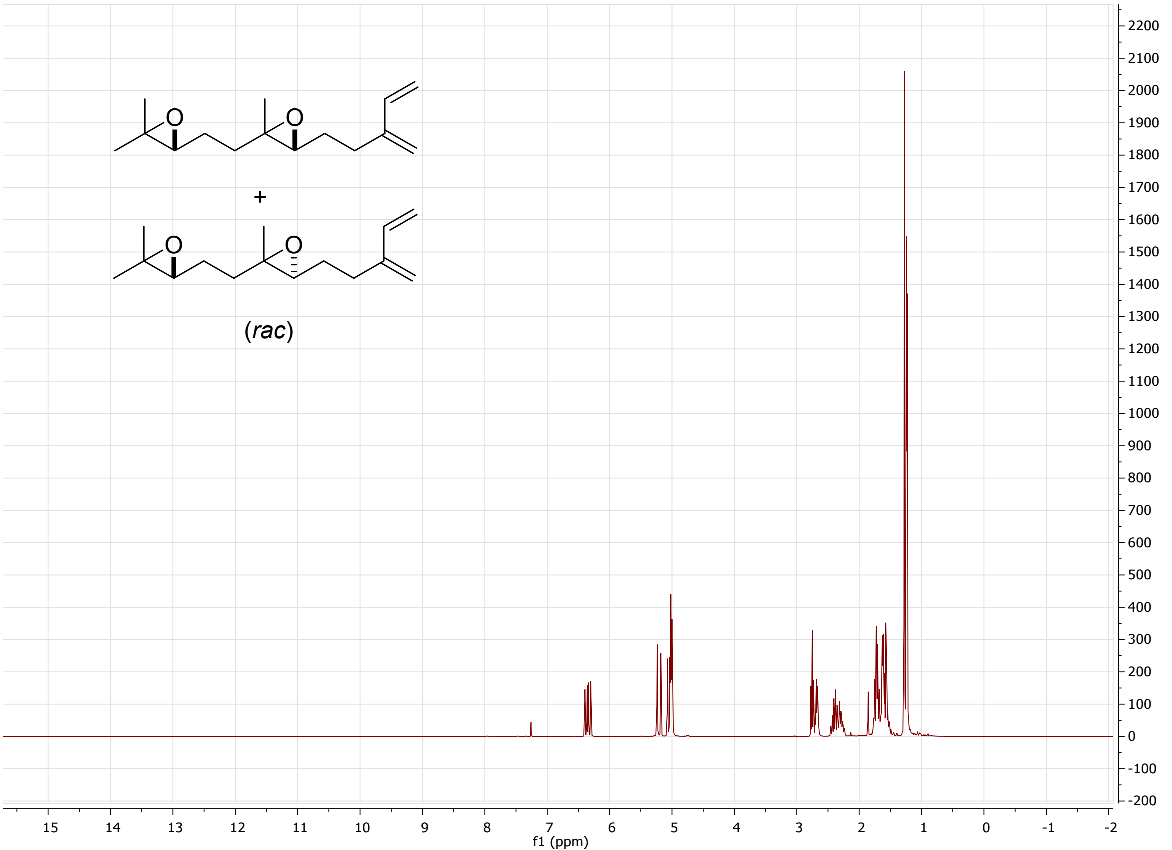


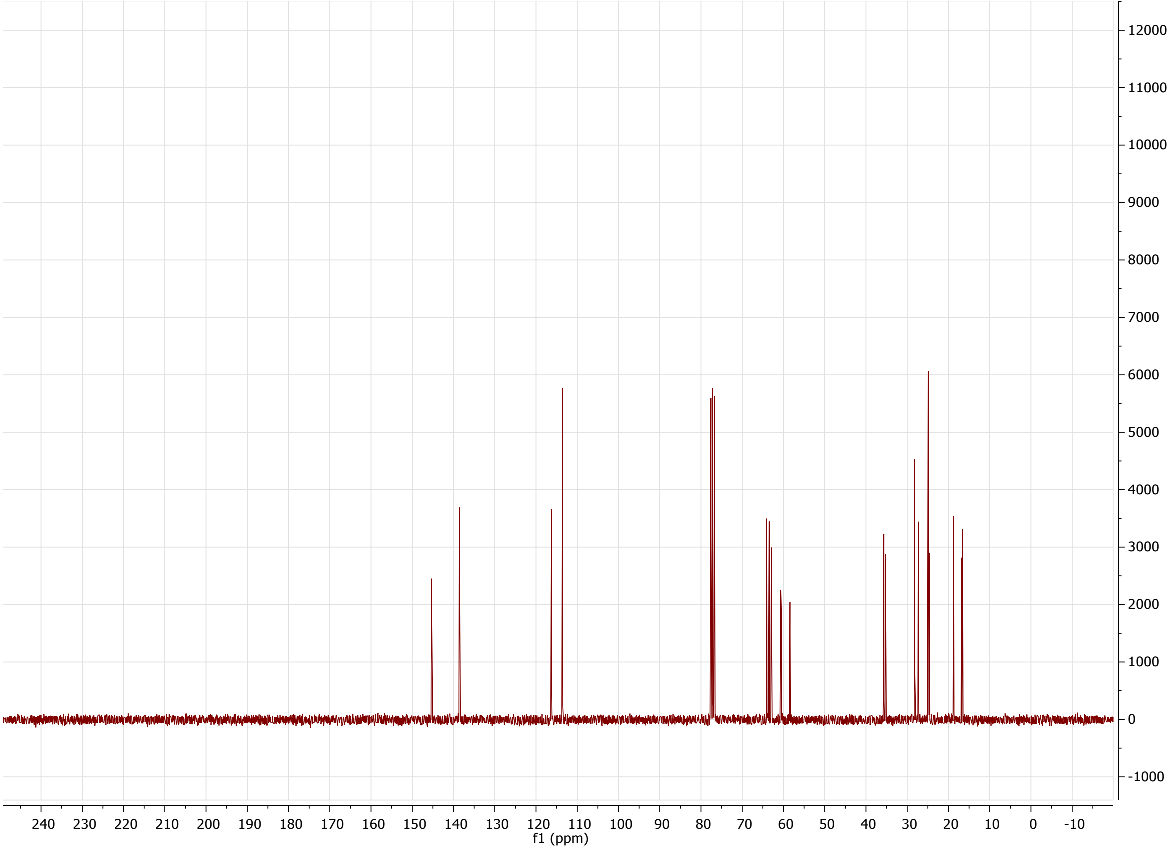
(*rac*)-γ-Terpinene *bis*-epoxide (12)



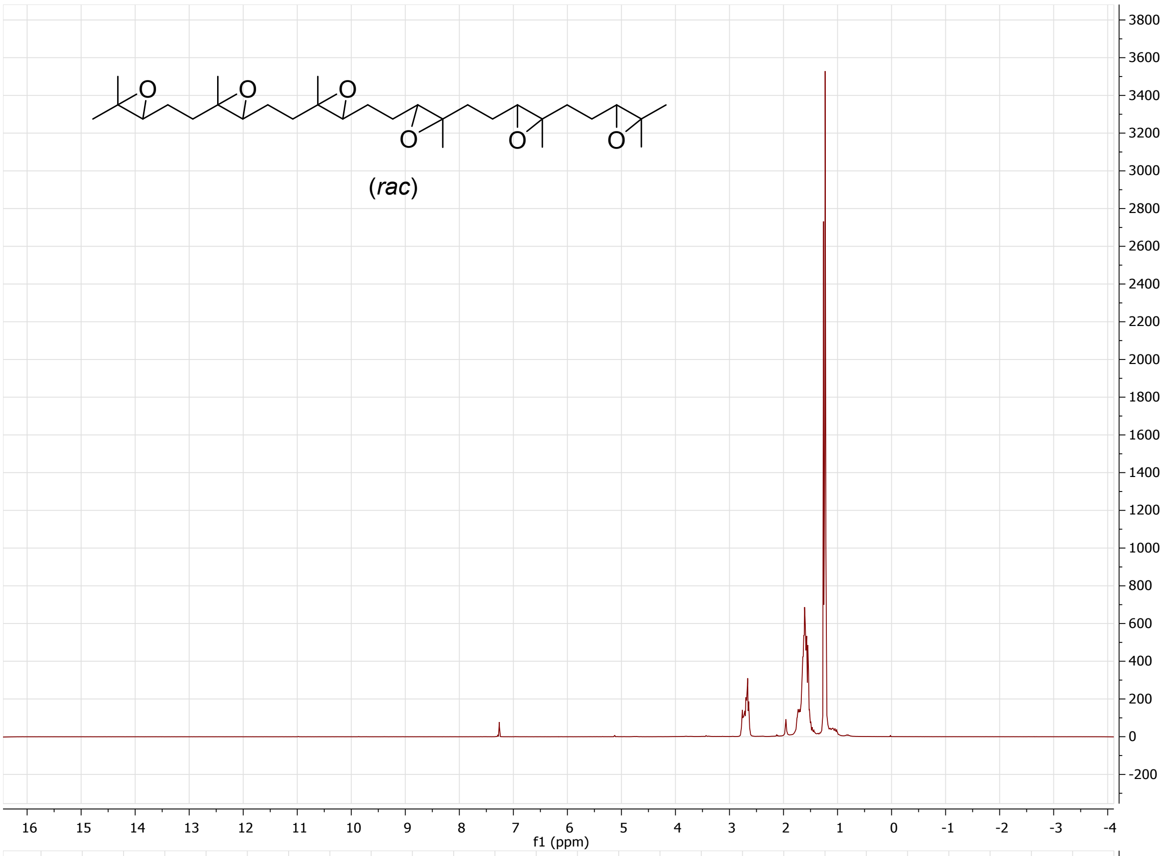


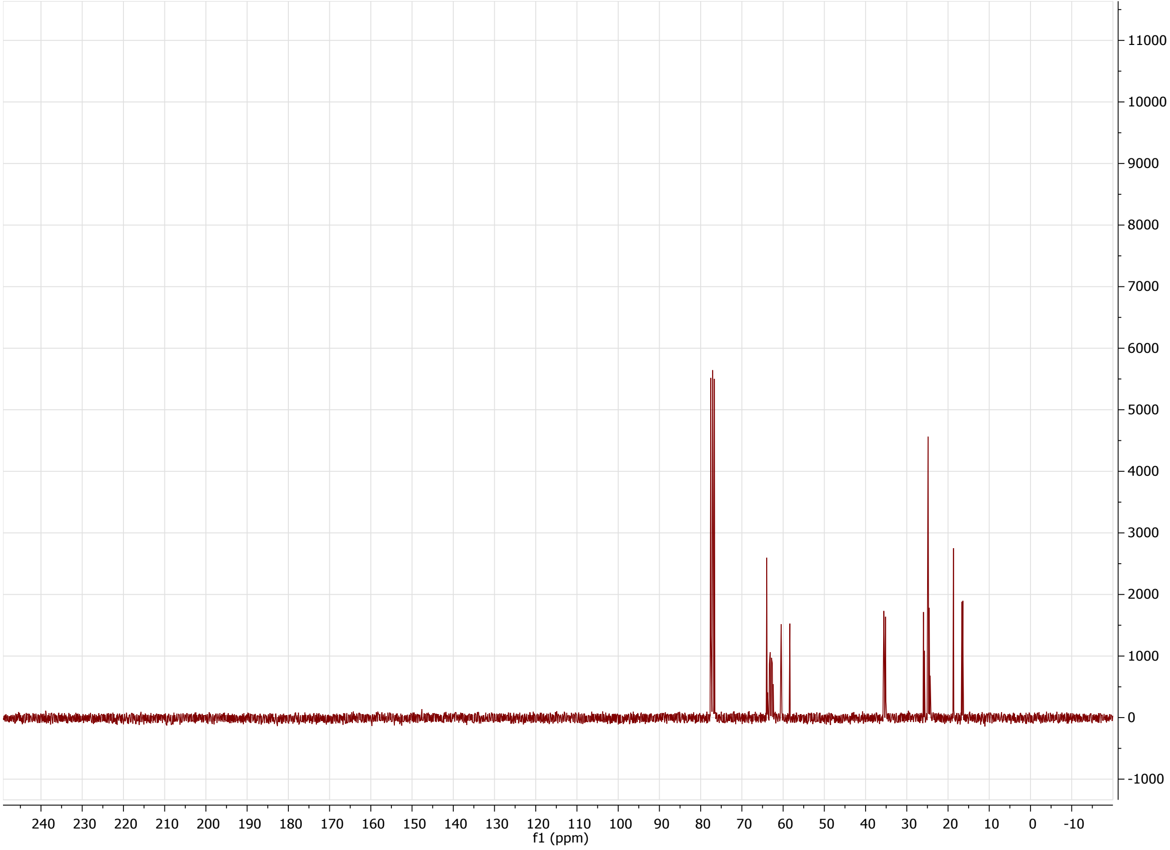
(*rac*)-Farnesene *bis*-epoxides (13a/b)



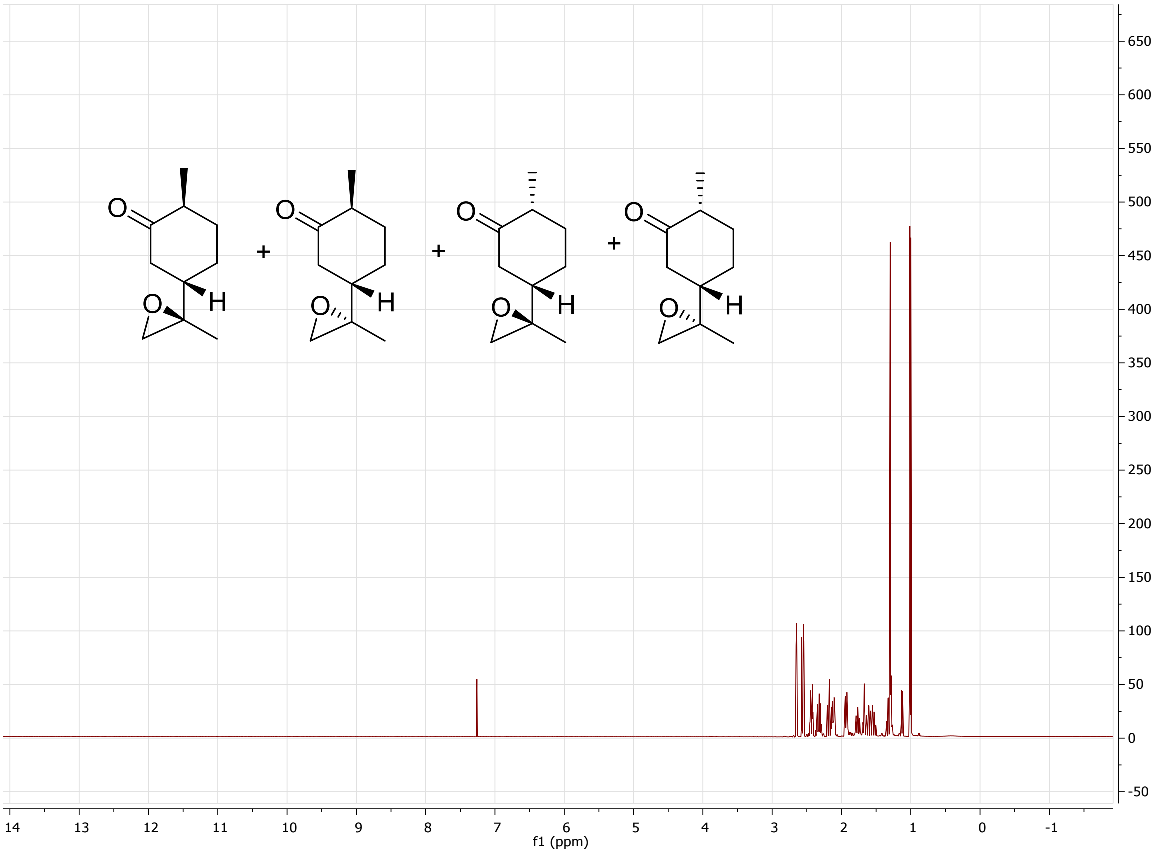


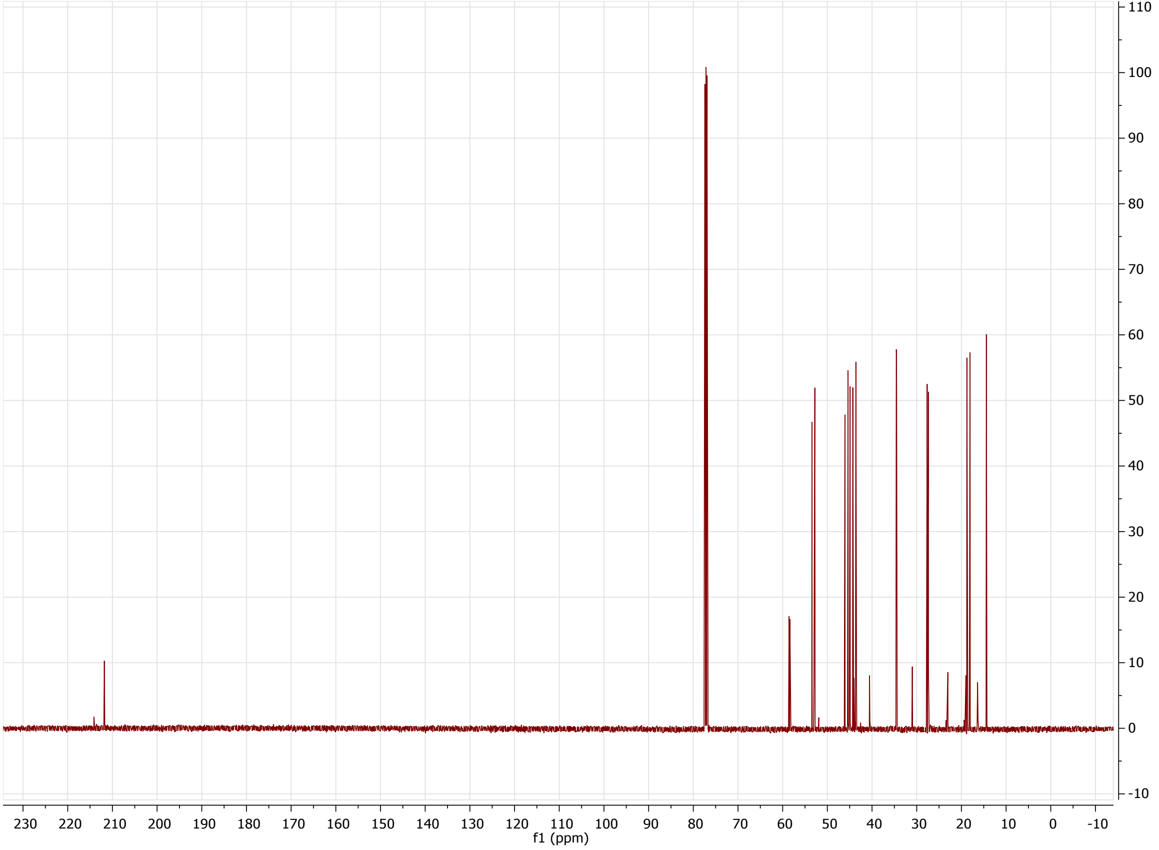
(*rac*)-Squalene epoxides (14)



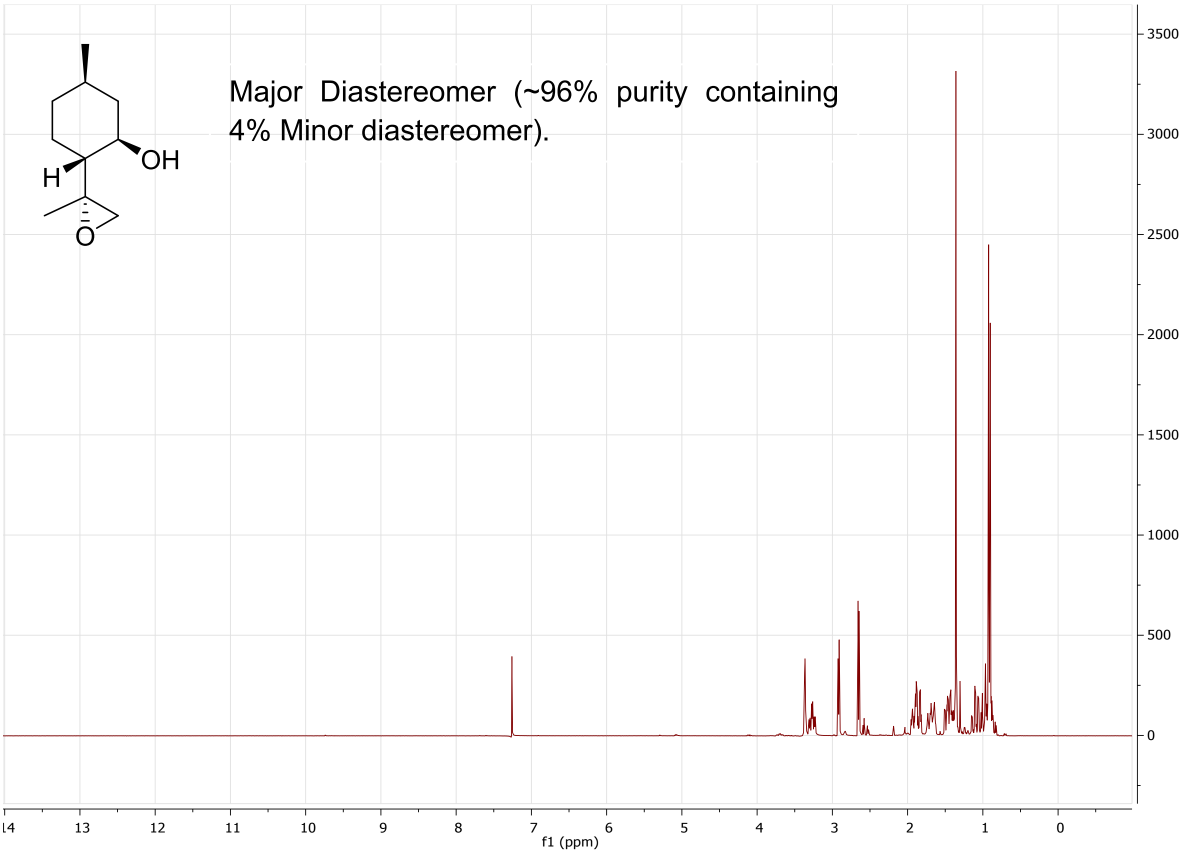


Dihydrocarvone epoxides (15a-d)

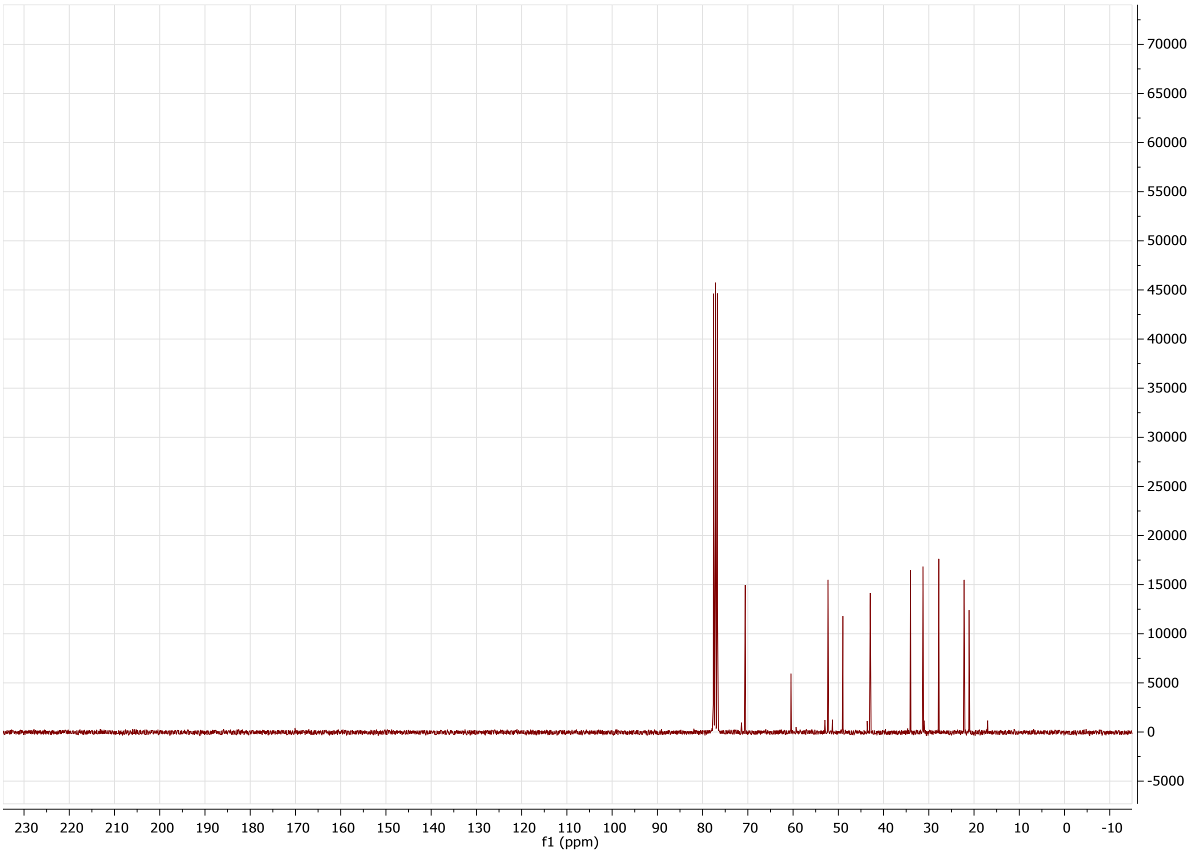


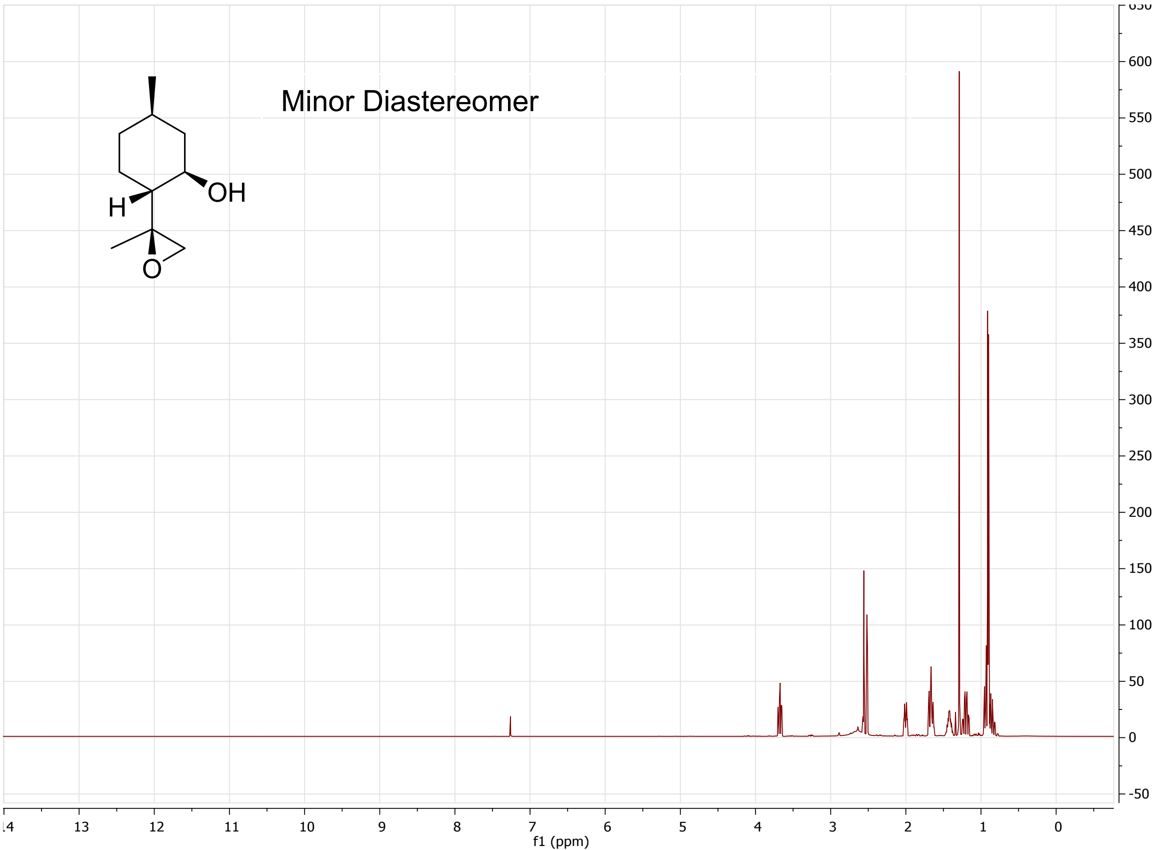


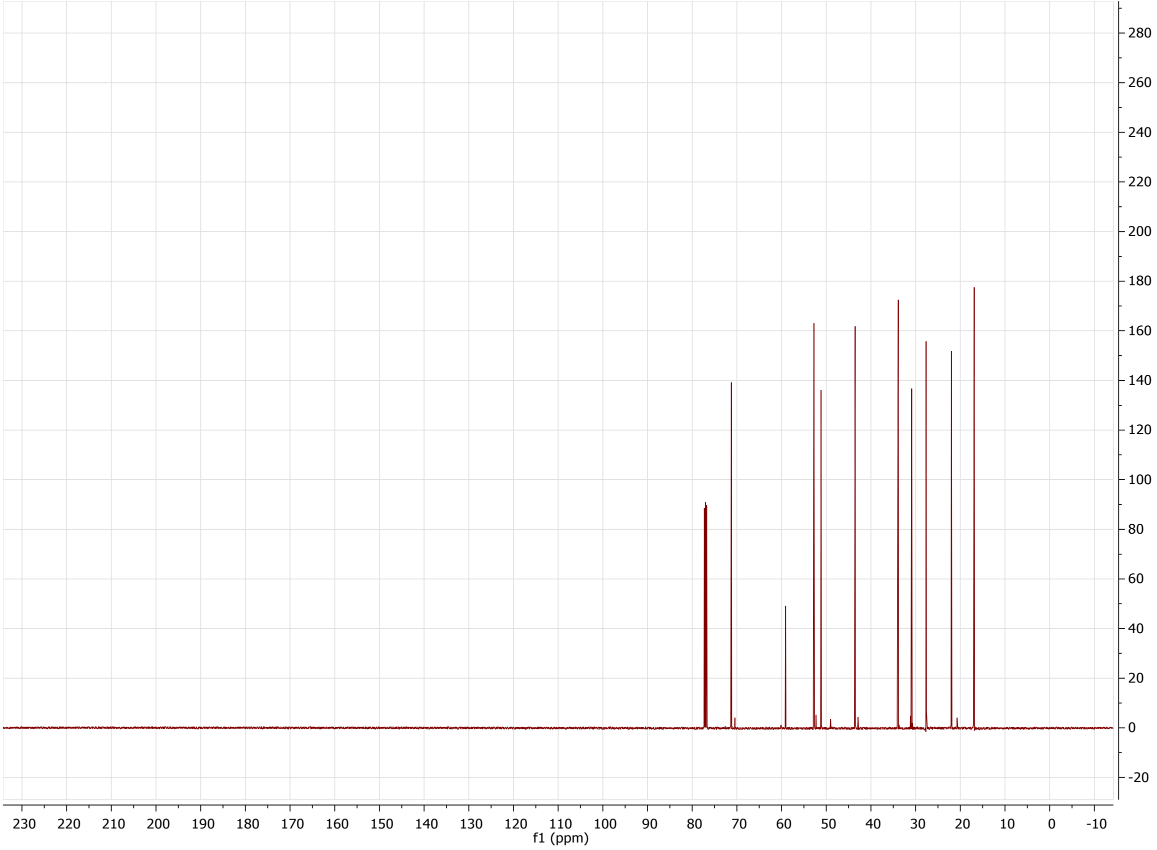
(-)-Isopulegol epoxides (16a/b)



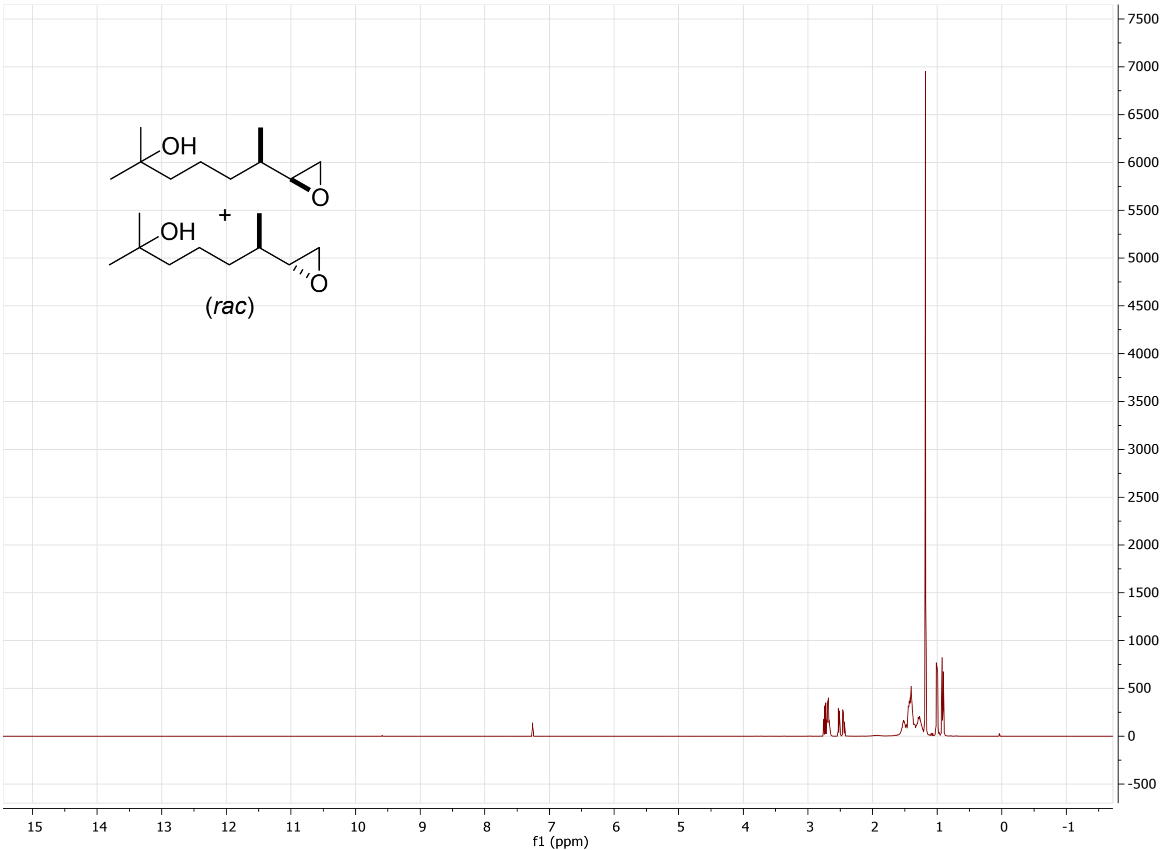
Major Diastereomer (~96% purity containing 4% Minor diastereomer).

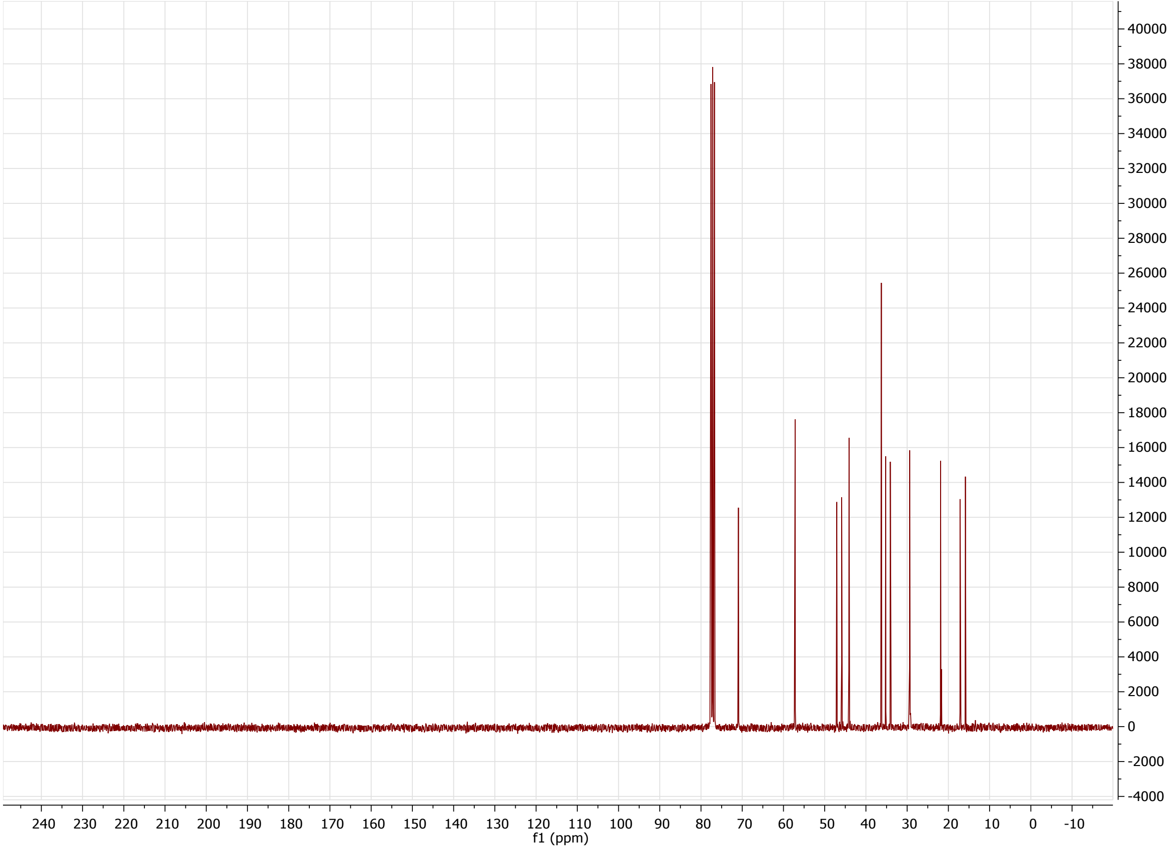



Minor Diastereomer
OH
H
O
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

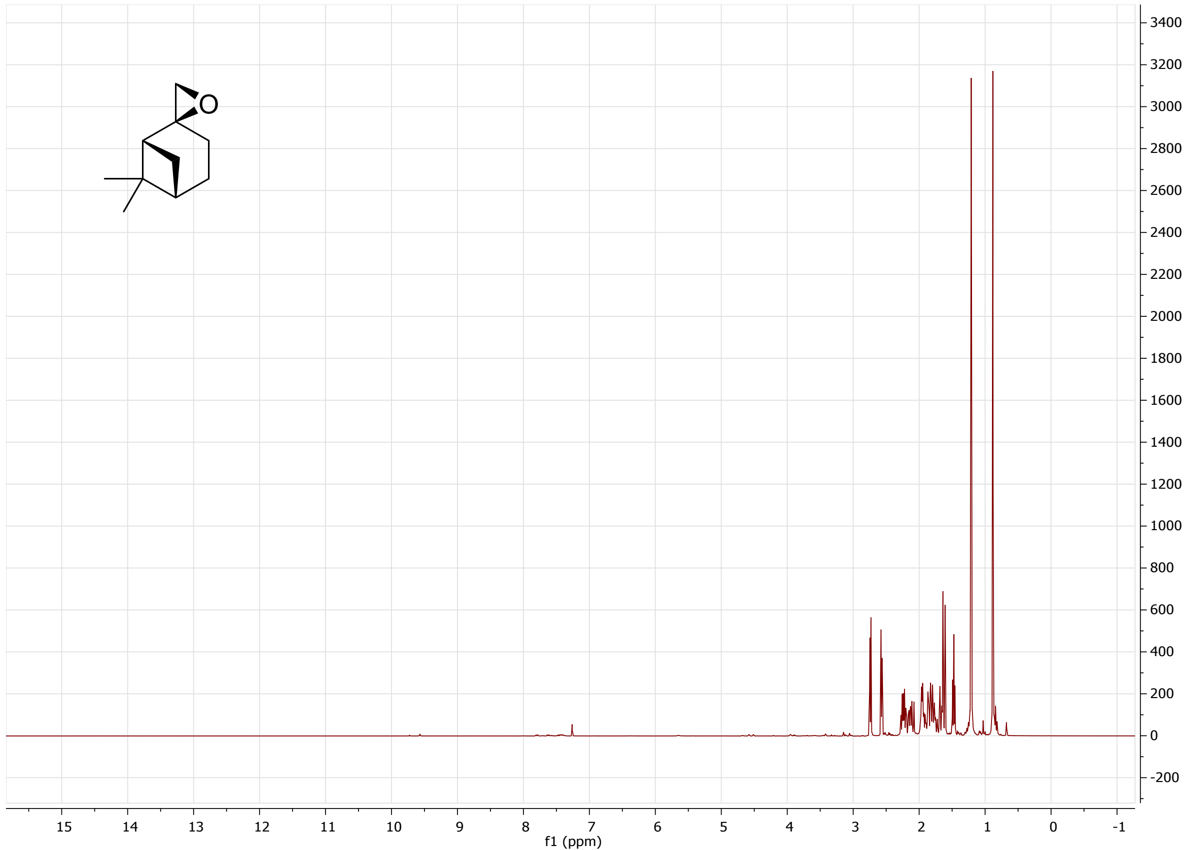

280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

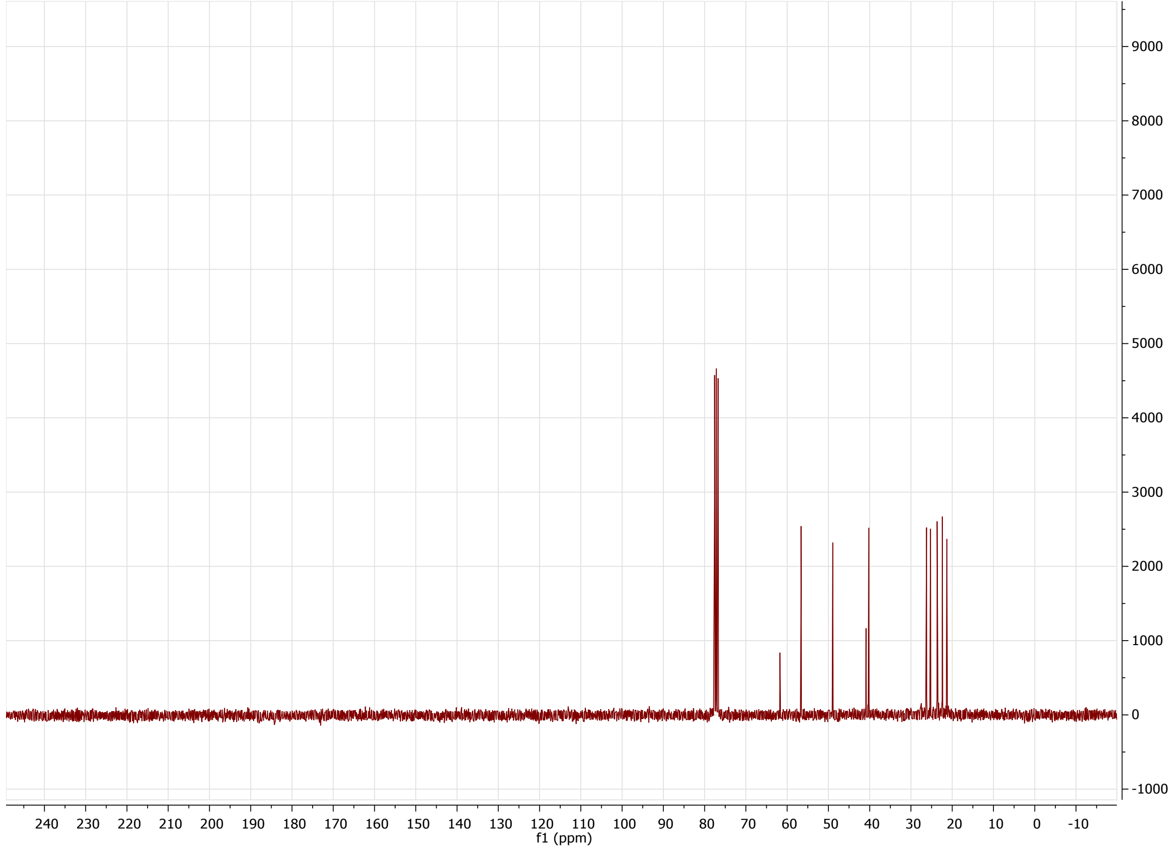
(*rac*)-Dihydromyrcenol epoxides (17a/b)



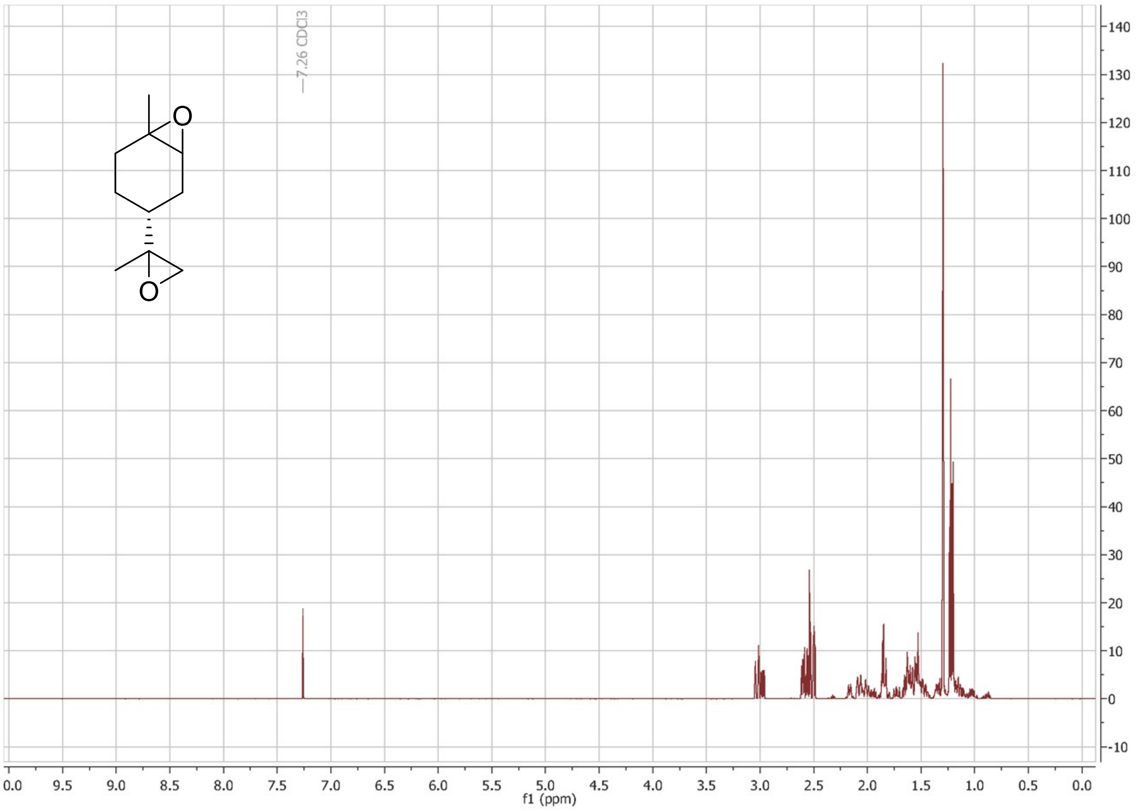


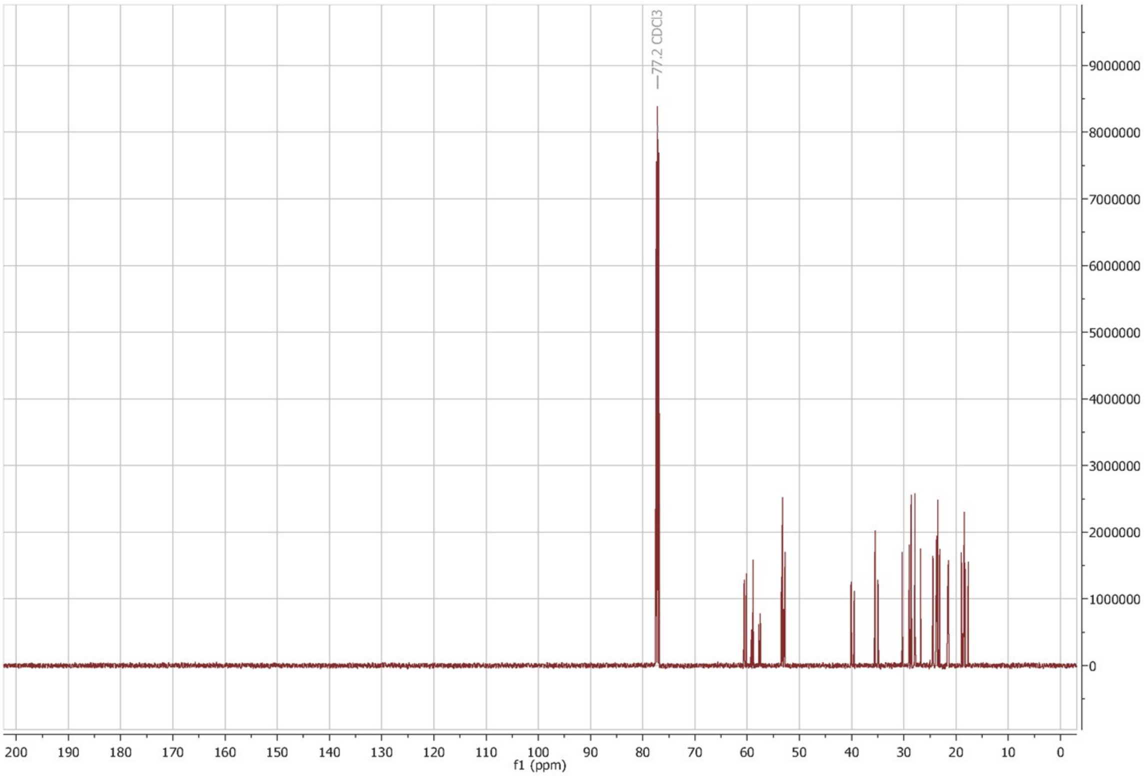
β-Pinene oxide (18)



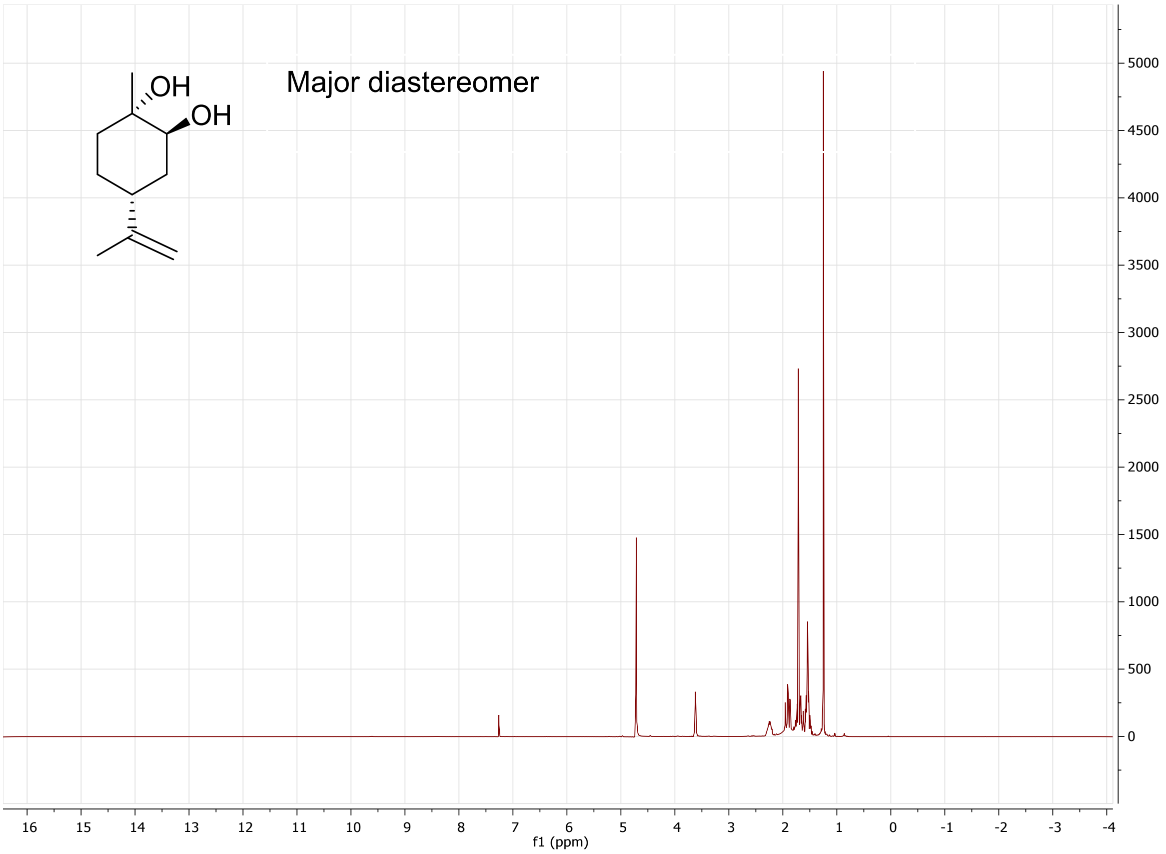


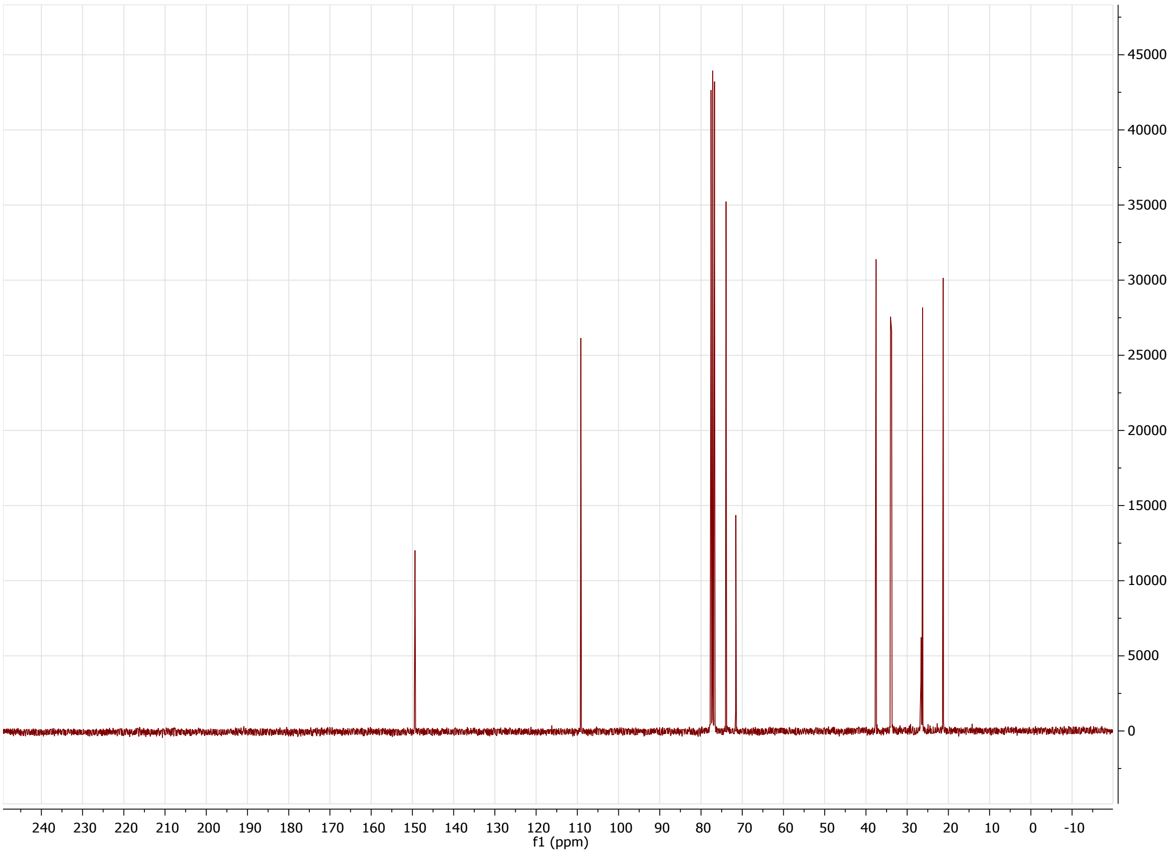
Limonene bis-epoxide (19)

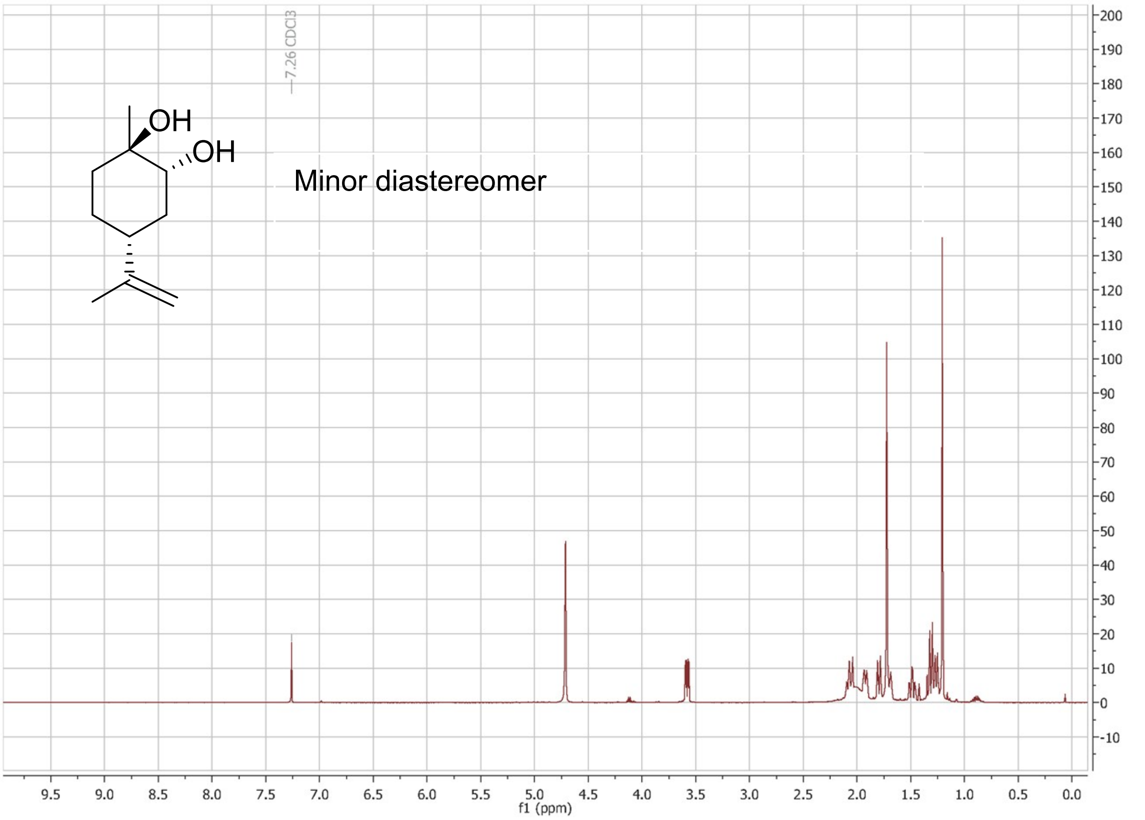


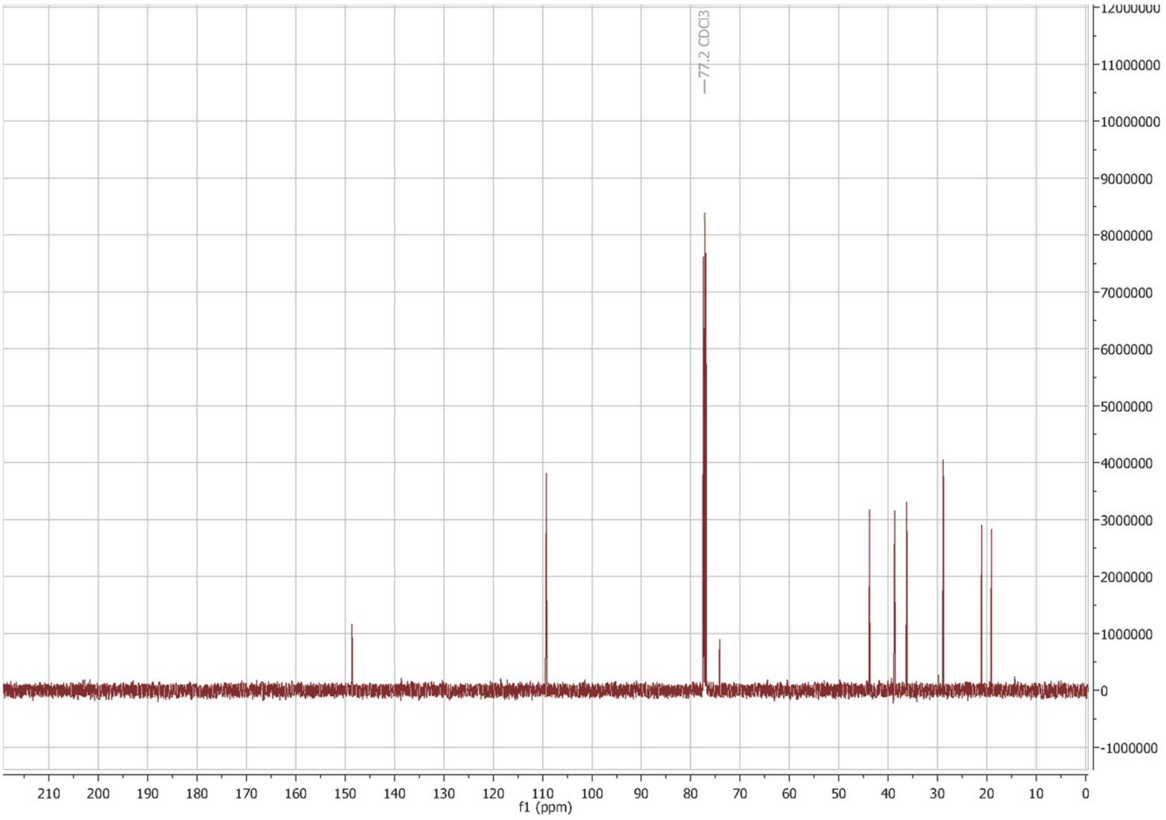


Limonene 1,2-*anti*-diols (20a/b)

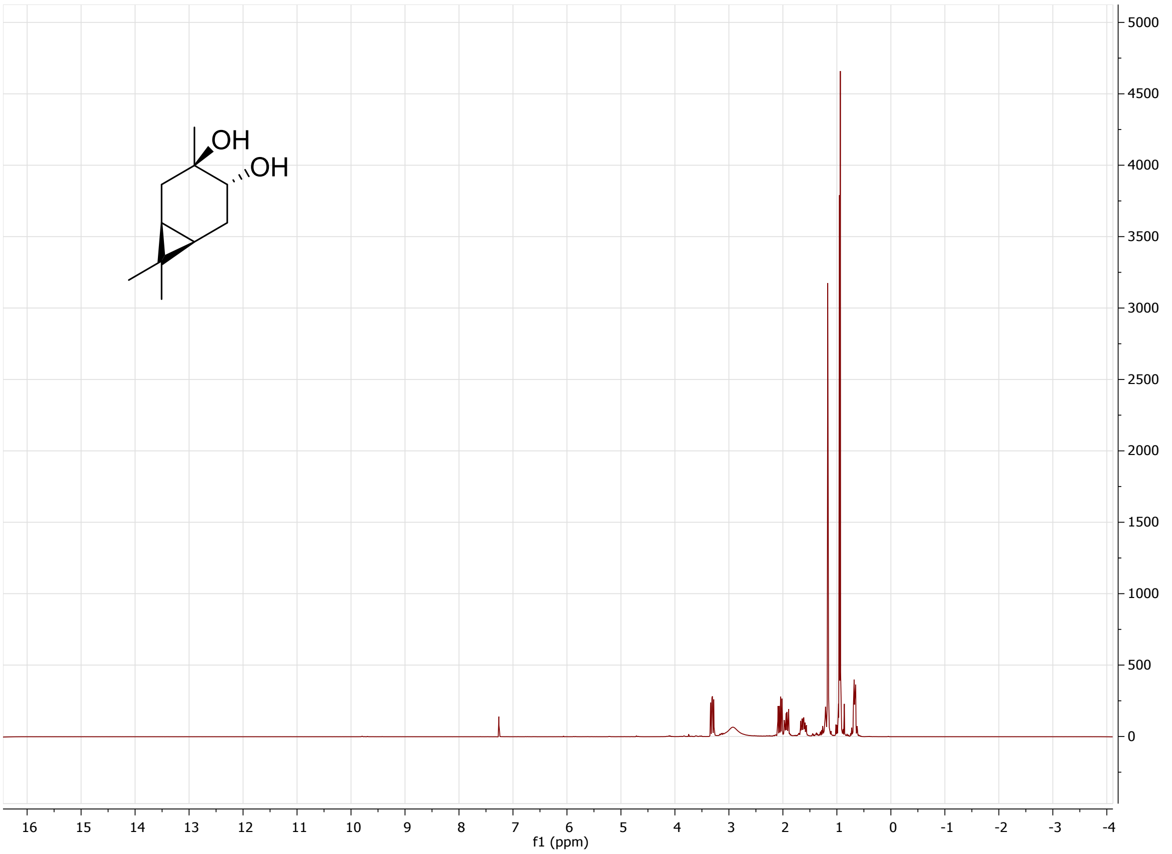


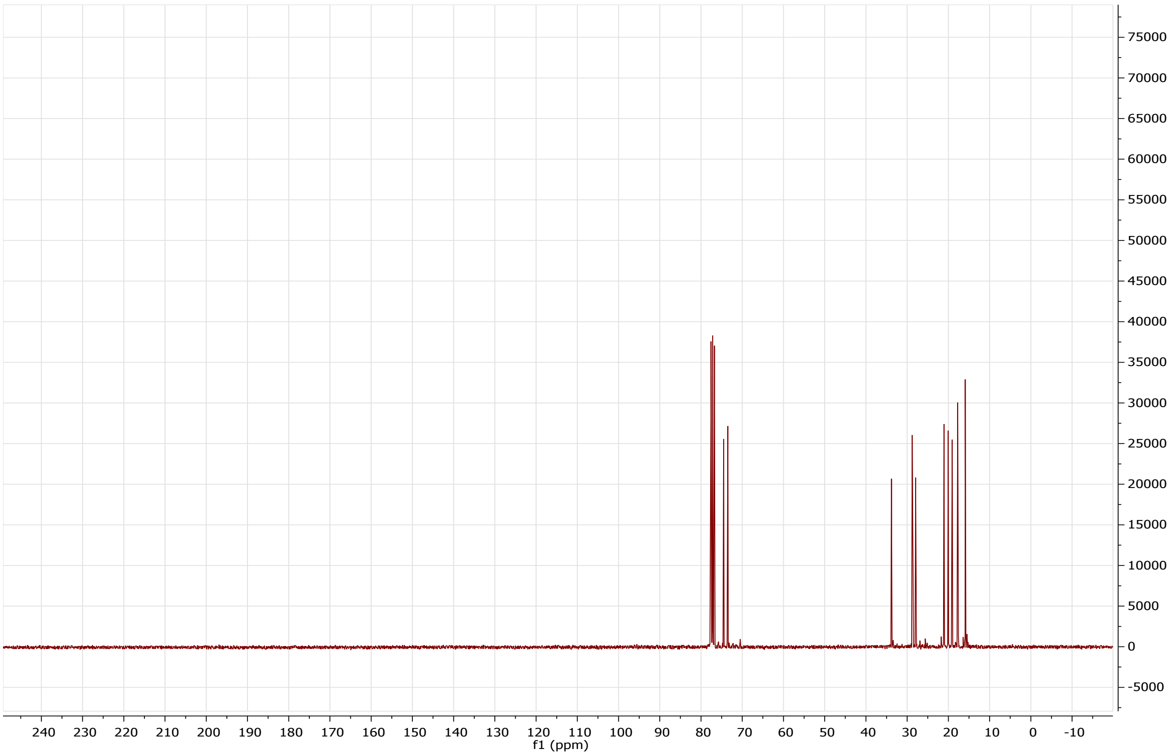



7.26 CDCl3
OH
OH
Minor diastereomer
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

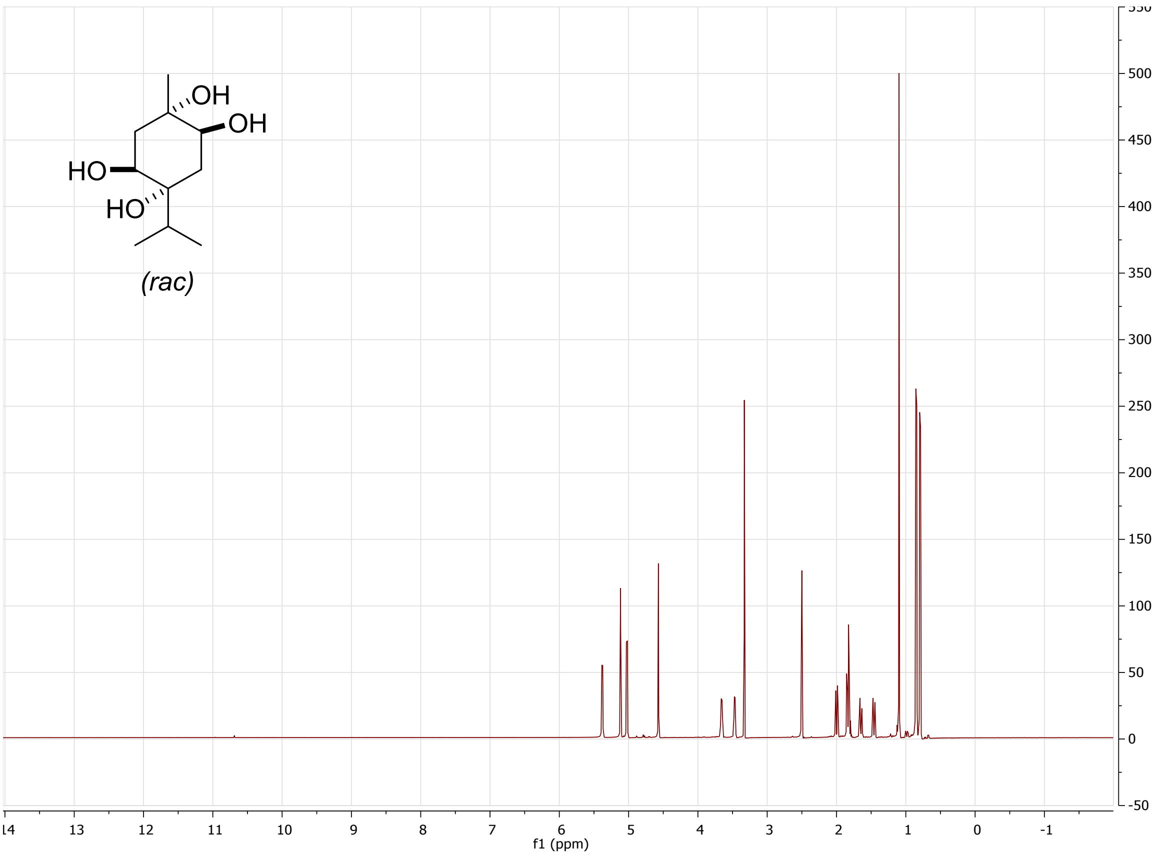

77.2 CDCl3
12000000
11000000
10000000
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
-1000000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

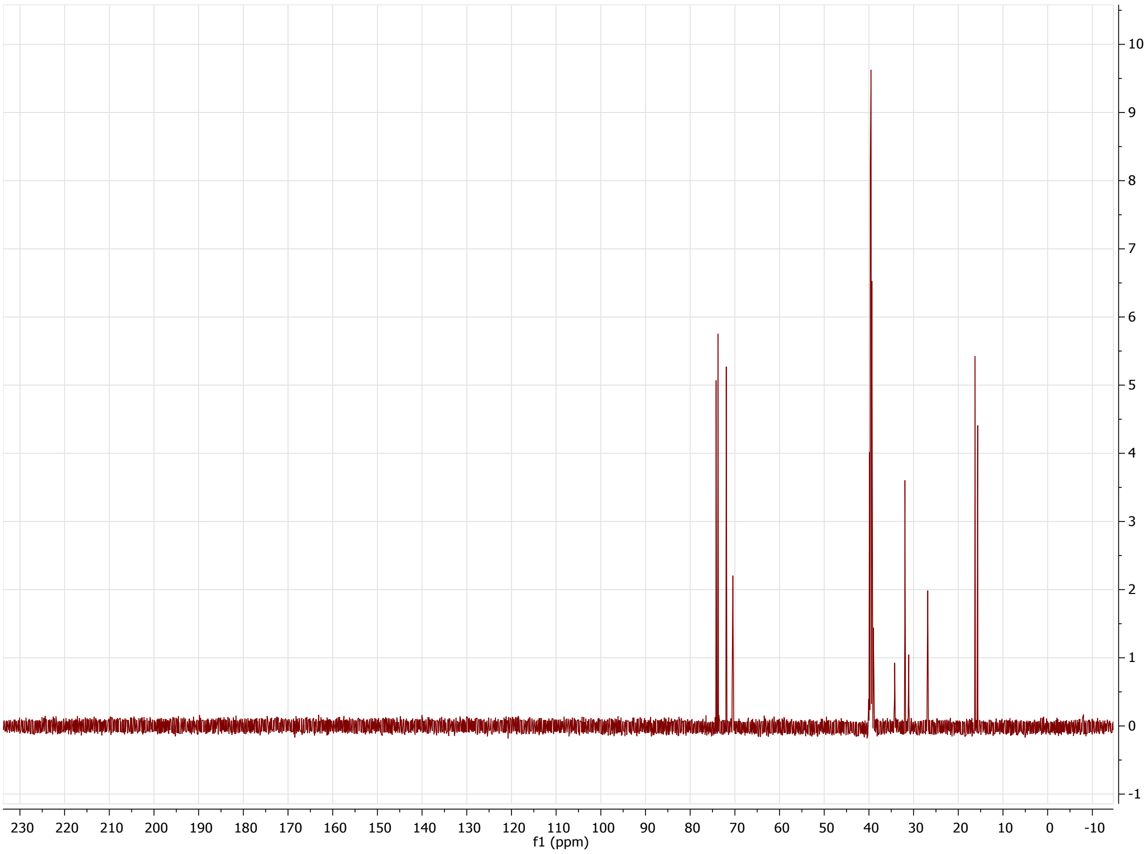
Carene-3,4-*anti*-diol (21)



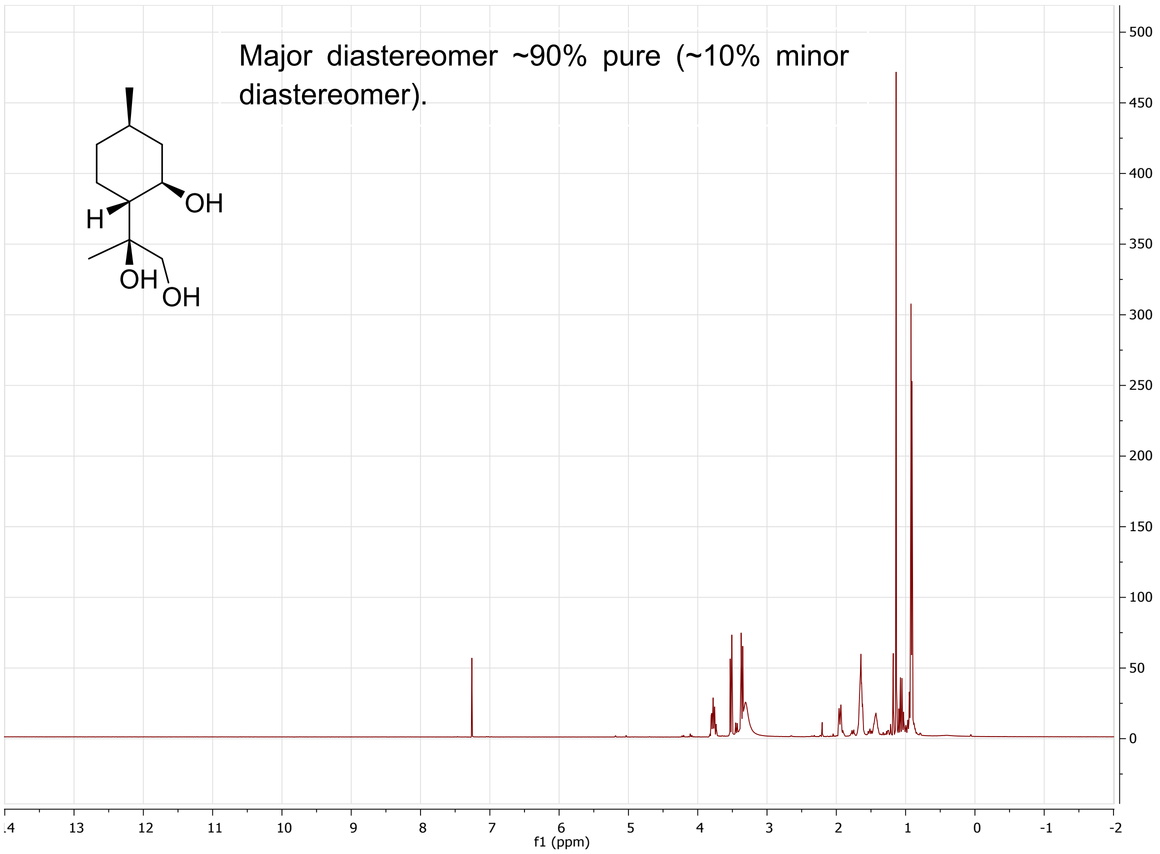


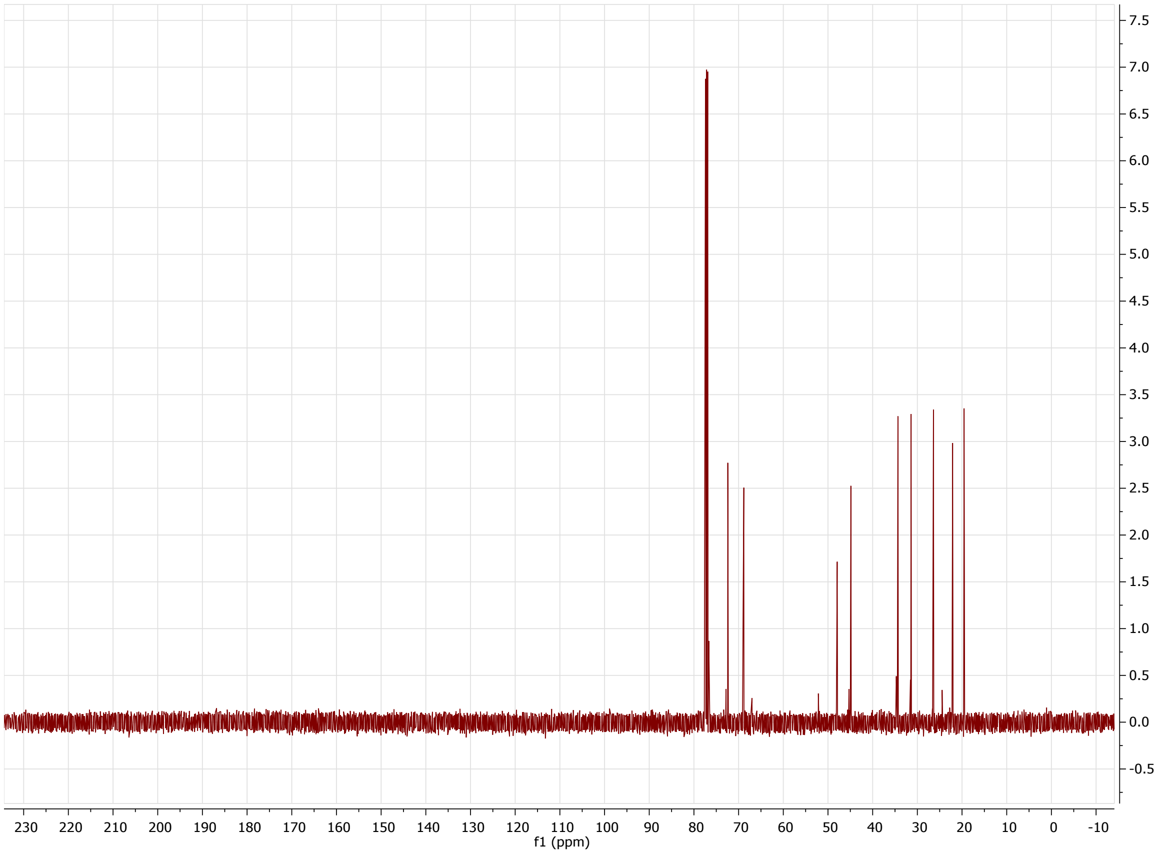
(*rac*)-γ-Terpinene-*anti*-tetrol 22

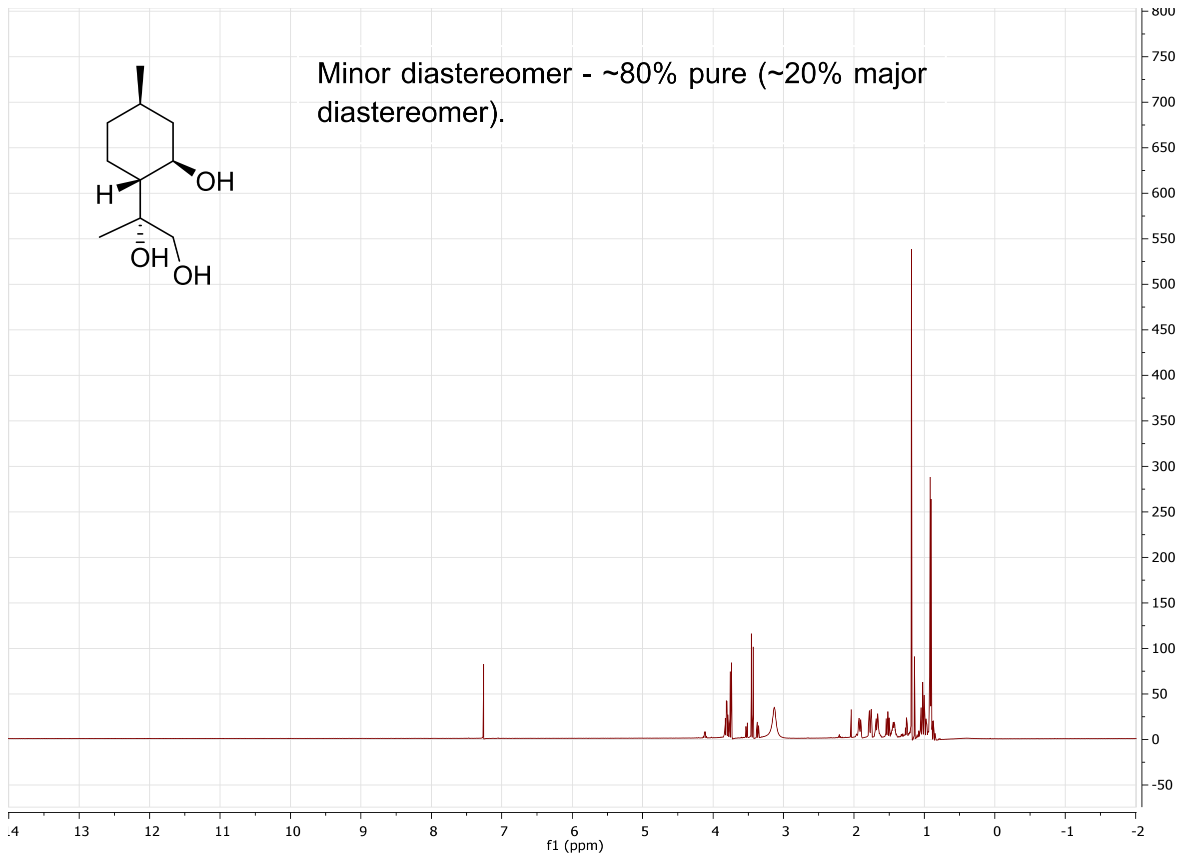




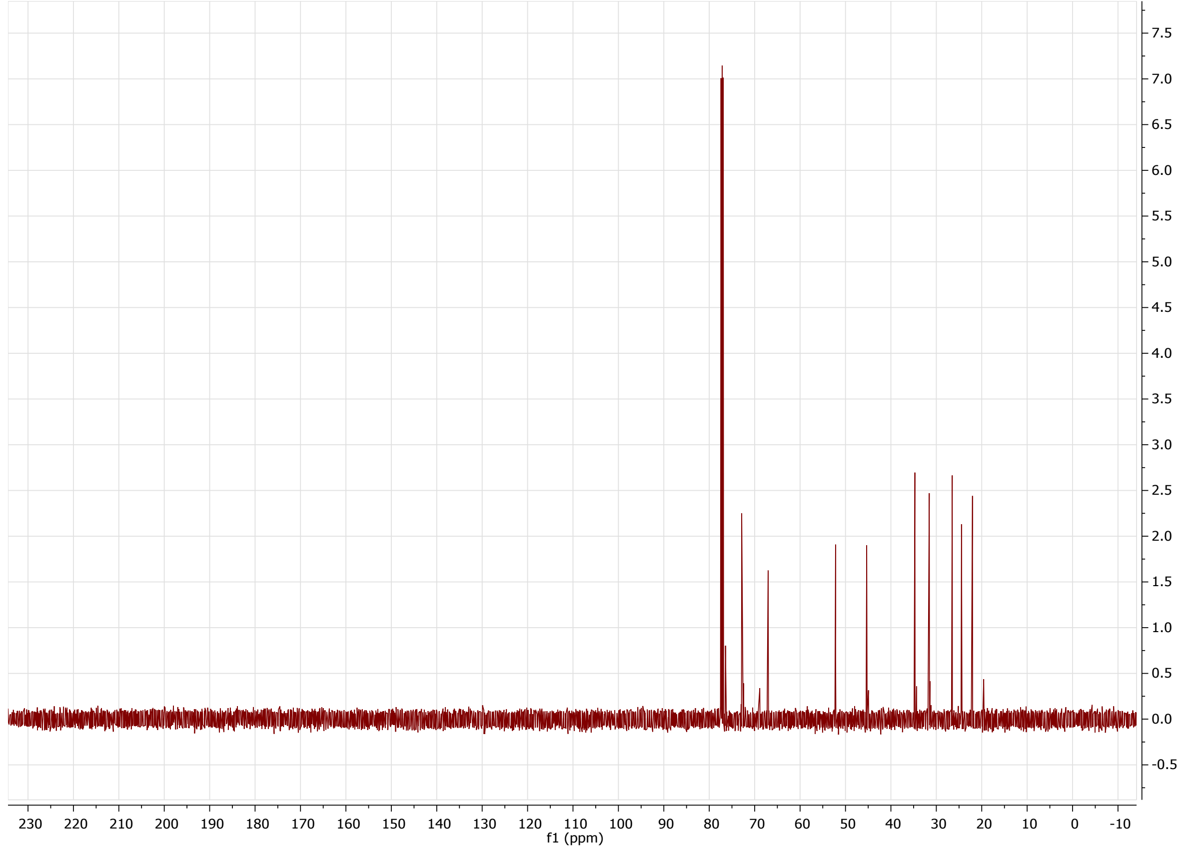
(-)-Isopulegol-8,9-*anti*-diols (23a/b)


Major diastereomer ~90% pure (~10% minor diastereomer).

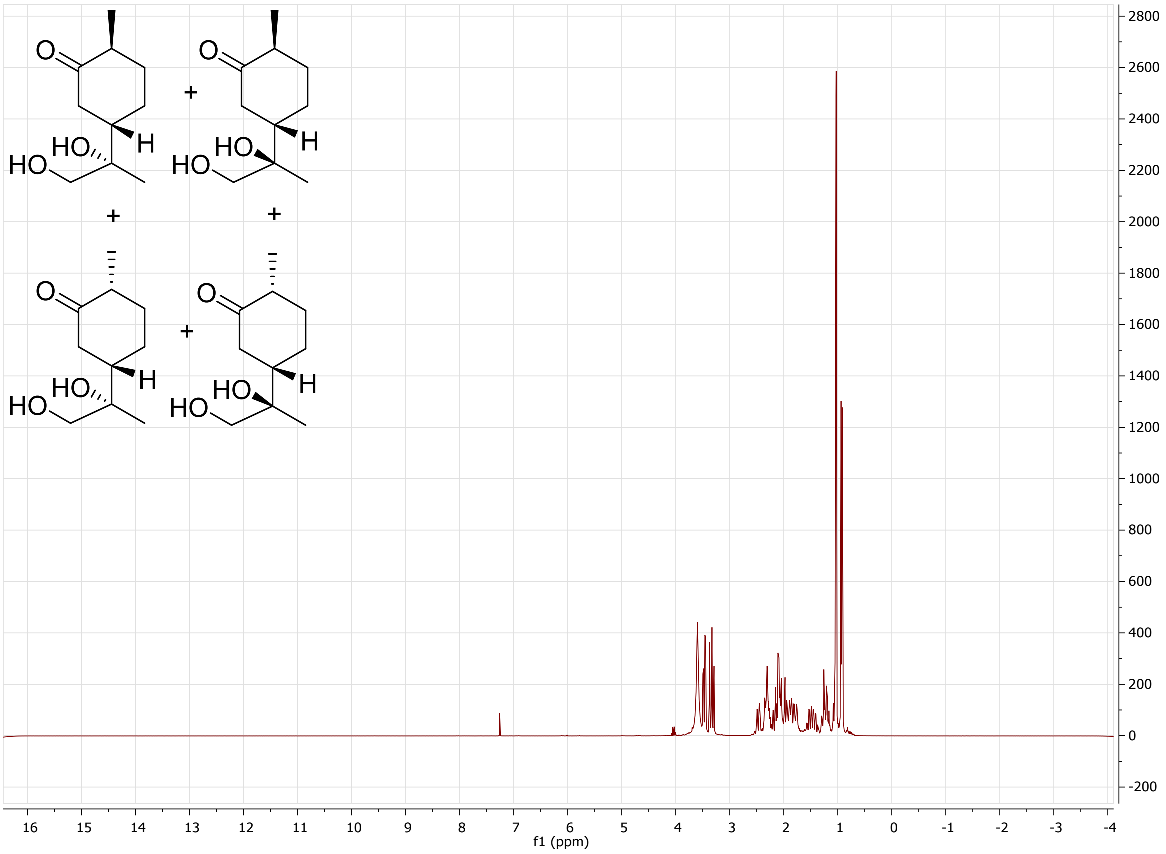


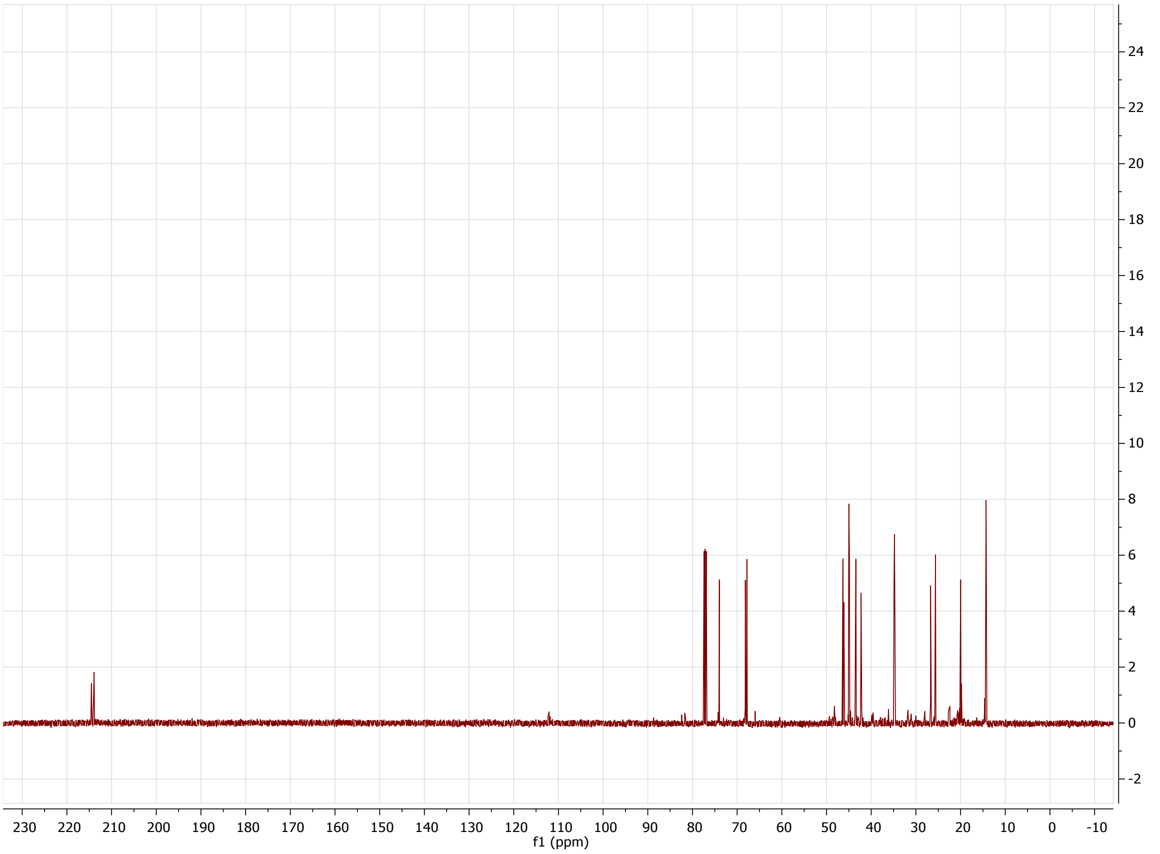


Minor diastereomer - ~80% pure (~20% major diastereomer).

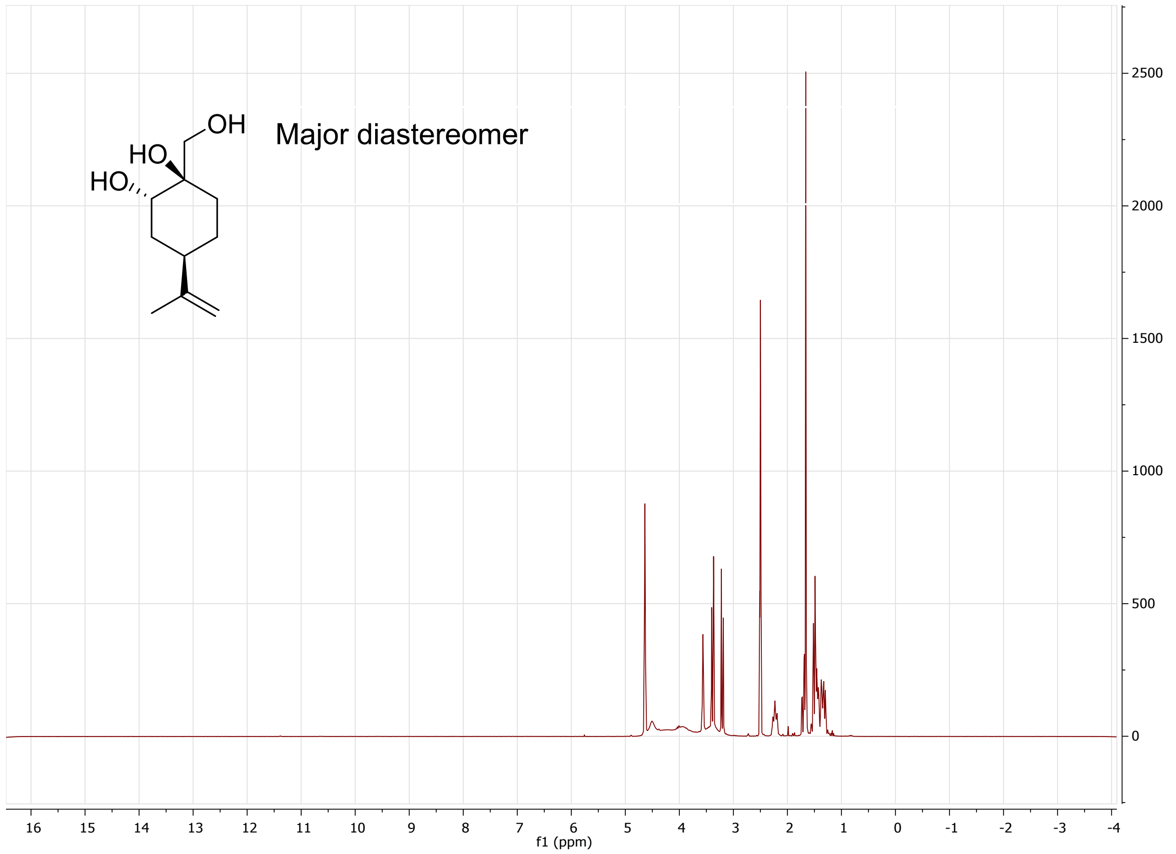


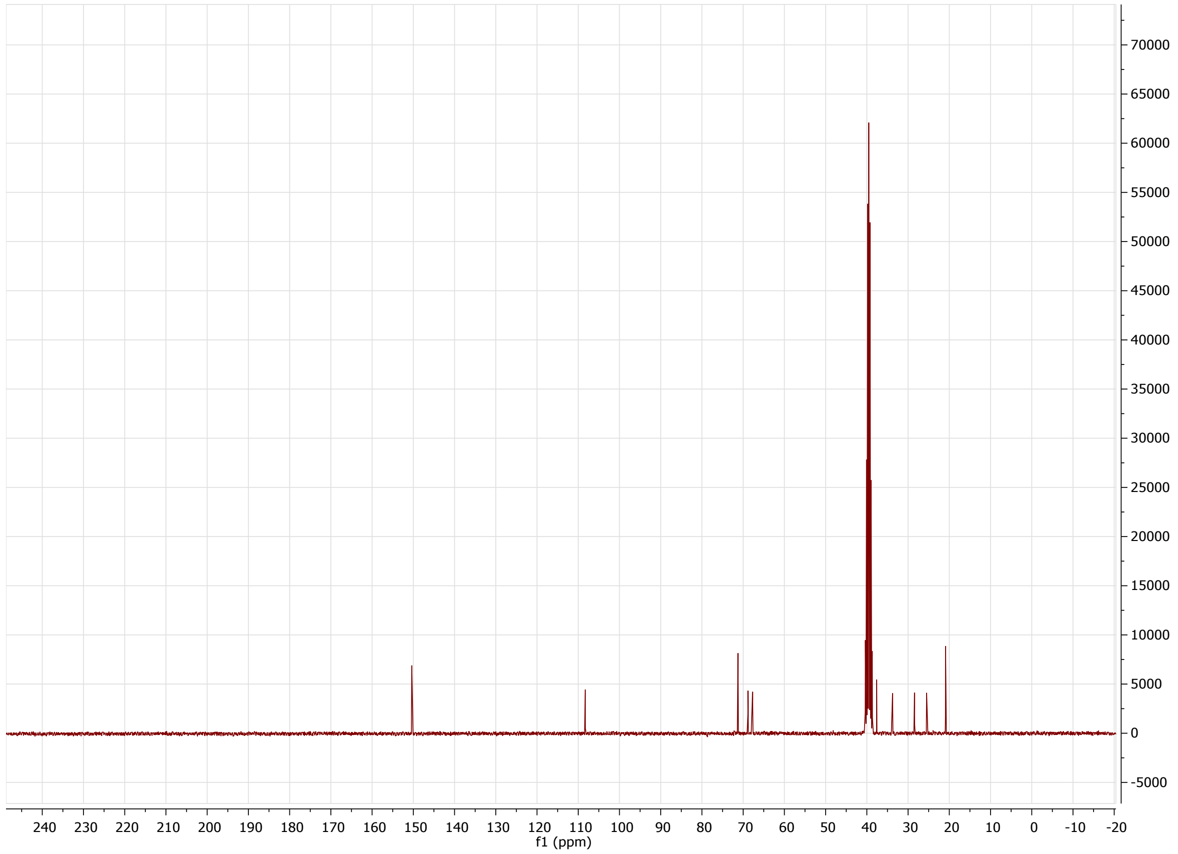
Dihydrocarvone-8,9-*anti*-diols (24a-d)



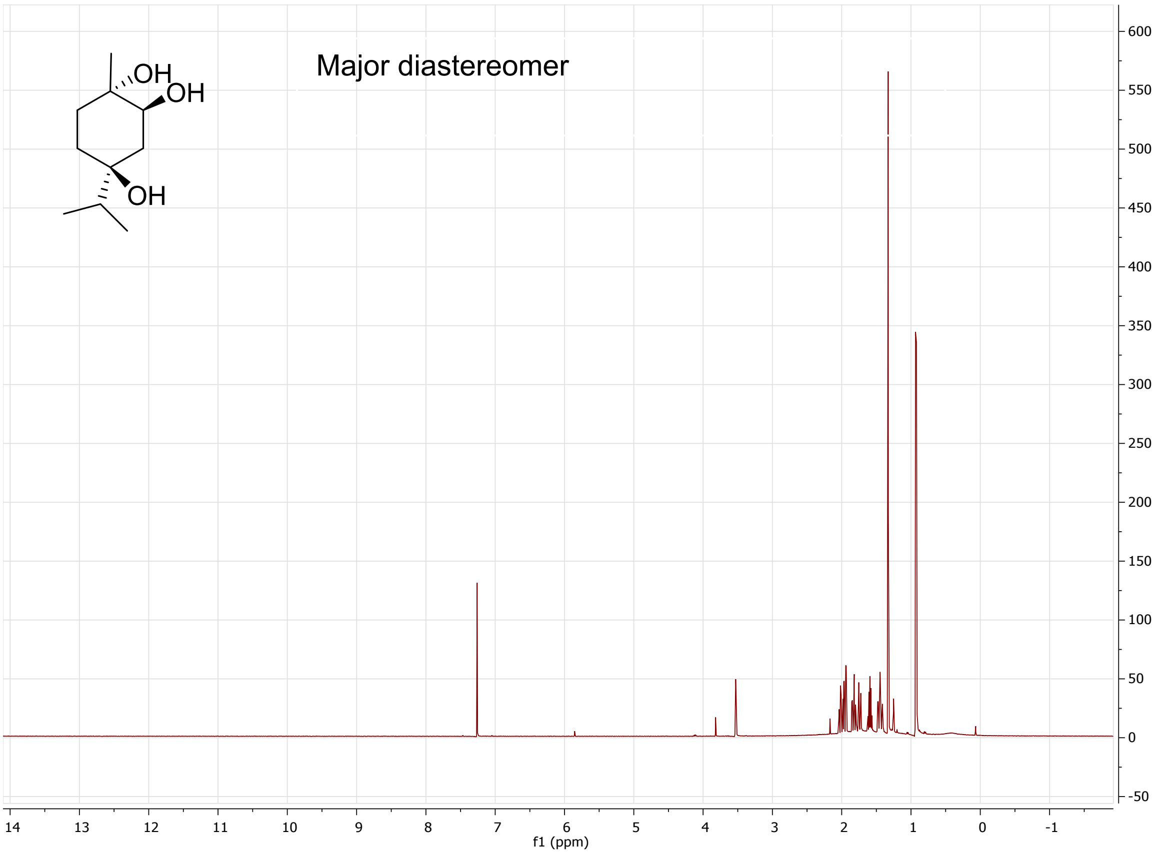


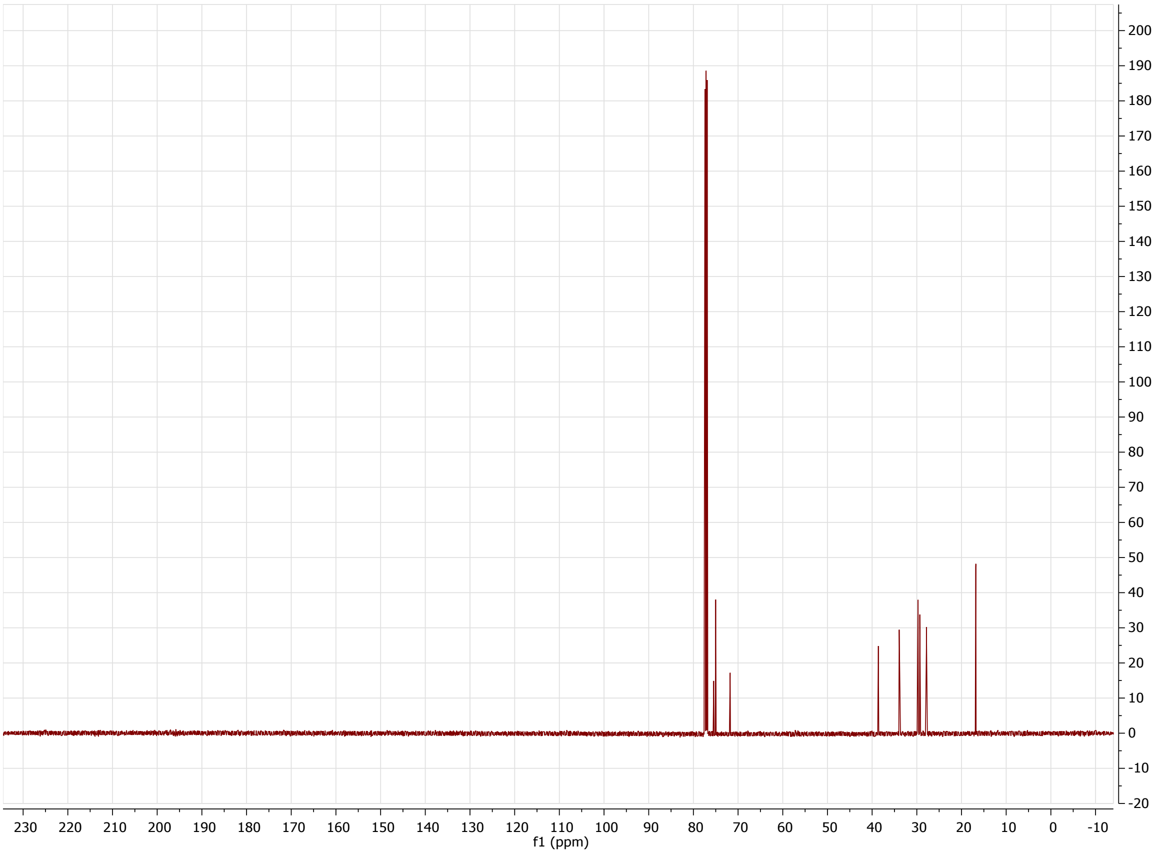
Perillyl alcohol 1,2-*anti*-diols (25a/b)



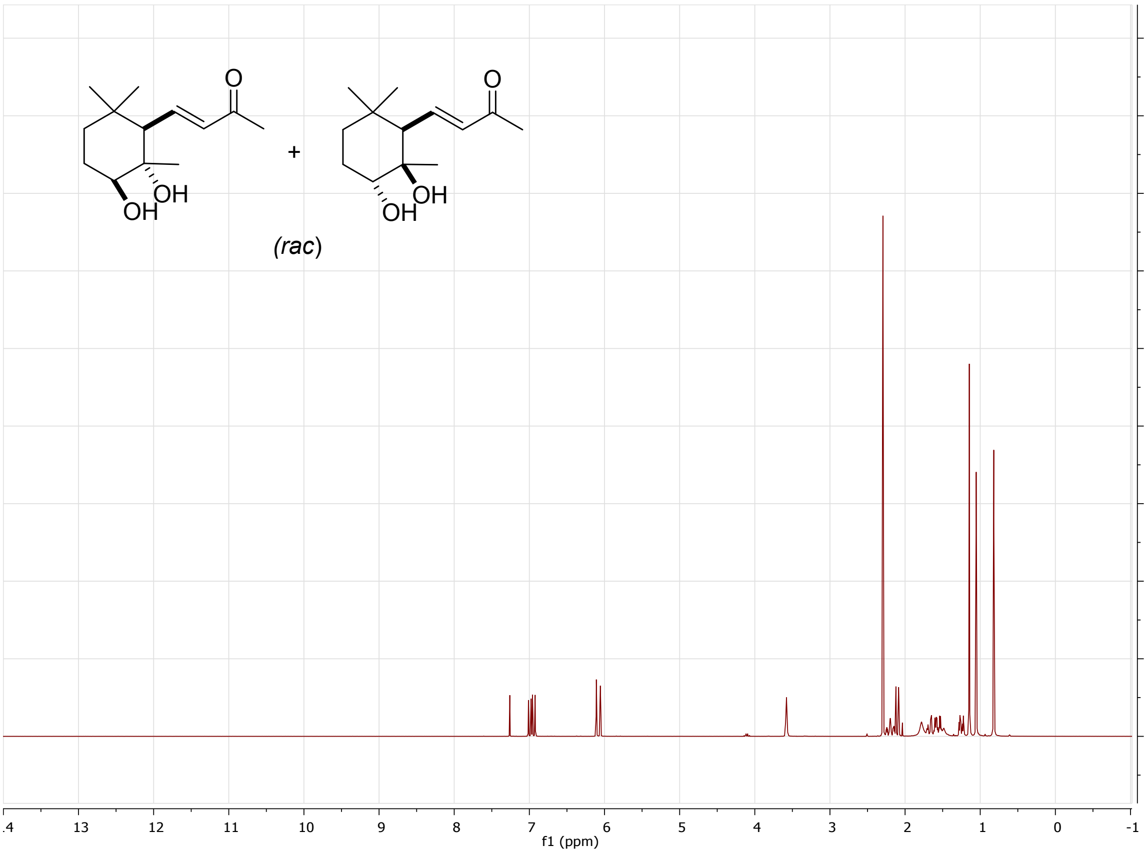


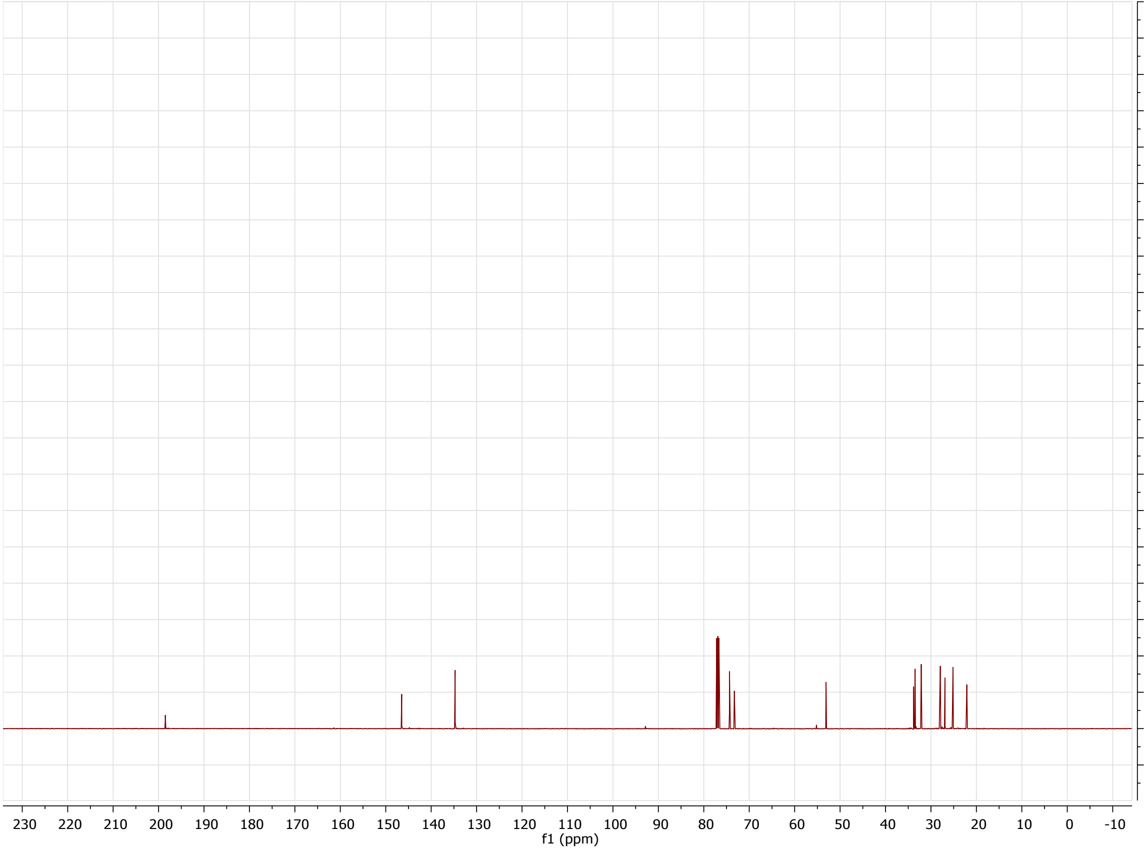
4-Carvomenthenol-*anti*-diols (26a/b)



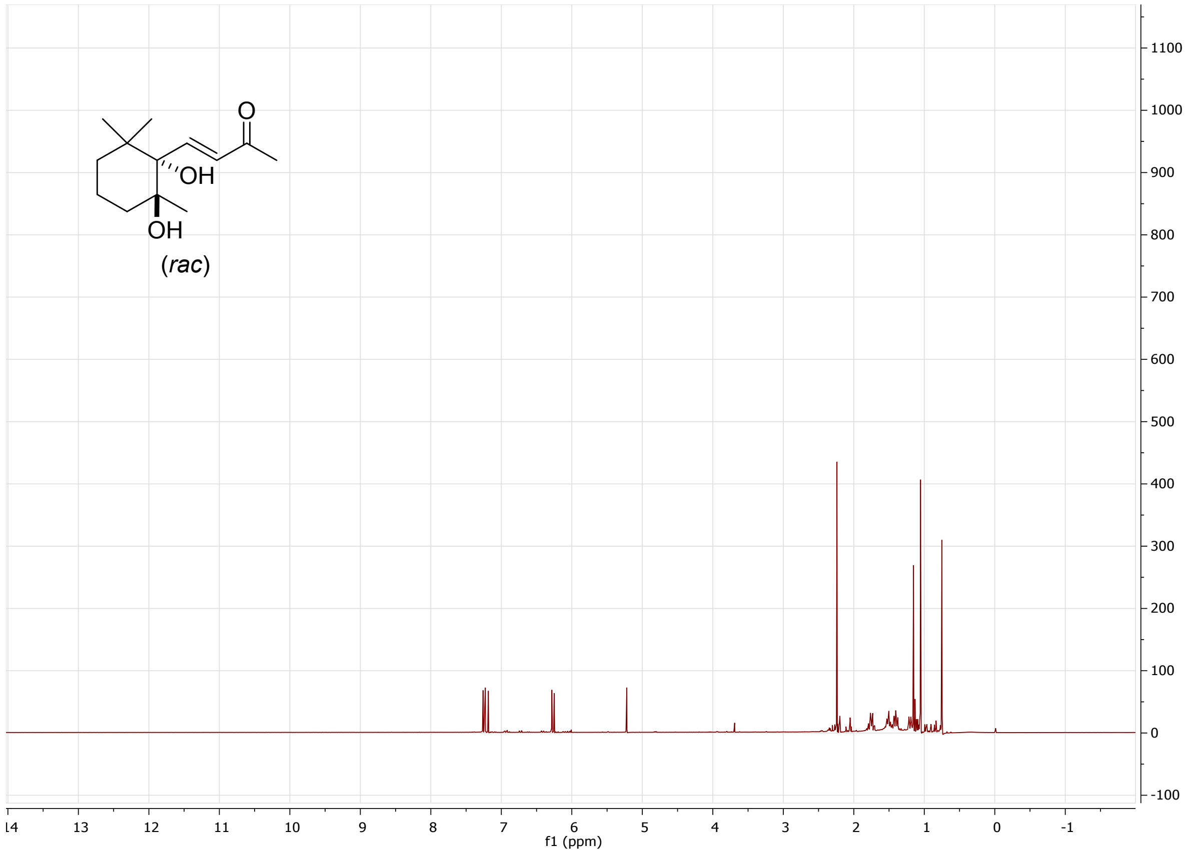


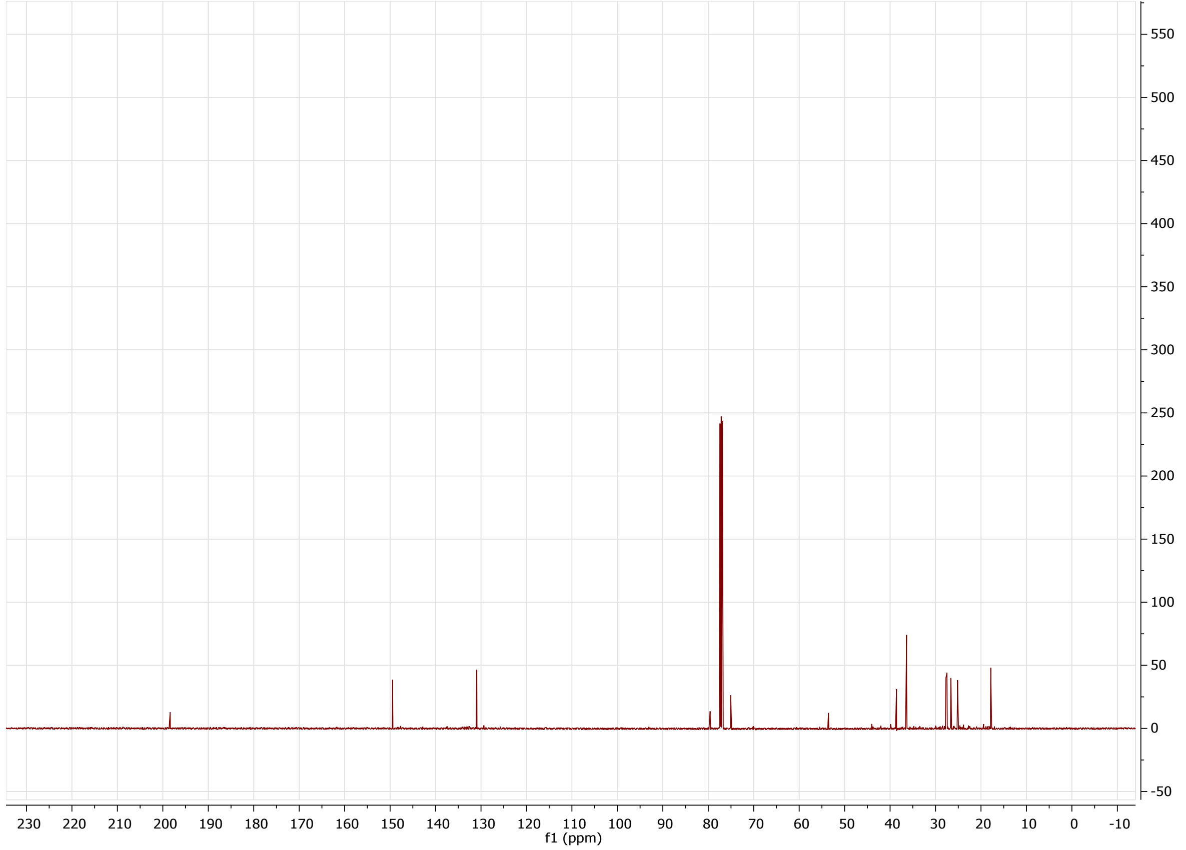
(*rac*)-α-Ionone-*anti*-diols (27a/b)





(*rac*)-β-Ionone-*anti*-diols (28)


O
OH
OH
(rac)
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)


550
500
450
400
350
300
250
200
150
100
50
0
-50
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

4 References

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