

**Synthesis and Coherent Vibrational Laser Spectroscopy of Putative Molecular Constituents in
Isoprene-Derived Secondary Organic Aerosol Particles**

Carlena J. Ebben,[%] Benjamin F. Strick,[%] Mary Alice Upshur, Hilary M. Chase, Jennifer L. Achtyl,
Regan J. Thomson,^{*} and Franz M. Geiger^{*}

¹Department of Chemistry, Northwestern University, Evanston, IL 60208, USA

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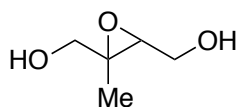
1. General Methods. All reactions were carried out under a nitrogen atmosphere in flame-dried glassware with magnetic stirring unless otherwise stated. THF, Et₂O and CH₂Cl₂ were purified by passage through a bed of activated alumina.¹ Reagents were purified prior to use unless otherwise stated following the guidelines of Armarego and Chai.² Purification of reaction products was carried out by flash chromatography using EM Reagent silica gel 60 (230-400 mesh). Analytical thin layer chromatography was performed on EM Reagent 0.25 mm silica gel 60-F plates. Visualization was accomplished with UV light and anisaldehyde stain, ceric ammonium molybdate stain, or potassium permanganate stain followed by heating. Film infrared spectra were recorded using a Bruker Tensor ATR. ¹H-NMR spectra were recorded on a Bruker Avance III 500 (500 MHz) or Varian Inova 400 (400 MHz) spectrometer and are reported in ppm using solvent as an internal standard (MeOD at 4.78 ppm). Data are reported as (app = apparent, obs = obscured, s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, h = hextet, sep = septet, o = octet, m = multiplet, b = broad; coupling constant(s) in Hz; integration. Proton-decoupled ¹³C-NMR spectra were recorded on a Bruker Avance III 500 (500 MHz) spectrometer and are reported in ppm using solvent as an internal standard (MeOD at 49.10 ppm). Mass spectra data were obtained on an Agilent 6210 Time-of-Flight LC/MS and a Thermo Finnegan Mat 900 XL High Resolution Magnetic Sector.

1. Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometal.* **1996**, *15*, 1518–1520.
2. Armarego W. L. F.; Chai, C. L. L. *Purification of Laboratory Chemicals*; 5th Ed., Butterworth-Heinemann, 2003.

2. Experimental Procedures

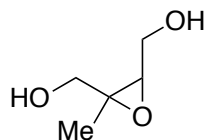
Synthesis of IEPOX molecules:

Syntheses of IEPOX compounds were carried out according to procedures reported by Surratt and coworkers.³ Any procedural modifications are reported below.



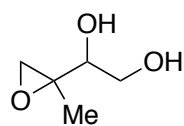
(trans-2-methyloxirane-2,3-diyl)dimethanol (1): IR (film) 3670, 2931, 1452, 1386, 1030, 860 cm^{-1} ; ^1H NMR (500 MHz, MeOD) 3.63 (dd, 1H, $J = 12.2, 4.6$ Hz); 3.50 (dd, 1H, $J = 12.2, 6.5$ Hz); 3.44 (d, 1H, $J = 12.2$ Hz); 3.37 (d, 1H, $J = 12.2$ Hz); 2.96 (dd, 1H, $J = 6.5, 4.6$ Hz); 1.17 (s, 3H); ^{13}C NMR (125 MHz, MeOD): δ 67.1, 62.1, 61.6, 14.4; HRMS (EI): Exact mass calcd for $\text{C}_5\text{H}_{10}\text{O}_3$ $[\text{M}-2\text{H}_2\text{O}]^+$, 82.0419. Found 82.0414.

Found 82.0414.



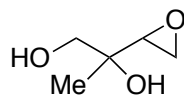
(cis-2-methyloxirane-2,3-diyl)dimethanol (2): Removal of small impurity as a result of over reduction of 3-methyl furan-2(5H)-one can be accomplished by flash column chromatography on silver impregnated silica gel with EtOAc as and eluent. IR (film) 3369, 2975, 2934, 2884, 1446, 1023, 866 cm^{-1} ; ^1H NMR (500 MHz, MeOD) 3.65 (dd, 1H, $J = 12.3, 4.3$ Hz); 3.50 (dd, 1H, $J = 12.3, 6.7$ Hz); 3.47 (s, 2H);

2.85 (dd, 1H, $J = 6.7, 4.3$ Hz); 1.25 (s, 3H); ^{13}C NMR (125 MHz, MeOD): δ 65.4, 64.5, 62.2, 61.3, 20.3 HRMS (ESI): Exact mass calcd for $\text{C}_5\text{H}_{10}\text{O}_3$ $[\text{M}-\text{H}]^-$, 117.0557. Found 117.0553.



1-(2-methyloxiran-2-yl)ethane-1,2-diol (3): IR (film) 3386, 2972, 2935, 2881, 1389, 1072, 1027 cm^{-1} ; ^1H NMR (500 MHz, MeOD) all signals reported 3.56 (dd, 1H, $J = 11.4, 3.8$ Hz); 3.50–3.40 (m, 3H) 3.33 (dd, 1H, $J = 6.7, 3.8$ Hz); 3.24 (dd, 1H, $J = 6.8, 5.8$ Hz); 2.67 (dd, 2H, $J = 18.6, 4.9$ Hz); 2.48 (dd, 2H, $J = 23.9, 4.9$ Hz); 1.19 (s, 3H);

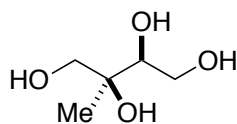
1.18 (s, 3H); ^{13}C NMR (125 MHz, MeOD): δ all signals reported 77.1, 75.5, 64.4(2), 63.3(7), 59.1, 58.3, 52.8, 52.5, 17.8, 16.6; HRMS (ESI): Exact mass calcd for $\text{C}_5\text{H}_{10}\text{O}_3$ $[\text{M}+\text{Na}]^+$, 141.0509. Found 141.0511.



2-(oxiran-2-yl)propane-1,2-diol (4): IR (film) 3393, 2924, 2853, 1045, 907, 866 cm^{-1} ; ^1H NMR (500 MHz, MeOD) all signals reported 3.40–3.31 (m, 4H); 2.93 (dd, 1H, $J = 4.1, 2.8$ Hz); 2.88 (dd, 1H, $J = 4.1, 2.8$ Hz); 2.71 (dd, 1H, $J = 5.3, 2.8$ Hz); 2.61 (dd, 1H, $J = 5.3, 2.8$ Hz); 2.58 (dd, 1H, $J = 3.8, 1.5$ Hz); 2.57 (dd, 1H, $J = 3.8, 1.6$ Hz);

1.05 (s, 3H); 1.03 (s, 3H); ^{13}C NMR (125 MHz, MeOD): δ all signals reported 71.4, 71.3, 68.9, 68.7, 57.0, 56.6, 44.6, 43.8, 21.4, 20.3 HRMS (ESI): Exact mass calcd for $\text{C}_5\text{H}_{10}\text{O}_3$ $[\text{M}+\text{Na}]^+$, 141.0522. Found 141.0528.

Synthesis of 2-methyltetraols:

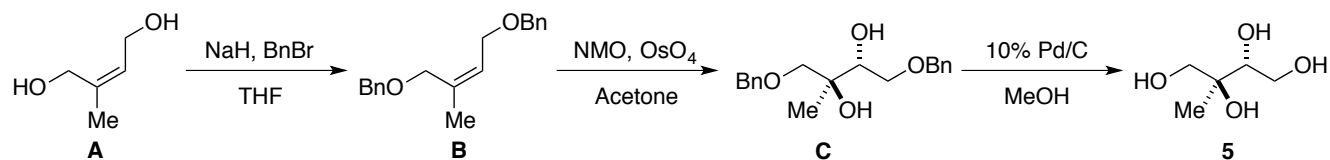


syn-2-methylbutane-1,2,3,4-tetraol (5): To a solution of *syn*-4-(benzyloxy)-3-methylbutane-1,2,3-triol⁴ (400 mg, 1.77 mmol) in MeOH (20 mL) was added 10% Pd/C (373 mg). Reaction was placed under H_2 and stirred for 24 hours. At this

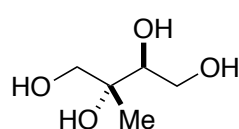
3. Zhang, Z.; Lin, Y. -H.; Zhang, H.; Surratt, J. D.; Ball, M.; Gold, A. *Atmos. Chem. Phys.* **2012**, *12*, 8529–8535.

4. Fontana, A.; Messina, R.; Spinella, A.; Cimino, G. *Tetrahedron. Lett.* **2000**, *41*, 7559–7562.

time, reaction was filtered through a pad of celite and solvent removed, giving the title compound as a viscous yellow oil (216 mg, 1.77 mmol, quant.): IR (film) 3314, 2975, 2937, 2883, 1467, 1042, 1012 cm^{-1} ; ^1H NMR (500 MHz, MeOD) 3.63 (dd, 1H, $J = 10.2, 2.5$ Hz); 3.51–3.54 (m, 2H); 3.41 (d, 1H, $J = 11.1$ Hz); 3.34 (d, 1H, $J = 11.1$ Hz); 1.04 (s, 3H); ^{13}C NMR (125 MHz, MeOD): δ 76.8, 75.0, 68.1, 63.7, 21.4; HRMS (ESI): Exact mass calcd for $\text{C}_5\text{H}_{12}\text{O}_4$ $[\text{M}+\text{Na}]^+$, 159.0628. Found 159.0631.

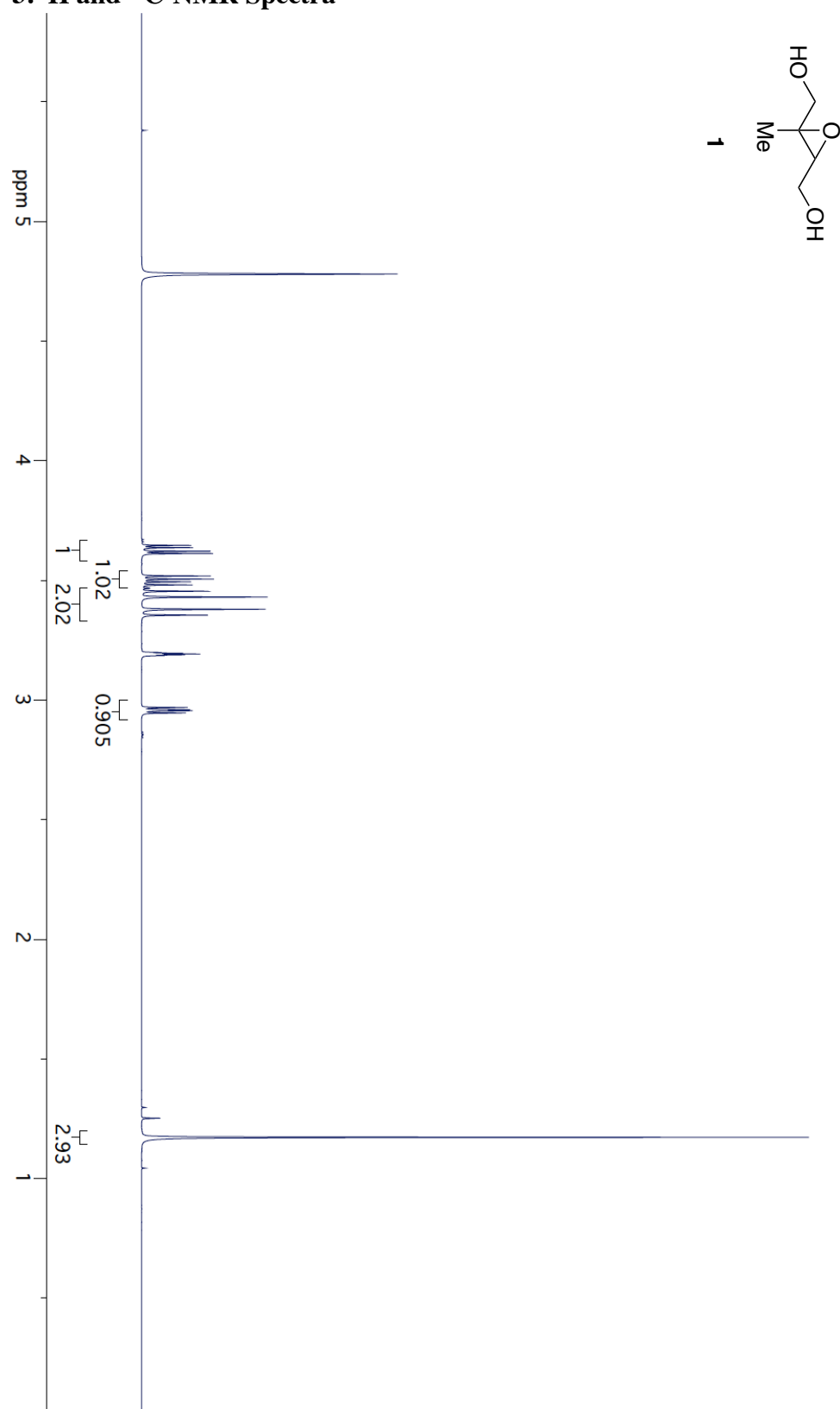


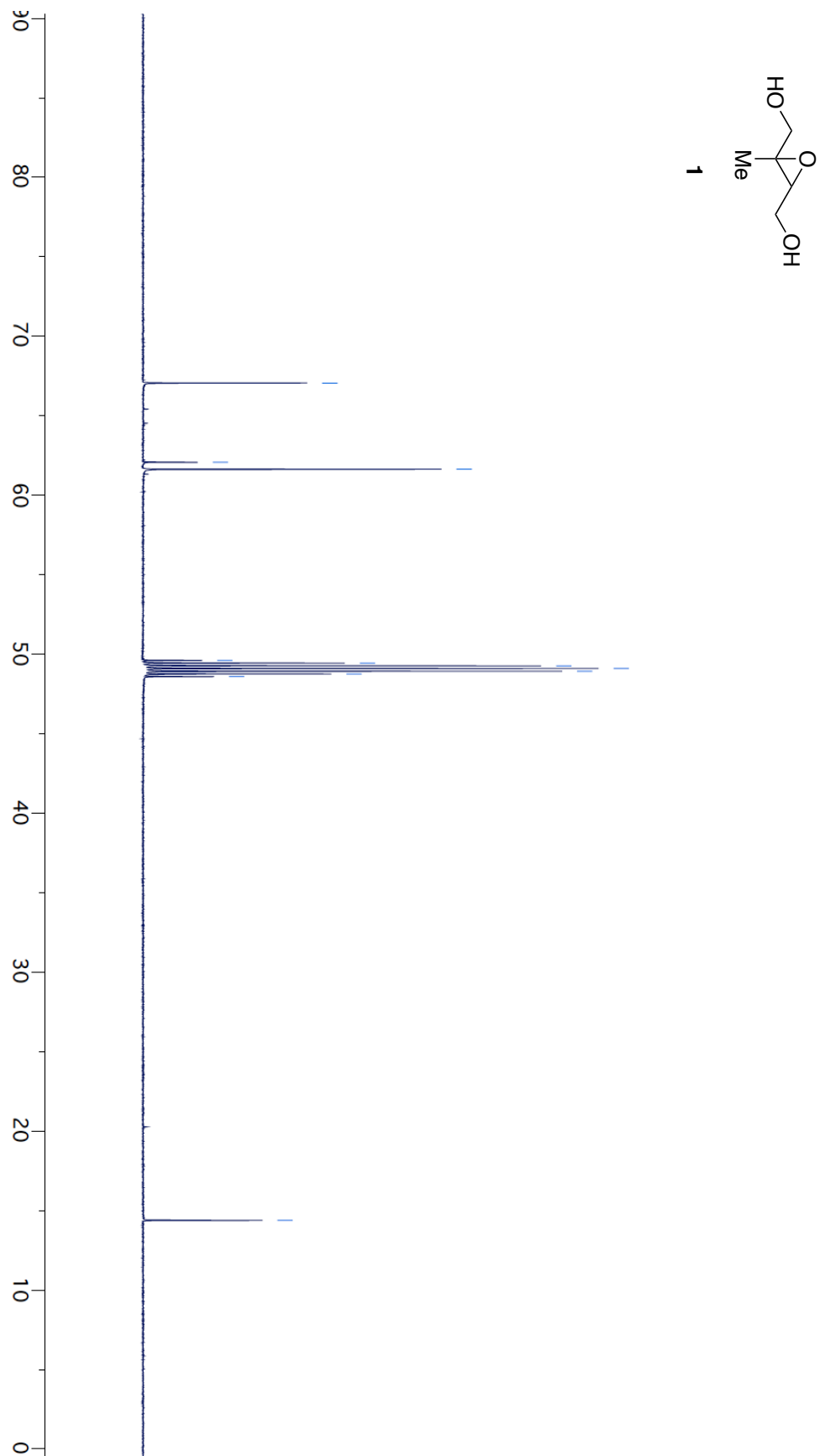
Scheme S1: Outline of *anti*-2-methylbutane-1,2,3,4-tetraol synthesis starting from the corresponding 1,4-diol.

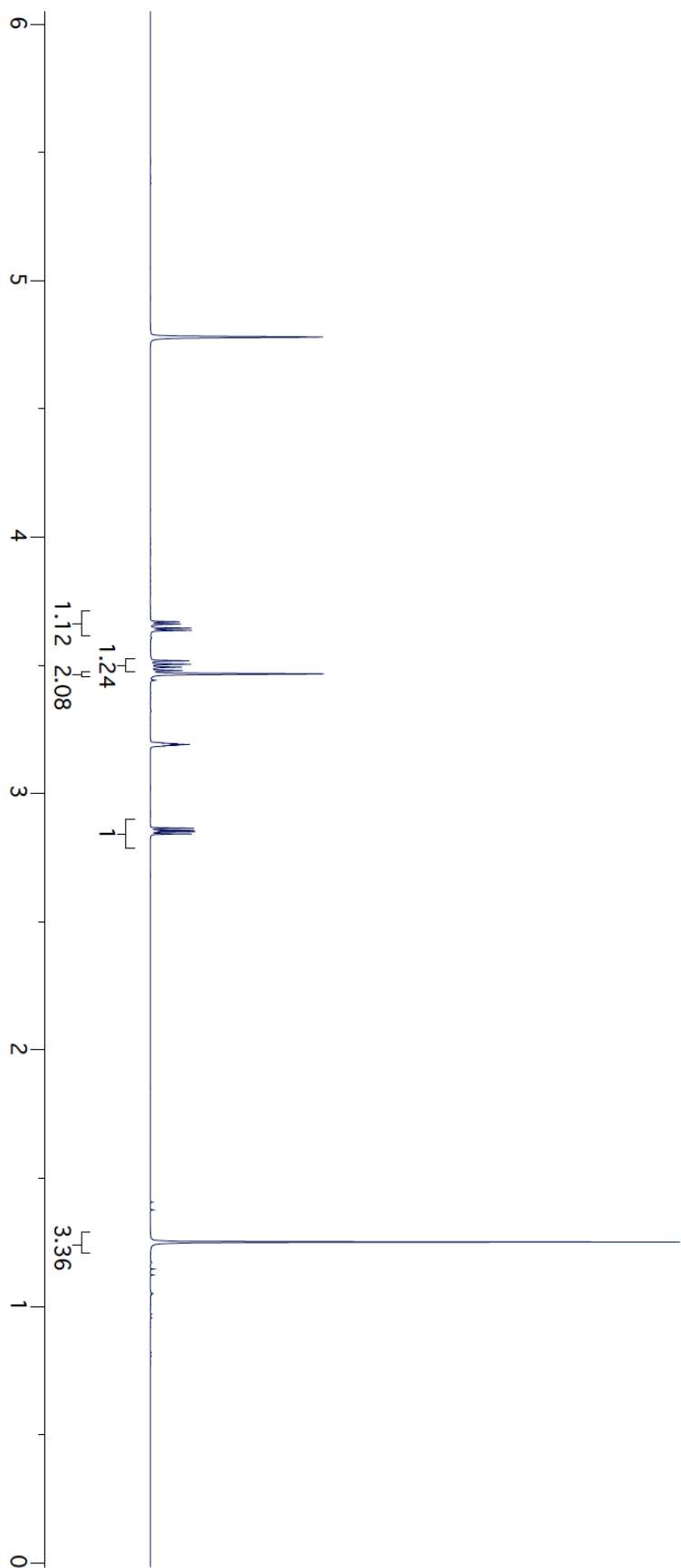
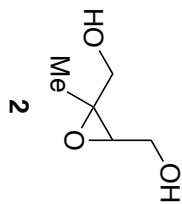


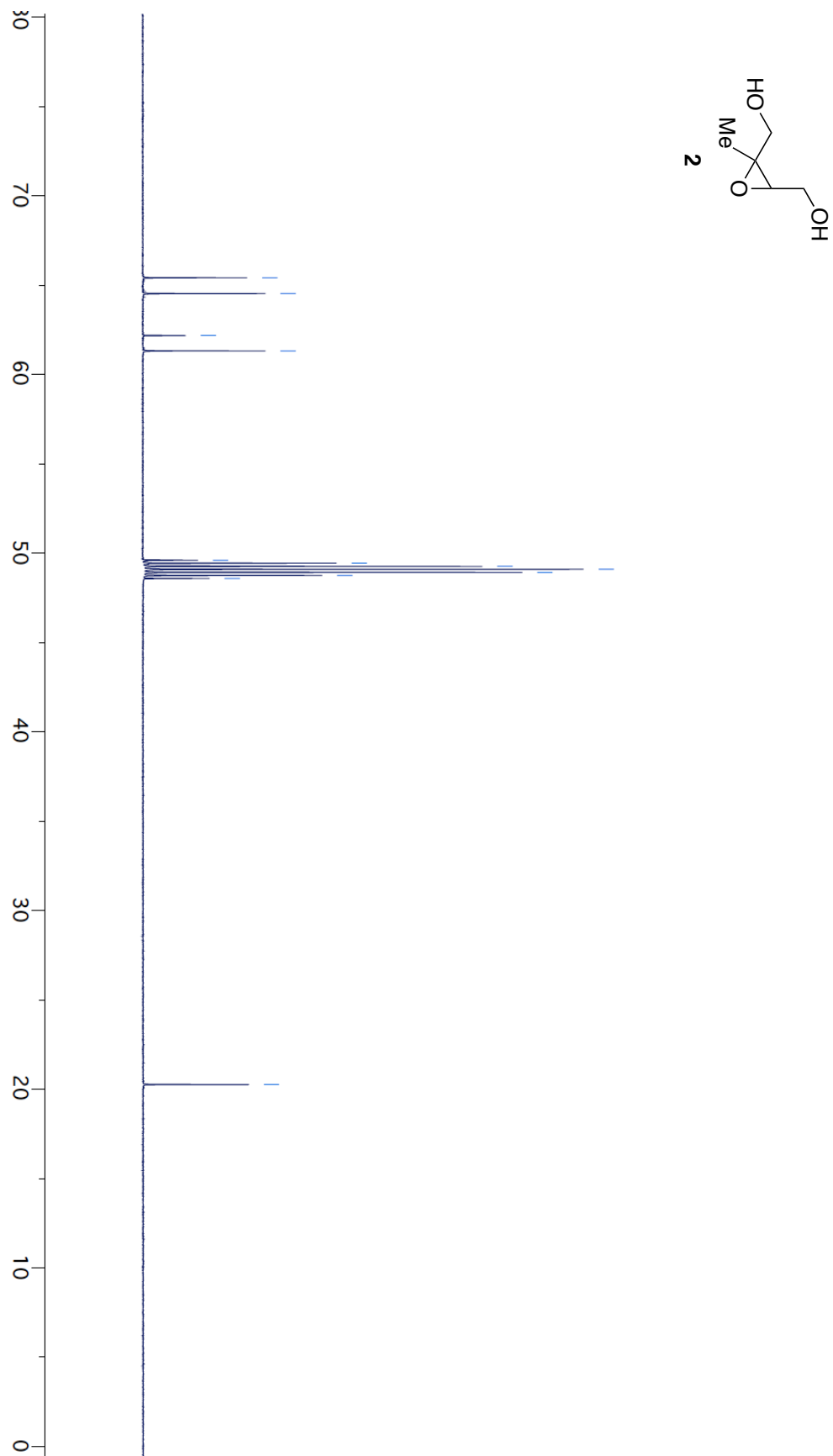
***anti*-2-methylbutane-1,2,3,4-tetraol (6):** To a solution of sodium hydride (512 mg, 12.8 mmol) in DMF (8 mL), under N_2 , at 0 °C was cannulated (*Z*)-2-methylbut-2-ene-1,4-diol³ (**A**) (500 mg, 4.9 mmol) in DMF (3 mL). Solution was warmed to room temperature and stirred for one hour. At this time benzyl bromide (2.0 mL, 17.1 mmol) was added and reaction stirred overnight. After 12 hours reaction was quenched with H_2O (10 mL) and transferred to a separatory funnel. Mixture was diluted with brine (20 mL) and extracted with a 1:1 mixture of EtOAc/Hexanes (3 x 10 mL). The combined organics were dried with Na_2SO_4 and solvent was removed under reduced pressure. Flash column chromatography on silica gel with 10→20% EtOAc in hexanes as the eluent afforded dibenzylated alcohol (**B**) as a clear oil (860 mg, 3.0 mmol, 62% yield). To a solution of **B** (800 mg, 2.83 mmol) in acetone (9 mL) was added *N*-methylmorpholine *N*-oxide (653 mg, 5.57 mmol) and osmium tetroxide (2.5 wt. % in H_2O , 378 μl). Reaction was stirred for 12 hours at which time it was diluted with EtOAc (10 mL) and transferred to a separatory funnel. Resulting mixture was washed with $\text{Na}_2\text{S}_2\text{O}_3$ (20 mL) and brine (20 mL). The combined organics were dried with Na_2SO_4 and solvent removed under reduced pressure. Flash column chromatography on silica gel with 30% EtOAc in hexanes as the eluent afforded *anti*-1,4-bis(benzyloxy)-2-methylbutane-2,3-diol (**C**) (590 mg, 1.9 mmol, 66%). To a solution of **C** (580 mg, 1.83 mmol) in MeOH (20 mL) was added 10% Pd/C (386 mg). Reaction was placed under H_2 and stirred for 24 hours.⁵ At this time, reaction was filtered through a pad of celite and solvent removed, giving the title compound as a viscous yellow oil (298 mg, 1.9 mmol, quant.): IR (film) 3314, 2976, 2941, 2884, 1459, 1045, 1022 cm^{-1} ; ^1H NMR (500 MHz, MeOD) 3.68 (dd, 1H, $J = 10.5, 2.7$ Hz); 3.50–3.43 (m, 2H); 3.40 (d, 1H, $J = 11.1$ Hz); 3.32 (d, 1H, $J = 11.1$ Hz); 0.99 (s, 3H); ^{13}C NMR (125 MHz, MeOD): δ 76.2, 75.1, 68.5, 63.9, 19.8; HRMS (ESI): Exact mass calcd for $\text{C}_5\text{H}_{12}\text{O}_4$ $[\text{M}+\text{Na}]^+$, 159.0628. Found 159.0630.

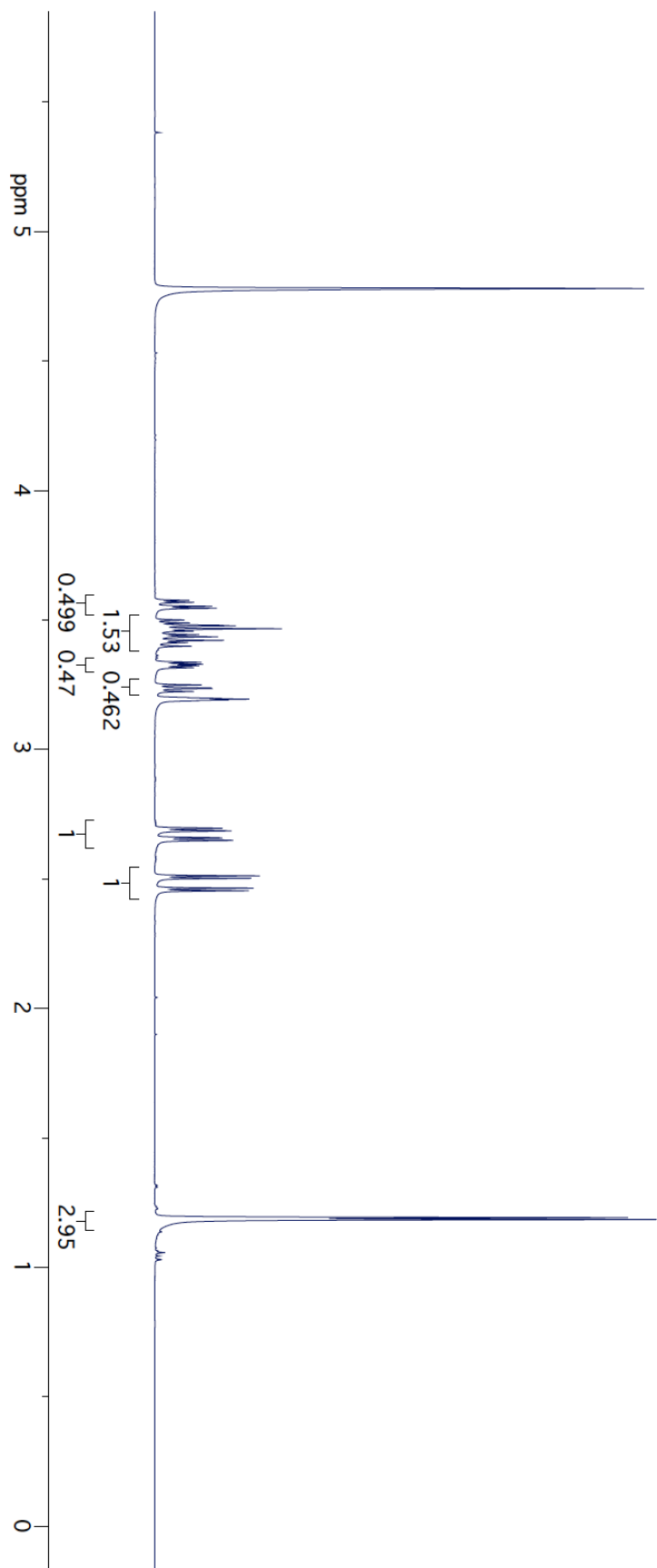
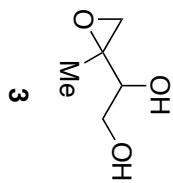
5. Hoefler, J. -F.; Grosdemange-Billiard, C; Rohmer, M. *Tetrahedron. Lett.* **2000**, *41*, 4885–4889.

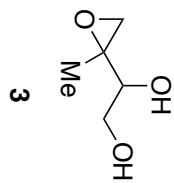
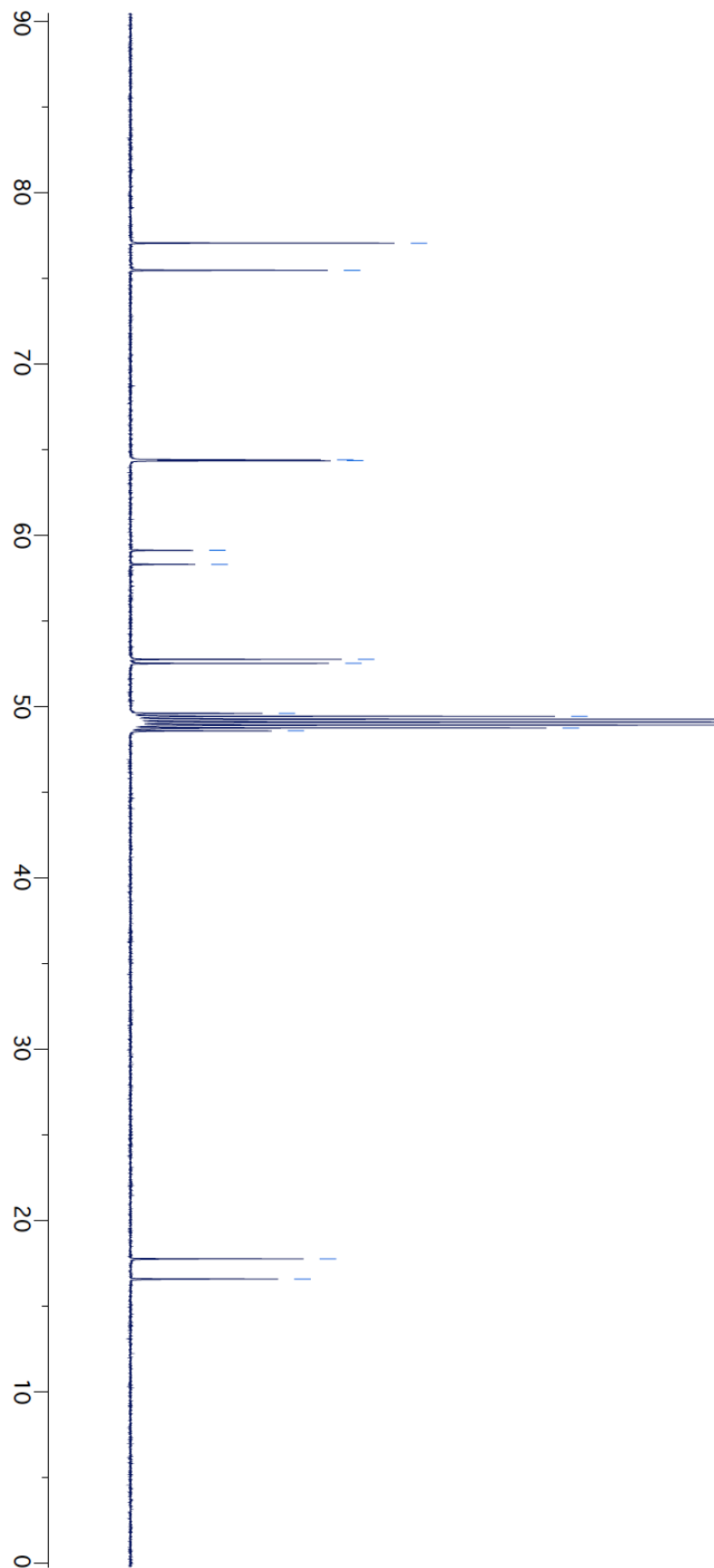
3. ^1H and ^{13}C -NMR Spectra

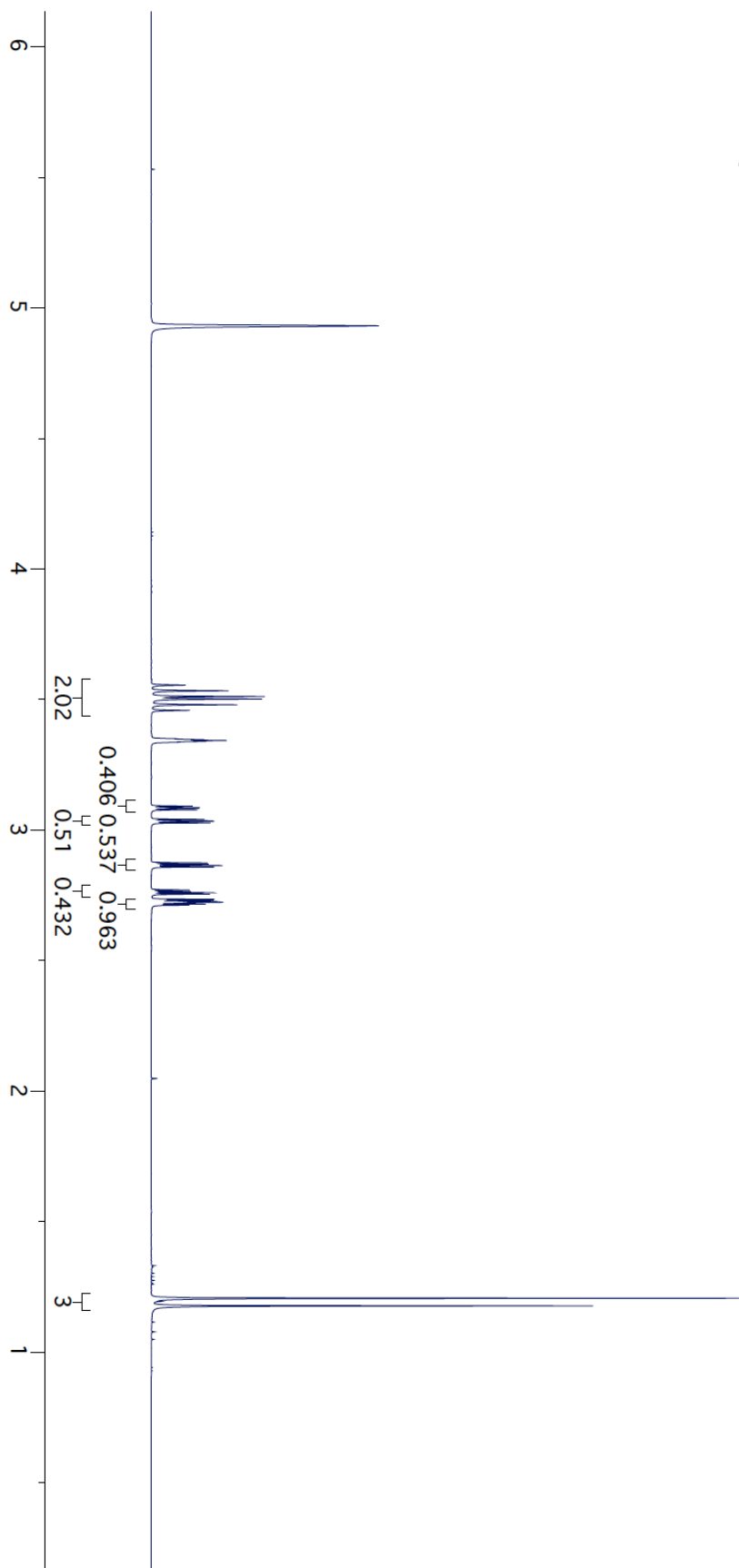
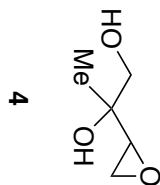


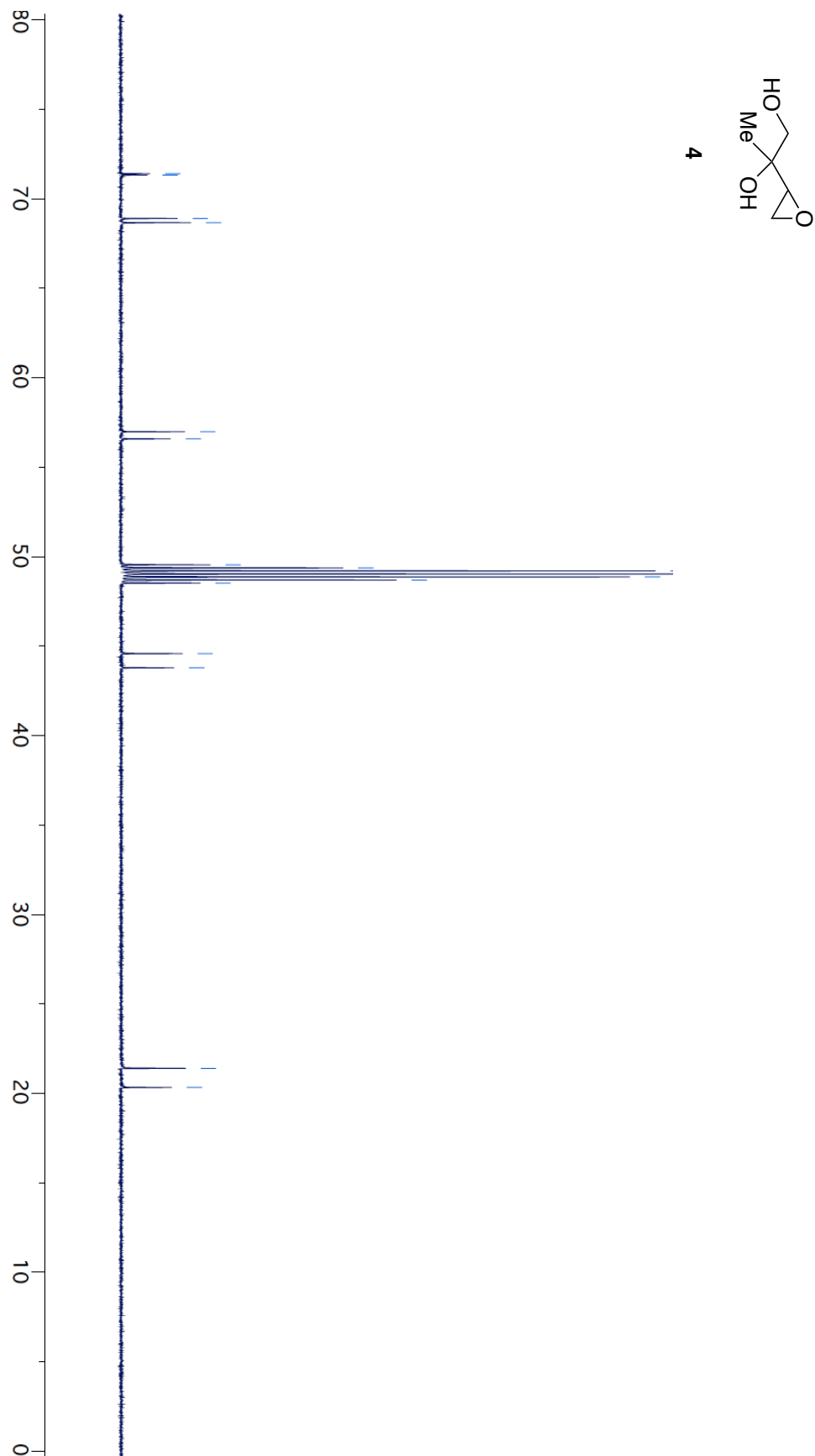


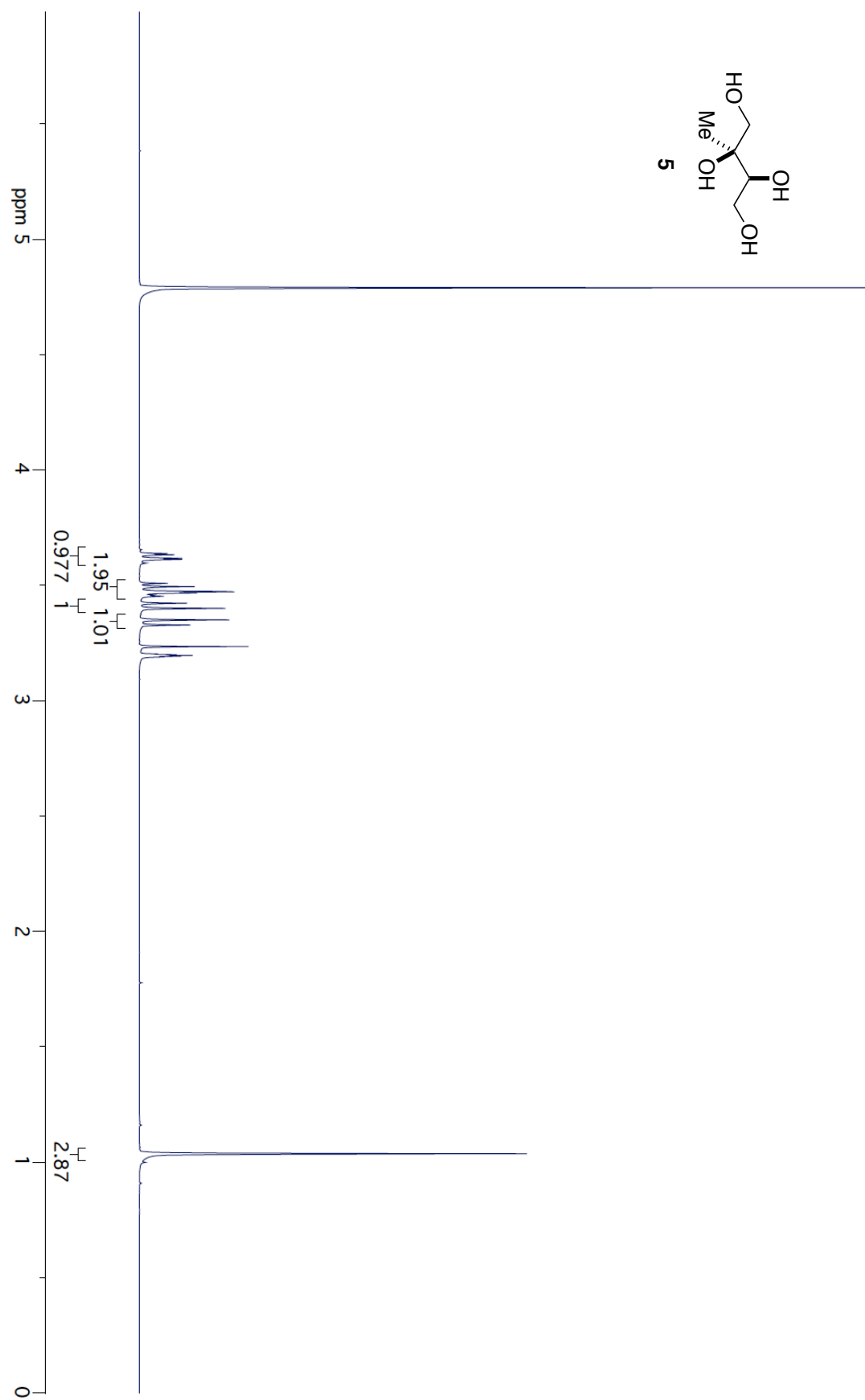


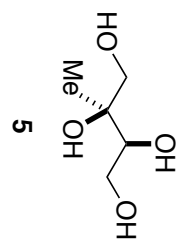


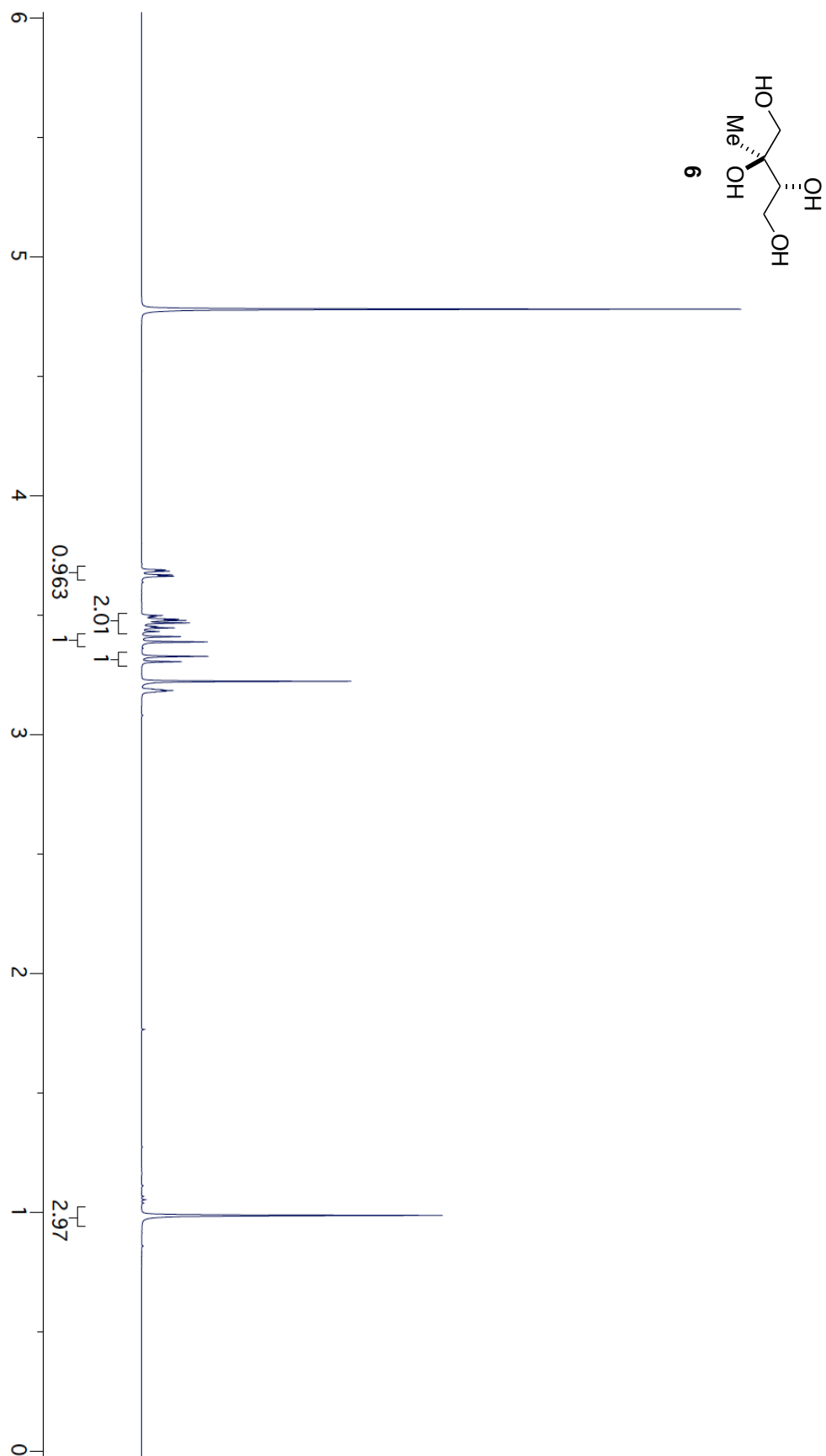


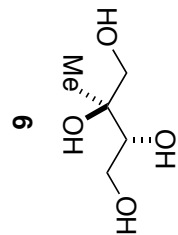


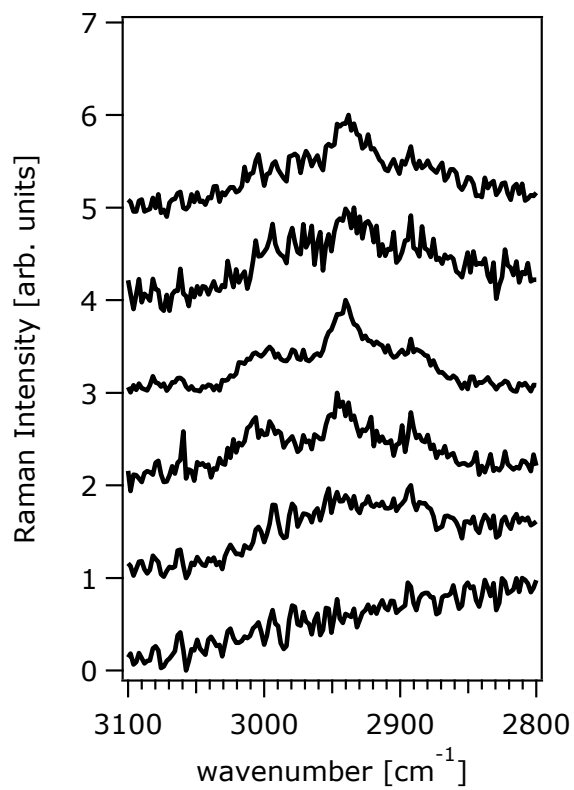
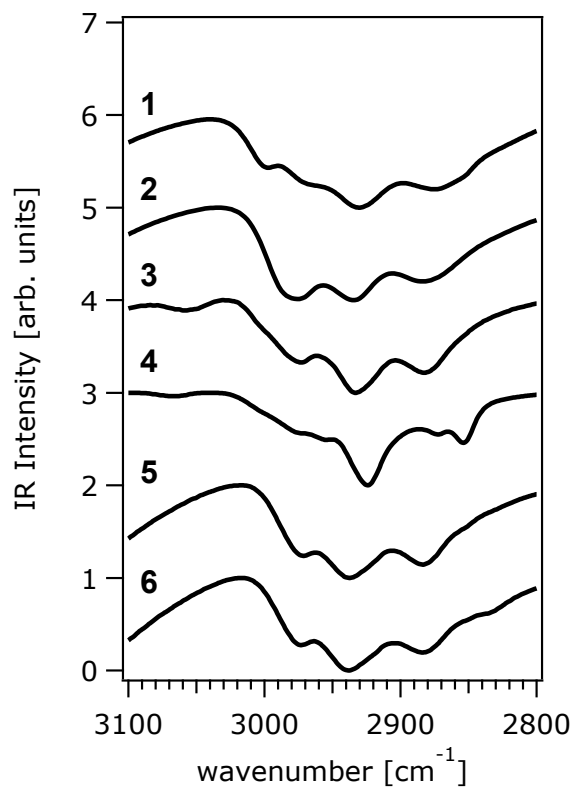




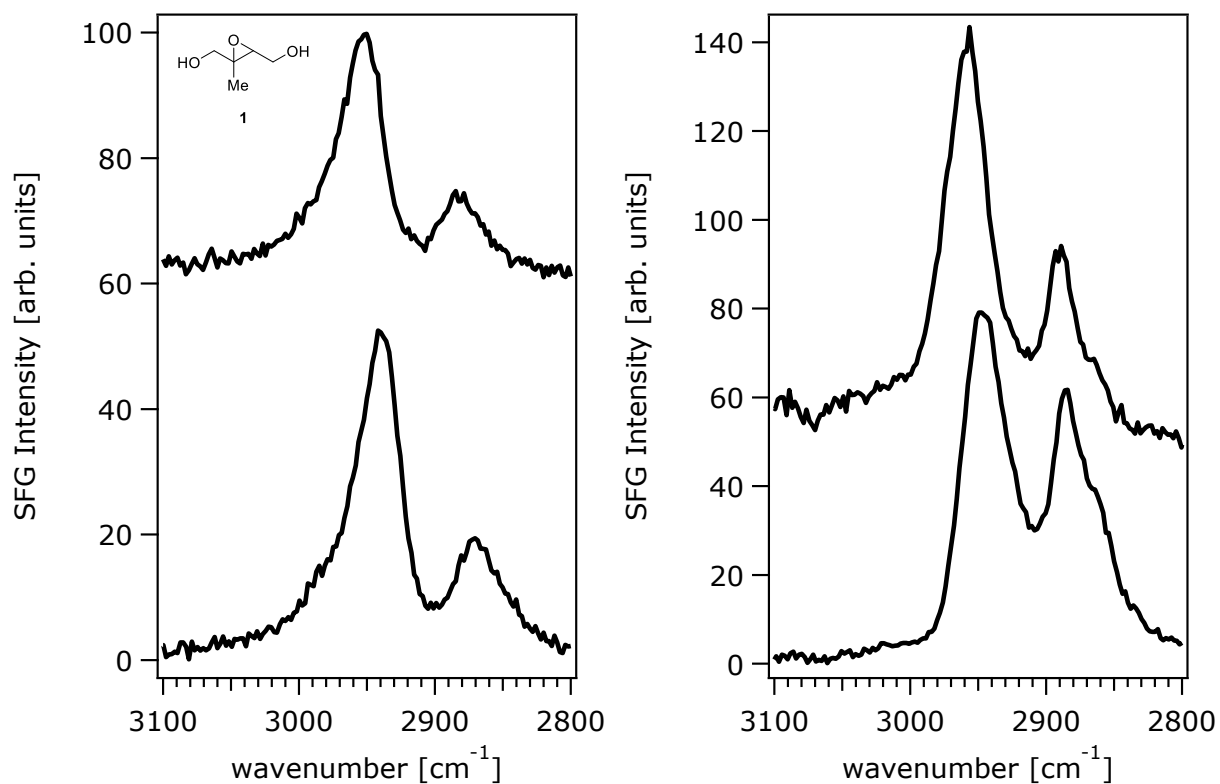


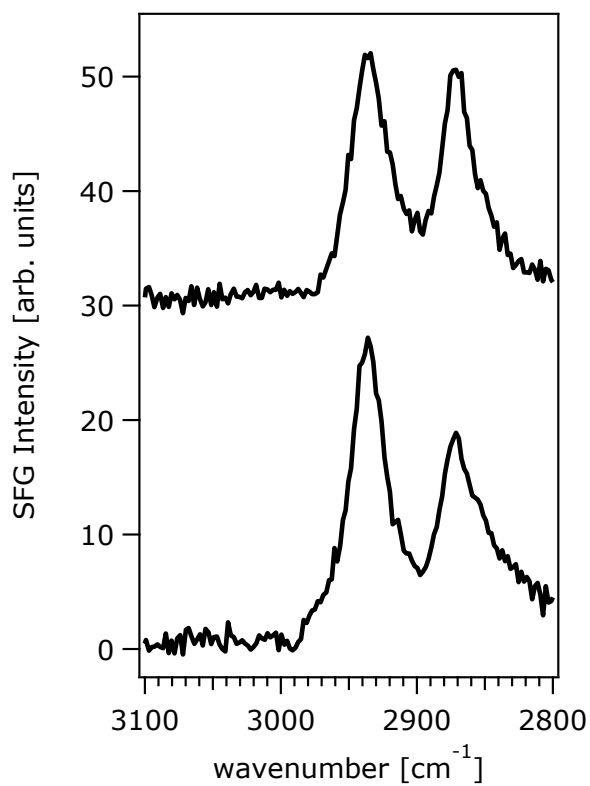
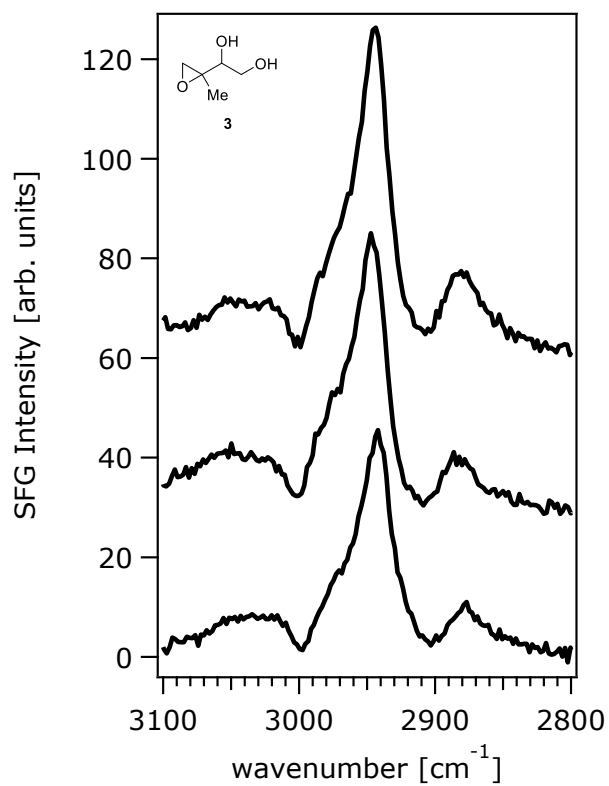
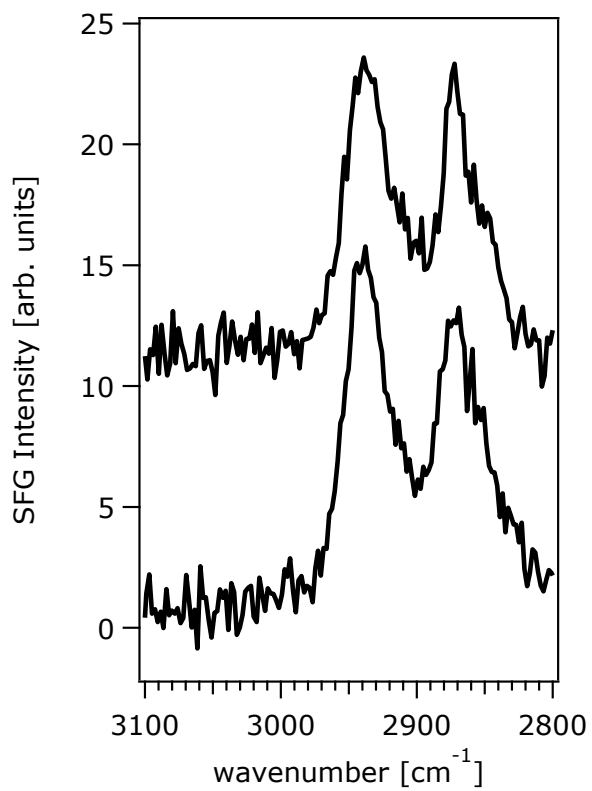
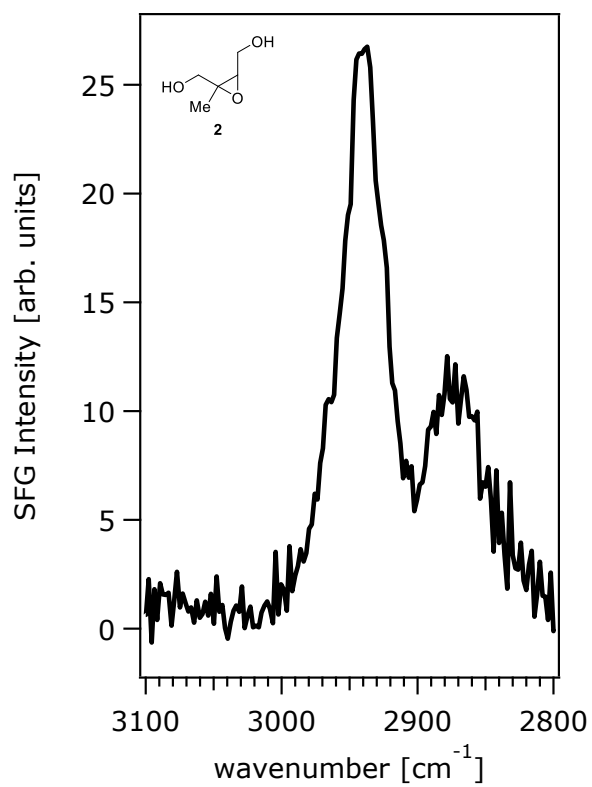


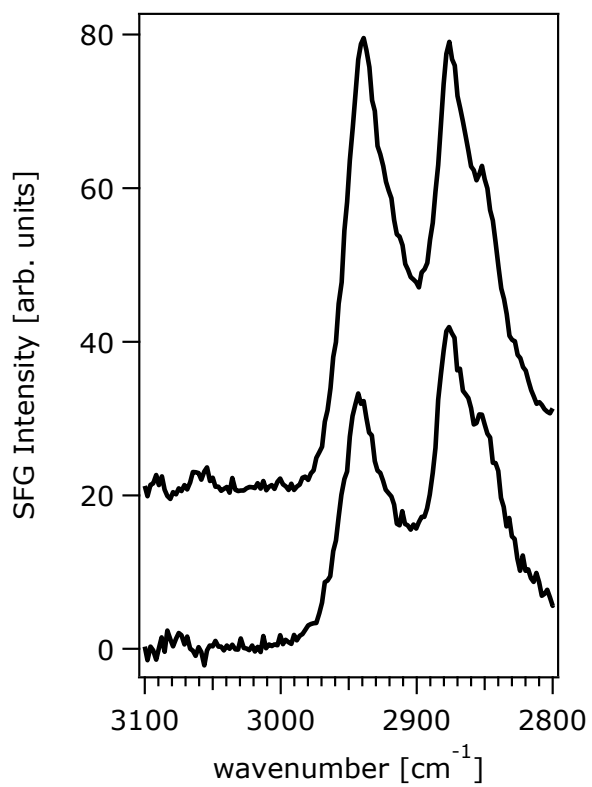
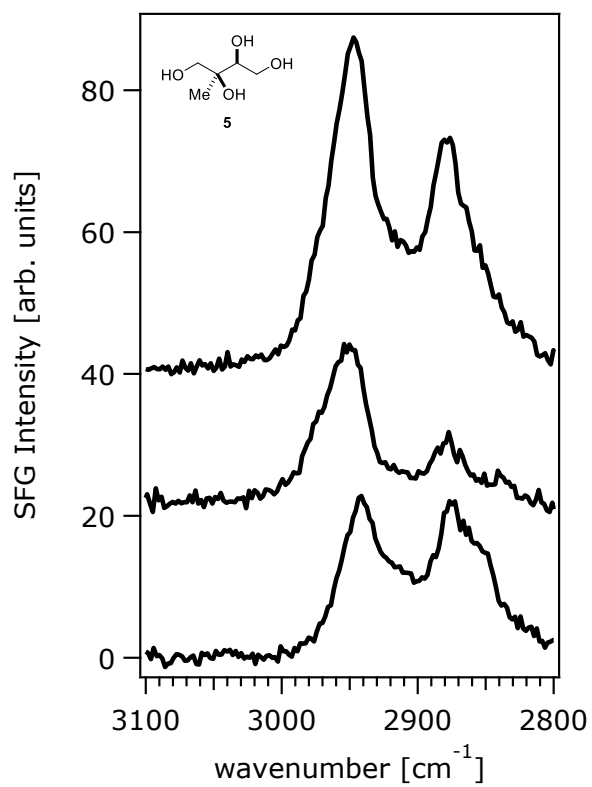
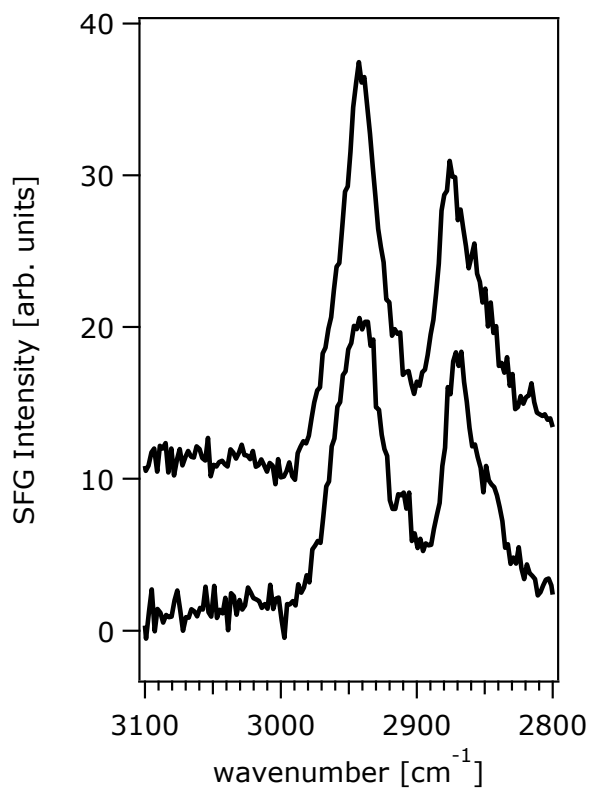
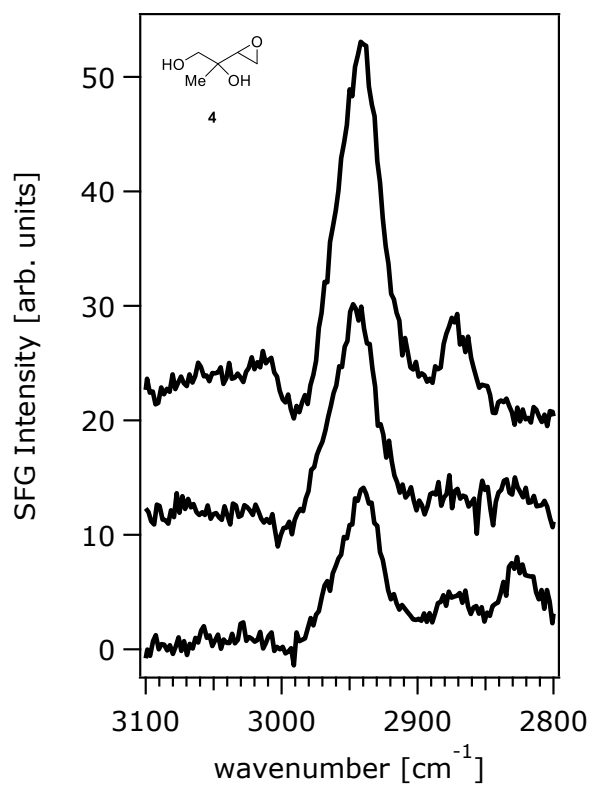


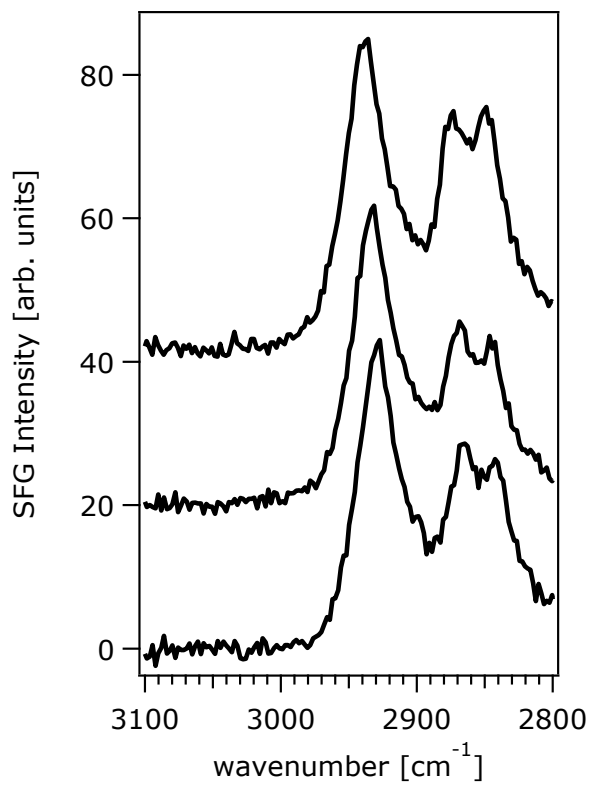
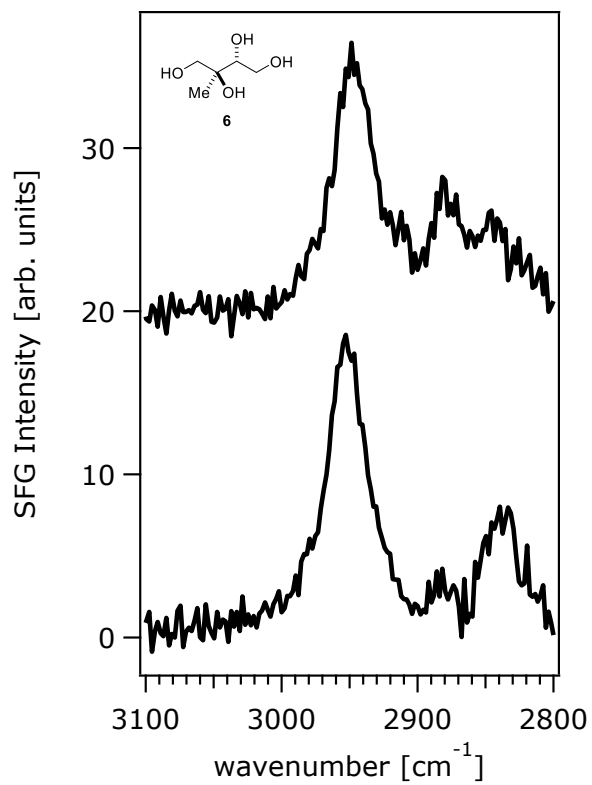
4. IR and Raman Spectra.

5. Individual SFG Spectra. SFG experiments were carried out multiple times on each compound under both vapor and condensed phase conditions. Repetition of these experiments allows us to account for variability in spectral responses. We find that, in general, the spectral line shapes are similar between experiments, and peak frequencies do not vary more than 8 cm^{-1} . Differences in absolute intensity may result from changes in alignment from day to day. Despite these differences, we find that spectra that result from averaging together individual spectra provide an accurate representation of the spectral features present in the individual spectra. Below, the individual ssp-polarized SFG spectra of compounds **1-6** are shown. Vapor-phase spectra are shown on the left, and spin-coated spectra are shown on the right. All spectra were collected under the same conditions and are offset for clarity.



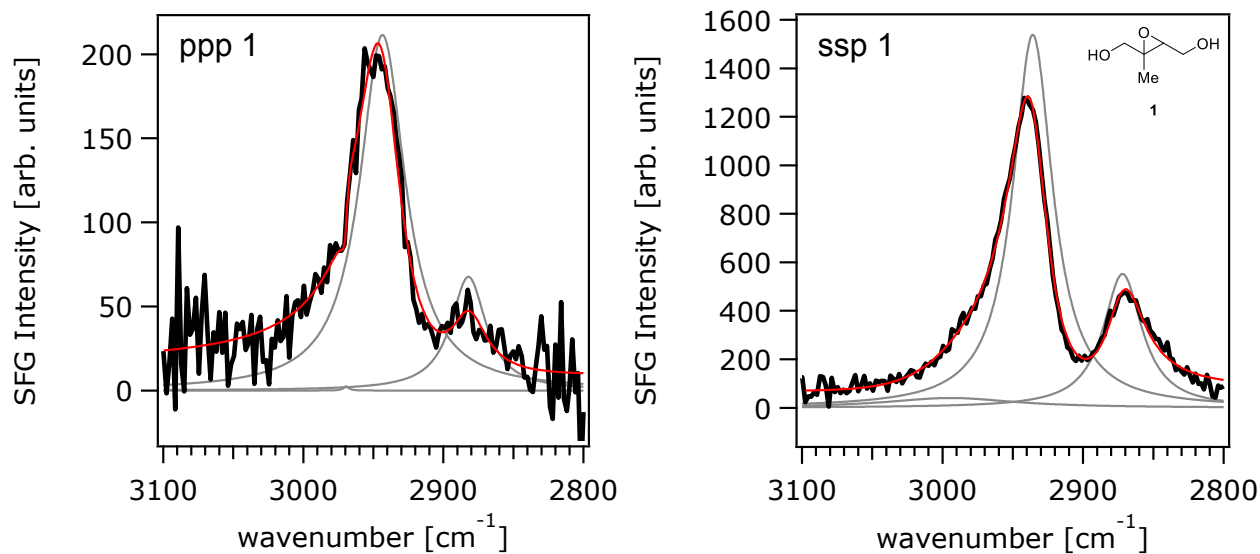




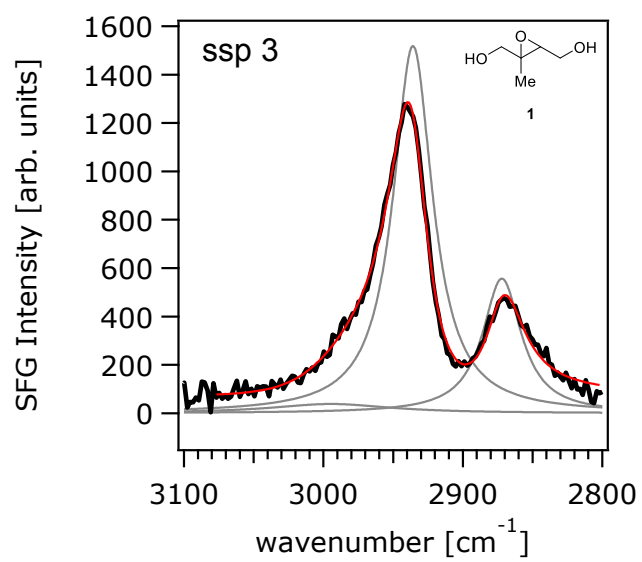
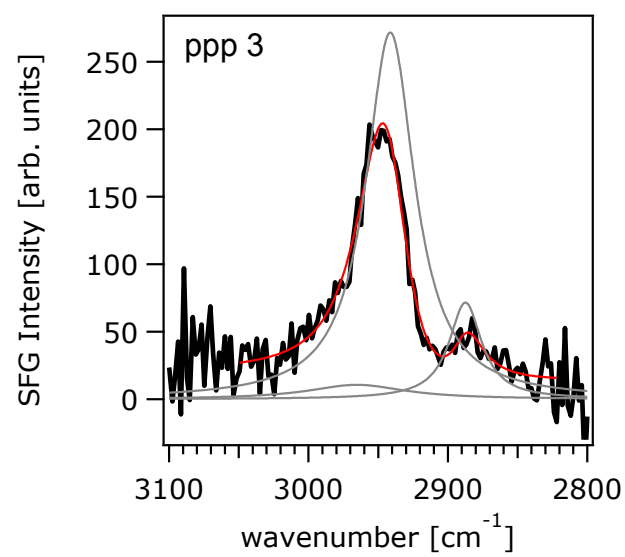
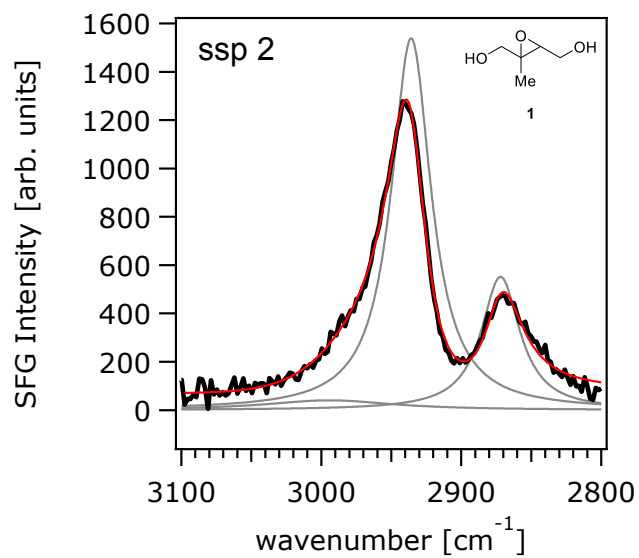
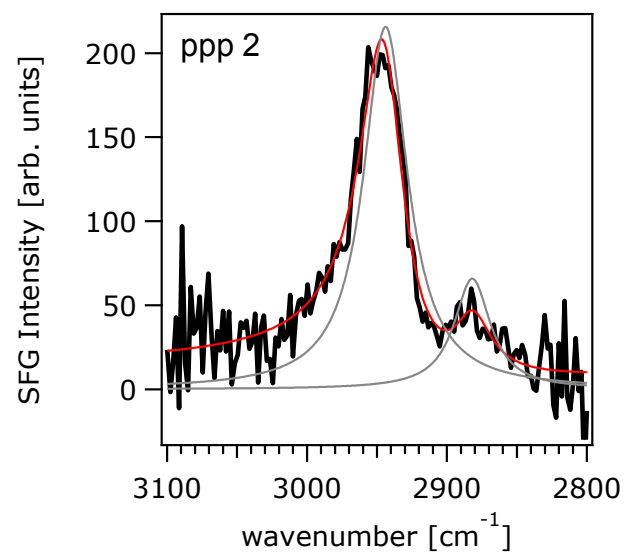


6. Fitting and Orientation Analysis. Comparison of SFG spectra of each of the epoxides and tetraols analyzed in this work with those of isoprene-derived SOA particle material indicates that trans- β -IEPOX (epoxide **1**) provides the best match to the particle material, and therefore, may be present at the surfaces of these particles. Based on this match, we carried out a thorough orientation analysis of both the vapor phase and spin-coated sample spectra of this compound. One experiment for each phase state was chosen as representative data, and the ssp- and ppp-polarized spectra of the compound under each phase condition were fit three times. Fits were carried out using a combination of in-phase and out-of-phase Lorentzians with a non-resonant contribution. The number of Lorentzians was varied between three and six, in order to assess which possible C–H stretches contribute to the spectral intensity. Each Lorentzian peak is made up of three parameters: peak position, amplitude, and width. The amplitudes associated with the methyl symmetric stretch, located near 2880 cm^{-1} in each of the spectra were then used to calculate $\chi_{\text{ppp}}/\chi_{\text{ssp}}$. The ratios of the three fits were averaged together for each phase state, and the average point estimates were added to the radial plots described and shown in the main text. Sigma values for the amplitudes in each fit were used to determine the standard error associated with each calculated ratio, and the average standard errors are also indicated on the radial plots in the main text.

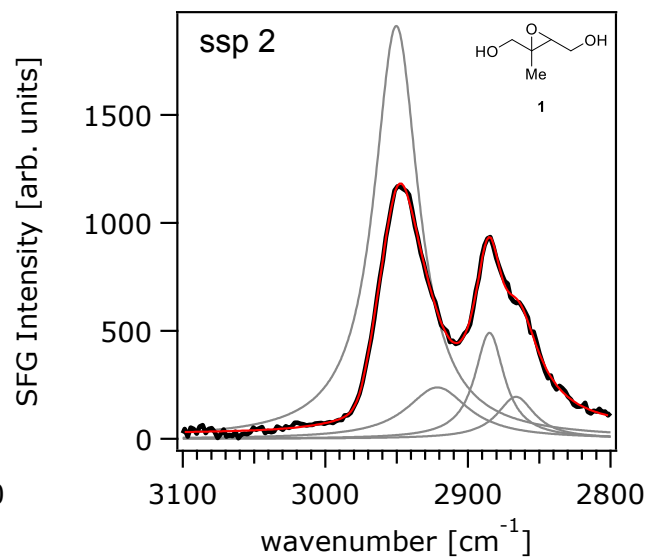
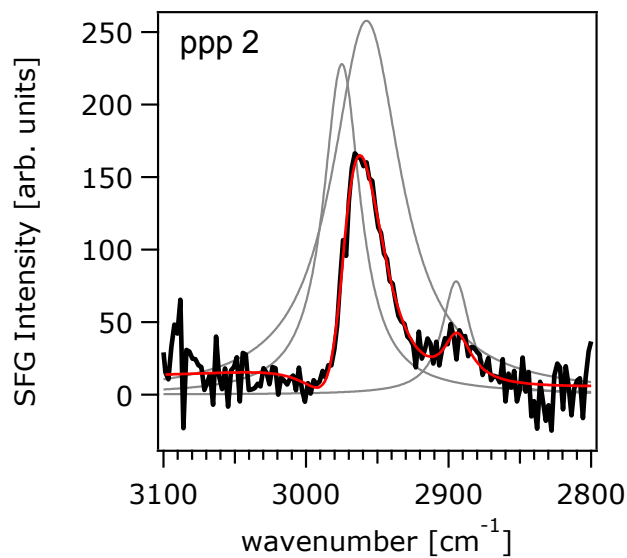
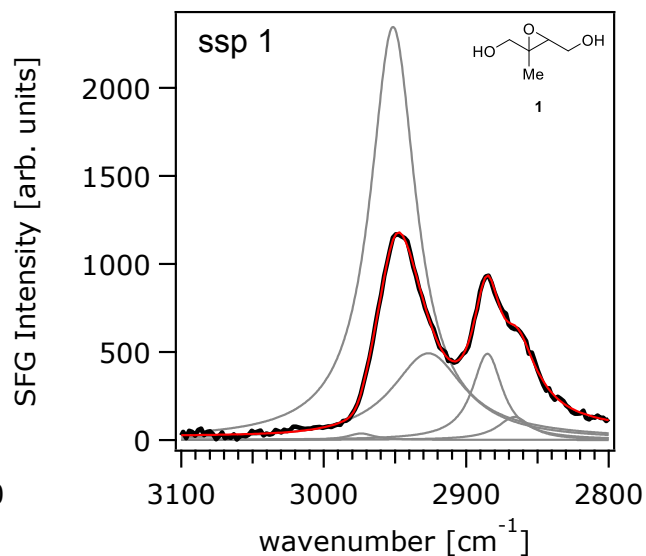
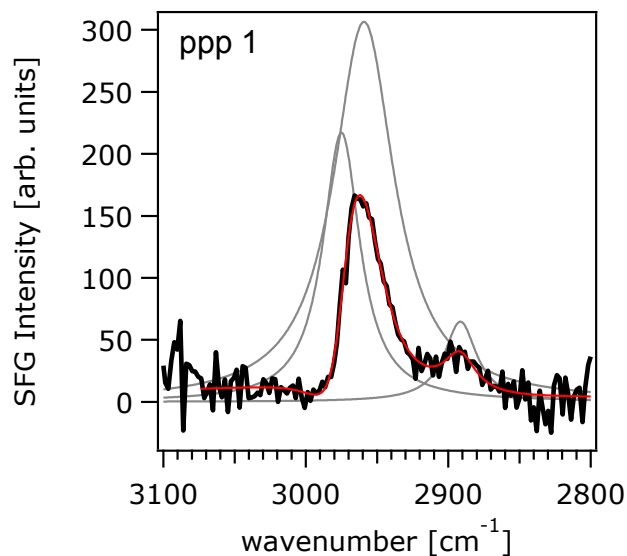
Vapor phase. ssp spectra are shown on the left and ppp on the right. Fits are shown in red, and individual Lorentzian peaks are shown in gray.



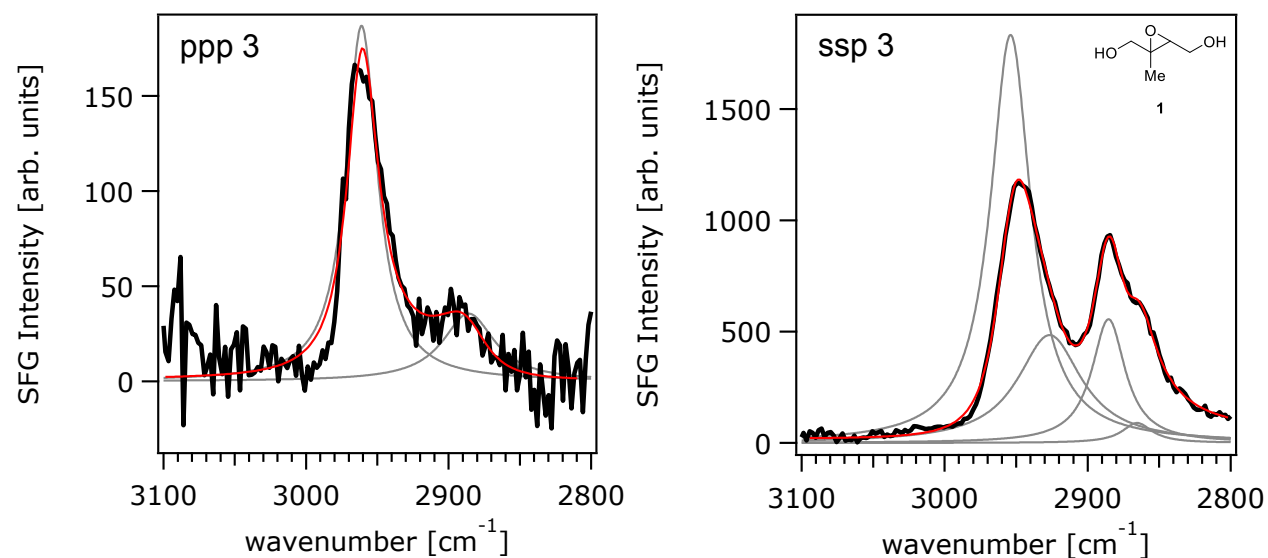
Vapor phase



Spin-coated. ssp spectra are shown on the left and ppp on the right. Fits are shown in red, and individual Lorentzian peaks are shown in gray.



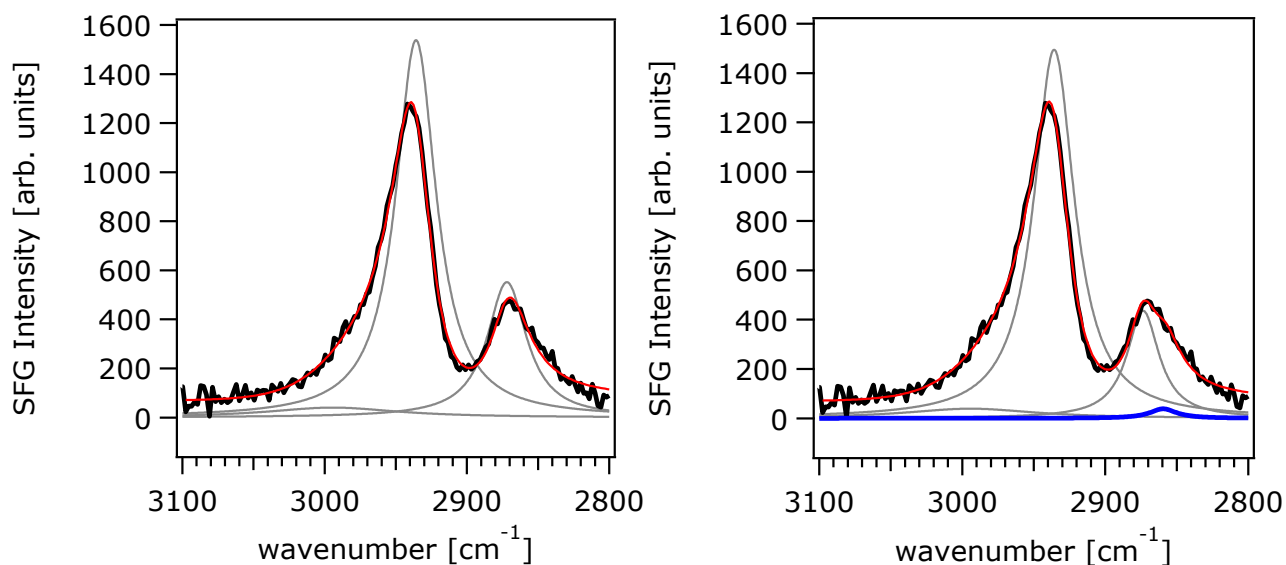
Spin-coated



Fit parameters and propagation of error.

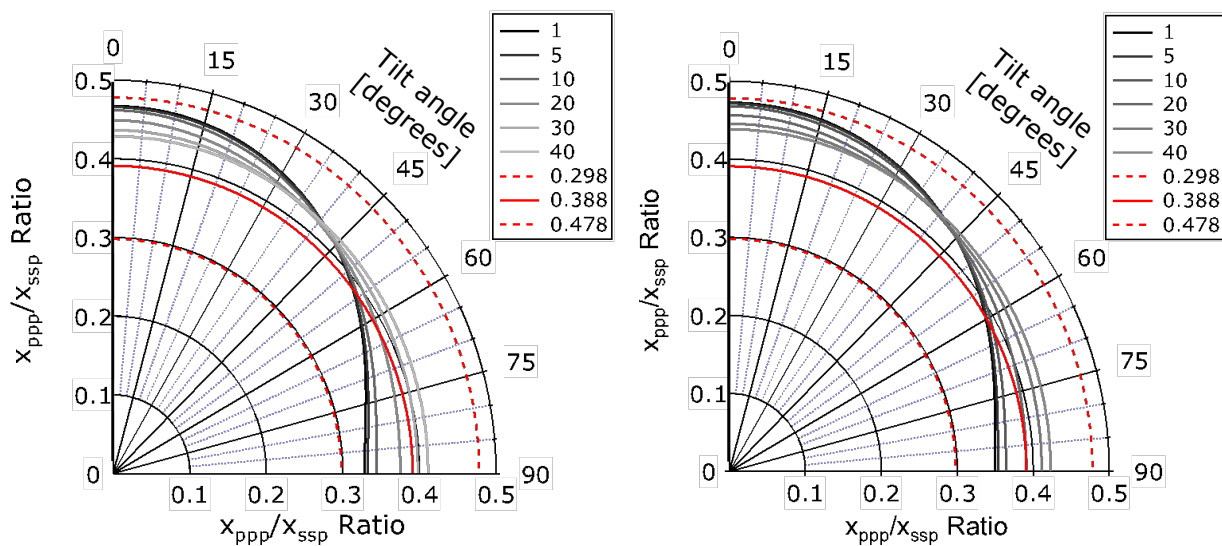
	trans- β -IEPOX, vapor			trans- β -IEPOX, spin-coated		
ssp amplitude	395.5	395.3	397.5	284.9	278.7	334.5
ssp sigma	12.2	12.2	11.2	54.7	33.3	30.2
ppp amplitude	125.3	128.3	120.2	111.3	105.2	132.5
ppp sigma	20.2	20.4	21.7	16.2	19.1	29.2
ppp/ssp ratio	0.317	0.325	0.302	0.391	0.378	0.396
Standard error	0.052	0.053	0.055	0.094	0.082	0.094
Average ratio	0.314			0.388		
Average error	0.053			0.090		
Upper bound	0.367			0.478		
Lower bound	0.261			0.298		

Methylene contributions. When methylene contributions are added to the spectral fits, we find that they are either low in amplitude or cause the parameters in the fit to have large sigma values associated with them. In particular, adding methylene contributions to the vapor phase spectral fits shown above decreases the effectiveness of the fit. For example, shown below are fits for ssp-polarized vapor phase trans- β -IEPOX (**1**) spectra, with (right) and without (left) an added methylene symmetric stretching contribution. The methylene peak is shown in blue. The parameters and sigma values associated with each fit are shown below. The amplitude of this peak is low with a large sigma value, and we were unable to obtain a better fit. In addition, adding this peak to the fit results in increase in the error associated with the methyl symmetric stretch amplitude. A similar attempt was made to add a methylene asymmetric stretching contribution to the fit; however, this led to results that were non-physical.



	without CH ₂ ss	sigma	With CH ₂ ss	sigma
freq 1, CH ₂ ss	0	0	2859.5	3.0
ampl 1	0	0	70.9	88.3
gamma 1	0	0	11.4	5.2
freq 2, CH ₃ ss	2871.9	0.6	2873.6	1.1
ampl 2	395.3	12.2	286.1	99.6
gamma 2	16.8	0.5	13.7	2.3
freq 3, CH ₂ as	0	0	0	0
ampl 3	0	0	0	0
gamma 3	0	0	0	0
freq 4, CH ₃ as	2935.8	0.4	2935.7	0.4
ampl 4	-677.4	25.1	-670.6	24.7
gamma 4	17.3	0.3	17.3	0.3
freq 5	2994.2	5.1	2994.1	5.1
ampl 5	358.0	91.8	350.2	89.3
gamma 5	56.2	9.7	56.0	9.4
chi NR	-8.7	0.2	-8.5	0.2

Sensitivity analysis. One parameter used in calculating theoretical tilt angle distributions is the interfacial refractive index. A sensitivity analysis was performed for spin-coated trans- β -IEPOX (**1**), using interfacial refractive indices of 1.42 (left) and 1.46 (right). These values were chosen based on the known refractive indices of similar compounds.⁶



⁶ Froyd, K. D.; Murphy, S. M.; Murphy, D. M.; de Gouw, J. A.; Eddingsaas, N. C.; Wennberg, P. O. *Proceedings of the National Academy of Sciences of the United States of America* **2010**, *107*, 21360.

7. Comparison of Fresh and Aged Isoprene-Derived SOA. Isoprene-derived SOA particles were collected on a Teflon filter at the Harvard Environmental Chamber in 2010 and shipped on ice to Northwestern for analysis by SFG. The sample was pressed with a fused silica window. The ssp-polarized SFG spectrum of the freshly collected SOA sample is shown below (black, bottom left). After analysis, the window was removed from the filter surface, and the filter was stored in a freezer at -12 °C. In 2013, a spectrum was collected from the aged isoprene-derived SOA sample. For this analysis, a clean, new fused silica window was pressed to the sample surface. The ssp-polarized SFG spectrum of the aged isoprene-derived SOA is shown below (gray, top left). The spectra on the left are offset for clarity. To allow for better comparison between the fresh and aged sample spectra, the plot on the right shows both spectra normalized to a maximum intensity of 1 and overlapped. We find that there is little change in the surfaces of the particle material over the course of several years of storage, at least as seen by SFG.

