Supporting Information

Isoprene Epoxydiols as Precursors to Secondary Organic Aerosol Formation: Acid-Catalyzed Reactive Uptake Studies with Authentic Compounds

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This supporting information contains 12 pages: 1 table, and 8 figures.

Table S1. Summary of IEPOX-derived SOA Tracers Characterized in This Study.

IEPOX-derived SOA tracers	Analytical Techniques [a]	Tracer Ion (*m/z*)	Retention Time (min)
3-methyltetrahydrofuran-3, 4-diols (3-MeTHF-3,4-diols)	GC/EI-MS	262	22.20
	GC/EI-MS	262	22.81
C_5-alkene triols	GC/EI-MS	231	27.30
	GC/EI-MS	231	28.35
	GC/EI-MS	231	28.71
2-methyltetrols	GC/EI-MS	219	34.73
	GC/EI-MS	219	35.58
dimers	GC/EI-MS	335	54.56
organosulfate derivatives of the 2-methyltetrols	UPLC/ESI-HR-Q-ToFMS	215	1.115
organosulfate derivatives of the dimers	UPLC/ESI-HR-Q-ToFMS	333	1.191

[a] Reaction products analyzed by GC/EI-MS are derivatized by trimethylsilylation.

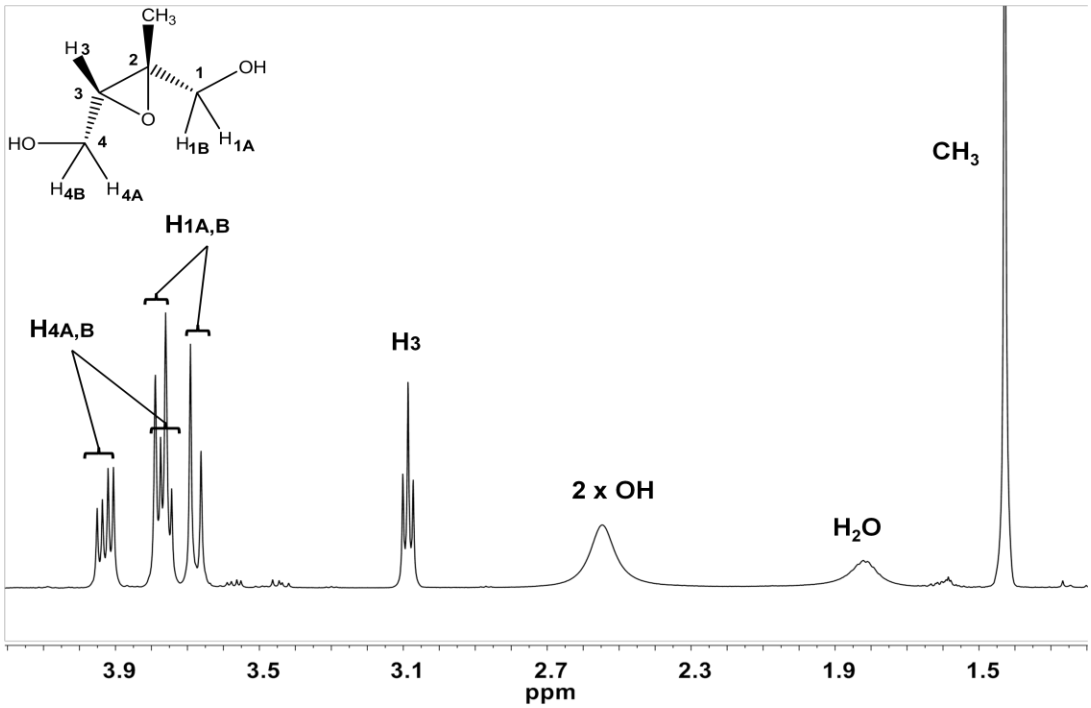


Figure S1A. ^{1}H NMR (400 MHz, chloroform-*d*) of (2-methyloxirane-2,3-diyl)dimethanol (*cis*-β-IEPOX).

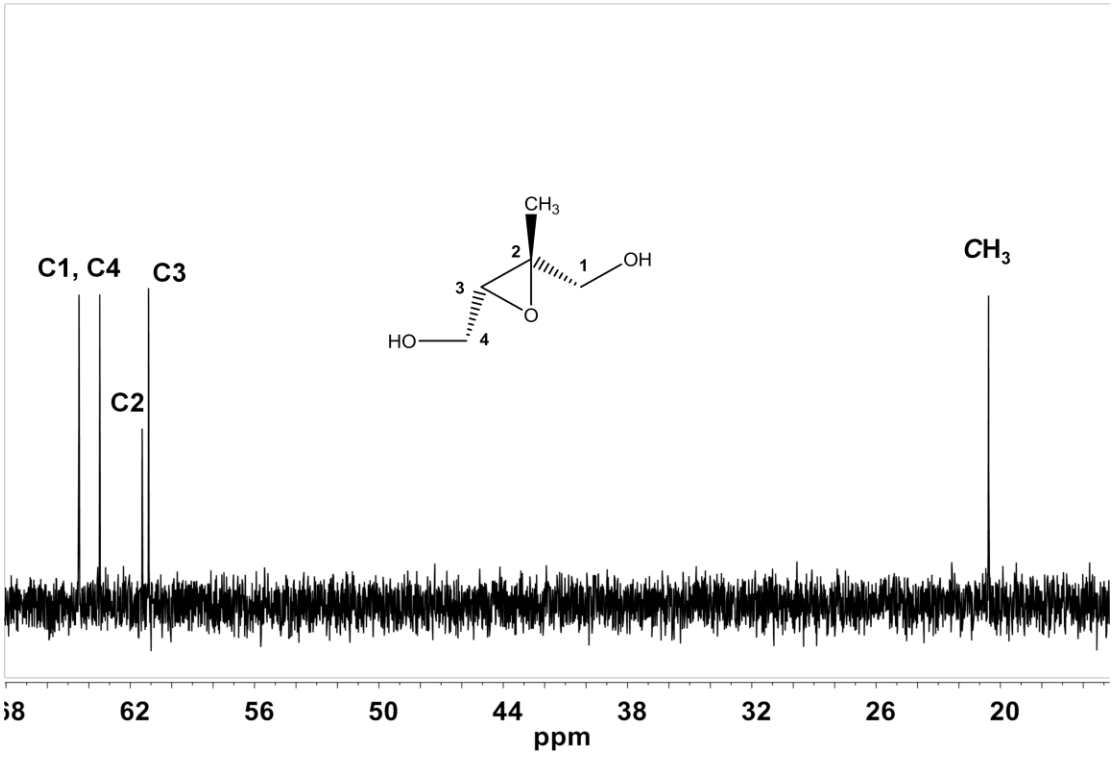


Figure S1B. ^{13}C NMR (100 MHz, chloroform-*d*), (2-methyloxirane-2,3-diyl)dimethanol(*cis*-β-IEPOX).

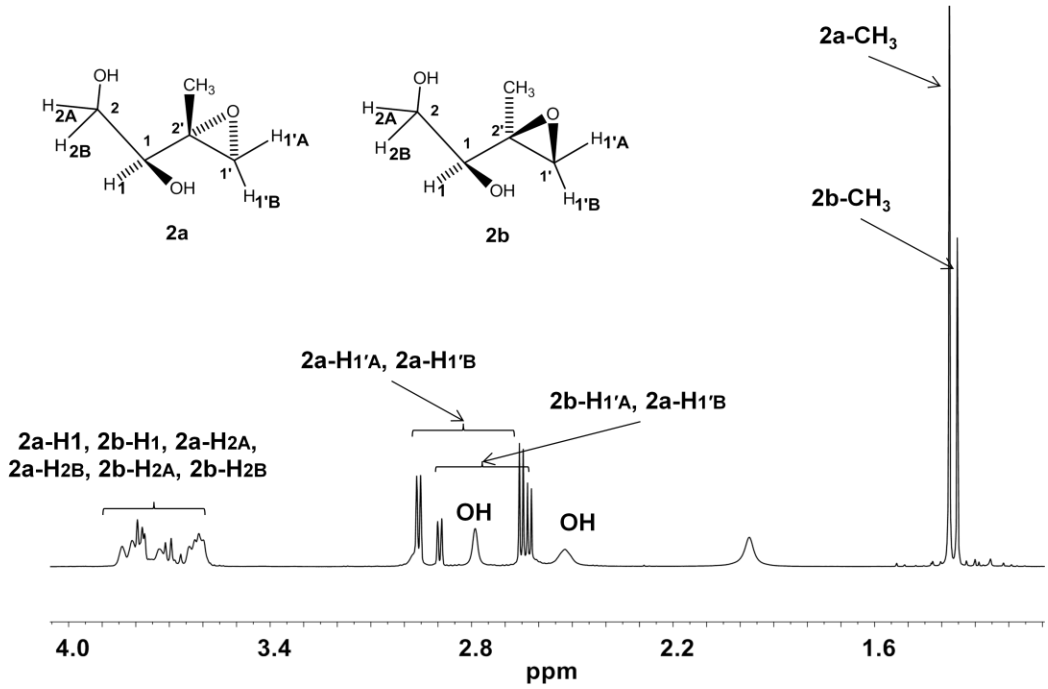


Figure S1C. ^{1}H NMR (400 MHz, chloroform-*d*) racemic mixture of δ-IEPOX diastereomers [(*2′R*)-*1S*]/[(*2′S*)-*1R*]-1-(2-methyloxiranyl)-1,2-ethanediol (**2a**) and [(*2′S*)-*1S*]/[(*2′R*)-*1R*]-1-(2-methyloxiranyl)-1,2-ethanediol (**2b**). Signal assignments are based on Adam et al.[1]

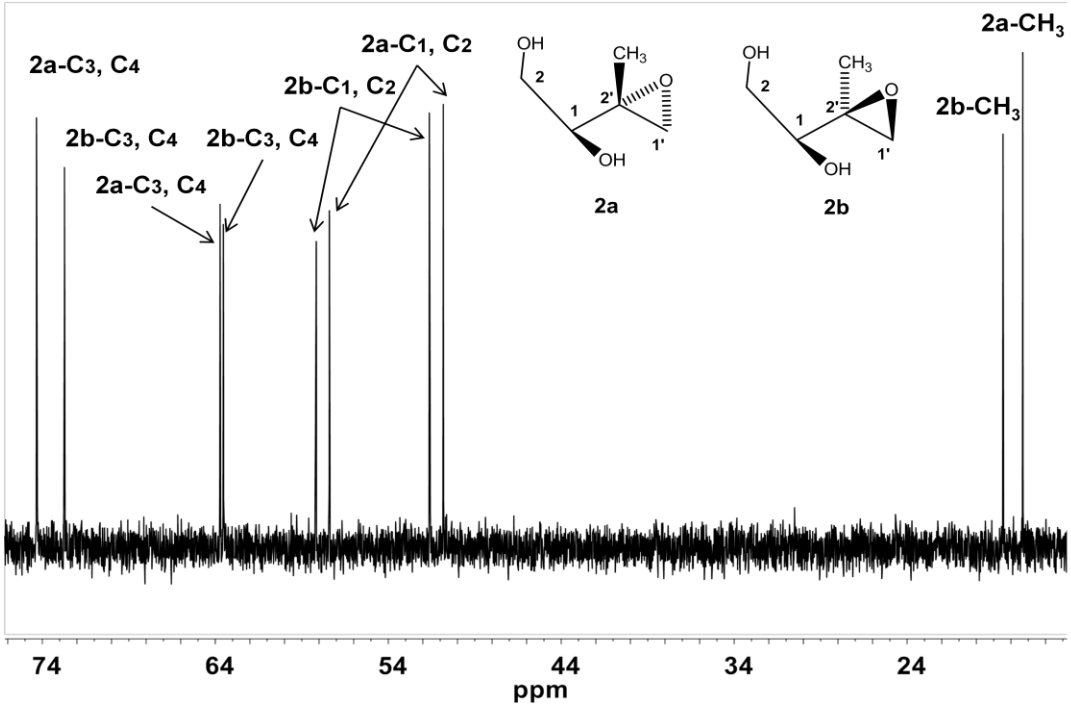


Figure S1D. ^{13}C NMR (100 MHz, chloroform-*d*), racemic mixture of δ-IEPOX diastereomers **2a** and **2b** ([(*2′R*)-*1S*]/[(*2′S*)-*1R*]- and [(*2′S*)-*1S*]/[(*2′R*)-*1R*]-1-(2-methyloxiranyl)-1,2-ethanediol, respectively).

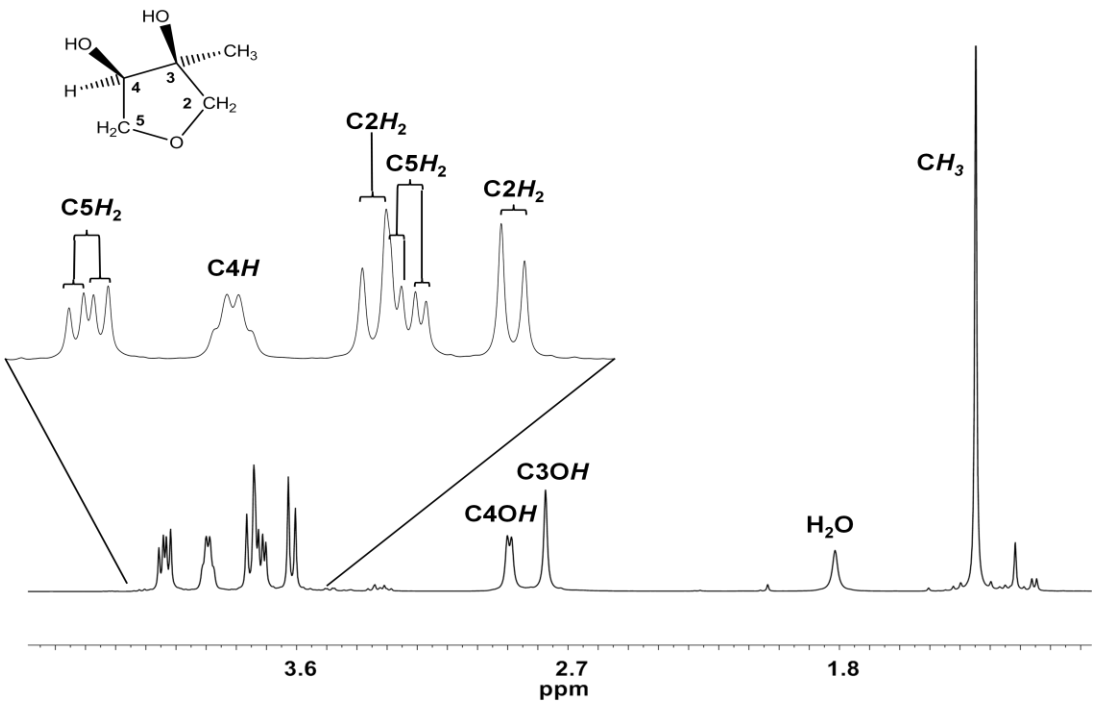


Figure S2A. ^{1}H NMR (400 MHz), chloroform-*d*) of *cis*-3-methyltetrahydrofuran-3,4-diol.

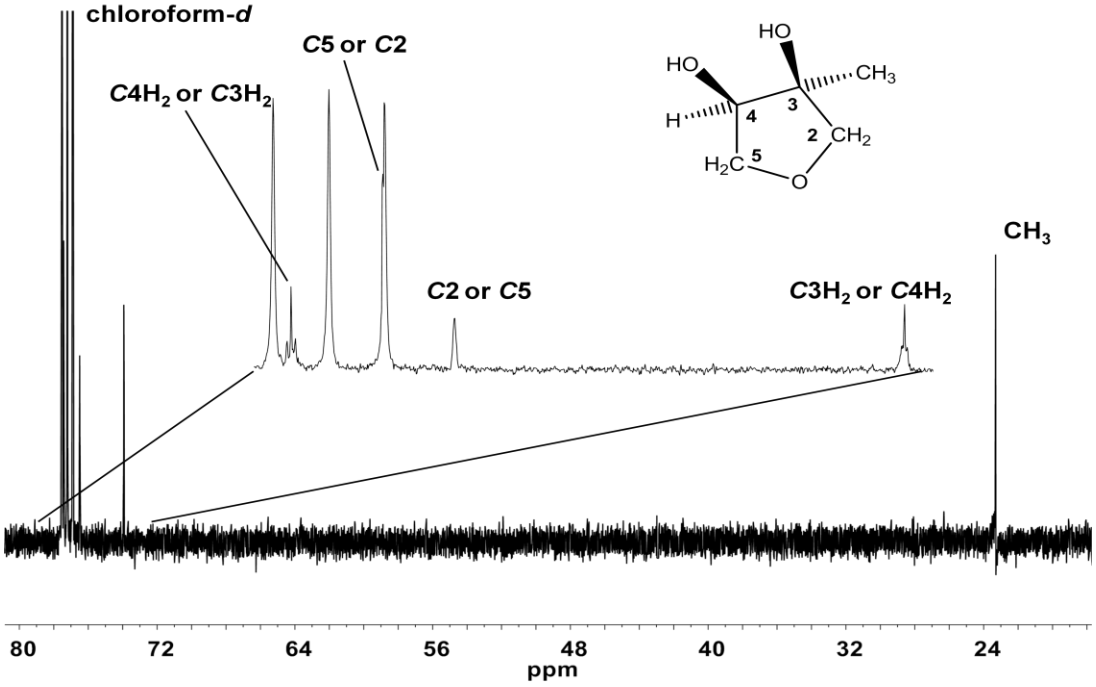


Figure S2B. ^{13}C NMR (100 MHz, chloroform-*d*) of *cis*-3-methyltetrahydrofuran-3,4-diol. Partial signal assignments are based on the presence of splittings consistent with $^{2}J_{C-H}$ or $^{3}J_{C-H}$ coupling,[2] possible only for signals of C3 and C4. The 1:1:1 triplet at 77.2 ppm is due to natural abundance ^{13}C-chloroform-*d*.

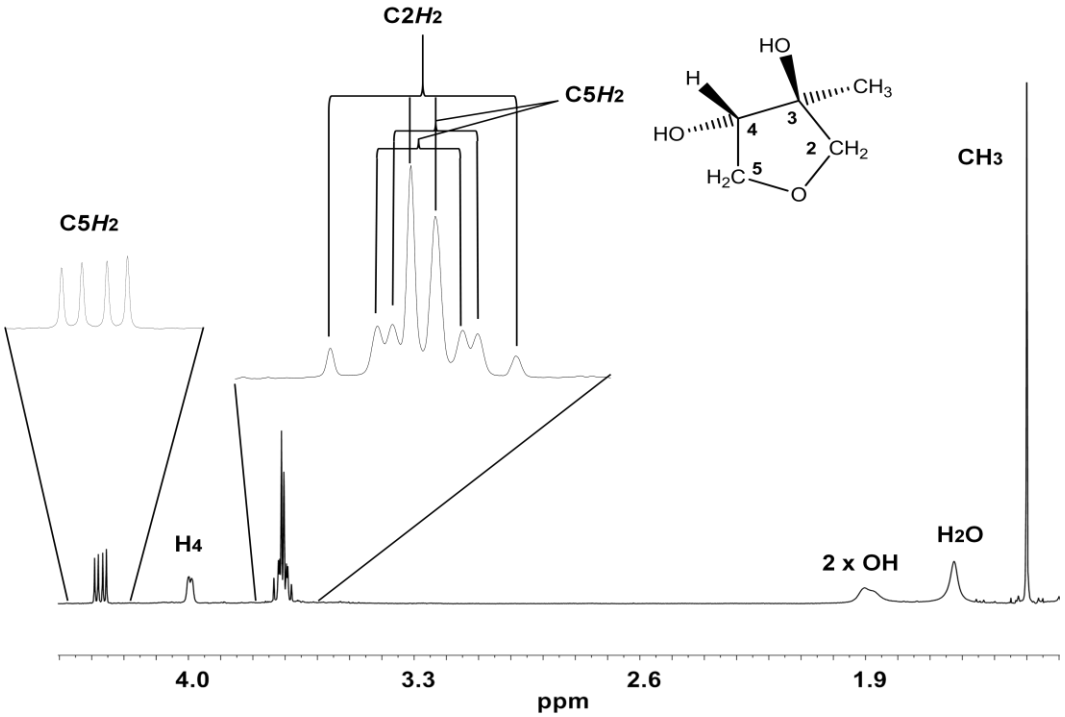


Figure S2C. ^{1}H NMR (400 MHz), chloroform-*d*) of *trans*-3-methyltetrahydrofuran-3,4-diol.

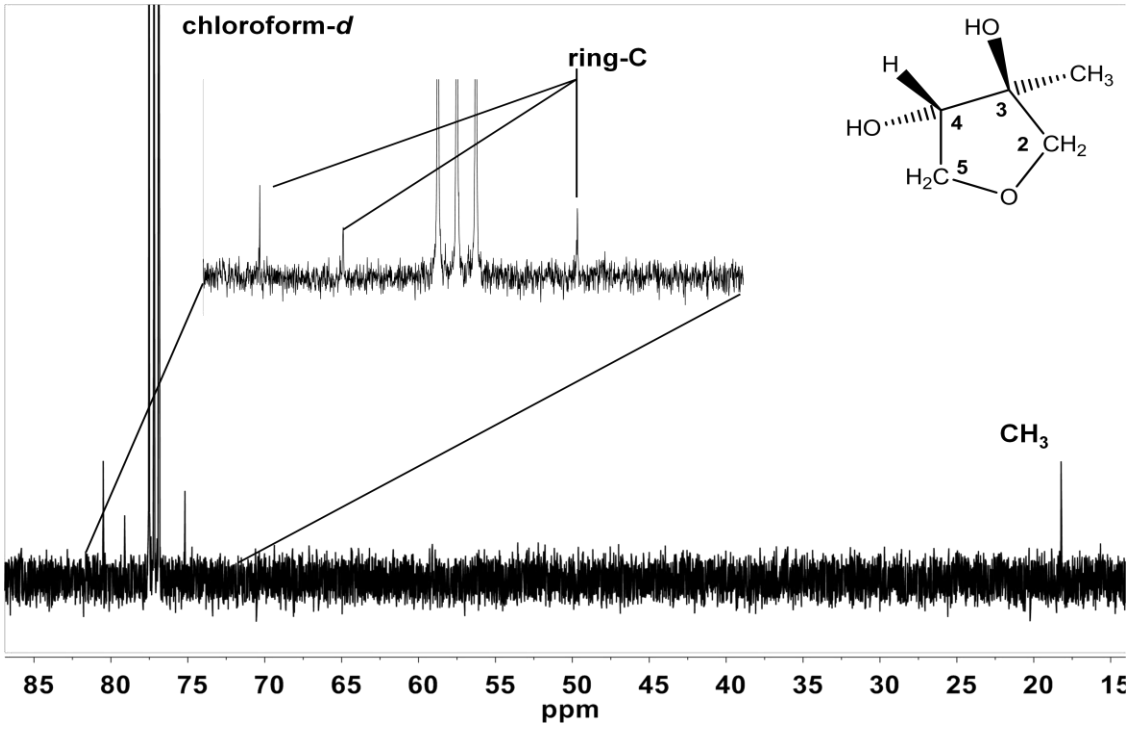


Figure S2D. ^{13}C NMR (100 MHz), chloroform-*d*) of *trans*-3-methyltetrahydrofuran-3,4-diol. One ring carbon signal is obscured by the ^{13}C-chloroform-*d* signals.

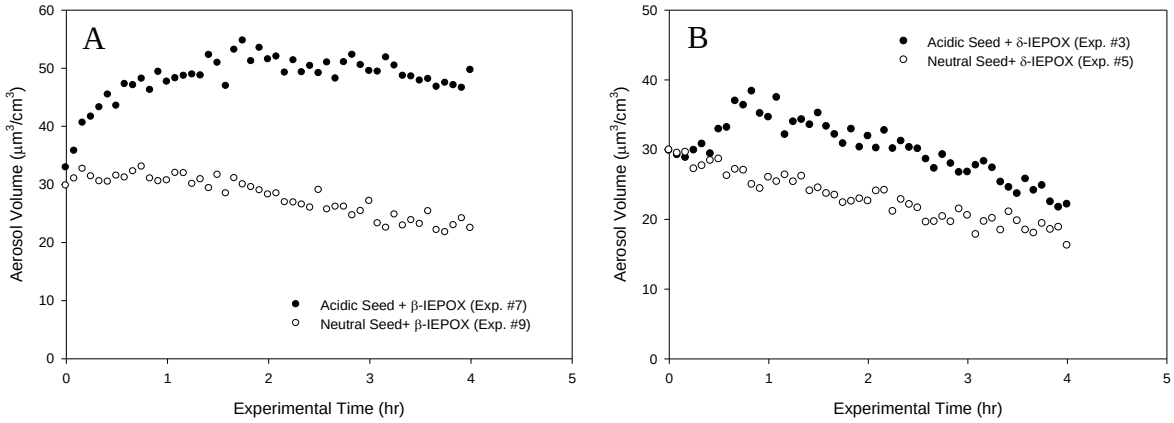
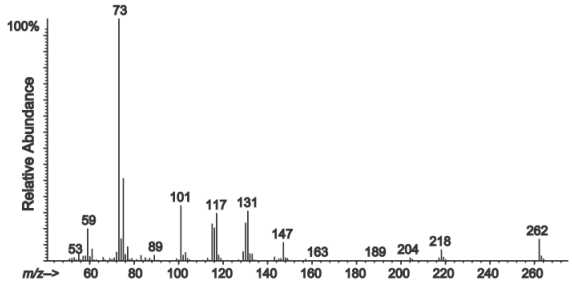
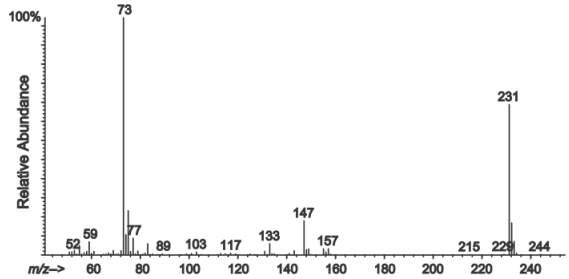


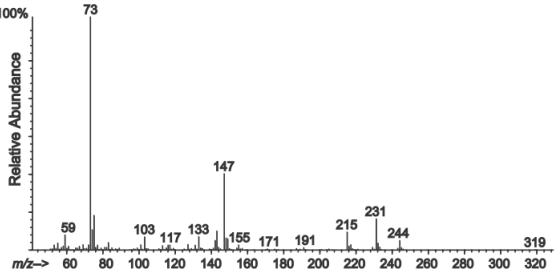
Figure S3. Evidence of SOA growth by acid-catalyzed reactive uptake from wall-loss uncorrected SMPS data. (A) β-IEPOX and (B) δ-IEPOX were introduced into the chamber with heated $N_{2\,(g)}$ from time zero.

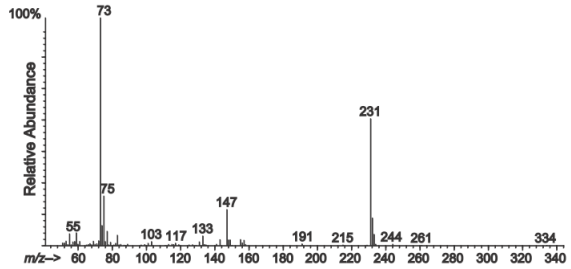
A



B







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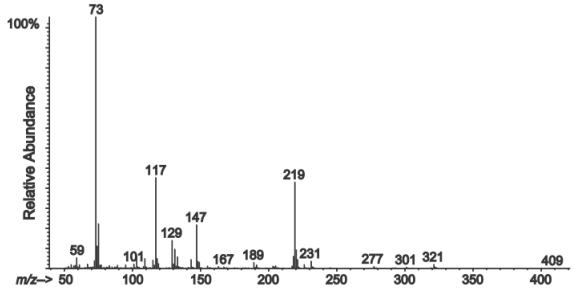


D

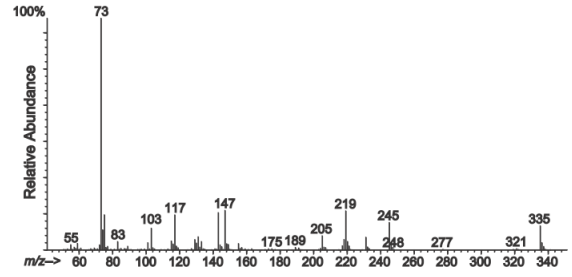
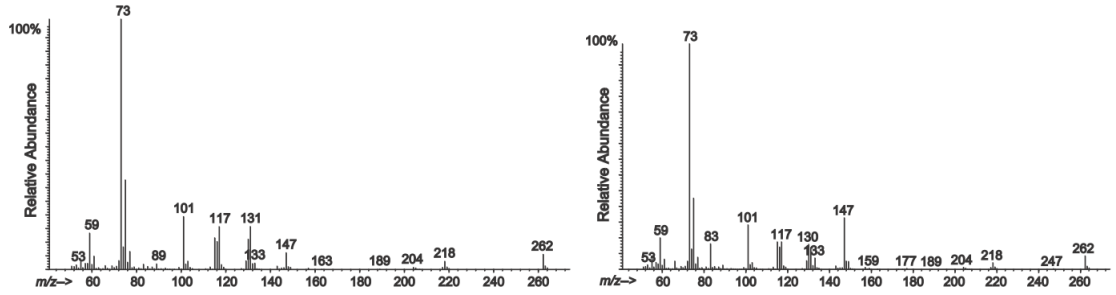


Figure S4. GC/MS EI mass spectra corresponding to reaction products formed in acidic seed aerosol from reactive uptake of *cis*-β-IEPOX. (A) EIC of *m/z* 262: 3-MeTHF-3,4-diol (B) EIC of *m/z* 231: C_5-alkene triols (C) EIC of *m/z* 219: 2-methyltetrols (D) EIC of *m/z* 335: dimers.

A



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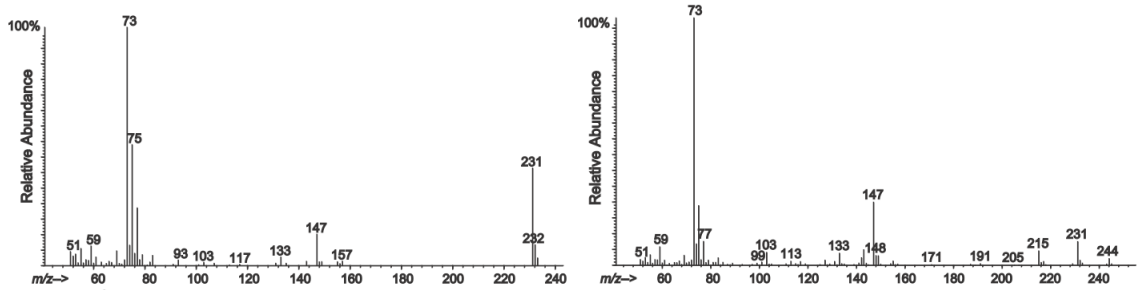

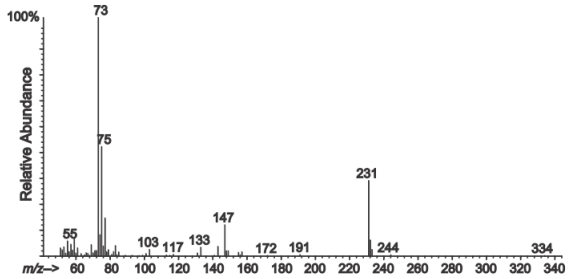

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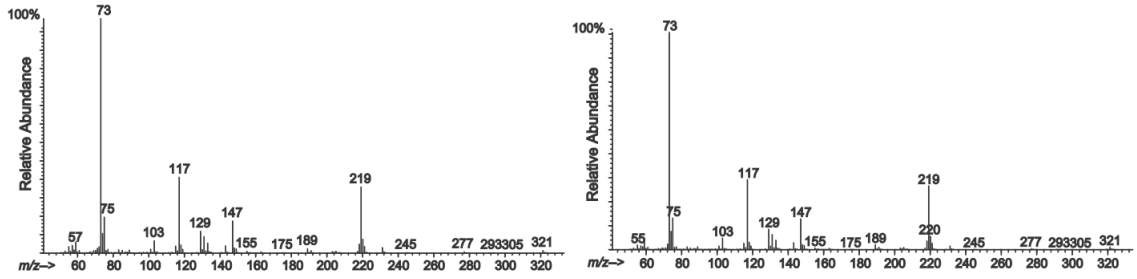


D

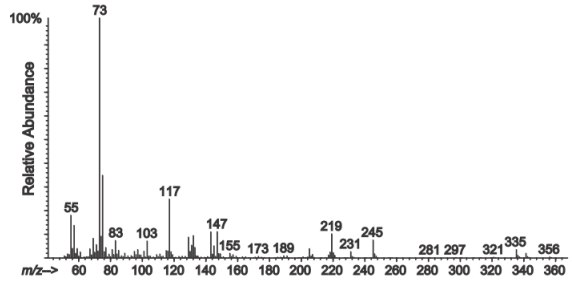
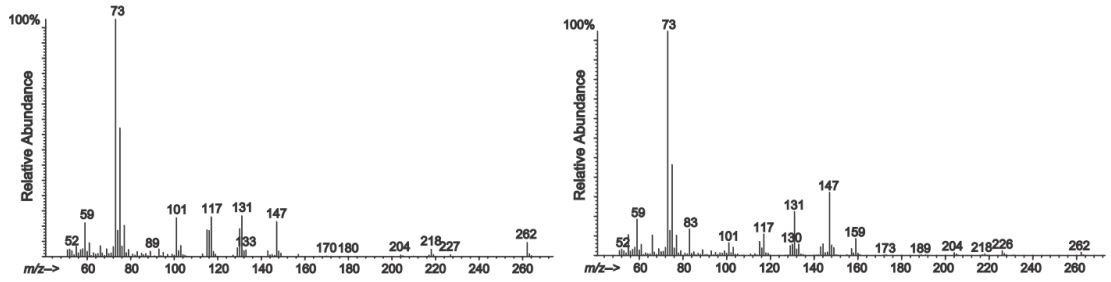


Figure S5. GC/MS EI mass spectra corresponding to aerosol-phase reaction products formed in acidic seed aerosol from reactive uptake of δ-IEPOX. (A) EIC of *m/z* 262: 3-MeTHF-3,4-diols (B) EIC of *m/z* 231: C_5-alkene triols (C) EIC of *m/z* 219: 2-methyltetrols (D) EIC of *m/z* 335: dimers.

A



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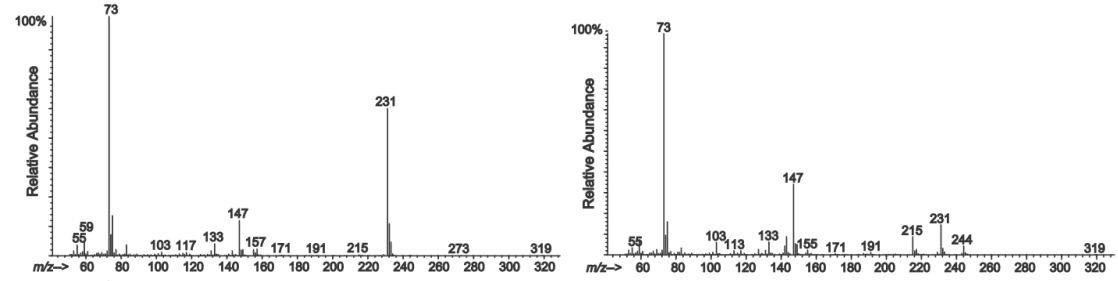

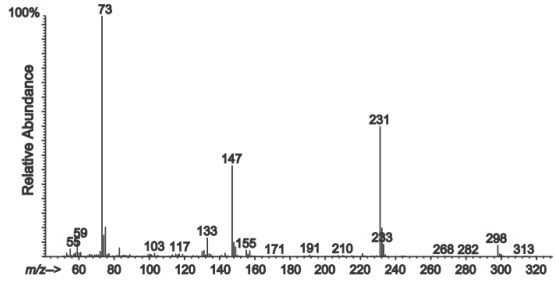

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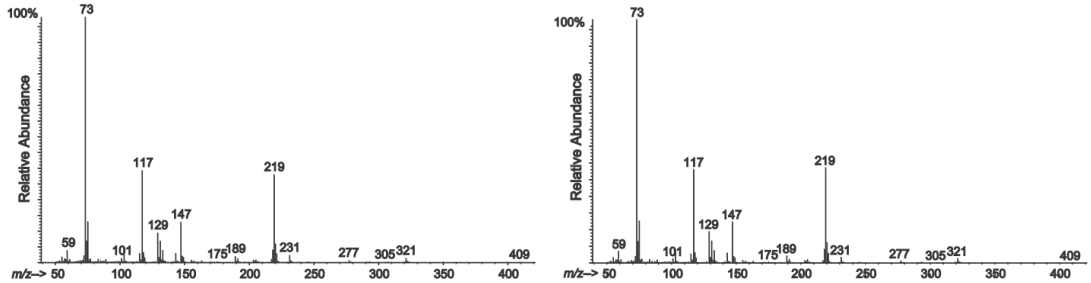

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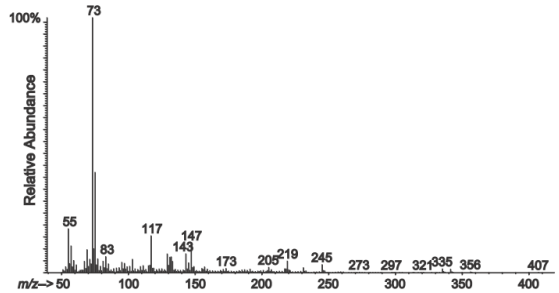
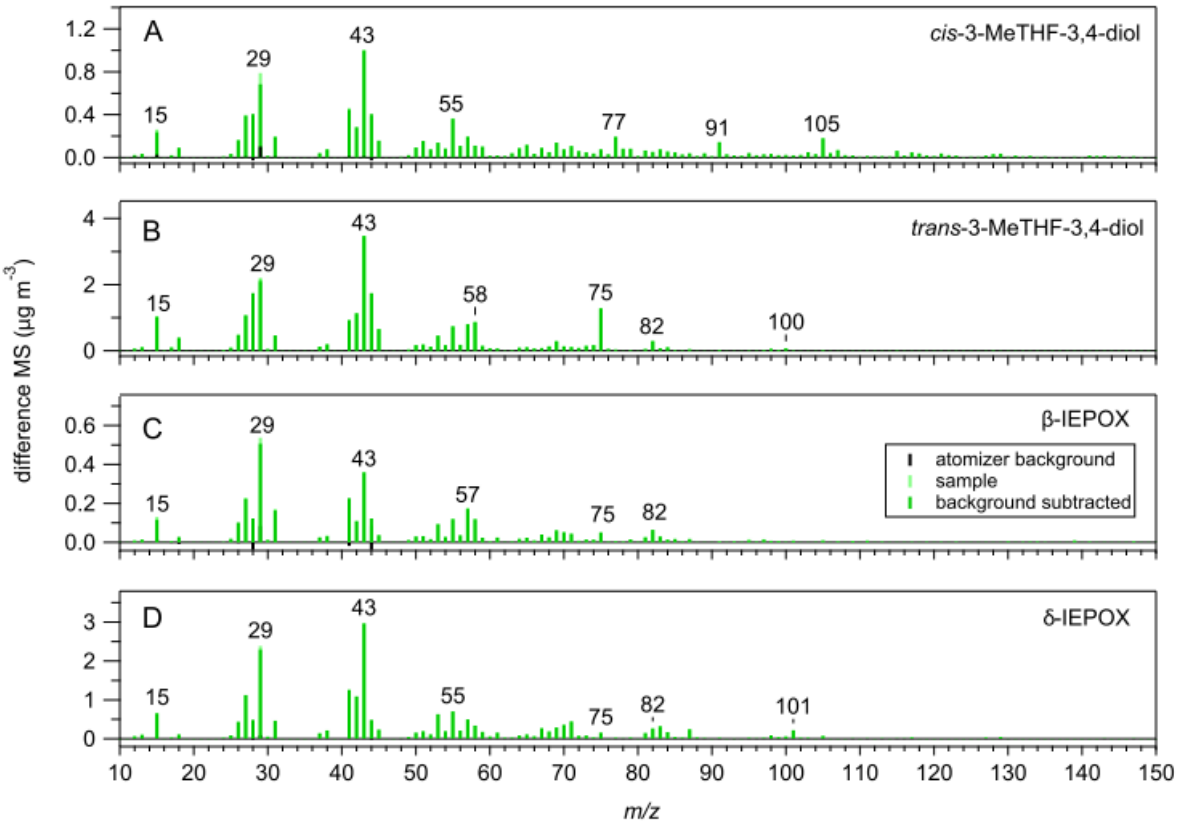


Figure S6. . GC/MS EI mass spectra corresponding to IEPOX-derived reaction products found in a representative field sample collected from the southeastern United States during the summer of 2010. (A) EIC of *m/z* 262: 3-MeTHF-3,4-diols (B) EIC of *m/z* 231: C_5-alkene triols (C) EIC of *m/z* 219: 2-methyltetrols (D) EIC of *m/z* 335: dimers.



91

92 **Figure S7.** HR-AMS unit mass resolution (UMR) mass spectra of synthesized standards (A) *cis*-
93 3-MeTHF-3,4-diol, (B) *trans*-3-MeTHF-3,4-diol, (C) β-IEPOX, and (D) δ-IEPOX. UMR spectra
94 of atomizer background, the synthesized standard, and that of the standard with the atomizer
95 background subtracted are shown.

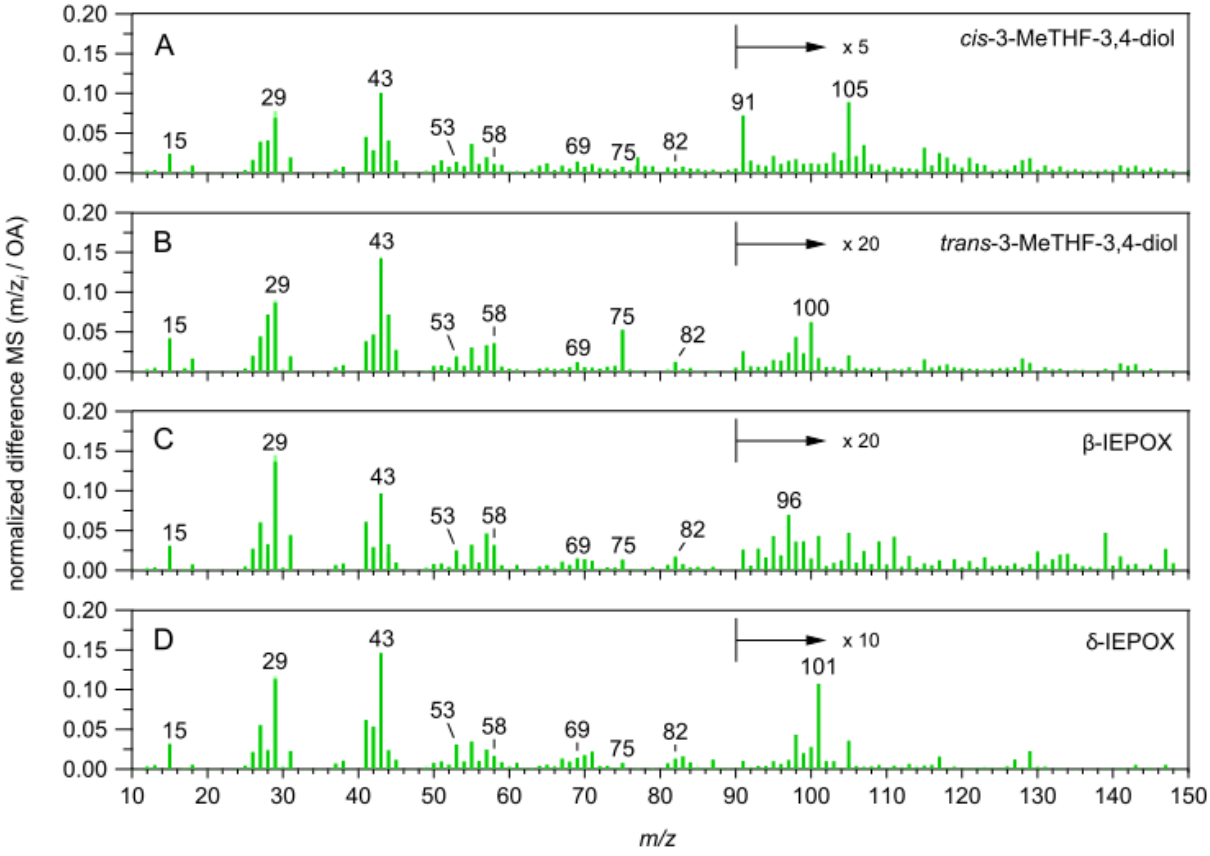


Figure S8. Background corrected HR-AMS unit mass resolution (UMR) mass spectra of synthesized standards (A) *cis*-3-MeTHF-3,4-diol, (B) *trans*-3-MeTHF-3,4-diol, (C) β-IEPOX, and (D) δ-IEPOX that have been normalized by the total organic signal (i.e., m/z_i/org). As such, these spectra show the relative contribution of each fragment to total organic signal. The intensities of *m/z* > 90 have been adjusted to clearly show the contribution and patterns of fragments in that mass range.

Reference:

(1) Adam, W.; Peters, K.; Renz, M., Titanium-Catalyzed Diastereoselective Epoxidations of Ene Diols and Allylic Alcohols with -Hydroperoxy Alcohols as Novel Oxygen Donors. *J. Org. Chem.* **1997,** *62* (10), 3183-3189.

(2) Wu, A.; Cremer, D., Extension of the Karplus Relationship for NMR Spin-Spin Coupling Constants to Nonplanar Ring Systems: Pseudorotation of Tetrahydrofuran. *Int. J. Mol. Sci.* **2003,** *4* (4), 158-192.