Supporting Information

Appearance of strong absorbers and fluorophores in limonene-O_3 secondary organic aerosol due to NH_4^+-mediated chemical aging over long time scales

David L. Bones,[1] Dana K. Henricksen,[1] Stephen A. Mang,[1] Michael Gonsior,[2] Adam P. Bateman,[1] Tran B. Nguyen,[1] William J. Cooper,[2] and Sergey A. Nizkorodov[1]*

*corresponding author: nizkorod@uci.edu

[1] Department of Chemistry, University of California, Irvine, Irvine, California 92697

[2] Department of Environmental and Civil Engineering, University of California, Irvine, Irvine, California 92697

Figure S1. pH dependence of absorption maxima, at 430 and 505 nm, observed in aged limonene SOA (base-10). For each measurement, 2 mL of SOA extract was added to 2mL of NH_4Cl solution. The pH was adjusted by adding HCl or NH_4OH dropwise to the samples. Samples were left to age for 20 hours. The pH was measured using an Oakton pH 1100 meter (Eutech instruments).

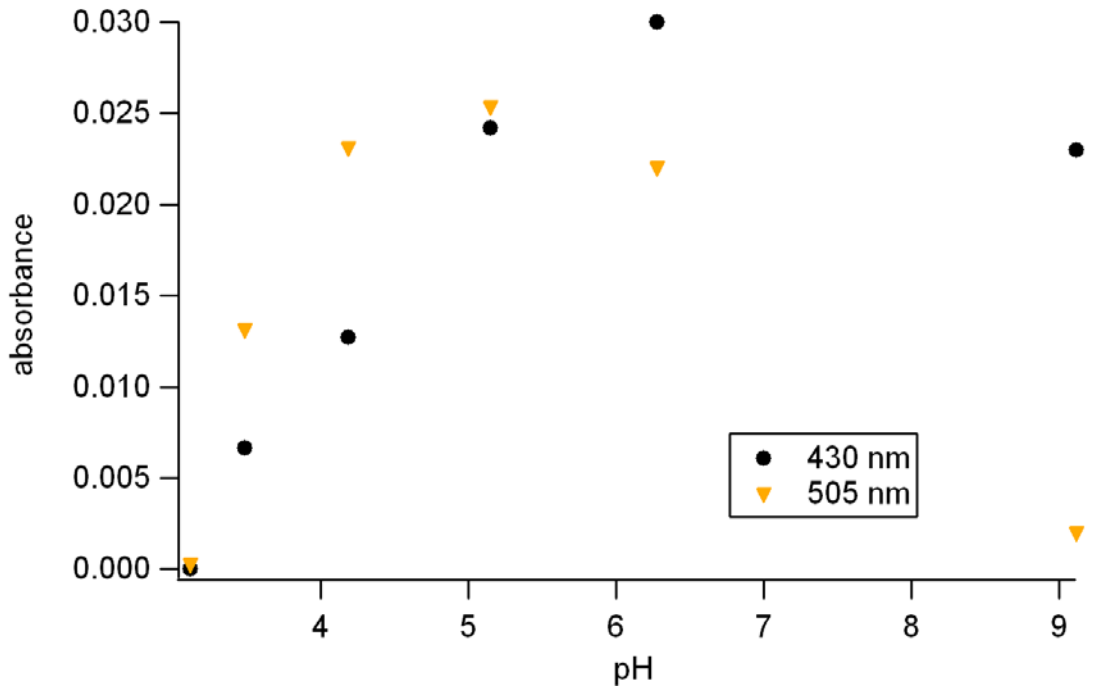

Figure S2. Three dimensional fluorescence excitation-emission spectra of terpene SOA samples extracted into water. Note the different scales (color coded): (a) limonene SOA + arginine; (b) limonene SOA + aspartic acid; (c) limonene SOA + NH_4Cl; (d) limonene SOA + cysteine; (e) β-pinene SOA + NH_4^+; (f) α-pinene SOA + NH_4^+; (g) limonene SOA + NH_4^+ aerosol (aged on foil); (i) myrcene SOA + NH_4^+.

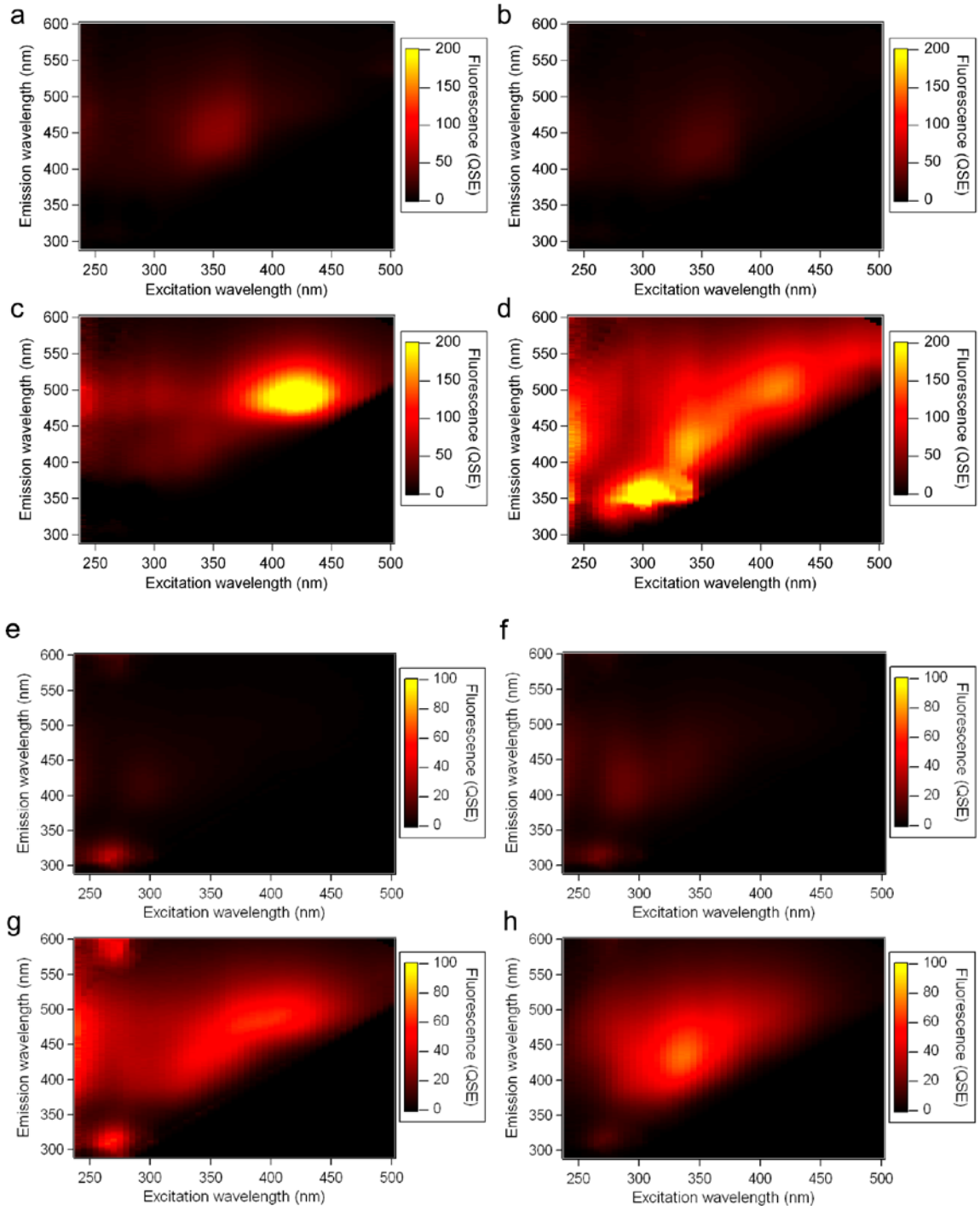

Figure S3. Expanded views of selected regions of mass spectra presented in Figure 7. (a) Fresh limonene SOA, m/z = 350 – 500. (b) Limonene SOA + NH_4^+, m/z = 350 – 500. (c) Fresh limonene SOA, m/z = 400 – 420. (d) Limonene SOA + NH_4^+, m/z = 400 – 420.

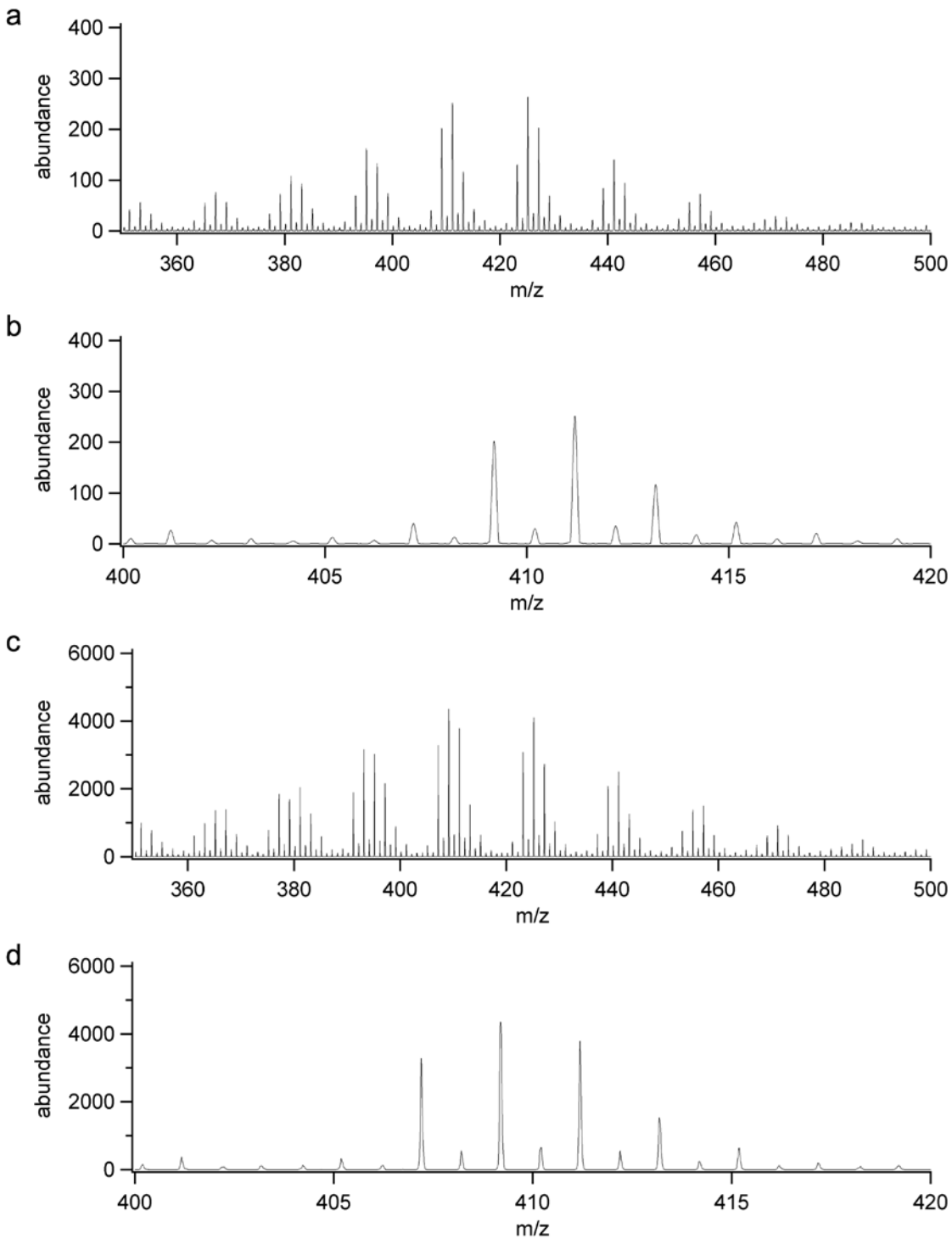
a
abundance
400
300
200
100
0
360
380
400
420
440
460
480
500
m/z
b
abundance
400
300
200
100
0
400
405
410
415
420
m/z
c
abundance
6000
4000
2000
0
360
380
400
420
440
460
480
500
m/z
d
abundance
6000
4000
2000
0
400
405
410
415
420
m/z

Figure S4. FTIR spectra of fresh and aged limonene SOA samples collected on ZnSe windows. The similarity of these spectra confirms that the major functional groups in SOA remain the same despite the fact that SOA changes color.

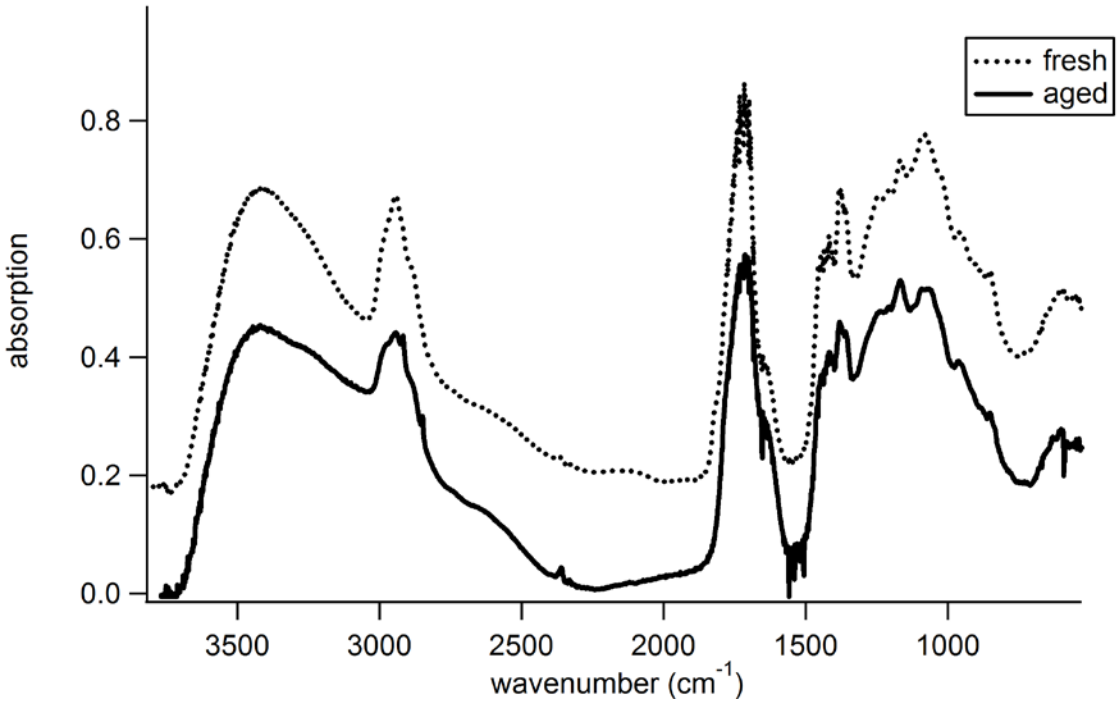

Figure S5. 2-D HMQC (^{1}H-^{13}C correlation) NMR of limonene SOA, aged 1 day then extracted in $CDCl_3$.

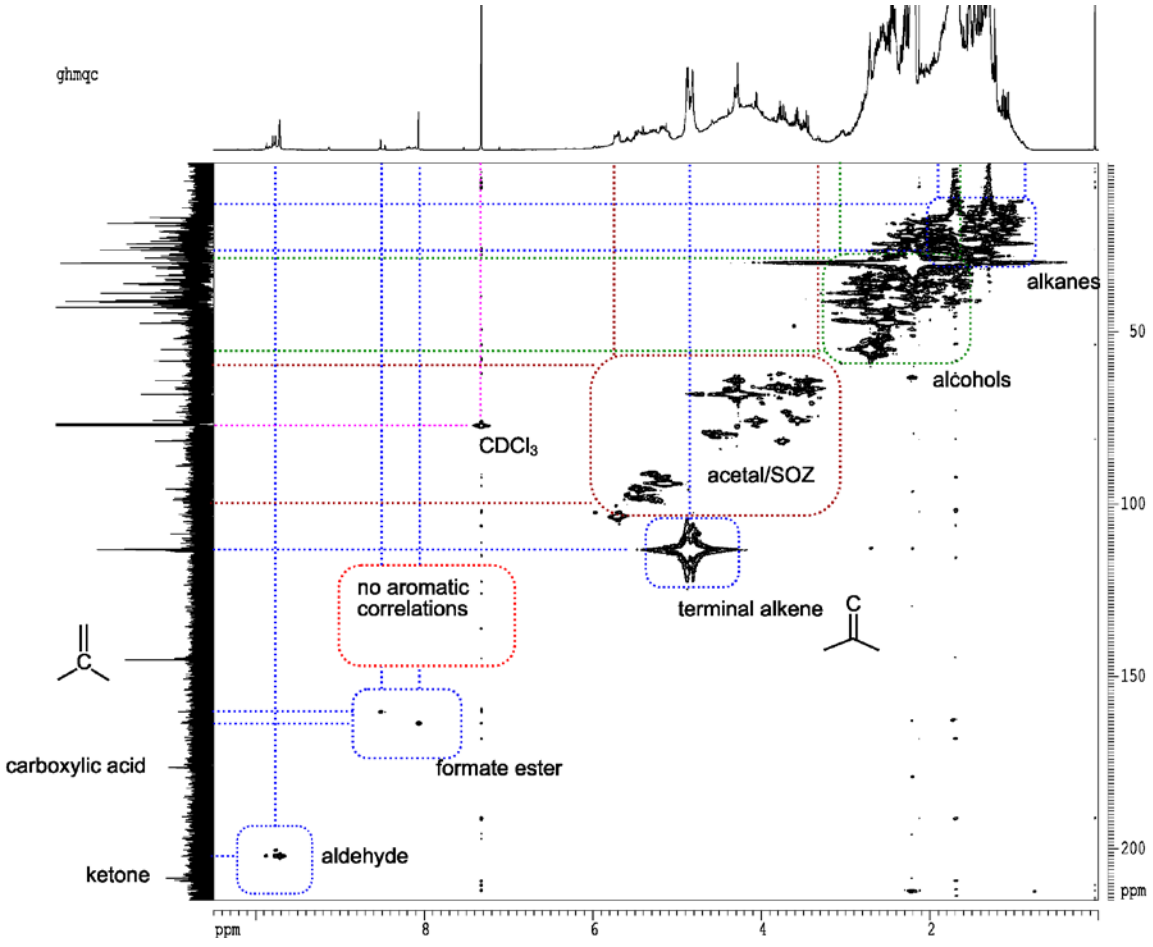

Figure S6. 2-D HMQC (^{1}H-^{13}C correlation) NMR of limonene SOA + NH_4^+ aerosol, aged 1 day then extracted in $CDCl_3$.

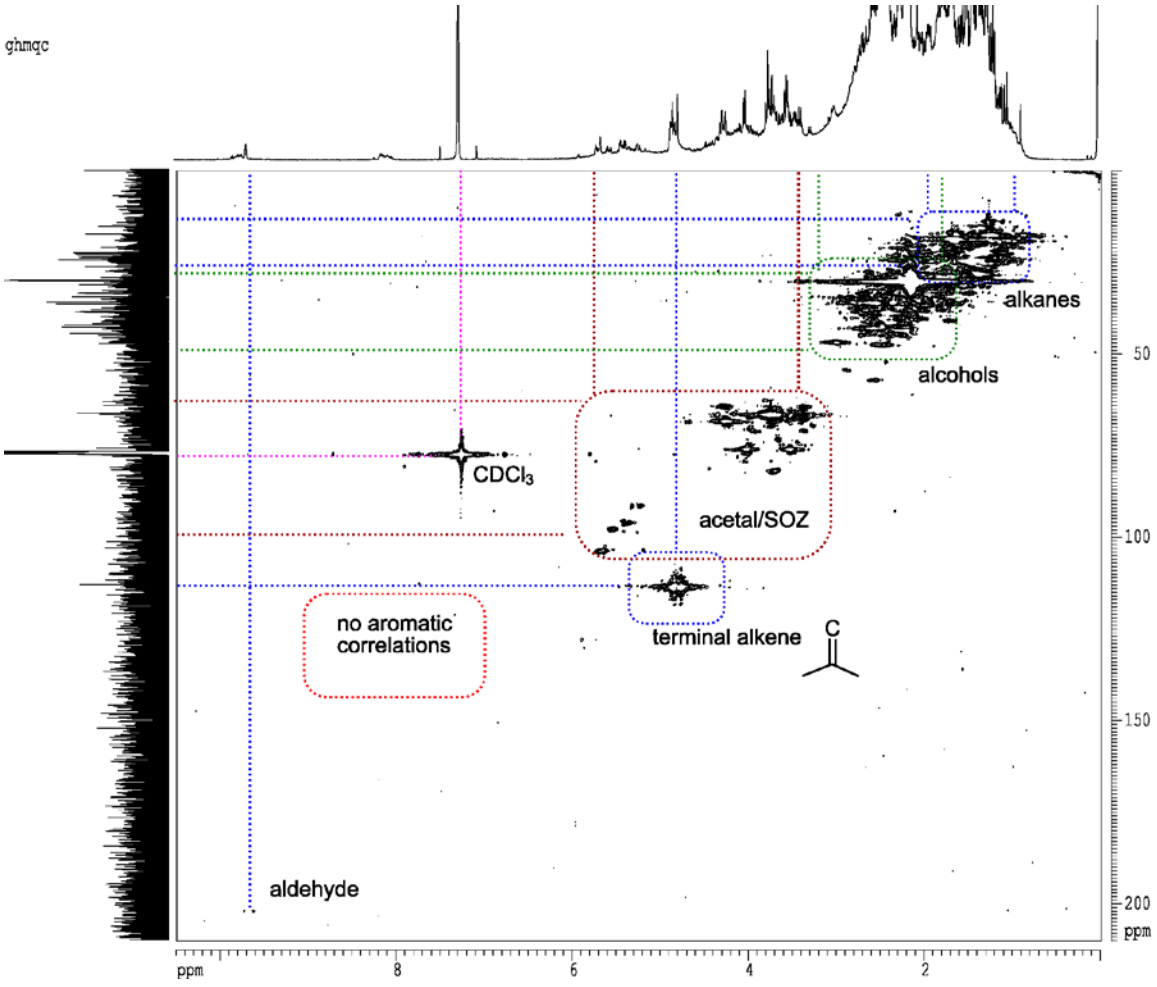

Figure S7. The absorption Ångström exponent can be extracted from the slope of the curves resulting from plotting the natural logarithm of wavelength versus the natural logarithm of absorbance, for fresh and aged aqueous extracts of limonene-O_3 SOA.