Supplementary Information:

Secondary organic aerosol formation from photooxidation of acyclic terpenes in an oxidation flow reactor

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Text S1: Oxidation Flow Reactor OH Exposure Calibration

Off-line calibration of the OH exposure in the OFR was performed by changing the UV light intensity through stepping the lamp voltage on the computer software. This experiment was performed under a similar range of relative humidity and O_3 concentration used in formal SOA experiments. Toluene was selected as an OH tracer gas since the fate of toluene reacting with O_3 is negligible compared to the reaction with OH. The toluene mixing ratio at the OFR inlet and outlet was measured each time the lamp setting was changed and are presented in the table S1. The OH exposure was calculated by applying the known reaction rate constant of OH with toluene ($k_{\mathrm{OH,toluene}}$= 5.63e-12 cm^3 molec^{-1} s^{-1})[1] as:

$$OH\ \text{exposure} = \frac{-1}{k_{OH,\ toluene}} \times \ln\left(\frac{\left[VOC_f\right]}{\left[VOC_i\right]}\right) \qquad \text{(Equation S1)}$$

where $\mathrm{VOC_{inlet}}$ and $\mathrm{VOC_{outlet}}$ represents inlet VOC and outlet VOC mixing ratio, respectively.

Text S2: VOC sample collection at the OFR inlet

For SOA mass yield experiments, duplicate VOC samples were collected onto stainless steel absorbent cartridges (multibed Carbograph/Tenax TA; Markes International, Inc.) at OFR inlet. All acyclic terpenes investigated in this study are expected to be fully reacted in the OFR when the inlet mixing ratio is less than 400 ppb at the OH exposure corresponding to the highest SOA mass yield. We have tested this hypothesis by increasing the inlet mixing ratio around 400 ppb and collected duplicate VOC samples both at OFR inlet and outlet. Results collected at the OFR outlet were carefully checked to make sure no VOC were detected in the cartridges analyzed with the TD-GC-MS. For all acyclic terpenes experiments, the inlet mixing ratio remained smaller than 99 ppb.

Text S3: Volatility and viscosity prediction

The volatility distribution for each SOA system is calculated based on the method developed by Li et al.[66] The equation is shown below:

$$\log_{10} C_0 = \left(n_C^0 - n_C\right)b_C - n_O b_O - 2\frac{n_C n_O}{n_C + n_O} b_{CO} \quad \text{(Equation S2)}$$

where n_C^O is the reference carbon number, and n_C and n_O refer to the number of C and O element, respectively, obtained from HRMS data. The values for parameters n_C^O, b_C, b_O, and b_{CO} are 22.6, 0.4481, 1.656, and -0.779, respectively, which is estimated for reference CHO compounds from Li et al.[67]

The viscosity for each SOA was determined following the methods from DeRieux et al.[68] In brief, the glass transition temperature ($T_{g,i}$), defined as a temperature range where phase transition between amorphous solid and semisolid states happens,[69] can be estimated based on the molecular composition from HRMS data by using the following equation:

$$T_{g,i} = \left(n_C^0 + \ln\left(n_C\right)\right)b_C + \ln\left(n_H\right)b_H + \ln\left(n_C\right)\ln\left(n_H\right)b_{CH} + \ln\left(n_O\right)b_O + \ln\left(n_C\right)\ln\left(n_O\right)b_{CO} \quad \text{(Equation S3)}$$

where n_C, n_H, and n_O are the numbers of carbon, hydrogen, and oxygen atoms, respectively. The values of parameters n_C^0, b_C, b_H, b_{CH}, b_O, and b_{CO} were 12.13, 10.95, -41.82, 21.61, 118.96, and -24.38, respectively, for reference CHO compounds.[68] Based on the Gordon–Taylor equation, the glass transition temperature of the SOA under dry conditions ($T_{g,org}$) are predicted by assuming the Gordon-Taylor constant (κ_{GT}) as 1 [70] for each organic component as the equation shown below:

$$T_{g,org} = \sum \omega_i T_{g,i} \quad \text{(Equation S4)}$$

where ωi represents the mass fraction of an organic compound I from HRMS data. The water content in SOA is determined using the effective hygroscopicity parameter (κ).[71] Based on Zhao et al.,[72] the κ values is derived from cloud condensation nuclei measurements of 0.15. Following the Gordon–Taylor equation, Tg of organic–water mixtures ($T_{g,mix}$) is estimated using a Gordon–Taylor constant (k_{GT}) of 2.5 [69,73]:

$$T_{g,\,\mathrm{mix}} = \frac{\left(1 - w_{org}\right)T_{g,H_2O} + \frac{1}{k_{GT}} w_{\mathrm{org}} T_{g,ORG}}{\left(1 - w_{org}\right) + \frac{1}{k_{GT}} w_{\mathrm{org}}}$$ (Equation S5)

where T_{g,H_2O} and $T_{g,org}$ refer to the glass transition temperatures of water and SOA organics and w_{org} denotes the mass fraction of the organic compound. The w_{org} could be calculated by the mass concentration of water (m_{H_2O}) and SOA (m_{SOA}) as $w_{org} = \frac{m_{SOA}}{(m_{SOA} + m_{H_2O})}$. The m_{H_2O} can be estimated using the effective hygroscopicity factor (κ) [57] with the following equation:

$$m_{H_2O} = \frac{\kappa \rho_w m_{SOA}}{\rho_{SOA}\left(\frac{1}{a_w} - 1\right)}$$ (Equation S6)

where the density of water (ρ_w) is 1 g cm^{-3}; the density of SOA is set to 1.3 g cm^{-3};[57–59] and the water activity, a_w, is calculated as a_w = RH/100.[74]

The temperature-dependence of viscosity is estimated with Vogel-Tammann-Fulcher (VTF) equation as function of $T_{g,mix}$:

$$\log(\eta) = -5 + 0.434\frac{T_0 D_f}{T - T_0}$$ (Equation S7)

where T_0 is the Vogel temperature calculated as $T_0 = \frac{39.17 T_g}{D_f + 39.17}$, assuming viscosity of 10^{12} Pa s at the glass transition temperature.[75] The fragility parameter (D_f) is set to 10 [75] for representing deviation of the temperature dependence of viscosity from the Arrhenius behavior [68,76] and the T is the temperature at which measurements were conducted, 291K.

Figure S1. Fate of RO_2 and HO_2 radicals determined in OFR experiments for β-myrcene, β-ocimene and linalool. RO_2 and HO_2 mixing ratios were estimated by OFR RO_2 Fate Estimator v1.0.[2]

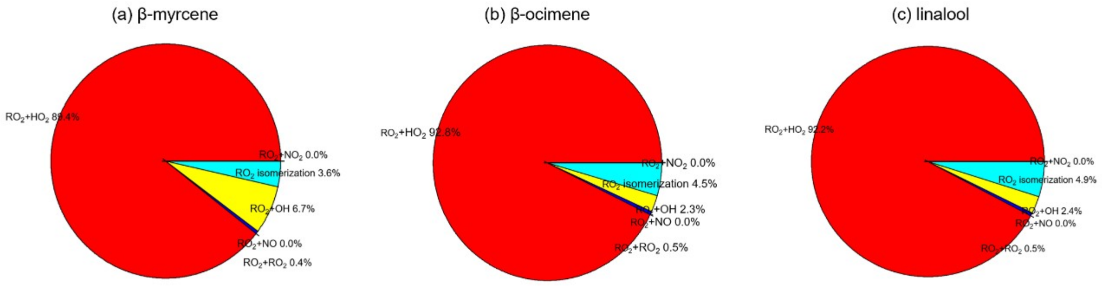


Figure S2. Relationship between the number of peaks and accumulated normalized intensities for α-pinene, β-myrcene, β-ocimene and linalool SOA based on HR-MS data analysis.

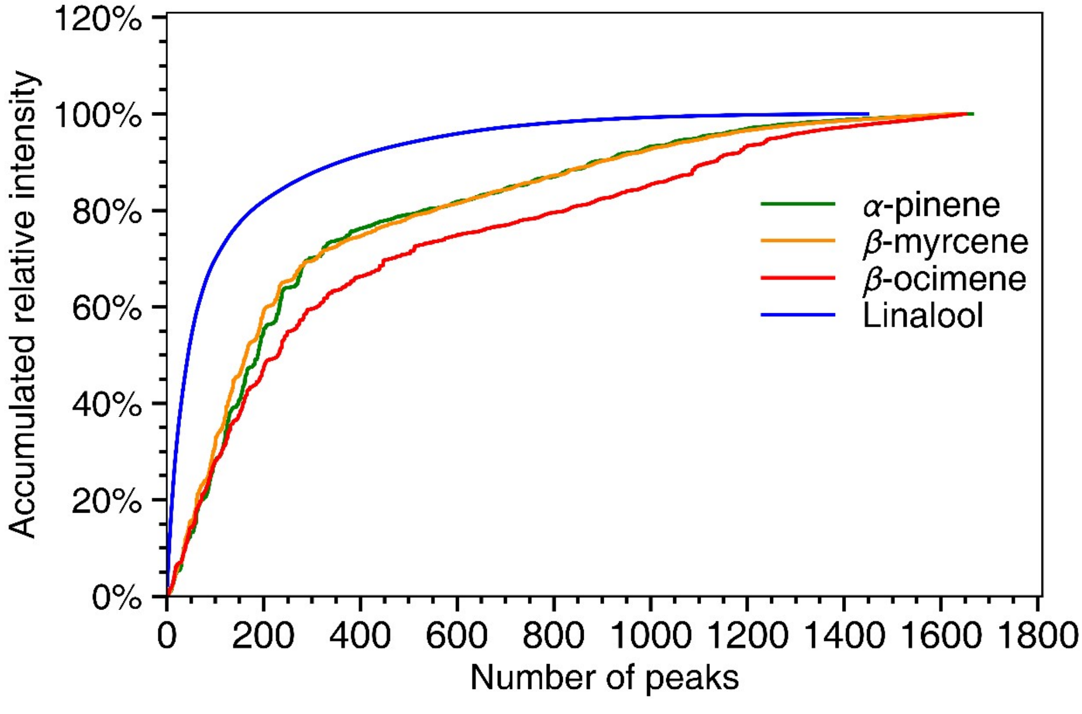


Figure S3. Gas-phase oxidation schemes for β-myrcene from GECKO-A model simulation. Note: this is not the full reaction mechanism but only include up to fourth generation oxidation products.

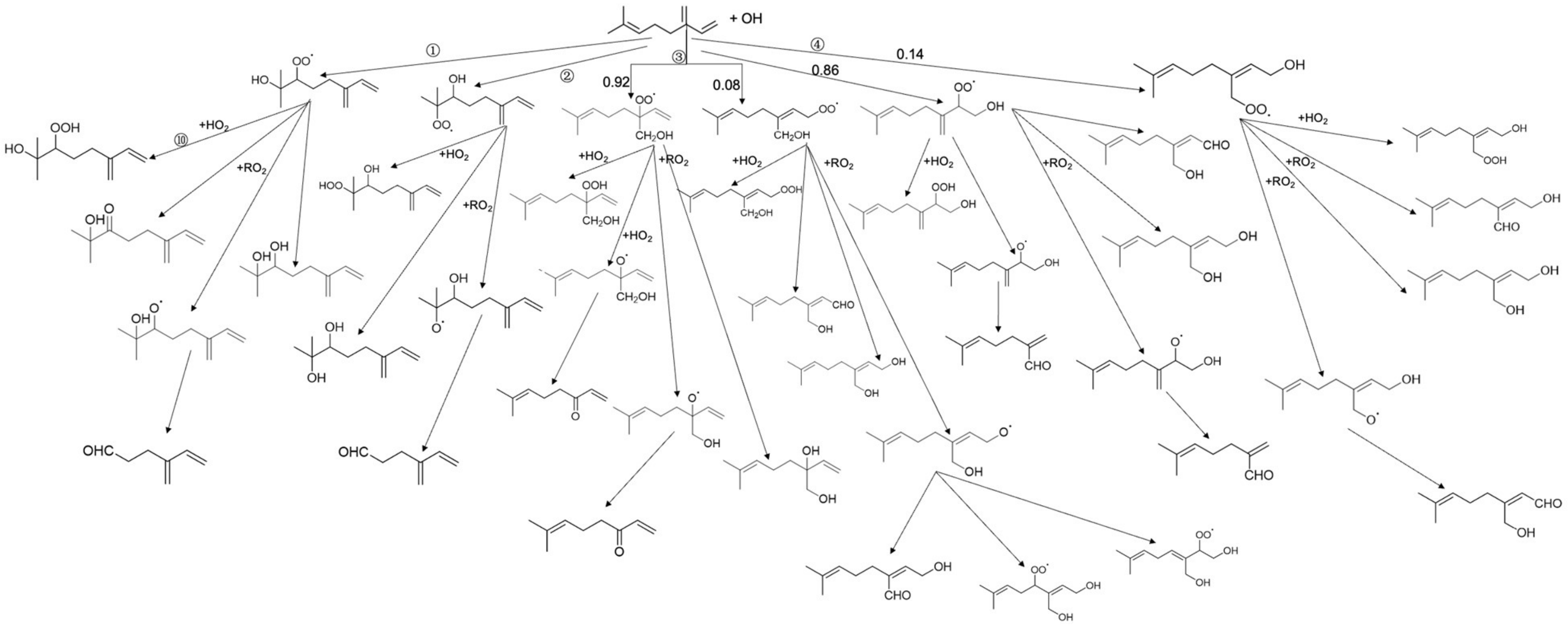


Figure S4. Gas-phase oxidation schemes for β-ocimene from GECKO-A model simulation. Note: this is not the full reaction mechanism but only include up to fourth generation oxidation products.

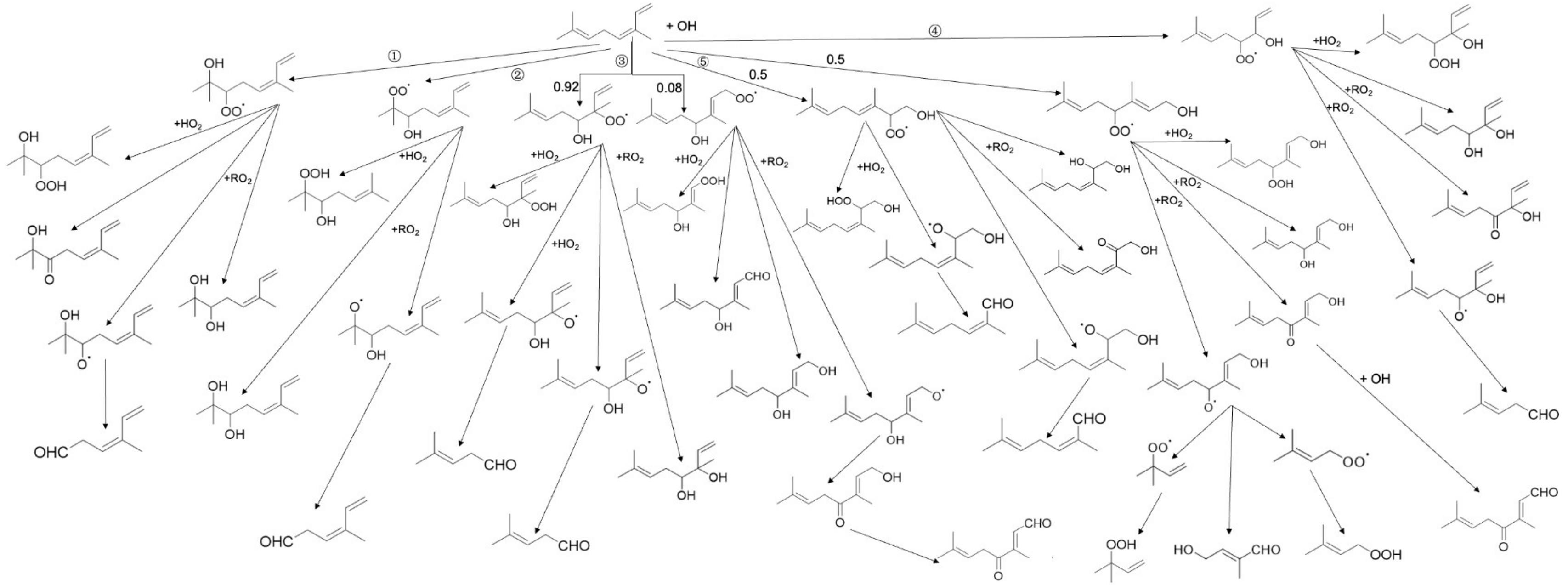


Figure S5. Gas-phase oxidation schemes for linalool from GECKO-A model simulation. Note: this is not the full reaction mechanism but only include up to fourth generation oxidation products.

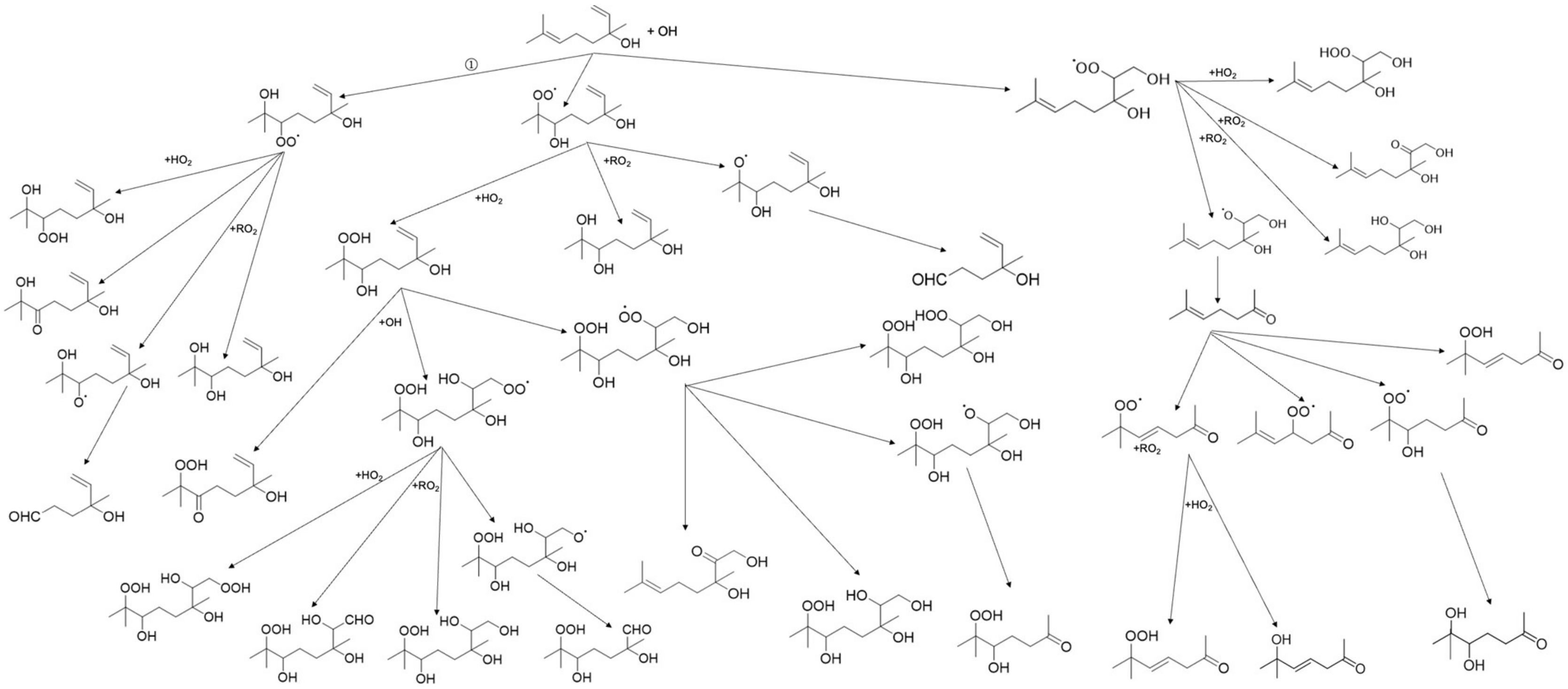


Figure S6. Elemental composition and volatility distribution for α-pinene, β-myrcene, β-ocimene and linalool SOA based on HR-MS data analysis. The sizes of the points correspond to the intensity of signal.

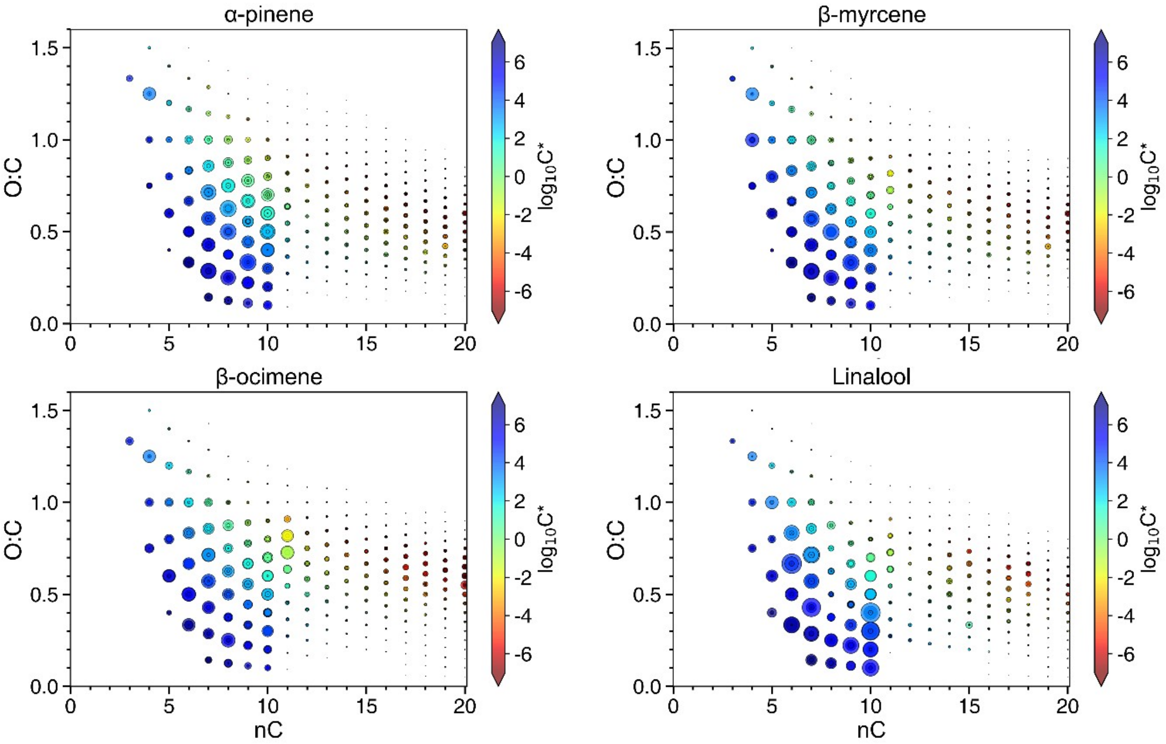


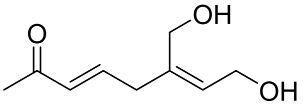
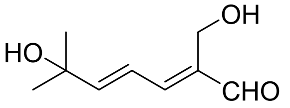
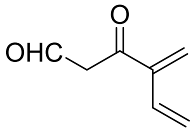
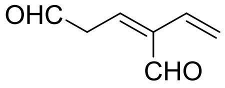
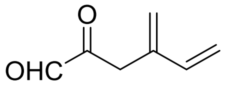
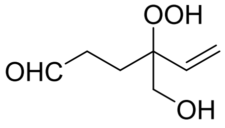
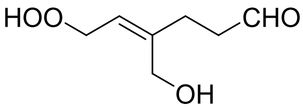
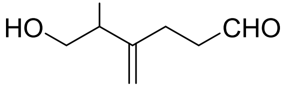
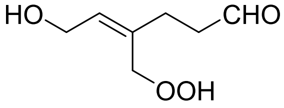
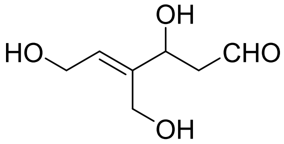
Table S1. OFR condition, inlet and outlet toluene mixing ratios for OH exposure calibration experiments at a constant RH with three lamp settings.

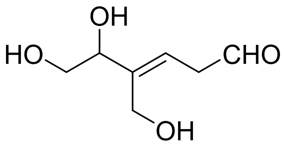
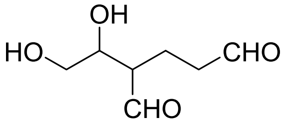
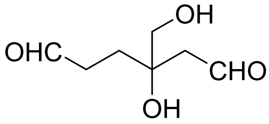
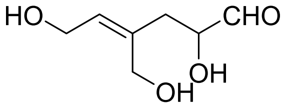
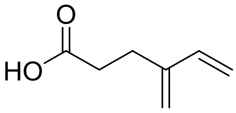
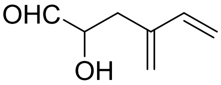
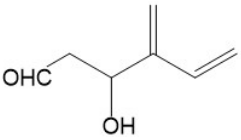
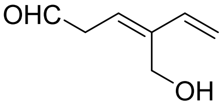
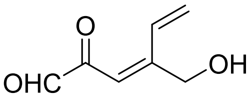
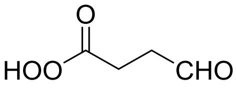
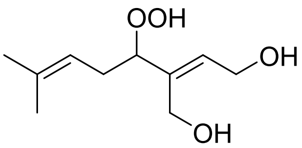
Irradiance ($\mu W/cm^2$)	RH (%)	Initial VOC (ppb)	Final VOC (ppb)	OH_{exp} (molec s cm^{-3})
1.48	60	641	73	3.87e+11
12.15		655	22	5.99e+11
51.17		782	10	1.01e+12

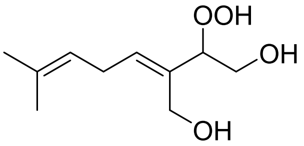
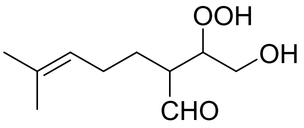
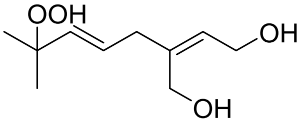
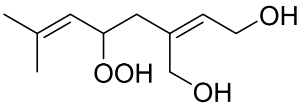
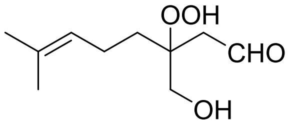
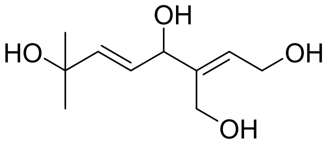
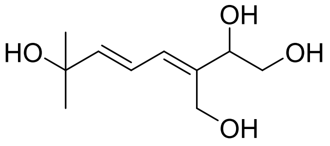
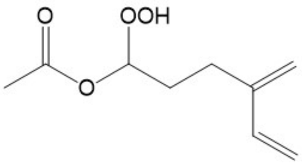
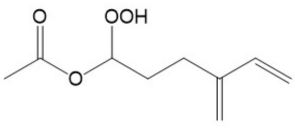
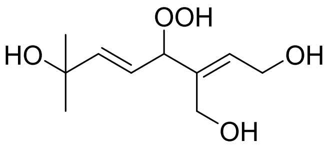
Table S2. Summary of experimental condition for SOA filter collection experiments.

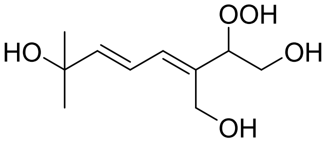
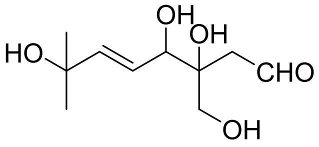
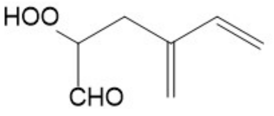
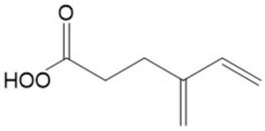
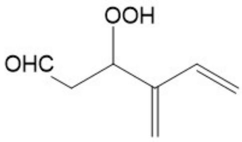
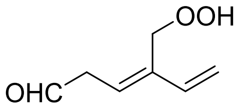
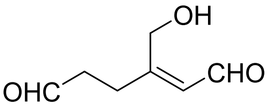
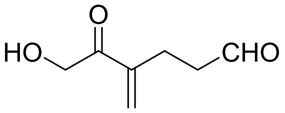
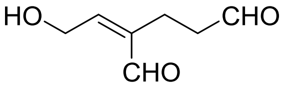
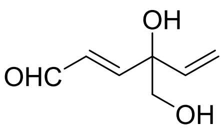
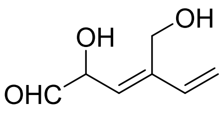
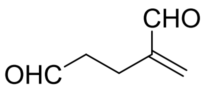
Experiment	**Precursor**	**Introduced VOC (ppb)**	**OH exposure (molec s cm^{-3})**	**RH (%)**	**O_3 (ppm)**	**SOA mass concentration (μg/m^3)**	**RO_2/HO_2 ratio**
SOA filter collection	α-pinene		5.5 ×10^{11}	60±3	6.5	50	□
	β-myrcene	29	4.3 ×10^{11}	61±2	2.5	45	0.67
	β-ocimene	70	4.1 ×10^{11}	62±2	2.1	48	0.77
	linalool	95	4.06 ×10^{11}	61±2	1.8	49	0.77

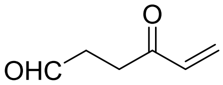
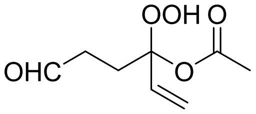
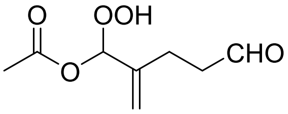
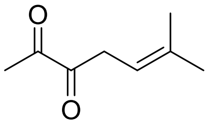
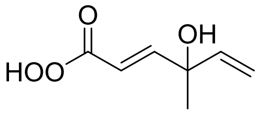
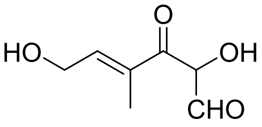
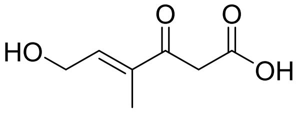
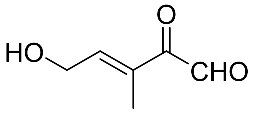
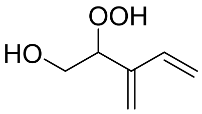
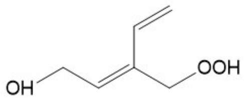
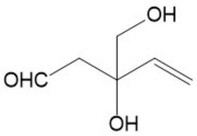
Table S3. Oxidation products detected by HR-MS from both ESI (-) and ESI (+) mode, and the corresponding chemical structure from GECKO-A for SOA formed from α-pinene, β-myrcene, β-ocimene and linalool.

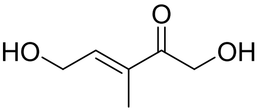
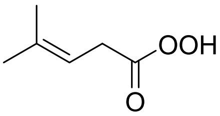
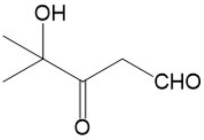
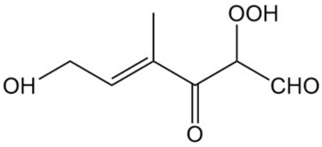
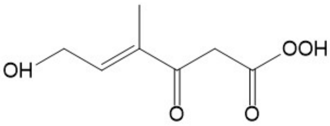
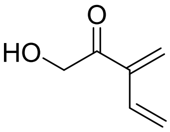
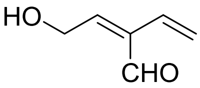
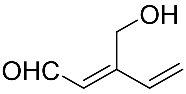
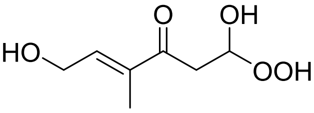
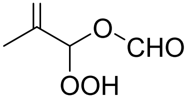
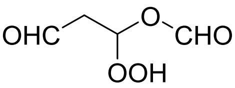
Sample	MW (Da)	Formula	Molecular structure from GECKO-A
β-myrcene	170.09	C9H14O3	 
	124.05	C7H8O2	  
	160.07	C7H12O4	    

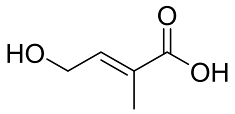
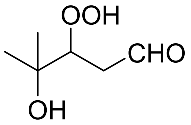
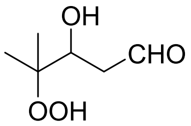
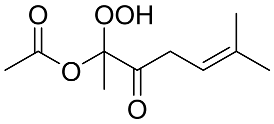
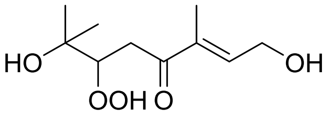
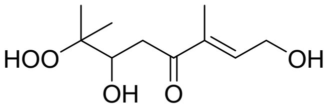
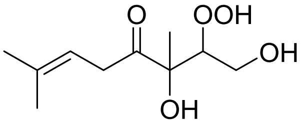
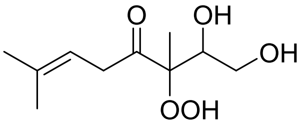
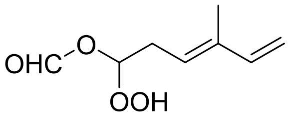
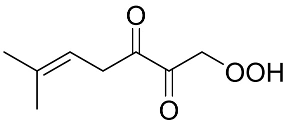
			   
	126.07	C7H10O2	   
	140.05	C7H8O3	
	118.03	C4H6O4	
	202.12	C10H18O4	

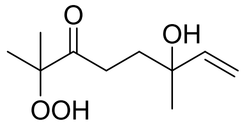
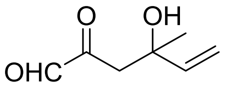
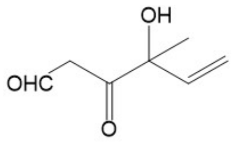
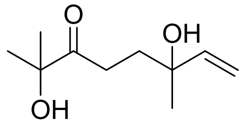
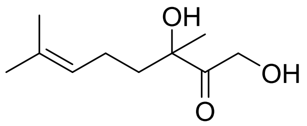
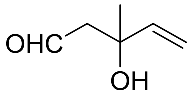
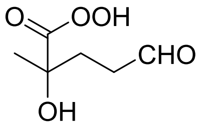
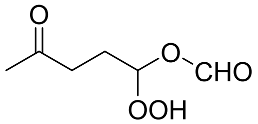
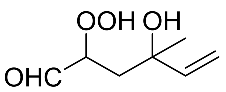
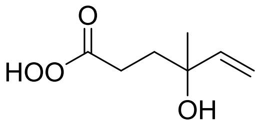
			      
	186.09	C9H14O4	 
	218.12	C10H18O5	

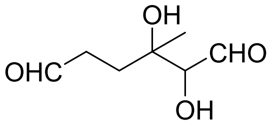
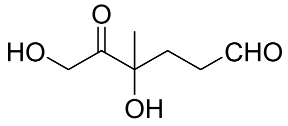
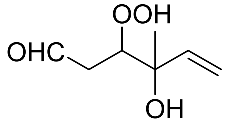
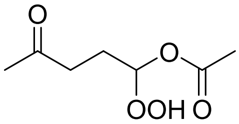
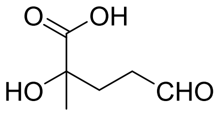
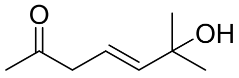
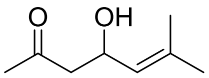
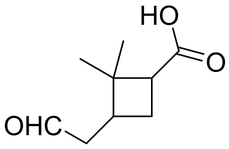
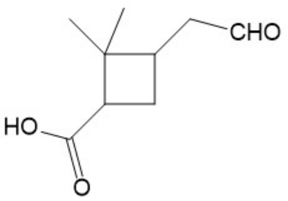
	142.06	C7H10O3	           

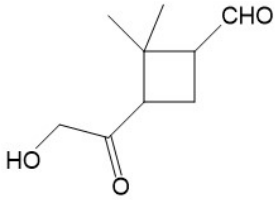
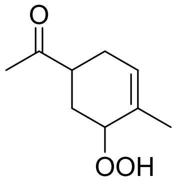
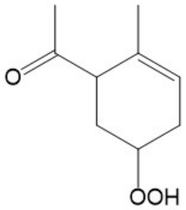
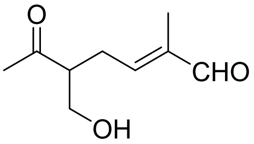
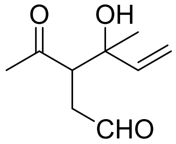
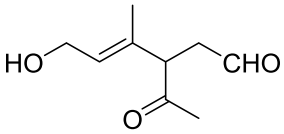
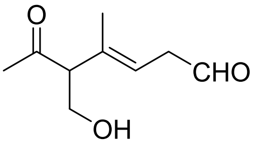
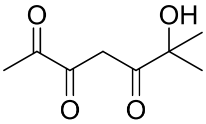
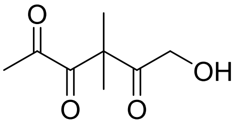
	112.05	C6H8O2	
	188.07	C8H12O5	 
β-ocimene	140.08	C8H12O2	
	158.06	C7H10O4	  
	128.05	C6H8O3	
	130.06	C6H10O3	  

			  
	174.05	C7H10O5	 
	112.05	C6H8O2	  
	176.07	C7H12O5	
	134.02	C4H6O5	 

	116.05	$C_5H_8O_3$	
	148.07	$C_6H_{12}O_4$	 
	216.10	$C_{10}H_{16}O_5$	
	218.12	$C_{10}H_{18}O_5$	   
	172.07	$C_8H_{12}O_4$	 

Linalool	202.12	$C_{10}H_{18}O_4$	
	142.06	$C_7H_{10}O_3$	 
	186.13	$C_{10}H_{18}O_3$	 
	114.07	$C_6H_{10}O_2$	
	162.05	$C_6H_{10}O_5$	 
	160.07	$C_7H_{12}O_4$	 

			  
	176.07	C7H12O5	
	146.06	C6H10O4	
	142.10	C8H14O2	 
α-pinene*	170.10	C9H14O3	 

			      
	172.07	C8H12O4	 
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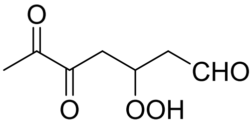
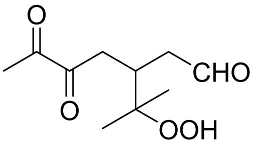
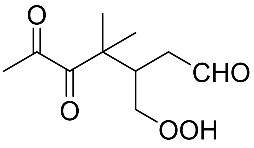
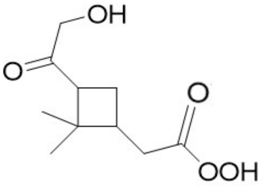
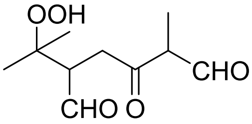
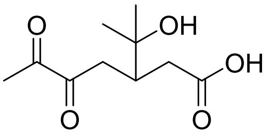
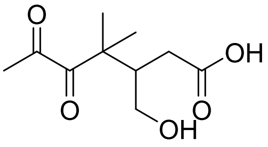
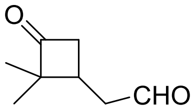
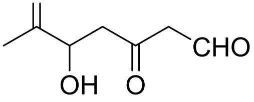
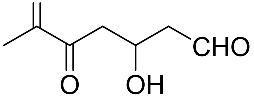
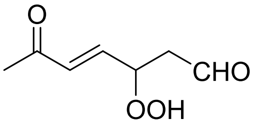
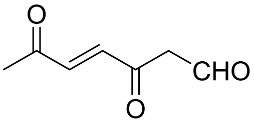
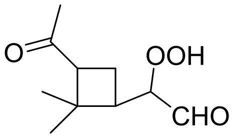
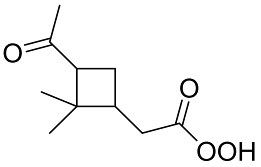
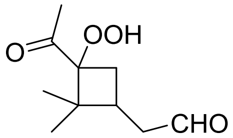
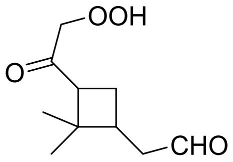
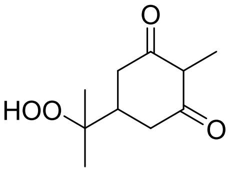
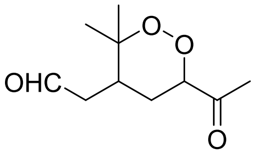
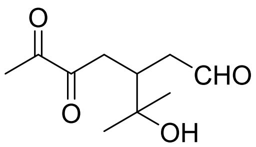
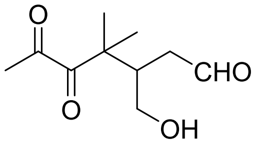
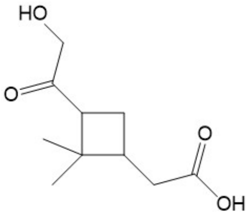
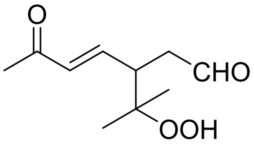
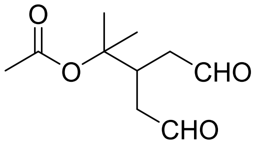
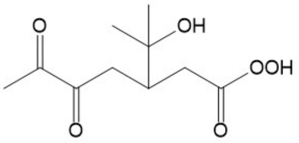
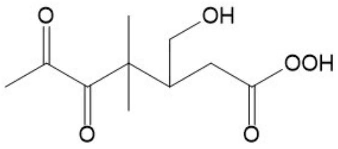
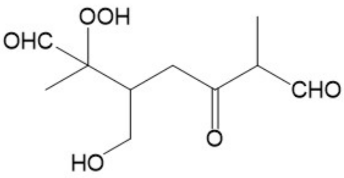
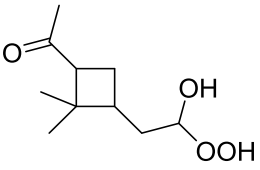
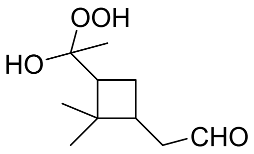
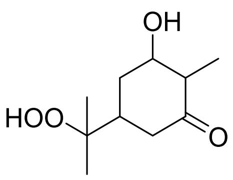
	216.10	C10H16O5	      
	140.08	C8H12O2	
	158.06	C7H10O4	 

			
	140.05	C7H8O3	
	200.10	C10H16O4	       

	232.10	C10H16O6	     
	202.12	C10H18O4	  

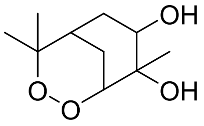
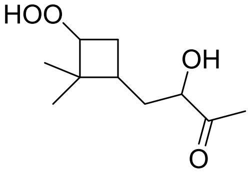
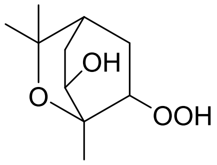
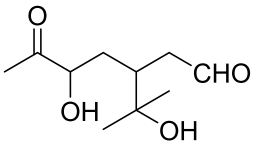
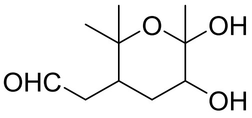
			    

Table S4. Summary of the fate of each VOC precursors from reactions with OH and O_3 for SOA filter collection experiments. [1,3-6]

Experiment	**Precursor**	**Introduced VOC** (ppb)	**K_{OH+VOC}** (10^{-10} cm^3 $molec^{-1}$ s^{-1})	**K_{O3+VOC}** (10^{-16} cm^3 $molec^{-1}$ s^{-1})	**Lifetime_OH (s)**	**Lifetime_O_3 (s)**
SOA filter collection	α-pinene	99	52.3	1.07	0.1	4.47
	β-myrcene	29	3.34	4.44	0.9	37.2
	β-ocimene	70	3.03	4.44	1	37.2
	linalool	95	1.70	4.30	0.01	55.1

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