



Supplement of

Aqueous secondary organic aerosol formation from the direct photosensitized oxidation of vanillin in the absence and presence of ammonium nitrate

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24 **Section S1. Materials.**

25
26 Initial solutions of 0.1 mM vanillin (VL, Acros Organics, 99%, pure), 0.1 mM guaiacol (GUA,
27 Sigma Aldrich, $\geq 98.0\%$), 1 mM ammonium nitrate (AN, Acros Organics, 99+%, for analysis),
28 and 1 mM sodium nitrate (SN, Sigma-Aldrich, $\geq 99.5\%$) were prepared in Milli-Q water. The pH
29 values of the samples were adjusted using sulfuric acid (H_2SO_4 ; Acros Organics, ACS reagent, 95%
30 solution in water).

31
32 **Section S2. UV-Vis spectrophotometric analyses.**

33
34 The absorbance changes for all samples were characterized using a UV-Vis
35 spectrophotometer (UV-3600, Shimadzu Corp., Japan). The absorbance values from 200 to 700
36 nm were recorded instantly after sample collection, and measurements were done in triplicate.
37 Absorbance enhancements were calculated as the change in the integrated area of absorbance from
38 350 to 550 nm. The increase of light absorption at this wavelength range, where VL and GUA did
39 not initially absorb light, suggests the formation of light-absorbing compounds (Zhou et al., 2019).

40
41 **Section S3. UHPLC-PDA analyses.**

42
43 An ultra-high performance liquid chromatography system (UHPLC, Waters Acquity H-
44 Class, Waters, Milford, USA) coupled to a photodiode array (PDA) detector (Waters, Milford,
45 USA) was used for the quantification of VL and GUA concentrations. The drawn solutions were
46 first filtered through a 0.2 μm Chromafil[®]Xtra PTFE filter (Macherey-Nagel GmbH & Co. KG,
47 Germany). Briefly, the separation of products was performed using an Acquity HSS T3 column
48 (1.8 μm , 2.1 mm \times 100 mm; Waters Corp.). The column oven was held at 30 °C, and the
49 autosampler was cooled at 4 °C. The injection volume was set to 5 μL . The binary mobile phase
50 consisted of A (water) and B (acetonitrile). The gradient elution was performed at a flow rate of

51 0.2 mL/min: 0–1 min, 10% eluent B; 1–25 min, linear increase to 90% eluent B; 25–29.9 min,
52 hold 90% eluent B; 29.9–30 min, decrease to 10% eluent B; 30–35 min, re-equilibrate at 10%
53 eluent B for 5 min. Standard solutions of VL and GUA ranging from 10 to 130 μM were analyzed
54 along with samples and blanks using the channels with UV absorption at 300 and 274 nm,
55 respectively. The calibration curves for VL and GUA standard solutions are shown in Figure S2.

56
57 **Section S4.** IC analyses of small organic acids.

58
59 The small organic acids were analyzed using an ion chromatography system (IC, Dionex
60 ICS-1100, Sunnyvale, CA) equipped with a Dionex AS-DV autosampler (Sunnyvale, CA). The
61 separation was achieved using an IonPacTM AS15 column (4 \times 250 mm) with an AG15 guard
62 column (4 \times 50 mm). The isocratic gradient was applied at a flow rate of 1.2 mL/min with 38 mM
63 sodium hydroxide (NaOH) as the eluent. The total run time was set at 20 min. The standard
64 solutions (1–50 μM) of formic, succinic, and oxalic acid were analyzed three times along with the
65 samples and water blank. Formic, succinic, and oxalic acid had retention times of 3.6 min, 8.3 min,
66 and 11.9 min, respectively.

67
68 **Section S5.** UHPLC-qToF-MS analyses.

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70 The characterization of reaction products was performed using a UHPLC system
71 (ExionLCTM AD, ABSciex, Concord, Canada) coupled to a quadrupole time-of-flight mass
72 spectrometer (qToF-MS) (TripleTOF 6600+, ABSciex). The settings (e.g., column, mobile phase,
73 gradient, oven temperature) in the UHPLC system were the same as those used in UHPLC-PDA
74 (Section S3). The mass spectrometer was equipped with an electrospray ionization (ESI) source
75 and operated in the positive ion mode (the negative ion mode signals were too low for our analyses)
76 at a resolving power (full width at half-maximum (fwhm) at m/z 300) of 30000 in MS and 30000

77 in MS/MS (high-resolution mode). Information-dependent acquisition (IDA) scanning was
78 adapted for product identification. The acquisition using IDA consisted of a ToF-MS scan and
79 information-dependent trigger events. The ToF-MS scan had an accumulation time of 250 ms and
80 covered a mass range of m/z 30–700 with a declustering potential (DP) of 40 and collision energy
81 (CE) of 10 eV. The accumulation time for the IDA experiment was 100 ms, and the MS/MS scan
82 range was set from m/z 30–700 in high-resolution mode. The IDA criteria were as follows: 5 most
83 intense ions (number of IDA experiments) with an intensity threshold above 50 cps, isotope
84 exclusion was switched off, and dynamic background subtraction was switched on. The automated
85 calibration device system (CDS) was set to perform an external calibration every four samples.
86 The ESI source conditions were as follows: temperature, 500 °C; curtain gas (CUR), 25 psi; ion
87 source gas 1 at 50 psi; ion source gas 2 at 50 psi; and ion-spray voltage floating (ISVF) at 4.5 kV.

88 All parameters in the liquid chromatography system and mass spectrometer were controlled
89 using Analyst TF Software 1.8 (ABSciex). The high-resolution LC-MS data were processed with
90 PeakView and Analyst in the SCIEX OS software 1.5 (ABSciex). Peaks from the blank sample
91 were subtracted from the sample signals. In addition to a minimum signal-to-noise ratio of 30, a
92 peak was determined as a product if the difference in peak area between the samples before and
93 after irradiation is ≥ 10 times. The formula assignments were carried out using the MIDAS
94 molecular formula calculator (<http://magnet.fsu.edu/~midas/>) with the following constraints: $C \leq$
95 35, $H \leq 70$, $N \leq 5$, $O \leq 20$, $Na \leq 1$, and the mass error was initially set at 10 ppm. The nitrogen
96 atom was removed in the constraints for the experiments without AN or SN. The detected adducts
97 in ESI positive ion mode have several types (e.g., $[M+H]^+$, $[M+Na]^+$), and their formation can be
98 influenced by the sample matrix (Erngren et al., 2019). For simplification purposes, we mainly
99 considered $[M+H]^+$ adducts for formula assignments, except for specific experiments with AN or

100 SN in which $[M+NH_4]^+$ adducts and $[M+Na]^+$ adducts were observed. The final assigned formulas
101 were constrained by a mass error of mostly < 5 ppm, which is a requirement for product
102 identification using positive ion mode (Roemmelt et al., 2015). The double bond equivalent (DBE)
103 values and carbon oxidation state (OS_c) of the neutral formulas were calculated using the following
104 equations (Koch and Dittmar, 2006):

$$105 \quad DBE = C - H/2 + N/2 + 1 \quad (\text{Eq. S1})$$

$$106 \quad OS_c = 2 \times O/C - H/C \quad (\text{Eq. S2})$$

107
108 where C, H, O, and N correspond to the number of carbon, hydrogen, oxygen, and nitrogen atoms
109 in the neutral formula, respectively. Based on the detected products, the average oxygen to carbon
110 (O:C) ratios, $\langle O:C \rangle$: ($\langle O:C \rangle = \sum_i(\text{abundance}_i)O_i / \sum_i(\text{abundance}_i)C_i$) and average hydrogen to
111 carbon (H:C) ratios, $\langle H:C \rangle$: ($\langle H:C \rangle = \sum_i(\text{abundance}_i)H_i / \sum_i(\text{abundance}_i)C_i$) after the reactions
112 were further estimated using the signal-weighted method (Bateman et al., 2012). The average OS_c
113 $\langle OS_c \rangle$, was calculated as follows:

$$114 \quad \langle OS_c \rangle = 2 \times \langle O:C \rangle - \langle H:C \rangle \quad (\text{Eq. S3})$$

115
116 Based on the typical MS/MS fragmentation behavior for individual functional groups (Table S1)
117 and DBE values, examples of structures for products detected from VL (and GUA) photo-
118 oxidation experiments were proposed (Table S2).

119 **Section S6.** Photon flux measurements.

120
121 In this work, 2-nitrobenzaldehyde (2NB), a chemical actinometer, was used to determine
122 the photon flux in the aqueous photoreactor. Briefly, the photolysis of 50 μM 2NB in the reactor
123 was monitored by determining its concentration every 5 min for a total of 35 min, during which

124 2NB was almost completely decayed. The concentration of 2NB was measured using UHPLC-
 125 PDA, and the settings (e.g., column, mobile phase, gradient, oven temperature) were the same as
 126 those for VL decay analysis (Section S3). The channel with UV absorption at 254 nm was used
 127 for the quantification of 2NB. The concentration of 2NB in the reactor followed exponential decay,
 128 and its decay rate constant was determined using the following equation:

$$129 \quad \ln\left(\frac{[2NB]_t}{[2NB]_0}\right) = -j(2NB) \times t \quad (\text{Eq. S4})$$

130
 131 where $[2NB]_t$ and $[2NB]_0$ are the 2NB concentrations at time t and 0, respectively. The calculated
 132 2NB decay rate constant, $j(2NB)$, was 0.0026 s^{-1} . The following equation can also be used to
 133 calculate $j(2NB)$:

$$134 \quad j(2NB) = 2.303 \times (10^3 \text{ cm}^3 \text{ L}^{-1} \times 1 \text{ mol}/N_A \text{ mlc}) \times \sum(I'_\lambda \times \Delta\lambda \times \varepsilon_{2NB,\lambda} \times \Phi_{2NB}) \quad (\text{Eq. S5})$$

135 where N_A is Avogadro's number, I'_λ is the actinic flux ($\text{photons cm}^{-2} \text{ s}^{-1} \text{ nm}^{-1}$), $\Delta\lambda$ is the
 136 wavelength interval between actinic flux data points (nm), and $\varepsilon_{2NB,\lambda}$ and $\Phi_{2NB,\lambda}$ are the base-10
 137 molar absorptivity ($\text{M}^{-1} \text{ cm}^{-1}$) and quantum yield ($\text{molecule photon}^{-1}$) for 2NB, respectively.
 138 Values of $\varepsilon_{2NB,\lambda}$ (in water) at each wavelength under 298 K and a wavelength-independent Φ_{2NB}
 139 value of 0.41 were adapted from Galbavy et al. (2010). Similar to Smith et al. (2014, 2016), we
 140 measured the spectral shape of the photon output of our illumination system (i.e., the relative flux
 141 at each wavelength) using a high-sensitivity spectrophotometer (Brolight Technology Co. Ltd,
 142 Hangzhou, China). Using a scaling factor (SF), this measured relative photon output, $I_\lambda^{\text{relative}}$, is
 143 related to I'_λ as follows (Hullar et al., 2020):

$$144 \quad I'_\lambda = I_\lambda^{\text{relative}} \times \text{SF} \quad (\text{Eq. S6})$$

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 146
 147 Substitution of Eq. S6 into Eq. S5 and rearrangement yields:

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 149
$$SF = \frac{j(2NB)}{2.303 \times (10^3 \text{ cm}^3 \text{ L}^{-1} \times 1 \text{ mol}/N_A \text{ mlc}) \times \sum(I_{\lambda}^{\text{relative}} \times \Delta\lambda \times \varepsilon_{2NB,\lambda} \times \Phi_{2NB})}$$
 (Eq. S7)

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 152 and substitution of Eq. S6 into Eq. S7 yields:

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$$I'_{\lambda} = I_{\lambda}^{\text{relative}} \frac{j(2NB)}{2.303 \times (10^3 \text{ cm}^3 \text{ L}^{-1} \times 1 \text{ mol}/N_A \text{ mlc}) \times \sum(I_{\lambda}^{\text{relative}} \times \Delta\lambda \times \varepsilon_{2NB,\lambda} \times \Phi_{2NB})}$$
 (Eq. S8)

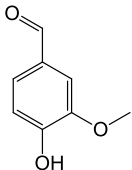
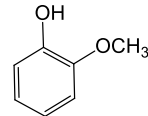
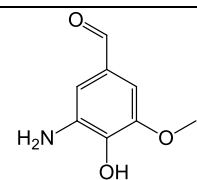
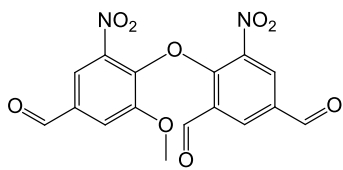
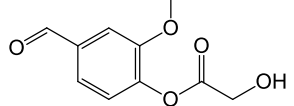
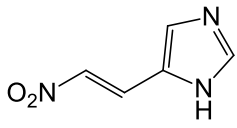
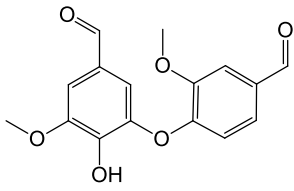
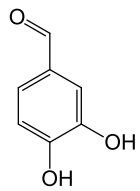
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 157 Finally, I'_{λ} was estimated through Eq. S8. The estimated photon flux in the aqueous reactor is shown
 158 in Fig. S1. The actinic flux during a haze event over Beijing (40° N, 116° E) on January 12, 2013,
 159 at 12:00 pm (GMT+8) (Che et al., 2014) estimated using the National Center for Atmospheric
 160 Research Tropospheric Ultraviolet-Visible (TUV) Radiation Model
 161 (http://cprm.acom.ucar.edu/Models/TUV/Interactive_TUV/) is also shown in Figure S2. The
 162 parameters used for the Quick TUV calculator were: Overhead Ozone Column: 300 du; Surface
 163 Albedo: 0.1; Ground Elevation: 0 km asl; Measured Altitude: 0 km asl; Clouds optical depth: 0,
 164 base: 4, top: 5; Aerosols optical depth: 2.5, single scattering albedo: 0.9, Angstrom exponent: 1;
 165 Sunlight direct beam, diffuse down, diffuse up: 1; 4 streams transfer model. For clear days, the
 166 actinic flux was estimated over Beijing (at the same date and time) using the default parameters.

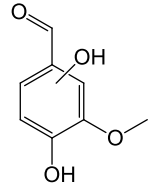
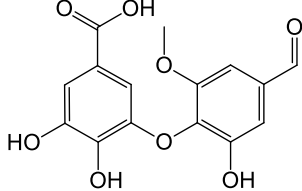
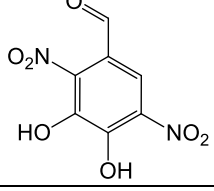
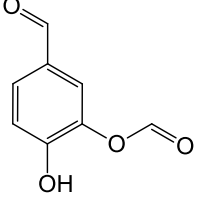
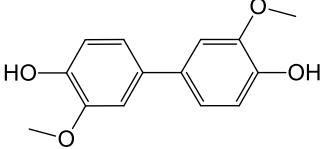
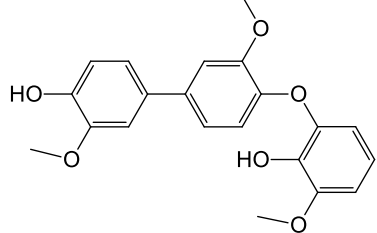
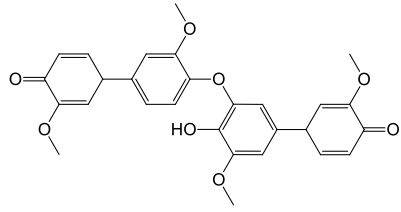
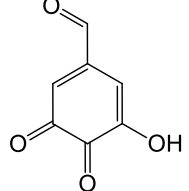
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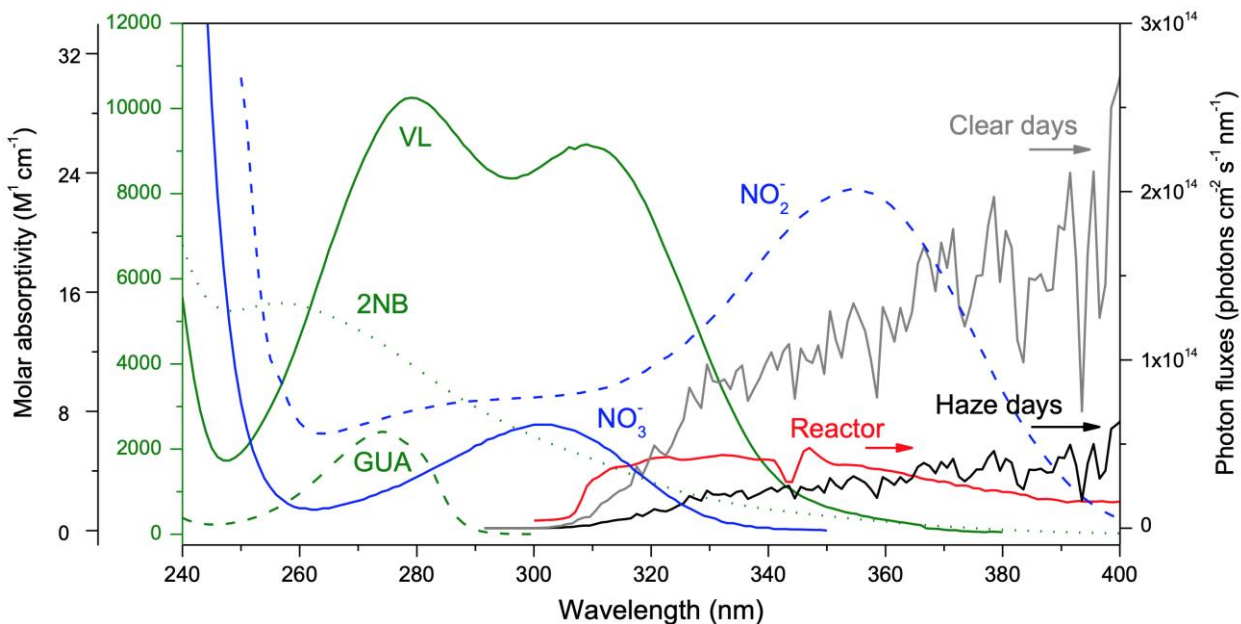
175 **Table S1.** Typical fragmentation behavior observed in MS/MS spectra for individual functional
 176 groups from Holčápek et al. (2010).

179 Functional group	Fragment ions	MS/MS loss	
180 Nitro (RNO ₂)	[M+H-OH] ⁺ *	-OH	
	[M+H-H ₂ O] ⁺	-H ₂ O	
	[M+H-NO] ⁺ *	-NO	
181	[M+H-NO ₂] ⁺ *	-NO ₂	
	Nitroso (RNO)	[M+H-NO] ⁺	-NO
	182 Carboxylic acid (ROOH)	[M+H-H ₂ O] ⁺	-H ₂ O
[M+H-CO ₂] ⁺		-CO ₂	
[M+H-H ₂ O-CO] ⁺		-H ₂ O-CO	
183 Phenol (ROH)	[M+H-H ₂ O] ⁺	-H ₂ O	
	[M+H-CO] ⁺	-CO	
184 Methoxy (ROCH ₃)	[M+H-CH ₃] ⁺ *	-CH ₃	
	[M+H-CH ₃ O] ⁺ *	-CH ₃ O	
	[M+H-CH ₃ OH] ⁺	-CH ₃ OH	
	[M+H-HCOH] ⁺	-HCOH	
185 Ester (R ¹ COOR ²)	[M+H-R ² OH] ⁺	-R ² OH	
	[M+H-R ² OH-CO] ⁺	-R ² OH-CO	
186 Amine	[M+H-NH ₃] ⁺	-NH ₃	
187 Aldehyde (RCHO)	[M+H-CO] ⁺	-CO	

204 **Table S2.** Examples of proposed structures for products detected from vanillin (and guaiacol)
 205 photo-oxidation experiments in this study.
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No.	Formula	DBE	Proposed structure	MS/MS fragment ions		
1	C ₈ H ₈ O ₃ (VL; triplet and aqSOA precursor)	5		-CO-CH ₃ OH	-CO	-CO- CH ₃ OH-CO
2	C ₇ H ₈ O ₂ (GUA; aqSOA precursor)	4				
3	C ₈ H ₉ NO ₃	5		-CO-CH ₃	-NH ₃	
4	C ₁₆ H ₁₀ N ₂ O ₉	13		-NO ₂		
5	C ₁₀ H ₁₀ O ₅	6		-CH ₃ OH	-CH ₃ OH- CO	
6	C ₅ H ₅ N ₃ O ₂	5		-NH		
7	C ₁₆ H ₁₄ O ₆	10		-CO-CH ₃ OH- CO	-CO- CH ₃ OH- CO-CH ₃ OH	-CO- CH ₃ OH- CO-CO
8	C ₇ H ₆ O ₃	5				

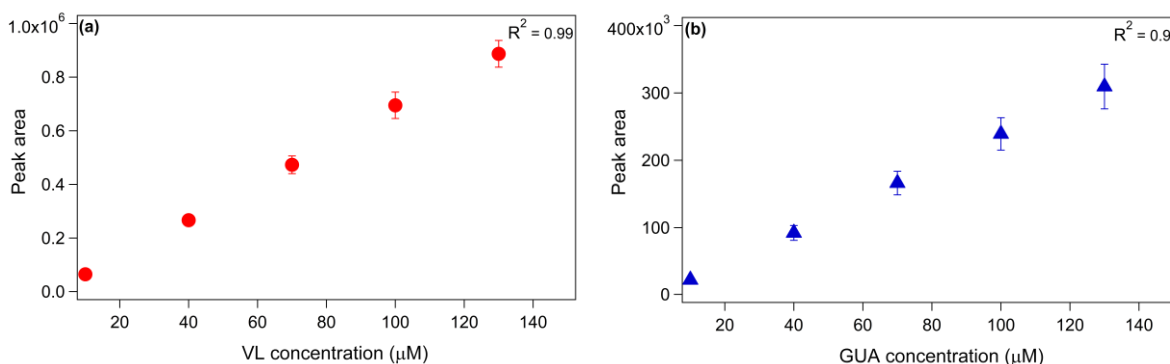
9	$C_8H_8O_4$	5		-CO-CH ₃ OH	-CO	-H ₂ O
10	$C_{15}H_{12}O_8$	10		-COOH		
11	$C_7H_4N_2O_7$	7				
12	$C_8H_6O_4$	6		-CO	-CO-CO	
13	$C_{14}H_{14}O_4$	8				
14	$C_{21}H_{20}O_6$	12				
15	$C_{28}H_{26}O_8$	16				
16	$C_7H_4O_4$	6		-CO	-CO-CO	



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211 **Figure S1.** The base-10 molar absorptivities (ϵ , $M^{-1} \text{ cm}^{-1}$) of vanillin (VL, green solid line), 2-
212 nitrobenzaldehyde (2NB, green dotted line), guaiacol (GUA, green dashed line), NO_2^- (blue
213 dashed line), NO_3^- (blue solid line), and photon flux in the aqueous reactor (red line) during typical
214 haze days (black line) or clear days (gray line) in Beijing, China. The ϵ values for 2NB and NO_2^-
215 were adapted from Galbavy et al. (2010) and Chu and Anastasio (2007), respectively.

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221 **Figure S2.** Calibration curves for (a) VL and (b) GUA standard solutions (10–130 μM). Error
222 bars represent 1 standard deviation.
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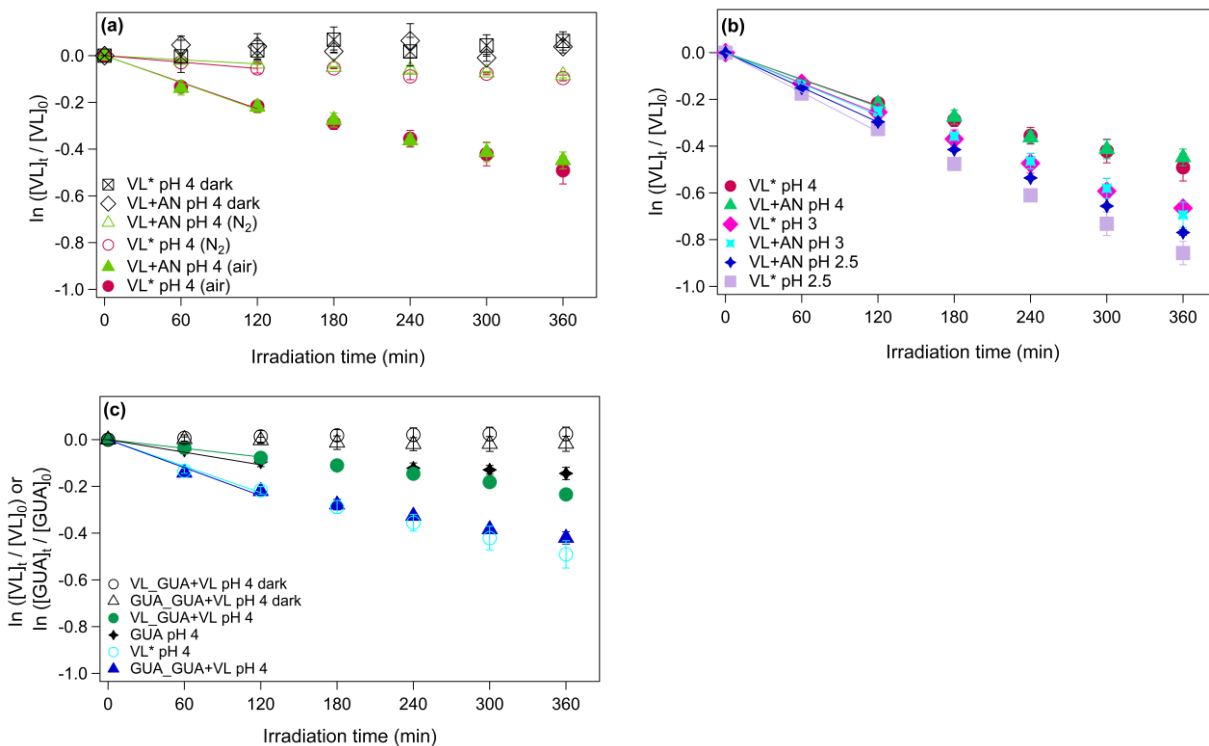
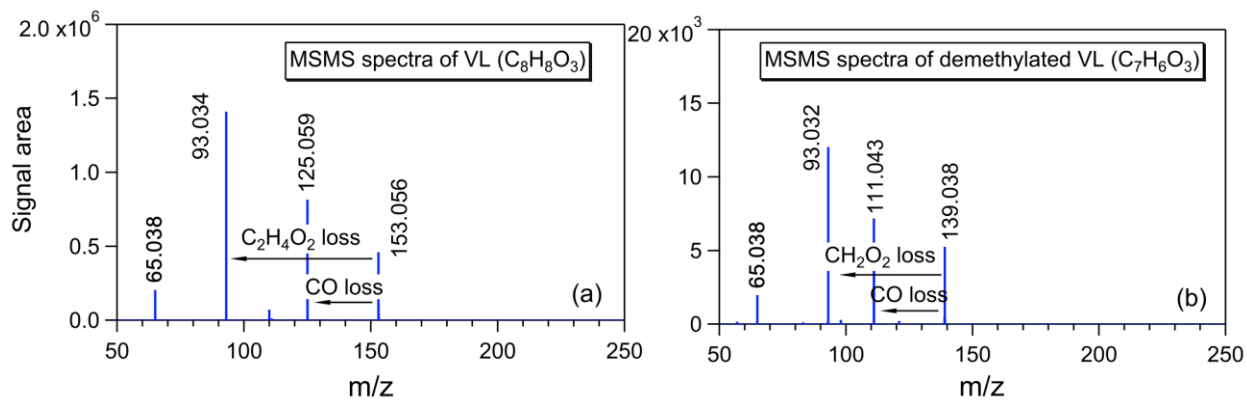
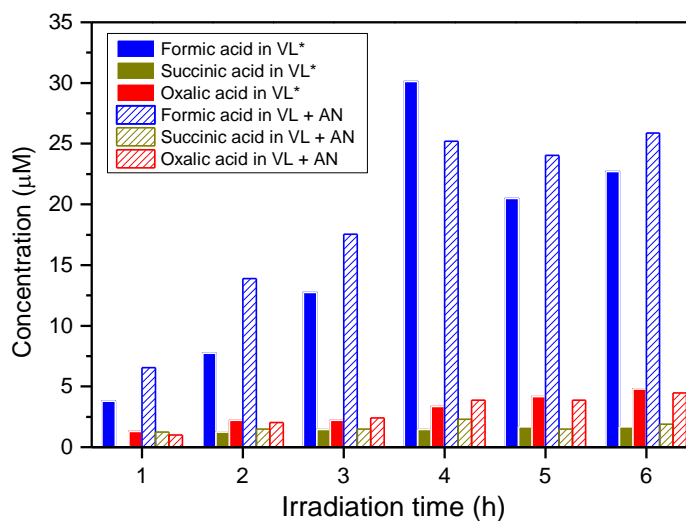


Figure S3. (a–c) The decay of VL under different experimental conditions for direct photosensitized oxidation of VL in the absence (VL*) and presence of ammonium nitrate (VL+AN): (a) VL* and VL+AN at pH 4 under N₂- (A6 and A8) and air-saturated (A5 and A7) conditions. No statistically significant difference ($p > 0.05$) was noted between VL+AN (A7) and VL+SN (A9; not shown here). (b) Effect of pH on VL* and VL+AN at pH 2.5 (A1 and A2), 3 (A3 and A4), and 4 (A5 and A7) under air-saturated conditions. (c) The decay of VL (and GUA) during direct GUA photodegradation (A13) and oxidation of GUA via photosensitized reactions of VL (GUA+VL; A14) at pH 4 under air-saturated conditions after 6 h of simulated sunlight irradiation. Error bars represent 1 standard deviation; most error bars are smaller than the markers.



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 253 **Figure S4.** MS/MS spectra of (a) VL and (b) demethylated VL. The arrows indicate possible
 254 fragmentation pathways of VL and demethylated VL.

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 258 **Figure S5.** The concentration of formic, oxalic, and succinic acid at different reaction times for
 259 VL* (A5) and VL+AN (A7) at pH 4 under air-saturated conditions.

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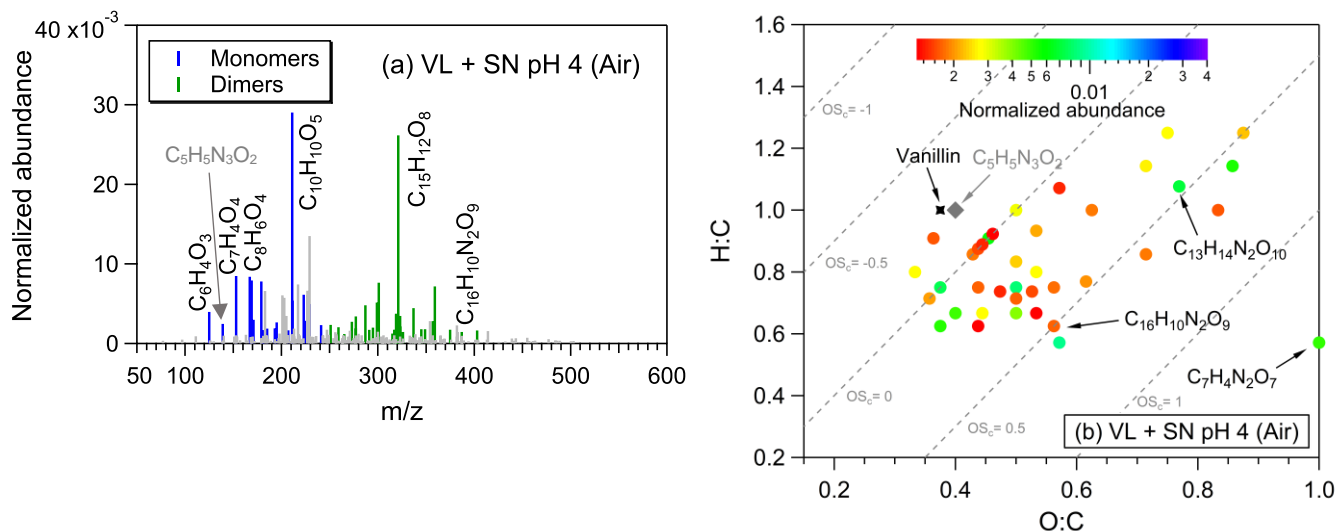
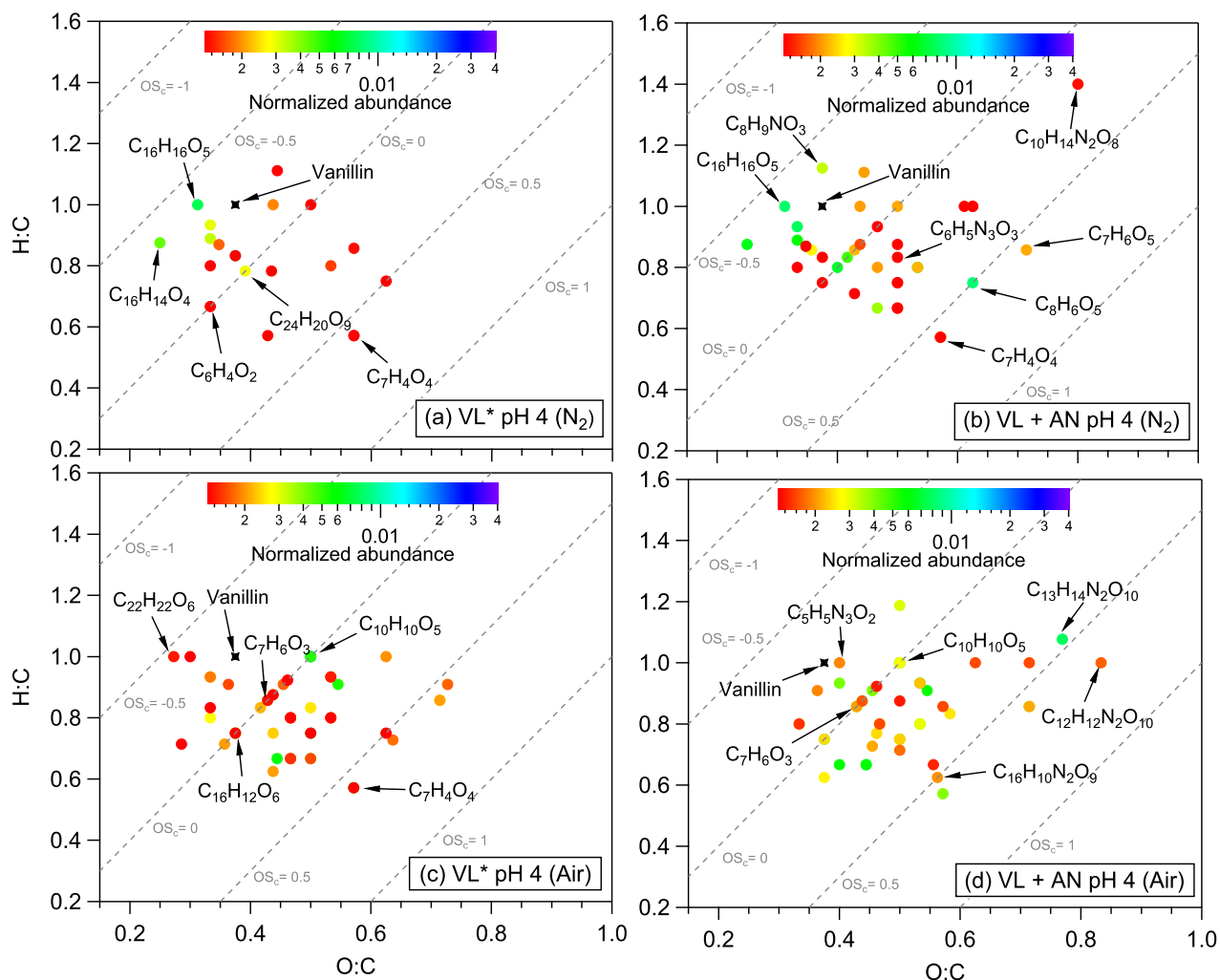


Figure S6. (a) Reconstructed mass spectra of assigned peaks and (b) Van Krevelen diagram of the 50 most abundant products from VL+SN (A9) at pH 4 under air-saturated conditions after 6 h of simulated sunlight irradiation. The normalized abundance of products was calculated using Eq. 2. The 50 most abundant products contributed more than half of the total normalized abundance of products, and they were identified as monomers (blue) and dimers (green). Gray peaks denote peaks with low abundance or unassigned formula. The gray arrows show where the potential imidazole derivative (C₅H₅N₃O₂) from VL+AN (A7) was observed. Examples of high-intensity peaks were labeled with the corresponding neutral formulas. The color bar denotes the normalized abundance of products. The gray dashed lines indicate the carbon oxidation state values (e.g., OS_c = -1, 0, and 1).



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289 **Figure S7.** Van Krevelen diagrams of the 50 most abundant products from (a) VL* (N₂-saturated;
 290 A6), (b) VL+AN (N₂-saturated; A8), (c) VL* (air-saturated; A5), and (d) VL+AN (air-saturated;
 291 A7) at pH 4 after 6 h of simulated sunlight irradiation. The color bar denotes the normalized
 292 abundance of products. The gray dashed lines indicate the carbon oxidation state values (e.g., OS_c
 293 = -1, 0, and 1).

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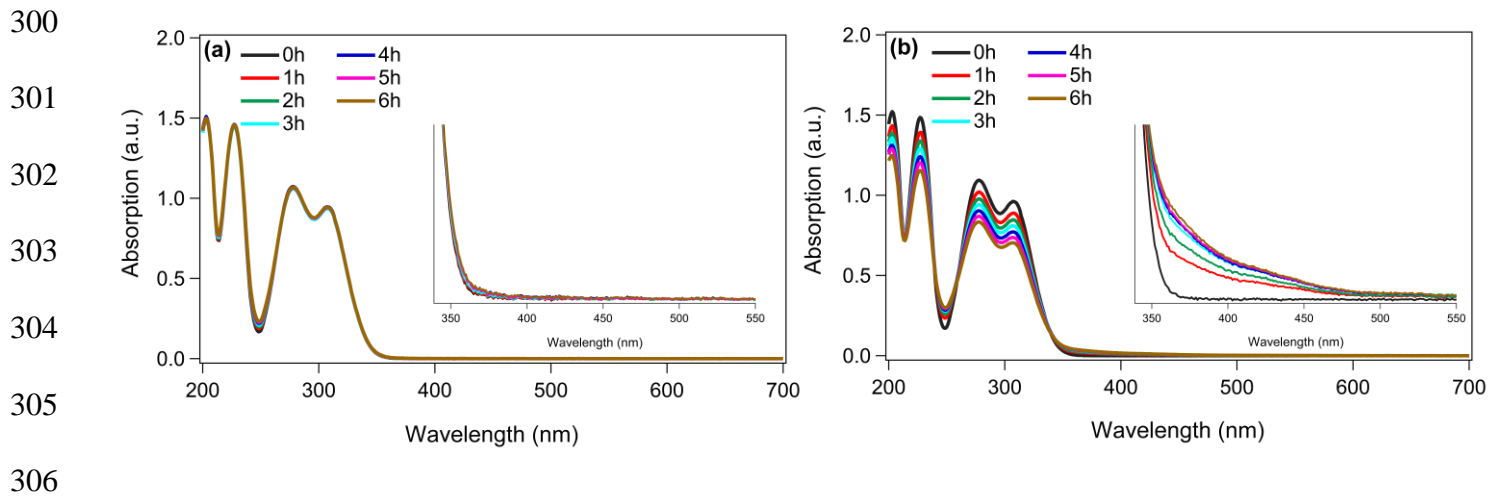
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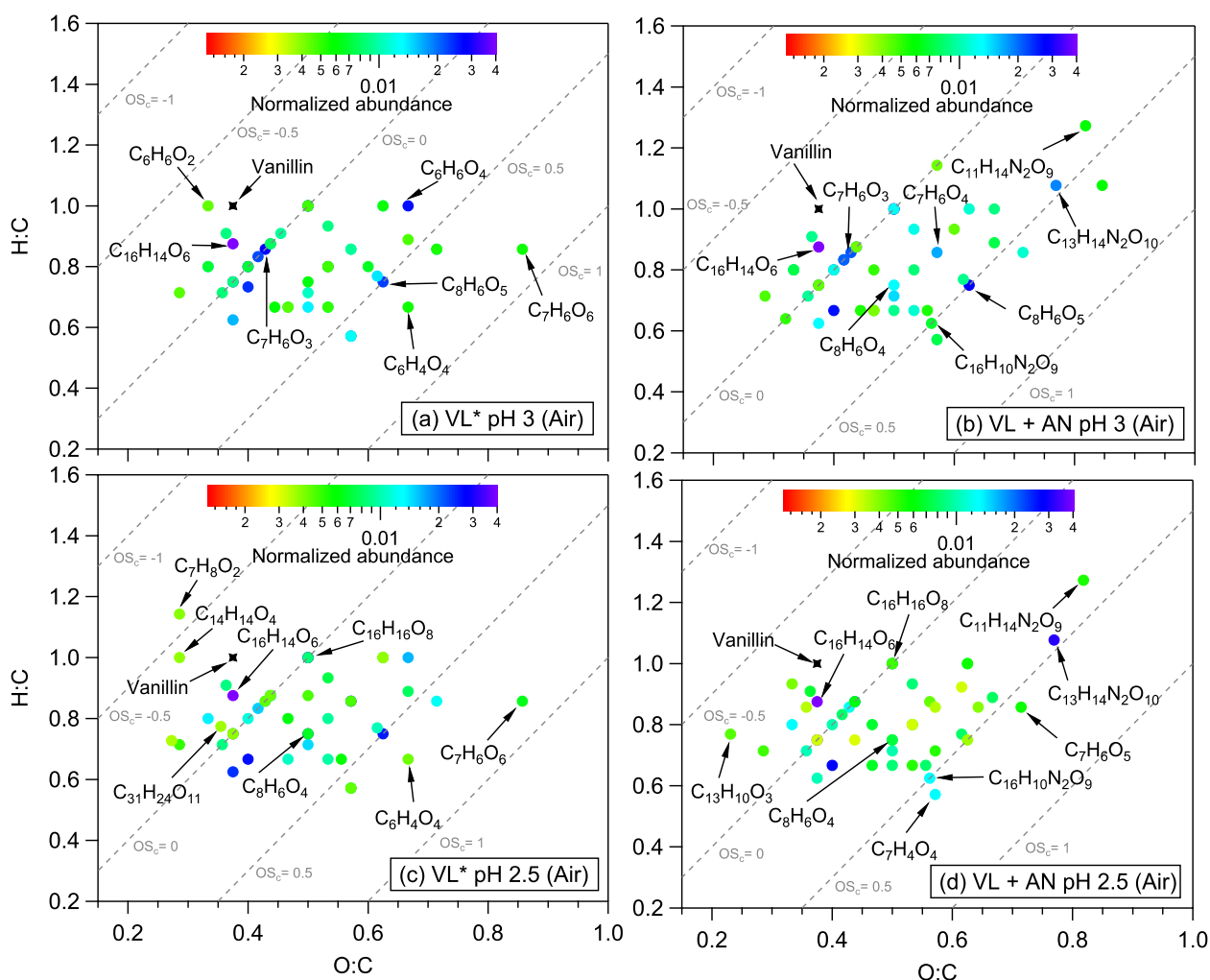
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307 **Figure S8.** UV-Vis absorption spectra of VL* (A6 and A5; pH 4) under (a) N₂- and (b) air-
 308 saturated conditions at different time intervals. The insets show the absorbance enhancement from
 309 350 to 550 nm.
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313 **Figure S9.** Van Krevelen diagrams of the 50 most abundant products from (a) VL* pH 3 (A3), (b)
 314 VL+AN pH 3 (A4), (c) VL* pH 2.5 (A1), and (d) VL+AN pH 2.5 (A2) under air-saturated
 315 conditions after 6 h of simulated sunlight irradiation. The color bar denotes the normalized
 316 abundance of products. The gray dashed lines indicate the carbon oxidation state values (e.g., OS_c
 317 =-1, 0, and 1).

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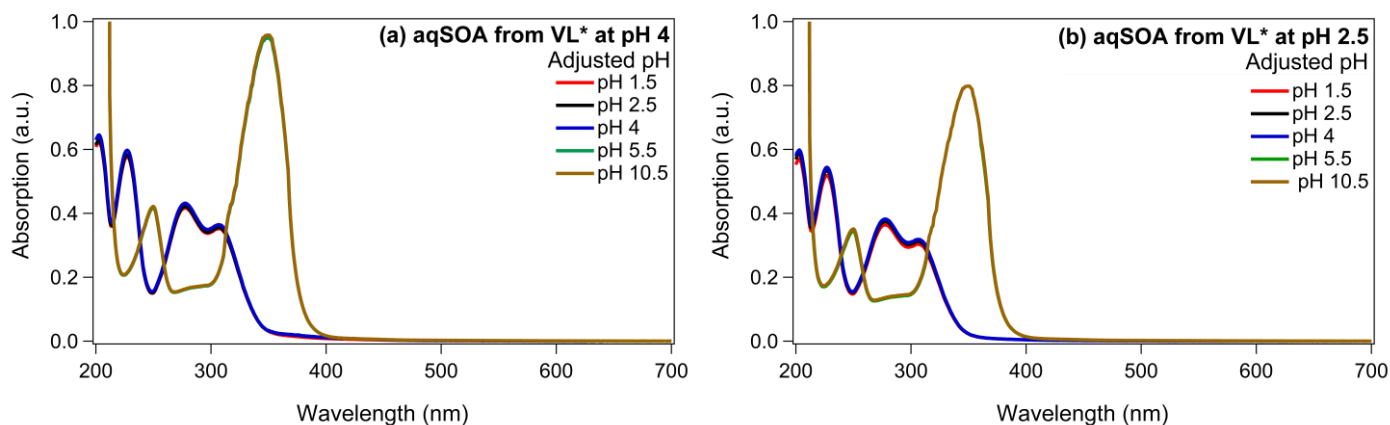
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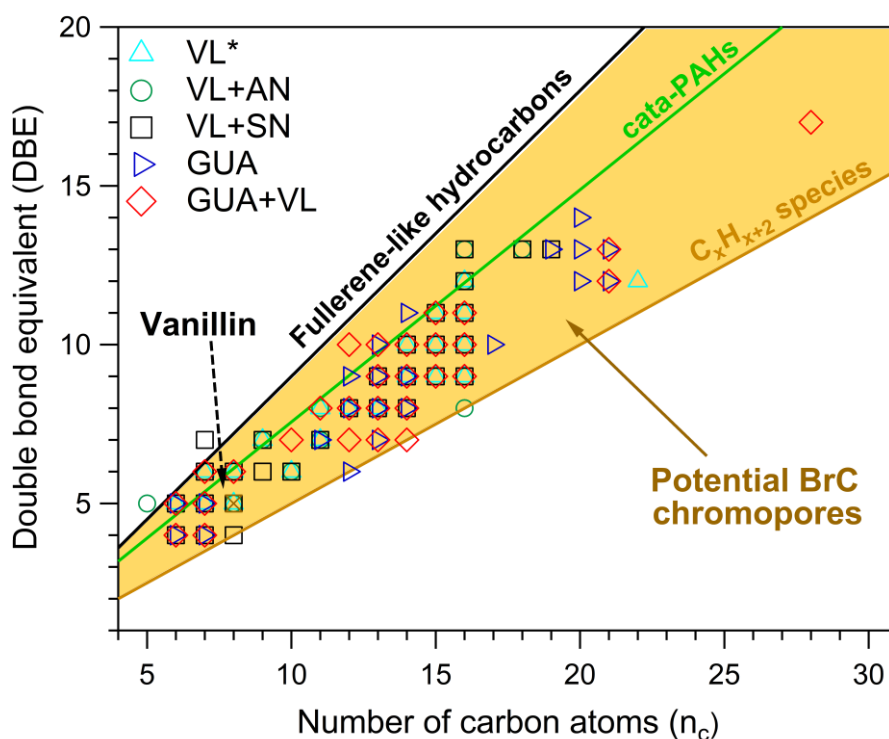
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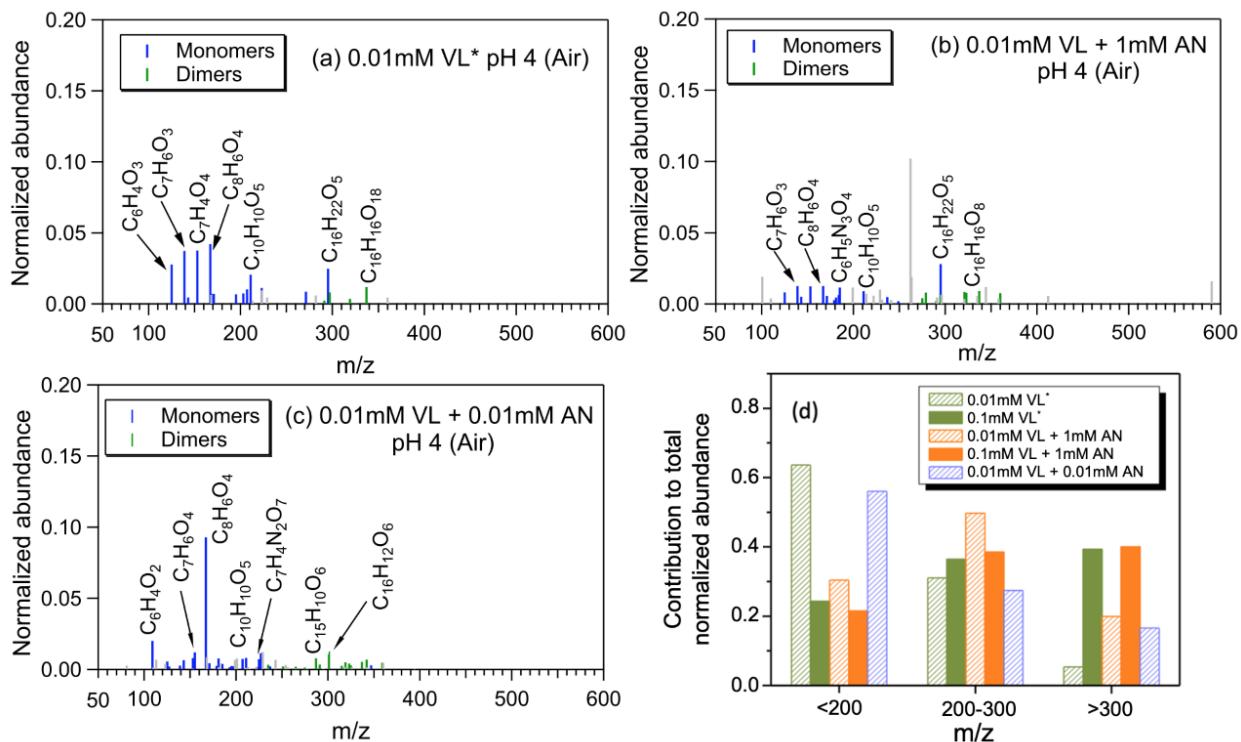
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 325 **Figure S10.** UV-Vis absorption spectra of VL*-derived aqSOA formed at (a) pH 4 and (b) pH
 326 2.5 over a range of pH conditions from 1.5 to 10.5.
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 343 **Figure S11.** The plot of the double bond equivalent (DBE) values vs. number of carbon atoms (n_C)
 344 (Lin et al., 2018) for the 50 most abundant products from pH 4 experiments under air-saturated
 345 conditions. Dashed lines indicate DBE reference values of fullerene-like hydrocarbons (black solid
 346 line; Lobodin et al., 2012), cata-condensed polycyclic aromatic hydrocarbons (PAHs) (green solid
 347 line; Siegmann and Sattler, 2000), and linear conjugated polyenes (general formula C_xH_{x+2})
 348 (brown solid line). Data points within the shaded area are potential BrC chromophores.



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350 **Figure S12.** Reconstructed mass spectra of assigned peaks from (a) 0.01 mM VL* (A10), (b) 0.01
 351 mM VL + 1 mM AN (A12), and (c) 0.01 mM VL + 0.01 mM AN (A11) at pH 4 under air-saturated
 352 conditions after 6 h of simulated sunlight irradiation. The normalized abundance of products was
 353 calculated using Eq. 2. The 50 most abundant products contributed more than half of the total
 354 normalized abundance of products, and they were identified as monomers (blue) and dimers
 355 (green). Gray peaks denote peaks with low abundance or unassigned formula. Examples of high-
 356 intensity peaks were labeled with the corresponding neutral formulas. (d) Contributions of
 357 different m/z ranges to the normalized abundance of products from experiments with low [VL] =
 358 0.01 mM (A10–A12) and high [VL] = 0.1 mM (A5 and A7) at pH 4 under air-saturated conditions
 359 after 6 h of simulated sunlight irradiation.

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