Supplementary Information

Nitrogen-Containing Organic Aerosols and Highly Oxidized Molecules Produced by Reaction of Ozone with Floor Cleaning Detergent

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This file contains six supplementary texts, nine figures, and two tables.

Test S1: Cleaning Procedure

The chamber was prepared by rinsing eight times with tap water followed by successive immersions into a bath of hydrochloric acid (HCl) 10%, sodium hydroxide (NaOH) 1M for 1h and further rinsing eight times in deionized water sequentially. Finally, it is wrapped in aluminum foil and baked in a 40°C oven to remove any residual moisture.

Test S2: Samples Preparation

The detergent used in this study is manufactured by large international company and readily available for purchase online and in most supermarkets in China and elsewhere. The active ingredients of the floor cleaner can be found on the company's website (water, ethoxylated alcohol, n-alkyl dimethyl benzyl ammonium chlorides, methylchloroisothiazolinone & methylisothiazolinone and colorant). However, the volatilities of these substances at room temperature are extremely low and mainly concentrate in liquid phase. In our previous research, we utilized TD-GC-MS to measure the volatile components of this floor cleaner. It was found that floor cleaners emit a large amount of C7~C10 VOCs, including compounds such as d-Limonene, dihydromyrcenol, α-terpineol, γ-terpineol, and decanal, among the others [1] These compounds are more likely to react with ozone, leading to the formation of particulate matter. Furthermore, the usage (dilution ratio) has not been marked out. Therefore, we diluted 1 part of detergent with 4 parts of ultrapure water (18 Mohm, H_2O-MM-UV-T, Germany) and injected 30ml of the diluted solution into the reactor through the upper exit.

Text S3: Experimental Process

The real-time measurements of the particle-phase composition were performed by the

EESI-TOF with 5s time resolution, and a SMPS was used to monitor the particle number size distribution and absolute mass concentration within 14-670 nm. At the beginning of each experiment, we first test the signal of tank zero air for 16 minutes, then shift the airflow through a three-ball valve to made it passed through the chamber. Twenty minutes later, the ozone generator was switched on and the ozone concentration increased to about 50 ppb. The ozonolysis-only experiment lasted about 2.5 hours, followed by an hour-long photooxidation reaction and a fifty minutes long light irradiation in the absence of ozone.

Text S4: Data Analysis

The elemental composition of these formulas was constrained as $C_{1–50}H_{0–100}O_{0–50}N_{0–5}$ and *m/z* tolerance was 3 ppm for ESI+ mode. To describe the chemical characteristics of the organic constituents of the generated particles in indoor air, several metrics including double bond equivalent (DBE), aromaticity equivalent (Xc), carbon oxidation state (OSc) and Kendrick mass defect (KMD) were applied. DBE represents the number of double bonds and rings in a molecule and was used to assess the degree of unsaturation. DBE can be expressed as follows:

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

where C, H, and N represent carbon, hydrogen and nitrogen atom numbers in the compound formula. Since DBE may not accurately identify the level of unsaturation for certain compounds, the aromaticity equivalent (X_C) was also calculated based on Eq-S2:

$$X_c = \frac{2C + N - H - 2mO}{DBE - mO} + 1 \quad \text{(Eq-S2)}$$

where O represents the number of oxygen atoms; m and n represent the fraction of oxygen/sulfur involved in the π bond structure of the compound formula. If [DBE-mO] ≤

0, Xc=0. Besides, compounds with DBE=0 should not be included in the X_C scale.[2] In this study, m=0 was used for the compounds with only hydroxyl, ether and peroxide group; m=1 was used for compounds with only carbonyl, isocyanate and amide group; m = 0.5 was used for all the other compounds. Since the identified compounds did not include S, the n parameter was not applied. Use of X_C value may help to improve the identification of aromatic compounds in the indoor air particles. Here the threshold values for X_C as X_C=0, 0 <X_C <2.50, 2.5 ≤X_C <2.7143, and $X_C \geq 2.7143$ were used as minimum criteria for the presence of aliphatic saturated compounds, aliphatic unsaturated compounds, monocyclic, and polycyclic aromatic compounds, respectively[2, 4, 52, 4, 5].

The carbon oxidation state (OS_C) was also used as another metric to describe the degree of oxidation of organic species. OS_C was defined as the charge a carbon atom would take if it was to lose all electrons in bonds with more electronegative atoms, but gain all electrons in bonds with less electronegative atoms. [6] For a certain compound OS_C can be obtained as follows:

$$OS_C = -\sum_i os_i \frac{n_i}{n_C} \qquad \text{(Eq-S3)}$$

where OS_i is the oxidation state associated with element $_i$, and n_i/n_C is the molar ratio of element i to carbon.[7] In this context, we presume that all oxygen atoms possess an oxidation state of -2 (excluding peroxides), and organic nitrogen is either in the nitrooxy group form (with an oxidation state of +5) when there are at least three oxygen atoms, or in the form of amines (with an oxidation state of -3) when there are fewer than three oxygen atoms. [8]

Text S5: Relative Number Abundances Analysis

Figure S5 shows the relative abundance of the compounds produced under different

conditions. The attributed elemental formulas are classified into four Xc categories. For the CHO compounds produced from ozone reaction, 37.4% belongs to the group Xc≥2.7143, followed by 27.0% belongs to the group 2.5≤Xc<2.7143, 21.1% belongs to unsaturated non-aromatic compounds that do not contain C=C or C-C triple bonds (DBE=0), 7.7 % belongs to 0<Xc<2.5and 7.37% belongs to group Xc=0. According to the estimated Xc values, the detected CHO species are mainly composed of polycyclic aromatic compounds, followed by monocyclic compounds. The pie chart of the detected CHNO compounds is entirely different from the one of CHO compounds (Figure S5). Regarding the CHNO product compounds, the highest percentage (53.0%) of the detected species is associated with polyaromatic compounds (Xc≥2.7143), followed by aliphatic saturated compounds (DBE=0, 22.4%) and aliphatic unsaturated compounds (0<Xc<2.5, 21.0%), the monoaromatic compounds with a benzene core structure(2.5≤Xc<2.7143) exhibits the lowest concentration(0.95%).[3]The distribution of species produced by photooxidation reaction is the same as that of dark reaction, but the proportions are slightly different.

Text S6: Estimation of Saturation Concentrations

An element-based method with parameterizations by EESI-ToF measurement was used to estimate the saturation concentrations (C*) (μg m^{-3}) of the detected compounds. [9] Here we classified the volatilities of compounds into four categories including extremely low volatility organic compounds (ELVOC, logC*≤-3.5), low volatility organic compounds (LVOC, -3.5 < logC* ≤ -0.5), semi-volatile organic compounds (SVOC, -0.5<logC*≤ 2.5), and intermediate volatility organic compounds (IVOC, 2.5 <logC*≤ 6.5).[10, 11]

Note the average values of the parameterization method of Li et al. (2016) and Daumit et

al. (2013) were applied here.[9, 12] The volatility shall be overestimated compared to the heating method according to Chen et al. (2024).[13] These low-volatility compounds are produced by the gas-phase oxidation of reactive organic compounds, which is initiated by the generation of organic radicals and followed by multiple additions of O_2 and isomerization.[14]

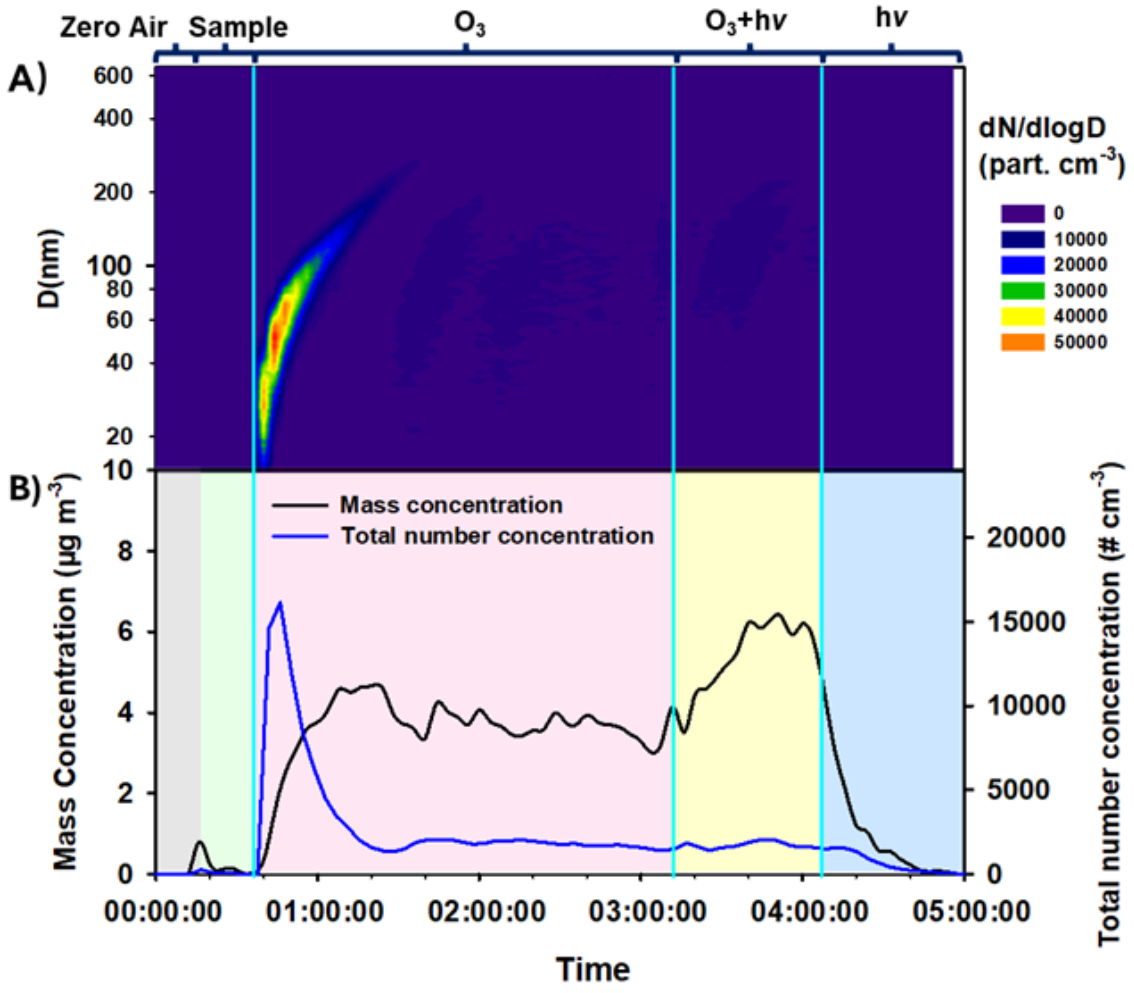


Fig. S1 A) Contours plots reporting particle number distribution evolutions measured through the O_3 reaction at 70%RH in dark and under light irradiation. B). Time profile of the mass concentration and total number concentration. For the conversion of size distributions to mass, an effective density of 1.4 g cm^{-3} was assumed. The light blue vertical lines in the figure delineate different experimental phases, which are the ozone oxidation phase (O_3, pink), the photo-oxidation phase (O_3+hν, yellow), and the

photoreaction phase (hν, blue). The corresponding experimental phases are marked at the top of the figure.

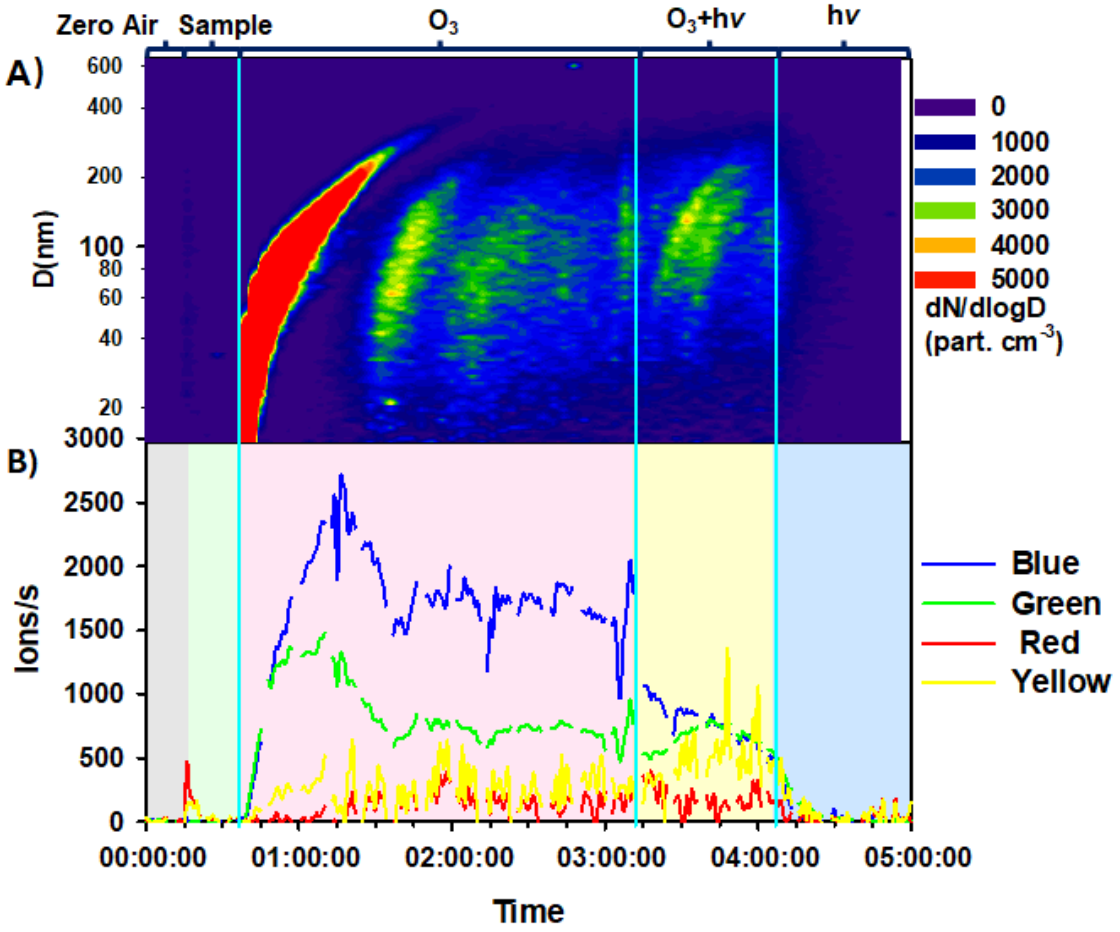
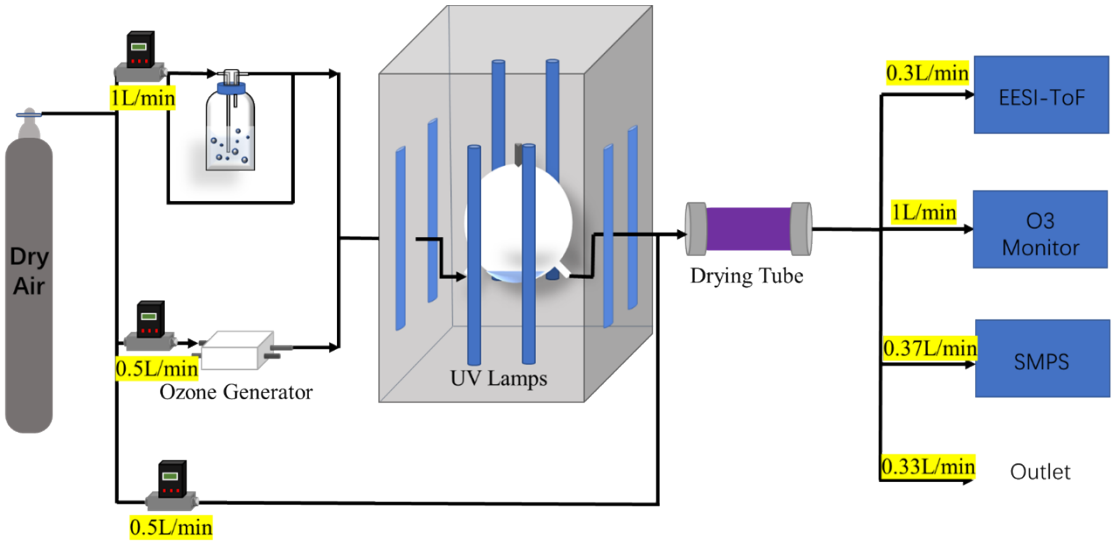


Fig. S2 Co-evolution diagram of particle formation and evolution patterns. A) Contour plots illustrate the progression of particle number distributions, as determined by ozone-induced reactions at 70% relative humidity in both the dark and light-exposed conditions. (Comparable to Fig. S1A yet featuring distinct concentration gradient labels for clarity.) B) Temporal profiles depicting the fluctuating intensities of various clusters, derived from a hierarchical cluster analysis approach.



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144 **Fig. S3** Experimental setup.

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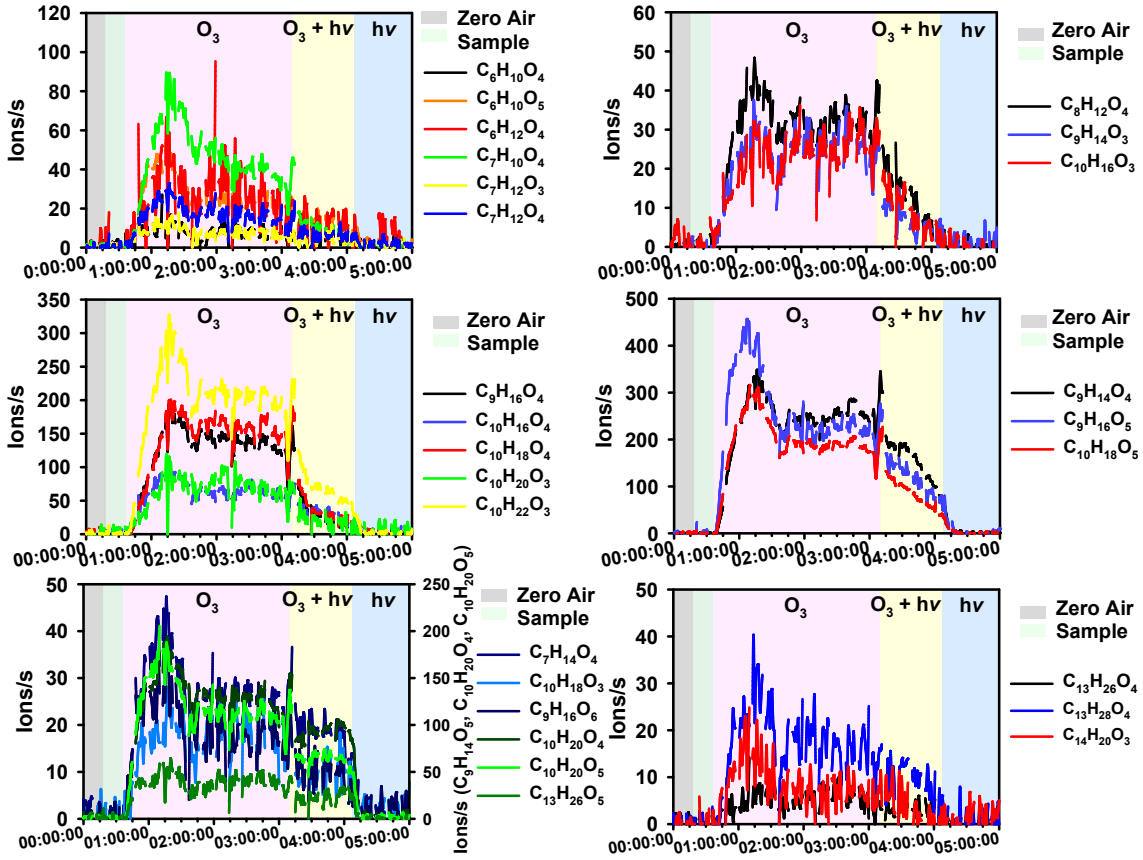

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147 **Fig. S4** Time profile of different species in each subgroup of group 'Blue'. These
148 subgroups show different trends of decreasing, indicating that substances in the same
149 subgroup have similar properties, particularly under the light irradiation.

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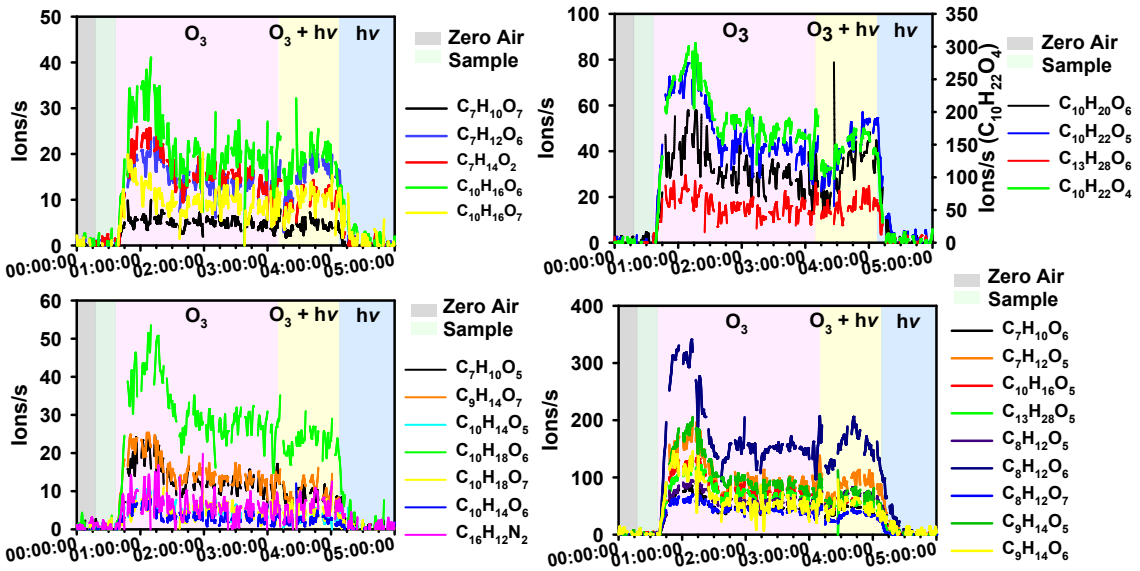

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152 **Fig. S5** Time profile of different species in each subgroup of group 'Green'. These
153 subgroups show different trends of decreasing, indicating that substances in the same
154 subgroup have similar properties, particularly under the light irradiation.
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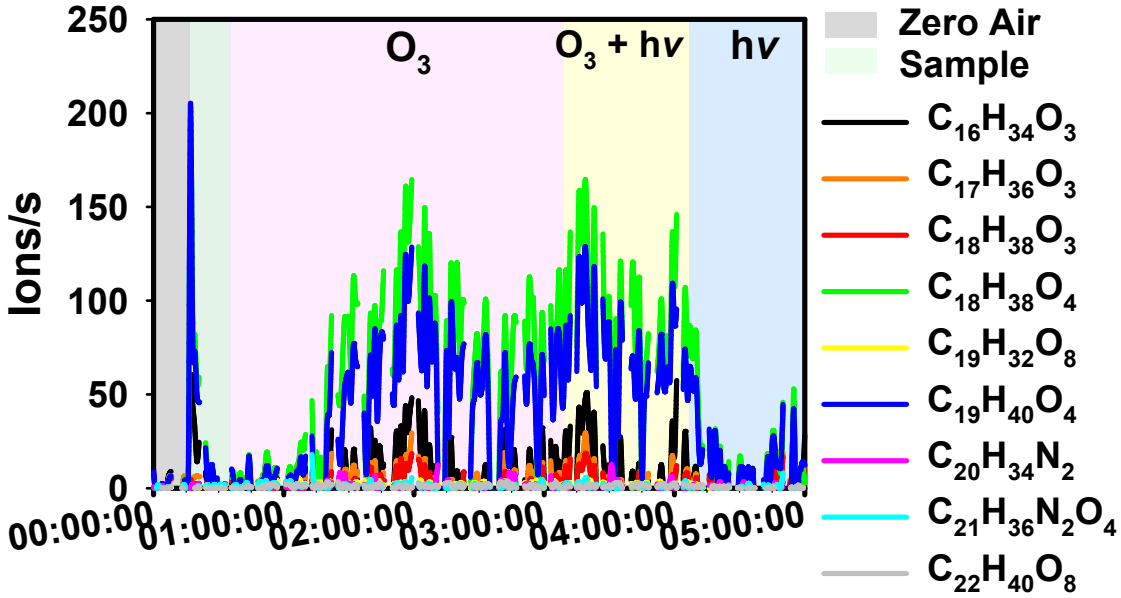

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157 **Fig. S6** Time profile of different species in the 'Red' group. Species with similar intensity-
158 time profiles may possess similar properties.
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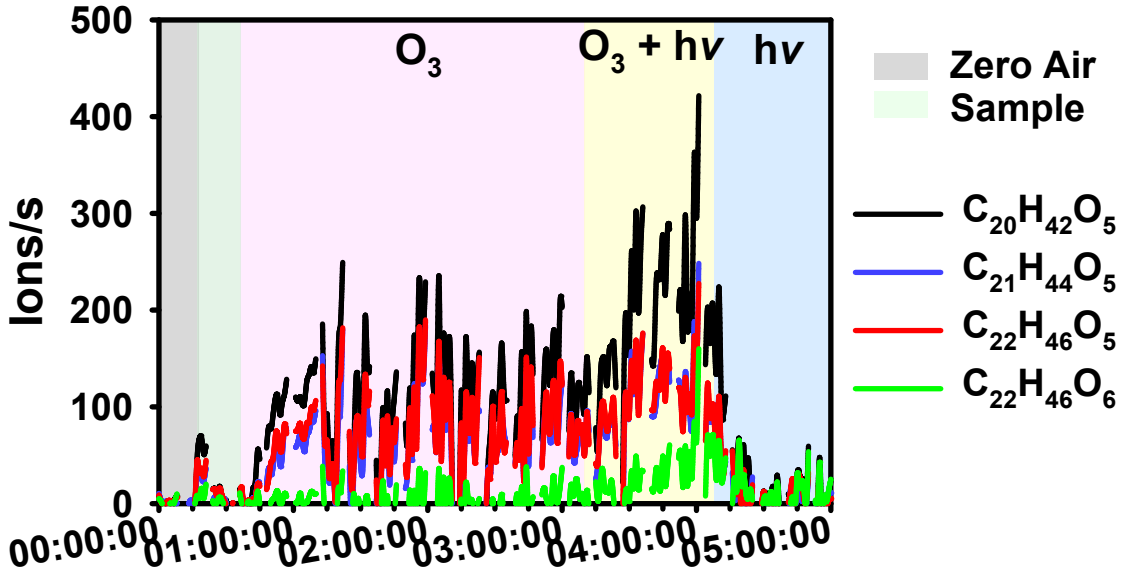

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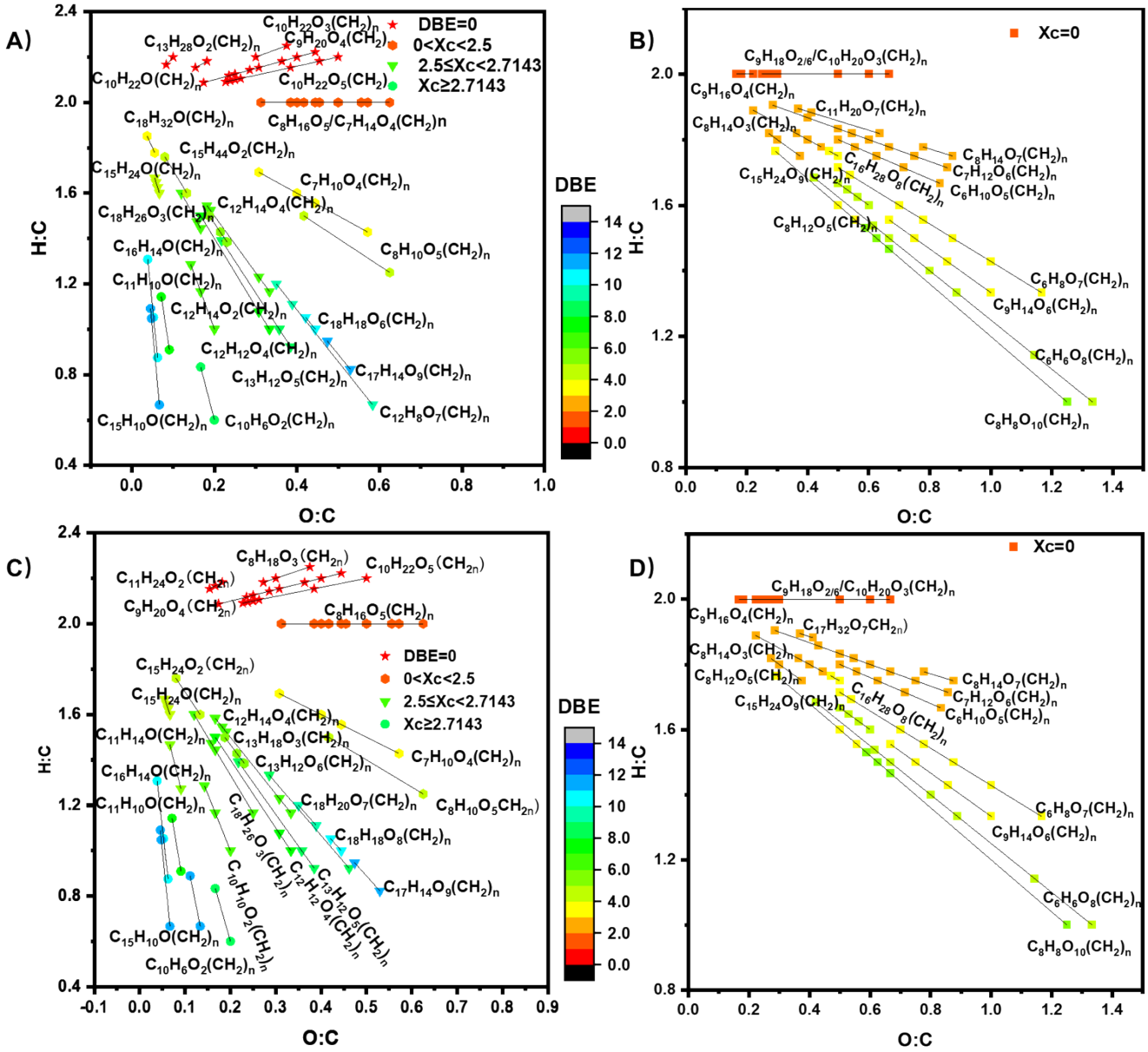
161 **Fig. S7** Time profile of different species in the 'Yellow' group. Species with similar
162 intensity-time profiles may possess similar properties.



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164 **Fig. S8** Van Krevelen plot for homologous series of CHO compounds produced from the
165 ozone reaction (A, B) and photooxidation reaction (C, D). The orange and green rectangles
166 correspond to aliphatic compounds and low oxidation aromatic compounds, respectively.
167 The "n" refers to the number of CH_2 groups in a given family.

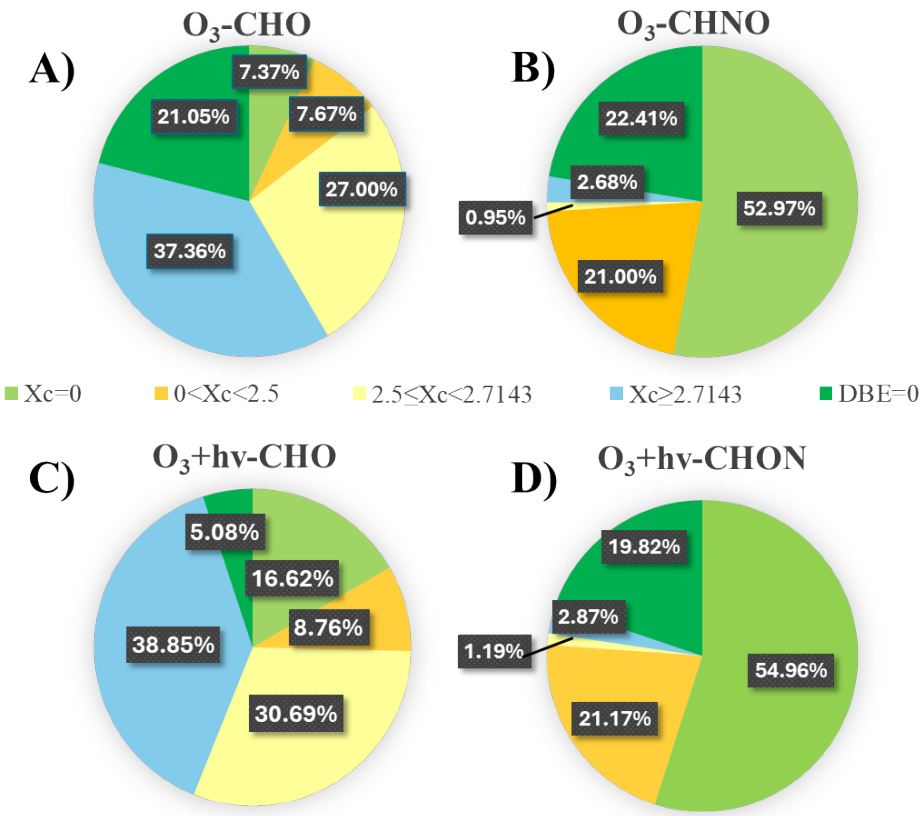

Fig. S9 Pie chart describing the proportion of different Xc groups under different conditions. A) CHO, and B) CHON compounds produced by ozone reaction with the floor cleaning detergent, C) CHO and D) CHON compounds produced under photooxidation reaction with the cleaning detergent.

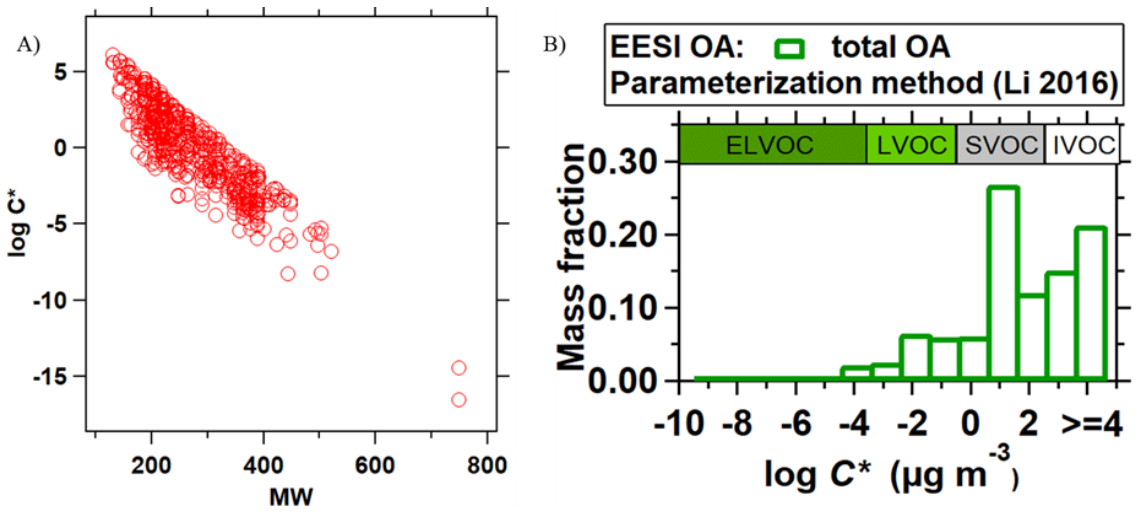

Fig. S10 A) Variation trend of estimated volatility vs. molecular weight. B) Estimated volatility distributions for identified compounds based on the element-based methods with parameterizations by EESI-ToF measurements.

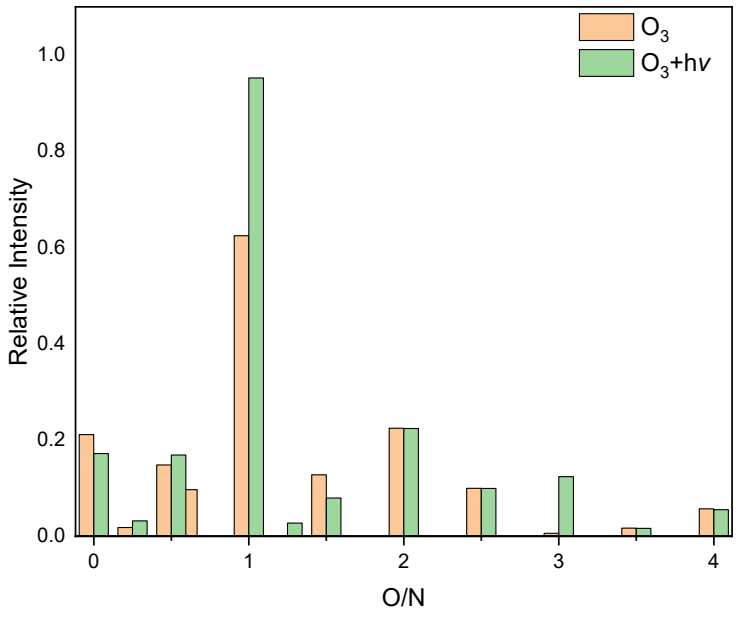

Fig. S11 Nitrogen containing organics separated into subgroups according to the O/N ratio in their chemical structures.

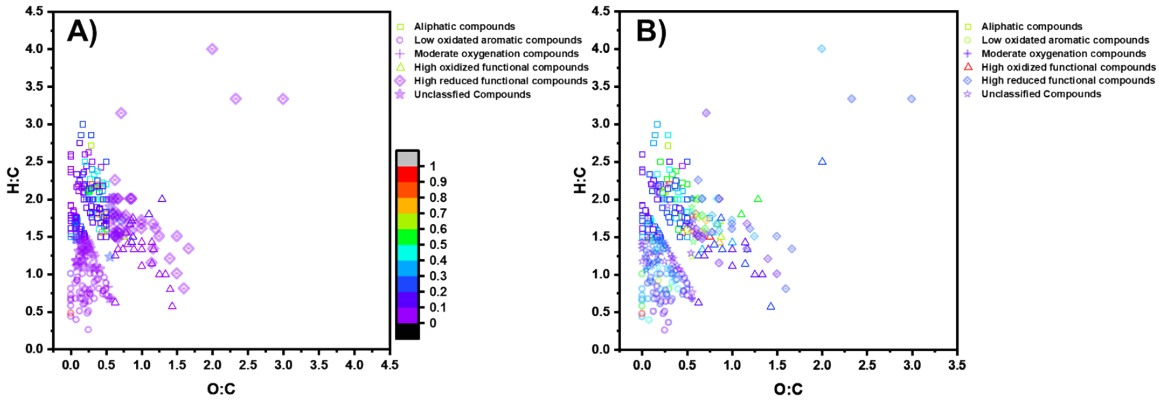

Fig. S12 Classification of the chosen substances based on their H/C, O/C, and OSc ratios under different conditions: A) Oxidation reaction, B) Photo-oxidation reaction. In the figure, square boxes depict aliphatic compounds, open circles denote lightly oxygenated aromatic compounds, crosses signify moderately oxygenated compounds, hollow triangles represent highly oxidized functional compounds, dotted diamonds stand for highly reduced functional compounds, and hollow five-pointed stars indicate unclassified compounds. The color gradient corresponds to the fourth root of the relative signal strength.

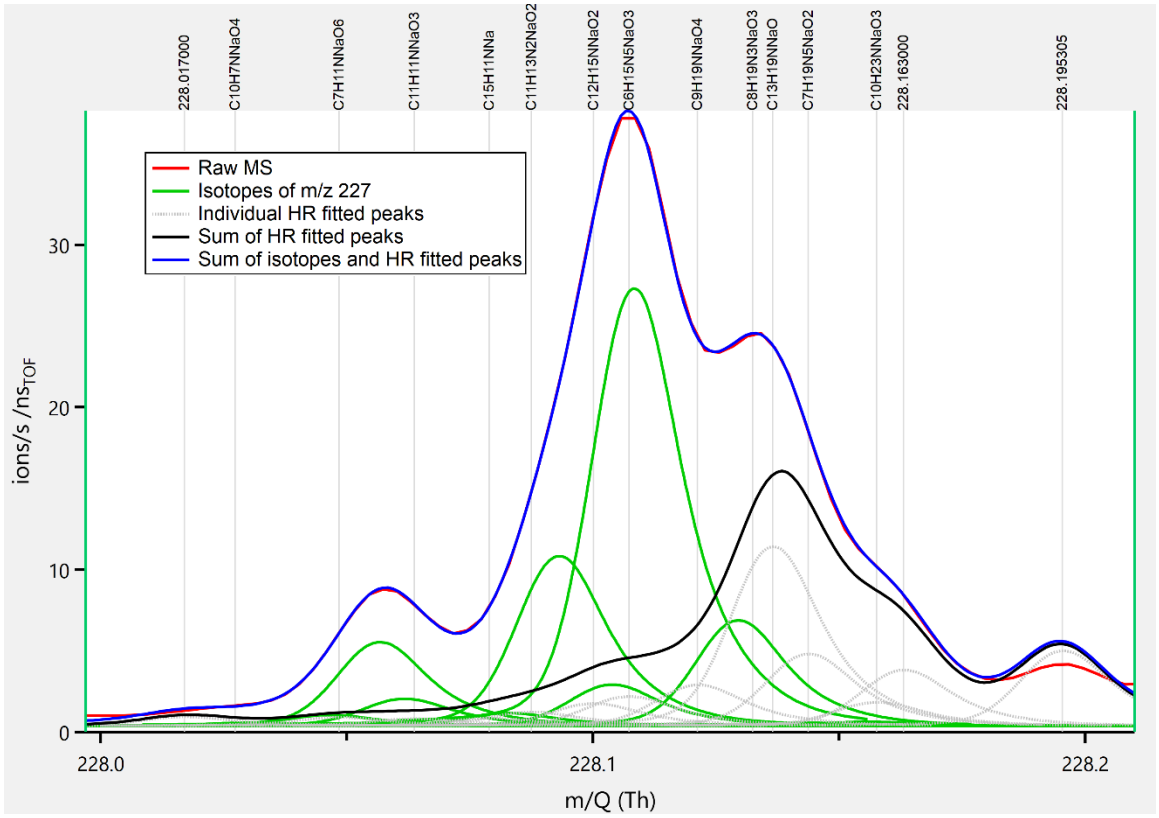

Fig. S13 A mass spectrum of the m/z 228. Both the isotope peaks of m/z 227 and the HR fitted peaks of m/z 228 are included.

Table S1. Four groups of compounds divided by the hierarchical cluster analysis. The molecular weight noted here does not include the molecular weight of Na^+.

	Formula	Molecular Weight		Formula	Molecular Weight
Blue	$C_6H_{10}O_4$	146.14	**Green**	$C_7H_{10}O_7$	206.15
	$C_6H_{10}O_5$	162.14		$C_7H_{12}O_6$	192.17
	$C_6H_{12}O_4$	148.16		$C_7H_{14}O_2$	130.18
	$C_7H_{10}O_4$	158.15		$C_{10}H_{16}O_6$	232.23
	$C_7H_{12}O_3$	144.17		$C_{10}H_{16}O_7$	248.23
	$C_7H_{12}O_4$	160.17		$C_{10}H_{20}O_6$	236.26
	$C_8H_{12}O_4$	172.18		$C_{10}H_{22}O_4$	206.28
	$C_9H_{14}O_3$	170.21		$C_{10}H_{22}O_5$	222.28
	$C_{10}H_{16}O_3$	184.23		$C_{13}H_{28}O_6$	280.36
	$C_9H_{16}O_4$	188.22		$C_7H_{10}O_6$	190.15
	$C_{10}H_{16}O_4$	200.23		$C_7H_{12}O_5$	176.17
	$C_{10}H_{18}O_4$	202.25		$C_8H_{12}O_5$	188.18
	$C_{10}H_{20}O_3$	188.26		$C_8H_{12}O_6$	204.18
	$C_{10}H_{22}O_3$	190.28		$C_8H_{12}O_7$	220.18
	$C_9H_{14}O_4$	186.20		$C_9H_{14}O_5$	202.20
	$C_9H_{16}O_5$	204.22		$C_9H_{14}O_6$	218.20
	$C_{10}H_{18}O_5$	218.25		$C_{10}H_{16}O_5$	216.23
	$C_7H_{14}O_4$	162.18		$C_{13}H_{28}O_5$	264.36
	$C_{10}H_{18}O_3$	186.25		$C_7H_{10}O_5$	174.15
	$C_9H_{16}O_6$	220.22		$C_9H_{14}O_7$	234.20
	$C_{10}H_{20}O_4$	204.26		$C_{10}H_{14}O_5$	214.21
	$C_{10}H_{20}O_5$	220.26		$C_{10}H_{14}O_6$	230.21
	$C_{13}H_{26}O_5$	262.34		$C_{10}H_{18}O_6$	234.25
	$C_{13}H_{26}O_4$	246.34		$C_{10}H_{18}O_7$	250.25
	$C_{13}H_{28}O_4$	248.36	**Yellow**	$C_{20}H_{42}O_5$	362.54
	$C_{14}H_{20}O_3$	236.31		$C_{21}H_{44}O_5$	376.58
Red	$C_{22}H_{40}O_8$	432.55		$C_{22}H_{46}O_5$	390.60
	$C_{21}H_{36}N_2O$	332.52		$C_{22}H_{46}O_6$	406.60
	$C_{20}H_{34}N_2$	302.50			
	$C_{19}H_{40}O_4$	332.52			
	$C_{16}H_{34}O_3$	274.44			
	$C_{17}H_{36}O_3$	288.47			
	$C_{18}H_{38}O_3$	302.49			
	$C_{18}H_{38}O_4$	318.49			
	$C_{19}H_{32}O_8$	388.45			

Table S2. Compounds categorized based on DBE and X_C. The structural formula and potential functional groups of each compound are acquired from the National Library of Medicine.

DBE Value	X_C Value	Classification	Compounds Series	DBE Value	X_C Value	Classification	Compounds Series
CHO Compounds				CHON Compounds			
0	/	Saturated alcohol or ether	$C_{10}H_{22}O_5(CH_2)_n$	0	0	Alcohols or ether compounds containing multiple amino groups	$C_6H_{18}N_4O(CH_2)_n$
			$C_9H_{20}O_4(CH_2)_n$				$C_8H_{21}N_3O_2(CH_2)_n$

DBE Value	X_C Value	Classification	Compounds Series	DBE Value	X_C Value	Classification	Compounds Series
			$C_8H_{18}O_3(CH_2)_n$				$C_7H_{20}N_4O_2(CH_2)_n$
			$C_{11}H_{24}O_2(CH_2)_n$			Saturated compounds with multiple hydroxyl or ether bonds and one or two amino group	$C_9H_{21}NO_3(CH_2)_n$
			$C_{10}H_{22}O(CH_2)_n$				$C_9H_{22}N_2O_4(CH_2)_n$
1		Aliphatic compounds with one unsaturated bond	$C_9H_{18}O_6(CH_2)_n$				
			$C_{10}H_{20}O_3(CH_2)_n$				
			$C_9H_{18}O_2(CH_2)_n$	1		Compounds with an unsaturated bond or ring	$C_8H_{18}N_2O(CH_2)_n$
2		Organic acid or organic alcohol with C=C/carboxyl/ester groups	$C_8H_{14}O_3(CH_2)_n$				$C_{10}H_{22}N_2O_2(CH_2)_n$
			$C_{11}H_{20}O_7(CH_2)_n$				$C_7H_{17}N_3O_3(CH_2)_n$
			$C_7H_{12}O_6(CH_2)_n$				$C_7H_{16}N_2O_4(CH_2)_n$
			$C_6H_{10}O_5(CH_2)_n$	2		Unsaturated aliphatic compounds containing one or more nitro/nitroso/imino/amino, carbonyl/carboxyl/hydroxyl/ether bonds	$C_6H_{12}N_2O_4(CH_2)_n$
			$C_8H_{14}O_7(CH_2)_n$				$C_6H_{12}N_2O_5(CH_2)_n$
			$C_9H_{16}O_4(CH_2)_n$				$C_7H_{14}N_2O_6(CH_2)_n$
3	0		$C_6H_8O_7(CH_2)_n$	3			$C_5H_8N_2O_5(CH_2)_n$
			$C_6H_8O_6(CH_2)_n$				$C_5H_8N_2O_6(CH_2)_n$
			$C_8H_{12}O_5(CH_2)_n$				$C_6H_{10}N_2O_7(CH_2)_n$
4			$C_{15}H_{24}O_9(CH_2)_n$	4		Unsaturated compounds containing multiple nitro and amide groups	$C_3H_4N_4O_5(CH_2)_n$
			$C_6H_6O_8(CH_2)_n$			Unsaturated compounds containing multiple amino and ester/carbonyl groups	$C_5H_6N_2O_7(CH_2)_n$
5			$C_8H_8O_{10}(CH_2)_n$	1	1	Unsaturated compounds containing multiple amino groups	$C_7H_{18}N_4(CH_2)_n$
1	1	Formulas with one equivalent double bond/circle and several ether bonds/alcohol groups	$C_7H_{14}O_4(CH_2)_n$			Compounds with an unsaturated bond or ring	$C_8H_{17}NO_4(CH_2)_n$
			$C_8H_{16}O_5(CH_2)_n$	4		Unsaturated aliphatic compounds or cyclic compounds with multiple nitro/nitroso/ imino/amino groups, carbonyl/ester/carboxyl/hydroxyl groups	$C_4H_6N_4O_6(CH_2)_n$
3	1	Organic acid or organic alcohol containing circles/C=C/carboxyl/ester groups	$C_7H_{10}O_4(CH_2)_n$	5			$C_7H_8N_2O_8(CH_2)_n$
4	1.667		$C_6H_6O_5(CH_2)_n$	3	2.333	Nitrogen heterocyclic compounds such as imidazole, pyrazine and pyrazole, or polycyclic compounds with multiple amino groups. May contain a benzene ring.	$C_{24}H_{46}N_2(CH_2)_n$
3	2.2	Aldehydes or alcohols with multiple unsaturated bonds/circles	$C_{18}H_{32}O(CH_2)_n$	4			$C_{13}H_{22}N_2O(CH_2)_n$
4	2.333	Aromatic compounds or aliphatic unsaturated compounds	$C_{14}H_{22}O_2(CH_2)_n$		2.5		$C_{14}H_{24}N_2(CH_2)_n$
5	2.429		$C_{13}H_{18}O_3(CH_2)_n$	5		Aromatic compounds with a ring/ unsaturated bonds, polycyclic compounds	$C_{11}H_{16}N_2O(CH_2)_n$
4	2.5	Aldehydes , ethers or alcohols containing multiple unsaturated bonds	$C_{15}H_{24}O(CH_2)_n$				$C_{13}H_{20}N_2O_2(CH_2)_n$
5	2.5	Aromatic compounds or aliphatic compounds with multiple unsaturated bonds/rings	$C_{11}H_{14}O(CH_2)_n$	6	2.556	Aromatic compounds with rings of unsaturated bonds, polycyclic compounds	$C_{12}H_{16}N_2O_3(CH_2)_n$

DBE Value	X_C Value	Classification	Compounds Series	DBE Value	X_C Value	Classification	Compounds Series
6	2.5	Aromatic compounds with multiple unsaturated functional groups or steroid compounds	$C_{12}H_{14}O_4(CH_2)_n$	5	2.6	Aromatic compounds with a ring/ unsaturated bonds, polycyclic compounds	$C_{11}H_{16}N_2(CH_2)_n$
6	2.556	Aromatic compounds or polycyclic compounds with multiple unsaturated functional groups or circles	$C_{18}H_{26}O_3(CH_2)_n$				$C_{12}H_{17}NO(CH_2)_n$
6	2.6		$C_{10}H_{10}O_2(CH_2)_n$	6		Aromatic compounds with rings or unsaturated bonds, polycyclic compounds	$C_9H_{10}N_2O(CH_2)_n$
7	2.6		$C_{12}H_{12}O_4(CH_2)_n$				$C_{11}H_{13}NO_2(CH_2)_n$
8	2.6		$C_{13}H_{12}O_6(CH_2)_n$				$C_{10}H_{12}N_2O_2(CH_2)_n$
8	2.636		$C_{13}H_{12}O_5(CH_2)_n$	7			$C_{11}H_{12}N_2O_4(CH_2)_n$
9	2.636		$C_{12}H_8O_7(CH_2)_n$	7	2.636		$C_9H_8N_2O_3(CH_2)_n$
10	2.667		$C_{18}H_{18}O_8(CH_2)_n$	8	2.636	Nitrogen heterocyclic compounds or aromatic compounds	$C_9H_6N_2O_5(CH_2)_n$
11	2.692		$C_{17}H_{14}O_9(CH_2)_n$	6	2.667		$C_{12}H_{16}N_2(CH_2)_n$
7	2.7143	Polyphenyl ring compounds	$C_{11}H_{10}O(CH_2)_n$	7			$C_8H_6N_2O_2(CH_2)_n$
8	2.7143		$C_{10}H_6O_2(CH_2)_n$	8			$C_{10}H_8N_2O_4(CH_2)_n$
10	2.789		$C_{16}H_{14}O(CH_2)_n$	9			$C_{18}H_{22}N_2O_6(CH_2)_n$
11	2.8		$C_{15}H_{10}O_2(CH_2)_n$	7	2.692		$C_{11}H_{12}N_2O(CH_2)_n$
11	2.810		$C_{15}H_{10}O(CH_2)_n$	9			$C_{11}H_8N_2O_5(CH_2)_n$
				10	2.692	Nitrogen heterocyclic compounds or aromatic compounds. May contain multiple benzene rings.	$C_{10}H_4N_2O_7(CH_2)_n$
				8	2.7143		$C_{10}H_8N_2O_2(CH_2)_n$
					2.733		$C_9H_6N_2O(CH_2)_n$
				11	2.818		$C_{14}H_{10}N_2(CH_2)_n$
				12	2.818		$C_{16}H_{12}N_2O_2(CH_2)_n$
					2.833		$C_{14}H_8N_2(CH_2)_n$

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