

Supplementary Material

**High molecular weight SOA formation during limonene ozonolysis:
Insights from ultrahigh-resolution FT-ICR mass spectrometry
characterization**

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Figure S1. Superimposition of the data from replicate analyses of an aerosol extract. Mixture of acetonitrile and water (1:1) is used as solvent. The symbol sizes represent the relative abundances of the chemical formulas. The higher is the size of symbol, the higher is the relative abundances. A majority of the data overlay well in terms of chemical identity and relative abundances. However, there are unique formulas between the replicate analyses. Also, the relative abundances of identical chemical formulas from the replicate analyses are not similar in some cases.

Figure S2. Superimposition of the data from aerosol samples from two different experiments. Relative humidity was maintained at 0% and 4% in the experiments. Other experimental conditions were identical. Mixture of acetonitrile and water is used as solvent. The symbol sizes represent the relative abundances of the chemical formulas. The higher is the size of symbol, the higher is the relative abundances. A majority of the data overlay well in terms of chemical identity and relative abundances. However, there are unique formulas between the aerosol samples. Also, the relative abundances of identical chemical formulas from two aerosol samples are not similar in some cases.

Figure S3. Averaged ESI FT-ICR negative ion mass spectra of acetonitrile and water (1:1) extracted aerosol sample from the ozonolysis of limonene. Four characteristic regions at $140 < m/z < 300$, $300 < m/z < 500$, $500 < m/z < 700$ and $700 < m/z < 850$ were observed.

Figure S4a. Schematic of the formation of a CH_2 -homologous series with double bond equivalents (DBE) 4. Alkoxy radical (XVIII) resulting from the limonene ozonolysis is converted to another alkoxy radical (XIX) with one more oxygen atom via oxygen-increasing-reactions (OIR) (isomerization $\rightarrow \text{O}_2 \rightarrow \text{RO}_2$). The number in parenthesis beside OIR indicates the repetition of OIR sequence. Cleavage of the alkoxy radical (XIX) followed by reactions with O_2 and RO_2 and OIR (1) reactions can form neutral molecule (XXI). Reaction with RO_2 with the alkoxy radical (XX) followed by the ozonolysis to the exocyclic double bond form a neutral molecule (XXII). Repetition of the OIR steps on (XIX) forms an alkoxy radical, which is converted to a neutral molecule (XXIII). Organic aerosol formation with C_{11} - C_{12} carbon occurs by the reactive absorption of gas phase organics (e.g., glyoxal) on aerosols as shown in the box.

Figure S4b. Schematic of the formation of O-homologous series with double bond equivalents (DBE) 4. Alkoxy radical (XXIV) resulting from the limonene ozonolysis is converted to another alkoxy radical (XXV) with one more oxygen atom via oxygen-increasing-reactions (OIR) (isomerization $\rightarrow \text{O}_2 \rightarrow \text{RO}_2$). Repetitions of the OIR steps on this radical forms alkoxy radicals such as XXVI, XXVII, XXVIII and XXIX. The number in parenthesis beside OIR indicates the repetition of OIR sequence. Neutral molecules are formed from these alkoxy radical to form homologous series.

Figure S5. The change of double bond equivalents (DBE) by 2 in (a) Criegee reaction pathway; Criegee radicals react with neutral molecules with the formation of peroxide ester and ozonide (b) hydroperoxide reaction pathway; hydroperoxides react with neutral molecules and (c) hemiacetal pathway, carbonyl compounds react with alcohols. All the participating building units shown are highly dominant in the mass spectra. The resulting accretion products are also the most dominant in the mass spectra. See the Table S1.

Figure S6. The change of double bond equivalents (DBE) by both 3 and 2 in (a) aldol condensation reaction pathway; reactions occur between carbonyl compounds and (b) esterification reaction pathway; reactions occur between carboxylic acids and alcohols. Water molecule can be eliminated in these reactions. All the participating building units and resulting oligomers are dominant in the mass spectra. See Table S1.

Figure S7. Reconstructed product ion spectra of the precursor peaks at the m/z of (a) 185, (b) 357, (c) 387, (d) 417, and (e) 541. Fragmentation was carried out using infrared multiphoton dissociation (IRMPD) technique. A normalized energy level of 100% was applied with an isolation width of 2 m/z units. Reconstruction of the mass spectrum was done following the co-addition of ~50 transients and formula assignments with a formula calculator (Composer, Sierra Analytics). The spectra show only the monoisotopic peaks. The inset shows the fragmentation processes and potential building units of each of the reaction channels that could form the prominent isobaric ions (shown in the inset) of the precursors.

Table S2. Formation of high abundance Group III compounds in the mass spectra. They are identified following different formation processes of high MW compounds.

Theoretical neutral mass	Chemical formula	Peak intensity (%) ^a	Hydroperoxide reaction ^b	Criegee reaction ^c	Hemi-acetal reaction ^d	Condensation reaction ^e
528.2571	C ₂₆ H ₄₀ O ₁₁	4	2	4	4	2
542.2727	C ₂₇ H ₄₂ O ₁₁	5	4	6	4	10
544.252	C ₂₆ H ₄₀ O ₁₂	6	5	1	7	3
546.2676	C ₂₆ H ₄₂ O ₁₂	5	3	1	6	2
556.2884	C ₂₈ H ₄₄ O ₁₁	5	4	2	5	2
558.2676	C ₂₇ H ₄₂ O ₁₂	8	4	1	6	4
560.2469	C ₂₆ H ₄₀ O ₁₃	6	3	3	5	6
560.2833	C ₂₇ H ₄₄ O ₁₂	6	2	2	5	2
562.2625	C ₂₆ H ₄₂ O ₁₃	5	4	1	6	3
572.2469	C ₂₇ H ₄₀ O ₁₃	5	4	2	6	7
572.2833	C ₂₈ H ₄₄ O ₁₂	8	5	1	6	3
574.2625	C ₂₇ H ₄₂ O ₁₃	9	4	1	6	6
574.2989	C ₂₈ H ₄₆ O ₁₂	6	4	2	6	1
576.2418	C ₂₆ H ₄₀ O ₁₄	4	3	1	7	5
576.2782	C ₂₇ H ₄₄ O ₁₃	7	2	1	4	3
586.2625	C ₂₈ H ₄₂ O ₁₃	6	3	1	5	8
586.2989	C ₂₉ H ₄₆ O ₁₂	6	3	2	6	2
588.2782	C ₂₈ H ₄₄ O ₁₃	11	9	5	12	22
590.2575	C ₂₇ H ₄₂ O ₁₄	8	1	2	3	6
590.2938	C ₂₈ H ₄₆ O ₁₃	7	3	×	3	2
592.2731	C ₂₇ H ₄₄ O ₁₄	6	3	1	×	4
600.2782	C ₂₉ H ₄₄ O ₁₃	5	4	1	7	8
602.2575	C ₂₈ H ₄₂ O ₁₄	6	2	2	4	8
602.2938	C ₂₉ H ₄₆ O ₁₃	9	2	3	3	4
604.2731	C ₂₈ H ₄₄ O ₁₄	11	3	1	6	6
604.3095	C ₂₉ H ₄₈ O ₁₃	6	2	2	7	2
606.2524	C ₂₇ H ₄₂ O ₁₅	5	3	2	5	7
606.2888	C ₂₈ H ₄₆ O ₁₄	7	2	2	4	4
616.2731	C ₂₉ H ₄₄ O ₁₄	6	4	1	10	7
616.3095	C ₃₀ H ₄₈ O ₁₃	5	2	1	4	3
618.2524	C ₂₈ H ₄₂ O ₁₅	5	2	1	7	7
618.2888	C ₂₉ H ₄₆ O ₁₄	10	2	1	4	5
620.268	C ₂₈ H ₄₄ O ₁₅	7	2	3	4	7
620.3044	C ₂₉ H ₄₈ O ₁₄	6	3	1	8	3
622.2837	C ₂₈ H ₄₆ O ₁₅	5	6	1	7	5
632.268	C ₂₉ H ₄₄ O ₁₅	5	4	1	9	10
632.3044	C ₃₀ H ₄₈ O ₁₄	6	2	1	6	4
634.2837	C ₂₉ H ₄₆ O ₁₅	8	4	1	9	7
636.2993	C ₂₉ H ₄₈ O ₁₅	5	4	×	6	3
648.2993	C ₃₀ H ₄₈ O ₁₅	5	2	2	3	6

^aIt is calculated with respect to the base peak in the mass spectra.

^bThe number of possible combinations between two hydroperoxides and a neutral molecule.

^cThe number of possible combinations between two Criegee radicals and a neutral molecule.

^dThe number of possible combinations between three neutral molecules.

^eThe number of possible combinations between three neutral molecules with elimination of two molecules of water by aldol condensation and esterification reactions.

Figure S1.

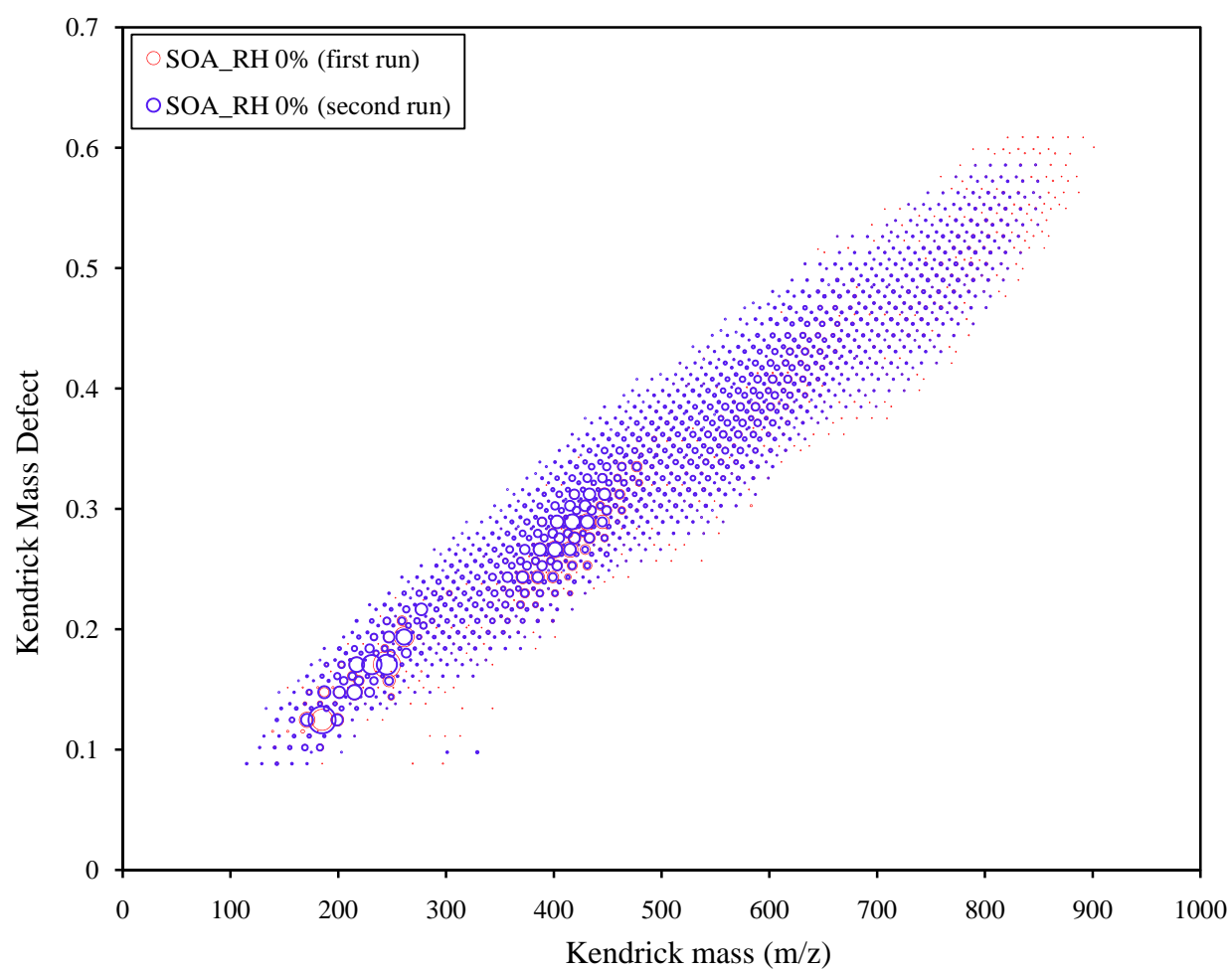


Figure S2.

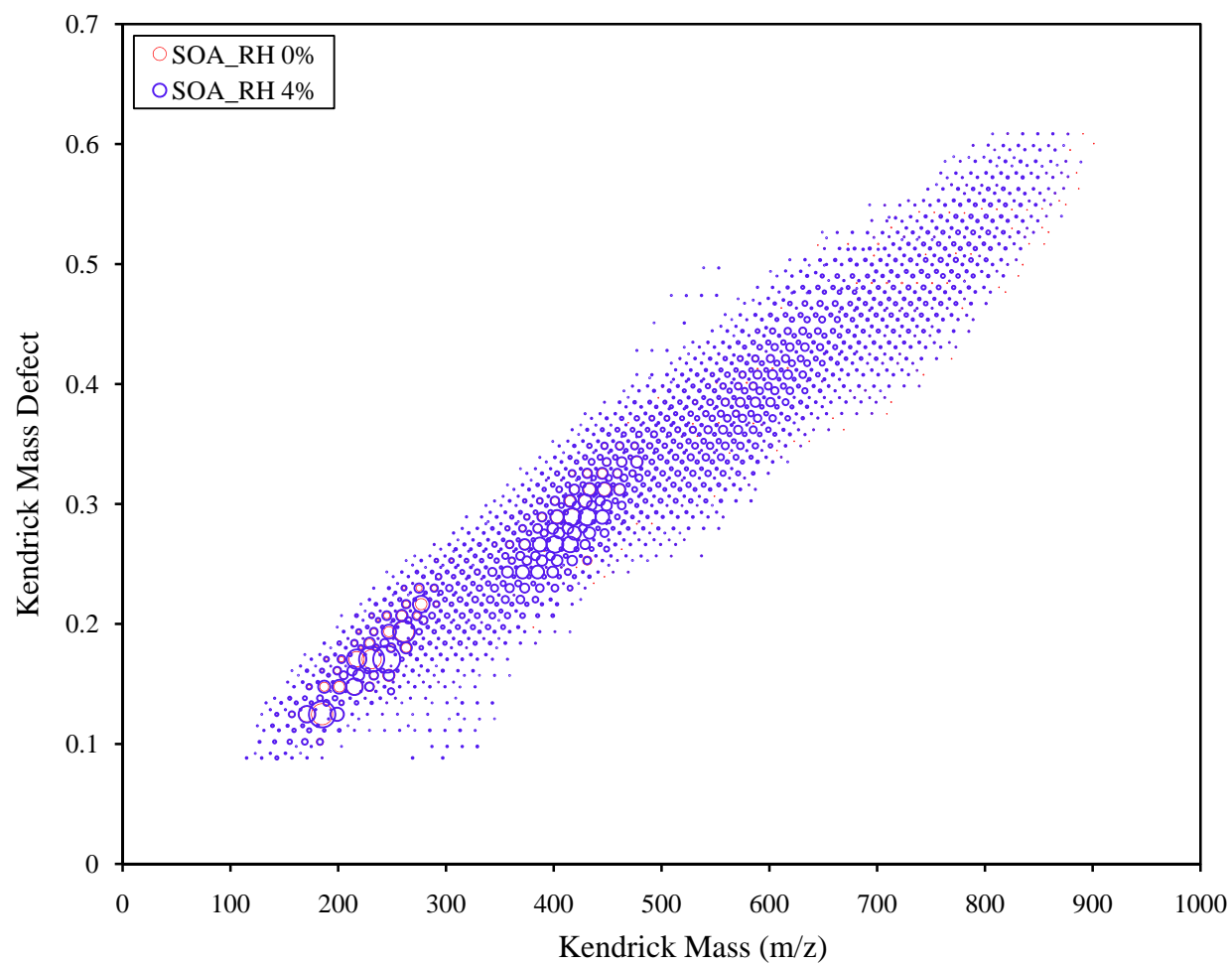


Figure S3.

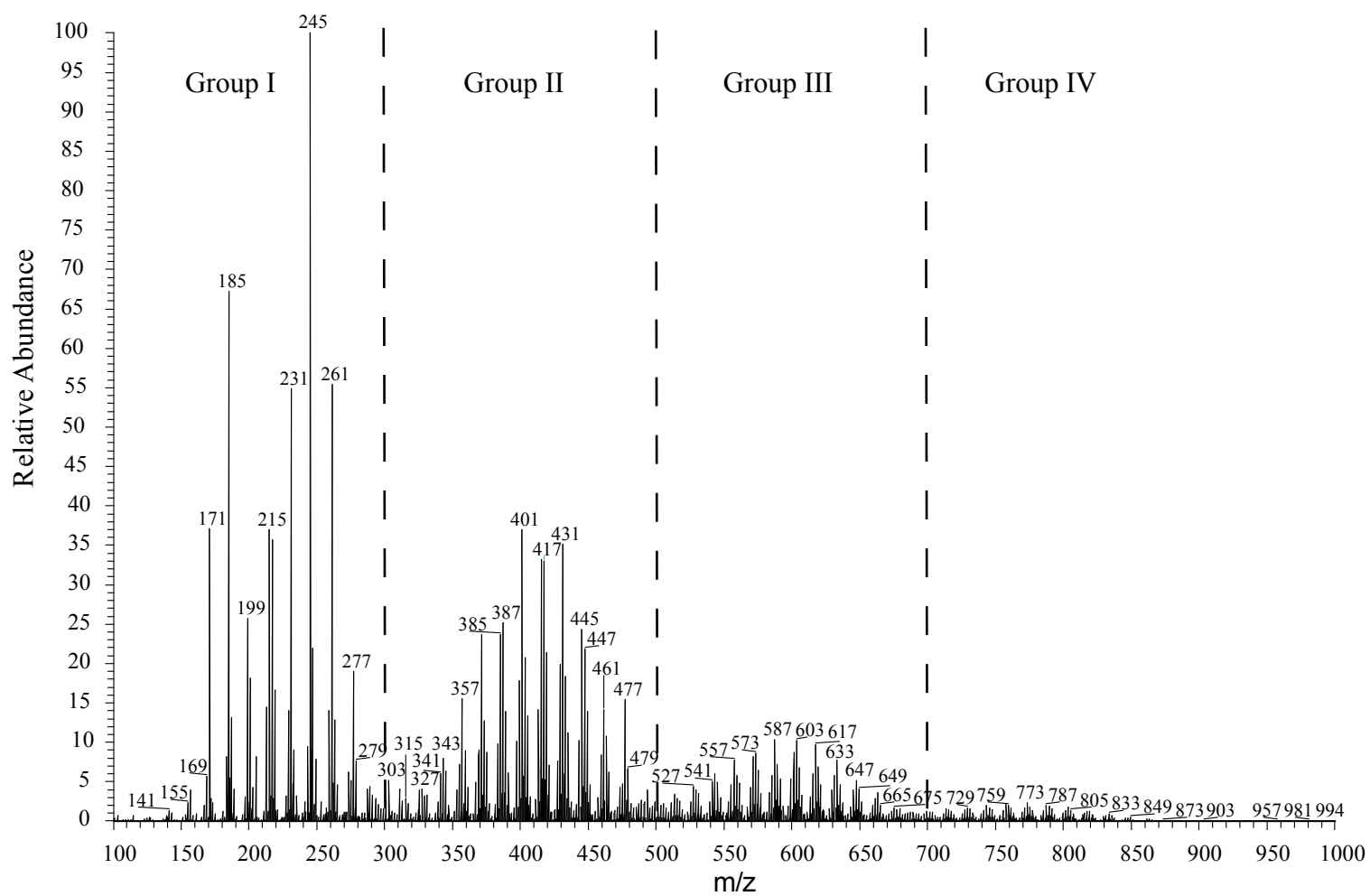


Figure S4a.

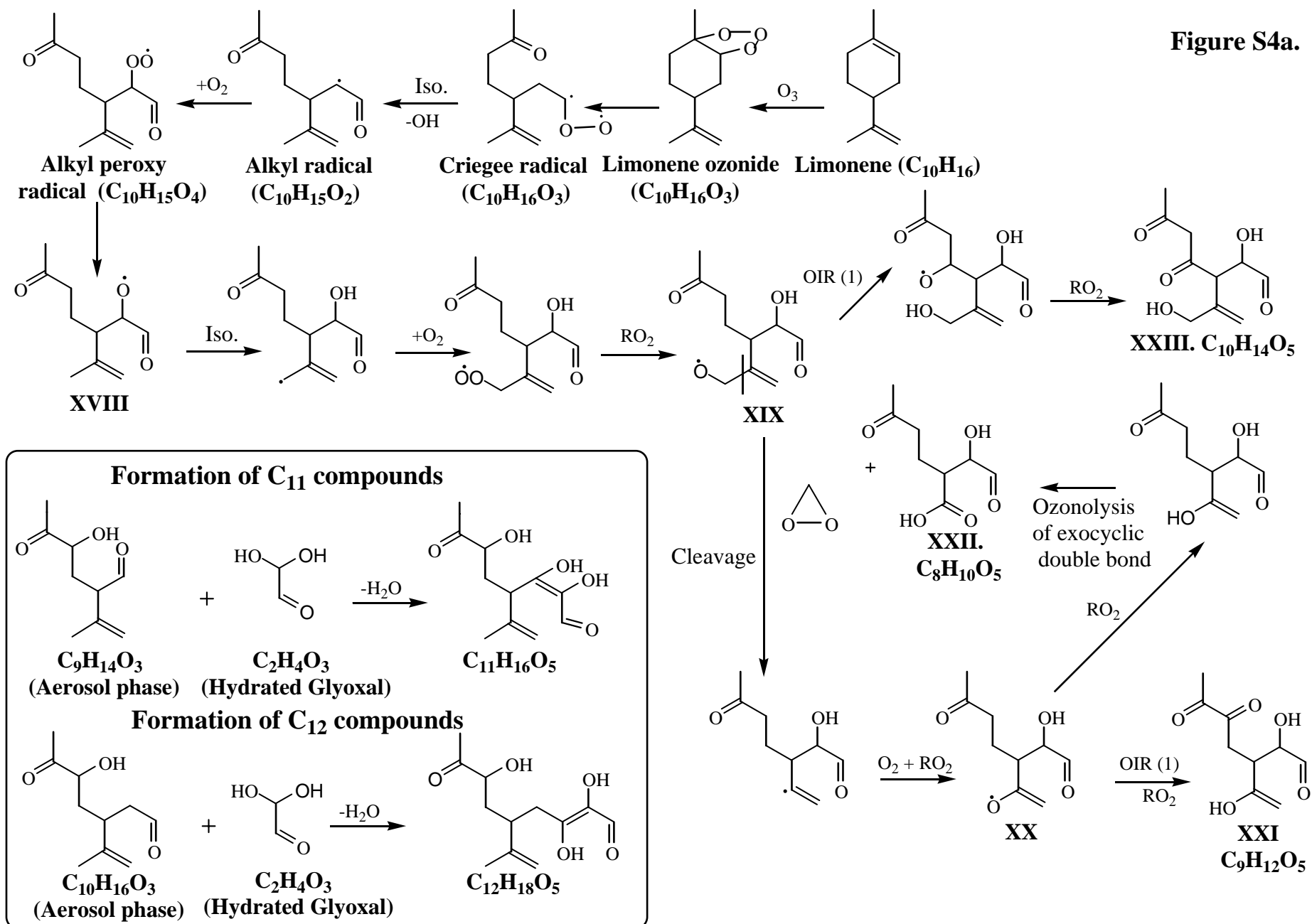


Figure S4b.

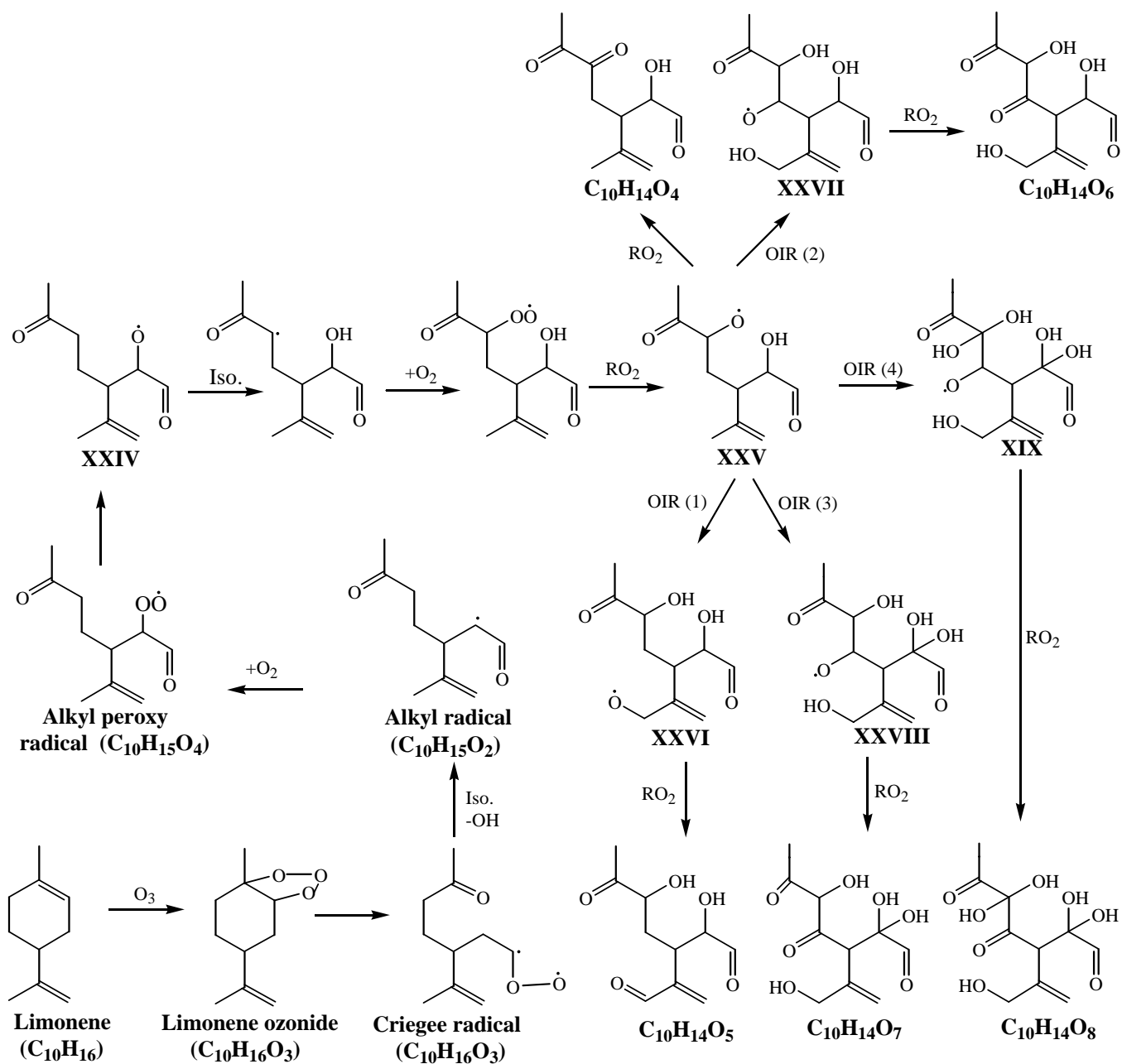


Figure S5.

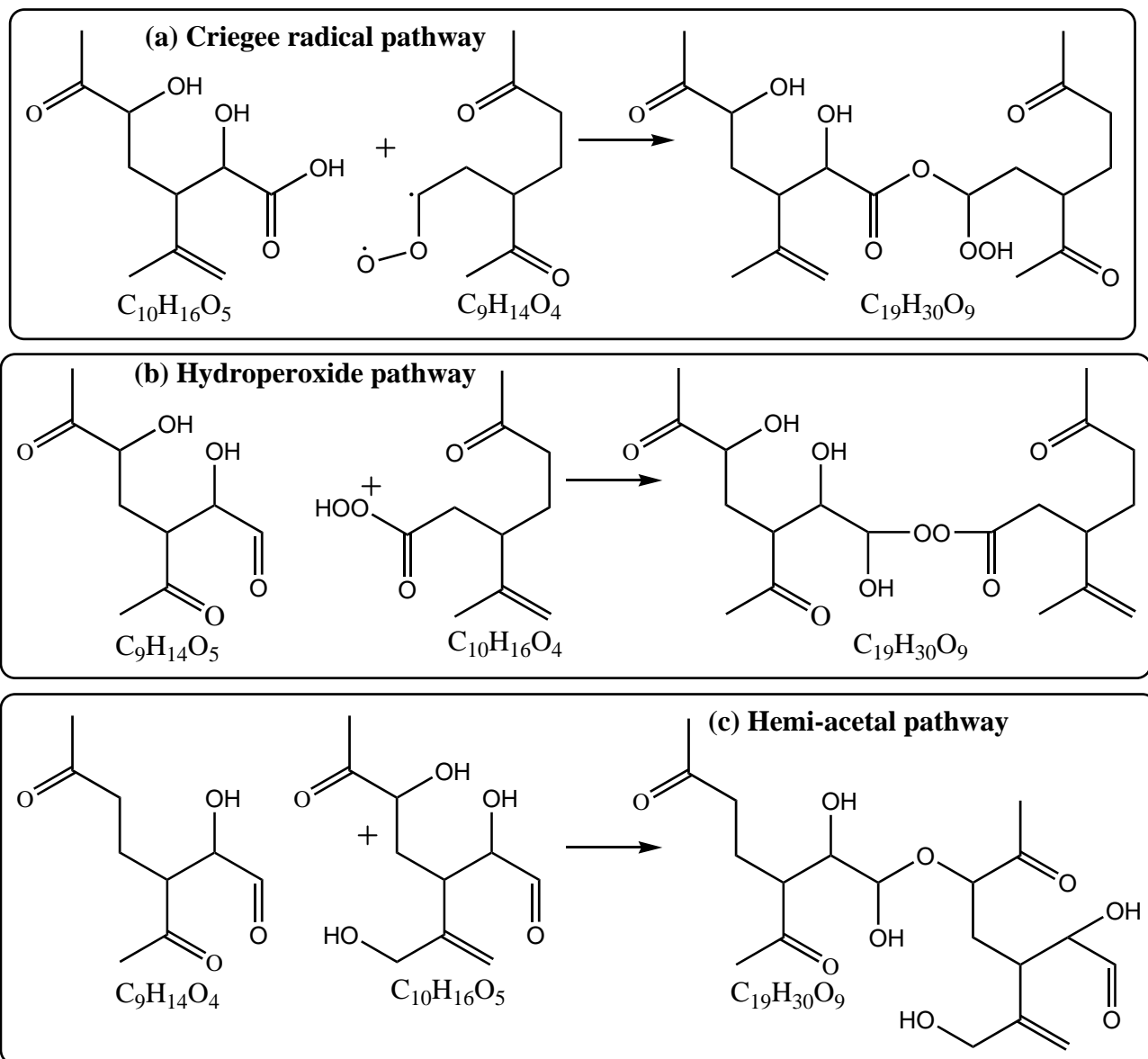


Figure S6.

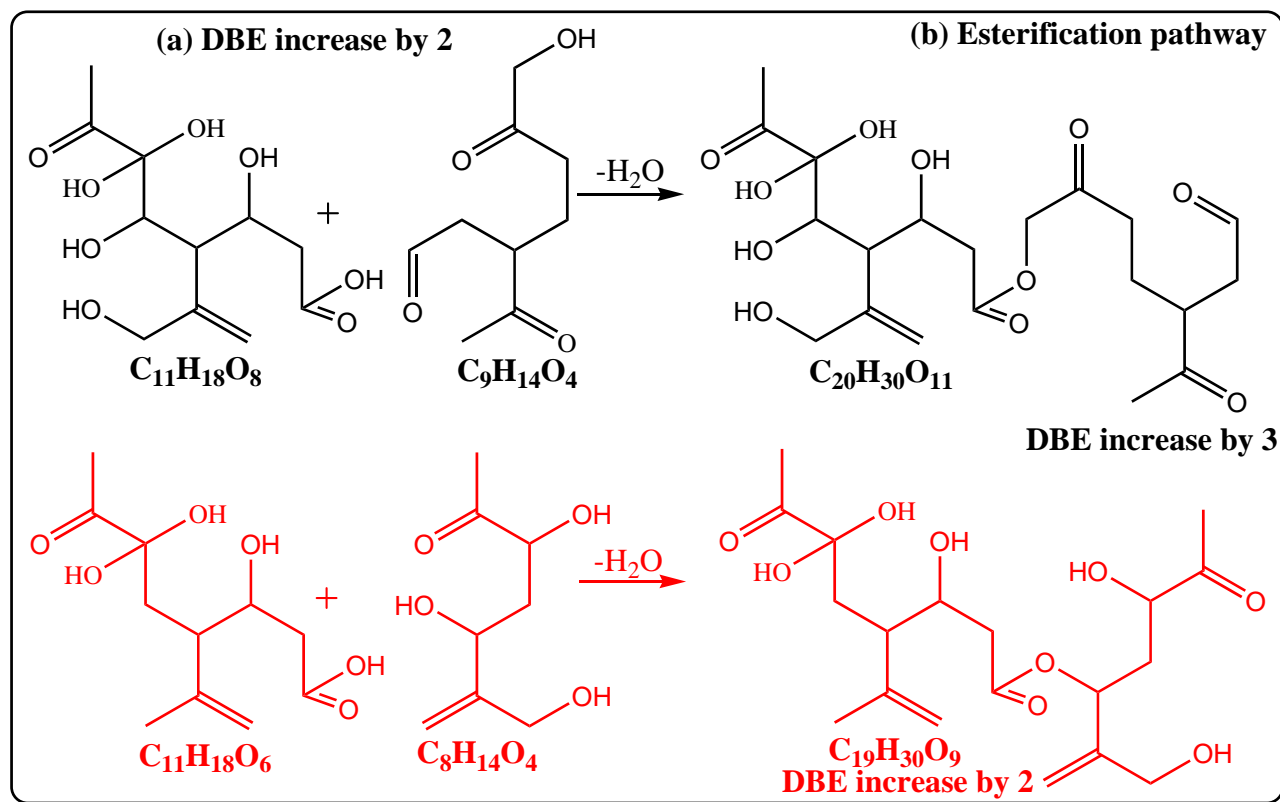
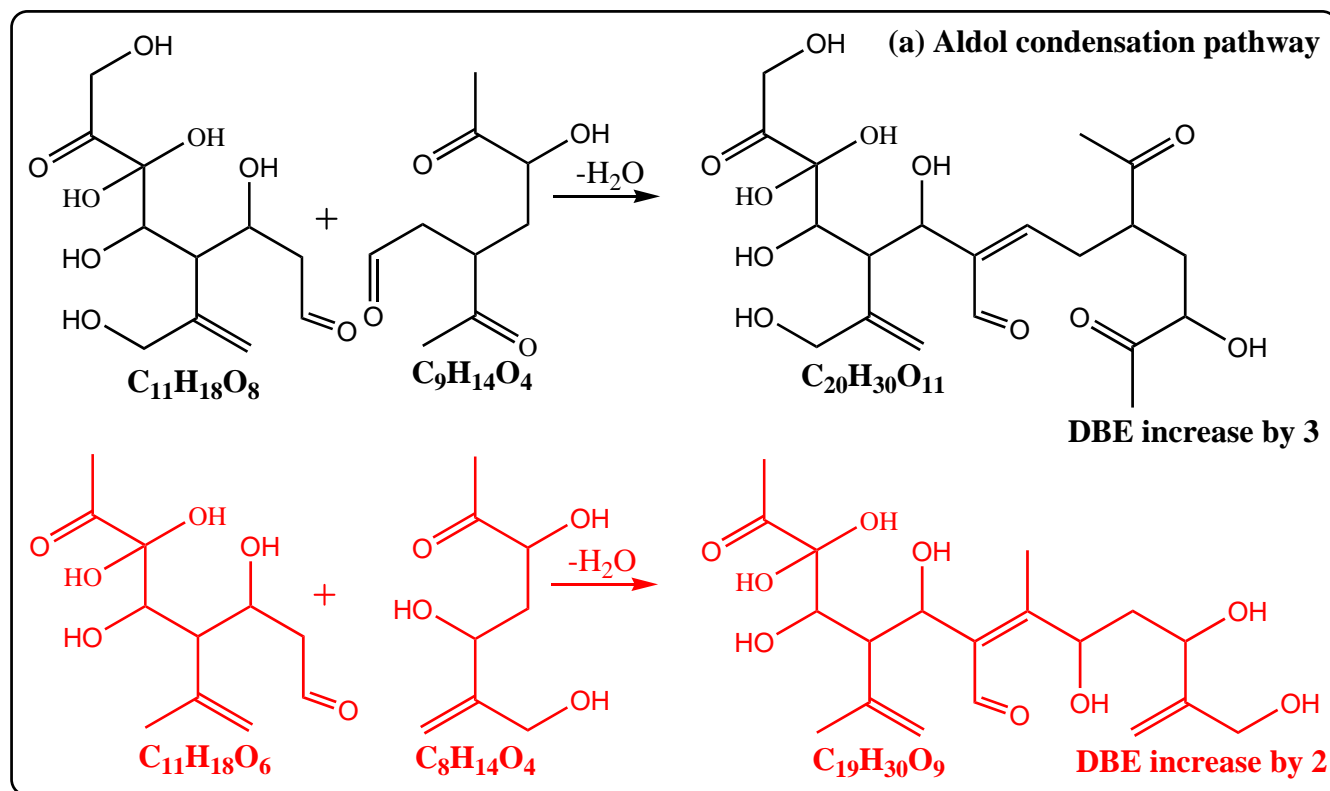


Figure S7.

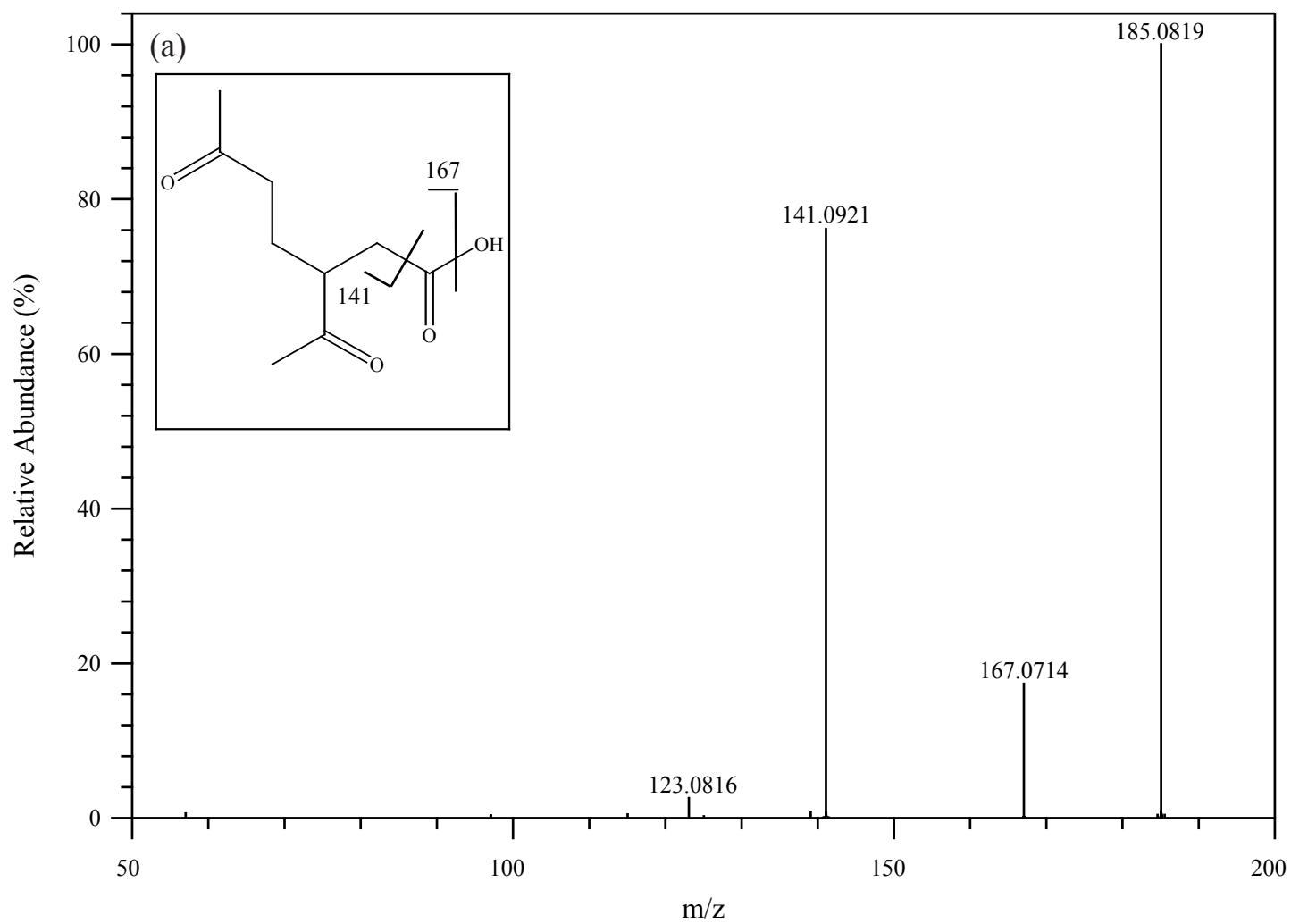


Figure S7.

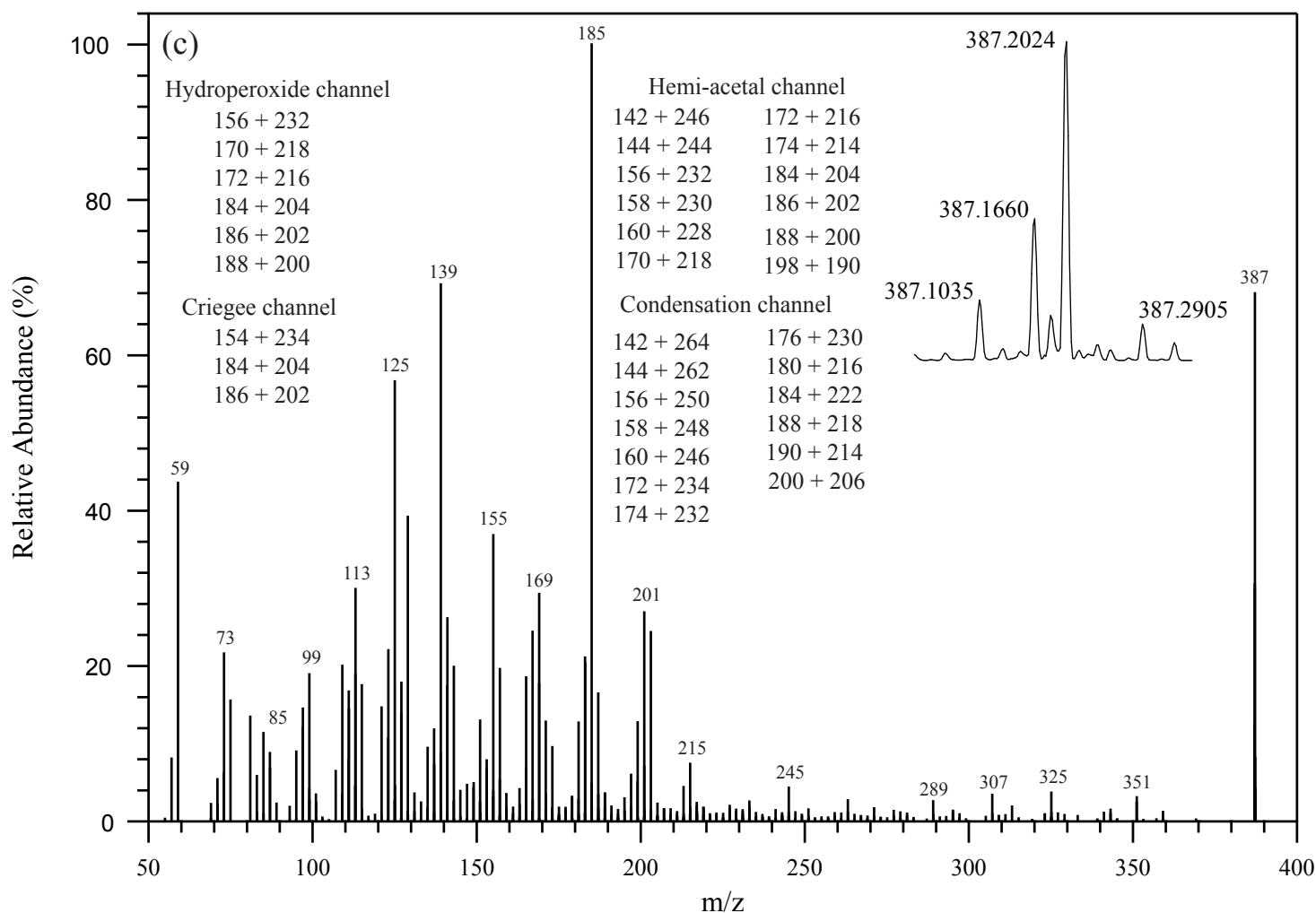
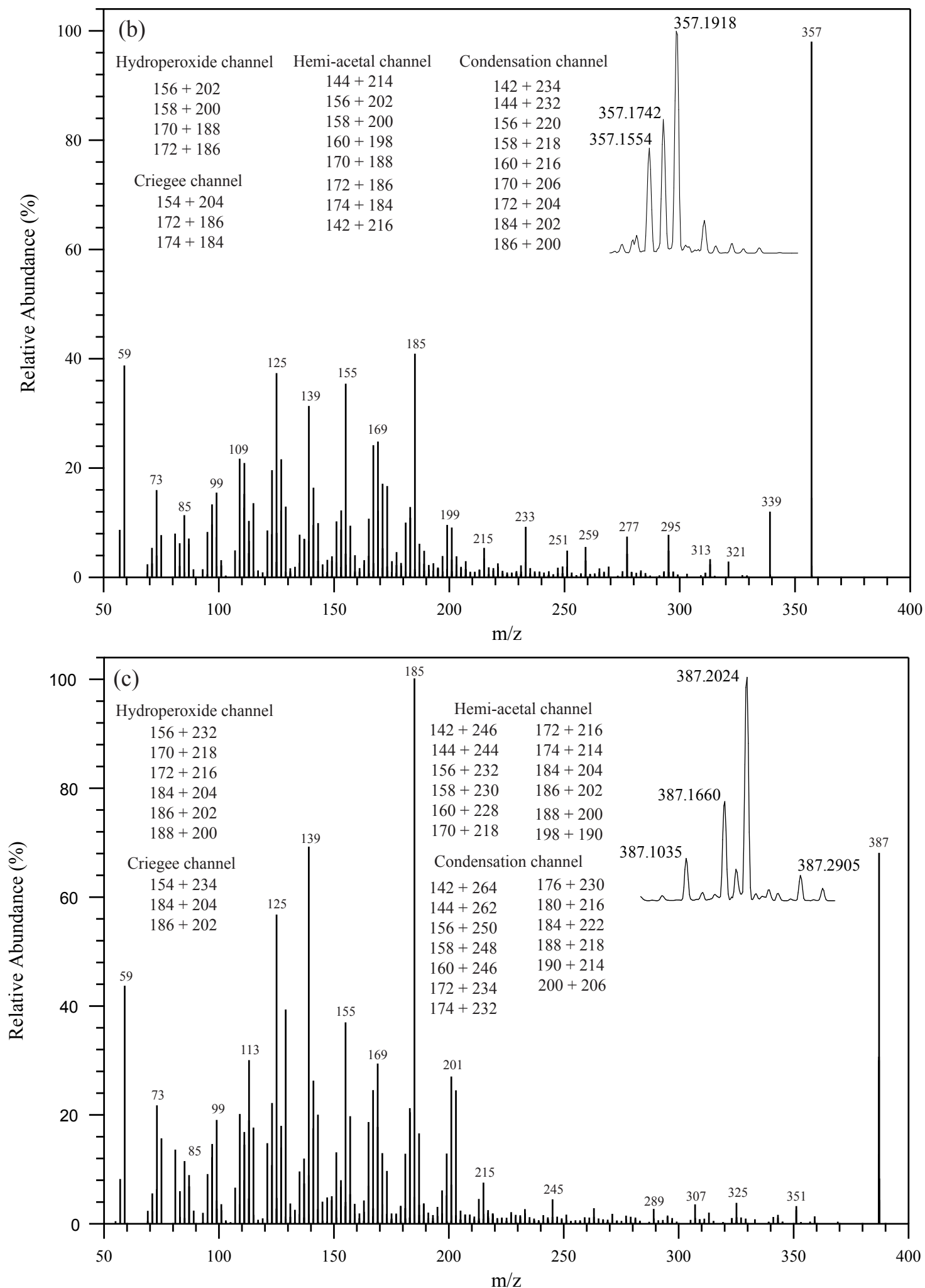


Figure S7.

