Supplement of

# On the formation of highly oxidized pollutants by autoxidation of terpenes under low temperature combustion conditions: the case of limonene and α-pinene.

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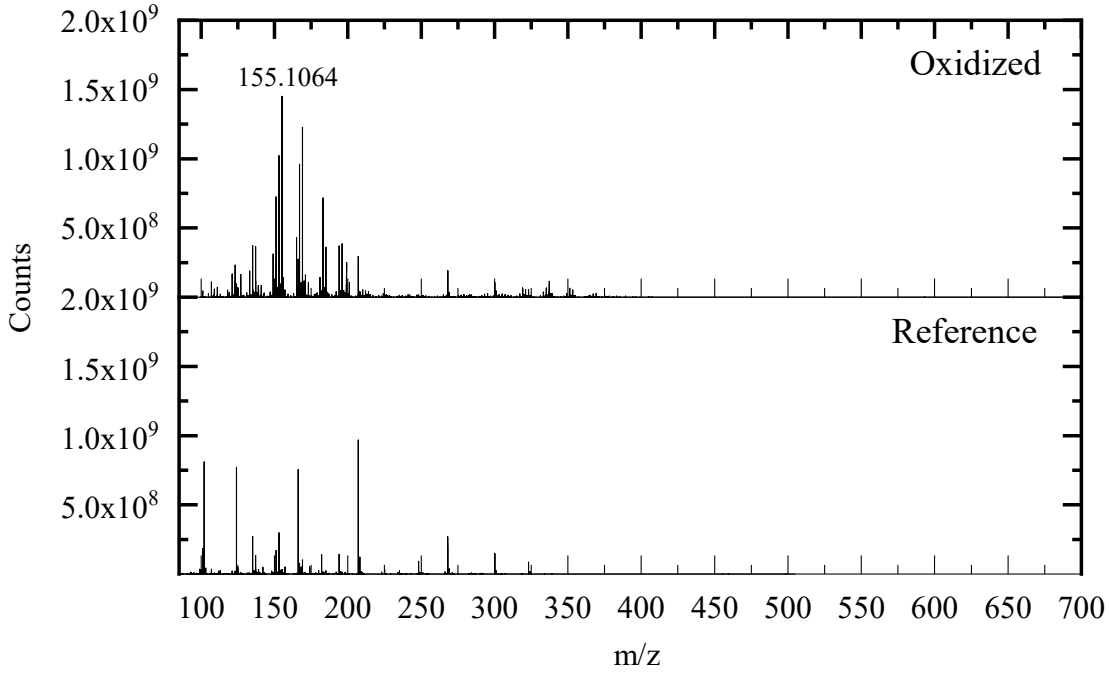



Fig. S1: Comparison of the mass spectra of pure (standard) and oxidated limonene

**Table S1.** Representation of the mass spectrometry data characterizing the oxidation of α-pinene and limonene (ionization source: APCI positive and negative mode, JSR experiments).

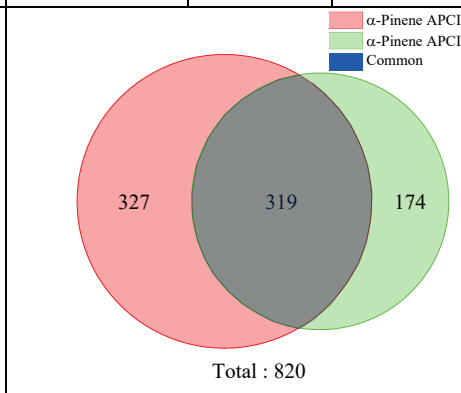
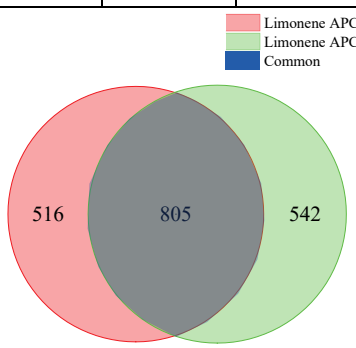
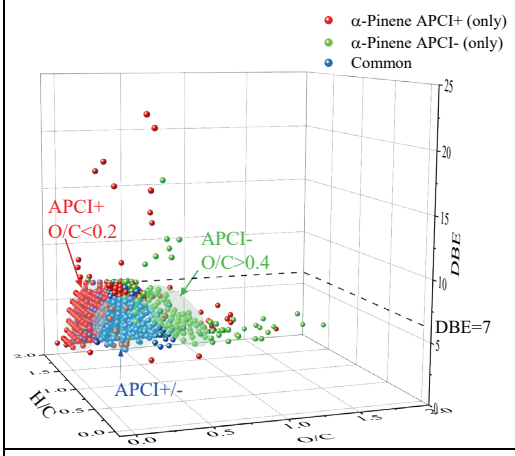
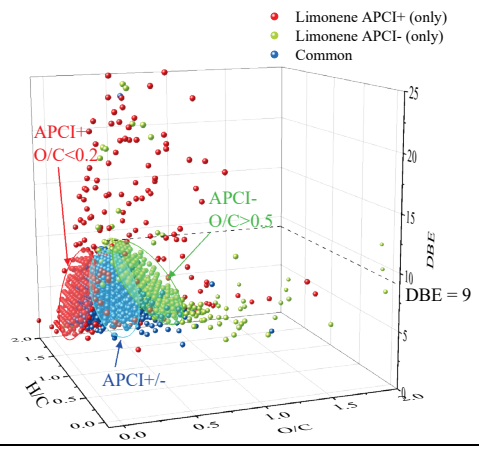
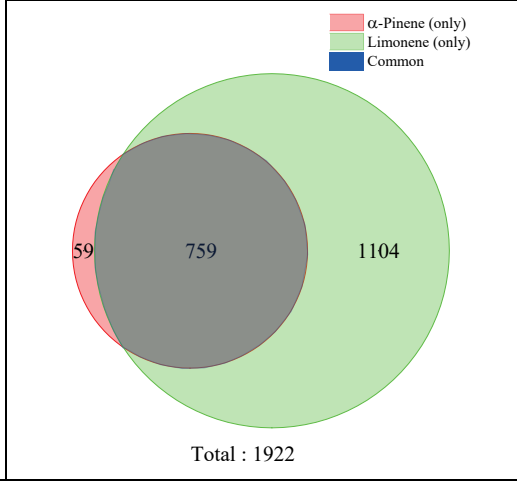
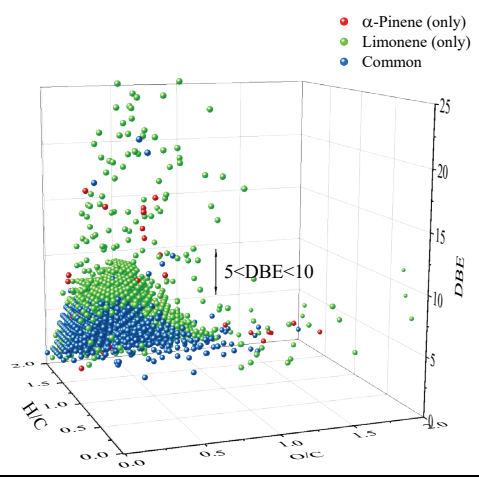
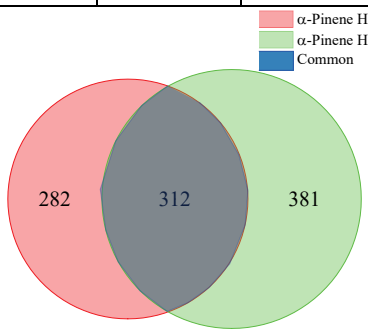
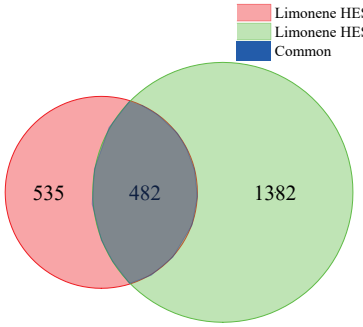
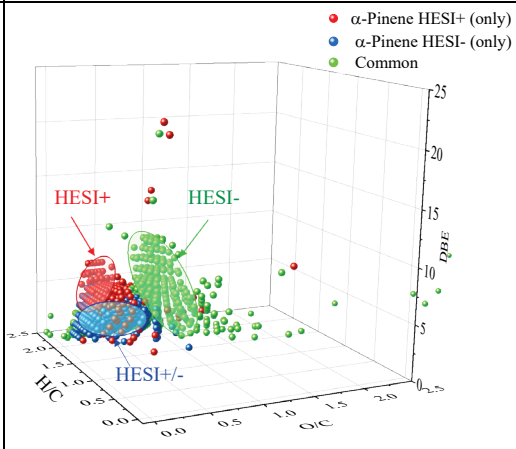
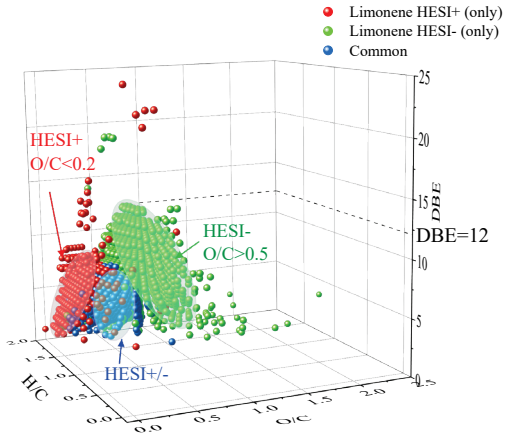
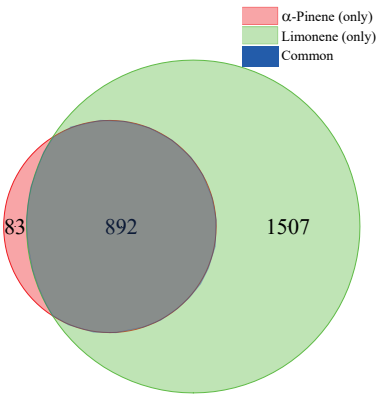
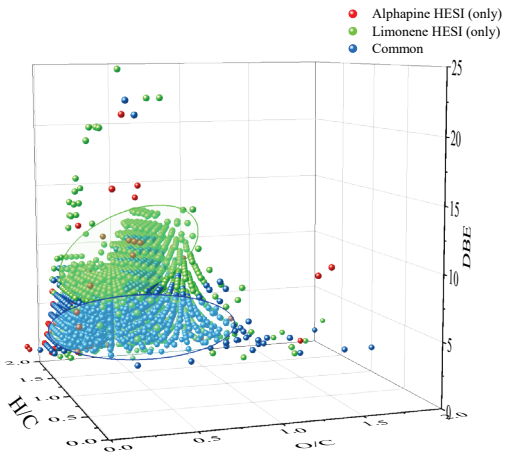
| | **α-Pinene** | | | **Limonene** | | |
|---|---|---|---|---|---|---|
| Source and mode | **APCI$^+$** | | **APCI$^-$** | **APCI$^+$** | | **APCI$^-$** |
| Number of compounds | 646 | | 503 | 1321 | | 1346 |
| Distribution | specific to positive mode 327 | common 319 | specific to negative mode 174 | specific to positive mode 516 | common 805 | specific to negative mode 542 |
| Venn graph |  Total : 820 | | |  Total :1863 | | |
| VK *vs* DBE |  | | |  | | |
| |  Total : 1922 | | |  | | |

**Table S2.** Representation of the mass spectrometry data characterizing the oxidation of α-pinene and limonene (ionization source: HESI positive and negative modes, JSR experiments).

| | **α-Pinene** | | | **Limonene** | | |
|---|---|---|---|---|---|---|
| Source and mode | **HESI$^+$** | | **HESI$^-$** | **HESI$^+$** | | **HESI$^-$** |
| Number of compounds | 594 | | 693 | 1017 | | 1864 |
| Distribution | specific to positive mode 282 | common 312 | specific to negative mode 381 | specific to positive mode 353 | common 482 | specific to negative mode 1342 |
| Venn Graph |  Total : 975 | | |  Total : 2399 | | |
| VK *vs* DBE |  | | |  | | |
| |  Total : 2482 | | |  | | |

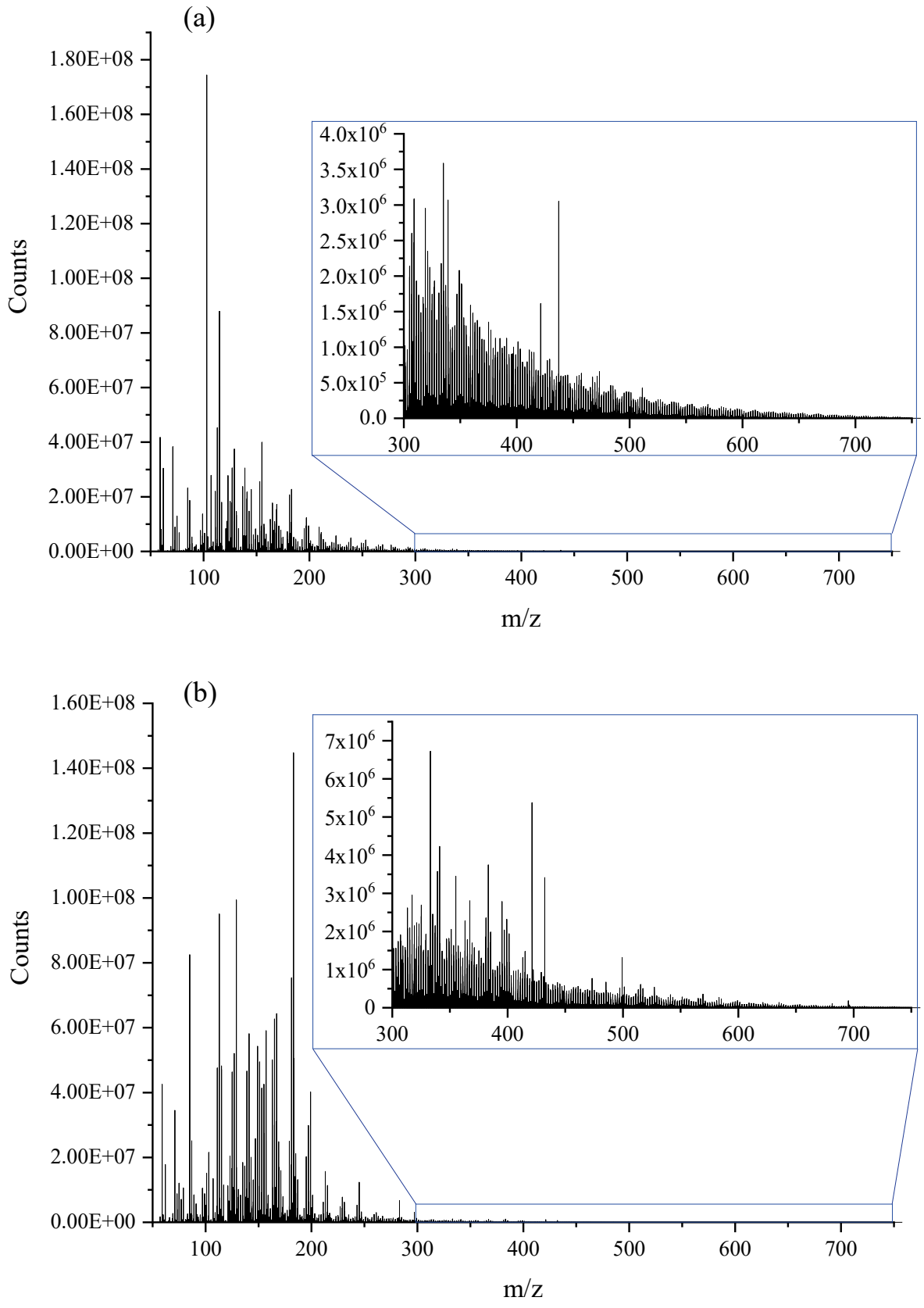



**Fig. S2:** α-pinene and limonene mass Spectra acquired with a HESI source in negative mode

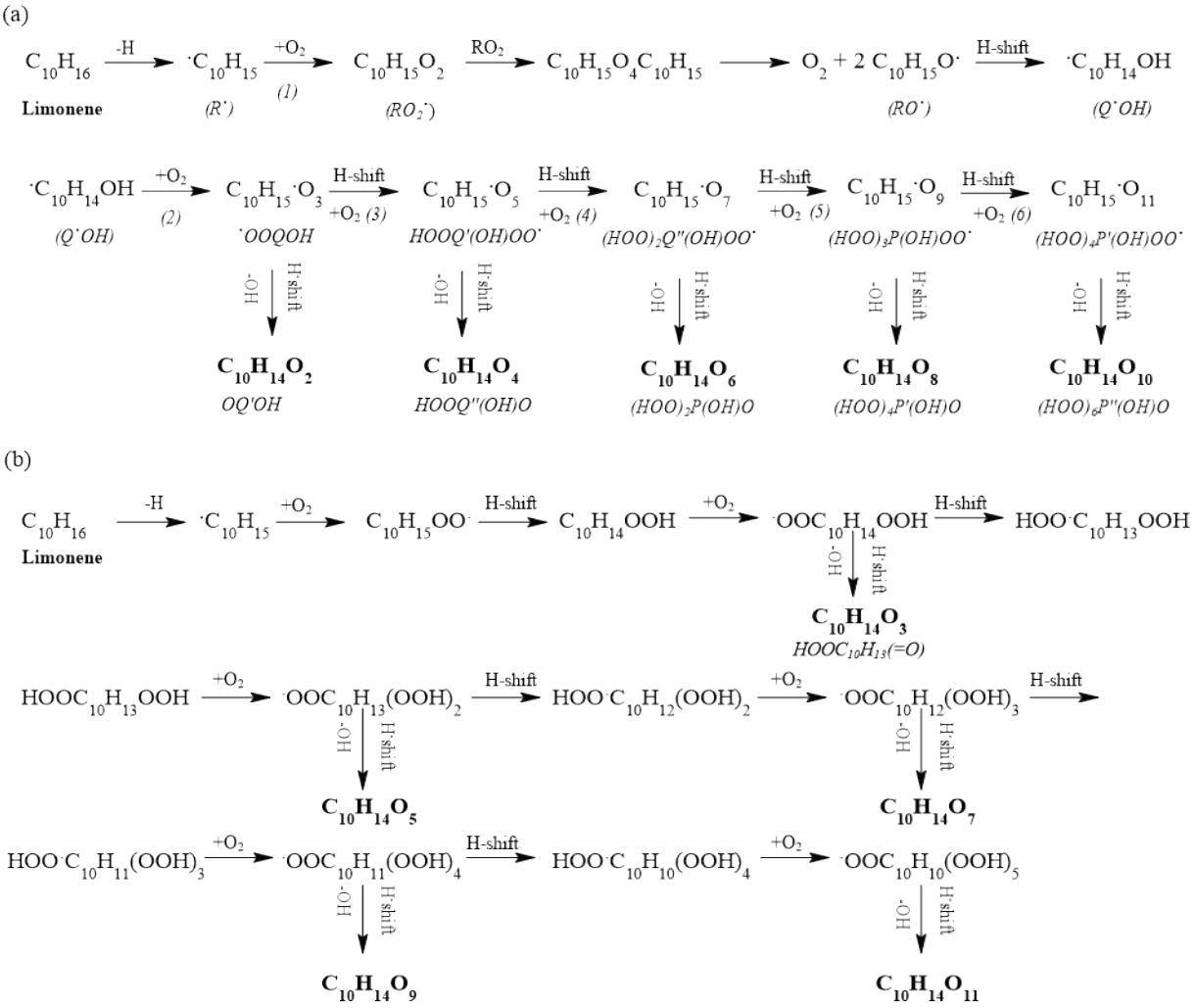



**Fig. S3:** Molecular forms resulting from an autoxidation mechanism of limonene: a) even number of oxygens b) odd number of oxygens.

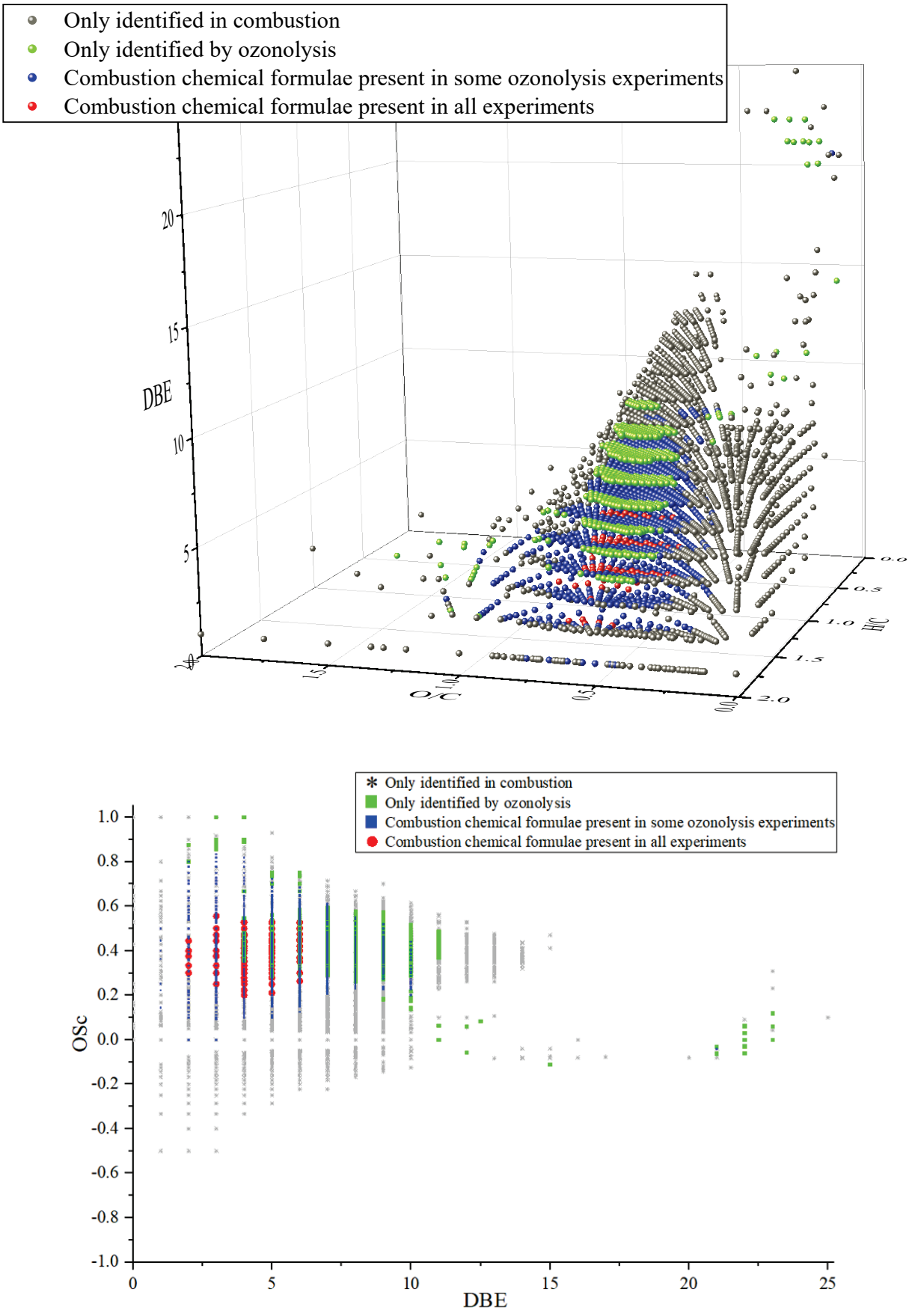



**Fig. S4:** a) 3-D representation of all limonene oxidation data where DBE is used as third dimension and b) OSc vs DBE graph

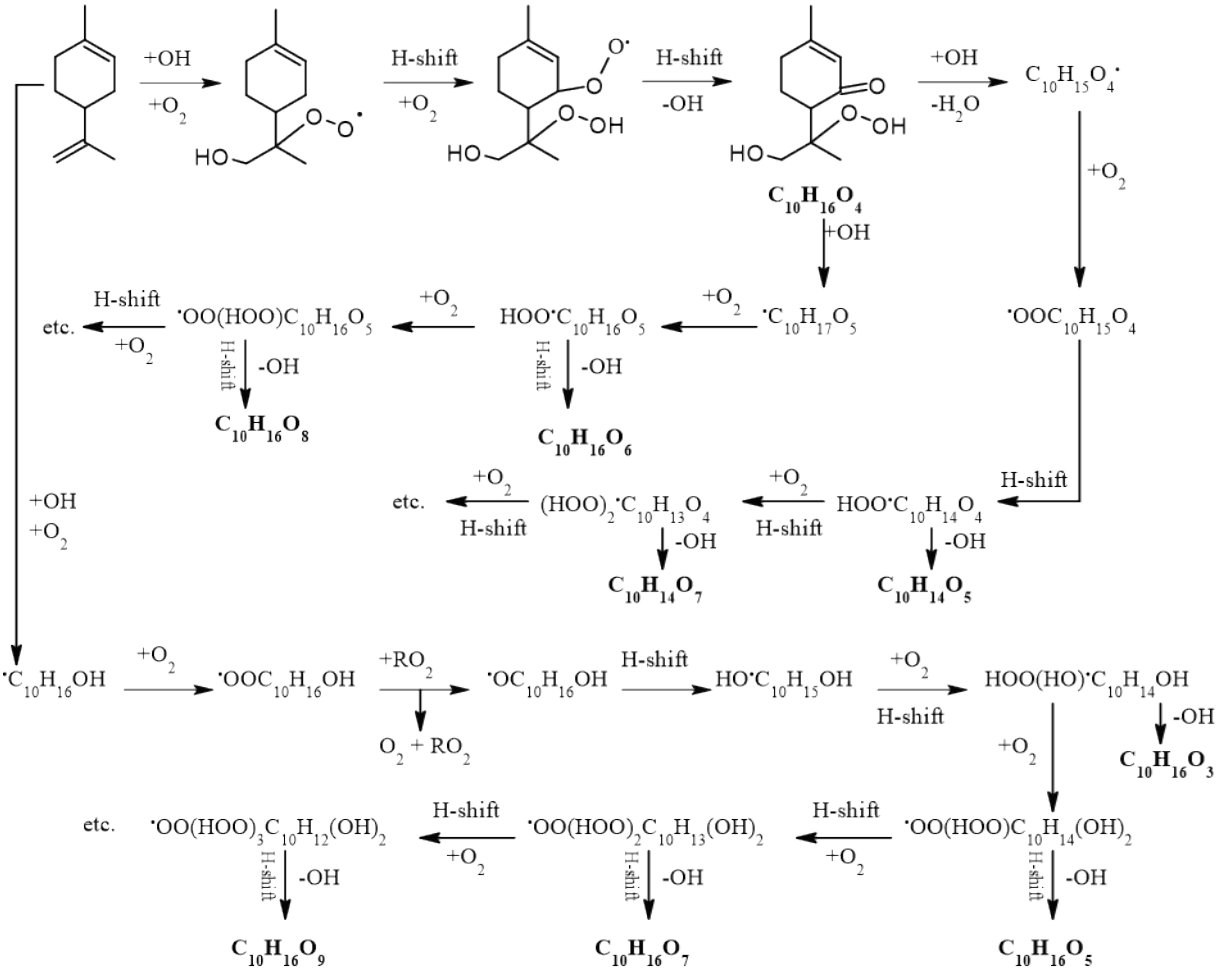



**Fig. S5**: Some proposed formation routes to $C_{10}H_{16}O_x$ species via autoxidation

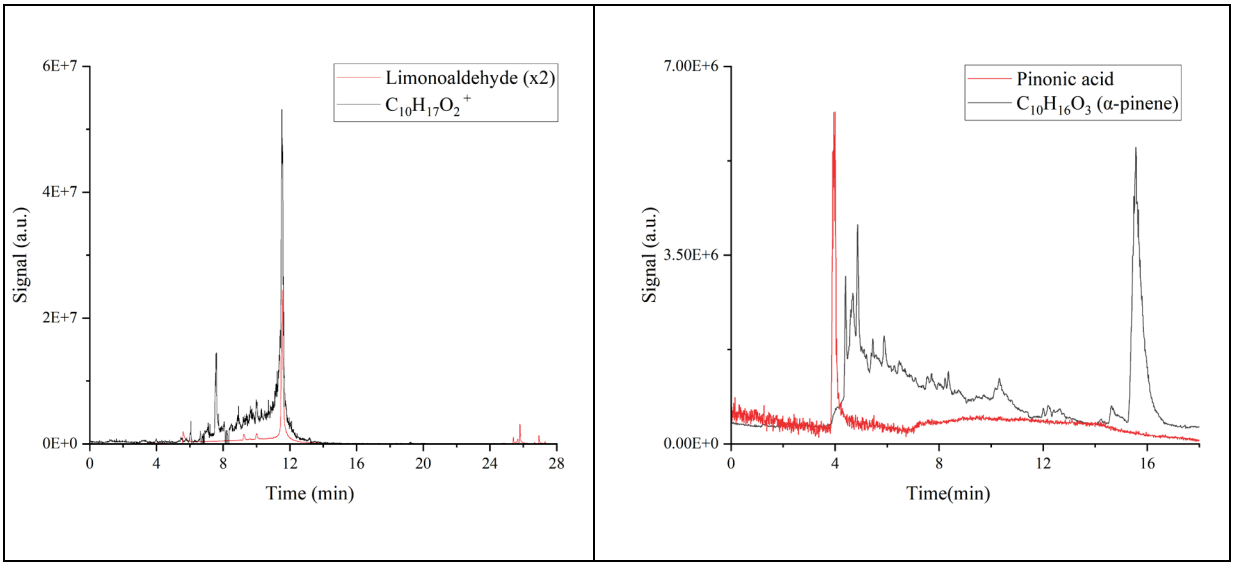



**Fig. S6**: Superposition of chromatographs (UHPLC) of limonoaldehyde (left) and pinonic acid (right) standards and $C_{10}H_{16}O_2$ and $C_{10}H_{16}O_3$ isomers (positive ionization mode).

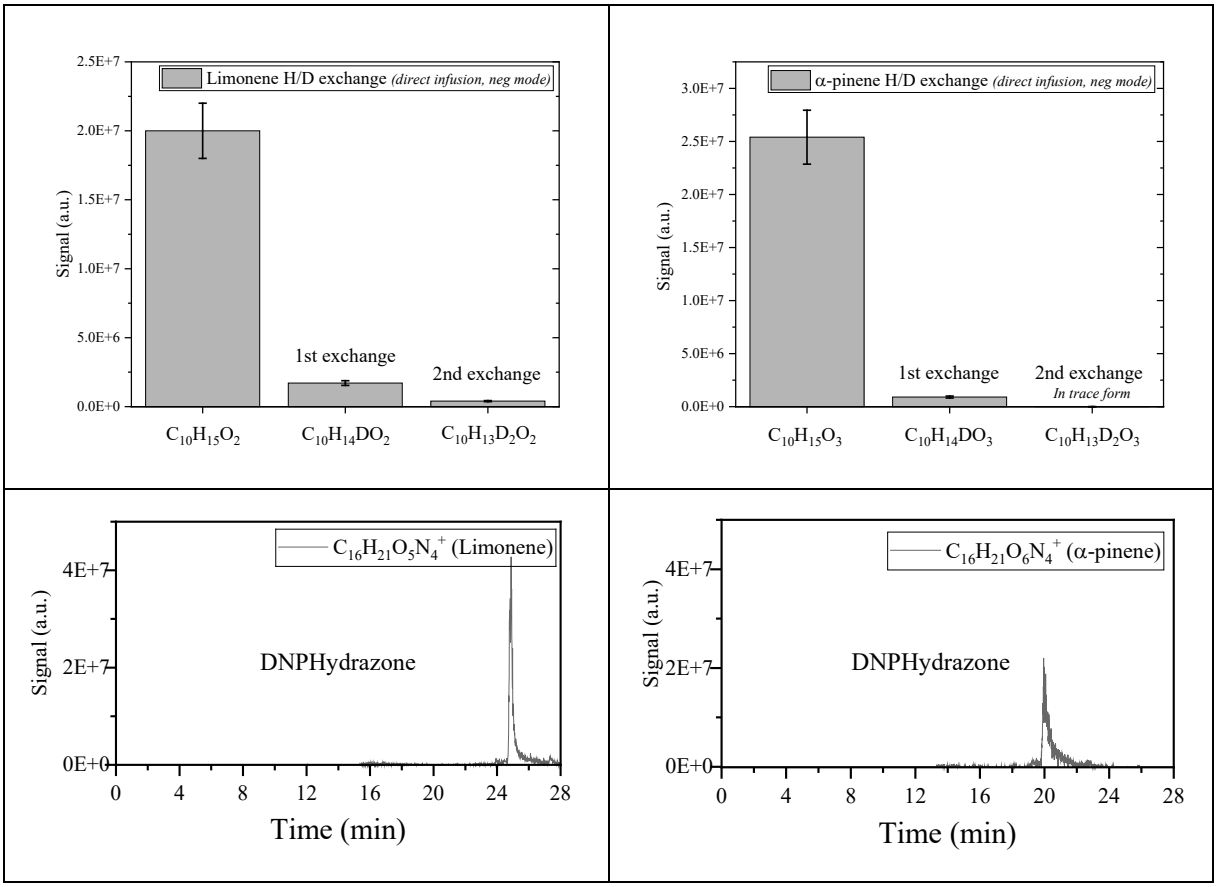



**Fig. S7**: $D_2O$ exchanges for limonene and α-pinene (direct infusion, negative ionization mode) - top; and derivatization of carbonyls in limonene and α-pinene oxidation samples using 2,4-DNPH (UHPLC, positive mode) – bottom.