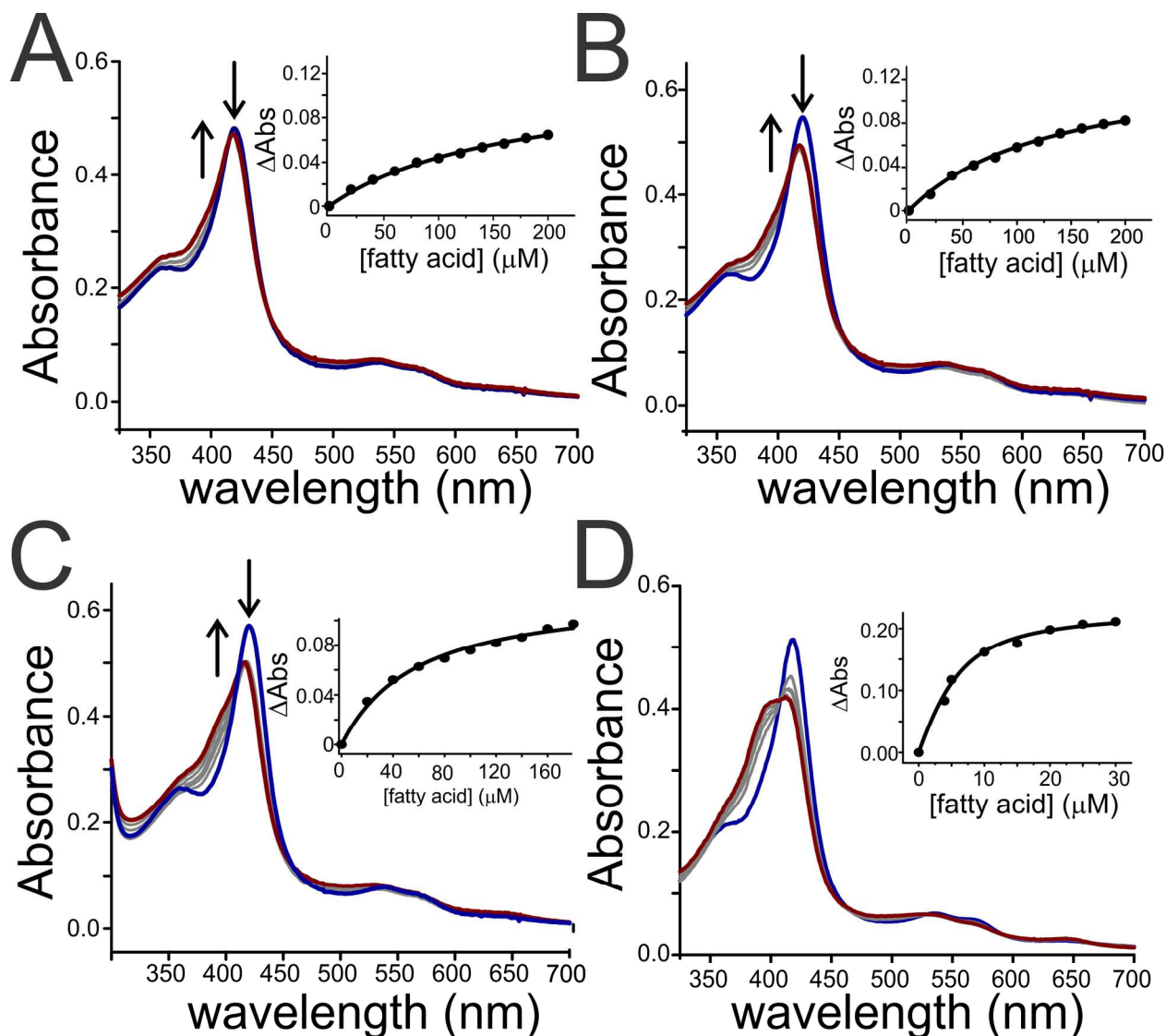


## SUPPORTING INFORMATION

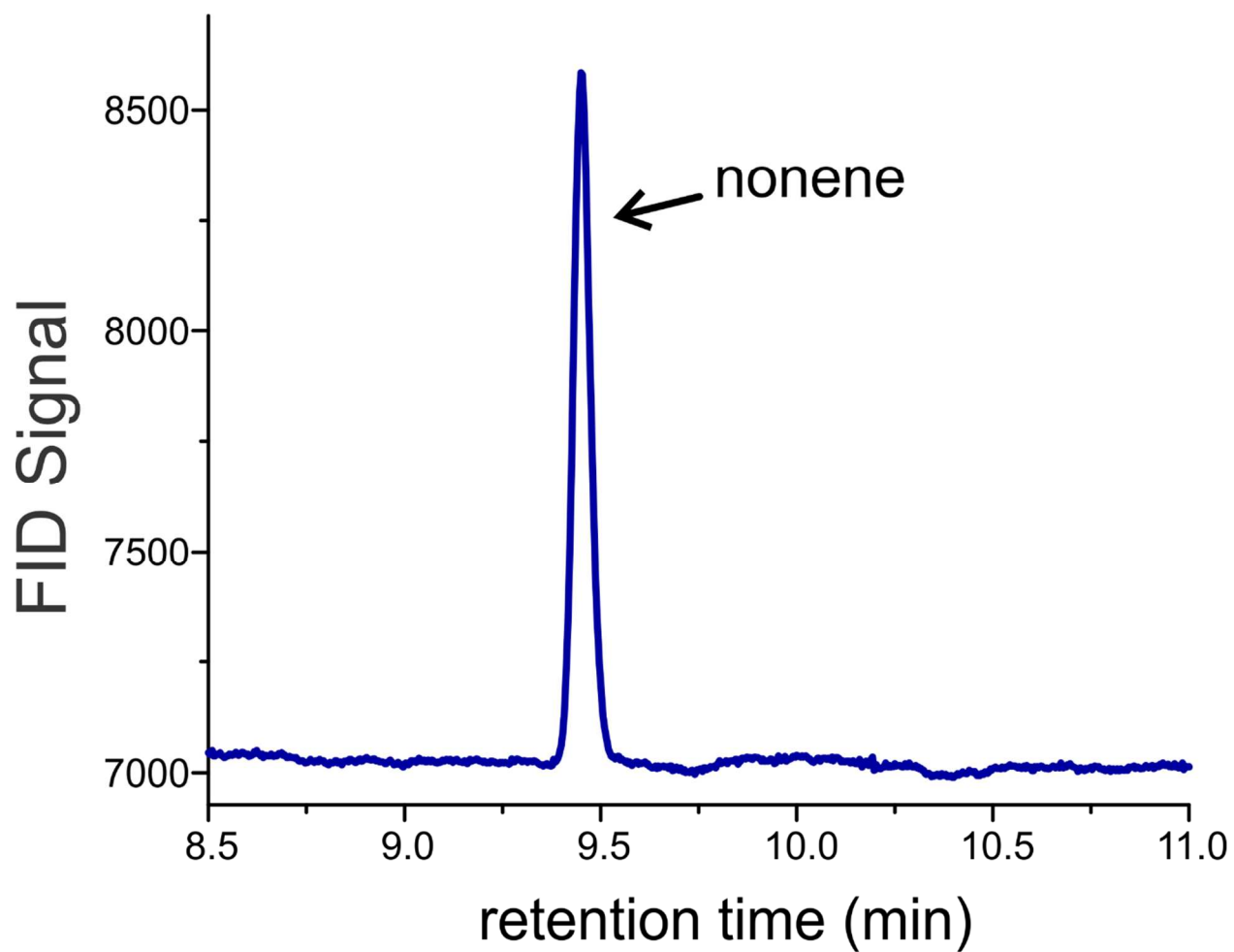
### The Enigmatic P450 Decarboxylase OleT is Capable of, but Evolved to Frustrate, Oxygen Rebound Chemistry

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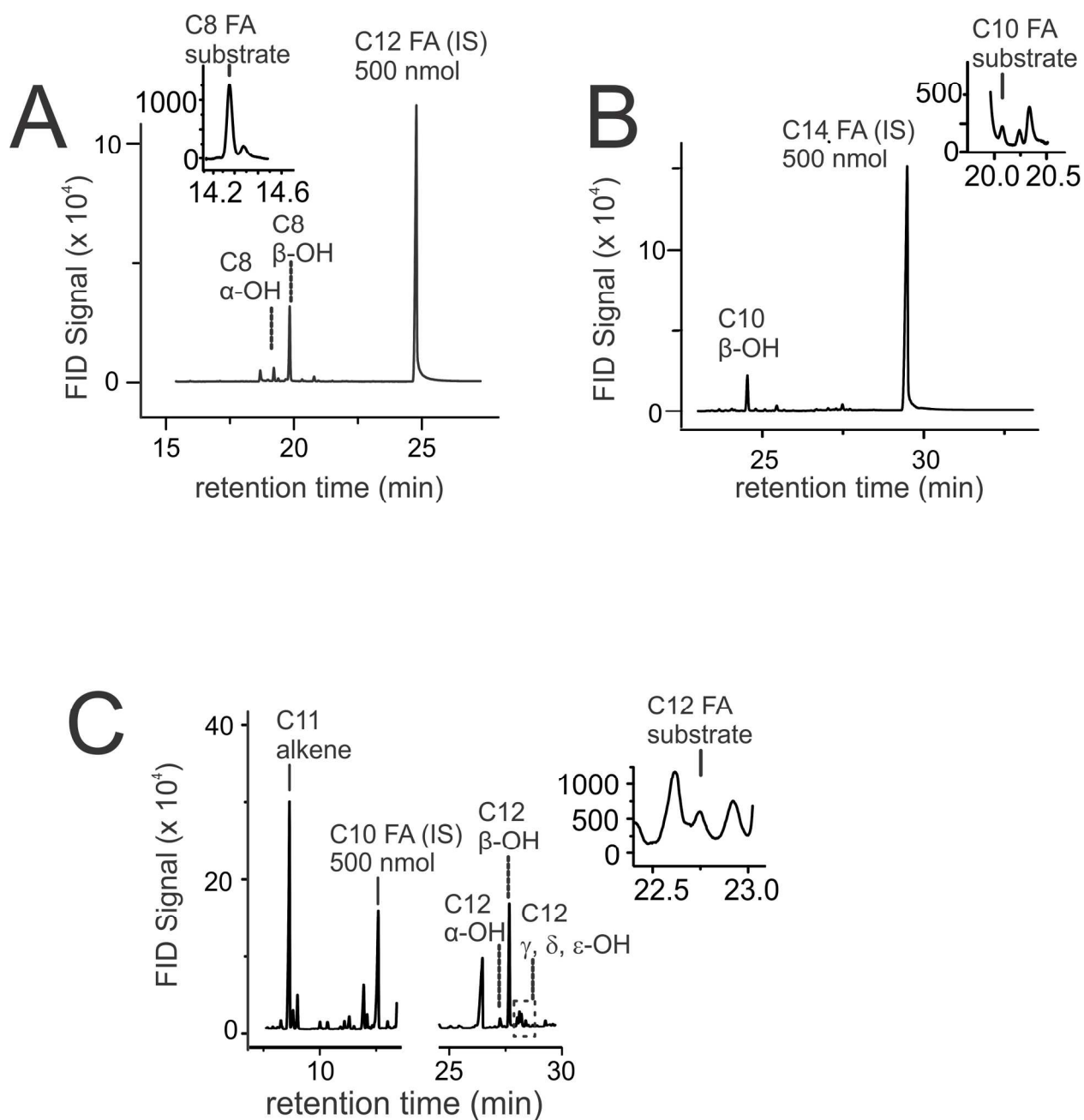
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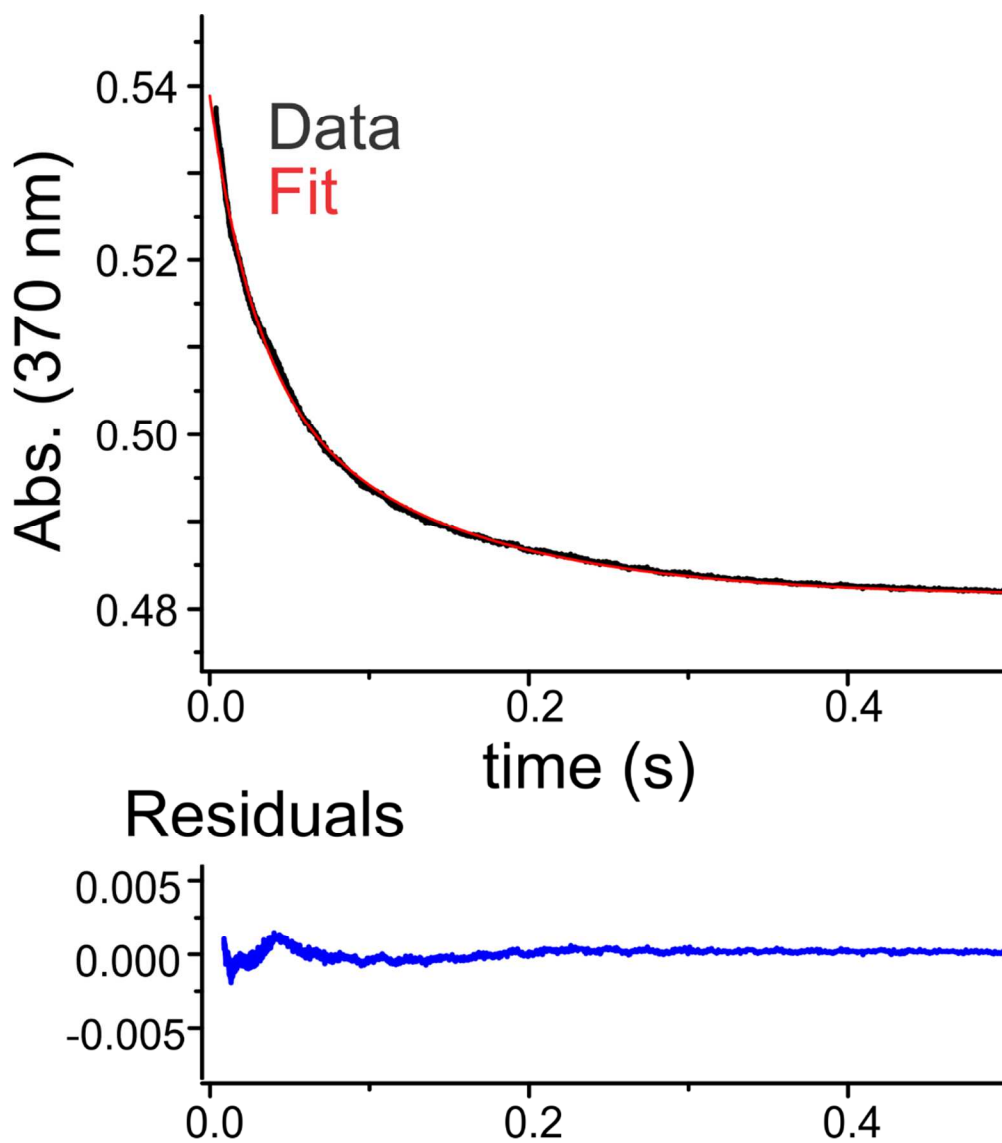
**Figure S1.** UV/visible binding titrations of 5  $\mu\text{M}$  OleT with (A)  $\text{C}_6$ , (B)  $\text{C}_8$ , (C)  $\text{C}_{10}$  and (D)  $\text{C}_{12}$  chain length fatty acids. The added absorbance changes at 417 and 392 nm were plotted against fatty acid concentration and fit to a hyperbolic binding (A, B) or Morrison expression (C, D) to determine dissociation constants ( $K_D$ ) that are summarized in Table 1.



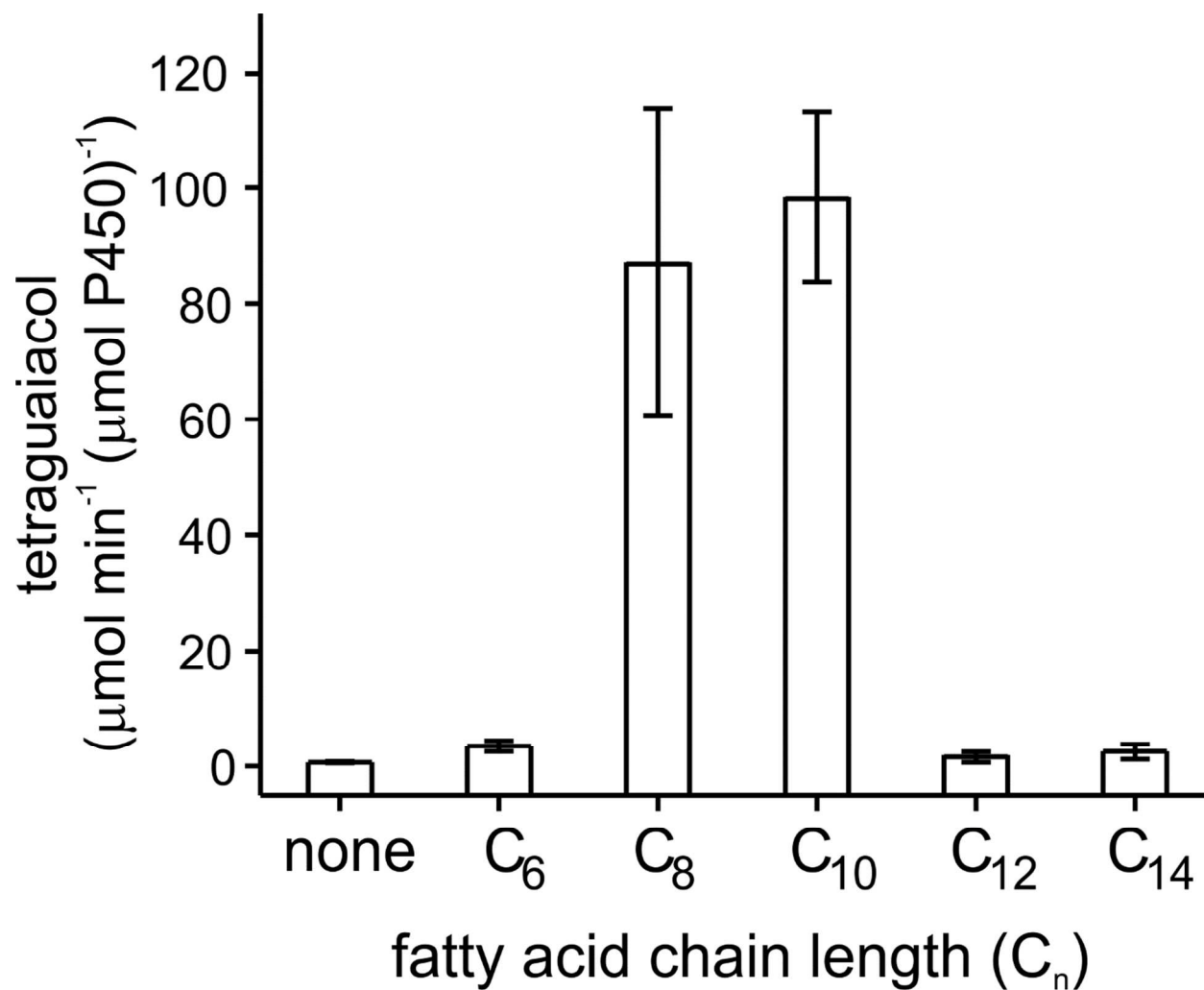
**Figure S2.** GC chromatogram of the reaction headspace of OleT and C<sub>10</sub> fatty acid after the slow introduction of H<sub>2</sub>O<sub>2</sub>.



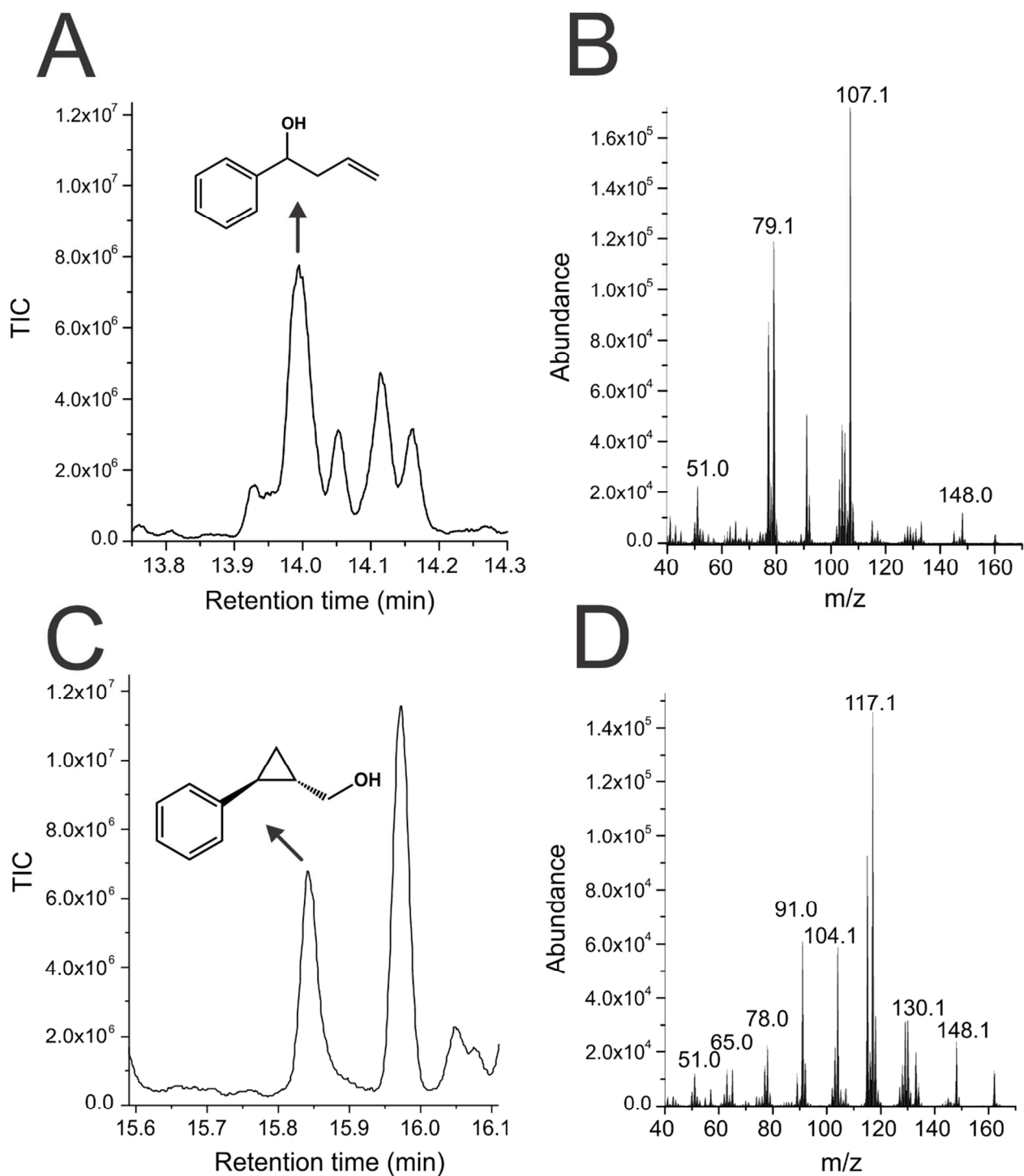
**Figure S3.** GC chromatogram of the reaction of OleT and (A) C<sub>8</sub>, (B) C<sub>10</sub> and (C) C<sub>12</sub> fatty acids. Following the slow addition of H<sub>2</sub>O<sub>2</sub>, samples were extracted in CHCl<sub>3</sub>, fatty acid and alkene internal standards (IS) were added to facilitate quantitation, and samples were derivatized by trimethylsilylation. The inset to each chromatogram shows the region corresponding to unmetabolized fatty acid substrate.



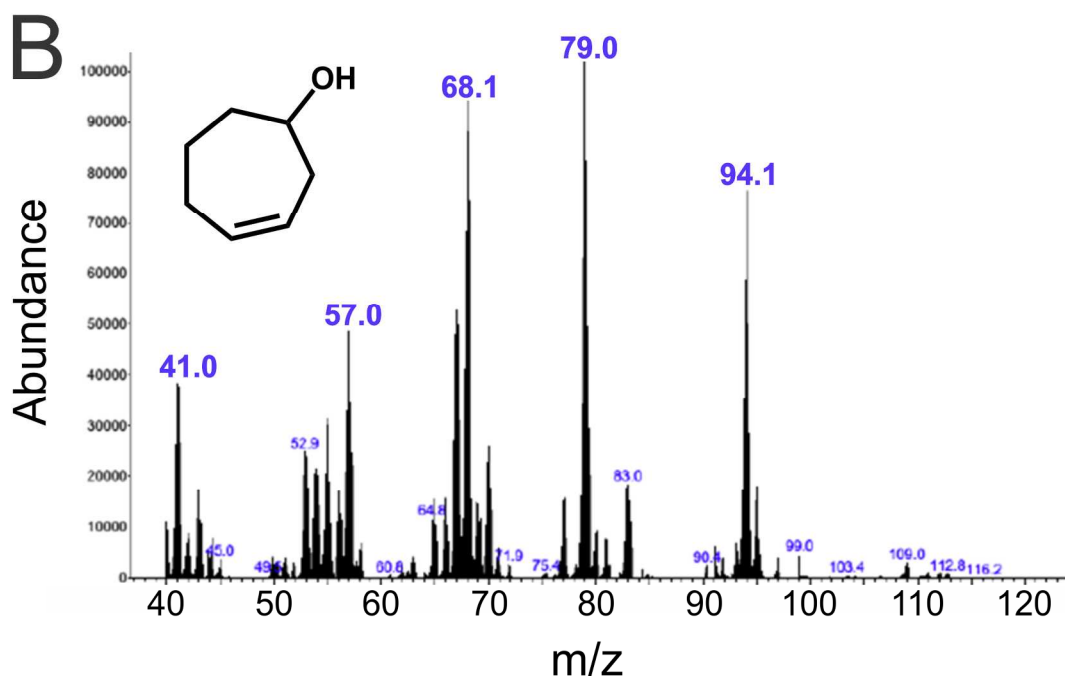
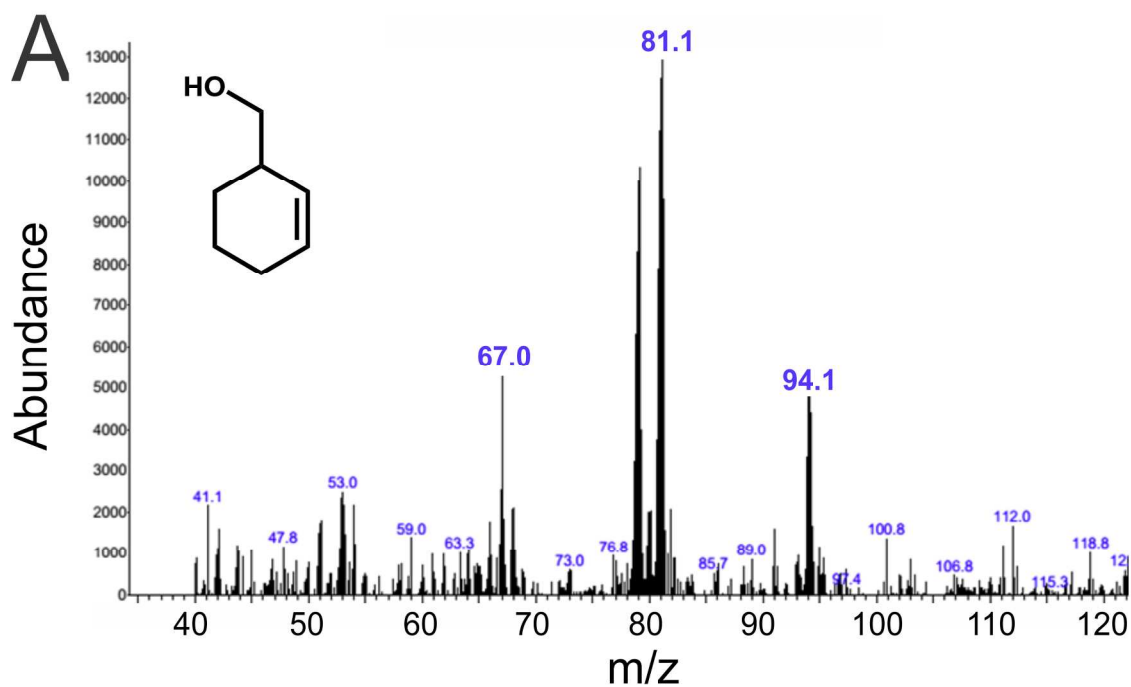
**Figure S4.** The decay of Compound I and Compound II in the reaction of OleT: DA- $d_{19}$  and 5 mM  $H_2O_2$  followed by the absorbance changes at 370 nm and photomultiplier detection. The timecourse was fit with a two-summed exponential expression described in the Methods. The faster and larger amplitude phase provides the decay rate constant of Ole-I and the slower phase provides the decay rate constant of Ole-II.



**Figure S5.** Optimization of the decoy strategy for OleT. Fatty acids of varying chain length were added to OleT in the presence of guaiacol. Following the addition of  $\text{H}_2\text{O}_2$ , the reaction was monitored at 470 nm, the absorbance maximum of the polymerized tetraguaiacol product.



**Figure S6.** Total ion chromatograms and mass spectral fragmentation patterns of the major ring opened (A, B) and unrearranged (C, D) products from the reaction of methylphenylcyclopropane and OleT with  $\text{H}_2\text{O}_2$  using perdeuterated decanoic acid (DA- $d_{19}$ ) to trigger the formation of OleT Compound I.



**Figure S7** Mass spectral fragmentation patterns of the radical ring opened (A) and cationic ring opened (B) products from the reaction of norcaradiene and OleT with  $\text{H}_2\text{O}_2$  using perdeuterated decanoic acid ( $\text{DA-d}_{19}$ ) to trigger the formation of OleT Compound I.