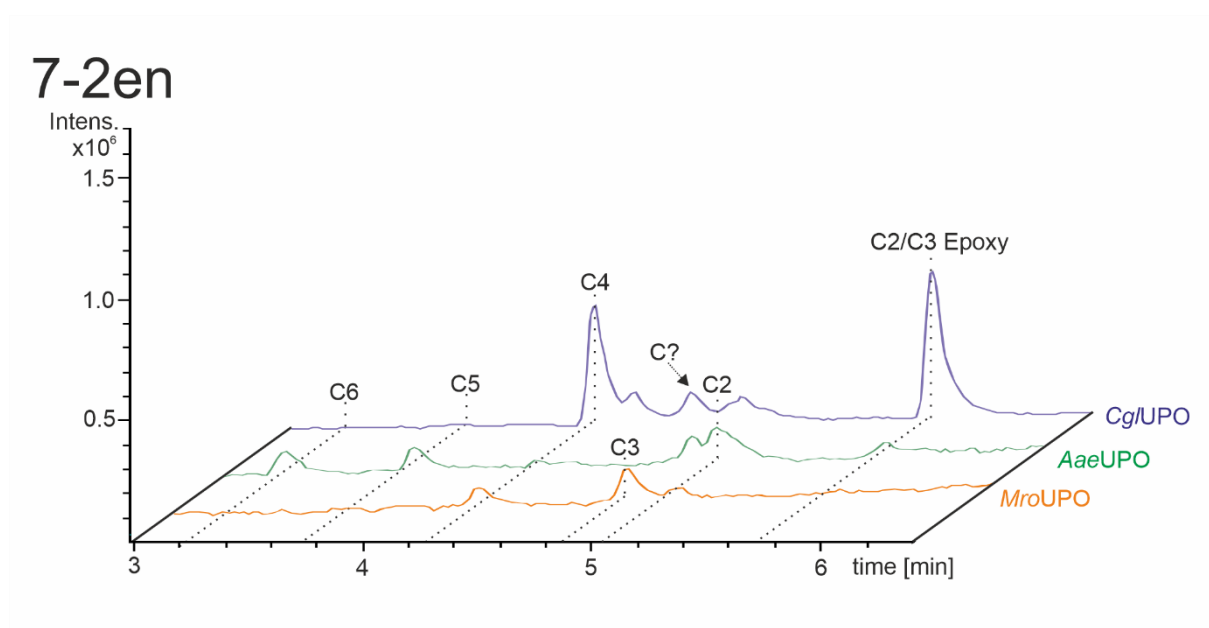


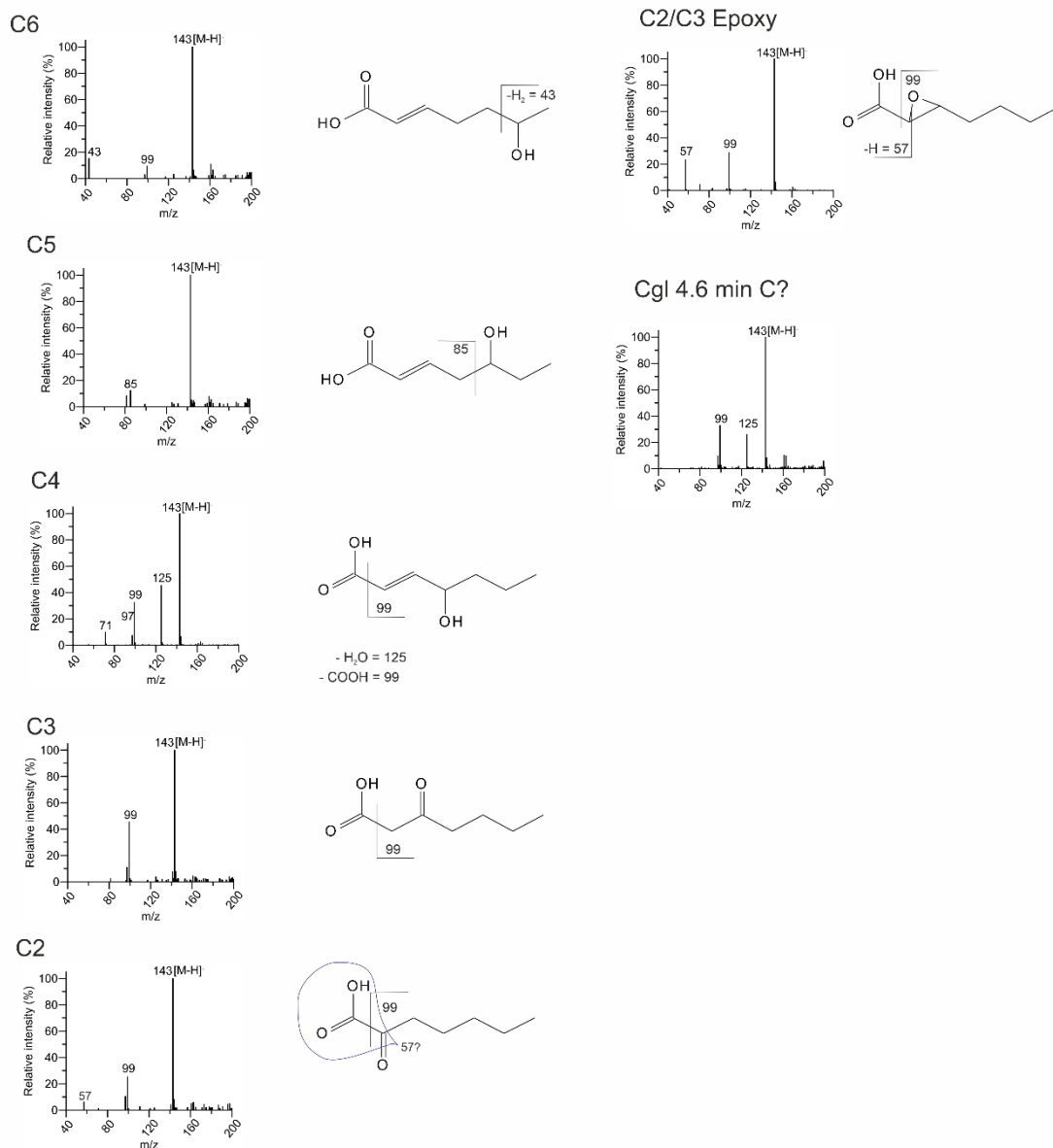
### Additional explanation to the UPOs applied:

*Aae*UPO – main abundant UPO of *Agrocybe aegerita*  
*Cab*MQ II – acidic UPO of *Candolleomyces aberdarensis*  
*Cab*MSII – neutral UPO of *Candolleomyces aberdarensis*  
*Cca*MQ2 – acidic UPO of *Candolleomyces candolleana* (Vietnam)  
*Ceu*MQ5 – acidic UPO of *Candolleomyces eurysporus*  
*Ceu*MS3 – neutral UPO of *Candolleomyces eurysporus*  
*Cgl*UPO – main abundant UPO of *Chaetomium globosum*  
*Cra*UPO – main abundant UPO of *Coprinellus radians*  
*Mro*UPO – main abundant UPO of *Marasmius rotul*  
*Mwe*UPO – main abundant UPO of *Marasmius wettsteinii*  
*rCab*2UPO – recombinant acidic UPO of *Candolleomyces aberdarensis*  
*rCab*1UPO – recombinant acidic UPO of *Candolleomyces aberdarensis*

### Supplemental Figures and Tables referring to results part:

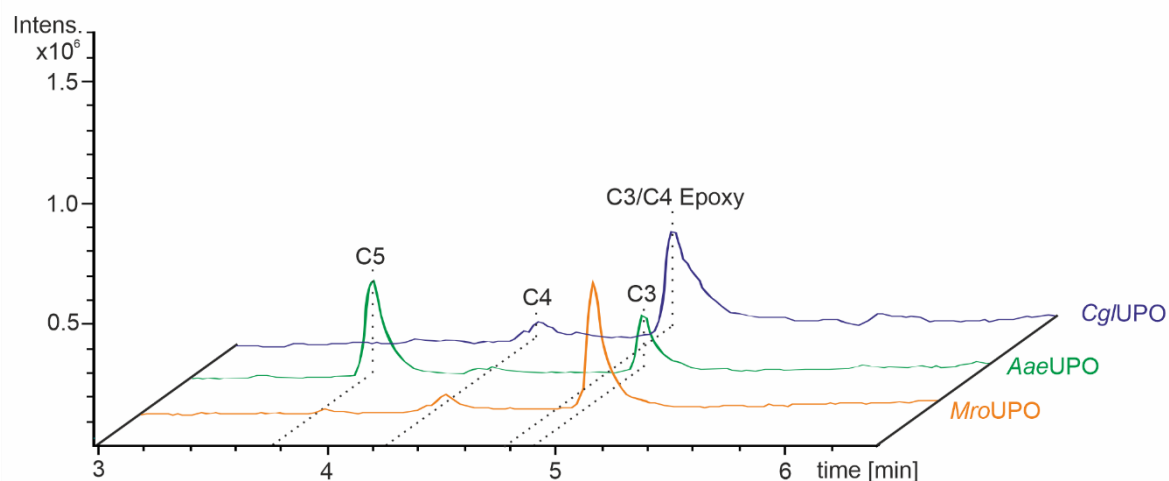


**Figure S1a.** MS-Chromatograms of reaction setups including 2-heptenoic acid and three different UPOs (*Cgl*UPO, *Aae*UPO and *Mro*UPO).

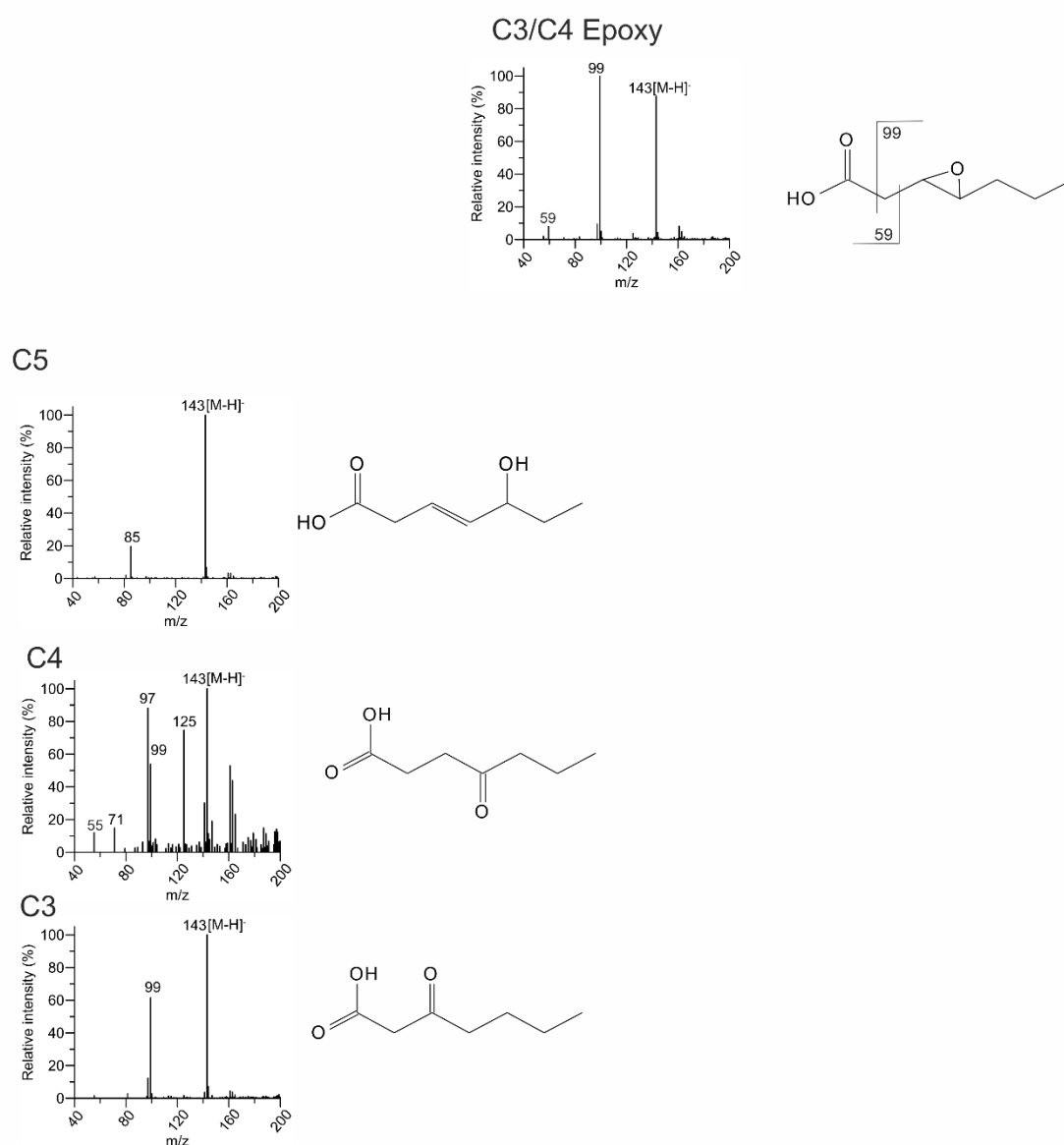


**Figure S1b.** MS-fragmentation patterns of products deriving from 2-heptenoic acid

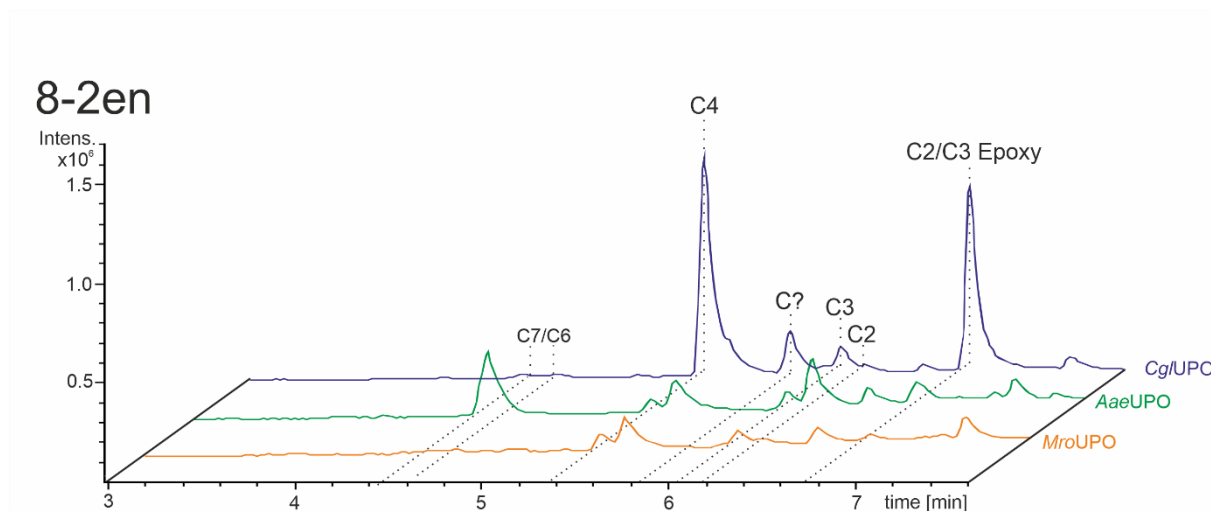
# 7-3en



**Figure S2a.** MS-Chromatograms of reaction setups including 3-heptenoic acid and three different UPOs (Cg/UPO, Aae/UPO and Mro/UPO).

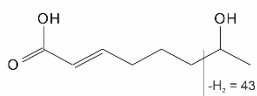
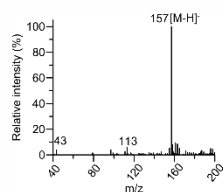


**Figure S2b:** MS-fragmentation patterns of products deriving from 3-heptenoic acid

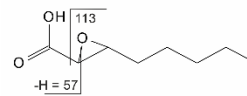
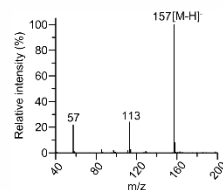


**Figure S3a.** MS-Chromatograms of reaction setups including 2-octenoic acid and three different UPOs (*Cg*/UPO, *Aae*UPO and *Mro*UPO).

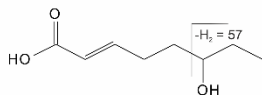
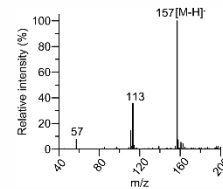
C7



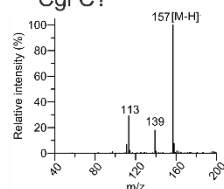
C2/C3 Epoxy



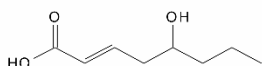
C6



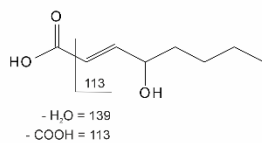
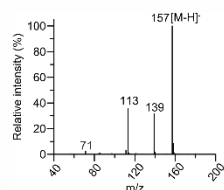
Cgl C?



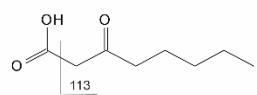
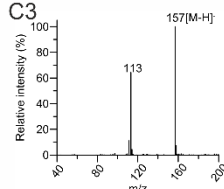
No C5



C4



C3



C2

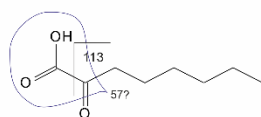
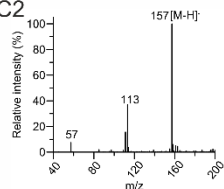
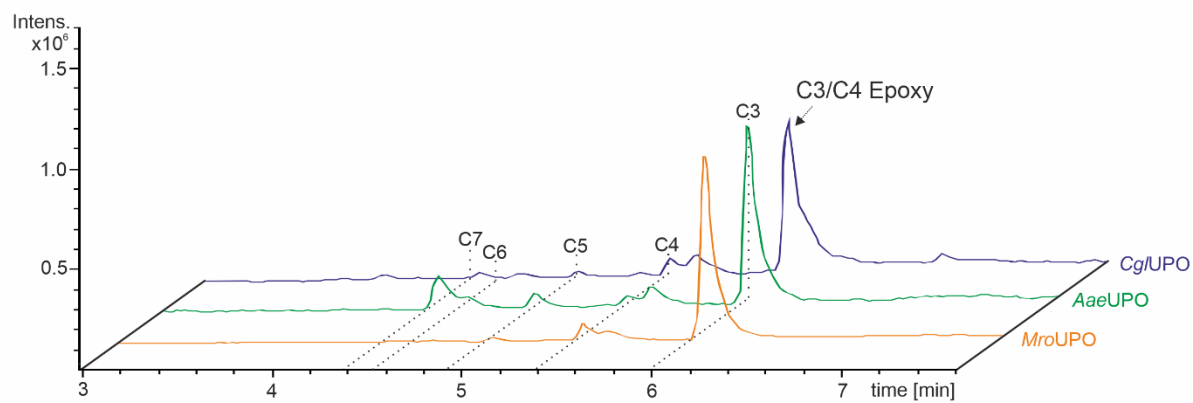
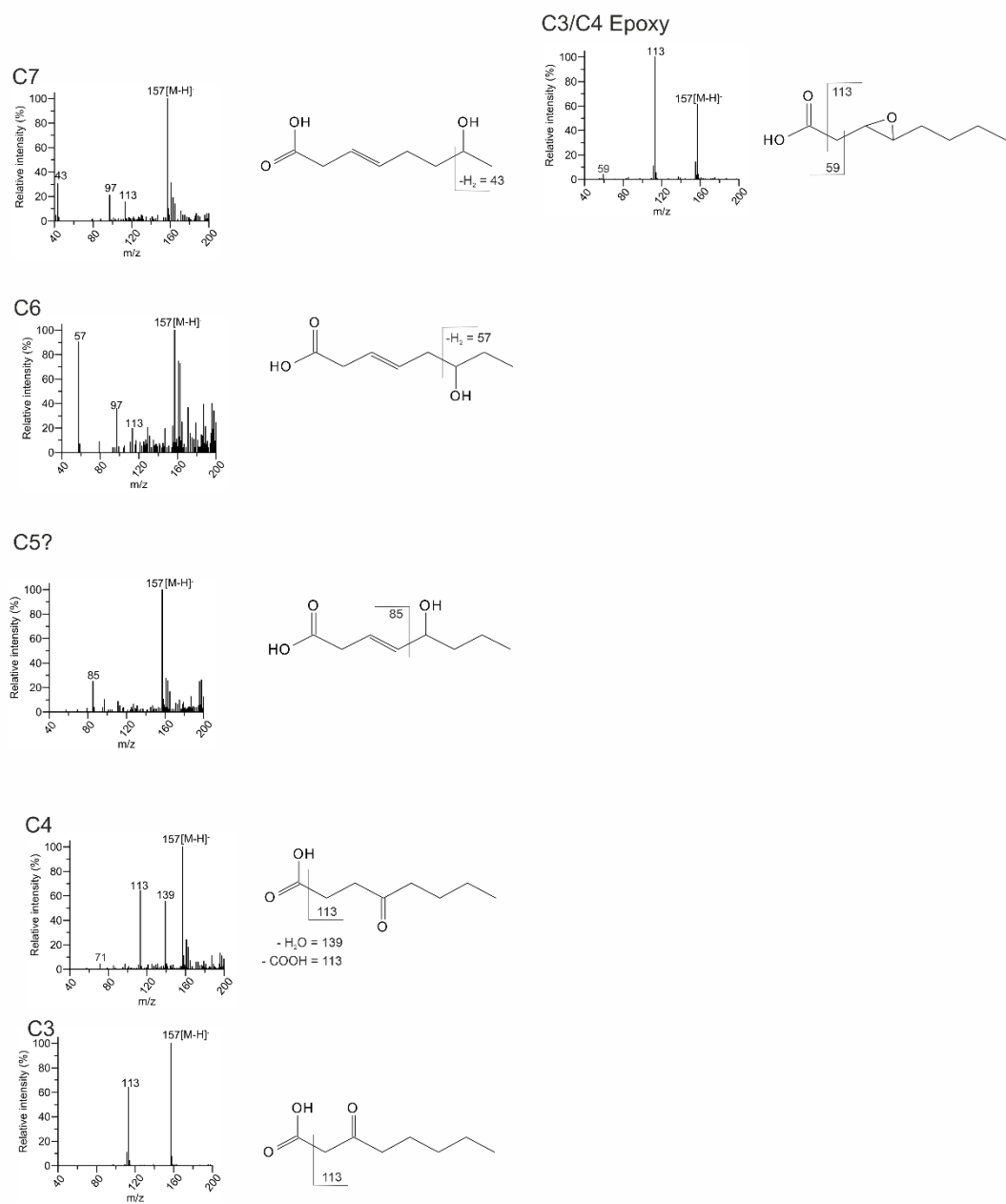


Figure S3b. MS-fragmentation patterns of products deriving from 2-octenoic acid

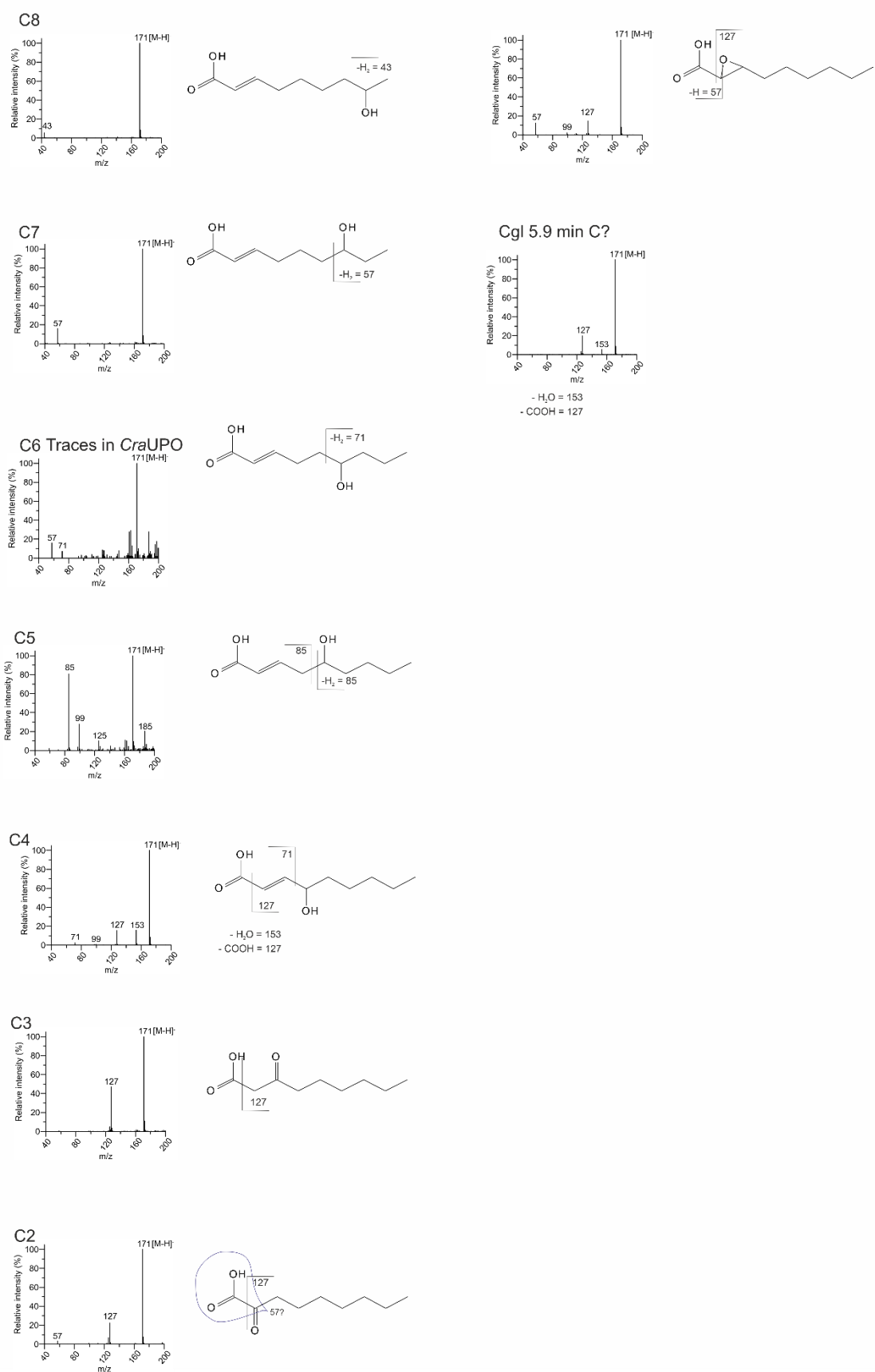
8-3en



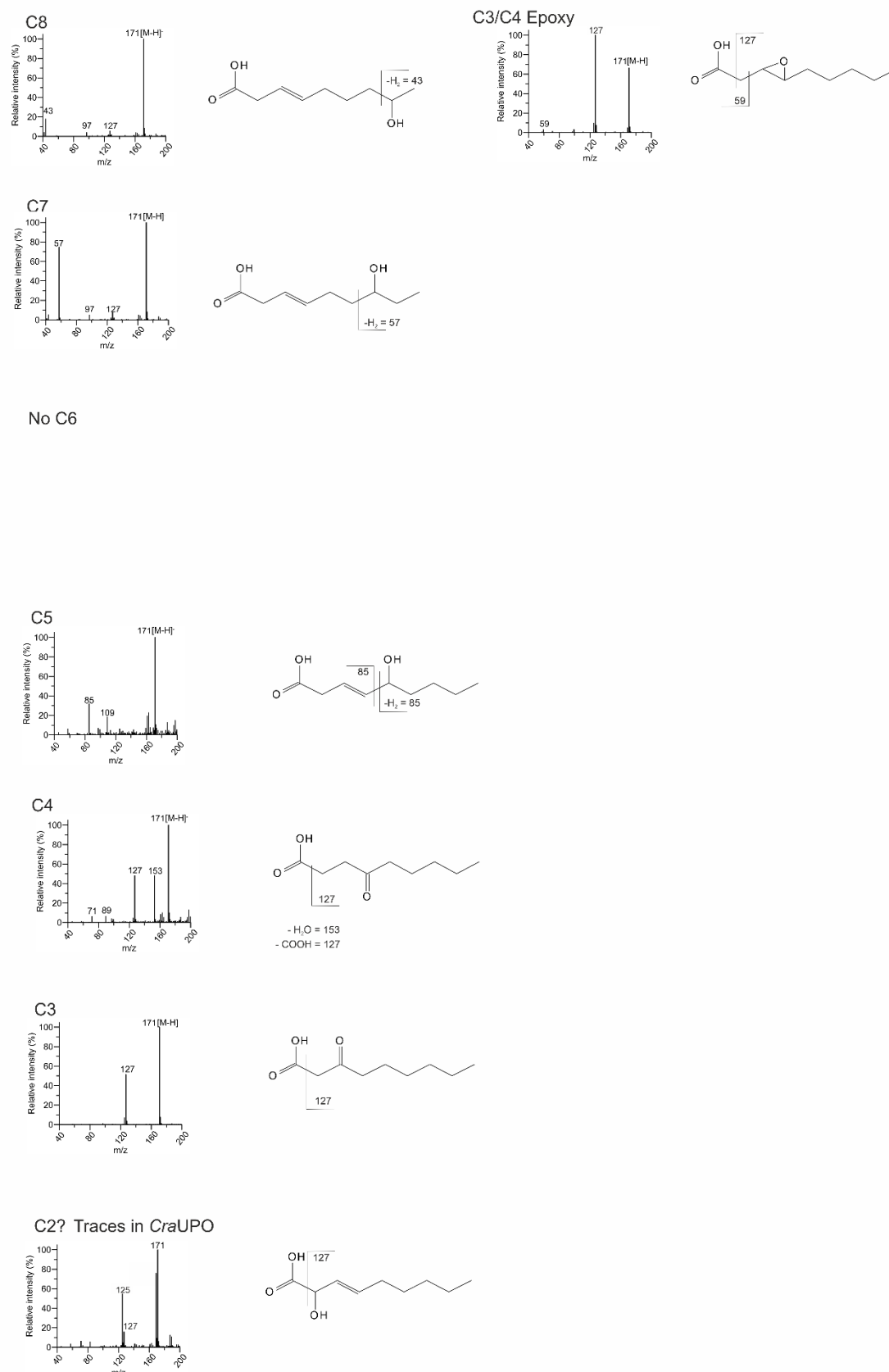
**Figure S4a.** MS-Chromatograms of reaction setups including 3-octenoic acid and three different UPOs (*Cgl*UPO, *Aae*UPO and *Mro*UPO).



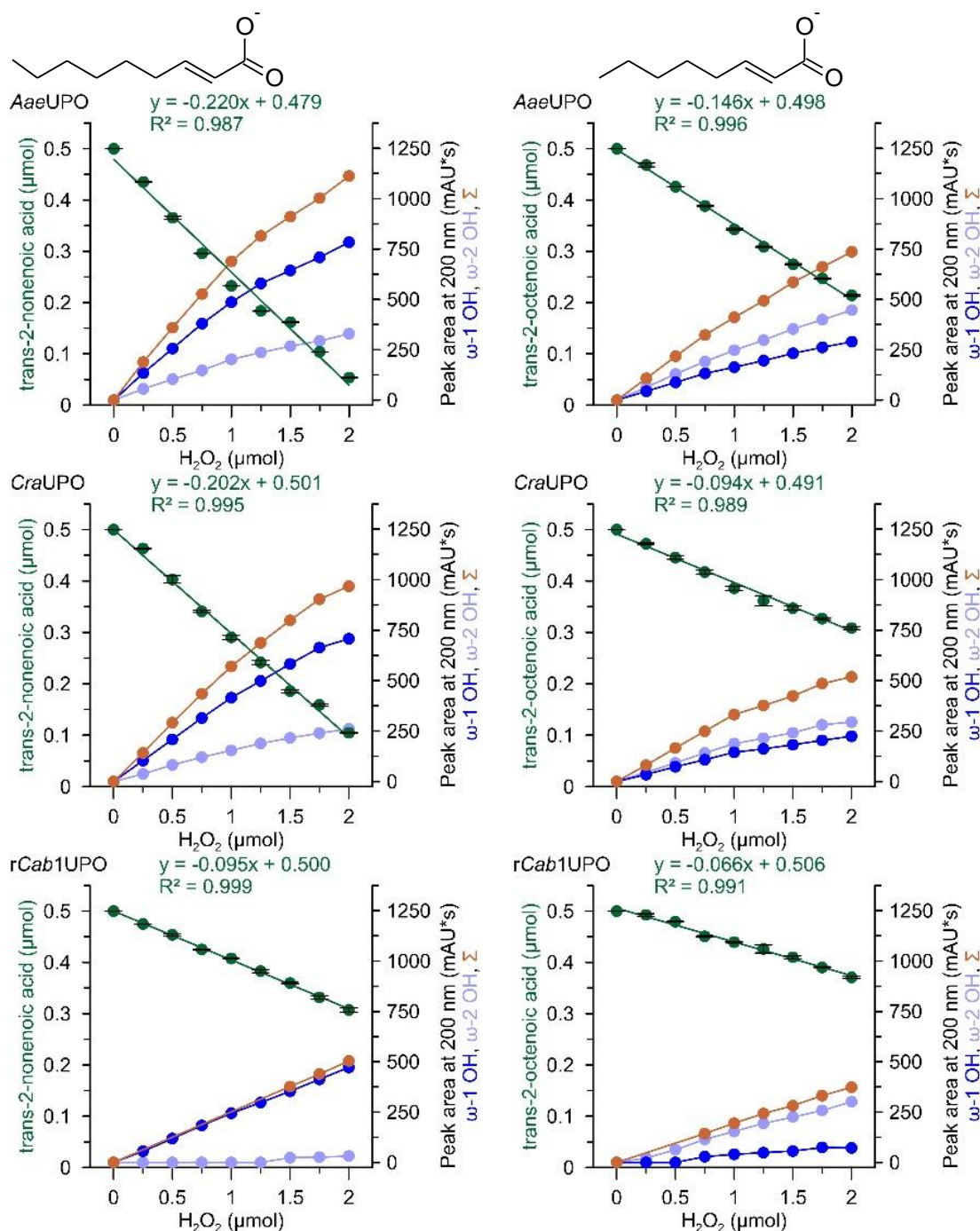
**Figure S4b.** MS-fragmentation patterns of products deriving from 3-octenoic acid.



**Figure S5.** MS-fragmentation patterns of products deriving from 2-nonenic acid.



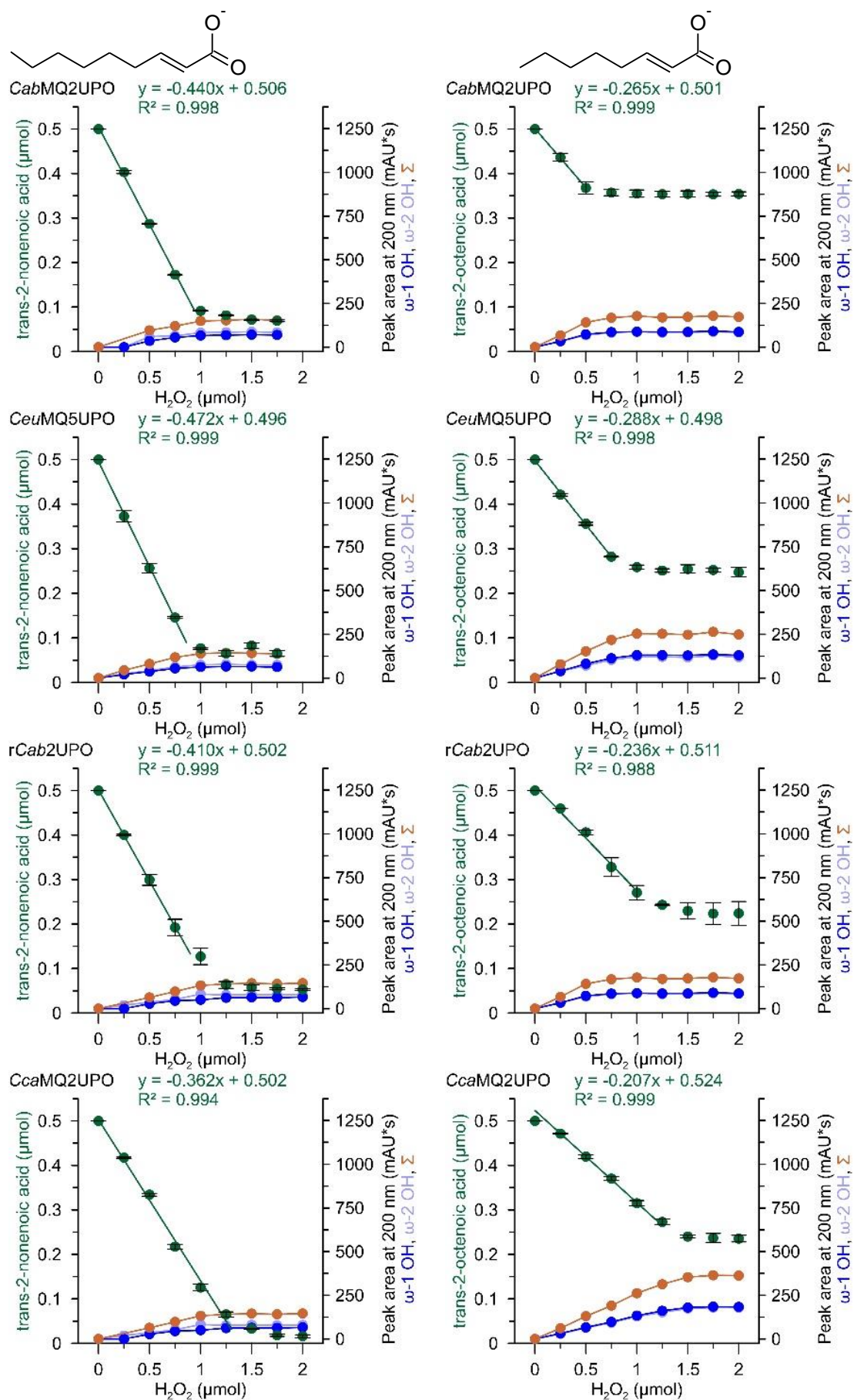
**Figure S6.** MS-fragmentation patterns of products deriving from 3-nonenic acid.



**Figure S7:** Amount of residual trans-2-nonenic acid (t-C9-2-en, left, green) or trans-2-octenoic acid (t-C8-2-en, right, green), as well as peak areas (relative for each product only) of the corresponding ω-1 (dark blue) and ω-2 (light blue) hydroxy products or further UV-absorbing products after different amount of  $H_2O_2$  dosage (orange represents the sum of both products). For MS-based product quantification refer to Tables 5 and 6.

Reaction setup: 0.5 μmol t-C9-2-en and t-C8-2-en, UPO 0.5 U (Valc), 10 mM  $KP_i$  pH 6 and 10% acetone. Formulas refer to the initial conversion rates of FA in μmol [C9-2-en]/μmol [ $H_2O_2$ ]

Conclusion: Continuous conversion of FA - TON was not reached under the conditions tested.



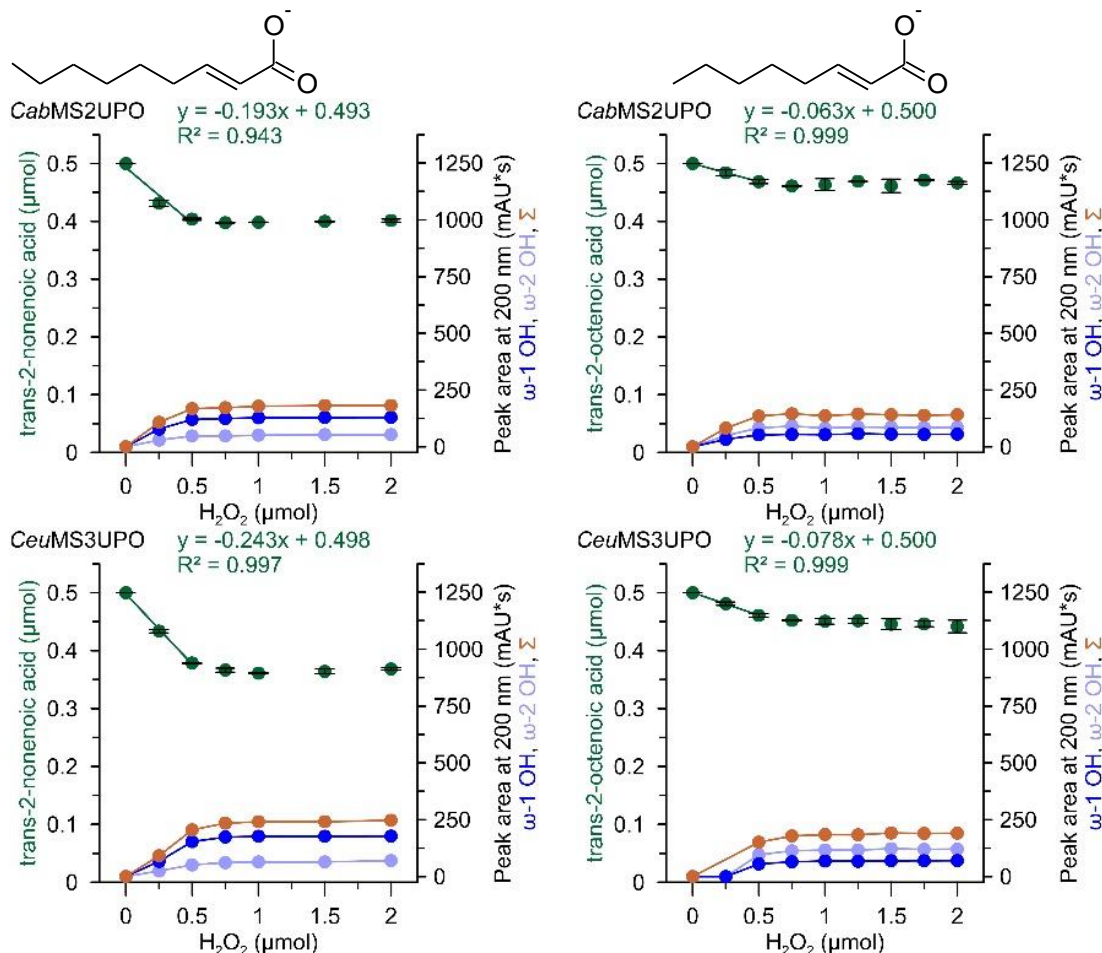
**Figure S8.** Amount of residual trans-2-nonenic acid (t-C9-2-en, left, green) or trans-2-octenoic acid (t-C8-2-en, right green), as well as peak areas (relative for each product only) of the corresponding  $\omega$ -1

(dark blue) and  $\omega$ -2(light lue) hydroxy products or further UV-absorbing products after different amount of  $\text{H}_2\text{O}_2$  dosage (orange represents the sum of both products). For MS-based product quantification refer to Tables 5 and 6.

Reaction setup: 0.5  $\mu\text{mol}$  t-C9-2-en and t-C8-2-en, UPO 0.5 U (Valc), 10 mM  $\text{KPi}$  pH 6 and 10% acetone.

Formulas refer to the initial conversion rates of FA in  $\mu\text{mol}$  [C9-2-en]/ $\mu\text{mol}$  [ $\text{H}_2\text{O}_2$ ]

Conclusion: Nearly “completed” conversion of FA C9-2en – but not in case of C8-2en.

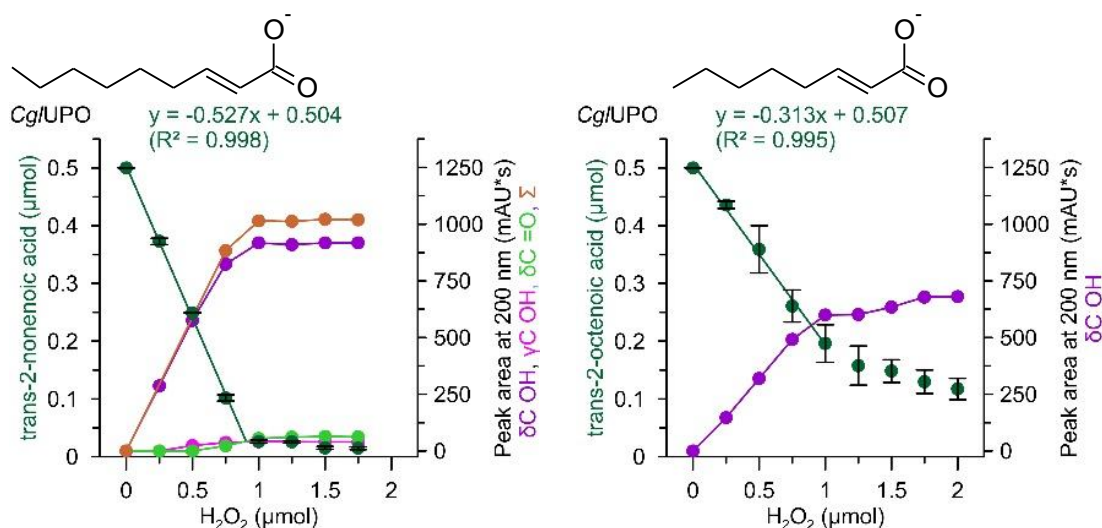


**Figure S9.** Amount of residual trans-2-nonenic acid (t-C9-2-en, left green) or trans-2-octenoic acid (t-C8-2-en, right, green), as well as peak areas (relative for each product only) of the corresponding  $\omega$ -1 (dark blue) and  $\omega$ -2 (light blue) hydroxy products or further UV-absorbing products after different amount of  $\text{H}_2\text{O}_2$  dosage (orange represents the sum of both products). For MS-based product quantification refer to Tables 5 and 6.

Reaction setup: 0.5  $\mu\text{mol}$  t-C9-2-en and t-C8-2-en, UPO 0.5 U (Valc), 10 mM  $\text{KPi}$  pH 6 and 10% acetone.

Formulas refer to the initial conversion rates of FA in  $\mu\text{mol}$  [C9-2-en]/ $\mu\text{mol}$  [ $\text{H}_2\text{O}_2$ ]

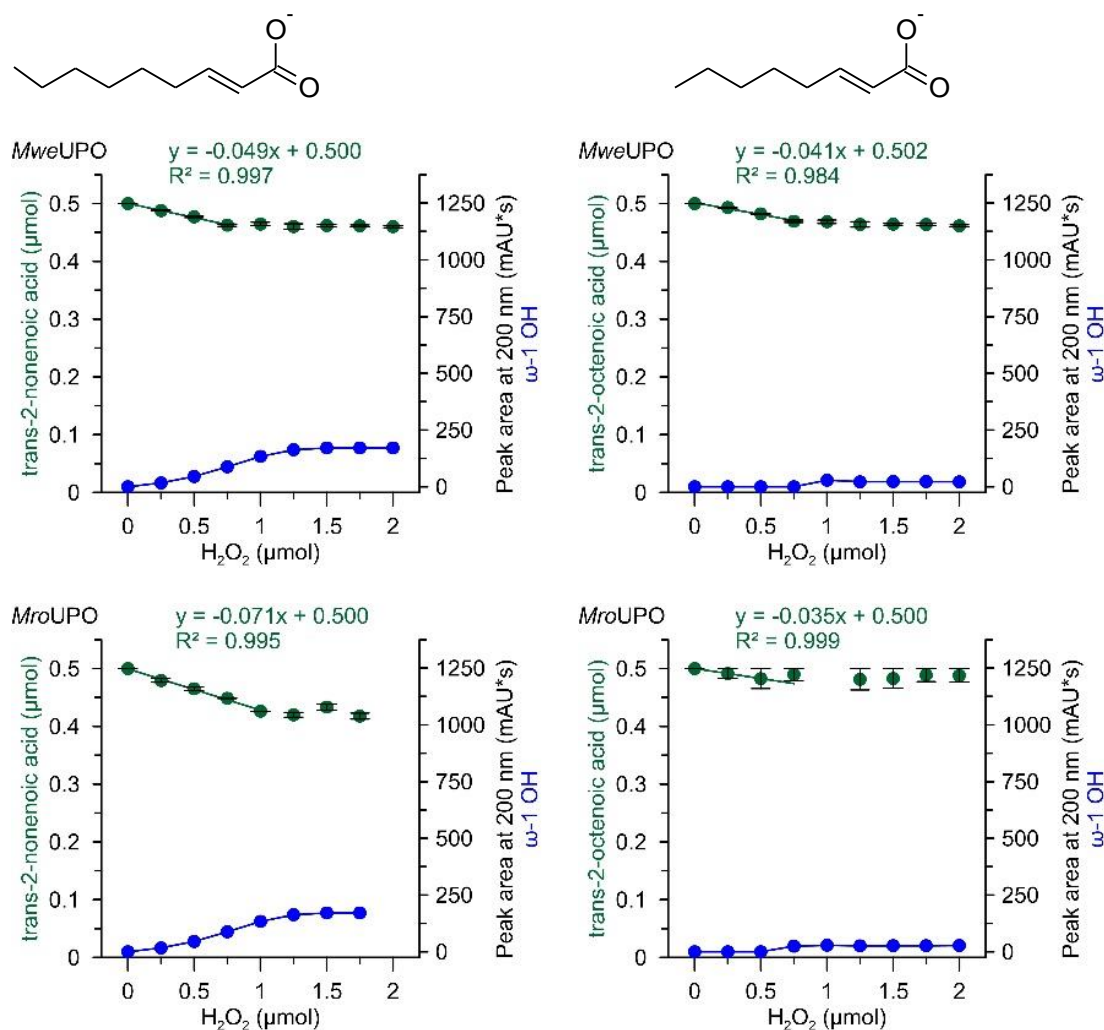
Conclusion: “incomplete” conversion of FA - TON was reached.



**Figure S10.** Amount of residual trans-2-nonenic acid (t-C9-2-en, left, green) or trans-2-octenoic acid (t-C8-2-en, right, green), as well as peak areas (relative for each product only) of the corresponding tentatively identified products after different amount of H<sub>2</sub>O<sub>2</sub> dosage ( $\delta$ -hydroxy violet,  $\gamma$ -hydroxy pink,  $\delta$ -keto green, sum of products, orange). For MS-based product quantification refer to Tables 5 and 6.

Reaction setup: 0.5  $\mu$ mol t-C9-2-en and t-C8-2-en, UPO 0.5 U (Valc), 10 mM KP<sub>i</sub> pH 6 and 10% acetone. Formulas refer to the initial conversion rates of FA in  $\mu$ mol [C9-2-en]/ $\mu$ mol [H<sub>2</sub>O<sub>2</sub>]

Conclusion: "complete" conversion of FA in case of C9-2en; but TON was reached for C8-en2



**Figure S11.** Amount of residual *trans*-2-nonenic acid (t-C9-2-en, left, green) or *trans*-2-octenoic acid (t-C8-2-en, right, green), as well as peak areas (relative for each product only) of the corresponding  $\omega$ -1 product (dark blue) after different amount of H<sub>2</sub>O<sub>2</sub> dosage. For MS-based product quantification refer to Tables 5 and 6.

Reaction setup: 0.5  $\mu$ mol t-C9-2-en and t-C8-2-en, UPO 0.5 U (Valc), 10 mM KPi pH 6 and 10% acetone. Formulas refer to the initial conversion rates of FA in  $\mu$ mol [C9-2-en]/ $\mu$ mol [H<sub>2</sub>O<sub>2</sub>]

Conclusion: Relatively “low” conversion

**Table S1.** additional, numeric data for table 2, rel. product yield with 3-nonenic acid and various UPOs – product in %, apparently identified according to MS-ionization.

	C2-OH	C3-OH	3,4-Epox	C4-OH	C5-OH	C6-OH	C7-OH	C8-OH	C9-OH	$\Sigma$ Keto
<i>Cgl</i> UPO	2.8	0.0	56.2	11.9	1.3	0.0	0.0	0.0	0.0	27.9
<i>Mro</i> UPO	0.0	80.5	0.0	6.5	0.0	0.0	0.0	0.0	0.0	12.9
<i>Mwe</i> UPO	0.0	68.9	0.0	5.7	0.0	0.0	0.0	0.0	0.0	25.5
<i>Aae</i> UPO	3.0	71.0	0.0	4.2	0.0	0.0	5.2	1.9	0.0	14.7
<i>Cra</i> UPO2	1.6	55.6	0.0	5.2	0.0	0.0	8.1	2.7	0.0	26.7
<i>Ceu</i> UPOMQ5	2.6	76.0	0.0	3.7	0.0	0.0	5.7	0.0	0.0	11.9
<i>Cab</i> UPOMQ2	3.2	72.4	0.0	3.7	0.0	0.0	5.2	0.0	0.0	15.4
<i>Ceu</i> UPOMS3	0.0	60.6	0.0	6.3	0.0	0.0	7.7	2.3	0.0	23.2
<i>Cab</i> UPOMS2	0.0	68.6	0.0	5.4	0.0	0.0	5.9	2.0	0.0	18.0
<i>rCab</i> UPO1	0.0	69.4	0.0	10.4	0.0	0.0	0.8	0.5	0.0	18.9
<i>rCab</i> UPO2	0.0	79.5	0.0	4.1	0.0	0.0	5.0	0.0	0.0	11.4

**Table S2.** additional, numeric data for table 3, rel. product yield with 3-octenoic acid and various UPOs – product in %, apparently identified according to MS-ionization.

	C2-OH	C3-OH	3,4-Epox	C4-OH	C5-OH	C6-OH	C7-OH	C8-OH	$\Sigma$ Keto
<i>Cgl</i> UPO	0.0	0.0	72.4	6.4	0.0	0.0	0.0	0.0	21.1
<i>Mro</i> UPO	0.0	89.0	0.0	5.4	0.0	0.0	0.0	0.0	5.6
<i>Aae</i> UPO	0.0	80.2	0.0	2.3	2.1	1.5	3.9	0.0	10.1

**Table S3.** additional, numeric data for table 4, rel. product yield with 3-heptenoic and various UPOs – product in %, apparently identified according to MS-ionization

	C2-OH	C3-OH	3,4-Epox	C4-OH	C5-OH	C6-OH	C7-OH	$\Sigma$ Keto
<i>Cgl</i> UPO	0.0	0.0	92.1	7.9	0.0	0.0	0.0	0.0
<i>Mro</i> UPO	0.0	92.1	0.0	7.9	0.0	0.0	0.0	0.0
<i>Aae</i> UPO	0.0	41.8	0.0	5.5	52.7	0.0	0.0	0.0

**Table S4.** additional, numeric data for table 5, rel. product yield with *trans*-2-nonenic and various UPOs – product in %, apparently identified according to MS-ionization. . \* refers to a product that has been hydroxylated at an unknown position.

	C2-OH	2,3-Epox	C3-OH	C*	C4-OH	C5-OH	C6-OH	C7-OH	C8-OH	C9-OH	$\Sigma$ Keto	di-OH
<i>Cgl</i> UPO	1.2	26.2	0.0	10.9	44.9	1.0	0.0	1.2	0.0	0.0	14.6	0.0

<i>Mro</i> UPO	30.3	8.0	16.6	0.0	4.3	0.0	0.0	0.0	0.0	0.0	0.0	40.9
<i>Mwe</i> UPO	39.6	5.5	31.1	0.0	4.8	0.0	0.0	4.2	0.0	0.0	0.0	14.8
<i>Aae</i> UPO	26.9	18.5	5.9	0.0	0.0	0.0	0.0	25.2	23.6	0.0	0.0	0.0
<i>Cra</i> UPO2	18.2	6.7	5.1	0.0	0.0	0.0	13.6	21.9	34.6	0.0	0.0	0.0
<i>Ceu</i> UPOMQ5	9.8	84.7	2.6	0.0	0.0	0.0	0.0	2.1	0.8	0.0	0.0	0.0
<i>Cab</i> UPOMQ2	12.4	80.3	2.8	0.0	0.0	0.0	0.0	3.3	1.3	0.0	0.0	0.0
<i>Ceu</i> UPOMS3	21.0	57.4	2.4	0.0	2.4	0.0	0.0	8.0	8.8	0.0	0.0	0.0
<i>Cab</i> UPOMS2	23.6	54.4	2.6	0.0	2.6	0.0	0.0	8.0	8.7	0.0	0.0	0.0
<i>rCab</i> UPO1	33.9	4.9	18.5	0.0	2.1	0.0	0.0	4.1	36.6	0.0	0.0	0.0
<i>rCab</i> UPO2	10.2	83.7	2.6	0.0	0.0	0.0	0.0	2.3	1.1	0.0	0.0	0.0

**Table S5.** additional, numeric data for table 6, rel. product yield with *trans*-2-octenoic acid and various UPOs – product in %, apparently identified according to MS-ionization. \* refers to a product that has been hydroxylated at an unknown position.

	C2-OH	2,3-Epox	C3-OH	C*	C4-OH	C5-OH	C6-OH	C7-OH	C8-OH	Σ Keto
<i>Cgl</i> UPO	2.3	35.3		8.9	9.2	44.2	0.0	0.0	0.0	0.0
<i>Mro</i> UPO	12.3	4.3		0.0	0.0	11.9	0.0	0.0	0.0	71.6
<i>Aae</i> UPO	30.8	10.7		0.0	0.0	4.0	0.0	15.5	6.2	0.0

**Table S6.** additional, numeric data for table 7, rel. product yield with 2-heptenoic acid and various UPOs – product in %, apparently identified according to MS-ionization. \* refers to a product that has been hydroxylated at an unknown position.

	C2-OH	2,3-Epox	C3-OH	C*	C4-OH	C5-OH	C6-OH	C7-OH	Σ Keto
<i>Cgl</i> UPO	0.0	60.2	0.0		10.6	29.2	0.0	0.0	0.0
<i>Mro</i> UPO	4.9	0.0	77.8		0.0	17.3	0.0	0.0	0.0
<i>Aae</i> UPO	52.3	11.1	0.0		0.0	4.9	9.2	11.0	0.0