Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting information

From tandem to catalysis – organic solvent nanofiltration for catalyst separation in the homogeneously W-catalyzed oxidative cleavage of renewable methyl 9,10-dihydroxystearate

Johanna Vondran, Marc Peters, Alexander Schnettger, Christian Sichelschmidt, Thomas Seidensticker*

Laboratory for Industrial Chemistry, Department of Biochemical and Chemical Engineering, TU Dortmund University, Emil-Figge-Straße 66, 44227 Dortmund, Germany.

[*] Dr. Thomas Seidensticker, E-Mail: thomas.seidensticker@tu-dortmund.de; Fax: +49 231 755 2311; Tel: +49 231 755 2310

Table of Contents

1. Materials

Most reactants are commercially available and used without further purification: methyl oleate (DAKO AG, 91.5 %), methyl 9,10-dihydroxystearate (abcr, 96%), phosphotungstic acid (Carl Roth, hydrate) hydrogen peroxide (35wt% aqueous solution, Acros Organics), acetonitrile (99.9%, Carl Roth). Methyl 9,10-epoxystearate was synthesized according to the method described in our previous work [1] and

obtained in a purity of 91.5%. Methyl 9-hydroxy-10-oxystearate/Methyl 9-oxy-10-hydroxystearate was synthesized according to the procedure described in section 9. The carboxylic acids pelargonic acid (Carl Roth, 97%) and mono methyl azelate (tci, 97%) and the cleavage aldehyde nonanal (Carl Roth, 97%) are commercially available and were used for GC-calibration and as a reference.

The composition of methyl oleate, given from the supplier, is as follows:

- 91.5% methyl oleate;
- 3.0% methyl palmitate;
- 2.0% methyl stearate;
- 2.5 % methyl linoleate;
- < 0.1 % methyl linolenate;
- 1% fatty acid methyl esters > C18

2. Analytical equipment and methods

The product samples were analysed by GC (Agilent 7890B with a HP-5 capillary column, 30 m x 0.25 mm x 0.25 mm) using an FID/MS in connection with an auto sampler. Conversion and yields were determined with dodecane as internal standard and tert-butanol as solvent. Iodometric analysis of peroxide was carried out with SI Analytics TitroLine 7000. Analysis of retentate and permeate was carried out using GC-TCD for determination of water/acetonitrile content. W and P content was quantified by inductively coupled plasma optical emission spectrometry (ICP-OES).

3. Reaction - experimental procedure

Experiments were carried out in 9 mL glass pressure tubes (ACE glass, see Figure S1) equipped with a magnetic stirrer bar. A stock solution of catalyst was prepared by dissolving phosphotungstic acid in acetonitrile. Methyl oleate/methyl 9,10-dihydroxystearate were added directly to the pressure tube and diluted with catalyst stock solution. Hydrogen peroxide was added just before placing the tube in the preheated steel block. The reaction mixture was stirred at 500 rpm and 100 °C for 24 h, if not otherwise specified. After cooling on ice, the reaction mixture was diluted with *tert*-butanol and dibutylether or dodecane was added as internal standard for GC-analysis.

Figure S1: steel block and pressure tubes on stirrer/heating plate

4. Further investigation on oxidative cleavage of methyl oleate

Before we carried out further experiments on oxidative cleavage of methyl 9,10-dihydroxystearate, we undertook some investigations on oxidative cleavage of methyl oleate without additional NaOH. However, those did not result in significant optimization and are therefore only mentioned as supplementary material.

4.1 Reaction temperature

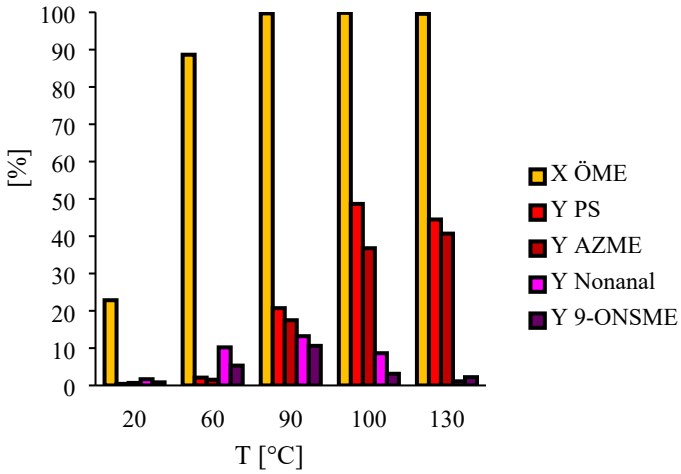


Figure S 2: effect of temperature on oxidative cleavage of methyl oleate

Reaction conditions: methyl oleate (1 mmol), H_2O_2 (35 wt% aqueous solution, 10 mmol), $H_3PW_{12}O_{40}$ (5 mol%), acetonitrile (3.04 g); t = 24 h. Conversion and yield determined via GC-FID-analysis with dodecane as internal standard.

4.2 H_2O_2 concentration

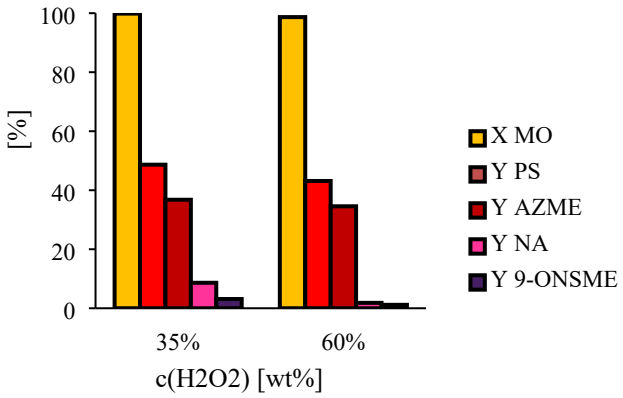


Figure S 3: effect of concentration of hydrogen peroxide on oxidative cleavage of methyl oleate

Reaction conditions: methyl oleate (1 mmol), H_2O_2 (10 mmol), $H_3PW_{12}O_{40}$ (5 mol%), acetonitrile (3.04 g); t = 24 h, T = 100°C. Conversion and yield determined via GC-FID-analysis with dodecane as internal standard.

4.3 Equivalents of H_2O_2

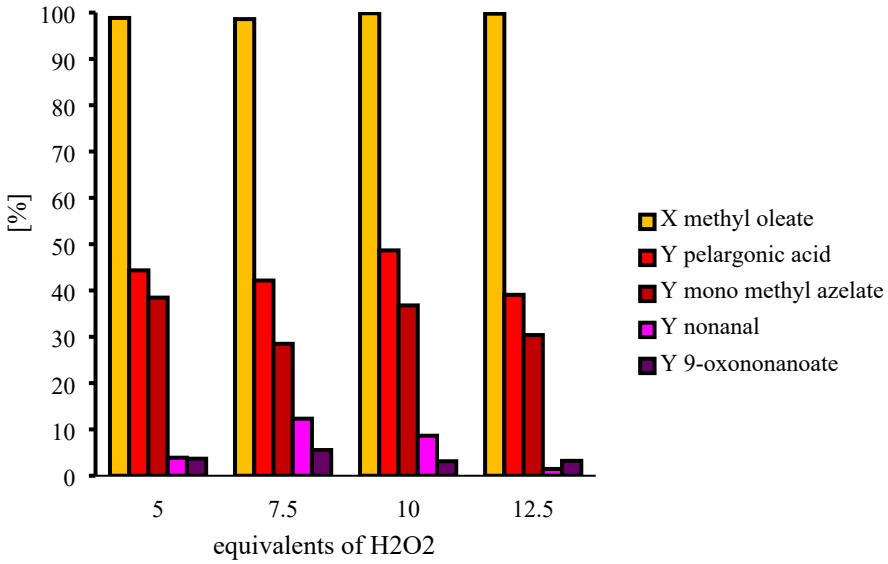


Figure S 4: effect of H_2O_2 equivalents on oxidative cleavage of methyl oleate

Reaction conditions: methyl oleate (1 mmol), H_2O_2 (35wt% aqueous solution), $H_3PW_{12}O_{40}$ (5 mol%), acetonitrile (3.04 g); t = 24 h, T = 100°C. Conversion and yield determined via GC-FID-analysis with dodecane as internal standard.

4.4 Concentration of methyl oleate

In order to avoid potential oligomerization as a side-reaction, we considered dilution of the reaction system. Thus, concentration of substrate (and also concentration of catalyst and oxidant) was investigated by variation of the amount of acetonitrile as a solvent.

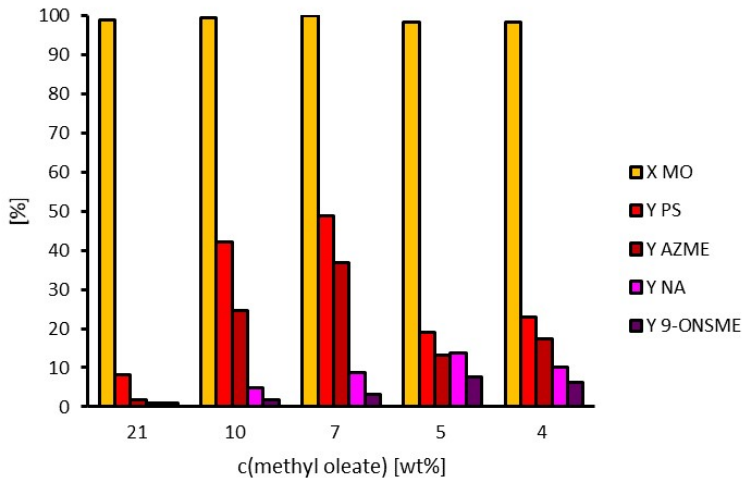


Figure S 5: effect of substrate concentration on oxidative cleavage of methyl oleate

Reaction conditions: methyl oleate (1 mmol), H_2O_2 (35wt% aqueous solution, 10 mmol), $H_3PW_{12}O_{40}$ (5 mol%), acetonitrile (experiment at substrate concentration of 21wt% is carried out without solvent); t = 24 h, T = 100°C. Conversion and yield determined via GC-FID-analysis with dodecane as internal standard.

4.5 Continuous feed of H_2O_2

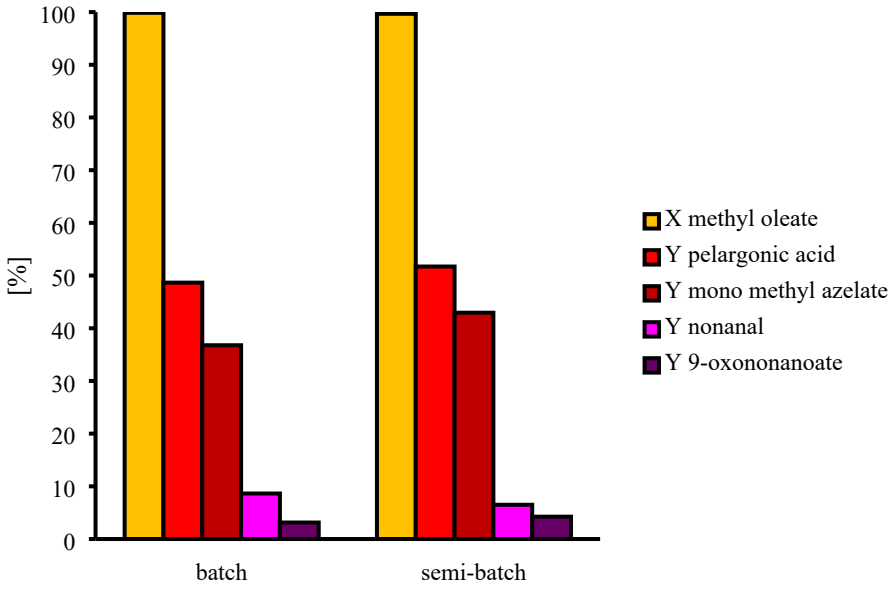


Figure S 6: comparison of batchwise and semi-batchwise addition of H_2O_2

Reaction conditions: methyl oleate (1 mmol), H_2O_2 (35wt% aqueous solution, 10 mmol), $H_3PW_{12}O_{40}$ (5 mol%), acetonitrile (experiment at substrate concentration of 21wt% is carried out without solvent); t = 24 h, T = 100°C. semi-batch: addition of H_2O_2 via peristaltic pump over 18 h. Conversion and yield determined via GC-FID-analysis with dodecane as internal standard.

4.6 Effect of additional water

Since the diol was not detected in significant amounts, we considered addition of water to the reaction system to improve hydrolysis of methyl 9,10-epoxystearate.

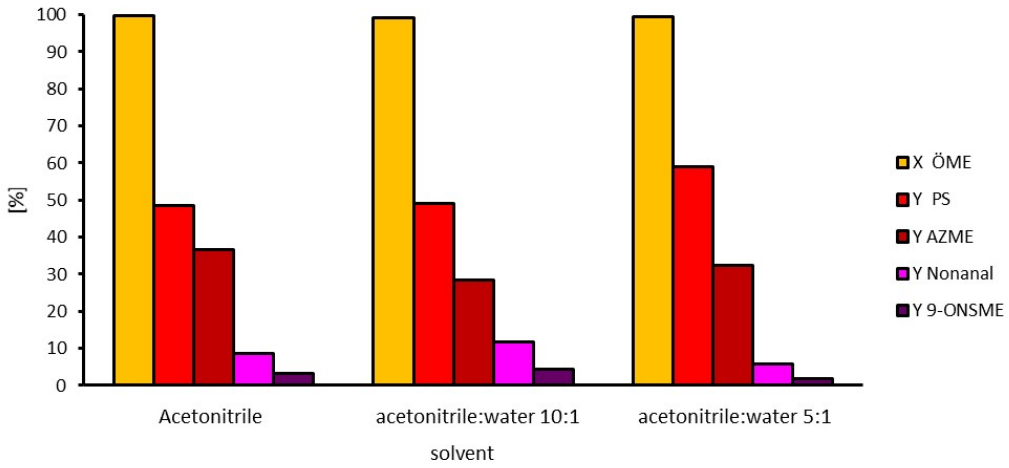


Figure S 7: effect of additional water on oxidative cleavage of methyl oleate

Reaction conditions: methyl oleate (1 mmol), H_2O_2 (35wt% aqueous solution, 10 mmol), $H_3PW_{12}O_{40}$ (5 mol%), acetonitrile/water (3.04 g); t = 24 h, T = 100°C. Conversion and yield determined via GC-FID-analysis with dodecane as internal standard.

4.7 Blind experiment: no oxidative cleavage of methyl 9,10-dihydroxystearate without catalyst

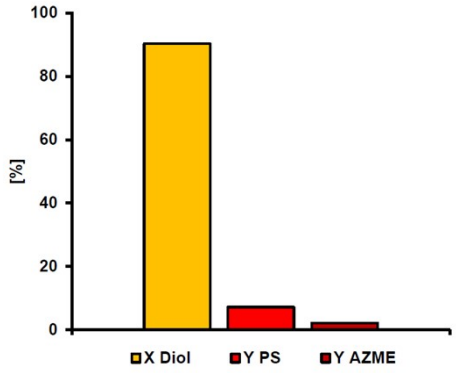


Figure S 8: Experiment in absence of catalyst

Reaction conditions: methyl 9,10-dihydroxystearate (0.5 mmol), H_2O_2 (35wt% aqueous solution, 5 mmol), acetonitrile (1.57 g); t = 24 h, T = 100°C, pH adjusted to 5 with 2M NaOH. Conversion and yield determined via GC-FID-analysis with dodecane as internal standard

4.8 Stability of methyl 9,10-epoxystearate, pelargonic acid and mono methyl azelate

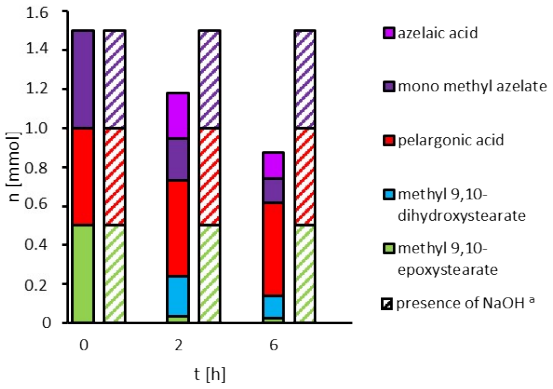


Figure S 9: stability of methyl 9,10-epoxystearate and oxidative cleavage products in absence and presence (striped) of NaOH

Reaction Conditions: methyl 9,10-epoxystearate **2** (0.15 g, 0.5 mmol), $H_3PW_{12}O_{40}$ (0.144 g; 0.05 mmol), H_2O (0.97) , acetonitrile (3.14 g), T = 100 °C. [a] NaOH (2 M, 0.1 g). Molar amounts determined via GC-FID-analysis with dibutyl ether as internal standard.

4.9 Addition of NaOH at catalyst loading of 3 mol%

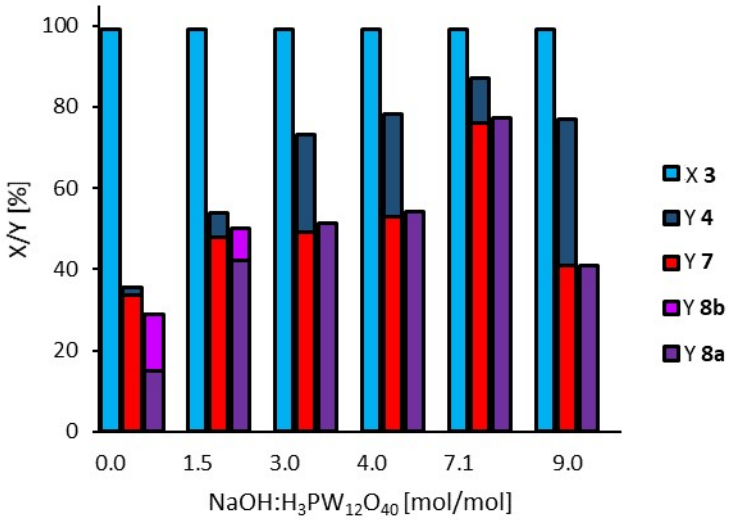


Figure S 10: oxidative cleavage of methyl 9,10-dihydroxystearate depending on molar ratio of NaOH:catalyst at catalyst loading of 3 mol%

Reaction Conditions: methyl 9,10-dihydroxystearate **3** (0.1 g, 0.3 mmol), $H_3PW_{12}O_{40}$ (3 mol%), H_2O_2 (35wt%, 10 eq.) , acetonitrile (1.02 g), NaOH (2 M), T = 100 °C, t = 24 h. Conversion (X) and yield (Y) determined *via* GC-FID-analysis with dibutyl ether as internal standard.

4.10 Effect of catalyst loading at optimized NaOH:$H_3PW_{12}O_{40}$ ratio of 7:1

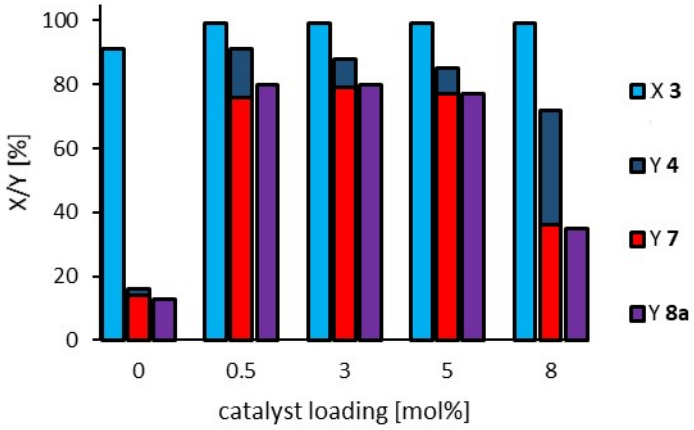


*Figure S 11: effect of catalyst loading on oxidative cleavage of methyl 9,10-dihydroxystearate **3** at optimized NaOH:$H_3PW_{12}O_{40}$ ratio of 7:1*

Reaction Conditions: methyl 9,10-dihydroxystearate (0.1 g, 0.3 mmol), $H_3PW_{12}O_{40}$, H_2O_2 (35wt%, 10 eq.), acetonitrile (1.02 g), NaOH (2 M, NaOH: $H_3PW_{12}O_{40}$ 7:1), T = 100 °C, t = 24 h. Conversion (X) and yield (Y) determined *via* GC-FID-analysis with dibutyl ether as internal standard.

4.11 Application of Na_2WO_4 as the catalyst

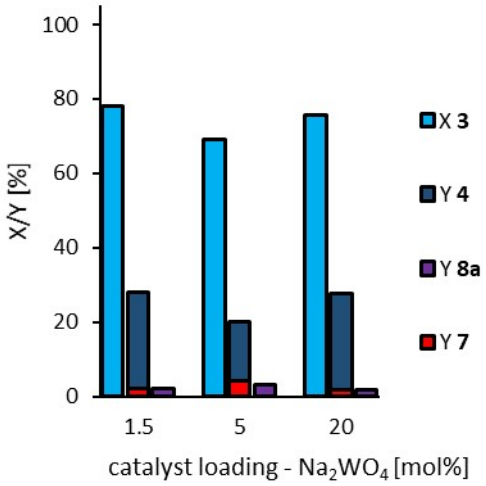


Figure S 12: variation of the catalyst: application of Na_2WO_4

Reaction Conditions: methyl 9,10-dihydroxystearate (0.1 g, 0.3 mmol), H_2WO_4, H_2O_2 (35wt%, 10 eq.), acetonitrile (1.02 g), T = 100 °C, t = 24 h. Conversion (X) and yield (Y) determined *via* GC-FID-analysis with dibutyl ether as internal standard.

4.12 Additional water at various equivalents of H2O2

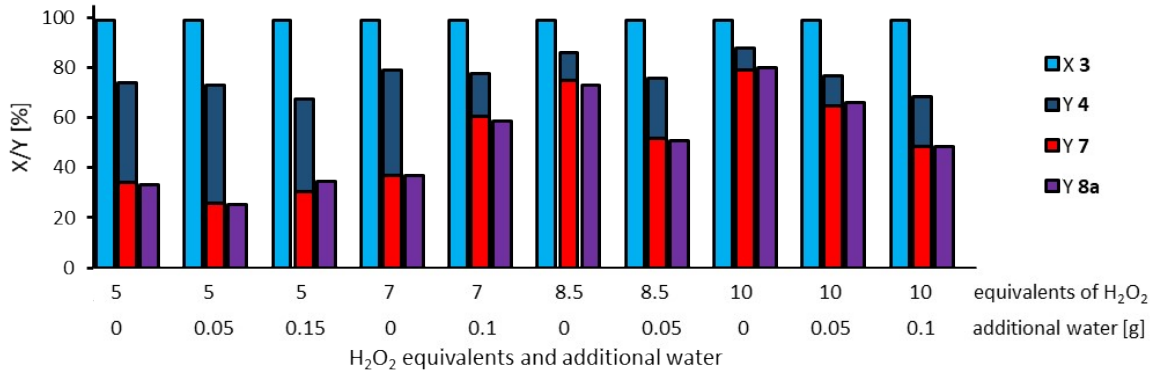


Figure S 13: influence of additional water on the oxidative cleavage of methyl 9,10-dihydroxystearate using various equivalents of oxidant

Reaction Conditions: methyl 9,10-dihydroxystearate (0.1 g, 0.3 mmol), $H_3PW_{12}O_{40}$ (3 mol%), H_2O_2 (35wt%) , acetonitrile (1.02 g), additional water, T = 100 °C, t = 24 h. Conversion (X) and yield (Y) determined *via* GC-FID-analysis with dibutyl ether as internal standard.

4.13 Decomposition of H_2O_2 in presence of phosphotungstic acid

Since we considered a correlation of catalyst loading and decomposition of hydrogen peroxide, we investigated O_2 gas release from a mixture of phosphotungstic acid, hydrogen peroxide and acetonitrile. Therefore, a stainless steel reactor, equipped with a glass inlay to exclude corrosion/decomposition was filled with the reagents. The reactor was also equipped with a pressure sensor and a digital pressure gauge (*BD sensors DM01)*. The initial and end concentration of hydrogen peroxide was analyzed via iodometric titration.

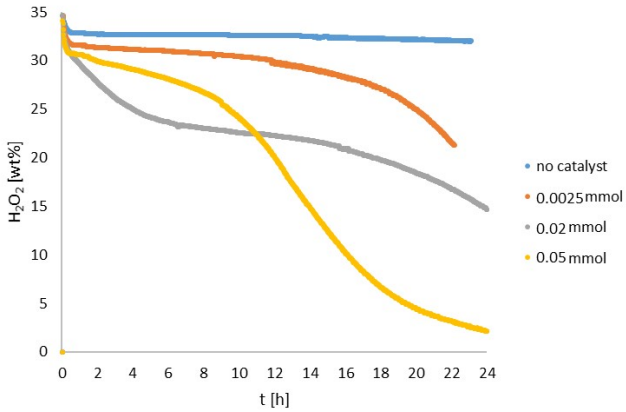


Figure S 14: Decomposition of H2O2 depending on the amount of catalyst

Reaction conditions: H_2O_2 (35wt% aqueous solution, 10 mmol), $H_3PW_{12}O_{40}$, acetonitrile (3.04 g); T = 100°C.

5. Higher molecular oligomers

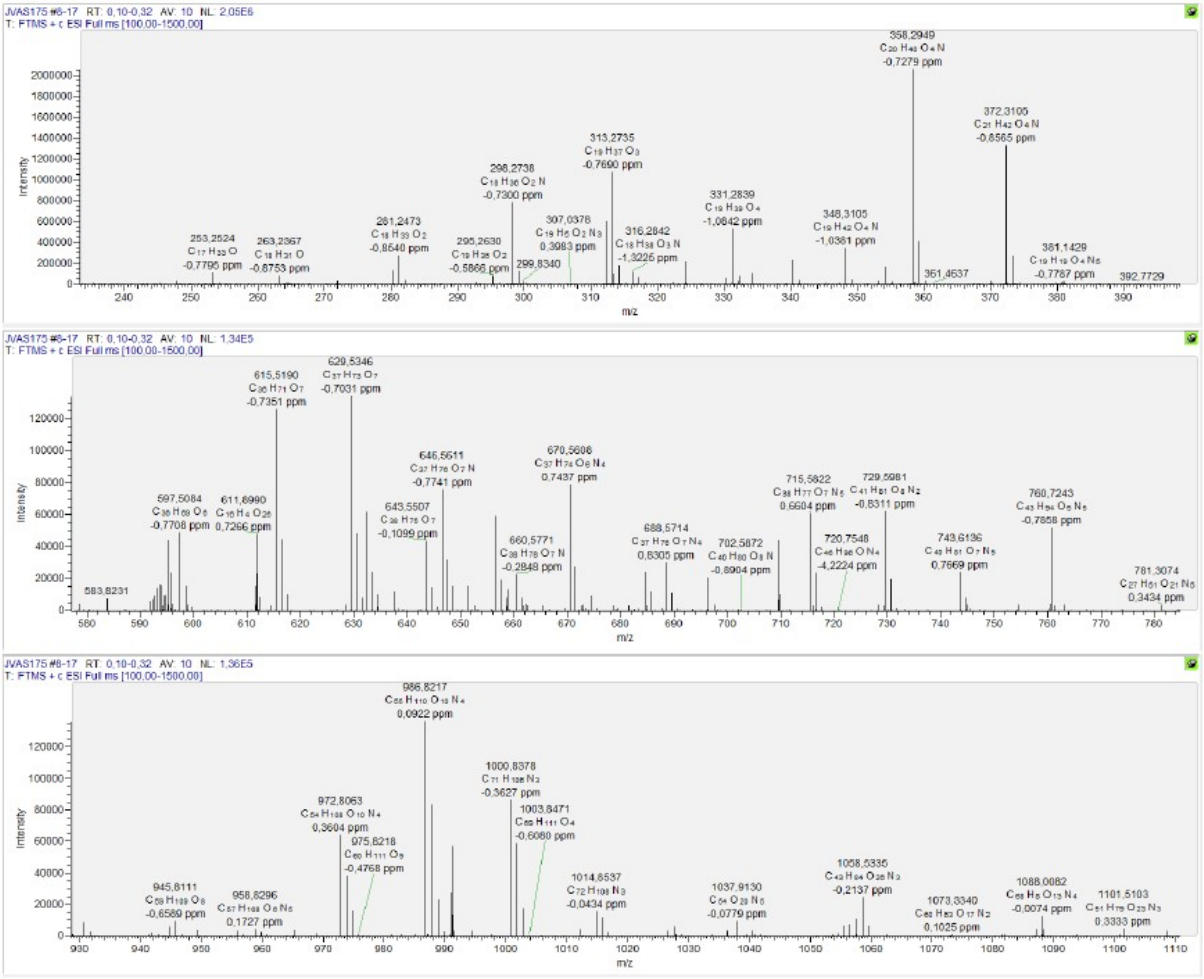


Figure S 15: HESI MALDI-MS of side-product

6. Organic solvent nanofiltration (OSN) – experimental procedure

The experiments were performed in a miniplant, specifically designed for OSN experiments. The setup contains a feed flask (heated and stirred), one HPLC pump for the feeding and the pressurization of the membrane loop and a gear pump for a proper flow in the membrane loop. The membrane itself is installed in the commercial Evonik 2.5" METcell lab scale module. Further equipment is a Coriolis mass flow meter for the flux measurement and a backpressure valve for the required transmembrane pressure. For more details s. Figure S 17 and Figure S 16. In the membrane screening experiments the retentate and permeate were recycled back to the feed flask. Therefore, the initial composition remained the same over the duration of one experiment. For the long-time experiment, only the retentate was recycled and therefore concentrated, while the permeate was discharged out of the system.

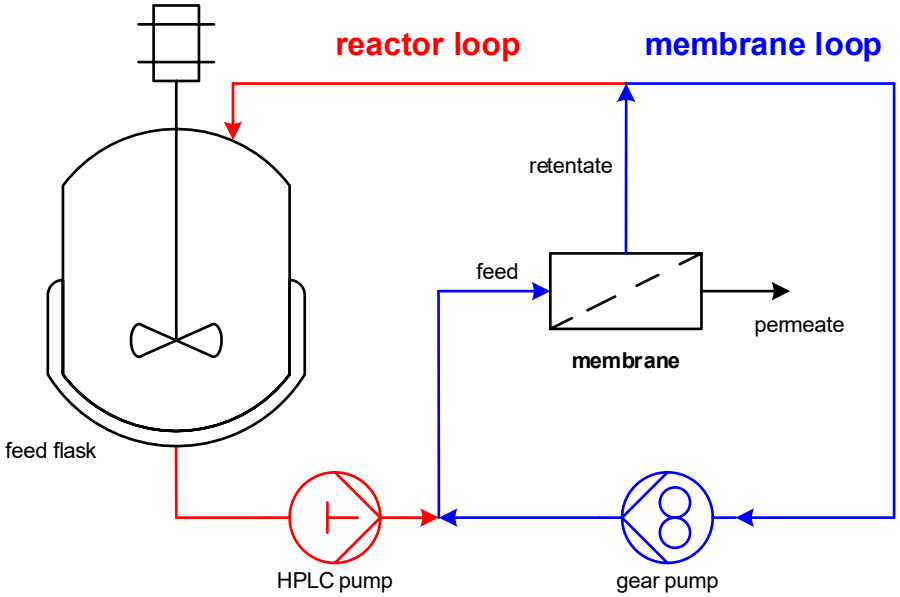


Figure S 16: Simplefied flow scheme of miniplant

Figure S 17: Photo of miniplant setup during membrane screening

The membranes were properly treated and conditioned (at least 4 h) according to the manufacturer prior to the start of the experiments. After 2h and 4h samples were taken from the retentate and the permeate and analyzed *via* ICP (s. section ICP-results) to determine the retention. The retention was calculated after equation (1). Note, that in literature the formula is also found as well for the catalyst concentration in the feed instead of in the retentate. In our case, $c_{cat,\ retentate}$ is close to $c_{cat,\ feed}$.

$$R = 1 - \frac{c_{cat,permeate}}{c_{cat,\ retentate}} \qquad (1)$$

7. GC-Analysis

GC-Analysis of reaction samples was carried out using an Agilent 7890A device, equipped with a flame ionization detector (FID) and an Agilent HP-5 column (30 m x 0.32 mm x 0.25 µm) (5% Phenyl Methyl Siloxan). Injection volume is 1 µL and split ratio is 70:1. The heating profile is given in Table S1. Dibutyl ether was used as an internal standard for quantification. An exemplary GC-calibration curve is given in Figure S 16.

Table S1: Heating profile

	Rate [°C/min]	Value [°C]	Hold time [min]
	-	50	3
Ramp 1	20	290	0
Ramp 2	45	320	3

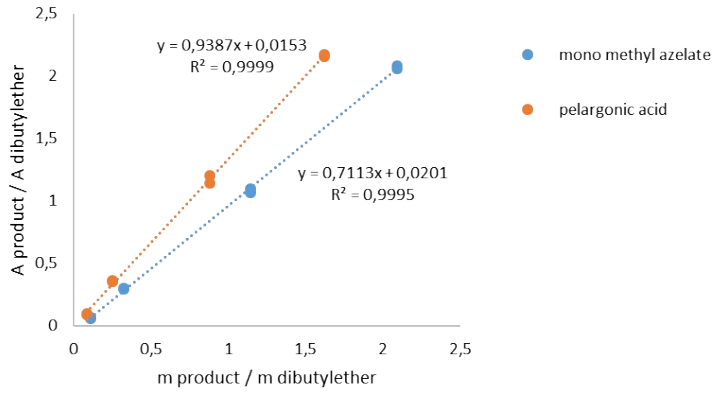


Figure S 18: GC-FID calibration of cleavage products

GC-analysis of retentate and permeate from organic solvent nanofiltration was carried out using Shimadzu GC-17A equipped with a FS-Supreme-5ms HT column (30 m x 0.32 mm x 0.25 µm). Injection volume was 0.5 µL and split ratio 180:1. Analysis was performed at a constant temperature of 70 °C.

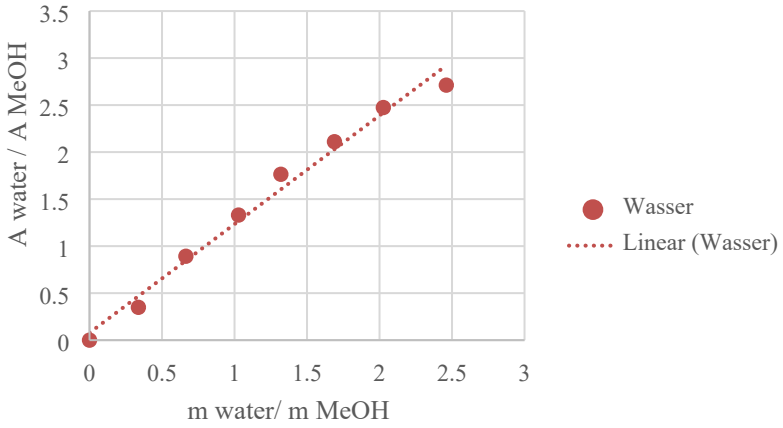


Figure S 19: GC-TCD calibration of water

8. ICP-results

ICP-OES-analysis was carried out using Analytik Jena PlasmaQuant PQ 9000 Elite.

Table S 2: ICP results for DuraMem 500

DuraMem 500	Phosphorus [ppm]	Tungsten [ppm]
Permeate 2h	13	935
Retentate 2h	41	2745
Permeate 4h	11	828
Retentate 4h	40	2777

Table S 3: ICP results for AMS Nanopro S-3012

AMS Nanopro S-3012	Phosphorus [ppm]	Tungsten [ppm]
Permeate 2h	2	137
Retentate 2h	41	2751
Permeate 4h	3	164
Retentate 4h	42	2814

Table S 4: ICP results for AMS Nanopro S-3012 in long-time experiment

AMS Nanopro	Phosphorus [ppm]	Tungsten [ppm]
Permeate 2h	1	196
Retentate 2h	40	3170
Permeate 4h	2	261
Retentate 4h	41	3211
Permeate 21h	4	403
Retentate 21h	50	3833
Permeate 45h	9	736
Retentate 45h	66	4956

9. Synthesis of acyloin

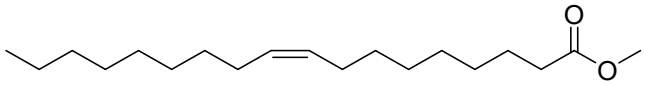
Using the reaction conditions reported in figure 10 (3 eq. of H_2O_2), the acyloin was obtained from the diol with high selectivity. Therefore, we repeated the procedure as follows to isolate the intermediate: six pressure tubes, equipped with a magnetic stirrer bar, were filled with methyl 9,10-dihydroxystearate (0.1 g; 0.3 mmol) and 1 g of a stock solution, consisting of 0.215 g of phosphotungstic acid and 7.9 g of acetonitrile, is added, corresponding to a catalyst loading of 3 mol%.

Sodium hydroxide is added as 2 M aqueous solution (0.0365 g). Water (0.06 g) is added to ensure solution of sodium hydroxide. Hydrogen peroxide (50wt%, 0.086 g, 3 eq.) is added right before placing the closed pressure tubes into a preheated block of steel on a stirrer plate. The reaction is run for 3 h at 100 °C. After cooling on ice, all six batches are combined and stored in an ice bath for 1 h. A white solid precipitates and is filtered off. The filtered solution is separated, before the solid is washed with cold water and dried under high vacuum (0.08 mbar). From GC-analysis, the white solid contains 70% of methyl 9,10-dihydroxystearate and 30% of acyloin. The filtered solution contains mainly acyloin and traces of carboxylic acids, but no more methyl 9,10-dihydroxystearate. It is then extracted with isooctane (3x, volumetric ratio of aqueous:organic phase of 1:1) and the organic layer is washed with water (3x, volumetric ratio of aqueous:organic phase of 1:1). The organic layer is then concentrated under reduced pressure (110 mbar at 50°C) and dried under high vacuum (0.08 mbar). Finally, 0.15 g of the acyloin (according to GC-FID and NMR) are obtained as a yellow oil, corresponding to an isolated yield of 26%.

10. Identification of intermediates and products

Known products and intermediates were identified by low resolution mass spectroscopy and commercially available references in GC-FID analysis. Methyl 9,10-epoxystearate was synthesized according to the procedure described in our previous work.[1] The acyloin methyl-9-hydroxy-10-oxy-octadecanoate/ methyl-9-oxy-10-hydroxy-octadecanoate was isolated from our reaction mixture according to the procedure described in section 9.

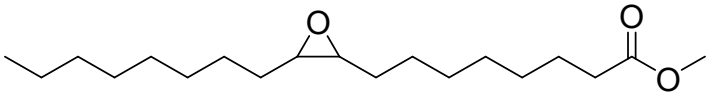
10.1 Methyl oleate



MS, (m/z): 296.3 (13.17); 265.3 (50.76); 264.3 (81.64); 235.2 (12.38); 222.2 (46.75); 221.2 (19.36); 220.2 (18.25); 207 (11.32); 181.1 (12.90); 180.1 (44.33); 179.1 (10.03); 169.1 (13.23);

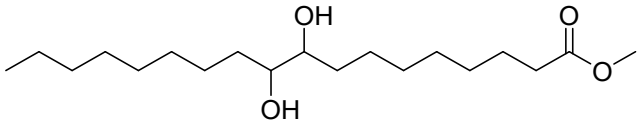
167.1 (11.70); 166.1 (28.13); 165.2 (19.95); 153.1 (19.96); 152.1 (35.64); 151.1 (35.44); 149.2 (17.4); 148.1 (17.01); 147 (13.81); 143.1 (16.08); 141.1 (31.75); 139.2 (29.29); 138.2 (33.28); 137.1 (42.04); 135.1 (22.66); 134.1 (22.83); 133 (15.3); 129.1 (15.49); 128 (15.37); 127.1 (12.19); 125.9 (10.69); 125.1 (45.46); 124.1 (47.44); 123.1 (63.79); 122.1 (13.9); 121.1 (28.86); 119 (17.43); 115 (23.34); 114.1 (18.24); 113.1 (14.72); 112.1 (39.73); 111.1 (100); 110.1 (96.19); 109.1 (74.6); 108.1 (24.6); 107 (21.86); 105 (10.41); 101 (31.28).

10.2 Methyl 9,10-epoxystearate



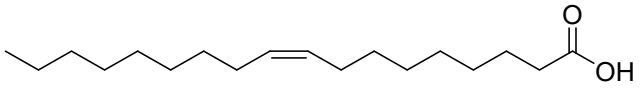
MS, (m/z): 294.1 (6.18); 281.2 (6.53); 264.2 (5.61); 199 (15.53); 185 (11.84); 171.1 (22.64); 170.2 (11.08); 168.1 (13.9); 167.1 (12.53); 158 (11.31); 157.1 (19.04); 156.2 (21.59); 155.1 (100); 154.1 (11.38); 153;1 (24.49); 150.1 (14.38); 149.1 (12.39); 143.1 (15.89); 142.1 (12.05). 141.1 (20.48); 140.1 (17.46); 139.1 (40.51); 138.1 (18.72); 137.1 (19.43); 136.1 (14.99); 135.1 (18.65); 127.1 (35.8); 126.1 (11.51); 125.1 (47.73); 124.1 (22.73); 123.1 (19.83); 121.1 (29.01); 120.1 (10.54); 111.1 (39.56); 110.1 (32.42); 109.1 (61;76); 107.1 (20.63); 101.1 (19.62)

10.3 Methyl 9,10-Dihydroxystearate



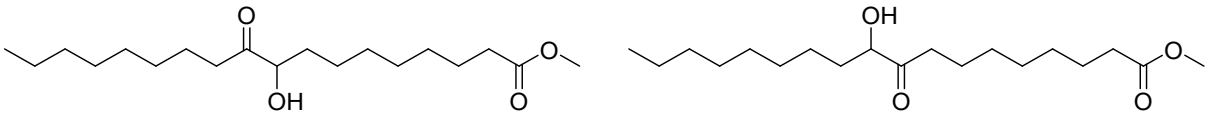
MS, (m/z): 281.2 (1.00), 188.2 (5.29), 187.2 (25.76), 156.1 (12.90), 155.1 (100), 143.2 (1.88), 138.1 (30.17), 127.1 (5.87), 115.0 (5.15), 110.1 (9.70), 109.1 (41.53), 101.1 (6.73), 96.1 (18.23), 95.1 (18.41), 87.1 (35.91), 84.1 (14.82), 83.1 (36.25), 81.1 (23.64), 74.1 (42.32), 71.1 (12.00), 69.1 (62.61), 67.1 (44.72), 57.1 (59.02), 55.1 (94.98), 43.1 (49.93), 41.1 (61.45).

10.4 Oleic acid



MS, (m/z): 265.4 (1.19), 264.3 (4.80), 235.2 (1.07), 222.3 (1.63), 220.2 (1.43), 207.4 (1.02), 180 (1.44), 165.1 (1.70), 152.1 (2.41), 151.2 (3.19), 148.1 (2.09), 147.1 (1.62), 138.1 (3.56), 137.1 (4.73), 133.0 (2.58), 125.1 (5.95), 123.1 (6.58), 119.1 (2.34), 114.0 (4.40), 111.1 (13.65), 110.1 (10.34), 97.1 (30.47), 96.1 (19.51), 87.1 (5.28), 83.1 (40.94), 81.1 (30.17), 79.28 (14.28), 69.1 (57.75), 67.1 (43.09), 60.1 (35.83), 57.1 (28.57), 56.1 (22.08), 55.1 (100), 54.1 (25.76), 45.1 (16.70), 43.1 (60.58), 42.1 (17.31), 41.1 (93.29).

10.5 Methyl-9-hydroxy-10-oxy-octadecanoate/ Methyl-9-oxy-10-hydroxy-octadecanoate



^{1}H NMR (600 MHz, CDCl3) δ 4.16 (s, 1H, -C**H**OH), 3.66 (s, 3H, C**H$_3$**OR-), 3.48 (s, 1H, -O**H**), 2.43 (m, 2H, -C**H$_2$**CO-), 2.29 (t, 2H, -C**H$_2$**COOMe, *J* = 6 Hz), 1.60 (m, 4H, -CH_2-), 1.45 (m, 2H, -C**H$_2$**-), 1.29 (m, 18 H, -CH_2-), 0.86 (t, 3H, C**H$_3$**-, *J* = 9 Hz).

^{13}C NMR (151 MHz, CDCl3) δ 212.73 (1C), 174.48 (1C), 76.61 (1C), 51.68 (1C), 38.06 (1C), 34.25 (1C), 33.98 (1C), 32.04 (1C), 29.67 (1C), 29.51 (1C), 29.30 (1C), 29.21 (2C), 29.10 (1C), 25.03 (1C), 23.86 (1C), 22.85 (1C), 14.30 (1C).

MS, (m/z): 329.30 (0.39), 279.30 (2.97), 188.10 (3.78), 187.10 (34.27), 185.10 (6.97), 171.10 (2.96), 158.10 (54.44), 155.10 (100), 141.10 (6.83), 129.10 (9.50), 125.10 (9.33), 115.10 (30.86), 109,10 (16.88), 101,00 (13.05), 97.10 (10.65), 87.00 (43.25), 83.10 (17.48), 81.10 (7.24), 74.00 (23.37), 69.10 (19.61), 67.00 (11.29), 57.10 (16.41), 55.10 (28.40), 43.10 (12.64), 41.00 (13.62).

HR-MS: $C_{19}H_{37}O_4$ $[M+H]^+$ = calculated: 329.26837, found: 329.26864.

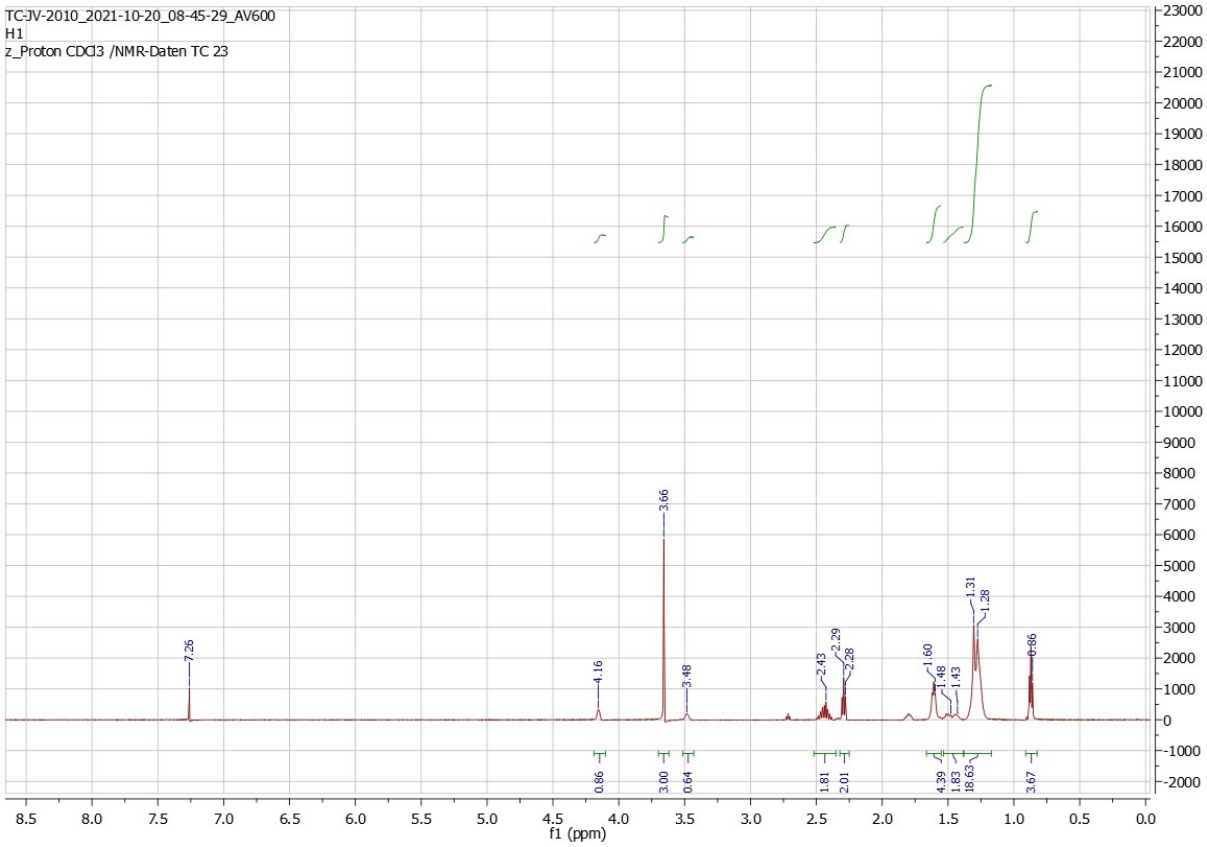


Figure S 20: ^{1}H-NMR of methyl 9-hydroxy-10-oxy-octadecanoate/ methyl 9-oxy-10-hydroxy-octadecanoate

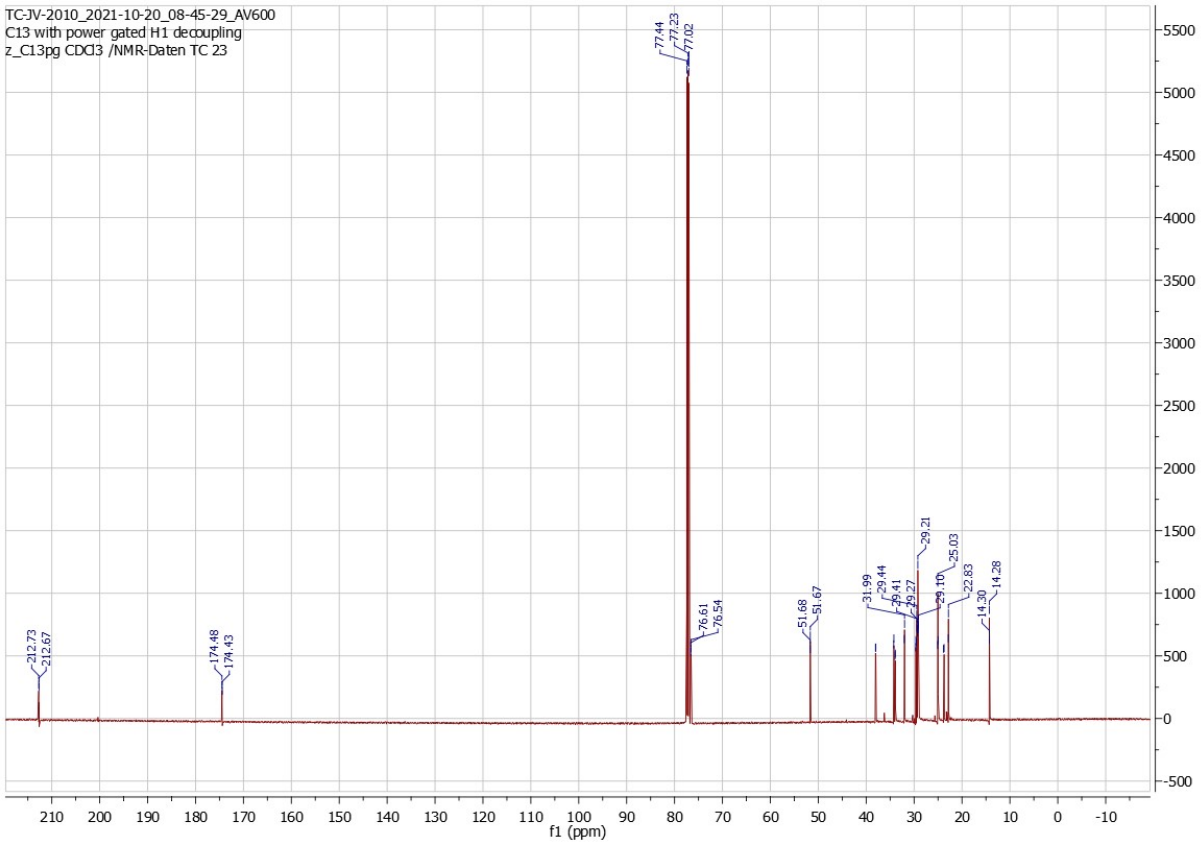
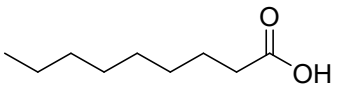


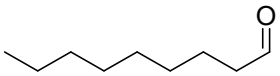
Figure S 21: ^{13}C-NMR of methyl 9-hydroxy-10-oxy-octadecanoate/ methyl 9-oxy-10-hydroxy-octadecanoate

10.6 Pelargonic acid



MS, (m/z): 130.0 (4.08), 129.0 (24.59), 115.1 (27.87), 100.9 (8.52), 98.0 (13.40), 82.9 (11.75), 74.1 (10.77), 73.0 (86.39), 69.1 (24.14), 61.0 (16.18), 60.0 (100), 57.0 (56.47), 56.1 (12.09), 55.1 (57.24), 53.1 (9.00), 45.0 (46.12), 43.1 (48.17), 42.1 (20.24), 41.1 (76.28).

10.7 Nonanal



MS, (m/z): 124.1 (1.33), 114.1 (3.87), 98.1 (18.76), 96.1 (14.57), 95.1 (15.08), 85.0 (2.41), 82.1 (19.49), 81.1 (18.76), 79.1 (3.08), 71.1 (10.60), 70.1 (24.69), 69.1 (21.53), 68.1 (19.46), 67.1 (19.39), 57.1 (62.44), 56.1 (35.80), 55.1 (44.43), 54.1 (11.82), 44.0 (29.76), 43.1 (52.68), 42.1 (100), 40.1 (7.74)

References

1 J. Vondran, J. Pela, D. Palczewski, M. Skiborowski and T. Seidensticker, Curse and Blessing—The Role of Water in the Homogeneously Ru-Catalyzed Epoxidation of Technical Grade Methyl Oleate, *ACS Sustainable Chem. Eng.*, 2021, **9**, 11469–11478.