

Biphasic Phase-Transfer Catalysis: Epoxidation of Vegetable Oils by Surface Active Ionic Liquids in Water

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Electronic Supplementary Information

Table of Contents

1. Experimental	S2
1.1. Materials, analytical methods and characterization techniques	S2
1.1.1. Materials	S2
1.1.2. Attenuated total reflectance infrared spectroscopy (ATR-IR)	S2
1.1.3. Transmission electron microscopy (TEM)	S2
1.1.4. Cryo-transmission electron microscopy (Cryo-TEM)	S2
1.1.5. Dynamic light scattering (DLS)	S3
1.1.6. Elemental analysis (EA)	S3
1.1.7. Inductively coupled plasma mass spectrometry (ICP-MS)	S3
1.1.8. Nuclear magnetic resonance spectroscopy (NMR)	S3
1.1.9. Titration experiments for determining substrate conversion and product selectivity	S4
1.1.10. Surface tension measurements	S6
1.2. Synthesis of the SAILs and their precursors	S7
1.2.1. Imidazolium bromides	S7
1.2.2. Imidazolium tungstate SAILs	S8
1.3. Catalysis experiments	S9
1.3.1. Epoxidation catalysis	S10
1.3.2. Catalyst recycling	S10
2. Materials characterization	S11
2.1. Critical micelle concentration	S11
2.2. Dynamic light scattering	S12
2.3. Transmission electron microscopy	S13
2.4. Nuclear magnetic resonance	S17
3. Epoxidation Catalysis	S19
3.1. EVO detection by ¹ H-NMR spectroscopy	S19
3.2. EVO detection by IR spectroscopy	S22
3.3. Kinetic data	S24
3.4. Determination of the activation energy	S27
4. References	S27

1. Experimental

1.1. Materials, analytical methods and characterization techniques

1.1.1. Materials

Chloroform (CHCl_3 , puriss), *n*-hexane (HPLC), 1-methylimidazole, 1,2-dimethylimidazole, 1-bromooctane, 1-bromodecane, 1-bromododecane, sodium hydroxide, potassium iodide, Wijs solution (0.1 M iodine monochloride solution in acetic acid), soybean and corn oil were purchased from Sigma Aldrich. Concentrated hydrogen chloride (HCl) solution was purchased from CLN GmbH. High oleic palm oil was provided by FEDEPALMA (Columbia). Hydrogen peroxide (H_2O_2 , 50 wt.% in water) and 8-dram vials for epoxidation catalysis (TraceClean®) were purchased from VWR. 1-Methylimidazole and all alkyl halides were distilled under vacuum and stored under an argon atmosphere until further use. All other purchased chemicals were used without further purification. Synthesis of imidazolium halides were carried out under Schlenk conditions, the following synthesis steps and catalysis runs were carried out under air, if not stated otherwise.

1.1.2. Attenuated total reflectance infrared spectroscopy (ATR-IR)

ATR-IR measurements were carried out on a *PerkinElmer* Frontier FT-IR spectrometer featuring an ATR plate with a diamond crystal with a 2 cm^{-1} resolution and 16 accumulated scans.

1.1.3. Transmission electron microscopy (TEM)

TEM measurements were carried out with a JEM 1400 plus microscope at 120 kV equipped with a Ruby CCD detector from JOEL. Prior to substrate loading the copper grids were glow discharged to increase the hydrophilicity of the carbon surface. Afterwards, 5 μL of the respective sample was coated onto a Micro to Nano grids (Carbon support film on copper, 300 mesh) by drop casting with an impregnation time of 5 s before flushing the grid with 20 μL water.

1.1.4. Cryo-transmission electron microscopy (Cryo-TEM)

Cryo-TEM measurements were carried out with a Jeol 1400 plus microscope at 120 kV equipped with a Ruby CCD detector. Blotting of the $[\text{DoMIM}]_2\text{WO}_4/\text{H}_2\text{O}_2$ and $[\text{DoMIM}]_2\text{WO}_4/\text{H}_2\text{O}_2/\text{palm oil}$ samples was performed with a FEI Vitrobot MK3 at 50 °C and 60% humidity on Micro to Nano grids (Carbon support film on copper, 300 mesh). The samples were heated to 50 °C before a sample of the aqueous phase (5 μL) was coated onto a TEM copper grid. The grid was blotted with two pieces of filter paper for approximately 4 s to form a solution thin film. Afterwards, the grid was quickly plunged into a reservoir of liquid ethane (cooled by liquid nitrogen) and stored in liquid nitrogen until the transfer of the grid to a cryogenic sample holder.

1.1.5. Dynamic light scattering (DLS)

DLS was performed on a Malvern Zetasizer Nano in quartz cuvettes using 173° angle backscattering mode. 2.5 mol% of the respective IL was dissolved in 1.4 mL aqueous H₂O₂ (25 mmol) and measured at 20 °C. In order to investigate the substrate interaction, the respective vegetable oil (10 mmol double bonds) was added to the mixture. The biphasic system was shaken and after phase separation the aqueous phase is used for the measurement after being filtered by a syringe filter (LLG-Syringe filters SPHEROS, PTFE, 0.22 µm, 13 mm diameter by Lab Logistics Group GmbH). Micelle size distributions were interpreted from the correlograms using a general-purpose method.

1.1.6. Elemental analysis (EA)

Elemental analyses were performed at the Microanalytical Laboratory of the Technical University of Munich, Germany on a HEKAtech Euro EA CHNSO-Analyzer and a Varian AA280FS fast sequential AAS spectrometer.

1.1.7. Inductively coupled plasma mass spectrometry (ICP-MS)

To determine if the catalyst [DoMIm]₂WO₄ fully remains in the aqueous phase or traces are contained in the organic phase after epoxidation catalysis of soybean oil, ICP-MS was conducted on a *Perkin Elmer* Nexlon 350D ICP-MS instrument. The sample was prepared by stirring 1.0 mL of the epoxidized soybean oil with 1.0 mL Millipore Milli-Q® water over night. Subsequently, the aqueous phase was separated and immersed in 7.5 mL concentrated nitric acid and 2.5 mL H₂O₂ 30 % (v/v) and treated in the microwave at 150 °C for 10 min. The microwave-digested samples were diluted 1/100 with Millipore Milli-Q® water. Each solvent was extra pure and checked for possible analyte contaminations before measurement. ¹⁸³W was used as target masses for the analyte and ¹¹⁵In as an internal standard. Analyte quantification was carried out in standard mode with correction equation to avoid polyatomic interferences. External calibration was performed and the detection limit for W was 0.6 µg/L. Each sample was measured with five measurement replicates, a dwell time per 50 ms and an integration time of 750 ms. The metal concentration was blank corrected via measurement of blank samples.

1.1.8. Nuclear magnetic resonance spectroscopy (NMR)

Liquid state NMR spectra were recorded on a *Bruker* AVIII 400 US (¹H: 400 MHz, 16 scans; ¹³C: 101 MHz, 1024 scans; ³¹P: 161 MHz, 32 scans) at ambient temperature (298 K). The ¹H-NMR spectroscopic chemical shifts are reported in ppm relative to tetramethylsilane. ¹H-NMR spectra are calibrated against the residual proton and natural abundance carbon resonances of the respective deuterated solvent as an internal standard (CDCl₃: δ (¹H) = 7.26 ppm). The following abbreviations are used to describe signal multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet. ¹⁸³W-NMR spectra were recorded on a *Bruker* AV 400 US in D₂O (16.6 MHz, 4096 scans).

1.1.9. Titration experiments for determining substrate conversion and product selectivity

To analyze the conversion and selectivity of vegetable oils (VOs) after the epoxidation the conventional method is the determination of the iodine and oxygen oxirane number (OON) by titration. Note that each titration is performed three times. The calculations were performed with the average values.

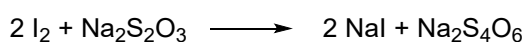
The iodine number (IN), which is needed to derive the conversion of the reaction, was determined by iodometric titration according to ISO 3961 (ISO, 2018). An excessive amount of Wijs reagent (0.1 N iodine monochloride solution in acetic acid) and 5 mL chloroform were added to the sample (0.06 g). After 30 min an excess of potassium iodide (2 ml, 10 wt.% in water) was added (producing molecular iodine with unreacted Wijs reagent). The iodine content of the sample was determined with a 0.1 N sodium thiosulfate solution, using a starch solution (1 wt.% in water) as indicator. The IN is expressed in terms of reacted I₂ in 100 g of the respective (epoxidized) vegetable oil ((E)VO), where one mole of double bonds (of the oil) reacts with one mole of iodine. The IN is calculated according to the following equation:

$$IN = \frac{(V_1 - V_2) \cdot C \cdot 12.69}{m}$$

The OON was determined by acid-base titration according to the ASTM standard method (ASTM, 2019). An excessive amount of hydrochloric acid (5 ml of a solution consisting of 1.5 mL concentrated HCl in 100 mL isopropanol) was added to the sample (0.1 g) and stirred for 15 min (ring opening of the epoxide ring). The solution was titrated with a 0.1 N sodium hydroxide solution using phenolphthalein as indicator to quantify the amount of unreacted HCl. The OON was calculated with the following equation:

$$OON = \frac{(V_1 - V_2) \cdot C \cdot 1.6}{m}$$

In both cases V₁ represents the blank, i.e., the volume of the respective titer needed to reach the equivalence point of a titration not containing any oil sample, and V₂ is the volume consumed for the titration of a catalytic epoxidation sample. C is the concentration of the respective titer and m is the sample mass. The factor 12.69 for the determination of the IN results from the stoichiometry and molar mass of the reaction between molecular iodine (I₂) and sodium thiosulfate (Na₂S₂O₃):



The mass equivalent of I₂ for 1 mL of a 0.1 M Na₂S₂O₃ solution (n = 0.0001 mol) is derived via the following equation and equals 0.01269 g I₂:

$$m(I_2) = 0.00005 \text{ mol} \cdot 253.84 \frac{\text{g}}{\text{mol}} = 0.01269 \text{ g}$$

The OON expresses the mass percentage of oxirane oxygen in the epoxidized vegetable oils (%m(O)/m(oil)), and therefore the factor of 1.6 results from the multiplication of the molar mass of oxirane oxygen (16 g/mol) with the fraction of 100 as the nominator (%) and 1000 as denominator (conversion of mL to L).

Followingly the conversion and the selectivity were calculated as follows:

$$\text{Conversion (\%)} = \frac{(IN_i - IN_s)}{IN_i} \cdot 100$$

$$\text{Selectivity (\%)} = \frac{OON/16}{(IN_i - IN)_s/253.8} \cdot 100$$

With IN_i representing the initial IN of the respective vegetable oil and IN_s being the IN of the titrated sample. For the calculation of the selectivity the mass of one mole oxirane oxygen and one mole molecular iodine (O, 16 g/mol and I_2 , 253.8 g/mol) are used, respectively, as one mole of double bonds produce one mole of oxirane oxygen (in case of 100 % selectivity).

The calculated errors for the conversion of the epoxidation reactions (using the minimum error of the burette) are generally low ($\pm 0.6 - 3.7\%$) and reproduceable across different titrations within aliquots of one data point of the same sample as well as among titrations of different sample. Furthermore, the calculated errors do not directly correlate to the respective degree of conversion. This is ensured by using aliquots with a sufficiently large sample mass (0.06 g). In case of low sample masses (e.g. 0.01 g) the error increases notably to $>\pm 5\%$ and therefore titration experiments with low sample loadings are not recommended.

In contrast, errors in terms of the selectivity towards epoxides strongly depend on the degree of conversion. The resulting errors decrease with reaction time and increasing conversion, while at full conversion the calculated errors value $\sim \pm 3\%$. However, at low conversions (below 20%) the resulting errors value up to $>\pm 35\%$ and are not further calculated. Similarly, to previous determinations for the conversion of the catalysis experiments the sample mass impacts the error value, therefore the sample mass is increased to 0.1 g in order to ensure coherent results and reproducibility. The high error values for the selectivity at low conversions result from the fractional calculation where both, the amount of reacted double bonds (nominator) and produced amount of oxirane moieties (denominator) in mole are involved. At low conversions both molar values are low, and therefore small deviations result in high errors when expressed in percentage.

Note that there is a certain uncertainty regarding the carbon balance, since the molecular weight of the epoxidized vegetable oil is increased. In case of high oleic palm oil (molar mass = 850 g/mol) at full conversion the difference in molecular weight equals up to 4.49% (depending on the selectivity), resulting from:

$$M(EVO) = M(VO) + 16 \cdot n(DB)$$

$$1 - \frac{850 \frac{g}{mol}}{850 \frac{g}{mol} + 16 \cdot 2.5} = 1 - \frac{850 \frac{g}{mol}}{890 \frac{g}{mol}} = 0.0449$$

Where 16 equals to the molar mass of oxirane oxygen, $n(\text{DB})$ is the average amount of double bonds in a molecule of the respective vegetable oil (2.5 for high oleic palm oil).

1.1.10. Surface tension measurements

The CMCs were determined by surface tension measurements with a K11 tensiometer (Krüss GmbH, Germany) according to the Wilhelmy plate method with an accuracy of 0.01 N m^{-2} . A vertically suspended plate touches the liquid, wets the plate and a force (F) can be measured. The surface tension is calculated according to the following equation:

$$\sigma = \frac{1}{4} F L \times \cos\theta$$

L is the length of the plate and θ the contact angle between liquid and solid surface of the plate. Due to the decomposition of hydrogen peroxide on platinum surfaces, the usually used platinum plates were substituted with glass plates. The data were drawn in a figure with surface tension over the logarithmic concentration of the surfactant to see a sharp break point at the CMC.

1.2. Synthesis of the SAILs and their precursors

1.2.1. Imidazolium bromides

The syntheses were carried out according to previous literature reports.^{S1} All 1,(2)-(di)alkyl-3-methylimidazolium bromides were synthesized by addition of 1-methylimidazole or 1,2-dimethylimidazole (1.0 equiv.) to the corresponding 1-bromoalkane (1.05 equiv.). The solution was degassed and stirred under an argon atmosphere for 24 h at 50 °C. Impurities were evaporated at 80 °C by using a turbomolecular pump (10⁻⁵ mbar) for 8 h. The resulting colorless ILs were stored under argon atmosphere due to their high hygroscopy.

1.2.1.1. 1-Octyl-3-methylimidazolium bromide [OMIm]Br

Colorless viscous liquid; 97 % yield

¹H-NMR (400 MHz, CDCl₃, 298 K) δ [ppm]: 10.28 (s, 1H), 7.61 (s, 1H), 7.43 (s, 1H), 4.27 (t, *J* = 7.4 Hz, 2H), 4.06 (s, 3H), 1.84 (pseudo-p, *J* = 7.3 Hz, 2H), 1.31 – 1.10 (m, 10H), 0.79 (t, *J* = 6.6 Hz, 3H).

¹³C-NMR (101 MHz, CDCl₃, 298 K) δ [ppm]: 137.51, 123.66, 121.87, 50.08, 36.65, 31.58, 30.28, 28.95, 28.84, 26.21, 22.49, 14.02.

1.2.1.2. 1-Dodecyl-3-methylimidazolium bromide [DoMIm]Br

White solid; 99 % yield

¹H-NMR (400 MHz, CDCl₃, 298 K) δ [ppm]: 10.30 (s, 1H), 7.61 (d, *J* = 1.8 Hz, 1H), 7.42 (d, *J* = 1.9 Hz, 1H), 4.25 (t, *J* = 7.4 Hz, 2H), 4.07 (s, 3H), 1.85 (pseudo-p, *J* = 7.3 Hz, 2H), 1.29 – 1.15 (m, 18H), 0.80 (t, *J* = 6.8 Hz, 3H).

¹³C-NMR (101 MHz, CDCl₃, 298 K) δ [ppm]: 137.31, 123.78, 121.99, 50.12, 36.71, 31.86, 30.33, 29.56, 29.47, 29.35, 29.29, 28.98, 26.23, 22.64, 14.10.

1.2.1.3. 1-Dodecyl-2,3-dimethylimidazolium bromide [DoMMIm]Br

White solid; 96 % yield

¹H-NMR (400 MHz, CDCl₃, 298 K) δ [ppm]: 7.74 (d, *J* = 2.1 Hz, 1H), 7.43 (d, *J* = 2.2 Hz, 1H), 4.17 (t, *J* = 7.5 Hz, 2H), 4.02 (s, 3H), 2.79 (s, 3H), 1.79 (pseudo-p, *J* = 7.6 Hz, 2H), 1.33 – 1.18 (m, 18H), 0.85 (t, *J* = 6.7 Hz, 3H).

¹³C-NMR (101 MHz, CDCl₃, 298 K) δ [ppm]: 143.83, 123.24, 121.11, 49.13, 36.35, 31.97, 29.96, 29.65, 29.58, 29.46, 29.40, 29.13, 26.47, 22.75, 14.20, 11.15.

1.2.2. Imidazolium tungstate SAILs

The imidazolium tungstates were synthesized according to our literature reported procedure. According to an anion exchange procedure, the respective imidazolium bromides (2.0 equiv.) were dissolved in 400 mL deionized water and rinsed over 250 g Amberlite 402 (Cl), freshly activated by 1 M NaOH solution. The basic fractions were collected, and tungstic acid (H_2WO_4 , 1.1 equiv.) was added. The solution was stirred at room temperature until a pH of 7 was reached. Excess of H_2WO_4 was removed by filtration and the water evaporated under reduced pressure. The products were dried at 80 °C for 8 h using a turbomolecular pump (10^{-5} mbar). The resulting colorless SAILs were stored under argon atmosphere due to the high hygroscopy.

1.2.2.1. 1-Octyl-3-methylimidazolium tungstate $[\text{OMIm}]_2[\text{WO}_4]$

Colorless viscous liquid; 97 % yield

$^1\text{H-NMR}^*$ (400 MHz, CDCl_3 , 298 K) δ [ppm]: 10.13 (s, 1H), 7.64 (s, $J = 1.9$ Hz, 1H), 7.29 (s, 1H), 4.22 (t, $J = 7.3$ Hz, 2H), 4.00 (s, 3H), 1.71 (pseudo-p, $J = 7.2$ Hz, 3H), 1.29 – 0.93 (m, 10H), 0.74 (t, $J = 6.8$ Hz, 3H).

*Intensity of the C2 proton is low due to high acidity and fast H/D exchange

$^{13}\text{C-NMR}^*$ (101 MHz, CDCl_3 , 298 K) δ [ppm]: 138.50, 123.80, 121.41, 77.45, 49.70, 36.47, 31.62, 30.34, 29.00, 26.23, 22.48, 13.97.

Elemental analysis calcd. (%) for $\text{C}_{24}\text{H}_{46}\text{N}_4\text{O}_4\text{W}$: C 45.15, H 7.26, N 8.77, O 10.02, W 28.79; found: C 45.57, H 7.68, N 8.83.

1.2.2.2. 1-Dodecyl-3-methylimidazolium tungstate $[\text{DoMIm}]_2[\text{WO}_4]$

Off-white solid; 96 % yield

$^1\text{H-NMR}^*$ (400 MHz, CDCl_3 , 298 K) δ [ppm]: 7.55 (d, $J = 1.8$ Hz, 1H), 7.24 (d, $J = 1.8$ Hz, 1H), 4.30 (t, $J = 7.3$ Hz, 2H), 4.11 (s, 3H), 1.81 (p, $J = 7.1$ Hz, 2H), 1.29 – 1.16 (m, 18H), 0.84 (t, $J = 6.7$ Hz, 3H).

$^{13}\text{C-NMR}^*$ (101 MHz, CDCl_3 , 298 K) δ [ppm]: 123.54, 121.21, 50.01, 36.77, 32.00, 30.55, 29.73, 29.72, 29.68, 29.57, 29.44, 29.27, 26.47, 22.78, 14.22.

$^{183}\text{W-NMR}$ (16.6 MHz, D_2O , 298 K) δ [ppm]: – 8.89 ppm.

Elemental analysis calcd. (%) for $\text{C}_{32}\text{H}_{62}\text{N}_4\text{O}_4\text{W}$: C 51.20, H 8.32, N 7.46, O 8.52, W 24.49; found: C 50.58, H 8.70, N 7.55.

1.2.2.3. 1-Dodecyl-2,3-dimethylimidazolium tungstate $[\text{DoMMIm}]_2[\text{WO}_4]$

Off-white solid; 95 % yield

$^1\text{H-NMR}^*$ (400 MHz, CDCl_3 , 298 K) δ [ppm]: 7.83 (d, $J = 2.1$ Hz, 0H), 7.41 (d, $J = 1.9$ Hz, 0H), 4.18 (t, $J = 7.4$ Hz, 1H), 4.03 (s, 1H), 1.72 (q, $J = 7.3$ Hz, 1H), 1.25 (d, $J = 5.8$ Hz, 2H), 1.29 – 1.16 (m, 18H), 0.84 (t, $J = 6.7$ Hz, 1H).

^{13}C -NMR* (101 MHz, CDCl_3 , 298 K) δ [ppm]: 143.51, 123.70, 121.05, 48.75, 35.96, 31.96, 30.07, 29.67, 29.61, 29.50, 29.40, 29.22, 26.52, 22.74, 14.19.

Elemental analysis calcd. (%) for $\text{C}_{34}\text{H}_{66}\text{N}_4\text{O}_4\text{W}$: C 52.44, H 8.54, N 7.19, O 8.22, W 23.61; found: C 51.58, H 8.69, N 7.33.

*Note the intensity of C2 protons in the ^1H -NMR is very low or not detectable due to fast H/D exchange and the signal of C2 in the ^{13}C -NMR is low in intensity and in some cases not detected due to C-D coupling.

1.3. Catalysis experiments

1.3.1. Epoxidation catalysis

Standard catalytic experiments were carried out on air in an 8-dram vial (TraceClean®). 2.5 mol% or 5 mol% of the catalyst and 5 mol% phenylphosphonic acid (PPA) were dissolved in 50 wt.% aqueous solution of hydrogen peroxide (1.4 mL, 25 mmol, 2.5 equiv.) before 69 µL mesitylene (5 mol%) as internal standard were added. The reaction vessel was closed and heated to reaction temperature in an oil bath under continuous stirring. Afterwards, the respective vegetable oil (10 mmol double bonds, 1.0 equiv. double bonds) was added, and the biphasic mixture was stirred in a closed vessel at 500 rpm. At respective time intervals the vessel was removed from the oil bath and after phase separation aliquots were taken from the organic top layer and analyzed by titration.

1.3.2. Catalyst recycling

The scale of the recycling experiment is doubled compared to standard catalytic experiments and carried out in a round bottom flask. Each run was stopped after 4 h reaction time. The oil phase was carefully removed with a pipette after the phase separation was ensured to be completed by a resting time of 3 h. To the residual 2 mL water was added before it was extracted with 3x 20 mL n-hexane before the aqueous phase is evaporated in vacuo. Afterwards, the catalytic run is performed as previously described using fresh H₂O₂, substrate and the recovered catalyst-PPA mixture.

2. Materials characterization

2.1. Critical micelle concentration

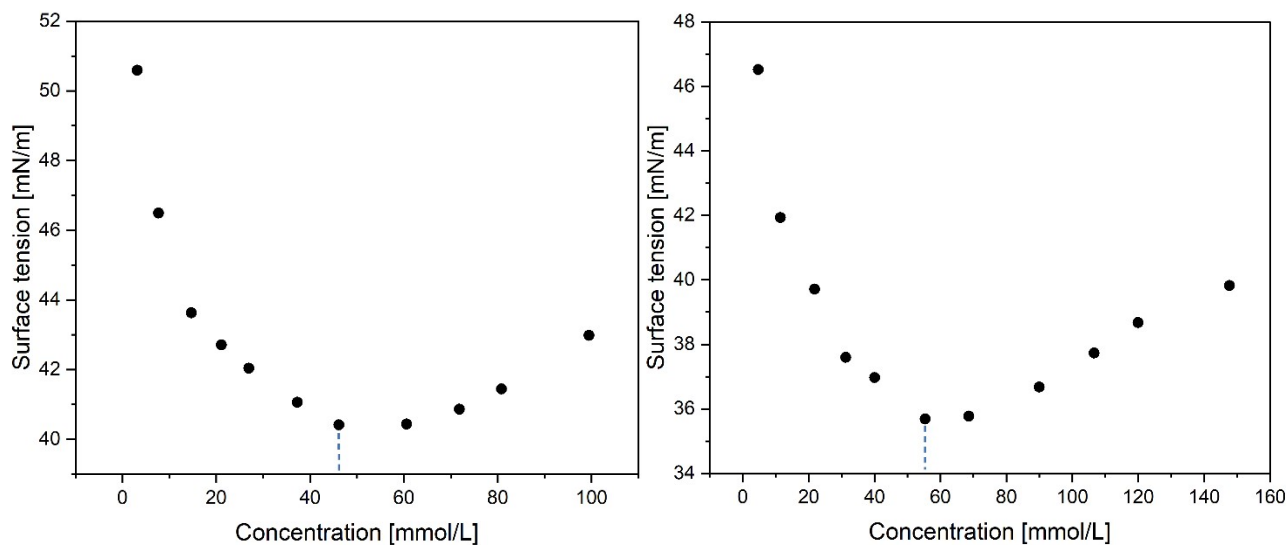


Figure S1 Surface tension measurements of [OMIm]₂[WO₄] at 25 °C (left) and 60 °C (right) in 50 wt.% H₂O₂, respectively. The dotted blue line indicates the CMC.

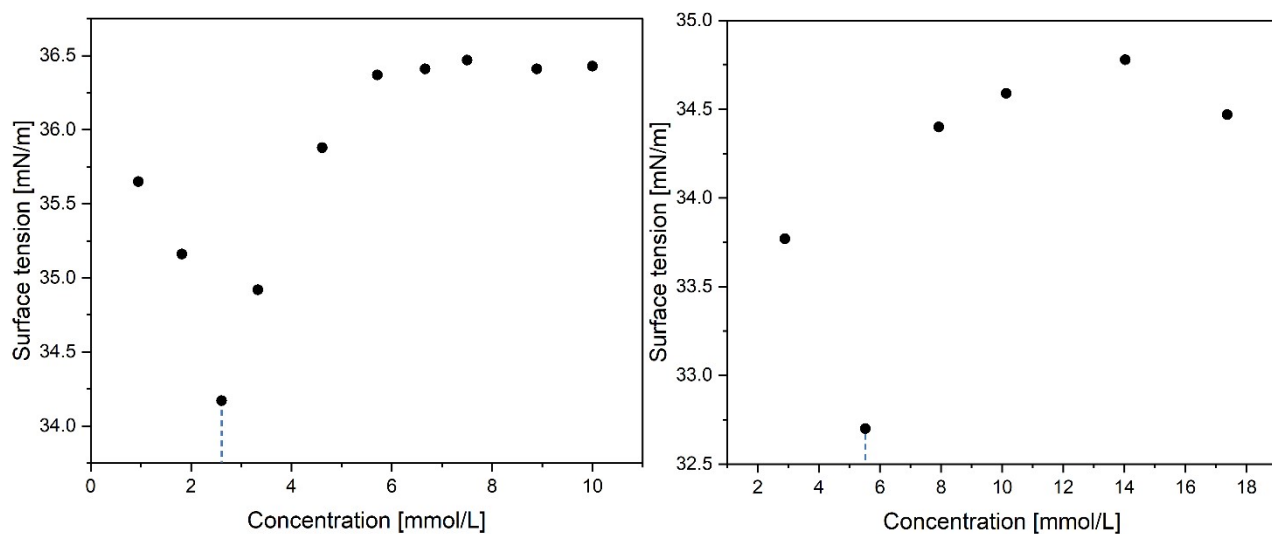


Figure S2 Surface tension measurements of [DoMIm]₂[WO₄] at 25 °C (left) and 60 °C (right) in 50 wt.% H₂O₂, respectively. The dotted blue line indicates the CMC.

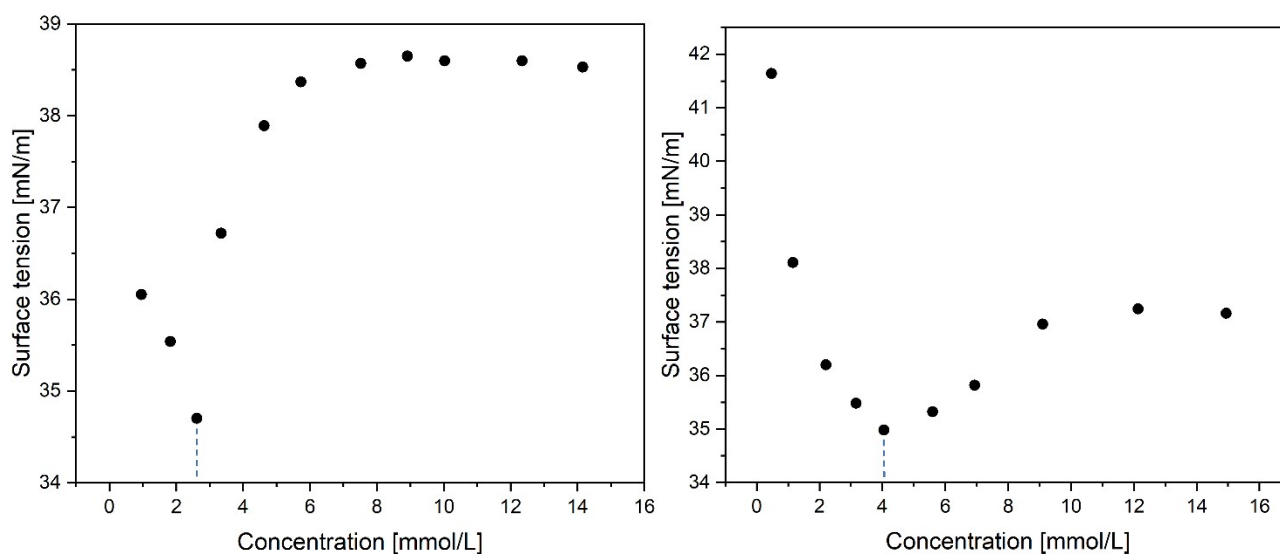


Figure S3 Surface tension measurements of $[\text{DoMIm}]_2[\text{WO}_4]$ at 25 °C (left) and 60 °C (right) in 50 wt.% H_2O_2 , respectively. The dotted blue line indicates the CMC.

2.2. Dynamic light scattering

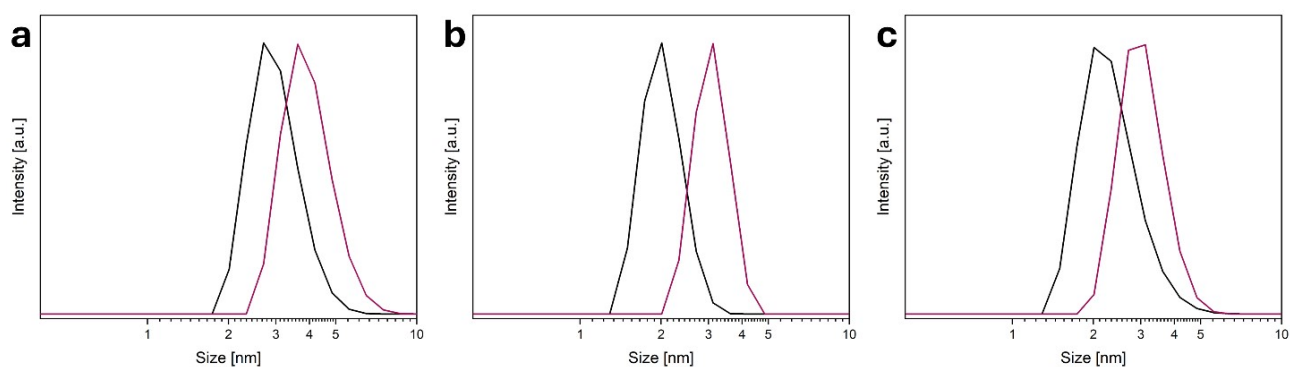


Figure S4 DLS measurements of IL catalysts at concentrations of 178 mmol/L in 50 wt.% aq. H_2O_2 at 20 °C prior (black) and after treatment with an excess of palm oil (purple), respectively. a) $[\text{OMIm}]_2[\text{WO}_4]$, b) $[\text{DoMIm}]_2[\text{WO}_4]$, c) $[\text{DoMIm}]_2[\text{WO}_4]$.

2.3. Transmission electron microscopy

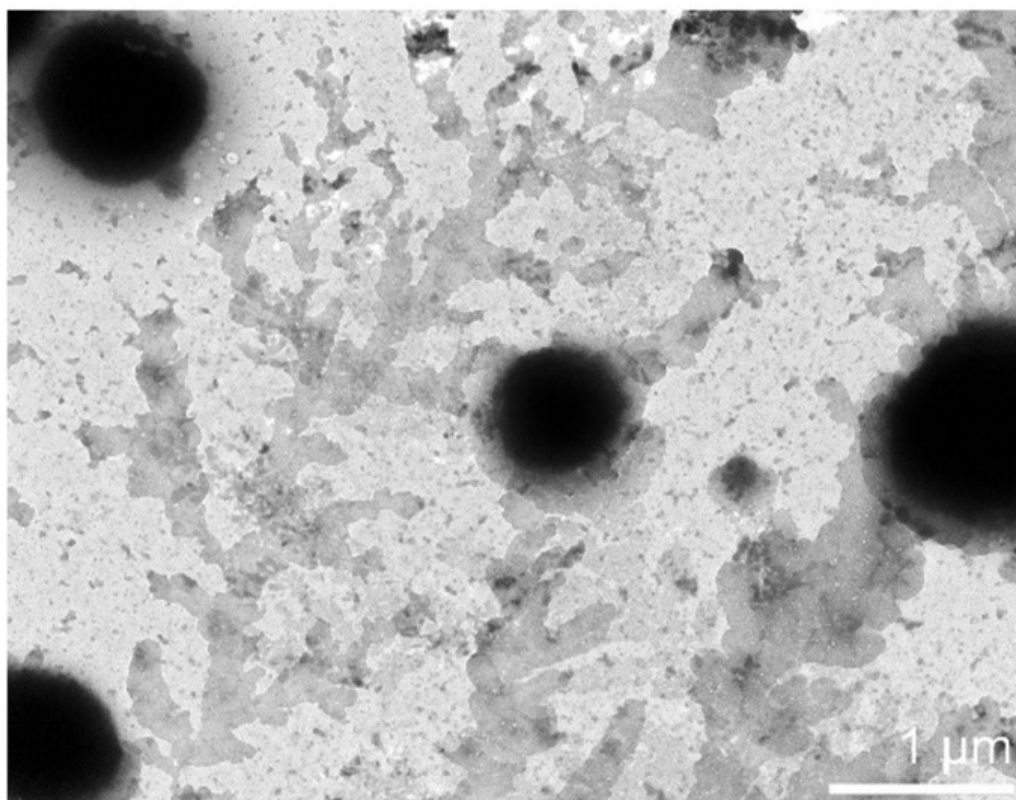


Figure S5 TEM image of [DoMIM]₂[WO₄] in 50 wt.% H₂O₂ at a concentration of 2.7 mmol/L.

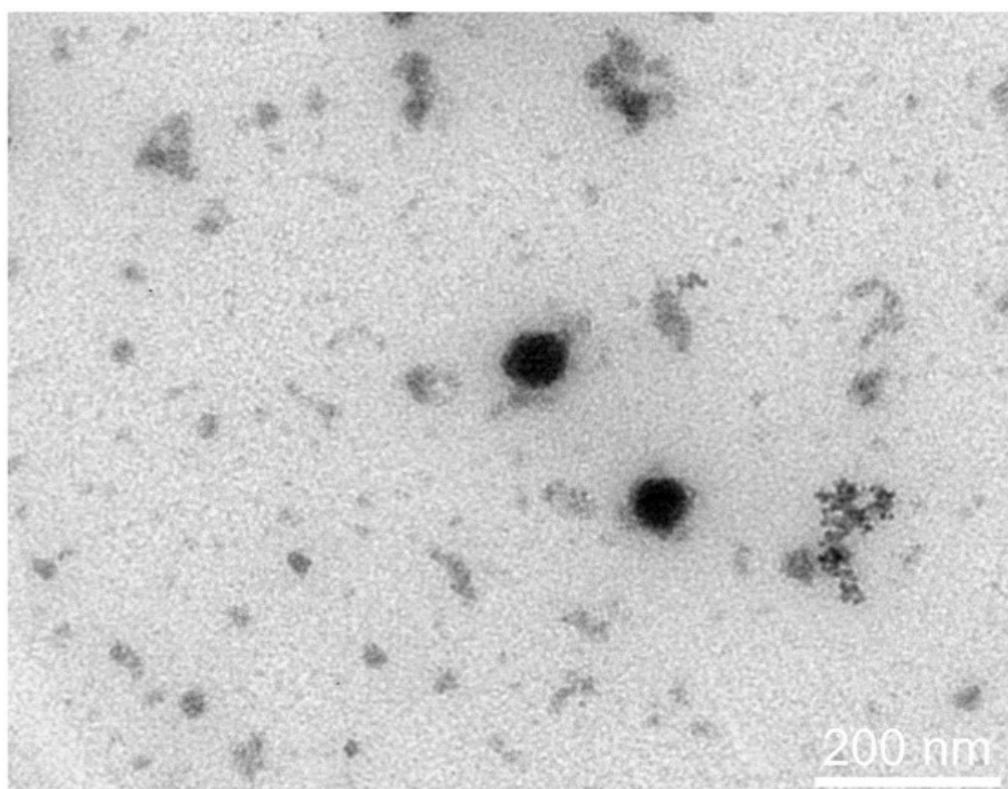


Figure S6 TEM image of [DoMIM]₂[WO₄] in 50 wt.% H₂O₂ at a concentration of 26 mmol/L.

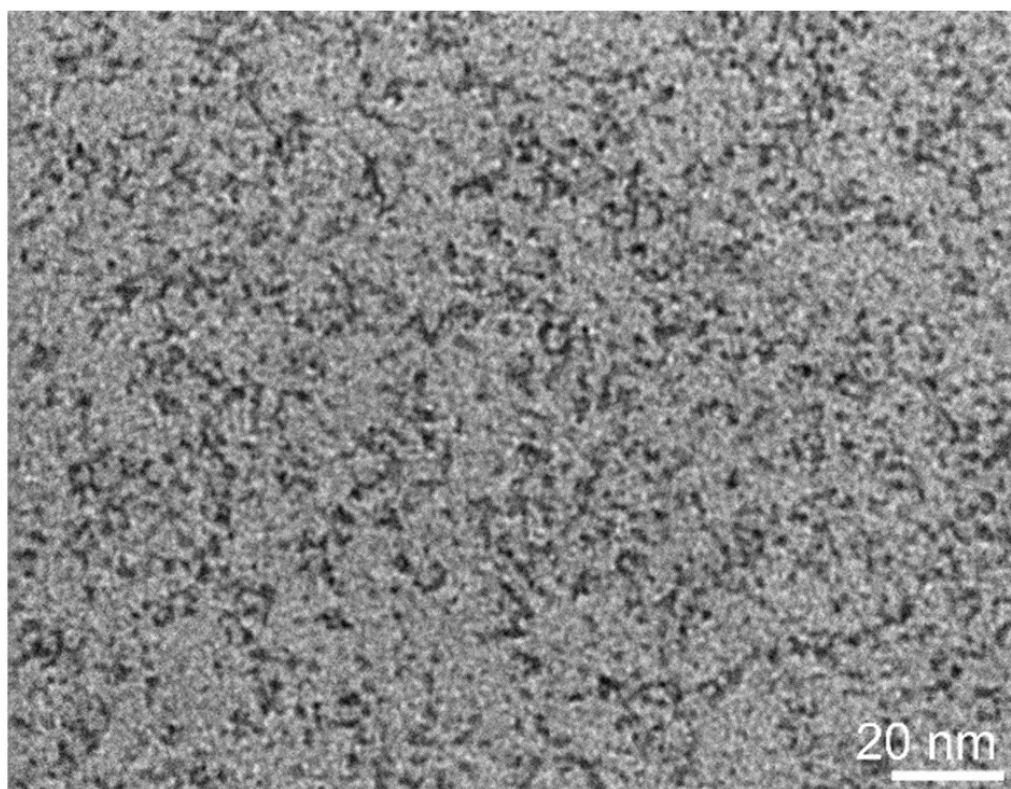


Figure S7 TEM image of [DoMIM]₂[WO₄] in 50 wt.% H₂O₂ at a catalytic concentration of 178 mmol/L.

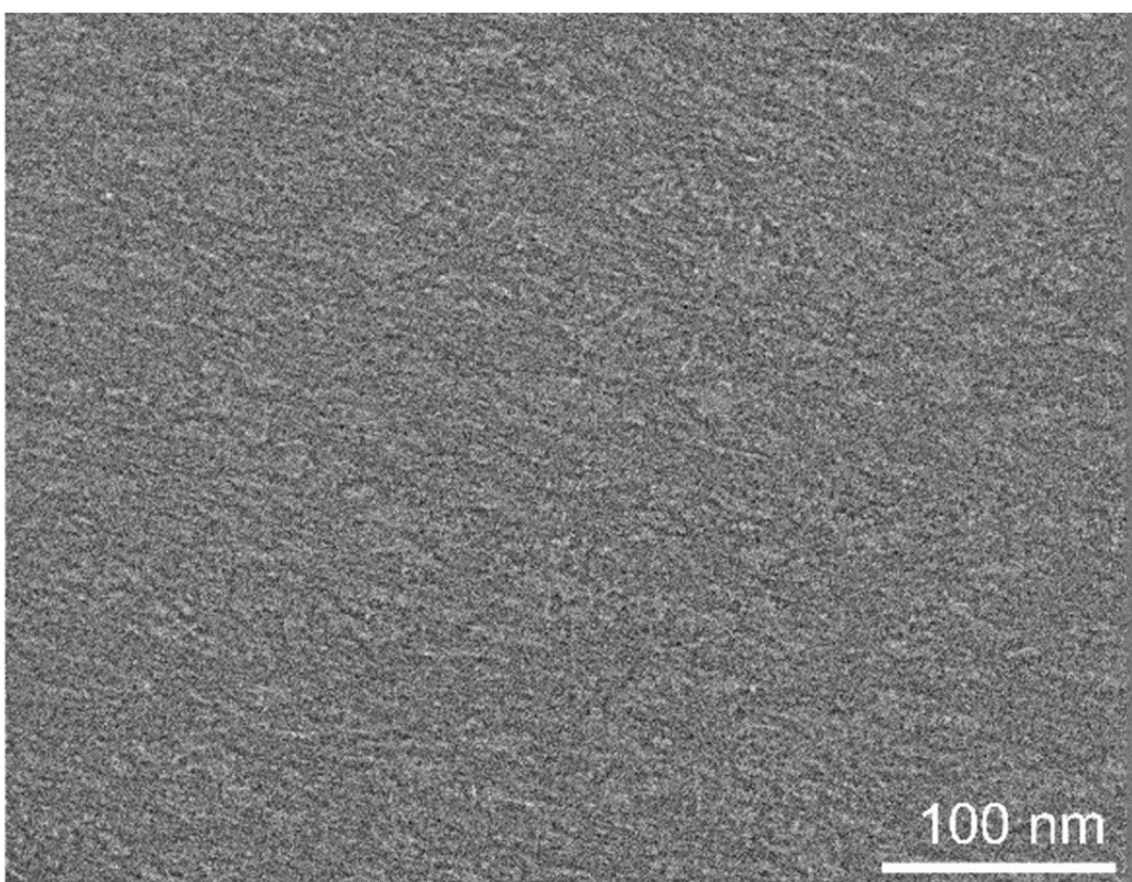
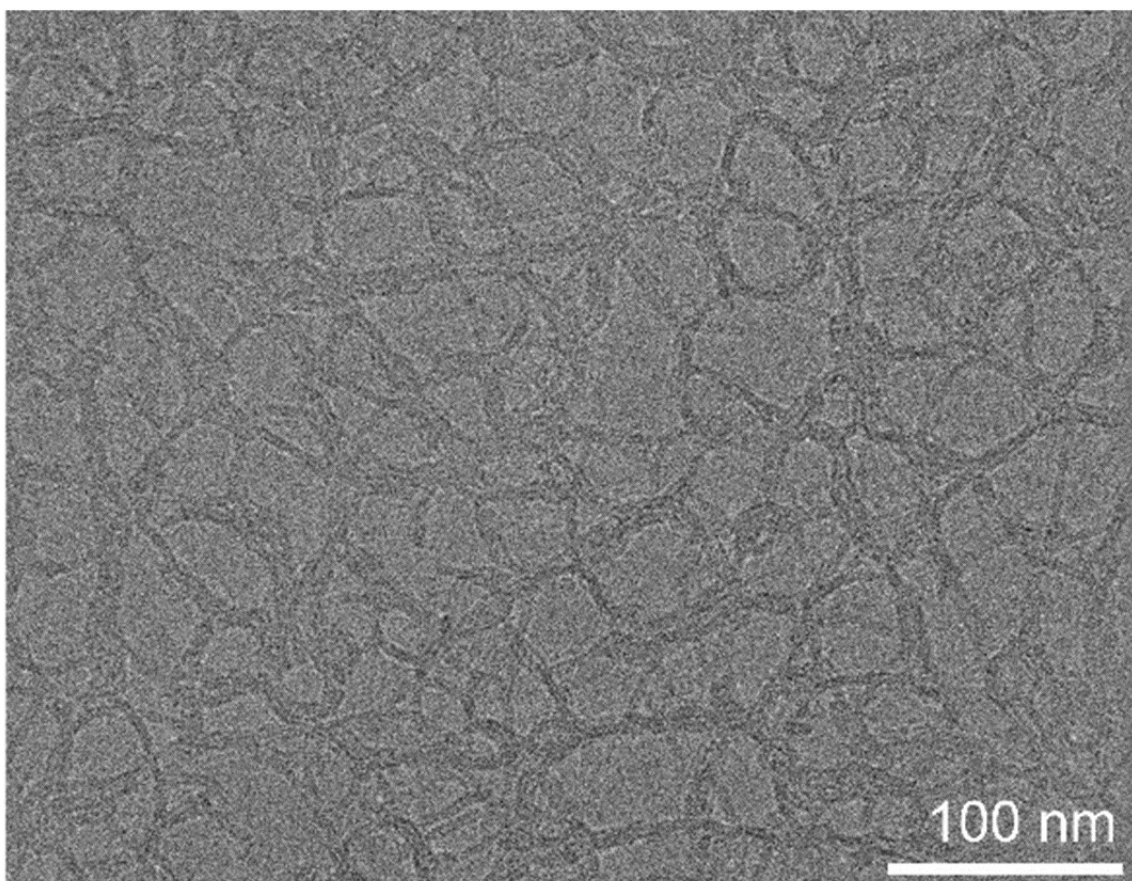


Figure S8 cryo-TEM images of $[\text{DoMIM}]_2[\text{WO}_4]$ in 50 wt.% H_2O_2 at a catalytic concentration of 178 mmol/L prepared at 50 °C (top) and an analogous sample that was treated with palm oil (bottom).

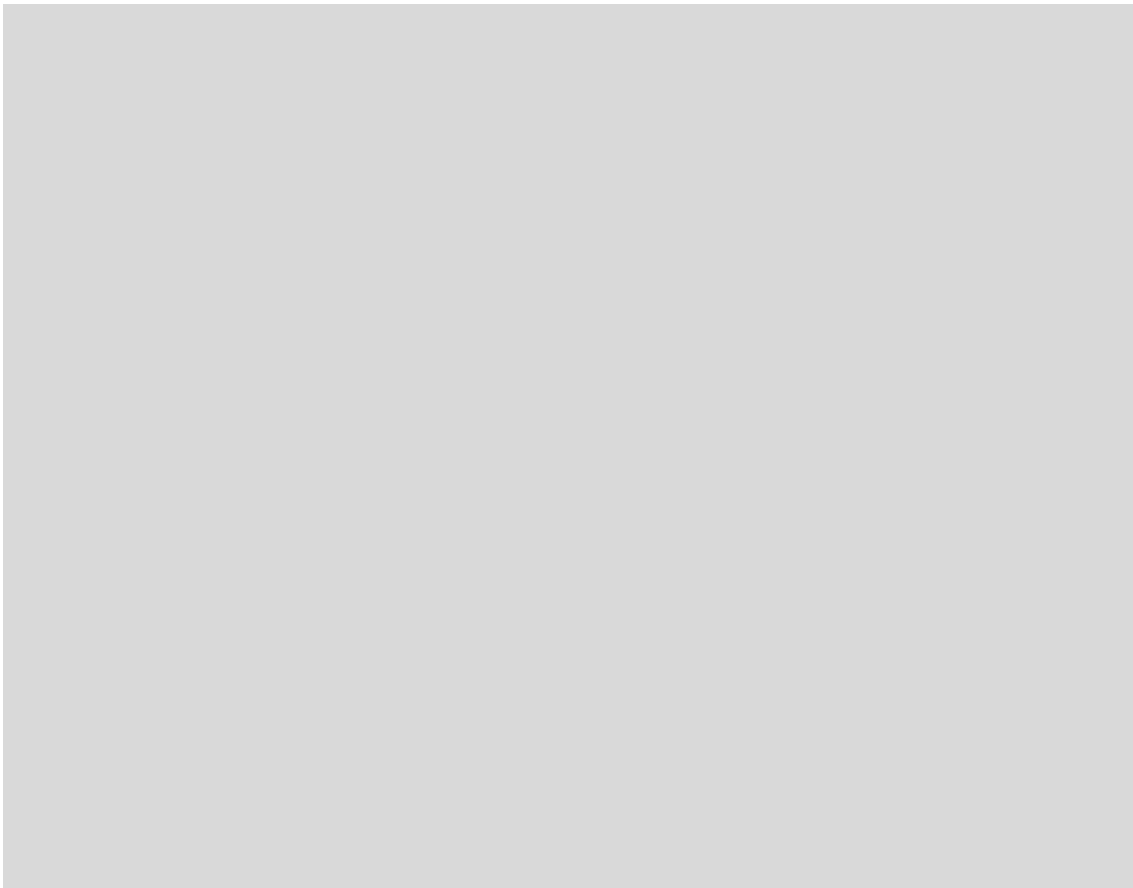


Figure S9 cryo-TEM image of $[\text{OMIM}]_2[\text{WO}_4]$ in 50 wt.% H_2O_2 at a catalytic conc. of 178 mmol/L prepared at 50 °C.

2.4. Nuclear magnetic resonance

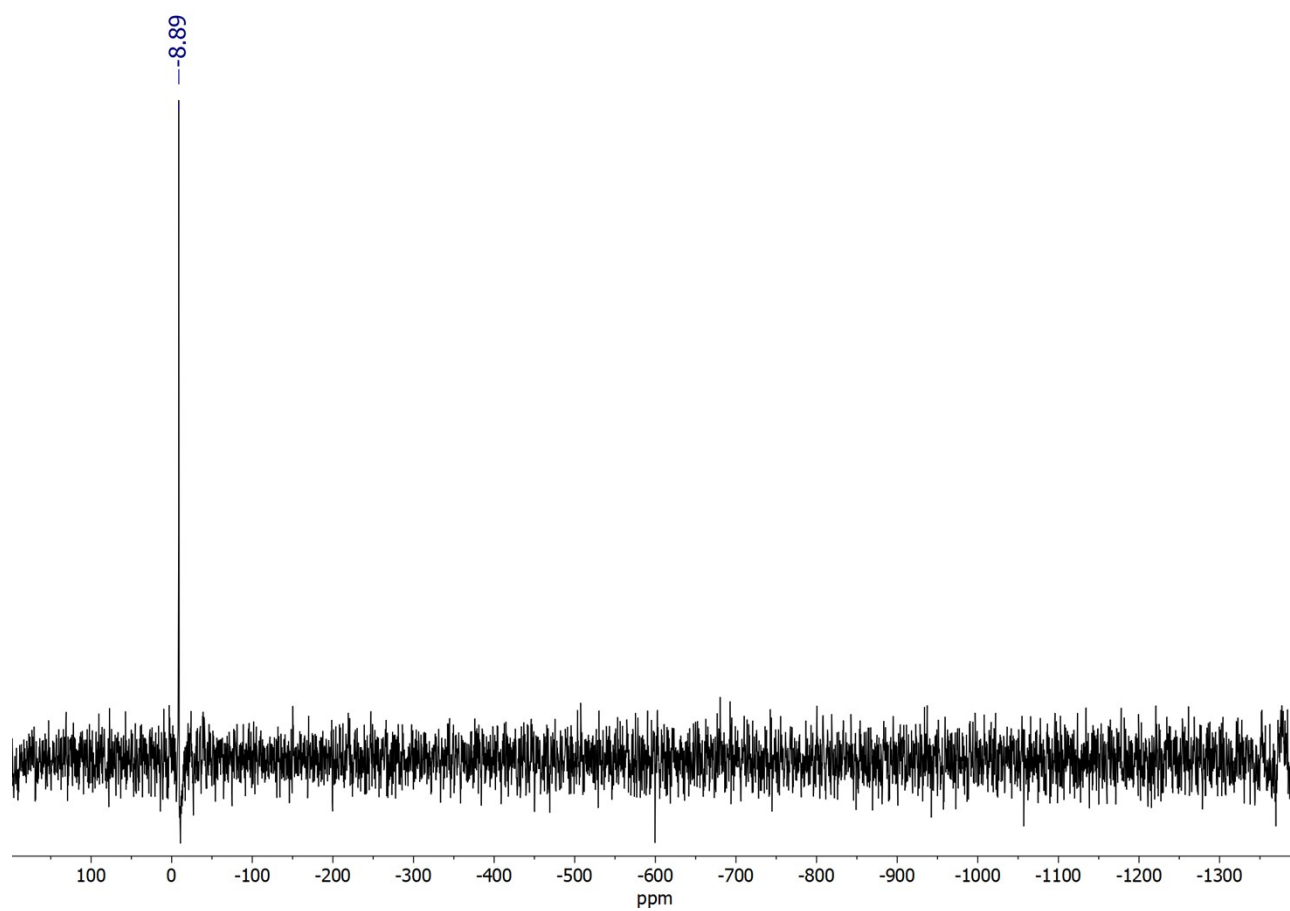


Figure S10 ^{183}W -NMR spectrum of a 1 M solution of $[\text{DoMIM}]_2[\text{WO}_4]$ in D_2O .

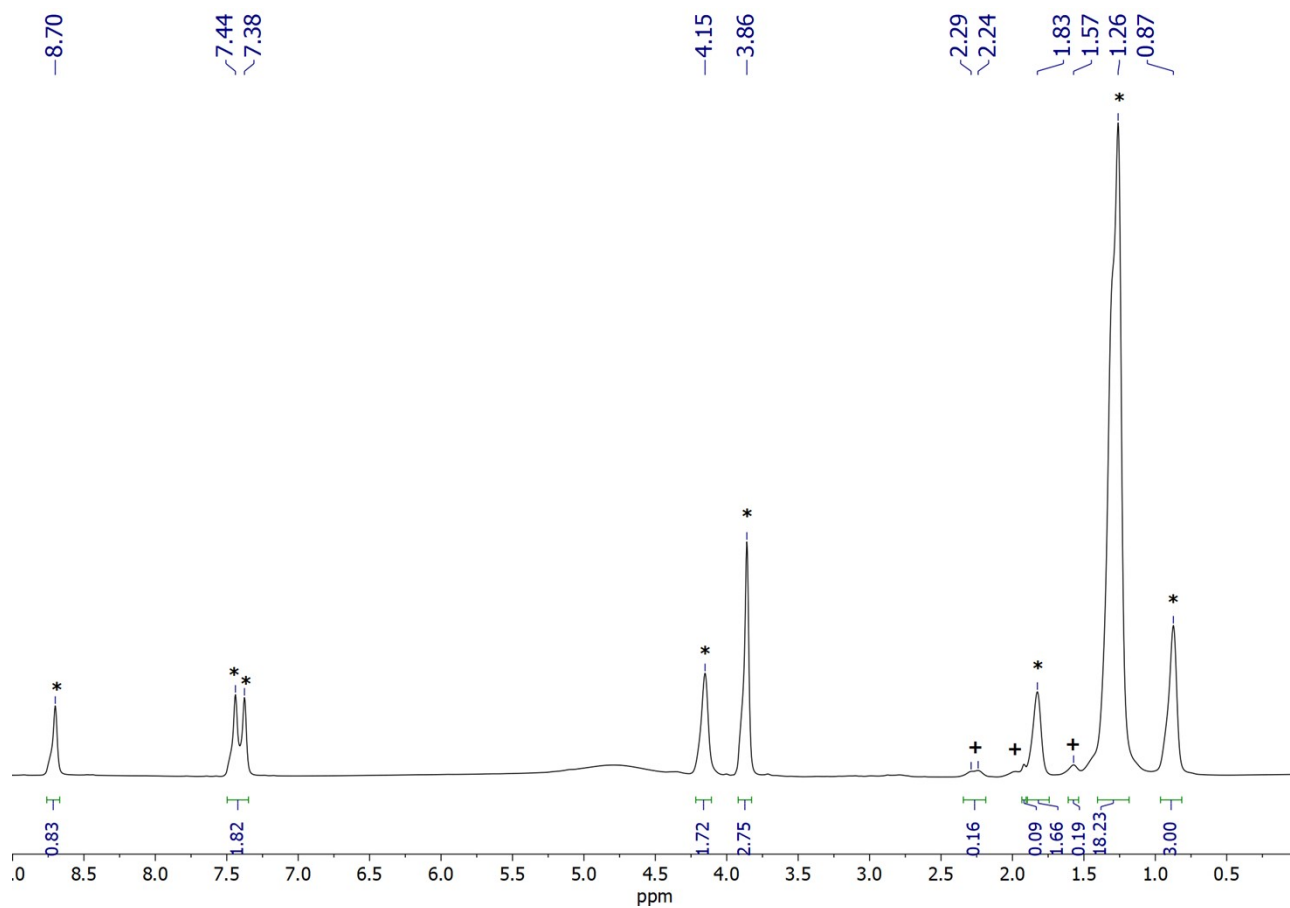


Figure S11 $^1\text{H-NMR}$ spectra of an aliquot of the aqueous phase of 2.5 mol% $[\text{DoMIM}]_2[\text{WO}_4]$ in 1.4 mL H_2O_2 (25 mmol) and 4.8 mL palm oil (4.5 mmol = 10 mmol double bonds) in D_2O . Note that the spectra was measured at water suppression mode. The signals attributed to the catalyst and palm oil are marked with * and +, respectively.

Palm oil signals in the range of 4.3–5.4 ppm are not integrable due to the water suppression mode and aliphatic resonances of the palm oil overlap with those of the catalyst. Therefore, the calculation was performed with the methyl group at 0.86 ppm from the catalyst and a CH_2 group of the substrate at 1.57 ppm.

3. Epoxidation Catalysis

3.1. EVO detection by $^1\text{H-NMR}$ spectroscopy

It has to be noted that a quantitative $^1\text{H-NMR}$ analysis of the vegetable oils and their epoxidation product is not possible due to the complex organic matrices; the integrals of the olefin and epoxide protons do not directly correlate and resonances of different functional groups overlap. The signals of the respective functional groups were assigned according to a literature report and indicated by color in the spectra.^{S2} Note that vegetable oils are natural products that contain various triglycerides with different chainlengths and a different constitution of unsaturated fatty acids. The structural representation used in the spectra is one possible unsaturated fatty acid derivative (R^1 and R^2 vary across the different samples) that is used for the assignment of the functional groups contained in every (E)VO.

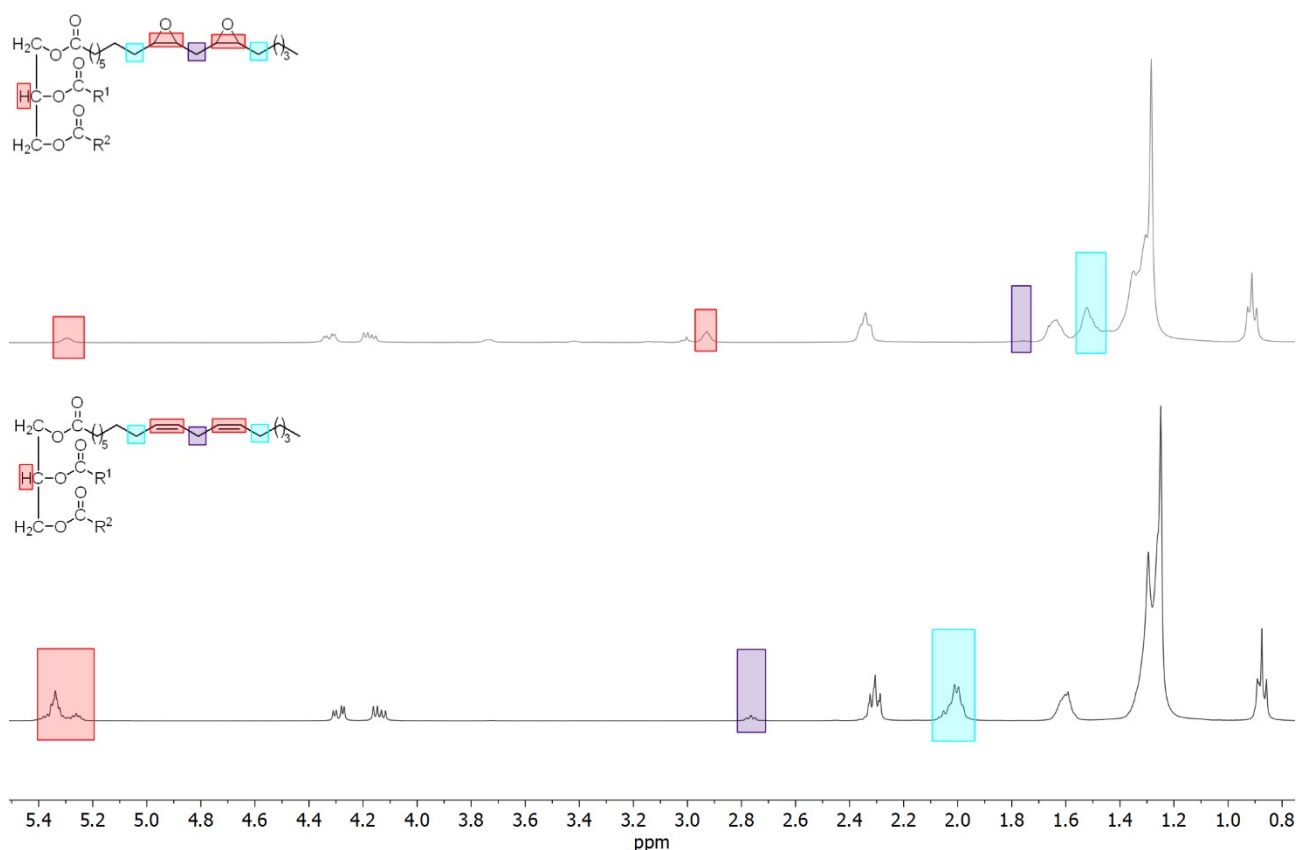


Figure S12 $^1\text{H-NMR}$ spectra of palm oil (bottom) and epoxidized palm oil (top).

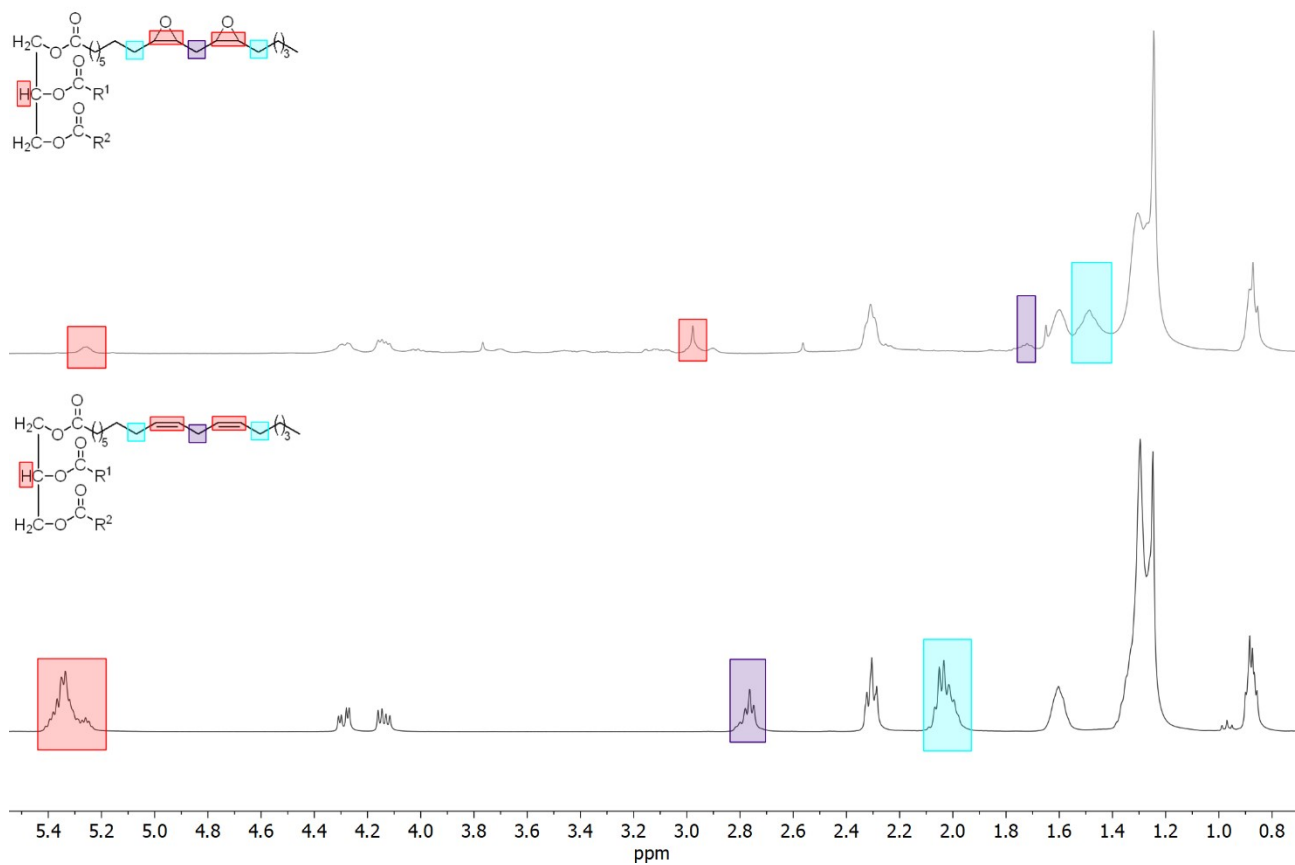


Figure S13 ¹H-NMR spectra of soybean oil (bottom) and epoxidized soybean oil (top).

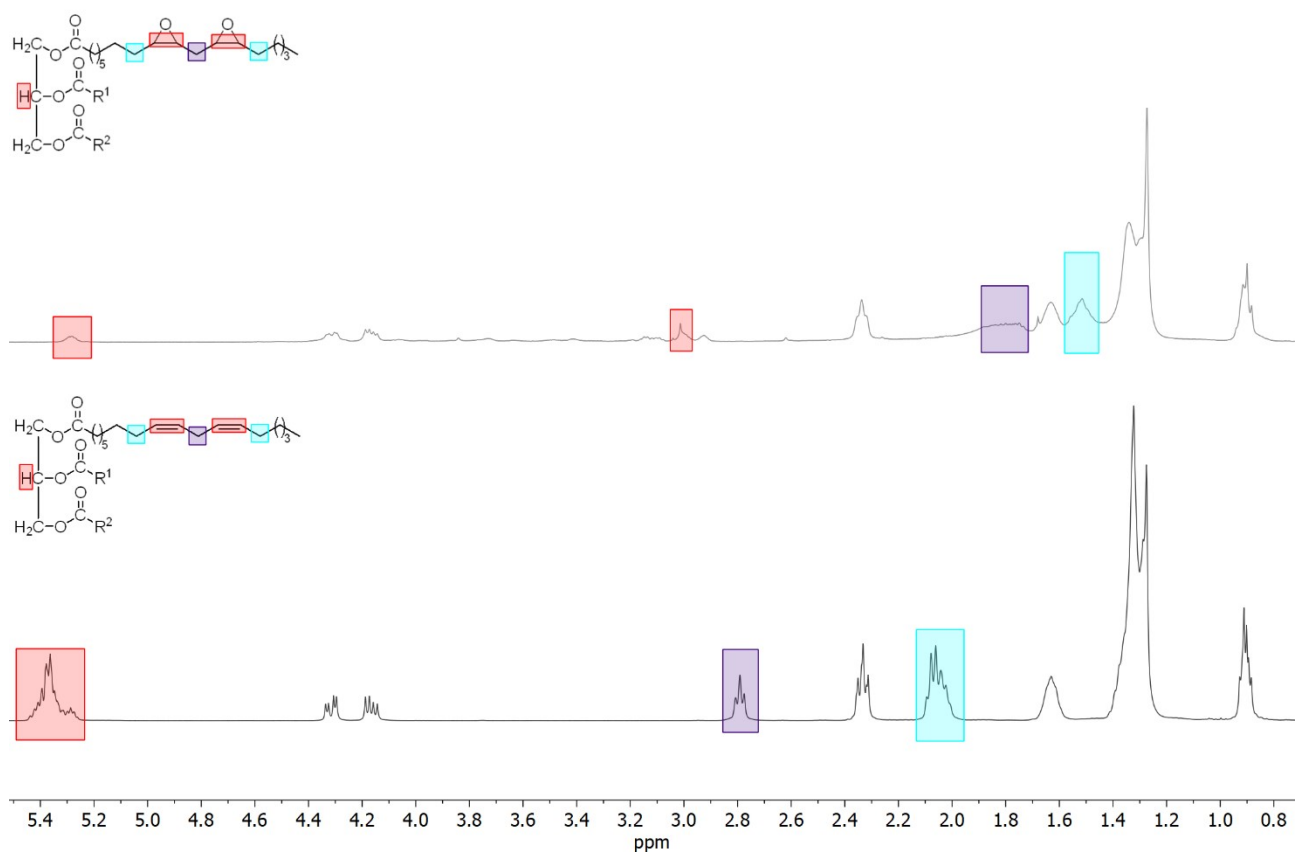


Figure S14 $^1\text{H-NMR}$ spectra of corn oil (bottom) and epoxidized corn oil (top).

3.2. EVO detection by IR spectroscopy

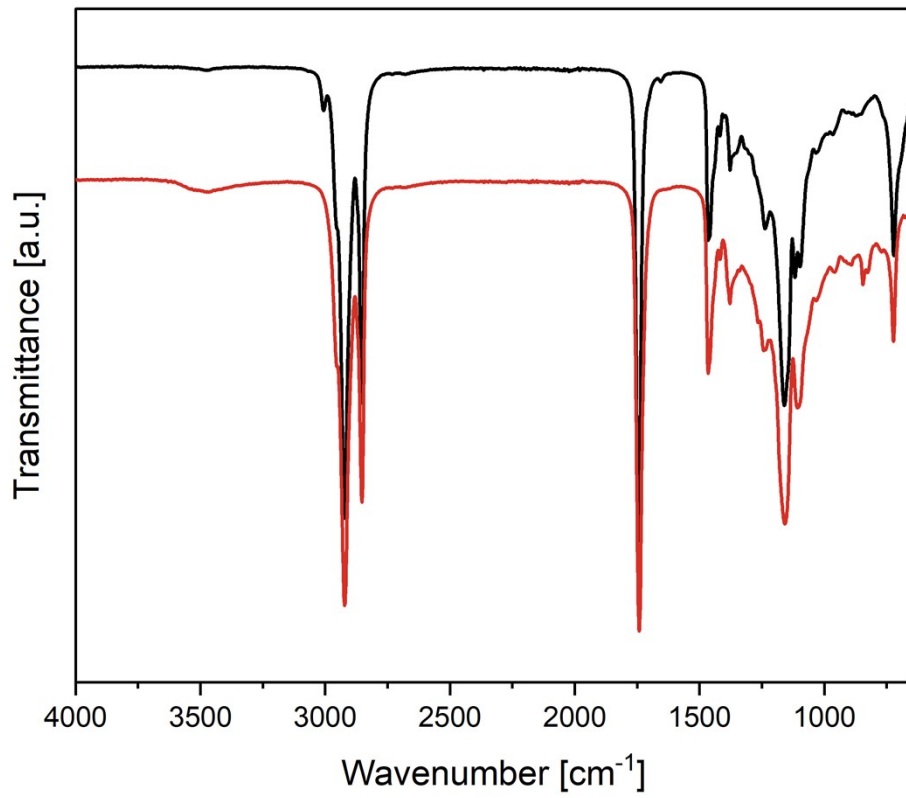


Figure S15 IR spectra of palm oil (black) and epoxidized palm oil (red).

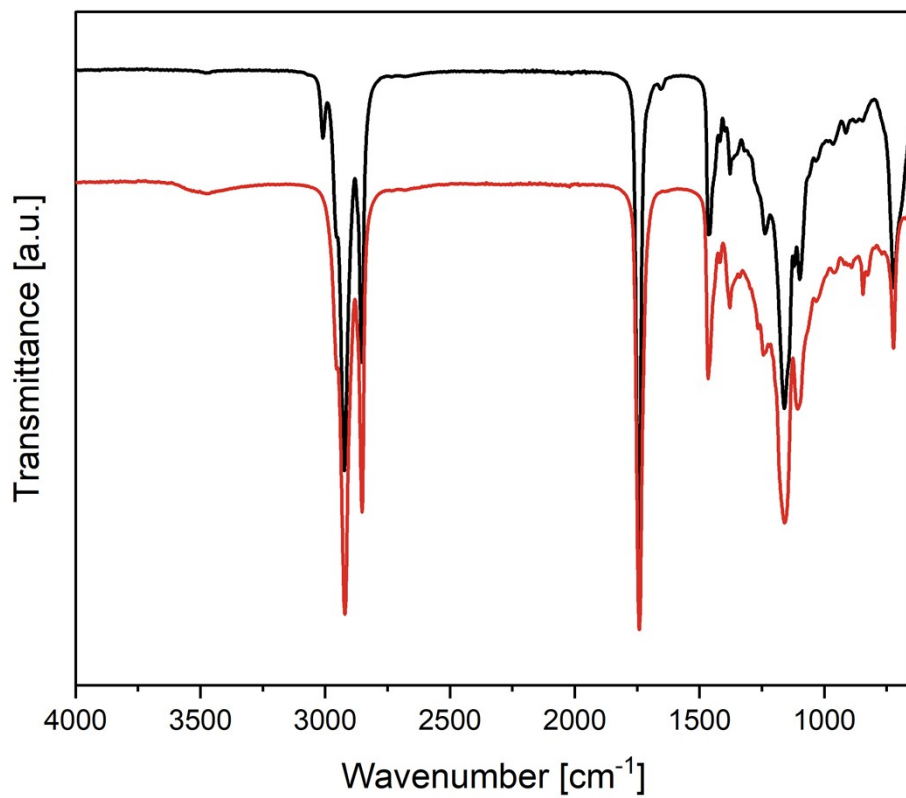


Figure S16 IR spectra of corn oil (black) and epoxidized corn oil (red).

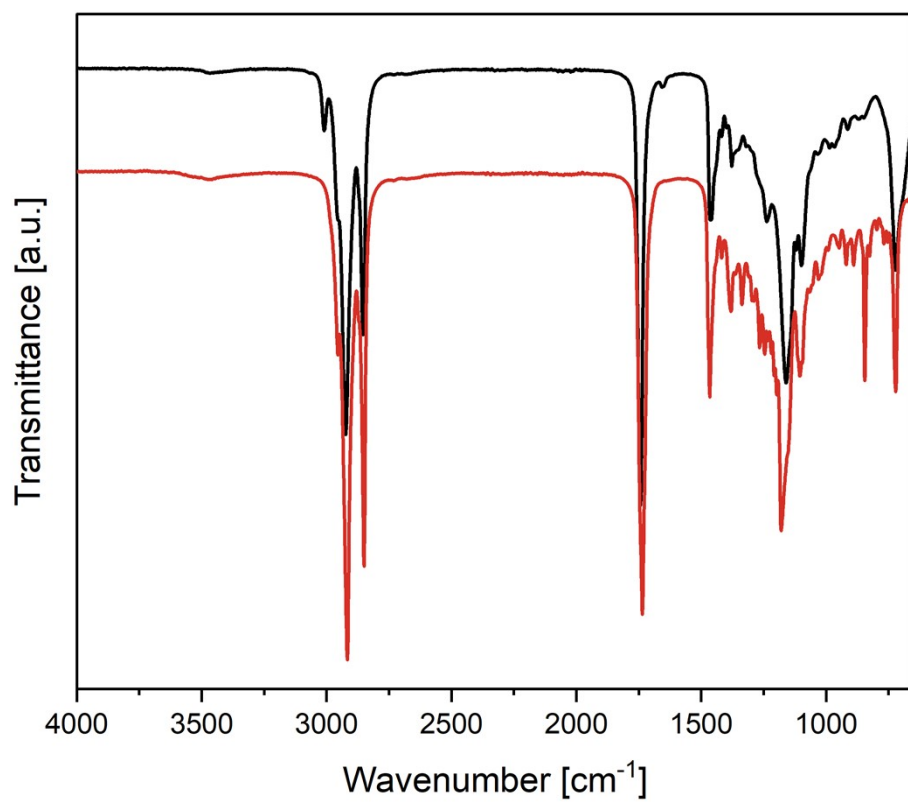


Figure S17 IR spectra of soybean oil (black) and epoxidized soybean oil (red).

3.3. Kinetic data

Note that the error of the selectivities is only calculated for conversions >30%. The value of the conversion is required for the selectivity calculation, while low conversions lead to highly overestimated error values.

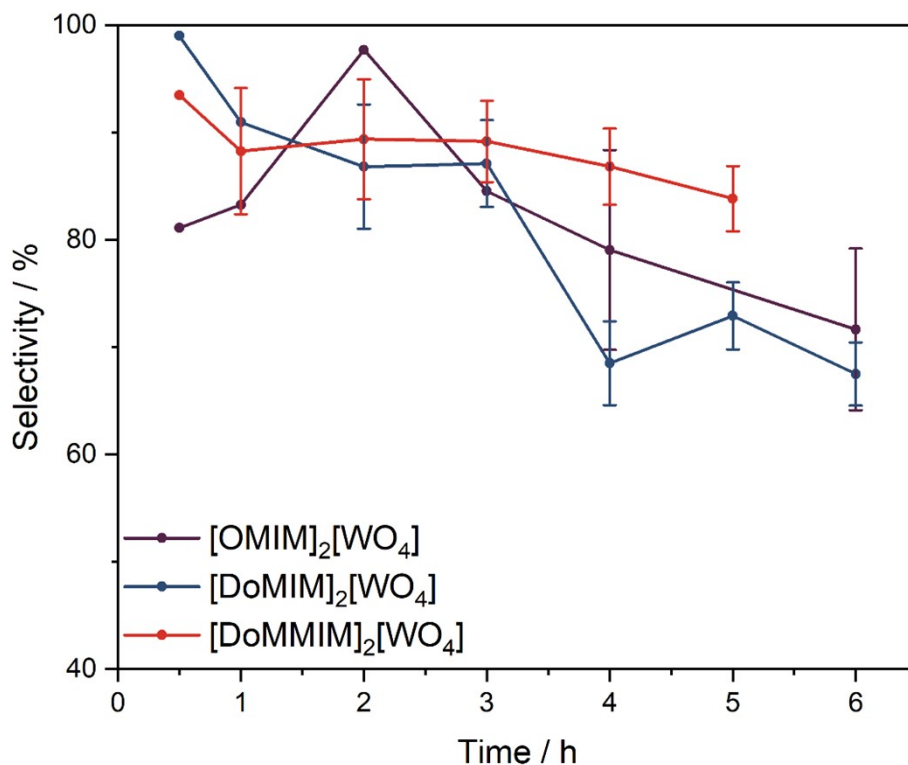


Figure S18 Selectivities of high oleic palm oil in the epoxidation catalysis with imidazolium tungstate SAILs with different alkyl chain lengths. Reaction conditions: 60 °C, 500 rpm, 3.8 mL palm oil (4 mmol, 100 equiv. double bonds), 1.4 mL aq. H₂O₂ solution (50 wt.%, 25 mmol, 250 equiv.), 2.5 mol% SAIL and 5 mol% PPA.

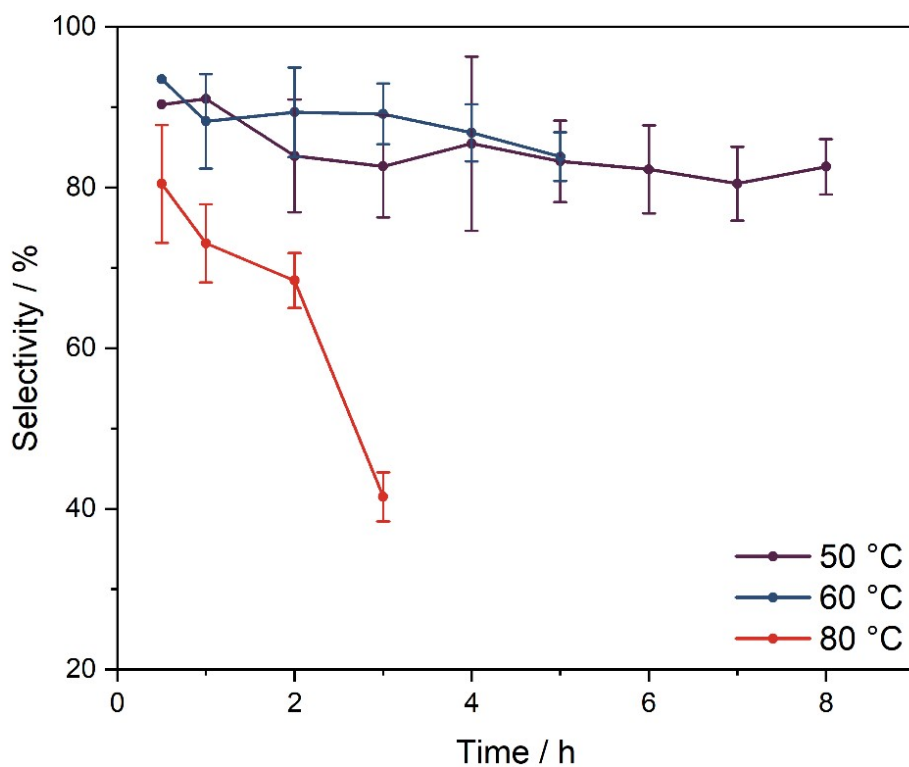


Figure S19 Selectivities of high oleic palm oil in the epoxidation catalysis with $[\text{DoMMIM}]_2[\text{WO}_4]$ at different temperatures. Reaction conditions: 500 rpm, 3.8 mL palm oil (4 mmol, 100 equiv. double bonds), 1.4 mL aq. H_2O_2 solution (50 wt.%, 25 mmol, 250 equiv.), 2.5 mol% SAIL and 5 mol% PPA.

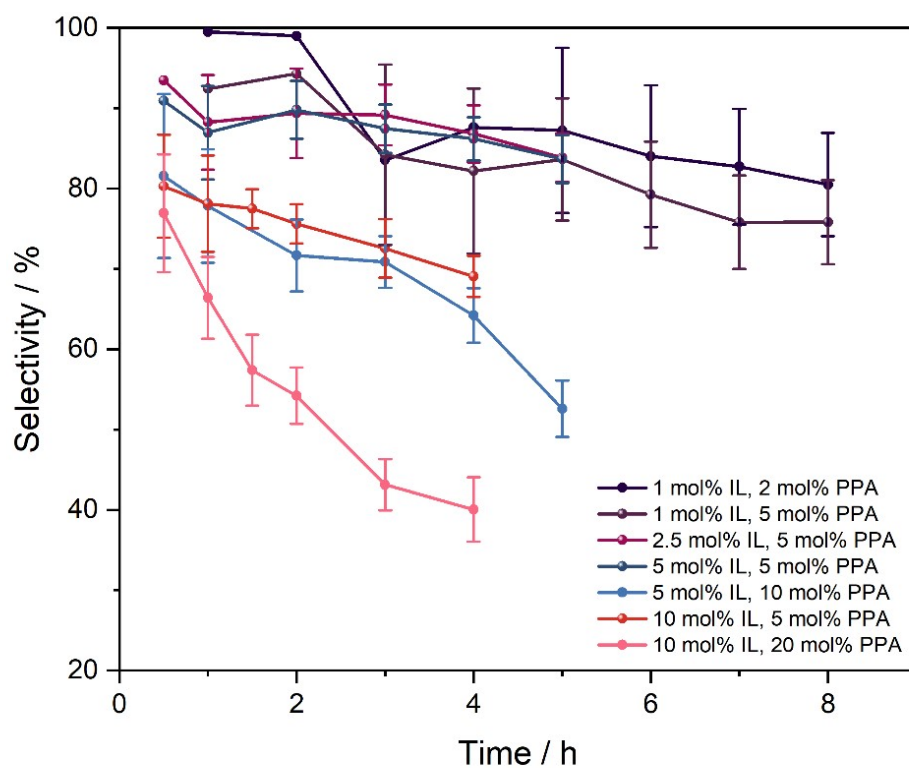


Figure S20 Selectivities of high oleic palm oil in the epoxidation catalysis with different $[\text{DoMMIM}]_2[\text{WO}_4]$ loadings and different PPA ratios. Reaction conditions: 500 rpm, 3.8 mL palm oil (4 mmol, 100 equiv. double bonds), 1.4 mL aq. H_2O_2 solution (50 wt.%, 25 mmol, 250 equiv.).

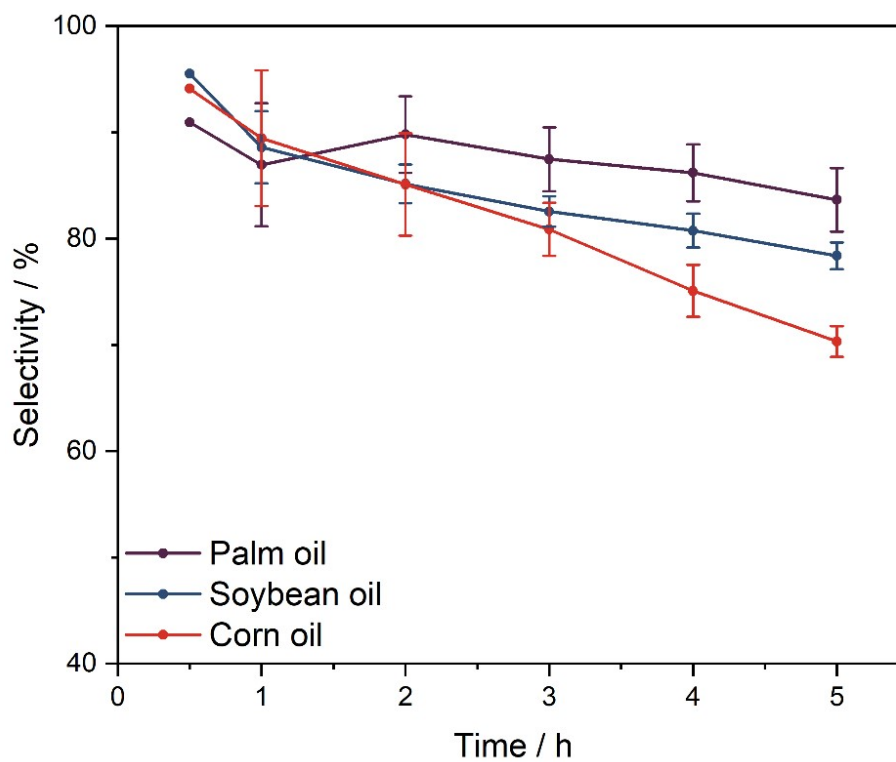


Figure S21 Selectivities of different vegetable oils in the epoxidation catalysis with [DoMMIM]₂[WO₄]. Reaction conditions: 62 °C, 500 rpm, 3.8 mL palm oil (4 mmol, 100 equiv. double bonds) / 2.3 mL soybean oil (2.22 mmol, 100 equiv. double bonds) / 3.0 mL corn oil (2.86 mmol, 100 equiv. double bonds), 1.4 mL aq. H₂O₂ solution (50 wt.%, 25 mmol, 250 equiv.), 5 mol% SAIL and 5 mol% PPA.

3.4. Determination of the activation energy

The activation energy of the epoxidation of high oleic palm oil with [DoMMIM]₂[WO₄] was determined by an Arrhenius plot of the initial reaction rates at different temperatures (50, 60 and 80 °C).

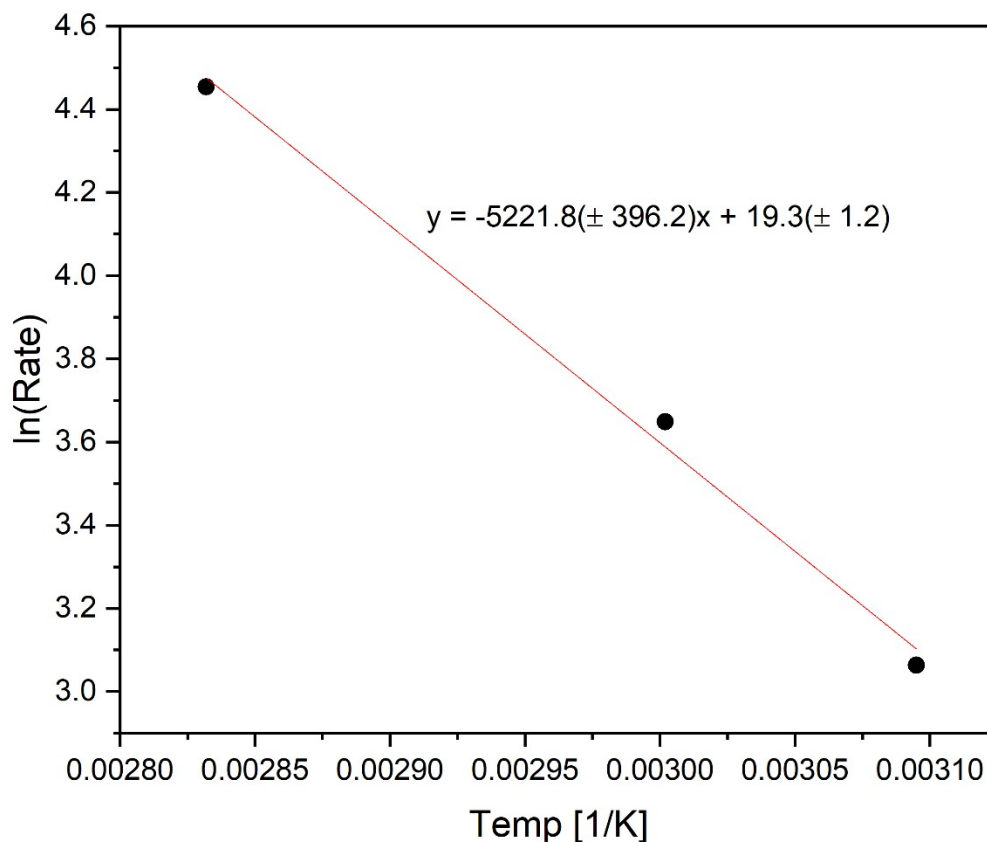


Figure S22 Arrhenius plot for the epoxidation of high palm oil with [DoMMIM]₂[WO₄].

The activation energy of the epoxidation is calculated by the multiplication of the slope of the Arrhenius plot with the ideal gas constant R (8.314 J/mol·K), resulting in an activation energy of 43.4±3.3 kJ/mol.

4. References

- S1 F. Schmidt, B. Zehner, W. Korth, A. Jess and M. Cokoja, *Catal. Sci. Technol.*, 2020, **10**, 4448–4457.
- S2 M. Farias, M. Martinelli and D. P. Bottega, *Appl. Catal., A*, 2010, **384**, 213–219.