Supplementary Information

Sustainable Electro-organic Synthesis of Dicarboxylic Acids from Biogenic Shellac

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1 General information

1.1 General information

All employed chemicals are of analytical grade, were purchased from commercial suppliers and were used as received unless stated otherwise. 20% H_2SO_4 and 1 M KOH solutions were prepared by dilution of 98% H_2SO_4 and dissolving 56.1 g KOH in 1 L of distilled water. A 0.1 M sodium meta-periodate solution was obtained by dissolving 2.139 g sodium meta-periodate (Sigma-Aldrich) in water and dilute it to 100 mL using a volumetric flask. The flask was wrapped in aluminium foil and stored under argon atmosphere. 0.1 M sodium thiosulfate solution was obtained by dissolving 24.8 g sodium thiosulfate pentahydrate (Sigma Aldrich) in water and dilute it to 1 L using a volumetric flask. A 1 wt% starch solution was obtained by boiling 100 mg soluble starch (Sigma Aldrich) in 10 mL distilled water for 10 min and cooling it down. Dewaxed bleached shellac was provided by A.F. Suter, United Kingdom. Electrodes were obtained from commercial suppliers: Stainless-steel VA1.4571 electrode, and nickel foam RCM-Ni4753.03 (Recemat™, Dodewaard, Netherlands) with an average pore size of 0.40 mm.

1.2 Instruments and analytical methods

Gas chromatography (GC)

Analysis of crude reaction mixtures and purified products were performed using a GC-2030 (*Shimadzu*, Kyoto, Japan) equipped with a flame ionization detector (FID) and a quartz capillary column HI-5MS (*Avantor VWR*, Radnor, USA) with following specification: length of 30 m, inner diameter of 0.25 mm and a stationary phase ((5%-phenyl)dimethylsiloxane) of 0.25 µm thickness. Hydrogen was used as carrier gas with a constant velocity of 40 cm/s. Measurements were performed at an injector temperature of 270 °C and a detector temperature of 320 °C, starting at 50 °C (holding for 1 min) and heating to 300 °C (holding for 4.71 min) with a temperature ramp of 17.5 °C/min.

Nuclear magnetic resonance (NMR) spectroscopy

^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded at 25 °C on a Bruker AVANCE II 400 MHz spectrometer equipped with a Prodigy probe (Bruker BioSpin GmbH, Rheinstetten, Germany) using $CDCl_3$ as the deuterated solvent. Chemical shifts (δ) are reported in parts per million (ppm) relative to the residual solvent peaks, which served as internal standards. Data are given as δ (multiplicity, coupling constant J in Hz, number of protons). Spectra were processed and analyzed using MestReNova 14 (Mestrelab Research S.L., Spain).

1.3 Electrochemical setup

Galvanostat

Electrochemical reactions were carried out using a multichannel galvanostat HMP4040 (*Rohde & Schwarz*, München, Germany). The cells used for screening or large-scale batch reactions are described below.

Screening and small-scale batch reactions

Screening reactions were carried out in undivided glass cells with a volume of 25 mL equipped with a cooling jacket, two electrodes (interelectrode gap: 12 mm) and a cross-shaped stirring bar (Figure S1). The described system is commercially available as SynLectro™ Jacketed Glass Cell (Merck S.A, an affiliate of Merck KGaA, Darmstadt, Germany). The electrosynthesis of pimelic and azelaic acid was performed in a batch cell set-up. A stainless-steel VA1.4571 electrode (A= 2 cm x 6 cm x 0.3 cm, Caravaggio, Italy) was used as a cathode. The anode consisted of nickel foam RCM-Ni4753.03 (A= 2 cm x 6 cm x 0.3 cm, pore size Ø 0.4 mm, Recemat™, Dodewaard, Netherlands). The temperature of the cell is controlled with a cryostat using water as cooling media (RC6 cryostat, Lauda, Lauda-Königshofen, Germany). The temperature was constantly monitored using a DS18B20 temperature sensor with a USB-connected cortex-M microcontroller (Diamex Produktion und Handel GmbH, Heidelberg, Germany). The applied current of the electrolysis was controlled using a HMP4040 galvanostat (Rohde & Schwarz, München, Germany) in constant current mode as a power source. The electrolysis can be controlled remotely via an open-source python-based user interface (https://github.com/marcodyga/power_supply_gui).

Figure S1 Undivided glass cells with a volume of 25 mL equipped with a cooling jacket available as SynLectro™ 25mL (Merck S.A, an affiliate of Merck KGaA, Darmstadt, Germany), two electrodes (interelectrode gap: 12 mm) and a cross-shaped stirring bar. [1] Cathode material consists of a stainless-steel VA1.4571 electrode and a nickel foam RCM-Ni4753.03 anode (Recemat™, Dodewaard, Netherlands).

Big-scale batch reactions

The scale-up experiments were performed in a jacketed undivided glass cell with a volume of 100 mL equipped with a PTFE stopper and sleeve, electrodes (interelectrode gap: 12 mm), electrode holders and a cross-shaped stirring bar (Figure S2a) as well as a non-jacketed undivided glass cell with a volume of 250 mL (Figure S2b). The described system is commercially available as SynLectro™ 100mL (Merck S.A, an affiliate of Merck KGaA, Darmstadt, Germany). The electrosynthesis of pimelic and azelaic acid was performed in a batch cell set-up. A stainless-steel VA1.4571 electrode (A= 3 cm x 7 cm x 0.3 cm) was used as a cathode for the 100 mL glass cell while the dimensions of the stainless-steel VA1.4571 electrode for the 250 mL glass cell was A= 4 cm x 9 cm x 0.3 cm. The anode consisted of nickel foam RCM-Ni4753.03 (A= 3 cm x 7 cm x 0.3 cm, pore size Ø 0.4 mm, Recemat™, Dodewaard, Netherlands) for the 100 mL glass cell while the dimensions of the for the nickel foam RCM-Ni4753.03 electrode used for the 250 mL glass cell was A= 4 cm x 9 cm x 0.3 cm.

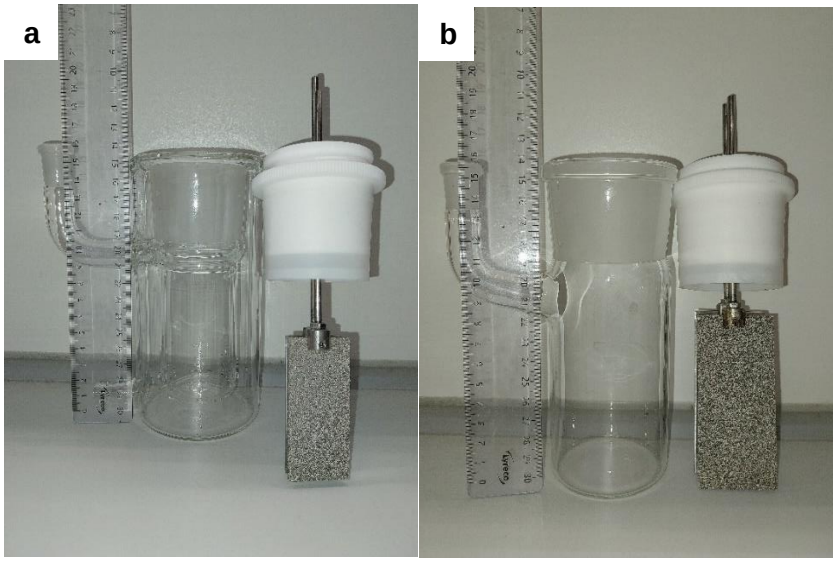


Figure S2 a. jacketed undivided glass cell with a volume of 100 mL, b. non-jacketed undivided glass cell with a volume of 250 mL. Cathode material consists of a stainless-steel VA1.4571 electrode and a nickel foam RCM-Ni4753.03 anode (Recemat™, Dodewaard, Netherlands).

2 General experimental procedures

2.1 Aleuritic acid content estimation

10 mL ethanol and 5 mL of a 20% (v/v) H_2SO_4 solution were transferred into an Erlenmeyer flask equipped with a magnetic stirrer. To the flask was added 4 mL of the hydrolyzed shellac solution

and the flask was cooled to 0 °C. 5 mL of a 0.1 M sodium meta-periodate solution in water was added and the Erlenmeyer was protected from light and stirred at room temperature for one hour. At the same time, a blank was prepared in the same way as stated above, however, with 4 mL of a 1 M KOH solution instead of a hydrolyzed shellac solution. Afterward, 5 mL of a saturated potassium iodide solution was added to the shellac sample and the blank and both solutions were titrated with 0.1 M sodium thiosulfate in water. Three drops of a starch solution were added near the endpoint as an indicator. The aleuritic acid **1** concentration was calculated according to formula (*5*):

$$\mathbf{1}_{(aq)} + IO_{4\,(aq)}^{-} \rightarrow aldehydes + IO_{3\,(aq)}^{-} \quad (1)$$

$$IO_{4(aq)}^{-} + 7I_{(aq)}^{-} + 8H^{+} \rightarrow 4I_{2(aq)} + 4H_2O_{(l)} \quad (2)$$

$$IO_{3(aq)}^{-} + 5I_{(aq)}^{-} + 6H^{+} \rightarrow 3I_{2(aq)} + 3H_2O_{(l)} \quad (3)$$

$$I_{2(aq)} + 2S_2O_{3(aq)}^{2-} \rightarrow 2I_{(aq)}^{-} + S_4O_{6(aq)}^{2-} \quad (4)$$

$$n(\mathbf{1}) = \frac{[V_{titration}(blank) - V_{titration}(sample)] \times C_{S_2O_3^{2-}}}{2} \quad (5)$$

The titration was performed five times on shellac and on 100 mg of aleuritic acid and the results are summarized in Table S1 and Table S2.

1	**ΔV [mL]**	**n(1) [mmol]**
1	6.4	0.325
2	6.7	0.335
3	6.9	0.345
4	6.7	0.335
5	6.9	0.345
AVG	6.7	0.337

Table S1 Titration of periodate after reaction with aleuritic acid.

Shellac	**ΔV [mL]**	**n(1) [mmol]**
1	4.2	0.210
2	4.6	0.230
3	4.8	0.240
4	4.7	0.235
5	5.0	0.250
AVG	4.6	0.232

Table S2 Titration of periodate after reaction with hydrolysed shellac

Out of the titration results, it was found that the **1** content in 100 mg aleuritic acid was 103±3% which is slightly higher, presumably due to some side reactions of periodate. The concentration of **1** in shellac was determined to be 35±2 wt%.

2.2 Calibration curve

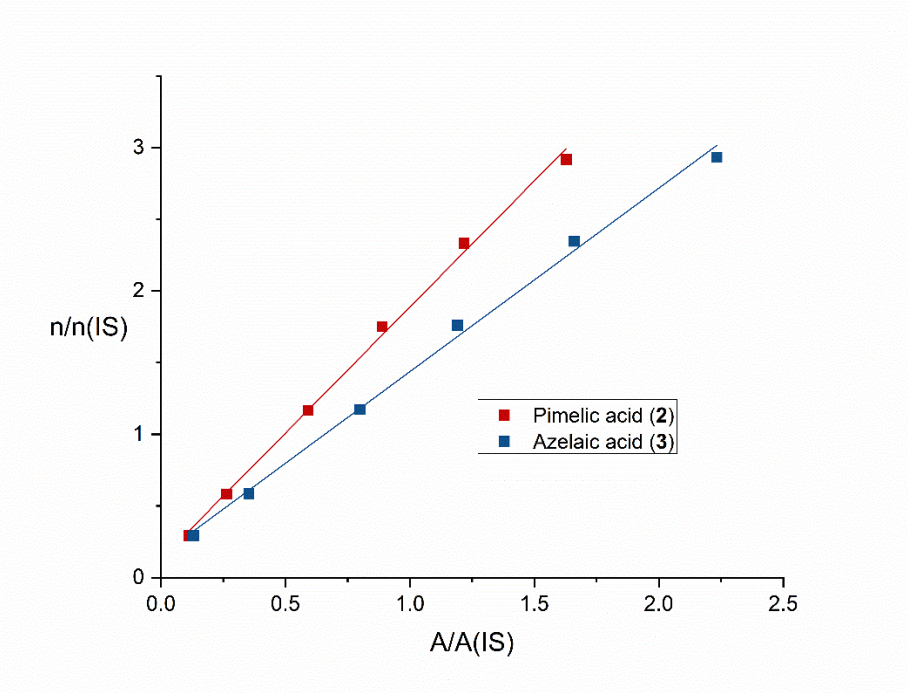
The evaluation of the GC yields was achieved by external calibration with dodecane as internal standard. Stock solutions of dodecane (IS), pimelic acid (**2**) and azelaic acid (**3**) were prepared in dry methanol (Table S3). Different quantities of the stock solutions were transferred to GC vials (Table S4) together with 0.75 mL dry toluene. Dry methanol was added to obtain a total volume of 1 mL (toluene:methanol 3:1). 0.1 mL trimethylsilyldiazomethane solution (2.0 M in hexanes) was added to each vial. After shaking for 30 min, 1 drop of acetic acid was added to the vials to quench the excess of trimethylsilyldiazomethane. Each vial was measured for each substance and the value of the peak areas A from these runs were used as a calibration point. Control points with samples prepared from dimethyl pimelate and dimethyl azelate confirmed that the esterification method is quantitative.

	$m_{measured}$ [mg]	V [mL]	C (mM)
Pimelic acid	238.7	25	59.6
Azelaic acid	282.0	25	59.9
Dodecane	171.1	10	100.4

Table S3 Concentration stock solutions

	Dodecane [µL]	Pimelic acid [µL]	Azelaic acid [µL]
1	50	25	25
2	50	50	50
3	50	100	100
4	50	150	150
5	50	200	200
6	50	250	250

Table S4 Quantities of stock solutions transferred into a GC vial



■ Pimelic acid (**2**) ■ Azelaic acid (**3**)

Equation	y = a + b*x
Intercept	0.12901 ± 0.04418
Slope	1.7594 ± 0.04678
R-Square (COD)	0.99718

Equation	y = a + b*x
Intercept	0.15703 ± 0.04909
Slope	1.28008 ± 0.03814
R-Square (COD)	0.99646

Figure S3 GC-FID calibration curve for the corresponding esters of **2** and **3**

2.3 General shellac hydrolysis protocol

5 wt% Shellac solutions were prepared by weighing 20 g shellac (SSB Stroever Schellac Bremen, Bremen, Germany) into a 500 mL round-bottom flask equipped with a magnetic stirrer and a reflux condenser. 400 mL 1 M KOH was added and the reaction was stirred at 60 °C for 48 h. Hydrolyzed shellac solutions were stored in the fridge prior to use.

2.4 General protocol for nickel activation to Ni(O)OH

Nickel foam, was cut into electrodes fitting the previously stated dimensions (2x6 cm for the screening reactions) with the anodes being pretreated by soaking the planar anode in 1 M NaOH followed by immersing it into the activation solution. Nickel activation towards Ni(O)OH was performed by reacting 0.1 M nickel(II) sulphate hexahydrate with 0.1 M sodium acetate trihydrate

and 5 mM NaOH to make up the activation solution. The nickel activation procedure required taking 25 mL of the activation solution and placing it into 25 mL undivided electrolysis glass cells with cooling jacket whilst using stainless-steel VA1.4571 cathode and a nickel foam RCM-Ni4753.03 anode with a geometrical current density of 5 mA/cm^2 and an applied charge of Q = 8 C/cm^2. Afterward, the activated nickel electrode was carefully rinsed with deionized water and immediately used.

2.5 General protocol for the oxidative degradation of shellac

In a glass cell equipped with a magnetic stirrer was added 25 mL of the hydrolyzed shellac solution. A clean stainless-steel VA1.4571 was used as cathode and a freshly activated nickel foam RCM-Ni4753.03 (prepared according to general protocol 2.4) were placed 3 cm deep in the shellac solution. The electrodes were immediately connected to a multichannel galvanostat HMP4040 (*Rohde & Schwarz*, München, Germany) and the reaction was electrolyzed at a geometrical current density of 5 mA/cm^2 with an applied charge of 2080 C (~19 h), corresponding to 15 *F* relative to the estimated aleuritic acid content. Afterwards, the reaction mixture was transferred into an extraction funnel and acidified with 1 M H_2SO_4. The reaction mixture was extracted 3 times with 50 mL ethyl acetate. The organic phase was washed with brine and dried with Na_2SO_4, filtered followed by solvent removal under reduced pressure at 50 °C.

2.6 Analysis of the dicarboxylic acid yields

After solvent removal, the crude reaction mixture was dissolved in 20 mL toluene and 5 mL dry methanol. 50 µL Dodecane (internal standard) was added using a Hamilton syringe. 0.5 mL of the homogeneous reaction mixture was transferred into a vial and 0.1 mL trimethylsilyldiazomethane solution (2.0 M in hexanes) was added dropwise (***caution, nitrogen is evolving from the reaction mixture***). The vial was gently swirled and left for 30 min. Afterwards, the excess of trimethylsilyldiazomethane was quenched by addition of 1 drop of acetic acid. The reaction mixture was filtered through a glass Pasteur pipette equipped with a cotton plug and silica into a GC vial. The silica plug was rinsed with acetone. Afterwards, the esterified dicarboxylic acids were analysed using GC-FID.

2.7 Optimized protocol for large-scale synthesis

2.7.1 Shellac 5 g scale in 100 mL batch

5 g shellac scale reactions were carried out in a glass cell equipped with a magnetic stirrer (Figure S2a). 100 mL of the hydrolyzed shellac solution was used (general protocol 2.3). A clean

stainless-steel VA1.4571 was used as cathode and a freshly activated nickel foam RCM-Ni4753.03 (prepared according to general protocol 2.4) were placed 5 cm deep in the shellac solution. The electrodes were immediately connected to a multichannel galvanostat HMP4040 (*Rohde & Schwarz*, München, Germany) and the reaction was electrolyzed at 5 mA/cm^2) with an applied charge of 11100 C (~41 h), corresponding to 20 *F* relative to the estimated aleuritic acid content. Afterwards, the reaction mixture was transferred into an extraction funnel and acidified with 1 M H_2SO_4. The reaction mixture was extracted 3 times with 200 mL ethyl acetate. The organic phase was washed with brine and dried with Na_2SO_4, filtered followed by solvent removal under reduced pressure at 50 °C.

2.7.2 Shellac 12.5 g scale in 250 mL batch

12.5 g shellac scale reactions were carried out in a glass cell equipped with a magnetic stirrer (figure S2b). 250 mL of the hydrolyzed shellac solution was used (general protocol 2.3). A clean stainless-steel VA1.4571 was used as cathode and a freshly activated nickel foam RCM-Ni4753.03 (prepared according to general protocol 2.4) were placed 7 cm deep in the shellac solution. The electrodes were immediately connected to a multichannel galvanostat HMP4040 (*Rohde & Schwarz*, München, Germany) and the reaction was electrolyzed at 5 mA/cm^2) with an applied charge of 28000 C (~77 h), corresponding to 20 *F* relative to the estimated aleuritic acid content. Afterwards, the reaction mixture was transferred into an extraction funnel and acidified with 1 M H_2SO_4. The reaction mixture was extracted 3 times with 200 mL ethyl acetate. The organic phase was washed with brine and dried with Na_2SO_4, filtered followed by solvent removal under reduced pressure at 50 °C.

2.8 Isolation

For the isolation of dimethyl pimelate and dimethyl azelate, the reaction was performed on 12.5 hydrolyzed shellac according to protocol 2.7. After extraction and removal of the solvent under reduced pressure, the crude mixture was dissolved in 250 mL methanol containing 2% H_2SO_4. 10 mL 2,2-dimethoxypropane was added as a water scavenger. The reaction was refluxed at 80 °C for 12 h. Afterward, the reaction was concentrated to a volume of 50 mL under reduced pressure at 50 °C. The mixture was diluted with 200 mL diethyl ether and extracted with water, saturated $NaHCO_3$ and brine. The organic layer was dried with Na_2SO_4, filtered and solvent was removed under reduced pressure at 40 °C. Next, dimethyl pimelate and dimethyl azelate were distilled using a fractionated vacuum distillation with an oil pump at 1 mbar. First, the reaction mixture was distilled at 120 °C to remove lower boiling side products. The collection flask was

switched to a cow receiver with three collection flasks and the mixture was further distilled at 160°C. The temperature at the top measured 67 °C for pimelic acid. When the temperature decreased, the cow receiver was turned to the next collection flask. The temperature increased to 72 °C and a fraction 2 was collected. When the temperature increased to 81 °C, three more drops where collected into the second flask before switching to the third collection flask. The reaction was further heated and the top of the Vigreux column was slightly heated with a heat gun to ensure that dimethyl azelate was completely distilled. GC-FID analysis showed that fraction one was dimethyl pimelate with traces of dimethyl suberate and dimethyl azelate ($m_{dimethyl\ pimelate}$ = 813 mg, 33%). Fraction two was a mixture of dimethyl pimelate and dimethyl azelate as well as dimethyl suberate. This fraction was not included in the isolated yield. The last fraction contained pure dimethyl azelate ($m_{dimethyl\ azelate}$ = 1.642 g, 55%).

2.9 Optimization of electrolysis parameters

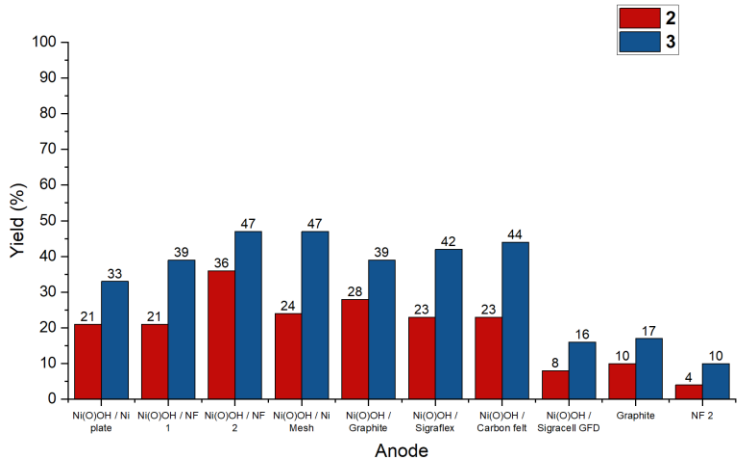


Figure S4 Optimization of the anode material for the electrochemical oxidation of shellac.

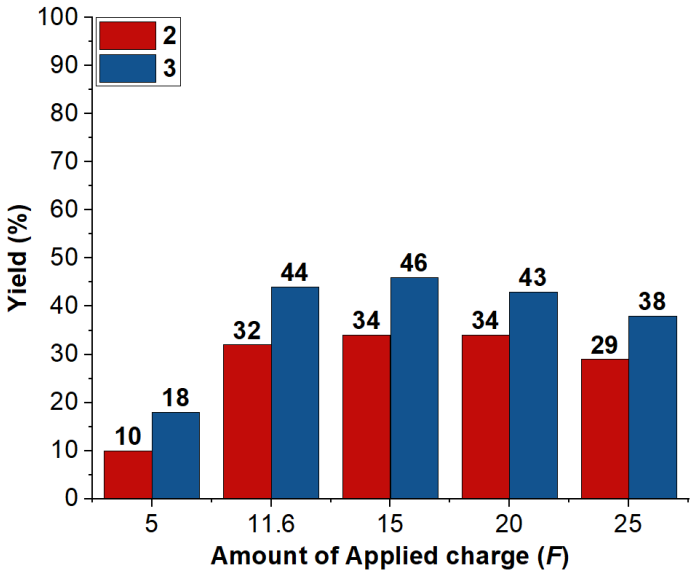


Figure S5 Optimization of the amount of applied charge.

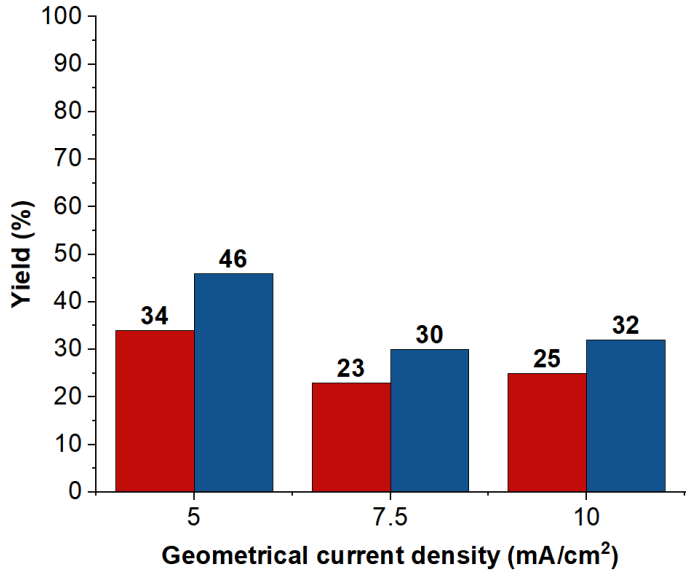


Figure S6 Optimization of the geometrical current density.

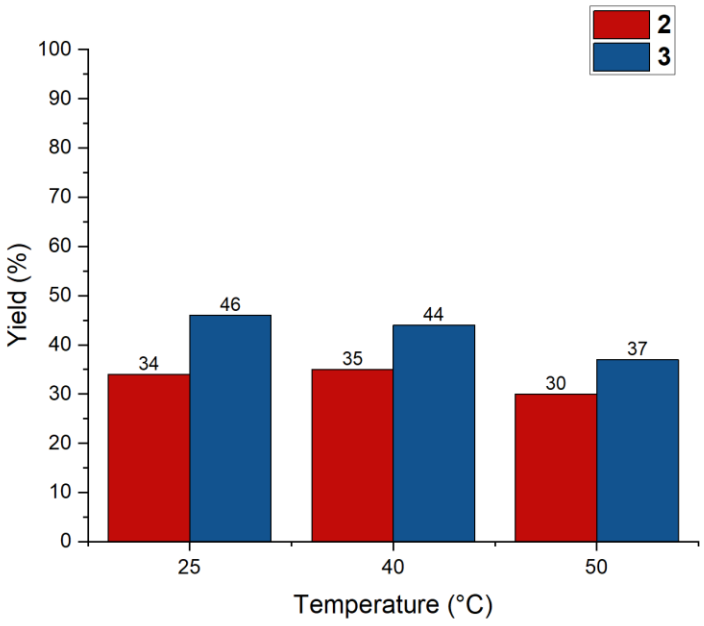


Figure S7 Optimization of the electrolysis temperature.

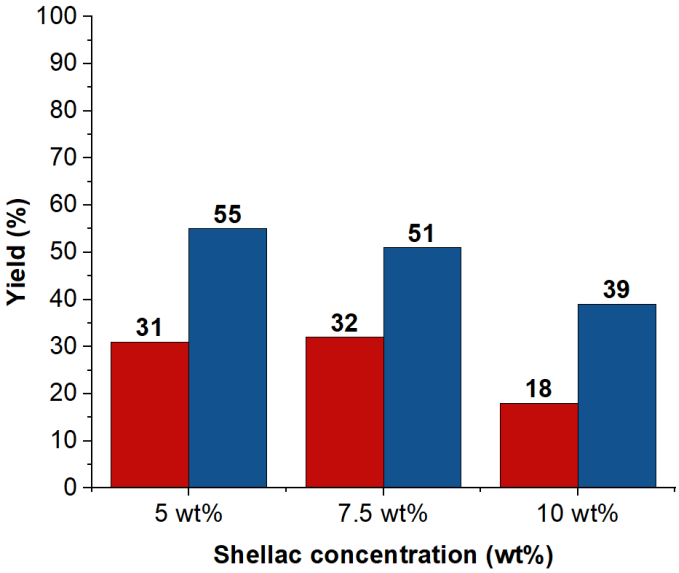


Figure S8 Optimization of the shellac concentration.

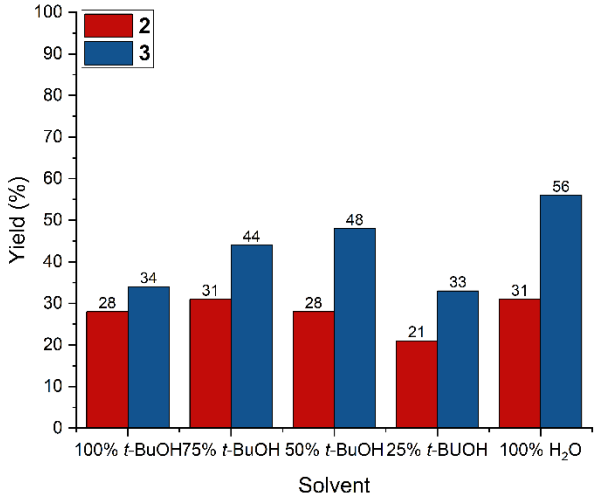


Figure S9 Optimization of the solvent used for the electrochemical oxidation of shellac.

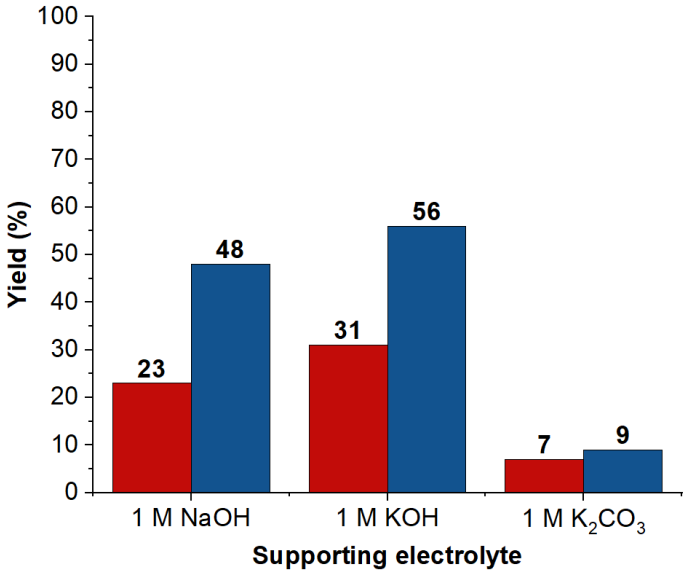


Figure S10 Optimization of the supporting electrolyte.

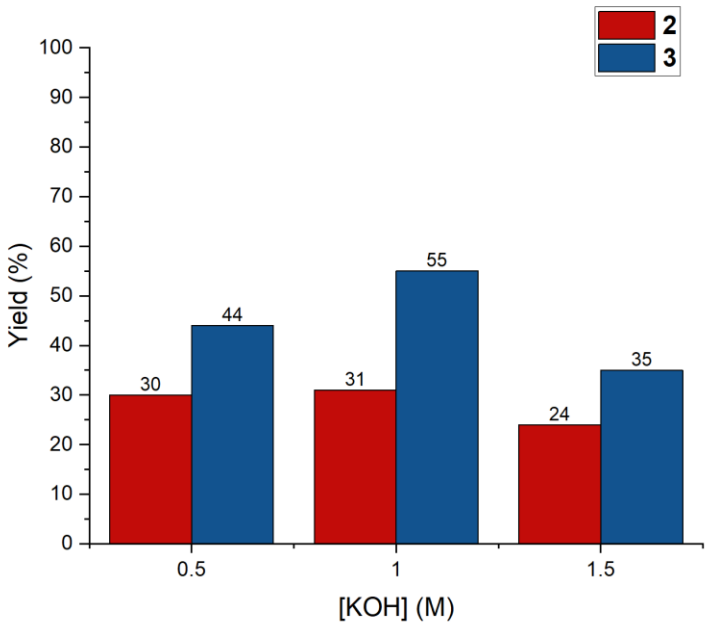


Figure S11 Optimization of the supporting electrolyte concentration.

2.10 Hydrolysis optimization

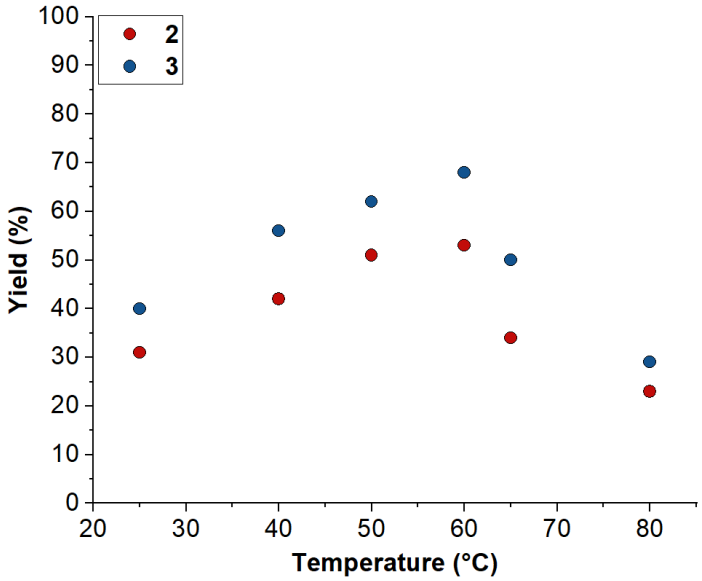


Figure S12 Optimization of the hydrolysis temperature after 48 h.

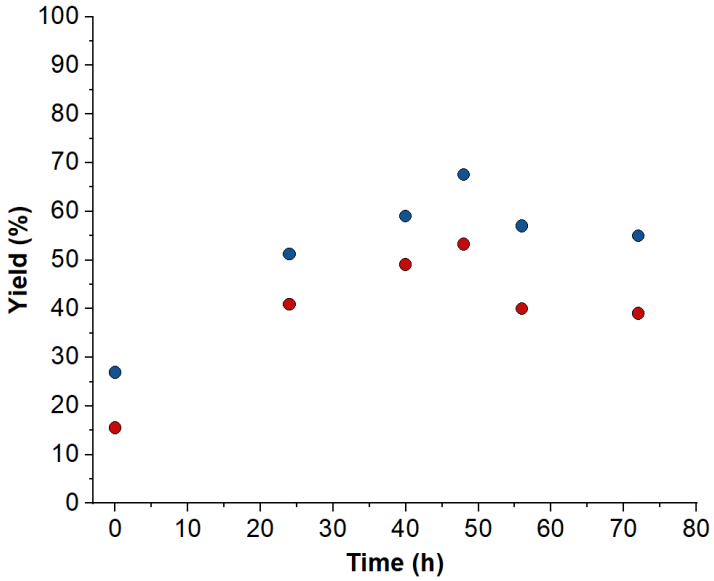


Figure S13 Optimization of the hydrolysis time at 60 °C.

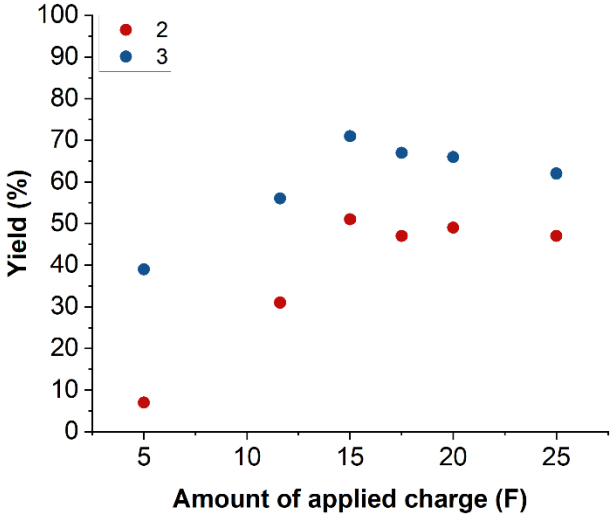


Figure S14 Optimization of the amount of applied charge using the optimal hydrolysis and electrolysis conditions.

3 Green metrics

3.1 Methodology

A combination of different metrics was chosen to evaluate the greenness of the reported procedure. As there is no reported literature method accessing pimelic acid **2** and azelaic acid **3**,

the ozonolysis reaction of oleic acid to form azelaic acid **3** and nonanoic acid.[2] To make a better comparison on the complete process, work-up and isolation considered with the calculations.

As the comparison is mostly done when only one product is formed, we define the carbon averaged yield according to following formula (*6*)

$$yield = \frac{\sum(\#C_{product} \cdot chemical\ yield\ \%)}{\#C_{starting\ product}} \qquad (6)$$

For economic considerations, it should be noted that this protocol is designed for the use of shellac waste-streams, which is normally incinerated or leached into waste-water streams. Therefore, the price per gram shellac is not considered. Solvents are not considered as these can be recycled. The economical factor (Eco) is calculated according to formula (*7*)

$$Eco = \frac{\sum(product\ value\ per\ mol \cdot yield)}{\sum(reagent\ value\ per\ mol \cdot equivalents)} \qquad (7)$$

A higher *Eco* value refers to a better cost balance between the reactants and the desired product.

The atom economy was calculated according to formula (*8*):

$$AE = \frac{\text{molecular mass of desired product}}{\text{molecular mass of all reactants}} \qquad (8)$$

For the calculation of the atom efficiency, the molecular weight of aleuritic acid is used.

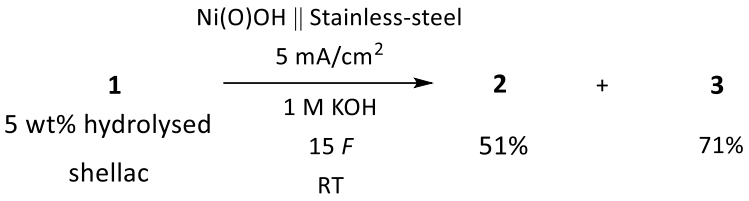
The safety of the reaction was calculated, by categorizing the used reagents according to table S5 and calculating the mean value:

GHS ranking	classification
1	explosive, oxidizing, toxic, health hazard
2	harmful, flammable, environmental, corrosive (combination of 3 hazards)
3	harmful, flammable, environmental, corrosive (combination of 2 hazards)
4	harmful, flammable, environmental, corrosive (1 hazard)
5	-

Table S5 GHS ranking of reagents.

The EcoScale score was calculated according to the procedure developed by Van Aken et al.[3]

3.2 Our method



Substance	M / g/mol	GHS classification	GHS ranking	Price €/g	Price €/mol	Specifications
Aleuritic acid	304.43	none	5	0.55	167.14	500 g, > 95% (Apollo Scientific)
Potassium hydroxide	56.11	corrosive	4	0.021	1.18	25 kg, >85%, p.a. (Carl Roth)
Sulfuric acid	98.08	corrosive	4	0.018	1.77	2.5 L, 95-98% (Carl Roth)
Pimelic acid	160.17			1.08	172.98	100 g, >98% TCI chemicals
Azelaic acid	188.22			0.56	104.65	250g, >98% TCI chemicals

Overall safety (average of GHS ranking): 4.3

Solvents for work-up were not considered as the comparable method is not defining the work-up procedure.

Calculations:

$$yield = \frac{(7 \cdot 51\%) + (9 \cdot 71\%)}{16} = 62\%$$

$$AE = \frac{160.17\ \frac{\mathrm{g}}{\mathrm{mol}} + 188.22\frac{\mathrm{g}}{\mathrm{mol}}}{304.43\ \frac{\mathrm{g}}{\mathrm{mol}} + 3 \cdot 18.0\frac{\mathrm{g}}{\mathrm{mol}}} \cdot = 97\%$$

Three equivalents of water are required as oxygen source for this reaction.

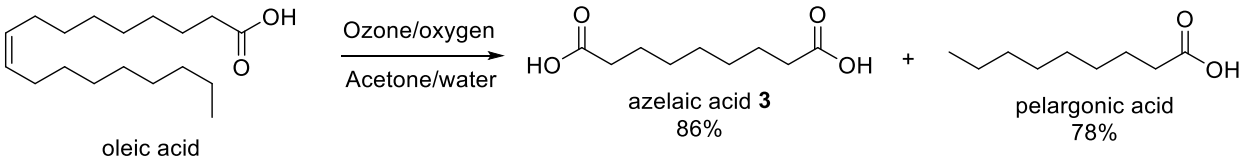
$$Eco = \frac{((172.98\ € \cdot 51\%) + (104.65€ \cdot 71\%))}{(1.18\ € \cdot 17.4\mathrm{eq})_{KOH} + (1.77€ \cdot 10\mathrm{eq})_{H_2SO_4}} = 4.3$$

The cost for solvents and electricity was not considered. Furthermore, the electrode material and its prior activation was not considered in the eco-factor as this can be reused.

Parameter	Penalty points
yield	= (100-62/)2 = 19
reagent costs	0
reagent safety	0
equipment	2 (electrode activation procedure)
conditions	3 (room temperature, > 1 h; heating, >1 h)
work up	9 (2x Liquid-liquid extraction; distillation)
Sum	33

The actual score is 67, with most penalty points originating from the mediocre yield and elaborate purification to avoid the need of column chromatography to make the procedure more interesting for industrial applications. The use of shellac waste-streams as a resource and only KOH as reagent makes up for this as well as the safety and mild reaction conditions.

3.3 Comparison method from the ozonolysis of oleic acid[2]



oleic acid

azelaic acid **3**
86%

pelargonic acid
78%

Substance	M / g/mol	GHS classification	GHS ranking	Price €/g	Price €/mol	Specifications
Oleic acid	282.47	none	5	0.08	22.22	1 L, ≥ 90% (Sigma Aldrich)
Ozone	48.00	Explosive, Oxidizing Toxic	1	0.04	2.24	1 kg, >85%, p.a. (Carl Roth)
Oxygen	32.00	Explosive Toxic	1	0.03	2.94	2.5 L, 95-98% (Sigma Aldrich)
Acetone	88.11	flammable	4			
Pelargonic acid	158.24			0.028	4.43	500 g, Fluorochem EU
Azelaic acid	188.22			0.56	104.65	250g, >98% TCI chemicals

Overall safety (average of GHS ranking): 2.7

Calculations:

$$yield = \frac{(9 \cdot 74\%) + (9 \cdot 86\%)}{18} = 80\%$$

$$AE = \frac{158.24\ \frac{\mathrm{g}}{\mathrm{mol}} + 188.22\frac{\mathrm{g}}{\mathrm{mol}}}{282.47\ \frac{\mathrm{g}}{\mathrm{mol}} + 48.00\frac{\mathrm{g}}{\mathrm{mol}} + 32.00\frac{\mathrm{g}}{\mathrm{mol}}} \cdot = 96\%$$

$$Eco = \frac{((4.43\ € \cdot 74\%)_{Pelargonic\ acid} + (104.65€ \cdot 86\%)_{Azelaic\ acid})}{22.22€_{\ oleic\ acid}} = 4.2$$

The solvent cost for solvents and electricity for ozone generation was not considered. Furthermore, work-up using column chromatography was not considered. It should be noted that the authors of the ozonolysis method used ≥99% oleic acid, which has a price of 1809 €/mol, lowering the *Eco* value to 0.5 making it not economically profitable. However, it is expected that this method also works on lower grade oleic acid. But this will have an effect on the required purification.

Parameter	Penalty points
yield	= (100-82/)2 = 9
reagent costs	0
reagent safety	10 (explosive)
equipment	3 (liquid/gas flow and additional ozone scrubber)
conditions	4 (cooling to 0 °C)
work up	10 (column chromatography)
Sum	36

The actual score is 64, with most penalty points originating from safety as a mixture of oxygen and ozone is used in combination of acetone, a highly flammable solvent. Furthermore, additional scrubbing equipment is required as well as pumps to minimize the safety risks. Purification was also done using column chromatography.

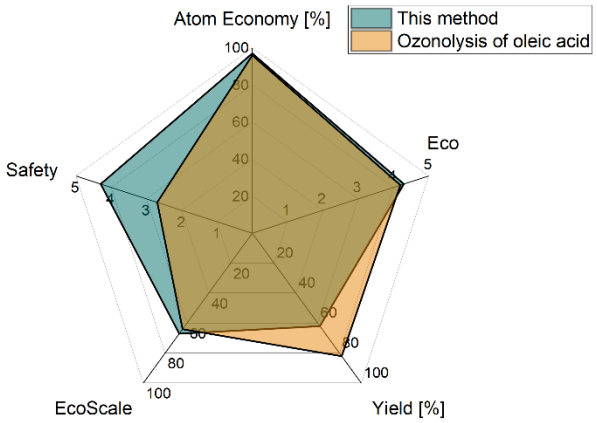
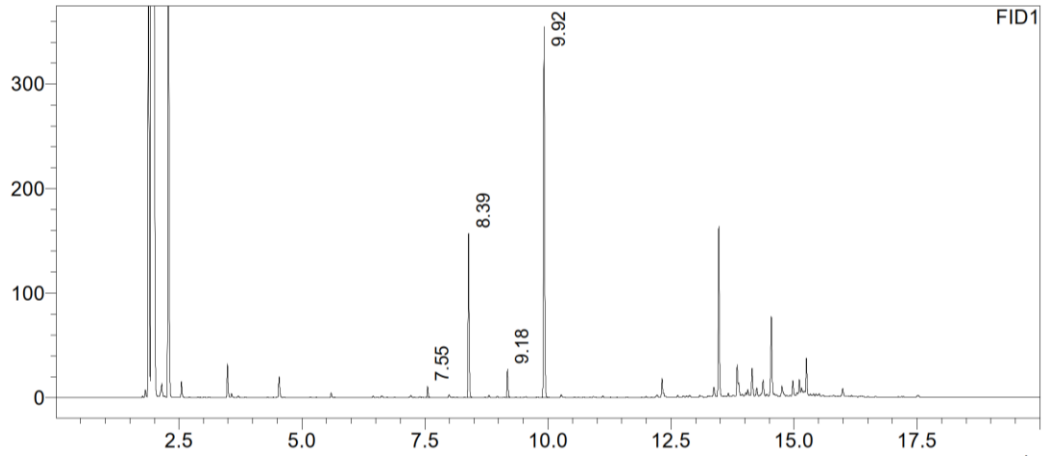


Figure S15 Green metrics comparison.

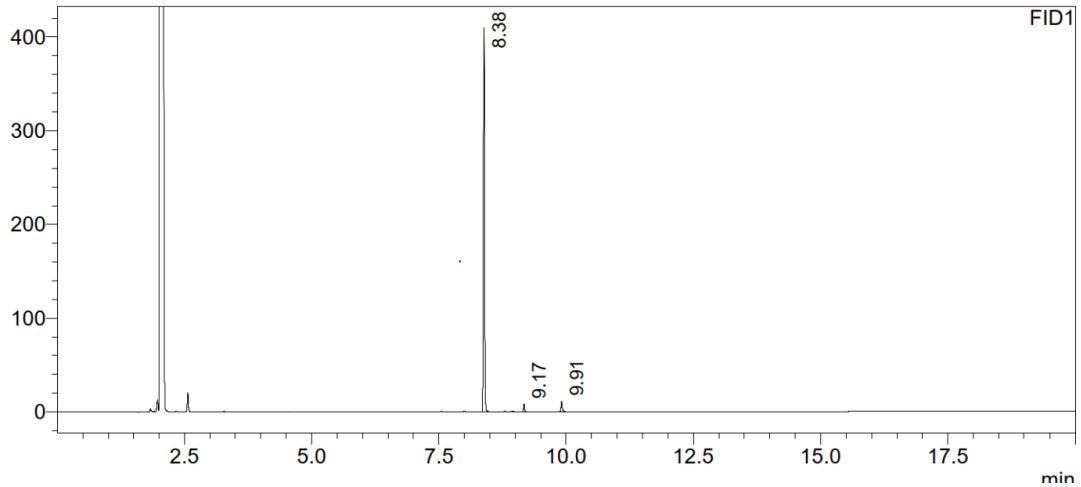
4 Compound characterization

4.1 GC chromatogram



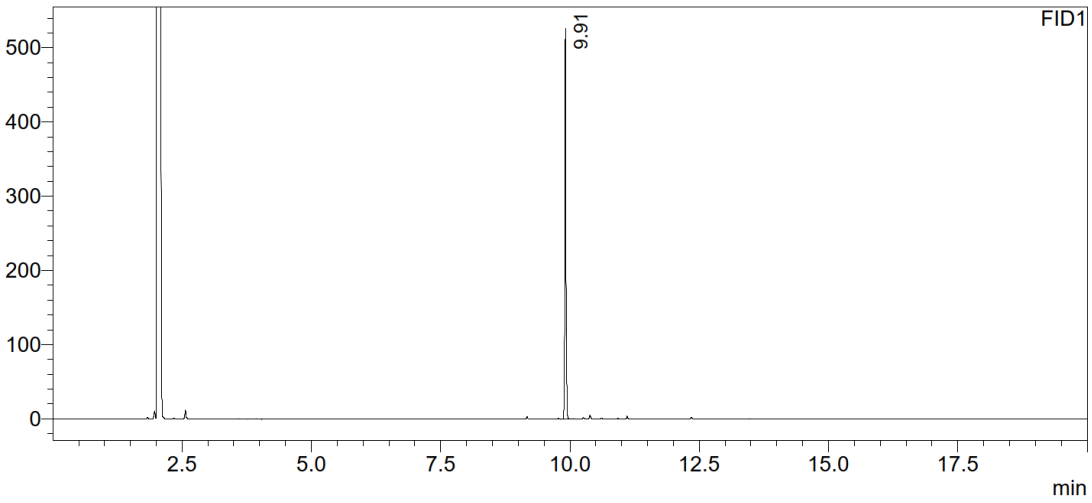
Retention time (min)	Product
7.55	Dimethyl adipate
8.39	Dimethyl pimelate
9.18	Dimethyl suberate
9.92	Dimethyl azelate

Figure S16 GC-FID chromatogram after esterification before distillation



Retention time (min)	Product
8.38	Dimethyl pimelate

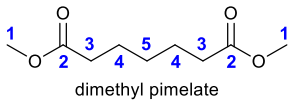
Figure S17 GC-FID chromatogram of the isolated dimethyl pimelate fraction after distillation (fraction 1)



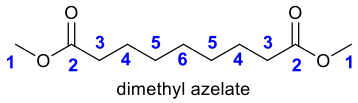
Retention time (min)	Product
9.91	Dimethyl azelate

Figure S18 GC-FID chromatogram of the isolated dimethyl azelate fraction after distillation (fraction 3)

4.2 NMR analysis



^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.61 (s, 6H, 1-*H*), 2.26 (t, 4H, 3-*H*), 1.59 (p, 4H, 4-*H*), 1.36 – 1.23 (m, 2H, 5-*H*). **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 174.0 (2-*C*), 51.5 (1-*C*), 33.8 (3-*C*), 28.6 (5-*C*), 24.6 (4-*C*) ppm. This NMR data agrees with the data previously reported in literature.[4]



^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.65 (s, 6H, 1-*H*), 2.28 (t, 4H, 3-*H*), 1.60 (p, 4H, 4-*H*), 1.38 – 1.25 (m, 6H, 5 & 6-*H*). **^{13}C NMR (101 MHz, CDCl3)** δ = 174.4 (2-*C*), 51.6 (1-*C*), 34.2 (3-*C*), 29.1 (5-*C*), 29.0 (6-*C*), 25.0 (4-*C*) ppm. This NMR data agrees with the data previously reported in literature.[5]

4.3 NMR

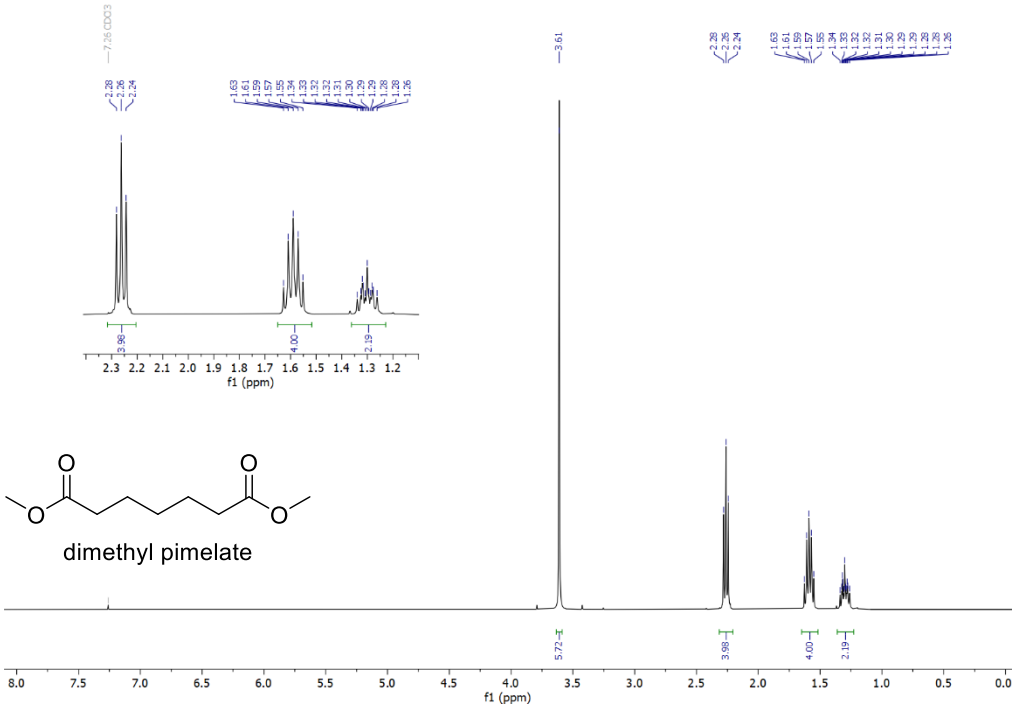


Figure S19 ^{1}H NMR of the dimethyl pimelate, purified by distillation.

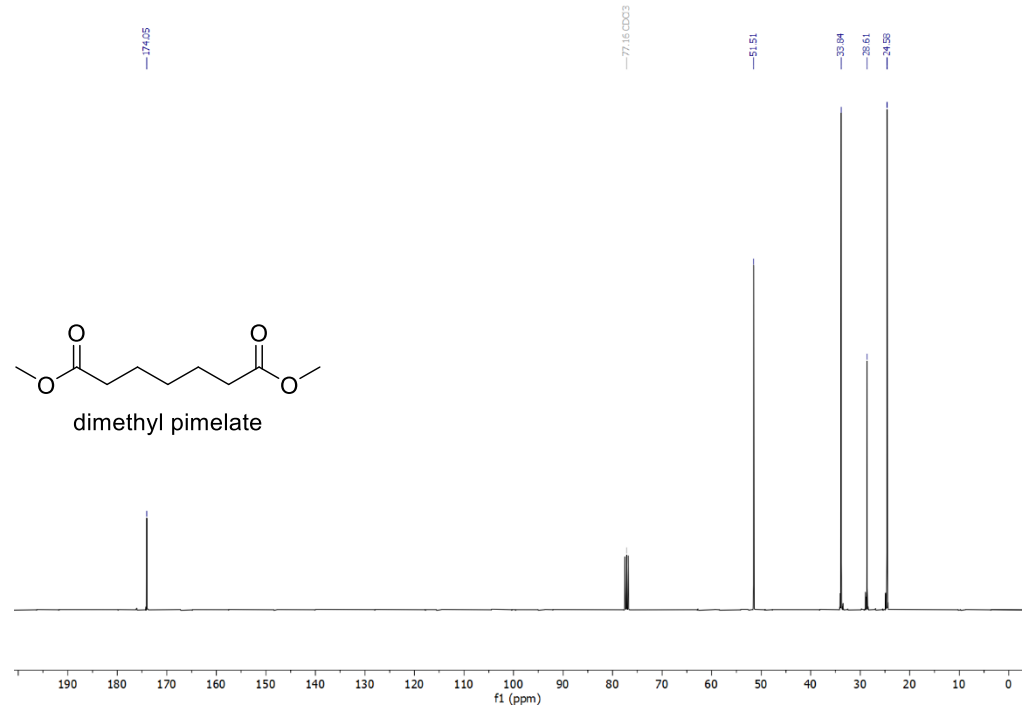


Figure S20 ^{13}C NMR of the dimethyl pimelate, purified by distillation.

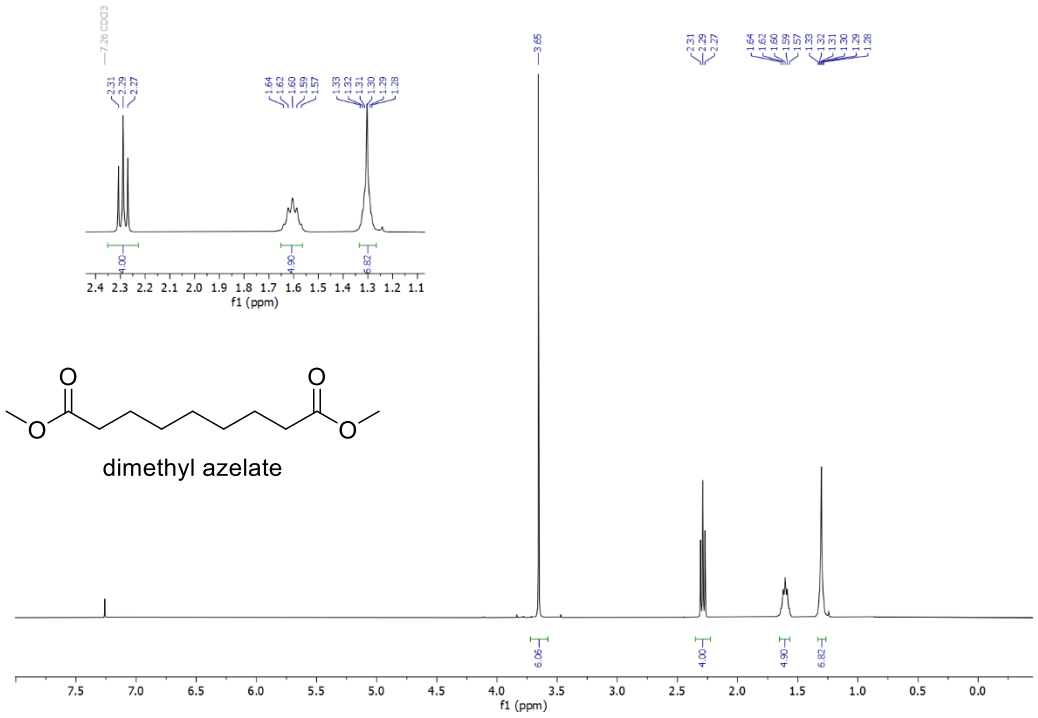


Figure S21 ^{1}H NMR of the dimethyl azelate, purified by distillation.

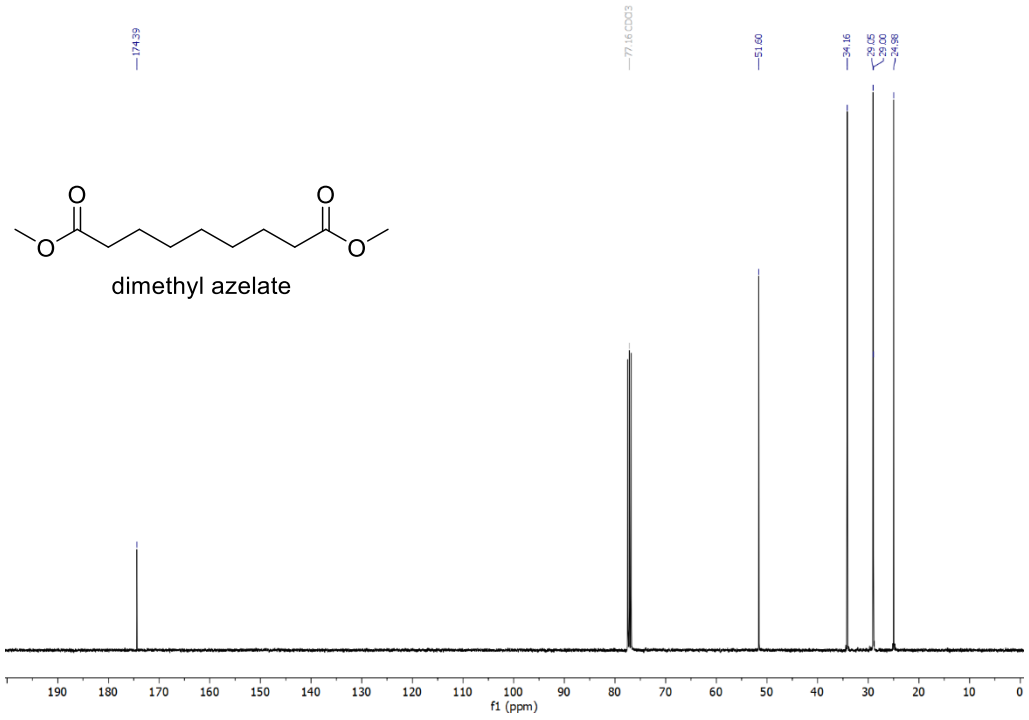


Figure S21 ^{13}C NMR of the dimethyl azelate, purified by distillation.

5 References

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