Beyond Kolbe and Hofer–Moest: Electrochemical Synthesis of Carboxylic Anhydrides from Carboxylic Acids

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SUPPORTING INFORMATION

Materials and Methods

Chemicals

All carboxylic acids, supporting electrolytes, solvents, and additives were used as received from commercial suppliers. For all experiments under ambient conditions, HPLC grade acetonitrile was used. For electrolysis under inert conditions, anhydrous acetonitrile was prepared by refluxing 500 mL acetonitrile with 1 g phosphorous pentoxide for 30 min, distilling it off under a nitrogen atmosphere, and storing it over activated 3 Å molecular sieves in the dark.

Gas Chromatography (GC-FID/GC-MS)

A GC-2010 (Shimadzu, Japan) equipped with a flame ionization detector (detector temperature: 583 K) was used for quantitative analysis. A GC-2010 in combination with a GCMS-QP2010 mass spectrometer (both Shimadzu, Japan) was used for qualitative analysis. Both gas chromatographs were equipped with a quartz capillary column ZB-5 (Phenomenex, USA, length: 30 cm, inner diameter: 0.25 mm, layer thickness of stationary phase: 0.25 μm, carrier gas: hydrogen, stationary phase: (5%-phenyl)methylpolysiloxane). For both, the following temperature program was used: 1 min@323 K, 15 K/min to 563 K, 8 min@563 K.

High Resolution Mass Spectrometry (ESI-MS/APCI-MS)

High resolution m/z were measured on a G6545A Q-ToF mass spectrometer (Agilent, Germany) with electrospray ionization (ESI) or chemical ionization at atmospheric pressure (APCI). The sample was introduced via a 1260 Infinity II HPLC system (Agilent, Germany) equipped with a G7111B 1260 Quaternary Pump, a G7129A 1260 Vialsampler, and a G7116A 1260 Multicolumn Thermostat. The mass calibration was performed on the day of the measurement using an external standard. The mass accuracy of the measurement is better than 5 ppm.

NMR Spectroscopy

NMR spectra were recorded on Avance III HD 300, Avance II 400, or Avance III 600 (Bruker, Germany) spectrometers. Chemical shifts are given as δ-values in ppm and are referenced to the residual proton signal of the deuterated solvent (CDCl₃: ¹H, s, 7.26 ppm; ¹³C, t, 77.1 ppm; DMSO-d₆: ¹H, p, 2.50 ppm; ¹³C, hept, 39.5 ppm. Coupling constants J are given in Hz. Multiplicities are abbreviated as: s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), hept (heptet), m (multiplet), dd (doublet of doublets), ddd (doublet of doublets of doublets). Data analysis was done with MestReNova (Ver. 14.2, Mestrelab Research S.L., Spain).

IR Spectroscopy

IR spectra were recorded on an Alpha spectrometer (Bruker, Germany) using ATR.

Electrolysis Setup

Experiments up to 5 mL electrolyte volume were carried out under ambient atmosphere in undivided beaker-type cells made from Teflon® developed by the Waldvogel lab. Dimensions of the electrodes are 7 cm × 1 cm × 0.3 cm. The electrodes were cleaned with water and acetone after each use and sanded in case of strongly adhesive residues. The immersion depth into 5 mL electrolyte is 1.7 cm and 0.9 cm into 3 mL electrolyte volume. The current density is given in mA/cm². The current set at the galvanostat is calculated as I [mA] = j [mA/cm²] × A [cm²]. The system including a magnetic stirrer, the electrolysis cells, and the galvanostat is commercially available from IKA®-Werke GmbH & CO. KG, Germany. For larger volume experiments, undivided beaker-type glass cells developed by the Waldvogel lab were used.
Optimization

Optimization of carboxylic anhydride yield was performed with isobutyric acid (1h, 99.0%). The yield was determined via $^1$H NMR (general procedure A, see experimental data) using 1,3,5-trimethoxybenzene (98.0%) as absolute internal standard, or via GC (general procedure B) using dibutyl fumarate (4% in DMF) as relative internal standard. Both methods have the same error of measurement.

**Anode Material**

![Graph showing yield comparison for different materials at 2 hours]

**Figure S1:** Reaction conditions: X||stainless steel, 0.7 M isobutyric acid (1h), 0.1 M KSCN, 5.0 mL MeCN, 1.1 $F$, 50 mA/cm$^2$, GC yields; X||Pt, 1.0 M isobutyric acid (1h), 0.1 M KSCN, 5.0 mL MeCN, 1.2 $F$, 50 mA/cm$^2$, NMR yields; X||stainless steel, 1.0 M isobutyric acid (1h), 0.1 M KSCN, 5.0 mL MeCN, 1.2 $F$, 50 mA/cm$^2$, GC yields.

**Cathode Material**

![Graph showing yield comparison for different materials at 2 hours]

**Figure S2:** Reaction conditions: graphite||X, 1.0 M isobutyric acid (1h), 0.1 M KSCN, 5.0 mL MeCN, 1.2 $F$, 50 mA/cm$^2$, GC yields; BDD||X, 1.0 M isobutyric acid (1h), 0.1 M KSCN, 5.0 mL MeCN, 1.2 $F$, 50 mA/cm$^2$, GC yields.
Supporting Electrolyte

**Figure S3:** Reaction conditions: BDD||Pt, 1.0 M isobutyric acid (1h), 0.1 M supporting electrolyte, 5.0 mL MeCN, 1.2 F, 50 mA/cm², GC yields; BDD||Pt, 1.0 M isobutyric acid (1h), 0.05 M KSCN + 0.1 M X, 5.0 mL MeCN, 1.2 F; 50 mA/cm², GC yields; graphite||stainless steel, 0.7 M isobutyric acid (1h), 0.1 M KSCN, 5.0 mL MeCN, 1.1 F, 50 mA/cm², NMR yield; BDD||stainless steel, 0.7 M isobutyric acid (1h), 0.1 M supporting electrolyte, 5.0 mL MeCN, 1.1 F, 50 mA/cm², NMR yields.

Carboxylic Acid Concentration

**Figure S4:** Reaction conditions: graphite||stainless steel, 0.1 M KSCN, 5.0 mL MeCN, 1.1 F, 50 mA/cm², circles: GC yields, squares: NMR yields.
Supporting Electrolyte Concentration

Figure S5: Reaction conditions: graphite||stainless steel, 0.7 M isobutyric acid (1h), 5.0 mL MeCN, 1.0 F, 50 mA/cm², GC yields.

Amount of Applied Charge Q [F]

Figure S6: Reaction conditions: graphite||stainless steel, 0.7 M isobutyric acid (1h), 0.1 M KSCN, 5.0 mL MeCN, 50 mA/cm², circles: GC yields, squares: NMR yields.
Figure S7: Reaction conditions: graphite||stainless steel, 0.7 M isobutyric acid (1h), 0.1 M KSCN, 5.0 mL MeCN, 1.0 F; GC yields.
**Mechanistic Studies**

**Analysis of Gaseous By-products**

Valeric acid (1d, 98.0%, 9.9 mL, 89 mmol, 0.89 M) and KSCN (0.972 g, 0.10 M) were dissolved in MeCN (100 mL) in an undivided glass cell equipped with a graphite anode and stainless steel cathode (active electrode area: 18 cm²). The electrolyte was degassed for 10 min by purging it with a stream of dry N₂. The headspace of the electrolysis chamber was purged with a slow stream of dry N₂ throughout the experiment. The mixture was electrolyzed at 80 mA/cm² and 288 K. The exhaust gas from the electrolysis cell was carried through two bubble counters in series (Figure S8), which were empty at the beginning of the electrolysis. After start of the electrolysis, the bubble counters were purged with the exhaust gas for 10 min. Each bubble counter was then filled under countercurrent from the electrolysis cell with 10 mL of a solution of pyrogallol (2.5 mg/mL) in aqueous 1 M NaOH, which was prepared under inert conditions. Until the end of the electrolysis after 1.1 F, no staining was visible in the bubble counters. Shortly after the end of the electrolysis, the N₂-stream was stopped. The solution in the right bubble counter (Figure S8) immediately started turning brown due to diffusion of air into the solution. 8 min after stopping the N₂-stream, the tubing from the electrolysis cell to the left bubble counter was removed. The solution in the left bubble counter immediately started turning brown (Figure S8, bottom right). We conclude that no O₂ is formed in the electrolysis cell.

**Electrolysis with Addition of Water**

The electrolysis of valeric acid (1d) was performed with addition of water to gain insight on the reaction mechanism (Table S1). Analogous to general procedure C, valeric acid (1d, 0.9 M) and KSCN (0.35 M) were dissolved in MeCN, and a defined amount of water was added. The mixture was electrolyzed, and the yield of valeric anhydride (2d) was determined via GC. As expected, the yield of 2d is lower in the presence of water. Importantly, water does not
suppress the anhydride formation but only slows it down. If the amount of charge is increased, the anhydride yield increases too. The reaction can be considered self-drying since any water present at the beginning will react with the anhydride and form the acid again. We conclude that anhydrous conditions are not necessary, but the reaction can be run under ambient conditions.

**Table S1:** Electrolysis of valeric acid (1d) with addition of water; Reaction conditions: graphite||stainless steel, 0.35 M KSCN, 5.0 mL MeCN, 80 mA/cm², GC yields.

| #  | H₂O [equiv.] | Q [F] | Yield 2d [%] |
|----|--------------|-------|--------------|
| 1  | 0.25         | 1.1   | 28           |
| 2  | 0.25         | 1.6   | 46           |
| 3  | 0.50         | 1.1   | 9            |
| 4  | 0.50         | 1.35  | 18           |

**In situ-NMR Study**

Isobutyric acid (1h, 99.0%, 0.47 mL, 5.0 mmol, 1.0 M) and KSCN (49 mg, 0.10 M) were dissolved in D₃CCN (5.0 mL) in an undivided Teflon cell equipped with a BDD anode and Pt cathode (active electrode area: 1.7 cm²). The mixture was electrolyzed at 50 mA/cm². Four aliquots of 0.2 mL each were taken consecutively from the electrolyte after 0.33 F, 0.75 F, 1.1 F, and 1.2 F. To each aliquot, one drop of dibromomethane (99%) and 0.35 mL D₃CCN were added. ¹H NMR spectra were recorded within 1 h after the aliquot was taken from the electrolyte. ¹³C NMR spectra were recorded within 12 h after end of the electrolysis. No stoichiometric by-product is visible in any of the recorded spectra (Figure S9, Figure S10).
**Figure S9**: In situ $^1$H NMR of the electrolysis of isobutyric acid (1h).

**Figure S10**: In situ $^{13}$C NMR of the electrolysis of isobutyric acid (1h).
Cyclic Voltammetry

Figure S11: Cyclic voltammetry of 10 mM KSCN and 10 mM valeric acid (1d) in MeCN; Working electrode: BDD, 1 mm²; Counter electrode: Pt coil; Reference electrode: Ag/AgCl in EtOH/sat. LiCl; Sweep rate: 0.2 V/s.

Electrolysis in a Divided Cell

Divided cells made from Teflon® with a ceramic frit as separator[1] were used to study the anodic reaction separately from the cathodic one. Each compartment was charged with KSCN (136 mg, 0.35 M), valeric acid (1d, 98.0%, 0.31 mL, 2.8 mmol, 0.70 M), and MeCN (4.0 mL). A graphite anode and stainless steel cathode were immersed into the cell, and the mixture was electrolyzed at 50 mA/cm² until 0.92 F had passed. During electrolysis, the cell voltage rose quickly to 32 V, the maximum output voltage of the used galvanostat, and consequently the current density dropped (Figure S14). In the anodic compartment, an orange solid was formed (Figure S15), which covered the anode completely. The anolyte was analyzed analogously general procedure A (Figure S12). No valeric anhydride (2d) was detected (ISTD: 27.9 mg ethylene carbonate (99%)). The conversion of 1d was 1%.

Following the same procedure but changing 1d in the anodic compartment to tetramethylammonium valerate (491 mg, 2.8 mmol, 0.70 M) gave a similar result (Figure S13). 2d was obtained in 7% yield (ISTD: 28.4 mg ethylene carbonate (99%)). The conversion of 1d was 23%.

The orange solid was filtered off and washed with H₂O and MeOH. The IR absorptions of the dried sample match those of (SCN)x (Figure S15).[2]

The experimental data suggest that the formation of the anhydride is a convergent paired electrolysis. No or only little anhydride is formed in a divided cell. Instead, the oxidation of SCN⁻ to (SCN)x becomes the main reaction in the anodic compartment. The small amount of anhydride formed with tetramethylammonium valerate can be explained by imperfect separation of the two half cells. The experiment did not reveal the electroactive species on the anode.
**Figure S12:** $^1$H NMR of the crude anolyte from electrolysis of valeric acid (1d) in a divided cell; 400 MHz, 296 K.

**Figure S13:** $^1$H NMR of the crude anolyte from electrolysis of tetramethylammonium valerate in a divided cell; 400 MHz, 296 K.
**Figure S14:** Cell voltage and current density during the electrolysis of 1d (a), and tetramethylammonium valerate (b) in a divided cell.

**Figure S15:** IR spectrum of (SCN)$_x$ formed during electrolysis of 1d or tetramethylammonium valerate in the anode compartment of a divided cell.
Experimental Procedures

General Procedure A
The supporting electrolyte and the starting material 1 were dissolved in MeCN in an undivided Teflon cell with a magnetic stirrer. A graphite anode and stainless steel cathode were immersed into the solution, and the mixture was electrolyzed without temperature control. An internal standard (ISTD) was added and the mixture was stirred for 5 min. An aliquot of 0.5–0.6 mL of the mixture was evaporated, and the residue was suspended in 0.5–0.6 mL CDCl₃. The suspension was filtered through a cotton plug into an NMR tube. The yield was determined via ¹H NMR with the following formula:

\[ \text{yield}_{\text{anhydride}} [%] = \frac{200 \times 0.980 \times I_{\text{anhydride}} \times m_{\text{ISTD}} [g] \times z_{\text{ISTD}}}{z_{\text{anhydride}} \times I_{\text{STD}} \times n_{\text{acid}} [mol] \times 168.19 \, g/mol} \]

- 0.980: purity of 1,3,5-trimethoxybenzene
- 168.19 g/mol: molecular weight of 1,3,5-trimethoxybenzene
- \( I_x \): surface integral \( NMR (x) \)
- \( z_x \): number of protons (x); in case of inverse-gated \(^{13}\)C NMR: number of carbon atoms (x)

General Procedure B
The supporting electrolyte and the starting material 1 were dissolved in MeCN in an undivided Teflon cell with a magnetic stirrer. A graphite anode and stainless steel cathode were immersed into the solution, and the mixture was electrolyzed without temperature control. The reaction mixture was transferred to a round-bottom flask and evaporated. Dibromomethane (99%) was added as internal standard (ISTD) and the mixture was shaken for 30 s. Ca. 30 mg of the mixture were dissolved in 0.5–0.6 mL CDCl₃. The yield was determined via ¹H NMR with the following formula:

\[ \text{yield}_{\text{anhydride}} [%] = \frac{200 \times 0.99 \times I_{\text{anhydride}} \times m_{\text{ISTD}} [g] \times z_{\text{ISTD}}}{z_{\text{anhydride}} \times I_{\text{STD}} \times n_{\text{acid}} [mol] \times 173.83 \, g/mol} \]

- 0.99: purity of dibromomethane
- 173.83 g/mol: molecular weight of dibromomethane
- \( I_x \): surface integral \( NMR (x) \)
- \( z_x \): number of protons (x); in case of inverse-gated \(^{13}\)C NMR: number of carbon atoms (x)

General Procedure C
The supporting electrolyte and isobutyric acid (1h, 99%) were dissolved in 5.0 mL MeCN in an undivided Teflon cell with a magnetic stirrer. The electrodes were immersed into the solution, and the mixture was electrolyzed without temperature control. 0.50 mL Dibutyl fumarate (4% in DMF) were added as internal standard (ISTD), and the mixture was stirred for 5 min. The mixture was added to 10 mL saturated aqueous NaHCO₃, and the mixture was shaken for 10 s. 0.8–1.0 mL of the organic phase were filtered through a plug of silica. 0.2 mL of the filtrate were diluted with 1 mL MeCN, and the yield was determined via GC-FID with the following formula:

\[ \text{yield}_{\text{2h}} [%] = \frac{I_{2h}}{\sqrt{0.0386 \times I_{\text{STD}}}} \times \frac{1 \, g \times 88.11 \, g/mol}{5 \times V_{1h} [mL] \times 0.990 \times 0.95 \, g/mL \times 158.19 \, g/mol} \]

- 88.11 g/mol: molecular weight of isobutyric acid
- 158.19 g/mol: molecular weight of isobutyric anhydride (2h)
The calibration curve was created as a power function \( \frac{I_{\text{anhydride}}}{I_{\text{ISTD}}} = a \times m_{\text{anhydride}}^b \) from five calibration points. The error of measurement was calculated as the mean deviation of six control points. For the calibration and control points, a defined amount of isobutyric anhydride (2h, 97%) was dissolved in 5.0 mL MeCN. 0.50 mL Dibutyl fumarate (4% in DMF) were added as internal standard, and the mixture was stirred for 5 min. 0.2 mL of the solution were diluted with 1 mL MeCN and measured three times (calibration points) or once (control points).

**Figure S16:** Calibration curve for isobutyric anhydride (2h).

**Acetic Anhydride (2a)**

Following general procedure A, electrolysis of acetic acid (1a, 100%, 0.35 mL, 6.1 mmol, 1.2 M) at 50 mA/cm² with KSCN (49 mg, 0.10 M) as supporting electrolyte in MeCN (5.0 mL) gave acetic anhydride (2a) in 37% yield after 1.1 F (ISTD: 43.6 mg 1,3,5-trimethoxybenzene (98.0%)).

**GC**

\( t_R = 1.947 \text{ min}; t_R (\text{acetic anhydride (2a), authentic sample}) = 1.949 \text{ min.} \)

**\(^1H\text{ NMR} (400 \text{ MHz, CDCl}_3) \delta 2.13 (s, 6H) \text{ ppm.} \)**

The analytic data is in agreement with previously reported data.\[3\]
**Figure S17:** $^1$H NMR of the crude mixture from electrolysis of acetic acid (1a); 400 MHz, 296 K.

**Propionic Anhydride (2b)**

Following general procedure B, electrolysis of propionic acid (1b, 99%, 0.38 mL, 5.0 mmol, 1.0 M) at 50 mA/cm² with KSCN (49 mg, 0.10 M) as supporting electrolyte in MeCN (5.0 mL) gave propionic anhydride (2b) in 46% yield after 1.1 F (ISTD: 92.0 mg dibromomethane (99%)).

$^1$H NMR The signals overlap partially with propionic acid (1b).

$^{13}$C NMR (101 MHz, CDCl₃) δ 170.4, 28.8, 8.5 ppm.

The analytic data is in agreement with previously reported data.[3]
**Figure S18:** $^1$H NMR of the crude mixture from electrolysis of propionic acid (1b); 400 MHz, 296 K.

**Figure S19:** $^{13}$C NMR of the crude mixture from electrolysis of propionic acid (1b); 101 MHz, 296 K; ISTD: CH$_3$Br$_2$. 
Butyric Anhydride (2c)

Following general procedure A, electrolysis of butyric acid (1c, 99%, 0.33 mL, 3.5 mmol, 0.71 M) at 50 mA/cm² with KSCN (49 mg, 0.10 M) as supporting electrolyte in MeCN (5.0 mL) gave butyric anhydride (2c) in 46% yield after 1.0 F (ISTD: 63.7 mg 1,3,5-trimethoxybenzene (98.0%)).

\(^1\)H NMR The signals overlap partially with butyric acid (1c).

\(^13\)C NMR (101 MHz, CDCl₃) δ 169.6, 37.2, 17.9, 13.5 ppm.

The analytic data is in agreement with previously reported data.\(^4\)

![Figure S20: \(^1\)H NMR of the crude mixture from electrolysis of butyric acid (1c); 400 MHz, 296 K.](image-url)
Figure S21: $^{13}$C NMR of the crude mixture from electrolysis of butyric acid (1c); 101 MHz, 296 K; ISTD: CH$_2$Br$_2$.

Valeric Anhydride (2d)

Following general procedure B, electrolysis of valeric acid (1d, 98.0%, 0.5 mL, 4.5 mmol, 0.90 M) at 80 mA/cm$^2$ with KSCN (170 mg, 0.35 M) as supporting electrolyte in MeCN (5.0 mL) gave valeric anhydride (2d) in 66% yield and 92% selectivity (72% conversion) after 1.1 F (ISTD: 90 mg dibromomethane (99%)).

The electrolysis of valeric acid was upscaled: Valeric acid (1d, 98.0%, 9.9 mL, 89 mmol, 0.89 M) and KSCN (3.401 g, 0.35 M) were dissolved in MeCN (100 mL) in an undivided glass cell equipped with a graphite anode and stainless steel cathode (active electrode area: 18 cm$^2$). The mixture was electrolyzed at 80 mA/cm$^2$ and 288 K until 1.1 F had been transferred. An aliquot was taken from the electrolyte and the yield of valeric anhydride (2d) was determined 55% by GC analogously general procedure C. The remaining electrolyte was diluted with EtOAc and washed with saturated aqueous NaHCO$_3$. The aqueous phase was extracted with EtOAc and the combined organic phases were dried with MgSO$_4$. The residue was distilled in high vacuum to afford 2.817 g (34%) valeric anhydride (2d) as colourless liquid.

$^1$H NMR (400 MHz, CDCl$_3$) δ 2.45 (t, $J = 7.5$ Hz, 4H), 1.71 – 1.59 (m, 4H), 1.45 – 1.32 (m, 4H), 0.93 (t, $J = 7.3$ Hz, 6H) ppm.

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 169.8, 35.1, 26.4, 22.1, 13.8 ppm.

The analytic data is in agreement with previously reported data.$^5$
**Figure S22:** $^1$H NMR of the crude mixture from electrolysis of valeric acid (1d); 400 MHz, 296 K.

**Figure S23:** $^{13}$C NMR of the crude mixture from electrolysis of valeric acid (1d); 101 MHz, 296 K.
Figure S24: $^1$H NMR of valeric anhydride (2d) after distillation; 400 MHz, 296 K.

Figure S25: $^{13}$C NMR of valeric anhydride (2d) after distillation; 101 MHz, 296 K.
Caproic Anhydride (2e)

Following general procedure B, electrolysis of caproic acid (1e, 98%, 600 mg, 5.1 mmol, 1.0 M) at 50 mA/cm² with KSCN (49 mg, 0.10 M) as supporting electrolyte in MeCN (5.0 mL) gave caproic anhydride (2e) in 60% yield and >100% selectivity (57% conversion) after 1.1 F (ISTD: 62.0 mg dibromomethane (99%)).

1H NMR The signals overlap partially with caproic acid (1e).

13C NMR (101 MHz, CDCl₃) δ 169.8, 35.4, 31.3, 24.0, 22.4, 14.0 ppm.

The analytic data is in agreement with previously reported data.[6]

Figure S26: 1H NMR of the crude mixture from electrolysis of caproic acid (1e); 400 MHz, 296 K.
Caprylic Anhydride (2f)

Following general procedure A, electrolysis of caprylic acid (1f, 99.5%, 507 mg, 3.5 mmol, 0.70 M) at 50 mA/cm² with EMIMSCN (85 mg, 0.10 M) as supporting electrolyte in MeCN (5.0 mL) gave caprylic anhydride (2f) in 37% yield and 79% selectivity (46% conversion) after 1.1 F (ISTD: 45.8 mg 1,3,5-trimethoxybenzene (98.0%)).

**GCMS (EI) t<sub>r</sub> = 12.970 min, [m/z] 127 (100%), 98 (7%), 57 (75%), 43 (25%), 42 (11%), 41 (26%).**

**<sup>1</sup>H NMR** The signals overlap partially with caprylic acid (1f).

**<sup>13</sup>C NMR** (101 MHz, CDCl₃) δ 169.8 ppm; The signals of the remaining carbon atoms cannot be assigned unambiguously.

The analytic data is in agreement with previously reported data.\[^{[7]}\]
Figure S28: $^1$H NMR of the crude mixture from electrolysis of caprylic acid (1f); 400 MHz, 296 K.

Figure S29: $^{13}$C NMR of the crude mixture from electrolysis of caprylic acid (1f); 101 MHz, 296 K.
Figure S30: GCMS of the crude mixture from electrolysis of caprylic acid (1f) after filtration through silica.

Lauric Anhydride (2g)

Following general procedure A, electrolysis of lauric acid (1g, 98%, 715 mg, 3.5 mmol, 0.70 M) at 50 mA/cm² and 313 K with EMIMSCN (85 mg, 0.10 M) as supporting electrolyte in MeCN (5.0 mL) gave lauric anhydride (2g) in 39% yield and 96% selectivity (41% conversion) after 1.1 F (ISTD: 42.9 mg 1,3,5-trimethoxybenzene (98.0%)).

1H NMR The signals overlap partially with lauric acid (1g).

13C NMR (101 MHz, CDCl₃) δ 169.7, 35.3 ppm; The remaining signals overlap with lauric acid (1g) or cannot be assigned unambiguously.

The analytic data is in agreement with previously reported data.[8]
Figure S31: $^1$H NMR of the crude mixture from electrolysis of lauric acid (1g); 400 MHz, 296 K.

Figure S32: $^{13}$C NMR of the crude mixture from electrolysis of lauric acid (1g); 101 MHz, 296 K.
Isobutyric Anhydride (2h)

Following general procedure A, electrolysis of isobutyric acid (1h, 99.0%, 0.33 mL, 3.5 mmol, 0.70 M) at 50 mA/cm² with KSCN (170 mg, 0.35 M) as supporting electrolyte in MeCN (5.0 mL) gave isobutyric anhydride (2h) in 61% yield after 1.1 F (ISTD: 37.4 mg 1,3,5-trimethoxybenzene (98.0%)).

**GC** \( t_R = 4.199 \text{ min}; \ t_R \) (isobutyric anhydride (2h), authentic sample) = 4.193 min.

**\(^1\)H NMR** The signals overlap partially with isobutyric acid (1h).

**\(^{13}\)C NMR** (101 MHz, CDCl₃) \( \delta \) 173.0, 35.2, 18.4 ppm.

The analytic data is in agreement with previously reported data.[3]

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**Figure S33:** \(^1\)H NMR of the crude mixture from electrolysis of isobutyric acid (1h); 400 MHz, 296 K.
Figure S34: $^{13}$C NMR of the crude mixture from electrolysis of isobutyric acid (1h); 101 MHz, 296 K; ISTD: CH$_2$Br$_2$.

Pivalic Anhydride (2i)

Following general procedure B, electrolysis of pivalic acid (1i, 99%, 516 mg, 5.0 mmol, 1.0 M) at 50 mA/cm$^2$ with KSCN 50 mg, 0.10 M) as supporting electrolyte in MeCN (5.0 mL) gave pivalic anhydride (2i) in 52% yield and 92% selectivity (57% conversion) after 1.1 F (ISTD: 66.1 mg dibromomethane (99%)). N-tert-Butyl acetamide was observed as side-product.

GCMS (EI) $t_R = 5.960$ min, [m/z] 85 (38%), 57 (100%), 41 (25%); $t_R$ (pivalic anhydride (2i), authentic sample) = 5.970 min, [m/z] 85 (41%), 57 (100%), 41 (24%).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.26 (s, 18H) ppm.

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 174.2, 40.3, 26.6 ppm.

The analytic data is in agreement with previously reported data.$^{[9,10]}$
Figure S35: $^1$H NMR of the crude mixture from electrolysis of pivalic acid (1i); 400 MHz, 296 K.

Figure S36: $^{13}$C NMR of the crude mixture from electrolysis of pivalic acid (1i); 101 MHz, 296 K; ISTD: 1,3,5-trimethoxybenzene.
3,3-Dimethylbutanoic Anhydride (2j)

Following general procedure B, electrolysis of 3,3-dimethylbutanoic acid (1j, 98%, 600 mg, 5.1 mmol, 1.0 M) at 50 mA/cm² with KSCN (50 mg, 0.10 M) as supporting electrolyte in MeCN (5.0 mL) gave 3,3-dimethylbutanoic anhydride (2j) in 53% yield and 90% selectivity (59% conversion) after 1.1 F (ISTD: 113.8 mg dibromomethane (99%)).

\(^1\)H NMR (400 MHz, CDCl_3) \(\delta\) 2.30 (s, 4H), 1.07 (s, 18H) ppm.

\(^{13}\)C NMR (101 MHz, CDCl_3) \(\delta\) 168.1, 48.7, 29.8, 29.6 ppm.

The analytic data is in agreement with previously reported data.[11]

Figure S37: \(^1\)H NMR of the crude mixture from electrolysis of 3,3-dimethylbutanoic acid (1j); 400 MHz, 296 K.
Figure S38: $^{13}$C NMR of the crude mixture from electrolysis of 3,3-dimethylbutanoic acid (1j); 101 MHz, 296 K; ISTD: 1,3,5-trimethoxybenzene.

2-Ethylhexanoic Anhydride (2k)

Following general procedure B, electrolysis of 2-ethylhexanoic acid (1k, 100%, 724 mg, 5.0 mmol, 1.0 M) at 50 mA/cm² with KSCN (50 mg, 0.10 M) as supporting electrolyte in MeCN (5.0 mL) gave 2-ethylhexanoic anhydride (2k) in 58% yield and >100% selectivity (51% conversion) after 1.1 F (ISTD: 95.0 mg dibromomethane (99%)).

GCMS (EI) $t_R = 11.453$ min, [m/z] 127 (75%), 99 (38%), 57 (100%), 43 (22%), 41 (25%).

$^1$H NMR The signals overlap partially with 2-ethylhexanoic acid (1k).

$^{13}$C NMR (101 MHz, CDCl₃) δ 171.9, 48.2, 31.0, 29.3, 24.8, 22.6, 13.9, 11.8 ppm.

The analytic data is in agreement with previously reported data. [12]
Figure S39: $^1$H NMR of the crude mixture from electrolysis of 2-ethylhexanoic acid (1k); 400 MHz, 296 K.

Figure S40: $^{13}$C NMR of the crude mixture from electrolysis of 2-ethylhexanoic acid (1k); 101 MHz, 296 K.
4-Pentenoic Anhydride (2l)

Following general procedure A, electrolysis of 4-pentenoic acid (1l, 100%, 0.36 mL, 3.5 mmol, 0.70 M) at 50 mA/cm² with KSCN (49 mg, 0.10 M) as supporting electrolyte in MeCN (5.0 mL) gave 4-pentenoic anhydride (2l) in 26% yield after 1.0 F (ISTD: 60.3 mg 1,3,5-trimethoxybenzene (98.0%)).

$^1$H NMR The signals overlap partially with 4-pentenoic acid (1l).

$^{13}$C NMR (101 MHz, CDCl₃) δ 168.8, 135.8, 116.3, 34.7, 28.2 ppm.

The analytic data is in agreement with previously reported data.[13]

![NMR spectrum](image)

**Figure S41**: $^1$H NMR of the crude mixture from electrolysis of 4-pentenoic acid (1l); 400 MHz, 296 K.
Figure S42: $^{13}$C NMR of the crude mixture from electrolysis of 4-pentenoic acid (1I); 101 MHz, 296 K.

10-Undecenoic Anhydride (2m)

Following general procedure A, electrolysis of 10-undecenoic acid (1m, 99%, 465 mg, 2.5 mmol, 0.50 M) at 30 mA/cm$^2$ and 313 K with EMIMSCN (178 mg, 0.20 M) as supporting electrolyte in MeCN (5.0 mL) gave 10-undecenoic anhydride (2m) in 24% yield and 71% selectivity (34% conversion) after 1.1 F (ISTD: 37.6 mg 1,3,5-trimethoxybenzene (98.0%)).

HRMS (ESI) [m/z] calc’d for C$_{22}$H$_{38}$NaO$_3$ [M + Na]$^+$, 373.2713; found, 373.2716; deviation: +0.8 ppm.

$^1$H NMR (400 MHz, CDCl$_3$) δ 2.39 (t, $J$ = 7.5 Hz, 4H) ppm; The remaining signals overlap with 10-undecenoic acid (1m).

The analytic data is in agreement with previously reported data.$^{[14]}$
3-Bromopropanoic Anhydride (2n)

Following general procedure A, electrolysis of 3-bromopropanoic acid (1n, 97%, 552 mg, 3.5 mmol, 0.70 M) at 50 mA/cm² with KSCN (49 mg, 0.10 M) as supporting electrolyte in MeCN (5.0 mL) gave 3-bromopropanoic anhydride (2n) in 29% yield and 74% selectivity (39% conversion) after 1.1 F (ISTD: 41.0 mg 1,3,5-trimethoxybenzene (98.0%)).

**1H NMR** The signals overlap partially with 3-bromopropanoic acid (1n).

**13C NMR** (101 MHz, CDCl₃) δ 166.0, 38.6, 24.2 ppm.

The analytic data is in agreement with previously reported data.\[15\]
**Figure S44**: $^1$H NMR of the crude mixture from electrolysis of 3-bromopropanoic acid (1n); 400 MHz, 296 K.

**Figure S45**: $^{13}$C NMR of the crude mixture from electrolysis of 3-bromopropanoic acid (1n); 101 MHz, 296 K.
11-Bromoundecanoic Anhydride (2o)

Following general procedure A, electrolysis of 11-bromoundecanoic acid (1o, 93%, 1426 mg, 5.0 mmol, 1.0 M) at 50 mA/cm² and 313 K with EMIMSCN (89 mg, 0.10 M) as supporting electrolyte in MeCN (5.0 mL) gave 11-bromoundecanoic anhydride (2o) in 39% yield and 92% selectivity (43% conversion) after 1.1 F (ISTD: 31.9 mg 1,3,5-trimethoxybenzene (98.0%)). For analytic purposes, the residual electrolyte was filtered through a mixture of silica (ca. 4 g) and K₂CO₃ (ca. 1 g) on a 4 µm frit. The silica layer was rinsed with 60 mL cyclohexane, and the filtrate was washed with cold aqueous K₂CO₃ (0.1 M, 20 mL). The organic phase was dried with MgSO₄ and the solvent was evaporated to give 465 mg of a mixture of 11-bromoundecanoic anhydride (2o, 95%) and 1,3,5-trimethoxybenzene (5%). The isolated amount of 11-bromoundecanoic anhydride (2o) corresponds to 34% yield.

HRMS (ESI) [m/z] calc’d for C₂₂H₄₀Br₁₂NaO₃⁺ [M + Na]⁺, 533.1236; found, 533.1239; deviation: +0.6 ppm.

¹H NMR (400 MHz, CDCl₃) δ 3.39 (t, J = 6.9 Hz, 4H), 2.43 (t, J = 7.4 Hz, 4H), 1.84 (dt, J = 14.5, 6.9 Hz, 4H), 1.64 (dt, J = 14.5, 7.4 Hz, 4H), 1.44 – 1.25 (m, 24H) ppm.

¹³C NMR (101 MHz, CDCl₃) δ 169.7, 35.4, 34.1, 32.9, 29.4, 29.3, 29.2, 28.9, 28.8, 28.2, 24.3 ppm.

No spectroscopic data for this compound has been reported before.

![1H NMR of the crude mixture from electrolysis of 11-bromoundecanoic acid (1o); 400 MHz, 296 K.](image)

Figure S46: ¹H NMR of the crude mixture from electrolysis of 11-bromoundecanoic acid (1o); 400 MHz, 296 K.
**Figure S47**: $^1$H NMR of 11-bromoundecanoic anhydride (2o) after filtration; 400 MHz, 296 K.

**Figure S48**: $^{13}$C NMR of 11-bromoundecanoic anhydride (2o) after filtration; 101 MHz, 296 K.
(S)-2-Chloroproanoic Anhydride (2p)

Following general procedure A, electrolysis of (S)-2-chloropropanoic acid (1p, 100%, 380 mg, 3.50 mmol, 0.70 M) at 50 mA/cm² with KSCN (49 mg, 0.10 M) as supporting electrolyte in MeCN (5.0 mL) gave (S)-2-chloropropanoic anhydride (2p) in 43% yield and 84% selectivity (51% conversion) after 1.1 F (ISTD: 39.0 mg 1,3,5-trimethoxybenzene (98.0%)).

1H NMR The signals overlap partially with (S)-2-chloropropanoic acid (1p).

13C NMR (151 MHz, CDCl₃) δ 164.5, 52.3, 20.8 ppm.

The analytic data is in agreement with previously reported data.[16]

Figure S49: 1H NMR of the crude mixture from electrolysis of (S)-2-chloropropanoic acid (1p); 400 MHz, 296 K.
**SUPPORTING INFORMATION**

**Figure S50:** $^{13}$C NMR of the crude mixture from electrolysis of (S)-2-chloropropanoic acid (1p); 151 MHz, 294 K.

### 1-Methylcyclohexanecarboxylic Anhydride (2q)

Following general procedure A, electrolysis of 1-methylcyclohexanecarboxylic acid (1q, 99%, 718 mg, 5.00 mmol, 1.0 M) at 50 mA/cm² with EMIMSCN (89 mg, 0.10 M) as supporting electrolyte in MeCN (5.0 mL) gave 1-methylcyclohexanecarboxylic anhydride (2q) in 34% yield after 1.1 F (ISTD: 40.5 mg 1,3,5-trimethoxybenzene (98.0%)). The yield was determined via inverse-gated $^{13}$C NMR because no isolated signal in the $^1$H NMR spectrum was available. For analytic purposes, the residual electrolyte was filtered through a mixture of silica (ca. 4 g) and K$_2$CO$_3$ (ca. 1 g) on a p4 frit. The silica layer was rinsed with 60 mL cyclohexane, and the filtrate was washed with cold aqueous K$_2$CO$_3$ (0.1 M, 20 mL). The organic phase was dried with MgSO$_4$ and the solvent was evaporated to give 262 mg of a mixture of 1-methylcyclohexanecarboxylic anhydride (2q, 87%) and 1,3,5-trimethoxybenzene (13%). The isolated amount of 1-methylcyclohexanecarboxylic anhydride (2q) corresponds to 34% yield.

**GCMS (EI) tR = 12.720 min, [m/z] 125 (22%), 97 (100%), 55 (34%), 41 (11%).**

**HRMS (ESI) [m/z] calc’d for C$_{16}$H$_{26}$NaO$_3$ $^+ [M + Na]^+$, 289.1774; found, 289.1766; deviation: -2.8 ppm.**

**$^1$H NMR (400 MHz, CDCl$_3$) δ 2.08 – 1.97 (m, 4H), 1.62 – 1.41 (m, 10H), 1.33 – 1.25 (m, 6H), 1.23 (s, 6H) ppm.**

**$^{13}$C NMR (101 MHz, CDCl$_3$) δ 173.5, 44.8, 35.3, 25.7, 25.6, 23.1 ppm.**

No spectroscopic data for this compound has been reported before.
**Figure S51:** $^1$H NMR of the crude mixture from electrolysis of 1-methylcyclohexanecarboxylic acid (1q); 400 MHz, 297 K.

**Figure S52:** Inverse-gated $^{13}$C NMR of the crude mixture from electrolysis of 1-methylcyclohexanecarboxylic acid (1q); 101 MHz, 296 K.
**Figure S53**: $^1$H NMR of 1-methylcyclohexanecarboxylic anhydride (2q) after filtration; 400 MHz, 298 K.

**Figure S54**: $^{13}$C NMR of 1-methylcyclohexanecarboxylic anhydride (2q) after filtration; 101 MHz, 298 K.
**Supporting Information**

**Adamantane-1-carboxylic Anhydride (2r)**

Following general procedure A, electrolysis of adamantane-1-carboxylic acid (1r, 98.0%, 460 mg, 2.5 mmol, 0.50 M) at 30 mA/cm² and 313 K with EMIMSCN (178 mg, 0.20 M) as supporting electrolyte in MeCN (5.0 mL) gave adamantane-1-carboxylic anhydride (2r) in 28% yield after 1.1 F (STD: 35.6 mg 1,3,5-trimethoxybenzene (98.0%)). The yield was determined via inverse-gated $^{13}$C NMR because no isolated signal in the $^1$H NMR spectrum was available.

$^1$H NMR The signals overlap with adamantane-1-carboxylic acid (1r).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 173.4, 42.2, 38.2, 36.5, 27.6 ppm.

The analytic data is in agreement with previously reported data.\(^9\)

![Figure S55: $^1$H NMR of the crude mixture from electrolysis of adamantane-1-carboxylic acid (1r); 400 MHz, 296 K.](image)
SUPPORTING INFORMATION

Figure S56: Inverse-gated $^{13}$C NMR of the crude mixture from electrolysis of adamantane-1-carboxylic acid (1r); 101 MHz, 296 K.

Levulinic Anhydride (2s)

Following general procedure A, electrolysis of levulinic acid (1s, 98%, 0.37 mL, 3.5 mmol, 0.71 M) at 50 mA/cm$^2$ with KSCN (49 mg, 0.10 M) as supporting electrolyte in MeCN (5.0 mL) gave levulinic anhydride (2s) in 21% yield after 1.3 $F$ (ISTD: 28.8 mg 1,3,5-trimethoxybenzene (98.0%)). The yield was determined via inverse-gated $^{13}$C NMR because no isolated signal in the $^1$H NMR spectrum was available. An unidentified side-product is visible in NMR.

GCMS (EI) $t_r = 11.067$ min, [m/z] 99 (100%), 71 (14%), 43 (57%).

$^1$H NMR The signals overlap with levulinic acid (1s) and an unidentified side-product.

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 206.8, 171.2, 37.7 ppm; The signals of the remaining methylene and methyl groups cannot be assigned unambiguously.

The analytic data is in agreement with previously reported data.$^{[17]}$
Figure S57: $^1$H NMR of the crude mixture from electrolysis of levulinic acid (1s); 400 MHz, 296 K.

Figure S58: Inverse-gated $^{13}$C NMR of the crude mixture from electrolysis of levulinic acid (1s); 101 MHz, 296 K.
3-((tert-Butyldimethylsilyl)oxy)-2,2-dimethylpropanoic Anhydride (2t)

Following general procedure A, electrolysis of 3-((tert-butyldimethylsilyl)oxy)-2,2-dimethylpropanoic acid (1t, 100%, 818 mg, 3.5 mmol, 0.70 M) at 50 mA/cm² with KSCN (121 mg, 0.25 M) as supporting electrolyte in MeCN (5.0 mL) gave 3-((tert-butyldimethylsilyl)oxy)-2,2-dimethylpropanoic anhydride (2t) in 36% yield and 52% selectivity (70% conversion) after 1.1 F (ISTD: 62.3 mg 1,3,5-trimethoxybenzene (98.0%)). An unidentified substance is visible in the NMR spectra.

**1H NMR** The signals overlap partially with 3-((tert-butyldimethylsilyl)oxy)-2,2-dimethylpropanoic acid (1t) and an unidentified substance.

**13C NMR** (101 MHz, CDCl₃) δ 172.1, 70.4, 45.9, -4.8 ppm; The signals of the remaining carbon atoms cannot be assigned unambiguously.

**HRMS** (ESI) [m/z] calc’d for C₂₂H₄₆NaO₅Si₂⁺ [M + Na]⁺, 469.2776; found, 469.2799; deviation: +4.9 ppm.

No spectroscopic data for this compound has been reported before.

Figure S59: ¹H NMR of the crude mixture from electrolysis of 3-((tert-butyldimethylsilyl)oxy)-2,2-dimethylpropanoic acid (1t); 400 MHz, 296 K.
Figure S60: $^{13}$C NMR of the crude mixture from electrolysis of 3-((tert-butyl(dimethyl)silyl)oxy)-2,2-dimethylpropionic acid (1t); 101 MHz, 296 K.

2-(2-Fluorophenyl)acetic Anhydride (2u)

Following general procedure A, electrolysis of 2-(2-fluorophenyl)acetic acid (1u, 98%, 330 mg, 2.1 mmol, 0.70 M) at 50 mA/cm² with KSCN (29 mg, 0.10 M) as supporting electrolyte in MeCN (3.0 mL) gave 2-(2-fluorophenyl)acetic anhydride (2u) in 17% yield and 38% selectivity (45% conversion) after 1.1 F (ISTD: 27.8 mg 1,3,5-trimethoxybenzene (98.0%)�.

$^1$H NMR The signals overlap partially with 2-(2-fluorophenyl)acetic acid (1u).

$^{13}$C NMR (101 MHz, CDCl₃) δ 166.1, 161.1 (d, $J = 247.2$ Hz), 131.6 (d, $J = 3.7$ Hz), 129.8 (d, $J = 8.2$ Hz), 124.4 (d, $J = 3.8$ Hz), 119.5 (d, $J = 15.8$ Hz), 115.6 (d, $J = 21.6$ Hz), 35.4 (d, $J = 3.1$ Hz) ppm.

$^{19}$F ($^1$H) NMR (377 MHz, CDCl₃) δ -118.0 ppm.

No spectroscopic data for this compound has been reported before.
Figure S61: $^1$H NMR of the crude mixture from electrolysis of 2-(2-fluorophenyl)acetic acid (1u); 400 MHz, 296 K.

Figure S62: $^{13}$C NMR of the crude mixture from electrolysis of 2-(2-fluorophenyl)acetic acid (1u); 101 MHz, 296 K.
**Figure S63**: Enlarged aromatic region of the $^{13}$C NMR of the crude mixture from electrolysis of 2-(2-fluorophenyl)acetic acid (1u); 101 MHz, 296 K.

**Figure S64**: Enlarged aliphatic region of the $^{13}$C NMR of the crude mixture from electrolysis of 2-(2-fluorophenyl)acetic acid (1u); 101 MHz, 296 K.
**SUPPORTING INFORMATION**

Figure S65: $^{19}$F ($^1$H) NMR of the crude mixture from electrolysis of 2-(2-fluorophenyl)acetic acid (1u); 377 MHz, 296 K.

**2-(4-(Trifluoromethyl)phenyl)acetic Anhydride (2v)**

Following general procedure A, electrolysis of 2-(4-(trifluoromethyl)phenyl)acetic acid (1v, 98%, 729 mg, 3.5 mmol, 0.70 m) at 80 mA/cm$^2$ with KSCN (49 mg, 0.10 m) as supporting electrolyte in MeCN (5.0 mL) gave 2-(4-(trifluoromethyl)phenyl)acetic anhydride (2v) in 20% yield and 37% selectivity (54% conversion) after 1.1 F (ISTD: 42.0 mg 1,3,5-trimethoxybenzene (98.0%).)

$^1$H NMR The signals overlap partially with 2-(4-(trifluoromethyl)phenyl)acetic acid (1v).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 166.1, 135.9, 129.9, 125.8 (q, $J = 3.9$ Hz), 41.7 ppm; The signals of the remaining carbon atoms overlap with 2-(4-(trifluoromethyl)phenyl)acetic acid (1v).

$^{19}$F ($^1$H) NMR (376 MHz, CDCl$_3$) $\delta$ -63.9 ppm.

The analytic data is in agreement with previously reported data.$^{[18]}$
Figure S66: $^1$H NMR of the crude mixture from electrolysis of 2-(4-(trifluoromethyl)phenyl)acetic acid (1v); 400 MHz, 296 K.

Figure S67: $^{13}$C NMR of the crude mixture from electrolysis of 2-(4-(trifluoromethyl)phenyl)acetic acid (1v); 101 MHz, 296 K.
Figure S68: $^{19}$F ($^1$H) NMR of the crude mixture from electrolysis of 2-(4-(trifluoromethyl)phenyl)acetic acid (1v); 376 MHz, 296 K.

Oleic Anhydride (2w)

Following general procedure A, electrolysis of oleic acid (1w, 99.0%, 0.48 mL, 1.5 mmol, 0.50 M) at 30 mA/cm² and 313 K with EMIMSCN (187 mg, 0.35 M) as supporting electrolyte in MeCN/EtOAc 2:1 (v/v, 3.0 mL) gave oleic anhydride (2w) in 16% yield and 48% selectivity (34% conversion) after 1.1 F (ISTD: 23.9 mg 1,3,5-trimethoxybenzene (98.0%)). For analytic purposes, the residual electrolyte of two different experiments was combined and filtered through a mixture of silica (ca. 4 g) and K₂CO₃ (ca. 1 g) on a p4 frit. The silica layer was rinsed with 60 mL cyclohexane, and the filtrate was washed with cold aqueous K₂CO₃ (0.1 M, 20 mL). The organic phase was dried with MgSO₄ and the solvent was evaporated to give a mixture of oleic anhydride (2w), traces of oleic acid (1w), and 1,3,5-trimethoxybenzene.

$^1$H NMR (400 MHz, CDCl₃) δ 2.44 (t, $J = 7.4$ Hz, 4H) ppm; The signals of the remaining protons overlap with oleic acid (1x).

$^{13}$C NMR (101 MHz, CDCl₃) δ 169.7, 130.2, 129.8, 35.4, 32.1, 29.9, 29.8, 29.7, 29.5, 29.5, 29.2, 29.2, 29.0, 27.4, 27.3, 24.4, 22.8, 14.3 ppm.

No spectroscopic data for this compound has been reported before.
Figure S69: $^1$H NMR of the crude mixture from electrolysis of oleic acid (1w); 400 MHz, 298 K.

Figure S70: $^{13}$C NMR of the crude mixture from electrolysis of oleic acid (1w); 101 MHz, 298 K.
**Figure S71:** $^1$H NMR of oleic anhydride (2w) after filtration; 400 MHz, 297 K.

**Figure S72:** $^{13}$C NMR of oleic anhydride (2w) after filtration; 101 MHz, 297 K.
Linoleic Anhydride (2x)

Following general procedure A, electrolysis of linoleic acid (1x, 99%, 555 mg, 2.0 mmol, 0.39 M) at 50 mA/cm² with EMIMSCN (178 mg, 0.20 M) as supporting electrolyte in MeCN/EtOAc 2:1 (v/v, 5.0 mL) gave linoleic anhydride (2x) in 15% yield and 51% selectivity (30% conversion) after 1.3 F (ISTD: 26.2 mg 1,3,5-trimethoxybenzene (98.0%)). For analytic purposes, the residual electrolyte of two different experiments was combined and filtered through a mixture of silica (ca. 4 g) and K₂CO₃ (ca. 1 g) on a p4 frit. The silica layer was rinsed with 60 mL cyclohexane, and the filtrate was washed with cold aqueous K₂CO₃ (0.1 M, 20 mL). The organic phase was dried with MgSO₄ and the solvent was evaporated to give a mixture of linoleic anhydride (2x), traces of linoleic acid (1x), and 1,3,5-trimethoxybenzene.

HRMS (APCI) [m/z] calc’d for C₂₆H₃₃O₅⁺ [M + O₂ + H]⁺, 575.4670; found, 575.4650; deviation: -3.5 ppm; [m/z] calc’d for C₁₈H₃₁O₃⁺ [(M - linoleate) + O₂ + H]⁺, 295.2268; found, 295.2262; deviation: -2.0 ppm; The formation of the postulated hydroperoxide is assumed to happen during the ionization process because the $^{13}$C NMR spectra of the crude reaction mixture did not show a hydroperoxide signal.

$^{1}H$ NMR (400 MHz, CDCl₃) δ 5.44 – 5.27 (m, 8H), 2.77 (t, $J = 6.2$ Hz, 4H), 2.44 (t, $J = 7.4$ Hz, 2H), 2.05 (q, $J = 6.8$ Hz, 8H), 1.72 – 1.59 (m, 4H), 1.38 – 1.26 (m, 30H), 0.89 (t, $J = 6.8$ Hz, 6H) ppm.

$^{13}C$ NMR (101 MHz, CDCl₃) δ 169.7, 130.4, 130.1, 128.2, 128.0, 35.4, 31.7, 29.7, 29.5, 29.2, 29.0, 27.3, 27.3, 25.8, 24.3, 22.7, 14.2 ppm.

The analytic data is in agreement with previously reported data.[19]

![Figure S73: $^{1}H$ NMR of the crude mixture from electrolysis of linoleic acid (1x); 600 MHz, 294 K.](image-url)
Figure S74: $^1$H NMR of linoleic anhydride (2x) after filtration; 400 MHz, 297 K.

Figure S75: $^{13}$C NMR of linoleic anhydride (2x) after filtration; 101 MHz, 297 K.
**Supporting Information**

**N-Benzyltrifluoroacetamide (3y)**

Following general procedure A, electrolysis of trifluoroacetic acid (1y, 100%, 0.27 mL, 3.5 mmol, 0.70 M) at 50 mA/cm² with KSCN (49 mg, 0.10 M) as supporting electrolyte in anhydrous MeCN (5.0 mL) gave trifluoroacetic anhydride (2y) after 1.1 F. Because of its fast hydrolysis, the anhydride 2y was directly converted to an amide in the electrolysis vessel. Benzylamine (100%, 0.38 mL, 3.5 mmol, 0.99 eqs.) was added and the mixture was stirred for 18 h. 2 N Hydrochloric acid was added, and the mixture was extracted with EtOAc. The organic phase was washed with saturated aqueous NaHCO₃ and dried with MgSO₄. The residue was chromatographed on silica to give 120.9 mg (34%) N-benzyltrifluoroacetamide (3y) as white solid.

\[ ^{1}H \text{ NMR (400 MHz, CDCl}_3 \delta 7.39 - 7.28 (m, 3H), 7.28 - 7.20 (m, 2H), 6.72 (s, 1H), 4.48 (d, J = 5.8 Hz, 2H) ppm.} \]

\[ ^{13}C \text{ NMR (101 MHz, CDCl}_3 \delta 157.3 (q, J = 37.0 Hz), 136.0, 129.2, 128.4, 128.1, 116.0 (q, J = 287.8 Hz), 44.0 ppm.} \]

\[ ^{19}F \text{ NMR (377 MHz, CDCl}_3 \delta -77.0 ppm.} \]

The analytic data is in agreement with previously reported data.[20]

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**Figure S76:** \(^{1}H\) NMR of \(N\)-benzyltrifluoroacetamide (3y); 400 MHz, 296 K.
Figure S77: $^{13}$C NMR of $N$-benzyltrifluoroacetamide (3y); 101 MHz, 296 K.

Figure S78: $^{19}$F NMR of $N$-benzyltrifluoroacetamide (3y); 377 MHz, 296 K.
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Author Contributions

A. P. H. discovered the reaction, performed the experiments, and supervised the project. B. R. S. performed experiments for the optimization and the scope. V. K. and J. S. helped with initial experimental work. A. P. H. and S. R. W. analyzed the data, and A. P. H., D. P. and S. R. W. wrote the manuscript.