Supplementary Information (SI) for Green Chemistry.
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Supporting Information

On the use of propylene carbonate and dimethyl carbonate as green solvents in organic electrosynthesis

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Content

1 General

The chemicals and solvents were purchased from commercial suppliers and were used without further purification unless mentioned otherwise. BU_4NBF_4 has been purchased from Carbolution and purified by precipitation from ethyl acetate with heptane and recrystallisation in water/ethanol.

NMR spectra were recorded on an Agilent Technologies 400-MR spectrometer at room temperature (400 MHz) or AV-III HD 300 (Bruker) also at room temperature (300 MHz). The chemical shifts (δ) are given in ppm relative to the NMR solvent signal. For estimation of NMR yields, mesitylene was used as internal standard.

GC-MS was carried out on a Shimadzu GC-2010 gas chromatograph with the mass detector GCMS-QP2010. The used column is a quartz capillary column (30 m x 250 µm x 0.25 µm) HP-5 supplied by Agilent using hydrogen as the carrier gas.

2 Physicochemical analysis

2.1 Polarity measurements

Polarities of solvent and electrolyte mixtures have been determined UV-vis-spectroscopically using Reichhardt's dye Betaine 30. Spectra were recorded using an Ava Spec 2048 fiber optical UV-vis spectrometer equipped with an Ava Light-DH-S-BAL light source. The spectra of pure propylene carbonate (PC) and dimethyl carbonate (DMC) are shown exemplarily below. For each medium *m*, the $E_T(30, m)$ value was calculated from the absorption maximum λ_{max} of the corresponding UV-vis spectrum according to the following equation.[1]

$$E_T(30, m) = 28591/\lambda_{max} \tag{1}$$

The $E_T(30, m)$ value was converted to E_{T}^{N} using the following relationship. The boundaries of this empirical scale are defined by water (E_{T}^{N}=1) and tetramethylsilane ($E_{\text{T}}^{\text{N}} = 0$).

$$E_{\text{T}}^{\text{N}} = [E_T(30, m) - 30.7]/32.4 \tag{2}$$

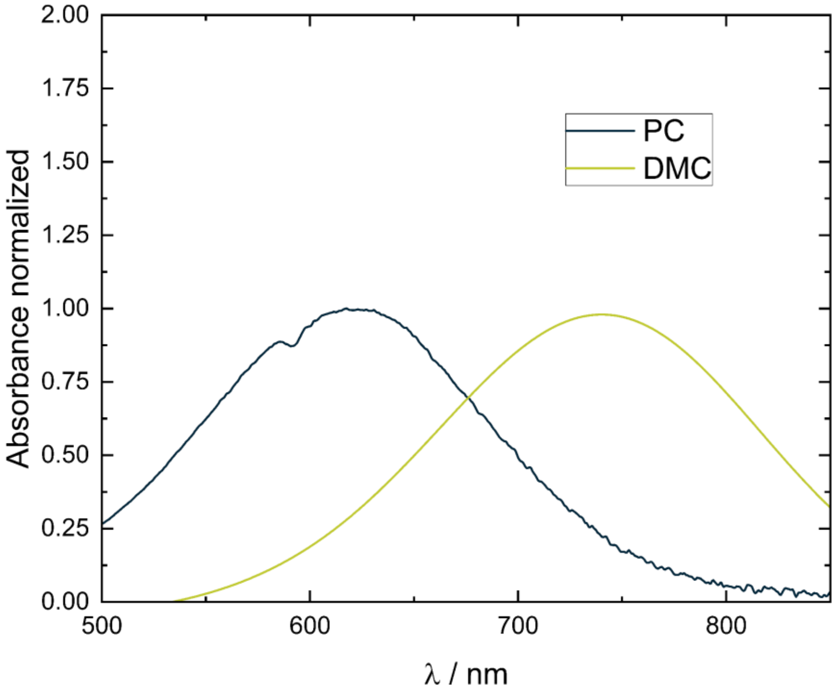

Figure S1: Normalized UV-vis spectra of Betaine 30 in propylene carbonate (PC) and dimethyl carbonate (DMC).

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[1] C. Reichardt, *Chem. Rev.*, **1994**, *94*, 2319-2358.

Table S1: Summary of the Polarity determined at 25 °C and different PC-DMC ratios (salt-free and in the presence of Bu_4NBF_4).

m% (PC)	salt-free E_T^0	0.1 M Bu_4NBF_4 E_T^0
0	0.245±0.007	0.390±0.010
10	0.349±0.007	0.402±0.004
20	0.375±0.007	0.407±0.011
30	0.417±0.010	0.417±0.002
40	0.426±0.007	0.431±0.004
60	0.438±0.007	0.447±0.009
80	0.450±0.005	0.460±0.003
100	0.483±0.004	0.490±0.009

2.2 Viscosity measurements

Density and viscosity of the media were measured using an Anton Paar Stabinger DSA 5000M and Lovis viscosimeter, respectively, the latter being equipped with a capillary (diameter: 1.59 mm) and a steel ball. Measurements were carried out with 0.1 M Bu_4NBF_4 solutions and salt-free solvent mixtures at temperatures of 15, 20, 25, 30, 35, and 40°C.

Table S2: Summary of the dynamic viscosities determined at different temperatures and PC-DMC ratios.

m% (PC)	η @ 15 °C [mm s^{-1}]	η @ 20 °C [mm s^{-1}]	η @ 25 °C [mm s^{-1}]	η @ 30 °C [mm s^{-1}]	η @ 35 °C [mm s^{-1}]	η @ 40 °C [mm s^{-1}]
0	3.013	2.697	2.431	2.206	2.013	1.842
10	2.053	1.855	1.691	1.547	1.424	1.317
20	1.479	1.354	1.244	1.151	1.066	0.993
30	1.103	1.018	0.943	0.878	0.819	0.766
40	0.962	0.891	0.828	0.772	0.722	0.678
60	0.841	0.781	0.729	0.682	0.640	0.602
80	0.741	0.690	0.646	0.605	0.570	0.539
100	0.649	0.609	0.571	0.538	0.507	0.480

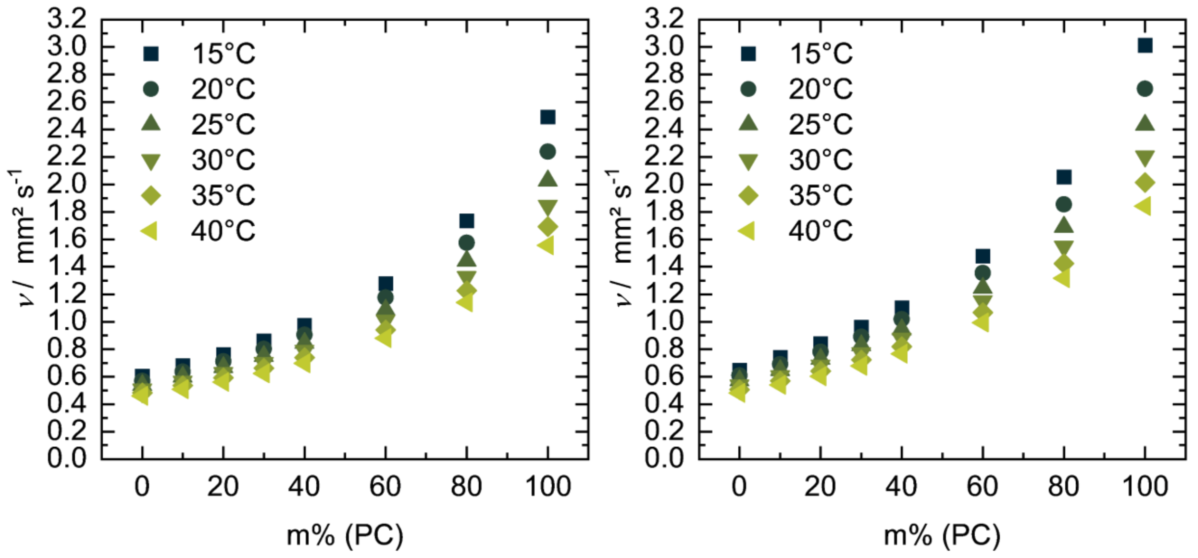

Figure S2: Kinematic viscosity of PC-DMC mixtures at different temperatures without (left) and with 0.1 M Bu_4NBF_4 (right).

Table S3: Summary of the dynamic viscosities determined at 25 °C and different PC-DMC ratios (salt-free and in the presence of Bu_4NBF_4).

m% (PC)	salt-free η [mPa s]	0.1 M Bu_4NBF_4 η [mPa s]
0	2.431	2.625
10	1.691	2.121
20	1.244	1.555
30	0.943	1.074
40	0.828	0.927
60	0.729	0.825
80	0.646	0.737
100	0.571	0.667

2.3 Conductivity measurements

Conductivity measurements were conducted in a temperature controlled glass cell with a Mettler Toledo SevenCompact™ Duo S213 Conductivity Meter. Each solution has been analyzed at least three times.

Table S4: Summary of the ionic conductivities determined at 25 °C and different PC-DMC ratios (0.1 M Bu_4NBF_4).

m% (PC)	0.1 M Bu_4NBF_4 σ [mS cm^{-1}]
0	0.067±0.01
10	0.589±0.02
20	1.521±0.03
30	2.270±0.05
40	2.625±0.03
60	2.839±0.02
80	2.561±0.04
100	2.148±0.02

3 Cyclic voltammetry

3.1 General procedure

The experiments were carried out in a custom-made three-electrode cell using a Vionic potentiostat (Metrohm Autolab). A glassy carbon disk (diameter: 1.6 mm) served as the working electrode and a platinum wire as the counter electrode. The glassy carbon disk was polished using polishing alumina suspension (0.05 µm) prior to each experiment. As reference, a Ag/AgNO$_3$ electrode (silver wire in 0.1 M Bu$_4$NClO$_4$/ CH$_3$CN solution; c(AgNO$_3$) = 0.01 M; E^0 = -87 mV vs. ferrocene/ferrocenium couple)[2] was used, and this compartment was separated from the rest of the cell with a Vycor frit. Bu$_4$NBF$_4$ (0.1 M, electrochemical grade) was employed as supporting electrolyte in different mixtures of propylene carbonate and dimethyl carbonate. The electrolyte was purged with argon for at least 5 min prior to recording. To account for the iR drop at high catalytic currents, positive feedback iR compensation was used. The resistance R was determined by electrochemical impedance spectroscopy prior to each experiment. Background corrections were made by subtracting the blank voltammograms from the CVs of the analytes. Each measurement was conducted at least twice, whereby one CV is shown exemplarily below for each case.

3.2 Determination of electrolyte stability

For determination of the solvent stability, cyclic voltammetry was conducted as described above. Solvents were purchased from Thermo Fischer and Merck (< 99% purity) and used as received. The scan rate was set to 10 mV s^{-1} and multiple scans were carried out. Due to first cycle effects occurring in some solvents, only the second and following cycles were evaluated. The chosen cut-off criterion for defining the boundaries of the electrochemical window is a current density of $|0.1 \text{ mA cm}^{-2}|$.[3]

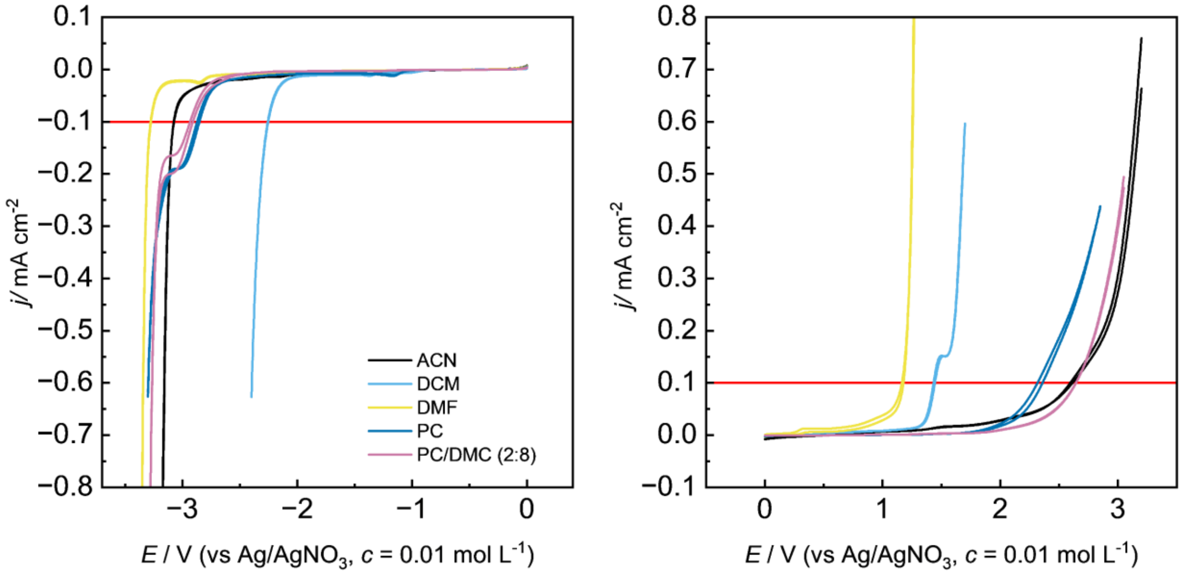

Figure S3: Blank CVs using different solvents in combination with 0.1 M Bu$_4$NBF$_4$ as a supporting electrolyte for determining the electrochemical window at v = 10 mV s^{-1}.

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[2] V. V. Pavlishchuk, A. W. Addison, *Inorg. Chim Acta* **2000**, *298*, 97.

[3] M. Ue, K.Ida, S. Mori, *J. Electrochem. Soc.* **1994**, *141*, 2989.

3.3 Voltammetric analysis of TEMPO under non-catalytic conditions

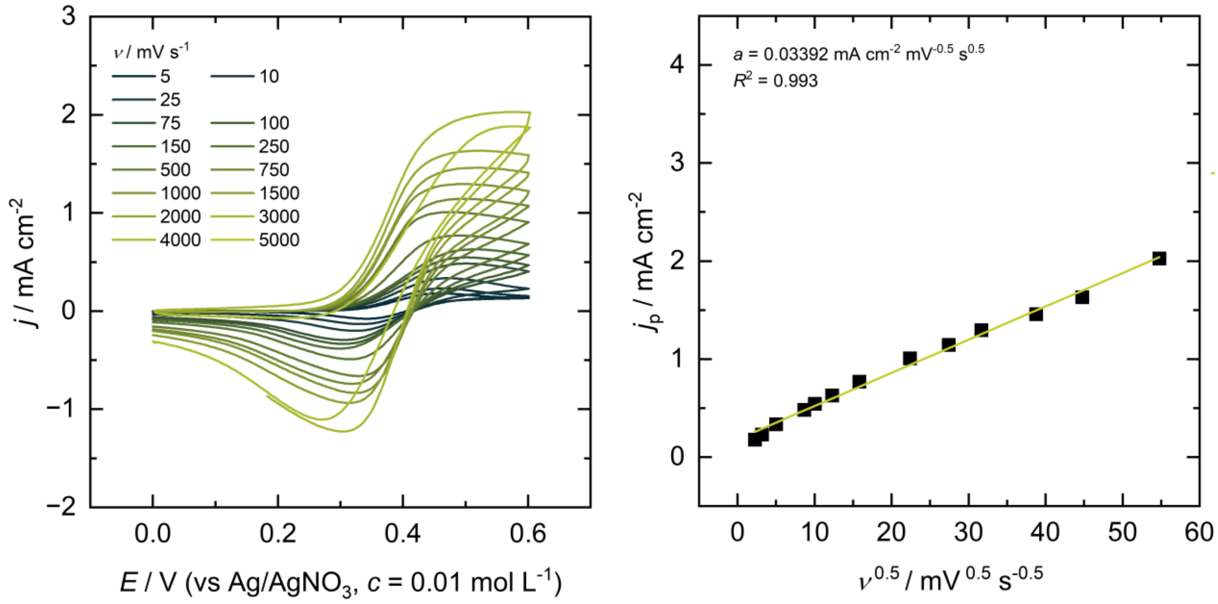

Figure S4. Cyclic voltammetry of 2.5 mM TEMPO in an electrolyte consisting of 0.1 M Bu_4NBF_4 in DMC.

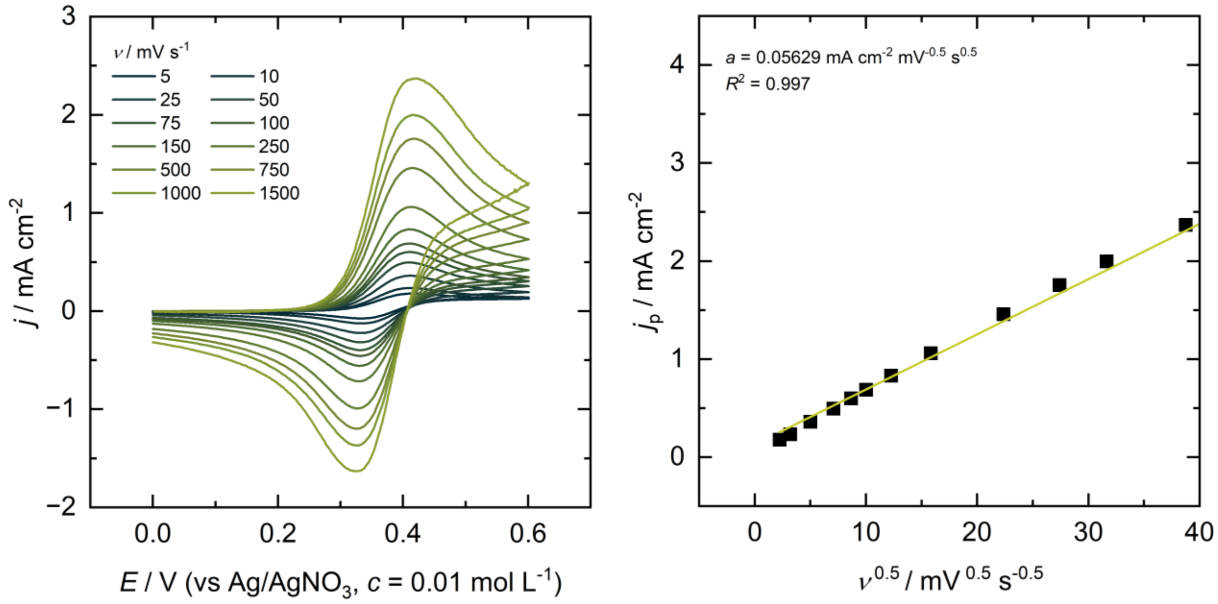

Figure S5: Cyclic voltammetry of 2.5 mM TEMPO in an electrolyte consisting of 0.1 M Bu_4NBF_4 in PC-DMC (9:1, w/w).

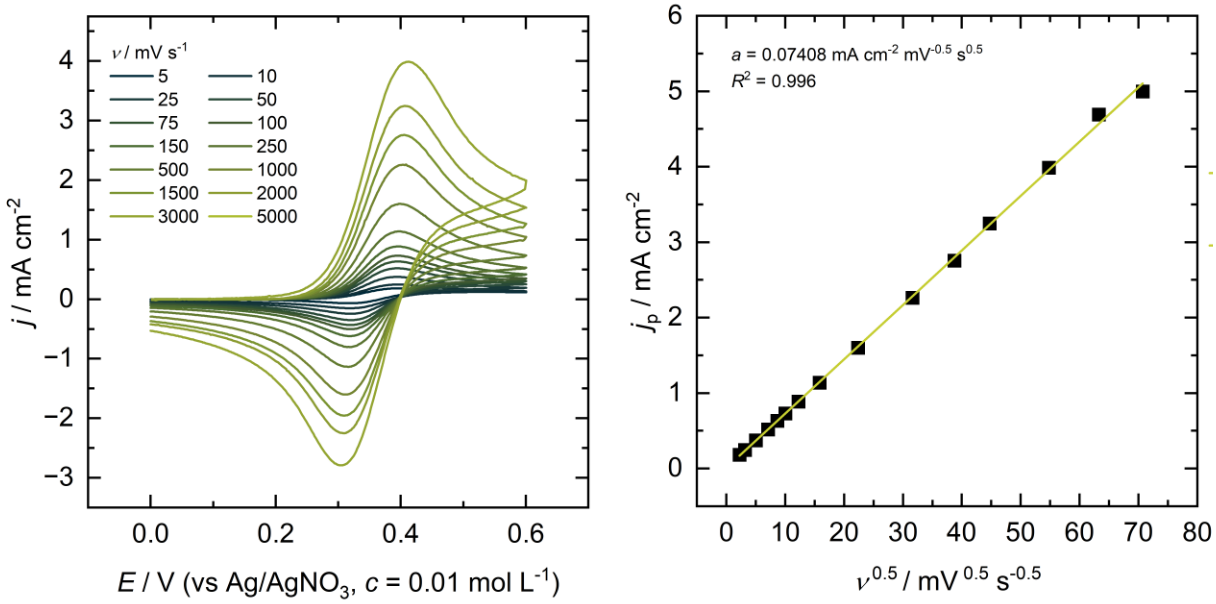

Figure S6: Cyclic voltammetry of 2.5 mM TEMPO in an electrolyte consisting of 0.1 M Bu_4NBF_4 in PC-DMC (2:8, w/w).

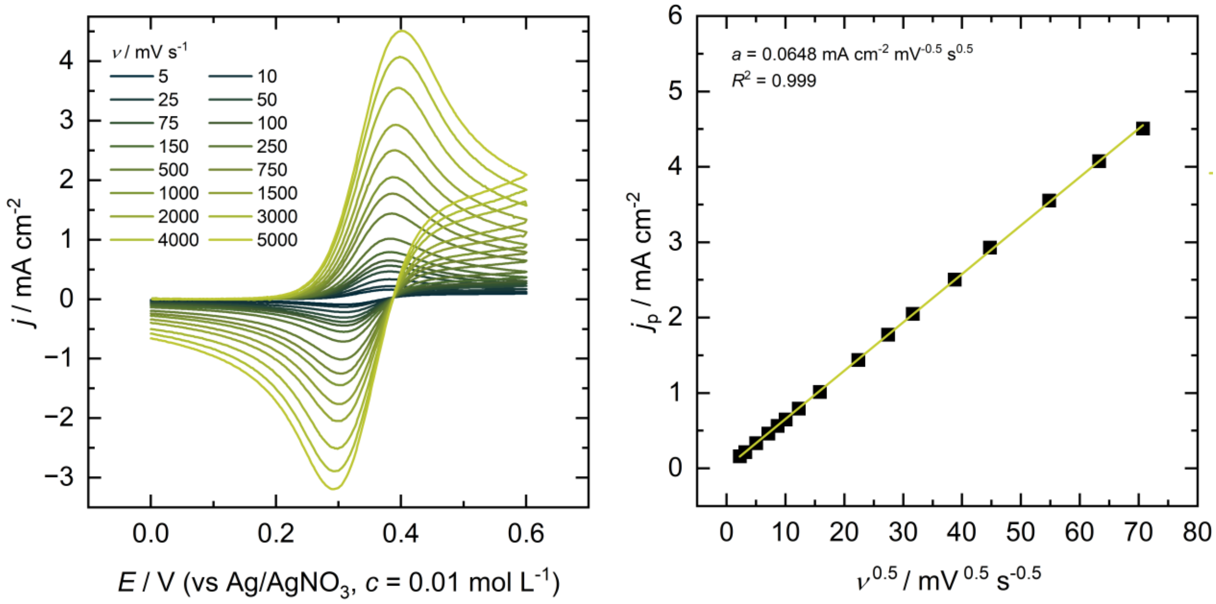

Figure S7: Cyclic voltammetry of 2.5 mM TEMPO in an electrolyte consisting of 0.1 M Bu_4NBF_4 in PC-DMC (3:7, w/w).

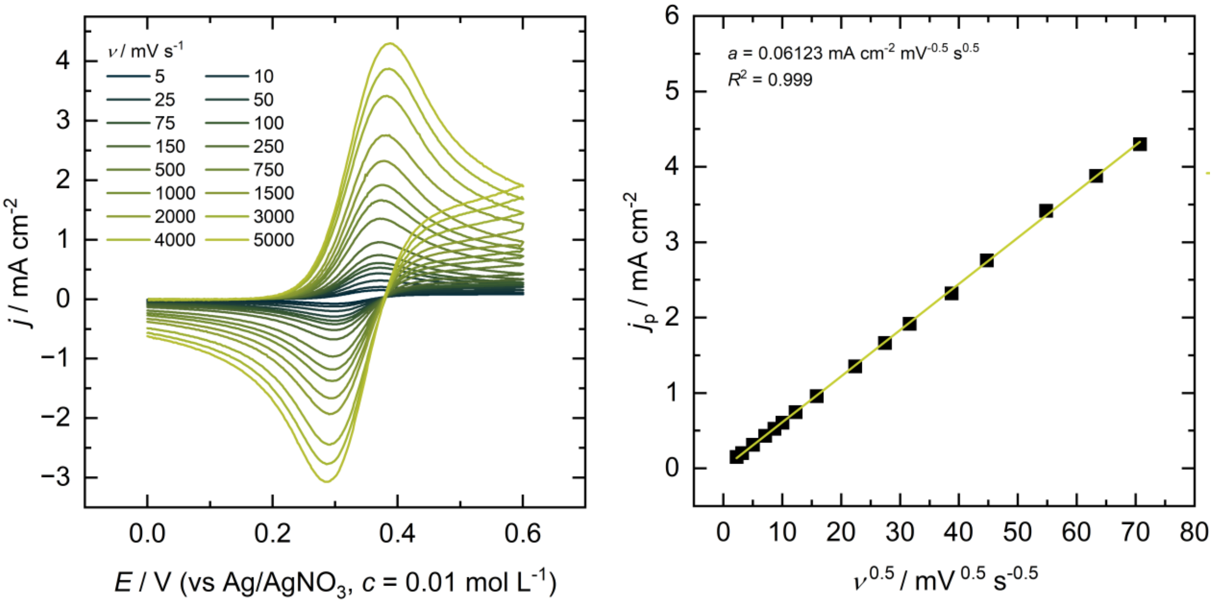

Figure S8: Cyclic voltammetry of 2.5 mM TEMPO in an electrolyte consisting of 0.1 M Bu_4NBF_4 in PC-DMC (4:6, w/w)

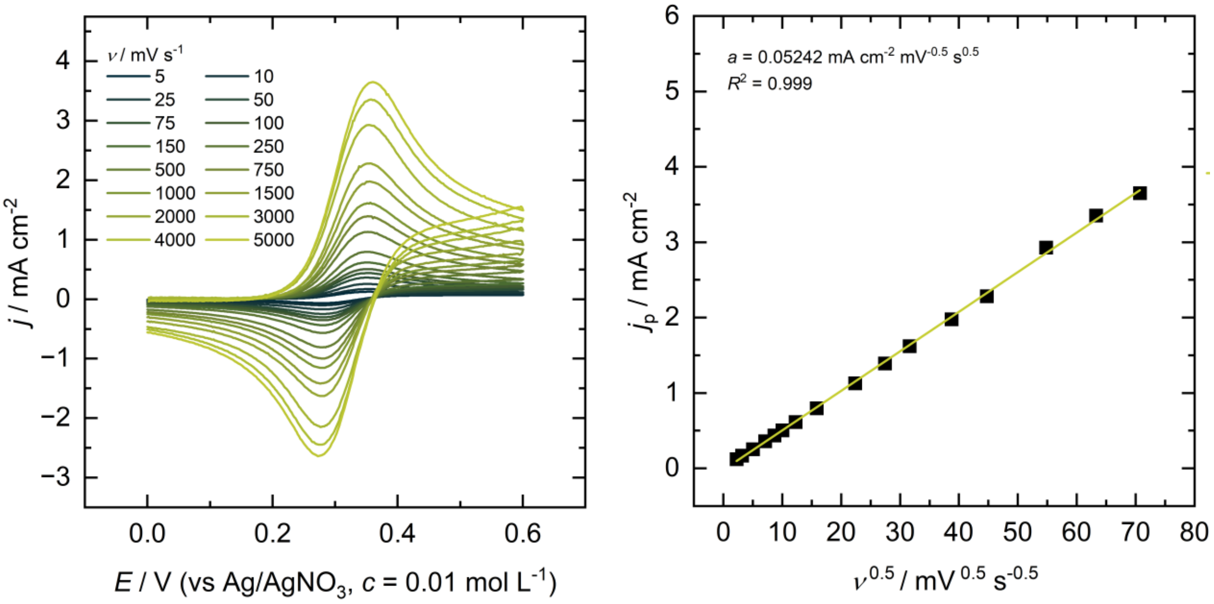

Figure S9: Cyclic voltammetry of 2.5 mM TEMPO in an electrolyte consisting of 0.1 M Bu_4NBF_4 in PC-DMC (6:4, w/w).

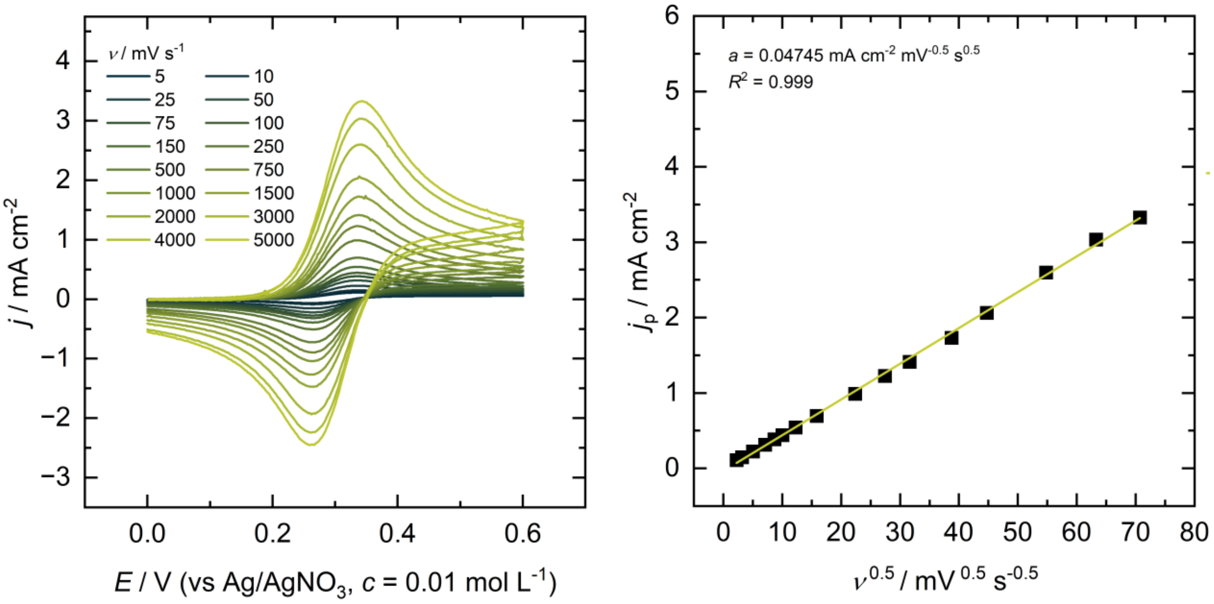

Figure S10: Cyclic voltammetry of 2.5 mM TEMPO in an electrolyte consisting of 0.1 M Bu_4NBF_4 in PC-DMC (8:2, w/w).

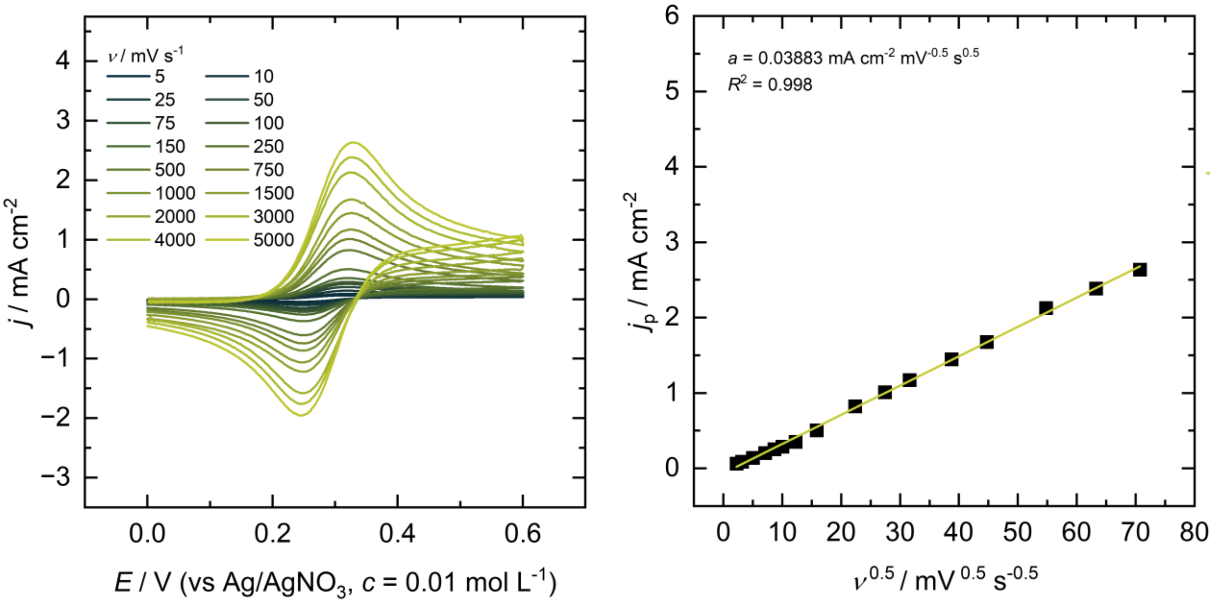

Figure S11: Cyclic voltammetry of 2.5 mM TEMPO in an electrolyte consisting of 0.1 M Bu_4NBF_4 in PC.

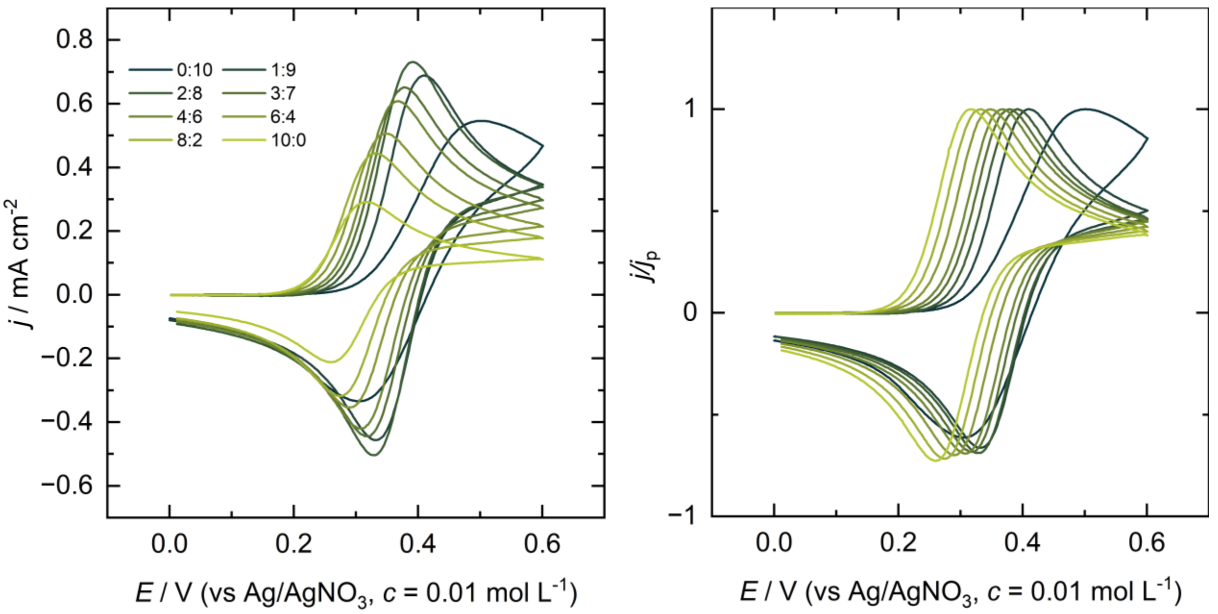

Figure S12. Comparison between the CVs of 2.5 mM TEMPO recorded in different mixtures of PC-DMC at 100 mV s^{-1} (supporting electrolyte: 0.1 M Bu_4NBF_4).

The diffusion coefficients were extracted from the slope of the plot of the peak current densities j_P vs. $v^{0.5}$ according to the Randles-Sevcik equation,[4]

$$j_\mathrm{P} = 0.4463 zFc_\mathrm{T}\sqrt{\frac{zFvD}{RT}} \tag{3}$$

where z is the number of transferred electrons (z = 1), F the Faraday constant, c_T the concentration of TEMPO (2.5 mM in all cases), R the gas constant, v the scan rate, and D the diffusion coefficient. The corresponding slopes, R^2 values, and diffusion coefficients are summarized in Table S5 (see section 3.5). The D values reported in the paper are mean values from these measurements.

3.4 Analysis of TEMPO under non-catalytic conditions

Cyclic voltammetry has been conducted as described in sections 3.1 and 3.3, but in the presence of 4-methoxybenzyl alcohol (4-MBA, c = 0.1 M) and *N*-methyl imidazole (NMI, c = 0.45 M). The concentration of TEMPO was 2.5 mM. As an electrolyte, 0.1 M NBu_4BF_4 was used in various mixtures of PC-DMC. The catalytic response was analyzed in each mixture two times, whereby one CV is shown exemplarily in each case. With increase of the scan rate, plateau formation of the maximum current density (j_P) was observed.[5] The plateau values j_max are summarized in Table S5.

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[4] A. J. Bard, L. R. Faulkner, *Electrochemical Methods. Fundamentals and Applications*, Wiley, 2001.

[5] J.-M. Savéant, C. Costentin, *Elements of Molecular and Biomolecular Electrochemistry: An Electrochemical Approach to Electron Transfer Chemistry*, Wiley, 2019.

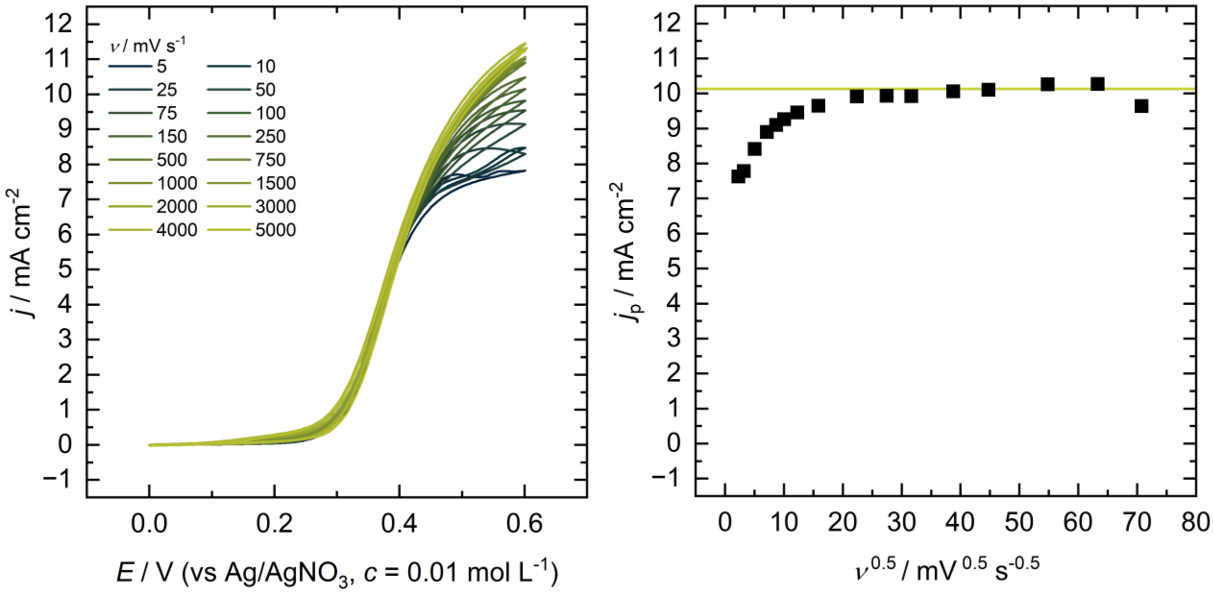


Figure S13: Cyclic voltammetry of 2.5 mM TEMPO with 100 mM 4-MBA and 450 mM 1-NMI in an electrolyte consisting of 0.1 M Bu_4NBF_4 in PC-DMC (1:9).

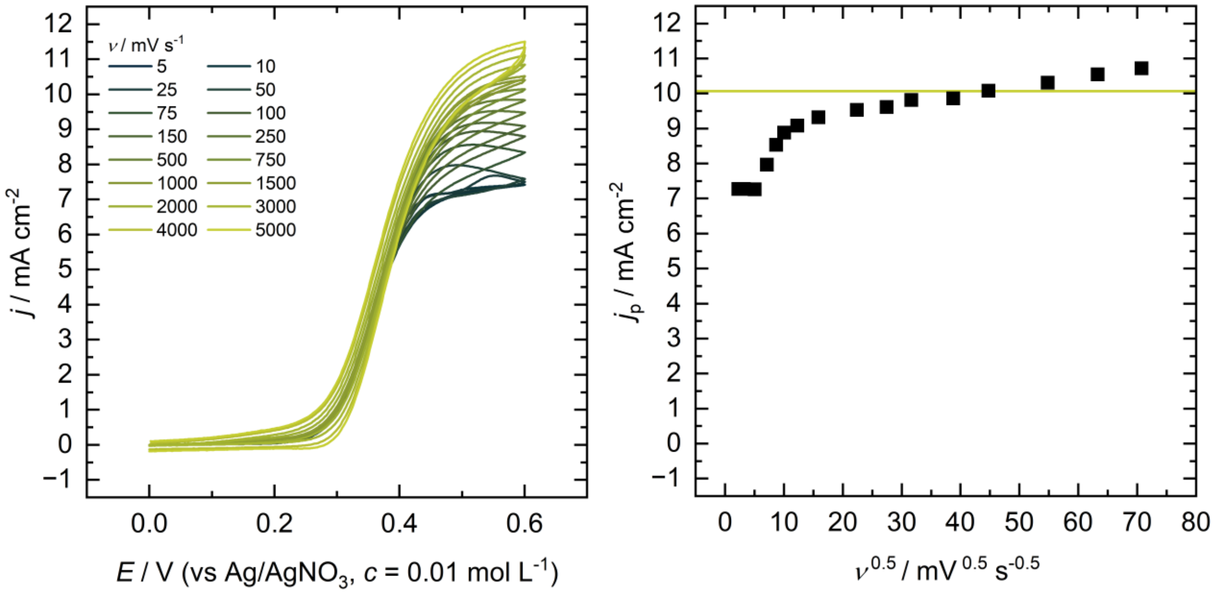


Figure S14: Cyclic voltammetry of 2.5 mM TEMPO with 100 mM 4-MBA and 450 mM 1-NMI in an electrolyte consisting of 0.1 M Bu_4NBF_4 in PC-DMC (2:8).

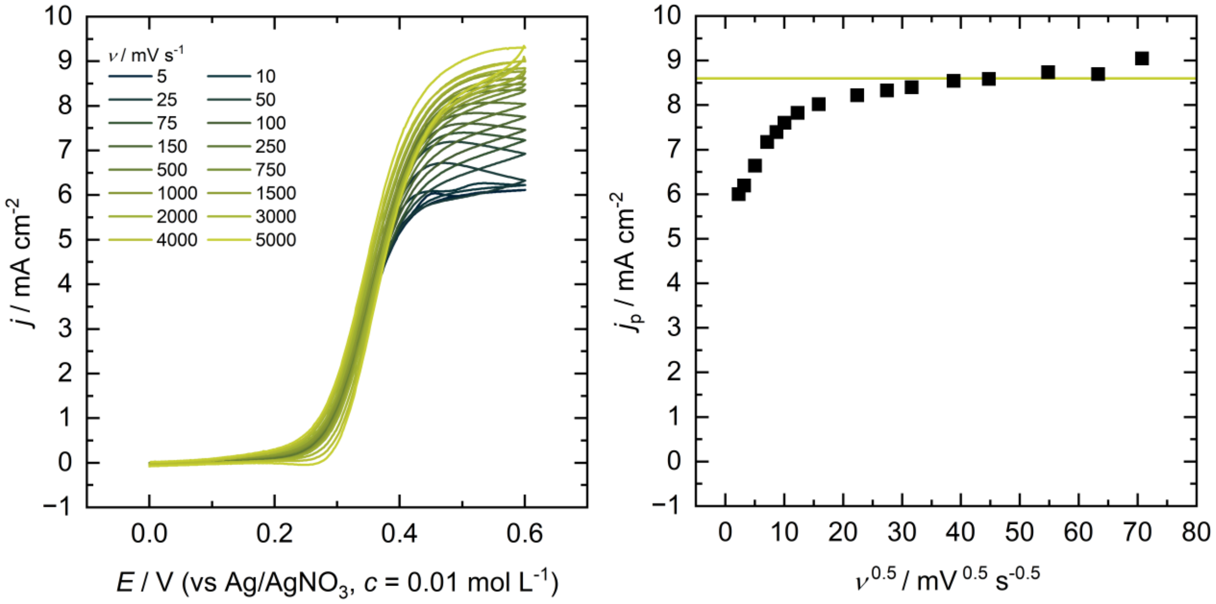


Figure S15: Cyclic voltammetry of 2.5 mM TEMPO with 100 mM 4-MBA and 450 mM 1-NMI in an electrolyte consisting of 0.1 M Bu_4NBF_4 in PC-DMC (3:7).

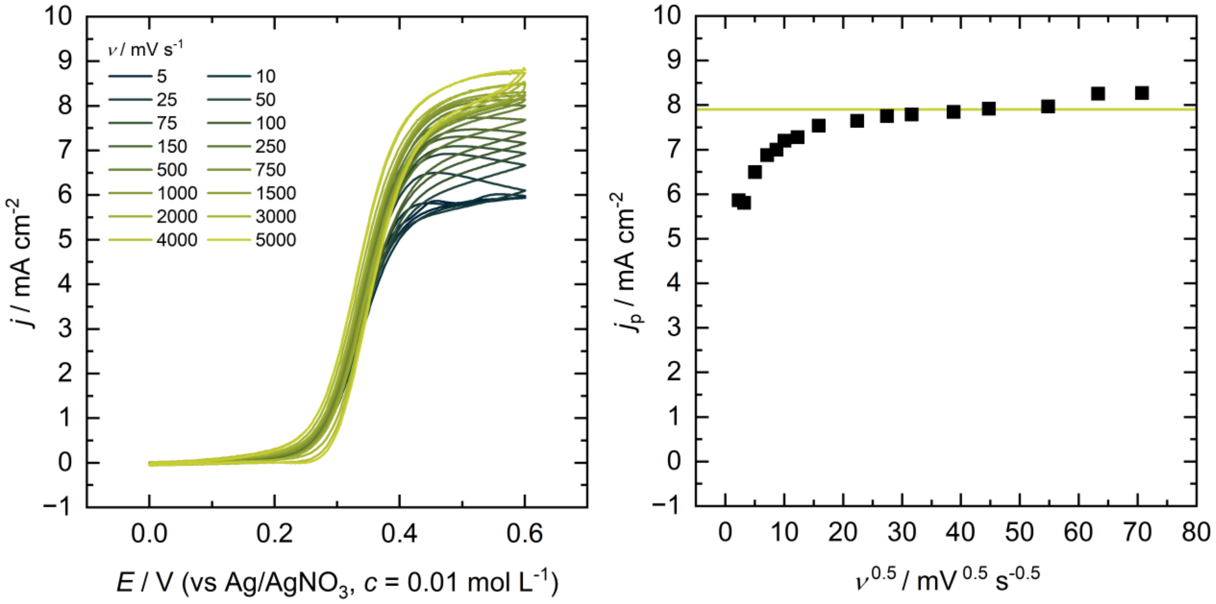


Figure S16: Cyclic voltammetry of 2.5 mM TEMPO with 100 mM 4-MBA and 450 mM 1-NMI in an electrolyte consisting of 0.1 M Bu_4NBF_4 in PC-DMC (4:6).

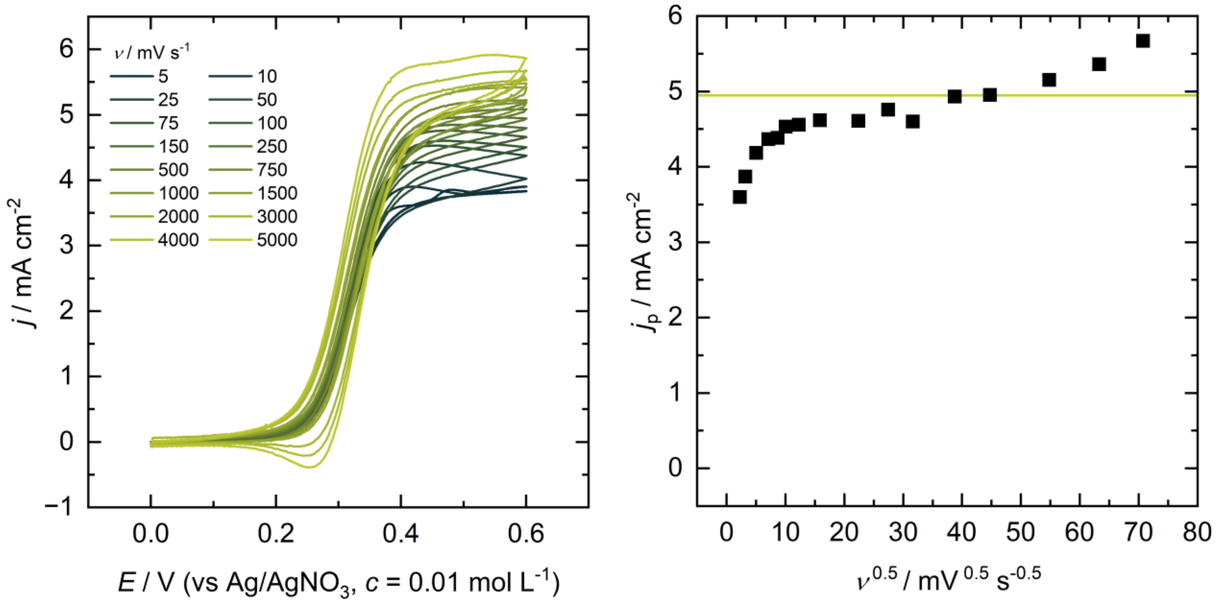


Figure S17: Cyclic voltammetry of 2.5 mM TEMPO with 100 mM 4-MBA and 450 mM 1-NMI in an electrolyte consisting of 0.1 M Bu_4NBF_4 in PC-DMC (6:4).

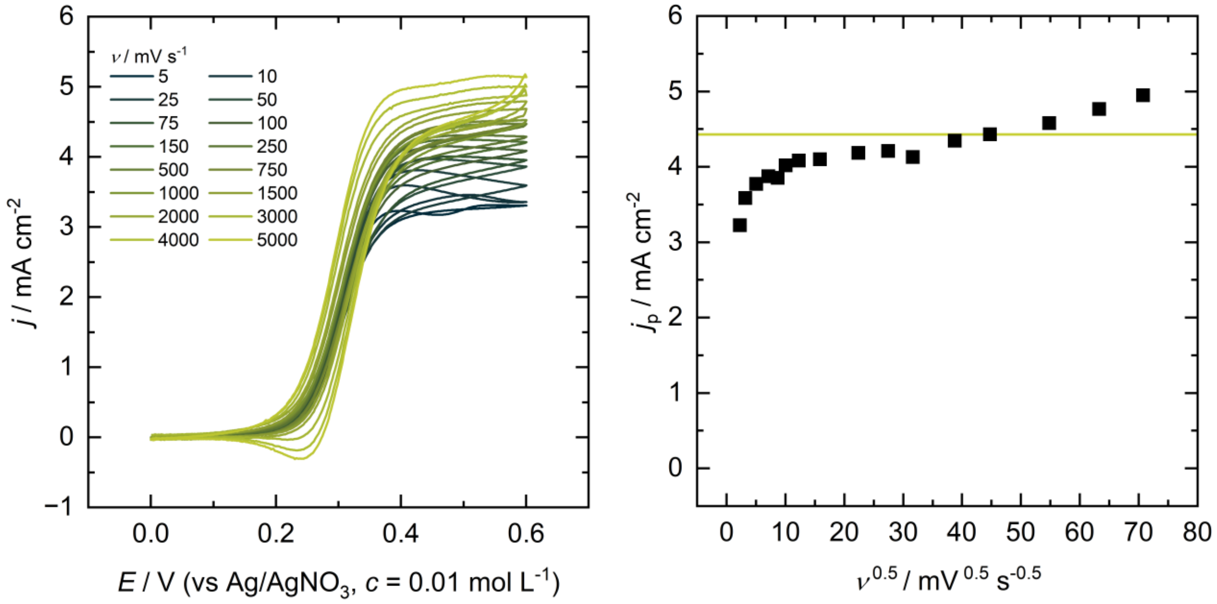


Figure S18: Cyclic voltammetry of 2.5 mM TEMPO with 100 mM 4-MBA and 450 mM 1-NMI in an electrolyte consisting of 0.1 M Bu_4NBF_4 in PC-DMC (8:2).

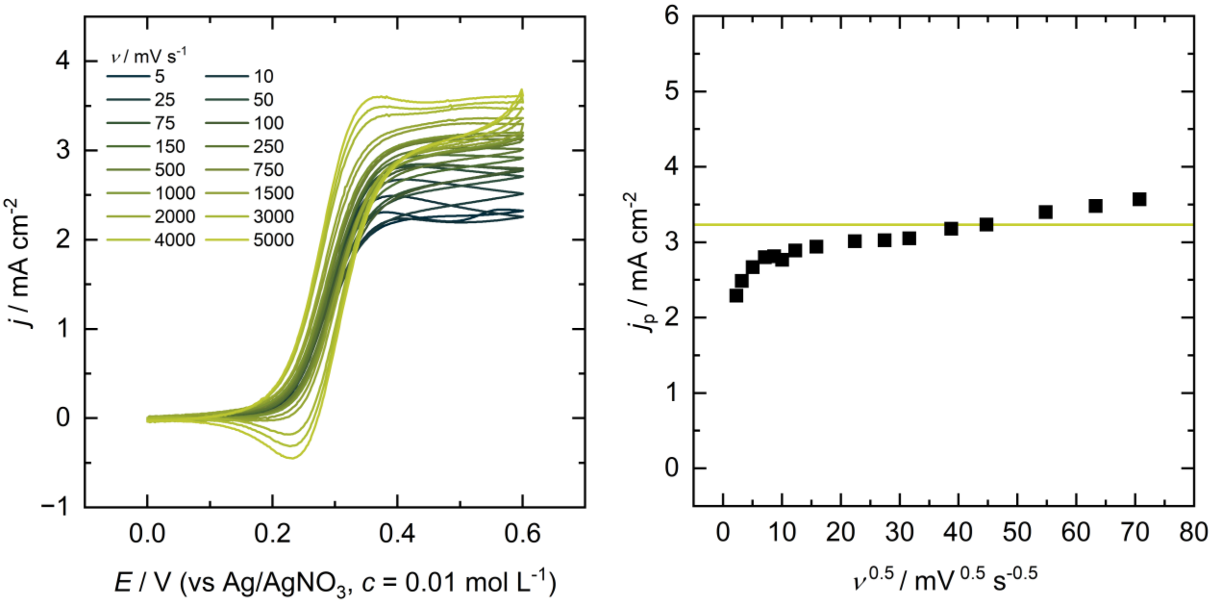


Figure S19: Cyclic voltammetry of 2.5 mM TEMPO with 100 mM 4-MBA and 450 mM 1-NMI in an electrolyte consisting of 0.1 M Bu_4NBF_4 in PC-DMC (10:0).

3.5 Summary of parameters extracted from CV data

Table S5: Summary of the values for D, E_0, and j_{max}, all of them determined using cyclic voltammetry.

PC/DMC (*m*:*m*)	D [m^2 s^{-1}]	a [mA cm^{-2} $mV^{-0.5}$ $s^{0.5}$]	R^2	E_0 [V]	j_{max} [mA cm^{-2}]
0:10	2.55E-10	0.03392	0.9928	0.409	
1:9	7.02E-10	0.05629	0.9976	0.373	10.12
1:9	7.19E-10	0.05697	0.9950	0.377	9.84
2:8	1.21E-09	0.07402	0.9957	0.348	8.89
2:8	1.01E-09	0.06743	0.9997	0.355	10.18
2:8	1.07E-09	0.06932	0.9989	0.362	9.53
2:8	9.82E-10	0.06655	0.9992	0.361	9.27
3:7	9.31E-10	0.64801	0.9998	0.346	8.59
3:7	1.02E-09	0.06791	0.9998	0.339	8.84
4:6	8.31E-10	0.06123	0.9997	0.336	7.92
4:6	7.81E-10	0.05937	0.9996	0.338	7.07
4:6	7.47E-10	0.05804	0.9994	0.34	6.68
6:4	6.09E-10	0.05242	0.9992	0.316	4.95
6:4	6.78E-10	0.05532	0.9994	0.316	5.26
6:4	6.77E-10	0.05527	0.9994	0.323	5.93
8:2	4.99E-10	0.04745	0.9992	0.301	4.43
8:2	4.99E-10	0.04744	0.9988	0.300	3.93
10:0	3.34E-10	0.03883	0.9985	0.285	3.23
10:0	3.28E-10	0.03847	0.9995	0.291	4.59

Table S6: Summary of average values of the parameters reported in Table S5 including standard deviations.

PC/DMC (*m*:*m*)	⌀ D [m² s^{-1}]	⌀ E_0 [V]	⌀ j_{max} [mA cm^{-2}]
0:10	2.55E-10	0.409	
1:9	7.11E-10 ±0.08E-10	0.375 ±0.002	9.977 ±0.140
2:8	10.67E-10 ±0.90E-10	0.356 ±0.005	9.466 ±0.471
3:7	9.77E-10 ±0.46E-10	0.343 ±0.003	8.292 ±0.603
4:6	7.86E-10 ±0.35E-10	0.338 ±0.002	7.223 ±0.519
6:4	6.55E-10 ±0.32E-10	0.318 ±0.003	5.150 ±0.533
8:2	4.99E-10 ±0.00E-10	0.301 ±0.000	3.981 ±0.350
10:0	3.31E-10 ±0.03E-10	0.289 ±0.002	3.707 ±0.622

3.6 Analysis of ferrocene

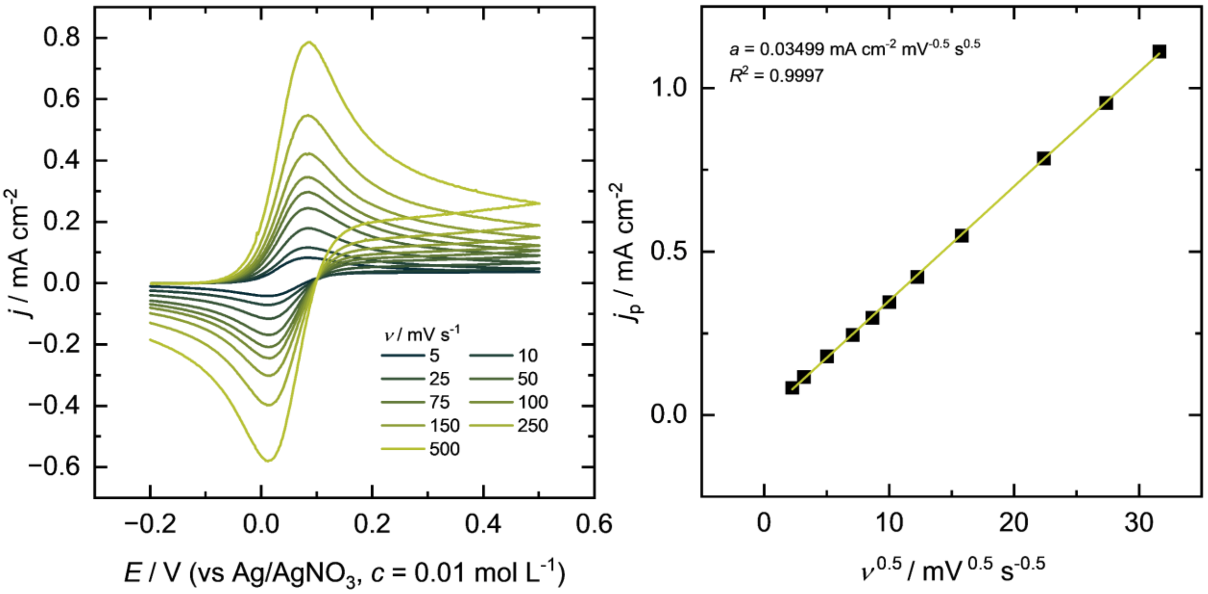


Figure S20: Cyclic voltammetry of 2.5 mM Ferrocene in an electrolyte consisting of 0.1 M Bu_4NBF_4 in PC.

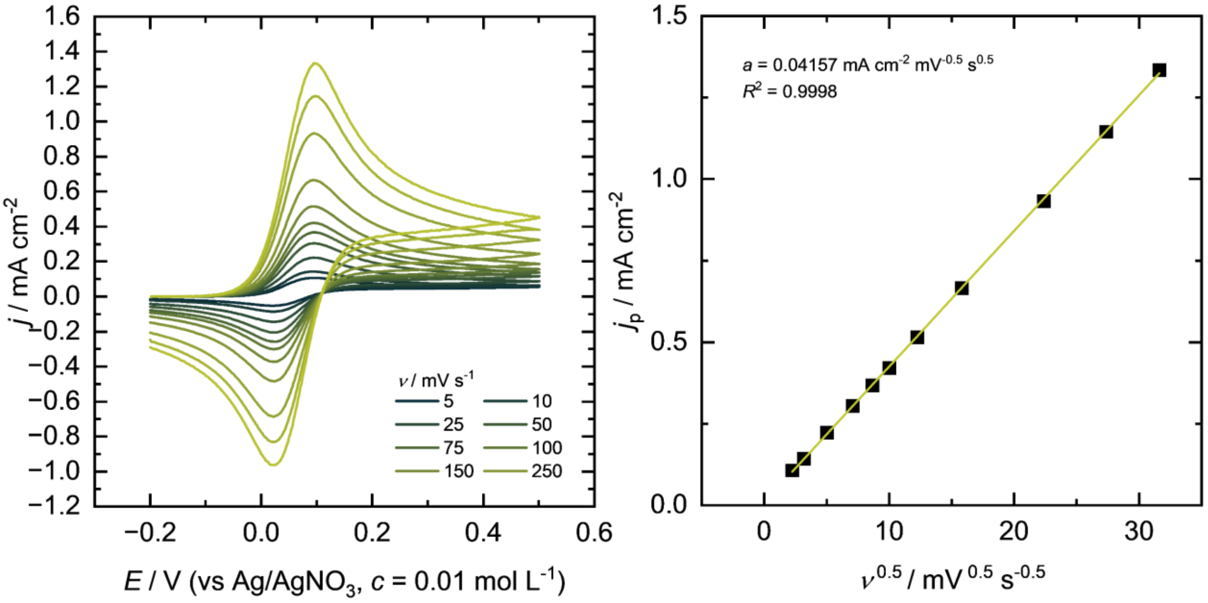


Figure S21: Cyclic voltammetry of 2.5 mM Ferrocene in an electrolyte consisting of 0.1 M Bu_4NBF_4 in PC-DMC (8:2).

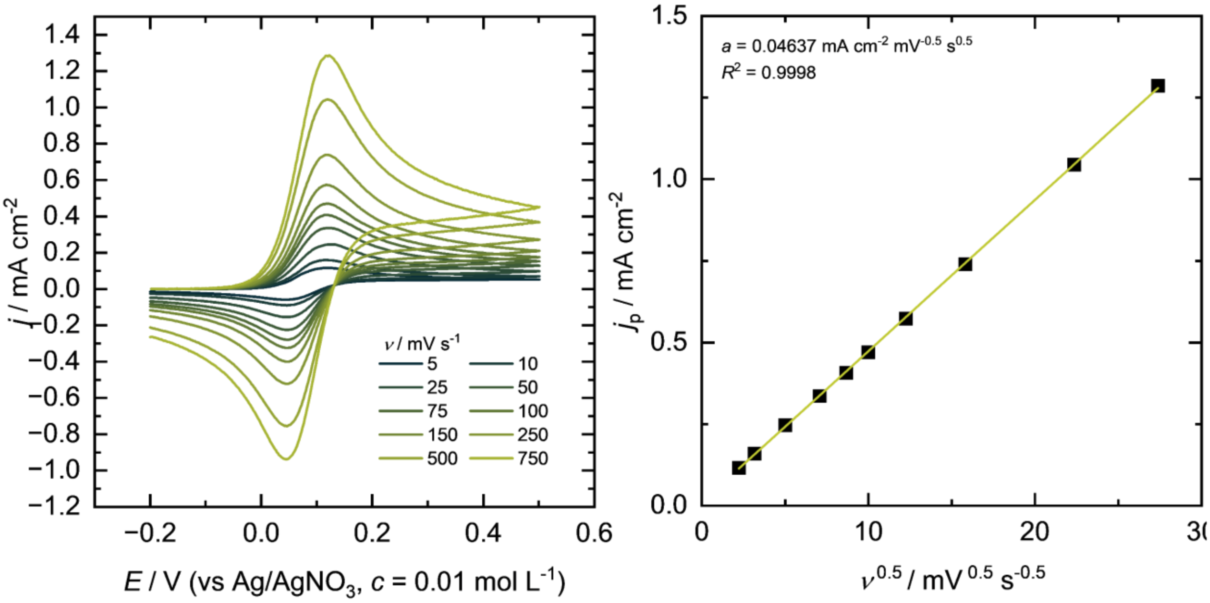


Figure S22: Cyclic voltammetry of 2.5 mM Ferrocene in an electrolyte consisting of 0.1 M Bu_4NBF_4 in PC-DMC (6:4).

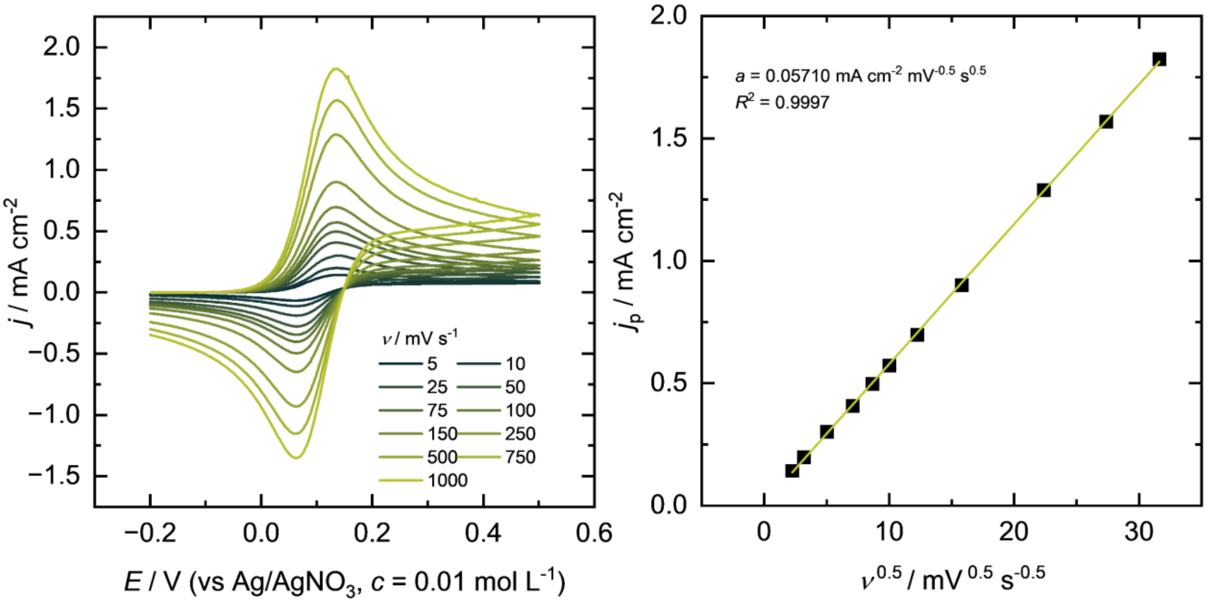


Figure S23: Cyclic voltammetry of 2.5 mM Ferrocene in an electrolyte consisting of 0.1 M Bu_4NBF_4 in PC-DMC (4:6).

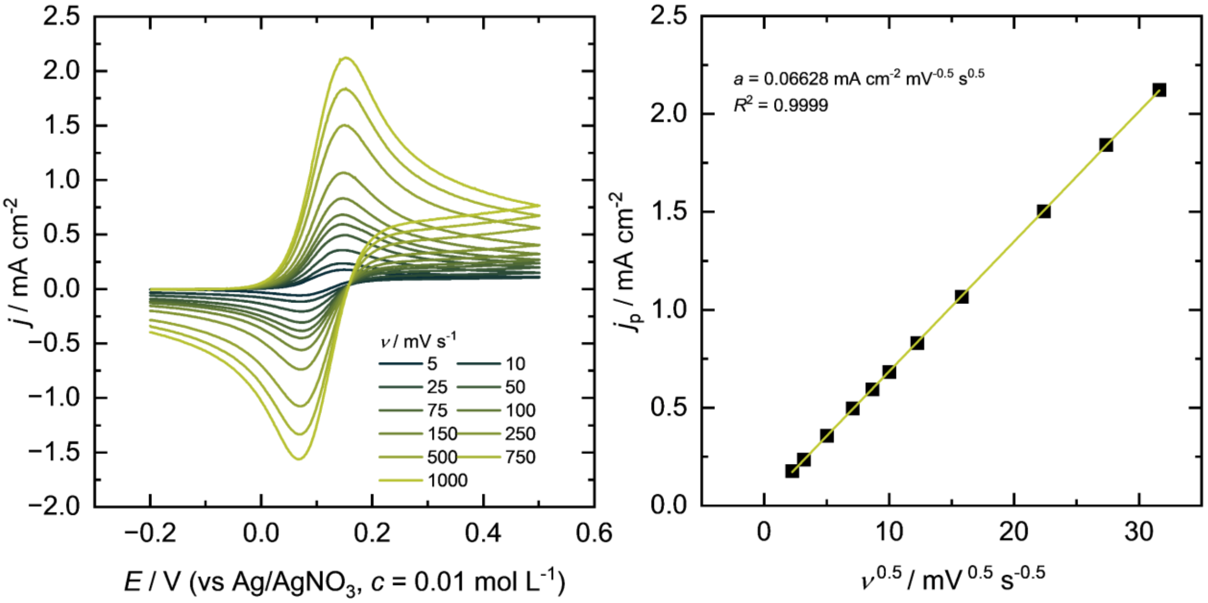


Figure S24: Cyclic voltammetry of 2.5 mM Ferrocene in an electrolyte consisting of 0.1 M Bu_4NBF_4 in PC-DMC (3:7).

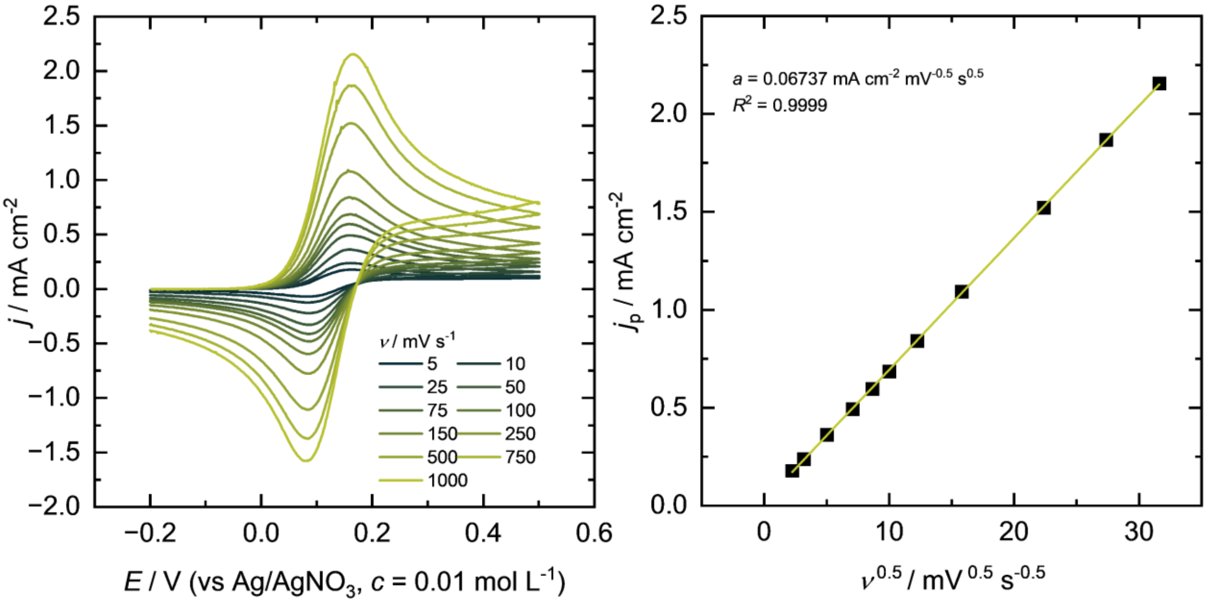


Figure S25: Cyclic voltammetry of 2.5 mM Ferrocene in an electrolyte consisting of 0.1 M Bu_4NBF_4 in PC-DMC (2:8).

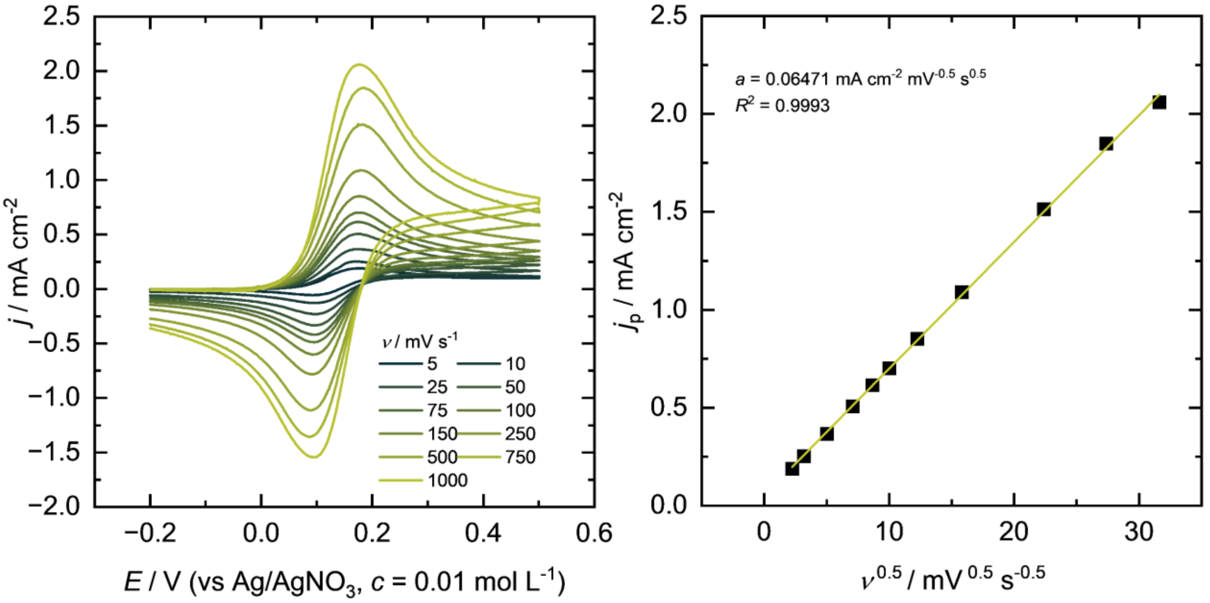


Figure S26: Cyclic voltammetry of 2.5 mM Ferrocene in an electrolyte consisting of 0.1 M Bu_4NBF_4 in PC-DMC (1:9).

3.7 Analysis of benzophenone reduction

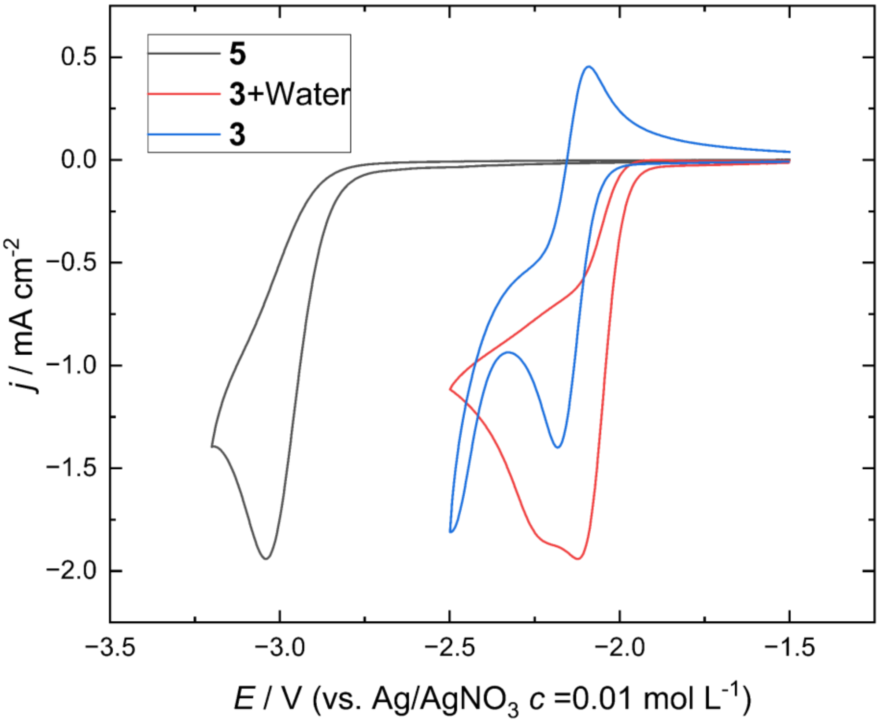


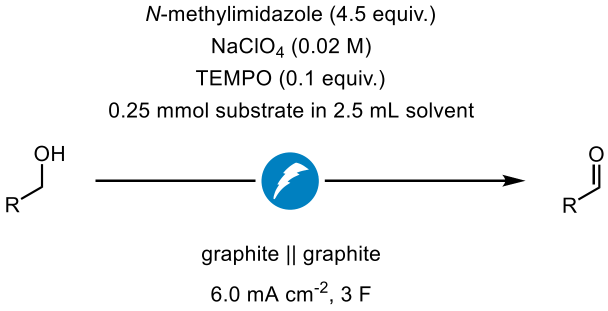
Figure S27: CVs of DPMC (**5**), benzophenone, and benzophenone in the presence of water in PC-DMC (2:8); $c(Bu_4NBF_4)$ = 0.1 M, c(analyte) = 5 mM, $c(H_2O)$ = 0.56 M.

4 Synthetic procedures

4.1 TEMPO-mediated anodic alcohol oxidation

All electrochemical reactions were conducted using an ElectraSyn 2.0 set-up (IKA). Reactions were performed in 5 mL and 10 mL vials purchased from IKA and the stirring rate was kept at 1000 rpm.

4.1.1 General procedure for TEMPO-mediated alcohol oxidations

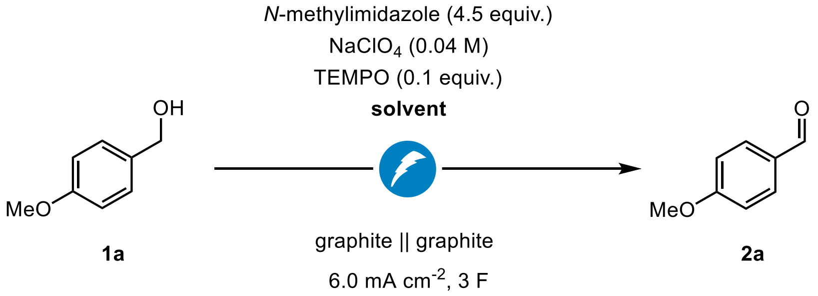


Scheme S1. Standard conditions for TEMPO-mediated alcohol oxidations in an ElectraSyn 2.0 electrolysis set-up.

To a 5 mL ElectraSyn 2.0 vial under ambient conditions, alcohol substrate (0.25 mmol, 1.0 equiv.), *N*-methylimidazole (90 µL, 1.13 mmol, 4.5 equiv.), $NaClO_4$ (12.2 mg, 0.1 mmol, 0.4 equiv., 0.04 M), and TEMPO (3.9 mg, 0.025 mmol, 0.1 equiv.) were directly added as solids or liquids. The reagents were dissolved in the optimized solvent mixture (2.5 mL) and pre-stirred briefly (ca. 5 min) to dissolve all solids prior to electrolysis. The vial was closed with an ElectraSyn 2.0 vial cap equipped with graphite electrodes (both anode and cathode) and placed on an IKA ElectraSyn 2.0 stir plate. Electrolysis was carried out at ambient temperature at 5 mA (j = 6.0 mA cm^{-2}) passing 3 F per mole starting material. After completion of the reaction, the electrodes were removed and mesitylene (0.25 mmol) was added to the mixture as internal standard for product quantification *via* ^{1}H NMR analysis in DMSO-d_6.

4.1.2 Solvent Optimization

A screening of different solvent mixtures using 4-methoxybenzyl alcohol (**1**) as the model substrate revealed that a 1:4 ratio (v/v) between PC and DMC affords higher yields compared to AN as traditional solvent (see Scheme S2). Furthermore, the 1:4 ratio showed the lowest cell voltage among the tested PC/DMC ratios.

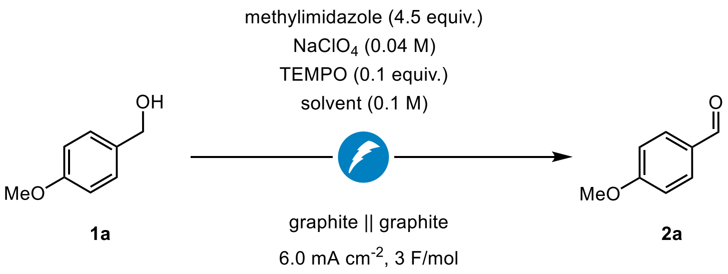


solvent	**ratio**	**average yield of 2a (%)**[a]
MeCN	-	47 ± 5.5
PC	-	71 ± 4.9
PC : DMC	4 : 1	62 ± 14.4
	3 : 2	70 ± 5.4
	1 : 1	61 ± 1.7
	2 : 3	71 ± 4.1
	1 : 4	74 ± 2.6[b]

Scheme S2. Optimization of the solvent ratio (v./v.). ^{1}H NMR yield of desired aldehyde **2** determined against mesitylene as internal standard. [a] All reactions were run in triplicate. [b] Lowest cell voltage.

4.1.3 Control reactions

Several control reactions were performed on the model reaction, to evaluate the influence of applied current, electrode materials, and substituent in position 4 of the TEMPO piperidinyl unit (Scheme S3). In the absence of current, some absorption of the substrate into the electrodes is observed (approx. 10%), but no formation of desired aldehyde **2a** is observed. Substituting graphite electrodes by glassy carbon (GC) electrodes diminished the yield of desired aldehyde **2a**. Substituting graphite electrodes by platinum sheets did not affect the yield. Using 4-acetamido-TEMPO did not improve the yield of the transformation. Carrying out the reaction in acetonitrile, DMF, and DCM, respectively, led to inferior results.

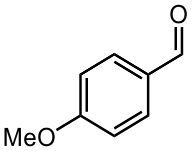


Modification	^{1}H NMR yield of 1a	^{1}H NMR yield of 2a
-	0%	74%
no current	88%	0%
GC || GC	0%	37%
Pt sheet || Pt sheet	0%	74%
4-acetamido-TEMPO	0%	53%
MeCN	0%	51%
MeCN, no current	62%	0%
DMF	0%	46%
DMF, no current	90%	0%
DCM	0%	68%
DCM, no current	100%	0%

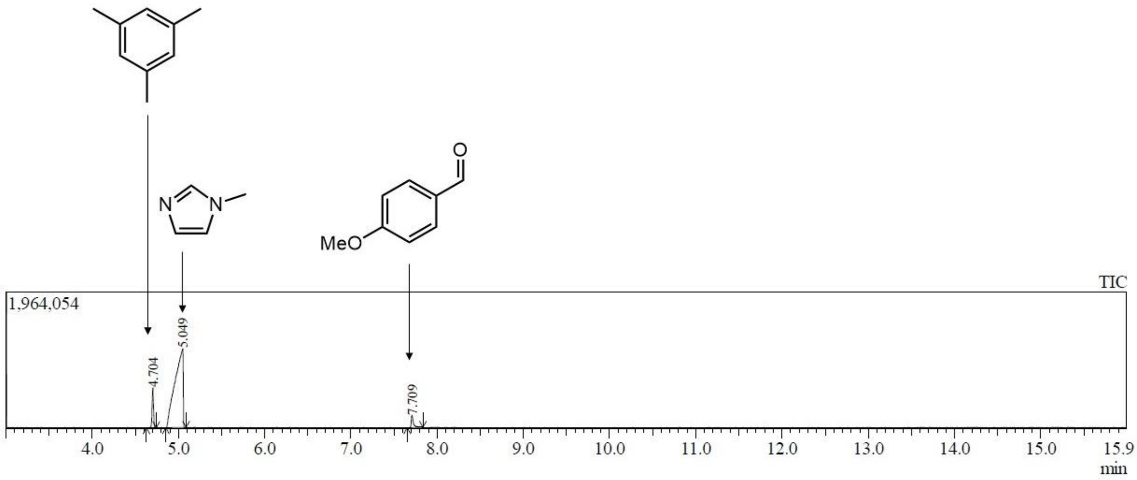
Scheme S3. Control reactions. ^{1}H NMR yield of desired aldehyde **2** determined against mesitylene as internal standard.

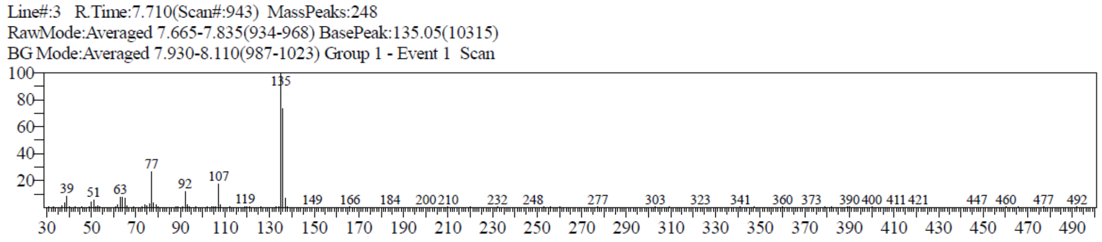
4.1.4 Substrate scope

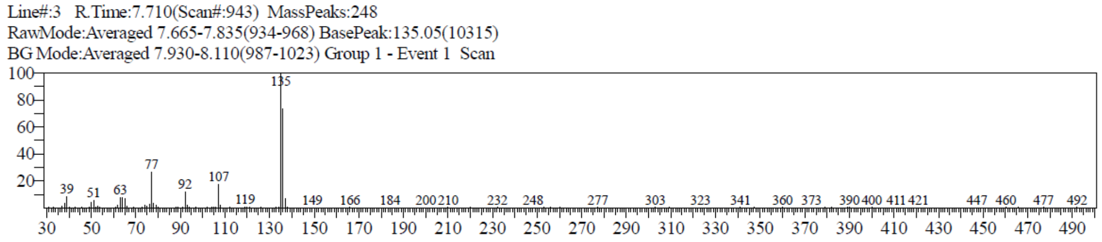
4-Methoxybenzaldehyde (2a)



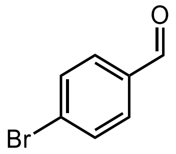
Following the general procedure, conversion of 4-methoxybenzyl alcohol (34.5 mg, 0.25 mmol, 1.0 equiv.), *N*-methylimidazole (90 µL, 1.125 mmol, 4.5 equiv.), $NaClO_4$ (12.2 mg, 0.4 equiv., 0.02 M), and TEMPO (3.9 mg, 0.025 mmol, 0.1 equiv.) in 1:4 PC-DMC (2.5 mL total volume) afforded compound **2a**. The ^{1}H NMR yield of **2** was determined in DMSO-d_6 against mesitylene as internal standard. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.87 ppm (C*H*O, 74%). GC-MS: R_t = 7.709 min.







4-Bromobenzaldehyde (2b)

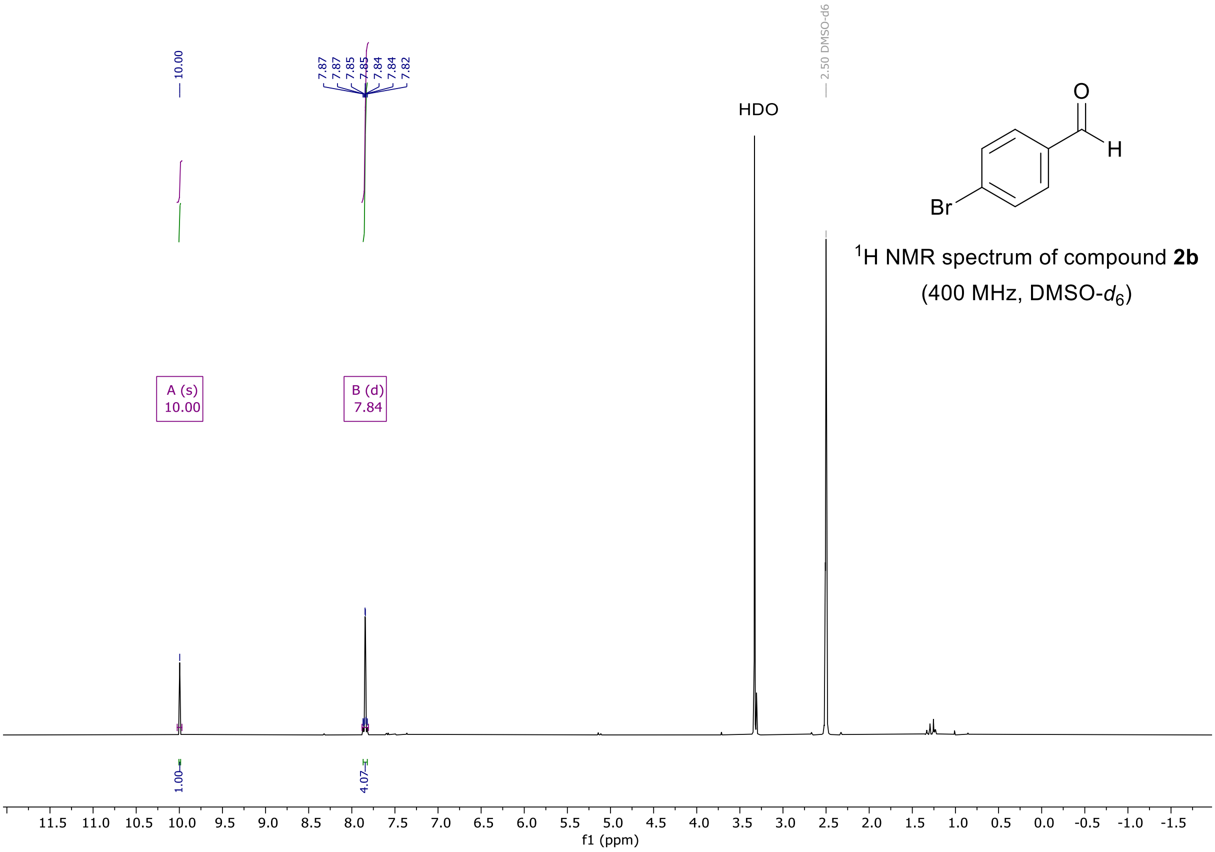


Following the general procedure, conversion of 4-bromobenzyl alcohol (46.8 mg, 0.25 mmol, 1.0 equiv.), *N*-methylimidazole (90 µL, 1.125 mmol, 4.5 equiv.), $NaClO_4$ (12.2 mg, 0.4 equiv., 0.02 M), and TEMPO (3.9 mg, 0.025 mmol, 0.1 equiv.) in PC-DMC (1:4 v/v, 2.5 mL total volume) afforded compound **2b**. The ^1H NMR yield of **2b** was determined in DMSO-d_6 against mesitylene as internal standard. ^1H NMR (400 MHz, DMSO-d_6): δ = 9.99 ppm (C*H*O, 78%).

For isolation of **2b**, another reaction was carried out under optimized conditions on a 0.5 mmol scale in a 10 mL ElectraSyn 2.0 vial (all components of the reaction mixtures were scaled up accordingly). After completed electrolysis, the reaction mixture was transferred into a separation funnel and partitioned by adding saturated aq. $NaHCO_3$ solution and pentane. After shaking vigorously, aqueous and organic layers were separated. The aqueous layer was extracted with pentane two times. The combined organic layers were washed sequentially with saturated aq. $NaHCO_3$, water, and brine. After drying over $MgSO_4$, the mixture was concentrated under reduced pressure using a rotary evaporator. After reducing the volume to about 2 mL, the residue was adsorbed on a short silica plug and eluted with small amounts of diethyl ether. The eluate was concentrated under reduced pressure and dried in vacuum to give the pure product as a colorless solid. Analytical data are in accordance with the literature.[6]

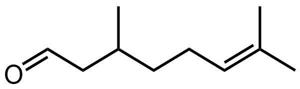
Yield: 70 mg (0.3 mmol, 76%).

^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 10.00 (s, 1H), 7.84 (d, J = 1.5 Hz, 4H).



^{1}H NMR spectrum of compound **2b** (400 MHz, DMSO-d_6)

Citronellal (2c)



Following the general procedure, conversion of citronellol (46 µL, 0.25 mmol, 1.0 equiv.), *N*-methylimidazole (90 µL, 1.125 mmol, 4.5 equiv.), $NaClO_4$ (12.2 mg, 0.4 equiv., 0.02 M), and TEMPO (3.9 mg, 0.025 mmol, 0.1 equiv.) in 1:4 (v/v) PC-DMC (2.5 mL total volume) afforded compound **2c**. The ^{1}H NMR yield of **2c** was determined in DMSO-d_6 against mesitylene as internal standard. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.66 ppm (CHO, 71%). GC-MS: R_t = 6.629 min.

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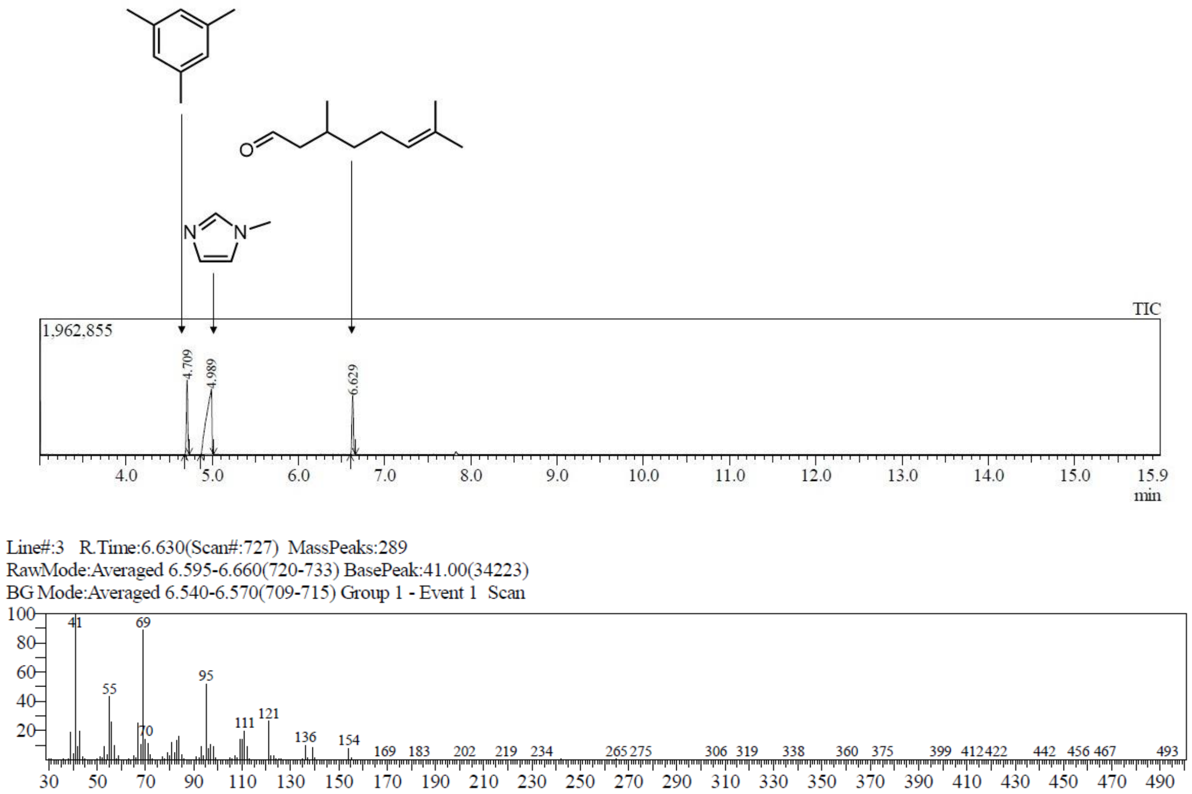
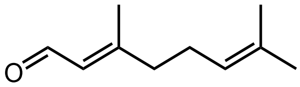
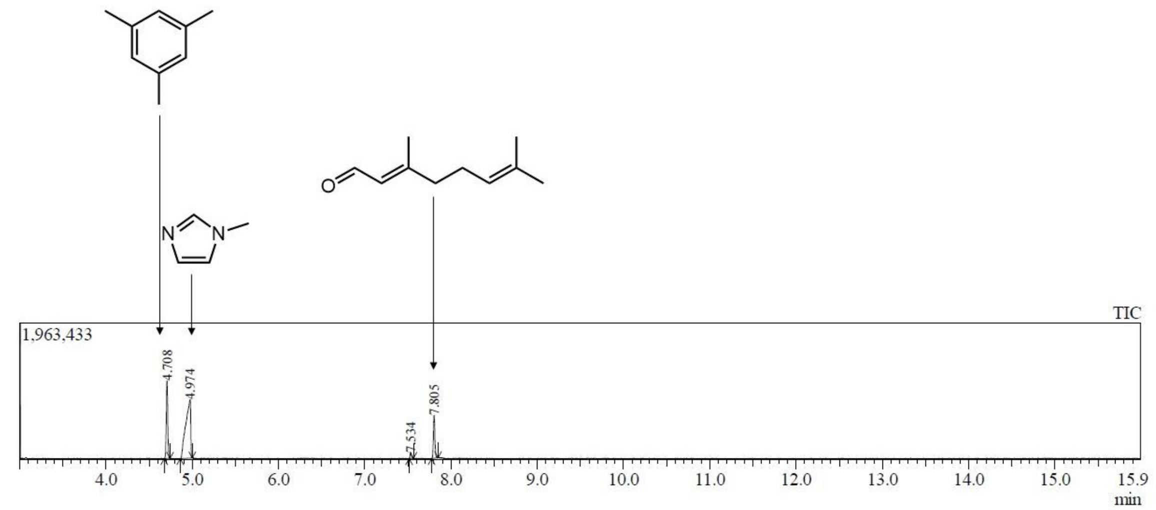
[6] X. Jia, Y. Zhang, P. Zhang, Z. Guo, *Tetrahedron Lett.* **2024**, *142*, 155079.



Geranial (2d)



Following the general procedure, conversion of geraniol (44 µL, 0.25 mmol, 1.0 equiv.), *N*-methylimidazole (90 µL, 1.125 mmol, 4.5 equiv.), $NaClO_4$ (12.2 mg, 0.4 equiv., 0.02 M), and TEMPO (3.9 mg, 0.025 mmol, 0.1 equiv.) in 1:4 (v/v) PC-DMC (2.5 mL total volume) afforded compound **2d**. The ^{1}H NMR yield of **2d** was determined in DMSO-d_6 against mesitylene as internal standard. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.94 ppm (C*H*O, 67%). GC-MS: R_t = 7.805 min.



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RawMode:Averaged 7.775-7.845(956-970) BasePeak:69.05(41213)
BG Mode:Averaged 7.870-7.905(975-982) Group 1 - Event 1  Scan
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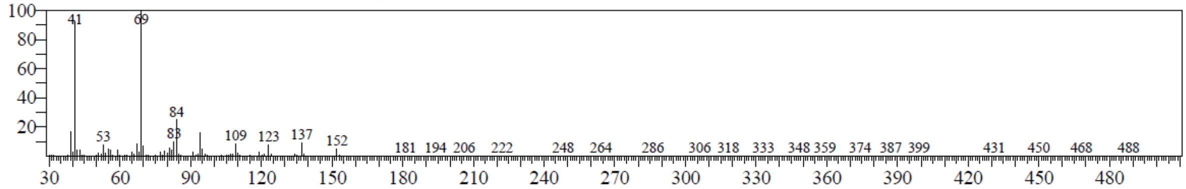

4.2 Cathodic reduction of benzophenone

The reactions were carried out at room temperature under stirring in an undivided cell using a Vionic Potentiostat (Metrohm). Two glassy carbon plates (7 cm x 1 cm x 3 mm, immersion depth: 1 cm, immersed surface area: 1 cm^2), both aligned in parallel to each other (interelectrode distance: 1.5 cm), were used as anode and as cathode, respectively. Solutions of 0.1 M NBu_4BF_4 (5 mL) in various mixtures of PC and DMC served as the electrolyte. Substrate and additives were added as described in Table S7. The yields were determined with ^1H NMR spectroscopy (internal standard: 1,3,5-trimethoxy benzene, added after electrolysis).

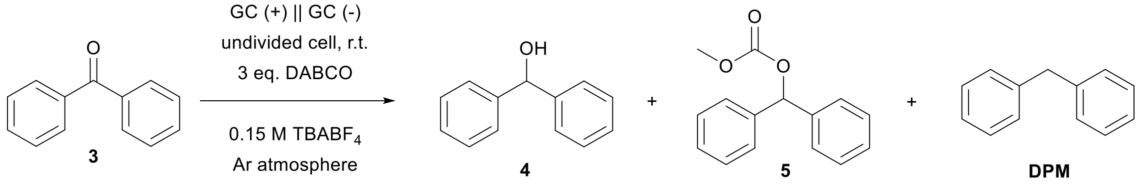

Table S7. Results of cathodic reduction of benzophenone in different solvents using an undivided cell. Working electrode: GC, counter electrode: GC, *n*(substrate) = 0.5 mmol, *c*(Bu_4NBF_4) = 0.12 M, *n*(DABCO) = 1.5 mmol (3 equiv.).

j [mA cm^{-2}]	medium	charge [F]	yield (**4**) [%]	yield (**5**) [%]	Y (**DPM**) [%]	Notes
10	DMF	6.2 F	79	-	-	ref. 7
5	Cyrene™/EtOH (1:1)	3.5 F	85	-	-	ref. 8
7.5	PC/DMC (2:8)	4.0 F	64	8	-	-
5	PC/DMC (2:8)	2.0 F	36	31	-	-
5	PC/DMC (2:8)	3.0 F	59	1	-	-
5	PC/DMC (2:8)	3.5 F	65	5	-	-
5	PC/DMC (2:8)	4.0 F	69	6	-	-
2.5	PC/DMC (2:8)	4.0 F	47	4	-	-
5	PC/DMC (2:8)	4.0 F	61	7	-	-
10	PC/DMC (2:8)	4.0 F	43	4	-	-
7.5	PC	4.0 F	72	0	-	-
7.5	PC/DMC (8:2)	4.0 F	55	4	-	-
7.5	PC/DMC (6:4)	4.0 F	63	6	-	-
7.5	PC/DMC (4:6)	4.0 F	48	5	-	-
7.5	PC/DMC (2:8)	2.2 F	45	32	-	b
7.5	PC/DMC (2:8)	2.2 F	83	-	-	b,c
CPE[a]	PC/DMC (2:8)	2.2 F	79	-	-	b-d
CPE[a]	PC/DMC (2:8)	2.02 F	95	2	-	b,c
7.5	AN/DMC (2:8)	2.2 F	13	46	43	b,e
7.5	AN/DMC (2:8)	2.2 F	15	55	32	b

[a] Controlled potential electrolysis with *E* = -2.20 V vs. Ag/0.01 M $AgNO_3$. [b] Exclusion of O_2 by electrolysis under Ar atmosphere. [c] 50µL water added (*c* = 0.56 M). [d] 6 equiv. triethylamine instead of 3 eq. DABCO. [e] In a control experiment, methylcarbonate species **5** was converted instead of **3**.

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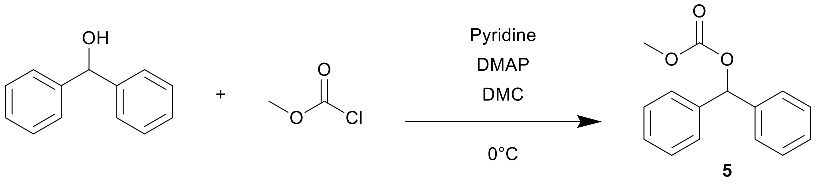
[7] L. Wang, X. Zhang, R. Y. Xia, C. Yang, L. Guo, W. J. Xia, *Synlett* **2022**, *33*, 1302-1308.

[8] J. M. Ramos-Villasenor, J. Sotelo-Gil, S. E. Rodil, B. A. Frontana-Uribe, *Faraday Discuss.* **2023**, *247*, 182-194.

Electrolysis with product isolation (Table 2, entry 6): The electrolysis was carried out under optimized conditions (Table 2, entry 5) but with twofold batch size. Benzophenone (1.0 mmol, 182 mg, 1.0 equiv.), DABCO (3.0 mmol, 336 mg, 3.0 equiv.), and *n*Bu_4BF_4 (1.2 mmol, 395 mg, 1.2 equiv., *c* = 0.12 mol L^{-1}) were placed in the electrolysis cell and dissolved in 10 mL of the solvent mixture (1:4 PC/DMC + 100 µL H_2O). The electrolyte was degassed by purging Ar through the solution for 20 minutes under stirring. The electrolysis was then performed at −2.2 V vs. Ag/0.1 M $AgNO_3$ (for details on the reference electrode, see section 3.1) until 2 F were transferred per mole benzophenone. After completed electrolysis, 10% of the total electrolyte volume was removed for estimation of the ^1H NMR yield (88%). The remaining electrolyte solution was subjected to workup and isolation. First, DMC was removed under reduced pressure using a rotary evaporator, followed by removal of propylene carbonate using a Kugelrohr distillation apparatus (BÜCHI Glass Oven B-585) at 80 °C and 10^{-2} mbar. The oily residue was subjected to flash column chromatography using an eluent mixture of 9:1 *n*-heptane/ethyl acetate. The product was obtained as a colorless solid (143 mg, 0.78 mmol, corresponds to 87% yield with respect to the total electrolyte volume).

Electrolysis of 3 on a 5 mmol scale (Table 2, entry 7): To improve the process mass intensity, the electrolysis was carried out under the conditions described above ("electrolysis with product isolation"), whereby the amount of **3** was increased to 5 mmol (911 mg, 1.0 equiv.) and the amount of DABCO was changed to 11 mmol (1.234 g, 2.2 equiv.). The amount of solvent (10 mL) and supporting electrolyte (*n*Bu_4BF_4, 1.2 mmol, 395 mg, *c* = 0.12 mol L^{-1}) were kept the same. After completed electrolysis, 4% of the electrolyte volume were removed for estimation of the ^1H NMR yield (89%). Product isolation was carried out as described above (728 mg, 3.95 mmol; corresponds to 82% yield with respect to the total electrolyte volume).

Synthesis of methyl carbonate species 5 as reference material



Chloroformate (0.62 mL, 1.1 equiv., 8 mmol) in 2.5 mL of CH_2Cl_2 was added dropwise to a solution of 1.34 g diphenylmethanol (1 equiv., 7.3 mmol), 0.73 mL pyridine (1.25 eq., 9.1 mmol), and 8.7 mg DMAP (0.01 eq., 0.08 mmol) in 4.75 mL CH_2Cl_2 over 30 minutes at 0°C. The solution was allowed to warm up to room temperature and stirred for two hours, followed by addition of water. The resulting layers were separated, and the aqueous layer extracted two times with CH_2Cl_2. The combined organic layers were washed with aqueous 1 M HCl solution and brine. After drying over sodium sulfate, the product was purified by flash chromatography with an eluent containing heptane / ethyl acetate (9:1 v/v). The analytical data are in agreement with the literature.[9]

Yield: 1.29 g (5.84 mmol, 73%).

^1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 3.80 (s, 3H), 6.71 (s, 1H), 7.26–7.40 (m, 10H).

^{13}C NMR (300 MHz, $CDCl_3$): δ (ppm) = 55.1, 81.0, 127.1, 128.3, 128.7, 139.8, 155.3.

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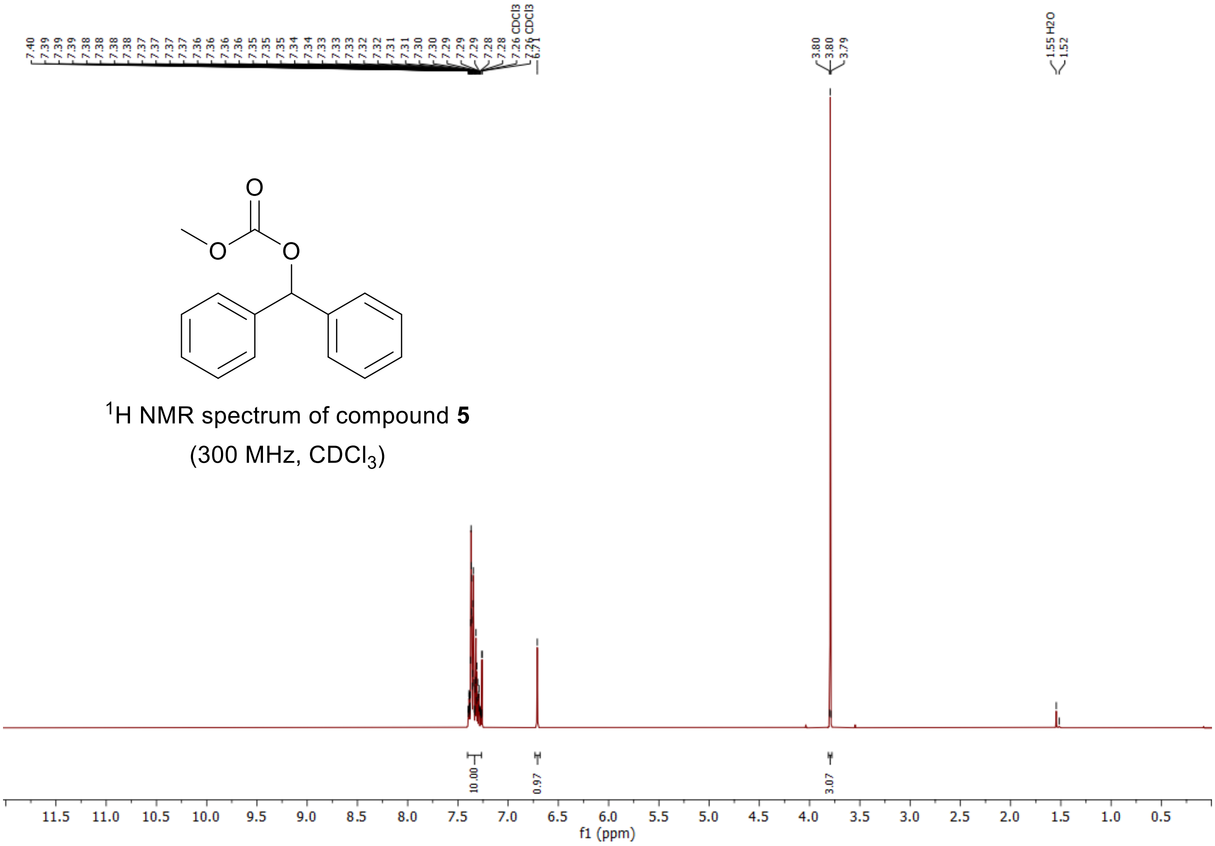
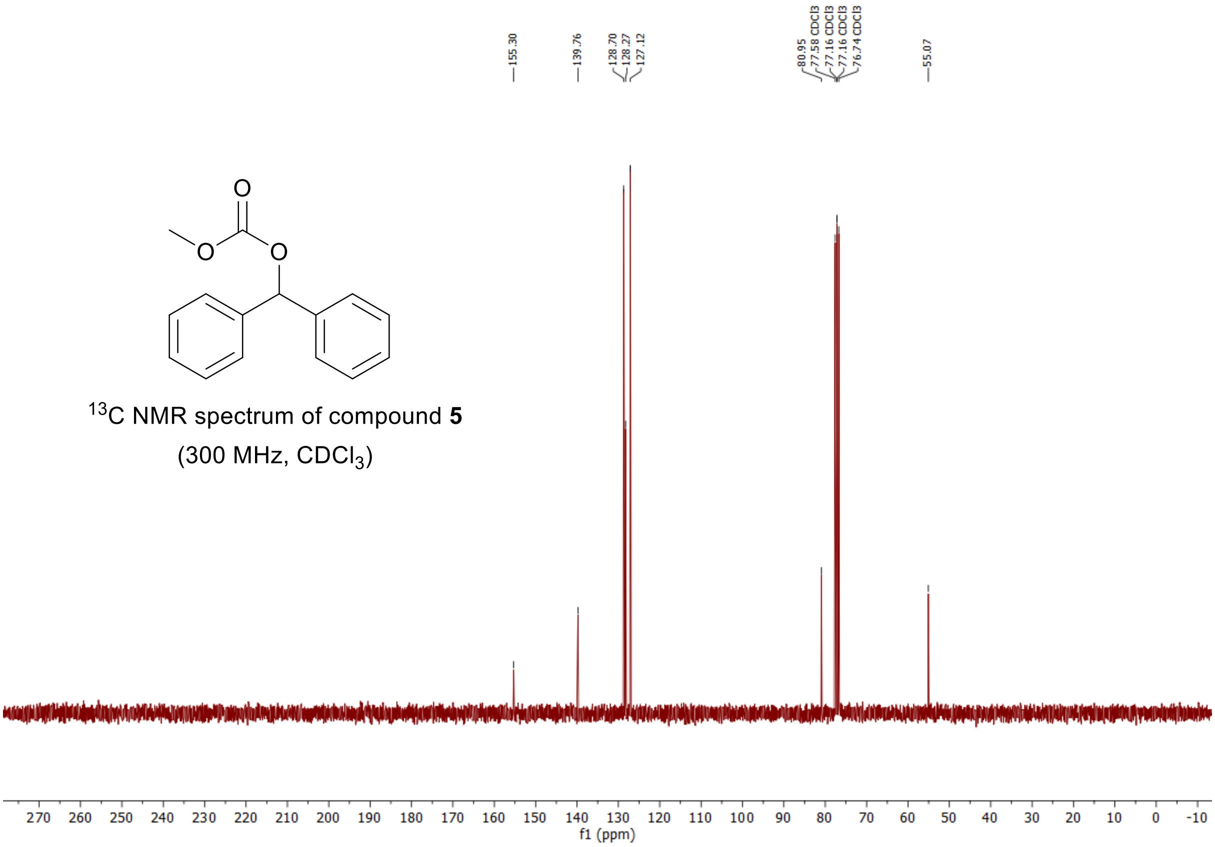
[9] R. Kuwano, H. Kusano, *Chem. Lett.* **2007**, *36*, 528-529.



^{1}H NMR spectrum of compound **5**
(300 MHz, $CDCl_3$)



^{13}C NMR spectrum of compound **5**
(300 MHz, $CDCl_3$)

4.3 Anodic synthesis of diaryliodonium compounds

For the synthesis of diaryliodonium compound **7**, a custom-made divided glass cell was used. A G4 glass frit served as the separator. A Wenking LPG-03 potentiostat-galvanostat was employed as the power source. A platinum sheet (immersion depth: 10 mm x 10 mm) was used as the anode and a glassy carbon plate as the cathode. A 1.0 M solution of $LiClO_4$ in PC-DMC served as the electrolyte, whereby both the anolyte and the catholyte volume was 5 mL. To the working electrode chamber, 1 mmol of 4-bromoiodobenzene and 5 mmol of benzene was added. After completed reaction, mesitylene was added as an internal standard for product quantification via ^{1}H NMR spectroscopy (see Table S8).

Table S8: Yields and conversion for the electrochemical synthesis of diaryliodonium species **7** in different mixtures of PC-DMC (j = 10 mA cm^{-2}, 4 F per mole of transferred charge).

Entry	PC content [w%]	Benzene [equiv.]	Conversion [%]	Yield [%]	Selectivity [%]
1	20	5	92	67	73
2	40	5	89	73	82
3	60	5	86	77	89
4	**80**	**5**	**82**	**82**	**100**
5	100	5	75	66	88
6	80	2	90	73	81

Based on entry 4 in Table S8, current density and charge were optimized. Better results were achieved at 5 mA cm^{-2} and 4 F per mole iodoarene, whereby the product was isolated. For this purpose, an aliquot of 90% of the total anolyte volume was passed through a silica gel column after completed electrolysis, followed by elution of the product with CH_2Cl_2/MeOH (97/3). After evaporation of the solvent, the product was obtained as an off-white solid (0.368 g, 0.80 mmol, 89%). The remaining 10% of the anolyte volume were used for ^{1}H-NMR spectroscopic product quantification, whereby the yield of 89% was confirmed. The analytical data are in agreement with the literature.[10]

^{1}H NMR (400 MHz, CD_3CN): δ 8.11 – 8.05 (m, 2H), 7.98 – 7.93 (m, 2H), 7.75 – 7.66 (m, 3H), 7.58 – 7.51 (m, 2H).

^{13}C NMR (101 MHz, CD_3CN): δ 137.9, 136.4, 136.4, 134.1, 133.5, 128.6, 114.7, 112.5.

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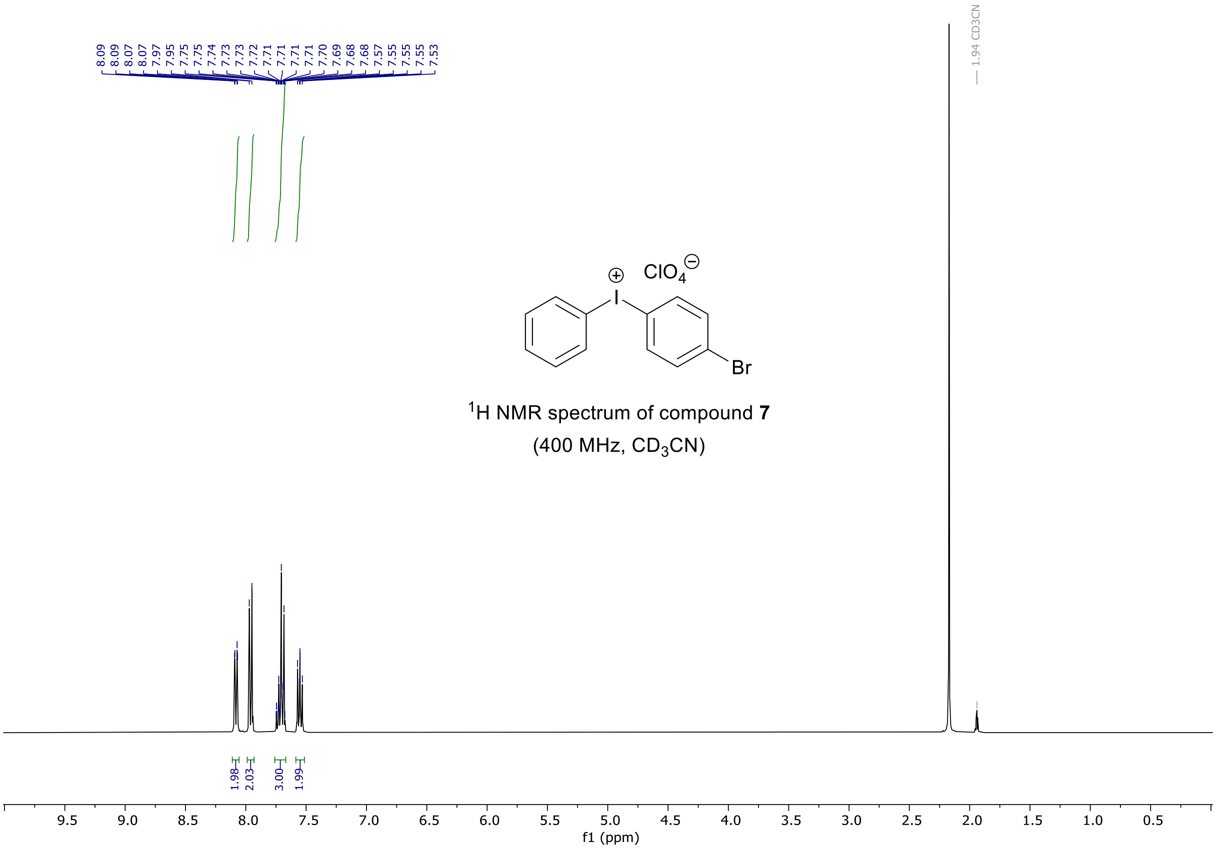
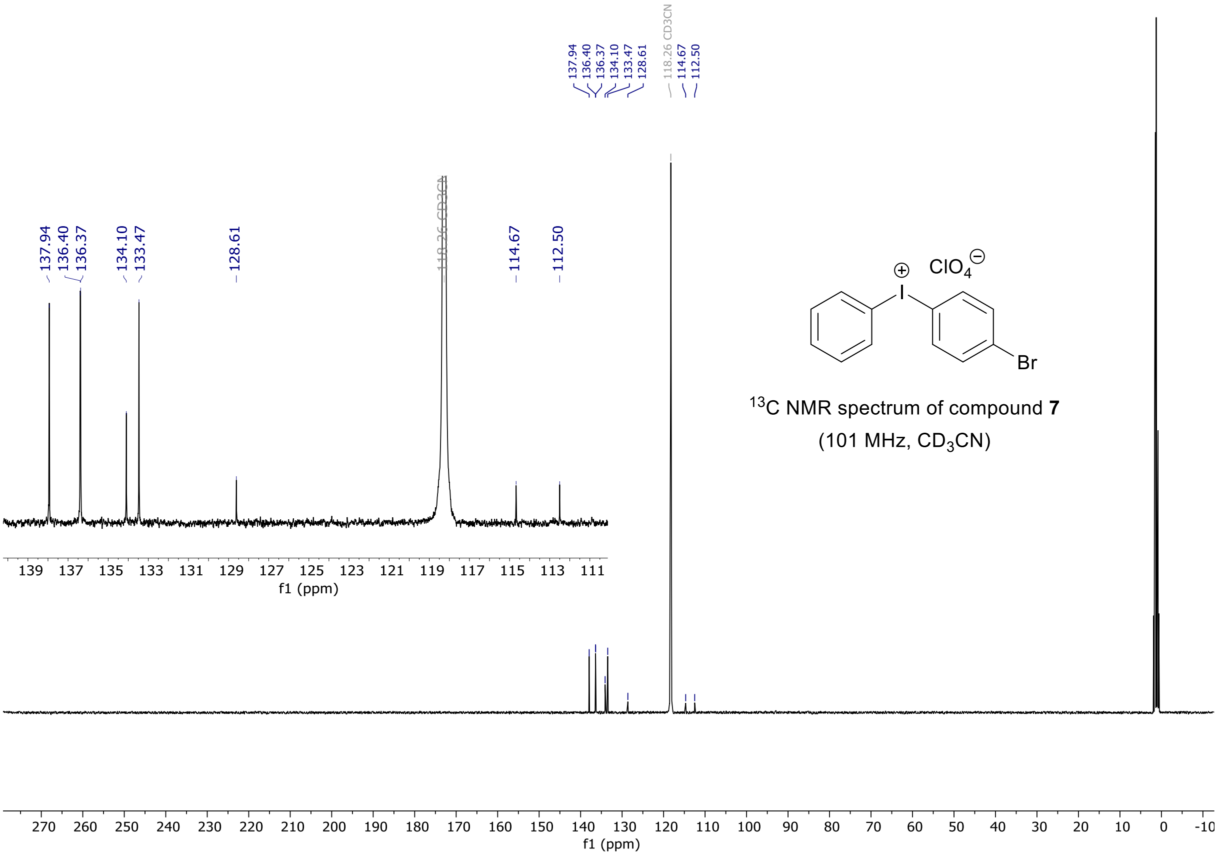
[10] M. Bielawski, *J. Org. Chem.* **2008**, 73, 12, 4602−4607.



^{1}H NMR spectrum of compound **7**
(400 MHz, CD_3CN)



^{13}C NMR spectrum of compound **7**
(101 MHz, CD_3CN)

5 Considerations with respect to sustainability

5.1 Details of solvent ratings

The color codes listed in Table 1 for assessing the sustainability of the solvents are taken from GSK's solvent selection guide.[11] To determine this, individual aspects (10 in total) are first rated with grades between 1 and 10. The individual aspects are then grouped into the categories waste, environment, health, and safety. A score is generated by forming the geometric mean of each of the aspect's scores (Eqs. 4-7), whereby the metrics *I*, *R*, *BT* and *VOC* evaluate the potential for different waste treatment methods (i.e., *incineration*, *recycling*, *biotreatment*), as well as potential *volatile organic compound* emissions. The parameters *F&E* and *R&S* rate the *fire and explosion* risk and the solvent's *reactivity and stability*, respectively.

The scores are summarized in Table S9, together with a composite score that is defined as the geometric mean of the four categories (eq. 8). For definition of the color coding, priority categories were determined and the decision tree in Figure S27 defined.

$$Waste = \sqrt[4]{I \cdot R \cdot BT \cdot VOC} \tag{4}$$

$$Environment = \sqrt{air \cdot aqueous} \tag{5}$$

$$Health = \sqrt{health\ hazard \cdot exposure\ potential} \tag{6}$$

$$Safety = \sqrt{F\&E \cdot R\&S} \tag{7}$$

$$Composite = \sqrt[4]{waste \cdot environment \cdot health \cdot safety} \tag{8}$$

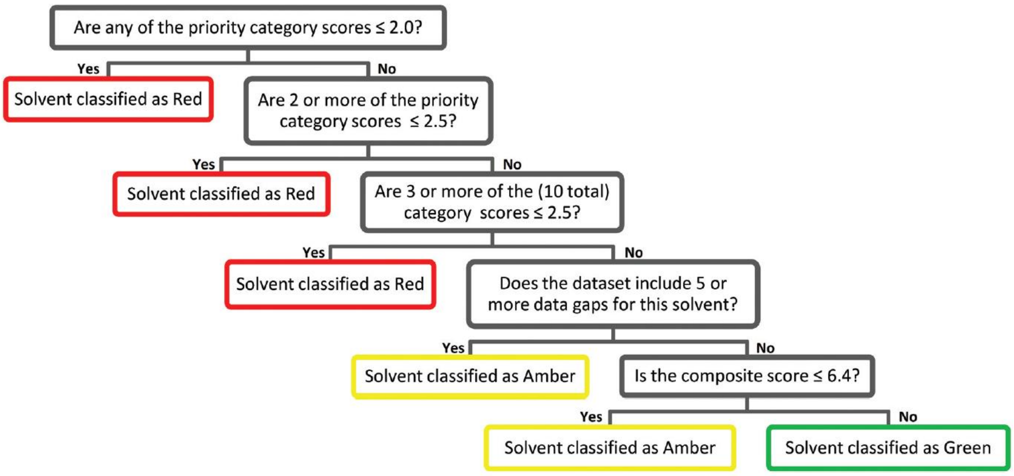


Figure S27: Decision tree for the definition of the color coding in GSK's solvent selection guide.[11]

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[11] C. M. Alder, J. D. Hayler, R. K. Henderson, A. M. Redman, L. Shukla, L. E. Shuster, H. F. Sneddon, *Green Chem.* **2016**, *18*, 3879-3890.

Table S9. Summary of the aspect, category, and composite scores of the solvents discussed in the papers. Calculations were carried out using eqs. 4-8.

Solvent	Incineration	Recycling	Biotreatment	VOC Emissions	**Waste Potential**	Aqueous	Air	**Environment.**	Health Hazard	Exposure potential	**Health**	Flammability/ Explosion.	Reactivity/ Stability	**Safety**	Composite
AN	3	5	1	4	**2.8**	10	8	**8.9**	7	5	**5.9**	6	10	**7.7**	5.8
DMF	3	6	3	8	**4.6**	10	4	**6.3**	1	6	**2.4**	9	9	**9.0**	5.0
DCM	2	10	4	1	**3.0**	8	6	**6.9**	7	4	**5.3**	4	10	**6.3**	5.1
PC	4	5	6	10	**5.9**	10	10	**10.0**	10	10	**10.0**	10	10	**10.0**	8.8
DMC	4	3	5	5	**4.2**	9	7	**7.9**	10	6	**7.7**	6	10	**7.7**	6.7

5.2 Mass-based metrics for evaluation of ketone reduction

The process mass intensity (PMI) values in Table 3 were calculated according to Constable et al.[12] and Monteith et al.[13] using the following equations. The values used for calculations are summarized in Tables S10-S12.

$$PMI = \frac{total\ mass\ used}{m_{product}} \tag{9}$$

$$= \frac{m_{reactants} + m_{reagents} + m_{catalyst}}{m_{product}} + \frac{m_{solvent}}{m_{product}} \tag{10}$$

$$= PMI_{RRC} + PMI_{solv} \tag{11}$$

Table S10. Summary of the parameters used for calculation of PMI, PMI_{RRC}, and PMI_{solv} values for electrochemical ketone reduction described in this work.

	Starting materials			**Product**	**Solvents**	
Compound	Benzophenone (**3**)	DABCO	Bu_4NBF_4	$(Ph)_2CHOH$ (**4**)	PC	DMC
MW [g mol^{-1}]	182.22	112.18	329.27	184.24	-	-
V [mL]	-	-	-	-	2.00	8.00
ρ [g mL^{-1}]	-	-	-	-	1.21	1.07
n [mmol]	5	11	1.2	4.1	-	-
m [g]	0.911	1.234	0.395	0.755	2.42	8.56

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[12] D. J. C. Constable, A. D. Curzons, V. L. Cunningham, *Green Chem.* **2002**, *4*, 521-527.

[13] E. R. Monteith, P. Mampuys, L. Summerton, J. H. Clark, B. U. W. Maes, C. R. McElroy, *Green Chem.*, **2020**, *22*, 123-135.

Table S11. Summary of the parameters used for calculation of PMI, PMI_{RRC}, and PMI_{solv} values for electrochemical ketone reduction in DMF.[7]

	Starting materials			**Product**	**Solvent**
Compound	Benzophenone (**3**)	DABCO	Bu_4NBF_4	$(Ph)_2CHOH$ (**4**)	DMF
MW [g mol^{-1}]	182.22	112.18	329.27	184.24	-
V [mL]	-	-	-	-	5.0
ρ [g mL^{-1}]	-	-	-	-	0.95
n [mmol]	0.3	0.9	0.25	-	
m [g]	0.055	0.101	0.082	0.044	4.75

Table S12. Summary of the parameters used for calculation of PMI, PMI_{RRC}, and PMI_{solv} values for chemical ketone reduction in EtOH using $NaBH_4$.[14]

	Starting materials		**Product**	**Solvent**
Compound	Benzophenone (**3**)	$NaBH_4$	$(Ph)_2CHOH$ (**4**)	EtOH
MW [g mol^{-1}]	182.22	37.83	184.24	-
V [mL]	-	-	-	50.0
ρ [g mL^{-1}]	-	-	-	0.79
n [mmol]	5.5	3.6	-	
m [g]	1.00	0.137	1.01	39.5

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[14] J. Desroches, P. A. Champagne, Y. Benhassine, J.-F. Paquin, *Org. Biomol. Chem.* 2015, **13**, 2243-2246.