Supporting Information

Concentrated Aqueous Peroxodicarbonate: Efficient Electrosynthesis and Use as Oxidizer in Epoxidations, S-, and N-Oxidations

A.-K. Seitz, P. J. Kohlpaintner, T. van Lingen, M. Dyga, F. Sprang, M. Zirbes, S. R. Waldvogel*, L. J. Gooßen*
# Table of Contents

1. General Methods.............................................................................................................. 3

2. **1H-NMR Method for in-situ Analysis of Reaction Mixtures** ........................................... 3

2.1 General Procedure ......................................................................................................... 3

2.2 NMR Method for Single Presaturation of H₂O with ¹³C-Decoupling ......................................................... 4

2.3 NMR Method for Double Presaturation.............................................................................. 5

3. Electrochemical Flow Cells and Setups.............................................................................. 6

3.1 Circular Flow Cell with Copper Contact ........................................................................ 6

3.2 Circular Flow Cell with Copper Contact & Heat Exchanger ........................................... 7

3.3 Copper Cooling Cell ........................................................................................................ 7

4. Screening of Electrolysis Conditions for the Electrosynthesis of Peroxodicarbonate .......... 9

5. Characterization of Peroxodicarbonate ........................................................................... 10

5.1 ¹³C-NMR .......................................................................................................................... 10

5.2 IR Spectroscopy ............................................................................................................... 12

5.3 Electronic Character ........................................................................................................ 13

6. Initial Oxidations with Low Concentrated Peroxodicarbonate ......................................... 14

7. Experimental Procedures ................................................................................................ 15

7.1 General Procedure for the Electrochemical Generation of Peroxodicarbonate ................. 15

7.2 General Procedure A for the Oxidation of Sulfides............................................................ 15

7.3 General Procedure B for the Oxidation of Sulfoxides ....................................................... 15

7.4 General Procedure C for the N-oxidation of Amines ........................................................ 15

7.5 General Procedure D for the Synthesis of Enones ............................................................ 15

7.6 General Procedure E for the Epoxidation of Enones ........................................................ 15

7.7 General Procedure F for the Epoxidation of Quinones ....................................................... 16

8. Synthesis and Characterization of Products ...................................................................... 17

8.1 Sulfones .......................................................................................................................... 18

8.2 Sulfoxides ....................................................................................................................... 18

8.3 N-Oxides ......................................................................................................................... 20

8.4 Enones ............................................................................................................................ 20

8.5 Epoxides ........................................................................................................................ 23

8.6 Multi-gram-scale Epoxidation of 2-Methyl-1,4-naphthoquinone .................................... 27

9. NMR-Spectra .................................................................................................................. 28

10. References .................................................................................................................... 66

11. Author Contributions ...................................................................................................... 66
1. General Methods

Commercial substrates were used as received unless otherwise stated. Solvents were purchased (puriss p.A.) from commercial suppliers. For electrochemical reactions BDD as anode and stainless steel as cathode were used.

$^1$H- and $^{13}$C($^1$H) NMR spectra were recorded on a Bruker Avance III 300, or Bruker Avance III 400 spectrometer using CDCl$_3$, DMSO-d$_6$ and (CD$_3$)$_2$CO) as deuterated solvents, with proton resonances at 300/400MHz and carbon resonances at 75/101 MHz, respectively. $^{19}$F NMR spectra were recorded on a Bruker DPX-250 or Magritek Spinsolve spectrometer, with fluorine resonances at 235 and 41 MHz, respectively. All values of the chemical shift are in ppm regarding the $\delta$-scale. To display multiplicities and signal forms correctly the following abbreviations were used: s = singlet, d = doublet, t=triplet, q = quartet, m = multiplet, dd = doublet of doublet, br = broad signal.

Optimization reactions were monitored by $^1$H-NMR analysis on Avance-400 spectrometers at 25 °C using DMSO as internal standard.

Mass spectrometric data were acquired using an HPLC-MS system consisting of an UltiMate 3000 HPLC (ThermoFisher) with an EC 4/2 Universal RP pre-column (Macherey-Nagel), eluting at 40 °C with acetonitrile/water/formic acid (3:1:0.01) and a flow rate of 0.3 mL/min, coupled with a maXisCompact high-resolution mass spectrometer (Bruker Daltonik GmbH). The MS ionization was achieved by ESI.

Fourier-transformed infrared (FT-IR) spectra for characterization of products were recorded at 20 °C on a Bruker Vertex 70 Spectrometer with Universal ATR Sampling Accessory, while those for the characterization of peroxodicarbonate were performed at 20 °C on a Bruker ALPHA ATR spectrometer.

Melting points were measured on a Mettler Toledo MP70.

Gas chromatography was performed using a Shimadzu GC-2010 using a ZB-5 column (Phenomenex, USA, dimensions 30 m x 0.25 mm x 0.25 µm, carrier gas: hydrogen) with a flame ionization detector (FID) at 310 °C. All samples were prepared through filtration through silica gel Geduran® Si 60 (0.063–0.200 mm, Merck) using acetonitrile as eluent.

2. $^1$H-NMR Method for in-situ Analysis of Reaction Mixtures

In cooperation with Martin Gartmann from the NMR-department of the Ruhr-Universität Bochum, we developed a special NMR method for in situ analytics of the reaction mixture after the oxidation with peroxodicarbonate to get quick, reliable reaction control even in highly diluted reactions in non-deuterated water.

2.1 General Procedure

If the reaction time was less than 5 hours, the reaction mixture was quenched by addition of 1 M Na$_2$S$_2$O$_3$ solution. If the reaction mixture was not homogeneous, it was diluted with H$_2$O until it became completely homogeneous solution. A precise amount of dimethylsulfoxide (DMSO) was added as standard and the mixture was thoroughly mixed. Since DMSO can be oxidized by peroxodicarbonate to dimethylsulfone, it was added after the peroxodicarbonate has either decomposed overnight or was quenched by a suitable reductant, e.g. Na$_2$S$_2$O$_3$. Then, 300 µL were transferred into a high-precision NMR tube (Wilmad 507-PP-7 or Deutero Boro600-5-7) and diluted with 300 µL of deuterated water. D$_2$O is used to maintain the lock during measurement. The sample was measured on a Bruker Avance III 400 spectrometer (400 MHz) using the pulse programs listed below. A relaxation delay (D1) of 20 seconds was configured. An example for the evaluation of the N-oxidation of N-methylmorpholine with peroxodicarbonate via $^1$H-NMR is given in Figure S1.

**Figure S1.** $^1$H-NMR spectrum of a reaction mixture of the N-oxidation of N-methylmorpholine with peroxodicarbonate.
2.2 NMR Method for Single Presaturation of H$_2$O with $^{13}$C-Decoupling

This method was used for samples containing only water as a solvent. The $^{13}$C decoupling suppresses the formation of $^{13}$C satellites in the $^1$H-NMR spectra, improving precision.

```
#include <Avance.incl>

"d12=20u"

"p0=p1*cnst12"

"acqt0=-(p1*6/PI)-4u"

1 ze
d11 pl12:f2
2 30m do:f2
d12 fq=fq1:f1 pl9:f1
d1 cw:f1 ph29
4u do:f1
d12 pl1:f1
p1 ph1
4u
p1 ph2
4u
p0 ph3
4u
p1 ph4
go=2 ph31 cpd2:f2
30m do:f2 mc #0 to 2 F0(zd)
exit

ph1=1 3 3 1 2 0 0 2
ph2=2 0 2 0 3 1 3 1
ph3=3 1 1 3 0 2 2 0
ph4=0 2 0 2 1 3 1 3
ph29=0
ph31=0 2 0 2 1 3 1 3
```

;pl1 : f1 channel - power level for pulse (default)
;pl9 : f1 channel - power level for presaturation
;p1 : 90 degree transmitter high power pulse
;d1 : relaxation delay; 1-5 * T1
;d12 : delay for power switching [20 usec]
;d11 : delay for disk I/O [30 msec]
;cnst12: as multiplier for flip angle (1 = 90o) [1]
;ns: 1 * n, total number of scans: NS * TD0
2.3 NMR Method for Double Presaturation

This method was used for samples containing water and one additional solvent which has one $^1$H-NMR signal (typically MeCN). $^{13}$C-decoupling is not used in this method, as the channel of the NMR spectrometer is needed for the second presaturation.

```plaintext
;cpd2: decoupling according to sequence defined by cpdprg2
;pcpd2: f2 channel - 90 degree pulse for decoupling sequence
;define FQ1LIST for presaturation frequency

prosol relations=<lcnmr>

#include <Avance.incl>

"d12=20u"
"d13=4u"
"acqt0=-p1*2/3.1416"

1 ze
d12 pl21:f2
2 30m
d12 pl9:f1
d1 cw:f1 ph29 cw:f2 ph29
d13 do:f1 do:f2
d12 pl1:f1
p1 ph1
go=2 ph31
30m mc #0 to 2 F0(zd)
exit
ph1=0 2 2 0 1 3 3 1
ph29=0
ph31=0 2 2 0 1 3 3 1

;pl1 : f1 channel - power level for pulse (default)
;pl9 : f1 channel - power level for presaturation
;pl21: f2 channel - power level for presaturation
;p1 : f1 channel - 90 degree high power pulse
;d1 : relaxation delay; 1-5 * T1 [ca. 1-2sec]
;d12: delay for power switching [20 usec]
;d13: short delay [4 usec]
;ns: 4 * n, total number of scans: NS * TD0
;ds: 4
```
3. Electrochemical Flow Cells and Setups

3.1 Circular Flow Cell with Copper Contact

The peroxodicarbonate solution was generated in a circular flow system (Figure S2). The cell design for the anode side is designed by Waldvogel and commercially available from IKA (ElectraSyn flow).\(^1\) The anode was a BDD electrode on silicon substrate with the dimensions 60×20×3 mm (DIACHEM\(^\circledast\), Condias GmbH). The cooled stainless-steel block serving as the cathode was fabricated from 1.4571 stainless steel by the metal workshop of Johannes Gutenberg-Universität Mainz. The PTFE spacer between the anode and cathode blocks determines the interelectrode gap and electrode surface.

The pump for the electrolyte was a small diaphragm pump, model HX100KTDC-T (Joto Fluid). The flow rate was controlled via the supply voltage of the pump motor. Calibration of the flow rate was performed by pumping water at a temperature of 0 °C at varying supply voltage. Before running an electrolysis, the flow rate was verified using water at 0 °C.

The electrolyte container was placed in an ice bath for cooling. A magnetic stir bar was added to the electrolyte, and the solution was stirred at 750 rpm during the electrolysis. Additional cooling was provided using a Lauda EcoLine RE206 cryostat, which was connected to the stainless-steel cathode. A commercial coolant mixture based on ethylene glycol and water was used (Nigrin Kühler-Schutz). For every electrolysis, the cryostat was set to a temperature of 0 °C. The inner temperature of the electrolyte was recorded using a DS18B20 temperature sensor in combination with a Diamex Temp-Sensor-Tester (Diamex GmbH). The constant current of electricity was supplied by a Rohde&Schwarz HMP4040.

![Figure S2. Schematic of the circular flow setup for carbonate electrolysis.](image)

![Figure S3. Exploded view of a circular flow cell modified with copper contact for peroxodicarbonate electrolysis.](image)
3.2 Circular Flow Cell with Copper Contact & Heat Exchanger

To reduce the temperature of the electrolyte, a heat exchanger was designed and assembled from a coil of stainless steel tubing and a 3D printed shell (Figure S4) and connected to the circular-flow setup as displayed in Figure S5. The heat exchanger and the cathode were connected to the same cryostat in parallel.

![Figure S4. Photo and half-section view of the heat exchanger](image)

![Figure S5. Schematic of the circular flow setup with heat exchanger.](image)

3.3 Copper Cooling Cell

The peroxodicarbonate solution was generated in a circular flow system (Figure S6). The cell design was drafted and milled by the Gooßen group. We designed copper blocks with a microchannel structure in proximity to the active electrode surface. The microchannels increase the surface area and promote heat transfer to the coolant. On the anode side, the BDD electrode was placed into a precisely milled groove. Electrically conductive thermal paste (Arctic Silver® 5) was applied to the backside of the electrode. On the cathode side, a copper block and a thin stainless-steel sheet (0.5 mm thickness) are used. The stainless-steel sheet was glued to the copper block using thermally conductive glue (Silverbead® SG100XS).

The PTFE spacer between the anode and cathode blocks determines the interelectrode gap and electrode surface and fully seals the electrolyte on the surface of the electrodes. Therefore, no additional O-ring gaskets are required to prevent corrosive electrolyte from reaching the copper parts.

The BDD electrode with silicon substrate had the dimensions 60×20×3 mm, whereas those with glassy carbon, tantalum, and niobium substrate had the dimensions 60×20×2 mm. The electrodes were manufactured by Condias GmbH (DIACHEM).

The pump for the electrolyte was a small diaphragm pump, model HX100KTDC-T (Joto Fluid). The flow rate was controlled via the supply voltage of the pump motor. Calibration of the flow rate was performed by pumping water at a temperature of 0 °C at varying supply voltage. Before running an electrolysis, the flow rate was verified using water at 0 °C.

The electrolyte container was placed in an ice bath for cooling. A magnetic stir bar was added to the electrolyte, and the solution was stirred at 750 rpm during the electrolysis. Additional cooling was provided using a Lauda EcoLine RE206 cryostat using a commercial coolant mixture based on ethylene glycol and water (Nigrin Kühter-Schutz). The cryostat was connected to both copper blocks in parallel. For every electrolysis, the cryostat was set to a temperature of 0 °C. The inner temperature of the electrolyte and of the cathode cooling block was recorded using a DS18B20 temperature sensor in combination with a Diamex Temp-Sensor-Tester (Diamex GmbH). The constant current of electricity was supplied by a Rohde&Schwarz HMP4040.
Figure S6. Schematic of the circular-flow setup using the copper cooling cell.

Figure S7. Exploded view of the copper cooling cell developed for carbonate electrolysis.
4. Screening of Electrolysis Conditions for the Electrosynthesis of Peroxodicarbonate

Table S1. Screening of Electrolysis Conditions

| # | c (electrolyte) [M] | Setup | BDD substrate | V [mL] | d [mm] | A [cm²] | j [A/cm²] | Flow rate [mL/min] | Cum. charge [F] | c (C₂O₄²⁻) [mL] | U [V] | Tₑ [°C] | FE [%] | EC [kWh/mol (C₂O₄²⁻)] |
|---|---------------------|-------|---------------|--------|--------|---------|-----------|-------------------|--------------|----------------|------|--------|-------|--------------------------|
| Reproduction of literature conditions[25] | | | | | | | | | | | | | | |
| 1[4] | 0 | 1.5 | 0 | A | Si | 35 | 1 | 10.8 | 0.80 | 100 | 1.5 | 266 | 5.5 | 23.0 | 23.7 | 1.25 |
| Screening of double- and triple-salt electrolyte | | | | | | | | | | | | | | |
| 2 | 1.5 | 0 | 0 | " | " | " | " | " | " | 258 | 5.1 | 12.6 | 23.0 | 1.19 |
| 3 | 2.25 | 0 | 0 | " | " | " | " | " | " | 275 | 5.0 | 10.2 | 16.3 | 1.65 |
| 4 | 1.25 | 1 | 0 | " | " | " | " | " | " | 337 | 5.2 | 11.3 | 19.9 | 1.40 |
| 5 | 1.225 | 0.98 | 0.045 | " | " | " | " | " | " | 346 | 5.1 | 10.8 | 20.5 | 1.34 |
| 6 | 1.2 | 0.96 | 0.09 | " | " | " | " | " | " | 384 | 5.1 | 12.5 | 21.5 | 1.27 |
| 7 | 1.125 | 0.9 | 0.225 | " | " | " | " | " | " | 406 | 5.1 | 11.6 | 24.0 | 1.14 |
| 8 | 1 | 0.8 | 0.45 | " | " | " | " | " | " | 398 | 5.2 | 11.3 | 23.5 | 1.16 |
| Improving cooling efficiency | | | | | | | | | | | | | | |
| 9 | 1.125 | 0.9 | 0.225 | B | " | " | " | " | " | 588 | 5.7 | 1.1 | 34.8 | 0.88 |
| 10 | " | " | " | " | " | " | " | " | " | 444 | 5.4 | 1.3 | 26.3 | 1.10 |
| 11 | " | " | " | " | " | " | " | " | " | 503 | 7.1 | 2.5 | 29.8 | 1.28 |
| 12 | " | " | " | C | " | " | " | " | " | 620 | 6.3 | 3.8 | 36.7 | 0.92 |
| 13 | " | " | " | D | " | " | " | " | " | 687 | 6.9 | 5.3 | 40.6 | 0.91 |
| Inter-electrode distance | | | | | | | | | | | | | | |
| 14 | " | " | " | " | " | " | " | " | " | 662 | 5.8 | 3.8 | 39.2 | 0.79 |
| 15 | " | " | " | " | " | " | " | " | " | 666 | 5.5 | 2.8 | 39.4 | 0.75 |
| Multiplying current density by reducing electrode surface | | | | | | | | | | | | | | |
| 16 | " | " | " | " | " | " | " | " | " | 709 | 6.5 | 5.8 | 41.9 | 0.83 |
| 17 | " | " | " | " | " | " | " | " | " | 354 | 8.4 | 10.1 | 20.9 | 2.15 |
| Cumulated charge | | | | | | | | | | | | | | |
| 18 | " | " | " | " | " | " | " | 3 | 2.88 | " | 0.5 | 344 | 6.3 | 6.2 | 61.2 | 0.55 |
| 19 | " | " | " | " | " | " | " | " | " | 1.0 | 533 | 6.4 | 6.0 | 47.4 | 0.72 |
| 20 | " | " | " | " | " | " | " | " | " | 1.5 | 709 | 6.5 | 5.8 | 41.9 | 0.83 |
| 21 | " | " | " | " | " | " | " | " | " | 2.5 | 791 | 6.1 | 6.8 | 28.1 | 1.16 |
| 22 | " | " | " | " | " | " | " | " | " | 4.0 | 827 | 6.2 | 3.8 | 18.4 | 1.81 |
| Fine-tuning of current density | | | | | | | | | | | | | | |
| 23 | " | " | " | " | " | " | " | " | " | 2.88 | " | 2.5 | 791 | 6.1 | 6.8 | 28.1 | 1.16 |
| 24 | " | " | " | " | " | " | " | " | " | 3.2 | " | 798 | 6.6 | 6.8 | 28.4 | 1.25 |
5. Characterization of Peroxodicarbonate

5.1 $^{13}$C-NMR

The $^{13}$C-NMR spectra of peroxodicarbonate were measured on a Bruker Avance III 400 spectrometer. A carbonate stock solution was prepared by dissolving K$_2$CO$_3$ (281 mmol, 1.125 M), Na$_2$CO$_3$ (225 mmol, 0.90 M), KHC$_2$O$_3$ (56.3 mmol, 0.225 M), and D$_2$O (50 mL) in H$_2$O, and diluting with H$_2$O to a volume of 250 mL in a volumetric flask. A 1 mL aliquot of the stock solution was added to a vial containing potassium methanesulfonate (20 mg). 0.6 mL of this solution were added to an NMR tube and the $^{13}$C-NMR (1024 scans) was measured at a temperature of 273 K (Figure S8, green trace).

35 mL of the carbonate stock solution were electrolyzed using the copper cooling cell at a constant current density of 3.33 A/cm$^2$ for 31.7 minutes, corresponding to a charge of 2.5 F. A flow rate of 100 mL/min, an interelectrode gap of 0.3 mm, and an electrode surface of 3 cm$^2$ were used. A 1 mL aliquot of the electrolyte was added to a cooled (0°C) vial containing potassium methanesulfonate (20 mg). 0.6 mL of this solution were added to an NMR tube and the $^{13}$C-NMR (1024 scans) was measured at a temperature of 273 K (Figure S8, blue trace). Furthermore, a second $^{13}$C NMR of the peroxodicarbonate solution after standing for 4 days at room temperature was measured (Figure S8, red trace).
Figure S8. $^{13}$C NMR spectra of carbonate solution under different conditions.
Another $^{13}$C-NMR was measured for a carbonate solution containing $\text{H}_2\text{O}_2$. The solution was prepared by weighing $\text{K}_2\text{CO}_3$ (783 mg, 5.65 mmol), $\text{Na}_2\text{CO}_3$ (479 mg, 4.52 mmol) and $\text{KHCO}_3$ (113 mg, 1.13 mmol) and adding $\text{D}_2\text{O}$ (1 mL) and water (ca. 2.5 mL). The salts were brought into solution by gentle heating, and the solution was subsequently cooled down to room temperature. Then, $\text{H}_2\text{O}_2$ (35% in $\text{H}_2\text{O}$, 1.0 mL, 11.3 mmol) was added to the solution, and the solution was diluted with water to 5 mL. The concentrations in the resulting solution were: 1.125 M $\text{K}_2\text{CO}_3$, 0.90 M $\text{Na}_2\text{CO}_3$, 0.225 M $\text{KHCO}_3$, and 2.25 M $\text{H}_2\text{O}_2$. A 1 mL aliquot of the solution was added to a cooled (0°C) vial containing potassium methanesulfonate (20 mg). 0.6 mL of this solution were added to an NMR tube and the $^{13}$C-NMR (1024 scans) was measured at a temperature of 273 K (Figure S8, purple trace).

To test the influence of acid and base within the stability range of peroxodicarbonate a 1 mL aliquot of the electrolyte was added to a cooled (0 °C) vial containing potassium methanesulfonate (20 mg). To this solution, aqueous NaOH (5 M, 0.86 mmol) was added and a pH value of 13.5 was determined. 0.6 mL of this solution were added to an NMR tube and the $^{13}$C-NMR (1024 scans) was measured at a temperature of 273 K (Figure S8, black trace). To another identical sample, sulfuric acid (0.22 mmol) was added and a pH value of 11 was determined. 0.6 mL of this solution were added to an NMR tube and the $^{13}$C-NMR (1024 scans) was measured at a temperature of 273 K (Figure S8, orange trace).

5.2 IR Spectroscopy

The IR spectra were measured on a Bruker ALPHA ATR spectrometer. The following samples were measured ($\text{H}_2\text{O}$ was recorded as background):

- electrolyte solution consisting of 0.90 M $\text{Na}_2\text{CO}_3$, 1.125 M $\text{K}_2\text{CO}_3$ and 0.225 M $\text{KHCO}_3$ (black trace)
- electrolyte solution consisting of 0.90 M $\text{Na}_2\text{CO}_3$, 1.125 M $\text{K}_2\text{CO}_3$ and 0.225 M $\text{KHCO}_3$ electrolyzed following the general procedure A in section 7.2 (blue trace)
- electrolyte solution consisting of 0.90 M $\text{Na}_2\text{CO}_3$, 1.125 M $\text{K}_2\text{CO}_3$ and 0.225 M $\text{KHCO}_3$ mixed with $\text{H}_2\text{O}_2$ (35%) in the ratio 1/1 (purple trace).

Figure S9. IR spectra of a 9:1 KNaCO$_3$/KHCO$_3$ electrolyte $\text{H}_2\text{O}_2$ solution prepared by mixing commercial $\text{H}_2\text{O}_2$ solution (35%) with the carbonate electrolyte in the ratio 1/1.
5.3 Electronic Character

We investigated the electronic character of peroxodicarbonate in the oxidation of methyl(methylthio)methyl sulfoxide (Table S2. $\chi_{SO}$ was calculated using the following equation:

$$\chi_{SO} = \frac{n_{SO}}{n_{SO} + n_S} = \frac{(n_{SSO_2} + n_{SOSSO_2})}{(n_{SSO_2} + n_{SOSSO_2}) + (n_{SO} + n_{SOSSO_2})}$$

(1)

$$n_{SO} = n_{SSO_2} + n_{SOSSO_2} \text{ total "SO" oxidation}$$

$$n_S = n_{SOSSO_2} + n_{SOSSO_2} \text{ total "S" oxidation}$$

Table S2. $\chi_{SO}$ values of oxygen-transfer agents assessed by the methyl(methylthio)methyl sulfoxide (SSO) probe

| #   | Conditions                           | pH value | Conv. SSO/ % [c] | Product composition/ % [d] | $\chi_{SO}$ |
|-----|--------------------------------------|----------|------------------|-----------------------------|-------------|
| 1[a] | $\text{C}_2\text{O}_6^2-$            | 12       | 43               | SSO$_2$: 46.5, SSO: 32.6, SO$_2$: 20.9 | 0.56        |
| 2[a] | $\text{C}_2\text{O}_6^2-$            | 12.5     | 36               | SSO$_2$: 28.7, SSO: 60.0, SO$_2$: 13.3 | 0.35        |
| 3[a] | $\text{C}_2\text{O}_6^2$ + 0.11 mmol p-TsOH | 12       | 48               | SSO$_2$: 11.1, SSO: 75.0, SO$_2$: 13.9 | 0.22        |
| 4[a] | $\text{C}_2\text{O}_6^2$ + 0.17 mmol p-TsOH | 11       | 40               | SSO$_2$: 10.3, SSO: 79.4, SO$_2$: 10.3 | 0.19        |
| 5[a] | $\text{C}_2\text{O}_6^2$ + 0.23 mmol p-TsOH | 11       | 46               | SSO$_2$: 8.2, SSO: 81.6, SO$_2$: 10.2 | 0.17        |
| 6[a] | $\text{C}_2\text{O}_6^2$ + 0.34 mmol p-TsOH | 11       | 55               | SSO$_2$: 7.6, SSO: 83.0, SO$_2$: 9.4  | 0.16        |
| 7[a] | $\text{C}_2\text{O}_6^2$ + 0.45 mmol p-TsOH | 11       | 56               | SSO$_2$: 6.6, SSO: 85.2, SO$_2$: 8.2  | 0.14        |
| 8[a] | $\text{C}_2\text{O}_6^2$ + 0.91 mmol p-TsOH | 11       | 67               | SSO$_2$: 5.9, SSO: 80.9, SO$_2$: 13.2 | 0.17        |
| 9[a] | $\text{C}_2\text{O}_6^2$ + 0.11 mmol NaOH (5M) | 13       | 34               | SSO$_2$: 55.0, SSO: 30.0, SO$_2$: 15.0 | 0.61        |
| 10[a] | $\text{C}_2\text{O}_6^2$ + 0.23 mmol NaOH (5M) | 13       | 33               | SSO$_2$: 69.0, SSO: 17.2, SO$_2$: 13.8 | 0.72        |
| 11[a] | $\text{C}_2\text{O}_6^2$ + 0.45 mmol NaOH (5M) | 13.5     | 36               | SSO$_2$: 70.3, SSO: 16.2, SO$_2$: 13.5 | 0.74        |
| 12   | H$_2$O in 0.6 mL acetic acid, RT      | 2        | >99              | SSO$_2$: <1.0, SSO: 100, SO$_2$: <1.0 | <0.01       |
| 13   | H$_2$O in 0.5 mL H$_2$O               | 4        | 79               | SSO$_2$: <1.0, SSO: 100, SO$_2$: <1.0 | <0.01       |
| 14   | H$_2$O in 0.5 mL of an aqueous solution of K$_2$CO$_3$ (1.125 M), Na$_2$CO$_3$ (0.90 M), and KHCO$_3$ (0.225 M) | 11       | 21               | SSO$_2$: 23.5, SSO: 64.7, SO$_2$: 11.8 | 0.32        |
| 15   | KMnO$_4$ in 2.388 mL acetone/H$_2$O (26:1), RT | -        | >99              | SSO$_2$: 100, SSO: <1.0, SO$_2$: <1.0 | 1.00        |
| 16   | 2 Na$_2$CO$_3$ · 3 H$_2$O in 0.5 mL H$_2$O | 11       | 36               | SSO$_2$: 15.4, SSO: 66.7, SO$_2$: 17.9 | 0.28        |

Reaction conditions: 0.5 mmol SSO, 1 equiv. oxygen-transfer agent, 20 mL crimp-cap vial, 0°C, 19 h. [a] C$_2$O$_6^2-$(>0.9 M) generated via electrolysis of an aqueous solution of K$_2$CO$_3$ (1.25 M), Na$_2$CO$_3$ (0.90 M), and KHCO$_3$ (0.225 M) [b] C$_2$O$_6^2-$(>0.9 M) generated via electrolysis of an aqueous solution of K$_2$CO$_3$ (1.125 M), Na$_2$CO$_3$ (0.90 M), and KHCO$_3$ (0.225 M) [c] conversion determined via $^1$H-NMR using DMSO as standard. [d] Relative yields (normalized to 100%), determined via $^1$H-NMR using DMSO as standard. Amount of additive calculated based on the remaining carbonate in solution (e.g.: 900 mmol PODIC, 450 mmol remaining carbonate).
6. Initial Oxidations with Low Concentrated Peroxodicarbonate

When we first tested our peroxodicarbonate solution (<0.2 M) on various substrates, the results were sobering (Figure S10).

**Attempted oxidations with low concentrated \( \text{C}_2\text{O}_6^{2-} \)**

| Oxidation Type | Reaction Equation | Product | Conversion |
|----------------|-------------------|--------|------------|
| N-Oxidation    | \( \text{C}_2\text{O}_6^{2-} \rightarrow \text{N-Oxide} \) | tertiary amine | low conversion |
| Epoxidation    | \( \text{alkene} \rightarrow \text{epoxide} \) | no conversion |

![Chemical structures and reactions](image)

**Figure S10. Attempted oxidations with low concentrated \( \text{C}_2\text{O}_6^{2-} \).**
7. Experimental Procedures

7.1 General Procedure for the Electrochemical Generation of Peroxodicarbonate

An aqueous electrolyte solution (35 mL) consisting of 0.90 M \( \text{Na}_2\text{CO}_3 \), 1.125 M \( \text{K}_2\text{CO}_3 \) and 0.225 M \( \text{KHCO}_3 \) was added into a 100 mL screw-cap glass container and placed in an ice bath or in the coolant mixture of the cryostat. A temperature sensor was placed inside of the electrolyte. The solution was circulated through the electrolysis system at a constant flow rate until the electrolyte temperature stayed constant. Then, the solution was electrolyzed using the copper cooling cell at a constant current density of 3.33 A/cm² for 126.76 minutes, corresponding to a charge of 10 F rel. to carbonate. A flow rate of 100 mL/min, an interelectrode distance of 0.3 mm, and an electrode surface of 3 cm² were used. After the electrolysis, the sample container was placed in an ice bath. A 4 mL volumetric pipette was pre-cooled by pumping 4 mL of cold electrolyte solution into the pipette and immediately returning it into the electrolyte three times. Then, up to three 4 mL aliquots of the electrolyte were transferred into Erlenmeyer flasks. The pH was adjusted to ~1 by addition of 20% (v/v) \( \text{H}_2\text{SO}_4 \) (4 mL each). To each flask, 5 mL of an aqueous solution of \( \text{KI} \) (1–3 mol/L, depending on the concentration of the oxidizer) and a drop of ammonium heptamolybdate solution (3% in \( \text{H}_2\text{O} \)) were added. The brown solution was titrated against a standard solution of \( \text{Na}_2\text{S}_2\text{O}_3 \) (0.1 – 0.4 M). The endpoint of the titration was determined by the complete disappearance of the yellow color of free \( \text{I}_2 \). The resulting average concentration of total oxidizer was then calculated by standard error calculations.

7.2 General Procedure A for the Oxidation of Sulfides

Based on the result of the titration, freshly prepared peroxodicarbonate solution (1.0 equiv., unless otherwise stated) and sulfuric acid (1.00 mmol) were added to a sulfide (1.00 mmol) in an ice-cooled 20 mL vial with a Teflon-coated stirring bar. The reaction mixture was stirred at 400 rpm for 16 h allowing the ice-bath to melt. Afterwards, the reaction mixture was acidified with \( \text{HCl} \) (if sulfide contains protic groups), extracted with \( \text{EtOAc} \) (4×20 mL), dried over \( \text{MgSO}_4 \) and the organic solvent was removed under reduced pressure. The residue was purified by column chromatography, yielding the corresponding sulfoxide.

7.3 General Procedure B for the Oxidation of Sulfoxides

Based on the result of the titration, freshly prepared peroxodicarbonate solution (5.0 equiv., unless otherwise stated) was added to a sulfoxide (1.00 mmol) in an ice-cooled 20 mL vial with a Teflon-coated stirring bar. The reaction mixture was stirred at 400 rpm for 16 h, allowing the ice-bath to melt. Afterwards, the reaction mixture was diluted with water or \( \text{HCl} \) (if sulfoxide contains protic groups), extracted with \( \text{EtOAc} \) (4×20 mL), dried over \( \text{MgSO}_4 \) and the organic solvent was removed under reduced pressure, yielding the corresponding sulfone.

7.4 General Procedure C for the N-oxidation of Amines

Based on the result of the titration, freshly prepared peroxodicarbonate solution (1.5 equiv., unless otherwise stated) was added to a tertiary amine (1.00 mmol) in an ice-cooled 20 mL vial with a Teflon-coated stirring bar. The reaction mixture was stirred at 400 rpm for 16 h, allowing the ice-bath to melt. The reaction mixture was transferred into a 50 mL flask and dried by freeze-drying (1 mbar vacuum) and the resulting solid was crushed, suspended in \( \text{CH}_2\text{Cl}_2 \) (20 mL) and filtered. The filter cake was washed with \( \text{CH}_2\text{Cl}_2 \) (4×20 mL) and the organic solvent was removed under reduced pressure, yielding the corresponding \( \text{N} \)-oxide.

7.5 General Procedure D for the Synthesis of Enones

To an ice-cool solution of the acetophenone compound (1.0 equiv.) in ethanol was added of \( \text{NaOH} \) (1.1 equiv.) in water. After 5 minutes the aldehyde compound was added via syringe. For solid aldehydes, the compound was dissolved in ethanol prior to addition. After the reaction was complete, and the mixture was diluted with ice-water. The precipitated product was collected on a Büchner funnel, recrystallized from either ethanol or ethanol/water (2:1) mixtures if necessary and dried under high vacuum.

7.6 General Procedure E for the Epoxidation of Enones

Based on the result of the titration, freshly prepared peroxodicarbonate solution (9.0 equiv.) was added to a solution of the enone (1.00 mmol) in 20–40 mL ethanol at room temperature and stirred until conversion was completed (1–3 h). This was monitored via GC-MS. The reaction mixture was diluted with water and extracted with \( \text{CH}_2\text{Cl}_2 \) (3×50 mL). The combined organic layers were washed with brine (1×40 mL), dried over \( \text{MgSO}_4 \), filtered, and evaporated under reduced pressure. The epoxide was then purified via column chromatography using \( \text{SiO}_2 \) and cyclohexane/ethyl acetate as eluent mixture.
Based on the result of the titration, freshly prepared peroxodicarbonate solution (2.0 equiv.) was added to a solution of the quinone (1 mmol) in CH$_2$Cl$_2$/EtOH/H$_2$O (2:1:1, 20 mL in total) at 0 °C. After complete conversion (1–3 h, monitored via GC-MS) the reaction mixture was extracted with CH$_2$Cl$_2$ (3x 50 mL), the combined organic layers were then washed with brine (1x 40 mL), dried over MgSO$_4$, filtered, and evaporated under reduced pressure, yielding the pure epoxide.
8. Synthesis and Characterization of Products

8.1 Sulfoxides

3-(Methylsulfinyl)benzoic acid (2a) [CAS: 90345-62-3]

\[
\text{HO} \quad \begin{array}{c}
\text{S} \\
\text{O} \\
\text{O}
\end{array} 
\quad \text{O} 
\]

Compound 2a was prepared following the general procedure A for the oxidation of \( m \)-(methylthio)-benzoic acid (172 mg, 1.00 mmol) and isolated as a colorless solid (148 mg, 0.80 mmol, 80%) after column chromatography (SiO\(_2\), CH\(_2\)Cl\(_2\)/MeOH/H\(\text{HCO}_2\)H = 95:5:0.1).

\text{m.p. (MeOH)} = 172-174 °C.

\(^1\text{H NMR (300 MHz, DMSO-}\text{d}_6\text{)} \delta = 8.27-8.18 (m, 1H), 8.08 (qd, \text{ } J = 0.9, 7.7 \text{ Hz, } 1H), 7.92 (ddd, \text{ } J = 1.1, 1.8, 7.8 \text{ Hz, } 1H), 7.70 (dt, \text{ } J = 0.5, 7.7 \text{ Hz, } 1H), 2.78 (s, 3H) \text{ ppm.}

\(^{13}\text{C}[^1\text{H}] \text{ NMR (75 MHz, DMSO-}\text{d}_6\text{)} \delta = 166.4, 147.2, 131.9, 131.3 129.6, 127.9, 124.2, 43.2 \text{ ppm.}

\text{IR: } \tilde{\nu} = 3079 (w), 3003 (w), 2915 (w), 2769 (w), 1706 (s), 1594 (w), 1575 (w), 1449 (m), 1426 (m), 1284 (s), 1131 (s), 969 (s) \text{ cm}^{-1}.

HRMS (ESI-TOF): [M + H]\(^+\) calcd. for C\(_8\)H\(_8\)O\(_3\)S: 185.0267; found: 185.0267.

The analytical data (NMR) matched those reported in the literature.[3]

Thiolane sulfoxide (2b) [CAS: 1600-44-8]

\[
\text{O} 
\quad \begin{array}{c}
\text{S} \\
\text{O}
\end{array}
\]

Compound 2b was prepared following the general procedure A for the oxidation of thiolane (89.1 mg, 1.00 mmol) and isolated as a colorless liquid (90.4 mg, 0.90 mmol, 90%) after column chromatography (SiO\(_2\), CH\(_2\)Cl\(_2\)/MeOH = 96:4).

\(^1\text{H NMR (300 MHz, CDCl}_3\text{)} \delta = 2.95-2.72 (m, 4H), 2.53-2.30 (m, 2H), 2.08-1.92 (m, 2H) \text{ ppm.}

\(^{13}\text{C}[^1\text{H}] \text{ NMR (75 MHz, CDCl}_3\text{)} \delta = 54.6, 25.6 \text{ ppm.}

HRMS (ESI-TOF): [M + H]\(^+\) calcd. for C\(_4\)H\(_9\)OS: 105.0369; found: 105.0368.

The analytical data (NMR) matched those reported in the literature.[3]

4,4’ Bisphenol sulfoxide (2c) [CAS: 1774-34-1][3]

\[
\text{HO} 
\quad \begin{array}{c}
\text{S} \\
\text{O} \\
\text{O}
\end{array} 
\quad \text{OH} 
\]

Compound 2c was prepared following the general procedure A for the oxidation of 4,4’-thiodiphenol (223 mg, 1.00 mmol) and isolated as a colorless solid (210 mg, 0.90 mmol, 90%) after column chromatography (SiO\(_2\), pentane/ acetone gradient).

\(^1\text{H NMR (300 MHz, DMSO-}\text{d}_6\text{)} \delta = 10.10 (br. s, 2H), 7.42 (d, \text{ } J = 8.6 \text{ Hz, } 4H), 6.86 (d, \text{ } J = 8.6 \text{ Hz, } 4H) \text{ ppm.}

\(^{13}\text{C}[^1\text{H}] \text{ NMR (75 MHz, DMSO-}\text{d}_6\text{)} \delta = 159.9, 135.5, 126.5, 116.1 \text{ ppm.}

HRMS (ESI-TOF): [M + H]\(^+\) calcd. for C\(_{12}\)H\(_{11}\)O\(_3\)S: 235.0423; found: 235.0413.

The analytical data (NMR) matched those reported in the literature.[4]
8.2 Sulfones

Dimethylsulfone (4a) [CAS: 67-71-0]

Compound 4a was prepared following the general procedure B for the oxidation of dimethylsulfoxide (78.1 mg, 1.00 mmol) and isolated as a colorless solid (85.1 mg, 0.90 mmol, 90%).

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta = 2.98\) (s, 6H) ppm.
\(^{13}\)C\(^{\text{[\text{\text{[1}H\]}}}\) NMR (75 MHz, CDCl\(_3\)) \(\delta = 42.8\) ppm.
HRMS (ESI-TOF): [M + Na]\(^+\) calcd. for C\(_2\)H\(_6\)NaO\(_2\)S: 116.9986; found: 116.9981.
The analytical data (NMR) matched those reported in the literature.\(^{[5]}\)

Sulfolane (4b) [CAS: 126-33-0]

Compound 4b was prepared following the general procedure B for the oxidation of tetramethylenesulfoxide (109 mg, 1.00 mmol) and isolated as a colorless liquid (118 mg, 0.98 mmol, 98%).

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta = 3.03\) (m, 4H), 2.22 (m, 4H) ppm.
\(^{13}\)C\(^{\text{[\text{\text{[1}H\]}}}\) NMR (75 MHz, CDCl\(_3\)) \(\delta = 51.3, 22.9\) ppm.
HRMS (ESI-TOF): [M + H]\(^+\) calcd. for C\(_4\)H\(_9\)O\(_2\)S: 121.0318; found: 121.0318.
The analytical data (NMR) matched those reported in the literature.\(^{[3]}\)

4,4' Bisphenol S (4c) [CAS: 80-09-1]

Compound 4c was prepared following the general procedure B for the oxidation of 4,4' Bisphenol sulfoxide (109 mg, 1.00 mmol) using 10 equiv. peroxodicarbonate and isolated as a colorless solid (210 mg, 0.84 mmol, 84%) after column chromatography (SiO\(_2\), pentane/MTBE gradient).

\(^1\)H NMR (300 MHz, (CD\(_3\))\(_2\)CO)) \(\delta = 9.27\) (s, 2H), 7.78 (m, 4H), 6.97 (m, 4H) ppm.
\(^{13}\)C\(^{\text{[\text{\text{[1}H\]}}}\) NMR (75 MHz, (CD\(_3\))\(_2\)CO)) \(\delta = 162.4, 134.7, 130.6, 116.8\) ppm.
HRMS (ESI-TOF): [M + H]\(^+\) calcd. for C\(_{12}\)H\(_{11}\)O\(_4\)S: 251.0373; found: 251.0373.
The analytical data (NMR) matched those reported in the literature.\(^{[6]}\)

8.3 N-Oxides

N-Methylmorpholine N-oxide (6a) [CAS: 7529-22-8]

Compound 6a was prepared following the general procedure C for the N-oxidation of 4-methylmorpholine (101 mg, 1.00 mmol) and isolated as a colorless solid (109 mg, 0.93 mmol, 93%).

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta = 4.50−4.39\) (m, 2H), 3.81−3.72 (m, 2H), 3.36 (dt, \(J = 3.7\) Hz, 11.4 Hz, 2H), 3.26 (s, 3H), 3.15−3.06 (m, 2H) ppm.
\(^{13}\)C\(^{\text{[\text{\text{[1}H\]}}}\) NMR (75 MHz, CDCl\(_3\)) \(\delta = 66.1, 61.8, 61.4\) ppm.
HRMS (ESI-TOF): [M + H]\(^+\) calcd. for C\(_5\)H\(_{12}\)NO\(_2\): 118.0863; found: 118.0863.
The analytical data (NMR) matched those reported in the literature.\(^{[7]}\)
**SUPPORTING INFORMATION**

**N-Methylpiperidine N-oxide (6b) [CAS:17206-00-7]**

![Chemical structure of N-Methylpiperidine N-oxide (6b)](image)

Compound 6b was prepared following the general procedure C for the N-oxidation of N-methylpiperidine (102 mg, 1.00 mmol) and isolated as colorless solid (110 mg, 0.95 mmol, 95%).

1^H NMR (300 MHz, CDCl₃) δ = 3.30−3.15 (s in m, 7H), 2.38−2.21 (m, 2H), 1.77−1.54 (m, 3H), 1.49−1.30 (m, 1H) ppm.

13C{¹H} NMR (75 MHz, CDCl₃) δ = 67.6, 59.7, 21.9, 21.5 ppm.

HRMS (ESI-TOF): [M + H]^+ calcd. for C₆H₁₄NO: 116.1070; found: 116.1073.

The analytical data (NMR) matched those reported in the literature.[8]

**N-(2-Hydroxyethyl)morpholine-N-oxide (6c) [CAS: 95925-60-3]**

![Chemical structure of N-(2-Hydroxyethyl)morpholine-N-oxide (6c)](image)

Compound 6c was prepared following the general procedure C for the N-oxidation of N-(2-hydroxyethyl)morpholine (132 mg, 1.00 mmol) using 4 equiv. peroxodicarbonate and isolated as colorless solid (130 mg, 0.88 mmol, 88%).

1^H NMR (300 MHz, CDCl₃) δ = 7.72 (br. s., 1H), 4.45 (ddd, J = 3.3 Hz, 10.4 Hz, 12.6 Hz, 2H), 4.17−4.09 (m, 2H), 3.85−3.76 (m, 2H), 3.46−3.39 (m, 2H), 3.37−3.22 (m, 4H) ppm.

13C{¹H} NMR (75 MHz, CDCl₃) δ = 70.2, 65.1, 61.4, 57.3 ppm.

HRMS (ESI-TOF): [M + H]^+ calcd. for C₆H₁₄NO₃: 148.0968; found: 148.0971.

The analytical data (NMR) matched those reported in the literature.[9]

**Triethylamine N-oxide (6d) [CAS: 2687-45-8]**

![Chemical structure of Triethylamine N-oxide (6d)](image)

Compound 6d was prepared following the general procedure C for the N-oxidation of triethylamine (102 mg, 1.00 mmol) using 4 equiv. peroxodicarbonate and isolated as a colorless solid (112 mg, 0.96 mmol, 96%).

1^H NMR (300 MHz, CDCl₃) δ = 3.19 (q, J = 7.2 Hz, 6H), 1.33 (t, J = 7.2 Hz, 9H) ppm.

13C{¹H} NMR (75 MHz, CDCl₃) δ = 59.5, 8.6 ppm.

HRMS (ESI-TOF): [M + H]^+ calcd. for C₆H₁₆NO: 118.1226; found: 118.1227.

The analytical data (NMR) matched those reported in the literature.[10]

**N,N-Dimethylbenzylamine N-oxide (6e) [CAS: 5400-82-8]**

![Chemical structure of N,N-Dimethylbenzylamine N-oxide (6e)](image)

Compound 6e was prepared following the general procedure C for the N-oxidation of N,N-dimethylbenzylamine (137 mg, 1.00 mmol) in 5 mL EtOH/H₂O (1:4 (v/v)) using 4 equiv. peroxodicarbonate and isolated as a colorless solid (143 mg, 0.95 mmol, 95%).

1^H NMR (300 MHz, CDCl₃) δ = 7.52−7.46 (m, 2H), 7.46−7.38 (m, 3H), 4.41 (s, 2H), 3.12 (s, 6H) ppm.

13C{¹H} NMR (75 MHz, CDCl₃) δ = 132.0, 130.7, 129.8, 128.9, 76.7, 57.9 ppm.

HRMS (ESI-TOF): [M + H]^+ calcd. for C₉H₁₄NO: 152.1070; found: 152.1070.

The analytical data (NMR) matched those reported in the literature.[10]
Compound 6f was prepared following the general procedure C for the N-oxidation of (S)-(−)-Nicotine (164 mg, 1.00 mmol) in 1 mL H₂O using 4 equiv. peroxidicarbonate and isolated as a beige solid (171 mg, 0.96 mmol, 96%).

Mixture of cis and trans (d.r. 81:19)

cis:

\[ \text{H NMR (300 MHz, CDCl}_3\] \( \delta = 8.63 \text{ (dd, } J = 4.8, 1.5 \text{ Hz, 1H}), 8.59 \text{ (d, } J = 1.8 \text{ Hz, 1H}), 8.31–8.20 \text{ (m, 1H), 7.42–7.30 \text{ (m, 1H), 4.35 (dd, } J = 11.3, 7.4 \text{ Hz, 1H)}, 3.83–3.59 \text{ (m, 2H), 3.00 (s, 3H), 2.82–2.43 \text{ (m, 2H), 2.41–2.01 (m, 2H)) ppm.} \]

\[ \text{C}^{13} \text{NMR (75 MHz, CDCl}_3\] \( \delta = 151.8, 151.2, 139.1, 128.1, 123.6, 77.5, 70.7, 54.3, 29.2, 23.3 \text{ ppm.} \]

trans:

\[ \text{H NMR (300 MHz, CDCl}_3\] \( \delta = 8.73 \text{ (d, } J = 2.0 \text{ Hz, 1H)}, 8.69–8.65 \text{ (m, 1H), 7.96 \text{ (m, 1H), 7.42–7.30 \text{ (m, 1H), 4.67 (t, } J = 8.3 \text{ Hz, 1H}), 3.83–3.62 \text{ (m, 2H), 2.82–2.43 \text{ (m, 2H), 2.41–2.01 (m, 2H)) ppm.} \]

\[ \text{C}^{13} \text{NMR (75 MHz, CDCl}_3\] \( \delta = 151.2, 150.2, 137.5, 129.5, 123.8, 81.2, 69.8, 51.9, 26.4, 20.2 \text{ ppm.} \]

HRMS (ESI-TOF): [M + H]^+ calc. for C₁₀H₁₅N₂O: 179.1179; found: 179.1173.

The analytical data (NMR) matched those reported in the literature.[11,12]

8.4 Enones

1,3-Diphenyl-propen-1-one (7e)

Compound 7e was synthesized according to the general procedure D using acetophenone and benzaldehyde. NaOH (2.262 g, 56.5 mmol, 1.1 eq.) was dissolved in water (20 mL) and added to a stirred ice-cold solution of acetophenone (6.0 mL, 51.4 mmol, 1.0 eq.) in ethanol (60 mL). Benzaldehyde (5.19 mL, 51.4 mmol, 1.0 eq) was added via syringe to the slightly yellow solution. After stirring overnight at room temperature, the precipitated solid was filtered off, washed with water giving the title compound as a bright yellow solid (9.168 g, 44.1 mmol, 86%).

m.p. (EtOH) = 54–55 °C, Lit.: 54–56 °C.

\[ \text{H NMR (400 MHz, CDCl}_3\] \( \delta = 8.10–7.99 \text{ (m, 2H), 7.82 (d, } J = 15.7 \text{ Hz, 1H), 7.69–7.63 \text{ (m, 2H), 7.63–7.49 \text{ (m, 4H), 7.47–7.38 \text{ (m, 3H)) ppm.} \]

\[ \text{C NMR (101 MHz, CDCl}_3\] \( \delta = 190.7, 145.0, 138.4, 135.0, 132.9, 130.7, 129.1, 128.8, 128.7, 126.2 \text{ ppm.} \]

HRMS (ESI-TOF): [M+H]^+ calc. for C₁₅H₁₂O: 209.0961; found: 209.0953.

The analytical data matches the reported literature.[13]

3-(4-Nitrophenyl)-1-phenyl-propen-1-one (7f)

Compound 7f was synthesized according to the general procedure D. Acetophenone (2.4 mL, 20.58 mmol) was dissolved in 10 mL of EtOH and NaOH solution (980 mg, 24.5 mmol in 15 mL H₂O) was added to the cooled mixture. After 5 minutes 4-nitro-benzaldehyde (3.11 g, 20.58 mmol) in 40 mL EtOH was added in one portion and the mixture stirred overnight. The collected precipitate was washed several times with water and recrystallized from pure ethanol to give the title compound as light orange crystals (4.196 g, 16.57 mmol, 81%).

m.p. (EtOH) = 163–164 °C, Lit.: 165 °C

\[ \text{H NMR (400 MHz, CDCl}_3\] \( \delta = 8.28 \text{ (m, 2H), 8.07–8.01 \text{ (m, 2H), 7.85–7.76 \text{ (m, 3H), 7.68–7.50 \text{ (m, 4H)) ppm.} \]

\[ \text{C NMR (101 MHz, CDCl}_3\] \( \delta = 189.8, 158.7, 141.7, 137.7, 133.5, 129.1, 129.0, 128.7, 125.9, 124.4 \text{ ppm.} \]

HRMS (ESI-TOF): [M+H]^+ calc. for C₁₅H₁₂NO₃: 254.0812; found: 254.0817.

The analytical data is in accordance with the literature.[14,15]
1-Phenyl-3-(4-(trifluoromethyl)phenyl)-propen-1-one (7g)

Compound 7g was synthesized according to the general procedure D. Acetophenone (1.75 mL, 15 mmol) was dissolved in 20 mL of EtOH and NaOH solution (660 mg, 16.5 mmol in 10 mL H₂O) was added to the cooled mixture. After 5 minutes 4-(trifluoromethyl)benzaldehyde was added in one portion via syringe (1.99 mL, 15 mmol) and the mixture stirred overnight. The collected precipitate was washed several times with water and recrystallized from 2:1 EtOH/H₂O to give the title compound as light green crystals (3.01 g, 10.9 mmol, 73%).

m.p. (EtOH/ H₂O) = 129–130 °C, Lit.: 129–130 °C.

1H NMR (400 MHz, CDCl₃): δ = 8.07–8.00 (m, 2H), 7.81 (d, J = 15.7 Hz, 1H), 7.78–7.65 (m, 4H), 7.65–7.56 (m, 2H), 7.57–7.49 (m, 2H) ppm.

13C NMR (101 MHz, CDCl₃): δ = 190.2, 142.9, 138.4, 137.9, 133.2, 132.2, 131.9, 128.9, 128.7, 126.1, 126.0, 125.3, 124.4, 122.6 ppm.

19F NMR (376 MHz, CDCl₃): δ = -64.0 ppm

HRMS (ESI-TOF): [M+H]+ calc. for C₁₅H₁₁NO₃: 277.0835; found: 277.0835.

The analytical data matches the reported literature.[16,17]

3-(4-chlorophenyl)-1-phenyl-prop-2-en-1-one (7h)

Compound 7h was synthesized according to the general procedure D. NaOH (145 mg, 3.62 mmol, 1.1 eq.) was dissolved in water (3 mL) and added to a stirred ice-cold solution of acetophenone (0.38 mL, 3.29 mmol, 1.0 eq.) in ethanol (15 mL). 4-chlorobenzaldehyde (463 mg, 3.29 mmol, 1.0 eq.) was added after 5 minutes. After stirring overnight at room temperature, the precipitated solid was filtered off and washed with water, giving the title compound as a bright yellow solid (750 mg, 3.1 mmol, 94%).

m.p. (EtOH) = 113–114 °C, Lit.: 113–114 °C.

1H NMR (400 MHz, CDCl₃): δ = 8.05–7.99 (m, 2H), 7.76 (d, J = 15.7 Hz, 1H), 7.63–7.56 (m, 3H), 7.54–7.48 (m, 3H), 7.42–7.37 (m, 2H) ppm.

13C NMR (101 MHz, CDCl₃): δ = 190.3, 143.4, 138.0, 136.5, 133.4, 133.0, 129.6, 129.3, 128.7, 128.5, 122.4 ppm.

HRMS (ESI-TOF): [M+H]+ calc. for C₁₅H₁₂ClO: 243.0571; found: 243.0562.

The analytical data is in accordance with the reported literature.[18,19]

3-(4-bromophenyl)-1-phenyl-prop-2-en-1-one (7i)

Compound 7i was synthesized according to the general procedure D. NaOH (377 mg, 9.43 mmol, 1.1 eq.) was dissolved in water (5 mL) and added to a stirred ice-cold solution of acetophenone (1.0 mL, 8.57 mmol, 1.0 eq.) in ethanol (20 mL). 4-bromobenzaldehyde (1.586 g, 8.57 mmol, 1.0 eq.) was added after 5 minutes. After stirring overnight at room temperature, the precipitated solid was filtered off and washed with water, giving the title compound as a bright yellow solid (2.314 g, 8.059 mmol, 94%).

m.p. (EtOH) = 122–124 °C, Lit.: 123.5 °C.

1H NMR (400 MHz, CDCl₃): δ = 8.05–7.98 (m, 2H), 7.74 (d, J = 15.7 Hz, 1H), 7.63–7.48 (m, 8H) ppm.

13C NMR (101 MHz, CDCl₃): δ = 190.3, 143.4, 138.0, 136.5, 133.8, 133.0, 129.8, 128.7, 124.8, 122.5 ppm.

HRMS (ESI-TOF): [M+H]+ calc. for C₁₅H₁₂BrO: 287.0066; found: 287.0055.

The analytical data is in accordance with the reported literature.[20,21]
1-Phenyl-3-(3-(trifluoromethyl)phenyl)-propen-1-one (7j)

Compound 7j was synthesized according to the general procedure D. Acetophenone (1.75 mL, 15 mmol) was dissolved in 20 mL of EtOH and NaOH solution (660 mg, 16.5 mmol in 10 mL H$_2$O) was added to the cooled mixture. After 5 minutes 3-(trifluoromethyl)-benzaldehyde was added in one portion via syringe (1.99 mL, 15 mmol) and the mixture stirred overnight. The collected precipitate was washed several times with water and recrystallized from 2:1 EtOH/H$_2$O to give the title compound as light green crystals (3.662 g, 13.26 mmol, 88%).

m.p. (EtOH/ H$_2$O) = 109–110 °C, Lit.: 109–110 °C.

$^1$H NMR (400 MHz, CDCl$_3$): δ = 8.08–8.01 (m, 2H), 7.92–7.87 (m, 1H), 7.86–7.78 (m, 2H), 7.69–7.50 (m, 6H) ppm.

$^{13}$C NMR (101 MHz, CDCl$_3$): δ = 190.2, 143.0, 138.0, 135.8, 133.3, 131.8, 131.5, 129.7, 128.9, 128.7, 127.0, 125.3, 124.8, 123.8, 122.6 ppm.

$^{19}$F NMR (376 MHz, CDCl$_3$): δ = -64.0 ppm.

HRMS (ESI-TOF): [M+H]$^+$ calc. for C$_{16}$H$_{12}$F$_3$O: 277.0835; found: 277.0831.

The analytical data is in accordance with the reported literature.

1-(4-bromophenyl)-3-phenyl-prop-2-en-1-one (7k)

Compound 7k was synthesized according to the general procedure D. NaOH (145 mg, 3.62 mmol, 1.1 eq.) was dissolved in water (3 mL) and added to a stirred ice-cold solution of 4-bromo-acetophenone (654 mg, 3.29 mmol, 1.0 eq.) in ethanol (15 mL). Benzaldehyde (0.34 mL, 3.29 mmol, 1.0 eq.) was added after 5 minutes via syringe. After stirring overnight at room temperature, the precipitated solid was filtered off and washed with water, giving the title compound as an off-white solid (621 mg, 3.1 mmol, 66%).

m.p. (EtOH/ H$_2$O) = 101–102 °C, Lit.: 103–104 °C.

$^1$H NMR (400 MHz, CDCl$_3$): δ = 7.93–7.87 (m, 2H), 7.82 (d, J = 15.7 Hz, 1H), 7.69–7.60 (m, 4H), 7.48 (d, J = 15.7 Hz, 1H), 7.45–7.38 (m, 3H) ppm.

$^{13}$C NMR (101 MHz, CDCl$_3$): δ = 189.5, 145.6, 137.0, 134.8, 130.9, 130.2, 129.15, 128.7, 128.1, 121.6 ppm.

HRMS (ESI-TOF): [M+H]$^+$ calc. for C$_{15}$H$_{12}$BrO: 287.0066; found: 287.0056.

The analytical data is in accordance with the reported literature.

1-(4-(trifluoromethyl)phenyl)-3-phenyl-prop-2-en-1-one (7l)

Compound 7l was synthesized according to the general procedure D. NaOH (396 mg, 9.896 mmol, 1.0 eq.) was dissolved in water (20 mL) and added to a stirred ice-cold solution of 4-trifluoromethyl-acetophenone (1.862 g, 9.896 mmol, 1.0 eq.) in ethanol (20 mL). Benzaldehyde (1.0 mL, 9.896 mmol, 1.0 eq.) was added after 5 minutes via syringe. After stirring overnight at room temperature, the precipitated solid was filtered off and washed with water, giving the title compound as a bright yellow solid (750 mg, 3.1 mmol, 94%).

m.p. (EtOH/ H$_2$O) = 122–123 °C, Lit.: 120–122 °C.

$^1$H NMR (400 MHz, CDCl$_3$): δ = 8.10 (dq, J = 7.8, 0.9 Hz, 2H), 7.84 (d, J = 15.7 Hz, 1H), 7.81–7.74 (m, 2H), 7.49 (d, J = 15.7 Hz, 1H), 7.46–7.41 (m, 3H) ppm.

$^{13}$C NMR (101 MHz, CDCl$_3$): δ = 189.8, 146.3, 141.2, 134.7, 134.3, 134.0, 131.1, 129.2, 128.9, 128.8, 125.8, 125.2, 122.5, 121.7 ppm.

$^{19}$F NMR (376 MHz, CDCl$_3$): δ = -64.2 ppm.

HRMS (ESI-TOF): [M+H]$^+$ calc. for C$_{16}$H$_{12}$F$_3$O: 277.0835; found: 277.0830.

The analytical data is in accordance with the reported literature.
8.5 Epoxides

2,3-Epoxy-2-methyl-2,3-dihydro-1,4-naphthoquinone (8a)

Epoxide 8a was synthesized according to general protocol F. A freshly prepared solution of peroxodicarbonate (2.0 eq. according to the result of the titration) was added to a stirred solution of 2-methyl-1,4-naphthoquinone (172 mg, 1.0 mmol, 1.0 eq.) in 20 mL of CH₂Cl₂/EtOH/H₂O (2:1:1) at 0 °C. The reaction was complete after 1 hour. Subsequent workup according to general protocol F and recrystallization from ethanol/water (2:1) gave the pure epoxide 8a as yellow needles (181 mg, 0.962 mmol, 96%).

m.p. (EtOH/H₂O) = 92–93 °C, Lit.: 94–96 °C.

¹H NMR (400 MHz, CDCl₃): δ = 8.04–7.98 (m, 1H), 7.97–7.91 (m, 1H), 7.77–7.70 (m 2H), 3.85 (s, 1H), 1.73 (s, 3H) ppm.

¹³C NMR (101 MHz, CDCl₃): δ = 192.1, 191.9, 134.7, 134.5, 132.2, 132.1, 127.6, 126.9, 61.6, 61.5, 14.8 ppm.

HRMS (ESI-TOF): [M+H]⁺ calc. for C₁₁H₉O₃: 189.0546; found: 189.0543.

The analytical data matches the reported literature.[26,27]

2,3-Epoxy-2,3-dihydro-1,4-naphthoquinone (8b)

Compound 8b was prepared according to general protocol F. Freshly electrolyzed peroxodicarbonate solution (2.0 eq.) was added to a stirred solution of 1,4-naphthoquinone (158 mg, 1.0 mmol, 1.0 eq.) in 20 mL of CH₂Cl₂/EtOH/H₂O (2:1:1) at 0 °C. After 1 h the reaction was complete and worked up according to general protocol F giving the pure epoxide as a light brown solid (164 mg, 0.941 mmol, 94%).

m.p. (CH₂Cl₂) = 129–130 °C, Lit: 134–136 °C.

¹H NMR (400 MHz, CDCl₃): δ = 7.99 (dd, J = 5.8, 3.3 Hz, 2H), 7.77 (dd, J = 5.8, 3.3 Hz, 2H), 4.02 (s, 2H) ppm.

¹³C NMR (101 MHz, CDCl₃): δ = 190.9, 134.9, 131.9, 127.4, 55.4 ppm.

HRMS (ESI-TOF): [M+H]⁺ calc. for C₁₀H₇O₃: 175.0390; found: 175.0391.

The analytical data is in accordance with the reported literature.[28,29]

2,3-Epoxy-3,5,5-trimethylcyclohexan-1-one (8c)

Isophorone (276 mg, 2.0 mmol, 1.0 eq) was dissolved in ethanol at 0 °C. Over the course of 0.5 h freshly prepared peroxodicarbonate solution (8.5 eq. according to the result of the titration) was added dropwise at 0 °C and stirred for 6.5 h. This process was repeated two times until full conversion of starting material was observed. After subsequent workup, the residue was passed through a silica gel column with cyclohexane/ethyl acetate (9:1) and gave 2,3-epoxy-3,5,5-trimethylcyclohexan-1-one as colorless liquid (210 mg, 1.4 mmol, 70%).

¹H NMR (400 MHz, CDCl₃): δ = 3.03 (s, 1H), 2.59 (dd, J = 13.2 Hz, 1.0 Hz, 1H), 2.05 (dd, J = 13.2 Hz, 1.0 Hz, 1H), 1.83–1.63 (m, 2H), 1.40 (s, 3H), 1.00 (s, 3H), 0.89 (s, 3H) ppm.

¹³C NMR (101 MHz, CDCl₃): δ = 208.18, 64.46, 61.57, 48.12, 42.88, 36.31, 30.96, 27.97, 24.18 ppm.

The spectral data is in accordance with the reported literature.[30]
Compound 8d was synthesized according to general protocol F. 2,5-dimethyl-1,4-benzoquinone was dissolved in CH₂Cl₂/EtOH/H₂O (2:1:1) at 0 °C and freshly prepared peroxodicarbonate solution (4.0 eq. according to the result of the titration) was added in one go. After three hours the reaction was complete (monitored via GC-MS) and worked up accordingly. After removal of the solvent, the target epoxide 8d was obtained as a brown solid (101 mg, 0.601 mmol, 60%).

Mixture of isomers (0.17:0.83):

m.p. (CH₂Cl₂) = 85–86 °C, Lit.: 86–88° C.

¹H NMR (400 MHz, CDCl₃): δ = 3.59 (s, 3H), 3.42 (s, 3H), 1.55 (s, 1H), 1.52 (s, 1H) ppm.

¹³C NMR (101 MHz, CDCl₃): δ = 197.5, 194.6, 64.7, 64.04, 57 ppm.

HRMS (ESI-TOF): [M-H]⁻ calc. for C₈H₈O₄: 167.0350; found: 167.0352.

The melting point matches the reported literature.[31]

Phenyl(3-phenyloxiran-2-yl)methan-1-one (8e)

Compound 8e was synthesized according to general protocol E. Freshly prepared peroxodicarbonate solution (9.0 eq. according to the result of the titration) was added to a stirred ethanolic solution of 1,3-diphenyl-prop-2-en-1-one (7e, 208 mg, 1 mmol, 1.0 eq.) at room temperature. After subsequent workup, the epoxide was passed through a column of silica using cyclohexane/ethyl acetate (9:1) as eluent. After evaporation of the solvent the title compound 8e was obtained as an off-white solid (190 mg, 0.847 mmol, 85%).

m.p. (EtOAc/Cy) = 87–89°C, Lit.: 87–89 °C.

¹H NMR (400 MHz, CDCl₃): δ = 8.02 (dd, J = 8.4, 1.3 Hz, 2H), 7.67–7.58 (m, 1H), 7.53–7.46 (m, 2H), 7.43–7.35 (m, 5H) 4.30 (d, J = 1.9 Hz, 1H), 4.08 (d, J = 1.9 Hz, 1H) ppm.

¹³C NMR (101 MHz, CDCl₃): δ = 193.2, 135.6, 134.1, 129.2, 129.0, 128.9, 128.5, 125.9, 61.2, 59.5 ppm.

HRMS (ESI-TOF): [M+Na]⁺ calc. for C₁₅H₁₂O₂: 247.0730; found: 247.0720.

The analytical data matches those reported in the literature.[32,33]

(3-(4-Nitro-phenyl)-oxiran-2-yl)-phenyl-methan-1-one (8f)

Epoxide 8f was synthesized according to general protocol E. A freshly prepared solution of peroxodicarbonate (9.0 eq. according to results from the titration) was added to a suspension of 7c (253 mg, 1.0 mmol, 1.0 eq.) in ethanol at ambient temperature. After 2 h the reaction turned colorless and was complete (confirmed via GC-MS) and worked up accordingly. The crude epoxide was purified via column chromatography (silica, ethyl acetate/cyclohexane 99:1 to 9:1) giving the title compound 8f as a white solid (252 mg, 0.936 mmol, 94%).

m.p. (EtOAc/Cy) = 150–151 °C, Lit.: 150 °C

¹H NMR (400 MHz, CDCl₃): δ = 8.34–8.19 (m, 2H), 8.05–7.97 (m, 2H), 7.71–7.61 (m, 1H), 7.59–7.47 (m, 4H) 4.28 (d, J = 1.8 Hz, 1H), 4.21 (d, J = 1.8 Hz, 1H) ppm.

¹³C NMR (101 MHz, CDCl₃): δ = 192.2, 148.9, 142.9, 135.3, 134.5, 129.2, 128.6, 126.8, 124.2, 61.0, 58.2 ppm.

HRMS (ESI-TOF): [M+Na]⁺ calc. for C₁₅H₁₁NNaO₄: 292.0580; found: 292.0578.

Analytical data matches those reported previously.[18,32]
Epoxide 8g was obtained via general protocol E. To an ethanolic solution of 7g (276 mg, 1.0 mmol, 1.0 eq.) was added freshly prepared peroxodicarbonate solution (7.0 eq.). After the conversion was completed, subsequent workup and purification via column chromatography (silica, cyclohexane/ethyl acetate (99:1 to 9:1)) gave the title compound 8g as a white solid (161 mg, 0.551 mmol, 55%).

\[
m.p. \text{ (EtOAc/ Cy) } = 91–93 \, ^\circ\text{C}, \text{ Lit.: } 93–96 \, ^\circ\text{C}.
\]

\[
\begin{align*}
\delta & = 8.04–7.98 \text{ (m, 2H)}, 7.70–7.65 \text{ (m, 2H)}, 7.65–7.61 \text{ (m, 1H)}, 7.54–7.47 \text{ (m, 4H)}, 4.27 \text{ (d, } J = 1.9 \text{ Hz, 1H)}, \\
& 4.15 \text{ (d, } J = 1.8 \text{ Hz, 1H) ppm.}
\end{align*}
\]

\[
19\text{F NMR (376 MHz, CDCl}_3\text{): } \delta = -63.8 \text{ ppm}
\]

HRMS (ESI-TOF): [M+H]\(^+\) calc. for C\(_{16}\)H\(_{12}\)F\(_3\)O\(_2\): 315.0609; found: 315.0604.

The analytical data matches the reported literature.\[34,35\]

1-Phenyl-3-(4-chlorophenyl)oxiran-2-yl-methan-1-one (8h)

The title compound 8h was synthesized according to general protocol E. 1-phenyl-3-(4-chlorophenyl)-prop-2-en-1-one (243 mg, 1.0 mmol, 1.0 eq.) was dissolved in ethanol. A freshly prepared solution of peroxodicarbonate (9.0 eq. according to the result of the titration) was added to the mixture and stirred at room temperature. After subsequent workup, the epoxide was purified via column chromatography (silica, cyclohexane/ethyl acetate (99:1 to 9:1)). After removal of the solvent 8h was obtained as a white solid (178 mg, 0.688 mmol, 69%).

\[
m.p. \text{ (EtOAc/ Cy) } = 73–75 \, ^\circ\text{C}, \text{ Lit.: } 78–79 \, ^\circ\text{C (EtOH)}.
\]

\[
\begin{align*}
\delta & = 8.05–7.97 \text{ (m, 2H)}, 7.63 \text{ (ddt, } J = 8.0, 6.9, 1.3 \text{ Hz, 1H)}, 7.54–7.46 \text{ (m, 2H)}, 7.42–7.35 \text{ (m, 2H)}, 7.35–7.28 \text{ (m, 2H)}, 4.25 \text{ (d, } J = 1.8 \text{ Hz, 1H)}, 4.06 \text{ (d, } J = 1.8 \text{ Hz) ppm.}
\end{align*}
\]

\[
19\text{F NMR (376 MHz, CDCl}_3\text{): } \delta = -63.8 \text{ ppm}
\]

HRMS (ESI-TOF): [M+Na]\(^+\) calc. for C\(_{15}\)H\(_{11}\)ClNaO\(_2\): 281.0340; found: 281.0329.

The analytical data is in accordance with the reported literature.\[34,36\]

3-(4-bromophenyl)-oxiran-2-yl-1-phenyl-methan-1-one (8i)

Compound 8i was synthesized according to general protocol E. 3-(4-bromophenyl)-1-phenyl-prop-2-en-1-one (7i, 287 mg, 1.0 mmol, 1.0 eq.) was dissolved in ethanol. A freshly prepared solution of peroxodicarbonate (9.0 eq. according to the results of the titration) was added to the mixture and stirred for 2 h until the reaction was completed (monitored via GC-MS). The reaction mixture was worked up accordingly and the crude epoxide purified via column chromatography (silica, cyclohexane/ethyl acetate 99:1). After evaporation of the solvent the title compound 8i was obtained as a white solid (162 mg, 0.534 mmol, 53%).

\[
m.p. \text{ (EtOAc/ Cy) } = 85–86 \, ^\circ\text{C, Lit.: } 85–86 \, ^\circ\text{C.}
\]

\[
\begin{align*}
\delta & = 8.00 \text{ (dd, } J = 8.4, 1.3 \text{ Hz, 2H)}, 7.69–7.59 \text{ (m, 1H)}, 7.58–7.45 \text{ (m, 4H)}, 7.30–7.21 \text{ (m, 2H)}, 4.25 \text{ (d, } J = 1.9 \text{ Hz, 1H)}, 4.05 \text{ (d, } J = 1.8 \text{ Hz, 1H) ppm.}
\end{align*}
\]

\[
19\text{F NMR (376 MHz, CDCl}_3\text{): } \delta = -63.8 \text{ ppm}
\]

HRMS (ESI-TOF): [M+H]\(^+\) calc. for C\(_{15}\)H\(_{12}\)BrO\(_2\): 303.0015; found: 303.0004.

The analytical data is in accordance with the published literature.\[32,37\]
1-Phenyl-3-(3-(trifluoromethyl)phenyl-oxiran-2-yl)methan-1-one (8j)

Compound 8j was synthesized according to general protocol E. A freshly prepared solution of peroxodicarbonate (9.0 eq. according to the result of the titration) was added to a solution of 7j in ethanol (276 mg, 1.0 mmol, 1.0 eq.) at room temperature. After 3 h the reaction mixture was worked up as described under general protocol E and passed through a column of silica (cyclohexane/ethyl acetate 99:1 to 9:1) giving the title compound 8j as a white solid (258 mg, 0.883 mmol, 88%).

m.p. (EtOAc/Cy) = 77–78 °C, Lit.: 76.5–78.5 °C.

1H NMR (400 MHz, CDCl3): δ = 8.04–7.99 (m, 2H), 7.67–7.48 (m, 7H), 4.29 (d, J = 1.8 Hz, 1H) 4.16 (d, J = 1.8 Hz, 1H) ppm.

13C NMR (101 MHz, CDCl3): δ = 192.6, 136.9, 134.4, 131.7, 131.4, 129.5, 129.3, 129.1 128.6, 126.0, 122.7, 61.0, 58.7 ppm.

19F NMR (376 MHz, CDCl3): δ = -63.9 ppm

HRMS (ESI-TOF): [M+H]+ calc. for C16H12F3O2: 293.0784; found: 293.0785.

The melting point matches the reported literature.  

1-(4-bromophenyl)-oxiran-2-yl-3-phenyl-methan-1-one (8k)

Epoxide 8k was synthesized according to general protocol E. 1-(4-bromophenyl)-3-phenyl-prop-2-en-1-one (215 mg, 0.731 mmol, 1.0 eq.) was dissolved in ethanol. A freshly prepared solution of peroxodicarbonate (9.0 eq. according to the results of the iodometric titration) were added to the solution and stirred at room temperature for 3 h. After subsequent workup, the crude product was purified by passing through a column of silica (cyclohexane/ethyl acetate 99:1). Removal of the solvent gave the title compound as a white solid (122 mg, 0.402 mmol, 55%).

m.p. (EtOAc/Cy) = 127–128 °C, Lit.: 128 °C.

1H NMR (400 MHz, CDCl3): δ = 7.89 (d, J = 8.6 Hz, 2H), 7.64 (d, J = 8.6 Hz, 2H), 7.48–7.32 (m, 5H), 4.23 (d, J = 1.9 Hz, 1H), 4.07 (d, J = 1.8 Hz, 1H) ppm.

13C NMR (101 MHz, CDCl3): δ = 192.4, 135.4, 134.2, 132.4, 130.0, 129.5, 129.3, 129.0, 125.9, 61.2, 59.5 ppm.

HRMS (ESI-TOF): [M+H]+ calc. for C15H12BrO2: 303.0015; found: 303.0004.

The analytical data is in accordance with the literature.[39,40]

(3-phenyloxiran-2-yl)-(4-(trifluoromethyl)phenyl)methan-1-one (8l)

Epoxide 8l was synthesized according to general protocol E. To a solution of 1-(4-(trifluoromethyl)phenyl)-3-phenyl-prop-2-en-1-one (7d) (276 mg, 1.0 mmol, 1.0 eq.) in ethanol a freshly prepared solution of peroxodicarbonate (9.0 eq according to the results of the titration) was added at ambient temperature. Subsequent workup according to general procedure E and purification of the crude using column chromatography (SiO2, cyclohexane/ethyl acetate 99:1 to 9:1) gave the title compound as a white solid (270 mg, 0.924 mmol, 92%).

m.p. (EtOAc/Cy) = 107–109 °C, Lit.: 108–109 °C (EtOAc).

1H NMR (400 MHz, CDCl3): δ = 8.17–8.08 (m, 2H), 7.76 (d, J = 8.2 Hz, 2H), 7.47–7.32 (m, 5H), 4.27 (d, J = 1.8 Hz, 1H), 4.09 (d, J = 1.8 Hz, 1H) ppm.

13C NMR (101 MHz, CDCl3): δ = 192.7, 138.1, 135.5, 135.2, 129.4, 129.0, 128.9, 12.9, 124.9, 122.2, 61.5, 59.7 ppm.

19F NMR (376 MHz, CDCl3): δ = -64.4 ppm

HRMS (ESI-TOF): [M+H]+ calc. for C16H12F3O2: 293.0784; found: 293.0785.

The analytical data are in accordance with the reported literature.[34]
8.6 Multi-gram-scale Epoxidation of 2-Methyl-1,4-naphthoquinone

To a solution of 2-Methyl-1,4-naphthoquinone (5.0 g, 29.04 mmol) in 200 mL of CH₂Cl₂/EtOH/H₂O (2:1:1) in a 500 mL three-necked round-bottom flask with mechanical stirrer and pre-cooled dropping funnel, a freshly prepared solution of peroxodicarbonate (2.0 eq., 58.08 mmol) was added quickly over 5 minutes. The required amount was calculated according to the result of the titration. The reaction was monitored via GC-MS and stirred overnight. After confirming complete conversion, the reaction mixture was diluted with water (100 mL) and transferred into a 1 L separatory funnel. The aqueous layer was extracted with dichloromethane (3x 100 mL), washed with brine (1x 120 mL) and dried over MgSO₄. After filtration the solvent was evaporated under reduced pressure giving the epoxide as a light brown solid. Recrystallization from ethanol/H₂O (3:2) gave the epoxide 8a as yellow needles (4.9 g, 90%). For analytical data, see section 8.5 compound 8a.
9. NMR-Spectra

3-(Methylsulfinyl)benzoic acid (2a)

$^1$H NMR (300 MHz, DMSO-d$_6$)

Chemical Shift (ppm)

$^{13}$C($^1$H) NMR (75 MHz, DMSO-d$_6$)

Chemical Shift (ppm)
Thiolane sulfoxide (2b)

1H NMR (300 MHz, CDCl$_3$)

13C{1H} NMR (75 MHz, CDCl$_3$)
4,4’ Bisphenol sulfoxide (2c)

\(^1\)H NMR (300 MHz, DMSO-\(d_6\))

\[^{13}\]C\(^{(1)}\)H\) NMR (75 MHz, DMSO-\(d_6\))
**Dimethylsulfone (4a)**

$^1$H NMR (300 MHz, CDCl₃)

$^{13}$C($^1$H) NMR (75 MHz, CDCl₃)
**SUPPORTING INFORMATION**

**Sulfolane (4b)**

$^1$H NMR (300 MHz, CDCl$_3$)

![Chemical Shift (ppm)](image-1)

$^{13}$C($^1$H) NMR (75 MHz, CDCl$_3$)

![Chemical Shift (ppm)](image-2)
4,4’ Bisphenol S (4c)

$^1$H NMR (300 MHz, (CD$_3$)$_2$CO)

$^{13}$C($^1$H) NMR (75 MHz, (CD$_3$)$_2$CO)
**SUPPORTING INFORMATION**

*N*-Methylmorpholine *N*-oxide (6a)

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C($^1$H) NMR (75 MHz, CDCl$_3$)
**N-Methylpiperidine N-oxide (6b)**

**$^1$H NMR (300 MHz, CDCl$_3$)**

Chemical Shift (ppm): 7.26, 3.19, 3.17, 2.27, 2.25, 1.63, 1.58

**$^{13}$C($^1$H) NMR (75 MHz, CDCl$_3$)**

Chemical Shift (ppm): 77.58, 77.58, 76.74, 67.58, 59.75, 21.46, 21.92, 21.46, 21.92
SUPPORTING INFORMATION

*N-(2-Hydroxyethyl)morpholine N-oxide (6c)*

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C($^1$H) NMR (75 MHz, CDCl$_3$)
Triethylamine N-oxide (6d)

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C($^1$H) NMR (75 MHz, CDCl$_3$)
\textbf{SUPPORTING INFORMATION}

\textit{N,N-Dimethylbenzylamine N-oxide (6e)}

$^1\text{H NMR (300 MHz, CDCl}_3\text{)}$

\begin{center}
\includegraphics[width=\textwidth]{n-h-nmr.png}
\end{center}

\textit{\textsuperscript{13}C($^1\text{H}$) NMR (75 MHz, CDCl$_3$)}

\begin{center}
\includegraphics[width=\textwidth]{c-nmr.png}
\end{center}
(S)-(-)-Nicotine N-1'-Oxide (6f)

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C$^1$H NMR (75 MHz, CDCl$_3$)
1,3-Diphenyl-propan-1-one (7e)
3-(4-Nitrophenyl)-1-phenyl-propen-1-one (7f)
1-Phenyl-3-(4-(trifluoromethyl)phenyl)-propen-1-one (7g)
3-(4-chlorophenyl)-1-phenyl-prop-2-en-1-one (7h)
3-(4-bromophenyl)-1-phenyl-prop-2-en-1-one (7i)
1-Phenyl-3-(3-(trifluoromethyl)phenyl)-prop-1-one (7j)
SUPPORTING INFORMATION

1-((4-bromophenyl)-3-phenyl-prop-2-en-1-one (7k)

[Chemical structure and NMR spectra are shown here, but not transcribed.]
1-(4-(trifluoromethyl)phenyl)-3-phenyl-prop-2-ene-1-one (7l)
2,3-Epoxy-2-methyl-2,3-dihydro-1,4-naphthoquinone (8a)
2,3-Epoxy-2,3-dihydro-1,4-naphthoquinone (8b)
2,3-Epoxy-3,5,5-trimethylcyclohexan-1-one (8c)
2,3,5,6-Diepoxy-2,5-dimethyl-1,4-benzoquinone (8d)
Phenyl(3-phenyloxiran-2-yl)methan-1-one (8e)
1-phenyl-3-(4-(trifluoromethyl)phenyl)oxiran-2-yl)-methan-1-one (8g)
1-Phenyl-3-(4-chlorophenyl)oxiran-2-yl-methan-1-one (8h)
3-(4-bromophenyl)-oxiran-2-yl-1-phenyl-methan-1-one (8i)
1-Phenyl-3-(3-(trifluoromethyl)phenyl)-oxiran-2-yl)methan-1-one (8j)
1-(4-bromophenyl)-oxiran-2-yl-3-phenyl-methan-1-one (8k)
(3-phenyloxiran-2-yl)-1-(4-(trifluoromethyl)phenyl)methan-1-one (8I)
10. References

[1] a) C. Gütz, A. Stenglein, S. R. Waldvogel, Org. Process Res. Dev. 2017, 21, 771–778. b) "ElectraSyn flow - Elektrosynthese Systeme," can be found under https://www.ikaprocess.com/en/Products/Electro-Organic-Synthesis-Systems-cph-45/ ElectraSyn-flow-csb-ES/, accessed 22.12.2021.

[2] C. P. Chardon, T. Matthée, R. Neuber, M. Fryda, C. Comninelis, ChemistrySelect 2017, 2, 1037–1040.

[3] C. Yang, Q. Jin, H. Zhang, J. Liao, J. Zhu, B. Yu, J. Deng, Green Chemistry 2009, 11, 1401.

[4] B. Karimi, M. Khorasani, ACS Catal. 2013, 3, 1657–1654.

[5] M. Dráčínský, R. Pohl, L. Slavětiñská, M. Budíñský, Magnetic Resonance in Chemistry 2010, 48, 718–726.

[6] H. Tanaka, H. Korishi, K. Marane, Chem. Lett. 2019, 48, 760–763.

[7] Y. Imai, H. Iida, S. Oho, S.-I. Murashii, J. Am. Chem. Soc. 2003, 125, 2868–2869.

[8] H. Völz, H. Gartner, Eur. J. Org. Chem. 2007, 2007, 2791–2801.

[9] D. Limnios, C. G. Kokotos, Chem. Eur. J. 2014, 20, 559–563.

[10] S. Zhang, J. Li, X. Deng, G. Zhao, X. Cui, Z. Tang, ACS Catal. 2010, 10, 245–252.

[11] T. Nishida, A. Pilotti, C. R. Enzelj, Org. Magn. Reson. 1980, 13, 434–437.

[12] G. Ollotina, S. Bianchi, B. Belloni, G. Carrea, B. Danieli. Tetrahedron Letters 1999, 40, 8483–8486.

[13] R. Gupta, R. P. Choudhary, Heterocyclic Communications 2013, 19, DOI 10.1515/hc-2013-0024.

[14] W. Wang, J. Wang, S. Li, C. Li, R. Tan, D. Yin, Green Chem. 2020, 22, 4645–4655.

[15] A. W. Johnson, H. Schubert, J. Org. Chem. 1970, 35, 2678–2680.

[16] C. Bérubé, X. Barbeau, P. Laguée, N. Voyer, Chem. Commun. 2017, 53, 5099–5102.

[17] N. Upadhyay, K. Titekar, F. Loidiotce, N. Yu, Anisimova, T. S. Spina, D. V. Sokolova, G. B. Smirnova, J. Choe, F.-J. Meyer-Almes, V. S. Pokrovsky, A. Lavecchia, C. Ramaa, Bioorganic Chemistry 2021, 107, 104527.

[18] E. Weitz, A. Scheffer, Ber. dsch. Chem. Ges. A/B 1921, 54, 2327–2344.

10. Supporting Information

https://www.ikaprocess.com/en/Products/Electro-Organic-Synthesis-Systems-cph-45/ElectraSyn-flow-csb-ES/, accessed 22.12.2021.

11. Author Contributions

A.-K. S. participated in testing of the cooled electrolysis cell, optimization of electrolysis conditions, mechanistic studies, optimization of the reaction conditions for the N-oxidation of amines, completely performed the isolation of the S-, S(O)- and N-Oxidation scope and revised the draft of this manuscript.

P. K. participated in the initial peroxodcarbonate synthesis, mechanistic studies, and application development, completely prepared the epoxidation scope and revised the draft of the manuscript.

T. v. L. participated in milling and testing of the cooled electrolysis cell, optimization of electrolysis conditions, mechanistic studies, optimization of the reaction conditions for the N-oxidation of amines and revised the draft of this manuscript.

M. D. participated in development and testing of the cooled electrolysis cell, optimization of electrolysis conditions, mechanistic studies, optimization of the reaction conditions for the N-oxidation of amines and wrote the first draft of this manuscript.

F. S. participated in the initial peroxodcarbonate synthesis and initial application development.

M. Z. participated in the initial peroxodcarbonate synthesis and initial application development.

S. W. supervised the experimental work, provided continuous input, and thoroughly revised the manuscript draft.

L. G. supervised the experimental work, provided continuous input, designed the final copper cell, and thoroughly revised the manuscript draft.