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Direct electrochemical deoxygenation reaction of ketones using leaded bronze cathode in formic acid

Sebastian Kissel, [ID] †[a] Marcel Nicolas Perner, [ID] †[a] Rok Narobe,[a] Kyra Hochadel,[a] Martin Klein, [ID] [b] Bertram Cezanne, [ID] [b] Philipp Schnieders,[c] Volker Derdau [ID] [d] and Siegfried R. Waldvogel [ID] *[a,e]

We report a mild and resource efficient electrochemical method for the deoxygenation reaction of ketones using a leaded bronze CuSn7Pb15 cathode in a very simple two-electrode undivided setup under galvanostatic conditions. The method is easy to conduct and applicable to a variety of ketones leading to deoxygenated products in yields up to 82% using a simple isolation protocol. The use of formic acid as a solvent and source of protons turned out to be crucial for the deoxygenation reaction. The scale-up experiments up to 100 mmol scale proved the practical relevance of the method and the potential use for industrial large-scale synthesis. Noteworthy, this method is sustainable in terms of process safety and re-usability of the components including the electrodes and solvent-supporting electrolyte mixture.

Green foundation

1. Conventionally, the reductive deoxygenation requires harsh reaction conditions, stoichiometric amounts or even larger amounts of reducing agents and the use of toxic heavy metals which lead to a significant environmental impact. By using electricity as renewable reducing agent in combination with reusable electrodes and electrolyte system we present a much more sustainable alternative method for the deoxygenation of ketones.

2. In this study, we report a mild and resource efficient electrochemical deoxygenation reaction of ketones using a leaded bronze cathode in a very simple two-electrode undivided setup. A simple workup by phase separation and the reusability of both electrolyte and electrodes provide all pre-requisites for a potential technical application.

3. In the future, the method can be further developed using metal free carbon-based electrodes and applying to other conversions as well.

Introduction

Deoxygenation reactions of ketones forming hydrocarbon species are fundamental reactions in organic chemistry having an important application in the valorisation of waste biomass to platform chemicals as well as in the synthesis of bioactive molecules.[1–4] In literature, there are only a few approaches known forming methylene groups from carbonyl compounds in a direct deoxygenation reaction.[5,6] The first approaches in classical chemistry were reported in the early 20th century in

the well-known Clemmensen and Wolff–Kishner reactions for the deoxygenation of carbonyl compounds.[7,8] The reported conditions in these pioneering works were rather harsh requiring high temperatures and strongly acidic or basic conditions which makes them unsuitable for a broad range of substrates (Scheme 1A). Nevertheless, hydrazone intermediates became frequently used in cross-coupling reactions.[9–15] Later advances were made by using metal hydride reagents in combination with Lewis acids which enabled broader functional group tolerance. However, the use of stoichiometric amounts of reducing agents still represents a limitation.[16–20]

More recent approaches are reported using transition-metal catalysts either in homogeneous or heterogeneous catalysis typically in combination with molecular hydrogen.[21–25] Although hydrogen is a very atom-efficient reagent the use of hydrogen is related to significant safety risks considering working with compressed flammable and potentially explosive gas mixtures especially in industrial production plants.[26] In this context, electrochemistry offers a neat solution circumventing the use of reducing agents, high temperatures and

[a]Max Planck-Institute for Chemical Energy Conversion, Stiftstraße 34–36, 45470 Mülheim an der Ruhr, Germany. E-mail: siegfried.waldvogel@cec.mpg.de; Tel: +49 208/306-3131

[b]Merck Electronics KGaA, 64293 Darmstadt, Germany

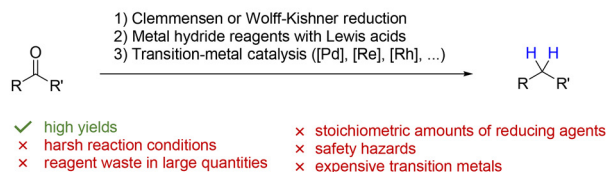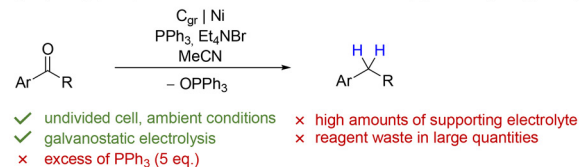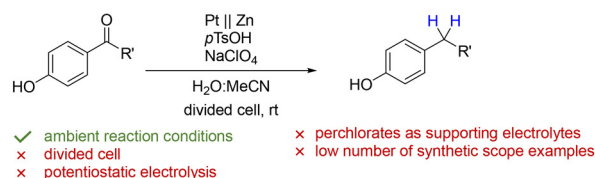[c]Deutero GmbH, Am Ring 29, 56288 Kastellaun, Germany

[d]Sanofi-Aventis Deutschland GmbH, Integrated Drug Discovery, Industriepark Höchst, 65926 Frankfurt am Main, Germany

[e]Karlsruhe Institute of Technology, Institute of Biological and Chemical Systems – Functional Molecular Systems (IBCS FMS), 76131 Karlsruhe, Germany
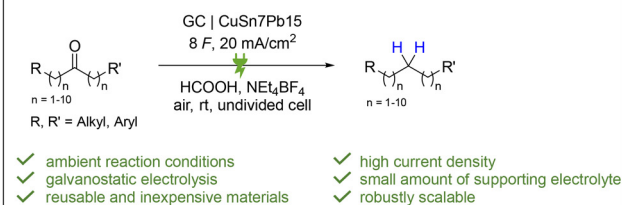
†Equal contribution.

A) Traditional deoxygenation reactions of ketones

1) Clemmensen or Wolff-Kishner reduction
2) Metal hydride reagents with Lewis acids
3) Transition-metal catalysis ([Pd], [Re], [Rh], ...)

✓ high yields
✗ harsh reaction conditions
✗ reagent waste in large quantities
✗ stoichiometric amounts of reducing agents
✗ safety hazards
✗ expensive transition metals

B) Triphenylphosphane-assisted electrochemical deoxygenation (Wang et al.)

C_{gr} | Ni
PPh_3, Et_4NBr
MeCN
$- OPPh_3$

✓ undivided cell, ambient conditions
✓ galvanostatic electrolysis
✗ excess of PPh_3 (5 eq.)
✗ high amounts of supporting electrolyte
✗ reagent waste in large quantities

C) Electrochemical Clemmensen reduction at Zn cathode (Choi et al.)

Pt || Zn
$pTsOH$
$NaClO_4$
H_2O:MeCN
divided cell, rt

✓ ambient reaction conditions
✗ divided cell
✗ potentiostatic electrolysis
✗ perchlorates as supporting electrolytes
✗ low number of synthetic scope examples

D) This work: Direct electrochemical deoxygenation reaction of ketones in formic acid using leaded bronze cathode

GC | CuSn7Pb15
8 F, 20 mA/cm²
HCOOH, NEt_4BF_4
air, rt, undivided cell

R, R' = Alkyl, Aryl
n = 1-10

✓ ambient reaction conditions
✓ galvanostatic electrolysis
✓ reusable and inexpensive materials
✓ high current density
✓ small amount of supporting electrolyte
✓ robustly scalable

Scheme 1 Approaches for the deoxygenation reactions of ketones in classical and electrochemical ways.

high hydrogen pressures.[27–31] Some early electrochemical approaches were reported by Cheng et al. using ammonia as a carbon-free and sustainable fuel, although the use of gaseous ammonia is highly challenging due to its toxicity and more complex reaction setup. Furthermore, the use of perchlorates as supporting electrolyte in a potentiostatic electrolysis is not favoured for a potential technical application.[32] Later, Wang et al. reported an electrochemical approach in an undivided cell using an excess of triphenylphosphane (5 eq.) to facilitate the deoxygenation of aromatic benzylic ketones (Scheme 1B), correlating with the formation of large amounts of reagent waste in the form of triphenylphosphine oxide.[33] The use of sacrificial reducing agents like diisopropylethylamine (DIPEA) is also known in literature, negatively impacting the atom economy of the reaction.[34] Choi et al. published an electrochemical Clemmensen reduction using a zinc cathode in a divided cell, although perchlorates are associated with safety risks in electrosynthesis (Scheme 1C).[35] Wang et al. reported a tuneable system for the electrochemical reduction of ketones using formic acid and sodium azide as the supporting electrolyte. However, the use of NaN_3 in acidic media is dangerous

due to the formation of hydrazoic acid.[36] Waldvogel et al. reported a method for the reductive deoxygenation of amides under acidic conditions using lead cathodes.[37] Lead cathodes are well known for its high overpotential for hydrogen evolution which is necessary especially when working under acidic conditions.[38] In this work (Scheme 1D), we report a mild method for an electrochemical deoxygenation reaction of non-benzylic ketones in an undivided cell using a simple two-electrode setup under galvanostatic conditions in acidic media. Leaded bronze cathode (CuSn7Pb15) was used as a sustainable alternative for elemental lead electrodes.[38–43] The features and surface studies of CuSn7Pb15 are reported in literature, highlighting the great potential for the deoxygenation reactions of ketones.[44,45] As the only solvent and source of protons, formic acid has excellent properties regarding the solubility of substrates and the acidity necessary for the chemical transformation.[46] Beside this, it acts like a sacrificial reducing agent on the anode forming CO_2, preventing the energy- and cost consuming separation of by-products after electrolysis and therefore enabling a simple isolation and purification procedure.[47–50] Insights in the mechanistic studies for the cathodic reduction are based on results from Choi et al. with a proposed mechanism shown in the SI (chapter 6, S23 and S24).[35]

Beside the addition of tetraethylammonium tetrafluoroborate (0.25 eq.) as a supporting electrolyte, no additives are needed in this reaction. Furthermore, alkylammonium salts are accumulating at the cathode minimizing the cathodic evolution of hydrogen.[51]

Results and discussion

Reaction development

Inspired by previous reports in literature, the electrochemical reductive deoxygenation of ketones was optimized using 1,3-diphenylpropan-2-one (**1a**) as a test substrate in formic acid both as a solvent and source of protons in a simple undivided batch-type cell.[52] Formic acid is considered as green solvent since it can be directly made from CO_2. Initial screening indicated leaded bronze CuSn7Pb15 and lead as the most promising cathodes, likely due to their high hydrogen evolution overpotential, affording the desired deoxygenated product 1,3-diphenylpropane (**1b**) in good yield (76% and 80%, Table 1, entries 1 and 2).[38] Interestingly, switching to different leaded bronze electrodes with higher (CuSn5Pb20) or lower (CuSn10Pb10) lead content resulted in significantly lower yields of product (<41%), highlighting the excellent features of this specific leaded bronze material CuSn7Pb15 (entry 3, Table S3).

Moreover, surface studies of the leaded bronze cathode CuSn7Pb15 used in this work were done using SEM-EDX. The electrode is composed of a copper matrix with lead clusters (yellow) on the surface. After electrolysis, the lead clusters are still preserved and additionally a thin layer of lead is distributed over the electrode surface (Fig. 1). This observation is in

Table 1 Optimized conditions for the electrochemical deoxygenation reaction of ketones[a]

Entry	Deviation from standard conditions	Yield [%]
1	None	76 (74)[b]
2	Pb cathode	80
3	CuSn5Pb20 or CuSn10Pb10 cathode	<41
4	DSA anode (IrO$_2$ at Ta)	70
5	Pure HOAc (1 eq. NEt$_4$BF$_4$)	Traces
6	Propylencarbonate : HCOOH (9 : 1)	Traces
7	HCOOH : H$_2$O (9 : 1)	60
8	NBu$_4$BF$_4$ (0.5 eq.)	57
9	Divided cell (glass frit)	16
10	No electricity	0

[a] Reaction conditions: undivided Teflon™ batch-type screening cell with 6 mL formic acid, 0.25 mmol NEt$_4$BF$_4$ and 1 mmol 1,3-diphenyl-propan-2-one. Reactions performed using glassy carbon anode and CuSn7Pb15 cathode, 20 mA cm^{-2}, 8 F at ambient reaction conditions. Reported current density is calculated based on the geometric area of the electrode immersed into the reaction mixture. [b] Isolated yield.
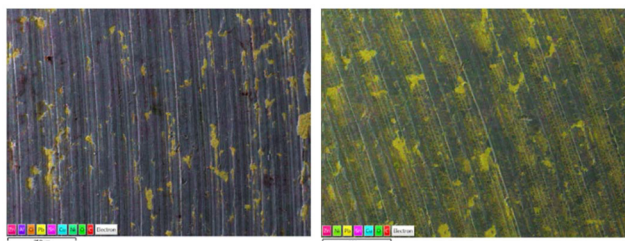

Fig. 1 Leaded bronze CuSn7Pb15 cathode prior electrolysis (left) and after electrolysis (right). Upon electrolysis, redeposited lead is visible on the surface.

accordance with literature, observing a redeposition of lead on the electrode surface during electrolysis, making the electrodes reusable.[43] The presence of lead clusters on the surface is advantageous and indicate the redeposition of lead. With CuSn5Pb20 the overall lead content may be higher but no clusters of lead are formed which is important for a low lead contamination.[45] Therefore, the reactivity of the substrate on the electrode surface is inferior, known from literature.[44,45]

As an anode material glassy carbon was used although dimensionally stable anodes (DSA) IrO$_2$ at Ta gave similar but slightly lower yields (entry 4, Table S4). The choice of solvent turned out to be significant for the deoxygenation reaction, since pure acetic acid and different non-protic solvents in combination with sulfuric acid or formic acid in over-stoichiometric amount, did not lead to any product formation or only traces of the desired product (entries 5 and 6, Table S5).

Notably, involving water in the system as a co-solvent resulted in only a bit lower yield, indicating the robustness of this protocol against moisture (entry 7, Table S5). Beside tetraethylammonium tetrafluoroborate as a supporting electrolyte in low quantities (0.25 eq.) no additives are needed, allowing the formation of **1b** at ambient reaction conditions. Supporting electrolytes involving halides revealed no product formation at all, whereas alkylammonium salts with higher alkyl chains (propyl, butyl, octyl) gave significantly lower yields (entry 8, Table S6). Higher concentrations of supporting electrolyte were linked to lower product formation while observing traces of remaining starting material (Table S7). Similarly, as observed in our previous work,[37] the coating layer consisting of alkylammonium ions is necessary to prevent the evolution of hydrogen as a major product, although at higher concentrations the accessibility of the substrate to the cathode may be hindered resulting in no full conversion of the starting material.[53,54] The current density proved to be rather insignificant for the deoxygenation reaction although the highest yields were observed at current densities of 20 mA cm^{-2} used in our case (Table S8). For 1,3-diphenylpropan-2-one as our test substrate, current densities up to 100 mA cm^{-2} could be used while still achieving yields up to 70%. Especially, industrial applications favor high current densities and short reaction times, proving the practical relevance of the developed method. However, because of the heat generated by electricity, current densities higher than 100 mA cm^{-2} were not tested. For the substrate scope and molecules containing different functional groups, a current density of 20 mA cm^{-2} was used, since higher current densities along with associated large overpotentials may result in lower functional group tolerance. The screening of the amount of applied charge indicated a rather linear trend, reaching full conversion of the starting material at 8 F (Table S9). The excess of applied charge is required because of hydrogen evolution as a parasitic side reaction. Nevertheless, since 4 F as the theoretical amount of applied charge is needed for the deoxygenation, the faradaic efficiency of about 40% still provides acceptable results. The concentration of the starting material had some effect on the product yield, since lower concentration (0.08 M) did not lead to full conversion of the starting material (Table S10). The concentration of starting material could be increased up to 0.83 M in batch-type screening cells while still achieving yields up to 46%. Running the reaction at lower temperatures (0 °C) gave slightly higher yields (78%) compared to room temperature although the additional energy consumption for cooling makes is less attractive for further optimization (Table S11). The result obtained in a divided Teflon™ batch-type cell equipped with a glass frit (porosity 4) gave moderate yields (16%) proving the importance of the undivided cell setup including the short electrode distances and cell geometry (entry 9).[55] The control reaction without electricity did not lead to any product formation (entry 10). With the optimized conditions for the electrochemical deoxygenation reaction of ketones under galvanostatic condition we isolated **1b** in 74% yield (entry 1). Beside the desired deoxygenated product, up to 15% of the corresponding ester

(formate) are observed as a minor by-product indicating at a clean electrochemical reaction.

Scale-up in batch cells

To show the general applicability of the method and the possible use in technical production plants, scale-up experiments were conducted for the test substrate **1a**. The developed optimized reaction conditions were applied and transferred into larger scale. The reactions were carried out in batch-type glass cells carrying up to 200 mL volume on 5–100 mmol scale while maintaining a concentration of 0.5 M in all cases at 20 mA cm^{-2} (Fig. 2, Fig. S7). On large scale, using the possibly highest concentration is favored, since less solvent is needed per run and more product can be obtained in shorter time. Higher concentrations of **1a** than 0.5 M leads to a decrease in yield (Table S10).

The following table shows the isolated yield of **1b** after column chromatography (Table 2). Detailed information about the cells, the general procedure and isolation method can be found in the SI.

Regarding the test substrate **1a**, the electrolysis is scalable to a 100 mmol scale while still achieving isolated yields above 70% proving the robustness for larger scale synthesis. The obtained product **1b** is not soluble in formic acid, forming a layer of product on top of the formic acid-based electrolyte (Fig. 3, Fig. S8).

By phase separation, the purity of the crude product is already about 90% determined by ^{1}H NMR (Fig. S8), which

Fig. 2 Scale-up experiments in batch-type cells up to 100 mmol scale.

Table 2 Scale-up experiments in batch of **1a** on 0.5 M concentration up to 100 mmol scale at 20 mA cm^{-2}. The active surface of the cathode was determined based on the area of the cathode immersed into the electrolyte

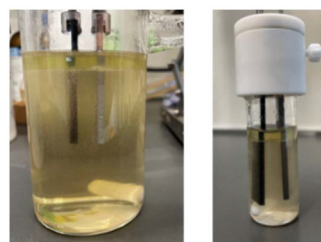| n(**1a**) [mmol]	Volume HCOOH [mL]	Active surface of cathode [cm^2]	Isolated yield (**1b**)
1	6	2	0.13 g (74%)
5	10	3.5	0.72 g (75%)
15	30	4	2.0 g (70%)
40	80	7	5.6 g (72%)
75	150	7	11.0 g (75%)
100	200	7	13.9 g (71%)

Fig. 3 Separated top layer of deoxygenated product **1b** on top of the formic acid on 100 mmol scale (left) and 5 mmol scale (right).

could be even increased on larger scale. Removing the product over time by phase separation from the cell while adding new starting material could be a possible application for technical process enabling continuous generation of product. Moreover, the electrolyte mixture is well recycled.

Synthetic application in batch

With the optimized conditions in hand, we started exploring the general applicability of the electrochemical transformation by testing different carbonyl compounds including electron-releasing, electron-withdrawing groups as well as halo containing substrates (Scheme 2). Noteworthy, substrates containing carbonyl groups in benzylic positions, like acetophenone or benzophenone, are generally not deoxygenated, instead the esters (formate) are formed (Scheme S2). Beside dibenzylketones, phenylacetones as well as longer carbon chain containing carbonyl compounds can be successfully deoxygenated. For substrates beside dibenzylketones, the amount of applied charge had to be doubled (16 F), since with 8 F there was still unreacted starting material left. To keep the reaction time the same, the current density was doubled to 40 mA cm^{-2} in these cases. Screening experiments indicated no significant decrease in yield at higher current densities (Table S8).

Evaluation of sustainability

Replacing lead with leaded bronze CuSn7Pb15 as a cathode material already improves the green aspects of a chemical reaction. Beside the electrode material, the atom economy, as well as necessary additives are from importance. In our method, only small amounts of NEt$_4$BF$_4$ (0.25 eq.) as a supporting electrolyte are needed while working in pure formic acid as a solvent and source of protons. Noteworthy, after electrolysis, the formic acid can be re-distilled and reused (Fig. S13). Due to phase separation the complete electrolyte can even be directly reused without any further purification (Fig. S12). All pre-requisites for continuous process are laid out enabling a cost-efficient downstream processing. The addition of new supporting electrolyte and fresh formic acid can be avoided and the waste formation is therefore minimized.

The minor by-product is the corresponding ester (formate) which is present in small quantities being dissolved in the formic acid upon electrolysis (Fig. S12). In 4 consecutive runs of electrolysis the formic acid can be reused while still achiev-
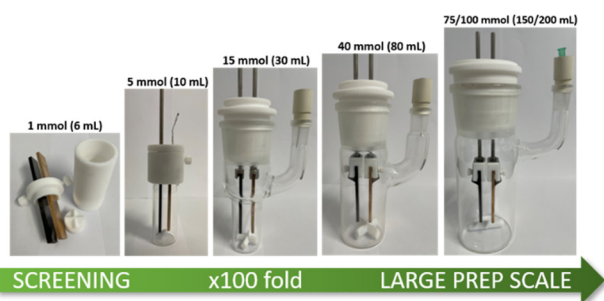
Scheme 2 Synthetic scope of the developed electrochemical deoxygenation reaction of carbonyl compounds. Reaction conditions: undivided Teflon™ batch-type screening cell with 6 mL formic acid, 0.25 mmol NEt_4BF_4 and 1 mmol substrate. Reactions performed using glassy carbon anode and CuSn7Pb15 cathode, 20 mA cm^{-2}, 8 F at ambient reaction conditions. Reported current density is calculated based on the geometric area of the electrode immersed into the reaction mixture. [a] GC yield, [b] 16 F, 40 mA cm^{-2}.

ing yields >65% (Fig. S11). Additionally, the electrodes can be reused multiple times (monitored up to 5 times) while observing minor fluctuations in yield (Table 3, entry 4, Fig. S9). A better evaluation of green chemistry aspects[56] of the developed method can be achieved in a spider plot comparing our

Table 3 Experiments emphasizing the sustainability and reusability aspects of the developed method[a]

Entry	Deviation from standard conditions	Yield [%]
1	None	76[b] (74)[c]
2	5 mmol scale (0.5 M) & re-distilled HCOOH	74[c]
3	5 mmol scale (0.5 M) & reused HCOOH without purification	65–72[c]
4	Reused electrodes (up to 5 reactions)	66–77[c]

[a] Reaction conditions: undivided Teflon™ batch-type screening cell with 6 mL formic acid, 0.25 eq. NEt_4BF_4 and 1 mmol 1,3-diphenylpropan-2-one. Reactions performed using glassy carbon anode and CuSn7Pb15 cathode, 20 mA cm^{-2}, 8 F at ambient reaction conditions. Reported current density is calculated based on the geometric area of the electrode immersed into the reaction mixture. [b] GC yield. [c] Isolated yield.

method with a classical approach like Wolff–Kishner reduction[57] and an electrochemical approach already known from literature by Wang *et al.*[33] The Wolff–Kishner reduction as well as already known electrochemical approaches in literature[32–35] are valuable reactions having an outstanding importance for chemical industry and scientific applications.

Noticeable from the spider plot (Fig. 4), our developed method is a superior addition to what is known from literature

Fig. 4 Spider plot for the better comparison of green chemistry aspects. In blue is shown our developed method, in orange the classical chemistry Wolff–Kishner reduction[57] and in green the electrochemical approach from literature by Wang *et al.*[33]

highlighting the sustainability, efficiency and practical relevance of this method (for more details: SI chapter 7, S25–S31).

Conclusions

A simple galvanostatic electrochemical method was established for the deoxygenation reaction of ketones in the simplest undivided batch-type cell set-up under constant current electrolysis. The method is based on formic acid, acting as a solvent and source of protons. Leaded bronze CuSn7Pb15 was used as cathode material preventing hydrogen formation as a major product especially when working under acidic conditions. Noteworthy, formic acid can be directly made from CO_2 and is considered as green reagent. The method is applicable to a broad range of substrates including electron-releasing, electron-withdrawing as well as halo compounds. Dehalogenation reaction was not observed. Beside this, all materials can be reused including the electrodes and formic acid. Scale-up experiments up to a 100 mmol scale proved the robustness of the method. The apolar nature of the product leads to phase separation upon electrolysis enabling a cost-efficient downstream processing and continuous use of the electrolyte for technical applications. Calculations for green chemistry aspects emphasizes the sustainability of the developed electrochemical method.

Author contributions

Sebastian Kissel: Conceptualization (leading), investigation (leading), methodology (leading), supervision (supporting), project Administration (supporting), writing – original draft preparation (leading). Marcel Nicolas Perner: Conceptualization (leading), investigation (leading), methodology (leading), supervision (supporting), project administration (supporting), writing – original draft preparation (leading). Dr Rok Narobe: Conceptualization (supporting), writing – original draft preparation (supporting). Kyra Hochadel: Investigation (supporting), methodology (supporting). Dr Martin Klein: Conceptualization (supporting). Dr Bertram Cezanne: Conceptualization (supporting), supervision (supporting). Dr Philipp Schnieders: Conceptualization (supporting). Dr Volker Derdau: Conceptualization (supporting). Prof. Dr Siegfried R. Waldvogel: Conceptualization (leading), supervision (leading), project administration (leading), funding acquisition (leading), writing – original draft preparation (supporting).

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the SI: general procedures and analytical data. See DOI: **https://doi.org/10.1039/d5gc03495g**.

Acknowledgements

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