

Manganese/Copper Co-catalyzed Electrochemical Wacker–Tsuji-Type Oxidation of Aryl-Substituted Alkenes

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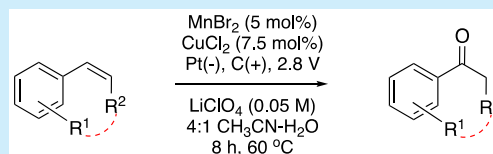


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Supporting Information

ABSTRACT: A manganese/copper co-catalyzed electrochemical Wacker–Tsuji-type oxidation of aryl-substituted alkenes has been developed. The process involves the use of 5 mol % MnBr_2 and 7.5 mol % CuCl_2 , in 4:1 acetonitrile/water in an undivided cell at 60 °C, with 2.8 V constant applied potential. α -Aryl ketones are formed in moderate to excellent yields, with the advantages of avoidance of palladium as a catalyst and any external chemical oxidant in an easily operated, cost-effective procedure.



The oxidation of olefins is a powerful tool for the industrial conversion of petrochemical feedstocks into high value-added chemicals.¹ Among the processes used with this purpose, the Wacker oxidation for the preparation of acetaldehyde from ethylene in aqueous media, with palladium(II) chloride and copper(II) as catalysts under oxygen, was one of the first homogeneous catalytic processes applied on an industrial scale.² The laboratory-scale modification, namely the Wacker–Tsuji oxidation, is one of the most useful methods for convert terminal olefins into methyl ketones.³ In this protocol, water serves as the oxygen source, and the reduced palladium generated in the process is reoxidized by copper(II) and ultimately by atmospheric oxygen.⁴ A variety of synthetic methods based on this reaction by modification of the palladium reoxidation process⁵ or the nature of the involved nucleophile⁶ have been reported during the past decades, and the process has found application in broadly different fields.⁷

Organic electrochemistry offers a mild and efficient alternative to conventional chemical approaches to redox chemistry, electricity representing (depending on its origin) a potentially *green* oxidizing or reducing agent⁸ with no limitations for large-scale application.⁹ Electrooxidation methods have already been used for the partial oxidation of ethylene on palladium electrodes¹⁰ and for the regeneration of recyclable oxidants such as quinone,¹¹ iron trichloride,¹² or triarylaminines,¹³ used for the regeneration of the Pd(II) catalyst in Wacker–Tsuji reactions. In these studies, divided cell systems have been normally used to avoid the deposition of palladium metal onto the cathode that could result in unsatisfactory conversion.¹⁴

Hitherto, progress in the Wacker-type oxidation has rarely escaped from the palladium catalysis paradigm. There are, however, important limitations in the Wacker–Tsuji oxidation still remaining, such as cost, toxicity of palladium compounds to humans, low activity for internal alkene substrates, moderate TON due to degradation of the palladium catalyst, and the formation of chlorinated byproducts,¹⁵ among others. There-

fore, the development of cost-effective, noble-metal-free procedures for the oxidation of alkenes offers considerable interest. In this respect, Lei and co-workers reported a direct anti-Markovnikov oxidation of β -alkylstyrenes to carbonyl compounds involving a dual photoredox-metal catalytic system,¹⁶ while the Han group reported the iron-catalyzed Wacker-type oxidation of olefins to ketones using ambient air as the sole oxidant under mild reaction conditions.¹⁷

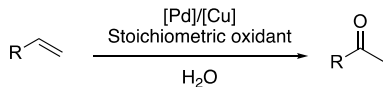
The electrochemical functionalization of olefins has received considerable attention in recent times,^{18–23} and the use of manganese catalysis, pioneered by Li, has played a central role in these developments.^{19–23} In light of these findings, we decided to explore the possibility of developing an electrochemical alternative to the Wacker–Tsuji process where toxic and expensive palladium could be replaced by abundant and less harmful metals used as catalysts. Herein, we report the successful development of an electrochemical Wacker–Tsuji-type oxidation of aryl-substituted alkenes through a manifold of parallel oxidative events taking place at a carbon felt anode in an undivided cell using cheap, environmentally friendly MnBr_2 and CuCl_2 as co-catalysts in acetonitrile/water under *forbidden* conditions (2.8 V) as shown in **Scheme 1**.

Our initial study targeted the oxidation of styrene (**1a**) to acetophenone (**2a**), as shown in **Table S1**. An undivided cell with Pt as cathode and carbon felt as anode was used in the experiments, operated at an applied voltage of 3.0 V. Since it has been previously reported that Mn(II) salts catalyze the coupling of styrenes and aliphatic alcohols under oxidative conditions (TBHP),²⁴ we wanted to discard first the operation

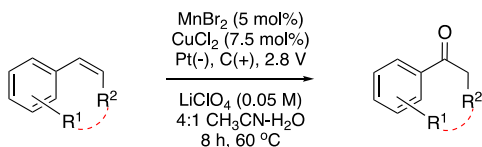
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Scheme 1. Standard and Electrochemical Wacker–Tsuji Oxidation

A. Standard Wacker–Tsuji oxidation



B. This work: [Mn]/[Cu] co-catalyzed electrochemical Wacker–Tsuji oxidation



of this mechanism under electrooxidative conditions. As shown in entries S1 and S2, no coupling took place between primary alcohols used as cosolvents and styrene **1a**, while acetophenone **2a** was detected in low yield when 1:1 2-propanol/water was used as a solvent in the presence of 5 mol % MnBr_2 as catalyst at 60 °C (entry S3). Binary mixtures of polar aprotic solvents and water also afforded poor results (entries S4 and S5), but the use of 4:1 vol/vol acetonitrile/water was somewhat promising, especially when performing the reaction at 60 °C (entries S7 and S8). The use of NiCl_2 (entry S9), FeCl_3 (entry S10), or even PdCl_2 (entry S11) instead of MnBr_2 , was deleterious. On the other hand, the combined use of MnBr_2 and CuCl_2 (5 mol % each) led to a very significant yield increase (67%, entry S12). Alternatively, the exclusive use of CuCl_2 did not produce any detectable amount of **2a** (entry S13).

Once we had established the determining roles in the reaction of MnBr_2 and CuCl_2 , we proceeded to optimize the relative amounts of these two species (Figures S1 and S2). The initial concentration of **1a** (Figure S4) and of the support electrolyte LiClO_4 (Figure S5) were also optimized.

Interestingly, the reaction gave a similar yield in the presence or in the absence of oxygen in the reaction cell. Besides the operative advantage in reaction practicality, this observation provides a clear indication that oxygen reduction is not involved in the observed reaction and that the oxygen atom in the final product arises from water. We accordingly studied the effect of the proportion of water in the solvent system on the efficiency of the process (Figure S3). As anticipated, the presence of water in the solvent is a requisite for the reaction to take place, and the optimal yield (77%) is achieved with a volumetric composition of 80% MeCN and 20% water. Further increases in the amount of water lead to a rather sharp decrease in yield, probably because of the insolubility of styrene in those solvent mixtures.

As a final parameter, we studied the effect of the applied potential on the reaction yield while working in constant voltage mode (Figure S6). The onset voltage for the reaction to proceed was shown to be 1.7 V. The yield slightly increased with the applied potential, and at ca. 2.5 V, a sudden increase in the slope of the yield vs voltage graph occurs, with a maximum 85% yield being achieved at 2.8 V.²⁵ These experiments were later repeated in a single-compartment, three-electrode cell including a AgCl reference electrode (see Figure S7). Interestingly, the results between 2.4 and 3.0 V are exactly duplicated, with the highest (85%) yield being achieved again at 2.8 V. The observed yield vs applied voltage behavior is strongly indicative of some additional redox process, on top

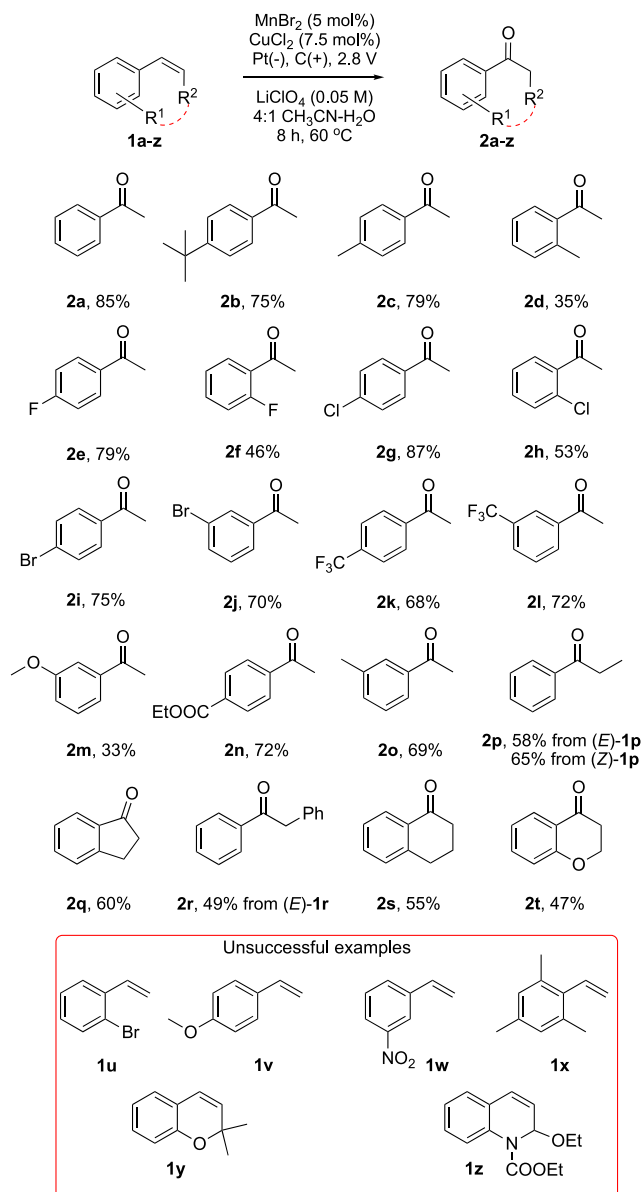
of $\text{Cu}^{\text{I}}/\text{Cu}^{\text{II}}$ and $\text{Mn}^{\text{II}}/\text{Mn}^{\text{III}}$, taking also place above 2.5 V. According to the known electrochemical oxidation behavior of acetonitrile at platinum electrodes in the presence of water, solvent oxidation appears as a logical, and in this case synergistic, candidate.²⁶

Once the optimization process was completed, different combinations of manganese and copper compounds were tested as potential catalytic systems (Table S2). It is interesting to note that combinations of chlorides and bromides of $\text{Mn}(\text{II})$ and $\text{Cu}(\text{II})$ are almost equally suitable catalysts for the process (entries S1, S5, and S15), with the combined use of both dibromides (entry S1) leading to the highest (86%) yield. On the contrary, the combination of both chlorides (entry S12) results in a mediocre catalyst. Thus, the presence of bromide ions is of primordial importance for catalytic activity. The reaction did not produce any **2a** when $\text{Cu}(\text{acac})_2$, involving a highly chelated $\text{Cu}(\text{II})$ species, was used as a co-catalyst (entry S6). It is also worth mentioning that polymerization of styrene was observed when $\text{Cu}(\text{OTf})_2$ replaced CuCl_2 as the $\text{Cu}(\text{II})$ source (entry S4).²⁷ As already mentioned, no acetophenone was detected in the absence of a $\text{Mn}(\text{II})$ source (entries S16–S20).

Once the optimal reaction conditions had been fully established, the applicability of the Mn/Cu co-catalyzed electrochemical oxidation was studied on a representative series of substrates **1a–z** containing in their structures an aryl group conjugated with a carbon–carbon double bond (Scheme 2). In general, the reaction tolerates alkyl groups and medium polarity substituents, such as halogen or trifluoromethyl groups and even groups with strong withdrawing character (**2n**). With respect to regiochemistry, *para*-substituted substrates are those leading to higher yields.

Also in this respect, the reaction appears to be sensitive to steric effects, since *ortho*-substituted substrates, like **1d**, **1f**, and **1h**, afford the corresponding oxidation products in lower yield than the corresponding *para*-isomers and heavily *ortho*-substituted substrates, like **1u** and **1x**, fail to react. Interestingly, substrates containing 1,2-disubstituted double bonds are efficiently oxidized, irrespective of their cyclic (**1q**, **1s**) or acyclic nature (**1p**, **1r**). In the case of **1p**, no appreciable bias exists with respect to the stereochemistry of the double bond in the substrate. 2*H*-Chromene (**1t**), a substrate belonging to an important class of natural substances, was successfully oxidized to chromanone **2t** (47% yield). However, the analogue 2,2-dimethyl-2*H*-chromene **1y** failed to react, thus indicating that heavy substitution on the double bond is deleterious to the reaction. On the other hand, when extension of the electrochemical oxidation to commercially available dihydroquinoline **1z** was attempted, fast deprotection of the carbamate moiety took place, but oxidation did not proceed. It is also worth mentioning that allylbenzene, a regioisomer of **1o** of nonstyrene nature, completely failed to provide the corresponding oxidation product.²⁸ Finally, *p*-methoxystyrene (**1t**) and *m*-nitrobenzaldehyde (**1u**) failed to provide the corresponding acetophenone products **2t** and **2u** for completely different reasons. While **1t** underwent a very fast reaction, but led to ill-defined products of oligomeric nature, **1u** was reluctant to electrochemical Wacker–Tsuji oxidation. This behavior can be rationalized through the tentative mechanistic proposal shown in Figure 1.

As can be seen, we propose that three parallel oxidative events could take place at the carbon felt anode: the standard oxidation of $\text{Mn}(\text{II})$ to $\text{Mn}(\text{III})$ [$E^\circ = 1.56 \text{ V}$ ²⁹ and peak at ca.

Scheme 2. Substrate Scope in the Mn/Cu Co-Catalyzed Wacker–Tsuji Electrochemical Oxidation^a


^aReaction conditions: Substrate (**1a–z**) (1 mmol), CuCl₂ (7.5 mol %), MnBr₂ (5 mol %), 4:1 acetonitrile:water (3 mL), Constant applied potential: 2.8 V (Pt cathode, Carbon felt anode, 0.05 M LiClO₄), 60 °C, 8 h. Isolated yield.

1.50 V in the cyclic voltammogram (CV, **Figure 2**), the oxidation of Cu(II) to Cu(III) [$E^\circ = 2.4 \text{ V}^{29}$ and peaks at ca. 1.85 and 2.45 V in the CV (**Figure 2**), and the oxidation of acetonitrile to its radical cation which, as discussed above (**Figure S6**), becomes possible at the high applied potential [$E^\circ = 1.78 \text{ V}^{23}$ and peak at ca. 2.32 V in the cyclic voltammogram (**Figure 2**)]. Interestingly, the peak at ca. 2.5 V in the CV which, according to our optimization studies appears to be very relevant to the overall oxidation process, cannot be observed when water is not present in the solvent system (see the **SI**). We discard the possibility that oxidation of Mn(III) to Mn(IV) can also occur, since MnO₂ does not appear to be a competent chemical oxidant in the overall process (see **Table S2**, entry **S11**) and no assignable peak is observed in the CV.

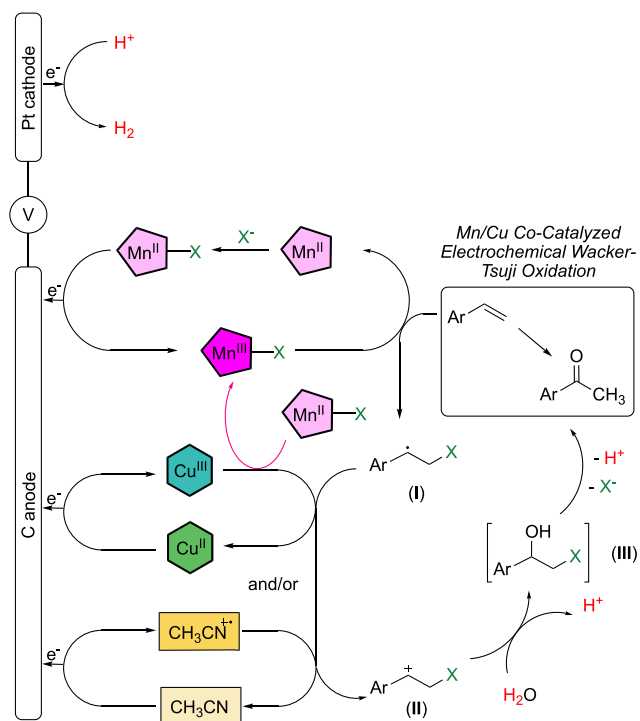


Figure 1. Tentative mechanistic proposal for the Mn/Cu co-catalyzed electrochemical oxidation of styrenes.

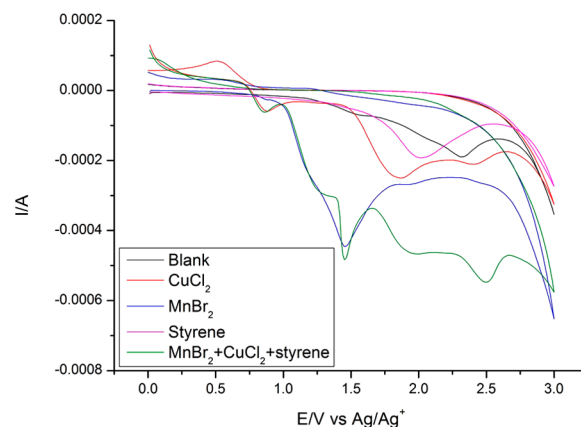


Figure 2. Cyclic voltammetry studies.

A chemically or electrochemically generated Mn(III) halide, preferably containing bromide anions ($X = \text{Br}$) according to our optimization studies (**Table S2**), would transfer a halogen atom onto the starting styrene, generating the intermediate radical (**I**). Evolution of this species toward the final ketone product requires hydration, but this is hardly conceivable at this oxidation level. We accordingly propose that **I** could be further oxidized to carbocation **II** by electrogenerated Cu(III) or, more probably, by electrogenerated acetonitrile radical cation.

Hydration of **II** would lead to bromohydrin **III**, already possessing the overall oxidation state of the product acetophenone **2**. Then either chemically or electrochemically promoted dehydrobromination would lead to the acetophenone product via keto–enol tautomerism. It is worth mentioning that **III** has been detected as a minor byproduct in most oxidation crudes (see the **SI**). On the other hand, independently prepared **III**³⁰ has been converted to

acetophenone under the electrochemical conditions employed in our study with high selectivity (91%, corresponding to 50% yield at 55% conversion, see the SI). Interestingly, this transformation also occurs, albeit in a less selective manner (70%), in the absence of any metal halide. The intermediacy of carbocation **II** is consistent with the behavior in the reaction of highly electron-deficient substrates like **1w**, where the highly electron-poor carbocation intermediate would be hardly available, and highly electron-rich ones like **1v**, where the exceeding electron density of the corresponding intermediate could trigger highly promiscuous behavior leading to oligomeric product mixtures.

In conclusion, we have developed an electrochemical Wacker–Tsuji-type oxidation of aryl-substituted alkenes, applicable to monosubstituted and 1,2-disubstituted substrates. The process relies on a dual Mn/Cu catalytic system with solvent (acetonitrile) participation and likely operates by means of three parallel electrochemical oxidative events where Mn(III), Cu(III), and acetonitrile radical cation are likely generated. By this process, α -aryl ketones are formed in moderate to excellent yields, with the advantages of avoidance of palladium as a catalyst and of any external chemical oxidant, in an easily operated cost-effective procedure.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.orglett.0c02670>.

Experimental procedures and spectral data (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) *Industrial Organic Chemistry*, 5th, completely revised ed.; Arpe, H.-J., Ed.; Wiley-VCH: Weinheim, 2010.
- (2) Jira, R. Acetaldehyde from Ethylene-A Retrospective on the Discovery of the Wacker Process. *Angew. Chem., Int. Ed.* **2009**, *48*, 9034–9037.
- (3) (a) Tsuji, J. Synthetic applications of the palladium-catalyzed oxidation of olefins to ketones. *Synthesis* **1984**, *1984*, 369–384. (b) Li, J. J. Wacker–Tsuji oxidation. In *Name Reactions for Functional Group Transformations*; Li, J. J., Corey, E. J., Eds.; Wiley-Interscience: Hoboken, NJ, 2007; pp 309–326. (c) Baiju, T. V.; Gravel, E.; Doris, E.; Namboothiri, I. N. N. Recent developments in Tsuji–Wacker oxidation. *Tetrahedron Lett.* **2016**, *57*, 3993–4000.
- (4) (a) Keith, J. A.; Henry, P. M. The Mechanism of the Wacker Reaction: A Tale of Two Hydroxypalladations. *Angew. Chem., Int. Ed.* **2009**, *48*, 9038–9049. (b) Vidossich, P.; Lledós, A.; Ujaque, G. First-Principles Molecular Dynamics Studies of Organometallic Complexes and Homogeneous Catalytic Processes. *Acc. Chem. Res.* **2016**, *49*, 1271–1278.
- (5) (a) Tsuji, J.; Nokami, J.; Mandai, T. Oxidation of Olefins to Ketones Catalyzed by Pd²⁺ Salts and Its Applications to Organic Synthesis. *Yuki Gosei Kagaku Kyokaiishi* **1989**, *47*, 649–659. (b) Cornell, C. N.; Sigman, M. S. Discovery of a Practical Direct O₂-Coupled Wacker Oxidation with Pd[(-)sparteine]Cl₂. *Org. Lett.* **2006**, *8*, 4117–4120. (c) Mitsudome, T.; Umetani, T.; Nosaka, N.; Mori, K.; Mizugaki, T.; Ebitani, K.; Kaneda, K. Convenient and Efficient Pd-Catalyzed Regioselective Oxyfunctionalization of Terminal Olefins by Using Molecular Oxygen as Sole Reoxidant. *Angew. Chem., Int. Ed.* **2006**, *45*, 481–485. (d) Michel, B. W.; Camelio, A. M.; Cornell, C. N.; Sigman, M. S. A general and efficient catalyst system for a Wacker-type oxidation using TBHP as the terminal oxidant: application to classically challenging substrates. *J. Am. Chem. Soc.* **2009**, *131*, 6076–6077. (e) DeLuca, R. J.; Edwards, J. L.; Steffens, L. D.; Michel, B. W.; Qiao, X.; Zhu, C.; Cook, S. P.; Sigman, M. S. Wacker-type oxidation of internal alkenes using Pd(Quinox) and TBHP. *J. Org. Chem.* **2013**, *78*, 1682–1686. (f) Wang, Y.-F.; Gao, Y.-R.; Mao, S.; Zhang, Y.-L.; Guo, D.-D.; Yan, Z.-L.; Guo, S.-H.; Wang, Y.-Q. Wacker-type oxidation and dehydrogenation of terminal olefins using molecular oxygen as the sole oxidant without adding ligand. *Org. Lett.* **2014**, *16*, 1610–1613. (g) Chaudhari, D. A.; Fernandes, R. A. Hypervalent Iodine as a Terminal Oxidant in Wacker-Type Oxidation of Terminal Olefins to Methyl Ketones. *J. Org. Chem.* **2016**, *81*, 2113–2121. (h) Xia, X.; Gao, X.; Xu, J.; Hu, C.; Peng, X. Selective Oxidation of Styrene Derivatives to Ketones over Palladium(0)/Carbon with Hydrogen Peroxide as the Sole Oxidant. *Synlett* **2017**, *28*, 607–610.
- (6) McDonald, R. I.; Liu, G.; Stahl, S. S. Palladium(II)-Catalyzed Alkene Functionalization via Nucleopalladation: Stereochemical Pathways and Enantioselective Applications. *Chem. Rev.* **2011**, *111*, 2981–3019.
- (7) Fong, D.; Luo, S.-X.; Andre, R. S.; Swager, T. M. Trace Ethylene Sensing via Wacker Oxidation. *ACS Cent. Sci.* **2020**, *6*, 507–512.
- (8) Frontana-Urbe, B. A.; Little, R. D.; Ibanez, J. G.; Palma, A.; Vasquez-Medrano, R. Organic electrosynthesis: a promising green methodology in organic chemistry. *Green Chem.* **2010**, *12*, 2099–2119.
- (9) (a) Cardoso, D. S. P.; Šljukic, B.; Santos, D. M. F.; Sequeira, C. A. C. Organic Electrosynthesis: From Laboratorial Practice to Industrial Applications. *Org. Process Res. Dev.* **2017**, *21*, 1213–1226. (b) Leow, W. R.; Lum, Y.; Ozden, A.; Wang, Y.; Nam, D.-H.; Chen, B.; Wicks, J.; Zhuang, T.-T.; Li, F.; Sinton, D.; Sargent, E. H. Chloride-mediated selective electrosynthesis of ethylene and propylene oxides at high current density. *Science* **2020**, *368*, 1228–1233.
- (10) (a) Blake, A. R.; Sunderland, J. G.; Kuhn, A. T. The partial anodic oxidation of ethylene on palladium. *J. Chem. Soc. A* **1969**, 3015–3018. (b) Goodridge, F.; King, C. J. H. Oxidation of ethylene at a palladium electrode. *Trans. Faraday Soc.* **1970**, *66*, 2889–2896. (c) Otsuka, K.; Kobayashi, A. Design of the Catalyst for Partial

Oxidation of Ethylene by Applying an Electrochemical Device. *Chem. Lett.* **1991**, *20*, 1197–1200.

(11) (a) Tsuji, J.; Minato, M. Oxidation of olefins to ketones in combination with electrooxidation. *Tetrahedron Lett.* **1987**, *28*, 3683–3686. (b) Bäckvall, J.-E.; Gogoll, A. Palladium-hydroquinone catalysed electrochemical 1,4-oxidation of conjugated dienes. *J. Chem. Soc., Chem. Commun.* **1987**, *0*, 1236–1238.

(12) Horowitz, H. H. Preliminary examination of an electrochemical process for converting olefins to ketones. *J. Appl. Electrochem.* **1984**, *14*, 779–790.

(13) Inokuchi, T.; Ping, L.; Hamaue, F.; Izawa, M.; Torii, S. Electrochemical Wacker Type Reaction with a Double Mediator System Consisting of Palladium Complex and Tri(4-bromophenyl)-amine. *Chem. Lett.* **1994**, *23*, 121–124.

(14) Wayner, D. D. M.; Hartstock, F. W. Electrode-mediated catalytic carbonylation of olefins. *J. Mol. Catal.* **1988**, *48*, 15–19.

(15) Stangl, H.; Jira, R. Die durch palladium(II) chlorid und kupfer(II) chlorid katalysierte oxychlorierung von äthylen zu äthylenchlorhydrin. *Tetrahedron Lett.* **1970**, *11*, 3589–3592.

(16) Zhang, G.; Hu, X.; Chiang, C. W.; Yi, H.; Pei, P.; Singh, A. K.; Lei, A. Anti-Markovnikov Oxidation of β -Alkyl Styrenes with H₂O as the Terminal Oxidant. *J. Am. Chem. Soc.* **2016**, *138*, 12037–12040.

(17) Liu, B.; Jin, F.; Wang, T.; Yuan, X.; Han, W. Wacker-Type Oxidation Using an Iron Catalyst and Ambient Air: Application to Late-Stage Oxidation of Complex Molecules. *Angew. Chem., Int. Ed.* **2017**, *56*, 12712–12717.

(18) Imada, Y.; Okada, Y.; Noguchi, K.; Chiba, K. Selective Functionalization of Styrenes with Oxygen Using Different Electrode Materials: Olefin Cleavage and Synthesis of Tetrahydrofuran Derivatives. *Angew. Chem., Int. Ed.* **2019**, *58*, 125–129.

(19) Fu, N.; Sauer, G. S.; Saha, A.; Loo, A.; Lin, S. Metal-catalyzed electrochemical diazidation of alkenes. *Science* **2017**, *357*, 575–579.

(20) Fu, N.; Sauer, G. S.; Lin, S. Electrocatalytic Radical Dichlorination of Alkenes with Nucleophilic Chlorine Sources. *J. Am. Chem. Soc.* **2017**, *139*, 15548–15553.

(21) Ye, K.; Pombar, G.; Fu, N.; Sauer, G. S.; Keresztes, I.; Lin, S. Anodically Coupled Electrolysis for the Heterodifunctionalization of Alkenes. *J. Am. Chem. Soc.* **2018**, *140*, 2438–2441.

(22) Zhang, Z.; Zhang, L.; Cao, Y.; Li, F.; Bai, G.; Liu, G.; Yang, Y.; Mo, F. Mn-Mediated Electrochemical Trifluoromethylation/C(sp²)-H Functionalization Cascade for the Synthesis of Azaheterocycles. *Org. Lett.* **2019**, *21*, 762–766.

(23) Tian, S.; Jia, X.; Wang, L.; Li, B.; Liu, S.; Ma, L.; Gao, W.; Wei, Y.; Chen, J. The Mn-catalyzed paired electrochemical facile oxychlorination of styrenes *via* the oxygen reduction reaction. *Chem. Commun.* **2019**, *55*, 12104.

(24) Zhang, W.; Wang, N. X.; Bai, C. B.; Wang, Y. J.; Lan, X. W.; Xing, Y.; Li, Y. H.; Wen, J. L. Manganese-Mediated Coupling Reaction of Vinylarenes and Aliphatic Alcohols. *Sci. Rep.* **2015**, *5*, 15250.

(25) Current intensity was also optimized for reactions run in constant current mode. A highest 80% yield was recorded in 8 h for a reaction run at 25 mA.

(26) Foley, J. K.; Korzeniewski, C.; Pons, S. Anodic and cathodic reactions in acetonitrile/tetra-*n*-butylammonium tetrafluoroborate: an electrochemical and infrared spectroelectrochemical study. *Can. J. Chem.* **1988**, *66*, 201–206.

(27) (a) Iroh, J. O.; Bell, J. P.; Scola, D. A. Mechanism of the electrocopolymerization of styrene and *N*-(3-carboxyphenyl)-maleimide onto graphite fibers in aqueous solution. *J. Appl. Polym. Sci.* **1993**, *47*, 93–104. (b) Lorandi, F.; Fantin, M.; Shanmugam, S.; Wang, Y.; Isse, A. A.; Gennaro, A.; Matyjaszewski, K. Toward Electrochemically Mediated Reversible Addition-Fragmentation Chain-Transfer (eRAFT) Polymerization: Can Propagating Radicals Be Efficiently Electrogenerated from RAFT Agents? *Macromolecules* **2019**, *52*, 1479–1488.

(28) However, when ethylbenzene was used as the starting material, acetophenone could be isolated in 20% yield. This is probably related to the behavior in the reaction of the allyl ether of *p*-vinylbenzyl

alcohol, where polymerization, and not selective oxidation of the aryl-substituted vinyl group, was the major reaction pathway.

(29) Bratsch, S. G. Standard Electrode Potentials and Temperature Coefficients in Water at 298.15 K. *J. Phys. Chem. Ref. Data* **1989**, *18*, 1–21.

(30) Das, B.; Venkateswarlu, K.; Damodar, K.; Suneel, K. Ammonium acetate catalyzed improved method for the regioselective conversion of olefins into halohydrins and haloethers at room temperature. *J. Mol. Catal. A: Chem.* **2007**, *269*, 17–21.