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Catalyst-Free Decarboxylation of Carboxylic Acids and Deoxygenation of Alcohols by Electro-Induced Radical Formation

Xiaoping Chen,[†][a] Xiaosheng Luo,[†][b] Xiao Peng,[†][a] Jiaojiao Guo,[b] Jiantao Zai[b] and Ping Wang*[b]

Abstract: *Electro-induced reduction of redox active esters and N-phthalimidoyl oxalates derived from naturally abundant carboxylic acids and alcohols provides a sustainable and inexpensive approach to radical formation via undivided electrochemical cells. The resulting radicals are trapped by an electron-poor olefin or hydrogen atom source to furnish the Giese reaction or reductive decarboxylation products, respectively. A broad range of carboxylic acid (1°, 2°, and 3°) and alcohol (2° and 3°) derivatives are applicable in this catalyst-free reaction, which tolerated a diverse range of functional groups. This method features simple operation, sustainable platform and broad applications.*

The discovery of Barton decarboxylation and Barton-McCombie deoxygenation via radical processes has led to numerous applications, albeit using toxic tin reagents under elevated temperature.[1] Recently, significant advances in radical generation have been achieved, allowing the use of easily accessible and abundant carboxylic acid or alcohol radical precursors. For example, stabilized carbon-centered radicals from α-hetero carboxylic acids can be directly generated under Ir-catalyzed photoredox conditions (Figure 1A).[2] Furthermore, decarboxylative fragmentation of redox active esters (RAEs) enables the generation of alkyl radicals under photoredox conditions using Ir, Ru, and other photocatalysts.[3] Meanwhile, transition metals such as Ni,[4] Fe,[5] Cu,[6] Co,[7] Cr,[8] and other metal species[9] have also been used to reduce RAEs via thermal single-electron transfer (SET) to form alkyl radicals. Through similar mechanisms, oxalate derivatives can produce tertiary radicals through Ir-, Ru-catalyzed photoredox conditions[10] or Zn metal and Ni with ligands.[11] However, these approaches mainly rely on precious or toxic metal catalysts, which is not ideal, especially during the preparation of medicinal intermediates. Moreover, the needs for strict reaction conditions such as anhydrous and anaerobic conditions are mandatory due to the properties of reactive transition metals. Several studies avoided the use of transition-metal catalysts and photo-catalysts.[3f-h, 12] Therefore, the development of catalyst-free and robust synthetic methods to generate radicals for synthetic application is still in high demand.

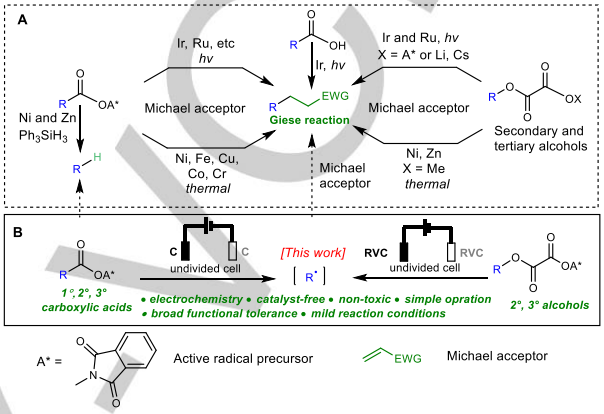

Figure 1. Decarboxylation and deoxygenation engaged Giese reactions under different conditions.

Meanwhile, electrochemistry has experienced a renaissance in recent years. Major advances on cross coupling,[13] annulation,[14] dehydrogenation[15] and other diverse reactions[16] have been accomplished by different groups.[17] However, conjugate addition from RAEs and oxalates were rare under catalyst-free and mild electrochemical conditions. Herein, we report an electro-induced, catalyst-free method for Giese reaction[18] and reductive decarboxylation. The features of this method include: 1) unprecedented electro-induced Giese reaction and reductive decarboxylation without toxic metal species, 2) operational simplicity and water-tolerant condition, 3) sustainable resources from carboxylic acid or alcohol derivatives (about $ 0.4 per mmol for Giese reaction, see Supporting Information), 4) robust and mild reaction condition with broad functional group tolerance (Figure 1B).

We began our exploration of the decarboxylation of RAE **1** by cathodic reduction, and using phenyl vinyl sulfone **2** as a trapping reagent under electrochemical conditions. Conducting the reaction under a constant voltage of 2.5 V with a graphite anode and cathode using nBu$_4$NBF$_4$ as the electrolyte in DMF in an undivided cell at room temperature provided product **3** in low yield with most of RAE **1** and acceptor **2** remaining unreacted (Table 1, entry 1). When the voltage was elevated to 5.0 V, **3** was produced in 69% yield (entry 2). Pleasingly, under 2.5 V with Hantzsch ester (HE) (1.2 equiv.), **3** was produced in 87% yield (entry 3). Here, HE could effectively lower the reaction potential by 2.5 V, which improved the reaction efficiency and minimized the side reactions caused by high voltage. Changing the reductant from HE to PhSiH$_3$ resulted in a low product yield (entry 4). Several other observations are worth noting during the reaction optimization: 1) DMF is much better when compared

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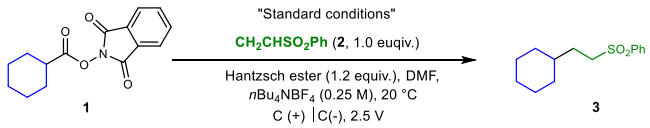
Table 1: Optimization experiments.



Entry[a]	Deviation from standard conditions	Yield (%)[b]
1	No reductant	trace
2	No reductant at 5.0 V	69
3	None	87
4	$PhSiH_3$ as reductant	trace
5	DME instead of DMF	53
6	ACN instead of DMF	34
7	Bu_4NOTf instead of nBu_4NBF_4	46
8	Bu_4NClO_4 instead of nBu_4NBF_4	36
9	$LiClO_4{\cdot}3H_2O$ instead of nBu_4NBF_4	32
10	Ni electrodes instead of graphite electrodes	51
11	Glassy carbon electrodes instead of graphite electrodes	44
12	Performed under an air atmosphere	61
13	No current	0
14	In the dark	85
15[c]	Under 450 nm irridiation, no current	53

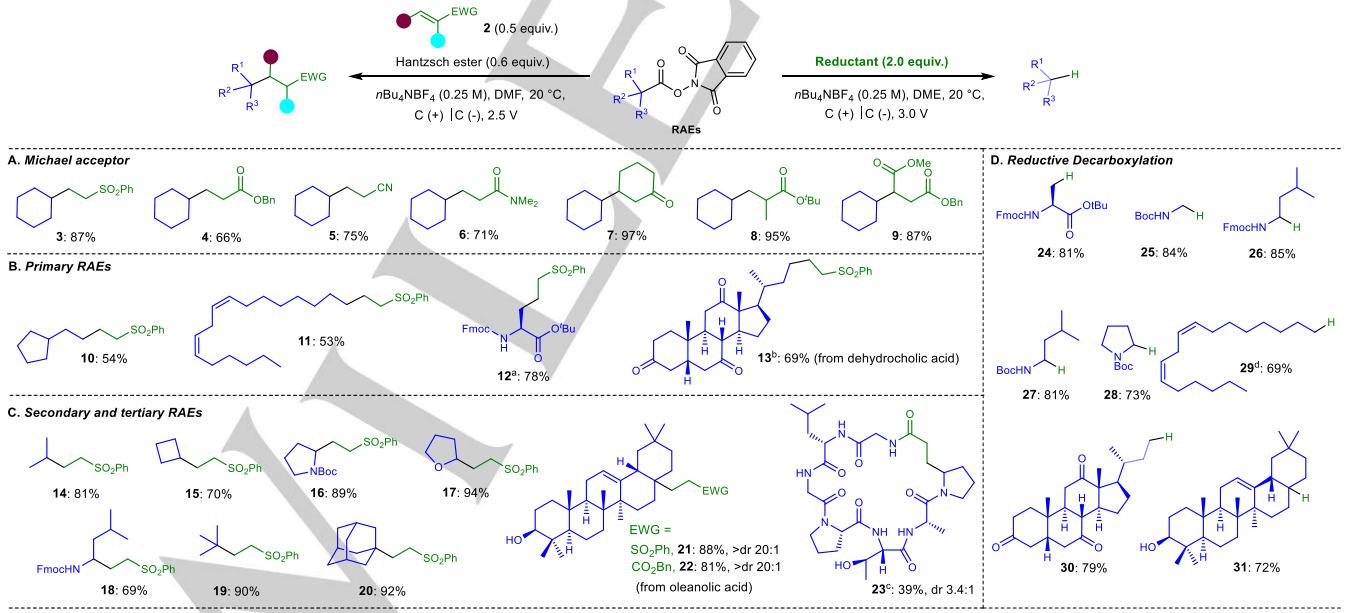
[a] Standard conditions (0.15 mmol). **1** (2.0 equiv.), **2** (1.0 equiv.), HE (1.2 equiv.), nBu_4NBF_4 (0.25 M), DMF (1.5 mL), graphite electrodes, 2.5 V, undivided cell, 20 °C, N_2 atmosphere, 2 h. [b] Isolated yield. [c] Reaction time: 12 h.

with the other solvents studied (entries 5, 6). 2) Low yields are obtained when different electrolytes are used (entries 7-9). 3) The material of electrode affects the yield (entries 10, 11). 4) Under open air conditions, the yield is slightly diminished (entry 12), indicating this reaction is insensitive to moisture and there is no requirement for the strict exclusion of oxygen. 5) An electric current is essential for this transformation, and visible light[12] is not critical in the reaction (entries 13-15).

Under the optimized conditions, the reaction of **1** with various Michael acceptors bearing different functional groups was examined (Scheme 1A). Products containing sulfones (**3**), esters (**4**), nitriles (**5**), amides (**6**), ketones (**7**) and α- or β-substituted adducts (**8** and **9**) were produced in excellent yields, demonstrating the broad functional tolerance. It was notable that **7** and **8** were obtained in near quantitative yield.

Non-stabilized primary alkyl radicals, which were less explored in other studies, were also investigated, yielding products **10**–**13** in good yields (Scheme 1B). Electron-rich olefin **11** was obtained in 53% yield with the internal alkene moieties in linoleic acid left intact. For complex substrates **12** and **13**, higher equivalents of the olefin and HE were required to give the desired products in good yields.

Excellent compatibility for a broad scope of secondary and tertiary alkyl RAEs bearing different functional groups was demonstrated (**14–22**) under standard conditions (Scheme 1C). The presence of α-heteroatom in cyclic substrates **16** and **17** resulted in higher yields (89 and 94%, respectively). Encouragingly, the formation of quaternary carbons (**19** and **20**) was highly efficient under electrochemical conditions when compared with photoredox and metal reagents.[19] Natural product derivatives (**21** and **22**) from steroid oleanolic acid were easily generated in excellent yields and high stereoselectivity. Furthermore, we extended this method to peptide macrocyclization.[2b, 20] Unprotected peptide **23** was readily accessed via an intramolecular Giese addition reaction in 39%



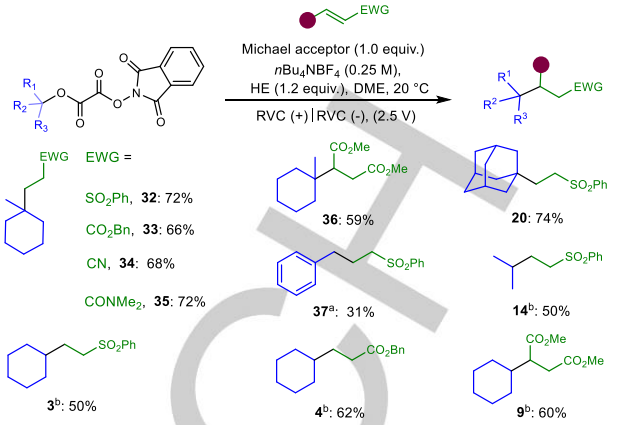
Scheme 1. Scope of the electro-induced Giese reaction and reduction of RAEs. Reaction conditions for the Giese reaction: RAE (2.0 equiv.), Michael acceptor (1.0 equiv.), HE (1.2 equiv.) nBu_4NBF_4 (0.25 M) in DMF (1.5 mL, 0.1 M for acceptor concentration), graphite electrodes, 20 °C, 2.5 V, undivided cell. Reaction conditions for reduction of RAEs: RAE (1.0 equiv.), DTT (2.0 equiv.), nBu_4NBF_4 (0.25 M) in DME (1.5 mL, 0.1 M), graphite electrodes, 20 °C, 3.0 V, undivided cell. [a]Using 1.0 equiv. of RAE, 5.0 equiv. of Michael acceptor and 2.4 equiv. of HE. [b]Using 1.0 equiv. of RAE and 2.0 equiv. of Michael acceptor. [c]Using the peptide derivative at 5 mM concentration. [d]Using 2.0 equiv. HE.

yield. Macrocyclic peptides are important therapeutics and this transformation suggests its potential value in peptide macrocyclization. Overall, the Giese reaction proceeded rapidly at ambient temperature.

As with the Giese reaction, a scope of primary, secondary and tertiary RAEs bearing a broad range of functional groups [Fmoc (**24** and **26**), Boc (**25**, **27–28**), olefins (**29**), ketone (**30**), and hydroxyl (**31**)] can be employed in reductive decarboxylation reaction in the presence of HE or DTT (1,4-dithiothrietol) as reductive reagents, producing **24–31** in excellent yields (Scheme 1D). In the case of primary product **29**, HE proved to be more efficient than DTT. Different from other Giese reaction protocols or decarboxylation conditions, a broad range of carboxylic acids (1°, 2°, and 3°) with no requisite for transition metal species features this transformation.

Next, we proceeded to investigate the potential application of alcohol-derived *N*-phthalimidoyl oxalates[10b, 21] in the electrochemical conditions. Despite an abundance of natural alcohols, direct methods for C(sp^3)-C(sp^3) bond formation from alcohols are rare due to the strong C–O bond.

Pleasingly, the Giese reaction of *N*-phthalimidoyl oxalates with a variety of Michael acceptors were also found to be efficient when reticulated vitreous carbon (RVC) electrodes were used in DME (Scheme 2). Quaternary carbons were formed to give products **20**, **32**–**36** in good yields. Primary benzylic and secondary alkyl oxalates failed to undergo the conjugate addition under the standard conditions. However, under an elevated voltage and reaction temperature (5 V, 50 °C), products **37**, **3**, **4**, **9** and **14** were obtained in moderate yield. This is an unprecedented example of the Barton deoxygenation reaction triggered by electrochemical process.



Scheme 2. Scope of the electro-induced Giese reaction of oxalate derivatives. Reaction conditions: Oxalate (2.0 equiv.), Michael acceptor (1.0 equiv.), HE (2.0 equiv.), nBu$_4$NBF$_4$ (0.25 M) in DME, RVC electrodes, 20 °C, 2.5 V, undivided cell. [a]Reaction run at 50 °C and 5.0 V with 1.0 equiv. of oxalate, 5.0 equiv. of Michael acceptor and 2.5 equiv. of HE. [b]Reaction run at 50 °C and 5.0 V.

To gain mechanistic understanding of this electrochemical reaction, control reactions were performed. First, no desired product was observed in the presence of TEMPO (2.0 equiv.) under the standard reaction conditions, and the TEMPO adduct was isolated with 24% yield, suggesting the involvement of radicals (Figure 2A). Next, reaction conducted with deuterated HE **38** gave product **3** in 71% yield with no formation of deuterated product **3′** (Figure 2B). However, when 10% D_2O was used as a co-solvent, deuterated product **3′** was produced in 83% yield with 89% deuterium incorporation. Furthermore, the

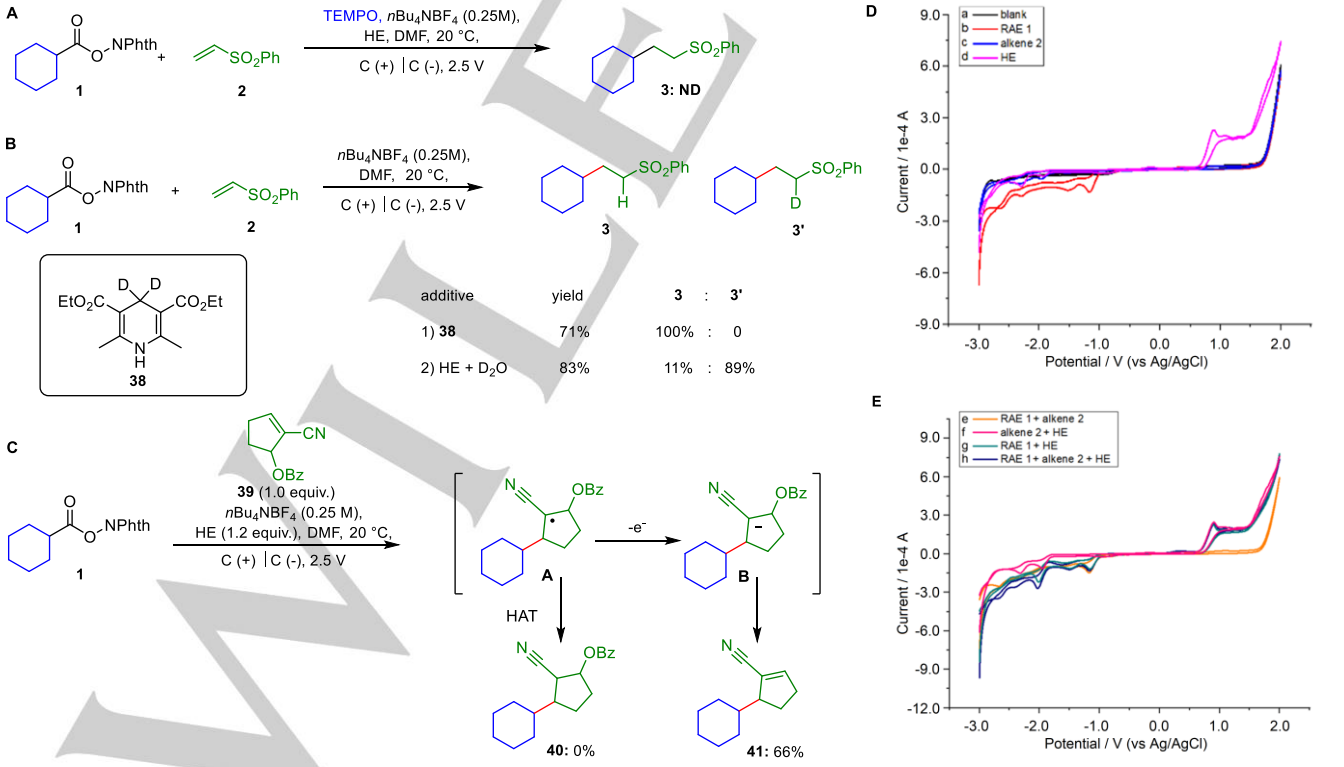


Figure 2. A) Giese reaction performed in the presence of 2.0 equiv. of TEMPO. B) Deuterium incorporation experiments. C) Giese reaction performed with acceptor **39** under the standard conditions. D) Cyclic voltammograms of different substrates at 10 mV/s in DMF, nBu$_4$NBF$_4$ (0.1 M). E) Cyclic voltammograms of different mixtures.

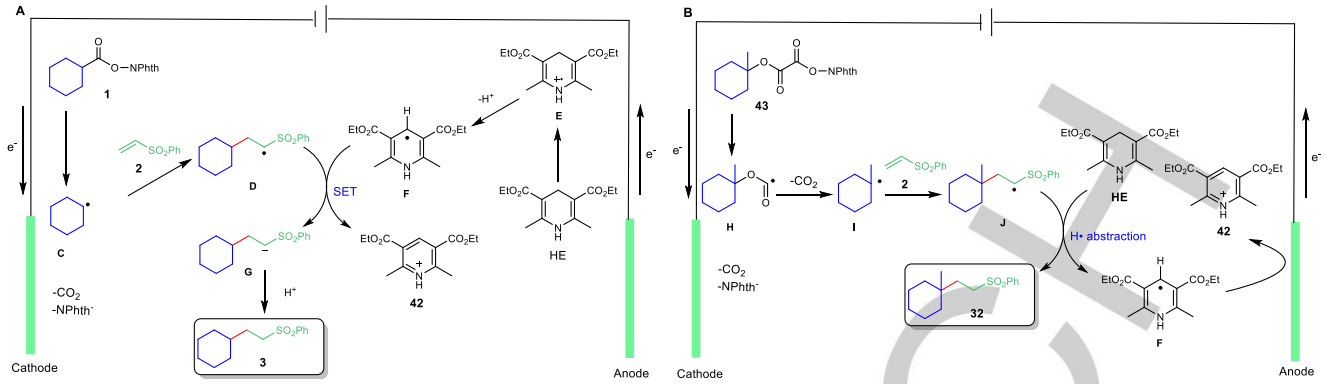


Figure 3. Proposed mechanisms for electrochemical C-C bond formation under the standard conditions using A) RAE **1** and B) oxalate **43** as a radical source.

reaction of RAE **1** with **39** bearing a leaving group (OBz) at allylic α′ position was performed using a method developed by Overman (Figure 2C).[22] Interestingly, product **41** was formed exclusively, indicating radical **A** was involved via single-electron reduction to α-cyanocarbanion intermediate **B**, followed by intramolecular elimination to give **41**. These results indicated that HE acted as an electron-donor, but not a H-donor in this reaction.

Subsequently, cyclic voltammetry (CV) experiments were examined to explore the redox behavior of these substrates. As shown in Figure 2, individual substrates **1** (curve b, −1.15 V), **2** (curve c, -1.95 V) and HE (curve d, +0.89 V) were recorded respectively (Figure 2D). The reduction peak of **1** (−1.15 V) indicates a reductive process at the cathode for the generation of alkyl radical. Furthermore, the mixtures of these substrates did not exhibit any significant change compared with each substrate alone (Figure 2E).

Based on these experiments, a plausible mechanism for this transformation is outlined in Figure 3. This process starts with the cathodic reduction of **1** to generate radical **C**, CO_2 and phthalimide (Figure 3A). Nucleophilic radical **C** couples with the terminal carbon of **2**, furnishing radical **D**. Meanwhile, anodic oxidation of HE produces radical cation **E**, followed by subsequent deprotonation to generate strongly reducing radical **F**. SET between radical **D** and intermediate **F** affords anion **G**, followed by protonation to give **3**. The plausible mechanism for the electro-induced Giese reaction under 5.0 V conditions is similar with that under 2.5 V conditions. In the absence of HE, radical **D** will be reduced at the cathode to provide anion **G** (see Supporting Information)**.** Interestingly, the mechanism for *N*-phthalimidoyl oxalate **43** is different to the RAE precursor (Figure 3B). After radical **I** is generated via cathodic reduction, it undergoes the Giese addition reaction with **2** to provide radical **J**. Instead of SET, hydrogen-atom abstraction (HAT) between **J** and HE generated the final adduct **32** together with intermediate **F** (see Supporting Information).

In summary, Giese reactions and reductive decarboxylations are enabled via the electro-induced decarboxylative and deoxygenative fragmentation of RAEs and *N*-phthalimidoyl oxalates. Mechanistic studies suggest that RAE and *N*-phthalimidoyl oxalate are initiated via cathodic reduction. It is notable that the robustness, environmental friendliness and wide applications of the decarboxylation of acids and the deoxygenation of alcohols avoid the use of toxic metal catalysts or expensive photoredox catalysts. Furthermore, the utilization of natural products and peptides has demonstrated its potential utility in the late-stage functionalization of complex natural products. Finally, the combination of ubiquitous carboxylic acids and alcohols with electrochemistry will facilitate their decarboxylation and deoxygenation in a sustainable and easily accessible way.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: electrochemistry • cathodic reduction • decarboxylation • deoxygenation • radical reaction

[1] a) D. H. R. Barton, D. Crich, G. Kretzschmar, *Tetrahedron Lett.* **1984**, *25*, 1055-1058; b) D. H. R. Barton, S. W. Mccombie, *J. Chem. Soc. Perkin I* **1975**, *6*, 1574-1585; c) S. W. McCombie, W. B. Motherwell, M. J. Tozer, in *Organic Reactions, Vol. 77*, John Wiley & Sons, Inc: Hoboken, NJ, **2012**, p. 161−591.

[2] a) L. Chu, C. Ohta, Z. Zuo, D. W. MacMillan, *J. Am. Chem. Soc.* **2014**, *136*, 10886-10889; b) S. J. McCarver, J. X. Qiao, J. Carpenter, R. M. Borzilleri, M. A. Poss, M. D. Eastgate, M. Miller, D. W. MacMillan, *Angew. Chem. Int. Ed.* **2016**, *56*, 728-732.

[3] Selected review: a) Y. Jin, H. Fu, *Asian J. Org. Chem.* **2017**, *6*, 368-385; Selected examples: b) W.-M. Cheng, R. Shang, Y. Fu, *ACS Catal.* **2017**, *7*, 907-911; c) J. Yang, J. Zhang, L. Qi, C. Hu, Y. Chen, *Chem. Commun.* **2015**, *51*, 5275-5278; d) R. Mao, A. Frey, J. Balon, X. Hu, *Nat. Catal.* **2018**, *1*, 120-126; e) X. Liu, Y. Liu, G. Chai, B. Qiao, X. Zhao, Z. Jiang, *Org. Lett.* **2018**, *20*, 6298-6301. f) J. Schwarz, B. König, *Green Chem.* **2016**, *18*, 4743-4749. g) Y. Jin, H. Yang, H. Fu, *Org. Lett.* **2016**, *18*, 6400-6403; h) L. Gao, G. Wang, J. Cao, D. Yuan, C. Xu, X. Guo, S. Li, *Chem. Commun.* **2018**, *54*, 11534-11537. i) K. Okada, K. Okamoto, N. Morita, K. Okubo, M. Oda, *J. Am. Chem. Soc.* **1991**, *113*, 9401-9402.

[4] a) T. Qin, J. Cornella, C. Li, L. R. Malins, J. T. Edwards, S. Kawamura,

B. D. Maxwell, M. D. Eastgate, P. S. Baran, *Science* **2016**, *352*, 801-805; b) X. Lu, X.-X. Wang, T.-J. Gong, J.-J. Pi, S.-J. He, Y. Fu, *Chem. Sci.* **2019**, *10*, 809-814

[5] F. Toriyama, J. Cornella, L. Wimmer, T. G. Chen, D. D. Dixon, G. Creech, P. S. Baran, *J. Am. Chem. Soc.* **2016**, *138*, 11132-11135.

[6] J. Wang, M. Shang, H. Lundberg, K. S. Feu, S. J. Hecker, T. Qin, D. G. Blackmond, P. S. Baran, *ACS Catal.* **2018**, *8*, 9537-9542.

[7] X.-G. Liu, C.-J. Zhou, E. Lin, X.-L. Han, S.-S. Zhang, Q. Li, H. Wang, *Angew. Chem. Int. Ed.* **2018**, *57*, 13096-13100.

[8] S. Ni, N. M. Padial, C. Kingston, J. C. Vantourout, D. C. Schmitt, J. T. Edwards, M. M. Kruszyk, R. R. Merchant, P. K. Mykhailiuk, B. B. Sanchez, S. Yang, M. A. Perry, G. M. Gallego, J. J. Mousseau, M. R. Collins, R. J. Cherney, P. S. Lebed, J. S. Chen, T. Qin, P. S. Baran, *J. Am. Chem. Soc.* **2019**, *141*, 6726-6739.

[9] a) K. M. M. Huihui, J. A. Caputo, Z. Melchor, A. M. Olivares, A. M. Spiewak, K. A. Johnson, T. A. DiBenedetto, S. Kim, L. K. G. Ackerman, D. J. Weix, *J. Am. Chem. Soc.* **2016**, *138*, 5016-5019; b) X. Lu, X.-X. Wang, T.-J. Gong, J.-J. Pi, S.-J. He, Y. Fu, *Chem. Sci.* **2019**, *10*, 809-814; c) L. Huang, A. M. Olivares, D. J. Weix, *Angew. Chem. Int. Ed.* **2017**, *56*, 11901-11905. c) T. Qin, L. R. Malins, J. T. Edwards, R. R. Merchant, A. J. Novak, J. Z. Zhong, R. B. Mills, M. Yan, C. Yuan, M. D. Eastgate, P. S. Baran, *Angew. Chem. Int. Ed.* **2017**, *56*, 260-265.

[10] a) X. Zhang, D. W. MacMillan, *J. Am. Chem. Soc.* **2016**, *138*, 13862−13865; b) G. L. Lackner, K. W. Quasdorf, L. E. Overman, *J. Am. Chem. Soc.* **2013**, *135*, 15342-15345; c) C. C. Nawrat, C. R. Jamison, Y. Slutskyy, D. W. C. MacMillan, L. E. Overman, *J. Am. Chem. Soc.* **2015**, *137*, 11270-11273; d) F. W. Friese, A. Studer, *Angew. Chem. Int. Ed.* **2019**, *58*, 9561-9564.

[11] Y. Ye, H. Chen, J. L. Sessler, H. Gong, *J. Am. Chem. Soc.* **2019**, *142*, 820-824.

[12] a) Y. Li, J. Zhang, D. Li, Y. Chen, *Org. Lett.* **2018**, *20*, 3296-3299; b) C. Zheng, G.-Z. Wang, R. Shang, *Adv. Synth. Catal.* **2019**, *361*, 4500-4505.

[13] Selected examples: a) T. Morofuji, A. Shimizu, J.-i. Yoshida, *Angew. Chem. Int. Ed.* **2012**, *51*, 7259-7262; b) Q.-L. Yang, X.-Y. Wang, J.-Y. Lu, L.-P. Zhang, P. Fang, T.-S. Mei, *J. Am. Chem. Soc.* **2018**, *140*, 11487-11494; c) P. Xiong, H. Long, J. Song, Y. Wang, J.-F. Li, H.-C. Xu, *J. Am. Chem. Soc.* **2018**, *140*, 16387-16391; d) S. Tang, S. Wang, Y. Liu, H. Cong, A. Lei, *Angew. Chem. Int. Ed.* **2018**, *57*, 4737-4741; e) R. Mei, N. Sauermann, J. C. A. Oliveira, L. Ackermann, *J. Am. Chem. Soc.* **2018**, *140*, 7913-7921; f) N. Sauermann, T. H. Meyer, C. Tian, L. Ackermann, *J. Am. Chem. Soc.* **2017**, *139*, 18452-18455; g) A. Wiebe, S. Lips, D. Schollmeyer, R. Franke, S. R. Waldvogel, *Angew. Chem. Int. Ed.* **2017**, *56*, 14727-14731; h) H. Li, C. P. Breen, H. Seo, T. F. Jamison, Y.-Q. Fang, M. M. Bio, *Org. Lett.* **2018**, *20*, 1338-1341; i) T. Koyanagi, A. Herath, A. Chong, M. Ratnikov, A. Valiere, J. Chang, V. Molteni, J. Loren, *Org. Lett.* **2019**, *21*, 816-820.

[14] Z.-J. Wu, S.-R. Li, H.-C. Xu, *Angew. Chem. Int. Ed.* **2018**, *57*, 14070-14074.

[15] a) K. Liu, S. Tang, T. Wu, S. Wang, M. Zou, H. Cong, A. Lei, *Nat. Commun.* **2019**, *10*, 639; b) H. Wang, X. Gao, Z. Lv, T. Abdelilah, A. Lei, *Chem. Rev.* **2019**, *119*, 6769-6787.

[16] a) D. Hui, P. L. Deroy, P. Christian, L. Alexandre, S. Arshad, C. G. Caldwell, H. Susan, P. G. Harran, *Angew. Chem. Int. Ed.* **2015**, *127*, 4900-4904; b) K. L. Jensen, P. T. Franke, L. T. Nielsen, D. Kim, J. R. Karl Anker, *Angew. Chem. Int. Ed.* **2010**, *49*, 129-133; c) X. H. Ho, S. I. Mho, H. Kang, H. Y. Jang, *Eur. J. Org. Chem.* **2010**, *2010*, 4436-4441; d) N. Fu, L. Li, Q. Yang, S. Luo, *Org. Lett.* **2017**, *19*, 2122-2125; e) B. H. Nguyen, A. Redden, K. D. Moeller, *Green Chem.* **2014**, *16*, 69-72; f) N. Fu, G. S. Sauer, A. Saha, A. Loo, S. Lin, *Science* **2017**, *357*, 575-579; g) K.-Y. Ye, G. Pombar, N. Fu, G. S. Sauer, I. Keresztes, S. Lin, *J. Am. Chem. Soc.* **2018**, *140*, 2438-2441.

[17] a) M. Yan, Y. Kawamata, P. S. Baran, *Chem. Rev.* **2017**, *117*, 13230-13319; b) T. H. Meyer, L. H. Finger, P. Gandeepan, L. Ackermann, *Trends Chem.* **2019**, *1*, 63-76.

[18] Z. Chami, M. Gareil, J. Pinson, J.-M. Saveant, A. Thiebault, *Tetrahedron Lett.* **1988**, *29*, 639-642.

[19] a) N. P. Ramirez, J. C. Gonzalez-Gomez, *Eur. J. Org. Chem.* **2017**, *2017*, 2154-2163; b) M. R. Garnsey, Y. Slutskyy, C. R. Jamison, P. Zhao, J. Lee, Y. H. Rhee, L. E. Overman, *J. Org. Chem.* **2018**, *83*, 6958-6976.

[20] X. Zhang, G. Lu, M. Sun, M. Mahankali, Y. Ma, M. Zhang, W. Hua, Y. Hu, Q. Wang, J. Chen, G. He, X. Qi, W. Shen, P. Liu, G. Chen, *Nat. Chem.* **2018**, *10*, 540-548..

[21] a) G. L. Lackner, K. W. Quasdorf, G. Pratsch, L. E. Overman, *J. Org. Chem.* **2015**, *80*, 6012-6024; b) Y. Slutskyy, L. E. Overman, *Org. Lett.* **2016**, *18*, 2564-2567.

[22] G. Pratsch, G. L. Lackner, L. E. Overman, *J. Org. Chem.* **2015**, *80*, 6025-6036.

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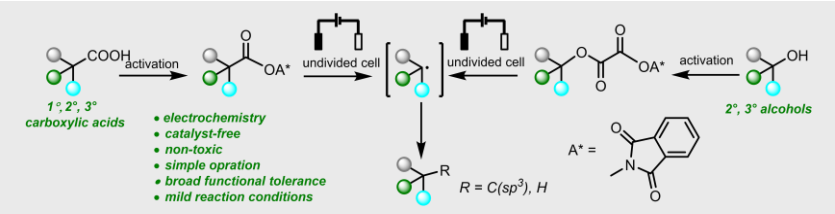

An electrochemical strategy produces alkyl radicals from readily accessible redox active esters and *N*-phthalimidoyl oxalates under catalyst-free and sustainable conditions within an undivided cell. The resulting carbon-centred radical was trapped by an electron-poor olefin or hydrogen atom source to furnish the new formed C(sp^3)–(sp^3) bond or reductive decarboxylation products, respectively.

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Catalyst-Free Decarboxylation of Carboxylic Acids and Deoxygenation of Alcohols by Electro-Induced Radical Formation