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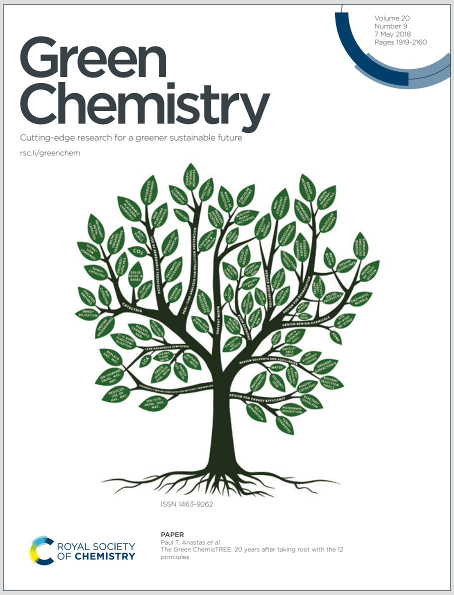

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ARTICLE

Electrochemical Esterification Reaction of Alkynes with Diols via Cleavage of Carbon-Carbon Triple Bonds Without Catalyst and Oxidant

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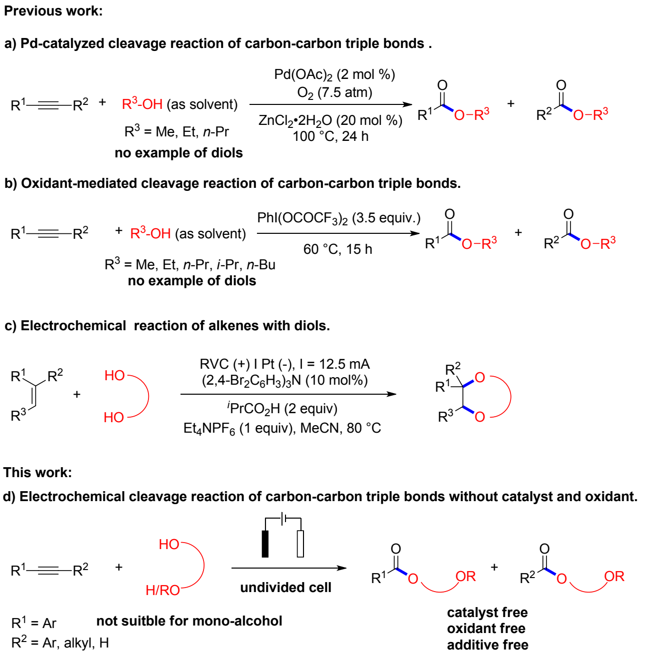
A novel electrochemical esterification of alkynes for the synthesis of esters was developed in which diols and their derivatives were used as the partent. This method is green for its characteristic of catalyst-free, oxidant-free, additive-free and atom-economy. This is the first example of electrochemical reaction via cleavage of carbon-carbon triple bonds. Meanwhile, this is also the first example of carbon-carbon triple bonds cleavage reaction of alkynes with diols.

Introduction

Cleavage reaction of carbon-carbon bond which is a usful synthetic tool for the construction of many valuable compounds has received widespread attention and been aplied in the field of agrochemicals, pharmaceuticals, and materials.[1] In the past decades, cleavage reactions of carbon-carbon sigle bond and carbon-carbon double bond have been developed intensively.[2,3] However, owing to the large bond energy of carbon-carbon triple bond, the cleavage reaction of it was developed slowly and it is still one of the most challenging subjects in organic synthesis. One of the example of cleavage reactions of carbon-carbon triple bond was metathesis of alkynes.[4] However, transiton-metal catalysts were needed, for example, Mo or W were commonly used. Beside metathesis reaction, examples of cleavage reactions of carbon-carbon triple bond were rare, and most of them involved the use of transition-metal catalysts and oxidants. Transition-metal catalysis played a important role in the carbon-carbon triple bond cleavage reaction. In 2001, Jun reported a rhodium-catalyzed hydroiminoacylation reaction via cleavage of carbon-carbon triple bonds.[5] After that, a serious of transition-metal catalyzed cleavage of carbon-carbon triple bonds were developed.[6] However, the use of expensive or toxic transiton-metal added the cost of product and the difficulty of purification. In addition, most of these reactions need harsh reaction conditions. A few examples of cleavage reaction of carbon-carbon triple bonds which can avoid the use of transiton-metal catalyst have been developed.[7] However, many of them still need plenty amount of oxidants.[8] Developing green and sustainable carbon-carbon triple bonds cleavage reactions is till challenging.

As for esterification reaction of alkynes via cleavage of carbon-carbon triple bonds, only two methods have been reported. In 2008, Jiang reported a palladium-catalyzed cleavage reaction of carbon-carbon triple bond with molecular oxygen promoted by lewis acid (scheme 1a).[9] However, there are many drawbacks of this reaction: (1) This reaction used the expensive transition-metal-catalyst $Pd(OAc)_2$; (2) the reaction conditions are harsh, which need high pressure and temperature; (3) the reaction need high pressure O_2 as the oxidant and $ZnCl_2{\cdot}2H_2O$ as an additive; (4) there was no example of diols as substrate. In 2014, Guo reported PIFA-mediated



Scheme 1 Methods for the construction of α,β-dialkoxy-stilbene and electrochemical reaction with diols.

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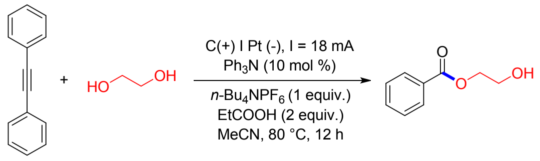
esterification reaction of alkynes with alcohols via oxidative cleavage of carbon triple bonds (scheme 1b).[10] However, plenty amount of oxidant (3.5 equivalent) was used and no example of diols was reported.

In recent years, electrochemical synthesis has been developed into one of the most fascinating synthetic methods because of its green and economical character.[9] Electrochemistry provides an economical way to transfer electrons directly at the electrode. Therefore, many reactions can be conducted by anode oxidation directly without use of a catalyst, redox medium or oxidant. In 2018, Xu's group realized an electrochemical coupling reaction with alkenes and diols (scheme 1c).[10] However, the electrochemical reaction of alkynes and diols has never been reported. It is worth mentioning that the cyclic product was obtained in Xu's work but our target product is esters. Therefore, how to avoid the formation of cyclic product is challenging. In addition, Xu's work needs amine as catalyst and acid as additive. Herein, we report a novel electrochemical esterification of diaryl acetylene with diols and their derivatives for the synthesis of esters in the absence of catalyst, oxidant and additive (scheme 1d). This is the first example of electrochemical reaction via cleavage of carbon-carbon triple bonds. Meanwhile, This is also the first example of carbon-carbon triple bonds cleavage reaction of alkynes with diols. Fortunately, the desired esters were formed with a yield of up to 80%.

Table 1 Electrochemical dialkoxylation of diaryl acetylenes: optimization of conditions[a,b]



1a 2a 3a

Entry	Variation from the above conditions	Yield (%)
1	none	66
2	I = 12 mA	52
3	I = 15 mA	56
4	I = 20 mA	63
5	C (+) ∣ C (-)	61
6	Pt (+) ∣ C (-)	0
7	Pt (+) ∣ Pt (-)	0
8	DMF instead of MeCN	trace
9	DMSO instead of MeCN	0
10	H_2O instead of MeCN	0
11	50 °C	55
12	Room temperature	38
13	n-Bu_4NBF_4 instead of n-Bu_4NPF_6	54
14	n-Bu_4NOAc instead of n-Bu_4NPF_6	0
15	no electric current	0
16[c]	double the amount of all reagents except for solvent	72
17[d]	triple the amount of all reagents except for solvent	76
18[d, e]	without EtCOOH and Ph_3N	**76**
19[d,e,f]	10 h	67
20[d, e, g]	1 mL of **2a**	66
21[d, e, h]	0.5 mL of **2a**	55
22[d, e, i]	under air	73

[a] Reaction conditions: C anode, Pt Cathode, constant current = 18 mA, undivided cell, **1a** (0.2 mmol), **2a** (0.5 mL), Ph_3N (0.02 mmol, 10 mol%), n-Bu_4NPF_6 (0.2 mmol, 1 equiv.), EtCOOH (0.4 mmol, 2 equiv.), MeCN (5 mL), 80 °C, 12 h, N_2. [b] Isolated yield. [c] **1a** (0.4 mmol), **2a** (1 mL), Ph_3N (0.04 mmol, 10 mol%), n-Bu_4NPF_6 (0.4 mmol, 1 equiv.), EtCOOH (0.8 mmol, 2 equiv.), MeCN (5 mL). [d] **1a** (0.6 mmol), **2a** (1.5 mL), Ph_3N (0.06 mmol, 10 mol%), n-Bu_4NPF_6 (0.6 mmol, 1 equiv.), EtCOOH (1.2 mmol, 2 equiv.), MeCN (5 mL). [e] without EtCOOH and Ph_3N. [f] 10 h. [g] 1 mL of 2a. [h] 0.5 mL of **2a**. [i] under air.

Results and discussion

We initiated our study by using diphenyl acetylene (**1a**) and glycol (**2a**) as model substrates under N_2 atmosphere in the presence of C as the anode, Pt as the cathode, 10 mol% of Ph_3N as a catalyst, 1 equivalent of n-Bu_4NPF_6 as an electrolyte, EtCOOH as an additive, and MeCN as a solvent at 80 °C. To our delight, the desired product ester **3a** was obtained in good yield (66%, entry 1, Table 1). Next, we assessed the effect of current intensity on the conversion and found that on increasing or decreasing the current intensity, the conversion was reduced (entries 2-4). Then, we assessed the effect of the electrode on the conversion and found that the anode material was crucial for this reaction. When a C anode was used, the different material of the cathode had a slight effect on the yield (entry 5). When a Pt anode was used, despite the cathode being C or Pt, no product was obtained (entries 6-7). The choice of solvent is also crucial for this reaction. Other solvents that are usually used in electrochemical synthesis such as DMF, DMSO, H_2O were tested, but almost no product was obtained (entries 8-10). The yield was reduced as the temperature was decreased (entries 11-12). Additionally, we surveyed electrolytes and found that the use of n-Bu_4NBF_4 reduced the yield to 54% and that n-Bu_4NOAc even led to no product formation (entries 13-14). As a control experiment, we conducted the reaction without electricity and found that none of the desired product **3a** was afforded (entry 15). To improve the yield further, we increased the concentration. When doubling the amount of all reagents except solvent, the yield was raised to 72% (entry 16). When tripling the amount of all reagents except for the solvent, the yield was raised to 76% (entry 17). Furthermore, we tested the necessity of the catalyst Ph_3N and additive EtCOOH. It is worth mentioning that without a catalyst and additive, the transformation proceeded as well as before, affording the desired product with a yield of 76% (entry 18). Shortening the reation time to 10 h lead to decrement of the yield (entry 19). The yield was reduced as the amount of **2a** was decreased (entries 20-21). Finally, we conducted this reaction under air in place of N_2, and the yield was found to be slightly lower (entry 22). Thus, through optimization of the conditions, we established the optimized reaction conditions to be as follows: C anode, Pt cathode, 18 mA of constant current, 0.6 mmol of **1a**, 1.5 mL of glycol, 1 equivalent of

Table 2 Substrate scope[a,b]

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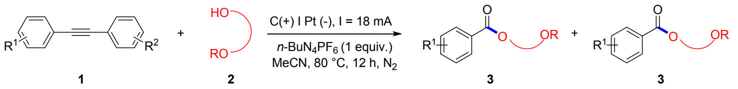

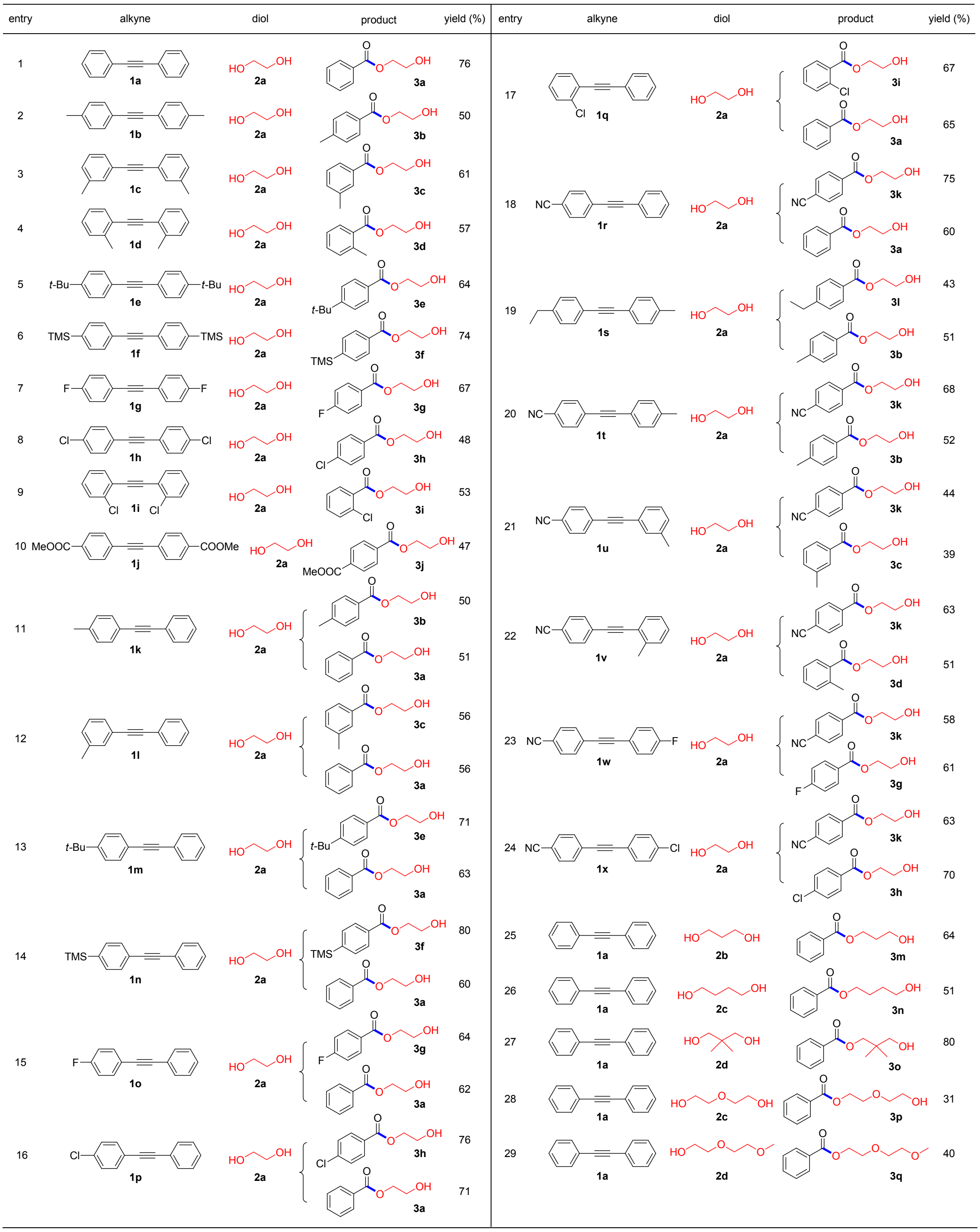

entry	alkyne	diol	product	yield (%)
1	**1a**	**2a**	**3a**	76
2	**1b**	**2a**	**3b**	50
3	**1c**	**2a**	**3c**	61
4	**1d**	**2a**	**3d**	57
5	**1e**	**2a**	**3e**	64
6	**1f**	**2a**	**3f**	74
7	**1g**	**2a**	**3g**	67
8	**1h**	**2a**	**3h**	48
9	**1i**	**2a**	**3i**	53
10	**1j**	**2a**	**3j**	47
11	**1k**	**2a**	**3b** **3a**	50 51
12	**1l**	**2a**	**3c** **3a**	56 56
13	**1m**	**2a**	**3e** **3a**	71 63
14	**1n**	**2a**	**3f** **3a**	80 60
15	**1o**	**2a**	**3g** **3a**	64 62
16	**1p**	**2a**	**3h** **3a**	76 71
17	**1q**	**2a**	**3i** **3a**	67 65
18	**1r**	**2a**	**3k** **3a**	75 60
19	**1s**	**2a**	**3l** **3b**	43 51
20	**1t**	**2a**	**3k** **3b**	68 52
21	**1u**	**2a**	**3k** **3c**	44 39
22	**1v**	**2a**	**3k** **3d**	63 51
23	**1w**	**2a**	**3k** **3g**	58 61
24	**1x**	**2a**	**3k** **3h**	63 70
25	**1a**	**2b**	**3m**	64
26	**1a**	**2c**	**3n**	51
27	**1a**	**2d**	**3o**	80
28	**1a**	**2c**	**3p**	31
29	**1a**	**2d**	**3q**	40

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[a] Reaction conditions: C anode, Pt cathode (1 cm x 1 cm), I = 18 mA, undivided cell, **1** (0.6 mol), **2** (45 equiv. 27 mmol), *n*-Bu_4NPF_6 (1 equiv. 0.6 mmol), MeCN (5 mL), 80 °C, 12 h, N_2. [b] Isolated yield.

n-Bu_4NPF_6 as electrolyte, and 5.0 mL of MeCN as solvent under N_2 at 80 °C for 12 h.

With the optimized conditions in hand, we moved on to explore the substrate scope by first varying the substituents on the diaryl acetylene, as shown in Table 2. For the symmetric diaryl acetylenes, substituents on the para-, meta- and ortho- position were well tolerated (**3b**-**3d**, entries 2-4). In addition to methyl, bulky groups substituent tert-butyl was also tolerated (**3e**, entry 5). In addition, the trimethylsily group substituted diaryl acetylene was found to be well tolerated in this esterification reaction, affording the corresponding product in good yield (**3e-3f**, entries 5-6). Moreover, a diverse range of halogen substituents on the various positions of the phenyl rings were also found to be compatible with this method (**3g**-**3i**, entries 7-9). The strong electron-withdrawing ester group was well tolerated in our catalytic system, affording the corresponding product **3j** in moderate yield (entry 10). The structure of **3j** was conformed by the X-ray (Figure 2). The electron poor system (**3j**) working as well as some of the more electron-rich systems is interesting, since the strong electron-withdrawing group would decrease the electron density of aromatic ring and its conjugate system, making the electron hard to lose and the substrate hardly be oxidized. To explain this phenomenon, a series of CV studies were carried out (Figure 2) and showed that the oxidation potentials of the **1a** (2.1 V) and ester group substituted substrate **1j** (2.2 V) were not so different. For the asymmetric diaryl acetylenes, we first assessed diaryl acetylenes that contained only one substituent (**1k**-**1r**, entries 16-24). In general, substituents on the para-, meta- and ortho- position were well tolerated. Alkyl groups were suitable for this reaction (**1k**-**1m**, entries 11-13). The trimethylsilyl group substituted diaryl acetylene proceeded smoothly to afford the corresponding product in good yield (**1n**, entry 14). Halogen substituents on the various positions of the phenyl rings were also found to be compatible with this method (**1o**-**1q**, entries 15-17). The strong electron-withdrawing cyano group substituted diaryl acetylene proceeded smoothly to afford the corresponding product in good yield (**1r**, entry 18). The asymmetric diaryl acetylenes, which contains different substituents on its two phenyl rings, were well tolerated (**1s**-**1x**, entries 19-24).

After screening the substrate scope for diaryl acetylenes, we next moved on to explore the substrate scope for alcohols. Linear diols, propane-1,3-diol and butane-1,4-diol were all found to be compatible with our newly developed protocol, affording the corresponding products in moderate yields (**3m**-**3n**). It is worth mentioning that with the extension of the chain length of the linear diols, the yield was reduced (**3a**, **3m** and **3n**). Interestingly, non-linear diol 2,2-dimethylpropane-1,3-diol was fully applicable to this catalytic system with excellent yield (80%, **3o**). Finally, we tested diethylene glycol and diethylene glycol monomethyl ether. To our delight, the desired products **3p** and **3q** were obtained smoothly, albeit in relatively low yields.

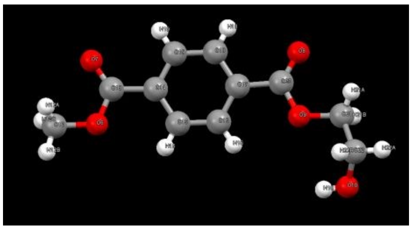

Figure 1 X-ray structure of **3j**

Table 3 Substrate scope[a,b]

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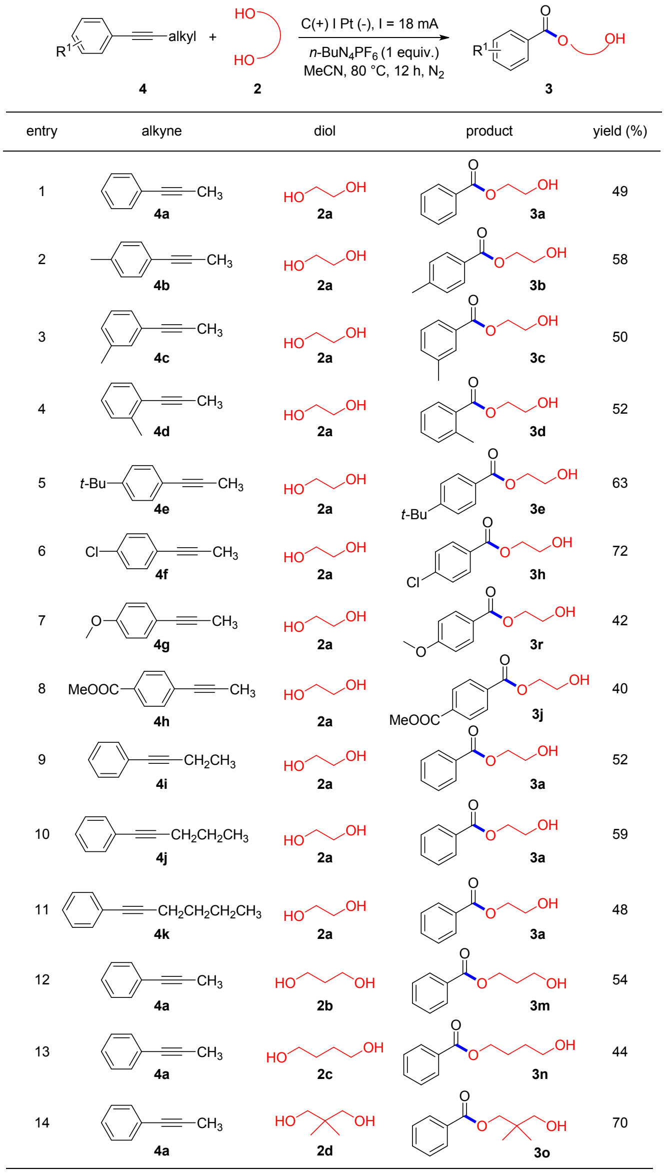
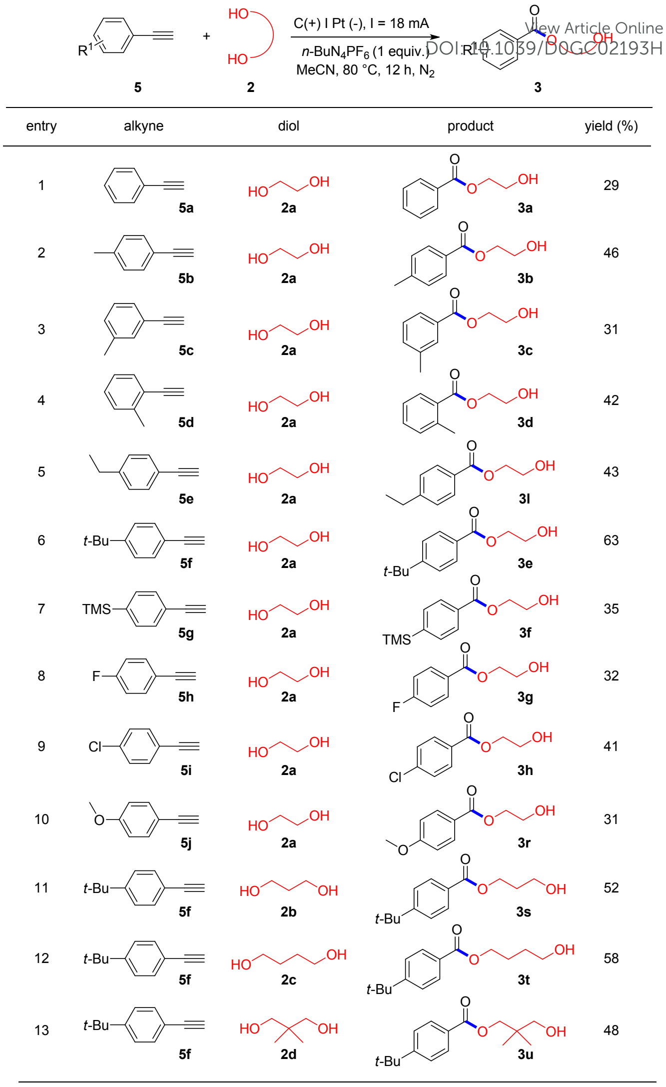


entry	alkyne	diol	product	yield (%)
1	**4a**	**2a**	**3a**	49
2	**4b**	**2a**	**3b**	58
3	**4c**	**2a**	**3c**	50
4	**4d**	**2a**	**3d**	52
5	**4e**	**2a**	**3e**	63
6	**4f**	**2a**	**3h**	72
7	**4g**	**2a**	**3r**	42
8	**4h**	**2a**	**3j**	40
9	**4i**	**2a**	**3a**	52
10	**4j**	**2a**	**3a**	59
11	**4k**	**2a**	**3a**	48
12	**4a**	**2b**	**3m**	54
13	**4a**	**2c**	**3n**	44
14	**4a**	**2d**	**3o**	70

[a] Reaction conditions: C anode, Pt cathode (1 cm x 1 cm), I = 18 mA, undivided cell, **4** (0.6 mol), **2** (45 equiv. 27 mmol), n-Bu_4NPF_6 (1 equiv. 0.6 mmol), MeCN (5 mL), 80 °C, 12 h, N_2. [b] Isolated yield.

Beside diaryl acetylenes, arylalkylalkynes were also suitable for this reaction (Table 3). We screened the substituents on the phenyl ring firstly. Substituents on the para-, meta- and ortho- position of the phenyl ring were well tolerated (**4b**-**4d**, entries 2-4). Alkyl and halogen substituents were found to be compatible with this method (**4b**-**4f**, entries 2-6). To our delight, the strong electron-donating substituents working as well as the strong electron-withdrawing substituents (**4g**-**4h**, entries 7-8). Next, we moved on to explore the alkyl group of the arylalkylalkynes and found that a serious of alkyl groups were compatible with this method (**4l**-**4k**, entries 9-11). At last, we explored the substrate scope for alcohols. Linear and non-linear diols were applicable to this catalytic system (**3m**-**3o**, entries 12-14).

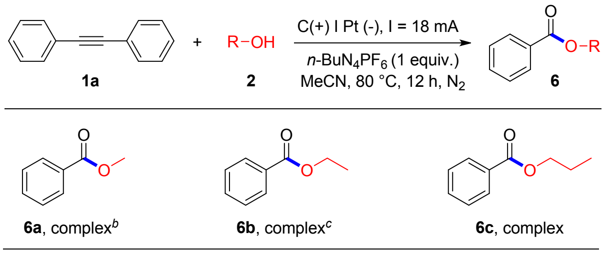
Table 4 Substrate scope[a,b]



entry	alkyne	diol	product	yield (%)
1	**5a**	**2a**	**3a**	29
2	**5b**	**2a**	**3b**	46
3	**5c**	**2a**	**3c**	31
4	**5d**	**2a**	**3d**	42
5	**5e**	**2a**	**3l**	43
6	**5f**	**2a**	**3e**	63
7	**5g**	**2a**	**3f**	35
8	**5h**	**2a**	**3g**	32
9	**5i**	**2a**	**3h**	41
10	**5j**	**2a**	**3r**	31
11	**5f**	**2b**	**3s**	52
12	**5f**	**2c**	**3t**	58
13	**5f**	**2d**	**3u**	48

[a] Reaction conditions: C anode, Pt cathode (1 cm x 1 cm), I = 18 mA, undivided cell, **5** (0.6 mol), **2** (45 equiv. 27 mmol), n-Bu_4NPF_6 (1 equiv. 0.6 mmol), MeCN (5 mL), 80 °C, 12 h, N_2. [b] Isolated yield.

Table 5 Substrate scope[a]



[a] Reaction conditions: C anode, Pt cathode (1 cm x 1 cm), I = 18 mA, undivided cell, **5** (0.6 mol), **2** (45 equiv. 27 mmol), n-Bu_4NPF_6 (1 equiv. 0.6 mmol), MeCN (5 mL), 80 °C, 12 h, N_2. [b] 60°C. [c] 75°C.

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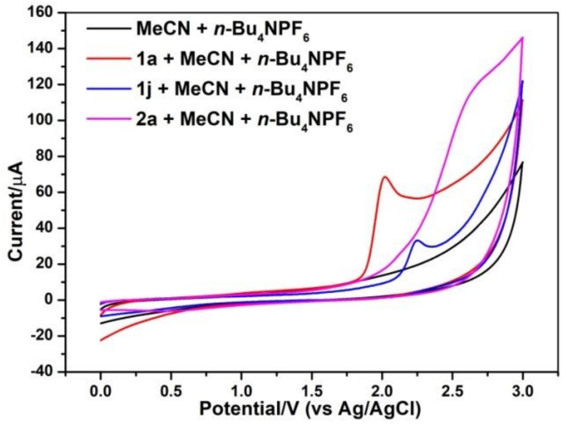


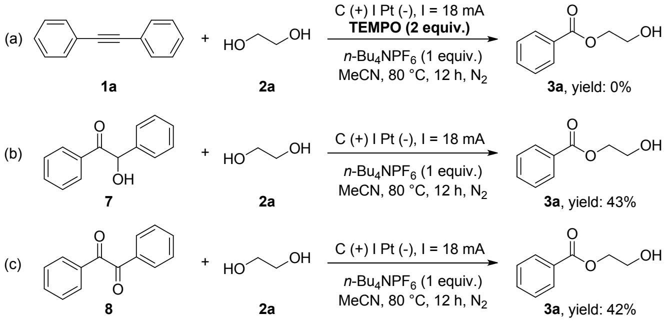
Figure 2 Cyclic voltammograms recorded in MeCN with 0.1 M *n*-Bu_4NPF_6 as the supporting electrolyte. **1a** (1 mM). **1j** (1 mM). **2a** (1 mM).

To our excitement, no only internal alkynes, but also terminal alkynes were suitable for this reaction (Table 4). Alkyl groups on the para-, meta- and ortho- position were well tolerated (**5b**-**5f**, entries 2-6). The trimethylsilyl group substituted phenylacetylene proceeded smoothly to afford the corresponding product (**5g**, entry 7). Halogen substituents were also found to be compatible with this method (**5h**-**5i**, entries 8-9). Strong electron-donating methoxy group was suitable for this reaction (**5j**, etries 10). Linear and non-linear diols were applicable to this catalytic system (**3s**-**3u**, entries 11-13).

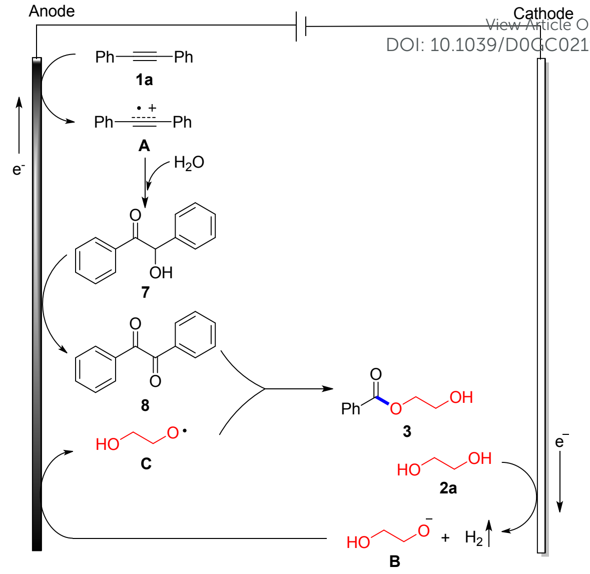
It is interesting that this reaction is suitable only for diols, not for mono alcohols. we tried to use the methanol, ethanol, propanol as he partners of the diphenylacetylene, but they were all failed. The reaction system was complex (Table 5).

To gain insight into the reaction mechanism, a series of CV studies were carried out (Figure 2). The oxidation peak for **1a** was found to occur at 2.1 V, The oxidation peak for **2a** was not obvious, but the curve of 2a was not the same as the black curve. It seemed that there was a peek at about 2.8V, which illustrated the fact that the glycol is electroactive. **1a** was oxidized more easily than **2a**.

To further probe the mechanism, a series of control experiments were carried out (scheme 2). Firstly, when TEMPO was added to the model reation, no desired product was obtained, which indicated that the reaction went through a radical pathway (scheme 2a). Furthermore, the plausible intermediate 2-hydroxy-1,2-diphenylethanone (**7**) and benzil (**8**) were subjected to the standard reaction conditions, and the desired product **3a** was obtained in 43% and 42% yields respectively.



Scheme 2 Control experiment



Scheme 3 Plausible reaction mechanism.

Based on the CV experiments, the control experiments and previous reports,[10-12] a plausible mechanism for the electrochemical esterification of alkynes is proposed in scheme 3. First, diaryl acetylene is transformed to the radical cation **A** by anode oxidation, which undergoes deprotonation with water from the reagents to generate the radical intermediate **7**. This is followed by further anode oxidation, where the cation intermediate **8** is formed. At the cathode, glycol (**2b**) was transformed to anion **B** and H_2. Then B was oxidized by anode to form the radical **C**. Finally, Further fragmentation of with radical **C** to generate the desired ester product **3**.

Conclusions

In conclusion, we developed the first electrochemical carbon-carbon triple bonds cleavage reaction. It provided a facile strategy for the synthesis of esters from alkynes. This is also the first example of carbon-carbon triple bonds cleavage reaction of alkynes with diols. No catalyst, oxidant and additive was used. The substrate scope was wide. Internal and terminal alkynes were all suitable for this reaction; Linear diols, non-linear diols, diol derivatives were also suitable for this reaction.

Conflicts of interest

The authors declare no competing financial interest.

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Notes and references

1 (a) R. H. Crabtree, *Chem. Rev.*, 1985, **85**, 245. (b) CarbocyclicThree- and Four-Membered Ring Compounds; A. de Meijere, Ed.; Houben-Weyl Methods in Organic Chemistry, Thieme: Stuttgart, 1996, Vol. E17a-c. (c) M. Murakami and Y. Ito, In Activation of Unreactive Bonds and Organic Synthesis; Murai, S., Ed.; Springer: Berlin, 1999; p 97. (d) B. Rybtchinski and D. Milstein, *Angew. Chem., Int. Ed.*, 1999, **38**, 870. (e) A. de Meijere, *Chem. Rev.*, 2003, **103**, 931. (f) C.-H. Jun, *Chem. Soc. Rev.*, 2004, **33**, 610. (g) Y. Horino, *Angew. Chem., Int. Ed.*, 2007, **46**, 2144. (h) M. Rubin, M. Rubina and V. Gevorgyan, *Chem. Rev.*, 2007, **107**, 3117. (i) L. J. Gooßen, N. Rodríguez and K. Gooßen, *Angew. Chem., Int. Ed.*, 2008, **47**, 3100. (j) M. Tobisu and N. Chatani, *Chem. Soc. Rev.*, 2008, **37**, 300. (k) Y. J. Park, J.-W. Park and C.-H. Jun, *Acc. Chem. Res.*, 2008, **41**, 222. (l) Y. J. Park, J.-W. Park and C.-H. Jun, *Acc. Chem. Res.*, 2008, **41**, 222. (m) C. Najera and J. M. Sansano, *Angew. Chem., Int. Ed.*, 2009, **48**, 2452. (n) A. Masarwa and I. Marek, *Chem.–Eur. J.*, 2010, **16**, 9712. (o) M. Murakami and T. Matsuda, *Chem. Commun.*, 2011, **47**, 1100. (p) C. Zhang, P. Feng and N. Jiao, *J. Am. Chem. Soc.*, 2013, **135**, 15257. (q) F. Chen, T. Wang and N. Jiao, *Chem. Rev.*, 2014, **114**, 8613. (r) C. Tang and N. Jiao, *Angew. Chem., Int. Ed.*, 2014, **53**, 6528. (s) W. Zhou, W. Fan, Q. Jiang, Y.-F. Liang and N. Jiao, *Org. Lett.*, 2015, **17**, 2542. (t) Q. Gao, S. Liu, X. Wu, J. Zhang and A. Wu, *Org. Lett.*, 2015, **17**, 2960. (u) L. Souillart and N. Cramer, *Chem. Rev.*, 2015, **115**, 9410. (v) S. Kollea and S. Batra, *Org. Biomol. Chem.*, 2016, **14**, 11048. (w) A. P. Y. Chan and A. G. Sergeev, *Coord. Chem. Rev.*, 2020, **413**, 213213.

2 For some selected examples on C-C single bond cleavage, see: (a) C.-H. Jun, H. Lee and S.-G. Lim, *J. Am. Chem. Soc.*, 2001, **123**, 751. (b) T. Takahashi, Y. Kuzuba, F. Kong, K. Nakajima and Z. Xi, *J. Am. Chem. Soc.*, 2005, **127**, 17188. (c) C. Wang, L. Deng, J. Yan, H. Wang, Q. Luo and Z. Xi, *Chem. Commun.*, 2009, 4414. (d) C. He, S. Gou, L. Huang and A. Lei, *J. Am. Chem. Soc.*, 2010, **132**, 8273. (e) T. Seiser and N. Cramer, *J. Am. Chem. Soc.*, 2010, **132**, 5340. (f) A. Sattler and G. Parkin, *Nature*, 2010, **463**, 523. (g) Y. Hirata, A. Yada, E. Morita, Y. Nakao, T. Hiyama, M. Ohashin and S. Ogoshi, *J. Am. Chem. Soc.*, 2010, **132**, 10070. (h) M. Waibel and N. Cramer, *Angew. Chem., Int. Ed.*, 2010, **49**, 4455. (i) H. Li, Y. Li, X.-S. Zhang, K. Chen, X. Wang and Z.-J. Shi, *J. Am. Chem. Soc.*, 2011, **133**, 15244. (j) R.-J. Song, Y. Liu, R.-X. Hu, Y.-Y. Liu, J.-C. Wu, X.-H. Yang and J.-H. Li, *Adv. Synth. Catal.*, 2011, **353**, 1467. (k) H. Li, W. Li, W. Liu, Z. He and Z. Li, *Angew. Chem., Int. Ed.*, 2011, **50**, 2975. (l) M. Baidya and H. Yamamoto, *J. Am. Chem. Soc.*, 2011, **133**, 13880. (m) P. Hu, M. Zhang, X. Jie and W. Su, *Angew. Chem., Int. Ed.*, 2012, **51**, 227. (n) C. Zhang, Z. Xu, T. Shen, G.Wu, L. Zhang and N. Jiao, *Org. Lett.*, 2012, **14**, 2362. (o) M. Tobisu, H. Kinuta, Y. Kita, E. Remond and N. Chatani, *J. Am. Chem. Soc.*, 2012, **134**, 115. (p) C. Zhang, P. Feng and N. Jiao, J. Am. Chem. Soc., 2013, **135**, 15257. (q) C. Qin, P. Feng, Y. Ou, T. Shen, T. Wang and N. Jiao, *Angew. Chem., Int. Ed.*, 2013, **52**, 7850. (r) Z.-Q. Lei, F. Pan, H. Li, Y. Li, X.-S. Zhang, K. Chen, X. Wang, Y-X. Li, J. Sun and Z.-J. Shi, *J. Am. Chem. Soc.*, 2015, **137**, 5012. (s) Z. Li, J. Dong, X. Chen, Q. Li, Y. Zhou and S.-F. Yin, *J. Org. Chem.*, 2015, **80**, 9392. (t) C. Zhu, F. Chen, C. Liu, H. Zeng, Z. Yang, W. Wu and H. Jiang, *J. Org. Chem.*, 2018, **83**, 14713. (u) T.-Y. Yu, Z.-J. Zheng, T.-T. Dang, F.-X. Zhang and H. Wei, *J. Org. Chem.*, 2018, **83**, 10589. (v) S. Wu, S. Luo, W. Guo, T. Wang, Q. Xie, J. Wang and G. Liu, *Organometallics*, 2018, **37**, 2335. (w) S. Wen, W. Lv, D. Ba, J. Liu and G. Cheng, *Chem. Sci.*, 2019, **10**, 9104. (x) M. Brendel, P. R. Sakhare, G. Dahiya, P.i Subramanian and K. P. Kaliappan, *J. Org. Chem.*, 2020, **85**, 8102.

3 For some selected examples on C-C double bond cleavage, see: (a) R. Criegee, *Angew. Chem., Int. Ed.*, 1975, **14**, 745. (b) H. R. Barton and W. Chavasiri, *Tetrahedron*, 1994, **50**, 19. (c) R. H. Grubbs, S. J. Miller and G. C. Fu, *Acc. Chem. Res.*, 1995, **28**, 446. (d) X. Baucherel, J. Uziel and S. Juge, *J. Org. Chem.*, 2001, **66**, 4504. (e) T. Takemori, A. Inagaki and H. Suzuki, *J. Am. Chem. Soc.*, 2001, **123**, 1762. (f) B. R. Travis, R. S. Narayan and B. J. Borhan, *J. Am. Chem. Soc.*, 2002, **124**, 3824. (g) J. W. Boer, J. Brinksma, W. R. Meetsma, A. Browne, P. L. Alsters, R. Hage and B. L. Feringa, *J. Am. Chem. Soc.*, 2005, **127**, 7990. (h) V. Kogan, M. M. Quintal and R. Neumann, *Org. Lett.*, 2005, **7**, 5039. (i) A. Dhakshinamoorthy and K. Pitchumani, *Tetrahedron*, 2006, **62**, 9911. (j) D. Xing, B. Guan, G. Cai, Z. Fang, L. Yang and Z. Shi, *Org. Lett.*, 2006, **8**, 693. (k) S.-T. Liu, K. V. Reddy and R.-Y. Lai, *Tetrahedron*, 2007, **63**, 1821. (l) K. Miyamoto, N. Tada and M. Ochiai, *J. Am. Chem. Soc.*, 2007, **129**, 2772. (m) A. H. Hoveyda and A. R. Zhugralin, *Nature*, 2007, **450**, 243. (n) N. M. Neisius and B. Plietker, *J. Org. Chem.*, 2008, **73**, 3218. (o) F. V. Singh, H. M. S. Milagre, M. N. Eberlin and H. A. Stefani, *Tetrahedron Lett.*, 2009, **50**, 2312. (p) M. O'Brien, I. R. Baxendale and S. V. Ley, *Org. Lett.*, 2010, **12**, 1596. (q) P. P. Thottumkara and T. K. Vinod, *Org. Lett.*, 2010, **12**, 5640. (r) R. Lin, F. Chen and N. Jiao, *Org. Lett.*, 2012, **14**, 4158. (s) T. Wang and N. Jiao, *J. Am. Chem. Soc.*, 2013, **135**, 11692. (t) M. Hu, R.-J. Song and J.-H. Li, *Angew. Chem., Int. Ed.*, 2015, **54**, 608. (u) Z. Wu, R. Ren and C. Zhu, *Angew. Chem., Int. Ed.*, 2016, **55**, 10821. (v) X. Tang and A. Studer, *Angew. Chem., Int. Ed.*, 2018, **57**, 814. (w) K. M. Nakafuku, S. C. Fosu and D. A. Nagib, *J. Am. Chem. Soc.*, 2018, **140**, 11202. (x) Q. Yu, Y. Zhang and J.-P. Wan, *Green Chem.*, 2019, **21**, 3436. (y) L. Gan, Y. Gao, L. Wei and J.-P. Wan, *J. Org. Chem.*, 2019, **84**, 1064. (z) Y. Liu, J. Xiong, L. Wei and J.-P. Wan, *Adv. Synth. Catal.*, 2020, **362**, 877.

4 For some reviews, see: (a) U. H. F. Bunz and L. Kloppenburg, *Angew. Chem., Int. Ed.*, 1999, **38**, 478. (b) A. Fürstner, C. Mathes and C. W. Lehmann, *Chem.-Eur. J.*, 2001, **7**, 5299. (c) U. H. F. Bunz, *Acc. Chem. Res.*, 2001, **34**, 998. (d) A. Fürstner and P. W. Davies, *Chem. Commun.*, 2005, 2307. (e) W. Zhang and J. S. Moore, *Adv. Synth. Catal.*, 2007, **349**, 93. (f) H. Villar, M. Frings and C. Bolm, *Chem. Soc. Rev.*, 2007, **36**, 55. (g) P. H. Deshmukh and S. Blechert, *Dalton Trans.*, 2007, 2479. (h) X. Wu and M. Tamm, *J. Org. Chem.*, 2011, **7**, 82. (i) A. Fürstner, *Angew. Chem. Int. Ed.*, 2013, **52**, 2794. (j) Y. Jin, Q.Wang, P. Taynton and W. Zhan, *Acc. Chem. Res.*, 2014, **47**, 1575. (k) M. Ortiz, C. Yu, Y. Jin and W. Zhang, *Top. Curr. Chem.*, 2017, **375**, 69.

5 C.-H. Jun, H. Lee, C.-W. Moon and H.-S. Hong, *J. Am. Chem. Soc.*, 2001, **123**, 8600.

6 (a) T. Shimada and Y. Yamamoto, *J. Am. Chem. Soc.*, 2003, **125**, 6646. (b) S. Datta, C.-L. Chang, K.-L. Yeh and R.-S. Liu, *J. Am. Chem. Soc.*, 2003, **125**, 9294. (c) A. Wang and H. Jiang, *J. Am. Chem. Soc.*, 2008, **130**, 5030. (d) T. Shen, T. Wang, C. Qin and N. Jiao, *Angew. Chem., Int. Ed.*, 2013, **52**, 6677. (e) W.-B. Sheng, Q. Jiang, W.-P. Luo and C.-C. Guo, *J. Org. Chem.*, 2013, **78**, 5691. (f) P. Bisseret, G. Duret and N. Blanchard, *Org. Chem. Front.*, 2014, **1**, 825. (g) X. Wang, D. He, Y. Huang, Q. Fan, W. Wu and H. Jiang, *J. Org. Chem.*, 2018, **83**, 5458. (h) J. Ni, Y. Jiang, Z. An and R. Yan, *Org. Lett.*, 2018, **20**, 1534.

7 (a) R. Tanaka and K. Yamabe, *J. Chem. Soc., Chem. Commun.*, 1983, 329. (b) N. Okamoto, M. Ishikura and R. Yanada, *Org. Lett.*, 2013, **15**, 2571. (c) K. Xu, Z. Li, F. Cheng, Z. Zuo, T. Wang, M. Wang and L. Liu, *Org. Lett.*, 2018, **20**, 2228. (d) P.

View Article Online
DOI: 10.1039/D0GC02193H

Zhou, J.-Y. Wang, T.-S. Zhang, G. Li, W.-J. Hao, S.-J. Tu and B. Jiang, *Chem. Commun.*, 2018, **54**, 164.

8 (a) K. Miyamoto, Y. Sei, K. Yamaguchi and M. Ochiai, *J. Am. Chem. Soc.*, 2009, **131**, 1382. (b) Q. Jiang, A. Zhao, B. Xu, J. Jia, X. liu and C. Guo, *J. Org. Chem.,* 2014, **79**, 2709. (c) X. Wang, G. Cheng, J. Shen, X. Yang, M. Wei, Y. Feng and X. Cui, *Org. Chem. Front.*, 2014, **1**, 1001. (d) S. Khamarui, R. Maiti and D. K. Maiti, *Chem. Commun.*, 2015, **51**, 384. (e) S. U. Dighea and S. Batra, *Adv. Synth. Catal.*, 2016, **358**, 500. (f) N. Katta, M. Ojha, A. Murugan, S. Arepally and D. S. Sharada, *RSC Adv.*, 2020, **10**, 12599.

9 For selected books and reviews of electrochemical synthesis, see: (a) J. Grimshaw, Electrochemical Reactions and Mechanisms in Organic Chemistry, Elsevier: Amsterdam, 2000. (b) H. Lund and O. Hammerich, Eds., Organic Electrochemistry. Marcel Dekker: New York, 4th ed., 2001. (c) J. B. Sperry and D. L. Wright, *Chem. Soc. Rev.,* 2006, **35**, 605. (d) B. A. Frontana-Uribe, R. D. Little, J. G. Ibanez, A. Palma and R. Vasquez-Medrano, *Green Chem.,* 2010, **12**, 2099. (e) R. Francke and R. D. Little, *Chem. Soc. Rev.,* 2014, **43**, 2492. (f) T. Fuchigami, S. Inagi and M. Atobe, Eds., Fundamentals and Applications of Organic Electrochemistry: Synthesis, Materials, Devices, Wiley-VCH: Chichester, West Sussex, 2015. (g) M. Yan, Y. Kawamata and P. S. Baran, *Chem. Rev.,* 2017, **117**, 13230. (h) S. Möhle, M. Zirbes, E. Rodrigo, T. Gieshoff, A. Wiebe and S. R. Waldvogel, *Angew. Chem., Int. Ed.,* 2018, **57**, 6018. (i) M. D. Kärkäs, *Chem. Soc. Rev.,* 2018, **47**, 5786. (j) K. D. Moeller, *Chem. Rev.,* 2018, **118**, 4817. (k) A. Wiebe, T. Gieshoff, S. Möhle, E. Rodrigo, M. Zirbes and S. R. Waldvogel, *Angew. Chem., Int. Ed.,* 2018, **57**, 5594. (l) P. Xiong and H.-C. Xu, *Accounts Chem. Res.,* 2019, **52**, 3339. (m) Y. Yuan and A. Lei, *Accounts Chem. Res.,* 2019, **52**, 3309. (n) C. Kingston, M. D. Palkowitz, Y. Takahira, J. C. Vantourout, B. K. Peters, Y. Kawamata and P. S. Baran, *Accounts Chem. Res.,* 2020, **53**, 72.

10 C.-Y. Cai and H.-C. Xu, *Nat. Commun.,* 2018, **9**, 3551.

11 J. Li, W. Huang, J. Chen, L. He, X. Cheng and G. Li, *Angew. Chem., Int. Ed.,* 2018, **57**, 5695.

12 B. Liu, S. Duan, A. C. Sutterer and K. D. Moeller, *J. Am. Chem. Soc.,* 2002. **124**, 10101.