



Cutting-edge research for a greener sustainable future

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: Y. Cao, Y. Yuan, Y. Lin, X. Jiang, Y. Weng, T. Wang, F. Bu, L. Zeng and A. Lei, Green Chem., 2020, DOI: 10.1039/D0GC00289E.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



rsc.li/greenchem

Journal Name



Cobalt catalyzed electrochemical [4+2] annulation for the synthesis of sultams

I Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Yangmin Cao,[†]a Yong Yuan,[†]b Yueping Lin,^a Xiaomei Jiang,^a Yaqing Weng,^a Tangwei Wang,^a Faxiang Bu,^b Li Zeng,^b and Aiwen Lei,^{*ab}

.

www.rsc.org/

Published on 07 February 2020. Downloaded by Universite Paris Descartes on 2/9/2020 8:15:56 AM.

Cobalt catalyzed electrochemical [4+2] annulation of sulfonamides with alkynes is demonstrated in this work, which provided a practical and environmentally friendly way to synthesize structurally diverse sultams. Notably, by employing anodic oxidation in an undivided cell to recycle the cobalt catalyst, this electrochemical method avoided the utilization of stoichiometric amount of metallic oxidant, delivering H₂ as the sole by-product. Moreover, this cobalt catalyzed electrochemical protocol proved to be practical and scalable. When model reaction was scaled up to 5.0 mmol, 86% yield of product could still be obtained.

Sultams are a class of very significant heterocyclic compounds, which are not only valuable synthetic precursors in synthetic chemistry,¹ but are also common motifs prevalent in many pharmaceuticals,² agrochemicals,³ and biologically active compounds.⁴ For these reasons, the development of efficient and practical approaches for synthesizing sultams has attracted considerable attention by organic chemists.5 Conventionally, sultams are prepared by the intramolecular cross-coupling or cascade cyclization of sulfonamide compounds.^{6,7} Though the intramolecular synthesis strategy presented an efficient route for constructing sultams, these procedures usually require multiple steps to synthesize the starting materials. Annulation reactions,⁸ especially transition metal-catalyzed oxidative C-H/X-H annulation reactions,⁹ are among the most straightforward ways for synthesizing cyclic compounds. In recent years, several examples for synthesizing sultams using oxidative annulation strategy have been developed.^{10,11} However, these methods largely require stoichiometric amounts of metallic oxidants as sacrificial reagents, inevitably generating some metal-containing byproducts. Furthermore, most of these reactions are carried out at high temperature (100 °C in 2,2,2-trifluoroethanol or 120 °C in 1,4-dioxane), which greatly limits the wide application of these methods, especially in large-scale synthesis. Therefore, developing a concise and practical synthetic approach to synthesize sultams at lower temperature under metallic oxidants-free conditions is highly desirable.



Scheme 1. Cobalt catalyzed electrochemical [4+2] annulation for the synthesis of sultams.

As a powerful and environmentally friendly synthetic protocol, electrochemical synthesis can realize the oxidative C-H functionalization¹² even oxidative C-H/X-H annulation under exogenous-oxidants-free conditions.13,14 Nevertheless, compared with the extensive study of metal-free electrochemical annulations,13 transition metal-catalyzed electrochemical annulations are relatively underexplored.14 For example, the transition metal-catalyzed electrochemical [4+2] annulation for synthesizing structurally diverse sultams has not been exploited until now. As a part of our recent research interest on electrochemical synthesis,¹⁵ we herein report the first example of transition metal-catalyzed electrochemical [4+2] annulation of sulfonamides with alkynes (Scheme 1). By employing a cobalt salt as the metal catalyst, a wide range of sultams were prepared using an undivided cell and with the evolution of hydrogen.

We started our investigation by employing 4-methyl-*N*-(quinolin-8-yl)benzenesulfonamide (**1**) and phenylacetylene (**2**) as the model substrates (Table 1). Gratefully, when the electrolysis was performed in an undivided cell in the presence of $Co(OAc)_2$ ·4H₂O (20 mol%) and NaOAc (2.0 equiv.) using the mixture of alcohol and acetic acid as the co-solvent, the desired [4+2] annulation product **3** could be isolated in 80% yield (Table 1, entry 1). Control experiments showed that electricity (Table 1, entry 2), cobalt catalysis (Table 1, entry 3), and NaOAc (Table 1, entry 4) were all crucial reaction partners. Increasing the operating current to 8 mA or decreasing the

^a National Research Center for Carbohydrate Synthesis, Jiangxi Normal University, Nanchang 330022, P. R. China. E-mail: aiwenlei@whu.edu.cn.

^b College of Chemistry and Molecular Sciences, Institute for Advanced Studies (IAS), Wuhan University, Wuhan 430072, P. R. China.

⁺ Yangmin Cao and Yong Yuan contributed equally to this work.

[‡] Electronic Supplementary Information (ESI) available: See DOI:

^{10.1039/}x0xx00000x.

Published on 07 February 2020. Downloaded by Universite Paris Descartes on 2/9/2020 8:15:56 AM.

Page 2 of 6

operating current to 2 mA delivered the annulation product **3** in low yield (Table 1, entries 5-6). Replacing $Co(OAc)_2$ ·4H₂O with $CoCl_2$, $Co(acac)_2$, or $Co(acac)_3$ also furnished the annulation product in low yield (Table 1, entries 7-9). Further investigation showed that NaOAc was the best choice for base and supporting electrolyte, using PhCOONa delivered the annulation product in 50% yield (Table 1, entry 10). Solvents were also investigated. MeCN/HOAc gave the annulation product in 33% yield (Table 1, entry 11); whereas CF₃CH₂OH/HOAc furnished the desired product in 85% yield (Table 1, entry 12). Given that CF₃CH₂OH is much more expensive than EtOH, we still decided to choose EtOH/HOAc as the co-solvent for the further studies.

Table 1: Optimization of the reaction conditions.^a

C C	$ \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \end{array}\\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\$	Ph + H ₂
Entry	Variation from the standard conditions	Yield (%) ^b
1	none	80
2	no electric current	0
3	no Co(OAc) ₂ ·4H ₂ O	0
4	no NaOAc (adding ⁿ Bu ₄ NBF ₄ as the electrolyte)	21
5	8 mA, 4 h	5
6	2 mA, 16 h	38
7	CoCl ₂	39
8	Co(acac) ₂	12
9	Co(acac) ₃	0
10	PhCO ₂ Na	50
11	MeCN/HOAc	33
12	CF ₃ CH ₂ OH/HOAc	85

 o Reaction conditions: carbon cloth (15 mm*20 mm*0.33 mm) anode, stainless steel plate (15 mm*20 mm*1.0 mm) cathode, constant current = 4 mA, **1** (0.25 mmol), **2** (2.0 equiv.), NaOAc (2.0 equiv.), Co(OAc)₂·4H₂O (20 mol%), EtOH (10.0 mL), HOAc (1.0 mL), Air, 75 °C, 8 h, Q = quinolin-8-yl. b Isolated yields.

Under the optimized reaction conditions, the generality and limitation for this cobalt catalyzed electrochemical [4+2] annulation reaction was then explored (Table 2). Initially, different alkynes were investigated. The phenylacetylenes with electron-neutral substituents afforded the corresponding annulation products in 73-80% yields (Table 2, 3-4). The phenylacetylenes bearing electron-withdrawing groups like 4-F, 3-F, 4-Br, even 4-CF₃ were also suitable substrates, generating corresponding [4+2] annulation products 5-8 in 73-81% yields. In addition to phenylacetylenes, alkyl alkynes were also tolerated in this transformation, producing the annulation products in moderate to high yields (Table 2, 9-19). It is worth noting that reactive functional groups such as C-C double bond and C-C triple bonds, cyclopropyl units, esters, TMS, and even hydroxyl groups, were all tolerated in the reaction (Table 2, 10, 14-19). Moreover, when an internal alkyne was employed as the reaction partner, corresponding [4+2] annulation product could still be obtained (Table 2, 19). Next, we explored different sulfonamides. Unfortunately, it seems that only electron-neutral substrates delivered the annulation products in high yields (Table 2, 20), most electron-rich and electrondeficient substrates gave the annulation products in low yields. Given that different substrates exhibited different of all the potential and one of the most important advantages of organic electrosynthesis is that the oxidation capacity of the electrochemical system can be optionally altered by varying the current or voltage, we tried to change the operating current to enhance the reaction yield. To our delight, by decreasing the operating current to 3 mA or increasing the operating current to 5 mA, both electron-rich and electrondeficient substrates could be converted to the annulation products in moderate to high yields (Table 2, **22-31**).

 Table 2: Substrate scope for the synthesis of sultams via cobalt catalyzed electrochemical [4+2] annulation.^a



This journal is © The Royal Society of Chemistry 20xx

Journal Name

COMMUNICATION

^{*a*} Reaction conditions: carbon cloth (15 mm*20 mm*0.33 mm) anode, stainless steel plate (15 mm*20 mm*1.0 mm) cathode, constant current = 4 mA, sulfonamides (0.25 mmol), alkynes (2.0 equiv.), NaOAc (2.0 equiv.), Co(OAc)₂·4H₂O (20 mol%), EtOH (10.0 mL), HOAc (1.0 mL), Air, 75 °C, 8 h, Q = quinolin-8-yl. ^{*b*} CF₃CH₂OH (10.0 mL), 3 mA, 10 h. ^{*c*} CF₃CH₂OH (10.0 mL), 5 mA, 8 h. ^{*d*} CF₃CH₂OH (10.0 mL).

To examine the practicability and scalability of this cobalt catalytic electrochemistry system, a gram scale reaction of 4-methyl-*N*-(quinolin-8-yl)benzenesulfonamide (1) with phenylacetylene (2) on 5.0 mmol was performed (Scheme 2). Gratefully, under electrochemical conditions the [4+2] annulation reaction occurred smoothly and 1.72 g product (86%) could be finally obtained (For details about gram scale synthesis, see ESI).



Scheme 2. Gram scale synthesis.

Based on literature reports, ^{11,14c,14e} we believe that this cobalt catalyzed electrochemical [4+2] annulation reaction possibly undergoes one of the two following pathways to access the Co(III) complex **B**: 1) Co(II) species is first oxidized to give a Co(III) species (Scheme 3, Path 1), which then coordinates with substrate **1** to afford the Co(III) complex **B**; 2) Co(II) species first coordinates with substrate **1** to generate Co(II) complex **A** (Scheme 3, Path 2), **A** then undergoes single electron oxidation to access the Co(III) complex **B**.



Scheme 3. The two pathways for accessing the Co(III) complex B.

To clarify which is the preferred pathway for generating the Co(III) complex **B**, cyclic voltammetry (CV) experiments were carried out (Figure. S3, for details about CV experiments, see ESI). The oxidation peaks of substrate **1** and Co(OAc)₂·4H₂O were observed at 1.86 V and 1.88 V, respectively; whereas the mixture of substrate **1**, Co(OAc)₂·4H₂O, and NaOAc showed a new oxidation peak at a less positive potential of 1.55 V. These results suggest that the reaction might occur via the pathway 2. That is to say, Co(II) species first coordinates with substrate **1** to produce the Co(II) complex **A**, **A** then undergoes single electron oxidation to generate the Co(III) complex **B**.



Scheme 4. Control experiments.

Nearly no [4+2] annulation product was observed when the electrolysis of 4-methyl-N-(quinolin-8-yl)benzenesulfonamide (1) and phenylacetylene (2) was performed under N_2 atmosphere (Scheme 4A), indicating that O₂ is important for this cobalt catalyzed electrochemical reaction. Increasing the amount of Co(OAc)₂·4H₂O to 1.0 equiv. only 21% yield of annulation product was obtained (Scheme 4B), further suggesting that besides electrochemical anodic oxidation, O2 also plays an important role in the conversion of Co(II) complex A to Co(III) complex B. Next, we tried our best to reveal how O_2 plays important role. Previous reports revealed that O_2 is easily reduced at cathode to generate the superoxide radical anion (O2⁻⁻).¹⁶ We propose that this reduction process might also be involved in our reaction system. Electron paramagnetic resonance (EPR) experiments were then conducted to verify this hypothesis (Figure 1, See ESI for details). Electrolyzing the model reaction under standard conditions for 15 min, desired superoxide radical anion (O2.) signal was not observed whereas an obvious alkoxy radical signal (g = 2.0068, A_N = 13.58 G, A_H = 7.48 G) was observed (Figure 1a). We speculate that this may be because the generated superoxide radical anion (O₂⁻⁻) easily abstracts a hydrogen atom from EtOH. Given that MeCN/HOAc could also furnish the [4+2] annulation product **3** in 33% yield (Table 1, entry 11), electron paramagnetic resonance (EPR) experiments were then conducted in MeCN/HOAc. Gratefully, when the model reaction was electrolyzed for 15 min, the desired superoxide radical anion (O_2^{-}) signal (g = 2.0068, A_N = 12.9 G, A_H = 10.7 G) was indeed observed (Figure 1b). These results indicated that our assumption is correct and the generated superoxide radical anion (O2-) would abstract a hydrogen atom from EtOH to generate the HOO⁻ intermediate. Given that 1.0 ml of HOAc was employed in the reaction, the generated HOO⁻ intermediate should be easily converted into the H₂O₂. That is

COMMUNICATION

een Chemistry Accepted mar

to say, H_2O_2 may be the ultimate active species of O_2 in promoting the conversion of Co(II) complex **A** to Co(III) complex **B**. Electrolyzing the model reaction under N_2 atmosphere in the presence of 2.0 equiv. of H_2O_2 (30 wt% solution in H_2O), 21% yield of annulation product **3** was obtained (Scheme 4C); whereas nearly no product was obtained when this reaction was performed without electric current (Scheme 4D). Adding 20 mol% of MnO₂ (a catalyst for decomposing H_2O_2) to the electrolysis of model reaction, only 13% yield of annulation product was obtained (Scheme 4E). These results indicated that the real active species of O_2 in promoting the conversion of Co(II) complex **A** to Co(III) complex **B** might be the H_2O_2 .



Figure 1. Electron paramagnetic resonance (EPR) spectra. a) Using EtOH/HOAc (10.5mL/0.5mL) as the co-solvent. b) Using MeCN/HOAc (10.5mL/0.5mL) as the co-solvent.

Taken together, a possible reaction mechanism for this cobalt catalyzed electrochemical [4+2] annulation reaction between **1** and **2** is illustrated in Scheme 5. Co(II) species first coordinates with substrate **1** to generate Co(II) complex **A**, which then is oxidized by anode and H_2O_2 to generate the Co(III) complex **B**. With the help of NaOAc, cyclic Co(III) complex **C** could subsequently be formed though the intramolecular C-H activation from Co(III) complex **B**. Next, phenylacetylene **2** insertion and following reductive elimination lead to the formation of annulation product **3** and Co(I) species. The generated Co(I) species is oxidized at anode to regenerate the Co(II) species. At the same time, O_2 is reduced at the cathode to generate the superoxide radical anion (O_2^{-}), which then gets a hydrogen atom from EtOH and a proton from HOAc to finally

access the H_2O_2 . In addition, the cathodic reduction ARE HOAC generates H_2 and AcO- might also be involved in the reaction of the section of the sec



Scheme 5. Proposed mechanism.

In conclusion, we have demonstrated the first example of cobalt catalyzed electrochemical [4+2] annulation of sulfonamides with alkynes. By employing anodic oxidation in an undivided cell to recycle the cobalt catalyst, a series of sultams were prepared with hydrogen evolution under metallic oxidants-free conditions. This electrochemical protocol proved to be practical and scalable. For example, when the model reaction was scaled up to 5.0 mmol, an 86% yield of [4+2] annulation product could still be obtained. Mechanistic insights suggest the cathodic reduction of O_2 might be involved in this annulation reaction.

We thank the Jiangxi Normal University for financial support.

Conflicts of interest

There are no conflicts to declare.

Notes and references

- (a) M. V. Pham and N. Cramer, *Chem. Eur. J.*, 2016, 22, 2270-2273;
 (b) H. Wang, T. Jiang and M.-H. Xu, *J. Am. Chem. Soc.*, 2013, 135, 971-974.
- (a) C. M. G. Azevedo, K. R. Watterson, E. T. Wargent, S. V. F. Hansen, B. D. Hudson, M. A. Kępczyńska, J. Dunlop, B. Shimpukade, E. Christiansen, G. Milligan, C. J. Stocker and T. Ulven, J. Med. Chem., 2016, 59, 8868-8878; (b) G. J. Wells, M. Tao, K. A. Josef and R. Bihovsky, J. Med. Chem., 2001, 44, 3488-3503.
- 3 K. Lei, X.-W. Hua, Y.-Y. Tao, Y. Liu, N. Liu, Y. Ma, Y.-H. Li, X.-H. Xu and C.-H. Kong, *Bioorg. Med. Chem.*, 2016, **24**, 92-103.
- (a) N. Ahmad, M. Zia-ur-Rehman, H. L. Siddiqui, M. F. Ullah and M. Parvez, *Eur. J. Med. Chem.*, 2011, **46**, 2368-2377; (b)
 S. Andrea, O. Takashi, M. Antonio and T. S. Claudiu, *Cur. Med, Chem.*, 2003, **10**, 925-953.
- (a) S. Debnath and S. Mondal, *Eur. J. Org. Chem.*, 2018, 2018, 933-956;
 (b) J. K. Laha, N. Dayal, R. Jain and K. Patel, *J. Org.*

4 | J. Name., 2012, 00, 1-3

Published on 07 February 2020. Downloaded by Universite Paris Descartes on 2/9/2020 8:15:56 AM

COMMUNICATION

Journal Name

Chem., 2014, **79**, 10899-10907; (c) N. Ishida, Y. Shimamoto, T. Yano and M. Murakami, *J. Am. Chem. Soc.*, 2013, **135**, 19103-19106; (d) S. Dadiboyena and A. Nefzi, *Tetrahedron Lett.*, 2012, **53**, 6897-6900.

- 6 (a) J. K. Laha, N. Dayal, K. P. Jethava and D. V. Prajapati, Org. Lett., 2015, 17, 1296-1299; (b) J. K. Laha, K. P. Jethava and N. Dayal, J. Org. Chem., 2014, 79, 8010-8019; (c) K. Geoghegan, S. Smullen and P. Evans, J. Org. Chem., 2013, 78, 10443-10451; (d) M. Yamagishi, K. Nishigai, A. Ishii, T. Hata and H. Urabe, Angew. Chem., Int. Ed., 2012, 51, 6471-6474.
- 7 (a) B. Song, C.-B. Yu, Y. Ji, M.-W. Chen and Y.-G. Zhou, *Chem. Commun.*, 2017, **53**, 1704-1707; (b) S. Mondal, S. Debnath, S. Pal and A. Das, *Synthesis*, 2015, **47**, 3423-3433; (c) T. M. Ha, B. Yao, Q. Wang and J. Zhu, *Org. Lett.*, 2015, **17**, 5256-5259; (d) K. Kaneko, T. Yoshino, S. Matsunaga and M. Kanai, *Org. Lett.*, 2013, **15**, 2502-2505.
- 8 (a) L. Wang, F. Wu, J. Chen, D. A. Nicewicz and Y. Huang, Angew. Chem., Int. Ed., 2017, 56, 6896-6900; (b) X. Hu, G. Zhang, F. Bu and A. Lei, Angew. Chem., Int. Ed., 2018, 57, 1286-1290; (c) J.-R. Chen, X.-Q. Hu, L.-Q. Lu and W.-J. Xiao, Chem. Rev., 2015, 115, 5301-5365; (d) R.-R. Liu, J.-J. Hong, C.-J. Lu, M. Xu, J.-R. Gao and Y.-X. Jia, Org. Lett., 2015, 17, 3050-3053; (e) M. Rueping, D. Leonori and T. Poisson, Chem. Commun., 2011, 47, 9615-9617.
- 9 (a) N. S. Upadhyay, V. H. Thorat, R. Sato, P. Annamalai, S.-C. Chuang and C.-H. Cheng, *Green Chem.*, 2017, **19**, 3219-3224;
 (b) S. Warratz, C. Kornhaaß, A. Cajaraville, B. Niepötter, D. Stalke and L. Ackermann, *Angew. Chem., Int. Ed.*, 2015, **54**, 5513-5517;
 (c) R. He, Z.-T. Huang, Q.-Y. Zheng and C. Wang, *Angew. Chem., Int. Ed.*, 2014, **53**, 4950-4953;
 (d) N. Guimond and K. Fagnou, *J. Am. Chem. Soc.*, 2009, **131**, 12050-12051.
- 10 (a) T. Lan, L. Wang and Y. Rao, Org. Lett., 2017, 19, 972-975;
 (b) N. Thrimurtulu, R. Nallagonda and C. M. R. Volla, Chem. Commun., 2017, 53, 1872-1875; (c) X. Li, Y. Dong, F. Qu and G. Liu, J. Org. Chem., 2015, 80, 790-798; (d) W. Xie, J. Yang, B. Wang and B. Li, J. Org. Chem., 2014, 79, 8278-8287; (e) M. V. Pham, B. Ye and N. Cramer, Angew. Chem., Int. Ed., 2012, 51, 10610-10614.
- 11 (a) Y. Ran, Y. Yang and L. Zhang, *Tetrahedron Lett.*, 2016, 57, 3322-3325; (b) D. Kalsi and B. Sundararaju, *Org. Lett.*, 2015, 17, 6118-6121; (c) O. Planas, C. J. Whiteoak, A. Company and X. Ribas, *Adv. Synth. Catal.*, 2015, 357, 4003-4012.
- (a) Q.-L. Yang, P. Fang and T.-S. Mei, *Chin. J. Chem.*, 2018, 36, 338-352; (b) M. D. Kärkäs, *Chem. Soc. Rev.*, 2018, 47, 5786-5865; (c) M. Yan, Y. Kawamata and P. S. Baran, *Chem. Rev.*, 2017, 117, 13230-13319; (d) J.-i. Yoshida, A. Shimizu and R. Hayashi, *Chem. Rev.*, 2018, 118, 4702-4730; (e) A. Jutand, *Chem. Rev.*, 2008, 108, 2300-2347; (f) Y. Jiang, K. Xu and C. Zeng, *Chem. Rev.*, 2018, 118, 4485-4540; (g) H. Wang, X. Gao, Z. Lv, T. Abdelilah and A. Lei, *Chem. Rev.*, 2019, 119, 6769-6787; (h) N. Fu, Y. Shen, A. R. Allen, L. Song, A. Ozaki and S. Lin, *ACS Catal.*, 2019, 9, 746-754; (i) Y.-Q. Li, Q.-L. Yang, P. Fang, T.-S. Mei and D. Zhang, *Org. Lett.*, 2017, 19, 2905-2908; (j) Y. Yuan, A. Yao, Y. Zheng, M. Gao, Z. Zhou, J. Qiao, J. Hu, B. Ye, J. Zhao, H. Wen and A. Lei, *iScience*, 2019, 12, 293-303.
- (a) S. Herold, D. Bafaluy and K. Muñiz, *Green Chem.*, 2018, 20, 3191-3196; (b) J. Li, W. Huang, J. Chen, L. He, X. Cheng and G. Li, *Angew. Chem., Int. Ed.*, 2018, 57, 5695-5698; (c) Z.-Q. Wang, X.-J. Meng, Q.-Y. Li, H.-T. Tang, H.-S. Wang and Y.-M. Pan, *Adv. Synth. Catal.*, 2018, 360, 4043-4048; (d) P. Qian, Z. Yan, Z. Zhou, K. Hu, J. Wang, Z. Li, Z. Zha and Z. Wang, *Org. Lett.*, 2018, 20, 6359-6363; (e) Y.-Y. Jiang, G.-Y. Dou, K. Xu and C.-C. Zeng, *Org. Chem. Front.*, 2018, 5, 2573-2577; (f) K. Liu, C. Song, J. Wu, Y. Deng, S. Tang and A. Lei, *Green Chem.*, 2019, 21, 765-769; (g) F. Xu, H. Long, J. Song and H.-C. Xu, *Angew. Chem., Int. Ed.*, 2019, 58, 9017-9021; (h) K.-Y. Ye, Z. Song, G. S. Sauer, J. H. Harenberg, N. Fu and S. Lin, *Chem.*

Eur. J., 2018, **24**, 12274-12279; (i) C.-Y. Cai and H.-C. Xu, *Nat. Commun.*, 2018, **9**, 3551. DOI: 10.1039/D0GC00289E

- (a) T. H. Meyer, J. C. A. Oliveira, S. C. Sau, N. W. J. Ang and L. Ackermann, ACS Catal., 2018, 8, 9140-9147; (b) M.-J. Luo, M. Hu, R.-J. Song, D.-L. He and J.-H. Li, Chem. Commun., 2019, 55, 1124-1127; (c) S. Tang, D. Wang, Y. Liu, L. Zeng and A. Lei, Nat. Commun., 2018, 9, 798; (d) R. Mei, N. Sauermann, J. C. A. Oliveira and L. Ackermann, J. Am. Chem. Soc., 2018, 140, 7913-7921; (e) L. Zeng, H. Li, S. Tang, X. Gao, Y. Deng, G. Zhang, C.-W. Pao, J.-L. Chen, J.-F. Lee and A. Lei, ACS Catal., 2018, 8, 5448-5453; (f) Y. Qiu, C. Tian, L. Massignan, T. Rogge and L. Ackermann, Angew. Chem., Int. Ed., 2018, 57, 5818-5822; (g) F. Xu, Y.-J. Li, C. Huang and H.-C. Xu, ACS Catal., 2018, 8, 3820-3824. (h) C. Tian, U. Dhawa, A. Scheremetjew and L. Ackermann, ACS Catal., 2019, 9, 7690-7696.
- (a) S. Tang, Y. Liu and A. Lei, *Chem*, 2018, **4**, 27-45; (b) Y. Yuan, Y. Yu, J. Qiao, P. Liu, B. Yu, W. Zhang, H. Liu, M. He, Z. Huang and A. Lei, *Chem. Commun.*, 2018, **54**, 11471-11474; (c) P. Huang, P. Wang, S. Wang, S. Tang and A. Lei, *Green Chem.*, 2018, **20**, 4870-4874; (d) Y. Yuan, Y. Chen, S. Tang, Z. Huang and A. Lei, *Sci. Adv.*, 2018, **4**, eaat5312; (e) Y. Yuan, Y. Cao, Y. Lin, Y. Li, Z. Huang and A. Lei, *ACS Catal.*, 2018, **8**, 10871-10875; (f) Y. Yuan and A. Lei, *Acc. Chem. Res.*, 2019, **52**, 3309-3324.
- 16 X. Han, K. Wang, G. Zhang, W. Gao and J. Chen, *Adv. Synth. Catal.*, 2019, **361**, 2804-2824.

Green Chemistry Accepted Manuscript

View Article Online DOI: 10.1039/D0GC00289E

