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Electrooxidative palladium- and enantioselective rhodium-catalyzed [3 + 2] spiroannulations†

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Despite indisputable progress in the development of electrochemical transformations, electrocatalytic annulations for the synthesis of biologically relevant three-dimensional spirocyclic compounds has as of yet not been accomplished. In sharp contrast, herein, we describe the palladaelectro-catalyzed C–H activation/[3 + 2] spiroannulation of alkynes by 1-aryl-2-naphthols. Likewise, a cationic rhodium(III) catalyst was shown to enable electrooxidative [3 + 2] spiroannulations *via* formal C(sp³)–H activations. The versatile spiroannulations featured a broad substrate scope, employing electricity as a green oxidant *in lieu* of stoichiometric chemical oxidants under mild conditions. An array of spirocyclic enones and diverse spiropyrazolones, bearing all-carbon quaternary stereogenic centers were thereby accessed in a user-friendly undivided cell setup, with molecular hydrogen as the sole byproduct.

Introduction

Spirocycles feature inherent three-dimensionality and represent a distinct structural scaffold. This privileged motif has been increasingly utilized in drug discovery, among others.¹ Thus, spirocyclic building blocks with an all-carbon quaternary center feature a higher fraction of sp³ hybridization (Fsp³), which was recently regarded as a new parameter for drug-likeness.² In addition, spirocycles with spirofluorenyl naphthalenone (SFNP) structures exhibit broad applications in organic optoelectronic materials (Fig. 1a).³ However, the synthesis of all-carbon spiro skeletons is not only associated with increased synthetic efforts, but has also been limited by broadly applicable and robust methods.⁴ Transition metal-catalyzed C–H functionalization⁵ has emerged as an increasingly efficient tool to construct spirocyclic compounds.⁶ Enol/enolate-directed ruthenium,⁷ rhodium,⁸ or palladium-catalyzed⁹ oxidative [3 + 2]/[3 + 3]/[4 + 1] annulations *via* C–H functionalization¹⁰ were thus reported. Similarly, transition metal-catalyzed C–H activation/dearomatization tandem processes of naphthols¹¹ and phenols¹² also proved to be viable (Fig. 1b). Despite the indisputable advances, the use of stoichiometric amounts of chemical oxidants has been necessary for the regeneration of the active catalyst. In the past few years, electricity has been recognized as an efficient tool for the assembly of two-dimensional ring scaffolds.¹³ In sharp contrast,

electrocatalytic methods are, thus far, unfortunately not available for the synthesis of 3D spirocyclic rings.¹⁴ Within our program on sustainable electrocatalytic C–H functionalizations,¹⁵ we have now developed the first electrocatalytically-enabled spiroannulation (Fig. 1c). Notable features of our strategy include (a) unprecedented electrooxidative C(sp²)–H

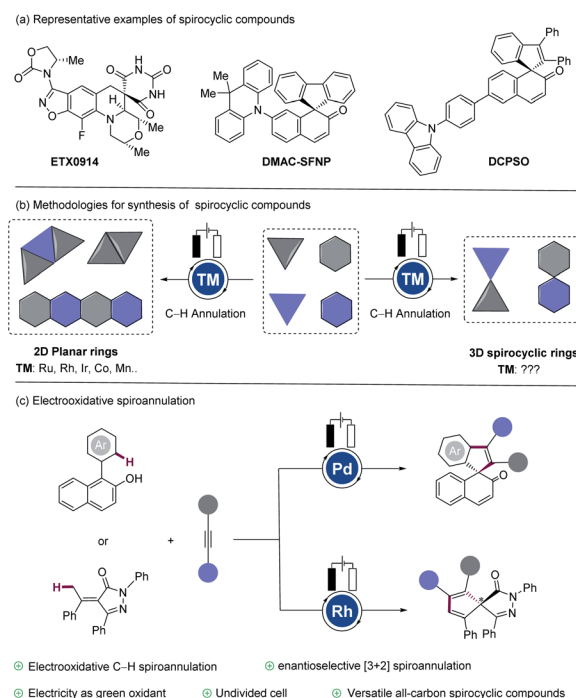


Fig. 1 (a) Representative examples of spirocyclic compounds. (b) Methodologies for synthesis of spirocyclic compounds. (c) Electrooxidative spiroannulations.

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activation/dearomatization by versatile palladium catalysis, (b) enantioselective [3 + 2] spiroannulation with a chiral rhodium catalyst, (c) electricity as a benign oxidant *in lieu* of stoichiometric chemical oxidants, (d) mild reaction conditions for high chemo- and enantio-selectivity, (e) and an operationally-convenient undivided cell setup.

Results and discussion

Optimization of the reaction conditions

We initiated our studies by probing different catalysts, among which only $\text{Pd}(\text{OAc})_2$ performed with encouraging catalytic efficacy. The desired dearomatization product **3aa** was thereby obtained in 50% yield. After considerable optimization of the supporting electrolyte (entries 6–13, for details see ESI†), we were pleased to find that the desired transformation was efficiently realized with NMe_4Cl and 2.0 equivalents of substrate **1a** in an undivided cell setup (entry 13). Replacing the electrolyte NMe_4Cl by $n\text{-Bu}_4\text{NOAc}$ led to a slight increase of the yield (entry 14). The conversion decreased significantly, when the catalyst loading was reduced (entry 16). Remarkably, the optimal result was obtained without K_2CO_3 , affording the product **3aa** in 87% yield (entry 17). Furthermore, control experiments showed the indispensability of the electricity (entries 18) (Table 1).

Table 1 Optimization of reaction conditions^a

Entry	Catalyst	Supporting electrolyte	Yield ^b /%
1	$[\text{RuCl}_2(p\text{-cymene})]_2$	$n\text{-Bu}_4\text{NOAc}$	Trace
2	$[\text{RhCp}^*\text{Cl}_2]_2$	$n\text{-Bu}_4\text{NOAc}$	Trace
3	$[\text{Cp}^*\text{Co}(\text{CO})\text{I}_2]$	$n\text{-Bu}_4\text{NOAc}$	Trace
4	$[\text{Cp}^*\text{Co}(\text{MeCN})_3](\text{SbF}_6)_2$	$n\text{-Bu}_4\text{NOAc}$	Trace
5	$\text{Pd}(\text{OAc})_2$	$n\text{-Bu}_4\text{NOAc}$	50%
6	$\text{Pd}(\text{OAc})_2$	$n\text{-Bu}_4\text{NPF}_6$	37%
7	$\text{Pd}(\text{OAc})_2$	$n\text{-Bu}_4\text{NBF}_4$	45%
8	$\text{Pd}(\text{OAc})_2$	NMe_4Cl	46%
9	$\text{Pd}(\text{OAc})_2$	KCl	25%
10	$\text{Pd}(\text{OAc})_2$	$n\text{-Bu}_4\text{NI}$	33%
11	$\text{Pd}(\text{OAc})_2$	Et_4NClO_4	44%
12	$\text{Pd}(\text{OAc})_2$	$n\text{-Bu}_4\text{NClO}_4$	39%
13 ^c	$\text{Pd}(\text{OAc})_2$	NMe_4Cl	71%
14 ^c	$\text{Pd}(\text{OAc})_2$	$n\text{-Bu}_4\text{NOAc}$	79%
15 ^{c,d}	$\text{Pd}(\text{OAc})_2$	$n\text{-Bu}_4\text{NOAc}$	64%
16 ^{c,e}	$\text{Pd}(\text{OAc})_2$	$n\text{-Bu}_4\text{NOAc}$	25%
17 ^{c,f}	$\text{Pd}(\text{OAc})_2$	$n\text{-Bu}_4\text{NOAc}$	87%
18 ^{c,f,g}	$\text{Pd}(\text{OAc})_2$	$n\text{-Bu}_4\text{NOAc}$	15%

^a Reaction conditions: **1a** (176 mg, 0.4 mmol), **2a** (70 mg, 0.4 mmol), catalyst (10 mol%), supporting electrolyte (1.0 equiv.), base (2.0 equiv.), DMF (4.0 mL) at 100 °C, 16 h, under air. ^b Yield of isolated product. ^c Using **1a** (0.8 mmol), **2a** (0.4 mmol). ^d 8 h. ^e Using $\text{Pd}(\text{OAc})_2$ (5 mol%). ^f Without K_2CO_3 . ^g Without current.

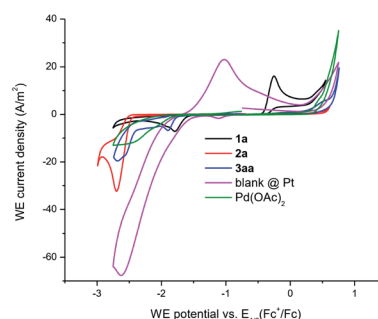
Mechanistic studies and gram-scale reaction

Then, we set out to study the working mode of the electro-oxidative palladium-catalyzed spiroannulation. First, cyclic-voltammetric analysis (Scheme 1a) of the substrates revealed an irreversible oxidation event of the 1-aryl-naphthalenol **1a** at $E_p = -0.3$ V. Compounds **2a** and **3aa** were found to be stable within the examined potential window. When employing Pt instead of glassy carbon as the working electrode (WE) material, a strong reduction current was observed at -1.5 V, being indicative of an efficient proton reduction as the cathodic event to form molecular hydrogen as the only stoichiometric byproduct (see ESI† for more details). Next, an intermolecular competition reaction was performed to determine the kinetic isotope effect (Scheme 1b). Thus, a KIE k_H/k_D of 3.0 was observed, suggesting that the C–H scission was involved in the rate-determining step. Finally, the robustness of the electrocatalysis was demonstrated by a gram-scale synthesis (Scheme 1c).

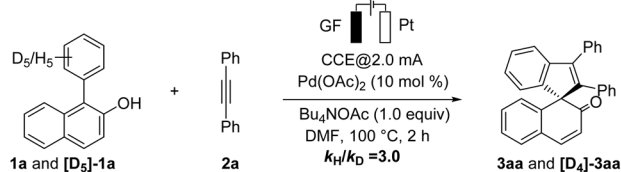
Substrate scope

With the optimal reaction conditions in hand, we explored the generality of the approach by testing different alkynes **2** (Scheme 2). Substrates with electron-donating groups, such as methyl and methoxy substituents, afforded products **3ab** and **3ac** in high yields. Alkynes with the electron-deficient trifluoromethyl and alkoxy carbonyl groups on the tolane could also be converted into the desired spirocycles **3ad** and **3ae**,

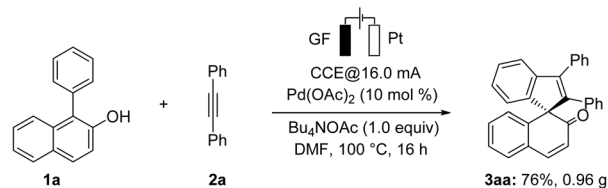
a) Cyclic voltammetry study



b) KIE study

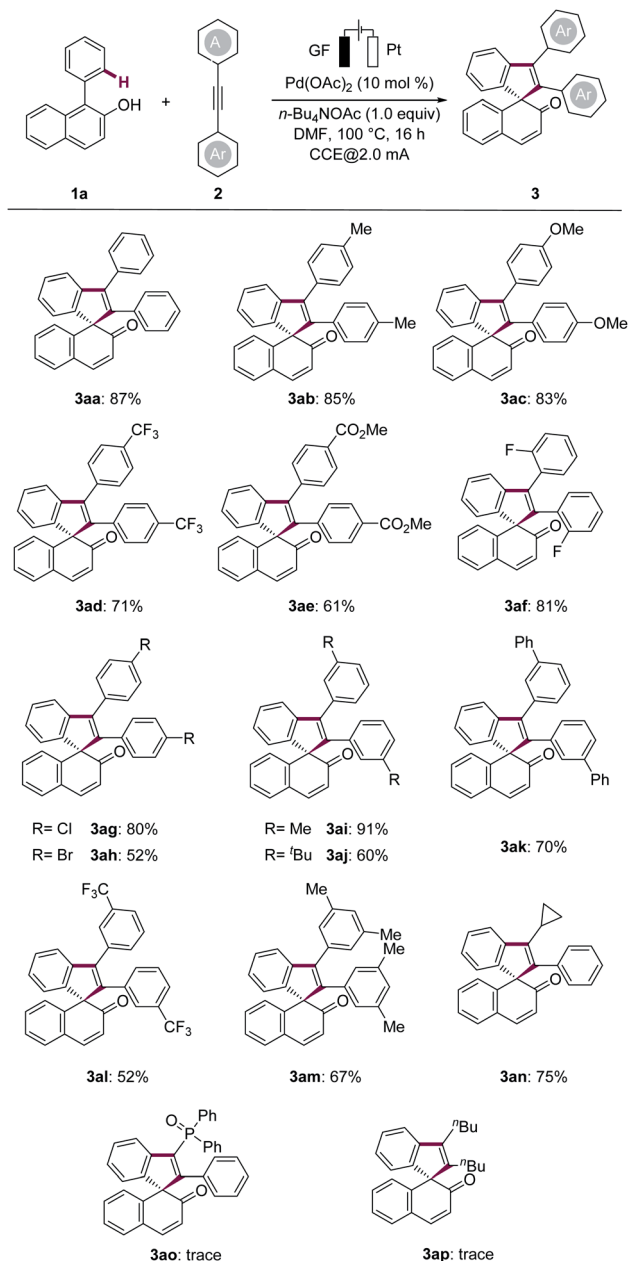


c) Gram scale reaction



Scheme 1 (a) Cyclic voltammetry, (b) KIE study, (c) gram-scale reaction.

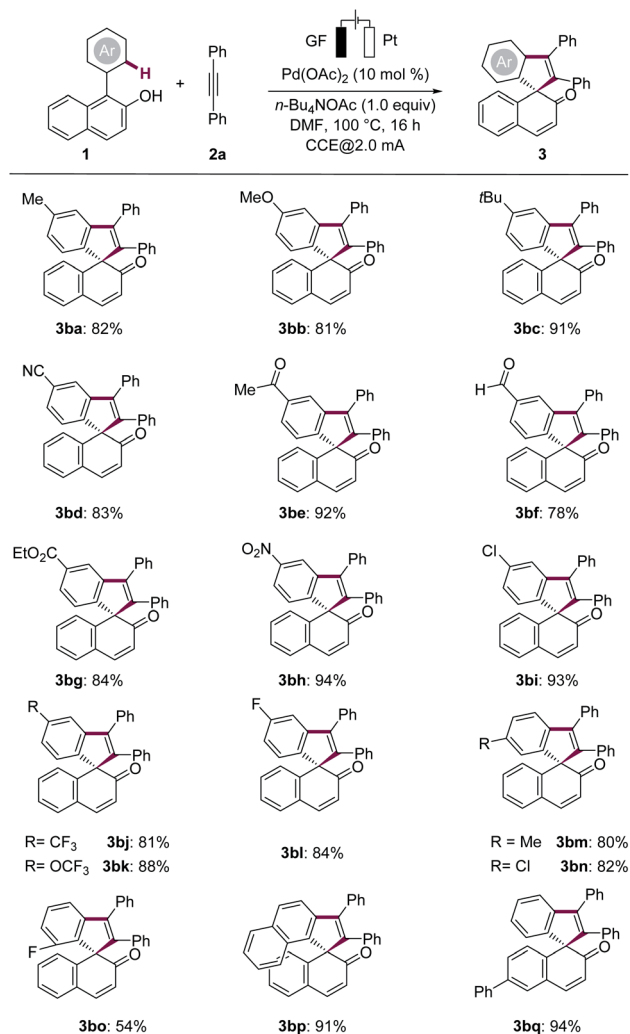




Scheme 2 Palladaelectro-catalyzed spiroannulation with alkynes 2.

albeit with slightly diminished yields due to the relatively low conversion of the alkynes. However, when the halogen substituents (3af–3ah) were examined, the bromoaryl-alkyne showed an apparent drop in the yield as compared with the fluoro or chloro analogs. Next, a series of alkynes bearing substituents at the *meta*- or *ortho*-position of the arene were found to be suitable to give products 3ai–3am. In addition, the unsymmetrical alkyne 2n was utilized for the dearomative spiroannulation, and the corresponding product 3an was selectively obtained, while products 3o and 3p were not observed under otherwise identical reaction conditions.

Subsequently, the reaction scope was further examined by varying the substitution pattern on the naphthols 1 (Scheme 3). An array of electron-donating groups on the arene motif was



Scheme 3 Palladaelectro-catalyzed spiroannulation with 1-aryl-naphthalenol 1.

found to be compatible with the electrocatalytic process (3ba–3bc). It is noteworthy that synthetically-useful electron-withdrawing groups, such as cyano (3bd), acetyl (3be), formyl (3bf), ester (3bg), nitro (3bh), chloro (3bi), and different fluoro-containing groups were tolerated well. The reaction of substrates with *meta*-substituents occurred regioselectively at the less sterically hindered position, delivering products 3bm and 3bn in 80% and 82% yield, respectively. The chloro group remained intact in products 3bi and 3bn, thus offering handles for further late-stage manipulations. The electrocatalysis enabled the transformation of *ortho*-fluoro-substituted substrate, affording the product 3bo in 54% yield. When binaphthalen-2-ol was subjected to the pallada-electrocatalysis, the spirocycle 3bp was furnished in excellent yield. An aryl-substituent on the naphthyl ring was tolerated likewise (3bq).

Given the topical interest in enantio-selective electrocatalyzed C–H activation,¹⁶ we explored an asymmetric electrocatalyzed oxidative palladium-catalyzed spiroannulation (Table 2). Thus, amino acid ligand 1 and chiral phosphoric acid diester ligand 2 were *inter alia* initially probed (entries 1 and 2). Unfortunately,

Table 2 Optimization of enantioselective electrocatalysis

a)

b)

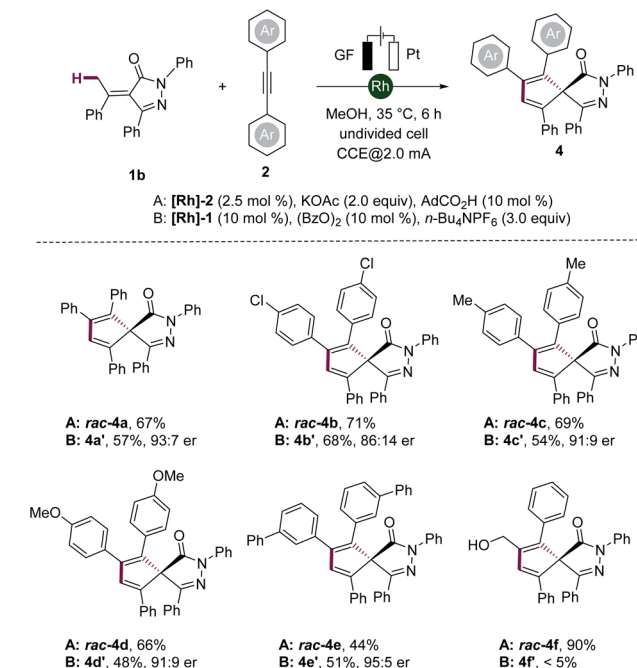
Ligand 1: L-Pyrroglutamic acid
Ligand 2: Chiral phosphoric acid
[Rh]-1: Chiral Rh(I) catalyst
[Rh]-2: Chiral Rh(I) catalyst

Entry	1a/1b	Catalyst	Additive	Yield/%
1 ^a	1a	PdCl ₂	Ligand 1	Trace
2 ^b	1a	PdCl ₂	Ligand 2	Trace
3 ^c	1a	[Rh]-1	(BzO) ₂	Trace
4 ^d	1b	[Rh]-2	AdCO ₂ H	67%
5 ^e	1b	[Rh]-1	(BzO) ₂	57%/93:7 er

^a Reaction conditions: **1a** (0.8 mmol, 2.0 equiv.), **2a** (0.4 mmol), PdCl₂ (10 mol%), **ligand 1** (20 mol%), NMe₄Cl (1.0 equiv.), DMF (4.0 mL) at 100 °C, 16 h, under air. ^b Reaction conditions: **1a** (0.8 mmol, 2.0 equiv.), **2a** (0.4 mmol), PdCl₂ (10 mol%), **ligand 2** (20 mol%), NMe₄Cl (1.0 equiv.), DMF (4.0 mL) at 100 °C, 16 h, under air. ^c Reaction conditions: **1a** (0.8 mmol, 2.0 equiv.), **2a** (0.4 mmol), [Rh]-1 (5.0 mol%), (BzO)₂ (5.0 mol%), *n*-Bu₄NOAc (1.0 equiv.), 1,4-dioxane/H₂O (3 : 1) (4.0 mL) at 100 °C, 16 h, under air. ^d Reaction conditions: **1b** (1.5 equiv., 0.3 mmol), **2a** (0.2 mmol), [Rh]-2 (2.5 mol%), KOAc (2.0 equiv.), AdCO₂H (10 mol%), MeOH (4.0 mL), at 35 °C, 6 h, under air. ^e Reaction conditions: **1b** (1.5 equiv., 0.15 mmol), **2a** (0.1 mmol), [Rh]-1 (10 mol%), (BzO)₂ (10 mol%), *n*-Bu₄NPF₆ (3.0 equiv.), MeOH (4.0 mL), at 35 °C, 6 h, under air.

no desired product was formed. As an alternative, chiral rhodium catalyst [Rh]-1 was examined, but exhibited no catalytic efficiency. Meanwhile, and inspired by a rhodium(III)-catalyzed enantioselective spiroannulation,^{8c} the substrate α -arylidene pyrazolone **1b** was, among others, considered for the envisioned rhodaelectro-catalyzed oxidative formal [3 + 2] annulation. It is noteworthy that the cationic rhodium(III) catalyst proved effective for this electrocatalytic transformation. Thereby, the desired biorelevant spiropyrazolone **4a** could be obtained in 67% yield (entry 4).¹⁷ Importantly, a minor adjustment of the catalytic system, set the stage for an enantioselective transformation. An excellent enantio-selectivity and a high conversion were hence observed under mild reaction conditions with the catalyst [Rh]-1 (entry 5).

Next, we investigated the functional group tolerance of the enantioselective rhodaelectrocatalysis (Scheme 4). Halogen groups, such as fluoro and chloro substituents, proved compatible with the rhoda-electrocatalysis (**4b** and **4b'**). Likewise, different substituents at the *para*- or *meta*-position were

Scheme 4 Enantio-selective rhoda-electrocatalyzed spiroannulation of pyrazolone **1b**.

examined, featuring high catalytic performance and selectivities (**4c–4e**, **4c'–4e'**). In addition, an unsymmetrically-substituted alkyne was tested to afford the product **4f** with excellent yield, while no conversion was found for the enantioselective electrocatalysis.

Conclusions

We have developed the first pallada-electrocatalyzed C–H activation/dearomative spiroannulation of 1-aryl-2-naphthols, as well as rhoda-electrocatalyzed enantioselective [3 + 2] spiroannulation. The electrocatalysis provided a facile route towards the assembly of a structurally distinct three-dimensional spirocyclic compounds. The unprecedented electrocatalysis was characterized by high chemo-selectivity as well as ample substrate scope, forming molecular hydrogen as the sole byproduct.

Data availability

All experimental data, procedures for data analysis and pertinent data sets are provided in the ESI.†

Author contributions

W. W. and L. A. conceived the project. W. W. conducted the experiments. A. S. performed the CV studies. W. W. and L. A. wrote the manuscript. All authors discussed the results.

Conflicts of interest

There are no conflicts to declare.



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Notes and references

- (a) K. Hiesinger, D. Dar'in, E. Proschak and M. Krasavin, *J. Med. Chem.*, 2021, **64**, 150–183; (b) T. T. Talele, *J. Med. Chem.*, 2020, **63**, 13291–13315; (c) Y.-J. Zheng and C. M. Tice, *Expert Opin. Drug Discovery*, 2016, **11**, 831–834; (d) Y. Zheng, C. M. Tice and S. B. Singh, *Bioorg. Med. Chem. Lett.*, 2014, **24**, 3673–3682.
- W. Wei, S. Cherukupalli, L. Jing, X. Liu and P. Zhan, *Drug Discovery Today*, 2020, **25**, 1839–1845.
- (a) T. P. I. Saragi, T. Spehr, A. Siebert, T. Fuhrmann-Lieker and J. Salbeck, *Chem. Rev.*, 2007, **107**, 1011–1065; (b) C. Poriel and J. Rault-Berthelot, *J. Mater. Chem. C*, 2017, **5**, 3869–3897.
- (a) A. J. Boddy and J. A. Bull, *Org. Chem. Front.*, 2021, **8**, 1026–1084; (b) L. Zheng and R. Hua, *Front. Chem.*, 2020, **8**, 580355.
- (a) T. Rogge, N. Kaplaneris, N. Chatani, J. Kim, S. Chang, B. Punji, L. L. Schafer, D. G. Musaev, J. Wencel-Delord, C. A. Roberts, R. Sarpong, Z. E. Wilson, M. A. Brimble, M. J. Johansson and L. Ackermann, *Nat. Rev. Methods Primers*, 2021, **1**, 43; (b) B. Liu, A. M. Romine, C. Z. Rubel, K. M. Engle and B.-F. Shi, *Chem. Rev.*, 2021, **121**, 14957–15074; (c) L. Guillemard, N. Kaplaneris, L. Ackermann and M. J. Johansson, *Nat. Rev. Chem.*, 2021, **5**, 522–545; (d) S. Rej, Y. Ano and N. Chatani, *Chem. Rev.*, 2020, **120**, 1788–1887; (e) P. Gandeepan, L. H. Finger, T. H. Meyer and L. Ackermann, *Chem. Soc. Rev.*, 2020, **49**, 4254–4272; (f) C. Sambiagio, D. Schönbauer, R. Blicke, T. Dao-Huy, G. Pototschnig, P. Schaaf, T. Wiesinger, M. F. Zia, J. Wencel-Delord, T. Besset, B. U. W. Maes and M. Schnürch, *Chem. Soc. Rev.*, 2018, **47**, 6603–6743; (g) Y. Park, Y. Kim and S. Chang, *Chem. Rev.*, 2017, **117**, 9247–9301; (h) Z. Dong, Z. Ren, S. J. Thompson, Y. Xu and G. Dong, *Chem. Rev.*, 2017, **117**, 9333–9403; (i) B. Ye and N. Cramer, *Acc. Chem. Res.*, 2015, **48**, 1308–1318; (j) T. Satoh and M. Miura, *Chem.-Eur. J.*, 2010, **16**, 11212–11222; (k) D. A. Colby, R. G. Bergman and J. A. Ellman, *Chem. Rev.*, 2010, **110**, 624–655; Y. Li and S. Xu, *Chem.-Eur. J.*, 2018, **24**, 16218–16245.
- Y. Li and S. Xu, *Chem.-Eur. J.*, 2018, **24**, 16218–16245.
- S. Reddy Chidipudi, I. Khan and H. W. Lam, *Angew. Chem., Int. Ed.*, 2012, **51**, 12115–12119.
- (a) Y. Wang, X. Huang, Q. Wang, Y. Tang, S. Xu and Y. Li, *Org. Lett.*, 2021, **23**, 757–761; (b) L. Kong, X. Han, S. Liu, Y. Zou, Y. Lan and X. Li, *Angew. Chem., Int. Ed.*, 2020, **59**, 7188–7192; (c) H. Li, R. Gontla, J. Flegel, C. Merten, S. Ziegler, A. P. Antonchick and H. Waldmann, *Angew. Chem., Int. Ed.*, 2019, **58**, 307–311; (d) J. Zheng, S.-B. Wang, C. Zheng and S.-L. You, *Angew. Chem., Int. Ed.*, 2017, **56**, 4540–4544; (e) J. Zheng, P. Li, M. Gu, A. Lin and H. Yao, *Org. Lett.*, 2017, **19**, 2829–2832; (f) S. Reddy Chidipudi, D. J. Burns, I. Khan and H. W. Lam, *Angew. Chem., Int. Ed.*, 2015, **54**, 13975–13979; (g) D. J. Burns, D. Best, M. D. Wiczysty and H. W. Lam, *Angew. Chem., Int. Ed.*, 2015, **54**, 9958–9962; (h) A. Seoane, N. Casanova, N. Quiñones, J. L. Mascareñas and M. Gulías, *J. Am. Chem. Soc.*, 2014, **136**, 7607–7610.
- (a) I. Khan, S. R. Chidipudi and H. W. Lam, *Chem. Commun.*, 2015, **51**, 2613–2616; (b) J. D. Dooley, S. Reddy Chidipudi and H. W. Lam, *J. Am. Chem. Soc.*, 2013, **135**, 10829–10836.
- W. K. Yuan and B. F. Shi, *Angew. Chem., Int. Ed.*, 2021, **60**, 23187–23192.
- (a) J. Wu, L. Bai, L. Han, J. Liu and X. Luan, *Chem. Commun.*, 2021, **57**, 1117–1120; (b) W. Liang, Y. Yang, M. Yang, M. Zhang, C. Li, Y. Ran, J. Lan, Z. Bin and J. You, *Angew. Chem., Int. Ed.*, 2021, **60**, 3493–3497; (c) J. Hao, Y. Ge, L. Yang, J. Wang and X. Luan, *Tetrahedron Lett.*, 2021, **71**, 153050; (d) B. Tan, L. Liu, H. Zheng, T. Cheng, D. Zhu, X. Yang and X. Luan, *Chem. Sci.*, 2020, **11**, 10198–10203; (e) L. Ding, W.-T. Wu, L. Zhang and S.-L. You, *Org. Lett.*, 2020, **22**, 5861–5865; (f) B. Tan, L. Bai, P. Ding, J. Liu, Y. Wang and X. Luan, *Angew. Chem., Int. Ed.*, 2019, **58**, 1474–1478; (g) L. Han, H. Wang and X. Luan, *Org. Chem. Front.*, 2018, **5**, 2453–2457; (h) G. Duarah, P. P. Kaishap, B. Sarma and S. Gogoi, *Chem.-Eur. J.*, 2018, **24**, 10196–10200; (i) L. Ding and S.-L. You, *Org. Lett.*, 2018, **20**, 6206–6210; (j) J. Zheng, S.-B. Wang, C. Zheng and S.-L. You, *J. Am. Chem. Soc.*, 2015, **137**, 4880–4883; (k) H. Zheng, L. Bai, J. Liu, J. Nan, Z. Zuo, L. Yang, Y. Wang and X. Luan, *Chem. Commun.*, 2015, **51**, 3061–3064; (l) S. Gu, L. Luo, J. Liu, L. Bai, H. Zheng, Y. Wang and X. Luan, *Org. Lett.*, 2014, **16**, 6132–6135; (m) J. Nan, Z. Zuo, L. Luo, L. Bai, H. Zheng, Y. Yuan, J. Liu, X. Luan and Y. Wang, *J. Am. Chem. Soc.*, 2013, **135**, 17306–17309.
- (a) Z. Zuo, J. Wang, J. Liu, Y. Wang and X. Luan, *Angew. Chem., Int. Ed.*, 2020, **59**, 653–657; (b) Y. Li, Z. Tang, J. Zhang and L. Liu, *Chem. Commun.*, 2020, **56**, 8202–8205; (c) Y. Ge, C. Qin, L. Bai, J. Hao, J. Liu and X. Luan, *Angew. Chem., Int. Ed.*, 2020, **59**, 18985–18989; (d) P.-P. Lin, X.-L. Han, G.-H. Ye, J.-L. Li, Q. Li and H. Wang, *J. Org. Chem.*, 2019, **84**, 12966–12974; (e) J. Nan, Y. Yuan, L. Bai, J. Liu and X. Luan, *Org. Lett.*, 2018, **20**, 7731–7734; (f) W. Hu, H. Wang, L. Bai, J. Liu and X. Luan, *Org. Lett.*, 2018, **20**, 880–883; (g) L. Luo, H. Zheng, J. Liu, H. Wang, Y. Wang and X. Luan, *Org. Lett.*, 2016, **18**, 2082–2085; (h) Z. Zuo, X. Yang, J. Liu, J. Nan, L. Bai, Y. Wang and X. Luan, *J. Org. Chem.*, 2015, **80**, 3349–3356; (i) L. Yang, H. Zheng, L. Luo, J. Nan, J. Liu, Y. Wang and X. Luan, *J. Am. Chem. Soc.*, 2015, **137**, 4876–4879; (j) S. Kujawa, D. Best, D. J. Burns and H. W. Lam, *Chem.-Eur. J.*, 2014, **20**, 8599–8602.
- (a) K. Yamamoto, M. Kuriyama and O. Onomura, *Acc. Chem. Res.*, 2020, **53**, 105–120; (b) F. Wang and S. S. Stahl, *Acc. Chem. Res.*, 2020, **53**, 561–574; (c) J. C. Siu, N. Fu and S. Lin, *Acc. Chem. Res.*, 2020, **53**, 547–560; (d) J. L. Röckl, D. Pollok, R. Franke and S. R. Waldvogel, *Acc. Chem. Res.*, 2020, **53**, 45–61; (e) Q. Jing and K. D. Moeller, *Acc. Chem. Res.*, 2020, **53**, 135–143; (f) K.-J. Jiao, Y.-K. Xing, Q.-L. Yang, H. Qiu and T.-S. Mei, *Acc. Chem. Res.*, 2020, **53**, 300–310;



- (g) T. Fuchigami and S. Inagi, *Acc. Chem. Res.*, 2020, **53**, 322–334; (h) P. Xiong and H.-C. Xu, *Acc. Chem. Res.*, 2019, **52**, 3339–3350; (i) H. Wang, X. Gao, Z. Lv, T. Abdelilah and A. Lei, *Chem. Rev.*, 2019, **119**, 6769–6787; (j) M. Elsherbini and T. Wirth, *Acc. Chem. Res.*, 2019, **52**, 3287–3296; (k) S. Tang, Y. Liu and A. Lei, *Chem.*, 2018, **4**, 27–45; (l) G. S. Sauer and S. Lin, *ACS Catal.*, 2018, **8**, 5175–5187; (m) J. E. Nutting, M. Rafiee and S. S. Stahl, *Chem. Rev.*, 2018, **118**, 4834–4885; (n) C. Ma, P. Fang and T.-S. Mei, *ACS Catal.*, 2018, **8**, 7179–7189; (o) M. Yan, Y. Kawamata and P. S. Baran, *Chem. Rev.*, 2017, **117**, 13230–13319; (p) R. Francke and R. D. Little, *Chem. Soc. Rev.*, 2014, **43**, 2492–2521; (q) A. Jutand, *Chem. Rev.*, 2008, **108**, 2300–2347.
- 14 (a) Y. Zhang, C. Ma, J. Struwe, J. Feng, G. Zhu and L. Ackermann, *Chem. Sci.*, 2021, **12**, 10092–10096; (b) W. C. Yang, M. M. Zhang, Y. Sun, C. Y. Chen and L. Wang, *Org. Lett.*, 2021, **23**, 6691–6696; (c) D. F. Chen, T. Y. He, Y. C. Jin and S. L. Huang, *Adv. Synth. Catal.*, 2022, **364**, 286–290.
- 15 (a) R. C. Samanta, T. H. Meyer, I. Siewert and L. Ackermann, *Chem. Sci.*, 2020, **11**, 8657–8670; (b) T. H. Meyer, I. Choi, C. Tian and L. Ackermann, *Chem.*, 2020, **6**, 2484–2496; (c) N. Sauermann, T. H. Meyer, Y. Qiu and L. Ackermann, *ACS Catal.*, 2018, **8**, 7086–7103.
- 16 (a) U. Dhawa, T. Wdowik, X. Hou, B. Yuan, J. C. A. Oliveira and L. Ackermann, *Chem. Sci.*, 2021, **12**, 14182–14188; (b) U. Dhawa, C. Tian, T. Wdowik, J. C. A. Oliveira, J. Hao and L. Ackermann, *Angew. Chem., Int. Ed.*, 2020, **59**, 13451–13457.
- 17 During the preparation of our manuscript, Mei and coworkers reported on an elegant electrochemical rhodium(III)-catalyzed enantioselective C–H activation through alkyne annulation, Y.-Q. Huang, Z.-J. Wu, L. Zhu, Q. Gu, X. Lu, S.-L. You and T.-S. Mei, *CCS Chem.*, 2021, **3**, 3501–3509.

