C–S Bond Formation

International Edition: DOI: 10.1002/anie.201700012
German Edition: DOI: 10.1002/ange.201700012

Electrocatalytic Oxidant-Free Dehydrogenative C–H/S–H Cross-Coupling

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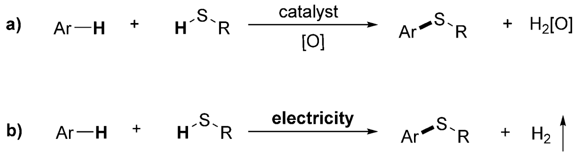
Abstract: *An environmentally friendly electrocatalytic protocol has been developed for dehydrogenative C–H/S–H cross-coupling. This method enabled C–S bond formation under catalyst- and oxidant-free conditions. Under undivided electrolysis conditions, various aryl/heteroaryl thiols and electron-rich arenes afforded the C–S bond-formation products in 24–99 % yield. A preliminary mechanistic study indicated that the generation of aryl radical cation intermediates is key to the success of this transformation.*

C–S bonds are important structural motifs in various biologically active molecules and functional materials.[1] Over the past decades, much attention has been paid to the development of efficient methods for their formation. The transition-metal-catalyzed cross-coupling of organic halides/triflates with thiols/thiophenols is one of the most widely applied methods for constructing C–S bonds.[2] Various transition metals, including palladium,[3] copper,[4] nickel,[5] cobalt,[6] and iron,[7] have been identified as catalysts to promote these transformations. Direct dehydrogenative C–H/S–H cross-coupling is a more attractive approach to C–S bond formation than traditional coupling reactions (Scheme 1 a).[8] It is well-known that thiols/thiophenols (RSH) are very good ligands, which can bind with transition metals tightly and usually poison transition-metal catalysts.[9] Furthermore, thiols/thiophenols can be easily over-oxidized to generate sulfoxides and sulfones.[10] These problems hamper the wide application of direct C–S cross-coupling. We envision that the use of electrolysis to drive hydrogen evolution could provide a solution to the above problems, since it avoids the use of transition-metal catalysts and oxidants.

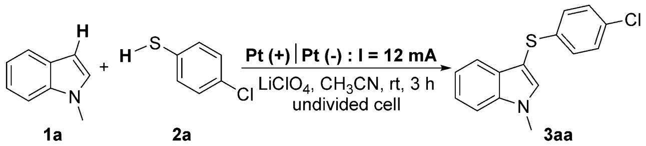
During the past decade, the application of electrochemical anodic oxidation in synthetic organic chemistry has received increasing attention.[11] However, only limited examples of oxidant-free dehydrogenative cross-coupling for C–C and C–N bond formation have been developed, since it is difficult to control the reaction selectivity under electrochemical conditions.[12] There is no precedent for electrocatalytic dehydrogenative C–H/S–H cross-coupling, possible because of the ready over-oxidation of thiols/thiophenols. Herein, we communicate our progress on an electrocatalytic oxidant-free dehydrogenative C–H/S–H cross-coupling in a simple undivided cell under constant-current conditions (Scheme 1 b).

N-Methylindole (**1a**) and 4-chlorothiophenol (**2a**) were chosen as model substrates to test the reaction conditions. By using a 12 mA constant current in an undivided four-necked bottle, we obtained the C–S bond-formation product **3aa** in 85 % yield (Table 1, entry 1). Both increasing and decreasing the constant current led to a decrease in the reaction yield (Table 1, entries 2 and 3). As for the choice of electrolyte, ammonium salts showed decreased reaction efficiency as



Scheme 1. Dehydrogenative C–H/S–H cross-coupling.

Table 1: Effects of reaction parameters.[a]



Entry	Variation from the standard conditions	Yield [%][b]
1	none	85
2	6 mA instead of 12 mA, 6 h	16
3	18 mA instead of 12 mA, 2 h	53
4	^{n}Bu$_4$NBF$_4$ instead of LiClO$_4$	81
5	^{n}Bu$_4$NClO$_4$ instead of LiClO$_4$	71
6	^{n}Bu$_4$NPF$_6$ instead of LiClO$_4$	60
7	THF instead of MeCN	4
8	MeOH instead of MeCN	67
9	C (+) | Pt (–) instead of Pt (+) | Pt (–)	25
10	Pt (+) | C (–) instead of Pt (+) | Pt (–)	59
11	under air	79
12	no electric current, under air	n.d.

[a] Standard conditions: Pt anode, Pt cathode, constant current = 12 mA, **1a** (0.50 mmol), **2a** (1.0 mmol), LiClO$_4$ (2.0 mmol), MeCN (8.0 mL), room temperature, 3 h. [b] The yield of **3aa** was determined by GC analysis with biphenyl as the internal standard; n.d. = not detected.

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Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under: http://dx.doi.org/10.1002/anie.201700012.

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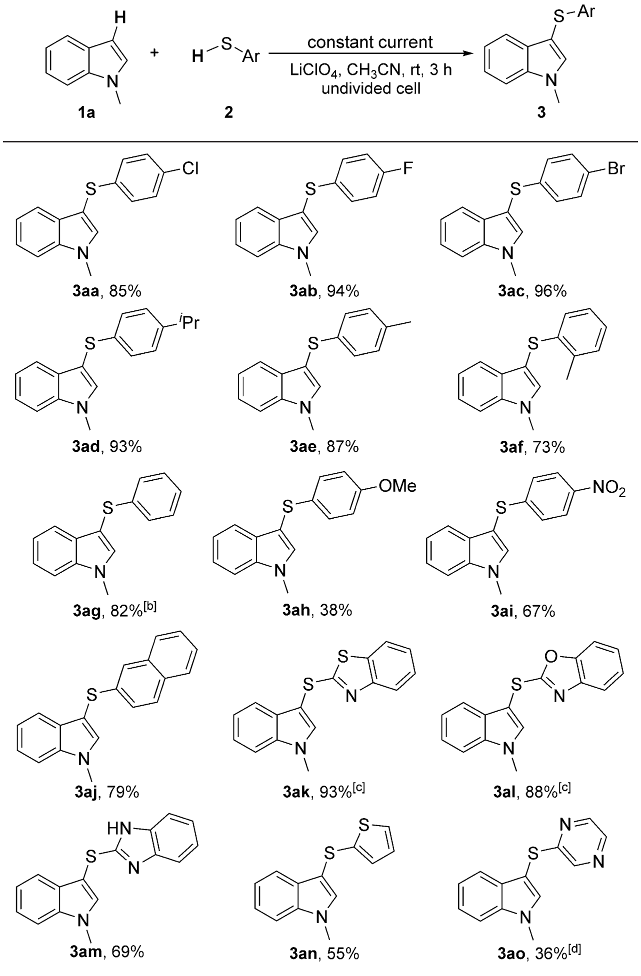
compared with lithium perchlorate (Table 1, entries 4–6). The choice of solvent was also important for this dehydrogenative C−H/S−H cross-coupling reaction. Tetrahydrofuran was not suitable for this transformation, and methanol afforded the desired product in lower yield (Table 1, entries 7 and 8). The effect of the electrode material was also explored. Lower reaction yields were observed when platinum was replaced with carbon as either the anode or cathode (Table 1, entries 9 and 10). However, a good reaction yield was still observed under atmospheric conditions (Table 1, entry 11). No desired product could be obtained without an electric current under atmospheric conditions (Table 1, entry 12).

To demonstrate the utility of this method, we applied different thiols as substrates in this electrocatalytic oxidant-free dehydrogenative C−H/S−H cross-coupling (Table 2). Thiophenols bearing electron-neutral substituents at the *para* position, such as an isopropyl or methyl group, also showed good reactivity in this transformation (products **3ad**, **3ae**). Notably, thiophenols bearing halide substituents were able to furnish the selective dehydrogenative C−H/S−H cross-coupling products in high yields (products **3aa**–**ac**). The reaction of *o*-methylthiophenol gave **3af** in a slightly decreased reaction yield, which might be due to the steric effect of the methyl group. Benzenethiol afforded the C−S bond-formation product **3ag** in 82% yield with a lower operating current, whereas electron-rich *p*-methoxythiophenol showed decreased reaction efficiency in this transformation (product **3ah**). The strongly electron withdrawing nitro group was also tolerated in this transformation, and the desired product **3ai** was obtained in good yield. Other aryl thiols were also applied as substrates in this transformation. 2-Naphthalenethiol afforded the desired C−S bond formation product **3aj** in 79% yield. Heteroaryl thiols were also suitable substrates: 2-Mercaptobenzothiazole, 2-mercaptobenzoxazole, and 2-mercaptobenzimidazole all furnished the desired products **3ak**–**am** in good to high yields. Moreover, 2-mercaptothiophene and 2-mercaptopyrazine were also able to give the products of C−S bond formation **3an** and **3ao**, though with decreased reaction yields. Only trace amounts of products were detected when aliphatic thiols were employed as substrates, possibly as a result of over-oxidation of these relatively unstable thiols.

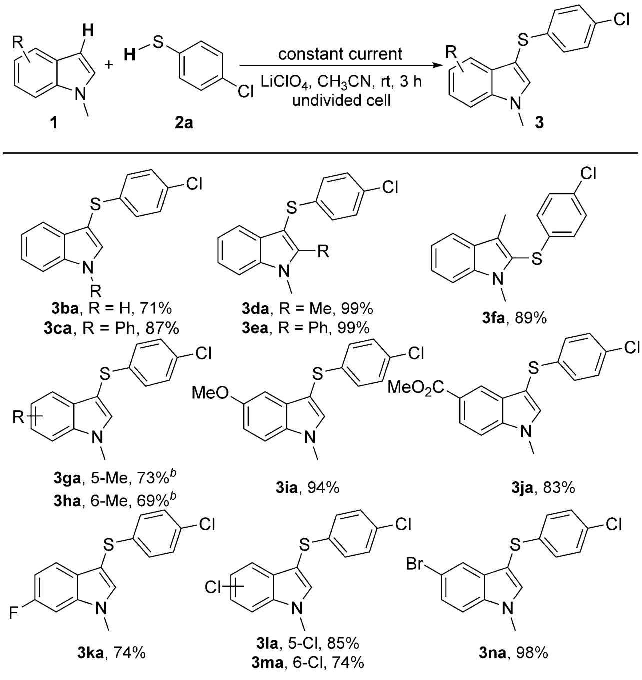
We next studied the tolerance of the reaction towards functional groups on the indole moiety (Table 3). Unprotected indole showed slightly lower reaction efficiency than N-protected indoles (products **3ba** and **3ca**). *N*-Methyl-

Table 2: Electrocatalytic oxidant-free dehydrogenative C−H/S−H cross-coupling with different thiols.[a]



[a] Standard conditions: Pt anode, Pt cathode, constant current = 12 mA, **1a** (0.50 mmol), **2** (1.0 mmol), $LiClO_4$ (2.0 mmol), MeCN (8.0 mL), room temperature, N_2, 3 h. Isolated yields are shown. [b] Constant current = 6 mA, 6 h. [c] The yield was determined by ^1H NMR spectroscopy with CH_2Br_2 as the internal standard. [d] A mixture of MeCN (4.0 mL) and CH_2Cl_2 (4.0 mL) was used as the solvent.

Table 3: Electrocatalytic oxidant-free dehydrogenative C−H/S−H cross-coupling with substituted indoles.[a]



[a] Standard conditions: Pt anode, Pt cathode, constant current = 12 mA, **1** (0.50 mmol), **2a** (1.0 mmol), $LiClO_4$ (2.0 mmol), MeCN (8.0 mL), room temperature, N_2, 3 h. Isolated yields are shown. [b] The yield was determined by ^1H NMR spectroscopy with CH_2Br_2 as the internal standard.

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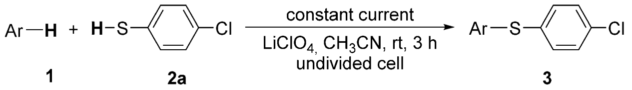
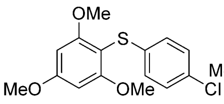
indoles bearing methyl and phenyl substituents at the C2 position showed excellent reactivity and afforded the desired product in quantitative yield (products **3da** and **3ea**). The reaction took place efficiently at the C2 position when the C3 position was substituted with a methyl group (product **3fa**). Moreover, 5- and 6-methyl substituted indoles were also suitable for this transformation (products **3ga** and **3ha**). Notably, an electron-donating methoxy group at the C5 position led to a higher reaction yield (product **3ia**). An electron-withdrawing ester group was also tolerated well in this transformation (product **3ja**). Halide-substituted indoles were also tested as substrates and selectively furnished the dehydrogenative C–H/S–H cross-coupling products **3ka–na** in good to high yields.

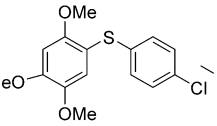
Besides indoles, other electron-rich arenes were also applied as substrates in this dehydrogenative C–H/S–H cross-coupling reaction (Table 4). The very electron rich benzenes 1,3,5-trimethoxybenzene and 1,3,4-trimethoxybenzene gave the desired products **3oa** and **3pa** in 74 and 50% yield, respectively. Furthermore, *N*,*N*-dimethylaniline and its derivatives were found to be reactive under the electrocatalytic conditions and afforded products **3qa–sa** of selective mono-thiolation in moderate yields. Electron-rich 3,5-dimethoxyphenol was also suitable for this transformation and afforded the thiolation product **3ta** in 54% yield. Less electron rich arenes, such as pentamethylbenzene, showed low reactivity in this transformation (product **3ua**). Electron-rich heteroarenes were also tested under the electrolysis conditions. For example, 2,5-dimethylpyrrole gave the product of C–H thiolation product at the C3 position in 51% yield (product **3va**). A thiophene bearing an electron-donating methoxy group at the C2 position could afford the product of C–S bond formation **3wa** at a lower operating current.

Table 4: Electrocatalytic oxidant-free dehydrogenative C–H/S–H cross-coupling with other electron-rich arenes.[a]

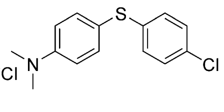




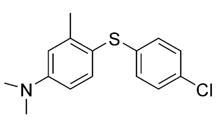
3oa, 74%



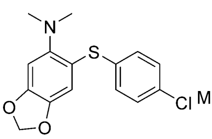
3pa, 50%



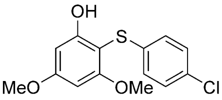
3qa, 44%[b]



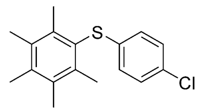
3ra, 58%[c]



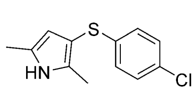
3sa, 40%



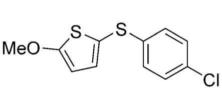
3ta, 54%



3ua, 24%



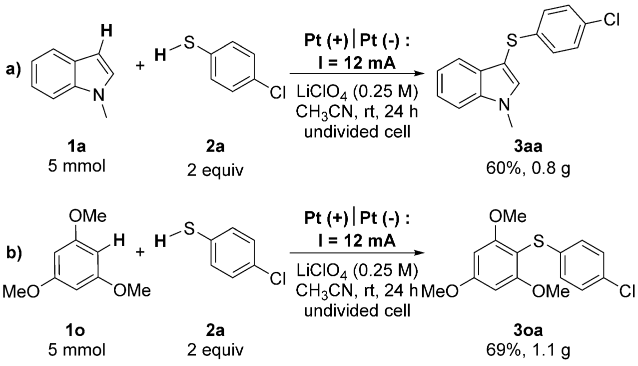
3va, 51%



3wa, 35%[d]

[a] Standard conditions: Pt anode, Pt cathode, constant current = 12 mA, **1** (0.50 mmol), **2a** (1.0 mmol), LiClO$_4$ (2.0 mmol), MeCN (8.0 mL), room temperature, N$_2$, 3 h. [b] **1** (0.80 mmol), **2a** (0.5 mmol), and LiClO$_4$ (3.0 mmol) were used. [c] The yield was determined by ^{1}H NMR spectroscopy with CH$_2$Br$_2$ as the internal standard. [d] Constant current = 10 mA, LiClO$_4$ (3.0 mmol).

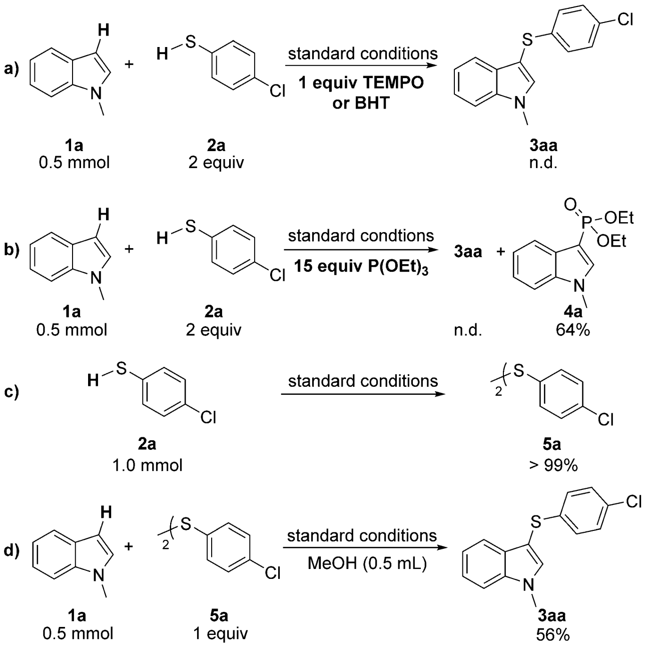
We evaluated the scalability of this electrocatalytic dehydrogenative C–H/S–H cross-coupling by performing reactions on a 5 mmol scale. The reaction with *N*-methylindole smoothly furnished the desired product **3aa** (0.8 g) in 60% yield (Scheme 2a). Similarly, a gram-scale reaction between **2a** and trimethoxybenzene afforded the desired product **3oa** (1.1 g) in 69% yield (Scheme 2b). These results show the great potential of this electrocatalytic dehydrogenative cross-coupling in practical synthesis.



Scheme 2. Gram-scale synthesis.

To gain an understanding of the reaction mechanism, we conducted experiments to explore the existence of radical intermediates. When 1 equivalent of (2,2,6,6-tetramethylpiperidin-1-yl)oxy (TEMPO) or butylated hydroxytoluene (BHT) was added in the reaction between **1a** and **2a** under the standard conditions, no desired C–S bond-formation product was observed (Scheme 3a). Thus, radical intermediates are possibly involved under the electrocatalytic conditions. We added an excess amount of triethyl phosphite to the reaction mixture to trap any radical intermediates. Interestingly, the indole-phosphorylation product **4a** was obtained in 64% yield, thus suggesting the generation of an indole radical during the reaction (Scheme 3b).[13]

In a control experiment in the absence of arene substrates, thiophenol **2a** underwent dimerization to afford disulfide **5a** in quantitative yield (Scheme 3c). We performed a sampling experiment of the reaction between **1a** and **2a** to further confirm the role of disulfide **5a** in this transformation (Figure 1a). Interestingly, the product **3aa** was formed slowly, whereas **5a** was generated fast but the amount remained nearly constant during the reaction. Since disulfides were found to be generated under the standard conditions, the reaction between **1a** and disulfide **5a** was conducted under the standard conditions. When a small amount of methanol was added as a proton source, **3aa** was obtained in 56% yield under the standard conditions (Scheme 3d). In the next step, we carried out cyclic voltammetry (CV) experiments to study the redox potential of the substrates (Figure 1b). An oxidation peak of **2a** in acetonitrile was observed at 1.27 V. At the same time, oxidation peaks of **1a** could also be observed



Scheme 3. Mechanistic studies.

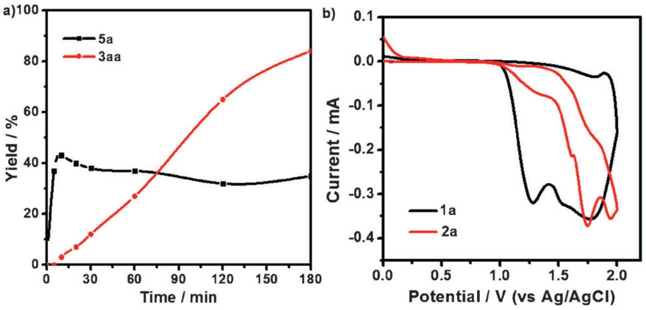
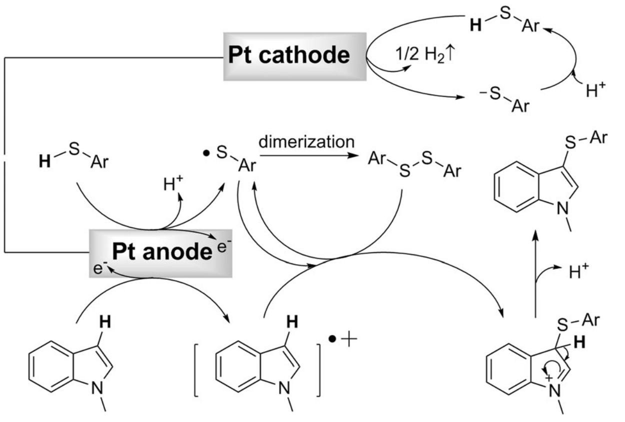


Figure 1. a) Sampling experiment of the reaction between **1a** and **2a**. b) Cyclic voltammetry of **1a** and **2a** in CH_3CN with $LiClO_4$ (0.2 M) under nitrogen at a platinum-disk electrode at a scan rate of $\nu = 0.1\ V s^{-1}$.

above 1.28 V. Since the operating voltage ranged from 1.8 to 2.2 V, the oxidation of both substrates was possible under the standard conditions.

On the basis of the above experimental results, a plausible mechanism for the reaction between **1a** and **2a** is shown in Scheme 4. Single-electron-transfer (SET) oxidation of the thiophenol by the anode leads to the formation of a sulfur radical, which undergoes rapid dimerization to generate a disulfide. At the same time, *N*-methylindole can also be oxidized by the anode to generate a radical-cation intermediate. The generated indole radical-cation intermediate can undergo either direct coupling with the sulfur radical or radical substitution with the generated disulfide **5a** to afford a hydroindole cation intermediate.[8h] Final deprotonation of the cation intermediate leads to the formation of the C–S bond-formation product. Concomitant cathodic reduction of thiophenol leads to the formation of hydrogen gas.



Scheme 4. Proposed mechanism.

In conclusion, an electrocatalytic dehydrogenative C–H/S–H cross-coupling has been developed that enables C–S bond formation under catalyst- and oxidant-free conditions. Various aryl/heteroaryl thiols and electron-rich arenes were suitable for this transformation. Importantly, the reaction can be conducted on a gram scale with good reaction efficiency. Mechanistically, anodic oxidative generation of an aryl cation radical was found to be the key to this transformation. Further application of electrocatalytic dehydrogenative cross-coupling in other useful transformations is under way in our laboratory.

Acknowledgements

This research was supported by the National Natural Science Foundation of China (21390402, 21520102003), the Ministry of Science and Technology of China (2012YQ120060), the Fundamental Research Funds for the Central Universities, and the Program of Introducing Talents of Discipline to Universities of China (111 Program).

Conflict of interest

The authors declare no conflict of interest.

Keywords: C–H functionalization · C–S bond formation · dehydrogenation · electrochemistry · radical cations

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[1] a) J. Dumas, D. Brittelli, J. Chen, B. Dixon, H. Hatoum-Mokdad, G. König, R. Sibley, J. Witowsky, S. Wong, *Bioorg. Med. Chem. Lett.* **1999**, *9*, 2531; b) R. Paramashivappa, P. Phani Kumar, P. V. Subba Rao, A. Srinivasa Rao, *Bioorg. Med. Chem. Lett.* **2003**, *13*, 657; c) L. Zhang, J. Fan, K. Vu, K. Hong, J.-Y. Le Brazidec, J. Shi, M. Biamonte, D. J. Busch, R. E. Lough, R. Grecko, Y. Ran, J. L. Sensintaffar, A. Kamal, K. Lundgren, F. J. Burrows, R. Mansfield, G. A. Timony, E. H. Ulm, S. R. Kasibhatla, M. F. Boehm, *J. Med. Chem.* **2006**, *49*, 5352; d) W. Huang, G.-F. Yang, *Bioorg. Med. Chem.* **2006**, *14*, 8280; e) G. Smith, G. Mikkelsen, J.

Eskildsen, C. Bundgaard, *Bioorg. Med. Chem. Lett.* **2006**, *16*, 3981; f) G. La Regina, M. C. Edler, A. Brancale, S. Kandil, A. Coluccia, F. Piscitelli, E. Hamel, G. De Martino, R. Matesanz, J. F. Díaz, A. I. Scovassi, E. Prosperi, A. Lavecchia, E. Novellino, M. Artico, R. Silvestri, *J. Med. Chem.* **2007**, *50*, 2865; g) M. C. Bagley, T. Davis, M. C. Dix, V. Fusillo, M. Pigeaux, M. J. Rokicki, D. Kipling, *J. Org. Chem.* **2009**, *74*, 8336.

[2] a) I. P. Beletskaya, V. P. Ananikov, *Chem. Rev.* **2011**, *111*, 1596; b) C.-F. Lee, Y.-C. Liu, S. S. Badsara, *Chem. Asian J.* **2014**, *9*, 706.

[3] a) M. A. Fernández-Rodríguez, Q. Shen, J. F. Hartwig, *J. Am. Chem. Soc.* **2006**, *128*, 2180; b) M. A. Fernández-Rodríguez, Q. Shen, J. F. Hartwig, *Chem. Eur. J.* **2006**, *12*, 7782; c) X. Moreau, J. M. Campagne, G. Meyer, A. Jutand, *Eur. J. Org. Chem.* **2005**, 3749.

[4] a) Y.-J. Chen, H.-H. Chen, *Org. Lett.* **2006**, *8*, 5609; b) L. Rout, T. K. Sen, T. Punniyamurthy, *Angew. Chem. Int. Ed.* **2007**, *46*, 5583; *Angew. Chem.* **2007**, *119*, 5679; c) P.-F. Larsson, A. Correa, M. Carril, P.-O. Norrby, C. Bolm, *Angew. Chem. Int. Ed.* **2009**, *48*, 5691; *Angew. Chem.* **2009**, *121*, 5801; d) Y. Jiang, Y. Qin, S. Xie, X. Zhang, J. Dong, D. Ma, *Org. Lett.* **2009**, *11*, 5250.

[5] Y. Zhang, K. C. Ngeow, J. Y. Ying, *Org. Lett.* **2007**, *9*, 3495.

[6] Y.-C. Wong, T. T. Jayanth, C.-H. Cheng, *Org. Lett.* **2006**, *8*, 5613.

[7] A. Correa, M. Carril, C. Bolm, *Angew. Chem. Int. Ed.* **2008**, *47*, 2880; *Angew. Chem.* **2008**, *120*, 2922.

[8] a) K. M. Schlosser, A. P. Krasutsky, H. W. Hamilton, J. E. Reed, K. Sexton, *Org. Lett.* **2004**, *6*, 819; b) S. Ranjit, R. Lee, D. Heryadi, C. Shen, J. E. Wu, P. Zhang, K.-W. Huang, X. Liu, *J. Org. Chem.* **2011**, *76*, 8999; c) C. Dai, Z. Xu, F. Huang, Z. Yu, Y.-F. Gao, *J. Org. Chem.* **2012**, *77*, 4414; d) Y. Liao, P. Jiang, S. Chen, H. Qi, G.-J. Deng, *Green Chem.* **2013**, *15*, 3302; e) Y. Liu, Y. Zhang, C. Hu, J.-P. Wan, C. Wen, *RSC Adv.* **2014**, *4*, 35528; f) J. Yuan, X. Ma, H. Yi, C. Liu, A. Lei, *Chem. Commun.* **2014**, *50*, 14386; g) S. K. R. Parumala, R. K. Peddinti, *Green Chem.* **2015**, *17*, 4068; h) Z. Huang, D. Zhang, X. Qi, Z. Yan, M. Wang, H. Yan, A. Lei, *Org. Lett.* **2016**, *18*, 2351; i) T. Gensch, F. J. R. Klauck, F. Glorius, *Angew. Chem. Int. Ed.* **2016**, *55*, 11287; *Angew. Chem.* **2016**, *128*, 11457.

[9] a) L. L. Hegedus, R. W. McCabe, *Catalyst Poisoning*, M. Dekker, New York, **1984**; b) J. R. Chang, S. L. Chang, T. B. Lin, *J. Catal.* **1997**, *169*, 338.

[10] a) G. K. S. Prakash, T. Mathew, C. Panja, G. A. Olah, *J. Org. Chem.* **2007**, *72*, 5847; b) S. Madabhushi, R. Jillella, V. Sriramoju, R. Singh, *Green Chem.* **2014**, *16*, 3125; c) H. Wang, Q. Lu, C. Qian, C. Liu, W. Liu, K. Chen, A. Lei, *Angew. Chem. Int. Ed.* **2016**, *55*, 1094; *Angew. Chem.* **2016**, *128*, 1106.

[11] a) J. B. Sperry, D. L. Wright, *Chem. Soc. Rev.* **2006**, *35*, 605; b) J.-i. Yoshida, K. Kataoka, R. Horcajada, A. Nagaki, *Chem. Rev.* **2008**, *108*, 2265; c) A. Jutand, *Chem. Rev.* **2008**, *108*, 2300; d) R. Francke, R. D. Little, *Chem. Soc. Rev.* **2014**, *43*, 2492; e) E. J. Horn, B. R. Rosen, P. S. Baran, *ACS Cent. Sci.* **2016**, *2*, 302; f) E. J. Horn, B. R. Rosen, Y. Chen, J. Tang, K. Chen, M. D. Eastgate, P. S. Baran, *Nature* **2016**, *533*, 77; g) A. Badalyan, S. S. Stahl, *Nature* **2016**, *535*, 406.

[12] a) C. Amatore, C. Cammoun, A. Jutand, *Adv. Synth. Catal.* **2007**, *349*, 292; b) A. Kirste, G. Schnakenburg, F. Stecker, A. Fischer, S. R. Waldvogel, *Angew. Chem. Int. Ed.* **2010**, *49*, 971; *Angew. Chem.* **2010**, *122*, 983; c) A. Kirste, B. Elsler, G. Schnakenburg, S. R. Waldvogel, *J. Am. Chem. Soc.* **2012**, *134*, 3571; d) T. Morofuji, A. Shimizu, J.-i. Yoshida, *Angew. Chem. Int. Ed.* **2012**, *51*, 7259; *Angew. Chem.* **2012**, *124*, 7371; e) B. Elsler, D. Schollmeyer, K. M. Dyballa, R. Franke, S. R. Waldvogel, *Angew. Chem. Int. Ed.* **2014**, *53*, 5210; *Angew. Chem.* **2014**, *126*, 5311; f) W.-J. Gao, W.-C. Li, C.-C. Zeng, H.-Y. Tian, L.-M. Hu, R. D. Little, *J. Org. Chem.* **2014**, *79*, 9613; g) Z.-W. Hou, Z.-Y. Mao, H.-B. Zhao, Y. Y. Melcamu, X. Lu, J. Song, H.-C. Xu, *Angew. Chem. Int. Ed.* **2016**, *55*, 9168; *Angew. Chem.* **2016**, *128*, 9314; h) S. Lips, A. Wiebe, B. Elsler, D. Schollmeyer, K. M. Dyballa, R. Franke, S. R. Waldvogel, *Angew. Chem. Int. Ed.* **2016**, *55*, 10872; *Angew. Chem.* **2016**, *128*, 11031; i) H. Gao, Z. Zha, Z. Zhang, H. Ma, Z. Wang, *Chem. Commun.* **2014**, *50*, 5034; j) Y. Li, H. Gao, Z. Zhang, P. Qian, M. Bi, Z. Zha, Z. Wang, *Chem. Commun.* **2016**, *52*, 8600.

[13] X.-Y. Jiao, W. G. Bentrude, *J. Am. Chem. Soc.* **1999**, *121*, 6088.

Manuscript received: January 2, 2017
Final Article published: ■■ ■■, ■■■■

Communications

C–S Bond Formation

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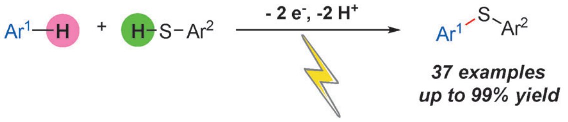
Electrocatalytic Oxidant-Free Dehydrogenative C–H/S–H Cross-Coupling



Evolutionary progress: An environmentally friendly electrocatalytic protocol for dehydrogenative C–H/S–H cross-coupling enabled C–S bond formation under catalyst- and oxidant-free conditions. The use of electrolysis in this way to drive hydrogen evolution enabled the direct cross-coupling of a variety of aryl and heteroaryl thiols with electron-rich arenes (see scheme).

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