

Electrocatalysis

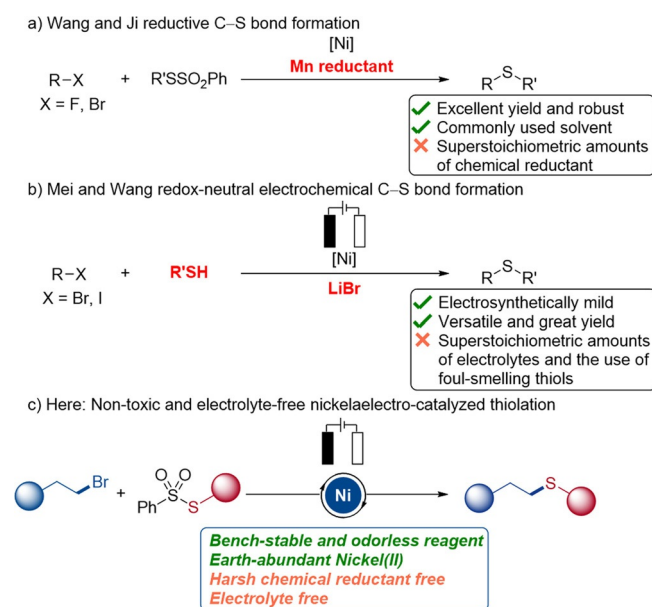
Electroreductive Nickel-Catalyzed Thiolation: Efficient Cross-Electrophile Coupling for C–S Formation

Nate W. J. Ang^[a] and Lutz Ackermann^{*[a, b]}

Abstract: Sulfur-containing molecules are of utmost topical importance towards the effective development of pharmaceuticals and functional materials. Herein, we present an efficient and mild electrochemical thiolation by cross-electrophile coupling of alkyl bromides with functionalized bench-stable thiosulfonates to access alkyl sulfides with excellent efficacy and broad functional group tolerance. Cyclic voltammetry and potentiostatic analysis were performed to elucidate mechanistic insights into this electrocatalytic thiolation reaction.

The vast amount of resources that has been directed to researches on nascent approaches for the formation of C–S bonds is caused by the influx of extensively useful sulfur-containing drug scaffolds.^[1] Alkyl sulfides have been recognized for their unique importance in pharmaceuticals and organic syntheses.^[2] Traditionally, the formation of alkyl sulfides largely required strong alkaline conditions that could hinder its use with limited substrate scope and low yielding products.^[3] Thus, it is desirable to develop facile and yet efficient methods for the C–S formation. Transition-metal-catalyzed C–S formations have undoubtedly eased the syntheses of alkyl sulfides dominated by precious metals, such as palladium, rhodium and gold.^[4] However, recently, 3d-transition metals have gained major attention and are well-sought after due to their low toxicities and earth-abundant nature.^[2c,4c,f,5] Thiols and their oxidized derivatives are predominantly used as the coupling partner. However, they are known to be highly toxic with foul-smelling odor and this impedes its functionality. In stark con-

trast, the use of simple, bench-stable and odorless electrophilic thiosulfonates for the formation of C–S bonds continues to be underdeveloped.^[5a–c,e,g,6] Cross-electrophile couplings have surfaced as an impressive alternative to conventional cross-couplings with preformed nucleophiles, providing an advantage in terms of step-economy.^[7] Notable examples for reductive cross-electrophile thiolation include defluorinative reductive cross-coupling of *gem*-difluoroalkenes with thiosulfonates and reductive thiolation of bromides (Scheme 1 a)^[5c,e] by using



Scheme 1. Electrochemical nickel-catalyzed cross-electrophile thiolation.

super-stoichiometric amounts of manganese as the chemical reductant. Recently, electrocatalysis combined with 3d-metal catalysis^[8] has emerged as a powerful tool for sustainable molecular syntheses.^[9] Pioneering studies for electrochemical thiolation feature independent reports from Mei and Wang/Pan on redox-neutral nickel-catalyzed electrochemical C–S bond formation with substituted thiols as coupling partners (Scheme 1 b).^[10] In addition to the impressive usage of electro-synthesis for the formation of C–S bonds, it is intriguing to unravel potent syntheses for thiolations that are mild and environmentally friendly. Herein, we report on a nickel-catalyzed cross-electrophile thiolation of alkyl bromides, featuring electricity as a mediator to access alkyl sulfides, which are common structural motifs in numerous drug scaffolds (Scheme 1 c).^[11]

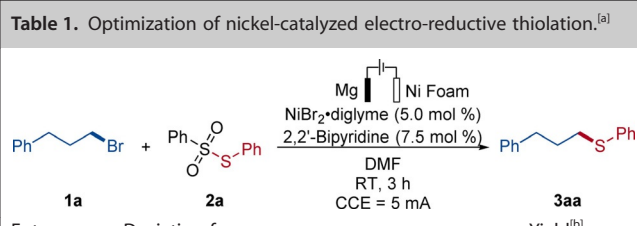
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<https://doi.org/10.1002/chem.202005449>.

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Table 1. Optimization of nickel-catalyzed electro-reductive thiolation.^[a]

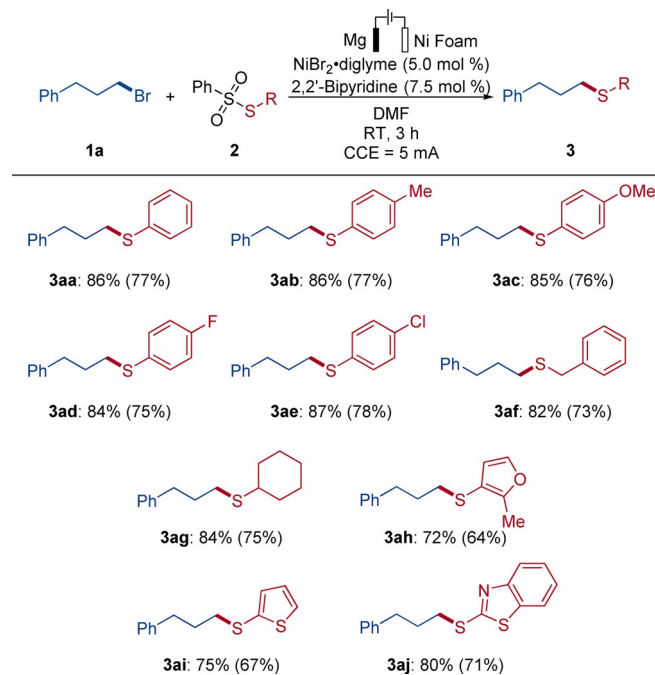


Entry	Deviation from standard conditions	Yield ^[b]
1	–	86%
2	bathocuproine instead of 2,2'-bipyridine	82%
3	neocuproine instead of 2,2'-bipyridine	67%
4	NiCl ₂ (5.0 mol %)	47% ^[c]
5	Fe anode	–
6	Zn anode	–
7	Cu anode	–
8	Pt cathode	70%
9	without catalyst	37% ^[d]
10	no electricity	–
11	Et ₄ NOTs (0.5 equiv) as electrolyte	51%
12	with IKA ElectraSyn 2.0	79%
13	PhS-SPh (4a) instead of 2a	–

[a] Undivided cell, **1a** (0.250 mmol), **2a** (0.275 mmol), NiBr₂·diglyme (5.0 mol %), 2,2'-bipyridine (7.5 mol %), solvent (5.0 mL), 25 °C, 3 h, Mg foil electrode (3.0 mm × 15 mm × 0.2 mm), Ni foam electrode (10 mm × 15 mm × 1.0 mm), constant current electrolysis (CCE) at 5 mA with an overall cell potential of 0.70–0.95 V. [b] Isolated yield. [c] 6 h reaction time. [d] High potential was observed.

We initiated our studies by optimizing the reaction conditions (Table 1) for the envisioned electro-thiolation of alkyl halides with benzenethiosulfonates. Bidentate nitrogen-containing ligands such as bathocuproine and neocuproine failed to give satisfactory yields (entries 2–3). Instead, the relatively inexpensive bipyridine outperformed them. Polar aprotic solvents, such as DMF and DMA, performed decently for the electro-thiolation (Table S-2).^[12] Various anode and cathode materials were tested for their efficacies (entries 5–8) but to no avail, these includes platinum cathode which provided the desired product with a lower yield. Control experiments (entries 9 and 10) substantiated the importance of electricity, and the essential role of the nickel catalyst for this cross-electrophile electro-thiolation (Table S-3).^[12] The use of electrolytes did not improve the yield as the potential of the optimized reaction remained stable throughout the entire course of electrolysis (entry 11). Notably, the commercially available IKA ElectraSyn 2.0 was used to exhibit the simplicity of the transformation, furnishing product **3aa** in comparable yield (entry 12). The use of diphenyl disulfide **4a** did not lead to product formation (entry 13).

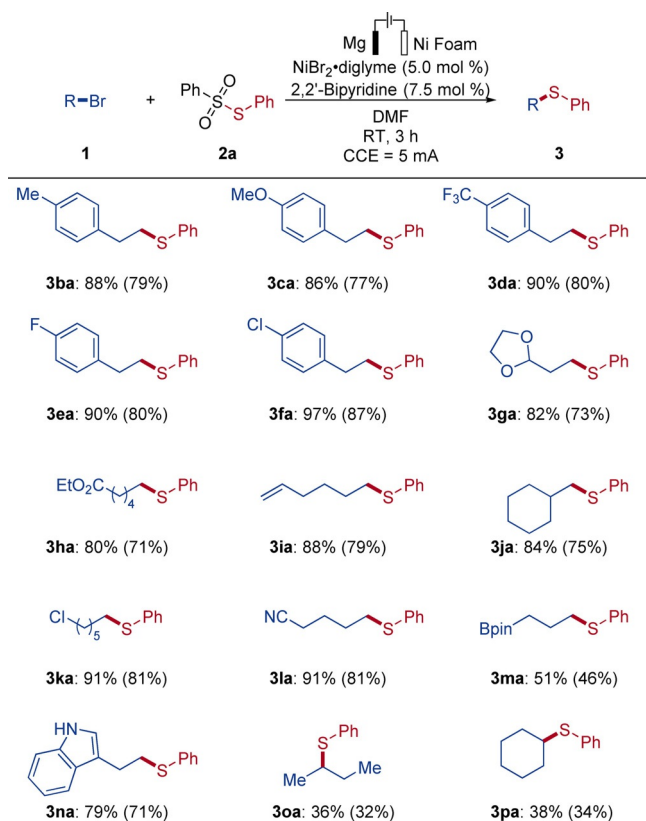
With the optimized reaction conditions in hand, we were keen on exploring the substrate scope of the nickel-electro-reductive thiolation reaction. We embarked on testing the robustness with various substituted bench-stable thiosulfonates (Scheme 2). Electron-donating groups such as *para*-substituted methyl **2b**, methoxy **2c**, provided the product with great efficacy. Halogen-containing substrates (**2d–e**) resulted in excellent yield of the thiolated products (**3ad** and **3ae**) without by-product formation from C–X cross-couplings. In addition, alkyl thiosulfonates, such as benzyl **2f** and cyclohexyl **2g**, delivered



Scheme 2. Nickel-catalyzed electro-reductive thiolation of alkyl bromide **1a** with substituted thiosulfonates **2**. Faradaic yield given in parentheses.

the desired products **3af** and **3ag** in very good yields. Moreover, heterocyclic thiosulfonates (**2h–j**) were well tolerated and furnished the thiolation products with high yield. The mild reaction conditions were highly versatile as various thiosulfonates were efficiently converted to the desired alkyl sulfide product **3**. Hence, we were intrigued to evaluate the performance of the electro-catalysis on differently substituted bromides (Scheme 3). To our delight, *para*-substituted electron-donating groups, such as methyl **1b**, methoxy **1c**, both gave the desired alkyl sulfide products with excellent yield. Electron-withdrawing trifluoromethyl arene **1d** also furnished the thiolated product with great yield, displaying no obvious preferences in terms of electronic influences. Various halogen-containing substrates (**1e–f**) gave the desired products (**3ea–3ef**) in a highly chemoselective fashion. Synthetically useful cyclic 1,3-dioxolane substituted bromide **1g** also underwent facile thiolation to give excellent yield of the desired product. In addition, ester-containing substrate **1h** provided the desired alkyl sulfide product (**3ha**) with good yield. Various functional groups such as terminal alkene (**1i**), sterically crowded 2-cyclohexyl (**1j**), alkyl chloride (**1k**), and cyano (**1l**) were efficiently transformed to products **3**. The otherwise highly labile boronic ester **1m** remained intact in the electro-thiolation regime to deliver the product (**3ma**). In addition, unprotected indole **1n** provided the desired product as well. Secondary bromides (**1o–p**) were also successfully thiolated, albeit lower yields were obtained.

In order to understand the mode of action for the nickel-electro-catalyzed thiolation reaction with alkyl bromides **1**, we sought to investigate the mechanism in detail. First, radical clock experiments also were performed with 6-bromo-1-



Scheme 3. Nickel-catalyzed electro-reductive thiolation with bromides **1**. Faradaic yield given in parentheses.

hexene to illustrate the formation of primary alkyl radical (Table 2).

Second, we elucidated various reduction potentials of the substrates and catalyst by means of cyclic voltammetry (CV) as disulfides were frequently present as by-product of the reaction. The cathodic reduction of thiosulfonates was important to determine the presence of an off-cycle pathway of this electro-catalysis. Cyclic voltammetry revealed that the reduction of the bipyridine ligated nickel pre-catalyst is more facile than the two-electron reduction of *S*-phenyl benzenethiosulfonate **2a** to the thiolate anion (Figure 1). The first reduction potential of thiosulfonate **2a** was shown to be irreversible at $E_p = -0.91$ V vs. Ag/AgCl and this could plausibly be assigned to the formation of the thiyl radical. Thiyl radicals are known to recombine

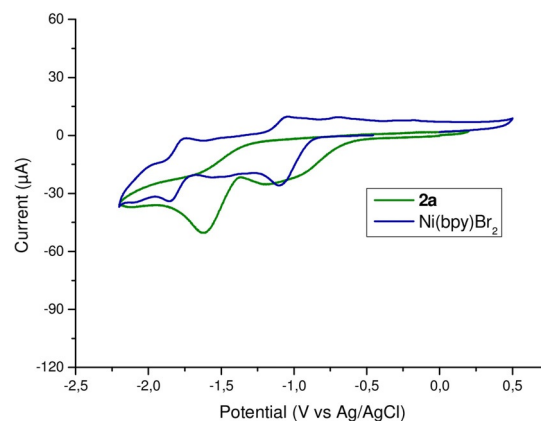
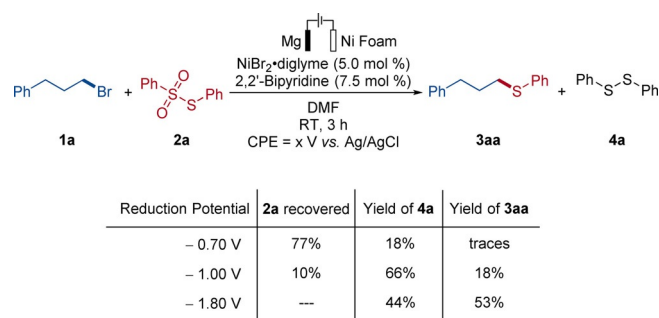


Figure 1. Cyclic voltammetry (DMF, 0.1 M $n\text{Bu}_4\text{NPF}_6$, 100 mVs^{-1}) with glassy carbon as the working electrode. Cyclic voltammograms of different reaction components.

systematically to disulfide due to their relative stability.^[13] In addition, a second reduction potential was found to be reversible at $E_p = -1.62$ V vs. Ag/AgCl and this would then be assigned to the thiolate anion after a two-electrons transfer process.^[14] The nickel pre-catalyst exhibits an irreversible reduction potential at $E_p = -1.27$ V vs. Ag/AgCl, which is lowered further to a reversible reduction potential of $E_p = -1.10$ V vs. Ag/AgCl by the ligation of the bipyridine ligand^[12] for the reduction of nickel(II) to nickel(I) analogous to previously reported observations.^[15] Additional observations postulate that the ligated nickel catalyst is found to undergo facile two electron reduction synergistically with the reduction of thiosulfonate. Further mechanistic studies by means of potentiostatic reactions were performed to illustrate the generation of thiyl radicals and the subsequent disulfide formation through radical recombination (Scheme 4). Potentiostatic reactions were conducted under the otherwise standard reaction conditions.^[16] As hypothesized, the desired product was not formed at CPE = -0.70 V vs. Ag/AgCl, but radical rebounded disulfide **4a** was formed with 18% yield, likely due to an early first onset potential of the thiosulfonate **2a** at $E_{\text{onset}} = -0.60$ V vs. Ag/AgCl. In contrast, the thiolated product **3aa** was formed at CPE = -1.00 V vs. Ag/AgCl, albeit with a considerable amount of by-product **4a**, plausibly by radical recombination. This observation is in good agreement with our CV studies indicating possible formation of thiyl radicals by initial reduction of substrate **2a**. When the

Table 2. Radical Clock Experiment.				
Entry	[Ni] (X mol %)	Ligand (Y mol %)	Yield ^[a]	3ia:3ia' ^[a]
1	2.50	3.75	69%	14:1
2	5.00	7.50	96%	> 20:1

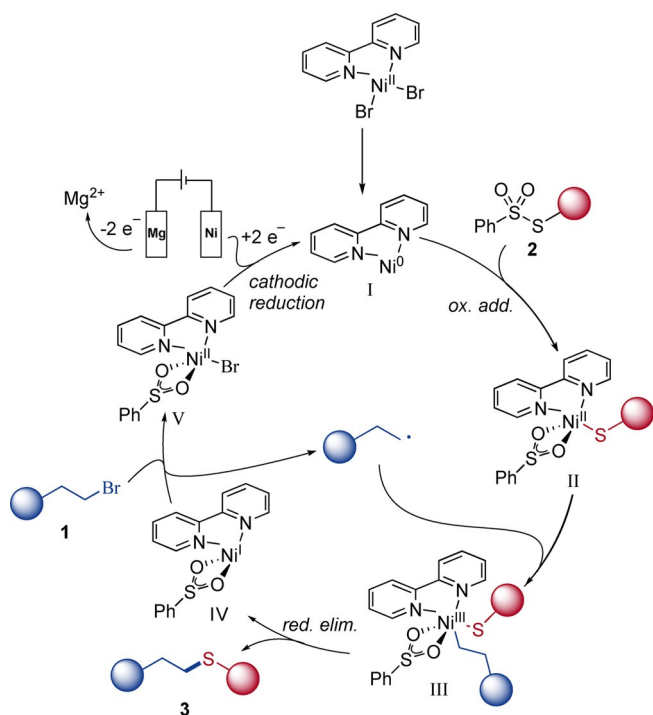
[a] Yield and ratio determined by ¹H NMR spectroscopy with 1,3,5-trimethoxybenzene as internal standard.



Scheme 4. Potentiostatic studies.

potential was higher than the second reduction potential of substrate **2a** at CPE = -1.80 V vs. Ag/AgCl, the desired thiolated product **3aa** was obtained with 53% yield, while by-product **4a** was formed with 44% yield.

A plausible catalytic cycle is proposed based on the obtained results (Scheme 5).^[5e,f,17] Initially, oxidative addition of **2** onto the active nickel(0) catalyst **I** occurs.^[8b,18] This formed intermediate **II** then combines with an alkyl radical formed in situ to give a nickel(III) complex. The complex **III** undergoes reductive elimination to provide the thiolation product **3** through a C–S bond formation. Nickel(I) complex **IV** would subsequently react with another molecule of alkyl bromide regenerating the alkyl radical and form nickel(II) intermediate **V**. This then undergoes cathodic reduction to reform the active catalyst.^[19]



Scheme 5. Plausible catalytic cycle.

In summary, we have developed an efficient and robust nickel-electrocatalyzed strategy for the cross-electrophile electrocoupling of alkyl bromides and thiosulfonates to access alkyl sulfides through C–S bond formation under ambient conditions, devoid of harsh chemical reductants. The mild electrothiolation provided a broad and versatile substrate scope with excellent yields. Cyclic voltammetry and potentiostatic investigations provided detailed mechanistic insights into the reaction mechanism.

Acknowledgements

Generous support by the DFG (Gottfried-Wilhelm-Leibniz award to LA) is gratefully acknowledged. Open access funding enabled and organized by Projekt DEAL.

Conflict of interest

The authors declare no conflict of interest.

Keywords: cross-electrophile coupling · electrocatalysis · nickel · reductive · thiolation

- [1] a) J.-M. Wang, G.-Z. Ding, L. Fang, J.-G. Dai, S.-S. Yu, Y.-H. Wang, X.-G. Chen, S.-G. Ma, J. Qu, S. Xu, D. Du, *J. Nat. Prod.* **2010**, *73*, 1240–1249; b) H. Guo, B. Sun, H. Gao, X. Chen, S. Liu, X. Yao, X. Liu, Y. Che, *J. Nat. Prod.* **2009**, *72*, 2115–2119; c) M. E. Thase, W. Macfadden, R. H. Weisler, W. Chang, B. Paulsson, A. Khan, J. R. Calabrese, *J. Clin. Psychopharmacol.* **2006**, *26*, 600–609; d) S. C. Piscitelli, T. F. Goss, J. H. Wilton, D. T. D'Andrea, H. Goldstein, J. J. Schentag, *Antimicrob. Agents Chemother.* **1991**, *35*, 1765–1771; e) L. P. Garrod, *Br. Med. J.* **1960**, *2*, 1695–1696; f) L. P. Garrod, *Br. Med. J.* **1960**, *1*, 527–529.
- [2] a) N. Wang, P. Saidharedy, X. Jiang, *Nat. Prod. Rep.* **2020**, *37*, 246–275; b) K. L. Dunbar, D. H. Scharf, A. Litomska, C. Hertweck, *Chem. Rev.* **2017**, *117*, 5521–5577; c) H. Liu, X. Jiang, *Chem. Asian J.* **2013**, *8*, 2546–2563; d) F.-Z. Wang, Z. Huang, X.-F. Shi, Y.-C. Chen, W.-M. Zhang, X.-P. Tian, J. Li, S. Zhang, *Bioorg. Med. Chem. Lett.* **2012**, *22*, 7265–7267; e) C.-S. Jiang, W. E. G. Müller, H. C. Schröder, Y.-W. Guo, *Chem. Rev.* **2012**, *112*, 2179–2207; f) F. C. Odds, C. E. Webster, A. B. Abbott, *J. Antimicrob. Chemother.* **1984**, *14*, 105–114.
- [3] H. Gilman, N. J. Beaver, *J. Am. Chem. Soc.* **1925**, *47*, 1449–1451.
- [4] a) Z. Lian, B. N. Bhawal, P. Yu, B. Morandi, *Science* **2017**, *356*, 1059–1063; b) S. D. Timpa, C. J. Pell, O. V. Ozerov, *J. Am. Chem. Soc.* **2014**, *136*, 14772–14779; c) C.-F. Lee, Y.-C. Liu, S. S. Badsara, *Chem. Asian J.* **2014**, *9*, 706–722; d) C.-S. Lai, H.-L. Kao, Y.-J. Wang, C.-F. Lee, *Tetrahedron Lett.* **2012**, *53*, 4365–4367; e) M. Sayah, M. G. Organ, *Chem. Eur. J.* **2011**, *17*, 11719–11722; f) I. P. Beletskaya, V. P. Ananikov, *Chem. Rev.* **2011**, *111*, 1596–1636; g) M. Jean, J. Renault, P. van de Weghe, N. Asao, *Tetrahedron Lett.* **2010**, *51*, 378–381; h) M. Arisawa, T. Suzuki, T. Ishikawa, M. Yamaguchi, *J. Am. Chem. Soc.* **2008**, *130*, 12214–12215; i) N. Morita, N. Krause, *Angew. Chem. Int. Ed.* **2006**, *45*, 1897–1899; *Angew. Chem.* **2006**, *118*, 1930–1933; j) M. A. Fernández-Rodríguez, Q. Shen, J. F. Hartwig, *J. Am. Chem. Soc.* **2006**, *128*, 2180–2181; k) T. Kondo, T.-A. Mitsudo, *Chem. Rev.* **2000**, *100*, 3205–3220.
- [5] a) P. Xu, Y.-M. Zhu, X.-J. Li, F. Wang, S.-Y. Wang, S.-J. Ji, *Adv. Synth. Catal.* **2019**, *361*, 4909–4913; b) J. Li, S.-Y. Wang, S.-J. Ji, *J. Org. Chem.* **2019**, *84*, 16147–16156; c) J. Li, W. Rao, S.-Y. Wang, S.-J. Ji, *J. Org. Chem.* **2019**, *84*, 11542–11552; d) G. Kibriya, S. Mondal, A. Hajra, *Org. Lett.* **2018**, *20*, 7740–7743; e) Y. Fang, T. Rogge, L. Ackermann, S.-Y. Wang, S.-J. Ji, *Nat. Commun.* **2018**, *9*, 2240; f) M. S. Oderinde, M. Frenette, D. W. Robbins, B. Aquila, J. W. Johannes, *J. Am. Chem. Soc.* **2016**, *138*, 1760–1763; g) P. Mampuy, Y. Zhu, T. Vlaar, E. Ruijter, R. V. A. Orru, B. U. W. Maes, *Angew. Chem. Int. Ed.* **2014**, *53*, 12849–12854; *Angew. Chem.* **2014**, *126*, 13063–13068; h) T.-J. Liu, C.-L. Yi, C.-C. Chan, C.-F. Lee, *Chem. Asian J.* **2013**, *8*, 1029–1034; i) M.-T. Lan, W.-Y. Wu, S.-H. Huang, K.-L. Luo, F.-Y. Tsai, *RSC Adv.* **2011**, *1*, 1751–1755; j) J.-R. Wu, C.-H. Lin, C.-F. Lee, *Chem. Commun.* **2009**, 4450–4452; k) A. Correa, M. Carril, C. Bolm, *Angew. Chem. Int. Ed.* **2008**, *47*, 2880–2883; *Angew. Chem.* **2008**, *120*, 2922–2925; l) Y.-C. Wong, T. T. Jayanth, C.-H. Cheng, *Org. Lett.* **2006**, *8*, 5613–5616; m) O. Baldovino-Pantaleón, S. Hernández-Ortega, D. Morales-Morales, *Adv. Synth. Catal.* **2006**, *348*, 236–242; n) N. Taniguchi, *J. Org. Chem.* **2004**, *69*, 6904–6906; o) F. Y. Kwong, S. L. Buchwald, *Org. Lett.* **2002**, *4*, 3517–3520.
- [6] a) W. Wang, X. Peng, F. Wei, C.-H. Tung, Z. Xu, *Angew. Chem. Int. Ed.* **2016**, *55*, 649–653; *Angew. Chem.* **2016**, *128*, 659–663; b) F. F. Fleming, S. Gudipati, V. A. Vu, R. J. Mycka, P. Knochel, *Org. Lett.* **2007**, *9*, 4507–4509; c) A. H. Stoll, A. Krasovskiy, P. Knochel, *Angew. Chem. Int. Ed.* **2006**, *45*, 606–609; *Angew. Chem.* **2006**, *118*, 621–623; d) G. Palumbo, C. Ferri, C. D'Ambrosio, R. Caputo, *Phosphorus Sulfur* **1984**, *19*, 235–238.
- [7] a) B. L. Truesdell, T. B. Hamby, C. S. Sevov, *J. Am. Chem. Soc.* **2020**, *142*, 5884–5893; b) G. S. Kumar, A. Peshkov, A. Brzozowska, P. Nikolaienko, C. Zhu, M. Rueping, *Angew. Chem. Int. Ed.* **2020**, *59*, 6513–6519; *Angew. Chem.* **2020**, *132*, 6575–6581; c) K.-J. Jiao, D. Liu, H.-X. Ma, H. Qiu, P. Fang, T.-S. Mei, *Angew. Chem. Int. Ed.* **2020**, *59*, 6520–6524; *Angew.*

- Chem.* **2020**, *132*, 6582–6586; d) N. W. J. Ang, J. C. A. Oliveira, L. Ackermann, *Angew. Chem. Int. Ed.* **2020**, *59*, 12842–12847; *Angew. Chem.* **2020**, *132*, 12942–12947; e) E. L. Lucas, E. R. Jarvo, *Nat. Rev. Chem.* **2017**, *1*, 0065; f) D. J. Weix, *Acc. Chem. Res.* **2015**, *48*, 1767–1775; g) T. Moragas, A. Correa, R. Martin, *Chem. Eur. J.* **2014**, *20*, 8242–8258; h) C. E. I. Knappke, S. Grupe, D. Gärtner, M. Corpet, C. Gosmini, A. Jacobi von Wangelin, *Chem. Eur. J.* **2014**, *20*, 6828–6842.
- [8] a) S.-K. Zhang, J. Struwe, L. Hu, L. Ackermann, *Angew. Chem. Int. Ed.* **2020**, *59*, 3178–3183; *Angew. Chem.* **2020**, *132*, 3204–3209; b) S.-K. Zhang, R. C. Samanta, A. Del Vecchio, L. Ackermann, *Chem. Eur. J.* **2020**, *26*, 10936–10947; c) J. C. Siu, N. Fu, S. Lin, *Acc. Chem. Res.* **2020**, *53*, 547–560; d) R. C. Samanta, T. H. Meyer, I. Siewert, L. Ackermann, *Chem. Sci.* **2020**, *11*, 8657–8670; e) K.-J. Jiao, Y.-K. Xing, Q.-L. Yang, H. Qiu, T.-S. Mei, *Acc. Chem. Res.* **2020**, *53*, 300–310; f) C. Zhu, M. Stangier, J. C. A. Oliveira, L. Massignan, L. Ackermann, *Chem. Eur. J.* **2019**, *25*, 16382–16389; g) T. H. Meyer, J. C. A. Oliveira, S. C. Sau, N. W. J. Ang, L. Ackermann, *ACS Catal.* **2018**, *8*, 9140–9147.
- [9] a) J. L. Röckl, D. Pollok, R. Franke, S. R. Waldvogel, *Acc. Chem. Res.* **2020**, *53*, 45–61; b) S. D. Minter, P. Baran, *Acc. Chem. Res.* **2020**, *53*, 545–546; c) L. Ackermann, *Acc. Chem. Res.* **2020**, *53*, 84–104; d) H. Wang, X. Gao, Z. Lv, T. Abdellilah, A. Lei, *Chem. Rev.* **2019**, *119*, 6769–6787; e) N. Shida, Y. Zhou, S. Inagi, *Acc. Chem. Res.* **2019**, *52*, 2598–2608; f) M. Elsherbini, T. Wirth, *Acc. Chem. Res.* **2019**, *52*, 3287–3296; g) N. Saueremann, T. H. Meyer, Y. Qiu, L. Ackermann, *ACS Catal.* **2018**, *8*, 7086–7103; h) N. Saueremann, T. H. Meyer, L. Ackermann, *Chem. Eur. J.* **2018**, *24*, 16209–16217; i) K. D. Moeller, *Chem. Rev.* **2018**, *118*, 4817–4833; j) Y. Jiang, K. Xu, C. Zeng, *Chem. Rev.* **2018**, *118*, 4485–4540; k) N. Fu, G. S. Sauer, S. Lin, *Nat. Protoc.* **2018**, *13*, 1725–1743; l) M. Yan, Y. Kawamata, P. S. Baran, *Chem. Rev.* **2017**, *117*, 13230–13319; m) E. J. Horn, B. R. Rosen, P. S. Baran, *ACS Cent. Sci.* **2016**, *2*, 302–308; n) R. Francke, R. D. Little, *Chem. Soc. Rev.* **2014**, *43*, 2492–2521; o) J. B. Sperry, D. L. Wright, *Chem. Soc. Rev.* **2006**, *35*, 605–621; p) T. Shono, *Tetrahedron* **1984**, *40*, 811–850.
- [10] a) Y. Wang, L. Deng, X. Wang, Z. Wu, Y. Wang, Y. Pan, *ACS Catal.* **2019**, *9*, 1630–1634; b) D. Liu, H.-X. Ma, P. Fang, T.-S. Mei, *Angew. Chem. Int. Ed.* **2019**, *58*, 5033–5037; *Angew. Chem.* **2019**, *131*, 5087–5091.
- [11] a) A. S. Surur, L. Schulig, A. Link, *Arch. Pharm. Chem. Life Sci.* **2019**, *352*, e1800248; b) M. Feng, B. Tang, S. H. Liang, X. Jiang, *Curr. Top. Med. Chem.* **2016**, *16*, 1200–1216; c) A. V. Bogolubsky, Y. S. Moroz, P. K. Mykhailiuk, E. N. Ostapchuk, A. V. Rudnichenko, Y. V. Dmytriv, A. N. Bondar, O. A. Zaporozhets, S. E. Pipko, R. A. Doroschuk, L. N. Babichenko, A. I. Konovets, A. Tolmachev, *ACS Comb. Sci.* **2015**, *17*, 348–354; d) H. L. Holland, *Nat. Prod. Rep.* **2001**, *18*, 171–181.
- [12] D. L. Davies, S. A. Macgregor, A. I. Poblador-Bahamonde, *Dalton Trans.* **2010**, *39*, 10520–10527.
- [13] a) C. Schöneich, *Molecules* **2019**, *24*, 4357; b) F. Dénès, M. Pichowicz, G. Povie, P. Renaud, *Chem. Rev.* **2014**, *114*, 2587–2693; c) R. P. Steer, B. L. Kalra, A. R. Knight, *J. Phys. Chem.* **1967**, *71*, 783–784.
- [14] a) G. Roos, F. De Proft, P. Geerlings, *Chem. Eur. J.* **2013**, *19*, 5050–5060; b) D. A. Armstrong, Q. Sun, R. H. Schuler, *J. Phys. Chem.* **1996**, *100*, 9892–9899; c) P. S. Surdhar, D. A. Armstrong, *J. Phys. Chem.* **1987**, *91*, 6532–6537; d) P. Surdhar, D. A. Armstrong, *J. Phys. Chem.* **1986**, *90*, 5915–5917.
- [15] a) Y. Kawamata, J. C. Vantourout, D. P. Hickey, P. Bai, L. Chen, Q. Hou, W. Qiao, K. Barman, M. A. Edwards, A. F. Garrido-Castro, J. N. deGruyter, H. Nakamura, K. Knouse, C. Qin, K. J. Clay, D. Bao, C. Li, J. T. Starr, C. Garcia-Irizarry, N. Sach, H. S. White, M. Neurock, S. D. Minter, P. S. Baran, *J. Am. Chem. Soc.* **2019**, *141*, 6392–6402; b) M. Durandetti, J. Maddaluno, in *Encyclopedia of Reagents for Organic Synthesis*, Wiley, **2014**, pp. 1–6; c) I. Zilbermann, E. Maimon, H. Cohen, D. Meyerstein, *Chem. Rev.* **2005**, *105*, 2609–2626; d) A. G. Lappin, A. McAuley, *Adv. Inorg. Chem.* **1988**, *32*, 241–295.
- [16] a) L. Muchez, D. E. De Vos, M. Kim, *ACS Sustainable Chem. Eng.* **2019**, *7*, 15860–15864; b) C. Li, X. Tong, P. Yu, W. Du, J. Wu, H. Rao, Z. M. Wang, *J. Mater. Chem. A* **2019**, *7*, 16622–16642; c) B. Shan, R. Schmehl, *J. Phys. Chem. A* **2014**, *118*, 10400–10406; d) S. Maity, N. Zheng, *Synlett* **2012**, *23*, 1851–1856; e) R. D. Richardson, E. J. Holland, B. K. Carpenter, *Nat. Chem.* **2011**, *3*, 301–303; f) D. R. Prasad, M. Z. Hoffman, *J. Phys. Chem.* **1984**, *88*, 5660–5665.
- [17] a) G. T. Venkanna, H. D. Arman, Z. J. Tonzetich, *ACS Catal.* **2014**, *4*, 2941–2950; b) S. Biswas, D. J. Weix, *J. Am. Chem. Soc.* **2013**, *135*, 16192–16197.
- [18] D. Vasudevan, *Russ. J. Electrochem.* **2005**, *41*, 310–314.
- [19] a) V. B. Mostardeiro, M. C. Dilelio, T. S. Kaufman, C. C. Silveira, *RSC Adv.* **2020**, *10*, 482–491; b) E. Dmitrieva, X. Yu, H. Hartmann, *Electrochem. Commun.* **2020**, *114*, 106706; c) B. Janhsen, C. G. Daniliuc, A. Studer, *Chem. Sci.* **2017**, *8*, 3547–3553.

Manuscript received: December 23, 2020

Accepted manuscript online: December 28, 2020

Version of record online: February 15, 2021