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# Paired Electrosynthesis of Aromatic Azo Compounds from Aryl Diazonium Salts with Pyrroles or Indoles

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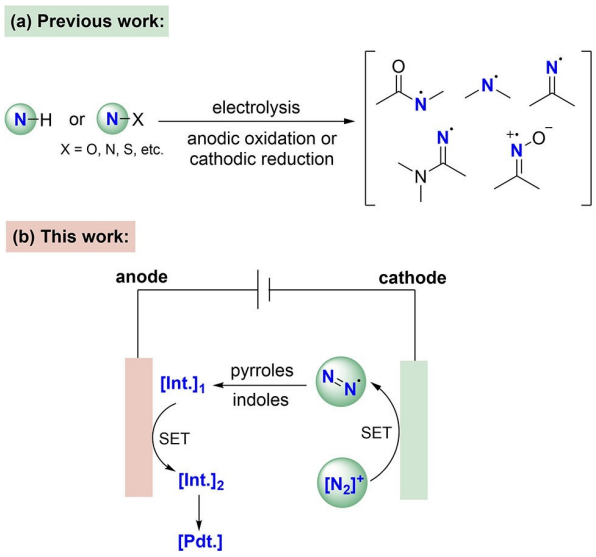
**Abstract:** An efficient paired electrosynthesis of functionalized aromatic azo compounds through a diazenyl radical pathway has been developed. The paired electrolysis simultaneously uses the anode and cathode reactions to avoid the electricity expense of oxidation/reduction of sacrificial substances, thereby maximizing energy efficiency and achieving high atom economy. The in vitro cytotoxicity of all compounds was evaluated against four cancer cell lines by MTT assay. Results showed that the aromatic azo compounds exhibited good antitumor activity in vitro, and one of the compounds induced tumor cell apoptosis.

**Keywords:** Paired electrolysis; N-centered radical; Diazenyl radical; Antitumor activity

Nitrogen-centered radicals are a class of universal intermediates that construct nitrogen-containing compounds in a wide range of chemical transformations.[1] Organic electrochemistry promotes chemical transformations through electron transfer, which has become an efficient synthetic technique to generate nitrogen-centered radicals in recent years.[2] At present, various N-centered radicals have been produced using electrochemical techniques, such as amidyl, amidinyl, iminyl and iminoxyl radicals, and many important skeletons have been synthesized by them (Scheme 1a).[2,3] For instance, Waldvogel and Moeller's group reported the electrochemical synthesis of amidyl radical from anilides to directly construct benzoxazoles.[4] Xu's group exploited amidinyl and iminyl radicals for the preparation of polycyclic imidazole derivatives and assorted pyridine-fused polycyclic N-heteroaromatic compounds under electrochemical conditions, respectively.[5,6] As an important structural motif of nitrogen-containing compounds, azo compounds are not only important synthetic colorants in the dye industry, but also used as indicators or food additives.[7] The electrophilic diazonium function allows the addition of nucleophiles to provide azo compounds, and the diazonium salts substituted with electron-withdrawing substituents show high chemical selectivity.[8] When the aryl diazonium salt undergoes a free radical mechanism reaction, the electron donating substitution generally obtains a higher yield.[9] Although many methods can be used to generate diazenyl radicals,[10] the synthesis of azo compounds by electrolysis-generating diazenyl radical has not been reported yet.

Organic electrosynthesis is a controllable and green synthesis tool.[11] In most electrochemical conversions, either anodic oxidation or cathodic reduction can obtain the desired products. However, only one electrode is used to convert the reaction substrate, and some sacrificial reagents (protic solvents, metal electrodes, and electrolytes) are usually required to promote the reaction on the counter electrode.[12] By contrast, paired electrolysis simultaneously uses both anode and cathode reactions to synthesize the target compound, which avoids the electricity expense of oxidation/reduction of sacrificial substances, thereby maximizing energy efficiency and achieving high atom economy.[13] Therefore, we report herein that the reduction reaction of aryl diazonium salts at the cathode produces diazenyl radical, which then dissociate to the anode and react with functionalized



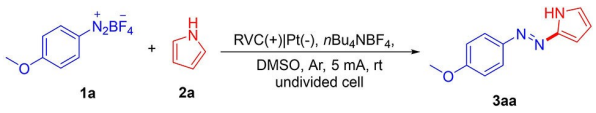

**Scheme 1.** Generation of various N-centered radicals via electrolysis.

pyrroles or indoles to construct pharmacologically active aromatic azo compounds (Scheme 1b).

We first chose aryl diazonium salt **1 a** and pyrrole **2 a** as model substrates to optimize the electrolysis reaction conditions (Tables 1 and S1). The results of electrolysis were optimal when the reaction was carried out at a constant current of 5 mA in an undivided cell equipped with reticulated vitreous carbon (RVC) anode and Pt plate cathode and when $n$Bu$_4$NBF$_4$ was the electrolyte in solvent DMSO at room temperature and under argon protection (entry 1). The control experiment verified the necessity of each reaction condition. In the absence of electricity, the desired product **3 aa** cannot be obtained (entry 2). Under air conditions, the yield of **3 aa** dropped to 73% (entry 3). The reaction at 60 °C resulted in a sharp decline in yield (entry 4). Other solvents such as EtOH (entry 5), $CH_3CN$ (entry 6), DMF (entry 7) and $CH_2Cl_2$ (entry 8) had lower reaction yields than DMSO. The changes of electrolyte had a negative effect on the yield of **3 aa** (entries 9–10). Under different constant currents, the results showed that increasing (Table S1, entry 1) and decreasing (Table S1, entry 2) the current both lead to a decrease in the yield. We also tested the yields change under different electrode conditions, and the yield decreased to different degrees (Table S1, entries 3–5).

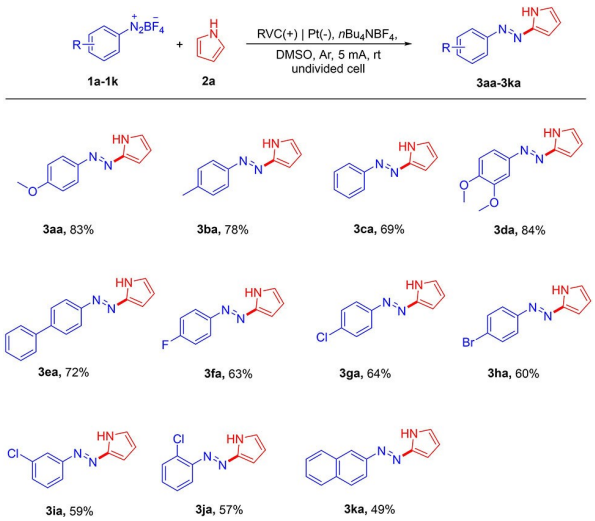
With the clarification of the optimal reaction conditions, we first conducted a substrate range analysis by changing the substituents of the aryl diazonium salt (Scheme 2). In the absence of substituents, aryl diazonium salt **1 c** reacts with pyrrole **2 a** to yield product **3 ca** at 69%. The para position of aryl diazonium salt can replace electron-donating OMe (**3 aa**, 83%), Me (**3 ba**, 78%), and electron-withdrawing halogens (e.g., F [**3 fa**, 63%], Cl [**3 ga**, 64%], and Br [**3 ha**, 60%]), which have good yields. Moreover, compound **3 ga** confirmed the crystal structure.[14] Given that the former has a strong electron-donating ability, the yield of electron-donating groups is higher than that of electron-withdrawing groups. Because

**Table 1.** Optimization of the reaction conditions.[a]




| Entry | Variation from standard conditions | Yield[b] (%) |
|---|---|---|
| 1 | none | 83 |
| 2 | no electricity | NR |
| 3 | under air | 73 |
| 4 | reaction at 60 °C | 42 |
| 5 | EtOH as solvent | 27 |
| 6 | $CH_3CN$ as solvent | trace |
| 7 | DMF as solvent | 64 |
| 8 | $CH_2Cl_2$ as solvent | 46 |
| 9 | $n$BuNPF$_6$ as electrolyte | 77 |
| 10 | Et$_4$NBF$_4$ as electrolyte | 79 |

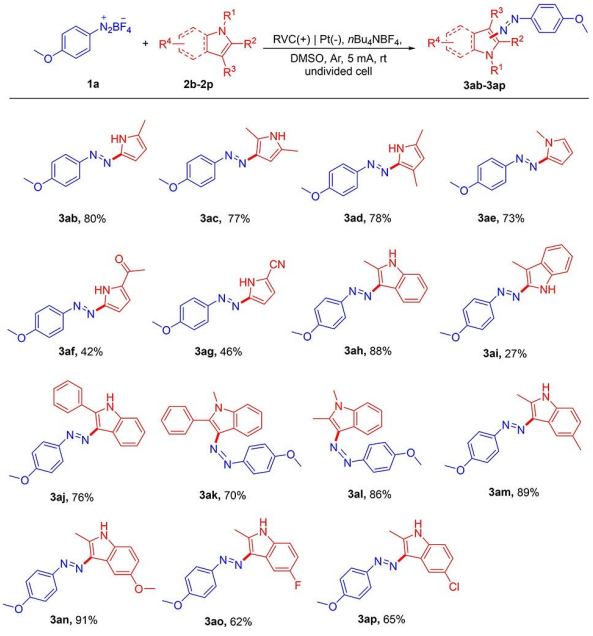
[a] Reaction conditions: Reticulated vitreous carbon (RVC) anode (100 PPI, 1 cm × 1 cm × 1.2 cm), Pt plate cathode (1 cm × 1 cm), undivided cell, **1 a** (0.3 mmol, 1.0 equiv.), **2 a** (0.9 mmol, 3.0 equiv.), electrolyte (1.0 equiv.), DMSO (6 mL), room temperature, argon, 5 mA, 2 h (1.2 F mol$^{-1}$).
[b] Isolated yields. NR = no reaction.




**Scheme 2.** Substrate scope of aryl diazonium salts. [a]Reaction conditions: reticulated vitreous carbon (RVC) anode (100 PPI, 1 cm × 1 cm × 1.2 cm), Pt plate cathode (1 cm × 1 cm), undivided cell, constant current = 5 mA, **1 a–1 k** (0.3 mmol, 1.0 equiv.), **2 a** (0.9 mmol, 3.0 equiv.), $n$Bu$_4$NBF$_4$ (1.0 equiv.), DMSO (6 mL), room temperature, argon, 5 mA, 2 h. Isolated yields.

diazenyl radicals are considered to be electrophilic species due to the negatively polarized N=N group, which require electron-donating substrate **1** to stabilize and then tend to react with electron-rich substrate **2**. The methoxy disubstituted product can be obtained with a yield of 84% (**3da**). Moderate yields were also obtained in the meta- and ortho-substitutions of aryl diazonium salts (**3ia**, 59%; **3ja**, 57%). Both biphenyl-diazonium salt (**3ea**, 72%) and naphthalene diazonium salt (**3ka**, 49%) reacted with pyrrole to obtain moderate yields.

A series of aryl azo compounds was synthesized by the reaction of aryl diazonium salt **1a** with pyrrole derivatives (Scheme 3). First, monomethyl and polymethyl substituted pyrroles can be involved in the reaction to obtain a good yield (**3ab**–**3ad**, 77%–80%). As a substrate, 1-methylpyrrole can also be used to obtain a good yield (**3ae**, 73%). Electron-withdrawing group-substituted pyrroles, such as 2-acetylpyrrole (**2f**) and pyrrole-2-carbonitrile (**2g**), react with **1a** to obtain lower yields. The aryl diazonium salt **1a** reacts with 2-methylindole (**2h**) and 3-methylindole (**2i**) to get a large difference, and the results showed that it is easier to attach to the third position of indoles. The participation of 2-phenylindole in the reaction also resulted in good yield (**3aj**, 76%). 1-Methylindole, which has a substituent at the 2-position can also give the products with a good yield (**3ak**, 70%; **3al**, 86%).

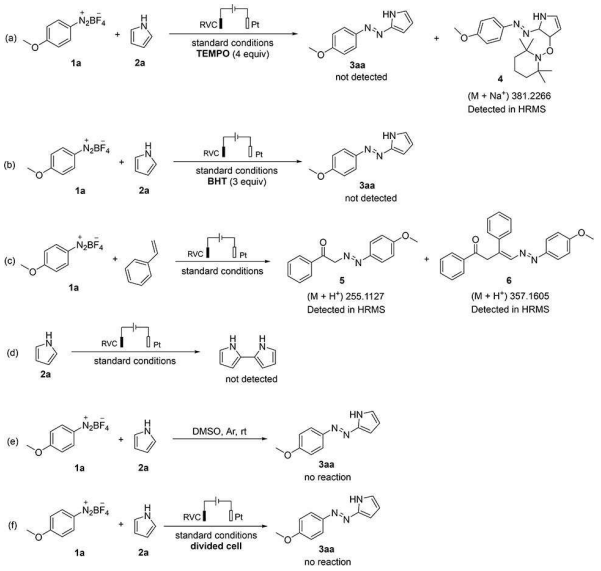



**Scheme 3.** Substrate scope of pyrroles. [a]Reaction conditions: reticulated vitreous carbon (RVC) anode (100 PPI, 1 cm × 1 cm × 1.2 cm), Pt plate cathode (1 cm × 1 cm), undivided cell, constant current = 5 mA, **1a** (0.3 mmol, 1.0 equiv.), **2b**–**2p** (0.9 mmol, 3.0 equiv.), $nBu_4NBF_4$ (1.0 equiv.), DMSO (6 mL), room temperature, argon, 5 mA, 2 h. Isolated yields.

The reaction of substrates with substituents on the indolebenzene ring with aryl diazonium salt **1a** resulted in a series of moderate yields (**3am**–**3ap**, 62%–91%). Among them, the electron-donating group-substituted substrates have a higher yield than the electron-withdrawing group substrates.

We conducted some control experiments to study the mechanism of this reaction (Scheme 4). The azo compound **3aa** was not detected by adding 4 equiv. TEMPO (Scheme 4a) or 3 equiv. BHT (Scheme 4b) to the optimal reaction system. Product **4** can be detected by HRMS when adding 4 equiv. TEMPO (Scheme 4a). The reaction of aryl diazonium salt **1a** with styrene was carried out under standard conditions, and the desired products **5** and **6** were detected by HRMS (Scheme 4c). According to the above experimental results, the radical intermediates are involved in the electrocatalytic reaction. In the absence of other reactants, pyrrole **2a** did not dimerize under standard conditions (Scheme 4d). This result indicated that pyrrole is not oxidized to the pyrrole radical cation on the anode.[15] In the absence of current and electrolyte, the reaction of **1a** and **2a** did not produce the target product **3aa** (Scheme 4e). We operated the reaction in the divided cell, and the results showed that the target product **3aa** was not produced at either anode or cathode (Scheme 4f). The above reaction results indicated that the aryl diazonium salt did not react with pyrrole in the form of a radical cation, but was reduced to a radical intermediate to participate in the reaction process.

Based on the above experiments and cyclic voltammetry experiments (Figure S2), we proposed a possible reaction mechanism with **1b** and **2a** as substrates under electrochemical conditions

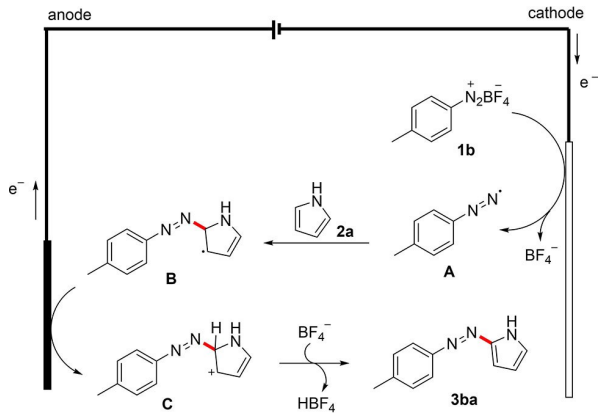



**Scheme 4.** Control Experiments.

(Scheme 5). First, the aryl diazonium salt **1b** was reduced to aryldiazenyl radical intermediate **A** at the cathode,[16] and the tetrafluoroborate anion was formed. Aryldiazenyl radical intermediate **A** reacted with pyrrole **2a** to generate radical intermediate **B**. Radical intermediate **B** was oxidized to cation intermediate **C** at the anode. Subsequently, intermediate **C** was deprotonated by tetrafluoroborate and finally formed the target azo product **3ba**.

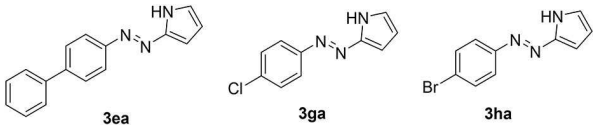
The proposed reaction mechanism can be demonstrated by the cyclic voltammetry experiment (Figure S2). According to the cyclic voltammograms, there is a reduction peak (−1.201 V vs. $Fc/Fc^+$) when only the aryl diazonium salt **1b** is present (Figure S2-1, curve b), indicating that it has undergone a cathodic reduction process without an anodic oxidation process. There is no redox peak when only pyrrole **2a** exists (Figure S2-2, curve c), showing that there is no redox process. In the cyclic voltammograms of **1b** in the presence **2a** (Figure S2-3, curve d), there is a reduction peak (−1.201 V vs. $Fc/Fc^+$) and an oxidation peak (1.294 V vs. $Fc/Fc^+$), implying that the aryl diazonium salt **1b** was reduced to intermediate **A** first, and intermediate **A** reacted with **2a** to form intermediate **B**, then intermediate **B** was anodized to intermediate **C**. Finally, the intermediate **C** was deprotonated to generate the target compound **3ba**. The curve of the synthesized compound **3ba** shows no redox peak (Figure S2-4, curve e), indicating that the synthesized compound has no further redox process.

As mentioned above, aromatic azo compounds can not only be used as dyes and photoswitches, but also have good biological activity. Here, compounds **3aa**–**3ka** and **3ab**–**3ap** were used to conduct in vitro cytotoxicity study of four cancer cell lines, Hela, T-24, SKOV3, and MGC-803, via MTT assay, which were screened using 5-FU as the positive control. As shown in Table 2, the $IC_{50}$ value of compound **3ga** was 3.3 ± 0.9 μM, showing good antitumor activity against the T-24 cell lines. In addition, the $IC_{50}$ value of compound




**Scheme 5.** Proposed mechanism.

**Table 2.** $IC_{50}$ (μM) values for compounds **3ea**, **3ga** and **3ha**.




| Compounds | HeLa | T-24 | SKOV3 | MGC-803 |
|---|---|---|---|---|
| **3ea** | 3.2 ± 1.2 | 1.5 ± 1.3 | 10.5 ± 0.8 | 5.4 ± 1.3 |
| **3ga** | 4.5 ± 1.4 | 3.3 ± 0.9 | 10.4 ± 1.5 | 6.2 ± 2.0 |
| **3ha** | 7.9 ± 1.3 | 5.8 ± 0.4 | 12.6 ± 0.7 | 9.5 ± 1.9 |

**3ea** on the T-24 cell line was 1.5 ± 1.3 μM, which indicated a significant inhibitory effect on tumor cells. On the basis of these results, the antitumor mechanism of **3ea** on the T-24 cell line was further studied. Detailed experimental results are described in the **Supporting Information**.

In summary, we have developed a method to synthesize pharmacologically active aromatic azo compounds through the reaction of functionalized pyrroles or indoles with aryl diazonium salts under paired electrolysis conditions. Under our paired electrosynthesis conditions, the diazonium salt was reduced to the diazenyl intermediate at the cathode to promote the reaction process, which uses both anode and cathode reactions to achieve high atom economy and maximize energy efficiency. The in vitro cytotoxicity of all compounds against four cancer cell lines was screened by using MTT assay. Among them, compounds **3ea**, **3ga**, and **3ha** all showed good antitumor activity against the T-24 tumor cell line. Preliminary analysis on the mechanism of action showed that compound **3ea** inhibited T-24 cell apoptosis.

## Experimental Section

### Synthesis of Aromatic Azo Compounds

A 10 mL three-necked round-bottomed flask was charged with aryl diazonium salts (0.3 mmol, 1.0 equiv.), pyrrole derivatives (0.9 mmol, 3.0 equiv.), and $nBu_4NBF_4$ (0.3 mmol, 1 equiv.). The flask was equipped with a reticulated vitreous carbon RVC (100 PPI, 1 cm × 1 cm × 1.2 cm) anode and a platinum plate (1 cm × 1 cm) cathode. DMSO (6 mL) was added. Electrolysis was carried out at room temperature using a constant current of 5 mA until the substrate was completely consumed (monitored by TLC, about 2 h). After the reaction was completed, the solvent was extracted with ethyl acetate. The aqueous phase was extracted with ethyl acetate (3 × 30 mL). The combined organic solution was washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The resulting solution was purified by silica gel column chromatography using ethyl acetate/petroleum ether to afford the desired products.

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## References

[1] a) S. Z. Zard, *Chem. Soc. Rev.* **2008**, *37*, 1603–1618; b) X.-Y. Yu, Q.-Q. Zhao, J. Chen, W.-J. Xiao, J.-R. Chen, *Acc. Chem. Res.* **2020**, *53*, 1066–1083; c) T. Xiong, Q. Zhang, *Chem. Soc. Rev.* **2016**, *45*, 3069–3087; d) J.-R. Chen, X.-Q. Hu, L.-Q. Lu, W.-J. Xiao, *Chem. Soc. Rev.* **2016**, *45*, 2044–2056; e) H. Jiang, A. Studer, *CCS Chem.* **2019**, *1*, 38–49; f) L.-Y. Xie, Y.-S. Bai, X.-Q. Xu, X. Peng, H.-S. Tang, Y. Huang, Y.-W. Lin, Z. Cao, W.-M. He, *Green Chem.* **2020**, *22*, 1720–1725.

[2] a) P. Xiong, H.-C. Xu, *Acc. Chem. Res.* **2019**, *52*, 3339–3350; b) M. D. Kärkäs, *Chem. Soc. Rev.* **2018**, *47*, 5786–5865.

[3] a) H.-B. Zhao, P. Xu, J. Song, H.-C. Xu, *Angew. Chem. Int. Ed.* **2018**, *57*, 15153–15156; b) S. Zhang, L.-J. Li, M.-Y. Xue, R. Zhang, K. Xu, C.-C. Zeng, *Org. Lett.* **2018**, *20*, 3443–3446; c) P. Zhang, B.-Y. Li, L.-W. Niu, L. Wang, G.-F. Zhang, X.-F. Jia, G.-Y. Zhang, S.-Y. Liu, G. Wei, D.-W. Qin, J.-B. Chen, *Adv. Synth. Catal.* **2020**, *362*, 2342–2347; d) S. Lv, X.-X. Han, J.-Y. Wang, M.-Y. Zhou, Y.-W. Wu, L. Ma, L.-W. Niu, G. Wei, J.-H. Zhou, W. Hu, Y.-Z. Cui, J.-B. Chen, *Angew. Chem. Int. Ed.* **2020**, *59*, 11583–11590; e) Y. Li, Z.-H. Ye, N. Chen, Z.-K. Chen, F.-Z. Zhang, *Green Chem.* **2019**, *21*, 4035–4039; f) N. Lei, Y.-L. Shen, Y.-J. Li, P. Tao, L.-Q. Yang, Z.-S. Su, K. Zheng, *Org. Lett.* **2020**, doi: 10.1021/acs.orglett.0c03158.

[4] T. Gieshoff, A. Kehl, D. Schollmeyer, K. D. Moeller, S. R. Waldvogel, *Chem. Commun.* **2017**, *53*, 2974–2977.

[5] H.-B. Zhao, Z.-W. Hou, Z.-J. Liu, Z.-F. Zhou, J. Song, H.-C. Xu, *Angew. Chem. Int. Ed.* **2017**, *56*, 587–590.

[6] H.-B. Zhao, Z.-J. Liu, J. Song, H.-C. Xu, *Angew. Chem. Int. Ed.* **2017**, *56*, 12732–12735.

[7] a) E. Merino, *Chem. Soc. Rev.* **2011**, *40*, 3835–3853; b) T. Fehrentz, M. Schönberger, D. Trauner, *Angew. Chem. Int. Ed.* **2011**, *50*, 12156–12182; c) S. H. Lee, E. Moroz, B. Castagner, J. C. Leroux, *J. Am. Chem. Soc.* **2014**, *136*, 12868–12871; d) B. Mondal, P. S. Mukherjee, *J. Am. Chem. Soc.* **2018**, *140*, 12592–12601.

[8] Z. Lu, O. Hennis, J. Gentry, B. Xu, G. B. Hammond, *Org. Lett.* **2020**, *22*, 4383–4388.

[9] a) P. Wang, Z. Yang, Z. Wang, C. Xu, L. Huang, S. Wang, H. Zhang, A. Lei, *Angew. Chem. Int. Ed.* **2019**, *58*, 15747–15751; b) Y.-Y. Jiang, G.-Y. Dou, L.-S. Zhang, K. Xu, R. D. Little, C.-C. Zeng, *Adv. Synth. Catal.* **2019**, *361*, 5170–5175.

[10] a) H. Othman Abdulla, S. Scaringi, A. A. Amin, M. Mella, S. Protti, M. Fagnoni, *Adv. Synth. Catal.* **2020**, *362*, 2150–2154; b) D. S. Barak, S. U. Dighe, I. Avasthi, S. Batra, *J. Org. Chem.* **2018**, *83*, 3537–3546; c) M. R. Heinrich, O. Blank, A. Wetzel, *J. Org. Chem.* **2007**, *72*, 476–484; d) M. N. Weaver, S. Z. Janicki, P. A. Petillo, *J. Org. Chem.* **2001**, *66*, 1138–1145; e) W. Adam, M. Dörr, *J. Am. Chem. Soc.* **1987**, *109*, 1240–1241.

[11] a) Y. Jiang, K. Xu, C.-C. Zeng, *Chem. Rev.* **2017**, *118*, 4485–4540; b) M. Yan, Y. Kawamata, P. S. Baran, *Chem. Rev.* **2017**, *117*, 13230–13319; c) P.-F. Zhong, H.-M. Lin, L.-W. Wang, Z.-Y. Mo, X.-J. Meng, H.-T. Tang, Y.-M. Pan, *Green Chem.* **2020**, *22*, 6334–6339; d) X.-Y. Wang, Y.-F. Zhong, Z.-Y. Mo, S.-H. Wu, Y.-L. Xu, H.-T. Tang, Y.-M. Pan, *Adv. Synth. Catal.* **2020**, 363, 208–214; e) X.-J. Meng, P.-F. Zhong, Y.-M. Wang, H.-S. Wang, H.-T. Tang, Y.-M. Pan, *Adv. Synth. Catal.* **2020**, *362*, 506–511; f) J.-S. Li, P.-P. Yang, X.-Y. Xie, S. Jiang, L. Tao, Z.-W. Li, C.-H. Lu, W.-D. Liu, *Adv. Synth. Catal.* **2020**, *362*, 1977–1981; g) Y.-Z. Zhang, Z.-Y. Mo, H.-S. Wang, X.-A. Wen, H.-T. Tang, Y.-M. Pan, *Green Chem.* **2019**, *21*, 3807–3811; h) H. Goljani, Z. Tavakkoli, A. Sadatnabi, D. Nematollahi, *Org. Lett.* **2020**, *22*, 5920–5924.

[12] a) Y. Yuan, A. Lei, *Acc. Chem. Res.* **2019**, *52*, 3309–3324; b) R. Francke, R. D. Little, *Chem. Soc. Rev.* **2014**, *43*, 2492–2521; c) Y. Yuan, A. Lei, *Nat. Commun.* **2020**, *11*, 802–804; d) M.-X. He, Z.-Y. Mo, Z.-Q. Wang, S.-Y. Cheng, R.-R. Xie, H.-T. Tang, Y.-M. Pan, *Org. Lett.* **2020**, *22*, 724–728; e) K. Sun, J. Lei, Y.-J. Liu, B. Liu, N. Chen, *Adv. Synth. Catal.* **2020**, *362*, 3709–3726.

[13] a) M. J. Llorente, B. H. Nguyen, C. P. Kubiak, K. D. Moeller, *J. Am. Chem. Soc.* **2016**, *138*, 15110–15113; b) T. H. Meyer, I. Choi, C. Tian, L. Ackermann, *Chem* **2020**, *6*, 1–13; c) T. Wu, B. H. Nguyen, M. C. Daugherty, K. D. Moeller, *Angew. Chem. Int. Ed.* **2019**, *58*, 3562–3565; d) R. S. Sherbo, R. S. Delima, V. A. Chiykowski, B. P. MacLeod, C. P. Berlinguette, *Nature Catalysis* **2018**, *1*, 501–507; e) X. Chong, C. Liu, Y. Huang, C. Huang, B. Zhang, *Natl. Sci. Rev.* **2020**, *7*, 285–295; f) Y. Zhao, C. Liu, C. Wang, X. Chong, B. Zhang, *CCS Chem.* **2020**, *2*, 507–515.

[14] "CCDC-2035295 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.".

[15] a) S. Sadki, P. Schottland, N. Brodie, G. Sabouraud, *Chem. Soc. Rev.* **2000**, *29*, 283–293; b) J. K. Laha, M. Kaur Hunjan, S. Hegde, A. Gupta, *Org. Lett.* **2020**, *22*, 1442–1447.

[16] a) R. Pazo-Llorente, C. Bravo-Díaz, E. González-Romero, *Fresenius J. Anal. Chem.* **2001**, *369*, 582–586; b) J. G. Green, G. R. Dubay, N. A. Porter, *J. Am. Chem. Soc.* **1977**, *99*, 1264–1265; c) T. Suehiro, T. Tashiro, R. Nakausa, *Chem. Lett.* **1980**, *11*, 1339–1342; d) T. Suehiro, S. Masuda, T. Tashiro, R. Nakausa, M. Taguchi, A. Koike, A. Rieker, *Bull. Chem. Soc. Jpn.* **1986**, *59*, 1877–1886.

## COMMUNICATIONS

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