

## REVIEW

View Article Online  
View Journal | View IssueCite this: *Org. Chem. Front.*, 2024,  
11, 4318

# Electroreduction strategy: a sustainable tool for the generation of aryl radicals

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Aryl radicals are important and versatile active intermediates in synthetic chemistry, and the chemical conversions involved are regarded as perfect complements to the transition-metal-catalyzed arylation reactions. The formation of aryl radicals is mainly achieved through reductive systems. Electrocatalysis has a safe and controllable potential range that can easily attain a reduction potential beyond the range of chemical reductants and excited photocatalysts, offering a synthetically attractive and environmentally friendly alternative for the production of aryl radicals. Remarkable achievements in the electrochemical functionalization of aryl radicals have been reported. This review primarily focuses on the generation of aryl radicals *via* an electroreduction strategy, and systematically elaborates on synthetic applications, scope, and limitations of the substrates. The full spectrum of aryl radical precursors applied in the electroreduction strategy, including aryl halides, aryl diazonium salts, arylazo sulfones, aryl amines, nitroarenes, aryl quaternary ammonium salts, aryl triflates, and aryl thianthrenium salts, is reviewed.

Received 12th May 2024,  
Accepted 14th June 2024

DOI: 10.1039/d4qo00846d

rsc.li/frontiers-organic

## 1. Introduction

Aryl radicals prove to be versatile active intermediates, playing a significant role in synthetic chemistry, agricultural chemistry, materials science, and pharmaceutical discovery.<sup>1</sup> Since the advent of the Meerwein arylation reaction in the 1940s,<sup>2</sup> a considerable number of synthetic chemists have employed the conversions of aryl radicals as ideal supplements to transition-metal-catalyzed arylation reactions, which has yielded novel, promising alternatives for the introduction of aryl and heteroaryl moieties into molecular scaffolds. Various compounds, such as aryl halides,<sup>3</sup> aryl diazonium salts,<sup>4</sup> aryl carboxylic acids,<sup>5</sup> aryl triflates,<sup>6</sup> hypervalent iodine(III) reagents,<sup>7</sup> aryl borates,<sup>8</sup> and aryl sulfonium salts,<sup>9</sup> have been successfully used as aryl radical precursors.

Historically, the generation of aryl radicals has relied primarily on the utilization of stoichiometric reagents (*e.g.*, reductants and oxidants), such as AIBN/*n*-Bu<sub>3</sub>SnH systems for aryl halides or stoichiometric transition-metal reductants for aryl diazonium salts.<sup>10</sup> Furthermore, these methods frequently suffer from poor selectivity, limited substrate and radical precursor scopes, and the formation of undesired by-products,

which substantially limit their widespread application in organic synthesis.

The “dual carbon goal” is driving the search for efficient and sustainable catalytic strategies in the generation of aryl radicals to meet the increasingly specific requirements of synthetic chemistry relating to conversion modes, catalytic activity, and reaction selectivity. Photoredox and electrochemical strategies, especially burgeoning electrochemical strategies, prove to be green and powerful alternatives for the generation of aryl radicals.<sup>1c</sup> Electrocatalysis is becoming increasingly popular for the synthesis of structurally diverse and high-value-added organic frameworks, as it employs “traceless” electrons as clean and renewable reagents.<sup>11</sup> This synthetic technology offers distinctive advantages for discovering new reactions and phenomena, as well as providing an environmentally benign and technically attractive platform for the generation of aryl radicals. Mechanistically, aryl radicals can be generated in two ways under electrochemical conditions: anodic oxidation and cathodic reduction of radical precursors. Currently, significant progress has been made in the generation of aryl radicals by anodic oxidation. Several types of aryl radical precursors, such as arylhydrazines, aryl trifluoroborates and electron-rich aromatics, have been developed for various arylation reactions.<sup>12</sup> However, research on this topic is still insufficient compared with extensive research on the generation of aryl radicals by cathodic reduction.

Electrocatalytic reactions have a safe and controllable potential range that can easily attain a reduction potential

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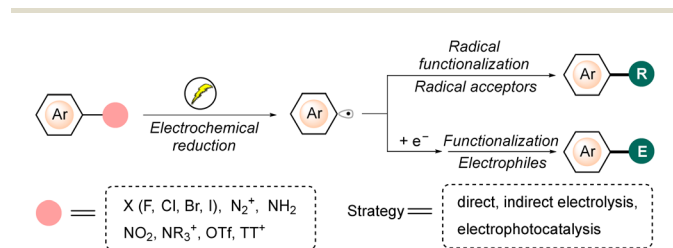
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beyond the range of chemical reductants and excited photocatalysts,<sup>13</sup> thus facilitating the reduction of aryl radical precursors. Over the last two decades, electroreductive aryl radical chemistry has been revisited and become a fast-growing research topic. Progress has primarily focused on the following several aspects: (i) the discovery of novel aryl radical precursors to expand known chemical transformations to novel molecular classes; (ii) the exploration of diverse transformations of aryl radicals to construct C(sp<sup>2</sup>)-carbon/heteroatom bonds; and (iii) the development of innovative catalytic systems to improve the practicality and efficiency of aryl radical formation (Scheme 1).

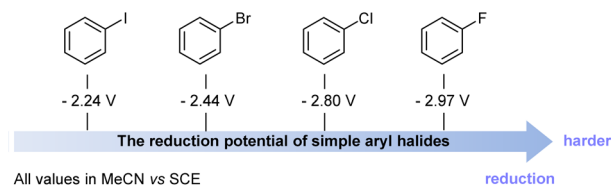
Considering the unique properties of aryl radicals and their fascinating applications in synthetic chemistry, we present herein a comprehensive survey of recent advances in the generation of aryl radicals through an electroreduction strategy. The full spectrum of aryl radical precursors applied in the electroreduction strategy, including aryl halides, aryl diazonium salts, arylazo sulfones, aryl amines, nitroarenes, aryl quaternary ammonium salts, aryl triflates, and aryl thianthrenium salts, is reviewed. Special emphasis is placed on the formation mechanisms, transformation processes, and application limitations of aryl radicals, aiming to stimulate the interest of synthetic chemists to develop novel catalytic systems and structurally diverse aryl radical precursors.

## 2. Aryl halides as aryl radical precursors

Aryl halides are a class of readily accessible, inexpensive, and versatile building blocks, which are routinely utilized in synthetic chemistry through transition-metal-catalyzed cross-coupling reactions, such as classic Suzuki–Miyaura coupling, Sonogashira cross-coupling, and the Ullmann reaction.<sup>14</sup> In recent years, the reductive dehalogenation of aryl halides has proved to be a productive synthetic strategy for producing aryl radicals.<sup>3</sup> Frequently, aryl halides have higher reduction potentials, especially aryl chlorides and fluorides, making their single-electron reduction extremely difficult (Scheme 2).<sup>15</sup> Therefore, it is still a formidable challenge to realize the downstream functionalization of inert aryl halides. The electroreduction strategy is considered a green, efficient, and controllable alternative for the reductive dehalogenation of aryl halides



**Scheme 1** Overview of the electroreductive diversity of aryl radical transformations.



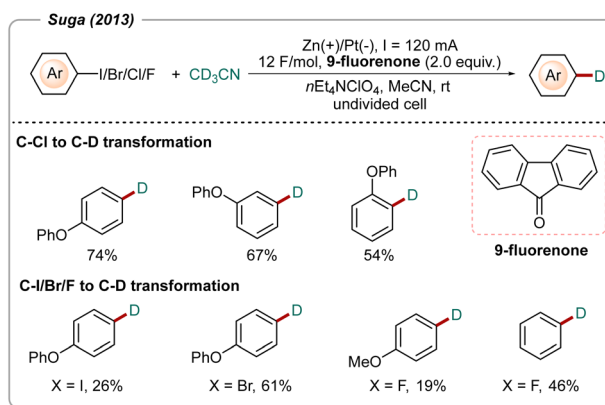
**Scheme 2** The reduction potential of some simple aryl halides.

owing to its extraordinary potential range. This section mainly illustrates the synthetic application of aryl radicals generated from the reductive dehalogenation of aryl halides by electrochemistry.

### 2.1 Dehalogenative hydrogenation/deuteration of aryl halides

Dehalogenative hydrogenation/deuteration of aryl halides plays a significant role in organic synthesis and drug discovery.<sup>16</sup> It not only enables the detoxification of environmentally hazardous aryl halides, but also offers a precise and controllable approach for the preparation of biologically valuable deuterated organic molecules.<sup>16</sup> Among the well-established dehalogenative hydrogenation/deuteration reactions, electrochemical strategies are favored by chemists owing to their unique advantages. Indeed, the electroreductive hydrogenation/deuteration of aryl halides was reported by Murray, Renaud, and Grimshaw in the 1970s.<sup>17</sup>

Although spectacular progress occurred decades ago, the development of novel and powerful electroreduction strategies for achieving the hydrogenation/deuteration of aryl halides remains challenging. In 2013, Suga *et al.* described an electrochemical dehalogenative deuteration of aryl halides using CD<sub>3</sub>CN as the deuterium source and 9-fluorenone as the redox mediator in an undivided cell (Scheme 3).<sup>18</sup> In this protocol, various aryl halides, including aryl iodides, bromides, chlorides, and fluorides, could be successfully converted into the corresponding deuterated products, although the conversion of aryl fluorides was less efficient owing to their thermodynamic stability. However, the requirements for stoichio-

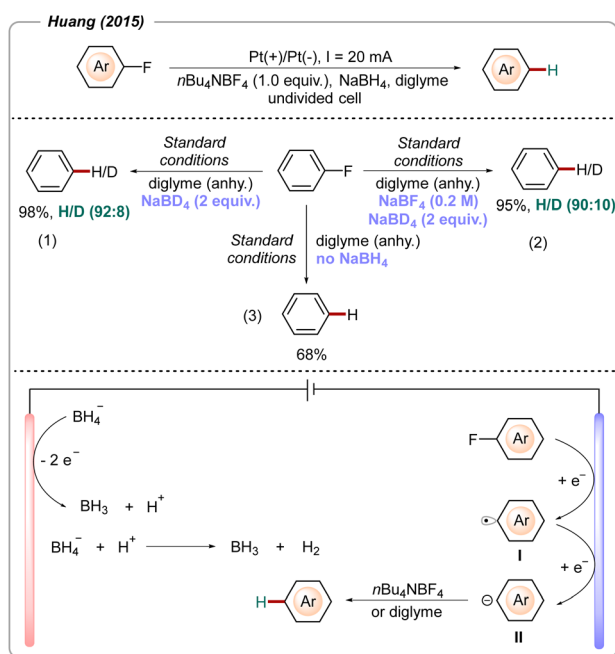


**Scheme 3** Electrochemical dehalogenative deuteration of aryl halides using CD<sub>3</sub>CN as the deuterium source.

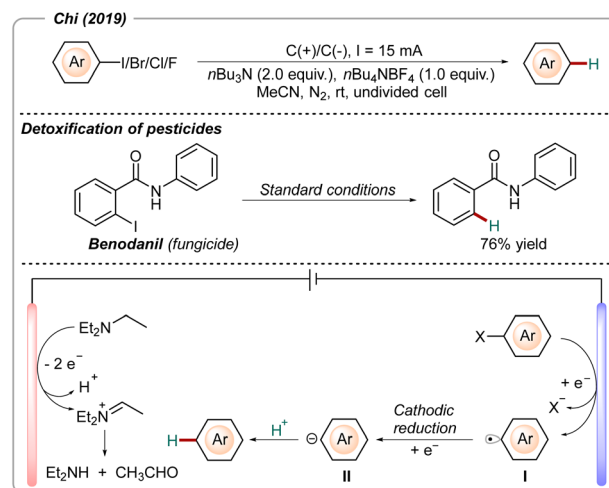
metric 9-fluorenone, excessively high electric current, and a sacrificial zinc anode are difficult to circumvent.

The high thermodynamic stability and kinetic inertness of C–F bonds make the defluorinative hydrogenation of aryl fluorides challenging.<sup>19</sup> In 2015, Huang *et al.* demonstrated an elegant NaBH<sub>4</sub>-promoted electrochemical defluorinative hydrogenation of aryl fluorides using platinum as the anode and cathode (Scheme 4).<sup>20</sup> Importantly, this strategy was not limited to monofluoroarenes; the reaction also proceeded smoothly for difluoro- and trifluoroarenes. The role of NaBH<sub>4</sub> in this system was discussed in detail through a series of deuterium-labeling experiments. Replacing NaBH<sub>4</sub> with NaBD<sub>4</sub>, the deuteration rate of arenes was extremely low, which indicated that both the solvent, diglyme, and electrolyte, *n*Bu<sub>4</sub>NBF<sub>4</sub>, could serve as hydrogen atom donors. Based on the above-mentioned outcomes and other control experiments, a plausible two-electron reduction mechanism is presented in Scheme 4. Initially, aryl fluoride is reduced at the cathode surface to form the aryl radical **I**, which then undergoes a second cathodic reduction to deliver the aryl anion **II**. Finally, the anion intermediate **II** abstracts H<sup>+</sup> from diglyme or *n*Bu<sub>4</sub>NBF<sub>4</sub> to produce the anticipated product. Concurrently, NaBH<sub>4</sub> works as a sacrificial material for oxidation of the anode, preventing the undesirable oxidation of intermediates and products.

Trialkylamines are typically utilized as terminal reductants and hydrogen atom donors in the dehalogenative hydrogenation of organic halides.<sup>21</sup> Building on these foundations, Chi *et al.* presented a homologous dehalogenative hydrogenation of aryl halides using *n*Bu<sub>3</sub>N/Et<sub>3</sub>N as efficient terminal reductants and hydrogen atom donors, offering a sustainable tech-



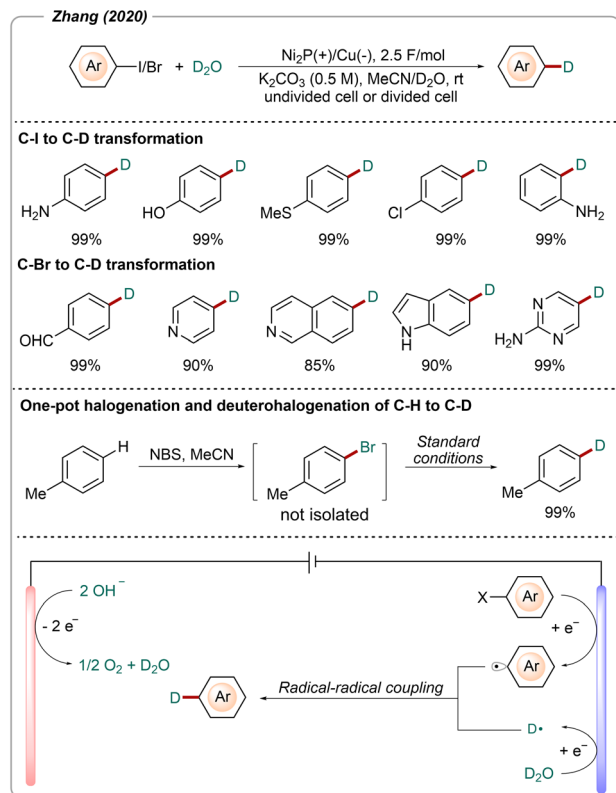
**Scheme 4** NaBH<sub>4</sub>-promoted electrochemical defluorinative hydrogenation of aryl fluorides.



**Scheme 5** Electrochemical dehalogenative hydrogenation of aryl halides.

nique for the detoxification of harmful organic halides, such as benodanil (a commercial fungicide) (Scheme 5).<sup>22</sup> Furthermore, the scalability of this electrochemical hydrogenation was assessed by conducting a 4 mmol scale reaction with 4,4'-dibromo-1,1'-biphenyl as the substrate. The single debrominated product, 4-bromobiphenyl, and fully debrominated product, biphenyl, were obtained in 33% and 50% yield, respectively. Mechanistically, this hydrogenation reaction involves a two-electron transfer process. The cathodic two-electron reduction of aryl halides occurs, resulting in the formation of aryl anions, which then react with acetonitrile or a trialkylamine *via* hydrogen atom transfer to yield the desired products. Conversely, the two-electron oxidation of a trialkylamine occurs at the anode, leading to the formation of an iminium, which can undergo hydrolysis to produce a dialkylamine and acetaldehyde.

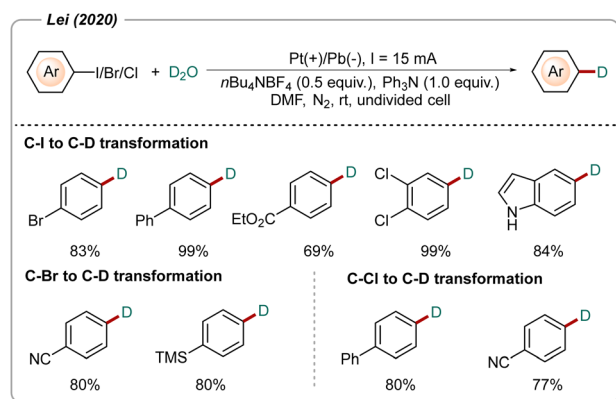
In 2020, Zhang *et al.* employed a noble-metal-free copper nanowire array with a weak active hydrogen species adsorption capacity as the cathode material to successfully achieve the dehalogenative deuteration of aryl halides with D<sub>2</sub>O, resulting in a wide range of deuterated compounds in up to 99% yield (Scheme 6).<sup>23</sup> Remarkably, this reaction also proceeded smoothly for aryl chlorides bearing unprotected NH<sub>2</sub> and OH groups, thus broadening the scope for late-stage functionalization. Moreover, this discovery was not only useful in the deuteration of less-active aryl bromides, but also provided an efficient route to the transformation of aryl halides containing pyridine, isoquinoline, indole, and pyrimidine skeletons. Satisfactorily, the conversion of aryl C–H to C–D was successfully performed in a high yield in a one-pot two-step halogenation–deuterodehalogenation process. Electron paramagnetic resonance (EPR) results verified that the aryl and hydrogen radicals were produced simultaneously with this protocol. Based on the results described above and other control experimental outcomes, a plausible radical–radical coupling mechanism was constructed. Mechanistically, the cathodic reduction



**Scheme 6** Electrochemical dehalogenative deuteration of aryl halides using  $\text{D}_2\text{O}$  as the deuterium source.

of aryl halides occurs, producing aryl radicals by releasing halogen anions. The formed aryl radicals then couple with the deuterium radicals produced from  $\text{D}_2\text{O}$  through electrocatalytic splitting at the cathode surface, resulting in the formation of deuterated compounds.

To enhance the practicability of reductive dehalogenation of aryl halides, in 2020, Lei *et al.* revealed a facile and economical  $\text{Ph}_3\text{N}$ -promoted electrochemical dehalogenative deuteration of aryl halides using  $\text{D}_2\text{O}$  as the deuterium atom donor under mild conditions (Scheme 7).<sup>24</sup> It should be



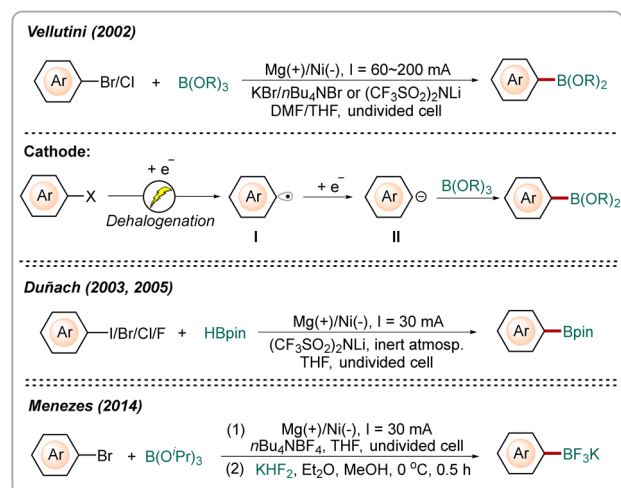
**Scheme 7**  $\text{Ph}_3\text{N}$ -promoted electrochemical dehalogenative deuteration of aryl halides with  $\text{D}_2\text{O}$ .

emphasized that the addition of anodic sacrificial reagents, such as  $\text{Ph}_3\text{N}$ ,  $\text{Et}_3\text{N}$ , and  $\text{Ph}_3\text{P}$ , is beneficial for this transformation. Interestingly, the deuteration of 2-bromonaphthalene also proceeded smoothly with three AA sized batteries as the power source, producing the corresponding deuterated compound in 80% yield. Similar to the well-established electrochemical dehalogenative deuteration of aryl halides by Zhang and co-workers,<sup>23</sup> as well as detailed EPR and control experimental results, this transformation proceeds *via* a radical-radical coupling mechanism.

## 2.2 Dehalogenative functionalization of aryl halides

The aryl radical-mediated reductive functionalization of aryl halides has been extensively studied, and offers a practical and straightforward avenue for the construction of structurally diverse functionalized arenes.<sup>3,25</sup> Recently, numerous synthetic chemists have exploited green electroreductive dehalogenation strategies to achieve the multifarious conversion of aryl radicals, which frequently serve as ideal complements to transition-metal-catalyzed arylation reactions.

Arylboronic acids and their derivatives play an important role in synthetic chemistry, especially in transition-metal-catalyzed cross-coupling reactions, such as the Chan–Lam and Suzuki–Miyaura coupling reactions.<sup>26</sup> The Miyaura boronation reaction is regarded as one of the most powerful tools to prepare versatile arylborates.<sup>27</sup> Recently, tremendous efforts have been devoted to investigating sustainable strategies for the dehalogenative radical borylation of aryl halides.<sup>28</sup> As early as 2002, Vellutini *et al.* reported an electrochemical borylation of aryl halides with trialkyl borates (Scheme 8).<sup>29</sup> This electrochemical borylation process was based on the direct two-electron reduction of aryl halides at the cathodic surface. At the anode, the magnesium electrode worked as a sacrificial reagent to prevent the oxidation of reaction intermediates and products. However, the high applied current limited further applications in synthetic chemistry. Subsequently, Duñach *et al.* employed pinacolborane (HBpin) as a borating reagent to

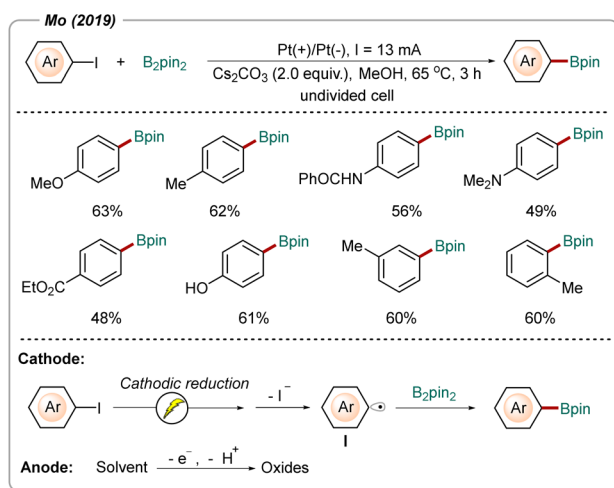


**Scheme 8** Electrochemical borylation of aryl halides.

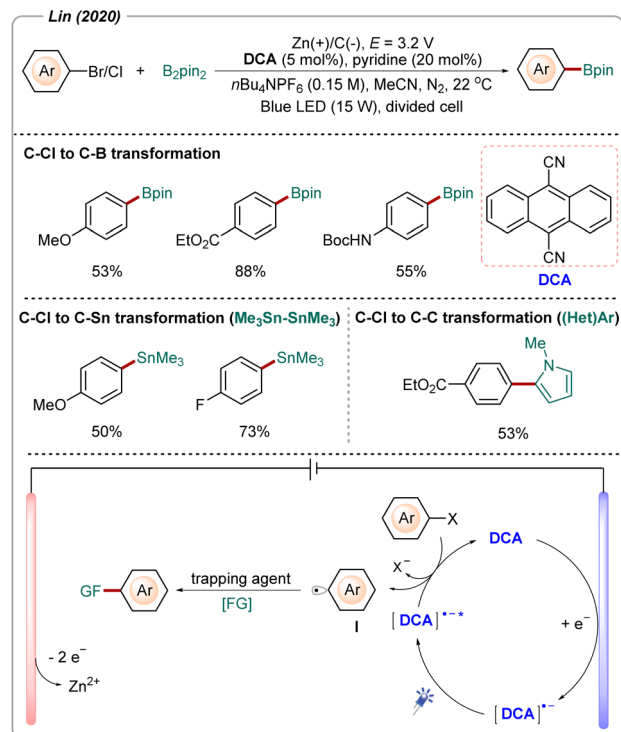
realize the electrochemical dehalogenative borylation of aryl halides (Scheme 8).<sup>30,31</sup> This meliorative method not only improved the reaction yield, but also expanded the types of borating reagent that could be used. Based on these finding, Menezes *et al.* utilized a well-established electroreductive borylation strategy to complete the construction of potassium aryltrifluoroborates in a one-pot two-step process in moderate yields (Scheme 8).<sup>32</sup>

In 2019, Mo *et al.* developed a sustainable electroreductive strategy for the dehalogenative radical borylation of aryl iodides with  $B_2pin_2$ , allowing access to arylboronic esters without any chemical reductants, transition-metal catalysts, or sacrificial reagents in an undivided cell (Scheme 9).<sup>33</sup> Mechanistically, the aryl radical **I** verified by the EPR experiment is initially generated from an aryl iodide *via* cathodic reduction and dehalogenation. The aryl radical **I** subsequently reacts with  $B_2pin_2$  to furnish the anticipated arylboronic esters. Regrettably, this established strategy is largely limited to aryl iodides with low reduction potential; the borylation of aryl bromides/chlorides remains incredibly problematic.

Generally, it is difficult to reduce aryl halides because of their inherently high reduction potential ( $E_{red} > -2.0$  V).<sup>15</sup> Therefore, developing efficient and general avenues for facilitating the radical borylation of aryl chlorides is of great significance.<sup>34</sup> In 2020, Lin, Lambert, and colleagues developed an unparalleled electrophotocatalytic strategy for realizing the dehalogenative radical borylation of aryl chlorides/bromides with  $B_2pin_2$  using 9,10-dicyanoanthracene (DCA) as the catalyst in a divided cell with constant voltage (Scheme 10).<sup>35</sup> Detailed control experimental outcomes proved that electricity, light, and DCA were all indispensable; without any one of these factors, the reaction almost did not occur. Notably, pyridine promoted the formation of B-centered radicals by coordinating with  $B_2pin_2$ , which was beneficial for reaction efficiency. This radical borylation project featured excellent functional group tolerance; both electron-donating and electron-withdrawing



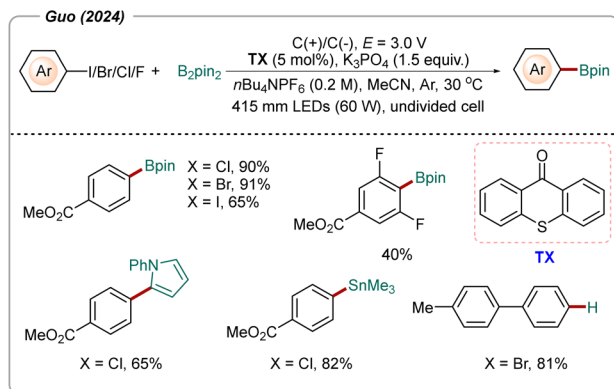
**Scheme 9** Electrochemical radical borylation of aryl iodides with  $B_2pin_2$ .



**Scheme 10** Electrophotocatalytic dehalogenative radical borylation of aryl chlorides/bromides with  $B_2pin_2$ .

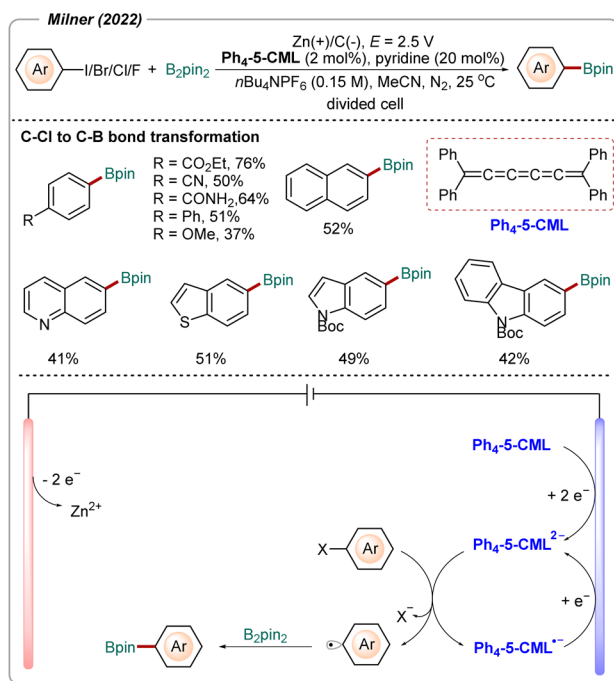
functional groups on the substrate are well-tolerated. Pleasingly, the synthetic utility of this established strategy was further extended to construct aryl C-Sn and aryl C-C bonds by using multifarious radical trapping agents, such as hexamethylditin, *N*-methylpyrrole, and 1,4-difluorobenzene. In this protocol, the key to success was combining the power of electricity and light to produce an excited radical anion species with a high reduction potential. Mechanistically, the catalyst **DCA** is initially reduced to the radical anion, **DCA**<sup>•-</sup>, with a relatively low reduction potential, which is then excited by visible light, giving the excited-state radical anion, **DCA**<sup>•-\*</sup> ( $E_{red} = -3.2$  V vs. SCE), with strong reducibility. Subsequently, the aryl halide reacts with **DCA**<sup>•-\*</sup> to deliver the key aryl radical **I** and the **DCA** catalyst. Finally, the aryl radical **I** is trapped by diverse radical receptors to furnish the desired functionalized arene.

Recently, Guo *et al.* discovered that 9-thioxanthene-9-one (**TX**) was a high performance photoelectroactive catalyst. The dehalogenative radical borylation of aryl halides by merging photocatalysis with electrocatalysis was realized in an undivided cell using carbon as the anode and cathode and **TX** as the catalyst (Scheme 11).<sup>36</sup> Compared with the electrophotocatalytic strategy reported by Lin and co-workers,<sup>35</sup> this method not only bypasses the utilization of a sacrificial anode, but can also proceed in a simple and inexpensive undivided cell. Furthermore, aryl fluorides also exhibited moderate reactivity. Identically, the generated aryl radical can be captured by various other radical acceptors, such as hexamethylditin, benzothioephene, and pyrrole.



**Scheme 11** Electrophotocatalytic dehalogenative radical borylation of aryl chlorides/bromides without a sacrificial anode.

Is light generally needed to achieve the electroreductive radical borylation of aryl chlorides? To answer this question, Millner *et al.* designed a redox mediator that could be reversibly reduced at the cathode surface, avoiding the use of visible light. In this electrochemical protocol, a tetraarylcumulene (**Ph<sub>4</sub>-5-CML**) was employed as a redox mediator to realize the radical borylation of (hetero)aryl chlorides/bromides using zinc as the sacrificial anode and porous carbon as the cathode (Scheme 12).<sup>37</sup> It is worth noting that aryl bromides and aryl chlorides exhibited similar dehalogenative borylation reactivity, but that of aryl iodides was significantly lower; this is in contrast to the traditional trends in the reactivity of photocatalytic and metal-catalytic methods. It is likely that the bulky

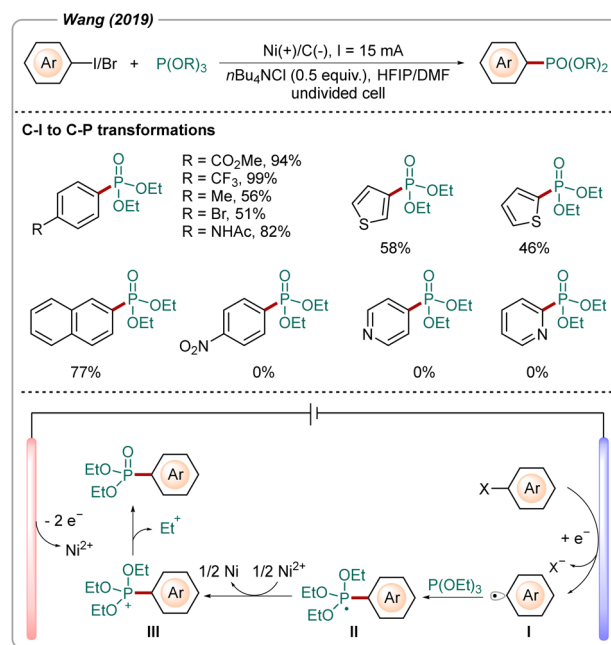


**Scheme 12** Tetraarylcumulene (**Ph<sub>4</sub>-5-CML**)-mediated electrochemical radical borylation of aryl halides.

nature of the iodide group disrupts the  $\pi$ -stacking between the aryl iodide and the reduced state of **Ph<sub>4</sub>-5-CML**, resulting in the observed decrease in reactivity. Mechanistically, the redox mediator **Ph<sub>4</sub>-5-CML** is reduced to **Ph<sub>4</sub>-5-CML<sup>2-</sup>** via a two-electron transfer process, which then in turn reduces the aryl halide to the corresponding aryl radical and **Ph<sub>4</sub>-5-CML<sup>\cdot-</sup>**. The generated **Ph<sub>4</sub>-5-CML<sup>\cdot-</sup>** can be re-reduced at the cathode to form the highly active **Ph<sub>4</sub>-5-CML<sup>2-</sup>**.

To enhance the application of electrochemical dehalogenative radical functionalization of aryl halides, Wang *et al.* established an efficient electrochemical dehalogenative phosphorylation of aryl bromides/iodides with trialkyl phosphites for the preparation of a series of structurally abundant aryl phosphates in up to 99% yield (Scheme 13).<sup>38</sup> A brief survey showed that the anode materials had a tremendous influence on reaction outcomes, and replacing the Ni anode with Fe, Mg, or Zn did not furnish the anticipated products. These findings revealed that the role of the Ni electrode extended far beyond serving as a sacrificial anode; the released nickel ions are active in promoting the reaction process. Furthermore, the removal of *N,N*-dimethylformamide (DMF) decreased the yield owing to the relatively poor solubility of the starting materials in hexafluoroisopropanol (HFIP). In this protocol, both electron-withdrawing and electron-donating functional groups on the aromatic ring of aryl iodides could provide access to the corresponding phosphorylation products in moderate yields. Unfortunately, 1-iodo-4-nitrobenzene, 4-iodopyridine, and 2-iodopyridine failed to furnish the corresponding aryl phosphates.

Mechanistic studies showed that the direct cathodic reduction of the aryl halide was the initial step, generating the



**Scheme 13** Electrochemical dehalogenative phosphorylation of aryl halides.

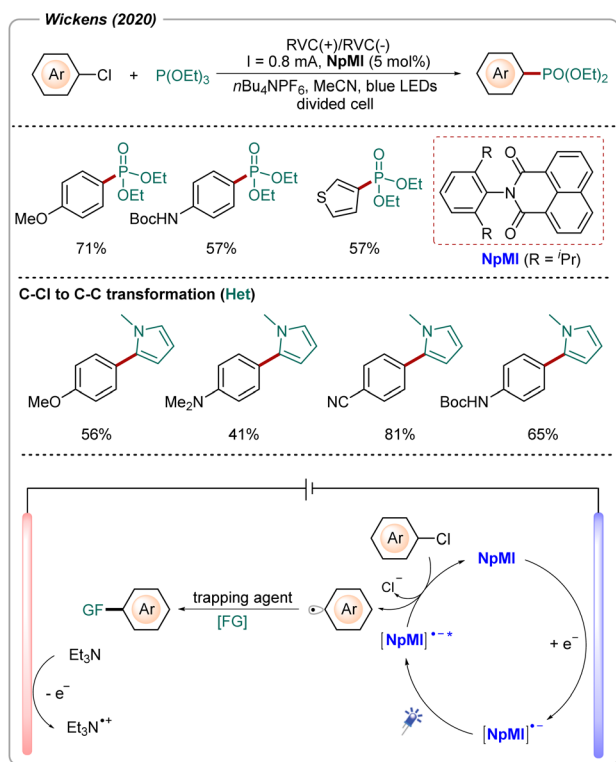
key aryl radical **I**. Subsequently, the aryl radical **I** reacts with triethyl phosphites to deliver the P-centered radical **II**, which is then oxidized by  $\text{Ni}^{2+}$  produced from the nickel anode to the cationic intermediate **III**. This is followed by the ethyl cation leaving, furnishing the desired product.

Despite the valuable electrochemical radical phosphorylation of aryl halides being well established, the precise activation of aryl chlorides remains challenging. In 2020, Wickens *et al.* screened a series of imide-based catalysts to establish an environmentally friendly and general electrophotocatalytic strategy for the dehalogenative radical phosphorylation of aryl chlorides (Scheme 14).<sup>39</sup> This protocol was performed in a divided cell, using reticulated vitreous carbon (RVC) as the anode and cathode, and naphthalene-based analogues (**NpMI**) as the catalyst. Importantly, aryl chlorides could be efficiently coupled with *N*-methylpyrrole, resulting in the formation of diverse arylated pyrroles in moderate to good yields. Compared with direct electrolysis and photocatalysis, it is found that direct electrolysis usually suffers from dechlorinative hydrogenation and unwanted aryl radical–radical coupling reactions, while photocatalysis hardly occurs. Similar to the electrophotocatalytic radical borylation of aryl halides established by Lin and co-workers,<sup>35</sup> this protocol also begins with the cathodic reduction of the catalyst **NpMI**, followed by irradiation with visible light to give the excited radical cation  $\text{NpMI}^{+\bullet}$ , which has a high reduction potential. Aryl chloride is reduced by  $\text{NpMI}^{+\bullet}$  to the corresponding aryl radical inter-

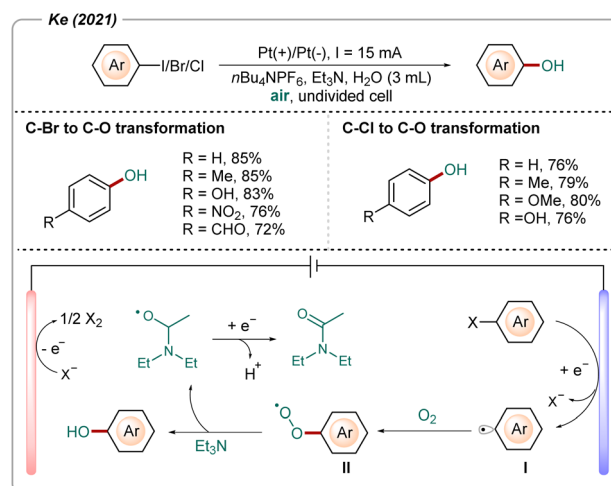
mediate, which then couples with radical acceptors to obtain the desired product.

In 2021, Ke *et al.* described an electrochemical hydroxylation of aryl halides using platinum as the anode and cathode, leading to a wide range of functionalized phenols in moderate to excellent yields (Scheme 15).<sup>40</sup> The electrolysis conditions used in this hydroxylation were relatively simple and environmentally friendly, neither a sacrificial anode nor transition-metal catalyst was required. Moreover, this reaction also proceeded smoothly for the hydroxylation of aryl chlorides, thus broadening the synthetic applications. It is worth noting that triethylamine played an indispensable role in this reaction, while other bases such as  $\text{K}_2\text{CO}_3$  and  $\text{NaOH}$  were inert, providing a key clue for further mechanistic studies. Furthermore, the scalability of this hydroxylation of aryl halides was assessed on a 10 mmol scale reaction, which led to the corresponding phenol being isolated in 87% yield. Mechanistically, the cathodic reduction of the aryl halide occurs preferentially, resulting in the corresponding aryl radical **I**, which is then captured by  $\text{O}_2$  to form the peroxy radical **II**. Afterward, the peroxy radical **II** reacts with  $\text{Et}_3\text{N}$  to afford the target product phenol and the O-centered radical **III**, which undergoes cathodic reduction to produce the amide.

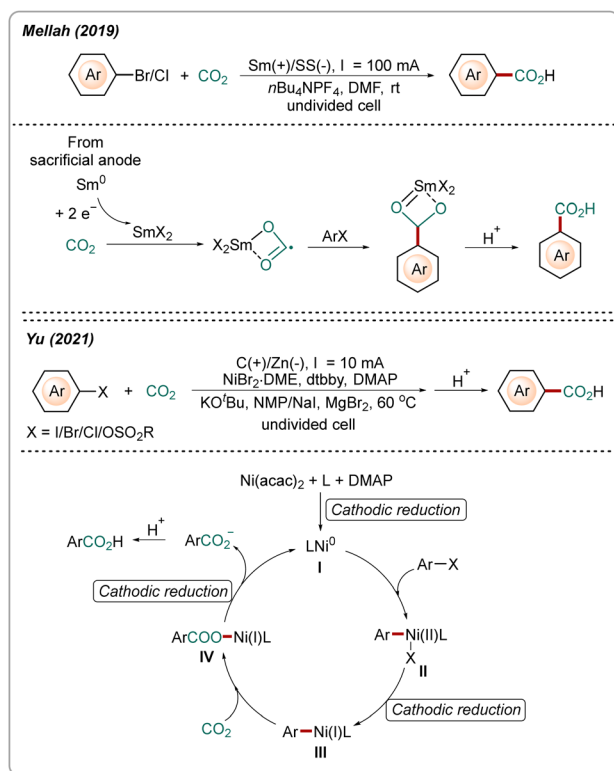
The carboxylation of aryl halides with the naturally abundant compound  $\text{CO}_2$  is considered a promising strategy to produce diverse aryl carboxylic acids.<sup>41</sup> By merging electrocatalysis with metal catalysis, the dehalogenative carboxylation of aryl halides with  $\text{CO}_2$  has been achieved by several research groups.<sup>42</sup> In 2019, Mellah *et al.* described an electrochemical carboxylation of aryl halides with  $\text{CO}_2$  in an undivided cell (Scheme 16).<sup>42a</sup> The samarium electrode used as a sacrificial anode dissolved during electrolysis and produced a  $\text{Sm}(\text{II})$  complex to activate  $\text{CO}_2$ , thereby achieving this electrochemical dehalogenative carboxylation. In 2021, Yu *et al.* also realized a dehalogenative carboxylation of aryl halides with  $\text{CO}_2$  by merging electrocatalysis with nickel catalysis (Scheme 16).<sup>42b</sup> Mechanistically, this electrochemical cycle



**Scheme 14** Electrochemical dehalogenative phosphorylation of aryl chlorides.



**Scheme 15** Electrochemical hydroxylation of aryl halides.

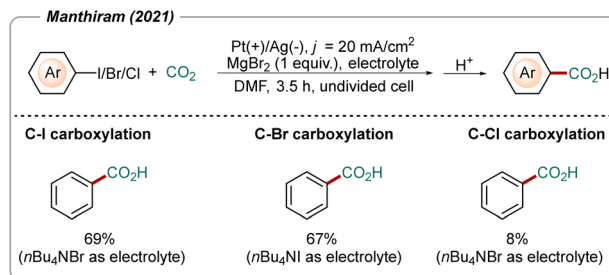


**Scheme 16** Metal-catalyzed electrochemical carboxylation of aryl halides with  $\text{CO}_2$ .

begins with the cathodic reduction of the Ni(II) catalyst to generate the Ni(0) species **I**, followed by oxidative addition with the aryl halide to form the Ar-Ni(II) species **II**. Subsequently, species **II** is reduced to the Ar-Ni(I) species **III**, which reacts with  $\text{CO}_2$  to produce the ArCOO-Ni(I) species **IV**. Finally, cathode reductive elimination from species **IV** delivers the desired carboxylation product.

The direct electroreductive carboxylation of aryl halides with  $\text{CO}_2$  is one of the important reactions to prepare carboxylic acids.<sup>43</sup> The general mechanism of this reaction is as follows: the aryl carbanion can be produced by two-electron reduction of aryl halides at the cathode, and then  $\text{CO}_2$  is captured to obtain carboxylic acids. Although these electroreductive carboxylation reactions employ  $\text{CO}_2$  as the carboxyl source and green electricity as the reaction driving force, the overall sustainability is limited by the use of sacrificial anodes (Mg and Al). In 2021, Manthiram *et al.* developed an electroreductive carboxylation of aryl halides with  $\text{CO}_2$  by using  $\text{MgBr}_2$  to replace the sacrificial anode (Scheme 17).<sup>44</sup> Control experiments using different electrochemical configurations proved that the magnesium ion could improve the reaction efficiency by inhibiting the formation of by-products. However, the authors mainly focused on the carbonylation of alkyl halides, and aryl halides were less studied.

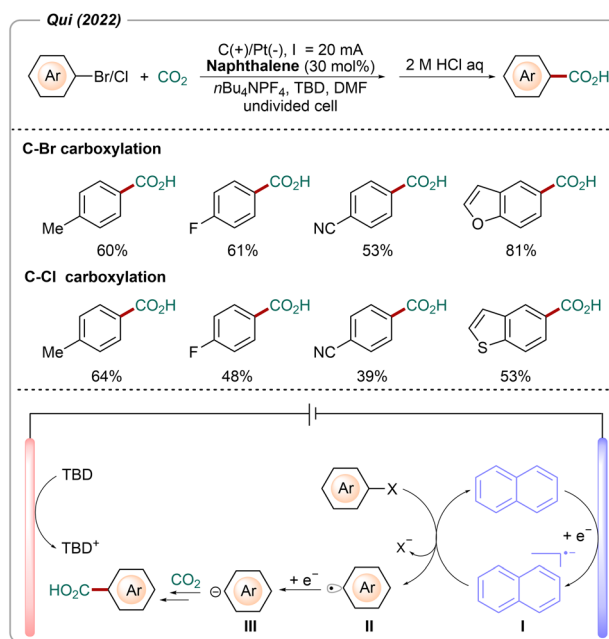
To enhance the practicality of electrocatalytic dehalogenation carbonylation of aryl halides, in 2022, Qiu *et al.* disclosed a novel naphthalene-mediated electroreductive strategy for the



**Scheme 17** Electrochemical carboxylation of aryl halides with  $\text{CO}_2$  by adding  $\text{MgBr}_2$  to replace the sacrificial anode.

carboxylation of aryl halides with  $\text{CO}_2$  using 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) as an anodic sacrificial reagent in a undivided cell, offering a metal-free avenue for building structurally rich aryl carboxylic acids (Scheme 18).<sup>45</sup> Control experiments showed that the redox mediator naphthalene was indispensable, otherwise the yields decreased tempestuously. Satisfactorily, the aryl halides containing biologically valuable skeletons, such as menthol, isoborneol, citronellol, phytol, and carveol, were well tolerated, which should facilitate the further application of the established electrochemical carboxylation method in synthetic chemistry and drug discovery. Importantly, the conversion could be performed with a lower concentration of  $\text{CO}_2$  atmosphere (30%), giving the desired product in an acceptable yield (54%).

Density functional theory (DFT) calculation outcomes proved that a naphthalene radical anion was favorable for the single-electron reduction of aryl halides. Meanwhile, detailed CV studies showed that the reduction potential of naphthalene



**Scheme 18** Naphthalene-mediated electrochemical carboxylation of aryl halides with  $\text{CO}_2$ .

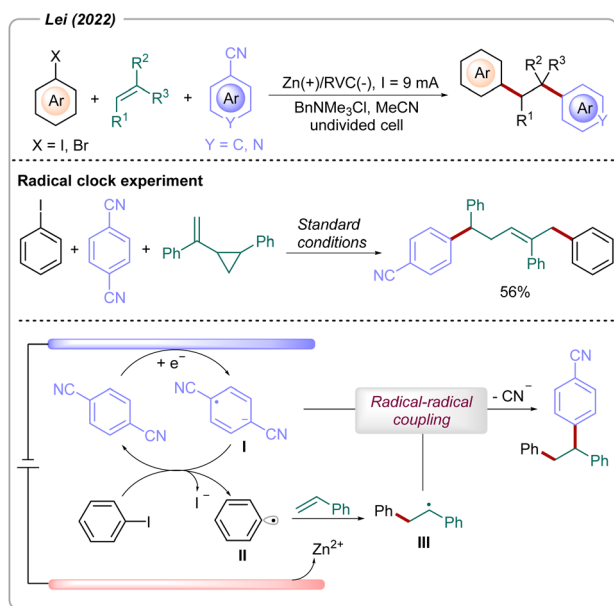
was lower than that of aryl halides. Mechanistically, the cathodic single-electron reduction of naphthalene affords the corresponding radical anion **I**, which then in turn reduces the aryl halide to the aryl radical **II**. Subsequently, the aryl radical **II** is further reduced to the aryl anion **III** at the cathode surface, followed by a nucleophilic attack on  $\text{CO}_2$ , producing the desired aryl carboxylic acid. It is worth mentioning that another possibility, in which the aryl radical couples with  $\text{CO}_2^{\cdot-}$  generated from the cathode, cannot be ruled out.

In 2023, Lei *et al.* established an elegant redox-mediated electroreductive intermolecular 1,2-diarylation of alkenes, aryl halides, and aryl nitriles using zinc as a sacrificial anode in an undivided cell, enabling the formation of a series of structurally diverse polyarylated alkanes in moderate to good yields (Scheme 19).<sup>46</sup> Remarkably, this electroreductive strategy was not limited to activated aryl alkenes, and inactivated alkyl alkenes also maintained good reactivity and selectivity. Furthermore, the alkenes containing biologically relevant skeletons were also assessed for this electrochemical 1,2-diarylation, and the corresponding products were produced in good yields. It should be noted that the aryl nitrile served as both the aryl radical precursor and redox mediator, as confirmed by detailed CV analysis. To acquire insights into the electroreduction mechanism, detailed control experiments were carried out. The result of the radical clock experiment presented clear evidence of a radical transformation process. Moreover, EPR results confirmed that an aryl radical was formed in this conversion.

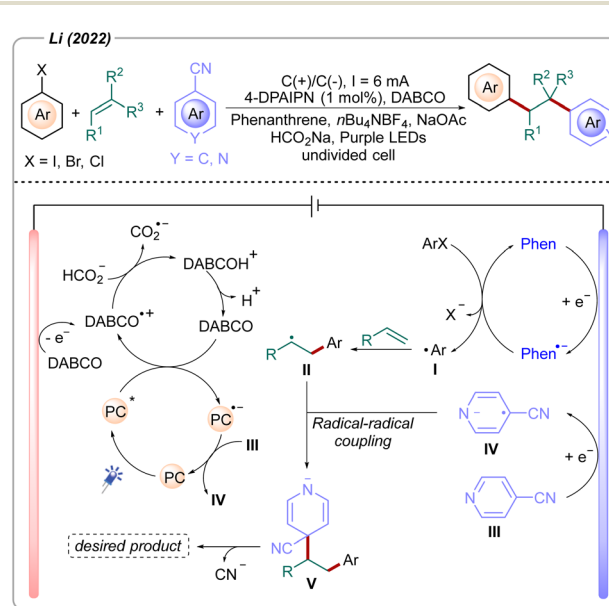
CV studies revealed that 1,4-dicyanobenzene had a lower reduction potential ( $E_{\text{red}} = -1.75 \text{ V}$ ) than iodobenzene ( $E_{\text{red}} = -2.5 \text{ V}$ ) or 1-methyl-4-vinylbenzene ( $E_{\text{red}} = -2.82 \text{ V}$ ), thus meaning that the cathodic single-electron reduction of 1,4-

dicyanobenzene was the initial step. Mechanistically, 1,4-dicyanobenzene is reduced at the cathode surface to the corresponding radical anion **I**, which has a higher reduction potential and in turn reduces the aryl halide, giving the crucial aryl radical intermediate **II**. Afterward, the aryl radical **II** reacts with an alkene to produce the alkyl carbon radical **III**, which ultimately couples with the cathode-generated radical anion **I** to yield the final product.

Despite impressive progress being made by Lei and co-workers in the field of electrochemical aryl radical enabled 1,2-diarylation of alkenes, many unresolved problems remain, for example, a sacrificial anode is hard to avoid. To address this limitation, Li *et al.* developed a novel electrophotocatalytic strategy for achieving a similar aryl radical-mediated 1,2-diarylation of alkenes (Scheme 20).<sup>47</sup> In the absence of light, the diarylation product was obtained in a yield of 13%. In addition, the reaction was not successful without electricity. These observations clearly demonstrated that electrocatalysis was critical to the reaction. Moreover, photoredox catalysis could significantly improve the reaction efficiency. Mechanistically, cathodic single-electron reduction of phenanthrene generates the corresponding radical anion, which quickly reacts with the aryl halide to give the aryl radical **I**. Then, the addition of the aryl radical to the alkene furnishes the alkyl radical **II**. Separately, 4-cyanopyridine is reduced to the corresponding radical anion **IV** either through a cathode or PC radical anion reduction. Afterward, a radical-radical coupling between the 4-cyanopyridine radical anion **III** and the alkyl radical **I** delivers the cation intermediate **V**. Finally, the decyanation of the cation intermediate **V** yields the anticipated diarylation product. It should be emphasized that DABCO is used as a sacrificial reagent at the anode.



**Scheme 19** Electroreductive intermolecular 1,2-diarylation of alkenes, aryl halides, and aryl nitriles.



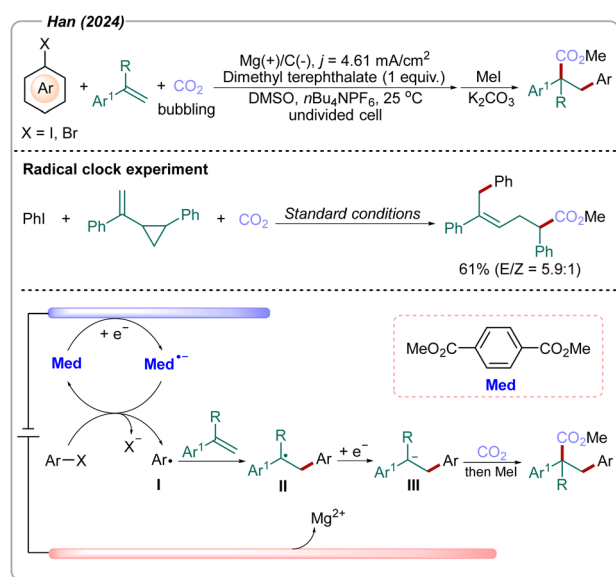
**Scheme 20** Electrophotocatalytic 1,2-diarylation of alkenes, aryl halides, and aryl nitriles.

The benzyl radicals generated from the addition of an aryl radical to alkenes are also easily reduced to benzyl anions, which subsequently react with CO<sub>2</sub> to achieve the arylcarboxylation of alkenes.<sup>48</sup> In 2024, Han *et al.* employed an electroreductive strategy to achieve the aryl radical enabled arylcarboxylation of alkenes and aryl halides with CO<sub>2</sub>, allowing access to a wide range of high-value 2,3-diarylpropanoic acids in moderate to good yields (Scheme 21).<sup>49</sup> This protocol was conducted in an undivided cell, using magnesium as the anode, carbon as the cathode, and dimethyl terephthalate as the redox mediator. The results of radical clock experiments supported the involvement of the aryl radical species in this reaction. The analysis of the electrochemical behavior of reaction components revealed that dimethyl terephthalate had two reduction peaks ( $E_{p1} = -1.83$  V and  $E_{p2} = -2.42$  V vs. Ag/AgCl), which indicated that this redox mediator could be reduced to the corresponding radical anion and dianion species. In addition, with increasing equivalents of iodobenzene, the oxidation current of the dimethyl terephthalate radical anion was decreased and the reduction current of dimethyl terephthalate was increased. These findings supported that dimethyl terephthalate served as a redox mediator for the single-electron reduction of aryl halides. Mechanistically, the cathodic single-electron reduction of dimethyl terephthalate occurs preferentially, resulting in the corresponding radical anion, which then in turn reduces aryl halides to the aryl radical I. Subsequently, the addition of the aryl radical I to the alkene delivers the benzyl radical II, which is reduced to the benzyl anion III. Finally, the generated benzyl anion III is trapped by CO<sub>2</sub> to produce the final product in the presence of MeI and K<sub>2</sub>CO<sub>3</sub>. Besides, the sacrifice of the anode is indispensable, otherwise the reduction of the benzyl radical will be threatened.

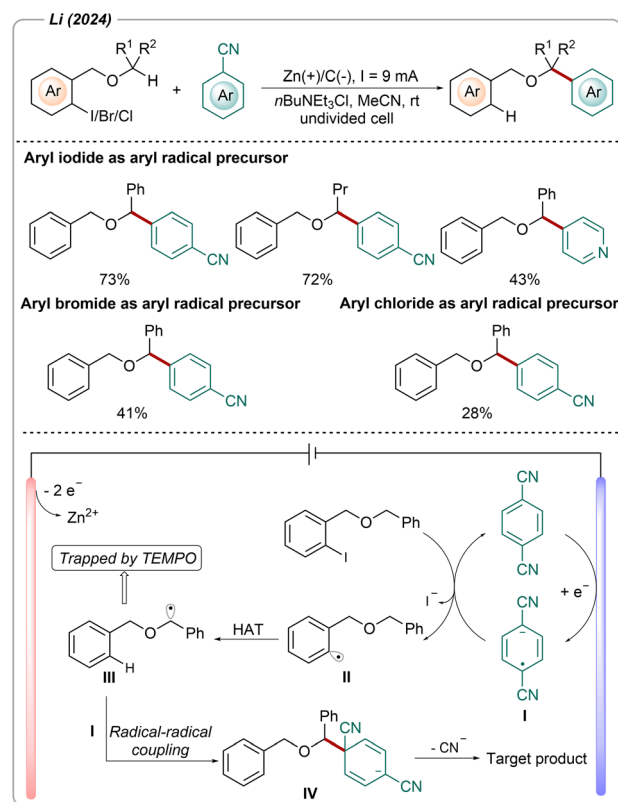
Compared with C(sp<sup>3</sup>)-H bonds, aryl C(sp<sup>2</sup>)-H bonds typically exhibit a higher bond dissociation energy (BDE), which

supports the strategy that employing aryl radicals to activate inert C(sp<sup>3</sup>)-H bonds *via* the hydrogen atom transfer (HAT) strategy is thermodynamically feasible.<sup>50</sup> As expected, this theory was confirmed by photocatalysis or transition-metal catalysis strategies.<sup>51</sup> For instance, Wu *et al.* realized the precise activation of  $\alpha$ -C(sp<sup>3</sup>)-H bonds by aryl radicals through a photocatalytic HAT strategy.<sup>51a</sup> Encouraged by these achievements, Li *et al.* described a novel electroreductive HAT strategy for the precise activation of remote C(sp<sup>3</sup>)-H bonds by aryl radicals generated from aryl halides, establishing a novel and environmentally sustainable route to remote C(sp<sup>3</sup>)-H aryl/heteroarylation (Scheme 22).<sup>52</sup> The reaction was conducted in a simply operated undivided cell equipped with zinc as the sacrificial anode and graphite rod as the cathode, and a series of C(sp<sup>3</sup>)-H aryl/heteroarylation products were synthesized in moderate to good yields. Note that besides aryl iodides, the aryl bromides/chlorides with high reduction potentials could also be used as aryl radical precursors to activate the molecular C(sp<sup>3</sup>)-H bonds, although the efficiency was lower.

Based on the control experiments and detailed CV analysis, a convincing mechanism is presented in Scheme 22. The cathodic single-electron reduction of 1,4-dicyanobenzene occurs initially, delivering the 1,4-dicyanobenzene radical anion I, which then in turn reduces the aryl halide to the corresponding aryl radical II. The facile 1,5-HAT process occurs between the aryl radical II and the intramolecular



**Scheme 21** Electroreductive 1,2-arylcaboxylation of alkenes and aryl halides with CO<sub>2</sub>.



**Scheme 22** Electrochemical remote C(sp<sup>3</sup>)-H arylation *via* the HAT strategy.

remote C(sp<sup>3</sup>)-H bond, giving the key alkyl radical intermediate **III**, which could be trapped by 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) in a control experiment. Subsequently, the aryl radical **III** couples with the cathode generated radical anion **I** to afford the cation intermediate **IV**. Finally, the decyanation of the cation intermediate **IV** gives the desired C(sp<sup>3</sup>)-H arylated product.

### 2.3 Dehalogenative cyclization of aryl halides

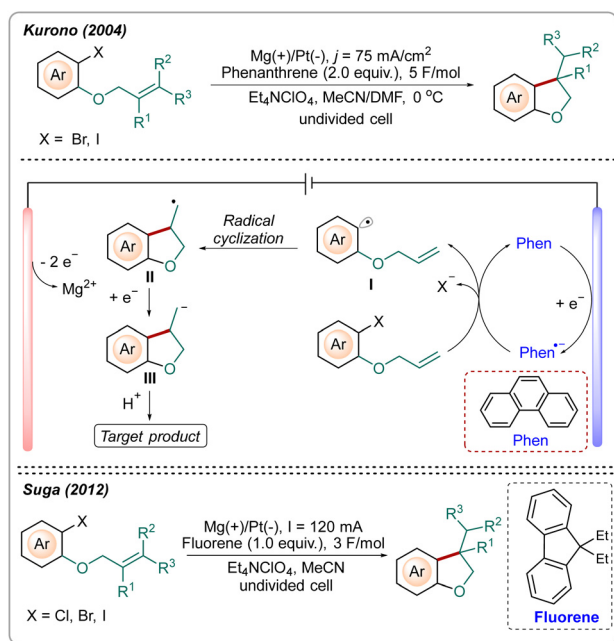
Expanding the synthetic applications outlined above, the electroreductive dehalogenation strategy can also be applied to synthesize various structurally and synthetically valuable cyclic molecular frameworks. As early as 2004, Kurono *et al.* reported a phenanthrene-mediated electrochemical dehalogenative intramolecular radical cyclization of aryl halides bearing an allyl moiety using magnesium as the sacrificial anode and platinum as the cathode in an undivided cell, providing a sustainable route for preparing functionalized 2,3-dihydrobenzofurans in moderate to good yields (Scheme 23).<sup>53</sup> Mechanistically, the cathodic reduction of phenanthrene (**Phen**) occurs preferentially, giving the radical anion **Phen<sup>•-</sup>** with a high reduction potential. Then, **Phen<sup>•-</sup>** reacts with the aryl halide to deliver the crucial aryl radical **I**, followed by successive 5-*exo* cyclization and cathodic reduction to yield the anion intermediate **III**. Finally, the cyclized product is obtained through the hydrogenation process. Notably, the anode dissolution of magnesium was a key factor in this system to effectively prevent the undesirable anodic oxidation of reaction intermediates and final products.

However, the substrate scope is limited to aryl iodides and bromides with lower reduction potentials, so the radical-

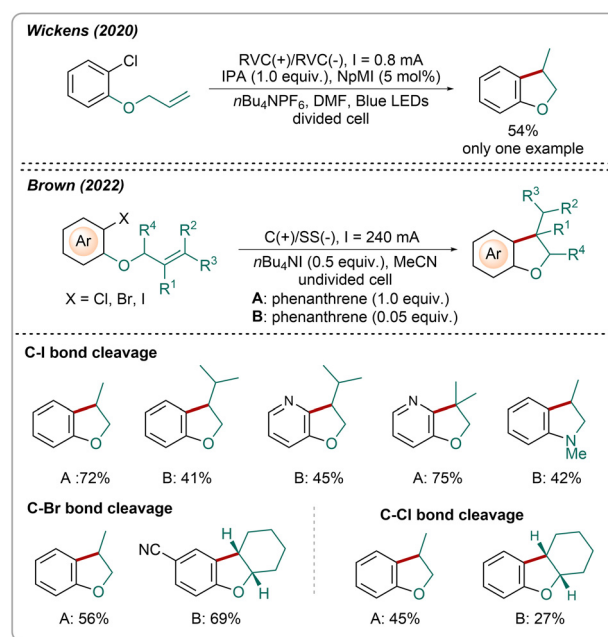
mediated intramolecular cyclization of aryl chlorides remains challenging. In 2012, Mitsudo, Suga and colleagues found that fluorene derivatives could work as efficient redox mediators to facilitate the above-mentioned electroreductive cyclization of aryl halides (Scheme 23).<sup>54</sup> In an undivided cell equipped with a magnesium anode and platinum cathode, a series of structurally diverse 2,3-dihydrobenzofurans were synthesized in up to 95% yield.

While several valuable approaches have been reported, the utilization of stoichiometric redox mediators and sacrificial anodes is inevitable. Therefore, developing an efficient and economic strategy for the radical-mediated intramolecular cyclization of aryl chlorides remains a challenging and highly studied topic. In 2020, Wickens *et al.* skillfully designed a novel electrophotocatalytic strategy to realize the above-described 5-*exo* cyclization reaction in a divided cell, which not only bypassed the sacrificial anode, but also avoided the participation of stoichiometric redox mediators (Scheme 24).<sup>39</sup> Regrettably, the authors did not investigate the scope of this transformation in detail; only one example was presented.

In 2022, Brown *et al.* illustrated an efficient phenanthrene-mediated electroreductive intramolecular 5-*exo* cyclization of aryl halides bearing an allyl moiety in an undivided continuous-flow cell using carbon as the anode and stainless steel as the cathode, thus resulting in the formation of various cyclic compounds in moderate to good yields (Scheme 24).<sup>55</sup> A thorough survey of the substrate scope of aryl halides containing electron-withdrawing and electron-donating groups revealed that the electronic effects exerted only a minor influence on the transformation. In this protocol, a suitable anode reaction is essential, such as the anodic oxidation of halide



**Scheme 23** Redox-mediated electrochemical radical cyclization of aryl halides bearing an allyl moiety.

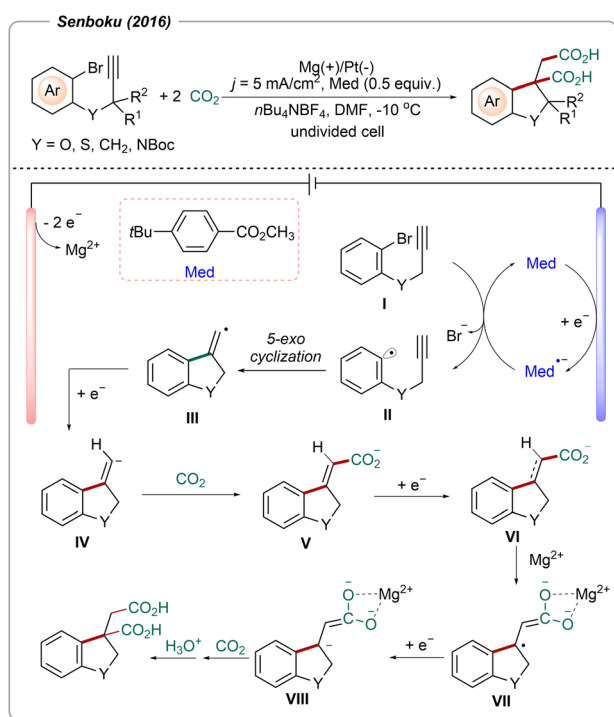


**Scheme 24** Redox-mediated electrochemical radical cyclization of aryl halides bearing an allyl moiety without a sacrificial anode.

ions generated from the dehalogenation of aryl halides. Furthermore, the utilization of the supporting electrolyte,  $\text{Bu}_4\text{NI}$ , is beneficial for the transformation, as it favors the supplementation of cathodic halide ions.

The aforementioned intramolecular radical cyclization usually relies on the protonation process to terminate the reaction. To further enrich the termination method, in 2016, Senboku *et al.* established a 4-*tert*-butylbenzoate-mediated electroreductive aryl radical cyclization and carboxylation of aryl bromides containing a propargyl moiety, offering a convenient approach for the rapid construction of structurally diverse cyclic dicarboxylic acids in up to 93% yield (Scheme 25).<sup>56</sup> Excitingly, electrolysis was also conducted by bubbling carbon dioxide through an undivided cell equipped with magnesium as the anode and platinum as the cathode.

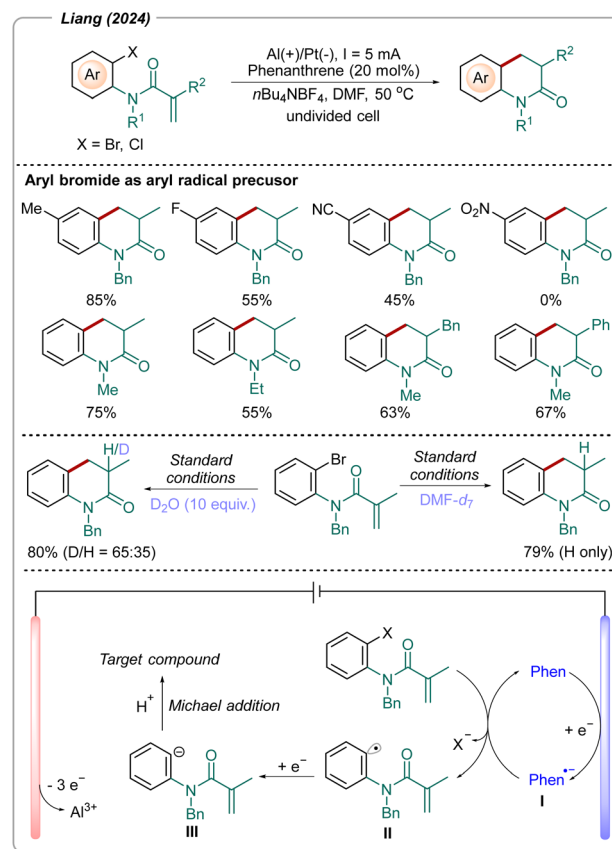
A plausible mechanism for the aryl radical-enabled cyclization followed by cascade carboxylation is summarized in Scheme 25. It is presumed that the protocol starts with the cathodic reduction of 4-*tert*-butylbenzoate (**Med**), resulting in a high reduction potential radical cation, **Med**<sup>•+</sup>, which then in turn reduces the aryl bromide **I** to the corresponding aryl radical **II**, thus causing the regeneration of the redox mediator. Subsequently, the intramolecular 5-*exo* cyclization of the aryl radical **II** takes place readily to afford the corresponding cyclized vinyl radical **III**. The subsequent single-electron reduction gives the vinyl anion **IV**, which then reacts with carbon dioxide ( $\text{CO}_2$ ) to furnish the carboxylate ion **V** bearing a cinnamic acid moiety. Afterward, further reduction of the electron-deficient intermediate **V** is likely to occur easily, thus



**Scheme 25** Redox-mediated electrochemical aryl radical cyclization and carboxylation of aryl bromides.

affording the corresponding radical anion **VI**, which is then converted into the stable radical anion **VII** assisted by a magnesium cation. This is followed by successive processes of single-electron reduction, electrophilic substitution, and protonation, resulting in the target cyclic dicarboxylic acid.

It is well known that the generated aryl radicals are also reduced easily at the cathode to generate aryl anions, followed by hydrogenation to terminate the reaction.<sup>57</sup> It is also a notable scientific concept to use aryl anions for diverse valuable transformations. In 2024, Liang *et al.* employed a cathodic two-electron reduction strategy to realize a practical phenanthrene-mediated intramolecular 6-*endo* cyclization of *o*-halophenylacrylamides, providing a convenient approach for the construction of a number of structurally diverse and valuable 3,4-dihydroquinolinone derivatives in moderate to good yields (Scheme 26).<sup>58</sup> Detailed deuterium-labeling experiments were carried out to elucidate the source of hydrogen atoms. Upon using *o*-bromophenylacrylamide as a substrate for this reaction in the presence of 10.0 equivalents of  $\text{D}_2\text{O}$ , 65% D-incorporation was observed at the terminal position of the alkene, while the target product without a deuterium label was isolated in 79% yield using  $\text{DMF-}d_7$  instead of  $\text{D}_2\text{O}$ . These findings supported that the hydrogen source was  $\text{H}_2\text{O}$ , not the reaction solvent DMF. Based on the above observations and detailed CV studies, a novel two-electron reduction mechanism



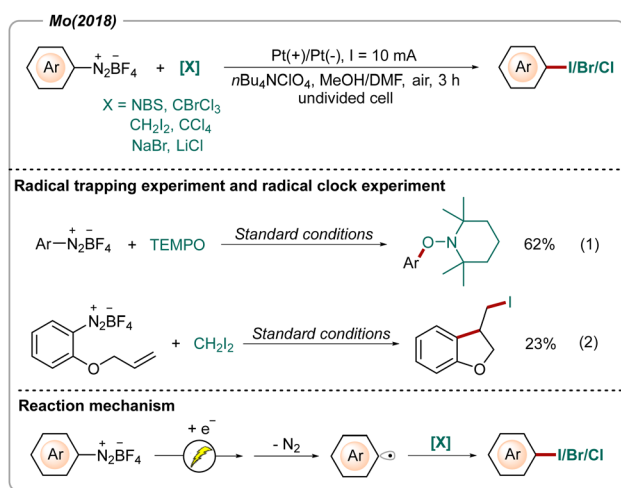
**Scheme 26** Phenanthrene-mediated electrochemical cyclization of *o*-halophenylacrylamides.

was identified, as shown in Scheme 26. At first, cathodic single-electron reduction of phenanthrene generates the radical anion **I**, which then reacts with aryl halides *via* a single-electron transfer (SET) process to deliver the aryl radical **II**. Subsequently, further reduction of the aryl radical **II** occurs, yielding the key aryl anion **III**, followed by intramolecular Michael addition and hydrogenation to obtain the final cyclization product.

### 3. Diazonium salts and their variations as aryl radical precursors

Over the past few decades, aryl diazonium salts have become indispensable synthons in synthetic chemistry, especially serving as aryl radical precursors in arylation reactions.<sup>4</sup> Recently, various catalytic strategies encompassing transition-metal, photoredox, and electrochemical catalysis systems were established for the precise reduction of aryl diazonium salts. Among the methods developed, electrocatalysis is undoubtedly attractive as an environmentally sustainable and promising reduction technology for the generation of aryl radicals. In this section, we mainly document the synthetic application of aryl radicals generated from aryl diazonium salts and their variations by electrochemistry over the past twenty years.

The Sandmeyer reaction is considered to be one of the most powerful tools to convert aryl diazonium salts into aryl halides.<sup>59</sup> In 2018, Mo *et al.* employed the burgeoning electrochemical strategy to achieve a Sandmeyer halogenation of aryl diazonium salts, which provided a metal-free route to the synthesis of structurally diverse aryl halides in up to 96% yield (Scheme 27).<sup>60</sup> This characteristic work featured a wide range of substrates, such as a variety of easily available and inexpensive halogen sources, including NBS, CBrCl<sub>3</sub>, CH<sub>2</sub>I<sub>2</sub>, CCl<sub>4</sub>, LiCl, and NaBr, which were efficiently converted into the

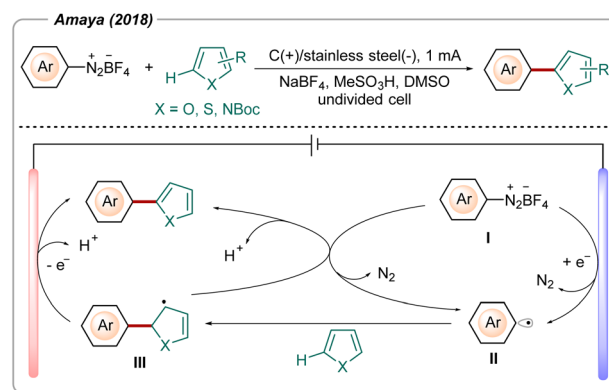


**Scheme 27** Electrochemical halogenation of aryl diazonium salts using diverse halogen sources.

relevant aryl halides in high yields. Moreover, this halogenation reaction could be easily scaled up to the three-gram level using large-sized graphite plate electrodes to decrease the current density ( $j = 2.78 \text{ mA cm}^{-2}$ ), thereby offering an opportunity for further synthetic applications.

A series of control experiments were performed to unravel the halogenation mechanism. Upon subjecting 2.0 equivalents of the radical scavenger TEMPO to the reaction system, a coupled product (Ar-TEMPO) was isolated in 62% yield. Furthermore, a radical clock experiment was carried out using a diazonium salt bearing an allyloxy group at the adjacent position, and this gave the cyclization product in 23% yield. These observations confirmed the formation of aryl radicals under standard conditions.

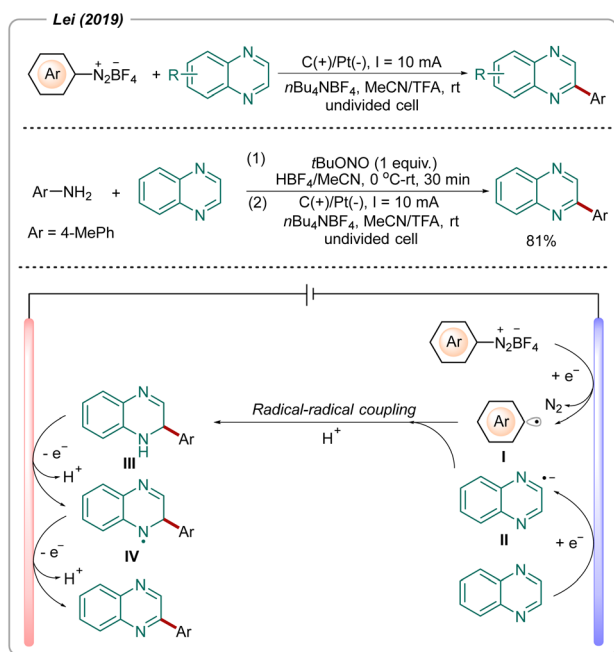
The addition of aryl radicals generated from aryl diazonium salts to aromatic compounds was first reported by Gomberg and Bachmann, providing a straightforward and powerful strategy for building diverse asymmetrical biaryls.<sup>61</sup> In 2018, Amaya *et al.* described a general electrochemical C(sp<sup>2</sup>)-C(sp<sup>2</sup>) cross-coupling of aryl diazonium salts with heteroarenes in the absence of any metal catalysts (Scheme 28).<sup>62</sup> This cross-coupling reaction occurred in an undivided cell equipped with carbon as the anode and stainless steel as the cathode, furnishing the coupled products in moderate to good yields. Importantly, a range of heteroarenes, including furans, pyrroles, and thiophenes, could all be coupled efficiently with aryl diazonium salts under standard conditions. Moreover, mesitylene was also applied as a coupling partner in this conversion. The proposed mechanism involves the initial generation of the aryl radical **II** by a cathodic single-electron reduction of the aryl diazonium salt **I**. Subsequently, the addition of the aryl radical **II** to a heteroarene affords the radical intermediate **III**, followed by anodic oxidation and deprotonation to afford the desired coupled product. Undeniably, the intermediate **III** can also react with the aryl diazonium salt to generate the radical intermediate **II** and the final product, as supported by theoretical calculations. However, the substrate scope of aromatics is limited to electron-rich heteroarenes; the arylation of electron-deficient heteroarenes remains challenging.



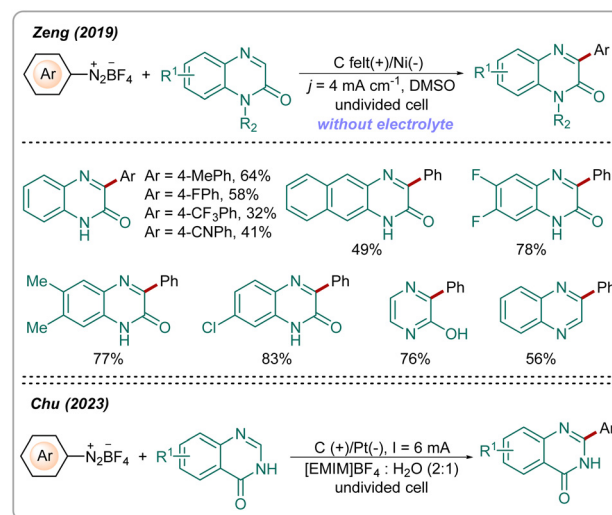
**Scheme 28** Electroreductive cross-coupling of aryl diazonium salts with electron-rich heteroarenes.

In 2019, Lei *et al.* utilized a similar electrochemical strategy to realize an elegant C(sp<sup>2</sup>)-C(sp<sup>2</sup>) cross-coupling of aryl diazonium salts with electron-deficient heteroarenes in an undivided cell without any metal catalysts and chemical reductants (Scheme 29).<sup>63</sup> A detailed survey of the substrate scope showed that various electron-deficient (hetero)arenes, including pyridazine, quinoxalinone, naphthyridine, pyrazine, quinoline, and isoquinoline, were amenable for this cross-coupling reaction. Furthermore, the transformation of commercially available anilines with aryl diazonium salts was successfully performed *via* a one-pot two-step process. The practicality of this method was also further demonstrated in a continuous-flow electrochemical reactor. Detailed mechanistic studies provided important evidence of two different cathodic reduction events involving both the aryl diazonium salt and quinoxaline, leading to the crucial aryl radical **I** and radical anion **II**, respectively. Subsequent radical-radical coupling delivers the intermediate 2-aryl-1,2-dihydroquinoxaline **III**, which then undergoes anodic single-electron oxidation and deprotonation processes twice to afford the final cross-coupled product.

In the same year, Zeng *et al.* depicted a similar electrochemical C(sp<sup>2</sup>)-C(sp<sup>2</sup>) cross-coupling of quinoxalinones with aryl diazonium salts using carbon felt as the anode and nickel as the cathode, resulting in the synthesis of a series of synthetically useful 2-aryl quinoxalinones in moderate to good yields (Scheme 30).<sup>64</sup> Notably, this electrochemical reaction proceeded in an undivided cell without any external supporting electrolyte. Interestingly, the cross-coupled product was isolated in a yield of 53% when the reaction was carried out in the cathodic compartment of a divided cell. This phenomenon supported the proposal that the reaction could be realized



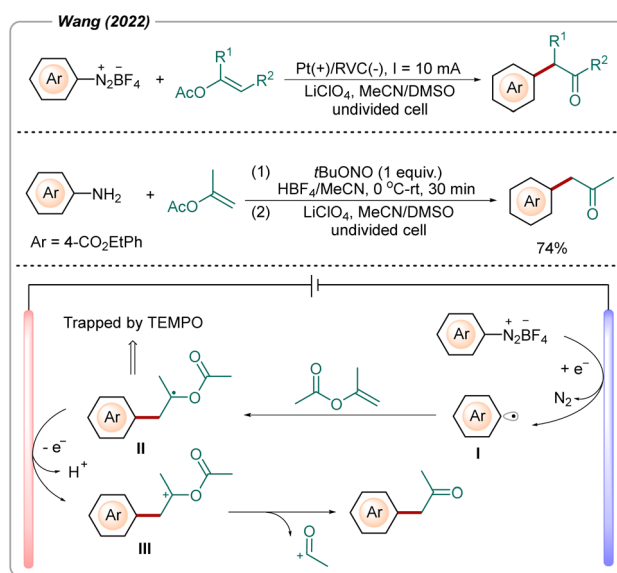
**Scheme 29** Electroreductive cross-coupling of aryl diazonium salts with electron-deficient heteroarenes.



**Scheme 30** Electroreductive heteroarylation of aryl diazonium salts.

without an anodic oxidation event, similar to the work of Amaya in 2018.<sup>62</sup> Based on the detailed CV analysis and control experimental outcomes, a Minisci-type reaction mechanism was proposed. Furthermore, in 2023, Chu *et al.* disclosed a similar electroreductive heteroarylation of aryl diazonium salts with quinazolinones in an aqueous solution of an ionic liquid, [EMIM]BF<sub>4</sub> (1-ethyl-3-methylimidazolium tetrafluoroborate), enriching the application of aryl diazonium salts in C(sp<sup>2</sup>)-C(sp<sup>2</sup>) cross-coupling reactions (Scheme 30).<sup>65</sup>

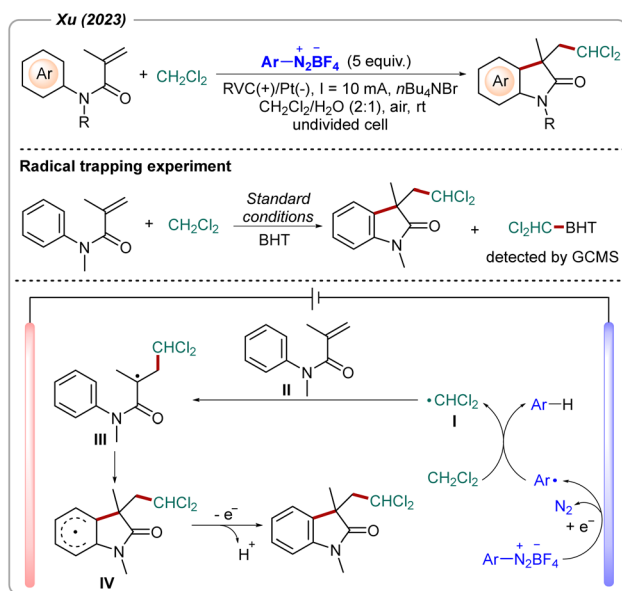
In 2022, Wang *et al.* illustrated a metal-free electrochemical method for the preparation of structurally diverse  $\alpha$ -arylketones by coupling aryl diazonium salts with enol acetates under mild conditions (Scheme 31).<sup>66</sup> Importantly, the



**Scheme 31** Electrochemical synthesis for the  $\alpha$ -arylation of ketones using enol acetates and aryl diazonium salts.

electrochemical transformation also proceeded smoothly using easily accessible anilines and enol acetates as the starting materials in a one-pot two-step process, resulting in the corresponding  $\alpha$ -arylketones in moderate to good yields. Mechanistically, the cathodic reduction of the aryl diazonium salt is preferred, followed by the loss of molecular  $N_2$  to give the aryl radical **I**. The aryl radical adds to the enol acetate to generate the radical intermediate **II**, which is trapped by TEMPO in the control experiment. Subsequently, anodic oxidation of the radical intermediate **II** occurs, resulting in the formation of the cation intermediate **III**. Finally, the release of the acyl cation from the cation intermediate **III** leads to the desired target product.

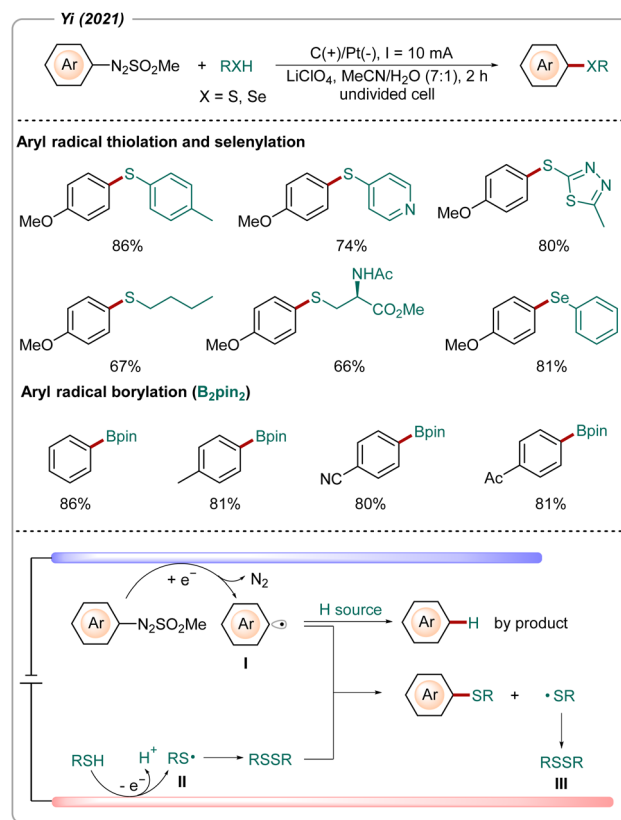
As mentioned earlier in this review, it is thermodynamically feasible for aryl radicals to activate inert  $C(sp^3)$ -H bonds *via* the HAT strategy. In 2023, Xu *et al.* employed this activation strategy to achieve an electrochemical polychlorinated alkylation cyclization of *N*-arylacrylamides with  $CH_2Cl_2$  using aryl diazonium salts as the reaction mediator (Scheme 32).<sup>67</sup> Notably, there was almost no reaction if  $H_2O$  was not used as a co-solvent; this may be related to the solubility of aryl diazonium salts. In addition, the reaction did not occur in the absence of aryl diazonium salts, which offered an important clue for proposing the HAT mechanism. In a radical trapping experiment, this cyclization was completely suppressed in the presence of stoichiometric BHT, wherein a cross-coupled product, BHT- $CHCl_2$ , was detected by GC-MS, indicating the generation of the  $\cdot CHCl_2$  radical intermediate in this protocol. Mechanistically, the aryl radical generated from the aryl diazonium salt by cathodic reduction reacts with  $CH_2Cl_2$  *via* a HAT process, resulting in the formation of the  $\cdot CHCl_2$  radical **I**. Subsequently, the addition of the radical **I** to the *N*-arylacrylamide **II** affords the alkyl radical intermediate **III**,



**Scheme 32** Electrochemical cyclization of *N*-arylacrylamide with  $CH_2Cl_2$  using a diazo salt as the mediator.

which quickly undergoes intramolecular cyclization to give the radical intermediate **IV**. Finally, the radical **IV** is oxidized at the anode and deprotonated to produce the desired product.

Arylazo sulfones are important variants of aryl diazonium salts, which can be easily prepared from commercially available and inexpensive anilines *via* a two-step reaction process.<sup>68</sup> Recent studies have found that arylazo sulfones usually work as effective aryl radical precursors to construct  $C(sp^2)$ -heteroatom bonds.<sup>69</sup> In 2021, Yi *et al.* developed an electroreductive radical thiolation/selenylation using arylazo sulfones as aryl radical donors, providing a transition-metal catalyst and reductant-free synthesis route to produce a series of decorated unsymmetrical thioethers and selenides (Scheme 33).<sup>70</sup> A hydrogenation product was isolated without a radical acceptor in 23% yield, which offered important evidence for the aryl radical mechanism. When the electricity was cut off at 0.5 h, the disulfide was detected by GC-MS in 37% yield. The isolated disulfide could react easily with arylazo sulfone, which indicated that disulfide was a key intermediate. More importantly, the cathode generated aryl radicals could also be trapped by  $B_2pin_2$ , resulting in a number of arylboronic esters in moderate to good yields. Mechanistically, the cathodic single-electron reduction of the arylazo sulfone leads to the formation of the aryl radical **I**. In the meantime, an anodic oxidation of a thiol occurs to generate the sulfur radical **II**, which then dimerizes



**Scheme 33** Electrochemical thiolation and borylation of arylazo sulfones with thiols and  $B_2pin_2$ .

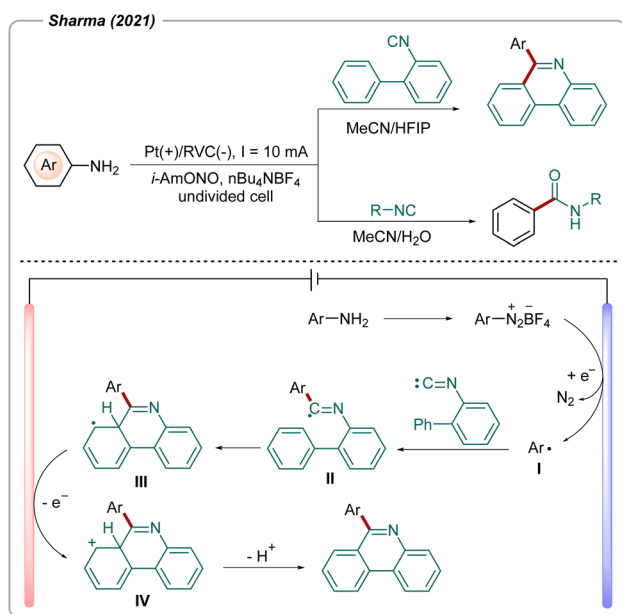
rapidly to deliver the crucial intermediate disulfide **III**. Then, the cathode-produced aryl radical **I** reacts with the disulfide **III** to obtain the desired product.

Aryl diazonium salts are usually prepared from the more stable and easily accessible aryl amines. Therefore, it is undoubtedly of great significance to utilize aryl amines as aryl radical precursors in organic synthesis.<sup>71</sup> In 2021, Sharma *et al.* established a highly atom-economical electrochemical strategy for the synthesis of diverse 6-aryl substituted phenanthridines in an undivided cell using aryl amines and 2-arylisocyanides as raw materials (Scheme 34).<sup>72</sup> Most importantly, the aryl amines could also react with a range of isocyanides without a phenyl group at the *ortho* position, yielding the corresponding amides in up to 81% yield. In this project, the key to success was the utilization of isoamyl nitrite (*i*-AmONO), which induced the conversion of aryl amines into the corresponding aryl diazonium salts. Mechanistically, the aryl diazonium salt **I** is initially generated from aryl anilines in the presence of *i*-AmONO. The single-electron reduction of the diazonium salt occurs at the cathode surface, producing the vital aryl radical **I**, which then couples with the 2-arylisocyanide to afford the radical intermediate **II**. The subsequent intramolecular radical cyclization and anodic oxidation gives the cation intermediate **IV**. Finally, the desired product is produced through deprotonated aromatization of the cation intermediate **IV**.

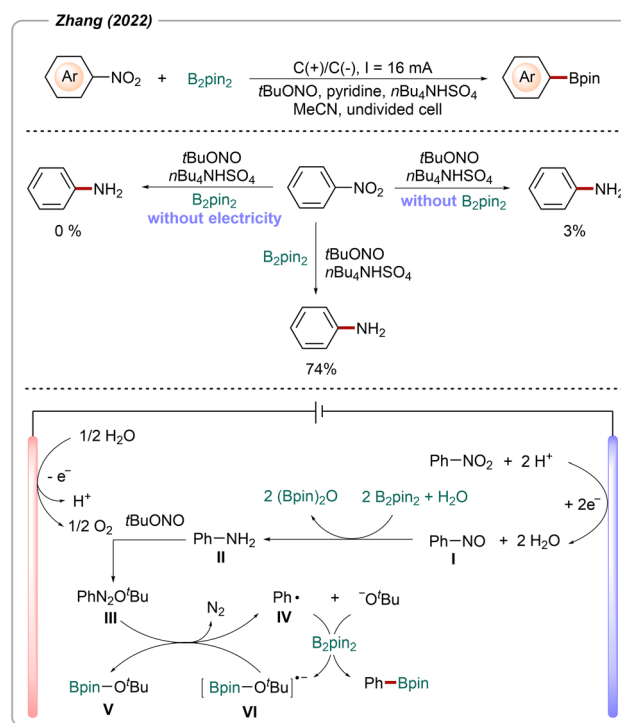
Nitroarenes are inexpensive and easily available chemical feedstocks that can be obtained by electrophilic nitration of arenes. Generally, nitroarenes can be readily reduced to aryl amines, indicating that nitroarenes are promising aryl radical precursors.<sup>73</sup> In 2022, Zhang *et al.* achieved a sustainable electrochemical denitrative radical borylation of nitroarenes

with  $B_2pin_2$  for the preparation of a series of synthetically useful arylboronic esters in moderate to good yields (Scheme 35).<sup>74</sup> In a brief survey of various borylation reagents, including  $B_2pin_2$ ,  $B_2neop_2$ ,  $B_2cat_2$ , and HBpin,  $B_2pin_2$  was the best choice to promote this transformation. Control experimental results provided evidence that both *t*BuONO and electricity were essential, otherwise the reaction was inert. In addition, the aryl amine was identified as a significant intermediate through a series of detailed confirmatory experiments. This denitrative radical borylation begins with the cathodic reduction of nitroarenes and the generated nitrosobenzene **I** subsequently reacts with  $B_2pin_2$  and  $H_2O$  to furnish the aryl amine **II**. In the presence of *t*BuONO, the aryl amine **II** is converted into the aryl diazonium salt **III**, which then undergoes single-electron transfer to afford the aryl radical **IV**. Finally, the aryl radical **IV** reacts with  $B_2pin_2$  and *tert*-butoxide anion to obtain the borylated product and the radical anion **VI**.

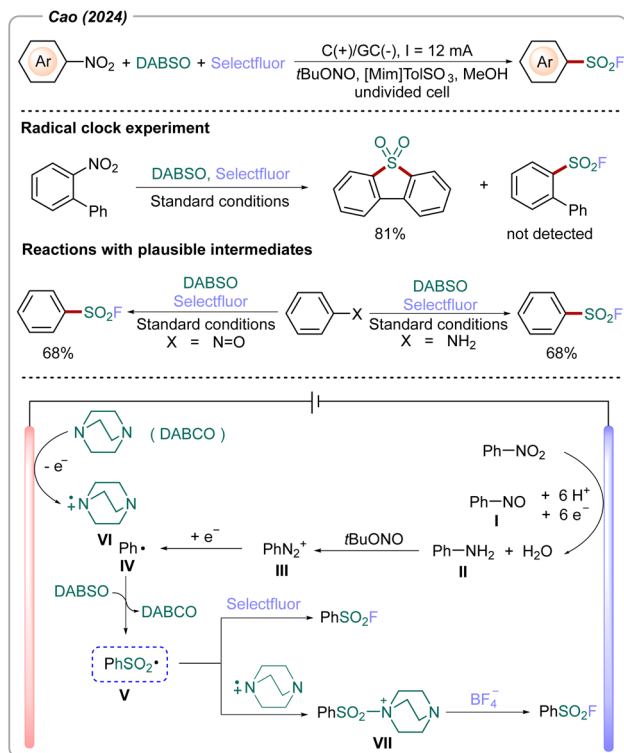
Encouraged by the success of the electrochemical denitration of nitroarenes, Cao *et al.* exploited an analogous electrochemical denitrative strategy to achieve an aryl radical-mediated three-component fluorosulfonylation of nitroarenes, DABSO, and Selectfluor, enabling the synthesis of structurally diverse aryl sulfonyl fluorides in moderate to good yields (Scheme 36).<sup>75</sup> The key to success relied on the assistance of the ionic liquid *N*-methylimidazolium *p*-toluenesulfonate ([Mim]TolSO<sub>3</sub>) as both a supporting electrolyte and additive to stimulate the selective reduction of nitroarenes. Furthermore, replacing MeOH with MeCN, DMF, EtOH, CF<sub>3</sub>CH<sub>2</sub>OH, or (CF<sub>3</sub>)<sub>2</sub>CHOH led to a lower or trace yield, which suggested that



**Scheme 34** Electrochemical coupling of aryl amines with 2-isocyanobiphenyls for the synthesis of phenanthridines.



**Scheme 35** Electrochemical denitrative radical borylation of nitroarenes with  $B_2pin_2$ .



**Scheme 36** Ionic liquid-promoted electrochemical reductive fluoro-sulfonylation of nitroarenes.

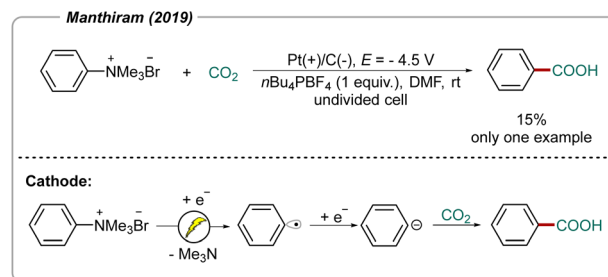
the solvent was a key factor for improving the reaction performance.

A radical clock experiment, which used 2-nitro-1,1'-biphenyl as a reaction substrate, provided clear evidence for an aryl-radical-based mechanism. Furthermore, the nitrosobenzene and aniline were converted into the corresponding aryl sulfonyl fluorides under standard conditions in good yields, which indicated that both nitrosobenzene and aniline were plausible reaction intermediates. Combined with the detailed CV analysis and other control experimental results, the possible reaction mechanism is shown in Scheme 36. Initially, the nitroarene undergoes a cathodic six-electron reduction assisted by the ionic liquid [Mim]TolSO<sub>3</sub>, along with protons, forming the aryl amine **II** via the ArNO intermediate **I**. The aryl amine **II** can be converted into the corresponding aryl diazonium salt **III** in the presence of *t*BuONO, which then undergoes single-electron reduction on the cathode surface, generating the key aryl radical **IV**. Then, the aryl radical **IV** is quickly captured by SO<sub>2</sub> formed from DABSO to produce the sulfonyl radical **V** and DABCO, the latter of which is oxidized at the anode to the corresponding radical cation **VI**. Notably, the sulfonyl radical **V** generally undergoes two different reaction pathways. In one case, the sulfonyl radical reacts directly with Selectfluor to yield the desired product. Apart from this, the radical-radical coupling of the sulfonyl radical with the anode-generated radical cation **VI** affords the cation intermediate **VII**, which is followed by nucleophilic substitution with BF<sub>4</sub><sup>-</sup> to give the anticipated product.

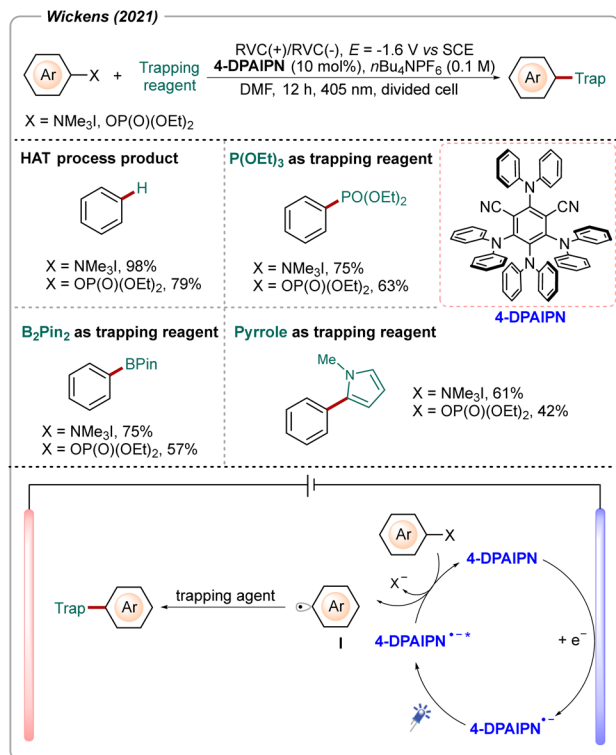
## 4. Other aryl radical precursors

Aryl quaternary ammonium salts have impressive application prospects in the arylation of fine chemicals owing to their inherent advantages, such as easy preparation from primary, secondary, or tertiary amines, as well as stability during storage and usage.<sup>76</sup> The cathodic reduction technology provides an extremely attractive alternative for the reductive cleavage of the aryl C–N bond to generate the aryl radical, avoiding the involvement of chemical reductants. In 2019, Manthiram *et al.* utilized the cathodic reduction of the aryl quaternary ammonium species to realize the synthesis of benzoic acid in the absence of a sacrificial anode (Scheme 37).<sup>77</sup> Regrettably, the authors did not investigate this electroreductive carboxylation of the aryl quaternary ammonium species with CO<sub>2</sub> in detail; only one product (benzoic acid) was obtained in 15% yield. Despite this limitation, there are important implications for promoting the development of electrocatalytic aryl radical chemistry.

The generation of aryl radicals *via* the electroreduction of aryl quaternary ammonium salts has attracted considerable research interest from many synthetic chemists. In 2021, Wickens *et al.* developed a novel electron-primed photoredox strategy for achieving the reductive functionalization of aryl quaternary ammonium salts (Scheme 38).<sup>78</sup> This protocol was conducted in a divided cell that was equipped with RVC as the anode and cathode. Using **4-DPAIPN** as the catalyst, the hydrogenation, phosphorylation, borylation, and heteroarylation products were all obtained in moderate to good yields. Excitingly, aryl C–O bonds were also easily activated to produce the corresponding aryl radicals, which further confirmed the superiority of this electrophotocatalytic strategy. Mechanistically, this electrophotocatalytic cycle begins with the cathodic single-electron reduction of the catalyst **4-DPAIPN**, producing the radical anion **4-DPAIPN<sup>•-</sup>**, which is then excited by visible light to produce the excited-state radical cation **4-DPAIPN<sup>•+</sup>\***, which has strong reducibility. Immediately, the aryl quaternary ammonium salt or aryl phosphate reacts with the excited-state radical cation, **4-DPAIPN<sup>•+</sup>\***, to deliver the aryl radical **I** and regenerate the catalyst. Finally, the aryl radical is captured by diverse trapping reagents to furnish decorated aryl(hetero) arenes.

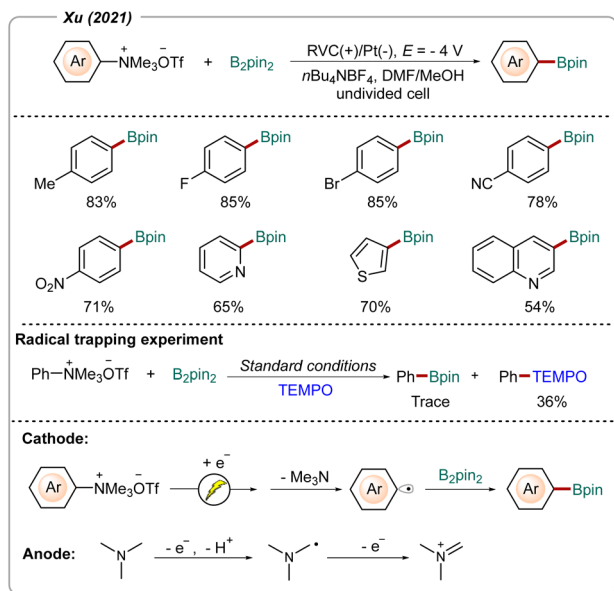


**Scheme 37** Electrochemical carboxylation of aryl quaternary ammonium salts with CO<sub>2</sub>.



**Scheme 38** Electron-primed photoredox functionalization of aryl ammonium salts and aryl phosphates.

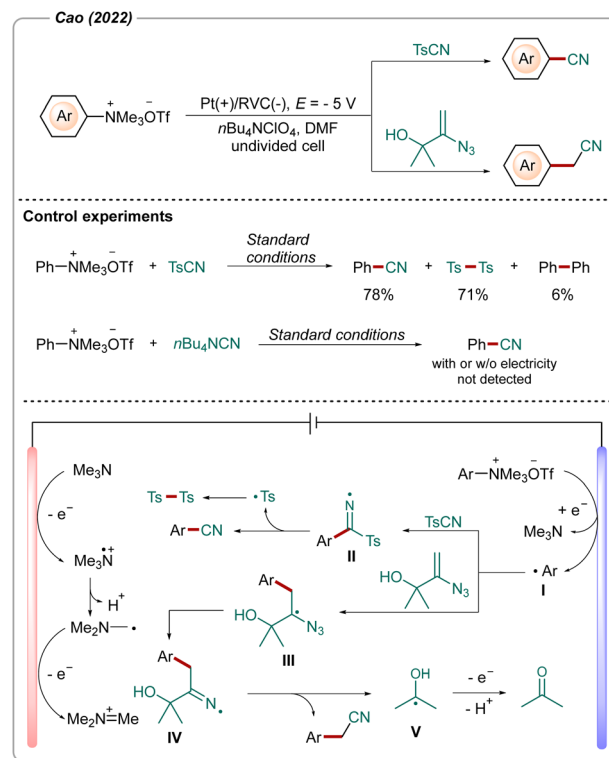
In 2021, Xu *et al.* developed a direct electroreductive strategy for the radical borylation of aryl quaternary ammonium salts with B<sub>2</sub>pin<sub>2</sub> (Scheme 39).<sup>79</sup> This protocol presented a straightforward and powerful route to the construction of



**Scheme 39** Electrochemical radical borylation of aryl quaternary ammonium salts with B<sub>2</sub>pin<sub>2</sub>.

various synthetically useful organoboronates in moderate to good yields. Notably, this aryl radical borylation reaction was almost suppressed in the presence of TEMPO, wherein a cross-coupled product (TEMPO-Ph) was isolated in 36% yield, which suggested that an aryl radical intermediate was involved in this protocol. Combining this information with CV analysis, a believable mechanism is outlined in Scheme 39. This transformation begins with the cathodic single-electron reduction of aryl trimethylammonium salts. After the loss of trimethylamine, the resulting aryl radical reacts with B<sub>2</sub>pin<sub>2</sub> to give the anticipated arylboronic esters. Additionally, the cathode-generated trimethylamine loses two electrons and a proton at the anode surface to form the imine cation.

To further strengthen the synthetic application of aryl quaternary ammonium salts as aryl radical precursors in organic electrochemistry, Cao *et al.* developed a novel strategy for the electrochemical cyanation and cyanomethylation of aryl trimethylammonium salts (Scheme 40).<sup>80</sup> This innovative approach utilized tosyl cyanide (TsCN) and an azido allyl alcohol as the cyanation and cyanomethylation reagents, respectively, offering a sustainable alternative to traditional metal-catalyzed reactions, and enabled the synthesis of various cyanated and cyanomethylated arenes in moderate to good yields. Under standard conditions, in addition to the cyanation product, some dimer products, including biphenyl and Ts-Ts, were isolated in yields of 6% and 71%, respectively. These observations provided clear evidence for the involvement of a



**Scheme 40** Electrochemical cyanation and cyanomethylation of trimethylammonium salts.

phenyl radical and a sulfonyl radical in this transformation. Furthermore, it was observed that the reaction between the aryl trimethylammonium salt and  $n\text{Bu}_4\text{NCN}$  did not occur under standard conditions, which ruled out the mechanism involving nucleophilic substitution.

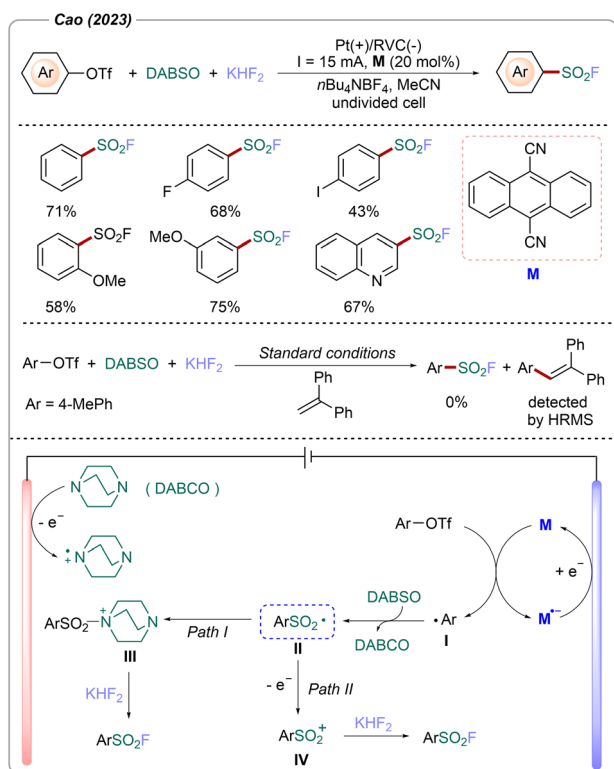
Based on the above-described results and CV investigations, a convincing mechanism is presented in Scheme 40. Initially, the aryl trimethylammonium salt is preferentially reduced to the aryl radical **I**. During the cyanation process, the desired product is synthesized through a Barton nitrile transfer reaction, which concomitantly leads to the formation of the sulfonyl radical. Conversely, the formed aryl radical **I** adds to the C=C bond in the azido allyl alcohol, which is followed by the release of molecular  $\text{N}_2$  to generate the nitrogen-centered radical intermediate **IV**. Eventually, the radical **IV** undergoes C–C bond cleavage, leading to the cyanomethylation product and the ketyl radical **V**, which then undergoes an anodic oxidation and deprotonation process to generate acetone.

Aryl triflates are important building blocks that are often used as aryl radical precursors in organic synthesis. Recently, a plethora of synthetic strategies realized the reduction of aryl triflates.<sup>6</sup> In 2023, Cao *et al.* described an attractive electroreductive strategy for the generation of aryl radicals from aryl triflates, providing an environmentally friendly and general approach for the synthesis of diverse decorated aryl sulfonyl fluorides in an operationally simple undivided cell (Scheme 41).<sup>81</sup> In this case, the utilization of the effective

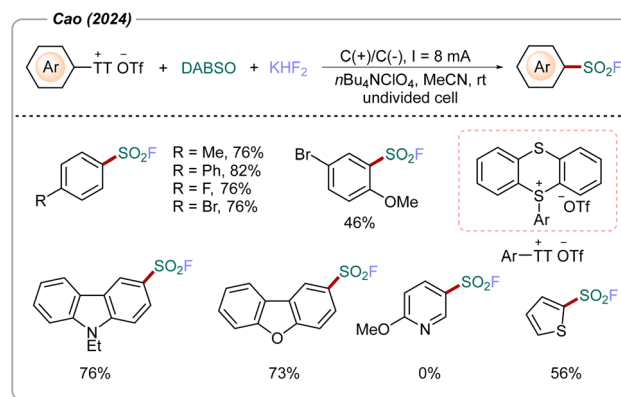
redox mediator 9,10-dicyanoanthracene was the key to achieving the fluorosulfonylation of aryl triflates, DABSO, and  $\text{KHF}_2$ . Notably, a trace amount of 4,4'-dimethyl-1,1'-biphenyl was detected by GC-MS analysis; this offers important evidence for the involvement of the 4-methylphenyl radical. Additionally, the aryl radical was also captured by ethene-1,1-diyldibenzene. Detailed CV studies revealed that 9,10-dicyanoanthracene had a lower reduction potential ( $E_{\text{red}} = -0.95 \text{ V vs. Ag/AgCl}$ ) than the aryl triflates; this supports the cathodic reduction of the redox mediator as the initial step.

Mechanistically, the redox mediator is initially reduced to the radical anion at the cathode surface, which in turn reduces the aryl triflate to the aryl radical **I**. Subsequently, the aryl radical **I** reacts with DABSO to generate the sulfonyl radical **II** and DABCO. Following path I, DABCO could be oxidized to the corresponding radical cation at the anode, which then couples with the sulfonyl radical **II** to deliver the cation intermediate **III**, followed by the nucleophilic substitution of  $\text{KHF}_2$ , furnishing the anticipated product. Following path II, the sulfonyl radical **II** can be oxidized to the sulfonyl cation **VI**, and the nucleophilic addition of  $\text{F}^-$  to form the target product is also possible.

Encouraged by previous studies on the electrochemically initiated fluorosulfonylation of aryl radicals, many chemists have focused on enriching the range of aryl radical precursors. Very recently, Cao *et al.* employed easily available aryl thianthrenium salts<sup>82</sup> as aryl radical precursors to realize a novel electrochemical fluorosulfonylation in the absence of any metal catalysts and chemical reductants in an undivided cell (Scheme 42).<sup>83</sup> This protocol exhibits excellent substrate compatibility, providing a sustainable and powerful approach for the construction of structurally diverse aryl sulfonyl fluorides. Furthermore, this strategy has been successfully applied in the fluorosulfonylation of drug molecules, such as gemfibrozil and epiandrosterone. Unfortunately, thianthrenium salts bearing a pyridine, pyrazole ring, or a cyclohexyl group could not be converted into the corresponding products. Similar to the previous work reported by the same group in 2023,<sup>81</sup> the aryl radical was first generated at the cathode surface.



Scheme 41 Electrochemical fluorosulfonylation of aryl triflates.



Scheme 42 Electrochemical fluorosulfonylation of thianthrenium salts, DABSO, and  $\text{KHF}_2$ .

## 5. Conclusions and outlook

Aryl radicals are versatile reaction intermediates for the assembly of C(sp<sup>2</sup>)-carbon/heteroatom bonds, and the chemical transformations involved are considered ideal complements to transition-metal-catalyzed arylation reactions. Attractive electroreduction strategies provide a sustainable alternative for the generation of aryl radicals. Given the typical inherent properties of aryl radicals and their synthetic application in organic chemistry and drug discovery, we have presented herein a comprehensive review of recent achievements in the generation of aryl radicals *via* electroreduction strategies. The full spectrum of aryl radical precursors, including aryl halides, aryl diazonium salts, arylazo sulfones, aryl amines, nitroarenes, aryl quaternary ammonium salts, aryl triflates, and aryl thianthrenium salts, is discussed in detail.

Although impressive progress has been achieved in the field of the electroreductive functionalization of aryl radicals, challenges and opportunities remain. Generally, aryl halides have a higher reduction potential than aryl radicals ( $E_{\text{red}} = +0.05$  V). This significant difference in potential means that aryl radicals are reduced easily at the cathode, which limits their wider application. Moreover, the activation of C(sp<sup>3</sup>)-H bonds by electroreductive aryl radicals has not been sufficiently applied in synthetic chemistry. To address these issues, future efforts in this field may focus on exploiting novel and powerful electroreductive systems, including the utilization of redox catalysts, and more specific approaches that merge with photocatalysis, metal catalysis, and Lewis acid catalysis. We also hope that this review will provide insights into this emerging research field and stimulate continued interest in the identification of new aryl radical precursors, expanding the known transformations into new molecular categories.

## Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

We thank the National Natural Science Foundation of China (no. 22261019), the Jiangxi Provincial Natural Science Foundation (no. 20224BAB213004, 20232BAB203007), the Jiangxi Province Key Laboratory of Organic Functional Molecules (no. 2024SSY05141), and the Jiangxi Science & Technology Normal University (no. 2021BSQD32, 2023KFJJ03) for financial support.

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