

## REVIEW

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# Modern photo- and electrochemical approaches to aryl radical generation

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Aryl rings appear in a plethora of natural products and drugs. The vast majority of arylation processes still rely on the utilization of transition-metal complexes as catalysts. Another important strategy for introducing aryl rings into an organic skeleton operates through a radical pathway. The chemistry of aryl radicals has witnessed rapid development during the last few decades, especially as these species are crucial intermediates in many synthetically meaningful organic transformations, such as the Sandmeyer or Pschorr reactions. Predominately, they are prepared employing conventional redox reagents (oxidants or reductants) that are often used in large excess. In turn, recent developments in photocatalysis and synthetic electrochemistry allow for the assembly of Ar<sup>•</sup> species in a more sustainable and straightforward way; however, these advancements have not been timely and critically summarised to date. This review fills this obvious gap and sums up recent advances in processes involving Ar<sup>•</sup> by highlighting some challenges and identifying potential areas for improvement, which might inspire future research endeavors in this topic.

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## 1. Introduction

Radicals are open-shell species that are crucial in the fields of synthetic organic chemistry,<sup>1</sup> materials chemistry<sup>2</sup> and

biology.<sup>3</sup> The very first example of the utilization of an aryl radical as an intermediate was reported in 1866 by Griess;<sup>4</sup> however, the first real development in radical chemistry in general was initiated in 1900 with a description of the triphenylmethyl radical.<sup>5</sup> Since then, many methods for the preparation and synthetic applications of these useful, but specific, intermediates have been developed.<sup>6</sup>

The analysis of the radical stabilization energies<sup>7</sup> (RSEs) of a variety of radicals along with bond dissociation energies<sup>8</sup> (BDEs) of different C–H bonds (Fig. 1a) leads to the conclusion

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that the phenyl radical is an exceptionally unstable, thus extremely reactive, open-shell intermediate of transient character,<sup>9</sup> with a remarkably short lifetime of about 150 ns regarding its disruptive hydrogen-atom transfer (HAT) process with the solvent (acetonitrile, MeCN).<sup>10</sup> Therefore, after its initial formation, it may undergo many follow-up processes, such as hydrogen removal from solvent or other molecules present nearby, halogen transfer or addition to various bonds (Fig. 1b).<sup>6a,b</sup> However, *in situ*-formed aryl radicals were successfully applied as mediators in the formation of more stable radicals, finally allowing catalytic functionalisation of amides<sup>11</sup> or aliphatic alcohols,<sup>12</sup> thus underlining their utility in synthetic organic chemistry.

In general, aryl radicals are produced *via* single-electron transfer (SET) with a variety of precursors (Fig. 1c).<sup>6,13</sup> A homolytic cleavage event that leads to the formation of an aryl radical can be induced by conventional (chemical) reagents, visible light (photocatalysis) or electric current (synthetic electrochemistry). Classical methods<sup>6,13</sup> for the generation of aryl radicals typically require the use of over-stoichiometric amounts of an oxidant or a reductant (expensive and/or toxic), as well as usually harsh reaction conditions (often elevated temperatures, *etc.*). While classical oxidative transformations are usually performed employing metal-based oxidants (Mn(III), Mn(VII), Fe(III), Mo(V) *etc.*), reductive transformations may be also initiated by a combination of an inorganic base and a small organic molecule.<sup>14</sup> Along with the terminology proposed by Studer and Curran,<sup>15</sup> these transformations can be classified as ‘electron-catalyzed reactions’. These seminal contributions set the stage for most developments within the modern reductive photochemistry.

During the last few decades, visible-light-photoinduced electron transfer methods (*e.g.* photoredox catalysis) and electrochemistry have enabled a tremendous array of new methods for the preparation of aryl radicals. In this way, these

intermediates were successfully employed in C–C, C–B, and C–F bond-forming processes.<sup>6,13,16</sup> Although some reviews<sup>6,13,17</sup> have appeared recently that partially cover examples presented in our work, none of them evaluate all of the possible precursors of aryl radicals, with special emphasis given to modern photochemical/electrochemical approaches. This article aims to fill this obvious gap.

Herein, we review and analyse recent achievements in the generation of aryl radicals through the modern synthetic methods of photochemistry and synthetic electrochemistry, and their combination, photoelectrochemistry. To realize that intention, the article is divided into two main sections which are dedicated to reductively and oxidatively induced methodologies. Obviously, the terms ‘reductive’ and ‘oxidative’ do not refer to the entire process, but describe the nature of the first electron transfer event relative to a given precursor. Within the abovementioned sections, we showcase differences between synthetic photochemistry and electrochemistry for a given precursor. We believe that this structure of the review will provide a comprehensive overview of modern aryl radical chemistry and possibly stimulate new ideas about how to improve existing methods or even develop other ones, employing other plausible precursors.

## 2. Photochemistry versus electrochemistry versus photoelectrochemistry

### 2.1. Photochemistry

In recent years, photochemistry has become a powerful tool for the activation of small molecules through their direct excitation (direct photochemistry) or *via* energy or electron transfer from the photocatalyst.<sup>20</sup> In the case of photon-coupled elec-



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tron transfer (photoredox catalysis) in the general sense, the *modus operandi* relies on the fact that photoexcited redox catalysts (PC\*) (such as metal complexes, organic dyes, or semiconductors) can simultaneously act as oxidants (reductive quenching catalytic cycle) and reductants (oxidative quenching catalytic cycle) (Scheme 1a). Therefore, photoredox catalysis makes it possible to continuously form small amounts of highly reactive species (radicals, radical ions, and charge transfer (CT) complexes) under mild conditions. The number of applications of photocatalysis grows every year because of the use of very mild conditions for highly selective and environmentally safe reactions. However, this methodology possesses some limitations: (1) challenges in scale-up due to limited light penetration; (2) a limited electrochemical potential window due to the energy limits resulting from the energy of visible photons; and (3) insufficient atom economy due to the addition of stoichiometric amounts of sacrificial reagents (oxidants and reductants). Nevertheless, it has indeed had a huge impact on aryl radical generation methods over the past decade.

## 2.2. Electrochemistry

Nowadays, more and more of the electrical energy produced by humans comes from renewable sources, such as wind or solar radiation. In this context, electrical energy has recently started to be considered as a green oxidant or a reductant in terms of synthetic methodology. Mainly due to the postulated green character of electricity, as well as the development of dedicated commercial equipment, the past decade has witnessed a renaissance in electrochemical organic synthesis.<sup>17b,21</sup>

Electrochemistry is one of the most powerful tools for performing electron transfers available to chemists, as its biggest advantages are the ability to strictly control the applied current or potential, as well as the fact that the redox window is in theory only limited by the tolerance of a given solvent.<sup>17b,21a,22</sup>



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More importantly, it constitutes a potent strategy for the generation of open-shell intermediates.<sup>21a,23</sup> From the standpoint of redox processes applied toward the formation of aryl radicals, these species can be obtained *via* reduction at a cathode or oxidation at an anode. To date, most known electrochemical methods for the generation of aryl radicals are based on the electrochemical reduction of a given organic precursor (section 3); however, oxidation-based methodologies are also established in the literature (section 4).

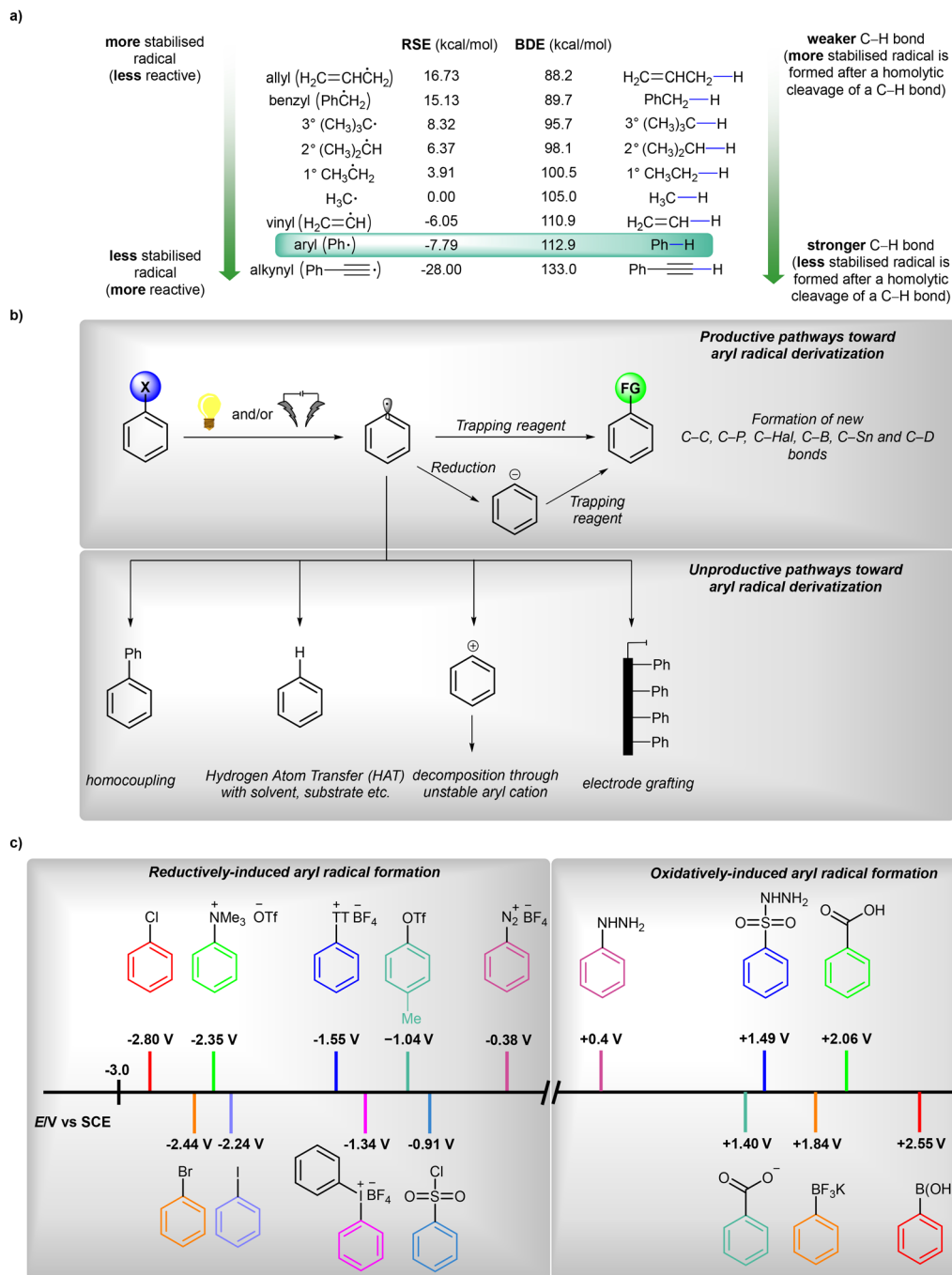
The obvious difference between a given photochemical transformation and an electrochemical one is the presence of electrodes immersed in the solution between which a potential is applied. Additionally, a supporting electrolyte should be added to a cell to facilitate charge flow between electrodes, when the potential difference between them is too high. Importantly, the existence of electrodes in contact with the solution causes the electron transfer between an electrode and a given species in a solution to be interfacial in nature, which undoubtedly has a huge impact on the result/success of a designed electrochemical process. To give an example, for many electrochemical processes, the reaction rates are strongly dependent on the applied currents, indicating that a turnover-limiting electron transfer is operative.<sup>24</sup> Therefore, the heterogeneous character of the electron transfer may affect the mechanistic aspects of the activation of a given precursor of aryl radicals.

Other major problems that chemists may encounter during an electrolysis toward aryl radicals are: (1) possible formation of phenyl anions ( $E^\circ(\text{Ph}^{\cdot-}/\text{Ph}^-) = 0.05 \text{ V vs. SCE}$ )<sup>10a</sup> – particularly in the case of reductively induced methods – and (2) the possibility of electrografting.<sup>25</sup> Still, many electrochemically based transformations toward aryl radicals were developed that produce these open-shell species in a selective and efficient manner (*vide infra*). Specifically, there are several experimental techniques that enable the efficient formation and transformation of aryl radicals. These include: (1) applying large excess (often >5 equivalents) of another reactant in order to immediately trap aryl radicals; (2) the presence of an electron mediator (a transfer of electrons occurs in a bulk solution, away from the electrode); (3) aryl radicals are trapped by a multiple bond within the same molecule in intramolecular radical cyclization reactions.

## 2.3. Photoelectrochemistry

Photoelectrochemistry is a constructive combination of both of the abovementioned methods (photochemistry and electrochemistry) (Scheme 1c). This merging seems to be the answer to the challenges of these two methods. From the point of view of aryl radical generation, two photoelectrochemical approaches can be involved: electrochemically-mediated photoredox catalysis (ePRC) and interfacial photoelectrochemistry (iPEC).<sup>26</sup> Electrochemically-mediated photoredox catalysis (ePRC) can operate *via* two different strategies: photoexcitation of electrochemically generated ions where, for example, a photocatalyst can be firstly oxidised (or reduced) at the electrode and then get excited to the excited state, forming a super-oxidant (or a super-reductant); or by replacing sacrificial





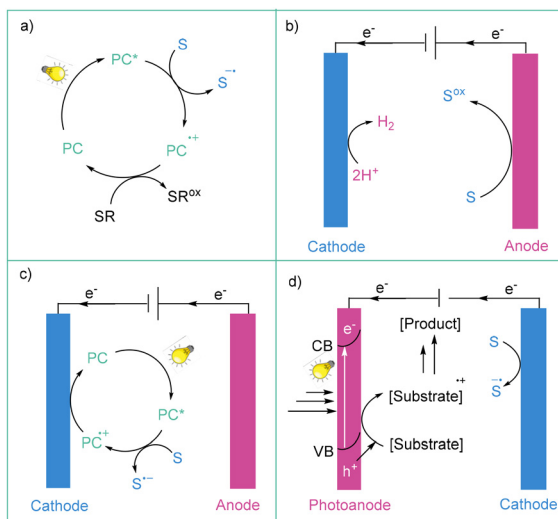
**Fig. 1** (a) General overview on generation and possible transformations of aryl radicals, (b) radical stabilization energies (RSE) and bond dissociation energies (BDE, given at 298 K) values for phenyl radical and its analogues and (c) comparison of oxidation<sup>18</sup> and reduction<sup>19</sup> potentials of typical aryl radical precursors. RSE values are given in reference to  $\cdot\text{CH}_3$ .

oxidants/reductants with the current (Scheme 1c).<sup>27</sup> In the case of iPEC, the most commonly used systems are based on two electrodes (cathode and anode), and one of them is a photoelectrode, which is coated in a photoresponsive material (typically a semiconductor). A semiconducting photoelectrode is exposed to visible light and generates electron-hole pairs that are used to drive a redox reaction. In such a system, the applied potential followed by the irradiation promotes an elec-

tron ( $e^-$ ) from the valence band (VB) to the conductive band (CB), generating a hole ( $h^+$ ), which is used for oxidation, and the flow of electrons in the CB, which is used for the reduction (Scheme 1d). Photoelectrochemical cells are widely studied for solar energy conversion; however, their use in organic synthesis is relatively underexplored.<sup>26,27</sup>

It should be emphasized that photoelectrochemical methods operate within low reduction or high oxidation





**Scheme 1** Comparison of (a) photoredox catalysis, (b) electrochemistry, (c) photoelectrocatalysis and (d) photoelectrochemical cells (PECs) for organic synthesis. PC – photocatalyst; S – substrate; SR – sacrificial reagent.

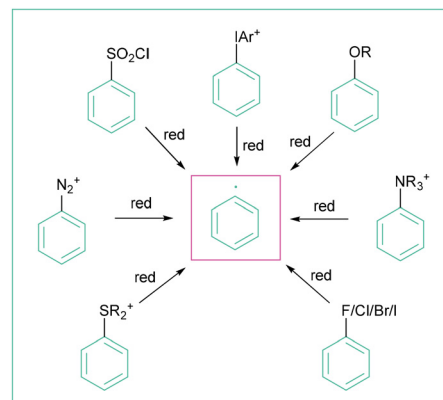
potentials, concomitantly avoiding over-reduction to aryl anions or over-oxidation to aryl cations of aryl radicals. This is because an electron transfer event between  $PC^{*+}$ / $PC^{*-}$  and substrate occurs in a bulk solution, that is, away from an electrode, therefore avoiding further reduction to the anion.

### 3. Reductively induced generation of aryl radicals

The formation of aryl radicals can generally be induced by a single-electron reduction of a given radical precursor. This can be realized by employing three different methodologies: photo-induced electron transfer (photoredox catalysis or through EDA complex formation and its subsequent reduction), organic electrochemistry<sup>28</sup> and photoelectrochemistry.<sup>26,29</sup> The reductively induced generation of aryl radicals is so far possible for aryl halides, aryl diazonium salts, sulfonyl chlorides, sulfonium salts, iodonium salts, aryl triflates and others (Scheme 2). The aforementioned precursors intrinsically differ in their ability to accept an electron, whereas charged species tend to be reduced much more easily than neutral molecules.<sup>30</sup> The reduction of charged precursors depicted in Scheme 2, however, is characterised by lower atom economy due to the liberation of higher-weight molecules, such as  $NR_3$ ,  $ArI$  or  $R_2S$ .

#### 3.1. Generation of aryl radicals from aryl halides

Aryl halides, although they are bench stable and readily available commercially and synthetically, have low reduction potentials (up to  $-2.8$  V vs. SCE for electron-rich chlorides), which severely limits the application of photocatalytically generated



**Scheme 2** Reductive generation of aryl radicals from different precursors.

aryl radicals. The most common applications of radicals generated photochemically from aryl halides include hydrodehalogenation, dehalogenative cyclization, intermolecular (hetero) arylation, phosphorylation, or borylation. Hereby, we present selected examples of pioneering and recent transformations of this type.

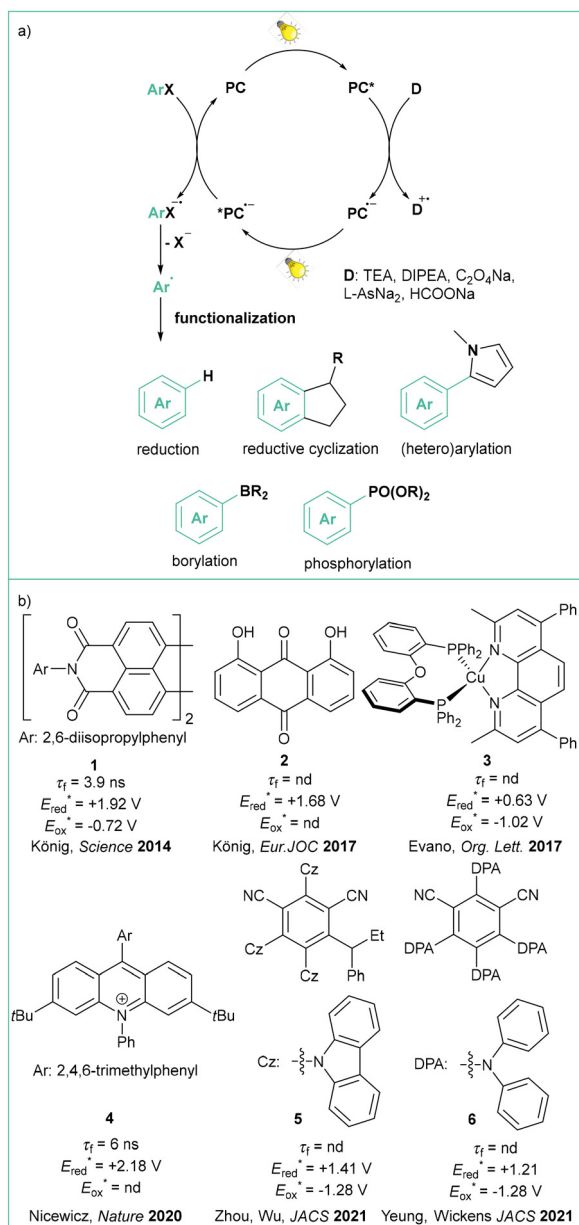
**3.1.1. Photochemistry.** Stephenson achieved the formation of aryl radicals from unactivated aryl iodides (alongside alkyl and vinyl iodides as well as some examples of intramolecular dehalogenative radical cyclization).<sup>31</sup> The system operates *via* a SET from the photoexcited iridium(III) to the aryl iodide forming an anion radical that decomposes into a halide anion and aryl radical which undergoes a HAT from tributylamine to give the hydrodehalogenated product. The same type of transformation using a different iridium complex  $[Ir(ppy)_2(dtbbpy)]PF_6$  was described independently in the same year by Lee.<sup>32</sup>

Less active halides, including chlorides, often require non-standard aryl radical generation strategies, which were recently summarised in an elegant review paper by Giedyk, Wenger, and Lu.<sup>33</sup>

As an example, aryl chlorides and fluorides were activated toward aryl radicals by employing indole thiolate organocatalyst, which upon excitation with 405 nm light, achieves strongly reducing properties.<sup>34</sup> Using this strategy, dehalogenation, Birch reduction, phosphorylation and borylation were achieved featuring broad substrate scopes and moderate to good efficiency.

In 2014, one of these approaches to overcome the high potential barrier was based on a two-photon excitation process (sometimes also called ‘consecutive photoinduced electron transfer’, ConPET, see: Scheme 3)<sup>35</sup> as seminal conceptualized by König.<sup>36</sup> The strategy is based on a single photocatalyst (PC), in this case commercially available *N,N'*-bis(3-pentyl)perylene-3,4,9,10-bis(dicarboximide), PDI (**1**), that is first excited by visible light ( $PC^*$ ) and then quenched by  $Et_3N$  to give an anion radical ( $PC^{*-}$ ), which is excited again, resulting in a highly reduced coloured anion radical ( $*PC^{*-}$ ) which can transfer an electron to aryl iodides, bromides and some activated chlor-





**Scheme 3** (a) General mechanism of ConPET in relation to the synthesis and functionalisation of aryl radicals from aryl halides and (b) selected photocatalysts studied in the ConPET reaction with aryl halides. Redox potentials are given vs. SCE.

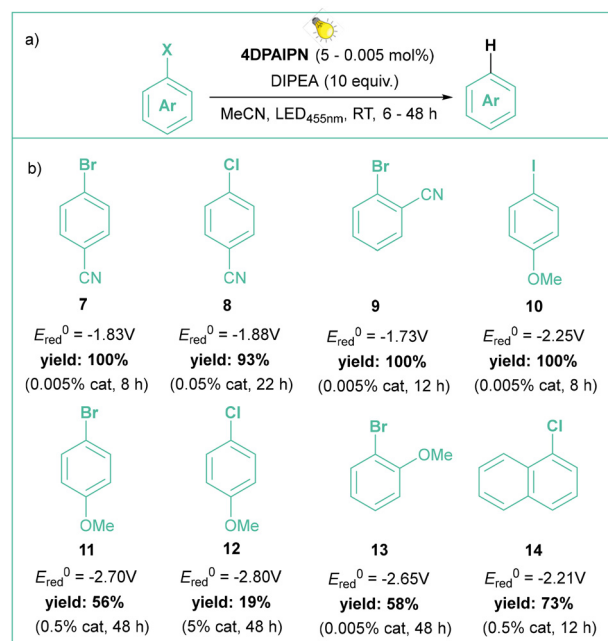
ides. The liberation of the halide anion results in an aryl radical that was subjected to a HAT from excess Et<sub>3</sub>N to give a hydrodehalogenation product or coupled with the pyrrole derivative when a radical trap was added in a very large excess (25–50 equiv.). A similar approach was later reported with the use of other photocatalysts (anthraquinone),<sup>37</sup> 9,10-dicyanon-thracene (DCA),<sup>38</sup> heteroleptic biphosphine/phenantroline Cu(I) complexes,<sup>39</sup> MesAcrBF<sub>4</sub>,<sup>40</sup> and 2,4,5-tri(9*H*-carbazol-9-yl)-6-(ethyl(phenyl)amino)isophthalonitrile, 3CzEPAIPN<sup>19a</sup>.

In the latter case, the authors successfully employed oxalate and ascorbate as inexpensive and environmentally friendly sacrificial electron donors. Gram-scale borylation of 4-chloro-

toluene was easily achieved by employing more intensive light irradiation and a longer reaction time. Independently, Yeung and Wickens developed a very similar system using 1,3-dicyano-2,4,5,6-tetrakis(diphenylamino)-benzene (4DPAIPN, **6**), 405 nm light irradiation, and sodium formate as an electron donor.<sup>41</sup> Besides typical dehalogenation, borylation, and phosphorylation (photo-Arbuzov) of aryl chlorides (with redox potential as low as -3.4 V vs. SCE), the authors also carried out successful hydroarylation of unactivated olefins. Of note, the reaction was viable with *tert*-butylvinylcarbamate, which gives access to the arylethylamine pharmacophore scaffold. Shortly afterwards, Jui *et al.* published a similar methodology for iodides and activated chlorides employing phenothiazine as photocatalyst.<sup>42</sup> Very recently, Gierschner, Wannemacher, and Kwon have studied the steric and photophysical parameters of popular cyanoarene catalysts including their related photodegradation processes (Scheme 4).<sup>43</sup> Careful investigation led to the development of systems capable of complete hydrodehalogenation of 4-bromobenzonitrile using as low as 0.005 mol% catalyst loading of 4DPAIPN under visible light irradiation (455 nm). At 0.05 mol% loading, the catalyst enabled facile gram-scale dehalogenation without degassing the reaction medium, which underlines its abnormally high oxygen tolerance.

Before the study of Yeung and Wickens was published, the ConPET mechanism was somewhat challenged by a similar examination of *in situ*-generated PC<sup>•-</sup>. The authors noted very short excited lifetimes of DCA analogues that would make them rather poor photocatalysts.<sup>44</sup>

Nocera studied the excited state of the radical anion produced from naphthalenemonoimide NpMI, proposing that



**Scheme 4** Hydrodehalogenation of aryl halides catalyzed by photo-excited 4DPAIPN: (a) model reaction and (b) representative products.



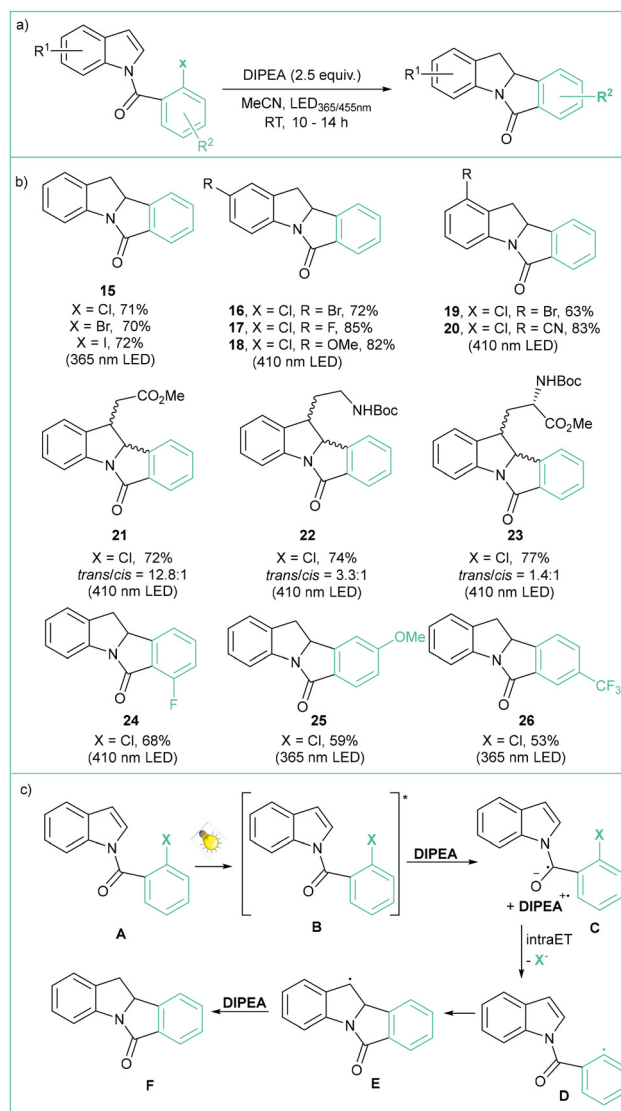
$\text{NpMI}^{\cdot-}$  is nonemissive and it rather derives from a Meisenheimer complex that is an active form of photocatalyst.<sup>45</sup>

In 2023, Scott's group managed to synthesize, isolate and fully characterize (including EPR and XRD) stable analogues of  $\text{NpMI}^{\cdot-}$  and  $\text{DCA}^{\cdot-}$  by reducing appropriate dyes with  $\text{KC}_8$  in the presence of a cryptand. Based on a series of simple experiments they proved their photostability and demonstrated that they are indeed active catalysts in visible light ConPET dehalogenation and phosphorylation of various aromatic chlorides, including electron-rich ones.<sup>46</sup>

In recent years, several groups found direct spectroscopic evidence for the thus far elusive pre-association of radical ions and substrate molecules that enables photoinduced electron transfer beyond the diffusion limit.<sup>47</sup> These reports may finally end the discussion about whether excited radicals with picosecond lifetimes can be catalytically active in ConPET processes.

An interesting example of ConPET, reported by Jing, used dicyanoanthracene (**DCA**) that was incorporated within a metal-organic framework (MOF).<sup>48</sup> The study proved that the ConPET was essential to form charge-transfer species and accelerate the conversion of interesting aryl halides (including relatively inactive species such as 1-chloro-4-methoxybenzene ( $E_{\text{red}} = -2.90$  V vs. SCE) in moderate to good yields). Upon generation of the aryl radical using visible light, it was subsequently quenched with *N*-methylpyrrole and  $\text{B}_2\text{pin}_2$  as radical traps. A similar incorporation of PDI into MOFs with further use in ConPET was performed by Duan and co-workers; however, it was limited to activated aryl chlorides that were employed in dehalogenation and heteroarylation reactions.<sup>49</sup> Another way to overcome the high potential barrier of these challenging substrates is to use metal-free carbon dots (B-CDots) as photocatalyst.<sup>50</sup> Namely, Yu and Huang achieved borylation of various aryl chlorides, iodides and bromides with very good to excellent yields. The authors proposed the aryl radical formation as a key step. Upon light irradiation B-CDots act as semiconductors – the electrons from the conductive band are able to reduce aryl halides toward radical anions followed by subsequent extrusion of a halide anion, eventually giving rise to aryl radicals that further react with a given boron source.

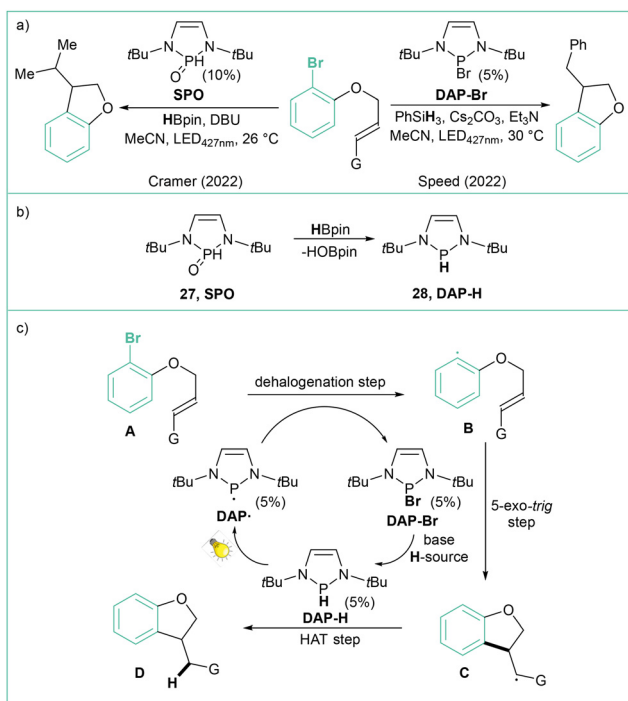
The application of photocatalyzed intramolecular aryl radical cyclizations toward the synthesis of polycyclic indolyl heterocycles was reported by Che and colleagues (Scheme 5a).<sup>51</sup> Direct irradiation of model *N*-(2-chlorobenzoyl)indole with visible light (410 nm) in the presence of DIPEA (2.5 equiv.), which acts as a sacrificial electron donor, led to a yield of 76% for the Heck-type intramolecular reaction product. Various substituted indoles were tested, and challenging reactions such as the use of aryl chlorides or the formation of quaternary carbon centres were indeed viable. This method has a high tolerance to functional groups, such as esters, amides, alcohols, or allyl moieties, and has been successfully applied in the synthesis of a number of complex natural product analogues (Scheme 5b). The use of UV light (365 nm) resulted in improved performance. According to the



**Scheme 5** Photocatalyzed synthesis of polycyclic indolyl heterocycles: (a) model reaction, (b) representative products and (c) mechanistic proposal.

proposed mechanism (Scheme 5c), a long-lived excited state **B** generated from **A** undergoes a bimolecular reaction with an electron donor resulting in the formation of the anion radical **C**, which then undergoes intramolecular C–Cl bond activation to give the aryl radical **D** and  $\text{Cl}^-$ . An intramolecular radical cyclization leads to the benzylic radical **E**, which then undergoes hydrogenation *via* a HAT or reduction/protonation to give the final product **F**. Abstraction of a bromide anion leading to aryl radicals that can further undergo intramolecular cyclization using diazaphospholene organocatalysts was recently reported independently by Cramer<sup>52</sup> and Speed<sup>53</sup> (Scheme 6a). The former approach relies on HBpin and DBU with **SPO** as a precatalyst, while the latter case uses  $\text{PhSiH}_3$ ,  $\text{Et}_3\text{N}$  and  $\text{Cs}_2\text{CO}_3$ ; in both cases visible light is required to regenerate the active DAP radical (**DAP**) (Scheme 6b). The reaction mechanism (Scheme 6c) is based





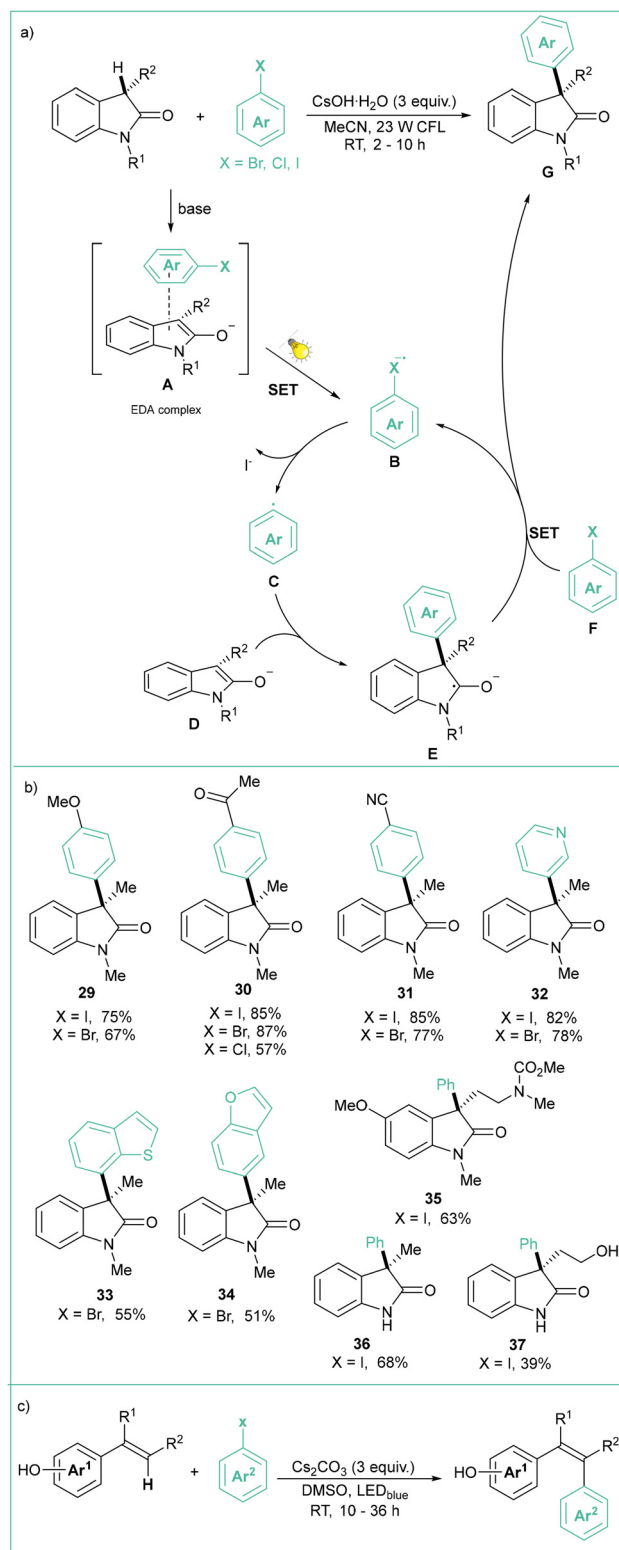
**Scheme 6** Approaches for intramolecular reductive cyclization using diazaphospholenes: (a) model reactions; (b) SPO pre-catalyst activation and (c) mechanistic proposal.

on the phosphalene cycle in which **DAP<sup>•</sup>** abstracts the bromine atom from the substrate leading to aryl radical **B** and **DAP-Br** that undergoes 5-*exo-trig* cyclization to the radical **C**. **DAP-Br** is converted to **DAP-H** via a reaction with a hydrogen donor (either **PSiH** or **HBpin**). **DAP-H** acts as a HAT reagent that converts **C** to the final product **D**, regenerating **DAP<sup>•</sup>** at the same time.

Aryl radicals can also be generated *via* photoexcitation of an EDA complex and subjected to intermolecular transformations, as was recently presented by Xia (Scheme 7a).<sup>54</sup> Namely, C-C cross-coupling of oxindoles and aryl halides was achieved under visible-light irradiation using **CsOH** as a base. The reaction of the aryl radical generated through a SET process from an excited EDA complex (**A**) leads to an anion radical **B** followed by loss of **I<sup>-</sup>** toward aryl radical **C**. Upon addition of **C** to **D**, the adduct **E** is formed which eventually gives the product **G** through a **S<sub>RN</sub>1**-type reaction<sup>55</sup> (Scheme 7b).

Shortly thereafter, the authors extended the scope of this reaction by testing a wide range of vinylphenol derivatives (Scheme 7c).<sup>56</sup> The protocol in general is very stereoselective (*E/Z* ratio 9:1 and higher) and found utility in the late-stage functionalisation of complex natural products.

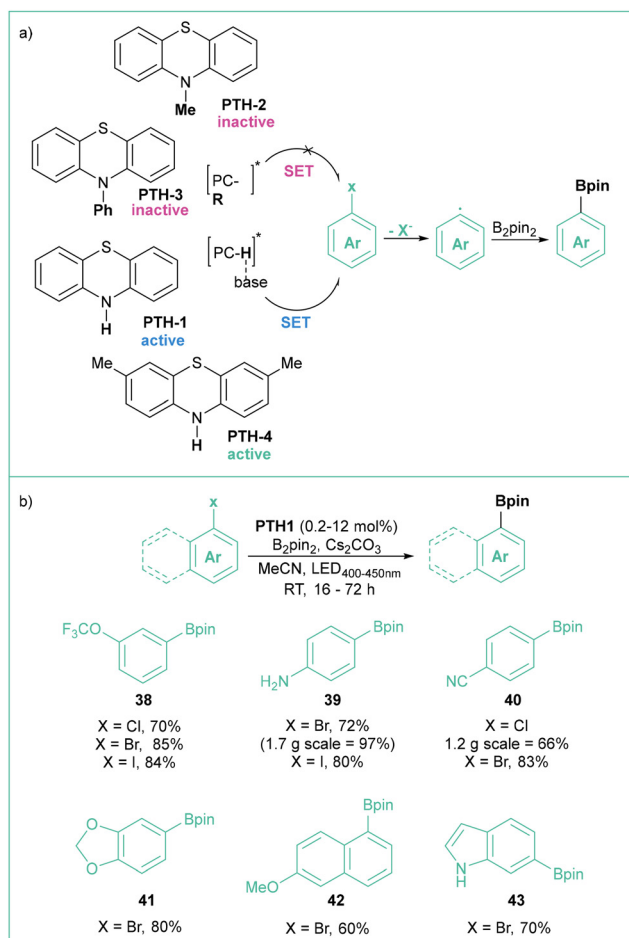
Recently, Larionov *et al.* developed a family of very potent SET photocatalysts based on simple, abundant and low molecular weight phenothiazines (Scheme 8).<sup>57</sup> These catalysts can generate aryl radicals from a number of halides, including inactivated bromides and chlorides, which were further converted into various boronic esters and trifluoroborates, with a



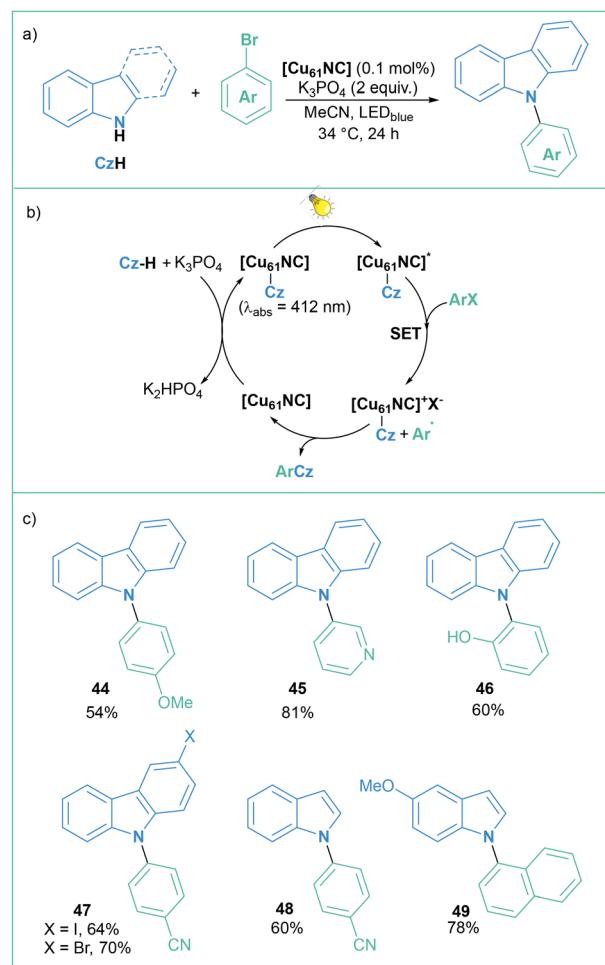
**Scheme 7** Photoarylation of oxindoles: (a) model reaction with mechanistic proposal, (b) representative products and (c) photoarylation of vinylphenols.







**Scheme 8** (a) Difference in the photocatalytic activity of phenothiazines in the generation of aryl radicals rationalized by the PCET mechanism. (b) Photoborylation of aryl halides using **PTH1**, model reaction, and representative products.



**Scheme 9** Photo-Ullmann reaction catalyzed by a copper(I) nanocluster: (a) model reaction, (b) mechanistic proposal and (c) representative products.

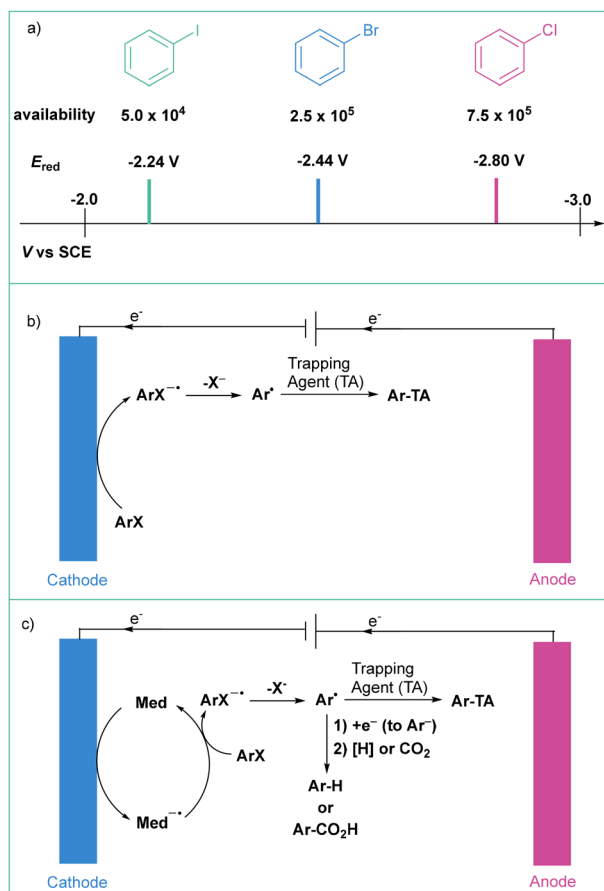
wide scope of functional groups tolerated and under visible light irradiation (Scheme 8b). The authors suggest that the reaction proceeds through a proton-coupled electron transfer (PCET) mechanism, where base-sensitive secondary ammonium catalysts **PTH-1** and **PTH-4** are more active than tertiary analogues **PTH-2** and **PTH-3** (Scheme 8a).

Bakr and Reuping presented an interesting example of the generation of aryl radicals through photoexcitation of an intermediate in the photo-Ullmann reaction catalyzed by a Cu nanocluster  $[\text{Cu}_{61}\text{NC}]$  (Scheme 9a).<sup>58</sup> According to the proposed mechanism (Scheme 9b), upon deprotonation of carbazole, a  $\text{Cu}_{61}$ -carbazolide complex  $[\text{Cu}_{61}\text{NC}]\text{-Cz}$  forms, that is activated under visible light irradiation ( $\lambda_{\text{abs}} = 412 \text{ nm}$ ), in striking contrast to an earlier example of the photoUllmann reaction presented by Fu<sup>59</sup> where higher-energy ultraviolet light was used for activation of the catalyst-nucleophile intermediate complex. A SET from the excited carbazolide-copper cluster  $[\text{Cu}_{61}\text{NC}]\text{-Cz}^*$  (via blue LED irradiation) to aryl halide generates the oxidised complex  $[\text{Cu}_{61}\text{NC}]^+\text{-Cz}$ , an aryl radical and a halide anion. This was rationalized by fluorescence and

lifetime quenching experiments. Then, the radical interacts with the oxidised cluster giving rise to C(arene)-N(carbazolide) bond formation *via* a radical-radical bound or reductive elimination pathway, as well as regeneration of the original  $[\text{Cu}_{61}\text{NC}]$ . The nucleophile scope includes carbazoles, indoles, and azaindole motifs. Moreover, electron-poor and electron-rich iodides, bromides and chlorides are well tolerated in this transformation (for selected examples, see Scheme 9c). The yields of the C-N coupling range from moderate to high, ranging from 48 to 87%, with 0.1 mol% catalyst loading, which translates to 6.1% clustered copper in the reaction medium.

**3.1.2. Electrochemistry.** As indicated previously and in Scheme 10a,<sup>19a</sup> aryl halides feature particularly low reduction potentials, therefore their electroreduction may be troublesome, leading mostly to undesired side products instead of selective transformations to value-added products.<sup>17a</sup> The formation of aryl radicals *via* electrolysis may be realized either in a direct (an electron is transferred from a cathode to  $\text{ArX}$  directly, Scheme 10b) or an indirect way – by employing an



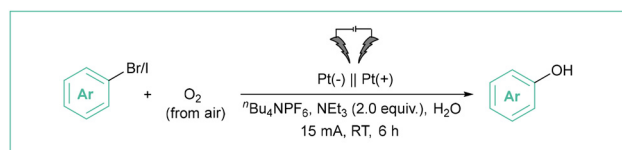


**Scheme 10** (a) Commercial availability of different arene sources (according to SciFinder, accessed April 2, 2021) and reduction potentials of PhCl, PhBr and PhI as reported by Zhou, Wu and others;<sup>19a</sup> (b) general scheme for the direct electroreduction of aryl halides and (c) general scheme for the indirect electroreduction of aryl halides.

electron mediator (**Med**, Scheme 10c). **Med** facilitates the electron transfer process from a cathode toward **ArX** in such a way that the SET does not occur at the electrode surface but in a bulk phase, therefore mitigating the direct further reduction of aryl radicals to aryl anions or electrografting. In fact, until very recently electroreduction of such species was explored mainly in terms of mechanistic studies,<sup>60</sup> electrolytic modification of electrodes (electrografting)<sup>61</sup> and hydrogen-atom abstraction.<sup>62</sup>

Aryl radicals that are produced from **ArX** via either a direct or indirect process may subsequently react with various trapping species such as  $B_2pin_2$ ,  $O_2$ , or  $H^+$  donor. If the reaction system allows, the radicals can be reduced immediately to aryl anions (Scheme 10c) that are then trapped by relevant electrophiles such as  $CO_2$ ,<sup>63</sup> an electrophile<sup>64</sup> or even  $H^+$  donor.<sup>65</sup>

Direct electrolysis of aryl halides is rarely used, as such challenging conditions may be harmful to many functional groups. As an example, the introduction of the OH group is a particularly relevant method as phenols are important species that are present in many biologically relevant molecules.<sup>66</sup> In the method developed by Ke *et al.*<sup>67</sup> (Scheme 11),  $O_2$  from the air was the source of the hydroxyl function whilst a non-sacrific-



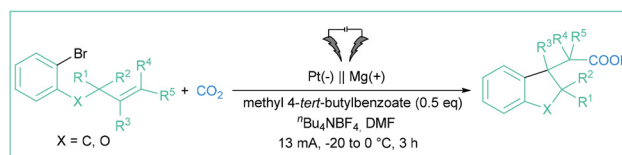
**Scheme 11** Hydroxylation of aryl halides via a direct electrolysis.

cial anode was used. A wide range of phenols was assembled in an undivided cell employing water as a green solvent. The electrolyses occurred with good to excellent efficiencies (up to 95%) employing aryl chlorides, bromides or iodides.

In 1991, Savéant and colleagues studied the electroreduction of aryl halides in the presence of olefinic acceptors (styrene, butylvinylether or acrylonitrile).<sup>68</sup> They found that the addition of some organic compounds (4,4'-bipyridine, naphthonitrile or methyl benzoate) significantly increases the efficiency of the hydroarylation reaction. Benzonitrile or *m*-tolunitrile were found to effectively mediate the electron transfer from a Pt-based cathode toward aryl halides in the preparation of 1-methylindans via an intramolecular cyclization of *o*-(3-butenyl)phenyl.<sup>69</sup> In turn, methyl 4-*tert*-butyl benzoate appeared to be an appropriate mediator for the assembly of 2,3-dihydrobenzofuran-3-ylacetic acids starting from olefins (Scheme 12).<sup>70</sup> Despite the rather narrow scope, the method constitutes an interesting example of employing aryl radicals in radical cascades, where the formed alkyl radical (via intramolecular addition of  $Ar^{\cdot}$  to a  $C=C$  double bond) is reduced to a carbanion which then attacks an electrophilic  $CO_2$  molecule, giving rise to carboxylic acid derivative.

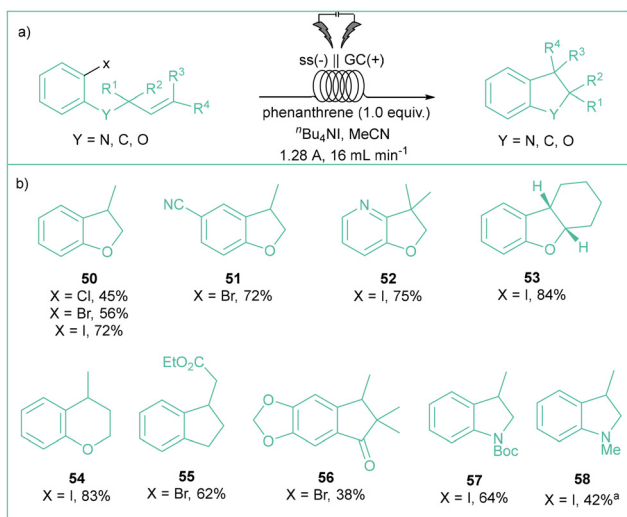
Direct arylation of pyrroles can be realized by indirect electroreduction of aryl halides bearing electron-withdrawing groups such as  $-COMe$ ,  $-CO_2Me$  or  $-CN$ .<sup>71</sup> In this case, a perylene bisimide dye was used as an electron mediator.

Some other similar contributions underlined the importance of polycyclic aromatic hydrocarbons (PAHs, such as phenanthrene<sup>72</sup> or fluorene derivatives<sup>73</sup>) as electron mediators in such cyclizations where the electroreduction of aryl halides constitutes an initial step. In 2022, Brown's group elegantly showcased the power of phenanthrene as an electron mediator in the assembly of cyclic derivatives (Scheme 13) by performing this transformation in flow.<sup>74</sup> Here, aryl chlorides, bromides and iodides are compatible, along with substrates bearing easily reducible groups. Importantly, the developed conditions allow for the formation of rings of various sizes including 5- or 6-membered ones, or even spirocycles. The



**Scheme 12** Synthesis of 2,3-dihydrobenzofuran-3-ylacetic acids described by Senboku *et al.*

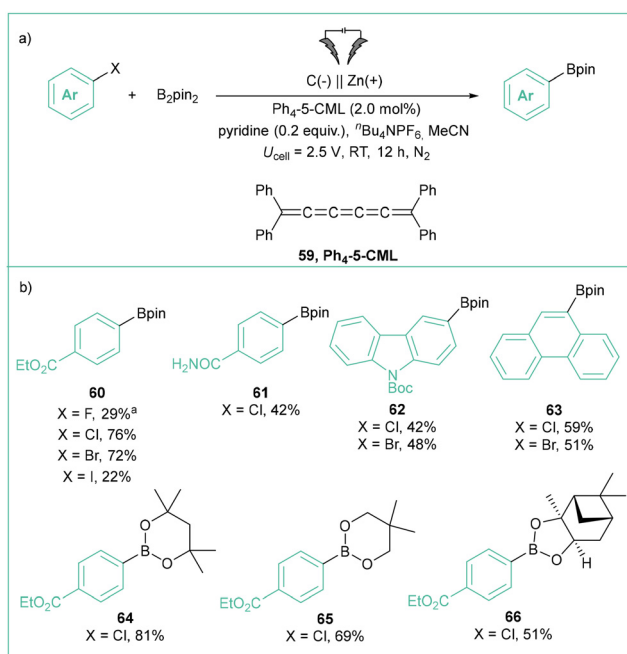




**Scheme 13** Synthesis of cyclic products **xx** in flow developed by Brown and colleagues in 2022: (a) model reaction and (b) representative products. <sup>a</sup> Reaction carried out on 7.0 mmol scale in THF/MeCN (7 : 1).

major difference between Brown's work and the aforementioned articles is the use of cost-effective electrodes and flow conditions, which should have positive impacts on the resource and energy economy of this process.

A new type of electron mediator, which is an analogue of cumulene (Ph<sub>4</sub>-5-CML, **59**), was proposed by Milner and others to mediate the borylation of aryl halides in a potentiostatic regime (Scheme 14).<sup>75</sup> The reaction tolerates a broad range of aryl halides (products **60–67**) as well as different boron-based



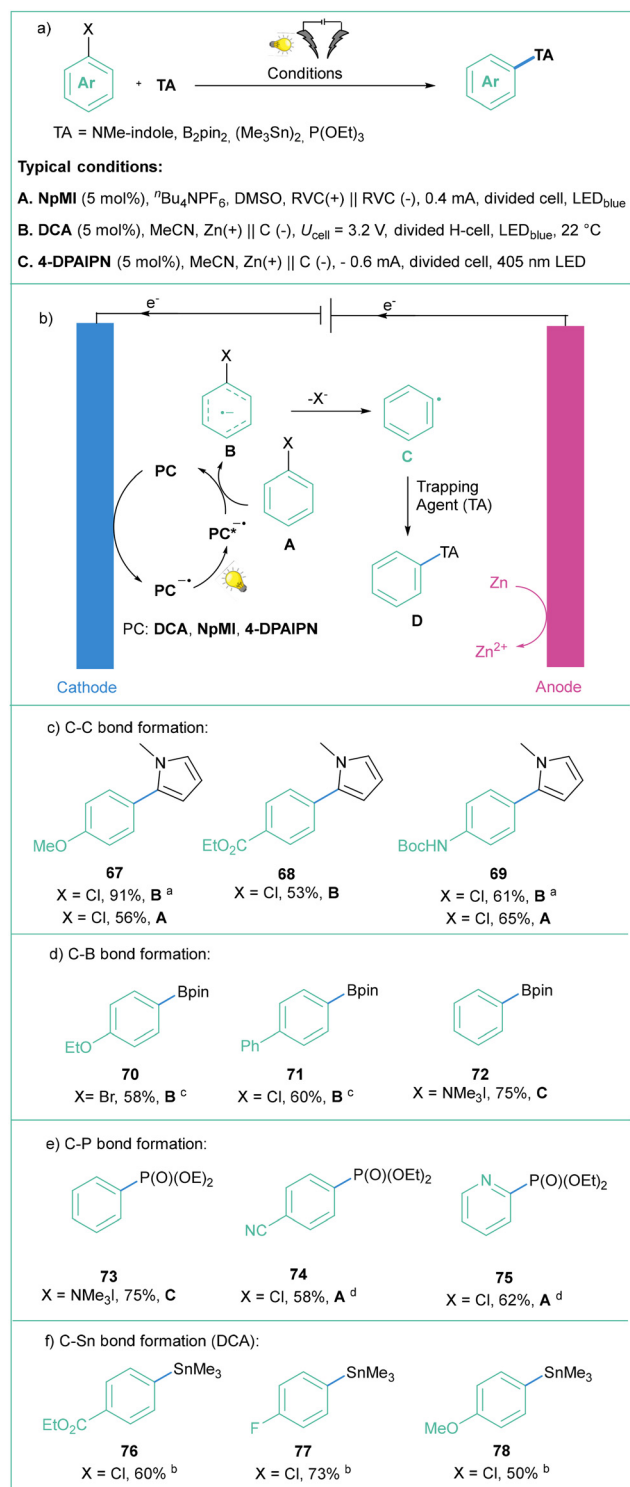
**Scheme 14** Employment of cumulenes as electron-mediators in borylation of aryl halides: (a) model reaction and (b) representative products.

reagents (products **64–65**). Despite the high reducing potentials needed for the ArX activation, all processes occur smoothly at relatively low cathodic potentials ( $U_{\text{cell}} = 2.5$  V, approximately  $-1.9$  V vs. Ag/AgCl) in comparison with those typically required for electrophotocatalytic or mediator-less electrochemical reactions. It should be emphasized here that even though the applied potential ( $-1.9$  V) is way lower than the potential for aryl radical reduction ( $E^\circ(\text{Ph}^\cdot/\text{Ph}^-) = 0.05$  V vs. SCE),<sup>10a</sup> the formation of Ar<sup>-</sup> is avoided by means of mediated electrolysis – that is, the reduction occurs in bulk solution, not near the cathode surface. This constitutes a general advantage of mediated electrolysis over direct electrolysis that should be taken into account in the designing of new (photo)electrochemical synthetic methods based on aryl radical chemistry.

**3.1.3. Photoelectrochemistry.** Photoelectrochemistry has proved to be a powerful strategy for the generation of photoexcited radical ions. Such an approach was applied for the efficient generation of aryl radicals toward the formation of C–C, C–P, C–Sn, and C–B bonds (Scheme 15).<sup>76,77</sup> In this approach, the first event is the reduction of the photocatalyst at the electrode to form a radical anion (**PC<sup>-</sup>**), which is subsequently photoexcited, enabling the formation of a super reductant radical anion (**\*PC<sup>-</sup>**). Such species are able to reduce aromatic halides **A** to a radical anion **B**, which after dehalogenation forms aryl radicals **C**, which readily react with trapping agents such as *N*-methylindole (Scheme 15c), B<sub>2</sub>pin<sub>2</sub> (Scheme 15d), P(OEt)<sub>3</sub> (Scheme 15e) and (Me<sub>3</sub>Sn)<sub>2</sub> (Scheme 15f). This methodology was applied with the use of different photocatalysts (**DCA**,<sup>78</sup> **NpMI**,<sup>76</sup> **4-DPAIPN**<sup>77</sup>) and is compatible with various aryl halides (Cl, Br).

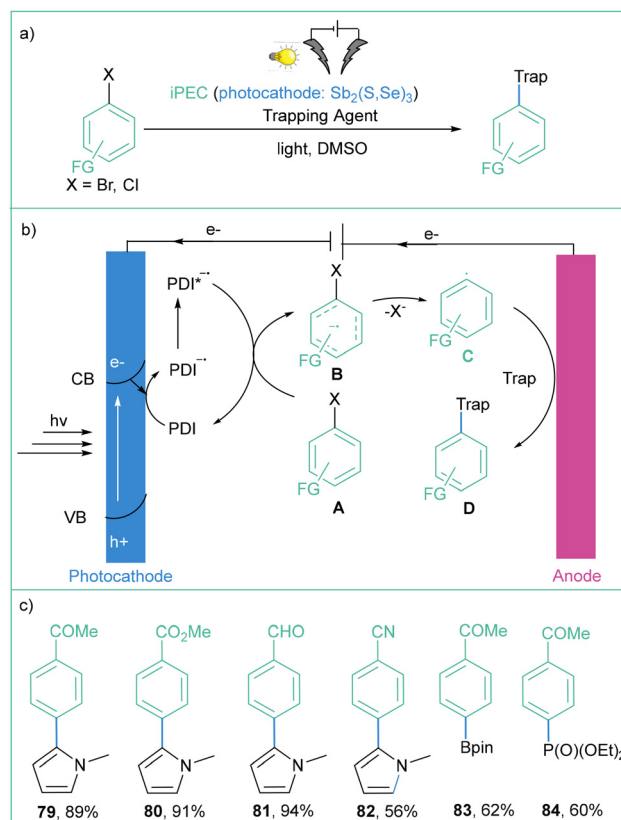
On the other hand, Wu and co-workers reported an iPEC/photoredox system consisting of a Sb<sub>2</sub>(S,Se)<sub>3</sub> photocathode and a PDI dye as a photoredox catalyst that was employed for very efficient and selective aryl functionalisations (Scheme 16).<sup>79</sup> The proposed mechanism for this transformation assumes that after light irradiation (Vis-NIR), the photocathode gets excited and an electron-hole pair is generated (Scheme 16a). The photogenerated electrons from the conductive band reduce **PDI** to a radical anion (**PDI<sup>-</sup>**), which is then excited to form a highly reductive species (**PDI<sup>-\*</sup>**). The photoexcited radical anion (**PDI<sup>-\*</sup>**) is now able to reduce different aryl halides **A** and **B**, which subsequently undergo mesolytic cleavage to generate aryl radical **C**, which reacts with trapping reagents to yield the functionalised product **D** (Scheme 16b). Such an approach allows for the functionalisation of different (hetero)aryl halides in good to excellent yields, with many functional groups being tolerated (–CN, –CHO, –CO<sub>2</sub>Me, –COMe). On the other hand, the reaction is also efficient with different trapping agents such as pyrrole derivatives, P(OEt)<sub>3</sub> and B<sub>2</sub>pin<sub>2</sub> (Scheme 16c). The application of a dual system with a photocathode and a photoredox catalyst allows the production of high-value products in good yields. However, the same transformation can be performed in more simple way and without the use of the toxic antimony-covered photocathode (see Scheme 16). Moreover, the authors reported





**Scheme 15** Photoelectrochemical generation of aryl radicals and subsequent C–C, C–B, C–P, and C–Sn bond-forming reactions. <sup>a</sup> 10 mol% of DCA was used. <sup>b</sup> <sup>1</sup>HNMR is given. <sup>c</sup> Pyridine (20 mol%) was used. <sup>d</sup> Constant current electrolysis at 0.8 mA was employed.

neither quantum efficiency measurements nor reusability studies for the Sb<sub>2</sub>(S,Se)<sub>3</sub> photoelectrode, while a high-energy Xe lamp (500 W) was used as a light source. It is worth men-



**Scheme 16** iPECs for the photoelectrochemical generation of aryl radicals: (a) model reaction, (b) mechanistic proposal and (c) representative products.

tioning that the reaction still proceeds without electricity, albeit with lower efficiency (57% for compound **86**).

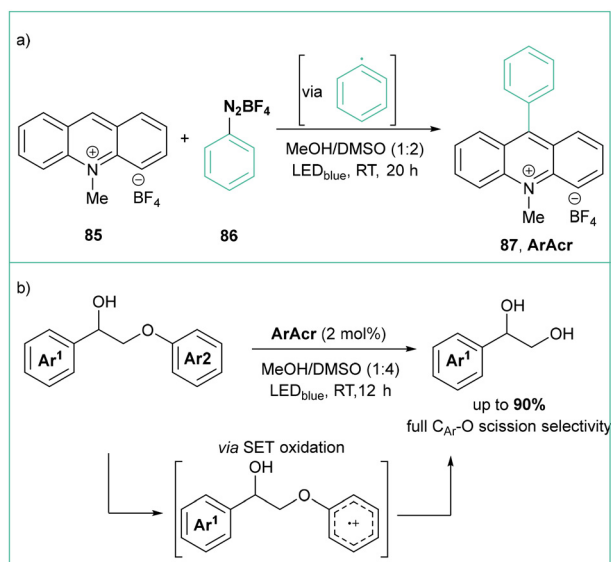
### 3.2. Generation of aryl radicals from diazonium salts

In comparison with aryl halides, aryl diazonium salts seem an even better source of aryl radicals due to their much lower redox potential and irreversible liberation of a nontoxic nitrogen molecule. Although they are certainly less stable than their respective halide analogues, they can be stored at low temperatures with good stability as long as a non-coordinating counterion, such as BF<sub>4</sub>, PF<sub>6</sub> or OTf, is being used. They are also quite simple and cost-effective reagents to synthesize starting from abundant anilines and are often generated *in situ*.

**3.2.1 Photochemistry.** Due to their low reduction potential, it is generally sufficient to photogenerate aryl radicals from diazonium salts either through direct excitation, irradiation of an EDA complex or by using a photoredox catalyst with a moderate reduction potential, such as xanthene dyes or ruthenium complexes.<sup>80</sup>

To give a recent example, Boixel, de Rouville, and Soulé developed a catalyst-free (or self-catalyzed) photoinduced arylation of *N*-substituted acridinium salts using various aryl diazonium tetrafluoroborates with high functional group tolerance (halide, ester, -CN, ketone and -NO<sub>2</sub>) (Scheme 17a).<sup>81</sup> The syn-





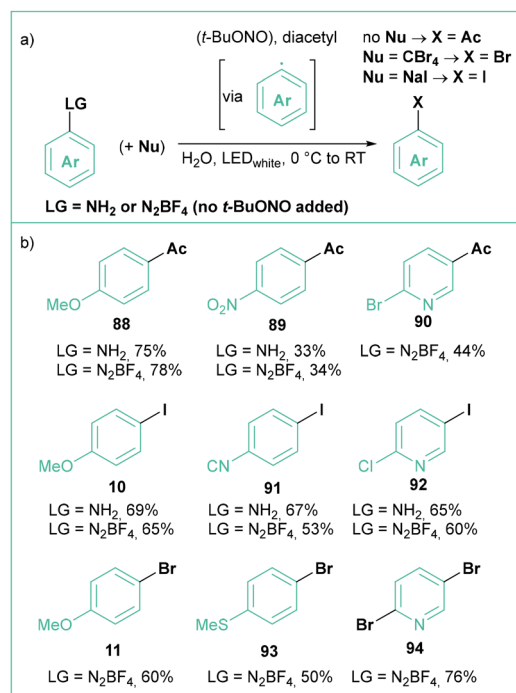
**Scheme 17** (a) Photoinduced arylation of *N*-methylacridinium salts to give new families of ArAc photocatalysts. (b) Application of ArAc in selective C–O bond fragmentation.

thesized acridinium salts were evaluated for their photoredox catalytic capabilities in the C–O bond fragmentation of ethers. The generation of the respective diol products was efficient, particularly when using the C9-(2-bromophenyl)-*N*-methyl dye, which was even able to outperform the commercial Fukuzumi catalyst for the reaction (Scheme 17b).

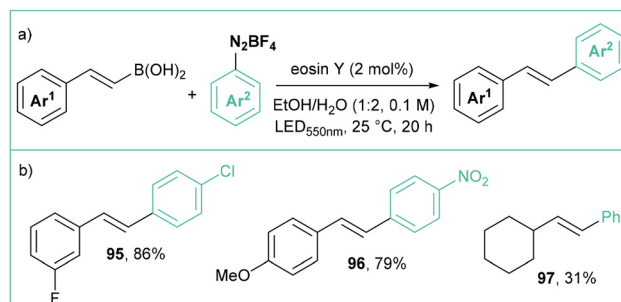
The photoredox version of the classical Sandmeyer-type halogenation was realized by Tang and Luo (Scheme 18).<sup>82</sup> They reported a facile conversion of anilines into acetates through the photoinduced generation of (hetero)aryl radicals using an excess of *t*-BuONO and simple diacetyl as a photosensitizer/trapping agent (Scheme 18a). More than 40 (hetero)aryl acetates were obtained this way with high functional group tolerance and moderate to good yields (Scheme 18b). Aryl bromides and iodides are also accessible when the appropriate trapping agent (CBr<sub>4</sub> or NaI, respectively) is present in the reaction mixture, although the scope was rather narrow and bromination required pre-synthesized aryl diazonium tetrafluoroborates rather than *in situ*-generated intermediates.

Another application of a reductive Sandmeyer-type reaction is the synthesis of sulfoxides from anilines under a photocatalytic regime.<sup>83</sup> An, Wu and Zheng presented efficient sulfinylation of a variety of arenediazonium salts (formed *in situ*). The proposed mechanism is very similar to that described in the current chapter.

Wu reported the photocatalytic synthesis of *E*-stilbenes by coupling arenediazonium tetrafluoroborates with cinnamyl boronates (Scheme 19a).<sup>85</sup> The reaction occurs employing only 2.0 mol% of a cost-effective organic dye (Eosin Y<sup>84</sup>), an EtOH/H<sub>2</sub>O mixture as a solvent and green (550 nm) light irradiation. More than 20 examples were presented, which mainly consisted of mono- and disubstituted stilbenes (Scheme 19b). Interestingly, changing the catalyst to a ruthenium complex



**Scheme 18** Photoredox approach for Sandmeyer reaction: (a) model reaction and (b) representative products.

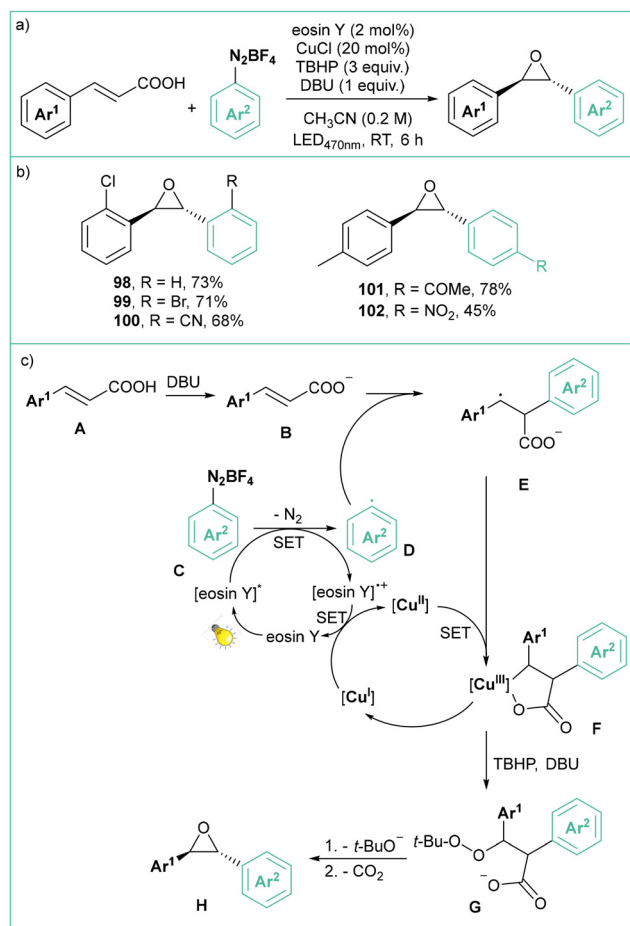


**Scheme 19** (*E*)-Selective photoredox synthesis of stilbenes from cinnamyl boronic acids using Eosin Y<sup>84</sup> as a catalyst: (a) model reaction and (b) representative products.

(Ru(bpy)<sub>3</sub>Cl<sub>2</sub>) switched the selectivity to provide predominantly *Z* isomers, which might suggest a subsequent *E/Z* isomerization through an energy transfer process, since Ru(bpy)<sub>3</sub>Cl<sub>2</sub> has a higher triplet state energy (Eosin Y ~44 kcal mol<sup>-1</sup>;<sup>84,86</sup> Ru(bpy)<sub>3</sub>Cl<sub>2</sub> ~49 kcal mol<sup>-1</sup> (ref. 87)).

Decarboxylative, visible-light photoredox synthesis of *trans*-oxiranes from (*E*)-cinnamic acids using arenediazonium salts was developed recently by Singh (Scheme 20a).<sup>88</sup> Eosin Y was also employed as a photocatalyst generating the aryl radical, while CuCl and TBHP served as the oxidant system. More than 20 examples of variously substituted diaryloxiranes, consisting mainly of mono and disubstituted products, were synthesized. The method tolerates many functionalities such as halides, nitro, cyano, ketone and ester groups. According to the pro-

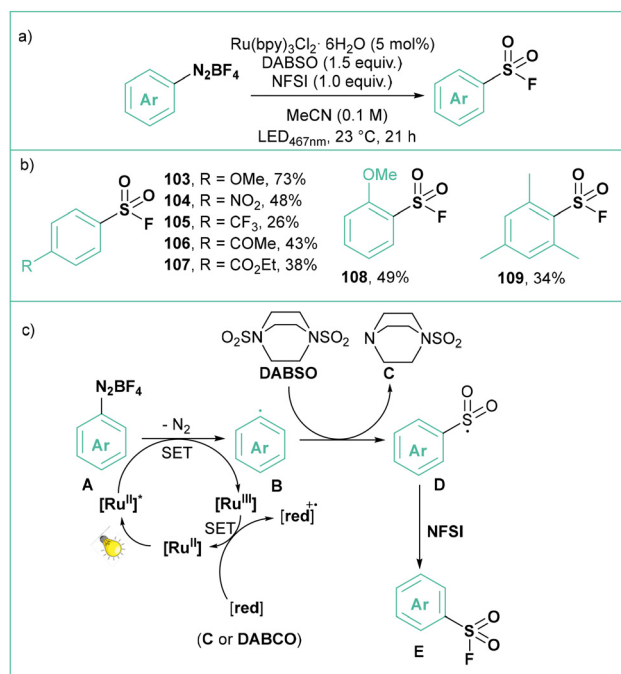




**Scheme 20** Decarboxylative photoorganometallic synthesis of *trans*-oxiranes using eosin Y and CuCl as co-catalysts: (a) model reaction and (b) representative products and (c) mechanistic proposal.

posed mechanism (Scheme 20c), the deprotonated cinnamate **B** reacts with the photogenerated aryl radical to give anion radical **E**. This intermediate forms a Cu(III) chelate **F** arising from a SET process with Cu(II). In the presence of TBHP and DBU, the chelate releases a Cu(I) species and a peroxide intermediate **G**, which liberates a *t*-butoxide anion and carbon dioxide, eventually leading to *trans*-oxirane product **H**.

Reactions based on sulfur(VI) fluoride exchange (SuFEx) are the basis of the second-generation click reactions developed by the Sharpless group and employed widely in biorthogonal processes including protein labelling.<sup>89</sup> The photocatalytic procedure for the conversion of aryl diazonium tetrafluoroborates to the corresponding sulfonyl fluorides was developed by Troian-Gautier and Tambar (Scheme 21a).<sup>90</sup> The optimised conditions employ Ru(bpy)<sub>3</sub>Cl<sub>2</sub>·6H<sub>2</sub>O as a catalyst, DABSO as a source of SO<sub>2</sub> and NFSI as a fluorinating agent in MeCN. Using this procedure, the authors synthesized 10 electron-rich and electron-poor mono-, di-, and trisubstituted arylsulfonyl fluorides with yields ranging from 26 to 73% (Scheme 21b). According to the proposed mechanism (Scheme 21c), the photogenerated aryl radical **B** reacts with DABSO to give the



**Scheme 21** Photocatalytic synthesis of arylsulfonyl fluorides from aryl diazonium salts (a) model reaction, (b) representative products and (c) mechanistic proposal.

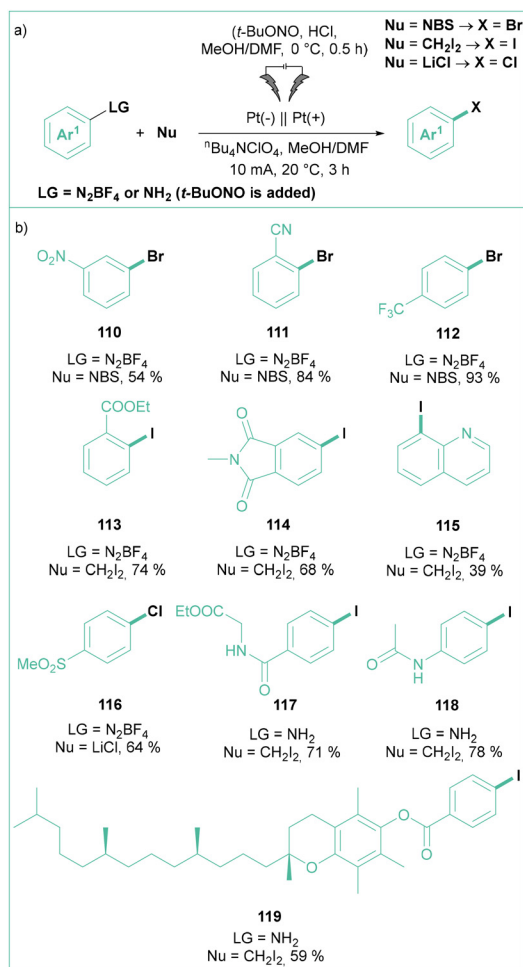
mono-(sulfur dioxide) adduct **C** and sulfonyl radical **D**, which is fluorinated by NFSI to the final product. According to the authors, the Ru(III) species, resulting from the oxidative quenching of the photoexcited catalyst with the aryl diazonium salt, is reduced back to the ground state from a SET process with either **C** or DABSO.

It is worth mentioning that aryl radicals can be liberated from aryl azosulfones; however, this transformation occurs through direct irradiation of the latter compounds.<sup>91–94</sup>

**3.2.2 Electrochemistry.** Until recently, arenediazonium salts were mainly considered to be excellent arylating reagents in electrografting<sup>80a,95</sup> due to their low reduction potentials and inert by-product, molecular N<sub>2</sub>. However, their huge synthetic potential has also started to be investigated in terms of electrochemically mediated synthesis,<sup>96</sup> although they are considered potentially dangerous due to the possibility of violent decomposition.<sup>97</sup>

In 2018, Mo and co-workers demonstrated that the classic Sandmeyer reaction can also be performed under the influence of electric power (Scheme 22a) using non-sacrificial Pt electrodes.<sup>98</sup> Namely, aryl diazonium salts are efficiently converted into their halogenated analogues using a variety of halogenation reagents such as NBS, NaBr, CH<sub>2</sub>I<sub>2</sub>, CBrCl<sub>3</sub> or LiCl (Scheme 22b). In contrast to the classical conditions, there is no need to use metal-based species, such as copper(I) salts. Importantly, the process can be performed on a large scale (up to 15 mmol of a substrate) with efficiencies reaching 70–80% (Scheme 22b). Here, Pt anodes were successfully replaced with cost-effective graphite plates. This process can also be per-





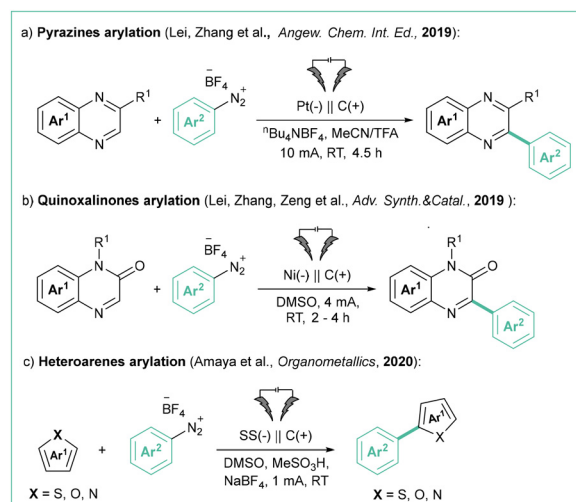
**Scheme 22** Electrochemically driven Sandmeyer reaction: (a) model reaction and (b) representative products.

formed in a two-step, one-pot fashion *via* the initial formation of an aryldiazonium salt followed by electrolysis. From the mechanistic point of view, the reaction was described as a cross-coupling between two radicals: a halogen-based radical that was produced *via* oxidation at an anode and an aryl radical produced *via* reduction of  $\text{ArN}_2^+$ .

A variety of heteroarenes can react with the aryl radicals produced by the electroreduction of aryl diazonium salts. Specifically, Zhang *et al.* employed diazonium tetrafluoroborates for the electrochemical arylation of electron-deficient arenes (Scheme 23a).<sup>99</sup> In this transformation, salts possessing electron-donating or withdrawing groups were reactive, although the latter featured reduced yields. A broad range of electron-deficient arenes, including quinoxalines, quinoxalinones, pyrazines, and other N-heteroarenes, were also tolerated.

Along this line, Zeng *et al.* reported the arylation of quinoxalinones with aryldiazonium salts (Scheme 23b).<sup>100</sup> The reaction shows very good scalability with high functional group tolerance, and proceeds without an electrolyte.

Similarly, Amaya *et al.* achieved the arylation of simple, electron-rich heteroarenes (Boc-protected pyrrole, thiophene,



**Scheme 23** Electrochemical coupling of different heteroarenes with aryldiazonium salts: (a) pyrazines arylation, (b) quinoxalinones arylation and (c) heteroarenes.

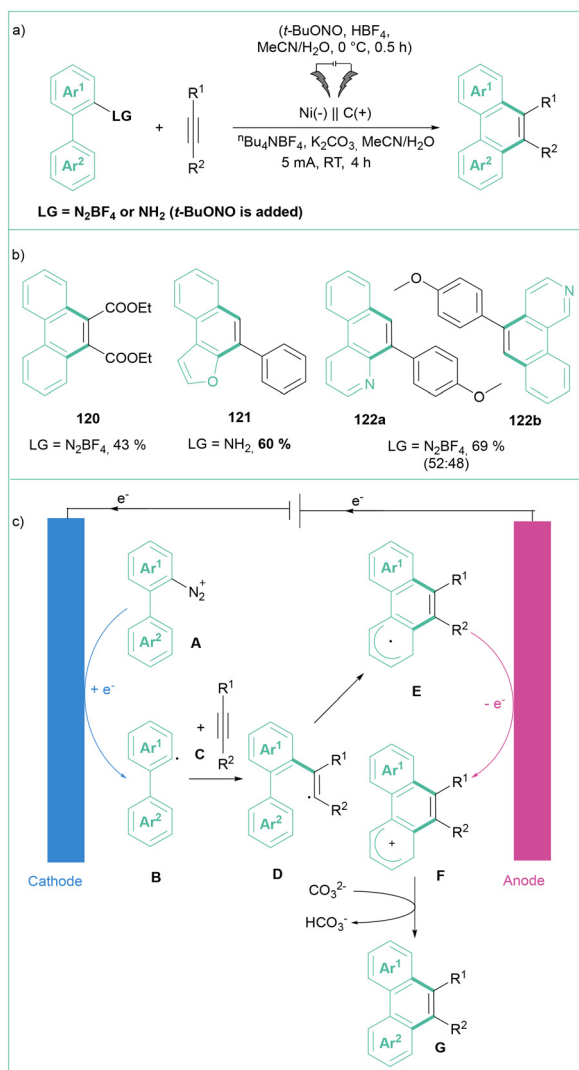
and furan) employing a stainless steel anode (Scheme 23c).<sup>101</sup> Unfortunately, the scope is rather limited, and only moderate yields can be achieved, probably due to the simultaneous decomposition of easily oxidisable heteroarenes at the anode.

In 2023, Wang, Zhou and co-workers developed a straightforward method to synthesize polycyclic (hetero)aromatic compounds *via* [4 + 2] benzannulation (Scheme 24a).<sup>102</sup> The reaction involved alkynes reacting with aryl diazonium salts, including 2-(hetero)aryl diazonium salts, or they can be generated *in situ* from the corresponding aniline. The reaction furnished the products in moderate to good yields, accepting differentiated substitution of both substrates but showed no selectivity for unsymmetrical heteroaryl diazonium salts (Scheme 24b). According to the proposed mechanism (Scheme 24c), the reaction starts with the reduction of the aryldiazonium salt **A** to an aryl radical **B**, which subsequently undergoes addition to an alkyne **C** giving rise to a vinyl radical **D**. The radical then undergoes cyclization followed by anodic oxidation, and bicarbonate-assisted deprotonation leads to products of type **G**. A similar transformation that led to a series of phenanthridines was developed by Sharma *et al.*<sup>19b</sup> Here, 2-isocyanobiphenyls were used as coupling partners for the *in situ*-formed aryldiazonium salts. The reaction occurs with good to excellent efficiencies at room temperature in an MeCN/HFIP (10 : 1) mixture employing a platinum cathode and an RVC anode.

### 3.3. Generation of aryl radicals from sulfonium salts

Sulfonium salts, which are in an isoelectronic relationship with phosphines, have attracted considerable attention as versatile reagents in organic synthesis for many years,<sup>103</sup> since they play an important role in various C–C bond-forming reactions that involve C–S bond cleavage.<sup>104</sup>





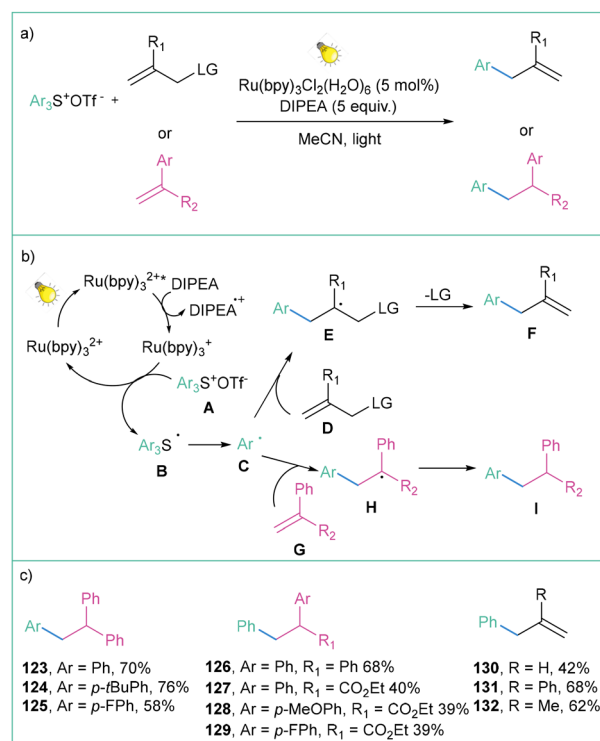
**Scheme 24** [4 + 2] Benzannulation of aryldiazonium salts and alkynes: (a) model reaction, (b) representative products and (c) mechanistic proposal.

Within this section, many methods that are based on thianthrenium chemistry are presented. Although extremely useful (*vide infra*), this kind of aryl radical precursor delivers high-weight by-product which may be re-isolated, however again with additional solvent waste. This should be also taken into account when planning the synthetic route involving aryl radical generation *via* reduction of thianthrenium salts.

**3.3.1. Photochemistry.** In recent years, photoredox catalysis has been proved to be an important and powerful approach for the generation of various C-centered radicals through cleavage of the C–S bonds *via* radical pathways.<sup>104</sup> Early reports regarding the photoinduced reaction of triarylsulfonium salts demonstrate that UV irradiation can trigger their decomposition toward the formation of, among others, new C–C bonds.<sup>105</sup> These findings set a stage for future studies on the reactivity of sulfonium salts under light irradiation. For example, they have been successfully applied for trifluoromethylation and alkyl-

ation of various species;<sup>106</sup> however, only recently they have also started to be used as suitable precursors for the photo-induced generation of aryl radicals.<sup>104c</sup> Arylsulfonium salts can easily undergo efficient, homolytic, photon-induced single-electron reduction under mild conditions toward aryl radical formation. The produced aryl radicals can then participate in the formation of carbon–carbon and carbon–heteroatom bonds. Oliver and co-workers demonstrated the successful application of triarylsulfonium salts as precursors of aryl radicals and their subsequent coupling with allyl sulfones or activated olefins (Scheme 25a).<sup>104a</sup> The mechanistic proposal assumes the initial photoexcitation of the photoredox catalyst ( $\text{Ru}(\text{bpy})_3\text{Cl}_2$ ) and its subsequent reduction by the secondary amine (DIPEA) to produce a strong reductant –  $\text{Ru}^{\text{I}}$ , that is capable of reducing the triarylsulfonium salt **A** to sulfuranyl radical **B** that immediately decomposes to aryl radical **C**. In the case of the reaction with the allylic partner **D**, radical **E** is formed, which undergoes  $\beta$ -fragmentation to form the allylated product **F**. When the aryl radical **C** reacts with activated olefin **G**, it forms radical **H**, which after protonation forms product **I** (Scheme 25b). Although the substrate scope is limited to only 16 examples, they confirmed the good efficacy of the developed method (39–70% yield) (Scheme 25c).

One of the most straightforward routes toward the synthesis of arylsulfonium salts is direct sulfonylation of C–H bonds with the use of thianthrene sulfoxide (**143a**). Such an approach was used for the preparation of arylsulfonium salts and their application as trifluoromethylation agents as well as electrophilic



**Scheme 25** Triarylsulfonium salts as radical precursors: (a) model reaction, (b) mechanistic proposal and (c) representative examples.



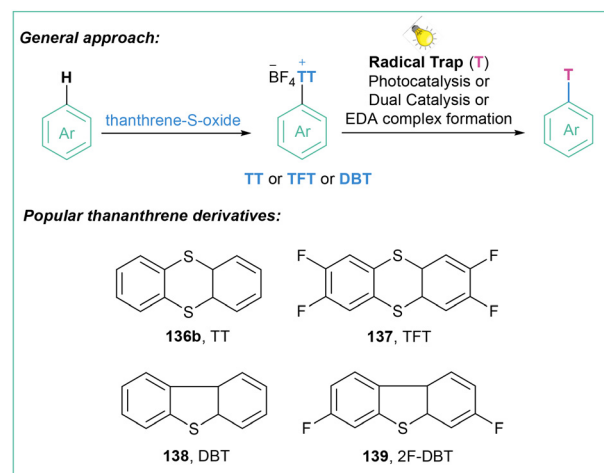


partners in transition-metal-catalyzed C–C cross-couplings.<sup>107</sup> Recently, Ritter with co-workers developed a highly *para*-selective C–H trifluoromethylation of arenes employing **136a** (Scheme 26).<sup>108</sup> In the next step, the generated salts were engaged in a dual catalytic system that involves a photochemical, Ru-catalyzed oxidation of Cu(I)–CF<sub>3</sub> to Cu(II)–CF<sub>3</sub> followed by copper-catalyzed C–C bond formation involving the Cu(III) intermediate.

The mechanistic proposal assumes that after light absorption, the ruthenium-based photocatalyst is excited to the excited state (Ru(bpy)<sub>3</sub><sup>2+\*</sup>), which is capable of oxidising Cu<sup>I</sup>CF<sub>3</sub> to Cu<sup>II</sup>CF<sub>3</sub>. The Ru<sup>I</sup> species subsequently reduces the tetrafluorothianthrene sulfonium salt **A** to radical **B**, which immediately decomposes to the aryl radical **C**. The generated radical **C** reacts with Cu<sup>II</sup>CF<sub>3</sub> during oxidative ligation to form complex **D**, after the subsequent formation of the reductive elimination product **E** (Scheme 26b). The reaction is generally high-yielding, and both electron-deficient and electron-donating groups are well tolerated (Scheme 26c).

The abovementioned findings set the stage for the general application of tetrafluorothianthrene sulfonium salts for the generation of aryl radicals under light irradiation in the presence of a photoredox catalyst. First, the synthesis of thianthrene sulfonium salts takes place, and then a photocatalyzed reduction to the aryl radical is performed, which subsequently can be engaged in further transformations (Scheme 27).

Such a methodology was already applied under different conditions (different photoredox catalyst and application of dual photoredox metal catalysis) in many transformations such as photocatalyzed trifluoromethylation<sup>108</sup> (Scheme 28a), Cu-catalyzed fluorination<sup>19c</sup> (Scheme 28b), borylation<sup>109</sup> (Scheme 28c),

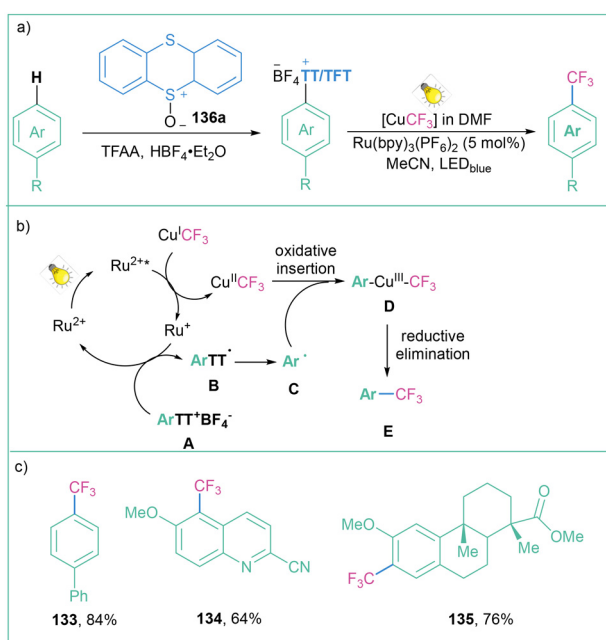


**Scheme 27** Generation of aryl radicals from tetrafluorothianthrene sulfonium salts.

Sonogashira-type reaction<sup>110</sup> (Scheme 28d), hydroarylation of vinyl acetamides<sup>111</sup> (Scheme 28e), arylation of indoles<sup>112</sup> (Scheme 28f), Meerwin-type bromoarylation<sup>113</sup> (Scheme 28g), gem-difluoroallylation<sup>114</sup> (Scheme 28h) and three-component synthesis of arenesulfonohydrazines<sup>115</sup> (Scheme 28i). All of the transformations are high yielding and site selective. The same methodology can also be expanded to the application of aryl selenium salts as aryl radical precursors.<sup>116</sup>

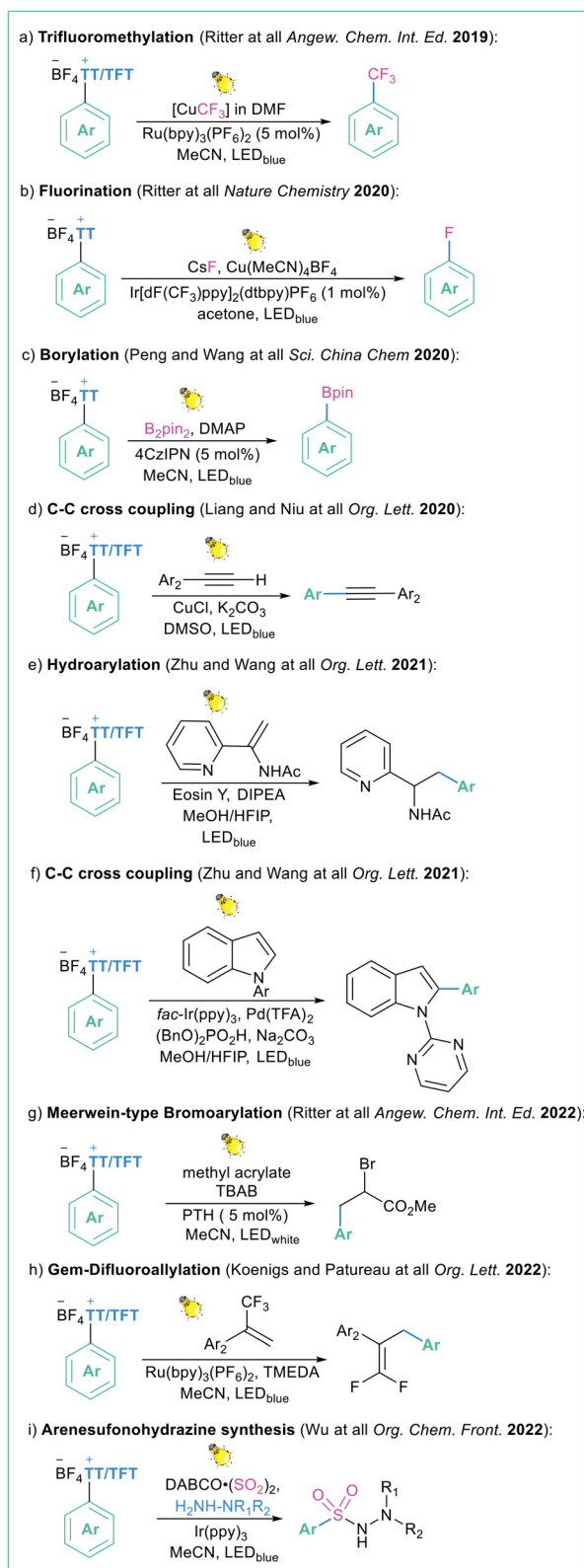
Importantly, all of the aforementioned transformations require prior salt synthesis and, in the next step, photoreduction of the sulfonium salt to finally assemble an aryl radical. Procter and co-workers described a successful modification of this approach, where the sulfonium salt is prepared *in situ* (Scheme 29).<sup>117</sup> The authors demonstrated a one-pot strategy for the rapid synthesis of (hetero)biaryls from non-prefunctionalised partners *via* merging photoredox catalysis (with the use of an organic dye (10-phenylphenothiazine) as a photocatalyst) and the activation of the substrate *via* an interrupted Pummerer reaction (Scheme 29a). The mechanism for this transformation assumes in the first step Pummerer activation of arene **A** with DBT-S-oxide **B** in order to form sulfonium salt **C**, which after single-electron reduction (by the photocatalyst in the excited state) forms aryl radical **D**. Subsequently, reaction with heteroarene **E** forms radical **F**, which is oxidised by the photocatalyst radical cation (PTH<sup>+</sup>) to form **G**. Finally, rearomatization leads to the biaryl product **H** (Scheme 29b). Generally, this metal-free, one-pot reaction proceeds with moderate to good yields for different radical traps (*N*-Me-pyrroles, *N*-Boc-pyrroles, furans, and thiophens) and also for different arene substrates. Worth mentioning is the 10 mmol-scale synthesis for **148**, performed with a yield similar to that performed for the smaller scale (0.2 mmol) (Scheme 29c).

Another useful application of sulfonium salts is the generation of alkyl radicals *via* direct irradiation of an EDA complex, as demonstrated for the first time by Shi *et al.* (Scheme 30a).<sup>118</sup> One year later, the same methodology was presented for the generation of aryl radicals.<sup>109b</sup> In this case,

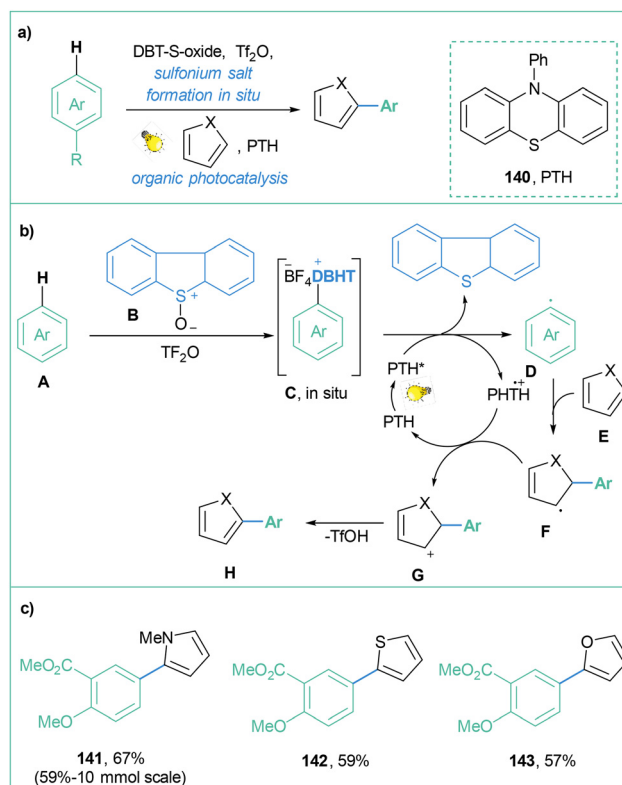


**Scheme 26** Aryl sulfonium salts for site-selective trifluoromethylation: (a) model reaction, (b) mechanistic proposal and (c) representative products.

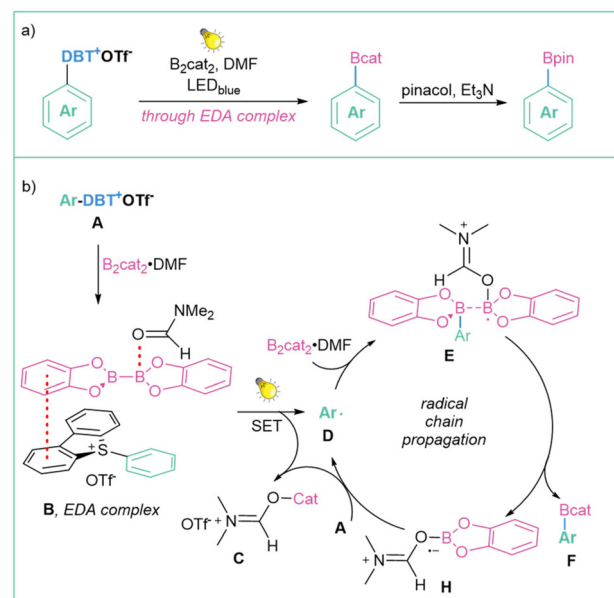




**Scheme 28** Scope of application of tetrafluorothianthrene sulfonium salts as arylating reagents.



**Scheme 29** One-pot, catalyst-free photoinduced synthesis of biaryls: (a) model reaction, (b) mechanistic proposal and (c) representative products.



**Scheme 30** Photoinduced desulfurative borylation: (a) model reaction and (b) mechanistic proposal.



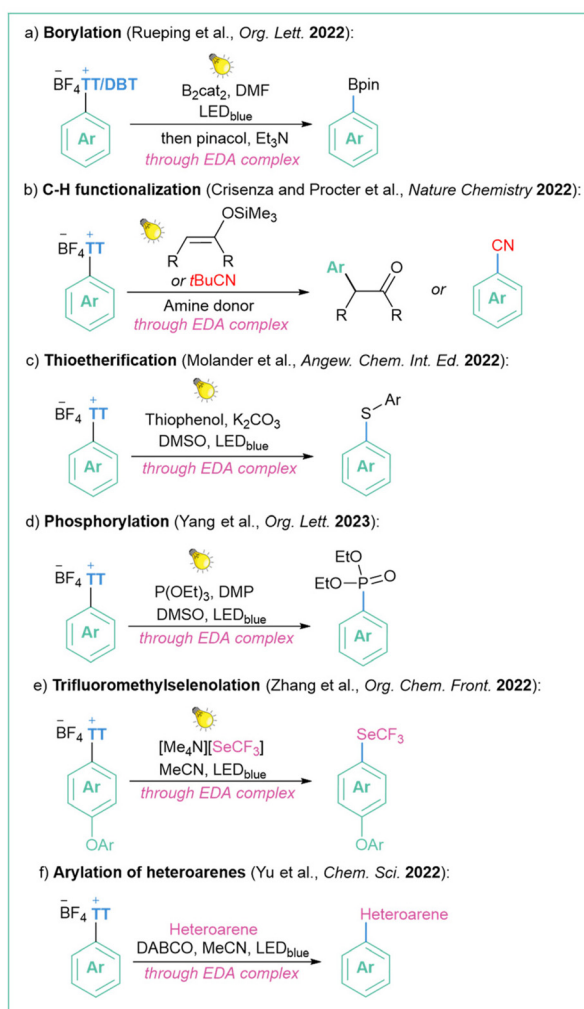
mechanistic studies suggest that the reaction begins with the formation of a straw-coloured EDA complex (**B**) between the DBT salt **A** and  $B_2cat_2$  in DMF. Under light irradiation, the EDA complex (**B**) triggers a single-electron transfer (SET) from  $B_2cat_2$  to DBT that forms the aryl radical **D**. After complexation with one molecule of DMF, the aryl radical **D** can interact with  $B_2cat_2$  to form a radical intermediate **E**. B–B bond cleavage produces product **F**, which after the addition of pinacol forms the final Ar–Bpin product. After B–B cleavage, the salt radical **H** is also formed. The subsequent SET event between **H** and another molecule of DBT salt **A** regenerates the aryl radical **D** and forms a stable ionic salt **C** to complete the cycle (Scheme 30b).

This methodology of irradiating an EDA complex containing a TT-based salt was already applied in many successful transformations such as borylation<sup>109b</sup> (Scheme 31a), C–H functionalisation<sup>119</sup> (Scheme 31b), synthesis of aromatic disulphides<sup>120</sup> (Scheme 31c), phosphorylation<sup>121</sup> (Scheme 31d),

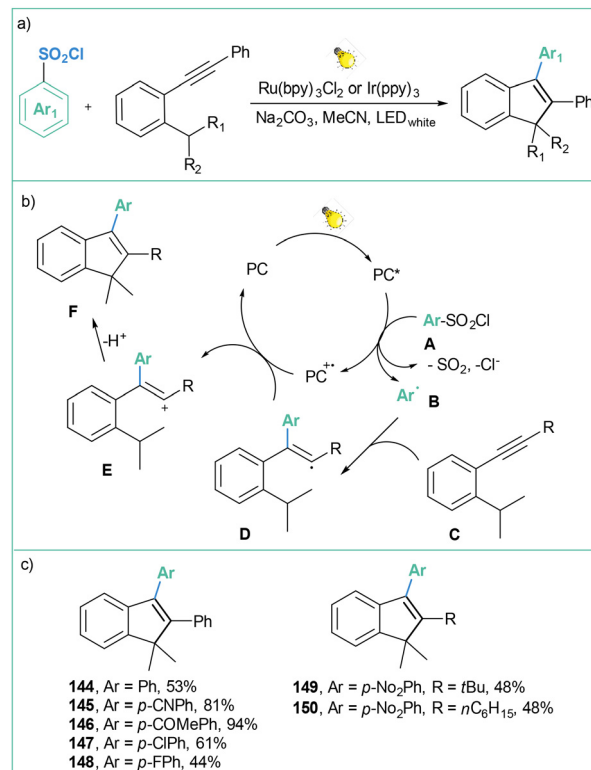
trifluoromethylselenolation<sup>122</sup> (Scheme 31e) and arylation of heteroarenes<sup>123</sup> (Scheme 31f). Even though such a strategy is limited to substrates that are able to form EDA-type complexes *in situ*, it is extremely useful, economical, and environmentally friendly (metal and photocatalyst-free).

### 3.4. Generation of aryl radicals from sulfonyl chlorides

**3.4.1. Photoredox catalysis.** Sulfonyl chlorides are versatile building blocks in organic synthesis since they are relatively inexpensive, commercially available, and provide only gaseous byproducts ( $SO_2$  or HCl); thus they are perfect examples of sustainable substrates. In single-electron transfer processes they produce either alkyl, aryl, or sulfonyl radicals. Most of the literature demonstrations refer to the generation of alkyl and sulfonyl radicals and their application; nevertheless, the activation of arylsulfonyl chlorides toward the generation of aryl radicals is also possible and can be achieved *via* a photo-induced single-electron reduction from the photocatalyst in the excited state (Scheme 32).<sup>124</sup> In 2012, Li and co-workers for the first time reported a protocol for the photocatalyzed generation of aryl radicals from arylsulfonyl chlorides and their subsequent application into carbocyclization toward the formation of 1*H*-indenes (Scheme 32a).<sup>125</sup> The mechanistic proposal assumes first photoexcitation of the photocatalyst and then single-electron transfer between the excited photocatalyst ( $PC^*$ ) and arylsulfonyl chloride **A** and subsequent generation



**Scheme 31** The scope of transformations is enabled via the formation of EDA complex: (a) borylation, (b) C–H functionalization, (c) thioetherification, (d) phosphorylation, (e) trifluoromethylselenolation and (f) arylation of heteroarenes.



**Scheme 32** Photocatalyzed reaction of arylsulfonyl chlorides with alkynes: (a) model reaction, (b) mechanistic proposal and (c) representative products.



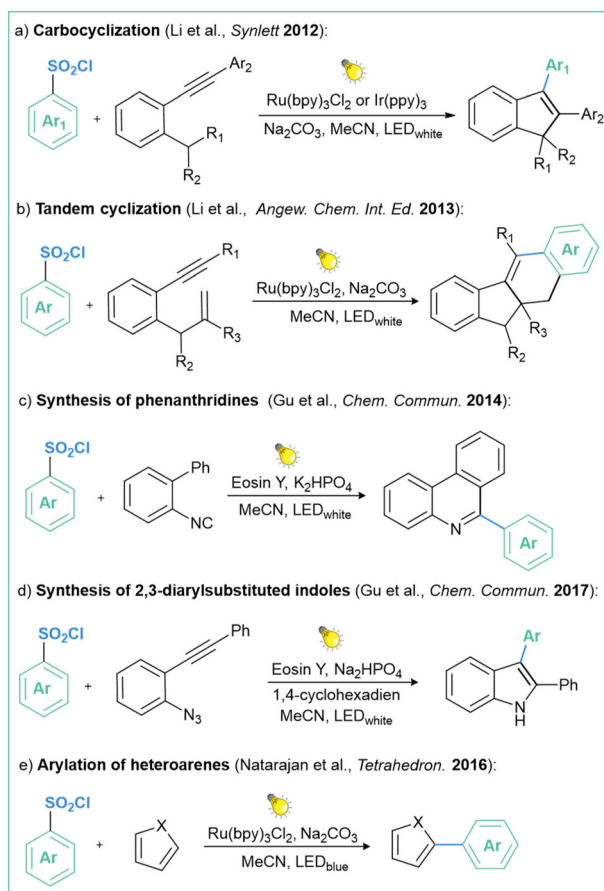
of the photocatalyst radical cation ( $PC^{\cdot+}$ ) and aryl radical **B**. Next, aryl alkyne **C** reacts with aryl radical **B** with the formation of radical **D**, which after oxidation and deprotonation forms product **F** (Scheme 32b). Generally, the reaction proceeds with good to high yields (44–94%) for different alkynes and aryl sulfonyl chlorides (Scheme 32c). This methodology was further utilized in a number of successful intramolecular cyclization reactions such as the synthesis of 10*a*,11-dihydro-10*H*-benzo[*b*]fluorenes<sup>126</sup> (Scheme 33b), phenanthridines<sup>127</sup> (Scheme 33c), and 2,3-diarylsubstituted indoles<sup>128</sup> (Scheme 33d). In 2016, Natarajan and co-workers also demonstrated the successful arylation of pyrroles, thiophenes and furans, where they showed that arylsulfonyl chloride can efficiently replace common aryl radical precursors such as diazonium salts and aryl halides (Scheme 33e).<sup>129</sup>

### 3.5. Generation of aryl radicals from phenol derivatives (aryl triflates, phosphates)

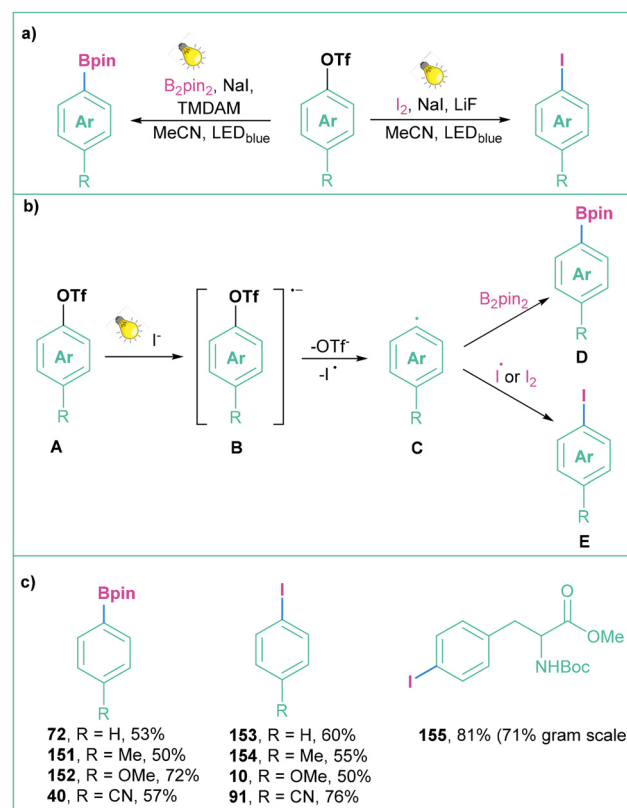
**3.5.1. Photochemistry.** Photoredox catalysis is responsible for an explosion of new synthetic applications for aryl halides, diazonium salts, sulfonium salts, and sulfonium chlorides as

aryl radical precursors in modern organic chemistry. On the other hand, the engagement of phenol and its derivatives could be even more appealing since they are easily available and inexpensive starting materials.<sup>6b,130</sup> In the case of photo-induced reductive transformations, the first demonstration of using phenol derivatives – aryl triflates as precursors of aryl radicals and their transformation into iodoarenes and borylated products – was presented by Li and co-workers (Scheme 34a).<sup>131</sup> The general mechanistic proposal (Scheme 34b) assumes that sodium iodide acts as an electron donor and is able to reduce aryl triflate **A** to radical anion **B** under UV-irradiation, which after C–O cleavage forms aryl radical **C**. The open-shell intermediate **C** can further react with  $B_2pin_2$  to form the borylated product **D**. Employing the iodide radical (or iodine molecule –  $I_2$ ) leads exclusively to iodoarene **E**. Although the protocol gives access to a variety of products in only moderate yields (36–70%), the methodology features good functional group compatibility and mild reaction conditions, as well as being metal- and photocatalyst-free. More importantly, it uses readily available and inexpensive aryl triflates as aryl radical precursors (Scheme 34c).

A similar mode of action was applied for the photoinduced Arbuzov-type reaction of aryl triflates with trialkyl phosphite, where NaI was replaced with TBAI (Scheme 35)<sup>132</sup> and for the deuteration of aryls.<sup>133</sup>

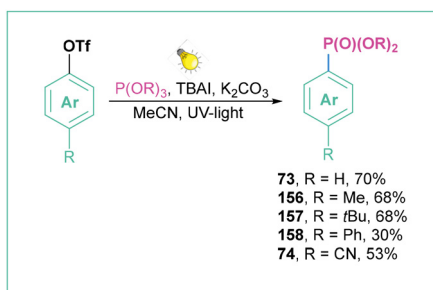


**Scheme 33** Photocatalyzed production of aryl radicals from arylsulfonyl chlorides and their application in (a) carbocyclization, (b) tandem cyclization, (c) synthesis of phenanthridines, (d) synthesis of 2,3-diarylsubstituted indoles and (e) arylation of heteroarenes.



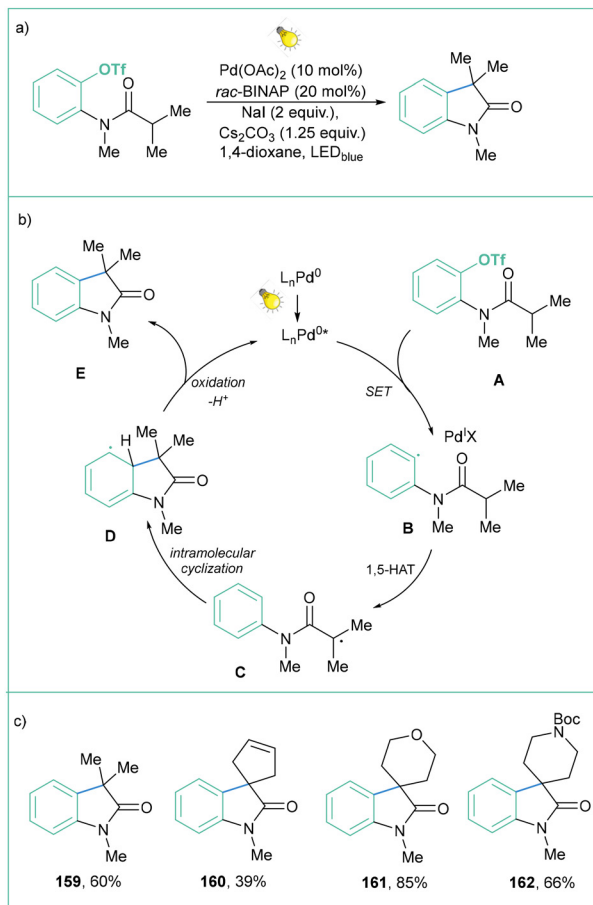
**Scheme 34** Generation of aryl radicals from aryl triflates: (a) model reaction, (b) mechanistic approach and (c) representative products.





**Scheme 35** Photoinduced Arbusov-type reaction of aryl triflates with trialkyl phosphite.

Another way of activating aryl triflates toward the generation of aryl radicals was presented by Gevorgyan and co-workers (Scheme 36a).<sup>134</sup> This methodology allows for efficient intramolecular C–H arylation of amides. The proposed mechanism depicted in Scheme 36b assumes the formation of a Pd-radical intermediate **B**, which after a 1,5-HAT produces radical **C**, which upon intramolecular cyclization and rearomatization forms product **E**. It is postulated that the formation of inter-

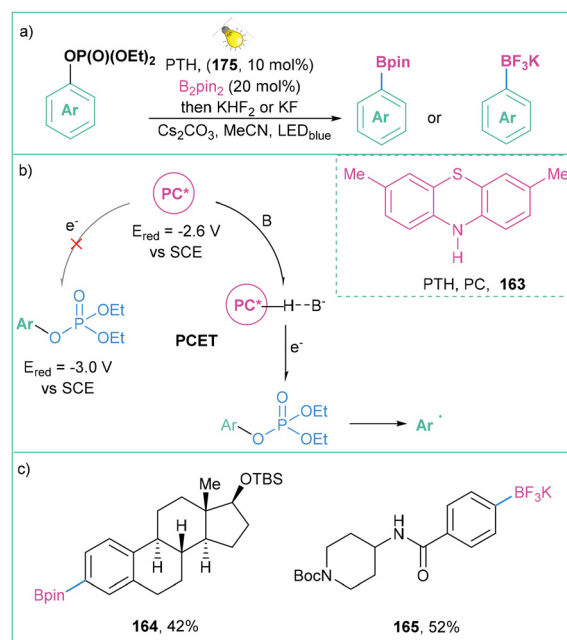


**Scheme 36** Visible-light-induced palladium-catalyzed generation of aryl radicals from aryl triflates: (a) model reaction, (b) mechanistic proposal and (c) representative products.

mediate **B** can occur through different pathways: (a) a SET between the Pd catalyst in the excited state and aryl triflate (via standard reduction to a radical anion and then C–O cleavage to an aryl radical); (b) oxidative addition of the Pd catalyst into substrate **A**, forming a Pd complex and after subsequent light absorption, formation of intermediate **B**; (c) ligand exchange, formation of the PdI-catalyst, and subsequent homolysis to form an aryl radical; or (d) reductive elimination and generation of an aryl iodide that undergoes SET with the photoexcited Pd-catalyst, leading to **B**. Although the mechanism has been studied in detail, it was not possible to determine which path is the most reliable one. However, this transformation proved to be very efficient in forming different oxindoles (Scheme 36c) and isoindoline-1-ones.

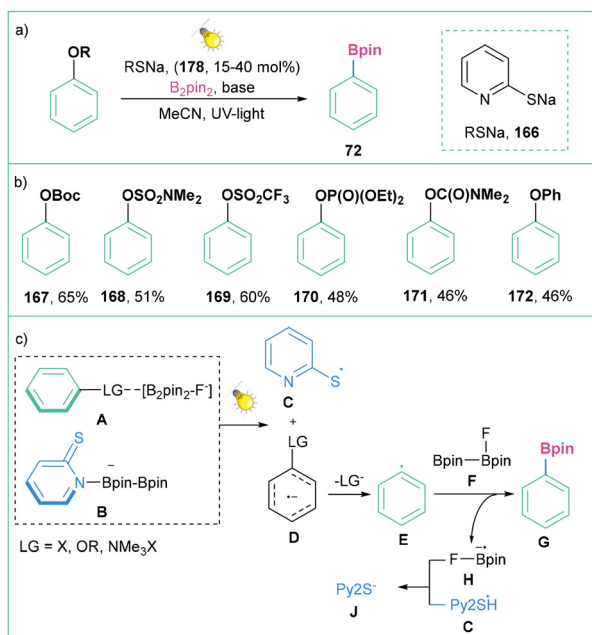
Aryl triflates are not the only phenol derivatives that can be activated to promote efficient aryl radical formation.<sup>135</sup> Larionov and co-workers proved that it is possible to photoactivate other derivatives such as aryl diethyl phosphates ( $E_{\text{red}} \sim -3.0$  V vs. SCE) (Scheme 37a), as well as aryl halides and quaternary aryl ammonium salts.<sup>57</sup> Proton-coupled electron transfer (PCET) was utilized in order to activate the substrates with strongly negative reduction potentials (Scheme 37b). Generally, this approach possesses an enormously broad scope of application: EDG, EWG, heteroarenes, and natural compounds, among them amino acids and hormones (Scheme 37c).

Another strategy for the activation of phenol derivatives that possess highly negative reduction potentials (OBoc, OSO<sub>2</sub>NMe<sub>2</sub>, OSO<sub>2</sub>CF<sub>3</sub>, OP(O)(OEt)<sub>2</sub>, OC(O)NMe<sub>2</sub>, OPh) is the application of thiolate as a catalyst (Scheme 38).<sup>136</sup> Here, the reaction is initiated by a photoinduced electron transfer



**Scheme 37** PCET as a mode of activation of phenol derivatives: (a) model reaction, (b) mechanistic proposal and (c) representative products.





**Scheme 38** PCET for the activation of phenol derivatives: (a) model reaction, (b) representative substrates and (c) mechanistic proposal.

process between an activated boryl-anion **A** (LG = X, O or N) and the adduct 2-PySNa/B<sub>2</sub>pin<sub>2</sub> **B** to generate a thiol radical **C** and radical anion **D**. The resulting radical anion **D** undergoes cleavage of the C-LG bond to form the aryl radical **E**, which then reacts with a diboron species [F, F-B<sub>2</sub>pin<sub>2</sub>] to give the borylation product **G** and the boryl radical anion **H**. Finally, the thiol radical **C** is reduced by the boryl radical anion **H** to regenerate thiolate **J** with the closure of the cycle (Scheme 38c).

Generally, this strategy allows for the activation of not only a very broad range of inert C-O bonds within phenol derivatives (carbonate, sulfamate, phosphate, and carbamate) but also non-activated C-F bonds, C-N bonds (ammonium salts), and C-S bonds (sulfone, sulfoxide, and sulfide), with very negative reduction potentials, which are challenging for photoredox activation. Despite the high reducing power generated, this reaction shows broad functional group tolerance and yields borylated products in moderate to very good yields (Scheme 38b).

### 3.6. Generation of aryl radicals from quaternary arylammonium salts

The application of unprotected amines as building blocks in organic synthesis has been a central research topic for decades. However, the C<sub>aryl</sub>-N bond cleavage of amines represents a very challenging problem, because of the high bond dissociation energy. The preactivation of the amine into other functional groups is one way to solve this problem. Transformation of an amine to the corresponding quaternary ammonium salts is easily achievable synthetically and relatively inexpensive. They show good reactivity in various organic transformations, especially *via* C-N bond cleavage.<sup>137</sup>

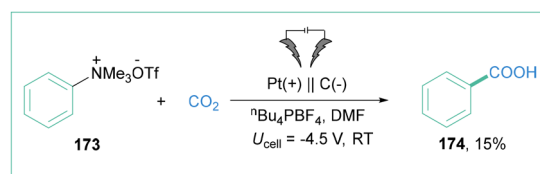
**3.6.1. Photochemistry.** Photoactivation of the strong C<sub>aryl</sub>-N bond in quaternary arylammonium salts has remained a challenge for a long time. In 2016, Larionov demonstrated that catalyst-free UV light-induced C-N borylation of quaternary arylammonium salts is possible.<sup>138</sup> The same group made a further improvement of this method a few years later with the use of phenothiazine as photocatalyst (for *modus operandi* see Scheme 37).<sup>57</sup>

**3.6.2. Electrochemistry.** The first examples of electrolyses of quaternary ammonium salts appeared in the literature in 1909;<sup>139</sup> however, the involvement of aryl radicals in these processes was suggested fifty years later.<sup>140</sup> Importantly, these studies primarily concentrated on mechanistic aspects rather than methodology, thus synthetic applications of these intriguing aryl radicals' precursors remained largely underexplored for a long time.

In 2019, Manthiram and colleagues investigated the electroreductive transformation of benzylammonium salts toward benzylic acids.<sup>141</sup> During the investigation, they also tested phenyltrimethylammonium triflate (**173**) (Scheme 39) as a possible aryl radical precursor. Indeed, benzoic acid (**174**) was isolated albeit in 15% yield, showcasing the synthetic potential of **180** at the same time. The important obstacle here is the high cell potential ( $U_{\text{cell}} = 4.5$  V) that was required for the indicated efficiency.

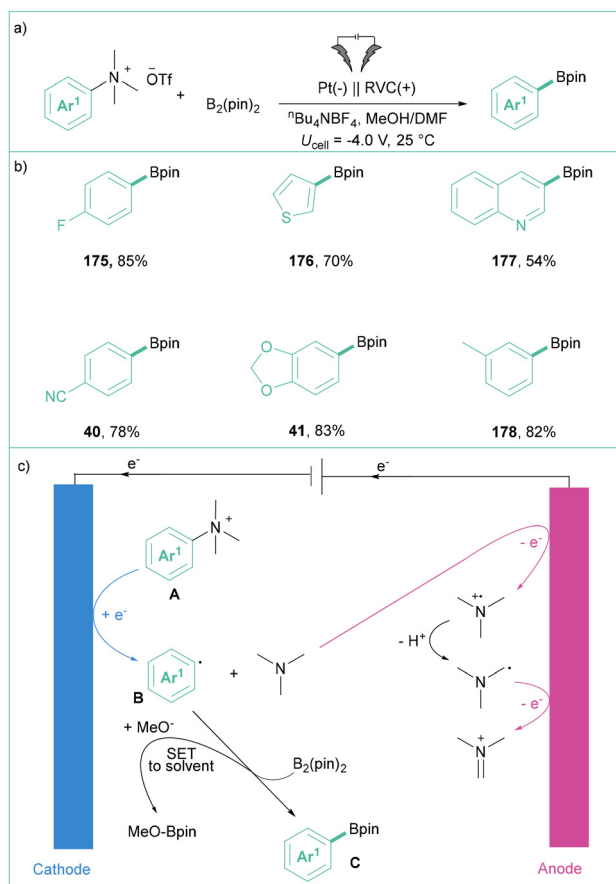
In 2021, Xu's group described the direct electrolysis of aryltrimethylammonium triflates toward synthetically meaningful organoboronates (Scheme 40a).<sup>142</sup> Here, potentiostatic conditions were applied to produce products in moderate to good yields showing broad applicability (Scheme 40b). They proved that the presence of MeOH is essential for this transformation as the efficiency dropped significantly in the absence of this protic solvent. Mechanistically, the process starts with the formation of an aryl radical *via* direct electroreduction along with Me<sub>3</sub>N. Subsequently, Ar<sup>•</sup> reacts with B<sub>2</sub>pin<sub>2</sub> in the presence of MeO<sup>-</sup>, giving rise to the expected product **C** and MeOBpin (Scheme 40c).

The same group also proved that quaternary arylammonium salts can be transformed into a variety of benzonitriles (**181**) as well as benzylnitriles (**182**) by employing tosyl cyanide (TsCN) or azido allyl alcohol as cyanation or cyanomethylation reagents (Scheme 41a).<sup>143</sup> The efficiency of cyanation was generally higher, in comparison with the cyanomethylation reaction. The method tolerates a broad range of substrates, including those bearing easily reducible functional groups (-CN, -CO<sub>2</sub>Alk, -NO<sub>2</sub>), S-, O- or N-based heterocyclic motifs, as well



**Scheme 39** Electrolysis of phenyltrimethylammonium triflate toward benzoic acid formation.



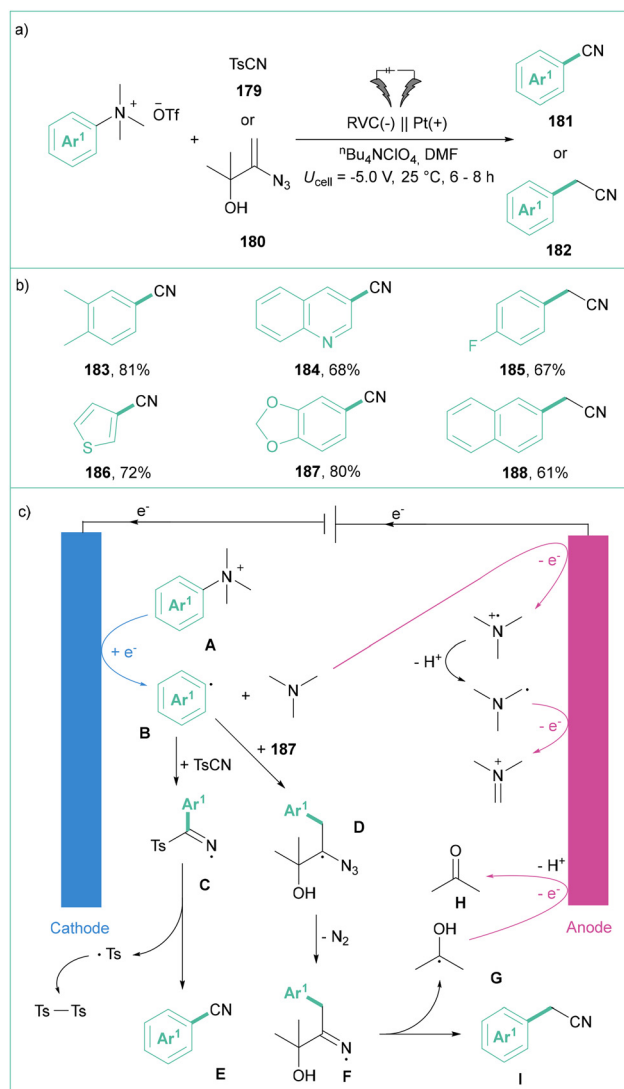


**Scheme 40** Electrolysis of phenyltrimethylammonium triflate toward benzoic acid: (a) model reaction, (b) representative products and (c) mechanistic proposal.

as natural product derivatives (Scheme 41b). Importantly, the authors found that the obtained nitriles of type **181–182** are stable during the electrolysis as they feature reversible electron-transfer characteristics (based on the CV studies). The proposed mechanism postulates the formation of an aryl radical **B** via a reductive process, which then reacts with electrophilic TsCN or **187**, giving rise to N-centered radicals in both cases (**C** or **D**). Finally, **E** and **I** are formed with the release of Ts-Ts or acetone (both assembled from the respective radicals) (Scheme 41c).

The common feature of the electrochemical methods described above is the extremely high working potential (up to  $-5.0$  V) that significantly hampers efficient energy utilization. Therefore, this sets the stage for more sustainable methods for the reduction of aryltrimethylammonium salts toward aryl radicals.

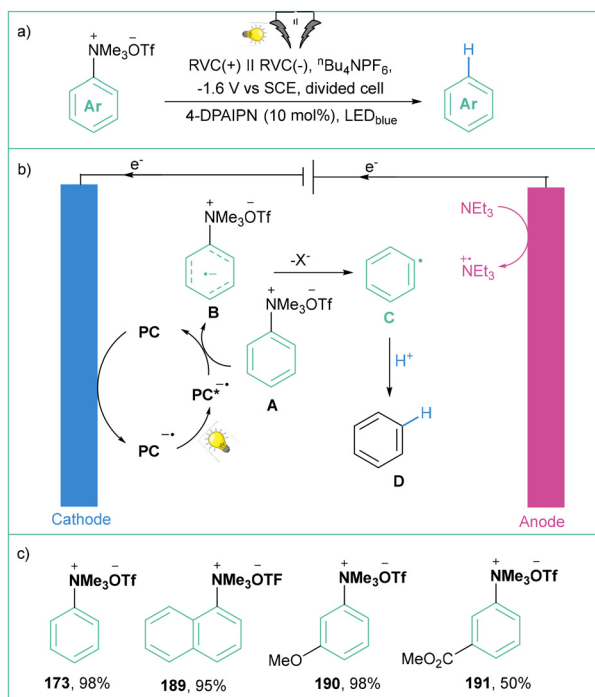
**3.6.3. Photoelectrochemistry.** As we mentioned in the photoredox part of this section, Larionov<sup>138</sup> and König<sup>136</sup> demonstrated the successful activation of challenging quaternary arylammonium salts ( $\sim -2.5$  V vs. SCE) via simple photoreduction. However, both approaches relied on the special characteristic of the boron partners, and therefore photoredox



**Scheme 41** Electrochemical cyanation and cyanomethylation of aryltrimethylammonium salts: (a) model reaction, (b) representative products and (c) mechanistic proposal.

transformations of these demanding substrates remain limited. On the other hand, photoelectrocatalysis has already been proved to be a powerful strategy for the generation of photoexcited radical ions that can behave as strong reductants under very mild conditions.<sup>77</sup> This approach has been utilized by Wickens and colleagues for the activation of quaternary arylammonium salts (Scheme 42a).<sup>77</sup> Generally, this approach assumes that first, the photocatalyst is reduced to its radical anion ( $\text{PC}^{\bullet-}$ ) at the cathode and as such it gets excited to form a super strong reducing agent ( $\text{PC}^{*\bullet-}$ ), which is able to reduce a quaternary arylammonium salt **A** to its radical anion **B**, which after dehalogenation forms the aryl radical **C**. Subsequent protonation forms product **D** (Scheme 42b). This strategy was demonstrated to be very efficient for various quaternary ammonium salts possessing electron-donating groups (excellent yields) and electron-withdrawing groups that were





**Scheme 42** Photoelectrocatalytic activation of quaternary arylammonium salts: (a) model reaction, (b) mechanistic proposal and (c) representative products.

slightly less reactive (moderate yields) (Scheme 42c) (for the stability of excited radical anions see paragraph 3.1 Con-PET vs. photoelectrochemistry).

### 3.7. Generation of aryl radicals from diaryliodonium salts

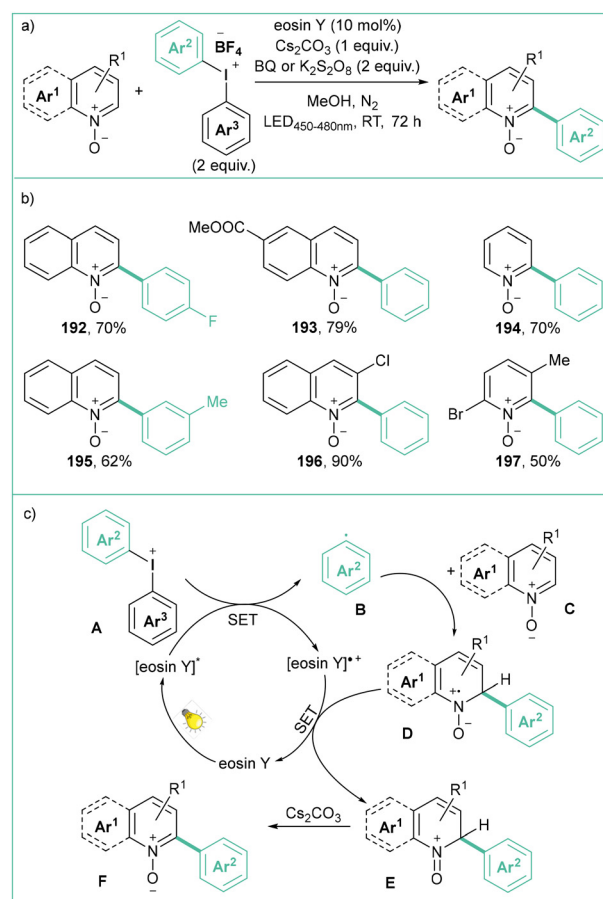
Diaryliodonium salts, similarly to diazonium salts, can also be used for the generation of aryl radicals, although they generally feature lower reduction potentials (usually  $-0.4$  to  $-0.8$  V vs. SCE in MeCN).<sup>144</sup> These compounds have recently received considerable attention as they are mild, nontoxic, selective, and compatible with many functional groups, and are low-cost reagents in organic synthesis. That's why diaryliodonium salts have become a good alternative to toxic, expensive, heavy-metal-based (Hg, Pb, Pd) catalysts in many organic transformations.<sup>145</sup>

**3.7.1 Photoredox catalysis.** The application of diaryliodonium salts in the preparation of aryl radicals under visible light irradiation is well established and widely described in the literature. The most important applications of these species include direct C–H arylation of alkenes and styrenes,<sup>146</sup> heteroarenes,<sup>147</sup> allyl tosylates,<sup>148</sup> *N*- or *C*-phenylamides,<sup>149</sup> preparation of sulfones,<sup>150</sup> sulfoxidation and sulfenylation,<sup>151</sup> synthesis of thiophosphates,<sup>152</sup> hydrophosphinylation<sup>20f</sup> and dehydrogenation.<sup>153</sup> The major limitation of methods involving diaryliodonium salts as aryl radical precursors is the production of ArI as a by-product, thus generating a lot of atom waste, especially since they are usually used in an excess (see below).

Li and co-workers developed a visible-light-promoted C2-selective arylation of quinoline and pyridine *N*-oxides using diaryliodonium tetrafluoroborates as arylation reagents (Scheme 43).<sup>154</sup> Here, the application of 10 mol% of eosin Y as a photocatalyst and 5 W blue LEDs (450–480 nm) ensures satisfactory yields. BQ (1,4-benzoquinone) or  $K_2S_2O_8$  were used as stoichiometric co-oxidants.

According to the mechanistic proposal, eosin Y undergoes excitation by visible light to its excited state and at the same time it reduces aryl iodonium salt **A** to aryl radical **B**. Then the radical **B** undergoes addition to pyridine *N*-oxide **C** (or quinoline) to form **D**, which after single-electron reduction forms **E**. Product **F** forms after rearomatization.

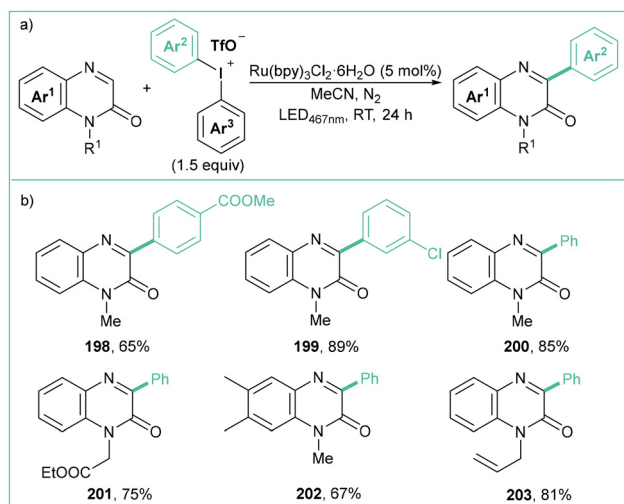
Similarly to the method mentioned above, the Ru(II)-based photocatalyst enables direct C3 arylation of quinoxalin-2-(1*H*)-ones employing easily available and stable diaryliodonium triflates (Scheme 44a).<sup>155</sup> Specifically, the reaction proceeds in the presence of  $Ru(bpy)_3Cl_2 \cdot 6H_2O$  (5 mol%) under blue LED irradiation (467 nm) in MeCN. The scope is rather broad, and allyl/propargyl groups are well tolerated in this protocol (Scheme 44b). Importantly, if non-symmetrical diaryliodonium salts are used, the selective transfer of an electron-deficient



**Scheme 43** Arylation of quinoline and pyridine *N*-oxides with diaryliodonium tetrafluoroborates: (a) model reaction, (b) representative products and (c) mechanistic proposal.







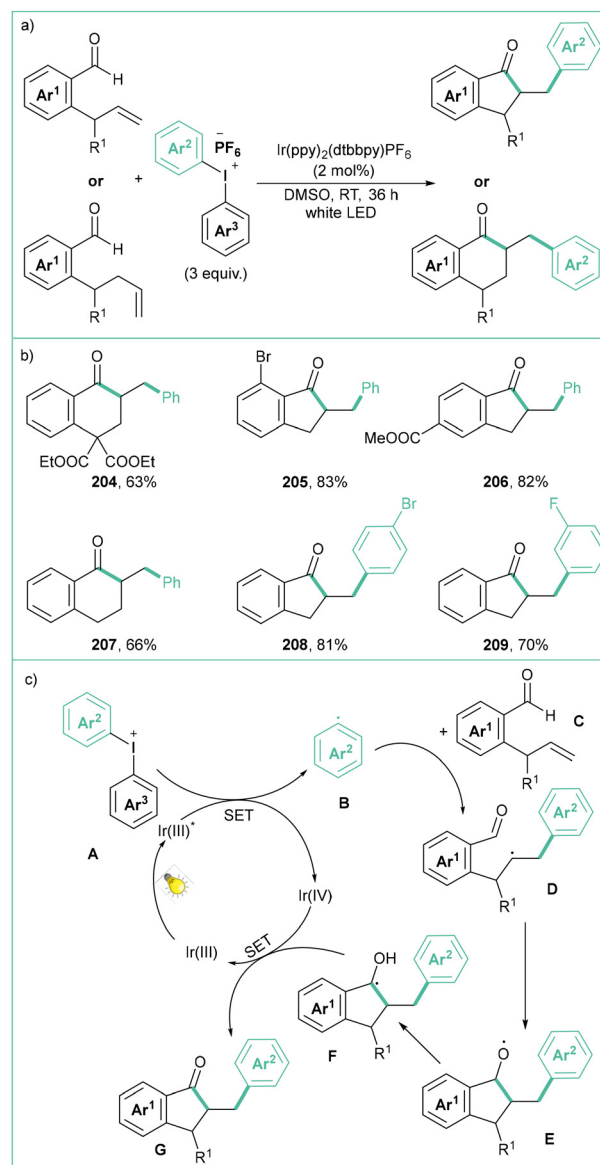
**Scheme 44** Arylation of quinoxalin-2(1*H*)-ones with diaryliodonium salts: (a) model reaction and (b) representative products.

and less sterically hindered part is preferred. In terms of mechanism, the reaction proceeds in a way analogous to that described earlier (see Scheme 43c).

In turn, the iridium-based catalyst  $(\text{Ir}(\text{ppy})_2(\text{dtbbpy})\text{PF}_6)$  proved to be effective in the photocatalytic acylarylation of unactivated alkenes to cyclic ketones (Scheme 45a).<sup>156</sup> The aldehyde substitution pattern has no significant impact on the reaction outcome and, at the same time, excellent *trans*-diastereoselectivity is observed. Initially, the Ir(III) catalyst is excited by visible light to the excited state  $\text{Ir}(\text{III})^*$ . Then, a SET process between  $\text{Ir}(\text{III})^*$  and **A** leads to an aryl radical **B**. Such an open-shell species **B** undergoes addition to the double bond within **C**, and the resultant radical **D** attacks the aldehyde functionality to form **E**. Oxidative quenching of Ir(IV) by this radical eventually gives rise to **G** (Scheme 45c).

*N*-Substituted 2-arylbenzimidazoles show a similar reactivity pattern toward diphenyliodonium triflates affording arylated-benzimidazo[2,1-*a*]isoquinolin-6(5*H*)-ones (Scheme 46a).<sup>155</sup> This cascade operates under mild conditions and offers a broad substrate scope with appreciable functional group tolerance (Scheme 46b). For non-symmetrical diphenyliodonium triflates, the transfer of an electron-deficient and sterically less hindered aryl ring prevails. The mechanism resembles the one described for the arylation of 2*H*-quinoxalines (Scheme 46c). The whole process is initiated by visible light photoexcitation of the Ru(II)-based photocatalyst in its excited form. Then, an aryl radical **B** is produced with the concomitant formation of the Ru(III) complex, which is reduced by a radical **D** formed *via* an addition of **B** to **C**. The final deprotonation step leads to **G**.

Liu and co-workers reported a three-component visible light photoredox-catalyzed synthesis of *N*-aminosulfonamides starting from diaryliodonium salts, hydrazines and different sulphur dioxide sources (Scheme 47).<sup>157</sup> Here, diaryliodonium salts react with 4-aminomorpholine and sulphur dioxide (gen-

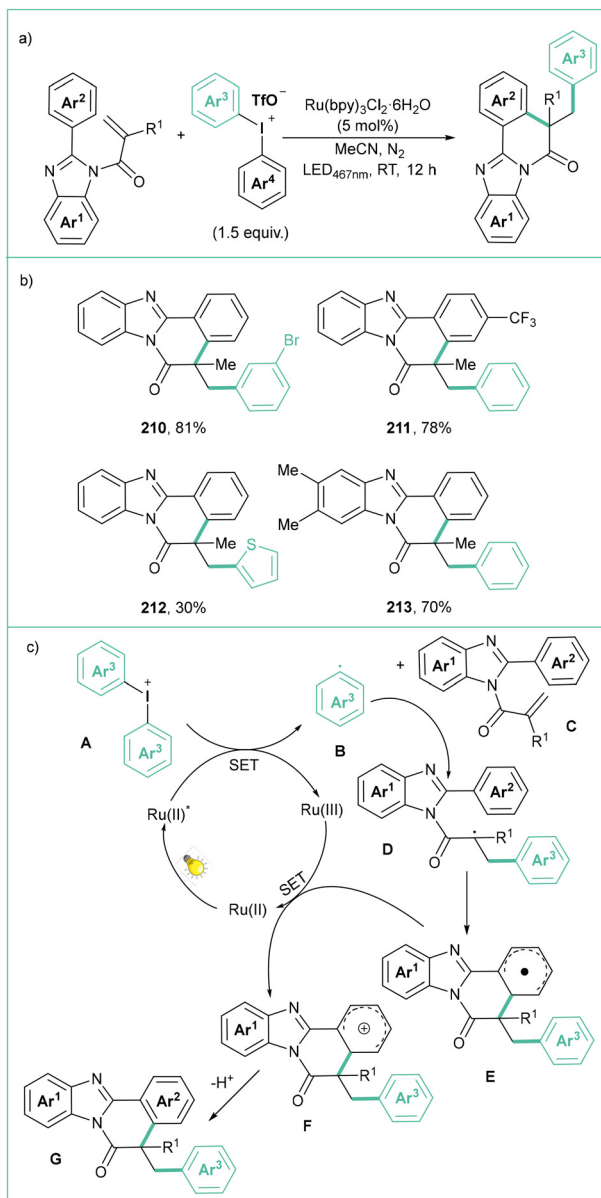


**Scheme 45** Acylarylation of unactivated alkenes with diaryliodonium salts: (a) model reaction, (b) representative products and (c) mechanistic proposal.

erated *in situ* from  $\text{K}_2\text{S}_2\text{O}_5$  and TFA) in the presence of 2 mol% **PDI1** upon blue light irradiation (445 nm), giving rise to *N*-aminosulfonamides in a selective manner (Scheme 47a). The proposed mechanism (Scheme 47c) starts with a **PDI1** photoexcitation and reductive quenching of **PDI1**\* with the hydrazine-sulphur dioxide complex **B** providing a radical adduct **C** and reduced catalyst **PDI1**<sup>-</sup>. Next, a SET between **PDI1**<sup>-</sup> and the diaryliodonium salt **E** gives an aryl radical **F** that then reacts with the sulphur-based radical **D** to finally give the expected product **G**.

An efficient protocol for the synthesis of aryl sulfonyl fluorides was presented by Ma and colleagues (Scheme 48a).<sup>158</sup> The reaction proceeds in MeCN under blue LED (440–445 nm) irradiation in the presence of a photosensitizer, namely cam-

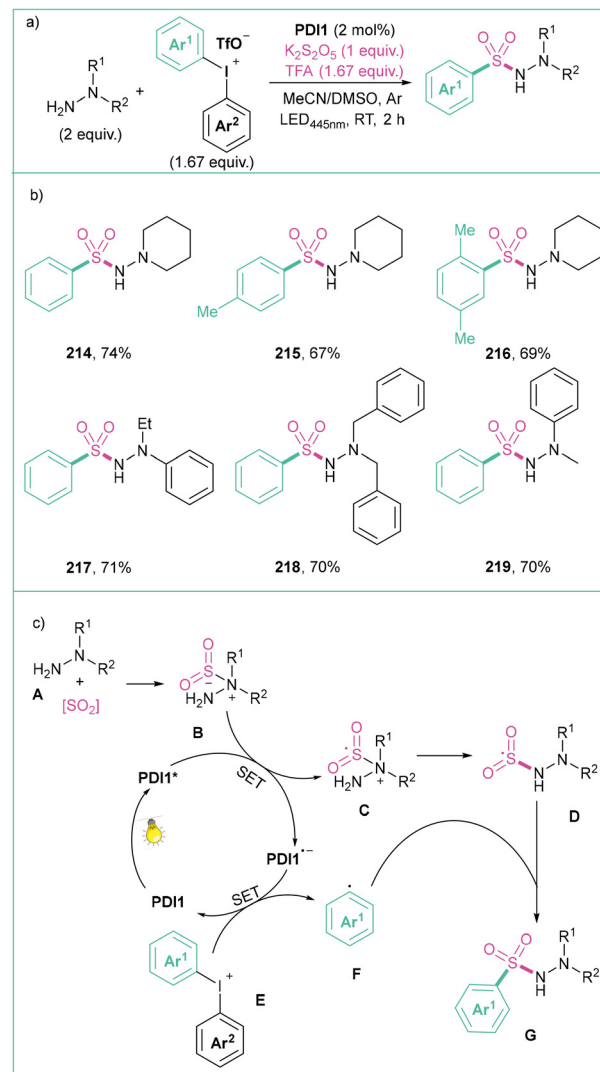




**Scheme 46** Arylative cyclization of *N*-acryloyl-2-arylbenzimidazoles with diaryliodonium salts: (a) model reaction, (b) representative products and (c) mechanistic proposal.

phorquinone (CQ), with diaryliodonium salts as a source of aryl radicals, alongside DABSO and  $\text{KHF}_2$  as the fluorine source. The process is compatible with a wide range of electron-donating, neutral, and electron-withdrawing functional groups that are tolerated in this transformation (Scheme 48b). The proposed reaction mechanism starts with the photoexcitation of CQ followed by a SET with salt A to give an aryl radical B. The radical B then interacts with DABSO (C), giving rise to a sulphur-based radical F. This species then reacts with the DABSO radical cation (E) which, under the influence of  $\text{KHF}_2$ , produces G.

**3.7.2 Electrochemistry.** Electrochemical generation of aryl radicals from diaryliodonium salts is well documented in the



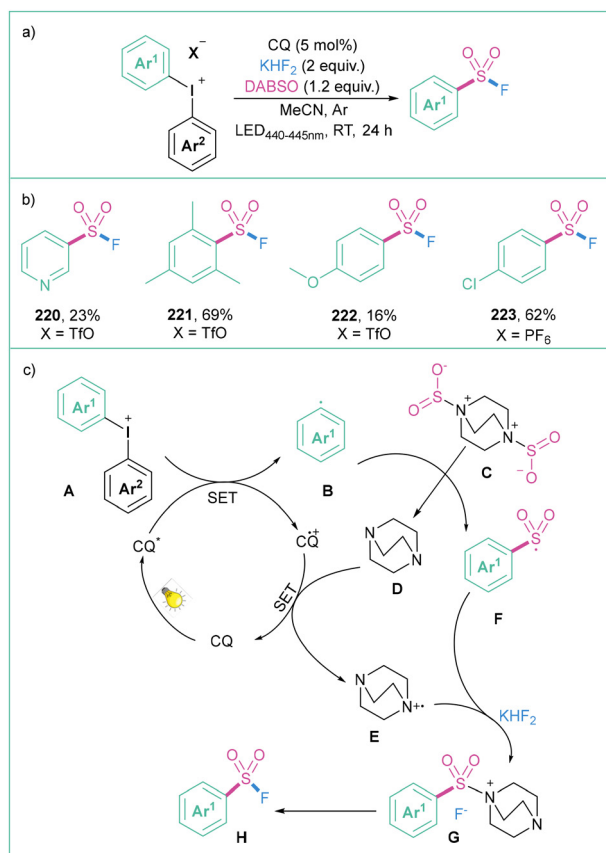
**Scheme 47** Synthesis of *N*-aminosulfonamides from diaryliodonium salts: (a) model reaction, (b) representative products and (c) mechanistic proposal.

literature but has been only applied in electrografting of different materials including carbon, gold, and tin oxide.<sup>144b,159</sup> It is worth noting that the grafting efficiency for diaryliodonium salts was found to be slightly lower than that noted for diazonium salts.<sup>144b,159b</sup> Notwithstanding, to the best of our knowledge, such electrochemically driven, purely methodological applications of diaryliodonium salts have not yet been developed.

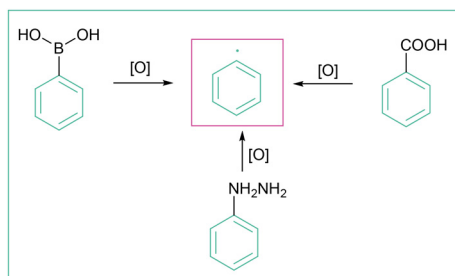
## 4. Oxidatively induced generation of aryl radicals

Taking into account three SET methods: PET (photoinduced electron transfer) (*e.g.* photoredox catalysis and reactions accruing through formation of EDA complexes), organic electrochemistry, and photoelectrochemistry, the oxidative





**Scheme 48** Synthesis of aryl sulfonyl fluorides from diaryliodonium salts: (a) model reaction, (b) representative products and (c) mechanistic proposal.



**Scheme 49** Oxidatively induced generation of aryl radicals from different precursors.

generation of aryl radicals is to date possible from aromatic boronic and carboxylic acids<sup>160</sup> as well as aryl hydrazines (Scheme 49). Synthetic methods that use electric current for oxidative functionalisation reactions<sup>21b,23,161</sup> have recently received considerable attention and aryl radicals can be generated in that way as well.

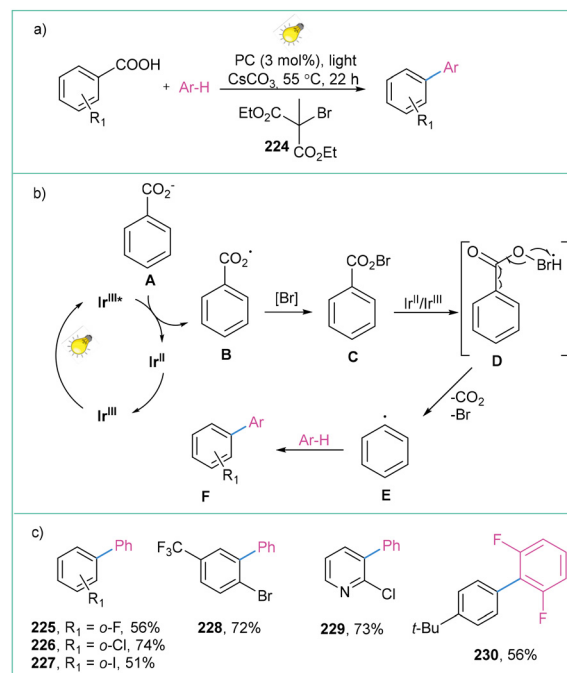
#### 4.1 Generation of aryl radicals from aromatic carboxylic acids and their derivatives

Benzoic acids seem to constitute the most promising precursors of aryl radicals, as they are easily accessible, bench-stable

and structurally diverse reagents. However, until very recently, decarboxylative transformations were largely mediated by the use of high temperatures and stoichiometric amounts of heavy metals.<sup>6a,160</sup> Among the biggest challenges associated with the oxidative decarboxylation of benzoic acids is the relative kinetic stability of the corresponding carboxyl radicals. Namely, PhCOO• was classified by Barton<sup>162</sup> as a ‘nondecarboxylating acyloxy radical’, that is, the decarboxylation process should occur only at temperatures above 120–130 °C, which can eventually lead to the formation of unwanted side products. Nevertheless, these shortcomings were resolved partially by means of photoredox catalysis (*vide infra*), while there is still no method for the generation of Ar• in a purely electrochemical way.

**4.1.1 Photochemistry (photoredox catalysis and formation of EDA complexes).** The first attempts for the light-induced generation of aryl radicals from carboxylic acid derivatives date back to 1988,<sup>163</sup> when Ingold and co-workers published the spectroscopic and kinetic characteristics of aryl radicals generated from different aromatic peroxides by laser flash photolysis. The authors observed that the production of aryl radicals through direct photolysis of dibenzoyl peroxides is more efficient compared with thermolysis. This important finding set the stage for future application of photoredox catalysis in the oxidative generation of aryl radicals from carboxylic acids. In 2017, the Glorius group showed the first example of aryl radical formation from aromatic carboxylic acids employing photoredox catalysis (Scheme 50a).<sup>164</sup>

The mechanistic scenario includes the initial oxidation of the deprotonated aromatic carboxylic acid **A** by the Ir-based



**Scheme 50** Decarboxylation of aryl carboxylic acids: (a) model reaction, (b) mechanistic proposal and (c) representative products.



catalyst in an excited state to form radical **B**. Then, *in situ* formation of an acyl hypobromite **C** occurs, which after reduction and concerted cleavage of the C–C and O–Br bonds produces CO<sub>2</sub> and aryl radical **E**. Subsequent trapping of the aryl radical **E** by a heteroarene generates the rearomatization product **F** (Scheme 50b). The described protocol is mild, high yielding, and tolerates a broad range of substrates (Scheme 50c); however, the application of an expensive and toxic Ir photocatalyst remains its limitation.

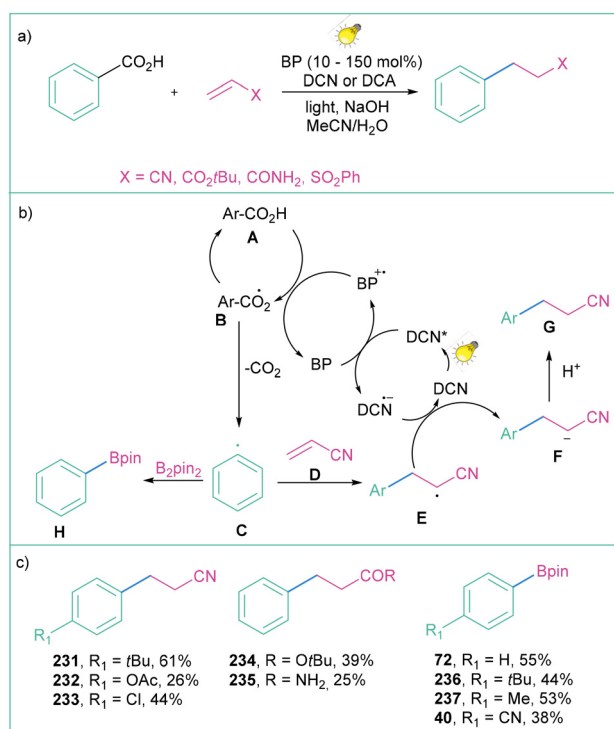
This problem was partially overcome by Yoshimi and co-workers with the use of two active organic photocatalysts: benzophenone and dicyanonaphthalene (**DCN**) or dicyanoanthracene (**DCA**) (Scheme 51a).<sup>18d</sup> Photon-induced electron transfer between benzophenone (**BP**) and **DCN** (or **DCA**) enables the oxidation of BP to its radical cation (**BP<sup>•+</sup>**), which can then oxidise carboxylic acid **A** to radical **B**, which after decarboxylation provides aryl radical **C**. The resultant aryl radical **C** reacts with electron-deficient olefins **D** to produce radical **E**, which after the reduction (enabled by the **DCN**-based radical anion formed by the catalytic cycle of **BP**) and protonation forms product **G**. When the aryl radical **C** is subjected to the reaction with B<sub>2</sub>pin<sub>2</sub>, borylated product **H** can be assembled employing this method (Scheme 51b). The methodology constitutes a facile synthetic protocol for alkylation and borylation of aromatic rings; however, yields remain moderate to good (Scheme 51c).

The search for a more efficient and sustainable photocatalyst for this transformation brought about an unexpected

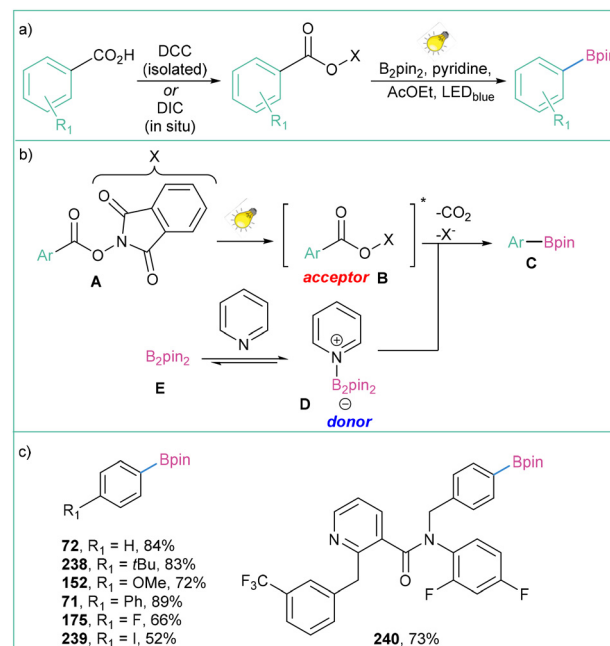
result: it is possible not to use a photocatalyst at all. The application of *N*-hydroxyphthalimide esters as aryl radical precursors enables catalyst-free conditions (Scheme 52a).<sup>165</sup> The proposed strategy assumes the formation of an EDA complex between the photoexcited acceptor (**B**) and pyridine adduct (**D**), which subsequently undergoes an electron transfer, rapid decarboxylation and finally borylation to produce the product **C** (Scheme 52b). Although in this approach aromatic carboxylic acids need to be functionalised with a NHPI group, the method remains relatively cost-effective and does not require the addition of a photocatalyst. The reaction is operationally simple, scalable, and tolerates a broad range of substrates (Scheme 52c), but most importantly, it is transition-metal- and photocatalyst-free.

Over the past decade, photoinduced intramolecular ligand to metal charge transfer (LMCT) has become a powerful strategy for the generation of oxygen-centred radicals through homolysis of oxygen–metal bonds,<sup>166</sup> and its applications in the decarboxylation of alkyl carboxylates have been well documented.<sup>167</sup> Ritter and co-workers proved that such an approach can also be applied for oxidative aryl radical generation. LMCT enables a mild and general decarboxylation of aryl carboxylic acids that works through high-valent arylcopper (iii) intermediates. Subsequently, when generated in this way, aryl radicals can further react, giving rise to fluorinated<sup>16</sup> (Scheme 53a) and hydroxylated<sup>168</sup> products (Scheme 53b).

For both processes, the mechanistic proposal assumes that irradiation of Cu(II) carboxylate **A** results in carboxylate to Cu<sup>II</sup> ligand to metal charge transfer (LMCT). Next, homolysis of the O–Cu<sup>II</sup> bond results in the formation of aryloxy radical **B**,

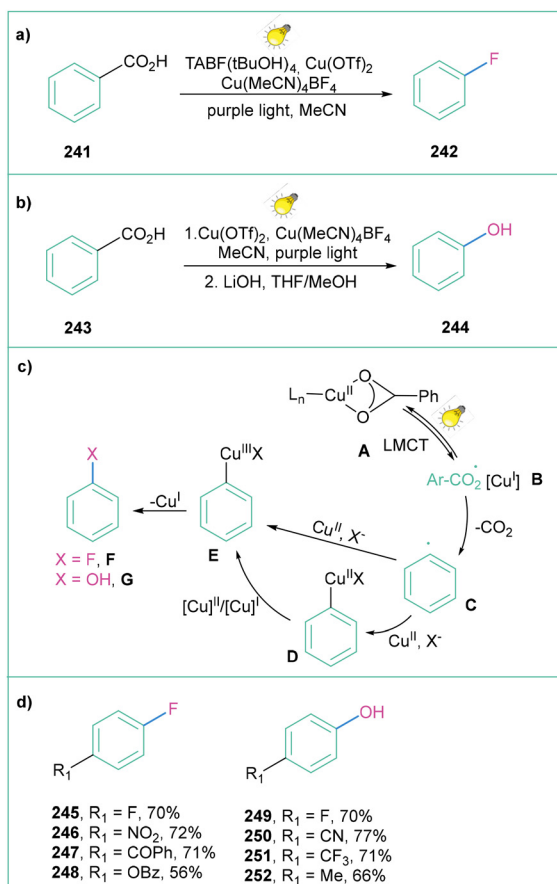


**Scheme 51** Photoinduced decarboxylative generation of aryl radicals from carboxylic acids: (a) model reaction, (b) mechanistic proposal and (c) representative products.

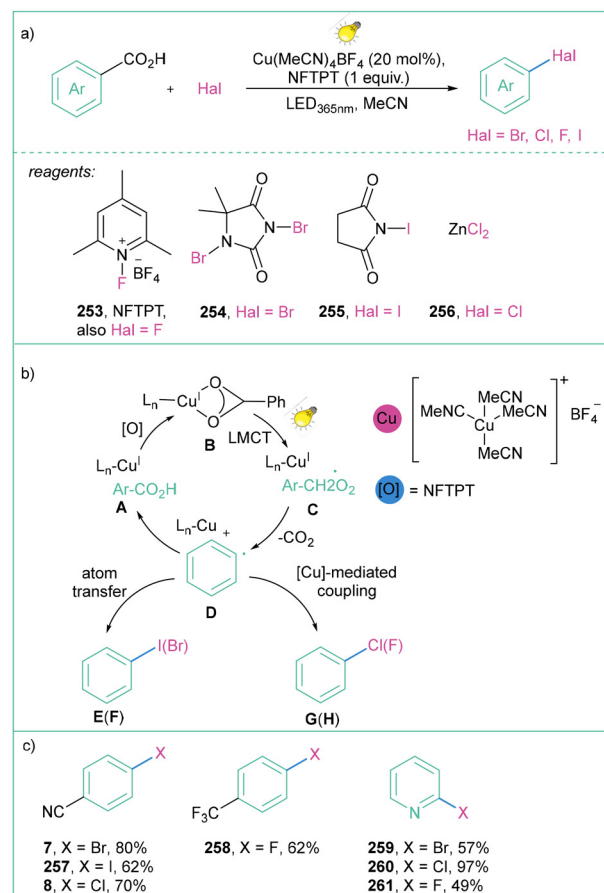


**Scheme 52** Decarboxylative borylation of aryl *N*-hydroxyphthalimide esters: (a) model reaction, (b) mechanistic proposal and (c) representative products.





**Scheme 53** Decarboxylative fluorination and hydroxylation enabled by Cu-LMCT catalysis: (a) fluorination, (b) hydroxylation, (c) mechanistic proposal and (d) representative products.



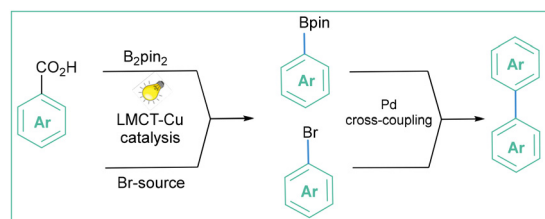
**Scheme 54** The general approach for the decarboxylative halogenation of aryl(heteroaryl) carboxylic acids: (a) model reaction, (b) mechanistic proposal and (c) representative products.

which after decarboxylation forms aryl radical C. The generated aryl radical C is trapped by a  $\text{Cu}^{\text{III}}\text{TC}$  complex or by a  $\text{Cu}^{\text{I}}\text{TC}$  complex with subsequent oxidation by  $\text{Cu}^{\text{II}}$  to afford arylcopper(III)TC. In both cases, reductive elimination of the C–O bond forms  $\text{Cu}^{\text{I}}$  and fluorinated product F or hydroxylated product G (depending on the reaction conditions) (Scheme 53c). Both protocols are operationally simple, Ir- and Ru-complex free, and moderate to high yielding (Scheme 53d).

MacMillan and co-workers presented a similar approach by developing a copper-catalyzed strategy for the decarboxylative halogenation (I, Br, Cl, F) of hetero(aryl) carboxylic acids (Scheme 54).<sup>169</sup> Later, they showed that the reaction could be used for borylations *via* the merging of Cu-LMCT borylation/bromination cross-coupling (Scheme 54a).<sup>170</sup> The proposed mechanism is similar to the one presented by the Ritter group (Scheme 53). The established methodology is general, mild, and moderate to high-yielding (see Scheme 54b); in addition, the synthesis of –Br, –Cl, –F and –I arenes and heteroarenes is compatible with a broad range of (hetero)aryl carboxylic acids (Scheme 54c).

The MacMillan group demonstrated further achievements in the area of Cu-LMCT catalysis for the oxidative aryl radical

generation and their subsequent application toward the synthesis of halogenated compounds and their cross-coupling. Namely, the authors established a methodology for the borylation of carboxylic acids.<sup>170</sup> These boron-based derivatives were subsequently merged with aryl halides (obtained by Cu-LMCT halogenation<sup>169</sup>) in Pd-catalyzed cross-coupling<sup>170</sup> (Scheme 55). Without a doubt, this approach facilitates the direct transformation of aryl carboxylic acid feedstocks into value-added products (pharmaceutically relevant compounds) under mild conditions.



**Scheme 55** Cu-LMCT decarboxylative borylation/Pd-cross coupling sequence toward value-added compounds.



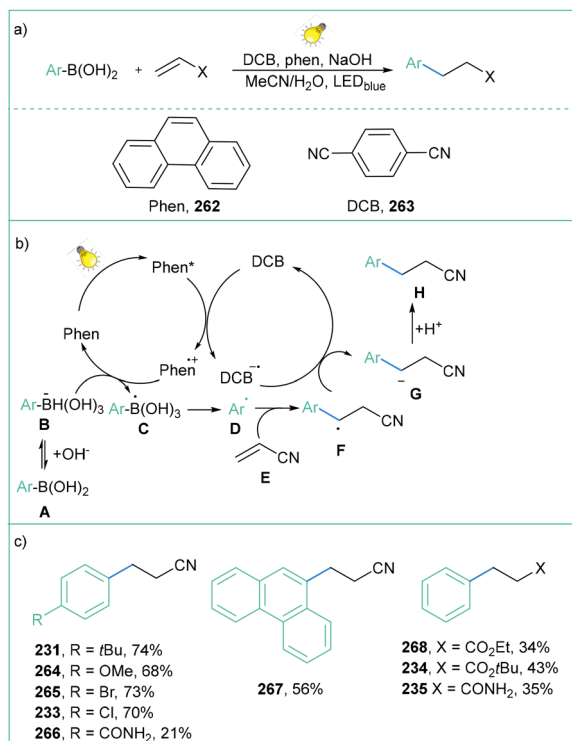
## 4.2 Generation of aryl radicals from aromatic boronic acid derivatives

Arylboronic acid derivatives are highly important chemical entities, both in organic synthesis<sup>171</sup> and medicinal chemistry.<sup>172</sup> The radical chemistry of boron-based compounds has been intensively studied over the past years, resulting in broad synthetic applications thereof.<sup>173</sup> Generally, organoboronic acids can serve as practical alkyl or aryl radical precursors *via* an oxidatively induced carbon–boron bond cleavage. Different catalytic systems based on metal catalysts, *e.g.* Mn(III), Ag(I), or Fe(II/III) have been demonstrated to be effective for such transformations;<sup>174</sup> however, these methods often depend on superstoichiometric amounts of co-oxidants.

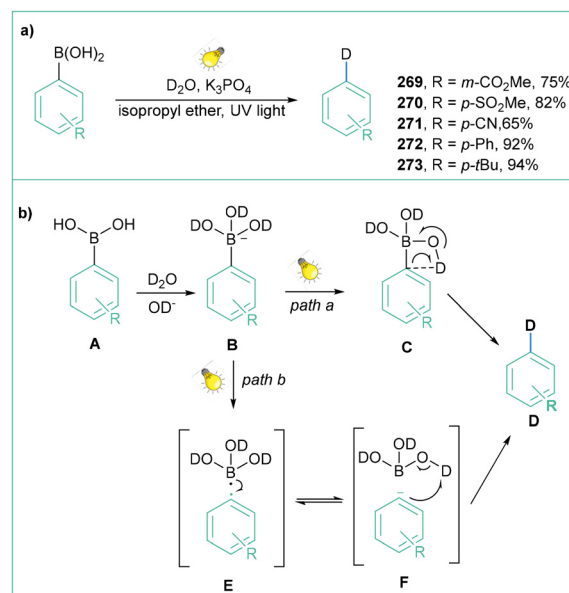
**4.2.1 Photochemistry.** Although many studies have focused on alkyl organoboronic acids and their utilization for the formation of C–C bonds, the use of aromatic boronic acids has received much less attention.<sup>173b</sup> Nevertheless, newly developed strategies for the arylation of various compounds from arylboronic acids deserve attention, since they offer highly atom economical approaches. Probably the most widely explored arylation reaction employing arylboronic acids as aryl radical precursors is the photoMeerwin-type arylation of electron-deficient alkenes (Scheme 56a).<sup>175</sup> The proposed mechanism for this transformation assumes that photoinduced electron transfer takes place between the excited state of Phen (**Phen\***), generated by direct light absorption, and dicyanobenzene (**DCB**) to form the radical cation of Phen (**Phen<sup>•+</sup>**) and the

radical anion of DCB (**DCB<sup>•-</sup>**). Subsequently, arylborate **B** (formed by the reaction of arylboronic acid **A** with NaOH) is oxidised to radical **C** by the **Phen<sup>•+</sup>**. In the next step, homolysis of the B–Ar bond occurs and aryl radical **D** is formed. Subsequently, the aryl radical **D** reacts with the electron-deficient olefin **E** to form the radical **F**, which after reduction and protonation gives the product **H** (Scheme 56b). The established methodology is metal-free, mild, and moderate to good yielding. The reaction of various boronic acids (with both EDG and EWG substituents) with acrylonitrile afforded the product in good yields; however, for other electron-deficient olefins, the results were diminished (Scheme 56c). A similar approach was also demonstrated with other photocatalysts, where the Phen/DCB pair was exchanged for acridinium,<sup>176</sup> flavin<sup>177</sup> or lumiflavin.<sup>178</sup> The same approach can be utilized not only for aryl boronic acids but also for aryl boronic esters.<sup>179</sup>

The generation of aryl radicals from aromatic boronic acids is also possible without the use of a photocatalyst. Zeng *et al.* have demonstrated that direct UV irradiation induced the generation of aryl radicals.<sup>135a</sup> Such an approach was applied toward the deuteration of aromatic compounds with D<sub>2</sub>O. Differently substituted arylboronic acids (both electron-withdrawing and electron-donating groups) were deuterated with very good yields (Scheme 57a). The mechanistic proposal assumes that the hydroxide ion coordinates to the empty p orbital of the boron and forms anion **B**. Subsequently, after promotion of the base, the hydroxyl hydrogens in the aryl boronic acid are exchanged for deuterium with D<sub>2</sub>O. Subsequently, two scenarios can occur: (a) upon UV irradiation, intermediate **C** is formed, which after rearrangement produces the deuterated product **D** (path a). On the other hand, intermediate **B** can undergo cleavage of the C–B



**Scheme 56** Photoinduced Meerwin reaction between the aryl boronic acids and electron-deficient olefins: (a) model reaction, (b) mechanistic proposal and (c) representative products.



**Scheme 57** UV-light-induced deuteration of arylboronic acids with D<sub>2</sub>O: (a) model reaction with representative products and (b) mechanistic proposal.



bond to form the aryl radical **E** and radical  $B(OD)_3$ , and then rapid electron transfer inside the cage between the aryl radical and the boric acid radical anion generates the aryl anion and the boric acid complex **F**. Finally, the phenyl anion captures deuterium from deuterated boric acid or  $D_2O$  to form the deuterated product **D** (Scheme 57b).

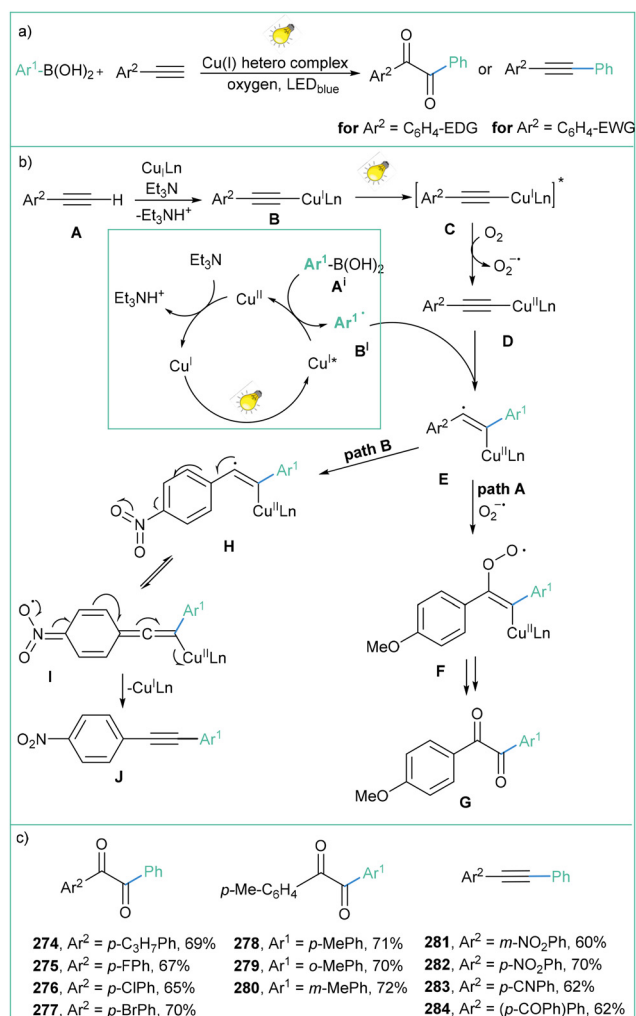
The application of arylboronic acid is not limited to only Meerwin-type reactions. Anandhan and co-workers displayed an efficient synthesis of 1,2-diketones and internal alkynes from terminal alkynes and arylboronic acids (Scheme 58a).<sup>135b</sup>

The Cu-based complex plays a dual role in this transformation: it acts as a photoredox catalyst and metal catalyst. In the photoredox cycle, the Cu complex is excited and acts as a photooxidant to form aryl radical **B'** from aryl boronic acid **A'**. At the same time, a phenylacetylene **A** forms phenylacetylide complex **B** in the presence of  $Cu(I)Ln$ . The formed complex **B** is excited under light irradiation and subsequently reacts with oxygen to form the  $Cu(II)Ln$ -phenylacetylide complex **D** and

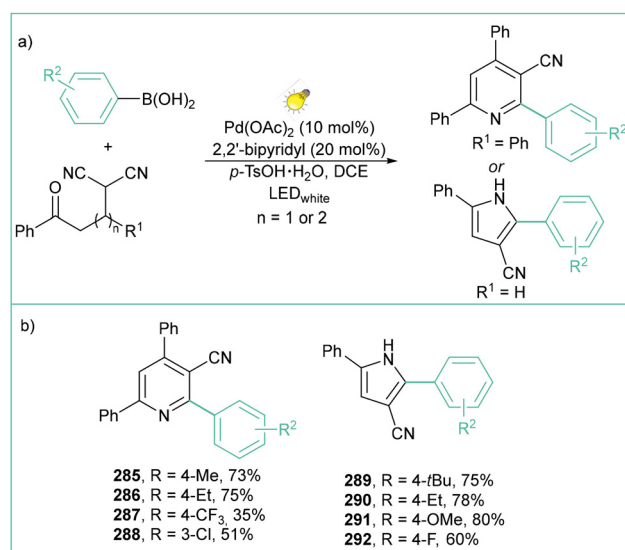
the oxygen radical anion ( $O_2^{\cdot-}$ ). Next, the independently generated phenyl radical **B'** attacks  $Cu(II)$ -phenylacetylide **D** to form  $\alpha$ -stilbene radical  $Cu(II)$ -complex **E**. The radical complex **E** can take part in two different reaction pathways (paths A, B) depending on the substitution pattern. Path A dominates for substrates with electron-withdrawing groups (such as  $-NO_2$ ), where complex **E** undergoes rearrangement to the more thermodynamically stable radical **F** and, following reductive elimination, generates internal alkyne **G** as the product with regeneration of the  $[Cu(I)Ln]$  complex (Scheme 58b). On the other hand, path B dominates for substrates with electron-donating substituents (such as *OMe*), where complex **E** undergoes a direct reaction with the oxygen radical anion, followed by rearrangement and elimination toward the formation of diketone **H**. The photoinduced, Cu-catalyzed reaction of aryl boronic acids with terminal alkynes is efficient, moderate to high yielding and, most importantly, it is chemoselective (depending on the substitution pattern) (Scheme 58c).

Another interesting example of the application of arylboronic acids as precursors of aryl radicals is the synthesis of 3-cyanopyridines (**285–288**) and 3-cyanopyrroles (**289–292**) (Scheme 59a).<sup>135c</sup> The reaction also proceeds *via* the merging of photo and metal catalysis, with the use of a Pd complex. The cascade reaction proceeds under visible-light irradiation of the Pd catalyst, which subsequently undergoes metal-to-ligand charge transfer (MLCT), followed by redox transmetalation with arylboronic acids. Both types of products are formed in good yields for both electron-withdrawing and electron-donating substituents within the aromatic ring of aryl boronic acid (Scheme 59b).

**4.2.2 Electrochemistry.** The oxidation potential of phenylboronic acid is equal to  $E_{ox} = 2.55$  V (vs. SCE)<sup>18a</sup> and is approxi-



**Scheme 58** Photoinduced synthesis of diketones and alkynes: (a) model reaction, (b) mechanistic proposal and (c) representative products.



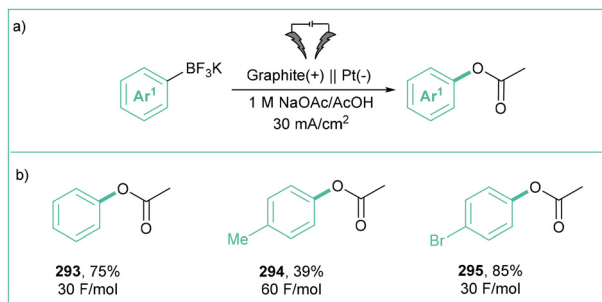
**Scheme 59** Synthesis of 3-cyanopyridines and 3-cyanopyrrole analogues from boronic acids: (a) model reaction and (b) representative products.



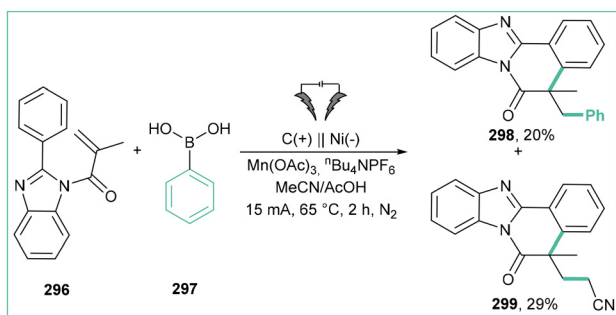
mately 0.7 V more positive than that measured for potassium phenyltrifluoroborate ( $E_{\text{ox}} = 1.87 \text{ V vs. SCE}$ ). Consequently, the direct electrochemical generation of aryl radical intermediates from phenylboronic acid or phenyl trifluoroborate constitutes a challenge itself.

In 2016, the first ever example of using arylboronic acid derivatives in order to electrochemically generate aryl radicals was published by Fuchigami and others.<sup>18a</sup> Namely, anodic oxidation of potassium aryltrifluoroborates in 1.0 M NaOAc/AcOH resulted in acetoxyated products (Scheme 60) in 39–85% yields. In the Fuchigami method, a large amount of electricity was needed to complete the electrolysis (up to 60 F mol<sup>-1</sup>), yet opening up room for new methods featuring more effective energy and resource utilization.

Later on, Lei's group developed a Mn(II)-mediated, electrochemically induced transformation toward functionalised benzo[4,5]imidazo[2,1-a]isoquinolin-6(5H)-one derivatives<sup>180</sup> where alkyl boronic acids were principally used as radical precursors. In this work, the authors also tested phenylboronic acid as a radical precursor, and it appeared that a mixture of products was obtained (Scheme 61). In addition to the expected product **298**, a side cyclization product **299** was obtained in 29% yield, where a reactive radical was derived from the interaction of an initially formed aryl radical and acetonitrile.



**Scheme 60** Electrochemical acetoxylation of trifluoroborates: (a) model reaction and (b) representative products.



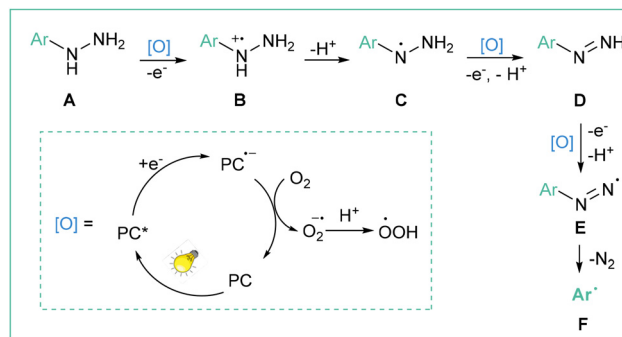
**Scheme 61** Mn(II)-catalyzed cascade reaction toward the formation of benzo[4,5]imidazo[2,1-a]isoquinolin-6(5H)-one derivatives.

### 4.3 Generation of aryl radicals from aryl hydrazines

The generation of aryl radicals from aryl hydrazines is an attractive methodology because the substrates can be readily synthesized *via* a variety of well-established methods. These include a diazotisation/reduction sequence of anilines, palladium or copper-catalyzed cross-couplings of aryl halides with hydrazine, or aromatic nucleophilic substitution of aryl halides with hydrazine.<sup>181</sup> Although synthetically useful, as described below, aryl hydrazines have been proved to be highly toxic/carcinogenic<sup>182</sup> which may limit their synthetic usefulness.

**4.3.1 Photoredox catalysis.** Irradiation of aryl hydrazines in the presence of a photocatalyst gives easy access to aryl radicals that can further undergo various transformations.<sup>135d</sup> A general mechanistic proposal for the generation of aryl radicals from aryl hydrazines assumes the initial photoexcitation of the photocatalyst (PC) to its excited state (PC\*) which is able to oxidise hydrazine **A** to radical cation **B** (Scheme 62). Next, proton abstraction generates radical **C**, followed by a sequence of oxidation and proton abstraction processes giving rise to aryl radical **F** through intermediates **D** and **E** (Scheme 62). Alternatively, it is postulated that intermediate **D** can be formed by a reaction with oxygen in its triplet state that is generated *via* an energy transfer process with a photocatalyst in the excited state.

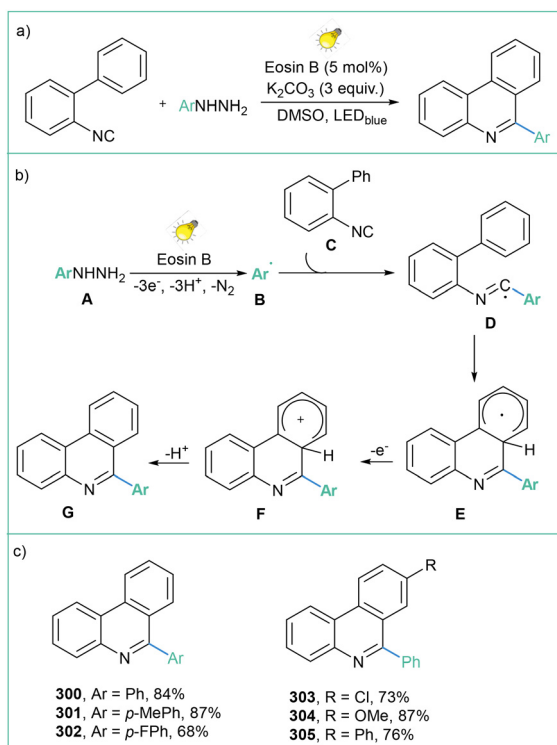
The construction of 6-substituted phenanthridines constitutes an early example of the use of aryl hydrazines as precursors of aryl radicals under light irradiation (Scheme 63a).<sup>135e</sup> The mechanistic proposal assumes the photocatalyzed formation of aryl radical **B** from aryl hydrazine **A** in a stepwise manner ( $-3e^-$ ,  $-3H^+$ ,  $-N_2$ ). Next, the aryl radical **B** reacts with 2-isocyanobiphenol **C** to form radical **D**, which after cyclization, oxidation, and deprotonation forms the product **G** (Scheme 63b). The photocyclization proceeds under mild conditions and is very efficient, since various functional groups are tolerant, and the reaction proceeds in moderate to good yields (Scheme 63c). Later, it was also demonstrated that the same transformation can also be catalyzed by the covalent organic framework (COF) as a photocatalyst.<sup>183</sup> The photo-induced reaction of aryl hydrazines with  $\alpha$ -substituted styrene derivatives in the presence of a photocatalyst and oxygen leads



**Scheme 62** General mechanistic proposal for the generation of aryl radicals from aryl hydrazines.



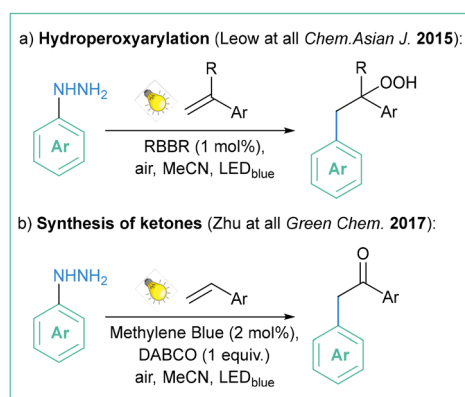




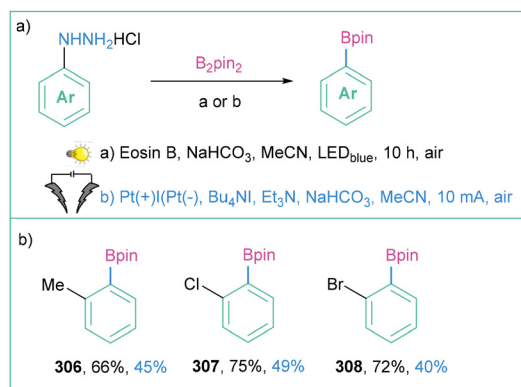
**Scheme 63** Synthesis of C6-substituted phenanthridines from aryl hydrazines: (a) model reaction, (b) mechanistic proposal and (c) representative products.

to hydroperoxyarylation of styrenes (Scheme 64a).<sup>184</sup> The same process, but applied to unsubstituted styrene derivatives, gives rise to benzyl ketones (Scheme 64b).<sup>185</sup>

Aryl hydrazines can also be used as radical precursors for transition metal-free borylation (Scheme 65a).<sup>186</sup> Zhang and co-workers demonstrated a comparison of photocatalyzed and electrochemical approaches for the borylation of aryl hydrazines. Generally, the photoredox approach is more efficient than the electrochemical one; however, the electrochemical method is more scalable (Scheme 65b).



**Scheme 64** Photoinduced reaction of aryl hydrazines with styrene derivatives: (a) hydroperoxyarylation and (b) synthesis of benzyl ketones.



**Scheme 65** Photochemical and electrochemical borylation of arylhydrazines hydrochlorides: (a) model reactions and (b) representative products.

### 4.3.2 Electrochemistry

**4.3.2.1 Oxidation of aryl hydrazines.** In 2018, Yu *et al.* developed a cobalt-catalyzed C–H/C–N oxidative coupling between arylhydrazines and *N*-arylacrylamides that gives oxindoles at room temperature (Scheme 66a).<sup>187</sup> The method tolerates a wide range of electron-withdrawing and electron-donating groups within both substrates, although no regioselectivity was observed for unsymmetrically substituted *N*-acrylamides (Scheme 66b).

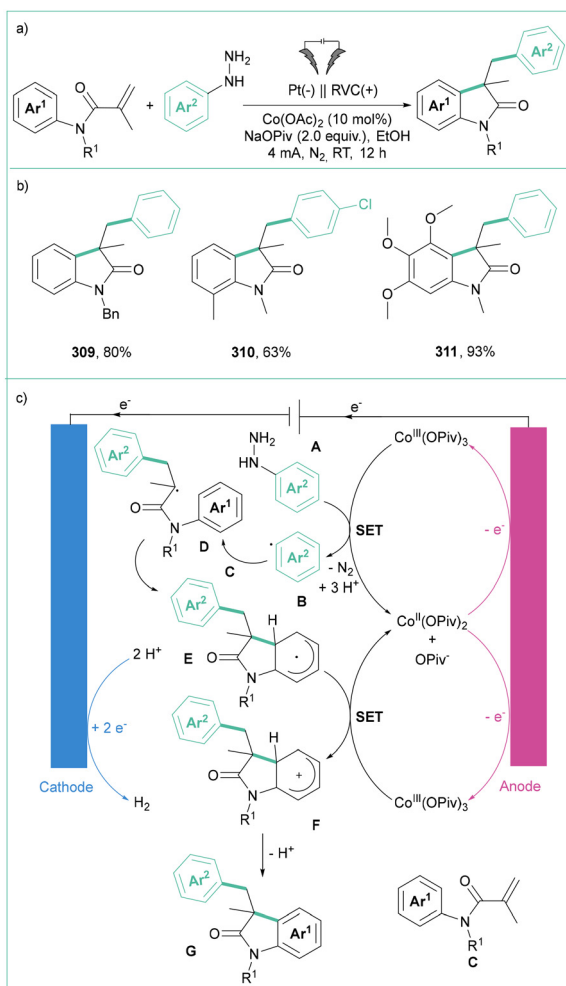
According to the proposed mechanism, once aryl radical **B** is generated from arylhydrazine **A** by Co-mediated anodic oxidation, it attacks *N*-arylacrylamide **C** to gain radical intermediate **D**. Intramolecular cyclization within **D** leads to **E**, which is further oxidised by Co(III)-based species to cationic intermediate **F**. Deprotonation of **F** provides the final product **G**. The presence of the cobalt(II) catalyst was shown to be crucial.

In 2022, Zhou and Li *et al.* reported an arylation of quinoxalin(on)es with arylhydrazine hydrochlorides under galvanostatic conditions (Scheme 67a).<sup>188</sup> The reaction demonstrates a broad functional group tolerance and provides the corresponding aryl products in moderate to excellent yields (Scheme 67b). This may be a result of self-coupling to Ar–Ar under oxidative conditions. The mechanism proposed by the authors closely reassembles the one shown in Scheme 66c, but this time no metal-based catalyst is necessary.

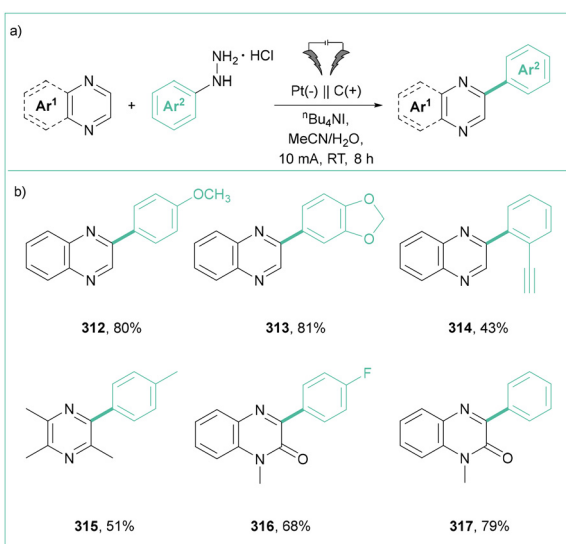
A similar reaction system proved viable in an electrochemical C–N borylation of arylhydrazines (Scheme 68a).<sup>186</sup> Substrates containing electron-withdrawing or electron-donating groups in the *ortho*, *meta* and *para* positions are well tolerated (Scheme 68b). The authors found that the use of <sup>n</sup>Bu<sub>4</sub>NI as an electrolyte is the key to ensure good efficiencies. As depicted in Scheme 68c, once the aryl radical **B** is formed, it then attacks adduct **F** (formed from B<sub>2</sub>pin<sub>2</sub> **E** and a bicarbonate ion) to give the desired product **D** and a radical anion **G**, which is then electrochemically oxidised toward the neutral species **H**.

**4.3.2.2 Oxidation of arylsulfonyl hydrazides.** Sulfonyl hydrazides are generally known to form sulfonyl radicals under

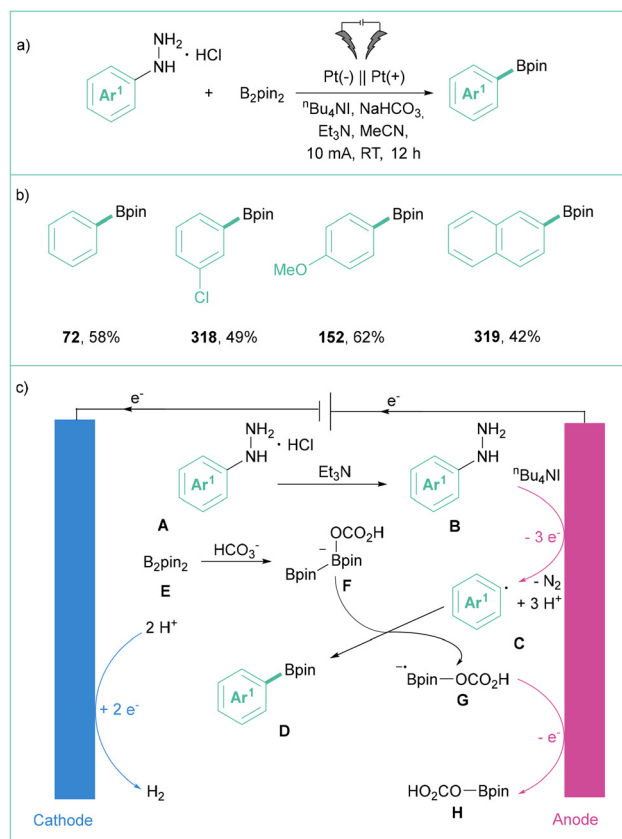




**Scheme 66** Synthesis of oxindoles via cobalt-catalyzed electrochemical C–H/C–N oxidation: (a) model reaction, (b) representative products and (c) mechanistic proposal.



**Scheme 67** Oxidative C–H arylation of quinoxalin(on)es: (a) model reaction and (b) representative products.



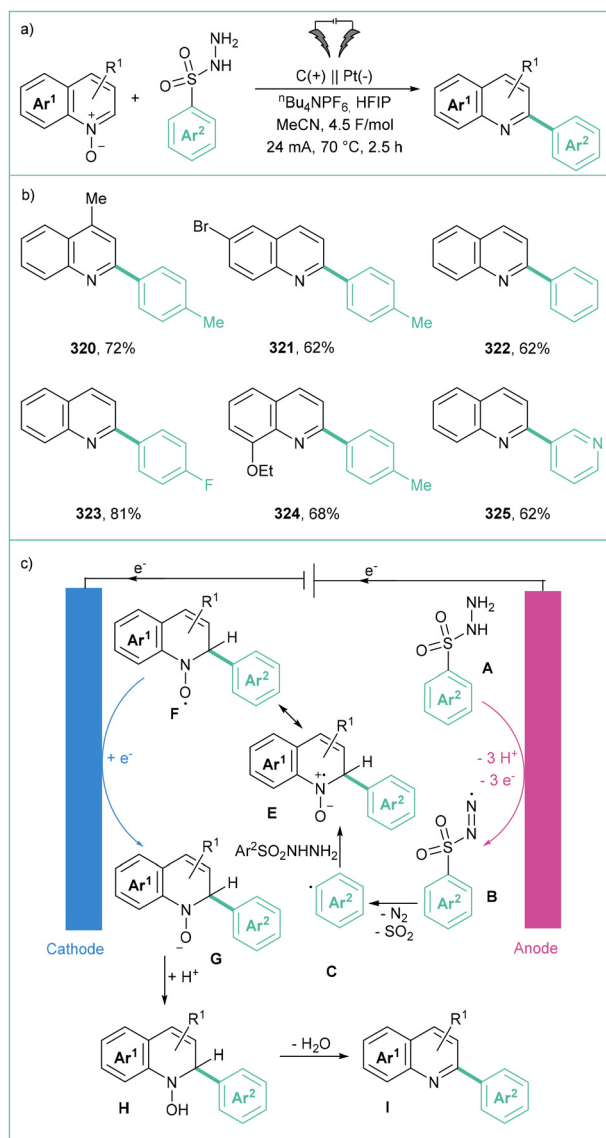
**Scheme 68** Electrochemical borylation of arylhydrazines: (a) model reaction, (b) representative products and (c) mechanistic proposal.

electrochemical conditions thus leading to a variety of sulfonylation reactions.<sup>189</sup> However, Lei and Wang *et al.* have proved that aromatic sulfonyl hydrazides possess the ability to readily form aryl radicals as well (Scheme 69a).<sup>190</sup> Namely, electrolysis of arylsulfonyl hydrazine in the presence of isoquinoline *N*-oxide in a MeCN/HFIP mixture leads to C2-arylated quinoxalines with moderate to good efficiencies (Scheme 69b). While the procedure tolerates a wide range of variously substituted quinoxaline *N*-oxides, isoquinoline *N*-oxide is not reactive at all. The reaction is initiated by the anodic oxidation of the hydrazine moiety, releasing N<sub>2</sub> and SO<sub>2</sub> and giving rise to an aryl radical C. This open-shell intermediate then undergoes addition to arylsulfonyl hydrazine leading to intermediate E which, after the reduction/protonation/dehydration sequence, gives the final arylation product H (Scheme 69c). This process constitutes an example of linear paired electrolysis where two electrode processes (oxidation and reduction) are essential to form the final product H. The application of such an approach undoubtedly increases the energy and resource economy of a given process.

## 5. Summary and outlook

Recent numerous achievements in the field of aryl radical chemistry place demand for a clear and systematized survey





**Scheme 69** Proposed mechanism for the deoxygenative C2 arylation of quinoline *N*-oxides: (a) model reaction, (b) representative products and (c) mechanistic proposal.

that critically and timely sums them up in terms of a given synthetic approach and sustainability (energy and resource utilization). In this review article, we summarise recent achievements in the field of aryl radical generation by means of photoredox catalysis, electrochemistry and their constructive combination – photoelectrochemistry. Importantly, the number of methods that use light or electric power to induce chemical transformations leading to aryl radicals is growing rapidly. The overwhelming majority of them are light-driven reactions. Despite the many benefits of photoredox catalysis, this approach also has some issues that should be solved: challenges in scale-up, due to the limited light penetration; limited electrochemical potential window, due to the energy limits resulting from the energy of visible photons; and insufficient

atom economy, due to the addition of stoichiometric amounts of sacrificial reagents.

In some cases electrochemistry and light-assistance electrochemistry started to be an answer to these problems. However, at this time, there are still no examples in the literature of electrochemically driven organic reactions that employ arylboronic acids, phenol derivatives, diarylsulfonium salts, diaryliodonium salts, or benzoic acids as precursors. This fact can be partially explained by limited access to suitable electrode materials, potentiostats, or cells. In the case of photoredox catalysis, only a source of light is needed to start research on this topic. As mentioned in the Introduction, the presence of electrodes that are immersed in a solution sets the stage for possible side reactions such as reduction of  $Ar^+$  to  $Ar^-$  or electrografting. These side reactions may be prevented by using a divided cell, different electrode material, or an electron mediator.<sup>63,191</sup> One may notice that for reductively induced aryl radical preparation, metal-based cathodes are crucial for a successful transformation. In contrast, oxidatively induced methods are based on carbon anodes, strongly increasing the possibility of electrografting occurring within the electrode surface. A possible solution for this particular challenge may be the application of electrodes with already modified surfaces, as in the work of Berben and others.<sup>192</sup> Such modification may prevent direct arylation of the surface as well as modulate the electron-transfer event itself.

Most of electrochemical reactions presented herein (besides photoelectrochemical ones) are performed in an undivided cell, which significantly simplifies the formation of aryl radical using electricity.

Still, redox potential mismatch is a serious problem; however, recent developments in photoelectrochemistry<sup>26,29</sup> have unlocked some challenging aryl radical precursors toward selective electrochemical transformations. Although some organic dyes have been already tested in photoelectrochemical transformations,<sup>26,29,79,193</sup> we believe that new types of photoelectrocatalysts, either organic or inorganic, will be found to unlock unexplored redox windows as well as dramatically expand the synthetic possibilities offered by this field.

Needless to say, stereoselective transformations are pivotal in assembling molecules with high structural complexity. Despite recent developments in the assembling of molecules *via* “an aryl radical” pathway, no stereoselective methods have been developed so far. This is a massively underexplored research area, and we believe that this review will contribute to its further development.

Importantly, an overwhelming number of reactions described in this review were performed in solvents featuring a similar value of dipole moment ( $\sim 3.9$  D) – MeCN or DMF (often as mixtures with protic solvents – MeOH, AcOH or H<sub>2</sub>O). This fact underlines the need for applying a polarized environment that will facilitate processes that occur *via* electron transfer and/or through charged intermediates.

Taking into account all of the above considerations, we certainly can say that electrochemistry has started to compete with photoredox catalysis in the area of aryl radical generation



research; however, it is still at the very early stage of development in practical organic synthesis. We hope that this review will help to advance research on the design of new reaction systems that will allow the generation of aryl radicals and their use in further transformations in a more efficient, selective and controllable way.

## Author contributions

Krzysztof Grudzień writing-original draft, writing-review & editing; Andrei Zlobin writing-original draft, writing-review & editing; Jan Zadworny writing-original draft; Katarzyna Rybicka-Jasińska conceptualization, funding acquisition, writing-original draft, writing-review & editing; Bartłomiej Sadowski conceptualization, funding acquisition, project administration, supervision, writing-original draft, writing-review & editing.

## 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.

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