Modern Photo- and Electrochemical Approaches to Aryl Radical Generation

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Abstract: Aryl rings appear in a plethora of natural products or drugs. A 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 operate through a radical pathway. The chemistry of aryl radicals has witnessed rapid development during the last century, 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 reductans) that are often used in large excess. In turn, recent developments in photocatalysis and synthetic electrochemistry allow for the assembly of $Ar^{\bullet}$ species in a more sustainable and straightforward way, however, these advancements have not been timely and critically summarised so far. This Review fills this obvious gap and sum up recent advances in processes involving $Ar^{\bullet}$ by highlighting some challenges and identifying potential areas of improvement, which might inspire future research endeavors in this topic.

1. Introduction

Radicals are open-shell species that are crucial in the fields of synthetic organic chemistry,[1] materials chemistry[2] or biology.[3] The very first example of the utilization of an aryl radical as an intermediate was reported in 1866 by Griess,[4] however the first proper development in radical chemistry in general was initiated in 1900 with a description of the triphenylmethyl radical.[5] Since then, many methods for the preparation and synthetic applications of these useful, but specific intermediates have been developed.[6]

The analysis of the radical stabilization energies[7] (RSE) of a variety of radicals along with bond dissociation energies[8] (BDE) of different C–H bonds (Fig. 1a) leads to the conclusion that phenyl radical is exceptionally unstable, thus extremely reactive open-shell intermediate of transient character,[9] with a remarkably short lifetime of about 50 µs.[10] Therefore, after its initial formation, they 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).[6a, 6b] However, *in situ* formed aryl radicals were successfully applied as mediators in the formation of more stable radicals, finally allowing catalytic functionalisation of amides[11] or aliphatic alcohols,[12] 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).[6, 13] A homolytic cleavage event that leads to the formation of an aryl radical can be induced by conventional (chemical) reagents, visible light (photo catalysis) or electric current (synthetic electrochemistry). Classical methods[6, 13] 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.[14] Along with the terminology proposed by Studer and Curran,[15] 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 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.[6, 13, 16] Although some reviews[6, 13, 17] 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.

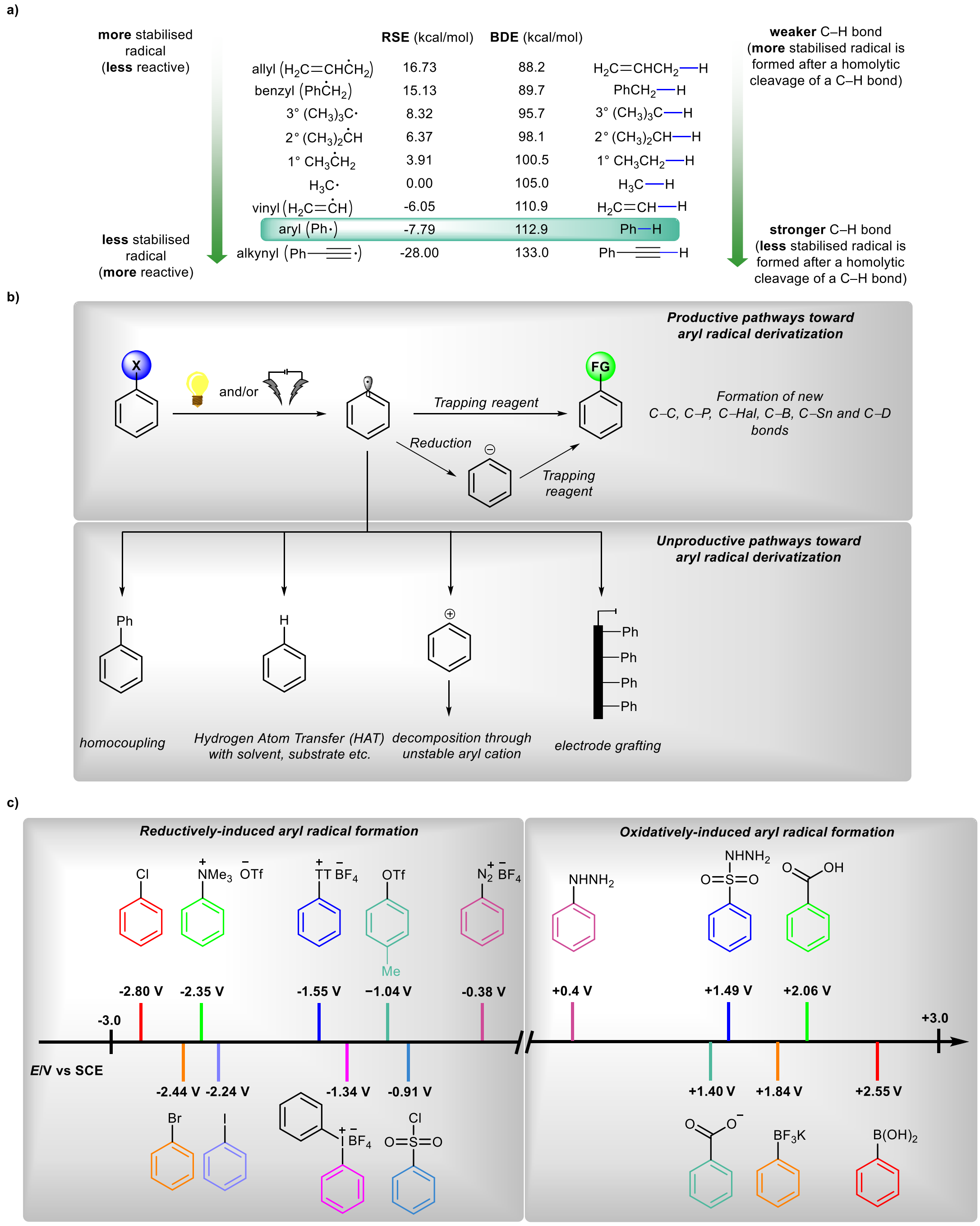

Fig. 1. a) General overview on generation and possible transformations of aryl radicals, b) radical stabilisation energies (RSE) and bond dissociation energies (BDE, given at 298 K) values for phenyl radical and its analogues and c) comparison of oxidation[18] and reduction[19] potentials of typical aryl radical precursors. RSE values are given in reference to $^{\bullet}CH_3$.

Herein, we review and analyse recent achievements in the generation of aryl radicals through modern synthetic methods: photochemistry and synthetic electrochemistry and their merger - photoelectrochemistry. To realize that intention, the article was 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 above-mentioned sections, we showcase differences between synthetic photochemistry and electrochemistry for a given precursor. We believe that such a structure of the review will provide a comprehensive overview of modern aryl radical chemistry and possibly induce new ideas of how to improve existing methods or even develop other ones, employing other plausible precursors.

Krzysztof Grudzień received his undergraduate training and M.Sc. degree in chemistry from the University of Warsaw (2012) under the guidance of Michał Barbasiewicz, then a Ph.D. degree (2018) under the supervision of Karol Grela at the Biological and the Chemical Research Centre, UW (development of NHC ligands for transition metal catalysis). He is currently a post-doctoral researcher in the Katarzyna-Rybicka Jasińska team at the Institute of Organic Chemistry, Polish Academy of Sciences, working in the field of photoelectrocatalysis.

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Bartłomiej Sadowski was educated in chemistry at the Warsaw University of Technology, Poland. He then obtained his Ph.D. from the Institute of Organic Chemistry of the Polish Academy of Sciences in 2019 under the supervision of Prof. Daniel T. Gryko. After completing his post-doctoral work at Georg-August-Universität Göttingen in the group of Prof. Lutz Ackermann, he began his independent career at the Centre of New Technologies, University of Warsaw. His research interests focus on the electrochemically-enabled synthesis of open-shell intermediates as well as chemistry of functional aromatic molecules, notably dipyrrolonaphthyridinediones.

2. Photochemistry *versus* Electrochemistry *versus* Photoelectrochemistry

Photochemistry

Over recent decades, 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.[20] In the case of photon-coupled electron transfer (photoredox catalysis) in general sense, 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 possible to continuously form small amounts of highly reactive species (radicals, radical ions, and charge transfer (CT) complexes) under mild conditions. The plethora of applications of photocatalysis grows every year because of the use of immensely 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.

Electrochemistry

Nowadays, more and more electric energy produced by humans comes from renewable sources, such as wind or solar radiation. In this context, electric 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.[17b, 21]

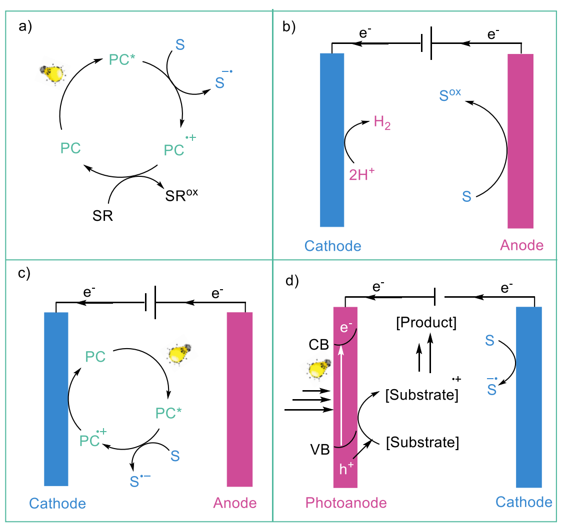
Electrochemistry is one of the most powerful tools for performing electron transfers available to chemists, as its biggest advantages are the ability to strictly control the applied current or potential, as well as the fact that the redox window is in theory only limited by the tolerance of a given solvent.[17b, 21a, 22] More importantly, it constitutes a potent strategy for the generation of open-shell intermediates.[21a, 23] 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. Up to now, 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 striking difference between a given photochemical transformation and an electrochemical one 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.[24] Therefore, the heterogenous character of the electron transfer may affect the mechanistic aspects of the activation of a given precursors of aryl radicals.

Other major problems that chemists may encounter during an electrolysis toward aryl radicals are: 1) possible formation of phenyl anions ($E°(Ph^{\bullet}/Ph^{-})$ = 0.05 V vs SCE)[25] – particularly in the case of reductively-induced methods and 2) the possibility of electrografting.[26] 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 enables 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 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.

Photoelectrochemistry

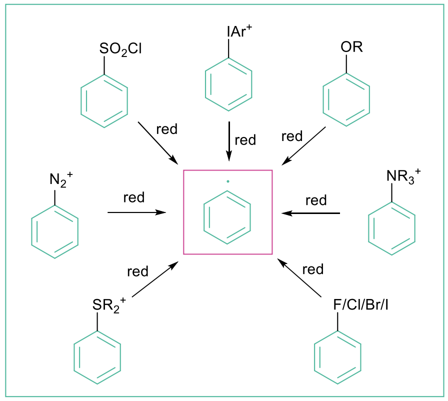
Photoelectrochemistry is a constructive combination of both of the above-mentioned methods (photo- and electrochemistry) (Scheme 1c). This merging seems to be the answer to the challenges of these two methods. From the point of view of aryl radical generation, two photoelectrochemical approaches can be involved: electrochemically mediated photoredox catalysis (*e*PRC) and interfacial photoelectrochemistry (*i*PEC).[27] Electrochemically-mediated photocatalysis (*e*PRC) can operate *via* two different strategies: photoexcitation of electrochemically generated ions (*e.g.* 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 replacing sacrificial oxidants/reductants with the current (Scheme 1c).[28] In the case of interfacial photoelectrochemistry (*i*PEC), 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 electron (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.[27-28]
It should be emphasized that photoelectrochemical methods operate within low reduction or high oxidation 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.



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.

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 could be realised by employing three different methodologies: photoinduced electron transfer (photoredox catalysis or through EDA complex formation and it subsequent reduction), organic electrochemistry[29] and photoelectrochemistry.[27, 30] 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 easier than neutral molecules.[31] The reduction of charged precursors depicted in Scheme 2 however, is characterised by lower atom economy due to liberation of higher-weight molecules, such as NR_3, ArI or R_2S.



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

3.1. Generation of aryl radicals from aryl halides

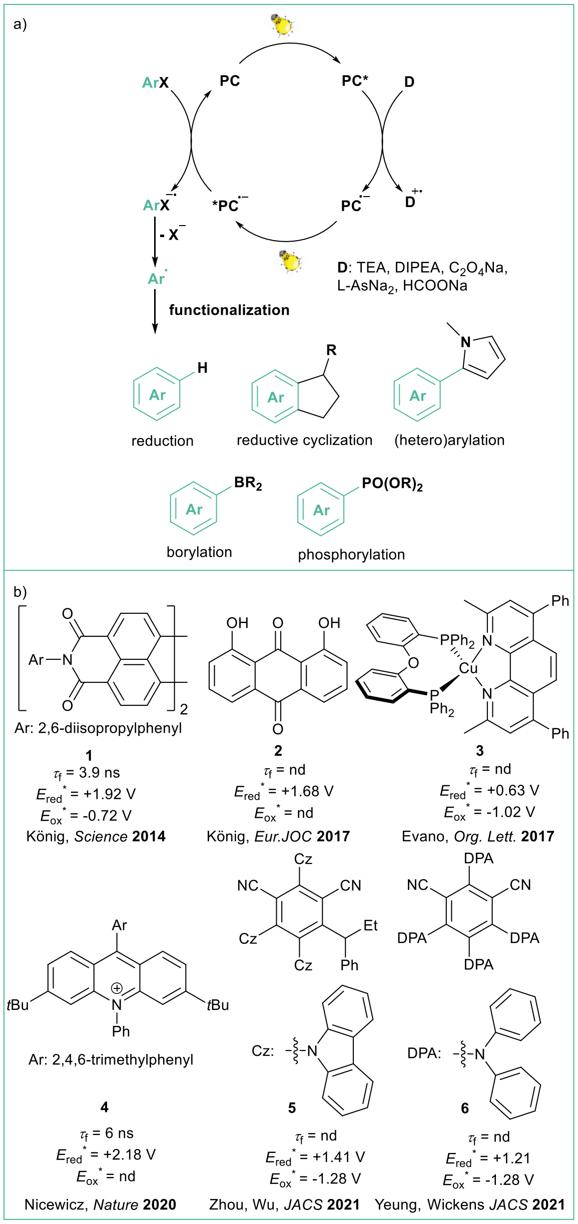
Aryl halides, although they are bench stable and readily available commercially and synthetically, have low reduction potentials (up to -2.8 V *vs* SCE for electron-rich chlorides), which severely limits the application of photocatalytically-generated aryl radicals. The most common applications of radicals 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).[32] 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 transformations using a different iridium complex $[Ir(ppy)_2(dtbbpy)]PF_6$ were described independently in the same year by Lee.[33]

Less active halides, including chlorides, often require nonstandard aryl radical generation strategies, which were recently summarised in an elegant review paper by Giedyk, Wenger, and Lu.[34]

As an example, aryl chlorides and fluorides were activated toward aryl radicals by employing indole thiolate organocatalyst, which upon excitation with 405 nm light, reaches strongly reducing properties.[35] Using this strategy, dehalogenation, Birch reduction, phosphorylation and borylation were achieved featuring broad substrate scope and moderate to good efficiency.



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.

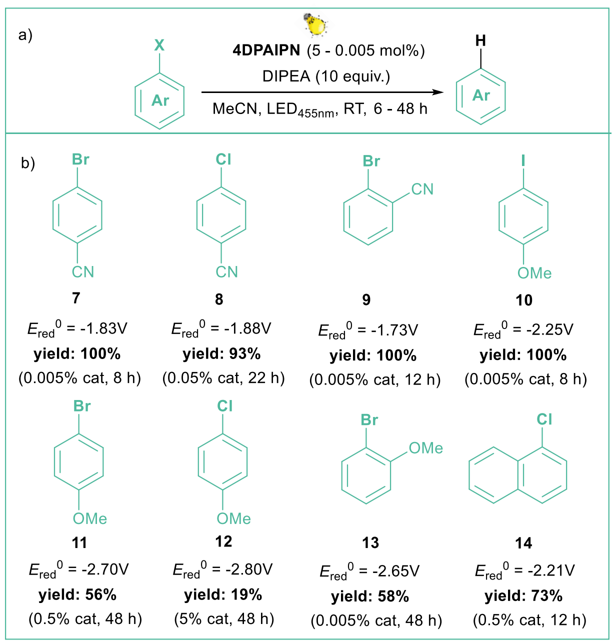
In 2014, one of these approaches to overcome the high potential barrier was based on a two-photon excitation process (sometimes also called 'consecutive photoinduced electron transfer', ConPET, see: Scheme 3)[36] as seminally conceptualized by König.[37] The strategy is based on a single photocatalyst (**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**$^{\cdot-}$), which is excited again, resulting in a highly reduced coloured anion radical (***PC**$^{\cdot-}$) which can transfer an electron to aryl iodides, bromides and some activated chlorides. The liberation of the halide anion results in an aryl radical that was subjected to a HAT from excess Et_3N 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)[38], 9,10-dicyanonthracene (**DCA**)[39], heteroleptic biphosphine/phenantroline Cu(I) complexes,[40] **MesAcrBF$_4$**,[41] 2,4,5-tri(9H-carbazol-9-yl)-6-(ethyl(phenyl)amino)isophthalonitrile, **3CzEPAIPN**[19a]).

In the latter case, the authors successfully employed oxalate and ascorbate as inexpensive and environmentally friendly sacrificial electron donors. Gram-scale borylation of 4-chlorotoluene 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.[42] Beside 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.[43] Very recently, Gierschner, Wannemacher, and Kwon have studied the steric and photophysical parameters of popular cyanoarene catalysts including their related photodegradation processes (Scheme 4).[44] 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, ConPET mechanism was somewhat challenged by likewise examination of *in situ* generated **PC**$^{\cdot-}$. The authors noticed very short excited lifetimes of **DCA** analogues that would deem them rather poor photocatalysts.[45]

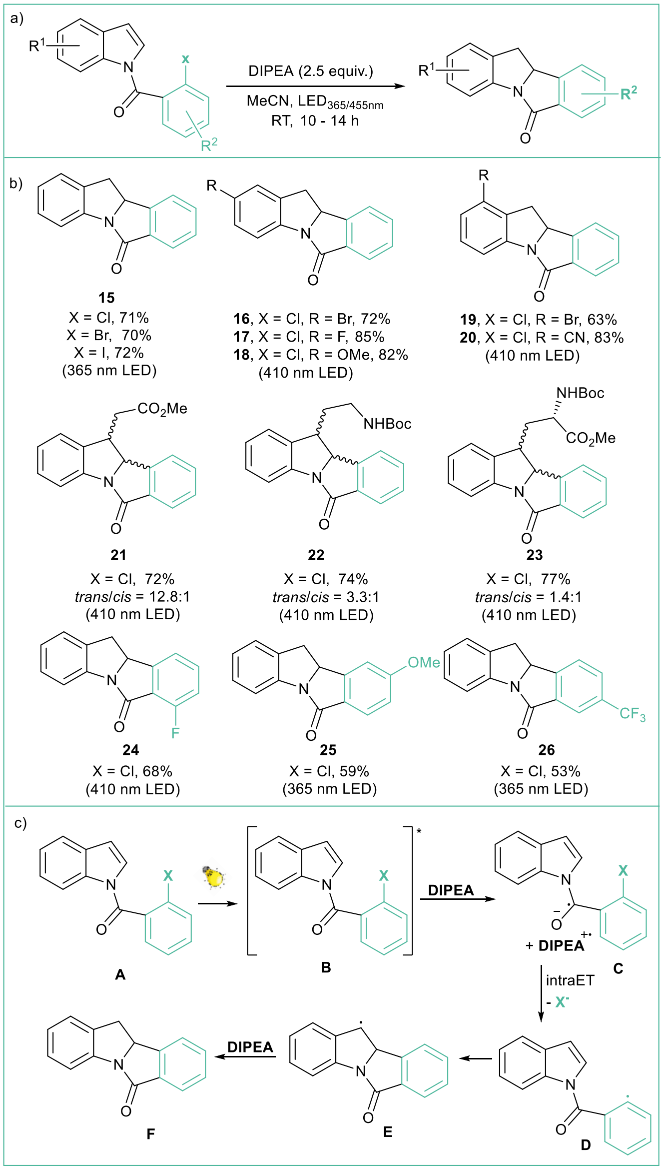
Nocera studied excited state of radical anion produced from naphthalenemonoimide **NpMI** proposing that **NpMI**$^{\cdot-}$ is nonemissive and it rather derives Meisenheimer complex that is an active form of photocatalyst.[46]

Finally in 2023 Scott's group managed to synthesize, isolate and fully characterize (including EPR and XRD) stable analogues of **NpMI**$^{\cdot-}$ and **DCA**$^{\cdot-}$ by reducing appropriate dyes with KC_8 in the presence of a cryptande. 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.[47]



Scheme 4. Hydrodehalogenation of aryl halides catalysed by photoexcited **4DPAIPN**: a) model reaction and b) representative products.

An interesting example of ConPET, reported by Jing, used dicyanoanthracene (**DCA**) that was incorporated within a metal-organic framework (MOF).[48] 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_{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 B_2pin_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.[49]



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

The application of photocatalyzed intramolecular aryl radical cyclizations toward the synthesis of polycyclic indolyl heterocycles was reported by Che and colleagues (Scheme 5a).[50] 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. Variously 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 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 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[51] and Speed[52] (Scheme 6a). The former

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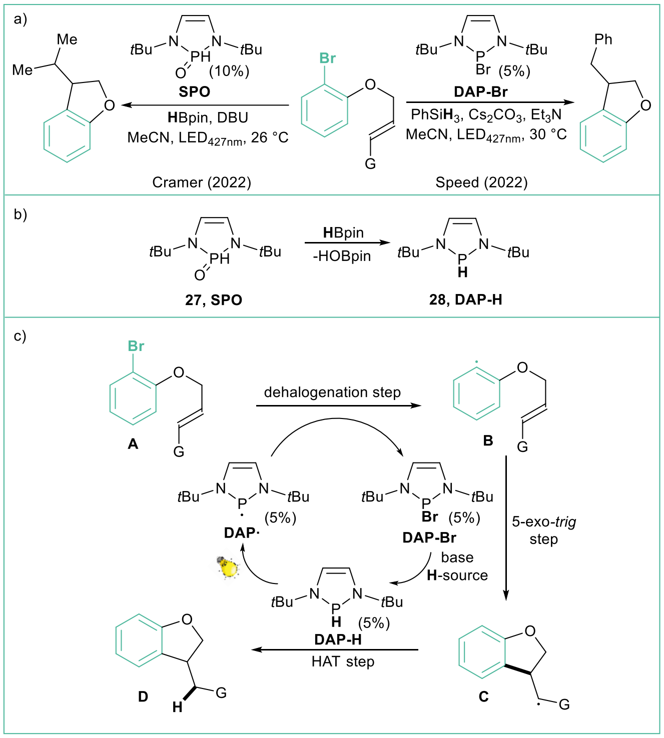
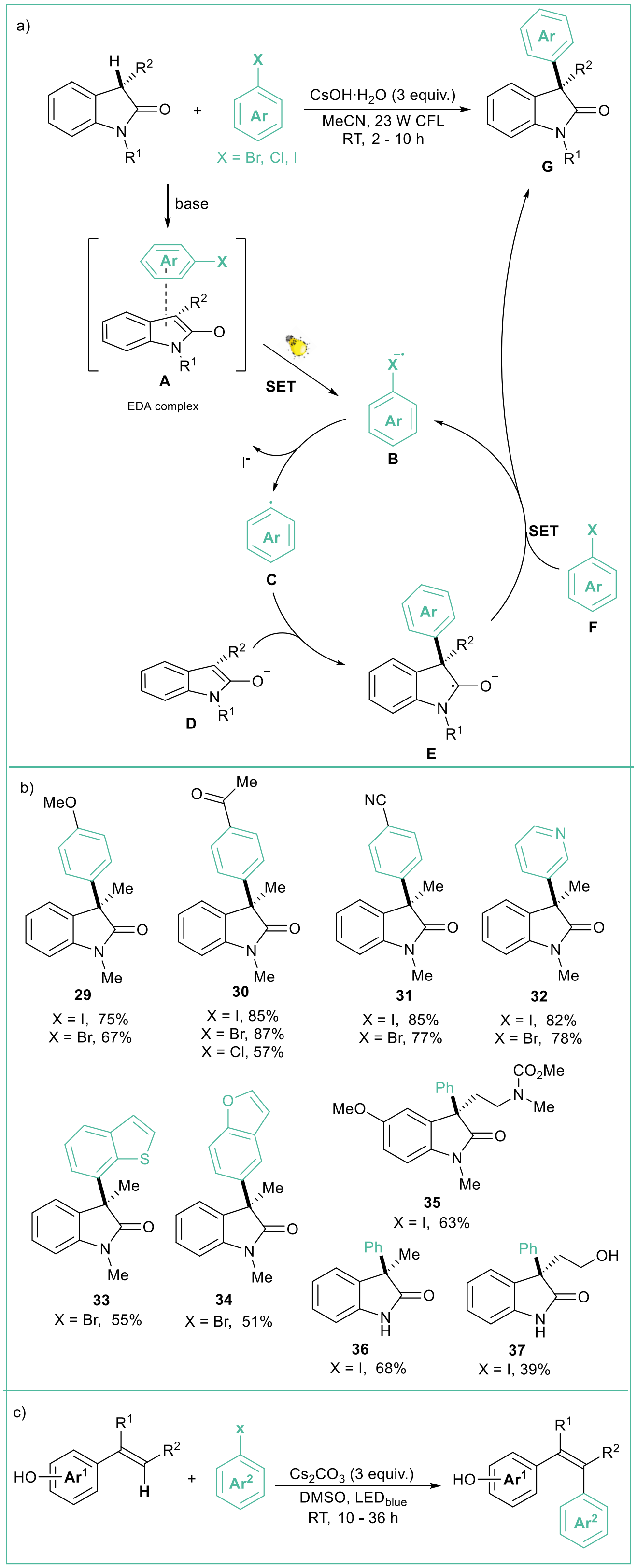
approach relies on HBpin and DBU with **SPO** as a precatalyst, while the latter case uses $PhSiH_3$, Et_3N and Cs_2CO_3, in both cases visible light is required to regenerate the active DAP radical (**DAP·**) (Scheme 6b). The reaction mechanism (Scheme 6c) is based on the phosphalene cycle in which **DAP·** 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 t*o* **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·** at the same time.



Scheme 6. Approaches for intramolecular reductive cyclization using diazaphosholenes: a) model reactions; b) **SPO** precatalyst activation and c) mechanistic proposal.

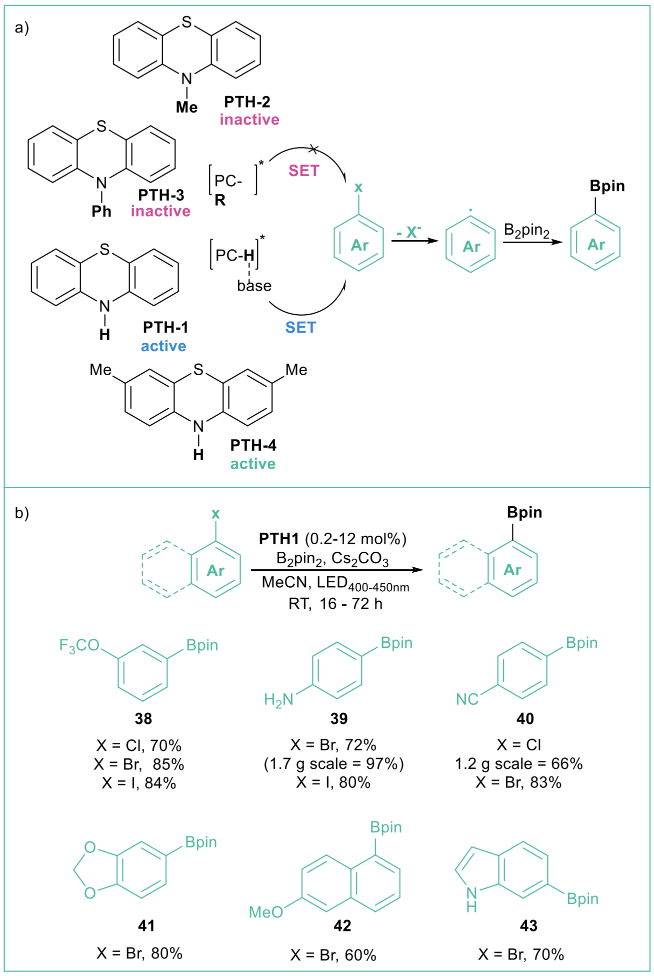
Aryl radicals can also be generated *via* photoexcitation of an EDA complex and subjected to intermolecular transformations, as was recently presented by Xia (Scheme 7a).[53] Namely, C–C cross-coupling of oxindoles and aryl halides was achieved under visible-light irradiation using CsOH as a base. The 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^- toward aryl radical **C**. Upon addition of **C** to **D**, the adduct **E** is formed which eventually gives the product **G** through a $S_{RN}1$-type reaction[54] (Scheme 7b).



Scheme 7. Photoarylation of oxoindoles: a) model reaction with mechanistic proposal, b) representative products and c) photoarylation of vinylphenoles.

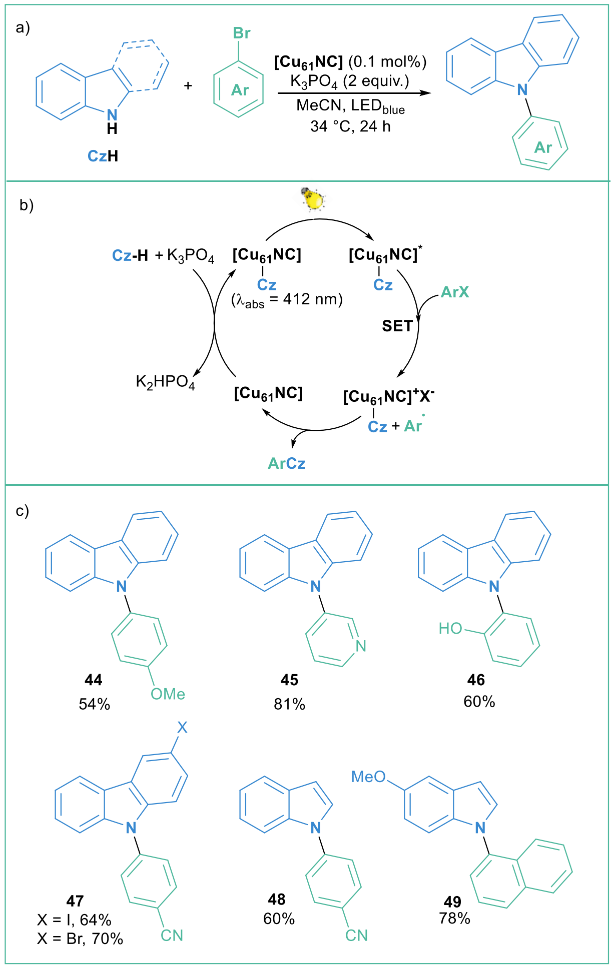
Shortly thereafter, the authors extended the scope of this reaction by testing a wide range of vinylphenol derivatives (Scheme 7c).[55] The catalytic system in general is very stereoselective (*E*/*Z* ratio 9:1 and higher) and found utility in the late stage functionalisation of complex natural products.

Recently, Larionov *et al.* developed a family of very potent SET photocatalysts based on simple, abundant and low molecular weight phenothiazines (Scheme 8).[56] 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 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).



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.

Bakr and Reuping presented an interesting example for the generation of aryl radicals through photoexcitation of an intermediate in the photo-Ullmann reaction catalysed by a Cu nanocluster **[Cu61NC]** (Scheme 9a).[57] According to the proposed mechanism (Scheme 9b), upon deprotonation of carbazole, a Cu_{61}-carbazolide complex **[Cu61NC]-Cz** forms, that is activated under visible light irradiation (λ_{abs} = 412 nm), in striking contrast to an earlier example of the photo-Ulmann reaction presented by Fu[58] where higher-energy ultraviolet light was used for activation of the catalyst-nucleophile intermediate complex. A SET from the excited carbazolide-copper cluster **[Cu61NC]-Cz*** (*via* blue LED irradiation) to aryl halide generates the oxidised complex **[Cu61NC]⁺-Cz**, an aryl radical and a halide anion. This was rationalized by fluorescence and lifetime quenching experiments. Then, the radical interacts with the oxidized 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 **[Cu61NC]**. The nucleophile scope includes carbazoles, indoles, and azaindole motifs. Moreover, electron-poor and electron-rich iodides, bromides and chlorides are well tolerated in this transformations (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.

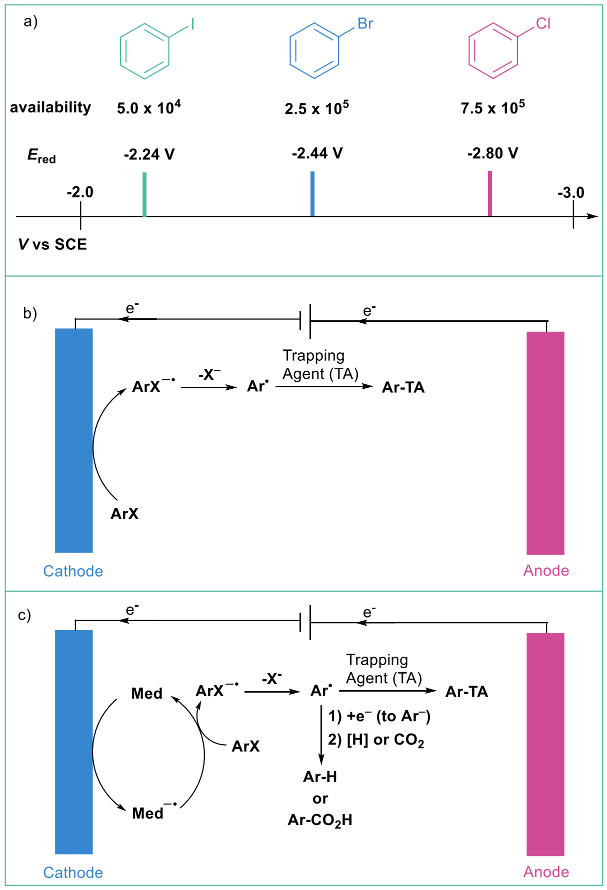


Scheme 9. Photo-Ullmann reaction catalysed by a copper(I) nanocluster: a) model reaction, b) mechanistic proposal and c) representative products.

3.1.2. Electrochemistry

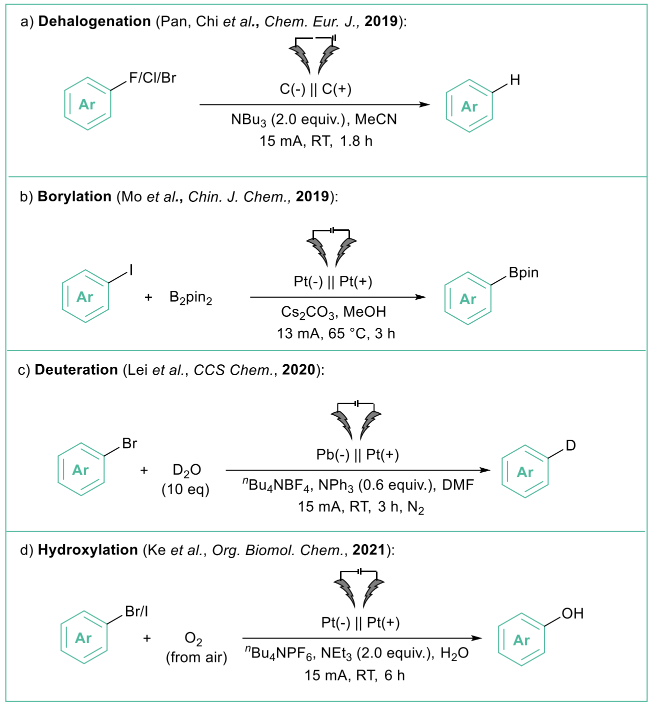
As indicated previously and on Scheme 10a,[19a] aryl halides feature particularly low reduction potentials therefore their electroreduction may be troublesome thus leading mostly to undesired side products instead of selective transformations to value-added products.[17a] The formation of aryl radicals *via* electrolysis may be realized either in a direct (an electron is transferred from a cathode to **ArX** directly, Scheme 10b) or an indirect way – by employing an 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 occurs 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,[59] electrolytic modification of electrodes (electrografting)[60] and hydrogen-atom abstraction.[61]

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 allow, the radicals can be reduced immediately to aryl anions (Scheme 10c) that are then trapped by relevant electrophiles such as CO_2 or H^+ donor.



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[19a]; b) general scheme for the direct electroreduction of aryl halides and c) general scheme for the indirect electroreduction of aryl halides.

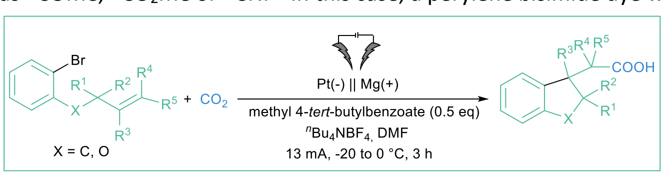
Direct electrolysis of aryl halides is rarely used as such challenging conditions may be harmful to many functional groups. Nevertheless, dehalogenation[62] (Scheme 11a), borylation[63] (Scheme 11b), deuteration[64] (Scheme 11c) or hydroxylation[65] (Scheme 11d) reactions of aryl halides have been developed. Among these methods, hydroxylation is a particularly relevant method as phenols are important species that are present in many biologically-relevant molecules.[66] In the method developed by Ke *et al.* [65] (Scheme 11d), O_2 from the air is the source of the hydroxyl function whilst a non-sacrificial anode was used. A wide range of phenols were 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.



Scheme 11. Synthetically-meaningful examples of direct electroreduction of aryl halides: a) dehalogenation, b) borylation, c) deuteration and d) hydroxylation.

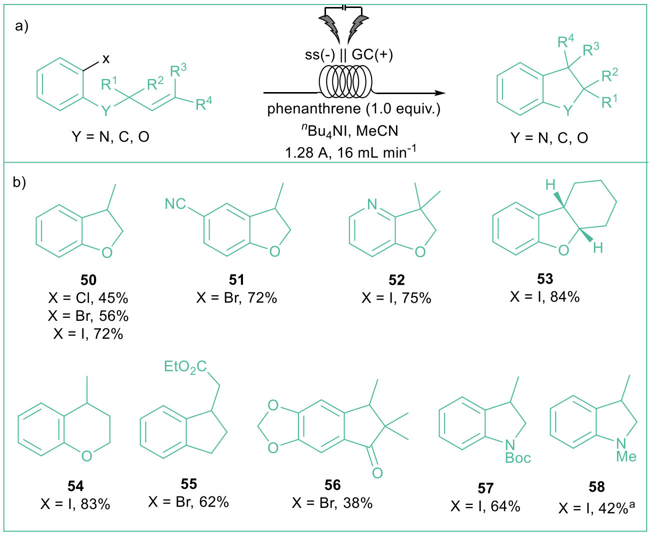
In 1991, Savéant and colleagues studied the electroreduction of aryl halides in the presence of olefinic acceptors (styrene, butylvinylether or acrylonitrile).[67] They found that the addition of some organic compounds (4,4'-bipyridine, naphthonitrile or methyl benzoate) significantly increases the efficiency 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.[68] 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).[69] 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• 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.[70] In this case, a perylene bisimide dye was used as an electron mediator.



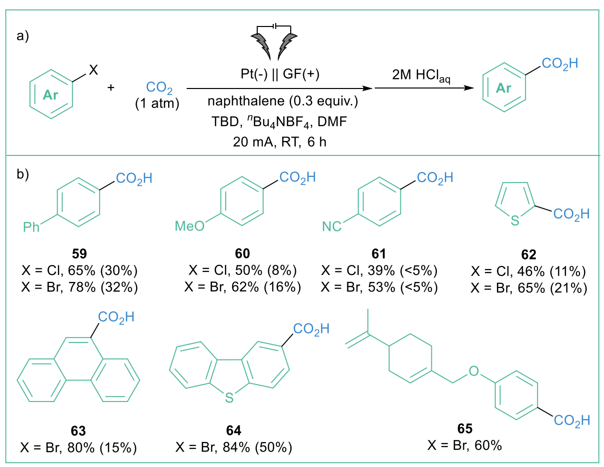
Scheme 12. Synthesis of 2,3-dihydrobenzofuran-3-ylacetic acids described by Senboku *et al.*

Some other similar contributions underlined the importance of polycyclic aromatic hydrocarbons (PAHs, such as phenanthrene[71] or fluorene derivatives[72]) 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.[73] 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 major difference between Brown's work and the aforementioned articles is the use of cost-effective electrodes and flow conditions which should have positive impact on resource and energy economy of this process.



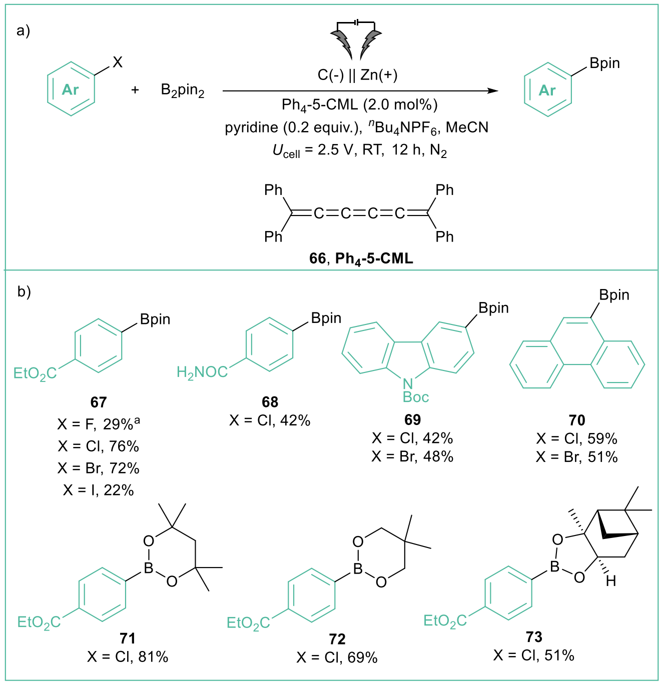
Scheme 13. Synthesis of cyclic products **xx** in flow developed by Brown and colleagues in 2022: a) model reaction and b) representative products. [a] Reaction carried out on 7.0 mmol scale in THF/MeCN (7:1).

A simpler analogue of PAHs – naphthalene, was found to smoothly mediate the carboxylation of a broad range of aryl halides (59 examples overall, Scheme 14).[74] Besides the easily-reducible functionalities present within the aryl chlorides/bromides tested, heterocycles and natural products/drug derivatives are also tolerated in this transformation, proving the huge potential of the developed methodology. Although an undivided cell was used, the carboxylic acids produced in this methodology exhibit high stability, which in turn, is in accordance with the lack of methods for the oxidatively-induced aryl radical generation employing ArCOOH (see section 4.2).



Scheme 14. Carboxylation of aryl halides developed by Qiu and others: a) model reaction and b) representative products.

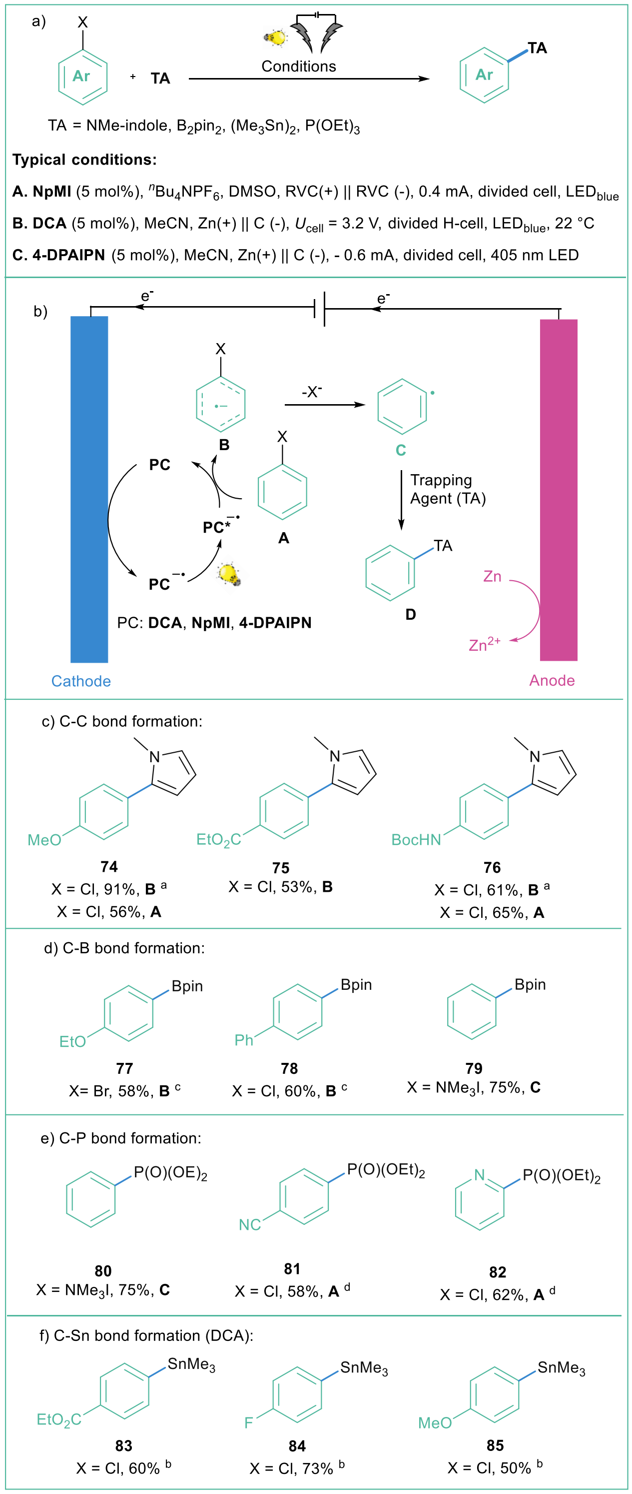
A new type of electron-mediator, which is an analogue of cumulene (Ph_4-5-CML, **66**), was proposed by Milner and others to mediate the borylation of aryl halides in a potentiostatic regime (Scheme 15).[75] The reaction tolerates a broad range of aryl halides (products **67**-**70**) as well as different boron-based reagents (products **71**-**73**). Despite the high reducing potentials needed for the ArX activation, all processes occur smoothly at relatively low cathodic potentials (U_{cell} = 2.5 V, approximately -1.9 V vs Ag/AgCl) in comparison to 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 potential for aryl radical reduction ($E°(Ph^•/Ph^–)$ = 0.05 V vs SCE)[25], the formation of $Ar^–$ 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.



Scheme 15. Employment of cumulenes as electron-mediators in borylation of aryl halides: a) model reaction and b) representative products.

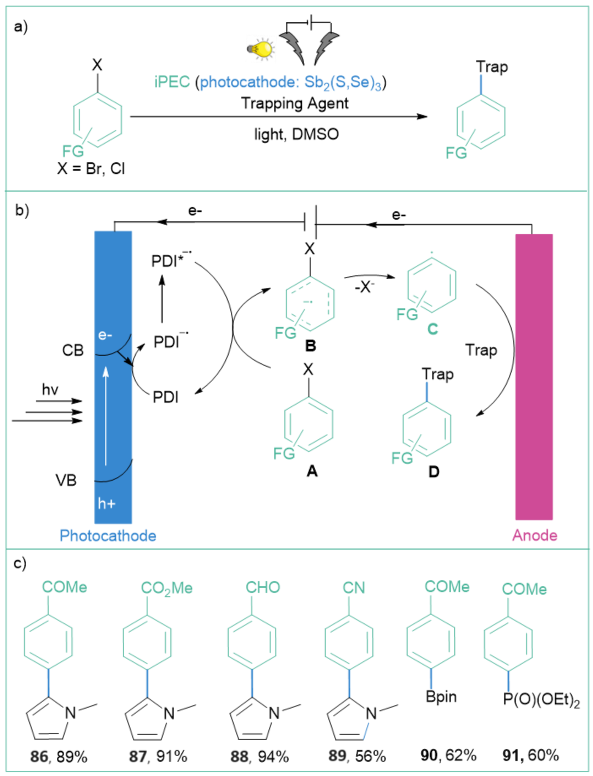
3.1.3. Photoelectrochemistry

Photoelectrochemistry has proven 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 16).[76,77] In this approach, the first event is the reduction of the photocatalyst at the electrode to form a radical anion (**PC**$^{\bullet-}$), which is subsequently photoexcited enabling the formation of a super reductant radical anion (***PC**$^{\bullet-}$). 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 16c), B_2pin_2 (Scheme 16d), $P(OEt)_3$ (Scheme 16e) and $(Me_3Sn)_2$ (Scheme 16f). This methodology was applied with the use of different photocatalysts (**DCA**,[78] **NpMI**,[76] **4-DPAIPN**[77]) and is compatible with various aryl halides (Cl, Br).



Scheme 16. Photoelectrochemial generation of aryl radicals and subsequent C–C, C–B, C–P, and C–Sn bond forming reactions. [a] 10 mol% of **DCA** was used. [b] ^{1}HNMR is given. [c] Pyridine (20 mol%) was used. [d] Constant current electrolysis at 0.8 mA was employed.

On the other hand, Wu and co-workers reported an iPEC/photoredox system consisting of a $Sb_2(S,Se)_3$ photocathode and a PDI dye as a photoredox catalyst that was employed for very efficient and selective aryl functionalizations (Scheme 17).[79] 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 17a). The photogenerated electrons from the conductive band reduce **PDI** to a radical anion (**PDI•⁻**), which is then excited to form a highly reductive species (**PDI*•⁻**). The photoexcited radical anion (**PDI*•⁻**) is now able to reduce different aryl halides **A** and **B**, which subsequently undergoes mesolytic cleavage to generate aryl radical **C**, which reacts with trapping reagents to yield the functionalised product **D** (Scheme 17b). Such an approach allows for the functionalisation of different (hetero)aryl halides in good to excellent yields, with many functional groups being tolerable (–CN, –CHO, –CO_2Me, –COMe). On the other hand, the reaction is also efficient with different trapping agents such as pyrrole derivatives, $P(OEt)_3$ and B_2pin_2 (Scheme 17c). 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 toxic antimony covered photocathode (see Scheme 17). Moreover, the authors reported neither quantum efficiency measurements nor reusability studies for $Sb_2(S,Se)_3$ photoelectrode, while high-energy Xe lamp (500 W) is used as a light source. It is worth to mention that the reaction still proceeds without electricity albeit with lower efficiency (57% for compound **86**).



Scheme 17. iPECs for the photoelectrochemical generation of aryl radicals: a) model reaction, b) mechanistic proposal and c) representative products.

3.2. Generation of aryl radicals from diazonium salts

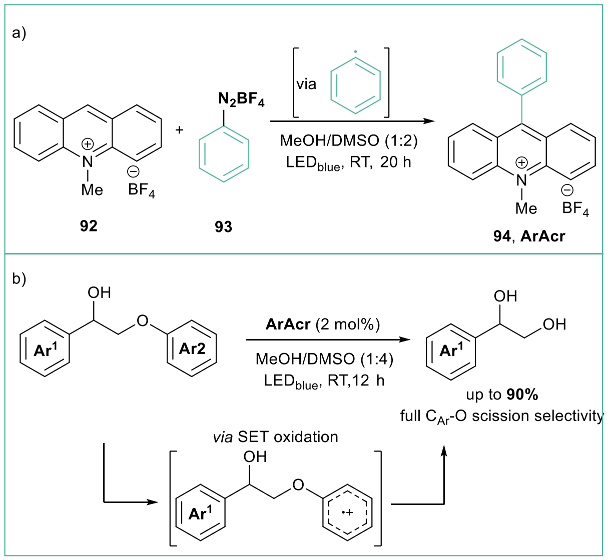
In comparison to aryl halides, aryl diazonium salts seem an even better source of aryl radicals due to their much lower redox potential and irreversible liberation of a nontoxic nitrogen molecule. Although, they are certainly less stable than their respective halide analogues, they can be stored at low temperatures with good stability as long as a non-coordinating counterion, such as BF_4, PF_6 or OTs, is being used. They are also quite simple and cost-effective reagents to synthesise 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.[80]

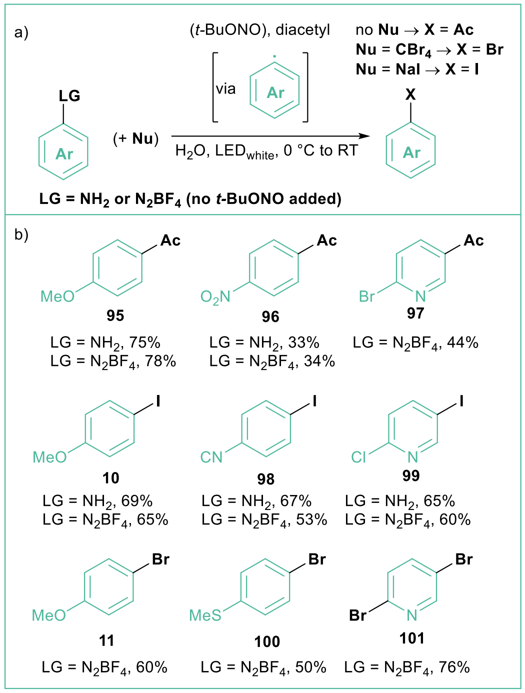
To give a recent example, Boixel, de Rouville, and Soulé developed a catalyst-free (or self-catalysed) photoinduced arylation of *N*-substituted acridinium salts using various aryl diazonium tetrafluoroborates with high functional group tolerance (halide, ester,

–CN, ketone and –NO_2) (Scheme 18a).[81] The synthesised 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 18b).

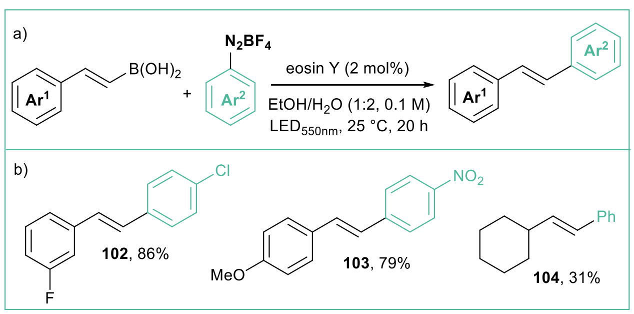


Scheme 18. a) Photoinduced arylation of *N*-methylacridinium salts to give new families of **ArAcr** photocatalysts. b) Application of **ArAcr** in selective C–O bond fragmentation.

The photoredox version of the classical Sandmeyer-type halogenation was realised by Tang and Luo (Scheme 19).[82] 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 photosensitiser/trapping agent (Scheme 19a). More than 40 (hetero)aryl acetates were obtained this way with high functional group tolerance and moderate to good yields (Scheme 19b). Aryl bromides and iodides are also accessible when the appropriate trapping agent (CBr_4 or NaI respectively) is present in the reaction mixture, although the scope was rather narrow and bromination required pre-synthesised aryl diazonium tetrafluoroborates rather than *in situ* generated intermediates.

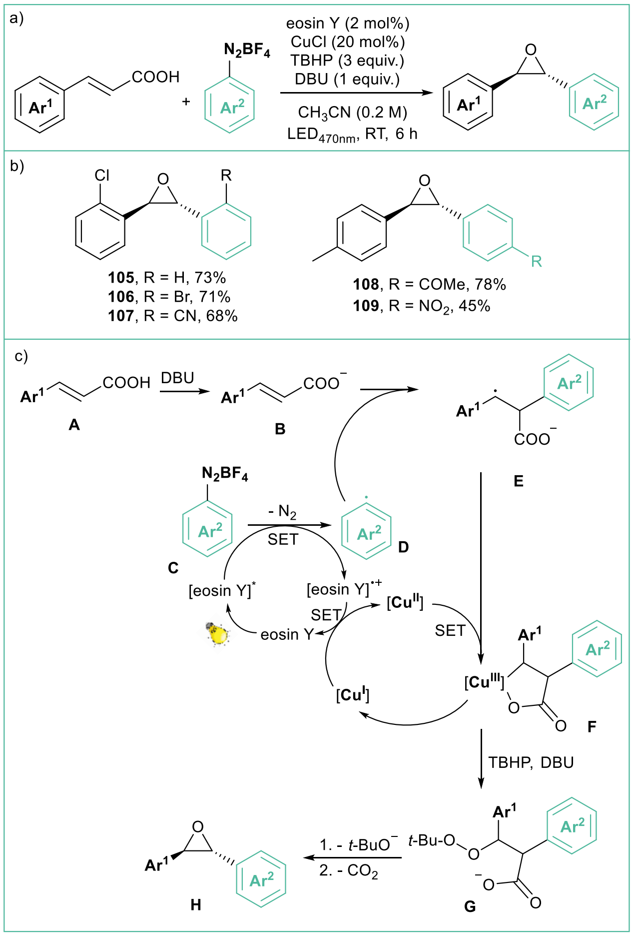


Scheme 19. Photoredox approach for Sandmeyer reaction: a) model reaction and b) representative products.



Scheme 20. (*E*)-selective photoredox synthesis of stilbenes from cinnamyl boronic acids using Eosin Y as catalyst: a) model reaction and b) representative products.

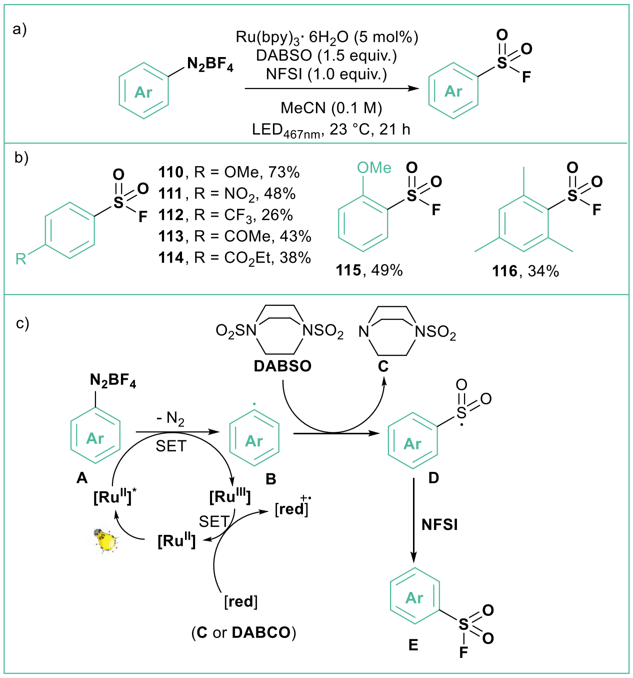
Wu reported the photocatalytic synthesis of *E*-stilbenes by coupling arenediazonium tetrafluoroborates with cinnamyl boronates (Scheme 20a).[83] The reaction occurs employing only 2.0 mol% of a cost-effective organic dye (eosin Y), an EtOH/H_2O mixture as a solvent and green (550 nm) light irradiation. More than 20 examples were presented which mainly consisted of mono- and disubstituted stilbenes (Scheme 20b). Interestingly, changing the catalyst to a ruthenium complex ($Ru(bpy)_3Cl_2$) switched the selectivity to provide predominantly *Z* isomers that might suggest a subsequent *E*/*Z* isomerization through an energy transfer process since $Ru(bpy)_3Cl_2$ has a higher triplet state energy (Eosin Y ~44 kcal/mol;[84] $Ru(bpy)_3Cl_2$ ~49 kcal/mol[85]).



Scheme 21. Decarboxylative photo-organometallic synthesis of *trans*-oxiranes using eosin Y and CuCl as co-catalysts: a) model reaction and b) mechanistic proposal.

Decarboxylative, visible-light photoredox synthesis of *trans*-oxiranes from (*E*)-cinnamic acids using arenediazonium salts was developed recently by Singh (Scheme 21a).[86] Eosin Y was also employed as a photocatalyst generating the aryl radical, while CuCl and TBHP serve as the oxidant system. More than 20 examples of variously substituted diaryloxiranes, consisting mainly of mono and disubstituted products, were synthesised. The method tolerates many functionalities such as halides, nitro, cyano, ketone and ester groups. According to the proposed mechanism (Scheme 21c), 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 TBHB 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 and employed widely in biorthogonal processes including protein labelling.[87] The photocatalytic procedure for the conversion of aryl diazonium tetrafluoroborates to the corresponding sulfonyl fluorides was developed by Troian-Gautier and Tambar (Scheme 22a).[88] The optimised conditions employ $Ru(bpy)_3Cl_2{\cdot}6H_2O$ as a catalyst, DABSO as a source of SO_2 and NFSI as a fluorinating agent in MeCN. Using this procedure, the authors synthesised 10 electron-rich and electron-poor mono-, di-, and trisubstituted arylsulfonyl fluorides with yields ranging from 26 to 73% (Scheme 22b). According to the proposed mechanism (Scheme 22c), the photogenerated aryl radical **B** reacts with DABSO to give the 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 aryldiazonium salt, is reduced back to the ground state from a SET process with either **C** or **DABSO**.



Scheme 22. Photocatalytic synthesis of arylsulfonyl fluorides from aryldiazonium salts a) model reaction, b) representative products and c) mechanistic proposal.

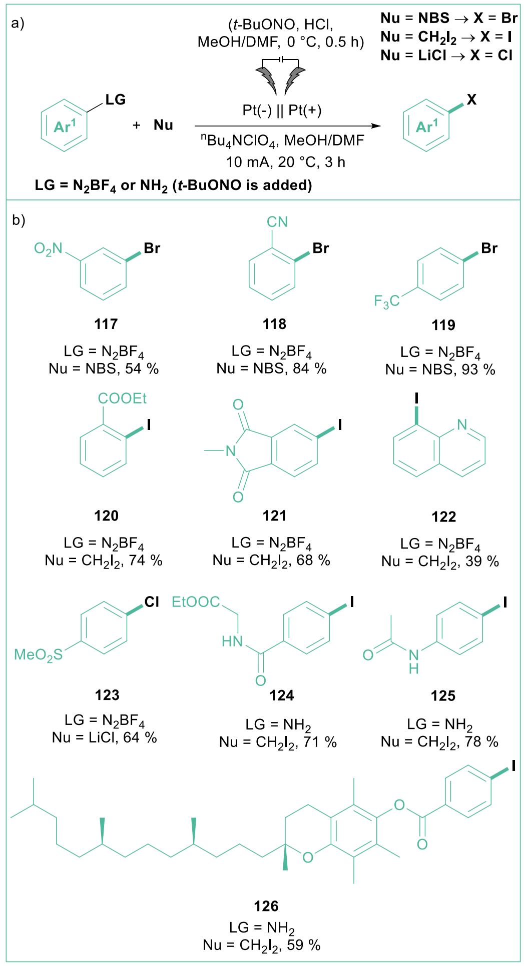
It is worth mentioning that aryl radicals can be liberated from arylazosulfones, however this transformation occurs through direct irradiation of the latter compounds. [89,90,91,92]

3.2.2 Electrochemistry

Until recently, arenediazonium salts were mainly considered to be excellent arylating reagents in electrografting[80a, 93] due to their low reduction potentials and inert by-product, molecular N_2. However, their huge synthetic potential has also started to be investigated in terms of electrochemically-mediated synthesis,[94] although they are considered potentially dangerous due to the possibility of violent decomposition.[95]

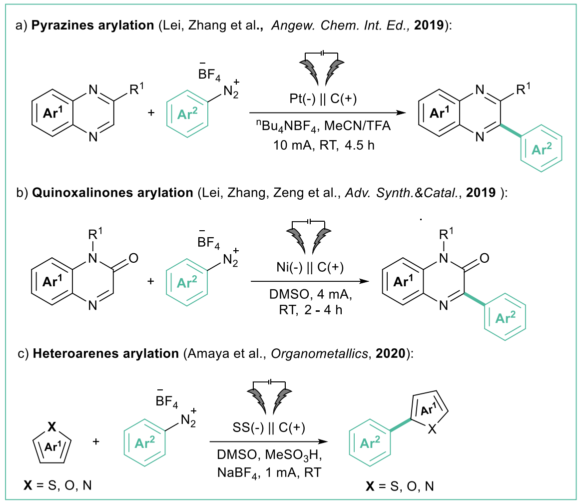
In 2018, Mo and co-workers demonstrated that the classic Sandmeyer reaction can also be performed under the influence of electric power (Scheme 23a) using non-sacrificial Pt electrodes.[96] Namely, aryl diazonium salts are efficiently converted into their halogenated analogues using a variety of halogenation reagents such as NBS, NaBr, CH_2I_2, $CBrCl_3$ or LiCl (Scheme 23b). 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 23b). Here, Pt anodes were successfully replaced with cost-effective graphite plates. This process can also be performed 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 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 24a).[97] 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.

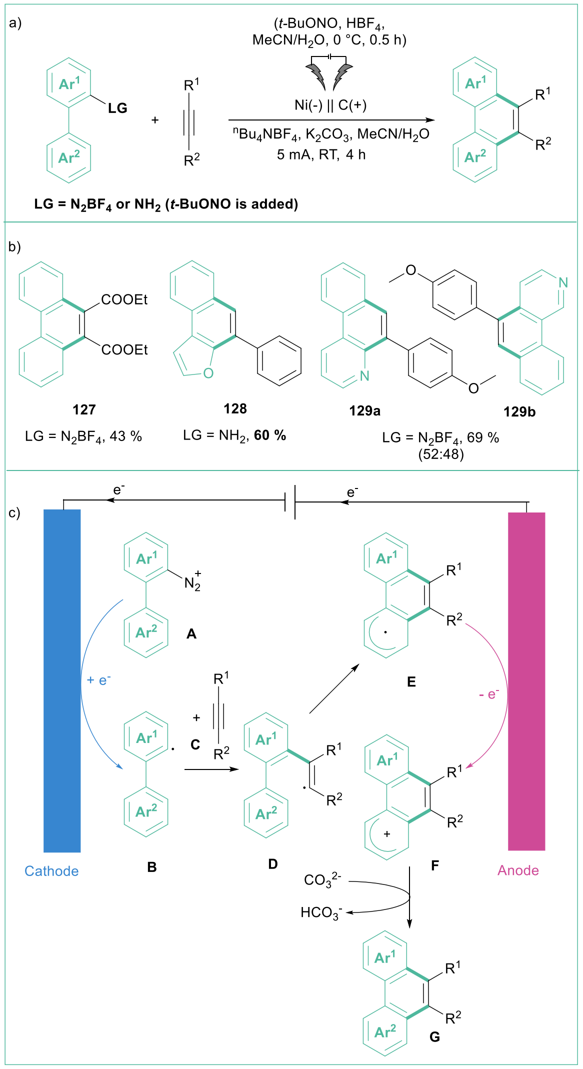


Scheme 23. Electrochemically driven Sandmeyer reaction: a) model reaction and b) representative products.

Along this line, Zeng *et al.* reported the arylation of quinoxalinones with aryldiazonium salts (Scheme 24b).[98] 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, and furan) employing a stainless steel anode (Scheme 24c).[99] Unfortunately, the scope is rather limited, and only moderate yields can be achieved, probably due to the simultaneous decomposition of easily oxidizable heteroarenes at the anode.



Scheme 24. Electrochemical coupling of different heteroarenes with aryldiazonium salts: a) pyrazines arylation, b) quinoxaliones arylation and c) heteroarenes.



Scheme 25. [4 + 2] Benzannulation of aryldiazonium salts and alkynes: a) model reaction, b) representative products and c) mechanistic proposal.

In 2023, Wang, Zhou and co-workers developed a straightforward method to synthesise polycyclic (hetero)aromatic compounds *via* [4+2] benzannulation (Scheme 25a).[100] 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 25b). According to the proposed mechanism (Scheme 25c), 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.*[19b] 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.

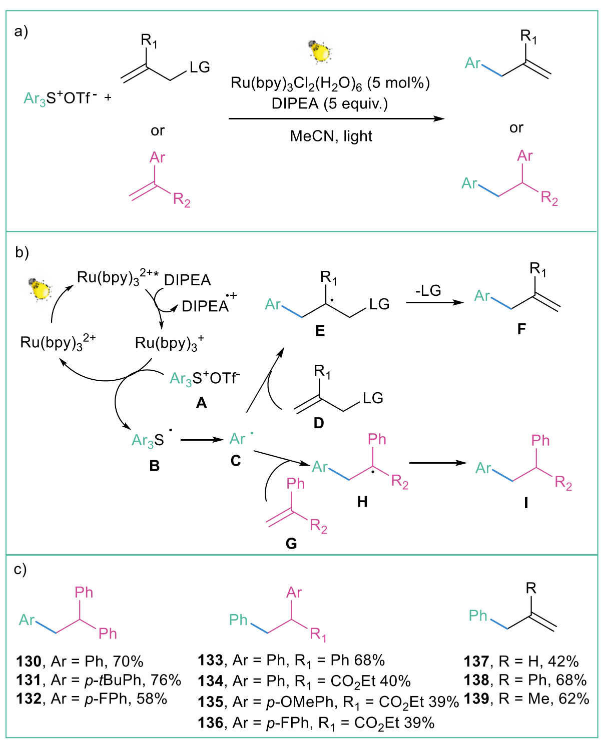
3.3. Generation of aryl radicals from sulfonium salts

Sulfonium salts, which are in an isoelectronic relationship with phosphines, have attracted considerable attention as versatile reagents in organic synthesis for many years,[101] since they play an important role in various C–C bond-forming reactions that involve C–S bond cleavage.[102]

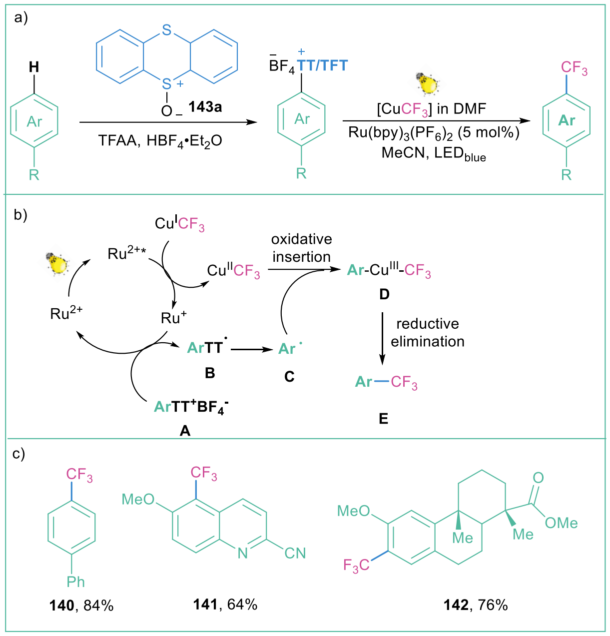
Within this chapter, many methods that are based on thianthrenium chemistry is presented. Although extremely useful (*vide infra*), this kind of aryl radical precursor deliver high weight by-product which may be re-isolated, however again with additional solvent waste. This should be also taken into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

3.3.1. Photochemistry

In recent years, photoredox catalysis has been proven to be an important and powerful approach for the generation of various C-cantered radicals through cleavage of the C–S bonds *via* radical pathways.[102] 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.[103] 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 alkylation of various species,[104] however only recently they have also started to be used as suitable precursors for the photoinduced generation of aryl radicals.[102c] Arylsulfonium salts can easily undergo efficient, homolytic, photon-induced single electron reduction under mild conditions toward the 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 26a).[102a] The mechanistic proposal assumes the initial photoexcitation of the photoredox catalyst ($Ru(bpy)_3Cl_2$) and its subsequent reduction by the secondary amine (DIPEA) to produce a strong reductant - Ru^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 β-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 26b). Although the substrate scope is limited to only 16 examples, they confirmed the good efficacy of the developed method (39-70% yield) (Scheme 26c).

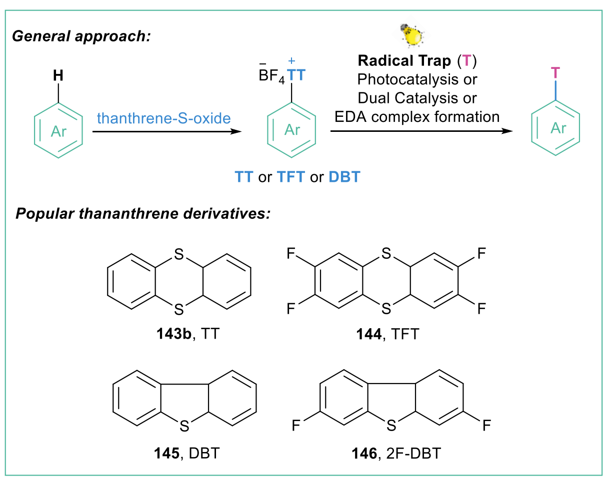


Scheme 26. Triarylosulfonium salts as radical precursors: a) model reaction, b) mechanistic proposal and c) representative examples.



Scheme 27. Aryl sulfonium salts for site-selective trifluoromethylation: a) model reaction, b) mechanistic proposal and c) representative products.

One of the most straightforward routes toward the synthesis of arylsulfonium salts is direct sulfenylation 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 trifluomethylation agents as well as electrophilic partners in transition-metal catalysed C–C cross-couplings.[105] Recently, Ritter with co-workers developed a highly *para*-selective C–H trifluoromethylation of arenes employing **143a** (Scheme 27).[106] In the next step, the generated salts were engaged in a dual catalytic system that involves a photochemical, Ru-catalysed oxidation of Cu(I)-CF_3 to Cu(II)-CF_3 followed by copper-catalysed C–C bond formation involving the Cu(III) intermediate.

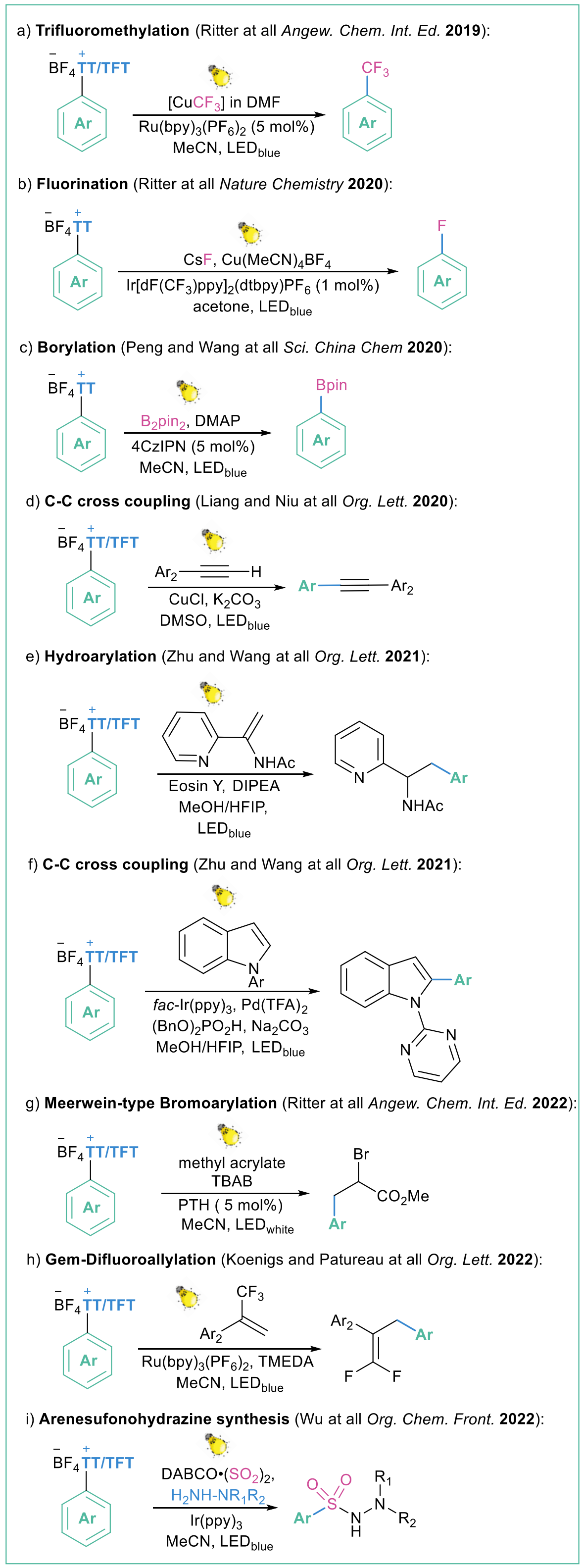


Scheme 28. Generation of aryl radicals from tetrafluorothianthrene sulfonium salts.

The mechanistic proposal assumes that after light absorption, the ruthenium-based photocatalyst is excited to the excited state ($Ru(bpy)_3^{2+*}$), which is capable of oxidising Cu^ICF_3 to $Cu^{II}CF_3$. The Ru^I 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 $Cu^{II}CF_3$ during oxidative ligation to form complex **D**, after the subsequent formation of the reductive elimination product **E** is formed (Scheme 27b). The reaction is generally high-yielding and both electron-deficient and electron-donating groups are well tolerated (Scheme 27c).

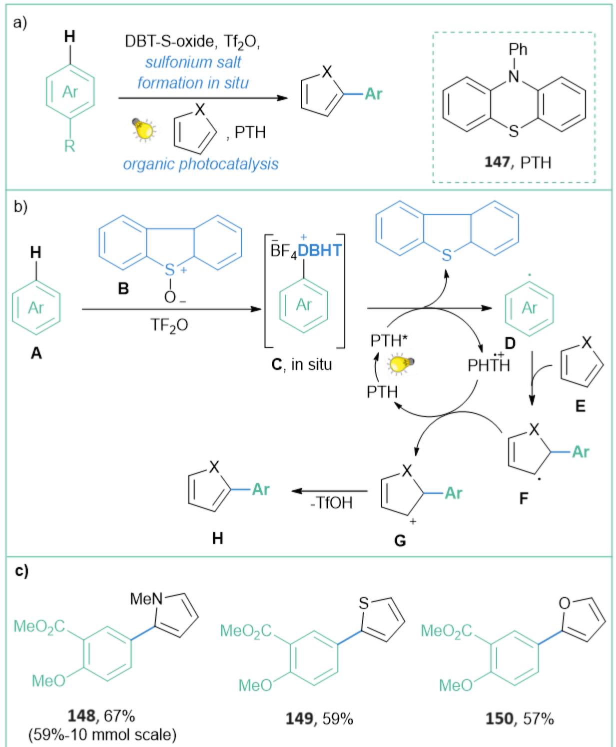
The above-mentioned findings set the stage for the general application of tetrafluorothianthrene sulfonium salts for the generation of aryl radicals under light irradiation in the presence of a photoredox catalyst. First, the synthesis of thianthrene sulfonium salts takes place, and then a photocatalysed reduction to the aryl radical is performed, which subsequently can be engaged in further transformations (Scheme 28).

Such a methodology was already applied under different conditions (different photoredox catalyst and application of dual photoredox metal catalysis) in many transformations such as photocatalysed trifluoromethylation[106] (Scheme 29a), Cu-catalysed fluorination[19c] (Scheme 29b), borylation[107] (Scheme 29c), Sonogashira-type reaction[108] (Scheme 29d), hydroarylation of vinyl acetamides[109] (Scheme 29e), arylation of indoles[110] (Scheme 29f), Meerwin-type bromoarylation[111] (Scheme 29g), gem-difluoroallylation[112] (Scheme 29h) and three-component synthesis of arenesulfonohydrazines[113] (Scheme 29i). 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.[114]

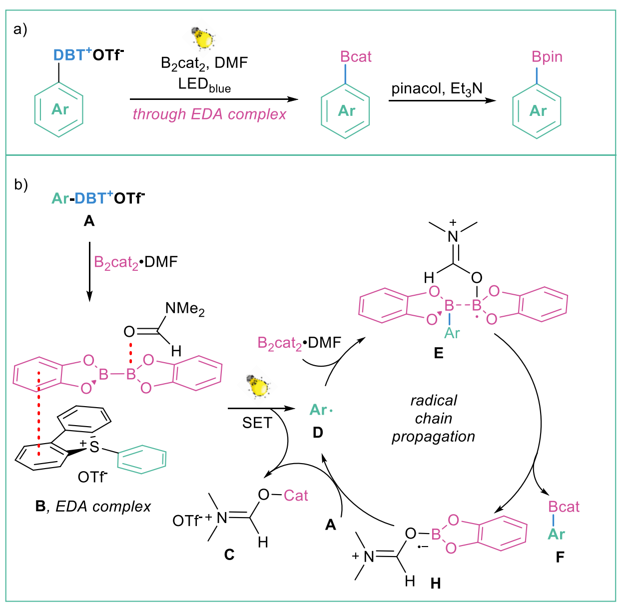


Scheme 29. Scope of application of tetrafluorothianthrene sulfonium salts as arylating reagents.

https://doi.org/10.26434/chemrxiv-2024-9nxdj **ORCID:** https://orcid.org/0000-0002-1323-2826 Content not peer-reviewed by ChemRxiv. **License:** CC BY-NC-ND 4.0

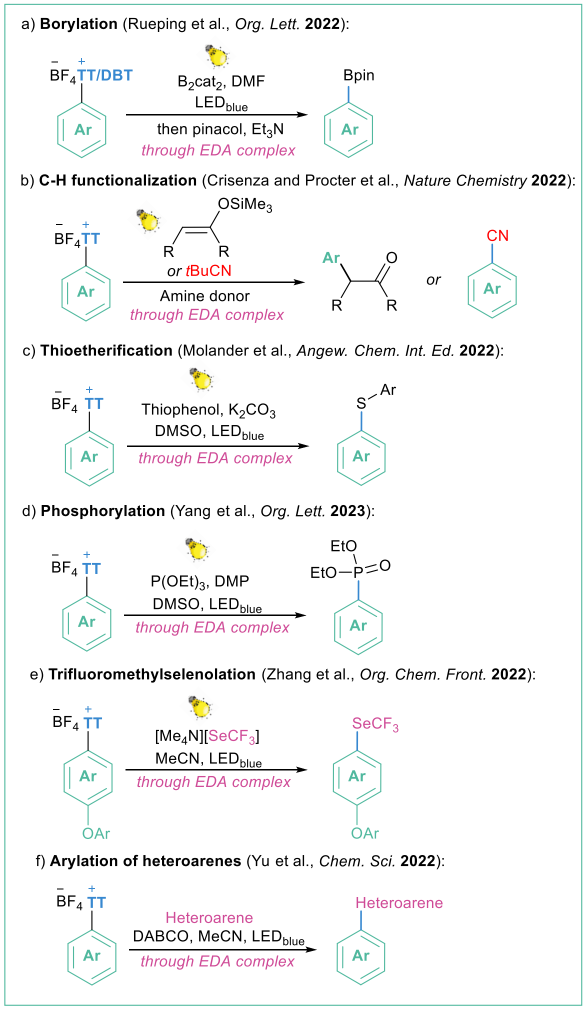


Scheme 30. One-pot, catalyst-free photoinduced synthesis of biaryls: a) model reaction, b) mechanistic proposal and c) representative products



Scheme 31. Photoinduced desulfurative borylation.

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 30).[115] The authors demonstrated a one-pot strategy for the rapid synthesis of (hetero)biaryls from non-prefunctionalized 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 30a). 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**$^{\bullet+}$) to form **G**. Finally, rearomatization leads to the biaryl product **H** (Scheme 30b). 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 30c).



Scheme 32. 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.

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 31a).[116] One year later, the same methodology was presented for the generation of aryl radicals.[107b] In this case, 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**. Upon 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 catalytic cycle (Scheme 31b).

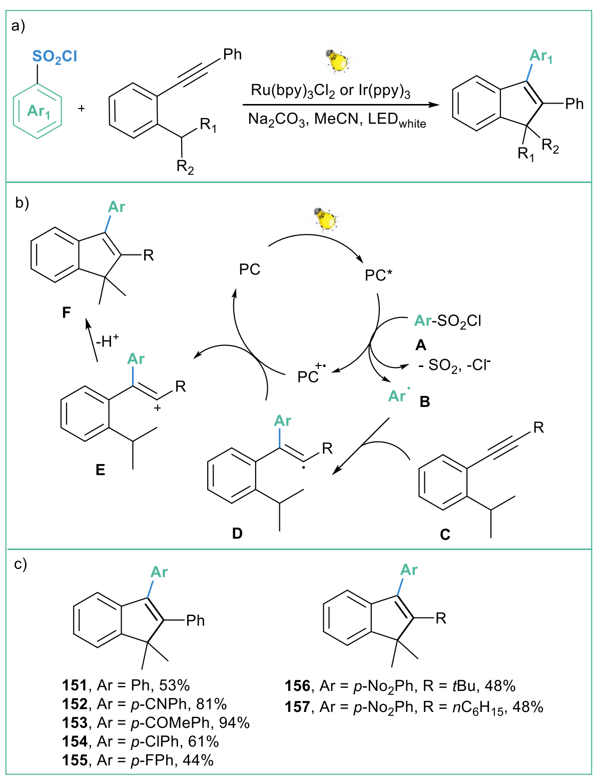
This methodology of irradiating an EDA complex containing a TT-based salt was already applied in many successful transformations such as borylation[107b] (Scheme 32a), C-H-functionalization[117] (Scheme 32b), synthesis of aromatic disulphides[118] (Scheme 32c), phosphorylation[119] (Scheme 32d), trifluoromethylselenolation[120] (Scheme 32e) and arylation of heteroarenes[121]

(Scheme 32f). 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).

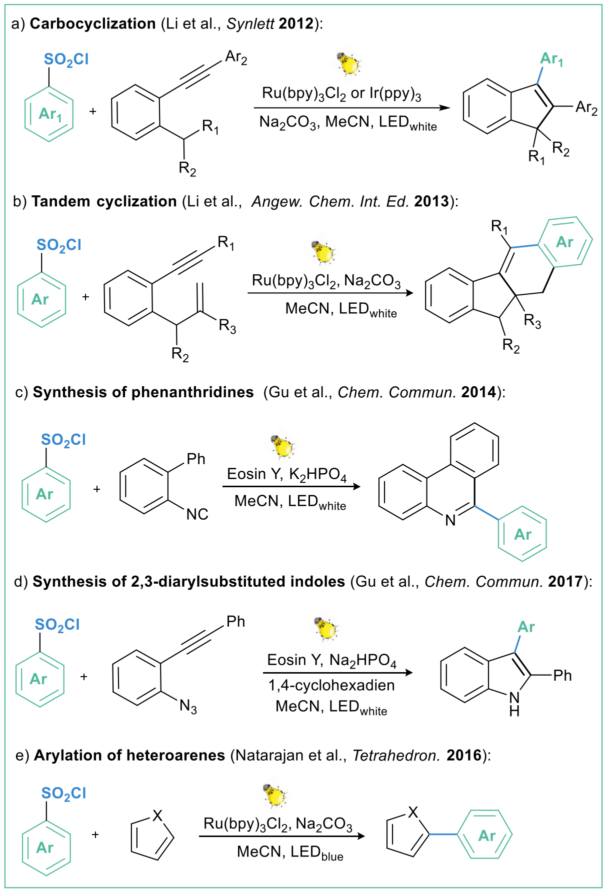
3.4. Generation of aryl radicals from sulfonyl chlorides

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 a 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 photoinduced single electron reduction from the photocatalyst in the excited state (Scheme 33).[122] In 2012, Li and co-workers for the first time reported a protocol for the photocatalyszed generation of aryl radicals from arylsulfonyl chlorides and their subsequent application into carbocyclization toward the formation of 1*H*-indenes (Scheme 33a).[123] 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 of the photocatalyst radical cation (**PC**$^{\bullet +}$) 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 33b). Generally, the reaction proceeds with good to high yields (44-94%) for different alkynes and aryl sulfonyl chlorides (Scheme 33c). This methodology was further utilised in a number of successful intramolecular cyclization reactions such as the synthesis of 10*a*,11-dihydro-10*H*-benzo[*b*]fluorenes[124] (Scheme 34b), phenanthridines[125] (Scheme 34c), 2,3-diarylsubstituted indoles[126] (Scheme 34d). In 2016, Natarajan and co-workers also demonstrated 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 34e).[127]



Scheme 33. Photocatalyzed reaction of arylsulfonyl chlorides with alkynes: a) model reaction, b) mechanistic proposal and c) representative products.

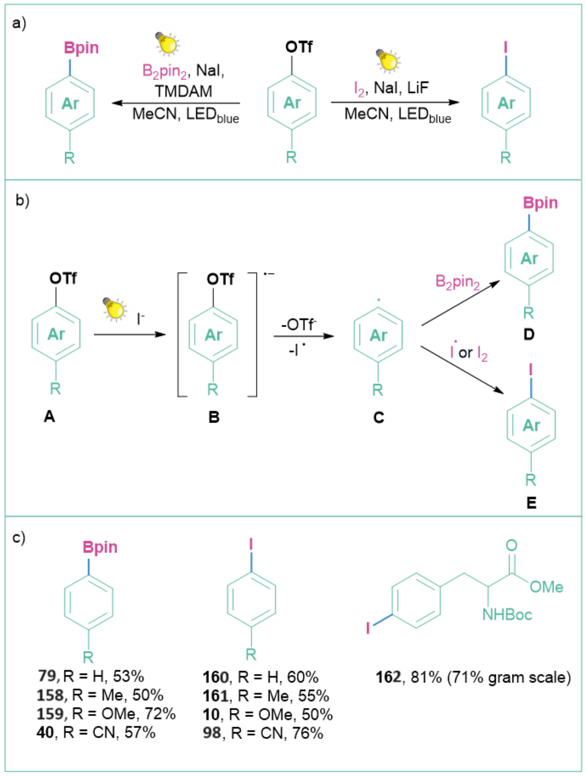


Scheme 34. Photocatalyzed production of aryl radicals from arylsulfonyl chlorides and their application in a) carbocyclization, b) tandem cyclization,
c) synthesis of phenanthridines, d) synthesis of 2,3-diarylsubstituted indoles and e) arylation of heteroarenes.

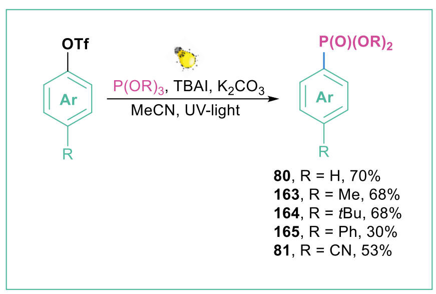
3.5. Generation of aryl radicals from phenol derivatives (aryl triflates, phosphates)

3.5.1. Photochemistry

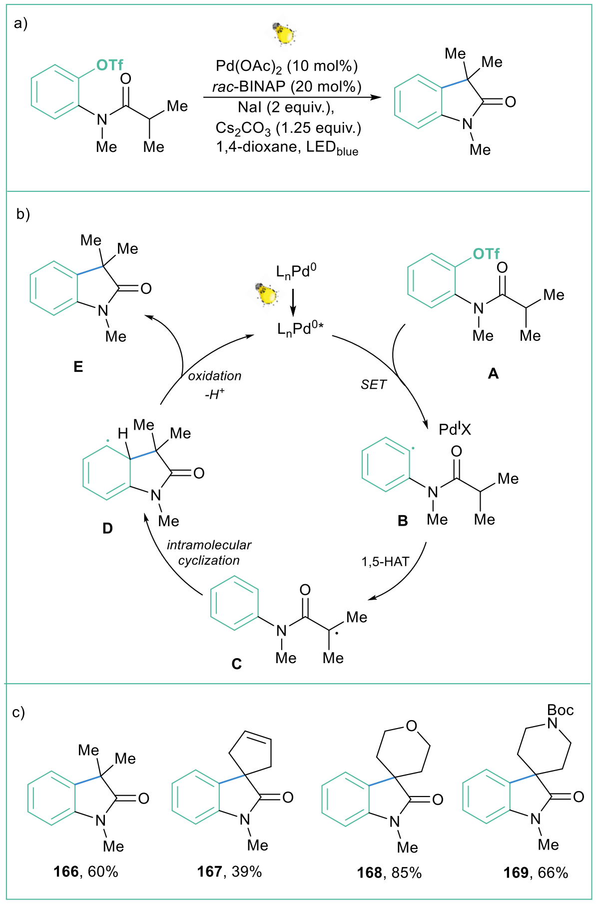
Photoredox catalysis is responsible for an explosion of new synthetic applications for aryl halides, diazonium salts, sulfonium salts, and sulfonium chlorides as aryl radical precursors in modern organic chemistry. On the other hand, the engagement of phenol and its derivatives could be even more appealing since they are easily available and inexpensive starting materials.[6b, 128]
In the case of photoinduced 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 35a).[129] The general mechanistic proposal (Scheme 35b) 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 an access to variety of products in only moderate yields (36-70%), the methodology features good functional group compatibility, mild reaction conditions, as well as is metal- and photocatalyst-free. More importantly, it uses readily available and inexpensive aryl triflates as aryl radical precursors (Scheme 35c).
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 36)[130] and for the deuteration of aryls.[131]



Scheme 35. Generation of aryl radicals from aryl triflates: a) model reaction, b) mechanistic approach and c) representative products.



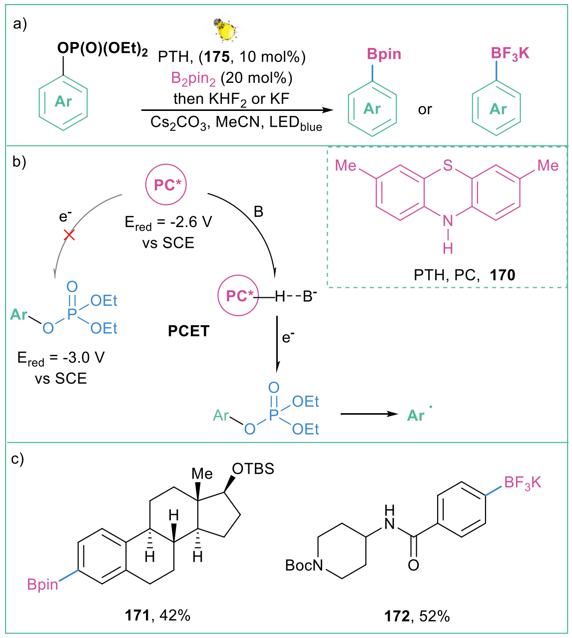
Scheme 36. Photoinduced Arbuzov-type reaction of aryl triflates with trialkyl phosphite.



Scheme 37. Visible-light-induced palladium-catalysed generation of aryl radicals from aryl triflates: a) model reaction, b) mechanistic proposal and
c) representative products

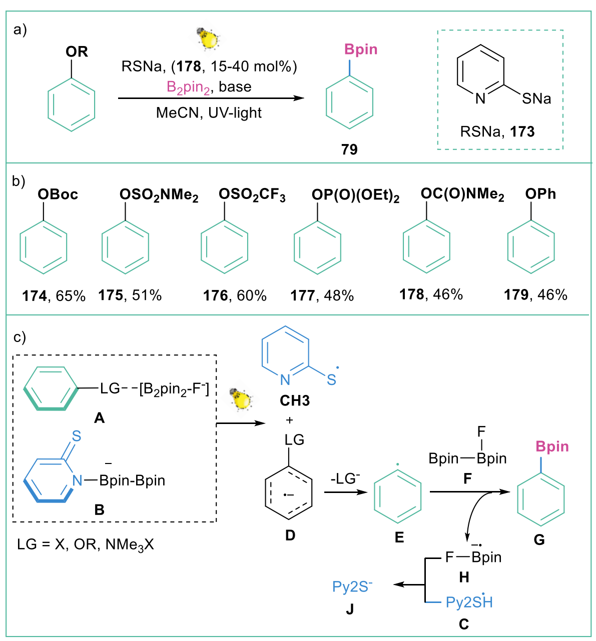
Another way of activating aryl triflates toward the generation of aryl radicals was presented by Gevorgyan and co-workers (Scheme 37a).[132] This methodology allows for efficient intramolecular C-H arylation of amides. The proposed mechanism depicted on Scheme 37b assumes the formation of a Pd-radical 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 intermediate **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 37c) and isoindoline-1-ones.

Aryl triflates are not the only phenol derivatives that can be activated to promote efficient aryl radical formation.[133] Larionov and co-workers proved that it is possible to photoactivate other derivatives such as aryl diethyl phosphates (E_{red} ~-3.0 V *vs* SCE) (Scheme 38a), as well as aryl halides and quaternary aryl ammonium salts.[56] Proton-coupled electron transfer (PCET) was utilised in order to activate the substrates with strongly negative reduction potentials (Scheme 38b). Generally, this approach possesses an enormously broad scope of application: EDG, EWG, heteroarenes, and natural compounds, among them amino acids and hormones (Scheme 38c).



Scheme 38. PCET as a mode of activation of phenol derivatives: a) model reaction, b) mechanistic proposal and c) representative products.

Another strategy for the activation of phenol derivatives that possess highly negative reduction potentials (OBoc, OSO_2NMe_2, OSO_2CF_3, $OP(O)(OEt)_2$, $OC(O)NMe_2$, OPh) is the application of thiolate as a catalyst (Scheme 39).[134] Here, the reaction is initiated by a photoinduced electron transfer process between an activated boryl-anion **A** (LG = X, O or N) and the adduct 2-PySNa/B_2pin_2 **B** to generate a thiyl 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_2pin_2] to give the borylation product **G** and the boryl radical anion **H**. Finally, the thiyl radical **C** is reduced by the boryl radical anion **H** to regenerate thiolate **J** with the closure of the catalytic cycle (Scheme 39c).



Scheme 39. PCET for the activation of phenol derivatives: a) model reaction, b) representative substrates and c) mechanistic proposal.

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 39b).

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_{aryl}–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.[135]

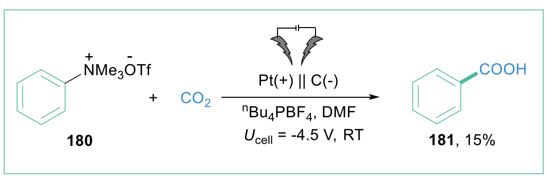
3.6.1. Photochemistry

Photoactivation of the strong C_{aryl}–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 arylamonium salts is possible.[136] 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 38).[56]

3.6.2. Electrochemistry

The first examples of electrolyses of quaternary ammonium salts appeared in the literature in 1909,[137] however the involvement of aryl radicals in these processes was suggested fifty years later.[138] 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.

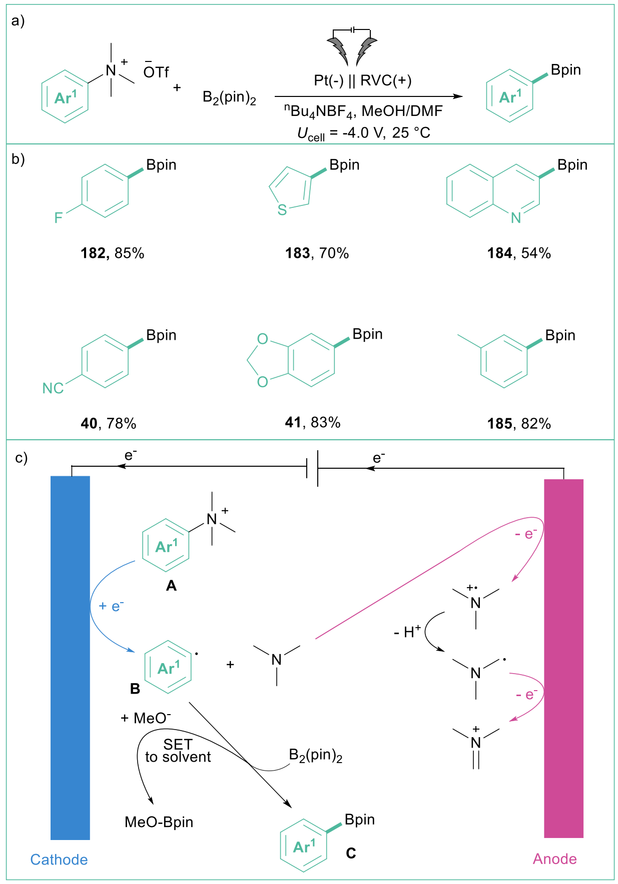
In 2019, Manthiram and colleagues investigated the electroreductive transformation of benzylammonium salts toward benzylcarboxylic acids.[139] During the investigation, they also tested phenyltrimethylammonium triflate (**180**) (Scheme 40) as a possible aryl radical precursor. Indeed, benzoic acid (**181**) 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_{cell} = 4.5 V) that was required for the indicated efficiency.



Scheme 40. Electrolysis of phenyltrimethylammonium triflate toward benzoic acid formation.

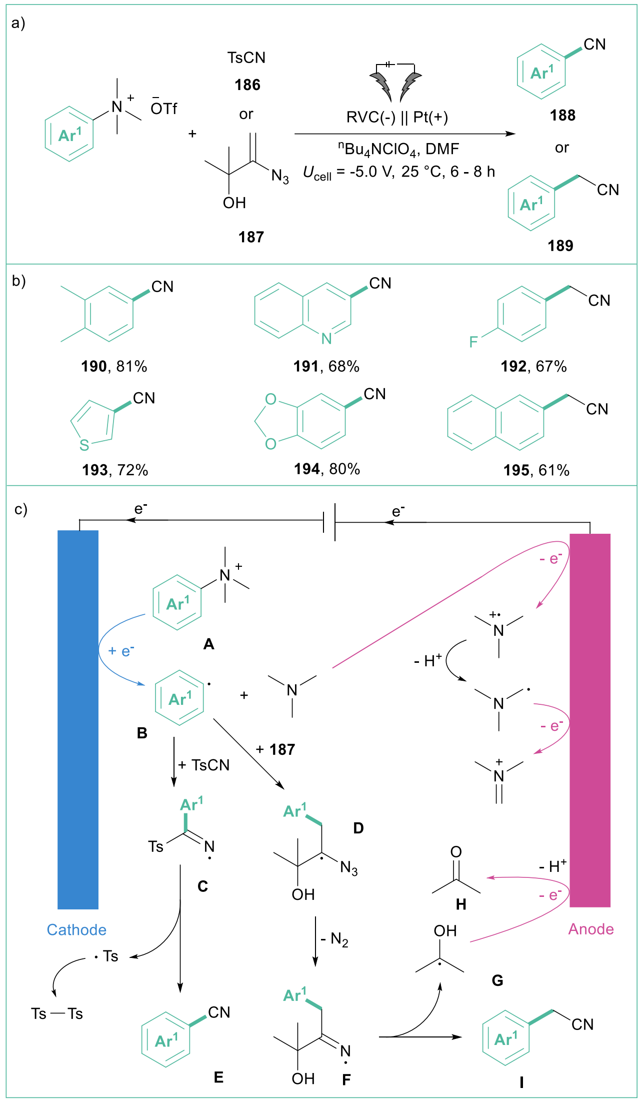
In 2021, Xu's group described the direct electrolysis of aryltrimethylammonium triflates toward synthetically-meaningful organoboronates (Scheme 41a).[140] Here, potentiostatic conditions were applied to produce products in moderate to good yields showing broad applicability (Scheme 41b). They proved 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_3N. Subsequently, $Ar^{\bullet}$ reacts with B_2pin_2 in the presence of MeO^- giving rise to the expected product **C** and MeOBpin (Scheme 41c).

The same group also proved that quaternary arylammonium salts can be transformed into a variety of benzonitriles (**188**) as well as benzylnitriles (**189**) by employing tosyl cyanide (TsCN) or azido allyl alcohol as cyanation or cyanomethylation reagents (Scheme 42a).[141] The efficiency of cyanation was generally higher, in comparison to the cyanomethylation reaction. The method tolerates a broad range of substrates, including those bearing easily-reducible functional groups (–CN, $–CO_2$Alk, $–NO_2$), *S*-, *O*- or *N*-based heterocyclic motifs, as well as natural product derivatives (Scheme 42b). Importantly, the authors found that the obtained nitriles of type **188**-**189** 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 42c).



Scheme 41. Electrolysis of phenyltrimethylammonium triflate toward benzoic acid: a) model reaction, b) representative products and c) mechanistic proposal.

https://doi.org/10.26434/chemrxiv-2024-9nxdj **ORCID:** https://orcid.org/0000-0002-1323-2826

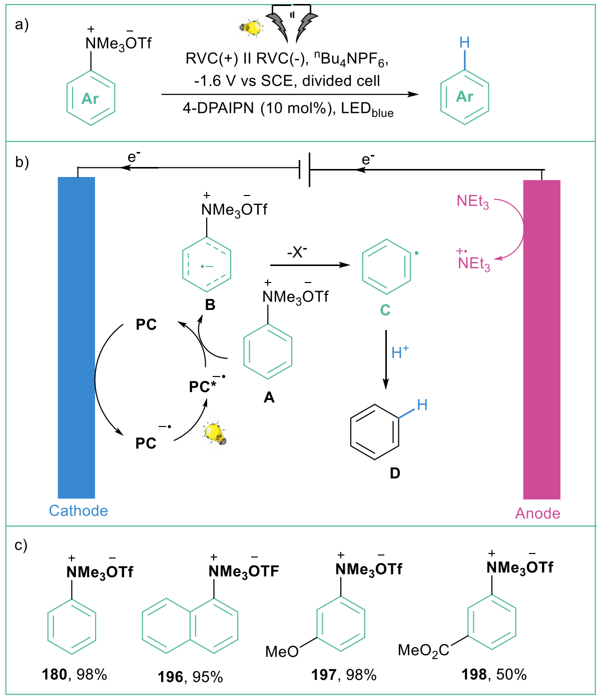


Scheme 42. Electrochemical cyanation and cyanomethylation of aryltrimethylammonium salts: a) model reaction, b) representative products and c) mechanistic proposal.

The common feature of electrochemical methods described above is extremely high working potential (up to -5.0 V) hampers significantly efficient energy utilization. Therefore, this set 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 chapter, Larionov[136] and König[134] demonstrated the successful activation of challenging quaternary arylammonium salts (~-2.5 V *vs* SCE) *via* simple photoreduction. However, both approaches relied on the special characteristic of the boron partners and therefore photoredox transformations of these demanding substrates remain limited. On the other hand, photoelectrocatalysis has already been proven to be a powerful strategy for the generation of photoexcited radical ions that can behave as strong reductants under very mild conditions.[77] This approach has been utilised by Wickens and colleagues for the activation of quaternary arylammonium salts (Scheme 43a).[77] Generally, this approach assumes that first, the photocatalyst is reduced to its radical anion (**PC**$^{\bullet-}$) at the cathode and as such it gets excited to form a super strong reducing agent (**PC***$^{\bullet-}$), which is able to reduce a quaternary arylamminium salt **A** to its radical anion **B**, which after dehalogenation forms the aryl radical **C**. Subsequent protonation forms product **D** (Scheme 43b). This strategy was demonstrated to be very efficient for various quaternary ammonium salts possessing electron-donating groups (excellent yields) and electron-withdrawing groups being slightly less reactive (moderate yields) (Scheme 43c) (for the stability of excited radical anions see paragraph 3.1 Con-PET *vs* photoelectrochemistry).



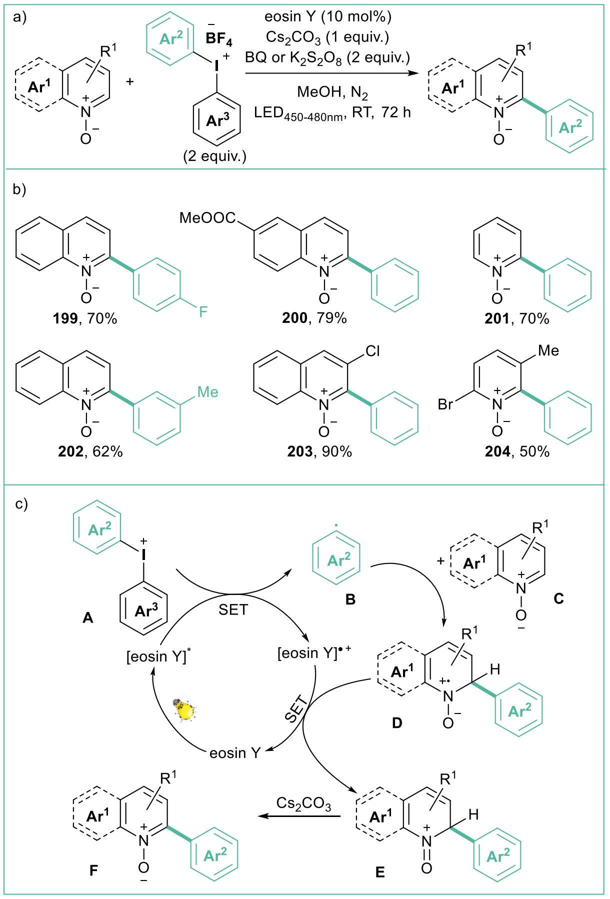
Scheme 43. Photoelectrocatalytic activation of quaternary arylammonium salts: a) model reaction, b) mechanistic proposal and c) representative products.

3.7. Generation of aryl radicals from diaryliodonium salts

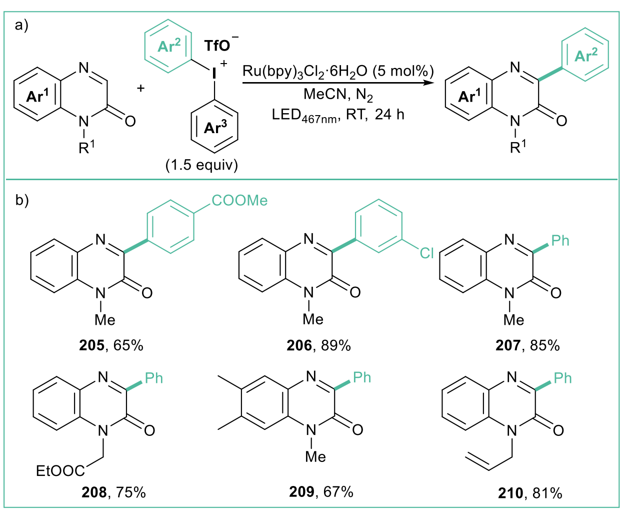
Diaryliodonium salts, similarly to diazonium salts, can also be used for the generation of aryl radicals, although they generally feature lower reduction potentials (usually -0.4 to -0.8 V *vs* SCE in MeCN).[142] These compounds have recently received considerable attention as they are mild, nontoxic, selective, compatible with many functional groups and 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.[143]

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,[144] heteroarenes,[145] allyl tosylates,[146] *N*- or *C*-phenylamides,[147] preparation of sulfones,[148] sulfoxidation and sulfenylation,[149] synthesis of thiophosphates,[150] hydrophosphinylation[20f] and dehydrogenation.[151] 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).

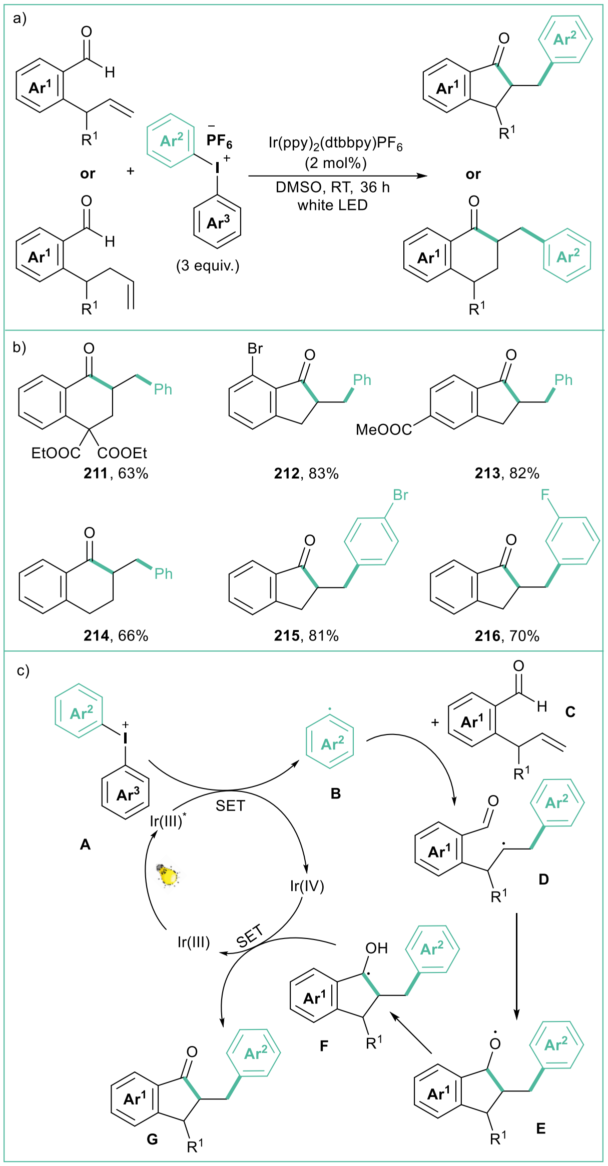


Scheme 44. Arylation of quinoline and pyridine *N*-oxides with diaryliodonium tetrafluoroborates: a) model reaction, b) representative products and c) mechanistic proposal.



Scheme 45. Arylation of quinoxalin-2(1*H*)-ones with diaryliodonium salts: a) model reaction and b) representative products.

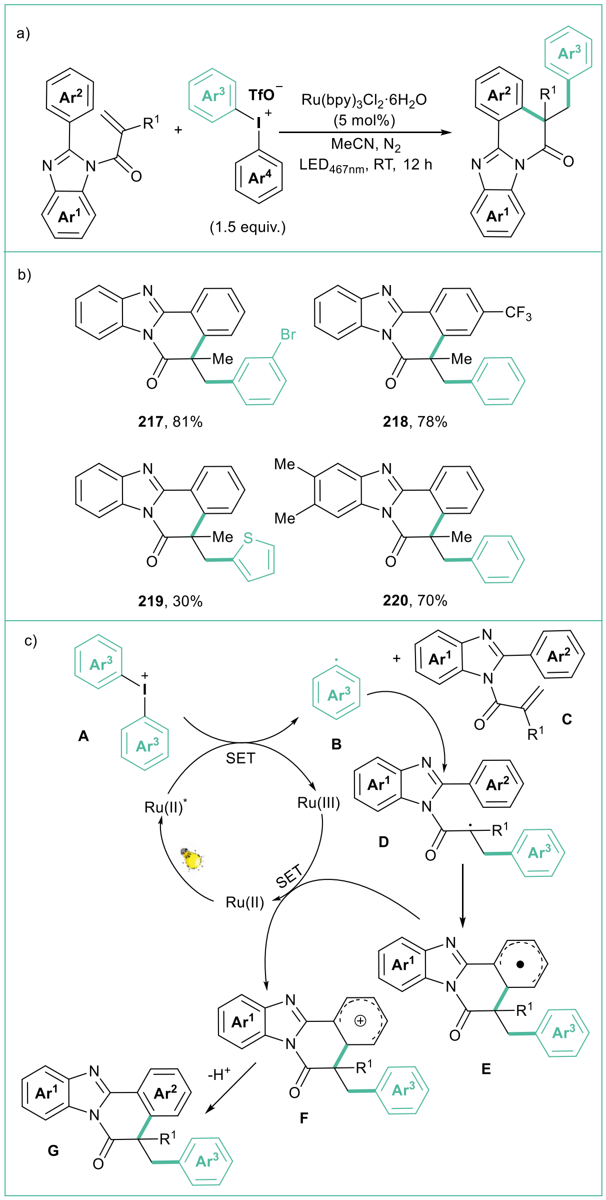
Li and co-workers developed a visible-light-promoted C2-selective arylation of quinoline and pyridine *N*-oxides using diaryliodonium tetrafluoroborates as arylation reagents (Scheme 44).[152] Here, the application of 10 mol% of eosin Y as a photocatalyst and 5 W blue LEDs (450-480 nm) ensures satisfactory yields. **BQ** (1,4-benzoquinone) or $K_2S_2O_8$ were used as stoichiometric co-oxidants.



Scheme 46. Acylarylation of unactivated alkenes with diaryliodonium salts: a) model reaction, b) representative products and c) mechanistic proposal.

According to the mechanistic proposal, eosin Y undergoes excitation by visible light to its excited state and at the same times 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.

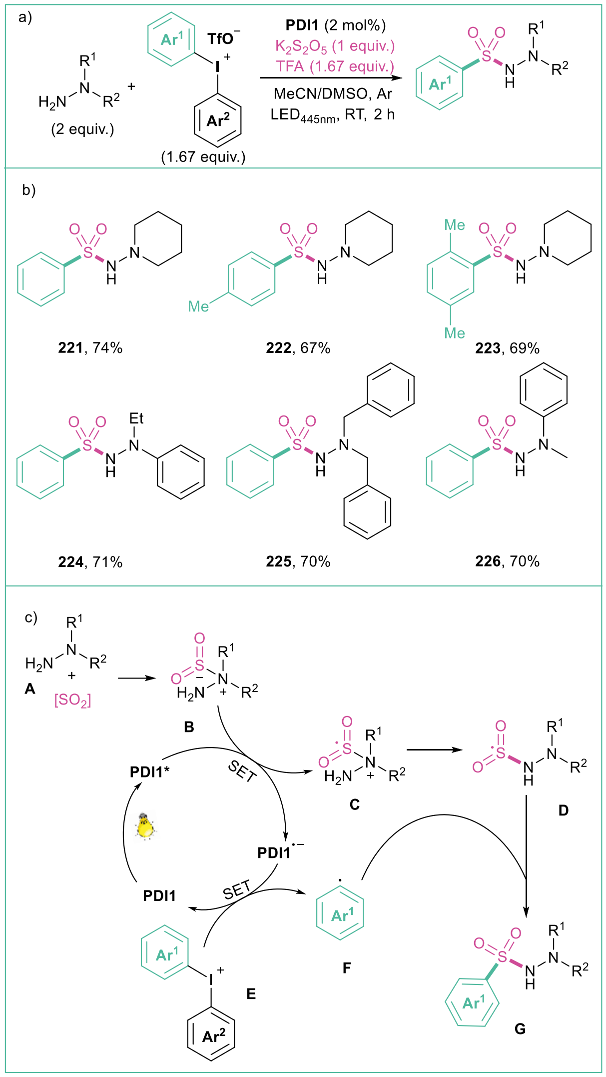
Similarly to the method mentioned above, the Ru(II) based photocatalyst enables direct C3 arylation of quinoxalin-2-(1*H*)-ones employing easily available and stable diaryliodonium triflates (Scheme 45a).[153] Specifically, the reaction proceeds in the presence of $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (5 mol%) under blue LED irradiation (467 nm) in MeCN. The scope is rather broad, and allyl/propargyl groups are well tolerated in this protocol (Scheme 45b). Importantly, if non-symmetrical diaryliodonium salts are used, the selective transfer of an electron-deficient and less sterically hindered part is preferred. In terms of mechanism, the reaction proceeds in an analogous way to that described earlier (see Scheme 44c).



Scheme 47. Arylative cyclization of *N*-acryloyl-2-arylbenzoimidazoles with diaryliodonium salts: a) model reaction, b) representative products and c) mechanistic proposal.

In turn, the iridium-based catalyst ($Ir(ppy)_2(dtbbpy)PF_6$) proved to be effective in the photocatalytic acylarylation of unactivated alkenes to cyclic ketones (Scheme 46a).[154] 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 Ir(III)*. Then, a SET process between Ir(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 46c).

N-Substituted 2-arylbenzoimidazoles show a similar reactivity pattern toward diphenyliodonium triflates affording arylated-benzimidazo[2,1-*a*]isoquinolin-6(5*H*)-ones (Scheme 47a).[153] This cascade operates under mild conditions and offers a broad substrate scope with appreciable functional group tolerance (Scheme 47b). 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 47c). 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**.

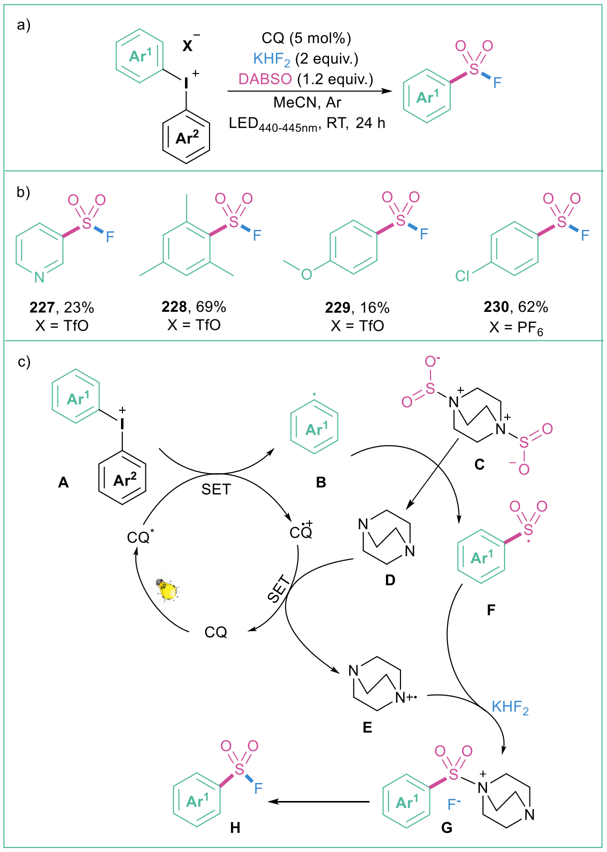


Scheme 48. Synthesis of *N*-aminosulfonamides from diaryliodonium salts: a) model reaction, b) representative products and c) mechanistic proposal.

Liu and co-workers reported a three-component visible light photoredox-catalysed synthesis of *N*-aminosulfonamides starting from diaryliodonium salts, hydrazines and different sulphur dioxide sources (Scheme 48).[155] Here, diaryliodonium salts react with 4-aminomorpholine and sulphur dioxide (generated *in situ* from $K_2S_2O_5$ 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 48a). The proposed mechanism (Scheme 48c) starts with a **PDI1** photoexcitation and reductive quenching of **PDI*** with the hydrazine-sulphur dioxide complex **B** providing a radical adduct **C** and reduced catalyst $\mathbf{PDI_1}^{-}$. Next, a SET between $\mathbf{PDI1}^{\bullet-}$ 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 49a).[156] The reaction proceeds in MeCN under blue LED (440-445 nm) irradiation in the presence of a photosensitizer, namely camphorquinone (**CQ**), with diaryliodonium salts as a source of aryl radicals, alongside DABSO and 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 49b). 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 KHF_2 produces **G**.



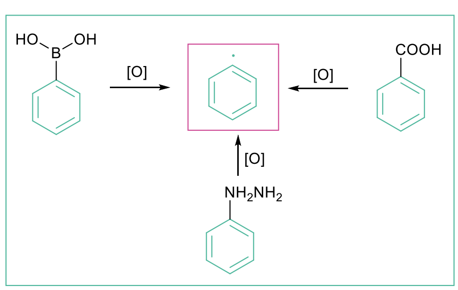
Scheme 49. Synthesis of aryl sulfonyl fluorides from diaryliodonium salts: a) model reaction, b) representative products and c) mechanistic proposal.

3.7.2 Electrochemistry

Electrochemical generation of aryl radicals from diaryliodonium salts is well documented in the literature but has been only applied in electrografting of different materials including carbon, gold, and tin oxide.[142b, 157] It is worth noting that the grafting efficiency for diaryliodonium salts was found to be slightly lower than that noted for diazonium salts.[142b, 157b] Notwithstanding, to the best of our knowledge, such electrochemically driven, purely methodological applications of diaryliodinium salts have not yet been developed so far.

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 EDA complexes formation), organic electrochemistry, and photoelectrochemistry, the oxidative generation of aryl radicals is so far possible from aromatic boronic and carboxylic acids[158] as well as aryl hyrazines (Scheme 50). Synthetic methods that use electric current for oxidative functionalisation reactions[21b, 23, 159] have recently received considerable attention and aryl radicals can be generated in that way as well.



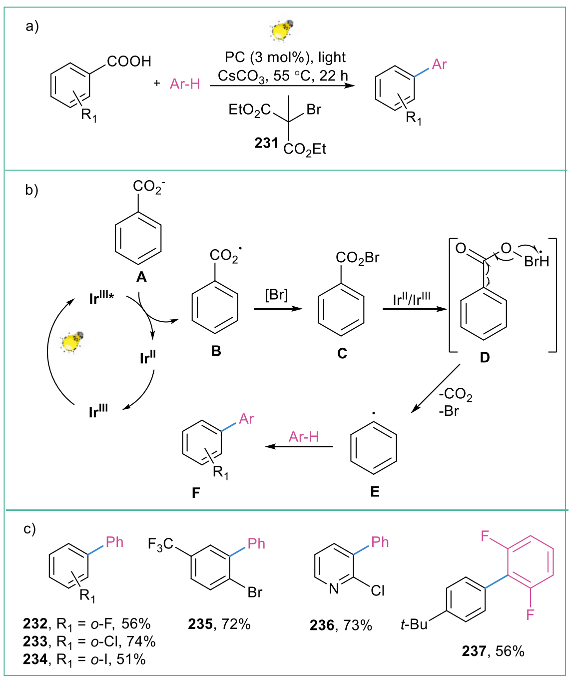
Scheme 50. Oxidatively-induced generation of aryl radicals from different precursors.

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.[6a, 158] 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[160] 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.

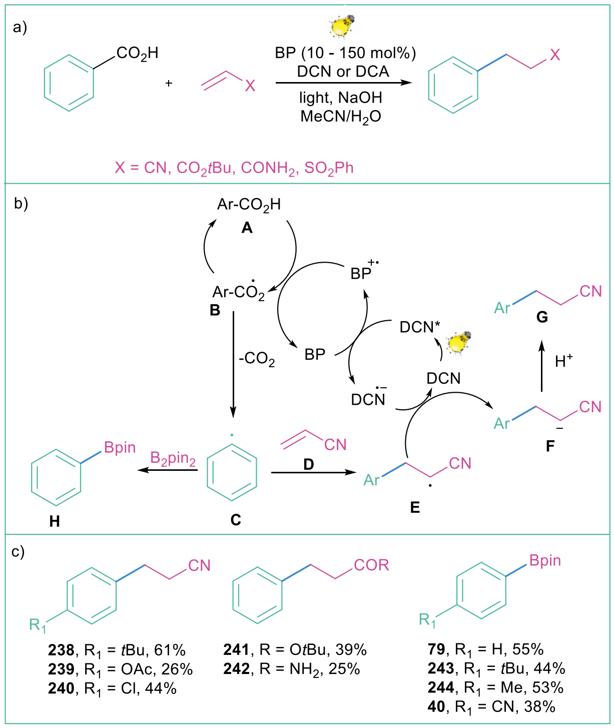
4.1.1 Photochemistry (photoredox catalysis and EDA complexes formation)

The first attempts for the light-induced generation of aryl radicals from carboxylic acid derivatives date back to 1988,[161] when Inglod 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 to thermolysis. This important finding sets the stage for future application of photoredox catalysis in the oxidative generation of aryl radicals from carboxylic acids. In 2017, the Glorious group showed the first example of aryl radical formation from aromatic carboxylic acids employing photoredox catalysis (Scheme 51a). [162]



Scheme 51. Decarboxylation of aryl carboxylic acids: a) model reaction, b) mechanistic proposal and c) representative products.

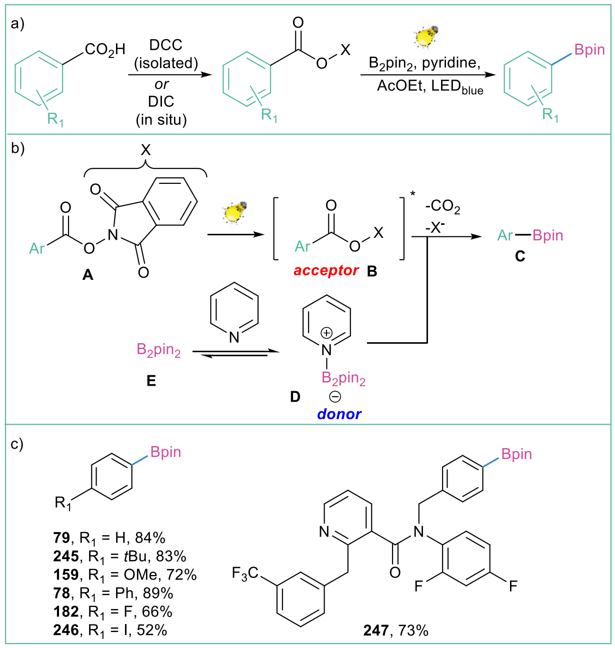
https://doi.org/10.26434/chemrxiv-2024-9nxdj **ORCID:** https://orcid.org/0000-0002-1323-2826 Content not peer-reviewed by ChemRxiv. **License:** CC BY-NC-ND 4.0



Scheme 52. Photoinduced decarboxylative generation of aryl radicals from carboxylic acids: a) model reaction, b) mechanistic proposal and c) representative products.

The mechanistic scenario includes the initial oxidation of the deprotonated aromatic carboxylic acid **A** by the Ir-based 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_2 and aryl radical **E**. Subsequent trapping of the aryl radical **E** by a heteroarene generates the rearomatization product **F** (Scheme 51b). The described protocol is mild, high yielding, and tolerates a broad range of substrates (Scheme 51c), however, the application of an expensive and toxic Ir photocatalyst remains its limitation.

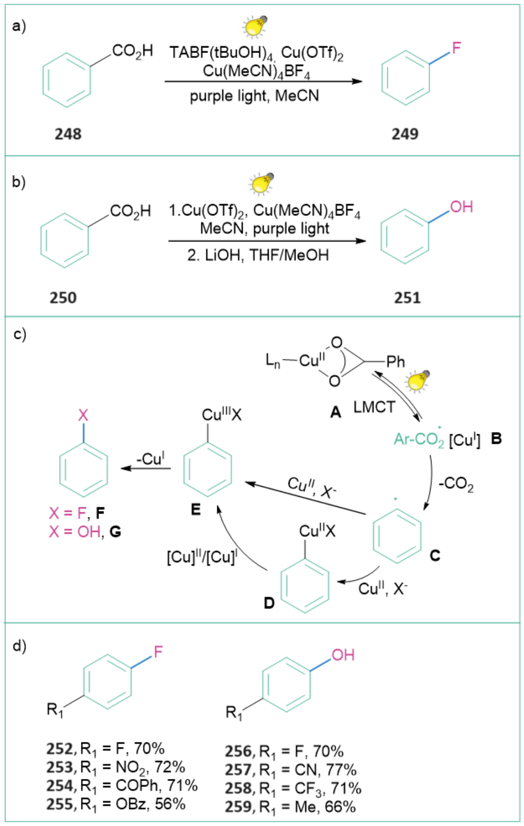
This problem was partially overcome by Yoshimi and co-workers with the use of two active organic photocatalysts: benzophenone and dicyanonaphthalene (**DCN**) or dicyanoanthracene (**DCA**) (Scheme 52a).[18d] Photon-induced electron transfer between benzophenone (**BP**) and **DCN** (or **DCA**) enables the oxidation of BP to its radical cation (**BP$^{\bullet+}$**), which can then oxidize 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_2pin_2, borylated product **H** can be assembled employing this method (Scheme 52b). The methodology constitutes an facile synthetic protocol for alkylation and borylation of aromatic rings, however, yields remain moderate to good (Scheme 52c).



Scheme 53. Decarboxylative borylation of aryl *N*-hydroxyphthalimide esters: a) model reaction, b) mechanistic proposal and c) representative products.

The search for 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 53a).[163] 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 53b). 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 53c) but most importantly, it is transition-metal- and photocatalyst-free.

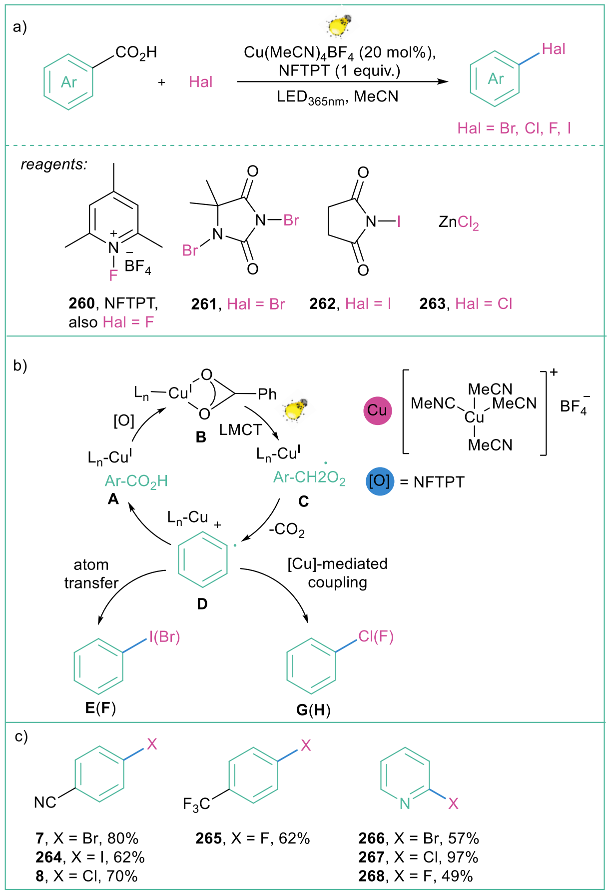
Over the past decade, photoinduced intramolecular ligand to metal charge transfer (LMCT) has become a powerful strategy for the generation of oxygen-centred radicals through homolysis of oxygen-metal bonds,[164] and its applications in the decarboxylation of alkyl carboxylates have been well documented.[165] 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[16] (Scheme 54a) and hydroxylated[166] products (Scheme 54b).



Scheme 54. Decarboxylative fluorination and hydroxylation enabled by Cu-LMCT catalysis: a) fluorination, b) hydroxylation, c) mechanistic proposal and d) representative products.

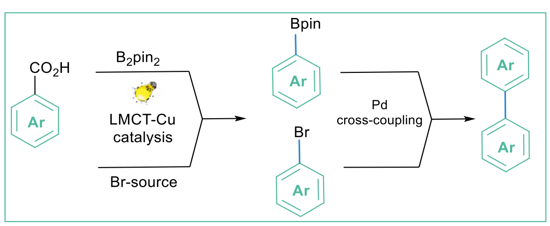
For both processes, the mechanistic proposal assumes that irradiation of Cu(II) carboxylate **A** results in carboxylate to Cu^{II} ligand to metal charge transfer (LMCT). Next, homolysis of the O–Cu^{II} bond results in the formation of aroyloxyl radical **B**, which after decarboxylation forms aryl radial **C**. The generated aryl radical **C** is trapped by a Cu^{III}TC complex or by a Cu^{I}TC complex with subsequent oxidation by Cu^{II} to afford arylcopper(III)TC. In both cases, reductive elimination of the C-O bond forms CuI and fluorinated product **F** or hydroxylated product **G** (depending on the reaction conditions) (Scheme 54c). Both protocols are operationally simple, Ir- and Ru-complex free, and moderate to high yielding (Scheme 54d).

MacMillan and co-workers presented a similar approach by developing a copper-catalysed strategy for the decarboxylative halogenation (I, Br, Cl, F) of hetero(aryl) carboxylic acids (Scheme 55).[167] Later, they showed that the reaction could be used for borylations *via* the merging of Cu-LMCT borylation/bromination cross-coupling (Scheme 55a).[168] The proposed mechanism is similar to the one presented by the Ritter's group (Scheme 54). The established methodology is general, mild, and moderate to high-yielding (see Scheme 55b), in addition, the synthesis of –Br, –Cl, –F and –I arenes and heteroarenes are compatible with a broad range of (hetero)aryl carboxylic acids (Scheme 55c).



Scheme 55. The general approach for the decarboxylative halogenation of aryl(heteroaryl) carboxylic acids: a) model reaction, b) mechanistic proposal and c) representative products.

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[168] These boron-based derivatives were subsequently merged with aryl halides (obtained by Cu-LMCT halogenation[167]) in Pd-catalysed cross-coupling[168] (Scheme 56). Without a doubt, this approach facilitates the direct transformation of aryl carboxylic acid feedstocks into value-added products (pharmaceutically active compounds) under mild conditions.



Scheme 56. Cu-LMCT decarboxylative borylation/Pd-cross coupling sequence toward value-added compounds.

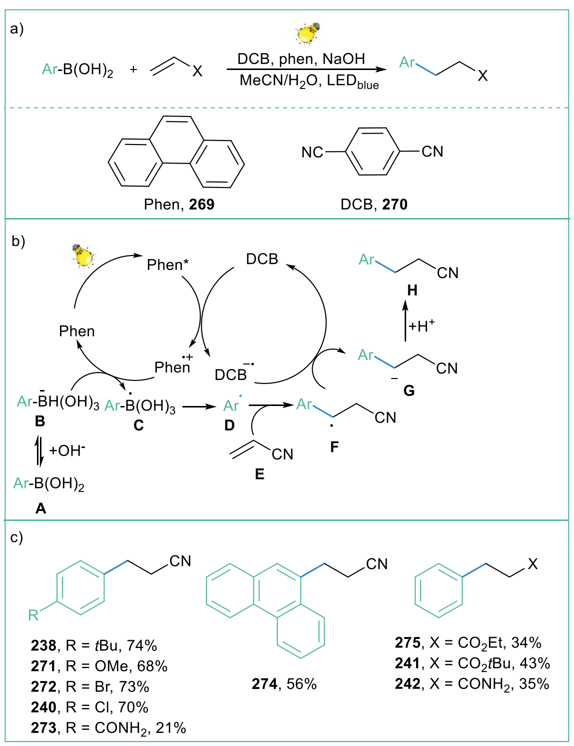
4.2 Generation of aryl radicals from aromatic boronic acid derivatives

Arylboronic acid derivatives are highly important chemical entities, both in organic synthesis[169] and medicinal chemistry.[170] The radical chemistry of boron-based compounds has been intensively studied over past years, resulting in broad synthetic applications thereof.[171] 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,[172] however, these methods often depend on superstoichiometric amounts of co-oxidants.

4.2.1 *Photochemistry*

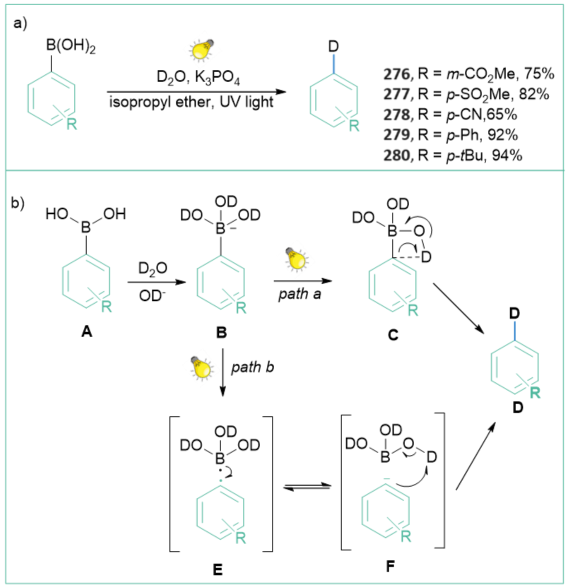
Despite many studies focused on alkyl organoboronic acids and their utilisation for the formation of C–C bonds, the use of aromatic boronic acids has received much less attention.[171b] Nevertheless, newly developed strategies for the arylation of various compounds from arylboronic acids deserve attention, since they offer high-atom economy approaches. Probably the widely explored arylation reaction employing arylboronic acids as aryl radical precursors is photo-Meerwin-type arylation of electron-deficient alkenes (Scheme 57a).[173] 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$^{\bullet+}$**) and the radical anion of DCB (**DCB$^{\bullet-}$**). Subsequently, arylborate **B** (formed by the reaction of arylboronic acid **A** with NaOH) is oxidised to radical **C** by the Phen$^{\bullet+}$. 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 57b). 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 57c). A similar approach was also demonstrated with other photocatalysts, where the Phen/DCB pair was exchanged for acridinium[174], flavin[175] or lumiflavin.[176] The same approach can be utilised not only for aryl boronic acids but also for aryl boronic esters.[177]

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.[133a] Such an approach was applied toward the deuteration of aromatic compounds with D_2O. Differently substituted arylboronic acids (both electron-withdrawing and electron-donating groups) were deuterated with very good yields (Scheme 58a). The mechanistic proposal assumes that the hydroxide ion coordinates to the empty orbital *p* 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_2O. 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 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 58b).

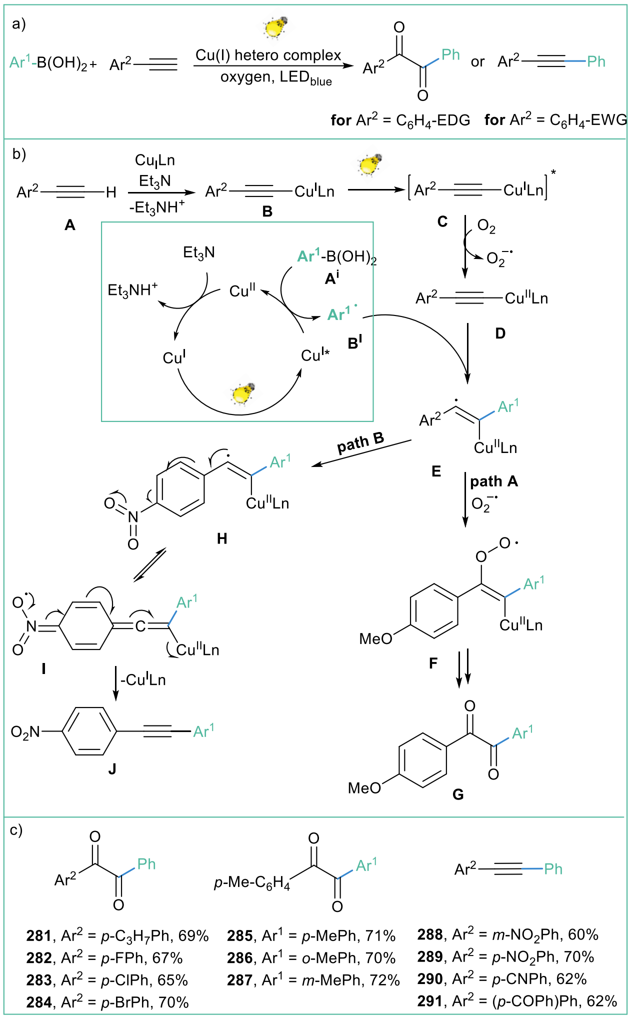


Scheme 57. Photoinduced Meerwin reaction between the aryl boronic acids and electron-deficient olefins: a) model reaction, b) mechanistic proposal and c) representative products.

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 59a).[133b]



Scheme 58. UV-light-induced deuteration of arylboronic acids with D_2O: a) model reaction with representative products and b) mechanistic proposal.

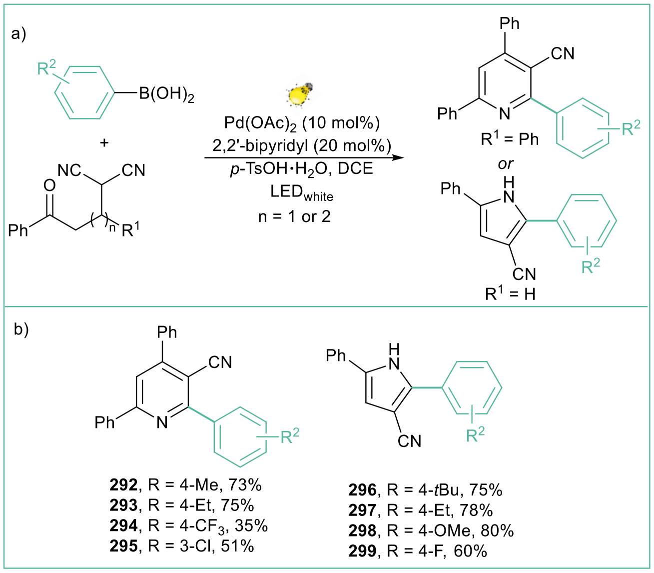


Scheme 59. Photoinduced synthesis of diketones and alkynes: a) model reaction, b) mechanistic proposal and c) representative products.

The Cu-based complex has 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 ($O_2^{\bullet -}$). Next, the independently generated phenyl radical **B'** attacked Cu(II)-phenylacetylide **D** to form α-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 59b). 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 **G**. The photoinduced, Cu-catalysed 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 59c).

Another interesting example for the application of arylboronic acids as precursors of aryl radicals is the synthesis of 3-cyanopyridines (**292**-**295**) and 3-cyanopyrroles (**296**-**299**) (Scheme 60a).[133c] 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 transmetallation 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 60b).

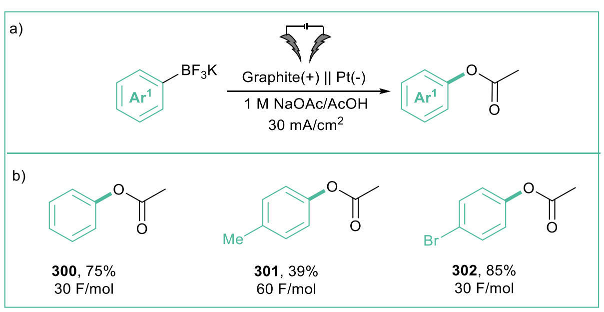


Scheme 60. Synthesis of 3-cyanopyridines and 3-cyanopyrrole analogues from boronic acids: a) model reaction and b) representative products.

4.3.2 Electrochemistry

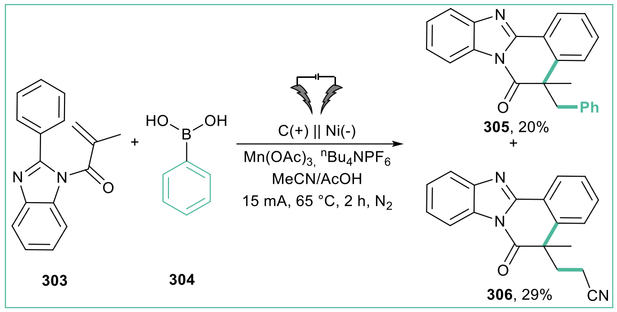
The oxidation potential of phenylboronic acid is equal to E_{ox} = 2.55 V (*vs.* SCE) [18a] and is approximately 0.7 V more positive than that measured for potassium phenyltrifluoroborate (E_{ox} = 1.87 V *vs* SCE). Consequently, the direct electrochemical generation of aryl radical intermediates from phenylboronic acid or phenyl trifluoroboronate 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.[18a] Namely, anodic oxidation of potassium aryltrifluoroborates in 1.0 M NaOAc/AcOH resulted in acetoxylated products (Scheme 61) in 39-85% yields. In the Fuchigami method, a large amount of electricity was needed to complete the electrolysis (up to 60 F·mol^{-1}), yet opening up room for new methods featuring more effective energy and resource utilisation.



Scheme 61. Electrochemical acetoxylation of trifluoroborates: a) model reaction and b) representative products.

Later on, Lei's group developed a Mn(II)-mediated, electrochemically-induced transformation toward functionalized benzo[4,5]imidazo[2,1-*a*]isoquinolin-6(5H)-one derivatives[178] 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 62). In addition to the expected product **305**, a side cyclization product **306** was obtained in 29%, where a reactive radical was derived from the interaction of an initially formed aryl radical and acetonitrile.



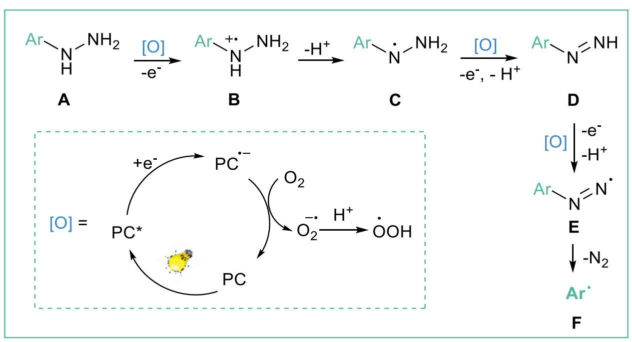
Scheme 62. Mn(II)-catalysed cascade reaction toward the formation of benzo[4,5]imidazo[2,1*a*]isoquinolin-6(5*H*)one derivatives.

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 synthesised *via* a variety of well-established methods. These include a diazotisation/reduction sequence of anilines, palladium or copper-catalysed cross-couplings of aryl halides with hydrazine, or aromatic nucleophilic substitution of aryl halides with hydrazine.[179] Although synthetically useful, as described below, aryl hydrazines have been proven to be highly toxic/carcinogenic[180] which may limit their synthetic usefulness.

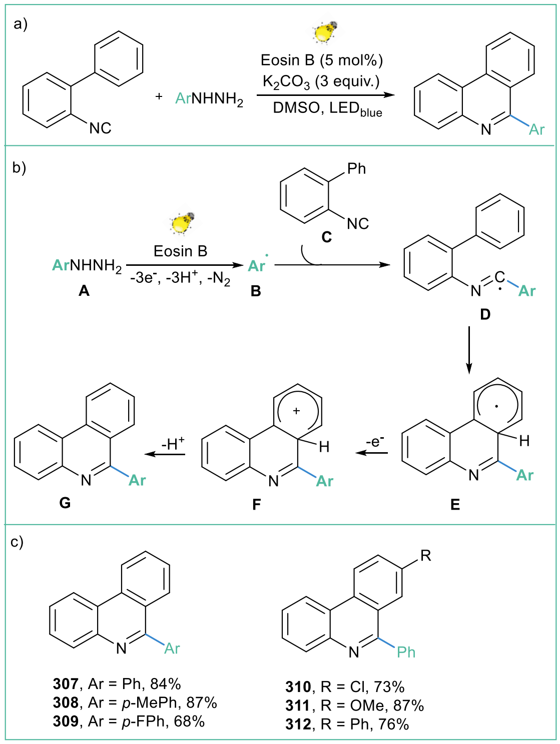
4.3.1 Photoredox catalysis

Irradiation of aryl hydrazines in the presence of a photocatalyst gives easy access to aryl radicals that can further undergo various transformations.[133d] 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 63). 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 63). 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.

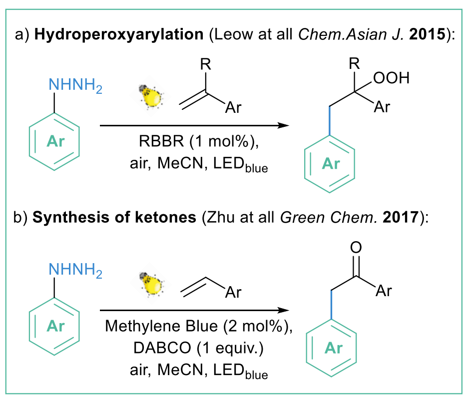


Scheme 63. General mechanistic proposal for the generation of aryl radicals from aryl hydrazines.

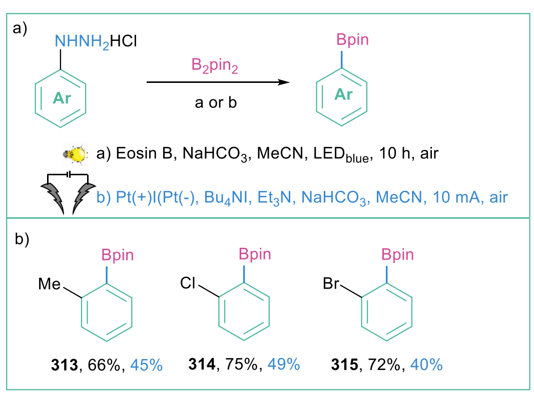
The construction of 6-substituted phenanthridines constitutes an early example of the use of aryl hydrazines as precursors of aryl radicals under light irradiation (Scheme 64a).[133e] The mechanistic proposal assumes the photocatalyzed formation of aryl radical **B** from aryl hydrazine **A** in a stepwise 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 64b). The photocyclization proceeded under mild conditions and is very efficient, since various functional groups are tolerant, and the reaction proceeds in moderate to good yields (Scheme 64c). Later, it was also demonstrated that the same transformation can also be catalysed by the covalent organic framework (COF) as a photocatalyst.[181] The photoinduced reaction of aryl hydrazines with α-substituted styrene derivatives in the presence of a photocatalyst and oxygen leads to hydroperoxyarylation of styrenes (Scheme 65a).[182] The same process, but applied to unsubstituted styrene derivatives, gives rise to benzyl ketones (Scheme 65b).[183]



Scheme 64. Synthesis of C6-substituted phenanthridines from aryl hydrazines: a) model reaction, b) mechanistic proposal and c) representative products.



Scheme 65. Photoinduced reaction of aryl hydrazines with styrene derivatives: a) hydroperoxyarylation and b) synthesis of benzyl ketones.



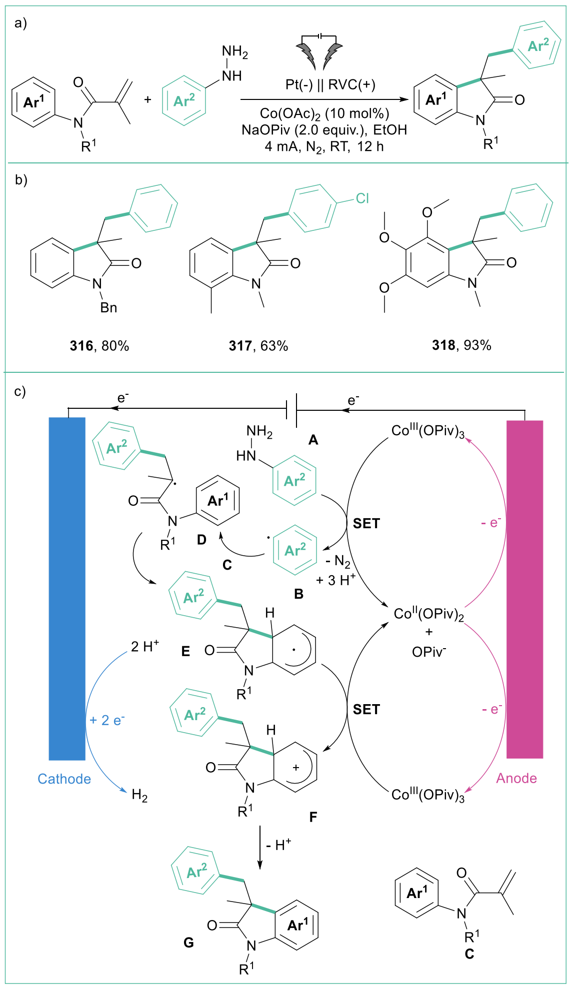
Scheme 66. Photochemical and electrochemical borylation of arylhydrazines hydrochlorides: a) model reactions and b) representative products.

Aryl hydrazines can also be used as radical precursors for transition metal-free borylation (Scheme 66a).[184] Zhang and co-workers demonstrated a comparison of photocatalysed and electrochemical approaches toward the borylation of aryl hydrazines. Generally, the photoredox approach is more efficient than the electrochemical one, however, the electrochemical method is more scalable (Scheme 66b).

4.3.2 Electrochemistry

4.3.2.1 Oxidation of aryl hydrazines

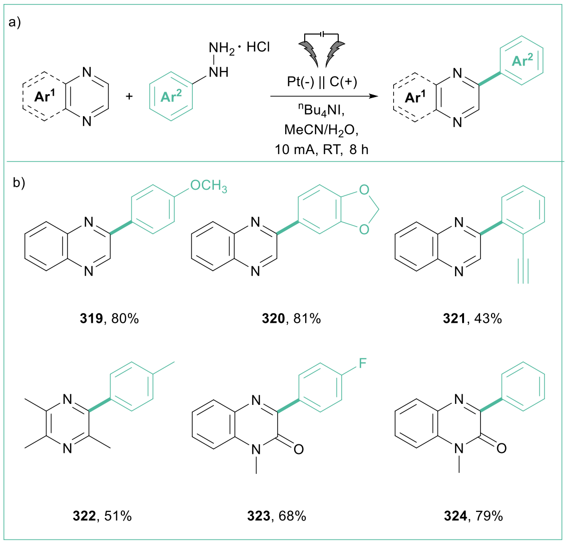
In 2018, Yu *et al.* developed a cobalt-catalysed C-H/C-N oxidative coupling between arylhydrazines and *N*-arylacrylamides that gives oxindoles at room temperature (Scheme 67a).[185] The method tolerates a wide range of electron-withdrawing and electron-donating groups within both substrates, although no regioselectivity was observed for unsymmetrically substituted *N*-acrylamides (Scheme 67b).



Scheme 67. Synthesis of oxoindoles *via* cobalt-catalysed electrochemical C–H/C–N oxidation: a) model reaction, b) representative products and c) mechanistic proposal.

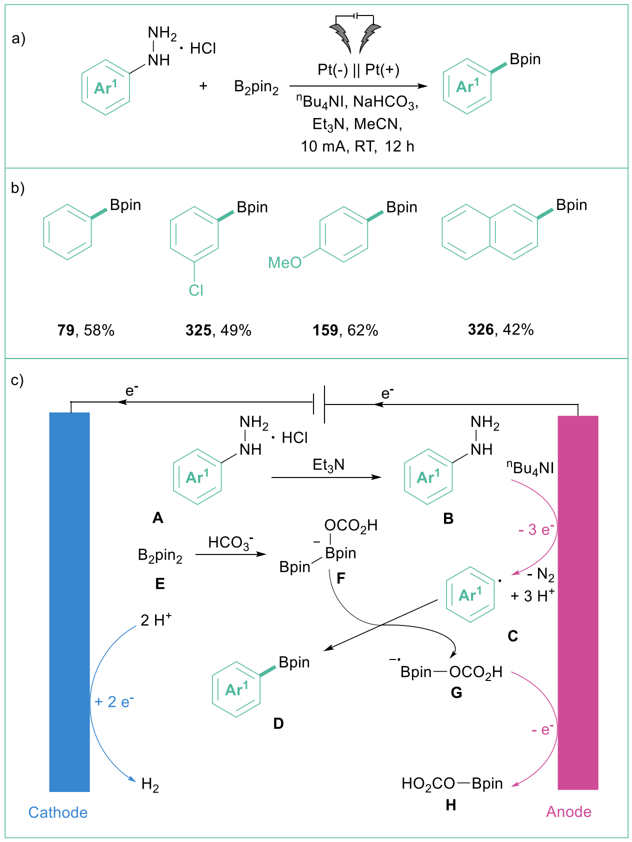
According to the proposed mechanism, once aryl radical **B** is generated from arylhydrazine **A** by Co-mediated anodic oxidation, it attacks *N*-arylacrylamide **C** to gain radical intermediate **D**. Intramolecular cyclization within **D** leads to **E**, which is further oxidised by Co(III)-based 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 68a).[186] The reaction demonstrates a broad functional group tolerance and provides the corresponding aryl products in moderate to excellent yields (Scheme 68b). 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 67c, but this time no metal-based catalyst is necessary.



Scheme 68. Oxidative C−H arylation of quinoxalin(on)es: a) model reaction and b) representative poducts.

A similar reaction system proved viable in an electrochemical C–N borylation of arylhydrazines (Scheme 69a).[184] Substrates containing electron-withdrawing or electron-donating groups in the *ortho, meta* and *para* positions are well tolerated (Scheme 69b). The authors found that the use of $^nBu_4NI$ as an electrolyte is the key to ensure good efficiencies. As depicted on Scheme 69c, once the aryl radical **B** is formed, it then attacks adduct **F** (formed from B_2pin_2 **E** and a bicarbonate ion) to give the desired product **D** and a radical anion **G**, which is then electrochemically oxidized toward the neutral species **H**.

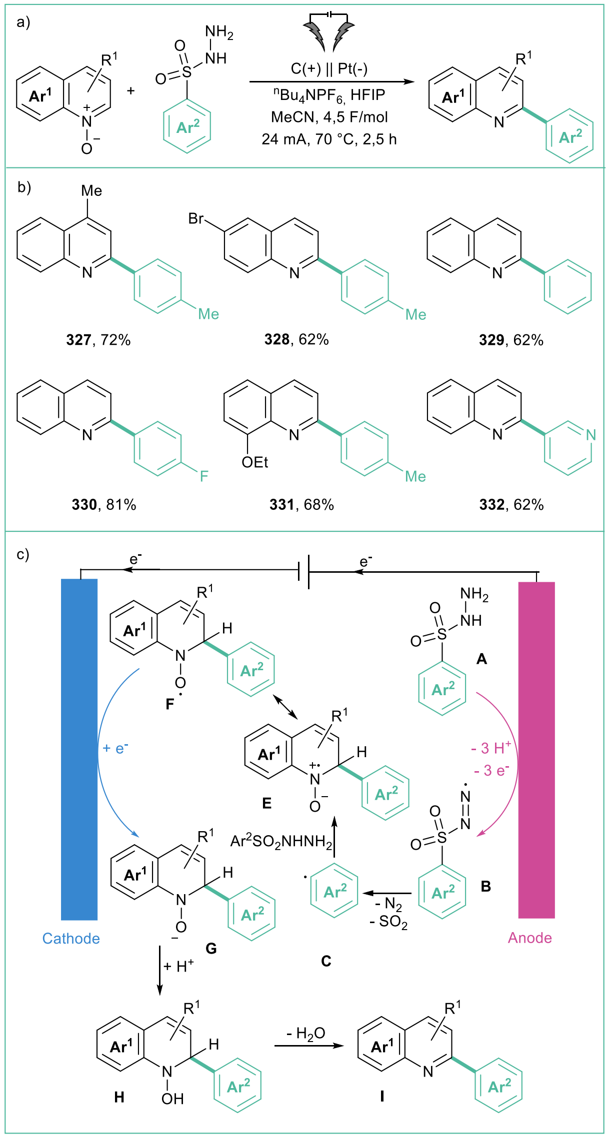


Scheme 69. Electrochemical borylation of arylhydrazines: a) model reaction, b) representative products and c) mechanistic proposal.

4.3.2.2 Oxidation of arylsulfonyl hydrazides

Sulfonyl hydrazides are generally known to form sulfonyl radicals under electrochemical conditions thus leading to a variety of sulfonylation reactions.[187] However, Lei and Wang *et al.* have proven that aromatic sulfonyl hydrazides possess the ability to readily form aryl radicals as well (Scheme 70a).[188] Namely, electrolysis of arylsulfonyl hydrazine in the presence of isoquinoline *N*-oxide in a MeCN/HFIP mixture leads to C2-arylated quinolines with moderate to good efficiencies

(Scheme 70b). While the procedure tolerates a wide range of variously substituted quinoline *N*-oxides, isoquinoline *N*-oxide is not reactive at all. The reaction is initiated by the anodic oxidation of the hydrazine moiety, releasing N_2 and SO_2 and giving rise to an aryl radical A**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 70c). 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.



Scheme 70. Proposed mechanism for the deoxygenative C2 arylation of quinoline *N*-oxides: a) model reaction, b) representative products and c) mechanistic proposal.

5 Summary and outlook

Recent numerous achievements in the field of aryl radical chemistry place demand for the clear and systematized survey that critically and timely sum 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 merge - 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 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 resulted from 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 proper 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 $Ar^{\bullet}$ to Ar^{-} or electrografting. These side reactions may be prevented by using a divided cell, different electrode material, or an electron mediator.[74, 189] 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 to occur within the electrode surface. Possible solution for this particular challenge may be the application of electrodes with already modified surface, as in the work of Berben and others.[190] Such modification may prevent direct arylation of the surface as well as modulate the electron-transfer event itself.

Most of electrochemical reactions presented herein (beside 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[27, 30] have unlocked some challenging aryl radical precursors toward selective electrochemical transformations. Although some organic dyes have been already tested in photoelectrochemical transformations,[27, 30, 79, 191] 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, that stereoselective transformations are pivotal in assembling of 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, overwhelming number of reactions described in this review was performed in solvents featuring similar value of dipole moment (~3.9 D) - MeCN or DMF (often as mixtures with protic solvents – MeOH, AcOH or H_2O). This fact underlines the need for applying polarized environment that will facilitate processes occurred via an electron transfer and/or through charged intermediates.

Taking into account all of the above consideration we certainly can say that electrochemistry started to complete photoredox catalysis in the area of aryl radical generation research, however it is still at the very early stage of the 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 to generate aryl radicals and employ them 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.

Conflicts of interest

There are no conflicts to declare.

Data availability statement

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

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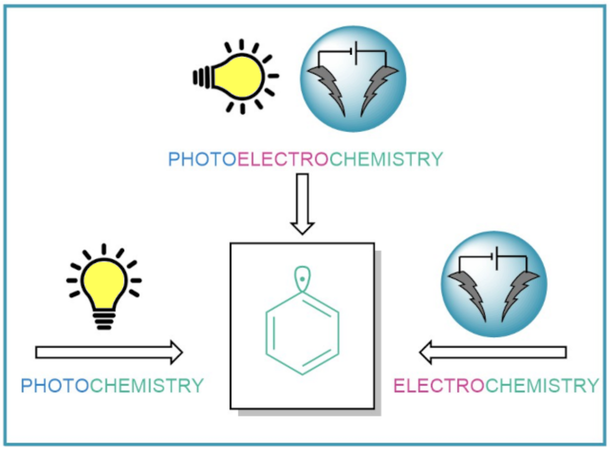
Graphical abstract

This review describes recent advances in the generation of aryl radicals using light and electricity. Such modern techniques allow for the efficient energy and resources utilization thus providing more sustainable radical arylation methods.



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