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Generation of aryl radicals by redox processes. Recent progress in the arylation methodology

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Arylation methods based on the generation and use of aryl radicals have been a rapidly growing field of research in recent years and currently represent a powerful strategy for carbon – carbon and carbon – heteroatom bond formation. The progress in this field is related to advances in the methods for generation of aryl radicals. The currently used aryl radical precursors include aryl halides, aryldiazonium and diaryliodonium salts, arylcarboxylic acids and their derivatives, arylboronic acids, arylhydrazines, organosulfur(II, VI) compounds and some other compounds. Aryl radicals are generated under mild conditions by single electron reduction or oxidation of precursors induced by conventional reagents, visible light or electric current. A crucial role in the development of the radical arylation methodology belongs to photoredox processes either catalyzed by transition metal complexes or organic dyes or proceeding without catalysts. Unlike the conventional transition metal-catalyzed arylation methods, radical arylation reactions proceed very often at room temperature and have high functional group tolerance. Without claiming to be exhaustive, this review covers the most important advances of the current decade in the generation and synthetic applications of (het)aryl radicals. Examples of reactions are given and mechanistic insights are highlighted.
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1. Introduction

Many organic compounds possessing useful properties and applied in the everyday life of people contain an aromatic moiety. Among these compounds are pharmaceutical drugs, agrochemicals, organic functional materials, natural products, *etc*. The key step of their synthesis is often the formation of a substituted aromatic moiety; therefore, the arylation reactions represent an important tool of modern organic synthesis.[1–3] Most of arylation methods used in synthetic practice are based on the formation of carbon – carbon and carbon – heteroatom bonds and proceed in the presence of transition metal catalysts based, first of all, on palladium, nickel, copper, rhodium and ruthenium. Particularly, the classical cross-coupling of aryl (pseudo)halides discovered in the second half of the 20th century and more

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recently discovered CH functionalization methods belong to this type of reactions.[4–6] In the last decades, considerable progress was made in the arylation with the use of aryl radicals. Despite their long history (in particular, Gomberg–Bachmann[7] and Meerwein[8] reactions were first mentioned almost 100 years ago), reactions of aryl radicals, like other free-radical reactions, were little used in synthetic practice: radical reactions rarely served as the basis for efficient general synthetic methods, although they still were employed in the syntheses of complex natural products.[9,10]

The key limitations hampering the use of aryl radicals were related to the difficulty of their generation. However, aryl radicals possess high reactivity,[11] and reactions characteristic of these species proceed under relatively mild conditions.[9,12]

The successful recent development of synthetic methods involving free radicals, including radical arylation, is inseparably connected with the progress in the (photo)redox catalysis[13–16] and with the use of visible light[17,18] and electrical current[19] for initiation of organic reactions. In addition, the development of new radical transformations was promoted by studies combining photoredox catalysis and organometallic catalysis by transition metal compounds.[20]

The progress in the synthetic use of aryl radicals was reflected in several recent analytical reviews. Among them, note the reviews addressing transition metal catalysis in the radical arylation,[21] reactions initiated by photochemical[22–26] and electrochemical[27,28] methods, successful synthesis of biaryl compounds[29–31] and radical reactions of diazonium salts.[7,8,32,33] A small chapter considering the radical arylation is included in a review[34] devoted to the recent advances in the functionalization of quinones. The generation of isomeric pyridyl radicals to be used in the synthesis of substituted pyridines is the subject of a mini review.[35]

Efficient development of the methodology of radical arylation is impossible without simultaneous development of methods for the generation of aryl radicals. To our knowledge, no integrated accounts of these methods including their comparative analysis and particular synthetic applications can be found in the literature. Meanwhile, the aryl radical generation step and selection of the appropriate precursor are the key aspects determining the efficiency of the arylation reaction as a whole. The present analytical review addresses particularly this aspect of radical arylation reactions and, in our opinion, this is a well-timed integration of numerous experimental data accumulated to date.

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Translation: Z.P.Svitanko

This review considers virtually all known precursors of aryl radicals and different methods for the generation of aryl radicals from the same precursors. Nevertheless, we do not claim to exhaustively cover all known examples. In our opinion, this would be impossible within a single review, because of the vigorous development of this synthetic strategy. For each precursor, we tried to collect most typical examples of generation and subsequent application of aryl radicals and to demonstrate the capabilities and limitations of both the radical generation technique and arylation reaction as a whole. We considered in detail the mechanisms of redox processes of aryl radical generation and formation of arylation products.

The classification of the material is based on the types of radical precursors. Depending on the chemical features of the precursors, methods of aryl radical generation can be divided into those using reduction and oxidation reactions (Fig. 1). The reductive conversion to aryl radicals can be carried out for aryl halides, aryldiazonium salts and related compounds, diaryliodonium salts, *N*-arylpyridinium salts, arylsulfonoium salts and aromatic sulfonyl chlorides. The oxidative generation of aryl radicals is characteristic of arylhydrazines and aromatic carboxylic and arylboronic acids. In both cases, applicable redox reactions can involve both ground and excited electronic states and can be both catalyzed and proceed without catalysts. The review mainly addresses the addition of aryl radicals to π-systems (carbo-

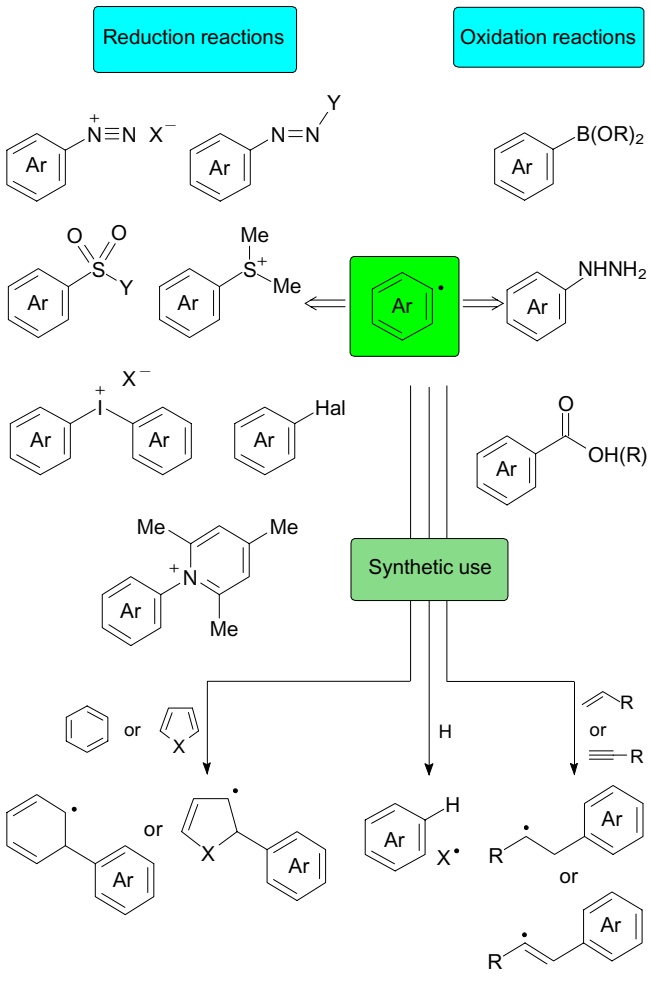


Figure 1. Generation methods and synthetic use of aryl radicals.

cyclic and heterocyclic aromatic compounds, alkenes and alkynes). These reactions give rise to new radical intermediates, which are finally converted to arylation products. In addition, cases are mentioned where aryl radicals serve for the generation of radicals of a different type *via* hydrogen atom elimination (see Fig. 1).

The following acronyms and designations are used in the review:

A — acceptor,
acac — acetylacetonate,
B — base,
bcp — 2,9-dimethyl-4,7-diphenylphenanthroline,
bpy — 2,2′-bipyridine,
bpz — 2,2′-bipyrazine,
Boc — *tert*-butoxycarbonyl,
BODIPY — 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene,
B_2pin_2 — bis(pinacolato)diboron,
BQ — benzoquinone,
Cat — catalyst,
CFL — compact fluorescent lamp,
Cp — cyclopentadienyl,
Cy — cyclohexyl,
D — donor,
DABCO — 1,4-diazabicyclo[2.2.2]octane,
DCA — 9,10- dicyanoanthracene,
DCC — dicyclohexylcarbodiimide,
DCE — 1,2-dichloroethane,
DCN — 1,4-dicyanonaphthalene,
DFT — density functional theory,
DIPEA — *N*,*N*-diisopropylethylamine,
DMA — dimethylacetamide,
dme — dimethoxyethane,
DMEDA — *N*,*N*′-dimethylethylenediamine,
DPEphos — bis[(2-diphenylphosphino)phenyl] ether,
dppb — 1,4-bis(diphenylphosphino)butane,
dppf — 1,1′-bis(diphenylphosphino)ferrocene,
dr — diastereomeric ratio,
dtbbpy — 4,4′-di-*tert*-butyl-2,2′-bipyridine,
E_{red} — reduction potential,
EDA — electron donor–acceptor complex,
EDG — electron-donating group,
EWG — electron-withdrawing group,
FG — functional group,
Hbipo — 2,3-bis(imidazo[1,2-*a*]pyridin)-2-one,
IBA — 2-iodosobenzoic acid,
IBX — iodoxybenzoic acid,
LED — light-emitting diode,
Mes — mesityl (2,4,6-thimethylphenyl),
MIDA — *N*-methyliminodiacetic acid,
MW — microwave irradiation,
Nu — nucleophile,
PANI — polyaniline,
PC — photocatalyst,
PDI — perylenediimide,
Phen — 1,10-phenanthroline,
Piv — pivaloyl,
PTH — 10-phenylphenothiazine,
ppy — 2-phenylpyridine,
Py — pyridyl,
rGO — reduced graphene oxide,
Rh-6G — Rhodamine 6G,
rt — room temperature,
SCE — saturated calomel electrode,
SET — single electron transfer,
Sub — substrate,
tap — tetrakis(4-anisylporphyrinato) dianion,
TBHP — *tert*-butyl hydroperoxide,
terpy — terpyridine,
Tf — trifluoromethanesulfonyl (triflyl),
TFA — trifluoroacetic acid,
TFE — 2,2,2-trifluoroethanol,
TFT — α,α,α-trifluorotoluene,
Th — thienyl,
TMEDA — *N*,*N*,*N*′,*N*′-tetramethylethylenediamine,
TMP — trimethoxyphenyl,
TMS — thimethylsilyl,
Ts — *p*-toluenesulfonyl (tosyl),
UV — ultraviolet radiation.

2. Reductive generation of aryl radicals

2.1. Generation of aryl radicals from aryl halides

Aryl halides are readily available and stable compounds, widely used as sources of aryl groups in transition metal-catalyzed arylation reactions.[4] The key step of these reactions is the two-electron reduction of aryl halides by transition metals (or metal ions) to give reactive organometallic compounds. The single-electron reduction of aryl halides with simultaneous elimination of halide ion results in the formation of reactive aryl radicals. The generation of these radicals from aryl halides is quite a challenge because of high strength of the carbon–halogen bond.[12,36] Traditional approaches to the generation of radicals from aryl halides make use of UV irradiation,[12] hydride reagents or other compounds possessing strong reducing properties and promoting halide elimination.[37–39] Drawbacks of these methods are related to the necessity to use stoichiometric amounts of toxic reagents or specific equipment.

This Section starts with the consideration of photoinitiated radical reactions of aryl halides. Subsequently, methods for generation of aryl radicals from aryl halides that do not use irradiation are presented, including reactions initiated by bases and/or organic electron donors.

2.1.1. Photoinitiated reactions of aryl halides

In the last several years, reactions of organic compounds initiated by visible light have attracted special attention of chemists. Most of reactions of this type are easily implemented under mild conditions at room temperature and require a relatively small amount of a photoredox catalyst and, in some cases, require no catalyst at all.[22,23,40–46]

Photoinitiated reactions can be divided into two types: those using (Fig. 2 *a*,*b*) and not using a photocatalyst (Fig. 2 *c*). In the former case, irradiation brings the photocatalyst (PC) to an electronically excited state (marked by an asterisk). The excited photocatalyst either participates in the redox reaction with a reagent as an electron donor (D) or electron acceptor (A) (reductant or oxidant, respectively, see Fig. 2 *a*)[47,48] or transfers energy to the reagent molecule, which is thus electronically excited (see Fig. 2 *b*).[49,50] Reactions of the latter type start with the formation of an electron donor–acceptor complex (EDA) between the reactant molecules. If EDA is able to absorb visible light (unlike the reactants), it acts as an endogenous photosensitizer.[51–53] The EDA absorbs a light quantum to be converted to an excited state, the subsequent single electron transfer (SET) from the donor to the acceptor and radical recombination afford the reaction product (see Fig. 2 *c*). In

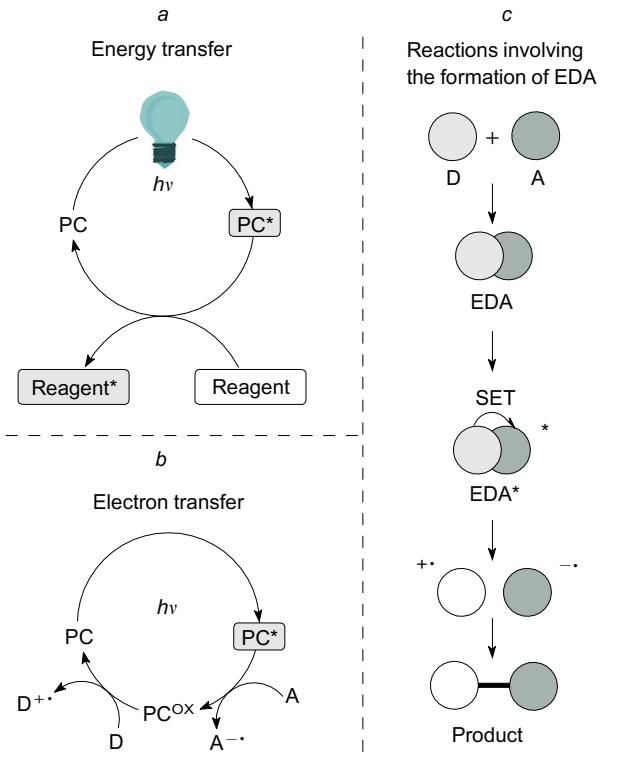


Figure 2. Key mechanisms of light-initiated reactions. PC^{OX} is the oxidized form of the photocatalyst.

some cases, EDA does not undergo intrasystem single-electron transfer, but transfers energy (as shown in Fig. 2 *b*).

Three key types of photocatalysts can be distinguished:

— transition metal complexes, mainly ruthenium(II) polypyridine complexes and related cyclometallated iridium(III) complexes [44] and also complex compounds of other transition metals;[54]

— organic dyes [26] (eosin,[55,56] fluorescein, rhodamine, fluorenone, anthraquinones,[57] phenothiazines [58] and so on);

— inorganic compounds possessing semiconductor properties (TiO_2, CdS and so on).

Photocatalysts based on transition metals possess high stability and long excited state lifetimes; moreover, the catalyst properties can be finely tuned by modification of ligands. Organic photocatalysts are attractive for their low cost, high structural diversity and, as a consequence, various redox properties. Methods that utilize organic photocatalysts are characterized by environmental friendliness and do not cause problems associated with the use of toxic heavy metals, in particular, there is no need to additionally purify reaction products for pharmaceutical purposes.[59,60]

The formation of aryl radicals from aryl halides is also induced by means of hybrid catalytic systems combining a transition metal-based catalyst and a photoredox catalyst.[60–69] In addition, some known radical reactions of aryl halides initiated by visible light proceed in the presence of classical catalytic systems based on transition metals (Pd, Cu, Fe) without additional photosensitizers.[69–72] Reactions of this type have been considered in detail in analytical reviews of Gevorgyan and co-workers [73,74] and are beyond the scope of this review.

Being reactions of compounds in electronically excited states, visible light-initiated reactions, which have been actively developed in recent years, offer wide opportunities for organic synthesis, since they allow transformations that are impossible or difficult for the ground electronic states of the same molecules. In particular, it was shown that the activity and selectivity can be controlled by changing the source of excitation for the same catalyst, which opens up the way for a step-by-step increase in the molecular complexity by changing the source of light.[75]

Unlike other precursors of aryl radicals, which are considered below, aryl halides are not readily reduced by photoinitiated electron transfer from the photoredox catalyst [the reduction potential (E_{red}) *versus* saturated calomel electrode (SCE) is less than -1.2 V, especially for aryl chlorides ($E_{red} \approx -2.8$ V)], which restricts the choice of the photocatalyst.[23,26]

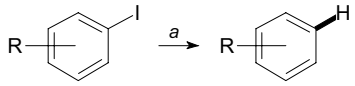
2.1.1.1. Formation of the C–H bond

The reductive hydrodehalogenation of aryl halides — an important process used for detoxification of products of organic synthesis — is traditionally carried out under harsh conditions or in the presence of transition metals.[76] The development of photoinitiated radical reactions of these compounds allows the reactions to be conducted under milder and more environmentally benign conditions.

The photochemically initiated reduction of aryl halides to arenes proceeds *via* the intermediate generation of aryl radicals. Stephenson and co-workers [77] reported an example of reduction of iodoarenes using the complex *fac*-$Ir^{III}(ppy)_3$ (ppy is 2-phenylpyridine) (Scheme 1; here and below the bond being formed is marked in bold). König and co-workers [78] developed a related method for the reduction of aryl halides ArX (X = I, Br, Cl) in the presence of perylenediimide (PDI, **1**), an organic photoredox catalyst (Scheme 2); the role of such catalyst can also be played by 10-phenylphenothiazine.[79] An alternative method for reductive hydrodehalogenation of aryl halides proposed by König and co-workers [80] is based on the use of chrysazine (1,8-dihydroxyanthraquinone) as a photoredox catalyst, irradiation at 455 nm and the presence of Et_3N (1 equiv.). Satisfactory or good yields of products were obtained for aryl bromides and iodides with electron-withdrawing substituents.

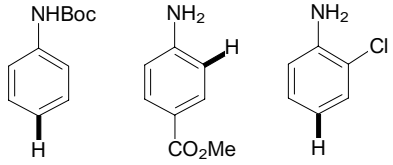
Catalytic systems composed of transition metal nanoparticles supported on inorganic semiconductors can act as photoredox catalysts for the generation of aryl radicals. The Au/CdS system was used for deuteration of aryl halides on exposure to visible light at >400 nm in the presence of D_2O as a source of deuterium. The method is equally efficient for

Scheme 1



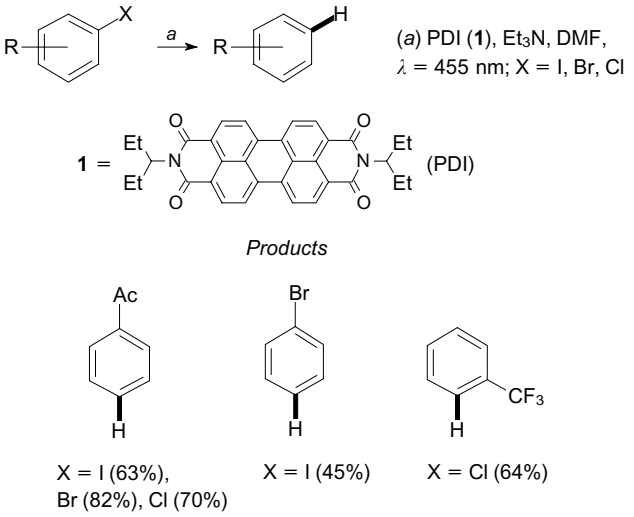
(*a*) *fac*-$Ir^{III}(ppy)_3$, Bu^n_3N, HCO_2H, MeCN, visible light; Boc is *tert*-butoxycarbonyl

Products



(97%) (93%) (94%)

Scheme 2



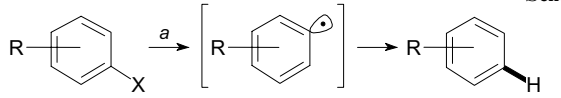
aryl iodides, bromides and chlorides. The deuteration follows a radical pathway, which includes the carbon–halogen bond activation upon ptotoinduced electron transfer from the catalyst to the aryl halide molecule to give the aryl radical.[81]

The reductive dehalogenation of aryl halides was induced by UV irradiation (λ = 254 nm) or heating at 250 °C in an excess of triethylamine or in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO). The reaction includes the electron transfer from the Et_3N molecule to the aryl halide molecule to generate the corresponding radical anion, which loses the bromide ion to be converted to the aryl radical.[82] The radical cation of the tertiary amine serves as the proton donor. This reaction can be performed for various aryl halides, including aryl chlorides.

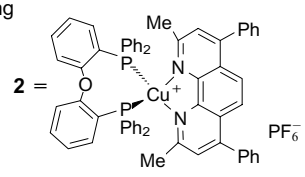
A method for radical reductive dehalogenation of aryl halides with tris(thimethylsilyl)silane upon irradiation with a compact fluorescent lamp (CFL) has been reported. This method is applicable only to aryl iodides and tolerates some sensitive functional groups.[83]

The formation of aryl radicals from aryl halides on irradiation with visible light takes place also in the presence of the copper-based photoredox catalyst $[(DPEphos)(bcp)Cu]PF_6$ (**2**) and an excess of *N*,*N*-diisopropylethylamine (DIPEA) (Scheme 3).[84] The best yields of reductive dehalogenation products were attained for aryl

Scheme 3



(*a*) $[(DPEphos)(bcp)Cu]PF_6$ (**2**),
DIPEA, MeCN, blue light; R = Ph, EDG, EWG;
DPEphos is bis[(2-diphenylphosphino)phenyl] ether,
bcp is 2,9-dimethyl-4,7-diphenylphenanthroline;
R = ED(W)G, electron-donating
(withdrawing) groups;



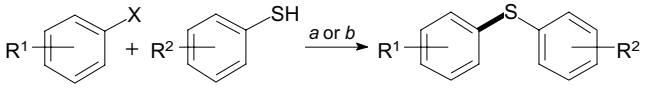
($[(DPEphos)(bcp)Cu]PF_6$)

halides with electron-withdrawing substituents, while in the case of strong electron-donating substituents, the corresponding arenes were formed in low yields. The yields also considerably depended on the halogen atom. Indeed, in the case of R = 4-CO_2Me, the yield was 90% for X = I, 55% for X = Br and only 15% for X = Cl.

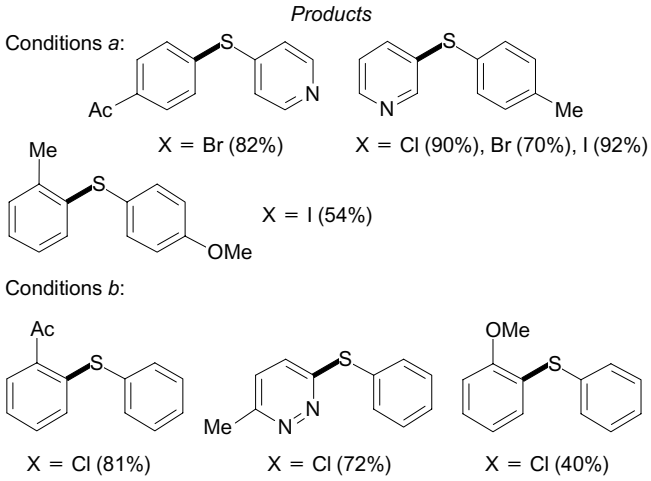
2.1.1.2. Formation of the C–S bond

Miyake and co-workers [85] developed a method for the synthesis of diaryl thioethers by visible light-initiated arylation of thiophenols at room temperature in the absence of photocatalysts. The reaction proceeded *via* the formation of EDA, which was detected in the absorption spectra (Scheme 4,† conditions *a*). This reaction is most efficient for aryl bromides and iodides that do not contain strong electron-withdrawing groups. Brominated pyridine, quinoline and pyrimidine derivatives can be used as aryl halides.[85,86] Fu and co-workers [87] proposed a synthesis of diaryl thioethers using the same starting compounds and the complex *fac*-Ir(ppy)$_3$ as the photocatalyst (see Scheme 4, conditions *b*). The same catalyst can be used to perform photoinitiated arylation of disulfides with aryl iodides to give aryl alkyl sulfides.[88]

Scheme 4



(*a*) for X = Cl, Br, I: Cs_2CO_3, DMSO, 25 °C, visible light;
(*b*) for X = F, Cl, Br, I: *fac*-$Ir^{III}(ppy)_3$ (**1**), Cs_2CO_3, DMF, 25 °C, visible light

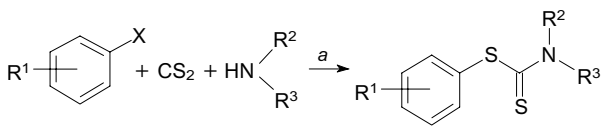


An efficient method was proposed for the preparation of *S*-aryl dithiocarbamates by the reaction of aryl iodides, carbon disulfide and primary amines (Scheme 5). The reaction proceeds without photocatalysts *via* the intermediacy of EDA.[89]

The visible light-initiated reactions of aryl halides form the basis of synthetic routes to aryl sulfones using sodium arenesulfinates. One of them includes the formation of an electron donor–acceptor complex from aryl halide and arenesulfinate; the complex absorbs light at 365 nm to be

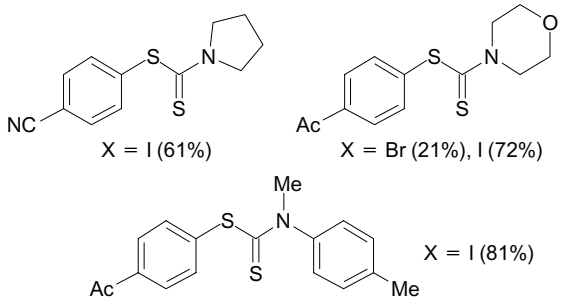
† Some Schemes show the main reaction for arenes, while the applicability of hetarenes is reflected in the structure of products.

Scheme 5



(*a*) Cs_2CO_3, DMSO, visible light, 25 °C; X = Br, I

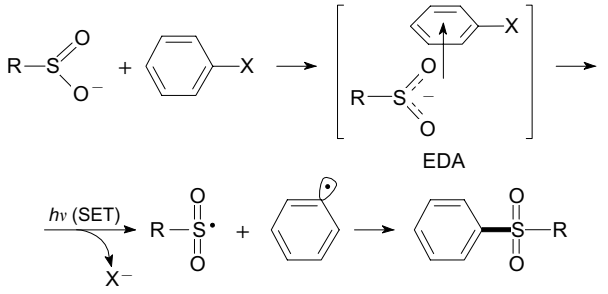
Products



X = I (61%) X = Br (21%), I (72%)

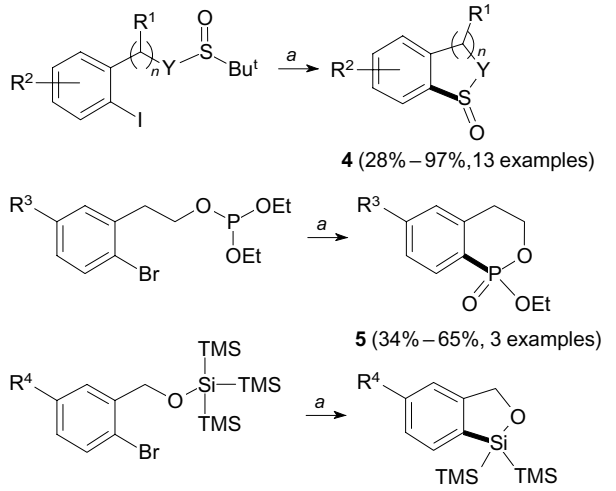
X = I (81%)

Scheme 6



EDA

Scheme 7

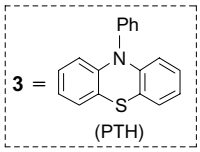


4 (28% – 97%,13 examples)

5 (34% – 65%, 3 examples)

6 (38% – 71%, 4 examples)

(*a*) PHT (**3**), DIPEA, MeCN, N_2, 25 °C;
4: *n* = 1, Y = NH, R^1 = H:
R^2 = H (66%), 5-CF_3 (68%);
n = 2, Y = NMe, R^1 = R^2 = H (28%), *etc.*;
5: R^3 = H (50%), OMe (34%), Cl (65%);
6: R^4 = H (71%), OMe (38%), CF_3 (62%), Cl (46%);
TMS is trimethylsilyl



(PTH)

brought to the excited state and undergoes an intrasystem single-electron transfer (Scheme 6).[90] A similar process takes place upon blue light irradiation (λ = 435 – 455) of a mixture of aryl halides and arenesulfinates in the presence of a base and a Hantzsch ester (diethyl 1,4-dihydro-2,6-dimethylpyridine-3,5-dicarboxylate) as the photoinitiator. According to the mechanism proposed by the authors, the photoinitiated electron transfer to the EDA formed by an aryl halide molecule and the Hantzsch ester anion gives rise to an aryl radical.[91] Both methods result in high yields of sulfones when conducted for aryl iodides and bromides with electron-withdrawing substituents and also for halo derivatives of electron-deficient heterocyclic compounds. For 4-Y-substituted iodobenzenes, the product yields were 86%, 61%, 64%, 42%, 49% and 71% for Y = CN, Ac, CO_2Me, CHO, F and CF_3, respectively.

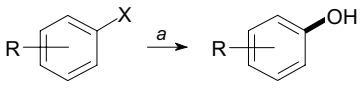
The photocatalytic single-electron reduction of aryl halides was used in the general synthesis of benzannulated heterocycles and their aza analogues (Y = N). The synthesis included the C – S, C – P or C – Si bond formation step (Scheme 7; the substituent position is indicated for the product).[92] The heterocyclizations were performed with 10-phenylphenothiazine (PTH, **3**) as the photoredox catalyst on exposure to light at 385 nm in the presence of DIPEA (2.5 equiv.) as an electron donor. The aryl radical is generated *via* single-electron reduction of the carbon – halogen bond by excited 10-phenylphenothiazine, while the subsequent interaction of the radical centre with the lone electron pair of the heteroatom or with the Si – Si bond leads to heterocyclic systems **4** – **6** and departure of the leaving group.

Ultraviolet irradiation was used to generate aryl radicals from aryl iodides in the synthesis of 2-arylsulfonylacetonitriles involving the complex of DABCO with SO_2. In the key step of the synthesis, the aryl radical adds to sulfur(IV) oxide to afford the arylsulfonyl radical.[93]

2.1.1.3. Formation of the C – O bond

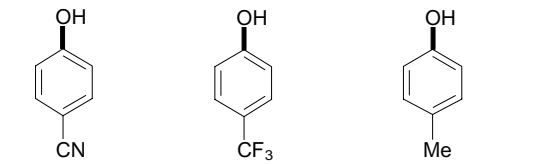
UV-initiated hydroxylation of aryl halides in the presence of sodium iodide, triethylamine and oxygen has been developed.[94] Substituted phenols with a variety of functional groups can be obtained in good yields using aryl chlorides, iodides or bromides (Scheme 8).[94]

Scheme 8



(*a*) Et_3N, NaI, MeCN, UV, O_2, 32 °C; UV is ultraviolet radiation

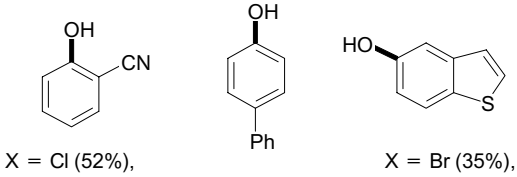
Products



X = Cl (60%), Br (75%), I (71%)

X = Cl (70%), Br (76%), I (81%)

X = Cl (35%), Br (42%), I (53%)

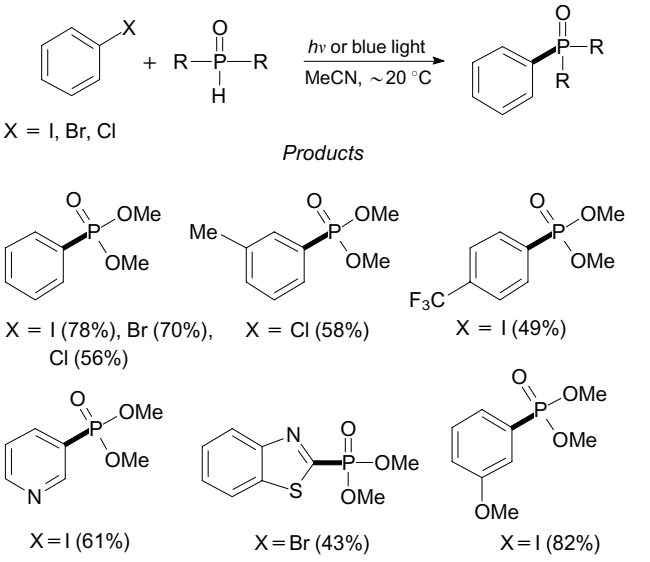


X = Cl (52%), Br (64%), I (67%)

X = Cl (37%), Br (43%), I (68%)

X = Br (35%), I (71%)

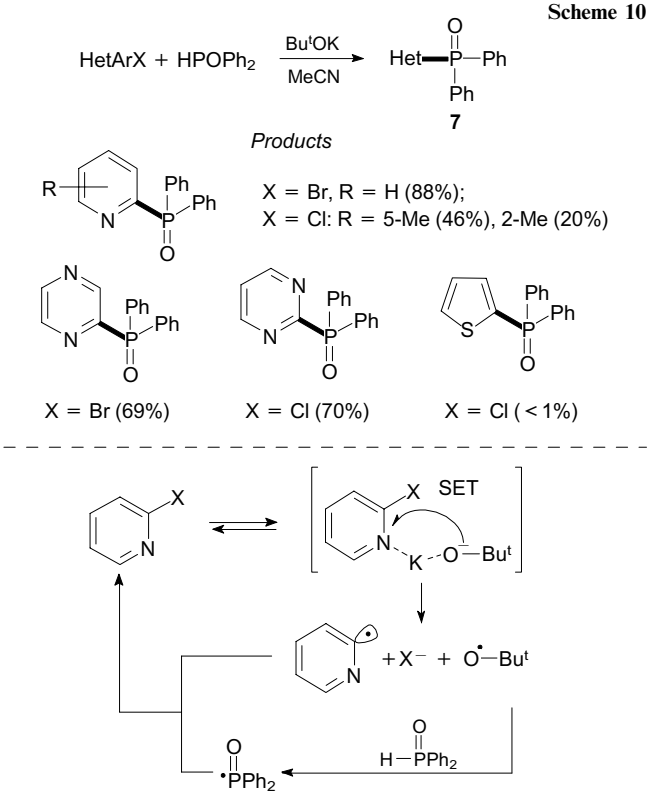
Scheme 9



2.1.1.4. Formation of the C – P bond

Homolysis of the carbon – halogen bond on exposure to UV radiation at 254 nm underlies the arylation of H-phosphonates with aryl halides (Scheme 9).[95] This method is applicable to various aryl halides, including aryl chlorides and structurally diverse heterocyclic halides. Visible light irradiation is ineffective for initiation of the reactions. König and co-workers [96] proposed a related reaction for the synthesis of aryl- and hetarylphosphonates from the corresponding halogen derivatives and trialkyl phosphites in the presence of DIPEA and rhodamine 6G (Rh-6G) as the photoredox catalyst under blue light irradiation at 455 nm. In the electronically excited state, rhodamine 6G oxidizes DIPEA to give the $[Rh\text{-}6G]^{-\bullet}$ radical anion, which, in turn, reduces aryl halides, thus generating the corresponding radicals. This approach is implemented for generation of aryl radicals with electronically different substituents and various hetaryl radicals.[96]

Scheme 10

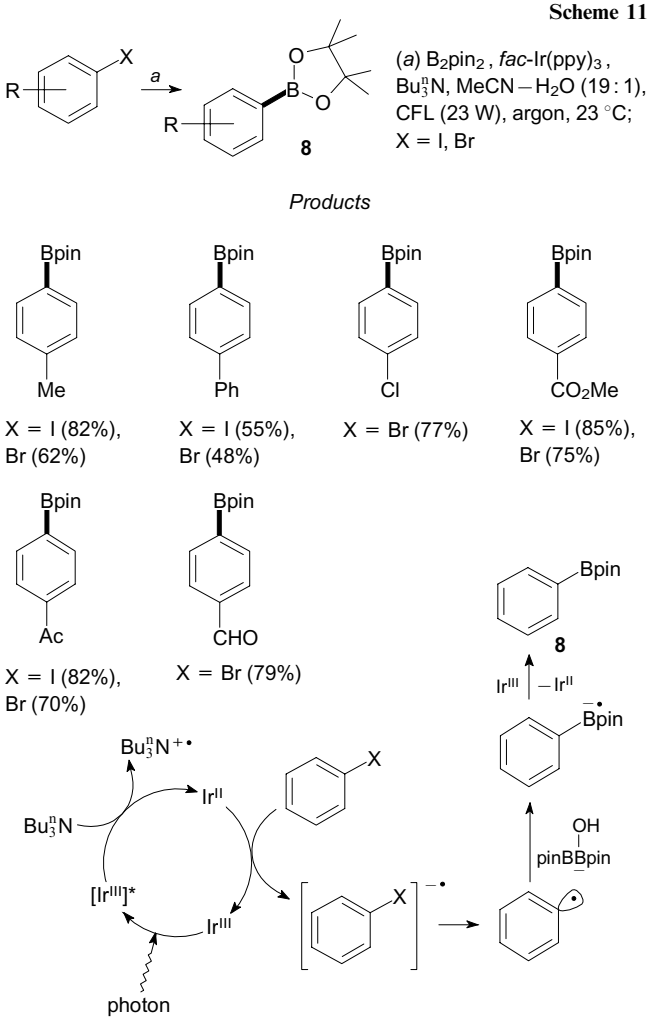


The reaction of hetaryl halides with diarylphosphine oxides performed in the presence of potassium *tert*-butoxide under blue light irradiation affords hetarylphosphine oxides **7** (Scheme 10).[97] The highest yields of arylation products were obtained in the case of bromides of electron-deficient heterocyclic compounds: pyridines, quinolines, pyrimidines and pyrazines. However, halogen derivatives of five-membered aromatic heterocycles are not converted to arylation products in high yields. According to the proposed mechanism, which is depicted in Scheme 10 for halopyridines, the donor – acceptor complex formed by hetaromatic halide and potassium *tert*-butoxide molecules is the key intermediate of this reaction; the formation of this complex was confirmed by electronic absorption spectra. The complex undergoes photoinduced electron transfer, which finally furnishes hetaryl and *tert*-butyl radicals. The latter participates in the generation of an organophosphorus radical, which recombines with the aryl radical to give the arylation product.

2.1.1.5. Formation of the C – B bond

Aryl bromides and iodides were utilized for the preparation of boronic acid esters by the photoinitiated reaction with bis(pinacolato)diboron (B_2pin_2) catalyzed by *fac*-Ir(ppy)$_3$ in the presence of Bu^n_3N under irradiation with a 23 W

Scheme 11



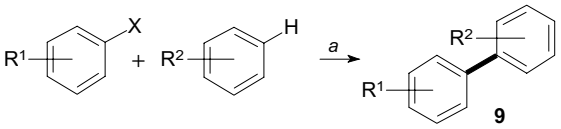
compact fluorescent lamp.[98] According to the proposed mechanism, excited iridium(III) is reduced by the amine to Ir^{II}, which serves as the electron donor for aryl halide. The aryl radical generated in this way reacts with activated B_2pin_2 (Scheme 11). The highest yields of borylation products **8** are obtained for aryl halides with electron-withdrawing substituents, although in this case, too, longer irradiation is required for bromides.

A similar photoinitiated borylation of aryl halides with bis(pinacolato)diboron can be carried out using a phenoxazine derivative as an organic photoredox catalyst.[99]

2.1.1.6. Formation of the C – C and C – N bonds

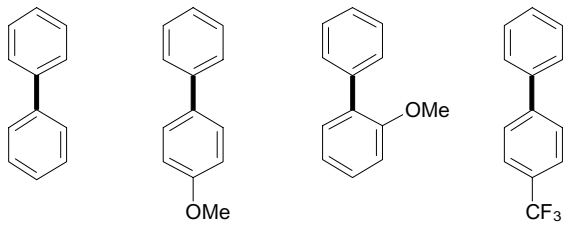
A method has been developed for the arylation of unactivated arenes with aryl halides in the presence of Bu^tOK under visible light irradiation and with *fac*-Ir(ppy)$_3$ as the photoredox catalyst (Scheme 12).[100] The aryl radicals are generated *via* photoinduced single-electron reduction of ArX to give the $[ArX]^{-\bullet}$ radical anion, which eliminates a halide anion. This furnishes biaryls **9**.

Scheme 12



(*a*) *fac*-Ir(ppy)$_3$, Bu^tOK, DMSO, visible light, 70 °C; X = I, Br

Products



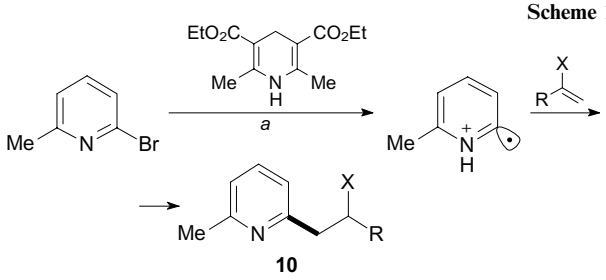
X = Br (79%) X = Br (80%) X = Br (77%) X = Br (40%)

The generation of aryl radical forms the basis for a synthesis of 1,3-dihydroisobenzofurans *via* intramolecular cyclization catalyzed by an iridium photoredox catalyst under irradiation by a compact fluorescent lamp or a source of blue light.[101] A similar intramolecular cyclization proceeds in the presence of gold complexes as photocatalysts[102] or in the presence of tris(thimethylsilyl)silane for photochemical generation of aryl radicals.[103]

The single-electron reduction of halopyridines in the presence of an iridium photocatalyst and Hantzsch ester affords the corresponding pyridinium radical, which then reacts with alkene (Scheme 13).[104] The role of the Hantzsch ester in this reaction is to reduce the photoexcited Ir^{III} complex to the Ir^{II} complex, which participates, together with 2,2,2-trifluoroethanol (TFE), in the concerted electron and proton transfer to a bromopyridine molecule. The yields of products **10** are moderate.

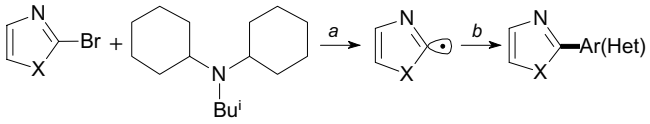
An iridium(III) complex, together with isobutyldi(cyclohexyl)amine, was used for the photoinitiated formation of 2-azolyl radicals from 2-bromoazoles. The heterocyclic radicals generated in this way serve as effective arylating agents towards several electron-rich arenes and hetarenes (Scheme 14).[105]

Scheme 13



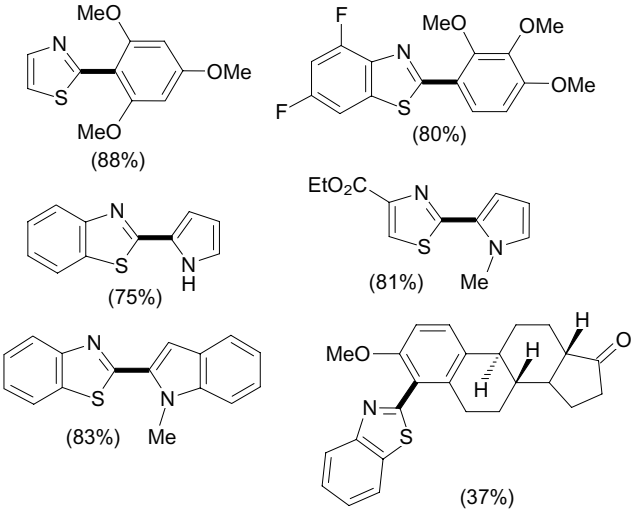
(*a*) Ir(ppy)$_2$(dtbbpy)$^+$, CySH, TFE, light; R = H: X = Br (78%), Bpin (58%), OAc (57%), O(CH$_2$)$_2$OH (72%); R = Me, X = Cl (70%); R = n-C$_6$H$_{13}$, X = F (65%); dtbbpy is 4,4′-di-*tert*-butyl-2,2′-bipyridine, Cy is cyclohexyl

Scheme 14



(*a*) *fac*-Ir(ppy)$_3$, K_2CO_3, MeCN, blue light, argon, 45 °C; (*b*) Ar(Het)H

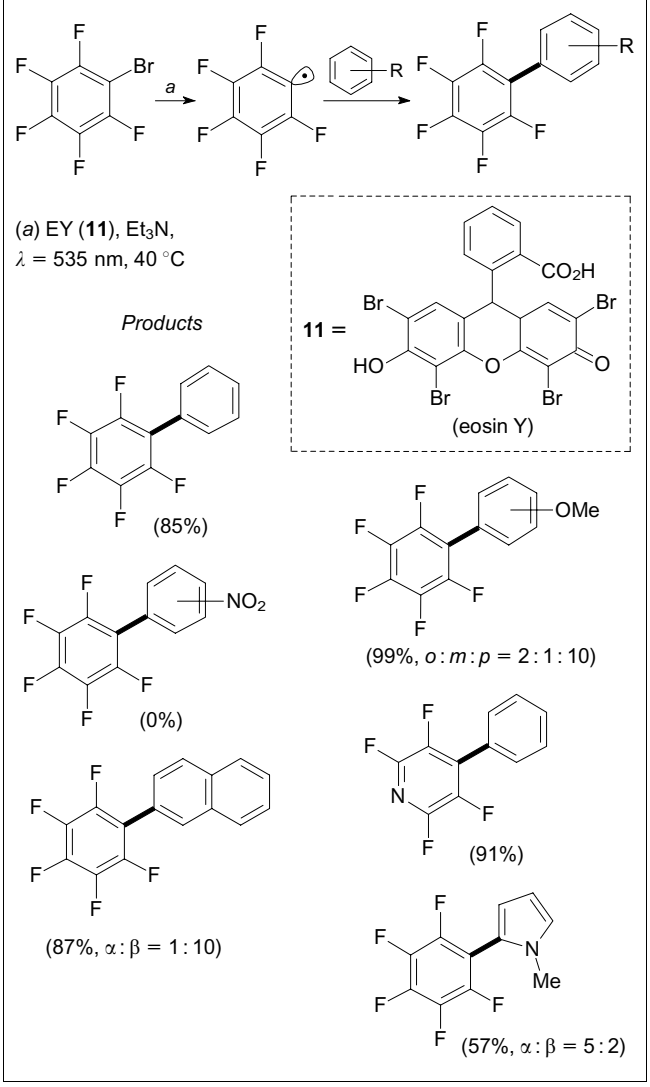
Products



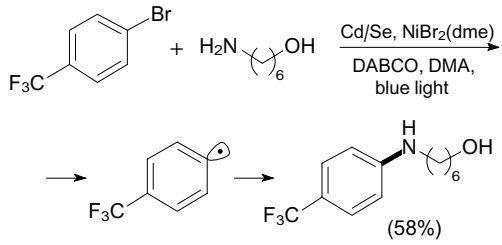
The generation of pentafluorophenyl radical from C_6F_5Br under irradiation with green light at 535 nm in the presence of eosin Y (**11**) as an organic photoredox catalyst and Et_3N as an electron donor provides the synthesis of polyfluorinated biaryls (Scheme 15).[106] Polyfluorinated aryl and pyridyl radicals were also generated from appropriate perfluoroarenes and perfluoropyridine under blue light irradiation in the presence of *fac*-Ir(ppy)$_3$ as a photocatalyst and *N*,*N*-diisopropylethylamine. These radicals were subsequently used in reactions with electron-rich (het)arenes for the synthesis of polyfluorinated bi(het)aryls.[107]

The photochemical generation of triplet aryl radicals from aryl halides can also take place in the presence of the decatungstate anion $[W_{10}O_{32}]^{4-}$ in polar protic solvents.[108] The colloidal nanocrystalline Cd/Se quantum dots of 3 nm size serve as efficient photoredox catalysts for the generation of aryl radicals from aryl bromides with C – N bond formation (Scheme 16).[109]

Scheme 15

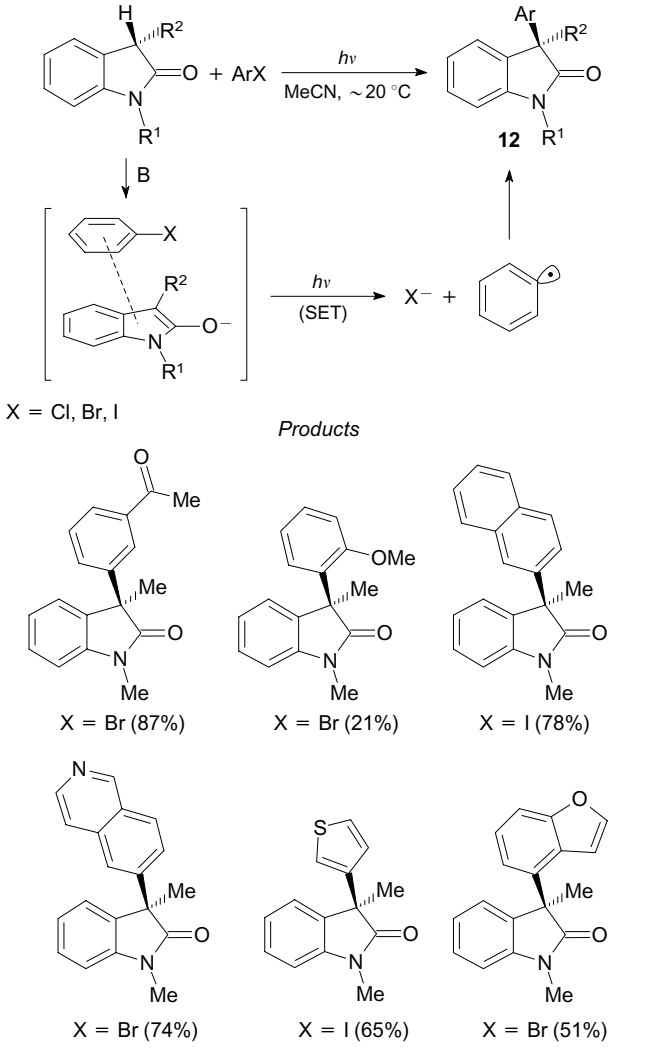


Scheme 16



dme is dimethoxyethane, DMA is dimethylacetamide

Scheme 17



The radical arylation of oxindoles at the position 3 with aryl halides in the presence of a base (B) under irradiation with a compact fluorescent lamp presumably involves the formation of a donor–acceptor complex (Scheme 17).[110] The maximum yields of arylation products **12** were attained for iodo and bromo derivatives, including heterocyclic ones.

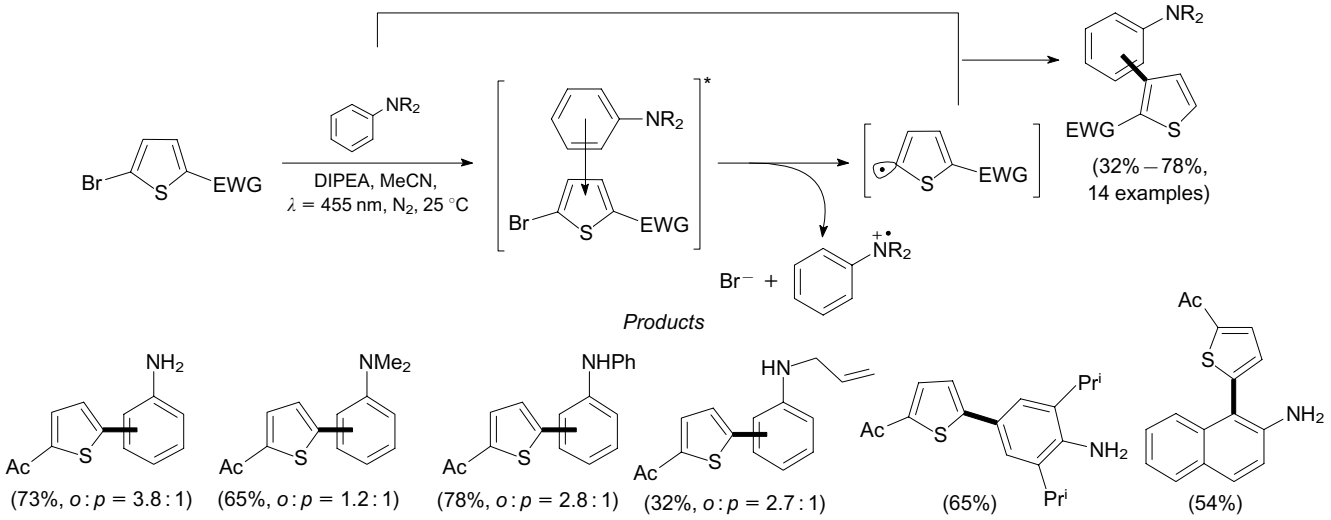
The formation of a donor–acceptor complex is also the key step in the radical arylation of thiophenes containing electron-withdrawing groups with aniline derivatives (Scheme 18).[111]

The radical cross-coupling of aryl bromides containing electron-withdrawing substituents with aromatic compounds occurs under irradiation with violet light at 390 nm in the absence of any photocatalysts.[112] Aromatic radicals are formed upon photoinitiated electron transfer from the arene molecule to the aryl halide molecule. Although the (het)aromatic compound functioning as the electron donor is taken in excess, this method is convenient for the synthesis of substituted biaryls, including those containing fused heterocyclic moieties.

The generation of aryl radicals from aryl iodides under irradiation (λ = 254 nm) also takes place in the presence of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) without any additives, transition metal-based catalysts or strong bases. The irradiation induces a single-electron transfer from the amine to aryl iodide to give the amine radical cation and the aryl iodide radical anion. The subsequent dissociation of the C–I bond affords the aryl radical.[113]

Aryl radicals can also be generated from electron-withdrawing-substituted aryl halides (iodides, bromides and chlorides) upon irradiation of their mixture with Et_3N at 400 nm.[114] According to authors assumption supported by experimental and theoretical data, the key role in the generation of aryl radicals belongs to the bond formed between the aryl halide and Et_3N. This gives rise to a complex that converts to the triplet state upon irradiation and undergoes an intrasystem homolytic cleavage of the

Scheme 18

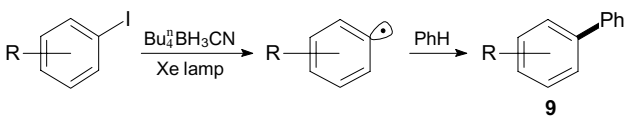


carbon – halogen bond. The aryl radicals generated in this way were allowed to react with pyrrole and 1-methyl- and 1-phenylpyrroles.

Light-initiated arylation of pyrroles with aryl bromides and chlorides without a photocatalyst has been reported.[115] The following mechanism was proposed for this reaction: photoinitiated disproportionation of pyrrole furnishes the pyrrole radical anion, which reacts with aryl halides as a reducing agent, with the single-electron transfer and C – Hal bond cleavage resulting in the formation of the expected aryl radical.

The radical coupling of aryl iodides containing substituents of any electronic nature with benzene can be induced by tetrabutylammonium cyanoborohydride and irradiation with a xenon lamp in air (Scheme 19).[116] A possible reaction mechanism includes the initial elimination of a hydrogen atom from the cyanoborohydride anion BH_3CN^- to yield the $BH_2CN^{-\bullet}$ radical anion, which reduces aryl iodide to the corresponding radical anion, converted subsequently to the aryl radical.

Scheme 19

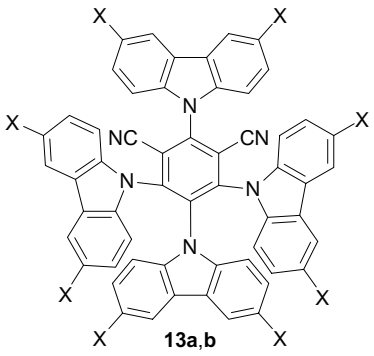


R = 4-OMe (78%), 4-CO_2Et (68%), 4-F (67%),
4-Ac (55%), 4-CF_3 (48%), 3-OMe (79%), 3-CO_2Et (62%)

The recent publication of MacMillan's group[117] about the generation of aryl radicals *via* halogen atom elimination from the aryl halide molecule on treatment with silyl radical prompted Molander and co-workers[118] to use tris(trimethylsilyl)silanol as the precursor of the silyl radical in the presence of a photocatalyst — 2,4,4,6-tetrakis(3,6-dichloro-9*H*-carbazol-9-yl)isophthalonitrile (Cl-4CzIPN, **13a**).

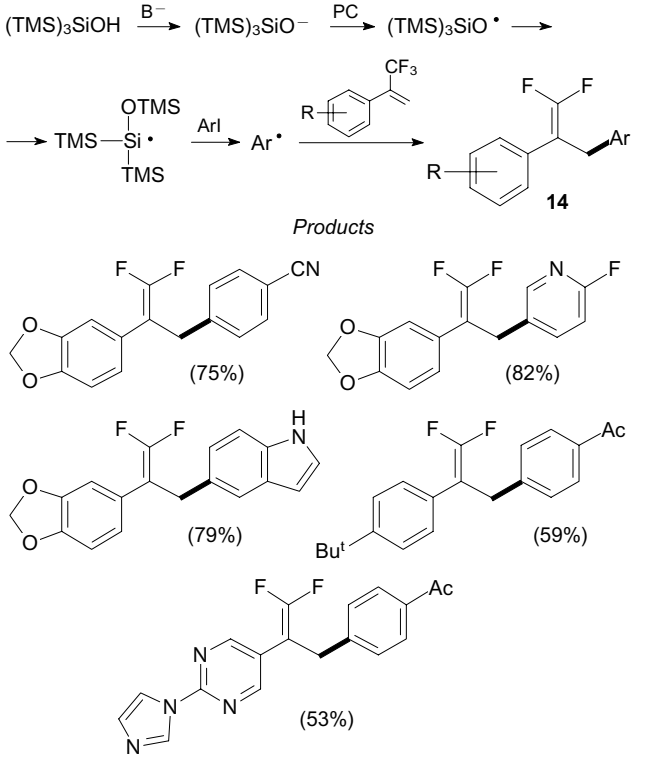
The catalytic cycle is initiated by deprotonation of silanol (Scheme 20), which is followed by the formation of the silyl radical as a result of oxidation and rearrangement. The developed method proved to be efficient for the preparation of phenyl-substituted *gem*-difluoroalkenes **14**,

Structures 13

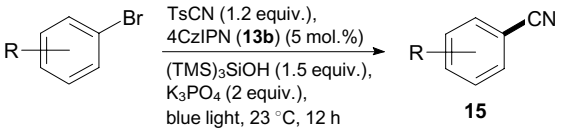


X = Cl (**a**), H (**b**)

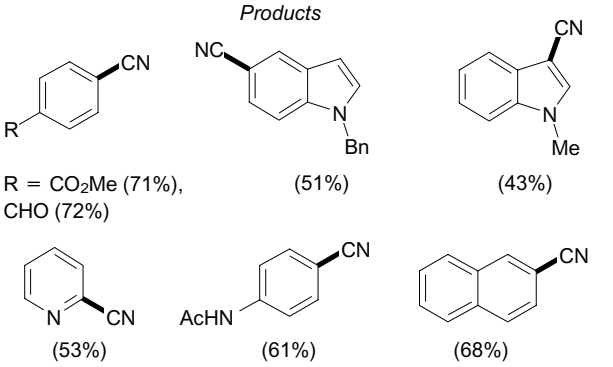
Scheme 20

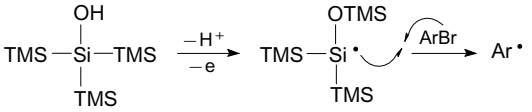


Scheme 21



Ts is *p*-toluenesulfonyl (tosyl)





difficult to obtain by other methods, by arylation of α-trifluoromethylstyrenes.

Aryl radical generation *via* silyl radical-initiated elimination of bromine was used in the synthesis of aryl cyanides **15** from aryl bromides and tosyl cyanide.[119] The reaction proceeds in the presence of 1,2,3,5- tetrakis(9*H*-carbazol-9-yl)-4,6-dicyanobenzene (4CzIPN, **13b**) as a photoredox catalyst under blue light irradiation (Scheme 21).

2.1.2. Electrochemically or photoelectrochemically initiated reactions of aryl halides

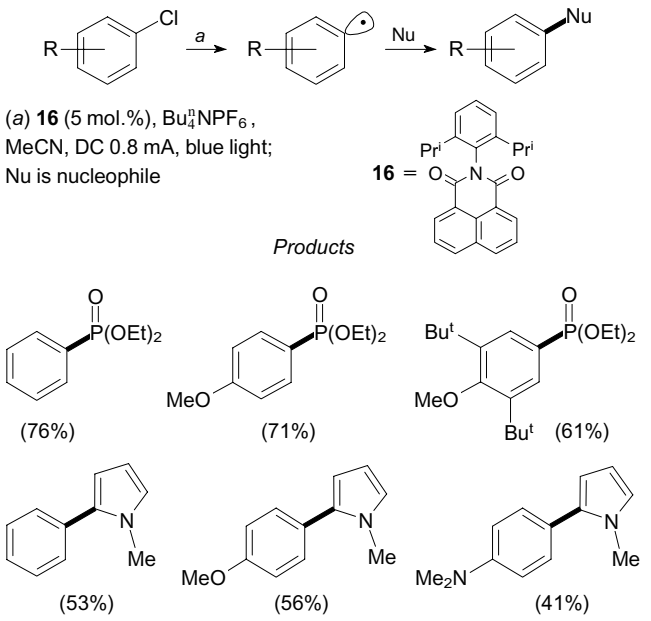
An alternative method of single-electron reduction of aryl halides, resulting in the generation of aryl radicals, is associated with the use of electrical current. The synthetic organic electrochemistry and photoredox catalytic reactions are modern methodologies of organic synthesis that complement each other and, in some sense, compete with each other. Quite a few synthetic transformations can be accomplished using either photoredox techniques or electrical current.[120]

The arylation using various reagents, including aryl halides, and initiated by electrical current was considered in detail in recent review papers;[19,27] therefore, here we do not discuss this type of reactions.

Particular attention is deserved by the hybrid method of generation of aryl radicals: the photoelectrochemical method based on the simultaneous use of photoredox catalysis and electrochemical activation.[121] A possible principle of this activation technique is photoexcitation of electrochemically generated ions. In this case, the basic level of redox capacity provided by the electrochemical reaction is enhanced by photoexcitation, which results in the formation of super-redox reagents, which can activate problematic poorly reactive substrates. In particular, using this technique, it is possible to carry out radical coupling reactions for aryl bromides, which are the most readily accessible aromatic halides. In the absence of electron-withdrawing substituents, aryl bromides and aryl chlorides have low reduction potentials (~ -1.9 to 2.9 *vs.* SCE) and often cannot be activated by photoredox catalysts on exposure to visible light (see examples given in the previous Section).

Wickens and co-workers [122] used *N*-(2,6-diisopropylphenyl)naphthalimide (**16**) as the redox catalyst for radical coupling of aryl chlorides, including those containing electron-donating substituents, with triethyl phosphite and 1-methylpyrrole (Scheme 22). The process was carried out in a divided electrochemical cell (DC).

Scheme 22



According to the concept proposed by the authors, initially, electrochemical reduction of the imide catalyst to give the corresponding radical anion takes place. The radical anion absorbs light to be photoexcited and acts as the reducing agent for aryl chlorides (Fig. 3).

Lambert and co-workers [123] reported the generation of aryl radicals from aryl chlorides and bromides on treatment with the the photoexcited radical anion obtained by cathodic reduction of 9,10-dicyanoanthracene (DCA). These

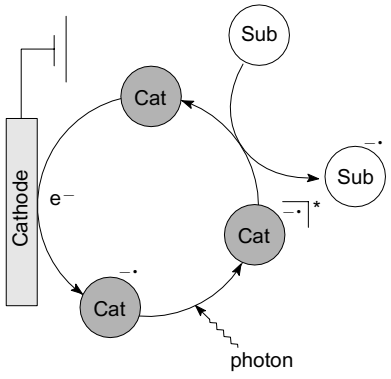


Figure 3. Combined photo- and electrochemical arylation. Cat is catalyst, Sub is substrate.

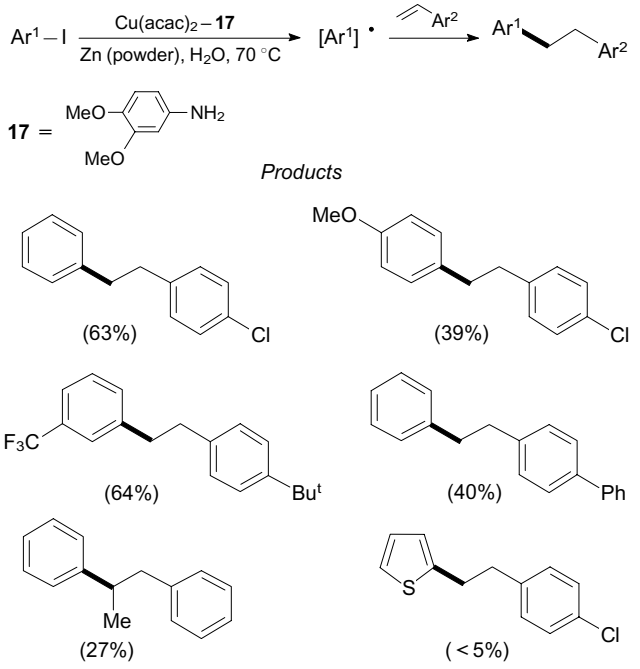
radicals were used to prepare pinacol esters of arylboronic acids, thimethylarylstannanes and 2-arylpyrroles.

2.1.3. Other initiation methods

The generation of aryl radicals from aryl halides can also be performed by means processes other than ultraviolet or visible irradiation of the reaction mixture.

For example, single-electron reduction of aryl iodides with zinc or a zinc/copper pair results in the generation of aryl radical (Scheme 23), which was used for the reductive arylation of styrenes in the presence of ligand **17**.[124]

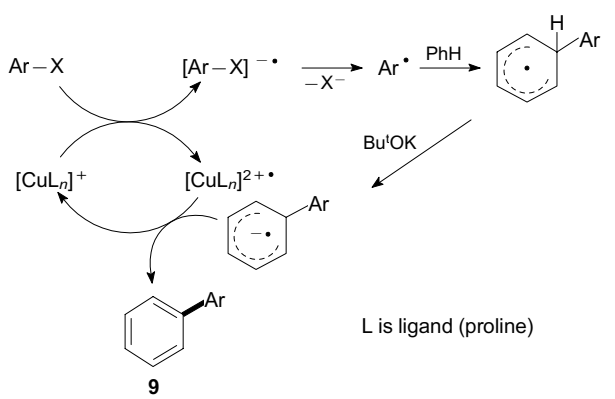
Scheme 23



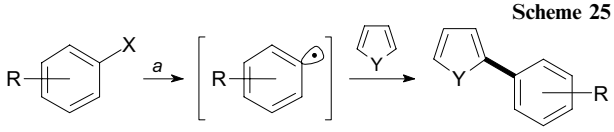
The CuBr – proline – Bu^{t}OK system catalyzes at 80 °C the conversion of aryl iodides to aryl radicals, which react with benzene. In the case of aryl iodides, the yields of substituted biphenyls **9** are high, while in the case of aryl bromides with electron-withdrawing substituents, the yields are moderate. Aryl bromides with electron-donating substituents and aryl chlorides are ineffective in this reaction (Scheme 24).[125]

A known method for generation of aryl radicals from aryl iodides and bromides uses catalysis with the Co^{II}(tap) complex [tap is tetrakis(4-anisylporphyrinato) dianion] without visible light irradiation and is suitable for the arylation of unactivated pyrroles and furans (Scheme 25).[126]

Scheme 24



Scheme 25



(*a*) Co^{II}(tap), KOH, Bu^{t}OK, N_2, dark, 200 °C

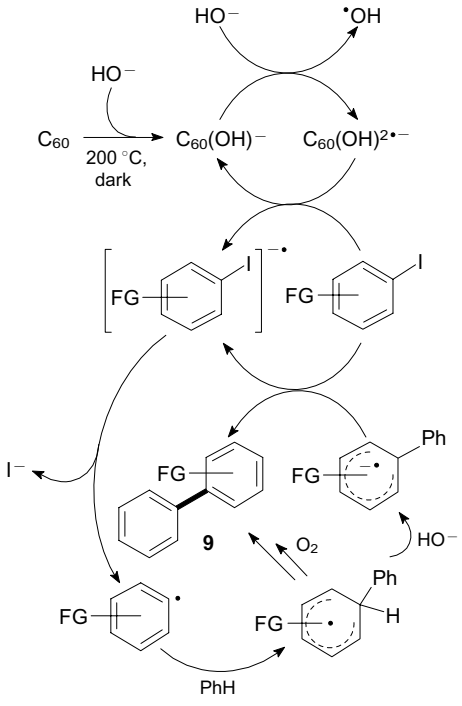
X	R	Yield (%)		X	R	Yield (%)	
		Y = NH	Y = O			Y = NH	Y = O
I	4-Me	74	62	I	H	69	52
Br	4-Me	52	42	I	4-OMe	66	62
I	4-Cl	54	49				

Rongalite (sodium hydroxymethanesulfinate dihydrate, Na^+ $HOCH_2SO_2^- \cdot 2H_2O$) initiates radical reactions of aryl halides proceeding under mild conditions. The single-electron reduction of the aryl halides with rongalite and the subsequent elimination of the halide anion result in the generation of aryl radicals, which can undergo coupling reactions giving C – C, C – S and C – P bonds. In particular, this method of radical arylation was used to prepare bi(het)aryls, phosphonates, sulfides and sulfones.[127]

The electron-rich diradical anion, $C_{60}(OH)^{2\bullet -}$, generated *in situ* from fullerene C_{60}, reduces aryl iodides with various functional groups (FG) to the corresponding aryl radicals. The large surface area and the spherical shape of C_{60} are favourable for this process (Scheme 26).[128]

The radical reactions initiated by a combination of an inorganic base and a small organic molecule have been substantially advanced in recent years. According to the terminology proposed by Studer and Curran,[129] these

Scheme 26

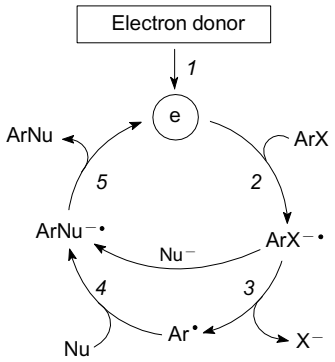


FG = H (78%), 4-Me (71%), 3-Me (79%), 2-Me (43%), 4-OMe (71%)

processes can be classified as 'electron-catalyzed reactions'. In their synthetic outcome, they are often similar to reactions catalyzed by transition metal compounds, *i.e.*, they convert the same initial aryl halides to the corresponding products, but do not require toxic and expensive catalysts. These processes are often conducted in the presence of small-size molecules — amines, amides, alcohols, *etc.*, which serve as electron donors either directly or as anions and accomplish the single-electron reduction and carbon–halogen bond activation. In some cases, reactions of this type efficiently proceed without any additives, with substrate and solvent molecules functioning as electron donors.

In terms of the considered concept, the general mechanism of carbon–halogen bond activation and formation of the coupling product in the electron-catalyzed reactions can be represented as follows (Scheme 27).[129, 130] The first step is the initiation of the catalytic cycle by the electron transfer from an electron-rich species, which can be considered to be the catalyst (electron) precursor. In the second step, the substrate molecule (ArX) is reduced to give the corresponding radical anion, which is split into the Ar$^{\bullet}$ radical and the halide ion (step *3*). The reaction of Ar$^{\bullet}$ with the nucleophile gives a new radical anion, ArNu$^{-\bullet}$ (step *4*), which in turn supplies an electron to the catalytic cycle, being converted to the cyclization product (step *5*). Steps *3* and *4* can occur in a concerted fashion; in this case, the intermediate formation of a free radical does not take place. In general, these reactions proceed by analogy with traditional aromatic radical substitution reactions, which follow the $S_{RN}1$ or $S_{RN}2$ mechanism [131, 132] and are initiated by metals or by irradiation, but do not require such conditions and are readily thermally activated. Many of these reactions give positive tests for the involvement of radical intermediates, but are unlikely to have a similar mechanism. The application of the concept proposed by Studer and Curran [129] suggests that these reactions are electron-catalyzed reactions of the same type.

Scheme 27



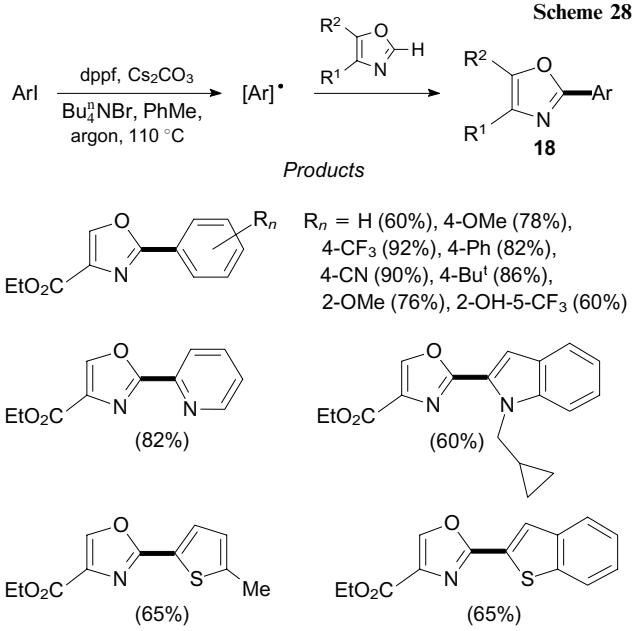
Since these reactions have been addressed in many review papers,[60, 133–135] only recently published examples will be considered in this Section.

Indoline, in combination with potassium *tert*-butoxide and trace amounts of air oxygen, was proposed as an additive for the generation of aryl radicals from not only aryl iodides or bromides, but also from considerably less reactive aryl chlorides containing no electron-withdrawing substituents. The high efficiency of indoline is attributable to its oxidative aromatization during the activation of aryl halides in the presence of a base and oxygen to give indole.[136]

For the generation of aryl radicals from aryl halides, phenanthroline derivatives were used, in several versions, as catalysts for the homolytic decomposition, in combination with potassium ethoxide,[137] potassium *tert*-butoxide [138] or iron acetate in the presence of potassium *tert*-butoxide.[139]

Ferrocene derivatives are also used to activate the single-electron transfer for the generation of aryl radicals from the corresponding aryl halides (Scheme 28). According to density functional theory (DFT) quantum chemical calculations, 1,1′-bis(diphenylphosphino)ferrocene (dppf) is complexed with Cs_2CO_3, which increases its single-electron reducing ability for radical generation from ArI. An example of using this method is (het)arylation of 2,3-disubstituted oxazoles at the position 2 to give products **18** in high yields.[140]

Scheme 28



The generation of aryl radicals from aryl halides is initiated by stable organic radicals or compounds prone to the single electron transfer (SET mechanism). From this standpoint, noteworthy is the stable 11π-electron zwitterionic radical anion of 2,3-bis(imidazo[1,2-*a*]pyridin)-2-one (Hbipo$^{-\bullet}$, **19**) (Scheme 29),‡ which initiates the formation of aryl radicals from aryl iodides in the presence of potassium *tert*-butoxide.[141] This reagent is used for arylation of various arenes.

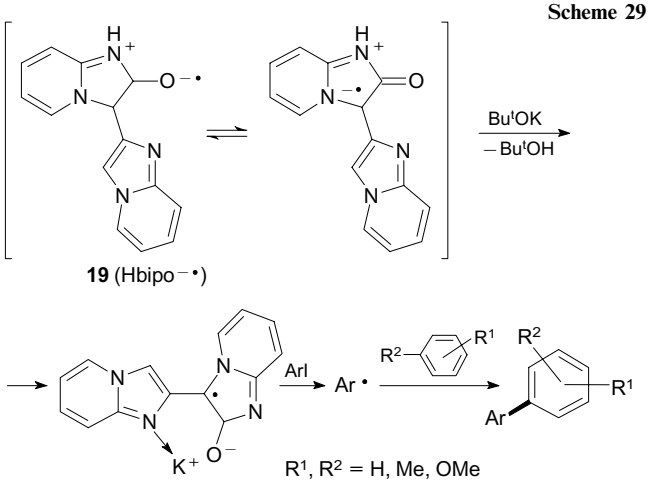
1,3-Diethylurea can catalyze the formation of (het)aryl radicals from (het)aryl iodides in the presence of potassium *tert*-butoxide (Scheme 30).[142]

In the presence of the n-butanol–potassium *tert*-butoxide system as the catalyst, aryl iodides and bromides are converted to aryl radicals upon single electron transfer (Scheme 31); this was used in the synthesis of unsymmetrical biphenyls.[143]

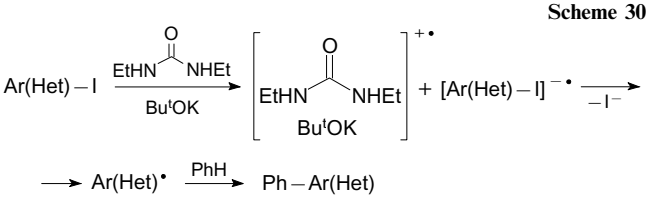
p-Toluenesulfonyl hydrazide also catalyzes the formation of aryl radicals and radical anions from aryl halides (Hal = I, Br, Cl) in the presence of potassium *tert*-butoxide (Scheme 32).[144]

‡ Here and below, unless otherwise indicated, substituents in different positions of the benzene ring are used.

Scheme 29

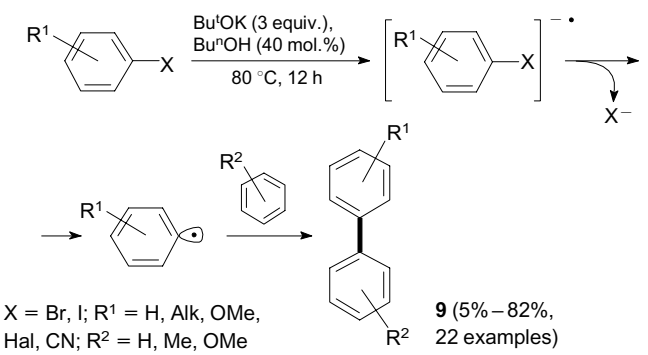


Scheme 30



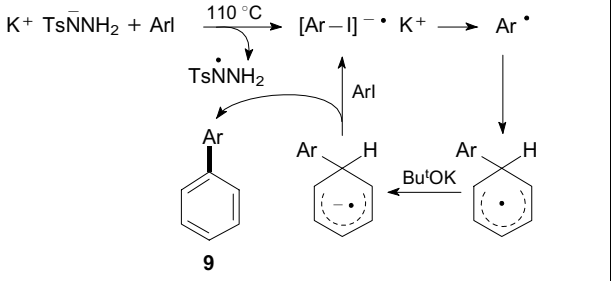
Ar = RC$_6$H$_4$ (R = H (95%), 4-OMe (94%), 4-Me (82%), 3-Me (82%), 4-CN (42%), 4-F (51%), 4-Cl (60%)); Het = 3-Th (85%), 2-Py (72%), 3-Py (52%), 4-Py (49%); Th is thienyl, Py is pyridyl

Scheme 31



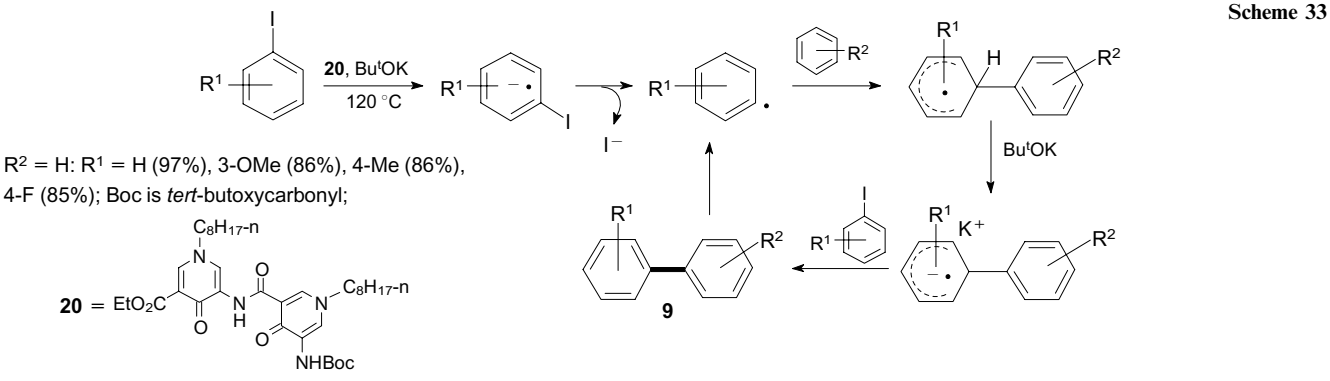
It was shown that a simple, but a well-designed pyridone dimer **20** (F-2) with two closely spaced oxygen atoms, which coordinate potassium cations, is an efficient organic catalyst for the generation of aryl radicals from aryl iodides in the presence of potassium *tert*-butoxide (Scheme 33). The yields of substituted biaryls **9** in this radical arylation reach 99%.[145] The arylation catalyzed by [2-(methylamino)phenyl]methanol with aryl iodides as substrates has also been reported.[146]

Scheme 32



The intramolecular arylation reactions initiated by bases are widely used for the preparation of various heterocyclic systems. An efficient method has been developed for the synthesis of indole-3-carboxylates,[147] well-known building blocks.[148] The intramolecular cyclization of *ortho*-halogen-substituted *N*-arylamidines initiated by potassium hydroxide in DMSO affords benzimidazole derivatives in moderate to high yields.[149] A reaction of this type was used to obtain pyrido[1,2-*a*]benzimidazoles from *N*-(2-halophenyl)-2-aminopyridines through the intramolecular formation of the C–N bond under irradiation.[150] Heterocyclization of *ortho*-iodo(bromo)-substituted *N*-arylureas serves as a convenient preparative route towards benzimidazol-2-ones, which possess a broad range of biological activities.[151] One of the earliest publications[152] related to the synthesis of heterocyclic compounds by amination of aryl halides without the use of transition metals describes the heterocyclization of (*Z*)-*o*-bromoacetophenone *N*-tosylhydrazone induced by potassium carbonate in the presence of 10 mol.% of *trans*-*N*,*N*′-dimethyl-1,2-diaminocyclohexane. The reaction takes place under very mild conditions at room temperature. It is noteworthy that other inorganic bases (KOH, Bu^{t}OK, Na_2CO_3) or amines were less effective or totally ineffective in this reaction. Similarly, cyclization of hydrazides of *ortho*-halobenzoic acids gives 1*H*-indazolones.[153] The base-initiated heterocyclization of *N*-acylated aryloxyanilines to give the carbon–heteroatom bond underlies an efficient synthesis of phenoxazines.[154] Related cyclization reactions proceeding without transition metal-based catalysts were used to obtain phenothiazines; an example is the tandem reaction of *N*-(2-iodophenyl)aceta-

Scheme 33



R^2 = H: R^1 = H (97%), 3-OMe (86%), 4-Me (86%), 4-F (85%); Boc is *tert*-butoxycarbonyl;

20 =

mide with 2-bromobenzenethiol in the presence of 4 equiv. of potassium carbonate in DMF.[155] Heating of 2-(2-bromophenyl)acetyl-*N*-tosylpyrroles in DMF in the presence of 2 equiv. of caesium carbonate results in the formation of dihydropyrrolizino[3,2-*b*]indol-10-ones.[156] A one-pot synthesis of pyrazolo[1,5-*a*]quinoxalines involving 1-(2-chlorophenyl-5-ethoxycarbonyl)pyrazole and primary aliphatic amines includes the initial step of formation of pyrazolecarboxylic acid amides and the subsequent intramolecular formation of the carbon – nitrogen bond.[157] Similar base-initiated heterocyclizations were also employed to prepare imidazo[1,5-*a*]quinoxalines from halogenated imidazole-2-carboxylic acid *N*-arylamides[158] and phenanthridinones from *o*-bromobenzoic acid anilides.[159] The generation of aryl radicals from aryl halides using *meso*-aryl-substituted porphyrins has been described.[160]

2.2. Generation of aryl radicals from aryldiazonium salts

Historically, aryldiazonium salts are widely used to generate aryl radicals.[7, 8, 12, 32, 33] Unlike other precursors, diazonium salts are easily reduced *via* single-electron transfer (E_{red} of ~ -0.1 to -0.3 V), which induces their irreversible decomposition to give an aryl radical and a nitrogen molecule. In addition, they have relatively low toxicity and are readily generated *in situ* from anilines.

2.2.1. Reactions without photoredox catalysts

The radical arylation of benzoquinone under mild conditions at room temperature is based on the use of aryldiazonium salts generated *in situ* by the reaction of appropriate anilines with *tert*-butyl nitrite.[161] For carrying out arylation with diazonium salts without any additives, the substrate should be a good acceptor of radicals such as, for example, benzoquinone[162] or quinoxalin-2(1*H*)-one.[163] 2-Arylbenzoquinones **21** are formed in high yields when the aryl radical contains an electron-withdrawing functional group (Scheme 34). However, the arylation of quinoxalin-2(1*H*)-ones **22** follows the opposite trend: the introduction of electron-rich groups is preferred. In both cases, the generation of aryl radicals from aryldiazonium cations is due to the reduction of the latter by components of reaction mixtures.

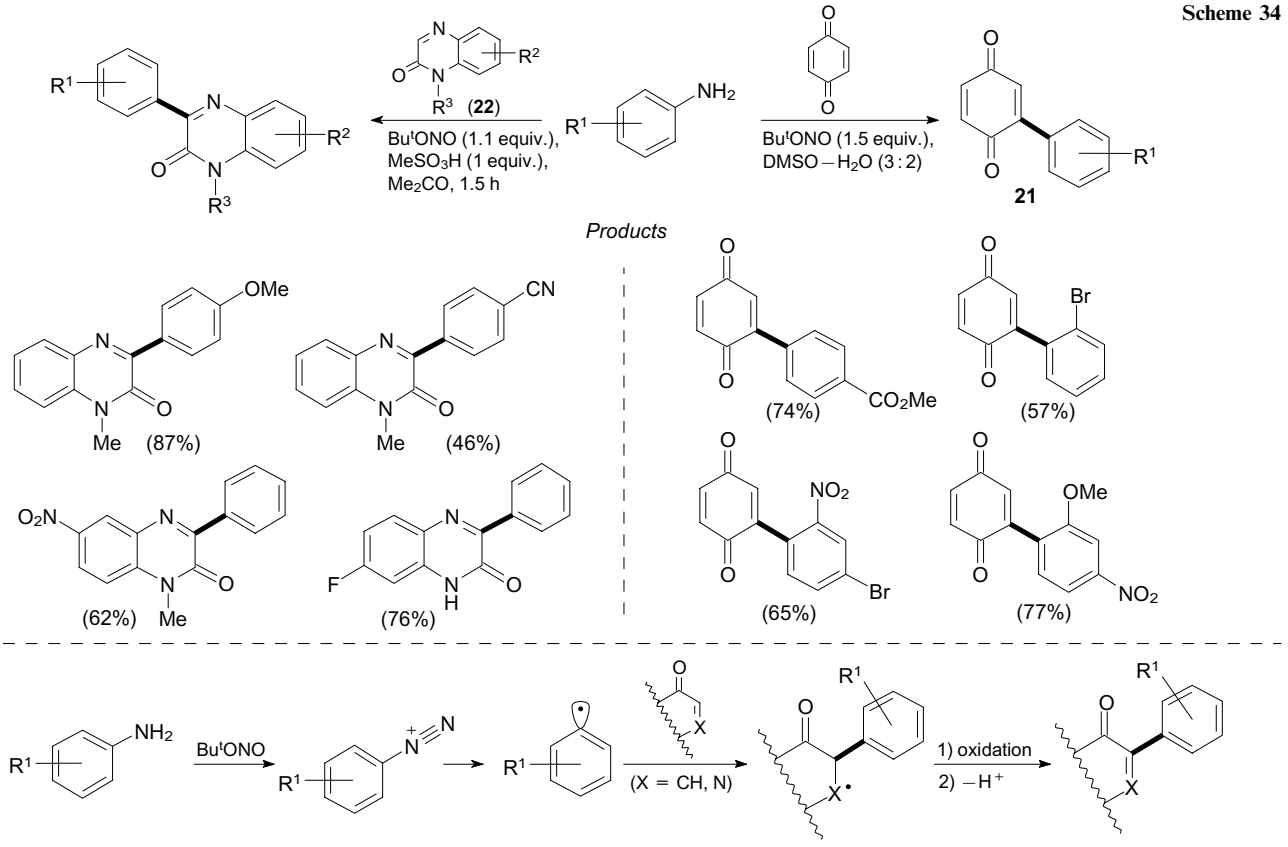
For the arylation of benzoxazoles, which are less reactive in radical reactions, catalysts based on copper(II) salts are necessary (Scheme 35).[164] The authors used substrates containing electron-withdrawing or nearly electron-neutral substituents. The latter were found to provide the highest efficiency of the reaction.

Five-membered aromatic heterocyclic compounds serve as convenient model substrates for the development of new arylation methods, because they are readily available and reactive towards radical addition reactions owing to the presence of an activated double bond. Several efficient arylation methods involving aryldiazonium salts as donors of aromatic radicals and various reducing agents were reported for these substrates (Scheme 36, see the main reaction).

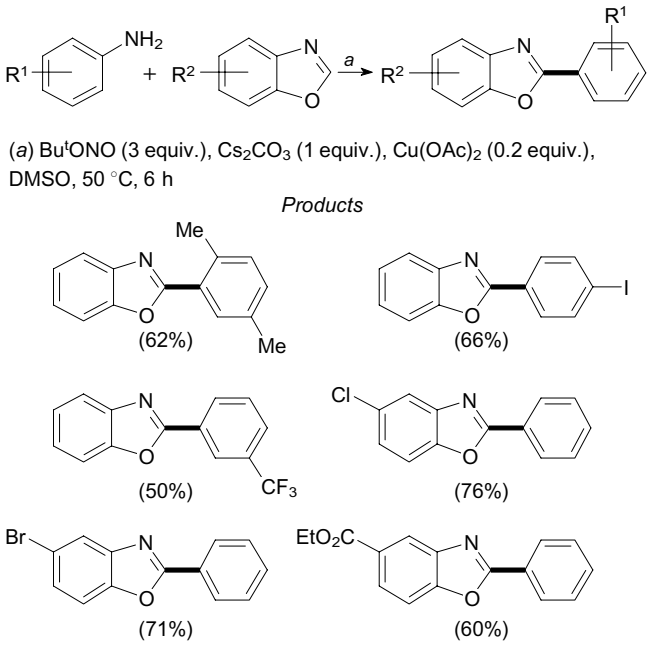
The generation of aryl radicals from diazonium salts was induced by cobaltocene Cp_2Co (Cp is cyclopentadienyl),[165] reduced graphene oxide (rGO)[166] and direct cathodic reduction (a stainless steel cathode and a carbon anode).[167] These methods are most efficient when electron-deficient diazonium salts are utilized (Table 1, rt is room temperature).

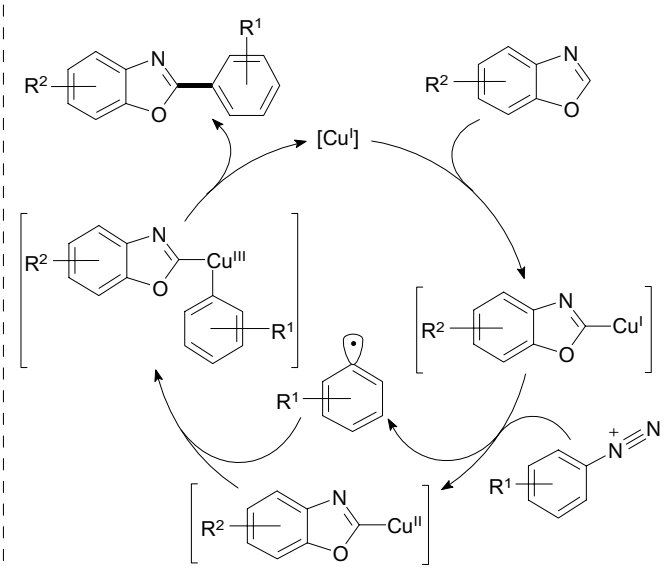
2-Chloro-*N*,*N*-dimethyl-10*H*-phenothiazine-10-propanamine hydrochloride (chlorpromazine hydrochloride, CP · HCl, **23**) was also used as the reducing agent (see Scheme 36).[168] This reagent allows conducting the arylation

Scheme 34

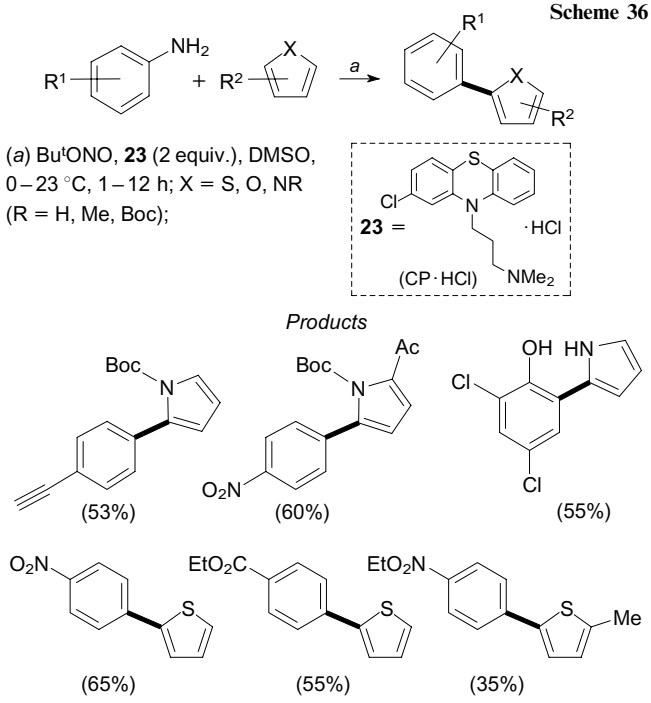


Scheme 35





Scheme 36



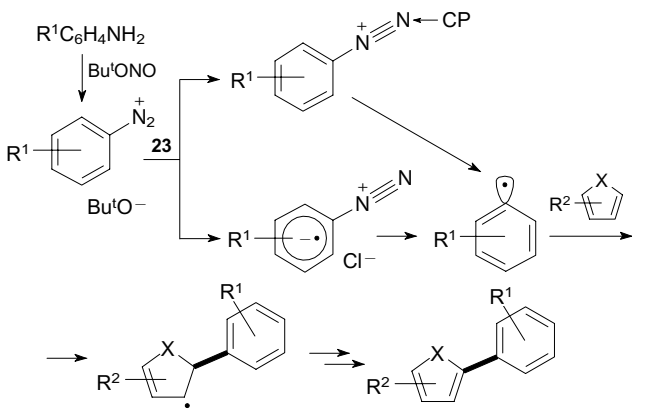


Table 1. Comparison of the efficiency of various methods for arylation of aromatic five-membered heterocycles with diazonium salts (see Scheme 36, R^1 = H).

X	R^2	Product yield (%)		
		see [a]	see [b]	see [c]
NBoc	4-NO_2	85	78	64
O	4-NO_2	–	81	56
NBoc	4-Br	45	–	61
S	4-Br	–	24	–
NBoc	4-OMe	27	–	36

Note. The dash means the absence of data. [a] Cp_2Co (5 mol.%), DMSO, rt, 30 min; [b] rGO (20 mg), DMSO, 40 °C, 6 h; [c] direct current, $NaBH_4$ (1 equiv.), $MeSO_3H$ (1 equiv.), DMSO, 20 min.

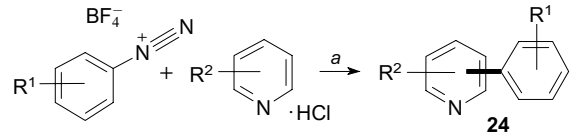
of five-membered heterocycles in good yields, even in the case of pyrrole with the unprotected nitrogen atom. The use of chlorpromazine is based on its ability to bind to the diazonium salt, thus facilitating the aryl radical generation.

The formation of aryl radicals catalyzed by microcrystalline metal-organic frameworks has been reported.[169]

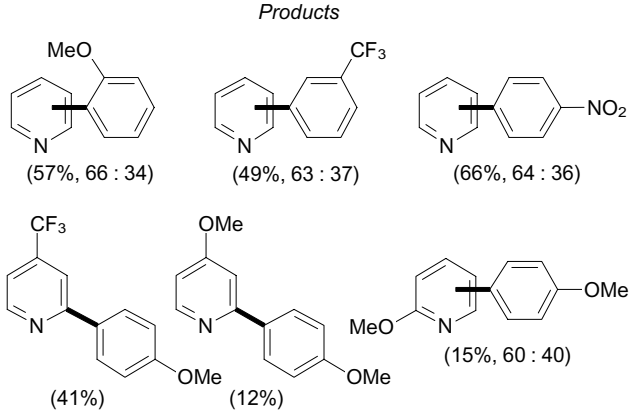
The arylation of pyridines with aryldiazonium tetrafluoroborate in water under the action of visible light was found to involve the intermediate formation of the donor – acceptor complex with pyridine, which absorbs visible light and, in the excited state, generates an aryl radical without a photocatalyst.[170] This reaction was used for the arylation of azines and their fused analogues (Scheme 37). Unfortunately, this method does not possess high regioselectivity: in all cases, the ratio of C(2)- and C(4)-substituted products (given in Scheme 37 in parentheses after the yield) is ~2 : 1, if the position 4 is vacant. Also, the total yield of products **24** decreases when the diazonium salt contains electron-donating functional groups.

Processes of the same type are also typical of the reactions of diazonium salts with benzene and its derivatives in the presence of pyridine.[171] In this case, the highest efficiency is attained on exposure to white light; however,

Scheme 37



(*a*) H_2O, O_2, blue light, 23 °C, 48 h

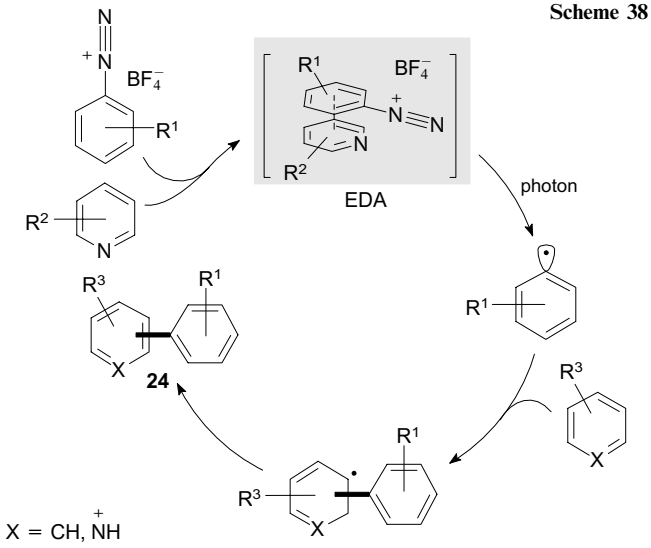


the general trend is the same: the reactions give product mixtures resulting from arylation of all positions of the benzene ring. The reaction mechanism is depicted in Scheme 38.

The aryl radicals generated from aryldiazonium chlorides in water and aqueous organic solvents were employed for the arylation of aromatic compounds containing hydrophilic amino and hydroxy groups. The reductive fragmentation of diazonium salts was induced by Ti^{III} compounds.[172]

The formation of a donor – acceptor complex between the aryldiazonium cation and tertiary amine is the key step in the synthesis of sulfonimidamides by the addition of aryl radicals to *N*-sulfinylamines.[173] Fluorosulfonylation of anilines in the absence of copper catalysts is based on reactions of the diazonium salts obtained *in situ* with $Na_2S_2O_5$ as a source of SO_2 group and Selectfluor [1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate)] as a source of fluorine. The mechanism of this reaction is similar to the mechanism of the Sandmeyer reaction: single-electron reduction of the diazonium cation generates an aryl radical, which adds sulfur(IV) oxide to give arylsulfonyl radical; the latter reacts with Selectfluor to give arylsulfonyl fluorides.[174]

Scheme 38



Hantzsch esters were used as activating reagents (hydride ion donors) for aryldiazonium salts. The diazenes formed upon the hydride transfer undergo oxidative fragmentation to give aryl radicals and a nitrogen molecule. The radicals generated in this way, containing substituents of various electronic nature, smoothly arylate aromatic heterocyclic compounds: furans, thiophenes, pyrroles, pyridines and their benzannulated analogues.[175]

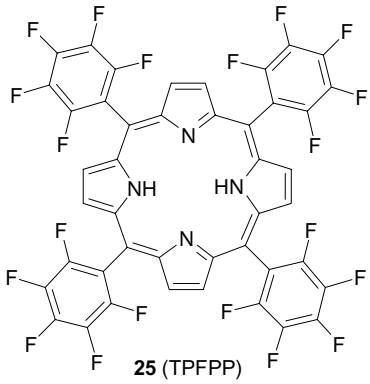
A method was developed[176] for photocatalyst-free arylation with diazonium salts generated *in situ* from anilines with subsequent lactonization of γ-alkenoic acids. The electrochemically activated arylation of electron-deficient arenes with diazonium salts has been described.[177]

2.2.2. Reactions involving organic photosensitizers

Photoredox reactions catalyzed by either organocatalysts or transition metal-based catalysts provide the most popular method for the generation of aromatic radicals.

Porphyrins are organic photoredox catalysts acting as SET photocatalysts. Electron-deficient *meso*-tetra(pentafluorophenyl)porphyrin (TPFPP, **25**) was found to exhibit the best photoactivity as an electron donor in the arylation of enol acetates. On irradiation, the porphyrin molecule is excited and easily transmits an electron to the diazonium salt, thus generating an aryl radical (Scheme 39).[178] This method was implemented in two designs: in a flask and in a flow reactor. This type of photocatalysis is successfully used to prepare various β-arylcarbonyl compounds; however, the introduction of strong electron-donating aryl substituents hampers the process.

Structure 25

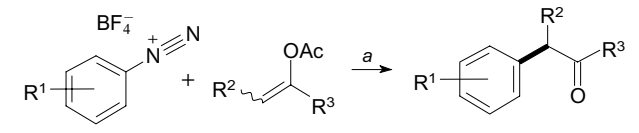


One more efficient redox catalyst is eosin Y (**11**). It was used for selective conversion of anilines to 2-aminobiphenyls (Scheme 40).[179] The electronic natures of both the substituents in the aniline aromatic ring and the diazonium salt do not have a significant effect on the yields of reaction products.

Eosin Y (**11**) was also successfully utilizad as a single-electron reducing agent for the arylation of five-membered heterocycles,[180,181] B_2pin_2 (Scheme 41),[182] diaryl diselenides[183] and organic sulfinates (to give diaryl sulfones).[184]

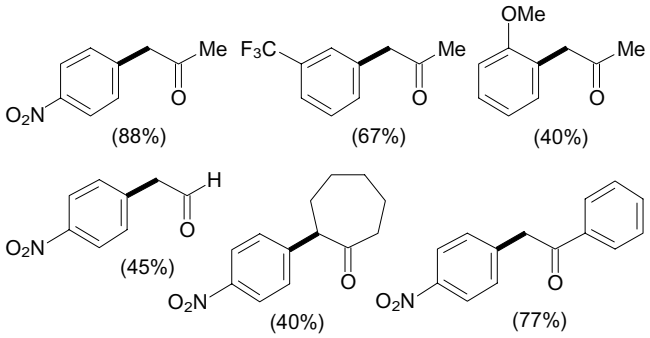
The generation of an aryl radical in a carbon monoxide atmosphere results in the formation of the benzoyl radical

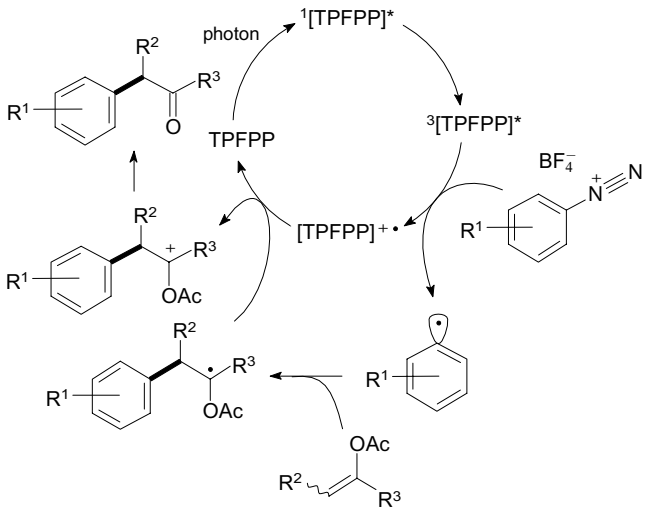
Scheme 39



(*a*) **25** (0.5 mol.%), $MeNO_2$ — DMF (5 : 1), blue light, 0 °C, 2 h

Products





(Scheme 42), which then attacks benzene [185] or an aliphatic alcohol.[186, 187]

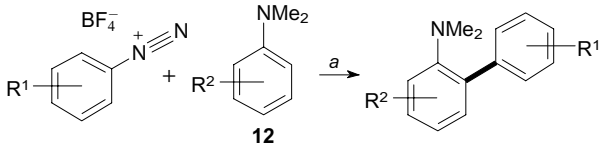
Apart from direct arylation reactions, eosin Y (**11**) can be used to carry out the photochemical radical annulation of 2-thioanisyldiazonium salts by alkynes to afford benzothiophenes **26** (Scheme 43).[188] If the methylsulfanyl group in the substrate is replaced by the phenyl group, it is possible to obtain phenanthrenes under these conditions.[189]

Green light irradiation (λ = 530 nm) for the generation of aryl radicals from aryldiazonium tetrafluoroborates in the presence of eosin Y was employed for the synthesis of diarylacetylenes by decarboxylative radical arylation of arylacetylenecarboxylic acids.[190]

The singlet excited state of boron(dipyrrolylmethene) dyes [4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (BODIPY) derivatives **27**], generated upon irradiation with visible light, induces the conversion of aryldiazonium salts to aryl radicals, which immediately arylate the dye (Scheme 44).[191] Depending on the excess amount of the diazo compound, both mono- and diarylation may take place.

A method was proposed for the synthesis of isoflavones by the reaction of *o*-hydroxyaryleneaminones with aryl

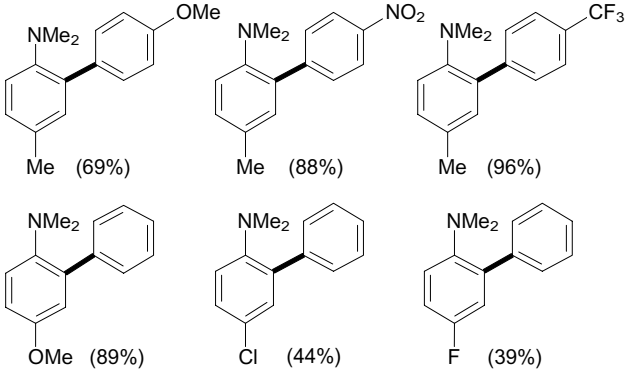
Scheme 40

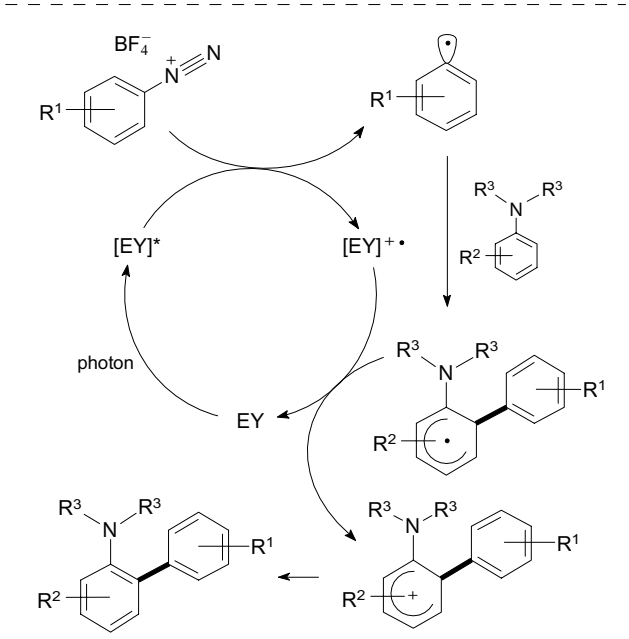


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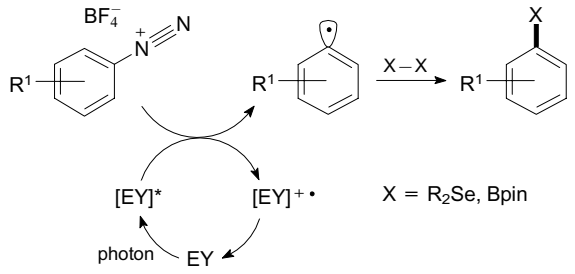
(*a*) EY (**11**) (1 mol.%), MeCN – H_2O (10 : 1), green LED, 23 °C, 14 h; LED is light-emitting diode

Products



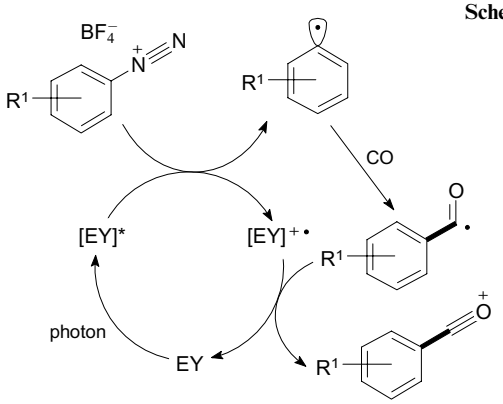


Scheme 41

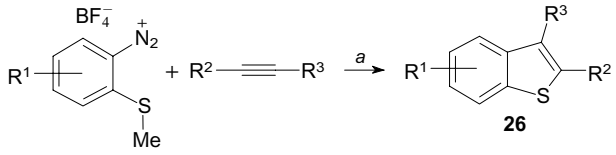


radicals, which are generated from diazonium salts upon green light irradiation in the presence of eosin Y (**11**) or from diaryliodonium salts upon blue light irradiation in the

Scheme 42

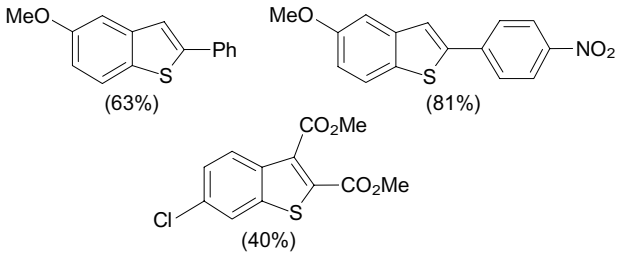


Scheme 43

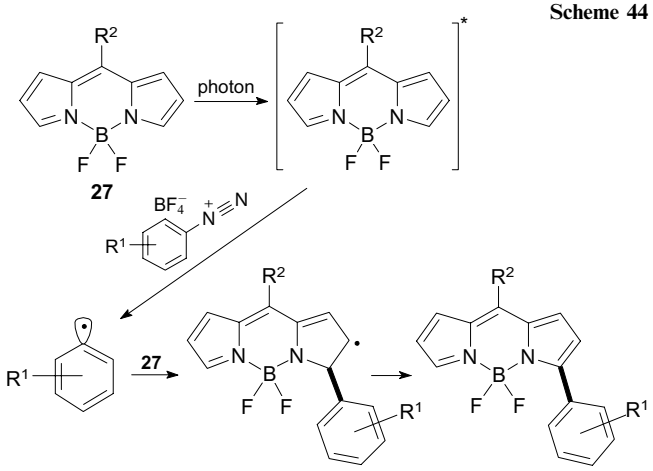


(*a*) EY (**11**) (5 mol.%), DMSO, green LED, 23 °C, 14 h

Products



Scheme 44



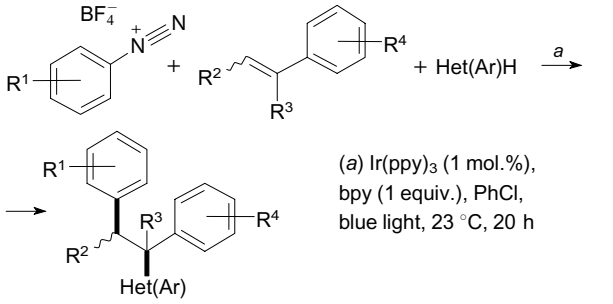
R^1 = Me, OMe, Cl; R^2 = Alk, Hal, EWG

presence of the complex $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (bpy is 2,2′-bipyridine).[192]

2.2.3. Reactions in the presence of metal-containing photoredox catalysts

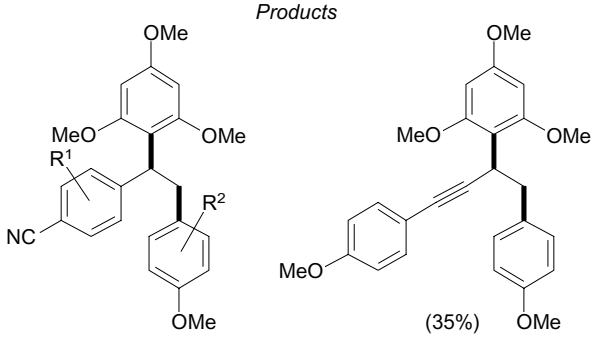
The use of iridium catalysts opened up the possibility of introducing an aryl group to the double bond of styrenes (Scheme 45).[193] Electron-rich aromatic systems (trimethoxybenzene, indole) were chosen as the third reaction component; the method proved to be equally efficient for both electron-rich and electron-poor substrates.

Scheme 45

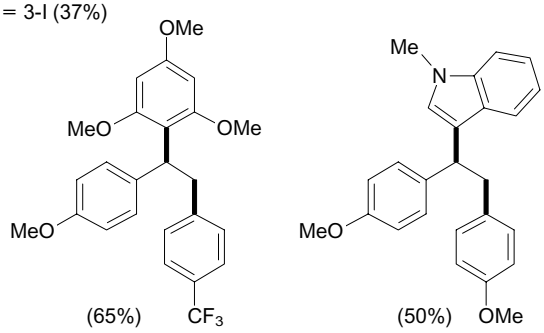


(*a*) $Ir(ppy)_3$ (1 mol.%), bpy (1 equiv.), PhCl, blue light, 23 °C, 20 h

Products



R^2 = H: R^1 = 4-CN (58%), 3-OMe (50%); R^1 = 4-OMe, R^2 = 3-I (37%)

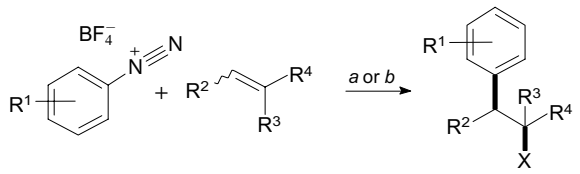


Ruthenium catalysts allow the use of simple nucleophiles such as methoxide anion,[194] thio- and selenocyanates[195] or nitriles[196] instead of aromatic compounds (Scheme 46). In the presence of air, the addition of an oxygen atom to the α-carbon atom of styrene takes place;[197] in the case of acrylonitriles, this affords arylacetic acid derivatives.[198] When DMSO employed as the solvent, the corresponding stilbenes are produced,[199] whereas the reaction in DMF gives formyloxylation products.[200]

The generation of aryl radicals from aryldiazonium salts assisted by the $[Ru(bpz)_3](PF_6)_2$ photoredox catalyst (bpz is 2,2′-dipyrazine) under irradiation with a compact fluorescent lamp was applied for Au^I-catalyzed alkoxycyclization of 1,6-enynes in the presence of alcohols to give five-membered carbocyclic compounds.[201]

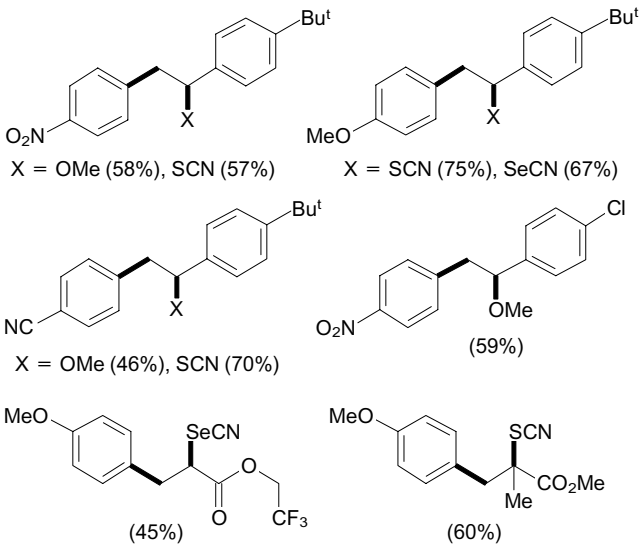
Since intramolecular nucleophilic substitution proceeds more easily than intermolecular substitution, in the presence of a carboxyl group in the alkene, the arylation – lactonization tandem process takes place (Scheme 47).[202] When *N*-arylacrylamides are used as the starting compounds, the reaction gives 3,3-disubstituted oxindoles.[203] This type of

Scheme 46



(*a*) $Ru(bpy)_3Cl_2$ (0.5 mol.%), MeOH — H_2O (1 : 1), blue light, 23 °C, 1 h; (*b*) NH_4SCN or KSeCN (3 equiv.), $Ru(bpy)_3(PF_6)_2$ (2 mol.%), MeCN, blue light, 23 °C, 6 h; X = OMe, SCN, SeCN

Products



X = OMe (58%), SCN (57%)

X = SCN (75%), SeCN (67%)

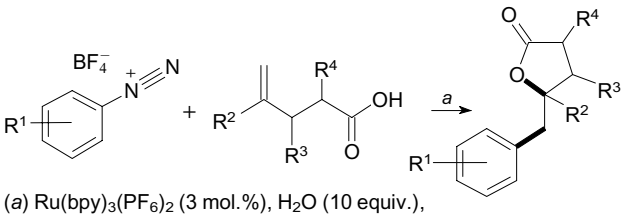
X = OMe (46%), SCN (70%)

(59%)

(45%)

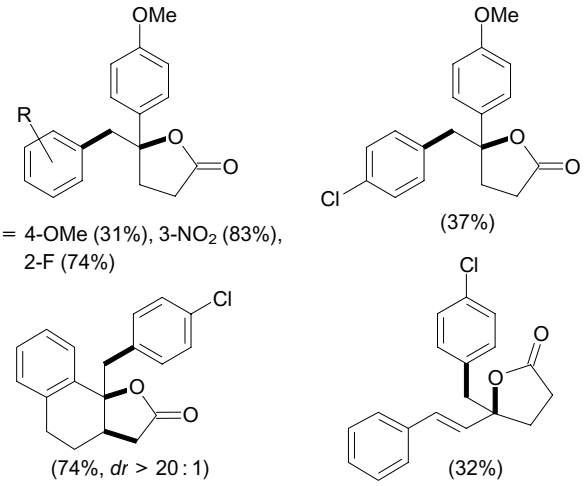
(60%)

Scheme 47



(*a*) $Ru(bpy)_3(PF_6)_2$ (3 mol.%), H_2O (10 equiv.), MeCN, white light, −20 °C, 19 – 72 h

Products



R = 4-OMe (31%), 3-NO_2 (83%), 2-F (74%)

(37%)

(74%, *dr* > 20 : 1)

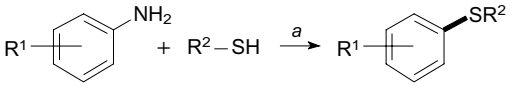
(32%)

dr is diastereomeric ratio

arylation of enol acetates in the presence of a ruthenium photocatalyst affords benzyl methyl ketones.[204]

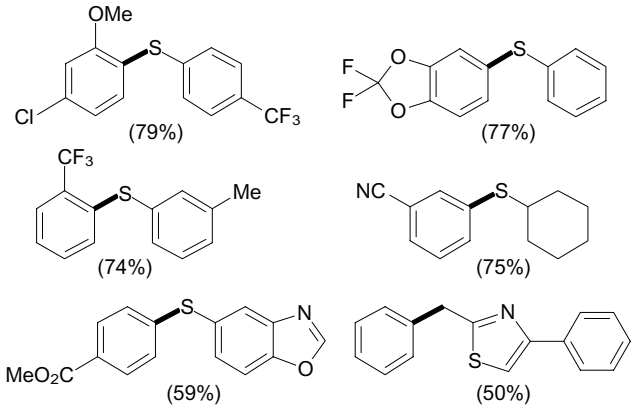
Apart from the arylation of substrates containing double bonds, the diazonium salt – $Ru(bpy)_2^{2+}$ combination proved to be efficient in the synthesis of diaryl and alkyl aryl sulfides (Scheme 48).[205] Conversely, in the C – H arylation of *N*-hetarenes, electron-donating aromatic radicals are most reactive.[206, 207]

Scheme 48



(*a*) Bu^tONO, $Ru(bpy)_3Cl_2$ (1 mol.%), $TsOH \cdot H_2O$ (1.5 mol.%), MeCN, blue light, rt, 5 – 6 h

Products



(79%)

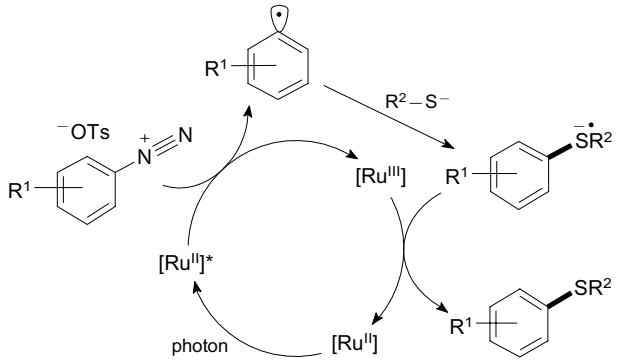
(77%)

(74%)

(75%)

(59%)

(50%)

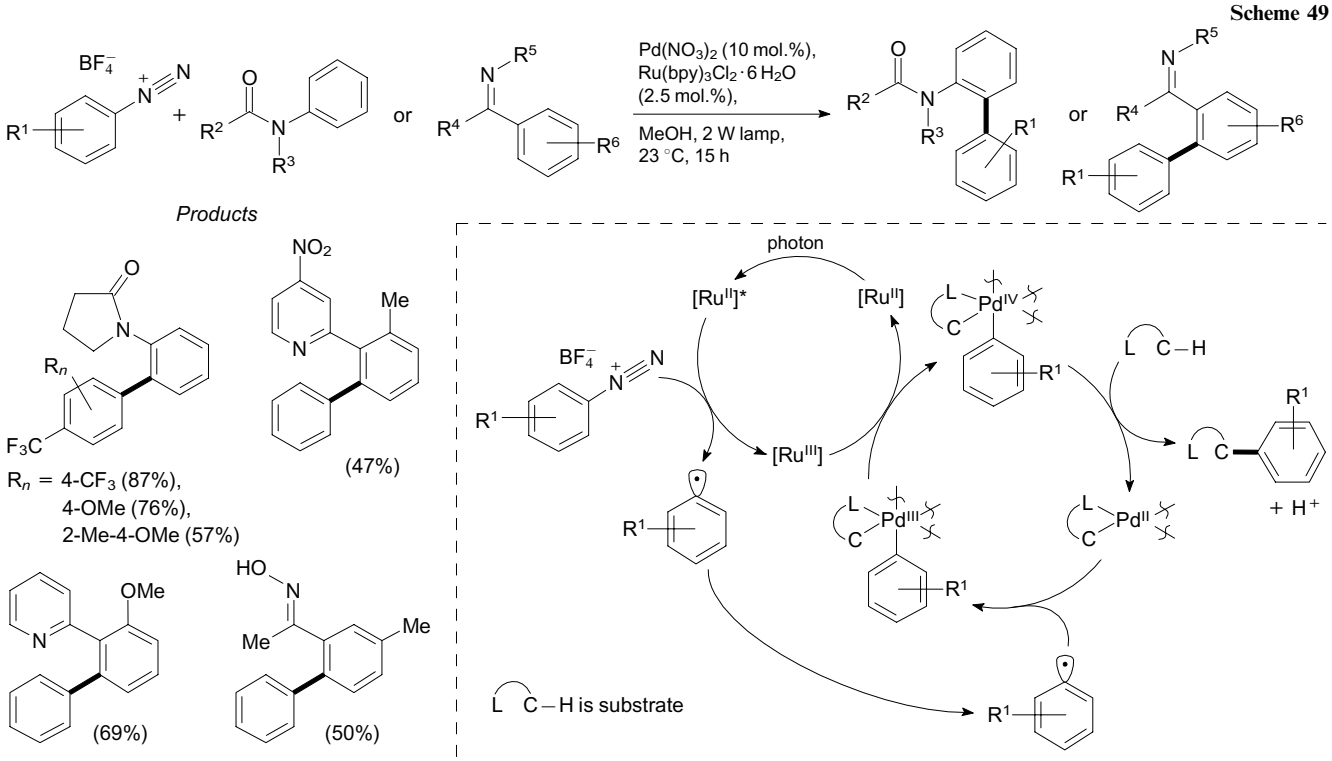


In the presence of the ruthenium photoredox catalyst $Ru(bpy)_3(PF_6)_2$, irradiation with white light induced the formation of aryl radicals from aryldiazonium tetrafluoroborates in the synthesis of trifluoromethoxyarenes.[208]

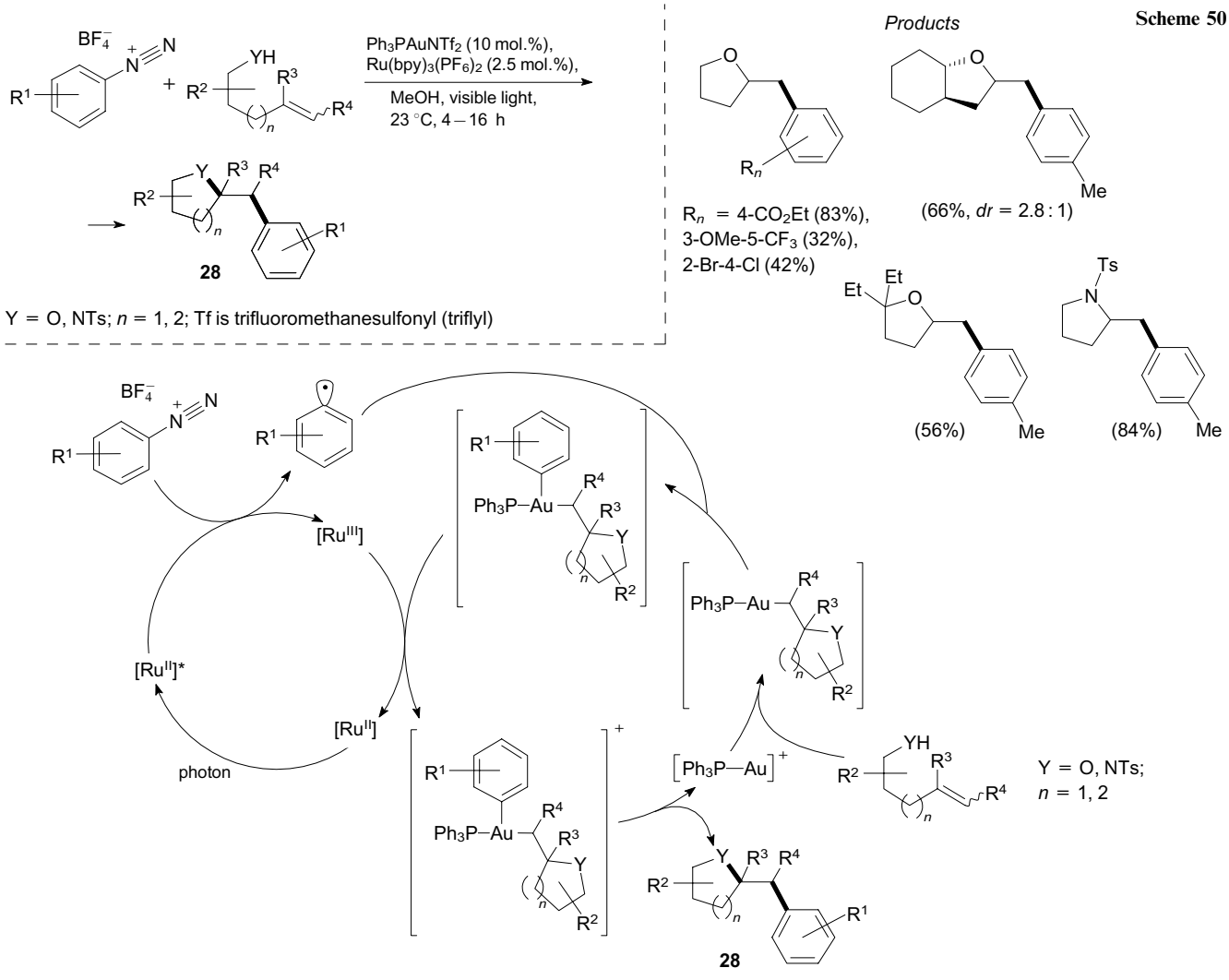
The ruthenium photocatalyst and the palladium catalyst were used together for the *ortho*-arylation of various electron-withdrawing group-substituted aromatic substrates, such as amides, oximes or pyridines (Scheme 49).[209] Electron-deficient and sterically uncrowded diazonium salts proved to be most efficient in this reaction, because the increase in the bulk of the introduced aryl moiety has an adverse effect on the oxidative addition of the aromatic radical to the Pd intermediate.

The use of a binary (Ru – Au) catalytic system makes it possible to conduct combined arylation and cyclization of ω-amino- and ω-hydroxyalkenes (Scheme 50).[210] Using this method, it is possible to prepare sterically crowded cyclic ethers and amines **28** in good yields. The same catalytic

Scheme 49



Scheme 50



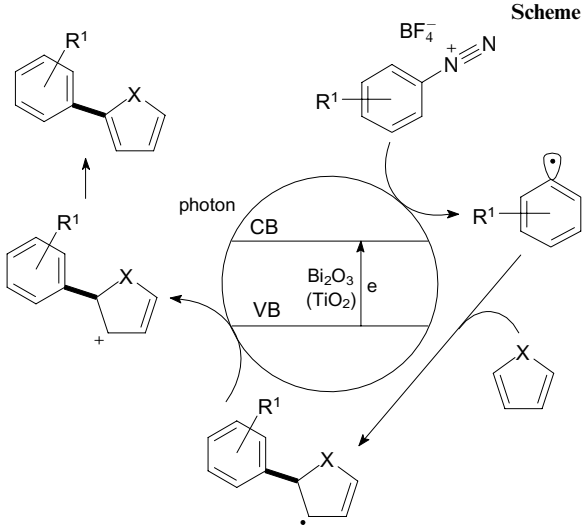
system proved to be suitable for arylation of diethoxyphosphine oxides to give the corresponding arylphosphonates.[211]

The successful use of bismuth(III) and titanium(IV) oxides as catalysts for the formation of aryl radicals from diazonium salts is due to their semiconducting properties (Scheme 51).[212, 213] After irradiation with a compact fluorescent lamp, an electron moves from the valence band of the catalyst to the conduction band, which allows electron transfer to the diazonium salt, generating an aryl radical.

The PANI–g-C_3N_4–TiO_2 photocatalyst (PANI is polyaniline, g-C_3N_4 is graphite carbon nitride) can also serve for the generation of radicals from diazonium salts, which was first demonstrated in the arylation of alkynes to give α-chloroaryl ketones **29** (Scheme 52).[214] The chlorine atom enters the product molecule *via* addition of the chloride ion to the radical cation of the formed enol. The reaction is applicable to substrates with different electronic properties; however, in the case of unsubstituted phenyldiazonium salt, the reaction product is formed in only trace amounts.

Efficient methods have been developed for the arylation of terminal alkynes with diazonium salts to give substituted acetylenes using a binary catalytic system comprising a gold-based catalyst and a photoredox catalyst.[215] These reactions are initiated by visible light. Subsequently, the range of applicability of this catalyst was extended to radical arylation of quinones, enol acetates and five-membered heterocycles.[216]

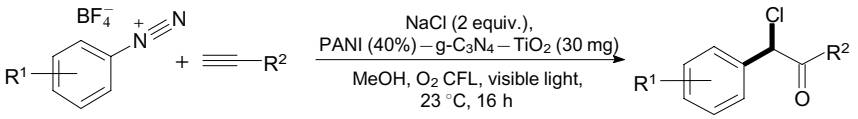
Scheme 51



X = O, S, N(Boc), HC═N; CB is conduction band; VB is valence band

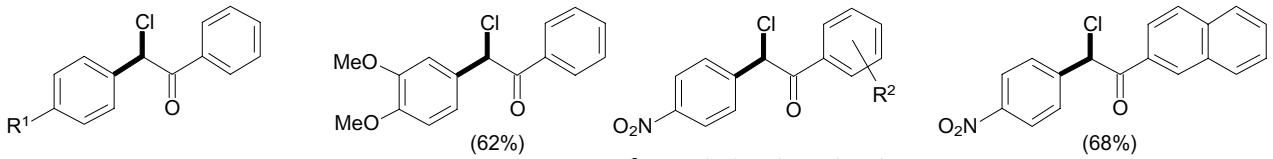
The $[Ru(bpy)_3][PF_6]_2$ photocatalyst proved to be applicable to the visible light-initiated arylation of pyridines at the position 2 with aryl radicals generated from aryldiazonium salts.[217]

Scheme 52



29

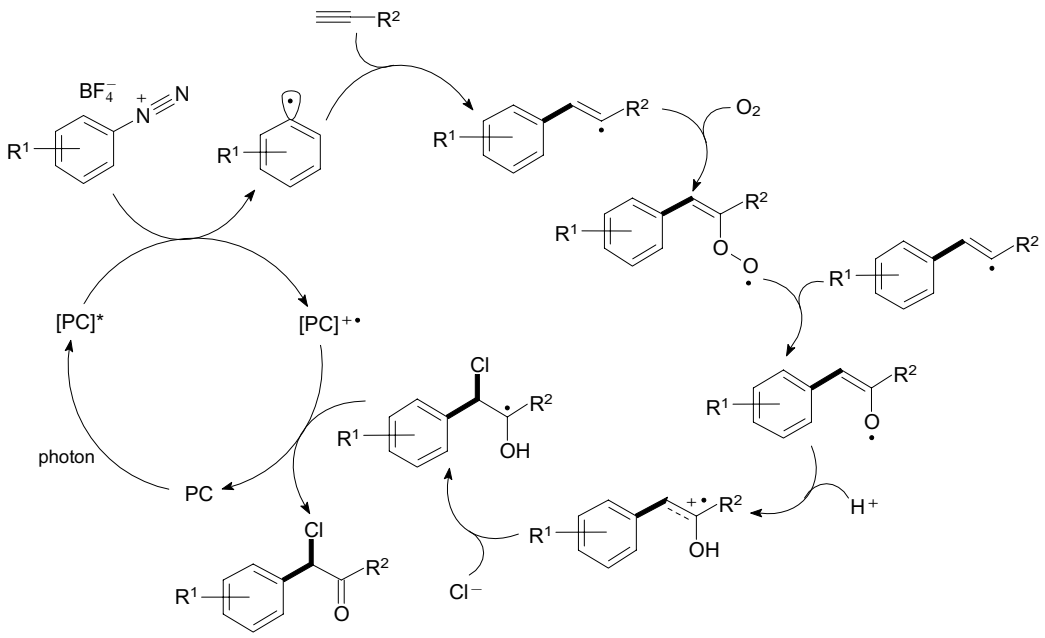
Products



(62%) (68%)

R^1 = Ac (68%), CN (78%)

R^2 = 4-NO_2 (76%), 2-F (56%)

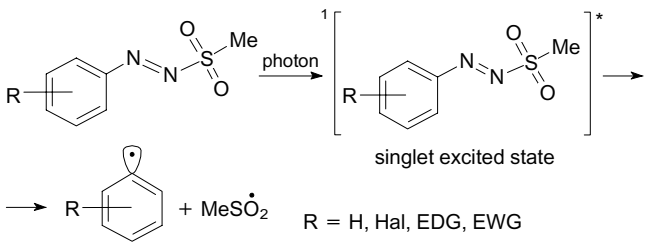


2.2.4. The use of various derivatives of aryldiazonium salts

In addition to aryldiazonium salts, some of their derivatives are also used for generating aryl radicals, which makes it possible to circumvent the key disadvantage of these compounds, that is, explosiveness.

Arylazo sulfones have been proposed as precursors of aryl radicals (Scheme 53). These compounds can be easily prepared in two steps from anilines by diazotization followed by the treatment of the aryldiazonium salt with sodium methanesulfinate. Visible light irradiation induces homolytic cleavage of the N – S bond to give the radical pair consisting of an aryl radical and a methanesulfonyl radical.

Scheme 53

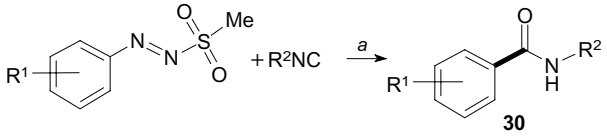


The application of arylazo sulfones as sources of aryl radicals for the subsequent arylation was first demonstrated in relation to the synthesis of *N*-substituted aromatic amides **30** (Scheme 54).[218]

Subsequently, these compounds were successfully used in the synthesis of 8-arylxanthines,[219] arylstannanes,[220] arylboronic esters and aryl sulfides.[221]

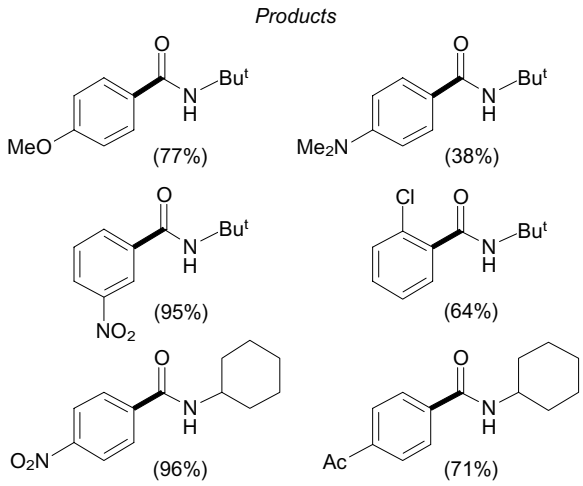
The generation of an aromatic radical from arylazocarboxylic *tert*-butyl ester in the presence of trifluoroacetic acid (TFA) and oxygen has been described (Scheme 55).[222] First, the Boc group is removed under the action of trifluoroacetic acid, which results in the formation of

Scheme 54

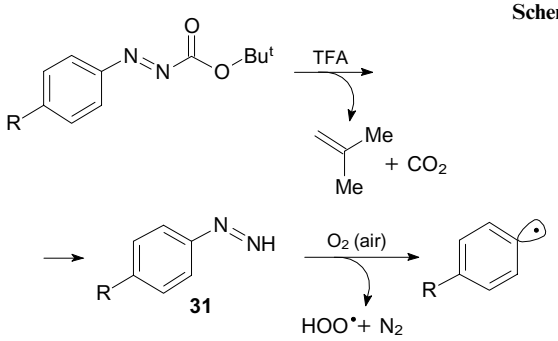


(*a*) $NaHCO_3$ (2 equiv.), MeOH – H_2O (9 : 1), blue ligh, 23 °C, 24 h

Products



Scheme 55

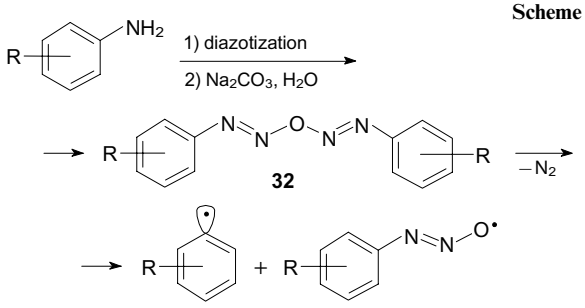


R = Br, NO_2, CN, OC_7H_{15}-n

aryldiazene **31**; this is followed by elimination of the terminal hydrogen atom with simultaneous elimination of the nitrogen molecule to give an aryl radical.

Aryl radicals are generated upon the addition of an aqueous solution of sodium carbonate to a diazonium salt, which is converted under these conditions to diazo anhydride **32**; the latter tends to undergo homolytic cleavage to an aromatic radical, diazenyloxyl radical and molecular nitrogen (Scheme 56).

Scheme 56



R = Hal, EDG, EWG

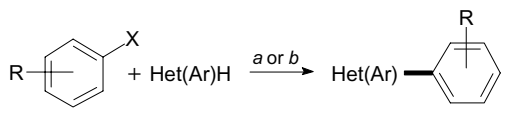
This method of generation of aryl radicals was applied to various (het)arenes. The maximum yields were obtained for hetaryl compounds, while biphenyl derivatives are formed in lower yields (Scheme 57).[223]

Photoactive diazo anhydrides were also generated *via* self-condensation of nitrosamines, which are formed *in situ* from anilines and alkyl nitrites (Scheme 58).[224] Diazo anhydrides are exceptionally unstable compounds, which decompose spontaneously or under illumination to give aryl radicals; under these conditions, the arylation is most efficient for electron-withdrawing substrates, *e.g.*, pyridine *N*-oxide.

Other derivatives of diazonium salts used to generate aryl radicals are diazotates, which are easily obtained by treatment of solutions of diazonium salts with a solution of sodium hydroxide (Scheme 59). Diazotates were successfully employed for the arylation of pyrroles and unsubstituted anilines.[225, 226]

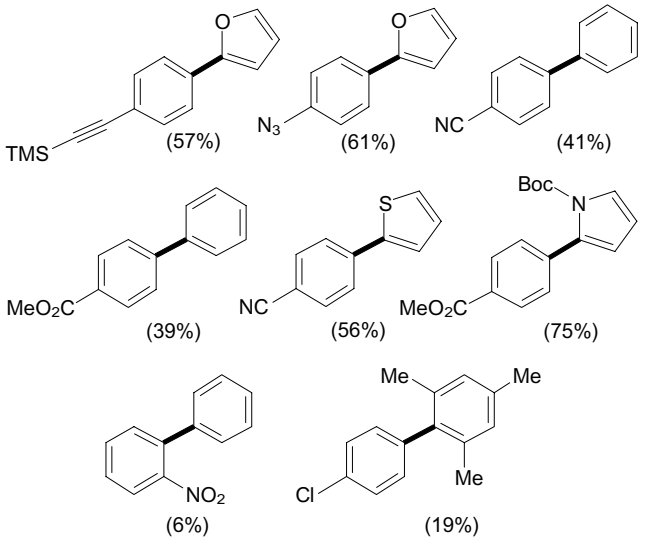
Diazotate derivatives, diazosalicylates, generated *in situ* from diazonium salts and salicylic acid, made it possible to perform α-arylation of enol acetates; salicylic acid was taken for this reaction in catalytic quantities (Schemes 60, 61).[227] The maximum yields of arylation products **33** were obtained in the case of electron-withdrawing group-substituted phenyldiazonium salts.

Scheme 57



(*a*) 1) Na_2CO_3 (1 M), MeCN, 23 °C; 2) 1 M HCl;
(*b*) Bu^{t}ONO, $MeSO_3H$, Na_2CO_3 (1 M), MeCN, 23 °C; 2) 1 M HCl;
X = NH_2, N_2BF_4

Products

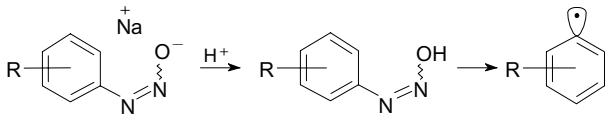


Similarly, the radical generation is catalyzed by gallic acid, which was used for the arylation of benzene and electron-rich five-membered heterocycles.[228]

Substituted aryltriazenes are much more stable than the corresponding aryldiazonium salts; many triazenes are stable at temperatures above 200 °C.[229]

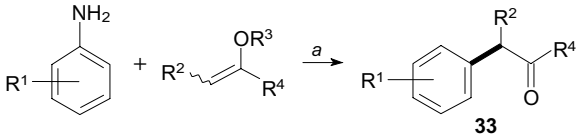
The aryl radicals generated from aryltriazenes under the action of the $AgNO_3 - K_2S_2O_8 -$ TFA system have found use for the arylation of various heterocyclic compounds such as substituted pyridines, pyrimidines, pyrazines, pyridazines, quinolines, isoquinolines, benzimidazoles, *etc.*

Scheme 59



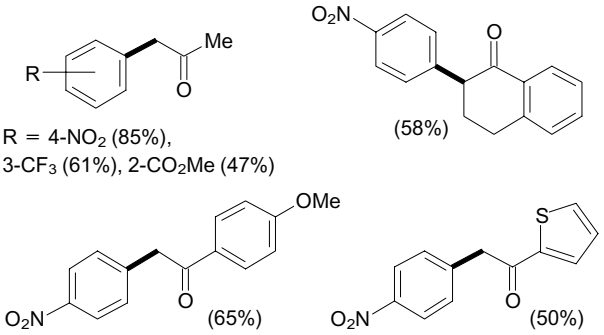
R = H, Hal, Me, OMe, CF_3

Scheme 60



(*a*) Bu^{t}ONO (1.5 equiv.), 2-$HOC_6H_4CO_2H$ (10 mol.%), MeCN – H_2O (2 : 1), 23 °C, 3 h

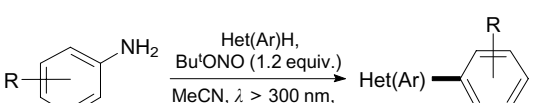
Products



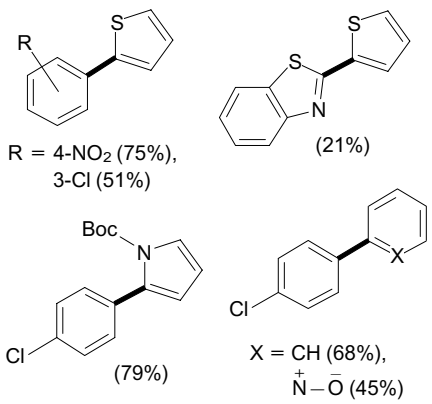
(Scheme 62). Despite the broad range of substrates, this method is not generally applicable, because it is not regiospecific and often gives mixtures of isomers.[230]

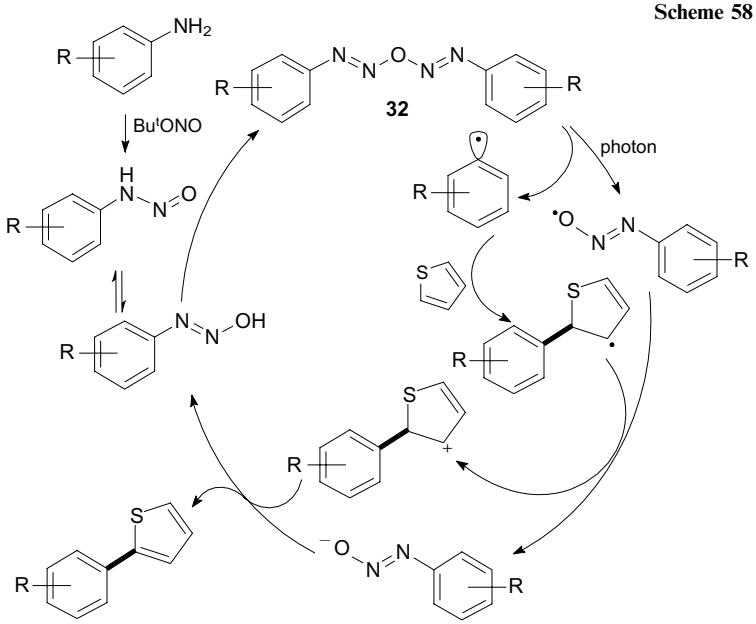
Thus, arylation methods based on the utilization of aryldiazonium salts and involving generation of aromatic radicals were markedly supplemented in recent years owing to the use of both diverse derivatives of diazonium salts and various methods for radical generation.

Scheme 58

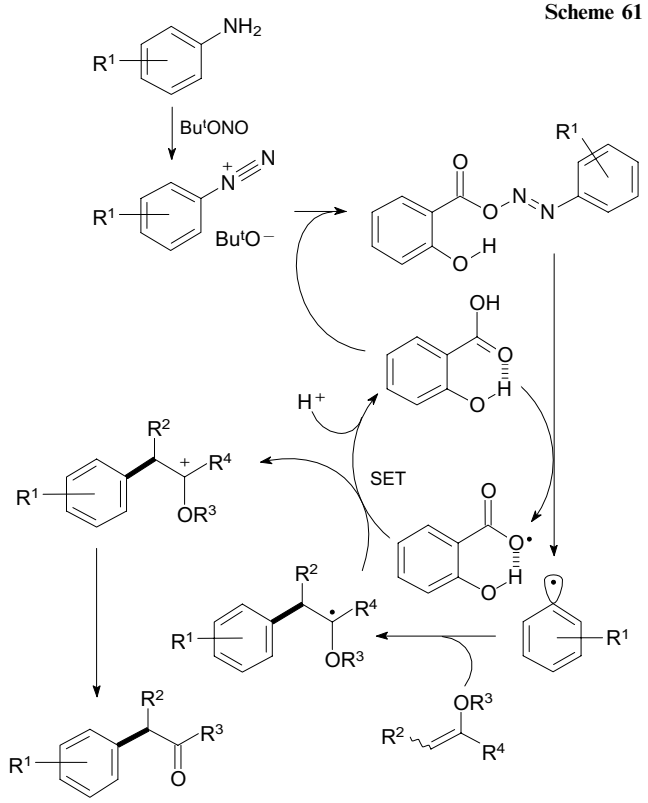


Products

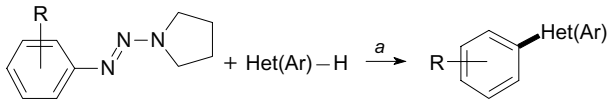




Scheme 61

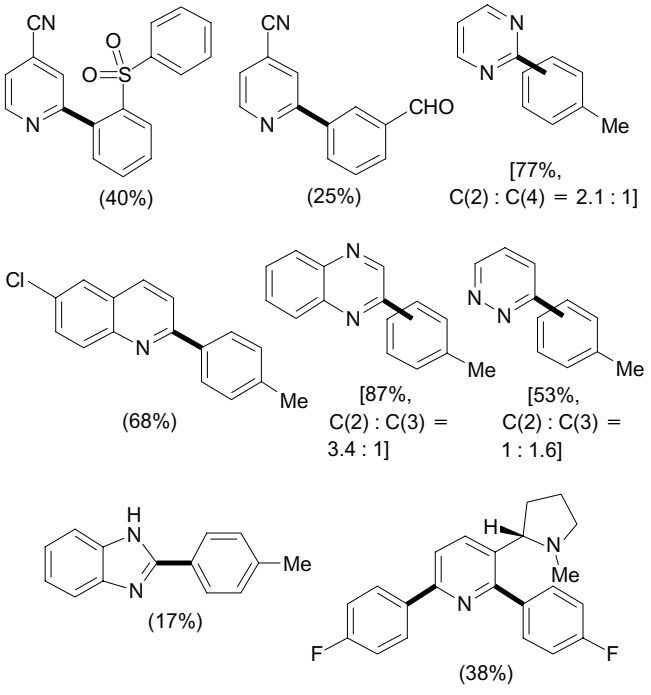


Scheme 62



(*a*) $AgNO_3$ (20 mol.%), $K_2S_2O_8$ (3 equiv.), TFA, CH_2Cl_2, H_2O, 23 °C

Products



2.3. Generation of aryl radicals from diaryliodonium salts

Hypervalent iodine compounds and synthetic methods employing these compounds have attracted great attention of researchers in the last decade. In particular, during this period, considerable advances have been made in the chemistry of diaryliodonium salts, which have found use as electrophilic arylating agents,[231–235] aryne precursors[236–238] and sources of aryl radicals.[239] The interest in diaryliodonium salts is primarily due to the fact that reactions of these compounds make a good alternative to methods using expensive and toxic catalysts based on transition metals.[240] Diaryliodonium salts are stable, nontoxic and highly reactive, demonstrating high selectivity and compatibility with many functional groups, and the safe methods for their synthesis developed in recent years make it possible to prepare large quantities of these compounds at low cost.[233] Although there are several analytical reviews addressing the chemistry of diaryliodonium salts, in particular, methods for their preparation and application in organic synthesis,[60,241,242] these publications do not consider radical transformations of diaryliodonium salts in detail. This Section describes reactions of diaryliodonium salts accompanied by intermediate formation of aryl radicals.

2.3.1. Reactions involving the formation of a donor–acceptor complex

Diaryliodonium salts, being Lewis acids,[243] are able to react with electron-donor molecules, which brings about the fragmentation of the diaryliodonium ion to the aryl radical and aryl iodide.

Aromatic radicals can be directly formed in the reaction between a donor of an aryl moiety and the substrate to be arylated. Like diazonium salts, diaryliodonium salts are used in the radical arylation of quinoxalin-2-(1*H*)-ones,[244] benzoquinones[245] and nitrogen heterocycles (in particular, pyrazines) (Scheme 63).[246]

Cyclic iodonium salts can react with molecular chalcogens to exchange the iodine atom, giving products **34** and **35**. In relation to the synthesis of cyclic sulfides, the authors demonstrated that this reaction has a radical mechanism (Scheme 64).[247]

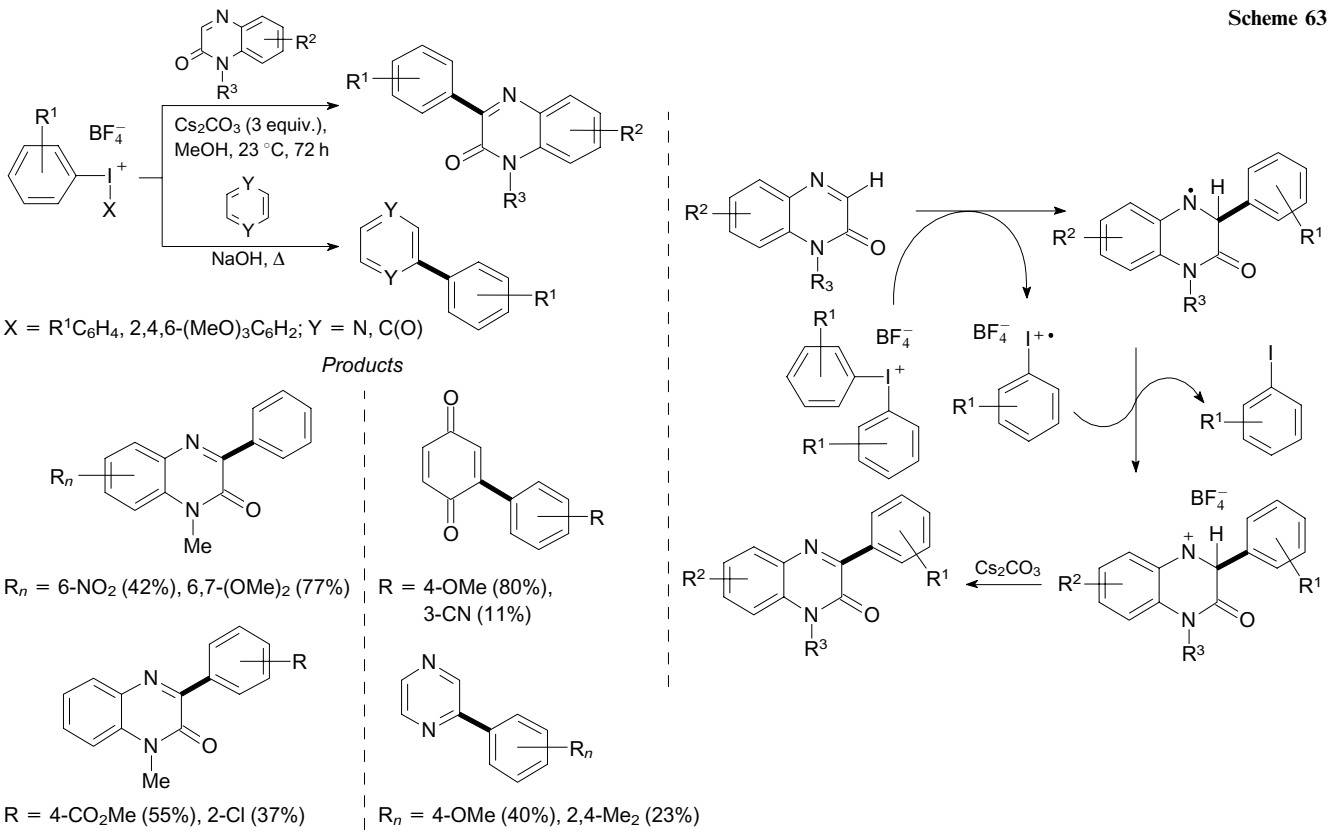
A possible route for the generation of aryl radicals from diaryliodonium salts is based on the formation of EDA with nucleophilic substrates. These complexes can undergo single electron transfer (SET), initiated either thermally or photochemically.[236,248,249] The SET induces decomposition of the complex with homolytic cleavage of the C–I bond, resulting in the generation of an aryl radical (Scheme 65).

Donor–acceptor complexes can be formed between a diaryliodonium salt and the molecule of an auxiliary reagent. In 2016, Lakhdar and co-workers[249] reported the thermal generation of the phenyl radical *via* the preliminary formation of the EDA from diphenyliodonium triflate and triethylamine. In this case, the aromatic radical does not participate in the formation of any arylation product, but only initiates a cascade of radical transformations (Scheme 66), resulting in the formation of 6-phosphorylated phenanthridines **36**.

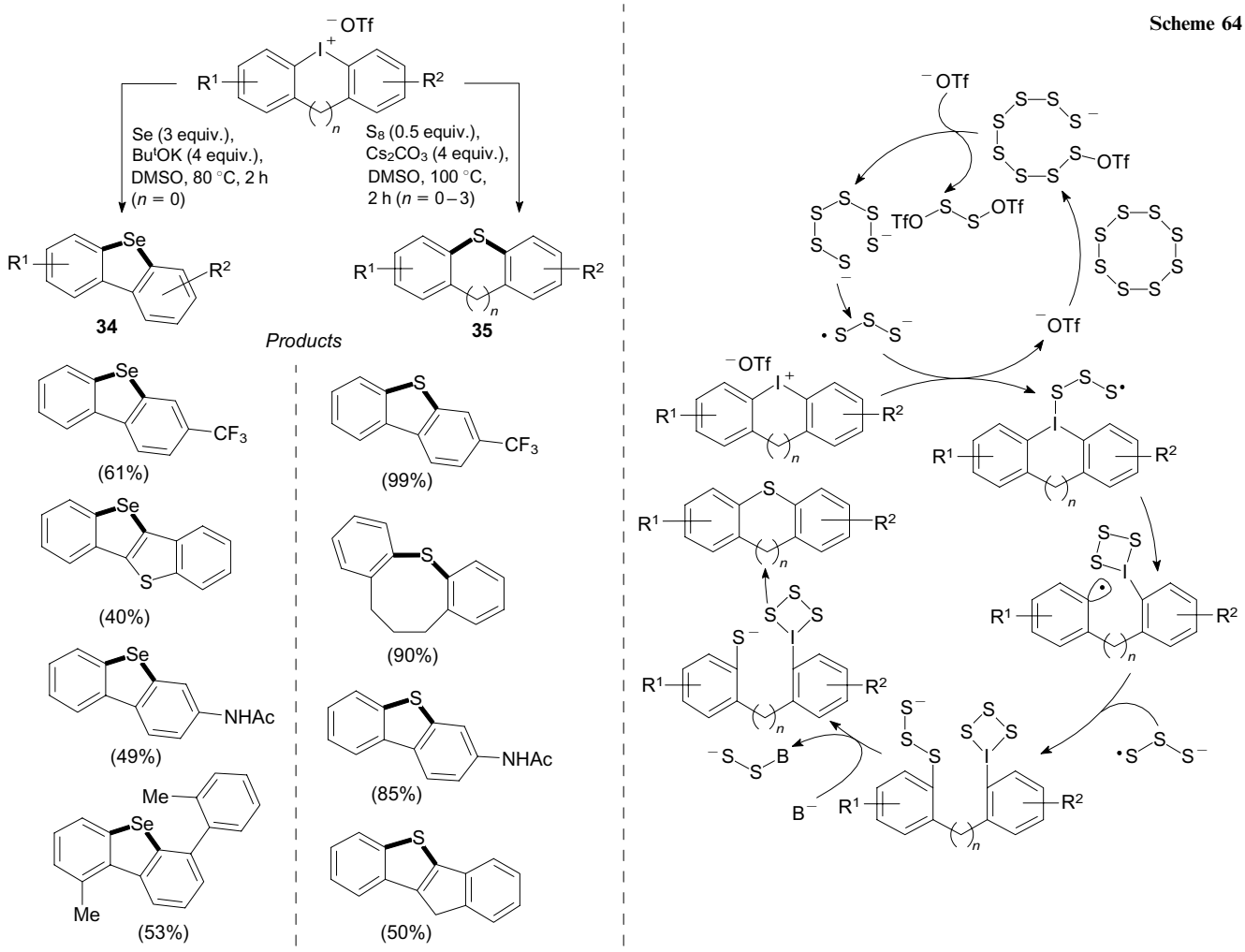
Later, the same research group[250] developed a synthetic route to phosphorylated enamides based on a similar transformation.

Potassium *tert*-butoxide can also serve as an auxiliary reagent for the homolytic cleavage of the C_{Ar}–I bond. As one of the probable mechanisms of this reaction, generation

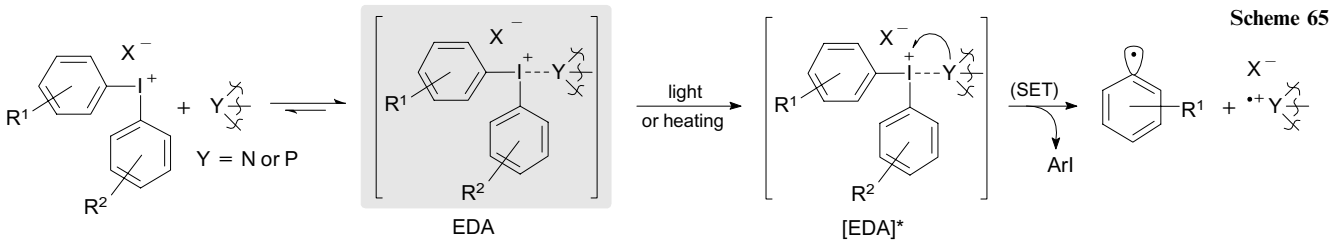
Scheme 63



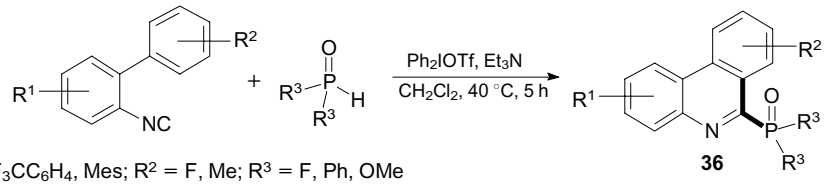
Scheme 64



Scheme 65

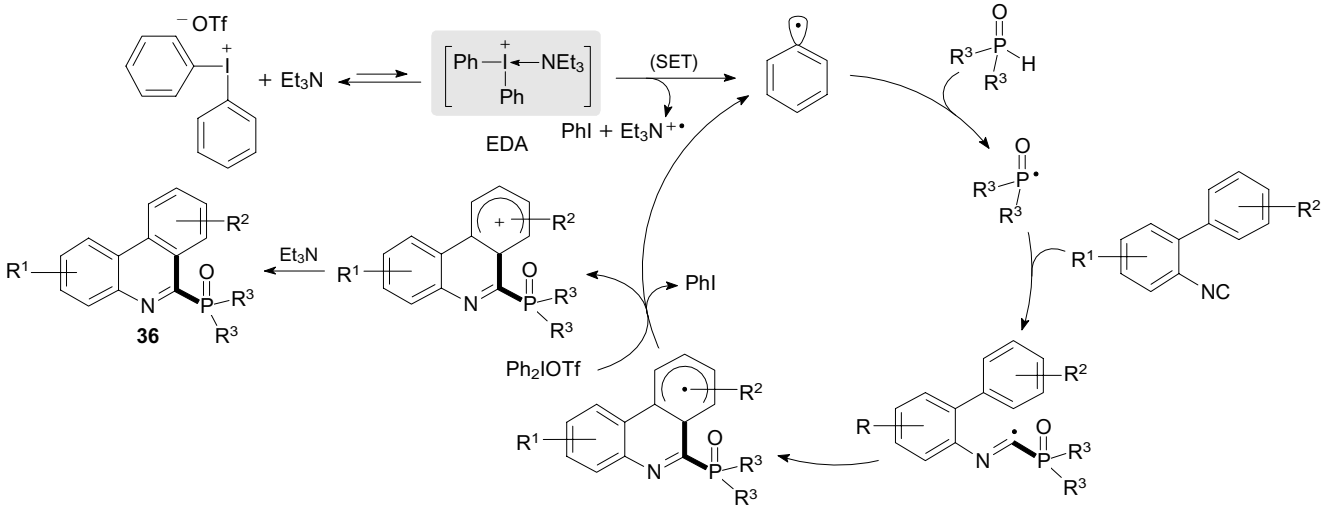


Scheme 66

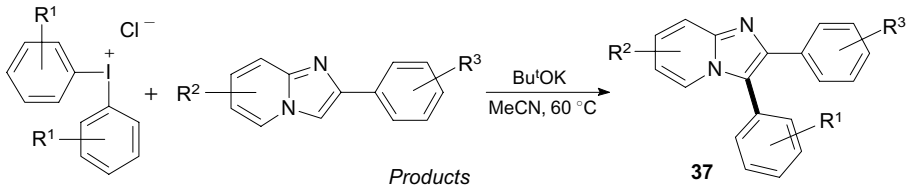


R^1 = Ph, 4-Bu^{t}C$_6$H$_4$, 4-F$_3$CC$_6$H$_4$, Mes; R^2 = F, Me; R^3 = F, Ph, OMe

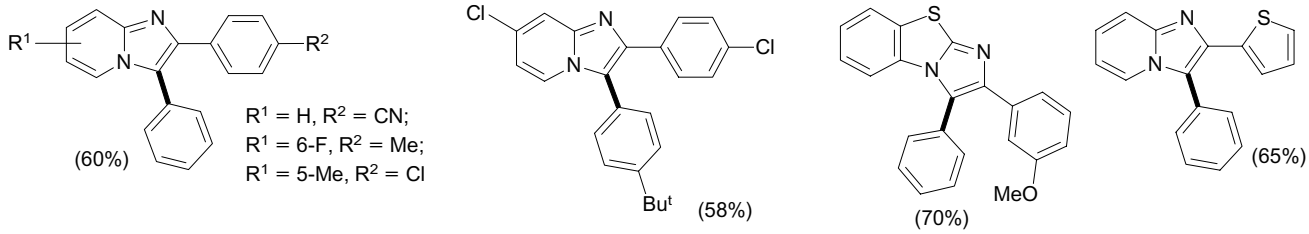
36

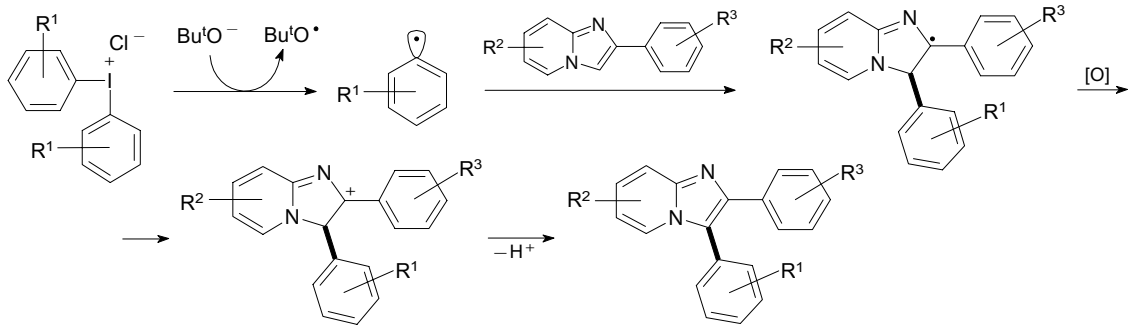


Scheme 67

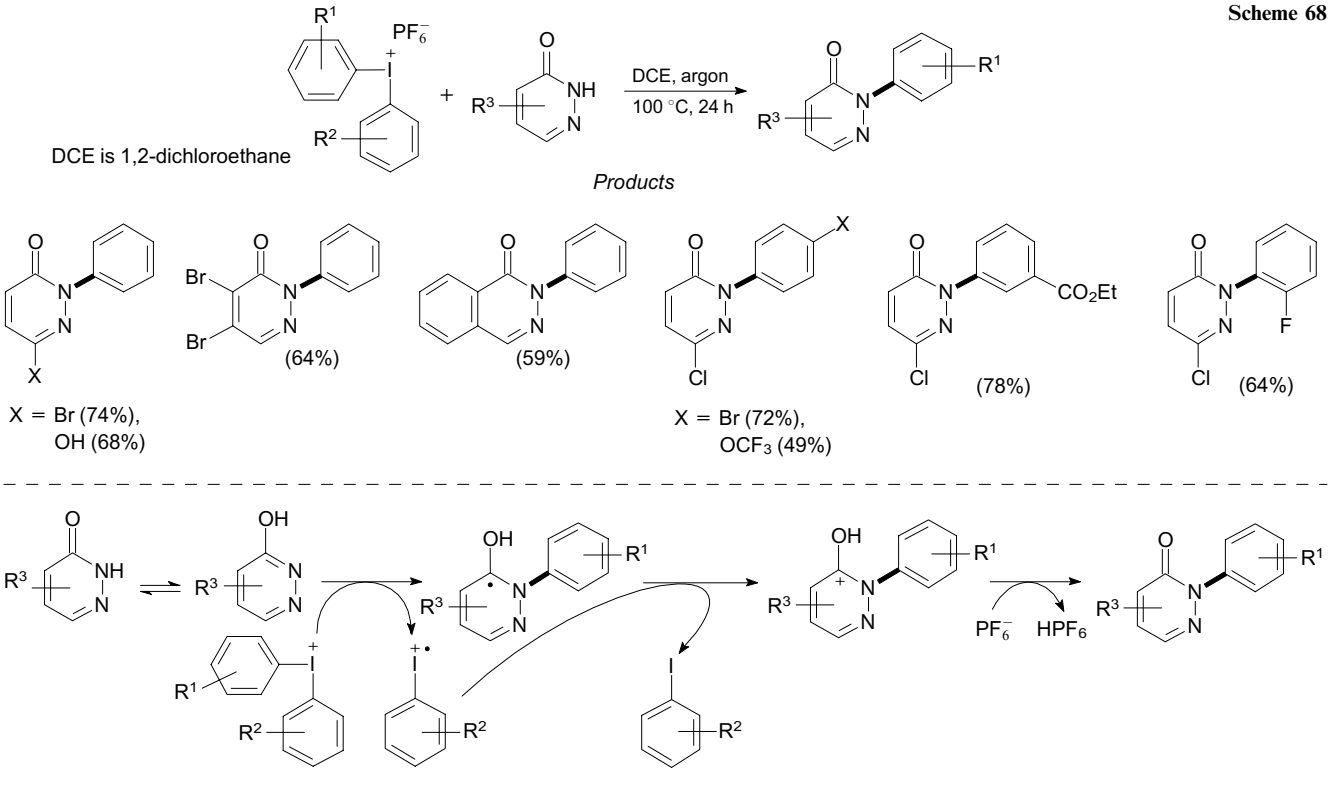


37

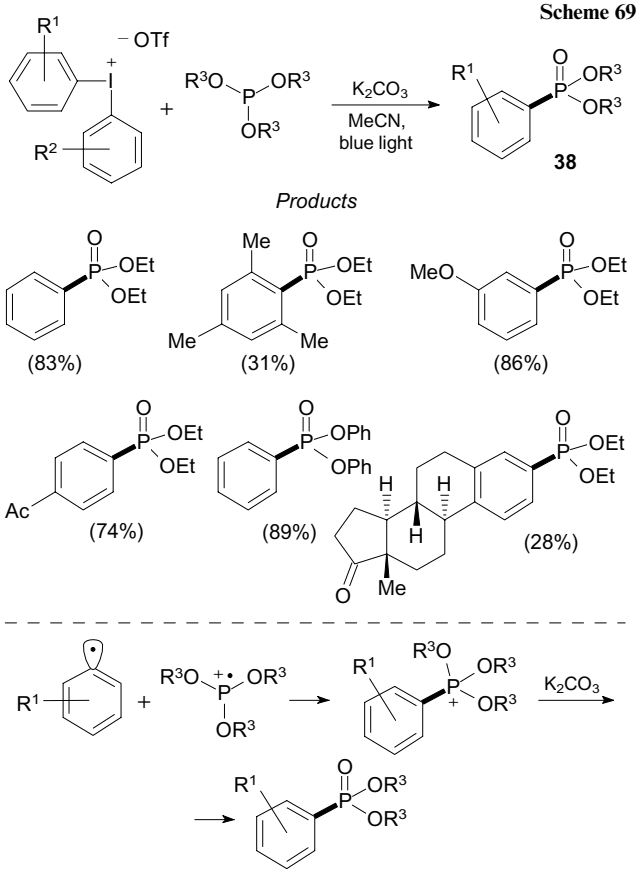




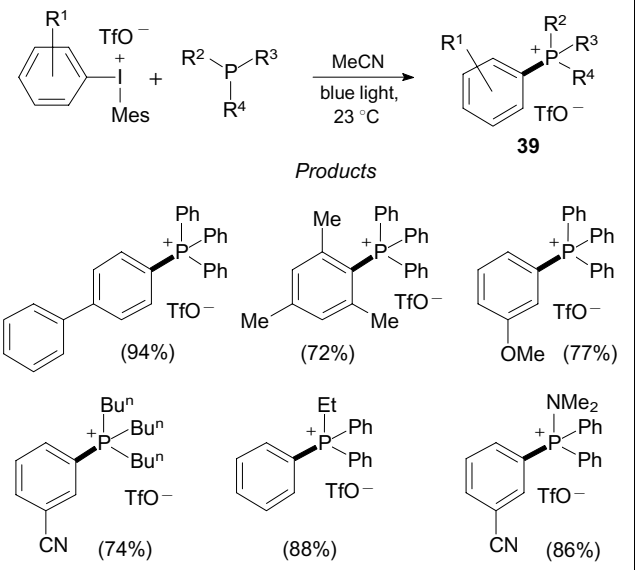
Scheme 68



Scheme 69



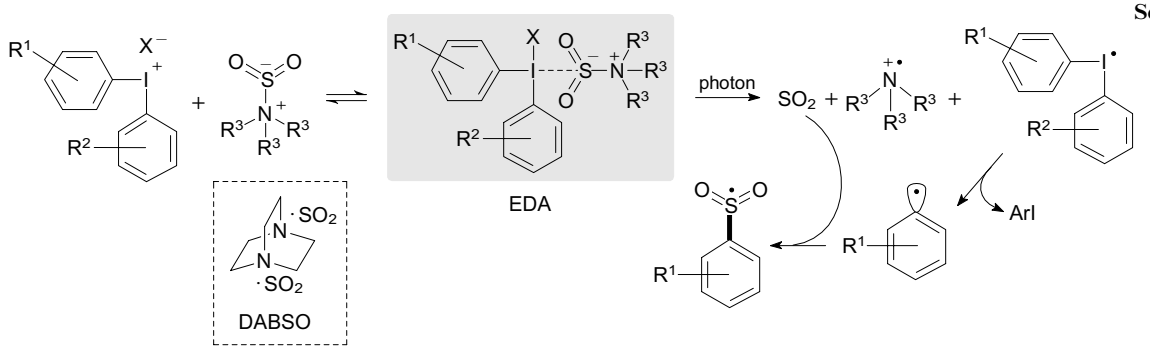
Scheme 70



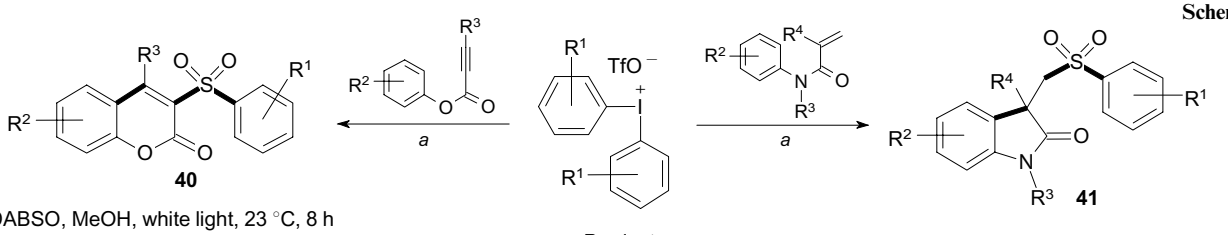
of aryl radicals according to Scheme 67 was proposed.[251] This method was used for the arylation of imidazo[1,2-*a*]-pyridines containing substituents of different electronic nature to give products **37**.

The formation of EDA between the iodonium salt and the substrate is actively utilized to form carbon – heteroatom bonds. For example, *N*-arylation of pyridazinones proceeds *via* thermal activation of the complex formed by the hydroxyl form of pyridazinone and the iodonium salt (Scheme 68).[252] The introduction of a halogen atom into the *ortho* position to nitrogen and introduction of electron-withdrawing substituents to the iodonium salt increase the yield of the product. In the case of iodonium salts containing electron-withdrawing substituents, symmetrical salts proved to be inefficient; therefore, the authors chose a mesityl (2,4,6-thimethylphenyl, Mes) group as an aryl auxiliary.

Scheme 71

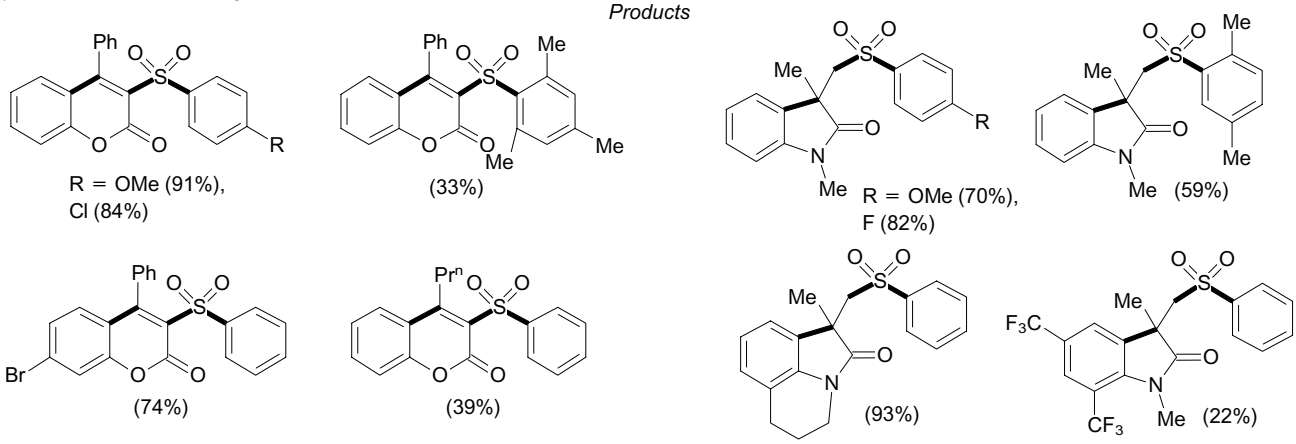


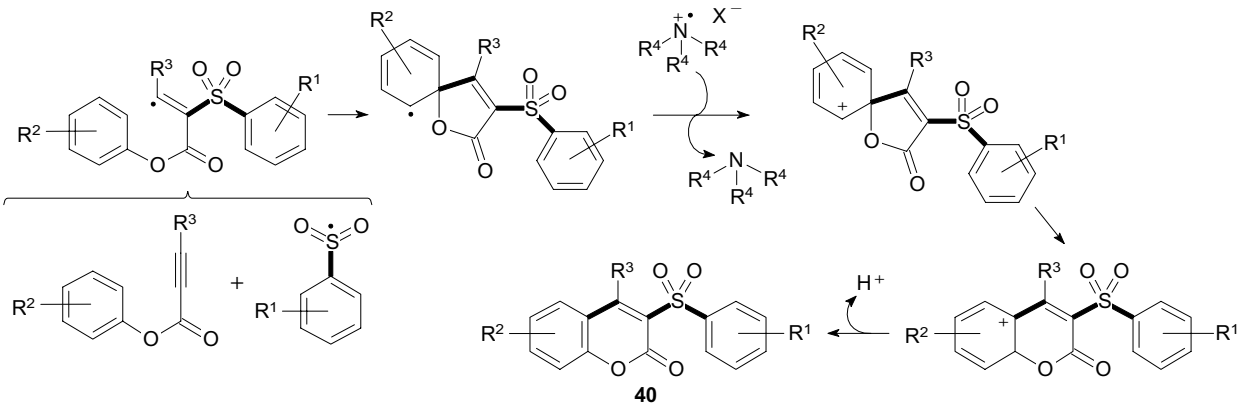
Scheme 72

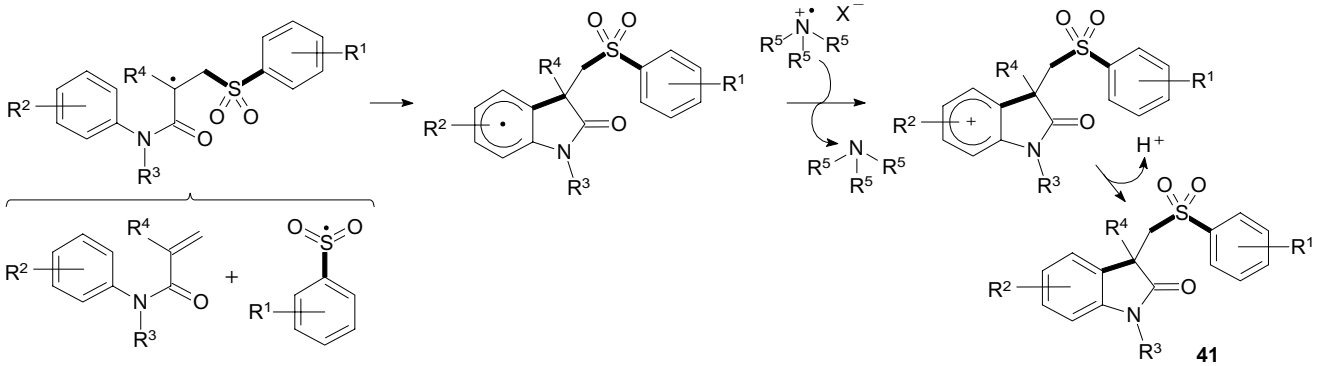


(*a*) DABSO, MeOH, white light, 23 °C, 8 h

Products







Selectivity of the transfer of an aromatic moiety is a key issue of the chemistry of unsymmetrical diaryliodonium salts. Although at the first glance, generation of radicals from unsymmetrical iodonium salts is difficult to control by either electronic or steric factors,[253] in the reactions of unsymmetrtical salts considered below, selective transfer of the aryl substituent takes place.

The Arbuzov-like reaction involving symmetrical diaryliodonium salts and trialkyl phosphites occurs upon irradiation with blue light (λ = 420 nm) (Scheme 69).[254] Under the action of irradiation, single-electron transfer takes place in the initially formed EDA, which results in the generation of an aryl radical and trialkyl phosphite radical cation. The subsequent recombination and base-induced elimination of the alkyl group affords arylphosphonates **38**. The phosphorylation of complex and expensive substrates was carried out using unsymmetrical aryl(mesityl) salts. The observed high selectivity of the transfer of an aryl substituent and the low yield of products in the case of di(mesityl)-iodonium triflate attest to steric control over the transfer of the aromatic moiety.

Karchava and co-workers [255] proposed a method for the arylation of tertiary phosphines in the absence of any additional reagents giving tetraaryl- and alkylarylphosphonium salts **39** in up to 90% yields. Steric factors do not significantly affect the yields of reaction products (Scheme 70).

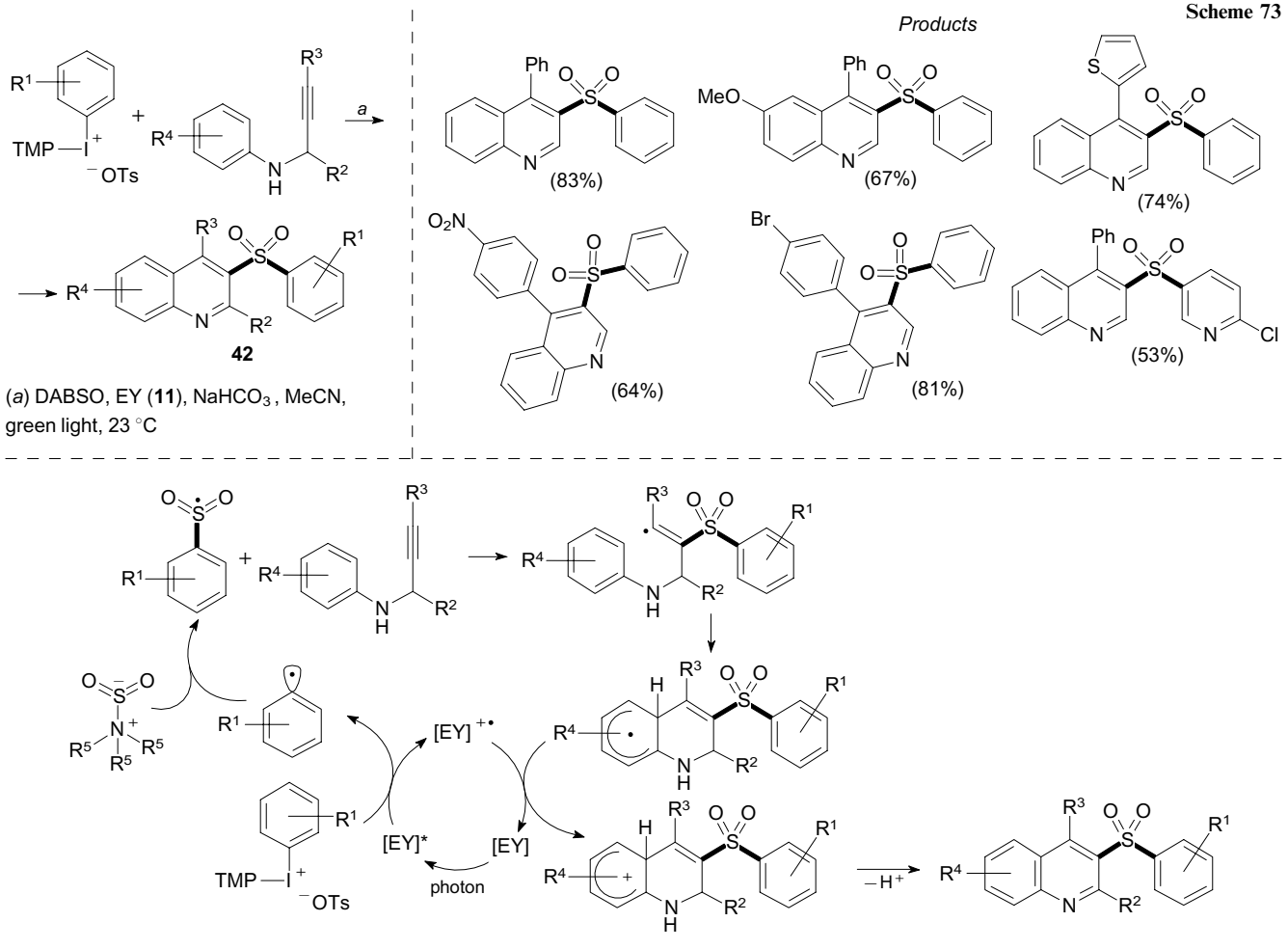
The formation of DAC is successfully utilized in three-component radical arylsulfonylation reactions initiated by visible light and based on the use of the 1,4-diazabicyclo[2.2.2]octane complex with two SO_2 molecules (DABSO) and diaryliodonium salts as sources of sulfonyl and aryl moieties, respectively (Scheme 71). The interaction of the electron pair of the sulfur atom with the vacant p orbital of the iodine gives the EDA. Then this complex is destroyed under visible light irradiation to give the reduced form of the iodonium salt, which undergoes fragmentation affording an aryl radical. The recombination of the aryl radical and sulfur(IV) dioxide furnishes the desired arylsulfonyl radical.

Using this pathway for generation of arylsulfonyl radicals, it is possible to convert unsaturated *O*-aryloxycarbonyl compounds and *N*-arylamides to arylsulfonylated coumarins **40** (Ref. 256) and arylsulfonylated indoles **41** (Ref. 257), respectively (Scheme 72). The irradiation with white light induces the cascade formation of arylsulfonyl radical, which attacks the double or triple bond to give fused heterocyclic systems. The presence of *ortho* substituents in the aryl moiety hampers both reactions; however, the preferable reaction pathway depends on electronic factors: coumarins **40** are predominantly formed in the presence of electron-donating substituents, whereas the highest yield of arylsulfonylated indoles **41** was detected for electron-deficient substrates.

2.3.2. Reactions involving photoredox catalysts or sensitizers

The synthesis of arylsulfonylquinolines **42** is based on the use of diaryliodonium salts, DABSO and eosin Y (**11**) as a photocatalyst (Scheme 73).[258] The visible light-excited eosin Y molecule acts as a reducing agent towards the iodonium

Scheme 73



salt molecule, giving rise to an aryl radical, which then participates in the reaction. The use of the electron-rich trimethoxyphenyl group (TMP) as a second aryl moiety determines high selectivity of transfer of the aryl rather than trimethoxyphenyl group (see Scheme 73).

The generation of aryl radicals by means of eosin Y (**11**) was also used in the synthesis of aryl sulfides and aryl sulfoxides.[259] Depending on the conditions of reactions between organic thiosulfates and diaryliodonium salts, the reactions give aryl sulfides **43** (white light, inert atmosphere) or sulfoxides **44** (green light, air) (Scheme 74). Sulfoxidation efficiently occurs for alkyl and aryl sulfides; however, the reaction with sterically crowded diaryliodonium salts is hampered, like in the case of sulfenylation. The reaction mechanism implies a double catalytic cycle for the photocatalyst: first, aryl sulfide is formed (electron transfer cycle), and then it is oxidized with singlet oxygen (energy transfer cycle).

The catalytic radical reactions of diaryliodonium salts proved to be applicable to arylation of azine *N*-oxides initiated by blue light in the presence of eosin Y (**11**).[260] The reaction follows the standard mechanism; however, it is necessary to additionally use an oxidant ($K_2S_2O_8$ or benzoquinone), the role of which is not entirely clear (Scheme 75).

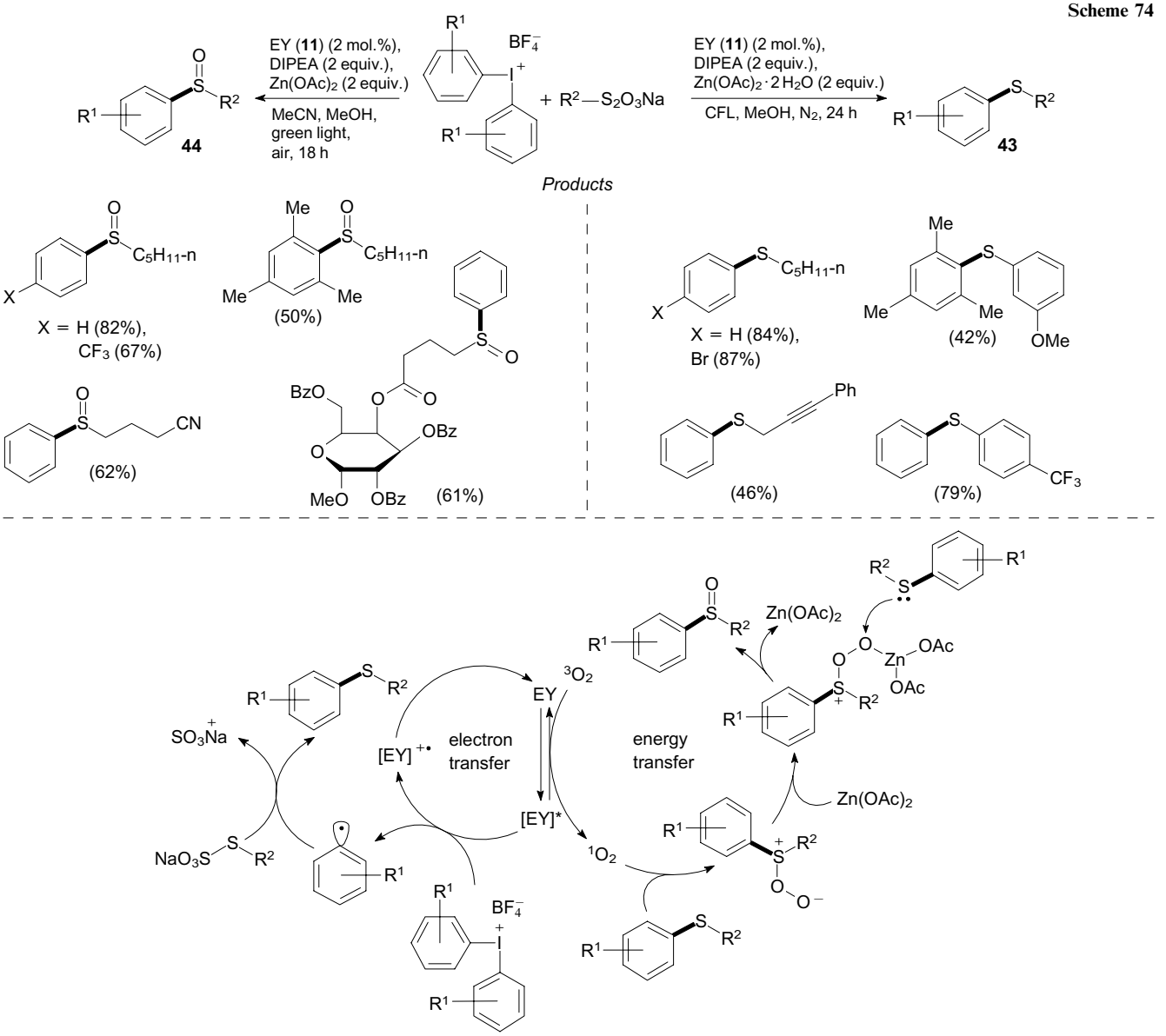
A photocatalyst is also needed for the reaction of diaryliodonium salts and hydrazines in the presence of SO_2 generated *in situ* in the $K_2S_2O_5$–TFA system; the perylene dye PDI (**1**) proved to be the most efficient photocatalyst in this case.[261] The mechanism of this reactions somewhat differs from the previous one: in this case, the aryl radical is formed upon the reaction of iodonium salt with the radical anion of the photocatalyst (Scheme 76).

The acridine catalyst Mes-Acr-Me (**45**) is also employed to prepare aromatic radicals from iodonium salts. The phenyl radical generated using this catalyst was applied for radical phosphorylation of alkenes (Scheme 77), similar to the above-described reactions involving Ph_2PHO,[262] and for aromatization of 1,2-dihydronaphthalenes.[263]

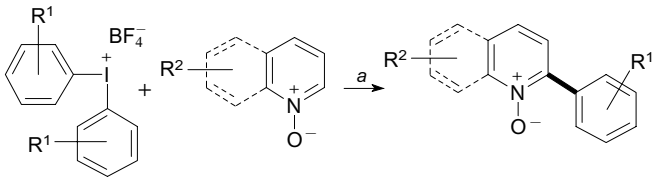
A number of publications address arylation of a variety of substrates with iodonium salts in the presence of photoredox catalysts based on transition metals (Ir, Ru and Cu).

An early example of application of metal-catalyzed radical reactions of iodonium salts is arylation of styrenes (Scheme 78).[264] The photoredox catalyst $Ir(ppy)_3$ in the

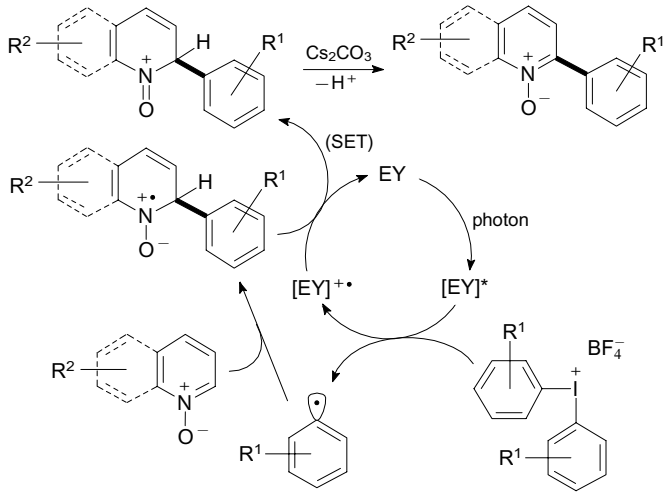
Scheme 74



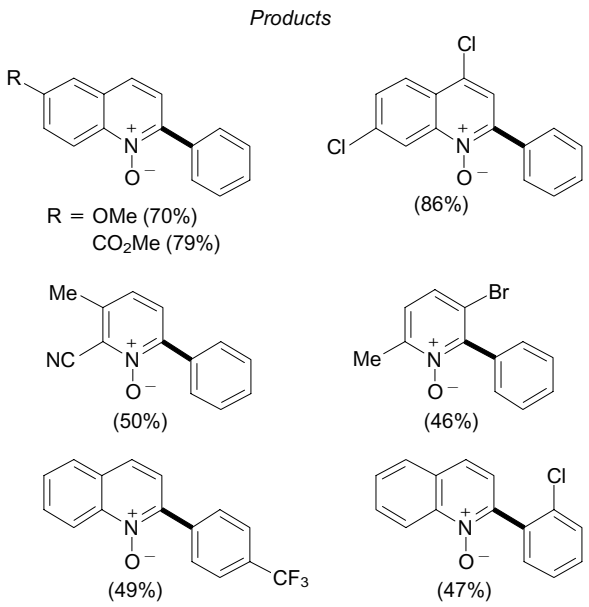
Scheme 75



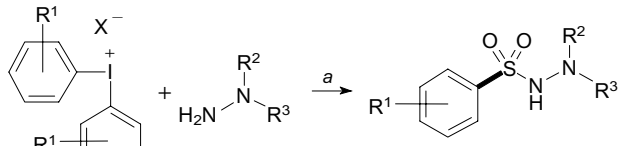
(*a*) EY (**11**) (10 mol.%), Cs_2CO_3 (1 equiv.), $K_2S_2O_8$ or BQ (2 equiv.), blue light, N_2, 3 days; BQ is benzoquinone



Products

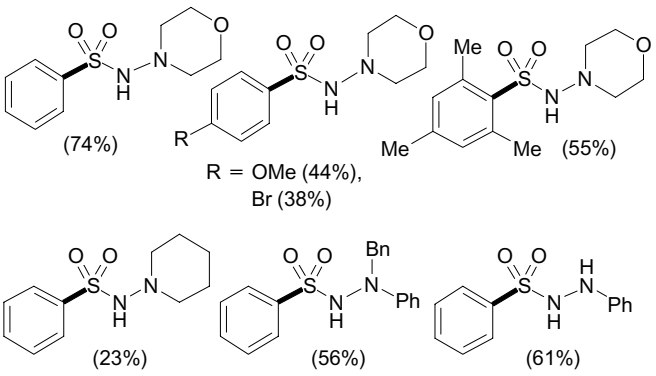


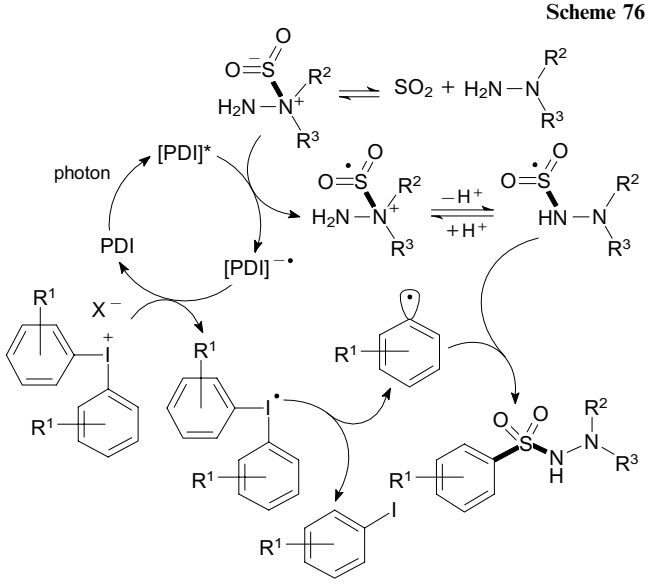
Scheme 76



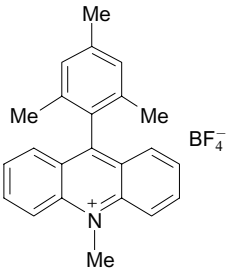
(*a*) $K_2S_2O_5$, TFA, PDI (**1**), MeCN, DMSO, blue light, 23 °C, 2 h

Products



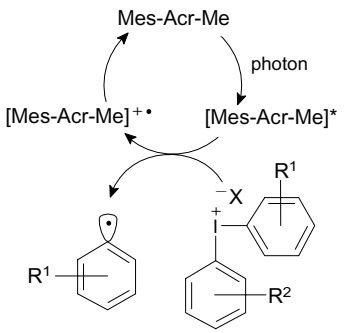


Structure 45

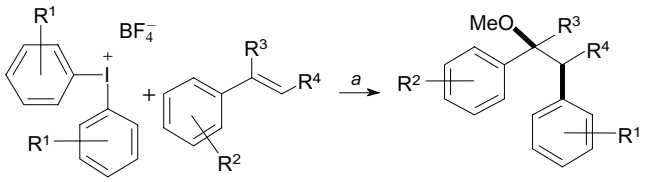


45 (Mes-Acr-Me)

Scheme 77

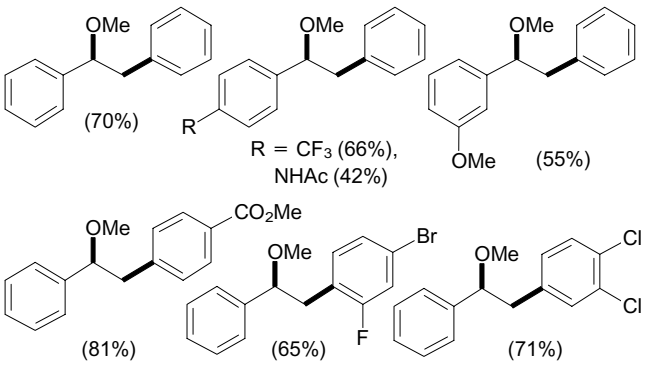


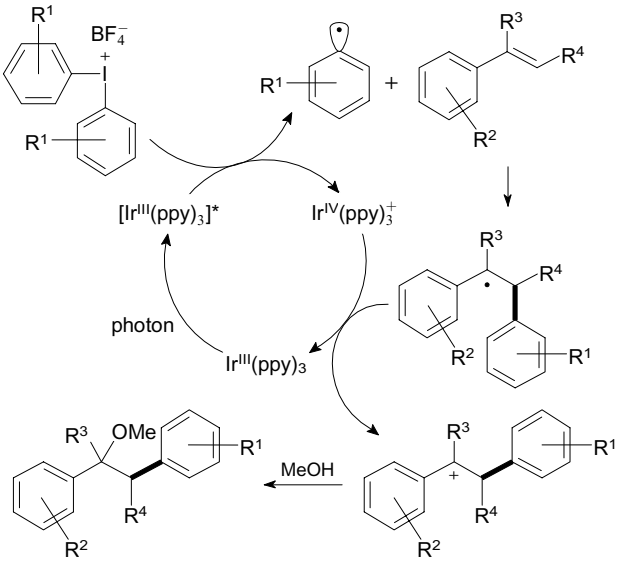
Scheme 78



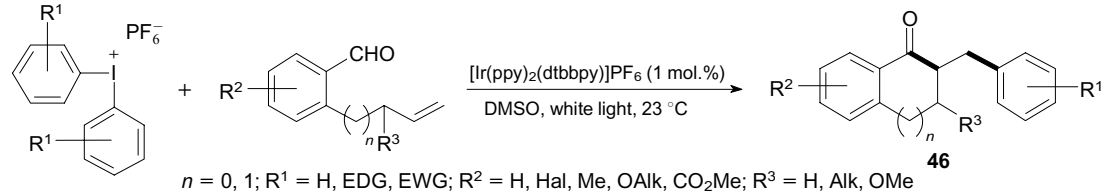
(*a*) $Ir(ppy)_3$ (1 mol.%), $Zn(OAc)_2$ (20 mol.%), MeOH, 30 W lamp, 23 °C, 18 h

Products



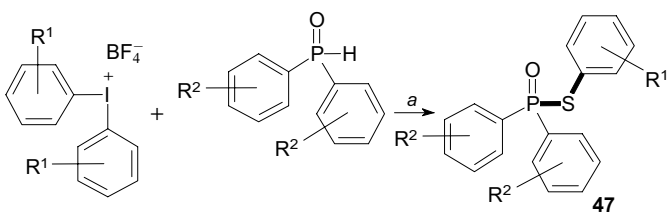


Scheme 79



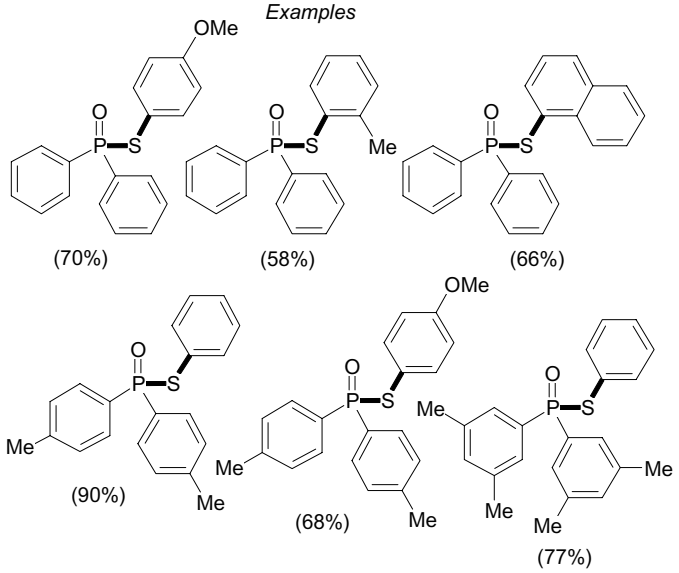
n = 0, 1; R^1 = H, EDG, EWG; R^2 = H, Hal, Me, OAlk, CO_2Me; R^3 = H, Alk, OMe

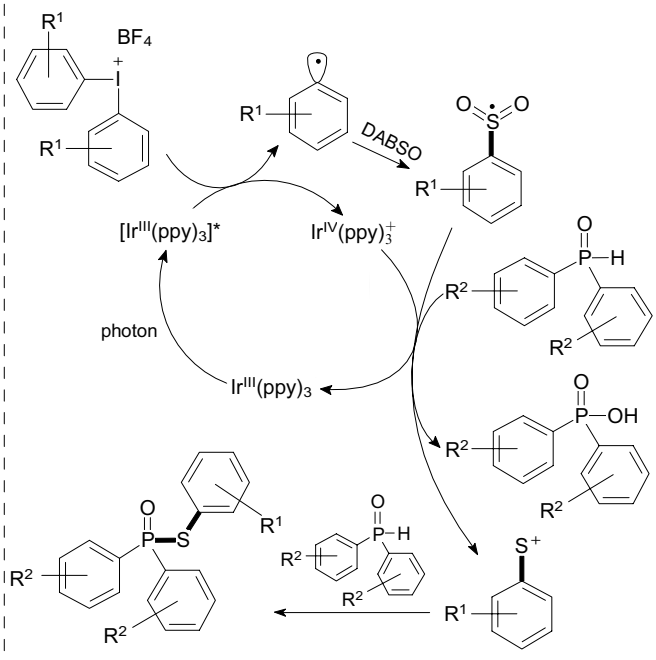
Scheme 80



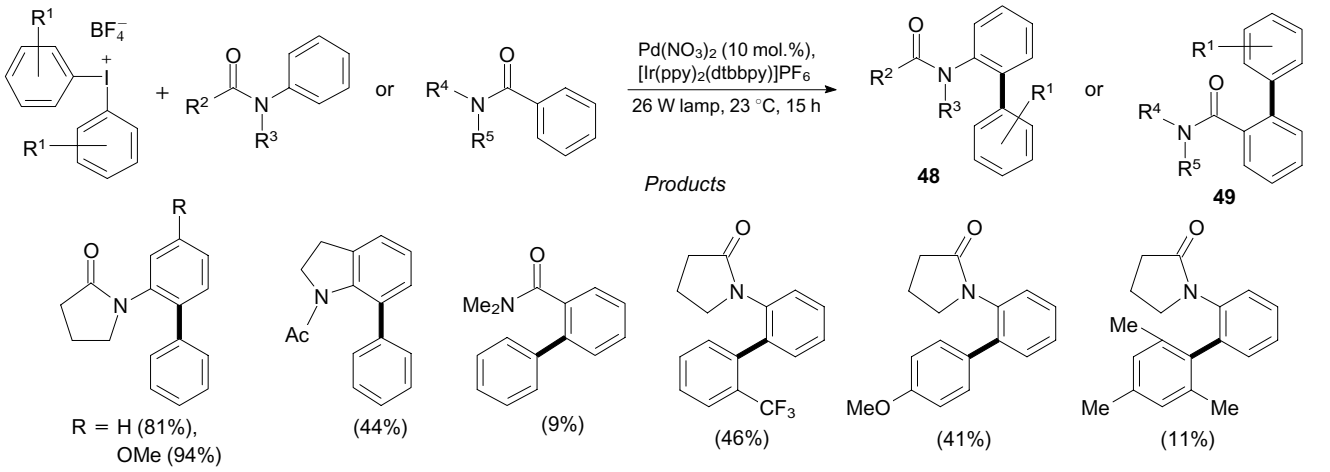
(*a*) DABSO, $Ir(ppy)_3$ (2 mol.%), MeCN, N_2, white light, 23 °C

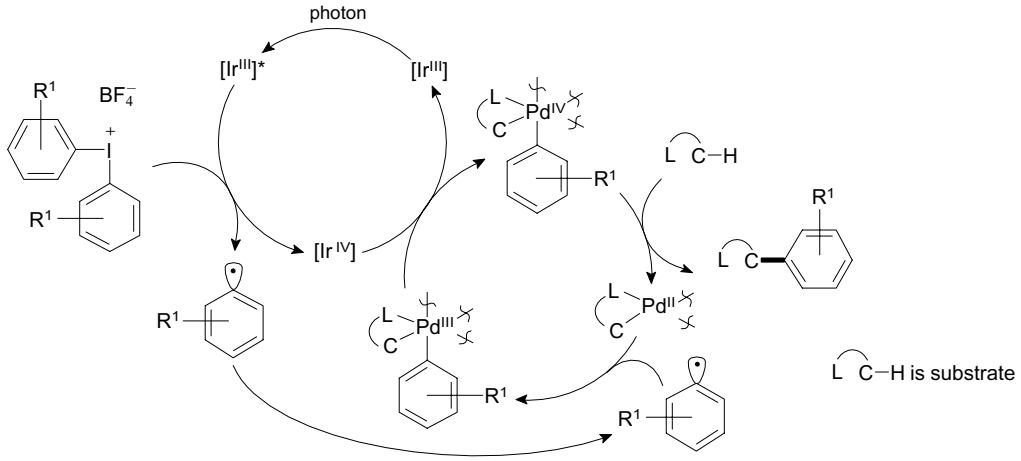
Examples



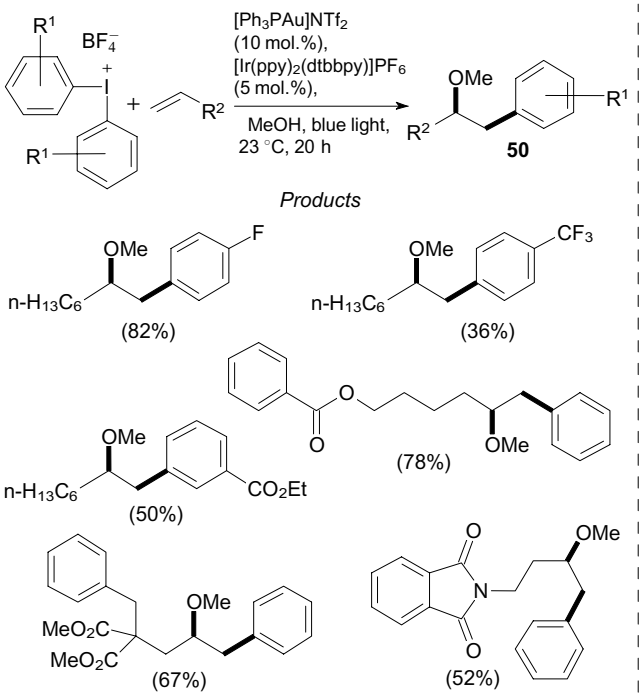


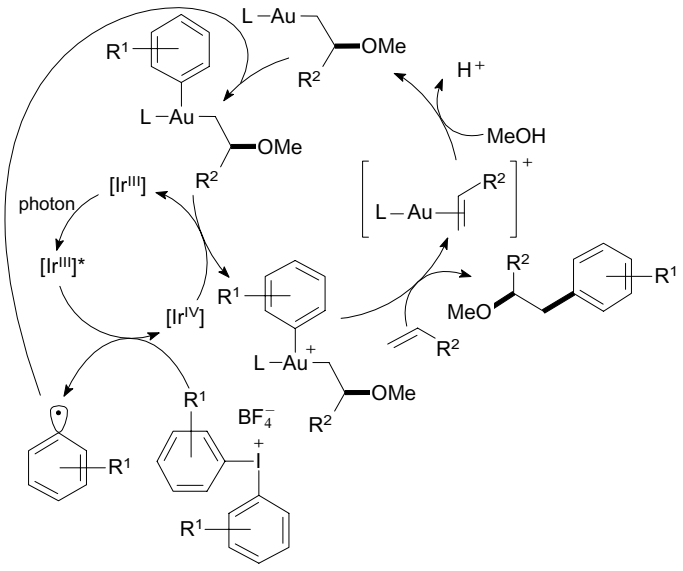
Scheme 81





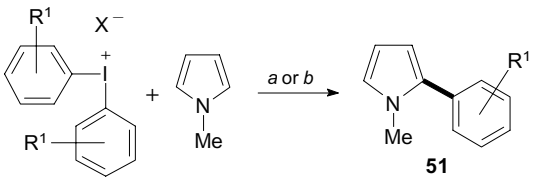
Scheme 82





electronically excited state (after green light irradiation) reduces the diaryliodonium salt, thus generating an aryl radical. This is followed by radical relay: the addition of the aryl radical to the double bond of styrene gives a more stable benzyl radical. The oxidation of the latter with the photocatalyst closes the catalytic cycle.

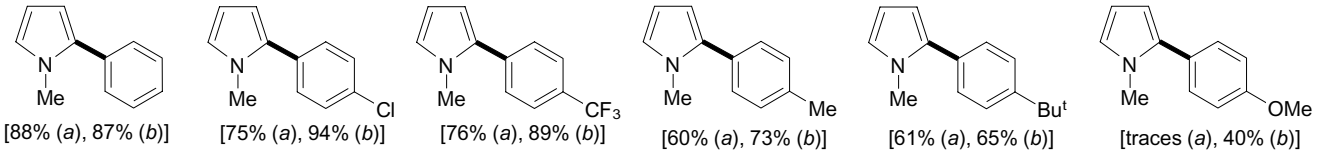
Scheme 83



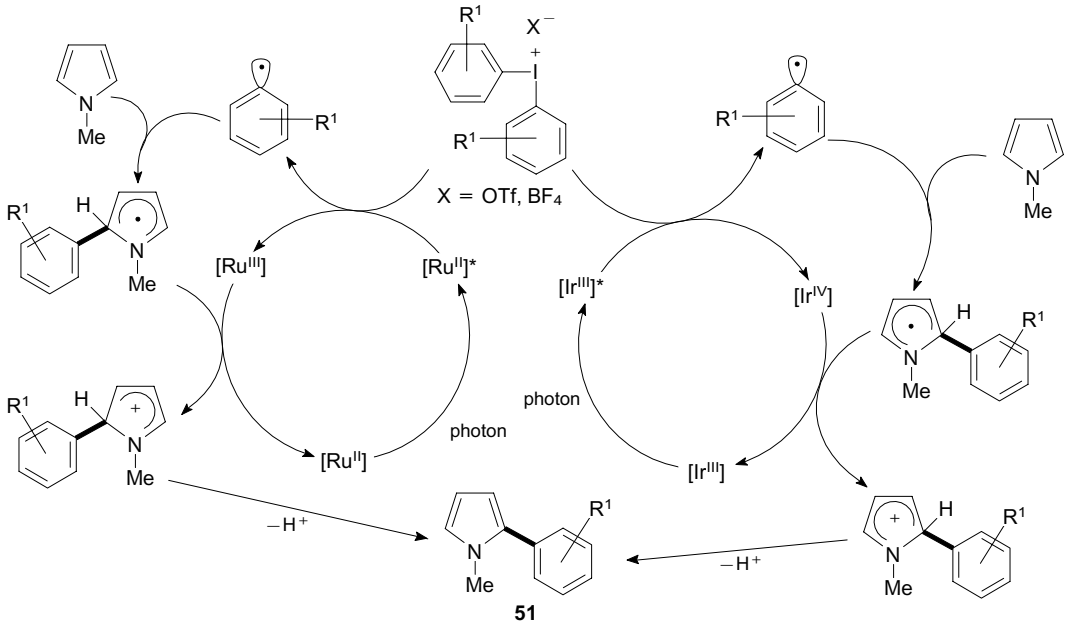
(*a*) $[Ir(ppy)_2(bpy)]PF_6$ (1 mol.%), white light, 23 °C, 16 h;
(*b*) $[Ru(bpy)_3]Cl_2 \cdot 6\,H_2O$ (1 mol.%), MeCN, blue light, 23 °C, 12 h

51

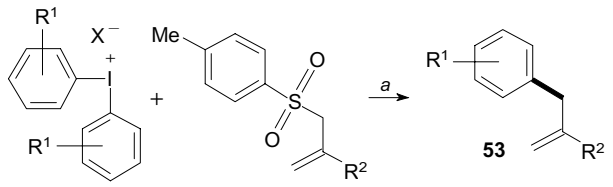
Products (conditions)



[88% (*a*), 87% (*b*)] [75% (*a*), 94% (*b*)] [76% (*a*), 89% (*b*)] [60% (*a*), 73% (*b*)] [61% (*a*), 65% (*b*)] [traces (*a*), 40% (*b*)]



Scheme 84

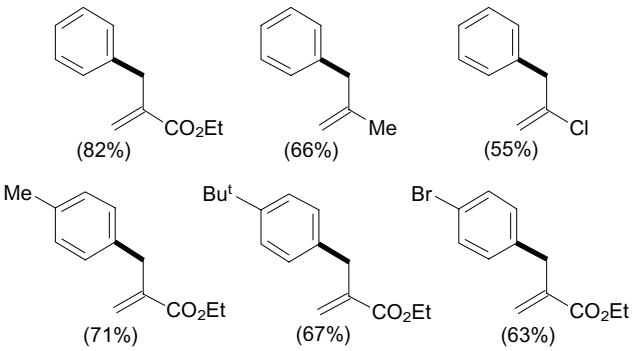


(*a*) $[Cu(dpp)_2]PF_6$ (**52**) (0.5 mol.%), DIPEA, MeCN, green light, 23 °C;

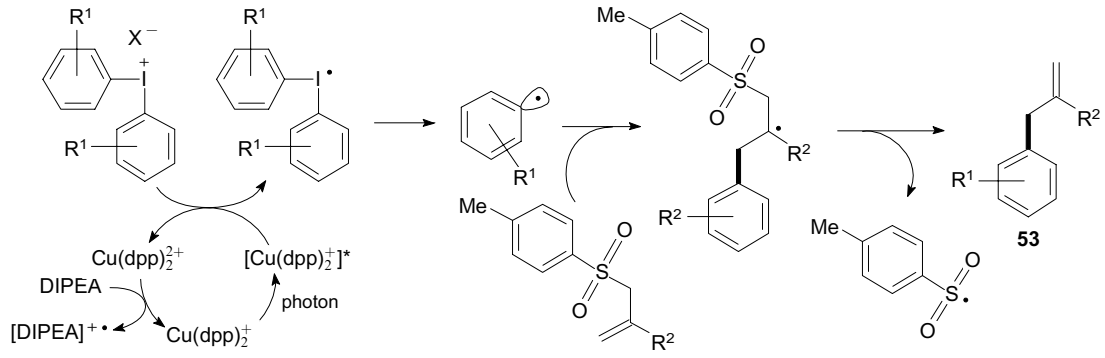
52 =

$[Cu(dpp)_2]PF_6$

Products



(82%) (66%) (55%) (71%) (67%) (63%)



The same principle of radical arylation of alkenes was used to develop an approach for transformation of aromatic aldehydes to cyclic ketones **46** (Scheme 79).[265]

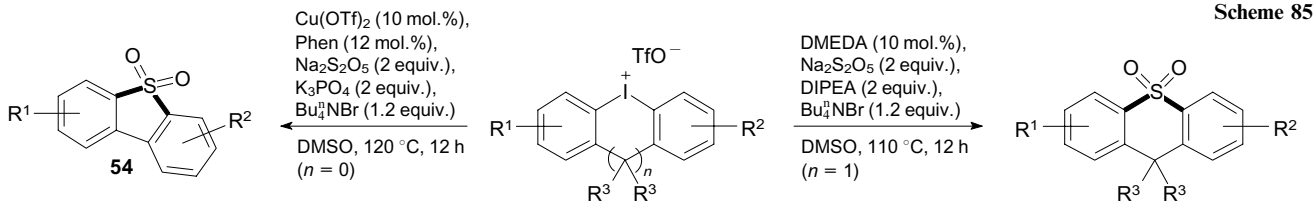
Functionalization of diphenylphosphine oxide is also possible in the presence of an iridium photocatalyst (Scheme 80).[266] The catalyst is necessary not only for generating the aryl radical under visible light irradiation, but also for reducing the sulfur atom of the arylsulfonyl radical. This method is applicable to sterically crowded phosphine oxides, but the presence of even a single methyl group in the *ortho* position of the introduced aryl moiety decreases the yield of product **47**.

The joint application of palladium and iridium catalysts allows direct C – H arylation of *N*-phenylamides and *C*-phenylamides (Scheme 81).[267] The aryl radical generated in a photoredox process undergoes oxidative addition to the palladium complex, which is followed by reductive elimination giving the target compound **48** or **49**. In this case, the success of arylation appreciably depends on steric factors.

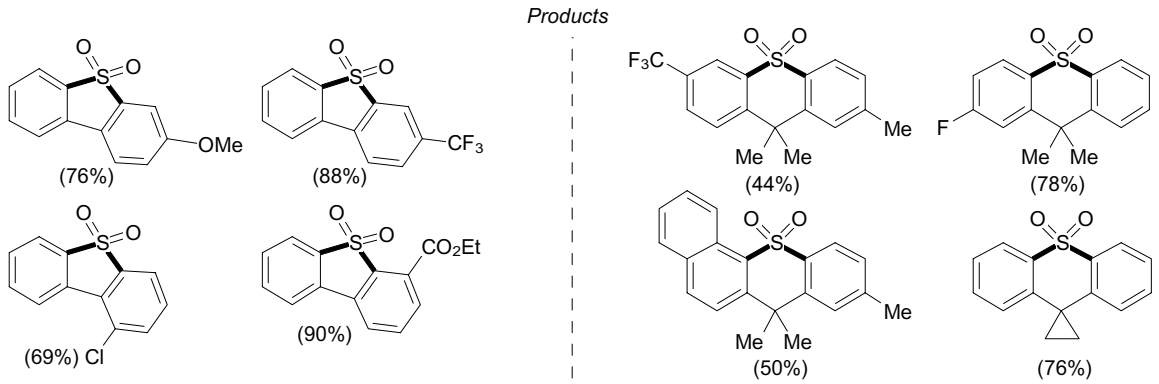
Glorius and co-workers[268] developed a binary catalytic system based on gold compounds and a photoredox catalyst and proposed a method for arylation of aliphatic alkenes giving substituted styrenes **50** (Scheme 82). The mechanism of this reaction implies two interacting catalytic cycles: a photoredox cycle with generation of the aryl radical and a cycle giving organometallic intermediates.

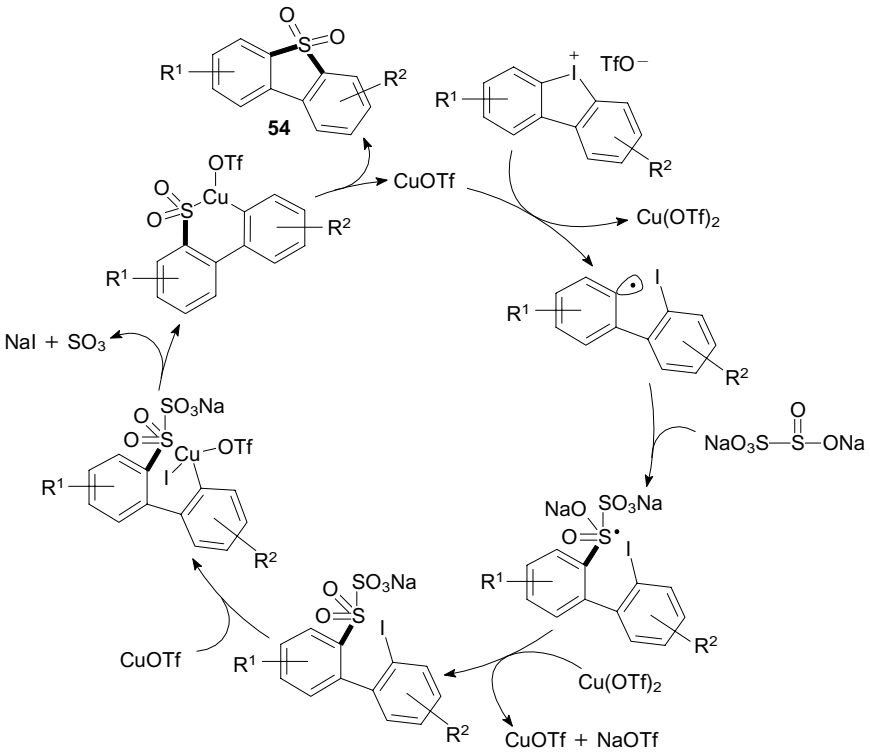
In 2013, direct C – H arylation of hetarenes with diaryliodonium salts was reported.[269, 270] In both studies, *N*-meth-

Scheme 85



Phen is 1,10-phenanthroline, DMEDA is *N*,*N*′-dimethylethylenediamine





ylpyrrole was used as the model substrate, while the photocatalysts were different: $[Ir(ppy)_2(bpy)]PF_6$ or $[Ru(bpy)_3]Cl_2$. As shown in Scheme 83, the ruthenium catalyst ensures higher yields of products **51**, especially in the case of electron-rich diaryliodonium salts for which the iridium catalyst is ineffective. It is noteworthy that the authors of the 'iridium methodology' found that arylation of pyrrole can also be induced by visible light without a catalyst. Presumably, this reaction involves the intermediate formation of EDA from the iodonium salt and the π-electron system of pyrrole.

The ruthenium photoredox catalyst $[Ru(bpy)_3](PF_6)_2$ was also used to generate (pentafluorosulfanyl)phenyl radicals from the corresponding diaryliodonium salts during the radical (pentafluorosulfanyl)phenylation of styrenes.[271]

The photochemical reduction of diaryliodonium salts to give aryl radicals is also possible in the presence of photocatalysts based on copper compounds, for example, complex **52**.[272] This approach was applied for arylation of allyl tosylates in which tertiary amine was used to close the catalytic cycle. The allylation products **53** were prepared in moderate yields by using symmetrical diaryliodonium salts. Meanwhile, unsymmetrical diaryliodonium salts with aryl substituents considerably differing in their electronic and steric properties did not provide a noticeable selectivity of the reactions (Scheme 84).

The replacement of the iodine atom in cyclic diaryliodonium salts by a sulfonyl moiety was accomplished using sodium metabisulfite (Scheme 85).[273] The key step of the process, which gives rise to cyclic sulfones **54** or **55** containing substituents of different electronic nature, includes, in the authors' opinion, the formation of 2-iodobiphenyl radical.

2.4. Generation of aryl radicals from *N*-arylpyridinium salts

Owing to well-known studies of Katritzky (see, *e.g.*, Ref. 274), *N*-alkylpyridinium salts are widely used to generate alkyl radicals in various organic reactions.[275] An example of such reactions is photoinduced deaminative borylation.[276] However, there are only few methods that use *N*-arylpyridinium salts for the formation of aryl radicals *via* a SET process. Three examples of using this approach for specific substrates were reported earlier,[277–279] but they have a narrow range of synthetic application, require harsh conditions for the pyrolysis of reactants (~200 °C) and give low yields of reaction products. Recently, conditions were proposed for the generation of aryl radicals from *N*-arylpyridinium salts in the borylation reaction involving diboranes such as bis(catecholato)diboron (B_2cat_2, **56**) in the presence of terpyridine (terpy, **57**) (Scheme 86).[280]

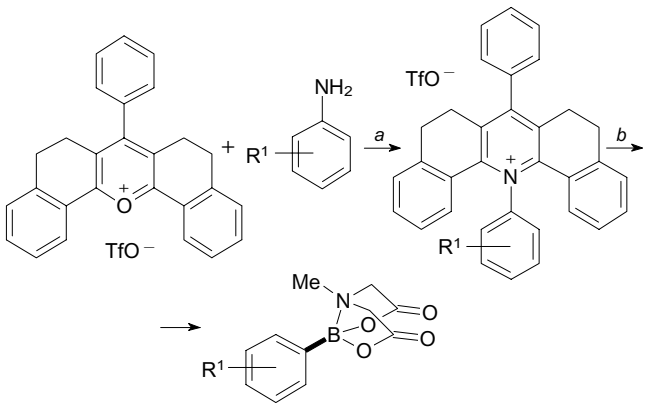
The crucial role in this process is played by the structure of the pyridinium salt and the use of diisopropylacetamide as the solvent. The unique nonplanar structure of the pyridinium salt provides the necessary driving force for the formation of the aryl radical (Scheme 87). This method was applied to perform borylation of diverse aromatic amines irrespective of their electronic structure (see Scheme 86).

2.5. Generation of aryl radicals from sulfonium salts

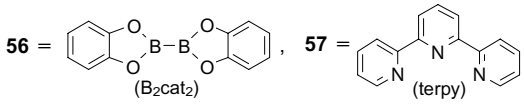
Sulfonium salts are often used as sources of structurally diverse carbon radicals, including aryl radicals.[281] In particular, the C–S bond is cleaved in the borylation reaction of substituted dimethylarylsulfonium salts in the presence of bis(pinacolato)diboron (Scheme 88).[282]

Ollivier and co-workers[283] developed a visible light-initiated process for the arylation of alkenes using arylsul-

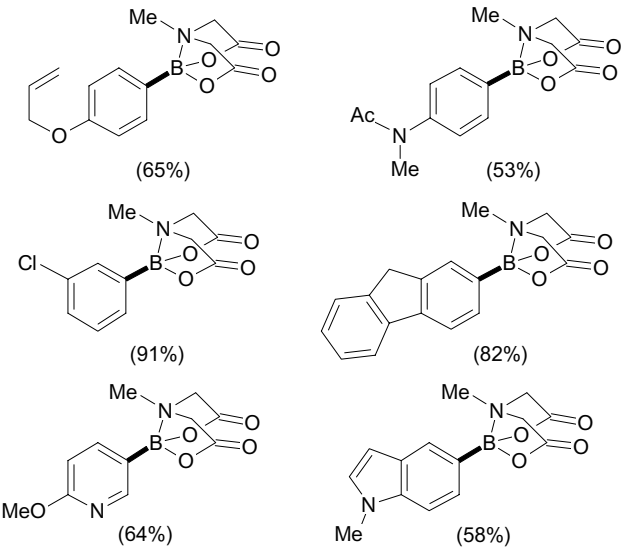
Scheme 86



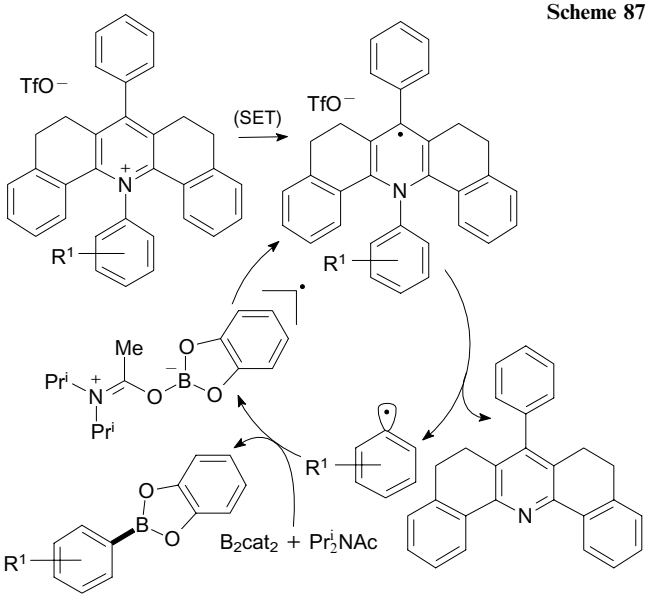
(*a*) NaOPiv, EtOH; (*b*) 1) B_2cat_2 (**56**) (3 equiv.), terpy (**57**) (10 mol.%), Pr^i_2NAc, 130 °C; 2) MIDA; Piv is pivaloyl, MIDA is *N*-methyliminodiacetic acid;



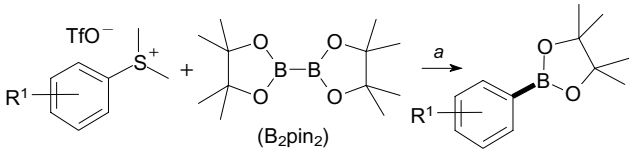
Products



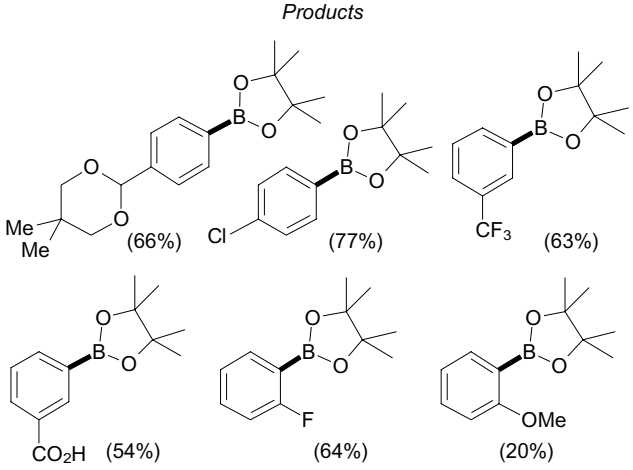
Scheme 87



Scheme 88



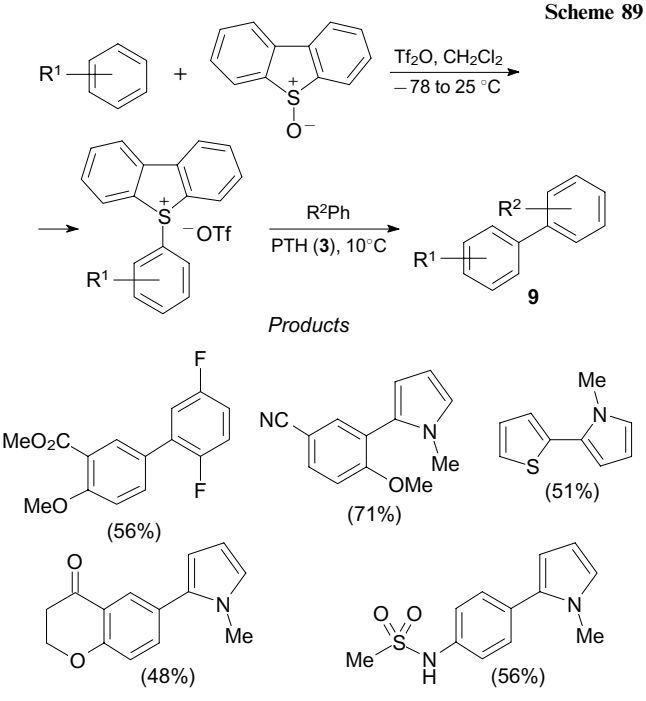
(*a*) PyH (5 equiv.), Me_2CO-H_2O (9 : 1), UV (λ = 254 nm), 23 °C, 12 h



fonium salts and $Ru(bpy)_3Cl_2 \cdot 6H_2O$ as the catalyst. An efficient method of trifluoromethylation of arenes includes the step of generation of aryl radicals from arylsulfonium salts in the presence of $Ru(bpy)_3(PF_6)_2$ as the photoredox catalyst.[284]

S-Aryldibenzothiazolium salts, prepared by the interrupted Pummerer reaction, were used as precursors of aryl radicals in the photoinitiated arylation of aromatic and heteroaromatic compounds. An organic dye, 10-phenylphenothiazine (**3**), served as the photoredox catalyst under blue light irradiation (Scheme 89).[285]

Scheme 89

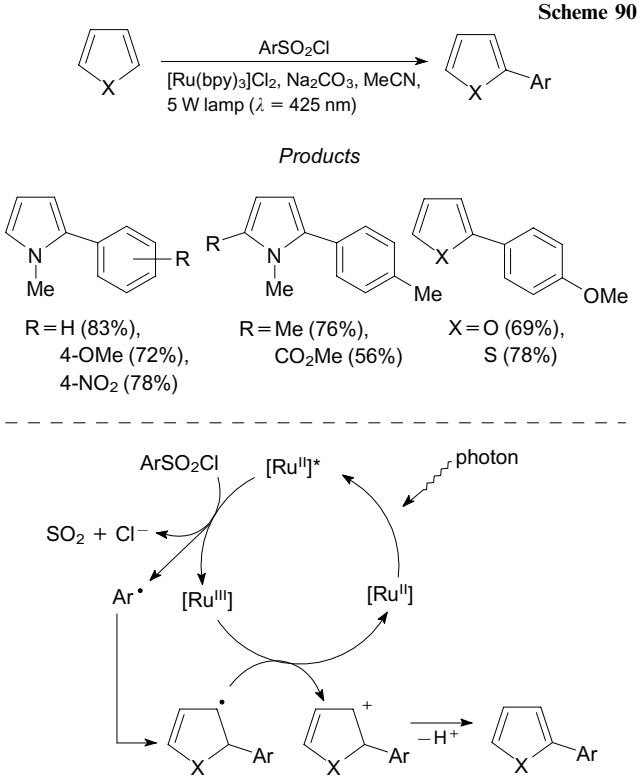


2.6. Generation of aryl radicals from aromatic sulfonyl chlorides

Aromatic sulfonyl chlorides are well-known reagents widely used in organic synthesis. Most often, they are stable and commercially available at a relatively low cost. Aromatic sulfonyl chlorides also serve as sources of aryl radicals.

The photochemically initiated arylation of pyrroles, thiophenes and furans reported by Bhasin and co-wokers [286] involves the generation of aryl radicals from arylsulfonyl chlorides initiated by blue light in the presence of $Ru(bpy)_3Cl_2$ acting as a photoredox catalyst. The single-electron reduction of an arylsulfonyl chloride molecule by the photoexcited catalyst and the subsequent ejection of SO_2 and Cl^- generate an aryl radical and a Ru^{3+} ion. The aryl radical adds to the electron-rich heterocyclic molecule, thus forming a radical intermediate, which is subsequently oxidized by Ru^{3+} to the corresponding cation, thus regenerating the initial photocatalyst (Scheme 90).[286]

Scheme 90



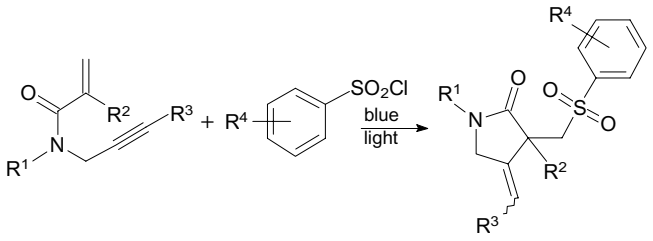
A number of intramolecular cyclizations were carried out with aromatic sulfonyl chlorides as sources of aryl radicals. For example, products **58** and **59** were obtained in this way (Scheme 91).[287, 288] In particular, blue light irradiation in the presence of $Ru(bpy)_3Cl_2$ [289] resulted in the synthesis of 1*H*-indenes **60**; the use of eosin Y gave phenanthridines **61**.[290] The intramolecular cyclization, initiated by aryl radicals generated from arylsulfonyl chlorides in the presence of eosin Y upon the activation with blue light, is utilized also in the synthesis of unsymmetrical 2,3-diaryl-substituted indoles **62**.[291]

3. Oxidative generation of aromatic radicals

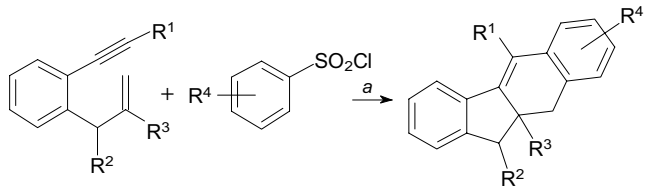
3.1. Reactions involving arylhydrazines

It is known that aromatic hydrazines as free bases are highly unstable; therefore, they are preferably stored and are commercially available as salts with protic acids. Arylhy-

Scheme 91

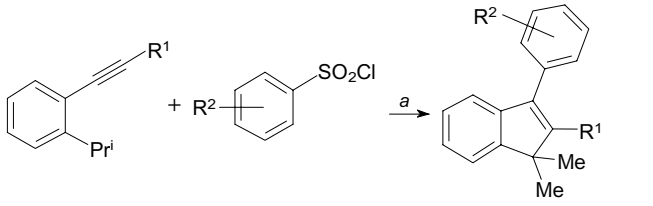


58 (52–90%) [288]



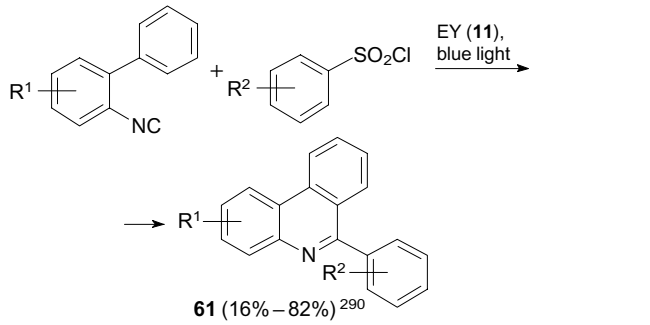
(*a*) $Ru(bpy)_3Cl_2$, blue light

59 (27–88%) [287]

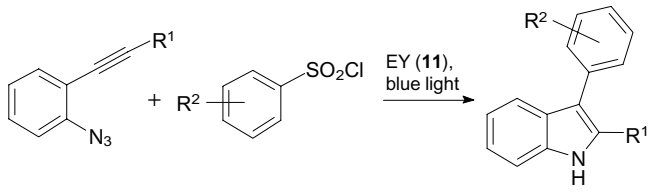


(*a*) $Ru(bpy)_3Cl_2$, blue light

60 (17–84%) [289]



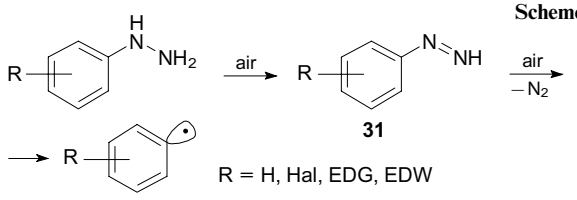
61 (16–82%) [290]



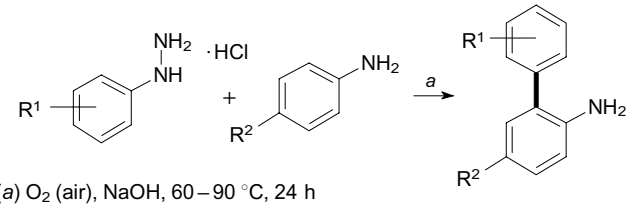
62 (57–84%) [291]

58: R^1 = Ar; R^2 = Me, Bn, Ph; R^3 = H, Me; R^4 = Alk, Ar;
59: R^1 = Ar; R^2 = OH, OAc, Et, CO_2Me; R^3 = Ph, EWG; R^4 = Cl, CN, EDG;
60: R^1 = Alk, Ar; R^2 = H, Hal, EDG, EWG;
61: R^1 = H, EDG; R^2 = Hal, EDG;
62: R^1 = Ar; R^2 = Hal, EDG

Scheme 92

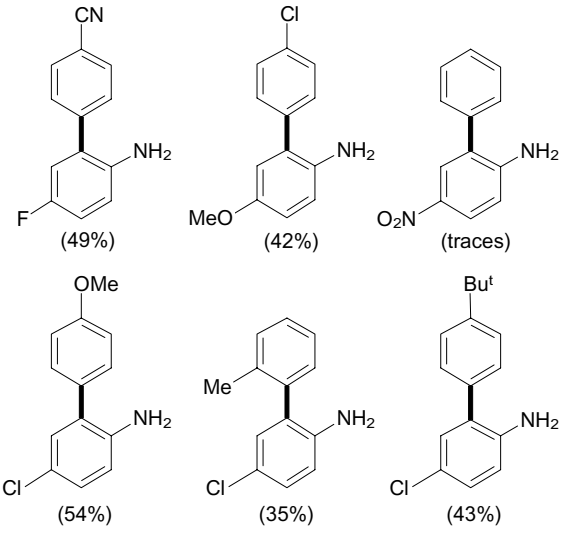


Scheme 93



(*a*) O_2 (air), NaOH, 60–90 °C, 24 h

Products



drazines are so easily oxidized that they can be converted to aryl radicals even on treatment with air oxygen (Scheme 92).

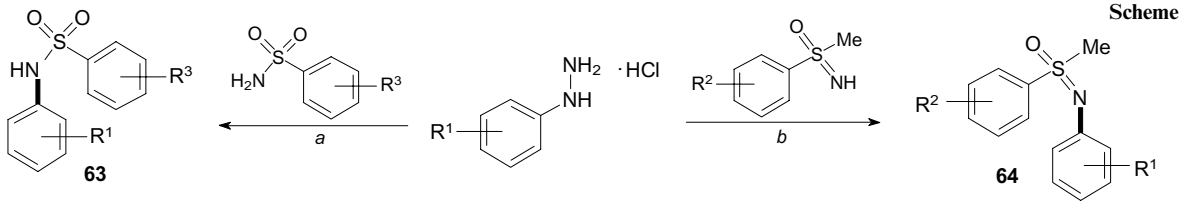
This oxidation reaction was utilized for C-arylation of anilines (Scheme 93).[292, 293]

The oxidation of arylhydrazines for generation of the corresponding aryl radicals was successfully used in the synthesis of diaryl selenides [294] and 2-arylpyrroles.[295] The related radical *N*-arylation of sulfoximines and sulfonamides was implemented using a copper-based catalyst (Scheme 94).[296] The arylation of sulfoximines is efficient for substrates containing substituents with different electronic and steric properties; however, *ortho* derivatives are formed in slightly lower yields due to steric hindrance. The arylation of sulfonamides requires more drastic conditions, in particular, the presence of a stronger oxidant, *tert*-butyl hydroperoxide (TBHP), which has an adverse effect on the yields of products **63** and **64**.[296]

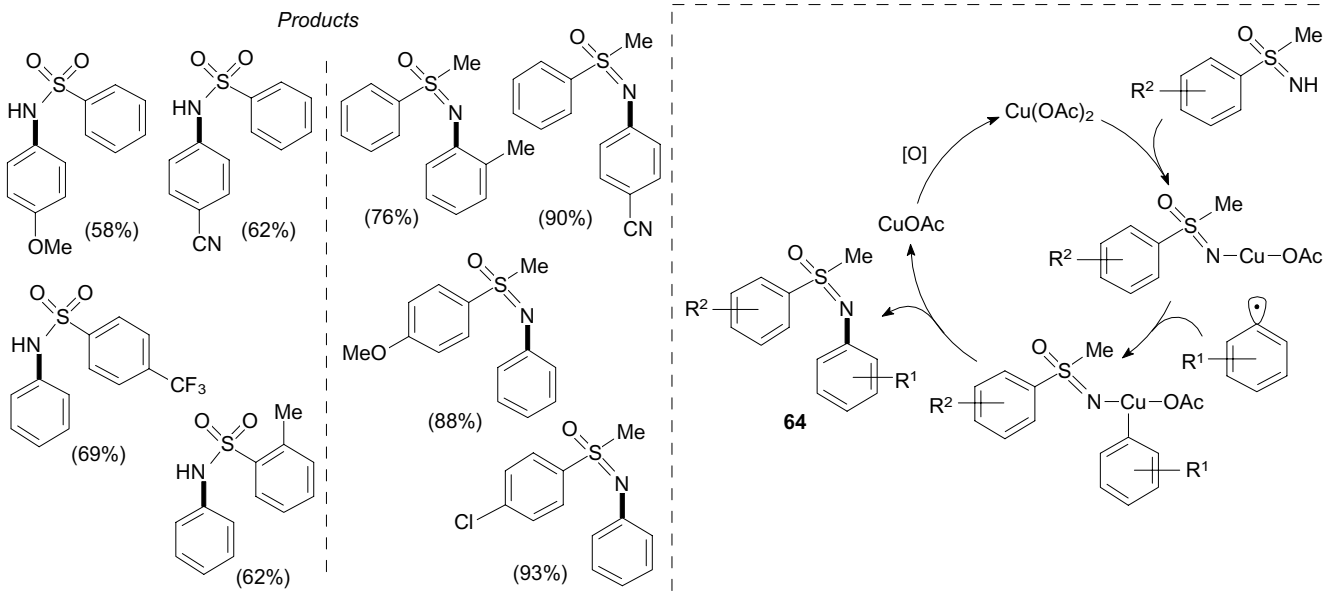
Aryl radicals can be generated from stable salts of arylhydrazines by successive deprotonation and oxidation with the K_2CO_3–air–DMSO system (Scheme 95). The efficiency of this system was demonstrated by the arylation of quinolin-4-ones,[297] aminopyridines [298] and benzoquinone.[299]

The use of arylhydrazines under these conditions proved to be efficient for the radical arylation of aromatic diamines, aminodiaryl sulfides and aminodiaryl ethers (Scheme 96).[300] The reaction is dependent on electronic factors: the use of aryl radicals with electron-withdrawing substituents increases the yields of arylation products **65** and **66** to nearly quantitative (92%). However, low regioselectivity of arylation was observed in the absence of substituent in the position 2 — the C(2) : C(4) isomer ratio was close to 1 : 1 in all cases.

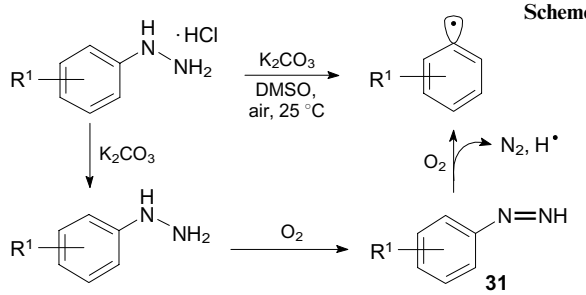
Scheme 94



(*a*) $Cu(acac)_2$, Cs_2CO_3, TBHP, MeCN, 100 °C, 24 h; (*b*) CuBr, KOAc, O_2, Me_2CO, 23 °C, 12 h; acac is acetylacetonate



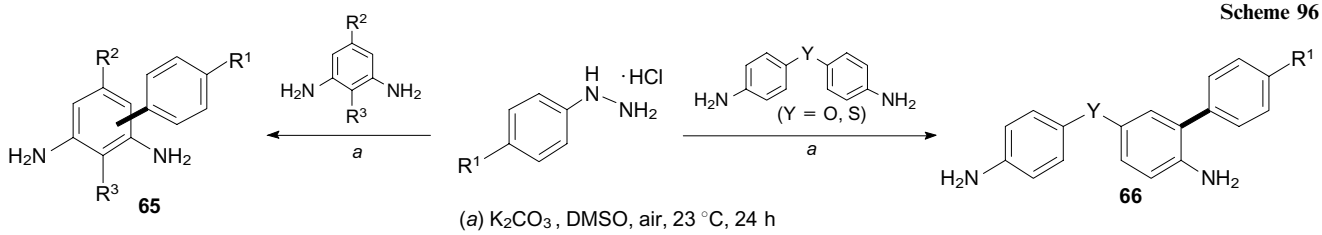
Scheme 95



31

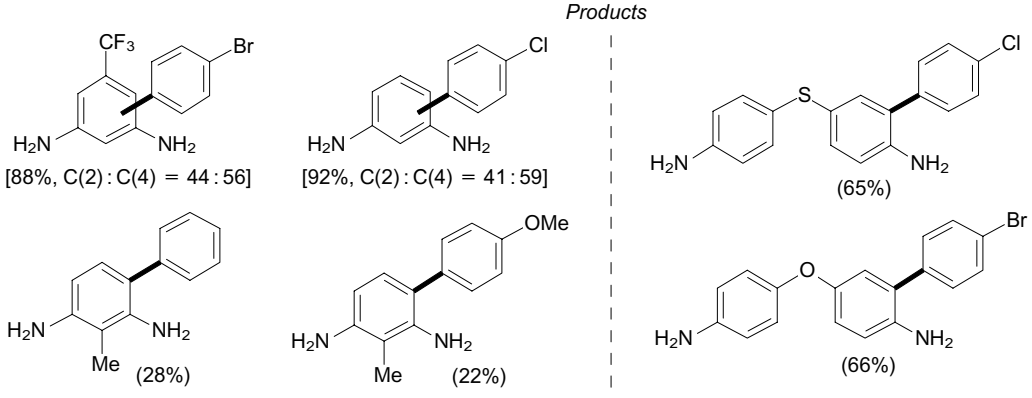
Compounds of manganese in higher oxidation states are also used for oxidative generation of aryl radicals from arylhydrazines. The introduction of an aryl moiety at the position 3 of coumarin is possible *via* generation of aryl radicals by oxidation of arylhydrazines by potassium permanganate (Scheme 97).[301] This reaction proceeds under relatively mild conditions (refluxing in acetonitrile for 3 h) and results in the synthesis of 3-arylcoumarins **67** in high yields, especially from arylhydrazines containing electron-donating substituents.

Scheme 96

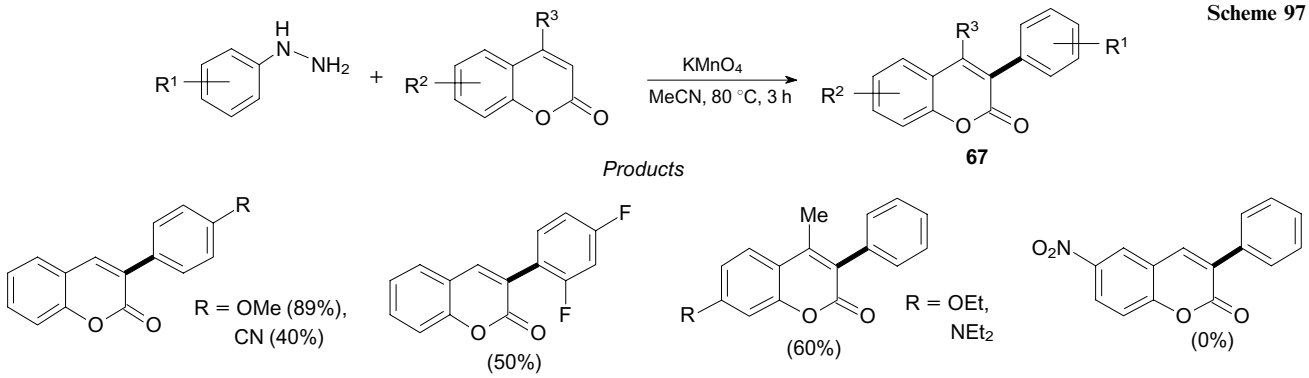


(*a*) K_2CO_3, DMSO, air, 23 °C, 24 h

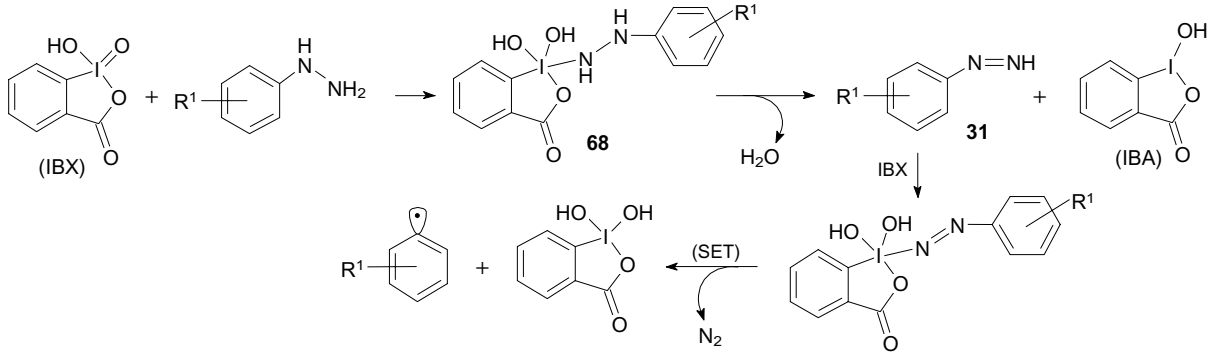
Products



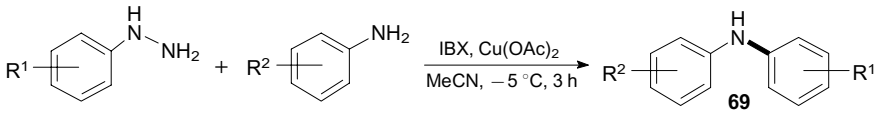
Scheme 97



Scheme 98



Scheme 99



Manganese(IV) oxide was also used for the generation of aryl radicals from arylhydrazines, as was demonstrated by the synthesis of 2-arylquinoline *N*-oxides [302] and 2-aminobiphenyls.[303]

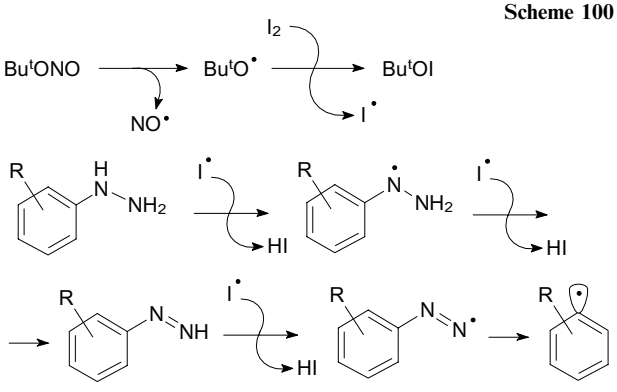
2-Iodoxybenzoic acid (IBX), a hypervalent compound of iodine, was also utilized for the generation of aryl radicals from arylhydrazines (Scheme 98). According to the mechanism proposed by the authors,[304] nucleophilic arylhydrazine adds to the electrophilic iodine atom of 2-iodoxybenzoic acid to give adduct **68**, which undergoes oxidative decomposition to be converted to phenyldiazene **31** and 2-iodosobenzoic acid (IBA). The subsequent oxidation of phenyldiazene with a second IBX molecule results in generation of a free aryl radical.

This method was utilized for the *N*-arylation of anilines in the presence of catalytic amounts of copper(II) acetate (Scheme 99).[304] In the authors' opinion, the role of copper(II) acetate is to stabilize the aryl radical and to be complexed with aniline, which leads to higher yields of arylation products **69**.

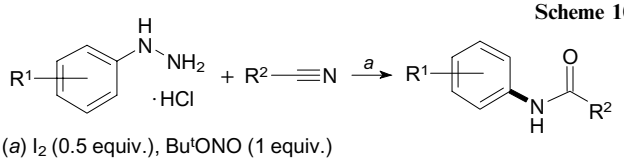
Naphthoquinones also react with aryl radicals formed in the arylhydrazine – IBX system.[305] In the radical arylation of quinoxalin-2(1*H*)-ones, aryl radicals were generated from the corresponding substituted phenylhydrazines on treatment with $K_2S_2O_8$ as an oxidant.[306]

A more exotic system for the generation of radicals from arylhydrazines is I_2 – Bu^{t}ONO (Scheme 100, R = H, Hal). The radical cleavage of *tert*-butyl nitrite affords the *tert*-butoxyl radical, which initiates decomposition of the iodine molecule into atoms. An iodine atom is an active oxidant, inducing the formation of aryl radicals from the corresponding arylhydrazines *via* a two-step process.[307]

Scheme 100

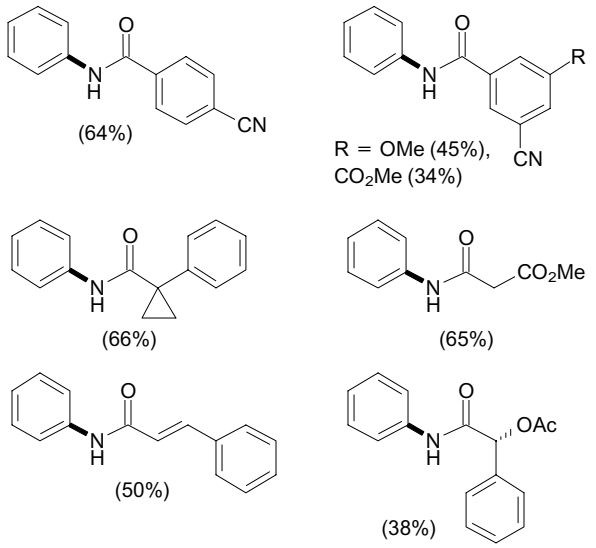


Scheme 101



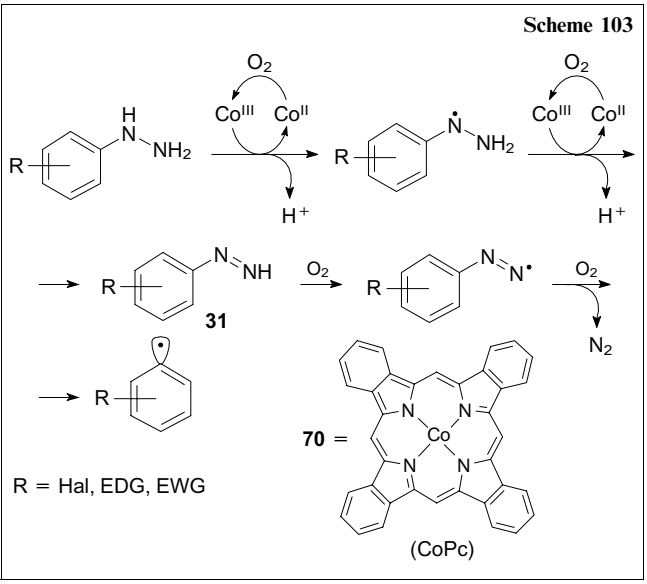
(*a*) I_2 (0.5 equiv.), Bu^{t}ONO (1 equiv.)

Products

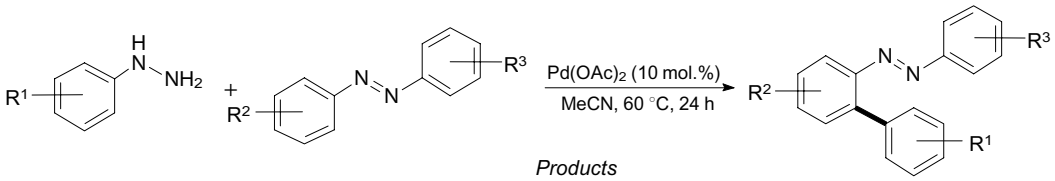


This method for the generation of aryl radicals was used to prepare arylamides from the corresponding nitriles as a result of addition of radicals to the nitrile nitrogen atom (Scheme 101).[307] This method tolerates a number of functional groups, including double bond-activated carbonyl groups and cyclopropane and heterocyclic moieties. The use of optically pure nitrile [(*R*)-cyano(phenyl)methyl ace-

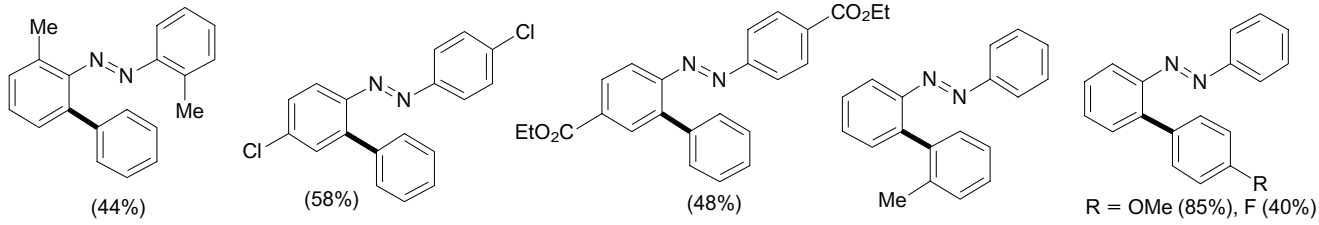
Scheme 103

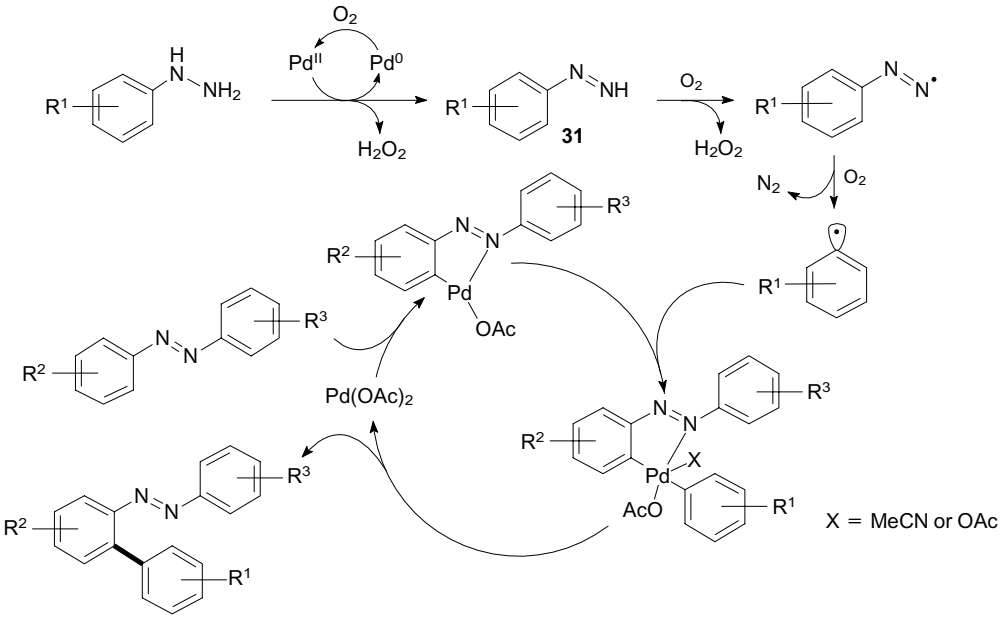


Scheme 102



Products





tate] is not accompanied by a considerable loss of optical purity.

Aryl radicals were also produced by oxidation of arylhydrazines with air oxygen in 2,2,2-trifluoroethanol catalyzed by molecular iodine, which was used for the arylation of 1,4-naphthoquinones.[308]

The generation of aryl radicals by catalytic oxidation of arylhydrazines with oxygen can be carried out in the presence of transition metal-based catalysts. For instance, palladium salts provide *ortho*-arylation of azoarenes; the azo group acts as the directing group, determining high *ortho*-selectivity of the reaction (Scheme 102).[309] The oxidation of arylhydrazines gives initially diazene **31**, which is further oxidized to afford the aryl radical.

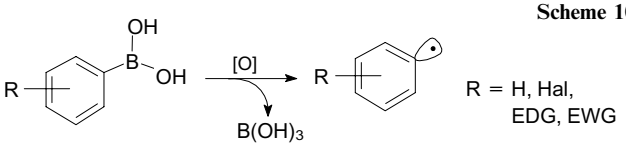
One more possible catalyst for the formation of aryl radicals from arylhydrazines is cobalt phthalocyanine (CoPc, **70**) (Scheme 103).[310, 311]

Apart from transition metal-based catalysts, an exotic green catalyst — the water extract of onion peel ash (WEOPA) — was proposed for the generation of aromatic radicals.[312]

3.2. Reactions involving arylboronic acids

Arylboronic acids generate aromatic radicals under oxidative conditions as shown in the general form in Scheme 104.

Scheme 104



An oxidant used for radical arylation is potassium persulfate. Upon a moderate temperature rise, it is converted to the sulfate radical anion, which initiates the formation of aryl radicals from arylboronic acids (Scheme 105).[313] This method is applicable to a broad range of naphtho- and benzoquinones; however, the use of arylboronic acids containing electron-donating substituents proved to be most efficient.

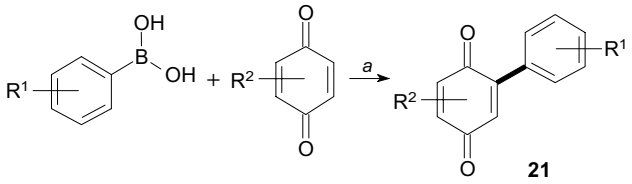
In the presence of transition metal salts, decomposition of $K_2S_2O_8$ occurs at lower temperature. The addition of only 0.2 equiv. of silver nitrate allows conducting the arylation of quinones even at room temperature.[314] The same system proved to be suitable for the arylation of pyridines; however, in this case, the addition of Selectfluor is necessary.[315]

The formation of aromatic radicals upon oxidation of arylboronic acids with potassium persulfate can also be catalyzed by iron salts.[316, 317] The sulfate radical anion, which initiates this reaction, is formed upon single electron transfer from Fe^{2+} to $S_2O_8^{2-}$ to give Fe^{3+}. Then the sulfate radical anion reacts with arylboronic acid, thus generating an aromatic radical (Scheme 106).

The oxidative formation of aryl radicals from arylboronic acids also takes place when iron(III) nitrate is used as the catalyst in the arylation of thiazoles, pyrazines, pyridines, quinones and their benzannulated analogues (Scheme 107).[318]

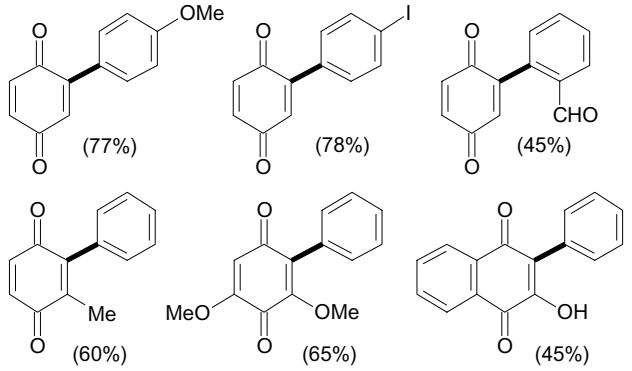
A similar reaction giving aryl radicals was used for the arylation of heterocyclic compounds and quinones in the presence of the iron(II) acetylacetonate complex (Scheme 108).[319]

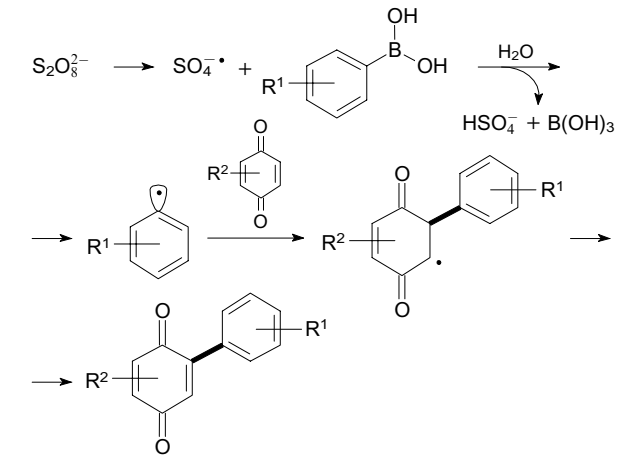
Scheme 105



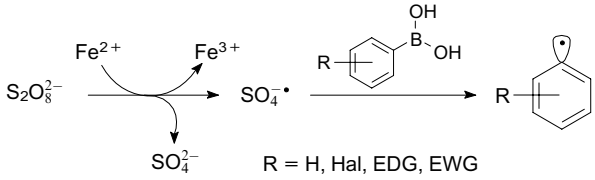
(*a*) $K_2S_2O_8$ (2 equiv.), DCE – H_2O (1 : 1), 80 °C

Products





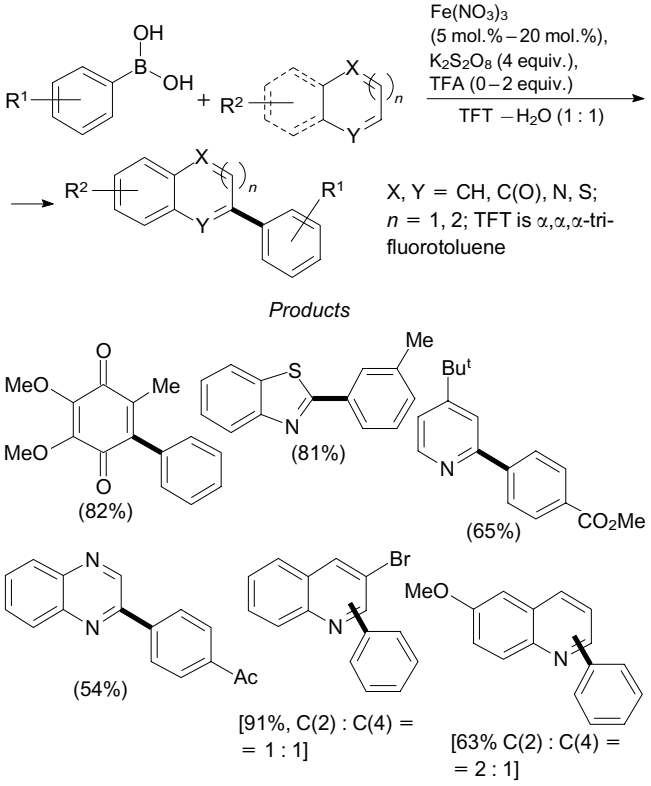
Scheme 106



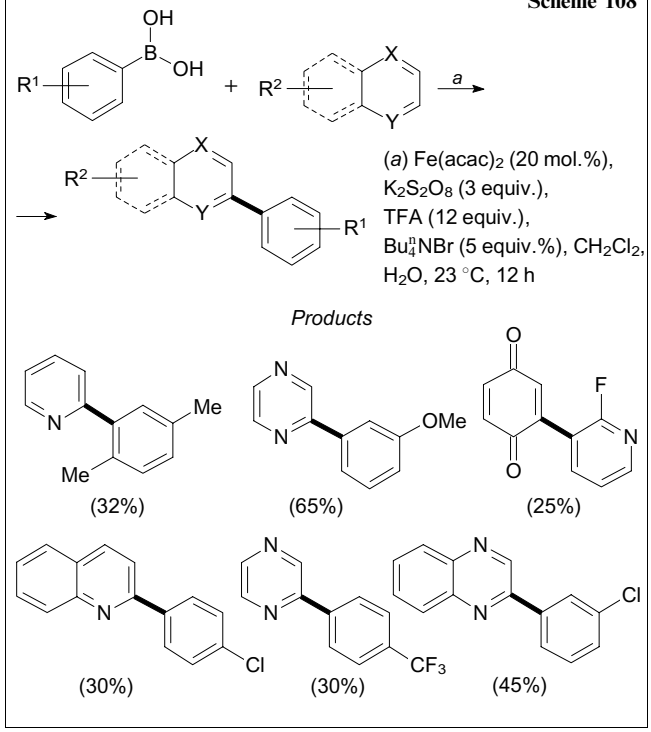
The role of iron compounds in reactions of this type is not limited to the catalysis of decomposition of the persulfate anion to give the sulfate radical; they can also act as oxidants of radical intermediates. Iron(III) nitrate serves as the catalyst for the arylation of *N*-methyl-2-pyridones with aryl radicals generated by oxidation of arylboronic acids with potassium persulfate. In the authors' opinion, the iron salt also participates in the oxidation of resonance-stabilized heterocyclic radical **71**, resulting from addition of the aryl radical to the position 3 of pyridone, to give the corresponding cation (Scheme 109).[320]

Manganese compounds are widely used for the oxidative generation of aryl radicals from arylboronic acids. For

Scheme 107



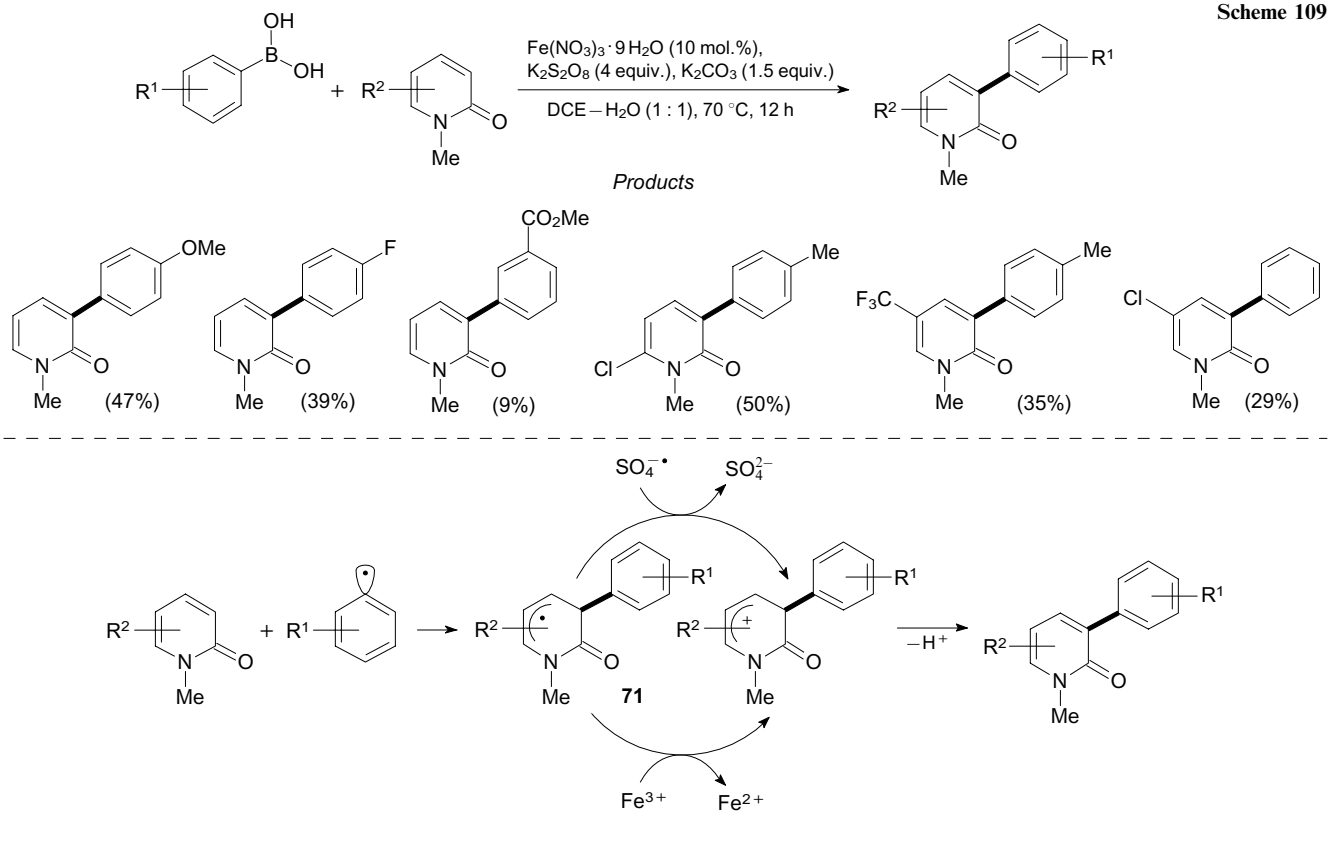
Scheme 108



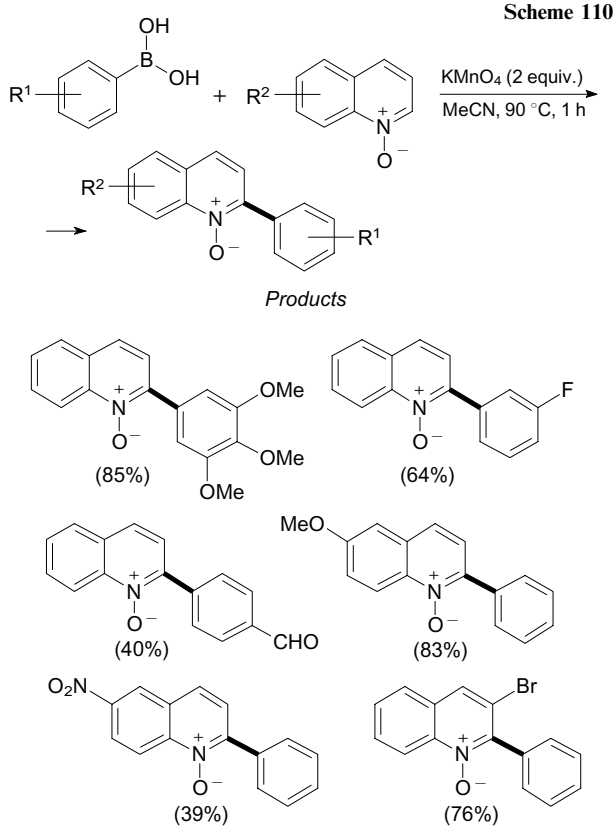
example, potassium permanganate was utilized as the oxidant for the arylation of quinoline *N*-oxides (Scheme 110).[321] The arylation of substrates containing electron-donating groups occurs most efficiently. Unlike the arylation of *N*-oxides, the arylation of proper quinolines gives a markedly lower yields of products.

Potassium permanganate in combination with acetic acid was proposed for the generation of aryl radicals from arylboronic acids. This system proved to be most efficient for the arylation of coumarins to give 3-aryl-substituted coumarins **72** (Scheme 111).[322] Like in the previous case, electron-donor substrates are arylated more readily. The

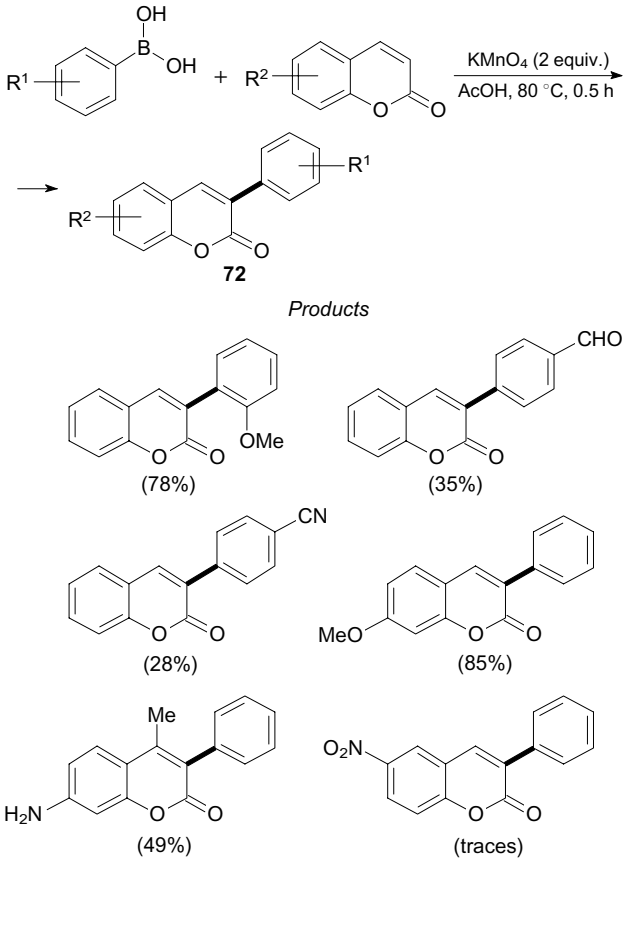
Scheme 109



Scheme 110



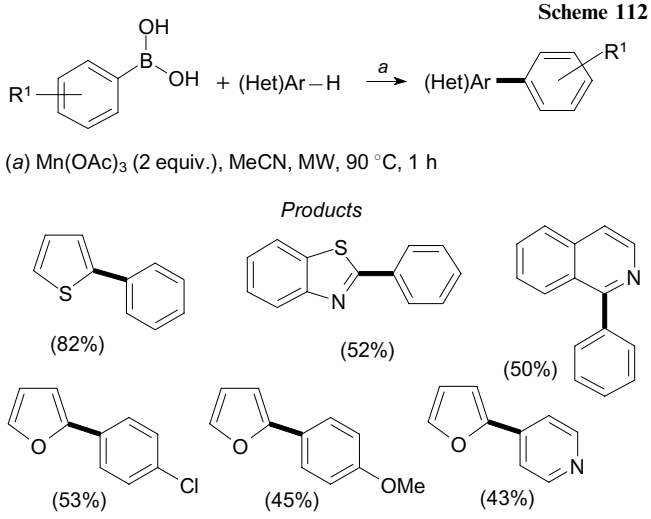
Scheme 111



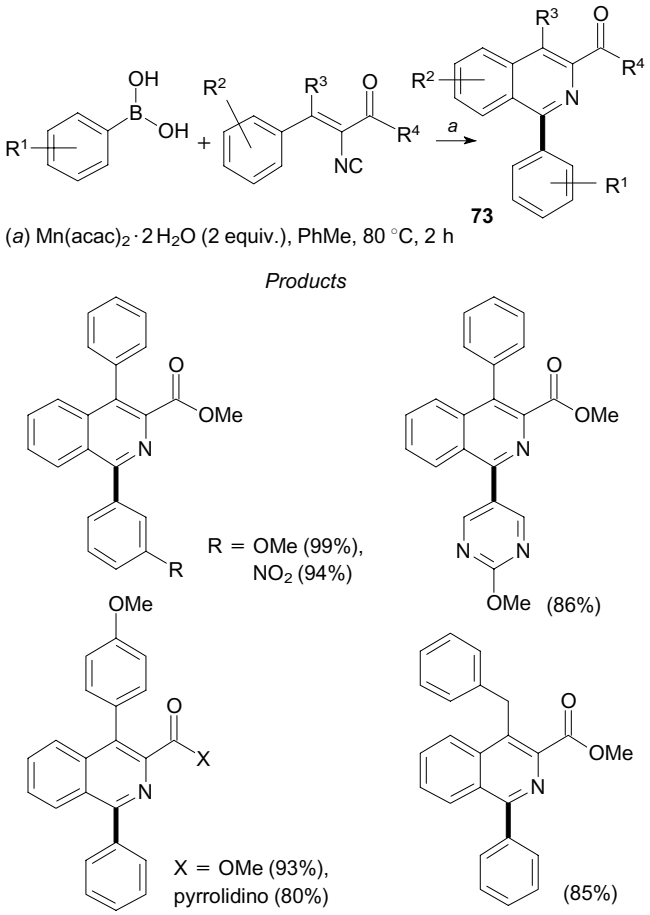
reaction is sensitive to steric hindrance: in the presence of substituents in the *ortho* position to the forming bond, the yields of arylation products decrease. This system was also utilized for regio- and diastereoselective acyloxyarylation of chalcones involving arylboronic acids as sources of aryl radicals.[323]

Manganese(III) acetate also serves for the oxidative generation of aryl radicals from arylboronic acids, for example, in the synthesis of substituted biphenyls under

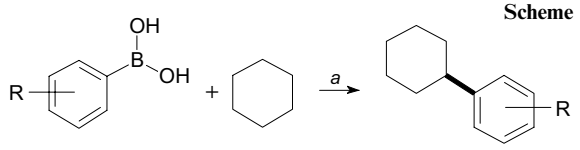
Scheme 112



Scheme 113

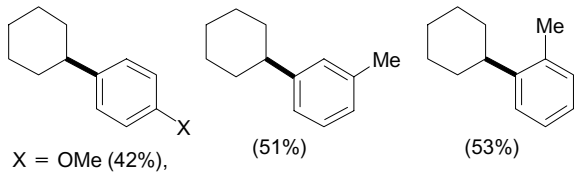


Scheme 114



(*a*) $Ni(acac)_2$ (10 mol.%), PPh_3 (20 mol.%), dppb (10 mol.%), K_3PO_4 (0.75 equiv.), DTBP (1 equiv.), 130 °C, 10 h;
dppb is 1,4-bis(diphenylphosphino)butane

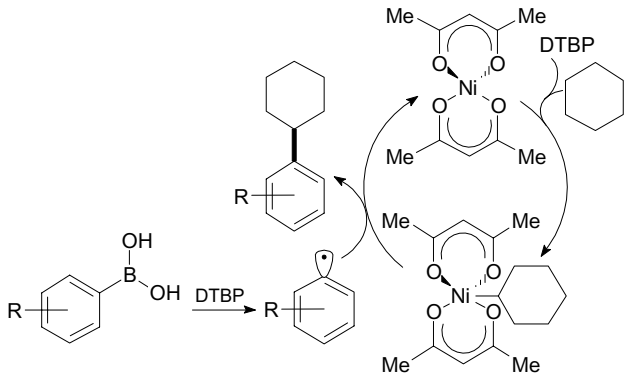
Products



X = OMe (42%), CN (67%), F (60%), Bu^t (51%)

(51%)

(53%)



microwave irradiation (MW)[324] and in the arylation of diverse heterocyclic compounds (Scheme 112).[325]

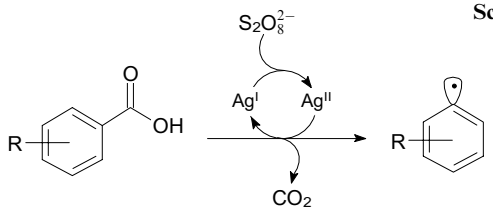
When aryl radicals are generated from arylboronic acids under the action of manganese(II) compounds, the reaction is carried out in the atmosphere of oxygen, which oxidizes Mn^{II} to Mn^{III}. This protocol was used to prepare isoquinolines **73** from vinyl isonitriles. This method is characterized by a broad diversity of substrates and low sensitivity to electronic factors (Scheme 113).[326] The $CuBr_2-O_2$ system was employed in the step of oxidative generation of aryl radicals from arylboronic acids in the catalytic synthesis of vinyl selenides from 1,1-diarylethylenes and selenium.[327]

A system consisting of nickel salt as a catalyst and di-*tert*-butyl peroxide as an oxidant was employed for the arylation of saturated oxygen-containing heterocycles (cyclic ethers) and cycloalkanes. The reactions involving tetrahydrofuran and dioxane take place under the same conditions and give products in good yields, but in the case of tetrahydrofuran, the radicals are generated more efficiently from arylboronic acids containing electron-donating substituents.[328] Conversely, in the arylation of cyclohexane, higher yields of arylation products are achieved in the presence of electron-withdrawing substituents in the arylboronic acids (Scheme 114).[329]

3.3. Reactions involving aromatic carboxylic acids

The radical generation from aromatic carboxylic acids is accomplished most often using the silver(I) $-K_2S_2O_8$ system. First, Ag^I is oxidized to Ag^{II} with the persulfate anion, while silver(II) salt, in turn, oxidizes the aromatic carboxylic

Scheme 115

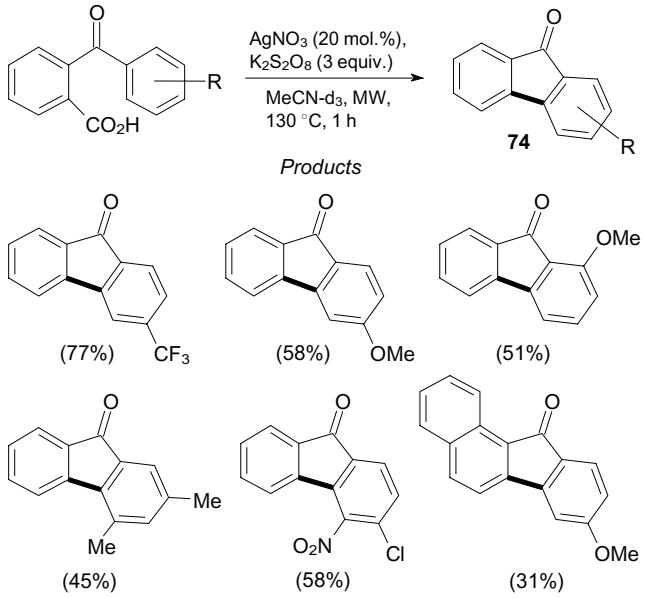


acid, which is accompanied by decarboxylation and generation of aryl radicals (Scheme 115).[330]

This method for the generation of aryl radicals was applied to prepare fluorenone derivatives **74** from the corresponding benzophenones containing a carboxyl group in the position 2. It is applicable to functionally substituted and sterically crowded substrates (Scheme 116).[330] The use of deuterated acetonitrile as a solvent and microwave irradiation proved to be critical for the smooth implementation of this reaction.

The same method for the preparation of aryl radicals was used to synthesize bi(het)aryls.[331, 332] It should be noted that this oxidative system is suitable for generation of radicals from benzyl alcohols and benzaldehydes. In this case, additional amounts of potassium persulfate and silver salt are necessary, since the formation of aryl radicals is

Scheme 116

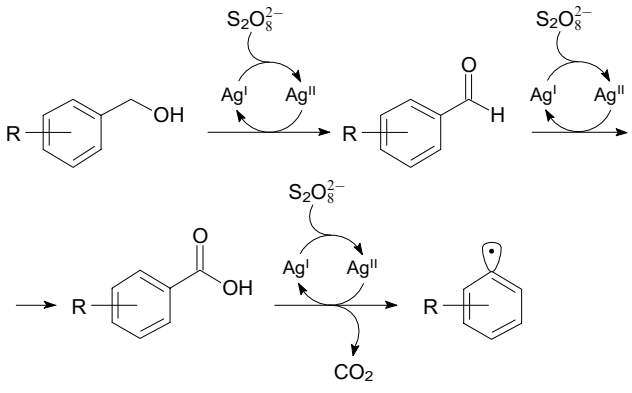


Products

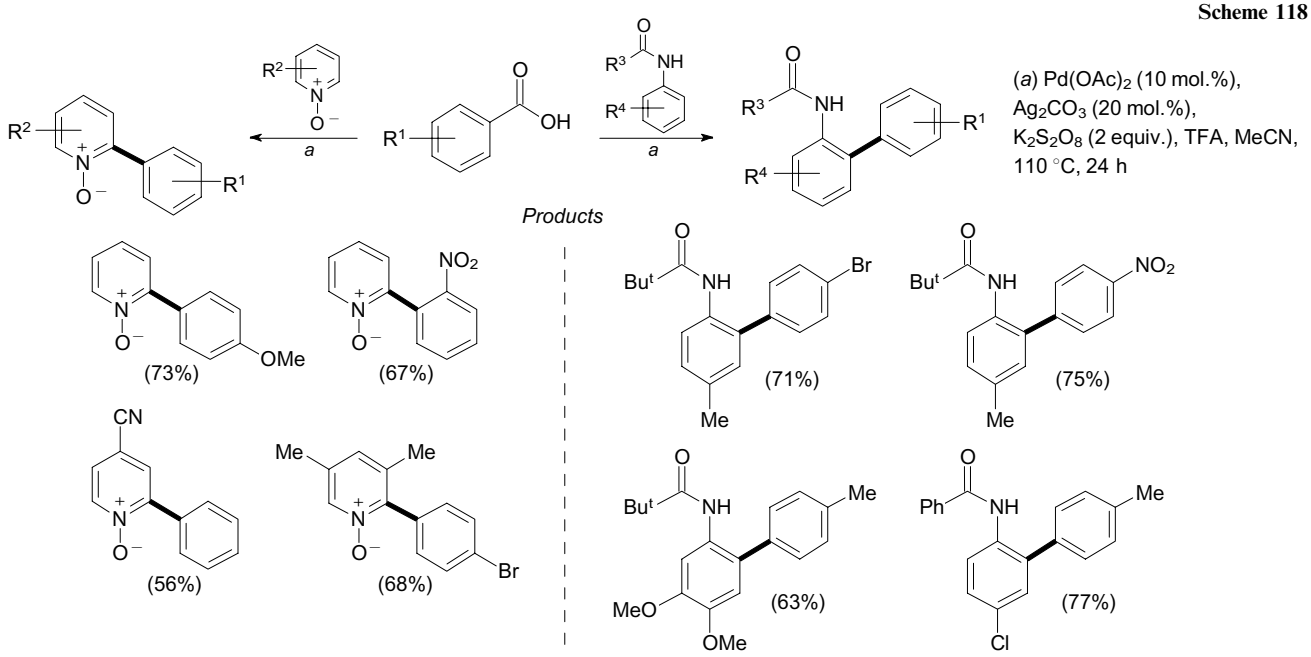
(77%) (58%) (51%)

(45%) (58%) (31%)

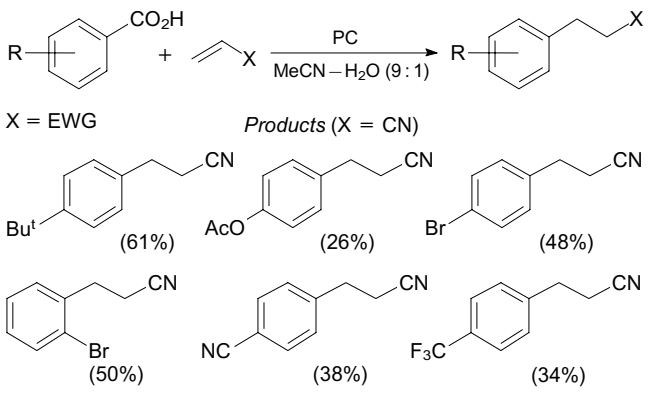
Scheme 117



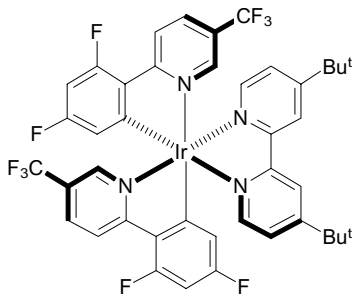
Scheme 118



Scheme 119

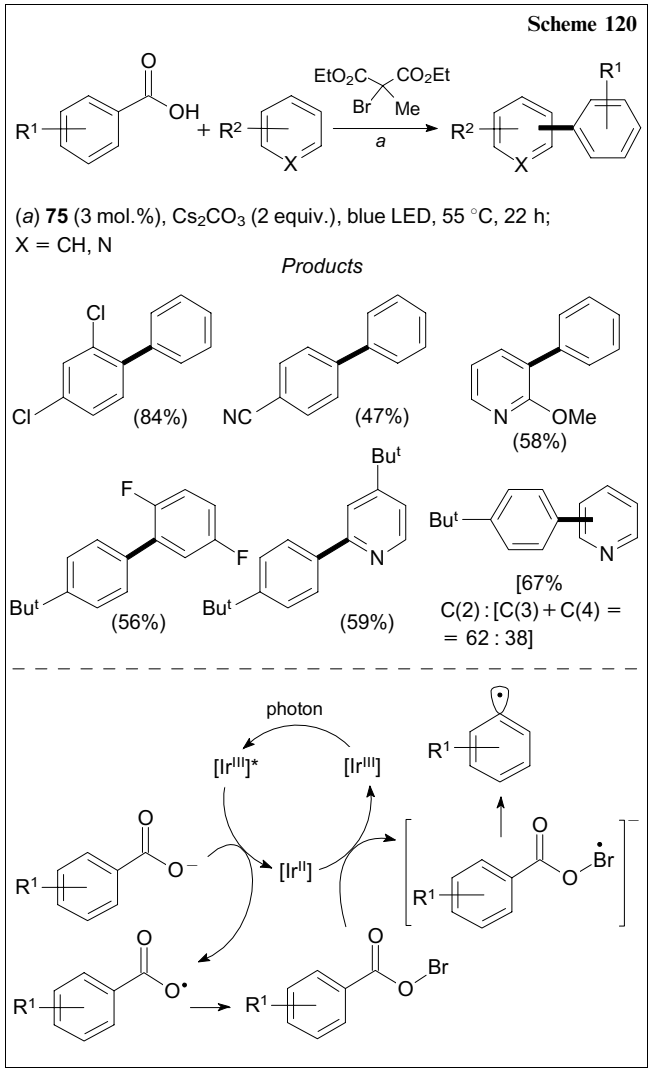


Structure 75



75 ([Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$)

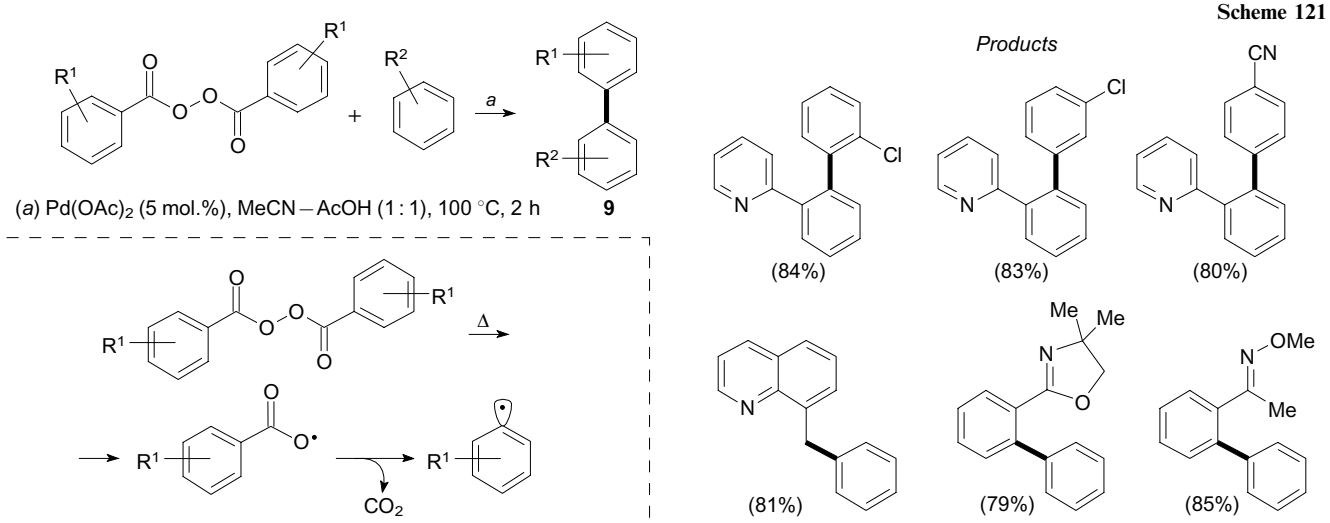
Scheme 120



preceded by substrate oxidation to the carboxylic acid (Scheme 117).[333]

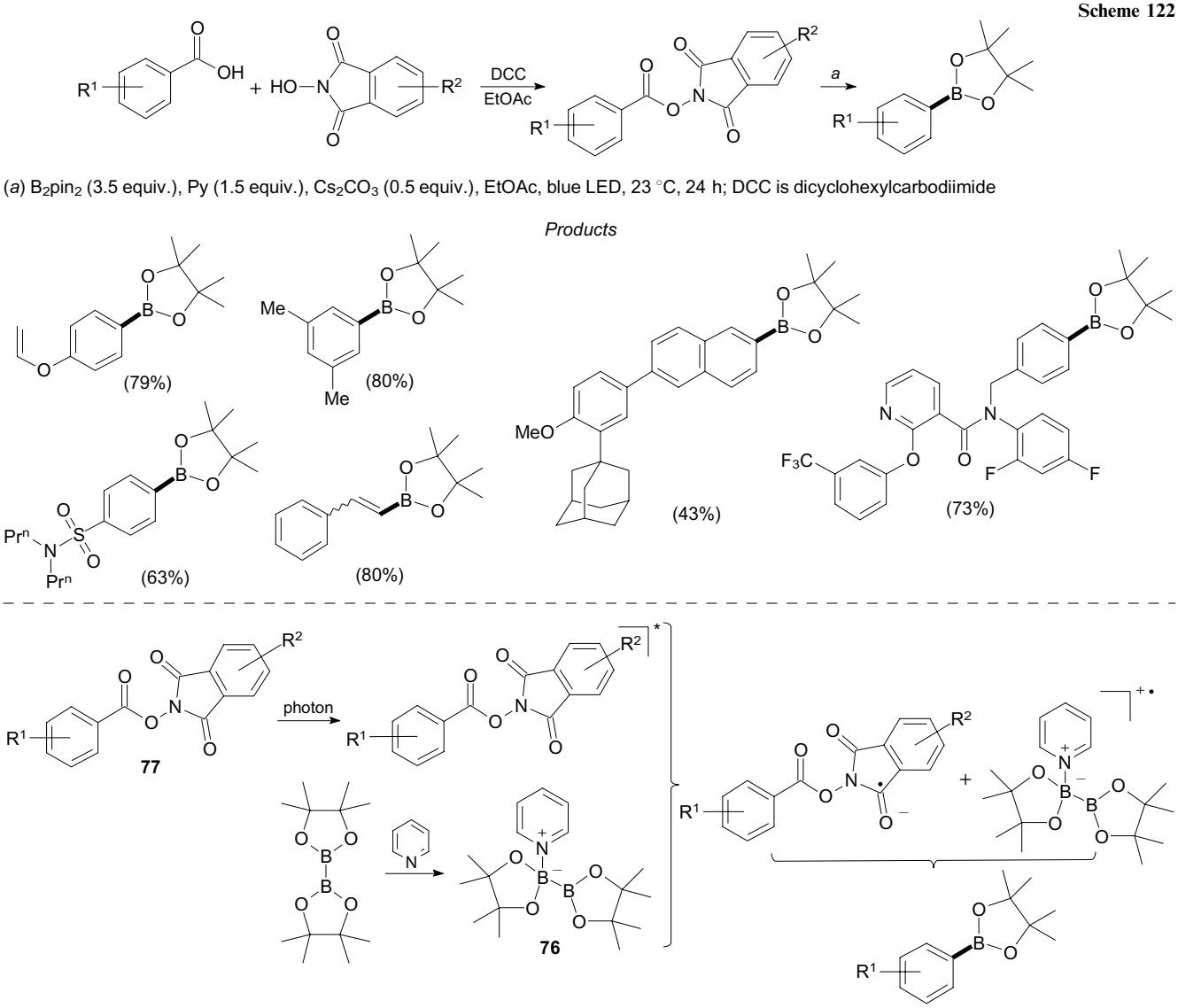
Using this oxidant in combination with the palladium complex Pd(OAc)$_2$, it is possible to carry out regioselective CH arylation of substituted anilides and pyridine *N*-oxides containing directing functional groups (Scheme 118).[334] The function of the palladium catalyst is to perform regioselective palladation and formation of the biaryl system *via* reductive elimination, while Ag^{I} ions and K$_2$S$_2$O$_8$ are responsible for the generation of aryl radicals.[334]

Scheme 121



The photoinitiated decarboxylative generation of aryl radicals from substituted benzoic acids is possible by using binary photoredox systems consisting of biphenyl and 1,4-dicyanonaphthalene (DCN) or 9,10-dicyanoanthraquinone and visible light irradiation at 405 nm. According to a proposed mechanism,[335] the photoinduced electron transfer between the Ph_2 and DCN or DCA molecules results in the formation of the excited biphenyl radical cation $[Ph_2]^{+}$*

Scheme 122



and the radical anion of the electron acceptor. Then $[Ph_2]^{+*}$ oxidizes the carboxylate anion to the corresponding radical, which is decarboxylated on gentle heating to give an aryl radical. Benzoic acids containing electron-withdrawing and moderately electron-donating substituents, including *ortho*-substituted ones, are usually employed. The aryl radicals generated in this way were allowed to react with electron-deficient alkenes, bis(pinacolato)diboron and CD_3CN to prepare alkylated derivatives and arylboronic acid esters in moderate yields and to introduce a deuterium label into the molecule (Scheme 119).

Glorius and co-workers[336] described the generation of aryl radicals from (hetero)aromatic carboxylic acids under the action of a photoredox catalyst based on iridium(III) complex **75** and under visible light irradiation in the presence of 2-bromo-2-methylmalonic ester as an additive. The reaction proceeds under mild conditions, presumably, *via* the formation of benzyl hypobromite, which is reduced by the iridium(II) complex to the corresponding radical anion, the source of the aryl radical (Scheme 120).

Substituted benzoyl peroxides are used for the generation of aryl radicals. At elevated temperature, the peroxide bond is homolytically cleaved to give arylcarboxyl radical, which is then decarboxylated. This method was applied in the CH arylation involving directing functional groups in the presence of palladium catalysts (Scheme 121).[337] The arylation products were obtained in good yields when benzoyl peroxides with electron-withdrawing substituents and moderately electron-donating substituents were used. The introduction of 4-methoxyphenyl and mesityl substituents to implement this method proved to be impossible, probably, because of the higher stability of arylcarboxyl radicals.[255]

Substituted benzoyl peroxides also serve as sources of aryl radicals for the arylation of unsubstituted and substituted benzenes to prepare biphenyl derivatives **9**. The aryl radicals are formed at 100 °C without any transition metal-based catalysts.[338]

An alternative approach to the generation of aryl radicals from carboxylic acid derivatives in the absence of transition metal complexes is based on the photoinduced decarboxylation of redox-activated *N*-hydroxyphthalimide esters of benzoic acids. *N*-Hydroxyphthalimide esters are stable compounds that are easily synthesized and behave as single-electron oxidants in the electronically excited state. This way of generation of aryl radicals was applied to prepare arylboronic acid esters upon decarboxylative borylation (Scheme 122).[339] The method is applicable to a broad range of functionally substituted benzoic acids, including biologically active ones. The reaction mechanism includes the formation of complex **76** from bis(pinacolato)-diboron molecule and pyridine; subsequently, the complex acts as an electron donor towards the electronically excited state of *N*-hydroxyphthalimide ester. The single-electron reduction of ester **77** followed by elimination of the phthalimide anion and carbon(IV) oxide give rise to an aryl radical. When the reaction is carried out in chlorobenzene, no product of solvent arylation was detected, which indicates that borylation takes place quickly in the solvent cage.[339] A similar reaction is implementable using *tert*-butyl isonicotinate as the donor compound for complex formation with B_2pin_2.[340] The *N*-hydroxyphthalimide esters of aromatic carboxylic acids can be generated *in situ* by oxidation of methylarenes with *tert*-butyl nitrite in the presence of *N*-hydroxyphthalimide and can be subsequently used in radical borylation.[341]

4. Conclusion

The arylation methods involving aryl radicals, which were developed in the last decades, made a considerable contribution to synthetic organic chemistry and related fields, first of all, for the design of new functional materials, pharmateuticals and other organic compounds with practically useful properties. This approach is an alternative to the classical arylation methods based on the use of compounds of transition metals (Pd, Ni, Cu, *etc.*) as catalysts. A benefit of radical arylation reactions is that they occur under mild conditions (as a rule, at room temperature), which accounts for a broad diversity of eligible functionally substituted substrates. Furthermore, radical arylation reactions do not require the search for a catalytic system or selection of a ligand.

The current development of methodology of radical arylation is directed towards new environmentally safe and economically feasible synthetic methods characterized by high efficiency. Many radical arylation reactions occur in the presence of an organic dye acting as a photoredox catalyst or in the absence of any catalyst. Among the latter type of reactions, noteworthy are reactions that involve the formation of donor–acceptor complexes, electrochemically activated reactions and reactions initiated by inorganic bases.

A variety of aromatic compounds can serve as precursors of aryl radicals — aryl halides; arylboronic and arylcarboxylic acids and their derivatives; aryldiazonium, diaryliodonium, arylsulfonium and *N*-arylpyridinium salts; arylhydrazines, arylsulfonyl chlorides; and other compounds. For each class of compounds, several ways of generation of aryl radicals are available, including initiation by visible light or electrical current and the use of organic or metal complex photosensitizers.

Radical arylation reactions were discovered rather long ago, but their synthetic application was limited by long-standing views on radical reactions as being uncontrollable and inefficient and resulting, in most cases, in mixtures of products. The achievements of recent years, related most of all to development of methods for generation of various radicals, crucially changed this situation. Now radical reactions, as a whole, and radical arylation, in particular, occupy an important place among the preparative methods of organic chemistry, together with traditional ionic methods, and this stimulates further development of radical methods.

The synthetic use of aryldiazonium and diaryliodonium salts, well-known sources of aryl radicals, has expanded in recent years because of the employment of photoredox catalysts. Aryl halides, which possess low reduction potentials and, therefore, represent substrates that are difficult to employ for the generation of aryl radicals under mild conditions, are used more and more often as radical arylating agents in the absence of UV irradiation owing to the design of new photoredox catalysts operating in the visible spectral range. A number of synthetic methodologies have been developed on the basis of aryl halides, such as electrophotochemical activation of carbon–halide bonds and reactions initiated by alkali metal bases. Processes of aryl radical generation utilizing aromatic carboxylic acids, their derivatives and arylboronic acids have also been substan-

tially advanced in recent years as a result of development of new oxidation processes. Meanwhile, radical arylation methods involving arylsulfonium salts, *N*-arylpyridinium salts and aromatic sulfonyl chlorides are still less studied, but their good prospects are quite obvious, which gives hope for the progress in this area in the near future

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