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# Transition metal-free cross-coupling reactions to form carbon – heteroatom bonds

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The formation of carbon – heteroatm bond is the key step of synthesis of numerous organic compounds, including socially important products such as pharmaceuticals, crop protection agents and organic functional materials. These reactions proceed most efficiently when catalyzed by compounds of transition metals, first of all palladium. However, this approach has considerable drawbacks, in particular, high cost and toxicity of transition metal compounds and harsh reaction conditions required in some cases, resulting in limited functional group tolerance. This review describes the recent advances in the development of methodology of transition metal-free carbon – heteroatom bond-forming cross-coupling. It is shown that single-electron transfer and homolytic bond cleavage result in the generation of highly reactive radical and/or radical ion intermediates, enable the formation of new carbon – heteroatom bonds. These intermediates are generated using either visible light or electricity as energy sources or simple organic compounds acting as electron donors. Methods for carbon – heteroatom bond formation based on radical reactions proceeding under mild conditions and in the presence of labile functional groups are considered. The key mechanistic aspects of the reactions are highlighted. The review mainly covers the original publications of the current decade.
The bibliography includes 302 references.

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## 1. Introduction

Cross-coupling reactions resulting in the formation of carbon – heteroatom bonds are among the key tools of organic chemistry used for the synthesis and functionalization of pharmaceuticals, organic functional materials and other practically useful organic compounds both in laboratory practice and on an industrial scale.[1,2]

Traditionally, these reactions are catalyzed by palladium, copper, nickel and some other transition metal compounds. Although catalytic transformations are characterized by high efficiency and reliability, they also suffer from certain drawbacks.[3] The first one is high and continuously growing cost of transition metals and their compounds, which leads to increase in the prime cost of the products synthesized with these catalysts by 5 – 20% every year.[4] For example, the price of palladium troy ounce increased from ~200 to >1500 US dollars in the period from 2005 to 2019.[4] In addition, some reactions require the use of expensive ligands, which may be even more expensive than transition metals.

One more important problem is the presence of transition metal trace impurities in the products of synthesis, because they have a pronounced toxicity and can promote decomposition and/or isomerization of organic com-

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pounds.[5] In addition, there are cases where impurities have caused considerable changes in the electric properties of organic compounds and in the performance of functional devices based on them[6] and were responsible for the erroneous results in medicinal chemistry studies.[7] When transition metal-catalyzed reactions are used for the synthesis of pharmaceuticals or for the design of functional materials for organic electronics, especially thorough purification of the products from transition metal traces is required; this is associated with significant time and material expenses.[8–10] Transition metal-catalyzed reactions also have a number of other drawbacks: as a rule, they proceed at elevated temperatures[11] and are sensitive to steric factors.[12] Furthermore, the possibility of activation of not only one carbon–halogen bond in polyhalo-substituted substrates brings about the problem of selectivity.[13,14]

In recent years, the synthetic community has made attempts to find efficient alternatives to catalytic processes, which resulted in the development of transition metal-free cross-coupling strategy. The most significant progress was noted for three main types of these transformations induced by visible light, electric current or alkali metal bases. Their key advantages are mild conditions and high selectivity in the activation of chemical bonds. This allows the use of more diverse functionally substituted substrates than in conventional catalytic cross-coupling reactions.

In the absence of transition metals, the alternative activation of chemical bonds in organic molecules is attained *via* single-electron transfer (SET) and, in some cases, *via* homolytic bond cleavage, which can be induced, for example, by visible light irradiation of organic compounds. The SET processes can be initiated by the energy of light (for visible light this is usually mediated by photocatalysts, see Section 2) or by electric current (see Section 3). In addition, organic electron donors can be introduced into the reactions to induce SET processes (see Section 4). Single-electron transfer processes involving organic molecules give rise to organic radicals, radical ion species or electron donor–acceptor complexes (EDA). All of these intermediates usually have high reactivity, which facilitates the formation of new bonds.

Upon the reaction with a photocatalyst (PC) in the electronically excited state (PC*), substrate (S) can be either reduced (Fig. 1, cycle A) or oxidized (cycle B). In this case, the starting molecule is activated as a result of photoinduced electron transfer.

Similarly, the substrate can be activated by electric current upon anodic oxidation (pathway C) or cathodic reduction (pathway D) (Fig. 2).

The formation of carbon–heteroatom bonds upon the substrate activation by the single-electron transfer mechanism can occur along three pathways (Fig. 3). Pathway *a* is typical of carbon substrates containing π-electron systems (compounds with carbon–carbon double bonds or aromatic derivatives) and possessing low oxidation potentials. In this case, the carbon substrate (CH) first undergoes photoinduced or anodic oxidation to be converted to the corresponding radical cation ($CH^{+\bullet}$), which then reacts with nucleophilic heteroatomic substrate (X) to give a C–X bond. Alternatively, heteroatomic substrate X can undergo single-electron oxidation, thus giving the corresponding radical cation ($X^{+\bullet}$), which reacts as an electrophile with electron-rich carbon substrate (pathway *b*). Transformations of the third type (pathway *c*) are inherent in carbon substrates containing an electron-withdrawing leaving group — a halogen atom. In this case the carbon substrate (CY) is first reduced to the corresponding radical anion ($CY^{-\bullet}$), which eliminates the leaving group ($Y^-$) to give the C$^\bullet$ radical. This radical reacts with the heteroatomic substrate to give a carbon–heteroatom bond. Figure 3 shows simplified transformation schemes in which the SET activation of organic molecules results in the formation of carbon–heteroatom bonds. In some cases, these schemes can be supplemented by the steps of formation and transformations of electron donor–acceptor complexes, redox transformations involving photocatalysts and intermediates, and hydrogen atom elimination or addition.

The intensive development of the strategy of cross-coupling free from organometallic catalysts was reflected in a number of analytical reviews. Among them, note the review by Sun and Shi[3] published in 2014 and covering the literature up to 2012. This review considers, in particular, reactions that have no analogues among transition metal-catalyzed processes. Various types of photoinduced[15] and electrochemically induced[16] processes are also subjects of short review publications. Some reviews analyze the photochemically and electrochemically driven formation of carbon–nitrogen[17–19] and carbon–sulfur[20] bonds. In addition, there are reviews[21,22] that give examples of reactions induced by alkali metal bases, but the reported data are limited to analysis of carbon–carbon bond-forming reactions.

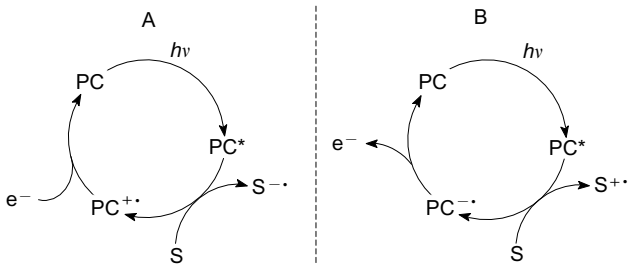



**Figure 1.** Substrate activation upon photoinduced electron transfer *via* substrate reduction or oxidation.

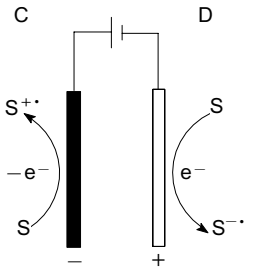



**Figure 2.** Substrate activation by electric current at the anode or cathode.

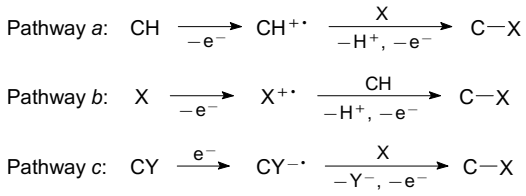



**Figure 3.** Transformations to form C–X bonds upon substrate activation *via* single-electron transfer.

The present review considers the key achievements of the last decade in the development of transition metal-free cross-coupling reactions that result in the formation of carbon–heteroatom bonds. Since this review is mainly addressed to synthetic chemists, we arranged the material according to the method used to activate organic compounds (visible light, electrical current and organic electron donors) and according to the type of carbon–heteroatom bond formed (nitrogen, sulfur, phosphorus and oxygen). Each part of the review discusses the formation of carbon–heteroatom bonds, first, as a result of functionalization of C–H bonds at $sp^3$- and $sp^2$-hybridized carbon atoms and, at the end, as a result of displacement of leaving groups. Without claiming to be exhaustive, we tried to demonstrate the most significant results of this type and the extensive possibilities of this strategy for the synthesis of structurally diverse organic compounds. For most of the considered reactions, the mechanisms of substrate activation and formation of carbon–heteroatom bonds are discussed and examples of compounds synthesized in this way are given.

## 2. Photoinduced reactions

In recent years, particular attention has been attracted by organic reactions induced by visible light, which represent an efficient and robust methodology of organic synthesis. The key step of these reactions is the formation of reactive radical type intermediates, which provide route to new products inaccessible by thermal activation of the substrates.[23]

### 2.1. Formation of C–N bond

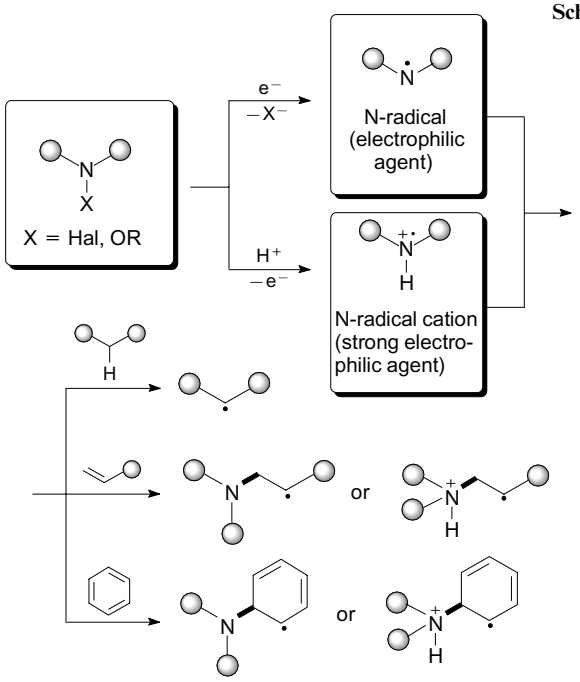
The C–N bond formation reactions induced by visible light are accomplished by generation of N-centred free radicals upon activation of amines, amides, hydrazones, and their N-derivatives. The reactivity of N-radicals depends on the type of hybridization of the nitrogen atom and the nature of substituents.[24] N-Centred radicals have been rarely used in organic synthesis for a long time because of the absence of selective methods for their generation under mild conditions. The development of photoredox-catalyzed reactions driven by visible light and based on single-electron transfer and energy transfer processes[25] crucially changed the situation in this field. In recent decades, significant progress has been attained in the development of photoredox generation methods of N-centred radicals and radical cations from diverse precursors containing labile N–O, N–N and N–halogen bonds and from compounds containing N–H bonds. In most of these reactions carried out to date, transition metal (iridium, palladium, ruthenium) complexes are used as photoredox catalysts.[26–28] Meanwhile, there are known examples of generation of N-radicals in the absence of transition metal catalysts, which form the subject of this part of the review.

N-Centred radicals are either converted to C-centred radicals upon hydrogen atom transfer (HAT) or add to electron-rich systems — compounds with multiple bonds or aromatic rings (Scheme 1).

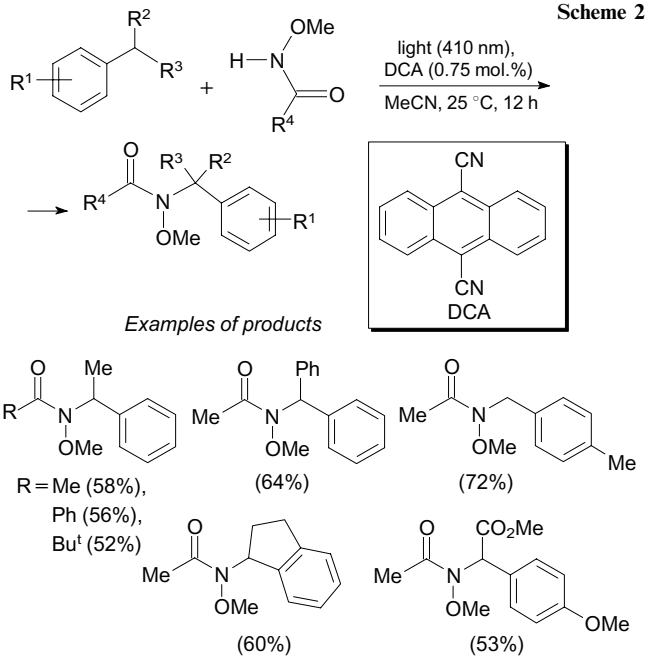
Among the former type reactions, mention should be made of cross-dehydrogenative benzylic C($sp^3$)–H amination using 9,10-dicyanoanthracene (DCA) as an organic photoredox catalyst and *N*-methoxyamides as precursors of amidyl radicals (Scheme 2).[29]

The putative reaction mechanism includes the step of formation of amidyl radical **1**, stabilized by the captodative

**Scheme 1**



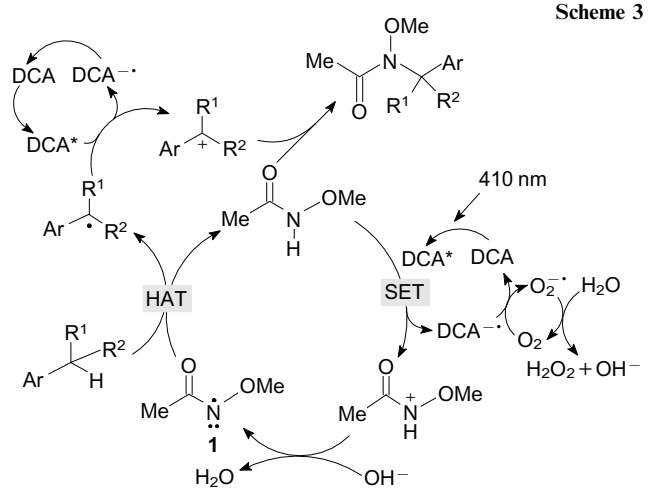

**Scheme 2**



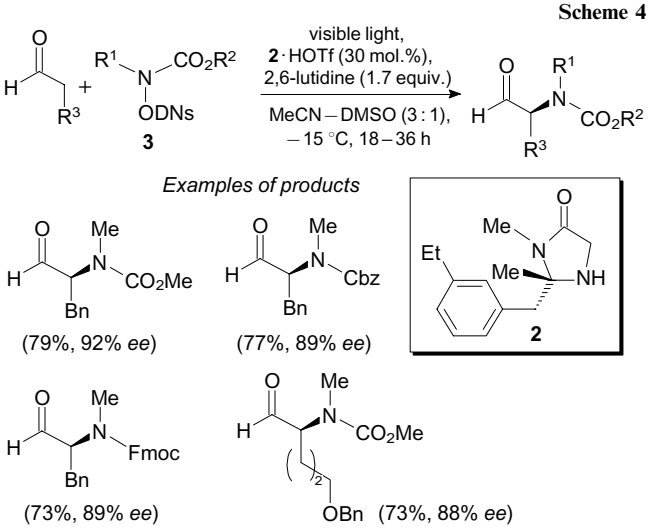

effect[30] (simultaneous presence of electron-donating and electron-withdrawing substituents at the radical centre), as a result of single-electron oxidation of *N*-methoxyamide with 9,10- dicyanoanthracene in the singlet excited state (DCA*) (SET process, Scheme 3). The hydrogen atom transfer from the benzylic substrate to the N-centred radical (HAT process) leads to a stable benzyl radical, which is then oxidized by DCA* to the corresponding benzyl cation. This cation reacts with *N*-methoxyamide to give the amination product.

The asymmetric α-amination of aldehydes is based on the reaction of electrophilic N-radicals with nucleophilic enamines, which are obtained *in situ* from aliphatic aldehydes and chiral imidazolidinone **2** (Scheme 4).[31] In this

**Scheme 3**

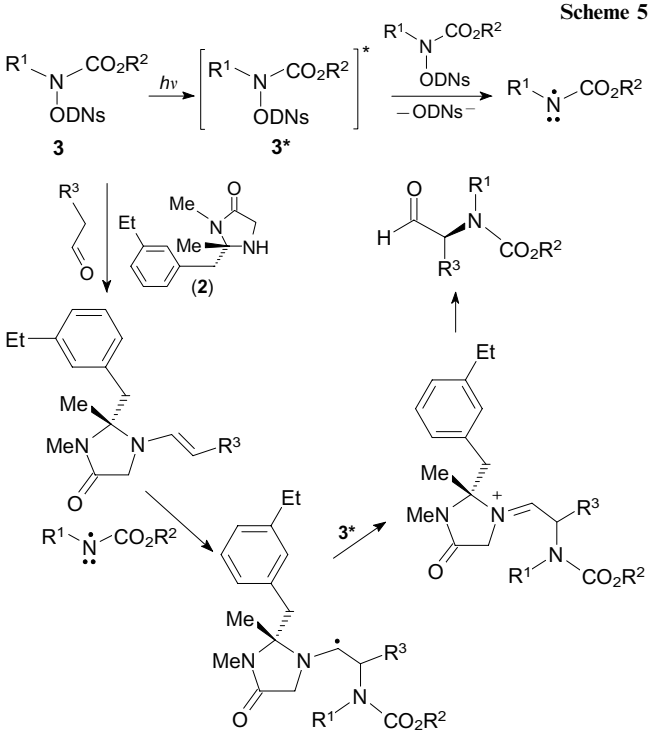



**Scheme 4**

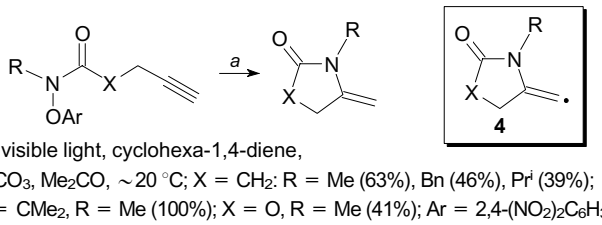



DNs is 3,5-dinitrobenzenesulfonyl, Tf is trifluoromethanesulfonyl (triflyl), Cbz is benzyloxycarbonyl, Fmoc is 9-fluorenylmethyloxycarbonyl, *ee* is enantiomeric excess

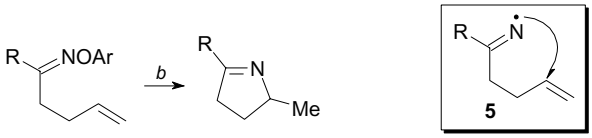
**Scheme 5**



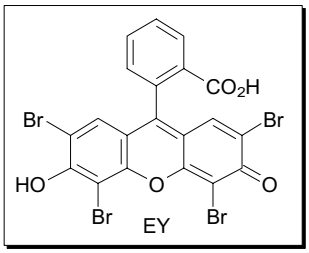

**Scheme 6**




(*a*) visible light, cyclohexa-1,4-diene, $K_2CO_3$, $Me_2CO$, ~20 °C; X = $CH_2$: R = Me (63%), Bn (46%), $Pr^i$ (39%); X = $CMe_2$, R = Me (100%); X = O, R = Me (41%); Ar = 2,4-$(NO_2)_2C_6H_3$




(*b*) EY (2 mol.%), visible light, cyclohexa-1,4-diene, $K_2CO_3$, $Me_2CO_2$, ~20°C; R = Ph (78%), 4-$MeOC_6H_4$ (94%), 4-$FC_6H_4$ (84%), $PhCH_2CH_2$ (72%), $MeO_2CCH_2$ (78%); Ar = 2,4-$(NO_2)_2C_6H_3$




case, the initial *N*-(2,4-dinitrobenzenesulfonyloxy)carbamates **3** serve as precursors of N-radicals.

The radicals are generated without a photoredox catalyst upon the single-electron reduction of the substrate in the electronically excited state (**3***) with the starting molecule **3**. The addition of N-radicals to enamines affords C-radicals, which undergo SET oxidation involving compound **3*** and are thus converted to the corresponding cations (Scheme 5).

A related generation of amidyl radicals upon irradiation of *N*-(2,4-dinitrophenyloxy)amides with a compact luminescent lamp provides the basis for the synthesis of pyrrolidinones.[32] Radical **4** formed upon 5-*exo*-*dig*-cyclization is converted to the corresponding pyrrolidine derivative *via* hydrogen atom transfer from cyclohexa-1,4-diene (Scheme 6).

Similarly, visible light-induced homolytic N – O bond cleavage in *O*-aryloximes and the subsequent 5-*exo*-*trig*-cyclization of the resulting N-radicals **5** provides the synthesis of five-membered N-heterocycles (see Scheme 6).[33]

Depending on the aryl group in *O*-aryloximes, the N – O bond activation giving rise to iminyl radicals **5** may be performed either in the presence of organic photoredox catalyst eosin Y (EY) or *via* the intermediate formation of the electron donor – acceptor complex with $Et_3N$ (not shown in Scheme 6; see Ref. 33).

The amidyl radicals generated upon green light irradiation of *N*-(2,4-dinitrophenyloxy)amides, which contain no multiple bonds, undergo intermolecular reactions with electron-rich aromatic compounds (substituted pyrroles, indoles, furans, thiophenes, naphthalenes, azulenes, *etc.*) in

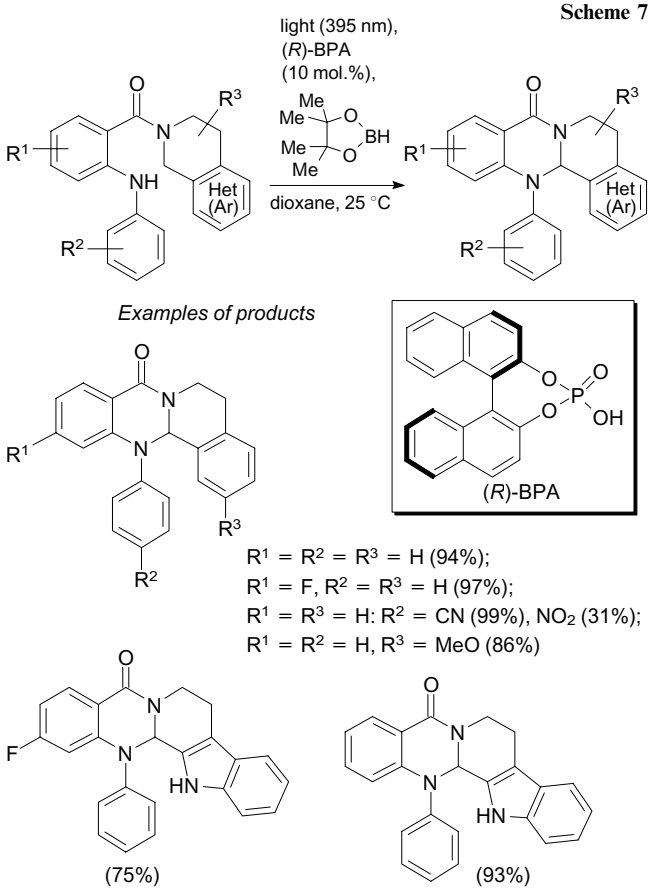
the presence of 2 mol.% eosin Y to give amination products.[34]

The photoinduced intramolecular amination of C(sp$^3$)—H bonds is also used to synthesize six-membered fused heterocyclic systems. The visible light-induced intramolecular formation of C—N bonds in benzamides in the presence of 1,1′-binaphthyl-2,2′-phosphoric acid (BPA) and pinacol borane yields fused heterocycles. This method was used to prepare the natural compounds tryptanthrin and rutaecarpine and related products (Scheme 7).[35]

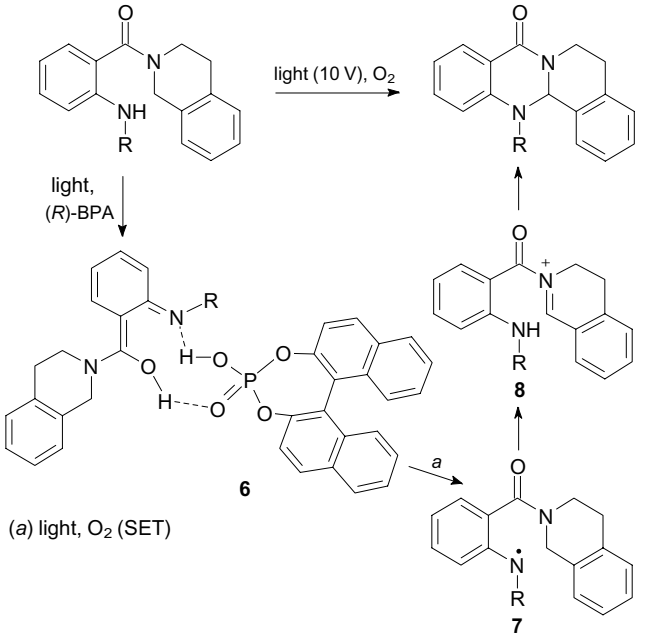
This reaction proceeds *via* photoinduced isomerization of amides to short-lived photoisomers **6** stabilized by intermolecular hydrogen bonds with the (*R*)-BPA molecule. As a result of SET processes, photoisomers **6** are converted first to N-radicals **7** and then to iminium ions **8** (Scheme 8).

Ethers can serve as substrates for the initiated photochemical amination of the C(sp$^3$)—H bonds, which was demonstrated in relation to THF.[36] In this case, the reaction involves 9-mesityl-10-methylacridinium perchlorate ([AcrMes]$^+$ClO$_4^-$) as the photoredox catalyst (Scheme 9). In the electronically excited state, the latter compound ([AcrMes]$^+$ClO$_4^-$)*, which is a potent oxidant, transforms azole molecules to the corresponding N-radicals. This reaction also involves air oxygen, which oxidizes the reduced form of the photoredox catalyst and promotes generation of C-radicals from THF. Pyrazoles and 1,2,3-triazoles can act as aminating agents.

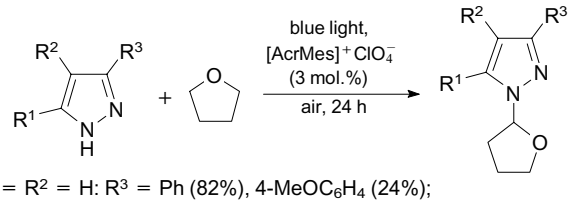
**Scheme 7**




**Scheme 8**




**Scheme 9**

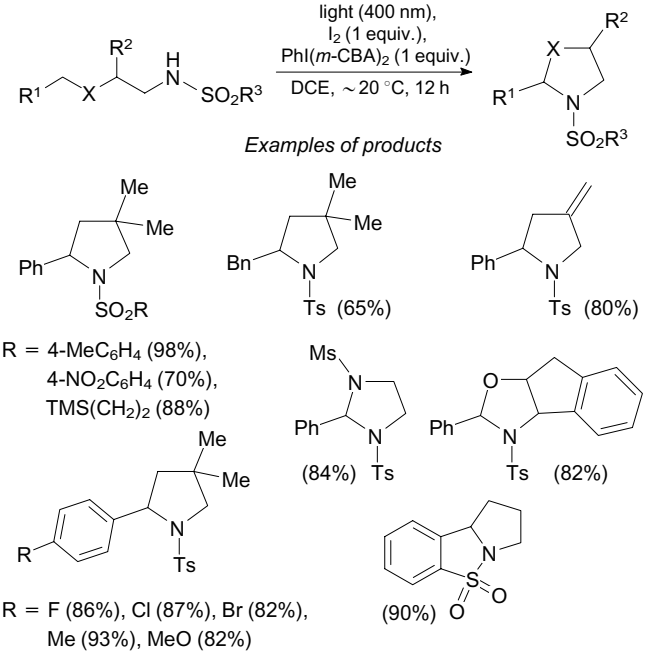



The acridinium photoredox catalyst [AcrMes]$^+$ClO$_4^-$ and oxygen as the terminal oxidant were used to generate hydrazonyl radicals from *N*-tosylhydrazones of β,γ-unsaturated ketones.[37]

An alternative approach to the formation of N-centred radicals is based on the application of iodine(III). In this case, the highly reactive N-radicals are generated as a result of photoinduced homolysis of the N—I bond. An example of this type is the intramolecular oxidative amination of tosylamides, giving rise to saturated nitrogen-containing heterocycles (Scheme 10).[38]

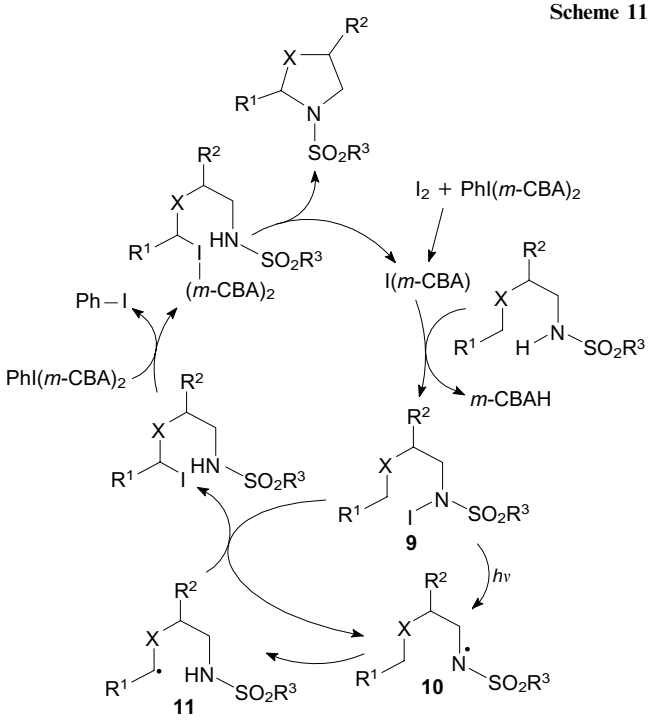
The putative mechanism of cyclization includes the initial reaction of molecular iodine with hypervalent iodine(III) compound to give I(*m*-CPB), which is the true catalyst of the process. The subsequent reaction of this compound with the substrate yields key intermediate **9**, containing an N—I bond and functioning as a photosensitizer. The irradiation of intermediate **9** affords N-radical **10**, which undergoes 1,5-transfer of hydrogen and thus isomerizes to C-radical **11**. The elimination of a iodine atom from intermediate **9** under the action of this radical initiates a radical chain reaction (Scheme 11).

**Scheme 10**



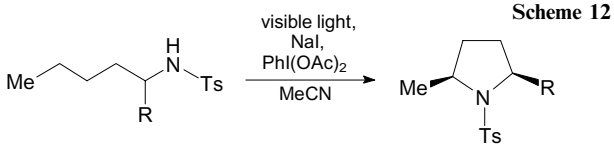

*m*-CBA is 3-chlorobenzoate, DCE is 1,2-dichloroethane, TMS is trimethylsilyl, Ts is *p*-toluenesulfonyl (tosyl), Ms is methanesulfonyl (mesyl)

**Scheme 11**




A synthetic strategy that makes it possible to avoid the drastic conditions of the Hofmann–Löffler reaction (cyclization of *N*-haloamines on heating in a strong acid[39]) is based on 1,5-cyclization of *N*-alkyltosylamines to give substituted pyrrolidines catalyzed by the $I_3^-$ anion (Scheme 12).[40] This anion is generated upon oxidation of the iodide anion under the action of $PhI(OAc)_2$. In this case, the amidyl radical is also formed upon the homolytic

**Scheme 12**



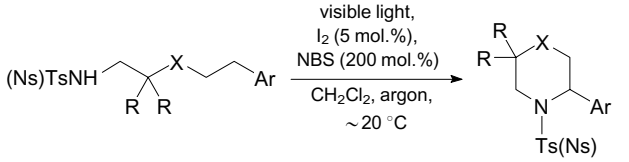

R = Me (80%, *dr* = 1.2 : 1 ), $CF_3$ (58%, *dr* = 2 : 1), $CO_2Me$ (65%, *dr* = 2 : 1); *dr* is diastereomeric ratio

cleavage of the N–I bond in the intermediate *N*-iodotosylamide induced by irradiation of the reaction mixture with a compact fluorescent lamp (CFL).

The $I_2$–$PhI(m\text{-CBA})_2$ system was used for photoinduced C–H amination of arenes.[41] The considered methods for the generation of compounds with a N–I bond are based on the use of iodine compounds and are accompanied by the formation of aryl iodides as by-products. This circumstance makes these methods uneconomical and somewhat cumbersome, since it is necessary to separate the target products from undesirable compounds formed in equimolar amounts.

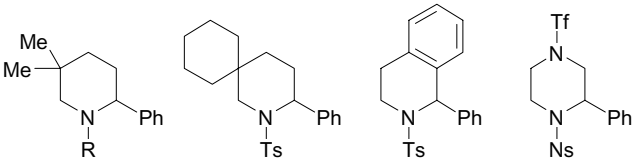
The cyclization of *N*-alkyltosylamides to give substituted pyrrolidines can also occur in the presence of *N*-iodosuccinimide for generation of photolabile compounds containing N–I bonds.[42] Using 2,4,6-triphenylpyrylium tetrafluoroborate as a photoredox catalyst for the oxidation of molecular iodine with air oxygen, it is possible to do without oxidants based on hypervalent iodine compounds.[43] A process of this type applied to *N*-alkylsulfonylamides containing an aryl substituent in position 5 leads to selective formation of substituted piperidines (Scheme 13).[44]

**Scheme 13**




NBS is *N*-bromosuccinimide, Ns is 4-nitrobenzenesulfonyl

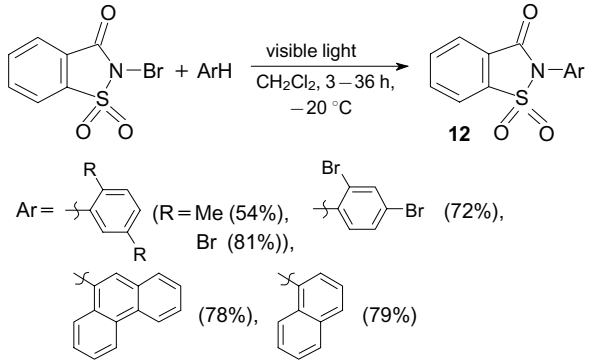
*Examples of products*




The generation of amidyl radicals upon the visible light-induced homolytic cleavage of the N–I bond is the key step of the benzylic C–H amination of aromatic hydrocarbons in the presence of chloramine T and molecular iodine.[45]

An alternative method for the generation of imidyl radicals comprises visible light irradiation of *N*-bromosaccharins.[46,47] The use of these radicals underlies the imidation of (hetero)arenes to give *N*-arylsaccharins **12** (Scheme 14).[46] This method is applicable to a wide range of (hetero)arenes containing electron-donating and weak electron-withdrawing (for example, halogen atoms) sub-

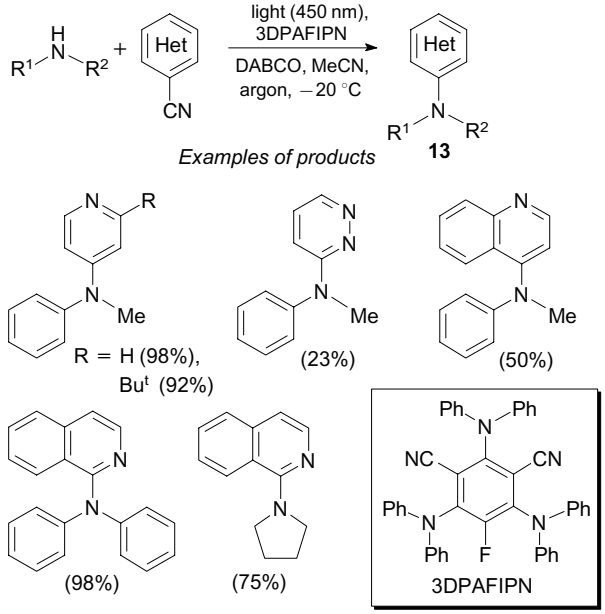
**Scheme 14**




stituents. A similar generation of amidyl radicals takes place in the case of substituted *N*-bromobenzamides,[48] although the synthetic use of the latter is not associated with the preparation of nitrogen compounds.

In the synthesis of an extensive series (58 examples) of azine-substituted tertiary amines **13**, the photoinduced generation of N-radical cations by single-electron oxidation of primary and secondary amines is followed by their coupling with the radical anions formed from the corresponding cyanoazines.[49] 3,5-Dicyano-2,4,6-tris(diphenylamino)fluorobenzene (3DPAFIPN) serves as the photoredox catalyst (Scheme 15).

**Scheme 15**

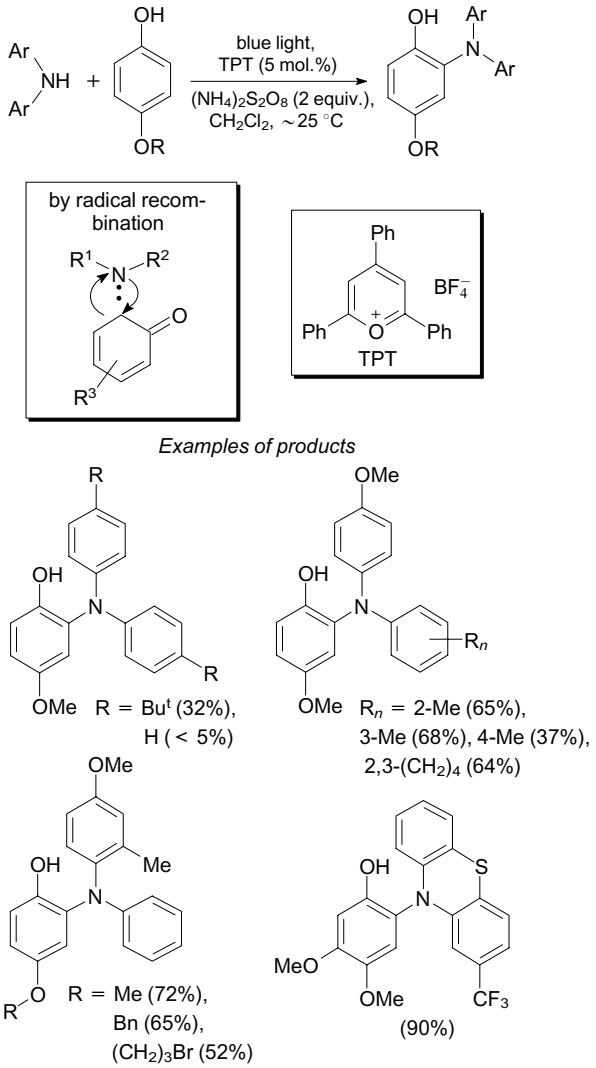



DABCO is 1,4-diazabicyclo[2.2.2]octane

The cross-dehydrogenative amination of 4-alkoxyphenols with diarylamines on exposure to blue light takes place in the presence of 2,4,6-triphenylpyrylium (TPT) tetrafluoroborate as the photocatalyst and ammonium persulfate as the oxidant (Scheme 16).[50] The mechanism of this reaction is based on radical coupling (shown in a frame in the Scheme).

The generation of the imidyl radical from phthalimide is the key step of the synthesis of phthalimide (PHTH-NH) derivatives of indole and some other five-membered heterocyclic compounds. The photoinduced dehydrogenative coupling of substrates with phthalimide takes place when the reaction mixture is irradiated by CFL in the presence of a base and 2-*tert*-butylanthraquinone (2-Bu$^t$-AQN) as the photoredox catalyst (Scheme 17).[51]

**Scheme 16**



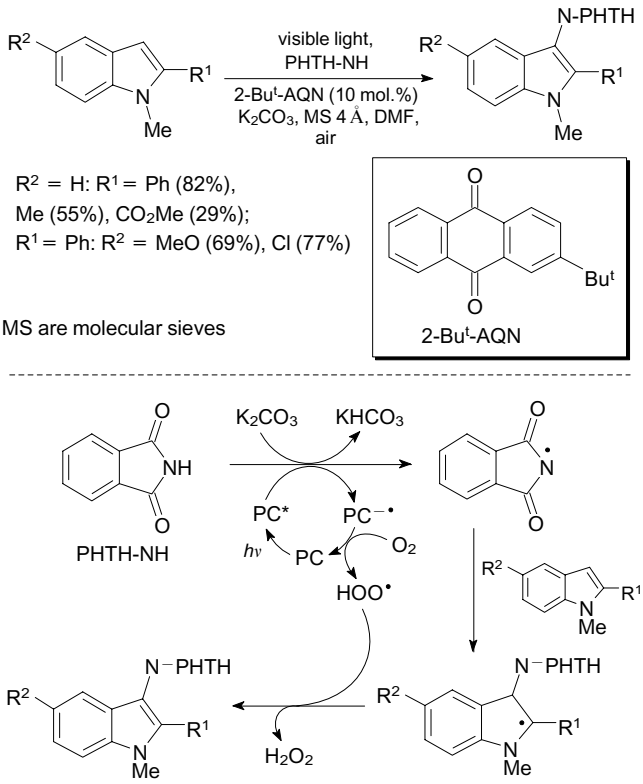

A similar mechanism of formation of the C–N bond is implemented in the amination of quinaxolin-2(1*H*)-ones with secondary amines induced by visible light at a 460–480 nm wavelength in the presence of eosin Y as the photocatalyst (1–5 mol.%) (Scheme 18).[52]

One more example of amination of an aromatic system is provided by regioselective cyclization of 2-styrylquinolines, resulting in quinolino[1,2-*a*]quinolinium salts **14**, potential biologically active compounds (Scheme 19).[53]

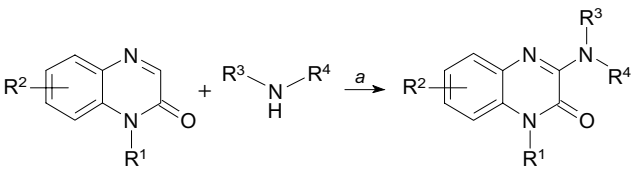
The visible-light induced dehydrogenative coupling of electron-deficient alkenes with azoles catalyzed by the rose bengal (RB) dye affords *N*-vinylazoles. In this case, the reaction mechanism includes the intermediate formation of azolyl N-radical. First, the single-electron oxidation of azole with the electronically excited photoredox catalyst yields the corresponding radical cation, which is then deprotonated to the N-radical (Scheme 20).[54]

The acridinium photoredox catalysts **15a**,**b** were used to generate alkylaminium radical cations upon oxidation of the corresponding primary aromatic alkylamines in an oxygen atmosphere under irradiation with light at 455 nm. The

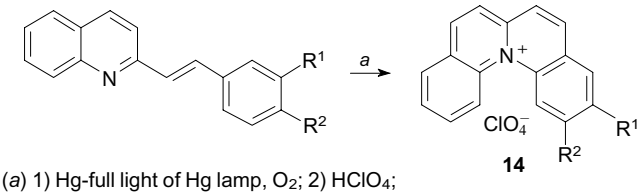
**Scheme 17**



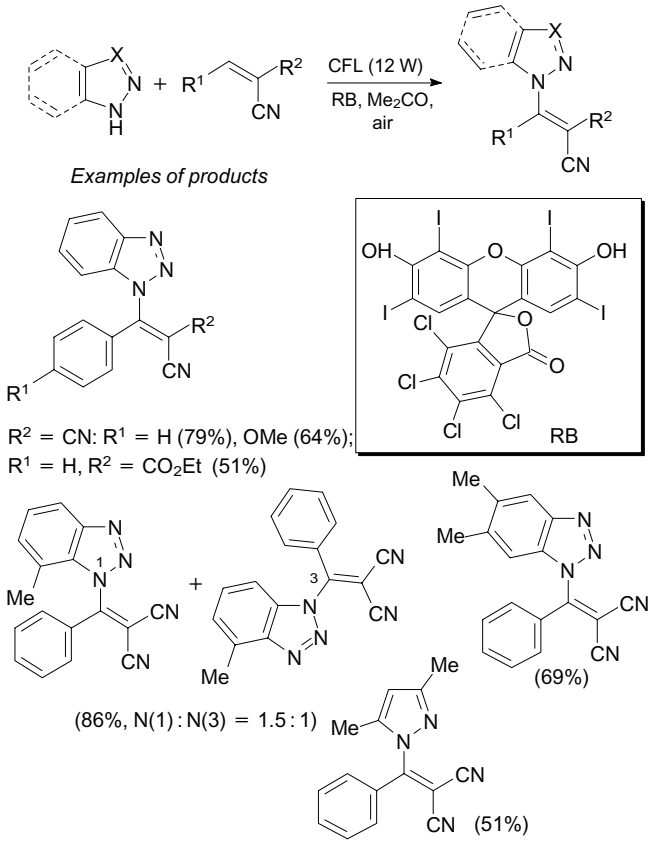

**Scheme 18**




**Scheme 19**

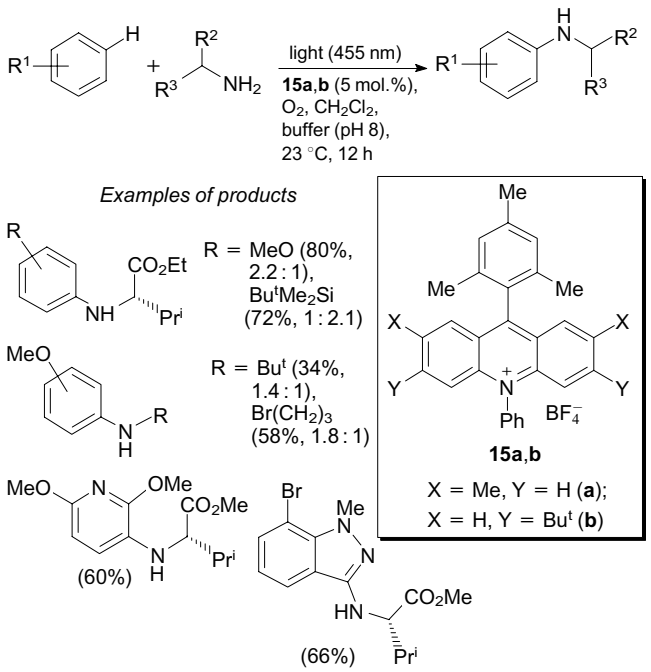



**Scheme 20**




N-radical cations generated in this way were used for direct C–H amination of aromatic compounds; amino acid ester hydrochlorides were also used as aminating agents in this case.[55] When optically pure chiral amines were used, their enantiomeric purity was retained. Although this method is fairly selective for the synthesis of monoamination prod-

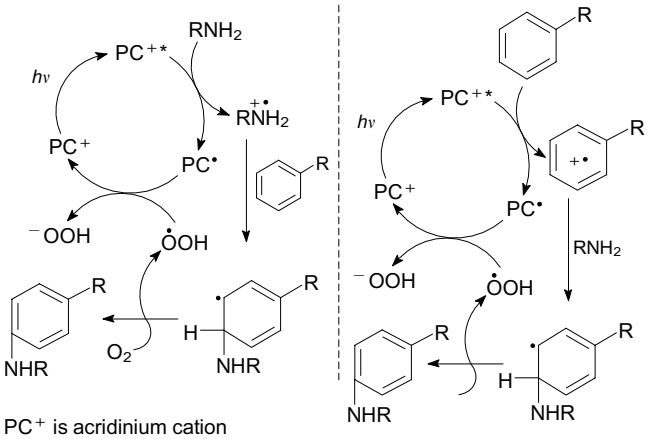
**Scheme 21**



ucts, the regioselectivity of C—H amination in the absence of pronounced steric restrictions remains moderate (Scheme 21; the value indicated in parentheses after the product yield is the ratio of *ortho*- and *para*-isomers). Meanwhile, the amination of heteroarenes is virtually regioselective under the same conditions.

A possible mechanism of C—H amination of aromatic compounds proposed by the authors includes the initial oxidation of the primary amine to the corresponding radical cation with the acridinium photoredox catalyst in the electronically excited state. The addition of the N-radical cation to the aromatic molecule results in the formation of cyclohexadienyl radical, which aromatizes under the action of oxygen (Scheme 22). However, since some aromatic compounds with electron-donating substituents have oxidation potentials close to the oxidation potentials of amines, an alternative mechanism is also possible. The mechanism includes the initial visible light-induced oxidation of aromatic substrate to give the C-radical cation, which then reacts with N-nucleophile (see Scheme 22).

**Scheme 22**

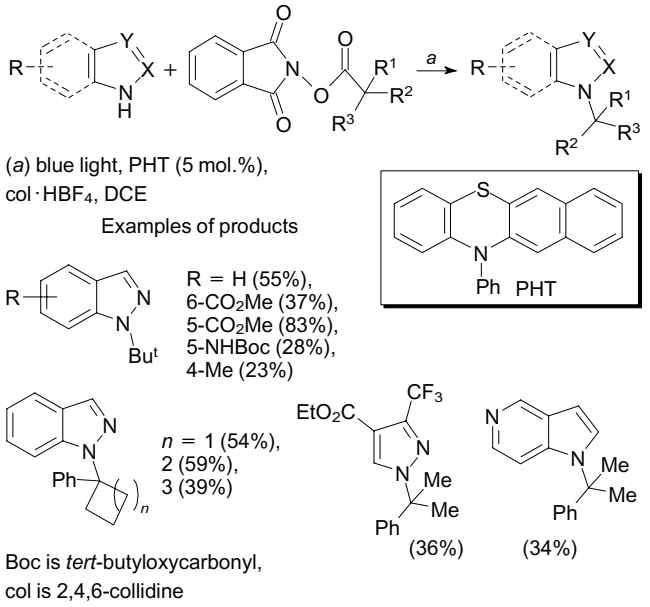



$PC^+$ is acridinium cation

Acridinium and xanthylium salts were employed as photoredox catalysts in the visible light-induced N-arylation of primary amines and azoles with fluoro- and methoxybenzenes *via* formal nucleophilic substitution with replacement of F atom[56] and MeO group.[57,58] In both cases, the probable mechanism implies the generation of C-radical cations (similar to that shown in Scheme 22), which then react with N-nucleophilic reagents. Unlike conventional aromatic nucleophilic substitution $S_NAr$, visible light-induced photocatalytic reactions proceed under mild conditions and in the absence of strong electron-withdrawing substituents in the substrate molecule.

The decarboxylative coupling of NH-azoles with redox-active *N*-acyloxyphthalimides[59,60] in the presence of *N*-phenylbenzo[*b*]phenothiazine (PHT) as a photoredox catalyst and collidinium tetrafluoroborate on blue light irradiation leads to the synthesis of azole derivatives containing a tertiary alkyl substituent at the nitrogen atom (Scheme 23).[61] The key intermediates of the reaction are alkyl radicals, formed as a result of photochemically induced fragmentation of *N*-acyloxyphthalimides. The collidinium salt is necessary to suppress the side elimination reaction involving phthalimide anion as the base.

**Scheme 23**



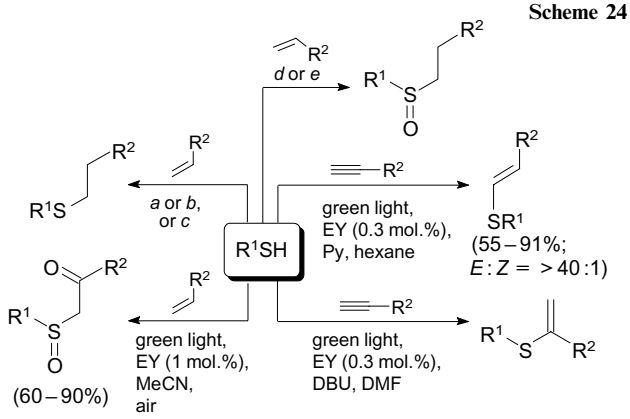

## 2.2. Formation of C—S bond

The photocatalytic reactions that give C—S bond in the presence of either photoactive transition metal complexes or organic photoredox catalysts are addressed in detail in a review[62] published in 2018. Another review[63] that appeared the same year considers the photocatalyzed formation of sulfones and sulfoxides. In this part of the present review, we mention only the most important reactions of this type described earlier and consider in detail the data obtained after 2018.

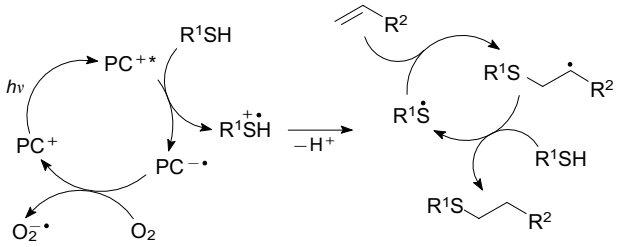
The visible light initiation was used to prepare the products of addition of aliphatic and aromatic thiols to multiple bonds (Scheme 24). Several photocatalysts were proposed for these reactions, including eosin Y,[64,65] phenylglyoxalic acid,[66] benzophenone,[67] 1,2-diphenylethane-1,2-dione,[68] 9-mesityl-10-methylacridinium salts[69–71] and the acridine orange dye, which acts simultaneously as a Lewis base.[72] Although the reaction mechanisms vary to some extent depending on the conditions and the nature of the photocatalyst, the key step is the single-electron oxidation of the starting thiol to the corresponding radical cation, which is converted to thiyl radical upon deprotonation.[73] The addition of S-radicals to alkenes or alkynes affords the corresponding C-centred radicals, which participate in the subsequent generation of S-radicals. It is noteworthy that the selectivity of addition of thiols to terminal alkynes depends on the base used. In the case of pyridine, the major reaction product is *E*-alkene formed upon the anti-Markovnikov addition,[65] whereas the use of 1,8-diazabicyclo[5.4.0]undec-1-ene (DBU) results in the formation of the Markovnikov addition product.[74] The reactions carried out in the presence of oxygen gave products of oxidative addition of thiols to alkenes (see Scheme 24).[64,75,76] The photoredox-catalyzed formation of C—S bonds induced by visible light was used for the synthesis of benzothiophenes[69] and for direct C—H sulfenylation of indoles,[77] quinoxalinones[78] and 4-hydroxycoumarins.[79]

The C—H sulfenylation of alkanes and cycloalkanes was accomplished on treatment with bis(2,3,5,6-tetrafluoropyridin-4-yl) disulfide under irradiation with light at 400 nm in the presence of an oxidant. The reaction was

**Scheme 24**

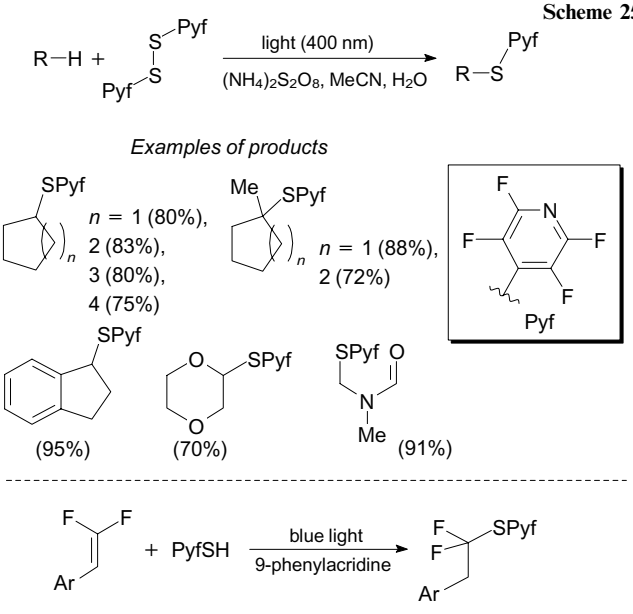



(*a*) CFL, $PhC(O)CO_2H$ (10 mol.%), THF, (74–90% yield);
(*b*) blue light, **15a** (1 mol.%), MeCN (73–90%);
(*c*) CFL, $Ph_2C{=}O$ (10 mol.%), MeCN (75–94%);
(*d*) white light, RB (5 mol.%), EtOH, $H_2O$, air (16–90%);
(*e*) green light, EY (2.5 mol.%), $CH_2Cl_2$, air (24–93%);
Py is pyridine




found to be highly selective to tertiary C–H bonds of alkanes. The presumed mechanism of sulfide formation includes the generation of alkyl radical upon hydrogen atom transfer (HAT) from an alkane molecule to the thiyl radical, formed upon the photolytic dissociation of the disulfide (Scheme 25).[80] The thiyl radical can be obtained

**Scheme 25**

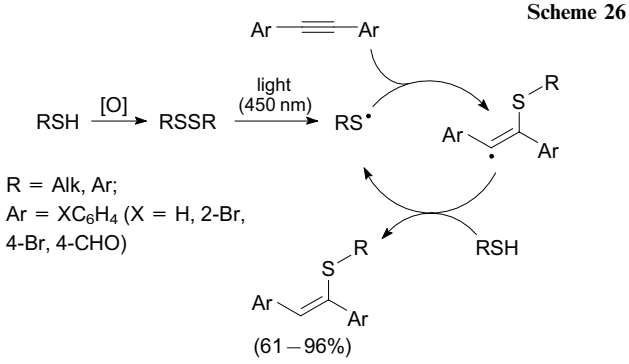



by blue light irradiation of the complex of 4-sulfanyl-2,3,5,6-tetrafluoropyridine with 9-phenylacridine *via* photo-induced proton coupled electron transfer (PCET). The thiyl radical generated in this way was used for the addition to *gem*-difluorostyrenes (see Scheme 25).[81]

One of the synthetic routes to benzothiazoles is based on cyclization of *N*-arylthiobenzamides upon C–H functionalization. First, thioamide or its deprotonated form is oxidized to give S-radical. The addition of the thiyl radical to the aromatic ring of the aniline moiety results in generation of a cyclohexadienyl radical, which aromatizes *via* hydrogen atom elimination. Although most transformations of this type are based on the use of ruthenium complexes as photoredox catalysts, catalytic systems that allow transition metal-free synthesis of benzothiazoles have been proposed in recent years. Reactions have been carried out in the presence of the following systems: riboflavin–$K_2S_2O_8$–blue light,[82] (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO)–light of CFL,[83] carbon nitride–air oxygen–red light,[84] eosin Y–diisopropylethylamine (DIPEA)–green light.[85]

Blue light irradiation at 450 nm in the absence of a catalyst stimulates the addition of alkane- and arenethiols to diarylacetylenes to give 1,2-diaryl-1-alkyl(aryl)ethylenes as mixtures of *cis*- and *trans*-isomers. According to the mechanism proposed by the authors, the reaction starts with the oxidative coupling of thiols to give the corresponding disulfides, which dissociate under irradiation *via* homolytic cleavage of the S–S bond to give S-radicals, which initiate a chain radical reaction (Scheme 26).[86]

**Scheme 26**

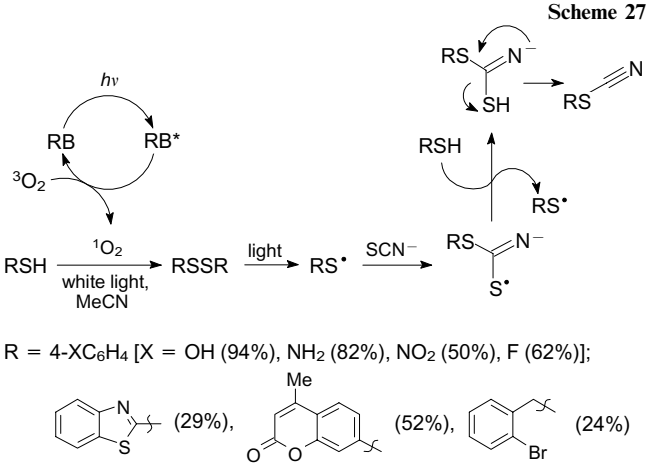



The addition of S-radicals generated from thiols to the thiocyanate anion under irradiation with white light in the presence of 1 mol.% rose bengal affords organic isothiocyanates. The mechanism of this reaction includes the initial generation of singlet oxygen $^1O_2$, which acts the oxidant for thiol and thus converts it to disulfide. Under irradiation, the latter dissociates into S-radicals, which add to the thiocyanate anion. Unlike other methods for the synthesis of organic isocyanates, this method is applicable to aromatic substrates containing substituents with different electronic properties and can be implemented under mild conditions requiring no toxic cyanide ion (Scheme 27).[87]

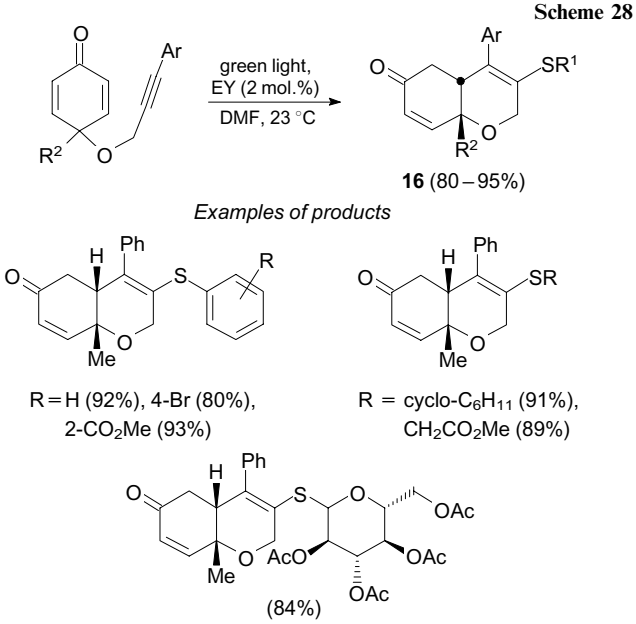
The addition of thiyl radicals to multiple bonds is the initial step of a number of cascade radical reactions that finally furnish complex molecules. An example is the synthesis of dihydrochromenones **16** by the sulfenylation–annelation cascade reaction (Scheme 28).[88]

Similar addition reactions to multiple bonds induced by visible light are also characteristic of thiocyanate anions

**Scheme 27**




**Scheme 28**

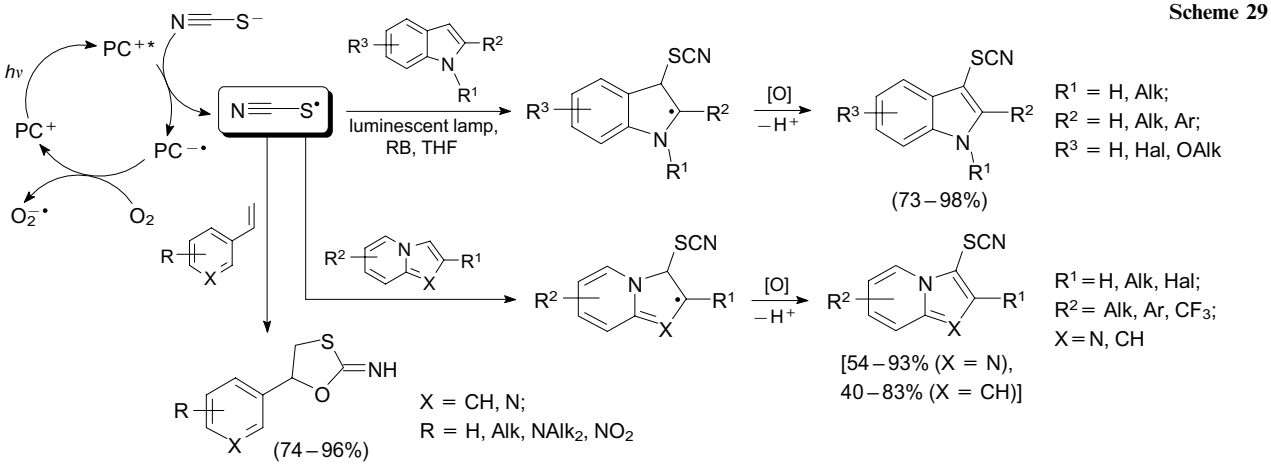



(Scheme 29). These reactions begin with single-electron oxidation to give a thiocyanyl radical, which then adds to carbon – carbon double bonds of styrenes[89] and electron-rich aromatic systems — indoles,[90] imidazopyridines[91] and indolizines.[92] The visible light-induced addition of N≡CS radical to 2-hydroxyaryl β-dialkylaminovinyl ketones in the presence of rose bengal furnishes 3-thiocyanochromenes.[93] In all of the above examples, reactions proceed under aerobic conditions, which facilitates regeneration of photoredox catalysts. When styrenes are used as the substrates, oxygen serves as the oxidant for the benzyl radical that is formed upon the addition of the S-radical to the C=C bond, and 5-(hetero)aryl-2-imino-1,3-oxathiolanes are isolated in the final step (see Scheme 29).[89]

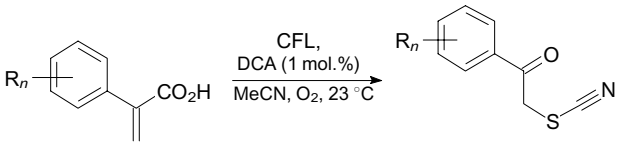
A similar oxidative transformation was observed upon the addition of the N≡CS radical generated from the thiocyanate anion to α-arylacrylic acids under irradiation with a fluorescent lamp in the presence of 9,10-dicyanoanthracene in an oxygen atmosphere.[94] In this case, the C–S bond formation followed by decarboxylation and oxidation of the benzylic position afford α-thiocyanato ketones (Scheme 30).

One more type of visible light-induced transformation involving thiocyanate anion takes place for cinnamic acids. The synthesis of vinyl thiocyanates is based on decarboxylative cross-coupling of cinnamic acids with potassium thiocyanate taking place upon irradiation with CFL in the presence of rose bengal as the photocatalyst under aerobic conditions (Scheme 31).[95] In the first step, the electronically excited dye molecule (RB*) oxidizes the thiocyanate anion to the corresponding radical, which adds to cinnamic acid thus giving a benzyl radical. The latter is oxidized with air oxygen to the benzyl cation, which is decarboxylated to yield vinyl thiocyanate. Air oxygen is also responsible for regeneration of the photoredox catalyst.

**Scheme 29**

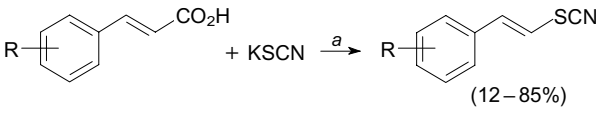


**Scheme 30**




R$_n$ = H (79%), 4-F (60%), 4-Br (74%), 4-CF$_3$ (24%), 4-MeS (40%), 2,5-Me$_2$ (20%)

**Scheme 31**



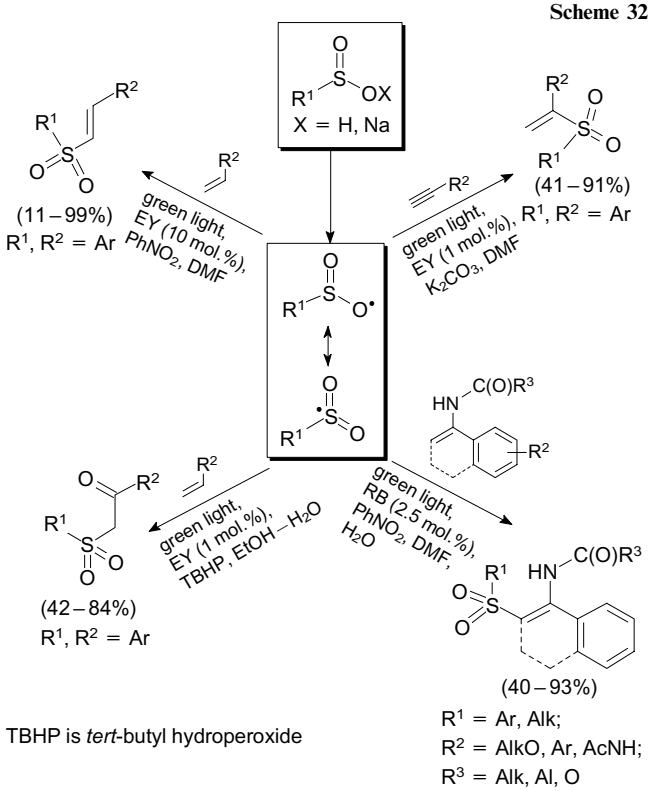

(*a*) visible light, RB, Cs$_2$CO$_3$, MeCN, air, ~20 °C;
R = 4-Me (82%), 4-OMe (71%), 2-Me (85%), 3-CF$_3$ (43%), 4-CHO (18%)

The generation of S-radicals *via* visible light-induced reactions of sulfinic acids and their salts followed by addition of the radicals to alkenes and alkynes underlies the synthesis of β-keto sulfones[96] and anti-Markovnikov[97] and Markovnikov isomers of vinyl sulfones[98] and β-acetaminovinyl sulfones (Scheme 32).[99]

Alternative routes to the generation of arenesulfonyl radicals include the addition of preliminarily generated aryl radicals to sulfur(IV) oxides. In turn, aryl radicals can be generated from arenediazonium and diaryliodonium salts.[25]

One of the synthetic routes to aryl alkyl sulfones and diaryl sulfones is based on the reaction of arenediazonium tetrafluoroborates with sodium aryl- and alkylsulfinates in the presence of eosin Y (1 mol.%) under irradiation with green light at 535 nm.[100] According to the mechanism

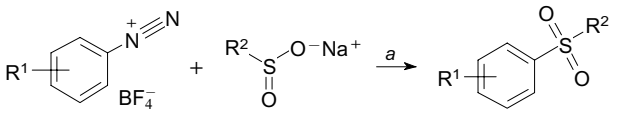
**Scheme 32**




TBHP is *tert*-butyl hydroperoxide

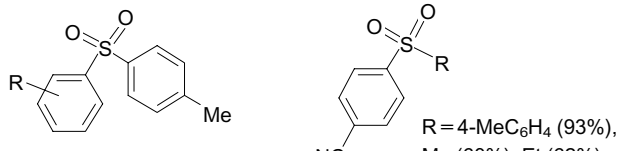
postulated by the authors, eosin Y is initially transferred to the excited state (EY*) upon photon absorption, while the excited state can act as a single-electron reducing agent for the arenediazonium cation. The electron transfer from EY* results in degradation of the arenediazonium cation to give an aryl radical and a nitrogen molecule and in the formation of the $EY^{+\bullet}$ radical cation. The $EY^{+\bullet}$ radical cation generated in this way serves as an oxidant for the arylsulfinate anion, which is thus converted to the $RSO_2^{\bullet}$ radical. The recombination of $Ar^{\bullet}$ and $RSO_2^{\bullet}$ radicals gives rise to sulfones (Scheme 33). There are examples of C–S bond formation upon coupling of sulfonyl radicals with stabilized tertiary alkyl radicals to give sulfones.[101]

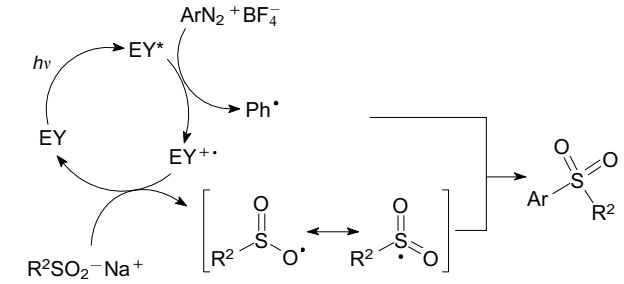
**Scheme 33**




(*a*) green light, EY (1 mol.%), MeCN, H$_2$O, 23 °C, N$_2$

*Examples of products*



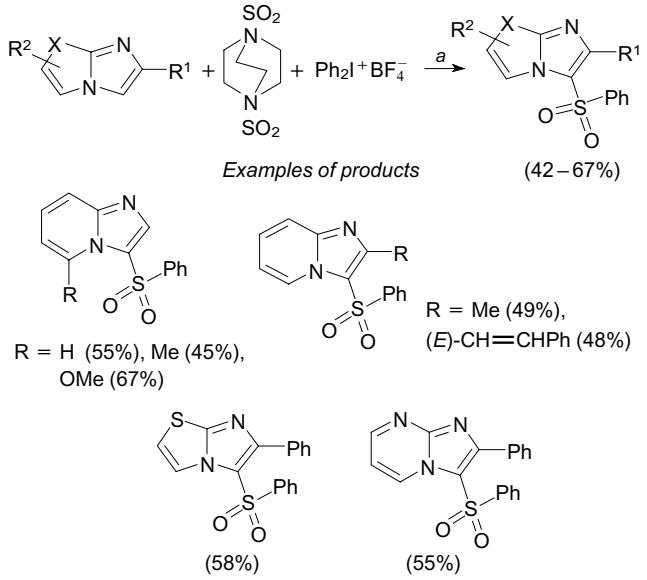



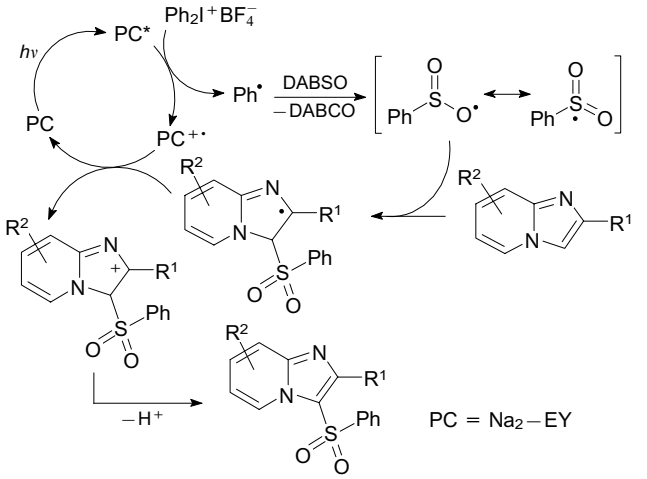

The generation of aryl radicals upon the photoinduced decomposition of diaryliodonium salts involving eosin Y and the subsequent reactions of the radicals with organic thiosulfates were used for the synthesis of aryl sulfides and aryl sulfoxides. The reaction selectivity was determined by the chosen conditions: the reaction carried out in an inert atmosphere under white light irradiation gave aryl sulfides, whereas green light irradiation in air promoted the formation of sulfoxides.[102]

In recent years, DABSO, the complex of 1,4-diazabicyclo[2.2.2]octane and sulfur(IV) oxide, has become a popular reagent in the practical organic synthesis as a stable, easily handled substitute for toxic sulfur dioxide gas.[103–105] In particular, the three-component reaction of diphenyliodonium salt, DABSO and substituted imidazopyridines induced by green light irradiation in the presence of the disodium salt of eosin Y ($Na_2$-EY) results in the formation of 3-sulfonylimidazopyridines in satisfactory yields (Scheme 34).[106]

One more alternative to sulfur dioxide used in organic synthesis is sodium or potassium pyrosulfite $M_2S_2O_5$

**Scheme 34**



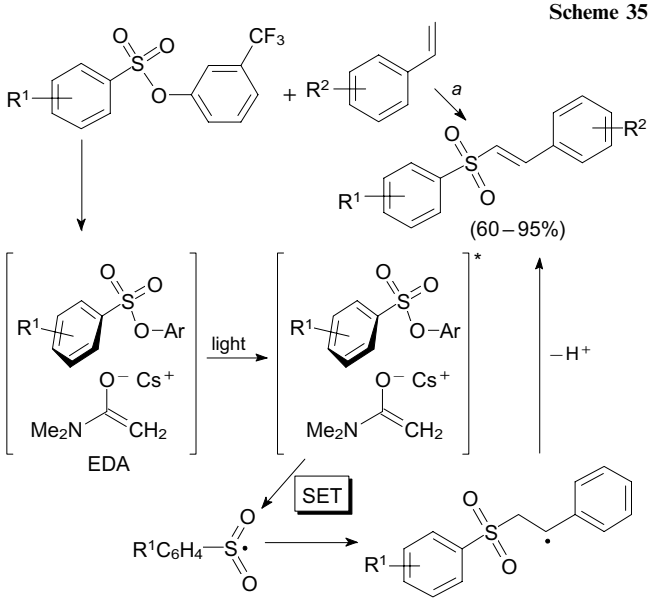




(M = K, Na).[107] For example, photoinduced three-component reaction of arenediazonium tetrafluoroborate, thiourea and $Na_2S_2O_5$ in MeCN under irradiation with CFL in the presence of rhodamine G results in the formation of *S*-aryl thiosulfonates in good yields. According to the mechanism postulated by the authors, the photoinduced decomposition of the diazonium salt leads to generation of an aryl radical, which is converted to arenesulfonyl radical upon the addition to sulfur dioxide. In parallel, the arenediazonium cation reacts with thiourea to give *S*-aryl isothiouronium salt, a source of the arenethiolate anion. The oxidation of this anion with a photoredox catalyst in the excited state gives rise to an arylthienyl radical, which recombines with the arenesulfonyl radical to give *S*-aryl thiosulfonate.[108] A related process is implemented when diaryliodonium salts, N,N-disubstituted hydrazines and $K_2S_2O_5$ are allowed to react under irradiation with blue light in the presence of perylene derivative as a photosensitizer, which results in the formation of sulfonyl hydrazides.[109]

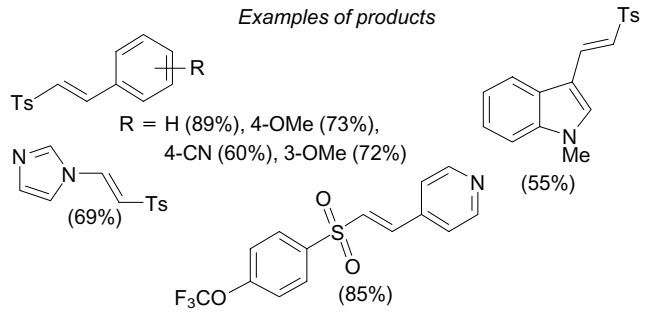
There are examples of cascade radical reactions involving arenesulfonyl radicals, which are generated upon the addition of aryl radicals to a $SO_2$ molecule. For example, 3-arenesulfonylquinolines were obtained by the green light-induced reaction of diaryliodonium salts, DABSO and *N*-arylpropargylamines in the presence of eosin Y.[110] Related cascade reactions that give C–S bond in the key step were used to prepare arylsulfonylcoumarins[111] and arylsulfonyl oxindoles.[112]

The reaction of 3-trifluoromethylphenyl esters of arenesulfonic acids with styrenes under blue light irradiation at 427 nm in *N*,*N*-dimethylacetamide (DMA) in the presence of $Cs_2CO_3$ furnishes *trans*-vinyl sulfones.[113] According to the proposed mechanism, the arenesulfonyl radical generated from arenesulfonate is the key intermediate in the formation of the C–S bond. In the first stage, the electron donor–acceptor complex is formed from arenesulfonate and a solvent molecule. The photoexcitation of this complex initiates a single-electron transfer from the DMA molecule to arenesulfonate, thus inducing S–O bond cleavage and giving an arenesulfonyl radical. The addition of this radical to styrenes to give benzylic radical and the subsequent elimination of the hydrogen atom yield vinyl sulfones (Scheme 35). The reactions of arenesulfonic acid esters with vinylheteroaryls proceed in a similar way.

**Scheme 35**

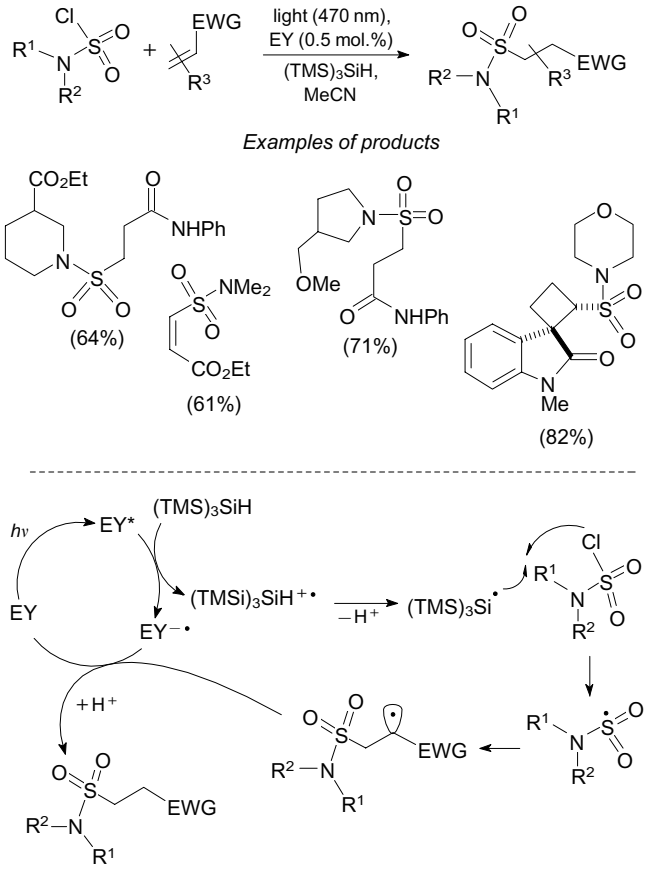



(*a*) $Cs_2CO_3$ (3 equiv.), light (427 nm), DMA; Ar = 3-$F_3CC_6H_4$




A method for activation of sulfamoyl chlorides to form the corresponding sulfamoyl radicals is based on elimination of a chlorine atom from the substrate under the action of tris(trimethylsilyl)silyl radical.[114] The latter radical is generated by photoinduced oxidation of tris(trimethylsilyl)-silane followed by deprotonation in the presence of eosin Y on exposure to blue light at 470 nm. The sulfamoyl radicals

**Scheme 36**



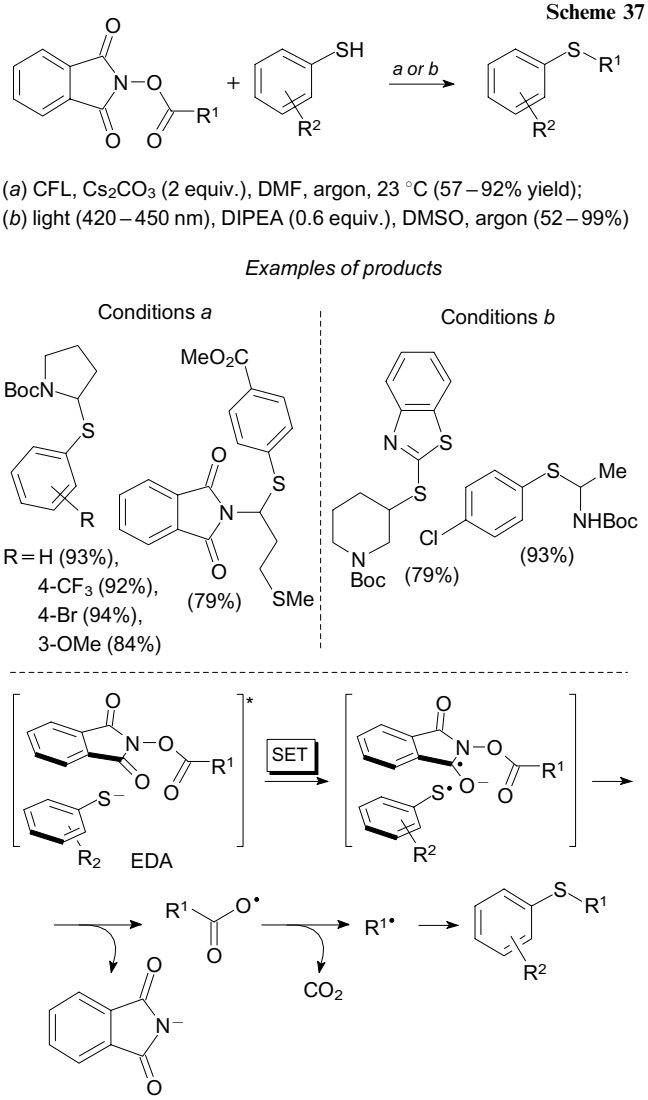

EWG is electron-withdrawing group

generated in this way were used in the addition reactions to compounds with multiple bonds to obtain sulfonamides (Scheme 36).

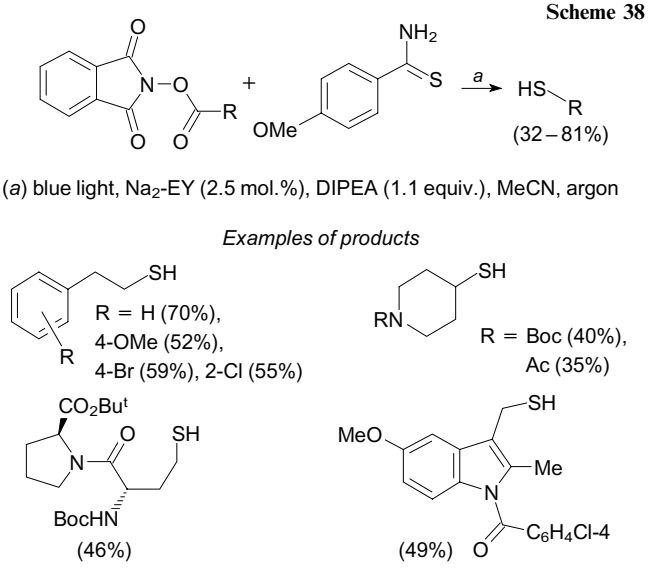
A number of methods have been developed to insert a C–S bond into the molecule *via* transformations of functional groups present in the molecule that contain no sulfur atoms, *e.g.*, carboxyl, carbonyl and amino groups. For example, reactions of redox-active *N*-(acetoxy)phthalimides,[59,60] which are readily formed from the corresponding carboxylic acids and *N*-hydroxyphthalimide, with thiophenols in the presence of $Cs_2CO_3$ or diisopropylethylamine under visible light irradiation furnish the products of decarboxylative S-alkylation of thiophenols.[115,116] This reaction proceeds without a photoredox catalyst *via* the preliminary formation of the electron donor–acceptor complex from the oxyphthalimide derivative and thiophenolate anion. The single-electron transfer from the thiophenolate anion to *N*-(acetoxy)phthalimide is accompanied by elimination of the phthalimide ion and generation of a carboxyl radical, which is decarboxylated to be converted to an alkyl radical. Coupling of the alkyl radical with an arylthiyl radical produces *S*-alkylthiophenols. An important synthetic application of this method is related to modification of natural amino acids to the corresponding sulfides *via* the intermediate formation of *N*-(acetoxy)phthalimides (Scheme 37). This approach is compatible with a number of protecting groups used in amino acid chemistry.

A similar reaction of the redox-active *N*-(acetoxy)-phthalimides with 4-methoxythiobenzamide under blue light irradiation in the presence of the disodium salt of eosin Y and DIPEA furnishes alkanethiols (Scheme 38).[117]

**Scheme 37**

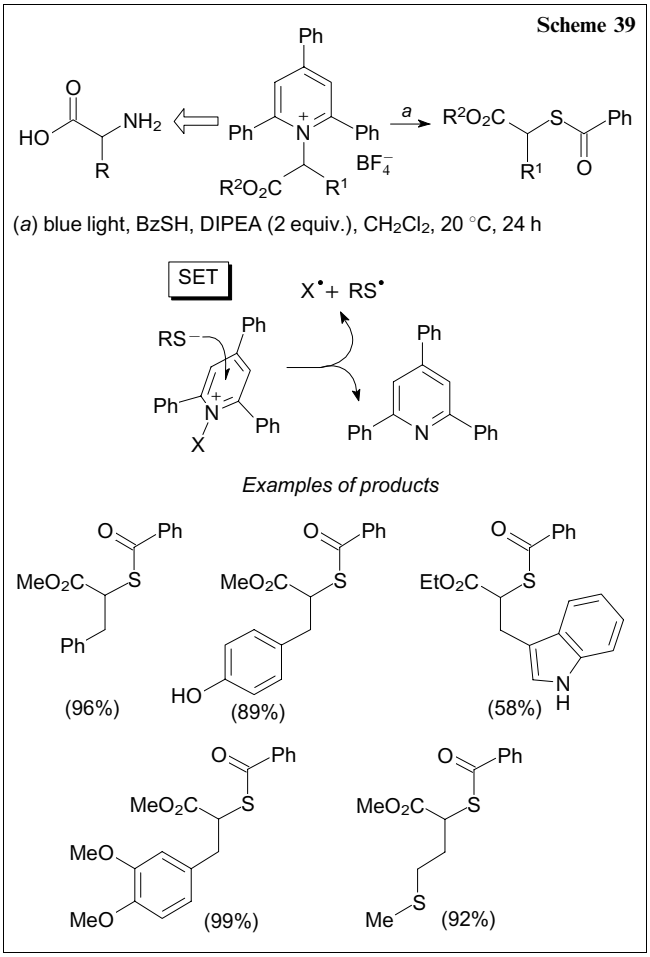



**Scheme 38**

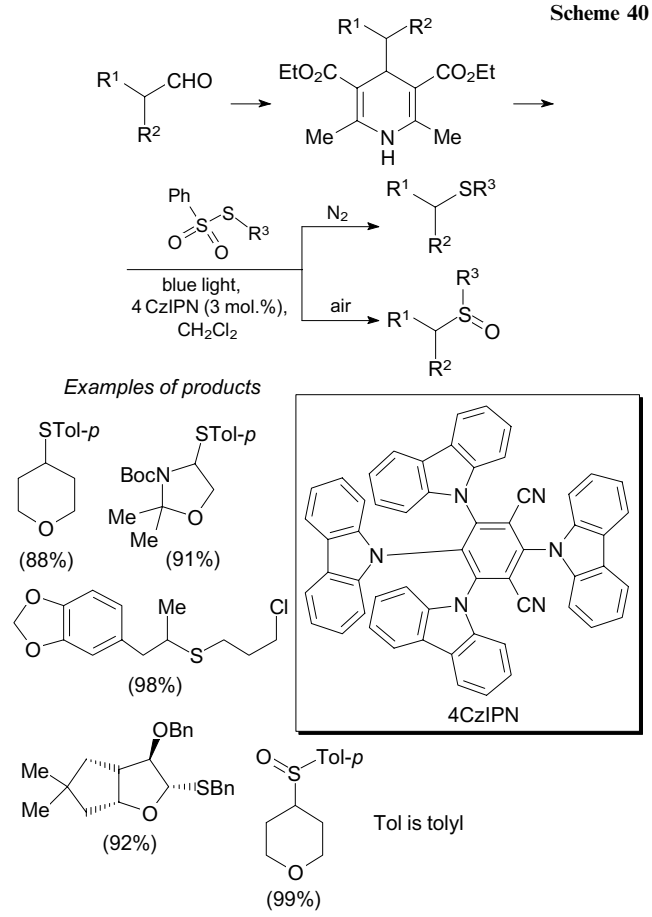



Yet another way for the introduction of sulfur functional groups into amino acid molecules is based on the visible light-induced deaminative thioesterification of thiobenzoic acid *via* the preliminary formation of 1-alkyl-2,4,6-

**Scheme 39**




**Scheme 40**




tetraphenylpyridinium tetrafluoroborate (Katritzky salts[118]) (Scheme 39).[119] The reaction also gives initially an electron donor–acceptor complex of the pyridinium cation and thiobenzoic acid anion. Upon the absorption of visible light, it is brought to the excited state and undergoes a single-electron transfer; elimination of 2,4,6-triphenylpyridine gives rise to two radicals: thienyl and alkyl radicals. Coupling of these radicals finally gives S-alkyl derivatives of thiobenzoic acid.

Photochemical transformations involving Hantzsch esters (4-alkyl-1,4-dihydropyridines), which are readily obtained from alkyl aldehydes, can also serve for the generation of C–S bond.[120] The reaction of 4-alkyl-1,4-dihydropyridines with *S*-aryl(alkyl)thiosulfonates induced by blue light irradiation in the presence of 1,2,3,5-tetrakis(carbazol-9-yl)-4,6-dicyanobenzene (4CzIPN) as a photoredox catalyst under inert atmosphere affords sulfides. When this reaction is conducted in air, with other conditions being the same, sulfoxides can be prepared (Scheme 40).[121]

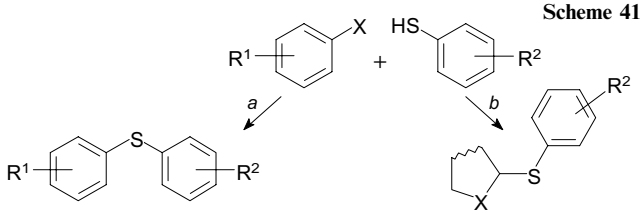
Several methods for the construction of C–S bond without transition metal catalysis were developed using aryl halides as the starting compounds. These methods are a good alternative to the approaches using transition metal-based catalysts, and, in most cases, they are favourably distinguished by environmental safety and cost efficiency. Diaryl sulfides were prepared by the visible light-induced cross-coupling of aryl halides with thiols without a photoredox catalyst.[122, 123] This reaction proceeds most efficiently for aryl bromides and iodides (Scheme 41). Conducting the reaction in the presence of aliphatic compounds capable of generating a stable radical upon hydrogen atom elimination furnishes aryl alkyl sulfides. In this case, aryl halides act as auxiliary reagents generating an aryl radical, which then detaches a hydrogen atom from the aliphatic substrate (HAT, see Scheme 41).[124]

This method for C–S bond formation was used for C–H sulfenylation of nitrogen-containing heterocycles. First, iodination of heterocyclic compounds with the $I_2$–TBHP system was carried out, and then the iodo derivative generated *in situ* was coupled with thiophenols in the presence of a base under visible light irradiation. This two-step one-pot procedure resulted in the synthesis of 4-arylthioisoquinolines, 3-arylthioquinolines and 3-arylthio-7-azaindoles in high yields.[125]

The cyclization of *N*-(2-bromophenyl)thioamides induced by CFL irradiation in the presence of $Na_3PO_4$ as a base has been reported. The method is applicable to the thioamides of various aromatic and aliphatic acids. Nearly quantitative yields of 2-substituted benzothiazoles **17** are attained in the cyclization of aromatic acid thioamides; the cyclization of thioamides of aliphatic acids is also fairly efficient (41–82% yields of products) (Scheme 42).[126]

A one-pot synthesis of *S*-aryldithiocarbamates **18** is based on the reaction of secondary amines with carbon disulfide and aryl iodides carried out under irradiation with CFL in the presence of caesium carbonate (Scheme 43).[127] The reaction consists of two steps: first, the secondary amine and $CS_2$ react to give an adduct, which reacts with aryl iodide *via* the preliminary formation of an electron donor–acceptor complex according to the mechanism considered above (see Scheme 41).

**Scheme 41**

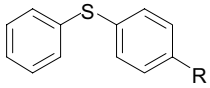


(*a*) visible light, $Cs_2CO_3$, DMSO, 25 °C;

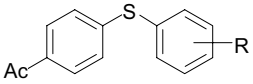
(*b*) , visible light, $Cs_2CO_3$, DMSO, 25°C

*Examples of products*

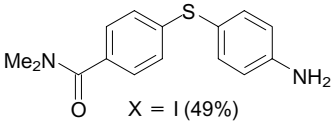
Conditions *a*



X = I: R = OMe (85%), $NH_2$ (37%), OH (25%)

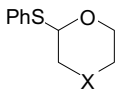


X = Cl, R = 4-Me (95%);
X = Br: R = 4-OMe (85%), 2-$CO_2H$ (64%)

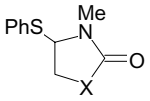


X = I (49%)

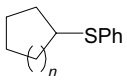
Conditions *b*



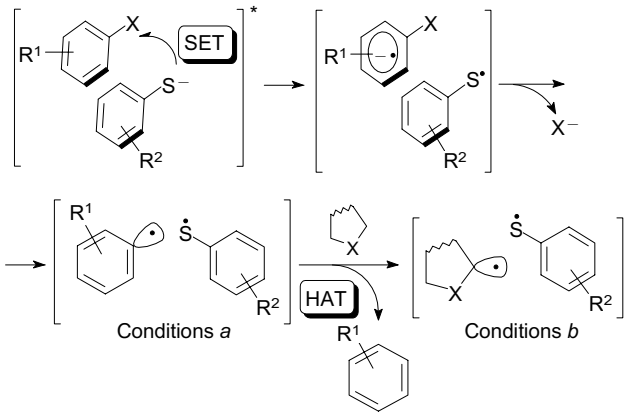
X = none (71%),
X = O (66%), $CH_2$ (28%)



X = $CH_2$ (41%),
NMe (43%)



*n* = 1 (43%), 2 (49%), 3 (27%)



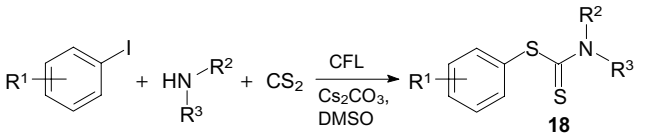

**Scheme 42**



$R^2$ = Ph: $R^1$ = H (98%), 6-Br (90%), 5-F (96%);
$R^1$ = H: $R^2$ = $Pr^n$ (75%), pyridin-4-yl (84%);
$R^1$ = 6-Cl, $R^2$ = $Bu^t$ (70%)

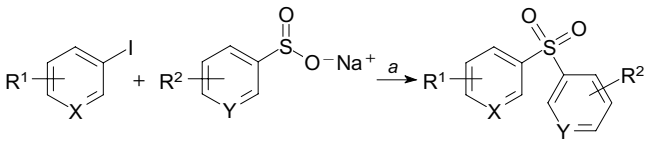
The visible light-induced C–S coupling of aryl iodides with potassium ethyl xanthate was used to prepare thiochromanes by intramolecular cyclization.[128] The formation of an electron donor–acceptor complex and the subsequent photoinduced single-electron transfer serve as the key steps of coupling of aryl halides with sodium arylsulfinates on exposure to light at 365 nm, resulting in the formation of

**Scheme 43**



| $R^1$ | $R^2$ | $R^3$ | Yield of **18** (%) |
|---|---|---|---|
| 4-CHO | Ph | Me | 74 |
| 4-Ac | Ph | Me | 78 |
| 4-Ac | $(CH_2)_5$ | | 70 |
| 4-CHO | Me | Me | 64 |
| 3-CHO | $(CH_2)_5$ | | 63 |
| 4-$NO_2$ | $(CH_2)_4$ | | 60 |

**Scheme 44**

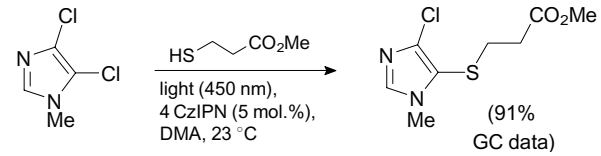


(*a*) light (365 nm), $Cs_2CO_3$, DMSO;
X = Y = CH, $R^2$ = 4-Me: $R^1$ = 4-CN (86%), 4-CHO (42%), 4-$NO_2$ (85%); X = Y = CH, $R^1$ = 4-CN, $R^2$ = 4-F (82%); X = N, Y = CH, $R^1$ = H, $R^2$ = 4-Me (80%); X = CH, Y = N, $R^1$ = 4-CN, $R^2$ = H (82%)

sulfones (Scheme 44). The highest yields of the coupling products are attained when aryl bromides and iodides were used.[129] A similar process takes place when a mixture of aryl halides and arylsulfinates is irradiated with light at 435–455 nm in the presence of diethyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (Hantzsch ester) and a base. The Hantzsch ester acts as an auxiliary reagent, which forms an electron donor–acceptor complex with aryl halide. On excitation with visible light, this complex undergoes a single-electron transfer and thus generates an aryl radical.[130]

The cross-coupling of aryl halides with S-nucleophiles of various types in the absence of photoredox catalysts usually gives high product yields in the case of aryl iodides and bromides with electron-withdrawing substituents and electron-deficient heterocyclic compounds. The coupling of halogenated electron-rich heterocycles with thiols requires the presence of a photoredox catalyst. Although iridium complexes are most efficient catalysts for this reaction, an organic photoredox catalyst based on isophthalonitrile, 4CzIPN, ensures the product formation in a relatively high yield and with high selectivity *via* selective coupling of dichloro-substituted substrate (Scheme 45).[131] The key step of formation of the C–S bond is redox-neutral homolytic aromatic substitution involving the thiyl radical generated from the corresponding thiols upon visible light-induced photochemical reaction involving 4CzIPN.

**Scheme 45**



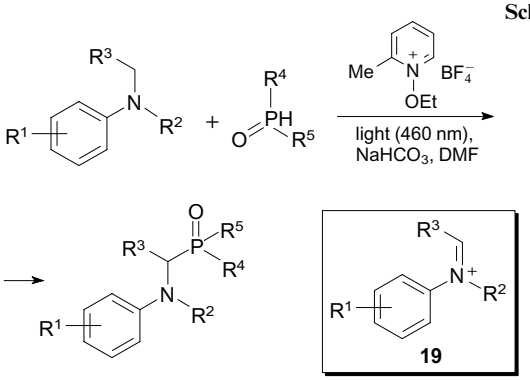
### 2.3. Formation of C—P bond

The important applications of organophosphorus compounds for various fields of human life activity stimulates the continuous search for effective methods for their synthesis. In recent years, new methodological approaches to C—P bond formation by visible light-induced reactions have been developed.[132, 133] These reactions can be divided into two main types. In reactions of the first type, a phosphorus-containing nucleophilic reagent reacts with a highly reactive intermediate (C-radical or C-cation) generated *via* a photochemical transformation. In the second type of reactions, the P-radical generated *via* a photochemical transformation reacts with compounds containing carbon—carbon multiple bonds or aromatic systems. Many reactions resulting in the formation of C—P bonds are similar in their mechanisms to the reactions of C—N bond formation considered above.

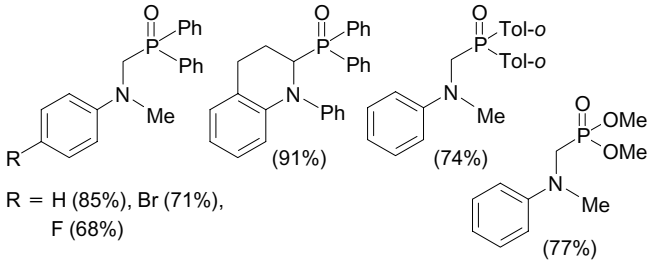
Quint *et al.*[134] reported α-phosphorylation of tertiary *N*-arylamines with secondary phosphine oxides in the presence of *N*-alkoxypyridinium salt. The reaction is induced by visible light irradiation at 460 nm and conducted in the presence of a base. In the key step, the amine molecule and the pyridinium cation form an electron donor–acceptor complex, which undergoes single-electron transfer on exposure to light thus giving the tertiary amine radical cation. The elimination of a hydrogen atom from the radical cation gives key intermediate **19**, an iminium cation, which subsequently reacts with secondary phosphine (Scheme 46).

The reaction of aryl halides with trialkyl phosphites in the presence of DIPEA and rhodamine 6G (Rh-6G) as the photoredox catalyst induced by blue light irradiation at

**Scheme 46**



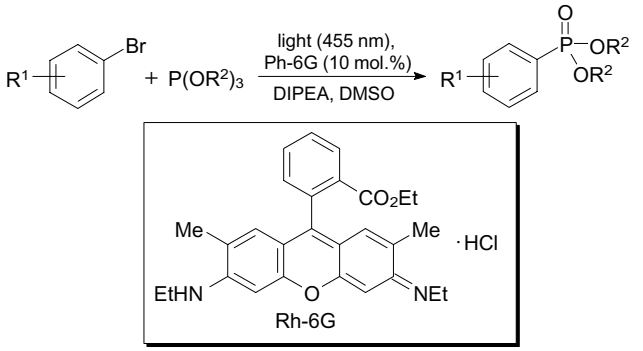

*Examples of products*



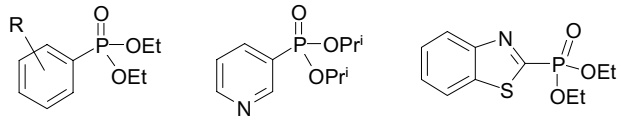

R = H (85%), Br (71%), F (68%)

455 nm gives rise to arylphosphonates. Electronically excited rhodamine 6G oxidizes DIPEA and is thus converted to the radical anion, which is able to reduce aryl halides to generate the corresponding aryl radicals (Scheme 47).[135] The reaction is efficient in the case of aryl halides and triflates of (hetero)arenes.

**Scheme 47**



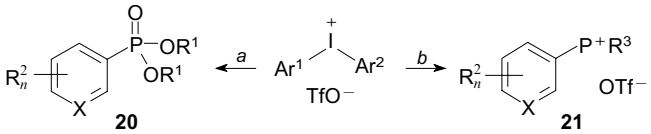

*Examples of products*




R = 2-CN (76%), 3-OMe (58%), 4-$CF_3$ (27%)

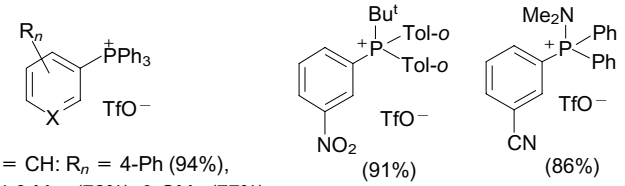
The P-arylation of trialkyl phosphites with diaryliodonium salts to give arylphosphonates is implemented upon blue light irradiation at 420 nm in the absence of photosensitizers. Presumably, the reaction proceeds through the preliminary formation of an electron donor–acceptor complex from the reactant molecules. The light-induced single-electron transfer from the phosphorus atom to the iodine atom in this complex finally gives the aryl radical and trialkyl phosphite radical cation. The subsequent recombination and elimination of the alkyl substituent gives arylphosphonates **20** (Scheme 48).[136] The successful arylation of the phosphorus atom can also be accomplished using unsymmetrical diarylphosphonium salts; in this case, the selectivity of the transfer of aryl substituent is controlled by steric factors. The arylation of tertiary phosphines involving aryl(mesityl)iodonium triflates affords structurally diverse quaternary arylphosphonium salts **21**. This reaction was also implemented without an external photosensitizer and

**Scheme 48**




(*a*) $P(OR^1)_3$, light (420 nm), $K_2CO_3$, MeCN (for $Ar^1 = Ar^2$ or $Ar^2$ = Mes);
(*b*) $PR_3$, light (405 nm), MeCN (for $Ar^2$ = Mes);
**20**: X = CH: $R^1$ = Et, $R^2_n$ = H (83%);
$R^1$ = Et, $R^2_n$ = 2,4,6-$Me_3$ (31%); $R^1$ = Et, $R^2_n$ = 2-OMe (57%);
$R^1$ = Pr$^i$, $R^2_n$ = 4-Ac (67%); $R^1$ = Et, $R^2_n$ = H, X = N (73%)

*Examples of products* **21**

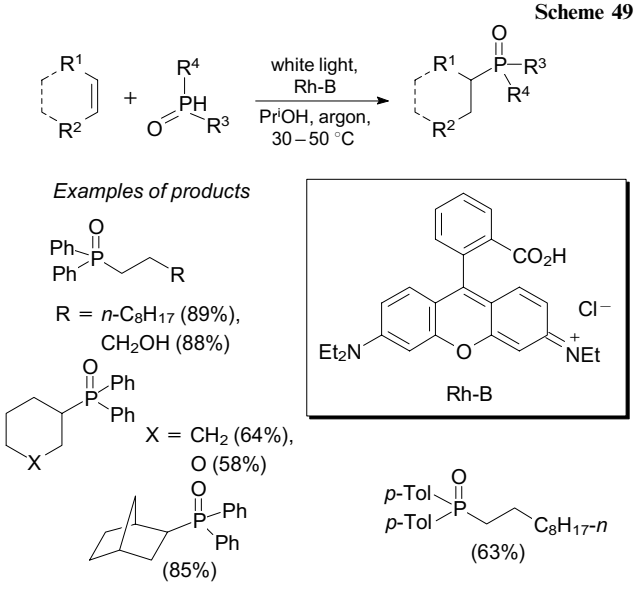



X = CH: $R_n$ = 4-Ph (94%), 2,4,6-$Me_3$ (72%), 3-OMe (77%), 3-CN (86%); R = H, X = N (88%)

apparently proceeds *via* the formation of a photosensitive electron donor–acceptor complex. Unlike other known methods for the arylation of tertiary phosphines, the course of arylation involving ArMesIOTf is not affected by bulky substituents at the phosphorus atom (see Scheme 48).[137]

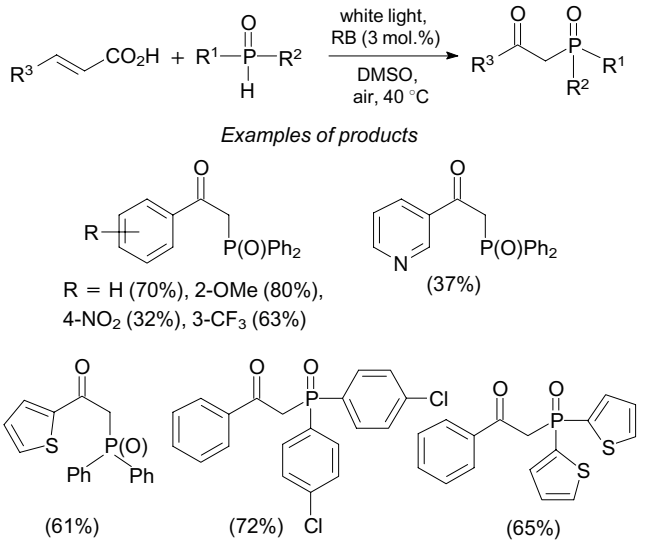
The synthesis of diaryl(heteroaryl)phosphine oxides is based on the reaction of aryl halides with diarylphosphine oxides in the presence of potassium *tert*-butoxide under blue light irradiation.[138] This procedure gives phosphine oxides in high yields when the substrates are bromides of electron-deficient heterocyclic compounds such as pyridines, quinolines, pyrimidines and pyrazines. The key step of the reaction is the formation of an electron donor–acceptor complex from heteroaryl halide and potassium *tert*-butoxide molecules. Upon visible light excitation, single-electron transfer takes place in the complex, resulting in aryl and *tert*-butyl radicals. The latter participates in the generation of P-radical, which in turn recombines with the aryl radical to give the reaction product.[138] Analogous reactions can be carried out for alkylphosphinates when 9-mesityl-1-methylacridinium perchlorate is used as the photoredox catalyst and diphenyliodonium triflate serves as the oxidant.[139] The addition of secondary phosphines to non-activated alkenes takes place in the presence of rhodamine B (Rh-B) as the photoredox catalyst and under irradiation with white light in an argon atmosphere.[140] In the key step of this reaction, P-radical is generated *via* single-electron oxidation of the secondary phosphine with excited rhodamine B (Scheme 49). Secondary phosphine oxides containing strong electron-donating substituents do not react in this way.

**Scheme 49**



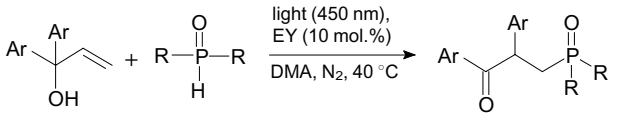

The reaction of cinnamic acids with diarylphosphine oxides under white light irradiation in air in the presence of rose bengal results in the formation of β-ketophosphine oxides *via* the decarboxylative oxidation (Scheme 50).[141] It is noteworthy that simple unsaturated carboxylic acids do not react in this way, nor secondary phosphines with potent electron-donating substituents. β-Ketophosphine oxides were also obtained upon the visible light-induced oxidative phosphinylation of terminal arylalkynes in an oxygen atmosphere using rhodamine B as the photoredox catalyst.[142]

**Scheme 50**




The reaction of 1,1-disubstituted allyl alcohols with secondary phosphine oxides induced by irradiation at 450 nm in the presence of eosin Y gives β-aryl-γ-ketophosphine oxides. This product is formed as a result of 1,2-migration of aryl group in the radical intermediate arising during the reaction (Scheme 51).[143]

**Scheme 51**

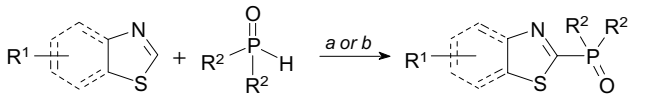



R = Ph: Ar = Ph (77%), *o*-Tol (76%), 4-$FC_6H_4$ (50%), 4-$BrC_6H_4$ (50%);
Ar = Ph, R = $Bu^n$ (34%)

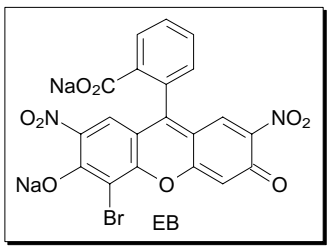
Direct C–H phosphorylation of thiazole derivatives with diarylphosphine oxides can be readily performed using eosin B (EB)[144] or eosin Y disodium salt[145] as the photoredox catalyst (Scheme 52).

Similar C–H phosphorylation reactions were described for quinoxalin-2(*1H*)-ones,[146] coumarins,[147] 2*H*-indazoles[148] and imidazopyridines[149] in the presence of oxidants and eosin B, eosin Y, rose bengal or rhodamine B,

**Scheme 52**



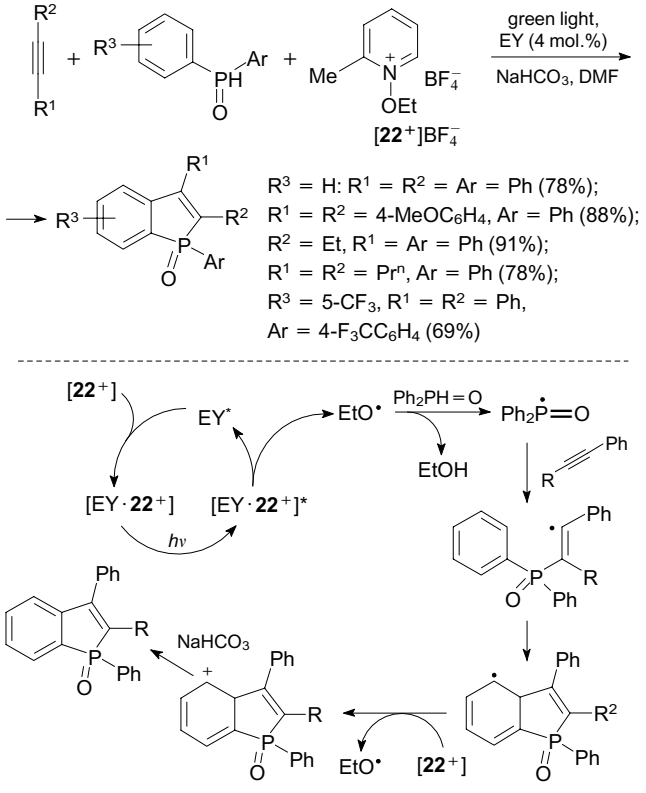

(*a*) white light, EB (5 mol.%), $CHCl_3$, $N_2$, 23 °C;
(*b*) white light, $Na_2$-EY (3 mol.%), $CHCl_3$, $O_2$, (52–99% yields);
$R^1$ = Alk, AlkO, Ar, Hal, $NO_2$, $CO_2$Alk; $R^2$ = (Het)Ar



respectively. The C–H phosphorylation of quinolinones and coumarins in the presence of 1-ethoxy-2-methylpyridinium tetrafluoroborate was accomplished in the absence of external photoredox catalysts or oxidants. In this case, the role of photosensitizer was played by the substrates and reaction products.[150]

The addition of P-radicals to multiple bonds forms the basis for the synthesis of (*Z*)-vinylphosphine oxides by the reaction of secondary phosphine oxides with terminal and internal alkynes in the presence of eosin Y in water under green light irradiation.[151] A similar reaction involving internal alkynes and diarylphosphine oxides induced by green light in the presence of 1-ethoxy-2-methylpyridinium tetrafluoroborate as the oxidant furnishes benzo[*b*]phosphole oxides. According to the reaction mechanism postulated by the authors, the donor–acceptor complex formed initially from eosin Y and pyridinium cation $\mathbf{22}^+$ undergoes an intramolecular single-electron transfer upon irradiation, which leads to its fragmentation to give an ethoxy radical. The latter detaches a hydrogen atom from diarylphosphine oxide, thus generating a P-centred radical. The P-radical adds to a triple bond to give an alkenyl C-radical, which cyclizes to form a C–C bond and cyclohexadienyl radical, which is then oxidized with the pyridinium salt to the corresponding cation and is deprotonated (Scheme 53).[152]

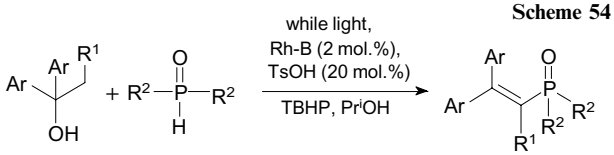
**Scheme 53**




An analogous cyclization reaction initiated by the addition of P-radical to alkynes and finally giving 3-phosphorylated coumarins has been reported.[153]

The reaction of 1,1-diarylethanols with secondary phosphine oxides catalyzed simultaneously by a protic acid and a photoredox catalyst (rhodamine B) furnishes (2,2-diarylvinyl)diarylphosphine oxides (Scheme 54).[154]

**Scheme 54**

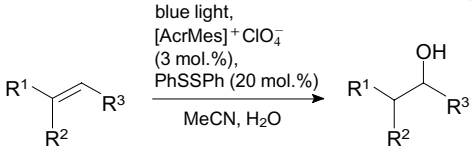



Ar = Ph: $R^1$ = H, $R^2$ = Ph (77%); $R^1$ = Me, $R^2$ = Ph (96%); $R^1$ = H, $R^2$ = $Bu^n$ (40%); $R^1$ = H, $R^2$ = Ph: Ar = 4-$MeC_6H_4$ (98%), 4-$ClC_6H_4$ (61%)

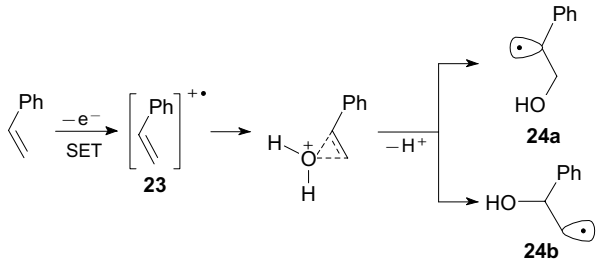
## 2.4. Formation of C–O bond

9-Mesityl-10-methylpyridinium perchlorate was used as the photoredox catalyst for the visible light-induced hydration of alkenes, which follows the anti-Markovnikov pathway in the presence of diphenyl disulfide.[155] The mechanism of this reaction (considered in relation to styrene) starts with the oxidation of alkenes to radical cation **23**, which directly participates in the C–O bond formation *via* the intermediate formation of hydroxyalkyl radicals **24a**,**b** (Scheme 55).

**Scheme 55**




$R^3$ = H: $R^1$ = $R^2$ = Ph (86%), 4-$BrC_6H_4$ (74%);
$R^2$ = Ph, $R^3$ = H: $R^1$ = 4-$F_3CC_6H_4$ (75%), 2-$MeOC_6H_4$ (48%);
$R^1$ = Ph: $R^2$ = Me, $R^3$ = H (76%); $R^2$ = Ph, $R^3$ = Me (76%)

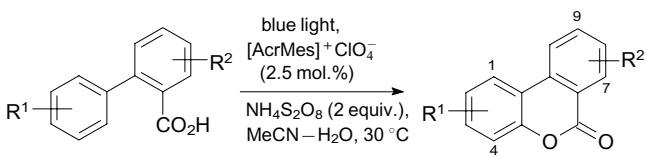



The intermolecular anti-Markovnikov addition of carboxylic acids to alkenes[156] and intermolecular and intramolecular cyclizations giving heterocyclic compounds[157,158] take place under similar conditions.

The $[AcrMes]^+ClO_4^-$ photocatalyst was also used for CH-lactonization of *o*-arylbenzoic acids giving benzo-3,4-coumarins.[159] According to the mechanism proposed by the authors, the intramolecular formation of C–O bond takes place as a result of 6-*endo*-*trig*-cyclization of the carboxyl radical generated upon elimination of a hydrogen atom from the carboxyl group (Scheme 56; positions of substituents in the product are indicated). It is noteworthy that in the case of $R^1$ = 3-OMe, $R^2$ = H, the reaction gave 2- and 4-methoxy isomers (92 : 8). A similar CH-lactonization preceded by *E*–*Z*-isomerization was described for (*E*)-cinnamic acid upon irradiation with light at 402 nm in the presence of (–)-riboflavin.[160]

The hydroxylation of imidazopyridines with primary and secondary alcohols is carried out by irradiation of a reactant mixture with white (visible) light in the presence of rose bengal.[161] This reaction is suitable for introducing both

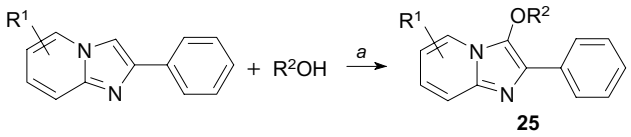
**Scheme 56**




$R^2$ = H: $R^1$ = H (87%), 3-F (70%), 3-OMe (73%);
$R^1$ = 3-F, $R^2$ = 8-Cl (79%); $R^1$ = 3-Me, $R^2$ = 9-Me (77%)

primary and secondary alkoxyl substituents, in particular containing halogen atoms, carbon–carbon multiple bonds and benzyl groups, into position 3 of product **25**. The C–O bond is formed upon the addition of an alcohol molecule to the radical cation, which is initially generated from imidazopyridine *via* single-electron oxidation with rose bengal in the electronically excited state (Scheme 57). This method is also effective for hydroxylation of benzimidazothiazoles.

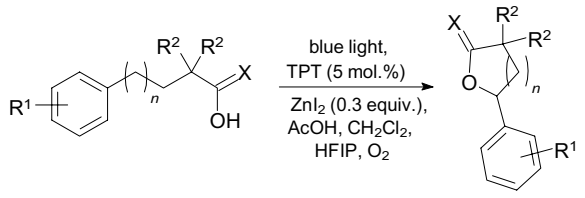
**Scheme 57**




(*a*) while light, RB (2 mol.%), DMF; $R^1$ = H, R = Me (88%);
$R^1$ = 8-Me: $R^2$ = Pr$^i$ (85%), All (87%), Bn (85%); All is allyl

One of approaches to the synthesis of cyclic ethers and lactones by cyclization of alcohols is based on visible light-induced generation of benzyl radicals. The authors proposed a mechanism according to which the initial reaction of electronically excited 2,4,6-triphenylpyrylium trifluoroborate with the substrate gives the C-radical cation *via* single-electron oxidation. The presence of a positive charge in the aromatic ring considerably increases the CH acidity of the benzylic position. The deprotonation of the radical cation results in generation of the benzyl radical (Scheme 58).[162]

**Scheme 58**

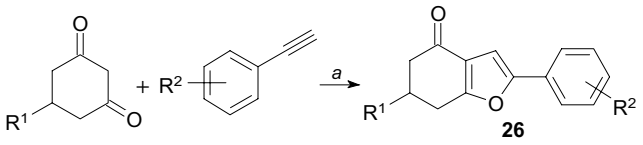



*n* = 1, X = $CH_2$: $R^1$ = $R^2$ = H (62%); $R^1$ = 2–F, $R^2$ = Me (55%);
*n* = 2, X = $CH_2$: $R^1$ = $R^2$ = H (80%); $R^1$ = 2-F, $R^2$ = Me (82%);
*n* = 1, X = O: $R^1$ = $R^2$ = H (77%); $R^1$ = H, $R^2$ = Me (74%);
*n* = 2, X = O, $R^1$ = H, $R^2$ = Me (80%);
HFIP is 1,1,1,3,3,3-hexafluoropropan-2-ol

The photooxidation of the benzylic position of diarylmethanes with oxygen proceeds *via* a similar step of generation of the benzyl radical; the expected ketones are formed when 9-mesityl-10-methylpyridinium perchlorate and blue light irradiation are used.[163]

The synthesis of furans **26** is based on oxidative cyclization of 1,3-dicarbonyl compounds and alkynes.[164] The reaction occurs when the reaction mixture is irradiated with blue light in the presence of methylene blue as a photoredox catalyst and ammonium persulfate as an oxidant. The mechanism of furan ring formation implies the initial radical generation from 1,3-dicarbonyl compound, the subsequent radical addition to alkyne to give vinyl radical and cyclization of the latter (Scheme 59).

**Scheme 59**




(*a*) blue light, methylene blue (6 mol.%),$NH_4S_2O_8$, MeCN;
$R^1$ = H: $R^2$ = H (83%), 4-$CO_2$Et (48%), 2-Me (80%), 4-OMe (70%), 3-Br (70%); $R^2$ = 4-Me: $R^1$ = Me (83%), Ph (70%)

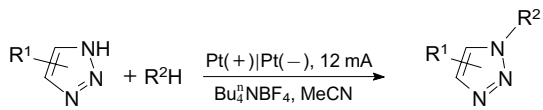
## 3. Electrochemical reactions

The oxidative cross-coupling is a strategy extensively used to form C–heteroatom bonds from accessible precursors. In the last two decades, huge research efforts have been concentrated in this field and great advances have been made. However, the formation of chemical bonds usually requires stoichiometric amounts of oxidants. Currently, considerable interest of the chemical community is attracted by oxidative cross-coupling reactions in the absence of external oxidants. Electrochemical synthesis is a potent and environmentally safe approach that not only provides the oxidative formation of chemical bonds without external oxidants,[165–177] but, in some cases, gives an additional valuable product, that is, hydrogen gas.[178]

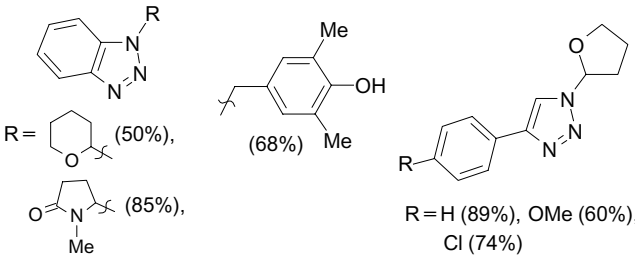
### 3.1. Formation of C–N bond

In recent years, electrochemical oxidation[179,180] has been used as a versatile and environmentally safe alternative synthetic tool for the formation of chemical bonds by direct C–H-activation.[181–188] Among direct oxidative electrochemical amination reactions of C–H bonds,[189–198] the C($sp^3$)–H/N–H cross-coupling involving the C($sp^3$)–H bond is used most rarely.[199] An example of this type is anodic oxidative coupling of azoles with tetrahydrofuran and some related aliphatic compounds (Scheme 60 †).[199]

**Scheme 60**



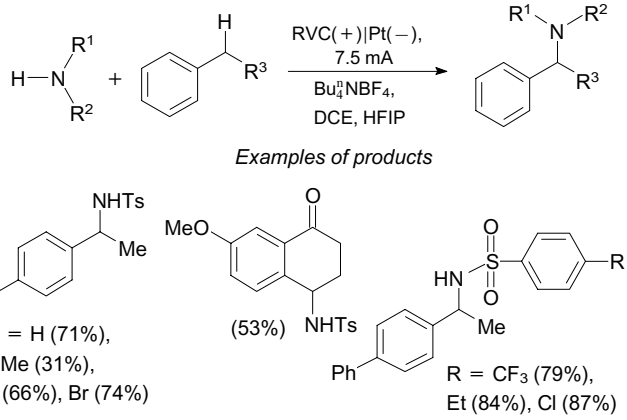

*Examples of products*




† The notation Pt(+)|Pt(–) means undivided electrochemical cell with the indicated anode and cathode.

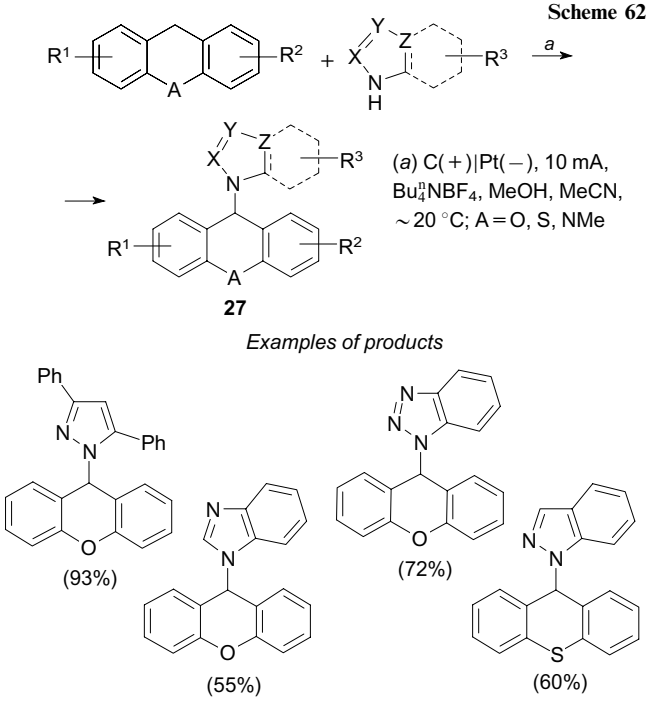
One more example of the C(sp$^3$)–H/N–H cross-coupling is the electrochemical amination of the benzylic carbon atom of alkylbenzene with $H_2$ evolution (Scheme 61).[200] This strategy implies anodic cleavage of the benzylic C–H bond to give a carbocationic intermediate, which is trapped by nitrogen-containing nucleophile, giving rise to the C–N bond.

**Scheme 61**




A new procedure for the preparation of 9-azoloxanthenes **27** by electrochemical C(sp$^3$)–H/N–H cross-coupling of xanthenes with azoles was reported (Scheme 62).[201]

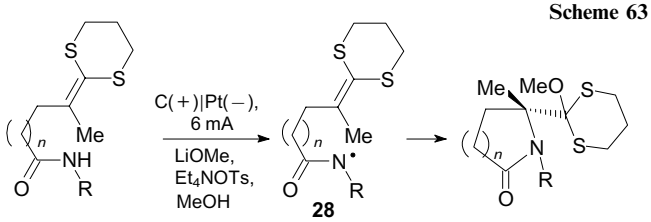
**Scheme 62**




The amidyl radical, which is generated from amides under mild electrooxidative conditions, can also serve as the source of nitrogen in such processes. For example, the cyclization of radicals **28** involving an electron-rich double bond gives five- and six-membered rings (for example, lactams) (Scheme 63).[202]

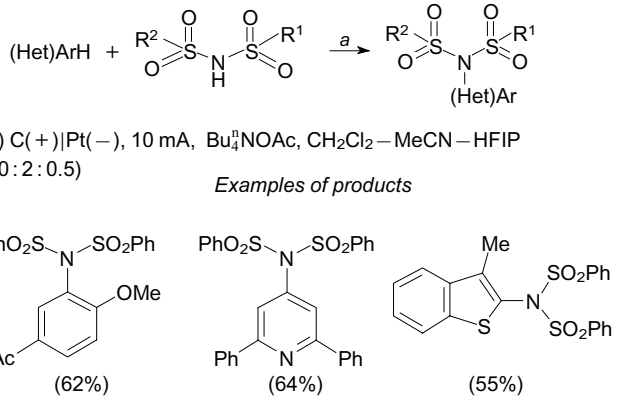
A similar reaction was used for regioselective electrochemical oxidative intermolecular cross-coupling of aromatic compounds with sulfonimides, which proceeds *via* the addition of the imidyl N-radical.[203] This reaction can be carried out for diverse arenes and heteroarenes (Scheme 64).

**Scheme 63**



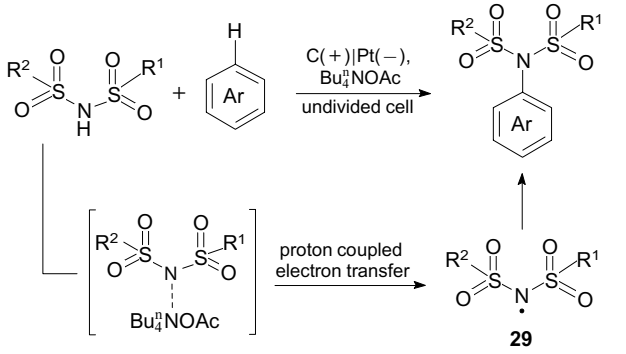

*n* = 1: R = BnO (80%), Ph (87%); *n* = 2: R = BnO (73%)

**Scheme 64**




Study of the mechanism of this reaction by cyclic voltammetry indicates that the imidyl radical **29** is generated as a result of proton coupled electron transfer (PCET) upon simultaneous action of tetra-n-butylammonium acetate and anodic oxidation (Scheme 65).

**Scheme 65**

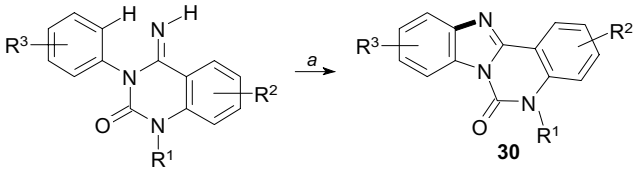



A method for the synthesis of formamides by decarboxylative N-formylation of primary and secondary aromatic and aliphatic amines in the presence of glyoxalic acids has been developed. The reaction proceeds in an undivided cell with platinum electrodes. A variety of functional substituents (F, Cl, Br and I atoms; $OCF_3$, CN, $CF_3$, $NO_2$, $CO_2Et$ and Ac groups) are tolerant to the reaction conditions, and the yields of products vary from 38 to 93%.[204]

In recent years, the electrochemical oxidative amination methodology has also been used to prepare nitrogen-con-

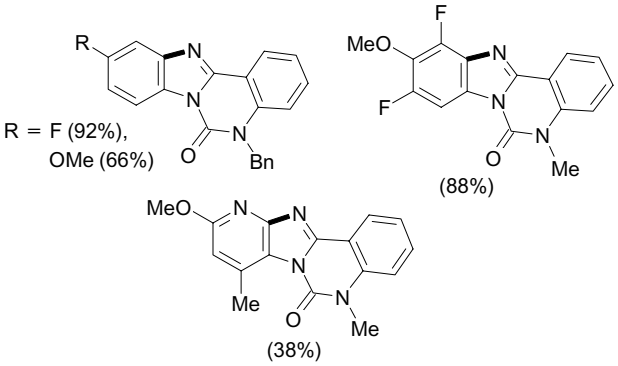
taining heterocyclic compounds *via* the formation of the C–N bond.[205] In particular, the preparation method for functionalized tetracyclic benzimidazoles **30** is based on the formation of N-radicals as a result of anodic cleavage of the N–H bond and the subsequent intramolecular cyclization of the N-radicals (Scheme 66).[206] This atom-economic C–H/N–H-cross-coupling reaction is suitable for substrates with diverse functional groups and is characterized by high regioselectivity.

**Scheme 66**



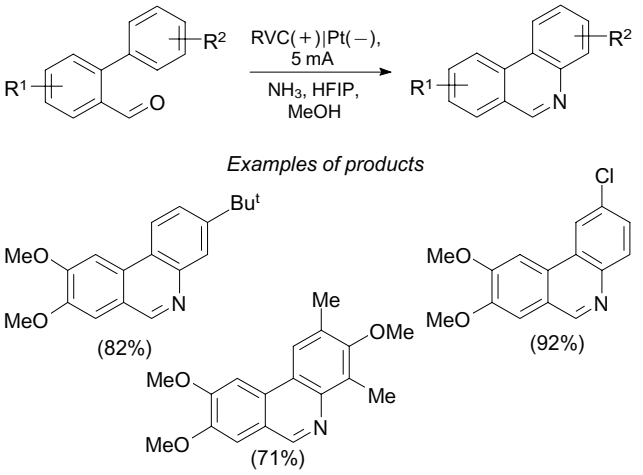

(*a*) RVC(+)|Pt(−), 10 mA, $Et_4NPF_6$, MeCN

*Examples of products*



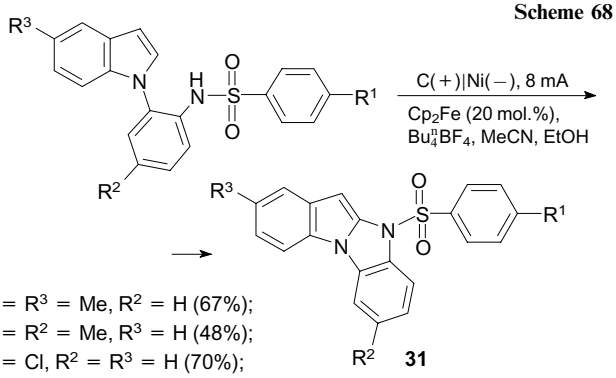

Yet another example of electrochemical amination is the synthesis of phenanthridines and related heterocyclic compounds from biaryl aldehydes and ammonia by C–H/N–H-cross-coupling (Scheme 67).[207]

**Scheme 67**




The electrochemical intermolecular amination was also used to prepare derivatives of nitrogen-containing fused systems — 10*H*-benzo[4,5]imidazo[1,2-*a*]indoles **31** (Scheme 68).[208]

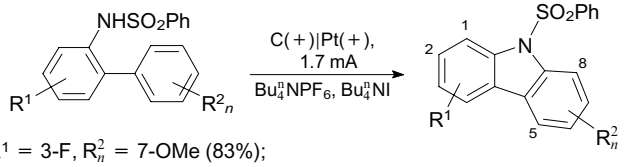
**Scheme 68**




$R^1 = R^3 = Me$, $R^2 = H$ (67%);
$R^1 = R^2 = Me$, $R^3 = H$ (48%);
$R^1 = Cl$, $R^2 = R^3 = H$ (70%);
Cp is cyclopentadienyl

The electrochemical dehydrogenative amination of the C–H bond served for the synthesis of *N*-benzenesulfonylcarbazoles (Scheme 69).[209]

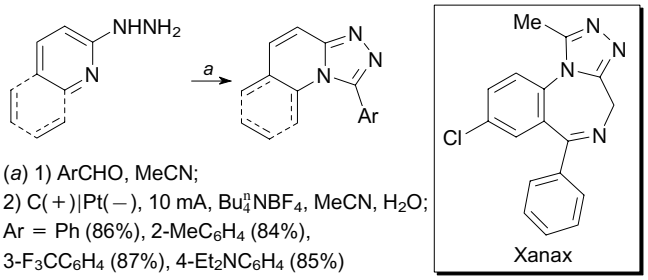
**Scheme 69**




$R^1 = 3\text{-F}$, $R^2_n = 7\text{-OMe}$ (83%);
$R^1 = H$: $R^2_n = 6\text{-Cl}$ (40%), $6,7\text{-OCH}_2O$ (85%)

The oxidative cyclization of hydrazones accompanied by C–N bond formation under the action of electrical current makes it possible to prepare 1,2,4-triazolo[4,3-*a*]pyridines and related heterocyclic systems from α-hydrazinoazines and aliphatic or (hetero)aromatic aldehydes (Scheme 70).[210] The process can be carried out in the one-pot version without isolation of the presynthesized hydrazones. This method was applied for the synthesis of a commercial anxiolytic drug Xanax (45% yield).

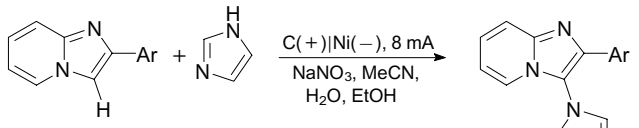
**Scheme 70**




(*a*) 1) ArCHO, MeCN;
2) C(+)|Pt(−), 10 mA, $Bu^n_4NBF_4$, MeCN, $H_2O$;
Ar = Ph (86%), 2-$MeC_6H_4$ (84%),
3-$F_3CC_6H_4$ (87%), 4-$Et_2NC_6H_4$ (85%)

Apart from being used for the synthesis of heterocyclic structures, electrochemical amination is equally widely employed to prepare anilines and heteroarylamines upon intermolecular cross-coupling reactions. A number of 3-amino derivatives of imidazo[1,2-*a*]pyridines were synthesized by electrochemical oxidative C–H/C–N-cross-coupling, with (benzo)imidazoles being used as the aminating agents (Scheme 71).[208] The corresponding amination products were also obtained in the case of morpholine, while attempts to carry out this reaction for n-butylamine were unsuccessful. According to the mechanism proposed by the authors, the product of amination is formed as a result of

**Scheme 71**

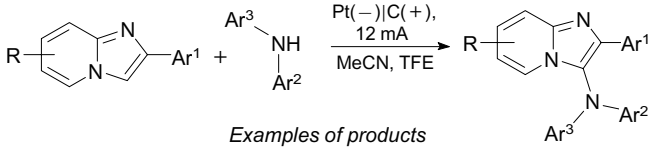



Ar = Ph (75%), 4-PhC$_6$H$_4$ (58%), 4-MeC$_6$H$_4$ (85%), 4-FC$_6$H$_5$ (57%), 4-CF$_3$C$_6$H$_4$ (59%)

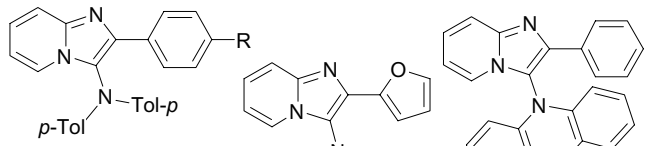
recombination of the N-radical, generated by anodic oxidation of deprotonated imidazole, with the C-radical, which is formed upon anodic oxidation of imidazopyridine and subsequent deprotonation.

The dehydrogenative C−H/C−N-cross-coupling of imidazopyridines with diarylamines of this type results in the regioselective formation of triarylamines (Scheme 72).[211]

**Scheme 72**




*Examples of products*

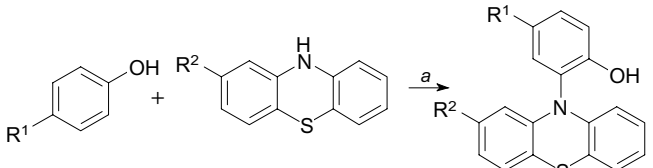



R = H (55%), OMe (48%), F (45%), $SO_2Me$ (54%); (87%) (60%)

TFE is 2,2,2-trifluoroethanol

The anodic oxidation of phenothiazines giving the corresponding radical cations is the key step of the electrochemical oxidative amination of phenols with phenothiazines, which gives products **32** (Scheme 73).[212] The amination proceeds most efficiently for phenols containing electron-donating groups, but it has low sensitivity to the electronic nature of substituents in phenothiazines. The amination of phenols with phenoxazine gives products in comparable yields.

**Scheme 73**

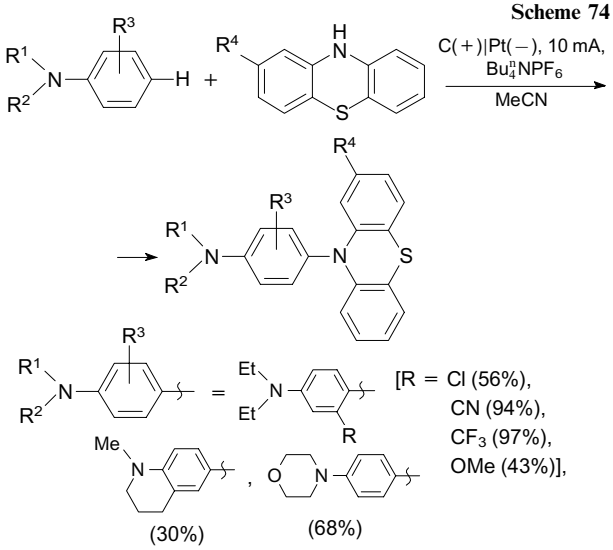



(*a*) C(+)|Ni(−), 7 mA, $Bu^n_4NBF_4$, MeCN, MeOH; $R^2$ = H: $R^1$ = NHAc (93%), Cl (71%), Ac (21%); $R^1$ = OMe, $R^2$ = Cl (91%)

**32**

Phenothiazines were also used as aminating agents for N,N-disubstituted anilines. The reaction occurs selectively involving the *para*-position of anilines and results in 10-aryl-10*H*-phenothiazines (Scheme 74).[213] Presumably, the process includes the electrochemical oxidation of anilines to give the corresponding radical cations, anodic

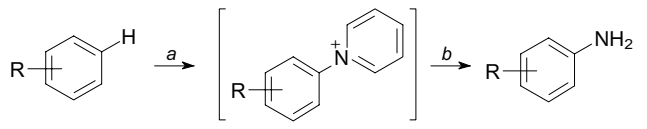
**Scheme 74**




oxidation of phenothiazines generating N-radicals and the subsequent radical recombination and deprotonation reactions.

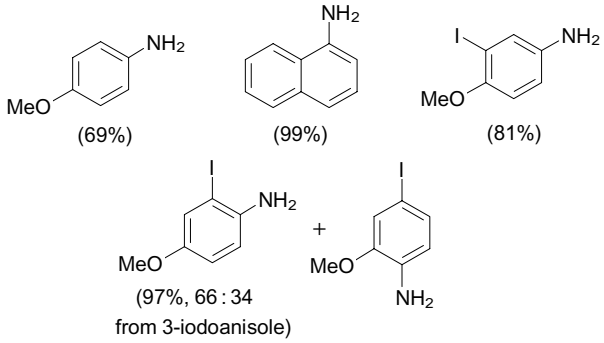
Morofuji *et al.*[189] developed a C−H-amination method for aromatic compounds based on their electrochemical oxidation in the presence of pyridine (divided H-cell, 10 mA). First, *N*-arylpyridinium salts are formed and then they are reacted with piperidine (pPy), which gives arylamines (Scheme 75). The key step of the reaction is anodic oxidation of aromatic systems to yield radical cations and cations.

**Scheme 75**




(*a*) C(+)||Pt(−), divided H-cell, anodic oxidation, Py, MeCN, $Bu^n_4NBF_4$, 25 °C; (*b*) pPy, MeCN, 80 °C

*Examples of products*



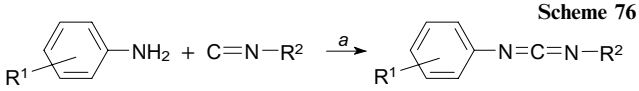
(69%) (99%) (81%)

(97%, 66 : 34 from 3-iodoanisole)

The electrochemical method for the synthesis of anilines by amination of arenes with aliphatic azides accompanied by C−C bond cleavage also includes anodic oxidation of the aromatic ring to give the corresponding radical cations. The reaction is carried out in an undivided electrochemical cell with graphite electrodes.[214]

The reaction reported by Malviya *et al.*[215] does not fit into the classification of electrochemical amination methods

**Scheme 76**



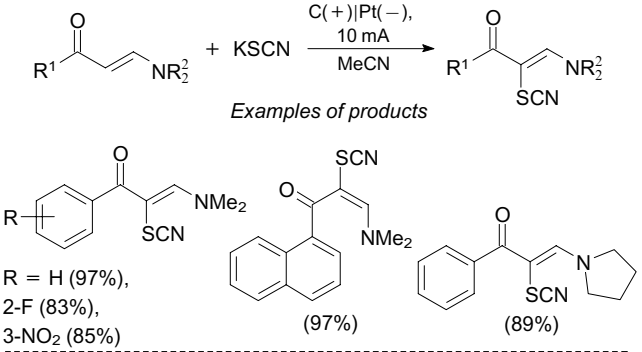
(*a*) C(+)|Pt(−), 12 mA, $Bu^n_4NI$, MeCN;
$R^2$ = $Bu^t$: $R^1$ = 4-$NO_2$ (86%), 3-OMe (80%); $R^1$ = 4-Cl, $R^2$ = cyclo-$C_6H_{11}$ (80%); $R^1$ = 4-Me, $R^2$ = n-$C_5H_{11}$ (67%)

accepted in this review. This is electrochemical oxidative cross-coupling of amines and aliphatic isonitriles, which affords carbodiimides in good yields (Scheme 76).

### 3.2. Formation of C−S bond

Electrochemical methods for the formation of C−S bond occupy an important place in the chemistry of organic sulfur compounds; however, virtually all examples of this type refer to cross-coupling of sulfur-containing reagents with unsaturated compounds. For example, Yang *et al.*[216] described a simple and efficient electrochemical thiocyanation of enaminones in an undivided electrochemical cell. This gives polyfunctionalized alkenes and chromenes in moderate to high yields with KSCN being used as the thiocyanating agent (Scheme 77).

**Scheme 77**



(*a*) C(+)|Pt(−), 10 mA, MeCN, ~20 °C;
R = 6-$Bu^t$ (98%), 7-Cl (88%), 6-Br (85%)

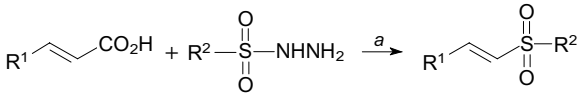
The electrochemical anodic thiocyanation involving inorganic thiocyanates was used for regioselective synthesis of thiocyanated derivatives of pyrrole, indole, pyrazole, isoxazole[217] and pyrazolo[1,5-*a*]pyrimidine.[218,219]

A stereoselective method for the synthesis of (*E*)-vinyl sulfones is based on the electrochemical oxidative cleavage of the N−S bond in aromatic sulfonylhydrazines followed by cross-coupling with cinnamic acids, which results in the formation of the C−S bond (Scheme 78).[220]

An electrochemical synthesis of vinyl thiocyanates from cinnamic acids and $NH_4SCN$ has been developed. The reaction proceeds in an undivided cell with platinum electrodes.[221]

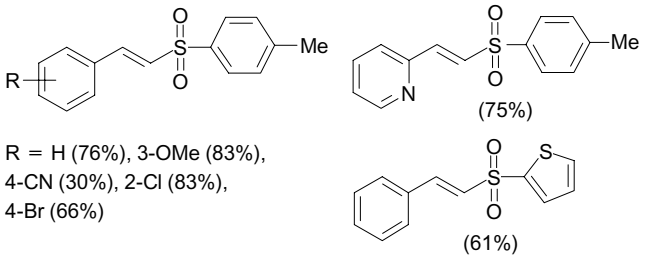
Electrochemical C($sp^2$)−H-sulfenylation of enaminones with thiophenols to give substituted vinylthiols in up to 87% yields is also known (Scheme 79).[222] It is notable that

**Scheme 78**



(*a*) Pt(+)|Pt(−), 5 mA, $Bu^tOLi$, $Bu^n_4NBF_4$, DMSO

*Examples of products*

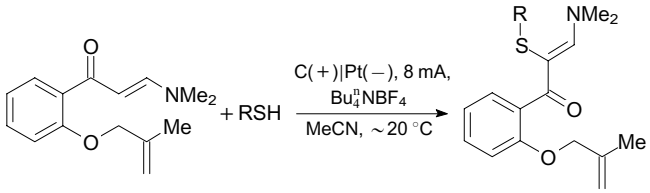


R = H (76%), 3-OMe (83%), 4-CN (30%), 2-Cl (83%), 4-Br (66%)

(75%)

(61%)

**Scheme 79**

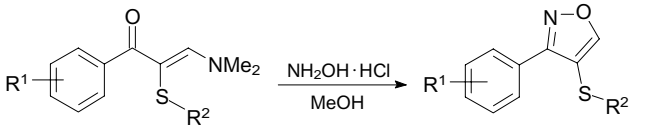


R = 4-$MeC_6H_4$ (82%), 4-$Pr^iC_6H_4$ (76%), 3-$MeOC_6H_4$ (45%), 4-$BrC_6H_4$ (87%), 3-$FC_6H_4$ (51%), 2-Naph (47%); Naph is naphthyl

thiophenols are selectively coupled with enaminones, even if the latter contain other alkenyl groups.

In addition, these products can be easily converted to α-sulfur-containing isoxazoles (Scheme 80), which exhibit various types of biological activity.[222]

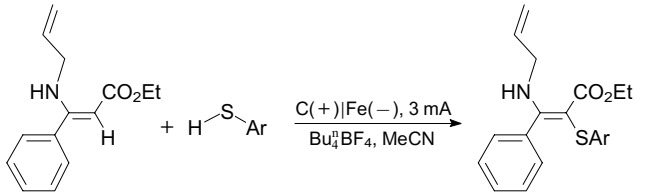
**Scheme 80**



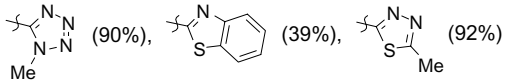
$R^1$ = 2-All: $R^2$ = *p*-Tol (82%), 4-$FC_6H_4$ (74%), 4-$BrC_6H_4$ (91%); $R^1$ = 4-$MeOC_6H_4$, $R^2$ = *p*-Tol (90%)

This is not the only example of application of compounds containing an enamine moiety in cross-coupling reactions to form C−S bonds. A method for electrochem-

**Scheme 81**



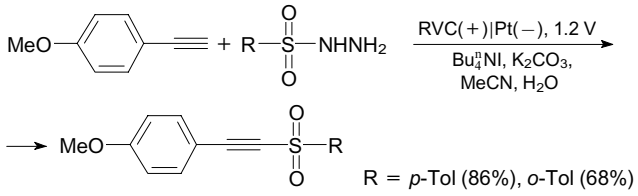
Ar = $RC_6H_4$ (R = 4-Cl (89%), 4-F(76%), 4-OMe (80%), 3-Br (80%)),



ical oxidative coupling of enamines with thophenols and hetarylthiols has been developed (Scheme 81).[223]

Mo *et al.*[224] reported electrochemical C(sp)–H/S cross-coupling of terminal alkynes and sulfonyl hydrazides to form alkynyl sulfones on a reticulated vitreous carbon electrode (Scheme 82). Most of products synthesized in this way possess antitumour activities on HeLa cells.

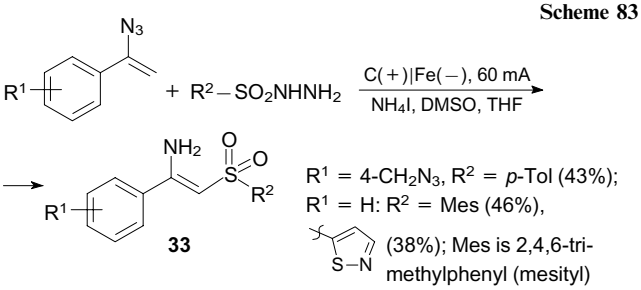
**Scheme 82**




In the electrochemical method for the synthesis of β-ketosulfones (51–90% yields) from substituted terminal alkynes or aryl methyl ketones, sodium arylsulfinates served as sources of S-radicals. The electrolysis of the reaction mixture was carried out at a constant current of 40 mA using a steel cathode and a graphite anode.[225]

A method for the synthesis of sulfonyl-substituted enamines with a free amino group has been developed.[226] The sulfonylation of vinyl azides involves the intermediate formation of electrophilic iodine-containing intermediates, which oxidize sulfonyl hydrazides to the corresponding S-radicals. The yields of products **33** reach 87% (Scheme 83).

**Scheme 83**

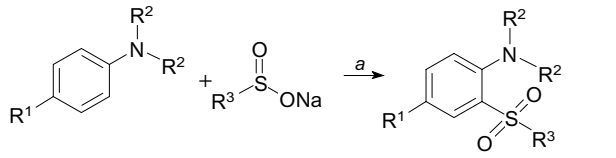



Terent'ev *et al.*[227] performed the sulfonylation of alkenes in which sulfonyl hydrazides served as the source of sulfonyl radicals. The reaction was carried out in an undivided cell with a C anode and an Fe cathode; the yields of vinyl sulfones were 25 to 95%. This reaction also proceeds in the presence of a number of functional groups in the substrate (F, Cl, Br, I, $NO_2$, OMe).

In most of the reported examples of oxidative electrochemical C($sp^2$)–H/S cross-coupling reactions, (hetero)-aromatic compounds were used both for introduction of sulfur-containing functional groups in the molecules and for the intramolecular cyclizations to give fused sulfur-containing heterocycles. Various sodium sulfinates were utilized in the electrochemical oxidative C–H sulfonylation of anilines, which gave the target *o*-aminoaryl sulfones in up to 96% yields (Scheme 84).[228]

Benzothiophenes with an arenesulfonyl group in position 3 were prepared using sodium sulfinates and 2-alkynylthioanisoles.[229] The reaction was carried out in an undivided electrochemical cell with C(+) and Pt(−) electrodes at a constant current of 8 mA. A variety of functional groups (F, Cl, Br, I, $CO_2Me$) were tolerant to these reaction conditions; the yields of products varied from 45 to 85%.

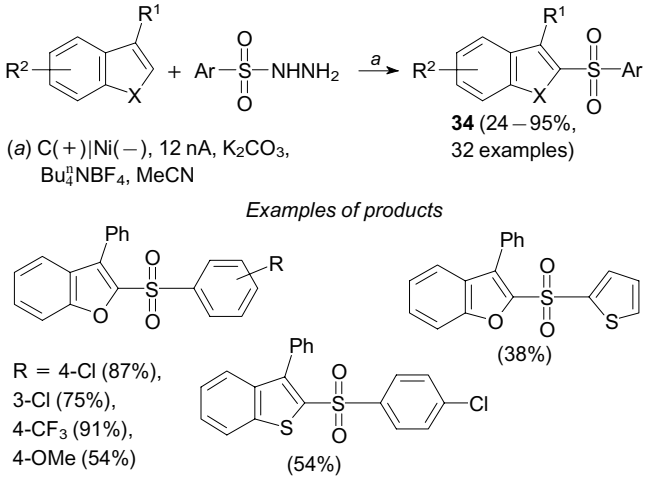
**Scheme 84**




(*a*) C(+)|Pt(−), 18 mA, MeCN–$H_2O$–AcOH (9 : 1 : 0.2);
$R^1$ = $R^2$ = Me: $R^3$ = Ph (90%), 4-$MeC_6H_4$ (93%), 4-$MeOC_6H_4$ (76%), 4-$Bu^tC_6H_4$ (57%), 2-Naph (36%); $R^1$ = Me, $R^2$ = Et, $R^3$ = Ph (96%)

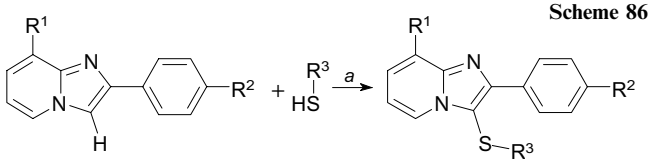
Heteroaryl sulfones **34** can also be obtained *via* radical electrochemical sulfonylation of C–H bonds in heteroarenes with arenesulfonyl hydrazides (Scheme 85).[230]

**Scheme 85**




The selective oxidative sulfenylation of imidazopyridines is efficiently attained by using both arene- and alkanethiols (Scheme 86).[231]

**Scheme 86**

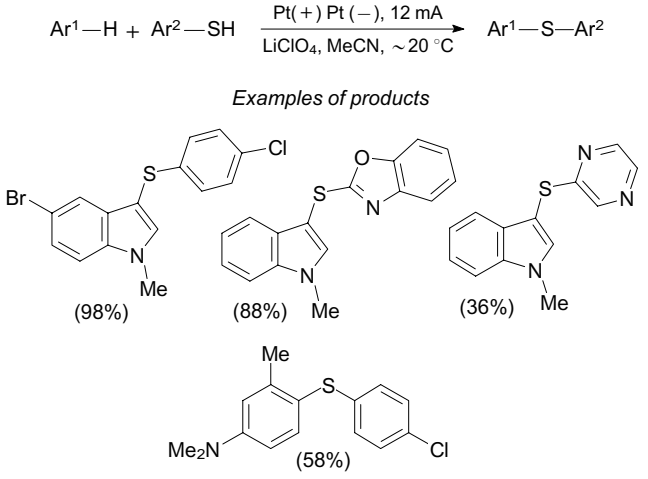



(*a*) C(+)|Pt(−), 12 mA; $Bu^n_4NPF_6$, MeCN, MeOH;
$R^1$ = H: $R^2$ = F, $R^3$ = 4-$ClC_6H_4$ (80%); $R^2$ = $CF_3$, $R^3$ = 4-$ClC_6H_4$ (54%); $R^2$ = OMe, $R^3$ = 4-$ClC_6H_4$ (86%); $R^2$ = H, $R^3$ = Et (59%); $R^1$ = $R^2$ = Me, $R^3$ = 4-$ClC_6H_4$ (90%)

Preliminary quantum chemical calculations for a similar reaction of indole derivatives demonstrated that the electrochemically generated aryl radical cation is the key intermediate (Scheme 87).[232]

A method for direct thiolation of arenes containing, in particular, alkoxy groups on treatment with aromatic thiols has been developed.[233] It should be emphasized that the product yields do not depend on the steric factors of either arenes or thiols: for example, the yield of the product in the reaction of MesH with *p*-TolSH is 95%, while for MeOPh

**Scheme 87**

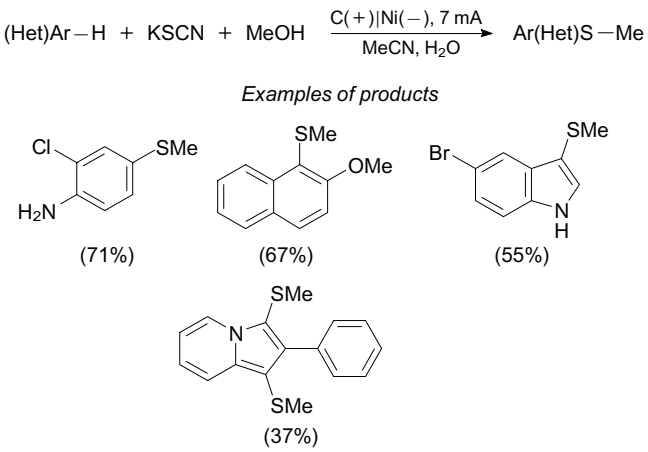



and 2,6-$Me_2C_6H_3SH$, the yield is 99%. The highest yield of reaction products is attained with platinum electrodes in the constant-current electrolysis at 5 mA.

The sulfonylation of 2*H*-imdazoles into position 3 was carried out using sulfonyl hydrazides as the source of sulfonyl radicals.[234] This reaction proceeds in the presence of air oxygen at room temperature; it can be scaled up to gram amounts and is characterized by high tolerance to the presence of several functional groups (F, Cl, $NO_2$, OMe) in the substrate. The electrolysis is conducted in an undivided cell at a constant current of 10 mA with a graphite anode and a nickel foam cathode. Similar products can be obtained by sulfonylation of 2*H*-indazoles with aryl- and alkylsulfinic acids in an undivided cell with C(+) and Pt(−) electrodes at 7 mA.[235]

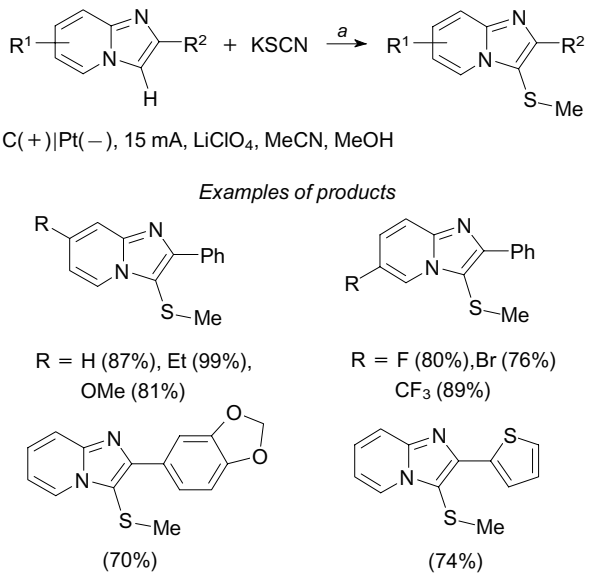
Three-component cross-coupling using thiocyanates as the source of sulfur atoms and methanol as the methylating agent formed the basis of the strategy of electrochemically induced regioselective thiomethylation of anilines, anisole, indole and indolizine (Scheme 88).[236]

**Scheme 88**




Under these conditions, many functional groups in the substrate are retained. This method was used for regioselective C(3)-thiomethylation of imidazopyridines (Scheme 89).[237]

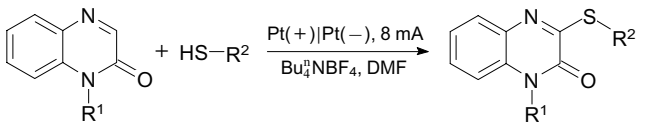
**Scheme 89**




A related sulfonylation–heteroarylation process involving sulfinic acids and alkenes is implemented *via* the step of *ipso*-migration of the heteroaryl moiety.[238]

Zhou *et al.*[239] described an electrochemical method for C($sp^2$)—H-functionalization of quinoxalin-2(1*H*)-ones with primary, secondary and tertiary thiols giving 3-alkylthioquinoxalin-2(1*H*)-ones (Scheme 90).

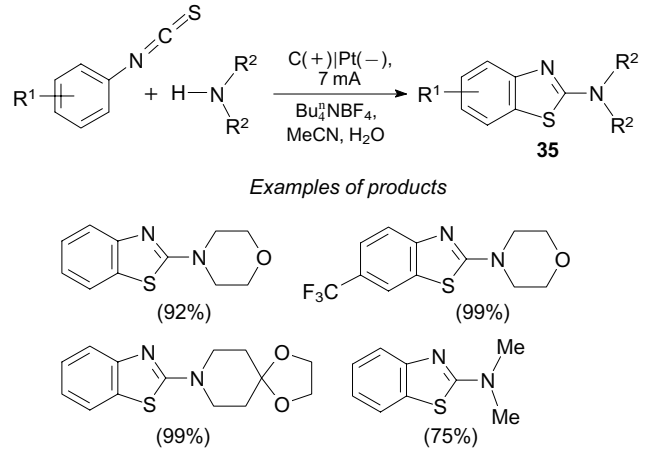
**Scheme 90**



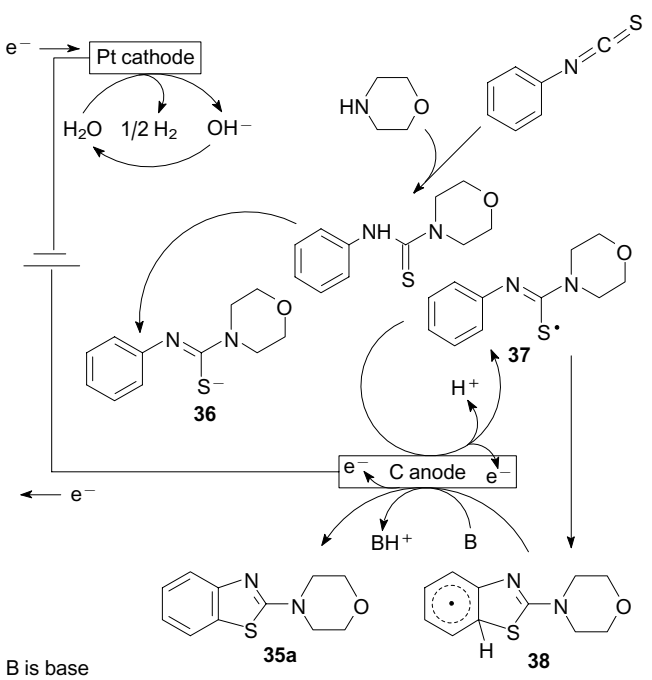

$R^2$ = $Bu^t$: $R^1$ = H (85%), $CH_2CCH$ (23%);
$R^1$ = H, $R^2$ = $CH_2CO_2Et$ (82%)

A series of substituted 2-aminobenzothiazoles **35** were prepared by electric current-induced intramolecular dehydrogenative C—H/C—S coupling involving *N*-aryl-*N*′,*N*′-dialkylthioureas, which are formed upon the reaction of secondary amines with aryl isothiocyanates (Scheme 91).[240]

**Scheme 91**



**Scheme 92**



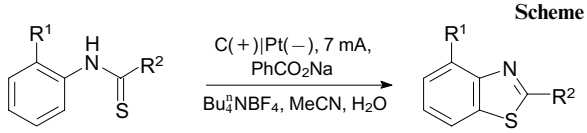

B is base

The mechanism proposed for this reaction is depicted in Scheme 92 in relation to the formation of 3-morpholinobenzothiazole (**35a**).

The nucleophilic addition of morpholine to isothiocyanate yields a thiourea derivative, which is then deprotonated with the hydroxide anion, generated by the cathodic reduction of water, thus giving ionic intermediate **36**. The anodic SET oxidation of intermediate **36** produces radical **37**, which rapidly undergoes intramolecular cyclization to be converted to intermediate **38**. The subsequent anodic oxidation and deprotonation of this intermediate furnishes the target product **35a**.

In the presence of sodium benzoate, the synthesis of benzothiazoles from *N*-arylthioamides can be carried out under the same conditions (Scheme 93).[240]

**Scheme 93**



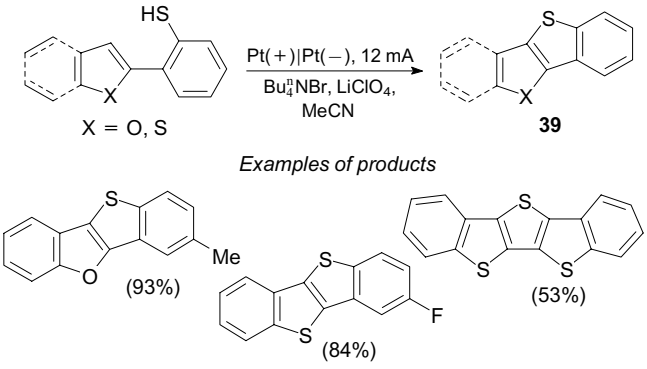

$R^1$ = Br, $R^2$ = Ph (98%); $R^1$ = H: $R^2$ = 4-$Bu^tC_6H_4$ (90%), cyclo-$C_6H_{11}$ (20%)

In addition, there is known TEMPO-catalyzed intramolecular cyclization of *N*-(hetero)arylthioamides, resulting in benzothioazoles and thiazolopyridines.[241] The reaction is carried out in an undivided electrochemical cell at 10 mA with a glassy carbon anode and a platinum cathode.

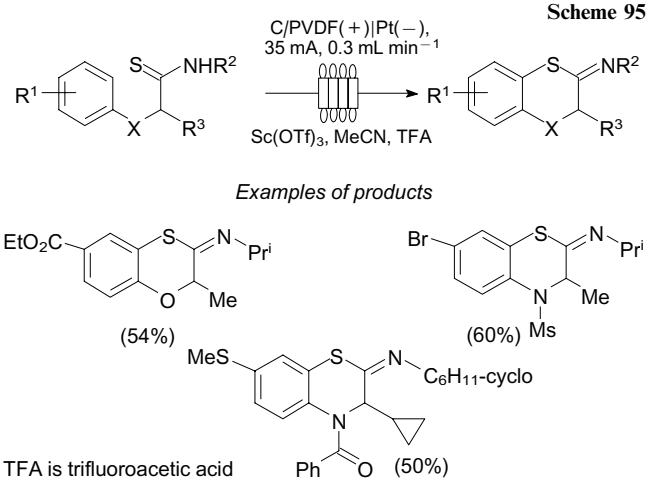
In the electrochemical dehydrogenative synthesis of fused systems **39** from sulfanylarenes, a significant factor is the addition of $Bu^n_4NBr$, which catalyzes the reaction and serves as the source of bromide ions (Scheme 94).[242]

Benzo-annulated six-membered S-heterocycles were synthesized by intramolecular dehydrogenative C−S coupling with appropriate thioamides in a modular flow electrolytic cell (Scheme 95).[243] The electrolysis was conducted at a

**Scheme 94**




**Scheme 95**




TFA is trifluoroacetic acid

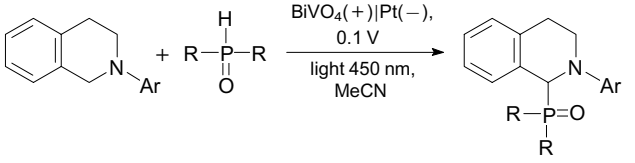
constant current of 35 mA; the flow cell was equipped with a Pt cathode and an anode made of graphite and poly(vinylidene fluoride) (PVDF).

A similar electrochemical aminoselenation of styrenes is based on participation of secondary amines, imides and azoles as aminating agents in the presence of diselenides. The reaction was carried out in an undivided electrochemical cell equipped with C(+) and Pt(−) electrodes.[244]

### 3.3. Formation of C−P bond

An original method for simultaneous of photo- and electrochemical processes was reported in 2019.[245] The authors designed a new photoelectric cell to carry out C−P cross-coupling with evolution of hydrogen. *N*-Aryltetrahydroisoquinolines and various phosphine oxides were used as the starting compounds (Scheme 96).‡

**Scheme 96**



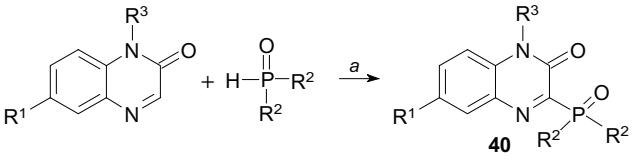

R = Ph: Ar = Ph (90%), 4-$MeOC_6H_4$ (88%), 3-$MeOC_6H_4$ (86%), 2-$MeOC_6H_4$ (91%), 4-$F_3CC_6H_4$ (85%); Ar = Ph: R = MeO (81%), $Bu^nO$ (64%)

‡ Note that the most recent achievements in the photoelectrochemistry are summarized in a review by Barham and König.[246]

The intramolecular cyclization of diarylphosphine oxides in an electrochemical process [Pt(+)|Pt(−) undivided cell, constant current of 2.5 mA] affords diarylphosphole oxides in good yields (24–72%).[247]

The other few examples of C−P bond formation in electrochemical processes are concerned with cross-coupling reactions involving aromatic compounds with C−H and C−halogen bonds. For example, an electrochemical approach was developed for the phosphorylation of the C(sp$^2$)−H bond in quinoxalin-2(1*H*)-ones *via* C−H/P−H cross-coupling. This procedure is applicable to a broad range of substrates and gives products **40** in high yields (up to 99%) (Scheme 97).[248]

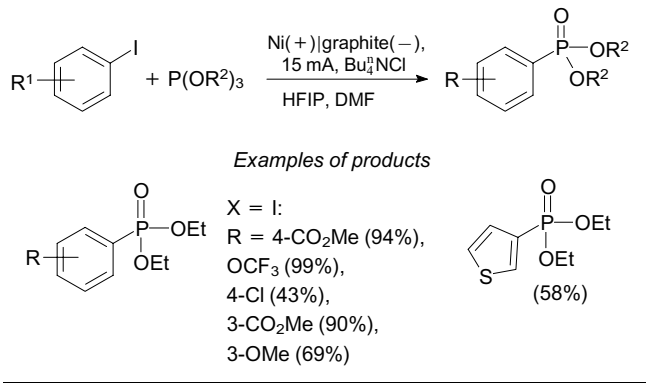
**Scheme 97**




(*a*) C(+)|Pt(−), $LiClO_4$, MeCN; $R^2$ = MeO: $R^1$ = Cl, $R^3$ = H (88%); $R^1$ = H, $R^3$ = 4-$MeOC_6H_4CH_2$ (53%); $R^1$ = $R^3$ = H, $R^2$ = Ph (99%)

The electrochemical cross-coupling of aryl halides with trialkyl phosphites gives arylphosphonates in moderate to good yields (Scheme 98).[249] In the case of aryl iodides, the products are formed in higher yields, whereas in the case of bromides, the yields are moderate. 4-Iodonitrobenzene and 4- and 2-iodopyridines do not give the expected coupling products, but are further reduced under conditions of electrolysis.

**Scheme 98**

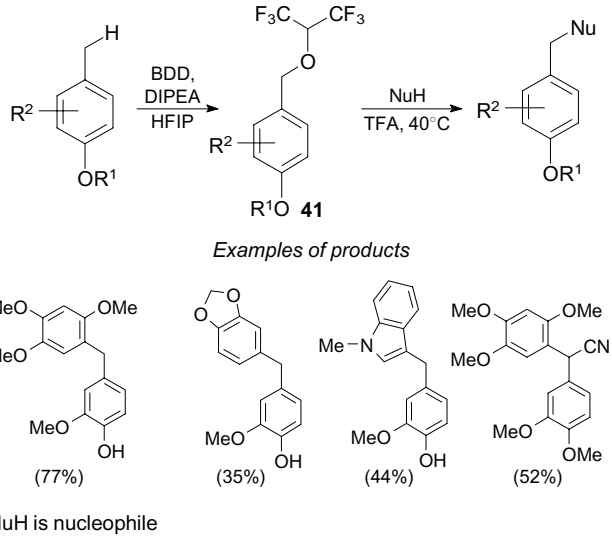



Cowper *et al.*[250] successfully performed the Arbuzov reaction of aryl chlorides under electrophotocatalytic conditions; the reaction included the intermediate formation of aryl radicals.

### 3.4. Formation of C−O bond

Although recent publications considering the use of electrochemical reactions for the formation of C−O bonds are few, they are nevertheless useful for evaluation of the future scope of applicability of this method. For example, a process has been developed for selective dehydrogenative electrochemical functionalization of substituted toluenes into the benzylic position to form the C−O bond using 1,1,1,3,3,3-hexafluoropropan-2-ol as the source of oxygen

**Scheme 99**

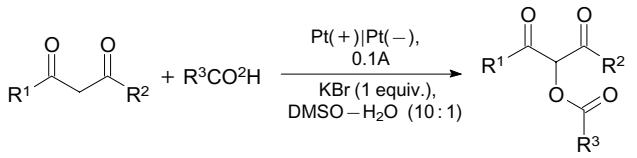


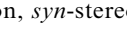

NuH is nucleophile

and boron-doped diamond (BDD) electrodes (Scheme 99).[251] The benzyl ethers **41** thus formed are versatile precursors for the subsequent functionalization, because in protic acids, they act as benzyl cations. The benzyl cations are generated on treatment of compound **41** with acids. The reactions with aromatic nucleophiles afford practically valuable diarylmethanes.

Bityukov *et al.*[252] developed an electrochemical method for the preparation of α-acyloxy-β-dicarbonyl compounds (36–92% yields) as a result of intermolecular C−O coupling of β-dicarbonyl compounds with carboxylic acids (Scheme 100).

**Scheme 100**



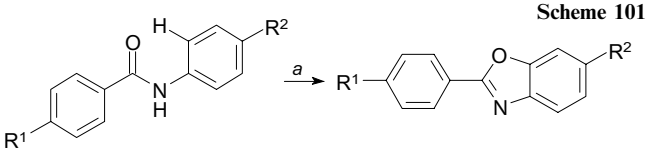

$R^1$ = Ph: $R^2$ = $R^3$ = Me (70%); $R^2$ = OEt, $R^3$ is thiophen-2-yl (38%); $R^2$ = OEt, $R^3$ =  (58%); $R^1$ = $R^3$ = Me, $R^2$ = OEt (73%)

In addition, *syn*-stereoselective acetoxyhydroxylation of alkenes under electrophotocatalytic conditions has been described.[253]

*O*-(Phthalimid-1-yl)oximes were obtained upon simultaneous formation of N−O and C−O bonds *via* the reaction of vinyl azides with *N*-hydroxyphthalimide.[254] During the reaction, O-radicals and N-imidoxyl radicals are generated.[255,256] This method is characterized by high yields of coupling products (up to 84%) and tolerates substrates with some labile and functional groups (F, $NO_2$, $CF_3$, $N_3$, OMe). Esters of aryl- and alkylcarboxylic acids, including sterically hindered ones, were synthesized from *N*-alkoxyamides by electrolysis in an undivided Pt(+)|Cu(−) electrochemical cell.[257]

The other examples of C−O bond formation are electrochemical intramolecular cross-coupling reactions of compounds containing aromatic C−H bonds; these reactions afford oxygen-containing heterocycles. An electrochemical synthesis of benzoxazoles from anilides giving

**Scheme 101**

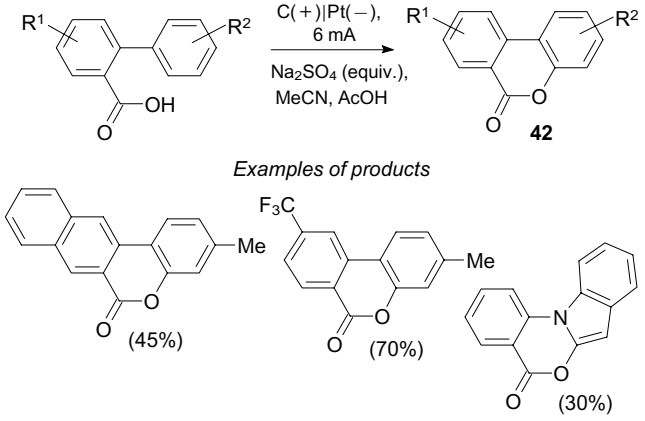


(*a*) RVC(+)|Pt(−) or C(+)|Pt(−), $Bu^n_4NPF_6$, HFIP;
$R^1$ = H: $R^2$ = Cl (66%), OMe (55%), OTf (60%), F (59%);
$R^1$ = Me: $R^2$ = OMe (56%), F (66%); $R^2$ = OMe, $R^1$ = Cl (80%)

products in good yields has been described (Scheme 101).[258] Presumably, the process is initiated by anodic oxidation of the deprotonated amide nitrogen atom to give an amidyl radical resonance-stabilized by the aromatic ring. The interaction of the radical centre with the carbonyl group leads to generation of a heterocyclic radical, which is converted to benzoxazole *via* the subsequent oxidation and deprotonation.[258]

Another example of activation of the aromatic C−H bond is the synthesis of lactones **42** from 2-diarylbenzoic acids (Scheme 102).[259] This reaction can also be carried out for 2-hetaryl-substituted benzoic acid and also can be scaled-up and used to prepare analogues of natural products.

**Scheme 102**



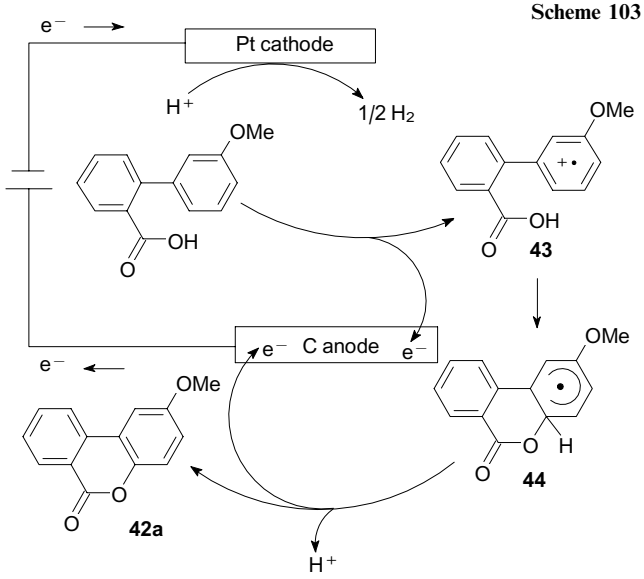
A putative mechanism of this reaction is depicted in Scheme 103 in relation to the formation of product **42a**. The initial anodic oxidation of the substrate *via* single-electron transfer gives rise to an aromatic radical cation **43**. Then this radical cation attacks the carboxyl group to form radical intermediate **44**, which rapidly aromatizes *via* SET and is deprotonated *via* the anodic oxidation step, thus giving target compound **42a**.

An analogous reaction was performed by electrolysis of solutions of 2-arylbenzoates in an undivided electrochemical cell using platinum electrodes and using a constant current of 23 mA.[260]

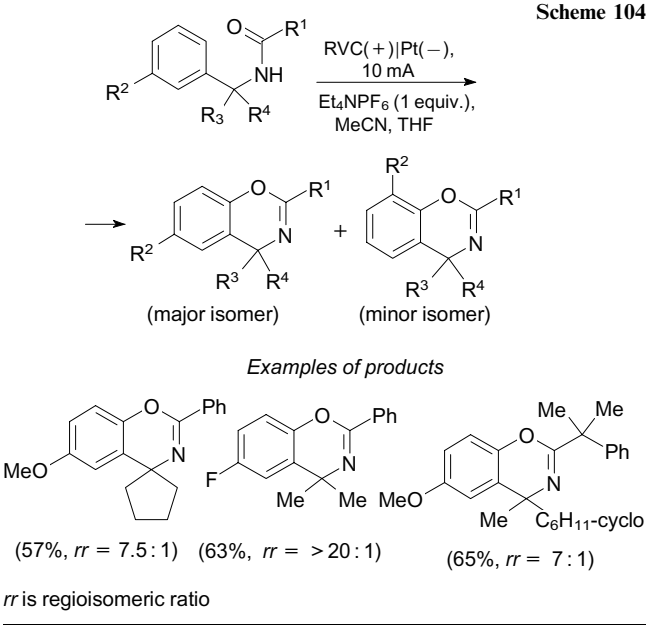
A highly regioselective synthesis of 4*H*-1,3-benzoxazines is based on the intramolecular cyclization of *N*-benzylacylamines, resulting in the formation of regioisomeric products (45–79%, 22 examples) (Scheme 104).[261]

The introduction of oxygen-containing functional groups into various molecules can be accomplished by cross-coupling involving not only the C−H bond, but also the carbon−heteroatom bond. The desulfurization and C−O bond formation take place, for example, in the

**Scheme 103**



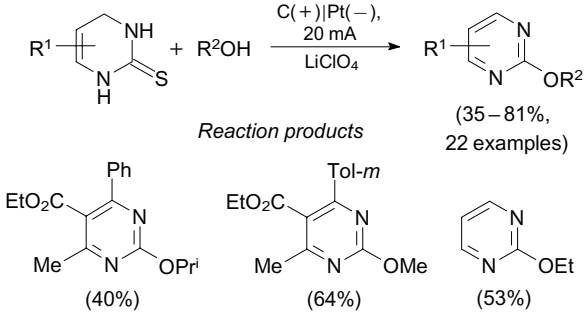
**Scheme 104**



*rr* is regioisomeric ratio

electrochemical oxidation of 3,4-dihydropyrimidine-2(1*H*)-thiones (including thiourea) in the presence of alcohols, which serve simultaneously as solvents and sources of alkoxy groups.[262] The reaction gives 2-alkoxypyrimidine derivatives (Scheme 105).

**Scheme 105**



Nokami *et al.*[263] reported a one-pot synthesis of oligosaccharides based on anodic oxidation of the thioglycoside residue. This residue is converted to the trifluoromethanesulfonic acid derivative, which reacts with another thioglycoside molecule containing a hydroxyl group to give diglycoside. Methods for hydroxylation of toluene derivatives were reported.[264] The synthesis of diaryl ketones, benzaldehydes and diketones[265] by electrochemical oxidation of diarylmethanes and alkenes, proceeding *via* the formation of alkoxysulfonium ions,[266] was developed.

The above successful examples of application of electrochemical methods for C—O bond formation attest to the necessity of further development of this area with the goal to synthesize practically useful products.

## 4. Reactions of aryl halides initiated by alkali metal bases

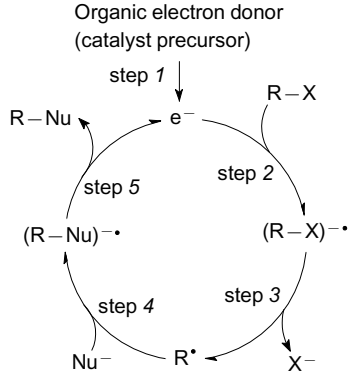
A mechanism of carbon—halogen bond activation in the absence of transition metals alternative to the photo- and electrochemical initiation is related to the single-electron reduction of aryl halide to give aryl radical anion and subsequent elimination of halide ion.[267] These reactions are initiated by alkali metal bases and organic additives (amines, diamines, diols and other organic compounds). Quite of few such reactions have been reported, which refer to cross-coupling to form the carbon–carbon bonds.[21,22,268–271] The initial reaction of the inorganic base with the additive furnishes a complex — a strong organic electron donor, which induces the reduction of aryl halide *via* the single-electron transfer. The role of the additive can also be performed by the organic solvent (DMSO, DMF) or the substrate.[272] Conversely, reactions of aryl halides that involve single-electron reduction of the carbon–halogen bond to give a C—N bond are few and are mainly limited to examples of intramolecular amination of aryl halides, resulting in the formation of heterocyclic products. Some transition metal-free reactions of aryl halides giving C—N bond are considered in this part of the review.

### 4.1. Electron as a catalyst concept

In 2014, Studer and Curran[273] introduced the paradigm according to which the electron is a catalyst to describe the mechanisms of some preparatively significant reactions discovered in the last decade. At the first glance, these reactions have little in common, except for two features: they are free from transition metal compounds and, most likely, they involve the formation of radical intermediates. In particular, various radical cascade reactions can be assigned to this type, *e.g.*, unimolecular radical aromatic substitution,[274,275] base-induced homolytic nucleophilic substitution,[276] radical Heck reaction[277] and so on.

According to this concept, the general mechanism of the carbon — heteroatom bond formation can be represented in the following way (Scheme 106). The first stage is initiation of the catalytic cycle by the electron transfer from an electron-rich species, which in this case can be considered as a catalyst precursor, *i.e.*, an electron (step *1*). Then the substrate ArX molecule is reduced to give the corresponding $(ArX)^{-\bullet}$ radical anion (step *2*), the fragmentation of which leads to the $Ar^{\bullet}$ radical and the $X^-$ halide ion (step *3*). The reaction of the $Ar^{\bullet}$ radical with a nucleophilic reagent yields a new radical anion, $(ArNu)^{-\bullet}$ (step *4*), which in turn lends an electron to the catalytic cycle and is thus converted to the final product (step *5*). Steps *3* and *4* may occur concertedly; in this case, free radical is not formed as an intermediate. In general, this reaction pathway is similar to the traditionally accepted mechanism of unimolecular aromatic nucleophilic substitution $S_{RN}1$, which can be considered as an example of electron-catalyzed reactions. Unlike classical metal- or radiation-induced reactions that follow the $S_{RN}1$ mechanism, the reactions discussed below usually do not require such conditions and readily proceed upon thermal activation. The participation of radical intermediates was shown experimentally for many of these reactions, despite the fact that they have little in common regarding the mechanism. The use of the Studer and Curran concept allows these reactions to be considered as examples of electron-catalyzed reactions.

**Scheme 106**



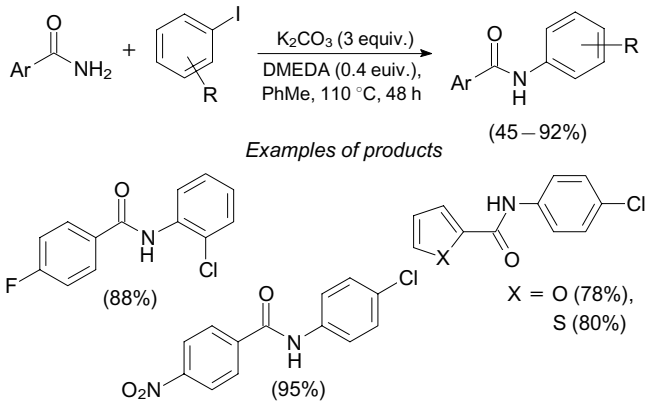

### 4.2. N-Arylation of benzamides

One of the few examples of intermolecular formation of C—N bond upon transition metal-free amination of aryl halides is related to the reaction of substituted benzamides and their heterocyclic analogues with aryl iodides in the presence of $K_2CO_3$ and *N*,*N*′-dimethylethylene-1,2-diamine (DMEDA). The arylation does not take place in the absence of DMEDA. As the arylating agents, *ortho*- and *para*-halo-substituted aryl iodides are used. No *cine*-substitution products are detected, which rules out the aryne mechanism of the reaction (Scheme 107).[278]

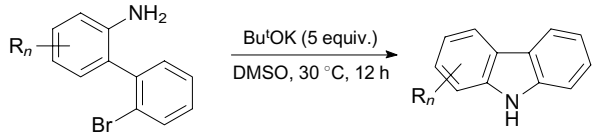
### 4.3. Synthesis of five-membered heterocyclic compounds

A feasible approach to the synthesis of substituted 9*H*-carbazoles is based on the heterocyclization of 2-amino-2′-bromobiphenyls. High yields of 9*H*-carbazoles are attained

**Scheme 107**



**Scheme 108**

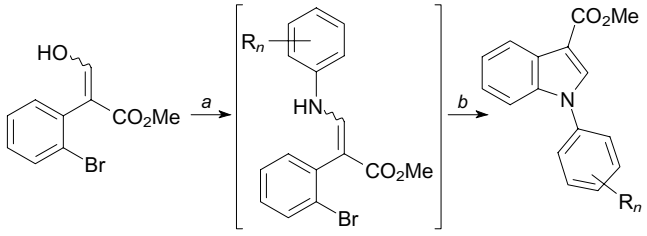



$R_n$ = H (88%), 4-Me (87%), 4-Cl (91%), 2,4-$Me_2$ (82%)

when potassium *tert*-butoxide is used as a base (Scheme 108; the position of substituents in the substrate is indicated).[279]

The cyclizaion of 3-amino-2-(2-bromophenyl)acrylates as a result of copper or iron salt-catalyzed intramolecular amination of aryl halides forms the basis of the known method for the synthesis of esters of N-substituted indole-3-carboxylic acids, valuable building blocks for the preparation of various indole derivatives, in particular, pharmacologically active compounds.[280, 281] The cyclization of the same substrates can be induced without transition metal catalysis (Scheme 109).[282] For example, indoles were prepared by initial conversion of enols to enamines and subsequent cyclization induced by the $Bu^tOK-DMF$ system. The efficiency of this method of synthesis of *N*-aryl indole derivatives is comparable with or is higher than the efficiency of known catalytic reactions.[280, 281] In addition, this reaction can be used to prepare indole in gram amounts and to synthesize a chiral product from (*S*)-(−)-α-methylbenzylamine without the loss of enantiomeric purity.

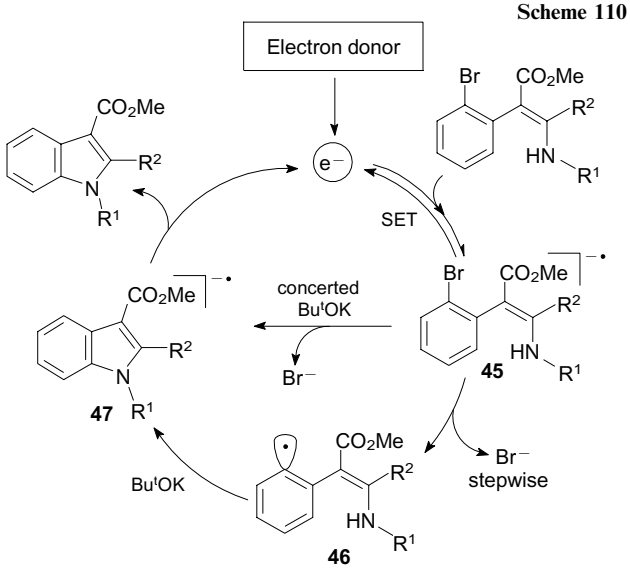
**Scheme 109**




(*a*) $R_nC_6H_4NH_2$, MeOH, Δ; (*b*) $Bu^tOK$, DMF, argon, 125 °C, 3 h;
$R_n$ = 4-OMe (94%), 3-Cl (91%), 4-I (88%), 2,4,6-$Me_3$ (94%)

Relying on the concept of electron-catalyzed coupling reactions, the authors proposed the following catalytic cycle for the formation of indole (Scheme 110). The transformation starts from the release of electron, which acts as the catalyst. The possible sources of electron are the $Bu^tOK-DMF$ system or the aza-allyl anion resulting from deprotonation of the substrate. The subsequent reduction of aryl bromide *via* single-electron transfer results in the corresponding radical anion **45**, which is converted to aryl radical **46** and bromide ion upon fragmentation. The intramolecular capture of radical **46** by N-nucleophilic moiety results in generation of radical anion **47**. In the final stage of the cycle, radical anion **47** is converted to the product and transmits an electron to a next substrate molecule, thus closing the catalytic cycle. This sequence is analogous to the $S_{RN}1$ mechanism. Alternatively, radical anion **47** can be obtained from radical anion **45** *via* a concerted process without intermediate formation of aryl radical **46**, which corresponds to the $S_{RN}2$ mechanism. Although the true mechanism of the reaction is not clear

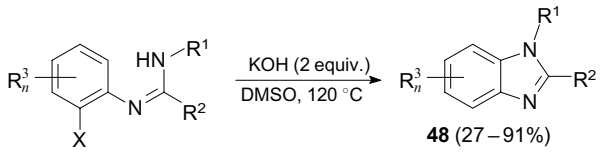
**Scheme 110**




as yet, high selectivity observed with the use of multihalo-substituted substrates suggests that conversion of radical anion **45** to radical anion **47** follows, most likely, a concerted mechanism.

The intramolecular cyclization of *ortho*-halo-substituted *N*-arylamidines induced by KOH in DMSO furnishes substituted benzimidazoles **48** (Scheme 111).[283] This method is suitable for substrates containing labile substituents and functional groups and efficient for the preparation of halo-substituted benzimidazoles. It is noteworthy that the heterocyclization may involve various halo derivatives. Fluoro- and iodo-substituted substrates have comparably high reactivities, whereas bromo and chloro derivatives are considerably less reactive. This indicates that the mechanism of heterocyclization depends on the nature of the halogen in the starting *ortho*-halo-substituted *N*-arylamidine. Apparently, in the case of fluorine-containing substrates, the reaction follows the $S_NAr$ mechanism, while iodo derivatives react through the formation of radical intermediates.

**Scheme 111**



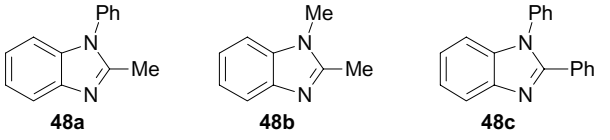

**48** (27–91%)

X = Br, $R^2$ = Me: $R^1$ = Bn, $R^3_n$ = H (28%);
$R^1$ = Me, $R^3_n$ = 4,6-$Me_2$ (89%); $R^1$ = Ph, $R^3_n$ = 4,6-$Br_2$ (79%);
X = F, $R^1$ = Ph, $R^2$ = Me, $R^3_n$ = 5-Me (90%), *etc.*

For comparison, given below are the yields of substituted benzimidazoles **48a–c** obtained upon the palladium-catalyzed intramolecular amination of aryl bromides under the following conditions: $Pd_2(dba)_3$ (0.5–1 mol.%), $Ph_3P$ (4–8 mol.%), NaOH (2 equiv.), $H_2O$, DME, MW, 160 °C; dba is dibenzylideneacetone, DME is dimethoxyethane, MW is microwave radiation.[284]

Although the product yields in the two types of processes are comparable, the catalyzed reaction requires the use of microwave radiation and tolerates a smaller range of

**Structures 48**



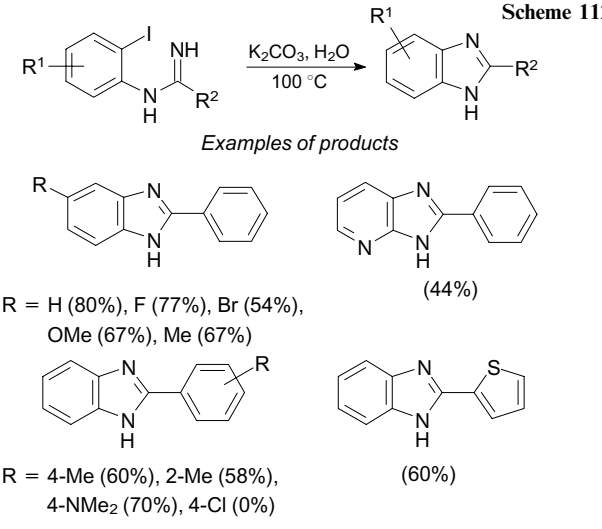
**48a** **48b** **48c**

| Conditions | Yield (%) (X) | | |
|---|---|---|---|
| | **48a** | **48b** | **48c** |
| No catalyst | 90 (X = F) | 73 (X = Br) | 90 (X = I) |
| Pd catalyst | 86 (X = Br) | 86 (X = Br) | 98 (X = Br) |

substituents (in particular, it is inapplicable for the preparation of bromo-substituted benzimidazoles). Furthermore, although the $Ph_3P$ ligand is used in the palladium-catalyzed reaction in a minor amount, the authors noted that traces of this compound were present in the reaction products. A special procedure using the Amberlist 15 ion exchange resin was developed for the removal of these impurities.[284]

A similar intramolecular cyclization of *N*-(2-iodophenyl)arylamidines carried out in the presence of $K_2CO_3$ (2 equiv.) in water at 100 °C for 30 h (Scheme 112) affords 2-(hetero)arylbenzimidazole derivatives in moderate to high yields.[285] This reaction smoothly proceeds for iodides and bromides, whereas chlorides and fluorides remain inert under the same conditions. In addition, the benzimidazole ring is not formed when strong electron-withdrawing groups are present in the benzene ring of the aromatic substituent $R^2$. The choice of base also considerably affects the efficiency of cyclization: for example, sodium derivatives and organic bases do not facilitate the formation of the desired product.

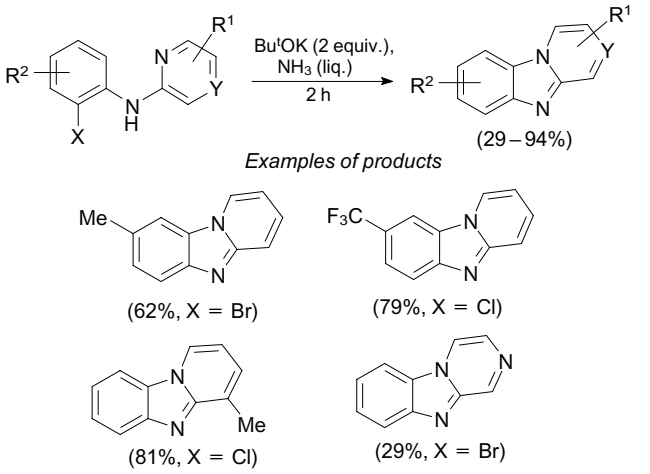
**Scheme 112**




A similar heterocyclization was used to prepare pyrido[1,2-*a*]benzimidazoles from *N*-(2-halophenyl)-2-aminopyridines (Scheme 113).[286]

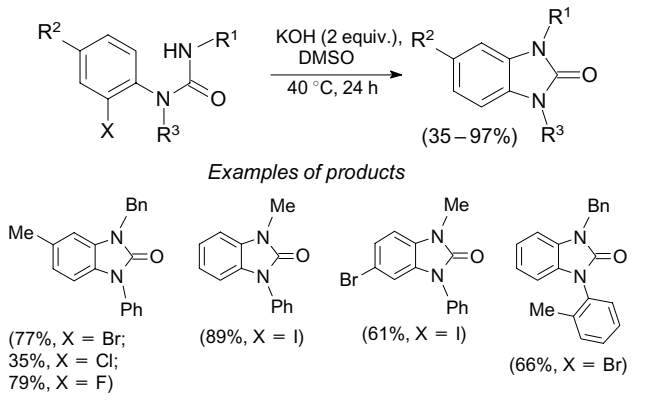
The transition metal-free intramolecular cyclization of *ortho*-iodo(bromo)-substituted *N*-arylureas serves as a convenient preparative route towards benzimidazol-2-ones (Scheme 114).[287] This method is applicable for the synthesis of structurally diverse benzimidazol-2-ones, including brominated derivatives and compounds with bulky substituents

**Scheme 113**




at the nitrogen atom. The use of ureas containing two unsubstituted NH groups as the starting compounds does not give the cyclization product. The highest yields of products are obtained for iodo- and bromo-substituted substrates. The cyclization of fluoro-substituted ureas proceeds smoothly, while chloro derivatives are least reactive. These facts suggest that the heterocyclization mechanism depends on the nature of the halogen atom acting as the leaving group. In the case of fluorinated substrates, the $S_NAr$ mechanism predominates, while the substitution of iodo and chloro derivatives involves radical intermediates.

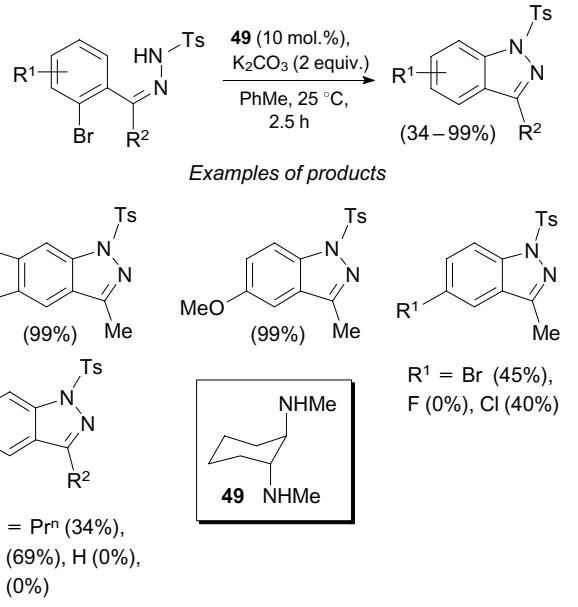
**Scheme 114**



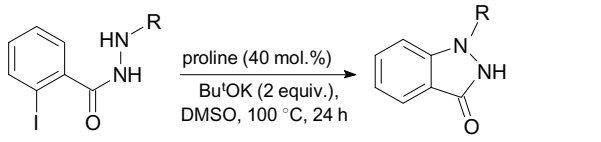

One of early studies[288] related to the synthesis of heterocyclic compounds by amination of aryl halides free from transition metal-based catalysts describes the heterocyclization of (*Z*)-*o*-bromoacetophenone *N*-tosylhydrazones (Scheme 115). The reaction takes place under the action of $K_2CO_3$ in the presence of 10 mol.% *trans*-*N*,*N*′-dimethyl-1,2-diaminocyclohexane (**49**) and yields N-substituted indazoles. Other bases (KOH, $Bu^tOK$, $Na_2CO_3$) and other amines were inefficient or less efficient. While analyzing the mechanisms of heterocyclization, the authors assumed the radical mechanism to be most likely, which was confirmed by studying the reaction mixture by EPR spectroscopy.

A similar heterocyclization reaction of hydrazides of *ortho*-halogenated benzoic acids gave 1*H*-indazolones (Scheme 116).[289] The heterocyclization proceeds most effi-

**Scheme 115**




**Scheme 116**



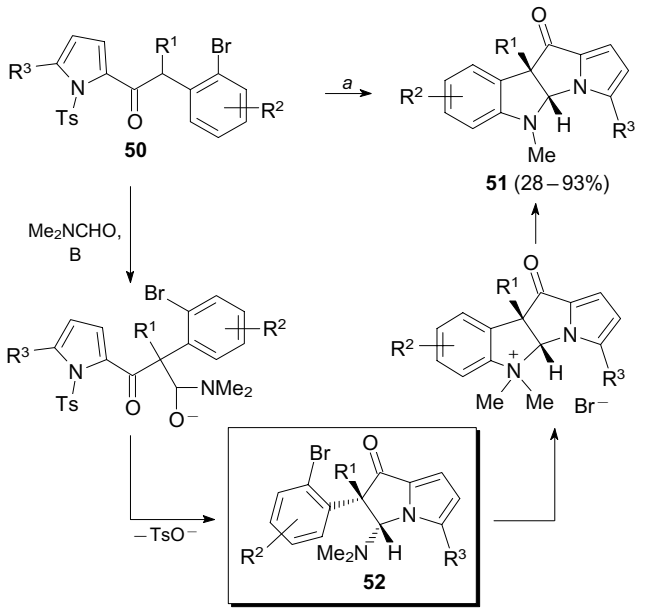

R = 2-MeOC$_6$H$_4$ (56%), 4-MeOC$_6$H$_4$ (72%), 4-ClC$_6$H$_4$ (51%), cyclo-C$_6$H$_{11}$ (61%)

ciently for hydrazones of *o*-iodobenzoic acids, whereas in the case of chloro- and fluorobenzoic acids, no cyclization products are formed. The optimal conditions include the use of potassium *tert*-butoxide as a base and DMSO as the solvent in the presence of 40 mol.% proline. The reaction is sensitive to the electronic nature of substituents: electron-withdrawing substituents present in either benzoic acid moiety or hydrazine moiety lead to decreasing yields of 1*H*-indazolones. The cyclization presumably follows a radical mechanism, as indicated by considerable decrease in the yield of the cyclization product upon the addition of radical scavengers into the reaction medium.[289]

Heating of 2-(2-bromophenyl)acetyl-*N*-tosylpyrroles **50** in DMF in the presence of 2 equiv. of $Cs_2CO_3$ affords dihydropyrrolizino[3,2-*b*]indol-10-ones **51** (Scheme 117).[290] In this reaction, DMF is not only a solvent, but also a reactant. The mechanism proposed for this reaction includes the formation of tricyclic intermediate **52** (see Scheme 117), which undergoes base-induced intramolecular cyclization. The subsequent demethylation of quaternary ammonium salt furnishes product **51**.

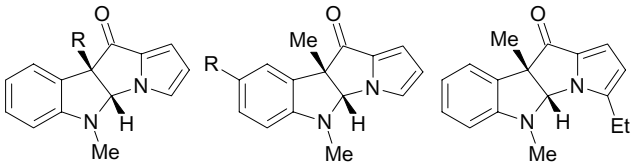
The reaction of bromoacetylenes with benzamidines in the presence of $K_2CO_3$, 2,2′-bipyridine (bipy) and water underlies the synthesis of substituted imidazoles (Scheme 118).[291] According to the mechanism proposed by the authors, the reaction starts with the formation of amidine and bromoacetylene adducts, compounds **53**, which then cyclize to substituted imidazoles. The reaction is applicable to substituted aromatic amidines and aryl- or alkyl-substituted bromoacetylenes; using *N*-monosubstituted amidines, the corresponding *N*-substituted imidazoles can be obtained only in low yields.

**Scheme 117**




(*a*) $Cs_2CO_3$ (2 equiv.), DMF, 120 °C, 24 h

*Examples of products*

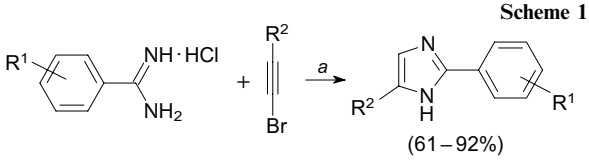


R = Me (87%), Et (93%), Bn (89%)

R = F (87%), Cl (90%), CF$_3$ (75%)

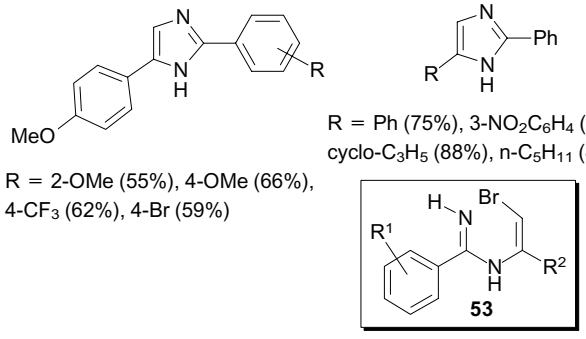
(42%)

**Scheme 118**




(*a*) $K_2CO_3$ (4 equiv.), bipy (5 mol.%), $H_2O$ (2.5 equiv.), PhMe, 120 °C, 12 h

*Examples of products*



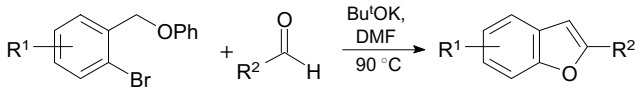
R = 2-OMe (55%), 4-OMe (66%), 4-CF$_3$ (62%), 4-Br (59%)

R = Ph (75%), 3-NO$_2$C$_6$H$_4$ (64%), cyclo-C$_3$H$_5$ (88%), n-C$_5$H$_{11}$ (86%)




The strategy towards the formation of nitrogen-containing five-membered heterocycles based on base-catalyzed intramolecular cross-coupling reactions can be successfully

**Scheme 119**

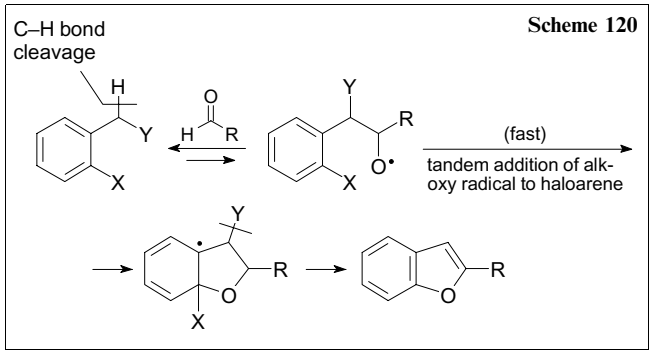


$R^2$ = Ph: $R^1$ = H (87%), 6-Br (84%), 5-$NO_2$ (33%);
$R^1$ = H, $R^2$ = Bu$^t$ (46%)

used to prepare benzofuran and its fused derivatives. For example, the intermolecular addition of the alkyl radical to the carbonyl group followed by the intramolecular addition of the alkoxy radical to *o*-phenoxymethylhaloarenes affords substituted benzofurans in high yields under catalysis with a strong base (Scheme 119).[292]

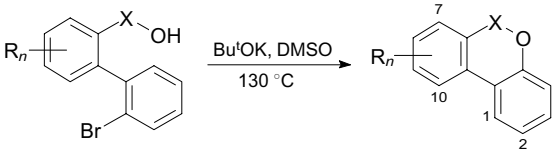
The radical mechanism of this reaction depicted in Scheme 120 was confirmed by free radical trapping experiments and analysis of EPR spectra.

**Scheme 120**




One more example of this type of C–O bond formation takes place in the Bu$^t$OK-initiated intramolecular cyclizations of 2-(2-bromoaryl)benzyl alcohols and -benzoic acids to give the corresponding 6*H*-benzo[*c*]chromene and 6*H*-benzo[*c*]chromen-6-one derivatives, respectively (Scheme 121).[279]

**Scheme 121**

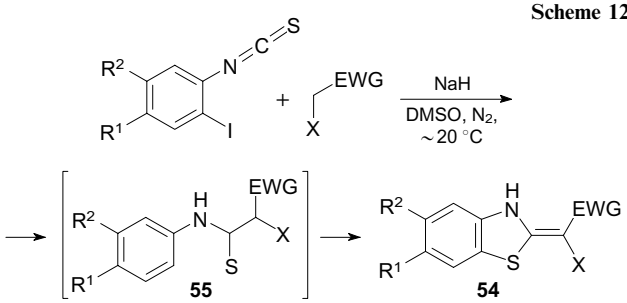


X = $CH_2$: $R_n$ = H (82%), 8-OMe (86%), 3-Me (81%), 9-$NO_2$ (21%);
X = C=O: $R_n$ = 3-Me (77%), 3-Cl (81%), 8,9-$(OMe)_2$ (86%)

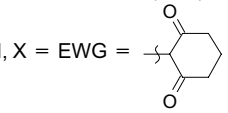
There are also known examples of the preparation of sulfur-containing five-membered heterocycles using the above-discussed reactions. The domino synthesis of 2-substituted benzothiazoles **54** includes base-induced one-pot addition of derivatives with an active methylene group to *o*-iodoaryl isothiocyanates and subsequent intramolecular formation of the C–S bond in the intermediate thioamidate anion **55** (Scheme 122).[293] A radical ($S_{RN}1$) mechanism was proposed for this cyclization. The reaction at room temperature proceeds within 1–3 h and gives products **54** in good yields.

The efficient synthetic pathway to 2,3-disubstituted benzothiophenes and their heterocyclic analogues developed by the same authors[294] (Scheme 123) includes a tandem reaction consisting of base-induced condensation

**Scheme 122**

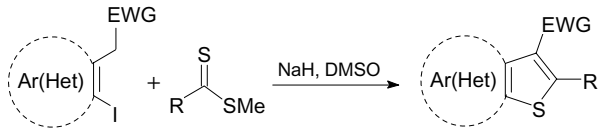


$R^1$ = $R^2$ = H: X = EWG = Ac (95%), Bz (95%);
X = CN, EWG is pyridin-2yl (96%);
$R^1$ = $R^2$ = OMe, X = EWG = Ac (67%);



$R^1$ = $CF_3$, $R^2$ = H, X = EWG = (93%)

**Scheme 123**



R is substituted aryl, Het, Alk, SMe,
OAlk, NHAr; EWG = CN, $CO_2$Et, COAr

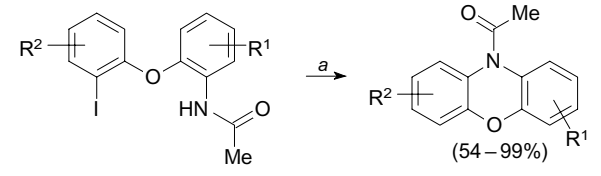
(80–98%,
28 examples)

of *o*-iodoarylacetonitriles, -acetates or -ketones with (hetero)aryl dithioesters and intramolecular C–S bond formation.

### 4.4. Synthesis of six-membered heterocyclic compounds

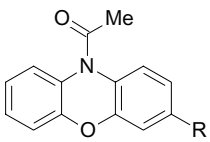
Non-catalyzed heterocyclization of N-acylated aryloxyanilines to give C–N bonds underlies an efficient approach to the synthesis of phenoxazines. The highest yields of cyclization products are attained with the $K_2CO_3$–DMEDA system (Scheme 124).[295] The cyclization products are obtained only from iodo derivatives. This method is inapplicable to substrates containing an alkyl or tosyl group

**Scheme 124**

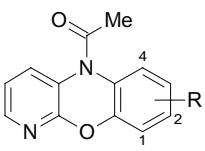


(*a*) $K_2CO_3$ (2 equiv.),
DMEDA (10 mol.%), PhMe, 135 °C, 24 h

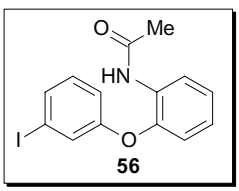
*Examples of products*



R = CN (64%),
OMe (79%),
Br (86%),
F (84%), $CF_3$ (84%)



R = H (100%),
3-Me (83%), 2-$CF_3$ (100%),
2-F (99%), 2-Br (98%)



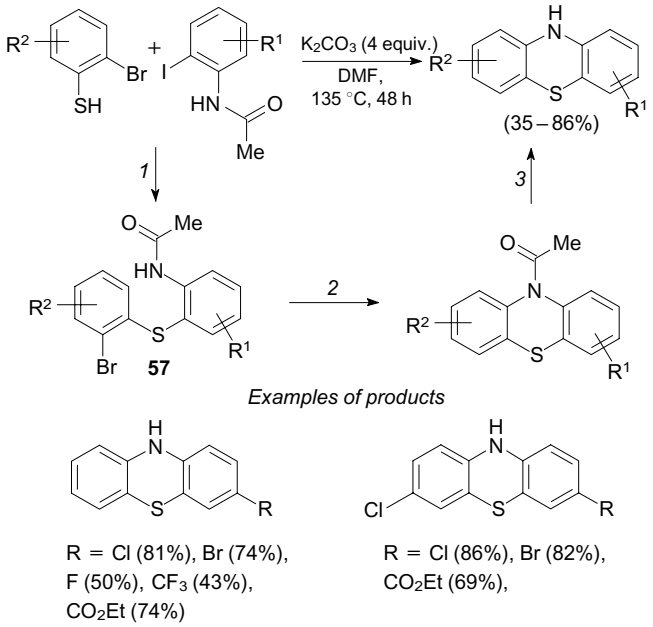
**56**

instead of the acetyl group at the nitrogen atom. The nature of the substituent in the aniline moiety of the starting compound barely influences the cyclization; conversely, the presence of electron-donating substituent in the iodoaryl moiety increases the yield of phenoxazines, although to a minor extent. This method is also applicable to the preparation of some aza analogues of phenoxazine.

In order to elucidate the mechanism of heterocyclization, the authors carried out a number of experiments, which did not unambiguously clarify the reaction mechanism, but provided the following conclusions. First, phenoxazines are formed exclusively in the presence of DMEDA or *trans*-*N*,*N*′-dimethyl-1,2-diaminocyclohexane (**49**). Second, the use of potassium carbonate of high purity (⩾99.999%, according to atomic absorption spectroscopy) virtually precluded the possibility of participation of trace amounts of transition metals in the reaction. Third, the aryne mechanism was also ruled out, because substrate **56** containing *m*-iodophenoxyl moiety (see Scheme 124) remained unchanged under the reaction conditions; particularly, it did not undergo cyclization and/or protodehalogenation. Fourth, the reaction proved to be insensitive to the presence of an equimolar mixture of radical scavengers in the reaction mixture; this indicates that the formation of radical intermediates is unlikely.

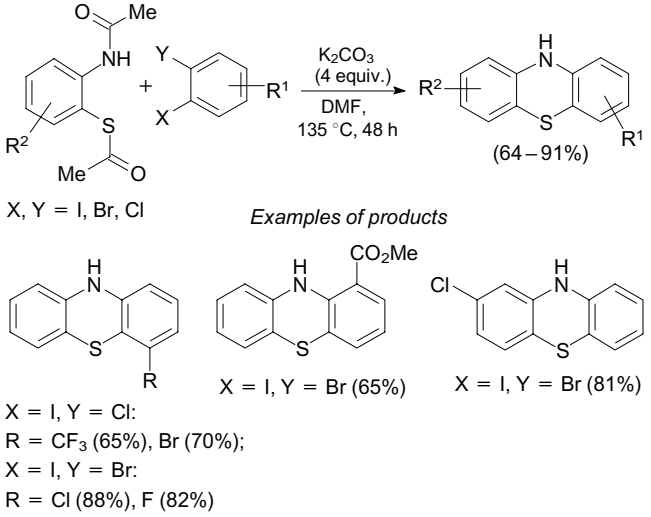
The tandem reaction of *N*-(2-iodophenyl)acetamides with 2-bromothiophenols in the presence of potassium carbonate in DMF gives rise to phenothiazines.[296] The reaction occurs without additional initiators and includes two successive steps of carbon–heteroatom bond formation. Initially, intermolecular formation of the carbon–sulfur bond takes place, yielding acyclic intermediate **57** (Scheme 125), which is the major product formed in the case of short-term heating. The second step is heterocyclization upon the intramolecular formation of the carbon–nitrogen bond, and the final step is the removal of the acetyl group. Experiments using radical scavengers demonstrated that the reaction apparently occurs without the formation of free radicals.

**Scheme 125**



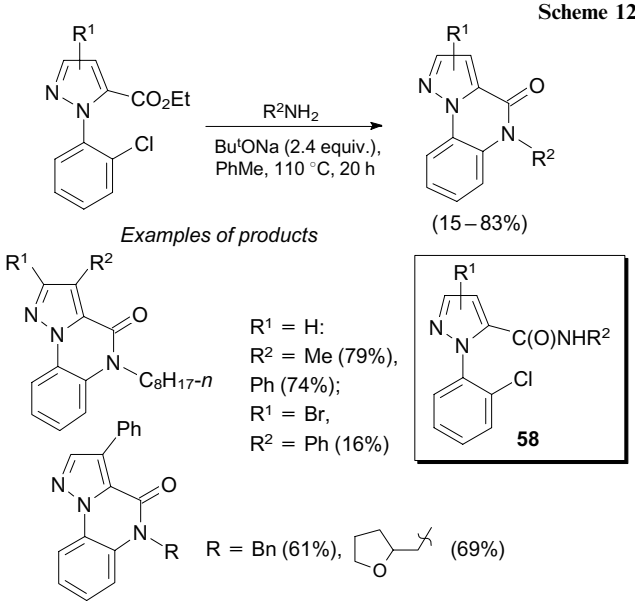

Phenothiazines are also formed as a result of a similar heterocyclization of *N*,*S*-diacetyl-2-aminobenzothiols with 1,2-dihalo-substituted benzenes induced by caesium carbonate in DMF (Scheme 126).[297] When radical scavengers were added to the reaction mixture, the yield of cyclization products significantly decreased. On the basis of experiments, the authors suggested that the reaction starts with base-promoted S-deacetylation of the substrate, which is followed by the intermolecular formation of the C–S bond. The heterocycle is formed upon the subsequent intramolecular formation of the C–N bond.

**Scheme 126**




One-pot synthesis of pyrazolo[1,5-*a*]quinoxalines from 1-(2-chlorophenyl)-5-(ethoxycarbonyl)pyrazoles and aliphatic primary amines includes the initial formation of pyrazolecarboxylic acid amides **58** (Scheme 127) and the subsequent intramolecular formation of carbon–nitrogen bond.[298] Experiments involving radical scavengers suggest that no radical intermediates are formed during this reaction. Base-promoted heterocyclizations of this type can also be used to prepare imidazo[1,5-*a*]quinoxaline derivatives

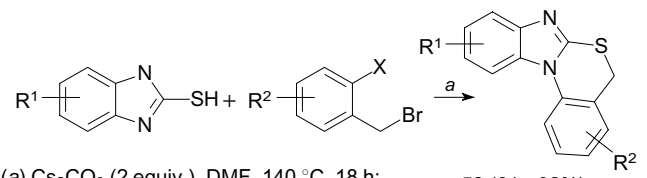
**Scheme 127**



upon cyclization of halo derivatives of imidazole-2-carboxylic acid *N*-arylamides.[299]

The domino reaction of 2-sulfanylbenzimidazoles with 2-halo-substituted benzyl bromides affords imidazobenzothiazines **59** *via* the successive formation of C–S and C–N bonds (Scheme 128).[300] The tetracyclic product is formed most efficiently in the presence of the $Cs_2CO_3$–DMF system. In the case of unsymmetrically substituted 2-sulfanylbenzimidazoles, the reaction gives a mixture of regioisomers.

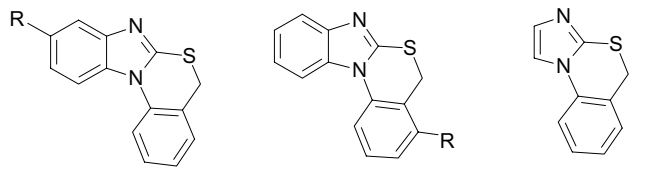
**Scheme 128**




(*a*) $Cs_2CO_3$ (2 equiv.), DMF, 140 °C, 18 h; X = I, Br

**59** (61–92%)

*Examples of products*



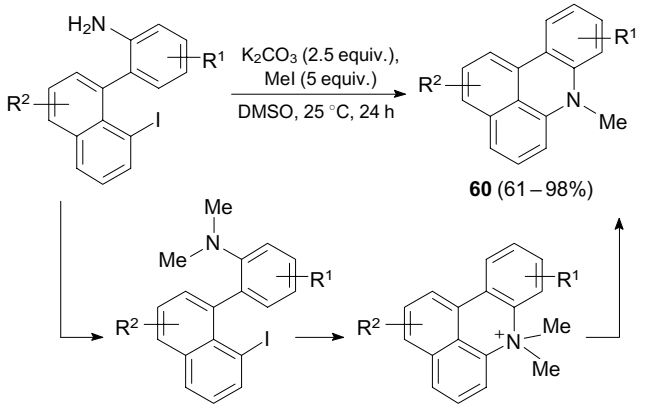

X = I: R = OMe (79%), $CF_3$ (72%), $NO_2$ (61%)

X = Br: R = $CF_3$ (87%), OMe (77%)

X = I (66%)

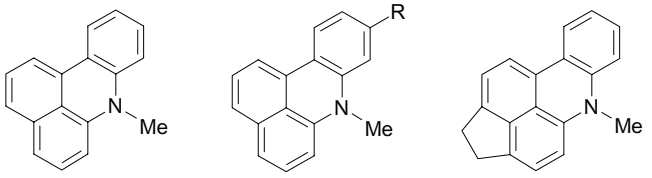
The reaction of substituted 1-(2-aminophenyl)-8-iodonaphthalenes with $K_2CO_3$ and excess MeI in DMSO furnishes π-fused systems **60** under mild conditions *via* intramolecular formation of the C–N bond. It was shown in special experiments that the N,N-dimethylation product is formed initially, and the subsequent heterocyclization of this compound involves tertiary amine and is accompanied by demethylation. Radical scavengers slightly decrease the yield of products **60**, but the experiments carried out by the authors rule out the aryne mechanism for the formation of cyclization products as well (Scheme 129).[301]

**Scheme 129**




**60** (61–98%)

*Examples of products*




(78%)

R = Me (86%), OMe (86%), Cl (98%)

(61%)

The papers considered in this part of the review were mainly published between 2010 and 2020, and the presented reactions are characterized by high preparative value owing to their efficiency, cost effectiveness and easy implementation. The key benefit of these reactions is that they do not require expensive and toxic catalysts based on transition metals, which can be successfully replaced by simple and readily available inorganic bases, organic ligands and solvents. Although special experiments aimed at making assumptions about the mechanism of amination of aryl halides were carried out almost in each study, reactions of this type cannot be assigned to any of known types of nucleophilic aromatic substitution. Nevertheless, the following general patterns can be distinguished for these reactions.

1. The reactions proceed efficiently in the presence of inorganic bases such as alkali metal carbonates, hydroxides and *tert*-butoxides. In most cases, the highest efficiency is attained by using potassium derivatives, although there are examples in which sodium and caesium bases perform better than potassium compounds.

2. The reactions proceed more easily in the case of iodo- and bromo-substituted substrates, while chloro derivatives have low reactivity. Fluoro-substituted substrates often show high reactivity, which may attest to a change in the reaction mechanism on going from iodo and bromo derivatives to fluorine compounds. In the latter case, the reactions may follow the $S_NAr$ mechanism or, more likely, the mechanism of concerted aromatic nucleophilic substitution.[302]

3. Apart from inorganic bases, for these reactions to proceed smoothly, special additives (aliphatic amines, heterocyclic compounds, *etc.*) should be present in the reaction mixture, or the reactions should be carried out in solvents containing donor heteroatoms (DMF, DMSO). The additives and solvents, in combination with the inorganic base used, play a key role in these reactions. In some cases, this role can probably be played by substrates; in these cases, the reactions successfully proceed in inert hydrocarbon solvents without the use of foreign additives.

## 5. Conclusion

The strategy of organic synthesis based on transition metal-free cross-coupling reactions has been intensively developed in recent years. A number of synthetic problems that could not be solved until recently without the use of transition metal-based catalysts are easily solved today using alternative methods for bond activation in organic molecules, in particular, SET processes. The use of visible light and electric current to induce single-electron oxidation and reduction of organic compounds allows the carbon–heteroatom bond-forming reactions to be conducted at room temperature for substrates containing functional groups incompatible with traditional cross-coupling reactions. In some cases, this activation increases the reactivity of organic molecules. The practical value of these methods is based on not only cost effectiveness associated with the absence of expensive catalysts. The reactions induced by

visible light and electric current can often proceed without strong oxidants. If these reactions are based on air oxygen as the oxidant, they can be assigned to green chemistry reactions. The attraction of these approaches to initiation of organic reactions is also related to the use of simple experimental equipment (glass reactors; diode and luminescent lamps, including household devices, as sources of visible light; and simple sources of direct current).

Special mention should be made of carbon–heteroatom bond formation reactions initiated by alkali metal bases. Despite the fact that these reactions often require drastic conditions, their main benefit is that they involve the same substrates and give the same products as classical cross-coupling reactions giving carbon–heteroatom bonds.

The further development of transition metal-free cross-coupling strategy is certainly of considerable fundamental and practical interest. In particular, a relevant task is the search for new reactions of this type that would provide efficient synthesis of compounds inaccessible by classical catalytic methods. In addition, it is worth concentrating on the development of new organic photoredox catalysts, in particular, to replace the expensive transition metal complexes that are widely used now. An equally important line of research is the development of new reagents that would allow reactions to be conducted using their own photochemical properties or without photocatalysts using electric current activation.

This review was prepared with the financial support of the Russian Foundation for Basic Research (Project No. 20-13-50056).

## 6. List of abbreviations and symbols

The following abbreviations and symbols are used in the review:

2-Bu$^t$-AQN — 2-*tert*-butylanthraquinone;
3DPAFIPN — 3,5-dicyano-2,4,6-tris(diphenylamino)-fluorobenzene;
4CzIPN — 1,2,3,5-tetrakis(carbazol-9-yl)-4,6-dicyano-benzene;
$[AcrMes]^+$ — 9-mesityl-10-methylacridinium cation;
All — allyl;
AQN — anthraquinone;
BDD — boron-doped diamond electrode;
Boc — *tert*-butyloxycarbonyl;
BPA — 1,1′-binaphthyl-2,2′-phosphoric acid;
bipy — 2,2′-bipyridine;
Cbz — benzyloxycarbonyl;
CFL — compact fluorescent lamp;
col — 2,4,6-collidine (2,4,6-trimethylpyridine);
Cp — cyclopentadienyl;
DABCO — 1,4-diazabicyclo[2.2.2]octane;
DABSO — DABCO complex with $SO_2$;
dba — dibenzylideneacetone;
DBU — 1,8-diazabicyclo[5.4.0]undec-1-ene;
DCA — 9,10-dicyanoanthracene;
DCE — dichloroethane;
DIPEA — *N*,*N*-diisopropylethylamine;
DMA — *N*,*N*-dimethylacetamide;
DME — dimethoxyethane;
DMEDA — *N*,*N*′-dimethylethylene-1,2-diamine;
DNs — dinitrophenylsulfonyl;
*dr* — diastereomeric ratio;
EB — eosin B;
EDA — electron donor–acceptor complex;
EWG — electron-withdrawing group;
*ee* — enantiometic excess;
EY — eosin Y;
Fmoc — 9-fluorenylmethyloxycarbonyl;
Fu — furyl;
HAT — hydrogen atom transfer;
HFIP — 1,1,1,3,3,3-hexafluoropropan-2-ol;
*m*-CBA — 3-chlorobenzoate;
Mes — 2,4,6-trimethylphenyl (mesityl);
Ms — methanesulfonyl (mesyl);
MS — molecular sieves;
MW — microwave radiation;
$Na_2$-EY — disodium salt of eosin Y;
Naph — naphthyl;
NBS — *N*-bromosuccinimide;
Ns — 4-nitrobenzenesulfonyl;
NuH — nucleophile;
PC — photoredox catalyst;
PC* — photoredox catalyst in the excited state;
PCET — proton coupled electron transfer;
PHT — *N*-phenylbenzo[*b*]phenothiazine;
PHTN-NH — *NH*-phthalimide;
pPy — piperidine;
PVDF — polyvinylidene fluoride;
Py — pyridine;
Tol — tolyl (methylphenyl);
Pyf — 2,3,5,6-tetrafluoropyridin-4-yl;
RB — rose bengal;
Rh-6G — rhodamine 6G;
Rh-B — rhodamine B;
*rr* — regioisomeric ratio;
RVC — is reticulated vitreous carbon electrode;
S — substrate;
SET — single-electron transfer;
TBHP — *tert*-butyl hydroperoxide;
TBP — tri-n-butyl phosphate;
TEMPO — (2,2,6,6-tetramethylpiperidin-1-yl)oxyl,
Tf — trifluoromethanesulfonyl (triflyl);
TFA — trifluoroacetic acid;
TFE — 2,2,2-trifluoroethanol;
TMS — trimethylsilyl;
TPT — 2,4,6-triphenylpyrylium tetrafluoroborate;
Ts — *p*-toluenesulfonyl (tosyl).

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