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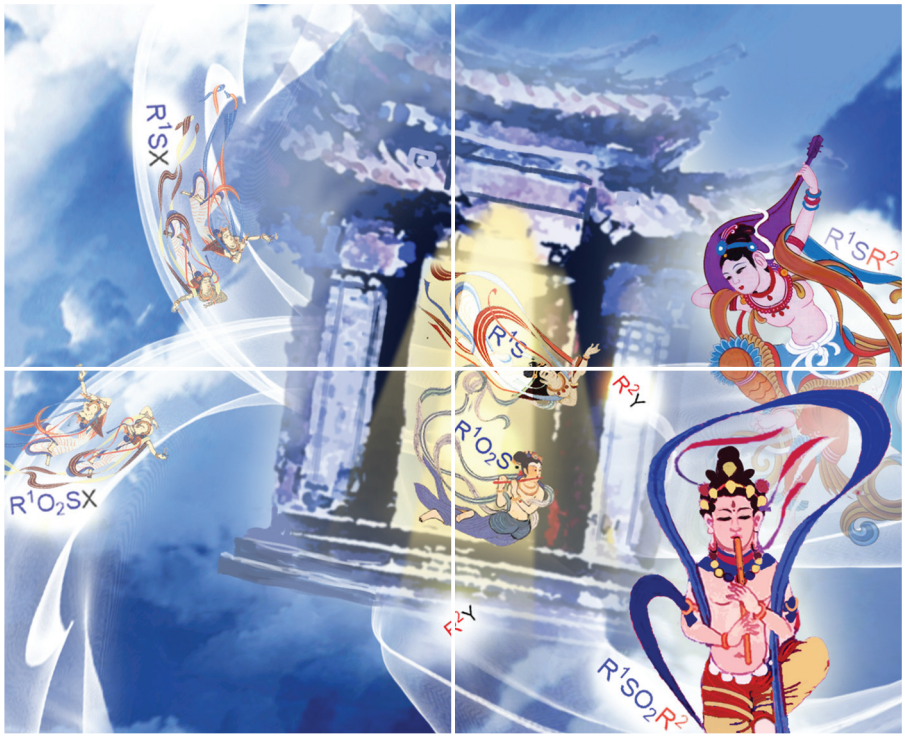

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REVIEW

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Recent advances in photocatalytic C–S/P–S bond formation *via* the generation of sulfur centered radicals and functionalization

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Thioyl and sulfonyl radicals are usually produced from various thiols and sulfonyl derivatives in high efficiency by single-electron-transfer (SET) oxidation. The generated sulfur (thioyl/sulfonyl) radicals are also highly reactive intermediates having various applications in the construction of organosulfur compounds in the field of organic synthesis. Recently, photoredox-catalyzed C–S/P–S bond formation *via* the generation of sulfur centered radicals has been studied extensively. In the photoredox catalytic process, a variety of S–H, S–S, S–C, S–N, and S–X (F, Cl, Br, I) bonds, and even active sulfone-containing skeletons can be easily transformed into the corresponding thioyl/sulfonyl radicals. Some of these transformations are achieved by a combination of photoredox catalysts (*i.e.*, TiO_2, Bi_2O_3, eosin Y, *fac*-$[Ir(ppy)_3]$, $[Ru(bpy)_3]^{2+}$) and other catalysts such as strong bases, Lewis acids, organocatalysts and transition metal catalysts. Compared with previous methods, photoredox catalysis is inexpensive and features the advantages of high efficiency and easy utilization in addition to being environmentally-benign. In this review, we have focused on the research on photoredox-catalyzed C–S/P–S bond formation *via* the generation of thioyl/sulfonyl radicals and further functionalization in the past few years. We hope to offer chemists the tools to open the door for further progress in organsulfur chemistry.

1. Introduction

Organosulfur compounds have been receiving increasing attention in medicinal chemistry, pharmaceuticals, chemical biology, and advanced functional materials.[1,2] Previous studies on the synthesis of organosulfur compounds require strong bases,

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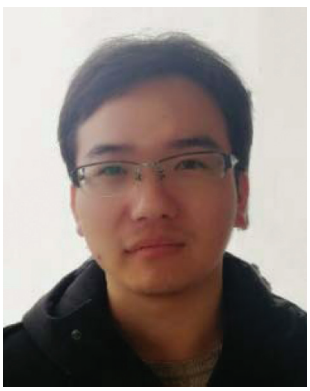

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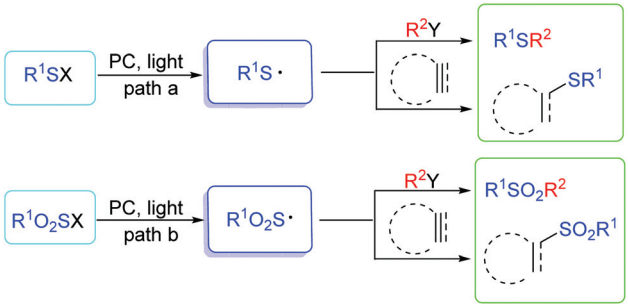
and/or stoichiometric oxidants, or rely on high reaction temperatures, or expensive and unavailable materials.[2e–h] Recently, sulfur centered radicals have served as important intermediates for the construction of organosulfur compounds.[3] Cahard's group also disclosed the redox potential of some sulfur precursors, which could help us understand the details.[4a] It is noted that the oxidation potential of some excited photocatalysts ($[Ru(bpz)_3^{2+}]^*$ = 1.4 V; rose bengal = 0.99 V; eosin Y = 0.83 V) are significantly more positive than that of the sulfur precursors.[4b–d] For example, the oxidation potential of benzyl thiol is +0.50 V,[4b,e] and for sodium benzenesulfinate it is −0.37 V.[4f,g] Thus, the direct photooxidation of thiol/sulfone-containing skeletons by photocatalysts is thermodynamically very favourable. Generally, there are many strategies to generate sulfur centered radicals for the synthesis of organosulfur compounds by the addition of peroxides, azo compounds, and organic catalysts (*e.g.*, $PhCOCO_2H$).[5] These transformations can be carried out under conditions of high temperature, UV irradiation or ultrasound, *etc.*[5,6] The functionalization of sulphur radicals in those strategies involve the addition of thioyl radicals to unsaturated bonds (alkenes, alkynes, *etc.*) or substitution with R–X (X = halides/H, *etc.*).[3d,5,6] For the past several years, photoredox catalysis has emerged as a useful tool for radical reactions for the synthesis of organosulfur compounds *via* visible-light induced processes.[7] Compared with previous methods, photoredox catalysis is inexpensive and features the advantage of being environmentally-benign in addition to high efficiency and ease of utilization. Commonly, visible-light photocatalysts mainly include metal-oxide-semiconductors, metal-ligand complexes, metal-organic frameworks, organic photosensitizers and so on. Among these photocatalysts, such as *fac*-$[Ir(ppy)_3]$ (bpy = 2,2′-bipyridine; ppy = 2-pyridylphenyl), $[Ru(bpy)_3]^{2+}$, eosin Y, eosin B, and rose bengal can be used to trigger the photooxidation or photoreduction process.

This review mainly highlights the recent advances in visible light induced C–S/P–S bond formation for the synthesis of organosulfur compounds *via* the generation of sulfur centered radicals. There are two major approaches for the construction of these organosulfur compounds including the highly reactive thioyl radical species (Scheme 1, path a), or the sulfonyl radical species in a controllable way (Scheme 1, path b). In the photoredox catalytic process, a variety of S–H, S–S, S–C, S–N, S–X (F, Cl, Br, I) bonds, and even active sulfone-containing skeletons can be easily transformed into the corresponding thioyl/sulfonyl radicals by single-electron-transfer (SET) oxidation. Further transformations could be divided into two types: radical substitutions and radical addition reactions. In this context, such catalytic strategies have also proved to be mild and general tools for the conversion of thioyl/sulfonyl radicals, thus enabling the achievement of a wide variety of new chemical reactions towards the synthesis of diversely functionalized organosulfur molecules. Elegant achievements from the most recent literature also demonstrate the significance of this fast developing area of research.



Scheme 1 Two major approaches for the generation of sulfur centered radicals and their functionalization.

2. Visible-light induced C–S/P–S bond formation *via* the generation of thioyl radicals

2.1. C(sp^3)–thioyl radicals coupling reactions

The majority of research studies on the thiolation of unactivated C(sp^3)–H bonds have focused on the transition-metal-

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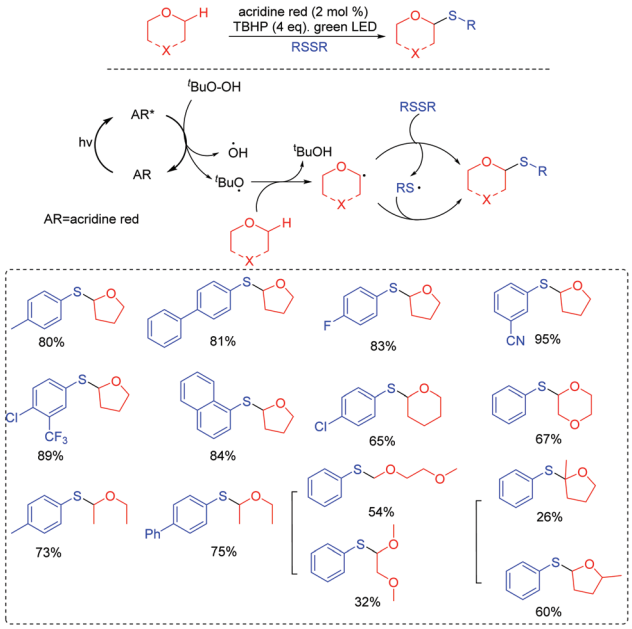
catalyzed process.[8] However, those transformations could demonstrate excellent functional group tolerances. It is noted that the use of transition metals would limit the suitability of its substrates in organic synthesis. To the best of our knowledge, visible-light photoredox-controlled C(sp^3)–H thiolations are particularly rare, especially the selective introduction of sulfur.[9] Wang and co-workers presented a protocol to access α-arylthioethers *via* visible-light induced direct thiolation at α-C(sp^3)–H of ethers with diaryl disulfides in the presence of acridine red (Scheme 2).[10] The reactions exhibited advantages including ambient conditions (room temperature and air), eco-energy sources, and good functional group compatibilities. It is the first example of a coupling reaction through the energy transfer method under visible light irradiation. In this case, the authors proposed that the formed excited state acridine red (AR)* interacted with ^{t}BuOOH (TBHP) *via* an energy transfer method to generate the ^{t}BuO$^\bullet$ species. Then, the trapping of ^{t}BuO$^\bullet$ with ethers resulted in the propagation and formation of the alkoxyalkyl radical. Finally, the alkoxyalkyl radical could couple with the thioyl radical to give the desired product.

In 2017, our group also succeeded in the utilization of thioyl radicals derived from thioureas for the construction of 2-iminothiazolidin-4-ones scaffolds *via* C(sp^3)–thioyl radical coupling reactions under visible-light promoted conditions (Scheme 3).[11] The reaction was also found to tolerate a range of functional groups, such as monosubstituted, disubstituted, trisubstituted, and heterocyclic benzylamines, various aliphatic amines, and even 3-morpholinopropan-1-amine, which provided potential applications in drug screening. Moreover, UV–vis spectroscopy revealed that an *in situ*-generated H-bonding electron donor–acceptor (EDA) complex probably acted as the photocatalyst, promoting the reaction process. On the basis of several control experimental results, we proposed a plausible reaction mechanism. First, the amine reacts with isothiocyanate to form intermediate **1**. Next, **1** couples with α-bromoester to deliver the H-bonding EDA complex **2**. Then, **2** releases radicals **3** and **4** through hemolytic dissociation.

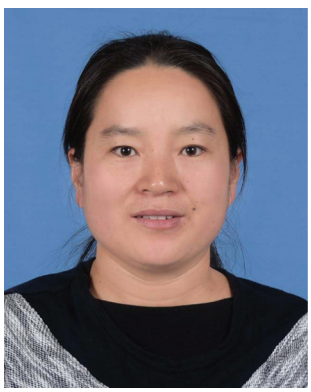


Scheme 2 Direct thiolation at α-C(sp^3)–H of ethers.

Furthermore, intermediate **1** can also be converted into intermediate **5** by isomerization, which is further oxidized to intermediate **6**. Subsequently, the radical coupling of thioyl radical **6** with radical **4** gives intermediate **7**. Finally, intermediate **7** can afford the desired product by intramolecular cyclization.

2.2. C(sp^2)–thioyl radical coupling reactions

2.2.1. Vinylic substitution reactions. The trifluoromethylthio (SCF_3) group has attracted increasing attention in the pharmaceutical and agrochemical fields because of its highly lipophilic and electron-withdrawing properties. Trifluoromethylthiolation of alkenes plays an important role in the synthesis of vinyl-SCF_3 compounds. This transformation could be successfully used to construct a wide range of SCF_3-containing compounds.



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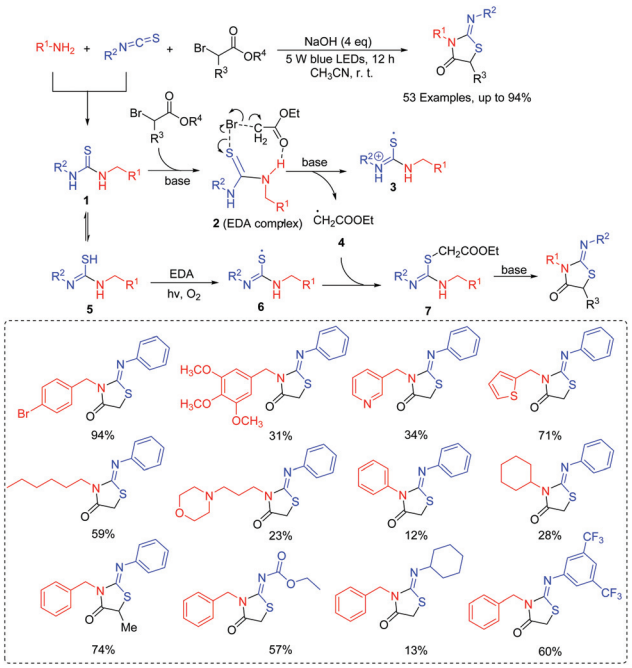
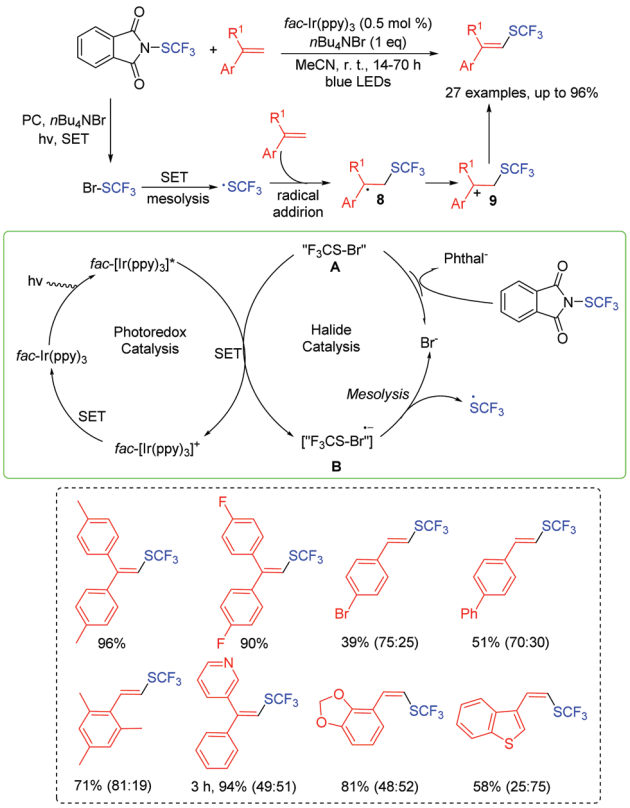


Scheme 3 Synthesis of 2-iminothiazolidin-4-ones.

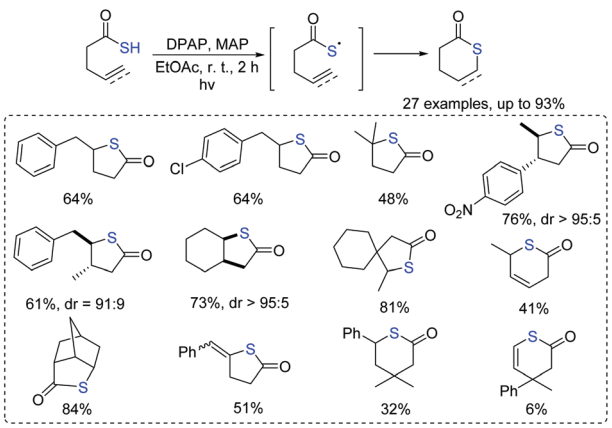
Glorius's group developed a visible-light photoredox-controlled C(sp^2)–H direct trifluoromethylthiolation with SCF_3 radicals to access various vinyl-SCF_3 products under mild conditions (Scheme 4).[12] This approach allowed for the efficient addition of the SCF_3 group to aryl-, alky- and heteroaryl substituted alkenes with yields up to 96%. The proposed mechanism for the formation of vinyl-SCF_3 products is shown in Scheme 4. SCF_3-halide species **A** initially interacts with the excited *fac*-Ir(ppy)$_3$ and undergoes a single-electron oxidation process to form species **B**. Then, the species **B** affords the SCF_3 radical and regenerates the halide *via* the mesolytic process. Subsequently, the SCF_3 radical is directly added to the alkene and further gives the alkyl radical **8**. Next, the alkyl radical **8** is successfully converted into the corresponding aryl-stabilized cation **9**, affording the desired product *via* deprotonation.



Scheme 4 Trifluoromethylthiolation of styrenes.

2.2.2. Addition to alkenes. Thiolactones play an important role in chemical biology,[13] medicinal chemistry,[14] drug discovery,[15] and materials science.[16] More attempts have also been developed to synthesise thiolactones due to its wide applications.[17] Various organosulfur compounds can be successfully obtained through the radical thiol–ene coupling of alkenes and thiols.[18–20] Furthermore, the difunctionalization of alkenes *via* a radical pathway also attracts much attention with the addition of visible light photoredox catalysts.[21] Therefore, alkenes are usually used as radical acceptors to react with S-radicals to provide radical addition products.

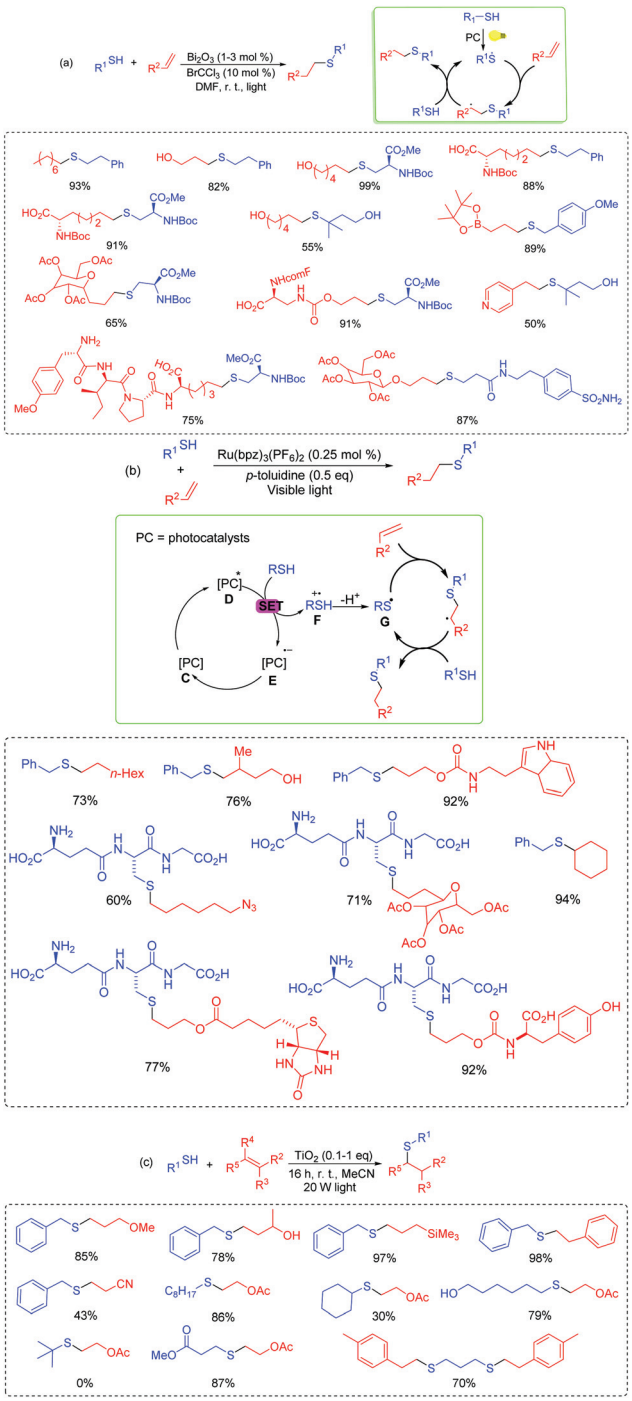
Scanlan *et al.* reported the intramolecular reactions of acylthioyl radicals with alkene or alkyne moieties to access thiolactones in the presence of visible light (Scheme 5).[18] The present methodology tolerated a wide range of functionalities, including alkyl, aromatic, and alkyne-containing groups.



Scheme 5 Synthesis of thiolactone derivatives.

Moreover, fused and spiro-bicyclic thiolactones could be prepared successfully in good yields.

Besides the intramolecular reactions, Robinson *et al.* developed a visible-light driven photocatalytic initiation system of hydrothiolation of alkenes using Bi_2O_3 as the photoredox catalyst (Scheme 6a).[19] This transformation facilitated widely functional group tolerances. Alkyl, benzyl, acyl, various Boc-protected cysteines, free hydroxyl, and even cyclohexyl tertiary thiols, all served good to excellent yields. Furthermore, the



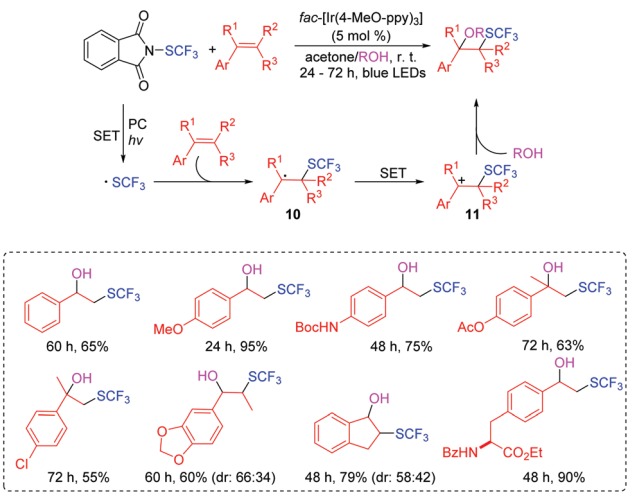
Scheme 6 Reactions of thiols and alkenes.

sulfur atoms have been successfully introduced to various complex biologically active relevant scaffolds and complex drug-like molecules, affording the corresponding active products in high yields.

Yoon and co-workers have also succeeded in the intermolecular reaction of radical thiol–ene conjugation from varied thiols and alkenes in the presence of photoredox catalysts (Scheme 6b).[4b] Not only aliphatic thiols, secondary thiols, and thiols with free hydroxyl could perform smoothly, but more importantly, glutathiones also reacted with a variety of coupling partners of potential biologically active molecules and gave the corresponding products in good yields.

Simultaneously, Greaney's group disclosed a titania photoredox route for the thiol–ene reaction *via* a visible-light induced transformation (Scheme 6c).[20] The reaction proceeded at room temperature for all kinds of aromatic and aliphatic thiols and alkenes, and tolerated various functionalized substrates (alcohols, esters, silanes, and nitriles). However, the *tert*-butyl thiol failed to react with the alkene and no desired product was detected. The proposed mechanism for the photocatalytic initiation of the radical thiol–ene reactions are clearly depicted in Scheme 6b. Thiol initially interacts with the excited organophotocatalyst **D** and undergoes a single-electron-transfer oxidation process to form intermediate **F**. Then the deprotonation of **F** gives thioyl radical **G**. Subsequently, the thioyl radical can initiate the thiol–ene cycle through the addition to an alkene and the generation of an alkyl radical, which propagates the reaction and affords the desired product by abstracting a hydrogen atom from the thiol starting material.

Organofluorine compounds have found increasing applications in the medicinal, pharmaceutical, agricultural, and materials sciences.[22,23] In 2016, Akita's group disclosed a photocatalytic radical oxy-trifluoromethylthiolation of aromatic alkenes under mild and simple reaction conditions at room temperature without the addition of any activators for the SCF_3 reagent (Scheme 7).[24] During the course of trifluoromethylthiolation of alkenes, the selective incorporation of oxygen-nucleophilic reagents such as water and alcohol were compatible, affording the corresponding products with good to excellent efficiencies. The proposed reaction mechanism is outlined in Scheme 7. The generated SCF_3 radical reacts with aromatic alkene to form product **10**, which is oxidized to give the carbocationic intermediate **11**. Intermediate **11** is attacked by water/or alcohol to afford the oxytrifluoromethylthiolated product.

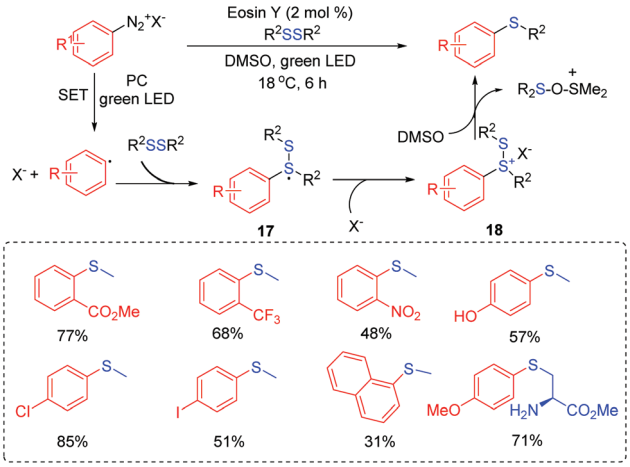


Scheme 7 Trifluoromethylthiolation of aromatic alkenes.

2.2.3. Addition to aldehydes. Besides the addition to alkenes, the thioyl radicals could also be added to aldehydes. In 2018, Lee and co-workers succeeded in the utilization of thioyl radicals for the thioacetalization of aldehydes *via* a visible-light photoredox-catalyzed process under metal-free and solvent-free conditions (Scheme 8).[25] This strategy widely facilitated functional group tolerance. Aromatic, heteroaromatic, and α,β-unsaturated aromatic rings all provided good to excellent yields. In the transformation, the generated intermediate **12** *via* a single-electron oxidation process can be further converted into the thioyl radical through the deprotonation process. Next, the radical addition of the thioyl radical to aldehydes produces intermediate **13**. Trapping of **13** with another thiol gives intermediate **14**, which subsequently affords intermediate **15** *via* the elimination of its water molecule. The other thioyl radical then reacts with **15** to afford intermediate **16**. Finally, the single-electron reduction of **16** affords the dithioacetal products.

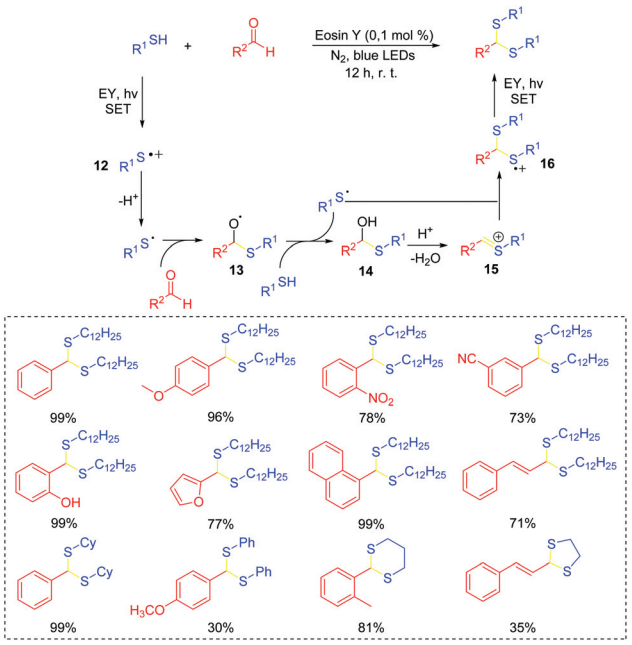
2.3. Aryl carbon–thioyl radicals coupling reactions

2.3.1. Ar–X substitution reactions. Generally, aryl sulfides have been synthesized through the transition metal-catalyzed cross-coupling of aryl halides with thiols. Herein, von Wangelin and co-workers developed a photocatalytic thiolation protocol for the synthesis of arylsulfides from arenediazonium salts in the presence of eosin Y (Scheme 9).[26] The reaction tolerated a variety of esters, nitro groups, and halides (F, Cl, Br, I) and so on, which could be used to perform further functionalization. The reaction pathway presumably initiates the formation of the aryl radical *via* the SET reduction by the excited photocatalyst. Next, the aryl radical is attacked by the nucleophilic disulfide to give a stable thioyl radical **17**. Then, the formed intermediate **17** can be further converted into intermediate **18** *via* one electron oxidation. Finally, **18** would be transformed into the desired products in the presence of a large excess of DMSO *via* the substitution process.

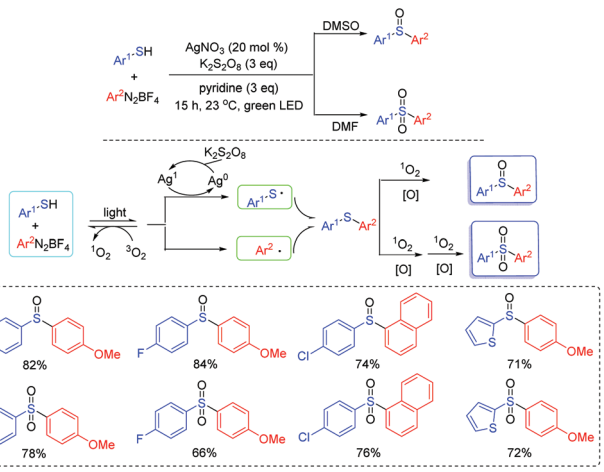


Scheme 9 Visible-light induced aryl sulfide reactions.

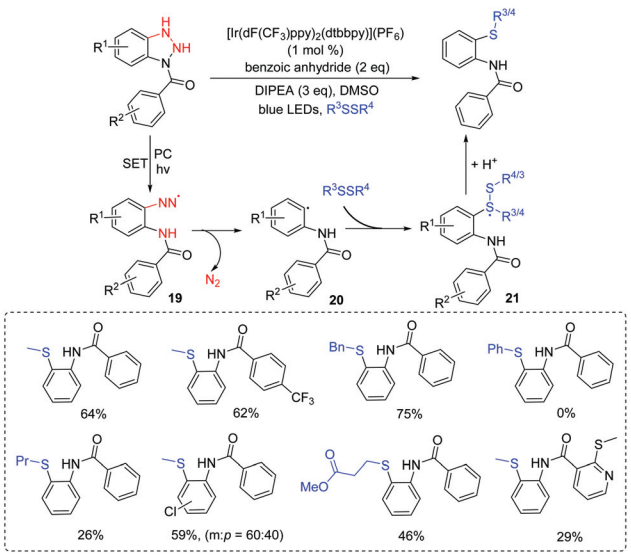
Aryl sulfoxides and aryl sulfones play a significant role in numerous organic compounds and drug candidates as building blocks[27] and exhibit many important biological activities.[28] In 2017, Lee's group developed a visible-light driven one-pot approach for the synthesis of diaryl sulfoxides and diaryl sulfones from aryl thiols and aryl diazonium salts using silver catalysis in the absence of a photocatalyst (Scheme 10).[29] As for the reaction mechanism, the thioyl radical and the aryl radical are initially generated by the silver catalyst through visible light irradiation. Then, the formed thioyl radical couples with the aryl radical to deliver the thioether intermediate. Finally, the thioether intermediate is oxidized to the desired product. The transformation does not require the pre-activation of aryl thiols. Therefore, the method facilitates the rapid access to various aryl sulfoxides and aryl sulfones.



Scheme 8 Thioacetalization of aldehydes.



Scheme 10 Synthesis of diaryl sulfoxides and diaryl sulfones.

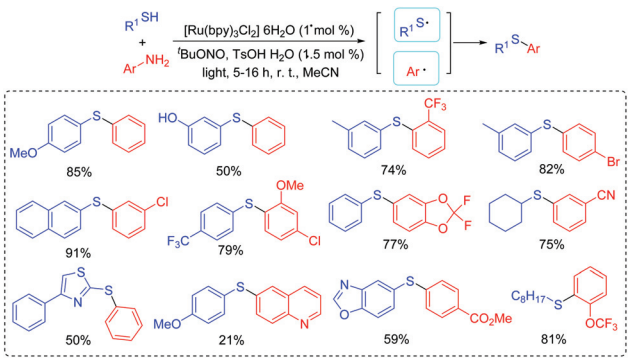


Scheme 11 Denitrogenative thiolation of benzotriazoles.

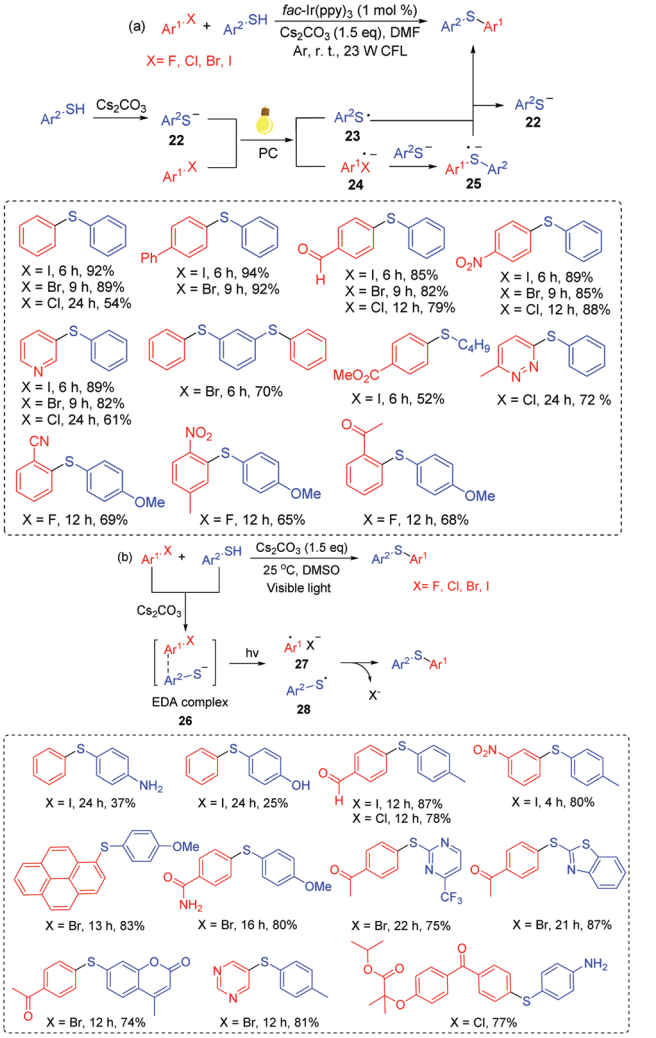
Glorius and co-workers reported a protocol for direct C–S bond-forming denitrogenative transformations to access *o*-thiolated *N*-arylbenzamide derivatives. The strategy facilitated a novel disconnection process *via* visible-light irradiation under mild conditions (Scheme 11).[30] Benzotriazoles with alkyl, halides, and heterocyclic groups were suitable coupling partners. Moreover, disulfide derivatives with alkyl and benzyl groups could react with benzotriazoles smoothly. However, aryl disulfides failed to give the corresponding products. For the reaction mechanism, the highly active intermediate **19** is generated *via* visible light irradiation under standard conditions, which immediately extrudes nitrogen to afford the aryl radical **20**. Intermediate **20** can add to the disulfide coupling partner to give the stabilized radical **21**. Trapping of the intermediate **21** with another proton affords the desired *o*-thiolated *N*-arylbenzamide product.

Noël's group developed a simple photoredox catalytic Stakler–Ziegler reaction to prepare arylsulfides from arylamines and aryl/alkylthiols at room temperature with minimum formation of diazosulfides (Scheme 12).[31] In this case, thiophenol with an active free hydroxy group gave the corresponding product in good yields, which could be subject to further modification. Notably, the generated diazonium salt intermediates were not isolated and afforded the aryl radicals. Subsequently, the radical coupling reactions of the generated thioyl radicals with the aryl radicals produced the desired products.

Fu and co-workers developed the representative arylation of thiols with aryl halides *via* a visible-light photoredox reaction at room temperature (Scheme 13a).[32a] This transformation explored readily available aryl halides as the arylating reagents and led to various desired products in good to high yields. In this process, the arylation of thiols tolerated various functional groups, including ether, ketone, aldehyde, ester, nitro, trifluoromethyl and an N-heterocycle. For the reaction mechanism, thiolate anion **22** is generated in the presence of Cs_2CO_3. Then, **22** can be converted into thioyl radical **23** through single-electron transfer (SET) oxidation. The reduction of aryl halides affords the radical anion **24**. Subsequently, the



Scheme 12 Reactions of arylamines and aryl/alkylthiols.



Scheme 13 Arylation of thiols with aryl halides.

transformation of **24** with another Ar^2S^- anion affords the sulfur-centered radical anion **25**. Finally, the reaction of **25** with thioyl radical **23** gives the desired product with the release of Ar^2S^- anion *via* the single-electron transfer process.

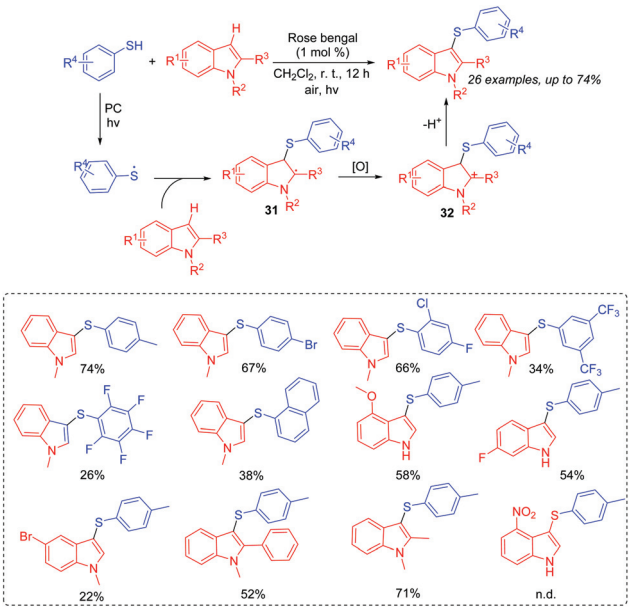
Miyake's group further managed to expand the strategy for the C–S cross-coupling of thiols and aryl halides without the use of either transition metals or photoredox catalysts (Scheme 13b).[32b] A wide range of organosulfur compounds were constructed under mild, efficient visible-light irradiation. Especially, a number of pharmaceutical ingredients and biologically active molecules have been modified, affording the desired products in high yields. In this case, an EDA complex **26** is generated from a thiolate anion and an aryl halide under Cs_2CO_3 conditions. Next, intermediates **27** and **28** are generated *via* electron transfer under visible-light induced conditions. Finally, the coupling reaction of **27** with **28** affords the target products.

2.3.2 Ar–H substitution reactions. In 2012, the visible-light photoredox synthesis of 2-substituted benzothiazoles by using $Ru(bpy)_3^{2+}$ as the photocatalyst under room temperature was developed by Li and co-workers (Scheme 14).[33] A series of 2-substituted benzothiazoles were obtained smoothly in good to excellent yields without any other reactive reagents. In this process, the generated sulfur radical **29** attacks the benzene ring to form intermediate **30**. Then, the re-aromatization of radical **30** provides the desired product.

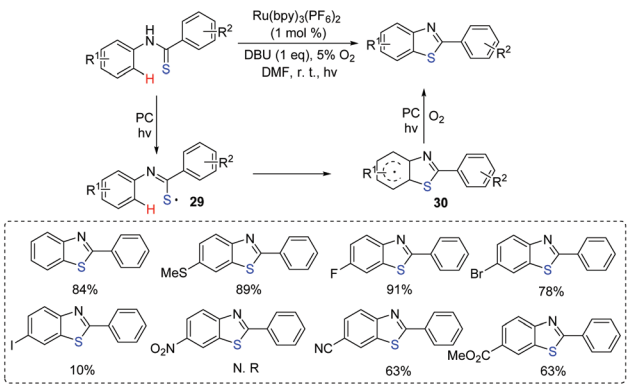
3-Substituted indoles compose an important skeleton in natural products, agrochemicals, and functional materials.[34] The development of simple and efficient procedures for the acquisition of 3-sulfenylindoles from easily available starting materials under mild conditions continues to attract the interest of organic chemists because of the remarkable application values of the targeting products. Photocatalytic direct construction of the C–S bond for the preparation of 3-sulfenylindoles is still an appealing process.

In 2017, our group reported the visible-light induced transformation of indoles into 3-sulfenylindoles (Scheme 15).[35] It is noted that the reaction system employed rose bengal as the photocatalyst, which provided a more convenient and environmentally friendly process compared with previous studies. Various indoles with electron-donating and electron-withdrawing groups were good coupling partners. Control experiments showed that the generated thioyl radical addition to the indole to form the radical intermediate **31** was a key step. The oxidation of **31** afforded intermediate **32**, which further underwent the deprotonation process to deliver the desired 3-substituted indole product. Subsequently, Barman's group also reported a similar strategy for the C-3 sulfenylation of imidazopyridine derivatives from the reaction of indoles with thiols (Scheme 16).[36]

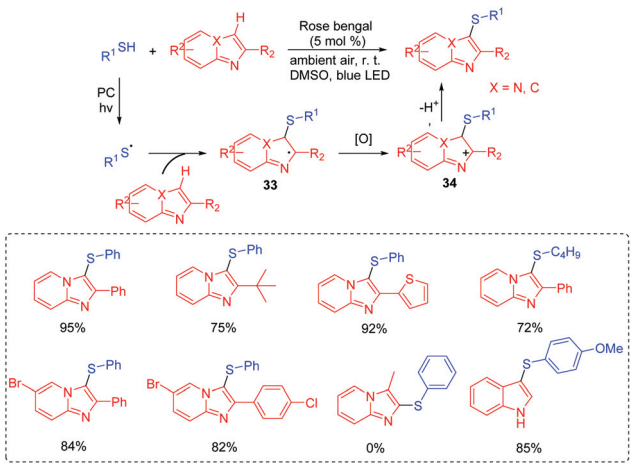
Additionally, Wang's group also developed a protocol for the regioselective C-3 sulfenylation of heteroaryl compounds to synthesize heteroaryl sulfides at room temperature using eosin



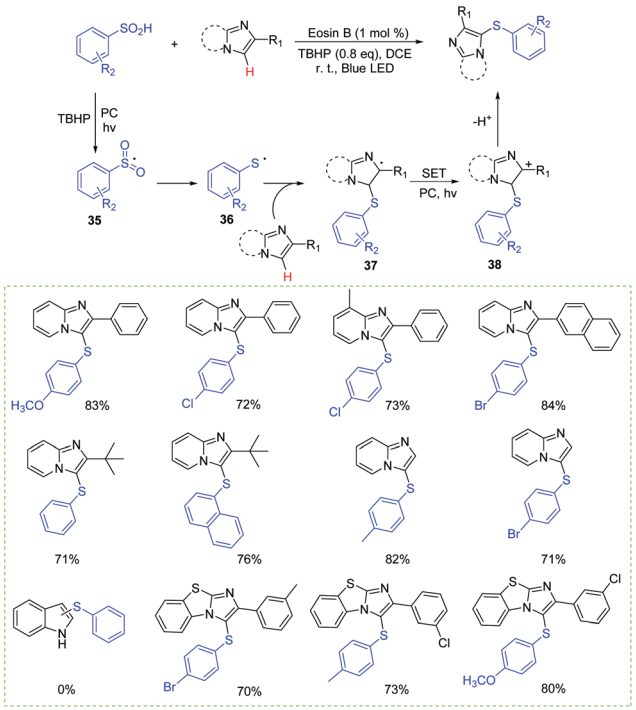
Scheme 15 Synthesis of 3-thioindoles.



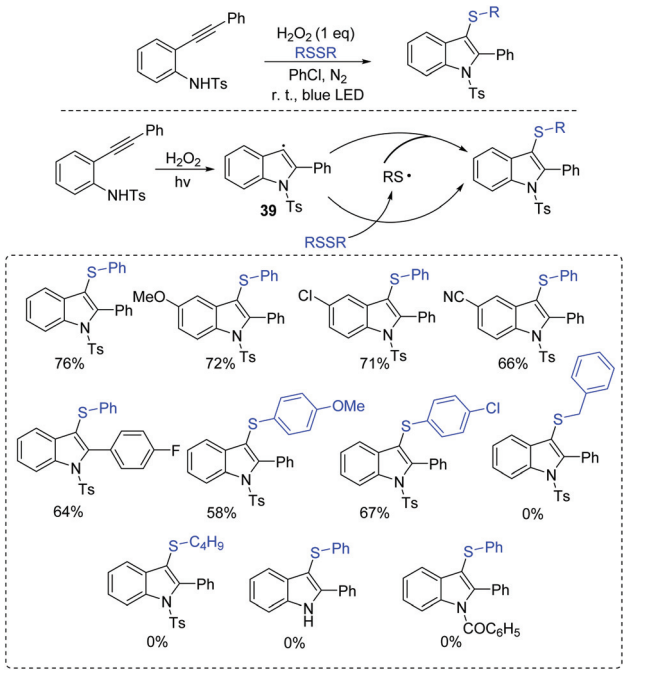
Scheme 14 Synthesis of 2-substituted benzothiazoles.



Scheme 16 Regioselective sulfenylation of imidazopyridines.



Scheme 17 Synthesis of heteroaryl sulphides.

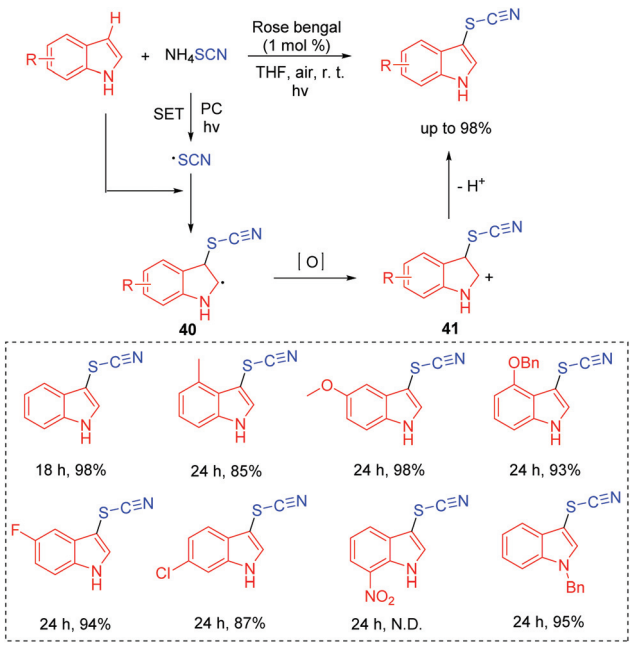


Scheme 18 Reaction of 2-alkynylanilines with disulfides.

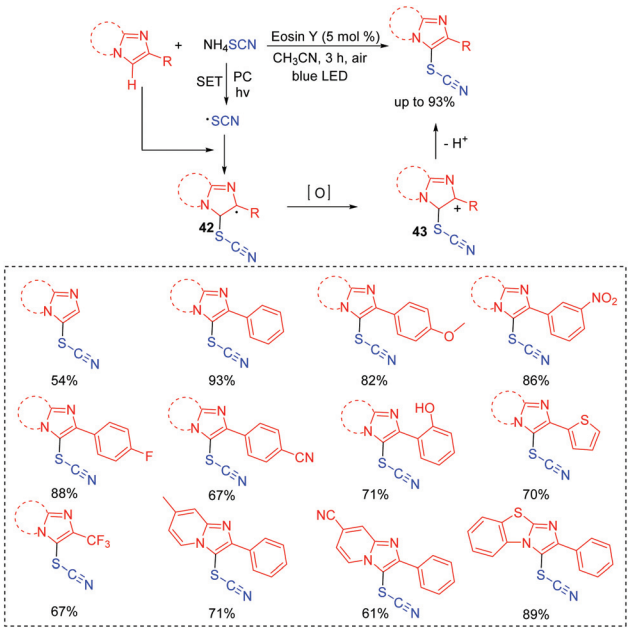
B as the photocatalyst (Scheme 17).[37] Generally, the desired products were obtained in moderate to good yields with a wide range of imidazopyridines, including those derived from the naphthalene group and the tertiary butyl group. Unfortunately, 1*H*-indole failed to react with sulfinic acids and no desired product was detected. A proposed mechanism for the formation of heteroaryl sulfide derivatives is shown in Scheme 17. Firstly, the generated sulfonyl radical **35** is converted into thioyl radical **36** *via* a sequence of reduction reactions. Then, the addition of thioyl radical **36** to a heteroaryl compound produces the radical intermediate **37**, which can be further transformed into intermediate **38** *via* the SET process. Finally, the attack of the sulfonic acid anion by the β-H of intermediate **38** affords the desired product.

In 2017, Wang *et al.* reported an improved strategy for the synthesis of 3-substituted indoles from 2-alkynylanilines with disulfides in the presence of H_2O_2 under transition-metal-free and photocatalyst-free conditions (Scheme 18).[38] In this process, the *in situ* generated indoles from 2-alkynylaniline deliver the aromatic carbon radical **39**. Finally, the formed intermediate **39** interacts with the disulfide/or thioyl radical to afford the desired product.

Thiocyanates are usually transformed into trifluoromethyl sulfides, sulfonyl chlorides, thiols, thiocarbamates, heterocycles, disulfides, and thioethers.[39–41] In 2014, Li and coworkers developed a direct C-3 thiocyanation of indoles in the presence of rose bengal at room temperature (Scheme 19).[4c] Generally, the reaction worked well either with weak electron-withdrawing group or with electron-donating group substituted indoles, affording the corresponding 3-thiocyanoindoles in good to excellent yields. A possible explanation for this transformation is illustrated in Scheme 18. Firstly, the formed SCN radical reacts with indole to afford intermediate **40**. Then, intermediate **40** is converted into intermediate **41** by oxidization, which further gives the desired product by losing a proton.



Scheme 19 C-3 Thiocyanation of indoles.



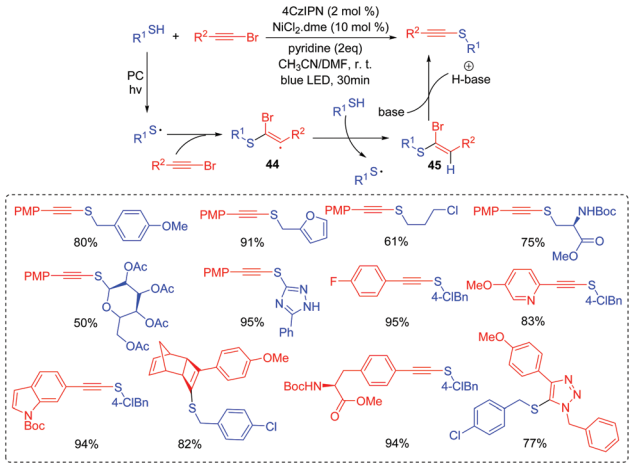
Scheme 20 Thiocyanation of imidazoheterocycles.

Additionally, Hajra's group also developed a similar protocol for the C-3 thiocyanation of imidazoheterocycles at room temperature *via* visible-light promoted by using eosin Y as the photocatalyst (Scheme 20).[4d] The reaction exhibited a wide range of functional group tolerances, such as imidazopyridines with the hydroxy group also afforded the desired product in a good yield. The transformation initiates the formation of the SCN radical by the SET mechanism. Then, the resulting SCN radical interacts with imidazoheterocycle to give intermediate **42**, which is oxidized to intermediate **43**. Finally, intermediate **43** is converted into the desired product *via* the aromatization process.

2.4. C(sp)–thioyl radical coupling reactions

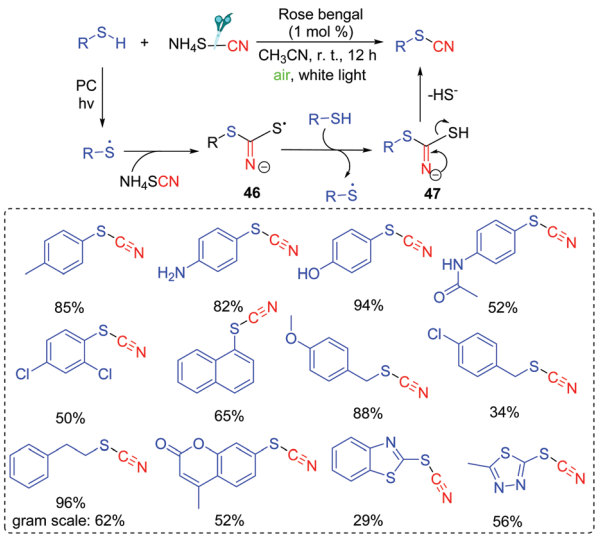
2.4.1. Alkynyl halide substitution reactions. Alkynyl sulfides play a significant role in organic synthetic chemistry, and has usually served as a synthetic precursor for the construction of organosulfur compounds.[42] In 2017, Collins and co-workers developed a novel strategy for the direct construction of alkynyl sulfides through a photochemical dual-catalytic system (Scheme 21).[43] It is the first example of the visible light photoredox-controlled process to construct a C(sp)–S bond. The method showed a wide range of functional group tolerances. The preparation of alkynyl sulfides bearing a wide range of electronically and sterically diverse aromatic alkynes and thiols can be achieved in good to excellent yields. In this study, the addition of the generated thiol radical into the bromoalkyne can form radical **44**. The coupling of another thiol with **44** produces intermediate **45**. Finally, the base-mediated elimination of **45** affords the expected product.

2.4.2. SCN substitution reactions. Recently, we reported a novel thiocyanation strategy for the synthesis of thiocyanates



Scheme 21 Synthesis of alkynyl sulfides.

through direct photocatalytic S–H bond cyanation from thiols and inorganic thiocyanate salts (Scheme 22).[44] Only 1.0 mol% of the photocatalyst (rose bengal) was required for the formation of the thiocyanate compounds up to 96% yield. This transformation features nontoxic and inexpensive green "CN" sources and shows excellent functional group tolerances. To further demonstrate the application value of this method, we successfully synthesized some potential drug intermediates and biologically active molecules to the corresponding skeletons in moderate yields. When benzeneselenol was used as the substrate under standard reaction conditions, selenocyanatobenzene was obtained. The result indicates that the CN unit of selenocyanatobenzene derives from the cleavage of the C–S bond in the NH_4SCN. As expected, the reaction of 4-methylbenzenethiol with NH_4SeCN also gave the corresponding desired 1-methyl-4-thiocyanatobenzene, which further shows



Scheme 22 Photocatalytic S–H bond direct cyanation.

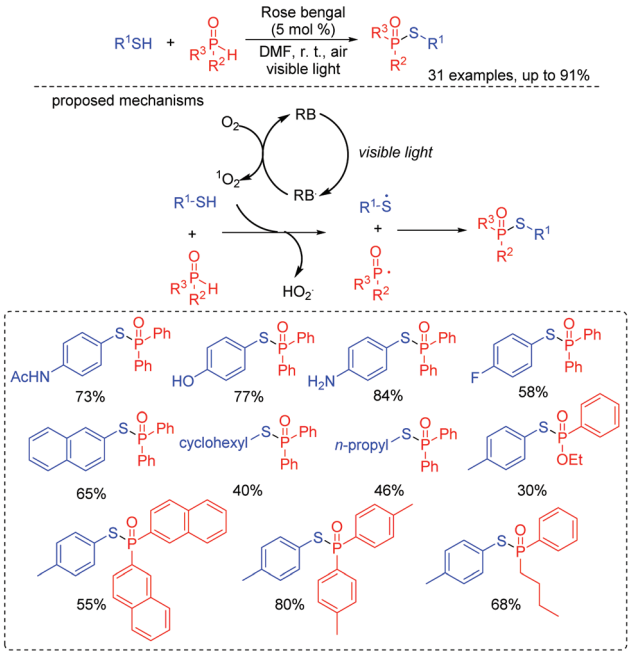
that the sulfur element of 1-methyl-4-thiocyanatobenzene derives from 4-methylbenzenethiol, rather than NH_4SCN.

A possible mechanism is shown in Scheme 22. The generated thioyl radical under the irradiation of visible light couples with SCN^- to form intermediate **46**. Trapping of intermediate **46** with another thiol can result in the propagation and formation of intermediate **47**. With the release of HS^-, **47** is further converted into the desired thiocyanate product.

2.4.3. Addition to nitriles. 2-Substituted benzothiazoles are important molecules used as medicinal agents and organic functional materials such as fluorescent dyes and liquid crystals.[45] Natarajan's group reported the synthesis of 2-substituted benzothiazoles from thiophenols and nitriles *via* the visible-light photoredox reaction under air (Scheme 23).[46] This method provided a wide range of 2-substituted benzothiazole derivatives in moderate to good yields. The transformation begins with the formation of the thioyl radical, which then reacts with nitrile to generate the iminyl radical **48**. Then, the iminyl radical **48** undergoes intramolecular cyclization affording intermediate **49**. Finally, the desired product is obtained from intermediate **49** through oxidation dehydrogenation.

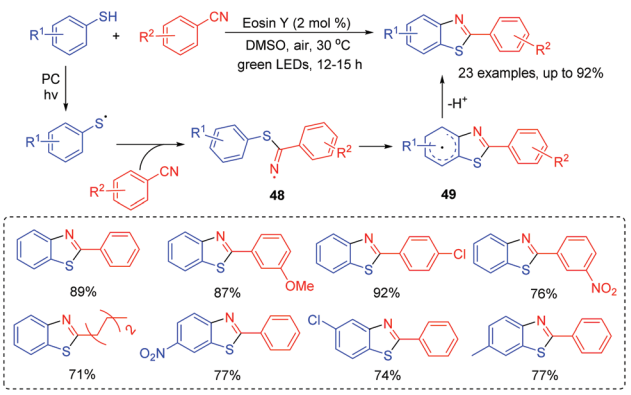
2.5. P(O)–H substitution reactions

Thiophosphates present important structural scaffolds, and usually serve as therapeutic molecules and agrochemicals.[47] Zhang and co-workers demonstrated an efficient S–P(O) bond formation protocol through the direct cross-coupling of thiols with P(O)H compounds using rose bengal as the photoredox catalysts (Scheme 24).[48] Various S–P(O) coupling products were easily constructed in moderate to excellent yields. Moreover, thiols with the active groups such as the free amine group and the hydroxy group were also performed smoothly, which could be further modified for more applications. In this process, $^1O_2$ is generated in the presence of rose bengal under visible light irradiation. Subsequently, the generated $^1O_2$ abstracts the hydrogen atom from thiol and affords the thioyl radical. At the same time, the P-centered radical is also generated from the P(O)H compound by a similar oxidation process. Finally, the coupling of the thioyl radical with P-centered radical produces the desired compound.

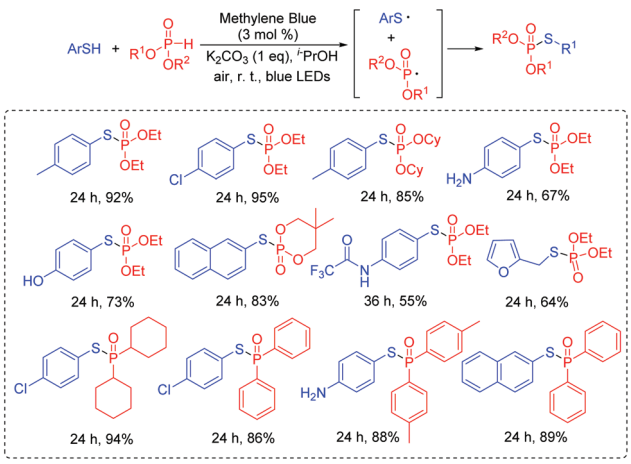


Scheme 24 Construction of S–P(O) bonds.

Wu's group also succeeded in the visible-light catalyzed dehydrogenative coupling reaction of thiols with phosphonates using methylene blue as a promoter to directly construct the S–P(O) bonds (Scheme 25).[49] The method provided a green route for the synthesis of thiophosphates under mild conditions. Moreover, thiols with different functional groups, including the halogen, amide, trifluoromethyl, free amine and the hydroxyl group, were successfully coupled with dialkyl phosphonates/or alkyl phosphine oxides, giving the desired products in good to excellent yields. In this photoredox catalysis process, the formed thioyl radical couples with the P-centered radical to produce the desired product.



Scheme 23 Synthesis of 2-substituted benzothiazoles.



Scheme 25 Synthesis of thiophosphates.

3. Visible-light induced C–S bond formation *via* the generation of the sulfonyl radical

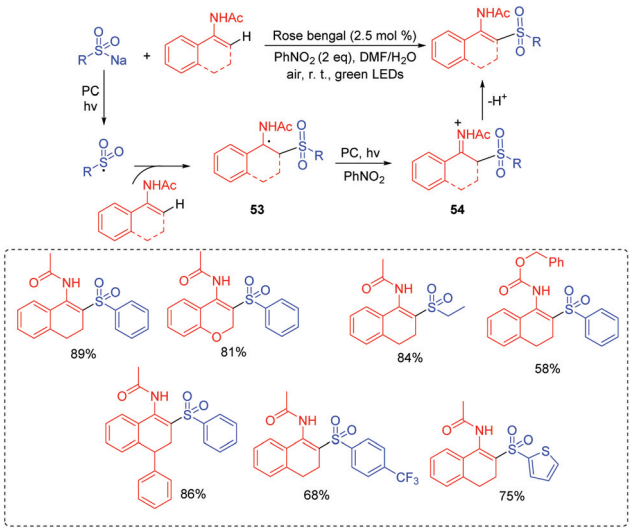
3.1. C(sp^2)–sulfonyl radicals coupling reactions

3.1.1. Substitution to alkenes. More and more chemists pay attention to the construction of sulfone-containing skeletons[50] for their appealing bioactivities and broad applications in synthetic methods.[51] Cai and co-workers described a decarboxylative cross-coupling reaction of sulfonyl hydrazides with cinnamic acids for the synthesis of vinyl sulfones through the visible-light photoredox catalysis process using oxygen as the sole terminal oxidant (Scheme 26).[52] Mechanistically, the generated highly active radical **50** is converted into sulfonyl radical **51** with the release of nitrogen. Then, a sequence of radical addition and transformation affords intermediate **52**. Finally, intermediate **52** undergoes an elimination reaction to yield the final sulfone product.

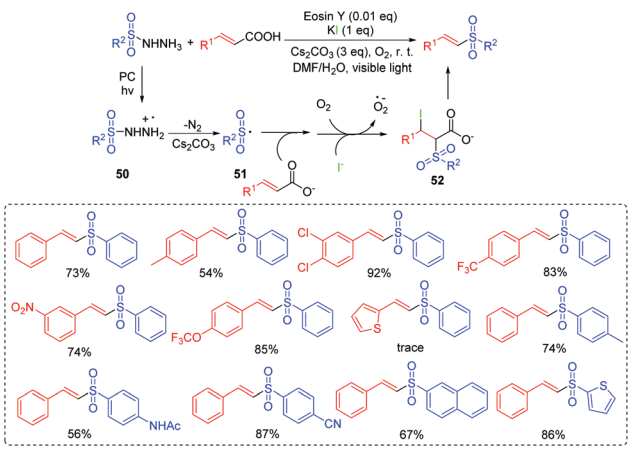
β-Amido sulfones are privileged scaffolds found in many natural products and biologically active compounds.[53] So far, the preparation of β-acetylamino acrylosulfone substrates relies on the several known methods, such as rearrangement reactions, the reduction of nitro alkenes or ketoximes, the acylation of imines, and the direct condensation of ketones with amides.[54] However, visible-light photoredox catalysis processes to access β-acetylamino acrylosulfones have been reported rarely. Zhang's group reported a visible-light induced oxidative cross-coupling strategy to access β-acetylamino acrylosulfones from enamides and sodium sulfinates using rose bengal as the photocatalyst at room temperature (Scheme 27).[55] In the transformation, the radical addition of the generated sulfonyl radical to enamide produces the carbon-centered radical **53**. Then, intermediate **53** is oxidated to the iminium ion **54**. Finally, **54** delivers the β-acetylamino acrylosulfone product *via* deprotonation.

3.1.2. Addition to alkenes. Allylic sulfones, are the useful building blocks of organic synthesis[56] and biologically important compounds that have potential applications for the treatment of Alzheimer's disease, cancer, and abnormal cell proliferation diseases, and in pharmaceuticals.[57,58] Moreover, significant progress toward this goal has been achieved.[59] In 2016, Lei and co-workers proposed a cross-coupling strategy to access allylic sulfones from α-methylstyrenes and sulfinic acids *via* a visible-light induced process (Scheme 28).[4g] Various allylic sulfone derivatives can be obtained with good yields and functional group tolerances. It is noted that the generated sulfonyl radical reacts with α-methylstyrene to generate the carbon-centered radical intermediate **55** through radical addition. Then, the radical intermediate **55** is oxidized to intermediate **56**. Finally, **56** is converted into the desired product through the deprotonation elimination reaction.

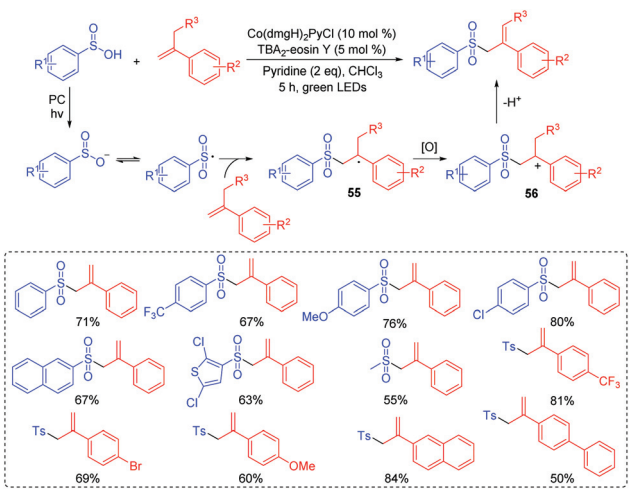
The importance of alkylsulfonyl compounds is known since some compounds with alkylsulfonyl units are marketed as drugs or biologically active molecules.[60] In 2018, Wu's group



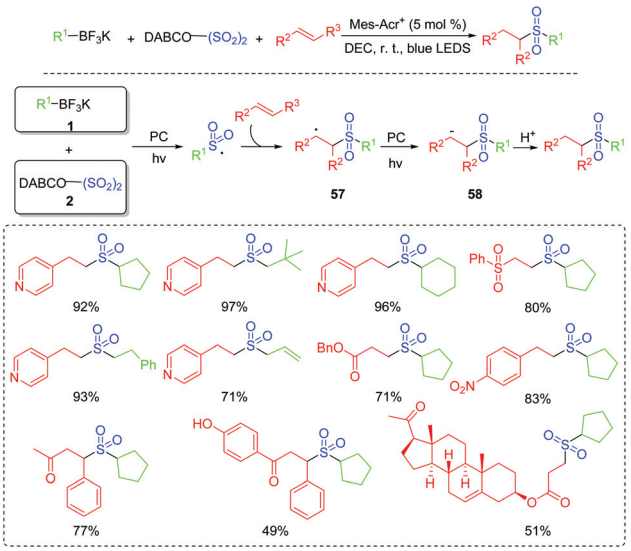
Scheme 27 Synthesis of β-acetylamino acrylosulfones.



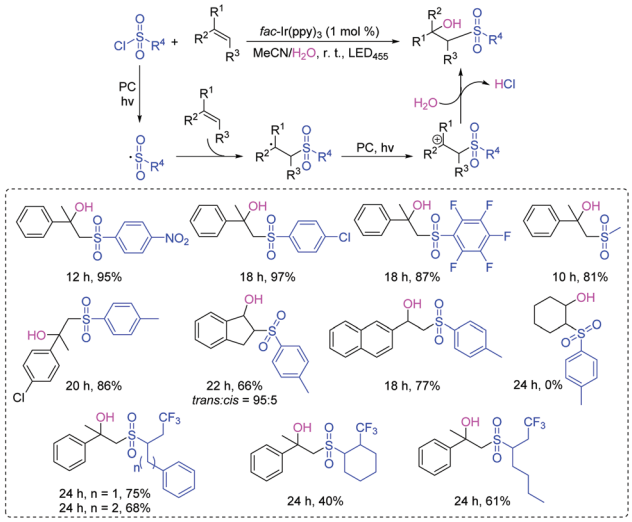
Scheme 26 Synthesis of α-substituted vinyl sulfones.



Scheme 28 Synthesis of allylic sulfones.



Scheme 29 Synthesis of alkylsulfonyl compounds.



Scheme 30 Synthesis of β-hydroxysulfones from sulfonyl chlorides and alkenes.

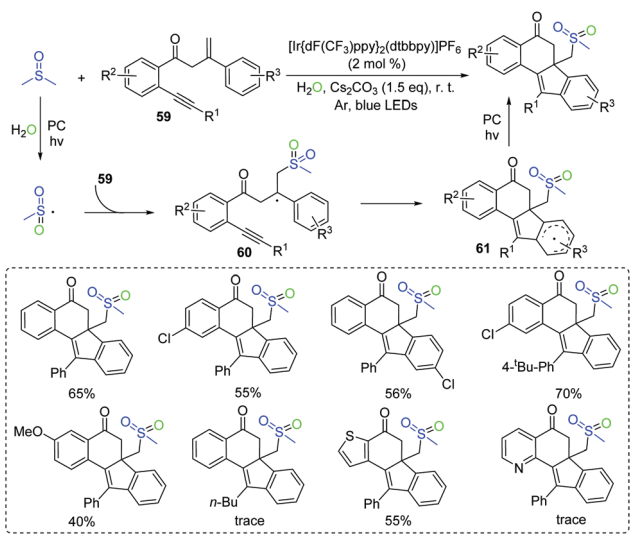
successfully explored a three-component reaction to access alkylsulfonyl compounds *via* photocatalysis at room temperature (Scheme 29).[61] This reaction worked efficiently with the use of potassium alkyltrifluoroborates, sulfur dioxide surrogate of DABCO·$(SO_2)_2$, and alkenes as the starting materials, affording diverse sulfones in good to excellent yields. Furthermore, sulfur dioxide was also successfully inserted into biologically active molecules. Mechanistic studies show that the alkylsulfonyl radical is a key intermediate. After that, the radical addition of an alkylsulfonyl radical to alkene produces the radical intermediate **57**, which is further transformed into intermediate **58**. Subsequently, the expected alkylsulfonyl product is generated by the protonation reaction.

The β-hydroxysulfone is an important scaffold for the synthesis of pharmaceutical drugs and various biologically active molecules.[62] Traditional methods for the preparation of β-hydroxysulfones are based on the opening of epoxides with sulfinate salts, the reduction of β-oxosulfones, or the hydroxylation of α,β-unsaturated sulfones.[63,64] In 2016, Reiser's group described a dual-catalyst-catalyzed reaction through a visible-light promoted process to synthesize β-hydroxysulfone derivatives from alkenes and sulfonyl chlorides in the presence of water (Scheme 30).[65] The reaction featured a wide range of functional group tolerances such as strong/weak electron-withdrawing/donating groups, alkyl and aryl groups, affording corresponding products in high yields. The authors proposed that the key step for the reaction was the radical addition of sulfonyl radicals to alkenes under visible-light irradiation.

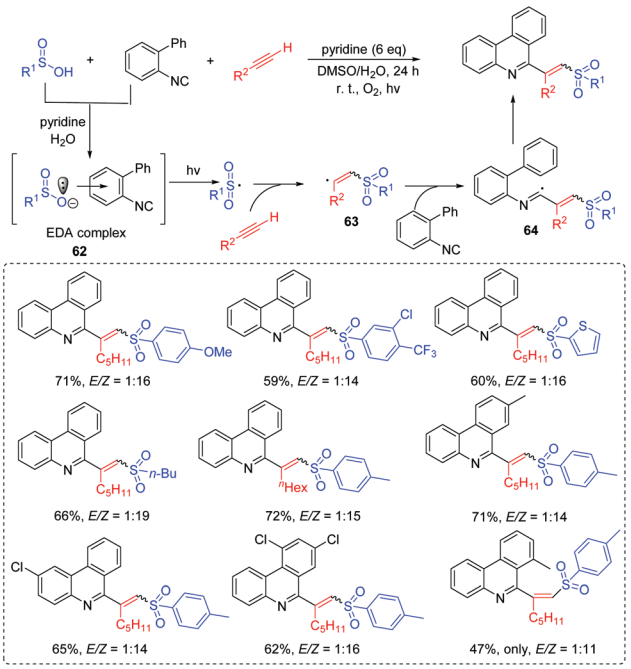
Dimethyl sulfoxide is the one of important organosulfur compounds. Due to its low cost and stability,[66] DMSO is usually utilized as a solvent and a versatile oxidant reagent in the organic synthesis reaction.[67] Furthermore, DMSO could be used as a common precursor for the methyl, formyl, cyano, methylmercapto, and so on.[68] In 2018, an elegant work for the synthesis of benzo[*a*]fluoren-5-one derivatives *via* the visible-light photocatalytic methylsulfonylation of 1,7-enynes under mild reaction conditions was reported by the group of Jiang (Scheme 31).[69] This method employed the DMSO/H_2O system as the methylsulfonyl synthon and afforded a broad range of functionalized benzo[*a*]fluoren-5-ones from readily available materials. The reaction of the generated sulfonyl radical with 1,7-enynes **59** delivers the radical intermediate **60**, which is further converted into the radical intermediate **61** *via* intramolecular 6-exo-dig/5-endo-trig bicyclization. The final benzo[*a*]fluoren-5-one product is obtained from **61** *via* the SET process.

3.2. Alkynes addition reactions

Wang's group developed a radical tandem process to synthesize (*E*)- and (*Z*)-C6-(vinyl sulfone) phenanthridines



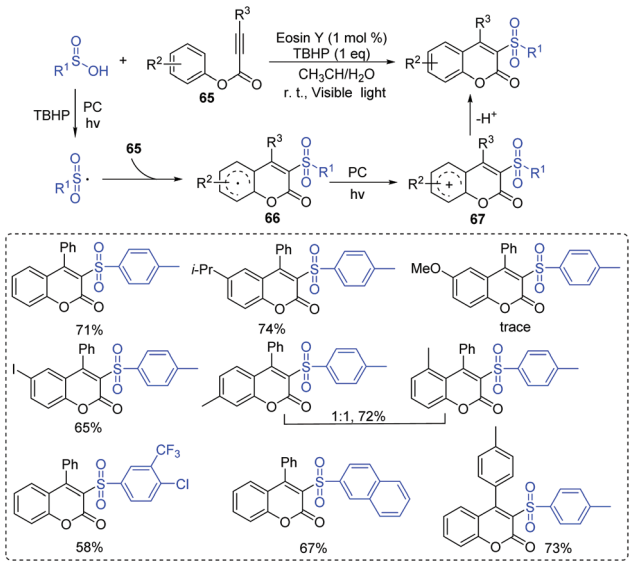
Scheme 31 Photocatalytic methylsulfonylation of 1,7-enynes.



Scheme 32 Synthesis of (*E*)- and (*Z*)-C6-(vinyl sulfone) phenanthridines.

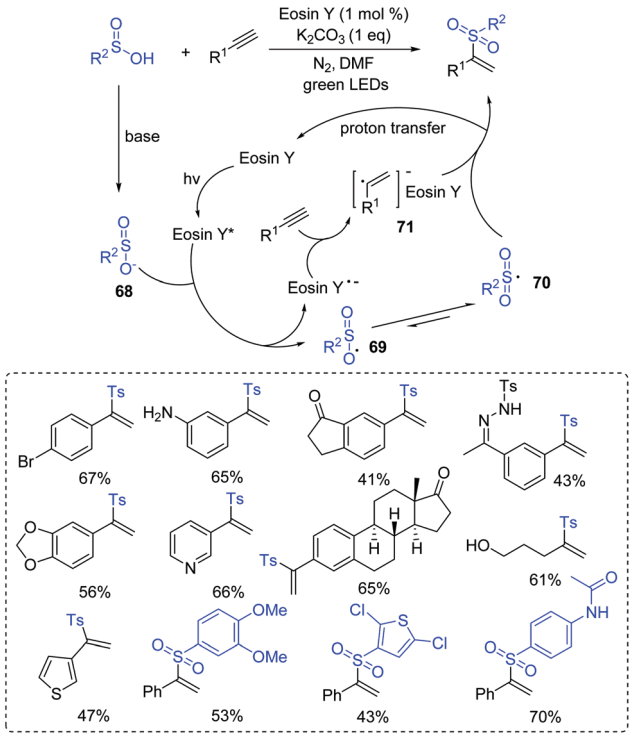
(Scheme 32).[70] The reaction was operationally simple using biaryl isocyanides, alkynes, and arylsulfinic acids as the starting materials *via* the light-controlled process under mild conditions. This approach exhibited a broad substrate scope, and provided the corresponding (*E*)- and (*Z*)-C6-(vinyl sulfone)phenanthridine derivatives in good yields. In this reaction, the novel electron donor–acceptor (EDA) complex **62** is generated from the reaction of arylsulfinic acid and biaryl isocyanide. Then, the generated sulfonyl radical reacts with the alkyne to afford vinyl radical **63**, which further performs an addition into the biaryl isocyanide to produce the imidoyl radical **64**. Finally, the desired product can be obtained *via* the intramolecular homolytic aromatic substitution and oxidation processes.

The coumarin skeleton plays a significant role in natural products, biologically active molecules, and it can serve as anti-HIV, and anti-diabetic drugs, and so on.[71] In 2015, Wang's group developed a visible-light initiated arylsulfonylation of alkynes with arylsulfinic acids to access 3-sulfonated coumarins (Scheme 33).[72] The method was compatible with a wide range of electron-rich aromatic compounds. More importantly, the halogens (F, Cl, Br and I) attached to the phenyl group of alkynes were well tolerated, which could be further modified in organic and medicinal chemistry. In this study, the addition of the generated sulfonyl radical to alkyne **65** delivers the radical intermediate **66**. Then, **66** is transformed into the carbon-cation intermediate **67** by the oxidation reaction. Finally, **67** is converted into a 3-sulfonated coumarin product by the deprotonation and rearomatization processes.



Scheme 33 Arylsulfonylation of alkynes.

Vinyl sulfones are known to be highly versatile encountered motifs, which have found widespread applications in biological research studies.[73] In 2016, Lei and co-workers reported a visible-light mediated Markovnikov-selective radical addition of sulfinic acids to terminal alkynes *via* the α-substituted vinyl radical/sulfonyl radical cross-coupling process (Scheme 34).[74] The transformation exhibited highly regioselective and broad functional-groups tolerance. It is noteworthy that a complex



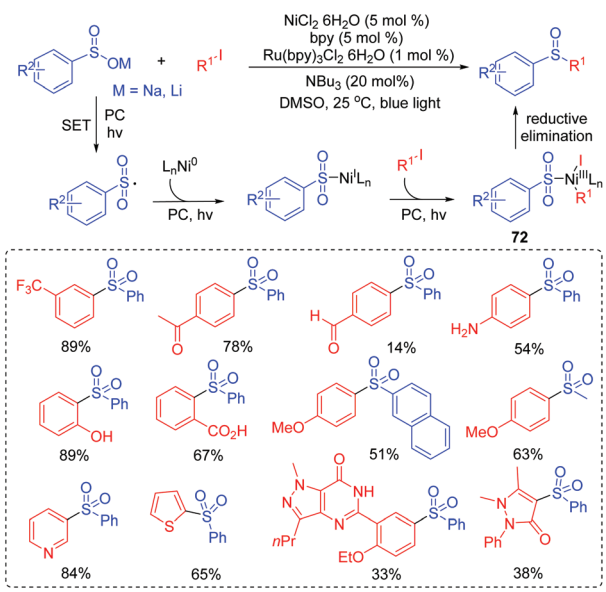
Scheme 34 Synthesis of α-substituted vinyl sulfones.

estrone derivative was also successfully generated. A plausible mechanism is illustrated in Scheme 34. The generated sulfinate **68** is generated from sulfinic acid with a base *via* an acid–base neutralization reaction. Then, the reaction of the formed species **68** with the excited state of eosin Y affords intermediate **69** along with the formation of eosin $Y^{\bullet-}$, which further resonates to intermediate **70**. Subsequently, the alkyne reacts with eosin $Y^{\bullet-}$ to give the α-vinyl carbon radical **71**. Finally, radical cross-coupling of **70** with **71** produces the desired Markovnikov product *via* the proton transfer process.

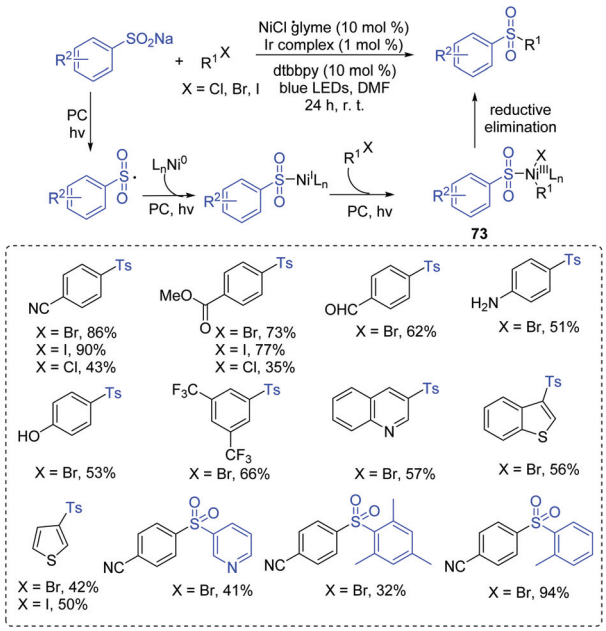
3.3. Aryl substitution reactions

Aryl sulfones could be served as a new class of human immunodeficiency virus type 1 (HIV-1) reverse transcriptase (RT) inhibitors acting at the non-nucleoside binding site of this enzyme.[75] In 2017, Manolikakes and co-workers reported the reactions of sulfinates with aryl iodides to give aryl sulfones under photoredox/nickel dual catalysts system conditions (Scheme 35).[76] Various sulfinates and aryl iodides were suitable for this transformation. The drug-like scaffolds also successfully realized diversification. In the same year, Rueping and coworkers developed a similar strategy for the synthesis of sulfones *via* the photoredox/nickel dual catalysis at room temperature (Scheme 36).[77] Coupling reactions of sodium sulfinates with various aryl halogen (Cl, Br, I) compounds were performed to synthesize the sulfones derivatives, giving the desired products in good to high yields.

The proposed catalytic pathway is initiated by the electron transfer process to form a sulfonyl radical. After that, a series of addition and oxidative addition reactions with nickel catalysts gives the Ni^{III} intermediate **72** (or **73**). Finally, the reductive elimination of the Ni^{III} intermediate **72** (or **73**) affords sulfone products.

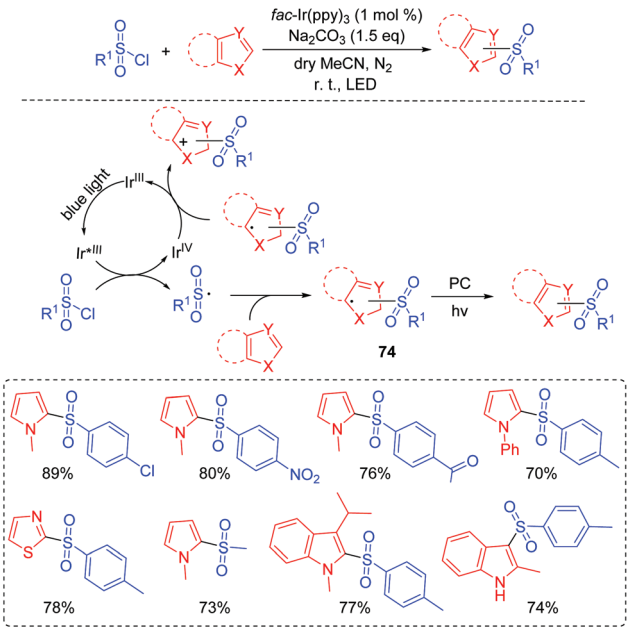


Scheme 35 Synthesis of aryl sulfones from sulfinic acid salts and aryl iodides.



Scheme 36 Synthesis of aryl sulfones from sulfinates and halides.

Furthermore, Reiser and co-workers demonstrated a visible-light induced photocatalytic strategy for the direct sulfonylation of heteroaromatic compounds at room temperature without pre-activating a heterocyclic ring and a sulfonyl source (Scheme 37).[78] All kinds of aryl and alkyl sulfonyl chlorides were good coupling partners for this transformation. Furthermore, indoles and pyrroles were also suitable substrates. A proposed mechanism is shown in Scheme 37. The key process for the reaction is the formation of the sulfonyl



Scheme 37 Sulfonylation of unactivated heterocycles.

radical by the oxidative quenching cycle of the Ir(III)-catalyst. The sulfonyl radical is sufficiently stable at room temperature to effectively undergo coupling with heteroarenes and then affords intermediate **74**. Finally, the desired product is obtained with the release of an electron and a proton from **74**.

4. Summary

In conclusion, visible-light photoredox catalysis has very rapidly been established as a powerful tool for the construction of organosulfur compounds. The reactions exhibited advantages including ambient conditions (room temperature or air atmosphere), eco-energy source, good functional group compatibility, and in some cases, the use of organic dyes as photocatalysts (*i.e.*, transition metal free conditions). In this review, we have described the two major approaches for the construction of these organosulfur compounds, including highly reactive thioyl/sulfonyl radical species substitution reactions and addition reactions in a controllable way. The transformation successfully provides diversely functionalized organosulfur compounds, which will be applied to the elaboration of pharmaceutical molecules and skeletons of natural products.

Although with unprecedented achievements of the C–S/P–S bond formation in hand, sulfur centered radicals chemistry still remains a fascinating hot topic.[79] However, the generated by-products (such as disulfide compounds) from the self-coupling of sulfur radicals are still challenging issues.[35,36] The exploration of novel and efficient photocatalysts, advanced reaction systems and the corresponding theoretical research represent an essential development field to improve the performance of sulfur centered radicals. The scale-up application for visible-light photoredox catalyzed transformations is another limitation, which could be adapted to continuous flow technology.[80] On the other hand, there is no doubt that some C–S/P–S bond formation and functionalization involving sulfur centered radicals mechanism have been carried out with the addition of transition-metal, I_2 or external oxidants.[3,81,82] Considering its great potential for synthetic applications, it is believed that the above strategies could be performed *via* the photoredox catalytic process. We envision that this strategy will help to promote continued interest in the visible light photoredox catalysis-controlled reactions involving the formation and further functionalization of sulfur centered radicals, which can be envisaged in the near future.

Conflicts of interest

The authors declare no competing financial interest.

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