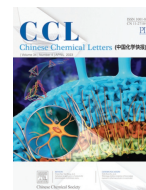




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Synthesis and applications of thiosulfonates and selenosulfonates as free-radical reagents

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ABSTRACT

Chalcogenative sulfones (thiosulfonates and selenosulfonates), as reactants for organic transformations, are widely used and interesting because of their potential to react with nucleophiles, electrophiles, and free radicals. As stable radical reagents, the synthesis and applications of chalcogenative sulfones have opened up a novel pathway to synthesize many kinds of compounds containing sulfur or selenium motifs. However, despite the numerous recent works on the synthesis and applications of thiosulfonates and selenosulfonates as radical reagents, no review has yet provided a summary of the literature. In this paper, we aim to review the synthesis and applications strategies of chalcogenative sulfones as radical reagents reported over the past several decades. Different types of catalysis are discussed in this review: (i) metal catalysis; (ii) visible-light catalysis; (iii) synergistic catalysis; and (iiii) other types. Concurrently, in visible-light catalysis and metallaphotoredox catalysis sections, we highlight that developing relatively environmentally friendly synthetic methods in this area is always a great challenge, but also a persistent pursuit. Finally, the scopes, limitations, mechanisms, and existing problems of some reactions are described briefly.

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1. Introduction

Organic sulfur and selenium compounds are omnipresent in a large number of natural products, pharmaceutical molecules, and chiral ligands, and they have received considerable attention over the past few decades on account of their wide range of biological and medicinal properties [1–11]. Sulfones have gradually become an indispensable part of modern organic chemistry and have been widely used in the transformation and synthesis of various drugs because of their special electronic and unique structural properties [12]. Particularly, chalcogenative sulfones are important organic compounds possessing both sulfonyl (R^1SO_2-) and sulfur (R^2S-)/selenium (R^3Se-) groups [13–16]. Four selenosulfonates synthesized from *o*-nitrobenzeneselenenyl bromide and sodium arenesulfonates were first proposed by Foss's group in 1947 [17]. Although thiosulfonates and selenosulfonates were first reported 70 years ago, research on their applications was not actively conducted at that time [18–27]. Thiosulfonates generally exhibit low toxicity and have served as efficient reactants for the synthesis

of many valuable sulfur-containing compounds over the last few years [5,28–30]. In addition, thiosulfonates and selenosulfonates can be used as practical sulfonating reagents in many chemical conditions [18,21,24]. For these reasons, thiosulfonates and selenosulfonates have become very valuable synthons. In recent years, considerable efforts have been made by chemists to develop new and efficient methods for synthesizing thiosulfonates and selenosulfonates, as well as applying them to new reactions to construct novel sulfur- or selenium-containing compounds.

At present, thiosulfonates and selenosulfonates are involved in a wide range of reactions, including electrophilic reactions, nucleophilic reactions, and radical reactions. Among them, the rapid development of free-radical chemistry is a hot spot in chemical synthesis that cannot be underestimated [31–43]. As new, effective, and stable free-radical reagents, chalcogenative sulfones are involved in some radical reactions that are worthy of special attention. Although there are several reviews on the applications of thiosulfonates and selenosulfonates, these related methodologies mainly highlight the synthesis, reactivity, and activation modes of fluoroalkyl thiosulfonates and selenosulfonates [44], or *S*-trifluoroethyl benzenesulfonothioates as bench-stable reagents for electrophilic trifluoroethylthiolation [45]. In 2020, Maes's group contributed a timely and elegant paper on the synthesis and appli-

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cations of thiosulfonates, in which nucleophilic, electrophilic, radical, coupling, polymerization, and multicomponent reactions were all briefly mentioned [46]. Herein, we mainly focus on and summarize the synthesis and applications strategies of thiosulfonates and selenosulfonates as stable radical reagents, which has not been reviewed so far in a general way. In this paper, the synthetic methods of chalcogenative sulfones are briefly summarized, and the research progress of radical reactions involving thiosulfonates and selenosulfonates is reviewed comprehensively. In addition, in order to further understand the recent research progress, reaction scopes, applications, limitations, and some mechanisms are also briefly discussed.

2. Synthesis of chalcogenative sulfones

As highlighted in the Introduction, thiosulfonates and selenosulfonates have interesting properties and are also widely used as versatile sulfonylating reagents in many organic transformations. For these reasons, chemists have made considerable efforts to design and develop new and effective methods for the construction of thiosulfonates and selenosulfonates. However, literature investigation indicates that the synthetic methods of thiosulfonates and selenosulfonates are limited. We briefly summarize some of the known synthetic strategies based on the precursors used to generate thiosulfonates and selenosulfonates. Each of these reactions will be discussed in summary in the following introduction.

In 1947, Foss's group first discovered the synthesis of selenosulfonates from *o*-nitrobenzeneselenenylbromide and sodium arenesulfonates (Scheme 1a) [17]. Unfortunately, only four examples of selenosulfonates have been successfully obtained in this way.

In 1972, Bentley and colleagues converted sodium sulfonates and alkyl disulfides directly into thiosulfonates using stoichiometric amounts of silver nitrate (Scheme 1b) [47]. However, the substrate range of this method was limited and only suitable for sodium methanesulfonates.

In 2012, Chen's group proposed the first example of sodium sulfonates with *N*-(organothio)succinimides catalyzed by Sc(OTf)₃ under ionic liquids and water cosolvent conditions, affording thiosulfonates with considerable yields (Scheme 1c) [48].

In 2014, Taniguchi *et al.* developed a method for the preparation of thiosulfonates catalyzed by copper using sodium sulfonates in an oxygen atmosphere (Scheme 1d) [49].

One year later, Natarajan's group introduced a new method in which oxone combines with MX (MX = KBr, KCl, NaBr, or NaCl) to oxidize aliphatic or aromatic disulfides containing electron-donating or electron-withdrawing groups into corresponding thiosulfonates (Scheme 1e) [50]. Compared with other synthetic methods, the outstanding advantages of this method include mild conditions, short reaction times, and avoiding the use of toxic and unstable reagents.

A practical synthesis of electrophilic thiosulfonates and disulfides in the presence of tetrabutylammonium iodide by selecting suitable solvents using cheap and readily available sulfonyl chlorides as starting materials was developed by Xu's and Huang's groups in 2016 (Scheme 1f) [51]. The method had high efficiency, economy, and mild conditions, which was attractive for the preparation of these two sulfur-containing compounds.

In 2017, Guo *et al.* used a Pd/ZrO₂ nanocomposite photocatalyst to catalyze the decomposition of sulfonyl hydrazines and synthesized thiosulfonates under mild conditions without oxidants or promoters (Scheme 1g) [52]. In the same year, Zou's group described a convenient *tert*-butyl hydroperoxide (TBHP)-mediated radical cross coupling of sulfonylhydrazides with thiols catalyzed by CuBr₂ to produce thiosulfonates with moderate to excellent yields (Scheme 1h) [53]. The method had a great tolerance for different functional groups and provided many kinds of thiosulfonates.

In 2018, Guan, Wu *et al.* proposed a novel, efficient, and environmentally friendly strategy for the preparation of thiosulfonates by the electrochemical oxidation of thiols (Scheme 1i) [54]. This method enabled the formation of thiosulfonates without catalysts and oxidants. The reaction conditions were simple and mild, and could be used at gram scale; they were also suitable for the late-stage synthesis of bioactive molecules.

In 2019, Sun, Liu *et al.* realized the electrochemical oxidative cross dehydrogenation coupling of arylsulfonic acids with thiophenol compounds by a radical method, providing a series of unsymmetrical thiosulfonates with excellent yields (Scheme 1j) [55]. At the same time, the electrochemical method could also be applied to the reaction of arylsulfonic acids and disulfides or diselenides to access thiosulfonates or selenosulfonates, respectively.

In 2021, Kumar and co-workers established a strategy for the successful synthesis of a series of symmetrical benzene thiosulfonates by irradiation of *N*-hydroxy sulphonamides under visible light induction in the presence of ethanol solvent (Scheme 1k) [56]. This method used ubiquitous blue light as the reaction condition, which was a relatively mild and environmentally friendly method.

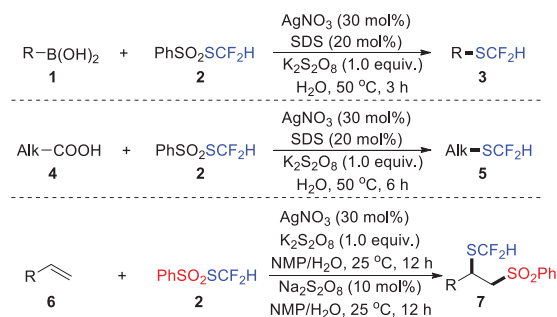
3. Applications of thiosulfonates and selenosulfonates

3.1. Applications of thiosulfonates and selenosulfonates based on metal catalysis

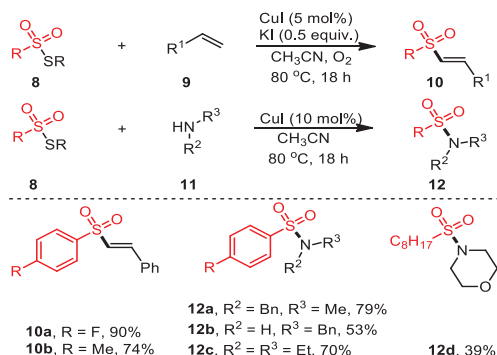
The transition metal-catalyzed radical reaction strategy of chalcogenative sulfones had become an indispensable tool for the construction of heteroatom-S(Se) bonds due to its rapid and efficient characteristics, especially in the construction of structurally diverse compounds [57–65]. In 2016, Shen and Lu's group discovered a stable radical reagent *S*-(difluoromethyl)benzenesulfonylthioate (PhSO₂SCF₂H), which could realize the radical difluoromethylthiolation of aryl and alkyl boronic acids **1**, the decarboxylative difluoromethylthiolation of aliphatic acids **4**, and the difunctionalization of alkenes **6** under mild conditions (Scheme 2) [66]. The strategy was characterized by simple operation, mild conditions, and the ability to access the target products in moderate to excellent yields. Due to the mild reaction conditions, various common functional groups such as fluorines, chlorines, bromines, amides, and nitros were com-

Reactants $\longrightarrow$ $\text{R}-\text{SO}_2\text{SR}$ $\text{R}-\text{SeSR}$		
(a) 1947, Foss Reactants = RSeBr + NaSO_2R EtOAc/MeOH	(b) 1972, Bentley Reactants = RSSR Oxidation	(c) 2012, Chen Reactants = RSeBr + NaSO_2R Sc(OTf) ₃ (5 mol%), [BMIM]PF ₆ /H ₂ O, 30 °C
(f) 2016, Xu, Huang Reactants = RSSR (<i>n</i> -Bu) ₄ Ni (3.0 equiv.) CH ₃ CN/acetone = 5:1 r.t., 20 h	(e) 2015, Natarajan Reactants = RSSR Oxone/MX CH ₃ CN/H ₂ O = 1:1, r.t.	(d) 2014, Taniguchi Reactants = RSSR + SHR [Cu], NH ₄ BF ₄ DMA/H ₂ O = 3:1 30 °C, 18 h
(g) 2017, Guo Reactants = RSSR + NH_2NH_2 Pd/ZrO ₂ , <i>hν</i> EtOH, 45 °C, O ₂ , 24 h	(h) 2017, Zou Reactants = RSSR + SHR CuBr ₂ , TBHP CH ₃ CN, 80 °C, 2 h	(i) 2018, Guan, Wu Reactants = RSSR Pt (+) 1 Pt (-) LiClO ₄ , CH ₃ CN r.t., 1.5 h
(k) 2021, Kumar Reactants = RSSR + NH_2NH_2 Blue Light, I ₂ , EtOH	(j) 2019, Sun, Liu Reactants = RSSR + SHR/RS-SR RSSR + RSe-SeR Pt (+) 1 Pt (-), LiClO ₄ , CH ₃ CN, 5 mA, r.t., 5 h	

Scheme 1. Different synthetic methods of thiosulfonates and selenosulfonates.



Scheme 2. Construction of difluoromethyl compounds catalyzed by copper.



Scheme 3. The synthesis of vinyl sulfones and sulfonamides catalyzed by copper catalyst.

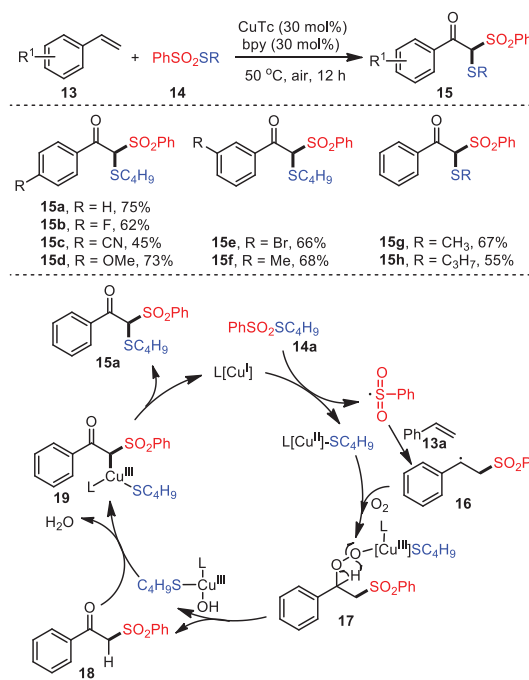
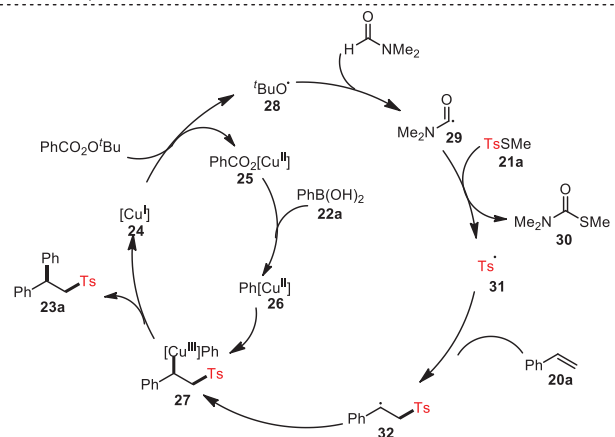
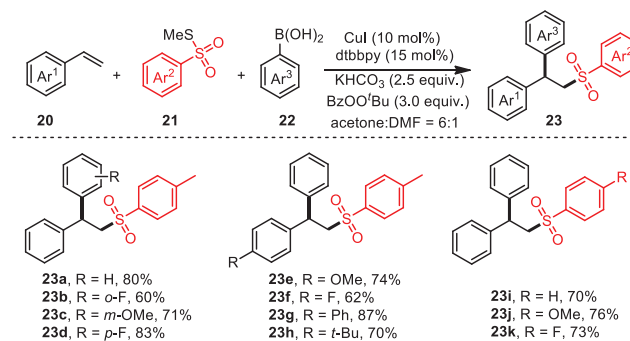
patible. The functionalization strategy involving $\text{PhSO}_2\text{SCF}_2\text{H}$ as a free-radical agent opened up a new direction for the construction of difluoromethyl compounds.

In 2017, Jang's group established a strategy of directly coupling thiosulfonates with alkenes and amines, respectively, breaking the original S-S bond and forming new C(sp²)-S/N-S bonds, thus constructing a series of synthetically and pharmaceutically useful vinyl sulfones **10** and sulfonamides **12** with synthetic and medicinal value (Scheme 3) [67]. Notably, thiosulfonate derivatives containing both electron-donating and electron-withdrawing groups offered the desired products with moderate to excellent yields. Surprisingly, octyl-substituted thiosulfonate yielded the desired product **12d** with 39% yield, where it was speculated that aliphatic thiosulfonate might not be suitable for this transformation.

A method to construct β -ketone thiosulfones **15** by oxidative trifunctionalization of olefins **13** was proposed by Xu's group in 2018 (Scheme 4) [68]. The conversion proceeded through molecular oxygen activation under the catalytic action of copper, forming two new C-S bonds in a single operation under mild conditions. Under standard conditions, various electronically rich, neutral, and poor styrenes were all well tolerated, and the corresponding β -keto thioether products were obtained in moderate yields.

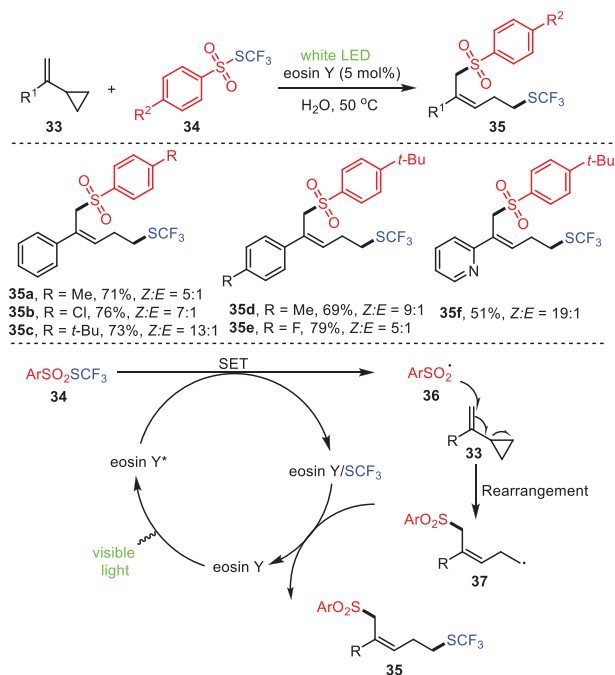
Based on the results of some control experiments and literature precedents, a plausible reaction mechanism was proposed, as shown in Scheme 3. *S*-Butyl benzenesulfonylthioate **14a** was catalyzed by copper(I) to form the sulfonyl radical, and then reacted with styrene to generate radical intermediate **16**. In the presence of L-[Cu]SC₄H₉, intermediate **16** was transformed into radical **17** through activating molecular oxygen. The fragmentation of radical **17** offered β -keto sulfone **18**, which reacted with the removed L-[CuOH]⁺ to form intermediate **19**, and subsequent reductive elimination revealed the cause of the formation of the final product **15a**.

In 2020, Jia *et al.* developed an effective strategy for the preparation of a wide range of 2,2-diarylethyl sulfone derivatives **23** by the Cu-catalyzed intermolecular difunctionalization of styrenes **20**

Scheme 4. The formation of functionalized β -keto thiosulfones.

Scheme 5. The preparation of 2,2-diarylethyl sulfones.

with methyl thiosulfonates **21** and arylboronic acids **22** (Scheme 5) [69]. Remarkably, the mild nature of the approach made it suitable for late-stage modification of biologically active natural products, and the different substrate scopes demonstrated the functional group's tolerance for this reaction. In addition, a series of relevant control experiments were carried out to verify the mechanism of this reaction. The formation of the product was significantly inhibited by the addition of the radical scavenger 2,2,6,6-



Scheme 6. Organocatalytic 1,5-trifluomethylthio-sulfonylation of vinylcyclopropane mediated by visible light in water phase.

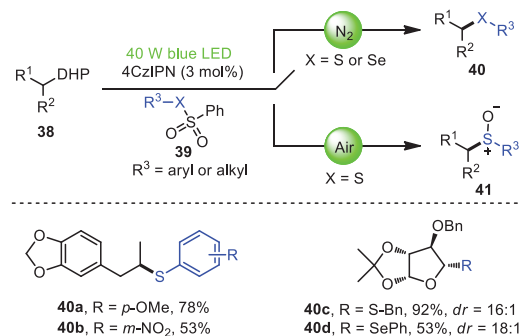
tetramethylpiperidiny 1-oxide (TEMPO) under standard conditions, demonstrating that the transformation involved a radical pathway.

At first, Cu(I) **24** reacted with BzOOCtBu to form copper complex **25** and radical **28**, which then extracted hydrogen from DMF to access formyl radical **29**. Afterwards, radical **31** obtained via a radical relay process was added to styrene **20a** to produce benzyl radical **32**. Cu(III) intermediate **27** was obtained by oxidative trapping of radical **32** and aryl copper(II) species **26** formed by the transmetalation of Cu(II) complex **25** with arylboronic acid **22a**. In the end, reductive elimination of the Cu(III) intermediate **27** accounted for the formation of final product **23a**.

3.2. Applications of chalcogenative sulfones under visible light irradiation

Over the past decade, many chemists have been devoted to researching atom transfer radical addition (ATRA) reactions catalyzed by visible light, as photoredox catalysis was characterized as a clean, efficient, and environmentally friendly method, and as an effective tool under mild conditions [70–76]. In recent years, visible light-induced chemical transformations had received increasing attention due to their important role in synthetic chemistry. Due to the special reaction mode of visible-light photoredox catalysis, many transformations that were previously unattainable by transition metal catalytic processes became possible. Next, the applications of visible light-induced chalcogenative sulfones as free-radical reagents are introduced in detail. This series of methods has also been successfully used in the construction of various chain or cyclic compounds, which fully reflects the bright prospects of photochemistry.

In 2020, Xu *et al.* reported a metal-free organocatalytic system mediated by visible light to achieve the remote difunctionalization of vinylcyclopropane **33** involving group migration with ArSO₂SCF₃ reagents **34**, accessing the expected difunctional products **35** with moderate yields (Scheme 6) [77]. This transformation demonstrated a good tolerance towards functional groups, as well as excellent regioselectivity and stereoselectivity. Obviously, substrates with electron-withdrawing groups at the *para* position of

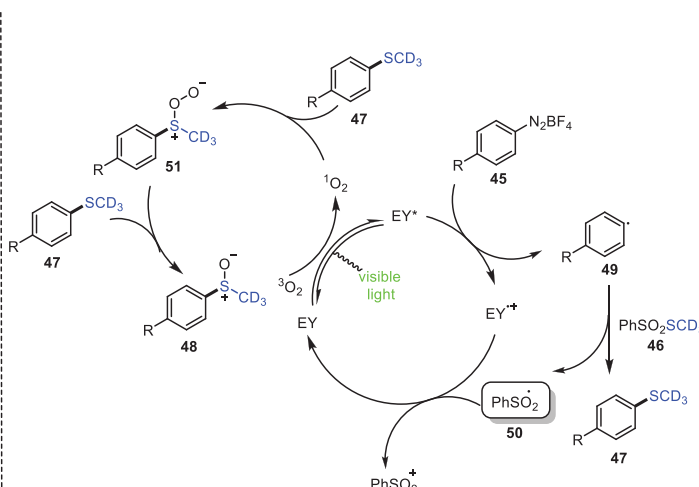
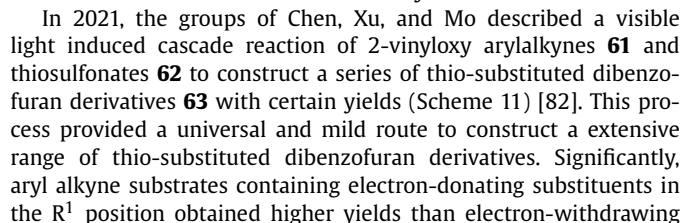
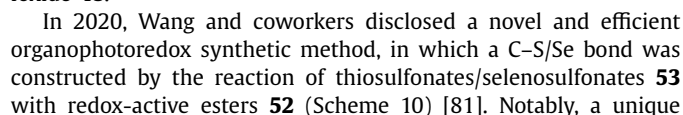


Scheme 7. Visible-light-promoted construction of thiolated and selenylated glycosides.

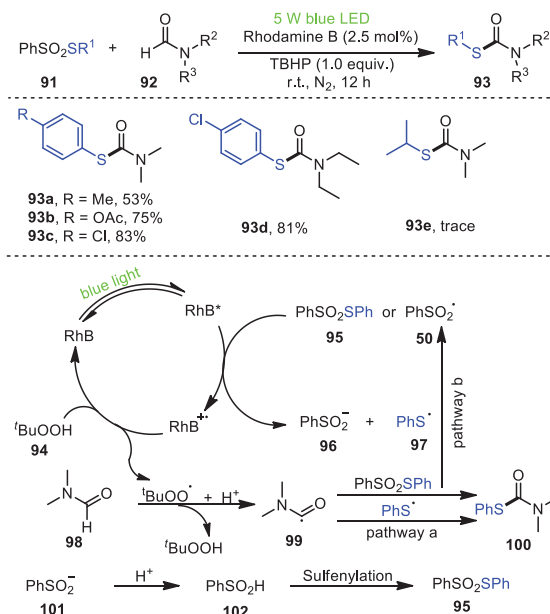
their phenyl rings had slightly higher yields than electron-donating groups. Fortunately, the stereoselectivity of the target product was significantly improved to 13:1 when *S*-(trifluoromethyl)-4-(*tert*-butyl)benzenesulfonate **35c** was used as a difunctionalization reagent. This pathway enabled the 1,5-trifluomethylthio-sulfonylation of vinyl-cyclopropane using eosin Y as a catalyst, which is cheaper and more tolerated than transition-metal or redox-catalyst systems, and water as a “green” solvent. Considering the mild conditions of this reaction, its atomic efficiency, its environmentally friendly solvent, and the recyclability of the catalytic system, it is speculated that this protocol has strong application prospects in terms of green indicators. Mechanistically, eosin Y went into its excited state eosin Y* by irradiation with visible light; then, substrate **34** was excited by it to generate radical **36**, and the eosin Y/SCF₃ complex was simultaneously formed. Further reaction of radical **36** with substrate **33** was followed by a rearrangement to form intermediate **37**, which was then reacted with the eosin Y/SCF₃ complex to obtain final product **35**.

In the same year, Wang, Ji *et al.* realized a novel synthesis route for the construction of C(sp³)–S or C(sp³)–Se bonds by the visible-light-promoted cross-linking of 4-alkyl-1,4-dihydropyridines **38** with thiosulfonates/selenosulfonates **39** in the absence of transition metals and additives, oxidants, or bases (Scheme 7) [78]. This strategy was characterized by readily available substrates, mild reaction conditions, and excellent chemoselectivity, which could also be well generalized to the synthesis of thiolated or selenylated glycosides that have not been explored before. Notably, both electron-donating (OMe) and electron-withdrawing (NO₂) substituents were well tolerated in the *para*- and *meta*-positions of *S*-aryl benzenesulfonothioates, so that products **40a** and **40b** could be isolated in 78% and 53% yields, respectively. Surprisingly, *S*-benzylbenzenesulfonate and *Se*-aryl benzenesulfonate were also suitable for this visible-light-promoted reaction in moderate to excellent yields and selectivity.

Soon after, Maes *et al.* developed a metal-free method of generating sulfonyl and sulfonyl radicals simultaneously through energy transfer of photo-organocatalysts excited by visible light followed by vicinal thiosulfonylation of unactivated olefins **42** under visible light irradiation (Scheme 8) [79]. This strategy provided a novel method for the synthesis of extensive 1,2-thiosulfonylation products **44** by using energy transfer rather than single electron transfer. It is worth noting that this method did not contain metals and oxidants and could be carried out in green solvents in an air atmosphere, which was suitable for the functionalization of alkenes. Additionally, the substituents could be successfully tolerated, whether they were electron-donating groups or electron-withdrawing groups, and target products could be obtained with moderate to excellent yields. Unfortunately, *S*-butyl benzenethiosulfonate did not yield the expected product **44d** under the same condition. This procedure can be carried out under mild conditions



Scheme 9. Synthesis of trideuteromethylated sulfides, sulfoxides and selenides under visible light irradiation.



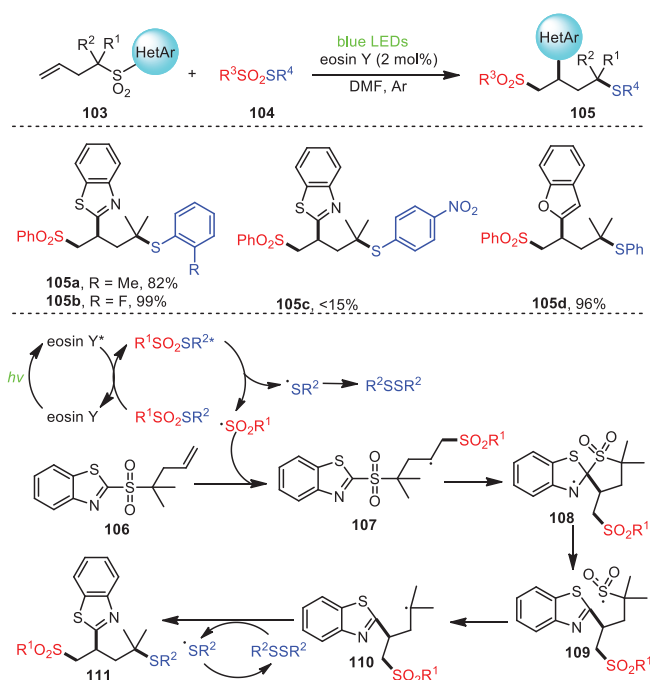
Scheme 15. Visible-light-promoted for the synthesis of secondary and tertiary thio-carbamates.

using thiosulfonates **91** and *N*-substituted formamides **92** as starting materials, Rhodamine B as a photocatalyst, and *tert*-butylhydrogen peroxide (TBHP) as an oxidant to obtain secondary and tertiary thio-carbamates **93** under blue-light irradiation at room temperature (Scheme 15) [85]. In particular, this method used *N*-monosubstituted formamides as amide sources to synthesize secondary thiocarbonates, as a first example. In addition, *S*-arylbenzene thiosulfonates bearing electron-withdrawing groups had higher yields than those bearing electron-donating groups, most likely due to the strong electron-donating groups inhibiting the reaction process. Unfortunately, *S*-alkyl benzenethiosulfonate **93e** was not suitable for this reaction under the optimized conditions, which was most likely caused by the instability of the sulfonyl radical.

Firstly, RhB^* and **95** underwent an SET process to form radical cations $\text{RhB}^{+\bullet}$, benzenesulfinic acid anion **96**, and benzenesulfonyl radical **97**. Afterwards, $\text{RhB}^{+\bullet}$ withdrew an electron from TBHP, resulting in the formation of RhB, the *tert*-butylperoxyl radical and H^+ . Ultimately, the final product was formed by the coupling of acyl radical **99** and **97**, in which acyl radical **99** was obtained by the extraction of hydrogen from DMF **98** by the *tert*-butylperoxyl radical (pathway a). Conversely, radical **99** reacted with **95** to form PhSO_2 radical **50** as well as **100** (pathway b).

Soon later, a method for the formation of new C–S/Se bonds between butenyl benzothiazole sulfones **103** with thiosulfonates or selenosulfonates **104** via radical sulfonylation/aryl migration/desulfonylation under visible light was established by Wang's group (Scheme 16) [86]. This process provided a new procedure for the acquisition of a series of 1,2,4-trifunctionalization products via a radical sulfonyl-smile rearrangement pathway. Notably, this strategy, using practical and economical eosin Y as the catalyst, could tolerate many functional groups, resulting in a series of 1,2,4-trifunctionalization products of butenyl benzothiazole sulfones. Surprisingly, *S*-(4-nitrophenyl) benzenesulfonothioate produced less than 15% of the expected product **105c** due to its strong electron-withdrawing group.

First of all, after irradiation, eosin Y was transformed into its excited state, which underwent energy transfer with thiosulfonate to generate its corresponding excited state, and the homolysis of the excited-state thiosulfonate produced a sulfonyl radical and a



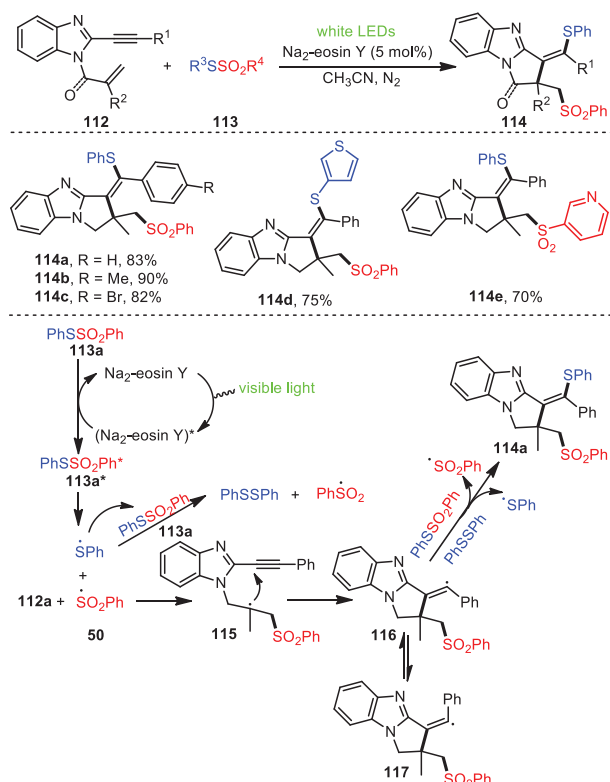
Scheme 16. Visible-light-triggered 1,2,4-trifunctionalization of butenyl benzothiazole sulfone with thiosulfonate/selenosulfonates.

sulfonyl radical. Subsequently, the five-membered ring intermediate **108** was formed by radical addition of the terminal double bond of **106** and subsequent intramolecular radical cyclization. The re-aromatization of intermediate **108** and cleavage of the C–S bond explained the formation of intermediate **109**. Eventually, **109** removed a molecule of SO_2 to produce radical intermediate **110**, which further reacted with disulfide to access the target product **111**.

In 2021, Xu and Chen's group investigated a radical cascade reaction of 1-allyl-2-ethynylbenzoimidazoles **112** with thiosulfonates **113** induced by visible light, providing thiosulfonylated pyrro[1,2-*a*]benzimidazoles **114** (Scheme 17) [87]. The transformation had the advantages of mild conditions, environmental friendliness, excellent functional group tolerance, and regioselectivity. The addition of radical inhibitor TEMPO under the standard reaction suggested that the transformation involved a radical process. Control experiments also showed that thiosulfonates were activated through a photocatalytic energy transfer pathway. Based on the results of relevant control experiments and previous references, a possible mechanism was depicted, as shown in Scheme 17.

3.3. Applications of thiosulfonates and selenosulfonates by synergetic metal/photoredox catalysis

Combining two distinctive catalytic systems, photoredox catalysis mediated by visible light and transition-metal catalysis, makes it possible to achieve unprecedented reactions [88–101]. The combination of photoredox catalysis with transition metal catalysis, known as metallaphotoredox catalysis or synergetic metal/photoredox catalysis, has become a mainstay in synthetic methodology in the past decade [102]. In addition, the use of inexpensive transition metals as catalysts for photoreactions was an innovation and breakthrough for a series of previous noble-metal catalysis and visible-light catalysis experiments. This combination of metal catalysis and photooxidation-reduction strategies shed light on the further development of metalloradical reactions in organic synthesis.

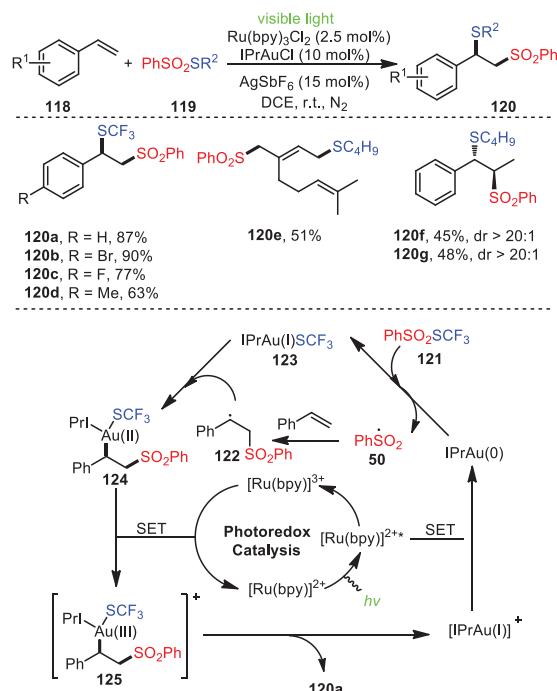


Scheme 17. Visible-light-induced construction of thiosulfonated pyrrolo[1,2-a]benzimidazoles.

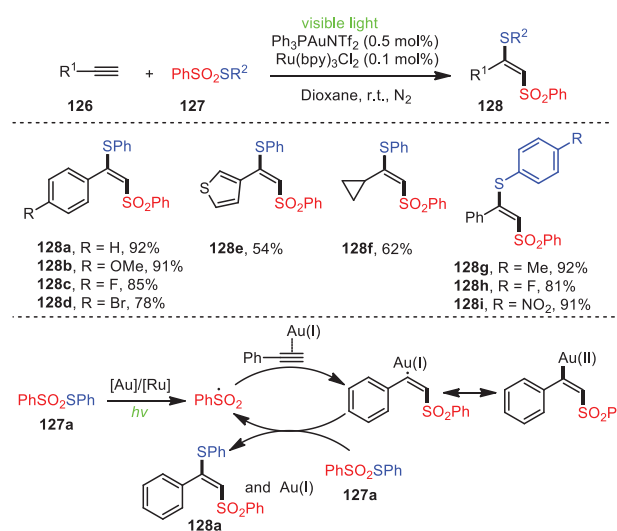
In 2017, Xu's group accomplished a unique gold and visible light photoredox synergistic catalysis difunctionalization of alkenes **118**, achieving a series of difunctional products **120** with moderate to excellent yields (Scheme 18) [103]. Particularly, the synergistic combination of gold catalysis and photoredox catalysis was the key for the selective introduction of thio groups together with sulfonyl groups into olefins. Interestingly, the main products of the *trans*-**120f** and *cis*-olefins **120g** had the same structure, as well as relatively similar yields with similar diastereoselectivity, which was an important advantage of this reaction.

The proposed mechanism is depicted in Scheme 18. First, irradiation of $\text{Ru}(\text{bpy})_3^{2+}$ obtained its excited state $\text{Ru}(\text{bpy})_3^{2+*}$, which underwent an SET reaction with cationic $\text{IPrAu}(\text{I})$ to generate $\text{Ru}(\text{bpy})_3^{3+}$ and $\text{IPrAu}(\text{0})$ and simultaneously initiate the catalytic cycle. Next, the highly active $\text{IPrAu}(\text{0})$ could reduce $\text{PhSO}_2\text{SCF}_3$ to $\text{IPrAu}(\text{I})\text{SCF}_3$ and a benzenesulfonyl radical **50**, which added to styrene, affording an alkyl radical **122**. The alkyl radical could oxidize **123** to form intermediate **124**, which was further oxidized by $\text{Ru}(\text{bpy})_3^{3+}$ to an $\text{Au}(\text{III})$ intermediate **125**, producing $\text{Ru}(\text{bpy})_3^{2+}$, thus completing the photoredox catalytic cycle. Finally, reductive elimination of the $\text{Au}(\text{III})$ intermediate **125** explained the formation of the desired product and led to the regeneration of the $\text{Au}(\text{I})$ catalyst.

In 2019, Xu, Wei and coworkers established a strategy for the rapid construction of thio-functionalized vinylsulfones **128** by gold-photooxidation-reduction co-catalyzed thiosulfonylation of alkynes **126** (Scheme 19) [104]. Remarkably, various alkynes, such as aromatic alkynes and aliphatic alkynes, could react with thiosulfonates to produce the corresponding thio-functional products. Furthermore, aromatic alkynes possessing electron-donating groups at their *para*-position gave higher yields than those bearing electron-withdrawing groups. Mechanistically, under the co-catalysis of a gold catalyst and photocatalyst, PhSO_2SPh underwent S–S bond



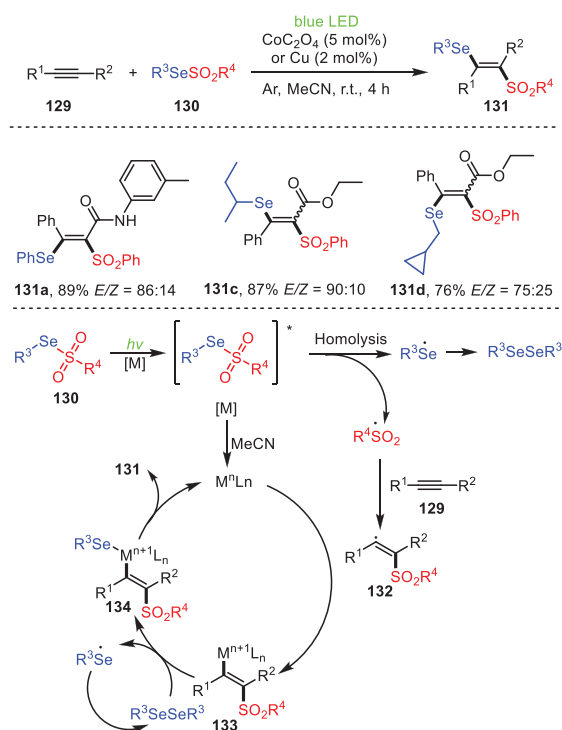
Scheme 18. Dual gold- and photoredox-catalyzed intermolecular atom transfer thiosulfonylation of alkenes.



Scheme 19. Gold/photoredox-cocatalyzed atom transfer thiosulfonylation of alkynes.

cleavage to form a sulfonyl radical, which added to alkyne's triple bond to form a vinyl radical in the presence of the gold catalyst. Finally, radical propagation was carried out with **127a** to obtain the target thiosulfonylation product and regenerate the $\text{Au}(\text{I})$ catalyst.

A visible-light-induced Co- or Cu-catalyzed 1,2-selenosulfonylation of alkynes **129** under mild conditions to construct a series of β -(seleno) vinyl sulfones **131** was proposed by Ji and Wang's group in the same year (Scheme 20) [105]. Notably, alkyamides possessing either electron-withdrawing groups or electron-donating groups reacted smoothly to produce a series of β -(seleno)vinyl sulfones with high yields. In addition, alkyl selenosulfonates (**131b**, **131c**) were also suitable for this reaction, with corresponding yields of 87% and 76%, respectively. Most importantly, the protocol used inexpensive transition metals as catalysts to achieve the visible-light catalysis cycle, which was an innovation in a series of previous ex-



Scheme 20. Visible-light-induced Co- or Cu-catalyzed selenosulfonylation of alkynes.

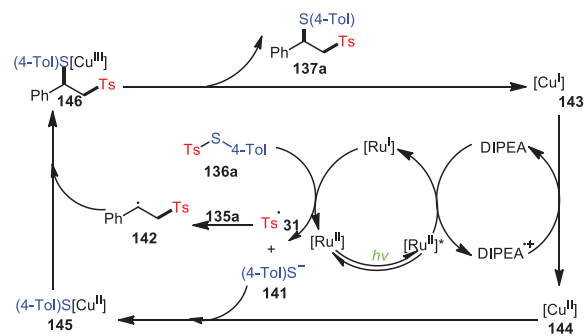
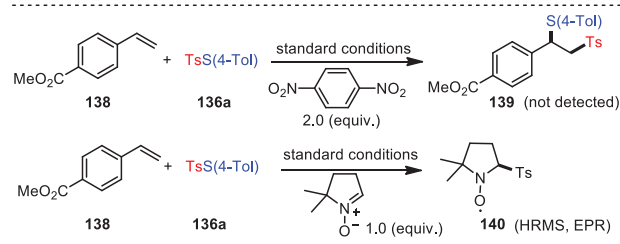
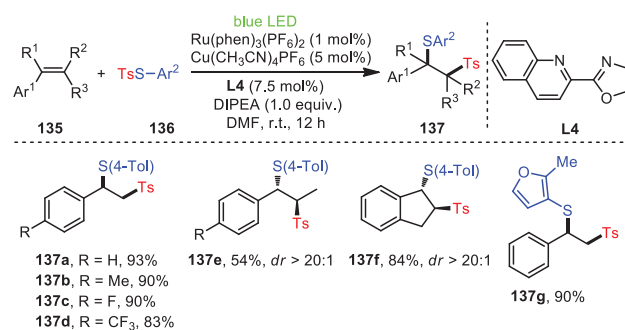
periments on the co-catalysis of precious metals and visible light, but also a new economical and environmentally friendly catalytic pathway following visible-light catalysis.

On the basis of controlled and competitive experiments, a reasonable mechanism was proposed, as shown in Scheme 20. Initially, in the catalysis of metal under visible light, **130** was transformed into its excited state, which underwent homolysis to form a sulfonyl radical and a seleno radical. Subsequently, the sulfonyl radical reacted with alkyne to access intermediate **132**, which underwent coordination with the metal to furnish intermediate **133**. Ultimately, reductive elimination of intermediate **134**, formed by the interaction between intermediate **133** and R^3SeSeR^3 , explained the formation of product **131** and regenerated the catalyst.

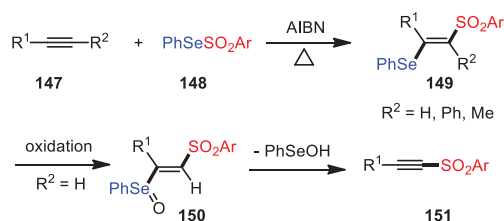
In 2021, Jia's and Liu's groups revealed the atom transfer radical addition of copper/photooxidation-reduction co-catalyzed styrenes **135** and thiosulfonates **136** (Scheme 21) [106]. Obviously, both the electron-withdrawing and electron-donating groups on styrenes exerted a negligible effect on the catalytic results. Furthermore, the styrene derivatives represented by β -methylstyrene **137e** and cyclic indene **137f** met the optimal catalytic conditions and had good regioselectivity and yields. In addition, the formation of **139** was completely inhibited by the addition of a radical scavenger (1,4-dinitrobenzene) from **138** and **136a** under standard conditions. As expected, when 1.0 equiv. of 5,5-dimethyl-1-pyrroline *N*-oxide was added to the same reaction system, the desired tosyl radical-trapped product **140** was found to be generated. The above mechanistic studies showed that the sulfonyl radical was the key intermediate of the transformation.

3.4. Other applications of chalcogenative sulfones under metal-free conditions

In this section, the reactions of selenosulfonates and thiosulfonates via breaking the original S(Se)-SO₂R bond with the assistance of azo compounds, peroxides, heating, and organic small molecules are discussed. In 1983, Miura and Kobayashi ob-



Scheme 21. The construction of dibenzofulvene derivatives.

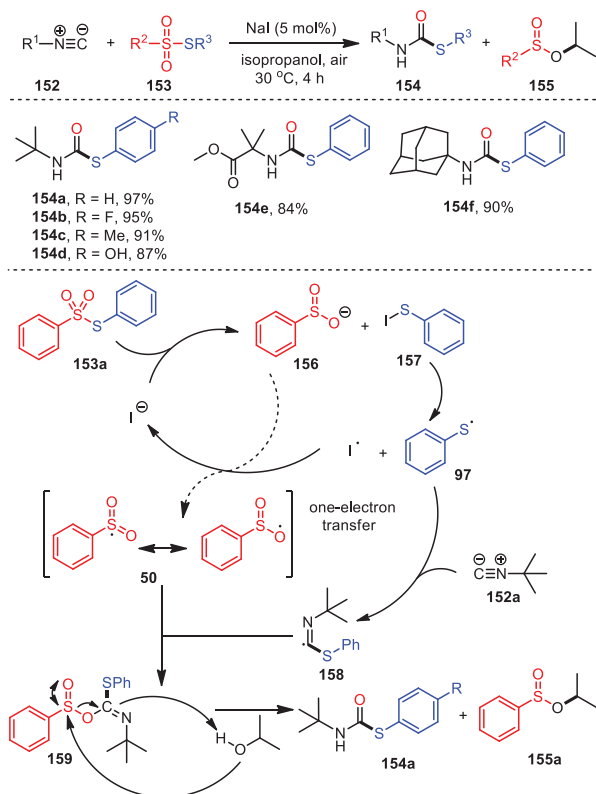


Scheme 22. The preparation of β -(phenylseleno)vinyl sulfones under metal-free conditions.

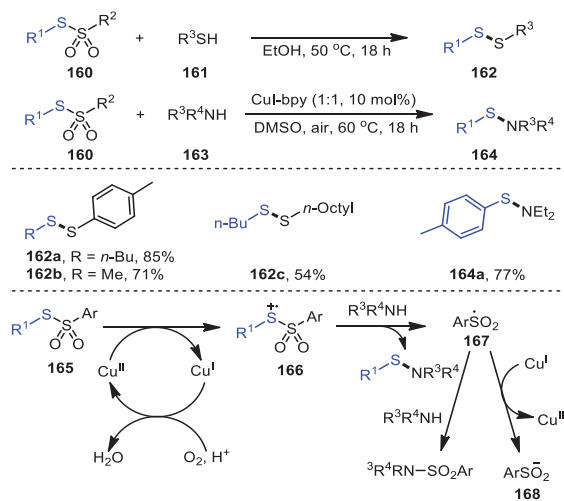
served that Se-phenyl *p*-tolueneselenosulfonates **148** underwent thermally induced 1,2-additions to acetylenes, producing novel β -(phenylseleno)vinyl sulfones **149** in high yields (Scheme 22) [107]. The reaction had excellent regioselectivity and stereoselectivity, and it occurred through a radical chain mechanism initiated by the thermal decomposition of selenosulfonates.

In 2016, Maes' and Ruijter's groups reported a new method for the construction of secondary thiocarbates **154** from isocyanides **152** and thiosulfonates **153** catalyzed by sodium iodide under mild conditions (Scheme 23) [108]. Remarkably, this reaction could be applied to substrates with electron-withdrawing or electron-donating substituents, resulting in a series of *S*-aryl *tert*-butylthiocarbamates with considerable yields. In addition to *tert*-butylisocyanide, other tertiary isocyanides could also participate in this transformation, and even adamantyl isocyanides **154f** could be applied.

Mechanistically, first, **153a** reacted with sodium iodide to form benzenesulfinate anion **156** and PhSI **157**, which underwent homolysis, forming radical **97**. Subsequently, the intermediate **159**



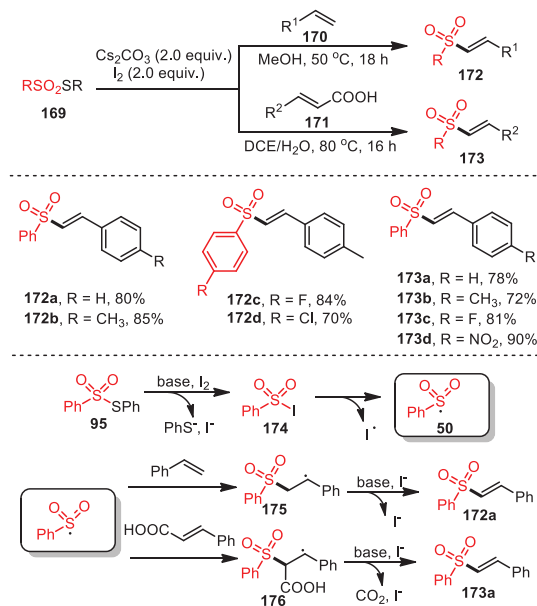
Scheme 23. The formation of secondary thiocarbamates.



Scheme 24. The construction of unsymmetrical disulfide and sulfenamide under metal-free conditions or promoted by copper.

was successfully obtained through the reaction of radical **158** and **50** obtained by the addition of **97** and isocyanide **152a**. Radical **158**, derived from the addition of **97** with isocyanide **153a**, reacted with intermediate **50** successfully to access intermediate **159**. Ultimately, the alcoholysis of intermediate **159** with isopropanol accounted for the formation of **154a** and **155a**.

One year later, Taniguchi's group investigated a protocol for producing unsymmetrical disulfides **162** in high yields by reacting thiosulfonates **160** as free-radical reagents with nucleophile thiol reagents **161** under metal-free conditions (Scheme 24) [109]. Meanwhile, the reaction of amines **163** and thiosulfonates **160** to produce sulfenamides **164** catalyzed by copper was also investigated. Notably, the conversion could obtain the desired unsym-



Scheme 25. The synthesis of vinyl sulfones mediated by iodine.

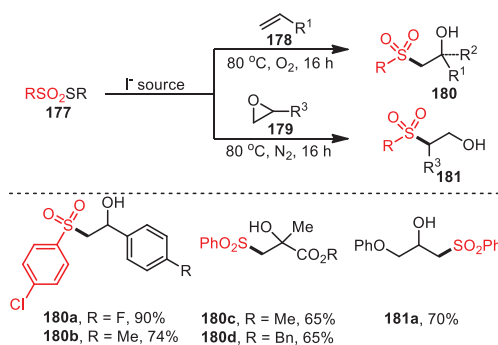
metrical disulfides at excellent yields for both aryl-substituted and alkyl-substituted thiosulfonates. The addition of TEMPO, a radical scavenger, significantly inhibited the reaction process, suggesting that thiosulfonates reacted with amine through a radical reaction. Mechanistically, sulfonamide and a sulfonyl radical **167** were produced by the reaction of amine with radical intermediate **166** originating from the oxidation of thiosulfonate by a copper catalyst in air. The sulfonyl radical reacted with amine or was reduced by CuI to further yield the final product sulfonamide.

A simple method to construct various vinyl sulfones **172** by sulfenylation of thiosulfonates **169** with styrenes **170** or cinnamic acid derivatives **171** was discovered by Jang's group in 2018 (Scheme 25) [110]. Notably, this sulfenylation appeared to be more functional for electron-deficient thiosulfonates and electron-rich styrene derivatives. In addition, under standard conditions, electron-deficient cinnamic acid derivatives could react with phenyl thiosulfonates smoothly, providing corresponding products in moderate to excellent yields. The strategy was characterized by mild conditions, environmental friendliness, and excellent functional group tolerance.

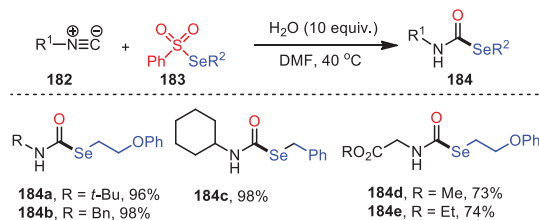
Some control experiments indicated that the above process may involve a radical pathway, and a rational mechanism was outlined as Scheme 25. First, sulfonyl iodide **174**, derived from the reaction of thiosulfonate with I_2 , underwent homolytic cleavage to form sulfonyl radical **50**, which was then added to either styrene or cinnamic acid. Finally, the radical intermediates **175** or **176** performed base-assisted elimination of HI or HI and CO_2 , resulting in vinyl sulfone **172a** or **173a**, respectively.

In the same year, the same group also studied the reactivity of thiosulfonates **177**, which could selectively generate β -hydroxysulfones with moderate to excellent yields under the condition of organic base KI and an aqueous solvent (Scheme 26) [111]. Obviously, this reaction could occur smoothly between either electron-withdrawing or electron-donating thiosulfonates and substituted styrenes, and the desired products were obtained successfully. In addition, electron-deficient alkenes, including methyl methacrylate and benzyl methacrylate, were obtained, with 65% yields of **180c** and **180d**, respectively.

In 2019, Ji, Wang and coworkers developed an effective method for the construction of secondary selenocarbamates **184** from isocyanides **182**, selenosulfonates **183**, and water by a radical-chain



Scheme 26. The synthesis of diverse β -hydroxysulfones under metal-free conditions.

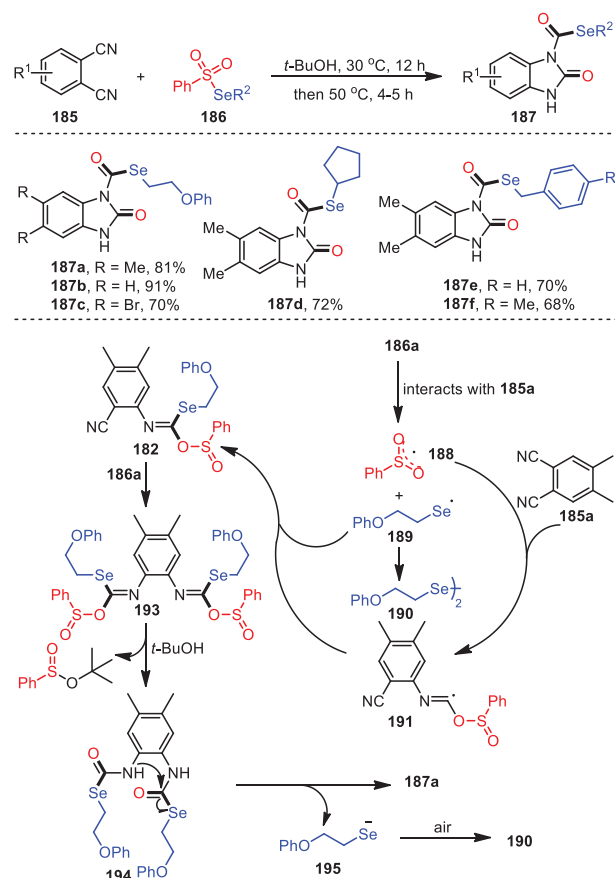


Scheme 27. The synthesis of selenocarbamates under metal-free conditions.

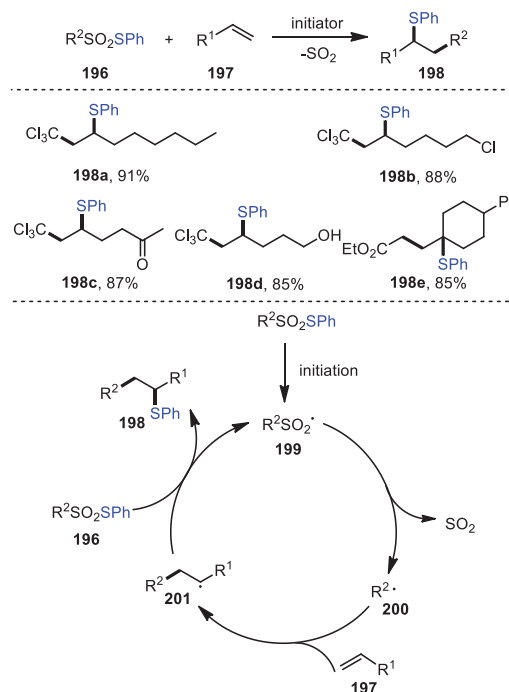
reaction under metal-free conditions (Scheme 27) [112]. This approach was characterized by simple operation, mild conditions, no need for additional catalysts, and good functional group tolerance. Obviously, either alkyl- or aryl-substituted isocyanides reacted smoothly under standard conditions and yielded corresponding products with considerable yields. This showed that the universality of the current process applied to both chain and ring compounds. Surprisingly, the primary isocyanides **184d** and **184e** target products were also smoothly obtained, with yields of 73% and 74%, respectively.

Later, a method of constructing 2-benzimidazolone derivatives **187** using the metal-free reaction of *ortho*-diisocyanoarenes **185** and selenosulfonates **186** was first developed by the same group (Scheme 28) [113]. The reaction was easy to handle and proceeded smoothly with moderate to excellent yields and tolerance of functional groups. Methyl- and bromide-substituted isocyanides all reacted successfully under standard conditions to obtain the target products with 81% and 70% yields, respectively. Furthermore, not only aryl-substituted selenosulfonates were suitable for this process, but cycloalkane-substituted selenosulfonates also had good tolerance under the same conditions. Based on the results of relevant control experiments and previous literature reports, a possible mechanism involving a radical process was described, as shown in Scheme 28. Herein, the formation of radical intermediate **188** was due to the intermolecular interaction between **185a** and **186a**.

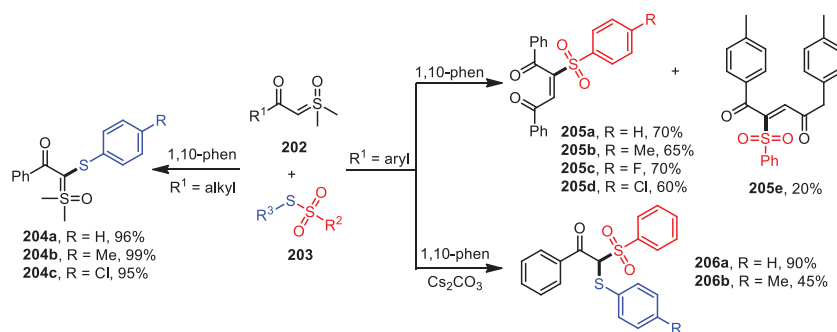
In 2020, Renaud's group introduced an efficient method for the thioalkylation of olefins by radical desulfuration sulfur-group transfer based on the use of readily available thiosulfonates **196** as starting materials (Scheme 29) [114]. Using $\text{Cl}_3\text{CSO}_2\text{SPh}$ as a starting material and diauryl peroxide (DLP) as an initiator, the desulfurative thioalkylation of 1-octene **197a** was attempted, and a 91% yield of corresponding product **198a** was successfully obtained. A considerable number of functional groups such as chlorines, ketones, and even alcohols could be well tolerated by this process. Mechanistically, a sulfonyl radical **199** was generated as a result of DLP, light, or V-40 initiation processes, which underwent a rapid desulfuration process resulting in an electrophilic radical **200** being added to the olefin **197**. The radical intermediate **201** then reacted with thiosulfinate to form a thioalkylated alkene.



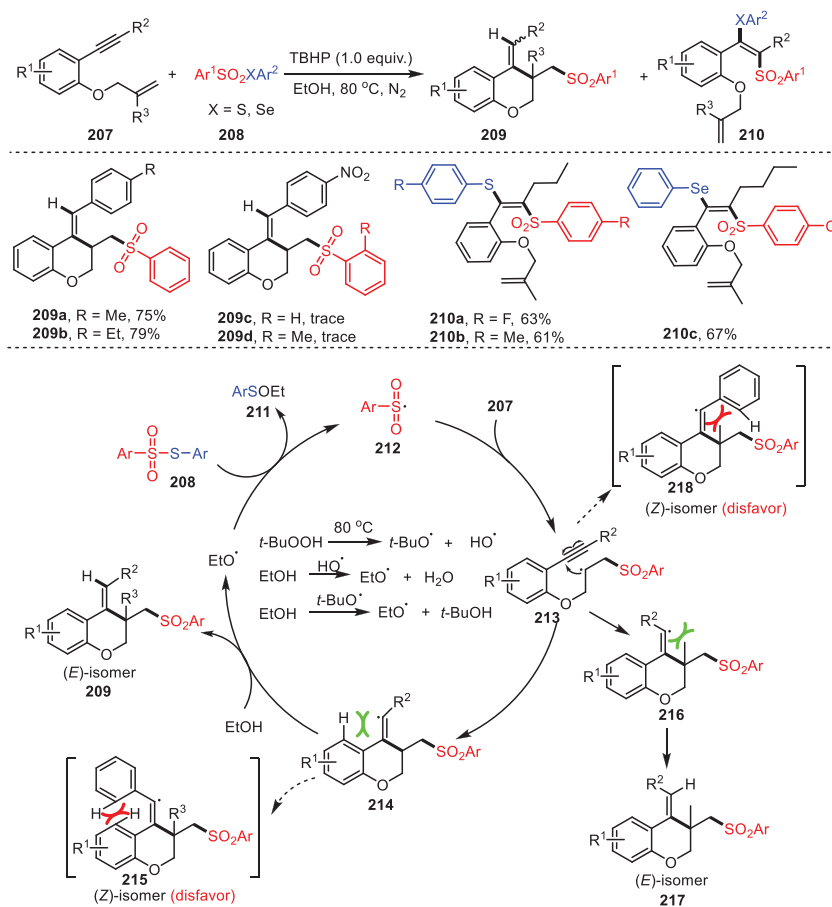
Scheme 28. The synthesis of *N*-(carboselenoate) benzimidazolones under metal-free conditions.



Scheme 29. Desulfurative thioalkylation of alkenes under metal-free conditions.



Scheme 30. The preparation of 1,4-diketone compounds, arylthiosulfoxide-ylides, and β-keto thiosulfones under metal-free conditions.



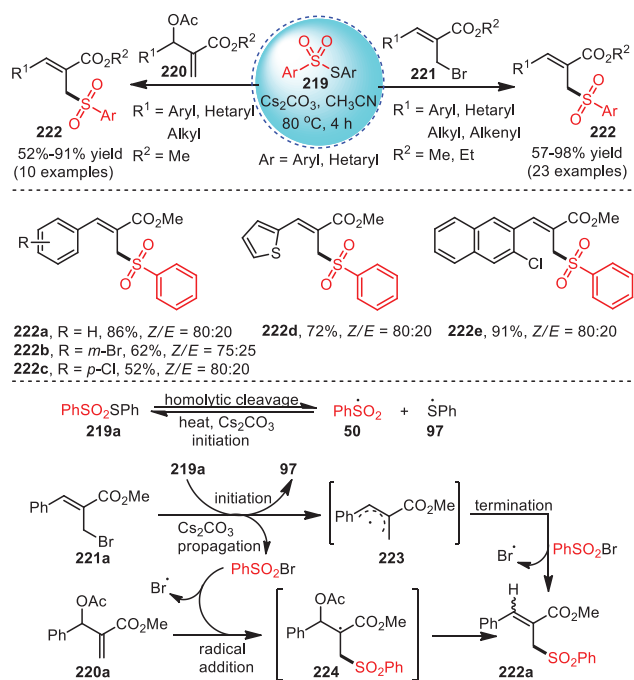
Scheme 31. The construction of (E)-3-((arylsulfonyl)-methyl)-4-substituted benzylidenemethylene derivatives under metal-free conditions.

In 2020, Wang and coworkers established a radical cascade reaction between sulfoxonium ylides **202** and thiosulfonates **203** in the absence of transition metals and smoothly selectively prepared 1,4-diketone compounds **204**, arylthiosulfoxide-ylides **205**, and β-keto thiosulfones **206** (Scheme 30) [115]. Notably, the desired products could be obtained successfully in moderate to excellent yields when using S-phenyl arylsulfonates possessing electron-withdrawing or electron-donating groups as substrates. However, when 2-(dimethyl(oxo)-λ⁶-sulfanylidene)-1-(p-tolyl)ethan-1-one **202e** was used as a starting material, the yield decreased to 20%. Mechanistic studies confirmed that this transformation was a free-radical reaction process, and 1,10-phenanthroline could stabilize free radicals in this route.

A method to successfully construct (E)-3-((arylsulfonyl)-methyl)-4-substituted benzylidenemethylene derivatives **209** through radical cyclization of oxygen-containing 1,7-enynes **207**

and thiosulfonates **208** with the assistance of TBHP was proposed by Wang, Rong and coworkers. (Scheme 31) [116]. Remarkably, different alkyl groups such as methyl as well as ethyl on the aromatic ring at the terminal alkyne (R²) could participate under standard conditions smoothly, obtaining corresponding products **209a** and **209b** with moderate yields. However, 1,7-enynes bearing a stronger electron-withdrawing group (NO₂) were not suitable for this reaction, indicating that the substituent properties of 1,7-enynes had a great impact on the reaction. The gram-scale reaction of this procedure was also verified, and the yield was good. A feasible mechanism was reported, as shown in Scheme 31, based on the results of control experiments.

In 2021, Reddy's group proposed a method for the synthesis of allyl sulfones **222** with high yields and stereoselectivity by radical sulfonation reaction of Morita-Bayis-Hillman adducts and thiosulfonates **219** promoted by Cs₂CO₃ (Scheme 32) [117]. Surpris-



ingly, aryl- and heteraryl-derived substrates could also tolerate this method, and the target products were successfully obtained with moderate to excellent yields. In addition, these allyl sulfones, especially allyl (hetero)aryl sulfones, had anticancer and abnormal cell-proliferation activities.

Mechanistically, at the very start, in the presence of Cs_2CO_3 , PhSSO_2Ph underwent homolytic cleavage resulting in the production of sulfonyl radical **50** and thiyl radical **97**. Afterwards, the propagation of **221a** explained the formation of allyl radical **223** and termination product sulfonyl bromide (PhSO_2Br). In the end, the desired allyl sulfone **222a** was obtained via the sulfonation of product **223** and PhSO_2Br . Similarly, the radical addition of substrate **220a** with sulfonyl radical generated radical **224**, which underwent elimination to access the desired allyl sulfone **222a**.

4. Conclusions and outlook

In this review, the recent progress in the synthesis and applications of thiosulfonates and selenosulfonates as radical reagents is reviewed, and the reaction scopes, limitations, and some mechanisms are also discussed. Depending on the reaction system, metal catalysis, visible-light catalysis, synergistic catalysis, and other types including azo compounds, heat, organic molecules, or peroxide-induced radical reactions were classified. After the above discussion, it can be found that thiosulfonates and selenosulfonates can utilize these methods to provide a stable and powerful platform for the efficient construction of various selenium- and sulfur-containing heterocyclic compounds and difunctional products. The successful examples described in this review convincingly demonstrate the high potential of thiosulfonates and selenosulfonates for drug discovery and applications. Among these synthesis methods, photochemistry and synergistic metal/photoredox catalysis techniques provide a more environmentally friendly and sustainable alternative for the applications of thiosulfonates and selenosulfonates and illustrate the development prospects of chalcogenative sulfones as free radicals.

Although significant progress has been made in this field over the last few years, several issues and challenges remain in fully

developing the potential applications of thiosulfonates and selenosulfonates, which should be further exploited and improved. First, more catalytic means should be explored in the applications of thiosulfonates and selenosulfonates as free-radical reagents, especially electrochemical synthesis methods, since electrochemical strategies have become increasingly powerful tools for the synthesis of organic compounds in recent years. Second, migration cyclization strategies involving thiosulfonates and selenosulfonates as radical reagents should be established to construct more complex polycyclic compounds, since polycyclic frameworks play an important role in medicinal chemistry and organic materials. In addition, the harmful consequences of metal catalysts and peroxides used in the reaction process cannot be ignored. Hopefully this paper will encourage more researchers to contribute to this emerging field by developing more environmentally friendly catalytic systems.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

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