Visible light-mediated synthesis of 1,3-benzothiazoles: A comprehensive review

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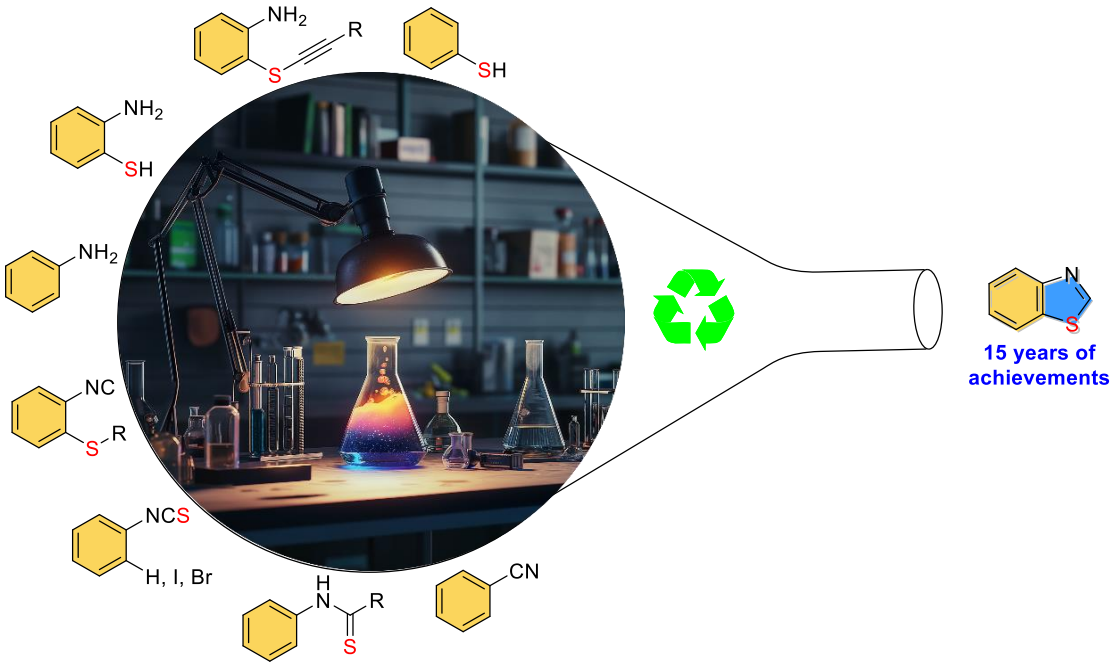
Highlights

- This review is the most comprehensive work to date on photochemical methods for the synthesis of 1,3-benzothiazoles completely covering developments in this field for the last 15 years
- A detailed summary for light-mediated synthesis of 1,3-benzothiazoles based on plausible reaction mechanisms is discussed
- Contributions of metal-based and organic photoredox catalysis, along with external photocatalyst-free conditions employed in benzothiazole synthesis are covered
- Possible ways of improving current synthetic methodology are outlined

Abstract

Photoredox catalysis has emerged as a powerful tool in organic synthesis, revolutionizing how chemists approach challenging bond-forming reactions. The importance of 1,3-benzothiazoles lies in their diverse roles in medicinal chemistry, materials science, and industrial applications, due to their stability, bioactivity, and versatility as building blocks. This review represents the most comprehensive work to date on photochemical methods for synthesizing 1,3-benzothiazoles, covering developments in this field from 2009 to 2024. It is organized by the types of starting compounds and discusses synthetic strategies for the target compounds alongside proposed reaction mechanisms. Notably, many established light-driven methods are photocatalyst-free and typically conducted under visible light (CFL, white, green, or blue LED) at room temperature. By exploring a range of synthetic methods, this review not only deepens our understanding of benzothiazole synthesis but also inspires possibilities for future advancements. We hope this review will motivate chemists to pursue new, environmentally friendly methods for synthesizing these and related biologically significant sulfur heterocycles.



Keywords: Photoredox catalysis; LED-light; Reaction mechanism; Green chemistry; 1,3-Benzothiazoles

1. Introduction

Photochemistry has ushered in a new era in the development of chemistry, and photoredox catalysis has become a hot topic, especially over the last fifteen years, with the combination of visible-light photoredox catalysis and radical reactions. Recently, visible-light photoredox catalysis has emerged as a powerful tool for the synthesis of densely substituted heterocycles that are difficult to prepare by traditional methods [1]. All these features make photoredox catalysis a sustainable alternative from the viewpoint of radical reactions and one that can be utilized as an elegant method to access reactive radicals giving practically valuable heterocyclic derivatives. Despite the recent publication of several large reviews on the photochemical formation of C–S bonds [2, 3, 4], the topic of photochemical synthesis of 1,3-benzothiazoles is very poorly described. Considering our constant interest in sulfur-containing heterocycles and their chemistry [5-11], we have found that more than 20 different types of such S-heterocycles can be obtained photochemically, and among them, the benzothiazoles are definitely the most developed. They are privileged and versatile heterocyclic scaffolds with extensive applications in pharmaceutical industry and materials science. As of November 2024, Reaxys® database showed approximately 340k compounds mentioned in >196k documents related to chemical space of 1,3-benzothiazoles. There are several early works published in 1982 [12] and 1997 [13] using ultraviolet (UV)-light-induced intramolecular aromatic substitutions of 2-bromo/iodo-thiobenzanilides to benzothiazoles. The application of quartz equipment, high-energy UV light and harsh conditions (in some cases a strong base in liquid ammonia) limits the substrate scope and causes unwanted side reaction products. Since the first ground-breaking work in 2009 [14], we found only 56 papers where benzothiazole motif was directly formed through photochemical event using visible light and in most cases at room temperature (Fig. 1). Thus, we believe this narrow area deserves separate consideration as a presented comprehensive review.

Since benzothiazoles are one of the best-known heterocycles, there are dozens of reviews devoted to their synthesis, including the most recent [15-26]. Despite this, photochemical methods for their synthesis are relatively rare and are not systematically presented in these and similar reviews. Thus, this comprehensive review highlights the 15-years progress in the synthesis of benzothiazoles mediated by visible light providing overview of their synthetic scope. This work is

structured based on the type of starting compounds used for the synthesis of benzothiazoles. In addition, the possible mechanisms of transformations are discussed.

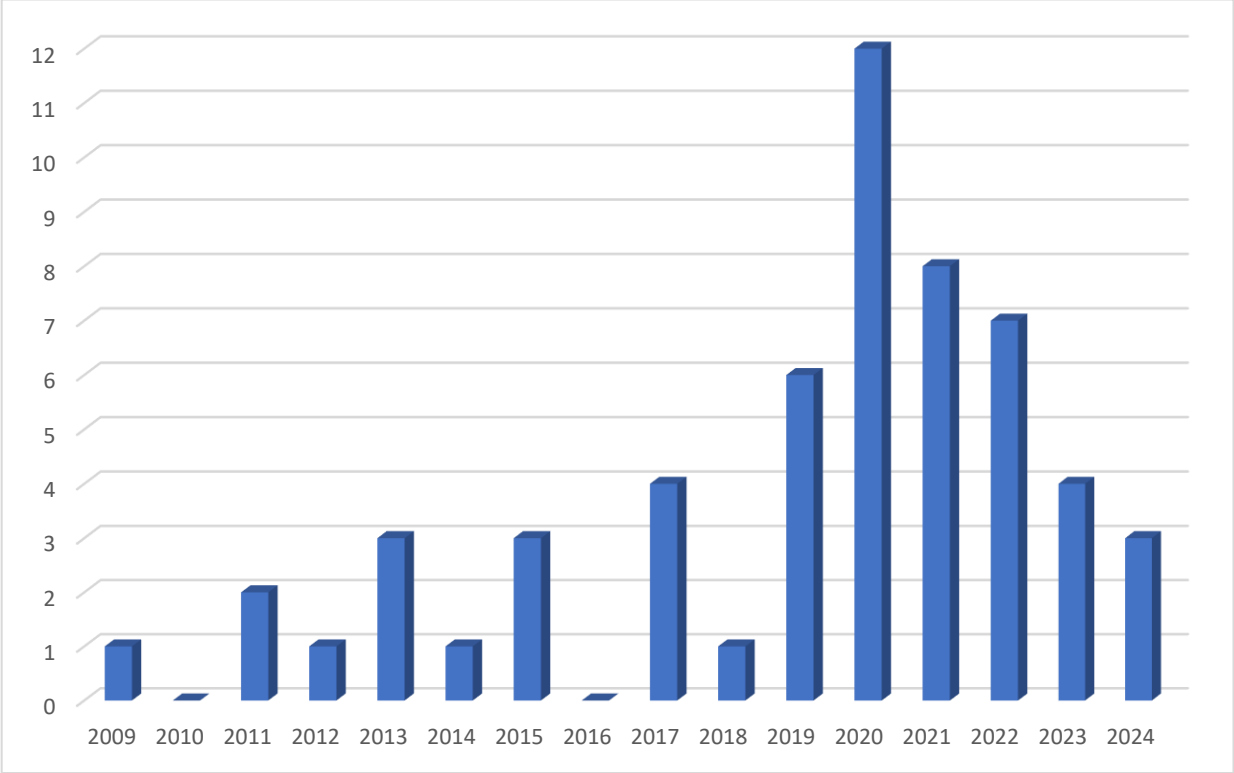


Fig. 1. Literature survey regarded photo-assisted methods for the synthesis of benzothiazole moiety (56 papers in total between 2009 and 2024)

The thiazole heterocycle itself is certainly a privileged structure and ranks 12th on the list of heterocyclic moieties most frequently found among FDA-approved drugs in 2013-2023 [27]. It is, therefore, not surprising that the wide range of pharmacological activities exhibited by benzothiazoles highlights their potential as key compounds for future drug development. Recently, research on benzothiazole-based medicinal chemistry has become a rapidly evolving and increasingly active subject. In particular, many benzothiazole-based compounds as clinical drugs have been widely used in practice to treat various types of diseases with high therapeutic efficacy (Fig. 2A). Among them anticancer [28-36], anti-inflammatory [28, 32, 33], antimicrobial [28, 30, 32, 33], antifungal [30], anticonvulsant [28, 33], antimalarial [28, 32, 33], antiviral [33, 37, 38], antidiabetic [32, 33], antihelmintic [32] agents. In addition to their application in different morbid conditions, they were also reported as inhibitors of such enzymes as α-glucosidase, carbonic anhydrase, acetylcholinesterase (AChE) and butyrylcholinesterase (BuChE), topoisomerase I and II, p38α-MAP kinase, β-glucuronidase, cytochrome P450 etc. [33].

Benzothiazoles are also present in many biologically important naturally occurring products (Fig. 2B). Unsubstituted benzothiazole itself was first isolated in 1967 from the volatiles of American cranberries *Vaccinium macrocarpon Ait. var. Early Black*. Since then, benzothiazole has been isolated from many different sources: the tail-gland of the red deer *Cervus elaphus*, French oak wood, the fungi *Aspergillus clavatus,* some tealeaves and wines, etc. [39]. Hu and MacMillan [40] reported the isolation of erythrazoles A and B from mangrove sediments of *Erythrobacter sp*. The erythrazole B had been investigated to possess potent cytotoxic activity against a panel of non-small cell lung cancer (NSCLC) cell lines. 6-Hydroxybenzothiazole-5-acetic acid, also known as antibiotic C304A, is a naturally occurring benzothiazole that was isolated from the cultured filtrate of the bacterium *Actinosynnema sp*. [39] and *Paecilomyces lilacinus*. The rifamycins are a group of antibiotics

(mycobacteria) that are synthesized naturally by the bacterium *Nocardia mediterranei*, and are therefore used to treat tuberculosis, leprosy, and Mycobacterium avium complex infections. Violatinctamine, bright orange alkaloid isolated in 2004 from a Kenyan marine tunicate of the genus *Cystodytes cf. violatinctus*, presents a unique heterocyclic skeleton that combines a benzothiazole core and a dihydroisoquinoline unit. It is interesting to note that the amino acid cysteine could be the source of the sulfur atom in all benzothiazole natural products [39].

In addition to this, benzothiazoles are widely used as fluorescent probes for analyte detection (Fig. 2C). Based on the mechanism of photoinduced electron transfer, excited-state intramolecular proton transfer (ESIPT), intramolecular charge transfer, aggregation-induced emission, the benzothiazole based fluorescent probes can specifically interact with the analyte (metal ions, anions, small molecules, biological macromolecules etc.), thereby changing their luminescence characteristics to achieve the detection of the analyte. Benzothiazole fluorescent probes can also be applied to the detection of harmful substances and cell imaging [41]. Benzothiazole-based Ir(III) complexes are well-known as phosphorescent emitters in OLED devices [42].

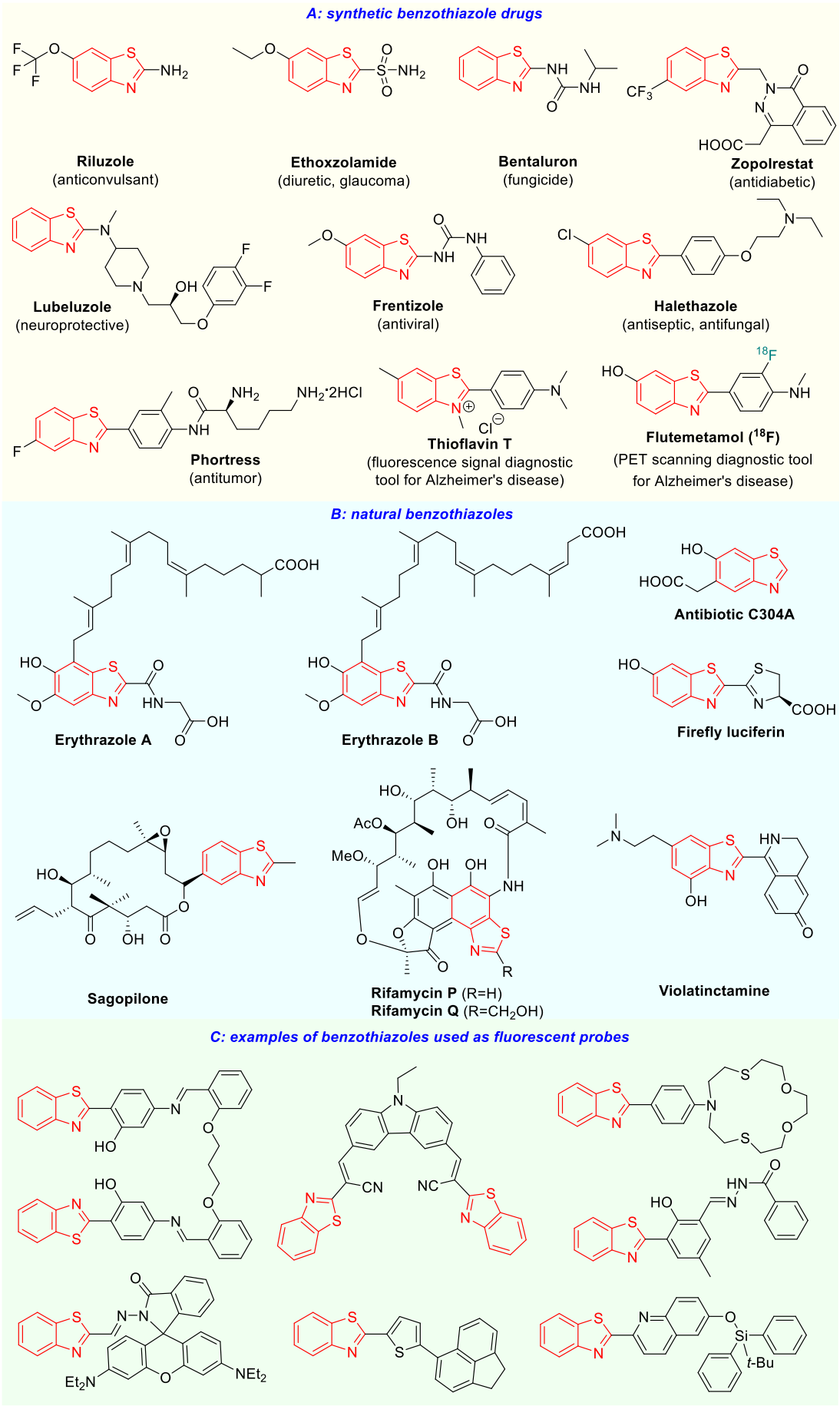


Fig. 2. Selected biologically important synthetic (A) and natural (B) products, and compounds (C) used as fluorescent probes for analyte detection bearing benzothiazole motif (*shown in red*)

2. Metal-based and organic photoredox catalysts/photosensitizers employed in benzothiazole synthesis

One of the major targets in modern synthetic chemistry is to develop green synthetic methods that take into account environmental impacts in the selection of reactants and reaction conditions. The use of visible-light to promote chemical processes is increasingly growing in importance as it represents an environmentally friendly alternative to the existing traditional synthetic methods. The employment of visible light has emerged as a powerful, selective, and sustainable tool for the construction and functionalization of 1,3-benzothiazole heterocyclic system. Fig. 3 contains list of catalysts/photosensitizers employed in benzothiazole synthesis discussed within this review. Among them, typical complexes like $Ru(bpy)_3Cl_2$ **1** [43-46], $Ru(bpy)_3(PF_6)_2$ **2** [47, 48], $Ru(phen)_3Cl_2$ **3** [49], *fac*-$Ir(ppy)_3$ **4** [50, 51], $Co(dmgH)_2PyCl$ **5** [52] and $Co(dmgH)_2(4\text{-}NMe_2\text{-}Py)Cl$ **6** [48], metal-based catalysts as Ba-dopped $CoMoO_4$ nanoparticles **7** [53], cetyl trimethylammonium bromide (CTAB)-coated Bi_2WO_4 **8** [54], CdSe/montmorillonite **9** [55], CdS nanosphere **10** [56], MIL-100(Fe) **11** [57], PhTeTePh **12** [58], and organic photoredox catalysts *p*-tolyl disulfide **13** [59] *p*-chloranil **14** [14], deprotonated mesoporous graphitic carbon nitride (mpg-C_3N_4) polymers **15** [60-62], TETPY **16** [63], PYTZ **17** [64], eosin Y **18** [65-72], rose bengal **19** [73, 74], fluorescein **20** [75], riboflavin 2',3',4',5'-tetraacetate (RFTA) **21** [76, 77], $[Acr^+\text{-}Mes]BF_4^-$ **22** [78], 4CzIPN **23** [79], 4CzIPN-^{t}Bu **24** [80], and two-dimensional porphyrin nanoplates (2DPNs) [81]. It is also important to know and worth mentioning, that many of known light-driven syntheses of benzothiazoles were conducted under external photocatalyst-free conditions [82-97]. A representation of individual groups of catalysts used in the synthesis of benzothiazoles is shown in Fig. 4.

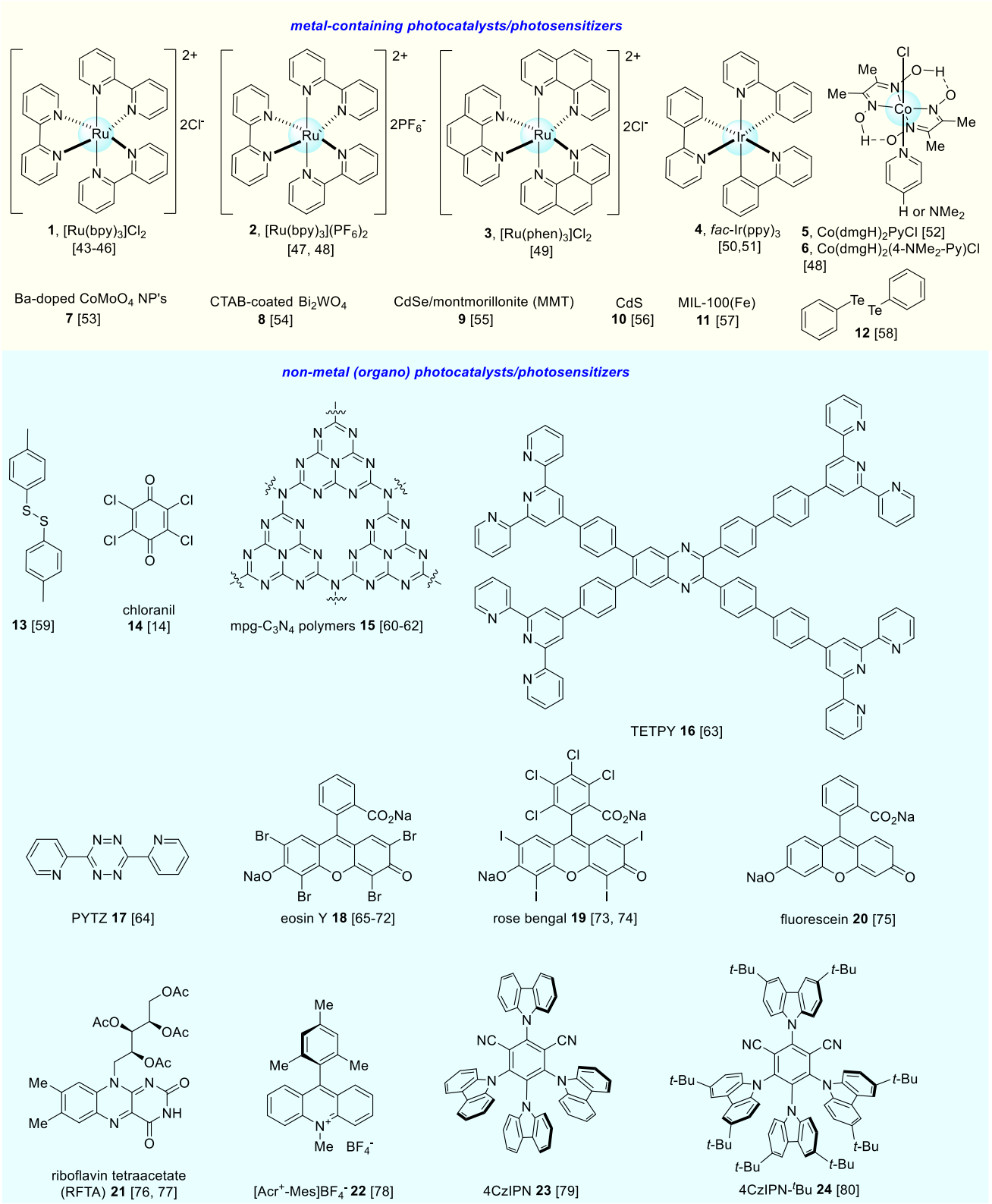


Fig. 3. Typical metal-based and organic photoredox catalysts/photosensitizers employed in benzothiazole synthesis.

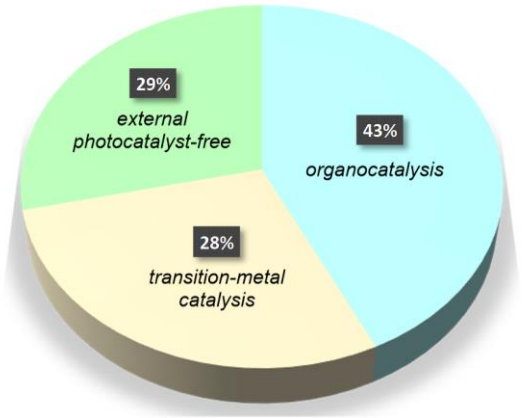
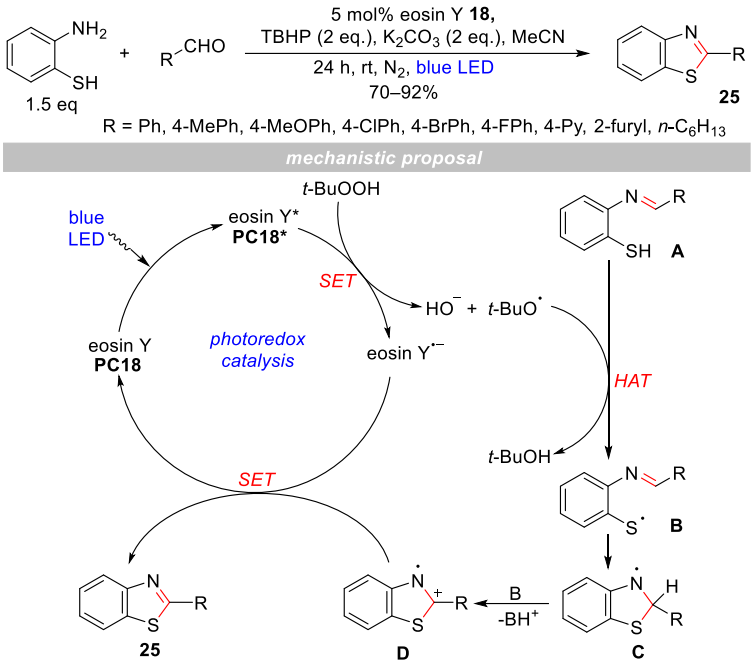


Fig. 4. A representation of individual groups of catalysts used in the photo-assisted synthesis of benzothiazoles

3. Cyclization of 2-aminothiophenols with aldehydes

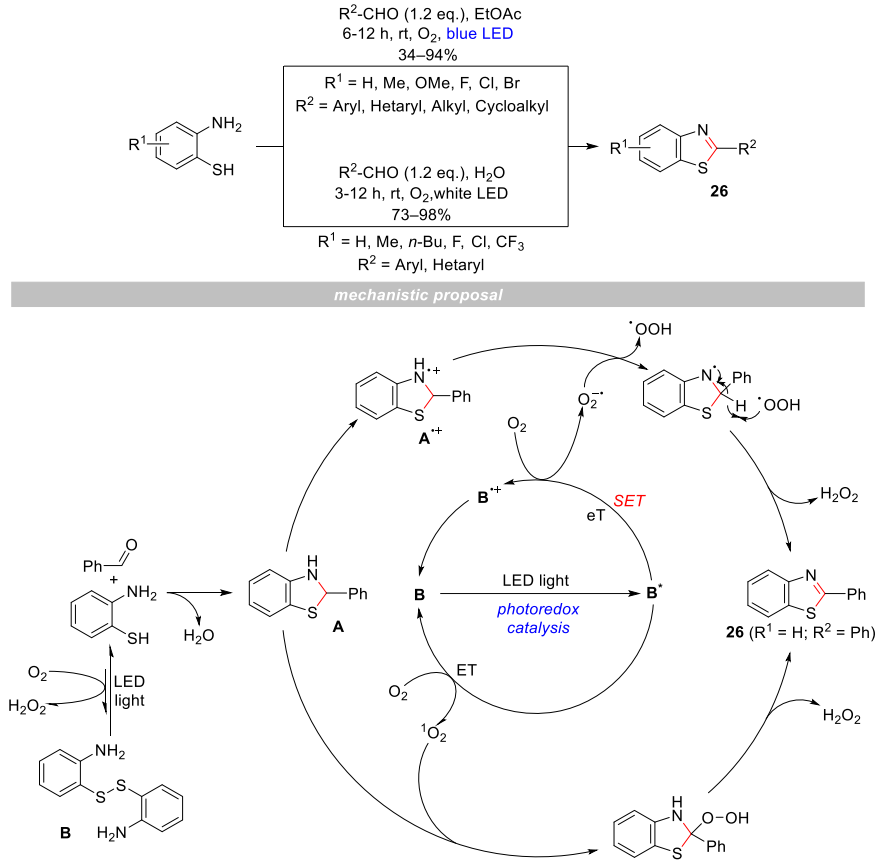
The photocatalyzed reaction of 2-aminothiophenols with different reagents (mostly aldehydes) is one of the most studied methodologies to obtain desired benzothiazoles due to its simplicity, mild reaction conditions, and the commercial availability of starting materials.

Among the numerous studies reporting the photochemical synthesis of benzothiazoles from aminothiophenols and aldehydes, only one has been conducted under anaerobic conditions [65]. In this study, a one-pot coupling reaction catalyzed by eosin Y **18** was performed using *tert*-butyl hydroperoxide (TBHP) as the oxidant in acetonitrile under blue LED irradiation (Scheme 1) [65]. Although the mechanism remains incompletely elucidated, a plausible pathway has been proposed to rationalize the formation of the desired products **25**. The suggested mechanism begins with the *in situ* condensation of the aldehyde and 2-aminophenol to form imine **A**, accompanied by the excitation of eosin Y **18** under visible light. The excited-state eosin Y* is proposed to interact with TBHP, generating a *tert*-butoxy radical (*t*-BuO$^{\bullet}$) and a hydroxide ion (OH^-). The *t*-BuO$^{\bullet}$ radical then abstracts a hydrogen atom from imine **A**, resulting in the formation of *tert*-butanol (*t*-BuOH) and the arylthiyl radical **B**. Radical **B** undergoes intramolecular 5-endo cyclization with the imine moiety, producing aminyl radical **C**. Subsequently, a tertiary carbanion intermediate **D** is generated, a process facilitated by the presence of a base. Finally, single electron transfer (SET) from **D** to the eosin Y radical anion restores eosin Y **18** to its ground state, ultimately yielding the benzothiazole products **25** (Scheme 1).



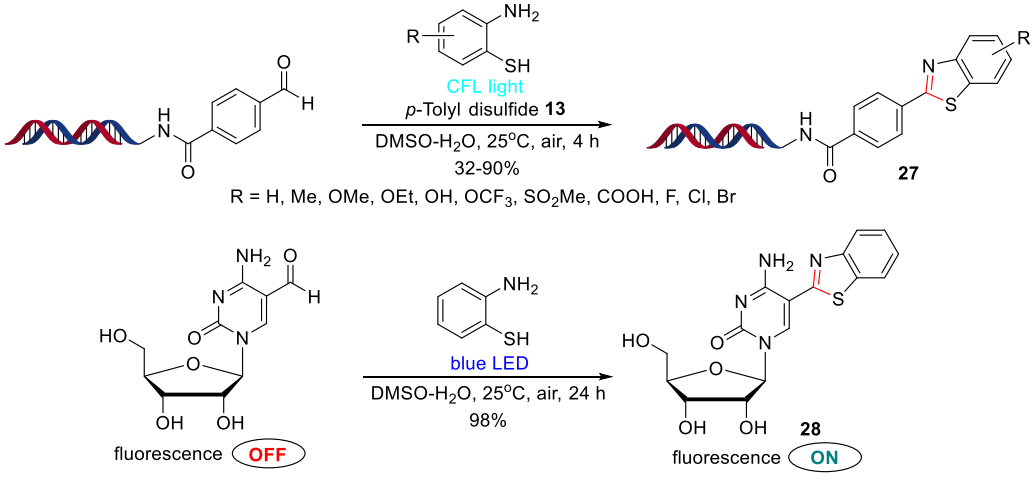
Scheme 1. Eosin Y **18** catalyzed synthesis of benzothiazoles **25.**

The use of a visible-light-absorbing intermediate as a photosensitizer simplifies and enhances the sustainability of chemical processes by eliminating the need for additional chemical additives. This strategy has been effectively employed in several studies (Scheme 2) [82, 88]. In the synthesis of benzothiazoles from 2-aminothiophenol and aldehydes, the formation of a photosensitizing disulfide intermediate was proposed and confirmed through detailed mechanistic investigations. Yan and co-workers successfully demonstrated the broad applicability of this method, employing a wide range of aromatic, heteroaromatic, and aliphatic aldehydes (40 examples) to synthesize benzothiazoles **26** under blue LED irradiation in ethyl acetate (Scheme 2) [82]. Subsequently, You and Cho showed that a similar scope of benzothiazole derivatives could be synthesized in water using white LED irradiation (Scheme 2) [88]. These reactions achieved good to excellent yields, irrespective of the electron density or substituent positions on the aldehydes. The mechanism begins with the reaction of benzaldehyde and 2-aminothiophenol to generate intermediates **A** and **B**. Under photoirradiation, **B**, which is in equilibrium with the starting materials, acts as a photosensitizer. It facilitates the production of reactive oxygen species, including superoxide anion ($O_2^{\bullet-}$) and singlet oxygen ($^1O_2$), *via* SET and energy transfer pathways, respectively. In the electron transfer pathway, photoexcited **B*** donates an electron to molecular oxygen (O_2), generating $O_2^{\bullet-}$ and the radical cation $\mathbf{B}^{\bullet+}$. The latter undergoes reduction, regenerating **B** through the oxidation of **A** to $\mathbf{A}^{\bullet+}$. The radical cation $\mathbf{A}^{\bullet+}$ is then deprotonated and reacts with $O_2^{\bullet-}$, resulting in the formation of benzothiazole **26** (R^1 = H; R^2 = Ph) along with hydrogen peroxide (H_2O_2). In the energy transfer pathway, $^1O_2$ undergoes insertion at the C–H bond at the 2-position of **A**, releasing H_2O_2 and forming **26** (R^1 = H; R^2 = Ph). The production of H_2O_2 during the reaction was confirmed using a peroxide indicator. Notably, even in the absence of light irradiation, the reaction still proceeds, albeit with low yields of 9–13%.



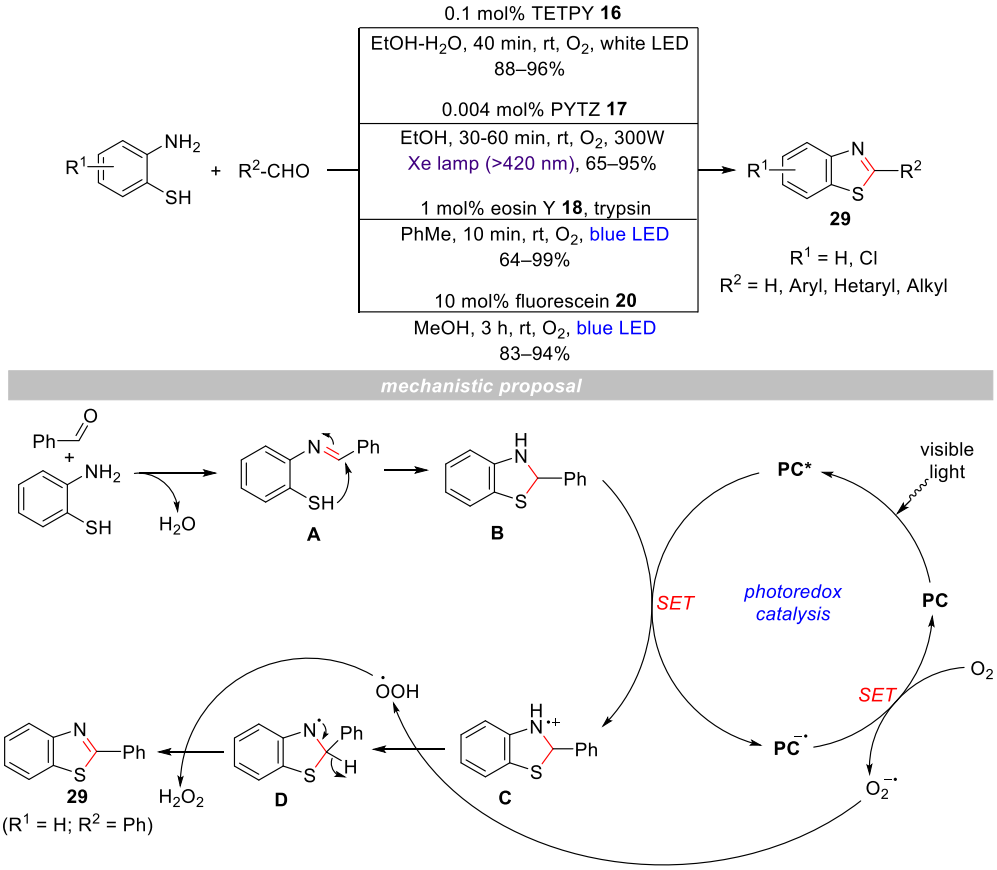
Scheme 2. External photocatalyst-free synthesis of benzothiazoles **26.**

Benzoheterocycles are extensively utilized as drug-like core scaffolds and have been effectively integrated into DNA-encoded chemical library technology to facilitate high-throughput hit discovery. Li and co-workers [59] successfully synthesized four types of DNA-conjugated benzoheterocycles, including benzothiazoles **27**, under light-promoted conditions with a broad substrate scope (Scheme 3). The authors [59] proposed that the reaction proceeds *via* the same mechanism previously established (Scheme 2) [88], with (*p*-TolS)$_2$ **13** serving as an external photosensitizer in this instance. The development of novel bioorthogonal reactions that enable the sensitive and efficient detection of 5-formylcytidine RNA in nucleic acids, both *in vitro* and *in vivo*, remains a significant challenge. To address this, a blue LED-triggered, catalyst-free photo-click condensation was employed to selectively label 5-formylcytidine with 2-aminothiophenol, resulting in the formation of the fluorogenic 5-(benzothiazol-2-yl) cytidine **28** (Scheme 3) [85].



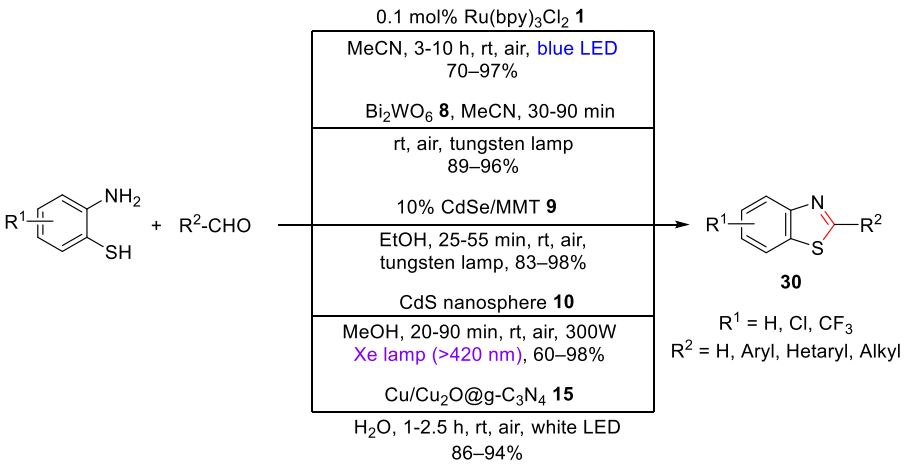
Scheme 3. Synthesis of DNA-conjugated benzothiazoles **27** and 5-(benzothiazol-2-yl) cytidine **28.**

Organophotocatalysts, including TETPY **16**, PYTZ **17**, eosin Y **18**, and fluorescein **20**, have been employed in the photo-assisted synthesis of benzothiazoles **29** under visible-light conditions (Scheme 4) [63, 64, 72, 75]. The work [72] represents the first example of combining enzymatic catalysis with visible-light photoredox catalysis for the synthesis of 2-substituted benzothiazoles. This innovative methodology achieves target compound yields up to 99% within just 10 minutes. The proposed mechanism, consistent across these methods, begins with the formation of imine **A** through the nucleophilic addition and dehydration of 2-aminothiophenol and benzaldehyde under visible-light irradiation. Imine **A** subsequently undergoes intramolecular cyclization to generate intermediate **B**. Under the photocatalyst (PC)/O_2 catalytic system, visible light excites PC, producing the species PC*. This excited state facilitates the SET that converts intermediate **B** into **C**. The photocatalyst radical anion ($PC^{\bullet-}$) is then oxidized back to its ground state by molecular oxygen (O_2). Finally, deprotonation of intermediate **D** *via* hydrogen abstraction yields the desired product **29** (R^1 = H; R^2 = Ph).



Scheme 4. Organophotocatalytic synthesis of benzothiazoles **29.**

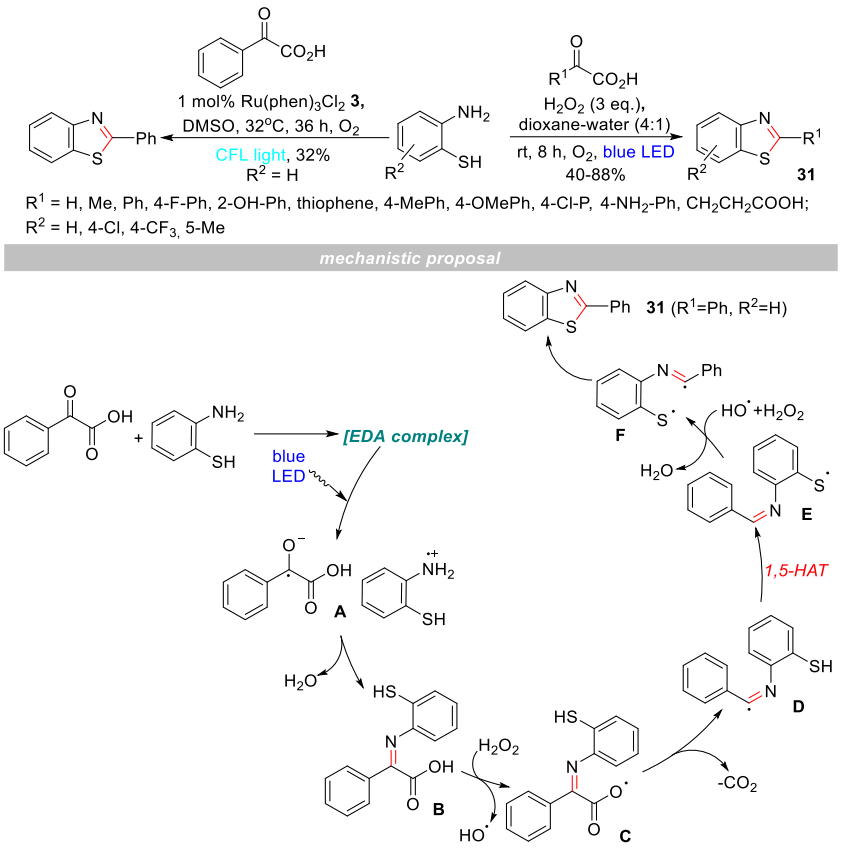
A variety of metal-based catalysts have also been employed in the synthesis of benzothiazoles **30**, including $Ru(bpy)_3Cl_2$ **1** [43], cetyl trimethylammonium bromide (CTAB)-coated Bi_2WO_4 **8** [54], CdSe/montmorillonite **9** [55], CdS nanosphere **10** [56], and Cu/Cu_2O@g-C_3N_4 **15** [62] (Scheme 5). These methodologies exhibit similar reaction scopes, yielding benzothiazoles **30**, and share a mechanistic pathway consistent with the intermediate steps described in Scheme 4.



Scheme 5. Metal-based catalytic synthesis of benzothiazoles **30.**

4. Cyclization of 2-aminothiophenols with *α*-ketocarboxylic acids

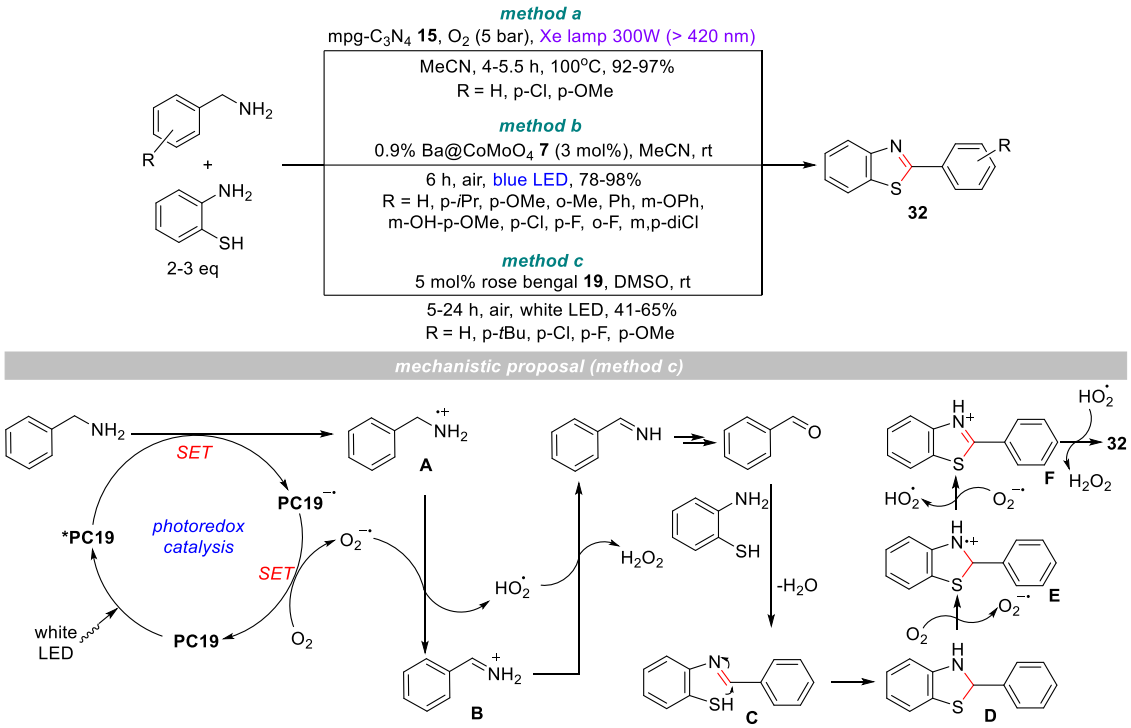
The first Ru-catalyzed synthesis of benzothiazoles *via* photooxidative decarboxylation of *α*-keto acids was reported in 2014 [49], demonstrating the synthesis of a single example, 2-phenylbenzothiazole (Scheme 6). This approach was further improved in 2020 with the discovery of a decarboxylative cross-coupling reaction between *α*-keto acids and 2-aminothiophenols to produce benzothiazoles **31** under blue LED irradiation without the use of any photocatalyst or metal, and at room temperature (Scheme 6) [86]. The mechanistic pathway for this improved protocol involves the initial formation of an electron donor-acceptor (EDA) complex between the starting materials. Upon irradiation, the EDA complex generates intermediate **A**, which is subsequently converted into imine **B**. Reaction of intermediate **B** with H_2O_2 forms radical **C**, which undergoes decarboxylation to yield intermediate **D**. A subsequent 1,5-hydrogen atom transfer (HAT) produces radical intermediate **E**, which is then converted to **F** by interaction with the hydrogen superoxide radical ($HOO^{\cdot}$). Finally, hetero-radical coupling at intermediate **F** results in the formation of the desired benzothiazole **31** (R^1 = Ph; R^2 = H).



Scheme 6. Syntheses of benzothiazoles **31.**

5. Cyclization of 2-aminothiophenols with benzylamines

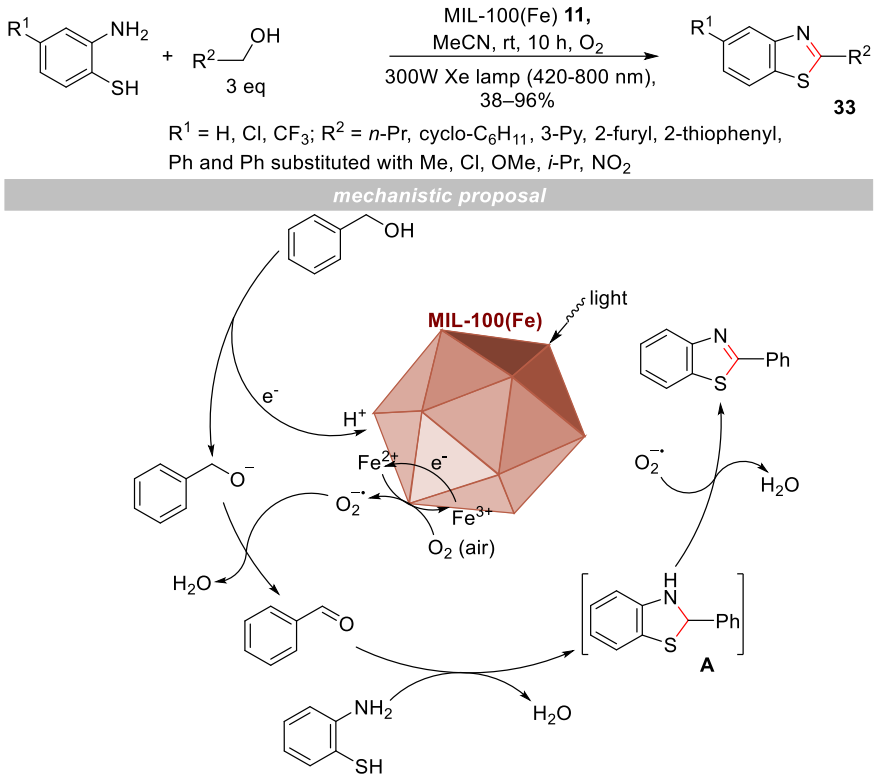
In 2011, a one-pot synthesis of benzothiazoles **32** (R = H, p-Cl, p-OMe) from benzylamines was developed (Scheme 7, method a) [60]. This protocol involves oxidative coupling to form imines, followed by intramolecular cycloaddition and subsequent oxidation to yield the target compounds. The process, catalyzed by mpg-C_3N_4 **15**, avoids the use of metals or organic oxidizing agents. However, the protocols main limitation is the requirement for high reaction temperature about 100°C, and only three products were reported. Recent advancements have addressed these limitations with more efficient methods [53, 74]. Baskar et al. introduced a protocol using 0.9% Ba-doped CoMoO4 nanoparticles **7** as a reusable and scalable catalyst under visible-light conditions, employing air as the oxidant (Scheme 7, method b) [53]. This approach provided benzothiazoles **32** (R = H, p-*i*Pr, p-OMe, o-Me, Ph, m-OPh, m-OH-p-OMe, p-Cl, p-F, o-F, m,p-diCl) with high efficiency. A representative mechanistic pathway is provided from a related work [74] (Scheme 7, method c), in which benzothiazoles **32** (R = H, p-*t*Bu, p-Cl, p-F, p-OMe) are synthesized *via* benzylamine oxidation. In this process, singlet oxygen generated by the excited photocatalyst oxidizes benzylamine to form the radical cation intermediate **A**. Further oxidation produces benzyl imine cation **B**, which reacts with the hydroperoxide radical. Hydrolysis of the resulting intermediate affords benzaldehyde, which couples with 2-aminothiophenol to form imine intermediate **C**. Intramolecular cyclization of **C** generates dihydrobenzothiazole **D**, which is oxidized in the presence of rose bengal **19** to yield the final benzothiazole product *via* intermediates **E** and **F**.



Scheme 7. Synthesis of benzothiazoles **32** using benzylamines.

6. Cyclization of 2-aminothiophenols with alcohols

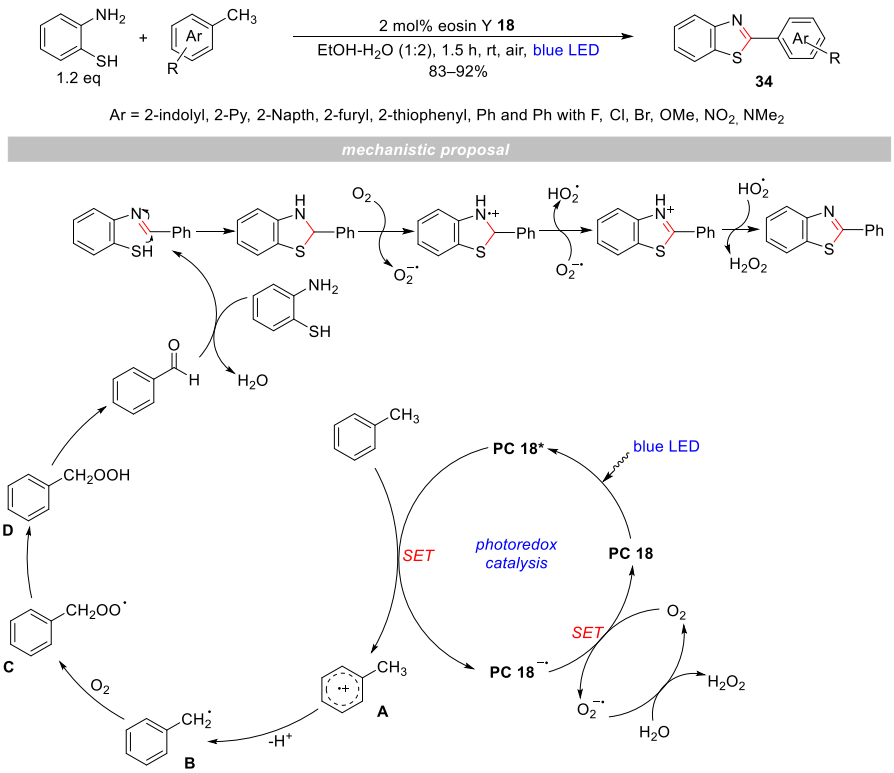
While aldehydes are commonly used as starting materials for benzothiazole synthesis (see Part 3), only one example has been reported where primary alcohols were directly employed [57]. MIL-100(Fe) **11** demonstrated catalytic activity in the oxidative condensation of alcohols with *o*-aminothiophenols to form 2-substituted benzothiazoles **33** under visible-light irradiation, using molecular oxygen (O_2) as the oxidant (Scheme 8). This reaction accommodates a wide substrate range, yielding medium to high product conversions. Mechanistic studies, including controlled experiments and ESR analysis, suggest a superoxide radical ($O_2^{\bullet-}$)-mediated pathway. The radicals are generated via the reduction of O_2 by photogenerated Fe^{2+} species within Fe–O clusters of MIL-100(Fe). The reaction rate-determining step involves the photo-oxidation of alcohols to aldehydes. Aromatic alcohols with electron-withdrawing groups (e.g., Cl, NO_2) exhibit lower conversions (46–56%) compared to those with electron-donating groups (e.g., *p*-OCH_3, *p*-CH_3), which show higher conversions (92–96%). However, steric hindrance, such as from *o*-OCH_3, *o*-CH_3, or *p*-$CH(CH_3)_2$ substituents, slightly reduces the conversion (78–85%) relative to unsubstituted benzyl alcohol. Aliphatic alcohols also react, but with significantly lower conversion rates (38–42%). The proposed mechanism (Scheme 8) involves the excitation of MIL-100(Fe) **11** under irradiation, leading to charge separation with electron transfer from O_2^- to Fe^{3+} in Fe_3O clusters, generating Fe^{2+}. The Fe^{2+} species reduces O_2 to $O_2^{\bullet-}$ radicals, with concurrent oxidation back to Fe^{3+}. Alcohols are oxidized to aldehydes *via* benzylic intermediates through $O_2^{\bullet-}$-mediated dehydrogenation. The *in situ* generated aldehyde undergoes condensation with *o*-aminothiophenol, facilitated by Lewis acidic Fe^{3+} sites in MIL-100(Fe). The resulting benzothiazoline intermediate is further oxidized by $O_2^{\bullet-}$ radicals to yield 2-phenylbenzothiazole. MIL-100(Fe) **11** thus functions both as a photocatalyst and a solid Lewis acid to enable this tandem reaction.



Scheme 8. MIL-100(Fe) **11** catalyzed synthesis of benzothiazoles **33**.

7. Cyclization of 2-aminothiophenols with methyl arenes

A highly efficient strategy for the synthesis of benzothiazoles **34** was introduced in 2023 (Scheme 9) [69]. This method involves the visible-light-induced reaction of 2-aminothiophenol with methylarenes in the presence of eosin Y **18** as a photocatalyst, using a green solvent mixture of ethanol and water, with atmospheric air as the oxidant under ambient conditions. Remarkably, both electron-donating and electron-withdrawing substituents on arenes exhibited comparable reactivity. The mechanism (Scheme 9) begins with the excitation of eosin Y **18** under blue light to form the highly reactive species EY*. A SET between EY* and methylarene generates a radical cation intermediate **A** while reducing EY to its ground state. Simultaneously, molecular oxygen is converted into superoxide ions, which react with water to produce hydrogen peroxide and regenerate O_2. Intermediate **A** undergoes proton abstraction to form benzylic radical **B**, which reacts with oxygen to form peroxy-species **C**. Further H-radical abstraction produces benzyl hydroperoxide **D**, which dehydrates to form benzaldehyde. The aldehyde subsequently reacts with 2-aminothiophenol, following mechanisms similar to earlier works [57, 63, 64, 74, 75], to yield the desired benzothiazole product.

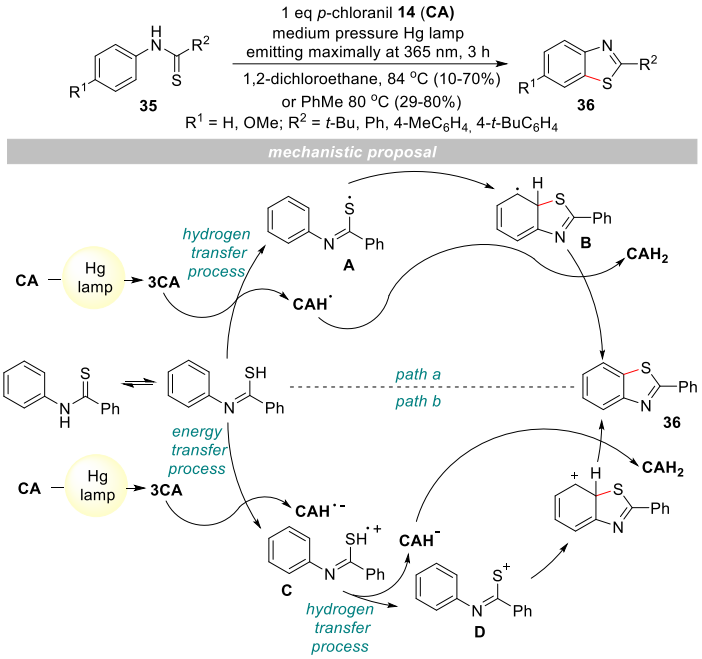


Scheme 9. Eosin Y **18** catalysed synthesis of benzothiazoles **34**.

8. Cyclization of N-aryl thioamides

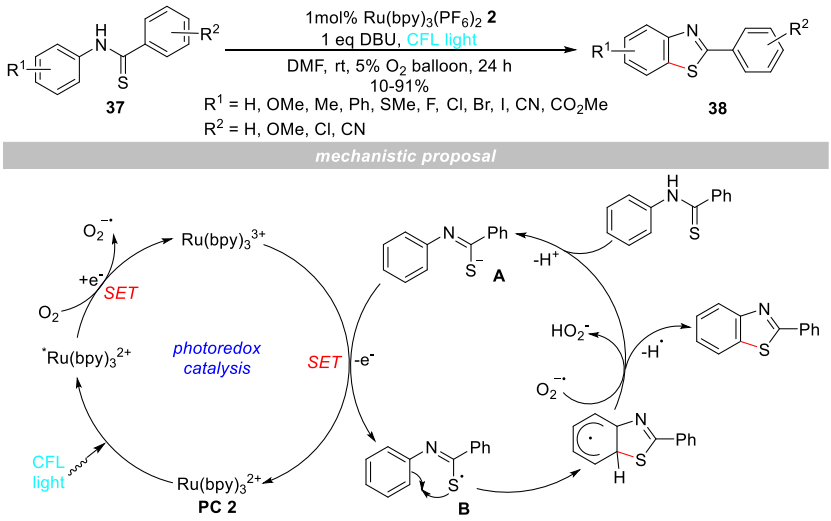
Over the last two decades, radical chemistry, particularly photoredox catalysis, has emerged as a prominent and versatile approach for C–H functionalization. Among its many applications, direct C(sp^2)–H activation followed by intramolecular C–S bond formation has been extensively investigated for the synthesis of 2-substituted 1,3-benzothiazoles. A groundbreaking study by Peñéñory and co-workers in 2009 demonstrated the cyclization of thiobenzanilides **35** to form 2-substituted 1,3-benzothiazoles **36**, using a stoichiometric amount of *p*-chloranil (CA) **14** under UV irradiation (365 nm) from a medium-pressure Hg lamp at 80 °C in non-polar solvents such as toluene or 1,2-dichloroethane (Scheme 10) [14]. The proposed mechanism begins with the generation of triplet-state *p*-chloranil (^{3}CA) under UV light, which acts as a hydrogen atom acceptor in non-polar solvents. This process produces a sulfur-centered radical from the substrate, which undergoes intramolecular cyclization and subsequent re-aromatization to yield the benzothiazole, with yields ranging from low to excellent. Specifically, the mechanism involves the formation of ^{3}CA **14**, followed by HAT from N-phenylbenzothioamide to ^{3}CA, generating the thiyl radical **A** and the hydroquinone radical CAH$^{\cdot}$ (Scheme 10, pathway a). Radical **A** adds intramolecularly to the aromatic ring, forming a cyclohexadienyl radical **B**, which undergoes a second HAT to CAH$^{\cdot}$ to furnish benzothiazole **36** (R^1 = H, R^2 = Ph). Alternatively, in polar solvents, an electron transfer (ET) mechanism is proposed (Scheme 10, pathway b). Energy transfer from N-phenylbenzothioamide to ^{3}CA forms the radical cation of thiobenzamide (**C**$^{+\bullet}$) and the radical anion CA$^{-\cdot}$. Subsequent deprotonation yields intermediate **C** and CAH$^{\cdot}$, while hydrogen transfer produces sulfur-centered cation **D**. Cation **D** undergoes intramolecular electrophilic addition to the phenyl ring, followed by deprotonation, to produce benzothiazole **36** (R^1 = H, R^2 = Ph). The experimental data suggest that the reaction mechanism is highly solvent-dependent. In non-polar solvents such as benzene or toluene, HAT (pathway a) is the dominant process, whereas electron transfer (pathway b) is favored in polar solvents such as MeCN. Interestingly, both mechanisms appear operative in 1,2-dichloroethane. These findings highlight the dual functionality of CA **14** as a hydrogen atom acceptor in non-polar media and as an electron

oxidant in polar environments. Moreover, HAT (pathway a) was determined to be more efficient for the synthesis of benzothiazoles **36**.



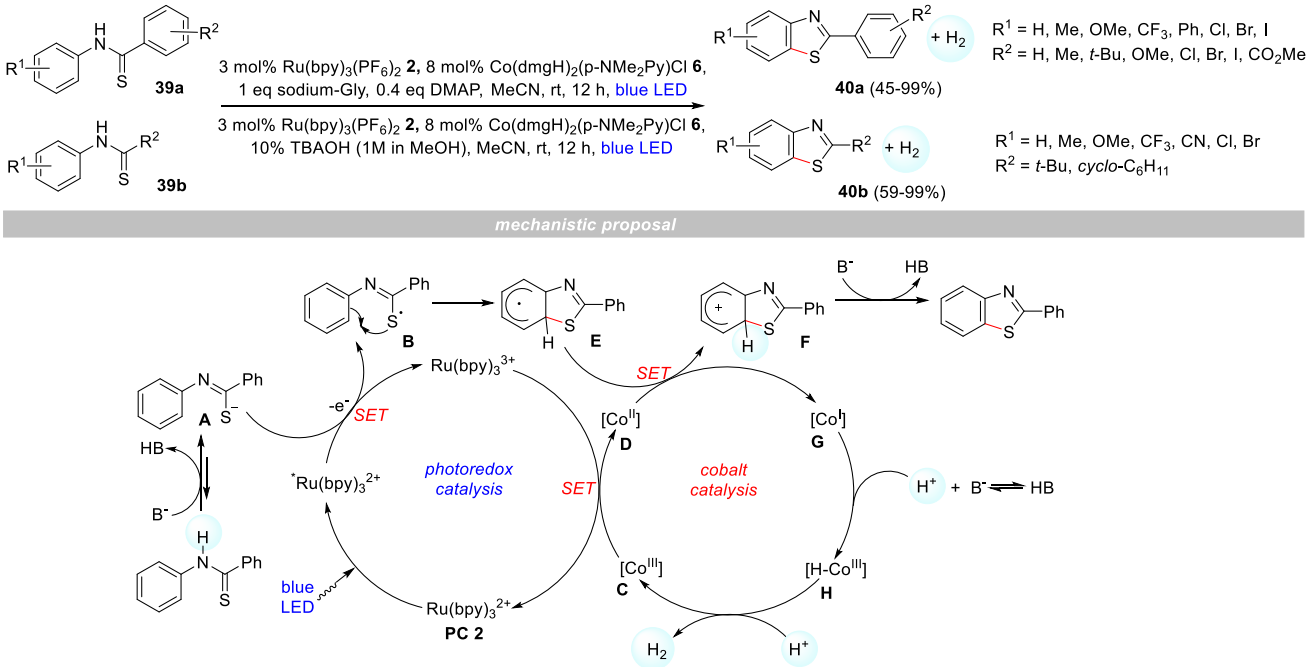
Scheme 10. *p*-Chloranil **14** catalyzed synthesis of benzothiazoles **36**.

Li et al. [47] developed a photoredox-catalyzed method for synthesizing benzothiazoles **38** *via* the cyclization of amides **37**. This process employs $Ru(bpy)_3(PF_6)_2$ **2** as the photocatalyst, with 1,8-diazabicycloundec-7-ene (DBU) serving as a base under an oxygen atmosphere (Scheme 11). Upon visible-light irradiation, $Ru(bpy)_3^{2+}$ is excited to $Ru(bpy)_3^{2+*}$, which undergoes electron transfer (ET) to molecular oxygen, forming $Ru(bpy)_3^{3+}$ and superoxide radicals ($O_2^{\bullet-}$). The base DBU facilitates the formation of a sulfur-centered anion **A**, which undergoes SET with $Ru(bpy)_3^{3+}$ to form the sulfur radical **B** while regenerating $Ru(bpy)_3^{2+}$. The sulfur radical **B** undergoes intramolecular cyclization, followed by $O_2^{\bullet-}$-mediated re-aromatization, to yield the final benzothiazole product. This method achieves moderate to excellent yields (up to 91%) and exhibits high functional group tolerance, including OMe, Me, Ph, SMe, F, Cl, Br, CO_2Me, but no product formation is observed with nitro-substituted substrates ($R^1 = NO_2$) [47].



Scheme 11. $Ru(bpy)_3(PF_6)_2$ **2** catalyzed synthesis of benzothiazoles **38.**

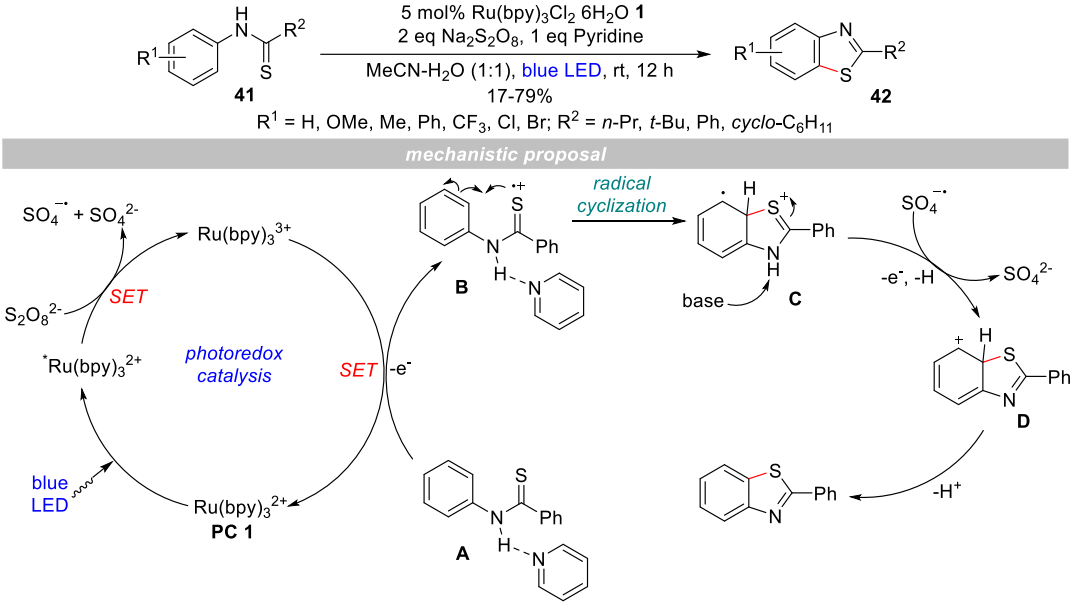
Lei and co-workers [48] introduced an innovative photoredox catalytic methodology combining the photocatalyst $Ru(bpy)_3(PF_6)_2$ **2** with a proton-reducing catalyst, $Co^{III}(dmgH)_2(4\text{-}NMe_2\text{-}C_5H_4N)Cl$ **6**. This system operates under mildly alkaline conditions and utilizes amides **39a,b** as substrates. The reaction, conducted under blue LED irradiation and using bases such as sodium glycinate/DMAP or TBAOH, yields products **40a,b** with high efficiency under oxidant-free conditions, accompanied by concurrent H_2 generation (Scheme 12). This approach demonstrates excellent performance with substrates bearing either electron-donating or electron-withdrawing substituents. However, the presence of strongly electron-donating groups (e.g., OMe) or strongly electron-withdrawing groups (e.g., CF_3) on the *N*-aryl ring reduces reactivity, and no product formation occurs when a nitro group ($R^1 = NO_2$) is present. Importantly, this catalytic system is scalable, achieving gram-scale synthesis with excellent yields. The mechanism begins with the excitation of $Ru(bpy)_3^{2+}$ by visible light, generating a long-lived excited state $*Ru(bpy)_3^{2+}$. While $*Ru(bpy)_3^{2+}$ is a strong oxidant, direct SET with *N*-phenylbenzothioamide is unlikely. Under alkaline conditions, however, an anionic intermediate **A** forms *via* acid-base equilibrium, significantly lowering its oxidation potential. Consequently, SET from intermediate **A** to the excited photosensitizer becomes feasible, generating $Ru(bpy)_3^{+}$ and a sulfur-centered radical **B**. $Ru(bpy)_3^{+}$, a potent reductant, donates an electron to the cobalt catalyst [Co^{III}] **C**, producing [Co^{II}] **D** while regenerating $Ru(bpy)_3^{2+}$, thus completing the photoredox cycle. Simultaneously, the sulfur radical **B** undergoes addition to the benzene ring, forming an aryl radical **E**. Radical **E** transfers an electron to [Co^{II}] **D**, yielding cation **F** and [Co^{I}] species **G**. Subsequent proton loss and rearomatization of **F** afford the desired benzothiazole, while [Co^{I}] **G** is protonated by the conjugate acid of the base to form [Co^{III}–H] species **H**. The hydride species **H** reacts with another proton to release H_2, regenerating [Co^{III}] **C**, thereby completing the proton reduction cycle. This dual functionality of the catalytic system enables efficient benzothiazole synthesis alongside hydrogen gas generation, demonstrating the versatility and practicality of this photoredox approach [48]. This advanced system highlights the synergy between photoredox and proton reduction catalysis, offering a scalable, sustainable, and efficient method for benzothiazole synthesis.



Scheme 12. $Ru(bpy)_3(PF_6)_2$ **2** catalyzed synthesis of benzothiazoles **40a,b.**

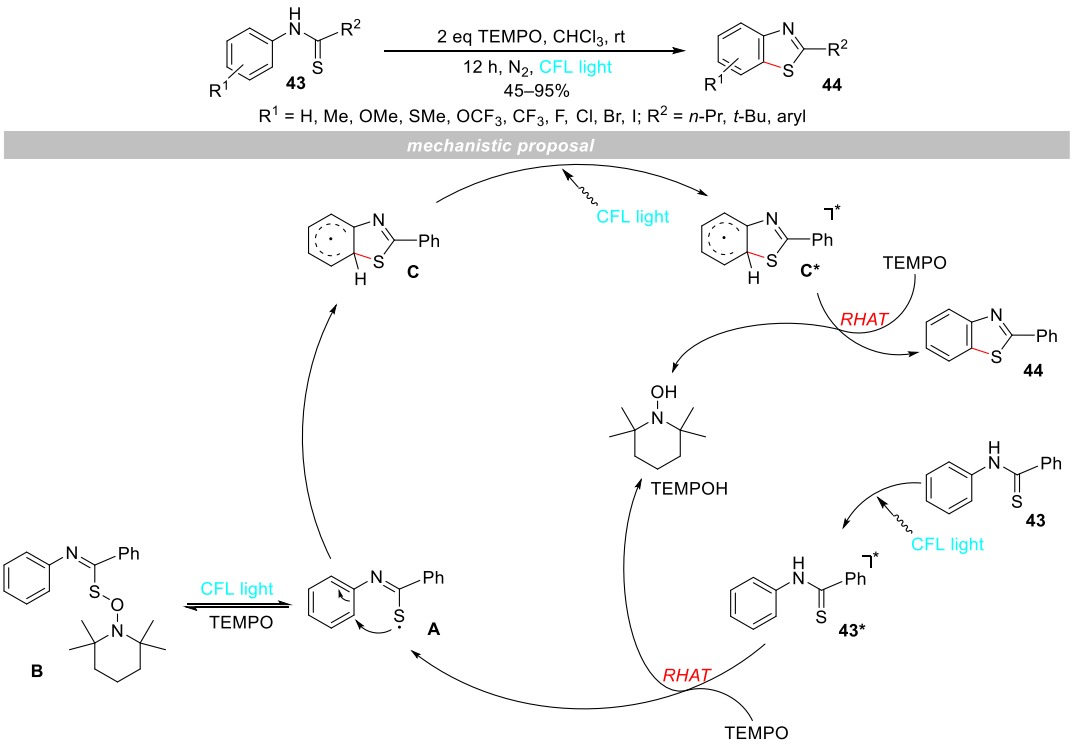
Using a ruthenium photocatalyst, Gustafson et al. [45] presented an oxidative C–H thiolation methodology for synthesizing benzothiazoles (Scheme 13). This approach utilizes thiobenzanilides **41** as substrates, $Ru(bpy)_3Cl_2$ **1** as a photocatalyst, sodium persulfate as an oxidant, and pyridine as a base, all under blue LED irradiation at room temperature. The proposed mechanism begins with the

activation of sodium persulfate by the excited photocatalyst, leading to the formation of the sulfate radical anion ($SO_4^{\bullet -}$) and Ru^{3+}. Together, these species act as potent oxidizing agents. Specifically, Ru^{3+} oxidizes the sulfur atom in thiobenzanilide **A** to produce the radical cation **B**. This species then undergoes intramolecular radical cyclization, generating intermediate **C**. Subsequent re-aromatization of intermediate **D** yields the final benzothiazole product. This method provides access to 2-alkyl and 2-aryl benzothiazoles **42** with yields ranging from moderate to good, reaching up to 79% [45].



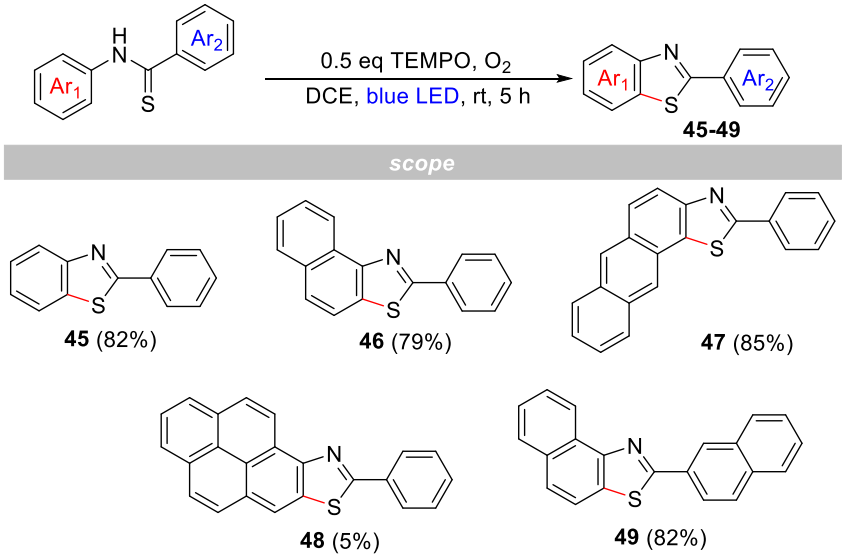
Scheme 13. $Ru(bpy)_3Cl_2$ **1** catalyzed synthesis of benzothiazoles **42**.

Lang, Li, and co-workers [83] developed a visible-light-driven C–H thiolation method that eliminates the need for photosensitizers, metal catalysts, or bases (Scheme 14). This innovative procedure involves the intramolecular cyclization of thiobenzanilides **43** *via* a reverse Hydrogen-Atom Transfer (RHAT) mechanism, employing TEMPO (2,2,6,6-tetramethylpiperidine N-oxide) as a mediator. Upon absorption of a photon, the substrate **43** (R^1=H, R^2=Ph) is excited to **43***. The excited state undergoes a reversible HAT process with TEMPO, forming a thiyl radical **A** and TEMPOH. Radical **A** can be trapped by TEMPO to create adduct **B**, which then undergoes homolytic cleavage, regenerating **A** and TEMPO. The S–O bond relatively weak dissociation energy facilitates this step. The thiyl radical **A** undergoes a 1,5-homolytic radical cyclization to generate aryl radical **C**. The final benzothiazole product **44** (R^1=H, R^2=Ph) is obtained *via* a photomediated RHAT process between the activated radical **C*** and TEMPO. This method achieves high efficiency, affording benzothiazoles **44** with electron-rich, -neutral, and -withdrawing groups in good to excellent yields, reaching up to 95%.



Scheme 14. Exogenous photosensitizer-, metal-, and base-free synthesis of benzothiazoles **44**.

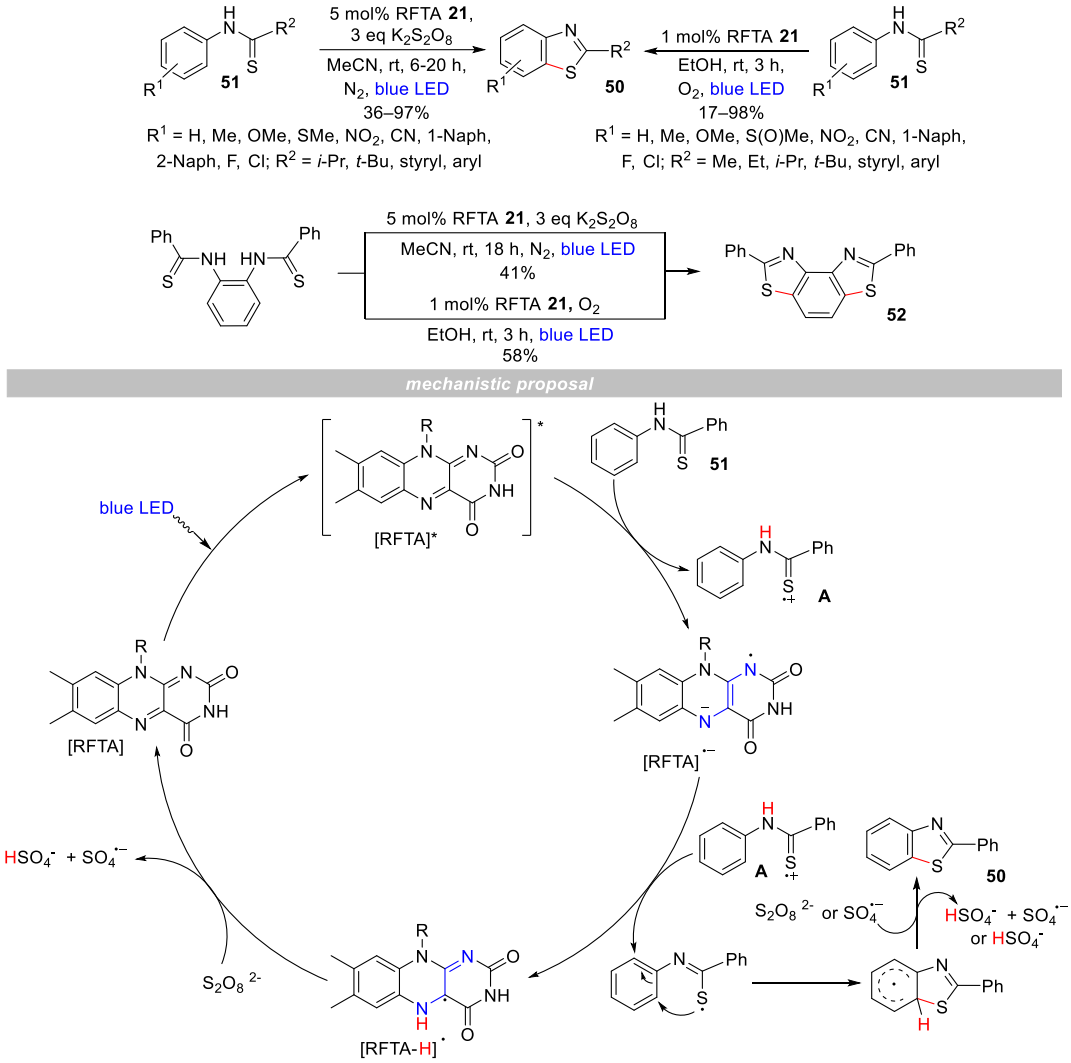
An adjusted version of the TEMPO-assisted RHAT method was employed for synthesizing benzothiazoles **45–49** with varying extents of π-conjugation (Scheme 15) [93]. These derivatives exhibited diverse luminescence properties in the solid state. Notably, compound **46** displayed unique white-light emission in its aggregated state, making it a promising candidate for applications in single-component light-emitting diodes (LEDs). This advancement demonstrates the versatility of the TEMPO-assisted methodology for not only efficient benzothiazole synthesis but also the generation of functional materials with potential technological applications.



Scheme 15. TEMPO-assisted synthesis of benzothiazoles **45-49**.

In 2020, Schmidt and Argüello introduced an efficient photochemical strategy for the synthesis of 2-substituted benzothiazoles **50** *via* visible-light-mediated aromatic C–H thiolation of thiobenzanilides **51**. This methodology employs riboflavin 2′,3′,4′,5′-tetraacetate (RFTA, **21**) as a photocatalyst and potassium persulfate as a sacrificial oxidant under a nitrogen atmosphere (Scheme

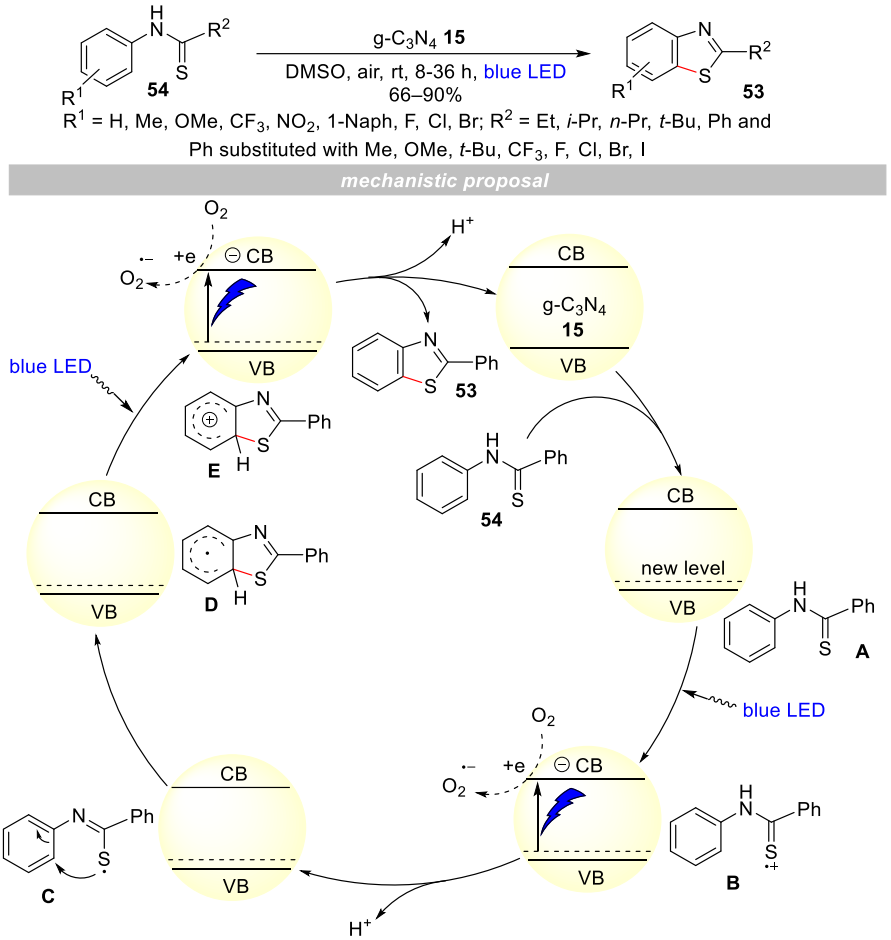
16) [76]. The key advantages of this approach include the utilization of a naturally derived organic dye (riboflavin) as a photocatalyst, the absence of transition-metal complexes or bases, and the use of blue light to drive the reaction, leading to benzothiazoles **50** in good to excellent yields (Scheme 16). This method demonstrates broad substrate tolerance, accommodating both electron-donating and electron-withdrawing substituents. Notably, it represents the first successful photochemical synthesis of nitro-substituted 2-phenylbenzothiazole. Additionally, several 2-alkylbenzothiazoles were produced in moderate to very high yields, and a double-cyclization product **52** was obtained with a yield of 41%. The proposed mechanism begins with the ET from thiobenzanilide (**51**, R^1=H, R^2=Ph) to the excited state of RFTA **21**, forming the radical cation of thiobenzanilide **A** and the radical anion $RFTA^{\bullet -}$. In the subsequent step, deprotonation of **A** is facilitated by $RFTA^{\bullet -}$. Cyclization followed by re-aromatization, driven by potassium persulfate, yields the desired benzothiazole **50** (R^1=H, R^2=Ph). The riboflavin catalyst is notable for its dual role, functioning as both a photocatalyst and a base (pKa of $[RFTA\text{-}H]^{\bullet}$ = 8.3). This property eliminates the need for an external base and enables the activation of substrates containing strong electron-withdrawing groups, such as nitro substituents. Peroxydisulfate is critical for closing the catalytic cycle, regenerating RFTA in its ground state[76]. In 2024, the same authors expanded on this work by developing a metal- and base-free aerobic photoredox protocol employing RFTA **21** for the synthesis of 2-substituted benzothiazoles **50** under similar conditions [77]. In this updated methodology, oxygen replaced potassium persulfate as the oxidant, offering enhanced efficiency. For instance, the yield of product **52** increased from 41% to 58%, while reaction time, catalyst loading, and solvent environmental impact were significantly reduced. This innovation represents a notable advance, achieving two cyclization reactions in a single reaction step with greater sustainability and efficiency.



Scheme 16. Riboflavin 2′,3′,4′,5′-tetraacetate (RFTA) **21** catalyzed synthesis of benzothiazoles **50, 52**.

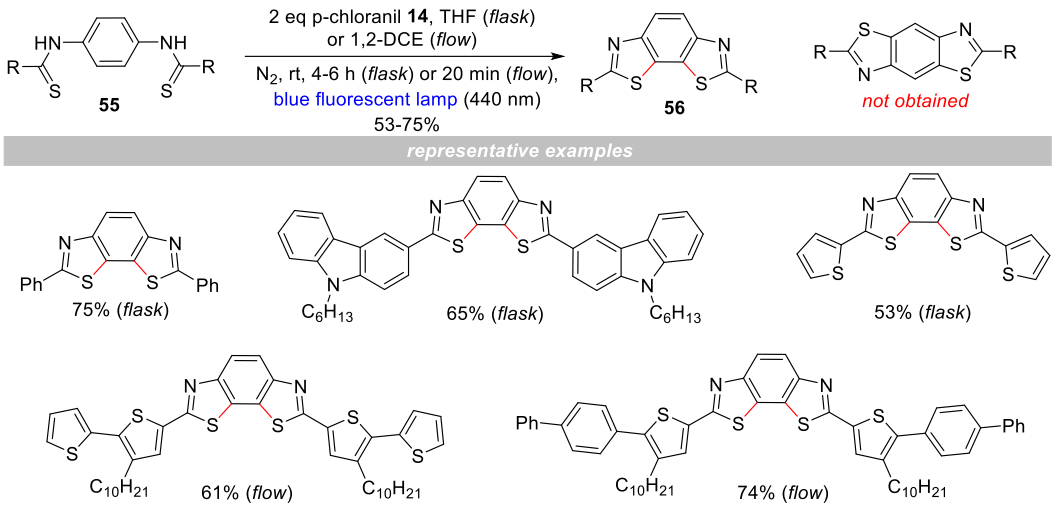
Zhou et al. reported the synthesis of benzothiazoles **53** *via* an intramolecular C–H functionalization and C–S bond formation of thiobenzanilides **54**, employing inexpensive graphitic carbon nitride g-C_3N_4 **15** as a photocatalyst under ambient air and blue LED irradiation (Scheme 17) [61]. This method is gram-scalable, operates at room temperature, and tolerates a wide range of functional groups, including nitro substituents. Moreover, it eliminates the need for strong bases or organic oxidants. Notably, the photocatalyst g-C_3N_4 **15** exhibited excellent stability and reusability, maintaining efficiency for at least five cycles. The proposed mechanism begins with the adsorption of N-substituted benzothioamide **54** (R^1=H, R^2=Ph) onto the surface of g-C_3N_4 **15**, forming a complex **A**. This adsorption creates a new donor energy level above the valence band of g-C_3N_4 **15**. Upon visible-light irradiation, an electron is promoted from the donor level of complex **A** to the conduction band of g-C_3N_4 **15**, resulting in the formation of a radical cation **B**. Subsequent quenching of the photogenerated electron by molecular oxygen (O_2) and deprotonation of **B** leads to the formation of a sulfur-centered radical **C**. This radical **C** then undergoes intramolecular cyclization, attacking the aromatic ring to form an aryl radical intermediate **D**. Further interaction of **D** with the conduction band of g-C_3N_4 **15** generates a cationic species **E**. Finally, deprotonation and rearomatization of **E** yield the desired benzothiazole **53** (R^1=H, R^2=Ph). In this reaction, molecular oxygen (O_2) functions as an electron scavenger, being reduced to superoxide radicals ($O_2^{\bullet-}$), which can further react with protons to form hydroperoxyl radicals (HOO$^\bullet$). These intermediates ultimately convert into hydrogen peroxide (H_2O_2) and regenerate molecular oxygen, sustaining the catalytic cycle. This environmentally

friendly, metal-free protocol underscores the utility of g-C_3N_4 **15** as a robust photocatalyst for sustainable organic transformations.



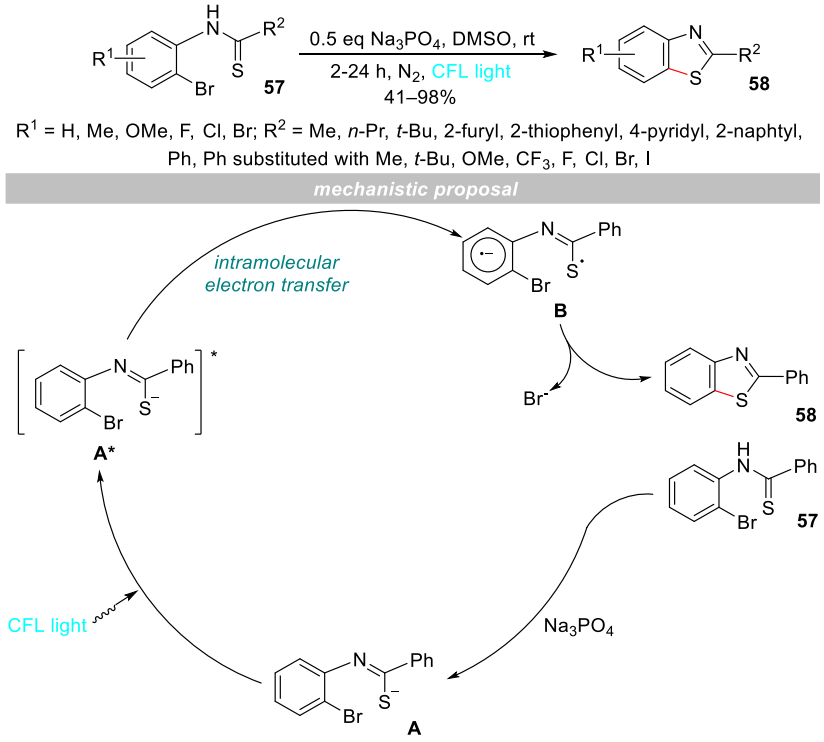
Scheme 17. Graphitic carbon nitride (g-C_3N_4) **15** catalyzed synthesis of benzothiazoles **53.**

A recent study (2022) explored the cyclization of thiobenzanilides through a blue light-induced (440 nm) photochemical reaction of N,N'-(1,4-aryl)dithioamides **55** in the presence of p-chloranil **14** as a mild oxidizing agent (Scheme 18) [92]. This method enables the selective synthesis of 2,7-diarylbenzo[1,2-d:4,3-d']bis(thiazoles) **56** without generating regioisomeric by-products. The high regioselectivity of the reaction underscores its synthetic utility, and the resulting compounds **56** exhibit intriguing photophysical and (spectro)electrochemical properties. These features highlight their potential applications in the field of organic electronics, offering promising avenues for the development of advanced materials.



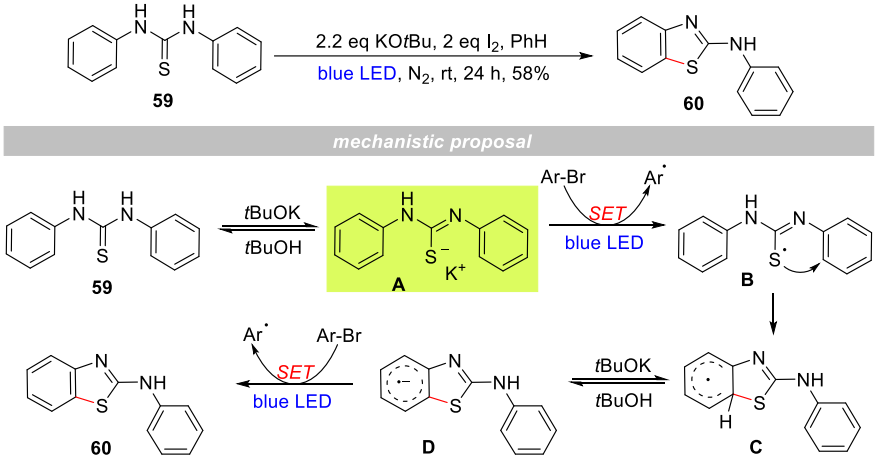
Scheme 18. Photochemical synthesis of 2,7-diarylbenzo[1,2-d:4,3-d']bis(thiazoles) **56**.

Halogenated thiobenzanilides **57** can undergo a photocatalyst- and transition-metal-free intramolecular cross-coupling to yield benzothiazoles **58** through a sequence involving photon absorption, electron transfer, and dehalogenative cyclization (Scheme 19) [89]. Brominated derivatives are predominantly utilized as starting materials, with the corresponding benzothiazoles **58** (R^1 = H, R^2 = Ph) achieved in excellent yields of up to 99%. Other halogens, including iodine, chlorine, and fluorine, afford yields of 99%, 24% and 9%, respectively. Notably, 2-aryl benzothiazoles are synthesized in high yields (90–98%) within 2–10 hours of irradiation. However, 2-alkyl benzothiazoles are obtained in relatively modest yields (41–82%) and require prolonged irradiation of up to 24 hours. Mechanistically, the substrate **57** or its anion **A** absorbs a photon to form an excited state **A***, which undergoes intramolecular electron transfer from the thiolate anion to the N-aryl moiety, generating an intermediate **B** containing both a thiyl radical and an aryl halide radical anion. This intermediate undergoes debrominative cyclization to yield the final benzothiazole **58** (R^1 = H, R^2 = Ph).



Scheme 19. A photocatalyst- and transition-metal-free synthesis of benzothiazoles **58**.

Adhikari and co-workers [95] introduced diphenylthiourea (DPTU) **59** as an effective photocatalyst that, in its deprotonated state, facilitates reductive bond cleavage in aryl bromides to enable Csp^2–Csp^2 and Csp^2–Csp^3 cross-coupling reactions (Scheme 20). Although DPTU **59** itself does not absorb visible light, *in situ* deprotonation alters the solution color to greenish-yellow, indicating the formation of the deprotonated species **A**. Upon photoexcitation, **A** undergoes SET to an aryl bromide, generating an aryl radical and a thiyl radical **B**. Radical **B** subsequently attacks the adjacent phenyl ring, forming a five-membered benzothiazole ring **C**. In the presence of a strong base (*t*BuOK), deprotonation of cyclohexenyl hydrogen in **C** yields radical anion **D**, a potent reducing species capable of further SET to cleave another aryl bromide bond. This sequence culminates in the formation of 2-anilinobenzothiazole **60**, a critical step confirmed through stoichiometric isolation of **60**. Notably, Schmidt and Argüello [77] achieved the same transformation **59**→**60** using 1 mol% riboflavin 2',3',4',5'-tetraacetate (RFTA) **21** under blue LED irradiation in ethanol, achieving a 41% yield within 3 hours.

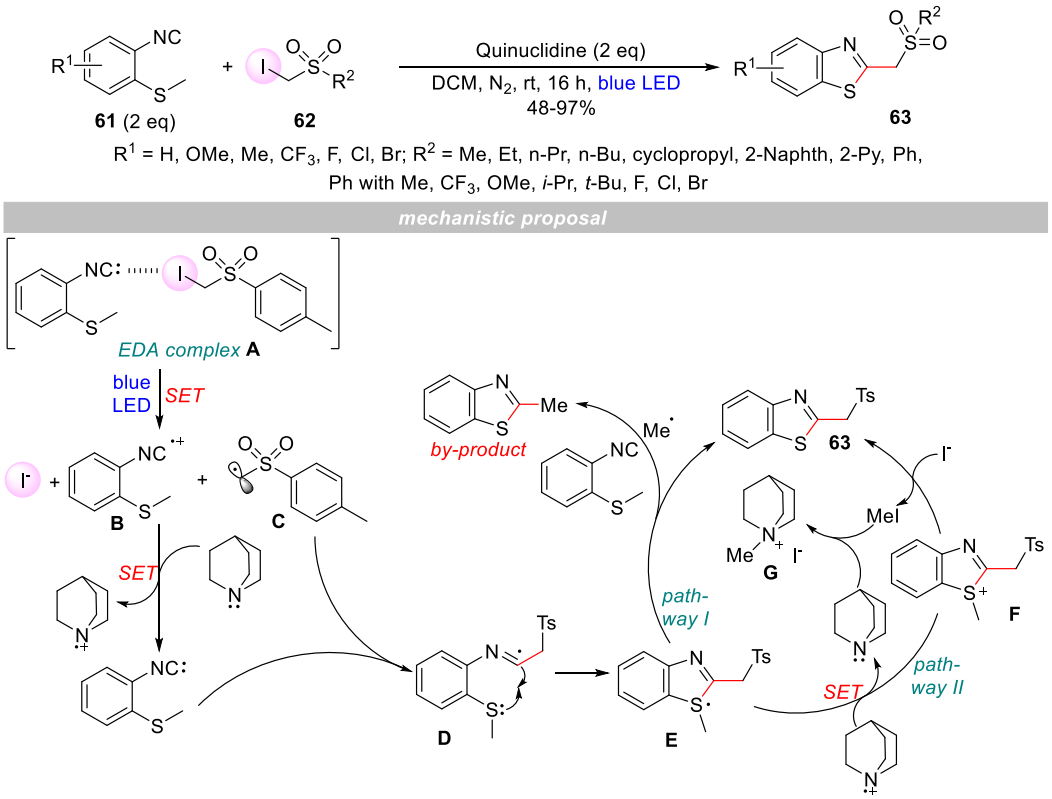


Scheme 20. Synthesis of N-phenylbenzo[d]thiazol-2-amine **60**.

9. Cyclization of 2-isocyanoaryl thioethers

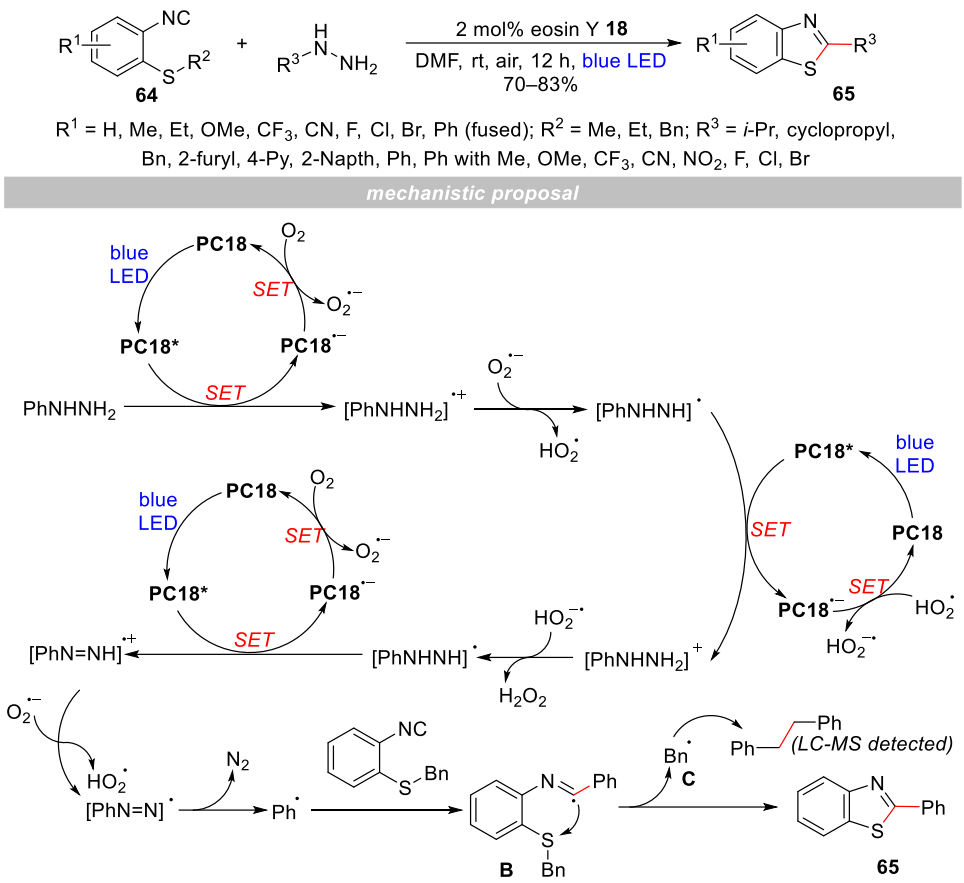
Another innovative method for synthesizing benzothiazoles involves the use of 2-isocyanoaryl thioethers as precursors. This strategy enables the incorporation of various functionalities at the 2-position, including fluorinated, alkyl, aryl, phosphine oxide, and ether substituents.

Very recently (2024), a photoinduced cascade sulfone alkylation/cyclization of 2-isocyanoaryl thioethers **61** was demonstrated (Scheme 21) [96]. This visible-light-driven reaction occurs under exceptionally mild conditions without requiring a photosensitizer. The process is initiated by the formation of an EDA complex **A** between (2-isocyanophenyl)(methyl)sulfane and α-iodosulfone **62**. Upon visible-light irradiation, this complex generates radical cation $\mathbf{B}^{+\cdot}$, a sulfone methyl radical **C** ($TsCH_2^{\cdot}$), and an iodine anion. Quinuclidine is oxidized by $\mathbf{B}^{+\cdot}$ to form a quinuclidinium radical cation, while the sulfone methyl radical **C** adds to the 2-isocyanoaryl thioether to produce imidoyl radical **D**. This intermediate undergoes intramolecular cyclization, yielding sulfonium radical **E**. Two possible pathways then emerge. In the first pathway, **E** releases a methyl radical, forming the target product **63** (R^1 = H, R^2 = 4-tolyl) alongside a by-product. In the second pathway, **E** is oxidized by the quinuclidinium radical cation to form sulfonium cation **F**. A subsequent nucleophilic attack by iodine anion on **F** generates the desired product **63** and methyl iodide, which reacts with quinuclidine to form quaternary ammonium salt **G**.



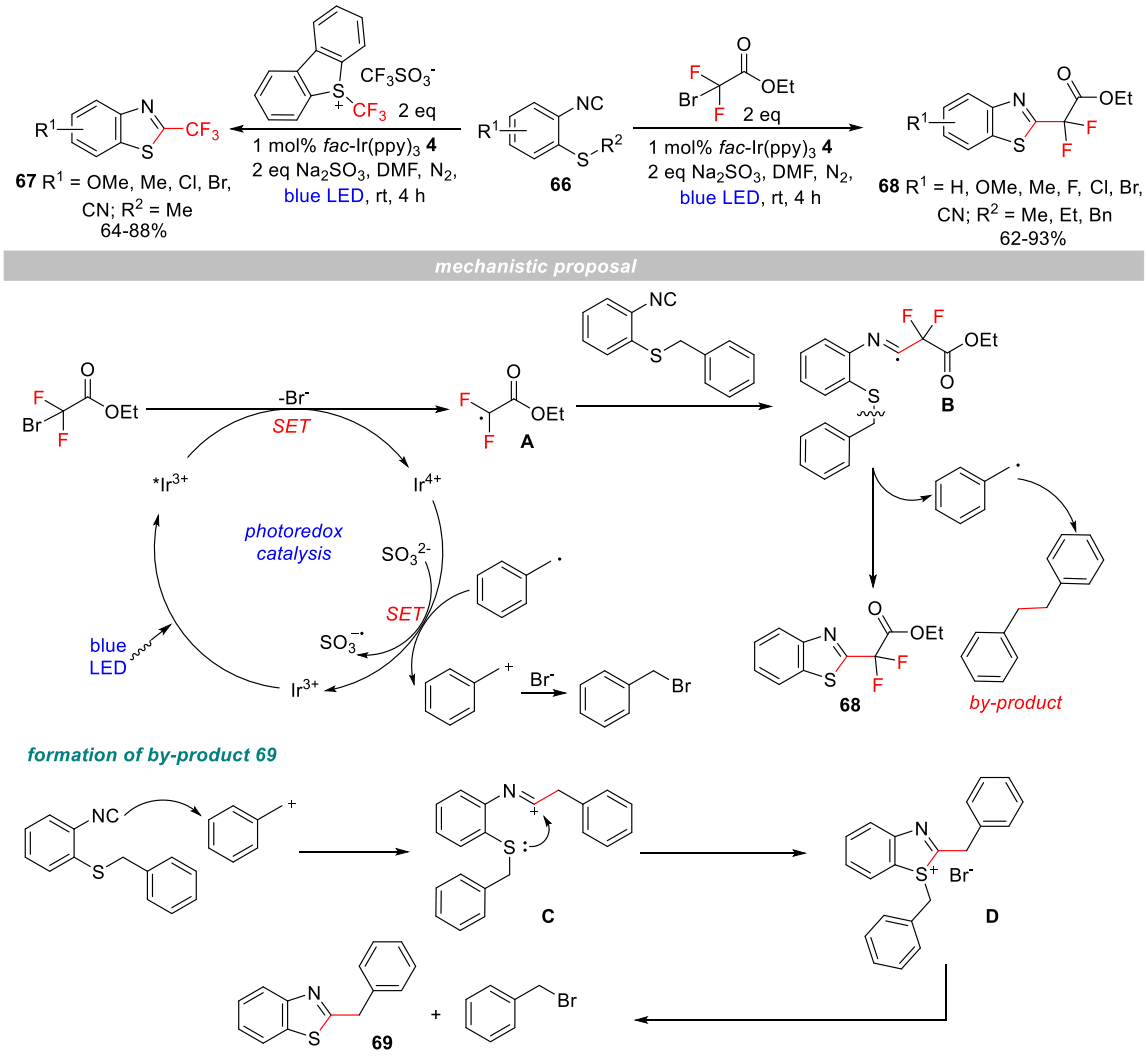
Scheme 21. EDA complex catalyzed synthesis of benzothiazoles **63**.

In 2023, a metal-free, visible-light-mediated cascade reaction was developed from 2-isocyanoaryl thioethers **64** (Scheme 22) [70]. This approach utilizes hydrazines as radical precursors, providing efficient access to a range of 2-aryl and 2-alkyl benzothiazoles **65** in high yields. Initially, phenyl hydrazine reacts with eosin Y **18** under visible-light irradiation to generate aryl radical **A**. This radical adds to the isocyanide moiety, yielding imidoyl radical intermediate **B**, which undergoes intramolecular cyclization to form the benzothiazole product **65** (R^1 = H, R^3 = Ph). Simultaneously, the benzyl radical **C** formed during the reaction is converted to 1,2-diphenylethane by-product. This efficient methodology underscores its potential for synthesizing structurally diverse benzothiazoles with broad applicability.



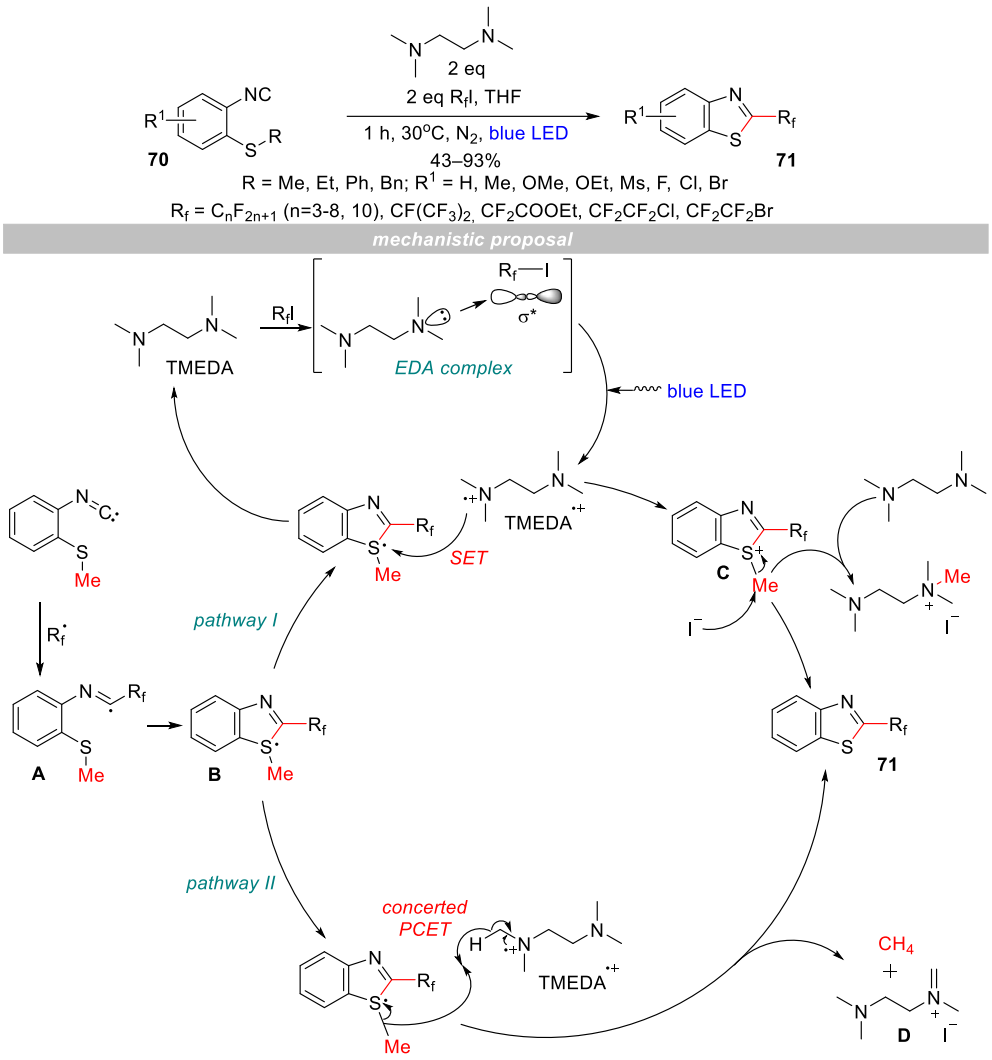
Scheme 22. Eosin Y **18** catalysed synthesis of benzothiazoles **65**.

Zhang and co-workers reported the cyclization of 2-isocyanoaryl thioethers **66** to synthesize 2-CF_3/2-CF_2-containing benzothiazoles **67**, **68** using *fac*-Ir(ppy)$_3$ **4** as a photocatalyst, with either the Umemoto reagent or ethyl 2-bromo-2,2-difluoroacetate as the fluoroalkyl source (Scheme 23) [50]. Unlike conventional methodologies employing tertiary amines as reductants for SET processes, sodium sulfite (Na_2SO_3) was utilized to regenerate Ir^{3+} from Ir^{4+}, enabling fluoroalkylation under mild reaction conditions. Mechanistically, visible-light irradiation of *fac*-Ir(ppy)$_3$ **4** produces its excited state (*fac*-Ir*(ppy)$_3$), which undergoes SET with ethyl 2-bromo-2,2-difluoroacetate to yield the CF_2COOEt radical **A** and Ir^{4+}. Radical **A** then reacts with the isonitrile group in the substrate, forming the imidoyl radical intermediate **B**. Subsequent intramolecular cyclization by the benzylthio moiety generates the target product **68** (R^1 = H) and benzyl radical. Concurrently, Ir^{4+} is reduced back to Ir^{3+} by Na_2SO_3, completing the catalytic cycle. The benzyl radical can undergo oxidation by Ir^{4+} to form a benzyl cation, which reacts with bromide (Br^-) to generate benzyl bromide or dimerizes to yield 1,2-diphenylethane by-product. In the absence of Na_2SO_3, the benzyl radical is predominantly oxidized to the benzyl cation, which may react with isonitrile to form cation intermediates **C** and **D**. These intermediates undergo intramolecular nucleophilic attack, ultimately producing benzyl bromide and a benzothiazole by-product **69**.



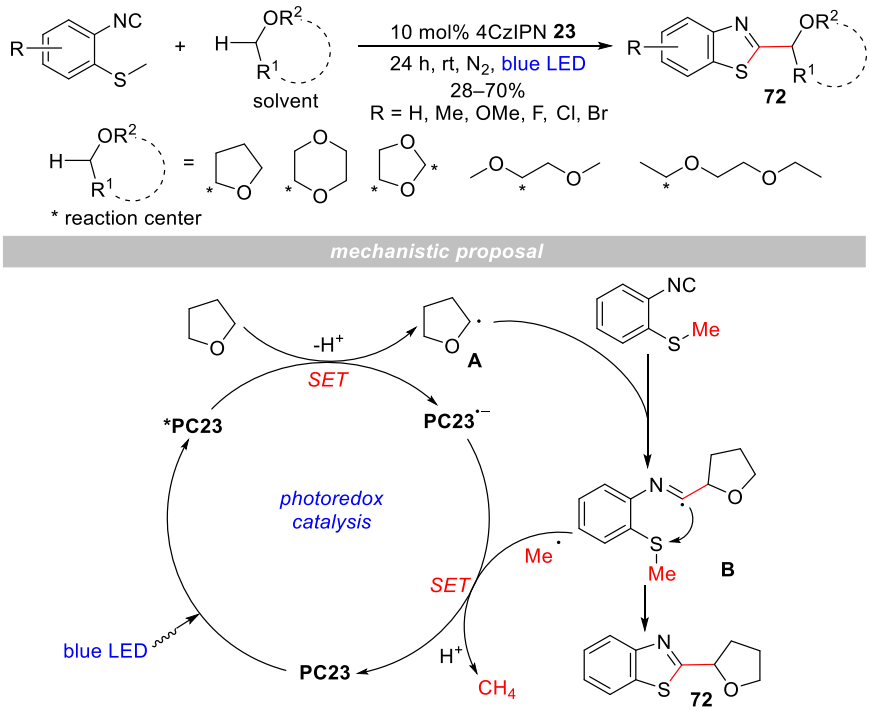
Scheme 23. Ir(ppy)$_3$ **4** catalyzed synthesis of benzothiazoles **67, 68.**

Yu et al. developed a robust protocol for the fluoroalkylation and cyclization of 2-isocyanoaryl thioethers **70** to synthesize 2-fluoroalkylbenzothiazoles **71** in yields up to 93% (Scheme 24) [84]. This methodology employs commercially available perfluoroalkyl iodides (e.g., IC_nF_{2n+1}, n = 3–8, 10, $ICF(CF_3)_2$, ICF_2COOEt, ICF_2CF_2Cl, or ICF_2CF_2Br), tetramethylethane-1,2-diamine (TMEDA), and visible-light irradiation, eliminating the need for external photocatalysts. The reaction is initiated by the formation of an EDA complex between perfluoroalkyl iodide and TMEDA. Visible-light irradiation of this complex generates perfluoroalkyl radicals ($R_f^{\bullet}$), $TMEDA^{+\bullet}$ radical cation, and iodide ions (I^-). Radical $R_f^{\bullet}$ reacts with the isonitrile group in the starting material, yielding the imidoyl radical intermediate **A**, which undergoes intramolecular cyclization to form sulfonium radical **B**. Two mechanistic pathways are proposed. In the first pathway, **B** undergoes SET with $TMEDA^{+\bullet}$, forming sulfonium cation **C**. A nucleophilic attack by iodide on **C** produces the target product **71** (R^1 = H) and methyl iodide (MeI), which reacts with TMEDA to generate a quaternary ammonium salt. Alternatively, in the second possible pathway, **B** undergoes a proton-coupled electron transfer (PCET) with $TMEDA^{+\bullet}$, yielding the target product **71** (R^1=H) and iminium ion **D**, along with methane formation.



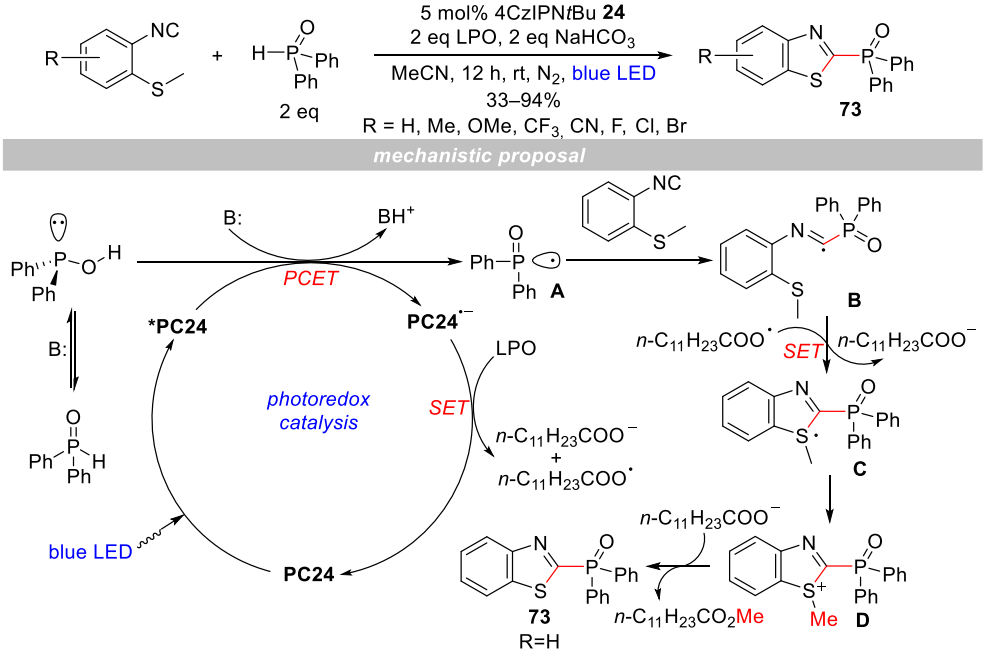
Scheme 24. A photocatalyst- and transition-metal-free synthesis of benzothiazoles **71**.

With the photocatalyst 4CzIPN **23** under blue LED light, an oxidant-free protocol was developed for synthesizing ether-functionalized benzothiazoles **72** from 2-isocyanoaryl thioethers (Scheme 25) [79]. Photoexcitation of 4CzIPN produces its excited state (4CzIPN*), which accepts an electron from tetrahydrofuran (THF) to generate an *α*-oxy radical **A** and the reduced form of the photocatalyst. Radical **A** reacts with the isonitrile substrate to form the imidoyl radical intermediate **B**, which undergoes cyclization to produce the benzothiazole product **72** and a methyl radical. The methyl radical combines with a proton to form methane, driven by the photocatalyst-mediated oxidative quenching process.



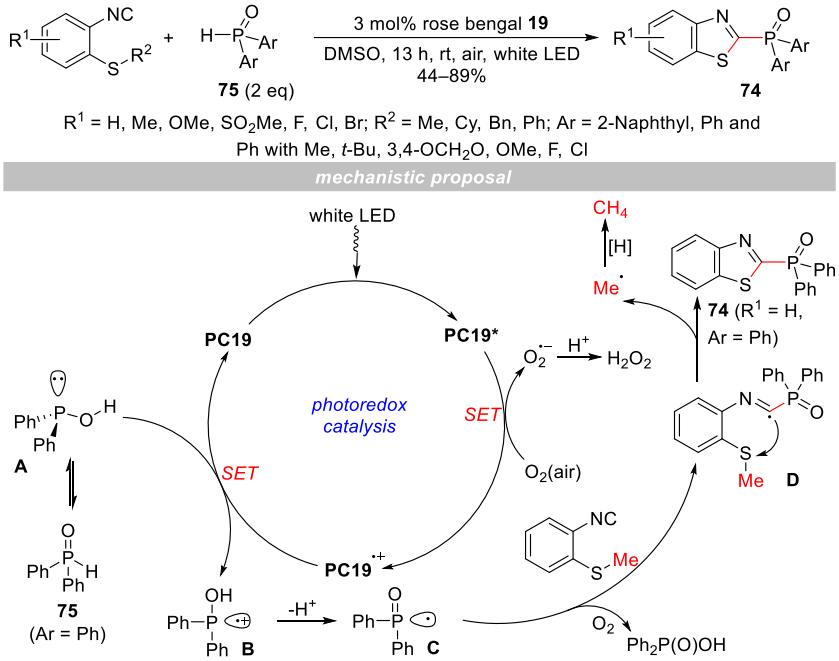
Scheme 25. A photocatalyst- and transition-metal-free synthesis of benzothiazoles **72**.

Chen, Yu, and collaborators extended this strategy using 2,4,5,6-tetrakis(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)-isophthalonitrile (4CzIPN*t*Bu) **24** as new photocatalyst to achieve a visible-light-induced PCET for generating phosphorus-centered radicals **A**. This method enabled the synthesis of 2-phosphorylated benzothiazoles **73** in moderate to excellent yields (Scheme 26) [80]. Mechanistically, dilauroyl peroxide (LPO) undergoes SET with the photocatalyst radical anion (**PC24**$^{\bullet-}$), generating a dodecanoyloxyl radical and a regenerated photocatalyst. Species **A** undergoes a radical addition to the isocyano group of (2-isocyanophenyl)(methyl)sulfane to afford the corresponding imidoyl intermediate **B**, which cyclizes to produce a benzothiazole radical **C**. The dodecanoyloxyl radical oxidizes **C** to benzothiazole cation **D**, which undergoes a nucleophilic S_N2 attack by *n*-$C_{11}H_{23}COO^-$, yielding the final product **73** (R=H) and by-products.



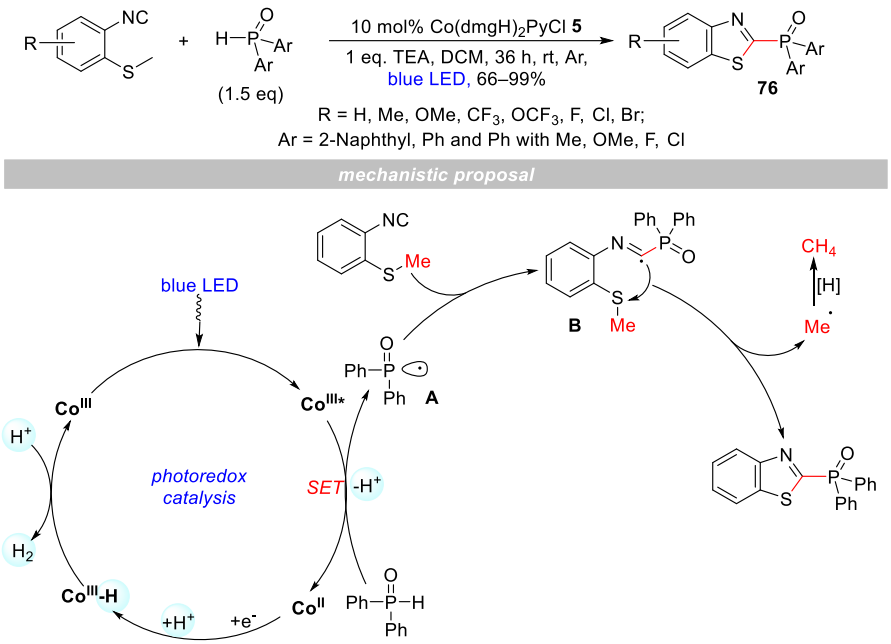
Scheme 26. 4CzIPN*t*Bu **24** catalyzed synthesis of benzothiazoles **73.**

In 2020, Feng and Yang were first who introduced a green method for the phosphorylation of 2-isocyanoaryl thioethers via visible-light-induced cascade reactions, employing rose bengal (RB) **19** as a photocatalyst (Scheme 27) [73]. This transition-metal-free process generates C2-phosphorylated benzothiazoles **74** under ambient conditions using aryl-substituted H-phosphorus oxides **75**. However, phosphonate esters, such as ethyl, isopropyl, and dicyclohexylphosphine oxides, were unsuitable substrates, resulting in no product formation. Mechanistically, diarylphosphine oxide **75** (Ar = Ph) exists in equilibrium with its phosphinous acid tautomer **A**. SET from the radical cation (**19**$^{\bullet+}$) to **A** generates species **B** and then **C**, which reacts with the isonitrile to form imidoyl radical intermediate **D**. Cyclization of **D** yields the final product **74** with the release of methane, driving the reaction to completion. Oxidation of the phosphinoyl radical **C** by O_2 produces a $Ph_2P(O)OH$ by-product.



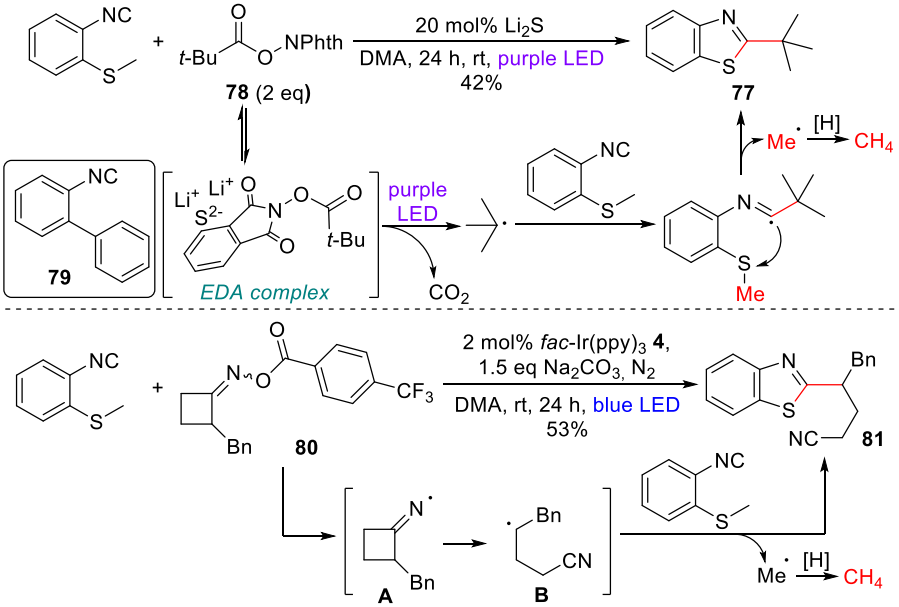
Scheme 27. Rose bengal **19** catalyzed synthesis of phosphoryl benzothiazoles **74.**

The generation of phosphorus-centered radicals through interactions with isocyano functional groups has been achieved *via* cobaloxime photocatalysis (Scheme 28) [52]. Utilizing $Co(dmgH)_2PyCl$ **5** as a photocatalyst, triethylamine (TEA) as a base, and dichloromethane (DCM) as a solvent under blue LED irradiation in an argon atmosphere, compounds **76** were synthesized with yields reaching 99%. Notably, similar reactions under sunlight resulted in excellent yields (88–98%) over 21 hours. Mechanistic investigations revealed that photoexcited cobaloxime oxidizes diphenylphosphine oxide to generate a phosphorus radical **A** and a Co^{II} species. Radical **A** subsequently adds to (2-isocyanophenyl)(methyl)sulfane to form the imidoyl intermediate **B**, which undergoes intramolecular cyclization, yielding the desired product.



Scheme 28. Co(dmgH)2pyCl **5** catalyzed synthesis of benzothiazoles **76**.

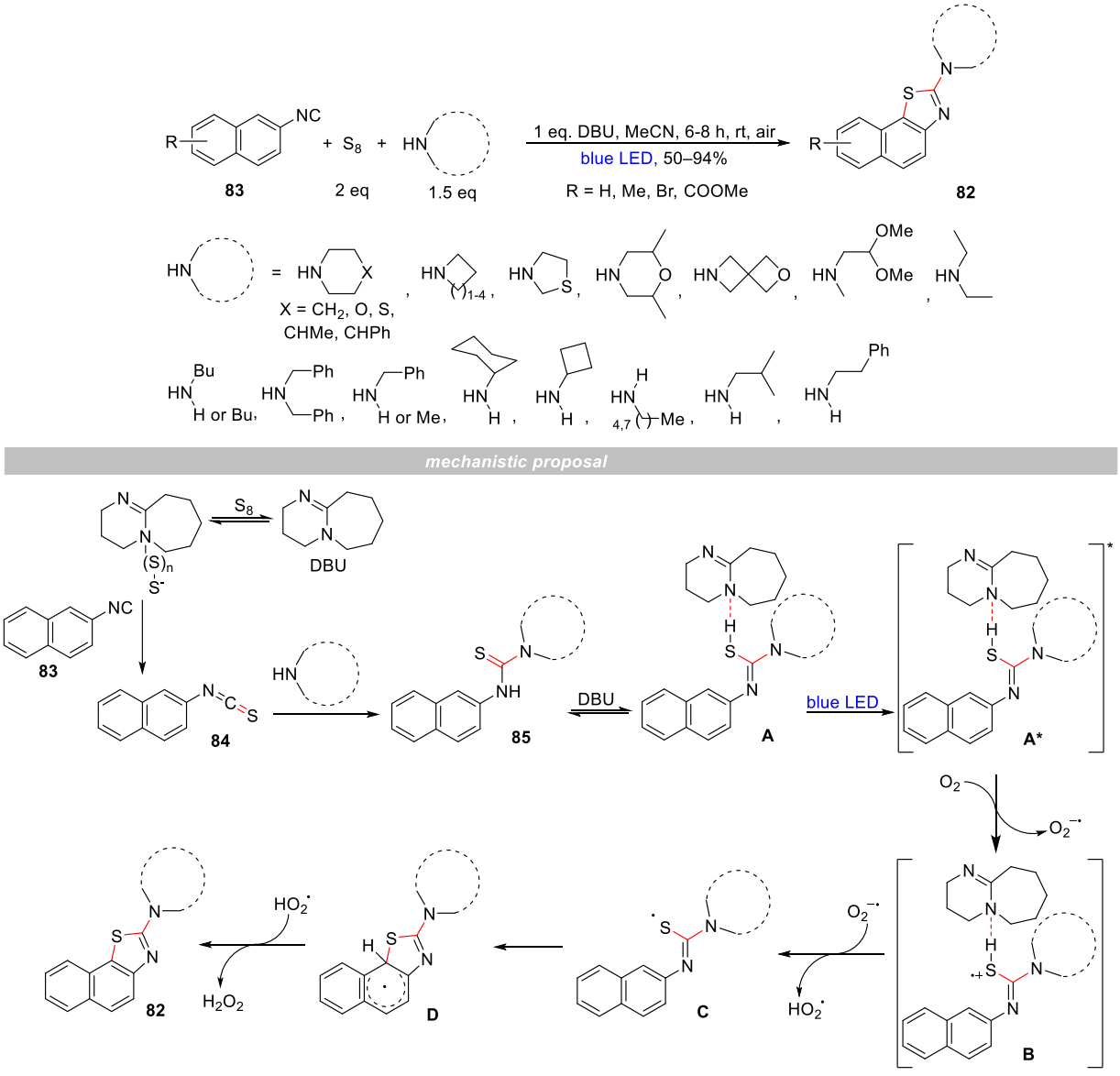
The incorporation of alkyl chains into benzothiazole motif through radical addition/cyclization cascades has also been demonstrated. Wang et al. synthesized compound **77** (Scheme 29) [94] using a redox-active ester **78** that forms a photoactive EDA complex with sulfide anions. This anion–π-assembled EDA complex, upon visible light absorption, transitions to an excited state and undergoes electron transfer, initiating the reductive decarboxylation to produce a *tert*-butyl radical. This radical adds to the isocyanide group of (2-isocyanophenyl)(methyl)sulfane, yielding an imidoyl radical, which then cyclizes intramolecularly with concurrent methyl radical release. Worth mentioning, that the substrate scope of this chemistry mainly involved *ortho*-isocyanobiaryls **79** giving the corresponding 6-alkylphenanthridines, with only compound **77** accessible using this methodology. A similar radical cascade process has been applied using cyclobutanone oxime ester **80** as a precursor (Scheme 29) [51]. Upon photoinduced electron transfer (PET) mediated by a photoredox catalyst like *fac*-Ir(ppy)$_3$ **4**, an iminyl radical **A** is generated, which undergoes selective C–C bond cleavage to form a γ-cyanoalkyl radical **B**. This strategy was mainly optimized for aryl isocyanides, although a single example, compound **81**, involved an isocyanoaryl thioether.



Scheme 29. Synthesis of benzothiazoles **77** and **81**.

10. Cyclization of aryl isonitriles/nitriles

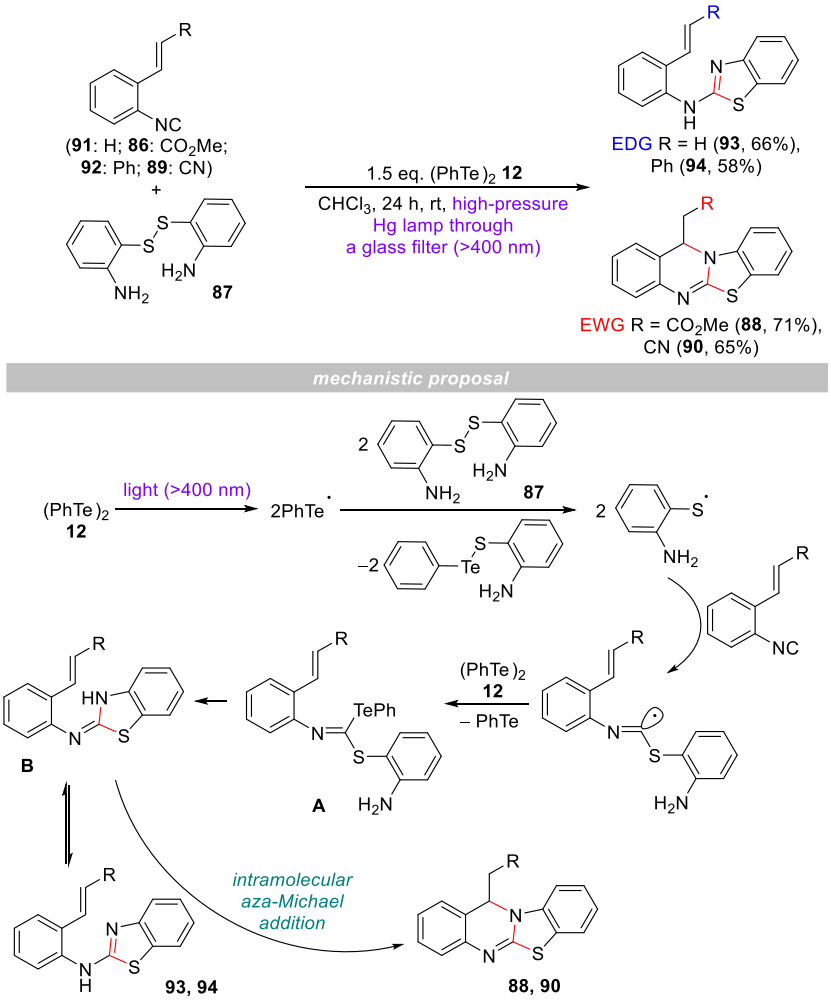
In a recent advancement (2024), an efficient three-component visible-light-mediated protocol was developed for synthesizing naphtho[2,1-d]thiazol-2-amines **82** by ortho-C–H sulfuration of 2-isocyanonaphthalenes **83** with elemental sulfur and amines (Scheme 30) [97]. Remarkably, this reaction proceeded under external photocatalyst-free conditions with an air atmosphere, although potassium persulfate $K_2S_2O_8$ (1 eq.) was occasionally added as an oxidant. Mechanistic studies suggested that a photoexcited species formed between a DBU-activated thiourea intermediate and visible light drives the reaction. The sequence involves reaction of 2-isocyanonaphthalene **83** with DBU-activated sulfur to yield 2-isothiocyanatonaphthalene **84**. Next, nucleophilic attack by an amine to form thiourea **85**, and excitation of the thiourea-DBU complex **A** under visible light to generate an activated species **A***. Oxidation of **A*** by oxygen produces sulfur radical cation **B**, which deprotonates to yield thiyl radical **C**. This radical undergoes regioselective intramolecular cyclization to form carbon-centered radical **D**, which abstracts a hydrogen atom to afford the desired product **82**.



Scheme 30. Synthesis of naphtho[2,1-d]thiazol-2-amines **82**.

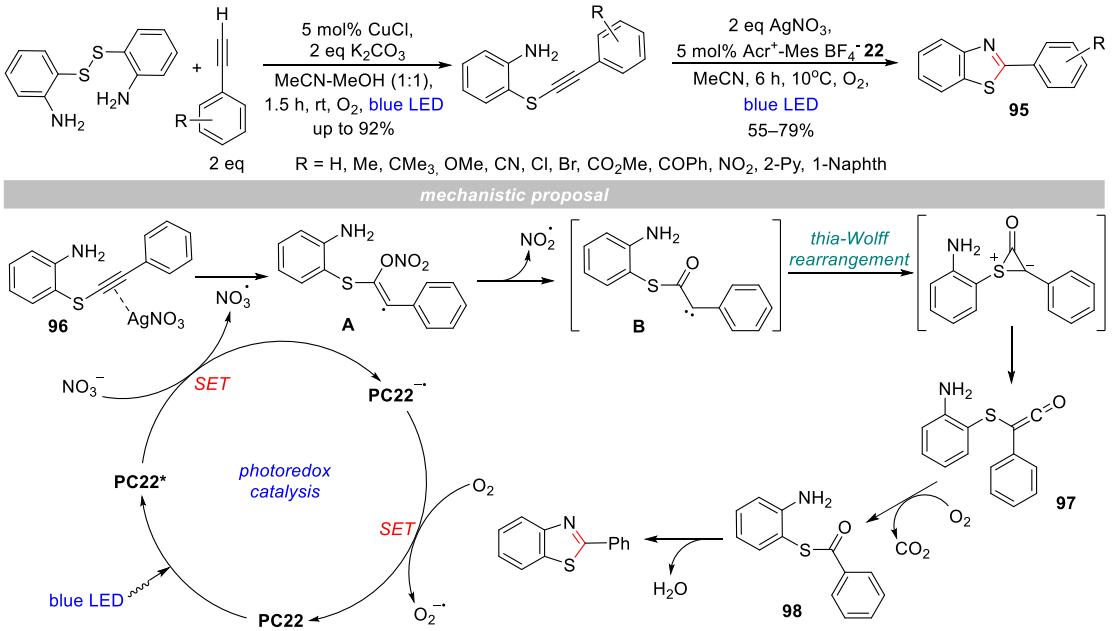
In the photochemical reaction of *o*-ethenylaryl isocyanides with organic disulfides, bisthiolated indole derivatives are formed *via* radical cyclization processes (Scheme 31) [58]. For example, when isocyanide **86** reacts with bis(2-aminophenyl) disulfide **87**, tetracyclic compound **88** containing dihydroquinazoline and benzothiazole units is obtained with a yield of 71%. Similarly, isocyanide **89**

yields compound **90** at 65%. However, when isocyanides **91** and **92** react with disulfide **87** in the presence of diphenyl ditelluride $(PhTe)_2$ **12**, benzothiazole derivatives **93** and **94** are formed with unreacted vinyl groups, achieving yields of 66% and 58%, respectively. The proposed mechanism involves photoinduced thiotelluration of *o*-ethenylaryl isocyanides toward the formation of intermediate **A**, nucleophilic substitution of the phenyltelluro group by an ortho-position amino group gives intermediate **B**. Next, intermediate **B** undergoes isomerization and aza-Michael addition to afford the tetracyclic compounds **88** and **90** or benzothiazole derivatives **93** and **94**.



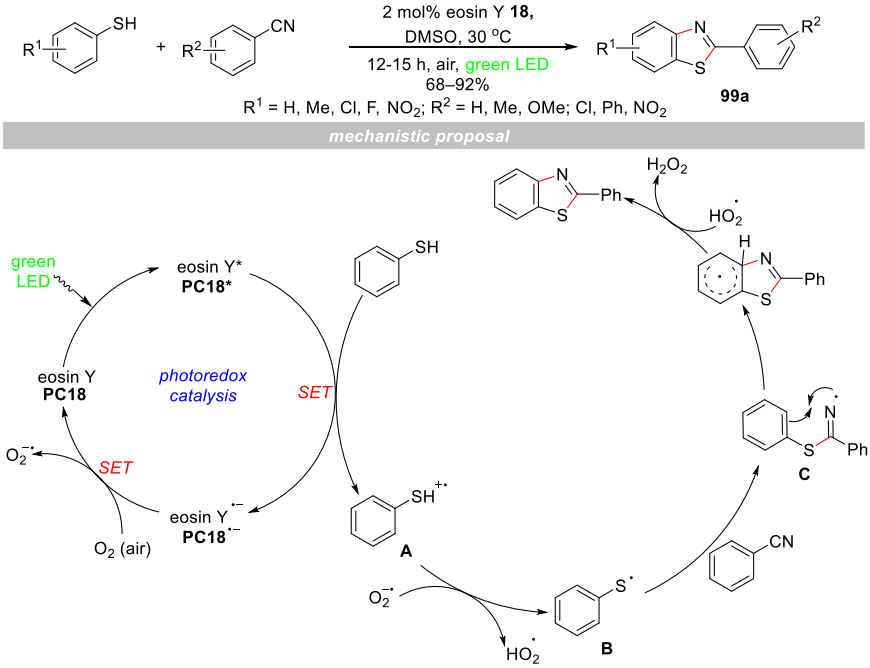
Scheme 31. Diphenyl ditelluride **12** catalyzed synthesis of benzothiazoles **88, 90** and **93, 94**.

A straightforward ortho-directed copper-catalyzed aerobic oxidative C(sp)–S coupling reaction has been reported using 2-aminothiophenol dimers and terminal alkynes under visible light (Scheme 32) [78]. This transformation exhibits excellent chemoselectivity and high yields, producing coupling products **95**. The methodology was extended to diverse thiol dimers and alkynes. These alkynyl sulfides serve as precursors for synthesizing 2-phenylbenzothiazoles via a thia-Wolff rearrangement mediated by silver nitrate ($AgNO_3$) under visible light with a photoredox catalyst system comprising 9-mesityl-10-methylacridinium tetrafluoroborate (Acr^+–Mes BF_4^-) **22**. Mechanistically, photoexcitation of catalyst **22** generates an oxidizing species **22*** capable of converting NO_3^- into $NO_3^{\bullet}$. The latter oxidizes a silver-coordinated alkynyl sulfide **96** to a vinyl radical **A**, which undergoes *γ*-fragmentation, releasing $NO_2^{\bullet}$ and forming a carbenoid **B**. This intermediate undergoes a mentioned rearrangement yielding ketene **97**, which then undergoes oxidative decarboxylation to the thioester **98**, followed by intramolecular condensation afforded the final 2-phenylbenzothiazole.



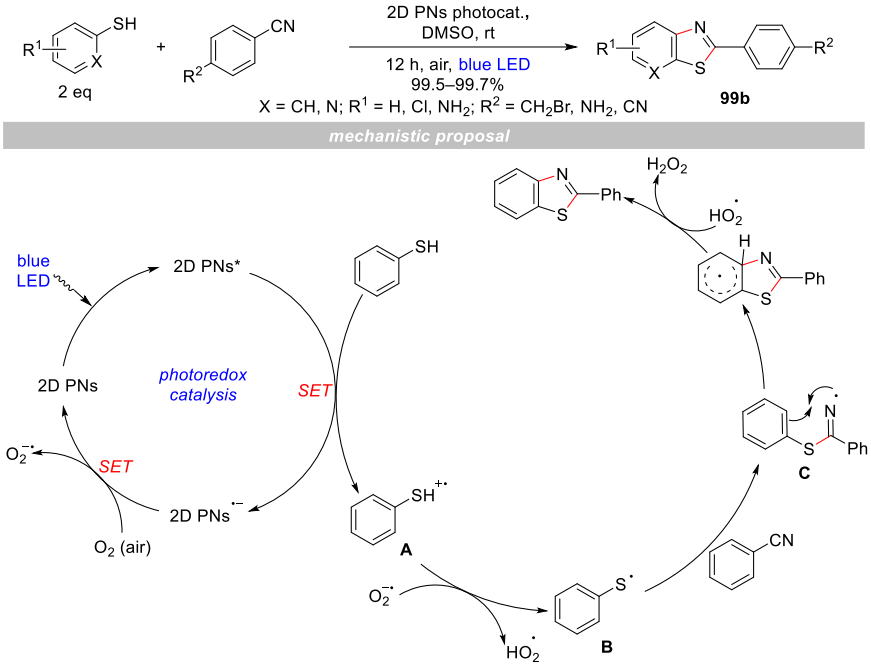
Scheme 32. 9-Mesityl-10-methylacridinium tetrafluoroborate **22** catalyzed synthesis of benzothiazoles **95**.

A novel visible-light photoredox methodology has been developed by Natarajan, Kim, Yadav, and colleagues for the efficient synthesis of 2-arylbenzothiazoles **99a,b** via sequential C–S and C–N bond-forming reactions from thiophenols and nitriles (Schemes 33 and 34) [67, 81]. Under green LED irradiation, eosin Y **18** is excited to its singlet state (eosin Y*), which undergoes reductive SET quenching by a thiophenol derivative, yielding the radical cation **A** and an eosin Y radical anion. The latter is subsequently oxidized back to its ground state by molecular oxygen, producing a superoxide radical anion ($O_2^{-\bullet}$). Radical **A** is deprotonated by $O_2^{-\bullet}$ to generate the thiyl radical **B**, which reacts with the carbon atom of the nitrile group to form the iminyl radical **C**. This intermediate undergoes intramolecular cyclization, followed by hydrogen radical elimination, to produce the benzothiazole **99a** [67].



Scheme 33. Eosin Y **18** catalyzed synthesis of benzothiazoles **99a.**

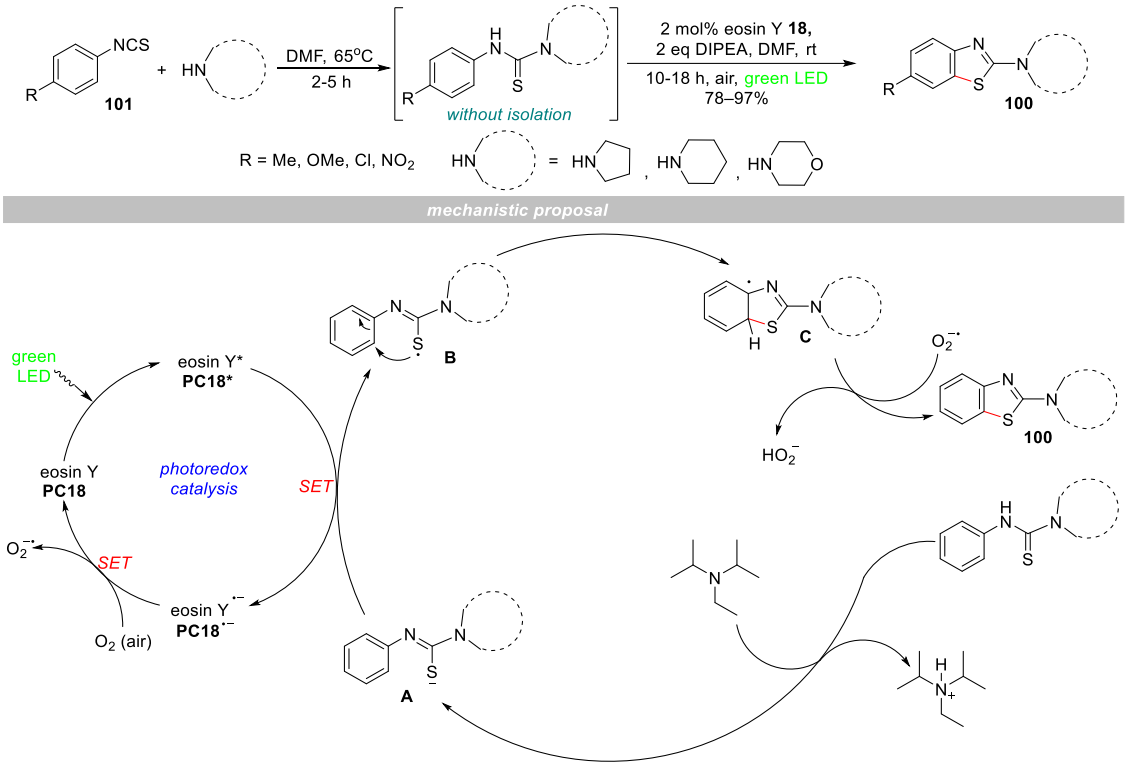
In a continuation of this methodology, ultrathin two-dimensional porphyrin nanoplates (2DPNs) have been identified as highly efficient photocatalyst for the quantitative conversion of thiophenols and nitriles into 2-substituted benzothiazoles **99b** (Scheme 34) [81] through mechanism, which is generaly the same as previously (Scheme 33) described.



Scheme 34. 2D PNs catalyzed synthesis of benzothiazoles **99b.**

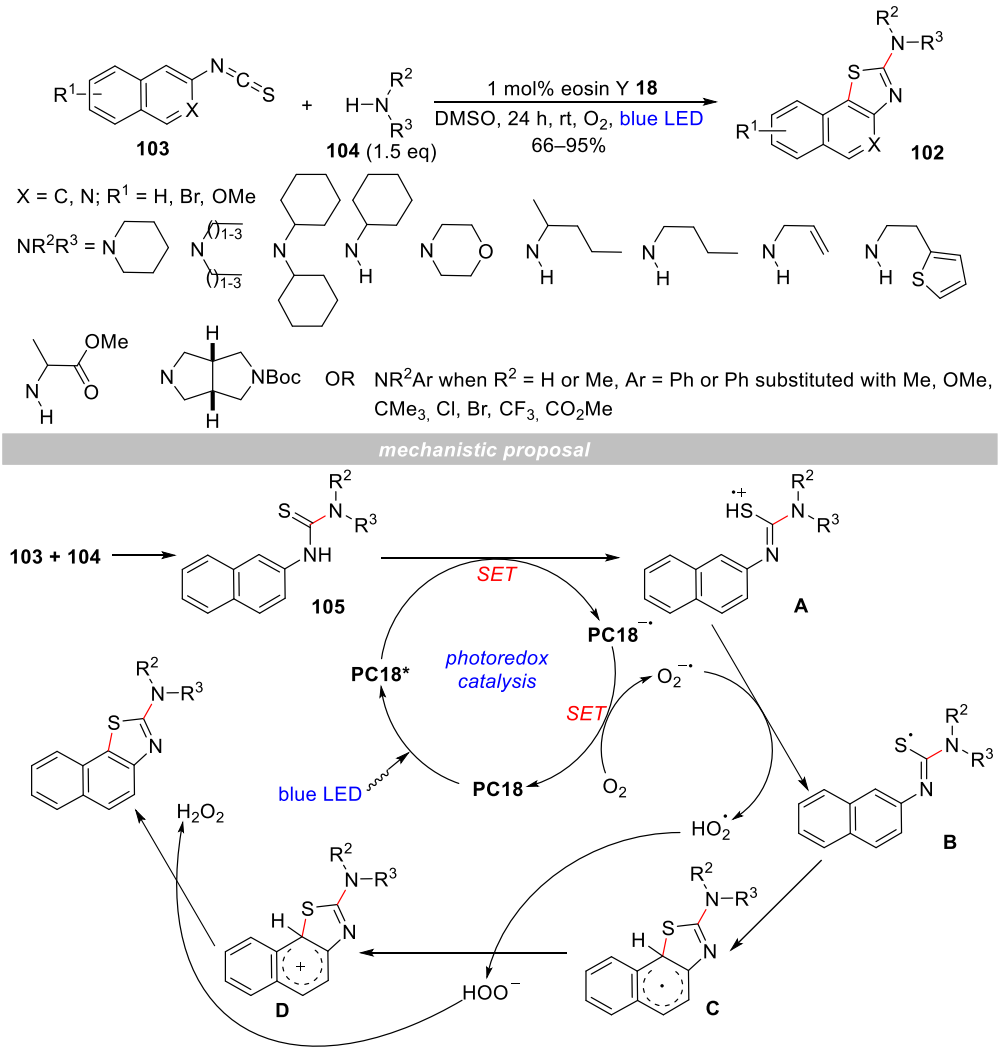
11. Cyclization of arylisothiocyanates

Singh and co-workers [66] introduced a one-pot method for the facile synthesis of 2-aminobenzothiazoles **100** directly from arylisothiocyanates **101** and secondary amines (Scheme 35). The reaction proceeds through initial heating of a solution of arylisothiocyanate and secondary amine in DMF at 65°C for 2–5 hours, generating the corresponding N-arylthioureas *in situ*. Subsequent photocatalysis using eosin Y **18** under green LED irradiation, along with N,N-diisopropylethylamine as a base and an air atmosphere, affords the products **100** in good to excellent yields (78–97%) at room temperature. This protocol is highly functional-group-tolerant, accommodating both electron-donating and electron-withdrawing substituents. However, arylisothiocyanates bearing electron-donating groups on the aromatic ring exhibit faster reaction rates and slightly improved yields compared to their electron-withdrawing counterparts. The proposed mechanism involves photoredox catalysis, where eosin Y is photoexcited to its singlet state (^{1}EY*), followed by intersystem crossing (ISC) to its more stable triplet state (^{3}EY*). A reductive SET from the intermediate **A** to ^{3}EY* generates the thioacyl radical **B**, which undergoes 5-endo-trig intramolecular cyclization to form intermediate **C**. Subsequent interaction with the superoxide radical anion leads to the final product.



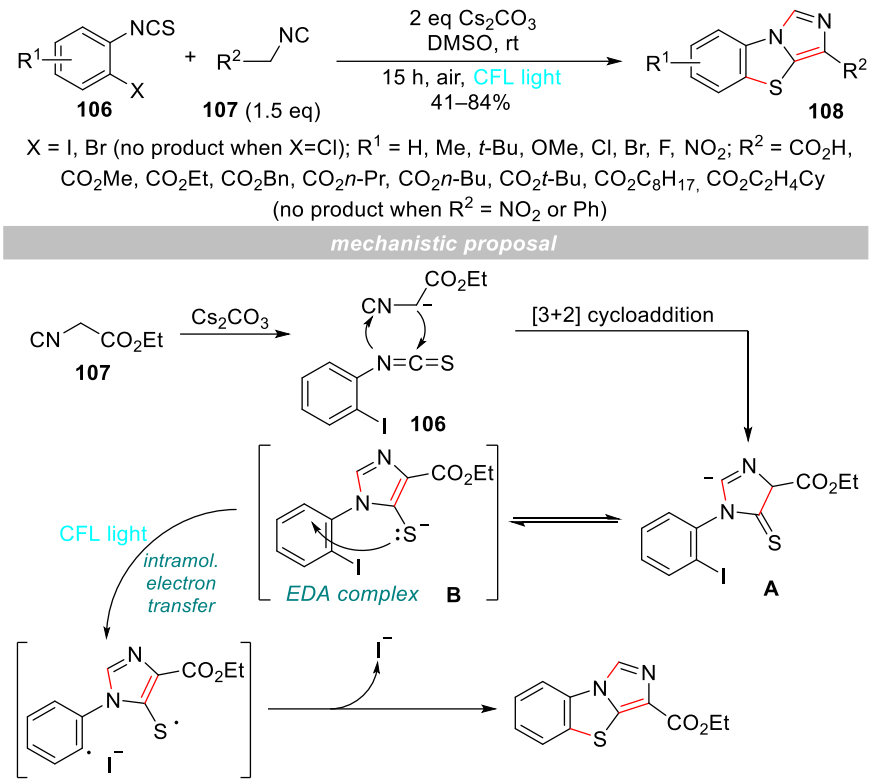
Scheme 35. Eosin Y **18** catalyzed synthesis of 2-aminobenzothiazoles **100**.

An environmentally friendly visible-light-mediated approach for synthesizing naphtho[2,1-d]thiazol-2-amines **102** has been reported *via* photoredox-catalyzed C(sp^2)–H/S–H cross-dehydrogenative coupling of 2-isothiocyanatonaphthalenes **103** and amines **104** (Scheme 36) [68]. This reaction efficiently forms new C–N and C–S bonds in a single step. Upon visible light excitation, eosin Y **18** transitions to its excited state (eosin Y*), which reacts with intermediate **105** (formed *in situ* from **103** and **104**) to generate radical cation **A** and eosin Y radical anion (eosin $Y^{\bullet-}$). This anion is reoxidized to its ground state by molecular oxygen, concurrently producing $O_2^{-\bullet}$. Deprotonation of **A** by $O_2^{-\bullet}$ results in the formation of thiyl radical **B**, which undergoes regioselective intramolecular radical addition to produce carbon radical **C**. A subsequent SET with $HO_2^{\bullet}$ yields intermediate **D**, which reacts with the superoxide anion to furnish the final cyclized product **102**. DFT calculations provide additional support for the proposed mechanism. Furthermore, He and co-workers [91] demonstrated that the same transformation can be achieved under DMSO/oxygen conditions using long-wavelength UVA light (385–390 nm), eliminating the need for a photocatalyst.



Scheme 36. Eosin Y **18** catalyzed synthesis of naphtho[2,1-d]thiazol-2-amines **102**.

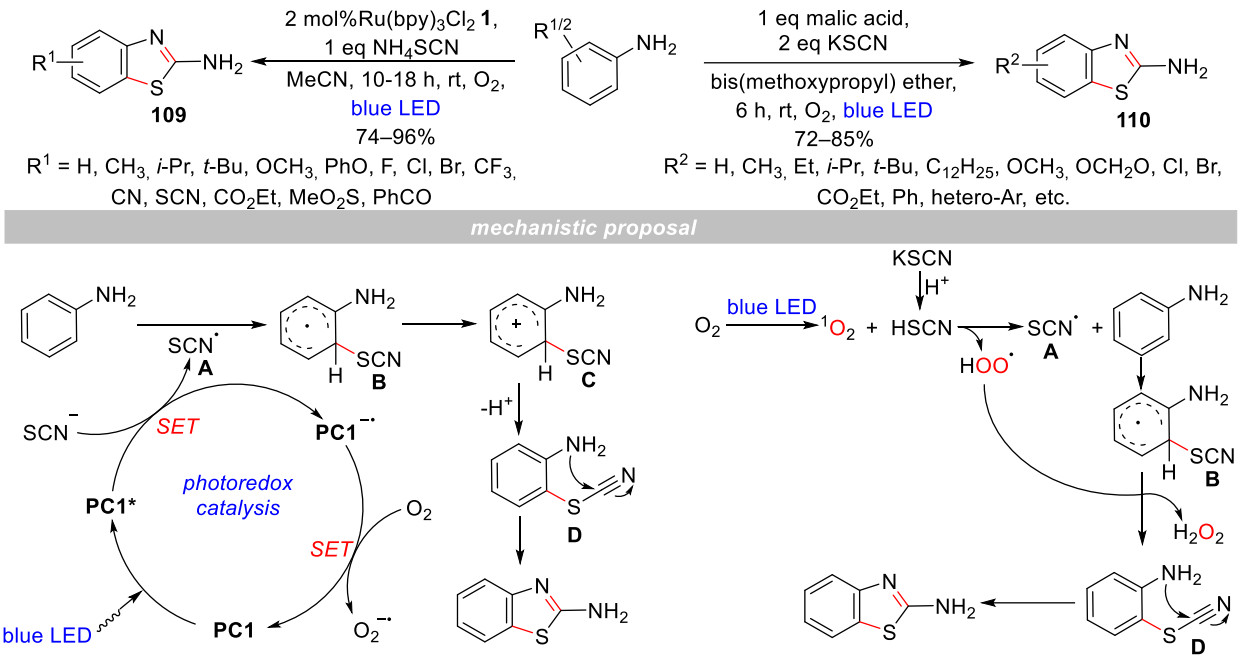
The visible-light-driven cascade cyclization of 2-haloaryl isothiocyanates **106** and isocyanides **107** into benzo[d]imidazo[5,1-b]thiazoles **108** has been accomplished under metal- and photocatalyst-free conditions (Scheme 37) [90]. The reaction begins with a base-promoted [3+2] cycloaddition between **106** and **107**, forming intermediate **A**, which subsequently undergoes isomerization to produce intermediate **B**. Within intermediate B, the electron-rich thiolate anion interacts with the electron-deficient aryl iodine moiety to form an EDA complex. Upon light irradiation, this EDA complex undergoes an intramolecular SET to generate an aryl radical, a sulfur radical, and an iodine anion. The reaction concludes with an intramolecular free radical coupling, yielding the desired product **108**.



Scheme 37. Metal- and photocatalyst-free synthesis of benzo[d]imidazo[5,1-b]thiazoles **108**.

12. Cyclization of anilines with thiocyanates

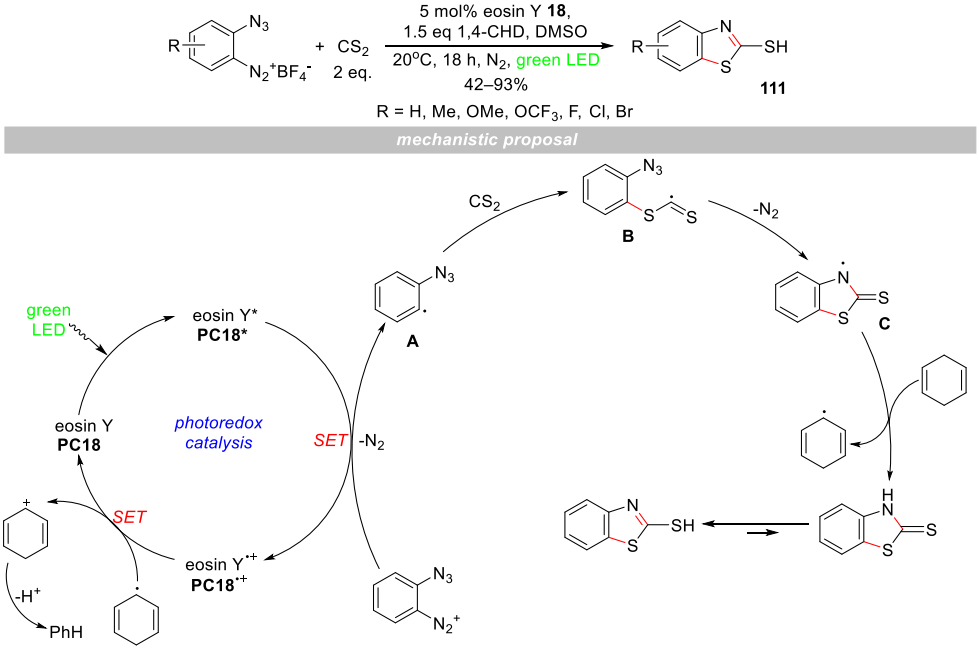
In 2020, Singh [46] and He [87] independently developed photochemical methodologies for synthesizing benzothiazoles directly from substituted anilines and inorganic isothiocyanates (Scheme 38). The first method utilizes a photoredox-catalyzed addition/cyclization cascade between thiocyanate radicals and anilines, employing $Ru(bpy)_3Cl_2$ **1** as the photocatalyst under visible-light irradiation [46]. This protocol is highly versatile, accommodating a wide range of substituents, including CH_3, *i*-Pr, *t*-Bu, OCH_3, PhO, F, Cl, Br, CF_3, CN, SCN, CO_2Et, MeO_2S, and PhCO, and affords 2-aminobenzothiazoles **109** in moderate to excellent yields. Upon visible-light excitation, Ru^{2+} is promoted to its excited state Ru^{2+}*, which undergoes SET with SCN^- to generate the thiocyanate radical **A** and Ru^+. Atmospheric oxygen oxidizes Ru^+ back to Ru^{2+}, completing the photoredox cycle while forming the superoxide radical anion ($O_2^{-\bullet}$). The thiocyanate radical reacts with aniline to form radical intermediate **B**, which is oxidized to cationic intermediate **C**. Deprotonation of **C** produces intermediate **D**, followed by an intramolecular cyclization where the nucleophilic amino group attacks the thiocyanate moiety, yielding the final product **109**. The second method involves a visible-light-initiated, malic acid-promoted cascade coupling/cyclization of anilines and KSCN with ambient air as the oxidant [87]. Singlet oxygen ($^1O_2$), generated from molecular oxygen (O_2) under visible-light irradiation, reacts with thiocyanic acid (produced in situ from KSCN and malic acid). This interaction generates the thiocyanate radical **A** and hydroperoxyl radical. The thiocyanate radical reacts with aniline to form intermediate **B**, which undergoes dehydro-aromatization to yield 2-thiocyanatoaniline **D**, accompanied by hydrogen peroxide formation. Intramolecular nucleophilic attack of the amino group in **D** on the thiocyanate group results in the final benzothiazole product **110**.



Scheme 38. Synthesis of 2-aminobenzothiazoles **109** and **110**.

13. Cyclization of 2-azidoarenediazonium tetrafluoroborates

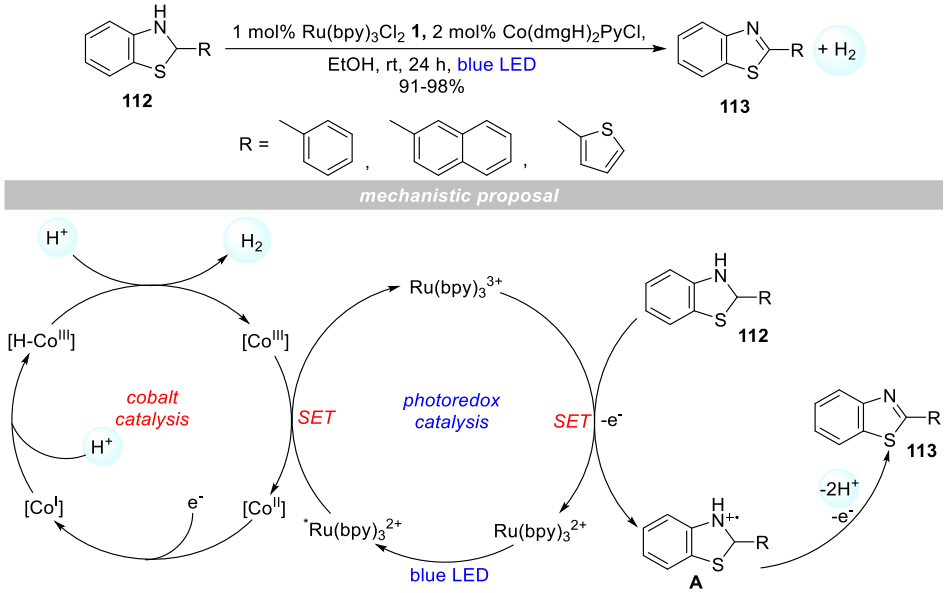
Natarajan and co-workers [71] reported an eosin Y-catalyzed visible-light-driven synthesis of 2-mercaptobenzothiazoles **111** from 2-azidoarenediazonium tetrafluoroborates and carbon disulfide (Scheme 39). Upon visible-light irradiation, eosin Y **18** transitions to its photoexcited state (EY*), which donates an electron to the diazonium salt. This step generates an aryl radical **A** and $[EY]^{\bullet+}$. Radical **A** then attacks the sulfur atom in carbon disulfide, forming intermediate **B**, which undergoes intramolecular cyclization with the azido group, extruding N_2 gas to yield the N-radical intermediate **C**. HAT from 1,4-cyclohexadiene (CHD) produces the desired product **111** while regenerating the CHD radical. The photoredox cycle is completed as the CHD radical transfers an electron to $[EY]^{\bullet+}$, regenerating eosin Y **18**.



Scheme 39. Eosin Y **18** catalyzed synthesis of 2-mercaptobenzothiazoles **111**.

14. Dehydrogenation of 2,3-dihydrobenzothiazoles

Li and co-workers developed a visible-light-promoted acceptorless dehydrogenation of 2,3-dihydrobenzothiazoles **112** using a combined photoredox and cobalt catalysis system to afford benzothiazoles **113** (Scheme 40) [44]. Under blue LED irradiation, $Ru(bpy)_3^{2+}$ transitions to its excited state $Ru(bpy)_3^{2+*}$, which is oxidatively quenched by Co^{III} to produce $Ru(bpy)_3^{3+}$ and Co^{II} *via* SET. A subsequent SET from **112** to $Ru(bpy)_3^{3+}$ generates intermediate **A**, regenerating $Ru(bpy)_3^{2+}$. The intermediate **A** undergoes deprotonation and electron loss to yield the final product **113**. Simultaneously, the Co^{II} formed is reduced to Co^{I}, which reacts with protons to form Co^{III}-H. This intermediate either undergoes protonation to produce H_2 or homolytic cleavage between two Co^{III}-H species to evolve H_2. This method, operating under mild reaction conditions at ambient temperature, provides a sustainable approach to synthesizing benzothiazoles and related azaheterocycles, with potential applications in reversible dehydrogenation-hydrogenation systems for H_2 storage.



Scheme 40. $Ru(bpy)_3Cl_2$ catalyzed synthesis of benzothiazoles **113**.

15. Conclusions and Future Outlook

This comprehensive review summarizes the advances in the photocatalytic synthesis of 1,3-benzothiazoles to date. The availability of cost-effective light sources, the utilization of visible light in the presence of photocatalytically active materials, and society growing emphasis on environmentally sustainable technologies have significantly accelerated the development of photochemical methods. The use of visible light in these processes not only overcomes many challenges, such as the need for high temperatures, but also achieves exceptional selectivity, often unattainable with conventional approaches. A survey of the literature reveals that among photochemical methods for synthesizing N,O,S-containing heterocycles, those targeting sulfur-based motifs remain the least represented. Nevertheless, sulfur-containing heterocycles are of paramount importance, particularly in the pharmaceutical field. As we can see, photocatalysis offers a straightforward and efficient route for assembling benzothiazoles under mild conditions, employing less toxic and more cost-effective sulfur sources compared to traditional strategies. Additionally, many methods have demonstrated scalability to gram-scale production, enhancing their practical utility. The proposed in original literature mechanisms, often presented in diverse ways, are unified in this review to offer a cohesive mechanistic perspective, fostering new ideas for heterocyclic synthesis. The cyclization of 2-aminothiophenols with aldehydes remains the most widely employed strategy for the photochemical synthesis of 1,3-benzothiazoles, with both organocatalysts and transition-metal-based catalysts proving effective. Other viable substrates for this cyclizations include benzylamines, *α*-ketocarboxylic acids, alcohols, and methyl arenes. Common starting materials include N-aryl thioamides, 2-isocyanoaryl thioethers, aryl isonitriles/nitriles, and aryl isothiocyanates. Notably, at least one-third

of reported light-driven syntheses of benzothiazoles have been conducted without external photocatalysts (Fig. 4). Certain reactions [59, 85, 88] satisfy bioorthogonality criteria and can be performed in water at physiological pH, making them promising for the *in vivo* modification of bioactive natural compounds. Beyond the construction of benzothiazole scaffolds, alternative strategies have emerged, such as the visible-light-driven arylation, alkylation, or acylation of 2-unsubstituted 1,3-benzothiazoles [98–100].

Despite substantial progress, several challenges remain in the photocatalytic synthesis of benzothiazoles. Key areas for future research include designing photocatalysts with enhanced efficiency, stability, affordability, broad spectral responsiveness, and recyclability is critical for advancing this field. Addressing the potential contamination of products by metal ions from photocatalysts is particularly important for pharmaceutical applications. Non-metallic dye- and polymer-based photocatalysts may offer promising solutions. Greater clarity is needed regarding the effects of solvents, substituents, and steric factors on reaction yields. Current findings are sometimes inconsistent and require further research. Developing environmentally friendly, photocatalyst-free methods using simple starting materials, such as anilines, thiophenols, and arylnitriles, should be prioritized. The underexplored area of C–S bond formation through electron donor-acceptor (EDA) complex formation is particularly promising. These complexes act as intrinsic light absorbers, enabling photochemical transformations without additional photosensitizers. Exploring such methods remains an open challenge.

The diversity of examples presented in this review highlights the potential of these methodologies in organic synthesis, drug discovery, and materials science. The reliance on inexpensive, transition-metal-free catalysts further underscores the practicality and industrial applicability of these protocols. Given that photoredox catalysis in benzothiazole chemistry has only been actively pursued for approximately 15 years, this field is still in its infancy. Innovative approaches leveraging photochemically generated radical intermediates are expected to emerge, offering greener and more efficient synthetic routes. With their inherent advantages and potential applications, these sustainable methodologies hold great promise for the pharmaceutical industry. Considering the biological importance of organosulfur heterocycles, the ongoing development of novel C–S bond formation strategies will remain a focus of the organic synthesis community.

Declaration of Competing Interest

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

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