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Recent advances in photochemical and electrochemically induced thiocyanation: a greener approach for SCN-containing compound formation

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Techniques utilizing photo- and electrochemically induced reactions have been developed to accelerate organic processes. These techniques use light or electrical energy (electron transfer) as a direct energy source without using an initiator or reagent. Thiocyanates are found in biologically active and pharmacological compounds and can be converted into various functional groups. It is one of the most prominent organic scaffolds. Significant development in photo- and electro-chemically induced thiocyanation procedures has been made in recent years for the conception of carbon-sulfur bonds and synthesis of pharmaceutically important molecules. This review discusses different photo- and electro-chemically driven thiocyanation $C(sp^3)$–SCN, $C(sp^2)$–SCN, and $C(sp)$–SCN bond conception processes that may be useful to green organothiocyanate synthesis. We focus on the synthetic and mechanistic characteristics of organic photo- and electrochemically accelerated C–SCN bond formation thiocyanation reactions to highlight major advances in this novel green and sustainable research field.

1. Introduction

Synthetic organic chemistry relies heavily on organo-thiocyanates.[1] In chemical synthesis and medicinal chemistry, the formation of C–SCN bonds is a common method for producing organothiocyanates,[1a] which are commonly used as synthetic precursors for a range of sulfur heterocycles and sulfur-containing compounds, such as sulfides, disulfides, thiols, thioethers, isothiocyanates, trifluoromethylthiolates, and thiocarbamates.[2] These organothiocyanates contain many biological features that are useful in various sectors, such as medicine, pesticides, and materials.[3] Organic synthetic chemists are fascinated by their remarkable biological activities and possible uses.

Organic chemists have concentrated their efforts into exploring thiocyanation reactions and applications, which mostly involve nucleophilic substitution, electrophilic substitution, and free radical thiocyanation (Fig. 1A) catalyzed by transition metals or nonmetals through a traditional technique or with the use of stoichiometric oxidants.[4,5] As a result, a number of well-established and highly successful methods for generating C–SCN bonds have been developed and are already well-reviewed, which is critical to the advancement of organic thiocyanate research.[1e]

The development of green, sustainable, efficient, and extremely atomic-economical C–S bond conception procedure is one of the most noteworthy research subjects in synthetic organic chemistry.[6] In this context, photoredox catalysis has lately appeared as a promising avenue for organic synthesis because it utilizes seemingly endless resources, such as visible light, air, and energy. Photocatalysis and electrocatalysis use light and electrical energy (electron transfer) as direct energy sources, respectively, and are thus in line with green chemistry principles. Photocatalytic approaches using air as a green antioxidant to perform thiocyanation reactions have been devised in recent years. Electrochemical synthesis is a novel and ecologically beneficial technology that uses continuous electron gain and loss rather than standard chemical redox reagents. Organic chemists have effectively leveraged this characteristic to construct a variety of metal-free and oxidant-free thiocyanation methods (Fig. 1B). The essential ideas of photocatalysis and
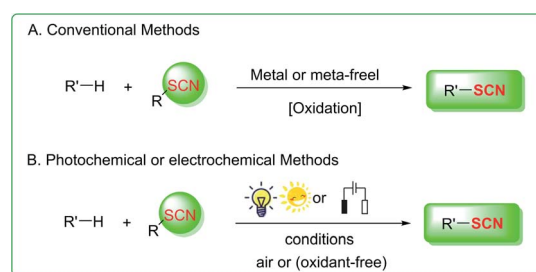
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Fig. 1 Strategies for C–SCN bond formation through thiocyanation.

electrocatalysis-induced processes for C–C and C–S bond formation have been thoroughly examined.[7] Nevertheless, novel photo- and electrochemically promoted strategies for generating carbon-thiocyano (C–SCN) bonds have recently been described. The purpose of this review is to describe the latest advances in this rapidly expanding field of photo- or electro-catalysis. This review article presents a concise summary of the most important photocatalysis- and electrocatalysis-driven thiocyanation strategies for the creation of C(sp^3)–SCN, C(sp^2)–SCN, and C(sp)–SCN bonds to increase understanding of the evolution of green and sustainable thiocyanation progression.

2. Photochemical-induced thiocyanation reactions

### 2.1 Photochemical-induced C(sp^3)–SCN bond formation through thiocyanation reaction

The direct thiocyanation of a stable C–H bond is one of the most advantageous routes because it facilitates the synthesis of organic thiocyanates with readily accessible C–H bond donors. Over the last decade, many catalytic techniques for the direct thiocyanation of stable C(sp^2)–H and C(sp^3)–H bonds have been satisfactorily established, allowing quick access to a wide range of thiocyanated molecules. The considerable activation energy required to activate inert C(sp^3)–H bonds increases the difficulty and challenge of C(sp^3)–H bond activation functionalization. Photocatalytic oxidative coupling of C(sp^3)–H thiocyanation reaction is an effective way to achieve C(sp^3)–H participation in thiocyanation reactions as compared to traditional C(sp^3)–H thiocyanation reactions processes.

To produce multi-substituted olefins 2, Yuan et al. invented a strategy that uses atmospheric oxygen as the terminating oxidant for the metal-free photochemical-induced amino-thiocyanation of activated ketones 1.[8] Ammonium thiocyanate has been used as the sole source of thiocyanate and amine, and water is the only secondary substance. This green approach may effectively and rapidly produce a range of multi-substituted olefins in high yields (Scheme 1a). The process starts with the SET oxidation of NH$_4$SCN by the incited photocatalyst fluorescein*, which produces ˙SCN and the decreased form fluorescein˙$^-$. In superoxide production, the photocatalyst can be regenerated by oxidizing fluorescein˙$^-$ with dioxygen. The ˙SCN radical then takes a hydrogen atom from 1A. This process results in a carbon-centered radical and thiocyanic acid (HSCN). ˙SCN or (SCN)$_2$ captures the α-carbonyl radical 1B to produce a bridging precursor 1C, which contains an electron-poor carbonyl group and may be conveniently targeted through nucleophilic NH$_3$. Eventually, the desired product 2 is obtained by removing water from the adduct of 1C and NH$_3$ (Scheme 1b).

The first example of an organo-photoredox catalyst-driven C(sp^3)–S bond formation through the thiocyanation reaction of tertiary amine 3 at ambient temperature was discovered by Yadav et al., who used ammonium thiocyanate as the source of thiocyanate.[9] The reaction is gentle, and oxygen and green light are environmentally friendly and cost-effective reagents; only a small amount of eosin Y (EY; 1 mol%) is required (Scheme 2a).
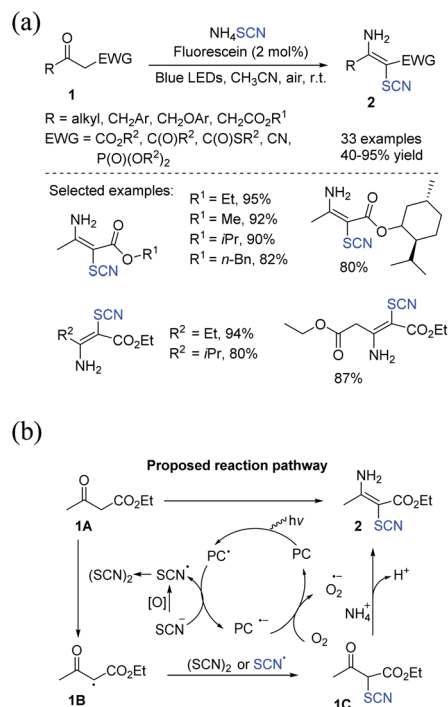
Scheme 1 a) Visible-light-induced amino-thiocyanation of activated ketones 1. (b) Proposed mechanism for visible-light-induced amino-thiocyanation of activated ketones 1.
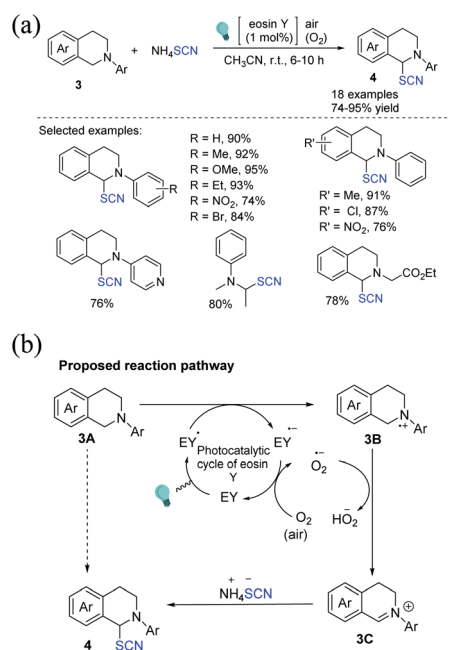
Scheme 2 a) Photoredox catalyst promoted α-C(sp^3)–H thiocyanation of tertiary amines 3. (b) Proposed reaction pathway for the α-C(sp^3)–H thiocyanation of tertiary amines 3.

When light is absorbed, EY transforms into its excited state (EY*). Compound 3B and EY˙$^-$ are formed by a single electron transfer between 3A and EY*, and the photoredox cycle of eosin Y occurs through the aerobic oxidation of EY˙$^-$ by O$_2$ to its

ground state (EY). The superoxide radical anion ($O_2^{-\bullet}$) produced *in situ* removes a proton from the α-position of **3B** to produce iminium ion **3C**, which is subsequently attacked by the SCN nucleophile to provide the final product **4** (Scheme 2b).

Zhu *et al.* created a distinctive approach for constructing δ-thiocyanato alcohols **6** in good to moderate yields. In this method, the reaction between *N*-alkoxypyridinium salts **5** and silyl isothiocyanate is catalyzed through dual photoredox or by copper.[10] A domino reaction includes alkoxy radical production, 1,5-hydrogen atom transfer (1,5-HAT), and copper-catalyzed thiocyanation of the ensuing C-centered radical (Scheme 3a). Three alternative approaches for functionalizing benzylic, aliphatic, and tertiary C(sp³)H are demonstrated. The authors claim that Ir(III)* excited species reduce substrates **5** in the production of radical **5C** and Ir(IV). In the presence of TMSNCS, Cu(I) is oxidized and produces Cu(II)SCN(OAc) salt. The process results in the regeneration of the Ir(III) species. After 1,5-HAT, radical **5C** fragments become alkoxy radical **5A**, which then fragments to form radical **5B**. Cu(II)SCN(OAc) forms the Cu(III) species **5D** when it interacts with Cu(III) species **5D**. With the release of Cu(I) salt, reductive elimination forms the thiocyanate molecule **6** (Scheme 3b).

## 2.2 C–S bond formation photochemical induced indirect thiocyanation reaction

Fan *et al.* proposed a direct photocatalyst-induced cyanation technique for the construction of thiocyanates **8** from thiols **7**.[11] This technique uses ammonium thiocyanate as an inorganic salt, which is a cheap and harmless and is a green cyano source and provides a wide range of thiocyanate products **8** in good to high yields (Scheme 4a). Under visible light, Rose Bengal (RB) can be used as a photocatalyst and air as an oxidant. RB is first stimulated to its excited state species (RB*) when released to visible light. Then, through energy transfer, RB* interacts with O_2 to produce $^1O_2$ and regenerates its ground state (RB). Under visible light irradiation, RB appears to be a better $^1O_2$-generating photosensitizer than other photocatalysts. The produced $^1O_2$ then captures a hydrogen atom from thiol, yielding the thioyl radical **7A**. Through radical coupling, radical **7A** is converted into intermediate **7B**. Owing to the instability of disulfides under light irradiation, the homolytic dissociation of **7B** produces radical **7A**. The intermediate **7C** is formed when thioyl radical **7A** combines with SCN⁻. The intermediate **7D** is propagated and formed when the intermediate **7C** is trapped by another thiol. Finally, **7D** is transformed into the desired product **8** with the release of HS⁻ (Scheme 4b).

2.3 Photochemical induced C(sp²)–SCN bond formation thiocyanation reaction

2.3.1 C(sp2)–SCN bond formation thiocyanation reaction of olefins and arenes. Bolm *et al.* proposed a method for synthesizing novel sulfur reagents as *N*-thiocyanato sulfoximines **10** from N–Br sulfoximines **9** and ammonium thiocyanate, which they then used in the photocatalytic difunctionalizations of styrenes **11** to obtain a variety of 1,2 difunctionalized compounds **12** carrying with a thiocyanato
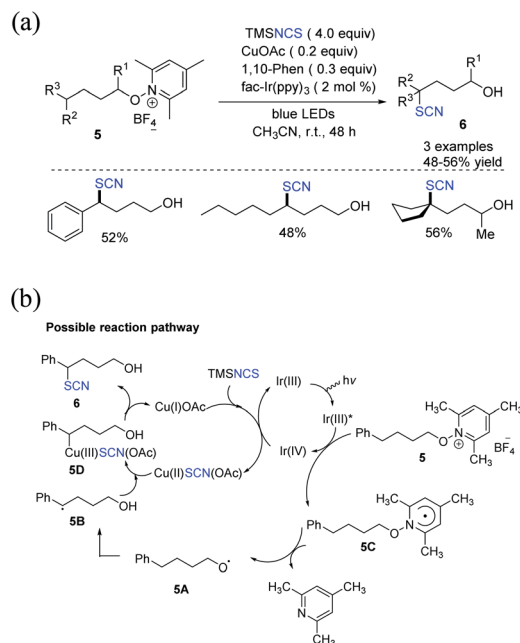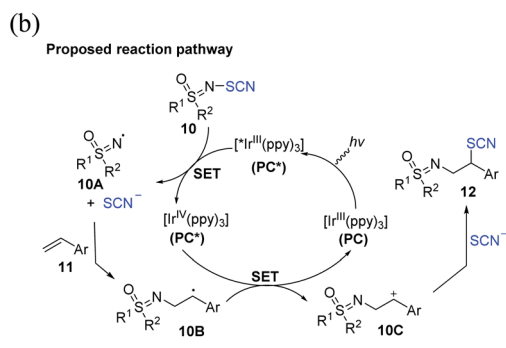

Scheme 3 a) Photoredox or copper-catalysis to access δ-thiocyanato alcohols **6**. (b) Proposed mechanism for photoredox or copper-catalysis to access δ-thiocyanato alcohols **6**.
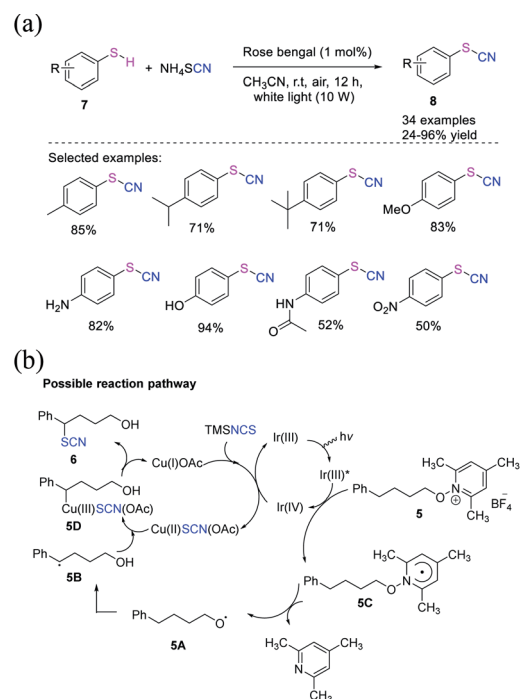
Scheme 4 a) Photocatalyst-promoted synthesis of thiocyanates **8** from thiols **7**. (b) Possible reaction pathway for synthesis of thiocyanates **8** from thiols **7**.

functions and a sulfoximine functions on vicinal positions in high to excellent yields (Scheme 5a).[12] According to the proposed reaction pathway, the photocatalyst *fac*-[Ir(ppy)₃] (PC) can efficiently receive a photon from poor fluorescent light. The

(a)

Selected examples:

R = Ph, 72%	R = p-tBuPh, 60%
R = o-Tol, 38%	R = p-BrPh, 66%
R = m-Tol, 51%	R = p-ClPh, 53%
R = p-Tol, 52%	R = p-FPh, 50%

R' = p-MeOPh, 81%	R' = m-MeOPh, 40%
R' = p-Tol, 71%	R' = m-BrPh, 44%
R' = p-BrPh, 66%	R' = m-ClPh, 43%
R' = p-ClPh, 62%	R' = o-BrPh, 38%
R' = p-FPh, 55%	R' = o-ClPh, 52%
	R' = 3,5-Cl₂Ph, 58%

(b)

Proposed reaction pathway

Scheme 5 a) Photocatalytic difunctionalization of alkenes **11** with *N*-SCN sulfoximines **10**. (b) Proposed mechanism for photocatalytic difunctionalization of alkenes **11** with *N*-SCN sulfoximines **10**.

process results in the incited state *fac*-[*Ir^{III}(ppy)$_3$] (PC*). PC$^+$ is formed through a single electron transfer (SET) from PC* to *N*-SCN sulfoximine **10**. A thiocyanate anion and the sulfoximidoyl radical **10A** are constructed. A novel radical, **10B**, is created, which is oxidized through PC$^+$ to produce the benzyle cation **10C** when **11** is added to **10A**. The photocatalyst then returns to its initial oxidation state (PC) and can initiate the original catalytic circle. When **10C** interacts in the midst of SCN$^-$, product **12** is produced (Scheme 5b).
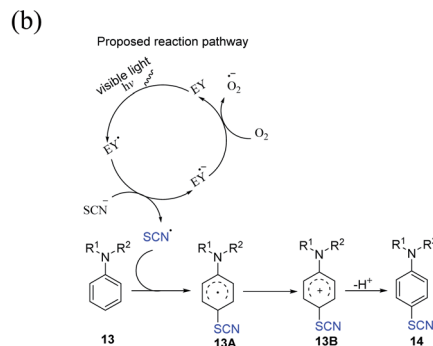
In 2020, Tan *et al.* developed a visible-light-assisted regioselective aerobic oxidative C(sp^2)–H thiocyanation process for aromatic substances **13**.[13] The process is ecologically benign, effective, and simple to operate. EY, which is an useful photocatalyst, and oxygen, which is a green terminal oxidant, were used to produce the required compounds **14** in good to high yields. A wide variety of aromatic amines, including primary, secondary, and tertiary amines, can be used in this process (Scheme 6a). In the author's opinion, a workable mechanism has been offered. After being photo-excited in the presence of green LED light, EY is converted to its excited state EY*, which is then oxidized to radical SCN˙ through single-electron transfer (SET). Subsequently, the SCN˙ radical attacks substrate **13**, promoting the formation of another radical intermediate **13A**, which is then swiftly oxidized to produce the cationic intermediate **13B**. The deprotonation of the cationic intermediate **13B** results in the formation of the desired product **14**. Furthermore,

(a)

FG = NH₂, NHR, NR₂, OH

Selected examples:

H-N-Bn	H-N-Me	H-N-Et	H-N-Ph	H-N-iPr
SCN	SCN	SCN	SCN	SCN
85%	81%	80%	90%	83%%

NH₂	NH₂	N-Me Me	iPr NH₂ iPr	OH
SCN	SCN	SCN	SCN	SCN
81%	92%	89%	95%	53%

(b)

Proposed reaction pathway

Scheme 6 a) Visible-light-assisted regioselective aerobic oxidative C(sp^2)–H thiocyanation of aromatic compounds **13**. (b) Proposed mechanism for visible-light-assisted regioselective aerobic oxidative C(sp^2)–H thiocyanation of aromatic compounds **13**.

oxygen may be important to the completion of the photoredox cycle by oxidizing the EY˙$^-$ radical anion abaft to its ground state (EY), which then enters the next catalytic cycle, as previously stated (Scheme 6b).

Yu *et al.* devised a metal-free and visible-light-mediated scheme for synthesizing thiocyanated heterocycles in green solvent, such as dimethyl carbonate (DMC), under an air atmosphere.[14] They used ammonium thiocyanate and graphitic carbon nitride (g-C₃N₄), which are inexpensive, readily available, and reusable semiconductor photocatalysts, in designing and synthesizing various types of thiocyanated heterocycles, such as indolo/benzimidazo[2,1-*a*]isoquinolin-6(5*H*)-ones **16**, thioflavones **18**, azaspiro[4,5]trienones **20**, and imidazo[1,2-*a*] pyridines **22** (up to 96%). The reusable g-C₃N₄ catalyst was reused many times before losing significant activity. They demonstrated the positive outcome of the protocol. They were able to use a reusable catalyst and a green solvent with a wide application without any metal or external oxidant (Scheme 7).

Guan and coworkers established an environmentally friendly photocatalytic additive-free decarboxylative reaction of acrylic acids **23** for the synthesis of a wide range of α-thiocyanate ketones **24**.[15] The author used a photocatalyst as an organic dye 9,10-dicyanoanthracene(DCA), instead of other photocatalysts.
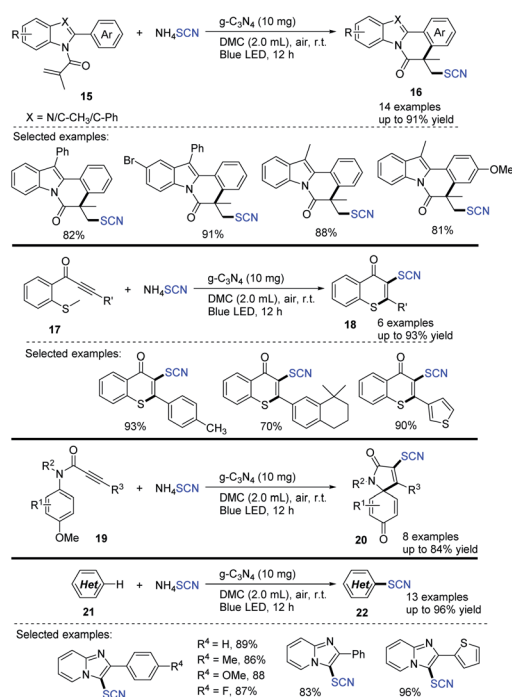
Scheme 7 Photocatalytic technique for the synthesis of thiocyanated heterocycles **16**.

The ammonium thiocyanate was used as both a sulfur source and a reductant, and molecular dioxygen serves as both an oxygen supply and an oxidant which is inexpensive, and environmentally benign. This approach has a lot of possibilities in organic and medicinal chemistry because of the ease with which the product α-thiocyanate ketones **24** can be transformed (Scheme 8).

Kapoor *et al.* demonstrated the photocatalytic denitrative thiocyanation of β-nitrostyrenes **25**.[16] They employed EY as a photocatalyst and ammonium thiocyanate as a thiocyanating agent in acetonitrile as an organic solvent in open air under visible light to create (*E*)-vinyl thiocyanates **26** in excellent to outstanding yields (Scheme 9a). They proposed that visible light stimulates EY, which then uses the SET mechanism to oxidize thiocyanate anion **B** to SCN radical **B'** through a reductive quenching circle. The carbon-centered radical intermediate **25A** is formed when the generated thiocyanate radical **B'** attacks the double bond of **25**. **25A** is subjected to denitration for the production of the desired product **26**. The involvement of
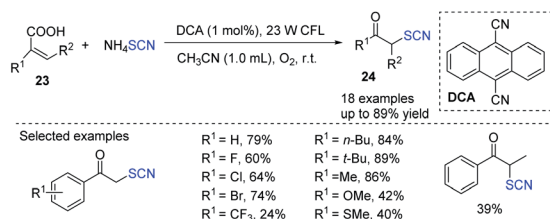
Scheme 8 Visible-light-mediated additive-free decarboxylative reaction of acrylic acid **23**.
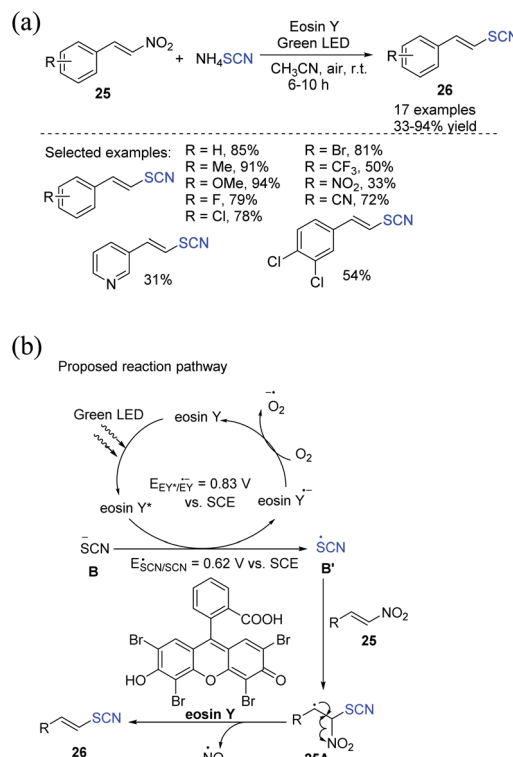
Scheme 9 a) Visible-light-induced denitrative thiocyanation of β-nitrostyrenes **25**. (b) Proposed mechanism for visible-light-induced denitrative thiocyanation of β-nitrostyrenes **25**.

aerobic oxygen in fulfilling the photoredox catalytic process is likely essential. It returns the EY radical anion to its ground state by oxidizing it (Scheme 9b).

Guan *et al.* disclosed a new Acr$^+$-MesClO$_4^-$-catalyzed thiocyanate radical addition or intramolecular cyclization cascade reaction from *N*-alkyl-*N*-methacryloylbenzamides **27** to obtain thiocyanato-containing isoquinolinediones **28** under gentle visible light photocatalytic conditions.[17] They used ammonium thiocyanate as a reagent to synthesize thiocyanate radicals through a SET pathway. They also used molecular oxygen as the sole oblational reagent. They obtained moderate to good yields of several new compounds **28** (Scheme 10a). Acr$^+$-Mes is stimulated to Acr$^+$-Mes* when exposed to visible light, which removes an electron from the thiocyanate anion and generates a thiocyanate radical while producing Acr$^•$-Mes. To complete the photocatalysis cycle, molecular oxygen oxidizes Acr$^•$-Mes back to Acr$^+$-Mes, releasing superoxide anion radical (O$_2^{•-}$), which accepts a proton from NH$_4^+$ and forms a hydroperoxyl radical (HO$_2^•$). When the thiocyanate radical is added to **27**, it forms a C–S bond, which results in alkyl radical intermediate **27A**. Intermediate **27A** undergoes cyclization on the aromatic ring, yielding the cyclic radical intermediate **27B**, which can then be oxidized and deprotonated by HO$_2^•$ to generate the product **28** (Scheme 10b).

Using diazonium salts **30** as an arylating agent and ammonium thiocyanate as a thiocyanate source, Hoque *et al.* established a highly effective photoredox-catalyzed process for the

(a)

(b)
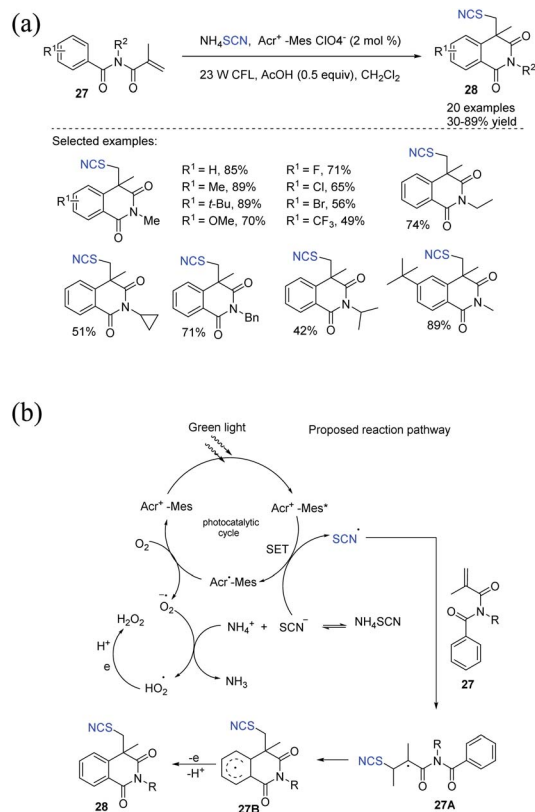
Scheme 10 a) Synthesis of isoquinoline-1,3-dione derivatives **28** through radical addition or cyclization cascade. (b) Proposed mechanism for the synthesis of isoquinoline-1,3-dione derivatives **28** through the radical addition or cyclization cascade.
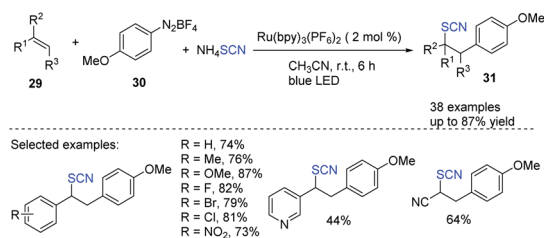
Scheme 11 Photoredox-catalyzed intermolecular radical arylthiocyanation of alkenes **29**.

intermolecular arylthiocyanation of alkenes **29**.[18] The process was found to be environmentally friendly and extremely efficient. Styrenes and acrylates produce diverse aryl-substituted alkylthiocyanates **31** good to excellent yields and in a variety of configurations (Scheme 11).

2.3.2 Photochemical-induced C(sp²)–SCN thiocyanation of aromatic heterocyclic compounds. Liu *et al.* identified an interesting approach for developing high-performance photocatalysts and novel isomorphic pyrene-based 2D-COFs (COF-JLU24) for the C-3 functionalization of indoles **32** with ammonium thiocyanate in tetrahydrofuran (THF) at room temperature (Scheme 12a).[19] One of the possible mechanisms is the conversion of COF-JLU24 to its excited state COF-JLU24* by

(a)

(b)
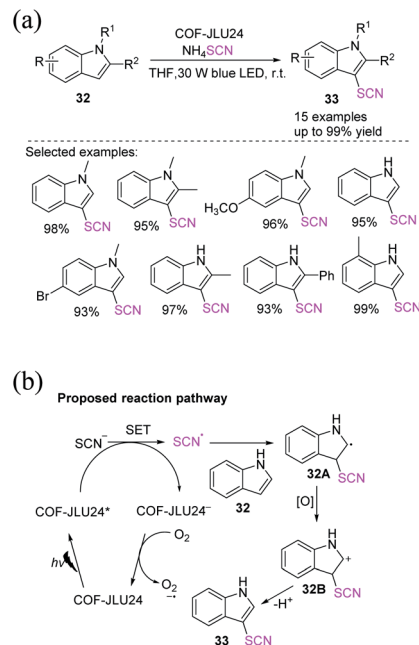
Scheme 12 a) C-3 functionalization reaction of indoles **32** with ammonium thiocyanate. (b) Proposed mechanism for C-3 functionalization reaction of indoles **32** with ammonium thiocyanate.

light irradiation. ˙SCN and COF-JLU24˙⁻ radicals are generated through SET from the thiocyanate anion SCN to COF-JLU24*. The produced COF-JLU24˙⁻ subsequently reacts with molecular oxygen to form the superoxide anion $O_2^{•-}$ and the ground state COF-JLU24. In the meantime, the newly formed radical ˙SCN attacks the substrate indole **32**, generating intermediate **32A**, which is subsequently oxidized to form cation intermediate **32B**, which in turn is deprotonated to form the final 3-thiocyanoindole molecule **33** (Scheme 12b).

Yue *et al.* devised a fast and efficient visible-light-induced difunctionalization process for alkenes **34** at ambient temperature.[20] The process uses ammonium thiocyanate and dioxygen. Owing to the generated carbon-sulfur and carbon–oxygen bonds and by using a nontoxic and cheap Na_2-EY photocatalyst, a range of α-thiocyanato ketones **35** can be rapidly and effectively synthesized in moderate to high yields. This green
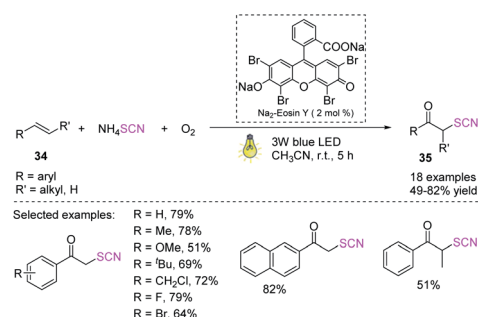
**Scheme 13** Visible-light-enabled method for the formation of α-thiocyanato ketones **35**.

technology offers an attractive alternative to obtaining different α-thiocyanato ketones **35** owing to its high functional flexibility, moderate reaction conditions, ecologically friendly energy source, and inexpensive and nontoxic catalyst (Scheme 13).

Using visible light and the widely available ammonium thiocyanate, Yang *et al.* found a novel photocatalyst-free oxidative C(sp^2)–H thiocyanation process for electron-rich heteroarenes and arenes **36**.[21] According to mechanistic research, singlet oxygen is created when light is irradiated and can be a vital stimulant for the reaction to continue. The most appealing aspect of the reaction is that it allows simple benchtop processes because it only requires simple and widely affordable compounds **37** and does not necessitate the use of a transition metal catalysts, photocatalysts, bases, or strong oxidants. In a nutshell, the approach offers new options for C(sp^2)–H thiocyanation reactions for medicinal and synthetic organic chemistry purposes (Scheme 14).

In recent years, chemists have designed energy-efficient photocatalytic thiocyanation processes that can directly use air as an oxidant in contrast to traditional free radical thiocyanation reactions and are thus more environmentally friendly. Li *et al.* invented a nontoxic and easy C-3 thiocyanation method for indoles **38**. The author utilized RB, an reasonably priced and readily accessible organic dye, as the photocatalyst, and air serves as the terminal oxidant (Scheme 15a).[22] When stimulated by visible light, RB transforms into excited RB*. A SET between –SCN and RB* produces the SCN radical **38A** and an RB$^{•-}$ radical anion. The photoredox cycle is completed when RB$^{•-}$ is oxidized to its ground state. Intermediate **38B** is formed after the electrophilic addition of radical **38A** to **38**. The oxidation of intermediate **38B** results in the formation of cation intermediate **38C**. Through the re-aromatization of intermediate **38C** with a proton loss, the final 3-thiocyanoindole product **39** is formed (Scheme 15b).
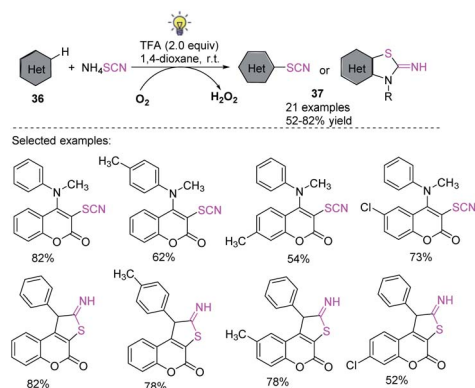
Using a green oxidant, Hajra *et al.* discovered an EY-catalyzed and visible-light-triggered C-3 thiocyanation of imidazoheterocycles **40** at room temperature.[23] The new strategy is potent and cost effective, can use an extensive series of substrates, and can accommodate a large number of functional groups. This technique may offer substantial contributions to

Scheme 14 Photocatalyst-free oxidative C(sp^2)–H thiocyanation of heteroarenes and arenes **36**.
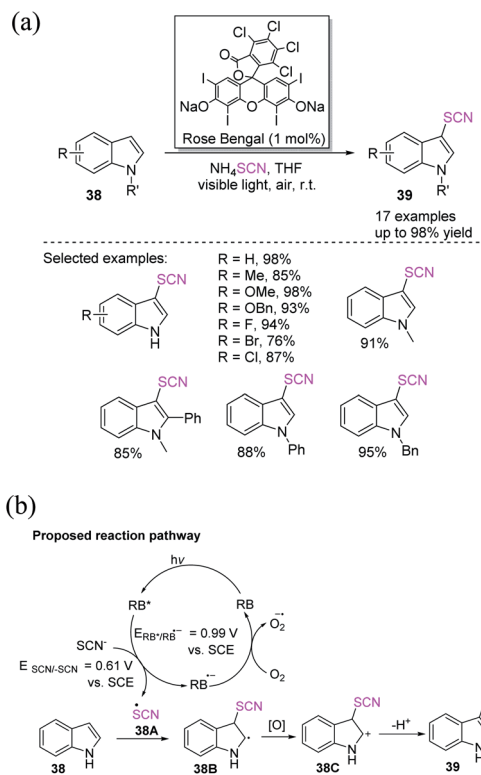
Scheme 15 a Photocatalyzed C-3 thiocyanation of indoles **38**. (b) Proposed reaction pathway for photocatalyzed C-3 thiocyanation of indoles **38**.
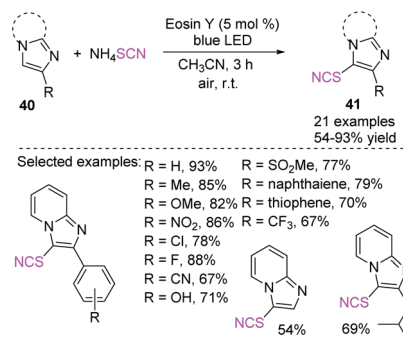
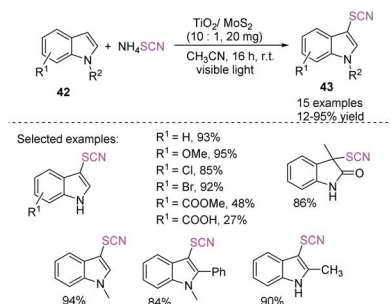Scheme 16 Eosin Y-catalyzed C-3 thiocyanation of imidazoheterocycles **40**.

the fields of chemical synthesis, medicinal chemistry, and material science (Scheme 16).

Ming-yang He *et al.* established a simple and nontoxic visible-light-assisted photocatalytic system for indole **42** thiocyanation.[24] The system uses a TiO$_2$/MoS$_2$ nanocomposite. MoS$_2$ is an effective photosensitizer, and its hybridization structure has a synergistic effect that boosts photocatalytic activity under visible light. This procedure is a practical and environmentally friendly choice to established techniques because of its high isolated yield and substrate compatibility and simple workup route and recyclability of the catalyst (Scheme 17).

Scheme 17 Visible-light-mediated photocatalytic thiocyanation for indole **42**.

Singh *et al.* reported that the eosin Y-catalyzed sequential radical cyclization and aromatization of 2-isocyanobiphenyls **44** with ammonium thiocyanate produces 6-thiocyanatophenan-thridines **45** through a simple, rapid, and metal-free mecha-nism.[25] They used inexpensive, efficient, and sustainable natural resources, such as visible light and oxygen, at room temperature in this one-pot technique, which is more favorable for the process (Scheme 18a). When visible light is absorbed, the excited state of EY is generated. A single-electron transition between SCN⁻ and EY* allows SCN and EY⁻ to exist. The production of a superoxide radical anion ($O_2^{\bullet-}$) by the aerial oxidation of EY⁻ to ground state EY⁻ completes the photo-redox cycle of EY. The imidoyl radical **44A** is formed when the thiocyanate radical generated *in situ* combines with 2-
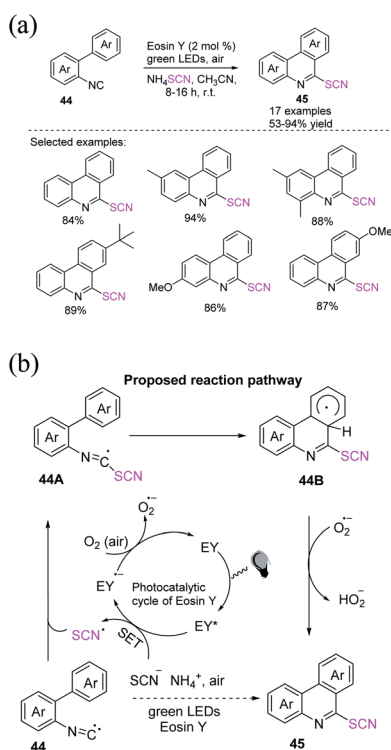
isocyanobiphenyl **44**. The imidoyl radical undergoes intra-molecular radical aromatic substitution and generates inter-mediate **44B**. $O_2^{\bullet-}$ aromatize intermediate **44B** by removing a hydrogen atom, resulting in the necessary 6-thiocyanato phenanthridine **45** (Scheme 18b).
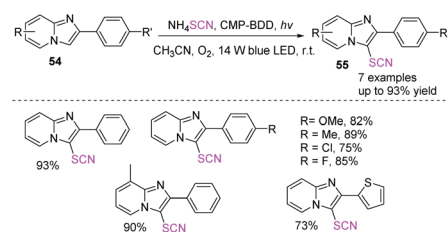
Sarvari *et al.* promoted the thiocyanation of anilines **46**, indoles **47**, pyrroles **48**, and 2-amino thiazoles **49** treated with ammonium thiocyanate at room temperature by utilizing Ag/TNT as a photoredox catalyst.[26] The produced thiocyano compounds had moderate to excellent yields under visible light. The convenience of usage, high to outstanding yields, gentle reaction conditions, and recyclability of the photoredox catalyst are the key benefits of this innovative approach (Scheme 19).

Zhang *et al.* exploited a commercially available molecule termed benzo[1,2-*b*:4,5-*b'*] dithiophene-4,8-dione (BDD) as a starting material to create a task-specific heterogeneous photocatalyst with a two-step process. The resulting BDD-based conjugated microporous polymer demonstrates effective visible light absorption as a result of the molecular engineering tech-nique using an electron-output BDD because of the inclusion of a BDD moiety and an extended π-conjugated structure. The conjugated microporous polymer (CMP)-BDD complex dis-played heterogeneous catalytic performance for common oxidative chemical reactions in the presence of light and oxygen, particularly in the selective thiocyanation of imidazo-heterocycles **54** (Scheme 20).[27]

On the route to thiocyanation and cyclization processes, Koohgard *et al.* discovered an ARS-TiO₂ photocatalyst that promotes the straightforward C–H functionalization of sp² C–H bridges.[28] They demonstrated the first visible-light-mediated phenol thiocyanation and synthesis of 2-aminobenzothiazole
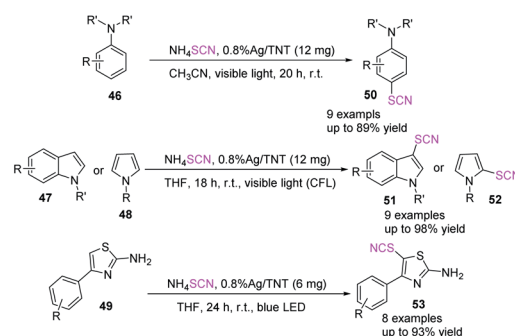
Scheme 19 Visible-light-promoted thiocyanation of aromatic and heteroaromatic compounds (**46–49**).

Scheme 18 a) Radical cyclization of 2-isocyanobiphenyls **44**. (b) Proposed mechanism for the radical cyclization of 2-iso-cyanobiphenyls **44**.


**Scheme 20** Thiocyanation of imidazoheterocycles **54**.

derivatives **64**. They also reported a method for treating various aromatic and heteroaromatic frameworks (2-phenylamino-thiazole **56**, phenol **57**, aniline **58**, pyrrole/indole **60** derivatives) with SCN⁻ at room temperature (Scheme 21).

Espino *et al.* outlined the synthesis of innovative Ir(III) bis-cyclometallated photosensitizers with β-carboline ligands and a facile and unique photocatalytic one-pot two-step process for the chemoselective and C-3 regioselective oxidative thiocyanation of indolines **66** and production of 3-thiocyanatoindoles **67** in good to high yields.[29] They used ammonium thiocyanate, molecular oxygen as a green oxidant, and Ir(III) photocatalysts in THF at room temperature in the presence of blue light as the energy source (Scheme 22).
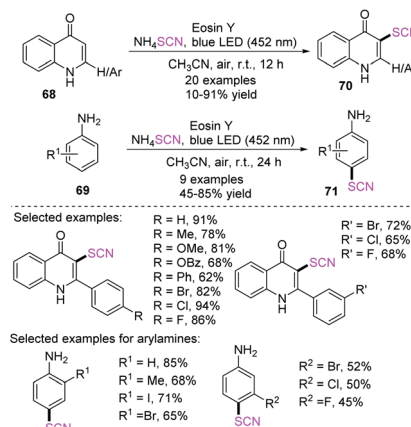
Jain *et al.* established an effective, easy, and metal-free regioselective C-3 thiocyanation process for 2-arylquinolin-4-ones **68** and a *para*-thiocyanation process for arylamines **69**. The processes resulted in good to outstanding yields.[30] They used eosin Y (EY) and air as the terminal oxidant in this photoredox process. The 3-thiocyanated quinolone derivatives **70** have many biological activities and can offer benefits to the field of pharmaceutical chemistry (Scheme 23).
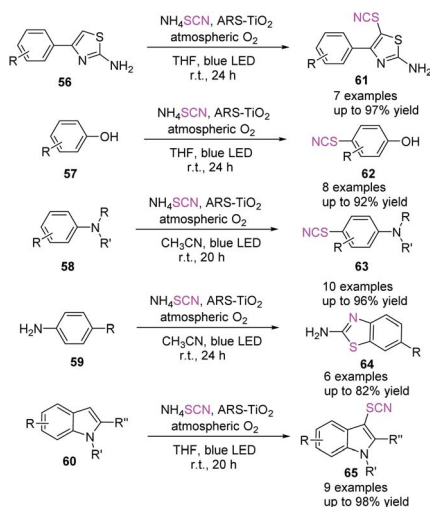
Scheme 21 Direct C–H functionalization of sp² C–H bonds on the way to thiocyanation and cyclization reactions.
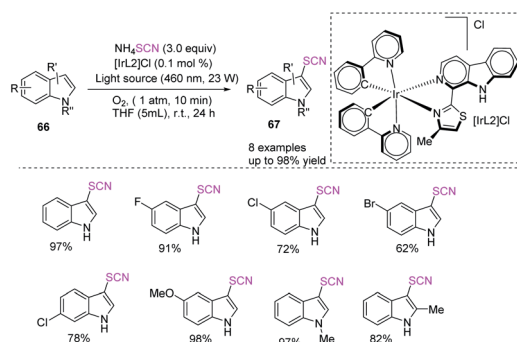
Scheme 22 Oxidative thiocyanation of indulines **66**.
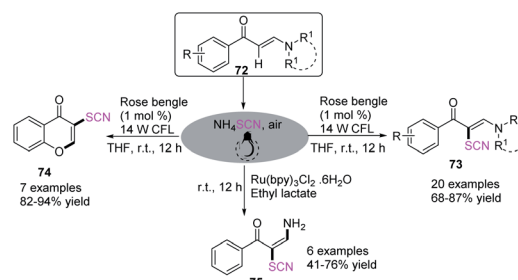

Scheme 23 Visible-light-promoted thiocyanation of heteroaromatics **68**.

Wan *et al.* described the metal-free photocatalyst-induced C–H bond thiocyanation of tertiary enaminones **72**. The process produced thiocyanated alkene derivatives **73** and chromones **74** with ammonium thiocyanate as the thiocyano source in an air atmosphere.[31] They used ammonium thiocyanate and Ru (bpy)3Cl₂·6H₂O as a photocatalyst to transform the reaction path and produce NH₂-functionalized thiocyanated enamines **75** through a difunctionalization route involving C–H bond thiocyanation and vinyl C–N bond *trans*-amination (Scheme 24).

Kar *et al.* succeeded in developing a novel synthetic process for the simple synthesis of a novel class of corrole ligands **77** with four thiocyanate groups at the four surrounding β-positions in the corrole framework.[32] They used an SCN radical created *in situ* to activate corrole macrocycles **76** at ambient temperature and fabricate tetrathio-cyanatocorroles **77** in high to excellent yields. The absorption properties of the modified corrole derivatives are strikingly similar to those of chlorophyll-a macrocycle. These compounds can be used as chlorophyll-a pigment spectroscopic model systems (Scheme 25).

Mai *et al.* proposed a template-free procedure for the synthesis of porphyrin-based CMP tubes (CMP-1), which are generated by the scrolling and shutting of ribbon-like structures. The author used CMP-1 as a metal-free photocatalyst that demonstrates outstanding photocatalytic efficiency for the
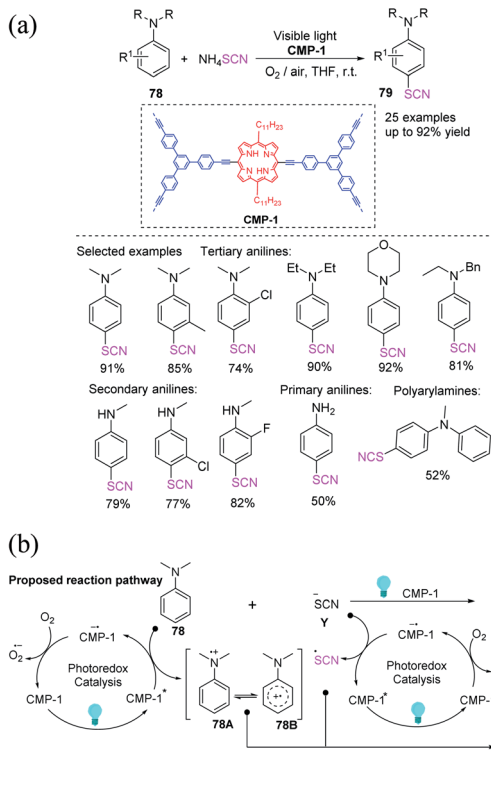

Scheme 24 Visible-light-induced thiocyanation of α-site of tertiary enaminones **72**.
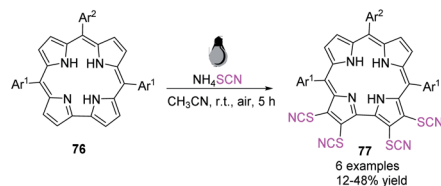
Scheme 25 Method for triggering corrole macrocycles **76**.

visible-light-driven chemoselective thiocyanation of anilines **78**, obtaining excellent to high yields **79** with respect to the transformation of various types of anilines under ambient conditions.[33] The photocatalyst can be used multiple times. CMP-1 plays two functions in photocatalytic thiocyanation according to the reaction mechanism. CMP tubes can be used as reusable carriers for single-atom catalysts in a variety of catalytic processes (Scheme 26a). Visible light is used to convert CMP-1 to CMP-1*. CMP-1* triggers two separate SET reactions: one that oxidizes an aromatic amine (**78**) to a radical cation, including intermediate **78A** and its resonance structure (**78B**), and another that transform the –SCN anion (Y) to a ˙SCN free radical. The excited CMP-1* is then transformed into the radical anion CMP-1˙⁻. CMP-1˙⁻ is a molecular oxygen oxidized to the initial state of CMP-1, completing the photoredox cycle. Additionally, the ˙⁻SCN free radical forms a cationic intermediate **78C** when it connect to the radical cation **78B**. The *para*-

thiocyanated product **79** is generated through the rearomatization of the intermediate **78C** by losing a proton (Scheme 26b).

2.4 Photochemical-induced C(sp)–SCN bond formation through thiocyanation reaction

Kshirsagar *et al.* designed a photoredox-catalyzed simple green synthetic technique that uses visible light as a green source in the production of 3-thiocyanatobenzothiophenes **81** with an extensive substrate capacity in good to high yields.[34] In the photoredox-catalyzed anion oxidation of the ammonium salt of a thiocyanate, they used EY and moleculer oxygen as a terminal oxidant, which incorporates the radical annulation of 2-alkynylthioanisoles **80** at room temperature (Scheme 27).

Gullapalli *et al.* reported a regio- and stereo-selective photocatalytic visible-light-mediated process for obtaining aryl α-thiocyanoketones **84** and α-thiocyanoalcohols **85** with excellent to high yields as of initiated aryl ultimate alkynes **82** and aryl conjugated dienes **83**.[35] They used ammonium thiocyanate as a thiocyanate source and sub-stoichiometric photocatalyst in ambient air. This technique is also suitable for the rapid one-pot synthesis of 2-hydroxy 4-substituted arylthiazoles, which is a potentially medicinal compound (Scheme 28).
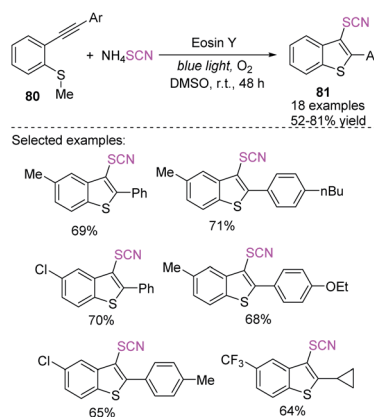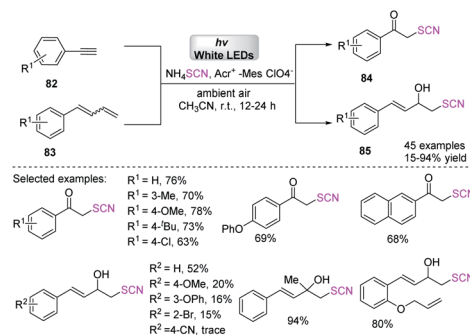
Scheme 26 a) Visible–light mediated thiocyanation of anilines **78**. (b) Proposed mechanism for the visible-light-mediated thiocyanation of anilines **78**.
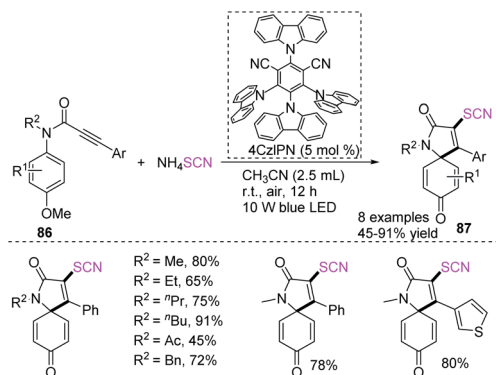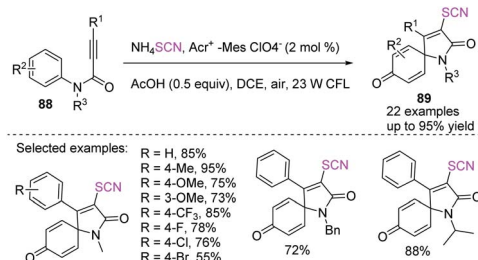
Scheme 27 Photoredox-catalyzed method for the synthesis of 3-thiocyanatobenothiophene **81**.

Scheme 28 Visible light promoted synthesis of aryl α-thiocyano ketones **84**/thiocyano alcohols **85**.

Scheme 29 Synthesis of 3-thiocyanato azaspiro [4,5] trienones **87**.

Scheme 30 Synthesis of thiocyanato-containing azaspirotrienediones **89**.

Yu and coworkers successfully created visible light mediated photocatalytic techniques for the synthesis of 3-thiocyanato azaspiro[4,5]trienones **87** with a wide reaction scope and high functional group acceptance using a radical-initiated cascade annulation reaction of *N*-arylpropiolamides **86** with ammonium thiocyanate and 2,4,5,6-tetra(9*H*-carbazol-9-yl)isophthalonitrile (4CzIPN) as an photocatalyst (Scheme 29).[36]

He *et al.* employed a visible-light-mediated metal-free thiocyanate radical addition/*ipso*-cyclization/oxidation cascade process to synthesize thiocyanato-containing azaspirotrienediones **89** in excellent to high yields.[37] They used *N*-phenylpropanamide **88** with ammonium thiocyanate as a precursor to the thiocyanate free radical, DCE (1,2-dichloroethane) as a solvent, and recyclable air oxygen as the only protective reagent and oxygen source (Scheme 30).

3. Electrochemical-induced C–SCN bond formation through thiocyanation reaction

Oxidative cross-coupling has emerged as one of the most basic strategies for forming novel chemical bonds in the last decade.[38] Without pre-functionalization, conveniently accessible starting materials are selected as substrates, significantly reducing the figure of synthetic processes. Nevertheless, an additional oblational oxidant is frequently needed to assist the oxidative cross-coupling procedure, resulting in significant material consumption and reduction in the atom economy of a complete

transformation. Furthermore, chemical oxidants may have undesirable side effects, such as over-oxidation. As a result, achieving oxidative cross-coupling in the absence of chemical oxidants is extremely desirable.

Therefore, oxidative coupling approaches that do not require the use of chemical oxidants are urgently needed. Organic synthetic chemists have been paying particular attention to electrochemical organic synthesis methods that are effective, green, and environmentally benign.[6,38] The exploit of electrons as mass-free reagents eliminates the need for a stoichiometric amount of chemical oxidant, resulting in no waste formation. Numerous electrochemical oxidation cross-coupling reactions have been exploited for the C–H bond activation through thiocyanation for the construction of C–S bonds in recent years.[38n]

3.1 Electrochemical-induced C(sp^3)–SCN bond formation through thiocyanation reaction

Liang *et al.* used NaI (sodium iodide) as a redox catalyst, sodium thiocyanate as a thiocyano source, and heterogeneous solid salt Amberlyst-15 (H) as a proton catalyst in a simple undivided cell to achieve the effective electrochemically oxidative α-C–H thiocyanation of ketones under constant current without the use of external conductive salts.[39] They demonstrated that solid salt can be reused up to five times without showing decrease in effectiveness in this electrochemical oxidation thiocyanation process, which does not require the addition of an additional conductive salt (Scheme 31a). The process occurs with the anodic oxidation of the iodide ion to produce molecular iodine, which then reacts with the enol isomer of ketone **90** to produce
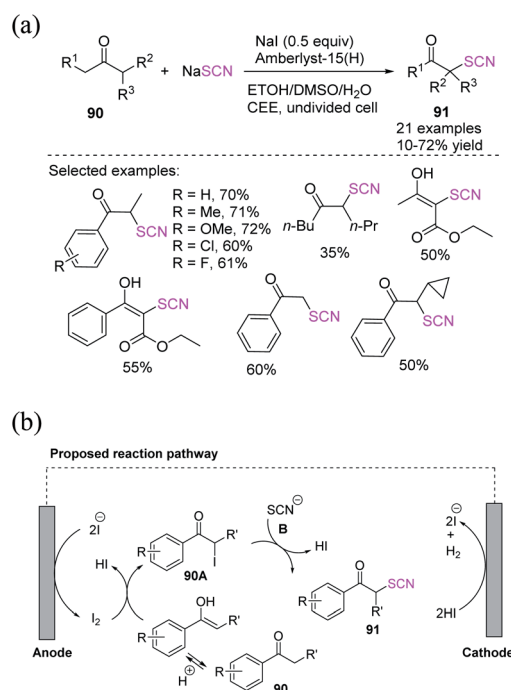
Scheme 31 a) Electrochemical oxidative α-thiocyanation of various ketones **90**. (b) Proposed mechanism for electrochemical oxidative α-thiocyanation of various ketones **90**.

α-iodo ketone **90A**, as well as one molecule of HI. After the essential intermediate **90A** is generated, it undergoes a nucleophilic substitution reaction with NaSCN or heterocyclic thiols. This process results in the final α-thiocyanation product **91**, which is followed by the formation of a second molecule of HI. Consequently, the HI produced *in situ* is reduced to H_2 on the cathode surface. The iodide ion is replenished during the reaction from stages of the α-iodination of ketone **90**, resulting in **90A**. After the nucleophilic substitution of **90A** to **91**, the iodide ion rejoins the redox catalyst process, requiring just a sub-stoichiometric or catalytic quantity of iodide ion (Scheme 31b).

Kang *et al.* developed an electrochemically induced technique for the synthesis of 3-amino-2-thiocyanato-α,β-unsaturated carbonyl derivatives **93**, using a single reagent or a mixture of ammonium acetate and potassium isocyanate without the use of any other conducting salt and a sub-stoichiometric amount of ammonium bromide.[40] Additionally, the procedure can be performed with catalytic concentrations of bromide salt. When ammonium thiocyanate was used as a redox catalyst and 1,3-dicarbonyl compounds **92** were combined in the presence of Et_4NBr (tetraethylammonium bromide), relevant adducts in moderate to good yields were obtained (Scheme 32).

3.2 Electrochemical-induced C(sp²)–SCN bond formation through thiocyanation reaction

### 3.2.1 Electrochemical-induced thiocyanation of olefins.
Electrocatalytic thiocyanation of olefins has been studied. In 1973, De Klein generated thiocyanate through the electro-oxidation of thiocyanate and generated dithiocyanation products **95** through the addition reaction of olefins **94**.[41] The authors stated that electrochemical thiocyanogen generation has several advantages over synthetic thiocyanogen sources in the thiocyanation of double bonds: initially, no process for the halogenation of the double bond is viable (this is particularly beneficial when a double bond responds slowly to thiocyanogen but reacts quickly with Cl or Br). Second, the oxidation potential

may be easily manipulated either through controlled potential electrolysis or by performing at a set current density and keeping the reactant concentration over a certain point, reducing the number of side products produced. A series of novel dithiocyanate products **95** were obtained in 16–80% yield through constant current electrolysis at 5–10 °C in an acetic acid environment, which laid the theoretical foundation for the study of electrocatalytic thiocyanation reactions (Scheme 33).

Becker *et al.* employed "the anodic one-pot approach" in a two-phase acidic environment of water and dichloromethane for the thiocyanation and isothiocyanation of polysubstituted olefins **96** in 2015.[42] They evaluated the effects of various acids, anodes, current densities, charge consumption, and electrolysis procedures on the reactions, using tetramethyl ethylene as the template substrate. The two main products (major **97** and minor **98**) were produced in moderate yields in two-phase media. Other alkyl-substituted olefins had similar addition products, but the two SCN addition products were the most important. The products of styrene and ninhydrin substrate reactions in a homogenous water-acetonitrile media were mostly SCN/OH adducts (Scheme 34).

Becker *et al.* devised a two-step anodic oxidation approach for the thiocyanation of olefins **102** in 2016.[43] First, ammonium thiocyanate was utilized as a source of thiocyanic acid in a separation cell with formic acid as a solvent and lithium perchlorate ($LiClO_4$), and thiocyanogen $(SCN)_2$ was formed through anodic oxidation in a constant voltage mode at 1.25 V. They used a platinum sheet as the anode, a steel sheet as the counter electrode, and Ag/AgCl as the reference electrode. Olefin derivatives were introduced and oxidized by free radicals. The desired product **103** was produced by a radical reaction pathway by using olefin derivatives (Scheme 35).

Under electrochemical oxidation, Wen *et al.* established an extremely effective and H_2O-controlled thiocyanation as well as alkenylation of ketene dithioacetals **104** with potassium

Scheme 33 Electrocatalytic dithiocyanation of olefins **94**.
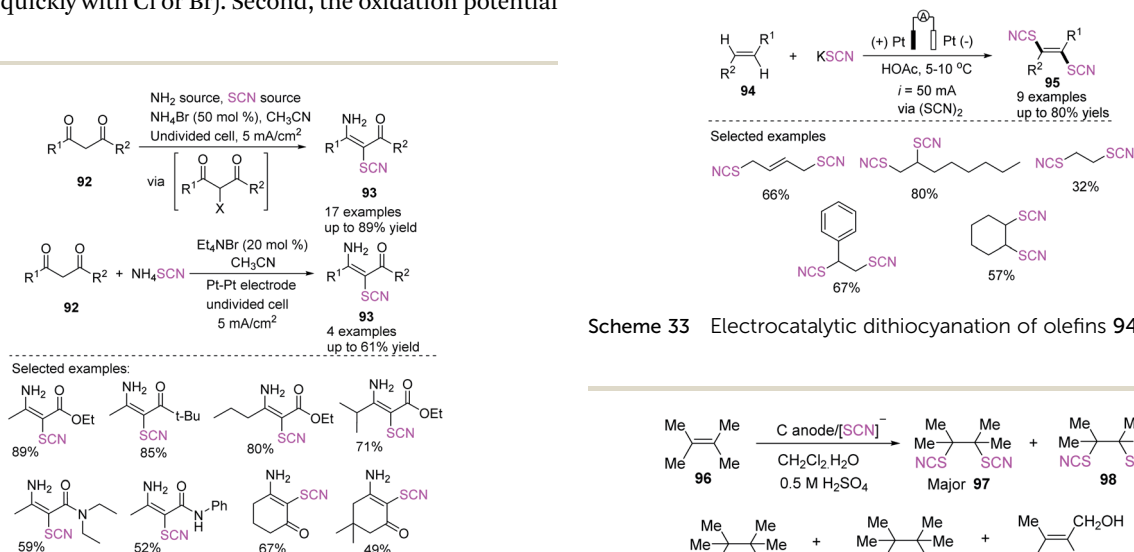
Scheme 32 Construction of precious 3-amino-2-thiocyanato-α,β-unsaturated carbonyl derivatives **93** by electro-synthesis.

Scheme 34 Thiocyanation of polysubstituted olefins **96**.
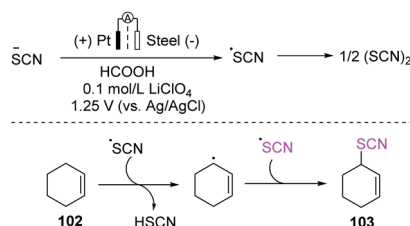
Scheme 35 Electrocatalytic thiocyanation of olefins 102.

thiocyanate in good to high yields and exceptional lenience to functional groups.[44] In contrast to previously disclosed strategies for fabricating internal alkenes, this electrochemical-oxidation-driven synthetic technique circumvents the use of transition metals and extrinsic oxidizing agents. This H_2O-controlled anodic oxidation synthesis approach is green and can scalable, which are useful feature for a variety of pharmaceutical purposes (Scheme 36a). In the presence of water, potassium thiocyanate might be oxidized to $(SCN)_2$ and is subsequently transformed into thiocyanate radical **A** through electrochemical anodic oxidation. The radical intermediate **104B** is then obtained through the radical insertion of thiocyanate radical **A** to ketene dithioacetal 104, from which a proton can be extracted by another thiocyanate radical **A**. The product 105 is finally produced (pathway 1). In the absence of water,
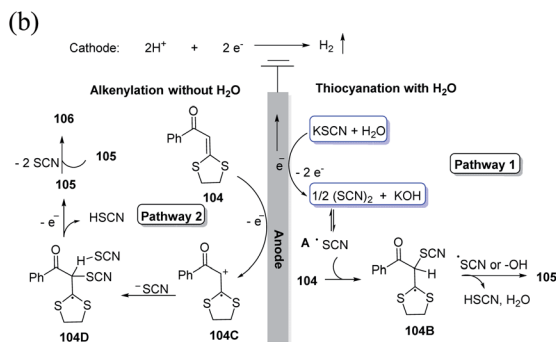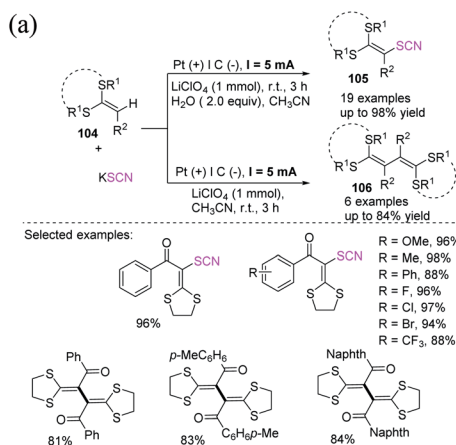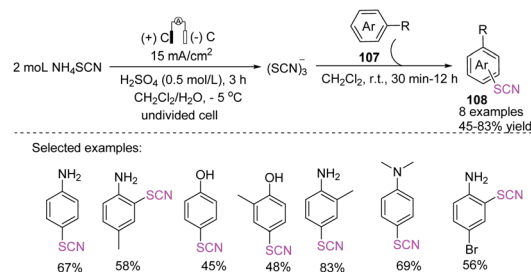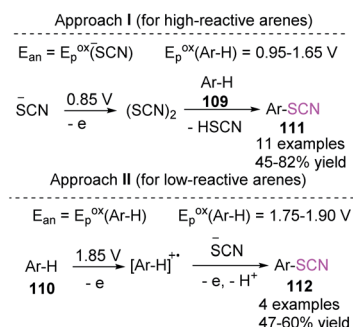
ketene dithioacetal 104 is oxidized on the anode's surface and generates a radical cation intermediate **104C**, which is then proceeded with the basic electrophile potassium thiocyanate to create intermediate **104D**, which loses an electron and a proton to create intermediate 105. After the removal of the pseudo-halogen group SCN, the home-coupling product 106 is produced (pathway 2; Scheme 36b).

3.2.2 Electrochemical-induced C(sp^2)–SCN bond formation through the thiocyanation of aromatic compounds. Thiocyanate derivatives are useful organic synthesis intermediates, especially in the creation of heterocyclic molecules. Gurjar et al. succeeded in selectively thiocyanating aniline and phenol derivatives 108 using a two-phase electrolysis of ammonium thiocyanate to generate $(SCN)_3^-$ thiocyanate in 1992 (Scheme 37).[45] Furthermore, they explored the effects of experimental parameters, such as electrolysis temperature, electrolysis time, non-aqueous solvent nature, and non-aqueous phase volume fraction on current efficiency. Cyclic voltammetry studies revealed that $(SCN)_3^-$ was generated in the aqueous phase and then carried into the non-aqueous phase to participate in the current.[46]

Kokarekin et al. evaluated the development of metal-free techniques for electro-oxidative C–H thiocyanation of a wide spectrum of high- and low-reactive (hetero) arenes (109, 110) in an undivided cell with GC electrodes. The desired aryl thiocyanates (111, 112) were obtained in moderate yields.[47] The proposed technique for forming carbon-sulfur bonds has the advantages of having simple reaction conditions and being easily accessible and environmentally sustainable materials.

(a)

(b)

Scheme 36 a) Thiocyanation and alkenylation of ketene dithioacetals 104. (b) Proposed mechanism for thiocyanation and alkenylation of alkenes 104.


Scheme 37 Thiocyanation of aniline and phenol derivatives 107.

Scheme 38 Electrochemical-induced synthesis of aryl thiocyanates 111, 112.

Additionally, the technique does not require chemical oxidants and metal-containing catalysts (Scheme 38).

Becker *et al.* explored an environmentally sustainable thiocyanation of aromatic compounds **113** containing different derivatives of anisole and aniline to obtain aromatic thiocyanates **114** in the presence of organic acids.[48] The initial electrochemical process is the anodic oxidation of the thiocyanate anion to its radical (SCN), followed by dimerization to thiocyanogen (SCN)$_2$. The acidic solvent polarizes the latter, leading to the thiocyanate derivative and attacking the aromatic nucleus of the substrate. Mono- and disubstituted aromatics have excellent regioselectivity and high isomer-selectivity in their single thiocyanate derivatives (Scheme 39).

Gitkis *et al.* examined the straightforward one-pot electrochemical-induced thiocyanation of methoxy benzene (anisole) **115**, which is highly regioselective in glacial acetic acid for the construction of 1-methoxy-4-thiocyanatobenzene **116**.[49] The yield of the product increases to over 80% at room temperature under the specified optimum conditions, and no detectable *para*-thiocyanogen owing to thiocyanogen polymerization is observed. Furthermore, controlled potential electrolysis is more effective than constant-current electrolysis in the synthesis of 1-methoxy-4-thiocyanatobenzene **116** (Scheme 40).
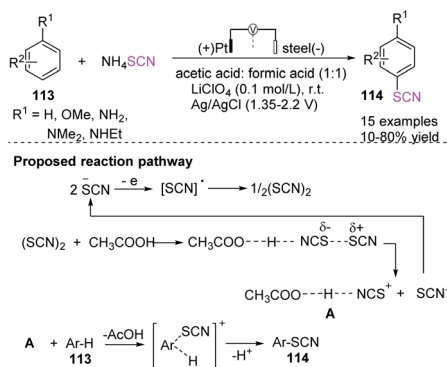
**Scheme 39** Electrochemical thiocyanation of aromatic compounds **113**.
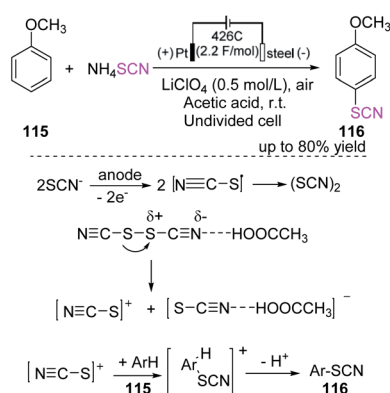
Scheme 40 One-pot electrochemical thiocyanation of methoxybenzene **115**.
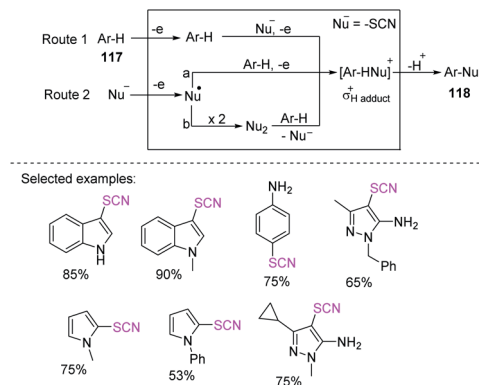
Scheme 41 Thiocyanation of heteroarenes **117** by anodic oxidation of ammonium thiocyanate.

3.2.3 Electrochemical-induced C(sp^2)–SCN bond formation thiocyanation of heteroaromatic heterocycles. In 2014, Petrosyan *et al.* successfully achieved the thiocyanation of *N*-heterocyclic derivatives **117**, such as indole, *N*-methylpyrrole, pyrazole, and aniline through the anodic oxidation of thiocyanate to produce thiocyanate heterocycles **118** and nucleophilic substitution in aromatic compounds with yields of up to 95%.[51] They utilized ammonium thiocyanate and acetonitrile as a solvent at 25 °C with a Pt anode in an undivided cell (Scheme 41).[50a] Notably, this method has a high yield (75%) for the construction of *para*-thiocyanoaniline compounds through a process that is more selective than that described by Krishnan *et al.*[45]

In 2018, Linhao Sun *et al.* achieved a low-cost and efficient technique for the thiocyanation and selenocyanation of electron-rich aromatics **119**.[50b] This method does not require the use of any catalyst or oxidant in the thiocyanation and selenocyanation reactions of diverse hetero-aromatic compounds, such as the derivatives of indole, aniline, pyrrole, and anisole, to construct thio-and selenocyanated aromatic heterocyclic compounds **120** with various substituents in 52–99% yields. Unfortunately, this method cannot generate the 1,3,5-trimethoxy-2-selenocyanatobenzene product and the selenocyanated *N*-methylpyrrole product. It produces 1-methyl-2,5-dithiocyanato-1H-pyrrole product but in low yields (Scheme 42). In 2019, Yaubasarova *et al.* proposed a two-step controlled
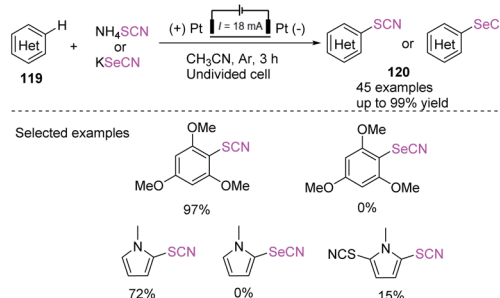
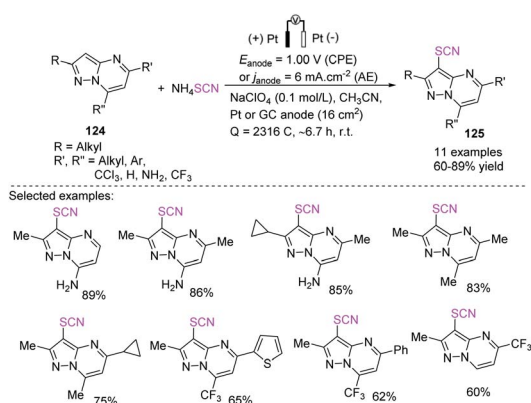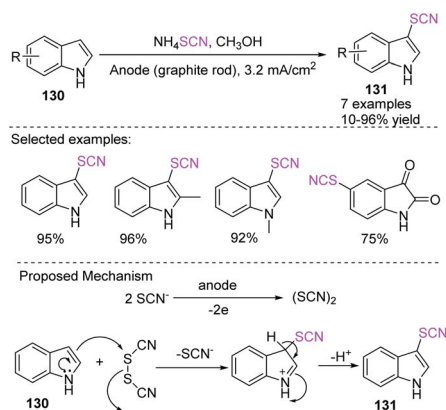**Scheme 42** Thiocyanation and seleno-cyanation techniques for electron-rich arenes **119**.
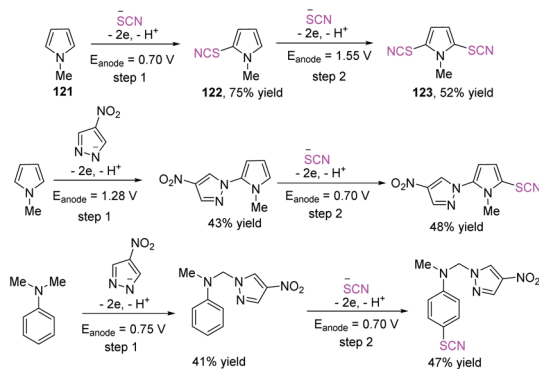
Scheme 43 Anodic C–H functionalization of N-methyl-1Hpyrrole **121** and N,N-dimethylaniline.

voltage electrolysis strategy based on this method and successfully achieved the double C–H bond activation thiocyanation of N-methylpyrrole **121** in 52% yield **123**.[51] They demonstrated that the procedure broadens the scope for the production of promising therapeutic drugs through direct C–S and C–N coupling, in which anode acts as a green oxidizing agent and contributes to the construction of polyfunctional hybrid molecules (Scheme 43).

Kokorekin et al. established successful electrooxidative C–H thiocyanation of pyrazolo[1,5-a]pyrimidines **124** that have high and low levels of reactivity and utilize ammonium thiocyanate or potassium thiocyanate as a thiocyanating agent at room temperature.[52] Owing to the moderate reaction conditions and excellent carbon-sulfur (C–S) bond-building efficiency, this method, which is based on the electrooxidative C–H thiocyanation of pyrazolo[1,5-a]pyrimidines **124**, is expected to offer benefits to future applications. The development of the thiocyanation procedure, conversion of aryl thiocyanates to new thiols, and the considerable improvement in the antifungal activity of arenes when the thiocyano group is introduced are extremely important (Scheme 44).

In 2020, Kokarekin et al. presented a novel facile metal-free electrochemical-mediated (anodic) C–H thiocyanation of 5-

aminopyrazoles **126** for the construction of 3-thiocyanatopyrazolo[1,5-a]pyrimidines **128** in good to high yields.[53] The author used ammonium thiocyanate as a thiocyanate ion source, obtaining 4-thiocyanato-5-aminopyrazoles **127** and then conducted chemical condensation with 1,3-dicarbonyl compounds or their derivatives. This innovative strategy for the two-stage synthesis of 3-thiocyanatopyrazolo[1,5-a]pyrimidines **128** is appealing because it combines electrochemical and chemical methodologies, has simple reaction conditions, uses widely accessible materials and solvents, is flexible, and conveniently isolates desired products (Scheme 45).

Petrosyan et al. established a method for the effective electrochemical-induced thiocyanation of pyrazolo[1,5-α]pyrimidines **129** in good to high yields.[54] They used ammonium thiocyanate as a source of thiocyanogen, which is electrochemically generated on a Pt anode in the presence of acetonitrile as a solvent. The oxidation potentiality of a substrate determines system performance, which can be controlled using Lewis acid additives (Scheme 46).

Nikoofar et al. discovered an easy and simple one-pot process for the electrochemical-mediated anodic thiocyanation of nitrogen-containing (hetero) aromatic compounds **130** in good to excellent yields **131** in methanol at ambient temperature.[55] They studied the thiocyanation of many aromatic compounds in the presence of ammonium thiocyanate in situ in an undivided cell, which is electrochemically generated thiocyanogen $(SCN)_2$ at a graphite electrode

Scheme 45 Synthesis of 3-thiocyanatopyrazolo [1,5-a]pyrimidines **128**.

Scheme 44 Electrooxidative C–H thiocyanation of pyrazolo[1,5-a]pyrimidines **124**.

Scheme 46 Thiocyanation of pyrazolo[1,5-a]pyrimidines **129**.

Scheme 47 Electrochemical-induced thiocyanation of indoles **130**.

(anode) without the use of any other supporting electrolyte, toxic material, or harmful reagent. According to the possible mechanism for this process, SCN is oxidized to a radical through a one-electron oxidation process, which then dimerizes at the electrode surface for the production of thiocyanogen. The product is formed when the electrogenerated precursor thiocyanogen (SCN)$_2$ interacts with substrates **130** (Scheme 47).

Cui *et al.* proposed an electrochemical approach for the oxidative C–H thiocyanation of imidazopyridines and electron-

rich arenes **132**, utilizing ammonium thiocyanate as a source of (thiocyanate) SCN for the formation of thiocyanated products **133** in moderate to excellent yields with a wide variety of substrates and functional groups.[56] This convenient approach has great advantages in terms of thiocyanated imidazopyridine production in the field of medicinal chemistry (Scheme 48a). In the postulated reaction pathway, the thiocyanate radical intermediate **B** is generated through the anodic oxidation of the thiocyanate anion. Imidazopyridine **132** traps radical **B**, yielding the radical intermediate **132C**, which is oxidized at the anode through SET to produce the cation intermediate **132D**. Finally, the deprotonation of cation **132D** produces **133** (Scheme 48b).

Chen *et al.* successfully formulated a simple and efficient electrochemical-induced oxidative thiocyanation process for imidazopyridines and imidazo[2,1-*b*] thiazoles **134** in a wide range of substrates.[57] The process has great functional group tolerance and moderate to outstanding yields **135** because of anodic oxidation and cathode hydrogen evolution processes that do not require the use of a catalyst or an oxidant (Scheme 49a). In the proposed reaction pathways, the anodic oxidation of 7-methyl-2-phenylimidazo [1,2-*a*] pyridine **134** produces the radical cation **134B**. Meanwhile, thiocyanate anion can be oxidized to thiocyanate radical **C** on the anode surface, which interacts with **134B**. The intermediate is promptly deprotonated to generate **135** (path 1). Furthermore, the radical cation intermediate **134B** has a low SOMO and a larger HOMO than the thiocyanate anion. The production of a radical
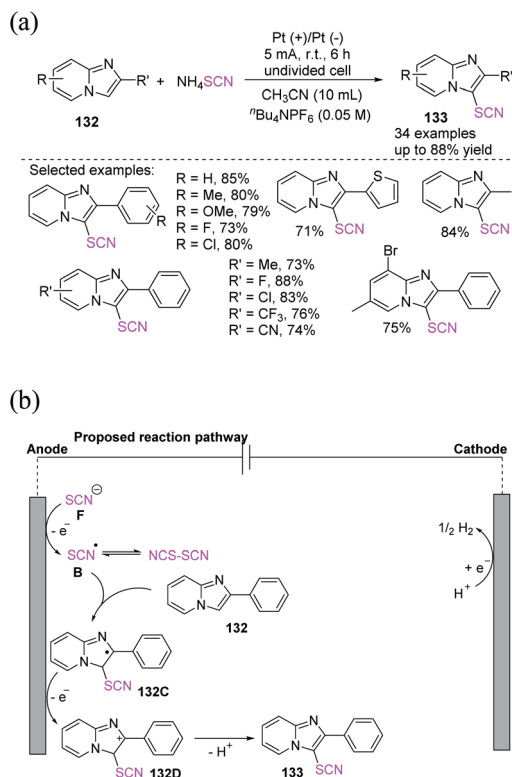
Scheme 48 a) Oxidative C–H thiocyanation of imidazopyridines **132**. (b) Proposed mechanism of oxidative C–H thiocyanation of imidazopyridines **132**.
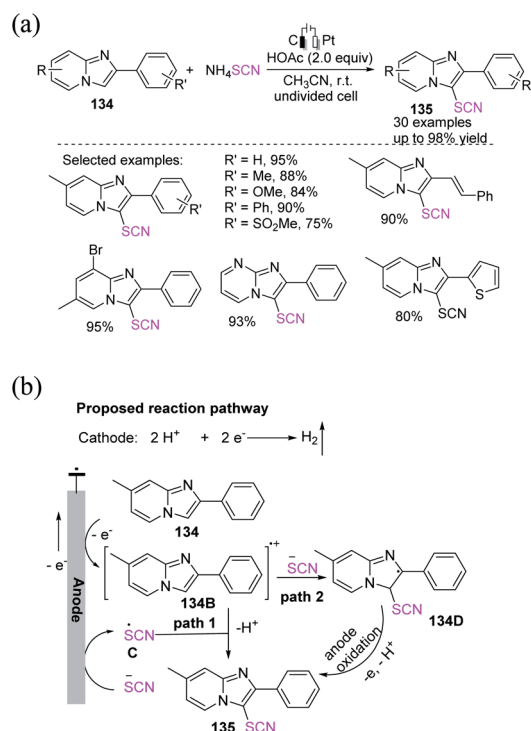

Scheme 49 a) Electrochemical oxidative thiocyanation of imidazopyridines **134**. (b) Proposed mechanism of electrochemical oxidative thiocyanation of imidazopyridines **134**.

intermediate **134D**, which will then swiftly gives an electron to the anode and is deprotonated to yield the product **135**, is expected to come from a substantial SOMO–HOMO interaction between the two species (path 2). Hydrogen gas is released as a result of the concurrent cathodic reduction of H$^+$ (Scheme 49b).
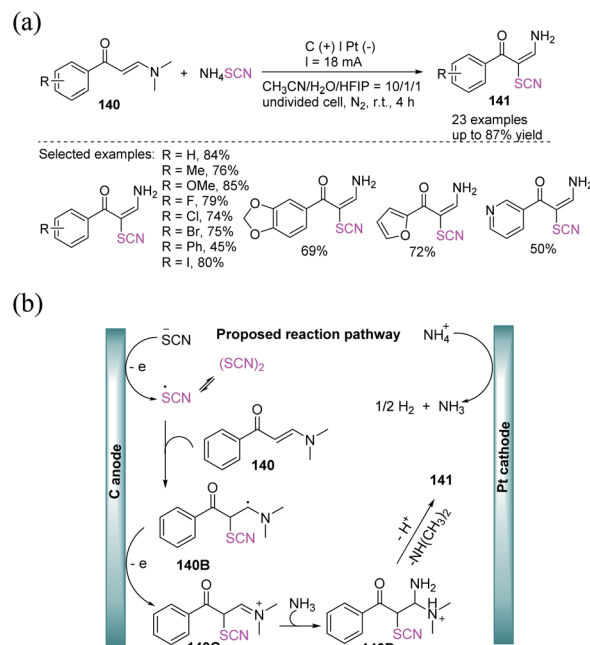
3.3 Electrochemical-induced C–SCN bond formation through the thiocyanation of enaminones

Under undivided electrolytic conditions, Zhou *et al.* produced a successful electrochemical-mediated thiocyanation of enaminones **136** or **137** by employing potassium thiocyanate as a thiocyanate source with a broad substrate scope and good to outstanding yields.[58] This protocol produces a catalyst-free and external oxidant-free procedure for the preparation of polyfunctionalized alkenes **138** and chromones **139**, in contrast to traditional methodologies for the thiocyanation of internal alkenes (Scheme 50).

Lei *et al.* accomplished a highly stereoselective electrochemical technique for the production of thiocyanated enaminones **141** in good to high yields. Interestingly, ammonium thiocyanate has been employed as an ammino and a thiocyanate source that comprises C–H bond thiocyanation and vinyl C–N bond *trans*-amination without the use of an extra oxidizing agent and a catalyst made of transition metal (Scheme 51a).[59] They depicted a probable pathway for this electrochemical thiocyanation. SCN$^-$ is first anodically oxidized to the thiocyanate radical, which is rapidly dimerized to form a disulfide. The thiocyanate radical is then added to substrate **140** to produce intermediate **140B**, which then undertakes single electron anodic oxidation to produce cation intermediate **140C**, which is easily attacked by nucleophilic NH$_3$ to generate **140D**. Consequently, *N*, *N*-dimethylamine and proton are removed from intermediate **140D** to produce the desired product **141**. During the reaction, ammonium ion can be reduced at the cathode, releasing ammonia gas and hydrogen gas (Scheme 51b).
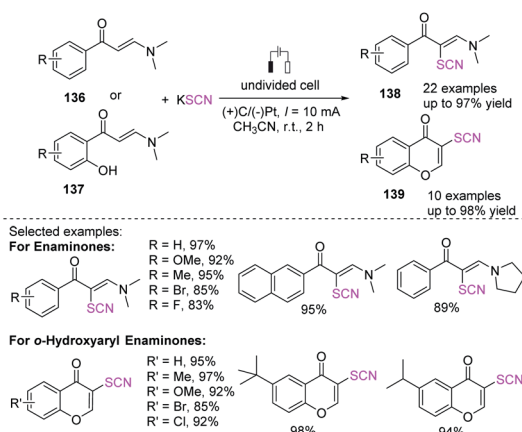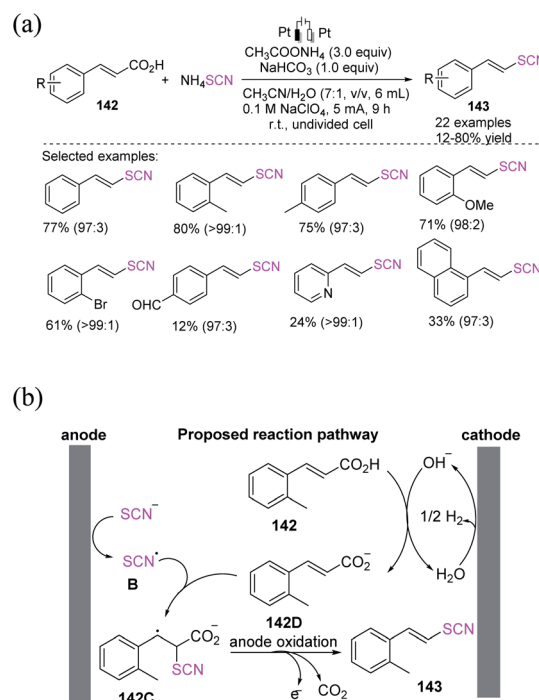

Scheme 50 Electrochemical-induced thiocyanation of enaminones **136** or **137**.

Scheme 51 a) Stereoselective electrochemical-induced synthesis of thiocyanated enaminones **141**. (b) Proposed mechanism of stereoselective electrochemical-induced synthesis of thiocyanated enaminones **141**.

3.3.1 Electrochemical-induced C–SCN bond formation through the thiocyanation of cinnamic and boronic acid compounds. Yang *et al.* proposed a simple and convenient
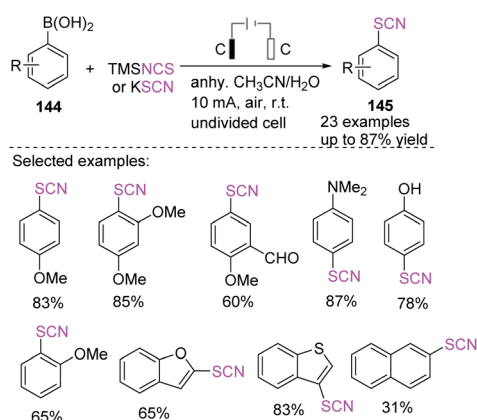

Scheme 52 a) Electrochemical decarboxylation of cinnamic acids **142**. (b) Proposed mechanism of electrochemical decarboxylation of cinnamic acids **142**.

electrochemical-induced decarboxylation process for cinnamic acids by utilizing ammonium thiocyanate as a thiocyanate source for the construction of vinyl thiocyanates in moderate to high yields (Scheme 52a).[60] The anodic electrode creates a thiocyanate radical intermediate **B** first when the thiocyanate anion is oxidized. By combining **B** and **142D**, the intermediate **142C** is produced. **142C** is finally decarboxylated to yield **143**, a vinyl thiocyanate. Anodic oxidation provides (SCN)$_2$, which then participates in the electrophilic addition to **142**, accompanied by the decarboxylation stage (Scheme 52b).

Cai *et al.* demonstrated green and simple electrochemical deborylative thiocyanation process for aryl boronic acids **144** to construct resulting aryl thiocyanates **145** in good to outstanding yields and with a broad range of functional groups.[61] This electrochemical deborylative thiocyanation system requires electricity, and a variety of aryl boronic acids **144** can be engaged. This straightforward and metal-free technique uses potassium thiocyanate or TMSNCS (trimethylsilyl)isothiocyanate as a thiocyanate source in an air atmosphere with no adverse chemicals (Scheme 53).

Scheme 53 Electrochemical deborylative thiocyanation of arylboronic acids **144**.
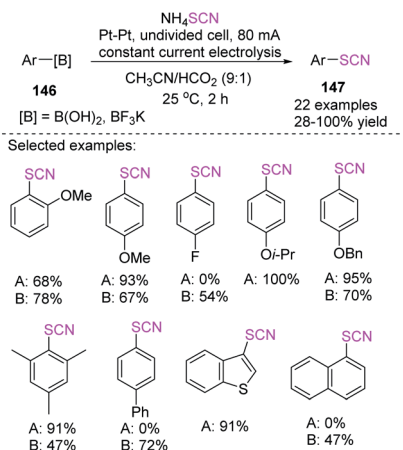
Scheme 54 Electrochemical induced synthesis of aryl thiocyanates **147**.

Without the use of any transition metals, Gooben *et al.* established a facile electrochemical technique for the *ipso*-thiocyanation of arylboronic acids with ammonium thiocyanate for the fabrication of aryl thiocyanates through excellent to high yields.[62] According to the mechanistic suggestion for the regiospecific thiocyanation of arylboron compounds, thiocyanate (SCN) is oxidized to pseudohalogen (SCN)$_2$, which then combines with the arylboron compound for the production of aryl thiocyanate. This reaction can be assisted by the coupling of SCN to boronic acid, which produces an anion, increasing the concentrations of reagents at the anode and activating the boron-based releasing group (Scheme 54).

4. Conclusion & viewpoint

Thiocyanates (SCN) are important organic intermediates in the advanced phases of bioactive molecule functionalization. Photo- or electrochemical-induced thiocyanation methods, which are novel methods for the environmentally sustainable, efficient, and safe synthesis of pharmaceuticals and functional materials, have garnered considerable interest in recent years. We have observed through previous discussions and published articles that photo- or electrochemical-induced synthesis in this field is sustainable and green and safer for the environment, thereby offering more significant contributions than previous conventional synthesis processes. In terms of future research, we can state that scientists will be able to conduct this type of photo- or electrochemical-triggered synthesis mode in a green and sustainable manner, opening new doors for the future where no toxic metals, oxidants, or other external catalysts are required. We have summarized entire research on photochemical- and electrochemical-induced thiocyanation techniques in this review, which is divided into three sections: (1) C(sp^3)–SCN bond formation, (2) C(sp^2)–SCN bond formation, and (3) C(sp)–SCN bond formation. We have discussed photochemically induced indirect thiocyanation of thiol compounds and electrochemically induced C–SCN bond formation of enaminones, cinnamic acid, and boronic acid compounds through thiocyanation. The construction of C–SCN bonds is finally described. The majority of photo- or electrochemical-mediated thiocyanation techniques seem to cover the conception of C(sp^2)–SCN and C(sp^3)–SCN bonds. Therefore, a wide range of thiocyanation approaches are available for C(sp^2)–H and C(sp^3)–H bonds. These strategies include undivided cell and metal-free (organic dye or EDA complex based) photocatalytic and electrocatalytic techniques. Photo- or electrochemistry-mediated C–SCN bond formation approaches are still limited. Organophoto- and electrocatalysis have attracted interest from academic and pharmaceutical laboratories. The development of potent and effective photo- and electrocatalysts ensures that the topic will remain an important subject of interest for many decades. Hence, C–SCN bond forming processes will be increasingly examined in the future.

Conflicts of interest

"There are no conflicts to declare".

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