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基于热、光以及电化学过程的无过渡金属碳–氢键硫氰化和硒氰化反应

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摘要 硫氰基和硒氰基均在有机合成中具有广泛应用的重要官能团. 这类结构也经常出现在具有生物药物活性、光学活性以及催化功能的分子中. 因此, 发展可用于合成具有结构多样性的有机硫氰化和硒氰化物及相关串联转化合成多样性杂环分子的方法持续吸引着研究者的兴趣, 总结了无过渡金属条件下的碳–氢键的硫氰化和硒氰化反应合成有机硫氰化物和硒氰化物以及相关串联环化反应的研究进展.

关键词 无过渡金属; 碳–氢键; 硫氰化; 硒氰化; 热化学; 光催化; 电化学

Transition Metal-Free C—H Thiocyanation and Selenocyanation Based on Thermochemical, Photocatalytic and Electrochemical Process

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Abstract Thiocyano and selenocyano are both important functional groups with broad application in organic synthesis. Such functional structures also occur frequently in molecules possessing valuable biological and pharmaceutical activities, optical functions, and catalytic profiles. Therefore, developing synthetic methods toward diverse organo thio-/selenocyanates as well as the tandem annulation for the construction of diverse heterocyclic scaffolds keep receiving high interests. The advances on the synthesis of organo thio-/selenocyanates via transition metal-free C—H thiocyanation or selenocyanation as well as the tandem annulation reactions based on such C—H functionalization are reviewed.

Keywords transition metal-free; C—H bond; thiocyanation; selenocyanation; thermochemistry; photocatalysis; electrochemistry

1 Introduction

The organo thiocyanates and selenocyanates bearing the S—C≡N/S—C≡N structure are useful organic compounds in both academic and industrial domains. The featured multiple carbon-nitrogen bond and the relatively active C—S/C—Se bonds in these compounds make them versatile building blocks in the synthesis of numerous organic products.[1] In addition, as key structural fragment, thiocyano and seleno groups also occur in many organic compounds possessing attractive biological or pharmacological profiles (Figure 1).[2] In the areas of material science,[3] catalysis,[4] as well as organometal complexes,[5] organo thio-/selenocyanates have also found interesting and distinctive applications. Therefore, it is not surprising that the synthesis of thiocyanated and selenocyanated organic products has been an issue of longstanding interest in the science of organic synthesis.

Presently, a plethora of different synthetic methods are available for the synthesis of thiocyanates and selenocyanates via various functional group transformation.[6] However, due to the inherent advantages in step economy and easy availability of substrates associated with C—H bond activation or functionalization,[7] the straightforward thiocyanation and selenocyanation of stable C—H bonds have been recognized as the particularly favourable tool in the synthesis of organic thio-/selenocyanates.

On the other hand, as the particularly attractive strategy, the transition metal-free functionalization of C—H bonds is

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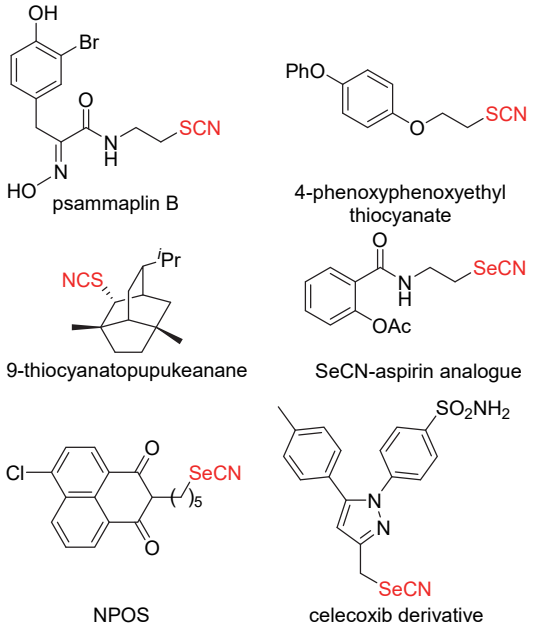


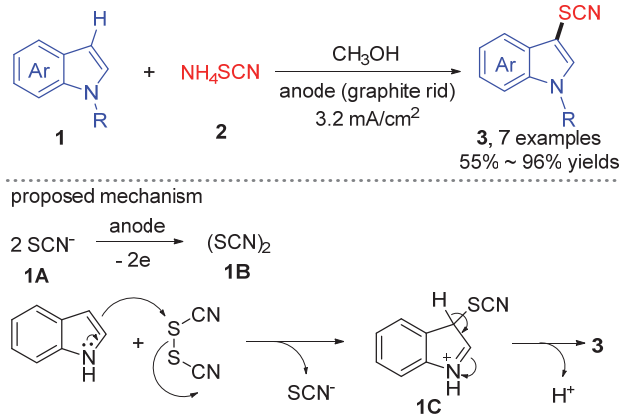
Figure 1 Selected drugs and bioactive molecules containing thio-/selenocyanate groups

of even higher superiority due to the inherent advantages of atom economy, environmental compatibility as well as the facile product purification.[8] Considering the significance of both thiocyanation reactions as well as the transition metal-free synthesis, herein the advances in the transition metal-free C—H thiocyanation and selenocyanation reactions are reviewed, including the direct synthesis of organo thiocyanates and selenocyanates by C—H bond functionalization as well as cascade reactions involving thiocyanation/selenocyanation as a key step. According to the status of this research area, the reactions employing conventional heating chemistry, the visible light photocatalytic and electrochemical reactions are covered.

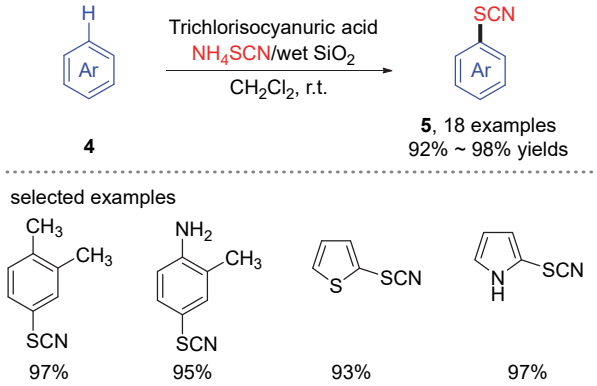
2 Thiocyanation and selenocyantion of aromatic C(sp²)—H bond

In 2013, Nikoofar *et al.*[9] developed the anodic thiocyanation reactions of indoles **1** and analogous nitrogen heterocycles. Under the condition of constant current at room temperature, thiocyano anions **1A** was oxidized to thiocyano dimers **1B** on the surface of the electrode. The electrophilic addition of **1B** to the heterocycle gave **1C**, and the deprotonation provided products **3** (Scheme 1). An advantage of this method was that ammonium thiocyanate was used as both thiocyano source and electrolyte, avoiding the employment of additional electrolyte.

In 2012, Akhlaghinia *et al.*[10] reported a method for the C—H thiocyanation of electron arenes and heteroarenes in the presence of combined trichloroisocyanuric acid (TCAA), NH_4SCN and wet silica. Arenes **4**, including electron rich phenyls, thiophene and pyrroles, could be transformed into corresponding thiocyanate products **5** by running the reactions in CH_2Cl_2 at room temperature (Scheme 2).

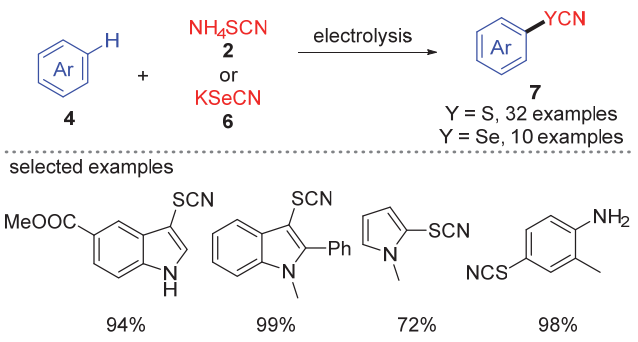


Scheme 1 Electrochemical C—H thiocyanation indoles and analogous heterocycles



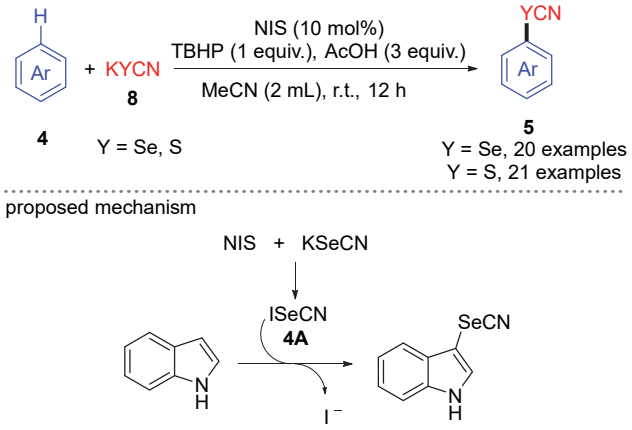
Scheme 2 Thiocyanation of electron rich arenes with the promotion of TCAA

In addition, Jiang and Sun *et al.*[11] reported the electrochemical thiocyanation and selenocyanation of the C—H bond in electron rich aromatic hydrocarbons **4** with NH_4SCN (**2**)/KSeCN (**6**) as the reaction partners. This strategy was applicable to various (hetero) aromatic compounds, such as indoles, pyrroles, anilines, anisoles *etc.* without any catalyst or oxidant. The reaction mechanism was hypothesized as identical in the reactions described in Scheme 1 based on the electrode oxidative dimerization of the thiocyano and selenocyano anion (Scheme 3).



Scheme 3 Electrochemical thiocyanation/selenocyanation of electron rich arenes

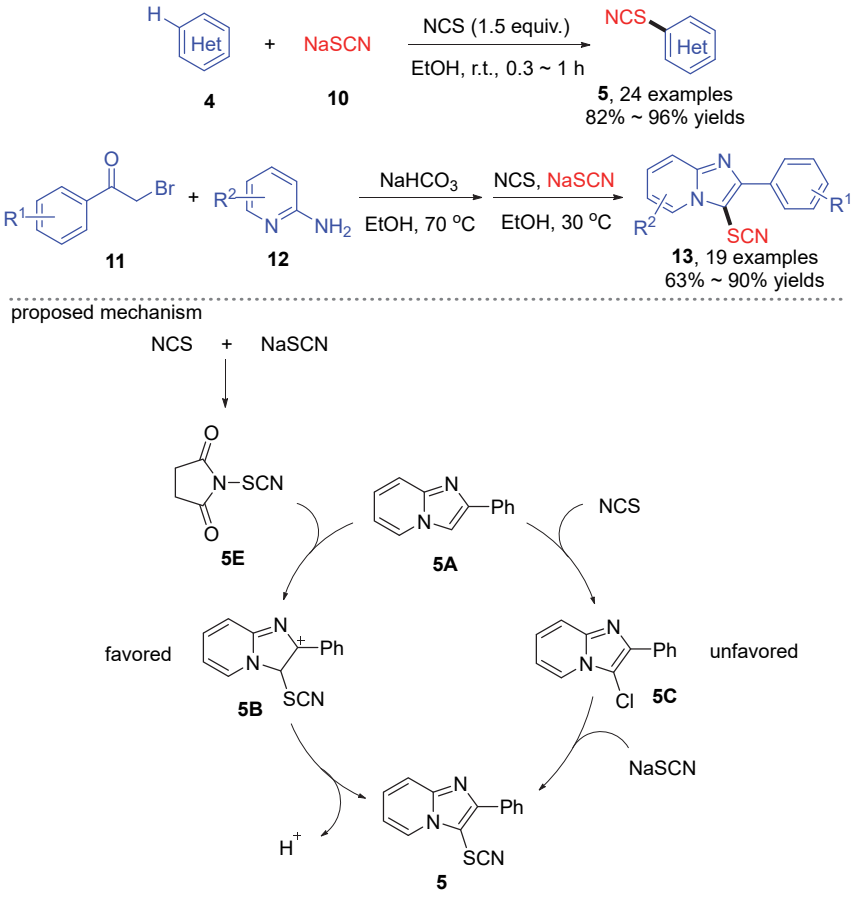
In 2016, Prabhu *et al*.[12] realized the selenocyanation and thiocyanation of electron rich aromatic hydrocarbons **4** at room temperature with *N*-iodosuccinimide (NIS) as catalyst and *tert*-butyl hydroperoxide (TBHP) as oxidant. This method was effective for indole, aniline, phenol and other electron rich aromatic systems, providing products with good to excellent yields with good regioselectivity. They proposed a tentative mechanism, in which NIS reacted with KSCN to generate highly electrophilic iodothiocyanate, which was trapped by nucleophilic indole on its C-3 position (*para*-position in the cases of aniline and phenol), followed by further re-aromatization to afford the seleno/thiocyano products (Scheme 4). Selenocyanation was more facile than the thiocyanation in this work because the *in situ* generated iodoselenocyanate was more electrophilic than equivalent iodothiocyanate.



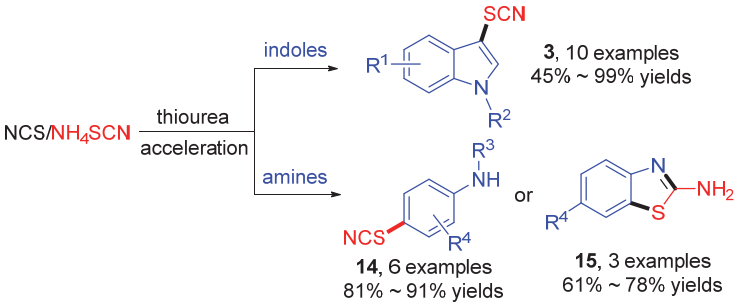
Scheme 4 NIS-catalyzed selenocyanation and thiocyanation of electron rich arenes

Wang *et al*.[13] developed a method for the C—H thiocyanation of heterocyclic arenes **4** with combined *N*-chlorosuccinimide (NCS) and NaSCN **12**, leading to the synthesis of 3-thiocyanatoimidazo[1,2-*a*]pyridines **13** by one-pot, two-step operation with bromoacetophenone **11** and diaminopyridines **12**. In the predominant mechanism, *N*-thiocyanatosuccinimide (NTS, **5E**) was formed via the reaction of NCS with NaSCN. Followed by regioselective electrophilic attack on the C-3 position of **5A**, imidazolinium intermediate **5B** was generated. The loss of a proton from **5B** gave the desired product and succinimide. Alternatively, but less likely, electrophilic substitution of **5A** with NCS resulted in the formation of **5C**, and then nucleophilic substitution of **5C** with NaSCN might also deliver product **5** (Scheme 5).

Additionally, Wang and He *et al*.[14] established a simple and effective thiourea/NCS/NH_4SCN system for the electrophilic thiocyanation of indoles and aromatic amines. The main characteristics of this system were the mild conditions, high yields, short reaction time and the use of easily available thiourea as organocatalyst (Scheme 6).

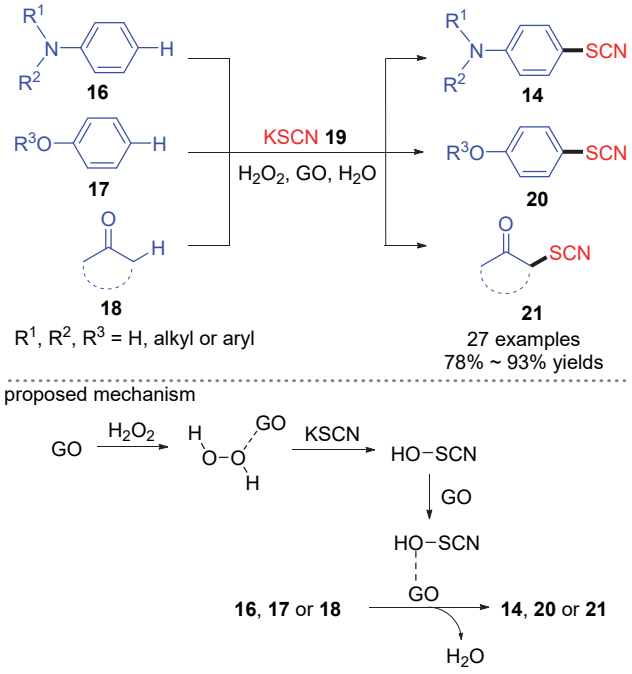


Scheme 5 Synthesis of 3-thiocyanatoimidazo[1,2-*a*]pyridines by the combination of NCS/NaSCN



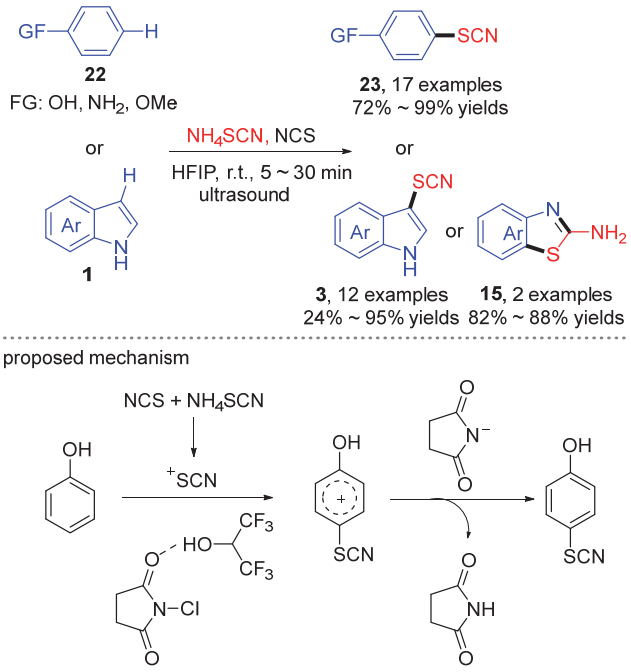
Scheme 6 Thiourea/NCS/NH_4SCN system for electrophilic thiocyanation of indoles and aromatic amines

Graphene oxide (GO), as a heterogeneous carbo-catalyst, could also catalyze the direct thiocyanation. In 2016, Khalili[15] developed a useful and simple method for the regioselective thiocyanation of various substrates in water in the presence of KSCN, GO and H_2O_2. It should be noted that alkenyl ketones **18** could also undergo the C(sp^3)—H thiocyanation with the catalytic conditions to donate the α-thiocyanoketones **21**. The reaction pathway began from the activation of H_2O_2 with GO. Then, the reaction of activated H_2O_2 with KSCN generated HO-SCN species which was reactivated on subsequent reaction with GO to produce thiocyanium ion SCN^+. Eventually, this electrophile was attacked by arene/enolizable ketone to afford the target products and water as a by-product (Scheme 7).



Scheme 7 Regioselective thiocyanation in water using GO/H_2O_2

In 2018, Wang *et al.*[16] developed an efficient ultrasonic promoted thiocyanation of phenols, indoles and anilines in the presence of NCS and NH_4SCN with 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) as solvent (Scheme 8). In this method, HFIP not only acted as a good solvent, but also activated NCS via hydrogen bond, which greatly accelerated the formation of SCN^+ cation.

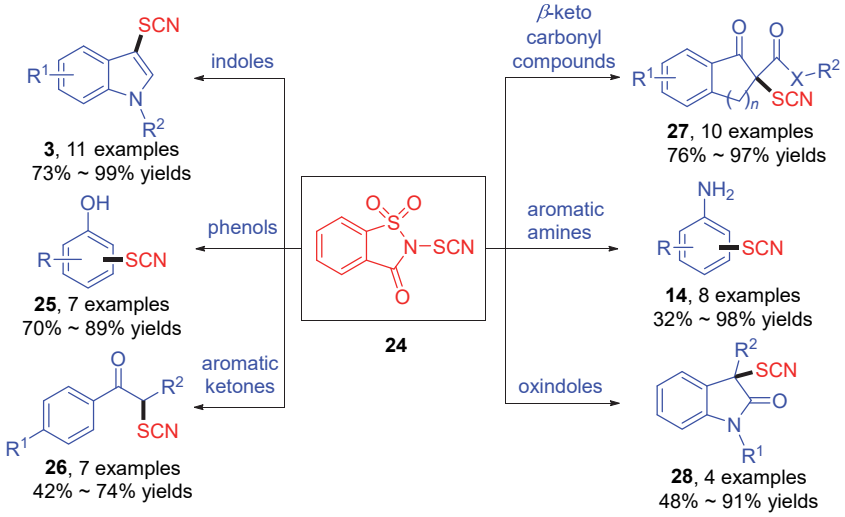


Scheme 8 Ultrasonic promoted thiocyanation with HFIP as solvent

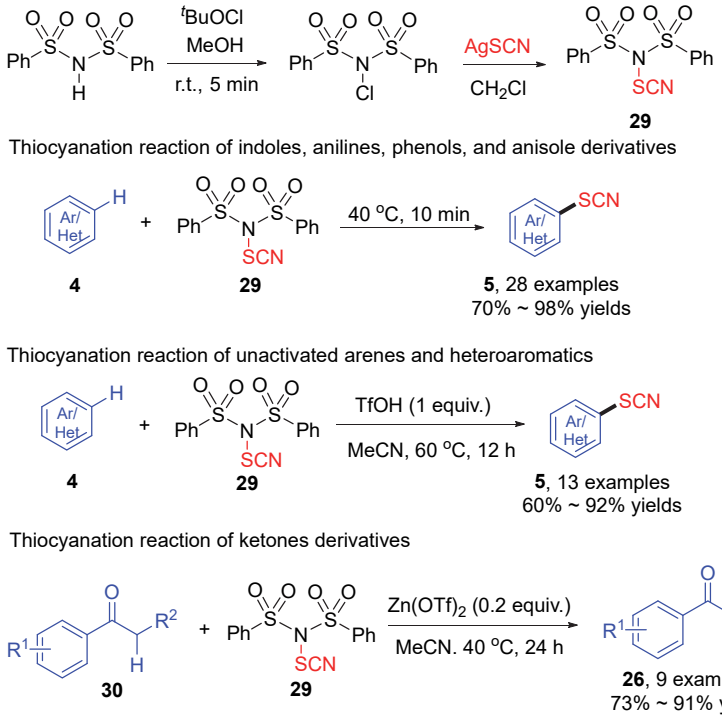
In 2018, Yin and Chen *et al.*[17] prepared a new cationic thiocyanation reagent, *N*-thiocyanatosaccharin **24**, and applied it to the direct electrophilic thiocyanation reaction of various nucleophiles. This method could be used for not only the thiocyanation of C(sp^2)—H bonds in aromatic substrates, such as benzothiophene, indole, oxindole, aromatic amine and phenol, but also the C(sp^3)—H bonds in substrates such as ketones (Scheme 9).

Moreover, the same group[18] reported the thiocyanation reactions with *N*-thiocyanatodibenzenesulfonimide **29** as electrophilic thiocyanating reagent. This reagent reacted with activated aromatic compounds such as phenol, indole, aniline and anisole without using any catalyst to provide the corresponding thiocyanation products **5** in high yields. For less active aromatic, heteroaromatic compounds and ketones, TfOH or $Zn(OTf)_2$ was required as additive for the thiocyanation (Scheme 10).

In 2020, Liu and Wei *et al.*[19] described the thiocyanation reaction of pyrrolo[1,2-*a*] quinoxaline **31** with the promo-



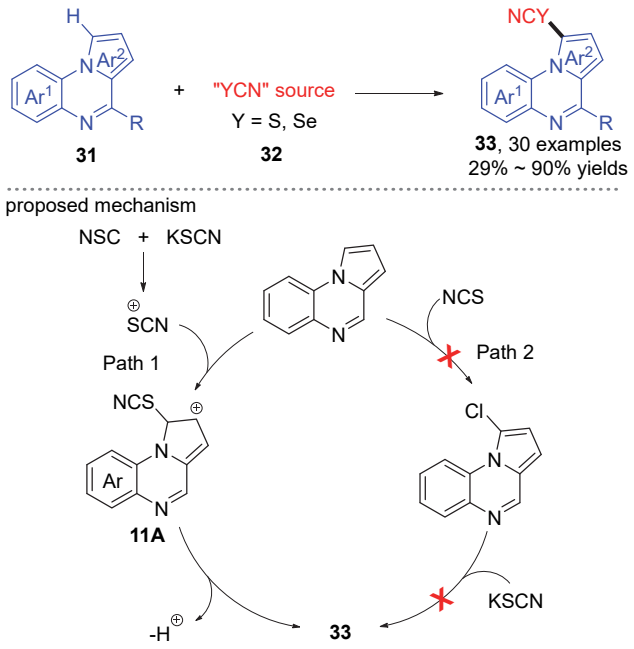
Scheme 9 Electrophilic thiocyanation reaction using *N*-thiocyanatosaccharin



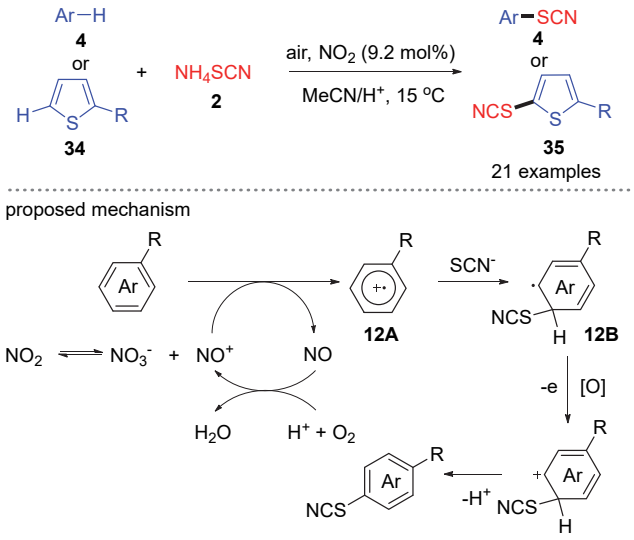
Scheme 10 Direct electrophilic thiocyanation reaction using *N*-thiocyanatodibenzenesulfonimide

tion of NCS by using NH_4SCN or KSCN as thiocyano-sources. With similar strategy, the selenocyanation of pyrrolo[1,2-*a*]quinoxaline **31** was also realized with KSeCN. The reactions might be achieved via path 1 wherein the thiocyanate cation was formed through the reaction of NCS with NH_4SCN. Subsequently, the pyrrolo[1,2-*a*]quinoxaline and thiocyanate cation underwent an electrophilic addition to form intermediate **11A**. Finally, intermediate **11A** lost one hydrogen ion to generate product **33**. On the other hand, the reaction involving the C—H chlorination as well as subsequent C—Cl bond thiocyanation (path 2) was not likely to be a possible pathway (Scheme 11).

In 2016, Ren and Wang *et al.*[20] developed the thiocyanation reaction of carbon aromatics **4** and thiophenes **34** with NH_4SCN under mild reaction conditions by using NO_2 as catalyst. The mechanism showed that the reaction might proceed via free radical pathway. The catalytic cycle started with the reaction between the aromatic ring and NO^+ to give the aromatic radical cation **12A** and NO. The latter was oxidized by O_2 to regenerate the catalytically active NO^+. The resulting aromatic radical cation **12A** reacted with SCN^- to form a neutral radical intermediate **12B**. The subsequent electron transfer and deprotonation gave the target aryl thiocyanate products (Scheme 12).

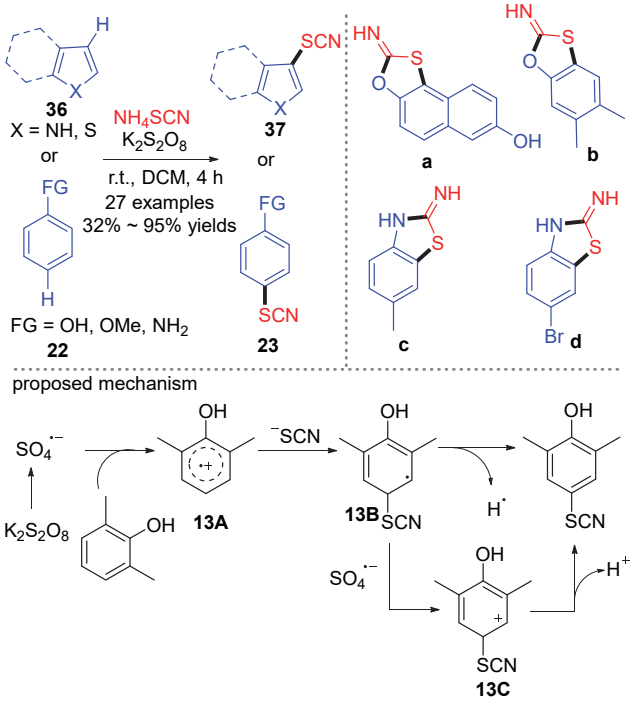


Scheme 11 Thiocyanation reaction of pyrrolo[1,2-*a*]quinoxaline promoted by NCS



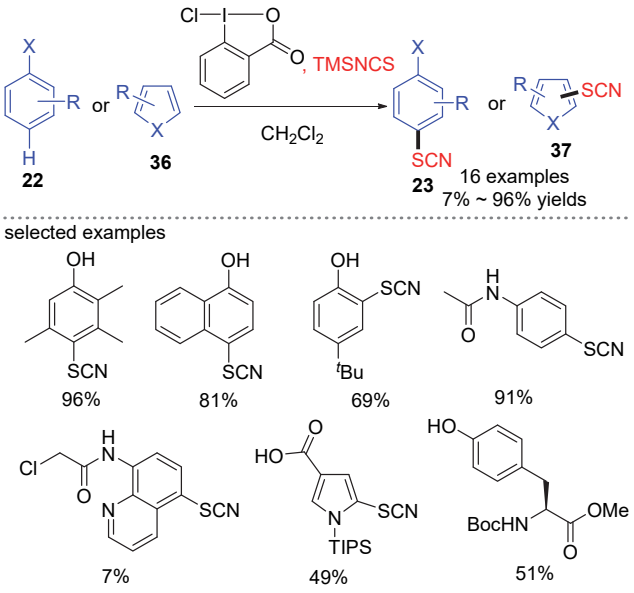
Scheme 12 NO_2-catalyzed thiocyanation aromatics and thiophenes

Alternatively, Bhat *et al.*[21] reported a simple regioselective synthesis of aryl thiocyanates with phenols, anilines or heteroaryls as C—H bond donors. The conversion was achieved in excellent yields by direct C—H thiocyanation at room temperature, without transition metals. Interestingly, stable cyclization products **a**~**d** of oxathioimines or azathioimines could be obtained by introducing substituents in the *para*-position of phenols or anilines. According to the proposed mechanism, potassium persulphate would decompose to generate sulphate radical anion ($SO_4^{\bullet-}$), which in turn oxidized the aromatic compound to form radical cation intermediate **13A**. Simultaneous nucleophilic addition of thiocyanate anion to the cation intermediate led to the formation of radical intermediate **13B**. Ultimately, the loss of hydrogen radical from **13B** would afford the desired compound. Alternatively, further oxidation of the intermediate **13B** might also take place to give intermediate **13C**. Finally, the elimination of H^+ from this intermediate could also afford the desired product (Scheme 13).



Scheme 13 Regioselective synthesis of thiocyanates using $K_2S_2O_8$ as oxidant

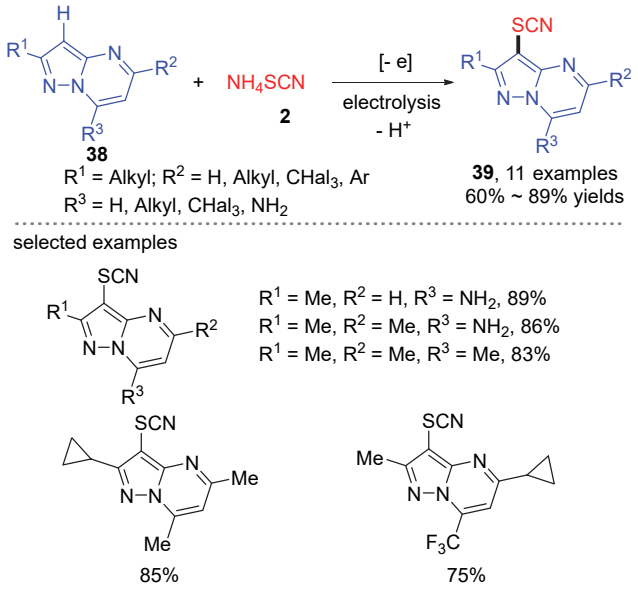
In 2019, Egami and Hamashima *et al.*[22] realized the thiocyanation reaction of aromatic compounds under mild conditions using the combination of 1-chloro-1,2-benziodine-3-(1*H*)-one and trimethylalkyl isothiocyanate (TMSSCN) (Scheme 14). The reaction of electron rich aromatic



Scheme 14 Thiocyanation reaction of aromatic compounds with TMSSCN

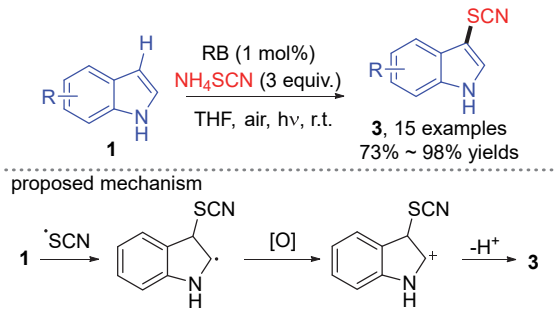
compounds proceeded smoothly to provide the thiocyanated products **23** or **37** in high yields, while electron deficient heteroaromatic compounds were not suitable for this reaction.

In 2019, Petrosyan *et al.*[23] developed a complementary method for the C—H thiocyanation of pyrazolo[1,5-*a*]-pyrimidine **38** by means of electrode oxidation. The reactions of both electron withdrawing and electron donating group functionalized substrates **38** could be transformed into the corresponding thiocyanates **39** with high regioselectivity (Scheme 15).



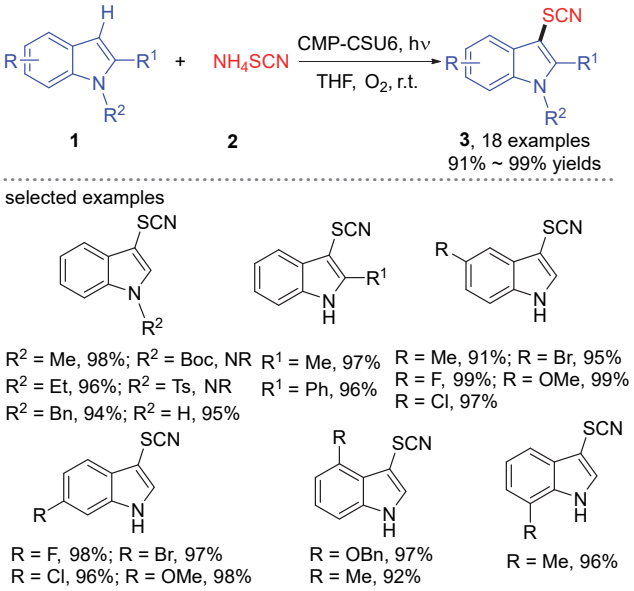
Scheme 15 Electrochemical thiocyanation of pyrazolo[1,5-*a*]-pyrimidines

As popular method featuring advantages in environmental friendliness and mild conditions, the photocatalysis has also been employed for C—H thiocyanation reaction. In 2014, Li *et al.*[24] established an effective visible light-induced method to promote indole C-3 thiocyanation in the presence of Rose Bengal (RB) under air atmosphere (Scheme 16). The target products were constructed through a sequence involving free radical addition, oxidation and elimination.

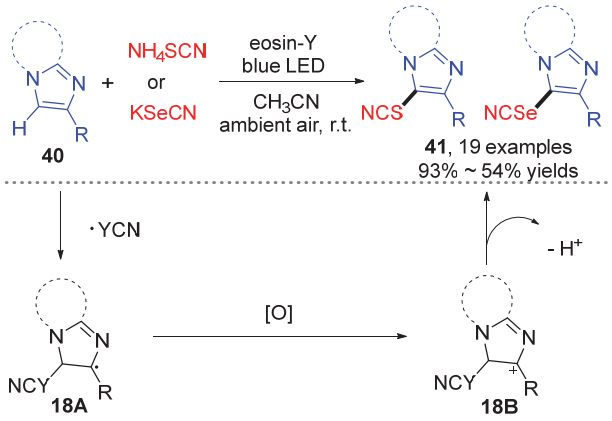


Scheme 16 Visible light method to promote indole C-3 thiocyanation

In 2018, Pan and Yu *et al.*[25] developed the thiocyanation of indoles with a series of conjugated microporous polymer (CMP) photocatalysts at room temperature (Scheme 17). Upon light irradiation, the CMP-CSU6 was excited to CMP-CSU6* and reductively quenched by oxygen to produce hydrogen peroxide and CMP-CSU6$^+$ via single electron transfer (SET) reaction. The thiocyano free radical generated therein added to the indole at C(3)-site as well as subsequent SET oxidation allowed the formation of indole cation which proceeded to products **3** by deprotonation (Scheme 17).



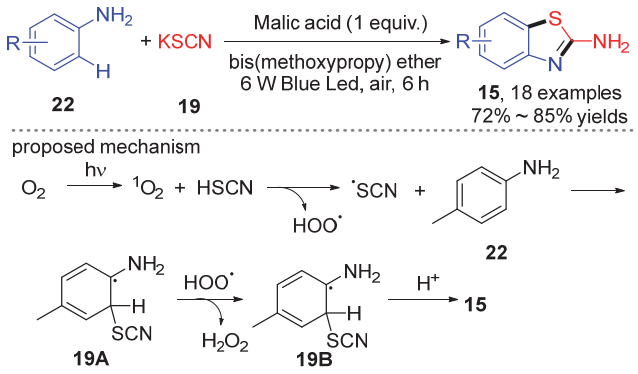
Scheme 17 Photocatalytic thiocyanation of indoles catalyzed by photocatalysts



Scheme 18 Photocatalytic imidazole heterocyclic thiocyanation

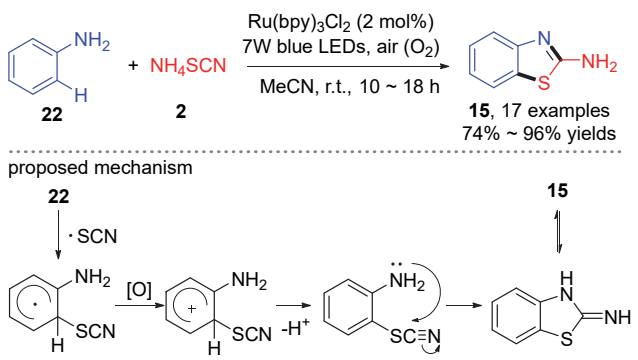
In 2015, Hajra *et al.*[26] developed a metal-free, visible light mediated method for C—H thiocyanation and selenocyanation of fused imidazoles. Using eosin-Y as photocatalyst, the 3-thiocyano/selenocyanoimidazo[1,2-*a*]pyridines **41** were obtained with high regioselectivity and wide substrate applicability by irradiating with 425 nm blue LED lamp for 3 h under ambient air. The reaction also proceeded via photocatalytic generation of thiocyano/selenocyano free radical **18A** and its SET oxidation to cation intermediate **18B** (Scheme 18).

In 2020, by using air as the oxidant and malic acid as the promoter, Xu and He *et al*.[27] established a practical method for the preparation of 2-aminobenzothiazoles **15** through visible-light-initiated cascade reactions of aromatic amines **22** and KSCN (**19**) in eco-friendly bis(methoxypropy) ether catalyzed by photocatalysis. Initially, the singlet oxygen $^1O_2$ was generated by the irradiation of visible-light to molecular oxygen. Meanwhile, the thiocyanic acid was generated *in situ* by the reaction of thiocyanate salts with malic acid. Subsequently, the active singlet oxygen abstracted one electron from thiocyanic acid to produce a thiocyano free radical and a hydroperoxyl radical. The thiocyano radical reacted with **19** to generate a free-radical intermediate **19A**, which underwent dehydro-aromatization to form 2-thiocyanatoaniline **19B** along with the generation of hydrogen peroxide in the presence of hydroperoxyl radical. Finally, the nucleophilic amino group of **19B** underwent deprotonation and intramolecular annulation to 2-aminobenzothiazole **15** (Scheme 19).



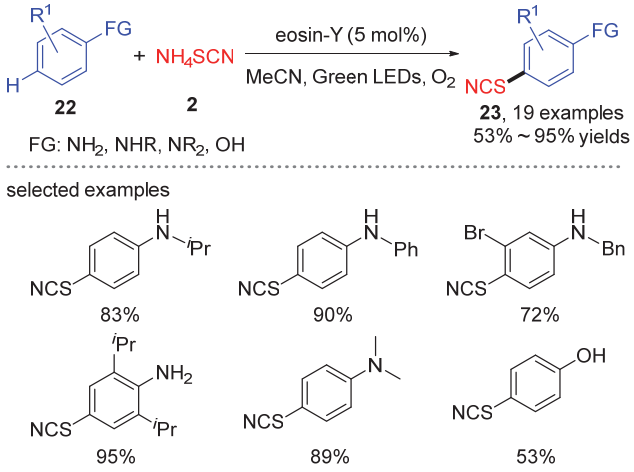
Scheme 19 Photocatalytic cascade C—H thiocyanation and thiazole annulation

In 2020, Yadav and Singh *et al*.[28] disclosed a new method for the direct synthesis of 2-aminobenzothiazole from aniline **22** and NH_4SCN under visible light irradiation (Scheme 20). Similar as the above work, the thiocyano free radical addition, deprotonation as well as the intramolecular annulation with amino group attack to the SCN fragment cascade were included in the presence of $Ru(bpy)_3Cl_2$.



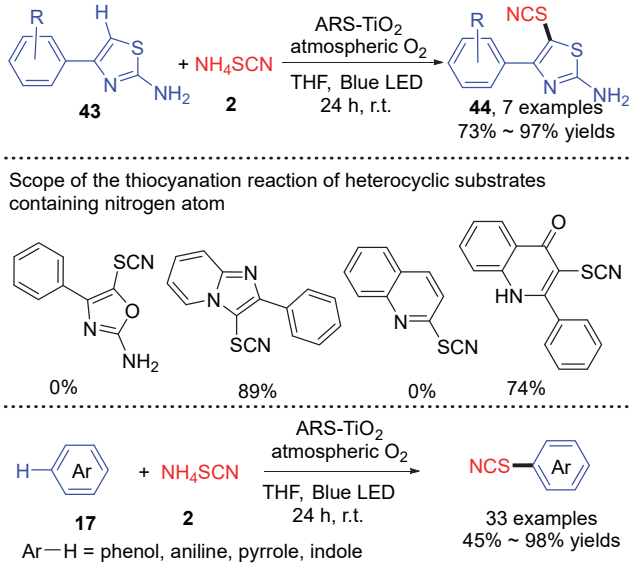
Scheme 20 Synthesis of 2-aminobenzothiazole via aniline C—H thiocyanation

In 2020, Yi, Xie and Tan *et al*.[29] developed the visible-light-enabled aerobic C(sp^2)—H thiocyanation of aromatic compounds **22** by employing eosin-Y as effective photocatalyst and oxygen as green terminal oxidant. The electron rich aromatics such as amines and phenols were practically tolerated and provided the corresponding products with moderate to excellent yields (Scheme 21).



Scheme 21 Visible-light aerobic aromatic C—H thiocyanation

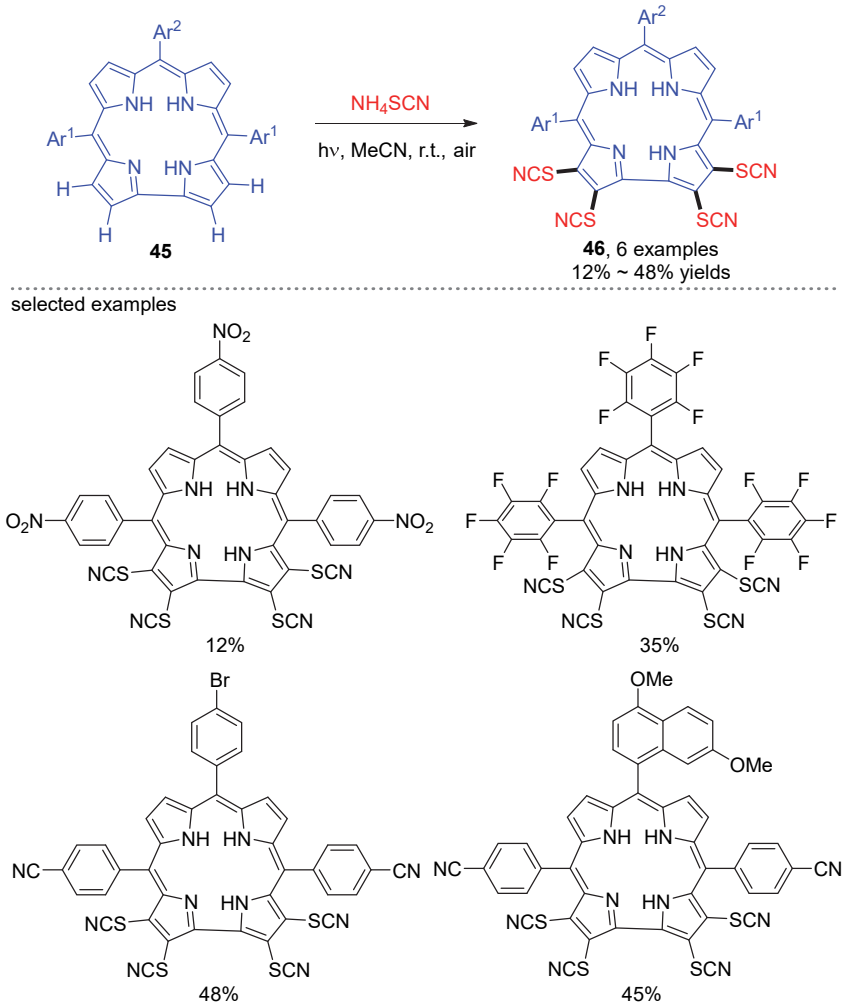
In 2020, Hosseini-Sarvari *et al*.[30] used alizarine red S (ARS) and TiO_2 to catalyze the C(sp^2)—H thiocyanation by the synergistic photocatalysis (Scheme 22). The method was compatible with a variety of C—H bond donors such as 2-phenylaminothiazoles, phenols, anilines, indoles, pyrroles and 4-quinolinones *etc*. Also, the oxygen in the air was utilized as the oxidant for the reactions.



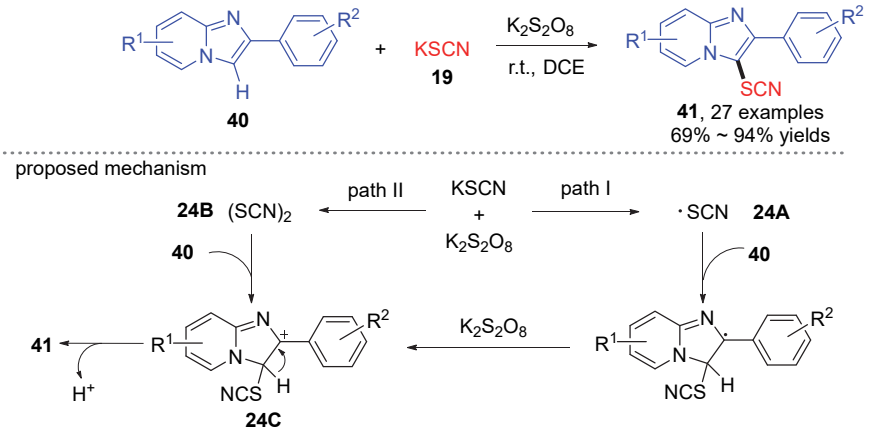
Scheme 22 ARS-TiO_2 as photocatalyst for the photocatalytic C(sp^2)—H thiocyanation

In 2021, Kar *et al*.[31] first reported a new method for activating corrole macrocycles **45** via an *in situ* generated SCN free radical at very mild conditions. This photooxidation reaction produced tetrathiocyanates **46** in high yields

(Scheme 23). In 2015, Wang *et al.*[32] first disclosed the method toward regioselective thiocyanation of pyridine fused imidazole heterocycles **40** by C(sp^2)—H functionalization with KSCN (**19**) as thiocyano source and $K_2S_2O_8$ as oxidant. The method allowed the synthesis of various C-3 thiocyanate imidazolopyridines **41** in moderate to good yields. Two possible reaction pathways were proposed. In path I, SCN radical **24A** was first generated by the oxidation of KSCN. As a complementary mechanism (path II), the oxidation of KSCN by $K_2S_2O_8$ generated electrophilic $(SCN)_2$ **24B** via dimerization. Subsequently, the electrophilic addition of electrophile **24B** to **40** could also give the same carbocation intermediate **24C** to provide the final products (Scheme 24).

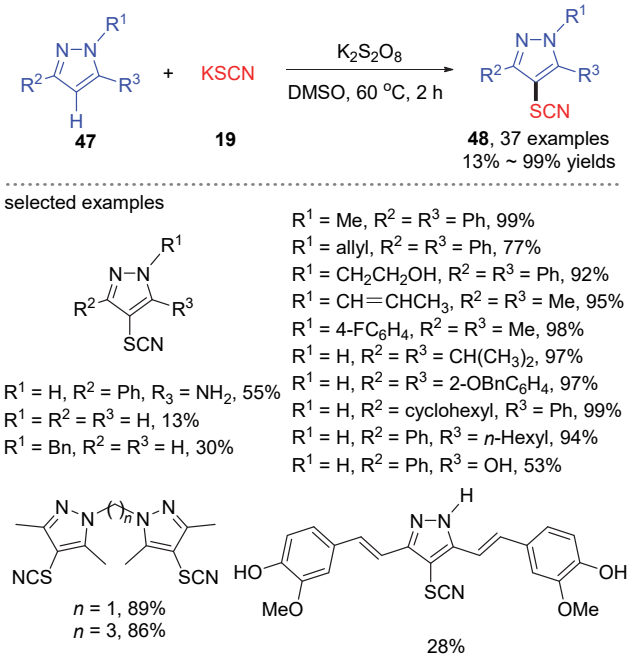


Scheme 23 Macrocycles C—H thiocyanation



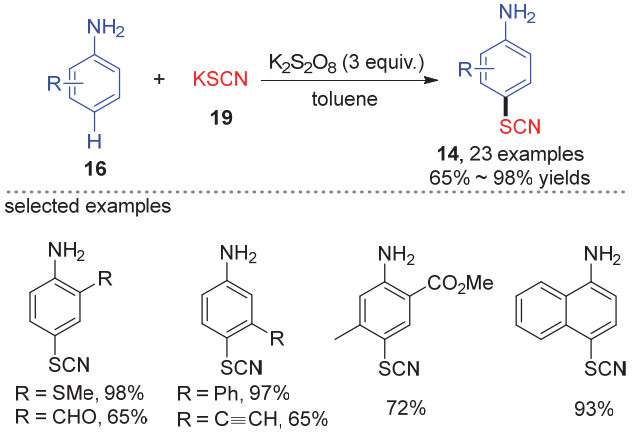
Scheme 24 Thiocyanation of imidazole heterocycles

In 2018, Kuhakarn *et al.*[33] reported a simple and practical method for the synthesis of pyrazole thiocyanates **48** with KSCN as thiocyano source in the presence of $K_2S_2O_8$. The reactions were run in dimethyl sulfoxide (DMSO) with pyrazoles **47** as the C—H bond donors and provided products with broad scope and up to 99% yield (Scheme 25).



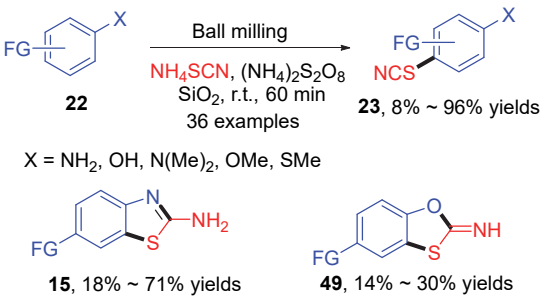
Scheme 25 Synthesis of pyrazole thiocyanate through C—H thiocyanation

In 2020, Zhang *et al.*[34] developed a method for the synthesis of *p*-thiocyanoanilines **14** at room temperature by the thiocyanation of the *para*-C—H bonds in anilines. The free radical thiocyanation of anilines was carried out in the presence of potassium persulfate without using transition metal reagent. A series of products **14** were synthesized thereby with good yields and regioselectivity by employing KSCN (**19**) as thiocyanating reagent (Scheme 26).



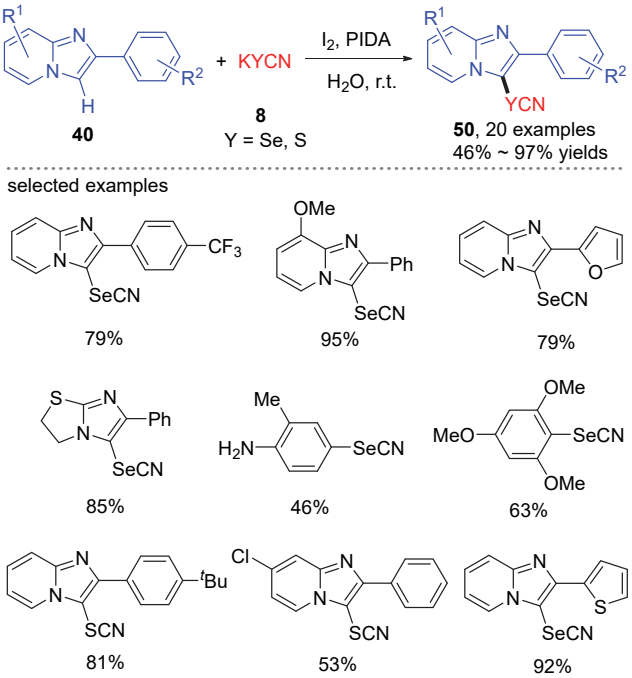
Scheme 26 Synthesis of *p*-thiocyanoaniline using $K_2S_2O_8$ as oxidant

In 2020, Malvestiti group[35] reported an example on the synthesis of aryl thiocyanates by ball milling promoted reactions of $(NH_4)_2S_2O_8/NH_4SCN$ and electron rich benzenes and heteroarenes with silica as grinding aids. The thiocyanated anilines, phenols, anisoles, thioanisoles and indoles **22** were obtained with moderate to excellent yields. Interestingly, products **15** and **49** could also be accessed by using corresponding aryl substrates (Scheme 27).



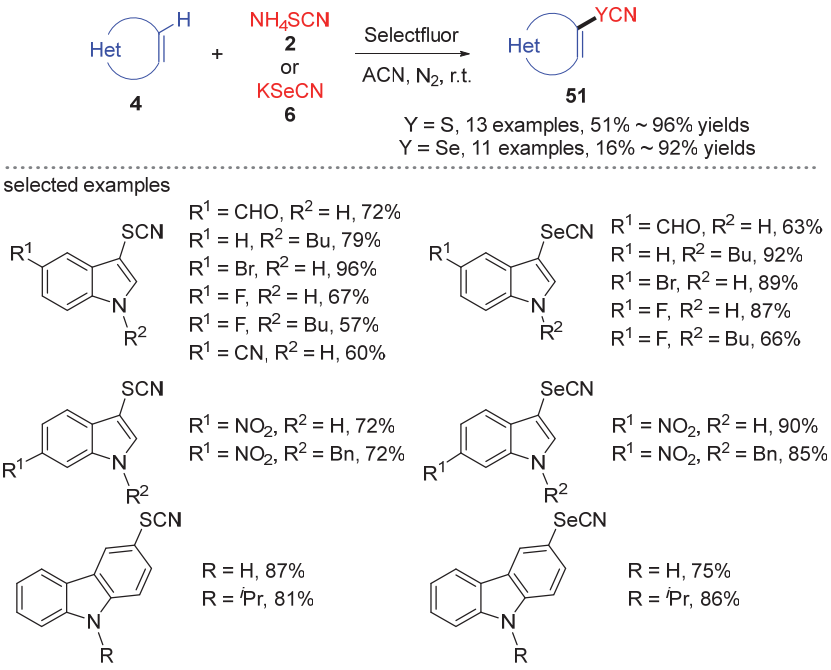
Scheme 27 Ball milling synthesis of aryl thiocyanates

To developed green access to organo thiocyanates, Hao and Song *et al.*[36] developed a method for C-3 thiocyanation of imidazolopyridines **40** by using KXCN **8** (X=S or Se) in water medium without transition metal catalysis. The reactions were run at room temperature and afforded products **50** with moderate to excellent yields (Scheme 28).



Scheme 28 Thiocyanation of imidazolopyridine in an aqueous medium

In 2019, Laali *et al.*[37] discovered that Selectfluor could catalyze the C—H thiocyanation and selenocyanation of heteroarenes such as indoles and carbazoles at room temperature by reacting with ammonium thiocyanate and potassium selenocyanate under nitrogen atmosphere, respectively (Scheme 29).

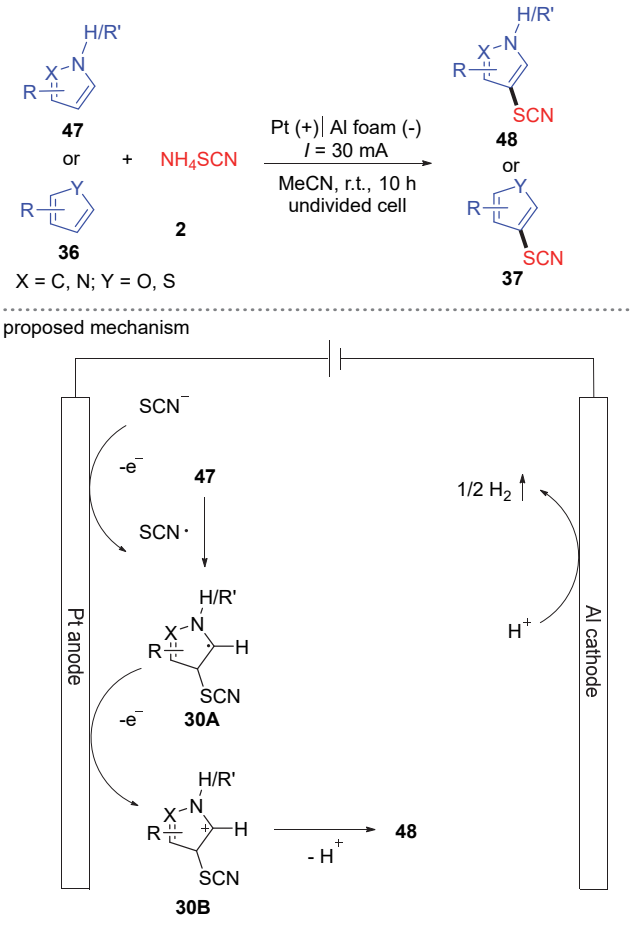


Scheme 29 Selectfluor mediated C—H thiocyanation and selenocyanation

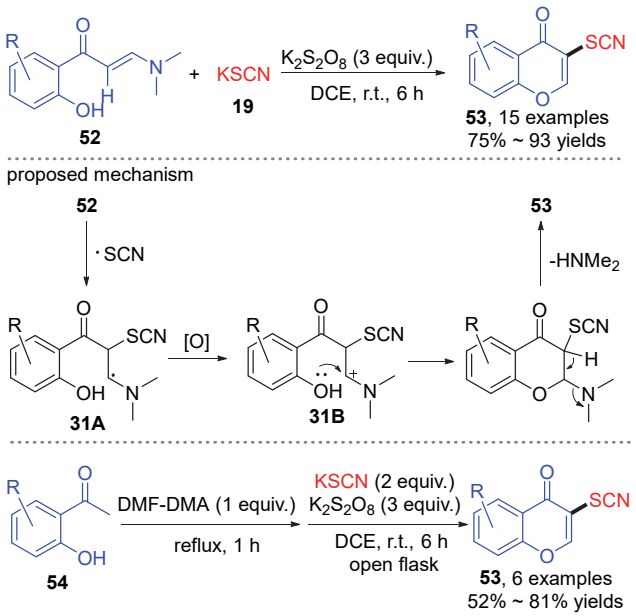
Recently, He and Peng *et al.*[38] reported an eco-friendly and practical method for the synthesis of thiocyanated five-membered heterocycles **48** and **37** through electrochemical C—H thiocyanation under chemical oxidant- and electrolyte-free conditions (Scheme 30). In the reactions, the thiocyanate ion was firstly oxidized at the surface of graphite plate anode to form a thiocyanate radical which regioselectively attacked the five-membered aromatic heterocycle **47** to yield a carbon-centered radical **30A**. Subsequently, the radical **30A** underwent anodic oxidation to afford the pyrazole cation intermediate **30B** by losing single electron. Finally, the deprotonation of intermediate **30B** provided the desired products **48**.

3 Thiocyanation and selenocyanation of nonaromatic C(sp^2)—H bond

In addition to aromatic C—H bonds, the nonaromatic C(sp^2)—H bonds in alkene derivatives and nonaromatic cyclic compounds could also undergo thiocyanation to provide corresponding thiocyanates. In 2016, Chen *et al.*[39] realized the thiocyanation of *o*-hydroxyarylenaminone **52** by using KSCN (**19**) and $K_2S_2O_8$ at room temperature, which gave 3-thiocyanated chromones **53** in high yields. In addition, a one-pot method for the synthesis of 3-thiocyanated chromone **53** from *o*-hydroxyacetophenone **54** and *N*,*N*-dimethylformamide (DMF)-dimethyl acetal (DMA) in one-pot, two-step operation was also developed. The possible mechanism of the reaction involved in the generation of SCN• free radical as key step. Subsequently, the addition of thiocyano radical to the double bond of **52** gave radical intermediate **31A**, and further SET oxidation provided carbocation intermediate **31B**. Finally, the intramolecular cyclization of **31B**, followed by the elimination of $HNMe_2$, afforded the desired product **53** (Scheme 31).

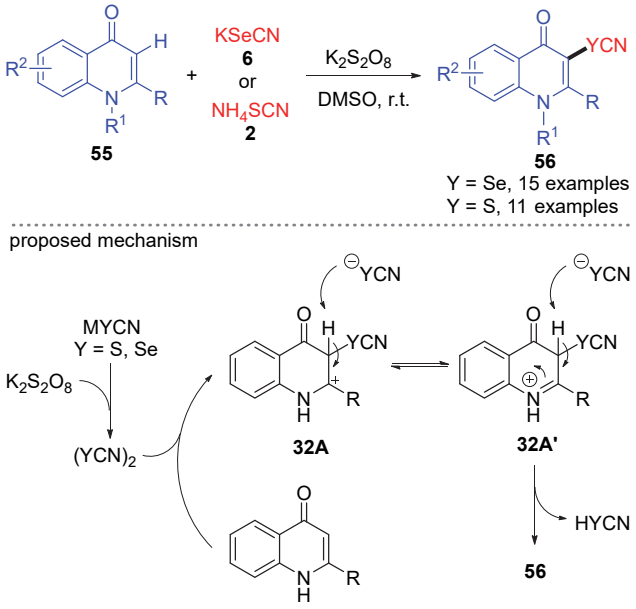


Scheme 30 Electrochemical thiocyanation of five-membered aromatic Heterocycles



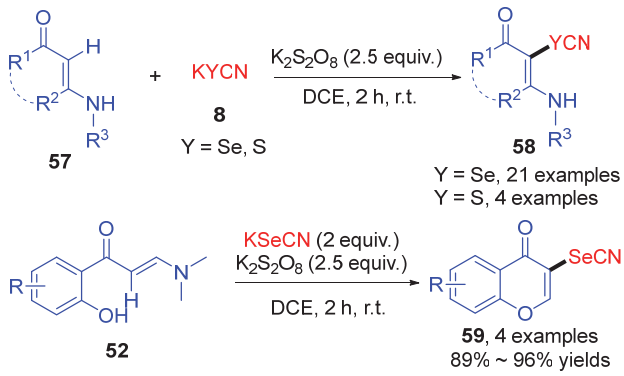
Scheme 31 Thiocyanation of *o*-hydroxyphenyl enaminones

In addition, Das *et al.*[40] developed a method to generate 4-thiocyanated quinolone derivatives **56** by using NH_4SCN (**2**) or KSeCN (**6**). In this route, the preliminary oxidation of NH_4SCN/KSeCN by $K_2S_2O_8$ first took place to afford the electrophile thiocyanogen $(SCN/SeCN)_2$. The intermediate $(SCN/SeCN)_2$ quickly reacted with 2-substituted-4-quinolones to afford the ionic species **32A**/**32A'** which could be stabilized by the adjacent nitrogen atom. With the loss of proton in the form of HSCN/HSeCN, the intermediate **32A** furnished the desired thiocyano/selenocyano 4-quinolones **56** (Scheme 32).



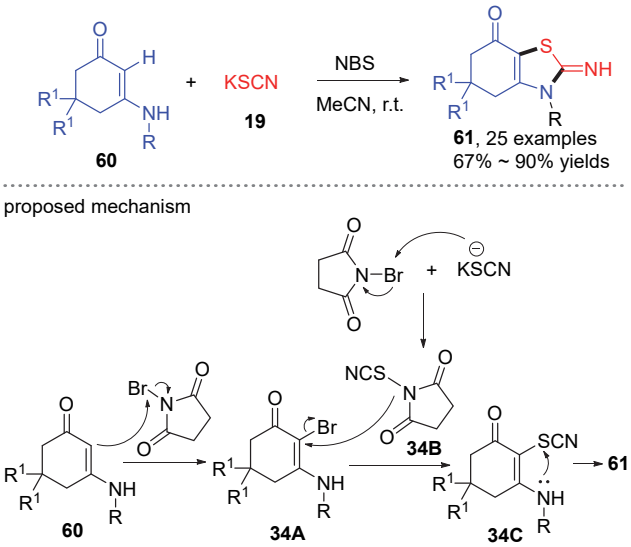
Scheme 32 Thiocyanation of 4-quinolones

Moreover, Sorabad and Maddani[41] achieved the regioselective selenocyanation of *N*-aryl enaminones **57** via C(sp^2)—H functionalization at room temperature. The KSeCN was used as the selenocyanating reagent and $K_2S_2O_8$ as the oxidant in the reactions. The present methodology was also applied for the synthesis of selenocyanated chromones **59**, indoles and anilines in good to excellent yields. In addition, replacing KSeCN with KSCN could yield the corresponding thiocyanated enamines **58** (Scheme 33).



Scheme 33 Regioselective selenocyanation of *N*-aryl enaminone

In addition, Chen, Huang and Liu *et al.*[42] developed a method for the synthesis of 2-iminothiazoles **61** via the reactions of enaminones **60** with KSCN (**19**) in the presence of *N*-bromosuccinimide (NBS). The reactions proceeded via the key *α*-bromoenaminone intermediate **34A** and *N*-thiocyanosuccinimide **34B**. The nucleophilic substitution of the thiocyano group to the C—Br bond in **34A** led to thiocyanated enaminone **34C**. The subsequent intramolecular annulation by the nucleophilic addition of the amino group to the thiocyano structure provided products **61** (Scheme 34).



Scheme 34 Regioselective synthesis of 2-iminothiazole via C—H thiocyanation

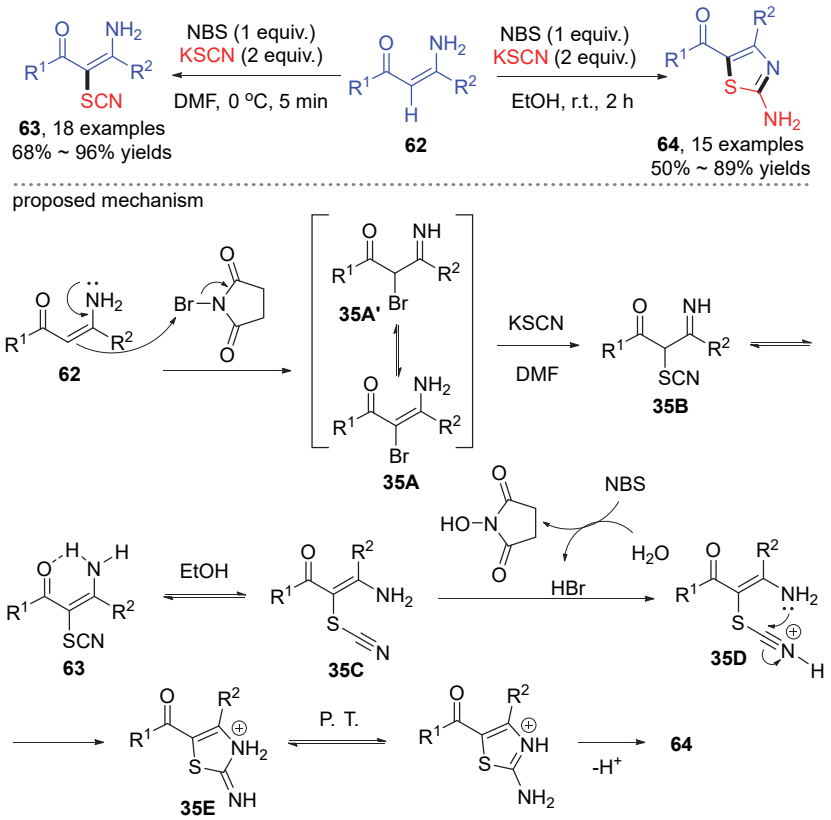
Later, with the starting materials of enaminones **62**,

KSCN and NBS, Duan *et al.*[43] developed the solvent-controlled synthesis of *α*-thiocyanoenamines **63** and 2-aminothiazoles **64**. NBS initially reacted with enaminones **62** to give intermediate **35A**. The nucleophilic substitution of KSCN to **35A** took place and resulted in the formation of imine **35B** which tautomerized into enaminones **63**. In aprotic solvents (DMF), the intramolecular hydrogens stabilized the isomer with the *cis*-arrangement of carbonyl and amino group. However, in the protic EtOH, this hydrogen bond would be broken, and *α*-thiocyanoenamines **63** tautomerized into its isomer **35C**. The excessive NBS reacted with a trace amount of water to produce 1-hydroxy-pyrrolidine-2,5-dione and HBr. Compound **63** reacted with HBr to generate intermediate **35D**, and a subsequent intramolecular cyclization donated **35E**. The hydrogen transfer in **35E** yielded final products **64** (Scheme 35).

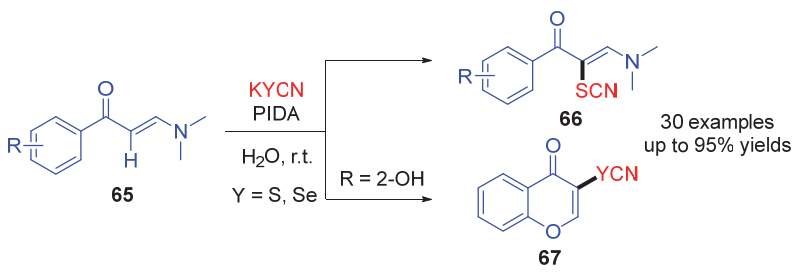
On the other hand, Zhou *et al.*[44] developed a metal-free protocol of enaminone *α*-C—H thiocyanation with PhI(OAc)$_2$ as oxidant. Depending on the structure of enaminones, various thiocyanated enaminones or chromones were synthesized in moderate to good yields. In addition, 3-selenocyanated chromones were synthesized by employing correspondingly KSeCN as the reaction partner (Scheme 36).

In 2020, Choudhury *et al.*[45] developed the additive- and metal-free methodology for the C—H thiocyanation of diverse amino (pyrazoles, isothaizoles, isoxazoles, and aminouracils) and enamines with the oxidation of H_2O_2. Interestingly, employing NaOH in one-pot enabled the tandem intramolecular annulation provided the corresponding pyrimidine-fused 2-amino thiazoles **73** in the case of aminouracils **68** (Scheme 37). The common feature of the substrates in the work was the intrinsically the enamine structure.

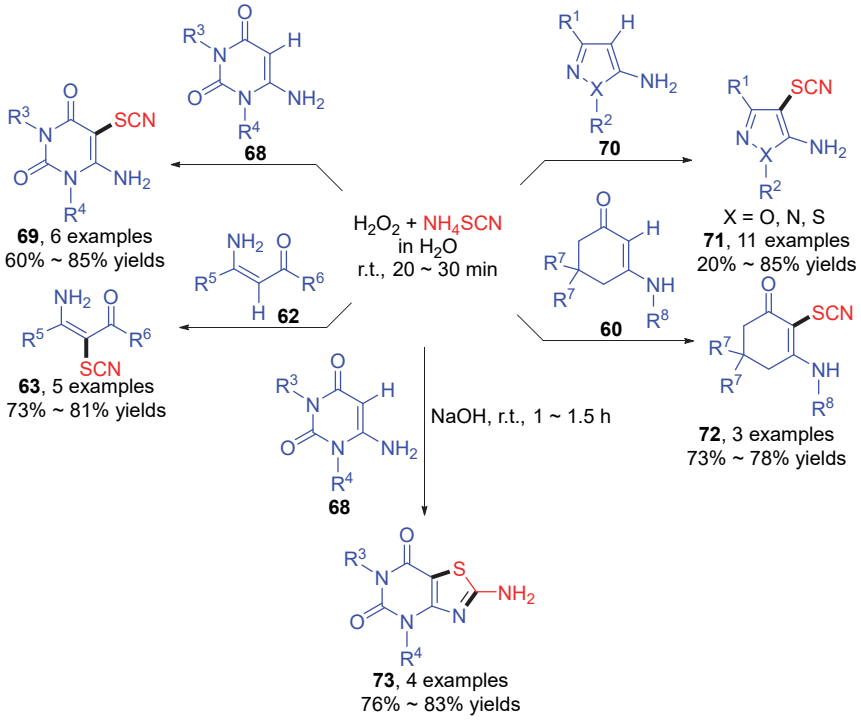
In 2019, Wan group[46] reported the first visible light induced C—H bond thiocyanation of tertiary enaminones **65** under metal-free conditions in the presence of Rose Bengal, enabling the synthesis of thiocyanated enaminones **66** and chromones **53** with NH_4SCN as the thiocyano source under air atmosphere (Scheme 38). In addition, employing



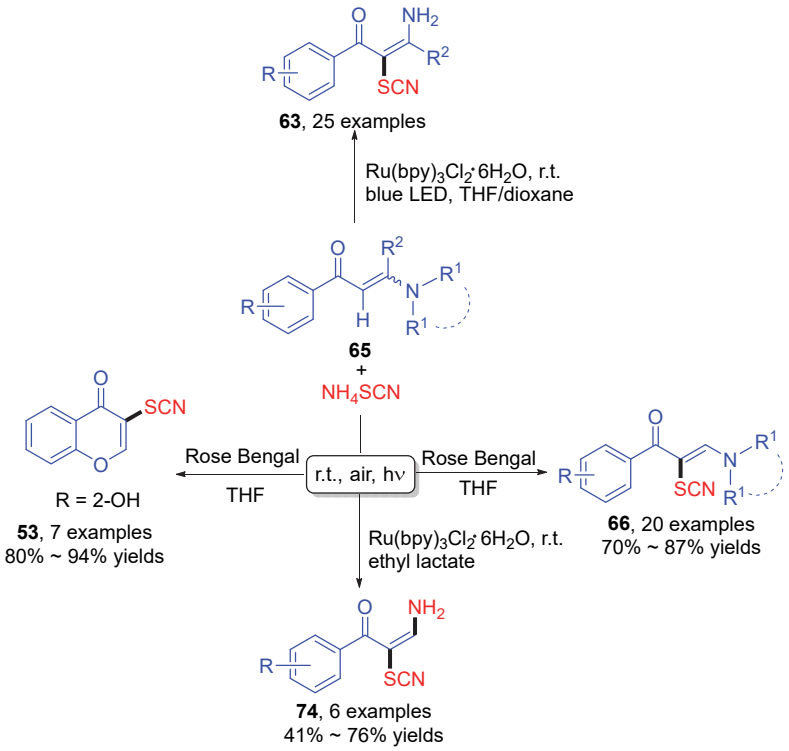
Scheme 35 Solvent-controlled synthesis of *α*-thiocyanoenamines and 2-aminothiazoles



Scheme 36 Thiocyanation of enaminones using PhI(OAc)$_2$ as oxidant



Scheme 37 Thiocyanation of diverse amino and enamine derivatives

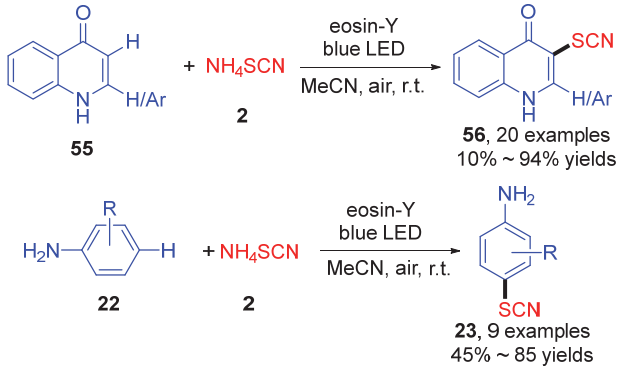


Scheme 38 Photocatalytic *α*-C—H thiocyanation of tertiary enaminones

$Ru(bpy)_3Cl_2$•$6H_2O$ as the photocatalyst switched the reaction pathway to provide NH_2-functionalized thiocyanated enamines **74** via the difunctionalization process consisting of C—H bond thiocyanation and vinyl C—N bond transamination. More recently, the direct *α*-thiocyanation of NH_2-enaminones with *β*-substitution enaminones has been realized for the first time by the same group with the catalysis of $Ru(bpy)_3Cl_2$•$6H_2O$, which led to the synthesis of products **63** with high efficiency.[47]

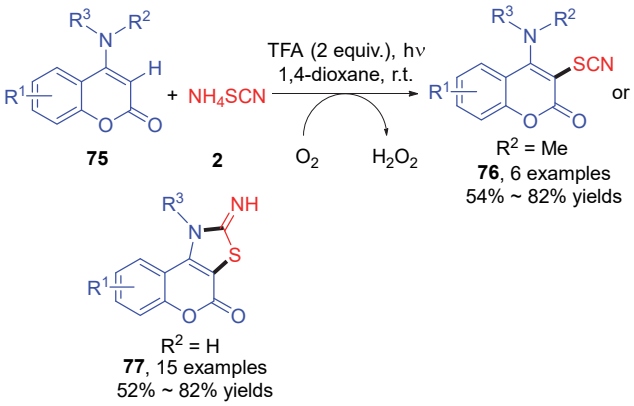
Complementarily, Jain *et al.*[48] reported the photocata-

lytic C-3 thiocyanation of quinolin-4-ones **55** in the presence of eosin-Y. The methodology allowed mild access to a variety of 3-thiocyano-quinolin-4-ones **56** with moderate to high yields. In addition, the catalytic method was also applicable for the *para*-C—H thiocyanation of anilines **22** for the synthesis of corresponding products **23** (Scheme 39).



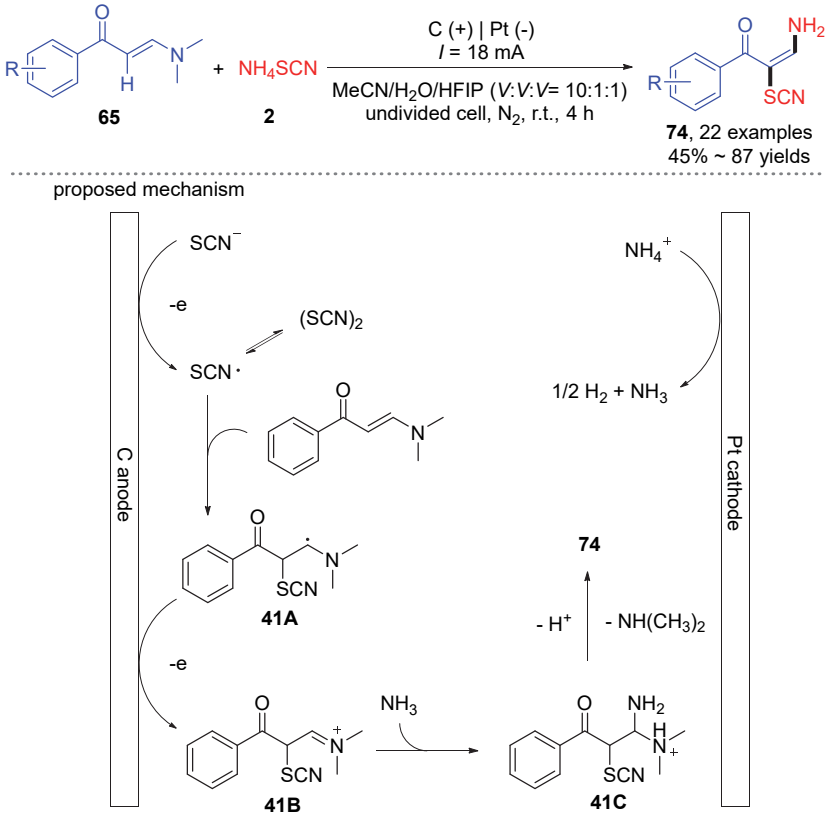
Scheme 39 Photocatalytic thiocyanation of 2-aryl-quinolin-4-ones and anilines

In 2019, Yang *et al.*[49] described the photocatalyst-free C(sp^2)—H thiocyanation reactions of 4-aminocumarins **75** with NH_4SCN under visible light irradiation. The direct thiocyanation in the enaminone structure allowed the formation of **76**. In addition, when NH-amino substrates (R^2 = H) were used, a further intramolecular nucleophilic annulation by the NH addition to C≡N bond afforded the cyclic products **77** (Scheme 40).



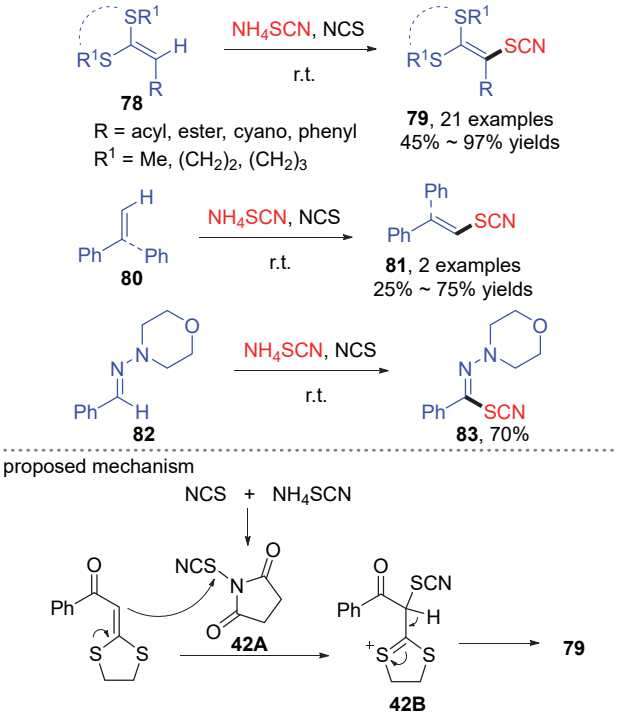
Scheme 40 Thiocyanation reaction of 4-aminocoumarins

Recently, Lei group[50] achieved the stereoselective synthesis of thiocyano enaminones by electrochemical C—H thiocyanation and C—N bond transamination (Scheme 41). The reactions of tertiary enaminones reacted with ammonium thiocyanate smoothly proceeded without employing external oxidant, electrolyte or transition metal reagent. In the reactions, SCN^- was anodically oxidized into the thiocyanyl free radical which added to the C=C double bond of enaminones to generate intermediate **41A**. Then **41A** underwent single electron anodic oxidation to provide cation intermediate **41B**, which would be easily attacked by the nucleophilic ammonium to produce the corresponding intermediate **41C**. Finally, the elimination of dimethylamine from **41C** afforded products **74**.



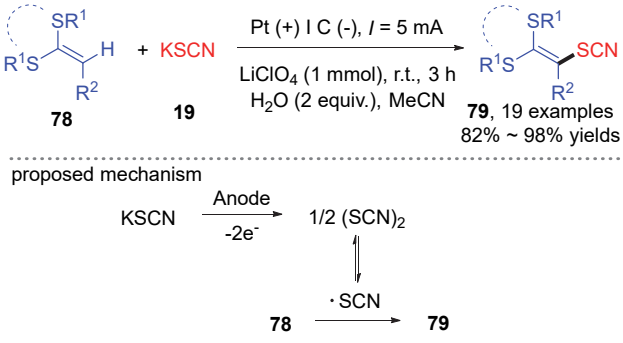
Scheme 41 Electrochemical thiocyanation and C—N transamination of enaminones

In 2016, Xu and Wang *et al.*[51] disclosed the C—H thiocyanation reactions of ketene dithioacetals **78** via the promotion of NCS by employing ammonium thiocyanate as reaction partner, leading to the synthesis of thiocyanates **79** with broad scope at room temperature. In addition, the C—H bond in terminal olefins **80** and aldehyde hydrazones **82** were also practically transformed into corresponding products **81** and **83**, respectively. The major transformation in the reactions was the generation of *N*-thiocyano succinimide **42A** via the coupling of NCS and NH_4SCN. The electrophilic C—H thiocyanation by the C—H bond and **42A** could afford **42B** which yielded products by tautomerization (Scheme 42).



Scheme 42 Thiocyanation of ketene disulfides, terminal olefins and hydrazine

In addition, Yang and Wang *et al.*[52] developed a H_2O-controlled selective thiocyanation reactions of internal olefins by electrochemical oxidation (Scheme 43). Notably, this transformation required neither additional oxidant nor

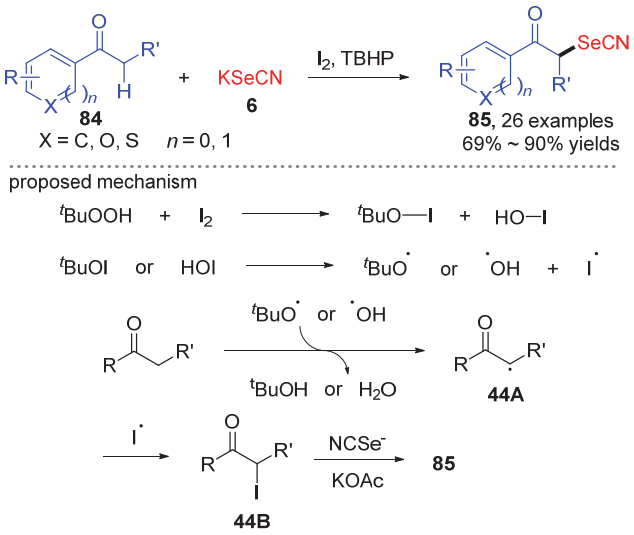


Scheme 43 H_2O-controlled selective thiocyanation of internal olefins

catalyst. Initially, KSCN could be oxidized into $(SCN)_2$ which was capable of providing thiocyano free radical by homolysis. Subsequently, the radical addition of the thiocyano radical to the C=C double bond in ketene dithioacetals **78** afforded the desired product **79** by means of cascade elimination.

4 Thiocyanation and selenocyantion of C(sp³)—H bonds

The thiocyanation of C(sp^3)—H bond is importance since such reactions provides alkyl thiocyanates. In 2017, Sun and Wang *et al.*[53] developed a method for the selenocyanation of aromatic ketones **84**. This C(sp^3)—H bond selenocyanation reactions avoided the requirement of using prior prepared *α*-halo ketone in traditional substitution protocols, providing a rapid access to the *α*-selenocyanated ketones **85**. As hypothesized, the initial reaction of ^{t}BuOOH with molecular iodine would lead to the formation of ^{t}BuOI and HOI. The homolytic cleavage of ^{t}BuOI (HOI) afforded a *tert*-butoxy (hydroxyl) free radical. The subsequent abstraction of an *α*-hydrogen from the ketone would enable the formation of the free radical intermediate **44A** accompanied by the liberation of ^{t}BuOH (H_2O). A further radical coupling of **44A** and iodine free radical gave **44B**. Finally, with the assistance of KOAc, **44B** would undergo a nucleophilic substitution with the selenocyano species to give product **85** (Scheme 44).



Scheme 44 Selenocyanation of aromatic ketones

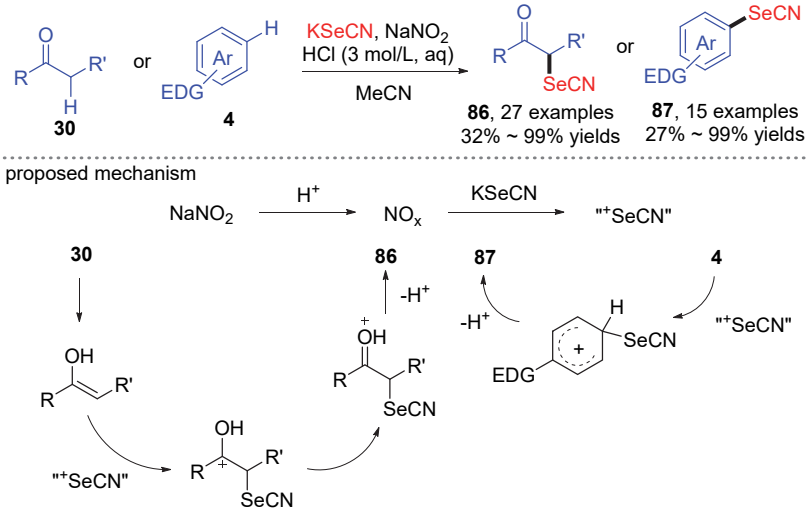
In 2020, Xiao and Huang *et al.*[54] developed a practical method for the umpolung selenocyanation of the C—H bond in aryl ketones, alkyl ketones, *β*-ketoesters and electron-rich arenes, affording various selenocyanates in moderate to excellent yields. These reactions proceeded through the nitrogen oxides-mediated electrophilic selenocyanation. Firstly, treating the sodium nitrite with aqueous hydrochloric acid afforded nitrogen oxide active species. Subsequently, $^+$SeCN ion was generated *in situ* through the reaction of nitrogen oxide and potassium selenocyanate. Fi-

nally, the α-carbonyl selenocyanates **86** and aryl selenocyanates **87** were delivered through the direct electrophilic selenocyanation of ketone α-C—H bond and the electron rich aryl C—H bond, respectively (Scheme 45).

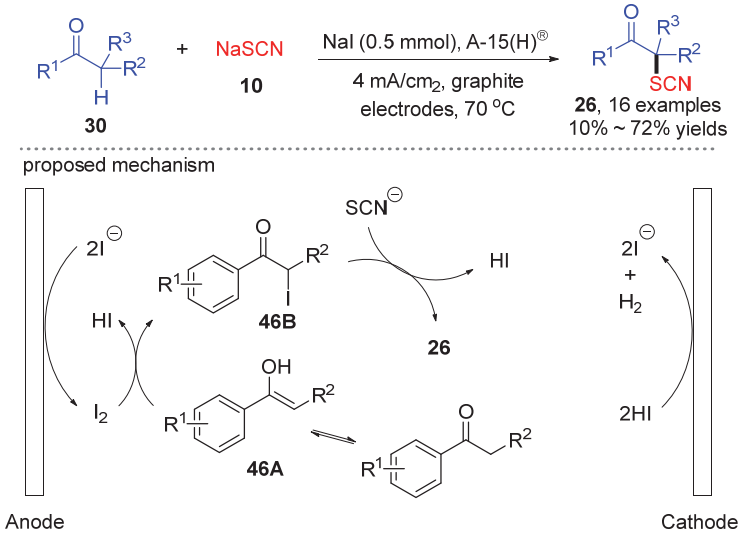
Later, Zeng and Sun *et al.*[55] developed an electrochemical method for the α-C—H thiocyanation of ketones **30** in an undivided cell under constant current condition. By using NaI as the redox catalyst and heterogeneous solid salt Amberlyst-15(*H*)® as proton catalyst, products **26** were synthesized with fair to good yields. The reaction began with the anodic oxidation of iodide ion to molecular iodine which could couple the ketone's enol isomer **46A** to form α-iodoketone **46B** along with HI. Once the key intermediate **46B** was formed, the nucleophilic substitution reaction with NaSCN **10** led to the final α-thiocyanation products **26**, accompanied with the generation of HI. Simultaneously, the *in situ* generated HI was reduced to evolve H_2 on the surface of cathode (Scheme 46).

In 2019, Xiao, Su and Yang *et al.*[56] prepared successfully a new electrophilic selenocyanating reagent, the selenocyano-benziodoxolone **90**, from 2-iodobenzoic acid **88** in two steps. A variety of α-selenocyanated ketones and β-ketoesters, including selenocyanated steroid derivatives, were achieved in good to excellent yields by using this selenocyanating reagent and simply grinding substrates under mild conditions. As for the mechanism, the selenocyanation reagent **90** was first attacked by enamine **47A** via an S_N2-like transition state to produce imine **47B** and 2-iodobenzoic acid **88**. Subsequently, the hemiaminoacetal **47C** was generated via hydrolysis, extruding $AcNH_2$ to deliver the products **93** (Scheme 47).

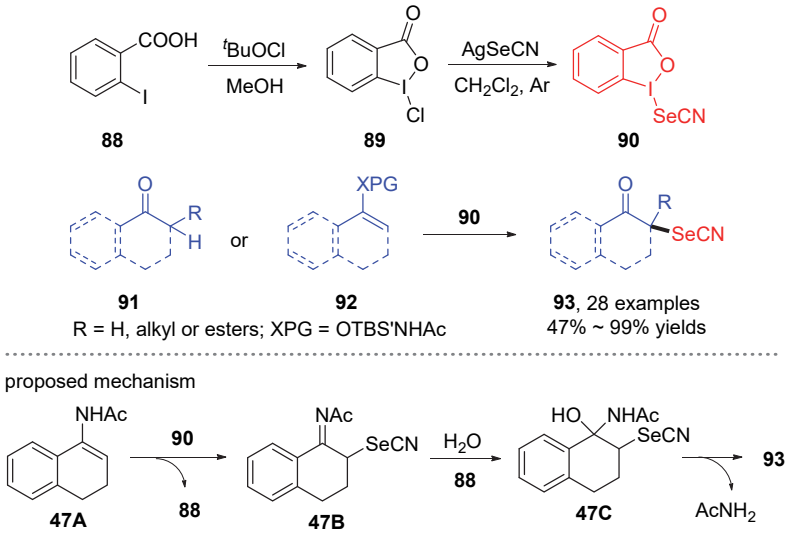
In 2020, Xu and Ding *et al.*[57] established an approach toward the synthesis of thiocyano pyrazoles by the direct thiocyanation of pyrazolin-5-ones **94**. A series of 4-thiocyanated 5-hydroxy-1*H*-pyrazoles **95** were synthesized in fair to good yields by $K_2S_2O_8$-promoted direct thiocyanation of pyrazolin-5-ones **94** with NH_4SCN (**2**) at room temperature. The generation of thiocyano free radical in the



Scheme 45 Electrophilic selenocyanation of different C(sp^3)—H and C(sp^2)—H bonds

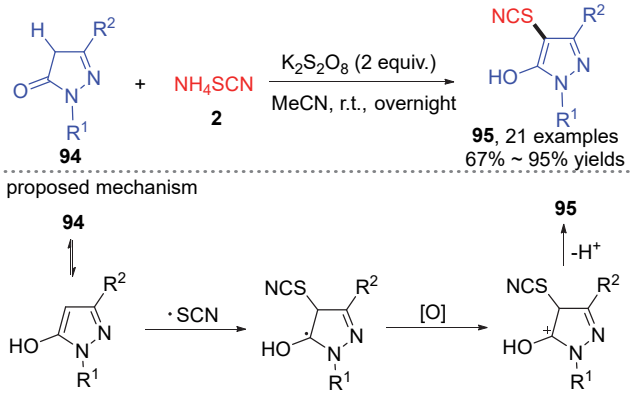


Scheme 46 Electrochemically thiocyanation of ketones



Scheme 47 Selenocyanation of ketones, *β*-keto esters and enamides silyl enolates

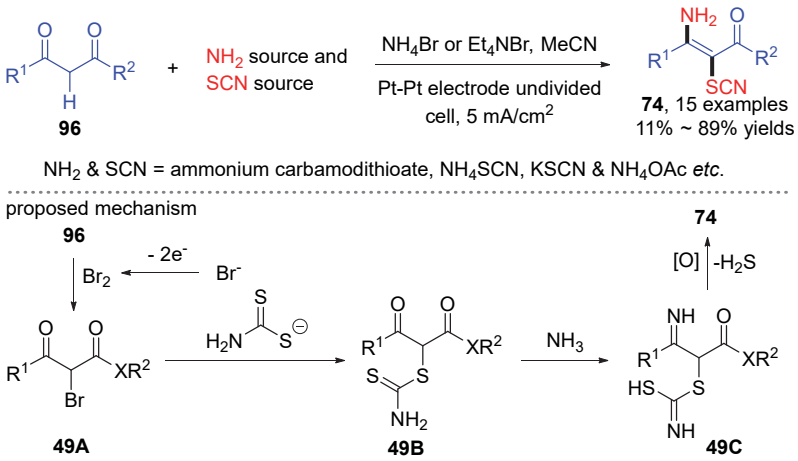
presence of $K_2S_2O_8$ was proposed as the initial step. The subsequent free radical addition, SET oxidation as well as deprotonation could provide the target product (Scheme 48).



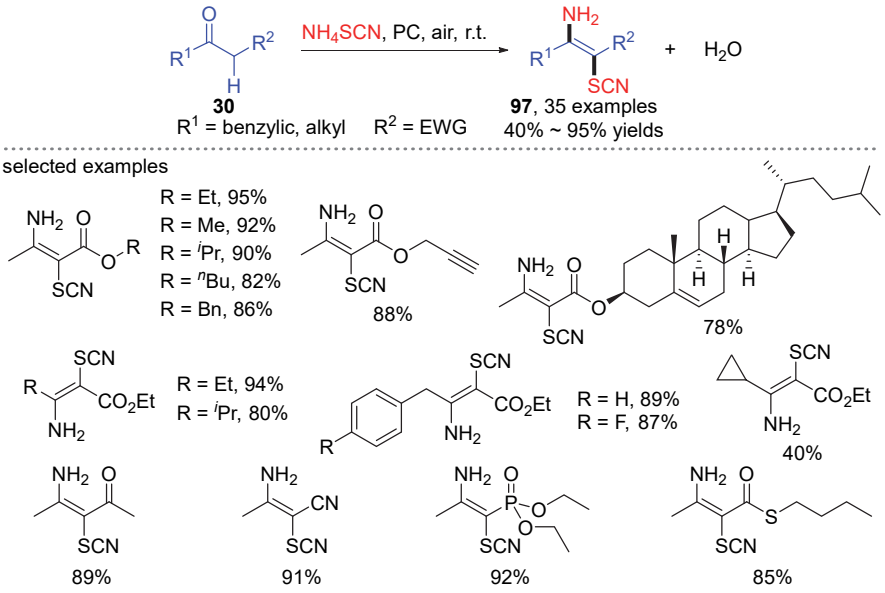
Scheme 48 Thiocyanation of pyrazolin-5-ones

In 2016, Zeng *et al.*[58] developed a electrochemical method for the synthesis of thiocyano enaminones **74**. To access products with diversity, different "SCN" and "NH_2" sources or combinatorial sources such as ammonium carbamodithioate, NH_4SCN and KSCN/NH_4OAc *etc*. were employed depending on the target products. Generally, the reactions started from the electrode oxidation of bromine anion to molecular bromine via paired electron transfer. The methylene C(sp^2)—H bond in diketones **96** was then brominated to provide **49A**. The nucleophilic substitution of the carbamodithioate to the C—Br bond afforded intermediate **49B**. With a followed ammonium elimination, **49C** was generated. The subsequent extrusion of H_2S and oxidation then yielded **74** (Scheme 49).

Later, Liu *et al.*[59] reported a direct photocatalytic, aerobic synthesis of similar polyfunctionalized alkenes **97** by reacting functionalized ketones **30** with NH_4SCN. Beside the sustainable and mild photocatalytic conditions, this work also featured the advantage in releasing water as the only by-product (Scheme 50).

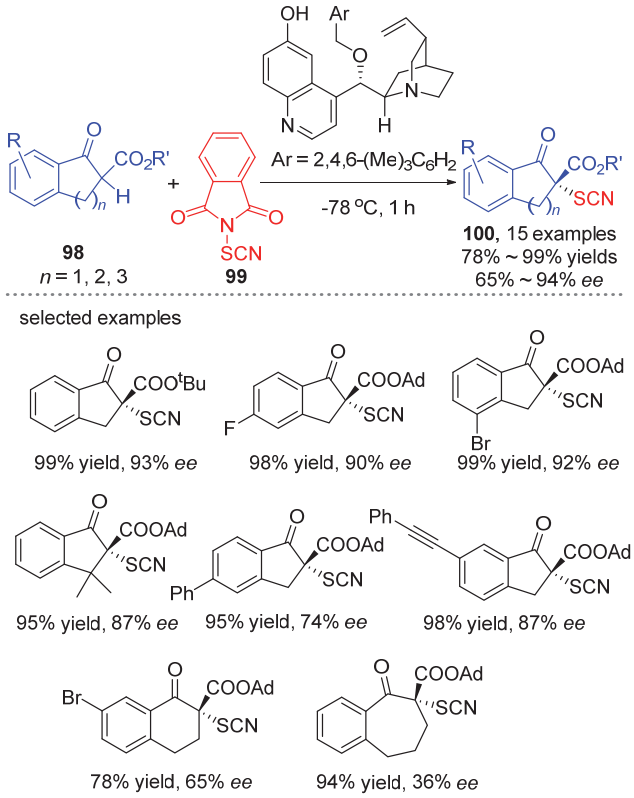


Scheme 49 Paired electrochemical thiocyanation of 1,3-diketones



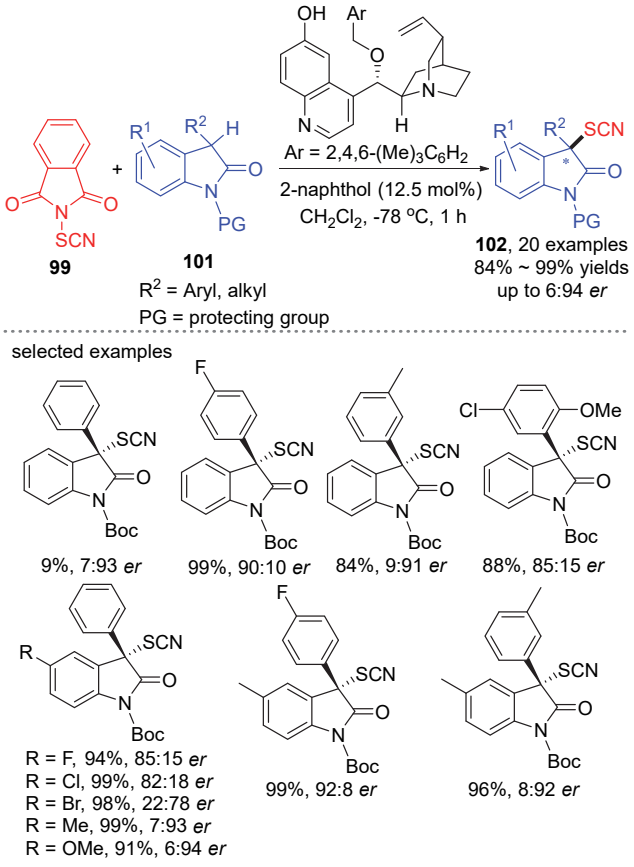
Scheme 50 Photocatalytic thiocyanation of ketones

On the other hand, Chen *et al.*[60] developed the asymmetrical C—H bond thiocyanation for the synthesis of thiocyanated products **100** by the reactions of cyclic ketoesters **98** and NTS **99** in the presence of a chiral cinchona alkaloid organocatalyst (Scheme 51). By running the reaction at −78 ℃, the products were acquired with good to excellent yields (up to 99%) and high enantioselectivity (up to 94% *ee*).



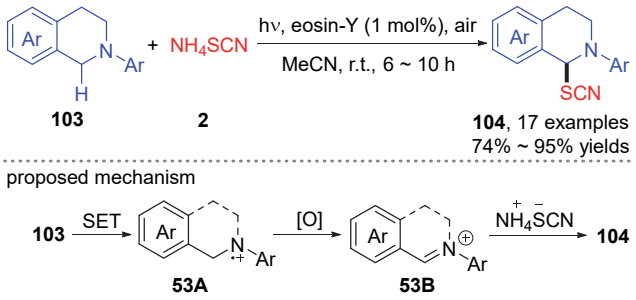
Scheme 51 Organocatalytic α-thiocyanation of cyclic β-ketoesters

In addition, the same group[61] also expanded the organic catalytic C—H thiocyanation to oxindoles **101** with the same thiocyano reagent and organocatalyst (Scheme 52). Various enantioenriched 3,3'-disubstituted oxindoles **102** were synthesized in generally excellent yields and satisfactory enantioselectivity (up to 6∶94 *er*).



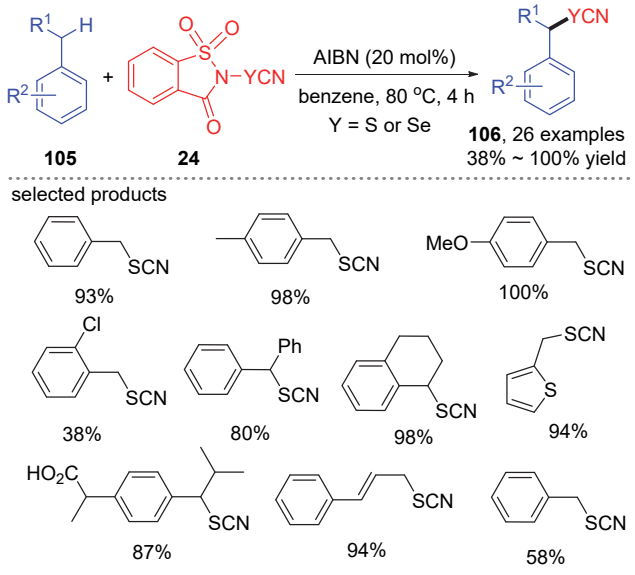
Scheme 52 Organocatalytic asymmetric α-thiocyanation of oxindoles

In 2015, Yadav *et al.*[62] reported the photocatalytic, aerobic oxidative α-C(sp^3)—H thiocyanation of tertiary amines **103** with eosin-Y as the photocatalyst. As proposed, the visible light promoted SET oxidation of amine **103** under air to give radical cation **53A** which underwent further oxidation to iminium cation **53B**. The nucleophilic addition of the thiocyano anion to the **53B** provided products **104** (Scheme 53).



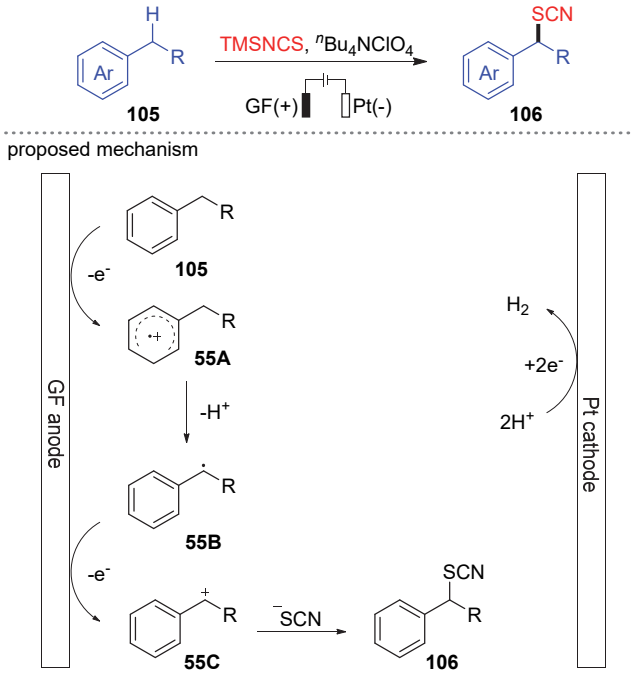
Scheme 53 Visible-light-induced α-C(sp^3)—H thiocyanation of tertiary amines

In 2021, Chen *et al.*[63] disclosed a method for the thiocyanation of benzyl C—H bond. With the thiocyanating reagent **24**, benzyl C—H bond donors **105** underwent thiocyanation to provide benzyl thiocyanates **106** in the presence of azodiisobutyronitrile (AIBN) by heating at 80 ℃ (Scheme 54). The results reported therein proved the broad tolerance of this method to the benzylic C—H bonds in different carbon aryl- and heteroaryl-based systems. The product resulting from the reaction of *p*-methoxyl toluene was obtained with up to 100% yield. Besides thiocyanation, the equivalent C — H selenocyanation by using *N*-selenocyanatosaccharin was also practical. Moreover, the allylic C—H bond could also be transformed into corresponding C—SCN bond under the standard reaction conditions.



Scheme 54 AIBN-initiated direct thiocyanation of benzylic C—H bond

Later, Wen and Guo *et al.*[64] also reported the benzylic C(sp^3)—H thiocyanation by means of electrochemical reactions. This protocol exhibited a unique site selectivity between different benzylic C—H bonds in one substrate (2°＞3°＞1°). As hypothesized, the reactions therein proceeded through a radical-polar crossover pathway. Initially, SET anodic oxidation on substrate **105** generated a radical cation **55A**. By releasing a proton, the benzylic radical intermediate **55B** was formed. This intermediate was further oxidized at the anode to form a carbocation **55C** via SET. Finally, intermediate **55C** was trapped by the thiocyanate anion to produce the corresponding thiocyanate **106** (Scheme 55).

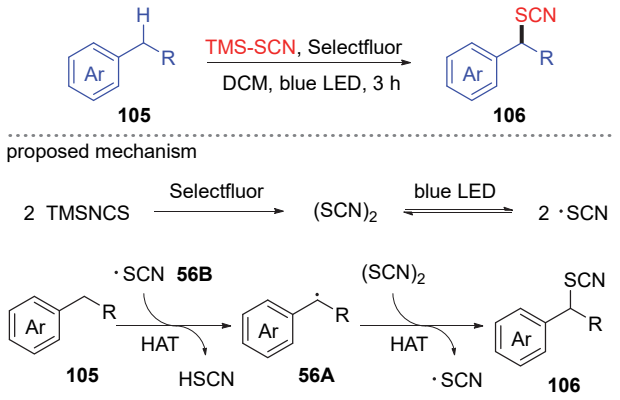


Scheme 55 Electrochemical thiocyanation of benzylic C—H bonds

Rather recently, Murakami *et al.*[65] reported a protocol of photo-induced benzylic C—H thiocyanation. The reaction of **105** with TMS-SCN was performed in the presence of selectfluor under blue LED irradiation. The reaction began with the oxidation of selectfluor to TMS-SCN to generate thiocyanogen via dimerization. The resulting thiocyanogen was able to donate thiocyanate radical under blue light irradiation. Subsequently, radical abstracted a hydrogen from the benzyl C—H bond to produce a benzyl free radical **56A**. Finally, the trapping of benzyl radical **56A** by thiocyanogen gave the desired thiocyanate **106** and release thiocyano free radical for repeated reaction rounds (Scheme 56).

5 Conclusions and outlook

Conclusively, as the environmentally benign and atom economic strategy, the transition metal-free thiocyanation/selenocynation reactions have emerged as favorable optional



Scheme 56 Photo-induced benzylic C—H thiocyanates

in the synthesis of thio-/selenocyanated molecules or other compounds resulting from the cascade annulation based on the thiocyanation/selenocyanation. As current state-of-art, the thiocyanation have been proved to be practical with conventional heating chemistry, as well as the energy source economical photocatalysis and electrochemical transformation, enabling the transformation of C(sp^3)—H and C(sp^2)—H bonds to different thiocyanates or derived heterocycles. Yet, the known results indicate the fact that the transition metal-free thiocyanation of inactivated C—H bond, including aryl and alkenyl C—H is yet a challenge. In addition, the synthesis of alkynyl thiocyanate by corresponding C(sp)—H bond has not yet been realized, either. In terms of the cascade reactions initiated by the C—H thiocyanation, the chromones and thiozoles are the major heterocyclic products in the known reported. Therefore, developing applicable method for the metal-free thiocyanation/selenocyanation in inactivated C—H bonds, as well as the construction of more diversified heterocyclic scaffolds by cascade reactions involving such transition metal-free thiocyanation consists of the major issues to address in this domain.

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