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POTASSIUM THIOCYANATE AS A VERSATILE INORGANIC SURROGATE FOR HETEROCYCLIC SYNTHESIS: A DECADE REVIEW

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ABSTRACT: Potassium thiocyanate (KSCN), an inexpensive and readily available inorganic source of the thiocyanate ion, has emerged as a practical and sustainable surrogate in heterocyclic synthesis. Owing to its unique ambident nucleophilicity, KSCN enables the construction of both C–S and C–N bonds, unlocking diverse mechanistic pathways such as oxidative cyclization, radical annulation, electrophilic substitution, and metal-catalyzed cross-coupling. This review summarizes with a focus on the development of KSCN-infused strategies for heterocycle construction over the past decade. The broad substrate tolerance, operational simplicity, and high atom economy of these methods highlight KSCN's growing role as a versatile reagent in modern synthetic organic chemistry.

KEYWORDS: Potassium thiocyanate, Heterocycles, Thiocyanation, C-N bod formation, C-S bond formation.

INTRODUCTION:

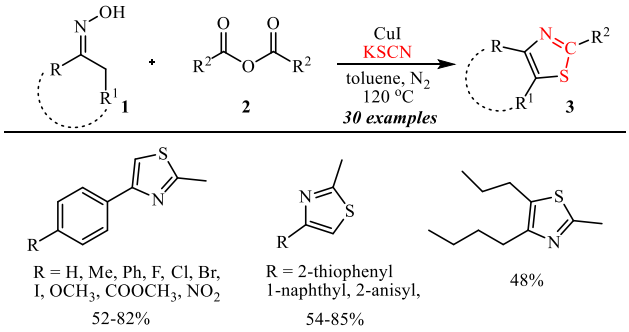
Heterocycles represent one of the most important classes of structural scaffolds in chemistry, with widespread applications in natural products, pharmaceuticals, agrochemicals, and functional materials.[i] Their remarkable diversity arises from the strategic incorporation of heteroatoms such as nitrogen, oxygen, and sulfur. Among these, nitrogen- and sulfur-containing heterocycles hold special significance due to their broad spectrum of biological and pharmacological activities.[ii] The assembly of these skeletons predominantly requires reagents capable of introducing both sulfur and nitrogen in a regioselective and controlled manner. The thiocyanate anion (SCN^-) is particularly well suited to this challenge owing to its ambident nucleophilicity, and it can be used as a bifunctional synthon for the formation of C–S and C–N bonds. Classical organic thiocyanates and thioureas have been used as SCN sources; however, these reagents are often marred by issues of limited availability, rising cost, and reduced operational stability.[iii]

Inorganic thiocyanates, particularly potassium thiocyanate (KSCN), have emerged as practical, inexpensive, and environmentally benign alternatives.[iv] It is readily available, thermally stable, and compatible with a wide range of reaction conditions via ionic as well as free-radical pathway. Its ambident reactivity established through nucleophilic attack either via sulfur or

nitrogen enables multiple mechanistic pathways, including oxidative cyclization, electrophilic substitution, radical-mediated annulation, and metal-catalyzed cross-coupling. Recent advances in catalytic systems, green oxidation protocols, and multicomponent strategies have significantly extended the scope of KSCN-mediated heterocycle synthesis, allowing rapid assembly of structurally diverse frameworks under mild and sustainable conditions. In the last two decades inorganic thiocyanates witnessed a paradigm shift, driven by the integration of KSCN into modern synthetic strategies such as visible-light photocatalysis, electrochemical oxidation, transition-metal catalysis, and solvent-free or aqueous-phase transformations.[v] These developments have not only expanded the diversity of accessible heterocyclic scaffolds but have also aligned SCN chemistry with the principles of green and sustainable synthesis. While many thiocyanate-based transformations have been described in recent years, only a limited number of reviews have focused on inorganic surrogate in heterocyclic synthesis, underscoring the need for a comprehensive summary of this area.[vi] To bridge this gap, we provide an exclusive survey of notable methodologies reported since 2016 that utilize KSCN as an only inorganic "SCN" or "S" source for heterocycle synthesis.

Synthesis of copper catalyzed thiazole derivatives (2016):

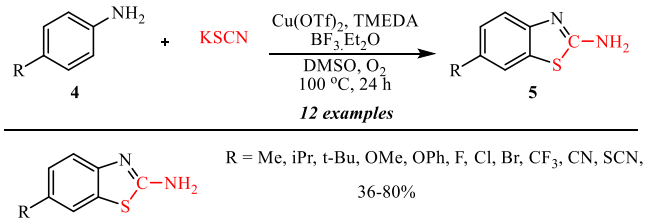
Jiang and co-workers reported a convenient protocol for the synthesis of thiazoles (**3**) through a copper-catalyzed [3+1+1] cyclization of oximes (**1**), anhydrides (**2**), and KSCN (Scheme **1**).[vii] The transformation proceeds via N–O and C–S bond cleavage, accompanied by C–S and C–N bond formation, as well as activation of the vinyl C-(sp^2) bond. Control experiments indicated that the reaction follows a free-radical pathway involving redox processes.



Scheme 1. Copper catalyzed thiazole derivatives

Synthesis of 2-aminobenzothiazoles (2016):

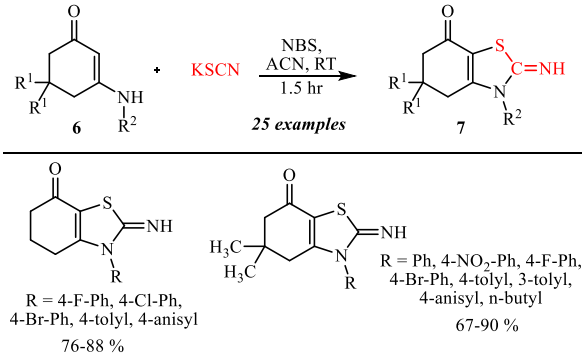
H. Jiang and co-workers developed a copper-catalyzed [3+1+1] aerobic oxidative regioselective thiocyanation of anilines (**4**) to access 2-aminobenzothiazoles (**5**) (Scheme **2**).[viii] This protocol shows good tolerance toward both electron-donating/-withdrawing substituents on a variety of anilines, delivering products in moderate to good yields. Mechanistic investigations suggest that the reaction proceeds through a copper-mediated single electron transfer (SET), where Cu(II) generates a thiocyanate radical. This radical is further captured by electron-rich aniline, and subsequent aromatization along with catalyst regeneration facilitated by the DMSO/O_2 system.



Scheme 2. Copper catalyzed synthesis of 2-aminobenzothiazoles

Synthesis of 2-iminothiazoles (2017):

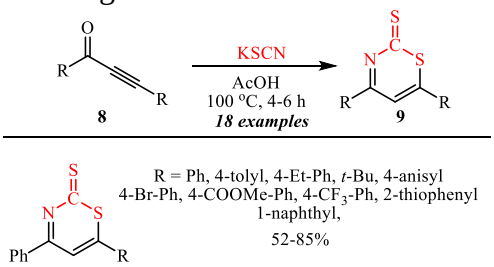
Xue-Bing Chen and co-workers reported a catalyst-free, cascade protocol for the regioselective synthesis of 2-iminothiazoles (**7**) from enaminones (**6**), *N*-bromosuccinimide (NBS) and KSCN (Scheme **3**).[ix] The reaction proceeds via α-bromo enaminone intermediates, followed by thiocyanation and intramolecular cyclization, efficiently forming C–N and C–S bonds under mild conditions. This operationally simple method shows broad substrate scope and provides access to biologically relevant thiazole scaffolds.



Scheme 3. Synthesis of 2-iminothiazoles via enaminones

Synthesis of thiazine-2-thiones (2017):

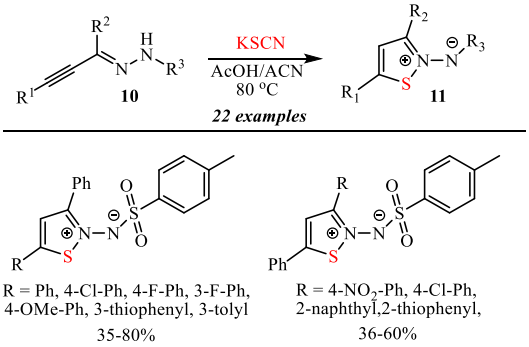
Maddi Sridhar Reddy and co-workers developed a diversity-oriented strategy for the synthesis of thiazine-2-thiones (**9**) from ynones **8** (**Scheme 4**).[x] This method involves thiocyanate addition to ynones followed by a thiocyanative cyclization. This tandem reaction proceeds efficiently across a broad range of substrates, affording the desired products in good to excellent yields. Furthermore, the resulting thiazine-2-thiones could be transformed into valuable isothiazole scaffolds through an iodine-mediated de-thio-carbonylation.



Scheme 4. Synthesis of thiazine-2-thiones from enaminones

Synthesis of N-iminothiazoliumylides (2018):

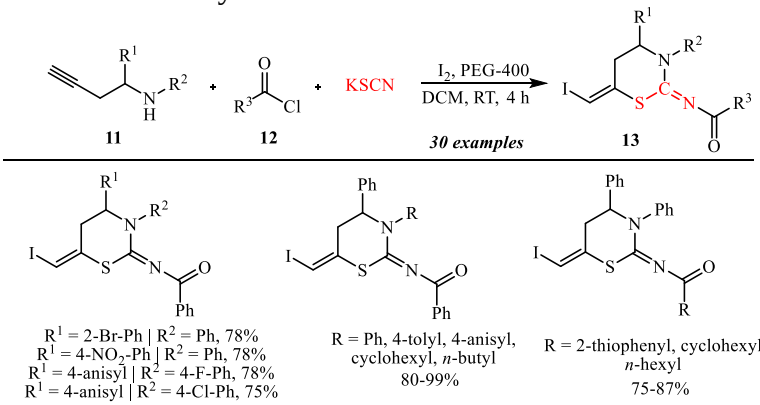
In 2018, Shen-Yi Wang and Shun-Jun Li co-workers developed a [4+1] cycloaddition strategy for the regioselective synthesis of *N*-iminoisothiazolium ylides (**10**) from *α,β*-alkynic hydrazones (**11**) and KSCN (**Scheme 5**).[xi] The method employs readily available precursors and delivers 22 examples in moderate to good yields, and also expanding access to useful isothiazolium scaffolds.



Scheme 5. Synthesis of N-iminoisothiazolium ylides from α,β-alkynic hydrazones

Synthesis of thiazine imides (2018):

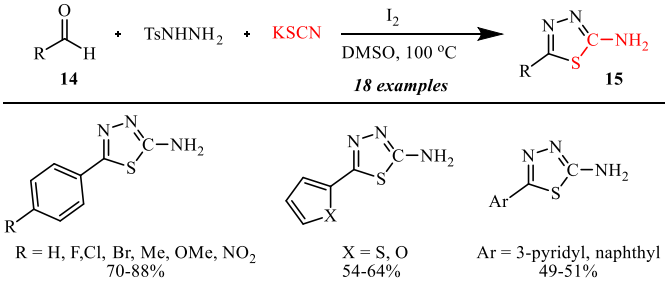
Jing Li and co-workers reported a metal-free, four-component cascade reaction of homo propargylic amines (**11**), acyl chlorides (**12**), KSCN, and iodine molecule to access thiazine imides **13** (Scheme **6**).[xii] The process involves a 6-*exo-dig* iodothiolation–cyclization, forming four new bonds in one pot under mild conditions with broad substrate scope and good atom economy. The products bear an exocyclic vinyliodide group, offering opportunities for further derivatization into diverse heterocycles.



Scheme 6. Synthesis of thiazine imides via multicomponent strategy

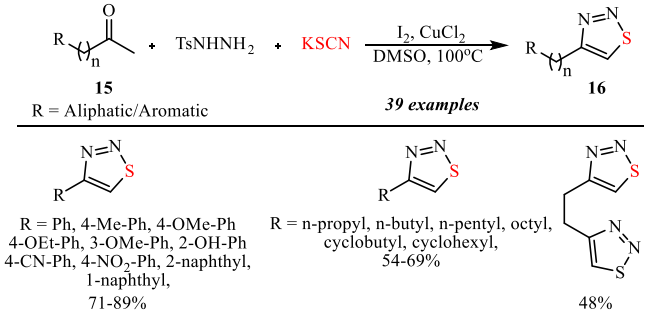
Synthesis of Iodine promoted 2-aminothiadiazoles (2019):

In 2019, Sen Lin and co-workers described an iodine-promoted multicomponent strategy for the synthesis of thiadiazole derivatives (**15**) from aromatic aldehydes (**14**), KSCN, and *p*-toluenesufonyl hydrazide (Scheme **7**).[xiii] The reaction, performed at 100 °C using DMSO as a solvent, proceeds efficiently with aromatic aldehydes bearing both electron-donating and electron-withdrawing substituents, affording products in 49–88% yield. Notably, the protocol was successfully extended to gram-scale synthesis, highlighting its synthetic practicality.



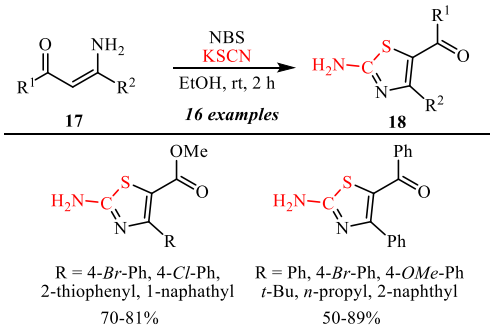
Scheme 7. Iodine-promoted synthesis of 2-aminothiadiazoles

Synthesis of 1,2,3-thiadiazoles (2019):
In 2019, An-Xin Wu and co-workers reported a one-pot, three-component synthesis of thiazoles (**16**) from aliphatic/aromatic ketones (**15**), *p*-toluenesulfonyl hydrazides, and KSCN under copper catalysis (Scheme **8**).[xiv] The reaction exhibited 39 examples with broad substrate tolerance, delivering the desired products in good yields. Importantly, the strategy was successfully applied to the natural product pregnenolone acetate, affording the corresponding thiazole derivative in good yield.



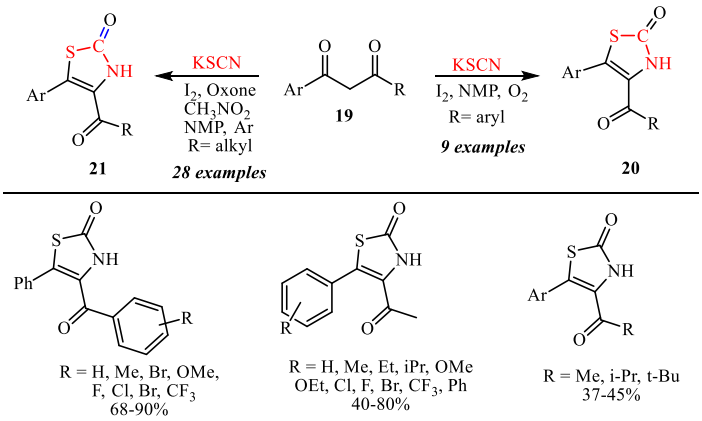
Scheme 8. Copper catalyzed synthesis of 1,2,3-thiadiazoles

Synthesis of 2-aminothiazoles (2019):
Xiyuan Duan and his research team presented an efficient protocol for the synthesis of 2-aminothiazoles (**18**) from enaminones (**17**), KSCN, and NBS (Scheme **9**).[xv] This divergent strategy proceeds under mild conditions, with simple operation, short reaction times, and offers 16 examples in good yields (50–89%). Interestingly, by altering the solvent, the method could also be tuned to afford thiocyanated enaminones, highlighting its diversity.



Scheme 9. Synthesis of 2-aminothiazoles

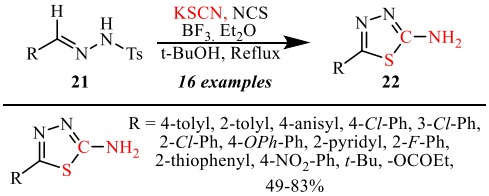
Synthesis of Thiozol-2(3*H*)-one derivatives (2021):
Rulong Yan and co-workers reported an iodine-catalyzed [3+2] cyclization of 1,3-diketones (**19**) with KSCN for the synthesis of thiazole-2(3*H*)-one (**20** & **21**) derivatives (Scheme **10**).[xvi] The reaction, performed at 140 °C in a mixed solvent system of *N*-methyl-2-pyrrolidone and nitromethane, employed iodine as the promoter with oxygen as the oxidant for aryl substrates, while Oxone was used for alkyl analogues. The protocol tolerated both electron-donating and electron-withdrawing substituents on the phenyl ring, although sterically hindered substrates provided comparatively lower yields.



Scheme 10. Iodine-catalyzed synthesis of thiazole-2(3*H*)-one from 1,3-diketones

Synthesis of 1,3,4-dithiazoles (2021):

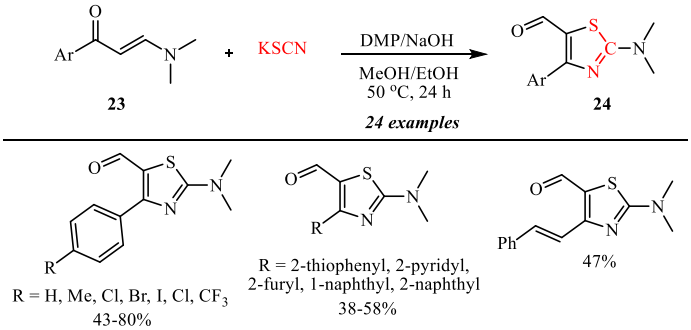
Meng Tang research group developed a diversity-oriented synthesis of 1,3,4-thiadiazol-2-amines (**22**) from *N*-tosylhydrazones (**21**) and KSCN in the presence of *N*-Chloro succinimide/$BF_3.Et_2O$ giving 16 examples in good yields (Scheme **11**).[xvii] The mechanistic studies revealed that the reaction proceeds via initial formation of *N*-tosylhyrazonoyl chloride followed by N-tosylhydrazonyl iminium salt formation (aided by $BF_3.Et_2O$), intramolecular cyclization, detosylation and 1,3-*H* shift.



Scheme 11. Diversity oriented synthesis of 1,3,4-dithiazoles

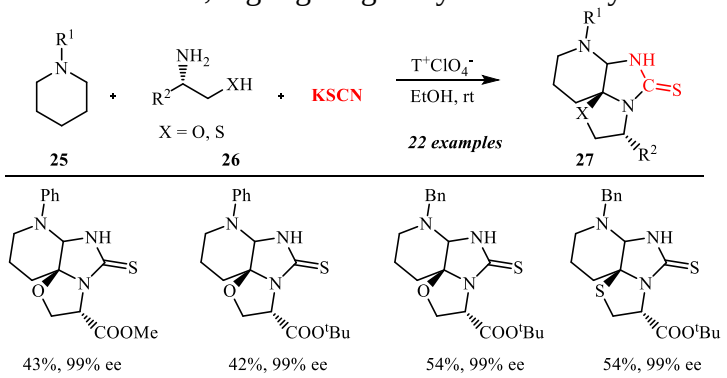
Synthesis of 5-thiazole-carbaldehyde (2022):

Liu, Wan, and co-workers developed a strategy for the synthesis of thiazole-5-carbaldehydes (**24**) via the annulation of enaminones (**23**) with KSCN using Dess–Martin periodinane (DMP) as the oxidant (Scheme **12**).[xviii] This high atom-economy protocol constructs the thiazole core and introduces an aldehyde functionality in a single step. The method exhibits broad substrate scope, tolerating diverse functional groups and substituents. Furthermore, the resulting heteroaryl aldehydes could be easily functionalized into various scaffolds underscoring the synthetic versatility.



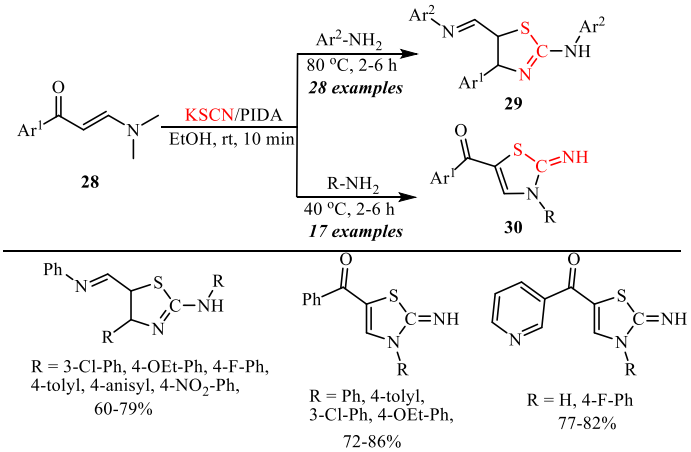
Scheme 12. Synthesis of 5-thiazoles carbaldehyde from enaminones

Synthesis of α, β-multifunctionalized azaheterocycles (2022):
Xuesen Fan et.al., reported a multicomponent strategy for the multiple C(sp^3)–H bond functionalization of saturated cyclic amines (**25**) via oxoammonium salt-promoted oxidation, generating a *β*-oxo cyclic iminium ion as the key intermediate (Scheme **13**).[xix] This species undergoes cascade addition with KSCN and aminoethanols or aminoethanethiols (**26**) in ethanol, furnishing *α,β*-multifunctionalized azaheterocycles (**27**). Remarkably, when cysteine or serine esters were employed as nucleophiles, the protocol delivered chiral spiro-aza polyheterocycles with excellent diastereoselectivity (>20:1 *dr*) and enantioselectivity (up to 99% *ee*). Furthermore, this method have significant potential for late-stage functionalization of diverse natural product derivatives, highlighting its synthetic utility.



Scheme 13. Synthesis of α,β-multifunctionalized azapolyheterocycles

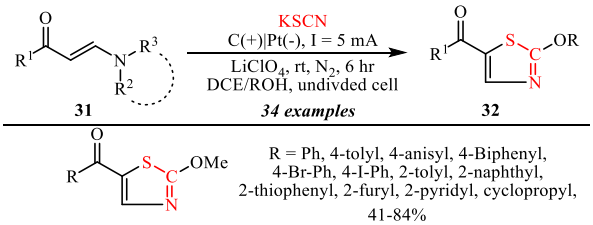
Temperature controlled synthesis of 2-aminothiazole/2-iminothiazolines (2022):
Jun Lin and co-workers reported a temperature-controlled synthesis of 2-amino thiazoles (**29**) and 2-iminothiazolines (**30**) from tertiary enaminones (**28**), anilines and KSCN using phenyliodine (III) diacetate oxidant (Scheme **14**).[xx] Interestingly, at high temperature, the reaction yields 2-amino thiazoles and low temperature yields 2-imino thiazolinos. Controlled experiments revealed that the radical intermediate generated converted into aminothiazoles via thermodynamic controlled and iminothiazoles via kinetic controlled.



Scheme 14. Temeprature controlles synthesis of 2-aminothiazoles/2-iminothiazolines

Electrochemical synthesis of 2-alkoxythiazoles (2023):
In 2023, Dandan Li and Jiangwei Wen group were investigated the electrochemical equipped synthesis of 2-alkoxy thiazoles (**32**) from enaminones (**32**), KSCN, and alcohols (Scheme

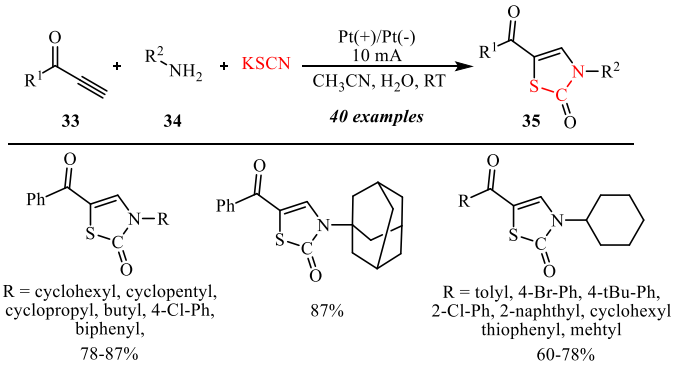
15).[xxi] This straightforward reaction proceeds seamlessly proceeds with 34 examples containing various functional groups/substituents.



Scheme 15. Electrochemical synthesis of -alkoxythiazoles

Synthesis of thiazole-2(3*H*)-ones (2024):

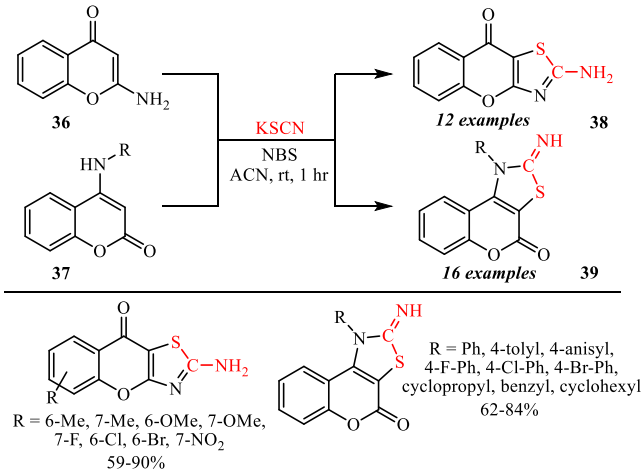
Youghui-He et.al., reported an electrocatalytic oxidative C-H bond thiolation and nucleophile cascade cyclization via [2+2+1] type from alkynones (**33**), amines (**34**), water and KSCN (Scheme **16**).[xxii] This protocol proceeds with various substituents and functional groups under mild conditions with short time.



Scheme 16. Electrocatalytic oxidative synthesis of thiazole-2(3H)-ones

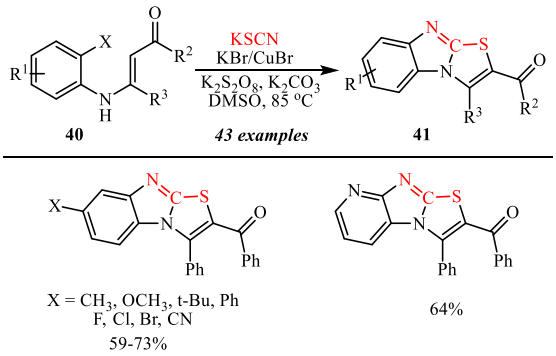
Synthesis of 2-amino/imino thiazolo fused chromene/coumarin (2024):

Nakula Shankariah and co-workers developed a tandem strategy for the synthesis of 2-amino/imino-fused chromene and coumarin scaffolds (**38** and **39**) from chromenes (**36**) and coumarins (**37**) using KSCN in the presence of NBS as an oxidant (Scheme **17**).[xxiii] The protocol employs simple reaction conditions and delivers the target products in good yields. Notably, the scalability of the method was demonstrated through gram-scale synthesis, while control experiments indicated that the transformation proceeds via an ionic mechanism.



Scheme 17. Synthesis of 2-amino/inimo thiazolo fused chromene/coumarin scaffolds

Synthesis of benzoimidazo[2,1-*b*]thaiazoles (2025):
Jinali Li and co-workers reported a synthesis of benzimadazo[2,1-*b*]thiazoles (**41**) via tandem insertion of thiocyanate to aryl enaminones (**40**) via Buchwald type copper catalysed C-N coupling reaction (Scheme **18**).[xxiv] This strategy well tolerates with various substituents giving 43 examples in good yields.



Scheme 18. Synthesis of benzimadazo[2,1-*b*]thiazoles from enaminones

CONCLUSION:

In summary, KSCN has established itself as a versatile, inexpensive, and sustainable reagent for the synthesis of diverse heterocyclic frameworks. Its unique ambident reactivity enables the efficient construction of both C–S and C–N bonds and seamlessly incorporating the sulfur atom, unlocking a wide range of mechanistic pathways such as oxidative cyclization, radical annulation, electrophilic substitution, metal-catalyzed cross-coupling and electrochemical pathway. The methods documented here developed over the past decade highlight its broad substrate tolerance, operational simplicity, and compatibility with green chemistry principles. The continued exploration of KSCN in combination with modern catalytic and electrochemical strategies is expected to further expand its role in heterocyclic chemistry, providing innovative and eco-friendly routes to biologically and functionally important molecules.

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