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Review

Recent Approaches in Transition Metal-Catalyzed Chalcogenative Heteroannulation of Alkenes and Alkynes

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Abstract: Organochalcogen-bearing heterocycles are important scaffolds in compounds under the spotlight of scientific interest in optoelectronic fields and for biological applications. The use of transition metals has been a versatile and reliable way to carry out the synthesis of these molecules efficiently, delivering products in high yields and with a wide functional diversity. In the last 10 years, many classes of heterocycles have been synthesized under the cyclization reaction of acyclic alkenes and alkynes with the incorporation of a chalcogen atom on its structure. Transition metal catalysts including Cu, Co, Pd, Ni, In, Ag, and Fe salts have been used in the development of new methodologies, the expansion of substrate scope, and mechanistic studies. This review provides an overview of these recent approaches with the aim of being a useful resource for interested researchers in this area.

Keywords: catalysis; cyclization reaction; heterocycles; organochalcogen; transition metal

Citation: Gutterres, E.L.; Anjos, T.; Santos, F.B.; Bandeira, P.T.; Penteado, F.; Schumacher, R.F. Recent Approaches in Transition Metal-Catalyzed Chalcogenative Heteroannulation of Alkenes and Alkynes. *Catalysts* **2023**, *13*, 1300. https://doi.org/10.3390/catal13091300

Academic Editors: Lianghua Zou and Xiaofeng Xia

Received: 8 August 2023
Revised: 7 September 2023
Accepted: 14 September 2023
Published: 16 September 2023

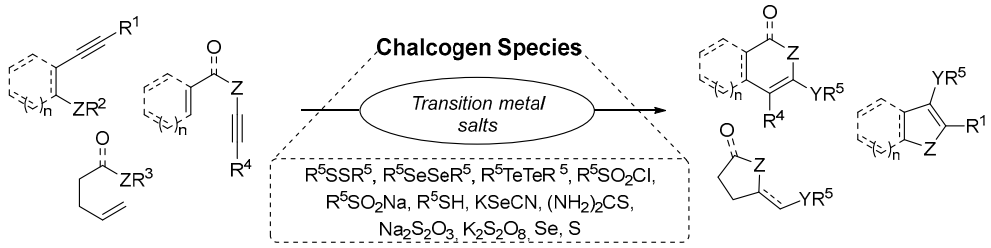
1. Introduction

The use of transition metal-catalyzed carbon-carbon and carbon-heteroatom bonds has long been considered a powerful and efficient tool in heterocycle synthesis. This strategy enables the efficient construction from simple to complex heterocyclic structures starting from acyclic materials [1,2]. In this context, the use of cheap, clean, and efficient catalytic systems to access heterocyclic compounds is always desired to design new bioactive compounds, functional materials, agrochemicals, or to synthesize naturally occurring molecules [3,4]. Transition metals have enabled the preparation of heterocyclic structures bearing a broad range of functionalities, in high selectivity and high yields [5–7]. Conventional metals used for this purpose include palladium, copper, iron, and ruthenium, which facilitate key transformations, including C-H or C-heteroatom bond activation, coordination to double and triple bond facilitating cyclization, and functional group manipulations [8–10]. The earliest traditional methods involving metals for the construction of new chemical bonds experienced several drawbacks, such as the need for stoichiometric amounts, low selectivity and efficiency, limited scope, and many side reactions. Over the past years, several advances have been reached to overcome these problems, further expanding the synthetic utility of catalytic systems. The development and use of innovative ligands, optimization of the reaction conditions, and the use of continuous methods or alternative energy sources are recent contributions in this area [11,12].

The preparation of organic chalcogenide compounds has experienced considerable breakthroughs in recent years. These compounds exhibit interesting physical, chemical, and biological properties which motivate studies from synthetic organic chemists and the pharmaceutical industry [13]. In addition, due to their unique physical and chemical properties, many of these compounds have been used as versatile building blocks in the synthesis of complex organic molecules, biologically active compounds, pharmaceuticals, and natural products [14–16]. From the viewpoint of biological activities, organochalcogen compounds

are known by their antioxidant [17,18], antitumoral [19–21], antimicrobial [22,23], and anti-inflammatory activities [24]. Several are heterocyclic systems containing sulfur on its structure available as FDA-approved drugs [25,26]. On the other hand, organoselenium and organotellurium derivatives display unique reactivity profiles, making them valuable as catalysts, ligands, and intermediates in synthetic methodologies [27–29]. In sum, the interesting properties presented by organochalcogen compounds offer wide research opportunities, considering the design of small molecules presenting pharmacological activity and toxicological safety to new materials.

The heterocyclization of alkenes and alkynes by using halogen- [30–33] or chalcogen-based electrophiles [34,35], or under photocatalysis and electrochemistry conditions involving radical intermediates, has been well documented [36,37]. Traditionally, these cyclization reactions are conducted for alkenes and alkynes neighboring nucleophilic substituents at an appropriate position, which can limit the applicability as most of them are not readily available starting materials, owing to its obtaining of a transition-metal catalysis in at least one reaction step. Although most of them are reliable methodologies, the unique reactivity and capacity of transition-metals to form C-C and C-Heteroatom bonds have not yet been overcome by the metal-free approaches. So, this review article intends to provide the readers with a comprehensive overview on the recent approaches to transition metal-catalyzed chalcogenative heterocyclization reactions, covering research articles published in the last ten years. The most common chalcogen-containing heterocycles explored in this review belong to five, six, and seven membered rings including *N*-, *O*-, *S*-, and *Se*-heterocycles (Scheme 1). This manuscript is organized into reactions catalyzed by transition metals, including copper, cobalt, iron, palladium, silver, indium, and nickel. Synthetic methodologies for the chalcogenative cyclization of alkenes and alkynes carried out with stoichiometric amounts of these substances are not covered in this review.



Scheme 1. Overview of transition metal-catalyzed chalcogenative heterocyclization reactions.

2. Transition Metal-Catalyzing Chalcogenative Heteroannulation

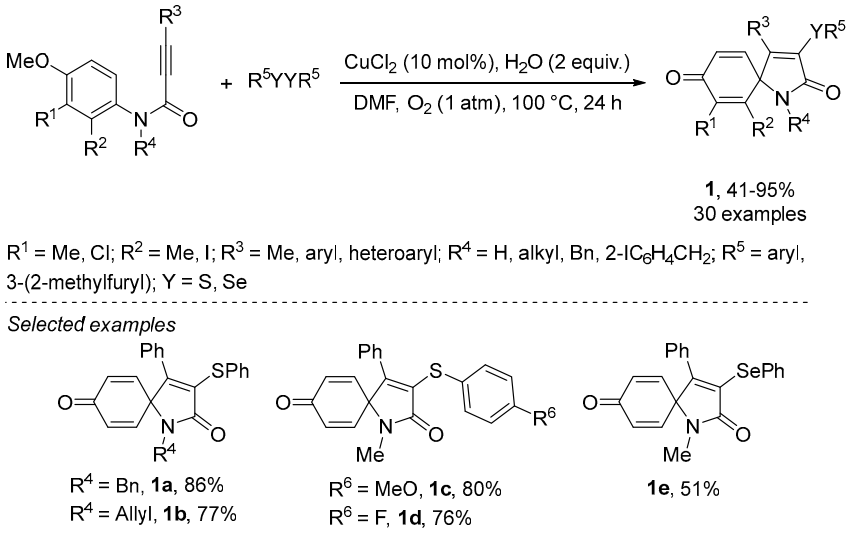
2.1. Using Copper as Catalyst

The chemistry of copper in organic synthesis is extremely rich and abundant, representing a significant field of research that is under constant development. The low cost, high abundance, high functional group tolerance, and capacity of copper to vary its oxidation state may represent attractive aspects involved in the application as a catalyst in cyclization reactions. The synthesis of a plethora of heterocyclic compounds by the copper-catalyzed chalcogen-chalcogen bond cleavage of disulfides or diselenides and the subsequent transfer of the ensuing chalcogen species to activated alkenes or alkynes is described. In this way, the use of copper catalysts represents a powerful synthetic tool to afford different classes of *N*-, *O*-, and *Chalcogen*-based heterocycles bearing an organochalcogen group.

2.1.1. N-Based Heterocycles

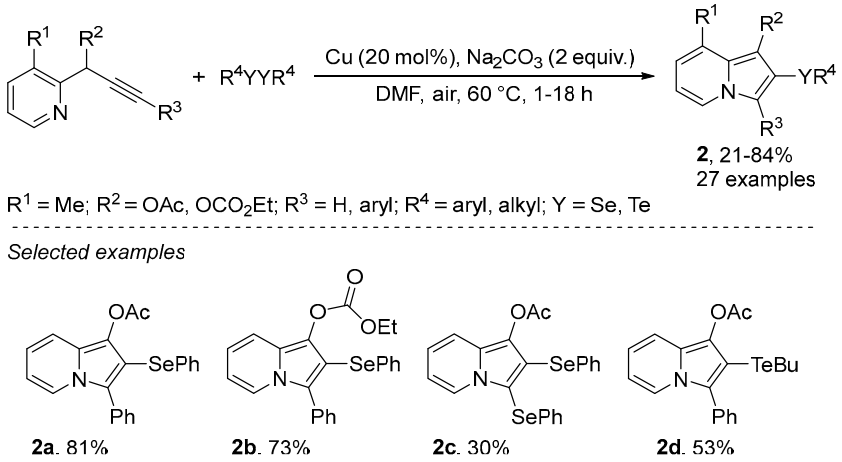
The synthesis of spiro[4.5]trienones **1** via sequential C-Chalcogen bond formation, *ipso*-cyclization, and dearomatization of *N*-(p-methoxyaryl)propiolamides catalyzed by $CuCl_2$ (10 mol%) has been reported (Scheme 2) [38]. The optimal conditions still include the use of O_2 atmosphere and H_2O (2 equiv.) in DMF as solvent at 100 °C for 24 h. The substrate scope covered diverse *N*-arylpropiolamides and diaryldisulfides containing halogen, alkyl, alkoxy, and nitrile as substituents, providing the spirocycles in yields ranging from 41% to

95%. Despite the broad scope and group compatibility, limitations on product formation were observed for alkyl-substituted terminal alkyne and in the presence of a free N-H group.



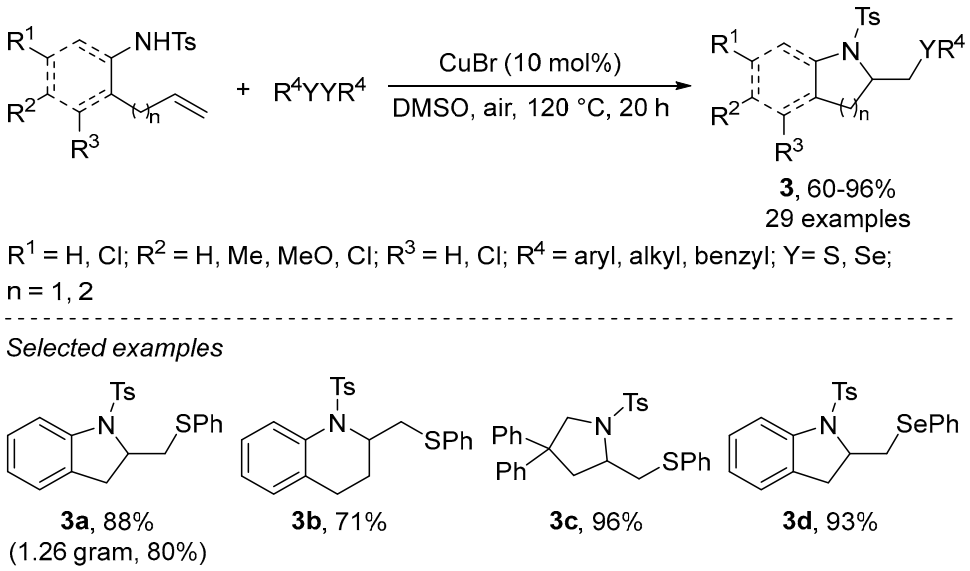
Scheme 2. Synthesis of 3-(arylthio)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-diones **1**.

The synthesis of 2-(chalcogenyl)indolizines **2** by copper-catalyzed chalcogenative cyclization of propargyl pyridines has been reported by Zeni and coworkers (Scheme 3) [39]. This protocol demonstrated the reaction of propargyl pyridines with diorganyl dichalcogenides via copper(I) iodide (20 mol%) catalysis in the presence of Na_2CO_3 as a base, and DMF as a solvent at 60 °C. This strategy was compatible with several propargyl pyridines bearing both acetate and carbonate groups directly bonded to the propargylic carbon, providing 2-chalcogenylindolizines **2** via 5-*endo-dig* cyclization by copper selenolate species activating the C-C triple bond to the anti-attack of the nitrogen atom of the pyridine nucleus. Moreover, differently substituted diorganyl diselenides and ditellurides were used, which delivered the target products in moderate to excellent yields. Exceptionally, when a terminal propargylpyridine was used to react with diphenyl diselenide, the coupling of two phenylselanyl groups at positions 2 and 3, in the indolizine structure was observed. In addition, the synthetic applicability of the Csp^2-tellurium bond on some 2-(butyltellurenyl)indolizines has been successfully evaluated in palladium-catalyzed Suzuki-type cross-coupling reactions.



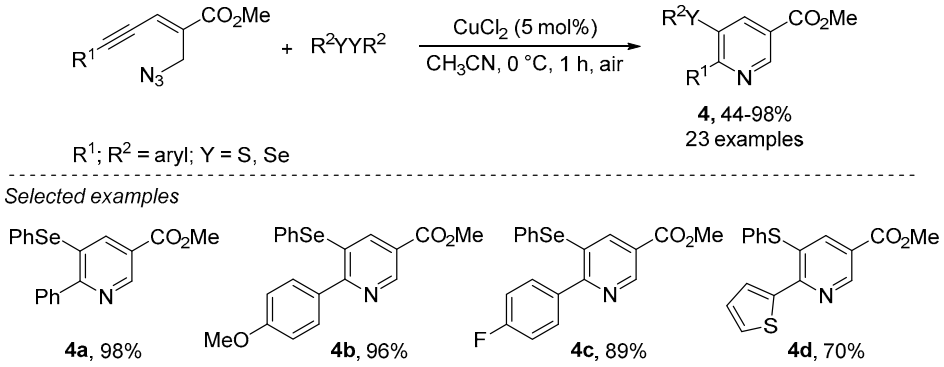
Scheme 3. Synthesis of 2-(chalcogenyl)indolizines **2**.

A novel copper-catalyzed oxidative alkene chalcogenofunctionalization starting from alkenyl *N*-Ts-protected amines and diorganyl dichalcogenides in the presence of $CuBr_2$ (10 mol%) as a catalyst was reported by Zhong and co-workers (Scheme 4) [40]. The substrate scope covered the synthesis of diverse indolines, tetrahydroquinolines, pyrrolines, and piperidines highly functionalized **3** in good to excellent yields. Furthermore, diorganyl disulfides and diselenides were used as a stable and highly available chalcogen source, which were well tolerated under optimal conditions and produced *N*-heterocycles **3** by *exo-trig* cyclization form. Still, the highlight of this methodology is the use of an inexpensive catalytic system based on copper(II) bromide and air oxygen as the oxidant.



Scheme 4. Chalcogenative cyclization of alkenyl amines catalyzed by $CuBr_2$.

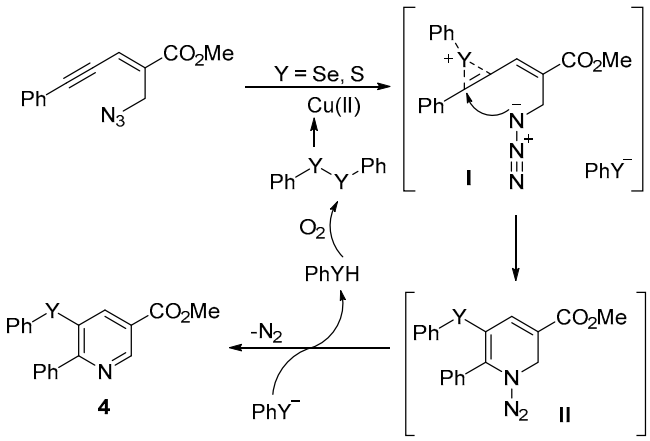
In 2019, Reddy and co-workers described the open-air synthesis of organochalcogenylated nicotinate derivatives by Cu-catalyzed intramolecular chalcogenamination reaction [41]. The one-pot aza-annulation of (*E*)-2-en-4-ynyl azides—which are readily prepared from the corresponding Morita–Baylis–Hillman acetate of acetylenic aldehydes—in the presence of diorganyl diselenides or disulfides and $CuCl_2$ (5 mol %) as the Cu(II) catalyst source provided direct access to a series of twenty-three structurally diverse 5-selanyl/sulfenyl nicotinates **4** in moderate to excellent yields (44–98%) (Scheme 5). Both electron-donating and electron-withdrawing groups were well-tolerated, demonstrating the versatility of this mild protocol.



Scheme 5. Synthesis of 5-organochalcogenated nicotinate derivatives **4**.

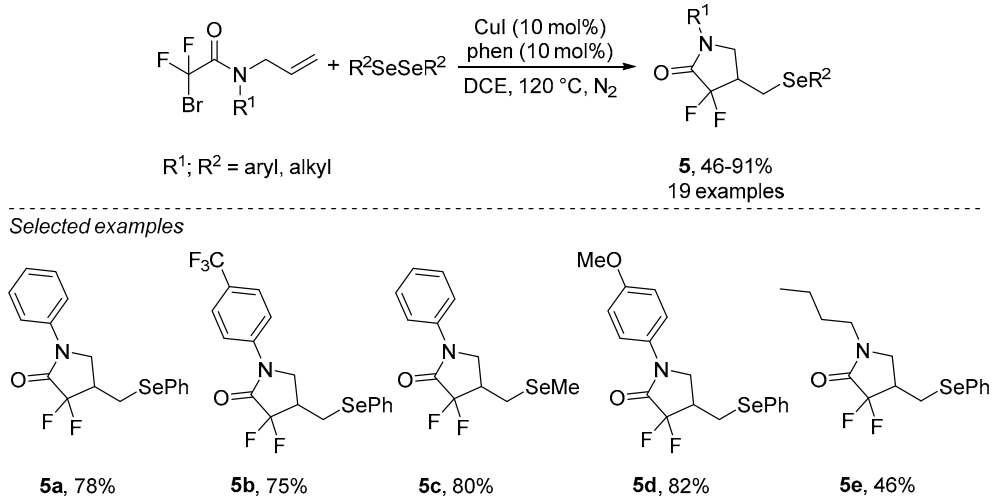
The proposed reaction mechanism is based on the activation of diorganyl dichalcogen by the copper salt (Scheme 6). Polarization of the chalcogen−chalcogen bond to a Cu(II)

complex promotes electrophilic regioselective addition to the alkyne moiety followed by intramolecular nucleophilic azide attack **I** (Scheme 6). Subsequent deprotonation of intermediate **II** leads to the desired nicotinate product **4** and seleno- or thiophenol, which promptly oxidizes to its corresponding diselenide/disulfide, completing the catalytic cycle.



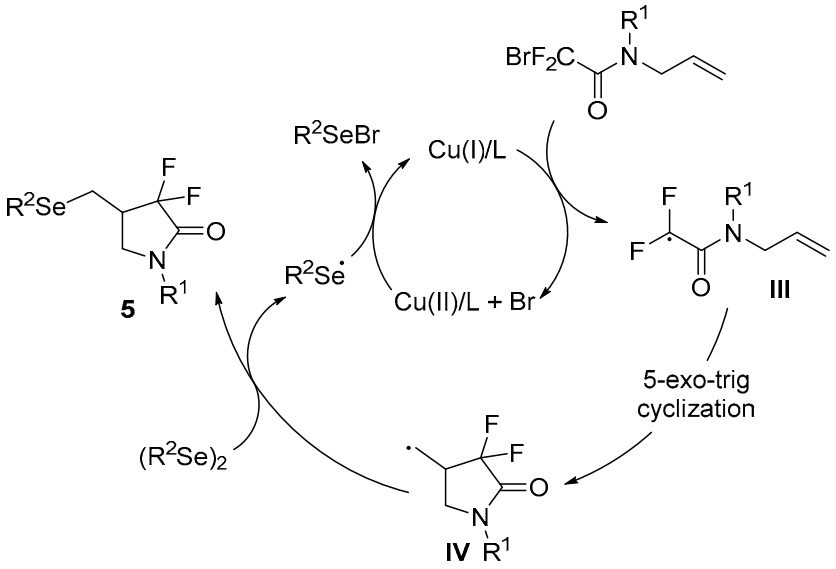
Scheme 6. Proposed mechanism for the synthesis of **4**.

A series of selenium-containing fluorinated γ-lactams **5** were synthesized by Sun, Zhang, and co-workers through Cu(I)-catalyzed radical cascade selenodifluoromethylation of *N*-allylphenylacetamides [42]. Using CuI/phenantroline as the catalytic system and diaryl, dialkyl, or diheteroaryl diselenides as the organochalcogen source, nineteen selenium-containing α,α-difluoro-γ-lactams **5** were prepared in moderate to excellent yields (46–91%) (Scheme 7).



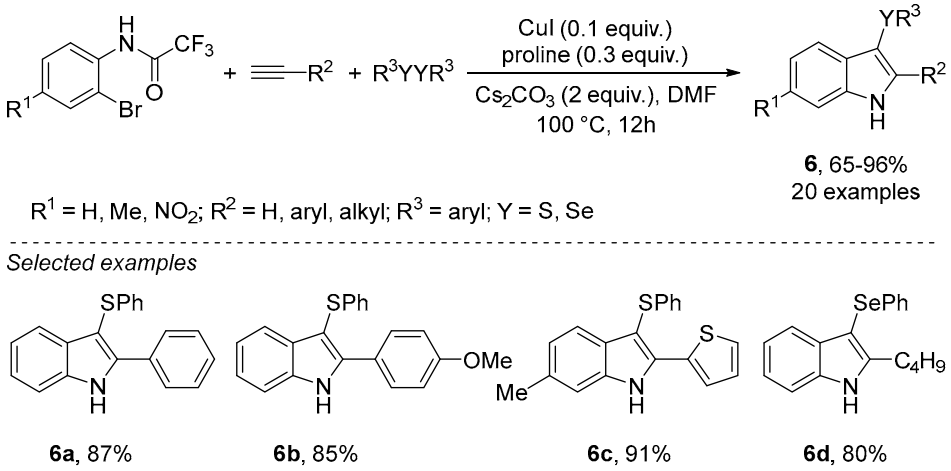
Scheme 7. Synthesis of 4-seleno-substituted α,α-difluoro-γ-lactams **5**.

Based on control experiments, a possible radical cascade cyclization mechanism was proposed. First, Cu(I) and *N*-allylphenylacetamide react via an SET (single-electron transfer) process producing Cu(II) species and the fluoroalkyl radical intermediate **III** (Scheme 8). Then, the cycle proceeds toward a *5-exo-trig* cyclization, leading to the radical intermediate **IV**, which is captured by the diorganyl diselenide to yield the desired product **5** and a selanyl radical. The latter is eventually reduced to selanyl bromide (RSeBr) and Cu(II) to Cu(I) to re-enter into the catalytic cycle.



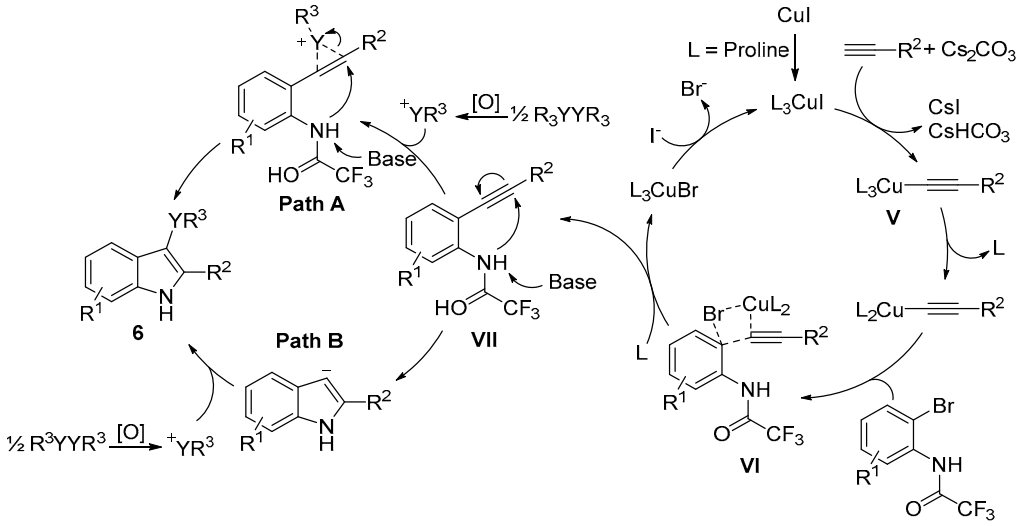
Scheme 8. Proposed radical cascade mechanism for the synthesis of **5**.

A series of polysubstituted 3-chalcogenated indoles **6** were synthesized by Liu and co-workers (2019) via a Cu-catalyzed multicomponent one-pot reaction involving Sonogashira coupling reaction, *N*-cyclization, and electrophilic sulfenyl/selanyl substitution [43]. Using *N*-(2-bromophenyl)trifluoroacetamides, an aryl or alkyl alkyne, diorganyl diselenide/disulfide, and CuI/proline as the catalyst system, the indole target products **6** were obtained in 65–96% yield (Scheme 9).



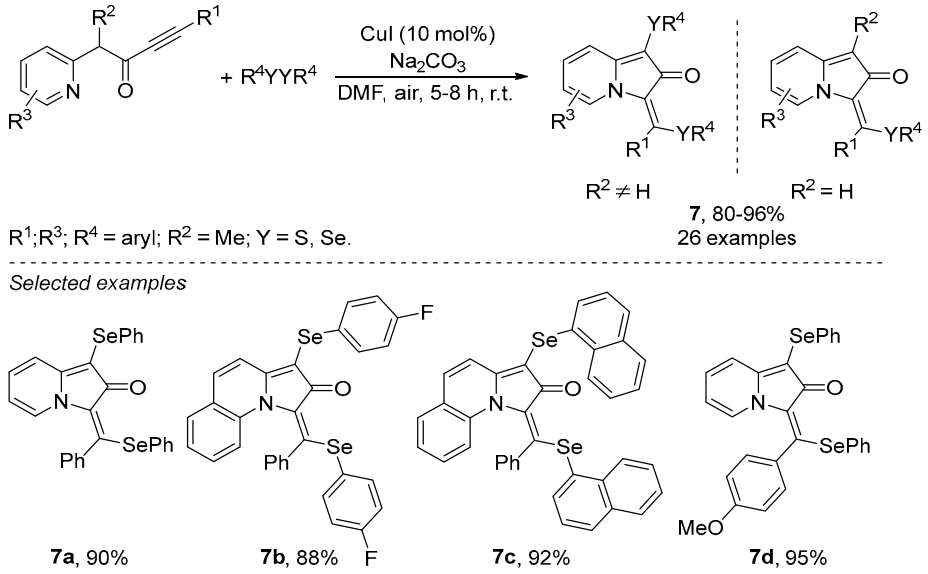
Scheme 9. Synthesis of polysubstituted 3-chalcogenated indoles **6**.

Two possible catalytic routes were proposed for this reaction (Scheme 10). First, the Cu-acetylide intermediate **V** is formed by the reaction of terminal alkyne with copper complex. Then, the in situ generated copper-acetylide reacts with aryl bromide to form the transition state **VI** leading to the key coupling intermediate **VII**, while the dichacolgen is oxidized to the corresponding cationic species. For pathway A, trifluoroacetyl-promoted annulation leads to the target 3-chalcogenated indole product **6**. For pathway B, the coupling intermediate **VII** undergoes intramolecular cyclization to afford an indole anion that traps the cationic chalcogen species, leading to the *N*-heterocycle product **6**.



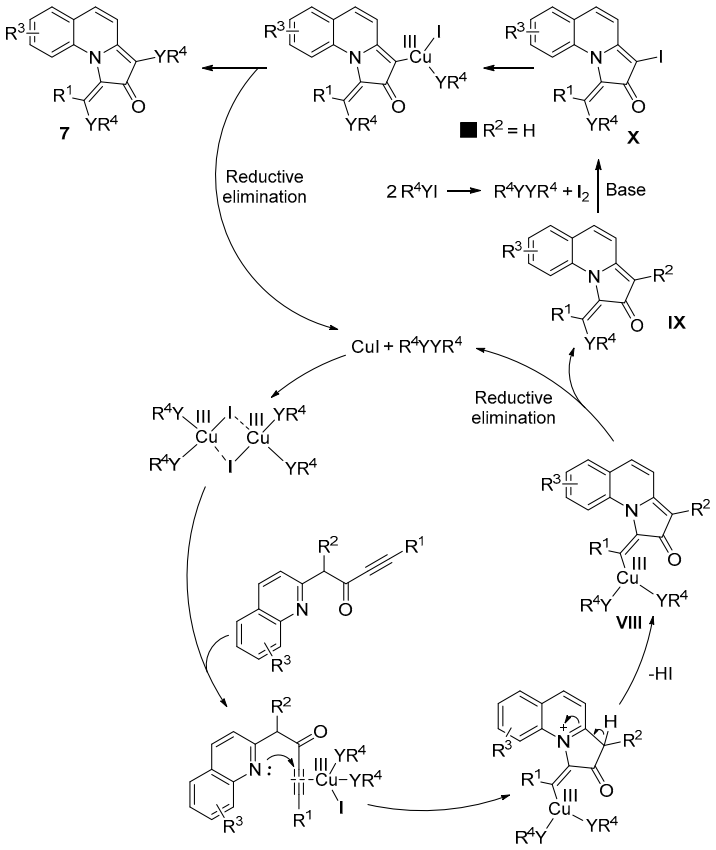
Scheme 10. Proposed mechanism for the synthesis of polysubstituted 3-chalcogenated indoles **6**.

In 2020, Sarkar and co-workers developed an interesting two-component Cu(I)-catalyzed regioselective cyclization cascade strategy for the synthesis of diorgano-chalcogenyl-substituted indolizinones **7** from a wide variety of substituted pyridine homologated ynones [44]. All reactions were carried out at room temperature and open-air atmosphere using CuI (10 mol %) as the catalyst and diorganyl dichalcogenides as the chalcogen source. Under these conditions, the desired chalcogen-decorated indolizinones **7** were obtained in high to excellent yields (80 to 96%) (Scheme 11).



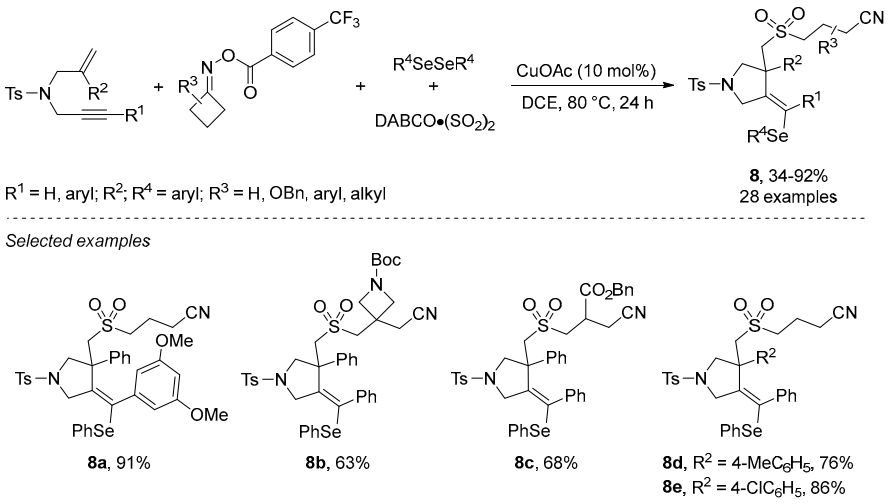
Scheme 11. Synthesis of diorgano-chalcogenyl-substituted indolizinones **7**.

The proposed reaction mechanism starts with formation of the dinuclear diorganochalcogen-Cu(III) complex, which is the species involved in the activation of starting ynone. The intramolecular *5-exo-dig* ring annulation followed by the reductive elimination of **VIII** furnishes the mono-organochalcogen-indolizinone intermediate **IX,** which had the acidic hydrogen exchanged by iodine with the aid of base, affording **X**. Finally, subsequent oxidative addition of the Cu(III)−organochalcogen species followed by reductive elimination leads to the target product **7** (Scheme 12).



Scheme 12. Proposed mechanism for the synthesis of **7**.

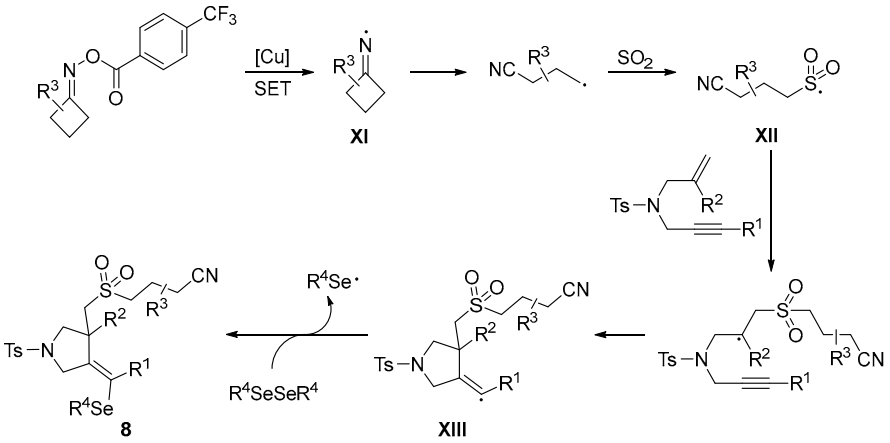
He, Wu, and co-workers (2021) developed an efficient copper(I)-catalyzed multicomponent radical cascade cyclization of 1,6-enynes, diorganyl diselenides, DABCO·$(SO_2)_2$ and cycloketone oxime esters for the regio- and chemoselective synthesis of cyanoalkylsulfonylated pyrrolidines **8** in moderate to good yields (34–92%) (Scheme 13) [45]. This mild protocol provided direct access to twenty-eight organoselenated pyrrolidines **8** employing CuOAc (10 mol%) as Cu(I) source and DCE as the solvent at 80 °C, demonstrating high functional group compatibility.



Scheme 13. Synthesis of cyanoalkylsulfonylated pyrrolidines **8**.

The suggested mechanism for this selenosulfonylation reaction starts with a single-electron transfer from Cu(I) to cycloketone oxime ester to form an iminyl radical **XI**

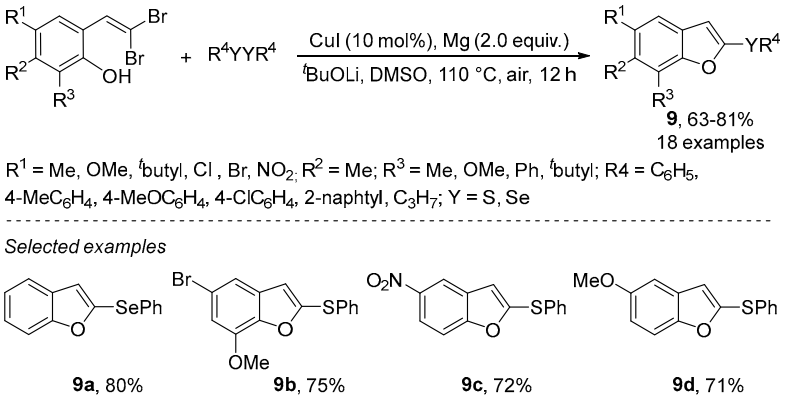
(Scheme 14). In the sequence, C–C bond cleavage results in the formation of a carbon radical intermediary, which is promptly captured by DABCO·$(SO_2)_2$ to produce the sulfonyl radical **XII**. Addition of **XII** to 1,6-enyne forms an alkyl radical intermediate that undergoes *5-exo-dig* cyclization to provide vinyl radical **XIII**. Finally, the reaction between radical species **XIII** and diphenyl diselenide affords the target pyrrolidine **8**.



Scheme 14. Proposed mechanism for the Cu-catalyzed selenosulfonylation of 1,6-enynes.

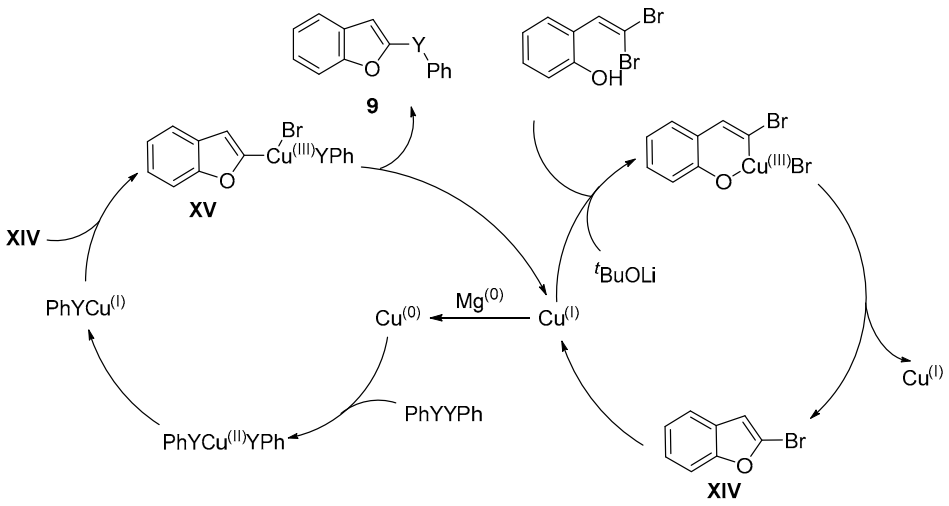
2.1.2. O-Based Heterocycles

In 2013, Wang and co-workers reported the synthesis of 2-chalcogenyl-benzofurans **9** by reacting 2-(*gem*-dibromovinyl)phenols with diorganyl dichalcogenides and using copper(I) iodide (10 mol%) as a catalyst (Scheme 15) [46]. The optimal conditions still consist of using *t*BuOLi as a base and metallic Mg as an additive in DMSO as solvent at 110 °C. The most striking feature of this protocol was the tolerance of both electron-donating and electron-withdrawing groups directly attached to the phenol moiety without apparent sensitivity to the electronic features of the substituents. Diorganyl disulfides and diorganyl diselenides were found to be efficient reagents to this reaction, affording the products **9** in good yields.



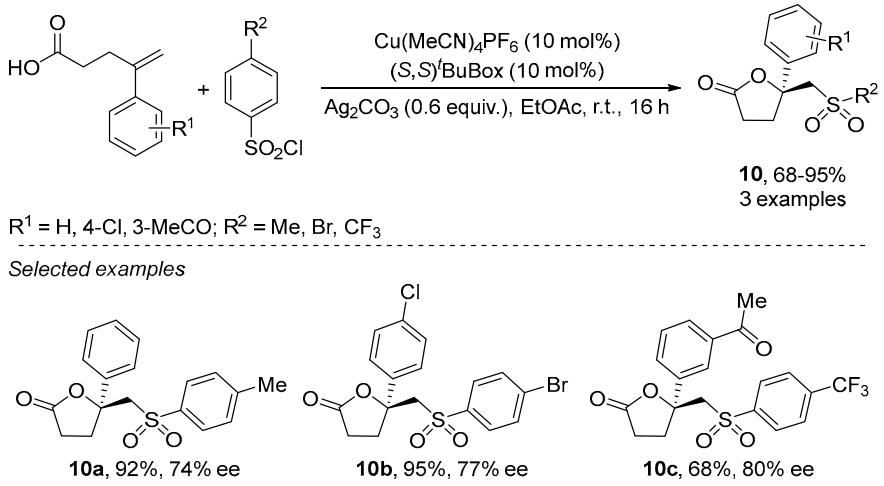
Scheme 15. Synthesis of 2-chalcogenyl-benzofuran **9**.

Based on detailed control experiments and the related literature, the authors proposed the following mechanism (Scheme 16). Initial Ullmann-type reaction catalyzed by copper furnishes 2-bromobenzofuran **XIV**. In parallel, reaction of diorganyl dichalcogenide with Cu(0), generated in situ from the reduction in Cu(I) with Mg(0), provides copper(II) and copper(I) intermediates, which reacts with **XIV** via oxidative addition, giving **XV**. Finally, the reductive elimination step regenerates the transition-metal and furnishes product **9**.



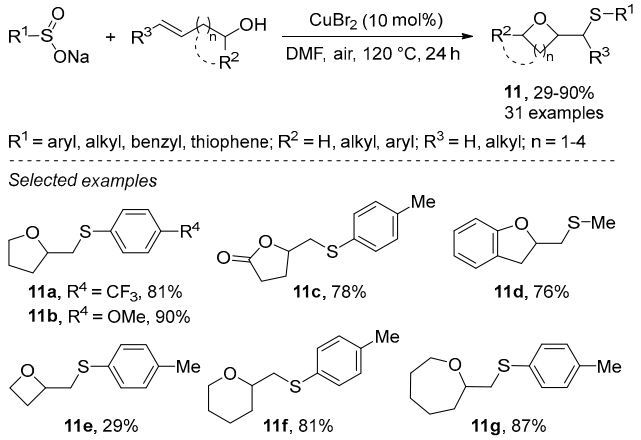
Scheme 16. Proposed mechanism for the synthesis of 2-chalcogenyl-benzofuran **9**.

In 2015, Buchwald and Zhu depicted the enantioselective radical cyclization of 4-arylpent-4-enoic acids to synthesize functionalized chiral lactones **10** via copper-catalyzed reaction (Scheme 17) [47]. Reactions were conducted using sulfonyl chlorides as sulfur sources in a catalytic system based on $Cu(MeCN)_4PF_6$ (10 mol %), (*S*,*S*)-^{t}BuBox (10 mol%) as ligand, and Ag_2CO_3 as base and chloride scavenger in ethyl acetate as solvent at room temperature. Under optimal conditions, enantiomerically-enriched sulfonyl-substituted lactones were obtained in high yields and good enantioselectivity. Finally, this key enantioselective lactonization still covered oxyazidation, oxyarylation, diacyloxylation, and oxyalkylation reactions.



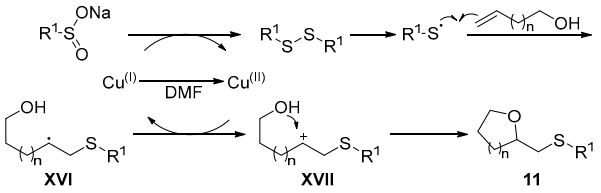
Scheme 17. Synthesis of sulfonyl-substituted lactones **10**.

A series of sulfonated cyclic ethers **11** were depicted via heterocyclization of enols with sodium sulfinates as an organic sulfur source that is readily accessible and stable (Scheme 18) [48]. The best reaction conditions involved the use of copper(II) bromide (10 mol%) in DMF as solvent at 120 °C under air for 24 h. The reactions were conducted using terminal and internal enols, which enabled the preparation of a series of four to seven membered cyclic ethers, including dihydrobenzofuran, lactone, and a norbornene derivative. Furthermore, the reaction conditions were compatible with several aryl and alkyl sulfinates bearing both bulky, electron-donating and electron-withdrawing groups at *orto*, *meta*, and *para* positions, which furnished the desired products **11** in good yields.



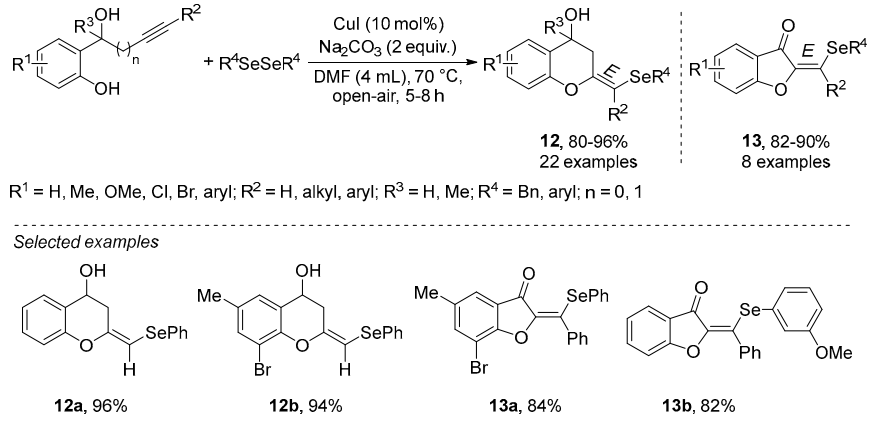
Scheme 18. Synthesis of sulfonated cyclic ethers **11**.

After screening several experiments, a radical mechanism was proposed. Initially, sodium sulfinate is reduced by Cu(I) resulting in Cu(II) species and reactive sulfur radical species via disulfide intermediate. Thereafter, addition of sulfur radical species to the enol double bond provides the alkyl radical species **XVI** which undergoes oxidation, resulting in a carbocation-type intermediate **XVII**. Subsequently, species **XVII** suffers an intramolecular nucleophilic attack of the neighboring oxygen atom, furnishing **11** and regenerating Cu(I) to the next catalytic cycle (Scheme 19).



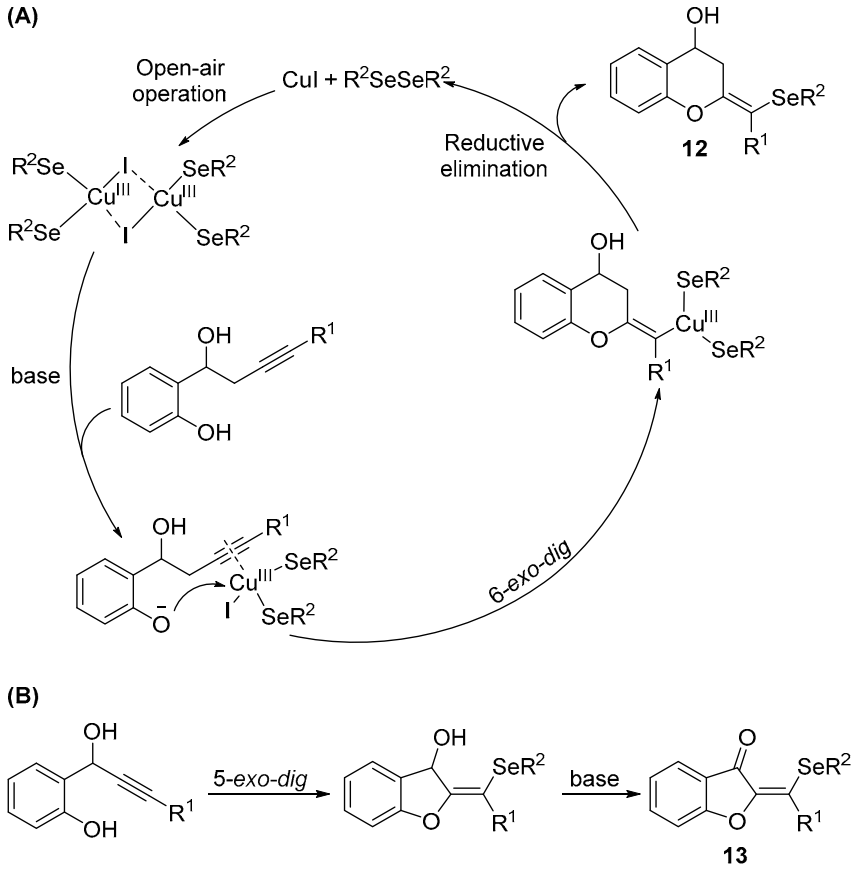
Scheme 19. Proposed mechanism for the synthesis of **11**.

The same research group developed a mild protocol for the regioselective synthesis of selanilated cromanol **12** and aurone **13** derivatives from homo-propargyl and propargyl alcohols, respectively [49]. The optimal reaction conditions involved the use of CuI (10 mol%) as catalyst, Na_2CO_3 as the base, and DMF as the solvent resulting in the selanyl methylene 4-chromanol **12** and selanyl aurone **13** products with an up to 96% yield (Scheme 20). The attempts to employ diorganyl ditellurides and disulfides as the chalcogen sources were unsuccessful.



Scheme 20. Cu-catalyzed regioselective synthesis of selanyl methylene 4-chromanol **12** and aurone derivatives **13**.

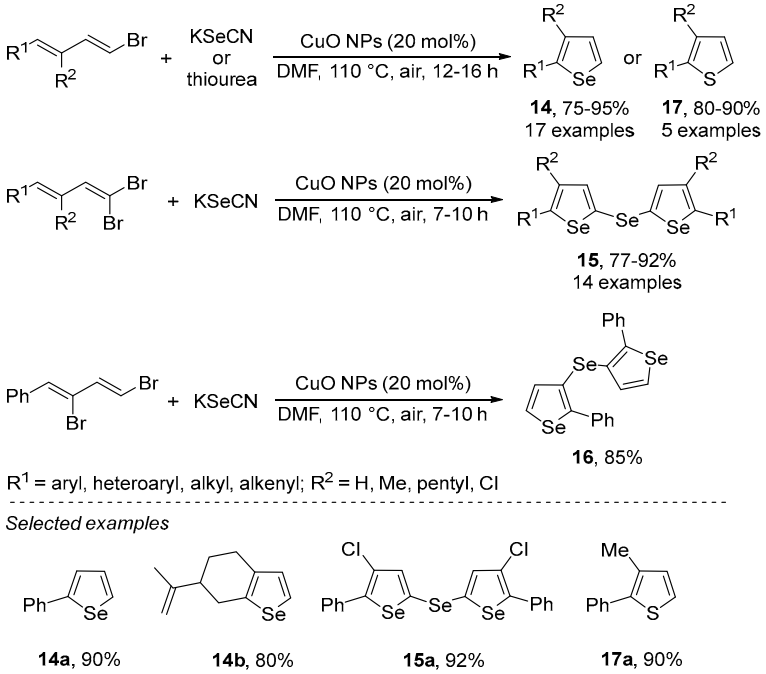
The proposed reaction mechanism proceeds through a similar pathway shown previously in Scheme 12, with the initial copper-organochalcogen complex formation. This dinuclear species is responsible for activating the starting ynol, which suffers a 6-*exo-dig* (Scheme 21A) or a 5-*exo-dig* (Scheme 21B) ring annulation, followed by a reductive elimination leading to the desired selanyl-substituted chromanols **12** and aurones **13**, respectively.



Scheme 21. Proposed mechanism for the synthesis of (**A**) chromanols **12** and (**B**) aurones **13**.

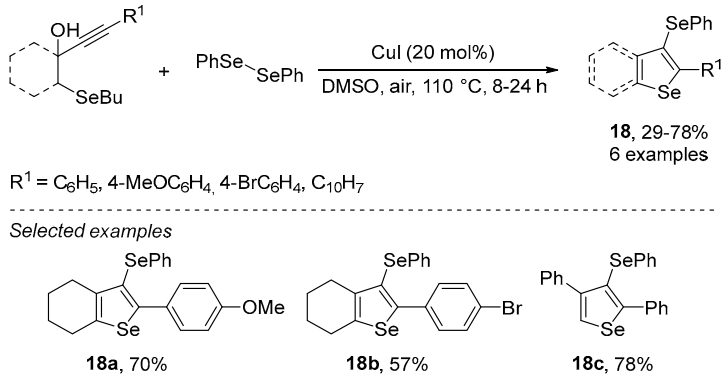
2.1.3. Chalcogen-Based Heterocycles

An efficient synthetic approach to the synthesis of highly functionalized selenophenes **14**, **15**, and **16** via Cu(II)-catalyzed reaction between several (*E*,*E*)-1,3-dienyl bromides and KSeCN as selenium source has been reported by Ranu and co-workers (Scheme 22) [50]. The standard condition uses 20 mol% of CuO Nps as catalyst and DMF as solvent, at 110 °C for 3 h to 12 h. Initially, a diversity of substituted 1,3-dienyl bromide derivatives underwent selanylation/cyclization reaction, producing the corresponding selenophenes **14** in 75% to 95% yields. Moreover, when 1,3-di-*gem*-dibromides were employed under optimal conditions in the presence of 3 equiv. of KSeCN, 2-selanyl bisselenophenes **15** were obtained as product. In addition, under the same conditions, the selanylation followed by cyclization reaction was extended to a 3-bromo-1,3-dienyl bromide which gave the 3-selanyl bisselenophene **16** in 85% yield. To complete the investigation, the synthesis of five differently substituted thiophenes **17** was explored in the presence of thiourea as a sulfur source under similar optimized reaction conditions obtaining the expected products in 80% to 90% yields. Particularly, KSCN was inefficient in providing the desired products.



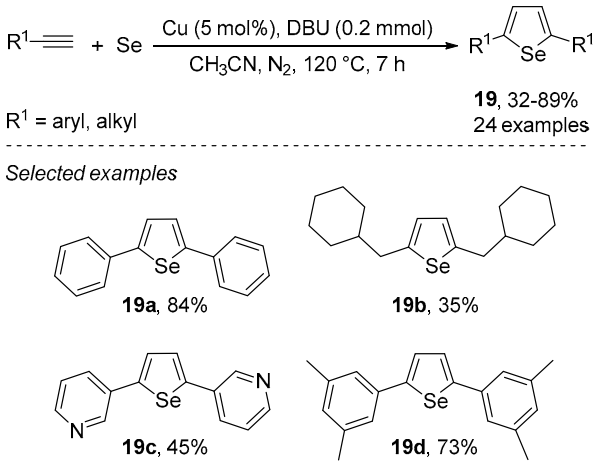
Scheme 22. Synthesis of chalcogenophene derivatives **14**–**17**.

In 2018, Zeni and co-workers described straightforward strategies to synthesize highly substituted selenophene scaffolds by direct incorporation of halogen and chalcogen as substituents (Scheme 23) [51]. Among them, the reaction of butylselanyl propargylic alcohols with diphenyl diselenide catalyzed by copper(I) iodide (20 mol%) was successfully employed to obtain diverse 3-(phenylselanyl)selenophenes **18** in moderate to good yields. Interestingly, simple electrophilic selenium sources, such as PhSeBr or $(PhSe)_2$/HCl or $(PhSe)_2/FeCl_3$, as promoters were inefficient, furnishing the expected product in satisfactory yields. In contrast, the formation of a copper π-complex favors the intramolecular cyclization, selanylation, and dehydration reaction of the starting propargylic alcohols.



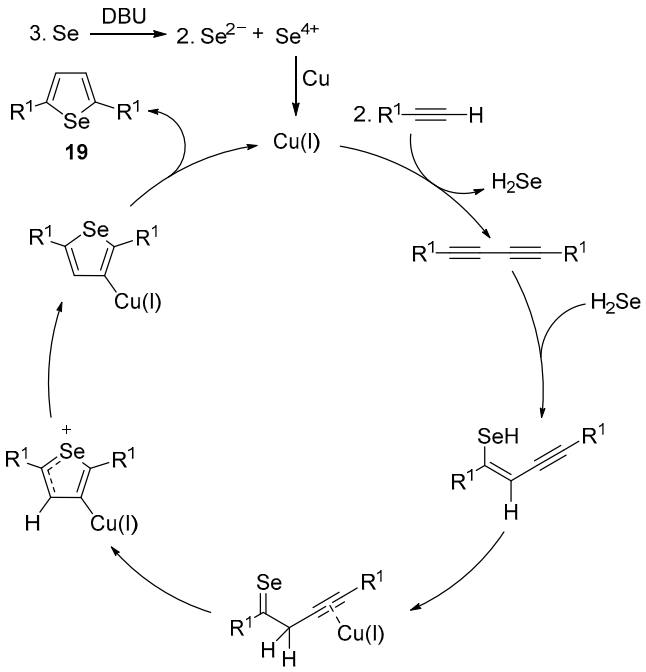
Scheme 23. Synthesis of 3-(phenylselanyl)selenophenes **18**.

Another notable example comes from a recent report by Wu and coworkers on the chemo- and regio-selective synthesis of selenophenes **19** via Cu(I)-catalyzed [2+2+1] cyclization of terminal alkynes and selenium powder [52]. This strategy applied stable and non-toxic elemental selenium as the chalcogen source, in contrast to the relatively unstable and unpleasant odour of commonly used dialkyl diselenides. Under the optimal reaction conditions, 2,5-disubstituted selenophenes **19** were prepared in 32–89% yields with a diversity of substituents, including aryl, alkyl, and heteroaryl groups (Scheme 24).



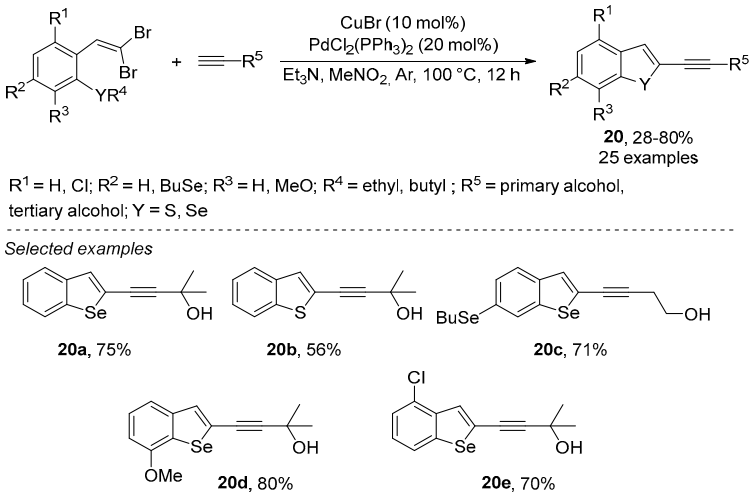
Scheme 24. Synthesis of 2,5-disubstituted selenophenes **19**.

The suggested mechanism starts with a DBU-promoted disproportionation of elemental selenium resulting in selenide anion (Se^{2-}) and selenite (Se^{4+}) (Scheme 25). In the sequence, Cu^0 is oxidized to Cu(I), which is responsible for catalyzing the homocoupling of two molecules of the terminal alkyne, followed by regioselective hydroselenation and subsequent cyclization to furnish the desired products **19**.



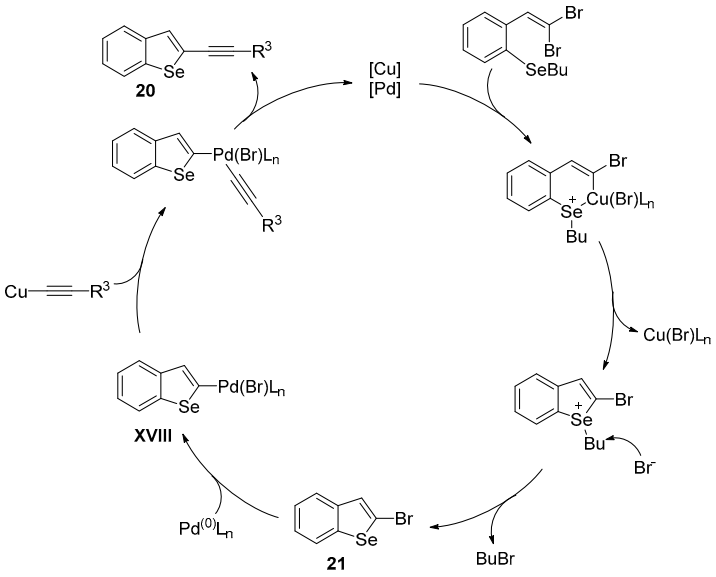
Scheme 25. Proposed mechanism for the synthesis of **19**.

While the strategies discussed above demonstrate intermolecular relationship between chalcogen species and unsaturated substrates, the copper(I)-catalyzed intramolecular cyclization of alkenes bearing a chalcogen (S or Se) group at an appropriate distance from the carbon−carbon double bond is also a versatile way to generate chalcogen-decorated heterocycles. The synthesis of several 2-alkynyl-benzo[*b*]chalcogenophenes **20** from 2-gem-dibromovinyl aryl chalcogenides has been described (Scheme 26) [53]. The highlights of this synthetic method are the intramolecular cyclization catalyzed by CuBr (20 mol%) providing 2-bromobenzo[*b*]chalcogenophenes **21** which subsequently undergoes one-pot palladium-catalyzed Sonogashira-type cross-coupling reaction with different terminal alkynyl alcohols.



Scheme 26. Synthesis of 2-substituted-benzo[*b*]selenophenes **20**.

Mechanistically, vinyl bromide undergoes initial cyclization via copper-catalyzed intramolecular Ullmann-type reaction, forming 2-bromochalcogenophene **21**, which was isolated and characterized by NMR spectroscopy. Then, oxidative addition of palladium species to Csp^2-Br bond generates intermediary **XVIII**, which undergoes transmetallation with alkynyl cuprate, delivering the coupling product **20** after a reductive elimination step. Notably, this methodology is selective for alcohol-containing alkynes, not being compatible with aliphatic or aromatic alkynes (Scheme 27).



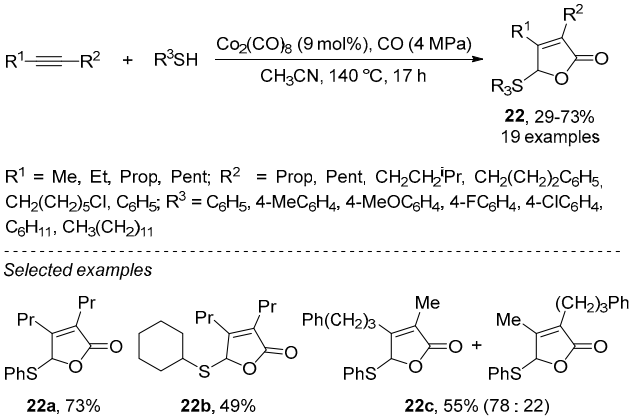
Scheme 27. Proposed mechanism for the synthesis of **20**.

2.2. Using Cobalt as Catalyst

The use of cobalt-catalyzing heterocyclization reactions with direct chalcogen incorporation is a field much less explored in organic synthesis. The most recent studies report the carbonylative reaction of terminal and internal alkynes with direct sulfenylation, achieving the synthesis of γ-lactones as product.

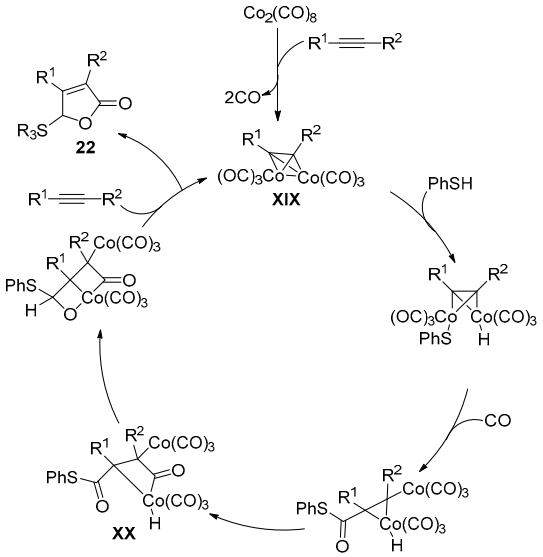
Ogawa and co-workers reported a unique method for the thiolative double carbonylation of internal alkynes by using $Co_2(CO)_8$ (9 mol%) as catalyst, affording α,β-unsaturated γ-thio γ-lactone derivatives **22** (Scheme 28) [54]. This multicomponent reaction was conducted in acetonitrile as solvent at 140 °C under 4 MPa of carbon monoxide for 17 h. Butenolides bearing both aryl and alkyl sulfides as substituents were synthesized in mod-

erate to good yields. The alkyl thiols reacted poorly in comparison to the aryl thiols having both electron-withdrawing and electron-donating groups at *para*-position. Interestingly, reactions conducted employing unsymmetrical internal alkynes provided moderate regioselectivity to the γ-lactones obtained, in which the carbonyl group bonded mainly to the less hindered acetylenic carbon. According to the authors, limitations were observed for internal alkynes containing carbonyl substituents which did not provide the desired products.



Scheme 28. Cobalt-catalyzing synthesis of α,β-unsaturated γ-thio γ-lactone derivatives **22**.

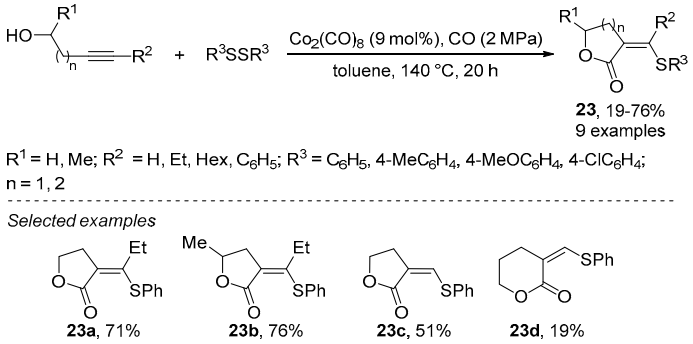
The reaction mechanism proposed by the authors shows the initial formation of a cobalt-alkyne complex **XIX**, which undergoes addition of the thiol derivative generating a sulfur–cobalt bond. After that, two subsequent CO insertions furnish the carbonyl intermediate **XX**. Finally, intramolecular cobalt–oxygen bond formation followed by reaction with internal alkyne provides lactone **22** and regenerates complex **XIX** to the next cycle (Scheme 29).



Scheme 29. Proposed mechanism for the synthesis of **22**.

Later, the same group reported the use of $Co_2(CO)_8$ as a catalyst for thiolative lactonization reactions of internal alkynes bearing a hydroxyl group with diorganyl disulfides under carbon monoxide (2 MPa) atmosphere (Scheme 30) [55]. The reaction was conducted in toluene as solvent at 140 °C for 20 h. Under these reaction conditions, nine γ- and δ-lactone derivatives **23** bearing an *exo*-methylene unit functionalized with sulfur were isolated in 19% to 76% yields. It is important to emphasize that for all synthesized products, the CO

entered regioselectively into the alkyne, and the sulfide remained preferentially located at the *cis* position in relation to the carbonyl group. Alternatively, the authors demonstrated the thiolative lactonization reaction of acetylenic alcohols catalyzed by $Pd(PPh_3)_4$ (5 mol%). This new protocol tolerated strong electron-donating and electron-withdrawing groups attached to both diaryl disulfides and aryl alkynes.



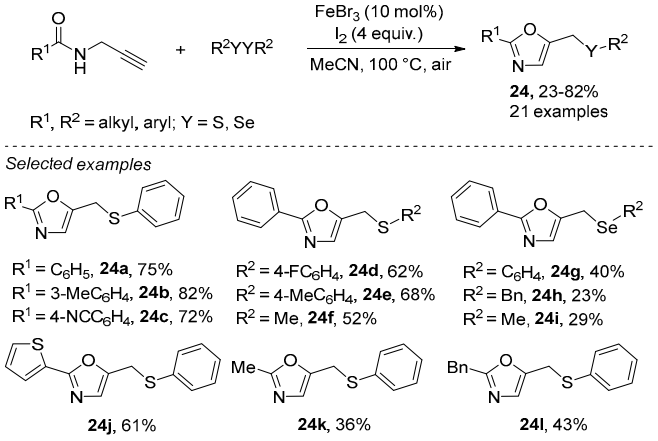
Scheme 30. Synthesis of thio-lactone derivatives **23**.

2.3. Using Iron as Catalyst

Iron salts promoting cyclization processes have been widely recognized in terms of their tolerance toward several functional groups. Moreover, reactions conducted in the presence of iron have reported advantages in terms of relative stability, abundance, low-cost, and low toxicity, when compared to other transition metals. The subsequent papers report on iron-catalyzed cyclization reactions leading to heterocyclic systems such as oxazole, isothiazolone, dihydrofuran, lactone, benzochalcogenophene, and several benzo-fused 6- to 8-membered rings.

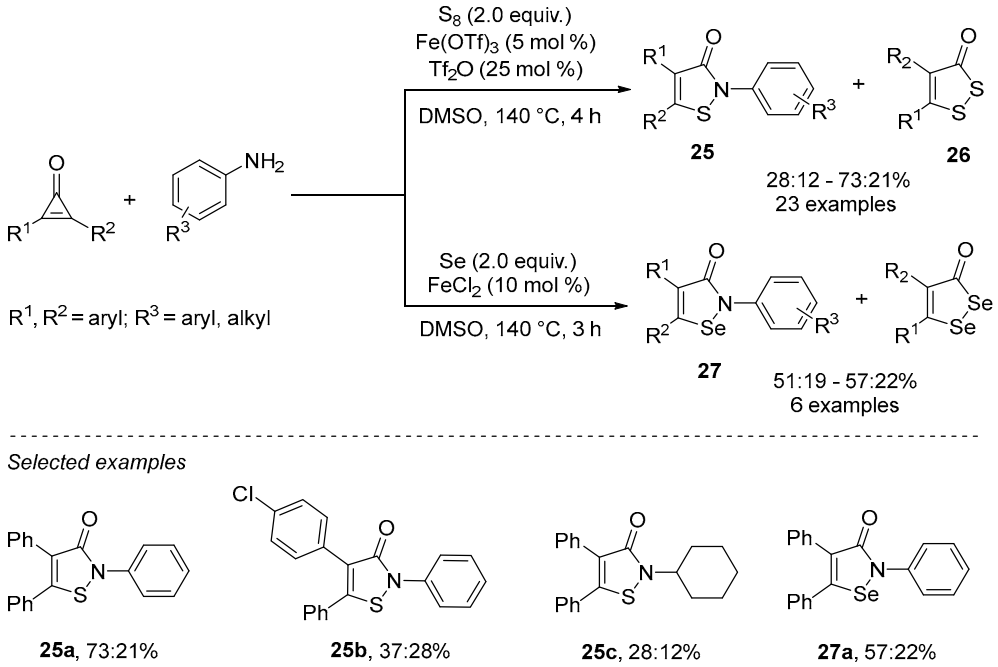
2.3.1. N-Based Heterocycles

Deng and coworkers have reported an elegant strategy to prepare methylsulfenyl oxazoles **24** by the tandem annulation of *N*-propargylamides in the presence of diorganyl disulfides [56]. The standard reaction condition was set under thermal conditions for 12 h, in the presence $FeBr_3$ (10 mol%), I_2 (4 equiv.), and anhydrous MeCN (2 mL), allowing the preparation of twenty-one methylsulfenyl oxazole derivatives **24** in poor to very good yields. Despite the good substrate tolerance, limitations were faced when alkyl substrates were submitted to the protocol, as well as when disulfides were replaced by diorganyl diselenides derivatives (Scheme 31).



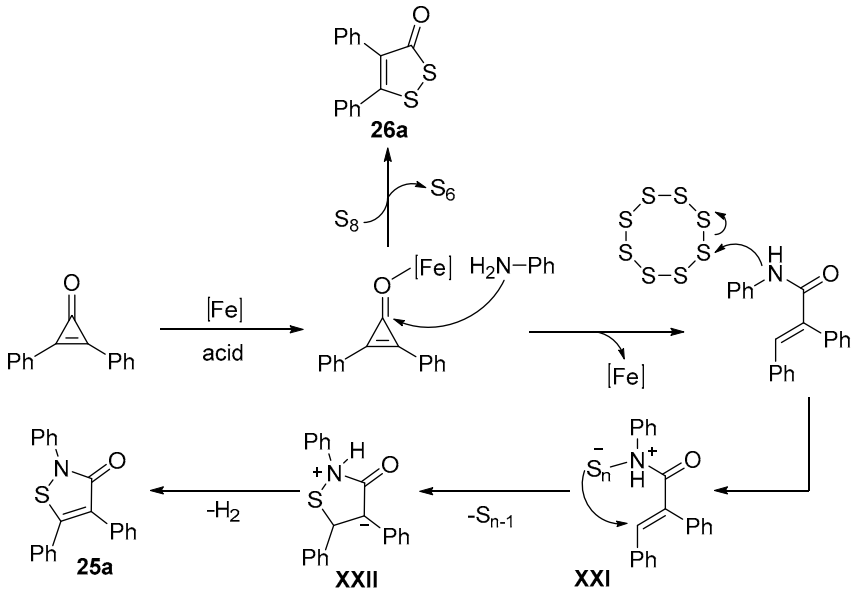
Scheme 31. $FeBr_3$-catalyzed annulation reaction of *N*-propargylamides for the synthesis of oxazole **24** derivatives.

In 2021, Yan and coworkers reported an ingenious synthetic approach to prepare isothiazolone derivatives **25** through an Fe-catalyzed multicomponent annulation of cyclopropenones, anilines, and elemental sulfur [57]. Thus, authors have set the best reaction condition by reacting the substrates in the presence of $Fe(OTf)_3$ (5 mol%), Tf_2O (25 mol%), and DMSO, with the resulting mixture stirred for 4 h at 140 °C. Therefore, the protocol allowed the synthesis of twenty-three isothiazolone derivatives **25** in moderate to good yields (28–73%), presenting an acceptable electronic and steric group tolerance. A huge limitation faced by the method is the simultaneous formation of the 4,5-diphenyl-3*H*-1,2-dithiol-3-ones **26** as a minor product, which were significantly yielded (12–37%) in all experiments. It is worth mentioning that the protocol was satisfactorily scaled-up from 0.2 mmol to 3 mmol, yielding the desired product **25a** in 60%. Additionally, the authors expanded the protocol for the synthesis of iso-1,2-selenazolones **27** by employing elemental selenium as reagent, in the presence of $FeCl_2$ (10 mol%) as a catalyst and DMSO as solvent. After being stirred for 3 h at 140 °C, six iso-1,2-selenazolones **27** were accessed in moderate yields (51–57%) (Scheme 32).



Scheme 32. Fe(III)- and Fe(II)-Catalyzing the synthesis of isothiazolone **25** and isoselenazolone **27** derivatives.

Based on control experiments, authors have proposed a plausible reaction mechanism which initially involves the Fe-catalyzed ring opening of the cyclopropenone, driven by the nucleophilic attack of the nitrogen lone electron pair. This step furnishes the α,β-unsaturated amide intermediate, which promotes the cyclooctasulfur activation by another ring opening event, generating the intermediate **XXI**. Thus, an intramolecular cyclization process releasing elemental sulfur to the reaction medium provides the cyclic ionic intermediate **XXII**, which is finally oxidized towards the desired product **25a** (Scheme 33).



Scheme 33. Proposed reaction mechanism for the synthesis of **25a**.

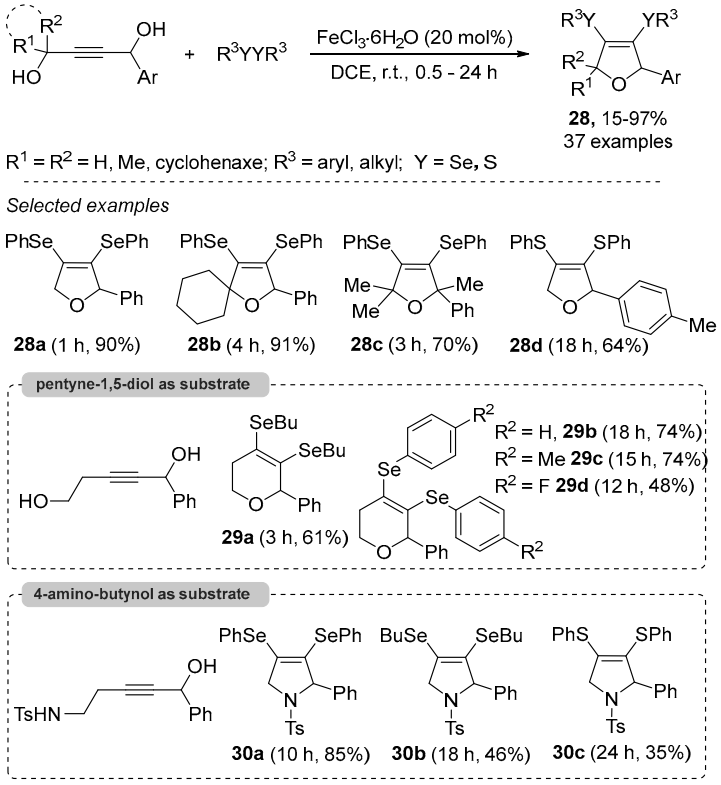
2.3.2. O-Based Heterocycles

In 2015, Zeni and coworkers reported a fashioned synthetic approach to construct 3,4-bis(organoselanyl)-2,5-dihydrofurans **28** by reacting 1,4-butyne-diols and diorganyl diselenides [58]. The optimized reaction condition was established by employing catalytic amounts of $FeCl_3 \cdot 6H_2O$ (20 mol%) and DCE as solvent, and the transformations were conducted from 0.5 h to 24 h to deliver a library of thirty-seven chalcogen-functionalized 2,5-dihydrofurans **28**. The protocol demonstrated excellent substrate tolerance once many 1,4-butyne-diol derivatives could be smoothly employed as substrates. Besides, electron-rich and electron-deficient diorganyl diselenides reacted efficiently to give the respective product **28** derivatives, as well as diphenyl disulfides, which were employed to prepare three sulfur-decorated 2,5-dihydrofuran **28** analogues (Scheme 34). In addition to these important results, authors also have expanded the reaction scope by employing pentyne-1,5-diol and 4-amino-butynol as substrate to prepare 4,5-bis(organoselanyl)-3,6-dihydro-*2H*-pyran **29** and 3,4-bis(organoselanyl)-2,5-dihydro-*1H*-pyrrole **30** derivatives, respectively. A total of four selenium-decorated 3,6-dihydro-*2H*-pyrans **29** were prepared in poor to moderate yields (48–74%), while five selenium- and sulfur-decorated dihydro-*1H*-pyrroles **30** were accessed in poor to very good yields (35–85%). It is worth mentioning that authors also have employed the 3,6-dihydropyran **29a** as a substrate to perform a Kumada-type coupling reaction using $Pd(PPh_3)_4$ (10 mol%) as catalyst, with the coupling product obtained in a yield of 57%.

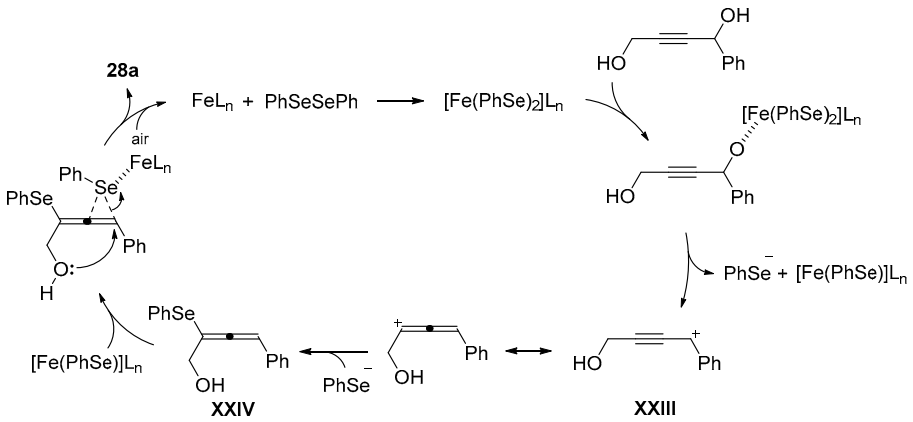
The authors proposed that the transformation is mainly triggered by the in situ formation of a reactive complex by the reaction between the Fe(III) species and diorganyl diselenides [57]. This species can coordinate with the benzyl hydroxyl unit, allowing the formation of a highly stabilized benzyl carbocation **XXIII**, which is quickly converted into the allene intermediate **XXIV**. Then, the product **28a** is reached by sequential events, e.g., a nucleophilic addition followed by an electrophilic annulation (Scheme 35).

Recently, Tang, Zhang, and coworkers published a process of lactonization of enoic acids catalyzed by $FeCl_3$ in the presence of diorganyl dichalcogenides to access chalcogen-decorated γ-lactones and δ-lactones **31** through a simple, atom-economic, and environmentally friendly protocol [59]. By the reaction optimization study, the authors set the best reaction condition by mixing the starting materials in the presence of $FeCl_3$ (10 mol%), KI (0.5 equiv.), and MeCN, stirring the resulting mixture for 24 h at 80 °C under open-air conditions. The developed protocol presented good substrate tolerance once a variety of electron-rich and electron-deficient enoic acids and diorganyl dichalcogenides could be

suitably employed as substrates. On the other hand, limitations were faced when a dialkyl disulfide derivative (R^2 = ^{t}Bu) was employed as substrate, in which the desired product was obtained in trace amounts. It is worth mentioning that the protocol was satisfactorily scaled up to a gram-scale, without significant lack of efficiency (Scheme 36).

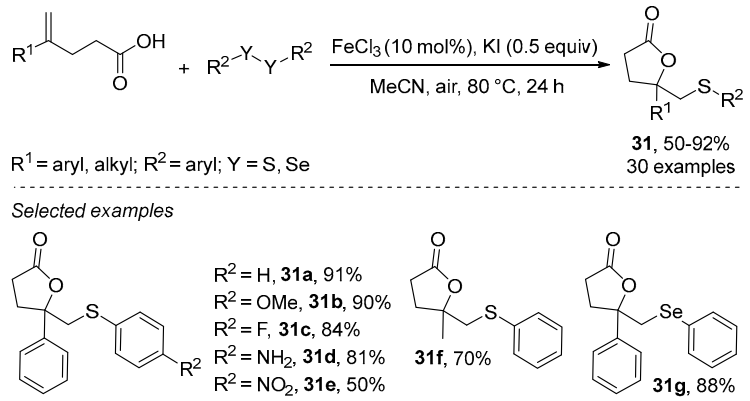


Scheme 34. Fe(III)-catalyzed annulation of alkynols.

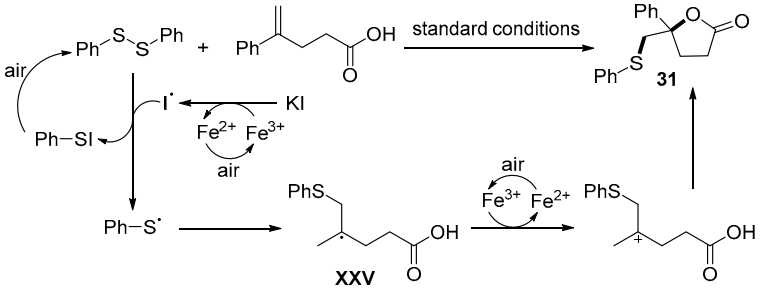


Scheme 35. Reaction mechanism for the Fe(III)-catalyzed annulation of alkynols.

Several control experiments were carried out, indicating that the process mainly follows radical chain events. Thus, authors have proposed a reaction mechanism which is triggered by an Fe(III)-mediated initial iodine anion (I^-) oxidation to the iodo-centered radical through an SET process. Then, the iodine radical species reacts with the S-S bond to afford a thiyl radical species which adds in the C-C double bond, yielding the benzyl radical intermediate **XXV**. Thereafter, this radical species undergoes an SET oxidation, being converted to the benzyl carbocation, which finally is converted into the desired lactone **31** by an intramolecular annulative process (Scheme 37).



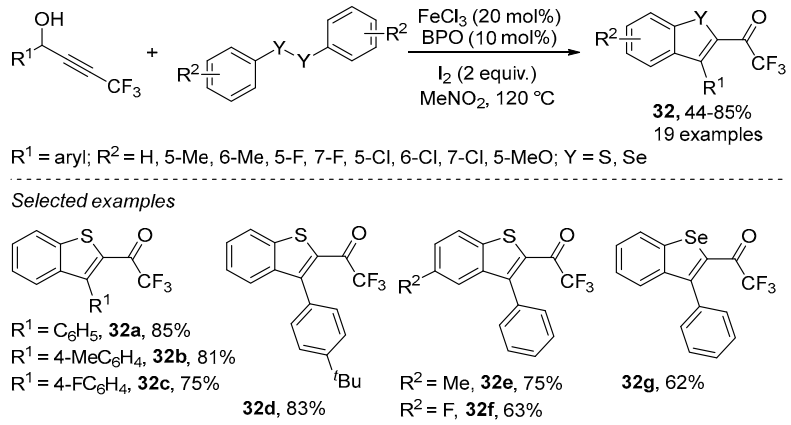
Scheme 36. $FeCl_3$-catalyzed radical cyclization of unsaturated carboxylic acids with disulfides and diselenides for the synthesis of γ-lactones **31**.



Scheme 37. Proposed mechanism for synthesis of lactones **31**.

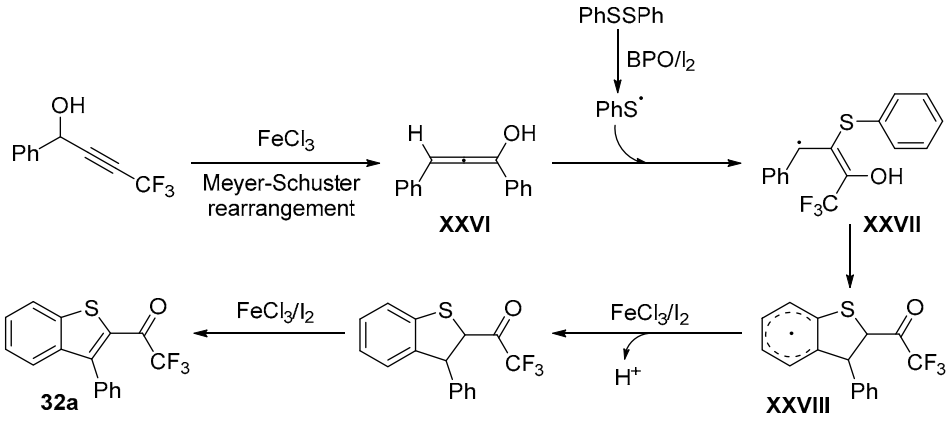
2.3.3. Chalcogen-Based Heterocycles

In 2017, Zhang and coworkers reported an elegant method to perform a thiocyclization of trifluoromethylated propynyls, in the presence of diorganyl disulfides, to construct the 2-trifluoroacyl benzothiophene derivatives **32** by the sequential formation of C-S and C-C bonds [60]. The reactions were carried out in the presence of $FeCl_3$ (20 mol%) as catalyst, benzoyl oxide (10 mol%) and I_2 (2 equiv.) as an oxidative system, and $MeNO_2$ as solvent, after which the resulting mixture was stirred for up to 12 h at 120 °C. Under these conditions, a library of 2-trifluoroacyl benzothiophenes **32** were satisfactorily prepared in moderate to very good yields. The methodology presented good substrate tolerance to electron withdrawing and donating groups, as well as to bulky and *ortho*-substituted substrates. In addition, the authors demonstrated the feasibility of the protocol to employ diphenyl diselenide as substrate, resulting in **32g** of a product in a yield of 62% (Scheme 38).



Scheme 38. $FeCl_3$-catalyzed cyclization of propynyls with disulfides and diselenides.

Based on control reaction experiments and on the literature, authors have proposed a plausible reaction mechanism which initially involves an $FeCl_3$-catalyzed Meyer-Schuster rearrangement to produce the active allenol intermediate **XXVI**. In parallel, the homolytic cleavage of the S-S bond, mediated by BPO and I_2, delivers the thiyl radical (PhS·) in the reaction medium, which promotes a selective addition to the allenol **XXVI**, reaching the allyl radical intermediate **XXVII**. Subsequently, a keto-enol tautomerism and an intramolecular radical electrophilic annulation affords the cyclohexadienyl radical intermediate **XXVIII**. Finally, a successive oxidation drives the reaction toward the formation of the desired aromatic product **32a** through an SET and deprotonation process (Scheme 39).

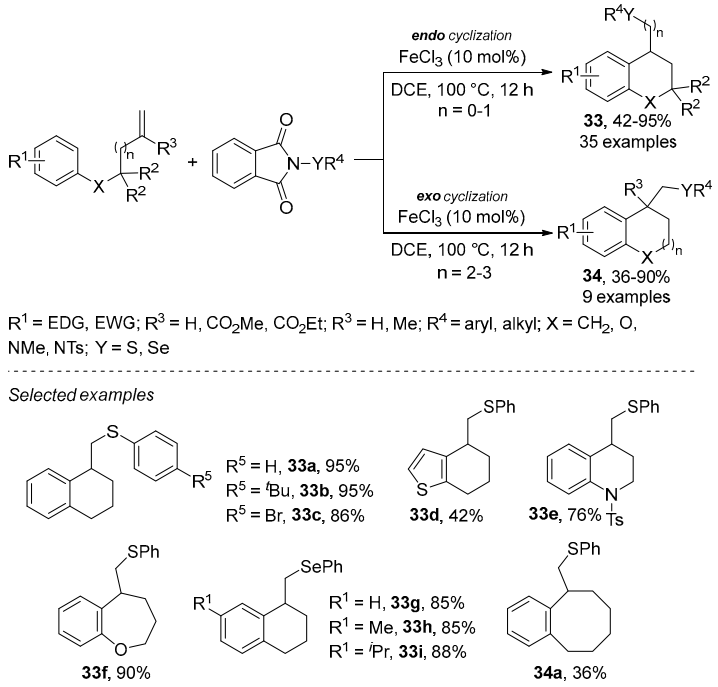


Scheme 39. Proposed mechanism for the synthesis of **32**.

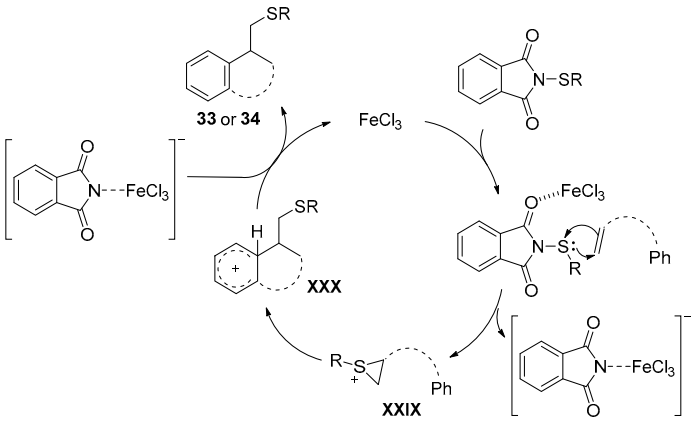
2.3.4. Miscellaneous

Lv, Li, and coworkers reported a regio-divergent carbochalcogenylation of inactivated alkenes through an $FeCl_3$-catalyzed annulation process in the presence of electrophilic *N*-chalcogenophatalimides as sulfur or selenium source reagents [61]. The protocol involves the application of simple reaction conditions by mixing the starting materials and $FeCl_3$ (10 mol%) in DCE and heating the resulting mixture for 12 h at 100 °C under N_2 atmosphere. The developed protocol provided the synthesis of a library of thirty-five medium-sized sulfur-decorated rings (6-, 7- and 8-membered rings) **33** and **34**, in addition to nine selenium-based derivatives **33** in poor to excellent yields. The methodology presented good scalability when scale up experiments were carried out. In general, the protocol presented good substrate tolerance to electron-rich alkenes and heteroaromatic derivatives. However, limitations were found when electron deficient substrates (R^1 = 4-NO_2) and heteroaromatic systems (quinoline) were employed, suppressing the formation of the desired products (Scheme 40).

The authors performed several control experiments, including kinetic isotopic effect and radical scavenger experiments, aiming to gain insights toward the role of iron in the reaction. Thus, a plausible reaction mechanism was initially proposed involving the activation of the *N*-sulfenylphtalimides by the $FeCl_3$ catalyst. Therefore, the alkene undergoes a sulfenyl addition to afford the thiiranium intermediate **XXIX**, as well as the Fe(III)-based anion. This event is followed by the intramolecular ring opening reaction by the attack of the aryl group, yielding the dearomatic intermediate **XXX.** It is worth mentioning that authors drew attention to the fact that the endo/exo selectivity in the ring opening event depends on the length of the carbon chain between the C-C double bond and the aryl ring. Finally, the Fe(III)-based anion performs a deprotonation of the intermediate **XXX,** affording the expected aromatic products **33** or **34** and releasing the $FeCl_3$ to restart the catalytic cycle (Scheme 41).



Scheme 40. Fe(III)-catalyzed carbosulfenylation of inactivated alkenes.

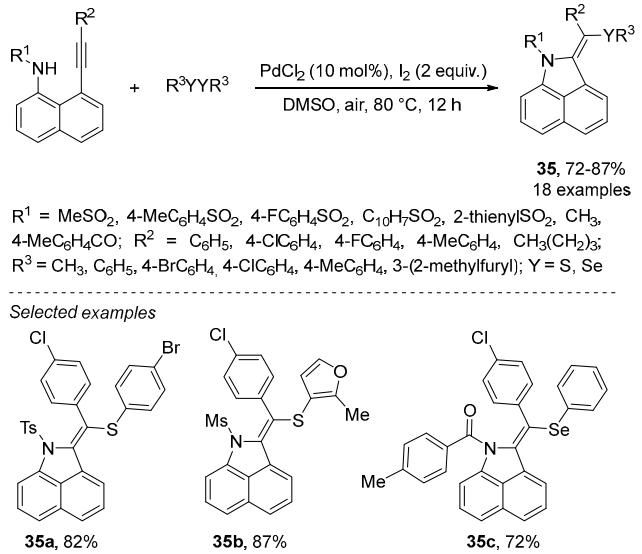


Scheme 41. Proposed reaction mechanism for the carbosulfenylation of alkenes.

2.4. Using Palladium as Catalyst

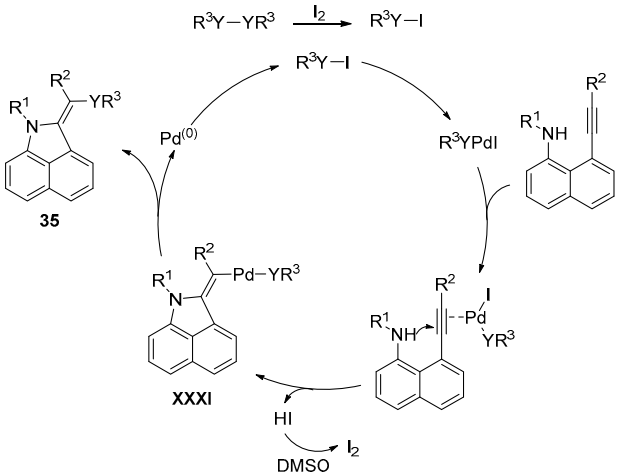
Palladium catalysis in organic synthesis is a powerful methodology to promote several transformations, including the C-C and carbon–heteroatom (C–N, C–O, C–S, and C–Se) bond formation. In addition, reactions involving palladium are used to provide high efficiency and excellent chemoselectivity. A special group of transformations is represented by palladium π-alkyne chemistry with the direct introduction of an organochalcogen unit into a newly formed *N*-heterocyclic system.

The synthesis of highly functionalized 1,2-dihydrobenzo[*cd*]indoles **35** was proposed by Zhang, Zhou, and co-workers under palladium(II) chloride-catalyzed thiolation/cyclization reaction of 8-alkynylnaphthalen-1-imines (Scheme 42) [62]. The main features of this work raise the fact that the reaction is regioselective, enabling the intramolecular 5-*exo-dig* cyclization and stereoselective, giving the 2-(arylthio)alkylene-containing *N*-heterocyle in (*E*)-configuration. The procedure was compatible with differently substituted sulfonyl, acyl, and alkyl groups directly bonded to the nitrogen atom. Moreover, the use of dialkyl disulfides, diaryl disulfides, and diphenyl diselenide was also evaluated, giving the corresponding products in moderate to good yields under optimal conditions.



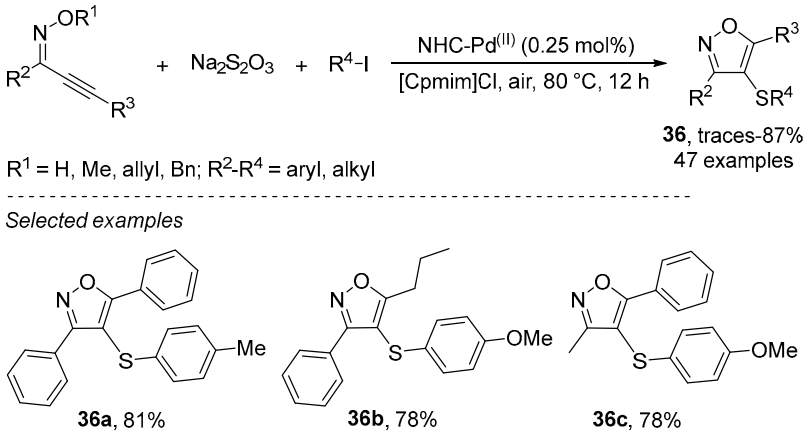
Scheme 42. Synthesis of (*E*)-2-(arylchalcogenyl)alkylene-1,2-dihydrobenzo[*cd*]indoles **35**.

A plausible pathway for this cyclization involves the formation of a sulfenylpalladium species, which subsequently coordinates with the Csp-Csp bond of the naphthalen-1-amine, becoming the triple bond available to intramolecular aza-cyclization. After cyclization, intermediate **XXXI** is formed, which allows the reductive elimination of palladium species, giving product **35** and regenerating the catalyst to the next cycle (Scheme 43).



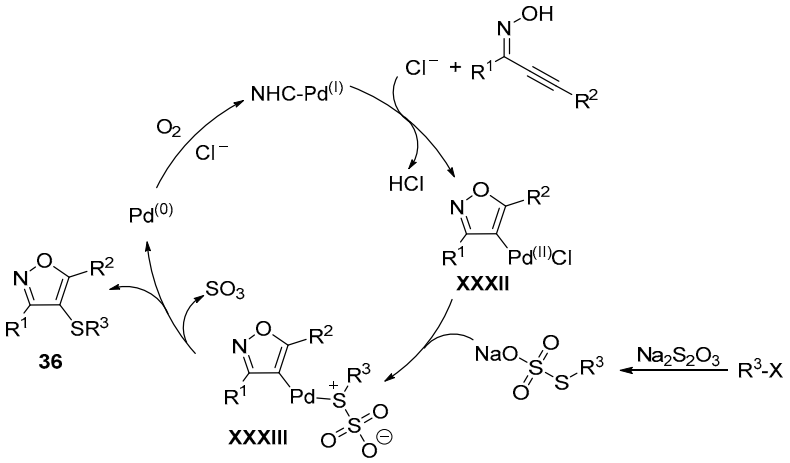
Scheme 43. Proposed mechanism for the synthesis of **35**.

In 2019, Li, Jiang, and co-workers reported an NHC-Pd(II) complex (0.25 mol%) catalyzing three-component reaction using acetylenic oximes, aryl iodide, and $Na_2S_2O_3$ as an inorganic, odorless, and stable sulfur source to prepare a wide array of 4-(organylthio)isoxazoles **36** (Scheme 44) [63]. The ionic liquid [Cpmim]Cl was elected as the best solvent at 80 °C under aerobic conditions. A range of 4-(organylthio)isoxazoles **36** bearing both electron-rich and electron-poor groups were obtained in moderate to good yields. Notably, aliphatic substituents in both terminal acetylenic position or directly bonded to the Csp^2 of the oxime were well tolerated. Moreover, the employment of *O*-alkyl oximes showed themselves to be promising as reaction partners, delivering the cyclic products in moderate yields. Despite the broad scope and group compatibility, limitations on product formation were observed for strong electron-withdrawing groups bonded to acetylenic oximes that hampered the sulfur-transfer to the isoxazole. Still, the use of alkyl iodides instead of aryl iodides were not compatible with the present protocol.



Scheme 44. Synthesis of 4-(organylthio)isoxazoles **36**.

Mechanistically, the authors proposed the *trans*-oxypalladation of oximes furnishing the isoxazole palladium(II) complex **XXXII**. Subsequently, the reaction of **XXXII** with sodium *S*-arylthiosulfate gives rise to a palladium thiosulfate intermediate **XXXIII**, which, via reductive elimination, delivers product **36**, releases SO_3, and regenerates palladium species to the next catalytic cycle (Scheme 45).



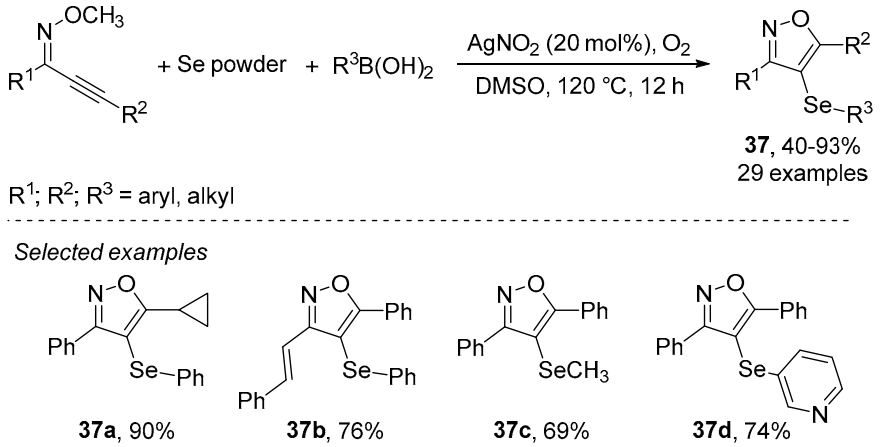
Scheme 45. Proposed mechanism for the synthesis of **36**.

2.5. Using Silver as Catalyst

Silver-catalyzed radical intramolecular cyclization reactions of unsaturated systems in the presence of elemental selenium or sodium sulfinates have been demonstrated. This synthetic tool has proven to be useful for the preparation of different chalcogen-containing heterocycles including isoxazoles, spiro-cyclohexadienones, lactones, isochromenones, and benzochalcogenophenes.

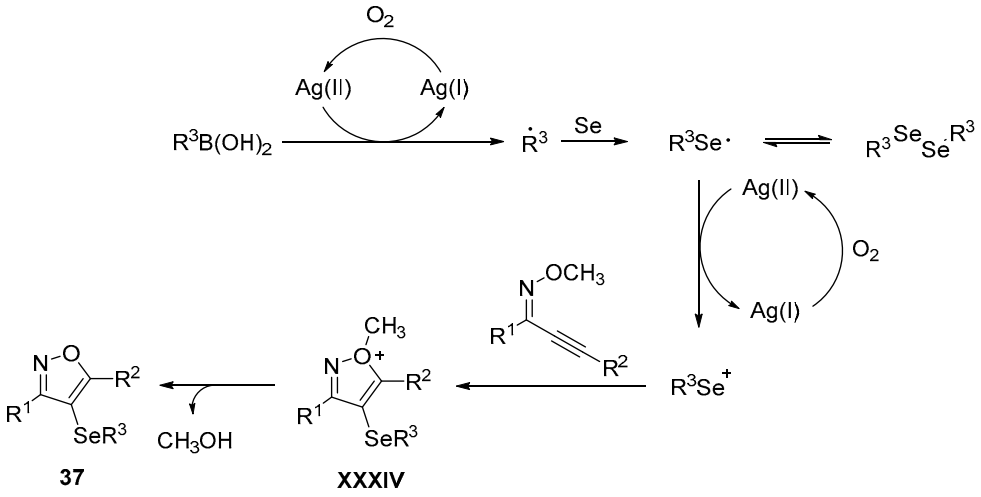
2.5.1. N-Based Heterocycles

Zhou, Liu, and co-workers reported an efficient and versatile protocol for the synthesis of a wide variety of selanyl-decorated isoxazoles **37** catalyzed by $AgNO_2$ from *o*-methyloximes, selenium powder, and organoboronic acids as reagents (Scheme 46) [64]. The reaction conditions involved the use of DMSO as solvent at 120 °C and the O_2 atmosphere proved to have a key role in this reaction. Using this protocol, a series of twenty-nine 4-organoselanylisoxazoles **37** were prepared in 40% to 93% yields.



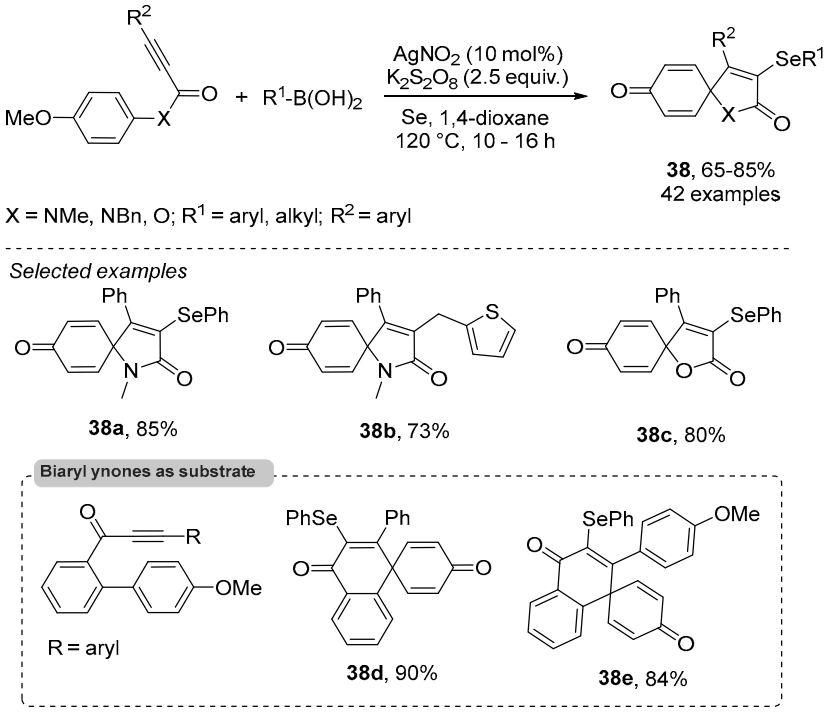
Scheme 46. Synthesis of selenated isoxazoles **37**.

The proposed mechanism is presented in Scheme 47. It involves the Ag-catalyzed formation of an aryl radical which is captured by Se^0, leading to the formation of an organylselenium radical intermediate. Then, this radical is oxidized to cationic selenium species, which reacts with the *o*-methyloxime, forming cationic species **XXXIV** and, after hydrolysis, yields the desired Se-containing cyclic product **37** and methanol as a by-product.



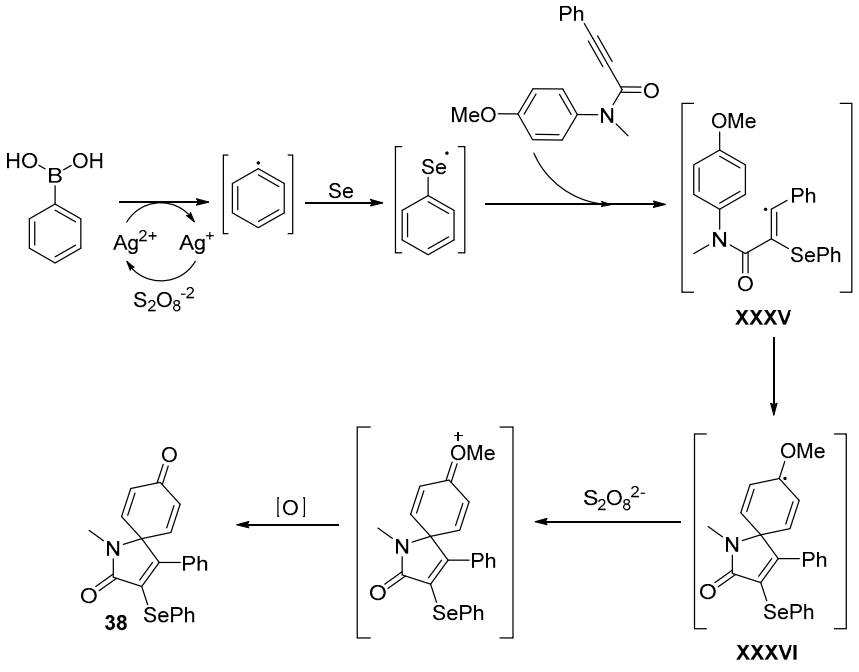
Scheme 47. Proposed mechanism for the $AgNO_2$-catalyzed cyclization reaction.

In 2022, Reddy and coworkers reported an elegant protocol to perform the simultaneous C-Se and C-C bond formation through Ag-catalyzed oxidative dearomatization multicomponent process by reacting carbonylated-alkynes with boronic acids and selenium powder [65]. The best reaction condition still employs $AgNO_2$ (10 mol%) as catalyst, $K_2S_2O_8$ (2.5 equiv.) as oxidant, and 1,4-dioxane as solvent, with the resulting mixture stirred at 120 °C, from 10 to 16 h. The developed protocol allowed the synthesis of forty-two spirocyclic products **38** in an up to 90% yield. This protocol presented a good substrate tolerance, since a wide diversity of electronic activated and deactivated boronic acids (aryl, heteroaryl, and alkyl) were suitably employed, as well as Csp-substituted groups (Scheme 48).



Scheme 48. Synthesis of selenium-spirocycles **38** via Ag-catalyzed selenylative annulation reaction.

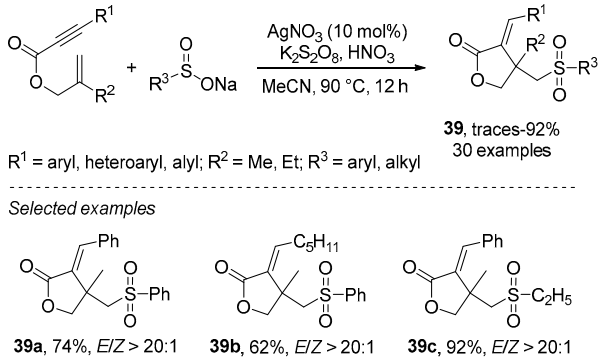
Based on control experiments and on the literature data, the authors have proposed a plausive reaction mechanism to describe the transformation events. Initially, persulfate ion ($S_2O_8^{-2}$) promotes the oxidation of Ag(I) to Ag(II), which triggers the homolytic cleavage of the C-B bond, yielding the aryl radical intermediate, which is trapped by Se^0 to produce the selenium-centered radical intermediate. Then, a radical addition to the C-C triple bond affords the key intermediate **XXXV**, which undergoes an intramolecular annulation to be converted into the radical intermediate **XXXVI**. Finally, oxidation promoted by the persulfate ion drives the reaction to the formation of the desired products **38** (Scheme 49).



Scheme 49. Proposed mechanism for the radical cascade cyclization catalyzed by $AgNO_2$.

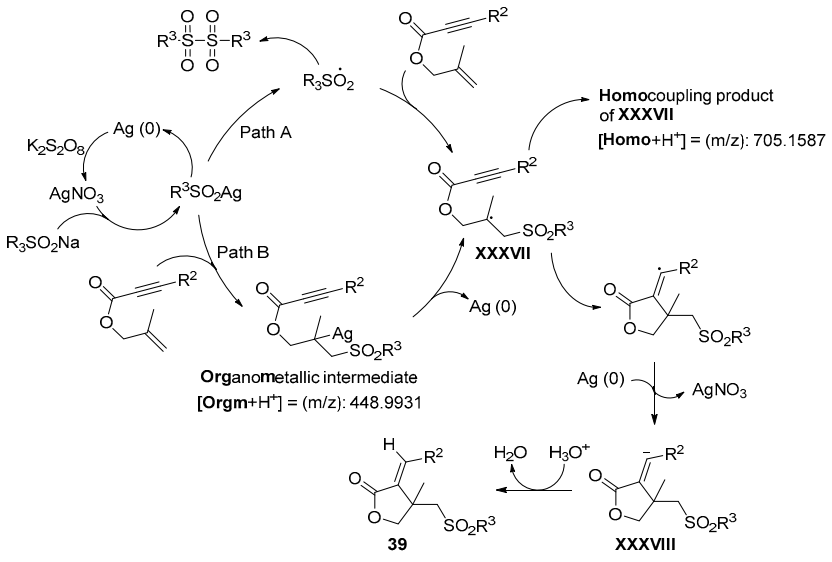
2.5.2. O-Based Heterocycles

Sulfonated α-methylene γ-lactones **39** were efficiently synthesized through silver-catalyzed radical addition followed by intramolecular cyclization reaction of 1,6-enynes with sodium sulfinates (Scheme 50) [66]. The protocol reports the use of $AgNO_3$ (10 mol%) as catalyst, $K_2S_2O_8$ as oxidant, and HNO_3 as additive, which is believed to accelerate the reaction, in acetonitrile at 90 °C for 12 h. Under these conditions, sodium alkyl- and arylsulfinates bearing both electron-donating and electron-withdrawing groups were compatible, resulting in the expected sulfonated butyrolactones in moderate to good yields and E/Z ratios higher than 20:1 in most cases. Additionally, different alkyl and aryl substituents attached to 1,6-enynes were tolerated under optimal conditions. The reaction scope demonstrated a good functional group tolerance and could be carried out even on a gram scale. Notably, heterocyclic-substituted sodium sulfinate, as well as terminal alkyne, did not undergo the reaction.



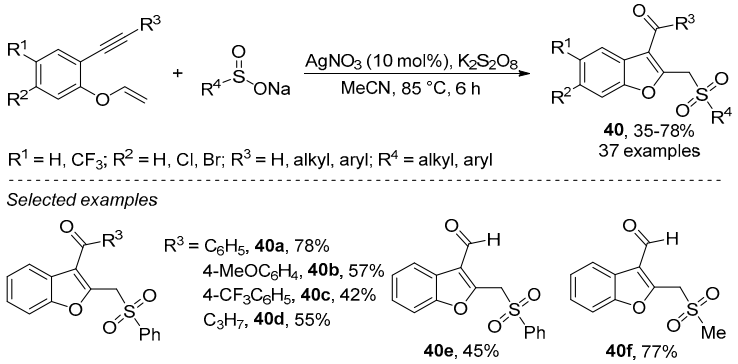
Scheme 50. Synthesis of sulfonated α-methylene γ-lactones **39**.

A reaction mechanism was proposed based on control experiments, electron spin resonance (ESR) experiments, and mass spectrometry (ESI-MS) analysis, as demonstrated in Scheme 51. First, the key intermediate sulfonyl-silver complex is formed by the reaction of sodium sulfinate with $AgNO_3$. Then, the reaction of 1,6-enyne by both sulfonyl radical (path A) or silver(I) species (path B) generates alkyl radical species **XXXVII**. Subsequently, an intramolecular radical addition/cyclization reaction provides the lactone-containing vinyl radical, which is reduced via Ag(II)-promoted SET process, producing **XXXVIII**. Finally, protonation of **XXXVIII** affords the desired lactone **39**.



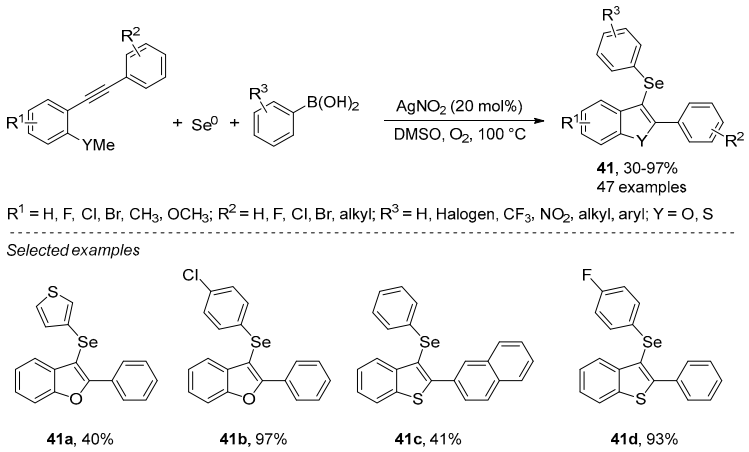
Scheme 51. Proposed reaction mechanism for the synthesis of **39**.

Soon after, the same group reported the efficient synthesis of sulfonated 3-carbonylbenzofurans **40** starting from alkynyl vinyloxy benzenes and sodium sulfinates (Scheme 52) [67]. The starting materials, $AgNO_3$ (20 mol%) as catalyst and $K_2S_2O_8$ as oxidant, were placed to react in acetonitrile at 85 °C for 6 h. The most striking features of this protocol are the wide tolerance for alkyl, electron-deficient, and electron-rich substituents attached to both 1,6-enynes and sulfinates, for the preparation of highly functionalized-benzofurans under mild conditions and in a step-economic process.



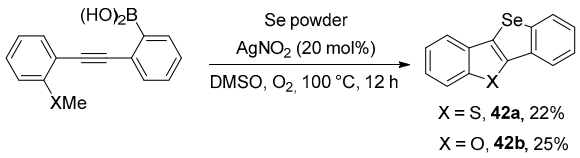
Scheme 52. Synthesis of sulfonated benzofurans **40**.

A concise methodology for the synthesis of Se-containing benzofurans and benzothiophenes **41** by Ag-catalyzed radical cyclization of 2-alkynyl(thio)anisoles, Se powder, and arylboronic acids was developed by Zhou, Liu, and co-workers in 2019 (Scheme 53) [68]. Under the optimal reaction conditions, which included $AgNO_2$ (20 mol %) as catalyst and DMSO as solvent under O_2 atmosphere at 100 °C, a series of selanylated heterocycles **41** were prepared in yields ranging from 30% to 97%.



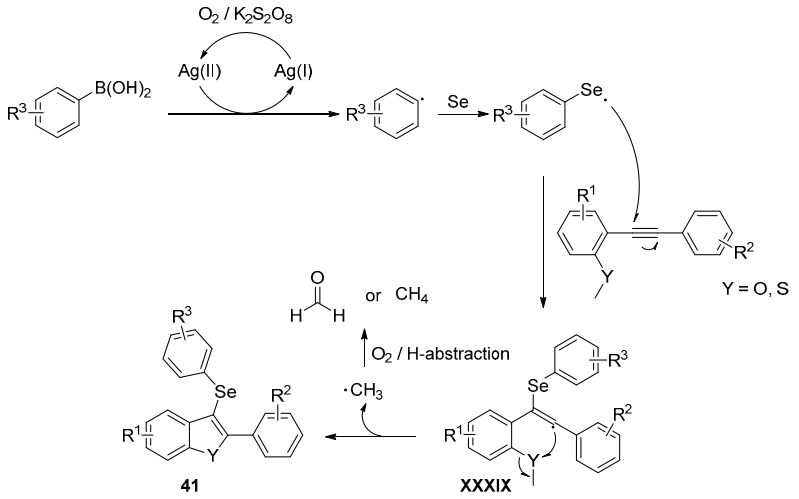
Scheme 53. Synthesis of selanylated benzofurans and benzothiophenes **41**.

This methodology was also applied to intramolecular silver-catalyzed radical cyclization, which afforded polycyclic selenium-containing heteroaromatics **42a** and **42b** in 22% and 25% isolated yields, respectively (Scheme 54).



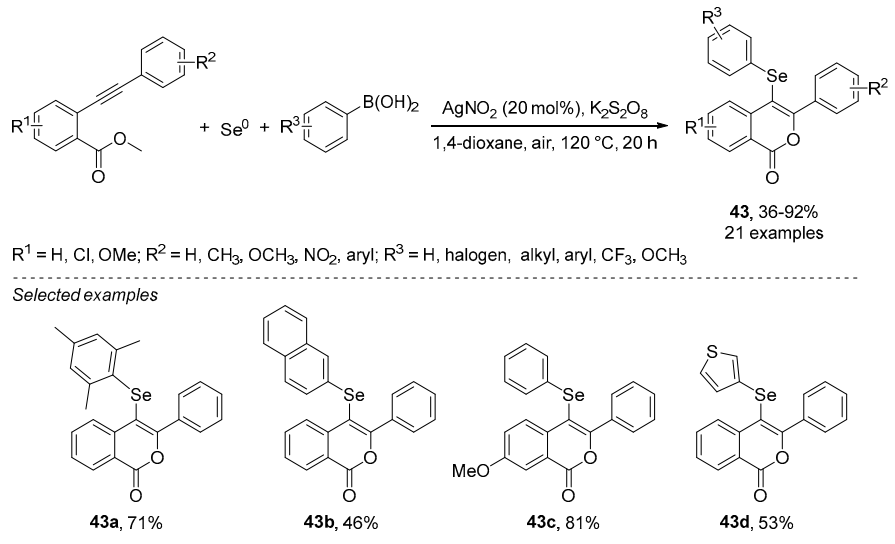
Scheme 54. Ag-catalyzed intramolecular cyclization for the synthesis of Se-containing heterocyles **42**.

According to the proposed mechanism (Scheme 55), initial conversion of arylboronic acid to the corresponding aryl radical species mediated by the catalytic system of $AgNO_2/O_2$ occurs. Then, in situ radical trapping by elemental selenium leads to the selenium-centered radical intermediate, which reacts with 2-alkynyl(thio)anisole, forming the alkenyl radical species **XXXIX**. Finally, intramolecular radical cyclization forms the desired Se-containing heterocycles **41**, while the remaining methyl radical is converted to formaldehyde or methane.



Scheme 55. Proposed radical reaction mechanism for the synthesis of **41**.

One year later, the same research group described the first synthesis of Se-containing isochromenones **43** by $AgNO_2$-catalyzed cyclization reaction (Scheme 56) [69]. This three-component protocol showed good efficiency for a series of alkynylarylesters and aryl-boronic acids bearing different substituents on the aromatic ring, using elemental selenium as chalcogen source. As the catalyst, $AgNO_2$ proved to give the best yield, although other silver salts such as $AgSbF_6$ and Ag_2SO_4 also catalyzed the cyclization reaction, albeit with lower yields. The optimum reaction conditions were dioxane as solvent at 120 °C under open-air atmosphere, resulting in a series of twenty-one selenated isochromenones **43** in 36–92% yield. The proposed mechanism for this reaction is similar to that described in Scheme 55, with the formation of selenium-centered radical as the key step.

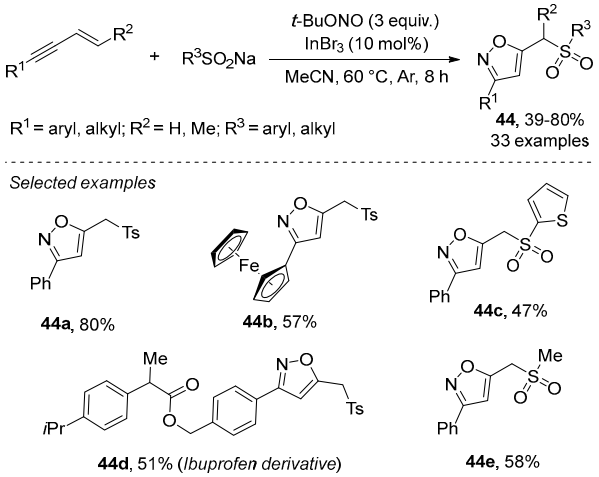


Scheme 56. Synthesis of Se-containing isochromenones **43** by $AgNO_2$-catalyzed cyclization reaction.

2.6. Using Indium as Catalyst

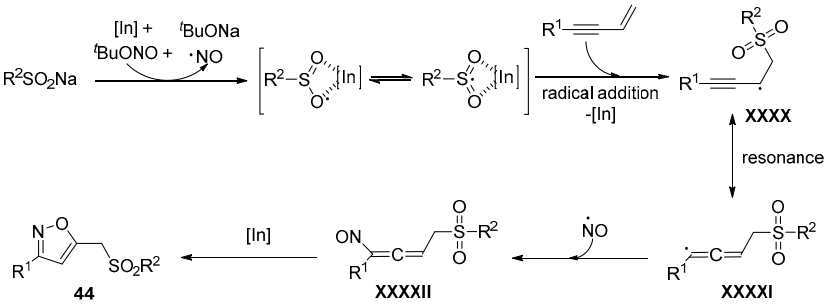
Indium salts have been widely recognized due to their high tolerance with oxygen- and nitrogen-containing functional groups. Furthermore, indium(III) exhibits catalytic activity as a soft Lewis acid, activating both C-heteroatom and C-C unsaturated systems, and finding application in the synthesis of organic cyclic compounds.

In 2020, Hu, Li, and coworkers reported a fashioned unprecedented protocol for the 1,3,4-trifunctionalization cascade of 1,3-enynes, allowing the simultaneous formation of C-S, C-N, and C-O bonds by a sequence of sulfonating, isomerization, nitration, and annulation events [70]. The authors have set the best reaction condition by reacting 1,3-enynes in the presence of sodium sulfinate, *t*-butyl nitrite (TBN), and $InBr_3$ (10 mol%), employing MeCN as solvent, with the resulting mixture stirred for 8 h at 60 °C under argon atmosphere. Through this reported method, thirty-three 5-sulfonylisoxazoles **44** derivatives were prepared in poor to very good yields, presenting an excellent substrate tolerance. Among the synthetized derivatives, an Ibuprofen analogue **44d** is a remarkable example which shows the potential of this protocol in a late-stage functionalization of natural products (Scheme 57).



Scheme 57. In(III)-promoted radical-mediated 1,3,4-trifunctionalization of 1,3-enynes.

After performing reactions in the presence of radical inhibitors, the authors proposed a plausible radical reaction mechanism. Thus, initially, sodium sulfinate reacts with ^{t}butyl nitrite, yielding a sulfonyl radical species and a NO radical species. After that, a selective radical addition across the C-C double bond of 1,3-enyne gives the intermediate **XXXX**, which is in resonance with radical allenyl species **XXXXI**. Then, a coupling with NO radical species produces the allenyl species **XXXXII**, which undergoes intramolecular nucleophilic cyclization, delivering the desired isoxazole **44**. According to the authors, the role of $InBr_3$ might be both as a Lewis acid to activate the sulfonyl radical intermediate and as facilitator to the cyclization step (Scheme 58).

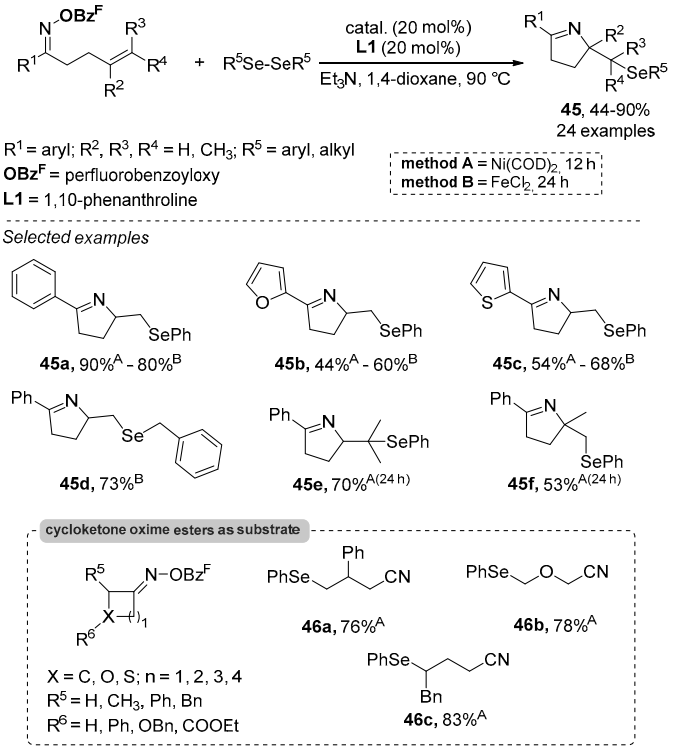


Scheme 58. Proposed mechanism for radical-mediated 1,3,4-trifunctionalization of 1,3-enynes.

2.7. Using Nickel as Catalyst

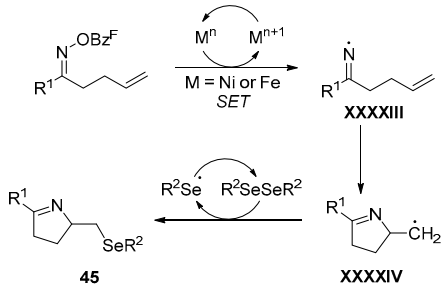
Nickel is an earth-abundant and low-cost transition metal, suitable to achieve several chemical transformations in organic synthesis. Although less used in organochalcogen chemistry when compared to copper and palladium, the synthetic utility of a nickel complex in a chalcogenative heterocyclization reaction has also been demonstrated.

Selander, Zhou, and coworkers have reported a strategy to perform a radical cyclization and ring opening of oxime esters in the presence of diorganyl diselenides, with the process catalyzed by Ni(0) or Fe(II) species [71]. In this sense, the authors developed two methods to perform the synthetic transformations efficiently. The method A involves mixing the oxime ester, diorganyl diselenides, and $Ni(COD)_2$ (20 mol%) as catalysts and 1,10-phenanthroline (20 mol%) as ligand in the presence of 1,4-dioxane as solvent and Et_3N as base, with the resulting mixture stirred for 12 h at 90 °C. On the other hand, the method B was set just by using $FeCl_2$ (20 mol%) instead of $Ni(COD)_2$ as catalyst, and extending the reaction time from 12 to 24 h. Under these conditions, the authors conducted the synthesis of organoselenium-decorated pyrrolines **45** and alkyl nitriles **46** by employing γ,δ-unsaturated oximes or cycloketone oximes, respectively. The protocol presented remarkable substrate tolerance, since a wide variety of electron-poor and electron-rich substituents were satisfactorily employed, despite being satisfactorily scaled-up from 0.2 mmol to 0.8 mmol (Scheme 59).



Scheme 59. Ni(0) or Fe(II)-catalyzed radical cyclization reactions of oxime esters with diselenides.

According to control experiments and the literature data, the authors proposed a similar reaction mechanism for both metal species (Ni and Fe). The transformation starts with the metal-promoted homolytic cleavage of the N-O bond via an *SET* process, giving the iminyl radical species **XXXXIII**, which quickly undergoes an intramolecular radical annulation, being converted into the cyclic intermediate **XXXXIV**. Finally, the carbon-centered radical intermediate **XXXXIV** reacts with diorganyl diselenide, yielding the desired product **45** and releasing selenium-centered radical species to the reaction medium, which are instantly oxidized to the respective diselenide (Scheme 60).



Scheme 60. Proposed mechanism for radical cyclization of oxime esters.

3. Conclusions and Perspectives

The structural diversity achieved in the transition metal-catalyzed synthesis of organochalcogen-containing heterocycles provides the direction to design and synthesize advanced molecules for biological and new material applications. The results summarized in this review demonstrate the importance and versatility of both alkenes and alkynes as starting materials to prepare differently functionalized heterocyclic compounds. The most recent approaches addressed the reactions of several organic and inorganic chalcogen species as precursors that enable the incorporation of a sulfur, a selenium, or a tellurium atom into five-, six- and seven-membered cycles. From this point of view, the chalcogenative annulation of acyclic unsaturated compounds catalyzed by transition metals represent a current opportunity to construct libraries of new molecules for fine applications. Transition metals are an indispensable toolbox for organic synthesis, but some drawbacks associated with their use can be evidenced: the low abundance and high cost of some noble metals, lack of mechanistic understanding of catalytic processes, toxicity, and environmental concerns. Although these are difficulties, they provide opportunities for researchers to achieve new chemical bonds and organic structures in high yields and selectivities not reached by other methods. In this sense, novel advancements arising from photo-redox chemistry, electrochemistry, flow chemistry, and the use of sustainable solvents are under intense development. From this point of view, future perspectives on chalcogenative heterocyclization reactions support applications of classical transition-metal catalysis in conjugation with environmentally friendly platforms. The current diversity of metals used for the synthesis of organocalcogen-decorated heterocycles also demonstrates the direction of using earth-abundant and low-cost metals. The big challenges are the development of stable, selective, and reusable catalysts applicable to rational chemo- and stereoselective transformations of interest to the fine chemical and pharmaceutical industry. Finally, the findings described here are very encouraging and we believe that they can help researchers interested in this area to conduct future developments in heterocycle synthesis and organochalcogen chemistry.

Author Contributions: Conceptualization, R.F.S., P.T.B. and F.P.; classification and analysis of the collected manuscripts and writing—original draft preparation, E.L.G., T.A. and F.B.S.; writing—review and editing, P.T.B. and F.P.; supervision, R.F.S.; project administration, R.F.S.; funding acquisition, R.F.S., P.T.B. and F.P. All authors have read and agreed to the published version of the manuscript.

Funding: This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior—Brasil (CAPES)—Finance Code 001. Fundação de Amparo à Pesquisa do Estado do Rio Grande do Sul (FAPERGS), grant number PqG 19/2551-0001947-5, ARD 23/2551-0000842-4, 23/2551-0000800-9; Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and Financiadora de Estudos e Projetos (FINEP) are acknowledged for financial support. CNPq is also acknowledged for the Fellowship for RFS.

Data Availability Statement: No new data were created or analyzed in this study. Data sharing is not applicable to this article.

Conflicts of Interest: The authors declare no conflict of interest.

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