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Recent advances in tandem selenocyclization and tellurocyclization with alkenes and alkynes

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Seleno-containing heterocycles exist widely in pharmaceutical molecules and the skeletons of natural products. The addition of organoselenium to alkenes and alkynes *via* intramolecular tandem selenocyclization is an efficient method for preparing selenofunctionalized heterocycles. In this protocol, multiple bonds are formed in a single reaction without the need to isolate intermediates. This review highlights recent progress in this rapidly growing area with an emphasis on the scopes, limitations and the mechanisms of these different reactions. Besides, tandem tellurocyclization with alkenes and alkynes is also briefly discussed.

1. Introduction

Organoselenium compounds are considered an important class of molecules in organic synthesis. These compounds are widely applied in materials and catalysis and as intermediates in organic synthesis.[1] In addition, organoselenium compounds have been shown to have pharmacological activities such as anticonvulsant, antioxidant, antidepressant, anticancer, antitumor, anti-inflammatory and antiviral properties.[2] The introduction of a selenium atom into a potentially bioactive molecule can dramatically increase the native biological activity of the substrate. Meanwhile, heterocycles, which exist in natural products and biologically active molecules, play significant roles in the pharmaceutical and agrochemical industries.[3] For all these reasons, continuous research effort has been devoted to the development of useful methods for synthesizing selenofunctionalized heterocycles. Currently, one way to access these compounds is the direct functionalization of the heterocycle precursor with a selenium source *via* transition metal catalysis.[4] However, this method is limited by its poor regioselectivity and direct use of preformed or commercially available heteroaromatic counterparts. Alternatively, the addition of organoselenium to alkenes and alkynes *via* intramolecular tandem selenocyclization is an efficient protocol for preparing selenofunctionalized heterocycles. In this protocol, multiple bonds are formed in a single reaction without the need to isolate intermediates.

Over the past decade years, the selenocylization of the selenium electrophiles (*e.g.*, ArSeCl, ArPhBr, and ArthSe) with alkenes or alkynes have been deeply developed.[5] However, the sensitivity to moisture and a short shelf life limited the appli-

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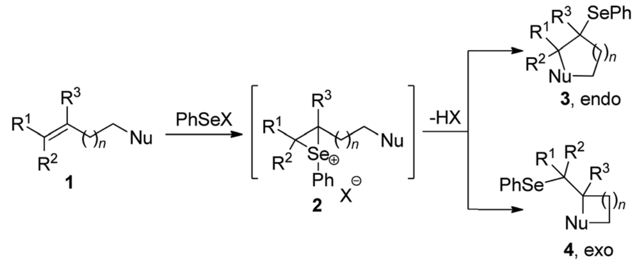
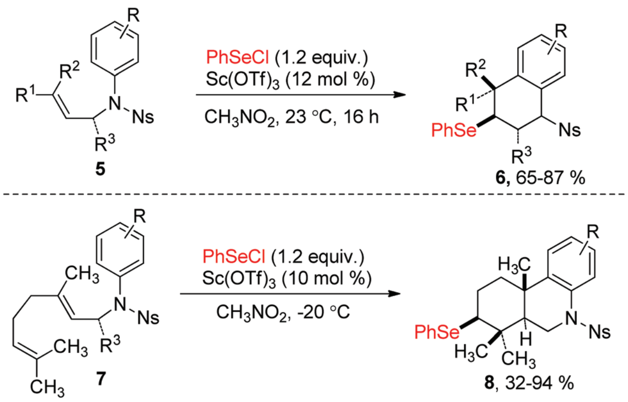
cation. In contrast, diselenides are easily accessible and operable selenium reagents in organic synthesis, making them a good choice for selenocyclization.[6] Although some approaches have been reported for the intramolecular tandem selenocyclization reactions of diorganyl diselenides with alkenes and alkynes, few efforts have systematically reviewed tandem selenocyclization with alkenes and alkynes. In consideration of recent research progress and to better understand selenium-based intramolecular tandem selenocyclization, this review article firstly introduce the traditional selenocylization with some selenium electrophiles, and then summarize the latest contributions to selenocyclization reactions of diorganyl diselenides with alkenes and alkynes between 2010 and 2020 and highlights the insights gained from previous methodological and mechanistic studies. The content is categorized by the type of catalysis, including metal catalysis, visible-light catalysis, electrochemical catalysis, organocatalysis, and other catalysis types involving hypervalent iodine- and peroxide-promoted reactions.

2. Traditional selenocyclization

Since the discovery in the late 1960s that species of type RSeX added stereospecifically to simple alkenes to the formation of a selenolactone,[7] these reactions were extensively developed to construct the selenofunctionalized heterocycles. Mechanistically, seleniranium ion **2** was formed by the addition of RSeX to unsaturation bond, which then was captured by a pendant nucleophilic group to generate a cyclic product with chemo-, regio-, stereo-specificity (Scheme 1).[8] For example, in 2013, the group of Shaw reported tandem monocyclization and bicyclization reactions between alkenes and PhSeCl in the presence of catalytic quantities of $Sc(OTf)_3$ to access polysubstituted tetrahydroquinoline **6** and octahydrophenanthridine **8** in moderate to high yields (Scheme 2).[9] In this process, two rings, three bonds, and three stereogenic centers were formed with excellent stereo- and regio-control in one step.



Scheme 1 Mechanism of traditional selenocyclization.



Scheme 2 PhSeCl promoted synthesis of selenyl tetrahydroquinoline and octahydrophenanthridine.

Moreover, *N*-(2-nitrophenylselenenyl)succinimide (NPSP) was also used as the electrophilic selenium source. In 2015, Yeung and co-workers described an enantioselective selenolactonization of olefinic acids **9** and NPSP, using hydroquinidine 1,4-phthalazinediyl diether ($(DHQD)_2PHAL$) as the catalyst (Scheme 3).[10] A series of functional groups were tolerant with this catalytic system, giving the corresponding selenolactones **10** with good yields and ee values. Additionally, heteroaromatic substrate was also reacted well in this catalytic system.

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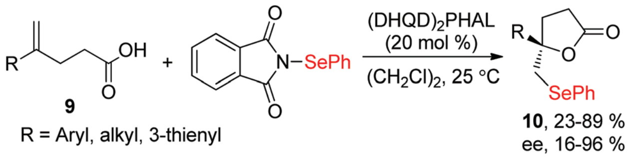


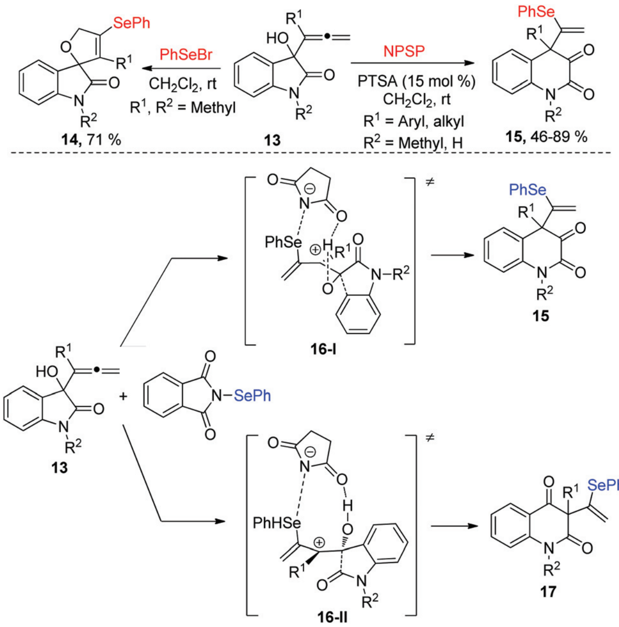
Scheme 3 NPSP promoted synthesis of enantioselective selenolactonization.

Scheme 4 PhSeCl promoted synthesis of β-organoselenium butenolides.

Although cyclohexyl substrate was accommodated in 89% yield, the ee was only 16% under this catalytic protocol. The mechanism study shows that the large catalyst pocket was required for this transformation to avoid racemization of the chiral episeleniranium ion, introducing high enantioselectivity.

Allenes owing to two cumulative carbon–carbon double bonds have some unique chemical properties.[11] For example, in 2004, the Ma's group demonstrated a electrophilic cyclization of 2,3-allenoic acids **11** with PhSeCl for the synthesis of β-organoselenium butenolides **12** (Scheme 4).[12] The reaction showed a broad substrate scope, and 4-mono-substituted, 2,4-disubstituted, and 2,4,4-trisubstituted 2,3-allenoic acids can all be applied to afford the corresponding products in 77–98% yields. Moreover, this protocol can also be compatible to the corresponding electrophilic cyclization of PhSCl.

In 2012, Alcaide and co-workers disclosed an electrophilic selenocyclization of 2-indolinone-tethered allenols **13** with various selenenylating reagents, affording different heterocycles, which was shown good chemoselectivity (Scheme 5).[13] PhSeBr, *N*-phenylselenosuccinimide (NPSS), or diphenyl diselenide as donors of PhSe$^+$ in reactions with 2-indolinone-tethered allenol XX delivered spirocyclic selenolactams **14**, and



Scheme 5 The selenocyclization of 2-indolinone-tethered allenols for the synthesis of spirocyclic selenolactams and quinoline-2,3-diones.

PhSeBr was the optimal selenenylating reagents, giving the target product with 71% yield in 1 hour without any additives Moreover, quinoline-2,3-diones **15** were obtained by using NPSP and catalytic amounts of *p*-toluenesulfonic acid (PTSA) in dichloromethane at room temperature. The mechanism of NPSP-promoted ring expansions was proposed in Scheme 5. First, the addition of PhSe$^+$ cation to the proximal allenic double bond produces the intermediate **16.** The intermediate **16** has two regioisomer: **16-I** and **16-II**, which occur a ring expansion to give the corresponding products **15** and **17.** The migration of the phenyl group is preferred to the migration of the carbonyl one, and **15** is the major product.

In subsequent work, Alcaide and coworkers reported a metal-free oxidative selenofunctionalized reaction between allenes and diphenyl diselenide (Scheme 6).[14] This reaction

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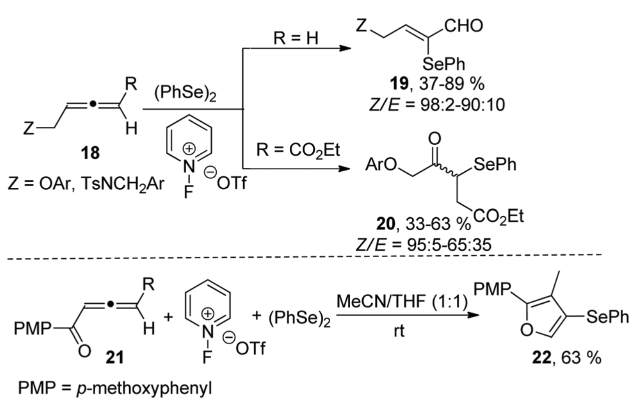


Scheme 6 The synthesis of α-seleno-α,β-unsaturated carbonyls and selenated furan.

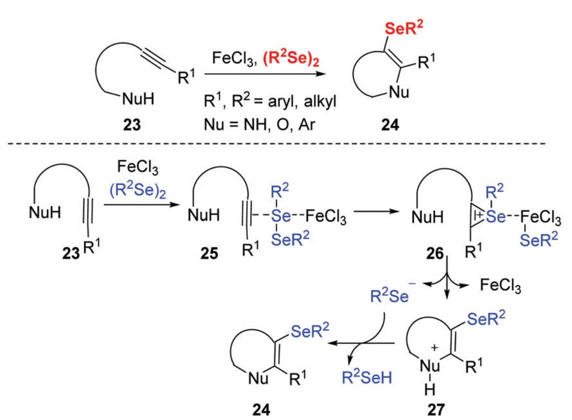
employed 1-fluoropyridinium compounds as oxidative functionalization reagents to access two types of α-seleno-α,β-unsaturated carbonyls (α-selenoenals **19** and α-selenoenones **20**) by changing the substituents at the allene end. In the case of allenone as a substrate, the α-selenoenone was failed to obtained, and the cyclized selenated furan **22** was afforded in 63% yield. The protocol disclosed the oxidation of $(PhSe)_2$ promoted by 1-fluoropyridinium triflate to generate the electrophilic species PhSe(OTf).

3. Diorganyl diselenides promoted selenocyclization

3.1 Transition metal-catalyzed selenocyclization

3.1.1 Iron(III)-promoted selenocyclization. Over the past decade, iron salts have appeared as alternative and promising catalysts for a wide range of organic transformations[15] due to their low cost, good stability, abundance, ease of handling, and excellent tolerance toward various functional groups.[16] The use of catalytic and stoichiometric quantities of iron(III) salts is a particularly efficient strategy to promote the selenocyclization of diselenides with alkenes or alkynes. Fundamentally, iron(III) salts act as Lewis acids and coordinate with selenium, which enhances the polarization of the diselenide bonds and facilitates electrophilic alkene selenocyclization with nucleophiles.

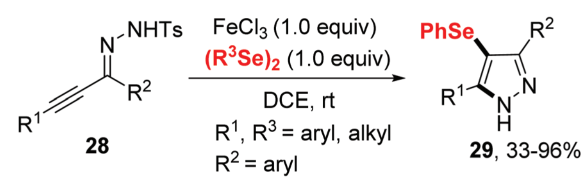
The group of Zeni reported a series of iron(III)-promoted cyclization of alkynes and diselenides. This strategy provides a new approach to obtain various selenofunctionalized heterocycles such as benzo[*b*]furans chromenones, indoles, isoxazoles, benzoxazines, dihydrofurans, isochromenimines, naphthalenes from readily accessible starting materials under mild conditions with efficiency and operability (Scheme 7).[17] The authors proposed the mechanism that the key of these selenocyclizations are the iron-seleno complex generated from the reaction of $FeCl_3$ and diorganyl diselenide $(RSe)_2$. The electrophilic portion of the selenium species coordinates to the triple carbon–carbon bond to generate the seleniranium ion **26**. The cyclized cationic intermediate **27** is then generated *via* intramolecular nucleophilic attack. Finally, deprotonation of **27** gives the selenocyclized product **24**.



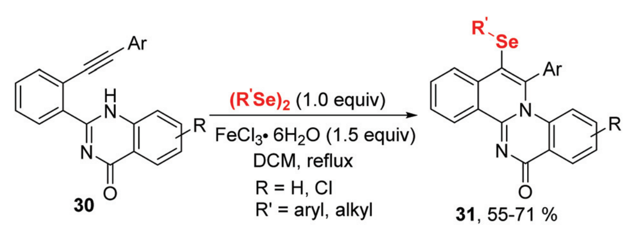
Scheme 7 Iron(III)-promoted selenocyclization of alkynes.

In 2020, the group of Ji established an iron(III) chloride-promoted cyclization between α,β-alkynic tosylhydrazones **28** and diselenides (Scheme 8).[18] The reaction proceeded efficiently in the presence of 1.0 equiv. $FeCl_3$ in 1,2-dichloroethane (DCE) at room temperature, providing a series of 4-(arylselanyl)-1*H*-pyrazoles **29** with good functional group tolerance. Meanwhile, Koketsu *et al.* reported seleno-cyclization of alkyne **30** and diselenides, furnishing a series of 6*H*-isoquinolino[2,1-*a*]quinazolin-6-one **31** (Scheme 9).[19] In this reaction, C–N and C–Se were constructed in one step using 1.5 equivalent of $FeCl_3·6H_2O$ in dichloromethane at room temperature. The plausible mechanisms of these two reactions are similar to above mentioned.

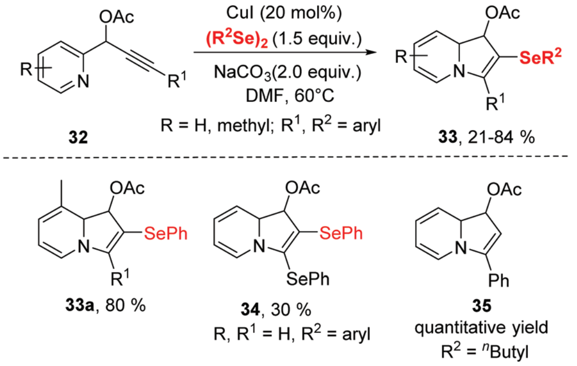
3.1.2 Copper catalyzed selenocyclization. Copper salts can act as catalytic cross-coupling agents, Lewis acids, and oxidizing agents in organic synthesis with the relatively low cost of copper and the realization of catalysis in many instances.[20] Among them, copper-facilitated selenocyclization reactions between the diselenides and alkenes or alkynes have been widely applied as one of the most powerful tools for the synthesizing of seleno-heterocycle. For example, in 2017, Zeni and coworkers accomplished copper catalyzed cyclization of propargyl pyridines **32** with diorganyl diselenides (Scheme 10).[21] The reaction was catalyzed by 20 mol% of CuI with 2 equiv. Na_2CO_3 as a base in DMF at 60 °C. A variety of propargyl pyridines and diorganyl diselenides were screened, and a wide range of 2-(organoselenyl)-indolizine **33** were obtained in generally good yields. Notably, when propargyl pyridines was equipped with a terminal alkyne, the indolizine with two phenyl selenium groups in the structure (**34**) was obtained in 30% yield. However, employing dibutyl diselenide as organoselenium source, the desired product was not



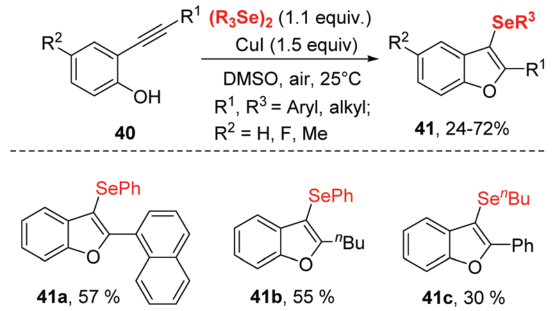
Scheme 8 Iron(III)-promoted synthesis of selenyl pyrazoles.



Scheme 9 Iron(III)-promoted synthesis of selenyl isoquinolino[2,1-*a*]quinazolin-6-one.



Scheme 10 CuI-catalyzed synthesis of selenyl indolizine.



Scheme 12 CuI-catalyzed synthesis of selenylated benzo[*b*]furan.

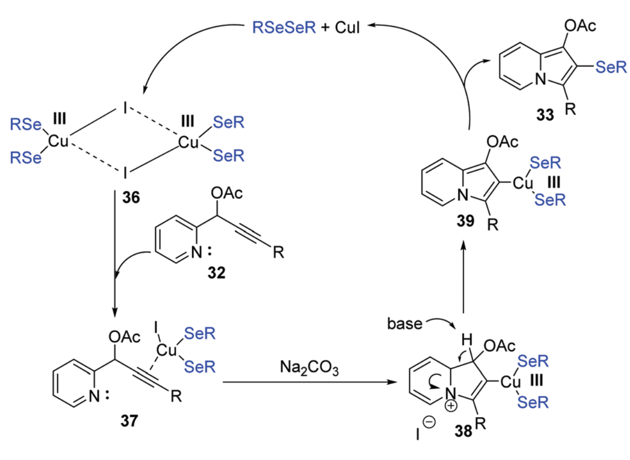
detected, and the corresponding 2-hydrogenated indolizine **35** was obtained *via* beta-selenoxide elimination.

To get insight the mechanism aspect of this cyclization, some control experiments were performed. These experiments revealed that the copper-selenolate species **36** generated by mutual action between copper(I) iodide and diorganyl diselenide was essential for the reaction. In the mechanism (Scheme 11), an intermediate **37**, as an electrophile through the activation by coordination of the Cu(I) ion to the alkyne, is formed. Intermediate **37** is then converted into **38** *via* intramolecular nucleophilic attack of N atom. Deprotonation then produces the 2-copper-indolizine **39**. The subsequent reductive elimination of copper leads to the formation of the final product **33**.

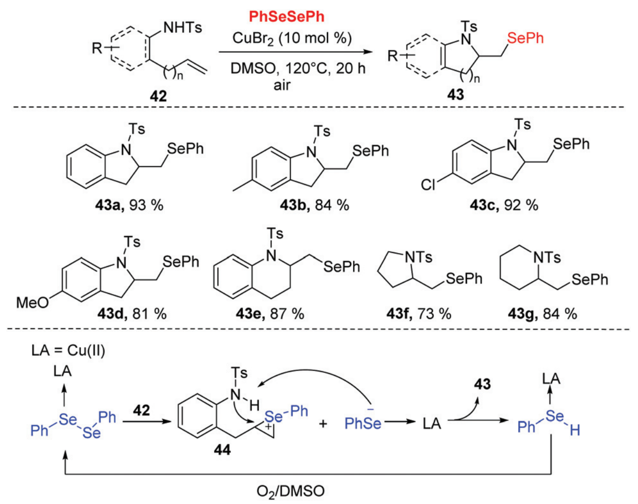
A similar transformation was achieved by Godoi.[22] The selenocyclization between 2-alkynylphenols and diorganyl diselenides enabled selenocyclization provided 3-organoselanylbenzo[*b*]furan derivatives in moderate to good yields (Scheme 12). In contrast to the Zeni's work,[21] this reaction did not need any base and worked smoothly in DMSO at room temperature by promotion of 1.5 equiv. CuI. The protocol performed excellent functionality tolerance. 2-Alkynylphenol, containing electron-donating groups, electron-withdrawing groups and halogen groups were all tolerated. Moreover, naphthyl-substituted alkyne also reacted well in this catalytic system. In particular, low reactive aliphatic alkyne was accommodated with moderate yields. Moreover, the dialkyl diselenides was proven to be applicable in this reaction.

Notably, 3-organoselanylbenzo[*b*]furan could be used to prepare for different functionalized benzo[*b*]furans, demonstrating the synthetic applicability of this protocol.

In 2018, Zhong and co-workers developed a copper-catalyzed tandem selenoamination reaction of alkenes, successfully affording a series of seleno-N-heterocycles (*e.g.*, indoline, tetrahydroquinoline, pyrroline, and piperidine derivatives) with 73–93% yields (Scheme 13).[23] In this approach, 10 mol% of $CuBr_2$ was utilized in DMSO at 120 °C in air. During the mechanistic investigation, oxygen and DMSO as co-oxidants were necessary for this transformation. Moreover, radical quenching experiments suggested a radical mechanism is not likely the case in the present catalytic system. As shown in Scheme 13, the Se–Se of diselenide could be polarized by $CuBr_2$ to access the coordination **44**, which undergoes an electrophilic addition to the olefin moiety of **42**. The intramolecular nucleophilic attack by nitrogen and deprotonation then furnish the desired product **43** and selenophenol.



Scheme 11 Proposed mechanism of CuI-catalyzed synthesis of selenyl indolizine.



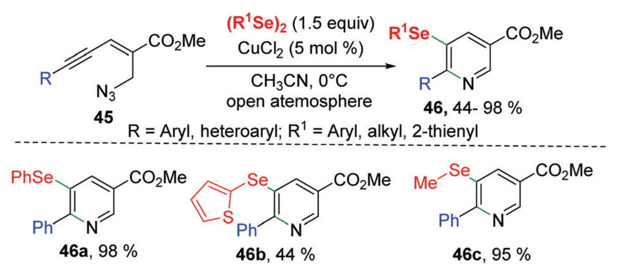
Scheme 13 $CuBr_2$-promoted synthesis of selenylated N-heterocycle.

Selenophenol is oxidized to diselenide by O_2 and DMSO, and re-enter to the catalytic cycle.

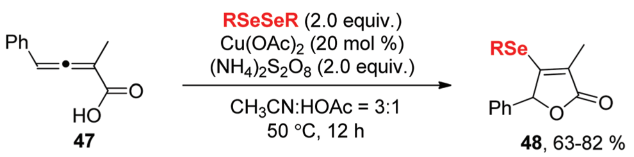
Soon after, Reddy's group reported a $CuCl_2$-catalyzed synthesis of selenyl nicotinates from enynyl azide **45** with diorganyl diselenides (Scheme 14).[24] The enynyl azide bearing aryl groups with different electron-donating or electron-withdrawing groups and 2-thienyl all underwent this transformation smoothly, leading to desired 5-selenyl nicotinates **46** with yields ranging from 78–98%. It is worth noting that aryl-substituted, heterocyclic, and alkyl-substituted diselenides are also compatible to this reaction. The mechanism for this intramolecular selenoamination is similar to that described in Zhong's work.[23]

In 2018, Xu and co-workers demonstrated a selenocyclization of 2,3-allenoic acids **47** with diselenides in the combination of CuCl and $(NH_4)_2S_2O_8$ as catalytic oxidation system (Scheme 15).[25] The reaction enabled sulfenylation/cyclization and subsequent oxidation to provide selenylated butenolides **48** in 63–82% yields. $(NH_4)_2S_2O_8$ played dual roles as a radical initiator as well as oxidant. Moreover, selenylated butenolides could be applied for synthesis of the corresponding furan derivatives.

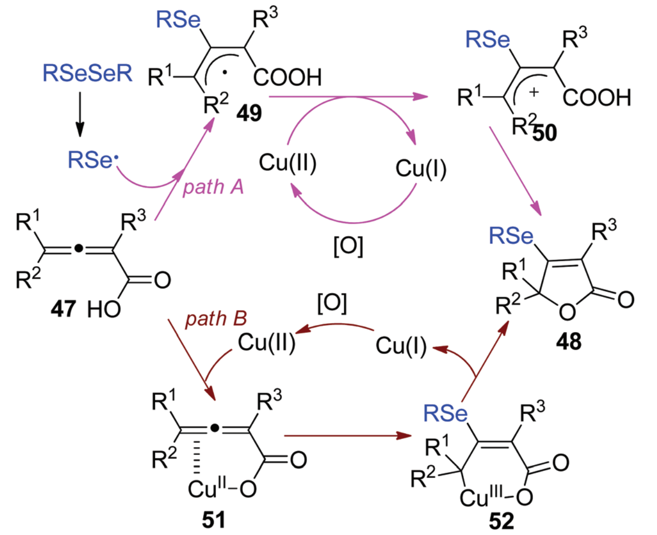
The proposed mechanism by the authors was depicted in Scheme 16. First, a selenyl radical is formed *via* the homolysis of RSeSeR in the presence of $(NH_4)_2S_2O_8$. The addition of selenyl radical to 2,3-allenoic acids gives the radical intermediate **49**. The further oxidation of intermediate **49** by Cu(II) affords the intermediate **50**. Finally, the intramolecular attack of intermediate **50** leads to the cyclized products **51**. Another pathway is also proposed. Cu(II) coordinated to 2,3-allenoic acids, generating the complex **51**. Then, the addition of selenyl radical to **51** gives Cu(III) intermediate **52**. Finally, reductive elimination is occurred to release the desired product **48**.



Scheme 14 $CuCl_2$-catalyzed synthesis of selenyl nicotinates.



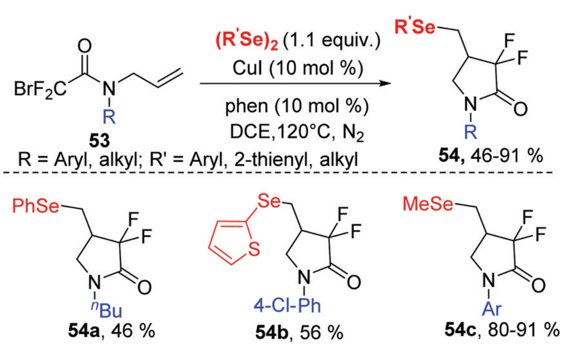
Scheme 15 $CuCl_2$-catalyzed synthesis of selenylated butenolides.



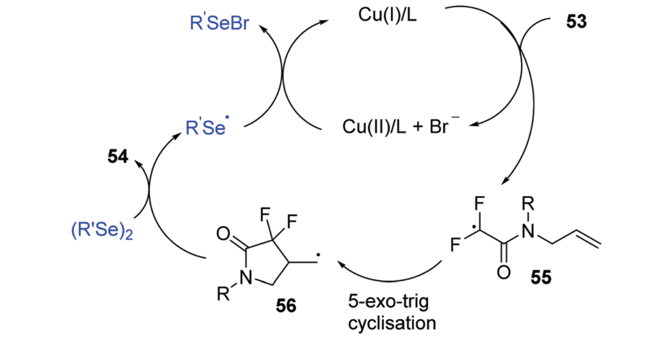
Scheme 16 Proposed mechanism $CuCl_2$-catalyzed synthesis of selenylated butenolides.

Organofluorine compounds constitute an attractive class of compounds that have attracted significant attention from researchers in a variety of disciplines. In 2019, the group of Sun successfully synthesized a series of 4-seleno-substituted α,α-difluoro-γ-lactams **54** using *N*-allyl-2-bromo-2,2-difluoroacetamides **53** and diorganyl diselenides catalyzed by 10 mol% CuI in DCE at 120 °C under external-oxidant-free conditions (Scheme 17).[26] Various *N*-aryl-substituents of bromodifluoroacetamides with different electron-donating or electron-withdrawing groups undergo this transformation smoothly, leading to desired products with yields ranging from 63–82%. Notably, *N*-alkyl-substituted bromodifluoroacetamide could proceed well in this reaction. Furthermore, diphenyl diselenides, 1,2-di(thiophen-2-yl)diselane and dimethyldiselenide were also compatible to this reaction.

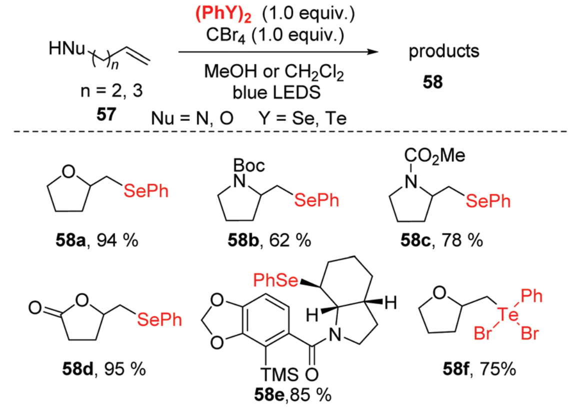
Regarding the mechanism, control experiments and radical quenching experiments demonstrated this process proceeded through a radical pathway. The authors proposed the following possible reaction mechanism (Scheme 18).



Scheme 17 CuI-catalyzed synthesis of 4-seleno-substituted α,α-difluoro-γ-lactams.



Scheme 18 Proposed mechanism of the CuI-catalyzed synthesis of 4-seleno-substituted α,α-difluoro-γ-lactams.



Scheme 19 Visible light-promoted synthesis of β-selenyl O-heterocycles and N-heterocycles.

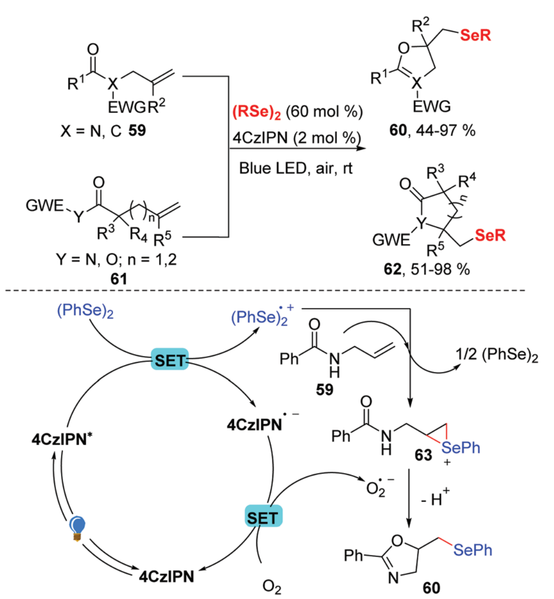
A single-electrontransfer (SET) between Cu(I) and **53** occurs to afford a Cu(II) species and radical intermediate **55**. Next, the addition of the fluoroalkyl radical to the unsaturated double bond affords alkyl radical intermediate **56** *via* a 5-*exo-trig* cyclization. The alkyl radical intermediate **56** reacts with diphenyl diselenide to form the desired product **54** and selenyl radical, which further reduces Cu(II) to Cu(I) and selenyl anion (PhSeX) to complete the catalytic system.

3.2 Visible light-promoted selenocyclization

Recently, photoredox catalysis has emerged as a useful tool for radical reactions *via* visible light-induced processes. Compared with previous methods, photoredox catalysis is inexpensive and has the advantages of environmentally-benign (it does not require excess amounts of transition metals or oxidants), high efficiency and easy to use.[27] Notably, diselenide bonds possess a lower bond energy (172 kJ mol^{-1}), which could facilitate the generation a selenium radical species *via* the homolytic cleavage of the Se–Se single bond under visible-light irradiation without any photocatalyst. Therefore, the construction C–Se to synthesize selenofunctionalized heterocycles under visible-light irradiation has become more appealing.

In 2013, Ragains and co-workers reported a visible light-promoted selenocyclization of alkenes at room temperature (Scheme 19).[28] In this reaction, bench-stable PhSeSePh is combined with CBr_4 under the irradiation of a 5 W blue light-emitting diode (LED), resulting in the *in situ* generation of reactive PhSeBr. This reaction showed a broad substrate scope, generating O-heterocycles in high yields along with N-heterocycles in moderate to high yields. Notably, diphenyl ditelluride was successfully suitable for this strategy to afford the tellurofunctionalization products in 53–75% yields in dichloromethane as solvent. To further demonstrate the application of this method, the Amaryllidaceae alkaloid γ-lycorane was synthesized. Mechanistic studies and DFT calculation suggested visible light irradiation promoted the phenylselenyl radical abstraction of bromine from CBr_4 to generate phenylselenyl bromide *in situ*. The detailed mechanism of these reactions is still under investigation.

Later, the group of Liu developed a visible light-driven selenocyclization of *N*-allylamides in MeCN in the presence of 2 mol% 4CzIPN under visible-light and in air (Scheme 20).[29] While dihydroisoxazole was produced in 73% yield without any photocatalyst under these optimized reaction conditions, the use of 4CzIPN as a photocatalyst promoted the reaction process. In contrast to other seleno cylization reactions, this protocol only needed 60 mol% diselenides. In addition, many substituted the allylic amides and various diselenides were well tolerated in this transformation and gave the corresponding products **60** in good to excellent yields. Inspired by this result, a series of heterocycles were prepared by investigating the scope of the nucleophilic reagent, generating the corresponding products 62 in 51–98% yields. A possible reaction mechanism (Scheme 20) was proposed based on fluorescence quenching experiments. In this mechanism, the ground state 4CzIPN is excited to *4CzIPN under visible light irradiation. The excited state then undergoes a SET reaction

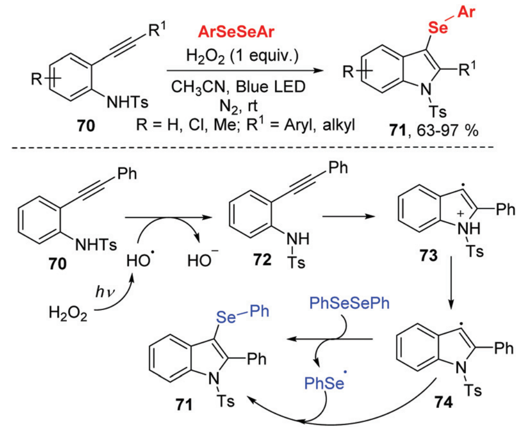


Scheme 20 Visible light-promoted synthesis of β-selenyl dihydroisoxazole.

with diphenyl diselenide to generate $(PhSe)_2^{\bullet+}$ radical cation and 4CzIPN$^{\bullet-}$ radical anion. Then, the molecular oxygen oxidized 4CzIPN$^{\bullet-}$ to the ground state completes the photoredox cycle. Meanwhile, the addition of diselane radical cation $(PhSe)_2^{\bullet+}$ to *N*-alkenylamide **59** produces seleniranium cation **63**, which undergoes intramolecular nucleophilic cyclization to obtain the desired product **60**.

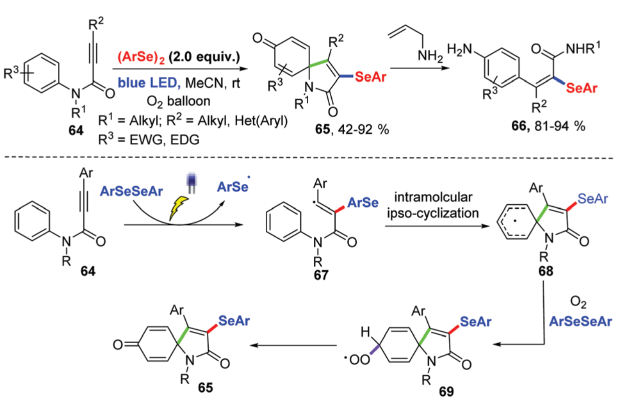
In 2017, an efficient approach for the preparation of selenium substituted spiro[4,5]trienones based on visible light-induced selenium radical-cyclization of *N*-aryl alkynamides **64** under oxygen atmosphere at room temperature without external photocatalyst was described for Baidya and coworkers (Scheme 21).[30] This reaction showed a wide range of functional groups tolerances. Diverse *N*-aryl alkynamide and diaryl diselenides bearing electron-donating as well as electron-withdrawing groups in aryl ring can achieve the products **65** in moderate to excellent yields. In addition, good yields were achieved in gram-scale reactions. A spiro-ring-opening strategy was realized to give fully substituted acryl amides **66**. Based on several control experiments, a possible radical pathway mechanism was proposed. First, under visible light irradiation, the addition of selenyl radical produced *via* homolytic cleavage of the Se–Se single bond to the triple bond produces a vinyl radical **67**. Subsequently, intramolecular radical *ipso*-cyclization affords **68**. Oxidative dearomatization would then occurs under oxygen atmosphere and in the presence of diaryl diselenide to afford the desired product.

In 2017, the group of Wang developed a facile route to prepare 3-selenylindoles from *N*-(2-(ethynyl)aryl)benzenesulfonamide **70** and diaryl diselenides under 3 W blue LED irradiation (Scheme 22).[31] The authors optimized reaction conditions and found that H_2O_2 (30% aqueous solution) as oxidant was necessary for this transformation. Moreover, this methodology exhibited good functional group tolerance, giving rise to the 3-selenylindoles **71** in moderate to excellent yields. With the result of radical-trapping experiment, a radical free mechanism was proposed. Initially, hydroxyl radical generates from the homolytic cleavage of H_2O_2 under blue LED irradiation. Then a single electron transfer between **70** and hydroxyl radical gives the intermediate **72**. After the intramolecular cyclization and deprotonation, radical intermediate **74** is formed. Finally, the reaction between diphenyl diselenide and **74** leads the desired product **71** and phenylselenyl free radical. The phenylselenyl free radical further reacts with **74**, delivering the final product.

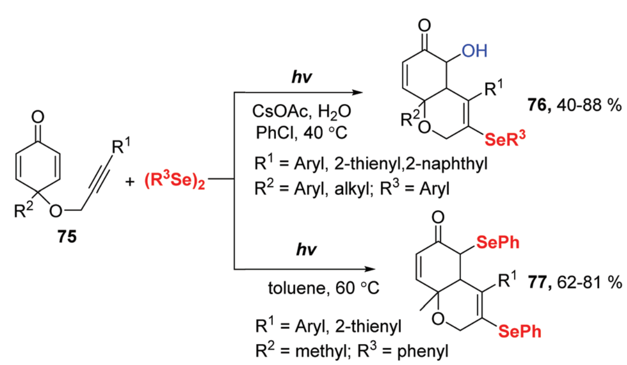


Scheme 22 Visible light-promoted synthesis of 3-selenylindoles.

In 2019, Xu and coworkers reported a Se radical-triggered multi-component tandem cyclization of alkyne-tethered cyclohexadienones **75** and diaryl diselenides under the irradiation of 25 W white LEDs at 40 °C temperature (Scheme 23).[32] This reaction gave 5-hydroxy-3-selenyl-4a,8a-dihydro-2*H*-chromen-6(5*H*)-ones **76** in 40–88% yields in the presence of 2 equiv. H_2O and CsOAc in chlorobenzene at 40 °C. Moreover, the reaction could be performed in the absence of a base in dry toluene at 60 °C, producing 3,5-diselenyl-4a,8a-dihydro-2*H*-chromen-6(5*H*)-ones **77** in 62–81% yields. These results demonstrate water is crucial for this transformation. To gain more insight into the effect of water, some control experiments were performed. First, decreasing the amount of H_2O to 1 equiv. provided **76** in 40% yield and **77** in 30% yield. Next, **77** was converted to the desired product **76** under the standard conditions indicating that **77** is a possible intermediate. ^{18}O-Labelling experiments showed that the oxygen atom of the hydroxyl group originated from water. Moreover, a radical-trapping experiment using 2,2,6,6-tetramethylpiperidine-1-oxyl



Scheme 21 Visible light-promoted synthesis of spiro[4,5]trienones.



Scheme 23 Visible light-promoted synthesis of selenyl chromenones.

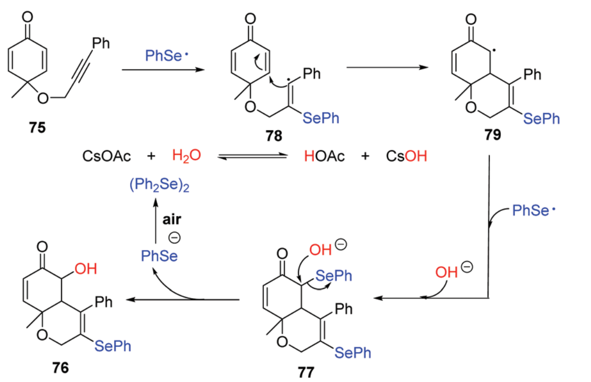
(TEMPO) was performed to probe the possibility of a radical mechanism in this transformation.

Through a series of experimental observations and surveys of previous literature, they proposed the following possible reaction mechanism (Scheme 24). First, under visible-light irradiation, phenylselenyl free radical generated from diphenyl diselenide undergoes a radical addition to substrate **75** to produce alkenyl radical **78**. Subsequently, intramolecular radical cyclization gives intermediate **79**, which is trapped by another phenylselenyl free radical to deliver the product **77**. In the presence of CsOAc, nucleophilic substitution occurs with water and **77**, leading to the desired product **76**. Interestingly, some products showed potent inhibition activities against cancer cell growth *in vitro*.

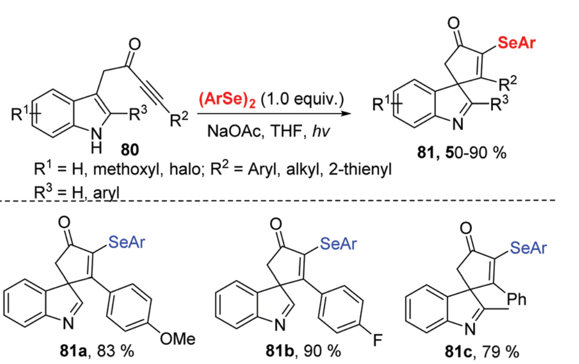
In 2020, Xu and coworkers further developed visible light-induced selenocyclization reaction of indolyl-ynones **80** with diselenides at room temperature under air atmosphere (Scheme 25).[33] Diverse 3-selenospiroindolenines bearing various functional groups were obtained in moderate to good yields. Similarly, phenylselenyl free radical is generated from diphenyl diselenide under visible-light irradiation. The desired product is then obtained through the radical addition/oxidation/deprotonation pathway. Compounds **81a** and **81b** were tested for *in vitro* anticancer activity by MTT assay and showed potent inhibitory activity against cancer cell growth.

Very recently, the group of Wang disclosed a regio- and chemoselective radical cascade cyclization of 1,6-enynes **82** and areneselenosulfonates **83a** under 34 W blue LED irradiation in the air without any photocatalysts (Scheme 26).[34] Numerous substrates (**82**) were examined, and the corresponding cyclized products (**84**) were obtained in good to excellent yields. This reaction also proceeded smoothly using diaryl diselenides **83b** with 1,6-enynes, and observed desired products with moderated to goods yields. However, this method was not applicable when the chain length was increased from one to two or three. The internal alkene and free amine in enyne were also not tolerant for this transformation. This protocol offers an efficient approach to build selenium substituted pyrrolidine derivatives *via* multiple chemical bond constructions in 5-*exo-dig* fashion, including one C–S bond, one C–Se bond, and one C–C bond.

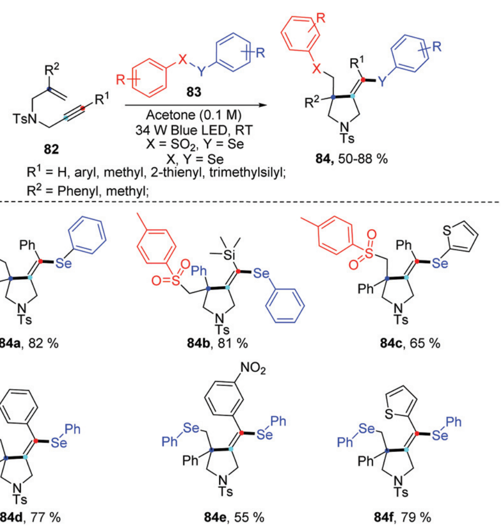
Notably, some control experiments indicated the reaction proceeded in a radical way, and the visible-light irradiation was necessary. The reactivity of the chalcogen group in the reaction was tested by the combination of **82a** with **83a** and **83b**. The result suggested that tosyl radical was more reactivity than phenylselenyl, demonstrating the regio- and chemoselectivity. The proposed mechanism is described in Scheme 27. The tosyl (**85**) and phenylselenyl free radical (**86**) are generated by visible light irradiation. Tosyl radical **85** is added to 1,6-enynes **82a** to generate alkyl radical intermediate radical **87**. Then intramolecular 5-*exo-dig* cyclization gives rise to the corresponding vinyl radical **88**, which is further trapped by phenylselenyl free radical (**86**) to generate desired product **84a**. The reverse transformation products were not observed, probably due to the higher stability of the tertiary alkyl radical intermediate **87** compared to the vinyl generated by the tosyl



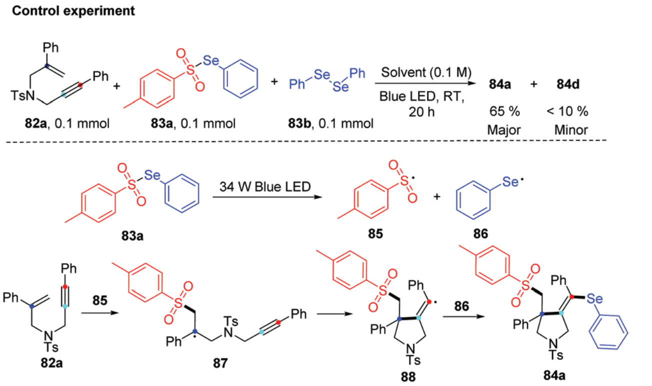
Scheme 24 Proposed mechanism of visible light-promoted synthesis of selenyl chromenones.



Scheme 25 Visible light-promoted synthesis of 3-selenospiroindolenines.



Scheme 26 Visible light-promoted synthesis of seleno-containing pyrrolidine.



Scheme 27 Control experiments and proposed mechanism of visible light-promoted synthesis of seleno-containing pyrrolidine.

radical addition to alkyne. This protocol showed excellent regio- and chemoselectivity, good functional tolerance.

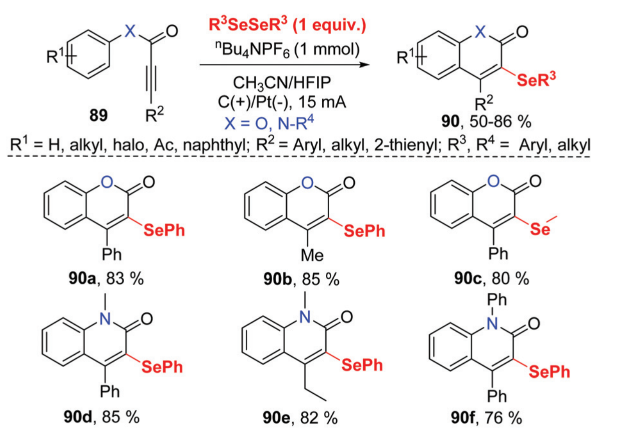
3.3 Electrochemically enabled selenocyclization

In the past few years, electrochemistry has been recognized as one of the most powerful and sustainable methods in organic chemistry since electrochemical methods avoid chemical oxidants, reductants, and transition-metal catalysts.[35] Compared to traditional chemical synthetic methods, electrochemically induced selenocyclization methods for the difunctionalization of alkenes and alkyne are relatively rare. More selenocyclization reactions for the synthesis selenyl heterocycles should be developed.

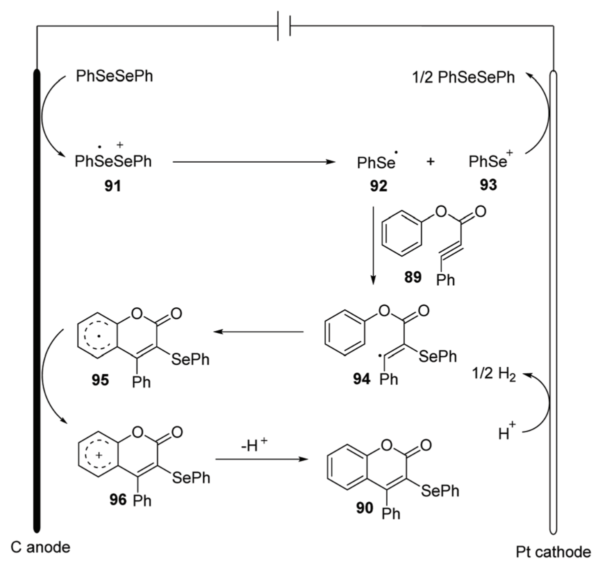
In 2019, Guo and co-workers reported an electrochemically induced oxidative cyclization of alkynoates or alkynamides with diselenides by using $^{n}Bu_4NPF_6$ as supporting electrolyte (Scheme 28).[36] In the cases of diselenides with aryl groups or alkyl groups, the reaction proceeded smoothly, giving the corresponding coumarins or quinolinones **90** in moderate to good yields. This protocol also demonstrated a broad substrate scope of alkynoates and alkynamides, except when *para*-OMe was substituted on the aryl group. However, terminal alkyne was ineffective for this transformation. Moreover, the reaction can be conducted on a gram scale with excellent efficiency, demonstrating the practical application in future industry. Comparing to the previous report on the related selenocyclization reaction of alkynoates and alkynamides by Zeni's[17e] and Liu's[49] work, this strategy requires no transition metals or chemical oxidants. Cyclic voltammetric (CV) experiments show that diphenyl diselenide had a lower oxidative potential than the substrate, indicating that diphenyl diselenide is more easily electrochemically oxidized to generate phenylselenium radical than the alkyne moiety.

Based on control experiments and radical quenching experiments, they proposed a possible reaction mechanism (Scheme 29). Diphenyl diselenide initially undergoes anodic oxidation to generate cationic radical intermediate **91**, which is decomposed to give phenylselenium radical **92** and phenyl selenium cation **93**. Thereafter, the radical addition of **92** to triple bond provides vinyl radical **94** in high regioselectivity. The resulting radical **94** participated in an intramolecular radical reaction to generate intermediate **95**, which is further oxidized on anode to afford the cation **96**. At last, deprotonation affords the final product **90**.

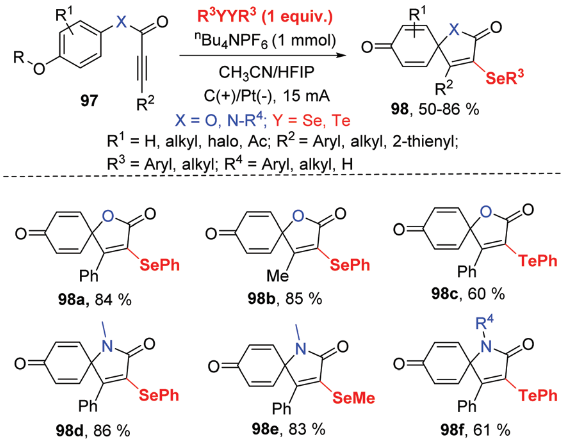
Inspired by this protocol, the group of Guo further developed the electrocatalytic oxidative radical dearomative spirocyclization for the preparation of selenation spiro[4.5]trienones **98** from alkynes **97** with diselenides (Scheme 30).[37] As mentioned above, when the substrates are alkynoates and alkynamides bearing a methoxy group at *para* substituted of aryl ring, the *ipso*-cyclization was occurred. Then, they optimized the reaction condition; the reaction worked well in CH_3CN/HFIP (v : v = 3 : 1) at room temperature with $n Bu_4NPF_6$ as electrolyte. The use of the optimized reaction parameters led to the corresponding 49 examples of selenation spiro[4.5]trien-



Scheme 28 Electrochemically induced synthesis of selenated coumarins and quinolinones.



Scheme 29 Proposed mechanism of electrochemically induced synthesis of selenated coumarins and quinolinones.



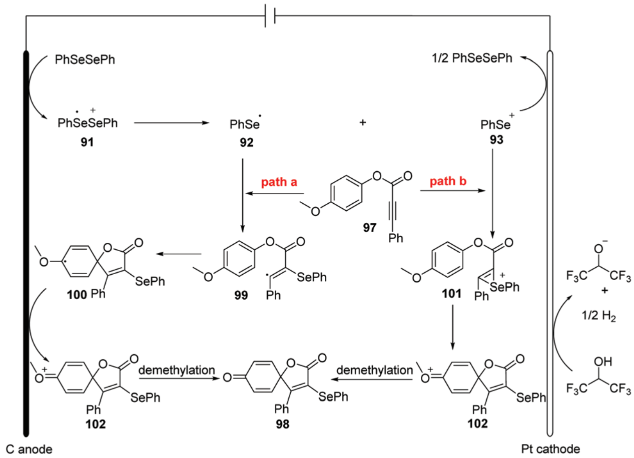
Scheme 30 Electrochemically induced synthesis of selenated spiro[4.5] trienones.

ones in moderate to good yields with broad substrate scope and high functional group tolerance. It is note that diphenyl ditelluride was also compatible for this transformation, giving tellurium-substituted products in good yields. It should be mentioned that terminal alkyne was not suitable for this system.

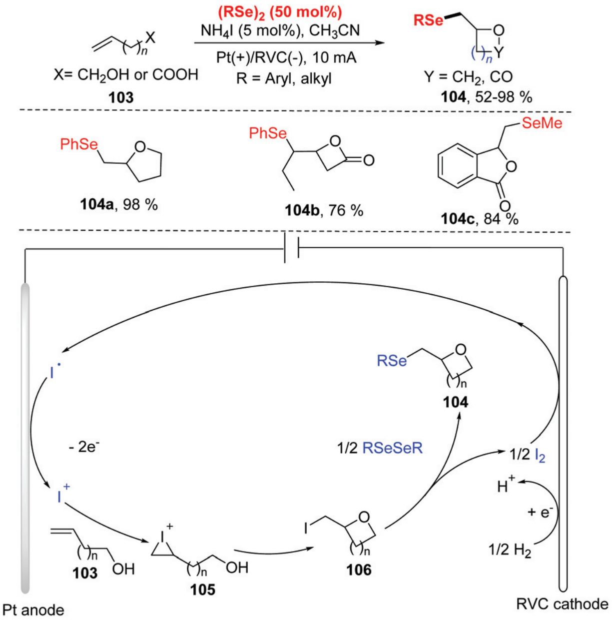
Notably, scale-up reaction was performed in electrochemical continuous flow system, and nearly the same yield was obtained (73% yield in nearly 15 h on the 10 mmol scale).

The authors also provided the possible mechanism (Scheme 31). Vinyl radical **99** is generated in the similar path and then undergoes intramolecular spirocyclization to provide **100**, different from their earlier work. Meanwhile, the anodic oxidation of the intermediate **100** generates oxygenium cation intermediate **102**. Finally, the sequential the demethylation of cation **102** and the dearomatization of the aromatic ring give access to the desired product.

In 2019, Pan and co-workers reported the electrochemical selenocyclization of olefins and diselenides for the generation



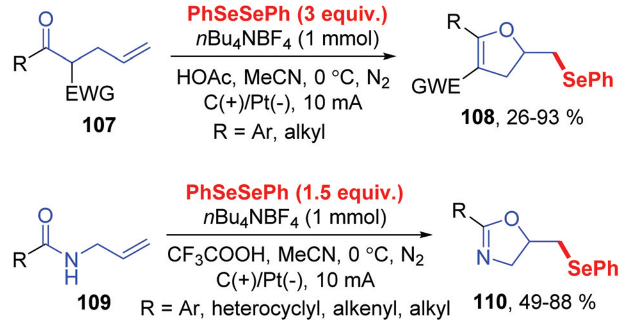
Scheme 31 Proposed mechanism of electrochemically induced synthesis of selenation spiro[4.5]trienones.



Scheme 32 Electrochemically induced synthesis of selenomethyl-substituted cyclic ethers, lactones and isobenzofuranones.

of selenomethyl-substituted cyclic ethers or lactones (Scheme 32).[38] The olefines including unsaturated alcohols and unsaturated carboxylic acids **103**, were all suitable for this reaction with NH_4I as electrolyte and electrocatalyst, affording the corresponding products **104** in good yields. Moreover, the difficult-to-synthesize medium-sized ethers (7-, 9-, and 11-membered rings) and 4–6-membered ring lactones could be obtained smoothly. However, the reaction was limited to diphenyl diselenides bearing electron-donating groups (OMe), failing to produce the desired product with 2-vinylbenzoic acid. According to the results of cyclic voltammetry studies and control experiments, the reaction mechanism is depicted in Scheme 32. Iodine ion is first oxidized at anode to produce I^+, which then reacts with olefinic alcohols to form iodonium cations intermediate **105**. Subsequently, intramolecular cyclization and deprotonation lead to intermediate **106**. Finally, rapid chemical selenation by diphenyl diselenide gives access to the desired product and a half molar equivalent of I_2. At the cathode, reduction of I_2 and proton to iodine anion and hydrogen completes the reaction cycle.

Dihydrofurans and oxazolines play important roles in numerous biologically active molecules, pharmaceuticals and agronomicals. As a straightforward and highly atom-economic method for synthesizing these derivatives, the selenocylization of olefinic carbonyls has attracted the attention of chemists. In 2019, the group of Lei realized an electrochemical oxidative cyclization between olefinic carbonyls and diaryl diselenides, providing a practical and enconomical approach to the preparation of selenium-functionalized dihydrofurans (Scheme 33).[39] This reaction could proceed smoothly in CH_3CN at room temperature with $^nBu_4NBF_4$ as electrolytes, HOAc as additive, graphite as the working anode, and plati-

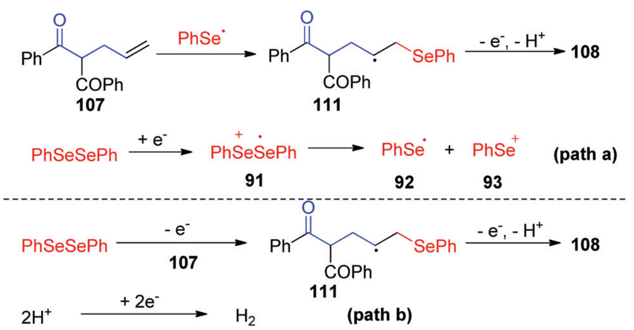


Scheme 33 Electrochemically induced synthesis of selenylated dihydrofurans and oxazolines.

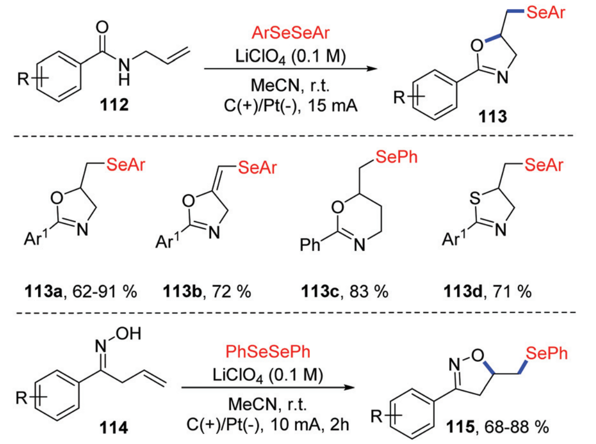
num as the cathode. This method shows good compatibility for symmetric and unsymmetric olefinic carbonyls **107** with different substituents, giving the corresponding dihydrofurans compounds **108** in moderate to good yields. In addition, this protocol also tolerated unsaturated amides **109**, affording the corresponding seleno oxazolines **110** in moderate to excellent yields.

To gain more insight into this cascade cyclization, they added stoichiometric radical inhibitor TEMPO to reaction systems and perform this reaction under standard conditions. The yield of the desired product decreased obviously, indicating that the process involves a free radical pathway. Based on mechanistic studies, cyclic voltammetry studies, and the literature, the authors proposed two possible reaction pathways (Scheme 34). In path a, the anion radical intermediate **91** is generated by cathode reduction, and then decomposes to give phenylselenium radical **92** and phenyl selenium anion **93**. Then, the radical addition of phenylselenium radical **92** to the alkene results in the formation of C-radical intermediate **111**, which is further oxidized at anode. Finally, an intramolecular cyclization is occurred by nucleophilic attack of the oxygen atom of carbonyl, subsequent deprotonation to render the final product **108**. In path b, the phenylselenium radical is generated by phenyl diselenide anode oxidation and decomposition.

The group of Sarkar reported the similar method for the electrochemical oxidative cyclization of *N*-allyl amides **112** and diaryl diselenides, providing a practical and flexible approach



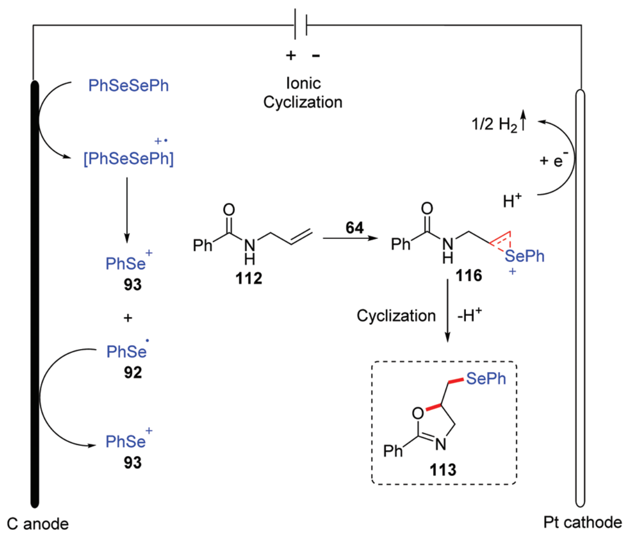
Scheme 34 Proposed mechanism of electrochemically induced synthesis of selenylated dihydrofurans and oxazolines.



Scheme 35 Electrochemically induced synthesis of selenylated oxazolines and isoxazolines.

for the preparation of selenium-functionalized oxazolines **113** (Scheme 35).[40] The reaction could proceed smoothly in CH_3CN at room temperature with $LiClO_4$ as electrolytes, and graphite and platinum as the working anode and cathode, respectively. A variety of substituents on both electronic and steric effects can tolerate the oxidative conditions well. Moreover, amides with varying chain length were also compatible in the oxidative cyclization process. Notably, the thiazoline derivative was synthesized from corresponding *N*-allylthiobenzamide **113d**. Comparing to the Lei's work,[39] this method could also be suitable for β,γ-unsaturated oximes **114** and various isoxazolines **115** were achieved under the standard reaction conditions.

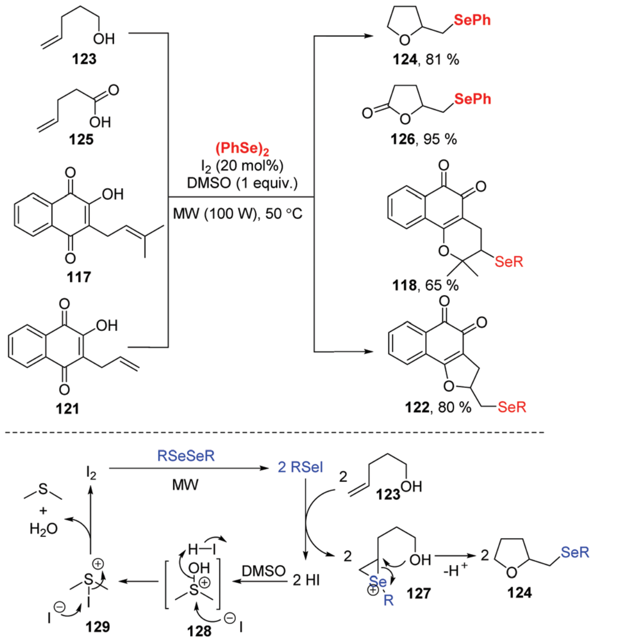
A plausible mechanism for this reaction was proposed based on mechanistic studies, cyclic voltammetry studies, and the literature (Scheme 36). In this mechanism, diphenyl diselenide is oxidized to generate cationic radical intermediate,



Scheme 36 Proposed mechanism of electrochemically induced synthesis of selenylated oxazolines and isoxazolines.

which is then decomposed to give phenyl selenium cation **93** and phenylselenium radical **92**. Further oxidation of phenylselenium radical **92** leads to phenyl selenium cation **93**. Subsequently, the addition of phenyl selenium cation **93** to alkenes **112** affords the cyclic seleniranium ion **116**, which then is captured by the nucleophile amide oxygen to afford the final product **113**. At the cathode, proton is reduced to the hydrogen, completing the reaction cycle.

Very recently, Ackermann and coworkers investigated an electrochemical oxidative cyclization of quinones and diaryl diselenides using a platinum plate anode and cathode under the constant current (10 mA) in an undivided cell (Scheme 37).[41] Using lapachol **117**, the quinone-hybrid compounds **118** were afforded with moderate to high yield *via* 6-*endo-trig* way. When this selenylation method was applied to the *C*-allyl lawsone **121**, 5-*exo-dig* cyclization occurred to give the corresponding products **122** in good to moderate yields. Unlike a previous report in which a I_2/DMSO oxidant system was employed,[42] this electrochemical reaction was conducted at room temperature without chemical oxidants. Moreover, some products exhibited considerable antitumor activity, indicating the promising in the application prospects.

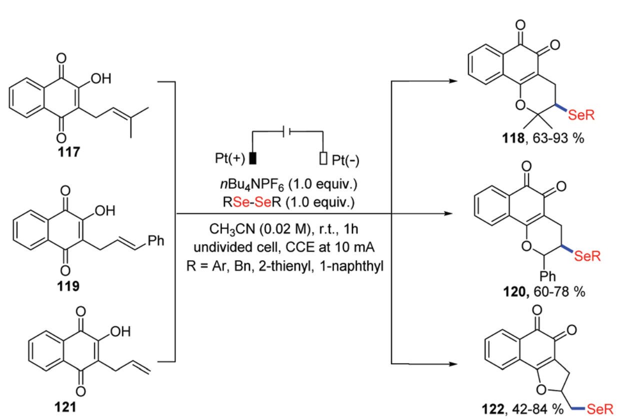


Scheme 38 I_2/DMSO catalyzed synthesis of seleno tetrahydrofuran and seleno-lactone.

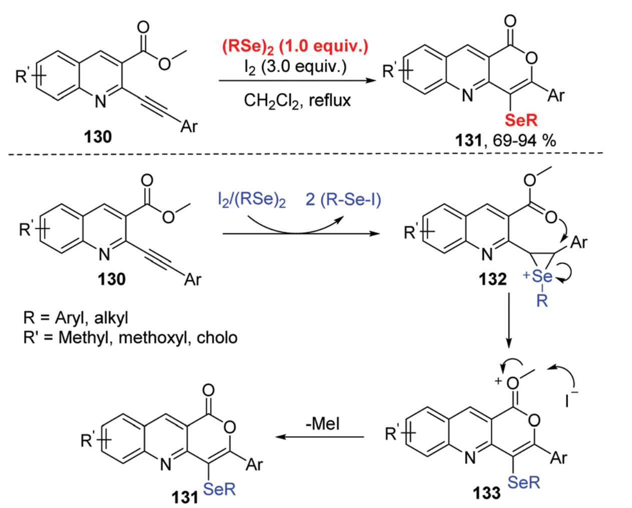
3.4. I_2 and hypervalent iodine-catalyzed selenocyclization

3.4.1 I_2 catalyzed selenocyclization. In 2013, Braga's group reported the synthesis of seleno O-heterocycle using molecular iodine as catalyst, DMSO as a stoichiometric oxidant under microwave irradiation without solvent (Scheme 38).[42] When using 4-penten-1-ol **123** or 4-pentenoic acid **125** as a substrate, the seleno tetrahydrofuran **124** or seleno-lactone **126** was obtained in excellent yield *via* the 5-*exo-trig* pathway. Moreover, lapachol **117** or *C*-allyl lawsone **121** was also suitable for this transformation, affording the corresponding product in good to high yields. However, nor-lapachol failed in this reaction. A plausible mechanism is proposed in Scheme 30. Initially, RSeI generated through the reaction of diorganyl diselenide with I_2 reacts with alkene to form seleniranium ion **127** and HI. Subsequently, intramolecular nucleophilic attack of the oxygen atom from the ester moiety on the carbon centre generates the final products. At the same time, HI is oxidized by DMSO to regenerate I_2.

In 2019, Koketsu and co-workers reported an iodine mediated selenocyclization of 2-phenylalkynylquinoline-3-carboxylate **130** with diorganyl diselenides to access seleno pyrano[4,3-*b*]quinolin-1-one **131** (Scheme 39).[43] The reaction featured a wide range of functional group tolerances, including strong/weak electron-withdrawing/donating groups along with alkyl and aryl groups, affording the corresponding products in high yields. The possible mechanism proposed by the authors



Scheme 37 Electrochemically induced synthesis of selenylated 3,4-dihydro-2*H*-benzo[*h*]chromene and 2,3-dihydronaphtho[1,2-*b*]furan.



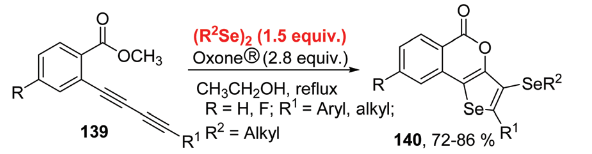
Scheme 39 I_2 mediated synthesis of seleno pyrano[4,3-*b*]quinoline-1-one.

is disclosed in Scheme 39. R–Se–I to is generated *in situ* by the reaction of I_2 and $(R–Se)_2$. The electrophilic addition of R–Se–I to compound **130** forms seleniranium ion **132**. The intramolecular nucleophilic attack by O atom gives the intermediate **133**. Finally, the elimination of Me–I leads to target compounds. In a control experiment, MeI was detected based on NMR spectroscopy.

3.4.2 Iodine(III)-mediated selenocyclization. β,γ-Unsaturated hydrazones and oximes are valuable and versatile building blocks for preparation of pyrazoline and isoxazoline derivatives. In 2017, the group of Cai reported the cascade radical selenocyclization of β,γ-unsaturated hydrazones **134** *via* the oxidation of phenyliodine(III) diacetate, giving rise to the corresponding pyrazoline and isoxazoline derivatives **135** in good yields without any metal (Scheme 40).[44] Due to the mild reaction conditions, this method had a wide tolerance for diorganyl diselenides. When a stoichiometric amount of TEMPO was added under standard conditions, the selenocyclization was completely suppressed, and the adduct was obtained in 84% yield. These results provide clear evidence that the process involves a C-centered radical intermediate formed by intramolecular cyclization. In these transformations, initially, the anionic intermediate is obtained by deprotonation of the β,γ-unsaturated tosyl hydrazone or oxime in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). Subsequently, a SET process between intermediate **136** and $PhI(OAc)_2$ occurs to generate radical **137**, which subsequently undergoes radical intramolecular cyclization to produce the C-centered radical **138**. The diselenide then captures the C-centered radical **138**, leading to the final product **135** and the phenylselenyl radical, which could recombine to diphenyl diselenide.

3.5 Peroxide-promoted selenocyclization

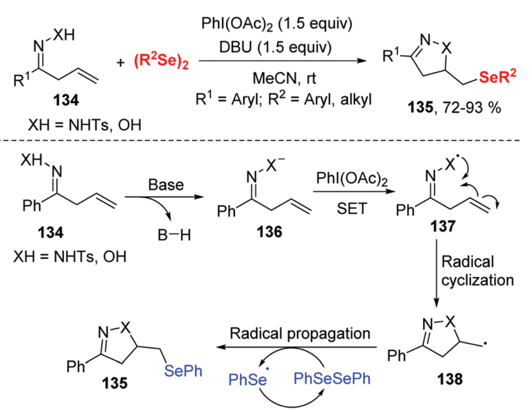
As an oxidant, Oxone® has been widely explored in organic synthesis due to its low cost, stability under various conditions, simple handling, and environmental nontoxicity. In 2019, Perin and coworkers described an efficient Oxone®-and dialkyl diselenides-promoted seleno-cyclization of 1,3-diynes **139** for the construction of diverse 5*H*-selenopheno[3,2-*c*]isochromen-5-ones **140** (Scheme 41).[45] This protocol enables the formation of four new chemical bonds, including one C–O bond and three C–Se bonds through a double intramolecular cyclization. Aryl-and alkyl-substituted 1,3-diynes were found to be suitable for this transformation. When 2-$CH_3OC_6H_4$-substituted 1,3-diyne was used as the substrate in the reaction, the yield of the target product was only 40% because of the competing reactions (intramolecular Se-cyclization and O-cyclization). A radical-trapping experiment using TEMPO and hydroquinone suggested this reaction does not involve a radical path. Furthermore, the ^{77}Se NMR experiment indicated that the active electrophilic selenium species are generated by the overoxidation of dibutyl diselenide by Oxone®.



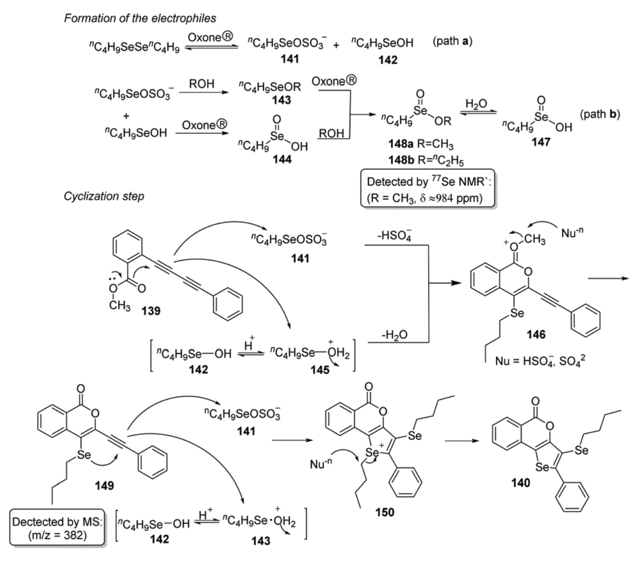
Scheme 41 Oxone® promoted synthesis of 5*H*-selenopheno[3,2-*c*]isochromen-5-ones.

Based on experimental findings, a plausible mechanism is proposed (Scheme 42). Firstly, the reaction of potassium peroxymonosulfate with diselenide affords two electrophilic selenium species $^nC_4H_9SeOSO_3^-$ (**141**) and $^nC_4H_9SeOH$ (**142**). $^nC_4H_9SeOH_2^+$ (**145**) is then formed by protonation of **142**. Both electrophiles **141** and **145** can react with 1,3-diyne **139** to deliver the cyclic intermediate **146** *via* the elimination of HSO_4^- or water. Subsequently, the methyl group leaves under the attack of nucleophile to produce intermediate **149**. Finally, the expected product **140** is afforded in the same way as above.

Subsequently, the authors further developed this methodology for the formation of 2,3-bis-organylselenylbenzo[*b*]chal-



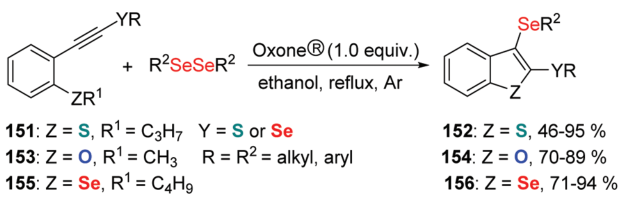
Scheme 40 Iodine(III)-mediated synthesis of β-selenyl pyrazoline and isoxazoline.



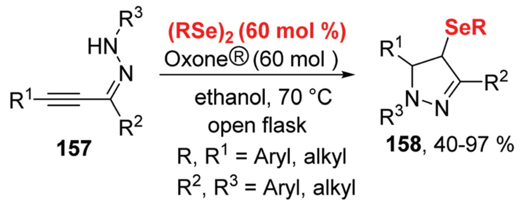
Scheme 42 Proposed mechanism of Oxone® promoted synthesis of 5*H*-selenopheno[3,2-*c*]isochromen-5-ones.

cogenophenes (Scheme 43)[46] and 4-organoselanyl-1*H*-pyrazoles (Scheme 44)[47] by employing chalcogenoalkynes and α,β-alkynyl hydrazones as substrates by promotion of Oxone® and diselenides.

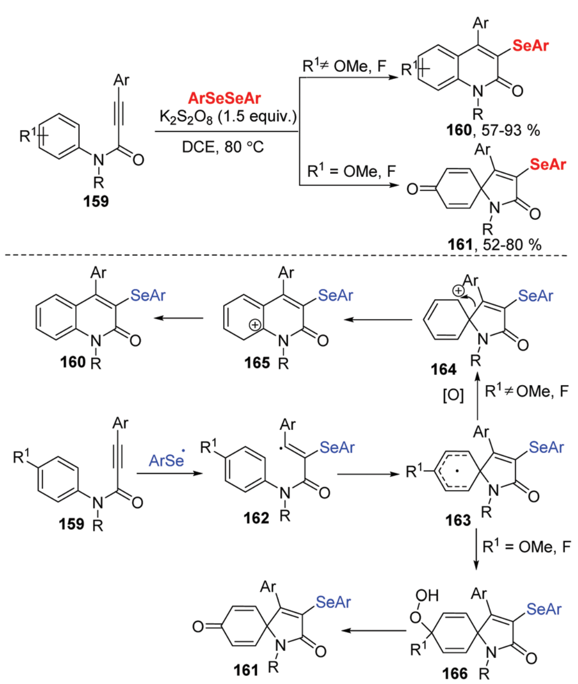
In 2019, the group of Baidya developed an efficient radical selenocyclization of *N*-aryl alkynamides **159** using $K_2S_2O_8$ as an oxidant in DCE at 80 °C (Scheme 45).[48] This method worked well in a switchable selectivity *ortho*/*ipso*-cyclization by



Scheme 43 Oxone® promoted synthesis of 2,3-bis-organylselenyl-benzo[*b*]chalcogenophenes.



Scheme 44 Oxone® promoted synthesis of 4-organoselanyl-1*H*-pyrazoles.



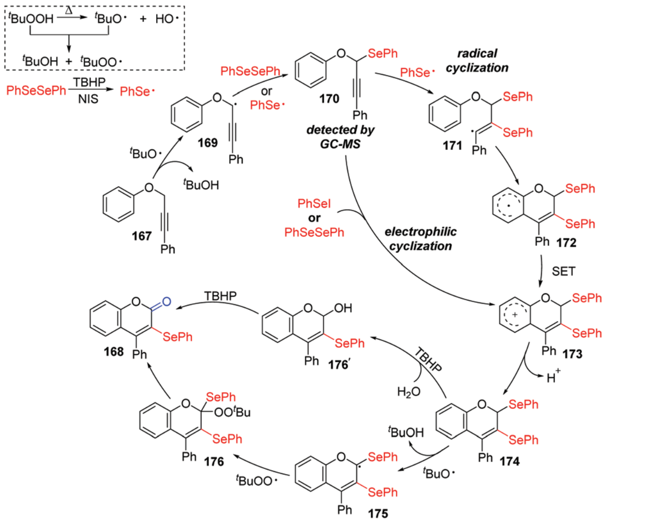
Scheme 45 $K_2S_2O_8$ initiated synthesis of 3-selenyl quinolin-2-ones and 3-selenospiro[4,5]trienones.

the change the substituent of *N*-aryl alkynamides **159**, resulting in a variety of 3-selenyl quinolin-2-ones **160** and 3-selenospiro[4,5]trienones **161** in good to excellent yields. Moreover, diaryl diselenides and dialkyl diselenides were well tolerated in *ortho* cyclization. When propiolamides bearing *para*-fluoro and *para*-methoxy in the *N*-aryl ring were reacted with diaryl diselenides, the spiro-cyclic products were isolated in good to high yields. Alkyl-substituted propiolamides were also suitable for the *ortho*/*ipso*-cyclization. Radical trapping experiments by using TEMPO, butylated hydroxytoluene (BHT) or 1,1-diphenylethylene indicated that the process involves a free radical pathway. The authors carried out the reaction between 4-phenyl-quinolin-2-one and diphenyldiselenide under the standard reaction conditions and found that the selenylation process occurred before the ring-closure step. A tentative radical mechanism was depicted in Scheme 37. Initially, the $K_2S_2O_8$-mediated cleavage of the Se–Se bond of diselenide forms an aryl selenium radical, which undergoes a radical addition to *N*-aryl alkynamide and intramolecular spirocyclization to give radical intermediate **163**. The intermediate **163** is oxidized to afford the intermediate **164**, which is rapidly converted into the desired quinolone product **160** through 1,2-C-migration and aromatization. When the *N*-aryl alkynamide bears *para*-F/OMe substituents, the intermediate **163** further reacts with solvated molecular oxygen to produce intermediate **166**, which undergoes defluorination/demethoxylation *via* O–O bond cleavage leading to the product **161**.

In 2019, Liu group reported the *tert*-butyl hydroperoxide (TBHP)-initiated radical cyclization of propargylic aryl ethers **167** with diaryl diselenides for the synthesis of diverse 3-organoselenyl-2*H*-coumarins **168** (Scheme 46).[49] The use of *N*-iodosuccinimid (NIS) could be *in situ* generation ArSeI with diaryl diselenides, increasing the reaction yield. For insight the mechanism, some control experiments were performed. TBHP was essential for this method, not only as radical initiator, but also with H_2O providing O atom proved *via* ^{18}O-labeling experiment.

According to the proposed mechanism (Scheme 47), aryl selenium radical and propargyl radical are generated *in situ* in the presence of TBHP as the oxidant and react with each other, leading to the key intermediate **170**, which was detected by GC. Aryl selenium radical then adds to alkyne triple bond **170** to produce the highly reactive alkenyl radical **171**. This radical undergoes intramolecular cyclization onto the phenyl moiety, giving intermediate **174**, which might be obtained by electrophilic cyclization of PhSeI in another path. Product **168** is gen-

Scheme 46 TBHP-initiated synthesis of 3-organoselenyl-2*H*-coumarins.



Scheme 47 Proposed mechanism TBHP-initiated synthesis of 3-organoselenyl-2*H*-coumarins.

erated by one of two pathways. In the first pathway, the solvent H_2O participates in the nucleophilic attack of **174** to generate an alcohol, which is further oxidized by TBHP to furnish **168**. In the second pathway, *tert*-butoxy radical gets an allylic hydrogen from **174** to generate radical intermediate **175**, which is subsequently trapped by the *tert*-butylperoxy radical to afford intermediate **176**. Finally, the cleavage of C–Se and O–O bonds intermediate **176** gives the targeted product **168**.

4. Conclusions

We have summarized recent advances in tandem selenocyclization and tellurocyclization between diselenides and alkenes or alkynes categorized by metal catalysis, visible-light catalysis, electrochemical catalysis, organocatalysis *etc*. Using such approaches, various important seleno-containing heterocycles can be efficiently accessed with high chemo- and regioselectivity and often with high atom economy. Additionally, the mechanistic features of these transformations have been discussed. The many successful examples presented in this review convincingly document the high potential of this approach in drug discovery, and some seleno-containing heterocycles have shown potent inhibitory activity against cancer cell growth. Despite the substantial advances in this area over the past few years, many challenges and problems remain to be solved. For instance, most of the tandem selenocyclization reactions discussed herein are based on two distinct reaction components. Reactions comprising three or even more components, which would further increase the structural space of the accessible compounds, are not well explored. Furthermore, designs for new diselenides should be developed. Asymmetric control also remains an important challenge. We hope that this review contributes to stimulating further advancement in the emerging research area of seleno cyclization reactions.

Conflicts of interest

There are no conflicts to declare.

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