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Review

Recent Developments in the Synthesis of Organoselenium Compounds Based on the Reactions of Organic Diselenides with Acetylenes †

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† Dedicated to Academician Prof. Boris A. Trofimov on the occasion of his jubilee.

Abstract: The last decade has witnessed significant progress in the development of novel synthetic methods for the preparation of a variety of new functionalized and condensed compounds via reactions of organic dichalcogenides with acetylenic derivatives. The present review highlights recent developments in the synthesis of organoselenium compounds based on the reactions of organic diselenides with acetylenes over the past few years. The discussion mainly focuses on the literature data for the last 5 years. It is worth noting that the lion's share of this material is devoted to catalytic and electrophile-mediated reactions with aromatic compounds, containing a triple bond and nucleophilic functional groups.

Keywords: acetylenes; annulation; cyclization; iron salts; organic diselenides; Lewis acids; condensed compounds

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1. Introduction

Selenium is identified as an essential micronutrient for mammals, including humans [1–5]. The discovery of the important physiological role of selenium in the human body gave a powerful impact to comprehensive studies on the syntheses and properties of various kinds of organoselenium compounds [6–11]. It is well known that selenium deficiency in the human body increases the incidence of cardiovascular diseases, cancer, arthritis, diathesis, and other common pathologies [1–11]. Organoselenium compounds exhibit various types of biological activity [12–27], including antiviral (anti-HIV and anti-SARS-CoV-2) [21,22], antibacterial [19,20], antitumor [16–19], and antioxidant glutathione peroxidase mimetic properties [23–25].

The selenium-containing drug ebselen (2-phenyl-1,2-benzisoselenazol-3(2H)one) exhibits cytoprotective, anti-inflammatory, and glutathione peroxidase-like activities [28–33]. A catalytic mechanistic cycle of ebselen as a glutathione peroxidase-like mimic has been investigated. This heterocyclic compound, containing a nitrogen–selenium bond, has also been found to show antiviral properties and inhibit the replication of the SARS-CoV-2 virus (Figure 1) [32,33]. An important property of ebselen is that it is a non-toxic compound. Ebselen is the first organoselenium compound that has been investigated in clinical trials as a glutathione peroxidase mimic and neuroprotective agent [28–33]. Recently, this compound has been used as a therapeutic agent in clinical trials in several areas, including the treatment of COVID-19, Meniere's disease, and bipolar disorder [28].

One of most important classes of organoselenium compounds are organic diselenides. These compounds are most widely used among other organoselenium reagents. Diorganyl diselenides serve as valuable starting materials for organic synthesis. They are used as

precursors of both electrophilic and nucleophilic selenium species, which are usually generated from organic diselenides in situ and involved in various useful transformations. Along with multifaceted applications in organic synthesis, organic diselenides exhibit various biological activities, including high glutathione peroxidase mimetic properties (Figure 1) [29,34–46].

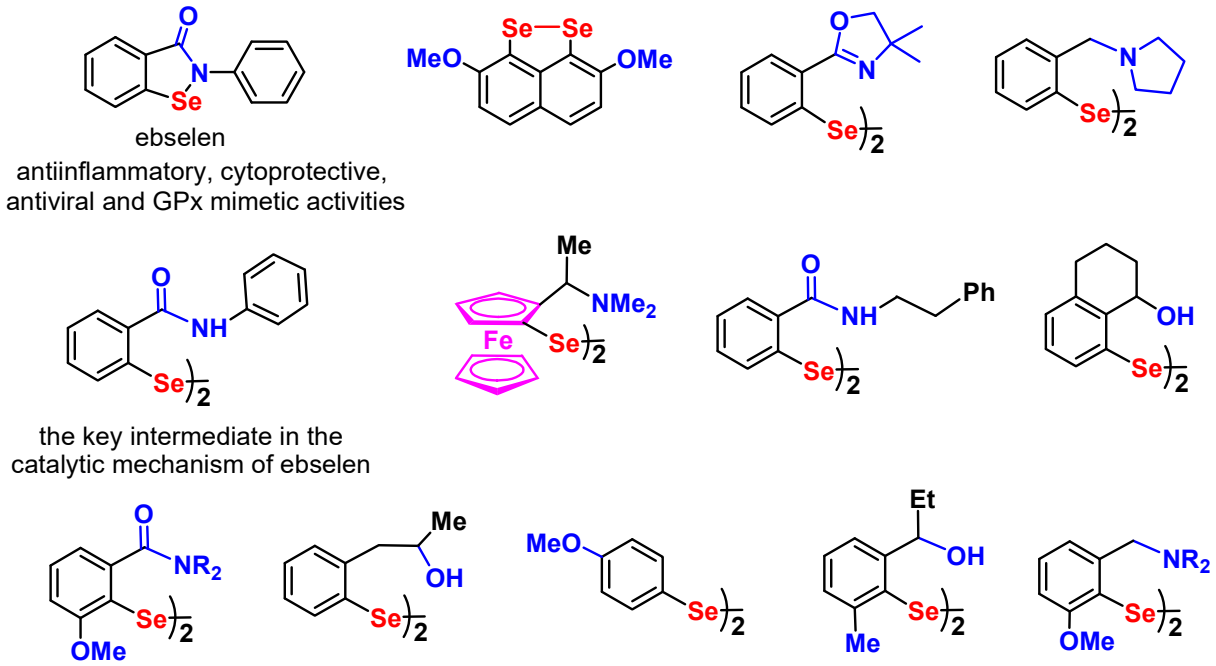


Figure 1. Examples of organic diselenides with glutathione peroxidase mimetic activity.

Bis(2-anilinocarbonylphenyl) diselenide (Figure 1) was found to be a key intermediate in the catalytic mechanistic cycle of ebselen as a glutathione peroxidase-like mimic [29]. It has been shown that the presence of a nitrogen–selenium bond is not necessary for the manifestation of high glutathione peroxidase-like activity. It has been demonstrated that a number of diaryl diselenides are superior to ebselen in terms of glutathione peroxidase-like mimetic properties (Figure 1) [29]. For example, diphenyl diselenide was shown to be twice as active as ebselen [41].

2. The Synthesis of Organoselenium Compounds Based on the Reactions of Organic Diselenides with Acetylenes

Organic diselenides, in addition to being a source of electrophilic and nucleophilic selenium species, serve as powerful multifaceted tools in a variety of reactions, primarily various catalytic reactions with unsaturated and aromatic compounds. The last decade has witnessed significant progress in the development of new synthetic methods for the preparation of organoselenium compounds based on reactions of organic diselenides with unsaturated and aromatic compounds. The present review discusses recent developments in the synthesis of organoselenium compounds based on the reactions of organic diselenides with acetylenes over the past few years. It mainly covers literature data for the last five years. It is worth noting that the lion's share of this material is devoted to the catalytic reactions of organic diselenides with acetylenes and with aromatic compounds, containing a triple bond and functional groups.

Acetylene and its derivatives are well-known versatile intermediates and building blocks of organic synthesis [47,48]. The Favorsky reaction of acetylenes with carbonyl compounds underlies a number of the methods used in industry for the production of valuable reagents and materials [47]. Developing Favorsky's scientific heritage in the A. E. Favorsky Irkutsk Institute of Chemistry, important fundamental contributions to the chemistry of acetylene and its derivatives were made by Trofimov and co-workers [49–56].

A number of important previous works on this topic deserve to be cited, including interesting articles and reviews on the reactions of organic diselenides with acetylenes [57–80]. A significant contribution to the research of transition metal-catalyzed reactions of organic diselenides with acetylenes was achieved by Beletskaya and Ananikov [57–63], Ogawa and Sonoda [64,65], and other scientists. A number of remarkable radical reactions of acetylenes with binary systems containing organic diselenides were developed by Ogawa [66–68].

The reactions of organic diselenides with acetylenes in the presence of reducing agents often led to vinylic selenides due to the generation of intermediate organylselenolate anions [69–71]. The base-catalyzed addition of diorganyl diselenides to terminal acetylenes proceeded in a stereoselective fashion, producing (*Z*)-1,2-bis(organylselanyl)ethenes [72–74]. Radical and electrophilic additions of organic diselenides to acetylenes, as well as other catalytic reactions of these reagents, were also reported [75–80].

2.1. Iron-Catalyzed and -Promoted Reactions

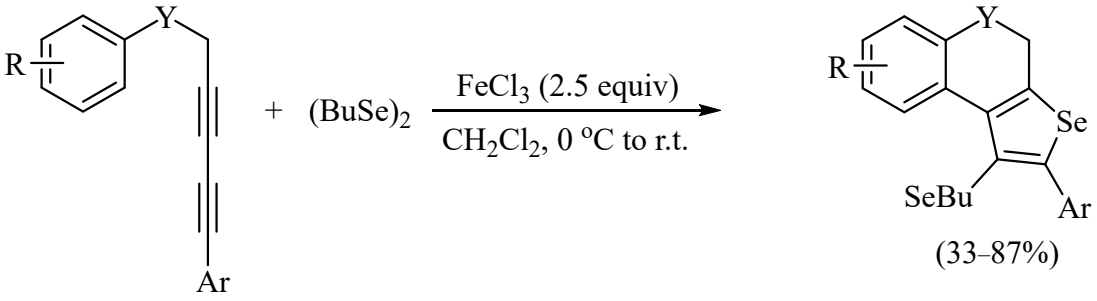
In the last few years, much attention has been paid to the reactions of diaryl diselenides with acetylenic compounds promoted by Lewis acids (e.g., salts of iron). The synthesis of novel organoselenium compounds based on the reactions of diorganyl diselenides with acetylenic compounds in the presence of iron salts has received significant development, and a number of diorganyl diselenide activation systems have been proposed [81–99]. For example, the diorganyl diselenide/Fe/I_2 system was used for the synthesis of novel *N*-methyl-3-chalcogeno-indoles via the iron-facilitated iodine-mediated electrophilic annulation reactions of 2-alkynylaniline derivatives with organic diselenides [81]. The iron-catalyzed addition of diorganyl diselenides to acetylenes led to (*E*)-1,2-bis(organylselanyl)ethenes [82].

The considerable contribution to the development of synthesis of novel organoselenium compounds based on iron-salt-promoted reactions of diorganyl diselenides with acetylenic compounds was made by Zeni and co-workers [82–94]. Inter alia, the synthesis of 3-organoselenylchromenones via the intramolecular 6-endo-dig cyclization of alkynyl aryl ketone derivatives was developed using a diorganyl diselenide-$FeCl_3$ system [83]. Based on the iron-promoted cyclization reaction of 1-benzyl-2-alkynylbenzenes with diorganyl diselenides, the efficient synthesis of 9-(organoselanyl)-5H-benzo[7]annulenes was developed [84]. The authors emphasized that the mutual action between diorganyl diselenides and iron(III) chloride was essential in order to achieve the maximal yields of the products.

A number of chromene-fused selenophene derivatives were synthesized by Zeni and co-workers based on 1,3-diynyl propargyl aryl ethers and dibutyl diselenide (Scheme 1) [90]. This remarkable methodology provides the formation of carbon-carbon, carbon-selenium, and selenium-carbon bonds in a one-pot protocol, using iron(III) chloride and dibutyl diselenide as promoters.

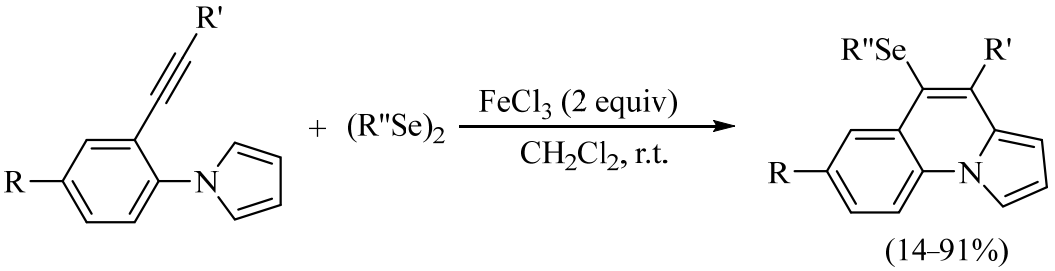
This approach was also implemented using propargyl anilines as a substrate, which made it possible to obtain a number of corresponding functional heterocycles containing a selenophene ring condensed with tetrahydroquinolines (Scheme 1) [90]. A mechanism for intramolecular electrophilic addition induced by an electrophilic selenium-containing intermediate was proposed. It was shown that the reaction proceeded through the ionic mechanism and did not include radical processes, and both diorganyl diselenide and $FeCl_3$ are necessary for the reaction to occur.

Zeni and co-workers reported an elegant method which made it possible to synthesize a series of 5-(organochalcogenyl)pyrrolo [1,2-*a*]quinolines based on N-(ortho-alkynyl)arylpyrroles. The heteroaromatic fragment, N-substituted pyrrole, acts as the electrophilic reaction center of intramolecular cyclization in this reaction (Scheme 2) [91].



Y = O; Ar = Ph, 4-MeC_6H_4, 3-MeC_6H_4, 4-MeOC_6H_4, 2-MeOC_6H_4, 4-ClC_6H_4, 2-BrC_6H_4, Napht;
R = H, 2-Me, 4-Me, 2-*t*-Bu, 4-Ph, 4-MeO, 4-I, 2-I, 3-Cl, 4-Me-2-Br, 2-Br-4-F;
Y = S; Ar = Ph; R = H;
Y = NTs; Ar = Ph, 4-MeOC_6H_4, 4-ClC_6H_4; R = H, 4-Me, 4-MeO, 4-Cl

Scheme 1. The iron-mediated cyclization of 1,3-diynyl propargyl aryl derivatives with dibutyl diselenide.



R = H, Me, Cl
R' = H, I, Si(Me)$_3$, Ph, 4-MeC_6H_4, 3-MeC_6H_4, 4-MeOC_6H_4, 2,4,6-Me$_3C_6H_2$, Napht-2-yl, Bu
R" = Ph, 4-MeC_6H_4, 4-ClC_6H_4, 4-FC_6H_4, 3-C$F_3C_6H_4$, Bu

Scheme 2. The cyclization of N-(ortho-alkynyl)aryl-pyrroles.

The reaction was carried out in methylene chloride at room temperature in a chemoselective fashion, giving the target products in up to 91% yields.

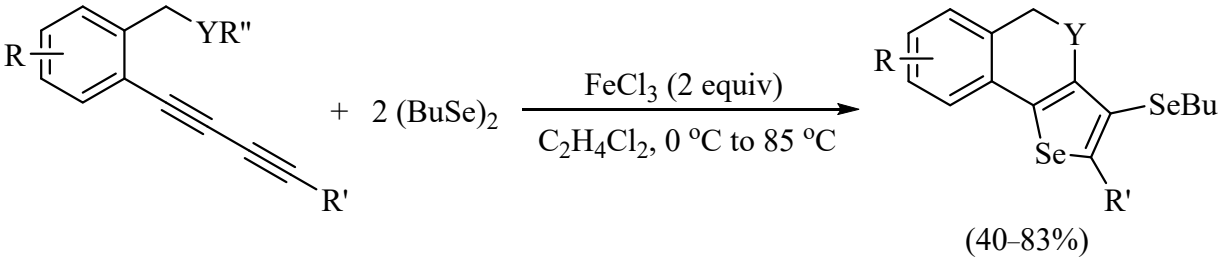
In the case of arylacetylenes, containing functional nucleophilic groups in the ortho position to the ethynyl substituent, the intramolecular cyclization reaction on the aromatic ring did not proceed, but involved the more active nucleophilic group. Thus, Zeni and co-workers synthesized a series of isochromene-fused selenophene derivatives based on the cascade cyclization reaction of *ortho*-diynyl benzyl chalcogenides as the substrate and a system of iron(III) chloride and diorganyl dichalcogenides under reflux in dichloroethane (Scheme 3) [92].

The best reaction conditions were found, which include ortho-diynyl benzyl chalcogenides (0.25 mmol), iron(III) chloride hexahydrate (2.0 equiv), and diorganyl diselenide (2 equiv) at the reflux of dichloroethane [92]. These conditions allow for obtaining the target products in good yields (40–83%).

A system of iron salts and diorganyl diselenides exhibits a dual action, consisting of both the promotion of the cyclization and the introduction of a new functionalization (the organylselanyl group) at the 3-position of chalcogenoisochromenes.

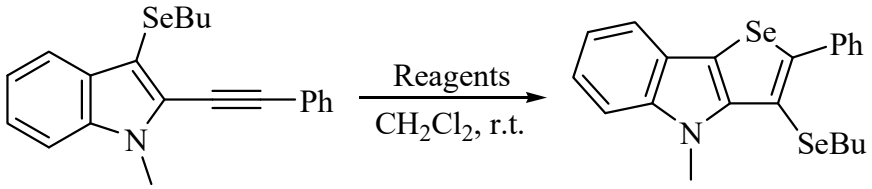
It is worth emphasizing that this methodology is highly regioselective and provides the formation of products exclusively through selective cyclization via a 6-endo-dig mode followed by a second 5-endo-dig cyclization. The syntheses were implemented as a one-pot procedure, in which three new carbon-chalcogen bonds were consecutively formed [92].

The treatment of 3-butylselanyl-2-phenylethynylindole with dibutyl diselenide and iron(III) chloride in methylene chloride at room temperature led to 3-(butylselanyl)selenophene indole in 68% yield (Scheme 4) [93].



Y = O; R" = Me; R = H;
R' = Ph, 4-MeC$_6$H$_4$, 3-MeC$_6$H$_4$, 2-MeC$_6$H$_4$, 2-MeOC$_6$H$_4$, 3-MeOC$_6$H$_4$, 2-ClC$_6$H$_4$, 4-ClC$_6$H$_4$, 4-FC$_6$H$_4$, Bu, Napht-2-yl, Thiophen-3-yl;
Y = S; R" = Et; R = H; R' = Ph;
Y = Se; R" = Bu; R = H, [d][1,3]dioxole, benzene;
R' = Ph, 4-MeC$_6$H$_4$, 3-MeC$_6$H$_4$, 2-MeC$_6$H$_4$, 4-MeOC$_6$H$_4$, 2-ClC$_6$H$_4$, 4-ClC$_6$H$_4$, 4-FC$_6$H$_4$, Napht-2-yl

Scheme 3. The FeCl$_3$/dialkyl diselenide-promoted cascade cyclization of ortho-diynyl benzyl chalcogenides.

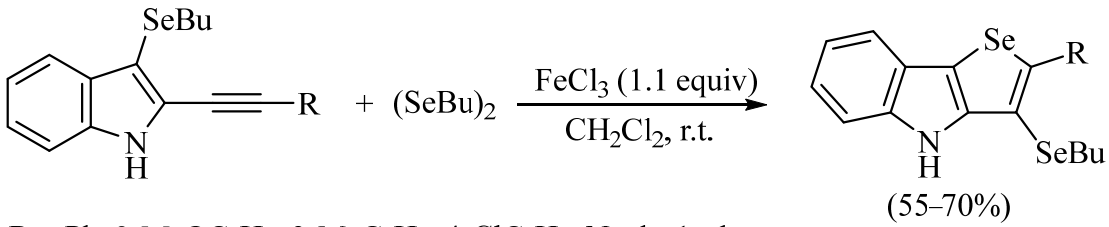


Reagents:	yield, %
FeCl$_3$, (SePh)$_2$	35
FeCl$_3$, (SeBu)$_2$	68

Scheme 4. The reactivity of dibutyl diselenide and diphenyl diselenide in the cyclization of 3-butylselanyl-2-alkynylindoles.

It was found that that dibutyl diselenide was superior to diphenyl diselenide in this reaction and produced the product in higher yield (Scheme 4) [93].

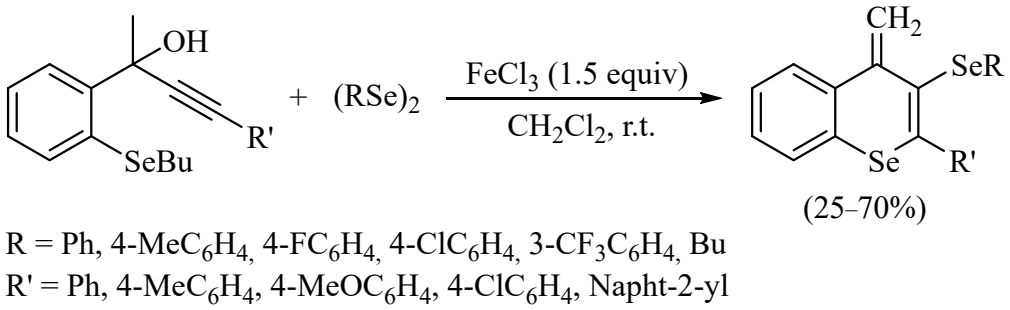
The convenient method for the preparation of 3-butylselanyl-selenophene-condensed indoles in 55–70% yields from 3-butylselanyl-2-alkynylindoles was developed at room temperature in methylene chloride using a iron(III) chloride/dibutyl diselenide system, which efficiently promoted the cyclization and functionalization of this heterocyclic system (Scheme 5) [93].



R = Ph, 2-MeOC$_6$H$_4$, 3-MeC$_6$H$_4$, 4-ClC$_6$H$_4$, Napht-1-yl

Scheme 5. The FeCl$_3$/dibutyl diselenide-promoted cyclization of 3-butylselanyl-2-alkynylindoles providing 3-butylselanyl-selenophene-condensed indoles.

The reaction of 2-(butylselanyl)phenylpropynols with the iron(III) chloride/diorganyl diselenide system was carried out in methylene chloride at room temperature, producing 4-methylene-3-(organoselanyl)-selenochromenes in 25–70% yields (Scheme 6) [94].



Scheme 6. The synthesis of 4-methylene-3-(organoselanyl)-selenochromenes from 2-(butylselanyl) phenylpropynols.

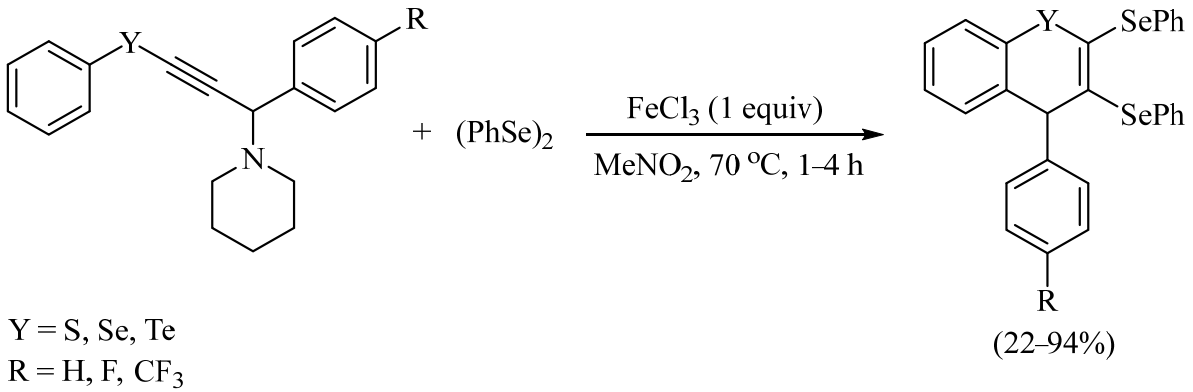
The results of the optimization of the reaction conditions showed that the effects of the solvent, the iron source, and the amount of diorganyl diselenides had a significant influence on the reaction process and yields of the products. On the basis of these studies, it was found that the products were formed in the best yields when using iron(III) chloride (1.5 equiv), diorganyl diselenides (1.0 equiv), and methylene chloride as the solvent, at room temperature [94].

The authors also found that these reaction conditions were suitable for substrates bearing electron-withdrawing and electron-donating groups in the aromatic ring at both the propargyl and alkyne positions [94].

Although the yields of the products obtained in some cases were low, these unusual transformations are very interesting, and these products, bearing an exo-methylene (as a part of the butadienyl fragment) and organylselanyl group, can be used as valuable starting materials in organic synthesis.

The authors indicated that the formation of 4-methylene-3-(organoselanyl)-selenochromenes was carried out via the regioselective 6-endo-dig cyclization of 2-(butylselanyl)phenylpropynols promoted by the cooperative action between diorganyl diselenides and iron(III) chloride [94].

The synthesis of polysubstituted 4*H*-chalcogenochromenes based on organochalcogenyl propargyl amines and diaryl diselenides in the presence of Fe^{3+} salts was developed [95]. The best results were obtained with $FeCl_3$. Nevertheless, the possibility of using $Fe(NO_3)_3$ and $Fe(acac)_3$ as catalysts was also shown (Scheme 7).



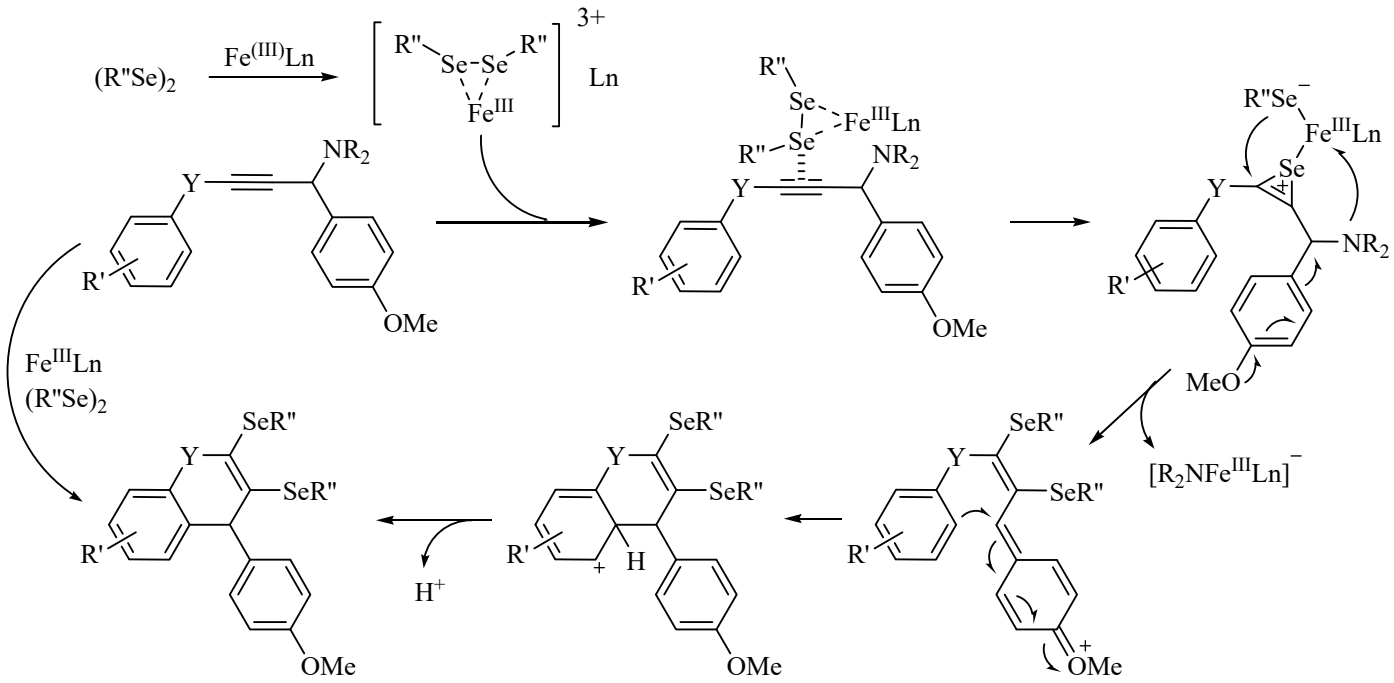
Scheme 7. The synthesis of polysubstituted 4H-chalcogenochromenes.

The piperidinyl substituent was found to be the best among the amine moieties when the effect of the leaving group R in the organoselenium propargylamine was studied [95]. A propargylamine containing the methyl group underwent decomposition when exposed to iron(III) chloride and no starting material was recovered from this reaction.

The scope of this reaction was also explored [95]. Organoselenium propargylamines containing electron-donating substituents at the benzene ring (methoxy and methyl groups)

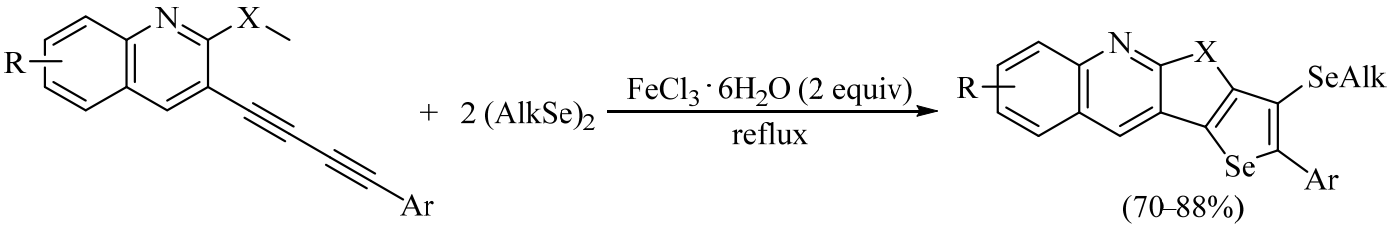
produced the products in good to excellent yields, whereas the reactions with substrates bearing electron-withdrawing substituents were sluggish. When a substrate with a strongly deactivating trifluoromethyl group was used, the expected product was not obtained.

The authors proposed a mechanism based on the tautomeric effect, which explains the formation of chromene structures containing two organylselanyl substituents (Scheme 8). The formation of a pseudo-quinoid structure with a main leaving group at the triple bond leading to a shift in the electrophilic center in the intermediate is important (Scheme 8) [95].



Scheme 8. The proposed mechanism for the formation of substituted 4*H*-chalcogenochromenes.

Very promising results were obtained by Koketsu and co-workers [96]. A remarkable ensemble of four- and five-cyclic selenophene-condensed, quinoline-based heteroacenes was synthesized based on iron-promoted intramolecular cascade cyclization reactions (Scheme 9) [96].



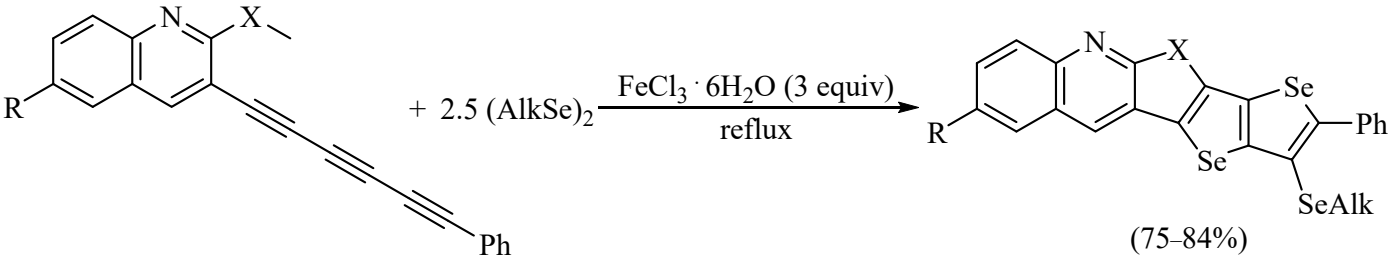
X = S; R = H, 6-Me, 7-Me, 8-Me;
Ar = Ph, p-MeC$_6$H$_4$; Alk = Pr, Bu
X = Se; R = H, 6-Me;
Ar = Ph, p-MeC$_6$H$_4$; Alk = Pr, Bu

Scheme 9. The synthesis of selenophene-condensed thieno [2,3-*b*]quinolines and selenopheno [2,3-*b*]quinolines.

Based on the optimization of the reaction conditions, the authors found that the process can be efficiently carried out at reflux in methylene chloride by using iron(III) chloride hexahydrate (2.5 equiv) and dialkyl diselenides (2 equiv) [96]. These conditions were used for the development of the synthesis of quinoline-based heteroacenes by the

Fe(III)-promoted linear intramolecular cascade cyclization of 3-(1,3-diynyl) quinolines. The target selenophene-condensed thieno [2,3-*b*]quinolines and selenopheno [2,3-*b*]quinolines were obtained in 70–88% yields (Scheme 9) [96].

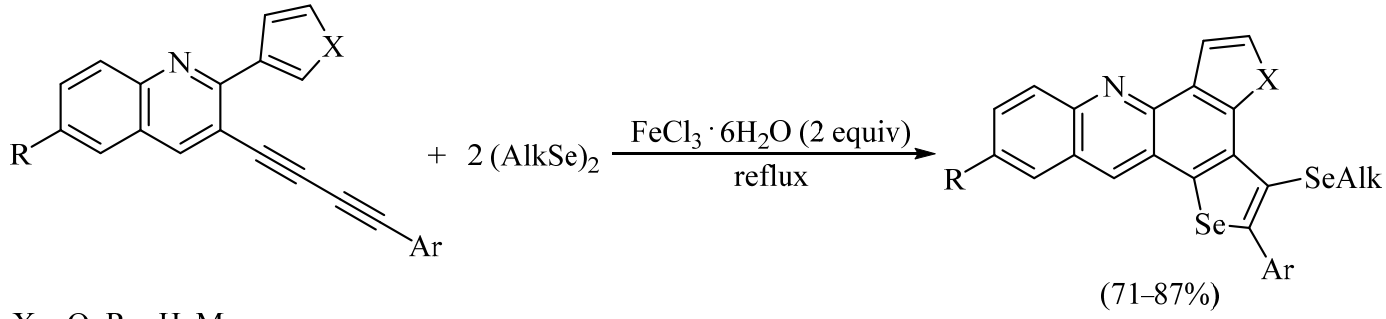
In the case of using similar substrates containing one more acetylenic group (3-(1,3,5-triynyl) quinolines), the favorable conditions for the preparation of five-cyclic selenophene-condensed, quinoline-based heteroacenes required an increase in the content of iron(III) chloride hexahydrate to 3 equivalents and dialkyl diselenides to 2.5 equivalents [96]. Using this ratio of the reagents, diselenophene-condensed thieno [2,3-*b*]quinolines and diselenopheno [2,3-*b*]quinolines were synthesized in 75–84% yields (Scheme 10) [96].



X = S; R = H, Me; Alk = Pr, Bu
X = Se; R = Me; Alk = Bu

Scheme 10. The synthesis of diselenophene-condensed thieno[2,3-*b*]quinolines and diselenopheno [2,3-*b*]quinolines.

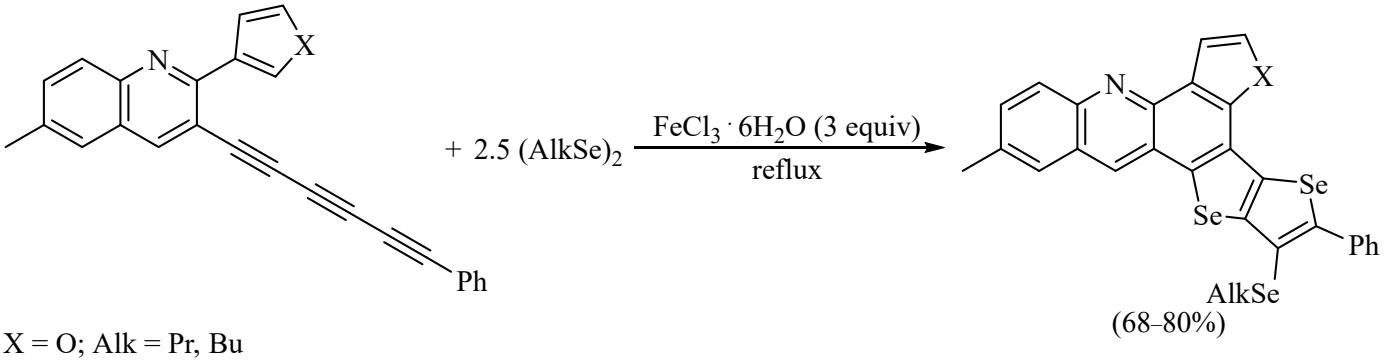
When the quinoline scaffold of the substrate contained the thiophene ring (the thien-3-yl substituent) in position 2, selenophene-condensed thieno [2,3-*c*]acridine and furo [2,3-*c*]acridine were successfully obtained in 71–87% yields under similar conditions (Scheme 11) [96].



X = O; R = H, Me;
Ar = Ph, 4-MeC$_6$H$_4$; Alk = Pr, Bu
X = S; R = H, Me;
Ar = Ph, p-MeC$_6$H$_4$; Alk = Pr, Bu

Scheme 11. The preparation of selenophene-condensed thieno [2,3-*c*]acridine and furo [2,3-*c*]acridine.

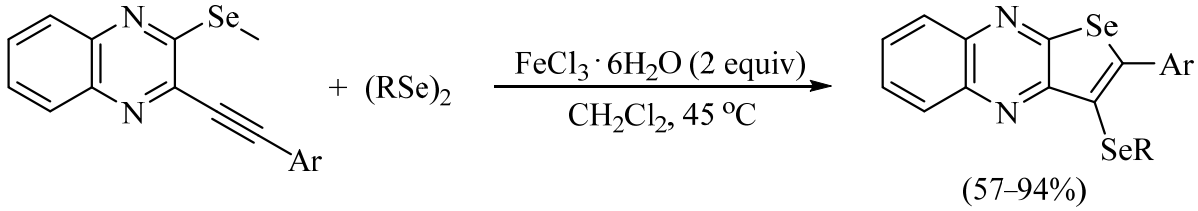
When the quinoline scaffold of the substrate contained the thiophene ring (the thien-3-yl substituent) in position 2, six-membered selenophene-condensed thieno [2,3-*c*]acridine and furo [2,3-*c*]acridine were successfully obtained in 68–80% yields under similar conditions (Scheme 12) [96].



X = O; Alk = Pr, Bu
X = S; Alk = Pr, Bu

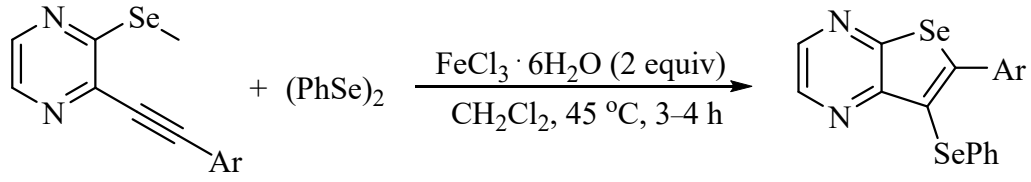
Scheme 12. The synthesis of six-membered diselenophene-condensed thieno [2,3-*c*]acridine and furo [2,3-*c*]acridine.

Another very interesting work by Koketsu and co-workers described the novel synthesis of three different heterocycles: 2-arylselenopheno [2,3-*b*]quinoxaline, 3-(aryl/alkylselanyl)-2-arylselenopheno [2,3-*b*]quinoxaline, and 6-phenyl-7-(arylselanyl)selenopheno [2,3-*b*]pyrazine derivatives based on 2,3-dichloroquinoxaline and 2,3-dichloropyrazine. The annulation reactions of 2-(methylselanyl)-3-(arylethynyl)quinoxaline (Scheme 13) and 2-(methylselanyl)-3-(arylethynyl) pyrazine (Scheme 14) were carried out in the presence of iron(III) chloride hexahydrate at reflux in methylene chloride, producing corresponding condensed heterocycles in 57–94% yields and 47–70% yields, respectively [97].



R = Ph; Ar = Ph, 4-MeC$_6$H$_4$, 4-MeOC$_6$H$_4$, 4-FC$_6$H$_4$, 3-FC$_6$H$_4$, 2-FC$_6$H$_4$
R = Me, Bu; Ar = Ph

Scheme 13. The annulation reaction of 2-(methylselanyl)-3-(arylethynyl)quinoxaline.

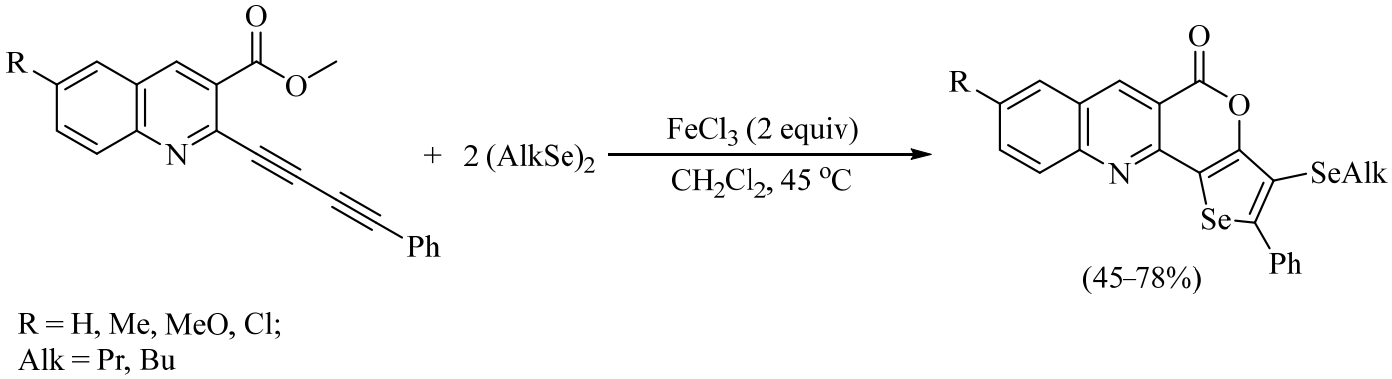


Ar = Ph, 4-MeC$_6$H$_4$, 4-MeOC$_6$H$_4$, 3-FC$_6$H$_4$, 2-FC$_6$H$_4$

Scheme 14. The annulation reaction of 2-(methylselanyl)-3-(arylethynyl) pyrazine.

The photophysical properties of 2-arylselenopheno [2,3-*b*]quinoxaline, 3-(aryl/alkylselanyl)-2-arylselenopheno [2,3-*b*]quinoxaline, and 6-phenyl-7-(arylselanyl)selenopheno [2,3-*b*] pyrazine derivatives were investigated to study the effect of heteroatoms on UV absorbance and fluorescence properties [97].

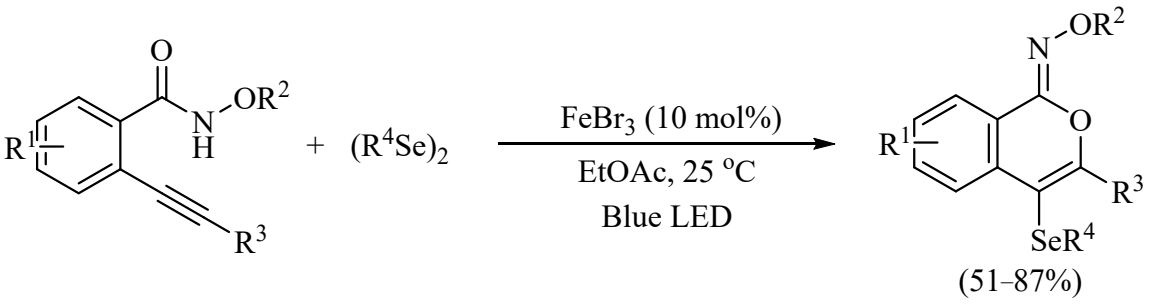
A new route for the convenient synthesis of a selenophene-condensed quinoline-based heterocycle was also developed by Koketsu and co-workers [98]. Iron(III) chloride and dialkyl diselenides generated the intramolecular cascade cyclization of methyl 6-methyl-2-(phenylbuta-1,3-diyn-1-yl)quinoline-3-carboxylate and other derivatives, which produced the target selenophene-condensed quinoline-based heterocycle derivatives in up to 78% yields (Scheme 15) [98].



R = H, Me, MeO, Cl;
Alk = Pr, Bu

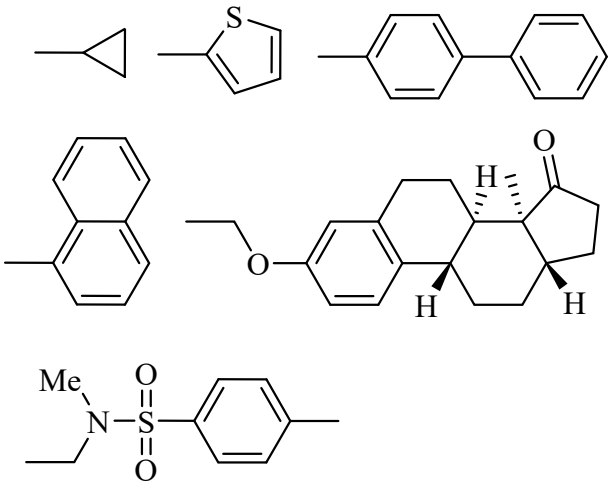
Scheme 15. The annulation reaction of methyl 2-(phenylbuta-1,3-diyn-1-yl)quinoline- 3-carboxylates.

A novel iron-catalyzed selenocyclization of *N*-methoxy-2-alkynylbenzamides enabled by visible-light irradiation was developed. Iron tribromide was used as the catalyst for the reaction between *N*-methoxy-2-alkynylbenzamide and diselenides, affording organylselanyl isocoumarin-1-imines in up to 87% yields (Scheme 16) [99].



R^4 = Et, Ph, 4-ClC_6H_4
R^1 = H, 6-Me, 7-Me, 7-MeO, 7-Cl,
R^2 = Me, Bn;

R^3 = t-Bu, n-Bu, Me_3Si, Ph, CH_2OMe, 4-MeC_6H_4, 4-$MeOC_6H_4$, 4-ClC_6H_4, 2-ClC_6H_4, 3-FC_6H_4,



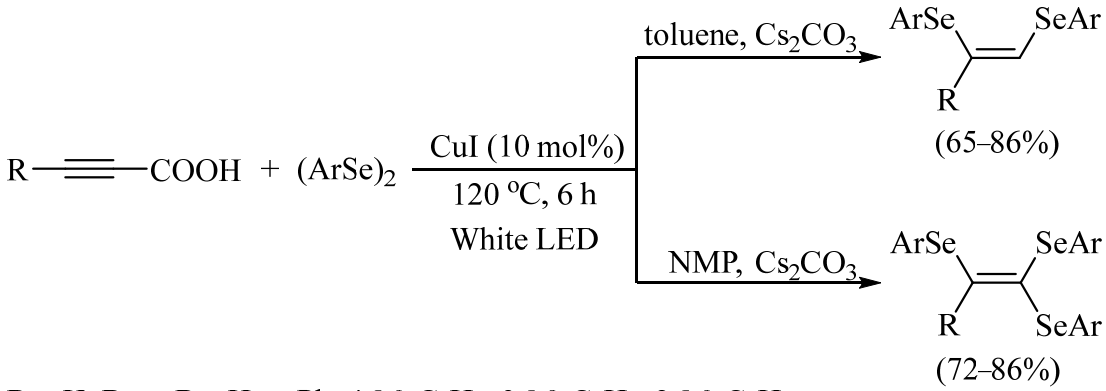
Scheme 16. The annulation reaction of *N*-methoxy-2-alkynylbenzamide and diselenides, producing selenated isocoumarin-1-imines.

A wide range of *N*-methoxy-2-alkynylbenzamides, and both aromatic and aliphatic diselenides, can serve as useful substrates, with the reaction conditions tolerating various functional groups (Scheme 16) [99].

Using this approach, several selenium-containing seven- and eight-membered-ring heterocycles were also synthesized [99].

2.2. Transition Metal-Catalyzed Reactions

The efficient synthesis of bis- and tris-selanyl alkenes based on alkynyl carboxylic acids and organic diselenides was developed. The reaction of alkynyl carboxylic acids with diaryl diselenides in a mixture of CuI, Cs_2CO_3, and toluene under white-light LEDs at 120 °C produced bis-selanyl alkenes in 65–86% yields (Scheme 17), whereas tris-selanyl alkenes were obtained in the CuI/Cs_2CO_3/N-methyl-2-pyrrolidone system at 120 °C in 72–86% yields (Scheme 17) [100].

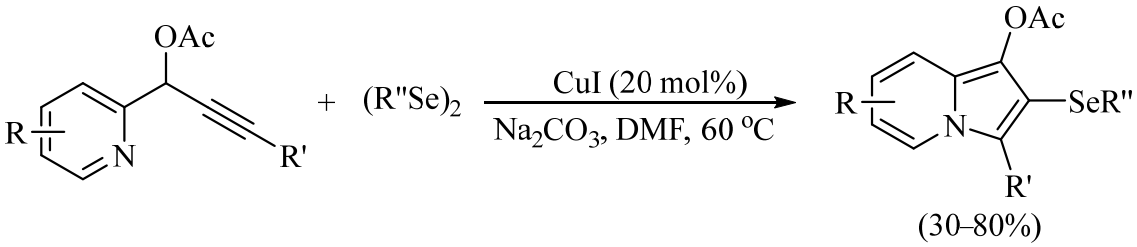


R = H, Bu, t-Bu, Hex, Ph, 4-MeC_6H_4, 3-MeC_6H_4, 2-MeC_6H_4, 4-PrC_6H_4, 4-$MeOC_6H_4$, 4-ClC_6H_4, 4-FC_6H_4, 4-$CF_3C_6H_4$;
Ar = Ph, 4-MeC_6H_4, 4-BrC_6H_4

Scheme 17. The reaction of alkynyl carboxylic acids with diaryl diselenides in the presence of CuI/Cs_2CO_3/toluene under white-light LEDs.

It is known that N-methyl-2-pyrrolidone is an aprotic bipolar solvent which accelerates the nucleophilic and some other reactions.

Copper(I) iodide and diorganyl dichalcogenides were found to be valuable cyclization promoters of propargylpyridines in preparing 2-(organochalcogenyl)-indolizines in up to 80% yields (Scheme 18) [101].



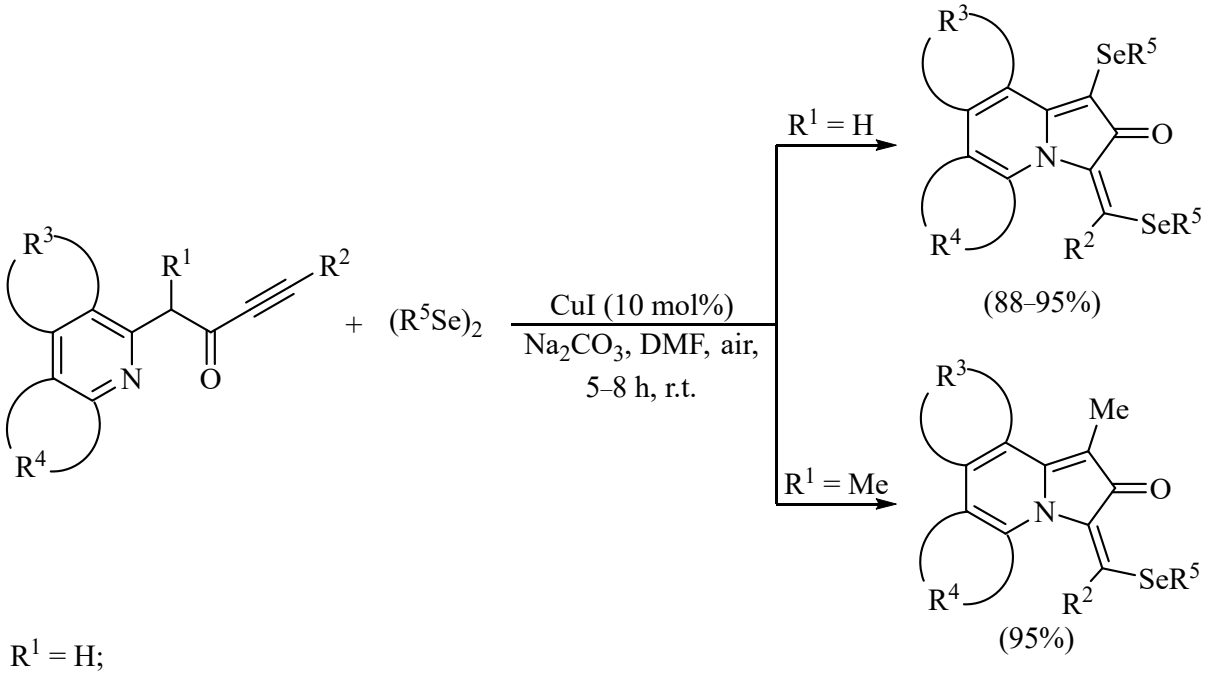
R = 3-Me; R' = Ph;
R" = Ph, 2-$MeOC_6H_4$, 4-ClC_6H_4;
R = H; R' = H, Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$;
R" = Ph, 3-$CF_3C_6H_4$, 4-MeC_6H_4, 2-MeC_6H_4, 4-$MeOC_6H_4$, 2-$MeOC_6H_4$, 4-ClC_6H_4

Scheme 18. The synthesis of 3-aryl-2-(arylselanyl)indolizin-1-yl acetates.

The obtained results pointed out that the mutual action between copper(I) iodide and diorganyl dichalcogenides is essential for the formation of indolizines in good yields and avoiding the undesirable formation of hydrogenated indolizine. The standard reaction conditions were compatible with many functional groups in the substrates, such as methyl, chlorine, fluorine, methoxy, and trifluoromethyl moieties. It is worth noting that this

methodology (Scheme 18) was efficient with diorganyl diselenides and ditellurides, but ineffective with diorganyl disulfides [101].

An efficient method for the preparation of functionalized indolizinone heterocycles based on the copper-catalyzed cascade reaction of pyridine, isoquinoline, and quinoline ynones in the system CuI/Na_2CO_3/NMP was developed (Scheme 19) [102]. The reaction occurred via 5-exo-dig cyclization.

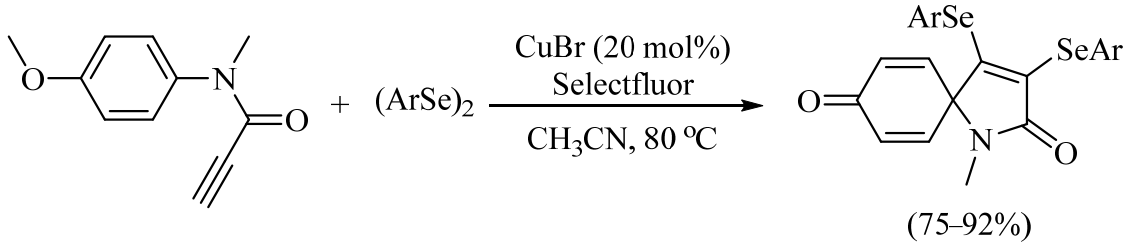


R^1 = H;
R^3, R^4 = H; R^5 = Ph
R^2 = Ph, 4-$MeOC_6H_4$, 4-FC_6H_4, 4-MeC_6H_4,
2-MeC_6H_4, 2-$CF_3C_6H_4$, 2-Me-4-$MeOC_6H_3$;
R^3 = H; R^4 = $(CH)_4$, CHC(Cl)CHCH; R^5 = Ph, Bn, 4-MeC_6H_4, 4-FC_6H_4;
R^2 = Ph, 4-MeC_6H_4;
R^3 = $(CH)_4$; R^4 = H; R^5 = Ph, Bn; R^2 = Ph
R^1 = Me;
R^3, R^4 = H; R^5 = Ph; R^2 = Ph

Scheme 19. Copper(I)-catalyzed diorganoselanyl-substituted indolizinone synthesis from substituted pyridine homologated ynones.

The obtained substituted indolizinones were involved in the reduction reaction. These compounds were converted into 1-(organylchalcogenyl)indolizin-2-ols, which are important building blocks in organic synthesis.

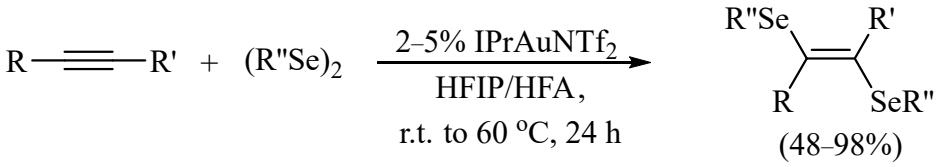
The cascade annulation reaction of terminal alkynyl amides with organic diselenides, leading to the construction of 3-arylselenenyl spiro [4.5]trienones, was realized under mild conditions (reflux in acetonitrile) with Selectfluor as the sole oxidant. 3,4-Bis(arylselanyl) spiro [4.5]trienones were synthesized by a cascade annulation reaction using copper bromide as a catalyst (Scheme 20) [103].



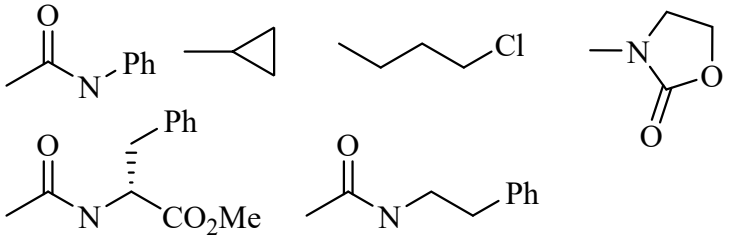
Ar = Ph, 4-EtC$_6$H$_4$, 4-MeOC$_6$H$_4$, 3-MeOC$_6$H$_4$, 4-ClC$_6$H$_4$, 4-BrC$_6$H$_4$, 2-BrC$_6$H$_4$, 4-*t*-BuC$_6$H$_4$, 4-CF$_3$OC$_6$H$_4$

Scheme 20. The synthesis of 3,4-bis(arylselanyl) spiro [4.5]trienones.

A gold-catalyzed reaction of aryl diselenides with alkynes and allenes was studied. The reactions with alkynes gave (*E*)-1,2-bis(arylselanyl)ethenes in up to 98% yields (Scheme 21). Excellent regio- and stereoselectivity (the formation of trans-adducts), as well as good to excellent yields, were achieved with a wide range of substrates and 2% catalyst loading [104].



R" = Bn, Ph, 4-MeC$_6$H$_4$, 4-MeOC$_6$H$_4$, 4-BrC$_6$H$_4$, 4-FC$_6$H$_4$, 4-CF$_3$C$_6$H$_4$, 3-FC$_6$H$_4$;
R = H, Me, COOMe, Br, Cl, Ph
R' = COOMe, COOBn, COOt-Bu, Ph, 4-MeC$_6$H$_4$, 4-MeOC$_6$H$_4$, 4-FC$_6$H$_4$, 4-CF$_3$C$_6$H$_4$, 4-BrC$_6$H$_4$, 4-FC$_6$H$_4$, 3-MeC$_6$H$_4$, 3-FC$_6$H$_4$, 2-MeC$_6$H$_4$



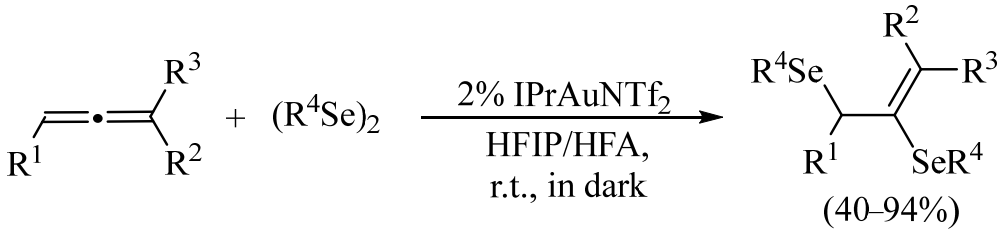
Scheme 21. The gold-catalyzed reaction of aryl diselenides with alkynes.

Based on the investigation of reaction mechanisms, the authors revealed the formation of a vinyl gold(I) intermediate followed by an intermolecular selenium cation migration [104].

The gold-catalyzed reaction of aryl diselenides with allenes produced corresponding vinyl selenides in 40–94% yields (Scheme 22).

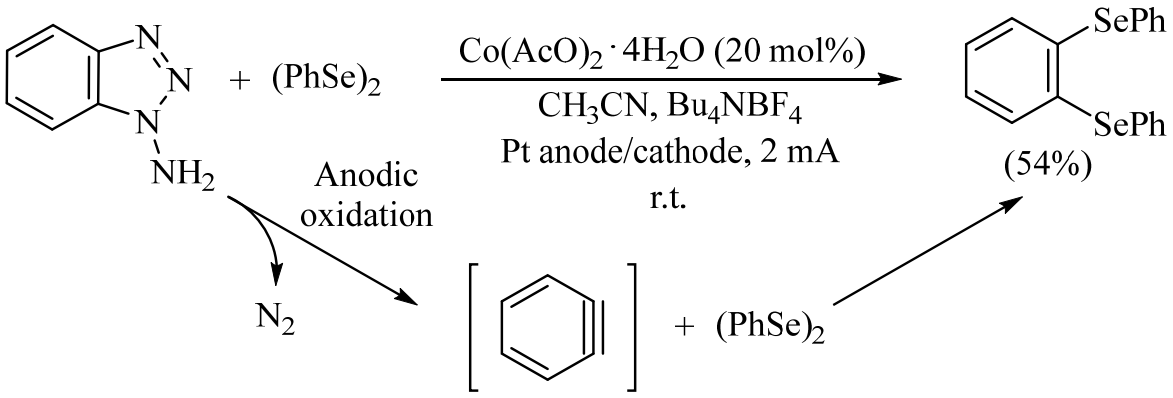
The reactions of the dithyilation and diselenylation of unsaturated compounds promoted by hexafluoroisopropanol (HFIP) were studied. The reactions of disulfides or diselenides with unactivated alkyne, alkene, and allene in HFIP led to corresponding 1,2-bis(organylchalcogenyl)ethenes, 1,2-bis(organylchalcogenyl)ethanes, and vinyl chalcogenides, respectively, in good to excellent yields (up to 96%). In contrast, other solvents, such as isopropanol and dichloroethane, could not promote the same reaction. These results exhibit examples of interesting HFIP-promoted transformations under mild conditions, which demonstrated the high reactivity and unique properties of this special solvent [105].

An interesting electrochemical approach for the oxidative generation of benzyne and its successful involvement in the reaction with diphenyl diselenide was recently described (Scheme 23) [106].



R^4 = Bn, Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$, 4-FC_6H_4;
R^1 = H, Ph
R^2 = H, Me, Ph
R^3 = Me, Ph, 4-BrC_6H_4, C_3H_6OTBS, 4-$CF_3C_6H_4$,
4-BrC_6H_4, 4-FC_6H_4, 3-MeC_6H_4, 3-FC_6H_4, 2-MeC_6H_4

Scheme 22. The gold-catalyzed reaction of aryl diselenides with allenes.



Scheme 23. The electrochemical approach for the oxidative generation of benzyne and its reaction with diphenyl diselenide.

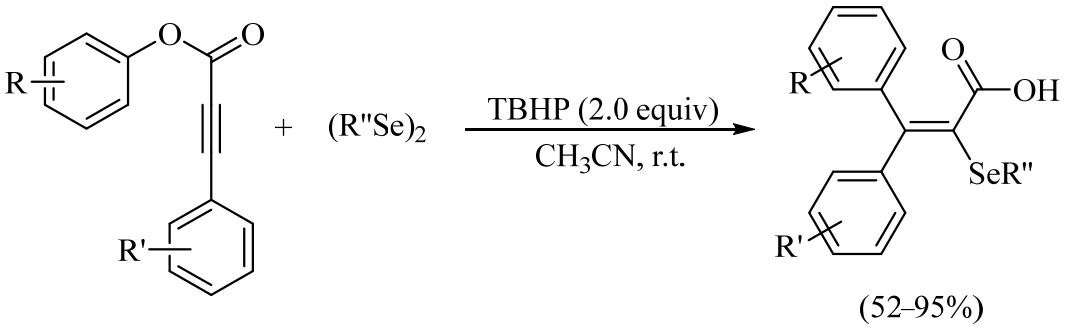
A very promising area of research is the development and application of nickel-based metal–organic frameworks as catalysts for the addition reactions of organic dichalcogenides [63].

2.3. Radical and Electrochemical Reactions

The oxidative difunctionalization of aryl alkynoates, providing stereodefined fully substituted α,β-unsaturated acids bearing a chalcogen functionality in high yields (up to 95%), was developed (Scheme 24) [107]. This radical-based cascade reaction was carried out at room temperature in the presence of tert-butyl hydroperoxide (TBHP) and studied with the use of devices.

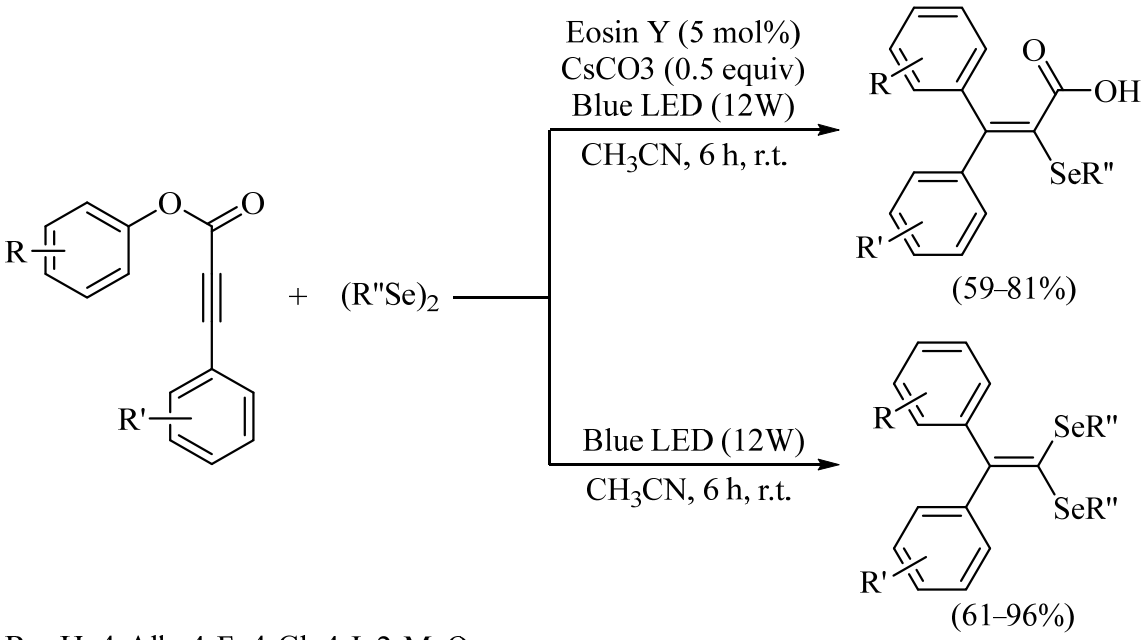
This methodology can be used in the synthesis of vinyl selenides and 1,1-dichalcogenyl olefins [107,108].

The synthesis of 1,1-diselanyl alkene derivatives and selenium-containing α,β-unsaturated carboxylic acid was achieved by a visible-light-induced selenium radical-mediated domino reaction of aryl alkynoates with organic diselenides (Scheme 25) [109]. The process is mild, metal-free, easy to handle, and scalable.



R = H, 4-Me, 4-MeO, 4-CN, 4-Br, 4-Cl, 4-Ph, 3-Me, 3-CF_3, 3-F, 2-MeO, 2-Cl, 3-Me;
R' = H, 4-Me, 4-MeO, 4-F, 3-MeO, 2-MeO;
R" = Ph, 4-$MeOC_6H_4$, 4-ClC_6H_4, 4-FC_6H_4, 4-EtC_6H_4, 3-$CF_3C_6H_4$

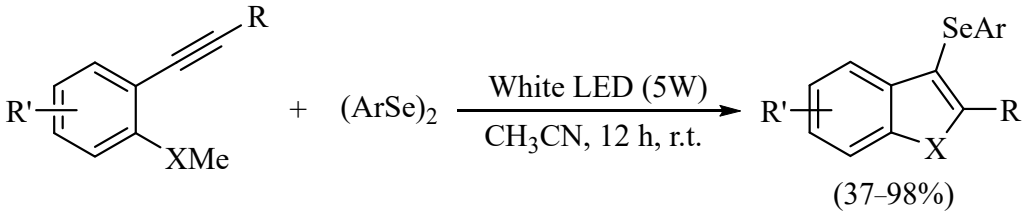
Scheme 24. The oxidative difunctionalization of aryl alkynoates.



R = H, 4-Alk, 4-F, 4-Cl, 4-I, 2-MeO;
R' = H, 4-Me, 4-MeO, 4-COOMe, 4-CHO, 4-Br, 4-F;
R" = Me, Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$, 4-BrC_6H_4, 4-FC_6H_4

Scheme 25. The synthesis of 1,1-diselenide alkene derivatives and selenium-containing α,β-unsaturated carboxylic acids.

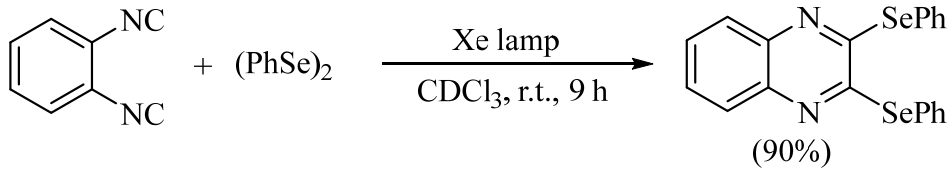
A simple and direct method for synthesizing 3-arylselanyl benzothiophenes was developed [110]. The reaction did not require any catalysts or additives, and the desired products were obtained under mild visible-light irradiation (5 W). This method provides a valuable alternative for the synthesis of 3-arylselanyl benzochalcogenophenes, which are important scaffolds of various bioactive compounds (Scheme 26) [110].



X = S, Se;
R' = H, 4-F, 4-Me
R = n-Pr, Bn, Ph, 2-MeC_6H_4, 3-MeC_6H_4, 4-MeC_6H_4, 4-MeOC_6H_4, 4-ClC_6H_4, 4-FC_6H_4, 4-CNC_6H_4, Pyridin-3-yl, Thiophen-3-yl;
Ar = Ph, 4-MeOC_6H_4, 2-MeOC_6H_4, 4-MeC_6H_4, 2-ClC_6H_4, 3-ClC_6H_4, 4-ClC_6H_4, 4-BrC_6H_4, 4-FC_6H_4, 4-$CF_3C_6H_4$, 4-CNC_6H_4, Pyridin-3-yl

Scheme 26. The synthesis of 3-arylselanyl benzochalcogenophenes.

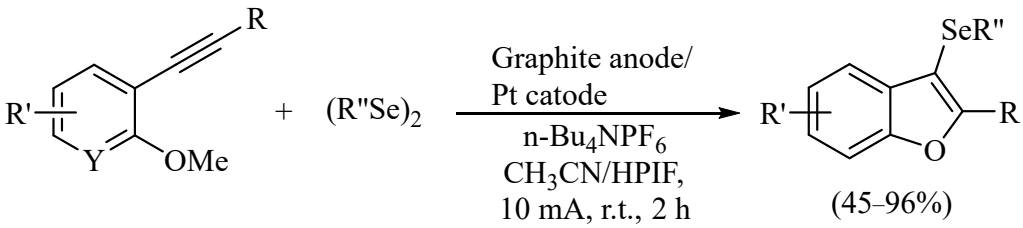
Chalcogenated quinoxalines were prepared via efficient photoinduced cyclization reactions of o-diisocyanoarenes with organic diselenides or thiols. The cyclization reaction with organic diselenides is believed to proceed via radical mechanisms. The developed methodology can be used to obtain a library of organylselanyl-substituted quinoxalines, which are known to be potential oxidants with promising biological activity (Scheme 27) [111].



Scheme 27. The synthesis of organylselanyl-substituted quinoxalines.

A series of electrochemical methods, including the direct electrooxidative selenylation/cyclization of alkynes [112] and the versatile electrochemical synthesis of selenylbenzo[*b*]furan derivatives [113], were developed.

An efficient electrochemical protocol for the formation of valuable organylselenylated benzo[*b*]furan derivatives via the cyclization of 2-alkynylanisoles through an electrooxidative process was developed. Various 3-substituted benzofurans were obtained in good to excellent yields under metal- and oxidant-free mild reaction conditions (Scheme 28) [112].

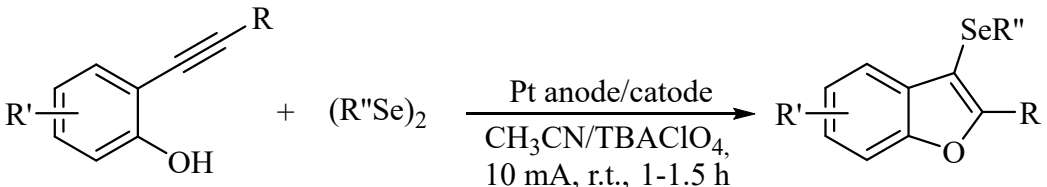


Y = C;
R" = Me, Et, 4-MeC_6H_4, 4-FC_6H_4, 4-ClC_6H_4, 4-BrC_6H_4, 3-MeC_6H_4, 3-ClC_6H_4, 3-BrC_6H_4, 3-$CF_3C_6H_4$, 2-MeC_6H_4, 2-ClC_6H_4, Thiophen-2-yl;
R' = H, 3-F, 4-Cl, 4-Me;
R = Ph, 4-MeC_6H_4, 4-EtC_6H_4, 4-FC_6H_4, 4-ClC_6H_4, 4-BrC_6H_4, 4-AcNHC_6H_4, 3-FC_6H_4, 2-BrC_6H_4, 2-ClC_6H_4, $(CH_2)_5OH$, Pyridin-3-yl, Thiophen-3-yl, Thiophen-2-yl;
Y = N; R' = H; R = Ph; R" = Ph

Scheme 28. The synthesis of organylselenylated benzo[*b*]furan derivatives via the cyclization of 2-alkynylanisoles.

This approach exhibited good functional group tolerance and could be easily scaled up with good efficiency, providing access to a diverse range of selenylated benzo[*b*]furans derivatives from available starting materials [112]. The possibility of using this methodology for a gram scale procedure was shown and a conceivable reaction mechanism was proposed.

An efficient regioselective electrochemical synthesis of 3-(organylselanyl) benzo[*b*]furan derivatives was achieved based on the cyclization of 2-alkynylphenols (Scheme 29) [113].

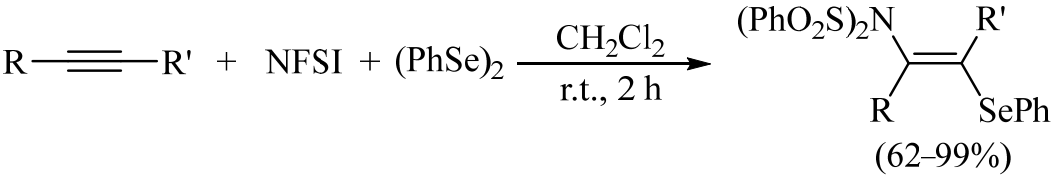


R" = n-Bu, Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$, 4-FC_6H_4, 4-ClC_6H_4, 3-$CF_3C_6H_4$, 2-MeC_6H_4, Thiophen-2-yl;
R' = H, 4-Br, 4-Me;
R = Ph, 4-MeC_6H_4, 4-ClC_6H_4, $(CH_2)_6$, Thiophen-2-yl

Scheme 29. The synthesis of 3-(organylselanyl)benzo[b]furan derivatives based on the cyclization of 2-alkynylphenols.

This procedure, driven by galvanostatic electrolysis using platinum electrodes assembled in an undivided cell, provided efficient transformation under oxidant-free, base-free, and transition metal-free conditions at room temperature. The method proved to be reliable and can be applied to gram scales. In addition, the wide applicability of this method was noted, since it can be used in the synthesis of 2,3-bis(organochalcogenyl)benzo[*b*]chalcogeno phenes [113].

An intermolecular selenoamination reaction of alkynes with diphenyl diselenide and N-fluorobenzenesulfonimide (NFSI) proceeded in a regio- and stereoselective fashion and produced vinyl selenides, containing the benzenesulfonamide group, in 62–99% yields (Scheme 30) [114].



R = H, Alk, Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$, 4-CNC_6H_4, 4-FC_6H_4, 4-$CF_3C_6H_4$, 4-$TsOC_6H_4$, 3-$MeOC_6H_4$, 3-$NO_2C_6H_4$, 2-*i*PrC_6H_4, 2-BrC_6H_4, 2,4-$Me_2C_6H_3$, Pyridin-2-yl, Pyridin-3-yl
R' = H, Alk, Bn, Ph, CH_2Br, CH_2OH, -CH(Me)OC(O)Ph, cyclopenten-1-ol-1-yl, $SiMe_3$

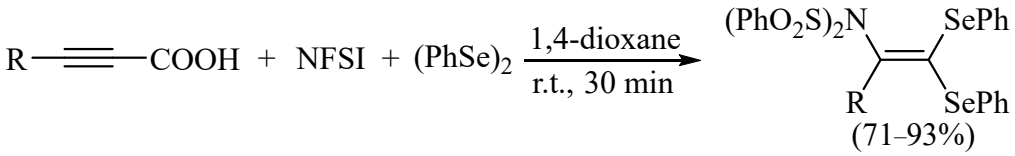
Scheme 30. The synthesis of vinyl selenides, containing the benzenesulfonamide group.

N-Fluorobenzenesulfonimide played the role of both the oxidant and the amination reagent. The reaction features mild conditions, selectivity, high yields of the products, and a broad substrate scope (Scheme 30) [114].

Mechanistic studies indicate that the in situ generated chalcogen imidates are the real reactive species, which clarified the mechanisms of related transformations [114]. These reactions represent a significant contribution to the development of the highly selective amino bisfunctionalization of alkynes.

The combination of organic diselenides with N-fluorobenzenesulfonimide made it possible to carry out a smooth decarboxylative tri- or tetrafunctionalization reaction of

alkynylcarboxylic acids under catalyst-free conditions at room temperature. A number of diseleno-substituted enamine derivatives were efficiently prepared in good to excellent yields (Scheme 31) [115].



R = H, Alk, Ph, C(O)OMe, CH_2OH, 4-MeC_6H_4, 4-EtC_6H_4, 4-FC_6H_4, 4-ClC_6H_4, 4-BrC_6H_4, 4-$CF_3C_6H_4$, 4-$MeOC_6H_4$, 3-MeC_6H_4, 2-FC_6H_4, 2-BrC_6H_4, 2-MeC_6H_4, Napht-2-yl, Thiophen-3-yl

Scheme 31. The synthesis of diseleno-substituted enamine derivatives.

This methodology offers a useful strategy for the simultaneous creation of one C–N bond and two or three C–Se bonds, and may be of practical value. The reaction opens up a new and simple way with which to obtain enamine derivatives containing two or three organylselanyl substituents [115].

2.4. Reactions with the Use of Oxone® and Iodine

A variety of efficient and very promising synthetic methods with the use of Oxone® were recently developed [116–124]. Oxone® is a commercially available reagent, consisting of $2KHSO_5$, $KHSO_4$, and K_2SO_4. This triple salt contains 50% (mol) of the active oxidant potassium peroxymonosulfate ($KHSO_5$) and can be used in various oxidation reactions, including oxidations of functional groups.

In the past few years, the use of Oxone® (potassium peroxymonosulfate) as an oxidizing agent and promoter of some reactions in organic synthesis has significantly increased [116]. This cheap and environmentally friendly reagent is an important alternative to many other commercially available oxidizing agents due to its useful chemical properties, availability, non-toxicity, and ease of handling. Over the past few decades, this green oxidative reagent has become a powerful tool in organic synthesis [116]. Recently, potassium peroxymonosulfate was successfully used in a number of promising transformations with the formation of valuable organoselenium compounds including heterocyclic products [118–128].

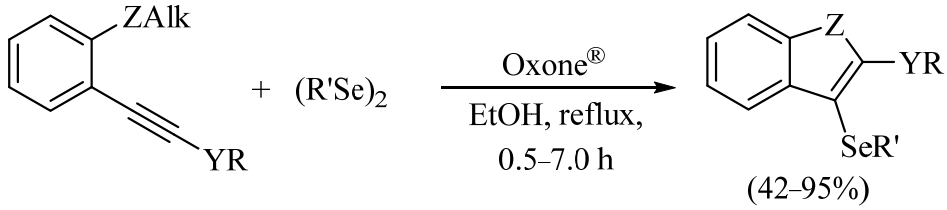
A review summarizing advances in the Oxone®-mediated synthesis of N-, O-, and chalcogen-containing heterocyclic compounds was recently published by Lenardão, Perin, and co-workers [116]. Various reactions starting from several types of substrates were discussed in this review, highlighting major synthetic differences, advantages, applications, and limitations. Some works using organic diselenides as substrates are included in the published review and therefore are not discussed in the present survey.

An important example is the selective synthesis of a number of new benzo[*b*]chalcogeno phenes (chalcogens are oxygen, sulfur, and selenium) via the reaction of diorganyl diselenides with 2-organylchalcogenyl-functionalized chalcogenoalkynes promoted by Oxone® under reflux in ethanol (Scheme 32) [124].

The environmentally friendly synthesis, mild reaction conditions, efficacy, and generality of the reaction are important features of this new approach.

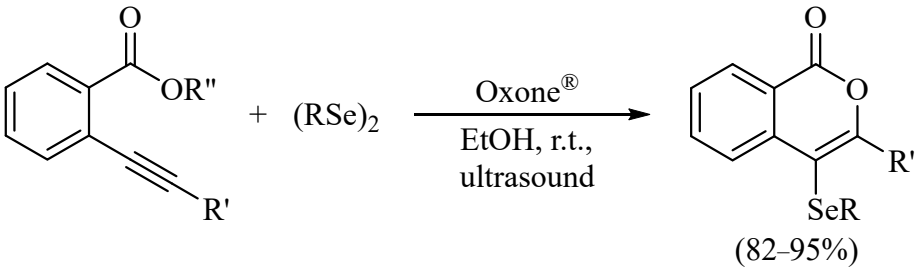
The obtained compound, 2-(butylselanyl)-3-(phenylselanyl)benzofuran, was involved in the Pd-catalyzed reaction with phenylacetylene to produce Sonogashira's coupling product in 50% yield [124].

Perin, Lenardão, and co-workers reported a new method for the preparation of 4-organylselanyl-1*H*-isochromen-1-ones in 82–95% yields from 2-alkynylaryl esters and diorganyl diselenides (Scheme 33) [125].



Z = O; Alk = Me;
Y = S; R = Ph; R' = Ph, 4-ClC_6H_4, 4-$MeOC_6H_4$;
Y = Se; R = Ph, Bu; R' = Ph, 4-ClC_6H_4, 4-FC_6H_4;
Z = S; Alk = Pr;
Y = S, R = Ph; R' = Ph, 4-ClC_6H_4, 4-$MeOC_6H_4$
Y = Se, R = Ph, 4-FC_6H_4, 4-MeC_6H_4;
R' = Ph, 4-ClC_6H_4, 4-FC_6H_4, 4-MeC_6H_4, 4-$MeOC_6H_4$
Z = Se; Alk = Bu; Y = Se; R = Ph; R' = Ph, p-MePh, p-ClPh, p-FPh

Scheme 32. The selective synthesis of new benzo[*b*]chalcogenophenes (O, S, and Se) via the simple reaction between diorganyl diselenides and 2-organylchalcogen-functionalized chalcogenoalkynes promoted by Oxone®.

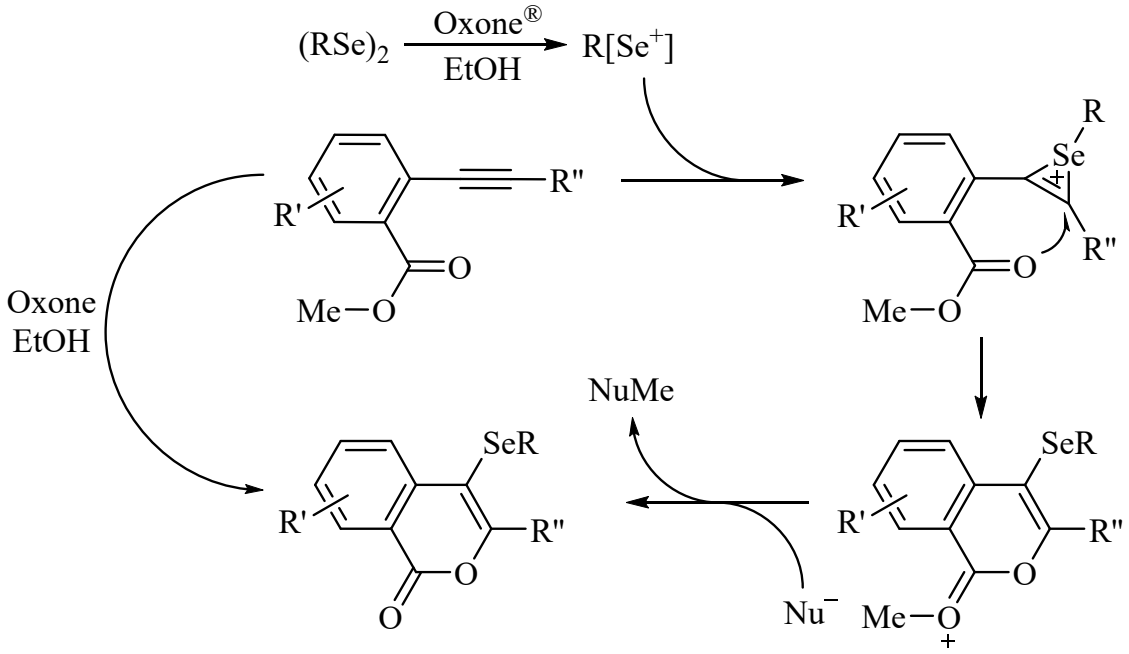


R' = H, Bu, CH_2OH, CH(Me)OH, $C(Me)_2OH$, Ph, 2-$MeOC_6H_4$,
4-ClC_6H_4, 4-$MeOC_6H_4$, 4-*t*BuC_6H_4, $SiMe_3$
R = Et, Bu, CH_2(Napht-2-yl), 4-FC_6H_4, 4-ClC_6H_4, 4-MeC_6H_4,
4-$MeOC_6H_4$, 3-$CF_3C_6H_4$, 2,3,6-$Me_3C_6H_2$;
R" = H, Me, Oct, Bn;

Scheme 33. The Oxone®-promoted synthesis of 4-organylselanyl-1*H*-isochromen-1-ones from 2-alkynylaryl esters and diorganyl diselenides.

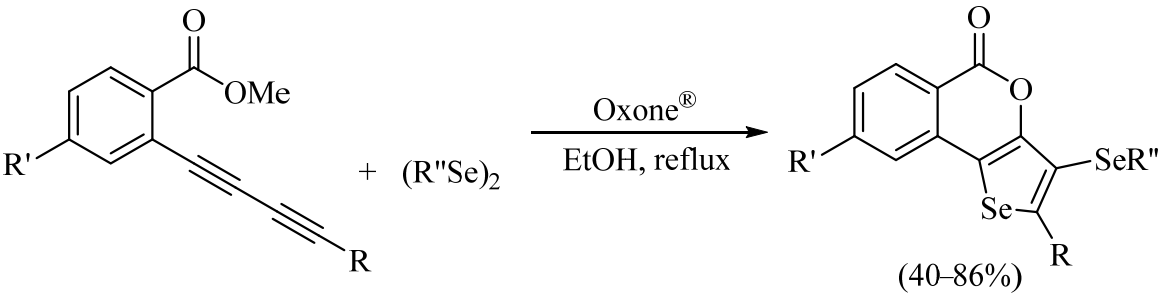
The reactions with the diselenides were carried out under mild conditions in ethanol, using Oxone® as a green oxidant under microwave irradiation. Organic ditellurides were also involved in the similar reaction in glycerol to produce 4-organylchalcogenyl-1*H*-isochromen-1-ones in 78–90% yields [125].

The possible mechanism of the reaction with diorganyl diselenides in a simplified form is shown in Scheme 34 [125]. The reactions proceeded via the 6-endo-dig electrophilic cyclization of 2-alkynyl aryl esters and diorganyl diselenide or ditelluride promoted by Oxone®. The main role of Oxone® is to generate electrophilic species in situ from diorganyl diselenides via the oxidative cleavage of the chalcogen−chalcogen bond. These electrophilic species react with 2-alkynylaryl esters to form selenirenium intermediates followed by an intramolecular nucleophilic attack of the carbonyl group at the selenirenium cation. In the last step, the substitution of the methyl group occurs to produce the target products [125].



Scheme 34. The proposed mechanism for the formation of 4-organylselanyl-1*H*-isochromen-1-ones.

Additionally, taking into account the importance of selenophene derivatives in material sciences and biochemistry, this protocol was used to the synthesis of novel isochromenones condensed to selenophenes via the Oxone®-promoted reaction of methyl 2-(4-phenylbuta-1,3-diyn-1-yl)phenyl ester and methyl 2-(octa-1,3-diyn-1-yl)phenyl ester with diorganyl diselenides (Scheme 35) [120].

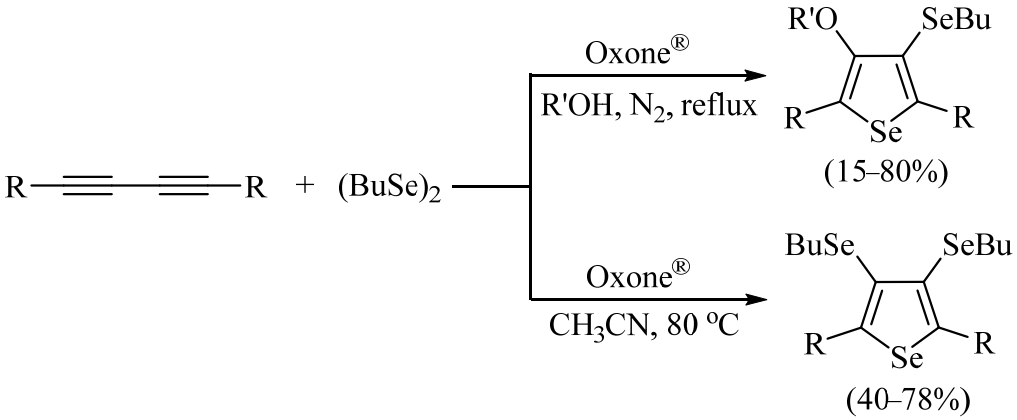


R = Bu, Oct, Ph, 4-ClC$_6$H$_4$, 4-MeC$_6$H$_4$, 4-MeOC$_6$H$_4$,
2-MeC$_6$H$_4$, 2-MeOC$_6$H$_4$, 2-MeO(O)CC$_6$H$_4$, Napht-1-yl;
R' = H, F;
R" = Et, Bu, Oct

Scheme 35. The Oxone®-promoted synthesis of 5*H*-selenopheno [3,2-*c*]isochromen-5-ones from 2-(1,3-diynyl)aryl esters and diorganyl diselenides.

Finally, the synthetic potential of this class of compounds was demonstrated by the example of the synthesis of isochromenethione analogues via the thionation reaction of the products obtained with Lawesson's reagent under microwave irradiation and solvent-free conditions.

Perin, Lenardão, and co-workers developed a transition metal-free method for the synthesis of 3,4-bis(butylselanyl)selenophenes via the electrophilic cyclization of 1,3-diynes with dibutyl diselenide using Oxone® as a green oxidant and acetonitrile as the solvent (Scheme 36) [126].



R = Bu, CH_2OH, Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$,
4-ClC_6H_4, 2-MeC_6H_4, 2-ClC_6H_4, Napht-2-yl;
R' = Me, Et, *i*-Pr, *t*-Bu, Ph

Scheme 36. The Oxone®-promoted synthesis of 3,4-bis(butylselanyl)selenophenes and 3-(butylselanyl)-4-alkoxyselenophenes via the electrophilic cyclization of 1,3-diynes with dibutyl diselenide.

The synthesis of 3-(butylselanyl)-4-alkoxyselenophenes was developed for the first time starting from several 1,3-diynes and dibutyl diselenide (Scheme 36) [126]. The reaction was carried out in the presence of Oxone® using aliphatic alcohols as the solvent and nucleophilic reagents.

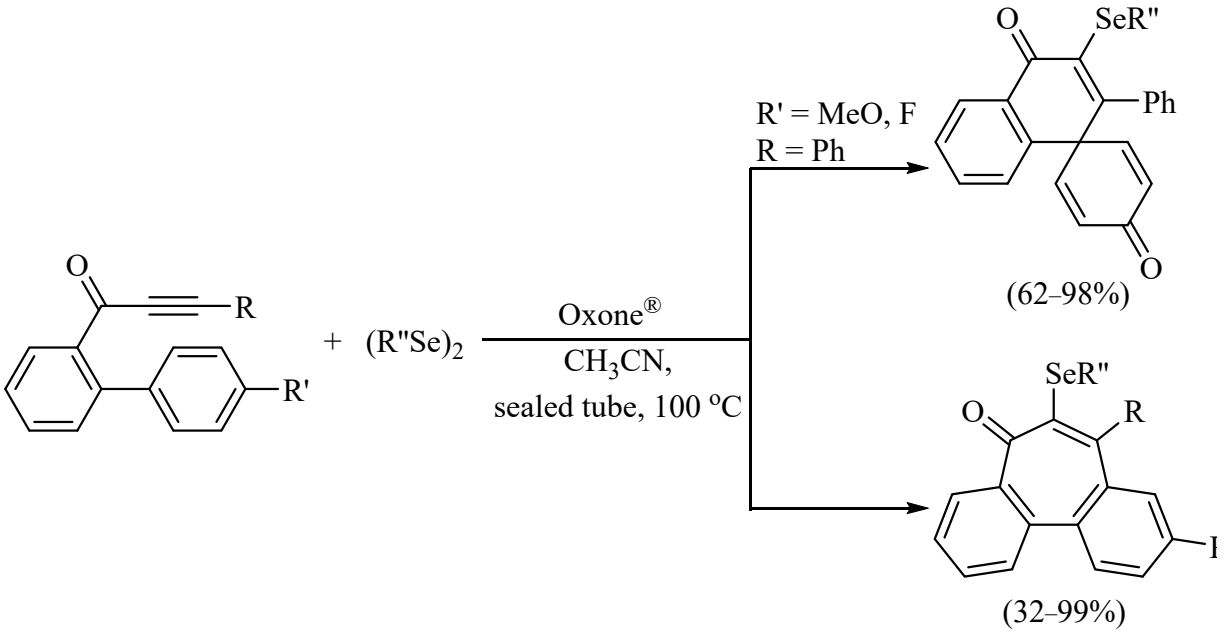
The reaction path included the 5-endo-dig electrophilic cyclization of 1,3-diynes promoted by electrophilic organoselenium species, generated in situ through the oxidative cleavage of the selenium-selenium bond of dibutyl diselenide by Oxone® as a green oxidant. This protocol was found to be sensitive to the electronic effect in the 1,3-diynes, as well as to the steric effects of the alkyl chain of the alcohols [126].

Lenardão, Perin, and co-workers recently reported very promising metal-free methods for the preparation of organylselanyl-functionalized dibenzocycloheptenones and selenospiro [5.5]trienones (Scheme 37) based on the radical cyclization of biaryl ethynyl ketones in the presence of diorganyl diselenides and Oxone® as an oxidizing agent [127].

These reactions were promoted by radical organoselenium species generated in situ from diorganyl dichalcogenides under the action of Oxone®. The processes were carried out in acetonitrile as the solvent in a sealed tube at 100 °C [127].

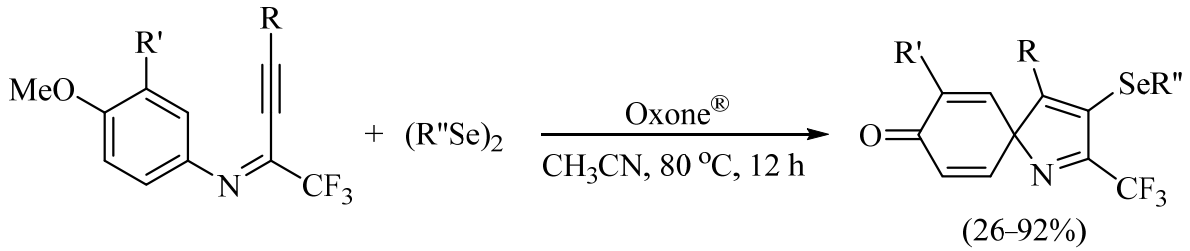
The reactions showed high regioselectivity and made it possible to synthesize 24 products in up to 99% yields. Additional synthetic transformations such as oxidation and reduction reactions were realized [127]. The developed method opened up opportunities to study the chemical and pharmacological properties of these new molecules. The deselenization of the prepared compounds can also lead to compounds with biological activity.

Very interesting regiodivergent syntheses of diversely functionalized azaspiro [4,5]tetraenones (26–92% yields, Scheme 38) and quinolines (38–99% yields, Scheme 39) via the radical cyclization reaction of trifluoromethyl propargyl imines with organic diselenides under the action of Oxone® were recently developed [128]. In the case of the preparation of azaspiro [4,5]tetraenones, the starting substrates contained a strong electron-donating 4-methoxy substituent (Scheme 38).



R = Pent, Ph, 4-ClC_6H_4, 4-MeC_6H_4, 3,5-$(MeO)_2C_6H_3$, $SiMe_3$, SePh;
R' = H, Me, Cl, Br, F;
R" = Bu, Ph, 4-FC_6H_4, 4-ClC_6H_4, 4-$MeOC_6H_4$, 4-MeC_6H_4,
3-$CF_3C_6H_4$, 2-MeC_6H_4, 2-$MeOC_6H_4$, 2-ClC_6H_4

Scheme 37. The Oxone®-promoted synthesis of organylselanyl-functionalized 3,4-bis(butylselanyl) selenophenes and selenospiro [5.5]trienones from biaryl ethynyl ketones and diorganyl diselenides.

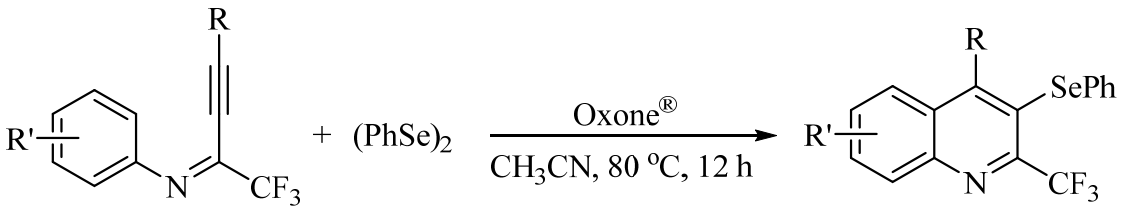


R" = Ph, 4-FC_6H_4, 4-ClC_6H_4, 4-$CF_3OC_6H_4$, 2,4-$Me_2C_6H_3$, Napht-1-yl;
R = Ph, 4-MeC_6H_4, 3-MeC_6H_4, 2-MeC_6H_4, 4-$MeOC_6H_4$, 4-ClC_6H_4, 4-BrC_6H_4,
4-FC_6H_4, 2-ClC_6H_4, Napht-1-yl, cyclopropyl, Hex, SePh;
R' = H, Me, MeO

Scheme 38. The Oxone®-promoted synthesis of functionalized azaspiro [4,5]tetraenones from trifluoromethyl propargyl imines and organic diselenides.

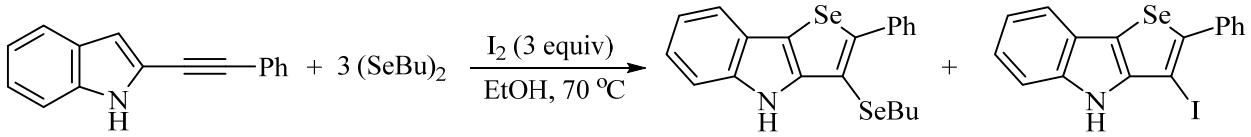
The method provided the dual incorporation of both selenium and trifluoromethyl groups into heterocyclic molecules via a one-pot procedure. The synthetic utility of this method was shown by a scale-up reaction and the further modification of the obtained products [128].

An example of an iodo-promoted reaction is the synthesis of 3-iodo-selenophene-condensed indole and 3-butylseleno-selenonophene-condensed indole from 2-phenylethyny lindole and dibutyl diselenide (Scheme 40). The formation of the former product was achieved via the selenation of the 3-position of indoles, followed by an iodine electrophilic cyclization, whereas the latter product was formed via the selenation of 2-alkynylindole with the subsequent electrophilic cyclization with BuSeI acting as the electrophilic source [93].



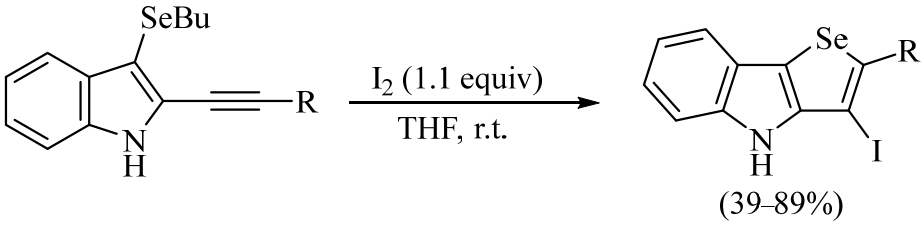
R = Ph, 4-MeOC$_6$H$_4$, 3-EtC$_6$H$_4$, Napht-2-yl, cyclohexen-1-yl, cyclopropyl;
R' = H, 4-Me, 4-*t*Bu, 2-Me

Scheme 39. The Oxone®-promoted synthesis of functionalized quinolines from trifluoromethyl propargyl imines and organic diselenides.



Scheme 40. The iodo-promoted reaction of 2-phenylethynylindole with dibutyl diselenide.

The synthesis of 3-iodo-selenophene-condensed indoles in 39–89% yields via the intramolecular electrophilic cyclization of 3-organoselanyl-2-alkynylindoles was also developed (Scheme 41) [93].



R = Ph, 4-MeC$_6$H$_4$, 3-MeC$_6$H$_4$, 4-MeOC$_6$H$_4$, 2-MeOC$_6$H$_4$, 4-ClC$_6$H$_4$, 2-ClC$_6$H$_4$, Napht-1-yl, Thien-3-yl, Pyridin-3-yl, Bu, Pent, Hex

Scheme 41. The synthesis of 3-iodo-selenophene-condensed indoles from 3-butylselanyl-2-alkynylindoles.

On the basis of the studies undertaken, the authors found the optimal conditions for the preparation of 3-iodochalcogenophene-fused indoles, which include the addition of iodine (I_2, 1.1 equiv) to a solution of 3-butylselanyl-2-alkynylindole (0.25 mmol) in THF at room temperature [93].

This method was extended to the synthesis of 3-iodo-thiophene-condensed indoles in a one-pot procedure consisting of the iodine-promoted thiolation of 2-alkynylindoles, followed by the electrophilic cyclization reaction [93].

Based on the results of additional experiments, a plausible mechanism of the reaction was proposed. The reaction was assumed to proceed through the formation of an iodonium ion, followed by a selenium 5-endo-dig cyclization to lead to the target products [93].

The 3-iodo-selenonophene-condensed indoles obtained were involved as substrates in copper-catalyzed cross-coupling reactions with thiols to produce 3-arylsulfanyl-selenophene-condensed indoles in good yields [93].

3. Conclusions

Significant progress in the synthesis of organoselenium compounds based on the reactions of diorganyl diselenides with acetylenes was achieved in the past few years. A number of remarkable interesting reactions and very promising results in this area have

been developed by Zeni, Lenardão, Perin, Ogawa, Koketsu, and other scientists. Depending on the structures of substrates, the reaction conditions, the substituents in substrates and diselenides, and the nature of heteroatoms, the reactions of organic diselenides with acetylenic compounds can lead to diverse products.

This very promising area of research is based on iron-catalyzed and -promoted reactions, which produce a variety of valuable products. These reactions are simple to run, occur under mild conditions (often at room temperature), and usually have a wide scope. Among the synthetic methods discussed, there are a number of excellent examples of reactions that are carried out under mild and environmentally friendly conditions in a very selective fashion, producing the target products in high yields. Dibutyl diselenide often outperformed diphenyl diselenide in these reactions, producing the products in higher yields.

Examples of efficient reactions proceeding with substrates bearing both electron-donating and electron-withdrawing groups in the aromatic ring were reported [94]; however, in the case of organoselenium propargylamines with electron-withdrawing substituents at the benzene ring, the reaction was sluggish [95]. When this substrate contained a strongly deactivating trifluoromethyl group, the expected product was not obtained.

The studies on reactions with the use of Oxone® have also made great achievements in the last decade. The Oxone®-promoted reactions are very efficient and usually have a wide scope. It is important that iron salts as well as Oxone®, which are used as catalysts or promoters, are readily available reagents.

A very promising reagent is N-fluorobenzenesulfonimide, which plays the role of being both an oxidant and amination reagent. The reactions with this reagent are characterized by mild conditions, selectivity, high yields of the products, and a broad substrate scope [114].

In the future, this area can expect to discover new remarkable reactions and develop novel functionalized and condensed compounds.

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