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Synthesis of vinyl selenides and tellurides: an updated review

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Over the past years organochalcogen compounds have attracted the attention of many research groups due to their powerful chemical and biological activities. Vinyl selenides and tellurides have proved to be useful in organic synthesis as important tools in different reactions. Noteworthy, this important class of compounds has been shown to possess important biological assets, making them promising drug candidates. Herein, we present a comprehensive and updated review on the state of the art of the available methods developed in the last seven years to obtain vinyl selenides and vinyl tellurides. More than 130 articles were accessed, and their contents were critically revised through three main sections, highlighting the metal-free and metal-promoted synthesis of this valuable class of compounds.
The bibliography includes 139 references.

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1. Introduction

The synthesis of organochalcogen compounds is increasingly being explored in organic chemistry, due to their applications in the pharmacological area.[1–7] More specifically, selenium is an essential trace element for human health,[8,9] which participates in several important metabolic pathways[10,11] and it is known to display a wide range of biological activities, such as hepatoprotective,[12] anticancer,[13] neuroprotective,[14] and anti-Alzheimer's disease.[15] In the field of antiviral research, Ebselen has been discovered to be the selenium compound with the most potent inhibitory activity against the main protease of the new coronavirus SARS-CoV-2.[16–18] In addition, chalcogen compounds are important chemical tools in organic synthesis, acting as nucleophiles,[19–22] electrophiles,[23–26] ligands,[27–33] catalysts,[34–39] and in materials science.[40–47]

Different classes of organochalcogen compounds have been prepared and studied, and among them, vinyl chalcogenides are versatile building blocks, applied in Negishi, Sonogashira, and Suzuki cross-coupling reactions,[48–52] in the reaction with Grignard reagents,[53] in the preparation of selenophenes,[54–57] N- and O-heterocycles,[58] among other valuable scaffolds. Furthermore, some vinyl selenides and tellurides exhibit antioxidant,[59–62] antinociceptive,[63,64] hepatoprotective[65,66] and antidepressant activities.[67] Consequently, several synthetic methods for the preparation of these valuable compounds have already been reported in review articles[68–79] and books,[80,81] which were published up to 2014.

Vinyl selenides can be reached through different reactions and from various substrates, such as terminal and internal alkynes and alkynyl selenides, *via* hydro-zirconation, -alumination, -stannation and -boration reactions. Starting from the same substrates, it is possible to obtain vinyl selenides using catalysis with copper, titanium or magnesium compounds, or by the addition of electrophilic or nucleophilic species of selenium. Moreover, alkenes and allenes can be suitable substrates to furnish vinyl selenides using electrophilic, nucleophilic and radical species of selenium. Also, Wittig, Horner and Knoevenagel reactions of carbonyl compounds were used as efficient approaches to the synthesis of a diversity of vinyl selenides.[76,78] Similar strategies were employed to prepare their analogues, vinyl tellurides, including the use of electrophilic, radical, and nucleophilic species of tellurium or elemental tellurium, or by Wittig and Wittig–Horner reactions.[74]

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Current interest of the authors: synthesis of organochalcogen compounds (sulfur, selenium and tellurium) using green protocols: alternative energy sources, green reagents and solvents, catalysis and biomass as feedstock.

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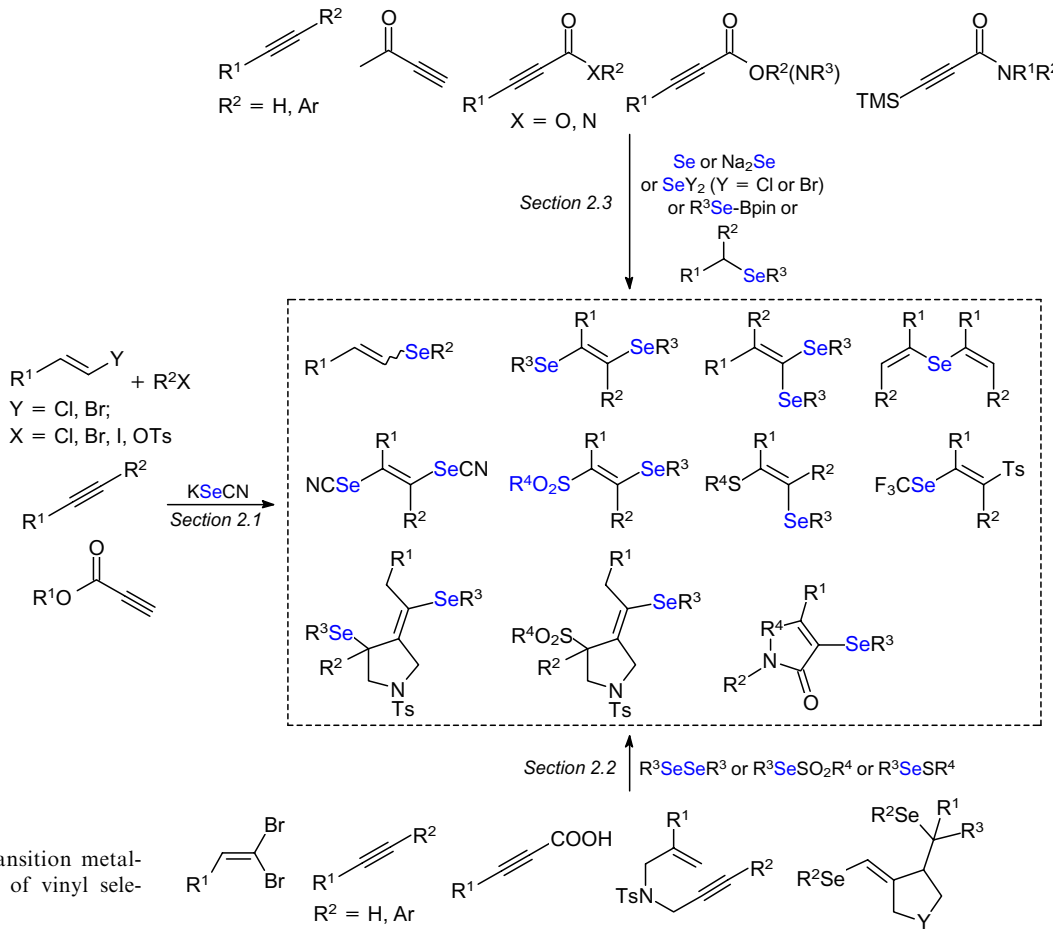


Figure 1. Transition metal-free synthesis of vinyl selenides.

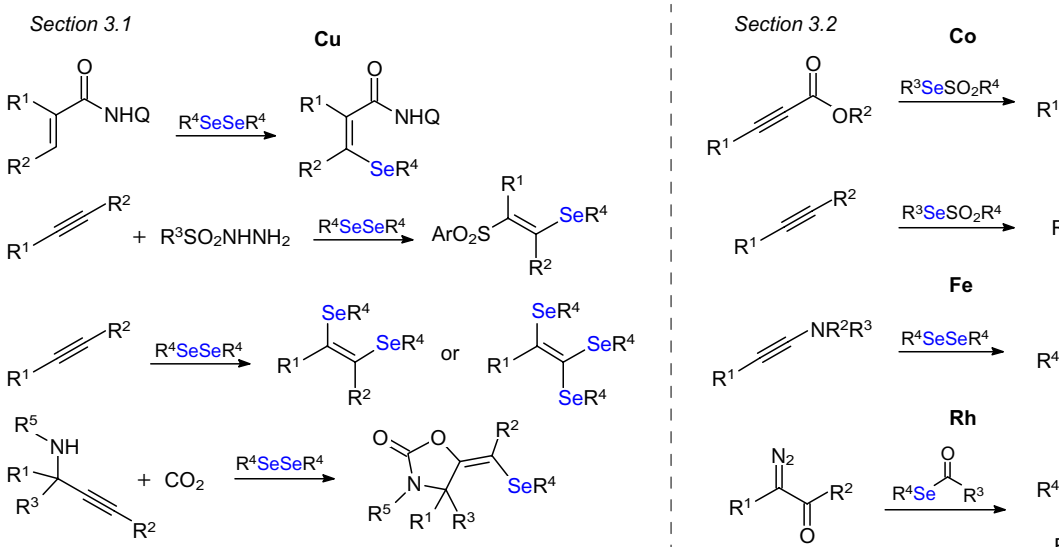


Figure 2. Transition metal-promoted synthesis of vinyl selenides.

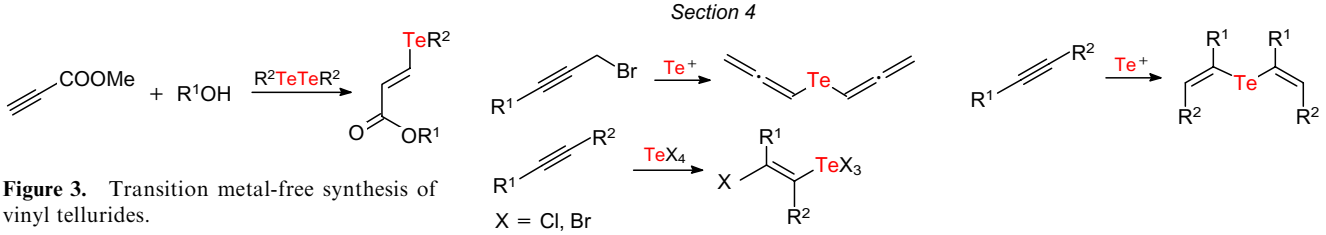


Figure 3. Transition metal-free synthesis of vinyl tellurides.

The present review describes an update of the available procedures for the synthesis of vinyl selenides and tellurides developed since 2015, including photo-induced reactions, discusses the aspects of reactivity and use of vinyl selenides for the preparation of more complex compounds, as well as β-(seleno)vinyl sulfones and cyclic compounds bearing vinyl selenide functionalities. Here, the known synthetic methods to obtain vinyl selenides and tellurides were divided into two main groups: transition metal-free reactions (Figs 1 and 3) and transition metal-catalyzed reactions (Fig. 2). The synthesis of vinyl sulfides will not be covered here, unless the discussed protocol to selenides and tellurides is extended to this class of compounds.

2. Transition metal-free synthesis of vinyl selenides

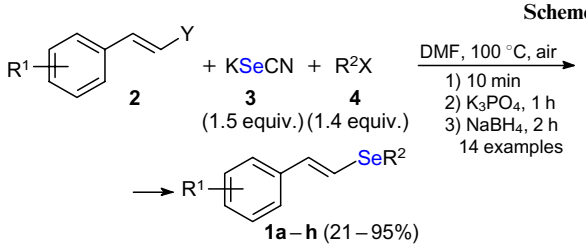
To date, several approaches to the synthesis of vinyl selenides have been established; however, many organic reactions suffer from the use of stoichiometric amounts of toxic reagents, hazardous solvents, and low atom-economic protocols. In this context, during the last seven years, a significant number of research groups have focused their efforts on the development of more sustainable approaches for the synthesis of this class of compounds. Thus, this Section will discuss methods employing safe and low-toxicity reagents, alternative solvents and reaction media, alternative energy sources, and atom-economic reactions. All transition metal-free procedures for the synthesis of vinyl selenides were divided into three main groups, according to the type of selenium species employed.

2.1. Reactions using potassium selenocyanate

This Section describes the synthesis of vinyl selenides from alkynes or vinyl halides using potassium selenocyanate as a source of selenium.

In 2015, Heredia and Peñéñory [82] reported the synthesis of alkyl styryl selenides **1** through a one-pot and three-step strategy, starting from aryl vinyl halides **2**, KSeCN **3** and alkyl halides **4**, in the presence of K_3PO_4 and $NaBH_4$ in DMF (Scheme 1). Besides being free of transition metal and ligand, this protocol uses selenocyanate instead of diselenide or the malodorous and air-sensitive alkyl selenols as starting materials and it proceeds in short reaction time and under air atmosphere. This method involves the *in situ* generation of selenolate anions and a bimolecular nucleophilic substitution between KSeCN **3**, vinyl halide **2** and alkyl halide **4**, affording the corresponding alkyl selenocyanate (RSeCN) in the first reaction step (Scheme 2). In the presence of K_3PO_4, RSeCN is hydrolyzed by traces of water present in DMF to produce the respective alkyl selenolate anion, which immediately attacks the selenium atom of another molecule of RSeCN to give the corresponding dialkyl diselenide. Subsequent reduction with $NaBH_4$ yields the alkyl selenolate anion, which reacts with the substituted (*E*,*Z*)-β-styryl halides **2** to reach the corresponding vinyl selenides **1** with retention of the double bond stereochemistry.

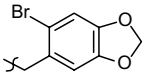
Scheme 1



X = Cl, Br, I, OTs; Y = Cl, Br; R^1 = H, 4-Cl, 4-Me, 4-MeO, 2-MeO; R^2 = Alk, Bn;

R^1 = H:

R^2 = n-Oct (71% for RX = n-OctBr, 83% for RX = n-OctOTs) (**a**); Me, 95% (**b**); $(CH_2)_2CH{=}CH_2$, 71% (**c**);
Bn, 44% (**d**); $CH_2C_6H_4$-F-4, 28% (**e**); $CH_2C_6H_4$-I-2, 25% (**f**); CH_2-Cy, 85% (**g**); Cy, 21% (**h**); Cy is cyclohexyl;

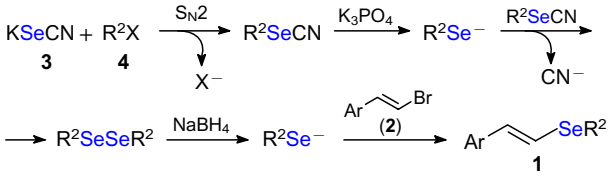


, 21% (**i**); Ph, 84% (**j**-*cis*);

R^2 = n-Oct:

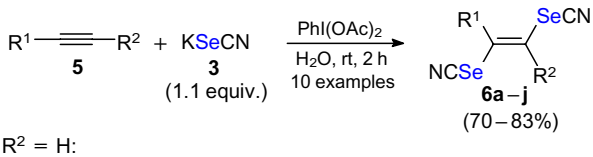
R^1 = 4-Cl, 80% (**k**); 4-Me, 83% (**l**); 4-MeO, 74% (**m**); 2-MeO, 52% (**n**); n-Oct = n-octyl, Bn is benzyl, Ts is tosyl

Scheme 2



In 2018, Lu *et al.*[83] described the $PhI(AcO)_2$-mediated 1,2-diselenocyanation of alkynes **5** with KSeCN **3** to form vinyl diselenocyanate **6** (Scheme 3). The reactions were carried out in the presence of $PhI(AcO)_2$ (1.1 equiv.), KSeCN **3** (1.1 equiv.) using H_2O as a solvent at room temperature. In general, various aromatic alkynes **5** substituted with both electron-donating and -withdrawing groups in the aromatic ring were well tolerated under the optimal conditions, affording products **6a**–**h** in moderate to good yields. Moreover, heterocyclic alkynes, such as 3-ethynylthiophene, and internal alkynes, such as prop-1-ynylbenzene, reacted smoothly to deliver the respective products **6i** and **6j** in 78% and 83% yields, respectively. To summarize, this reaction involves a relatively broad substrate scope, excellent functional group compatibility, mild conditions, cheap and low-toxicity oxidant.

Scheme 3



R^2 = H:

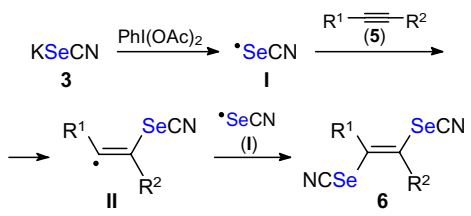
R^1 = Ph, 81% (**a**); C_6H_4Me-4, 78% (**b**); C_6H_4Me-3, 79% (**c**); C_6H_4Me-2, 72% (**d**); C_6H_4OMe-4, 73% (**e**); C_6H_4F-4, 70% (**f**); C_6H_4Cl-4, 72% (**g**); C_6H_4Br-4, 74% (**h**); 2-Th, 78% (**i**);

R^2 = Me: R^1 = Ph, 83% (**j**); Ac = C(O)Me; Th is thienyl

The first step of the reaction mechanism is the formation of the $^{\bullet}$SeCN radical **I**, generated from KSeCN **3** in the presence of $PhI(OAc)_2$ (Scheme 4). Subsequently, the *anti*-Markovnikov addition of radical **I** to alkyne **5** occurs to generate the vinyl radical **II**. Finally, the vinyl radical **II** is trapped by another $^{\bullet}$SeCN radical **I** to give product **6**.

In 2019, Wu *et al.*[84] reported the selenocyanation of alkynes **7** to prepare (*Z*)-vinyl selenolates **8** in the presence of a deep eutectic solvent (DES). The desired products **8** were obtained in high yields under sonication in the deep

Scheme 4



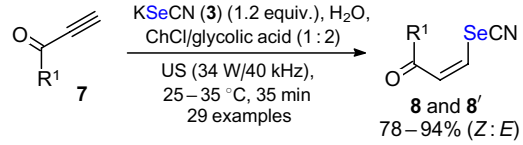
eutectic aqueous solution of choline chloride (ChCl)/glycolic acid (Scheme 5). All investigated substrates **7** were suitable for the reaction, including alkyl-, cycloalkyl- and aryl-substituted compounds, as well as internal propargylic esters containing halogen, alcohol or ether functionalities. Moreover, one-pot selenocyanation followed by reduction and alkylation was performed to give compound **9** in 72% yield (see Scheme 5). Finally, the authors demonstrated that the DES could be recovered and reused five times without loss in its activity.

In the proposed reaction mechanism, intermediate **I**, which is in resonance with species **II**, is first generated through the formation of two hydrogen bonds between substrate **7** and DES. Consequently, intermediate **II** undergoes an attack by the selenocyanate anion to give species **III**. At this point, product **8** is formed due to the capture of a proton by intermediate **III** from the less sterically hindered side (Scheme 6). The proton arises from the ultrasound-promoted self-ionization of H_2O.

Also in 2019, Lu *et al.*[85] described a sustainable protocol for the preparation of various (*Z*)-3-selenocyanatoacrylates **8** through the selenocyanation of activated alkynes **7** using lactic acid as both a reusable catalyst and the reaction medium (Scheme 7). The substrate scope of lactic acid-catalyzed selenocyanation reactions was extended to several terminal and internal alkynoates **7**, such as those based on bioactive natural alcohols (piperonyl, and cinnamyl alcohols), and also ynone, propargylic thioesters, affording twenty-two (*Z*)-β-vinyl selenolates **8** in excellent yields. The principal advantage of this protocol is that it can completely avoid the use of organic volatile compounds. Moreover, the conversion of substrate **7** is almost quantitative with a minimal amount of lactic acid used as the

Scheme 5

a



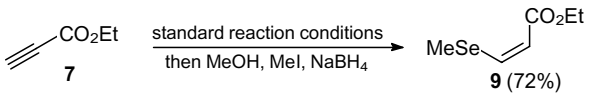
R = Alk, Ar, Het, sesamol derivative, perillyl derivative, vit E derivative; R^1 = H, Me, Br, CF_3, CO_2Et; ChCl is choline chloride

Selected examples

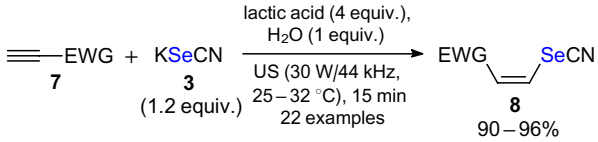
R^1 = OBn, 93% (27 : 1) (**8a** : **8a′**); Ph, 78% (26 : 1) (**8b** : **8b′**); OMe, 94% (32 : 1) (**8c** : **8c′**); SBn, 84% (18 : 1) (**8d** : **8d′**)



b

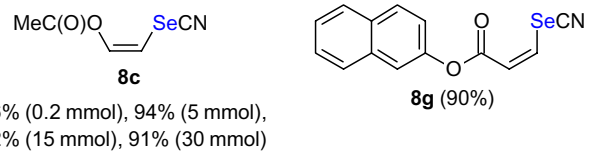


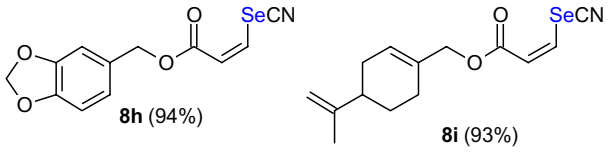
Scheme 7

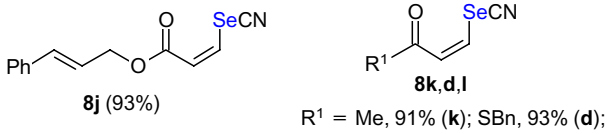


EWG = CO_2R^1, Ac, $C(O)SR^1$, SO_2R^1

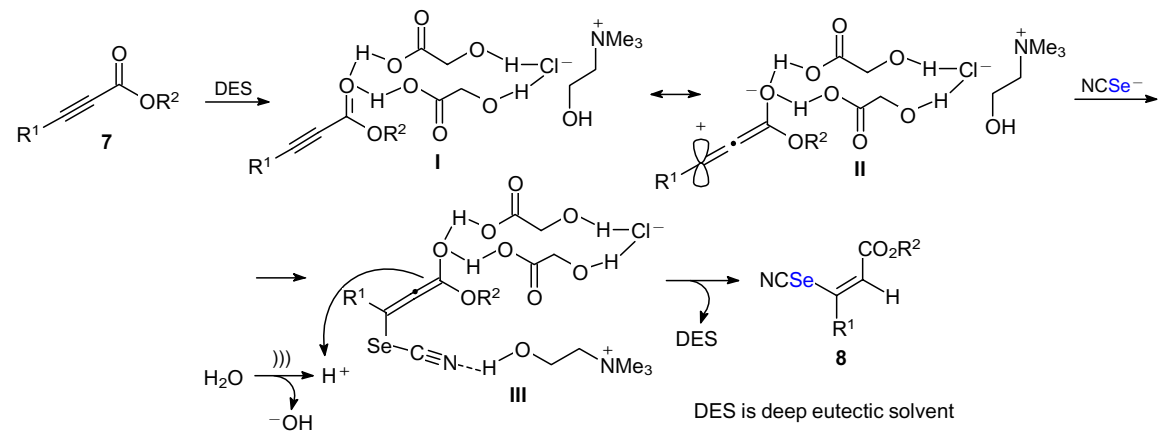
Selected examples







Scheme 6



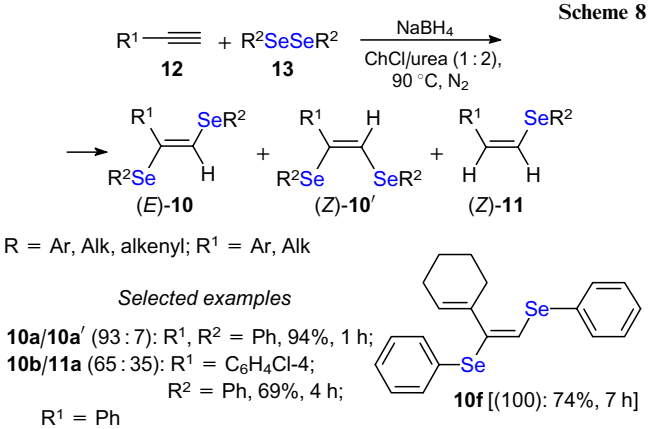
reaction medium. Additionally, the insolubility of selenocyanation products **8** in lactic acid allowed their facile isolation by simple extraction without traditional silica gel chromatographic purification. In the case of scaled up (5 mmol) preparations, pure products **8** were obtained using the water precipitation method. To further demonstrate the utility of this reaction, the selenocyanation of ethyl propiolate **7** was carried out in 15 mmol and 30 mmol scales, giving (*Z*)-ethyl 3-selenocyanatoacrylate **8c** in 92% and 91% yields, respectively.

2.2. Reactions using diorganyl diselenides

In this Section, the synthesis of vinyl selenides through the addition of different nucleophilic, electrophilic or radical selenium species to alkynes will be considered. The selenium reactive species were generated *in situ* from diorganyl diselenides and sodium borohydride or hypophosphorous acid, or diorganyl diselenides and *N*-fluorobenzenesulfonimide (NFSI), sulfonyl hydrazides or SelectFluor, benzoyl peroxide (BPO), *tert*-butyl hydroperoxide (TBHP) or di-*tert*-butyl peroxide (DTBP), and by a photocatalytic reaction of diorganyl diselenides or selenosulfonates.

In 2015, our research team [86] developed a procedure to prepare 1,2-bis-organylselenoalkenes **10** from terminal alkynes **12** and diaryl or dibutyl diselenides **13** in the presence of $NaBH_4$, and ChCl/urea 1 : 2 as a deep eutectic solvent (Scheme 8). The reaction optimization study revealed the possibility of obtaining three products: (*E*)-1,2-bis-organylselenoalkenes **10**, the *Z*-isomer **10′** and mono-selenide **11**. Several alkynes **12** and diselenides **13** were used under the optimal conditions, and the results showed that the DES–$NaBH_4$ system can be successfully used to produce selectively (*E*)-1,2-bis-organylselenoalkenes **10** in most cases. This reaction system allows the use of alkyl and alkenyl monosubstituted alkynes in a very efficient way, which is not possible for other so-called green solvents.

Scheme 8



R = Ar, Alk, alkenyl; R^1 = Ar, Alk

Selected examples

10a/10a′ (93 : 7): R^1, R^2 = Ph, 94%, 1 h;
10b/11a (65 : 35): R^1 = C_6H_4Cl-4;
R^2 = Ph, 69%, 4 h;
R^1 = Ph
10c/11b (67 : 33): R^2 = $C_6H_4CF_3$-3, 79%, 3 h;
10d/10b′ (59 : 41): R^2 = C_6H_4Me-4, 74%, 2 h;
10e/11c (82 : 18): R^2 = Bu^n, 82%, 2 h

10f [(100): 74%, 7 h]

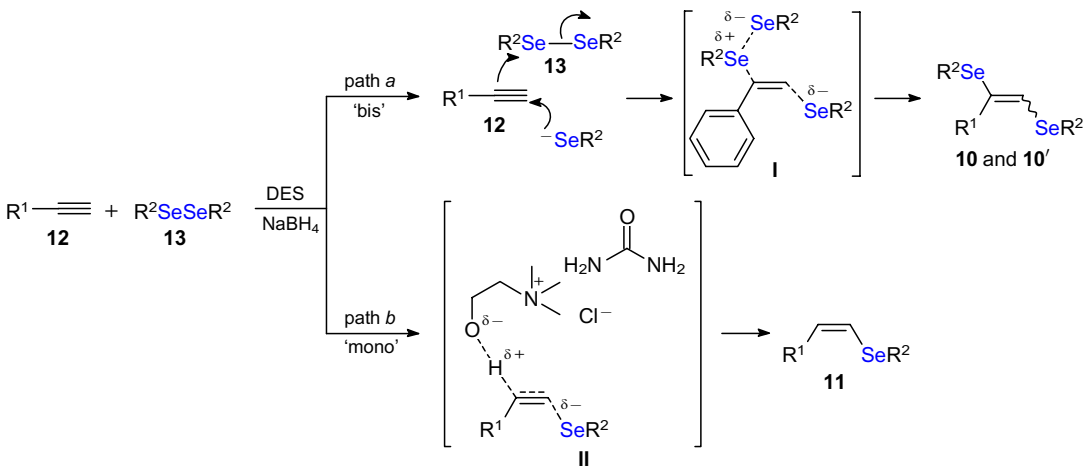
In a follow-up study,[87] we published a method for the synthesis of new vinyl selenides **14** and vinyl telluride **15**, starting from the previously prepared diselenide **16** and ditelluride **17**. To obtain the chalcogen-alkenes **14** and **15**, the reaction was carried out in PEG-400, in the presence of $NaBH_4$ at 30 °C under nitrogen atmosphere (Scheme 10). Initially, the starting materials **16** and **17** were synthesized from glycerol, and then they were allowed to react with alkynes **12**. A wide range of substrates **12** were investigated, such as electron-rich and electron-poor aryl-substituted and aliphatic alkynes, and all of them were well tolerated in the formation of vinyl selenides **14**. Limitations were only found in the reaction using 4-ethynyltoluene and ditelluride **17**, which produced a complex inseparable mixture of products. The aliphatic 1-hexyne did not react under the optimal conditions, even after 48 h. Noteworthy, alkyne bearing the strong electron-withdrawing trifluoromethyl group in the aromatic moiety afforded vinyl selenide **14d** in excellent yield (see Scheme 10).

Moreover, the new water-soluble vinyl selenide **18** was obtained in 78% yield after the deprotection of **14c**, using acidic cation exchange resin Dowex-(H^+) in methanol (Scheme 11).

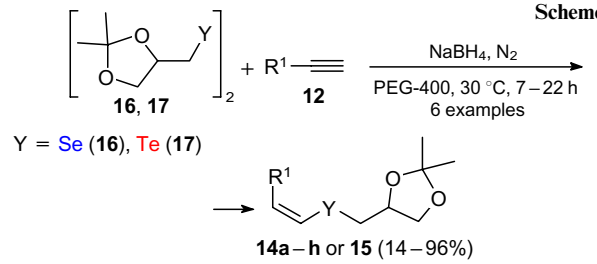
Concerning the mechanism, the authors suggested the reaction to occur *via* the transition state **I**, formed from alkynyl and chalcogenolate, which evolves to the desired products **14** (Scheme 12).

Also, a procedure for the regioselective preparation of (*E*)-1-bromo-1-arylselanoalkenes **19** and ketene selenoace-

Scheme 9

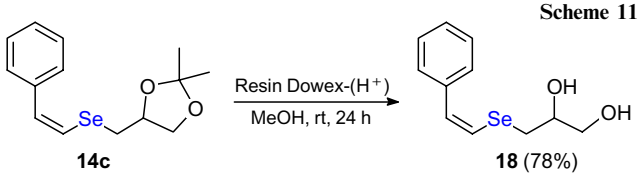


Scheme 10

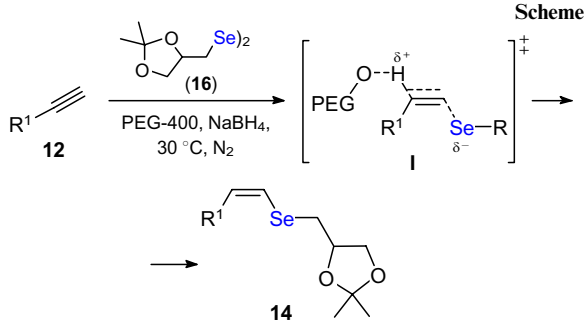


Y = Se:
14a: R^1 = C_6H_4Me-4; 14 h, complex mixture of products;
14b: R^1 = Bu^n, NR, 14 h;
14c: R^1 = Ph, 80%, 7 h;
14d: R^1 = $C_6H_4CF_3$-4, 96%, 14 h;
14e: R^1 = C_6H_4CN-4, 80%, 7 h;
14f: R^1 = C_6H_4OMe-4, 14%, 22 h;
14g: R^1 = C_6H_4F-4, 32%, 22 h;
14h: R^1 = C_6H_4Me-2, 52%, 14 h;
Y = Te:
15: R^1 = Ph, 20 h, complex mixture of products

Scheme 11

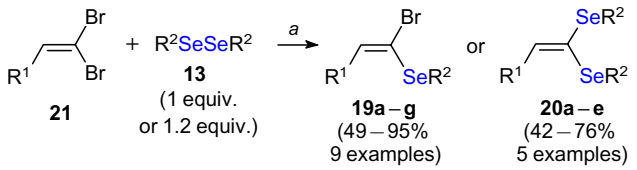


Scheme 12



tals **20** using diaryl diselenides **13** and1,1-dibromoalkenes **21** in PEG-400 was developed (Scheme 13).[88] It was shown that the selenation of 1,1-dibromoalkene **21** providing the selective formation of products **19** or **20** can be easily

Scheme 13



(*a*) $NaBH_4$, PEG-400, Ar, temperature; R = Ar, Het; R^1 = Ar

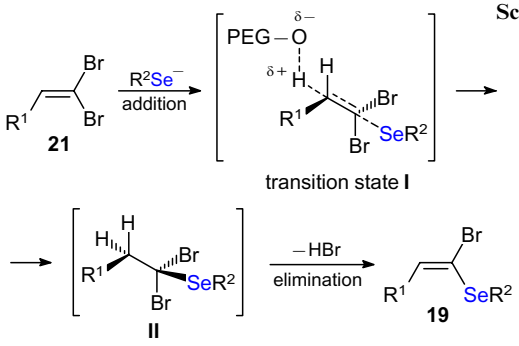
Selected examples

19: R^2 = Ph:
R^1 = C_6H_4Cl-4, 94%, 0.5 h (**a**); C_6H_4OMe-4, 49%, 2 h (**b**); C_6H_4Cl-2, 95%, 0.5 h (**c**); Ph, 88%, 0.5 h (**d**);
R^1 = Ph:
R^2 = C_6H_4F-4, 87%, 0.5 h (**e**); C_6H_4OMe-4, 65%, 1 h (**f**);
R^1 = 2-Fu, R^2 = Ph, 58%, 2 h (**g**); Fu is furyl
20: R^2 = Ph:
R^1 = C_6H_4Cl-4, 61%, 1 h (**a**); C_6H_4Me-4, 65%, 2 h (**b**);
R^1 = Ph:
R^2 = C_6H_4F-4, 42%, 1 h (**c**); C_6H_4OMe-4, 55%, 1 h (**d**);
R^1 = R^2 = Ph, 76%, 1 h (**e**)

controlled by varying the reaction conditions, the amount of diaryl diselenide **13** (1 equiv. to obtain products **19** or 1.2 equiv. for products **20**) and adjusting temperature (50 °C for products **19** or 120 °C for products **20**). A variety of electron-rich and electron-deficient 1,1-dibromoalkenes **21** and diaryl diselenides **13** were efficiently used and selectively converted to the corresponding products in good yields and in short reaction times (see Scheme 13). However, in this study, the efficacy of the method was not tested with dialkyl- and diheteroaryl diselenides.

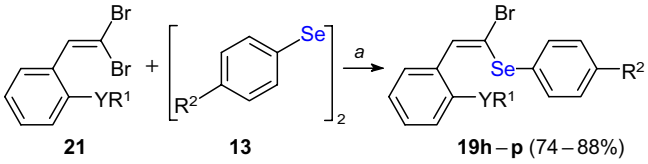
The proposed reaction mechanism starts with the addition of the arylselenolate to the double bond of 1,1-dibromoalkenes **21** *via* PEG-stabilized transition state **I**, which is responsible for the formation of saturated intermediate **II**. Then, elimination of HBr, through an *anti*-periplanar conformation, affords product **19** (Scheme 14).

Scheme 14



In another study developed in 2019, we reported the synthesis of (*E*)-1-bromo-1- arylselenoalkenes **19**, using the reaction of 1-(2,2-dibromovinyl)-2-chalcogenylbenzenes **21** with diaryl diselenides **13** in the presence of $NaBH_4$ as a reducing agent and PEG-400 as a solvent (Scheme 15).[89] The reaction scope was studied for substituted diaryl diselenides **13** and 1-(2,2-dibromovinyl)-2-chalcogenylbenzenes **21** to afford the desired products **19** with high regioselectivity (>99% of *E*-isomer) and in good yields. However, dialkyl- and diheteroaryl diselenides were not evaluated as substrates.

Scheme 15

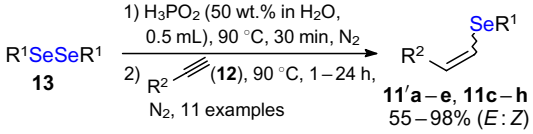


(*a*) $NaBH_4$, PEG-400, Ar, rt to 50 °C, 1 h, 9 examples;
YR^1 = $SeBu^n$: R^2 = H, 88% (**h**); Me, 74% (**i**); F, 80% (**j**);
YR^1 = OMe: R^2 = H, 78% (**k**); Me, 76% (**l**); F, 84% (**m**);
YR^1 = SPr^n: R^2 = H, 85% (**n**); Me, 76% (**o**); F, 78% (**p**)

In 2016, the synthesis of mono-**11**, **11′** or bis-selanyl alkenes **10**, **10′** starting from diorganyl diselenides **13** and terminal alkynes **12** was described (Scheme 16).[90] Products **11** and **11′** were obtained in good to excellent yields and predominantly with *Z*-configuration (**11**), using 2 equiv. of terminal alkynes **12**, in the presence of an excess of H_3PO_2 (50 wt.% in H_2O) as reducing agent for the Se–Se bond, within 1–24 h at 90 °C under nitrogen atmosphere (see Scheme 16 *a*).

a

Scheme 16

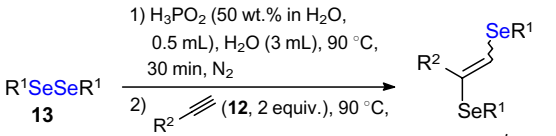


R^1 = Ar; R^2 = Ar, Alk

Selected examples

R^2 = Ph:
11a′ + **11d** (10 : 90): R^1 = Ph, 80%, 1 h;
11b′ + **11c**: R^1 = Bu^n, traces, 24 h;
11c′ + **11e** (25 : 75): R^1 = $C_6H_2Me_3$-2,4,6, 98%, 1 h;
R^1 = Ph:
11d′ + **11f** (20 : 80): R^2 = C_6H_4Me-4, 55%, 1 h;
11e′ + **11g** (20 : 80): R^2 = n-C_5H_{11}, 65%, 2 h;
11h (**11f′**/**11g** = 0 : 100): R^2 = C_6H_4Me-2, 55%, 2 h;

b



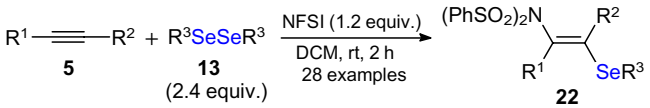
10a + **10a′** (85 : 10): R^1 = R^2 = Ph, 96%, 3 h;
10b + **10c′** (95 : 5): R^1 = Ph, R^2 = C_6H_4Cl-4, 90%, 3.5 h;
10d + **10b′** (86 : 14): R^1 = C_6H_4Me-4, R^2 = Ph, 93%, 3 h;
10g (**10g**/**10d′** = 100 : 0): R^1 = C_6H_4Cl-4, R^2 = Ph, 56%, 5 h;
10h + **10e′** (10 : 90): R^1 = Ph, R^2 = n-C_5H_{11}, 74%, 24 h;
10i + **10f′** (90 : 10): R^1 = Ph, R^2 = C_6H_4Me-4, 91%, 3.5 h

On the other hand, compounds **10** and **10′** were obtained in similar yields, but preferentially in *E*-configuration (**10**), using only 1 equiv. of terminal alkynes **12**, in the presence of H_2O as a solvent within 3–24 h, with other reaction conditions being the same (see Scheme 16 *b*). Moreover, the system $H_2O-H_3PO_2$ could be recovered and reused in four subsequent cycles without decreasing the yields and efficiency. The reaction started with *in situ* generation of organyl selenol (30 min, 90 °C under nitrogen atmosphere), and then alkyne **12** was added. Various diorganyl diselenides **13** and alkynes **12** were employed to produce compounds **11** and **11′** in good yields, except for dibutyl diselenide, which was unreactive. This reaction well tolerated all investigated diselenides **13** and alkynes **12** (see Scheme 16 *b*).

Zheng *et al.*[91] reported the first protocol of intramolecular selenoamination of alkynes **5** with NFSI and diorganyl diselenides **13** to prepare seleno enamides **22**. The reaction proceeds under very mild conditions and affords products **22** with high regio- and stereoselectivities (Scheme 17). A series of arylalkynes **5** bearing electron-donating, electron-withdrawing and sterically hindered substituents were investigated, and all of them proved to be suitable substrates in this reaction. Additionally, dibenzyl diselenide **13** was successfully used to give the respective product **22a** in 74% yield, while 3-fluoro-derivative of NFSI afforded vinyl selenide **22b** in 72% yield (see Scheme 17).

Based on several control experiments, a mechanism was proposed, as depicted in Scheme 18. The amination of arylalkynes **5** occurs on the benzylic carbon atom of the arylalkynes, while for aliphatic compounds, the terminal carbon is involved.

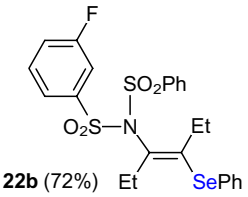
Scheme 17



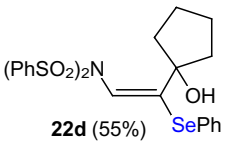
R^1 = H, Ar, Alk, Het; R^2 = H, Alk, Ar;
R^3 = Ph, Bn; NFSI = $FN(SO_2Ph)_2$; DCM = CH_2Cl_2

Selected examples

22: R^1 = R^2 = Et, R^3 = Bn, 74% (**a**);
R^1 = C_6H_4OTs-4, R^2 = Bu^n, R^3 = Ph, 92% (**c**);
R^1 = R^2 = Et, R^3 = Ph, 85% (**e**);
R^1 = Ph, R^2 = Pr^n, R^3 = Ph, 75% (**f**)

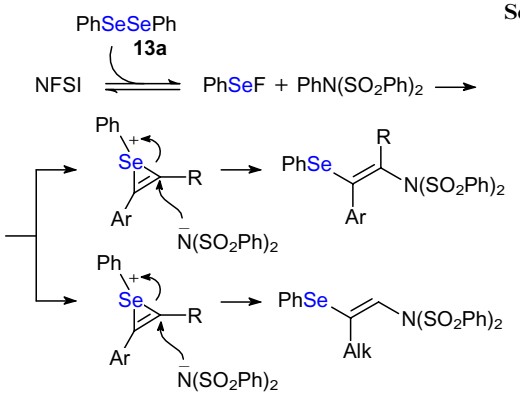


22b (72%)



22d (55%)

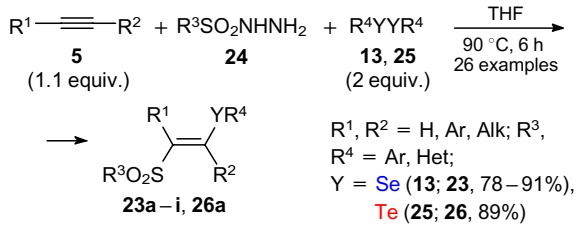
Scheme 18



In 2017, Sun *et al.*[92] described the preparation of β-(seleno)vinyl sulfones **23** through the 1,2-selenosulfonylation of alkynes **5** *via* a cationic species formed *in situ* by the reaction between benzenesulfonyl hydrazides **24** and diorganyl diselenides **13** (Scheme 19). This reaction avoids the need for the pre-prepared Se–S reagents; it was satisfactorily applied to a series of aromatic and aliphatic alkynes **5**, benzenesulfonyl hydrazides bearing both electron-withdrawing and electron-donating substituents **24**, diaryl and diheteroaryl diselenides **13** to afford a total of 25 vinyl selenides **23** in good yields with high regio- and stereoselectivity under metal-free conditions. The advantages of this process include a broad substrate scope, excellent functional group tolerance, the use of readily available reagents and amenability to the gram-scale synthesis. However, a limitation of this methodology is the use of high temperatures. Importantly, the scope of this reaction was expanded to diphenyl ditelluride **25a**, which efficiently reacted to afford β-[(phenylsulfonyl)vinyl]tellane **26a** in 89% yield (see Scheme 19).

Based on control experiments, a plausible reaction mechanism was proposed, which starts with the reaction of the benzenesulfonyl hydrazide **24** with diaryl diselenide **13** to give Se-aryl arylsulfonyl selenoate **I** as the active species (Scheme 20). The subsequent electrophilic attack of the phenylselenyl cation, arising from the heterolysis of **I**, on the alkyne **5**, furnishes the seleniranium cation **II**. Finally,

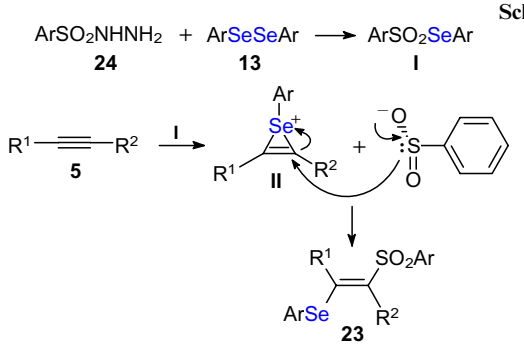
Scheme 19



Selected examples

23: R^1 = H, R^3 = Ts, R^4 = Ph:
R^2 = C_6H_4F-2, 91% (**a**), $C_6H_4CF_3$-4, 90% (**b**), C_6H_4Me-4, 88% (**c**);
R^1 = Bu^n, R^2 = Ph, R^3 = Ts, R^4 = Ph, 85% (**d**);
R^1 = H, R^2 = R^4 = Ph:
R^3 = C_6H_4Br-4, 78% (**e**);
R^3 = C_6H_4F-4, 78% (**f**);
R^3 = C_6H_4OMe-4, 80% (**g**);
R^1 = H, R^3 = Ts:
R^2 = Ph, R^4 = $C_6H_4CF_3$-4, 89% (**h**),
R^2 = H, R^4 = 2-Th, 79% (**i**);
26a: R^1 = H, R^2 = R^4 = Ph, R^3 = Ts, 89%

Scheme 20



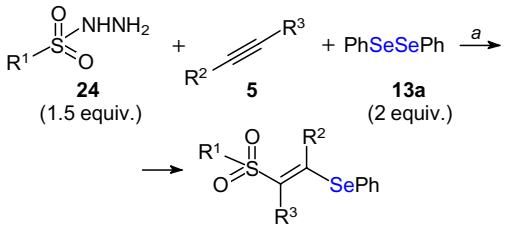
the S_N2 reaction of the benzenesulfonyl anion with **I** generates the *anti*-Markovnikov *trans*-1,2-selenosulfonylation product **23**.

In 2020, Kong *et al.*[93] reported a protocol to prepare β-(seleno)vinyl sulfones **23** through a metal-free electrochemical oxidative selenosulfonylation of alkynes **5** using diphenyl diselenide **13a** and sulfonyl hydrazides **24**. The electrochemical cell parameters included: C anode, Pt cathode, (both $10 \times 10 \times 0.2$ mm), constant current = 12 mA (3.7 F mol^{-1}) (Scheme 21). The products **23** were obtained in moderate to good yields. A wide range of diversely substituted alkynes **5** and various sulfonyl hydrazides **24** were employed, with good results in all the cases. Interestingly, when alkenes were tested as substrates under air atmosphere, the resulting products were β-ketosulfones.

The reaction mechanism involves, first, the formation of the sulfonyl radical **I** through the electrooxidation of alkyne **5**. Then **I** reacts with **5** to give intermediate **II**, which undergoes an atom transfer to afford product **23** (Scheme 22, path *a*). Alternatively, species **III**, derived from diselenide **13a**, can split into radical **IV** and cation **V**. Then, species **IV** adds to **II** to form product **23** (Scheme 22, path *b*).

In 2021, Ban *et al.*[94] developed the selenenylation/rearrangement of propargyl alcohols **5** promoted by the SelectFluor/RSeSeR system to obtain multisubstituted α-selenoenals and selenoenones **27** (Scheme 23). The main characteristics of this reaction are an atom-economical approach, mild and broadly applicable protocol using readily accessible substrates, and good *Z*/*E*-selectivity. Several substituted diorganyl diselenides **13** and internal or terminal propargyl alcohols **5** were employed, affording the desired products **27** in poor to excellent yields.

Scheme 21

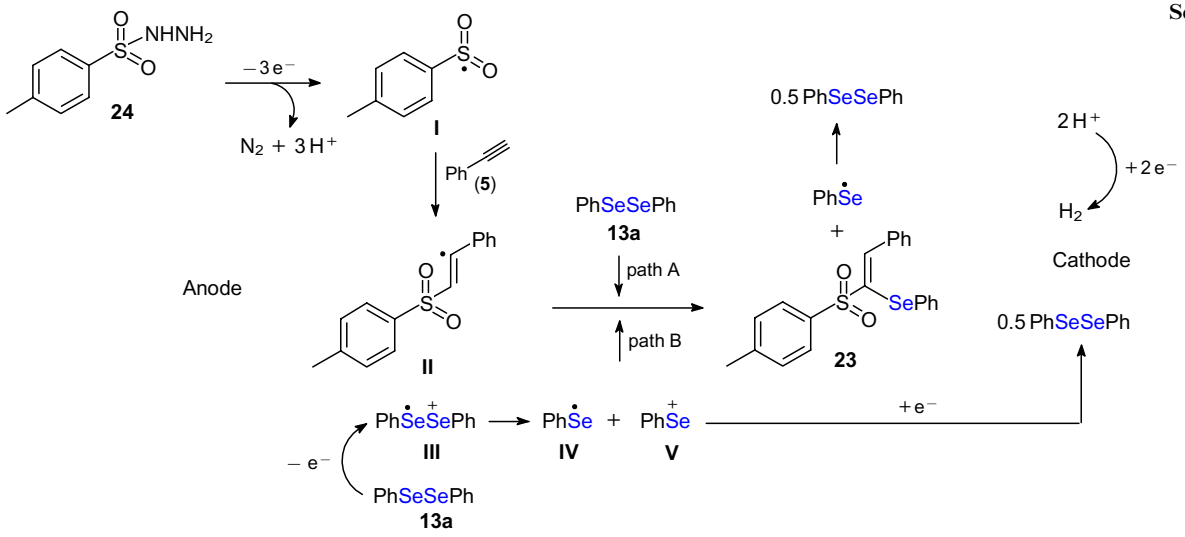


(*a*) C(+)–Pt(−), *I* = 12 mA, $Bu^n_4NBF_4$, rt, 4 h, MeCN, N_2, 34 examples;
R^1 = Ar, Alk, Het; R^2 = aryl, alkyl; R^3 = H, Ar, Alk

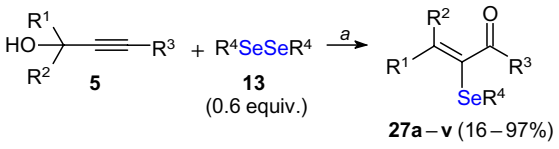
Selected examples

23: R^1 = C_6H_4Me-4, R^3 = H:
R^2 = Ph, 81% (**j**); $(CH_2)_3$Cl, 64% (**k**); C_6H_4OMe-3, 88% (**l**);
2-Naph, 77% (**m**);
R^2 = Ph, R^3 = H:
R^1 = $C_6H_2Me_3$-2,4,6, 45% (**n**); 2-Naph, 85% (**o**); Naph is naphthyl

Scheme 22

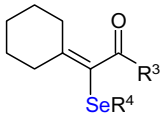


Scheme 23

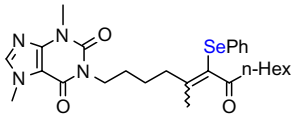


(*a*) SelectFluor (0.6 equiv.), MeCN, rt, 12 h, 45 examples;
R^1 = Alk, Ar; R^2 = H, Alk, Ar; R^3 = H, Alk, Ar, Het; R^4 = Alk, Ar

Selected examples



27: R^3 = Me:
R^4 = Ph, 94% (**a**);
C_6H_4OMe-4, 72% (**b**);
C_6H_4CN-4, 41% (**c**);
Bn, 78% (**d**); Me, 72% (**e**);
Cy, 81% (**f**);
R^4 = Ph:
R^3 = Bu^n, 82% (**k**);
C_6H_4CN-4, 81% (**l**);
2-Th, 85% (**m**);



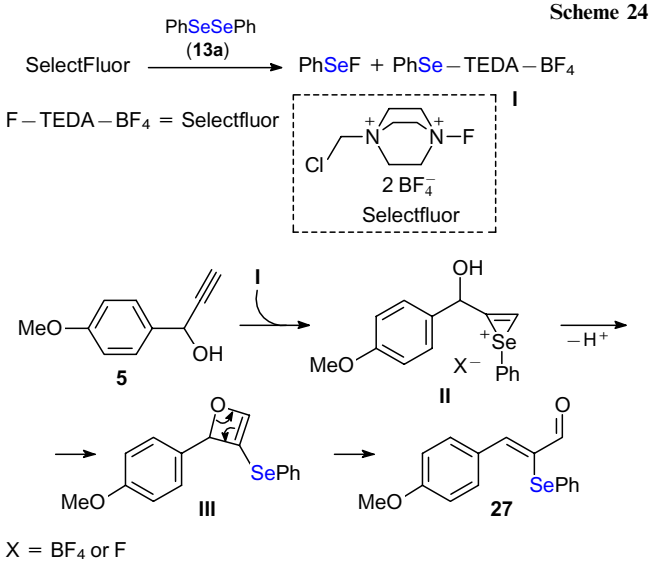
27j: 95% (*Z*/*E* = 1 : 1)

R^3 = R^4 = Ph:
R^1 = Bu^n,
R^2 = H, 80% (*Z*/*E* > 20 : 1) (**g**);
R^1 = Me,
R^2 = Et, 75% (*Z*/*E* = 1 : 1) (**h**);
R^1 = Me,
R^2 = Ph, 86% (*Z*/*E* = 2.6 : 1) (**i**);
R^2 = R^3 = H, R^4 = Ph:
R^1 = Ph, 64% (*Z*/*E* > 20 : 1) (**n**);
C_6H_4OH-4, 97% (*Z*/*E* > 20 : 1) (**o**);
$C_6H_4NO_2$-4, 16% (*Z*/*E* = 3.5 : 1) (**p**);
2-Naph, 60% (*Z*/*E* > 20 : 1) (**q**);
Me, 83% (*Z*/*E* > 20 : 1) (**r**);
R^1 = R^4 = Ph, R^3 = H:
R^2 = Me, 73% (*Z*/*E* = 4.2 : 1) (**s**);
cyclo-C_3H_5, 81% (*Z*/*E* > 20 : 1) (**t**);
Ph, 77% (**u**);
R^1 = R^2 = Me, R^3 = H,
R^4 = Ph, 88% (**v**)

The proposed mechanism for the selenofunctionalization/Meyer–Schuster type rearrangement of propargyl alcohols is outlined in Scheme 24. First, diphenyl diselenide **13a** is oxidized by Selectfluor to give the electrophilic C_6H_5SeX species **I** and PhSeF. Subsequently, the electrophilic attack of $C_6H_5Se^+$ across the triple bond of propargyl alcohols **5** generates intermediate **II**, which instantly undergoes an intramolecular attack by oxygen to form oxetene **III**, which is spontaneously converted into product **27**.

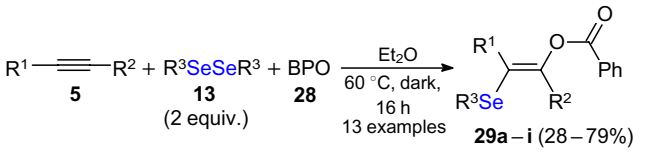
In 2017, Kodama *et al.*[95] reported the benzoyloxyselenation of internal alkynes **5** using the binary system of benzoyl peroxide **28** and diorganyl diselenides **13** to prepare

Scheme 24



X = BF_4 or F

Scheme 25

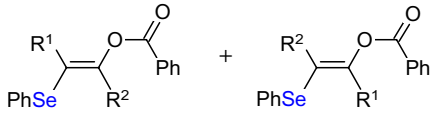


R^1, R^2, R^3 = Alk, Ar; BPO = $[PhC(O)O]_2$

Selected examples

29: R^3 = Ph:
R^1 = R^2 = Pr^n, 79% (**a**);
Ph, 64% (**b**);
CH_2OMe, 60% (**c**); Cl, 48% (**d**);
OH, NR (**e**);
R^1 = R^2 = CO_2Me, R^3 = Ph, NR (**f**);
NR is not recorded

R^1 = R^2 = Pr^n:
R^3 = C_6H_4OMe-4, 57% (**j**);
$C_6H_4CF_3$-4, 44% (**k**);
Bu^n, 68% (**l**);
R^2 = Me:
R^1 = Bu^t, 28% (**j**);
n-C_5H_{11}, 61% (56 : 44) (**h**);
$(CH_2)_3Ph$, 70% (55 : 45) (**i**)

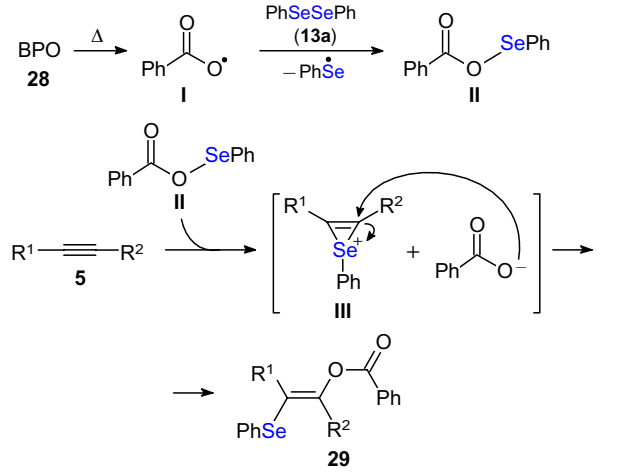


the corresponding β-(benzoyloxy)alkenyl selenides **29** (Scheme 25). The reactions were performed under air in the absence of light to provide a total of thirteen functionalized vinyl selenides **29** in good yields and with excellent regio- and stereoselectivities. The substrate scope included alkynes **5** bearing alkyl, aryl, methoxy or chlorosubstituents, which successfully afforded the corresponding β-benzoyloxy-substituted alkenyl selenides **29a**–**d** in good yields and with excellent *E*-stereoselectivity. Unfortunately, propargyl alcohol and acetylenedicarboxylate were unsuitable substrates in this reaction. Under the optimal conditions, 4,4-dimethylpent-2-yne was converted into the corresponding product **29g** in as low as 28% yield. Moreover, the unsymmetrical alkynes oct-2-yne and 6-phenylhex-2-yne provided the corresponding *trans* adducts **29h**,**i** and their regioisomers in good yields. Diaryl and dialkyl diselenides **13** were suitable substrates, giving products **29j**–**l** in acceptable yields (44–68%).

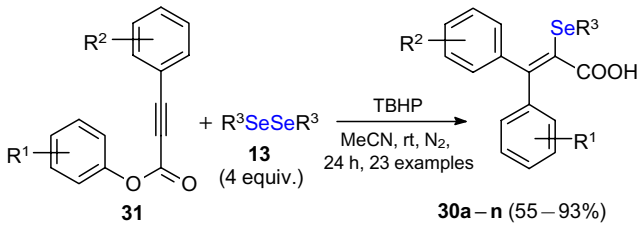
Using ^{77}Se NMR, the authors identified the generation of Se-based electrophilic species *in situ*, which are the key intermediates in this *anti*-addition reaction. The probable mechanism involves a thermal decomposition of BPO producing the benzoyloxy radical **I**, which reacts with diphenyl diselenide **13a** to yield the Se-based electrophile benzoyloxy selenide **II**. The subsequent benzoyloxyselenation reaction may then proceed *via* an ionic mechanism by the addition of the phenylselenenyl ion ($C_6H_5Se^+$) to alkyne **5**, leading to the *epi*-seleniranium ion **III**, which undergoes a nucleophilic attack of the benzoate anion on the opposite side to the selenium ion to reach *trans* adduct **29** (Scheme 26).

In 2018, Sahoo *et al.*[96] reported the synthesis of selenium-containing α,β-unsaturated acids **30** (Scheme 27). Through an optimization study, the best reaction conditions were to react aryl alkynoates **31** with diaryl diselenides **13** (2 equiv.) in the presence of *tert*-butyl hydroperoxide as an oxidant, at room temperature in acetonitrile. The protocol is operationally simple, scalable, displays a broad substrate scope, and overcomes the usual CO_2 exclusion phenomenon. This methodology was satisfactorily applied to a wide range of aryl alkynoates **31** and diaryl diselenides **13**, affording tetrasubstituted α,β-unsaturated acids **30** in moderate to very good yields. However, aryl diselenides bearing

Scheme 26



Scheme 27



R^1 = H, 4-Me, 4-MeO, 4-Br, 4-CN, 3-F, 3-CF_3, 3-Me, 2-MeO, 2-Cl, 2-Naph; R^2 = H, 4-Me, 4-MeO, 4-F, 3-MeO, 2-MeO; R^3 = Ar

Selected examples

30: $R^2 = R^3$ = Ph:
R^1 = Ph, 93% (**a**); C_6H_4Me-4, 91% (**b**); C_6H_4Br-4, 72% (**c**); C_6H_4F-3, 88% (**d**); C_6H_4Me-3, 78% (**e**); C_6H_4OMe-2, 62% (**f**); C_6H_4Cl-2, 55% (**g**); 2-Naph, 66% (**h**);

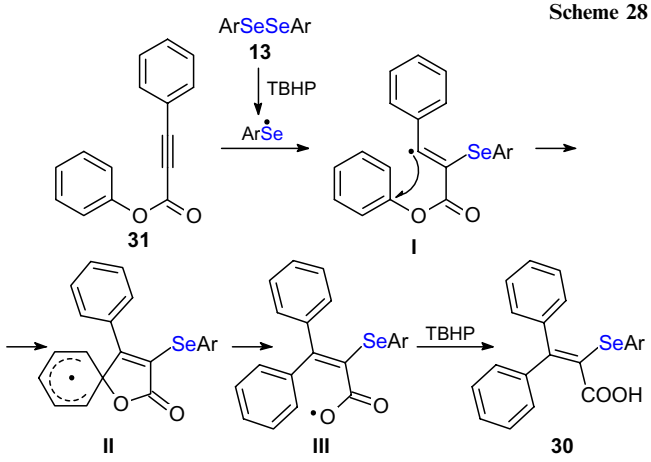
$R^1 = R^3$ = Ph:
R^2 = C_6H_4Me-4, 92% (**i**); C_6H_4F-4, 65% (**g**); C_6H_4OMe-3, 62% (**k**); C_6H_4OMe-2, 57% (**l**);
$R^1 = R^3 = C_6H_4$Cl-4,
R^2 = Ph, 89% (**m**);
$R^1 = C_6H_4$Cl-4, R^2 = Ph,
R^3 = C_6H_4Et-4, 71% (**n**);

electron-donating substituents and dialkyl- and diheteroaryl diselenides were not investigated in this study.

The first step of the reaction mechanism is the formation of the arylselanyl radical generated upon treatment of diaryl diselenides **13** with *tert*-butyl hydroperoxide (TBPH) (Scheme 28). This radical then reacts with the triple bond of **31** and produces the vinyl radical **I**. This latter undergoes an intramolecular radical *ipso*-cyclization to afford **II**, which, upon aryl migration from the oxygen to carbon centre, gives the carboxyl radical **III**. Finally, intermediate **III** extracts a hydrogen radical from TBHP to form the desired product **30**.

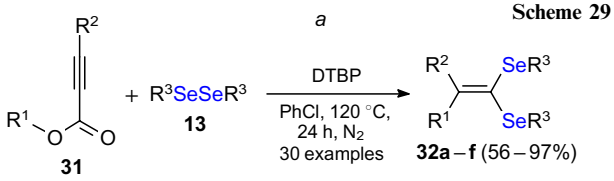
Later, a metal-free simple protocol was developed to access tetrasubstituted alkenes **32** and **33** (Scheme 29).[97] The best conditions for the reaction between aryl alkynoates **31** and diselenides **13** included the use of 2 equiv. of DTBP at 120 °C for 24 h in C_6H_5Cl under nitrogen atmosphere (see Scheme 29 *a*). When substituted aryl alkynoates **34** were employed, 4 equiv. of the oxidant DTBP were necessary to afford acceptable yields of the respective products (see Scheme 29 *b*). This method proved to be reliable for a wide range of substrates **31**, such as those bearing electron-

Scheme 28



TBPH = Bu^tOOH

Scheme 29

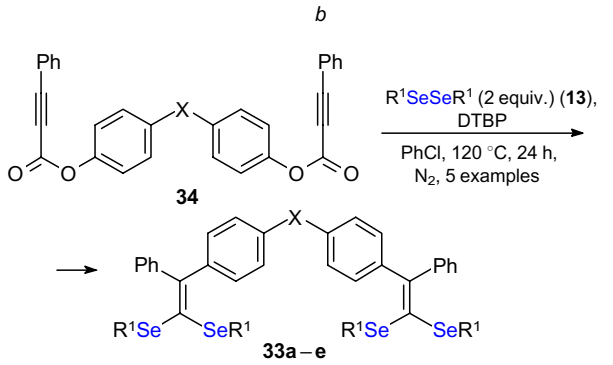


R^1, R^2 = aryl; R^3 = Ar, Het, Alk; DTBP = Bu^tOOBu^t

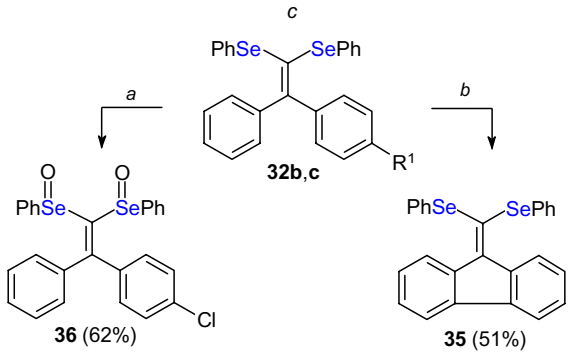
Selected examples

32: $R^1 = R^2$ = Ph:
R^3 = C_6H_4Br-2, 62% (**a**); Ph, 97% (**b**); 2-Th, 56% (**c**); C_6H_4F-3, 87% (**d**);

$R^2 = R^3$ = Ph:
R^1 = C_6H_4Cl-4, 78% (**e**); 2-Naph, 82% (**f**)



33: X = SO, R^1 = Ph, 69% (**a**);
X = S: R^1 = Ph, 73% (**b**); C_6H_4Cl-4, 54% (**c**); C_6H_4F-3, 44% (**d**); C_6H_4Br-2, 59% (**e**)

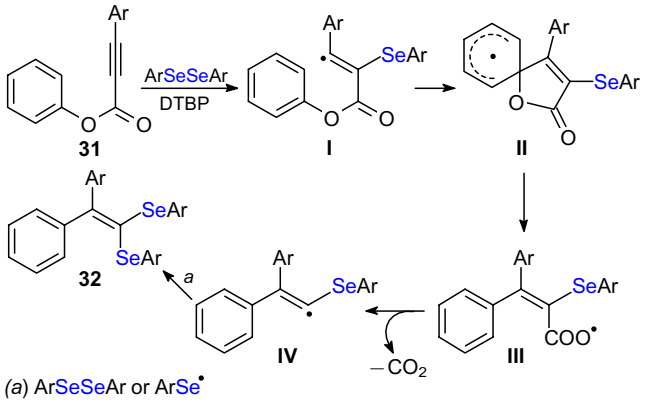


(*a*) *m*-CPBA, DCM, 30 min, 0 °C (R^1 = Cl);
(*b*) $Pd(OAc)_2$ (5 mol.%), Ag_2CO_3, K_2CO_3, TFA, 140 °C, 24 h (R^1 = H);
m-CPBA = 3-$ClC_6H_4C(O)OOH$, TFA = CF_3CO_2H

donating and -withdrawing groups, sterically hindered and aliphatic ones, except for 2-butynoic acid, which was unreactive. Moreover, various diselenides **13** were tested and products **32** were formed in good to high yields (see Scheme 29 *a*). No reaction was observed when ditelluride **25** was used instead of diselenide. The utility of this new approach was demonstrated in a gram scale reaction to afford product **32a**, which was obtained in 89% yield. Several aryl alkynoates **34** were investigated in the reaction with diselenide **13**, and the respective products **33** were isolated in good yields (see Scheme 29 *b*). Noteworthy, to demonstrate the synthetic applicability, the compound **32b** was subjected to a palladium-catalyzed cross-dehydrogenative annulation reaction to reach products **35** in 51% yield and compound **32c** was treated with *m*-CPBA to form product **36** in 62% yield (see Scheme 29 *c*).

The proposed mechanism starts with the reaction of diselenide **13** with DTBP to form the aryl selenium radical, which reacts with the substrate **31** to produce intermediate **I**. In this sequence, **I** undergoes an intramolecular radical *ipso*-cyclization to afford species **II**. After a sequential 1,4-aryl migration and decarboxylation, the vinyl radical **IV** is formed. Finally, the reaction of species **IV** with diselenide **13** or aryl selenium radical formed in the reaction medium affords product **32** (Scheme 30).

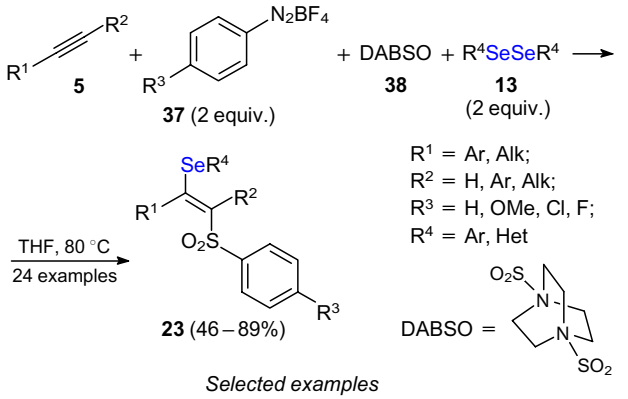
Scheme 30



In 2018, Sun *et al.*[98] offered an access to β-(seleno)vinyl sulfones **23** through a multicomponent reaction between alkynes **5**, aryldiazonium tetrafluoroborates **37**, 1,4-diazabicyclo[2.2.2]octane bis(sulfur dioxide) adduct (DABSO) **38** and diaryl diselenides **13** (Scheme 31). In general, aromatic terminal alkynes bearing electron-withdrawing (F, Cl and Br) or electron-donating groups (Me and OMe) on the phenyl ring, as well as internal alkynes, were well tolerated under the optimized conditions, affording the expected (*E*)-β-selenovinyl sulfones **23** in 71–89% yield. The selenovinyl sulfones **23q**,**r**, derived from aliphatic alkynes, were obtained in moderate yields. Additionally, various aryldiazonium tetrafluoroborates **37** and diaryl diselenides **13** were also satisfactorily employed as substrates, giving the desired products **23** in good yields. To summarize, this procedure involves readily available reagents, shows good regio- and stereoselectivity, excellent functional group tolerance, and amenability to the scale-up synthesis.

The authors hypothesized that the multicomponent reaction mechanism starts by the combination of an aryldiazonium cation with DABSO **38**, generating complex **I**. The unstable complex **I** decomposes to form sulfur dioxide,

Scheme 31

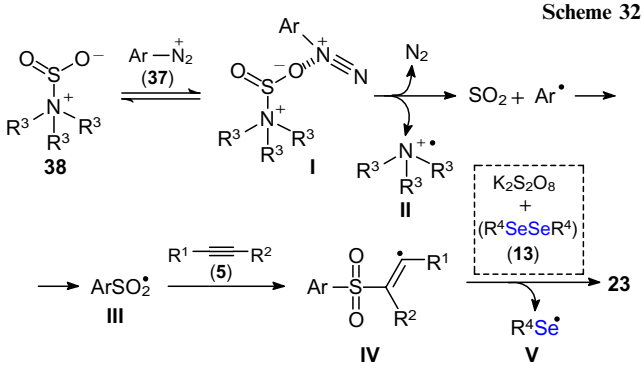


Selected examples

23: R^2 = H, R^3 = Me, R^4 = Ph:
R^1 = Ph, 84% (**j**); C_6H_4F-2, 81% (**a**); C_6H_4Cl-2, 86% (**p**); C_6H_4F-4, 83% (**q**); C_6H_4Br-4, 89% (**r**); C_6H_4Me-4, 76% (**c**); C_6H_4OMe-4, 80% (**s**);
R^1 = R^4 = Ph, R^3 = Me: R^2 = Ph, 71% (**t**); Me, 80% (**u**);
R^2 = R^3 = H, R^4 = Ph: R^1 = Bu^n, 51% (**v**); cyclo-C_3H_5, 46% (**w**);
R^1 = C_6H_4Cl-4, R^2 = H, R^4 = Ph:
R^3 = H, 85% (**x**); Cl, 84% (**y**); OMe, 81% (**z**);
R^1 = Ph, R^2 = H, R^3 = Me:
R^4 = C_6H_4Br-4, 73% (**aa**); C_6H_4Cl-4, 77% (**ab**); C_6H_4OMe-4, 70% (**ac**); 2-Th, 80% (**i**)

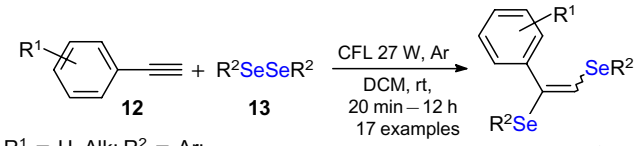
nitrogen, aryl radical and the tertiary amine radical cation **II** (Scheme 32). Then, the aryl radical is added to sulfur dioxide affording arylsulfonyl radical **III**, which regiospecifically adds to alkyne **5** to form the β-sulfonyl vinyl radical **IV**. In the last step, diaryl diselenide **13** reacts with $K_2S_2O_8$ to give intermediate **V**, which couples with **IV** affording (*E*)-β-selenovinyl sulfone **23**.

Scheme 32



Weber *et al.*[99] reported in 2018 the synthesis of (*E*)-1,2-bis-selanylalkenes **10** by the photoinduced reaction of arylacetylenes **12** with diaryl diselenides **13** (Scheme 33). Under the optimal conditions, a series of seventeen substituted bis(selanyl)alkenes **10** were accessed in up to 95% yield. The key features of this method include photocatalysis, broad substrate scope, low cost and low environmental impact. Besides, it is fast, efficient, and highly selective to (*E*)-1,2-bis-selanyl alkenes **10**, avoids the use of metal catalysts or additives, high temperatures, long reaction times and complex reagents. Equally good results were obtained starting from electron-rich or electron-poor arylalkynes **12** and diaryl diselenides **13**. Lower yields (31–42%) of 1,2-bis-selanyl alkenes **10j**,**k**,**r** were obtained

Scheme 33



R^1 = H, Alk; R^2 = Ar;
CFL is compact fluorescent lamp

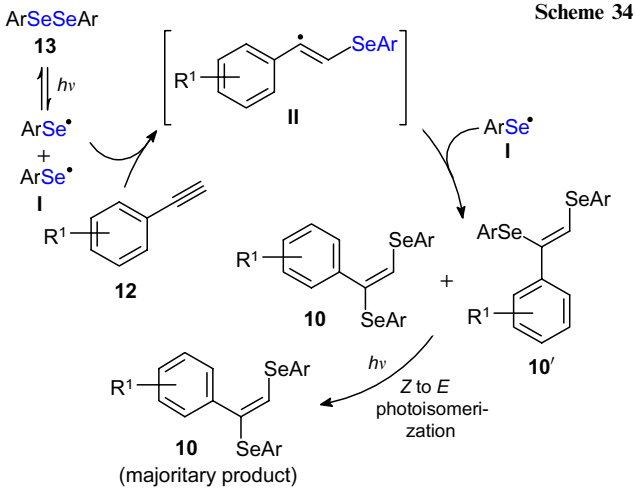
Selected examples

R^1 = Ph:
10a : **10a′** (97 : 3): R^2 = Ph, 95%, 20 min;
10g : **10d′** (85 : 15): R^2 = C_6H_4Cl-4, 88%, 20 min;
10d : **10b′** (> 99 : 1): R^2 = C_6H_4Me-4, 71%, 71 h;
10j : **10g′** (75 : 25): R^2 = C_6H_4OMe-4, 31%, 31 h;
10k : **10h′** (> 99 : 1): R^2 = C_6H_4Me-2, 35%, 12 h;
R^2 = Ph:
10i : **10f′** (99 : 1): R^1 = C_6H_4Me-4, 63%, 20 min;
10b : **10c′** (94 : 6): R^1 = C_6H_4Cl-4, 93%, 20 min;
10l : **10i′** (95 : 5): R^2 = $C_6H_4NO_2$-2, 89%, 12 h;
10m : **10j′** (94 : 6): R^1 = C_6H_3Me-3-OMe-5, 40%, 20 min;
10n : **10k′** (96 : 4): R^1 = C_6H_4Ac-4, 85%, 20 min;
R^1 = $C_6H_4NO_2$-4:
10o : **10l′** (50 : 50): R^2 = C_6H_4OMe-4, 81%, 12 h;
10p : **10m′** (66 : 34): R^2 = $C_6H_4CF_3$-3, 44%, 12 h;
R^1 = C_6H_4Me-4:
10q : **10n′** (89 : 11): R^2 = C_6H_4Cl-4, 93%, 20 min;
10r : **10o′** (80 : 20): R^2 = C_6H_4Me-2, 42%, 12 h

when *ortho*-functionalized diselenides were employed as substrates.

The reaction mechanism to prepare bis-arylselanyl olefins **10** and **10′** is depicted in Scheme 34. Initially, the reversible homolytic cleavage of the Se – Se bond in diaryl diselenide **13** occurs to form the selenium radical species **I**, which is added to the triple bond of alkyne **12** leading to the *anti*-Markovnikov adduct intermediate **II**. A second insertion of the selenium radical moiety produces both *E*- and *Z*-olefins **10** and **10′**. The last step of photoisomerization of *Z* to *E* affords mainly *E*-product **10**.

Scheme 34



In 2019, Chen *et al.*[100] reported a multicomponent visible light-promoted synthesis of β-sulfonylvinylselanes **39** of *E*-configuration starting from diselenides **13**, alkynes **12** and sulfur dioxide (Scheme 35). The reaction was carried out under the irradiation with blue LED at room temperature. Various diselenides **13** worked well in the reaction. In the case of 1,2-di(thiophen-3-yl) diselenide **13**, the corresponding product **39a** was formed only in trace amounts. Various alkynes **12** were investigated and demonstrated to be suitable for the reaction. When 3-ethynylpyridine was used, the respective product **39b** was obtained in 42% yield. With diphenyl disulfide **40a**, the expected product **39c** could not be isolated (see Scheme 35 *a*). Also, product **39d** (YR^1 = SePh) was subjected to oxidation with *m*-CPBA, and then treated once with $KHCO_3$ in THF/H_2O or THF/$NH_3 \cdot H_2O$ systems to form **41** and **42** in 70% and 56% yield, respectively (see Scheme 35 *b*). Additionally, product **39e** (YR^1 = SeMe) was converted to 1,3-dioxolane **43** in 64% yield after treatment with *m*-CPBA and $KHCO_3$ in ethylene glycol. Interestingly, the nine-membered heterocycle **44** was not detected (see Scheme 35 *c*), and no reaction occurred in ethanolamine.

The proposed reaction mechanism begins with the visible light-promoted formation of the selenium radical, which reacts with alkyne **12** to generate intermediate **I**. The latter species reacts with sulfur dioxide to give the sulfonyl radical **II**, which forms the vinyl radical **III** in the presence

Scheme 35

a

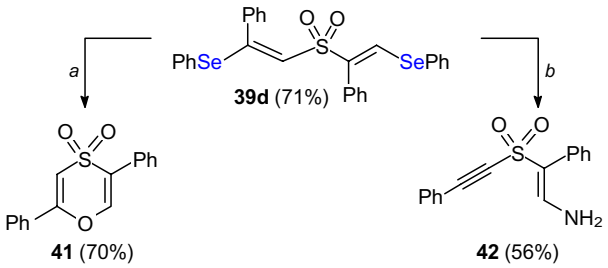


R^1, R^2 = Ar, Het; Y = Se, S

Selected examples

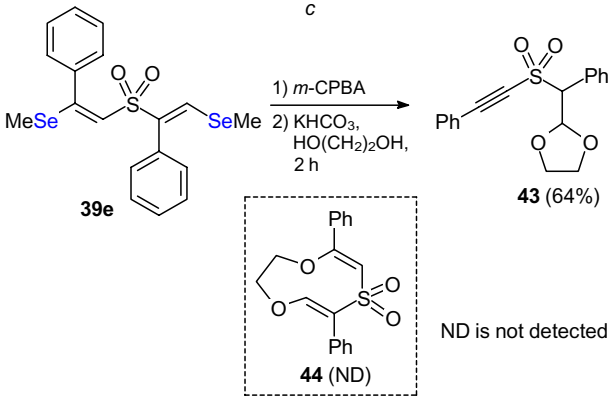
39: Y = Se:
R^1 = Ph, R^2 = 2-Th, traces (**a**); R^1 = Ph, R^2 = Me, 64% (**e**);
R^1 = 3-Py, R^2 = Ph, 42% (**b**); R^1 = $C_6H_4CO_2$Me-4, R^2 = Ph, 35% (**f**);
R^1 = R^2 = Ph, 71% (**d**); Y = S: R^1 = R^2 = Ph, traces (**c**)
Py is pyridyl

b

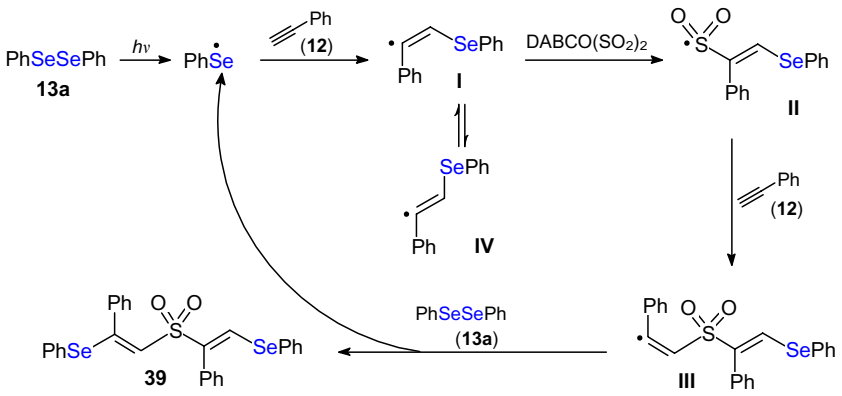


(*a*) *m*-CPBA, $KHCO_3$, THF/H_2O, 2 h;
(*b*) *m*-CPBA, $KHCO_3$, THF/$NH_3 \cdot H_2O$, 2 h

c



Scheme 36



of alkyne **12**. Finally, the species **III** reacts with diselenide **13** affording the desired product **39** and selenium-centred radical (Scheme 36).

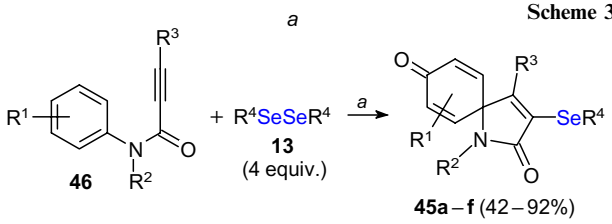
In 2018, Sahoo *et al.*[101] developed a metal-free synthesis of 3-selenospiro[4,5]trienones **45** through a radical oxidative dearomatization under blue LED irradiation (Scheme 37 *a*). The reaction was carried out in MeCN, under oxygen atmosphere using very mild conditions, and products **45** were achieved in 42–92% yields. The reaction proceeded smoothly for different *N*-aryl alkynamides **46** with various substituents both in the *N*-aryl ring and in the alkyne aryl moiety, like electron-donating and electron-withdrawing groups, sterically hindered and aliphatic ones. Also, various diaryl diselenides **13**, such as containing halogen, alkyl and electron-withdrawing groups, were suitable for the reaction. The heteroaryl derivative 2,2′-dithienyl diselenide afforded the expected product **45a** in 52% yield (see Scheme 37 *a*). Alkynylamides **46** substituted with fluorine or methoxy at the *para*-position of the pendant phenyl ring afforded product **45b** in 80% and 72% yields, respectively, after the cleavage of the C–F or C–OMe bonds (Scheme 37 *b*). Compounds **45** were further reacted with allylamines **47** to give the ring-opened products **48**. The formation of substituted aniline **48** involves the initial formation of ketimine **I**, which rearranges to aldimine **II** and is finally hydrolyzed (see Scheme 37 *c*).

Moreover, compound **45b** was subjected to several chemical transformations. Its treatment with $LiBH_4$ afforded compound **49**, while *m*-CPBA was used to prepare selenoxide **50**. Ketoxime **51** was obtained *via* the reaction of **45b** with methoxyamine (Scheme 38).

A plausible mechanism for the conversion of **46** into **45** involves initially the visible light-promoted homolytic cleavage of the Se–Se bond in diselenide **13** to generate a selenium radical, which reacts with substrate **46** to form the vinyl radical **I**. This species undergoes an intermolecular radical *ipso*-cyclization to produce intermediate **II**, which is transformed in the reaction medium to species **III**. The latter undergoes a O–O bond cleavage leading to the desired product **45**. This assumption is supported by the fact that intermediate **IV** was not detected (Scheme 39).

In 2021, a similar visible light-promoted protocol was described by Hou *et al.*[102] as a strategy to prepare the same class of vinyl selenide-substituted pyrrolidines **52** (Scheme 40). Advantages achieved in this synthesis include mild reaction conditions, no need for transition metal catalyst or oxidant, broad scope, excellent *Z*/*E*-selectivity and valuable arylselanyl-containing cyclic compounds. The radical addition/cyclization/selenation of 1,6-enynes **53** with

Scheme 37

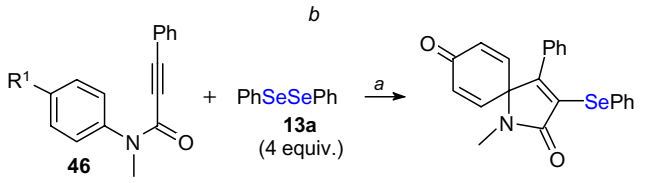


(*a*) MeCN, O_2, blue LED, rt, 24–36 h, 25 examples;
R^1 = H, 9-Me, 9-Br, 9-Cl, Ph; R^2 = Me, Et;
R^3 = Ph, C_6H_4Me-4, Me, 2-Th; R^4 = Ar, Het

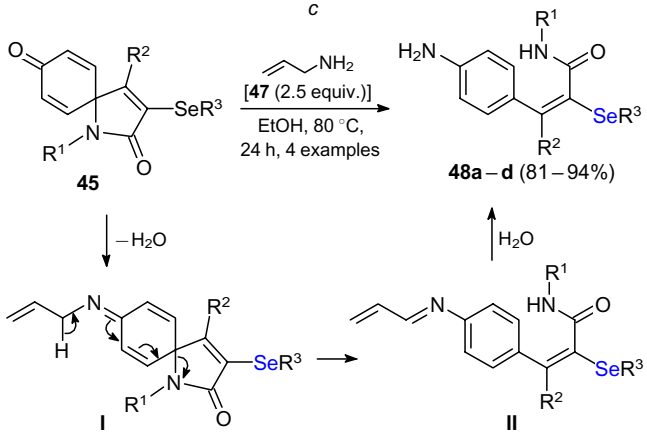
Selected examples

45: R^1 = H, R^2 = Me:
R^3 = Me, R^4 = 2-Th, 52% (**a**);
R^3 = R^4 = Ph, 85% (**b**);
R^3 = Ph, R^4 = C_6H_4Me-4, 42% (**c**);
R^1 = 3,5-Me_2, R^2 = Me,
R^3 = R^4 = Ph, 92% (**d**);

R^1 = H:
R^2 = R^3 = 2-Th,
R^4 = C_6H_4Cl-4, 63% (**e**);
R^2 = Et, R^3 = R^4 = Ph, 78% (**f**)



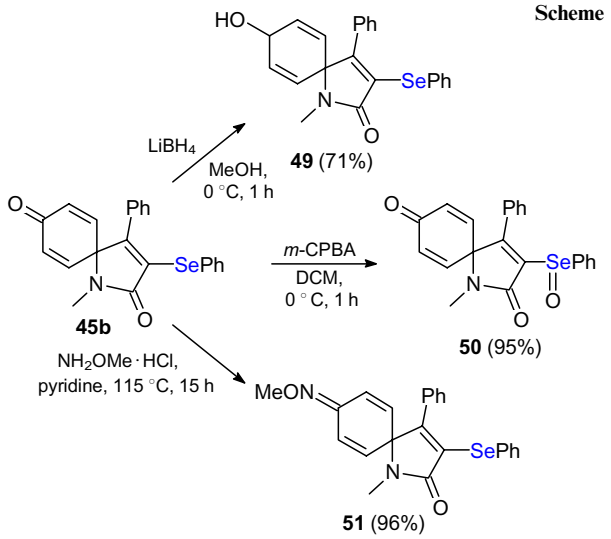
(*a*) MeCN, O_2, blue LED, rt, 24–36 h



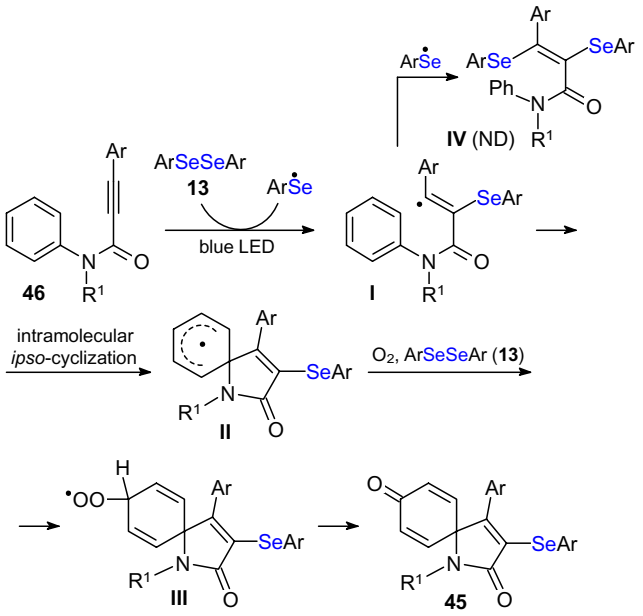
48: R^1 = Me:
R^2 = R^3 = Ph, 90% (**a**);
R^2 = 2-Th, R^3 = C_6H_4Cl-4, 94% (**b**);
R^2 = Ph, R^3 = C_6H_4Cl-4, 81% (**c**)

R^1 = Et, R^2 = Ph,
R^3 = C_6H_4Cl-4, 94% (**d**)

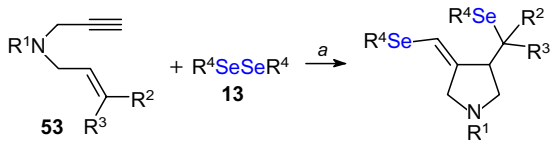
Scheme 38



Scheme 39



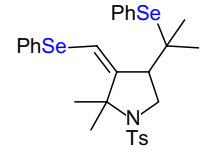
Scheme 40

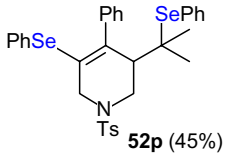


(*a*) 23 W fluorescent bulb, N_2, toluene, rt, 12 h, 16 examples;
R^1 = Ts, BPS ([1,1′-biphenyl]-4-sulfonyl), C(O)Me, C(O)Ph;
R^2, R^3 = Alk; R^4 = Ar

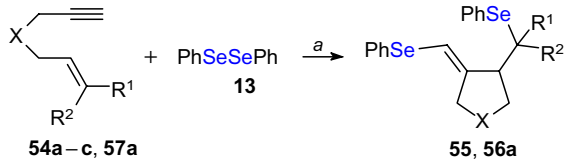
Selected examples

52: R^2 = R^3 = Me, R^4 = Ph:
R^1 = Ts, 82% (**e**); BPS, 71% (**f**);
Ac, 46% (**g**); C(O)Ph, 70% (**h**);
R^1 = Ts, R^2 = Me, R^3 = $(CH_2)_2Ph$,
R^4 = Ph, 63%, *dr* 1 : 1 (**j**);
R^1 = Ts, R^2 = R^3 = Me:
R^4 = C_6H_4OMe-4, 57% (**k**);
$C_6H_4CF_3$-4, 35% (**l**);
2-Naph, 39% (**m**); C_6H_4F-4, 76% (**n**);
$C_6H_3F_2$-2,4, 52% (**o**)

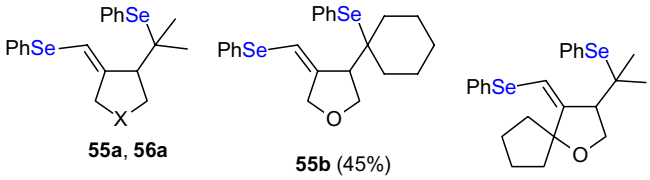




Scheme 41



(*a*) 23 W fluorescent bulb, N_2, toluene, rt, 12 h, 4 examples;
X = O (**54a–c**; **55a–c**, 45–52%), $C(CO_2Me)_2$ (**56a**, 40%; **57a**)



X = O (**55a**, 46%), $C(CO_2Me)_2$ (**56a**, 40%)

diorganyl diselenides **13** was carried out under N_2 atmosphere and irradiation with a 23 W household fluorescent bulb. Under these conditions, fifteen pyrrolidines bearing vinyl selenide moieties **52a–j** were obtained in poor to good yields, employing several 1,6-enynes **53** and diorganyl diselenides **13**. When an internal nitrogen tethered 1,6-enyne **53** was used, the tetrahydropyridine **52h** was obtained.

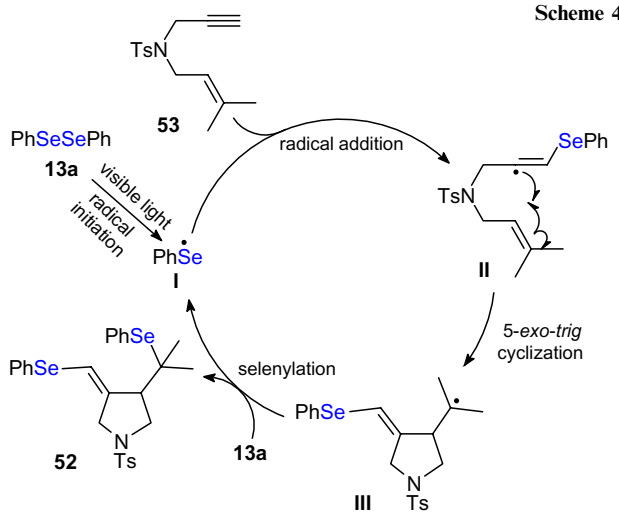
The replacement of the nitrogen atom in 1,6-enynes with an oxygen one, as in **54**, allowed the formation of tetrahydrofuran-containing selenides **55a,b** in moderate yields (Scheme 41). The spirocyclic **55c** was obtained by the reaction of 1-ethynylcyclopentanol-derived enyne **54c** with **13a**. In addition, the cyclopentane-based **56a** was formed by using dimethyl 2-isopentyl-2-(prop-2-yn-1-yl)malonate **57** as substrate (see Scheme 41). All these compounds were obtained in moderate yields.

The proposed mechanism for the cyclization reaction starts with the generation of the selenium-centred radical **I** upon the homolytic cleavage of the Se–Se bond promoted by the visible light irradiation of diphenyl diselenide **13a**. The radical addition of **I** to 1,6-enyne **53** gives the vinyl radical intermediate **II**, which undergoes an intramolecular 5-*exo-trig* cyclization to produce the tertiary carbon alkyl radical **III**. Finally, the direct phenylselenylation of radical **III** by diphenyl diselenide **13a** affords the desired product **52** and releases the phenylselenyl radical **I** (Scheme 42).

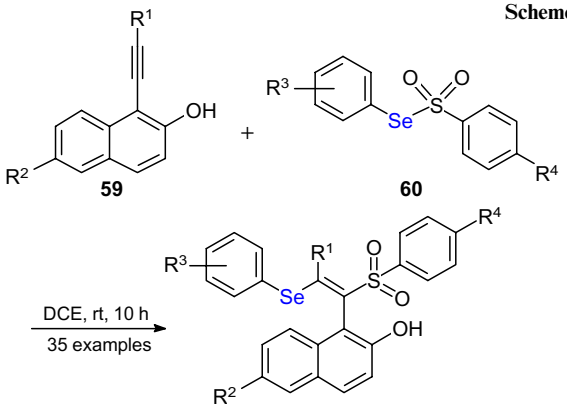
In 2019, Huang *et al.*[103] reported the synthesis of β-(seleno)vinyl sulfones **58** *via* the spontaneous selenosulfonylation of 1-(organylethynyl)naphthalen-2-ols **59** in the presence of selenosulfonates **60** (Scheme 43). The reaction was carried out under mild conditions without any catalysts or additives, affording thirty-five β-(seleno)vinyl sulfones **58** in moderate yields with excellent *E*-selectivity (> 99 : 1).

However, the standard reaction conditions were not suitable for 2-(organylethynyl)phenols **59j,k**, probably due to the fact that the formation of the vinylidene *ortho*-quinone methide (VQM) analogue **I** from phenol derivatives is more difficult than from naphthol ones (see the mecha-

Scheme 42



Scheme 43

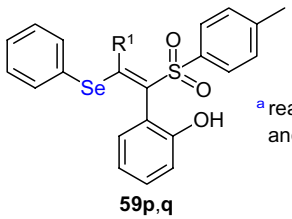


58a–q, 20–85% (*E*/*Z* > 99 : 1)

R^1 = Ar, Het; R^2 = H, Br; R^3 = H, 4-Me, 4-F, 4-Cl, 3-Me, 3-Cl, 3-Br, 2-Me, 2-Cl, 2-Br; R^4 = H, Me, F, Cl, Br; DCE = $Cl(CH_2)_2Cl$

Selected examples

58: R^2 = R^3 = H, R^4 = Me:
R^1 = Ph, 85% (**a**); C_6H_4Me-4, 44% (**b**); C_6H_4OMe-4, 76% (**c**); C_6H_4F-4, 81% (**d**); C_6H_4Cl-4, 47% (**e**); C_6H_4Me-3, 51% (**f**); C_6H_4Br-2, 47% (**g**); 2-Th, 46% (**h**);
R^1 = R^3 = Ph, R^2 = Br, R^4 = Me, 76% (**i**);
R^1 = Ph, R^2 = R^4 = H:
R^3 = H, 59% (**j**); 4-Cl, 75% (**k**); 2-Me, 61% (**l**); 2-Cl, 66% (**m**);
R^1 = Ph, R^2 = R^3 = H: R^4 = F, 64% (**n**); Cl, 76% (**o**)



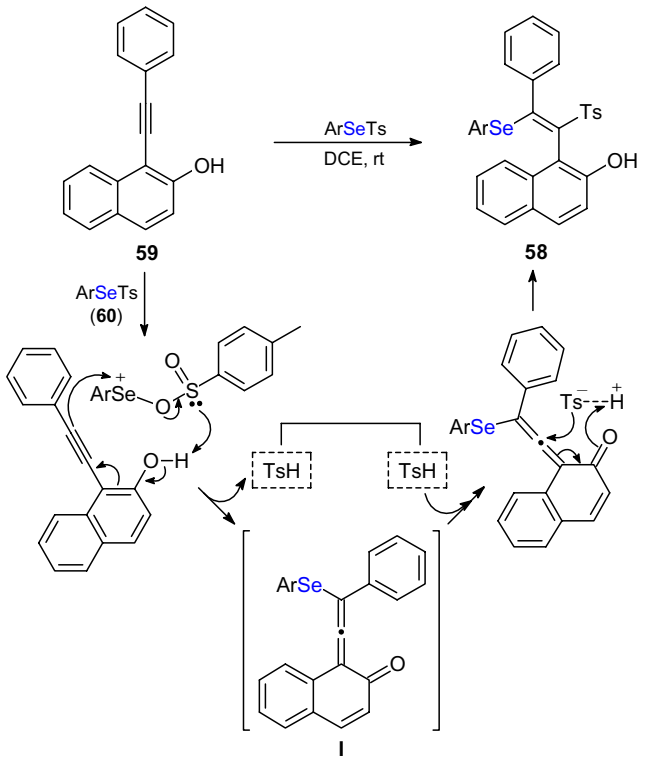
59p,q

R^1 = Ph, 20% [a] (**p**);
C_6H_4OMe-4, 26% [a] (**q**)

[a] reaction carried using Et_3N (1.0 equiv.) and toluene under reflux for 16 h

nism below). The products **58p,q**, derived from phenols, were obtained in 20% and 26% yield, respectively, using Et_3N under reflux in toluene for 16 h (see Scheme 43). In the proposed mechanism, the initial cleavage of selenosulfonate **60** by 1-(phenylethynyl)naphthalen-2-ol **59** affords the VQM intermediate **I** and releases one molecule of

Scheme 44



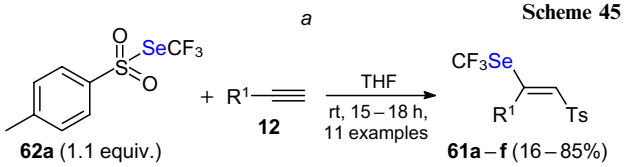
p-toluenesulfinic acid (TsH). Finally, intermediate **I** is attacked by TsH, leading to product **58** (Scheme 44).

In 2017, Ghiazza *et al.*[104] developed a synthetic approach to (perfluoroalkylselenyl) vinyl sulfones **61** using *Se*-(trifluoromethyl)-4-methylbenzenesulfonoselenoate **62** as a stable and easy to handle source of selenium (Scheme 45). Different alkynes **12** were employed and were well tolerated, except for aliphatic dec-1-yne, which produced the product **61a** in as low as 16% yield (see Scheme 45 *a*). Additionally, long-chain perfluorinated selenium reagents **62b,c** were successfuly used to afford the corresponding products **61g,h** both in 61% yield (see Scheme 45 *b*).

The authors hypothesized that the mechanism of the reaction involves the formation of the complex intermediate **I**, the trifluoromethylselenonium ion, as the first step. In the

Scheme 45

a



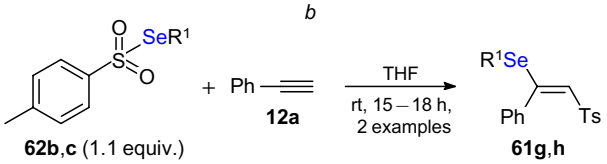
62a (1.1 equiv.) **61a–f** (16–85%)

R^1 = Ar, Alk

Selected products

61: R^1 = n-Oct, 16% (**a**); C_6H_4Cl-2, 85% (**b**); $C_6H_4OCF_3$-2, 53% (**c**); $C_6H_3(CF_3)_2$-3,5, 42% (**d**); $C_6H_4CH_2CN$-4, 64% (**e**); C_6H_4Ac-4, 65% (**f**)

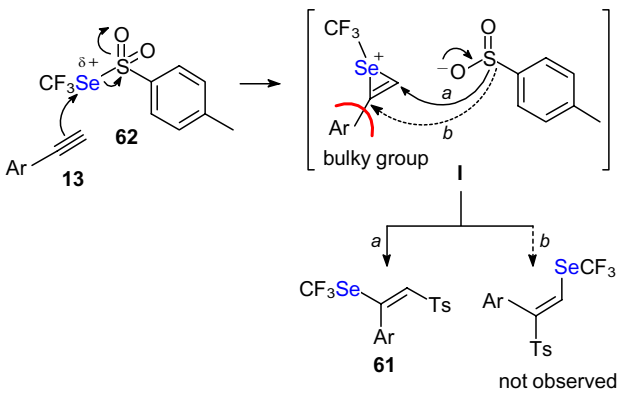
b



62b,c (1.1 equiv.) **61g,h**

R^1 = C_2F_5, 61% (**g**); n-C_6F_{13}, 61% (**h**)

Scheme 46

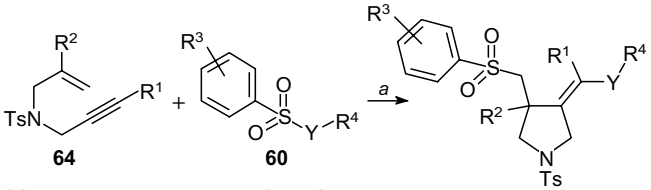


sequence, **I** suffers an *anti*-opening, due to the steric hindrance, leading to product **61** (Scheme 46).

In 2020, Mutra *et al.*[105] published the synthesis of (*Z*)-3-phenyl-4-[phenyl(arylselanyl)methylene]-3[(arylsulfonyl)-methyl]-1-tosylpyrrolidine derivatives **63** *via* regio- and chemoselective light-induced reactions of non-activated 1,6-enynes **64** with areneselenosulfonates **60** (Scheme 47). The key features of this protocol are broad substrate scope, environmentally friendly conditions (metal- and oxidant-free, no use of stoichiometric amounts of additives or harsh reaction conditions and expensive metal photocatalysts), operational simplicity, atom economy and no toxic waste generation. The optimal conditions involved the irradiation of a mixture of reactants in acetone with a 34 W blue LED at room temperature. The cyclization scope was extended to a series of diversely substituted terminal and internal alkynes **64** and (un)symmetrical chalcogenides **60** to produce the respective polysubstituted pyrrolidines **63** bearing vinyl selenide moieties in good yields. The reaction was also performed using the sulfide derivative (Ts–S–Ph) to afford the corresponding vinyl sulfide **63m** in 78% yield within 9 h.

In addition, when areneselenosulfonates **60** were replaced by diphenyl diselenide **13a**, the reaction with

Scheme 47

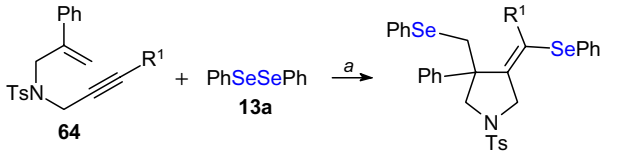


(*a*) 34 W blue LED, acetone (0.1 M), rt, 7–12 h, 19 examples;
R^1, R^2 = Ar, Alk, Het; R^3, R^4 = Alk, Ar; Y = Se, S

Selected examples

63: Y = Se:
R^3 = Me,
R^2 = R^4 = Ph:
R^1 = H, 75%, 8 h (**a**);
Ph, 82%, 9 h (**b**);
TMS, 81%, 8 h (**c**);
2-Th, 88%, 10 h (**d**);
Me, 77%, 8 h (**e**);
R^1 = R^4 = Ph,
R^2 = R^3 = Me, 77%, 8 h (**f**);
TMS = $SiMe_3$
R^1 = R^2 = R^4 = Ph:
R^3 = H, 77%, 12 h (**g**);
4-CF_3, 70%, 12 h (**h**);
2-Naph, 66%, 10 h (**i**);
R^1 = R^2 = Ph, R^3 = Me:
R^4 = C_6H_4Me-4, 80%, 10 h (**j**);
C_6H_4F-3, 62, 10 h (**k**);
2-Th, 65%, 7 h (**l**);
Y = S:
R^1 = R^2 = Ph, R^3 = Me,
C_6H_4Me-4, 78%, 9 h (**m**)

Scheme 48

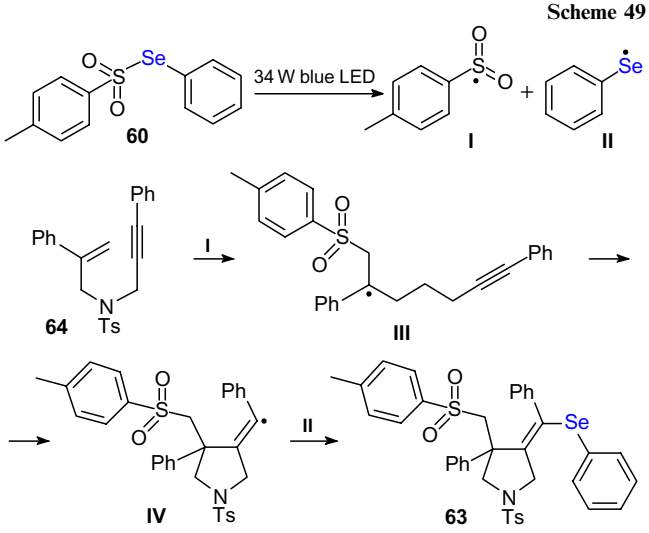


(*a*) 34 W blue LED, acetone (0.1 M), rt, 10–30 h, 4 examples;
65: R^1 = Ph, 77%, 24 h (**a**); $C_6H_4NO_2$-3, 50%, 30 h (**b**); $C_6H_4CO_2Me$-4, 55%, 30 h (**c**); 2-Th, 79%, 10 h (**d**)

1,6-enynes **64** under the optimal conditions gave compounds **65** in slightly lower yields within 10–30 h (Scheme 48).

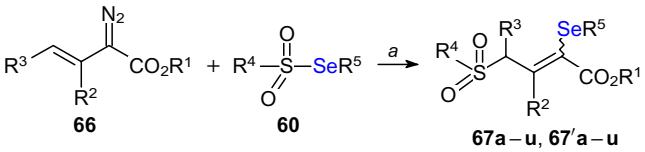
The proposed reaction mechanism involves the light-promoted homolytic cleavage of the SO_2–Se bond in Se-phenyl 4-methylbenzenesulfonoselenoate **60** to generate the tosyl **I** and phenylselenyl **II** free radicals. Then, a regio- and chemoselective tosyl radical addition to 1,6-enyne **64** occurs, producing the alkyl radical intermediate **III**. The latter undergoes a 5-*exo*-*dig* cascade cyclization to afford the vinyl radical intermediate **IV**, which is finally captured by phenylselenyl radical **II** to give the desired product **63** (Scheme 49).

Scheme 49



In 2021, Li and Zhou [106] reported the visible light-driven radical 1,3-selenosulfonylation of vinyldiazo compounds **66** with selenosulfonates **60** to prepare γ-seleno allylic sulfones **67**. The reaction proceeds at room temperature in an open flask under irradiation with a 5 W blue LED for 2 h (Scheme 50). The substrate scope included several vinyldiazoacetates **66** substituted at the vinyl and ester group and selenosulfonates **60** bearing a wide range of functional groups; a diversity of γ-seleno allylic sulfones **67** were produced in good to very good yields. The green features of this protocol include low process-mass intensity (it is an efficient addition reaction in a green solvent, such as ethyl acetate, using a 1:1 ratio of reactants; moreover, the reaction catalyst, base, and other additives are not needed), energy efficiency (the reaction proceeds at room temperature under irradiation with a 5 W blue LED for 2 h) and operational simplicity.

Scheme 50



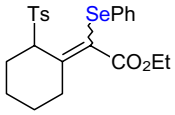
66 **60** **67a–u, 67′a–u**
63–86% (*Z* : *E*)

(*a*) 5 W blue LED, EtOAc, rt, 2 h, 33 examples;
R^1 = Alk, Ar, All, propargyl; R^2, R^3 = H, Alk, Ar;
R^4 = Ar, Alk, Het; R^5 = Alk, Ar

Selected examples

$R^2 = R^3$ = H,
$R^4 = C_6H_4Me$-4, R^5 = Ph:
67a : **67a′** (4 : 1) R^1 = Bu^t, 85%;
67b : **67b′** (4.5 : 1) R^1 = Bu^n, 85%;
67c : **67c′** (4.5 : 1) R^1 = Ph, 83%;
67d : **67d′** (4 : 1) R^1 = All, 77%;
67e : **67e′** (4 : 1) R^1 = propargyl, 71%;
R^1 = Et, $R^4 = C_6H_4Me$-4,
R^5 = Ph:
67f : **67f′** (1.8 : 1) R^2 = H,
R^3 = Me, 79%;
67g : **67g′** (2 : 1) R^2 = Me,
R^3 = H, 81%;
67h : **67h′** (1.5 : 1) R^2 = H,
R^3 = Ph, 68%;
67i : **67i′** (1.3 : 1) R^2 = H,
$R^3 = C_6H_4Me$-4, 70%;
67j : **67j′** (1.2 : 1) R^2 = H,
$R^3 = C_6H_4F$-2, 77%;
All is allyl

$R^1 = Bu^n$, $R^2 = R^3$ = H,
$R^4 = C_6H_4Me$-4:
67l : **67l′** (4.3 : 1) $R^5 = C_6H_4Bu^t$-4, 86%;
67m : **67m′** (4.3 : 1) $R^5 = C_6H_4Br$-4, 86%;
67n : **67n′** (4 : 1) $R^5 = C_6H_4Me$-3, 85%;
67o : **67o′** (5.7 : 1) $R^5 = C_6H_4Cl$-2, 83%;
67p : **67p′** (2 : 1) R^5 = Me, 78%;
67q : **67q′** (1 : 1) R^5 = 2-Th, 79%;
$R^1 = Bu^n$, $R^2 = R^3$ = H,
R^5 = Ph:
67r : **67r′** (4 : 1) $R^4 = C_6H_4Bu^t$-4, 85%;
67s : **67s′** (4 : 1) $R^4 = C_6H_4I$-4, 82%;
67t : **67t′** (4.6 : 1) R^4 = Naph, 76%;
67u : **67u′** (4 : 1) R^4 = Me, 79%

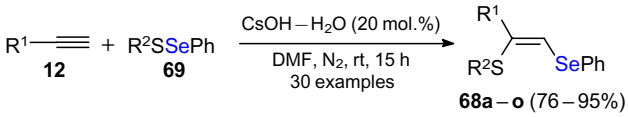


67k : **67k′**: 63% (2.1 : 1)

The above reaction has three possible paths. First, the decomposition of vinyldiazoacetate **66** under blue light irradiation affords the free vinyl carbene **I**. Then, carbene **I** reacts with **60** to give selenium ylide **II**, which is converted to the 1,3-selenosulfonylation product **67** *via* transition state **III** (Scheme 51, path *a*). Alternatively, the homolytic cleavage of the SO_2–Se bond of **II** generates the tosyl radical **IV** and the allyl radical **V**, which is in resonance with **VI**. Subsequently, product **67** is obtained *via* the combination of tosyl radical **IV** and allyl radical **VI** (see Scheme 51, path *b*). Alternatively, the photo-irradiation of **60** produces the tosyl radical **IV** and phenylselenyl radical **VII**. A radical pathway, initiated by the addition of tosyl radical **IV** to the C=C of the vinyldiazoacetate **66**, forms the vinyl radical **IX**, through the loss of nitrogen gas from intermediate **VIII**, a resonance structure of **VII**. The reaction of vinyl radical **IX** with $TsSeC_6H_5$ **60** gives the product **67** eliminating the tosyl radical **IV** to participate in another radical propagation process (see Scheme 51, path *c*).

Peng *et al.*[107] developed the regioselective synthesis of (*Z*)-vinyl selenosulfides **68** through the thioselenation of alkynes **12** with unsymmetrical diorganoyl dichalcogenides **69** catalyzed by cesium hydroxide monohydrate (Scheme 52). The method was efficiently performed with various terminal alkynes **12**, including propargyl alcohols and arylacetylenes containing electron-donating and electron-withdrawing groups at the *ortho*-, *meta*- or *para*-

Scheme 52



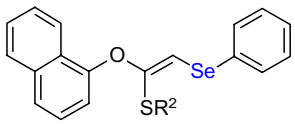
12 **69** **68a–o** (76–95%)

R^1 = Ar, Alk; R^2 = Ar, Alk, Het

Selected examples

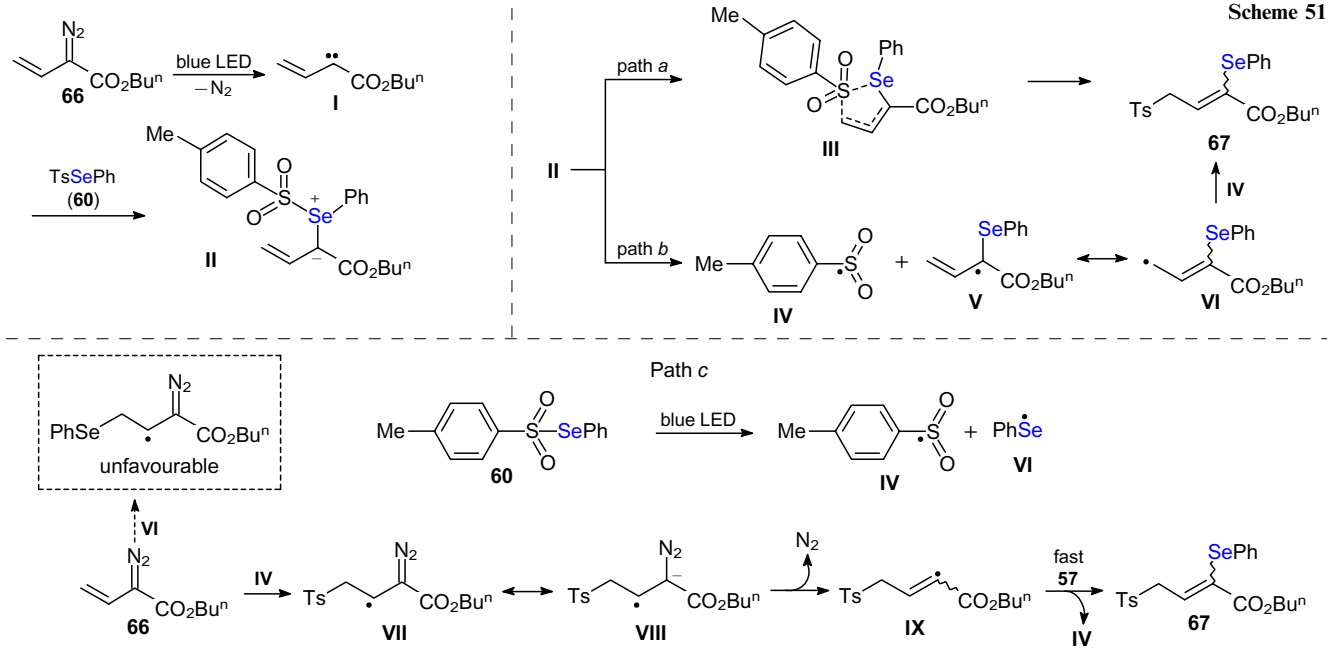
68: R^2 = Ph:
$R^1 = CH_2OH$, 90% (**a**);
CMe_2OH, 86% (**b**);
CH_2OMe, 90% (**c**);
Ph, 92% (**d**);
C_6H_4Me-4, 90% (**e**);
C_6H_4F-4, 95% (**f**);
$C_6H_4NH_2$-3, 83% (**g**);
C_6H_4Cl-2, 88% (**h**); Pr^n, NR (**i**);
$R^1 = CMe_2OH$,
$R^2 = C_6H_4Cl$-2, 85% (**j**)

R^1 = OBn:
$R^2 = C_6H_4Me$-4, 89% (**k**);
C_6H_4OMe-4, 85% (**l**);
C_6H_4Cl-4, 90% (**m**)



68n,o
R^2 = Bn, 76% (**n**); Pr^n, 87% (**o**)

Scheme 51



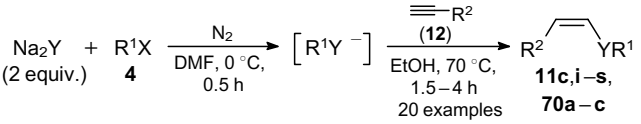
positions, and the products were obtained with high stereoselectivity and in excellent yields. However, the observed limitation of the substrate scope comprised n-pentyne, which gave no expected product **68i**. The reaction was suitable for both alkyl- and aryl-phenylselenosulfides, affording the corresponding products **68j-o** in good to excellent yields. It is worth to mention that the protocol was satisfactorily scalable to 20 mmol, providing the (*Z*)-vinylic selenosulfide **68a** in 90% yield.

2.3. Reactions using other selenium species

Several approaches have been established for the synthesis of vinyl selenides from alkynes. In addition to the selenium species discussed in Sections 2.1 and 2.2, other selenium sources can be used in the synthesis of vinyl selenides, such as sodium selenide, selenium dichloride and dibromide, elemental selenium in the presence of $NaBH_4$, PhSe-Bpin, β-hydroxy-, β-amino-, and β-mercapto-selenols.

Thus, in 2019, Pistoia *et al.*[108] described the stereoselective synthesis of (*Z*)-vinyl selenides **11** through the reaction of sodium selenide with organic halides **4**, followed by the addition of the selenolate intermediate to alkynes **12** (Scheme 53). The reaction of sodium borohydride with elemental selenium in DMF at 0 °C for 30 min produced sodium selenide, which reacted with organic halides **4** under a nitrogen atmosphere, giving the selenolate. The nucleophilic addition of selenolate to alkynes **12** afforded vinyl selenides **11** in a one-pot reaction, in good yields and with high *Z*-stereoselectivity. The advantage of this method over other hydroselenation reactions is that it avoids preliminary preparation or handling of diorganyl diselenides or very unstable selenols, and also the use of transition-metal catalysts. This protocol was applied to a variety of alkynes **12**, both substituted with electron-withdrawing and electron-donating groups, as well as to benzyl-, heteroaryl-, and alkyl halides **4**, achieving the corresponding (*Z*)-vinyl selenides **12**. However, secondary halides **4** showed no reaction. The recovering of unreacted secondary halides is an indication that the product formation was hampered in the selenolate generation step, probably due to steric hindrance in the reaction with sodium selenide. The reaction was extended to n-butyltellurols, which were reacted with terminal alkynes **12** to give the corresponding (*Z*)-vinyl tellurides **70** in moderate yields.

Scheme 53



R^1 = Bn, Alk; R^2 = Ar, Alk; X = Br or Cl;
Y = Se, 31–80% (**11**), Te, 34–50% (**70**)

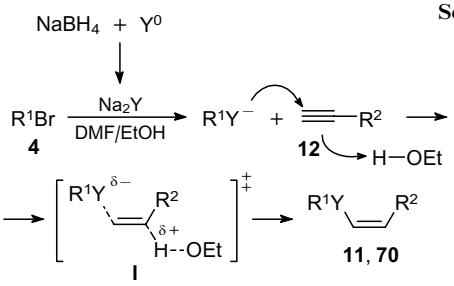
Selected examples

11: R^2 = Ph:
R^1 = Bu^n, 66%, 1.5 h (**c**);
Bn, 66%, 2.3 h (**i**);
$CH_2C_6H_4Me$-4, 50%, 4 h (**j**);
$CH_2C_6H_4Cl$-4, 50%, 4 h (**k**);
n-C_6H_{13}, 80%, 4 h (**l**);
$(CH_2)_2OH$, 54%, 4 h (**m**);
2-Py, X = Cl, 31%,
X = Br, 41% (**n**);
Pr^i, NR (**o**); Bu^i, NR (**p**);

R^1 = Bu^n:
R^2 = $CH_2C_6H_4Me$-4, 64%, 4 h (**q**);
C_6H_4Cl-4, 67%, 4 h (**r**);
$(CH_2)_2OH$, 50%, 4 h (**s**);
70: R^1 = Bu^n:
R^2 = Ph, 50%, 4 h (**a**);
$CH_2C_6H_4Me$-4, 37%, 4 h (**b**);
C_6H_4Cl-4, 34%, 4 h (**c**)

The proposed mechanism of the synthesis of vinyl chalcogenides **11** and **70** involves an *anti*-Markovnikov addition of a selenolate or tellurolate anion onto the triple bond of alkyne **12**, with a concomitant capture of a proton from EtOH giving intermediate **I** (Scheme 54). Thus, the *Z*-selectivity is attributed to the fact that this may be a concerted reaction, in which the carbon–selenium and the carbon–hydrogen bonds are formed in a single step.

Scheme 54

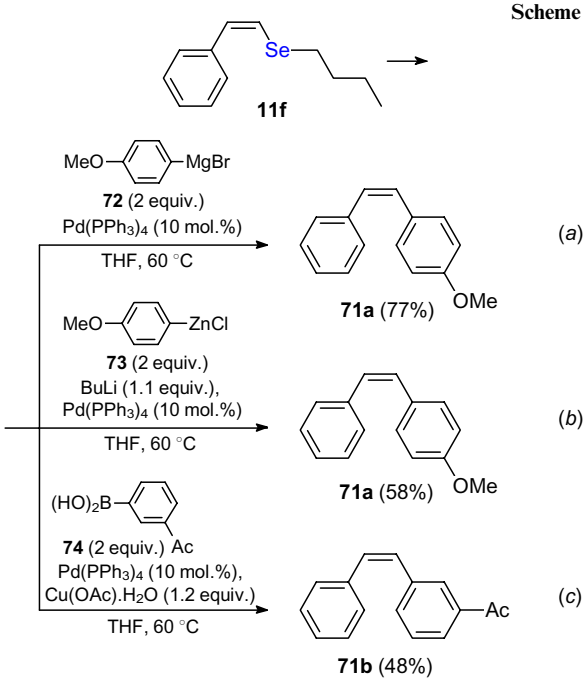


Y = Se (**11**), Te (**70**)

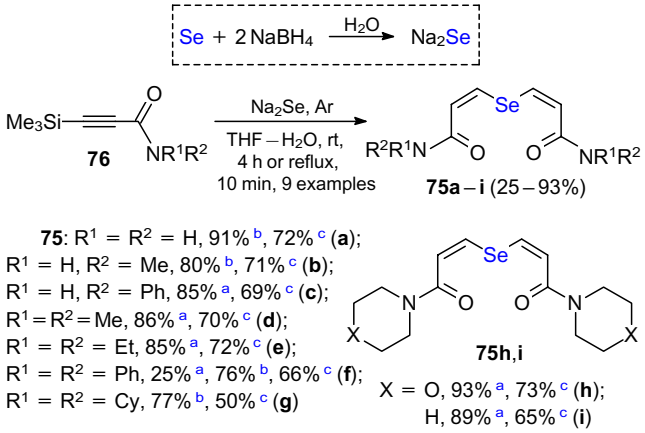
The synthetic application of the prepared vinyl selenides **11** was proven by the reaction of **11f** with Kumada,[109] Negishi[110] and Suzuki[111] substrates, affording the corresponding cross-coupled products **71a**,**b** in good yields (Scheme 55). The palladium-catalyzed Kumada cross-coupling between vinyl selenide **11f** and 4-methoxyphenyl magnesium bromide **72** afforded styrene derivative **71a** in 77% yield (Scheme 55 *a*). In the Negishi cross-coupling of **11f** with 4-methoxyphenyl zinc chloride **73**, bisaryl alkene derivative **71a** was obtained in 58% yield (Scheme 55 *b*). The Suzuki coupling of **11f** with 3-acetylphenylboronic acid **74**, in turn, afforded (*Z*)-(3-acetylaryl)styrene **71b** in 48% yield (Scheme 55 *c*).

In 2020, Andreev *et al.*[112] described the synthesis and evaluated the biological properties of (*Z*,*Z*)-selanediyl-bis(2-propenamides) **75** (Scheme 56). Bis(alkenyl) selenides **75** were obtained by the addition of sodium selenide to 3-(trimethylsilyl)-2-propynamides **76** in a THF — water

Scheme 55



Scheme 56

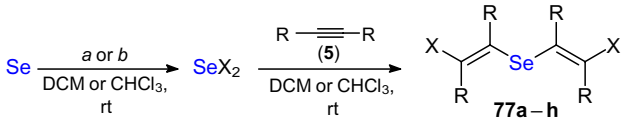


[a] THF/water ~ 1 : 3. A solution of **76** in THF was added to a hot aqueous solution of sodium selenide and the mixture was refluxed for 10 min.
[b] THF/water ~ 3 : 1. A solution of **76** in THF was added to a hot aqueous solution of sodium selenide and the mixture was refluxed for 10 min.
[c] Sodium borohydride was added portionwise to a mixture of **76**, selenium, THF and water and the mixture was stirred at room temperature for 4 h.

mixture under argon. In search for optimal reaction conditions, tests were carried out employing 3-(trimethylsilyl)-2-propynamides bearing various substituents (*e.g.*, phenyl, alkyl, cyclohexyl, morpholine and piperidine) in the amide moieties **76**, varying the ratio of the solvents in the THF–water system and the temperature. The higher yields of (*Z*,*Z*)-selanediylbis(2-propenamides) **75** (76–93%) were obtained when the reaction mixtures were refluxed for 10 min in 1 : 3 and 3 : 1 THF–water mixtures (see Scheme 56, conditions a, b). Additionally, the glutathione peroxidase-like activity of compounds **75** was evaluated, and very promising results were found.

In 2022, Musalov *et al.*[113] published the click-synthesis of bis[(*E*)-2-chlorovinyl] selenides **77a**–**d** and bis[(*E*)-2-bromovinyl] selenides **77e**–**h** in quantitative yields *via* the reaction of selenium dichloride or dibromide with alkynes **5** (Scheme 57). The reactions proceeded at room temperature through an *anti*-addition, achieving products exclusively with *E*-stereochemistry. Promising results were obtained in the studies on the glutathione peroxidase-like activity of the compounds **77**.

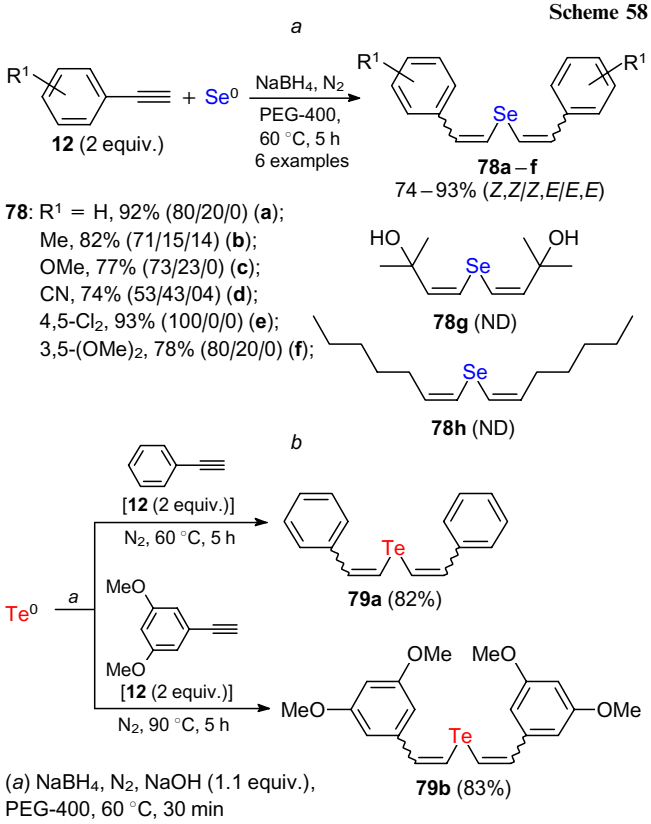
Scheme 57



(*a*) SO_2Cl_2; (*b*) Br_2; R = Me, Et, Pr^n, Bu^n;
77: X = Cl, 100% (**a**–**d**); Br_2, 100% (**e**–**h**)

In 2017, we reported the addition of sodium selenide species to aryl alkynes **12**, affording several divinyl selenides **78** (Scheme 58 *a*).[114] The nucleophilic species was generates *in situ* from the reaction of elemental selenium with $NaBH_4$ in PEG-400. The main advances achieved in this synthesis include the use of a green solvent, high selectivity, base-free

Scheme 58



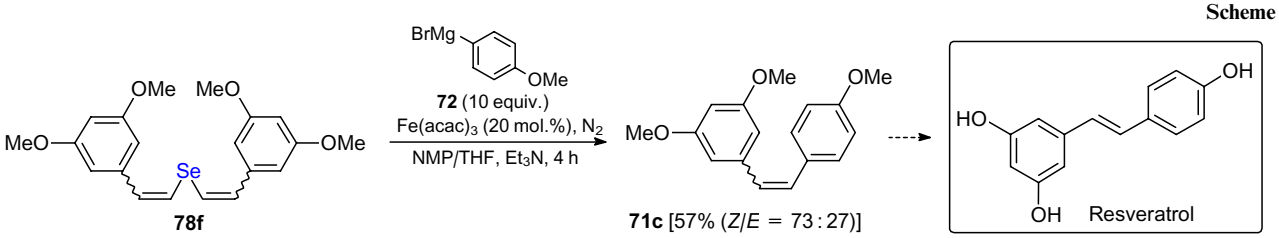
(*a*) $NaBH_4$, N_2, NaOH (1.1 equiv.), PEG-400, 60 °C, 30 min

and one-pot procedure, higher atomic efficiency compared to other protocols and fewer by-products. The reaction scope comprised various aryl alkynes **12**, and the desired products **78a**–**f** were obtained in good to excellent yields, with high selectivity to the (*Z*,*Z*)-isomer.

The presence of the strong electron–donating MeO substituent in the acetylene counterpart reduced its reactivity, and to attain good yields of the respective divinyl selenides **78c**,**f**, higher temperature (90 °C) was required. In contrast, 3,4-dichlorophenyl acetylene **12** produced the respective (*Z*,*Z*)-divinyl selenide **78e** in 93% yield as the single isomer, while 4-ethynylbenzonitrile **12** afforded the corresponding divinyl selenide **78d** as a mixture of (*Z*,*Z*)-, (*Z*,*E*)- and (*E*,*E*)-isomers in a 53 : 43 : 4 ratio in 74% overall yield (see Scheme 58 *a*). On the other hand, 1,1-dimethylpropargyl alcohol and hept-1-yne proved to be unsuitable substrates. This protocol was extended to elemental tellurium to form (*Z*,*Z*)-divinyl tellurides **79a**,**b** in good yields using the system $Te^0/NaBH_4$/PEG-400 in the presence of NaOH at 60 °C (see Scheme 58 *b*). Furthermore, the Fe-catalyzed stereoconservative cross-coupling reaction of bis(3,5-dimethoxystyryl) selenide **78f** with (4-methoxyphenyl)magnesium bromide **72** was carried out to produce the polymethoxylated stilbene **71c**, which is a pharmaceutically relevant precursor of resveratrol (Scheme 59).

García-Lopez *et al.*[115] described the *anti*-3,4-selenoboration of electron-deficient alkynes to prepare β-vinyl selenides **80**. The reaction occurred between α,β-acetylenic esters **31** or amides **46**, in the presence of C_6H_5Se-Bpin at 50 °C for 16 h, and the products **80** were obtained in good yields, only with *Z*-configuration (Scheme 60 *a*). Moreover, with the addition of a catalytic amount of PCy_3, the *anti*-3,4-selenoboration occurred to form the α-vinyl selenides **81**, which can undergo a protodeboronation with K_2CO_3 to

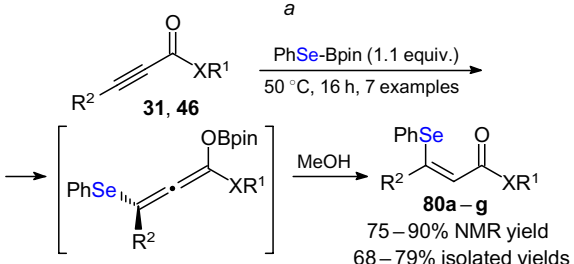
Scheme 59



acac is acetylacetonate, NMP is *N*-methylpyrrolidone

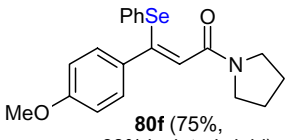
Scheme 60

a



80: X = O, R^1 = Et:
R^2 = Ph, 82%, 74% [a] (**a**);
C_6H_4OMe-4, 89%, 78% [a] (**b**);
n-Hex, 90%, 79% [a] (**c**);
R^2 = C_6H_4OMe-4:
R^1 = Pr^n, 75%, 72% [a] (**d**);
Pr^i, 88%, 69% (**e**);
X = N, R^1 = Me,
R^2 = C_6H_4OMe-4, 89%, 76% [a] (**g**)

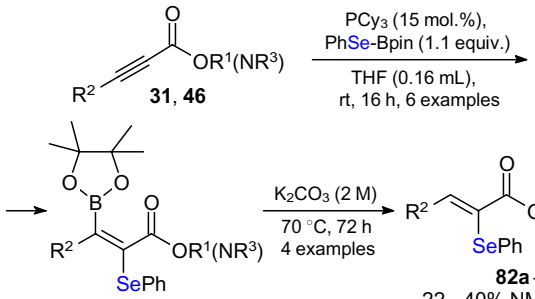
[a] Isolated yield



80f (75%, 68% isolated yield)

Bpin is pinacolboryl

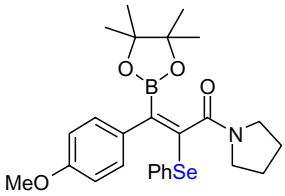
b



Compound	X	R^1	R^2	Yield (%)	
				81	**82**
a	O	Et	Ph	63	22
b	O	Et	C_6H_4OMe-4	60, 5 [a]	33, 21 [a]
c	O	Pr^n	C_6H_4OMe-4	79, 23 [a]	22, 13 [a]
d	O	Pr^i	C_6H_4OMe-4	66, 31 [a]	40, 31 [a]

[a] Isolated yield.

R^3 = Me, R^2 = C_6H_4OMe-4, 81% (**81e**)



81f (85%)

generate the respective α-hydroselenated compounds **82** (Scheme 60 *b*).

Tanini *et al.*[116] developed an approach to unsymmetrical functionalized alkyl vinyl selenides **83** by the reaction of β-hydroxy- (**84**), β-amino- (**85**) or β-mercapto-selenols **86** with electron-deficient alkynes **87** (Scheme 61). The best reaction conditions included the use of Al_2O_3 in toluene at room temperature, affording products **83** in good yields with moderate diastereoselectivity (see Scheme 61 *a*).

Compounds **83a**,**b** were shown to be unstable in $CHCl_3$, giving the products **88a**,**b** in 96% and 98% yields, respectively, by an intramolecular oxa-Michael reaction (see Scheme 61 *b*). The compound **83c** suffered an intramolecular thia-Michael reaction to form compound **89a** in 92% yield (see Scheme 61 *c*). Additionally, substrate **90** generated compound **89b** in 83% yield by reacting with but-3-yn-2-one **91** through sequential seleno-Michael and thia-Michael reactions (see Scheme 61 *d*). The same starting material **90**, after reaction with diethyl but-2-ynedioate **87b**, afforded heterocyclic compound **92** in 57% yield *via* vinyl selenide intermediate **I** (see Scheme 61e). Products **83** cyclized in the presence of NaH in THF at low temperature (−30 to −15 °C) to form 2-oxo-1,4-oxaselenane **93** in 63–78% yield. Instead, if the reaction temperature is allowed to reach room temperature, products **94a** and **94b** are obtained in 77% and 55% yield, respectively (see Scheme 64 *f*). In the same study, the catalytic antioxidant activity as GPx mimics of 2-oxo-1,4-oxaselenanes **93** was evaluated, and compound **93a** proved to be a more active catalyst.

3. Transition metal-promoted synthesis of vinyl selenides

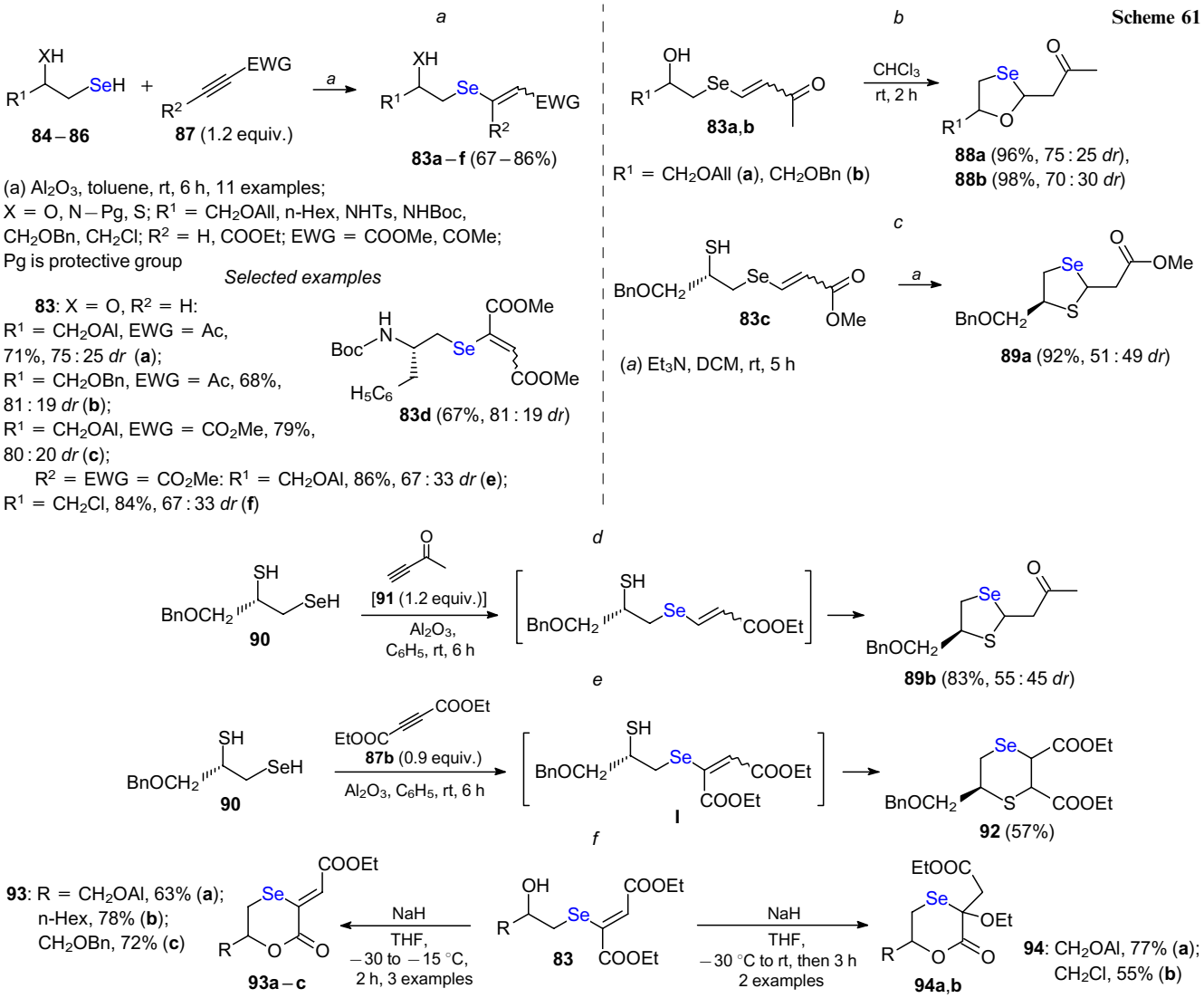
Transition metal-catalyzed transformations have become a powerful tool for the synthesis of vinyl selenides, allowing the formation of C–Se bond with high stereo- and regioselectivity under mild reaction conditions. This approach avoids the need of prefunctionalization of the starting material, allowing expanding the substrate scope. To a better discussion, this Section was divided into two subsections relating to the use of copper catalysts (3.1) and other transition metal catalysts (3.2).

3.1. Copper-catalyzed reactions

Due to its low cost, abundance, and relatively low toxicity, copper appears in numerous publications describing the synthesis of vinyl selenides. Different species of copper, such as halides, carboxylates and tetrakis(acetonitrile)copper(I)-hexafluorophosphate have been used as catalysts.

In 2017, Singh *et al.*[117] described the preparation of (*Z*)-vinyl selenides **95** *via* C–H selenynation of acrylamides **96** with diorganyl diselenides **13** using a copper – manganese

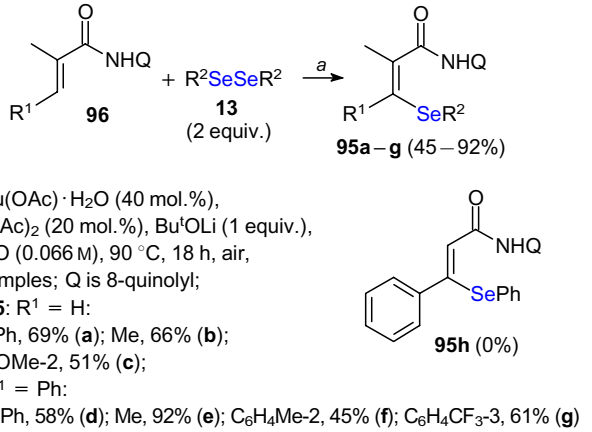
Scheme 61



dual catalytic system (Scheme 62). This protocol takes advantage of the direct C–H activation strategy, avoiding additional prefunctionalization steps, the use of stoichiometric metal oxidants, and expensive ruthenium, rhodium or palladium catalysts. However, with α-unsubstituted acrylamide **96**, the expected product **95h** was not obtained.

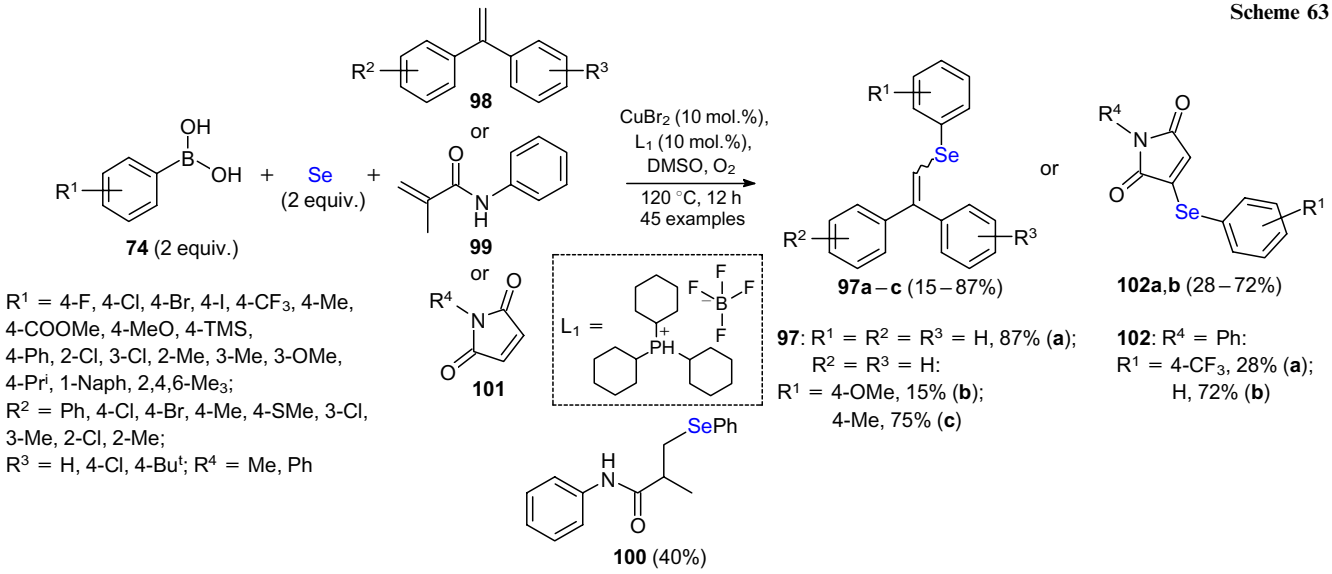
Yang *et al.*[118] developed a three-component Cu-catalyzed synthesis of vinyl selenides **97**. For the first time, easily accessible selenium powder was used as a selenium source in the reaction of arylboronic acids **74** with diarylethylenes **98** to give the corresponding products **97** (Scheme 63). The reaction well tolerated diversely substituted arylboronic acids **74**, such as bearing halogens, electron-donating, and electron-withdrawing groups. Moreover, various diarylethylenes **98** were employed, including unsymmetric ones, which gave 1 : 1 mixtures of *E*- and *Z*-isomers in most cases. Unfortunately, with heterocyclic and alkylboronic acids, the reaction did not occur. In the case of heterocycles, reason for the lack of reactivity is probably the coordination of the metal with the heteroatom. Interestingly, *N*-phenylmethacrylamide **99** reacted under optimal conditions to afford the addition product **100** instead of the expected vinyl selenide, while maleimides **101** were converted to selenol ethers **102**.

Scheme 62

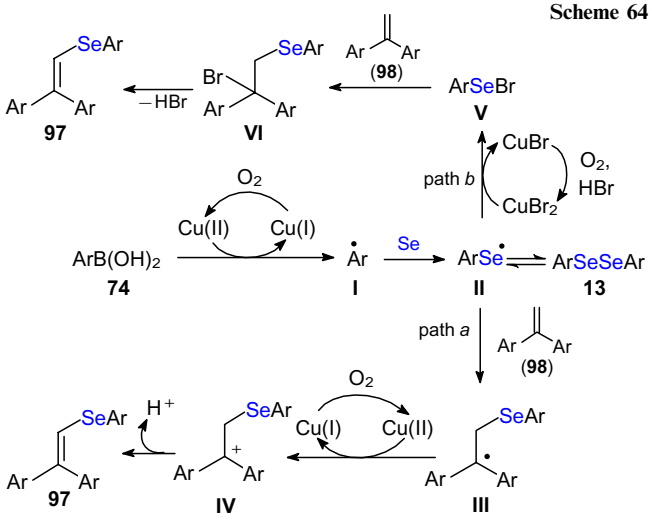


A plausible mechanism for the formation of vinyl selenides **97** involves firstly the reaction between arylboronic acid **74** and Cu(II) to generate the aryl radical **I** (Scheme 64). Next, this radical activates selenium to form intermediate **II**, which adds to diarylethylene **98**, giving the radical species **III**. A single electron transfer occurs between **III** and Cu(II) affording intermediate **IV**, which is deprotonated to give product **97** (see Scheme 64, path *a*). In parallel, another mechanism is possible, which implies the reaction

Scheme 63



Scheme 64

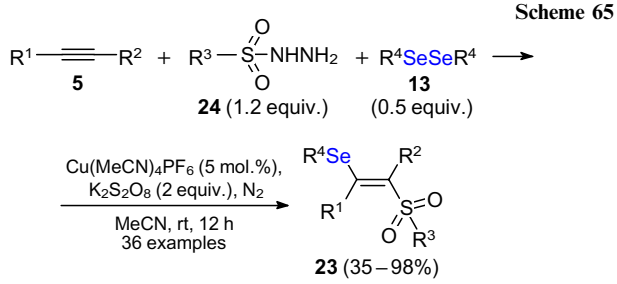


of radical **II** with $CuBr_2$ to form the electrophilic species ArSeBr (**V**). Then, **V** adds to substrate **98** forming intermediate **VI**, which eliminates HBr to afford product **97** (see Scheme 64, path *b*).

In 2017, Liu *et al.*[119] reported the copper-catalyzed regio- and stereospecific selenosulfonation of alkynes **5** with arylsulfonohydrazides **24** and diorganyl diselenides **13** as an approach to (*E*)-β-selenovinyl sulfones **23** (Scheme 65). The optimized reaction conditions include the use of $Cu(MeCN)_4PF_6$ as a catalyst and $K_2S_2O_8$ as an oxidant in MeCN. Both internal and terminal alkynes **5** bearing alkyl or aryl substituents react with arylsulfonylhydrazides **24** (and diorganyl diselenides **13** to provide thirty-six (*E*)-β-selenovinyl sulfones **23** in poor to excellent yields. The main advantages of this protocol are the use of mild reaction conditions (room temperature) and a broad scope of substrates. However, its utility is limited to the use of diphenyl and dimethyl diselenides **13**.

The plausible reaction mechanism comprises the generation of the sulfonyl radical **I** in the presence of copper salt and $K_2S_2O_8$ *via* a single electron transfer (SET) and deprotonation process, along with the release of N_2 from the aryl sulfonohydrazides **24** (Scheme 66). Then, the sulfonyl radical **I** regiospecifically adds to alkyne **5**, producing the relatively stable β-sulfonyl vinyl radical **II**. Subsequently, the phenyl selenol group is transferred from diphenyl diselenide **13a** to **II** through the coupling between **II** and phenyl selenol radical to afford thermodynamically stable (*E*)-β-selenovinyl sulfone **23**. Alternatively, the phenyl selenol group transfer might be faster than the inversion of **II**, thus forming a single isomer **23**.

Scheme 65



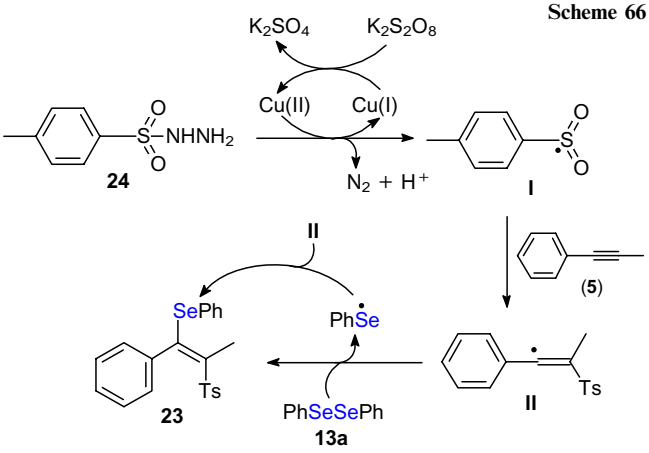
R1 = Ar, Alk; R2 = Alk, H; R3 = Ar; R4 = C_6H_5, Me

Selected examples

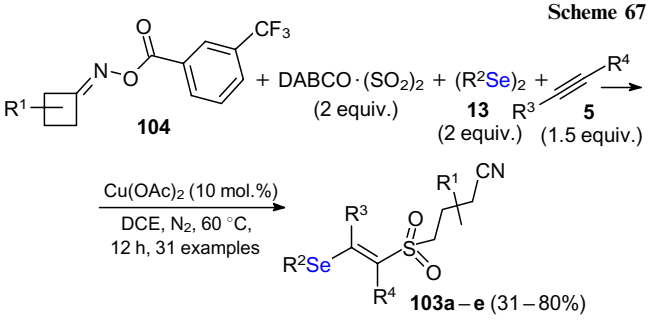
23: R1 = R4 = Ph, R3 = C_6H_4Me-4:
R2 = Me, 98% (**u**); H, 95% (**j**); Prn, 93% (**ad**); Ph, 42% (**t**);
R1 = $C_6H_3Me_2$-3,4, R2 = Prn, R4 = Ph, 79% (**ae**);
R2 = Prn, R3 = C_6H_4Me-4, R4 = Ph:
R1 = C_6H_4OMe-2, 88% (**af**); $C_6H_3F_2$-2,4, 75% (**ag**); C_6H_4Br-4, 93% (**ah**);
R4 = Ph, R2 = Me:
R3 = C_6H_4OMe-4, 79% (**ai**); $C_6H_2Me_3$-2,4,6, 82% (**aj**); C_6H_4Cl-4, 75% (**ak**);
R2 = H, R3 = C_6H_4Me-4, R4 = Ph:
R1 = C_6H_4Cl-4, 92% (**al**); C_6H_4CN-4, 63% (**am**); $C_6H_4NO_2$-3, 42% (**an**); C_6H_4Me-4, 94% (**c**); C_6H_4Me-3, 86% (**ao**);
R3 = C_6H_4Me-4, R4 = Ph:
R1 = R2 = Et, 47% (**ap**); R1 = Bun, R2 = H, 85% (**v**);
R1 = TMS, R2 = H, 64% (**aq**); R1 = Ph, R2 = H, 35% (**ar**)

In 2021, He *et al.*[120] described the copper-catalyzed synthesis of β-cyanoalkylsulfonylated vinyl selenides **103** *via* a four-component reaction between cycloketone oxime esters **104**, $DABCO(SO_2)_2$, diselenides **13**, and alkynes **5** (Scheme 67). A broad scope is an advantage of this method, and different alkynes **5**, such as terminal and internal ones bearing electron-rich, -neutral or -poor substituents, includ-

Scheme 66

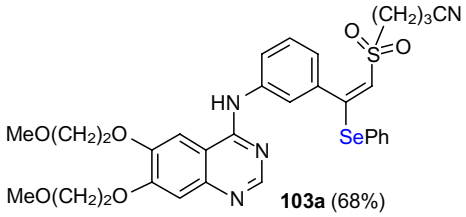


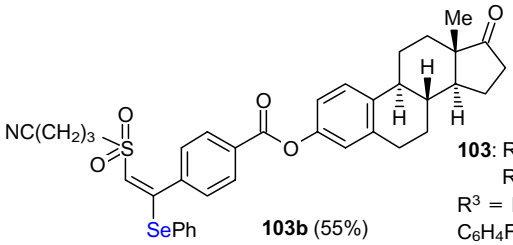
Scheme 67



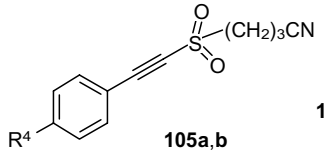
R^1 = H, CO_2Bn, CO_2Bu^t, Ph, OCH_2Ph, CH_2OCH_2Ph, NHC(O)OBn, cycloalkyl; R^2 = Ar; R^3 = H, Ar, Alk, Het; R^4 = H, Me, Ph, CO_2Me

Selected examples





103: R^1 = R^4 = H, R^2 = Ph: R^3 = Ph, 70% (**c**); C_6H_4F-2, 80% (**d**); Cy, 31% (**e**)

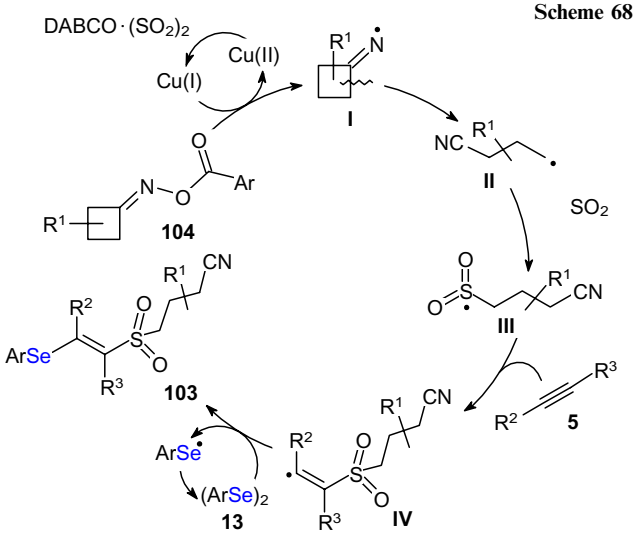


105: R^4 = H, 57% (**a**); Cl, 72% (**b**)

ing heteroaryl and aliphatic moieties, were employed and all of them afforded vinyl selenides **103** in moderate to good yields. Additionally, diversely substituted cycloketone oxime esters **104** along with several disubstituted diselenides **13** were well tolerated. A late-stage functionalization of drug derivatives afforded products **103a** and **103b** in 68% and 55% yields, respectively. Noteworthy, the oxidation of selected vinyl sulfides **103** with H_2O_2 in THF afforded alkynyl sulfones **105a**,**b**, which are elusive by other known methods (see Scheme 67).

The first step of the reaction is the formation of intermediate **I** through a copper-catalyzed single electron reduction of substrate **104**. Once formed, species **I** undergoes the ring-opening to give intermediate **II**, which reacts with SO_2 to generate radical **III**. In the sequence, **III** adds to alkyne **5** leading to the vinyl radical **IV**, which reacts with diselenide **13** to give the desired product **103** and radical ArSe$^{\bullet}$ (Scheme 68).

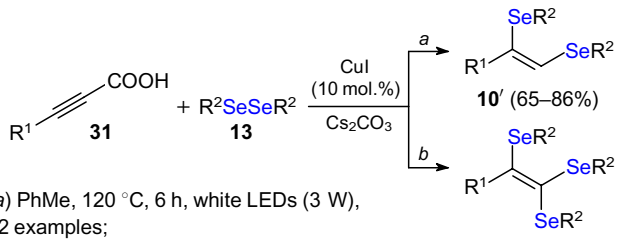
Scheme 68



In 2018, Chen *et al.*[121] reported a novel highly efficient synthesis of 1,2-bis- (**10′**) and tris-selanyl alkenes **106** through the reaction between available and cheap alkynyl carboxylic acids **31** and diselenides **13** under mild conditions (Scheme 69). The best reaction conditions include irradiation of the reaction mixture with a white LED (3 W).

The 1,2-bis-selanyl alkenes **10′** were obtained in good to very good yields (see Scheme 69 *a*). A wide range of substrates **31** proved to be well tolerated in this process, such as

Scheme 69



(*a*) PhMe, 120 °C, 6 h, white LEDs (3 W), 12 examples;
(*b*) NMP, 120 °C, 6 h; **13** (1.33 equiv.), 11 examples;
R^1 = H, Ar, Alk; R^2 = Ar

10: R^1 = H, R^2 = Ph, 77%, 72% (**p′**); R^1 = Ph: R^2 = C_6H_4Me-4, 70% (**b′**); C_6H_4Br-4, 65% (**q′**); R^2 = Ph: R^2 = C_6H_4Me-4, 86% (**f′**); $C_6H_4CF_3$-4, 84% (**r′**); Bu^t, 68% (**s′**)

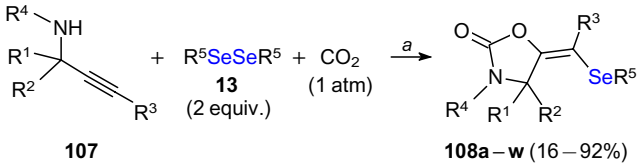
106: R^2 = Ph: R^1 = H, 87% (**a**); C_6H_4Me-4, 72% (**b**); n-Hex, 86% (**e**); $C_6H_4Pr^n$-4, 78% (**f**); R^1 = Ph: R^2 = C_6H_4F-3, 79% (**c**); C_6H_4Cl-2, 77% (**d**)

aromatic, bearing both electron-donating and -withdrawing groups, *e.g.*, halogens, and aliphatic propiolic acids. When propiolic and but-2-ynedioic acids **31** were used, product **10p′** was obtained in 77% and 72% yields, respectively. Instead, with hept-2-ynoic acid **31**, the corresponding product did not form. Moreover, alkenes **10b′** (Ar = 4-MeC_6H_4) and **10q′** (Ar = 4-BrC_6H_4) were obtained in 70% and 65% yields from the appropriate diphenyl diselenides **13**. To prepare tris-selanyl alkenes **106**, 2 equiv. of Cs_2CO_3 and NMP as a solvent were used, without the LED irradiation (see Scheme 69 *b*). Good results were obtained for all studied substrates **31**. Interestingly, product **106a** was obtained in 87% yield starting from both propiolic and propionic acids. Under these conditions, 1,2-bis(3-fluorophenyl) diselenide and 1,2-bis(2-chlorophenyl) diselenide were converted to the respective tris-selanyl alkenes **106c** and **106d** in 79% and 77% yield.

The reaction mechanism starts with the generation of intermediate **I** through the reaction of acid **31** and the base in the presence of the copper salt; in parallel, the PhSe$^{\bullet}$ radical species is formed from diphenyl diselenide **13a** under light irradiation. Then, intermediate **I** and selenium radical react to give intermediate **II**, which undergoes a decarboxylation to afford species **III**. Following protonation, it forms product **10′**. When an excess of base is used in the absence of light irradiation, intermediate **IV** is generated *via* the reaction of the selenolate anion and substrate **31**. In the sequence, species **IV** is decarboxylated to give **V**, which undergoes a reductive elimination affording compound **VI**. Then, it reacts with selenium cation, thus generating seleniranium intermediate **VII**, which is ring-opened by the selenolate anion to give **VIII**, thereby finally affording product **106** after releasing copper(I) for a new reaction cycle (Scheme 70).

In 2020, Chen *et al.*[122] described the electrophilic oxyselenation of propargyl amines **107** with diorganyl diselenides **13** and CO_2 under atmospheric pressure promoted by copper/DTBP, to obtain selanyl 2-oxazolidinones **108** (Scheme 71). The carboxylative cyclization reaction between propargylic amines and CO_2 is an attractive strategy to construct valuable 2-oxazolidinones. However, the previously reported methods have certain restrictions, such as high reaction temperature, high CO_2 pressure, complicated catalytic systems, or limited substrate scopes. In contrast, the above-mentioned protocol offers mild reaction conditions and high atom- and step-economy, broad substrate scope and good yields of the products. The protocol was suitable to terminal and internal propargyl amines **107**, with both electron-donating and electron-withdrawing groups in the pendant phenyl ring of the *N*-moiety. The substrates **107** containing *N*-cyclohexyl, *N*-phenyl, *N*-butyl,

Scheme 71

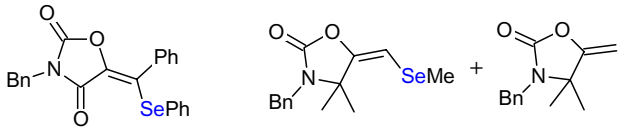


107 **108a – w** (16 – 92%)

(*a*) CuOAc (20 mol.%), DTBP (1 equiv.), Cs_2CO_3 (2 equiv.), DMSO, rt, 11 h, 42 examples;
R^1 = H, Alk; R^2 = H, Alk, Ar; R^3 = H, Ar, Alk;
R^4 = H, Bn, Alk; R^5 = Ar, Alk, Het

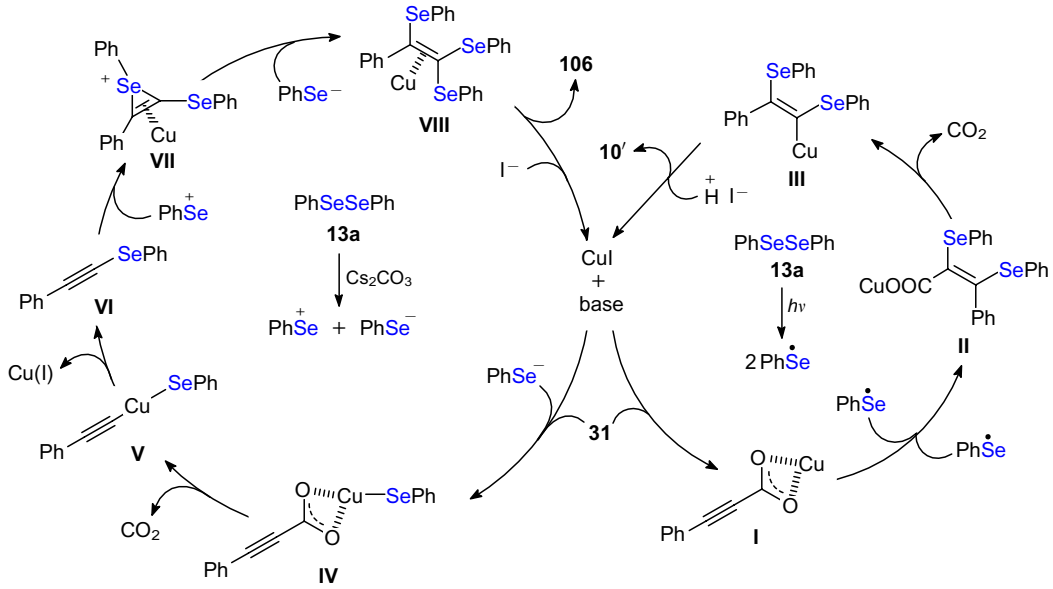
Selected examples

108: R^1 = R^2 = Me, R^3 = H, R^5 = Ph:
R^4 = Bn, 90% (**a**); $CH_2C_6H_4OMe$-4, 90% (**b**); $CH_2C_6H_4Cl$, 79% (**c**); Cy, 75% (**g**); Ph, 92% (**h**);
R^1 = R^2 = Me, R^3 = R^5 = Ph:
R^4 = Bn, 81% (**d**); $CH_2C_6H_4OMe$-4, 75% (**e**); $CH_2C_6H_4Cl$, 85% (**f**); Bu^n, 80% (**i**); H, 0% (**j**);
R^1 = R^2 = Me, R^3 = Bn, R^5 = Ph:
R^3 = n-Hex, 77% (**k**); $CH_2C_6H_4OMe$-4, 90% (**l**); $CH_2C_6H_4Br$-4, 76% (**m**);
R^1 = Me, R^2 = Et, R^3 = H, R^4 = Bn, R^5 = Ph, 88% (**n**);
R^1 = R^2 = R^3 = H, R^4 = Bn, R^5 = Ph, 79% (**o**);
R^1 = R^2 = Me, R^3 = H, R^4 = Bn:
R^5 = $CH_2C_6H_4OMe$-4, 57% (**q**); $CH_2C_6H_4Cl$-4, 72% (**r**); $CH_2C_6H_4Me$-2, 51% (**s**); 1-Naph, 69% (**t**); Py, 47% (**u**);
R^1 = R^2 = Me, R^3 = Ph, R^4 = Bn, R^5 = Me, 42% (**w**)



108p (16%) **108v** (30%) **109** (30%)

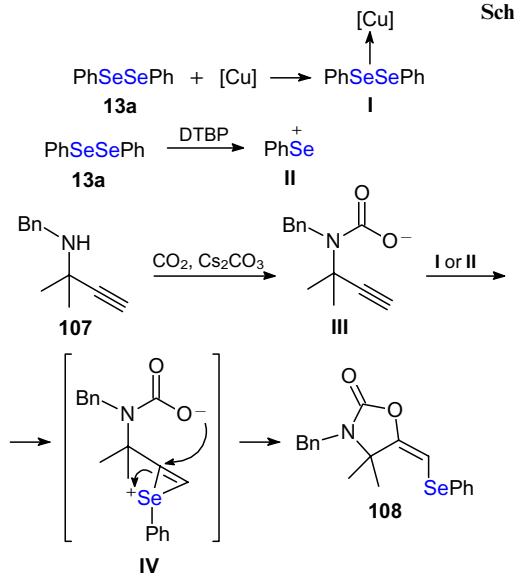
Scheme 70



as well as the aliphatic propargyl amine reacted smoothly to produce the desired products **108g**–**i**,**k** in 75–92% yield. However, the primary propargyl amine **107j** proved to be an unstable substrate and decomposed under the standard conditions, thus the corresponding product **108j** could not be obtained. Good results were obtained using terminal propargyl amines **107n**,**o** with both di- and unsubstituted propargylic position and *N*-benzylprop-2-yn-1-amine afforded the respective products **108n** and **108o** in 88% and 79% yields. Interestingly, *N*-benzyl-3-phenylpropiolamide reacted under the optimized conditions to give the desired selanyl oxazolidine-2,4-dione **108p** in as low as 16% yield. A variety of diaryl- and diheteroaryl diselenides **13** successfully reacted with **107q**–**u** to give products **108q**–**u** in moderate to good yields. It is worth to mention that dimethyl diselenide reacted with *N*-benzyl-4-methyl-4-phenylpent-1-yn-3-amine to afford a 1 : 1 mixture of **108v** (30%) and **109** (30%). This problem was not observed when *N*-benzyl-2-methyl-4-phenylbut-3-yn-2-amine was used instead of the terminal compound, yielding the respective product **108w** in 42% yield.

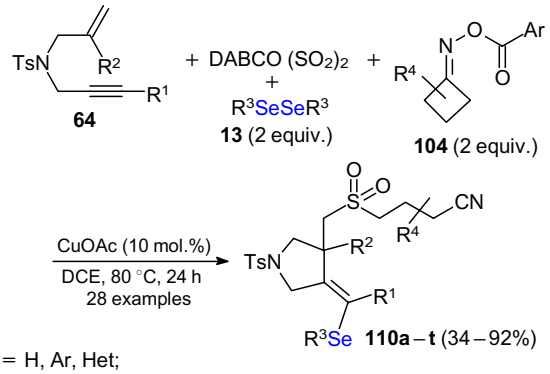
The proposed mechanism involves, initially, the reaction of the copper salt and diphenyl diselenide **13a** to give a copper-seleno complex **I**, which can enhance the electrophilicity of the selenium atom (Scheme 72). Alternatively, diselenide **13a** can be oxidized by DTBP to generate a $C_6H_5Se^+$ intermediate **II**. Moreover, propargyl amine **107** reacts with CO_2 in the presence of Cs_2CO_3 to form carbamate **III**. Subsequently, **I** or **II** promotes an electrophilic addition to the triple bond of carbamate **III**, affording intermediate **IV**, which undergoes an intramolecular nucleophilic attack to produce the corresponding product **108**.

Scheme 72



Recently, He *et al.*[123] reported a copper-catalyzed regio- and chemoselective multicomponent reaction of 1,6-enynes **64**, diaryl diselenides **13**, DABCO·$(SO_2)_2$, and cycloketone oxime esters **104** (Scheme 73). This radical-triggered cyclization leads to the formation of four new bonds including the C–SO_2, C–C and C–Se ones in a single step. 1,6-Enynes **64** bearing aryl groups with different electron-donating, electron-withdrawing and heteroaromatic substituents underwent this transformation smoothly, leading to desired cyanoalkylsulfonylated pyrrolidines **110** in moderate to good yields. Noteworthy, substrates with versatile functional groups, such as trifluoromethoxy, cyano, fluoro, chloro, aldehyde or ester ones, were compatible with this reaction. The scope was expanded to various cycloketone oxime esters **104** affording the expected products **110** in good yields. Despite the significant advances, the scope of the diorganyl diselenides could have been further explored, since only three aryl diselenides were used in the study.

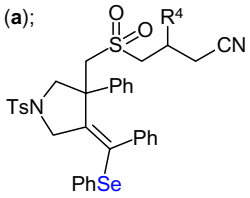
Scheme 73



R^1 = H, Ar, Het;
R^2, R^3 = Ar; R^4 = Ph, OBn, CO_2Bn, CO_2Bu^t; Ar = $C_6H_4CF_3$-4

Selected examples

110: R^1 = R^2 = R^3 = Ph, R^4 = H, 86% (**a**);
R^1 = R^4 = H, R^2 = R^3 = Ph, 34% (**b**);
R^2 = R^3 = Ph, R^4 = H:
R^1 = C_6H_4Me-4, 82% (**c**);
$C_6H_4OCF_3$-4, 72% (**d**);
$C_6H_4OCF_3$-3, 82% (**e**);
C_6H_4CN-4, 67% (**f**);
C_6H_4F-4, 77% (**g**); C_6H_4Cl-4, 83% (**h**);
C_6H_4CHO-4, 69% (**i**);
$C_6H_4CO_2Me$-4, 72% (**j**); 3-Py, 54% (**k**);
2-Th, 74% (**l**);
R^1 = R^3 = Ph, R^4 = H:
R^2 = C_6H_4Me-4, 76% (**m**);
C_6H_4Cl-4, 86% (**n**);
R^1 = R^2 = Ph, R^4 = H:
R^3 = C_6H_4Me-4, 67% (**o**); C_6H_4Br-4, 81% (**p**)



dr = 1 : 1 all:
R^4 = Ph, 75% (**q**);
CH_2OBn, 92% (**r**);
CO_2Bn, 68% (**s**);
CO_2Bu^t, 57% (**t**)

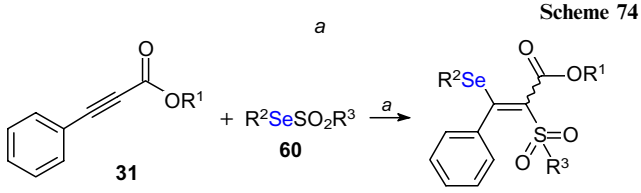
3.2. The use of other transition metal catalysts

In addition to copper, other metal catalysts were used in the synthesis of vinyl selenides. These include cobalt oxalate, iron(III) chloride and rhodium(II) acetate, which found application in reactions with a wide range of substrates under mild reaction conditions (room temperature, photocatalysis and short reaction times).

In 2019, Zhang *et al.*[124] developed the visible light-induced Co- or Cu-catalyzed selenosulfonylation of alkynes **31** and **46** with selenosulfonates **60** to produce β-(seleno)-vinyl sulfones **111** and **112** (Schemes 74, 75). Key features of the reaction include excellent functional group tolerance and the use of readily available reagents and inexpensive transition metals, instead of precious metals, as catalysts in a photoreaction. The reaction between various types of alkyne esters **31** and aryl(or alkyl) selenosulfonates **60** was carried out using CoC_2O_4 as a catalyst in acetonitrile and under argon atmosphere and under irradiation with blue LED to give β-(seleno)vinyl sulfones **111a**–**j** in poor to good yields (see Scheme 74 *a*).

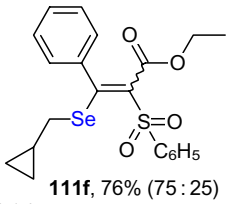
In the same work, selenosulfonylation of alkynamides **46** with selenosulfonates **60** was also studied using Cu(0) as

Scheme 74

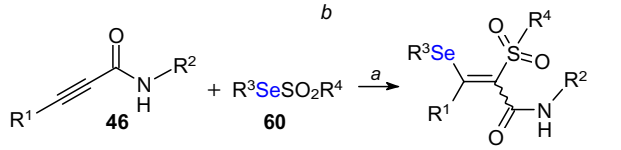


(*a*) CoC_2O_4 (5 mol.%), Ar, blue LED, MeCN, rt, 4 h, 10 examples

111: R^1 = Et, R^3 = H: R^2 = Ph, 86% (75 : 25) (**a**); C_6H_4Br-4, 70% (62 : 38) (**b**); R^2 = R^3 = Ph: R^1 = $(CH_2)_2Ph$, 75% (50 : 50) (**c**); $CH_2C_6H_4OMe$-3, 39% (70 : 3) (**d**); R^1 = Et, R^2 = Bu^s, R^3 = Ph, 87% (90 : 10) (**e**); R^1 = Et, R^2 = Ph: R^3 = C_6H_4Cl-4, 80% (67 : 33) (**g**); C_6H_4F-4, 80% (70 : 30) (**h**); C_6H_4Me-4, 82% (62 : 38) (**i**); Me, 66% (62 : 38) (**j**)



111f, 76% (75 : 25)



(*a*) Cu (2 mol.%), Ar, blue LED, MeCN, rt, 4 h, 14 examples; R^1 = Ar, Het; R^2, R^3, R^4 = Alk, Ar

112a–**k**, 45–96% (*E* : *Z*)

Selected examples

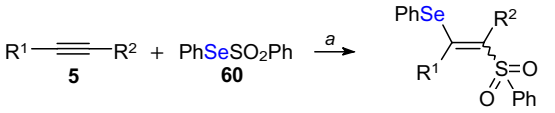
112: R^1 = R^3 = R^4 = Ph: R^2 = Bu^t, 87% (89 : 11) (**a**); Bu^n, 86% (67 : 33) (**b**); $C_6H_4CF_3$-4, 86% (67 : 33) (**c**); C_6H_4Me-3, 89% (86 : 14) (**d**); R^1 = R^3 = Ph, R^2 = Bu^t: R^4 = Me, 75% (69 : 31) (**e**); C_6H_4Cl-4, 78% (59 : 41) (**f**); C_6H_4Me-4, 96% (60 : 40) (**g**); R^1 = R^4 = Ph, R^2 = Bu^t, R^3 = Bu^s, 45% (81 : 19) (**h**); R^1 = C_6H_4OMe-4, R^2 = Bu^t, R^3 = R^4 = Ph, 92% (62 : 38) (**i**); R^2 = Bu^t, R^3 = R^4 = Ph: R^1 = 3-Py, 71% (67 : 33) (**j**); $C_6H_4CO_2Me$-4, 88% (67 : 33) (**k**)

a catalyst instead of CoC_2O_4 (see Scheme 74 *b*). A total of fourteen β-(seleno)vinyl sulfones **112** were obtained in poor to good yields from alkynamides **46** bearing both electron-withdrawing and -donating groups, as well as aryl or alkyl selenosulfonates **60** as substrates.

In addition, the authors investigated the formation of β-(seleno)vinyl sulfones **113** from differently substituted alkynes **5**, under cobalt oxalate and copper catalysis (see Scheme 75). Curiously, but-3-yn-1-yl-4-methylbenzenesulfonate and the terminal alkyne bearing a heterocyclic ring gave the desired products **113a**–**c** with high regio- and stereoselectivities.

The proposed reaction mechanism involves, first, the homolysis of selenosulfonate **60**, generating the sulfonyl and selanyl radicals in the presence of the metal catalyst and light irradiation (Scheme 76). The homocoupling of the selanyl radical forms R^3SeSeR^3 (**13**), while the sulfonyl radical reacts with alkynes **31**, **46** or **5** to produce intermediate **I**. Then, intermediate **I** and the metal atom coordinate to form intermediate **II**, which in turn interacts with the R^3SeSeR^3 giving intermediate **III** and releasing a selanyl radical. The reductive elimination of intermediate **III** affords products **111**, **112** or **113** and regenerates the catalyst.

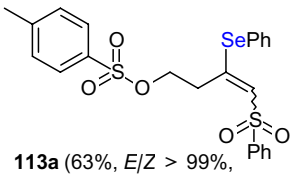
Scheme 75



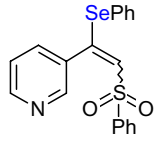
(*a*) CoC_2O_4 or Cu, Ar, blue LED, MeCN, rt, 4 h, 8 examples; R = Ar, Het; R^1 = H, SePh, Alk

113a–**f** (22–89%)

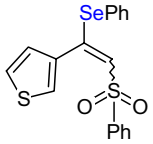
Selected examples



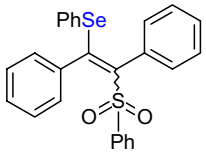
113a (63%, *E*/*Z* > 99%, catalyst: CoC_2O_4)



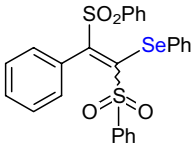
113b [89%, *E*/*Z* > 99%, catalyst: Cu(0)]



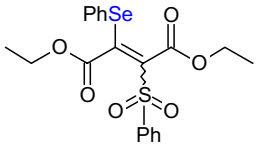
113c (71%, *E*/*Z* > 99%, catalyst: Cu(0)]



113d [69%, *E*:*Z* = 50:50 catalyst: Cu(0)]

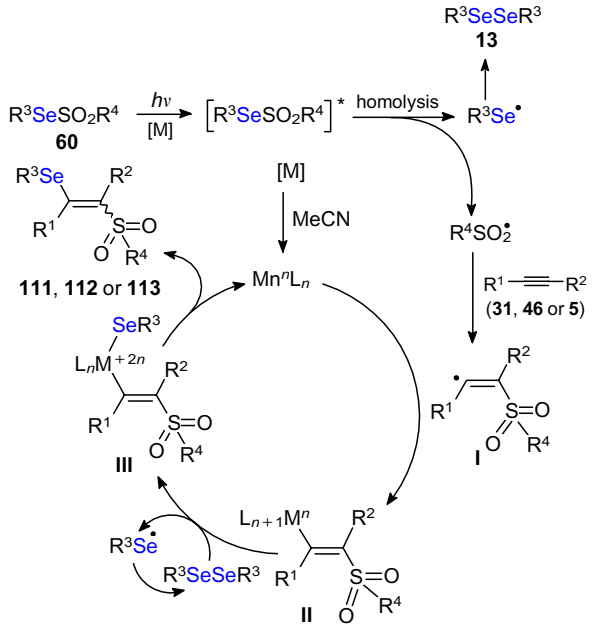


113e [22%, *E* : *Z* = 67 : 33, catalyst: Cu(0)]



113f (38%, *E* : *Z* = 75 : 25, catalyst: CoC_2O_4)

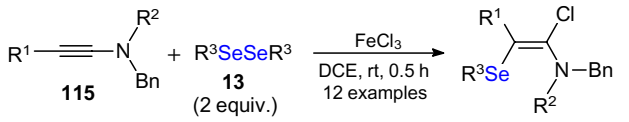
Scheme 76



affords products **111**, **112** or **113** and regenerates the catalyst.

In 2021, Goulart *et al.*[125] reported a strategy to prepare (*E*)-α-chloro-β-(organoselanyl) enamides **114** from ynamides **115** and diorganyl diselenides **13** in the presence

Scheme 77



R^1, R^3 = Ar; R^2 = Ts, Ms

Selected examples

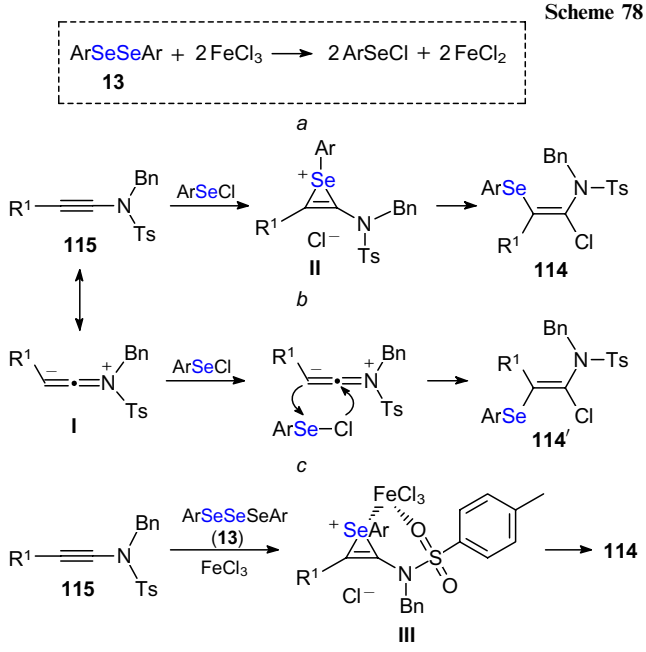
114: R^1 = R^3 = Ph, R^2 = Ts, 60% [a] (84%) [b] (**a**);
R^1 = Ph, R^2 = Ts:
R^3 = C_6H_4F-4, 32% [a] (75%) [b] (**b**); C_6H_4Me-4, 47% [a] (60%) [b] (**c**);
Bu^n, 0% (**d**);
R^1 = Ph, R^2 = Ms:
R^3 = Ph, 70% [a] (99%) [b] (**e**); C_6H_4F-4, 49% [a] (88%) [b] (**f**);
R^2 = Ts, R^3 = Ph:
R^1 = C_6H_4Cl-4, 46% [a] (76%) [b] (**g**); C_6H_4OMe-4, < 5% (**h**);
Ms is mesyl

[a] The reaction was carried out using $FeCl_3$ (3 equiv.).
[b] The reaction was carried out using $FeCl_3$ (1 equiv.).

of iron(III) chloride (Scheme 77). The authors optimized reaction conditions and found a significant difference in the selectivity and yields obtained using 1 or 3 equiv. of $FeCl_3$. The use of 3 equiv. of the iron salt favoured the selective formation of the *E*-isomer **114** in poor yields, while the use of 1 equiv. of this salt provided an isomeric mixture of β-(organoselanyl) enamides **114** in moderate to very good yields. Various ynamides **115** and diaryl diselenides **13** with different substituents were tolerated, leading to twelve different products **114**. However, no reaction using dibutyl diselenide **13** was observed, and the product **114d** did not form. In summary, the method is operationally simple, allowed the use of room temperature and led to the desired products in short reaction times.

According to the proposed mechanism, the main step for the formation of the *E*- and *Z*-isomer mixture is related to the ability of ynamide **115** to form the transient ketenimi-nium ion **I** (Scheme 78). The reaction of the electrophilic selenium species with ynamide **115** begins with the gener-

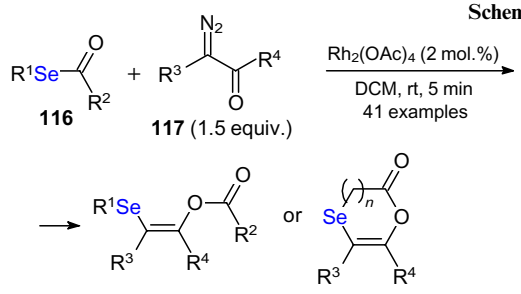
Scheme 78



ation of the seleniranium ion **II**, which undergoes a subsequent *anti*-attack of the nucleophilic portion, leading to the (*E*)-α-chloro-β-(phenylselanyl) enamide **114** (see Scheme 78 *a*). The formation of (*Z*)-α-chloro-β-(phenylselanyl) enamide **114′**, in turn, follows the *syn*-addition of the electrophilic selenium species to the keteniminium ion **I** (see Scheme 78 *b*). The high selectivity obtained when 3 equiv. of iron(III) chloride was used is related to the contribution of the iron salt to the formation of the electrophilic species of selenium and its complexation with selenium and oxygen atoms (intermediate **III**), thereby blocking the nucleophile attack from this side (see Scheme 78 *c*).

In 2022, X.-S.Liu *et al.*[126] described the stereoselective rhodium-catalyzed [1,4]-acyl rearrangement of selenoesters **116** and α-diazo carbonyl compounds **117** to prepare tetra-substituted vinyl selenides **118** (Scheme 79). This reaction features mild conditions, high atom economy, short reaction times, simple operation, efficient conversion, low catalyst loading, formation of a single *Z*-isomer, and is applicable to a broad substrate scope. Starting from selenoesters **116**, α-diazo carbonyl compounds **117** and $Rh_2(OAc)_4$ catalyst, fourty-one examples of (*Z*)-vinyl selenides **118a–t** were obtained in moderate to excellent yields. Furthermore, this protocol was applied to the late-stage modification of molecules with complex structures. Thus, vinyl selenides **118u–x** containing the motifs of natural products and drugs, including gemfibrozil, L-menthol, cholesterol, and ibuprofen, were produced.

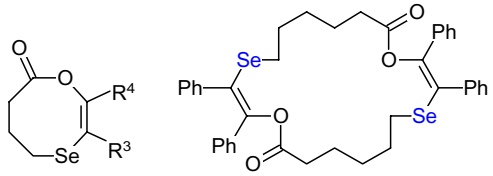
Scheme 79



R^1 = Ar, Alk; R^2 = Alk, Ar, ether; R^3 = Ar, H; R^4 = Ar, Alk, Het, OAlk, alkynyl

Selected examples

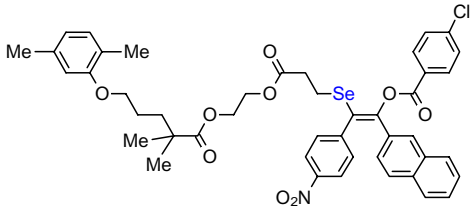
118: R^1 = R^4 = Ph,
R^2 = Me:
R^3 = Ph, 84% (**a**);
C_6H_4Br-4, 79% (**b**);
C_6H_4Br-3, 81% (**c**);
H, 30% (**d**);
R^1 = R^3 = Ph,
R^2 = Me:
R^4 = C_6H_4Me-4, 94% (**e**);
C_6H_4Cl-2, 96% (**f**);
Cy, 78% (**g**); 2-Th, 73% (**h**)
R^1 = Ph, R^2 = Me,
R^3 = C_6H_4Cl-4:
R^4 = Et, 42% (**i**); Pr^i, 52% (**j**);
R^1 = Me, R^2 = C_6H_4Cl-4,
R^3 = C_6H_4Br-4, R^4 = Ph, 51% (**k**);
R^2 = Me, R^3 = R^4 = Ph:
R^1 = C_6H_4Me-4, 76% (**l**);
C_6H_4F-4, 90% (**m**);
R^1 = R^2 = R^3 = R^4 = Ph, 89% (**n**);
R^1 = R^3 = R^4 = Ph:
R^2 = Et, 89% (**o**); Bu^t, 78% (**p**)



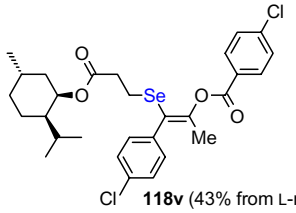
118t (46%)

R^3 = Ph, R^4 = C_6H_4Cl-3, 61% (**q**); R^3 = C_6H_4Cl-4:
R^4 = 1-Naph, 63% (**r**), Me 52%, (**s**)

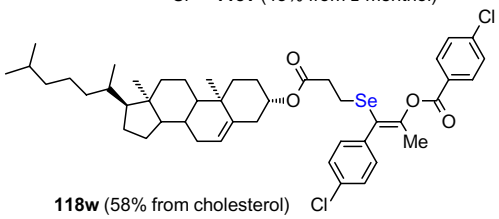
Structures 118u – x



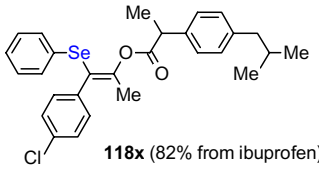
118u (55% from gemfibrozil)



118v (43% from L-menthol)



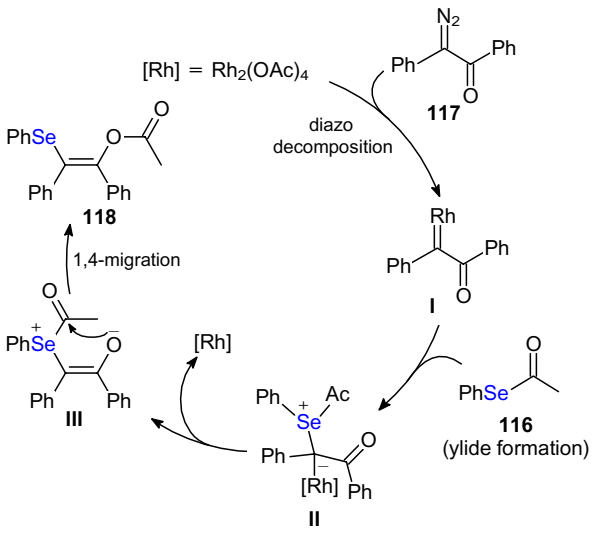
118w (58% from cholesterol)



118x (82% from ibuprofen)

The reaction mechanism suggests the formation of the rhodium carbene **I** due to the decomposition of diazo ketone **117** catalyzed by $Rh_2(OAc)_4$. This intermediate reacts with selenoester **116** to afford metal-bound ylide **II**. Then, free ylide **III**, which is formed *via* the departure of metal, undergoes the final [1,4]-shift of the acetyl group to produce vinyl selenide **118**. The excellent stereoselectivity of this reaction stems from the intramolecular migration of selenium ylide **III** (Scheme 80).

Scheme 80

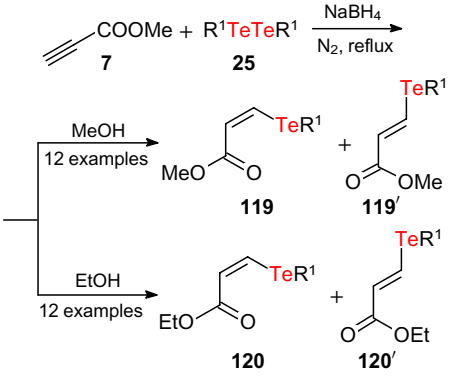


4. Transition metal-free synthesis of vinyl tellurides

Due to the importance and utility of vinyl tellurides in the field of organic synthesis, this Section highlights the progress made over the last five years in the synthesis of this class of compounds. Their production is based on the addition of various tellurium species, such as nucleophilic ones, generated *in situ* using the $R_2Te_2-NaBH_4$ system, or organotellurium trihalides, to alkynes under green reaction conditions.

In this context, Singh *et al.*[127] reported the synthesis of ester-functionalized vinyl tellurides **119** and **120** from methyl propiolate **7**. When substrate **7** was treated with $R_2Te_2-NaBH_4$ in methanol, a mixture of stereoisomers of methyl β-(aryltelluro)acrylates **119** and **119′** was formed. Instead, when the reaction was conducted in ethanol, isomeric mixtures of the corresponding ethyl esters **120** and **120′** were obtained (Scheme 81). Using isopropanol or *tert*-butanol as the reaction medium, however, a competing reaction occurred, the detelluration of the ditelluride to monotelluride.

Scheme 81



R^1 = C_6H_4OMe-4, 1-Naph, $C_6H_2Me_3$-2,4,6, $CpFeC_5H_4$, $C_6H_4NMe_2$-4, 2-Th

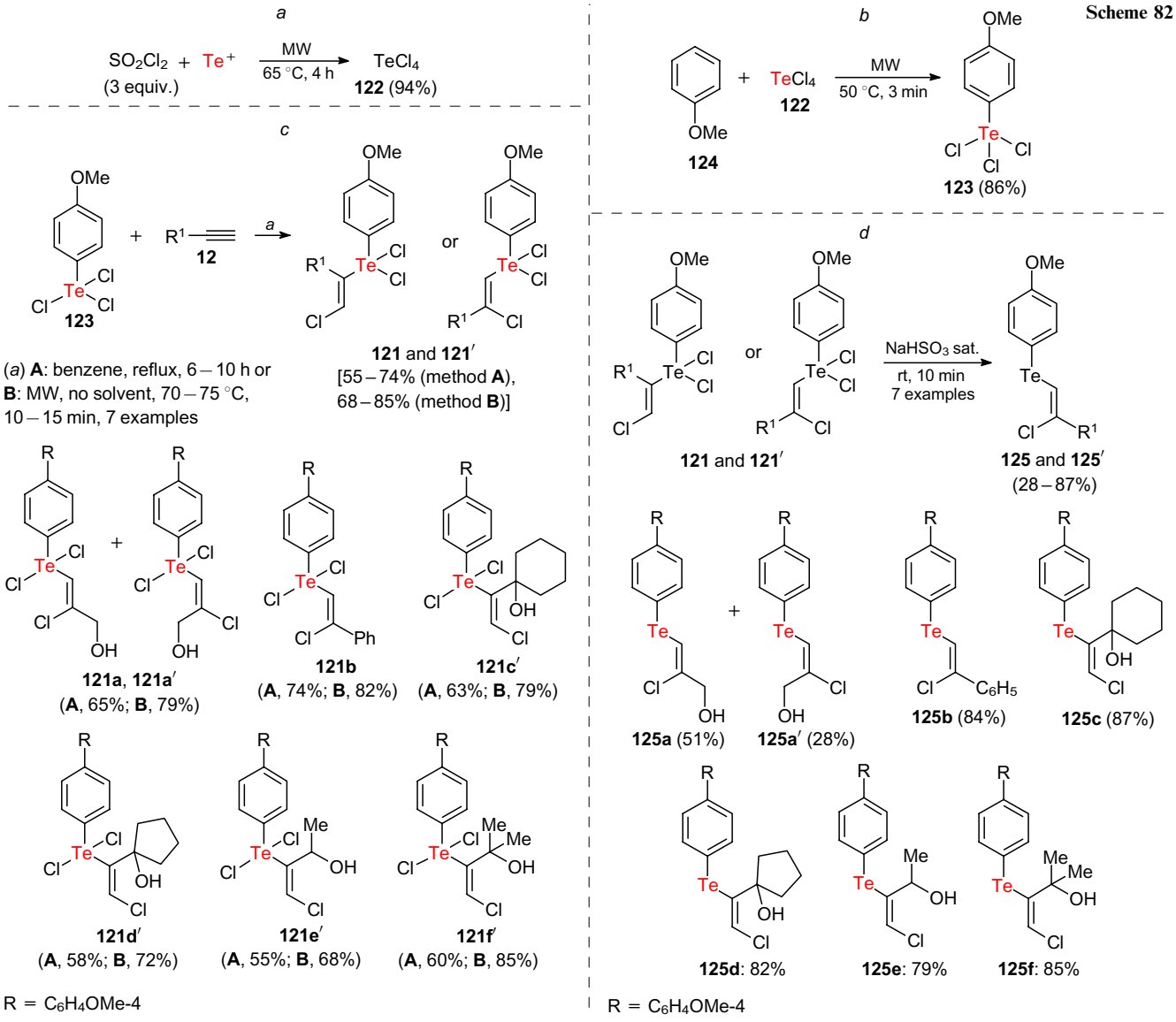
Selected examples

R^1 = C_6H_4OMe-4,
119a: 55% + **119a′**: 2%
R^1 = $C_6H_4NMe_2$-4,
119b: 59% + **119b′**: 5%

R^1 = C_6H_4OMe-4,
120a: 50% + **120a′**: 2%
R^1 = $C_6H_4NMe_2$-4,
120b: 53% + **120b′**: 4%

In 2015, Princival *et al.*[128] developed the synthetic route to tellurium(IV) compounds **121** using microwave (MW) irradiation under solvent-free conditions. Tellurium tetrachloride **122** was prepared in advance from elemental tellurium and an excess of SO_2Cl_2 under MW (100 W) (Scheme 82 *a*). Then, reagent **122** was employed to prepare *p*-methoxyphenyltellurium trichloride **123** in the reaction with anisole **124w** (see Scheme 82 *b*). Compound **123** was reacted with different alkynes **12**, using both conventional heating and microwave irradiation. According to the classical protocol, the reaction was carried out in refluxing benzene for 6 – 10 h, and products **121** were obtained in moderate to good yields (see Scheme 82 *c*). Using the new procedure, products **121** were obtained within 10 – 15 min of microwave irradiation in good yield in the absence of solvent. Only in the case of propargyl alcohol, was a mixture of two products, **121a** and **121a′**, observed. Finally, all products were reduced to tellurium(II) compounds **125**

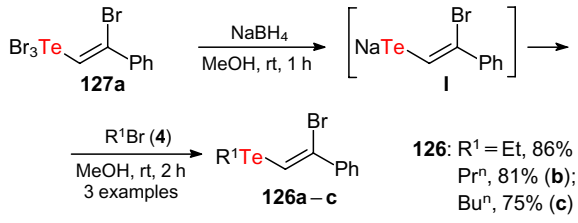
Scheme 82



with saturated solution of sodium bisulfite (see Scheme 82 *d*).

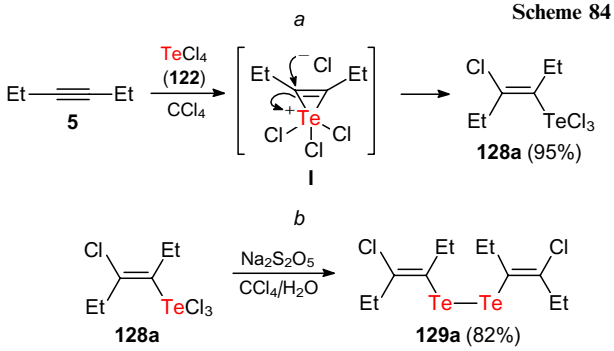
In 2015, Potapov *et al.*[129] reported the synthesis of (*Z*)-2-bromo-2-phenylvinyl tellurides **126** (Scheme 83). As the starting material, (*Z*)-2-bromo-2-phenylvinyltellurium tribromide **127a** was used, which was reduced *in situ* with $NaBH_4$ in MeOH, generating (*Z*)-2-bromo-2-phenylethene-tellurolate **I**. This species undergoes a nucleophilic substitution with alkyl halides **4** to afford the desired products with retention of the configuration of the substrate. The yield of the products decreased with increasing length of the alkyl substituent, probably due to the steric factor.

Scheme 83



Between 2015 and 2019, Potapov *et al.*[130 – 139] published a series of works on the addition of TeX_4 (X = Cl, Br) to acetylenes, aiming at the preparation of vinyl tellurides. Thus, in 2015, the synthesis of (*E*)-(4-chlorohex-3-en-3-yl)tellurium trichloride **128a** by the Markovnikov *anti*-addition of tellurium tetrachloride to the internal hex-3-yne **5** was described.[130] This reaction involves the formation of a three-membered tellurirenium intermediate **I** (Scheme 84 *a*). According to the developed procedure, equimolar amounts

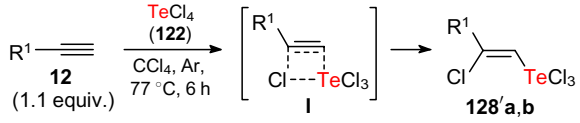
Scheme 84



of tellurium tetrachloride **122** and alkyne **5** are reacted in tetrachloromethane to afford product **128a** in excellent yield with high stereoselectivity towards *E*-configuration. In addition, the hitherto unpublished bis[(*E*)-4-chlorohex-3-en-3-yl] ditelluride **129a** was prepared in 82% yield by the reduction of compound **128a** with sodium metabisulfite in the CCl_4-H_2O two-phase system (see Scheme 84 *b*).

In 2016, the regio- and stereoselective synthesis of trichloro[(*Z*)-2-chlorohex-1-en-1-yl]-λ^4-tellane **128a′** and trichloro[(*Z*)-2-chlorooct-1-en-1-yl]-λ^4-tellane **128b′** *via* the reaction of tellurium tetrachloride **122** with hex-1-yne and oct-1-yne, respectively, was reported (Scheme 85).[131] The reaction was performed by refluxing a mixture of tellurium tetrachloride with hex-1-yne or oct-1-yne in carbon tetrachloride under an argon atmosphere, affording the unprecedented monoadducts **128a′** and **128b′** in 94% and 96% yield, respectively. The stereoselective *syn*-addition of tellurium tetrachloride to terminal alkylacetylenes **12** proceeds through the four-membered cyclic transition state **I**. Presumably, the addition of the bulky trichlorotellanyl group to the terminal carbon atom of the alkylacetylene substrate is more favourable due to steric effects.

Scheme 85

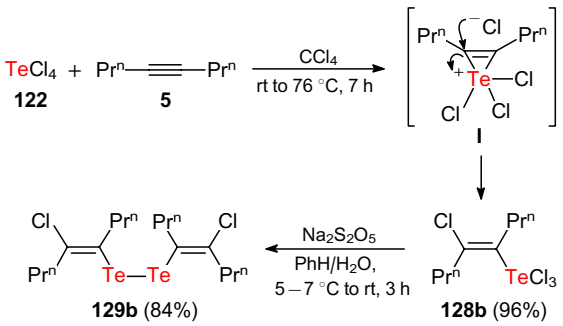


R^1 = Bu^n, 94% (**a**); n-Hex, 96% (**b**)

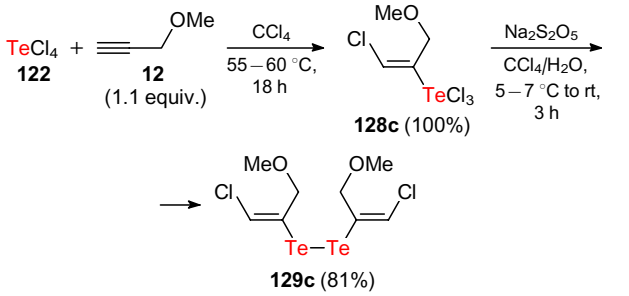
In 2017, a similar strategy was applied to the stereoselective *anti*-addition of tellurium tetrachloride **122** to a symmetric disubstituted acetylene **5** (Scheme 86).[132] As a result, trichloro[(*E*)-1-propyl-2-chloropent-1-enyl]tellane **128b** was produced in 96% yield after carrying out the reaction in CCl_4 (2 h at room temperature and 5 h under reflux). It was assumed that the *anti*-addition occurs *via* a three-membered tellurirenium intermediate **I**, the formation of which is more energetically favourable than that of a four-membered cyclic transition state, which would afford the *Z*-isomer (see Scheme 86). Additionally, the reduction of compound **128b** with sodium metabisulfite in the $C_6H_6-H_2O$ two-phase system was also studied, and bis[(*E*)-1-propyl-2-chloropent-1-enyl]ditellane **129b** was obtained in 84% yield.

The use of methyl propargyl ether **12** as an alkyne counterpart enabled the synthesis of (*E*)-trichloro(3-methoxy-1-chloroprop-1-en-2-yl)-λ^4-tellane **128c** (Scheme 87).[133] This reaction was performed in carbon

Scheme 86



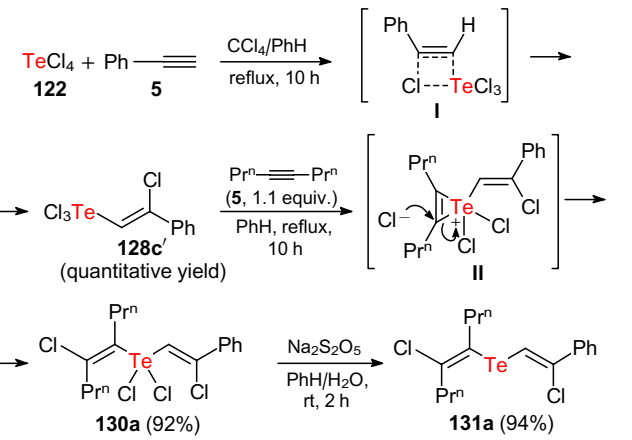
Scheme 87



tetrachloride to provide a quantitative yield of product **128c**. In this study, the reduction of compound **128c** with sodium metabisulfite to (*E*,*E*)-bis(3-methoxy-1-chloroprop-1-en-2-yl)ditellane **129c** was carried out without isolation of tellane **128c**, after adding of an aqueous solution of sodium metabisulfite to the reaction mixture followed by vigorous stirring of the two-phase system for 3 h.

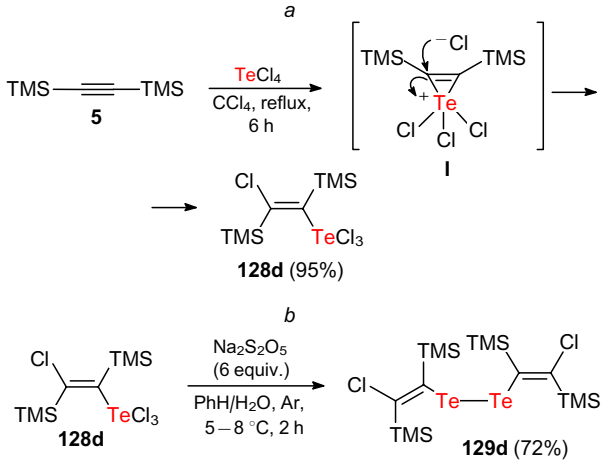
Using a sequential one-pot strategy, unsymmetrical bisalkenyl tellurides, trichloro[(*Z*)-2-chloro-2-phenylethenyl]-λ^4-tellane **128c′** and dichloro[(4*E*)-5-chlorooct-4-en-4-yl][(*Z*)-2-chloro-2-phenylethenyl]-λ^4-tellane **130a**, were prepared (Scheme 88).[134] Initially, the reaction of tellurium tetrachloride **122** with phenylacetylene **5** in a 9 : 1 (v/v) CCl_4-PhH mixture) proceeded through a *syn*-addition pathway, presumably *via* the four-membered cyclic transition state **I**, giving the trichloro[(*Z*)-2-chloro-2-phenylethenyl]-λ^4-tellane **128c′** in a quantitative yield. The monoadduct **128c′** was then reacted with oct-4-yne **5** (*anti*-addition) to afford dichloro[(4*E*)-5-chlorooct-4-en-4-yl][(*Z*)-2-chloro-2-phenylethenyl]-λ^4-tellane **130a** in 92% yield. Finally, compound **130a** was reduced by sodium metabisulfite to [(*Z*)-2-chloro-2-phenylethenyl]-[(4*E*)-5-chlorooct-4-en-4-yl]tellane **131a** in 94% yield.

Scheme 88



In the same 2017, Potapov *et al.*[135] reported the stereoselective *anti*-addition of tellurium tetrachloride **122** to bis(trimethylsilyl)acetylene **5** to give [(*E*)-2-chloro-1,2-bis(trimethylsilyl)-vinyl]trichlorotellane **128d** *via* the formation of a tellurirenium intermediate **I** (Scheme 89 *a*). Noteworthy, the bis-adduct was not formed even with an excess of alkyne. In addition, the reduction of **128d** under the action of a two-phase system of aqueous sodium metabisulfite-benzene at 5–8 °C led to bis[(*E*)-2-chloro-

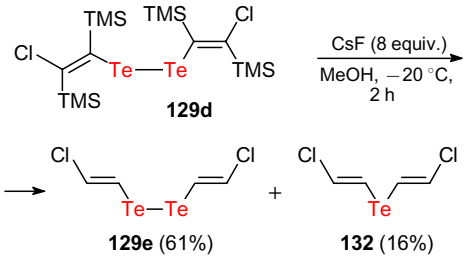
Scheme 89



1,2-bis(trimethylsilyl)vinyl]ditellane **129d** in a good yield (see Scheme 89 *b*).

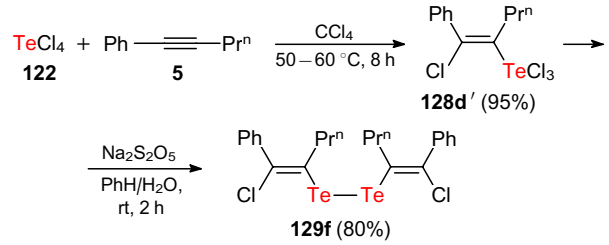
The stereoconfiguration of the products was confirmed by desilylation of ditelluride **129d** to provide a mixture of bis[(*E*)-2-chlorovinyl]ditellane **129e** and bis[(*E*)-2-chlorovinyl]tellane **132** (Scheme 90). Curiously, the formation of tellane **132** is a result of tellurium atom elimination from ditellane **129d**.

Scheme 90



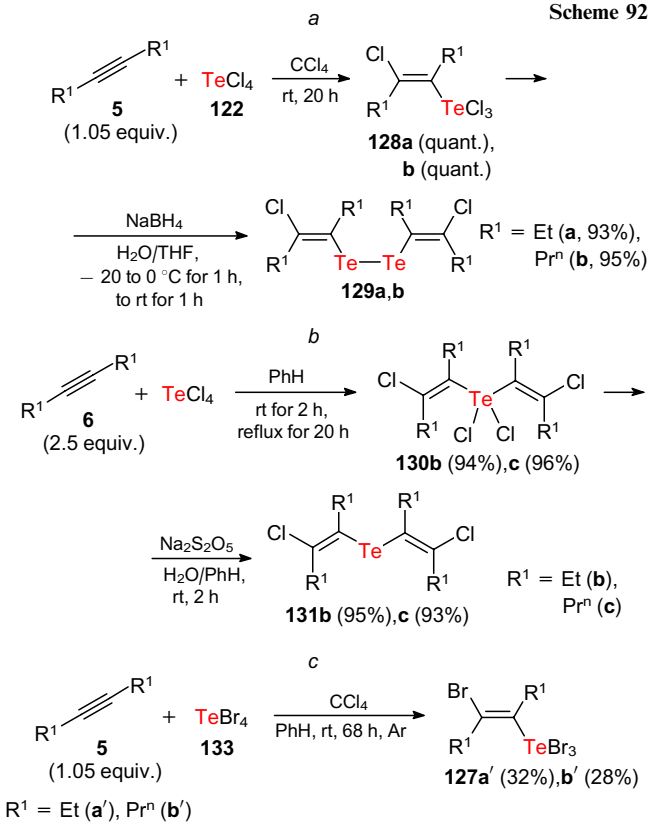
(*Z*)-2-Chloro-2-phenyl-1-propylethenyltellane **128d′** was prepared in excellent yield by the reaction of tellurium tetrachloride **122** with an unsymmetrical internal alkyne, 1-phenylpent-1-yne (Scheme 91).[136] Then, compound **128d′** was reduced by sodium metabisulfite to 1,2-bis[(*Z*)-2-chloro-2-phenyl-1-propylethenyl]ditellane **129f** in 80% yield.

Scheme 91



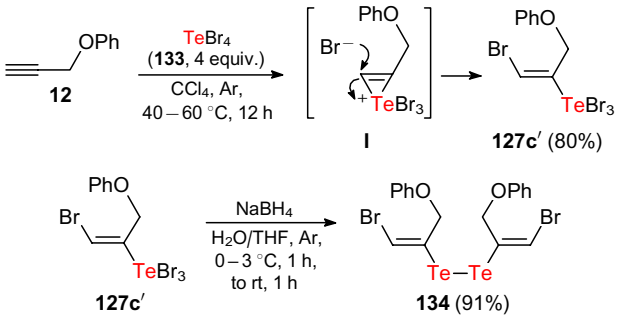
In 2018, the efficient stereoselective synthesis of (*E*)-2-halovinyltellanes **128a**,**b** and -ditellanes **129a**,**b**, through an *anti*-addition reaction, was described for the first time (Scheme 92).[137] First, tellanes **128a**,**b** were prepared in quantitative yield from tellurium tetrachloride **122** and hex-3-yne or oct-4-yne (CCl_4, rt, 20 h). Subsequently, the products **128a**,**b** were reduced to **129a**,**b** using a $NaBH_4-H_2O-THF$ system (see Scheme 92 *a*). Moreover, compound **122** reacted stereoselectively with an excess of hex-3-yne or oct-4-yne in benzene, affording for the first time bis-adducts **130b**,**c** in excellent yields. Then, these compounds were reduced to bis[(*E*)-2-chloro-1-ethyl-1-butenyl]tellane **131b** and bis[(*E*)-2-chloro-1-propyl-1-pentenyl]tellane **131c** in 95% and 93% yield, respectively (see Scheme 92 *b*). When $TeBr_4$ **133** was used instead of $TeCl_4$, the so far unknown products **127a′**,**b′** were formed in poor yields (see Scheme 92 *c*).

Scheme 92



The strategy based on the addition of tellurium tetrabromide **133** was extended in 2019 to the regio- and stereoselective synthesis of tribromo[(*E*)-2-bromo-1-(phenoxymethyl)vinyl]tellane **127c′** using propargyl phenyl ether **12** as an alkyne component (Scheme 93).[138] The product **127c′** is formed *via* the *anti*-addition proceeding against the Markovnikov rule, through the intermediate tellurirenium

Scheme 93

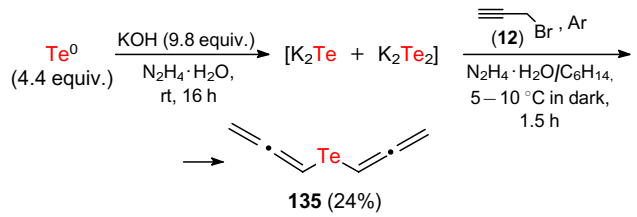


cation **I**, with the nucleophilic attack of the bromide ion on the unsubstituted carbon atom of the three-membered ring.

Additionally, the authors investigated the reduction of tellane **127c′** with sodium borohydride in a water/THF medium, producing bis[(*E*)-2-bromo-1-(phenoxymethyl)-vinyl]ditellane **134** in excellent yield (see Scheme 93).

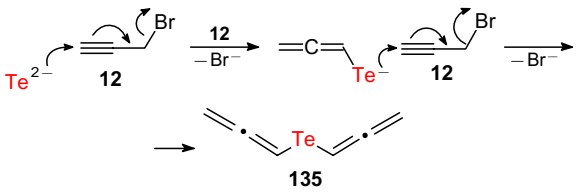
Moreover, in 2017, Potapov *et al.*[139] developed the synthesis of dipropadienyl telluride **135** from elemental tellurium and propargyl bromide **12** (Scheme 94). The reaction involves the reduction of tellurium with hydrazine hydrate in the presence of potassium hydroxide leading to the *in situ* generation of telluride and ditelluride anions, which react with propargyl bromide **12** in the hydrazine hydrate — hexane two-phase system under argon atmosphere, in the dark at 5–10 °C for 1.5 h to afford telluride **135** in a poor yield. The hydrazine hydrate serves as both a reducing agent and an inorganic solvent to solubilize potassium telluride, formed in the first step.

Scheme 94



The mechanism for the selective formation of the dipropadienyl telluride **135** is depicted in Scheme 95. Due to steric factor, the bulky highly nucleophilic telluride anion attacks not the substituted carbon of the bromomethyl group, but the terminal carbon of the triple bond with the shift of electrons and the formation of a propadienyl moiety and bromide anion. It is possible that the 1,3-nucleophilic substitution occurs, rather than the usual 1,1-nucleophilic substitution, in one step as a synchronous six-electron process.

Scheme 95



5. Conclusion

Herein, an overview of various methods developed over the last seven years to produce vinyl selenides and tellurides are presented. The discussed procedures are both metal-promoted and transition metal-free. The wide range of encountered protocols demonstrate the importance of this class of compounds due to their chemical and biological properties. Thus, the attention of the research groups is always focused on the search for new, green, and reliable methods to obtain structurally diverse vinyl selenides and tellurides. Despite all the advances that have been reported in recent years, there is still a lot of improvements required, especially regarding the synthesis of vinyl tellurides, a field that is still unexplored compared to that of the selenide analogues. Additionally, the green chemistry approach to the synthesis of vinyl chalcogenides is still in its infancy, and there are many opportunities to be explored in the coming years in this area. We hope that this review can inspire colleagues working in organic synthesis to add some 'greenery' in their reactions. The use of green solvents or solvent-free procedures, alternative energy sources (microwave, ultrasound, mechanics, light), atom-economic reactions, and catalytic approaches should stop being exceptions and become common procedures in our laboratories.

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6. List of acronyms

Ac — acyl,
All — allyl,
Bn — benzyl,
Bpin — pinacolboryl,
BPO — benzoyl peroxide,
Ch — choline,
Cy — cyclohexyl,
DABSO — 1,4-diazabicyclo[2.2.2]octane bis(sulfur dioxide),
DCE — dichloroethane,
DCM — dichloromethane,
DES — deep eutectic solvent,
dr — diastereomeric ratio,
DTBP — di-*tert*-butyl peroxide,
Hex — hexyl,
LED — light emitting diode,
Ms — mesyl (methanesulfonyl),
MW — microwave irradiation,
Naph — naphthyl,
NFSI — *N*-fluorobenzenesulfonimide,
Oct — octyl,
Py — pyridyl,
rt — room temperature,
TBHP — tert-butyl hydroperoxide,
Th — thienyl,
TMS — trimethylsilyl,
Ts — tosyl (p-toluenesulfonyl),
US — ultrasonication.

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