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Mini Review

Selenium Reagents as Catalysts

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Organoselenium chemistry is now become an important tool in synthetic and medicinal chemistry. Organoselenium reagents are more commonly known as electrophiles but there are few organic transformations where they act as nucleophiles. These reagents have been successfully employed to achieve number of synthetically important transformations such as oxyselenenylations, selenocyclisation and selenoxide eliminations etc. In past two decades, another episode of their success is introduced as they have developed as potential catalysts in organic synthesis. Various selenium-catalysed approaches such as oxidation, reduction, cyclisation, rearrangement and stereoselective reactions have been successfully investigated. During these reactions, a number of organic and inorganic oxidants have been employed to regenerate different active catalytic species *in situ*. In this review article, recently developed selenium-catalysed reactions are covered including stereoselective reactions.

Introduction

Although first organoselenium compound was synthesized in 1847 by F. Wohler, C. Siemens[1] but the progress of organoselenium chemistry was quite slow until the discovery of selenoxide eliminations in 1970s.[2] Organoselenium reagents are known to exhibit some toxicity and first time it was disclosed in 1930s.[3a] Eventually, the selenium was found as an essential dietary trace element.[3a] Probably, the toxicity of organoselenium species arises due to their exposure for longer period. Notably, the toxicity profile of organoselenium compounds is more safer compare to inorganic selenium compounds.[3b,c]

Additionally, few mammalian enzymes have been discovered which contain selenocysteine moiety.[4] Despite the toxicity issues with them, the chemistry of these reagents is now well established due to their wide applications in organic synthesis[5,6] and chemical biology.[7,8] Organoselenium reagents have been used to achieve various synthetic transformations such as selenenylations, seleno-cyclisations, selenoxide eliminations and 2,3-sigmatropic rearrangements under mild reaction conditions.[9-11] The utility of these reagents in catalysis provide a new dimension to organoselenium chemistry.[12] In most of the selenium-catalysed organic transformations, the diselenides are used as catalyst which exhibit moderate toxicity.[3c] This review highlights the recent progress of organoselenium reagents in catalysis.

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Selenium reagents as catalyst

Selenium compounds can exist as both inorganic and organic compounds. More commonly, organic selenium reagents have been used to catalyse organic reactions but there are few reports in the literature where inorganic selenium species are used as catalyst. Inorganic selenium species have been employed to catalyse few organic reactions such as carbonylation of electron-rich and electron-deficient arenes,[13] selective reduction of double bonds in α,β-unsaturated compounds,[14] dihydroxylation of alkenes,[15] oxidation of aromatic amines[16] and synthesis of *N*-containing heterocycles.[17] In past decade, the organoselenium catalysts have been identified as an asset in organoselenium chemistry and various organic transformations have been developed using these catalysts.

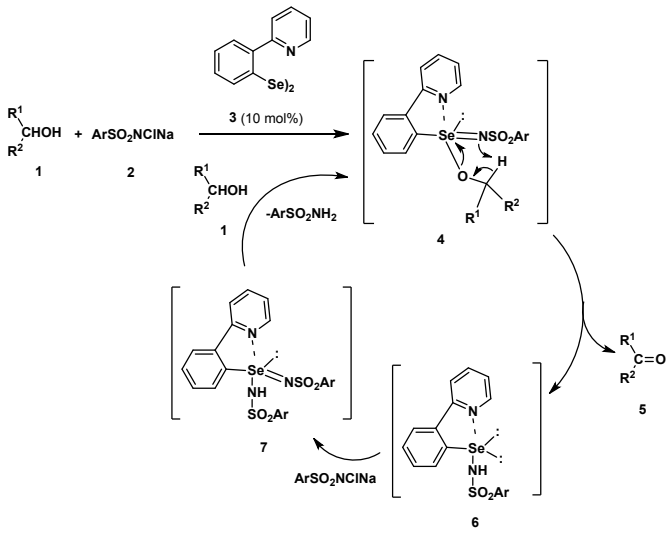
Selenium-catalysed oxidation reactions

Since long time, organoselenium reagents are known for their powerful oxidizing behaviours.[18] Various oxidation reactions have been developed by using the combination of organoselenium catalyst with some selective terminal oxidants such as hydrogen peroxide,[19] *tert*-butyl hydroperoxide (TBHP)[20] and iodoxybenzene ($PhIO_2$)[21] and ammonium persulfate.[22]

Selenium-catalysed oxidation of alcohols

The oxidations of alcohols can be used to achieve various synthetically important carbonyl compounds and carboxylic acids which make this reaction more suitable in organic chemistry.[23] In the beginning, the oxidation of alcohols was achieved by using stoichiometric amounts of selenium-based oxidants[18] while the first catalytic use of selenium reagents was reported in the oxidation of alcohols in 1996 by Onami and his coworkers.[24] Furthermore, the same research group achieved the oxidation of alcohols **1** to carbonyl

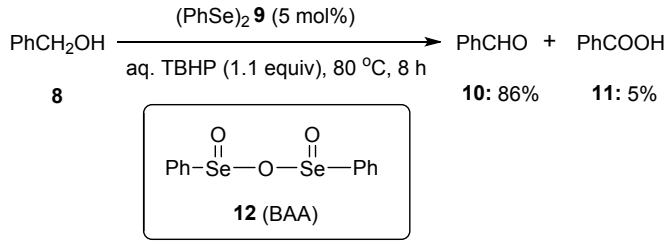
compounds **5** using catalytic amount of bis[2-(2-pyridyl)phenyl] diselenide **3** in the presence of *N*-chloro-4-chlorobenzenesulfonamide sodium salt **2** as oxidant (Scheme 1).[25]



Scheme 1. Selenium-catalysed oxidation of alcohols **1** to carbonyl compounds **5** using bis[2-(2-pyridyl)phenyl] diselenide **3** as catalyst and *N*-chloro-4-chlorobenzenesulfonamide sodium salt **2** as oxidant.

The mechanism for the selenium-catalysed oxidation of alcohols **1** to carbonyl compounds **5** is shown in Scheme 1. The catalytic cycle is initiated via formation of an intermediate **4** by the reaction of alcohol **1** with bis[2-(2-pyridyl)phenyl] diselenide **3** and *N*-chloro-4-chlorobenzenesulfonamide sodium salt **2**. Intermediate **4** undergoes oxidative cleavage and forms carbonyl compound **5** while generating another selenium intermediate **6**. Furthermore, the intermediate **6** reacts with *N*-chloro-4-chlorobenzenesulfonamide sodium salt **2** to form intermediate **7** which subsequently reacts with alcohol **1** to continue the catalytic cycle.

In 2009, the oxidation of benzyl alcohol **8** was achieved by replacing terminal oxidant *N*-chloro-4-chlorobenzenesulfonamide sodium salt **2** with *tert*-butyl hydroperoxide (TBHP) using diphenyl diselenide **9** as catalyst (Scheme 2).[26] The oxidation was investigated in different polar and non-polar solvents and benzaldehyde **10** was obtained in highest yields using toluene as solvent (Scheme 2). Additionally, the over oxidized product benzoic acid **11** was also observed but only as a minor product. Probably, benzeneseleninic acid anhydride (BAA) **12** is operating as active catalytic species which was generated by the oxidation of pre-catalyst diphenyl diselenide **9** with oxidant TBHP.

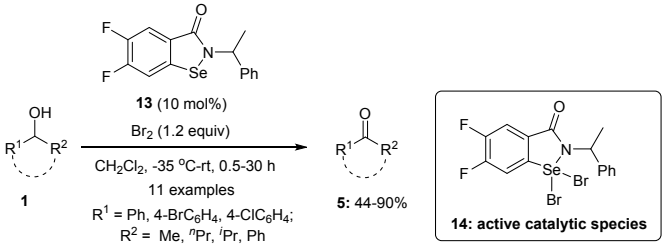


Scheme 2. Selenium-catalysed oxidation of benzyl alcohol **8** to benzaldehyde **10** using diphenyl diselenide **9** as catalyst in the presence oxidant TBHP.

Furthermore, piano-stool type complexes of ruthenium with arenes and *N*-[2-(arylseleno)ethyl]morpholines were used as new catalytic systems for the oxidation of alcohols **1** to carbonyl compounds **5**. Various terminal oxidants such as *tert*-butyl hydroperoxide (TBHP), *N*-methylmorpholine *N*-oxide and sodium periodate were successfully used during these oxidations.[27] Interestingly, 1.0 mol% catalyst was sufficient to achieve the oxidation products in high yields. Moreover, this catalytic approach was quite effective for both primary and secondary alcohols. Additionally, the catalytic species was recovered almost quantitatively and reused in further oxidation reactions without losing much catalytic activity.

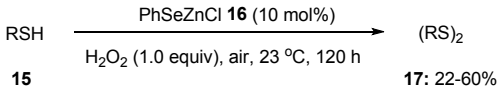
Moreover, Santi and others reported the oxidation of benzyl alcohol to benzoic acid using seleninic acid as catalyst with Oxone as terminal oxidant in water.[28] Notably, H_2O_2 was used as an oxidant under similar reaction and conditions but complete conversion of benzyl alcohol could not be observed.

In 2012, the oxidation of secondary alcohols **1** to ketones **5** was developed by using the combination of isoselenazolone catalyst **13** and bromine as an oxidant (Scheme 3).[29] Various acyclic and cyclic alcoholic substrates were successfully oxidized to corresponding ketones in high yields during these investigations. The mechanistic studies suggest that the isoselenazolone catalyst **13** oxidized by bromine to form isoselenazolone(IV) dibromide **14**, which is the key intermediate for the oxidation of alcoholic substrates **1**.



Scheme 3. Selenium-catalysed oxidation of secondary alcohols **1** to ketones **5** using isoselenazolone **13** as catalyst bromine as an oxidant.

Selenium-catalysts are not only limited to oxidation of alcohols but successfully applied for the oxidation of thiols. In 2012, Santi and co-workers introduced the selenium-catalysed oxidation of thiols **12** to disulfides **17** using PhSeZnCl **16** as catalyst in the presence of hydrogen peroxide (Scheme 4).[30] The course of oxidation reaction depends on the nature of substrates used and no reaction was observed when cysteine and homocysteine were used as substrates. Notably, the oxidation of aliphatic thiols proceeded in higher yields compared to aromatic thiols. This is one of the rare cases of selenium catalysis where nucleophilic organoselenium species were employed as catalysts.



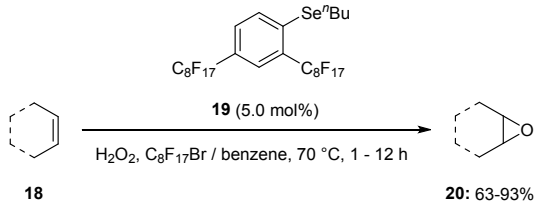
Scheme 4. Selenium-catalysed oxidation of thiols **12** to disulfides **17** using PhSeZnCl **16** as catalyst in the presence of H_2O_2.

Selenium-catalysed oxidation of alkenes

Oxidation of alkenes is an important reaction for synthetic organic chemists because it leads various synthetically important products such as epoxides, diols and carbonyl compounds. The nature of oxidants used during the oxidation of alkenes usually dictates the formation of oxidation products.

Selenium-catalysed epoxidation of alkenes

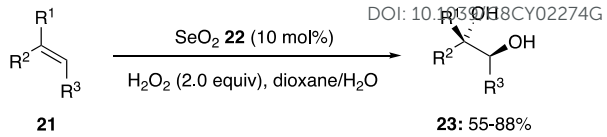
The progress of organoselenium reagents in catalysis began with the epoxidation of alkenes by Hori and Sharpless in 1978.[31] In this report, various arylseleninic acids were investigated as catalysts for the epoxidation of olefins in the presence of hydrogen peroxide. Another report on selenium-catalysed epoxidation of alkenes was published in 1999 where 2,4-bisperfluorooctylphenyl butylselenide **19** was used to catalyse the epoxidation of both cyclic and acyclic olefins **18** using 60% H_2O_2 as an oxidant in fluorous biphasic system. The epoxidation products **20** were isolated in moderate to excellent yields (Scheme 5).[32] Interestingly, the catalytic species was recovered successfully by phase separation and reused up to ten times without reducing product yields and increasing reaction times. Furthermore, the selenoxides were found as effective catalysts for the epoxidation of unsaturated substrates using same terminal oxidant.[33] In 2009, Arends and co-workers employed glycerol-based solvents as green reaction media to develop the selenium-catalysed approach for the epoxidation of olefins using the combination of the catalyst bis[3,5-bis(trifluoromethyl)-diphenyl]diselenide and hydrogen peroxide as oxidant.[34a] Additionally, the toxicity profile of solvents and catalysts used in this reaction was also studied. Both solvents and catalysts were found safe to perform these oxidation reactions.[3c,34b]



Scheme 5. Selenium-catalysed epoxidation of alkenes **18** using fluorous selenide **19** as catalyst in the presence of hydrogen peroxide.

Selenium-catalysed hydroxylation of alkenes

The chemistry of selenium-catalysed hydroxylation of alkenes was reported by Knochel and coworkers.[32] *Trans*-hydroxylations of olefins were achieved in useful yields using a fluorous biphasic system. Later on, the combination of SeO_2 catalyst with H_2O_2 was demonstrated as an effective catalytic system for *trans*-dihydroxylations of olefins **21**. Olefinic substrates **21** installed with aliphatic and aromatic functionalities were successfully oxidized to *trans*-diols **23** in good yields under mild reaction conditions (Scheme 6).[35] Additionally, the mechanistic studies revealed that the oxidation reactions were working via formation of perselenic acid as an active catalytic species, which was generated *in situ* by the reaction of SeO_2 with water followed by H_2O_2.



Scheme 6. Selenium-catalysed *trans*-dihydroxylations of olefins **21** using SeO_2 as catalyst in the presence of H_2O_2.

Furthermore, the similar alkenes **21** were oxidized to *trans*-diols in useful yields by a catalytic amount of diphenyl diselenide **9** with terminal oxidant hydrogen peroxide. The reaction products **23** were obtained with good selectivity but most of reactions required long reaction time and few of them were completed in more than a week. The reaction begins with oxidation of diselenide **9** to peroxy benzeneseleninic acid which was probably acting as an active catalytic species for the synthesis of *trans*-diols.[36] Additionally, the selenium catalyst **9** was quite stable and fully recovered using crystallization process.

Furthermore, three different selenium catalysts **9**, **24** and **25** (Figure 1) were employed for hydroxylation of cyclohexene **18** in the presence of hydrogen peroxide and results are summarized in Table 1.

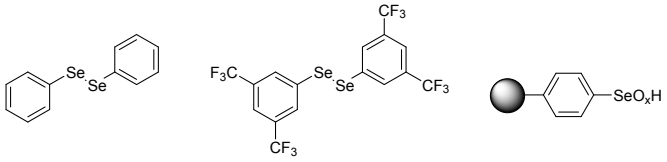
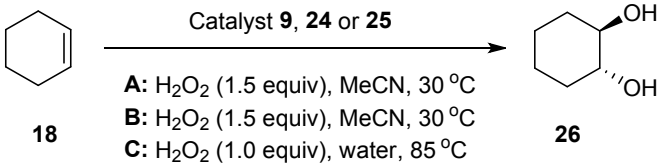


Figure 1. Structures of organoselenium catalysts **9**, **24** and **25**.

The catalyst **9** showed high catalytic activity at 1.0 mol% catalytic loading (see Scheme 7 and Table 1, entry 1).[37] The reaction time was reduced significantly when diaryl diselenide **24** equipped with CF_3 groups was used as catalytic selenium species (Table 1, entry 2).[38] Moreover, the same hydroxylation reaction was performed at 100 mmol scale and oxidation product **26** was obtained in 82% yield. Further the recyclable nature of catalyst **24** makes this approach more suitable for industrial applications. In 2016, Zhu and others introduced polymer-supported organoselenium catalyst **25**, which exhibited good catalytic activity with cyclohexene in water.[39] Moreover, the catalytic reactions were performed at different catalytic loadings and it was observed that the catalytic loading directly influences the rate of reaction (Table 1, entries 3 - 5). Notably, the catalytic species was recovered and reused without losing its catalytic potential.



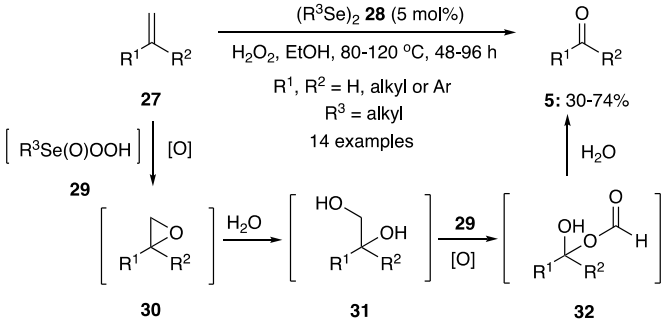
Scheme 7. Selenium-catalysed *trans*-hydroxylation of cyclohexane **18** using different catalysts **9**, **24** and **25**.

Table 1. Selenium-catalysed *trans*-hydroxylation of cyclohexane **18** under different reaction conditions.

Entry	Catalyst	Reaction conditions	Reaction time (h)	**26** yield (%)
1	**9** (1.0 mol%)	A	42	96
2	**24** (1.0 mol%)	B	5	96
3	**25** (1.0 mol%)	C	20	98
4	**25** (5.0 mol%)	C	5	99
5	**25** (10 mol%)	C	3	99

Selenium-catalysed cleavage of olefinic double bond

Oxidation of olefinic double bond is a useful reaction in synthetic organic chemistry because it provides an easy access for the synthesis of different carbonyl compounds. First time, the involvement of selenium-catalyst for oxidative cleavage of olefinic double bond to carbonyl compounds was introduced by Konwar and co-workers in 2007.[35] Recently, Yu and co-workers demonstrated a highly efficient selenium-catalysed approach for the oxidative cleavage of terminal alkenes **27** using 5.0 mol% of dialkyl diselenide **28** in the presence of hydrogen peroxide using environmentally friendly solvent ethanol.[40] The cleavage reactions were found quite slow but carbonyl products **5** were isolated in useful yields (Scheme 8). Various dialkyl diselenides **28** were investigated during these oxidations and dicyclohexyl diselenide **28** (R = *c*-C_6H_{11}) exhibited best catalytic activity. Additionally, this catalytic species **28** (R = *c*-C_6H_{11}) was found to be an efficient catalyst for the cleavage of terminal cyclic alkenes affording cyclic ketones in good yields.

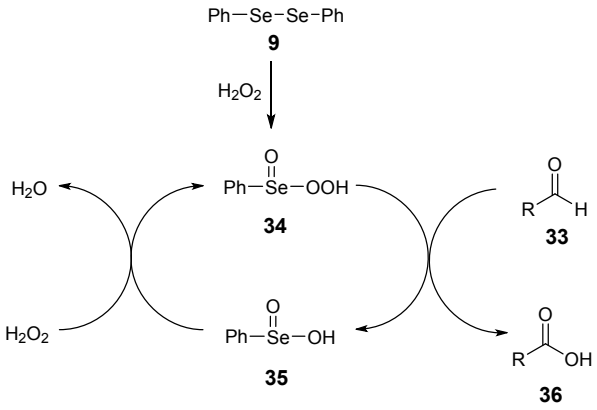


Scheme 8. Selenium-catalysed oxidative cleavage of alkenes **27** to ketones **5** using catalytic dialkyl diselenides **28**.

On the basis of GC-MS analysis, it was proposed that the cleavage reaction was initiated *via* the selenium-catalysed epoxidation of alkene **27**. Epoxide intermediate **30** undergoes hydrolysis to form diol **31**. Diol **31** then forms the further oxidized product **32**. On hydrolysis, oxidized product **32** degraded into ketone **5**. The active catalytic species **29** generated *in situ* was probably playing a key role during the synthesis of epoxide intermediate **30** and oxidized product **32**.

Selenium-catalysed oxidation of carbonyl compounds

Oxidation of carbonyl compounds is the key reaction in organic synthesis that leads various oxidation products such as carboxylic acids and esters. Organoselenium reagents have been received a particular attention as catalyst for the oxidation of aldehydes and ketones. In the first report on selenium catalysis, the oxidation of carbonyl compounds to carboxylic acids was achieved by using benzeneseleninic acid as catalyst in the presence of H_2O_2.[41] In 2000, selenium(IV) oxide was used as catalyst to develop similar oxidations.[42] Ebselen (5-mol%) was used to catalyse the oxidation of aldehydes to arenecarboxylic acids in the presence of *t*-butyl hydroperoxide (THBP).[43] In 2015, Santi and co-workers developed a green approach for the oxidation of various aliphatic and aromatic aldehydes in water using 2.5 mol% $(PhSe)_2$ **9** in the presence of hydrogen peroxide (Scheme 9).[44] This oxidative catalytic approach was applicable for substrates having electron-donating and electron-withdrawing functionalities but better yields were obtained with substrates having electron-withdrawing groups. Moreover, the catalytic diselenide species **9** was recovered from the aqueous layer obtained from the extraction of reaction mixture and used in further oxidation reactions. The catalytic cycle is initiated with the formation of benzeneperseleninic acid **34** by the oxidation of diphenyl diselenide **9** that oxidizes aldehydes **33** to corresponding carboxylic acids **36** along with the formation benzeneseleninic acid. Finally, benzeneseleninic acid is reoxidized to benzeneperseleninic acid **35** by H_2O_2 to continue the catalytic cycle.



Scheme 9. The mechanism for the selenium-catalysed oxidation of aldehydes **33** to carboxylic acids **36**.

In several selenium-catalysed reactions, the oxidation of carbonyl compounds leads the formation of various cyclic and acyclic esters. Different selenium reagents **24**, **37** and **38** were newly synthesized and used as catalyst during the investigations of various selenium-catalysed Baeyer–Villiger oxidations (Figure 2).

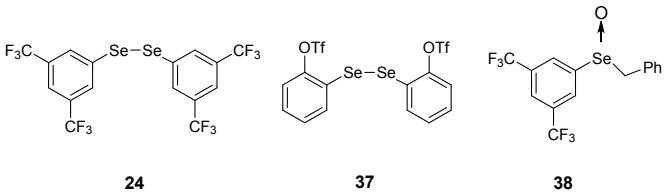


Figure 2: Structures of organoselenium catalysts **24**, **37** and **38**.

In 2001, Sheldon and co-workers developed Baeyer–Villiger oxidations of ketones **5** using 1 mol% of bis(trifluoromethyl)phenyl] diselenide **24** in the presence of hydrogen peroxide. The cyclic ketones **5** were oxidized to cyclic esters **39** in excellent yields while

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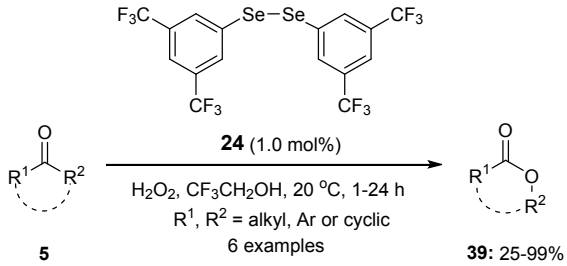
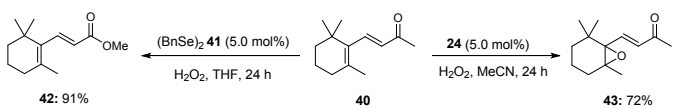
acyclic ketones could produce their corresponding esters in quite poor yields under similar reaction conditions (Scheme 10).[45] Various diaryl diselenide-based selenium-catalysts were tested during these oxidations and diselenides bearing electron-withdrawing groups showed better selectivity and reactivity compare to other diselenides. Probably, *in situ* generated seleninic and perseleninic acids are working as an active catalytic species. The electron-withdrawing nature of diselenides promotes the nucleophilic attack by the oxygen of hydrogen peroxide to form seleninic and perseleninic acid intermediates. Moreover, aldehydes were successfully oxidized into corresponding carboxylic acids in high yields using similar conditions.



Scheme 10. Baeyer-Villiger oxidations ketones **5** to lactones **39** using 1.0 mol% of bis(trifluoromethyl)phenyl] diselenide **24** in the presence of hydrogen peroxide.

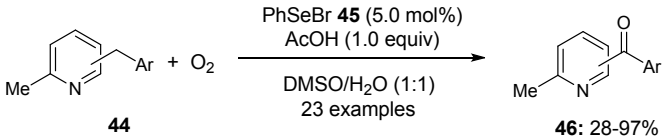
Other cyclic ketones **5** were successfully converted into the corresponding lactones **39** in high yields using 5 mol% diselenide **37** in the presence of hydrogen peroxide.[46] Moreover, Baeyer-Villiger oxidation products **39** were also obtained in excellent yields using selenoxide **38** as catalyst.[33] α,β-Unsaturated ketones can also be used as substrates in selenium-catalysed Baeyer-Villiger oxidations to achieve various substituted vinyl esters in moderate yields.[47] The recycling nature and reusing ability of selenium-catalyst makes this approach more attractive for synthetic organic chemists. Additionally, the selenium-catalysed approach was successfully applied in the synthesis of butanolides by Baeyer-Villiger oxidation of cyclobutanones.[48] Yu and others investigated an interesting selenium-catalysed approach for the oxidation of β-ionone where the selectivity of products was switchable according the choice of organoselenium catalyst.[49] During these oxidations, diaryl diselenide **24** and dibenzyl diselenide **41** were used as catalyst and oxidation of β-ionone with **24** could furnish to epoxide **43** while catalyst **41** leads the formation of corresponding Baeyer-Villiger oxidation product **42** (Scheme 11). Additionally, oxidation reactions were performed up to 40 mmol scale and yields was remained high in both reactions (86% for ester **42** and 70% for epoxide **43**). Moreover, the *in situ* generated benzyl seleninic acid was further used as catalyst in next four cycles of Baeyer-Villiger oxidation reaction although a significant decrease in the yield was observed in each cycle. Albeit the *in situ* generated catalytic species was peroxyseleninic in both reactions.



Scheme 11. Selenium-catalysed approach for the oxidation of β-ionone **40** to epoxide **43** and ester **42** using selenium-catalysts **24** and **41**, respectively.

Selenium-catalysed oxidation of sp^3 C–H bonds

Oxidation of sp^3 C–H bonds to carbonyl compounds is an important synthetic protocol in organic chemistry. Recently, a selenium-catalysed oxidation approach benzylic C–H bond was developed where benzylpyridines **44** were treated with 5 mol% of PhSeBr **45** in DMSO/H_2O under oxygen atmosphere (1 atm). Additionally, 1.0 equivalent of AcOH was required to activate the sp^3 C–H bond and oxidation products **46** were obtained in poor to excellent yields (Scheme 12). The wide range of functional groups on aromatic in substrates were successfully tolerated and the selenium-catalytic oxidation approach follow the free radical mechanism.[50]

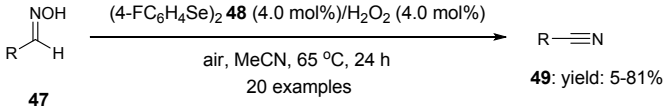


Ar = Ph, 4-MeC_6H_4, 4-$C_2H_5C_6H_4$, 4-FC_6H_4, 4-ClC_6H_4, 4-CNC_6H_4, 4-$CF_3C_6H_4$, 4-$CHOC_6H_4$, 1-Nap etc.

Scheme 12. Selenium-catalysed oxidation of benzylpyridines **44** to benzophenones **46** using PhSeBr **45** as catalyst.

Selenium-catalysed oxidation of oximes

The oxidation of oximes is another quite useful reaction in synthetic organic chemistry. Selenium-catalysed oxidation of aldoximes lead variety of oxidation products. Aldoximes **47** can be dehydrated to their corresponding organonitriles **49** using catalytic amounts of diaryl diselenide (3-$FC_6H_4Se)_2$ **48** and hydrogen peroxide as an oxidant (Scheme 13).[51] The effect of different aliphatic and aromatic substituents in the substrates was studied and the reaction would not work well with most of the aldoximes having aliphatic substituents.

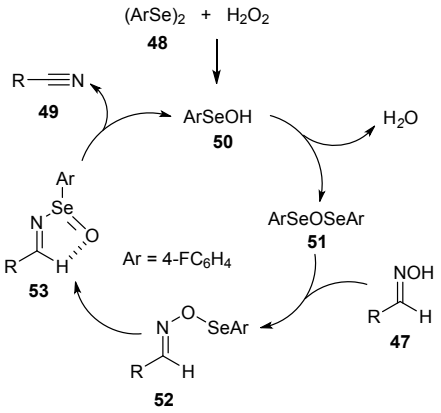


R = Ph, 4-FC_6H_4, 2-ClC_6H_4, 3-ClC_6H_4, 4-ClC_6H_4, 4-BrC_6H_4, 4-$CF_3C_6H_4$, 3-MeC_6H_4,4-MeC_6H_4, 4-$OMeC_6H_4$, ^{i}Pr, ^{t}Bu etc.

Scheme 13. Selenium-catalysed oxidation of aldoximes **47** to organonitriles **49** using (3-$FC_6H_4Se)_2$ **48** as catalyst.

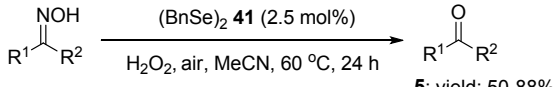
Additionally, the reactions were performed at large scale also and catalyst residue was reused in similar reactions up to 5-6 times without losing much catalytic efficiency. The possible catalytic cycle for the selenium-catalysed dehydration of aldoximes **47** to organonitriles **49** is shown in Scheme 14. According to the catalytic cycle, the reaction was initiated with the formation of selenenic acid intermediate **50** by *in situ* oxidation of catalytic species **48** with H_2O_2. Subsequently, the acid intermediate **50** undergoes dehydration and formed corresponding selenenic anhydride intermediate **51**. Furthermore, the anhydride intermediate **51** reacts with aldoxime **47**

to form another intermediate **52**, which subsequently rearranged to its selenoxide isomer **53**. Finally, the selenoxide isomer **53** facilitates the *syn*-elimination to form final product **49** and selenenic acid **50** to continue the catalytic cycle.



Scheme 14. Mechanism for the selenium-catalysed dehydration of aldoximes **47** to organonitriles **49** using diselenide **48** as catalyst.

In 2015, Yu and co-workers modified the same approach by using seleninic acid as pre-catalyst and air as an oxidant.[52] A similar selenium-catalysed dehydration reaction was achieved under solvent free conditions.[53] Recently, the same research group explored the catalytic utility of dibenzyl diselenide **41** in deoxyamination of oximes **54** to carbonyl compounds **5** in the presence of hydrogen peroxide (Scheme 15).[54] Notably, the reaction was scaled-up up to 50 mmol and recycled catalyst was reused more five times but slight lowering was observed in the yields. Interestingly, both aldoximes and ketoximes exhibited the same potential in this reaction and oxidation products were obtained in good yields. Notably, peroxyselenenic acid was probably working as an active catalytic species. This reaction provides an opportunity to organic chemist for the deprotection of oximes.

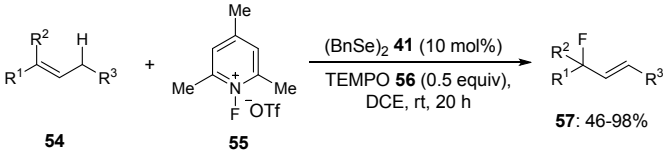


R^1 = Ph, 4-FC_6H_4, 2-ClC_6H_4, 3-ClC_6H_4, 4-ClC_6H_4, 4-$NO_2C_6H_4$, 3-MeC_6H_4,4-MeC_6H_4, 4-$OMeC_6H_4$, 1-Nap, 2-Nap; R^2 = H, Me, Ph, 4-ClC_6H_4, 4-MeC_6H_4, 4-$OMeC_6H_4$

Scheme 15. Deoxyamination of oximes **54** to carbonyl compounds **5** using dibenzyl diselenide **41** as catalyst.

Selenium-catalysed Halogenation

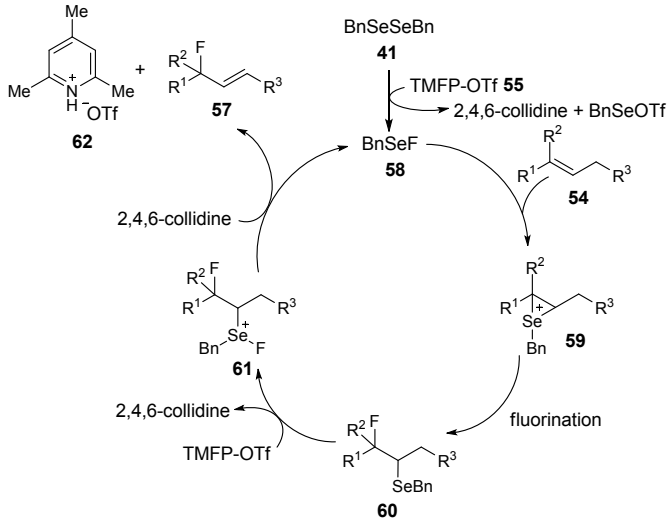
Few organoselenium catalysts have been successfully used to achieve halogenation of alkenes using halide ions in the presence of hydrogen peroxide. This chemistry began in 1979 when organoselenium catalysts were used for the chlorination of olefins using *N*-chlorosuccinimide (NCS) as chlorine source and hydrogen peroxide as an oxidant.[55] The same chlorine source was employed to achieve selenium-catalysed allylic chlorination[56] and chloroamidation of olefins.[57] In 2013, polymer supported selenenyl bromide was developed as a catalyst for chlorinations.[58] The importance of organoselenium catalysts is not limited to chlorination and catalysed few other halogenation reactions also. In 2015, Detty and co-workers synthesized few xerogel-sequestered silanated organoselenides which showed effective catalytic activity towards the bromination of alkenes using sodium bromide as bromine source.[59] Furthermore, the diarylselenides have been used as co-catalyst with DMAP to achieve bromolactonizations.[60] Recently, Zhao and co-workers introduced an organoselenium-catalysed approach for the allylic fluorination of functionalized alkenes **54** using 10 mol% of dibenzyl diselenide **41** using *N*-fluoro-2,4,6-trimethylpyridinium triflate (TMFP-OTf) **55** as an oxidant and as a source of fluoride ions.[61] The fluorinated products **57** were isolated in good to excellent yields (Scheme 16). Notably, TEMPO **56** was used as an additive that combines with diselenide catalyst and facilitates the fluorination process. Interestingly, the reaction did not proceed well in the absence of TEMPO as it was found to inhibit the decomposition of diselenide species. The catalytic diselenide species 41 was not recovered probably due to the instability of $(BnSe)_2$ species.



R^1 = H, Me; R^2 = Me, Et, Ph, Ar;
R^3 = COOMe, COOBn etc.

Scheme 16. Selenium-catalysed allylic fluorination of alkenes **54** with 10 mol% of dibenzyl diselenide **41** using TMFP-OTf **55** as an oxidant and fluorine source.

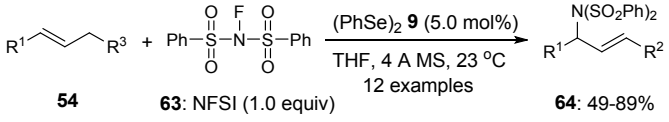
The catalytic cycle for the fluorination of alkenes **54** is depicted in Scheme 17. The catalytic cycle was initiated by the oxidative cleavage of diselenide **41** to more electrophilic selenium species BnSeF **58** by the reaction with TMFP-OTf **55**. The newly generated electrophile **58** activates the olefinic double bond of substrate **54** to form seleniranium ion intermediate **59**. Furthermore, intermediate **59** is attacked by fluorine anion to form fluoroselenenylated intermediate **60**. Then, another molecule of TMFP-OTf **55** oxidizes the selenium functionality of intermediate **60** to facilitate its elimination and form intermediate **61**. On elimination of a proton and the selenium moiety, the intermediate **61** forms fluorinated product **57** and regenerates the electrophilic species BnSeF **58** which continues the catalytic cycle.



Scheme 17. The catalytic cycle for the fluorination of alkenes **54** to **57** with catalyst **41** using TMFP-OTf **55** as an oxidant and fluorine source.

Selenium-catalysed Amination of C-H Bonds

The amination of C-H bonds is an important synthetic tool for the formation of new C-N bonds in different organic compounds. In the past, various synthetic strategies have been used to construct such C-N bonds including transition-metal-catalysed protocols,[62] hypervalent iodine[63] and selenium(IV)-mediated amination of alkenes.[64] In 2013, Breder and co-workers achieved the first selenium-catalysed amination of alkenes.[65] In this reaction, various unactivated olefins **54** were aminated to allylic amides **64** in good to excellent yields. Interestingly, phenylselenenyl bromide was found to be an inefficient catalyst for the amination reaction in the presence of NFSI **63** under similar reaction conditions. Additionally, diphenyl diselenide **9** was found to be an attractive catalyst for the amination of unactivated cyclic olefins under similar reaction conditions.

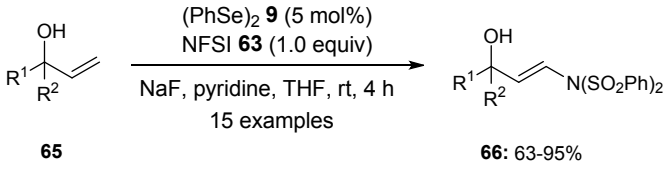


R^1 = Me, Pr, Hept, Ph, Bn; R^2 = COOMe, COOEt, COOBn, $PO(OEt)_2$, SO_2Ph

Scheme 18. Selenium-catalysed amination of alkenes **54** using NFSA **63** as an oxidant and source of nitrogen.

The same catalyst/oxidant [($PhSe_2$ **9**/NFSI **63**)] combination was employed for the amination of terminal alkenes **65** in the presence of a base and the amination occurred selectively at position C-3. 3-Amino allyl alcohols **66** were isolated in good to high yields (Scheme 19).[66a] Interestingly, the reaction site was switched completely from terminal to the other side of double bond when the reaction performed with substrates without an alcoholic group. A mixture of amination products was observed when substrates bearing protected alcohols were employed under similar reaction conditions.

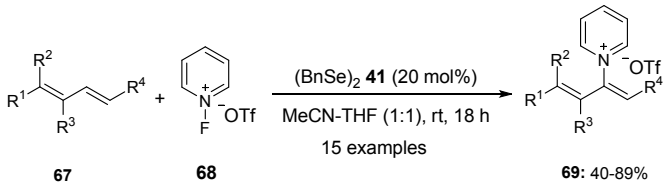
Notably, the presence of hydroxyl groups is mandatory to achieve a selective amination at the C-3 position. Moreover, the same catalytic system was able to aminate disubstituted alkenes at C-3 position with similar catalytic potential.



R^1 = ^{n}Pent, Ph, Bn, CH_2Bn, 4-ClC_6H_4, 4-BrC_6H_4, 4-$CF_3C_6H_4$, 2-$OMeC_6H_4$, 3-$OMeC_6H_4$, 4-MeC_6H_4, 4-$OMeC_6H_4$, 2-Nap; R^2 = H, Me, Et

Scheme 19. Selenium-catalysed amination of terminal alkenes **65** using diphenyl diselenide **9** as catalyst and NFSI **63** as oxidant and nitrogen source.

Recently, Zhao and co-workers developed a selenium-catalysed direct C-H pyridination of 1,3-dienes.[66b] In this report, 1,3-dienes **67** were treated with *N*-fluoropyridinium triflate **68** in the presence of 20 mol% $(BnSe)_2$ **41** and pyridinium triflates of 1,3-dienes **69** were obtained in good to excellent yields (Scheme 20). *N*-Fluoropyridinium triflate **69** was used as an oxidant and pyridine source in this reaction.

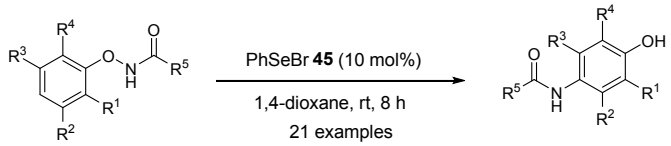


R^1 = Pent, Hept, Ph, Cy, 4-ClC_6H_4, 4-BrC_6H_4, 4-MeC_6H_4, 4-$OMeC_6H_4$, R^2 = R^3 = R^4 = H, Me

Scheme 20. Selenium-catalysed C-H pyridination of 1,3-dienes **67** using $(BnSe)_2$ **41** as catalyst and *N*-fluoropyridinium triflate **68** as oxidant and pyridine source.

Furthermore, the impact of *N*-fluoropyridinium salts on pyridination of 1,3-dienes was also studied. It was found that the reaction did not work with sterically hindered salts. Notably, the yields were slightly lowered when *N*-fluoropyridinium tetrafluoroborates was replaced with the oxidant **69**. Additionally, the same C-H pyridination was successfully performed with both acyclic and cyclic olefins. The catalytic cycle is based on usual selenenylation–deselenenylation pathway.

Phenylselenyl bromide **45** was found to catalyse the amination of *N*-aryloxyacetamides **70** *N*-acetyl *p*-aminophenols **71** under mild reaction conditions. The amination occurred at *para* position and *N*-acetyl *p*-aminophenols **71** were obtained in good to excellent yields (Scheme 21). Moreover, dearomatization occurred when *para*-substituted *N*-aryloxyacetamides were treated under similar reaction conditions.[67]



R^1 = H, Me, Et, Br, Cl; R^2 = H, Me, Br, Cl, F, OMe; R^3 = H, F; R^4 = H, Me; R^5 = Me, ^{t}Bu, Pent, Ph, 2-Py, Bn, 4-MeC_6H_4

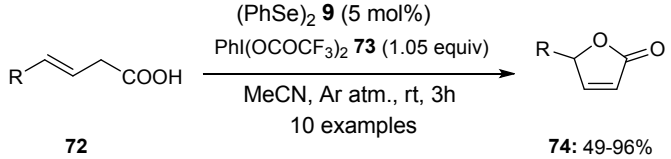
Scheme 21. Selenium-catalysed conversion of *N*-aryloxyacetamides **70** *N*-acetyl *p*-aminophenols **71** using phenylselenyl bromide **45** as catalyst.

Selenium-catalysed Cyclisation Reactions

Various selenium-catalysed cyclisation reactions have been successfully achieved under different reaction conditions. Usually, functionalized olefinic acids, amines or amides are found attractive substrates to develop diverse selenium-catalysed cyclisation reactions.

Selenium-catalysed Lactonisation

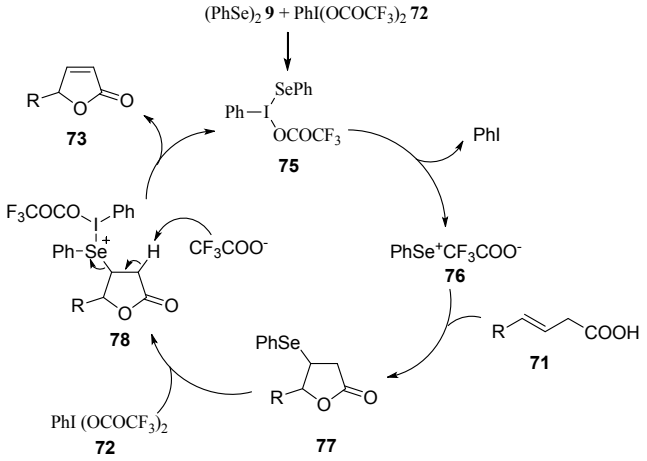
The chemistry of selenium-catalysed lactonization is quite new compare to other selenium-catalysed reactions. The first report on the application of selenium catalyst in lactonization was come in 2002[68] but detailed studies were carried out in 2007 by Wirth and co-workers.[69] The combination of diphenyl diselenide **9** catalyst and [bis(trifluoroacetoxy)iodo]benzene (PIFA) **73** was used to achieve the lactonization of β,γ-unsaturated carboxylic acids **72** to butenolides **74** in good yields (Scheme 22).[69] Other iodine(III) reagents such as PIDA and Koser's reagents can be used oxidant but PIFA showed superiority probably due its better solubility in acetonitrile and the higher electrophilic nature compare to other iodine(III) oxidants.



R = ^{n}Pr, ^{n}Bu, ^{n}Pen, ^{n}Dec, Ph, Bn, 4-MeC_6H_4, 4-BrC_6H_4, 2-Nap

Scheme 22. Selenium-catalysed lactonization of β,γ-unsaturated carboxylic acids **72** to butenolides **74** using diselenide **9** as catalyst and PIFA **73** as an oxidant.

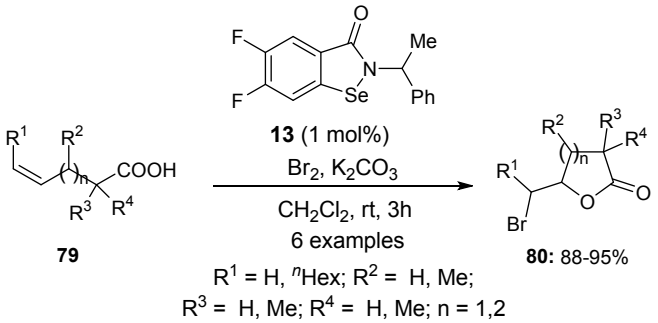
It is important to discuss the mechanistic pathway of this reaction to understand the role of hypervalent iodine species. The possible catalytic cyclic for selenium-catalysed lactonization of β,γ-unsaturated carboxylic acids **72** to butenolides **74** is presented in scheme 23.[69] Initially, PIFA **73** reacts with catalytic species **9** to form another hypervalent iodine species **75**, which converts into more electrophilic species phenylselenenyl trifluoroacetate **76**. Furthermore, the phenylselenenyl trifluoroacetate **76** activates the double bond of β,γ-unsaturated carboxylic acid **72** to form selenolactone **77**. The selenide functionality of lactone **77** was oxidized by another molecule of PIFA **73** to facilitate its elimination *via* intermediate **78**. Finally, intermediate **78** transforms to the butenolides **73** and regenerated iodine(III) species **75** to continue the catalytic cycle.

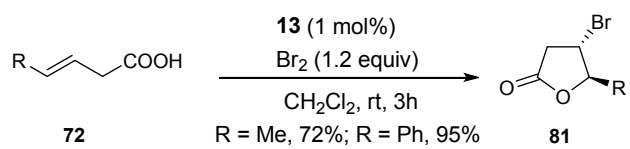


Scheme 23. Mechanism for the selenium-catalysed lactonisation of β,γ-unsaturated carboxylic acids **72** to butenolides **74**.

After this entry, the combination of same catalyst with hypervalent iodine reagents was explored for the synthesis of functionalized isocoumarins[70] and dihydropyranones[71] equipped with different electron-withdrawing and donating functionalities. Later on, Braga and others achieved similar selenium-catalysed lactonizations with the $NaBr/H_2O_2$ combination.[72] Recently, Breder and others replaced hypervalent iodine based oxidants with air in similar selenium-catalysed lactonizations.[73] Additionally, the selenium-catalysed cyclisation approach was used during the synthesis of naturally occurring Greek tobacco lactone.[74]

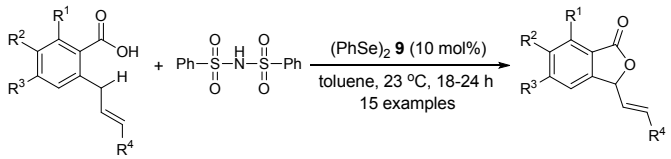
In 2012, Kumar and others developed the synthesis of isoselenazolone **13** and employed this compound as catalyst for the bromolactonisation of functionalized γ,δ-unsaturated acids **79** using bromine or *N*-bromosuccinimide (NBS) as bromine source in the presence of a base (Scheme 24). All the reactions worked smoothly and *exo*-cyclic lactone products were isolated in good yields. Notably, *endo*-cyclic lactones **81** were obtained as reaction products when β,γ-unsaturated acids **54** were treated under similar reaction conditions (Scheme 24).[29]





Scheme 24. Selenium-catalysed lactonization of alkenoic acids **79** and **72** to five-membered lactones **80** and **81** respectively using 1.0 mol% isoselenazolone **13** with bromine or NBS.

In 2015, *ortho*-allyl benzoic acids **82** were cyclised to bicyclic lactones **83** by unusual selenium-catalysed intramolecular oxidative acyloxylation using diphenyl diselenide **9** as catalyst and NFSI **63** as oxidant (Scheme 25).[75] The cyclisation reactions were performed in toluene and functionalized isobenzofuranones **83** were isolated in good yields. The scope of this reaction was further expanded with variety of functionalities in the benzene ring and electron-donating groups showed better results compare to electron-withdrawing substituents. Surprisingly, an 1,2-oxyselenation of the double bond was observed when an aryl group was replaced with sterically less-demanding and electronically less-stabilizing alkyl group in substrates. Probably, NFSI **63** reacts with catalytic species to form an electrophilic selenonium species, which might be used to activate the olefinic double bond.



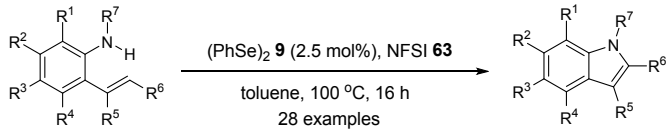
82 NFSI **63** **83:** 6-81%

R^1 = H, OMe; R^2 = H, Me, OMe, PivNH, CF_3; R^3 = H, CF_3; R^4 = Et, Ph, 4-MeC_6H_4; 4-FC_6H_4; 4-$CF_3C_6H_4$; 1-Nap, 2-thienyl

Scheme 25. Selenium-catalysed intramolecular oxidative acyloxylation of *ortho*-allyl benzoic acids **82** using catalyst **9** and oxidant NFSI **63**.

Selenium-catalysed Aminocyclisations

In the previous section, we have discussed the selenium-catalysed amination reactions using different nitrogen sources as an external nucleophile in the presence of terminal oxidants. There are few reports in the literature where selenium-catalysed aminocyclisations have been achieved using substrates having internal nitrogen nucleophiles. In 2015, Ortgies and Breder developed selenium-catalysed aminocyclisation of *ortho*-vinyl anilines **84** using 2.5 mol% of diphenyl diselenide **9** in the presence of *N*-fluorobenzenesulfonimide (NFSI) **63** as oxidant.[76] The aminocyclisation reactions were performed in toluene and functionalized indoles **85** were obtained in good yields (Scheme 26).

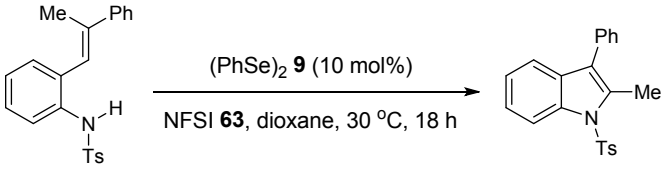


84 **85:** 42-99%

R^1 = H, Br; R^2 = H, CF_3; R^3 = H, Me, Cl, ^{n}Pr, CN, COOMe, R^4 = H, F; R^5 = H, 4-$OMeC_6H_4$; R^6 = Me, ^{n}Pr, Cy, CH_2OMe, $CH_2{}^c$Pent, ^{c}Pr, Ph, Bn; R^7 = Ts, Ns, Ms, Ac, $COCCl_3$

Scheme 26. Selenium-catalysed aminocyclisation of *ortho*-vinyl anilines **84** to indoles **85** using diphenyldiselenide **9** as catalyst in the presence of NFSI **63**.

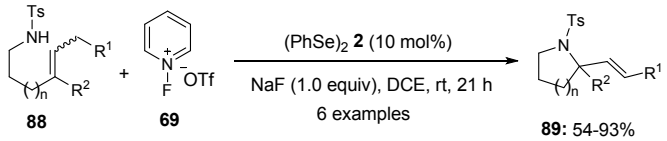
Moreover, the reaction conditions were modified slightly and similar cyclisations were obtained in dioxane at 30 °C but required 10 mol% catalytic loading.[77] Surprisingly, 1,2-phenyl migration product **87** with cyclisation was obtained exclusively when trisubstituted alkene **86** was used as the substrate (Scheme 27).[77]



86 **87:** 99%

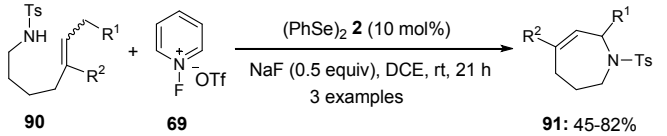
Scheme 27. Selenium-catalysed 1,2-phenyl migration with cyclisation of trisubstituted alkene **86** using diphenyl diselenide **9** as catalyst in the presence of NFSI **87**.

Zhao and co-workers developed the selenium-catalysed cyclisation of olefinic sulphonamides **88** to five- and six-membered tosyl amines **89** in good to excellent yields using catalyst **9** and *N*-fluoropyridiniumtriflate **69** (Scheme 28).[78] Surprisingly, seven-membered amines **91** were isolated in 45-82% yields under slightly modified reaction conditions (Scheme 28). Moreover, the same catalytic approach was applicable for the cycloetherification of olefinic alcohols.[78]



88 **69** **89:** 54-93%

R^1 = H, Et, Bn; R^2 = H, Me, Ph, 4-MeC_6H_4; n = 1 or 2

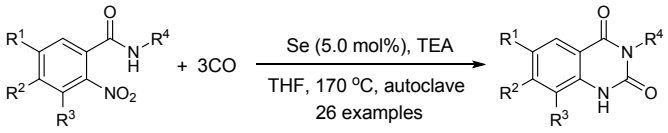


90 **69** **91:** 45-82%

R^1 = Et, Bn; R^2 = Ph, 4-ClC_6H_4; 4-MeC_6H_4

Scheme 28. Selenium-catalysed cyclisation of olefinic sulfonamides **88** and **90** to cyclic amines **89** and **91**.

The reductive carbonylation of *ortho*-nitrobenzamides **92** was successfully used to achieve aminocyclisations.[78] In 2010, Wu and Yu developed selenium-catalysed carbonylation of *ortho*-nitrobenzamides **92** to 1*H*-quinazoline-2,4-diones **93** using Se powder as catalyst with CO at 2.0 MPa in the presence of triethylamine.[79] The carbonylation reactions were performed in stainless steel autoclave at 170 °C and cyclic products **93** were isolated in good to excellent yields (Scheme 29). Notably, neither 1.0 MPa nor 3.0 MPa pressure of CO was suitable to achieve these cyclisations.

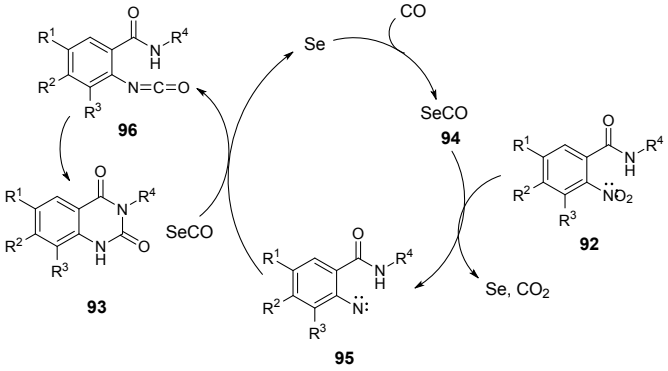


92 **93**: 67-96%

$R^1 = R^2$ = H, Cl, OMe; R^3 = H, Me; R^4 = H, Me, Et, ^{i}Pr, Bu, Allyl, Bn, Ph, 4-Py, 4-MeC_6H_4, 2-BrC_6H_4, 2-ClC_6H_4, 4-$OEtC_6H_4$;

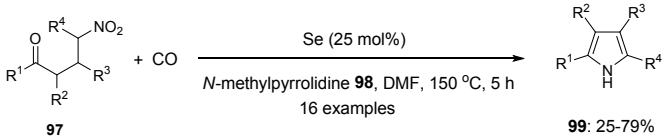
Scheme 29. Selenium-catalysed carbonylation of *ortho*-nitrobenzamides **92** to 1*H*-quinazoline-2,4-diones **93** using Se power as catalyst with CO at 2.0 MPa.

The catalytic cycle for the selenium-catalysed carbonylation of *ortho*-nitrobenzamides **92** to 1*H*-quinazoline-2,4-diones **93** is described in Scheme 30. The catalytic cycle was initiated with the *in situ* generation of carbonyl selenide (SeCO) **94** by the reaction of elemental selenium with CO. After that the carbonyl selenide species **94** reacts with *ortho*-nitrobenzamide **92** to form nitrene intermediate **95**. The nitrene intermediate **95** reacts with another molecule of carbonyl selenide (SeCO) **94** and forms isocyanate intermediate **96** along with Se. Finally, the isocyanate intermediate **96** undergoes intramolecular hydrogen transfer to yield the final cyclic product **93**. Probably, the role of triethylamine was to stabilize the *in situ* generated carbonyl selenide species.



Scheme 30. The catalytic cycle for selenium-catalysed carbonylation of *ortho*-nitrobenzamides **92** to 1*H*-quinazoline-2,4-diones **93**.

The selenium-catalysed synthesis of highly functionalized pyrroles **99** was achieved by the reaction of γ-nitro substituted carbonyl compounds **97** with carbon monoxide using selenium as catalyst and *N*-methylpyrrolidine **98** as a base (Scheme 31).[80] The cyclisation reactions were carried out with CO at 30 atm pressure and the yields were further reduced at lower CO pressure. Probably, *in situ* generated carbonyl selenide (SeCO) **94** was initiating the catalytic cycle.



97 **99**: 25-79%

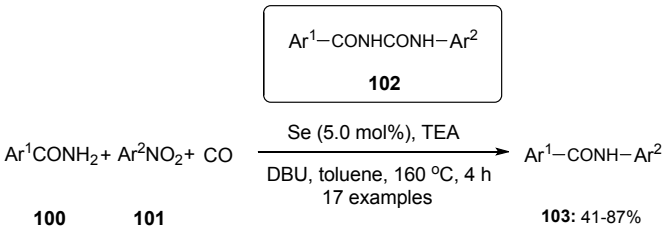
R^1 = Hex, Ph, 2-MeC_6H_4, 3-MeC_6H_4, 4-MeC_6H_4, 4-$OMeC_6H_4$, 4-ClC_6H_4; R^2 = H, Me, COOEt; R^3 = Bu, Ph, 2-MeC_6H_4, 3-MeC_6H_4, 4-MeC_6H_4, 4-$OMeC_6H_4$, 4-ClC_6H_4; R^4 = H, Me

Scheme 31. Selenium-catalysed synthesis of pyrroles **99** by the reaction of γ-nitro substituted carbonyl compounds **97** with CO using Se as catalyst in the presence of a base **98**.

View Article Online DOI: 10.1039/C8CY02274G

Selenium-catalysed carbonylations

Selenium-catalysed carbonylation reactions received a particular attention due to easy accessibility of catalysts and mild reaction conditions. Initially, few reports on the selenium-catalysed carbonylations were published by Sonoda and coworkers.[9,17] After that the combination of catalytic amount of elemental selenium with carbon monoxide was used for the selective reduction of nitro arenes.[10] The same catalytic approach was employed for the synthesis of 1,3-diaryl urea under different reaction conditions.[11,12] In 2004, selenium-catalysed carbonylation was applied in the synthesis of *N*-arylamides **103** in good yields by the reaction of arylamides **100** with nitroarenes **101** in the presence of carbon monoxide using a mixture of organic bases TEA and DBU (Scheme 32).[81] Additionally, elemental selenium was recovered and reused in further reactions. The role of these two organic bases was entirely different in this reaction. The intermediate **102** was found the key intermediate in the reaction. Interestingly, TEA was not sufficient to cleave the intermediate **102** into final product **103** and required stronger base DBU. The role of TEA was to promote this reaction and it was used as co-catalyst. In 2009, Zhang and Jing applied similar selenium-catalysed carbonylation approach for the synthesis of naphthyl carbamates by replacing amides with alcohols.[82]



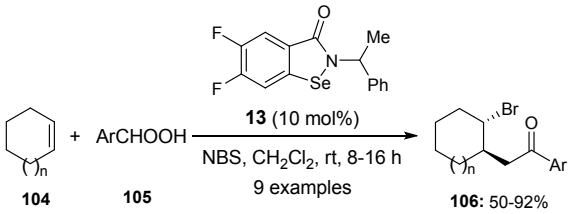
100 **101** **103:** 41-87%

Ar^1 & Ar^2 = Ph, 2-MeC_6H_4, 3-MeC_6H_4, 4-MeC_6H_4, 2-ClC_6H_4, 4-ClC_6H_4, 4-EtC_6H_4, 4-ClC_6H_4, 3-BrC_6H_4, 4-$OMeC_6H_4$, 4-$OEtC_6H_4$, 4-$OPhC_6H_4$

Scheme 32. Selenium-catalysed carbonylation of arylamides **100** to *N*-arylamides **103** by the reaction of nitroarenes **101** elemental Se and CO in the presence of bases.

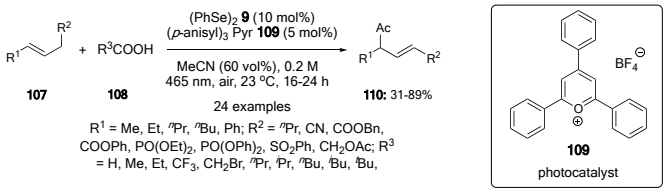
Selenium-catalysed Esterification

In 1992, organoselenum catalysts were used for the first time in esterification reactions by Iwaoka and Tomoda.[83] The next report on selenium-catalysed esterification was published only in 2012 by Kumar and co-workers.[29] In this report, the catalytic potential of isoselenazolone was explored for the bromoesterification of cyclic olefins **104** in good to excellent yields (Scheme 33). *N*-Bromosuccinimide (NBS) was used as bromine source and bromo esters **106** were obtained in single *trans*-isomer. Notably, the mixture of both *trans*- and *cis*-isomers was obtained when acyclic alkenes were used as substrates in this reaction.



Scheme 33. Selenium-catalysed bromoesterification of cyclic olefins **104** using NBS as bromine source.

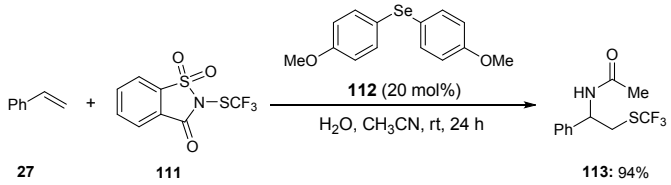
In 2016, the combination of diphenyl diselenide catalyst **9** with photocatalyst **109** was used to develop the esterification of functionalized olefins **107**. In order to achieve these esterification reactions, the mixture of alkenes **107** with different aliphatic carboxylic acids **108** in acetonitrile was irradiated in the presence of 10 mol% diphenyl diselenide **9** and 5.0 mol% of photocatalyst 2,4,6-tris(4-methoxyphenyl)pyrylium tetrafluoroborate **109**. In most of the reactions, allylic esters **110** were obtained in high yields except aromatic alkenes (Scheme 34).[84] Probably, the photocatalyst **109** was activated on irradiation at 465 nm and initiates the formation of more electrophilic active organoselenium species.



Scheme 34. Selenium-catalysed photo-induced allylic esterification of disubstituted alkenes **107** to allylic esters **110**.

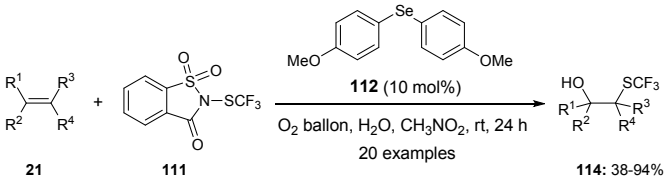
Selenium-catalysed Trifluoromethylthiolation

The selenium-catalysed trifluoromethylthiolation is a relatively new reaction compared to other selenium-catalysed reactions. The aminotrifluoromethylthiolation of styrene **27** (R^1 = Ph and R^2 = H) was achieved by the reaction with 20 mol% of di(4-methylphenyl)selenide **111** in water/acetonitrile using *N*-CF_3S-saccharin **112** as source of SCF_3. The trifluoromethylthiolated product **113** was obtained in 94% yield (Scheme 35). Various electron-rich and electron-withdrawing diarylselenides **112** were used as catalyst and electron-rich diarylselenides exhibited high catalytic efficiency. Notably, the selenide catalyst activates the CF_3S reagents to generate more reactive CF_3S^+ cation and stabilizes the trifluoromethylthiiranium ion intermediate. The electronic properties of selenide catalyst play a vital role in this aminotrifluoromethylthiolation reaction.[85]



Scheme 35. Selenium-catalysed trifluoromethylthiolation of styrene **27** using di(4-methylphenyl)selenide **112** as catalyst in water/acetonitrile using *N*-CF_3S-saccharin **111**.

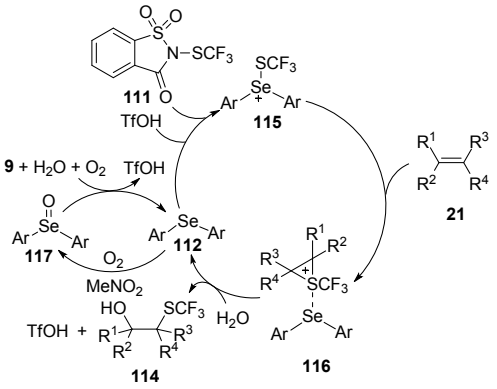
Furthermore, the same research group developed the hydroxytrifluoromethylthiolation of alkenes **21** using a similar reagent combination in nitromethane under oxygen atmosphere.[86] Notably, 10 mol% of di(4-methylphenyl)selenide **112** catalyst was found sufficient to catalyse this reaction. The hydroxytrifluoromethylthiolated products **114** were isolated in moderate to excellent yields (Scheme 36). The scope of reaction was further expanded with variety of olefinic substrates and reaction products were obtained in higher yields with electron-withdrawing aromatic olefins compare to other substrates. The same catalytic combination was successfully applied for the trifluoromethylthiolactonizations of nucleophile-tethered alkenes.



R^1 = H, Me, Et, Pr, ^{i}Pr, Ph, Bn; R^2 = Ph, 4-MeC_6H_4, 3-MeC_6H_4, 2-MeC_6H_4, 4-$OMeC_6H_4$, 4-FC_6H_4, 4-BrC_6H_4, 4-ClC_6H_4, 4-$CF_3C_6H_4$, 2-Nap; R^3 = H, Me, Pr; R^4 = H, Me

Scheme 36. Selenium-catalysed trifluoromethylthiolation of alkenes **21** using di(4-methylphenyl)selenide **112** as catalyst in water/nitromethane using *N*-CF_3S-saccharin **111**.

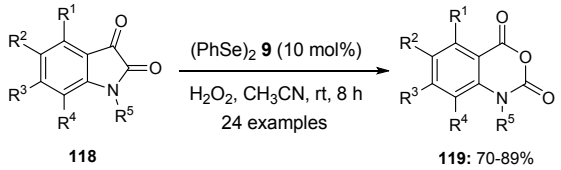
The possible catalytic cycle for the selenium-catalysed trifluoromethylthiolation of alkenes **21** is depicted in Scheme 37. The catalytic cycle is initiated with oxidation of catalytic selenide species **112** to diaryl selenoxide **117** by oxygen in nitromethane. After that the selenoxide **117** is further reduced to **112** by *N*-CF_3S-saccharin **111** along with the formation of TfOH. Furthermore, the formation of an intermediate **115** occurs by the co-activation of selenide **112** and *in situ* generated TfOH. The intermediate **115** further reacts with alkene **21** to form episulfonium ion intermediate **116**. Finally, the intermediate **112** reacts with H_2O to form final product **114** and regenerates catalyst **112** to continue the catalytic cycle.



Scheme 37. The possible catalytic cycle for the selenium-catalysed trifluoromethylthiolation of alkenes **21**.

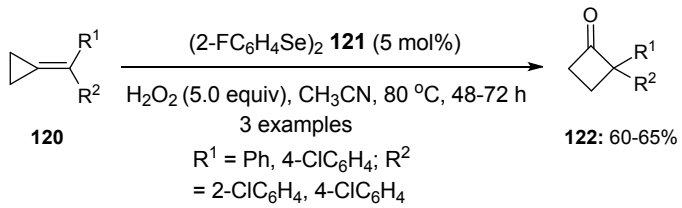
Selenium-catalysed Ring Expansions

Recently, several research groups have identified the application of organoselenium catalysts in rearrangements. In 2015, ring expansion was achieved during the oxidation of functionalized isatins **118** using catalytic amount of diphenyl diselenide **9** in the presence of terminal oxidant H_2O_2.[87] The oxidation reactions were found quite slow and isatoic anhydrides **119** (ring expansion products) were obtained in high yields (Scheme 38). Moreover, the reaction was scaled-up with up to 50 mmol and rearranged products **119** were obtained in healthy yields. Furthermore, the catalytic species was recovered simply by filtration of reaction mixture and catalyst was recovered in its mother liquid. The mother liquid was further charged up with the substrate **118** and hydrogen peroxide and process was successfully repeated up to seven times. Surprisingly, a significant increase in the yield of rearranged products **119** was observed in first five cycles while slightly lowered in remaining two cycles. An easy work-up procedure and recyclability of the catalyst makes this procedure more suitable for industrial purpose.



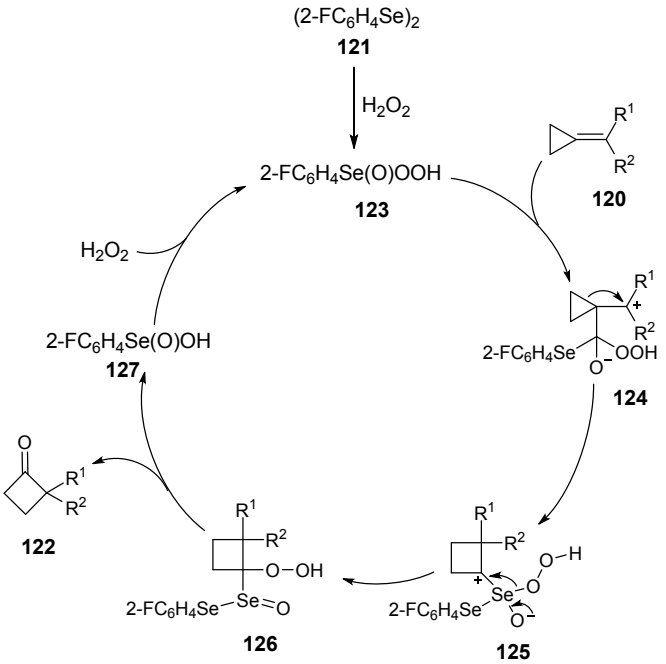
Scheme 38. Selenium-catalysed ring expansion of isatins **118** to isatoic anhydrides **119** using diphenyldiselenide **9** as catalyst and H_2O_2 as an oxidant.

Another approach to organoselenium-catalysed oxidative ring expansions was developed by Yu and co-workers.[88] In their report, various highly active disubstituted methylenecyclopropanes **120** were treated with 5 mol% of $(2\text{-}FC_6H_4Se)_2$ **121** in the presence of hydrogen peroxide and substituted cyclobutanones **122** (ring expansion products) were obtained in moderate yields (Scheme 39). Various diarylmdiselenides bearing electron-rich and electron-deficient moiety but diselenides catalyst with electron-deficient moiety exhibited better catalytic activities compare to electron-rich species. Notably, monosubstituted methylenecyclopropanes could find the suitable substrates under oxidative reaction conditions used in this reaction.



Scheme 39. Selenium-catalysed ring expansion of cyclopropanes **120** cyclobutanones **122** using diselenide **121** as catalyst and H_2O_2 as oxidant.

The catalytic cycle for the selenium-catalysed ring expansion of methylenecyclopropanes **120** to cyclobutanones **122** is described in Scheme 40. According to the catalytic cycle, the reaction was initiated with the oxidation of catalytic species **121** to seleninoperoxoic acid species **123** by hydrogen peroxide. The intermediate **123** activates the double bond of methylenecyclopropane **120** to form cationic intermediate **124**. After that the cationic intermediate **124** rearranged to another cationic intermediate **125**. Furthermore, the intermediate **125** undergoes an intramolecular rearrangement to forms another reaction intermediate **126**. Finally, intermediate **126** decomposes to the ring expansion product **122** along with the formation of organoseleninic acid [E]. The organoseleninic acid species [E] oxidizes to selenoperoxoic acid [A] to continue the catalytic cycle.



Scheme 40. The catalytic cycle Selenium-catalysed ring expansion of cyclopropanes **120** cyclobutanones **122** using diselenide **121** as catalyst and H_2O_2 as oxidant.

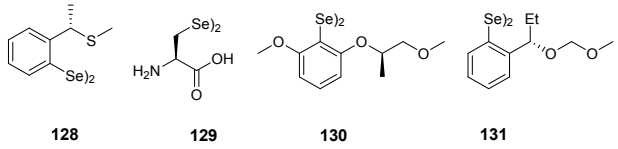
Selenium-catalysed Stereoselective Reactions

The chemistry of selenium-catalysed stereoselective reactions is particularly less developed research area compare to its racemic reactions but the history of these reactions is become quite old now. The first report on the application of chiral selenium catalyst in asymmetric synthesis was introduced by Uemura and co-workers in 1994.[89] Since this report, various chiral organoselenium catalysts have been successfully employed during the development of wide range of stereoselective reactions. In 2006, Braga and his research group compiled a review article where they covered various aspects selenium-catalysed symmetric reactions including selenium-ligated reactions.[90]

Wirth and co-workers employed various nitrogen containing chiral diselenides to achieve the synthesis of enantiomerically enriched secondary alcohols *via* the addition of diethylzinc to aldehydes.[91-93] Moreover, the other research groups have discovered few more chiral selenium catalysts for similar reactions.[94-96] Notably, the catalytic amount of few chiral organoselenium reagents have been used as ligand in transition metal-catalysed reactions.[90] Few

selenium-based chiral ligands have been used to achieve the Cu-catalysed enantioselective conjugate addition of organometallic reagents to enantiomerically rich enones.[97] Some selenium-based ligands have received a wide range of applications in Pd-catalysed stereoselective allylic alkylations.[98-105] Additionally, few other organoselenium reagents have been identified as successful catalysts for different stereoselective reactions such as Aldol reaction,[106] Darzen reaction[107] and Baeyer-Villiger oxidations.[108] High selectivities were obtained in case of Aldol and Darzen reactions while Baeyer-Villiger oxidations could only be achieved in low yields.

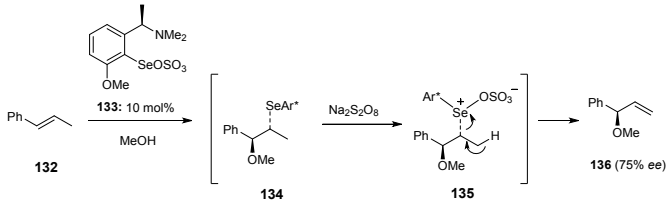
Chiral diselenides **128**-**131** were used as catalysts in stereoselective dihydroxylation of cyclohexene (Figure 3). Dihydroxylation was achieved in 20% enantiomeric excess when reaction was performed using sulfur-containing chiral diaryl diselenide **128** at room temperature.[109] Moreover, the high selectivities were obtained at low temperature with the same chiral catalyst.[36] Selenium-catalysts **129**-**131** were used in the hydroxylation of cycloalkenes and L-selenocystine based-catalyst **129** exhibited superior catalytic activity over catalysts **130** and **131**.[110] Unexpectedly, poor or no selectivity was observed when acyclic alkenes were hydroxylated using similar catalysts.[110]



128 **129** **130** **131**

Figure 3. The structures of various chiral selenium reagents **128**-**131**.

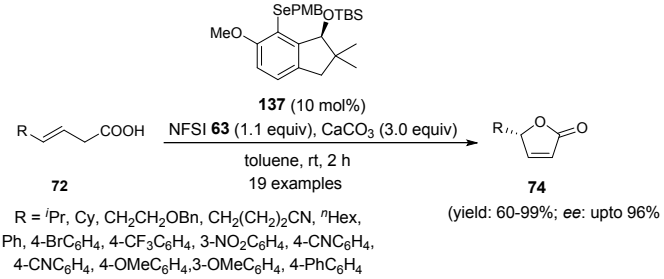
In 1998, Wirth and co-workers developed a selenium-catalysed asymmetric reaction based on stereoselective selenenylation-elimination reaction sequence.[111] In this report, they developed a sequence of methoxyselenylation and oxidative *β*-hydride elimination of alkenes **132** using nitrogen-containing chiral diselenide **133** as catalyst and sodium persulfate as terminal oxidant (Scheme 41). The reaction products **136** were obtained in low yields with up to 75% enantiomeric excess.[111] Initially, the diselenide species **133** activates the olefinic double bond of alkene **132** to form selenide intermediate **134**. Furthermore, the selenium functionality of intermediate **134** was oxidized to intermediate **135** by sodium peroxodisulfate. Finally, the intermediate **135** undergo β-hydride elimination and form final product **136** along with the regeneration of catalytic species. Later on, the asymmetric electrochemical selenenylation-elimination reaction sequence was developed with moderate enantiomeric excess using catalytic amount of chiral diselenides.[112]



132 **134** **135** **136** (75% *ee*)

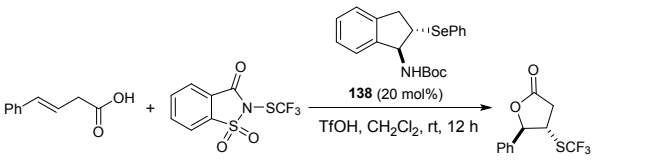
Scheme 41: Selenium-catalysed asymmetric reaction based on the stereoselective selenenylation-elimination reaction of β-methyl styrene **132**.

The same selenenylation-elimination sequence was utilized to achieve enantioselective lactonization of β,γ-unsaturated carboxylic acids **72** to γ-butenolides **74** using different enantiomerically pure diaryl diselenides. Notably, the limited success was achieved in terms of enantiomeric excess during these lactonizations.[69,113] In 2016, Maruoka and coworkers reported the first highly enantioselective lactonizaton of β,γ-unsaturated carboxylic acids **72** to enantioenriched γ-butenolides **74** using indane-based chiral electrophilic selenide **137**. During these lactonizations NFSI **63** was used as terminal oxidant and γ-butenolides were obtained in excellent yields with up to 96% enantiomeric excess (Scheme 42).[114] Probably, the rigidity of an indane-based chiral selenium catalyst **137** was playing a vital role in achieving γ-butenolides **74** with high enantiomeric excess. Moreover, the synthesized γ-butenolides **74** were reduced to chiral (*Z*)-allyl alcohols without any notably decrease of optical purity.[114]



Scheme 42. Selenium-catalysed enantioselective lactonizations β,γ-unsaturated acids **72** using 10 mol% of chiral catalyst **137** in the presence of oxidant NFSI **63**.

Furthermore, the indane-based chiral selenide **138** was used to catalyse the lactonization of (*E*)-4-phenylbut-3-enoic acid **71** using *N*-CF_3S-saccharin **111** as source of SCF_3 in the presence of triflic acid (TfOH). The trifluoromethylthiolated lactone **139** was obtained in excellent yield with 72% enantiomeric excess (Scheme 43).[115] Notably, the indane-based chiral sulfide catalysts showed better selectivity compare to selenide **138**. Triflic acid was used to make the salt of catalytic species which activates the SCF_3 reagent.

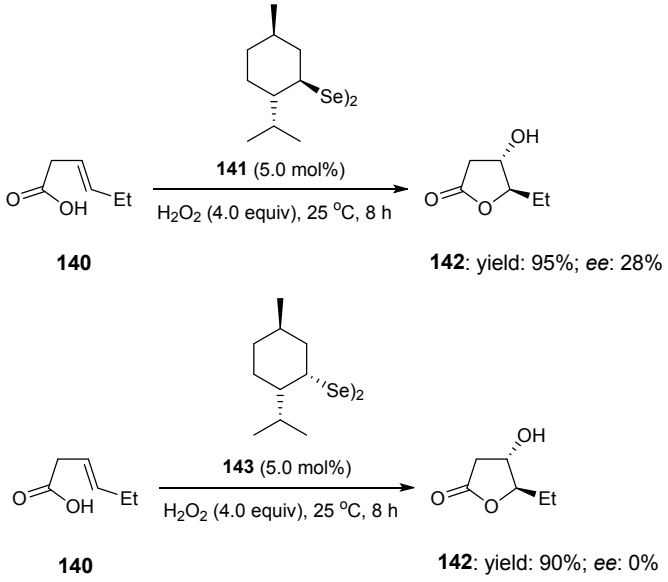


71 **111** **139**: yield: 94%; *ee*: <72%

Scheme 43: Selenium-catalysed enantioselective trifluoromethyl-thiolating lactonizations (*E*)-4-phenylbut-3-enoic acid **71** using 20 mol% of indane-based chiral catalyst **138** and *N*-CF_3S-saccharin **111** as source of SCF_3.

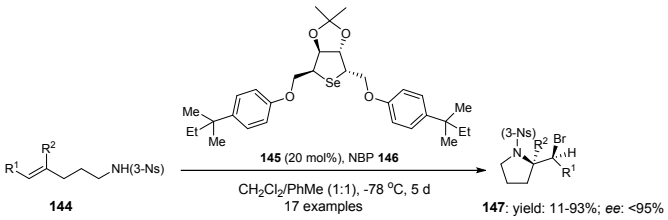
Recently, menthane-based selenium catalyst **141** was used to transfer the chiral information during the catalytic oxylactonization of β,γ-unsaturated acids **140**.[116] The cyclised product **142** was obtained in 95% yield with up to 28% enantiomeric excess (Scheme 44). Moreover, the structurally similar catalyst **143** could produce

only the racemic mixture, probably due to the steric hindrance on the selenium atom (Scheme 44).[116]



Scheme 44: Selenium-catalysed enantioselective oxylactonizations of β,γ-unsaturated acids **140** using 5.0 mol% of menthane-based chiral catalyst **141** and **143** in the presence of H_2O_2.

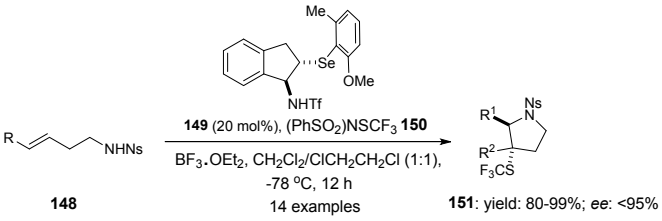
In 2013, Yeung and co-workers synthesized new chiral C_2-symmetric mannitol-derived cyclic selenium catalyst **145** in four chemical steps staring from mannitol.[117] This catalyst **145** was used to develop enantioselective bromocyclisation of trisubstituted olefinic amides **144** using stoichiometric amount of *N*-bromophthalimide (NBP) **146** as bromine source.[117] The cyclisation reactions proceeded *via* an *endo*-cyclic process and the resulting functionalized pyrrolidines **147** were obtained with up to 95% enantiomeric excess (Scheme 45). Interestingly, the nature bromine source and position of attachment with nosylamide influence the selectivity. The presence of *N*-bromophthalimide (NBP) exhibited the superiority over other bromine source while the 3-nitrobenzenesulfonamide showed far batter selectivity compare to its 2- and 4-nosyl analogues.



R^1 = Me, Et, Pr, Bu, Ph, Bn, EtPh, allyl; R^2 = Ph, 4-ClC_6H_4, 3-ClC_6H_4, 4-FC_6H_4, 4-$CF_3C_6H_4$, 4-MeC_6H_4, 3-MeC_6H_4, 2-MeC_6H_4, 4-$OMeC_6H_4$,

Scheme 45: Selenium-catalysed enantioselective bromocyclisation of trisubstituted olefinic amides **144** using 20 mol% of C_2-symmetric mannitol-derived cyclic selenium catalyst **145** and NBP.

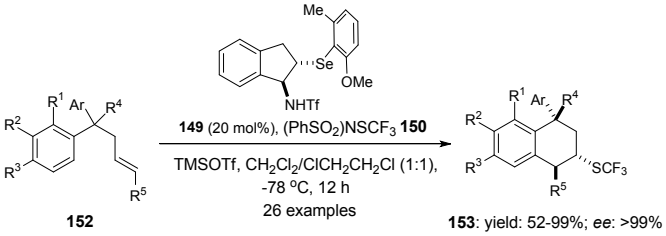
Recently, Zhao and co-workers modified the indane-based selenium catalyst **145** to **149** and applied for the catalytic trifluoromethylthiolating aminocyclisation of γ,δ-unsaturated nosylated amines **148** in the presence of Lewis acid.[118] During these cyclisations, $(PhSO_2)_2NSCF_3$ **150** was used as source of SCF_3 and the trifluoromethylthiolated pyrrolidines **151** were obtained in high yields with up to 95% enantiomeric excess (Scheme 46).[118] Additionally, indane-based chiral sulfides were also explored in this reaction but could produce only low enantiomeric excess. Expectedly, the cyclisations were proceeded *via* an *exo*-cyclic process when reactions were performed with substrates having one more carbon atom.



R^1 = Et, ^{t}Bu, Ph, Bn, CH_2Bn, 4-MeC_6H_4, 3-MeC_6H_4, 2-MeC_6H_4, 4-$OMeC_6H_4$, 4-ClC_6H_4, 2-BrC_6H_4, 2-Naphthyl, 2-Thienyl

Scheme 46: Selenium-catalysed enantioselective trifluoromethylthiolating aminocyclisation γ,δ-unsaturated nosylated amines **148** using 20 mol% of indane-based chiral catalyst **149** in the presence of a Lewis acid.

Very recently, the same indane-based selenium catalyst **149** was further explored by Zhao and co-workers to develop highly enantioselective desymmetrization and carbotrifluoromethylthiolation approach.[119] In this approach, various *gem*-diaryl-tethered alkenes **152** were cyclised to tetrahydronaphthalenes **153** using catalytic species **149** in the presence of TMSOTf. The same SCF_3 source was used and enantiomerically pure trifluoromethylthiolated tetrahydronaphthalenes **153** were isolated in >99% enantiomeric excess (Scheme 47).[119]



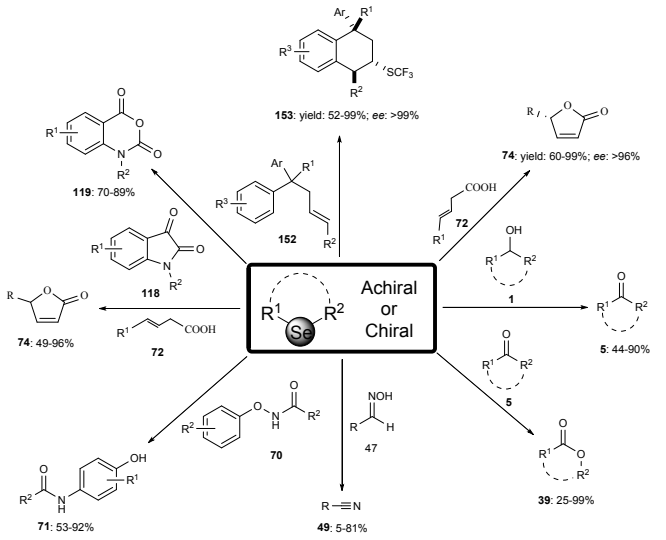
R^1 = H, Me; R^2 = H, Me, OMe; R^3 = H, Me, Ph; R^4 = H, NHBz, NXNs, CH_2OH, OBz, OAc; R^5 = Me, Ph, 2-MeC_6H_4, 4-MeC_6H_4, 4-ClC_6H_4, 4-BrC_6H_4, 3-$OMeC_6H_4$, 2-Naphthyl; Ar = Ph, 2-MeC_6H_4, 2-MeC_6H_4, 3-$OMeC_6H_4$, 4-MeC_6H_4, 4-PhC_6H_4

Scheme 48: Selenium-catalysed enantioselective carbotrifluoromethylthiolation of *gem*-diaryl-tethered alkenes **152** using indane-cored chiral catalyst **149** in the presence of TMSOTf.

Conclusions

In this review, we have covered various synthetically important organic transformations using variety of achiral and chiral orgaselenium catalysts (Scheme 48). Various synthetic transformations such as oxidation of alcohols, olefins and carbonyl compounds, cyclisations and ring expansions have been successfully achieved using different organoselenium catalysts in the presence of mild oxidants. Few of these selenium-catalysed reactions have been successfully achieved at large scale with high yields and catalysts were recovered and

reused several times without losing much catalytic efficiency. These catalytic approaches would be more suitable for industrial purpose. Recently, few chiral organoselenium catalysts have been investigated to achieve different stereoselective cyclisations including carbocyclisations with prodigious selectivity. Moreover, few products obtained during these catalytic transformations are important synthetic intermediates for the construction of biologically active synthetic and natural products.



Scheme 48: Highlights of selenium-catalysed reactions using achiral and chiral selenium catalysts.

Conflicts of interest

There are no conflicts to declare.

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