Organoselenium Chemistry

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1. Introduction

Organoselenium chemistry has been established as valuable research area in synthetic and medicinal chemistry.[1-11] After the discovery of the selenoxide elimination reaction in early 1970s,[12-14] organoselenium reagents received the great success in organic synthesis including asymmetric synthesis.[15-18] More commonly, synthetic transformations such as selenenylations, selenocyclizations and 2,3-sigmatropic rearrangements have been successfully achieved using these reagents under mild reaction conditions.[19-33] The application of these reagents in catalysis makes them more suitable reagents in organic synthesis.[34-39] Several books,[1-7, 41-43] book chapters[8-11, 44-48] and review articles[49-64] have been published to explain the utility of organoselenium reagents in synthesis. This chapter highlights the application of organoselenium reagents in organic synthesis including asymmetric synthesis.

2. Organoselenium Reagents As Electrophiles

Organoselenium reagents play different roles in organic reactions but mainly known for their electrophilic behaviour. The electrophilic selenium species can be generated by the cleavage of the Se-Se bond of diselenides and can be used to activate the olefinic double bonds. Due to their electrophilic character, selenium electrophiles react with olefinic double bonds to form three membered seleniranium ion intermediate. Furthermore, the seleniranium ion intermediate can be employed to achieve various selenenylation reactions with different nucleophiles.

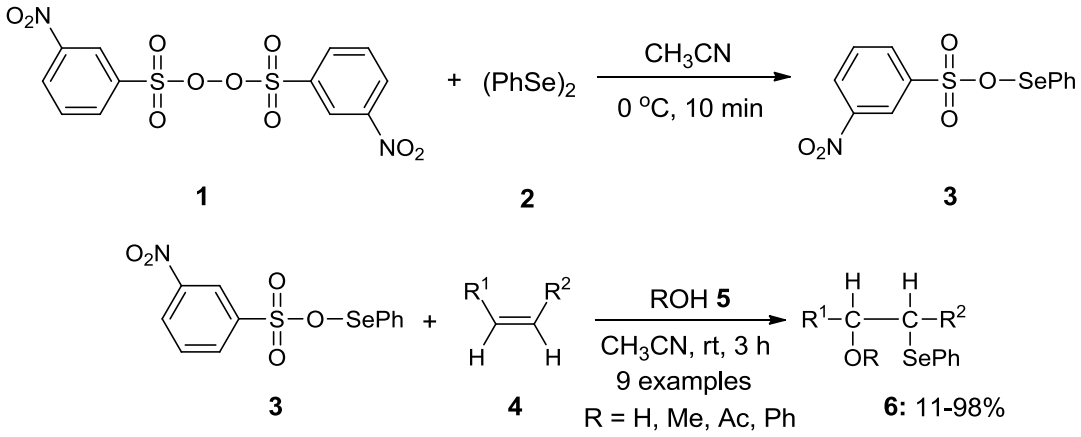
2.1. Selenenylation Reactions

Selenium electrophiles have been successfully used to achieve various selenylation reactions such as selenylation of olefins, arenes and other organic species. In the section, various selenylation reactions achieved in current decade will be highlighted.

2.1.1 Selenenylation of Alkenes

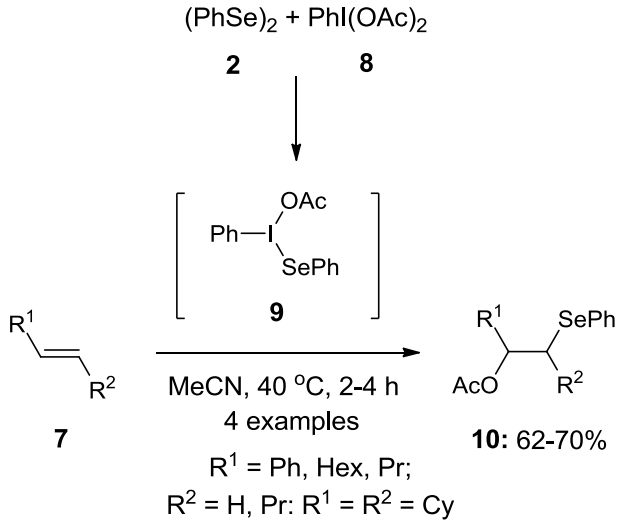
The addition of selenium electrophiles to alkenes is an important reaction after the discovery of selenoxide eliminations. In the beginning, Nicolaou and coworkers introduced two selenenylating agents *N*-phenylselenophtalimide (*N*-PSP) and *N*-phenylselenosuccinimide (*N*-PSS) and employed these for the selenenylation of olefins.[65,66] Hydroxyselenation of alkenes was observed with commercially available selenium electrophile PhSeCl under aqueous reaction conditions.[67] Furthermore, the conjugated and non-conjugated dienes were selenenylated under similar reaction conditions.[68] Phenylselenyl chloride (PhSeCl) was found good carrier to transfer the PhSe functionality but the involvement of a nucleophilic chloride anion in the side reactions limit the scope of this reaction.

Latter on, diphenyl diselenide **2** was oxidized with ammonium peroxydisulphate to generate the electrophilic species which was further used in methoxyselenenylations of functionalized alkenes in good yields.[69] In 1991, diphenyl diselenide **2** was oxidized to *m*-nitrobenzenesulfonate **3** with benzeneselenenyl *m*-nitrobenzenesulfonyl peroxide **1** and used as a carrier to transfer the PhSe moiety during the selenenylation of various olefinic substrates in moderate yields (Scheme 1).[70] Different nucleophiles **5** were utilized during the selenenylation of olefinic substrates **4** and methanol was found the best nucleophile.



Scheme 1. Selenenylation of alkenes **4** with selenium electrophile *m*-nitrobenzenesulfonate **3**.

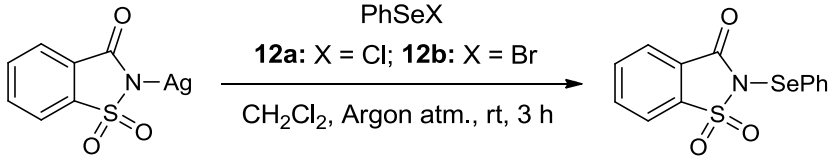
In 1998, an iodine(III)-mediated selenenylation of olefinic substrates **7** was developed by Tingoli and coworkers. In this report, alkenes **7** were reacted with diphenyl diselenide **2** and (diacetoxyiodo)benzene **8** in acetonitrile and acetoxyselenenylation was observed in good yields (Scheme 2).



Scheme 2. Acetoxyselenenylation of alkenes **7** by the reaction with diphenyl diselenide **2** and (diacetoxyiodo)benzene **8**.

More probably, the hypervalent iodine(III) reagent (diacetoxyiodo)benzene **8** was used to oxidize diselenide **2** to the more electrophilic selenium species **9**, which activates the olefinic double bond to form three membered selenarium ion intermediate. Furthermore, the three membered intermediate reacts with acetate ions to yield the addition product. Additionally, $PhI(OCOCF_3)_2$ (PIFA) was also used instead of PIDA **8** but similar success could not observed probably due the presence of comparatively less nucleophilic triflate species.[71]

Furthermore, same research group reported the synthesis of another selenium electrophile *N*-phenylselenosaccharin (NPSSac) **13** by the reaction of commercially available phenylselenium halide **12** and silver saccharin (AgSac) **11** in dichloromethane at room temperature (Scheme 3). Additionaly, newly synthesized selenium electrophile **13** exhibited good selenylating properties with olefinic substrates **7**.[72]

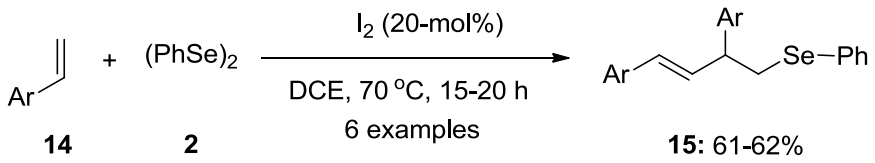


11 **13**

Scheme 3. Synthesis of selenium electrophile *N*-phenylselenosaccharin (NPSSac) **9** by the reaction of phenylselenium halide **12** and silver saccharin (AgSac) **11**.

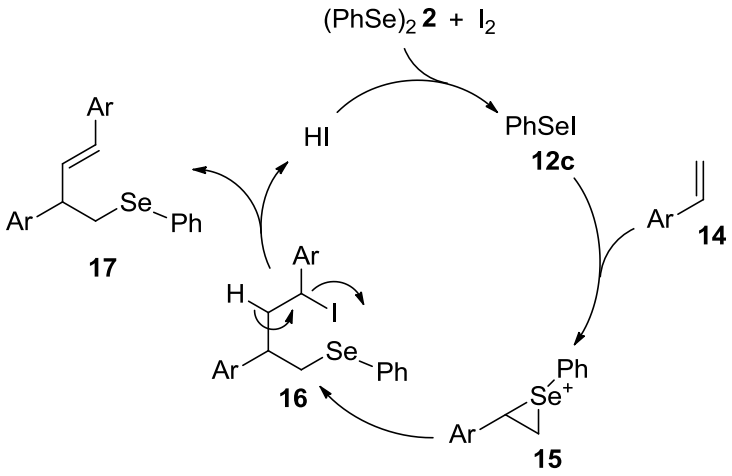
In 2012, Wirth and coworkers developed an iodine-catalyzed approach for the selenenylation of terminal alkenes **14** in good yields by the reaction with diphenyldiselenide **2** using catalytic amount of molecular iodine (Scheme 4).[73] Probably, PhSeI **12c** was playing the role of active catalytic species generated by the reaction of diphenyldiselenide **2** with molecular iodine in dichloromethane. Notably, additional

external nucleophile was not used during the reaction and terminal alkenes **14** were acting as nucleophile.[73]



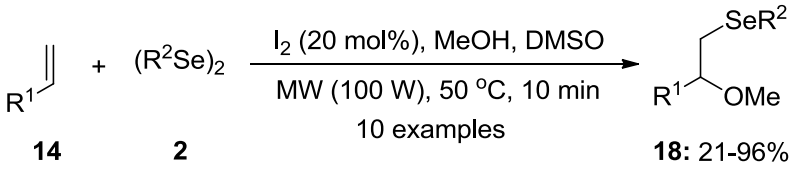
Scheme 4. Iodine-catalyzed selenenylation of terminal alkenes **14** by the reaction diphenyldiselenide **2** using catalytic amount of molecular iodine.

The catalytic cycle for iodine-mediated selenenylaion of terminal alkenes **14** is depicted in scheme 5. According that the catalytic cycle was initiated by the reaction of diphenyl diselenide **2** with iodine to form the active catalytic species phenylselenium iodide **12c**. Furthermore, the active catalytic species **12c** activates the olefinic double bond of **14** to form three membered seleniranium ion intermediate **16**. Latter on, the nucleophilic attack of alkene **14** to intermediate **16** could facilitate the formation of addition product **16**. On elimination, the intermediate **16** furnished the final product **15** along with HI. Finally, HI could further react with diphenyldiselenide **2** to regenerate the active catalytic species phenylselenyl iodide **12c** to continue the catalytic cycle.



Scheme 5. Catalytic cycle for iodine-catalyzed selenenylation of terminal alkenes **14** by the reaction diphenyldiselenide **2** using catalytic amount of molecular iodine.

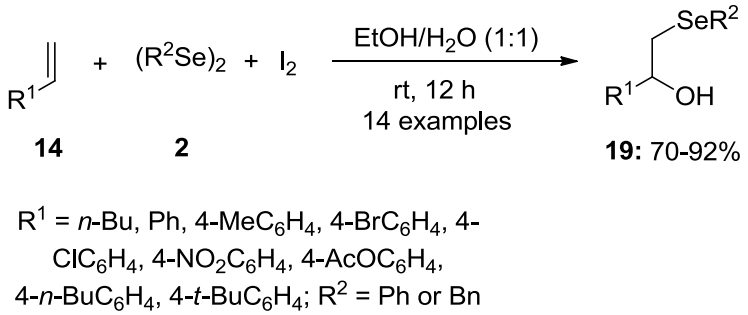
Furthermore, the scope of similar iodine-catalyzed reaction was expanded for the methoxyselenenylation of terminal olefinic substrates **14** using methanol of source of nucleophile under microwave conditions. All the reactions were completed in few minutes and selenenylated products **18** were obtained in good yields (Scheme 6).[74] Notably, the reaction was found to be quite effective for aromatic substrates but could not be applied to aliphatic olefinic substrates under similar reaction conditions. The mechanistic pathway was quite similar to that depicted in scheme 5 and similar active catalytic species PhSeI **12c** was generated *in situ* to activate the double bond of olefinic substrates **14**.



R^1 = Ph, 4-MeC_6H_4, 4-ClC_6H_4, 4-$(Me)_3COC_6H_4$; R^2 = *n*-Bu, Ph, 4-MeC_6H_4, 4-$OMeC_6H_4$, 4-ClC_6H_4, 3-$CF_3C_6H_4$

Scheme 6. Iodine-catalyzed microwave-assisted methoxyselenenylation of terminal alkenes **14**.

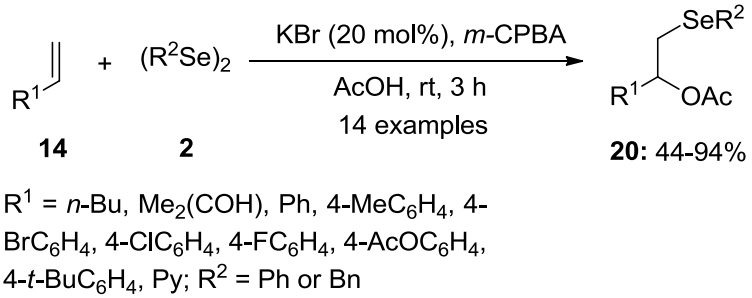
Recently, the electrophilic nature of phenylselenium iodide **12c** was explored by Yan and coworkers for the hydroxyselenenylation of similar terminal alkenes **14**.[75] In this report, the alkenes **14** were reacted with stoichiometric amount of diaryl diselenide **2** and molecular iodine in MeCN/H_2O (1:1) under an oxygen atmosphere. β-Hydroxyselenides were isolated in good to excellent yields (Scheme 7).[75] The scope of iodine-mediated hydroxyselenenylation of alkenes was expanded with different olefinic substrates having electron withdrawing and donating functionalities on the aromatic ring. Additionally, selenenylation reaction exhibited similar potential with aliphatic olefinic substrates.



Scheme 7. Iodine-mediated hydroxyselenenylation of styrenes **14** with diaryldiselenide **2** in MeCN/H_2O (1:1).

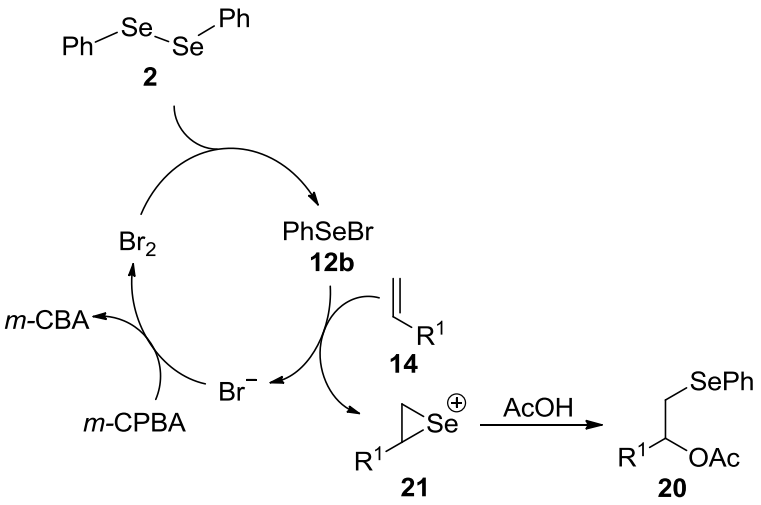
In 2015, a similar electrophilic selenium species (PhSeBr) **12b** was generated *in situ* by using a different catalytic system and was employed for the selenenylation of similar terminal olefins **14**.[76] In this approach, the acetoxyselenelynation of alkenes **14** was achieved by the reaction of diaryl diselenide **2** and catalytic amount of KBr using stoichiomtric amount of external oxidant *m*-CPBA (Scheme 8). The role of external oxidant was to oxidize bromide ion to molecular bromine which was further reacted with diphenyldiselenide **2** to generate the active catalytic species **12b**. The combination of

KBr and *m*-CPBA with diphenyldiselenide **2** was found quite effective catalytic system for the selenenylation of both aliphatic and aromatic olefinic substrates.



Scheme 8. KBr-catalyzed acetoxyselenylation of alkenes **14** by the reaction of diaryl diselenides **2** with *m*-CPBA as a catalyst.

The catalytic cycle for KBr-catalyzed acetoxyselenylation of alkenes **14** is described in scheme 9. The catalytic cycle initiates with oxidation of bromide ion to bromine using *m*-CPBA as an oxidant. Bromine was further reacted with diselenide **2** to form the more electrophilic species phenylselenyl bromide **12b**. Electrophilic selenium species **12b** activates the double bond of terminal alkene **14** to three membered selenarium ion intermediate **21** alongwith the formation of bromide ion. Finally, intermediate **21** reacts with acetic acid to yield final product **20** while bromide ion was further oxidized to continue the catalytic cycle.



Scheme 9. The catalytic cycle for KBr-catalyzed acetoxyselenylation of terminal alkenes **14** using *m*-CPBA as an external oxidant.

2.1.2. Stereoselective Selenenylation of Alkenes

The scope of organoselenium electrophiles is not limited to achieve racemic selenenylation but a number of highly stereoselective selenenylations have been developed extensively using a variety of chiral selenium electrophiles. Various enantiomerically pure chiral diselenides **22**-**39** have been synthesized and applied to transfer chirality in the stereoselective methoxyselenenylations of alkenes (Figure 1). Some new chiral binaphthyl-cored diselenides **22** were synthesized by Fujita and his research group and used in different stereoselective methoxyselenenylation of styrene **14** (R = H) (Scheme 10).[77-82] The methoxyselenenylated product **41** was obtained with up to 49% diastereomeric excess (Table 1, entry 1).[79] Furthermore, C_2 symmetric chiral diselenides **23** and **24** were synthesized and employed for the methoxyselenenylation of styrene **14** (R = H) at low temperature using methanol as source of nucleophile.[83-86] These two chiral auxiliaries **23** and **24** showed upto 77% diastereomeric excess during these methoxyselenenylations (Table 1, entries 2 and 3).[84,86]

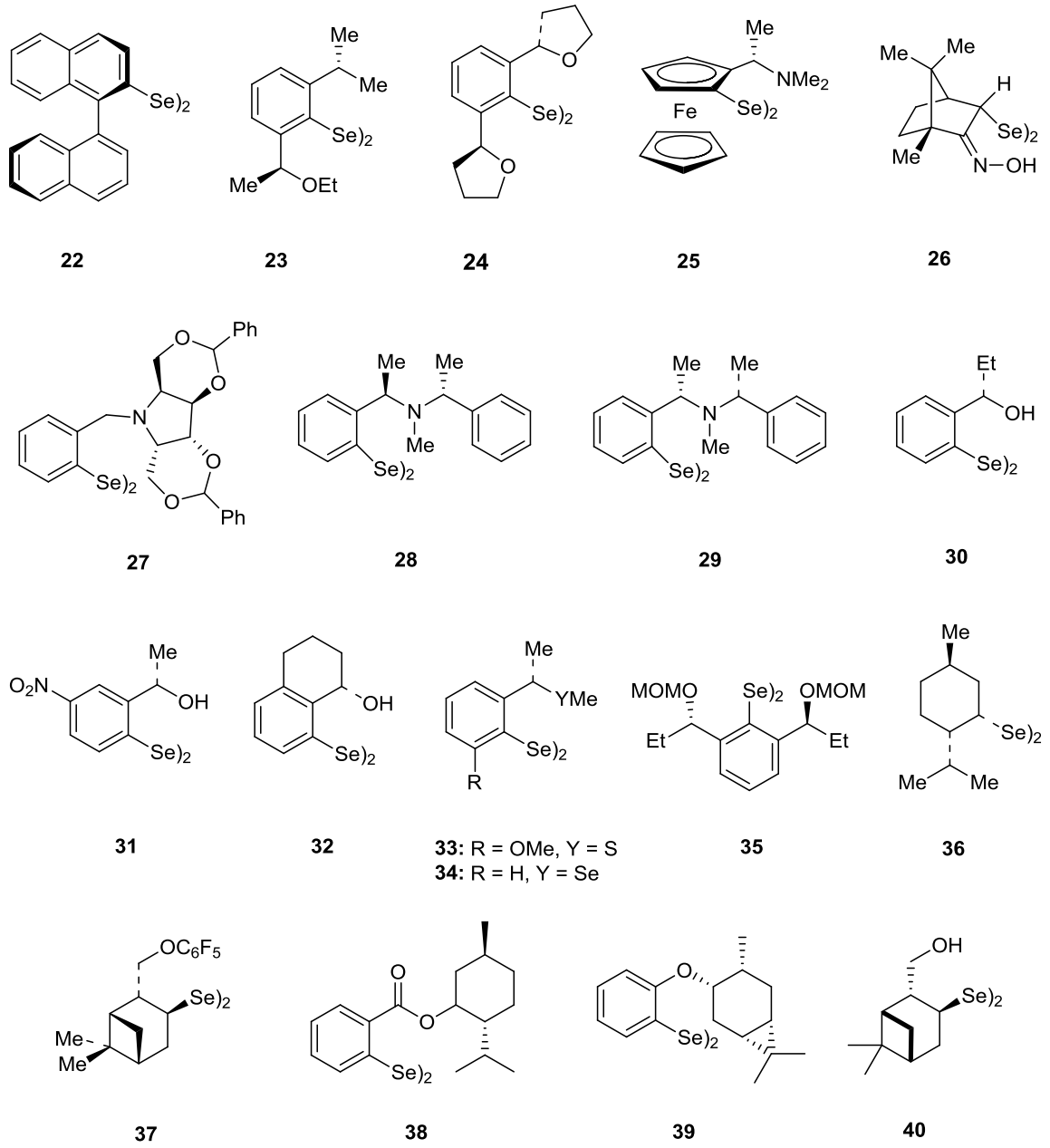
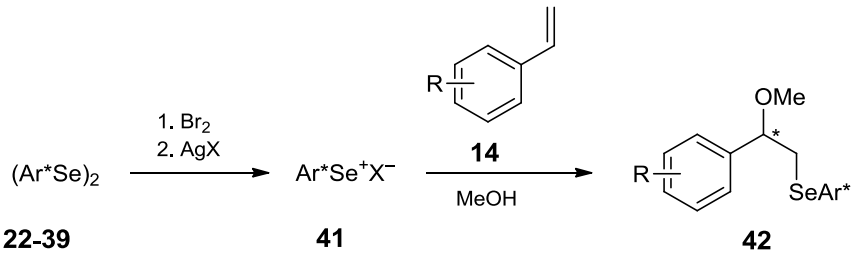


Figure 1. The structures of selective chiral selenium diselenides **22**-**40**.

Furthermore, ferrocenyl-cored chiral diselenides of type **25** were introduced by Uemura and coworkers and showed high selectivities in stereoselective methoxyselenenylations.[87-92] The reaction products **42** were observed in good yields with upto 97% diastereomeric excess (Table 1, entry 4).[87]



Scheme 10. Asymmetric methoxyselenenylation of styrenes **14** using chiral diselenides **22**-**40**.

Table 1. Stereoselective methoxyselenenylation of styrenes **14**.

Entry	**Chiral Diselenide**	**Counterion X**	**Reaction Conditions**	**41** de (%)	**Ref.**
1	**22**	Br	MeOH, 25 °C	49	79
2	**23**	OTf	Et_2O, –78 °C	77	84
3	**24**	OTf	Et_2O, –78 °C	73	86
4	**25**	Br	CH_2Cl_2, 25 °C	97	87
5	**26**	OTf	CH_2Cl_2/MeOH, –78 °C	92	97
6	**27**	PF_6	CH_2Cl_2/MeOH, –78 °C	42	101
7	**28**	OTf	MeOH, –78 °C	94	105
8	**29**	OSO_3H	MeOH, 25 °C	62	105
9	**30**	OTf	MeOH, –114 °C	92	102, 103
10	**31**	OTf	MeOH, –114 °C	95	103
11	**32**	OTf	MeOH, –100 °C	93	103
12	**33**	OTf	CH_2Cl_2/MeOH, –78 °C	92	107
13	**34**	OTf	CH_2Cl_2/MeOH, –78 °C	81	109
14	**35**	OTf	Et_2O/MeOH, –100 °C	95	110

15	**36**	OTf	MeOH, –78 °C	40	113
16	**37**	OTf	MeOH, –78 °C	72	115
17	**38**	Br	MeOH, rt	40	117
18	**39**	OTf	MeOH, CH_2Cl_2, –78 °C	36	118
19	**40**	OTf	MeOH, –78 °C	44	119

Additionally, camphor-based chiral diselenide **26** and its derivatives were tested in similar reactions[93-98] and up to 92% diastereoselectivity was obtained (Table 1, entry 5).[97] Furthermore, various C2 symmetric chiral diselenides **27** having cyclic amines as chiral moieties were synthesized by Fujita and coworkers and used as an electrophile in stereoselective methoxyselenenylation reactions with different alkenes.[99-101] It was observed that moderate selectivity was obtained with styrene (Table 1, entry 6) but high selectivity was observed when (*E*)-β-methylstyrene was used as substrate. The presence of the nitrogen atom at the position segregated by four bonds in diselenides **27** makes them more suitable for strong Se---N interactions which are necessary for a transfer of the chirality in asymmetric selenenylation reactions.[101]

After knowing the impact of strong Se---N interactions on the selectivity, Wirth and others reported the synthesis of diselenides **28**, **29** and **30-32** having nitrogen and oxygen atom respectively at the position segregated by four bonds from the selenium atom.[102-106] All the synthesized diselenides **28**, **29** and **30-32** showed high selectivities (up to 95% *de*) in the methoxyselenylation of styrene **14** (R = H) (Table 1, entries 7-11). Furthermore, chiral diselenide **33** and its derivatives were synthesized by Tiecco and coworkers where sulfur atom was used at the position segregated by four bonds from the

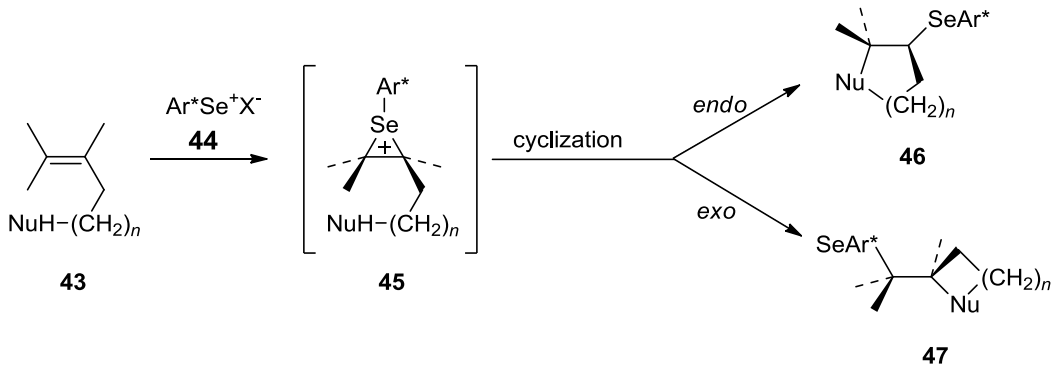
selenium atom. The methoxyselenenylation of styrene **14** was achieved in 96% diastereomeric excess when diselenide **33** was used as chiral source (Table 1, entries 7-11).[107,108] In 2005, the heteroatom sulfur was replaced with selenium by Cox and Wirth to synthesize a new selenium-stabilized diselenide **34**.[109] It was used for the stereoselective methoxyselenenylation of styrene and could show up to 81% *de* which was slightly lower compared with diselenides having other heteroatoms sulfur **33** and oxygen **30**, **31** (Table 1, entry 13). In 2009, Uehlin and Wirth reported the synthesis of another novel chiral dislenide **37** having C-2 symmetry and produce methoxyselenenylion of (*E*)-ethoxystyrenes with up to 95% *de* (Table 1, entry 14).[110] In the next year, Wirth and coworkers introduced sulfoxide-containing diselenides but could not produce the high selectivities during similar methoxyselenenylations.[111] Additionally, menthane- and terpene-cored chiral diselenides **35** and **36** were also tested in similar reactions but low and moderate selectivities were observed respectively (Table 1, entries 15 and 16).[112-116] In 2012, Santi and coworkers developed another new chiral diselenide **38** having ester chiral functionality at *ortho*-position in which exhibited low selectivities in similar methoxyselenenylations (Table 1, entry 17).[117] In 2016, *ortho*-functionalized optically active diaryldiselenides **39** were prepared by Scianowski and coworkers where similar selenenylation reactions could only achieve with up to 36% diastereomeric excess (Table 1, entry 18).[118] Recently, dipinanyl-cored diselenides **40** were prepared by same research group and induced slightly better selectivity in methoxyselenenylations compared to diselenides **39** (Table 1, entry 19).[119] Additionally, a variety of counterions have been successfully used during these methoxyselenenylations and the nucleophilicity of the counterion plays a crucial role for the selectivity in these reactions. The counterions

having lower nucleophilicity induce the higher selectivity in the methoxyselenenylation of olefins.[95, 100, 101]

Oxygen nucleophiles can also be replaced with nitrogen and carbon nucleophiles during the oxyselenenylations of alkenes. Furthermore, few stereoselective azidoselenenylations[120,121] and carboselenenylations[122-124] have been achieved with high selectivities using nitrogen and carbon nucleophiles respectively.

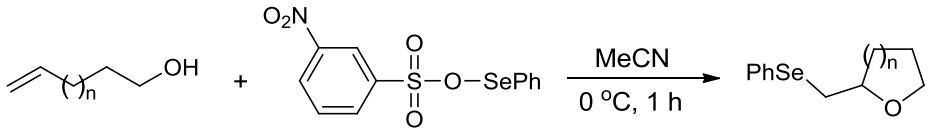
2.1.3. Selenocyclizations

Selenocyclizations are an important approach in organic chemistry which are frequently used to construct various bioactive heterocyclic compounds.[30,31,125] Several reaction products such as selenolactones obtained from selenocylization reactions have been successfully used as substrates in selenium-catalyzed cyclization reactions.[37] In addition, the selenocyclization reaction has been applied in the total synthesis of natural products.[126-129] The selenocyclization process is quite similar to the oxyselenenylation of alkenes as schown in scheme 11. The reaction begins with activation of the double bond in **43** with the selenium electrophile **44** to form seleniranium ion intermediate **45**. The seleniranium ion intermediate **45** then reacts with an internal nucleophile to lead the formation of a selenocyclization product. The formation of cyclic product **46** occurrs through *endo*-cyclization while the other cyclic product **47** occurrs via *exo*-cyclization. This is depend on ring-size of newly formed product and reaction conditions applied (Scheme 11). Additionally, the selenium moiety in the products **46** and **47** can be oxidized to develop selenium-catalyzed cyclization reactions.



Scheme 11. Selenocyclization of olefins **43** to *endo*- and *exo*-cyclization products **46** and **47** using selenium electrophles **44**.

A variety of alkenes bearing internal nucleophile have been successfully cyclized to different selenocyclic products such as selenolactone and selenoethers using various selenium electrophiles. Intially, different benzene selenenyl sulphates were used as electrophiles to achieve the selenocyclization of unsaturated alcohols and unsaturated carboxylic acids under mild reaction conditions.[130-132] In 1991, benzeneselenenyl *m*-nitrobenzenesulfonate **3** was used to achieve the cyclization of unsaturated alcohols **48** and **49** to the corresponding five- and six-membered cyclic ethers **50** and **51** respectively in high yields (Scheme 12).[70] The cyclization reactions were completed in short reaction times and proceeded via an *exo*-cyclization process. Interestingly, the cyclization of unsaturated alcohol **48** (n = 1) produced the *exo*-cyclic product **50** exclusively at -40 ^{o}C while the *endo*-cyclic product was only observed as minor product at 0 ^{o}C. Additionally, only the *exo*-cyclic product **51** was obtained during the cyclization of olefinic alcohol **49** even at 0 ^{o}C.



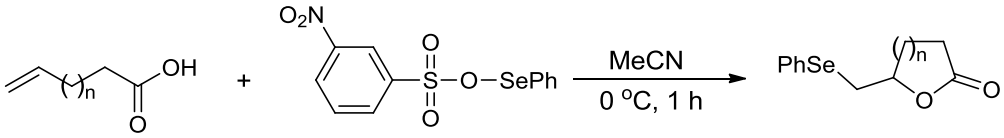
48: n = 1
49: n = 2

3

50: n = 1; 85%
51: n = 2; 100%

Scheme 12. Selenocyclization of unsaturated alcohols **48** and **49** to generate *O*-heterocyclic compounds **50** and **51** using selenium electrophiles **3**.

In a similar vien, the unsaturated carboxylic acids **52** and **53** were cyclized to five- and six-membered lactones **54** and **55** respectively using the same selenium electrophile **3** in excellent yields (Scheme 13).[70] During these cyclizations, only e*xo*-cyclic products were obtained and the selenocyclizations could not proceed via e*ndo*-cyclization process.



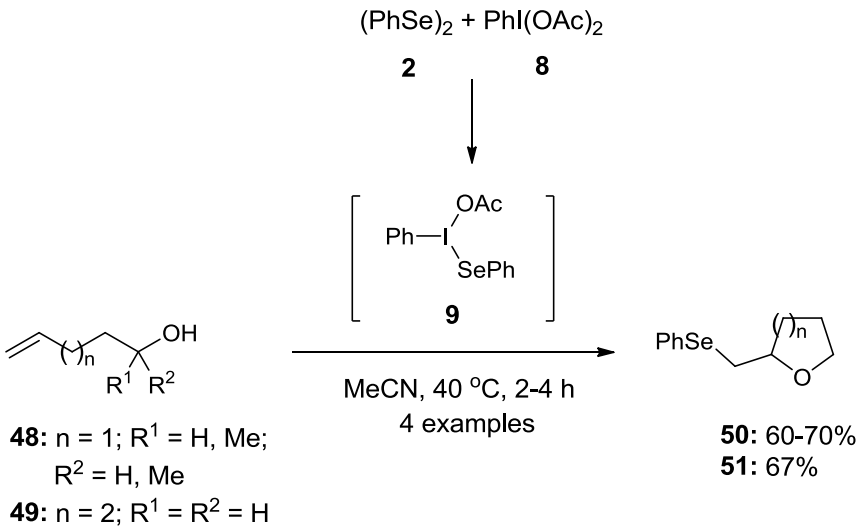
52: n = 1
53: n = 2

3

54: n = 1; 93%
55: n = 2; 96%

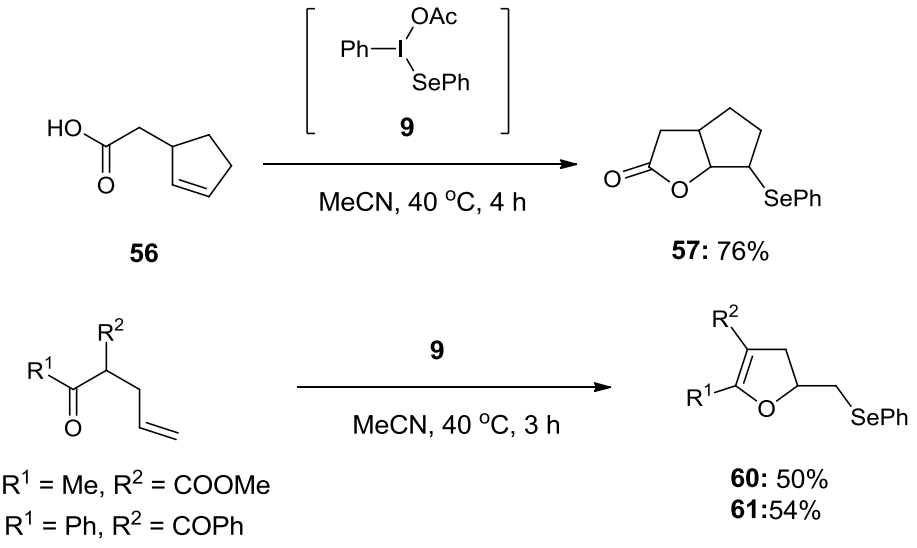
Scheme 13. Selenocyclization of unsaturated carboxylic acids **52** and **53** to lactones **54** and **55** respectively using the selenium electrophile **3**.

In 1998, the oelfinic substrates **48** and **49** were cyclized to corresponding cyclic ethers **50** and **51** by Tingoli and coworkers.[71] In this report, more electrophilic selenium species **9** was generated *in situ* by the oxidation of diselenide **2** with iodine(III) reagent **8** and used to activate the double bond of the unsaturated alcohol (Scheme 14). The cyclization reactions proceeded via an *exo*-cyclization process and reaction products **50** and **51** were obtained in good yields.



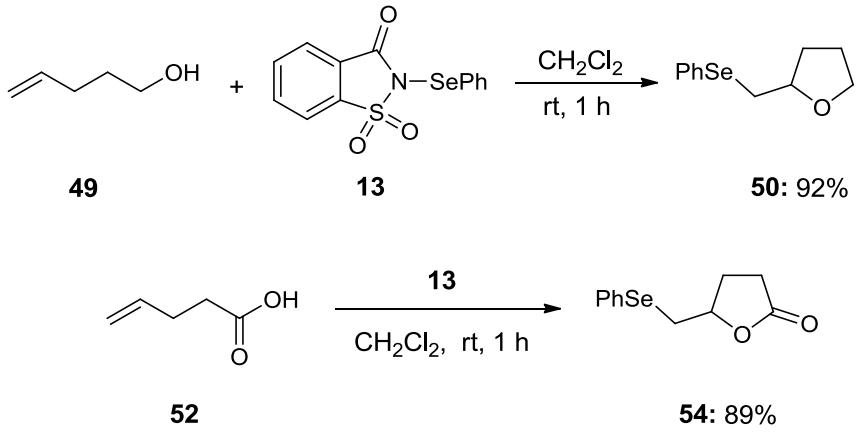
Scheme 14. Iodine(III)-mediated selenocyclization of unsaturated alcohols **48** and **49** to selenocyclic ethers **50** and **51** by the reaction of diphenyl diselenide **2** with PIDA **8** as an oxidant.

The selenocyclization of 2-(cyclopent-2-en-1-yl)acetic acid **56** under reaction conditions also proceeded by an *exo*-cyclization reaction. The fused bicyclic compound 6-(phenylselanyl)hexahydro-2*H*-cyclopenta[b]furan-2-one **57** was obtained in 76% yield (Scheme 15).[71] Additionally, similar *exo*-cyclizations were observed during the selenocyclization of unsaturated ketonic substrates **58** and **59** (Scheme 15).[71]



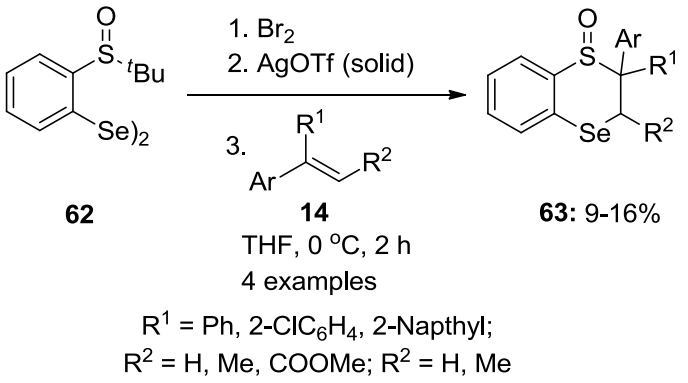
Scheme 15. Iodine(III)-mediated selenocyclization of unsaturated carboxylic acid **56** and ketones **58** and **59** to cyclic compounds **57**, **60** and **61** respectively using selenium electrophile **9**.

Furthermore, the similar selenocyclizations of unsaturated alcohol **49** and acid **52** were achieved by Tingoli and coworkers.[72] In this report, active selenium electrophilic species *N*-phenylselenosaccharin (NPSSac) **13** was generated *in situ* and used during these cyclization reactions. Cyclic ether **50** and lactone **54** were obtained as the reaction products in excellent yields (Scheme 16).



Scheme 16. Selenocyclization of the unsaturated alcohol **49** and acid **52** to the corresponding cyclic ether **50** and lactone **54** respectively using *N*-phenylselenosaccharin (NPSSac) **13** as an electrophile.

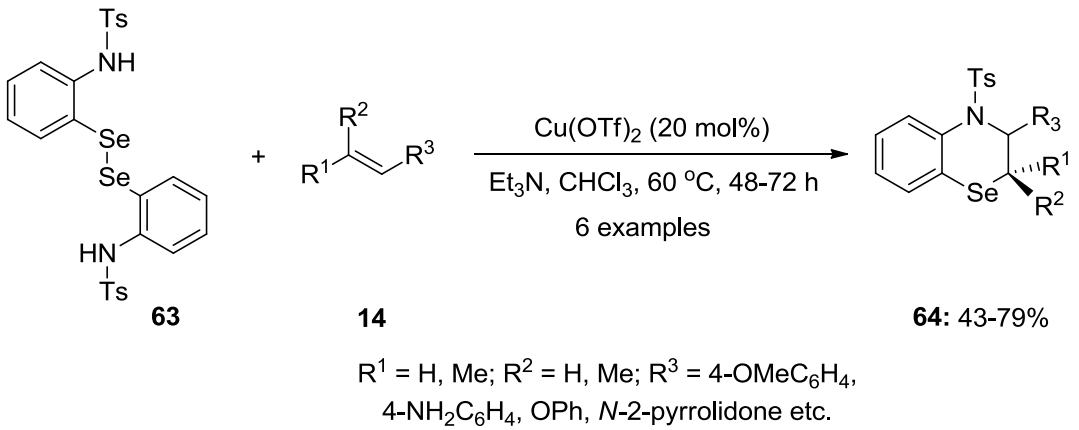
In 2010, Wirth and coowrkers developed an approach for intermolecular selenocyclization of alkenes **14** and *in situ* generated aryl selenium triflate by the reaction of diselenide **62** and bromine followed by the addition of silver triflate in THF at 0 ^{o}C (Scheme 17).[111]



Scheme 17. Intermolecular selenocyclization of alkenes **14** and the electrophilic species aryl selenyl triflate **62**.

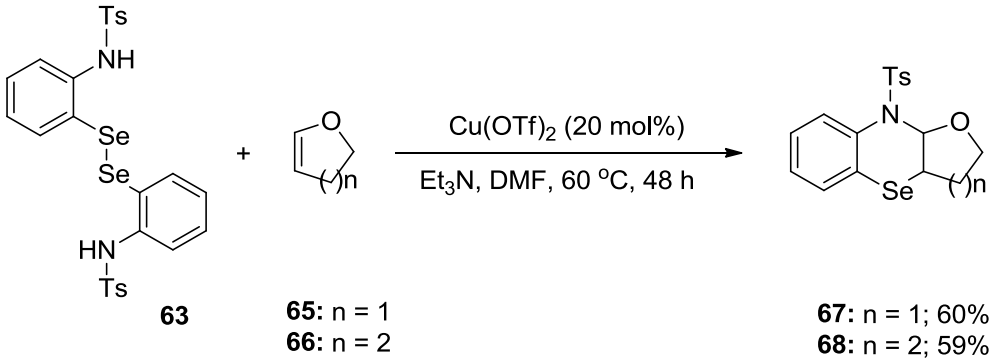
Interestingly, an external nucleophile was not used during this selenocyclization approach and the formation of the cyclic product was achieved by the activation of the double bond to form a selenarium ion followed by subsequest cyclization involving the sulfoxide moiety of an *in situ* generated electrophile (Scheme 17). Notably, the reaction worked with terminal styrenes albeit in low yields, but β-substituted styrenes could not be utilized as substrate during these cyclizations.[111]

In 2012, Menichetti and coworkers reported an intermolecular selenocyclization of 2-*N*-sulfonylamino diselenides **63** with alkenes **14** *via* copper(II)-catalyzed activation of the Se-Se bond in the presence of triethylamine. All the reactions were found to be quite slow and took 2-3 days to complete yielding benzo[*b*] [1,4]selenazines **64** in 43-79% yields (Scheme 18).[133]



Scheme 18. Cu(II)-catalyzed intermolecular selenocyclization of 2-*N*-sulfonylamino diselenides **63** with alkenes **14** to form benzo[*b*] [1,4]selenazines **64**.

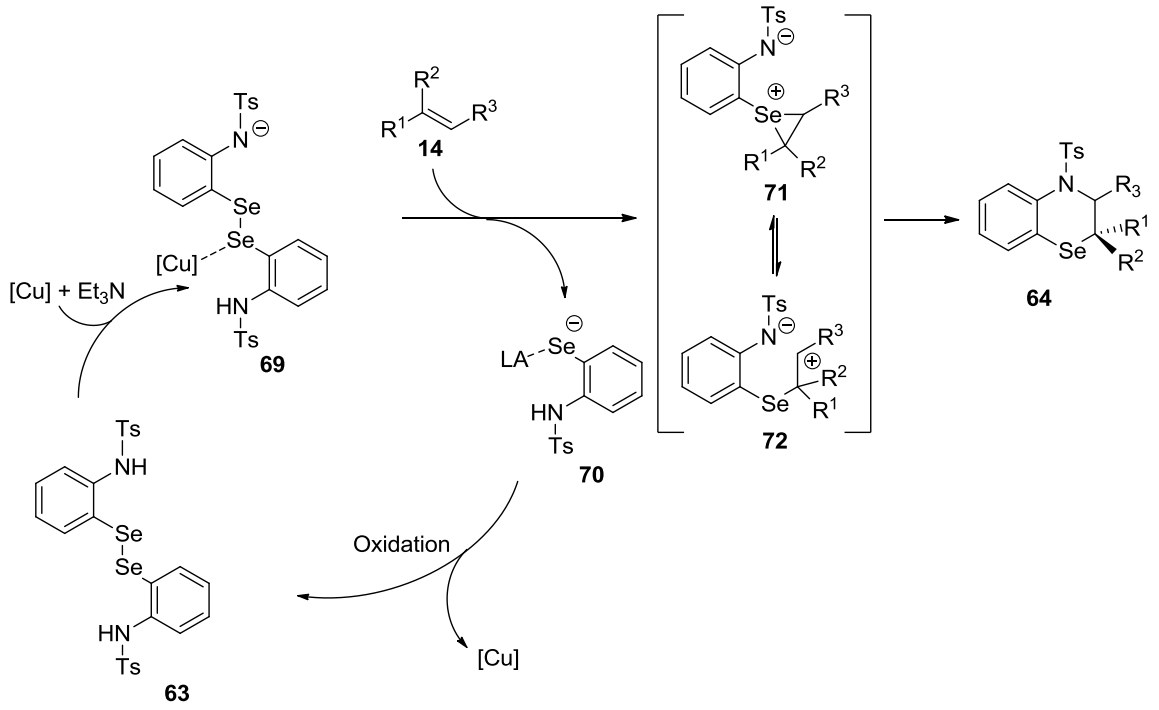
Additionally, cyclic alkenes **65** and **66** were found to be suitable substrates for the cyclization reaction under similar conditions and Se-contaning tricyclic compound **67** and **68** were obtained in 60% and 59% yields respectively (Scheme 19).[133]



Scheme 19. Cu(II)-catalyzed intermolecular selenocyclization of 2-*N*-sulfonylamino diselenides **63** with cyclic olefinic substrates **65** and **66** to Se-containing tricyclic compounds **67** and **68** respectively.

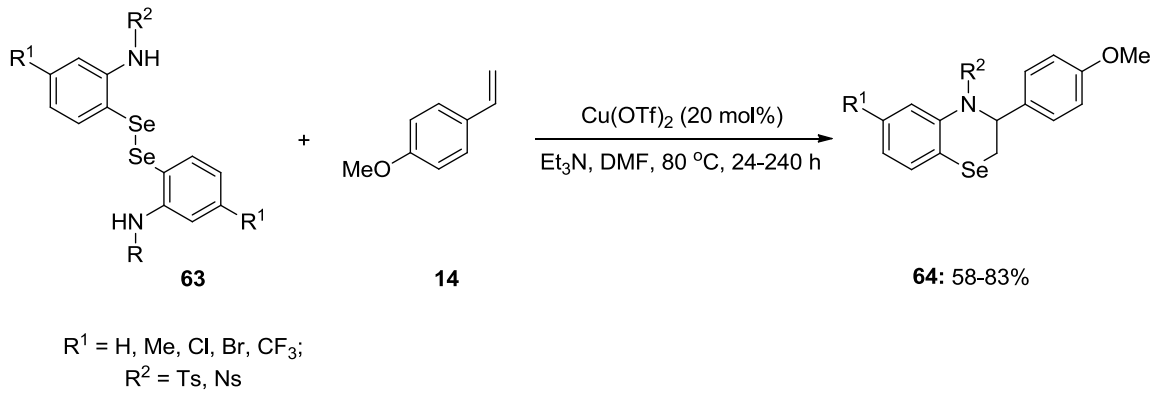
The catalytic cycle for the Cu(II)-catalyzed intermolecular selenocyclization of 2-*N*-sulfonylamino diselenides **63** with alkenes **14** to Se-containing heterocyclic compounds **64** is depicted in scheme 20.[133] According the proposed catalytic cycle, Cu(II)-species activates the diselenide **63** in the presence of a base and the formation of

intermediate **69** occurs. The activated diselenide **69** reacts with alkene **14** forming the episelenarium ion intermediate **71** which is probably in equabilibrium with the open carbocationic intermediate **72**. Intermediate **72** can then undergo an intramolecular cyclization to yield the final product **64**. Finally, selenolate ion intermediate **70** generated during the formation of episelenarium ion intermediate **71** can then be oxidized to regenerate the diaryl diselenide **63** to continue the catalytic cycle.



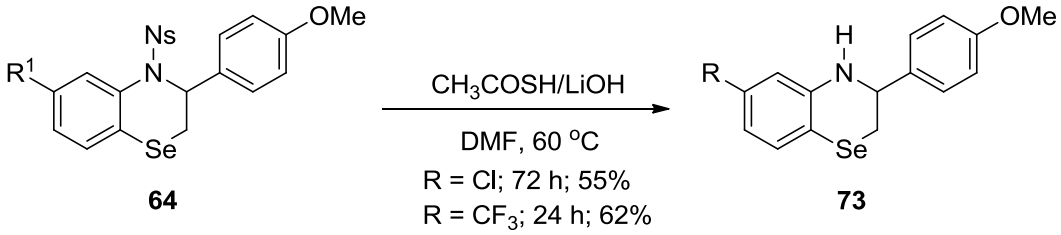
Scheme 20. Catalytic cycle for the Cu(II)-catalyzed intermolecular selenocyclization of 2-*N*-sulfonylamino diselenides **63** with alkenes **14** to benzo[*b*] [1,4]selenazines **64**.

In 2016, Viglianisi and coworkers expanded the scope of the selenocyclization reaction of *p*-methoxystyrene **14** with 2-*N*-sulfonylamino diselenides **63** which have different electron-withdrawing and donating functionalities. The reactions were observed to be quite slow and took 1-10 days to complete but benzo[*b*] [1,4]selenazines **64** could produce in good yields (Scheme 21).[134]



Scheme 21. Cu(II)-catalyzed synthesis of benzo[*b*] [1,4]selenazines **64** by the reaction of 2-*N*-sulfonylamino diselenides **63** with *p*-methoxystyrene **15**.

Additionally, the denosylation of synthesized benzo[*b*] [1,4]selenazines **64** was performed with thioacetic acid and LiOH in dry DMF. The course of reaction was found to be relatively slow once again and *N*-unsubstituted selenazines **73** were obtained in good yield (Scheme 22).[134] Recently, the selenocyclization approach was applied by Wang and Bates for the synthesis of one intermediate during the total synthesis of natural product allahabadolactone **A**.[135]

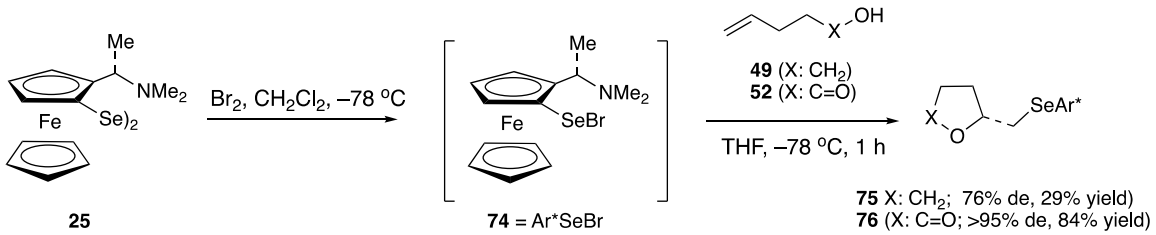


Scheme 22. Denosylation of compound **64** with with thioacetic acid and LiOH in DMF.

2.1.4. Stereoselective Selenocyclizations

Various chiral diselenides have been successfully used to achieve different stereoselective selenocyclization reactions of olefins bearing internal nucleophiles. In 1995, Uemura and coworkers achieved the distereoselective selenocyclization of unsaturated alcohol **49** and carboxylic acid **52** using chiral ferrocene-based selenium

electrophiles **74.** The cyclized products **75** and **76** were obtained with high diastereomeric excess (Scheme 23).[135] As usual, the selenium electrophile **74** was generated *in situ* by the reaction of chiral diselenide **25** with bromine in dichloromethane at low temperature.



Scheme 23. Stereoselective selenocyclization of unsaturated alcohol **49** and carboxylic acid **52** using chiral ferrocene-based selenium electrophiles **74**.

The camphor-based chiral selenium electrophiles **77** and **78** were synthesized *in situ* and tested in the diastereoselective selenofunctionalizations of alkenols and alkenoic acids by Back and coworkers (Figure 2). Selenoetherifications were achieved with up to 90% diastereoselectivity while poor selectivities were observed in case of selenolactonizations.[96,98,136] Insterestingly, the selenocyclization reactions proceeded quite efficiently with high selectivities using camphorselenenyl chlorides unlike the asymmetric oxyselenenylation reactions.[98]

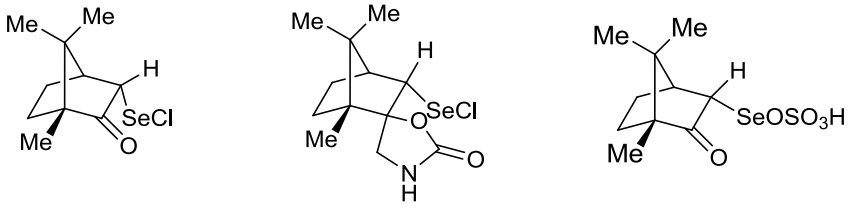
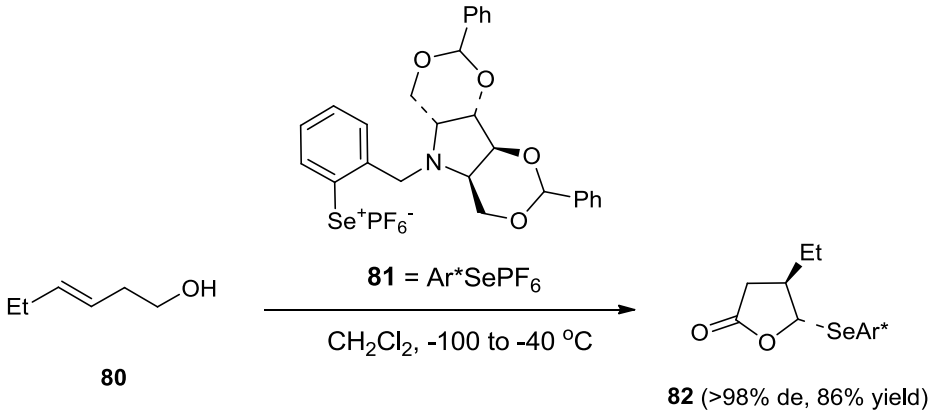


Figure 2. Structures of camphor-based chiral selenium electrophiles **77**, **78** and **79**.

Fruthermore, the chiral camphor-derived diselenide **25** was transfered into the corresponding camphorselenenyl sulfate **79** by *in situ* oxidation with ammonium persulfate in the presence of a stoichiometric amount of trifluoromethanesulfonic acid.[137] Additionally, the newly generated selenium electrophile **79** was successfully employed during the the synthesis of enantiomerically pure trisubstituted perhydrofuro[2,3-*b*]furans[138] and 1,6-dioxaspiro[4.4]nonane derivatives (spiroacetals).[139]

In 1997, Tomoda and coworkers synthesized selenium electrophile **81** with hexafluorophosphate as the counter ion *in situ* by the reaction of chiral cyclic amine-based diselenide **27** with bromine at low temperature followed by the addition of silver hexafluorophosphate. Selenium electrophile **81** was then applied in the selenocyclization of different di- and trisustituted olefins of type **80** containing oxygen nucleophiles with cyclized products **82** being obtained in excellent diastereoselectivities (Scheme 24). Notably, poor selectivities were observed during the cyclization of terminal alkenes.[101]



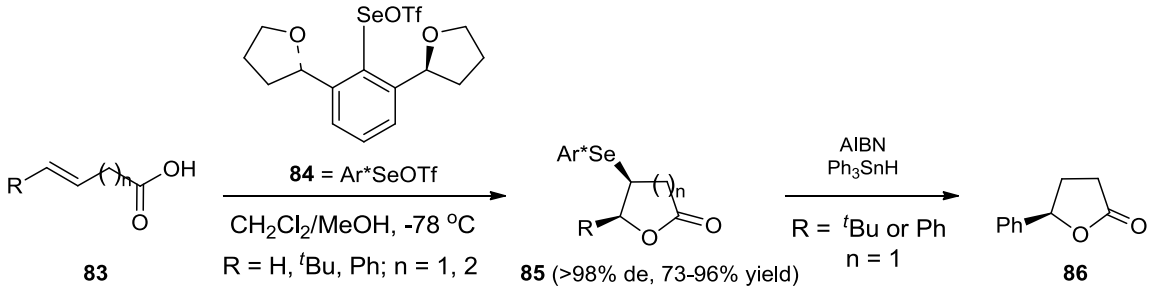
80

82 (>98% de, 86% yield)

Scheme 24. Asymmetric selenocyclization of different di- and trisustituted olefins of type **80** using chiral selenium electrophile **81**.

Furthermore, C_2-symmetrical chiral diselenide **24** was converted into corresponding arylselenyl triflate **84** and used in stereoselective selenolactonization of

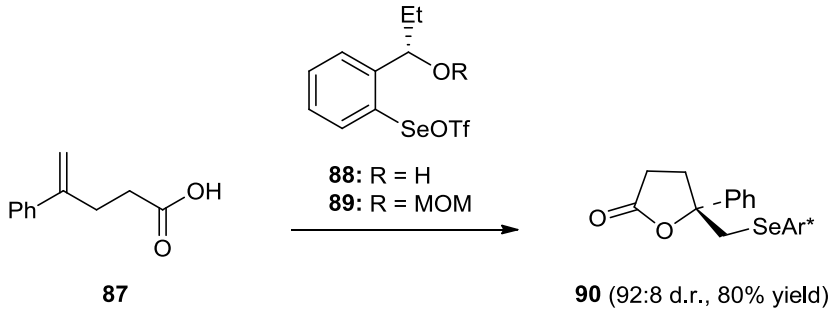
unsaturated carboxylic acids **83**. Five-membered selenolactones **85** were obtained with more than 98% diastereomeric excess (Scheme 25). Once again, terminal alkenes could not show the promising selectivities under similar reaction conditions. Chiral selenium electrophile **84** has selenium and oxygen atoms in close proximity, allowing a Se···O intramolecular interaction. The stereochemistry of lactone **85** was assigned by the formation of lactone **86** by deselenenylation and comparison of the optical rotation of the resulting lactone **86** with the literature value.[83] The element of C_2 symmetry was another vital factor for obtaining high facial selectivity during these cyclization reactions.[83,84] The same electrophilic species **84** was also applicable for the selenoetherifications of of unsaturated alcohols but comparatively lower distereoselectivities were observed.



Scheme 25. Stereoselective selenocyclization of unsaturated carbozylic acid **83** using chiral selenium electrophiles **84**.

Some highly stereoselective selenolactonizations of unsaturated carboxylic acids of type **87** (dr up to 92:8, product **90**) were developed by Wirth and coworkers using chiral selenium electrophiles **88** and **89** (Scheme 26).[106] Additionally, polymer-bound chiral selenium electrophilic reagents were introduced by Uehlin and Wirth and were used in stereoselective selenofunctionalizations. However, the cyclized products were unfortunately observed in moderate selectivities.[140] Sulfur-containing

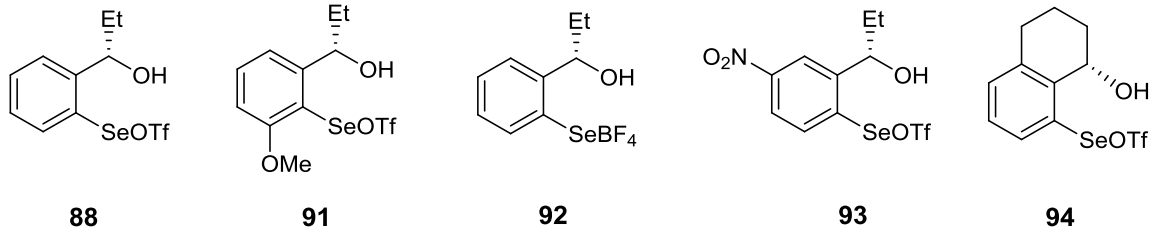
arylselenylbromides were investigated by Tiecco and coworkers in the stereoselective selenocyclizations of γ-alkenyl oximes.[141]



Scheme 26. Stereoselective selenocyclization of unsaturated carboxylic acid **87** using chiral selenium electrophiles **88** and **89**.

In the past few years, various terpene-derived chiral diselenides have been converted into corresponding selenium electrophiles and have been tested in different stereoselective selenocyclizations.[113,115,119] Notably, these chiral electrophiles could achieve only limited success in the stereoselective cyclizations compared with the other electrophiles.

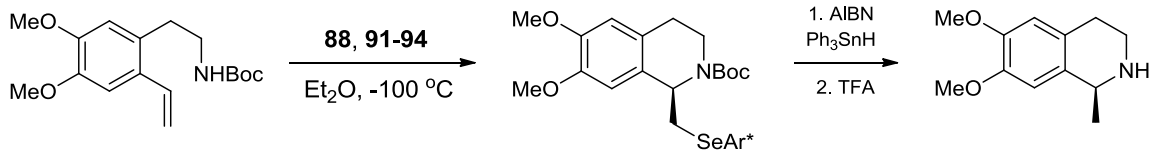
There are few selenocyclization reactions reported in the literature where olefins containing nitrogen nucleophiles were successfully cyclized to enantiomerically rich nitrogen-containing heterocycles using chiral selenium electrophile. In 1998, Wirth and coworkers introduced different chiral selenium reagents (Figure 3) and compound **91** was used to develop stereoselective aminoselenocyclizations.[142] Furthermore, the carbamate **95** was cyclized by using different electrophile **88**, **92**-**94** and the cyclized nitrogen-containing product **96** was obtained in the highest *de* with electrophile **94** (Scheme 27).[143]



88 **91** **92** **93** **94**

Figure 3. The structures of chiral selenium electrophiles **88** and **91-94.**

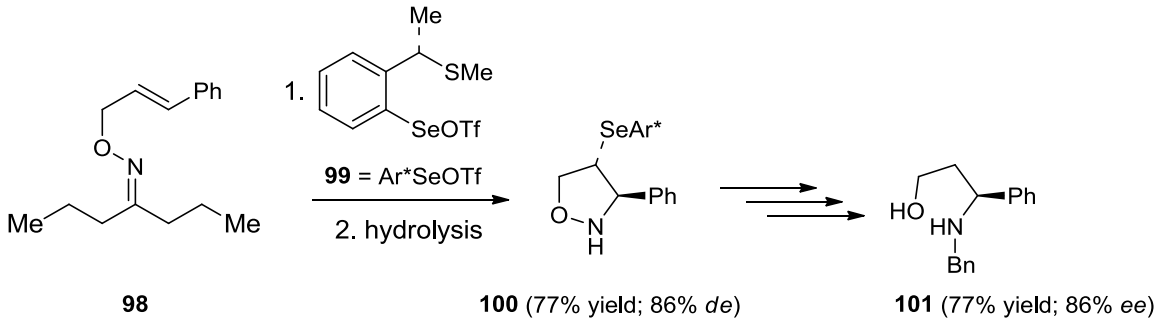
Finally, cyclized product **96** was converted into naturally occurring compound salsolidine **97** with 90% enantiomeric excess following deselenylation and deprotection of the Boc functionality (Scheme 27).[143]



95 **96** **97:** 90% *ee*

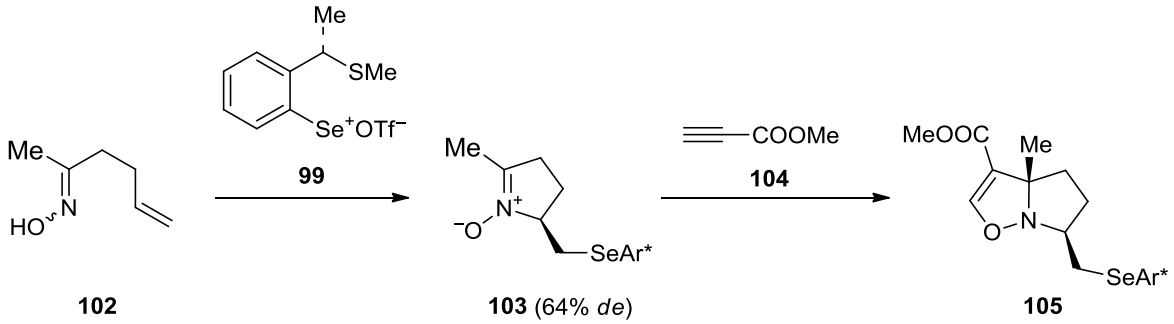
Scheme 27. Stereoselective Synthesis of salsolidine **97** by aminoselenocyclization of carbamate **95** followed by deselenylation and deprotection.

In 2000, Tiecco and coworkers used a camphor-derived chiral selenium electrophile (not shown here) to achieve aminocyclizations with high selectivities.[144] Furthermore, the sulfur containing chiral selenium electrophile **99** was generated *in situ* from corresponding diselenide and used to achieve the synthesis of isoxazolidines **100** with up to 86% *de* by aminoselenocyclization of olefinic substrates **98** (Scheme 28). The chiral isoxazolidine **100** was subsequently converted into 1,3-amino alcohol **101** in three chemical steps with 86% enantiomeric excess.[145]



Scheme 28. Stereoselective synthesis of enantiomerically enriched65 1,3-amino alcohol **100** by aminoselenocyclization of oximes **98** using chiral selenium electrophile **99**.

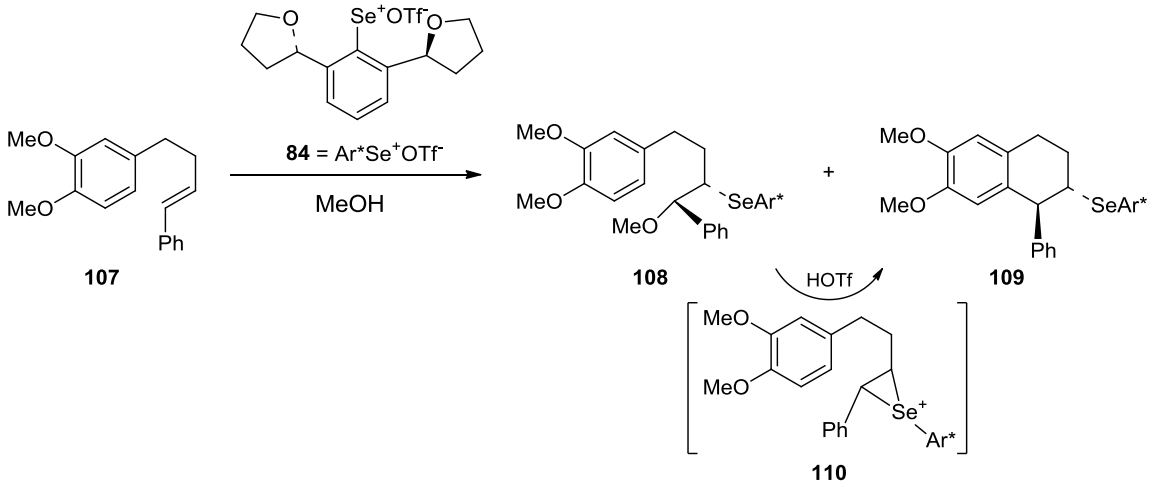
Addionally, same chiral selenium electrophile **99** was used to achieve cyclic nitrones **103** by the aminoselenocyclization of olefinic oximes **102** with up to 64%. The cyclic nitrones **103** were then converted into the bicyclic compounds **105** through a dipolar cycloaddition with methyl propiolate (Scheme 29).[146]



Scheme 29. Stereoselective synthesis of cyclic nitrones **103** by aminoselenocyclization of oximes **102** using chiral selenium electrophile **99**.

There are few selenocyclization reactions reported in the literature where alkenes bearing carbon nucleophiles have been successfully employed as substrates. The chemistry of carboselenocyclization is already matured[147, 148] In the beginning, various functionalized cyclic products were obtained by carboselenocyclization of *β*-dicarbonyl compounds using selenium electrophiles.[149,150] The first report on stereoselective

carboselenocyclizations was introduced in 1998 by Déziel and coworkers.[151] In this report, olefinic substrates **107** were cyclized into tetrahydronaphthalene scaffolds **109** using chiral selenium electrophile **84**. Initially, the methoxyselenenylation product **108** (with 98% de) and the cyclized product **109** were obtained in a 1:1 ratio. Treatment on 108 with triflic acid resulted in a complete conversion to **109** *via* the seleniranium intermediate **110** (Scheme 30).



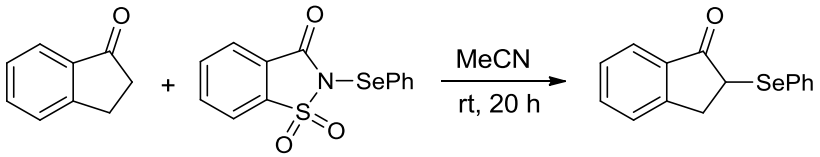
Scheme 30. Stereoselective synthesis of tetrahydronaphthalene scaffolds **109** by carboselenocyclization of alkene **107** using chiral selenium electrophile **84**.

2.1.5. Selenenylation of C-H Bonds

2.1.5.1. Selenenylation of Aliphatic C-H

In the past few years, selenium electrophiles have been successfully applied for the selenenylation of both aliphatic and aromatic C-H bonds. The selenenylation of C-H bonds is now a useful reaction in organic synthesis. The selenenylation of 1-indanone **111** at α-position was achieved in 2006 by Tingoli and coworkers using selenium electrophile *N*-phenylselenosaccharin (NPSSac) **11**. The α-selenenylated product of 1-indanone **112**

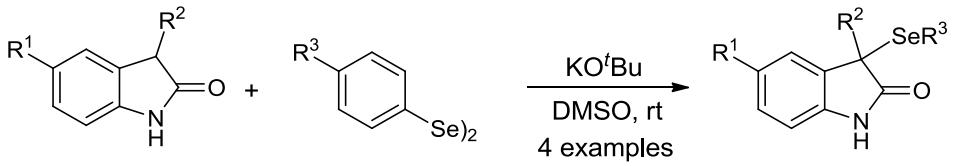
was obtained in 72% yield (Scheme 31).[72] The same reaction was also applied for the selenenylation of acyclic ketones at α-position in high yields.



111 **13** **112:** 72%

Scheme 31. Functionalization of 1-indanone **111** at α-position using *N*-phenylselenosaccharin (NPSSac) **13** as an electrophile.

Furthermore, the selenylation of cyclic amides **113** was achieved by Kumar and coworkers using diphenyldiselenide **2** as source of electrophile in the presence of potassium *tert*-butoxide in DMSO. α-Selenenylated cyclic amides **114** were obtained in moderate to good yields (Scheme 32).[152] The scope of this approach was not limited to cyclic amide and acyclic amides were found to be potential substrates for this reaction.

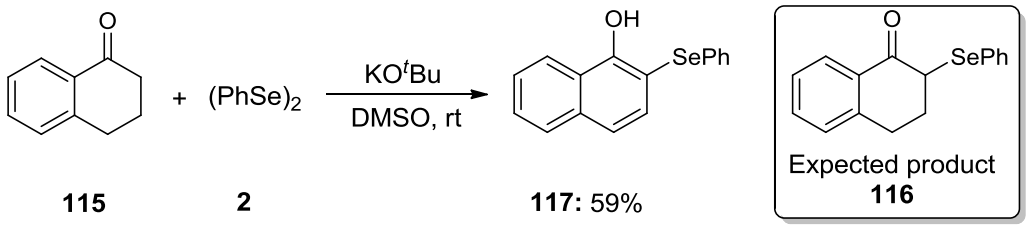


113 **2** **114:** 46-79%

R^1 = H, Cl; R^2 = H, Bn; R^3 = H, OMe

Scheme 32. Selenenylation of cyclic amides **113** at the α-position using diphenyldiselenide **2** in the presence of potassium *tert*-butoxide in DMSO.

Notably, expected selenenylation product **116** was not obtained when α-tetralone **115** was used as substrate in the same reaction under similar reaction conditions. In this reaction, the formation of 2-phenylselanyl-1-naphthol **117** occurred by concomitant chalcogenation and aromatization (Scheme 33).[152]



Scheme 33. Conversion of α-tetralone **115** to 2-phenylselanyl-1-naphthol **117** using diphenyldiselenide **2** in the presence of potassium *tert*-butoxide in DMSO.

2.1.5.2. Selenenylation of Aromatic C-H

There are few reports in which selenium electrophiles have been used for the selenenylation of aromatic C-H bonds. In few approaches, transition metals have been used to initiate the reaction while few reactions proceeded without using any transition metal.

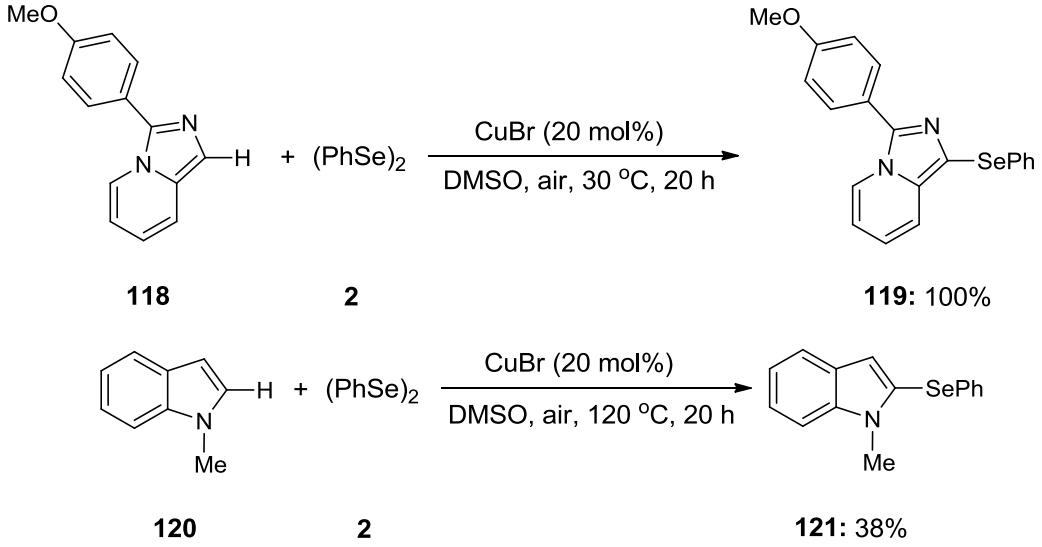
2.1.5.2.1. Metal-mediated Selenenylation of Aromatic C–H

Various metals have been successfully introduced into the selenenylation of aromatic C-H bonds. In 1995, Kim and Lee achieved the selenenylation of pyrimidones using diphenyldiselenide **2** as source of electrophile in the presence of catalytic amount of $Mn(OAc)_3$ in DMSO. The approach however could only provide selenenylaion products in low yields.[153]

2.1.5.2.1.1. Copper-Mediated Selenenylation of Aromatic C–H

In 2014, Cu(I)-catalyzed approach for the selenenylation of 3-(4-methoxyphenyl)imidazo[1,5-*a*]pyridine **118** was reported by Shibahara and coworkers using diphenyldiselenide **2** as an electrophile in the presence of catalytic amounts of CuBr. The reaction product **119** was obtained in quantitative yields (Scheme 34).[154] Additionally, 1-methylindole was tested as substrate under similar reaction conditions. Selenenylation was observed at C-2 position but reaction product **121** was obtained in

low yield compare to selenenylation of 3-(4-methoxyphenyl)imidazo[1,5-*a*]pyridine **118** (Scheme 32).[154]



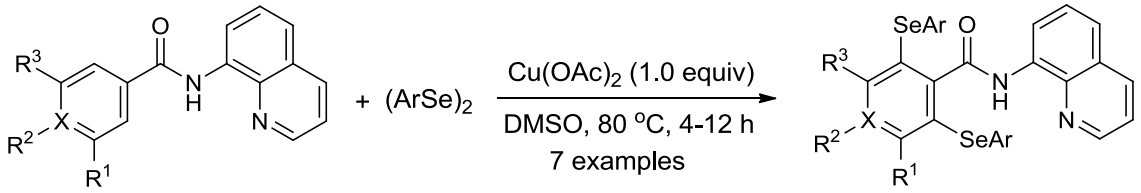
Scheme 34. Cu(I)-catalyzed selenenylation of 3-(4-methoxyphenyl)imidazo[1,5-*a*]pyridine **118** and 1-methylindole **120** using diphenyldiselenide **2** as an electrophile.

Selenenylation of 8-aminoquinolones **122** was achieved at the C-5 position by using various diselenides of type **2** as electrophilic source and 1.5 equivalents of $CuBr_2$ in DMSO under an oxygen atmosphere. Notably, the selenenylation reactions were found to be slightly sluggish and require higher temperature to precede while corresponding diarylselenides **123** were obtained in good yields (Scheme 35).[155] This approach was found to have equal potential to selenenylate substrates having both electron-donating and withdrawing groups.

R = Me, ^{t}Bu, cyclopentyl; Ar = Ph, 4-ClC_6H_4, 2,6-$Me_2C_6H_3$, 2,4,6-$Me_3C_6H_2$

Scheme 35. Cu(II)-Mediated selenenylation of 8-aminoquinolones **122** to corresponding diarylselenides **123** using diaryldiselenides **2**.

In 2016, the diselenenylation approach was developed where benzamides **124** (X = CH) or nicotinamides **124** (X = N; R^2 = H) were used as substrates by Baidya and coworkers.[156] In this report, diselenenylation of benzamides **124** was achieved by the reaction with different diaryldislenides **2** in the presence of $Cu(OAc)_2$ in DMSO. The selenenylation occurred at the C-2 and C-6 positions on the benzene ring and 2,6-bis(phenylselanyl)-*N*-(quinolin-8-yl)benzamides **125** were obtained in good yields (Scheme 36). In case of *N*-(quinolin-8-yl)isonicotinamides **124** (X = N; R^2 = H) the diselenenylation occurred at the C-3 and C-5 position on the pyridine ring and 3,5-bis(phenylselanyl)-*N*-(quinolin-8-yl)isonicotinamides were obtained in useful yields. The course of reaction was not to found change much when using different electron-donating and withdrawing groups on aromatic ring on the substrate.



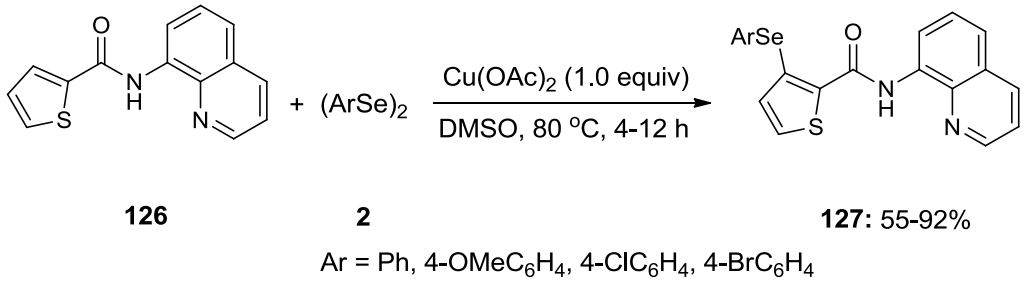
124 **2** **125:** 52-70%

R^1 = H, Me; R^2 = H, Me, OMe, Cl; R^3 = H, Me, OMe; Ar = Ph, *t*-BuC_6H_4; X = CH, N

Scheme 36. Cu(II)-Mediated diselenenylation of benzamides **124** using diaryldiselenides **20** and $Cu(OAc)_2$ in DMSO.

Monoselenenylation was observed in case of *N*-(quinolin-8-yl)thiophene-2-carboxamide **126** as a substrate by using various diaryldiselenides **2** under similar reaction conditions. The selenenylation was occurred at the C-3 position on the thiophene

ring and 3-(arylselanyl)-*N*-(quinolin-8-yl)thiophene-2-carboxamides **127** were obtained 55-92% yields (Scheme 37).[156]

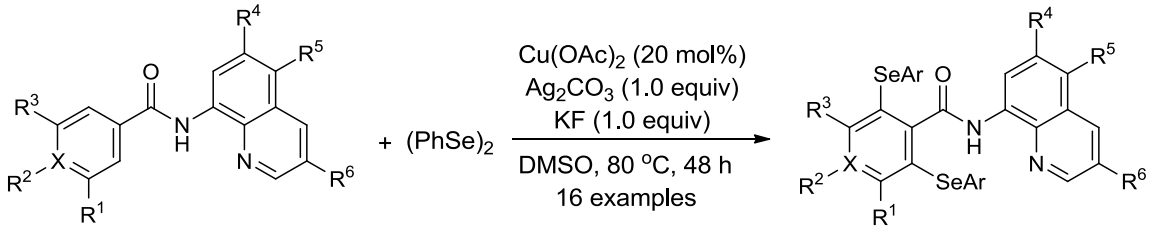


126 **2** **127:** 55-92%

Ar = Ph, 4-OMeC$_6$H$_4$, 4-ClC$_6$H$_4$, 4-BrC$_6$H$_4$

Scheme 37. Cu(II)-Mediated selenenylation of *N*-(quinolin-8-yl)thiophene-2-carboxamide **126** using diaryldiselenides **2** and $Cu(OAc)_2$ in DMSO.

Other selenenylations were also achieved using $Cu(OAc)_2$ as catalyst in same report.[156] Similar amide substrates **124** were treated with diphenyldiselenide **2**, 20 mol% of $Cu(OAc)_2$, KF as an additive and silver carbonate as an oxidant in DMSO. The diselenenylated products **125** were obtained in moderate to good yields (Scheme 38).[156] Unlike *N*-(quinolin-8-yl)thiophene-2-carboxamide **126**, diselenenylation was observed when *N*-(quinolin-8-yl)thiophene-3-carboxamide **126** (3-thienyl) was used as substrate. Probably, silver carbonate was used to regenerate the Cu(II) species *in situ* by oxidation of the reduced Cu(I) species.



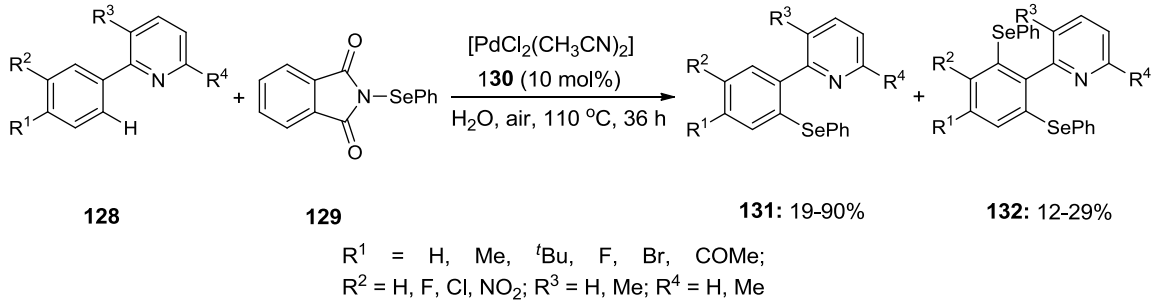
124 **2** **125:** 45-80%

R^1 = H, Me, OMe; R^2 = H, Me, OMe, Cl, F, Br; X = CH, N; R^3 = H, Me, OMe; R^4 = H, OMe; R^5 = H, I; R^6 = H, Br

Scheme 38. Cu(II)-Catalyzed mono-/diselenenylation of benzamides **124** using diphenyldiselenides **2** and $Cu(OAc)_2$ as catalyst and Ag_2CO_3 as an oxidant.

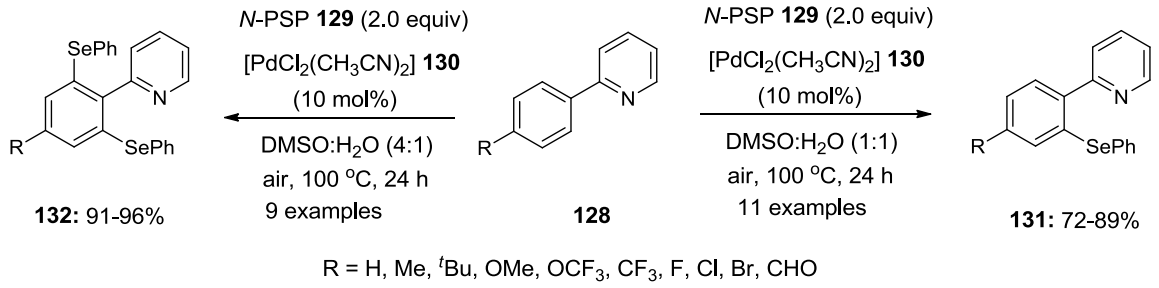
2.1.5.2.1.2. Palladium-Catalyzed Selenenylation of Aromatic C–H

Recently, the selenenylation of aromatic species have been developed using selenium electrophiles in the presence of a palladium catalyst. In 2015, the selenenylation of arenes **128** was developed by Law and others using *N*-(phenylseleno)phthalimide (*N*-PSP) **129** as an electrophile and $[PdCl_2(MeCN)_2]$ **130** as catalyst in an environmentally friendly solvent water. Monoselenenylated products **131** were obtained in low yields as major reaction products while diselenenylated products **132** were isolated as minor product in few of the reactions (Scheme 39).[157]



Scheme 39. Pd-Catalyzed selenenylation of arenes **128** using *N*-(phenylseleno)phthalimide (*N*-PSP) **129** and 10 mol% of $[PdCl_2(MeCN)_2]$ **130**.

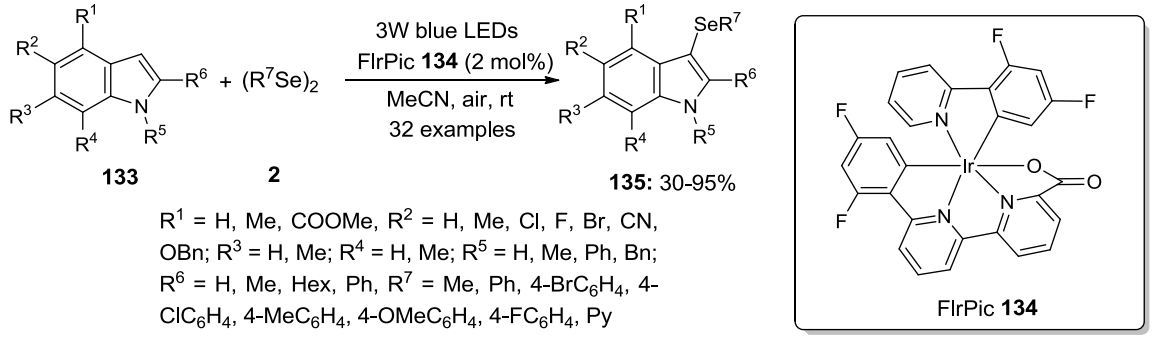
Furthermore, interesting observations were seen when two parallel reactions were performed with similar arenes **128** and electrophilic selenium species **129** in the presence of same catalyst **130** using different ratios of same solvent (DMSO/H_2O) combination (Scheme 40).[158] Monoselenenylated products **131** were obtained when reactions were attempted in a 1:1 ratio of DMSO and water as the solvent while diselenenylation products **132** were achieved where a 4:1 ratio of the same solvent combination was used (Scheme 40). The other reaction conditions were kept the same in both cases and the products **131** and **132** were both isolated in high yields.



Scheme 40. Pd-Catalyzed mono-/diselenenylation of arenes **128** using *N*-(phenylseleno)phthalimide (*N*-PSP) **129** and 10 mol% of $[PdCl_2(MeCN)_2]$ **130**.

2.1.5.2.1.3. Iridium-Mediated Selenenylation of Aromatic C–H

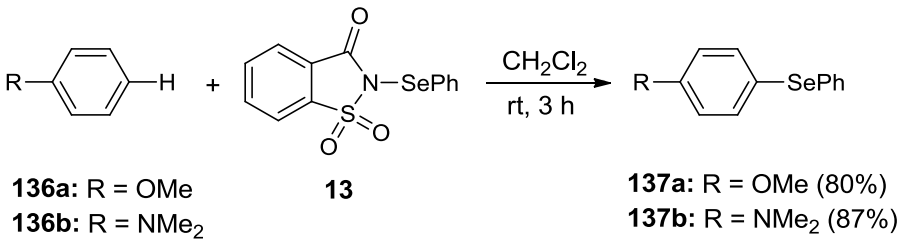
Recently, iridium-complex (FlrPic) **134** was found as an efficient catalyst for the selenenylation of functionalized indoles **133**. The selenenylations of indoles **133** were performed with diaryldiselenides **2** using 2.0 mol% of catalyst **134** in the presence of visible-light. Selelenylation occurred at the C-3 position and the unsymmetrical diarylselenides **135** were obtained in high yields (Scheme 41).[159] Notably, reaction products **135** were obtained in comparatively lower yields with diheteroaryldiselenides **2** (R^7 = Pyridyn-4-yl, thiophene-2-yl and thiophene-3-yl). Additionally, the selenenylation reactions were unsuccessful when R^5 = Ts and R^6 = 2-methoxycarbonyl were used as substrates **133**.



Scheme 41. Ir-Catalyzed selenenylation of functionalized indoles **133** using diaryldiselenides **2** and 2 mol% of FlrPic **134**.

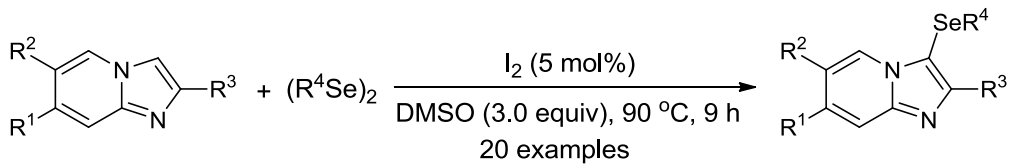
2.1.5.2.2. ***Metal-Free Selenenylation of Aromatic C–H***

There are few reports where the selenenylation of aromatic C–H bonds have been achieved without using toxic metals. Initially, a metal-free selenenylation of aromatic species was developed by Yoshida and coworkers using benzeneselenenyl *m*-nitrobenzenesulfonate **3** as source of selenium electrophile.[70] In 2006, (NPSSac) **13** was used as source of selenium electrophile to develop the similar selenenylations of aromatic species **136a** and **136b** (Scheme 42).[72] Notably, both approaches were suitable only for the selenenylation of electron-rich arenes and electron-dificient arenes were found to be unsuccessful in this reaction.



Scheme 42. Metal-free selenenylation of electron-rich arenes **136a** and **136b** using *N*-phenylselenosaccharin (NPSSac) **13** as an electrophile.

In 2016, Braga and coworkers used molecular iodine as a catalyst to develop the selenenylation of imidazo[1,2-a]pyridines **138** using diaryldiselenides **2** in the presence of DMSO as an oxidant under solvent free conditions. The selenenylation of substrates **138** occurred at the C-3 position selectively and unsymmetrical diarylselenides **139** were isolated in high yields (Scheme 43).[160] Additionally, this approach was successfully applied to the selenenylation of aromatic substrates having both electron-donating and withdrawing substituents.

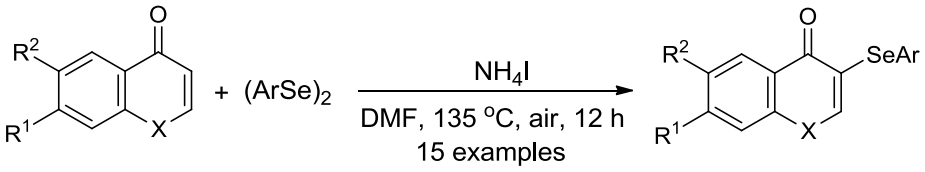


138 **2** **139:** 69-91%

R^1 = H, Me; R^2 = H, Me; R^3 = H, Ph, 3-BrC_6H_4, 4-FC_6H_4, 4-ClC_6H_4, 4-CNC_6H_4, 4-$OMeC_6H_4$, R^4 = ^{n}Bu, Ph, 2-MeC_6H_4, 4-MeC_6H_4, 2-$OMeC_6H_4$, 4-$OMeC_6H_4$, 4-FC_6H_4, 4-ClC_6H_4, 4-$CF_3C_6H_4$, Np, Thio

Scheme 43. Iodine-catalyzed selenenylation of imidazo[1,2-a]pyridines **138** using diaryldiselenides **2**.

In 2017, a NH_4I-mediated approach for the selenenylation of chromones **140** was investigated by the reaction of electrophilic selenium species **2** and ammonium iodide in the presence of air. The selenenylation of chromones **140** occurred at the C-3 position selectively and chromone-based unsymmetrical diarylselenides **141** were isolated in moderate to good yields (Scheme 44).[161] Additionally, quinolin-4(1*H*)-one **140** (R^1 = R^2 = H; X = NH) was successfully used as a substrate and the corresponding selenenylation product **141** was obtained in 53% yield.



140 **2** **141:** 45-73%

R^1 = H, Me, OMe, Br; R^2 = H, Me, Cl, F, Br, NO_2; Ar = Ph, 4-BrC_6H_4, 4-ClC_6H_4, 4-MeC_6H_4, 4-$OMeC_6H_4$, 4-FC_6H_4, 1-Nap; X = NH or O

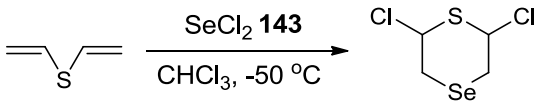
Scheme 44. NH_4I-mediated selenenylation of chromones **140** to diarylselenides **141** by using diaryldiselenide **2**.

Regarding the reaction mechanism, NH_4I decompose to NH_3 and HI at 135 °C which gets further oxidized to iodine in the presence of atmospheric oxygen. Molecular iodine then reacts with diselenide species **2** to form active selenium electrophilic species PhSeI **12c** that can be used for selenenylation of the substrates.

2.2. Cyclization Reactions

2.2.1. Metal-Free Cyclization Reactions

Selenium electrophiles have been involved in different cyclization reactions with or without using transition metals. In 2009, Amosova and coworkers developed an $SeCl_2$-mediated cyclization of divinyl sulfide **142** to 2,6-dichloro-1,4-thiaselenane **144** in quantitative yield (Scheme 45).[162] In addition, the synthesized compound **144** was used as key precursor during the the systhesis of selenium-containing heterocycles.



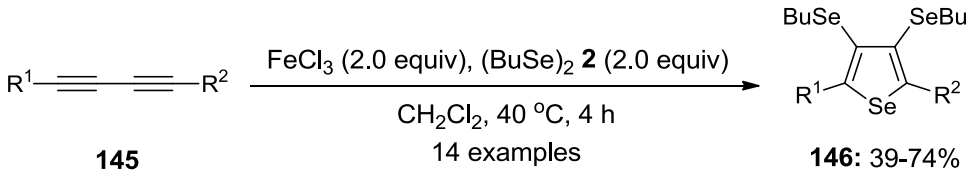
Scheme 45. $SeCl_2$-mediated cyclization of divinyl sulfide **142** to 2,6-dichloro-1,4-thiaselenane **144**.

2.2.2. Metal-Mediated Cyclization Reactions

2.2.2.1. Iron-Mediated Cyclization Reactions

Various metals have been used either in stoichiometric or catalytic amounts to achieve different cyclization reactions using selenium electrophiles. During these cyclizations, neither metal not diselenide species were able to activate the triple bond. Generally, the metal salt reacts with the diselenide to form a complex which further activates the triple bond. In 2015, Zeni and coworkers reported the synthesis of selenophenes **146** in good yields by the cyclization of functionalized 1,3-diynes **145** with

2.0 equivalents of dibutyldiselenide **2** and 2.0 equivalents of $FeCl_3$ (Scheme 46).[163] Additionally, the cyclization reaction was attempted with catalytic amounts of $FeCl_3$ but this proved unsuccessful. Probably, the $FeCl_3$ reacts with diselenide species to form a more electrophilic species which can further activate the triple bond of substrates **145**.

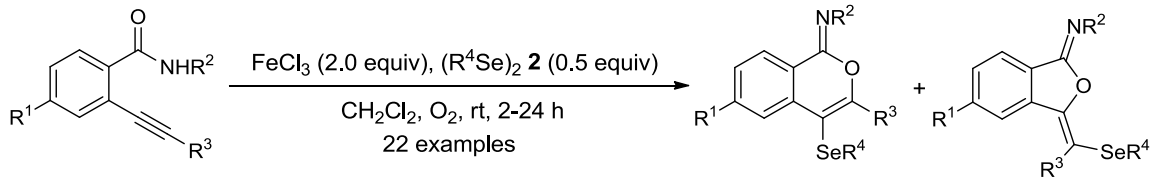


145 **146:** 39-74%

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

Scheme 46. $FeCl_3$-Mediated cyclization of functionalized 1,3-diynes **145** to selenophenes **146** using dibutyldiselenide **2** and $FeCl_3$.

The cyclization of substituted *o*-alkynylbenzamides **147** to 4-(phenylselanyl)-1*H*-isochromen-1-imines **148** was also developed by the reaction diaryldiselenide **2** with $FeCl_3$. The cyclized products 4-(phenylselanyl)-1*H*-isochromen-1-imines **148** were obtained in good yields (Scheme 47).[164] In few a reactions, the exocyclic products (functionalized isobenzofuran-1(3*H*)-imines **149**) were observed as a minor product.

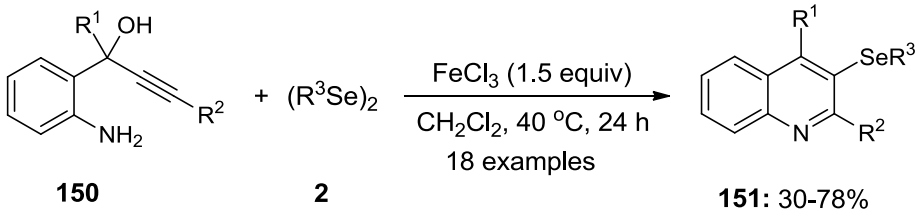


147 **148** major **149** minor

R^1 = H, 4-FC_6H_4, 4-$OMeC_6H_4$; R^2 = ^{t}Bu, Ph, 4-$OMeC_6H_4$, 4-ClC_6H_4; R^3 = ^{n}Bu, Ph, 4-FC_6H_4, 4-$OMeC_6H_4$, 4-ClC_6H_4; R^4 = ^{n}Bu, Ph, 4-FC_6H_4, 4-$OMeC_6H_4$, 3-$CF_3C_6H_4$, 4-ClC_6H_4

Scheme 47. The cyclization of functionalized *o*-alkynylbenzamides **147** using dibutyldiselenide **2** and $FeCl_3$ in dichloromethane.

Furthermore, functionalized quinolines **151** could be synthesized in good yields by the cyclization of 2-aminophenylprop-1-yn-3-ols **150** using similar reagent combinations (a diaryldiselenide **2** and $FeCl_3$) in dichloromethane (Scheme 48).[165] It was observed that Selenocyclizations worked well with substrates bearing both electron-donating and withdrawing substituents.

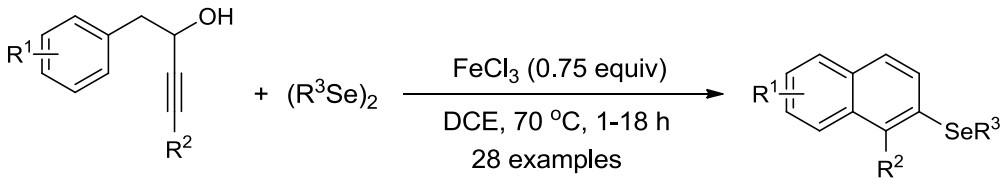


150 **2** **151:** 30-78%

R^1 = Me, Ph, 4-MeC_6H_4, 4-ClC_6H_4; R^2 = ^{n}Bu, Me, Ph, 4-MeC_6H_4, 4-$OMeC_6H_4$; R^3 = ^{n}Bu, Ph, 4-FC_6H_4, 4-ClC_6H_4, 4-MeC_6H_4, 4-$OMeC_6H_4$, Bn

Scheme 48. The synthesis of functionalized quinolines **151** from the cyclization of functionalized 2-aminophenylprop-1-yn-3-ols **150** with diaryldiselenides **2** and $FeCl_3$.

Recently, the same reagent combination (diaryldiselenide **2** and $FeCl_3$) was explored to achieve the carbocyclization of benzylic-substituted propargyl alcohols **152** to 2-organoselenyl-naphthalenes **153** (Scheme 49).[166] The reactions were performed in dichloroethane (DCE) and cyclized products **153** were isolated in moderate to good yields.

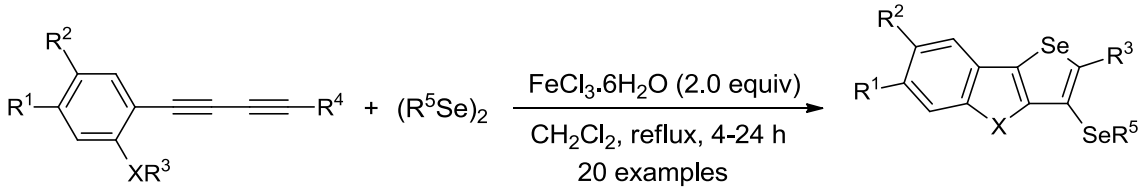


152 **2** **153:** 41-90%

R^1 = H, Me, OMe, Cl; R^2 = ^{n}Bu, Ph, 2-$OMeC_6H_4$, 4-$OMeC_6H_4$, 4-FC_6H_4, 4-ClC_6H_4, 1-Nap, 2-Nap; R^3 = ^{n}Bu, Ph, 2-Py, 4-BrC_6H_4, 3-$CF_3C_6H_4$, 4-ClC_6H_4, 4-MeC_6H_4, 4-$OMeC_6H_4$, 4-FC_6H_4, 2-Nap

Scheme 49. The cyclization of propargyl alcohols **152** to 2-organoselenyl-naphthalenes **153** using diaryl diselenides **2** and $FeCl_3$.

In 2016, 1,3-diynyl derivatives **154** were cyclized to benzo[*b*]furan-fused selenophenes (**114**: X = O) by using similar reagents. The cyclic products **155** were obtained in modrate to good yields (Scheme 50).[167] Additionally, this approach was successfully applied for the synthesis of benzo[*b*]thiophene-fused selenophenes (**155**: X = S) or benzo[*b*]seleno-fused selenophenes (**155**: X = Se).[167]



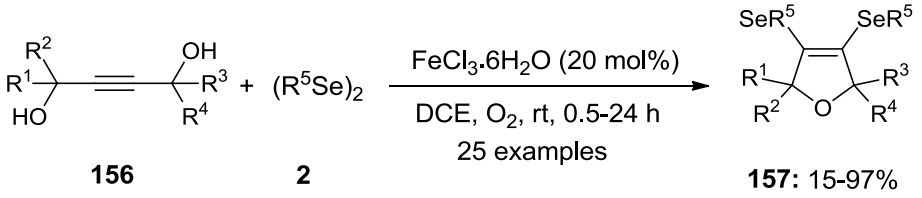
154 **2** **155:** 35-89%

R^1 = H, Me; R^2 = H, F, Me; R^3 = Me, Et, ^{n}Bu; R^4 = ^{n}Bu, Ph, 4-MeC_6H_4, 4-ClC_6H_4; 2-ClC_6H_4; 4-BrC_6H_4; 2-Nap; R^5 = Et, ^{n}Pr, ^{n}Bu, ^{n}Oct; X = O, S, Se

Scheme 50. The cyclization of 1,3-diynyl chalcogen derivatives **154** to benzo[*b*]chalcogen-fused selenophenes **155** by the reaction with diaryldiselenides **2**.

In 2015, Zeni and coworkers developed a high yielding Fe(III)-catalyzed approach for the synthesis of 3,4-bis(organoselanyl)-2,5-dihydrofurans **157** by the cyclization of 1,4-butyne-diols **156** with diaryldiselenides **2** using 20 mol% of $FeCl_3.6H_2O$ in DCE in the presence of an oxygen atmosphere (Scheme 51).[168] Additionally, the same catalytic approach was found to be useful for the synthesis of 3,6-dihydro-2*H*-pyrans and 2,5-dihydro-1*H*-pyrroles. It is important to note that neither the selenium species nor the iron salt alone was sufficient to promote these cyclizations and both reagents were required for the reaction to proceed. The diselenide species **2** reacts

with $FeCl_3$ to form more electrophilic species which occur further coordinate with one of hydroxyl group to initiate the catalytic reaction.



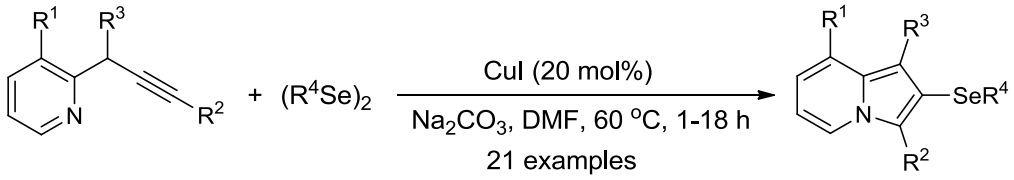
156 **2** **157:** 15-97%

R^1 = H, Me; R^2 = H, Me; R^3 = H, Me; R^4 = Me, Ph, 4-$OMeC_6H_4$, 2-ClC_6H_4, 2-Nap; R^5 = Ph, 4-FC_6H_4, 4-MeC_6H_4

Scheme 51. Fe(III)-catalyzed cyclization of 1,4-butyne-diols **156** to 3,4-bis(organoselanyl)-2,5-dihydrofurans **157**.

2.2.2.2. Copper-Mediated Cyclization Reactions

Recently, Zeni and coworkers developed similar cyclizations using CuI as catalyst. In this report, functionalized 2-(phenylselanyl)indolizines **159** were synthesized in good yields by the cyclization of substituted propargylpyridines **158** with diaryldiselenides **2** using 20 mol% of CuI in the presence of Na_2CO_3 base (Scheme 52).[169] Like $FeCl_3$, CuI coordinates with diselenide species **2** and formed a complex which activates the triple bond in substrates **158**. In addition, the similar cyclization reaction was tested by using dibutyldiselenide **2** (R = ^{n}Bu) as source of electrophile but could not promote these cyclizations successfully.



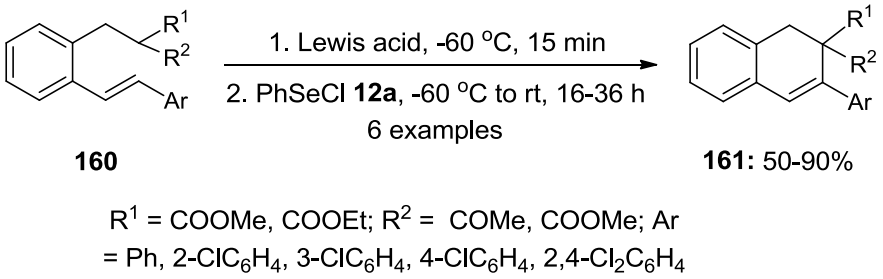
158 **2** **159:** 32-84%

R^1 = H, Me; R^2 = H, Ph, 4-MeC_6H_4, 4-$OMeC_6H_4$; R^3 = OAc, OCOOEt; R^4 = Ph, 2-MeC_6H_4, 4-MeC_6H_4, 4-ClC_6H_4, 2-$OMeC_6H_4$, 4-$OMeC_6H_4$, 3-$CF_3C_6H_4$

Scheme 52. Cu(I)-catalyzed cyclization of functionalized propargylpyridines **158** to 2-(phenylselanyl)indolizines **159** using diselenide **2** as an electrophile.

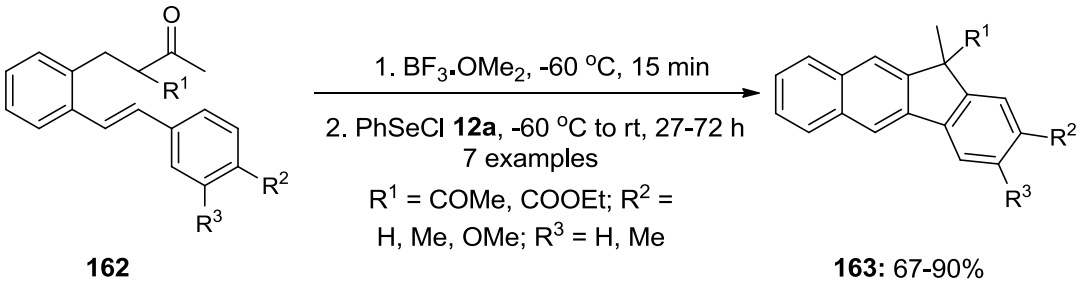
2.2.3 Lewis Acid-Mediated Cyclization Reactions

The combination of Lewis acid with phenylselenyl chloride **12a** was found an efficient reagent system to achieve the carbocyclization of stilbenes **160** to dihydronaphthalenes **161**. The cyclized products **161** were obtained in moderate to high yields (Scheme 53).[170] Two different Lewis acids $SnCl_4$ and $BF_3.OMe_2$ were used during these cyclizations with BF_3•OMe_2 was found superior over $SnCl_4$.



Scheme 53. Selenium-mediated approach for the carbocyclization of stilbenes **160** to dihydronaphthalenes **161**.

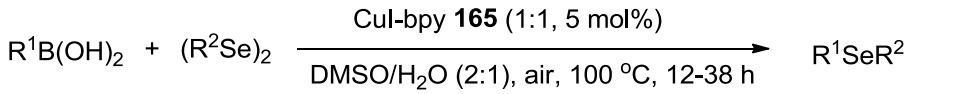
Benzo[*b*]fluorenes **163** were synthesized in useful yields by double carbocyclization of stilbenes **162** under similar reaction conditions using $BF_3.OMe_2$ as an Lewis acid (Scheme 54).[170] Most of the reactions were found to be quite slow and a few of them took 3 days to complete. The reaction products **163** were observed in slightly lower yields when electron-donating substituents were used at the aromatic ring in the substrates.



Scheme 54. Selenium-mediated synthesis of benzo[*b*]fluorenes **163** by double carbocyclization of stilbenes **162**.

2.3. Metal-Catalyzed Coupling Reactions

Organoselenium reagents have received attention due to their applications as electrophilic partners in metal-catalyzed coupling reactions with different organonucleophiles. The coupling reactions of organoselenium reagents provide access to symmetrical and unsymmetrical diorganoselenides. In 2007, the Cu(I)-catalyzed cross-coupling reaction of diaryldiselenides **2** was achieved with alkyl- or arylboronic acids **164** using 5.0 mol% of CuI-bpy (bpy = 4,4'-bipyridine) **165** (1:1) in DMSO:H_2O (2:1) at 100 °C under an oxygen atmosphere. The approach provides symmetrical and unsymmetrical diorgoselenides **166** in high yields (Scheme 55).[171] This approach showed the tolerance to different electron-donating and withdrawing functionalities at the aromatic ring on the organoboronic acid substrates.



R^1 = Me, ^{n}Bu, Ph, 2-MeC_6H_4, 4-MeC_6H_4, 4-FC_6H_4, 2-$OMeC_6H_4$, 4-$OMeC_6H_4$, 2-ClC_6H_4, 4-ClC_6H_4, 4-OHC_6H_4, 4-$CHOC_6H_4$, 4-OHC_6H_4, 4-$MeO_2CC_6H_4$; R^2 = Ph, Bn

Scheme 55. Cu(I)-catalyzed coupling reaction of diaryldiselenides **2** with alkyl- or arylboronic acids **164** using 5.0 mol% of CuI-bpy **165** (1:1) in DMSO:H_2O (2:1).

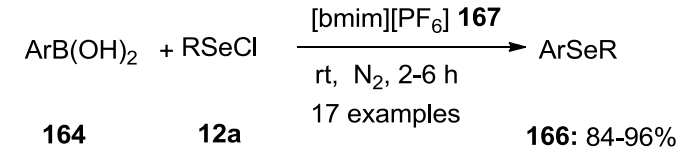
In 2009, the similar cross-coupling reaction was developed by Alves and other using CuO nanoparticles (CuO Nps) as catalyst and various diarylselenides **166** were obtained in excellent yields.[172] The recyclable nature of the catalyst makes this approch more advantageous over other cross-coupling approaches. Furthermore, CuI was used as catalyst by Alves and other to achieve similar reactions in high yields.[173] Interestingly, glycerol was used as solvent and the mixture of CuI-glycerol was reused in similar cross-coupling reactions.[173] In 2013, the combination of 3.0 mol% of $CuSO_4$ and 3.0 mol% of 1,10-Phen.H_2O (Ph = phenanthroline) was used by Xu and coworkers as new catalytic system to catalyze the similar coupling reactions in good yields.[174]

In 2009, Wang and coworkers showed that 10 mol% of Fe powder could be efficient catalyst to achieve similar coupling reaction of diaryldiselenides **2** and arylboronic acids **164**.[175] In the same year, 10 mol% of $InBr_3$ was introduced by similar research group as an efficient catalyst to achieve similar coupling reactions.[176] Recently, Alves and coworkers developed similar coupling reactions in good yields by using 10 mol% of $AgNO_3$ as catalyst.[177]

2.3.1. Coupling Reactions Using Ionic Liquids

In past few years, ionic liquids have received a particular attention in organic synthesis due to applications as versatile solvent in several organic reactions. In 2011, Alves and coworkers reported the cross-coupling reaction of organoselenyl chloride **12** with arylboronic acids **164** in an ionic liquid [bmim][PF_6] (bmin = 1-butyl-3-methylimidazolium) **167** without using any metal catalyst. This approach provides the accessibility of both unsymmetrical and symmetrical diaryldiselenides **166** in moderate to excellent yields (Scheme 56).[178] The course of similar reaction was tested in other

imidazolium ionic liquids such as [bmim][BF_4] and [bmim][NTf_2] but cross-coupling products **166** could obtain in lower yields compare to [bmim][PF_6] **167**. Additionally, arylselenyl bromides **12** were successfully used electrophilic partners with arylboronic acids under similar coupling reaction conditions.

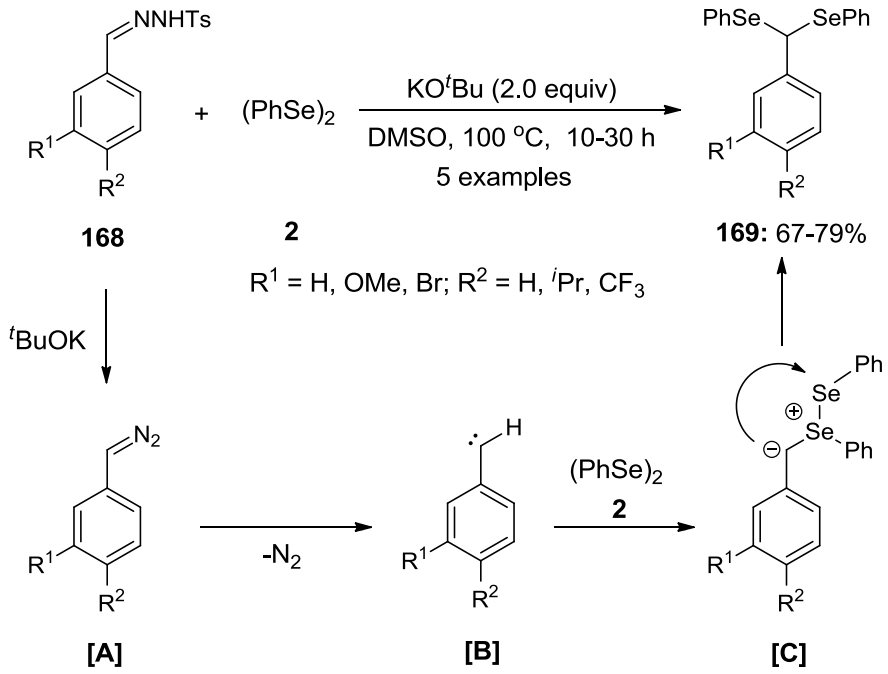


Ar = Ph, 2-MeC_6H_4, 3-MeC_6H_4, 4-MeC_6H_4, 2-$OMeC_6H_4$, 3-$OMeC_6H_4$, 4-$OMeC_6H_4$, 3-$CF_3C_6H_4$, 4-FC_6H_4, 2-ClC_6H_4, 4-ClC_6H_4, 2-BrC_6H_4, 4-BrC_6H_4, 2-Nap; R = ^{n}Bu, Ph, 2-Py, 2-MeC_6H_4, 4-MeC_6H_4, 4-FC_6H_4, 4-ClC_6H_4, 3-$CF_3C_6H_4$, 2,4,6-$Me_3C_6H_2$, 4-$OMeC_6H_4$

Scheme 56. Synthesis of diorgoselenides **166** by the coupling of arylselenyl chloride **12a** with arylboronic acids **164** in ionic liquid [bmim][PF_6] **167**.

2.4. Carbene Insertion Reactions

In 2016, a metal-free approach for insertion of carbene in Se-Se bonds was introduced by Arunprasatha and Sekar.[179] This carbene-insertion approach was used for the synthesis of bis(phenylseleno)acetals **169** in good yields by the reaction of *N*-tosylbenzylidenehydrazines **168** with diphenyldiselenide **2** in the presence of potassium *tert*-butoxide



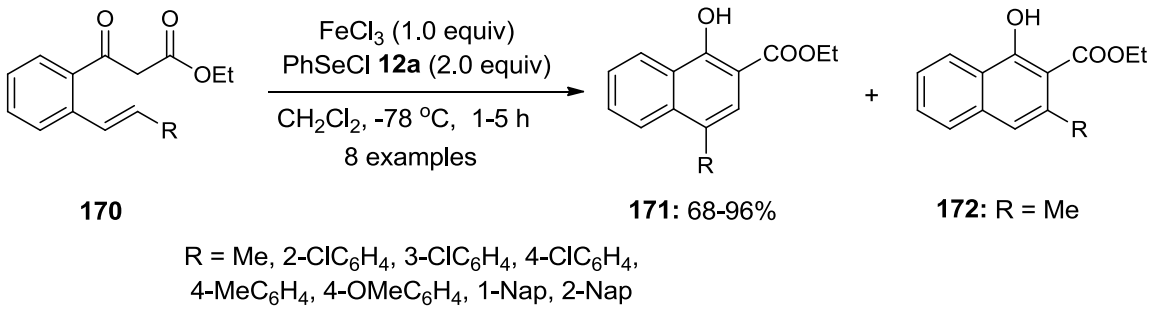
Scheme 57. Metal-free and base-mediated approach for carbene insertion in Se-Se bonds.

All the carbene-insertion reactions were performed in DMSO at 100 °C and proceeded well (Scheme 57).[179] In addition, the same carbene-insertion approach was successfully applied for the synthesis of thioacetals via insertion of carbenes in S-S bonds.

The possible reaction mechanism for carbene insertion reaction is depicted in Scheme 57. According that the reaction was initiated with the formation of diazo intermediate [**A**] by heating of tosylhydrazone **168** in the presence of a base. The diazo intermediate [**A**] converts to free carbene intermediate [**B**] with elimination of nitrogen. Furthermore, free carbene intermediate [**B**] reacts with diselenide 2 to form ylide intermediate [**C**]. Finally, intermediate [**C**] undergo 1,2-migration and form desired product **169**.

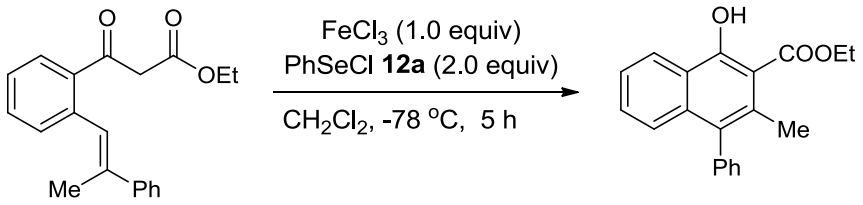
2.5. Rearrangements

In 2010, Wirth and coworkers investigated the role of PhSeCl **12a** in rearrangement reactions. In this report, the synthesis of functionalized naphth-1-ols **171** was developed by the cyclization of stilbenes **170** (R = Ar) having β-keto ester functionality with phenylselenyl chloride **12a** followed by the 1,2-migration of aryl group (Scheme 58).[180] Interestingly, this approach was not suitable for the substrates **170** (R = 4-$OMeC_6H_4$) bearing electron-donating groups at the benzene ring. The cyclization of stilbene **170** (R = 4-$OMeC_6H_4$) could be achieved only by using *in situ* generated more electrophilic selenium species such as phenylselenenyl trifluoracetate. In addition, styrene **170** (R = Me) was also used as substrate and the mixture of cyclic product with 1,2-methyl migration **171** (R = Me) and without migration **172** (R = Me) was obtained in overall 50% yield with 2:1 ratio (Scheme 56).[180]



Scheme 58. The cyclization of stilbenes **170** to cyclic products **171**.

Tancock and Wirth also explored the same reagent combination ($FeCl_3$ and PhSeCl **12a**) to synthesize tetrasubstituted naphthalenes **174** by the cyclization of stilbenes **173** bearing β-keto ester moiety (Scheme 59).[181] The course of the reaction is similar to the reaction described in Scheme 58.



173 **174:** 96%

Scheme 59. The cyclization of stilbenes **173** to cyclic products **174** with 1,2-aryl migration.

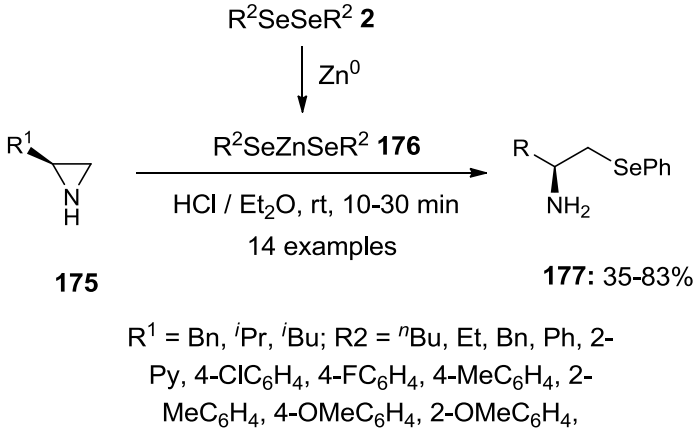
Various chiral selenides undergo stereoselective [2,3]-sigmatropic rearrangements in the presence of different terminal oxidants. These stereoselective [2,3]-sigmatropic rearrangements provide access to a variety of allyl alcohols and amines with high selectivities.[182-186] There are several review articles[15-17] and a book chapter[18] available in the literature where different stereoselective [2,3]-sigmatropic rearrangements are covered.

3. Organoselenium Reagents as Nucleophiles

There are few reactions available in the literature where organoselenium reagents have been used as a nucleophile. The utility of these reagents as nucleophile was developed in 1970s.[19,187,188] Since then various organoselenium reagents have been used as nucleophiles to develop several organic transformations. There are various inorganic selenium nucleophiles such as Li_2Se_2, Na_2Se, Na_2Se_2 and KSeCN which can be used to introduce a selenium atom in organic molecules. KSeCN is commercially available while others can be synthesized easily *in situ* by starting from metallic selenium.

Diaryldiselenides **2** reacts with Zn in the presence of $AlCl_3$ or $RuCl_3$ and form the nucleophilic zinc selenolate $Zn(SeAr)_2$ that can used for the synthesis of selenoethers, selenol esters and carboxylic acids.[191-194] In 2009, Braga and coworers developed the

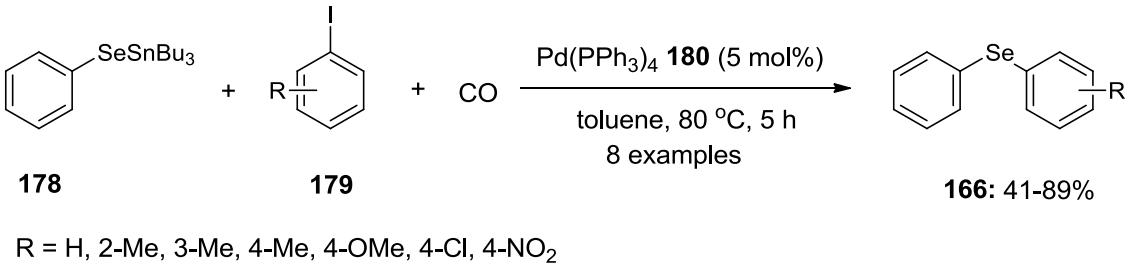
synthesis of chiral β-seleno amines **177** in useful yields by the using *in situ* generated zinc selenolate species $Zn(SeR)_2$ **176** in a biphasic system (Scheme 60).[195] Both electron-withdrawing and donating groups at the aromatic ring in diaryldiselenides **2** were used and substrates installed with an electron-withdrawing group were found to be more effective. Additionally, diferent type of zinc selenolate species PhSeZnX could be prepare by the reaction of metallic znic with phenylselenyl chloride or bromide and has been successfully applied as a nuclephile for the ring opening of epoxides.[196] Additionally, aryl zinc selenolates were successfully used for the synthesis of diarylselenides **166** with the reaction of hypervalent iodine salts in aqueous media.[197]



Scheme 60. The synthesis of chiral β-seleno amines **177** by the reaction with zinc selenolate species $Zn(SeR)_2$ **176** in biphasic system.

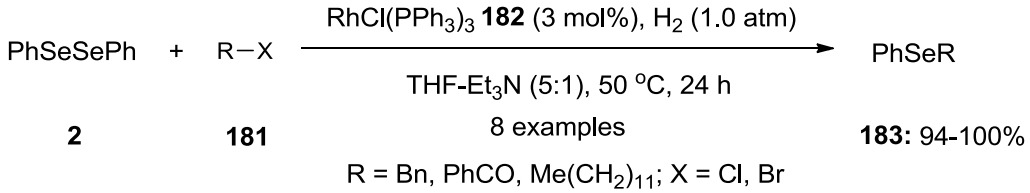
The chemistry of these reagents as nucleophiles was began with nucleophilic substitution reactions[188] but the main focus has been in their application in the synthesis of symmetrical and unsymmetrical diarylselenides via metal-catalyzed C-Se bond formating reactions. In 2002, Nishiyama and Sonoda introduced the application of these reagenets as a nucleophilic partner in Pd(0)-catalyzed cross-coupling reactions.[198] In this reaction, phenyl tributylstannyl selenide **178** was treated with aryl iodides **179** in the

presence of 5 mol% of $Pd(PPh_3)_4$ **180** in toluene and diarylselenides **166** were isolated in good yields (Scheme 61).[198]



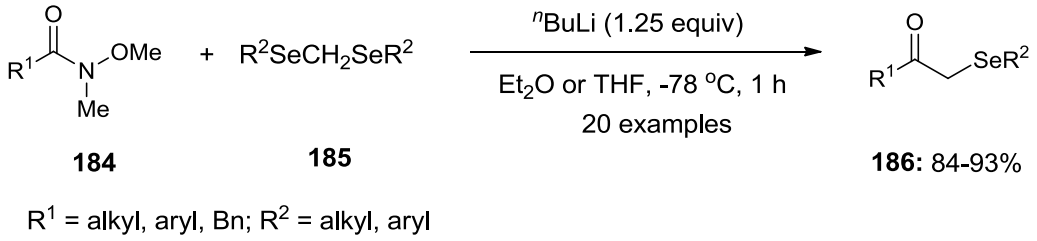
Scheme 61. Pd(0)-catalyzed coupling reaction of phenyl tributylstannyl selenide **178** with aryl iodides **179** using 5.0 mol% of $Pd(PPh_3)_4$ **180** in toluene.

Furthermore, Gujadhur and Venkataraman replaced phenyl tributylstannyl selenide **178** with phenyl selenol and achived the coupling reaction with electron-rich aryl iodides **179** using CuI as catalyst.[199] In 2004, phenyl selenol was used in Pd-catalyzed cross-coupling reactions with bromoporphyrins under mild reaction conditions.[200] In the next year, Tanoka and coworkers developed the Rh-catalyzed reductive coupling of diselenides **2** with alkyl halides **181** in the presence of triethylamine using hydrogen as a reducing agent. The reaction products **183** were obtained in excellent yields (Scheme 62).[201] The role of hydrogen is to generate Rh-SeR species by the reaction with catalyst $RhCl(PPh_3)_3$.



Scheme 62. Rh(I)-catalyzed reductive coupling of diphenyldiselenide **2** with alkyl halides **181** using 3.0 mol% of $Pd(PPh_3)_4$ **182** in the presence of triethylamine using hydrogen as a reducing agent.

Recently, Pace and coworkers developed synthesis of α-aryl- and α-alkyl seleno methylketones **186** in excellent yields by the reaction of Weinreb amides **184** with diselenoacetals **185** in the presence of ^{n}BuLi in ether or THF at -78 ^{o}C (Scheme 63).[202] The diselenoacetals **185** provide corresponding seleno carbanions on selenium/lithium exchange with ^{n}BuLi. Furthermore, the *in situ* generated selenocarbanions added to Weinreb amides **185** to form final products **186**. In addition, several chiral organoselenium reagents have been used as nucleophile to develop different stereoselective reactions.[18]



Scheme 63. The synthesis of α-aryl- and α-alkyl seleno methylketones **186** by the reaction of Weinreb amides **184** with diselenoacetals **185** in the presence of ^{n}BuLi.

4. Catalytic Reactions

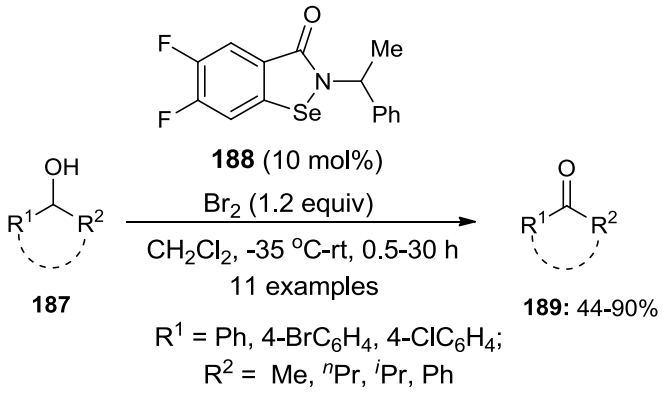
The popularity of organoselenium reagents have been enhanced dramatically in past two decades especially due to their utility in organic synthesis as a catalyst. In the past, several review articles[34-36,203,204] and book chapter[18,37] have covered different aspects of selenium-catalyzed organic reactions. In this section, catalytic transformations using organoselenium reagents are described.

4.1. Selenium-Catalyzed Oxidations of Alcohols

The first report on selenium-catalyzed the oxidation of alcohols to carbonyl compounds was reported in 1996 by Onami and his coworkers.[205] After that, similar

oxidations were achieved by using the combination of bis[2-(2-pyridyl)phenyl] diselenide as catalyst and *N*-chloro-4-chlorobenzenesulfonamide sodium salt as terminal oxidant.[206] In 2009, Arends developed the oxidation of benzyl alcohol by replacing the *N*-chloro-4-chlorobenzenesulfonamide sodium salt with *tert*-butyl hydroperoxide (TBHP).[207]

In 2012, the secondary alcohols **187** were oxidized to corresponding ketones **189** in good yields by reacting secondary alcohols **187** with bromine in the presence of catalytic amount of isoselenazolone **188** (Scheme 64).[208] Notably, the oxidation reaction was equally useful for the oxidation of both cyclic and acylic alcohols. Additionally, organoselenium reagents have been successfully used as catalyst for the oxidation of thiol substrates.[209]

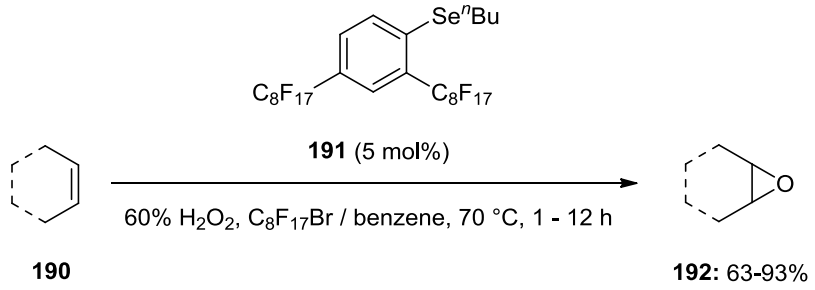


Scheme 64. Selenium-catalyzed oxidation of secondary alcohols **187** to corresponding ketones **189** using catalytic amount of isoselenazolone **188** with bromine.

4.2. Selenium-Catalyzed Oxidation of Alkenes

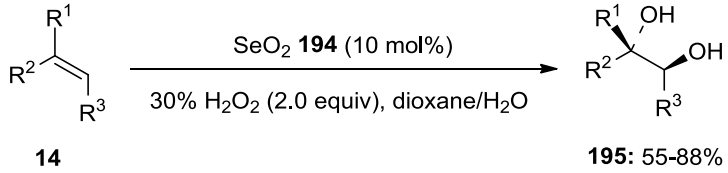
Oxidation of alkenes is more commonly leads the synthesis of different epoxides and diols. Various selenium-catalyzed oxidations of alkenes are existing in the literature which provides corresponding epoxides and diols in useful yields. The application of these reagents in catalysis was begun with the epoxidation of alkenes and first report came in 1978 by Hori and Sharpless.[210] Later, similar selenium-catalyzed epoxidation of

alkene was came after long wait in 1999.[211] In this report, the 2,4-bisperfluorooctylphenyl butylselenide **191** was used to catalyze the epoxidation of cyclic and acyclic alkenes **190** using 60% H_2O_2 as an oxidant in a fluorous biphasic system and functionalized epoxides **192** were isolated in high yields (Scheme 65).[211] Notably, the catalyst was recovered by phase separation and could be reused without losing its catalytic activity. The similar oxidations were achieved by using aryl benzyl selenoxides with the combination of same oxidant.[212] Furthermore, glycerol-based recyclable solvents were used as as green reaction media and found significant success in similar oxidations.[213]



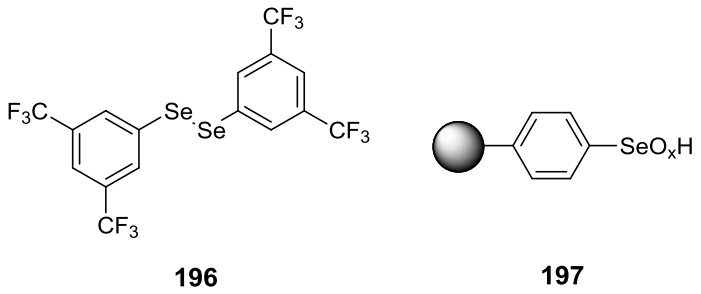
Scheme 65. Selenium-catalyzed epoxidation of alknes **190** to epoxides **192** using catalytic amount of butylselenide **191**.

Like selenium-catalyzed epoxidation reactions, the chemistry of selenium-catalyzed hydroxylation of alkenes is quite old and first report came in 1999.[210] Furthermore, the olefinic substrates **14** were treated with combination of catalyst SeO_2 and H_2O_2 oxidant and functionalized *trans*-diols **195** were obtained in moderate to good yields (Scheme 66).[214] The catalytic cycle of these oxidations suggested that the perselenic acid was working as the active catalytic species.



Scheme 66. Selenium-catalyzed hydroxylation of alknes **14** to *trans*-diols **195** using 10 mol% of SeO_2.

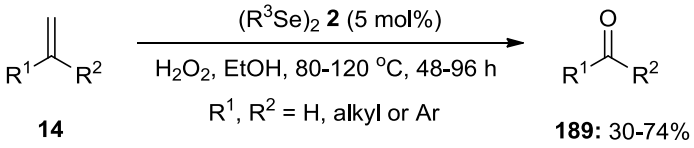
In 2008, 10 mol% of diphenyl diselenide **2** with hydrogen peroxide was also used to achieve hydroxylations alkene **14** in good yields but most of the reactions required longer time to consume the staring material.[215] Furthermore, selenium catalysts **2**, **196** and **197** were used for the dihydroxylation of cyclohexene **196** and 1.0 mol% of catalyst **2** required 42 h to achieve full conversion.[216] On the other hand, more electrophilic diselenide catalyst **196** at same loading required only 5 h to achieve the complete conversion.[216] Additionally, full conversion was observed in 3 h at 10 mol% catalytic loading of polymer-supported selenium catalyst **197** in water.[217]



196 **197**

Figure 4. The structures of organoselenium catalysts **2**, **196** and **197**.

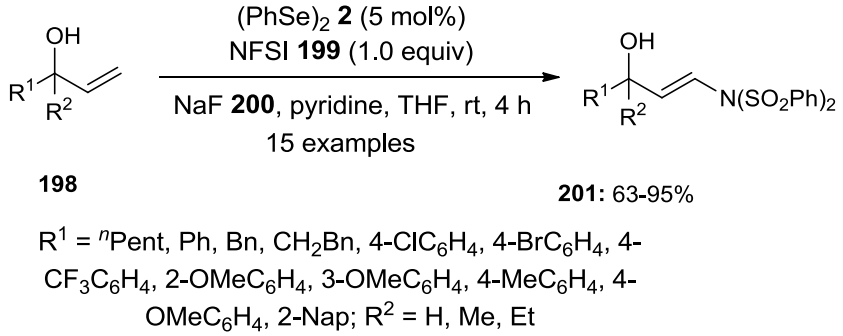
In 2007, Konwar and coworkers introduced the first selenium-catalyst for the cleavage of olefinic double bond to carbonyl compounds.[210] Recently, Yu and co-workers developed another selenium-catalyzed oxidation of terminal alkenes **14** to corresponding carbonyl compounds **189** using dialkyldiselinide **2** as catalyst and hydrogen peroxide as oxidant in ethanol. The cleavaged products **189** were obtained in useful yields (Scheme 67).[218]



Scheme 67. Selenium-catalyzed oxidation of terminal alkenes **14** to ketones **189** using dialkyl diselenides **2** as catalyst.

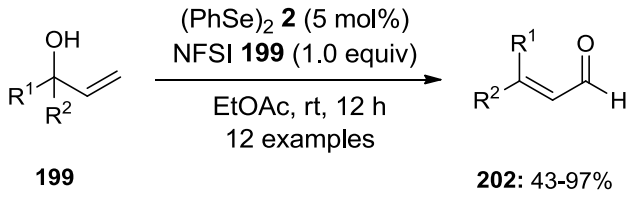
4.3. Selenium-Catalyzed synthesis of Allylic Alcohols

In 2015, Zhao and coworkers employed diphenyldiselenide **2** as catalyst to achieve the synthesis of 3-amino allylic alcohols **201** in high yields by reaction of terminal alkenes **198** using NFSI **199** as oxidant and NaF as an additive (Scheme 68).[219] It was found that the presence of hydroxyl group was essential to achieve the synthesis of compounds **201**.



Scheme 68. Selenium-catalyzed synthesis of 3-amino allylic alcohols **201** by the reaction of terminal alkenes **198** using diphenyldiselenide **2** as catalyst and NFSI **199** as an oxidant.

The alkenes **198** were found as useful substrates for the synthesis of α,β-unsaturated aldehydes **202** when same reaction was performed in EtOAc without using any base and additive. Carbonyl compounds **202** were isolated in moderate to high yields (Scheme 69).[219]

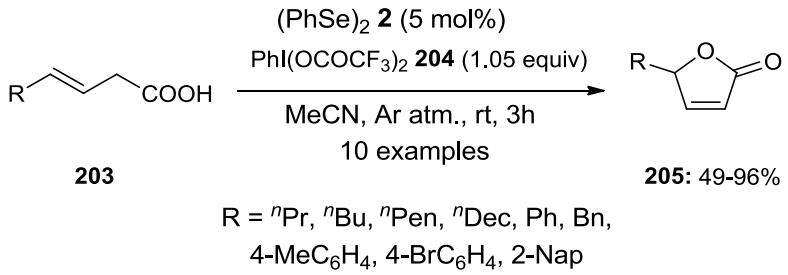


Scheme 69. Selenium-catalyzed synthesis of α,β-unsaturated aldehydes **202** by the reaction of alkenes **198** using diphenyldiselenide **2** as catalyst and NFSI **199** as an oxidant.

4.4. Selenium-Catalyzed Cyclization Reactions

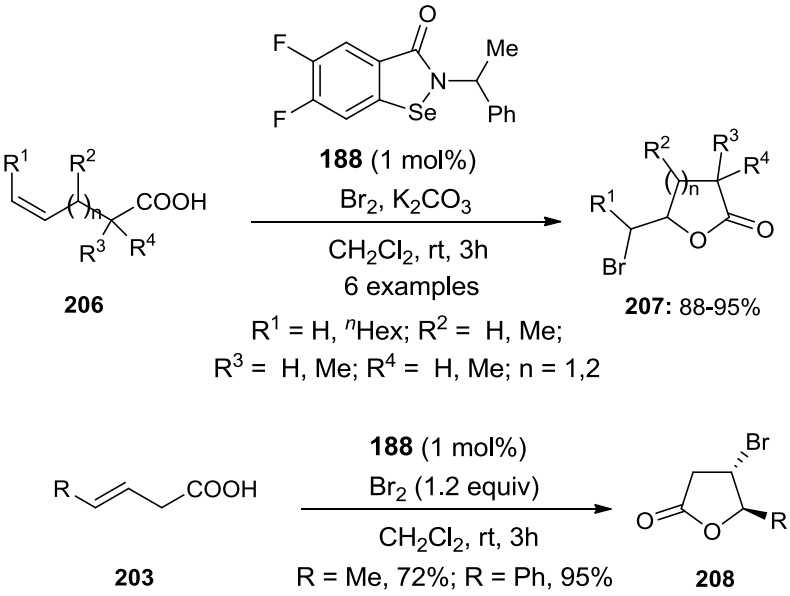
4.4.1. Selenium-Catalyzed Lactonization Reactions

In past decade, organoselenium reagents have been suceesfully introduced as catalysts in lactonization reactions. In 2007, Wirth and coworkers reported selenium-catalyzed lactonization of carboxylic acids **203** to butenolides **205** using diphenyl diselenide **2** as catalyst and [bis(trifluoroacetoxy)iodo]benzene (PIFA) **204** as an oxidant. The cyclized products **205** were isolated in moderate to high yields (Scheme 70).[220] Other iodine(III) reagents such as PIDA and Koser's reagents were tested also as an oxidant but best result was obtained with PIFA **204**. The role of hypervalent iodine species is to activate the selenium functionality (SePh) of corresponding selenolactone intermediate for selenoxide elimination process. Additionally, efforts were made to develop the asymmetric version of same catalytic lactonization but low selectivites were observed.[220, 221] Furthermore, the same catalytic approach was expanded for the synthsis of functionalized dihydropyranones[222] and isocoumarins[223] by same research group.



Scheme 70. Selenium-catalyzed lactonization of *β,γ*-unsaturated carboxylic acids **203** to butenolides **205** using diphenyl diselenide **2** as catalyst and [bis(trifluoroacetoxy)iodo]benzene (PIFA) **204** as an oxidant.

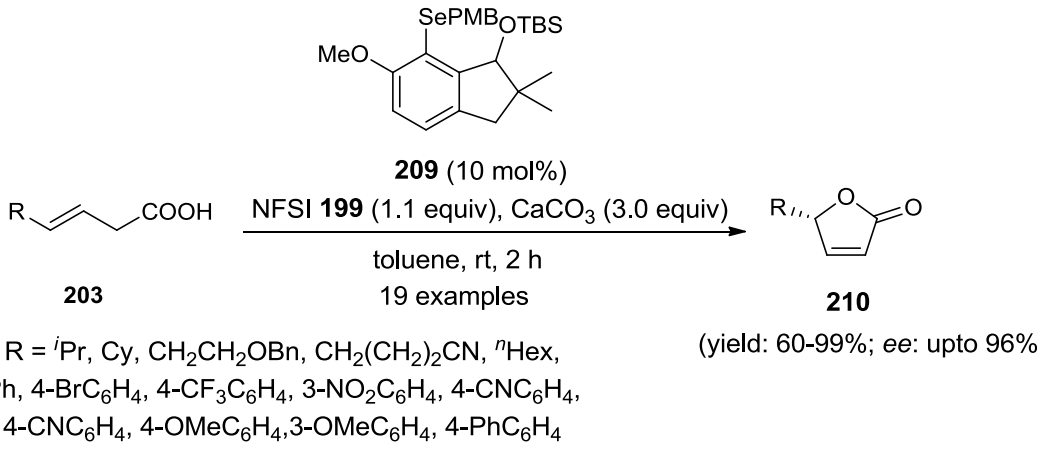
In 2012, the bromolactonization of substituted γ,δ-unsaturated acids **206** was achieved in excellent yields by using isoselenazolone **188** as catalyst with bromine or *N*-bromosuccinimide (NBS) in the presence of a base. Notebly, γ,δ-unsaturated acids **206** undergo *exo*-cyclization while *endo*-cyclization products were observed when γ,δ-unsaturated acids **203** were treated under similar reaction conditions (Scheme 71).[208]



Scheme 71. Selenium-catalyzed lactonization of alkenoic acids **206** and **203** to five-memebered lactones **207** and **208** respectively using 1.0 mol% isoselenazolone **188** with bromine or NBS.

4.4.2. Selenium-Catalyzed Stereoselective Lactonization Reactions

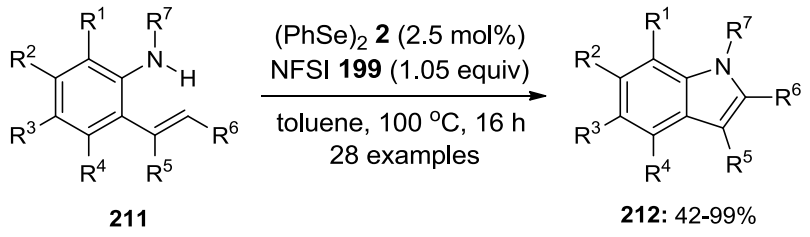
In 2016, Maruoka and coworkers developed the synthesis of indane-cored chiral selenide **209** and used as catalyst in enantioselective lactonizations β,γ-unsaturated acids **203**. The lactonization of acids **203** were performed with 10 mol% of chiral catalyst **209** in the presence of oxidant NFSI **199**. The cyclized products **211** were obtained in high yields with upto 96% enantiomeric excess (Scheme 72).[224]



Scheme 70. Enantioselective lactonizations β,γ-unsaturated acids **203** using 10 mol% of chiral catalyst **209** in the presence of oxidant NFSI **199**.

4.4.3. Selenium-Catalyzed Aminocyclizations

In 2015, Ortgies and Breder reported an aminocyclization of styrenes or stilbenes **211** bearing amino functionality at *ortho*-position using using diphenyldiselenide **2** as catalyst.[225] The aminocyclization reactions of substrates **211** were performed using selenium catalyst **2** in the presence of *N*-fluorobenzenesulfonimide **199** in toluene and cyclized compounds **212** were obtained in good yields (Scheme 73).[225,226]



Scheme 73. Selenium-catalyzed aminocyclization of styrenes or stilbenes **211** to indoles **212** using diphenyldiselenide **2** as catalyst and NFSI **199** as an oxidant.

5. Conclusion

This book chapter summarizes the key applications of organoselenium reagents in organic synthesis. Several synthetic transformations such as addition reactions with alkenes and selenocyclizations, selenenylations of aliphatic and aromatic species, metal-catalyzed C-C bond formation reactions, carbene-insertion and rearrangement reactions are discussed. The developments of catalytic reactions using catalytic amounts are described in detail. Additionally, the asymmetric variants of various synthetic transformations using stoichiometric or catalytic amounts organoselenium reagents are also covered. Several reaction products obtained during these reactions would be important synthetic intermediates for the synthesis of various biologically active synthetic and natural products.

6. References

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