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Selenium and Tellurium Electrophiles in Organic Synthesis

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Abstract:
This chapter highlights the utility of electrophilic achiral and chiral organoselenium reagents in organic synthesis. A range of reactions from alkene functionalizations, the functionalization of aliphatic and aromatic C–H bonds using stoichiometric and catalytic approaches as well as rearrangement reactions are described. In addition, the utility of organotellurium reagents in organic synthesis is covered in this chapter.

Keywords: selenium electrophiles, selenenylation, selenium-catalyzed reactions, chiral selenium electrophiles, tellurium electrophiles

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1 Introduction

The chemistry of organoselenium compounds has been identified as an important portfolio in synthetic and medicinal chemistry [1]. In the beginning, the development of organoselenium chemistry was quite limited but several synthetically important organoselenium reagents have been discovered after the selenoxide elimination in the early 1970s [2]. In past few decades, various synthetic transformations including selenenylations, selenocyclizations, selenoxide eliminations and 2,3-sigmatropic rearrangements have been successfully achieved using organoselenium reagents [2, 3]. Furthermore, the application of these reagents as catalysts and ligands provides an additional asset to the organic chemists [4]. The chemistry of organoselenium reagents has now become a well-established research area and books [5], book chapters [6] and review articles [7] have appeared to describe their chemical potential. This chapter highlights the utility of electrophilic achiral and chiral organoselenium reagents in organic synthesis. In addition, the utility of organotellurium reagents in organic synthesis is also covered in this chapter.

2 Selenium electrophiles

Organoselenium reagents are mainly known for their electrophilic nature but there are several reports in which these reagents have been used as nucleophile. Variety of selenium electrophiles can be generated by the cleavage of Se–Se bond of diselenides. Selenium electrophiles are quite powerful reagents and react with olefins to form three-membered seleniranium ion intermediate. Furthermore, seleniranium ion intermediate reacts with different nucleophiles to undergo various selenenylation reactions. The scope of these selenium electrophiles is not limited to selenylation of alkenes but selenation of other aliphatic and aromatic species has been successfully achieved using these electrophiles.

2.1 Selenenylation reactions

2.1.1 Selenenylation of Alkenes

The addition of selenium electrophiles to alkenes is one of the oldest reactions in the area of organoselenium chemistry. Initially, commercially available PhSeCl was successfully used to achieve the selenenylation of alkenes but this reaction was suffered with some side reactions due to nucleophilic chlorine anion [8]. In 1989, Tiecco and coworkers developed methoxyselenenylation of various acyclic and cyclic alkenes in good yields [9].

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In this report, active selenium electrophilic species was generated by the oxidation of diphenyl diselenide using ammonium peroxydisulfate as an oxidant. Furthermore, *N*-phenyl selenophthalimide (*N*-PSP) and *N*-phenyl selenosuccinimide were successfully used as selenenylating agents in oxyselenation of alkenes [10, 11]. In 1991, Yoshshida and coworkers developed a new selenenylating agent benzeneselenenyl *m*-nitrobenzenesulfonate **3** by oxidation of diphenyl diselenide **2** using benzeneselenenyl *m*-nitrobenzenesulfonyl peroxide **1** as oxidant (Figure 1) [12].

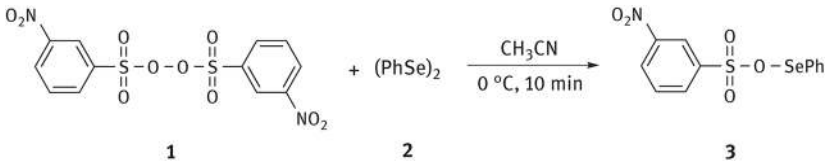


Figure 1: Synthesis of the selenenylating agent benzeneselenenyl *m*-nitrobenzenesulfonate **3**.

Compound **3** was synthesized *in situ* and used in various oxyselenenylation reactions of functionalized alkenes **4** using different nucleophiles (Figure 2, Table 1, entries 1–16) [12]. Initially, benzeneselenenyl *m*-nitrobenzenesulfonate **3** was used for the methoxyselenenylation of alkenes **4** using methanol as nucleophile (Figure 2, Table 1, entries 1–3). All reactions were performed in acetonitrile and selenenylated products **6** were isolated in excellent yields.

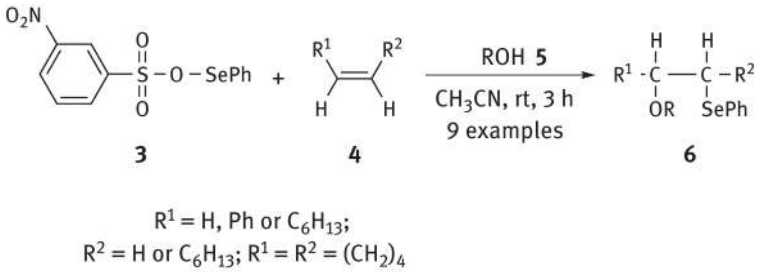


Figure 2: Oxyselenenylation of alkenes **4** using benzeneselenenyl *m*-nitrobenzenesulfonate **3**.

Table 1: Oxyselenenylation of alkenes **4** using benzeneselenenyl *m*-nitrobenzenesulfonate **3**.

Entry	4		5	Solvent	6
	R^1	R^2	R		Yied (%)
1	Ph	H	Me	CH_3CN	98
2	Hex	H	Me	CH_3CN	83
3	R^1=R^2=$(CH_2)_4$		Me	CH_3CN	92
4	R^1=R^2=$(CH_2)_4$		Ac	CH_3CN	25
5	R^1=R^2=$(CH_2)_4$		Ac	CH_3NO_2	70
6	Ph	H	Ac	CH_3NO_2	11
7	Hex	H	Ac	CH_3NO_2	73
8	Ph	H	H	CH_3NO_2	61
9	Ph	H	H	CH_3NO_2	77
10	R^1=R^2=$(CH_2)_4$		H	CH_3CN	33
11	R^1=R^2=$(CH_2)_4$		H	CH_3NO_2	72
12	Hex	H	H	CH_3NO_2	–
13	Hex	H	Ph	CH_3CN	25
14	Hex	H	Ph	CH_3NO_2	62
15	R^1=R^2=$(CH_2)_4$		Ph	CH_3CN	38
16	R^1=R^2=$(CH_2)_4$		Ph	CH_3NO_2	64

After achieving the methoxyselenenylations, acetoxyselenenylation of similar alkenes was achieved using organoselenium reagent **3** and AcOH as a sources of acetoxy ions (Figure 2, Table 1, entries 4–7) [12]. Initially, acetoxyselenylation was performed in acetonitrile but the reaction did not proceed well (Figure 2, Table 1, entries 4). The reaction products **6** were obtained in moderate yields when reaction was performed in nitromethane (Figure 2, Table 1, entries 5 and 7). Poor yields were observed when styrene was treated with electrophile **3** under similar reaction conditions (Figure 2, Table 1, entry 6).

The same reagent **3** was successfully used for the hydroxyselenenylation of similar alkenes (Figure 2, Table 1, entries 8–11) [12]. Hydroxyselenenylations were working in both acetonitrile and nitromethane but nitromethane was found to be a more effective solvent than acetonitrile. Interestingly, hydroxyselenenylation did not proceed when 1-octene was used as substrate (Figure 2, Table 1, entry 12). Finally, phenoxyselenenylation of 1-octene and cyclohexene was also achieved successfully using selenium electrophile **3** (Figure 2, Table 1, entries 13–16). The reactions were performed in both acetonitrile and nitromethane but nitromethane was well suited over acetonitrile.

In 1998, Tingoli and coworkers developed an approach for acetoxyselenenylation of alkenes **8** by the reaction of diphenyl diselenide **2** with PIDA [(diacetoxyiodo)benzene] **7** in acetonitrile (Figure 3). In addition, hydroxyselenenylation of similar alkenes **8** was also achieved in moderate yields when alkenes were treated with diphenyl diselenide **2** and PIDA **7** in MeCN/H_2O (5:1). PIDA **7** was used as an oxidant to oxidize diphenyl diselenide **2** to more electrophilic selenium species [13].

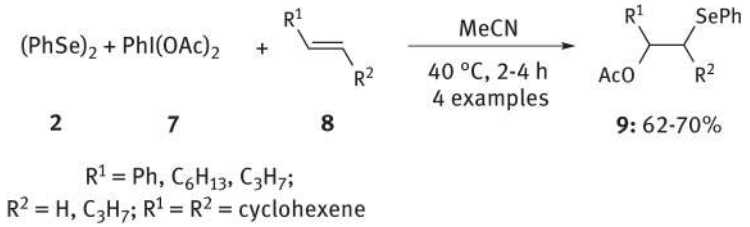


Figure 3: Acetoxyselenenylation of alkenes **8** by the reaction with diphenyl diselenide **2** and PIDA **7**.

In 2006, Tingoli and coworkers synthesized a new selenium electrophile *N*-phenyl selenosaccharin (NPSSac) **12** by the reaction of commercially available phenyl selenium halide **11** and silver saccharin (AgSac) **10** in dichloromethane at room temperature (Figure 4). The synthesized selenium reagent **12** was further used for methoxyselenenylation of olefins **13**. All the reactions were performed in dichloromethane at room temperature and reaction products **14** were isolated in moderate-to-high yields (Figure 4) [14].

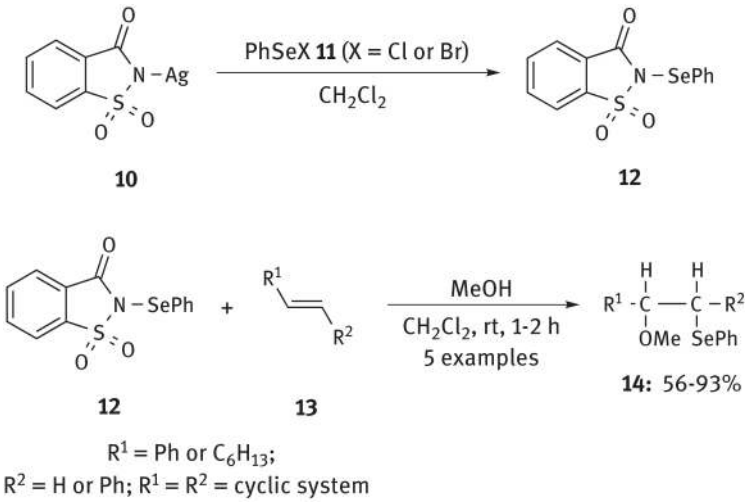


Figure 4: Methoxyselenenylation of alkenes **13** using selenium electrophile *N*-phenyl selenosaccharin (NPSSac) **12**.

In 2012, Thomas and coworkers reported an iodine catalyzed addition of functionalized styrenes **15** using *in situ*-generated electrophilic species PhSeI. In this reaction, 20 mol% of iodine was used as catalyst for the addition of styrenes **15** with diphenyl diselenide **2** in dichloromethane at 70°C and excess of styrene was used as nucleophile (Figure 5) [15].

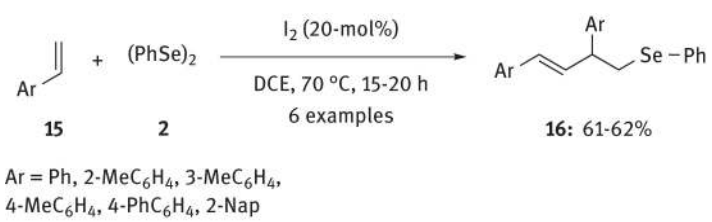


Figure 5: Iodine-catalyzed addition of styrenes **15** using *in situ*-generated electrophilic species PhSeI.

The catalytic cycle for iodine-mediated addition of styrenes is described in Figure 6. According to that, the catalytic cycle was initiated by the reaction of diphenyl diselenide **2** with iodine to forms active catalytic species phenyl selenium iodide **17** which further reacts with styrene **15** and form three-membered seleniranium ion intermediate **18**. Furthermore, intermediate **18** could be attacked by the styrene nucleophile to form addition product **19**. After that, the reaction intermediate **19** undergoes elimination reaction and HI with final product **16**. Finally, HI could further react with diphenyl diselenide to phenyl selenyl iodide **17** to continue the catalytic cycle.

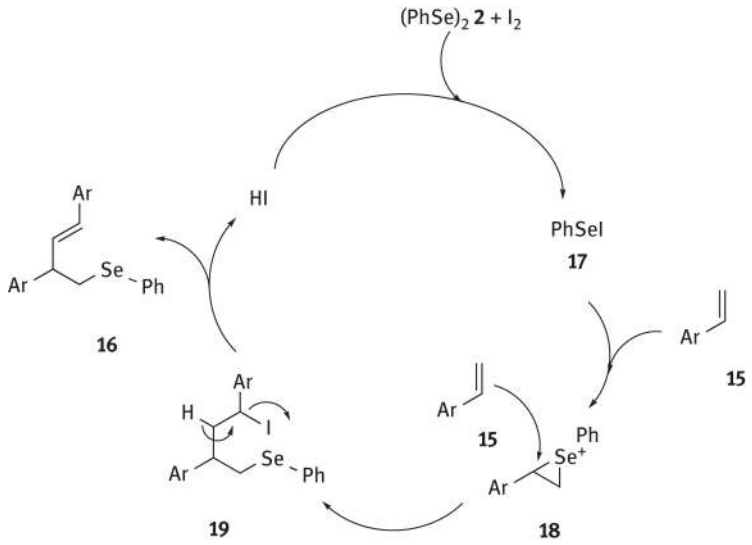


Figure 6: Catalytic cycle for iodine-mediated addition of styrenes **15** using *in situ*-generated electrophilic species PhSeI **17**.

In 2015, Yan and coworkers developed an approach for the acetoxyselenenylation of alkenes **15** by the reaction with diorganyl diselenide **20** and catalytic amount of KBr using *m*-CPBA as an oxidant. All the reactions were performed in AcOH and reaction products **21** were isolated in good-to-high yields (Figure 7) [16]. Various aliphatic and aromatic olefins were successfully tolerated under mild reaction conditions. In addition, NaCl was also used as catalyst under similar reaction conditions.

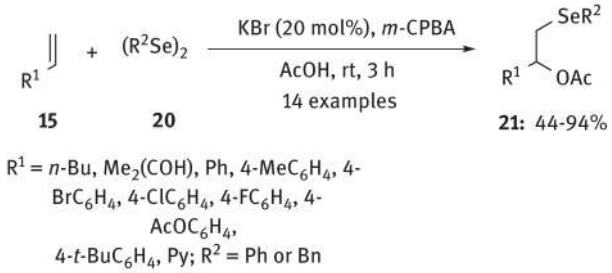


Figure 7: KBr-catalyzed acetoxyselenylation of alkenes **15** by the reaction of diorganyl diselenides **20** with *m*-CPBA as catalyst.

The catalytic cycle for KBr-catalyzed acetoxyselenylation of alkenes **15** is shown in Figure 8. The catalytic cycle initiates with oxidation of bromide ion to bromine using *m*-CPBA as an oxidant. Bromine was further reacted with diselenide **20** to form more electrophilic species phenyl selenium bromide **22**. Electrophilic selenium species **22** activates the double bond of styrene **15** to the three-membered seleniranium ion intermediate **23** along with the formation of bromide ion. Finally, intermediate **23** reacts with acetic acid to yield the final product **21** while the bromide ion was further oxidized to continue the catalytic cycle.

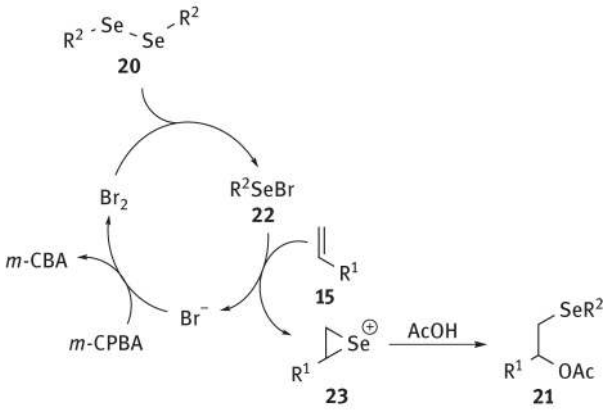


Figure 8: The catalytic cycle for KBr-catalyzed acetoxyselenylation of alkenes **15**.

In 2015, Braga and coworkers developed an iodine-catalyzed microwave-assisted methoxyselenenylation of alkenes **15** by the reaction of diorganyl diselenide **20**, catalytic amount of iodine in DMSO using methanol as source of nucleophile. All the reactions were completed in very short reaction time while reaction products **24** were isolated in poor-to-excellent yields (Figure 9) [17]. It was observed that methoxyselenenylated products **24** were obtained in high yields when diorganyl diselenides having electron-donating substituents were used. Various styrenes were successfully employed as substrates but the methoxyselenenylation of aliphatic alkenes was not successful. Molecular iodine reacts with diphenyl diselenide to form more electrophilic species PhSeI **17** which was used to activate the double bond of styrenes **15**. In addition, various other oxyselenenylations of alkenes were successfully achieved under similar reaction and conditions.

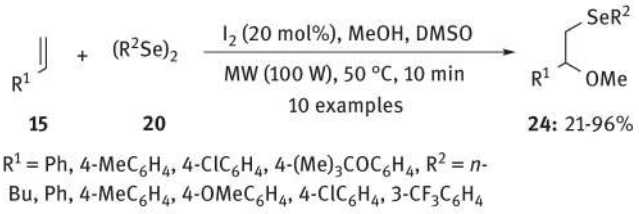


Figure 9: Iodine-catalyzed microwave-assisted methoxyselenenylation of alkenes **15**.

Recently, Yan and coworkers developed an iodine-mediated hydroxyselenenylation of alkenes **15** with the reaction of diorganyl diselenide **20** in the presence of molecular iodine in solvent mixture of EtOH and H_2O (1:1) under oxygen atmosphere. β-Hydroxyselenides **25** were isolated in good-to-excellent yields (Figure 10) [18]. Various electron withdrawing and donating functionalities at aromatic ring in styrenes were successfully tolerated under mild reaction conditions. The same approach was successfully applied for the hydroxyselenenylation of aliphatic and cyclic alkenes.

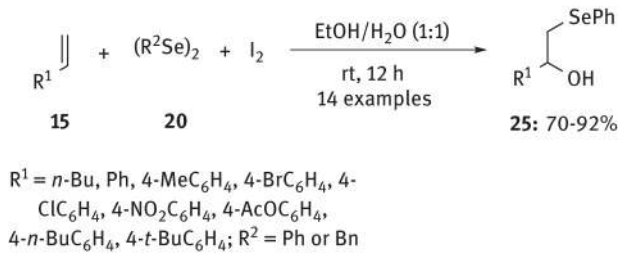


Figure 10: Iodine-mediated hydroxyselenenylation of styrenes **15** with diorganyl diselenide **20** in EtOH/H_2O (1:1).

The mechanism for the iodine-mediated hydroxyselenylation of alkenes **15** is shown in Figure 11. The reaction initiates with the formation of more electrophilic species phenyl selenium iodide **17** by the reaction of molecular iodine with diorganyl diselenide **20**. Electrophilic selenium species **22** activates the double bond of styrene **15** to form three-membered selenarium ion intermediate **27** along with the formation of iodide. Finally, intermediate **27** reacts with water to yield the product **25**.

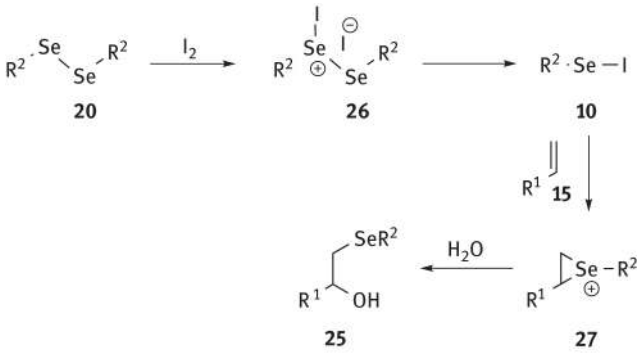


Figure 11: Mechanism for the iodine-mediated hydroxyselenenylation of styrenes **15** with diorganyl diselenide **20** in $EtOH/H_2O$ (1:1).

2.1.2 Selenocyclizations

Selenocyclization is an approach for the synthesis of various biologically active heterocyclic compounds (3f, 3g) [19]. The selenocyclization process is a quite similar process to oxyselenenylations of alkenes as shown in Figure 12. Initially, the selenium electrophile **29** activates the double bond of alkene **28** to form seleniranium intermediate **30**. Furthermore, seleniranium intermediate is then opened by an intramolecular nucleophilic attack of the internal nucleophile resulting in an *anti*-addition of the selenium moiety to yield cyclization product. Depending on ring size and reaction conditions, the seleniranium intermediate **30** can undergo either *endo*-cyclization to product **31** or *exo*-cyclizations yielding other heterocyclic derivatives such as compounds of type **32** (Figure 12). The selenium moiety in the products **31** and **32** can be used to develop selenium-catalyzed cyclization reactions.

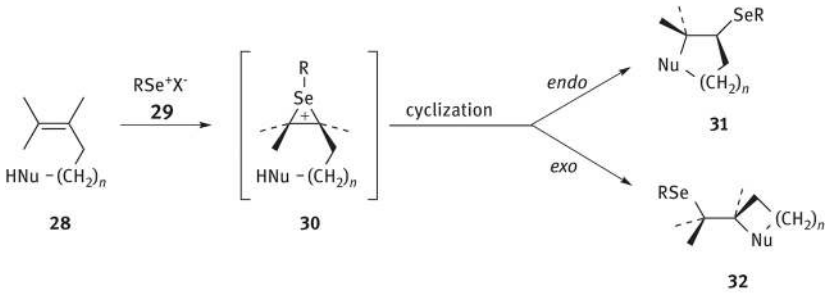


Figure 12: Selenocyclization of alkenes **28** to *endo*- and *exo*-cyclization products **31** and **32** using selenium electrophiles **29**.

Various selenium electrophiles have been successfully used to achieve the selenocyclization of alkenes having internal nucleophile. Initially, different benzene selenenyl sulfates were used as electrophiles to achieve the selenocyclization of unsaturated alcohols and unsaturated carboxylic acids under mild reaction conditions [20–22]. In 1991, benzeneselenenyl *m*-nitrobenzenesulfonate **3** was synthesized *in situ* and used in the selenocyclization of unsaturated alcohols **33** and **34** in acetonitrile at 0°C (Figure 13) [12]. Both reactions were completed in 1 h and *exo*-cyclic products **35** and **36** were isolated in excellent yields (Figure 13). Interestingly, *endo*-cyclic products were also observed during the selenocyclization of unsaturated alcohol **33** ($n = 1$) while *exo*-cyclic product **35** formed at −40°C.

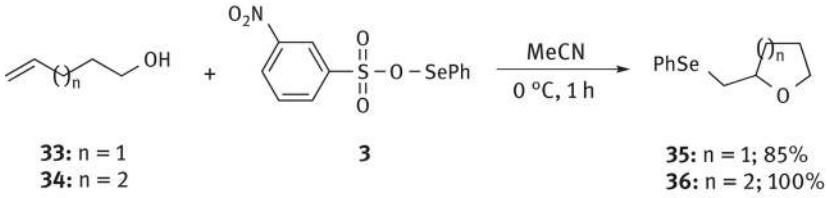


Figure 13: Selenocyclization of unsaturated alcohols **33** and **34** to *O*-heterocyclic compounds **35** and **36** using selenium electrophiles **3**.

Selenium electrophile **3** was also used for the selenocyclization of unsaturated carboxylic acids **37** and **38** in acetonitrile at 0°C (Figure 14) [12]. *exo*-Cyclizations were observed and selenolactones **39** and **40** were isolated in excellent yields (Figure 14). The *endo*-cyclic product was not observed during these selenocyclizations.

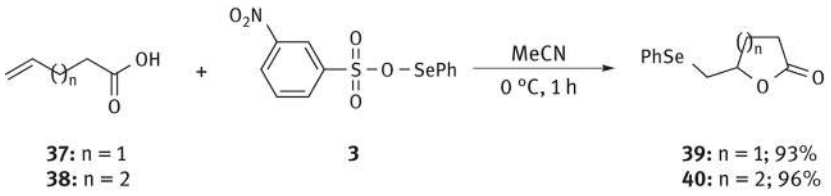


Figure 14: Selenocyclization of unsaturated carboxylic acids **37** and **38** to selenolactones **39** and **40** using selenium electrophile **3**.

In 1998, Tingoli and coworkers developed an approach for the selenocyclization of unsaturated alkenes **33** and **34** by the reaction of diphenyl diselenide **2** with PIDA **7** in acetonitrile (Figure 15). The cyclic products **35** and **36** were isolated in good yields. The electrophilic selenium species was generated *in situ* by the oxidation of diphenyl diselenide **2** using PIDA **7** as an oxidant [13].

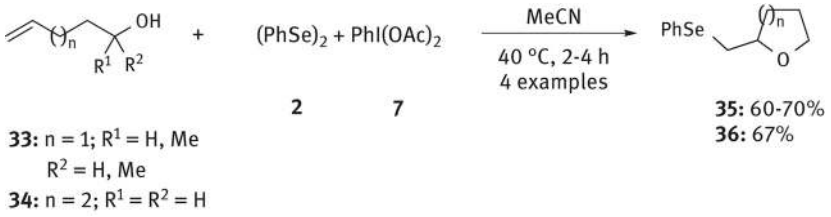


Figure 15: Iodine(III)-mediated selenocyclization of unsaturated alcohols **33** and **34** to selenoethers **35** and **36** by the reaction of diphenyl diselenide **2** with PIDA **7** as an oxidant.

In addition, similar reaction conditions were used for selenocyclization of unsaturated carboxylic acids **37** and **41** in acetonitrile at 40°C (Figure 16) [13]. Both cyclic and acyclic unsaturated carboxylic acids were successfully used as substrates but better yields were observed with acyclic substrates **37**.

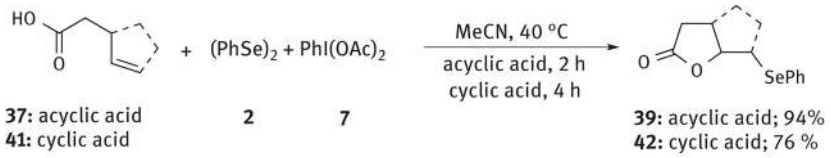


Figure 16: Iodine(III)-mediated selenocyclization of unsaturated carboxylic acids **37** and **41** to selenolactones **39** and **42** by the reaction of diphenyl diselenide **2** with PIDA **7** as an oxidant.

Functionalized ketones **43** and **44** were cyclized to corresponding 2,3-dihydrofurans **45** and **46** under similar reaction conditions. Both reactions proceeded well and 2,3-dihydrofurans **45** and **46** were isolated in moderate yields (Figure 17) [13].

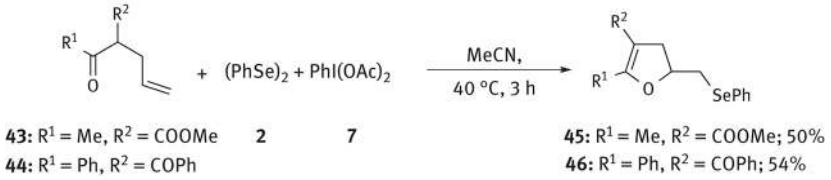


Figure 17: Iodine(III)-mediated selenocyclization of ketones **43** and **44** to 2,3-dihydrofurans **45** and **46**, respectively, by the reaction of diphenyl diselenide **2** with PIDA **7** as an oxidant.

Finally, substituted benzamide **47** was cyclized to the corresponding 4,5-dihydrooxazole **48** under similar reaction conditions. The product was isolated in 65 % yield (Figure 18) [13].

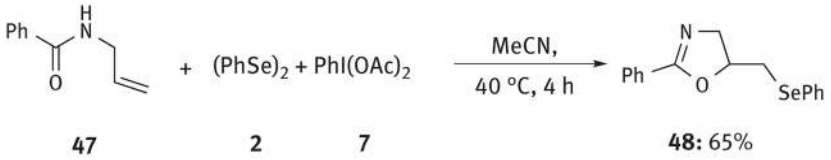


Figure 18: Iodine(III)-mediated selenocyclization of amide **47** to 4,5-dihydrooxazole derivative **48** by the reaction of diphenyl diselenide **2** with PIDA **7** as an oxidant.

In 2006, Tingoli and coworkers used another selenium electrophile NPSSac **12** for selenocyclization of unsaturated alcohol **33**. The cyclization reaction was performed in dichloromethane at room temperature for 1 h and cyclic ether **35** was isolated in 92 % yield (Figure 19) [14].

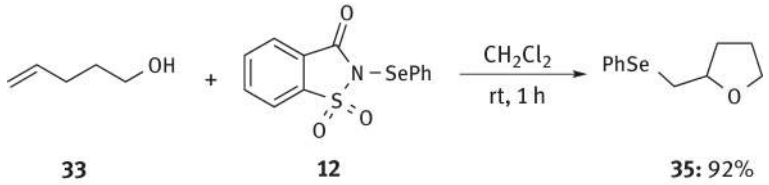


Figure 19: Selenocyclization of unsaturated alcohol **33** to cyclic ether **35** using *N*-phenylselenosaccharin (NPSSac) **12** as an electrophile.

In addition, a similar approach was used to cyclize the unsaturated carboxylic acid **37** to selenolactone **39** under similar reaction conditions. The selenolactone **39** was isolated in 89 % yield (Figure 20) [14].

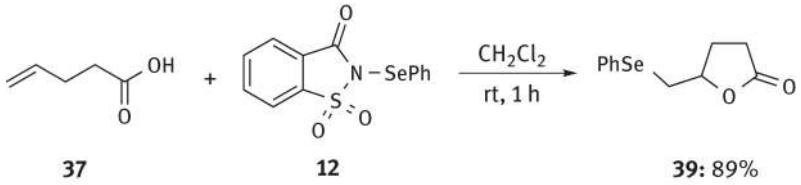


Figure 20: Selenocyclization of unsaturated carboxylic acid **37** to corresponding selenolactone **39** using *N*-phenyl selenosaccharin (NPSSac) **12** as an electrophile.

In 2010, Wirth and coworkers developed the intermolecular selenocyclization of alkene **15** and *in situ* aryl selenium triflate by the reaction of diselenide **49** and bromine followed by the addition of silver triflate in THF at 0°C (Figure 21) [23].

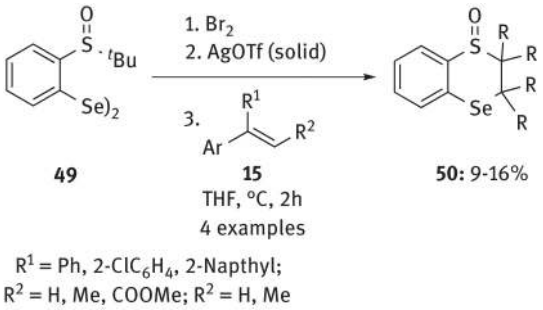


Figure 21: Intermolecular selenocyclization of alkenes **15** and electrophilic species aryl selenium triflate.

This reaction was performed without using any external nucleophile and the formation of cyclic product occurs by the activation of double bond to form selenarium ion followed by the cyclization involving sulfoxide moiety of the *in situ*-generated electrophile. The cyclic products **50** were only formed in poor yields (Figure 21). Notably, the cyclization reaction was proceeding only with α-substituted styrenes not with β-substituted styrenes [23].

In 2012, Menichetti and coworkers developed the synthesis of benzo[*b*][1,4]selenazines **52** by the reaction of 2-*N*-sulfonylamino diselenides **51** with alkene **15***via* copper(II)-catalyzed activation of the Se–Se bond in the presence of a base. All the reactions were performed in chloroform and benzo[*b*][1,4]selenazines **52** were isolated moderate-to-good yields (Figure 22) [24]. The course of reaction was quite slow and most of reactions were completed in 2–3 days.

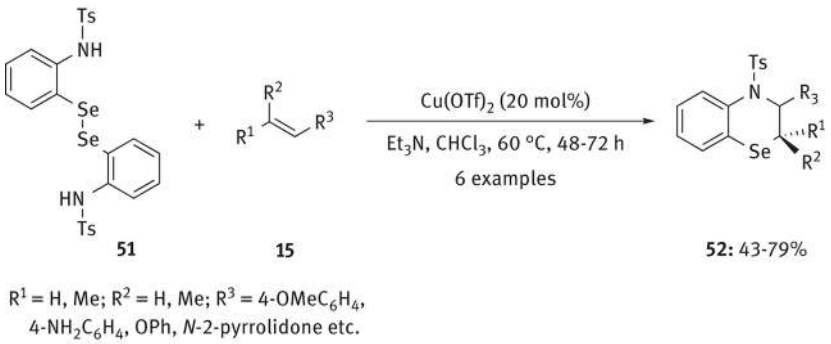


Figure 22: Cu(II)-catalyzed synthesis of benzo[*b*][1,4]selenazines **52** by the reaction of 2-*N*-sulfonylamino diselenides **51** with alkene **15**.

Additionally, similar cyclization reactions were performed with cyclic alkenes **53** and **54** under similar reaction conditions. The cyclic reaction was working well and Se-containing tricyclic compound **55** and **56** were isolated in 60 % and 59 % yield, respectively (Figure 23) [24].

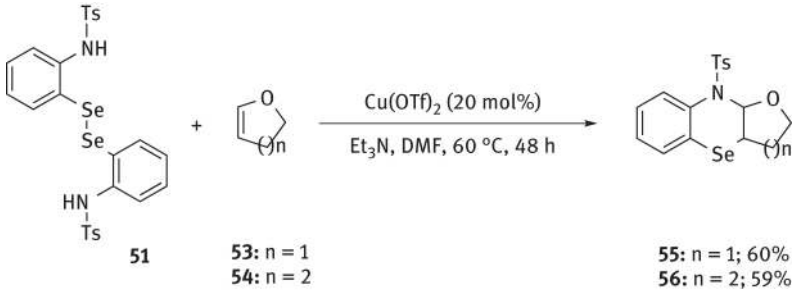


Figure 23: Cu(II)-catalyzed synthesis of Se-containing tricyclic compounds **55** and **56** by the reaction of 2-*N*-sulfonylamino diselenides **51** with cyclic alkenes **53** and **54**.

Furthermore, Viglianisi and coworkers synthesized various types of 2-*N*-sulfonylamino diselenides **57** having different electron-withdrawing and donating functionalities. The synthesized diselenides **57** were treated with 4-methoxystyrene using $Cu(OTf)_2$ as catalyst and triethyl amine as base in DMF. The reactions were completed in 1–10 days and benzo[*b*][1,4]selenazines **58** were isolated good-to-high yields (Figure 24) [25]. It was noted that the course of reaction was slow when diselenides with electron-withdrawing group was used in the aromatic ring in substrates. Recently, Supuran and coworkers reported the synthesis of benzo[*b*][1,4]selenazines of type **58** and identified as carbonic anhydrase inhibitors [26].

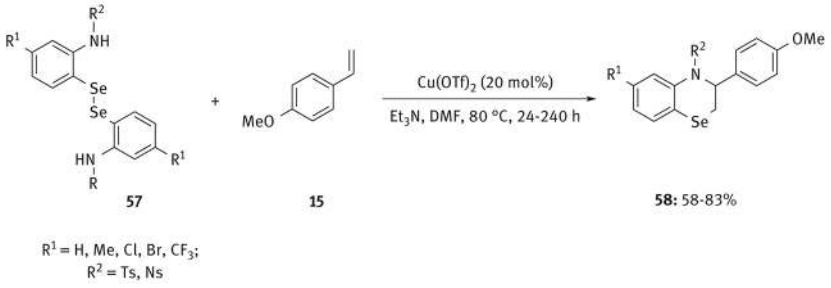


Figure 24: Cu(II)-catalyzed synthesis of benzo[*b*][1,4]selenazines **58** by the reaction of 2-*N*-sulfonylamino diselenides **57** with 4-methoxystyrene **15**.

The catalytic cycle for the synthesis of Se-containing heterocyclic compounds **52** by the reaction of diaryl diselenide **51** and alkenes **15** is shown in Figure 25 [25]. The catalytic cycle was initiated with the formation of intermediate **59** by reaction of $Cu(OTf)_2$ in the presence of a base. Intermediate **59** reacts with alkene **15** and forms selenarium ion intermediate **61** along with the formation of selenolate ion intermediate **60**. The seleniranium ion intermediate **61** converts into another intermediate **62**, which undergoes intramolecular cyclization to form the final product **52**. Finally, selenolate ion intermediate **60** was oxidized to diaryl diselenide **51** to restart the catalytic cycle.

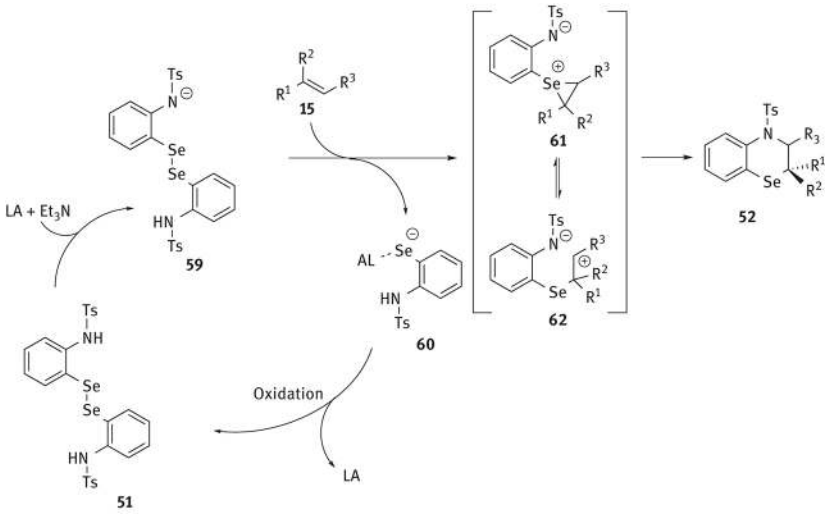


Figure 25: Cu(II)-catalyzed synthesis of benzo[*b*][1,4]selenazines **52** by the reaction of 2-*N*-sulfonylamino diselenides **51** with alkene **15**.

Furthermore, the synthesized benzo[*b*][1,4]selenazines **58** were treated with thioacetic acid and LiOH in dry DMF and a clean denosylation reaction was observed. The course of reaction was slightly slow once again but *N*-unsubstituted selenazines **63** were isolated in useful yields (Figure 26) [25].

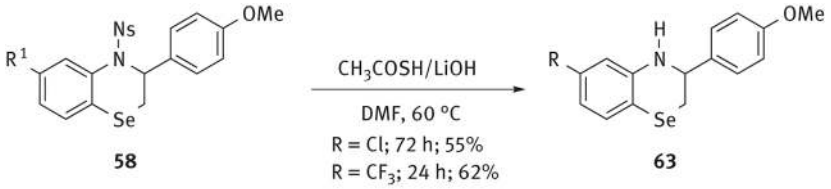


Figure 26: Denosylation of compound **58** with thioacetic acid and LiOH in DMF.

Recently, Wang and Bates used the selenocyclization approach for the synthesis of one intermediate during the total synthesis of naturally occurring compound allahabadolactone **A** [27].

2.2 Selenenylation of aliphatic C–H bonds

There are only few reports in which selenium electrophiles have been used for the selenenylation of aliphatic C–H bonds. In 2006, Tingoli and coworkers used selenium electrophile NPSSac **12** for the functionalization of 1-indanone **64** in the α-position. The reaction was performed in acetonitrile at room temperature for 20 h and reaction product **65** was isolated in 72 % yield (Figure 27) [14].

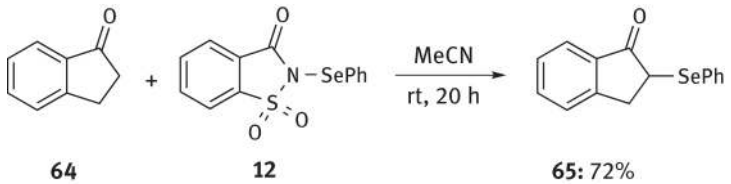


Figure 27: Functionalization of 1-indanone **64** at α-position using *N*-phenyl selenosaccharin (NPSSac) **12** as an electrophile.

A similar reaction was used for the functionalization of heptanal **66** in the α-position with selenium electrophile **12** and α-selenenylated heptanal **67** was isolated in 91 % yield (Figure 28) [14].

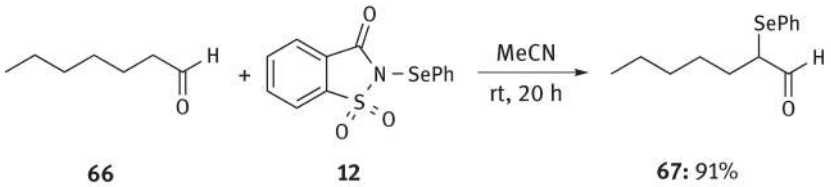


Figure 28: Functionalization of heptanal **66** at α-position using *N*-phenyl selenosaccharin (NPSSac) **12** as an electrophile.

Recently, Kumar and coworkers developed another approach for the α-functionalization of cyclic amides using diorganyl diselenide **20** and potassium *tert*-butoxide in DMSO at room temperature. The reaction products **69** were isolated in moderate to good yields (Figure 29) [28].

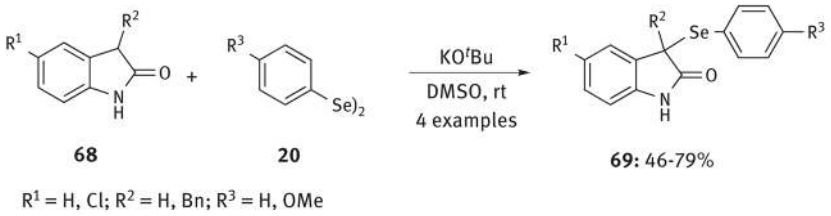


Figure 29: Functionalization of cyclic amides **68** in the α-position using diorganyl diselenide **20** and potassium *tert*-butoxide in DMSO.

In addition, acyclic amide **70** was used as a precursor under similar reaction conditions and reaction product **71** was isolated in 75 % yield (Figure 30). It was observed that the course of reaction was quite similar to cyclic amides [28].

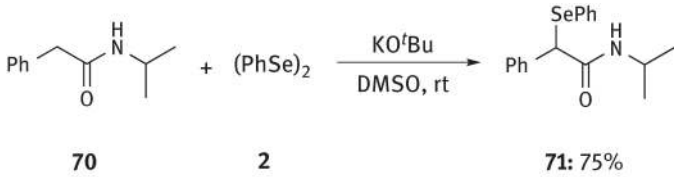


Figure 30: Functionalization of acyclic amides **70** at α-position using diphenyl diselenide **2** and potassium *tert*-butoxide in DMSO.

Furthermore, the reaction was performed for the functionalization of α-tetralone **72** at α-position but the expected reaction product **74** was not observed. The isolated product was characterized as 2-phenylselanyl-1-naphthol **73** by its spectroscopic analysis and obtained in 73 % yield (Figure 31) [28].

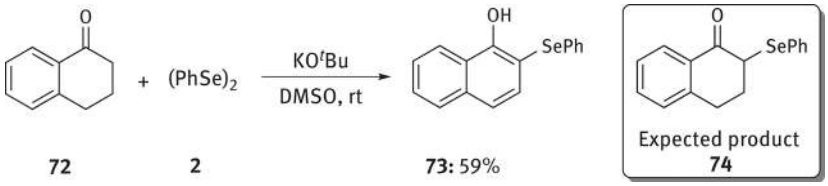


Figure 31: Conversion of α-tetralone **72** to 2-phenylselanyl-1-naphthol **73** using diphenyl diselenide **2** and potassium *tert*-butoxide in DMSO.

2.3 Selenenylation of aromatic C–H bonds

There are some 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.

2.3.1 Metal-mediated selenenylation of aromatic C–H bonds

2.3.1.1 Copper-mediated selenenylation of aromatic C–H bonds

In 1995, Kim and Lee developed an approach for the selenenylation of pyrimidones using diphenyl diselenide as source of electrophile and $Mn(OAc)_3$ as catalyst in DMSO but this approach suffered from poor reaction yields [29]. In 2014, Shibahara and coworkers reported Cu(I)-catalyzed selenenylation of 3-(4-methoxyphenyl)imidazo[1,5-*a*]pyridine **75** using diphenyl diselenide **2** as source for the electrophile and CuBr as catalyst in DMSO at 30°C. The selenenylated product phenylimidazopyridyl selenide **76** was obtained in quantitative yield (Figure 32) [30].

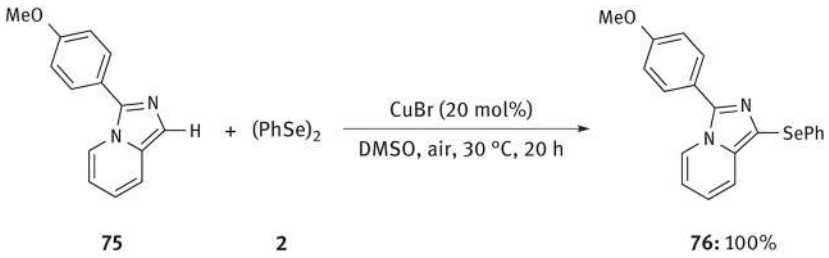


Figure 32: Cu(I)-catalyzed selenenylation of 3-(4-methoxyphenyl)imidazo[1,5-*a*]pyridine **75** using diphenyl diselenide **2** as an electrophile in DMSO.

In addition, a Cu(I)-catalyzed approach was used for the selenenylation of *N*-methylindole **77** under similar reaction conditions. The selenenylated product phenyl indolyl selenide **78** was isolated in 38 % yield (Figure 33) [30].

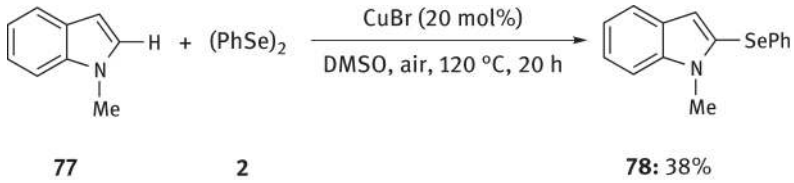


Figure 33: Cu(I)-catalyzed selenenylation of *N*-methylindole **77** using diphenyl diselenide **2** as an electrophile in DMSO.

Furthermore, a Cu(II)-mediated approach was developed for the selenenylation of quinolones [31]. In this approach, 8-aminoquinolones **79** were reacted with various diorganyl diselenides **20** using 1.5 equivalents of $CuBr_2$ in DMSO under oxygen atmosphere at 160°C leading to the corresponding diaryl selenides **80** in good yields (Figure 34) [31]. Various electron-donating and withdrawing groups at the aromatic ring in diselenide substrates were successfully tolerated in this reaction.

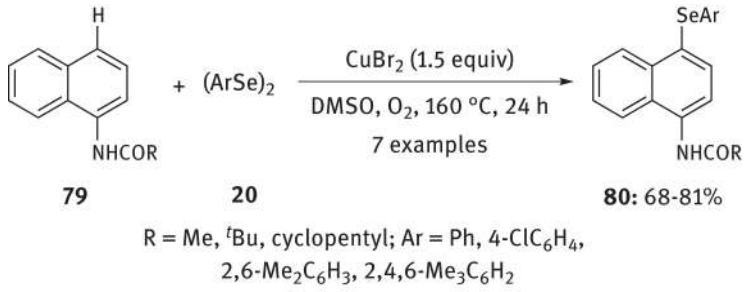


Figure 34: Cu(II)-mediated selenenylation of 8-aminoquinolones **79** to the corresponding diaryl selenides **80** using diorganyl diselenide **20** in DMSO.

In 2016, Baidya and coworkers developed another Cu(II)-mediated approach for the diselenenylation of benzamides **81** using diorganyl diselenide **20** and $Cu(OAc)_2$ in DMSO at 80°C. The reaction products **82** were isolated in moderate-to-good yields (Figure 35) [32]. Various electron-donating and withdrawing groups on aromatic ring in substrates **81** were tolerated in this reaction.

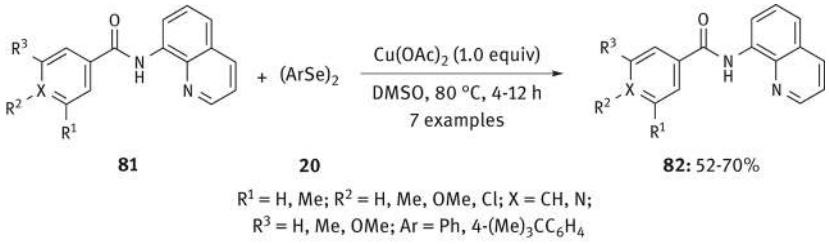


Figure 35: Cu(II)-mediated diselenenylation of benzamides **81** using diorganyl diselenides **20** and $Cu(OAc)_2$ in DMSO.

In addition, *N*-(quinolin-8-yl)thiophene-2-carboxamide **83** was treated with diorganyl diselenides **20** under similar reaction conditions. The selenenylation of the thiophene functionality was observed at C-3 position and reaction products **84** were isolated in moderate-to-excellent yields (Figure 36) [32]. The selenenylation reaction was working well with diaryl diselenides having both electron-donating and withdrawing groups at the aromatic ring but better yields were obtained with diorganyl diselenides having electron-donating functionalities.

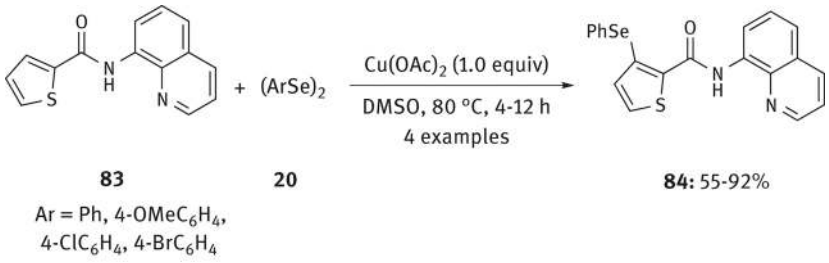


Figure 36: Cu(II)-mediated diselenenylation of *N*-(quinolin-8-yl)thiophene-2-carboxamide **83** using diorganyl diselenides **20** and $Cu(OAc)_2$ in DMSO.

The catalytic version of the same selenenylation reaction was developed by reacting benzamides **81** with diselenide **20** using $Cu(OAc)_2$ as catalyst and KF as an additive in the presence of silver carbonate in DMSO. The reaction products **82** were isolated in moderate-to-good yields (Figure 37) [32]. Silver carbonate served as an oxidant to reoxidize the Cu(I) to the Cu(II) species. Substrates **81** bearing various electron-donating and withdrawing groups on phenyl, pyridyl and quinoline rings were successfully used in this catalytic reaction.

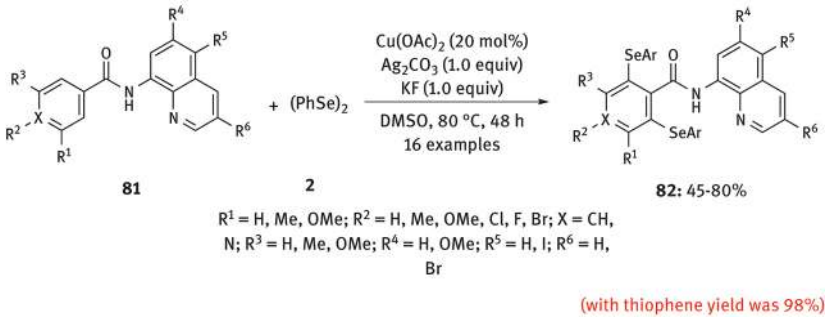


Figure 37: Cu(II)-catalyzed mono-/diselenenylation of benzamides **81** using diphenyl diselenides **2** and catalytic amounts of $Cu(OAc)_2$ in DMSO.

2.3.1.2 Palladium-mediated selenenylation of aromatic C–H bonds

Recently, some selenium electrophiles have been successfully used to achieve selenenylation of aromatic species in the presence of palladium catalysts. In 2015, Law and others developed a Pd-catalyzed approach for the selenenylation of arenes **85** using *N*-PSP **86** in the presence of 10 mol% of $[PdCl_2(MeCN)_2]$ **87** in water at 110°C. Unsymmetrical diaryl selenides **88** were isolated in poor-to-excellent yields (Figure 38) [33]. In addition, diselenenylated products **89** were isolated in reactions with up to 29 % yield (Figure 38) [33].

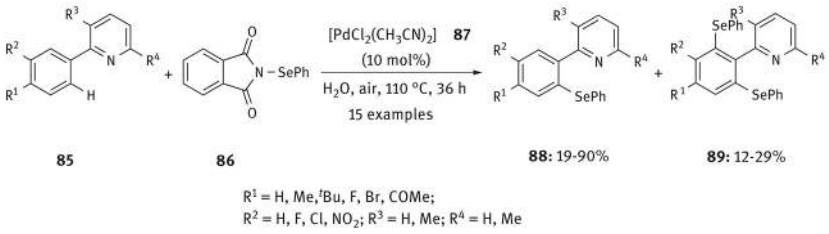


Figure 38: Pd-catalyzed mono-/diselenenylation of arenes **85** using *N*-(phenylseleno)phthalimide (*N*-PSP) **86** and 10 mol% of $[PdCl_2(MeCN)_2]$ **87**.

The same research group developed a Pd-catalyzed approach for the mono- or diselenenylation of arenes selectively using *N*-PSP **86**. Monoselenenylation of arenes **85** was achieved by the reaction with selenium electrophile *N*-PSP **86** in the presence of 10 mol% $[PdCl_2(CH_3CN)_2]$ **87** in DMSO:H_2O (1:1) at 100 C. The reaction products **88** were isolated in good-to-excellent yields (Figure 39). Additionally, diselenenylation of similar arenes **85** was achieved in excellent yields by using electrophilic species **86** and catalyst **87** in a similar solvent combination DMSO:H_2O in a different ratio (4:1) (Figure 39) [34].

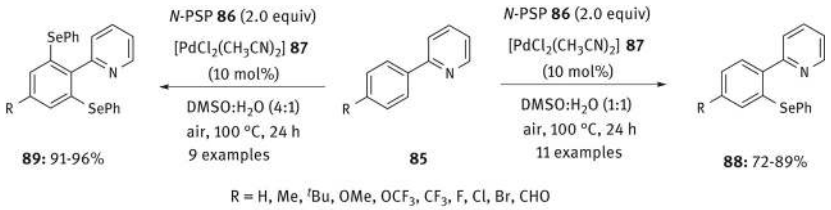


Figure 39: Pd-catalyzed mono-/diselenenylation of arenes **85** using *N*-(phenylseleno)phthalimide (*N*-PSP) **86** and 10 mol% of $[PdCl_2(MeCN)_2]$ **87**.

2.3.1.3 Iridium-mediated selenenylation of aromatic C–H bonds

Recently, Liu and coworkers reported a selenenylation of (hetero)arenes **90** by the reaction with diorganyl diselenide **20** using 2.0 mol% of FlrPic **91** as catalyst in the presence of visible light in acetonitrile under open atmosphere. Unsymmetrical diaryl selenides **92** were isolated (Figure 40) [35]. Various electron-donating and withdrawing substituents are tolerated in both, (hetero)arene and diorganyl diselenide substrates.

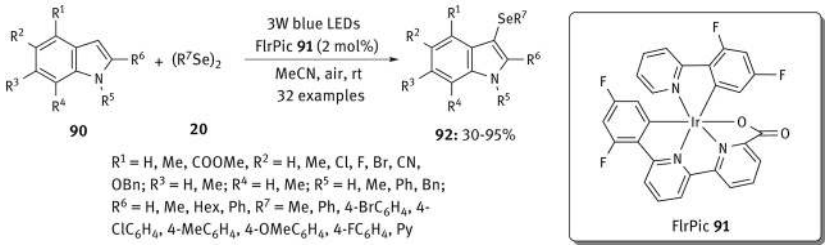


Figure 40: Ir-catalyzed selenenylation of (hetero)arenes **90** using diorganyl diselenides **20** and 2 mol% of FlrPic **91**.

2.3.2 Metal-free selenenylation of aromatic C–H bonds

In 1991, Yoshshida and coworkers developed a metal-free selenenylation of aromatic species using benzeneselenenyl *m*-nitrobenzenesulfonate **3** as selenium electrophile [12]. In 2006, Tingoli and coworkers developed another metal-free reaction for the selenenylation of electron-rich arenes **93a** and **93b** using selenium electrophile NPSSac **12** in acetonitrile at room temperature. The reaction products **94a** and **94b** were isolated in 80 % and 87 % yield, respectively (Figure 41) [14].

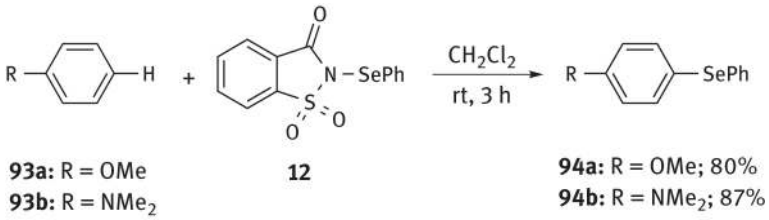


Figure 41: Metal-free selenenylation of electron-rich arenes **93a** and **93b** using *N*-phenylselenosaccharin (NPSSac) **12** as an electrophile in acetonitrile.

In 2016, Braga and coworkers reported a molecular iodine-catalyzed selenenylation of imidazo[1,2-*a*]pyridines **95** using diorganyl diselenides **20** as source of electrophile and DMSO as an oxidant under solvent-free conditions. The selenenylation of substrates **95** occurred at the C-3 position selectively and unsymmetrical diaryl selenides **96** were obtained in high yields (Figure 42) [36]. Various electron-donating and withdrawing substituents are tolerated in arene and diorganyl diselenide substrates. Additionally, dibutyl diselenide was also used successfully as source of electrophile in this reaction.

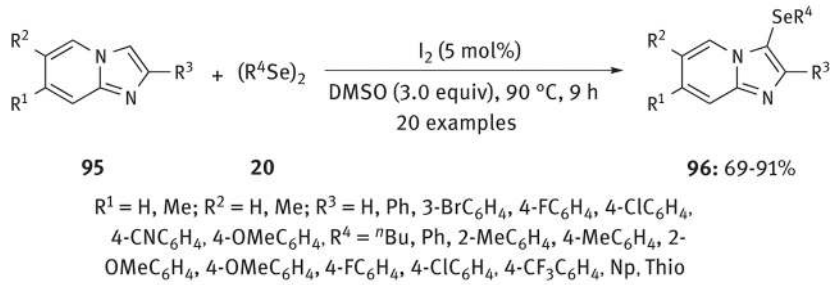


Figure 42: Iodine-catalyzed selenenylation of imidazo[1,2-*a*]pyridines **95** using diorganyl diselenides **20** as source of electrophile and DMSO as an oxidant.

Recently, another metal-free approach for the selenenylation of chromones **97** was developed by the reaction with diorganyl diselenide **20** and ammonium iodide in DMF at 135°C under open atmosphere [37].

The selenenylation of chromones **97** takes place at the C-3 position selectively and unsymmetrical diaryl selenides **98** are obtained in moderate-to-good yields (Figure 43) [37]. The selenenylation reaction was proceeding well when electron-donating and withdrawing substituents were used in both arene and diaryl diselenide substrates.

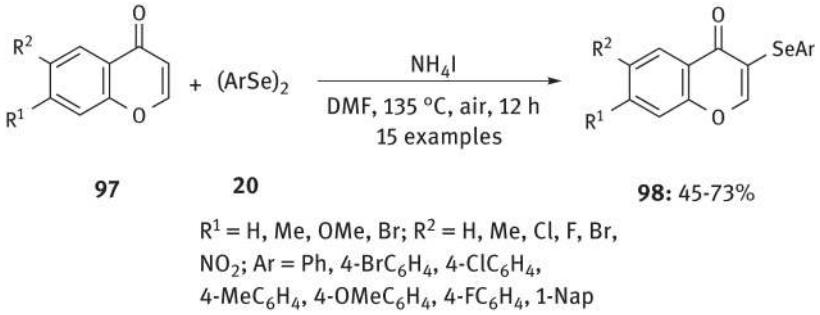


Figure 43: Ammonium iodide-mediated selenenylation of chromones **97** by the reaction with diorganyl diselenide **20** and ammonium iodide in DMF.

Additionally, the same approach was used for the selenenylation of quinolone **99** under similar reaction and conditions. Similar to chromones, the selenenylation of quinolone **99** occurred selectively at the C-3 position and 3-(phenylselanyl)quinolin-4(1*H*)-one **100** was isolated in 53 % yield (Figure 44) [37].

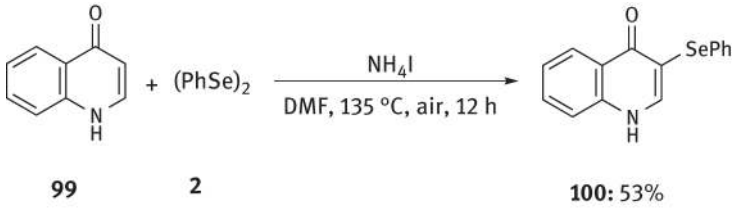


Figure 44: Ammonium iodide-mediated selenenylation of quinolone **99** by the reaction with diphenyl diselenide **2** and ammonium iodide in DMF.

2.4 Cyclizations

2.4.1 Metal-free cyclizations

Selenium electrophiles have been used to achieve various cyclization reactions with or without transition metals. In 2009, Amosova and coworkers reported the synthesis of the cyclic compound 2,6-dichloro-1,4-thiaselenane **103** in quantitative yield by the reaction of divinyl sulfide **101** with selenium dichloride **102** in chloroform at –50°C without using any metal salt (Figure 45) [38]. In addition, the synthesized compound **103** was further used as substrate for the synthesis of other selenium-containing heterocycles.

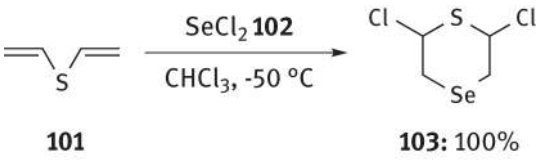


Figure 45: Synthesis of 2,6-dichloro-1,4-thiaselenane **103** by the reaction of divinyl sulfide **101** with selenium dichloride **102**.

2.4.2 Metal-mediated cyclizations

2.4.2.1 Iron-mediated cyclizations

Other cyclization reactions have been achieved using selenium electrophiles in the presence of transition metals in either stoichiometric or catalytic amounts. In 2015, Zeni and coworkers developed an Fe(III)-mediated approach for the cyclization of functionalized 1,3-diynes **104** by the reaction of two equivalents of dibutyl diselenide **20** and 1.5 equivalents of $FeCl_3$ in dichloromethane at 40°C. The isolated products were characterized as selenophenes **105** and obtained in moderate-to-good yields (Figure 46) [39]. This approach was used to prepare of various symmetrical and unsymmetrical selenophenes using easily accessible precursors.

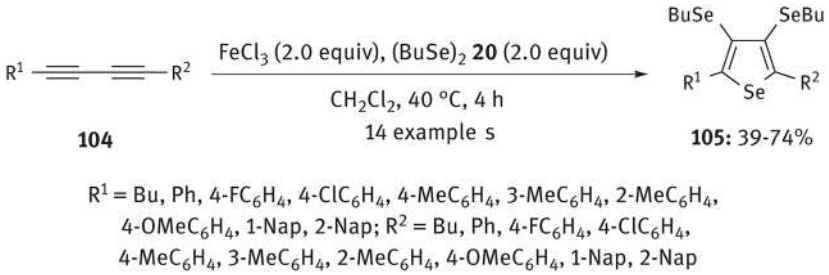


Figure 46: The cyclization of functionalized 1,3-diynes **104** to selenophenes **105** by the reaction of dibutyl diselenide **20** and $FeCl_3$ in dichloromethane.

The same research group developed another Fe(III)-mediated approach for the cyclization of functionalized *o*-alkynylbenzamides **106** by the reaction of 0.5 equivalents of diorganyl diselenide **20** and 2.0 equivalents of $FeCl_3$ in dichloromethane at room temperature under oxygen atmosphere. The cyclic products 4-(phenylselanyl)-1*H*-isochromen-1-imines **107** were isolated in moderate-to-good yields as major reaction products (Figure 47) [40]. In some reactions, functionalized isobenzofuran-1(3*H*)-imines **108** were observed as minor reaction products.

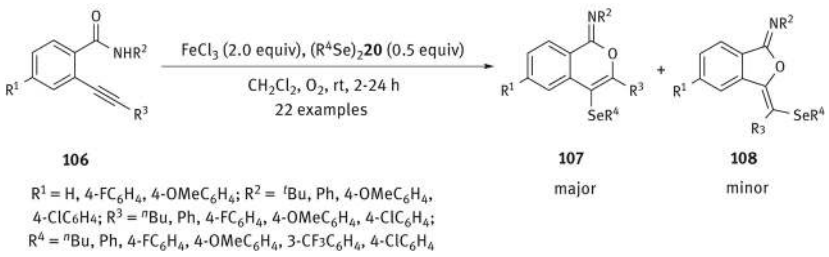


Figure 47: The cyclization of functionalized *o*-alkynylbenzamides **106** by the reaction of diorganyl diselenide **20** and $FeCl_3$ in dichloromethane.

Furthermore, a similar reagent combination (diorganyl diselenide **20** and $FeCl_3$) was used to achieve the aminocyclization of functionalized 2-aminophenylprop-1-yn-3-ols **109** in dichloromethane at 40°C. The cyclic products, 3-organoseleno-substituted quinolines **110**, were isolated in poor-to-good yields (Figure 48) [41]. The cyclization is proceeding well when electron-donating and withdrawing substituents were used in both arene and diorganyl diselenide substrates.

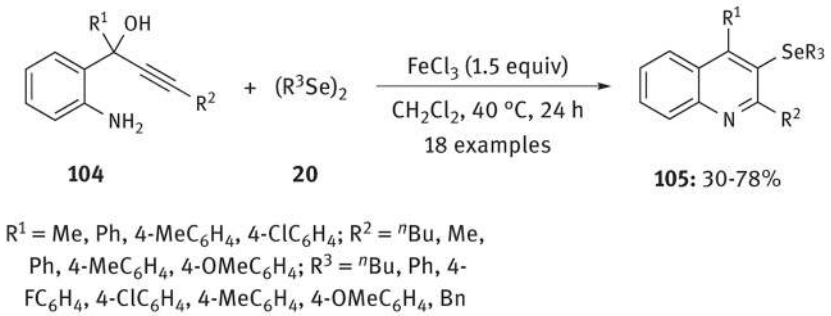


Figure 48: The cyclization of functionalized 2-aminophenylprop-1-yn-3-ols **109** to 3-organoseleno-substituted quinolines **110** by the reaction of diorganyl diselenides **20** and $FeCl_3$ in dichloromethane.

Recently, Zeni and coworkers used a similar reagent combination (diorganyl diselenide **20** and $FeCl_3$) to achieve the carbocyclization of benzylic-substituted propargyl alcohols **111** in dichloroethane (DCE) at 70°C under oxygen atmosphere. The cyclic products 2-organoselenyl-naphthalenes **112** were obtained in moderate-to-excellent yields (Figure 49) [42]. Various electron-donating and withdrawing substituents were successfully tolerated in both alcohol and diorganyl diselenide substrates.

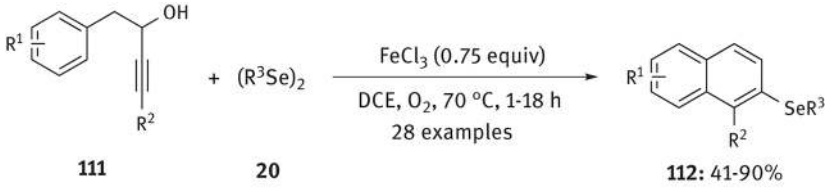


Figure 49: The cyclization of benzylic-substituted propargyl alcohols **111** to 2-organoselenyl-naphthalenes **112** by the reaction of diorganyl diselenides **20** and $FeCl_3$ in DCE.

In 2016, Zeni and coworkers developed an Fe(III)-mediated cyclization of 1,3-diynyl chalcogen derivatives **113** with diorganyl diselenides **20** and $FeCl_3{\cdot}6H_2O$ in dichloromethane at reflux temperature. The cyclic products benzo[*b*]furan-fused selenophenes (**114**: X=O) were isolated in moderate-to-excellent yields (Figure 50) [43]. In addition, the synthesis of benzo[*b*]thiophene-fused selenophenes (**114**: X=S) or benzo[*b*]seleno-fused selenophenes (**114**: X=Se) was also achieved using a similar approach.

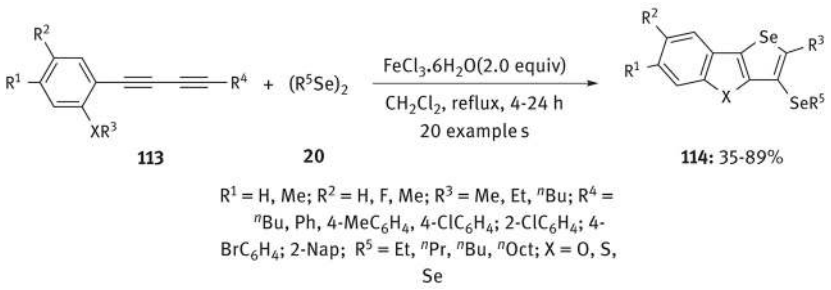


Figure 50: The cyclization of 1,3-diynyl chalcogen derivatives **113** to benzo[*b*]chalcogen-fused selenophenes **114** by the reaction of diorganyl diselenides **20** and $FeCl_3$ in dichloromethane.

Another Fe(III)-catalyzed approach was developed by Zeni and coworkers for the cyclization of 1,4-butynediols **115** with diorganyl diselenides **20** using 20 mol% of $FeCl_3{\cdot}6H_2O$ in DCE at room temperature under oxygen atmosphere. The 3,4-bis(organoselanyl)-2,5-dihydrofuran products **116** were isolated in poor-to-excellent yield (Figure 51) [44]. In addition, the same catalytic approach was also applied to the synthesis of 3,6-dihydro-2*H*-pyrans and 2,5-dihydro-1*H*-pyrroles.

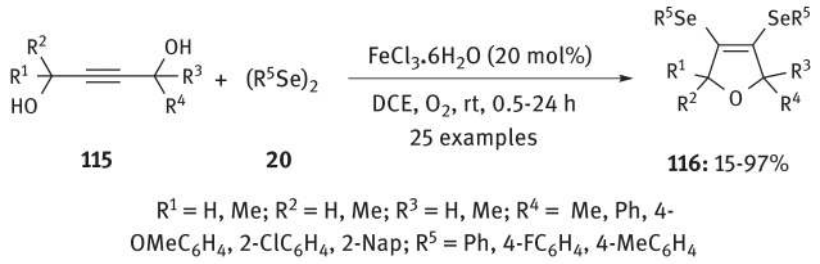


Figure 51: Fe(III)-catalyzed cyclization of 1,4-butyne-diols **115** to 3,4-bis(organoselanyl)-2,5-dihydrofurans **116**.

2.4.2.2 Copper-mediated cyclizations

Recently, Zeni and coworkers reported a Cu(I)-catalyzed approach for the cyclization of functionalized propargylpyridines **117** with diorganyl diselenides **20** using 20 mol% of KI in the presence of Na_2CO_3 base in DMF at 60 C. The functionalized 2-(phenylselanyl)indolizines **118** were isolated in poor-to-excellent yields (Figure 52) [45]. Various electron-donating and withdrawing substituents are tolerated in both alcohol and diorganyl diselenide substrates. In addition, a similar cyclization reaction was investigated with dibutyl diselenide **20** (R=^{n}Bu) as source of electrophile but no cyclization could be observed.

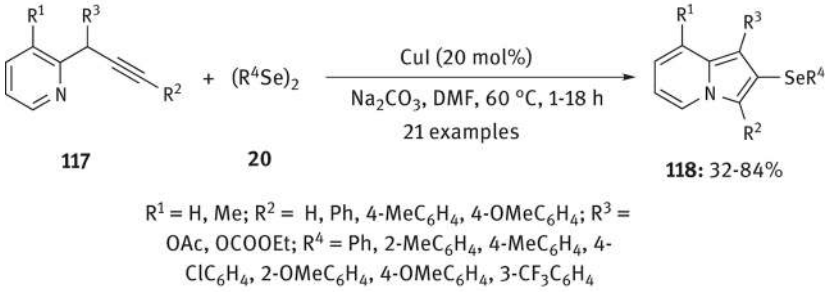


Figure 52: Cu(I)-catalyzed cyclization of functionalized propargylpyridines **117** to 2-(phenylselanyl)indolizines **118**.

2.4.2.3 Lewis acid-mediated cyclizations

In 2009, Shahzad and Wirth developed an approach for the carbocyclization of stilbenes **119** to dihydronaphthalenes **120** with the combination of a Lewis acid and phenylselenenyl chloride. The cyclic products **120** were isolated in good-to-excellent yields (Figure 53) [46]. Both $SnCl_4$ and $BF_3{\cdot}OMe_2$ can be used as Lewis acid in this reaction but cyclic product **120** was obtained in higher yields with $BF_3{\cdot}OMe_2$.

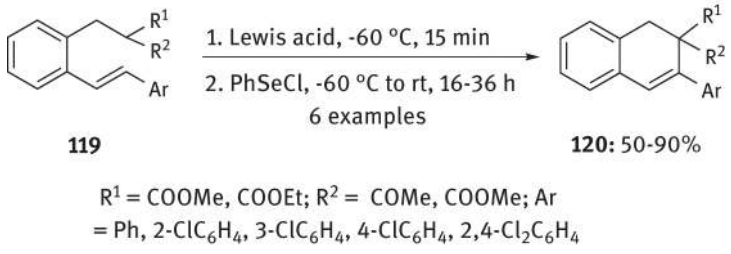


Figure 53: Selenium-mediated approach for the carbocyclization of stilbenes **119** to dihydronaphthalenes **120**.

In addition, the double carbocyclization of stilbenes **121** was achieved by using the combination of the Lewis acid $BF_3{\cdot}Me_2$ and phenylselenenyl chloride under similar reaction conditions. The cyclic products benzo[*b*]fluorenes **122** were isolated in reasonable yields (Figure 54) [46].

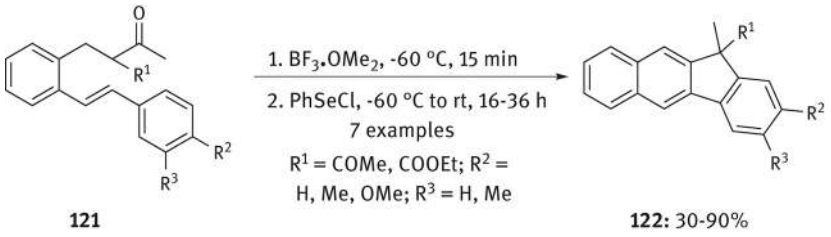


Figure 54: Selenium-mediated approach for the double carbocyclization of stilbenes **121** to benzo[*b*]fluorenes **122**.

2.5 Metal-catalyzed coupling reactions

Metal-catalyzed coupling reactions of organonucleophilic species with selenium electrophiles have been used to construct new C–Se bonds. The synthesis of various symmetrical and unsymmetrical diorganoselenides has been achieved using these coupling reactions.

2.5.1 Copper-catalyzed coupling reactions

In 2007, Taniguchi reported a Cu(I)-catalyzed coupling reaction of diorganyl diselenides **20** with alkyl- or arylboronic acids **123** using 5.0 mol% of CuI–bpy (1:1) in DMSO:H_2O (2:1) at 100°C under oxygen atmosphere. Symmetrical and unsymmetrical selenides **124** were isolated in good-to-excellent yields (Figure 55) [47]. In this reaction, organoboronic acid and diorganyl diselenide species were used as nucleophilic and electrophilic partners, respectively. Various electron-donating and withdrawing functionalities are tolerated at the aromatic ring of the organoboronic acid substrates.

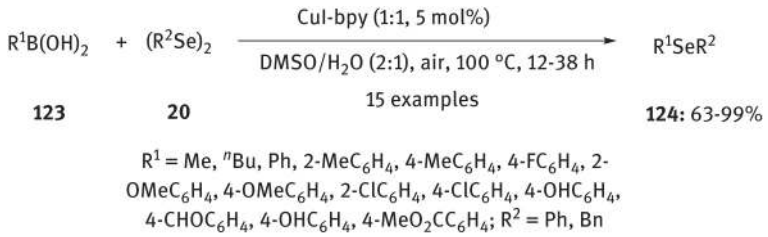


Figure 55: Cu(I)-catalyzed coupling reaction of diorganyl diselenides **20** with alkyl- or arylboronic acids **123** using 5 mol% of CuI–bpy (1:1) in DMSO:H_2O (2:1).

CuO nanoparticles (CuO Nps) have been used to catalyze similar coupling reactions of diorganyl diselenides **20** and arylboronic acids **123**. The coupling reaction of substrates **20** and **123** was performed in DMSO using 3 mol% CuO Nps at 100°C under open atmosphere. Symmetrical and unsymmetrical diaryl selenides **124** were isolated in excellent yields (Figure 56) [48]. Various electron-donating and withdrawing functionalities are acceptable in both substrates, the organoboronic acid and the diorganyl diselenides. This approach was advantageous over other catalytic approaches because the catalyst can be easily recovered and reused with almost similar catalytic efficacy.

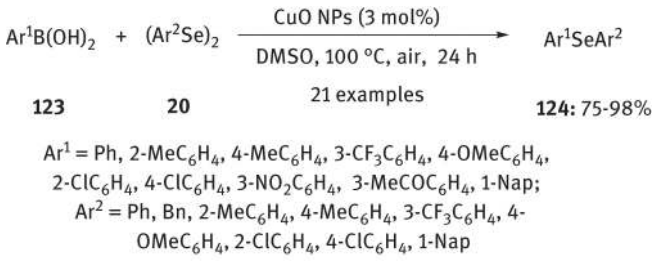


Figure 56: CuO nanoparticle-catalyzed coupling reaction of diorganyl diselenides **20** with arylboronic acids **123** using 3 mol% of CuO Nps in DMSO.

In 2012, Alves and others reported a CuI-catalyzed coupling reaction of diaryl diselenides **20** with arylboronic acids **123** using CuI as catalyst and DMSO as an additive in glycerol at 100°C under oxygen atmosphere. Diaryl selenides **124** bearing electron-donating and withdrawing group were obtained in good-to-excellent yields (Figure 57) [49]. Various substituents are tolerated on the aromatic ring in organoboronic acid substrates. Additionally, the glycerol–CuI mixture was reused in the cross-coupling reactions.

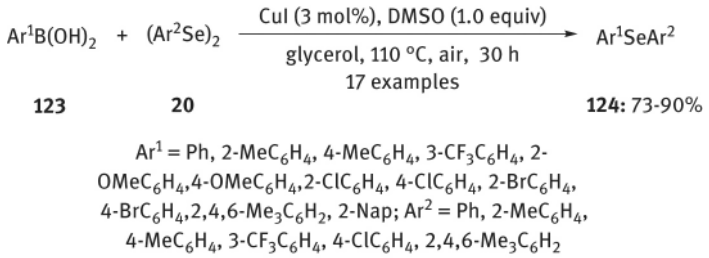


Figure 57: Cu(I)-catalyzed coupling reaction of diaryl diselenides **20** with arylboronic acids **123** using 3.0 mol% of CuI in glycerol.

In 2013, Xu and coworkers developed an efficient catalytic approach for the coupling of diphenyl diselenide **2** with arylboronic acids **123** using 3 mol% of $CuSO_4$ and 3 mol% of 1,10-Phen·H_2O in the presence of sodium carbonate in ethanol at 100°C under open atmosphere. Diaryl selenides **124** bearing electron-donating or -withdrawing groups were obtained in good-to-excellent yields (Figure 58) [50].

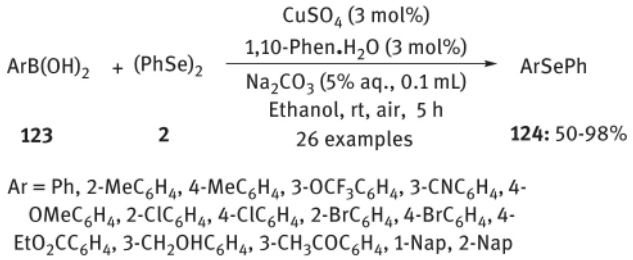


Figure 58: Cu(II)-catalyzed coupling reaction of diphenyl diselenide **2** with arylboronic acids **123** using 3 mol% of each $CuSO_4$ and 1,10-Phen·H_2O in ethanol.

2.5.2 Iron-catalyzed coupling reactions

In 2009, Wang and coworkers developed coupling reactions of diorganyl diselenides **20** and arylboronic acids **123** using 10 mol% of Fe powder in DMSO at 130°C. Symmetrical and unsymmetrical aryl selenides **124** were obtained in high yields (Figure 59) [51]. In addition, dibutyl diselenide **20** (R=Bu) was also used successfully in this reaction but coupling products were isolated in lower yields in the comparison with diaryl diselenides. Various electron-donating and withdrawing functionalities are tolerated in both substrates organoboronic acid and diaryl diselenide.

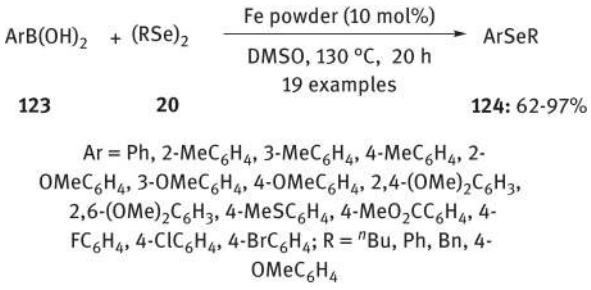


Figure 59: Fe(0)-catalyzed coupling reaction of diorganyl diselenides **20** with arylboronic acids **123** using 10 mol% of Fe powder in DMSO at 130°C.

2.5.3 Indium-catalyzed coupling reactions

An $InBr_3$-catalyzed approach for the coupling of diorganyl diselenides **20** and arylboronic acids **123** has been reported using 10 mol% of $InBr_3$ in DMSO at 130°C. Symmetrical and unsymmetrical diaryl selenides **124** were obtained in high yields (Figure 60) [52]. Additionally, dibutyl diselenide **20** (R=Bu) was also used successfully in this reaction but coupling product was isolated comparatively in low yield.

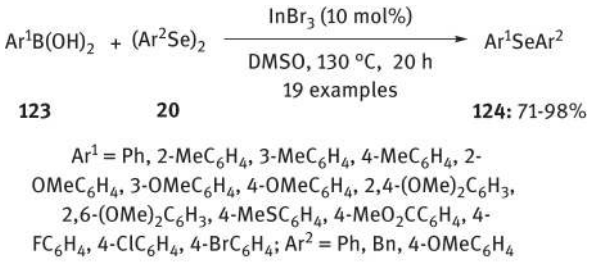


Figure 60: $InBr_3$-catalyzed coupling reaction of diorganyl diselenides **20** with arylboronic acids **123** using 10 mol% of $InBr_3$ in DMSO at 130°C.

2.5.4 Silver-catalyzed coupling reactions

In 2016, Alves and coworkers achieved the same coupling reaction of diorganyl diselenides **20** and arylboronic acids **123** using 10 mol% of $AgNO_3$ in DMSO at 130 °C. The coupling products **124** were isolated in moderate-to-excellent yields (Figure 61) [53]. This catalytic approach was equally working with both electron-withdrawing and donating substituents at the aromatic ring in both substrates.

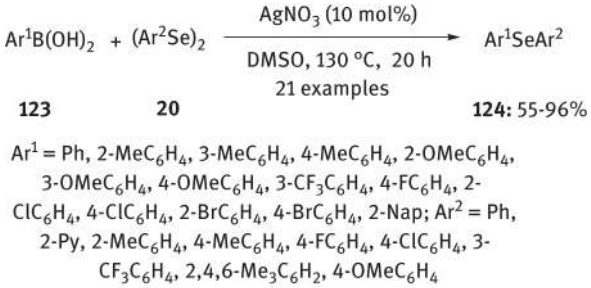


Figure 61: Ag(I)-catalyzed coupling reaction of diorganyl diselenides **20** with arylboronic acids **123** using 10 mol% of $AgNO_3$ in DMSO at 130°C.

2.5.5 Coupling reactions using ionic liquids

In 2011, the same research group achieved a coupling reaction of aryl selenenyl chlorides **125** and arylboronic acids **123** in ionic liquids [54]. The coupling of aryl selenenyl chlorides **125** and arylboronic acids **123** was performed in imidazolium ionic liquid [bmim][PF_6] without using any metal catalyst. Unsymmetrical and symmetrical diorganyl selenides **124** were isolated in moderate-to-excellent yields (Figure 62) [54]. Other imidazolium ionic liquids such as [bmim][BF_4] and [bmim][NTf_2] were used but lower yields of coupling products **124** were obtained in comparison with [bmim][PF_6]. The coupling reaction was working well with both alkyl- and aryl selenyl chlorides. In addition, aryl selenyl bromides can be used as electrophilic substrates under similar reaction conditions.

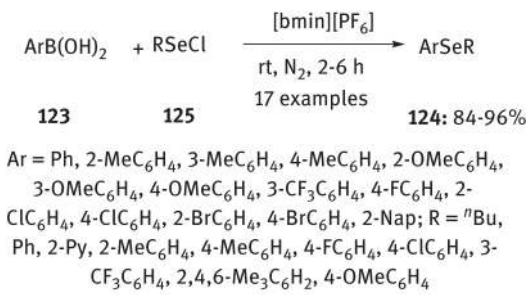


Figure 62: Synthesis of diorganyl selenides **124** by the coupling of aryl selenenyl chlorides **125** with arylboronic acids **123** in ionic liquid.

2.6 Carbene insertion reaction

In 2016, Arunprasatha and Sekar reported a metal-free approach for carbene insertion in Se–Se bonds [55]. In this report, *N*-tosylbenzylidenehydrazines **126** were treated with diphenyl diselenide **2** in the presence of potassium *tert*-butoxide in DMSO at 100°C. The carbene insertion reaction proceeded well and bis(phenylseleno)acetals **127** were isolated in good yields (Figure 63) [55]. In addition, a similar approach was applied for the carbene insertion in S–S bonds where thioacetals were obtained as reaction products. It was noted that the course reaction was quite similar when both electron-withdrawing and donating groups were used at the aromatic ring in substrates **126**.

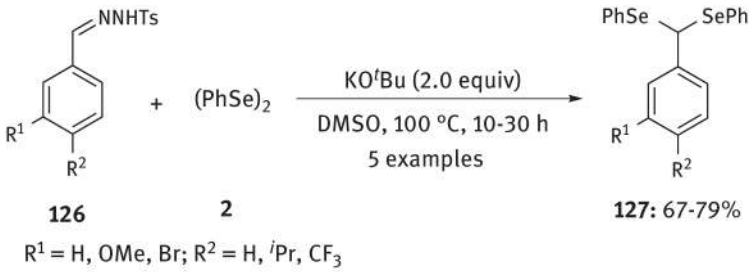


Figure 63: Metal-free and base-mediated approach for carbene insertion in Se–Se bonds.

2.7 Rearrangements

In 2010, Wirth and coworkers developed a new approach for the cyclization of stilbenes **128** (R=Ar) having β-keto ester functionality using phenyl selenenyl chloride in the presence of the Lewis acid $FeCl_3$. The cyclic products were obtained with a 1,2-migration of the aryl group and rearranged 1-naphthols **129** were isolated in good yields (Figure 64) [56]. Interestingly, the cyclization reaction could not proceed under similar conditions when electron-donating moieties at the benzene ring in stilbene **128** (R=4-MeO-C_6H_4) were used. The cyclization of stilbene **128** (R=4-MeO-C_6H_4) was achieved by the reaction with *in situ* generated more reactive selenium electrophilic species phenyl selenenyl trifluoracetate by the reaction of bis(trifluoroacetoxy)iodobenzene with stoichiometric amounts of diphenyl diselenide. In addition, styrene **128** (R=Me) was also used as substrate and the mixture of cyclic product with 1,2-methyl migration **130** (R=Me) and without migration **129** (R=Me) was obtained in overall 50 % yield with 2:1 ratio (Figure 64) [56]. During the cyclization of **128** (R=Ar), a cyclic product without 1,2-aryl migration **130** (R=Ar) was not observed.

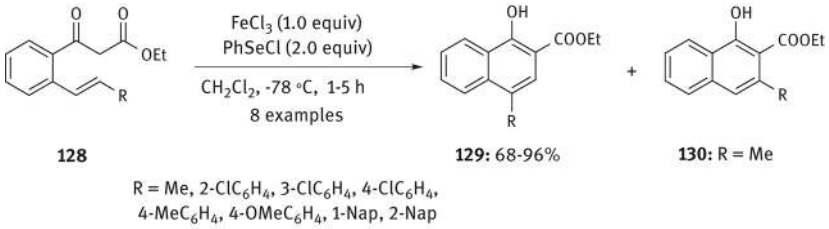


Figure 64: The cyclization of stilbenes **128** to cyclic products **129** with 1,2-alkyl- or aryl migration in dichloromethane.

The identical reagent combination ($FeCl_3$ and PhSeCl) was used by Tancock and Wirth to cyclize stilbene **131** bearing a β-keto ester moiety to yield the tetrasubstituted naphthalene **132** in dichloromethane at –78°C. The cyclic product **132** was obtained with 1,2-migration of aryl group in 96 % yield (Figure 65) [57].

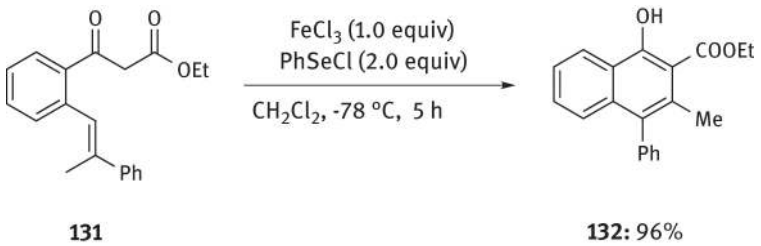


Figure 65: The cyclization of stilbenes **131** to cyclic products **132** with 1,2-aryl migration in dichloromethane.

2.8 Catalytic reactions

The scope of organoselenium electrophiles is not limited to their stoichiometric reactions as various catalytic protocols have been developed using organoselenium catalysts [4, 58–63]. In this section, catalytic transformations using organoselenium electrophiles developed in last decade are covered.

2.8.1 Selenium-catalyzed lactonization reactions

In 2007, Wirth and coworkers developed the catalytic lactonization of β,γ-unsaturated carboxylic acids **133** to butenolides **135** using 5 mol% of diphenyl diselenide **2** and [bis(trifluoroacetoxy)iodo]benzene (PIFA) **134** as stoichiometric oxidant. The reaction products **135** were isolated in moderate-to-excellent yields (Figure 66) [64]. Both aliphatic and aromatic substituents on alkene functionality in substrates **133** are tolerated in this catalytic reaction.

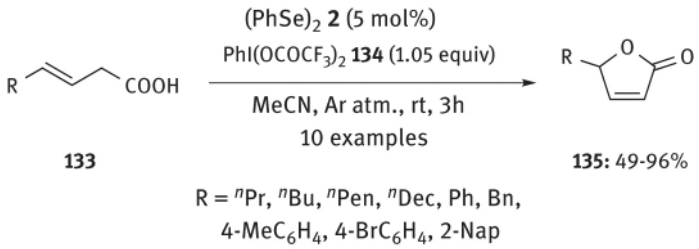


Figure 66: Selenium-catalyzed lactonization of β,γ-unsaturated carboxylic acids **133** to butenolides **135** using diphenyl diselenide **2** as catalyst and [bis(trifluoroacetoxy)iodo]benzene (PIFA) **134** as oxidant.

In 2011, Singh and Wirth extended the same selenium-catalyzed approach for the cyclization γ,δ-unsaturated carboxylic acids **136** to 3,6-dihydro-2*H*-pyran-2-ones **137** using 10 mol% of diphenyl diselenide **2** and [bis(trifluoroacetoxy)iodo]benzene (PIFA) **134** as stoichiometric oxidant in acetonitrile under argon atmosphere. All the lactonization reactions were proceeding well and 3,6-dihydro-2*H*-pyran-2-ones **137** were isolated in good yields (Figure 67) [65].

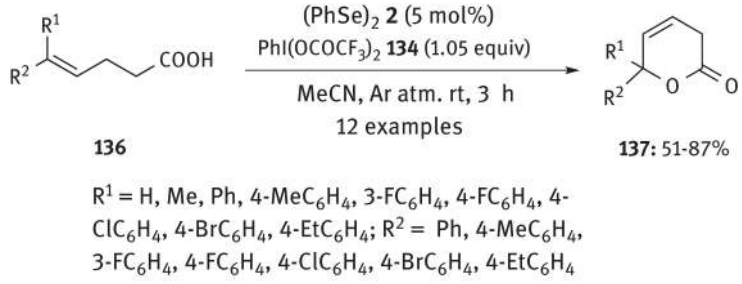


Figure 67: Selenium-catalyzed lactonization of γ,δ-unsaturated carboxylic acids **136** to 3,6-dihydro-2*H*-pyran-2-ones **137** using diphenyl diselenide **2** as catalyst and [bis(trifluoroacetoxy)iodo]benzene (PIFA) **134** as oxidant.

In addition, the lactonization of carboxylic acids **138** was performed under similar reaction conditions. Interestingly, the expected seven-membered lactone was not observed but six-membered lactones **139** were obtained in good yields via an *exo*-cyclization process (Figure 68) [65].

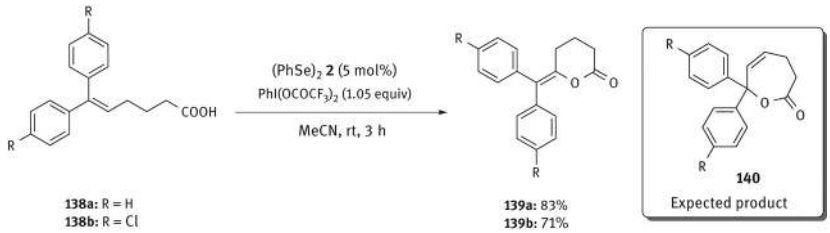


Figure 68: Selenium-catalyzed lactonization of carboxylic acids **138** to the corresponding 6-(diarylmethylene)tetrahydro-2*H*-pyran-2-ones **139** using selenium electrophile **2** as catalyst and PIFA **134** as oxidant.

The possible reaction mechanism for the selenium-catalyzed lactonization of γ,δ-unsaturated carboxylic acids **136** to 3,6-dihydro-2*H*-pyran-2-ones **137** is shown in Figure 69 [65]. According to the catalytic cycle, the reaction is initiated by the formation of the more electrophilic species phenyl selenenyl trifluoroacetate **141** by reaction of diphenyl diselenide **2** with PIFA **134**. Phenyl selenenyl trifluoroacetate **141** then reacts with the γ,δ-unsaturated carboxylic acid **136** to form selenolactone **144**. The selenide functionality of lactone **144** is then activated for elimination by [bis(trifluoroacetoxy)iodo]benzene *via* intermediate **145** and forms 3,6-dihydro-2*H*-pyran-2-ones **137**. The selenium electrophile **141** is regenerated by this process to continue the catalytic cycle.

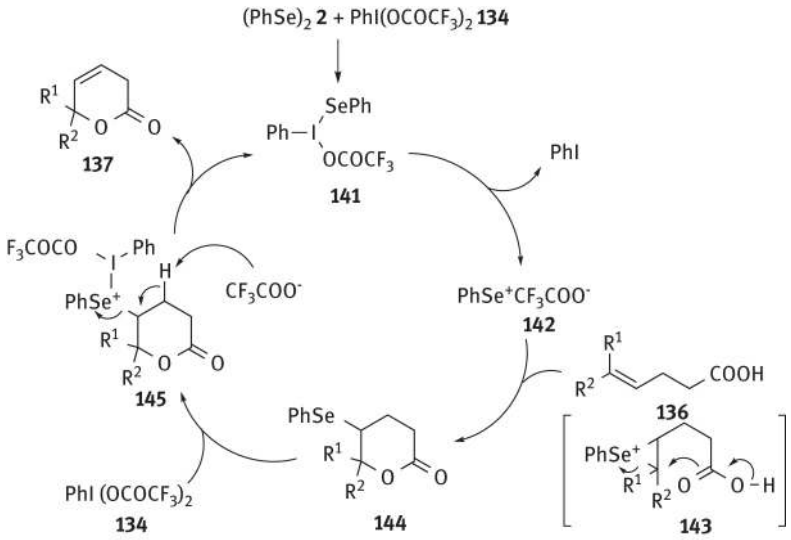


Figure 69: The possible reaction mechanism for the selenium-catalyzed lactonization of γ,δ-unsaturated carboxylic acids **136** to 3,6-dihydro-2*H*-pyran-2-ones **137**.

In 2010, Wirth and coworkers used a similar selenium-catalyzed approach for the lactonization of (*E*)-2-styrylbenzoic acids **146** to 3-aryl-1*H*-isochromen-1-ones **147** with 5 mol% diphenyl diselenide **2** and [bis(trifluoroacetoxy)iodo]benzene (PIFA) **134** as stoichiometric oxidant. These lactonizations were proceeding well and 3-aryl-1*H*-isochromen-1-ones **147** could be isolated in good yields (Figure 70) [66].

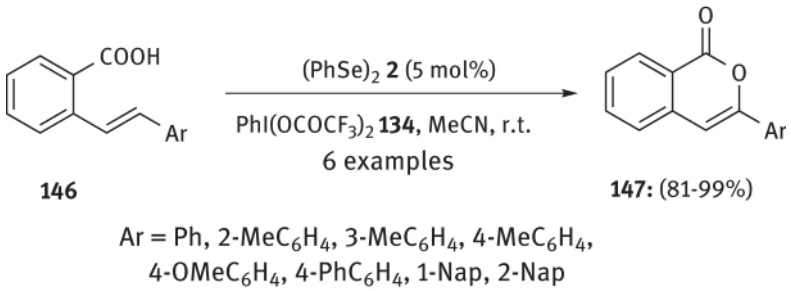


Figure 70: Selenium-catalyzed lactonization of (*E*)-2-styrylbenzoic acids **146** to corresponding 3-aryl-1*H*-isochromen-1-ones **147** using selenium electrophile **2** as catalyst and PIFA **134** as oxidant.

In 2012, Kumar and coworkers reported another selenium-catalyzed approach for the bromolactonization of functionalized alkenoic acids **148** using catalytic amounts of isoselenazolone **149** with bromine or *N*-bromosuccinimide (NBS) in the presence of potassium carbonate in dichloromethane at room temperature. The lactonization proceeded via an *exo*-cyclization and lactones **150** with different ring sizes were isolated in excellent yields (Figure 71) [67].

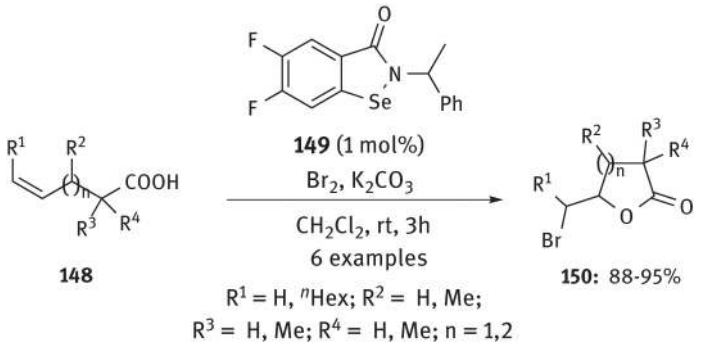


Figure 71: Selenium-catalyzed lactonization of alkenoic acids **148** to corresponding 3-lactones **150** using catalytic amount of isoselenazolone **149** with bromine or NBS.

The same approach was used in the bromolactonization of β,γ-unsaturated acids **151** under similar reaction conditions. The lactonization proceeded via an *endo*-cyclization process and lactones **152a** and **152b** were isolated in 72 % and 95 % yield, respectively (Figure 72) [67].

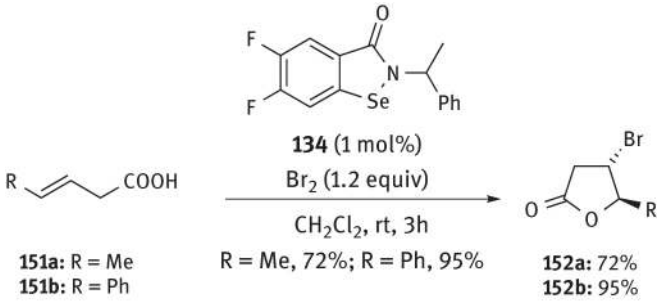


Figure 72: Selenium-catalyzed lactonization of β,γ-unsaturated acids **151** to corresponding bromolactones **152** using catalytic amount of isoselenazolone **149** with bromine or NBS.

2.8.2 Selenium-catalyzed oxidations of alcohols

In addition, isoselenazolone **149** was used to catalyze the oxidation of secondary alcohols **153**. In this approach, secondary alcohols **153** were reacted with bromine in the presence of catalytic amount of isoselenazolone **149** in dichloromethane. The oxidation reactions were proceeding well and functionalized ketones **154** are obtained as oxidation products in moderate-to-excellent yields (Figure 73) [67]. Both cyclic and acylic alcohols were successfully used as substrates in this isoselenazolone-catalyzed oxidation reaction.

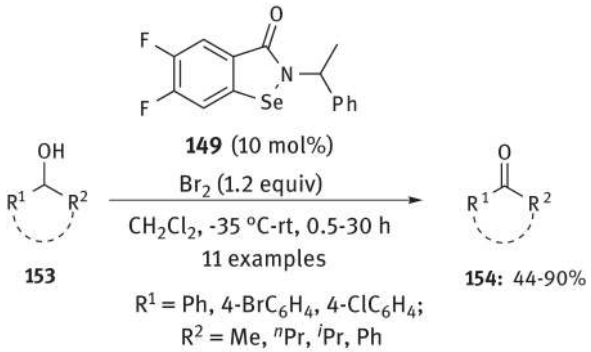
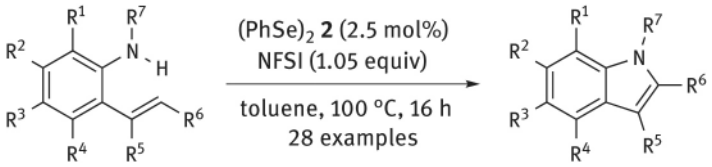


Figure 73: Selenium-catalyzed oxidation of secondary alcohols **153** to functionalized ketones **154** using catalytic amount of isoselenazolone **149** with bromine.

2.8.3 Selenium-catalyzed aminocyclizations

In 2015, Ortgies and Breder developed a new selenium-catalytic approach for the aminocyclization of styrenes or stilbenes **155** having an amino functionality in the *ortho*-position using 2.5 mol% of diphenyl diselenide **2**

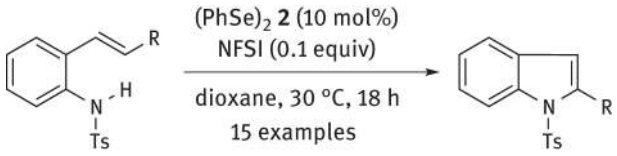
and *N*-fluorobenzenesulfonimide as an oxidant in toluene at 100°C. Various functionalized indoles **156** were obtained as reaction products in high yields (Figure 74) [68]. The aminocyclization reaction was tolerant to various electron-donating and withdrawing groups at different positions in the substrates **155**.



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

Figure 74: Selenium-catalyzed aminocyclization of styrenes or stilbenes **155** to functionalized indoles **156** using diphenyl diselenide **2** as catalyst and NFSI as oxidant.

In 2015, Zhao and coworkers extended this approach to the aminocyclization of styrenes or stilbenes **155** using 10 mol% of diphenyl diselenide **2** and *N*-fluorobenzenesulfonimide as an oxidant in dioxane at 30°C. Similar functionalized indoles **156** were isolated in poor-to-excellent yields (Figure 75) [69]. The aminocyclization reaction was tolerant to various electron-donating and withdrawing groups R at the double bond in the substrates **155**. Additionally, this approach was also applicable for the synthesis of *N*-tosyl-2-substituted indoles under similar reaction conditions.

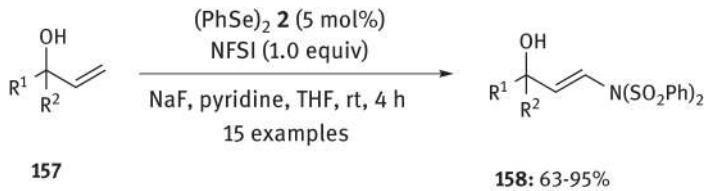


R = H, ^{n}Pr, ^{n}Pent, Ph, Bn, CH_2Bn, $CH_2(CH_2)_2CN$, 4-ClC_6H_4, 4-FC_6H_4, 4-$NO_2C_6H_4$, 4-MeC_6H_4, 4-$OMeC_6H_4$

Figure 75: Selenium-catalyzed aminocyclization of styrenes or stilbenes **155** to functionalized indoles **156** using diphenyl diselenide **2** as catalyst and NFSI as oxidant.

2.8.4 Selenium-catalyzed synthesis of allylic alcohols

In 2015, Zhao and coworkers developed a selenium-catalyzed approach for the synthesis of 3-amino allylic alcohols **158** by reaction of terminal alkenes **157** using catalytic amounts of diphenyl diselenide **2** and NFSI as oxidant in the presence of base in THF at room temperature. The reaction products **158** were isolated in good-to-excellent yields (Figure 76) [70]. Notably, the presence of hydroxyl group for coordinating the selenium reagent seems to be crucial in this reaction.



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

Figure 76: Selenium-catalyzed synthesis of 3-amino allylic alcohols **158** by the reaction of terminal alkenes **157** using diphenyl diselenide **2** as catalyst and NFSI as oxidant.

Additionally, terminal alkenes **157** were reacted with the catalyst diphenyl diselenide **2** and oxidant NFSI in EtOAc without using any base and additive. Interestingly, 3-amino allylic alcohols **158** were not obtained and

the isolated compounds were characterized as α,β-unsaturated aldehydes **159** by spectroscopic analysis. The reaction products **159** were obtained in moderate-to-high yields (Figure 77) [70].

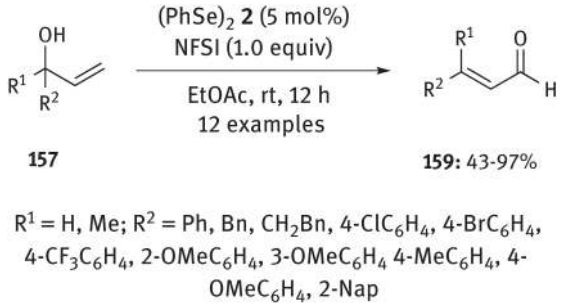


Figure 77: Selenium-catalyzed synthesis of α,β-unsaturated aldehydes **158** by the reaction of terminal alkenes **157** using diphenyl diselenide **2** as catalyst and NFSI as oxidant.

2.8.5 Selenium-catalyzed allylic esterification

Recently, Breder and coworkers developed a selenium-catalyzed photo-induced allylic esterification of disubstituted alkenes **160**. In this report, the reaction of alkenes **160**, carboxylic acid **161**, 10 mol% diphenyl diselenide **2** and 5 mol% of photo-catalyst 2,4,6-tris(4-methoxyphenyl)pyrylium tetrafluoroborate **162** in acetonitrile was irradiated at 465 nm for 16–24 h. Allylic esters **163** were obtained as reaction products in reasonable yields (Figure 78) [71]. Actually, the photo-catalyst **162** was activated after irradiation at 465 nm and initiated the process of forming the electrophilic selenium species.

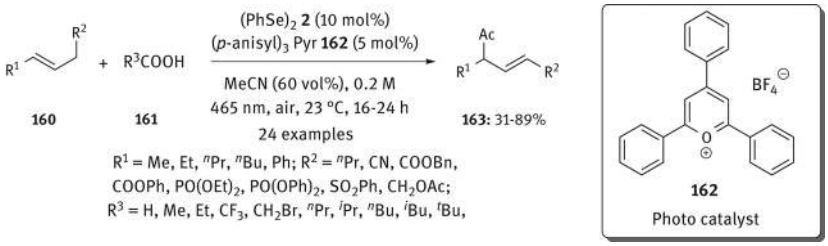


Figure 78: Selenium-catalyzed photo-induced allylic esterification of disubstituted alkenes **160** to allylic esters **163**.

3 Chiral selenium electrophiles in stereoselective reactions

In last decades, different chiral organoselenium electrophiles have been developed and used to achieve stereoselective selenenylations of alkenes including selenocyclizations [3f, 3g, 3j, 3m, 6e]. Additionally, several chiral selenium electrophiles have been successfully used as catalysts to develop catalytic stereoselective transformations [4a, 4d]. Various chiral organoselenium electrophiles **164**–**181** have been synthesized and used in asymmetric selenenylation reactions (Figure 79). Some new chiral binaphthyl diselenides **164** were synthesized by Fujita and his research group and used in stereoselective methoxyselenenylation of styrene **15** (R=H) (Figure 80) [72–77]. The methoxyselenenylated product **184** was obtained with up to 49 % diastereomeric excess (Table 2, entry 1) [74]. Déziel and coworkers reported the synthesis of C_2 symmetric chiral diselenides **165** and **166** and used in methoxyselenenylation of styrene **15** (R=H) in diethyl ether at –78°C using methanol as source of nucleophile [78, 80, 81]. The methoxyselenenylated product **184** was obtained in 77 % and 73 % diastereomeric ratio with chiral diselenides **165** and **166**, respectively (Table 2, entries 2 and 3) [79, 81].

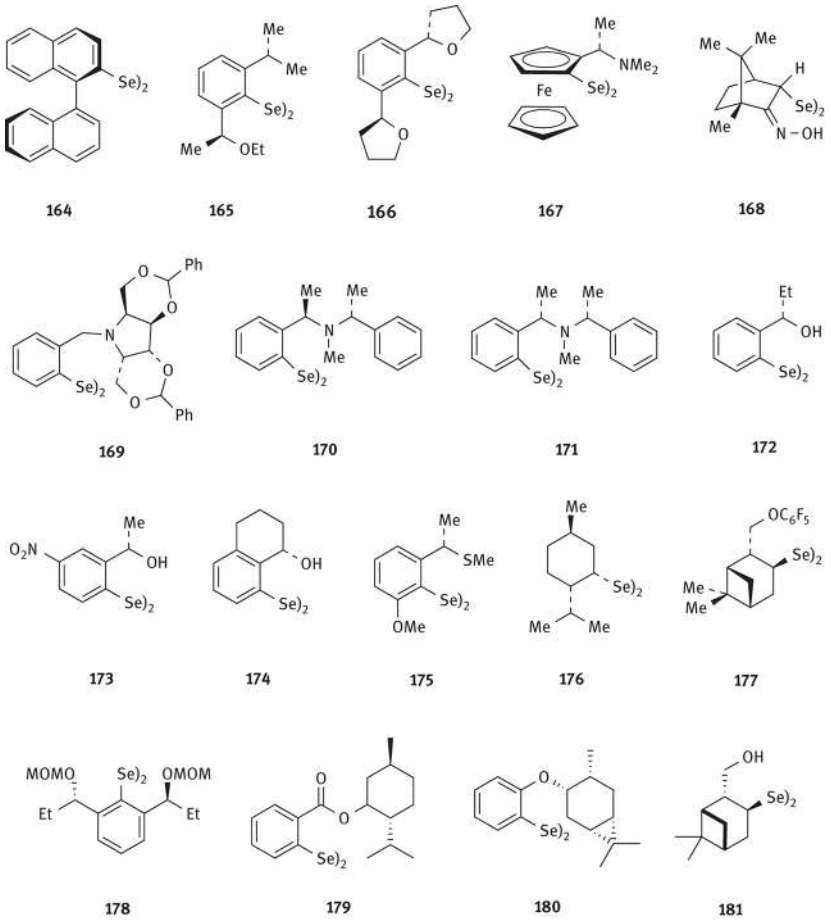


Figure 79: The structures of selective chiral selenium electrophiles **164–181**.

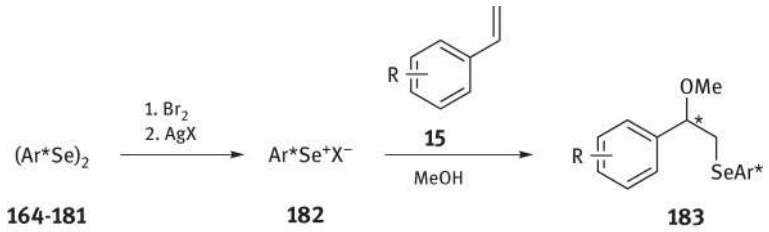


Figure 80: Asymmetric methoxyselenenylation of styrene using chiral electrophiles **164–181**.

Table 2: Stereoselective methoxyselenenylation of styrenes **15**.

Entry	Chiral diselenide	Counterion X	Reaction conditions	184 de (%)	Reference
1	**164**	Br	MeOH, 25°C	49	[74]
2	**165**	OTf	Ether, −78°C	77	[81]
3	**166**	OTf	Ether, −78°C	73	[79]
4	**167**	Br	CH_2Cl_2, 25°C	97	[82]
5	**168**	OTf	CH_2Cl_2/MeOH, −78°C	92	[96]
6	**169**	PF_6	CH_2Cl_2/MeOH, −78°C	42	[101]
7	**170**	OTf	MeOH, −78°C	94	[107]
8	**171**	OSO_3H	MeOH, 25°C	62	[103]
9	**172**	OTf	MeOH, −114°C	92	[103]
10	**173**	OTf	MeOH, −114°C	95	[103]
11	**174**	OTf	MeOH, −100°C	93	[103]
12	**175**	OTf	CH_2Cl_2/MeOH, −78°C	92	[109]
13	**176**	OTf	MeOH, −78°C	40	[111]
14	**177**	OTf	MeOH, −78°C	72	[112]c
15	**178**	OTf	MeOH, −100°C	72	[113]

16	**179**	Br	MeOH, rt	40	[114]
17	**180**	OTf	MeOH, CH_2Cl_2, −78°C	36	[115]
18	**181**	OTf	MeOH, −78°C	44	[116]

Furthermore, Uemura and coworkers developed the synthesis of ferrocenyl-cored chiral diselenide of type **167** and used successfully in stereoselective reactions [82–88]. The methoxyselenenylation of styrene **15** (R=H) was performed in dichloromethane at room temperature and selenenylated product **184** was obtained with up to 97 % de (Table 2, entry 4) [85].

The synthesis of camphor-based chiral diselenide **168** and its derivatives was developed by Back and others and successfully used in asymmetric selenenylation reactions [89–97]. The methoxyselenenylated product **184** was obtained in 92 % diastereomeric excess using chiral diselenide **168** (Table 2, entry 5) [98]. Tomoda and his research group developed the synthesis of chiral diselenides of type **169** containing cyclic amines as chiral moieties and used in different stereoselective reactions [98–101]. These diselenides have a nitrogen atom at the position segregated by four bonds from the selenium atom. Chiral diselenide **169** showed the best selectivity in asymmetric methoxyselenenylation of styrene **15** (R=H) (Table 2, entry 6) [101].

In addition, Wirth and others have developed the synthesis of nitrogen and oxygen-containing chiral diselenides **170, 171** and **172–174**, respectively [102–108]. Asymmetric methoxyselenylation of styrene **15** (R=H) was obtained with high selectivities using nitrogen and oxygen containing chiral diselenides **170, 171** and **172–174** (Table 2, entries 7–11). The selenenylation reactions were performed in different solvent systems at different temperatures and best result was observed at −114°C [107]. Furthermore, Tiecco and coworkers synthesized sulfur-containing chiral diselenide of type **175** and asymmetric methoxyselenenylation reaction styrene was obtained with up to 96 % diastereomeric excess [109]. In 2010, Wirth and coworkers synthesized new sulfoxide-containing diselenides and used in asymmetric methoxyselenenylation reactions of alkenes [23]. In addition, Cox and Wirth have reported the synthesis of selenium-stabilized diselenides and used them in stereoselective selenenylation reactions [110].

Furthermore, Scianowski and his research group reported the synthesis of menthol- and terpene-cored chiral diselenides **176** and **177** and used them in asymmetric selenenylation reactions (Table 2, entries 13 and 14) [111, 112]. In 2009, Cox and Wirth developed the synthesis of C-2 symmetric chiral diselenide **178** and asymmetric selenenenylation of styrenes **15** was achieved with up to 95 % *de* by employing this diselenide **178** (Table 2, entry 15) [113]. In 2012, Santi and coworkers achieved asymmetric methoxyselenenylation of styrene with up to 40 % *de* by using chiral diselenide **179** (Table 2, entry 16) [114]. In 2016, Scianowski and coworkers reported the synthesis of optically active *ortho*-substituted diaryl diselenide **180** which was further used in similar asymmetric reactions with up to 36 % *de* (Table 2, entry 17) [115]. Recently, the same research group developed the synthesis of various dipinanyl diselenides of type **181** which were used in asymmetric methoxyselenenylations with moderate diastereoselectivities (Table 2, entry 18) [116].

The scope of chiral organoselenium reagents is not only limited to asymmetric selenenylation reactions but also several other synthetically important asymmetric transformations such as selenocyclizations [117], aminoselenocyclizations [118], carboselenocyclizations [119] and α-functionalizations of carbonyl compounds [120] have been successfully achieved using these electrophiles. Additionally, stereoselective catalytic reactions have also been developed using selenium electrophiles as catalysts [4, 67, 121].

4 Tellurium electrophiles in organic synthesis

The chemistry of tellurium electrophiles is by far not as well explored as other chalcogen electrophiles and the applications of these electrophiles in organic synthesis are quite limited [122]. In 1996, Uemura and coworkers reported the application of tellurium electrophiles in coupling reactions [123]. Furthermore, Zeni and Comasseto synthesized few *Z*-vinylic tellurides which were used as electrophiles in coupling reactions with alkynes [124]. In 2000, some unsaturated organotellurium electrophiles were applied in the palladium-catalyzed C–C bond formation with nucleophilic species such as diethylzinc [125]. Furthermore, Zeni and others reported the synthesis of geminal enediynes by palladium-catalyzed coupling reaction of alkynes with electrophilic ketene butyl telluroacetals [126].

In 2003, Braga and others developed Sonogashira cross-coupling reactions of terminal alkynes **184** using vinylic tellurodichlorides **185** in the presence of a catalytic combination of $PdCl_2$/CuI (1:1) in methanol. Enynes **186** were isolated as cross-coupled products and obtained in good yields (Figure 81) [127].

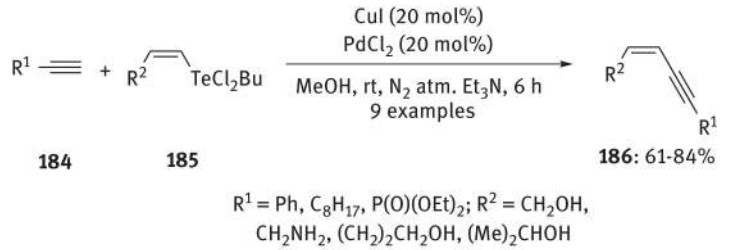


Figure 81: Pd-catalyzed coupling of alkynes **184** with vinylic tellurodichlorides **185** in methanol.

Furthermore, Stefani and coworkers developed a Suzuki-type coupling reaction of (*Z*)-vinylic tellurides **187** with potassium alkynyltrifluoroborate salts **188** using catalytic combination $Pd(acac)_2$/CuI (1:2) in methanol. Enynes **186** were isolated as cross-coupled products in good yields (Figure 82) [128].

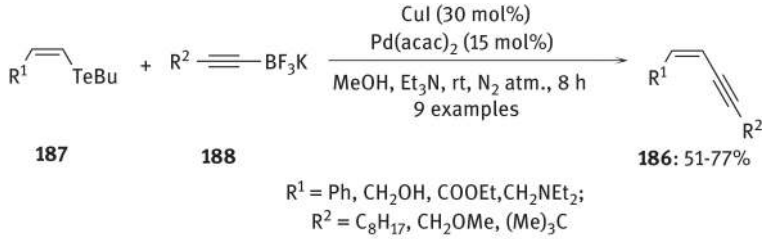


Figure 82: Pd-catalyzed coupling of potassium alkynyltrifluoroborate salts **188** with vinylic tellurides **187** in methanol.

Also, vinylic tellurides **187** were used for the synthesis of 1,3-dienes by Pd-catalyzed coupling with potassium vinylic trifluoroborates [129]. In 2006, Cella and Stefani used similar (*Z*)-vinylic tellurides **189** for the synthesis of (*Z*)-stilbenes **191** by Pd-catalyzed Suzuki coupling with potassium organotrifluoroborate salts **190**. All the coupling reactions were performed in ultrasonic bath at room temperature and (*Z*)-stilbenes **191** were obtained in good-to-excellent yields (Figure 83) [130]. Both electron-donating and withdrawing groups at the aromatic ring in substrates **189** and **190** were tolerated in the reaction conditions shown in Figure 83.

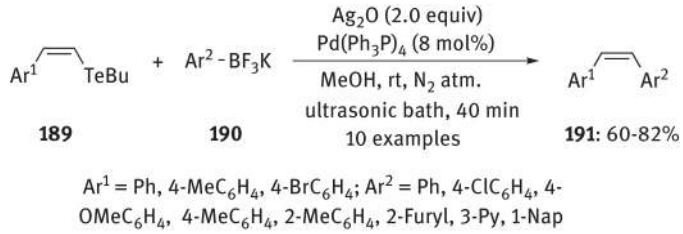


Figure 83: Ultrasound-assisted Pd-catalyzed coupling of vinylic tellurides **189** with potassium aryltrifluoroborate salts **190** in methanol.

In addition, aryl butyl tellurides **193** were synthesized and used as an electrophilic species in Pd-catalyzed Suzuki coupling with potassium (*E*)-vinyl trifluoroborate salts **192** under the reaction conditions mentioned in Figure 83. The coupling products (*E*)-stilbenes **194** were isolated in good-to-excellent yields (Figure 84) [130]. Both electron-donating and withdrawing groups at the aromatic ring in substrates **192** and **193** are tolerated in this coupling reaction. The role of Ag_2O was to reoxidize the Pd(0) to Pd(II) species.

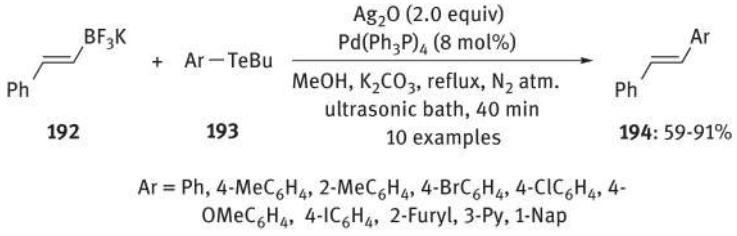


Figure 84: Ultrasound-assisted Pd-catalyzed coupling of aryl butyl tellurides **193** with potassium (*E*)-vinyl trifluoroborate salts **192** in methanol.

In 2006, Stefani and others developed the palladium-catalyzed Suzuki–Miyaura cross-coupling of aryl butyl tellurides **193** with potassium aryltrifluoroborate salts **190** using 10 mol% of $Pd(Ph_3P)_4$ in methanol at reflux

temperature. Symmetrical and unsymmetrical biaryls **195** were isolated in moderate-to-excellent yields (Figure 85) [131]. The reaction was working efficiently when coupling was performed with the substrates having both electron-donating and withdrawing substituents on the aromatic ring.

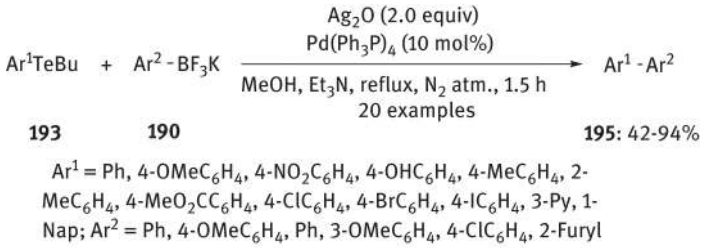


Figure 85: Pd-catalyzed Suzuki–Miyaura cross-coupling of aryl butyl tellurides **193** with potassium aryltrifluoroborate salts **190** in methanol.

In 2008, a different organotellurium electrophile, α-*n*-butyl tellurostyrene **196**, was synthesized and used in palladium-catalyzed coupling reaction with potassium alkynyltrifluoroborate salts **188** using 10 mol% of $Pd(Ph_3P)_4$ in methanol at room temperature in an ultrasonic bath. The coupling products 1,3-enynes **197** were isolated in high yields (Figure 86) [132].

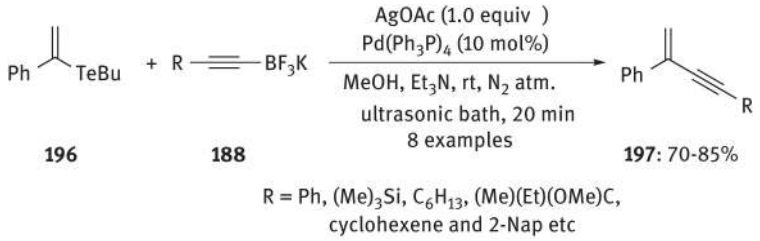


Figure 86: Pd-catalyzed Suzuki–Miyaura cross-coupling of α-*n*-butyltellurostyrene **196** with potassium alkynyltrifluoroborate salts **188** in methanol.

Alkynyl butyl tellurides **199** were used in similar coupling reactions with potassium α-styryltrifluoroborate salt **198**. Functionalized 1,3-enynes **197** were obtained in good yields (Figure 87) [132].

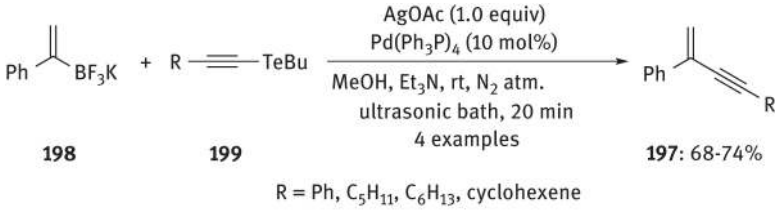


Figure 87: Pd-catalyzed Suzuki–Miyaura cross-coupling of alkynyl butyl tellurides **199** with potassium α-styryltrifluoroborate salt **198** in methanol.

The electrophilic species **193** was also employed in palladium-catalyzed coupling reactions with potassium α-styryltrifluoroborate salt **198** with 10 mol% of $Pd(Ph_3P)_4$ and 1 equiv of AgOAc as an additive in methanol at room temperature. The reaction mixture was irradiated in an ultrasonic bath and functionalized 1,1-diarylethenes **200** were isolated in high yields (Figure 88) [133]. Both electron-withdrawing and donating groups at the aromatic ring in tellurides **193** were tolerated.

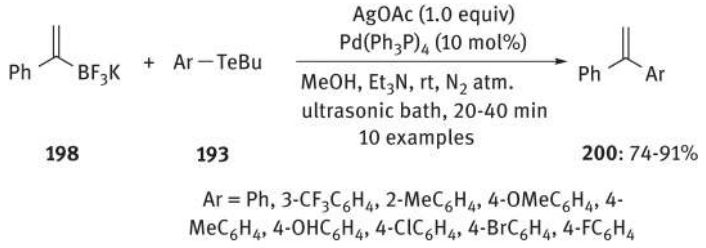


Figure 88: Pd-catalyzed Suzuki–Miyaura cross-coupling of aryl butyl tellurides **193** with potassium α-styryltrifluoroborate salt **198** in methanol.

Furthermore, Stefani and coworkers synthesized a new tellurium electrophile **201** having tellurium and chlorine moiety and used in Pd-catalyzed coupling reaction with potassium aryltrifluoroborate salts **190** using 10 mol% of $Pd(Ph_3P)_4$ and 1 equiv of AgOAc as an additive in methanol at room temperature. The coupling products **202** were obtained in good-to-excellent yields (Figure 89) [134]. Interestingly, the chlorine substituent remained in the coupling products while the tellurium moiety was participating in the reaction.

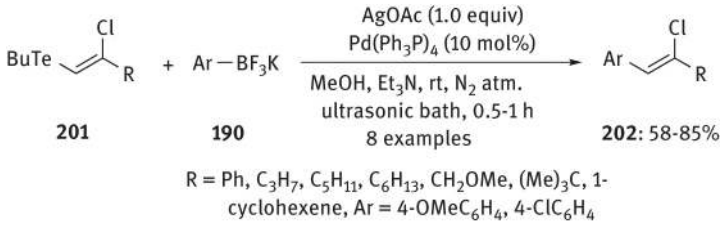


Figure 89: Pd-catalyzed Suzuki–Miyaura cross-coupling of alkenyl butyl tellurides **201** with potassium aryltrifluoroborate salts **190** in methanol.

Stefani and coworkers synthesized diaryl tellurides **203** and used them as electrophilic partners in Pd-catalyzed coupling reactions with arylzinc chloride **204** with 10 mol% of $Pd(dppf)_4$ and 2 equiv of CuI as an additive in THF at reflux temperature. Symmetrical and unsymmetrical biaryls **197** were isolated in good yields (Figure 90) [135].

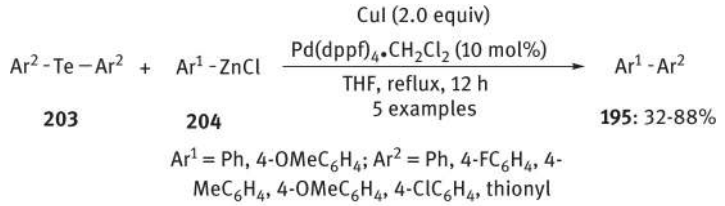


Figure 90: Pd-catalyzed Suzuki–Miyaura cross-coupling of diaryl tellurides **203** with arylzinc chloride **204** in THF.

In the same report, diaryl tellurides **203** were used in Pd-catalyzed coupling reaction with alkynylzinc chloride **205** under similar reaction conditions and 1,3-substituted alkynes **206** were obtained in good-to-excellent yields (Figure 91) [135]. Both electron-withdrawing and donating substituents at the aromatic ring in diaryl tellurides **206** are tolerated in the coupling with organozinc reagents **204** and **205**.

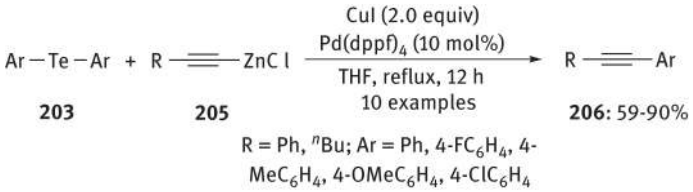


Figure 91: Pd-catalyzed Suzuki–Miyaura cross-coupling of diaryl tellurides **203** with alkynylzinc chloride **205** in THF.

Stefani and coworkers also developed palladium-catalyzed homo-coupling reactions successfully using aryl butyl tellurides **193** and alkynyl butyl tellurides **199** under mild reaction conditions [136]. Additionally, few organotellurium electrophiles have been successfully used in cycloaddition reactions with both cyclic and acyclic olefins [137, 138].

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