Chem Rev Lett 7 (2024) 677-688

Review Article

Chemical Review and Letters
journal homepage: www.chemrevlett.com
ISSN (online): 2645-4947 (print) 2676-7279

Recent Advances in Vicinal Fluorochalcogenation of Olefins

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ARTICLE INFO

Article history:
Received 16 July 2024
Received in revised form 8 September 2024
Accepted 9 September 2024
Available online 9 September 2024

Keywords:
Alkenes, 1,2-difunctionalization
Fluorosulfenylation
Fluoroselenation, β-fluoro
Thioethers, β-fluoro selenoethers

ABSTRACT

This review highlights progress made for the direct 1,2-fluorochalcogenation of olefins C–C bonds for the one-pot synthesis of biologically important β-fluoro thioether and β-fluoro selenoether derivatives. For clarity, the topic is divided into two major parts. The first section covers methods of fluorosulfenylation reactions, while the second focuses exclusively on the fluoroselenation reactions.

1. Introduction

Organofluorine compounds play an exceptionally important role in the field of medicinal chemistry and related areas due to the beneficial effects of the optimizing the pharmacological parameters, like metabolic stability, bioavailability lipophilicity, and membrane permeability [1,2]. Interestingly, up to one-fourth of the current blockbuster drugs [3] and near half of contemporary agrochemicals [4] contain at least one fluorine atom in their structures. In a similar way, organochalcogen compounds containing C–S/Se bond are important structural motifs in in pharmaceutical and agrochemical chemistry because of their intriguing biological active properties [5,6]. In the light of unique properties of fluorine and chalcogen atoms, fluorine-containing organochalcogen compounds have recently gained special popularity in medicinal chemistry and drug design. Currently, there are several FDA-approved drugs that containing both sulfur and fluorine atoms in their structures (e.g., Flovent, Faslodex, and Glecaprevir) [7, 8] and many researchers around the world are working to are working to design and develop new classes of drugs based on fluorine-containing organoselenium compounds [9]. Therefore, it is highly desirable to develop synthesis protocols to simultaneously introduce fluorine and chalcogen (S/Se) elements into targeted molecules within a single click.

The direct vicinal difunctionalization of alkenes, a cheap and abundant feedstock, has emerged as one of the most attractive strategy to increase molecule complexity by simultaneous installation of two different functional groups across the ubiquitous olefinic double bonds [10-15]. In this context, the development of 1,2-fluorofunctionalization of C-C double bonds has emerged as a hot topic of interest over the past few decades [16-25]. Along this line, several methods have been reported for the synthesis of synthetically and biologically important β-fluoro thioethers and β-fluoro selenoethers through vicinal fluorosulfenylation and fluoroselenation of alkenes, respectively (Figure 1). Needless to say that this page of β-fluoro thio-/seleno-ether synthesis has several key benefits over the classical approaches, namely shorter reaction steps, high atom economy and

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https://doi.org/10.22034/crl.2024.468181.1383

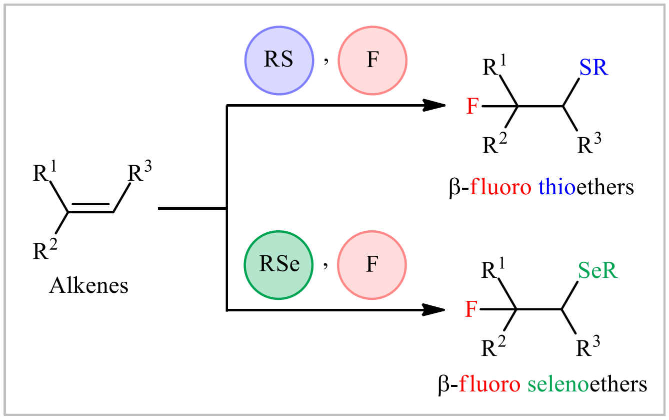
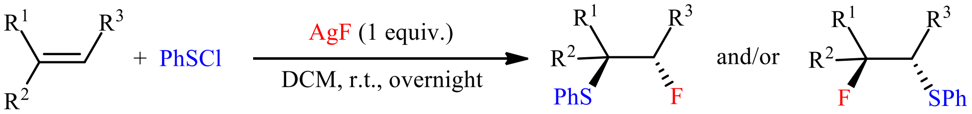


Figure 1. Vicinal fluorochalcogenation of olefins.

high environmental friendliness [26-37]. Since a number of important developments and discoveries in this domain have taken place in the last few decades, seems it is an appropriate time to summarize those achievements. In this Focus-Review, we intend to highlight the literature reports on the vicinal fluorochalcogenation of alkenes from 1985 till today.

2. Vicinal fluorosulfenylation of alkenes

The fabrication of β-fluoro thioethers through the direct vicinal fluorosulfenylation of alkenes was accomplished first in 1986 by Purrington and Correa [38]. They showed that treatment of simple, unactivated alkenes **1** with benzenesulfenyl chloride **2** in the presence of silver fluoride (AgF) in MeCN furnished corresponding β-fluoro phenyl thioethers **3** in relatively poor to high yields (Scheme 1). The reaction is notable in that both terminal (alkyl, aryl) and internal alkenes were tolerated. However, toxicity of benzenesulfenyl chloride and AgF can be considered as the main disadvantages of this protocol. Generally, the reaction was regioselective, favoring the formation of the anti-Markovnikov regioisomers, except for internal alkenes and styrene derivatives, which favored the formation of Markovnikov products. The mechanism of this reaction probably involves the initial formation of thiiranium ion intermediate through sulfenylation of alkene with sulfenyl chloride, which after reaction with fluoride ion leads to the target products. Subsequently, in a closely related investigation, Saluzzo and co-workers synthesized a library of β-fluoro phenyl/methyl thioethers in moderate to high yields *via* the reaction of corresponding alkenes with phenyl/methyl sulfenyl chlorides and subsequently with $Et_3N.3HF$ [39].



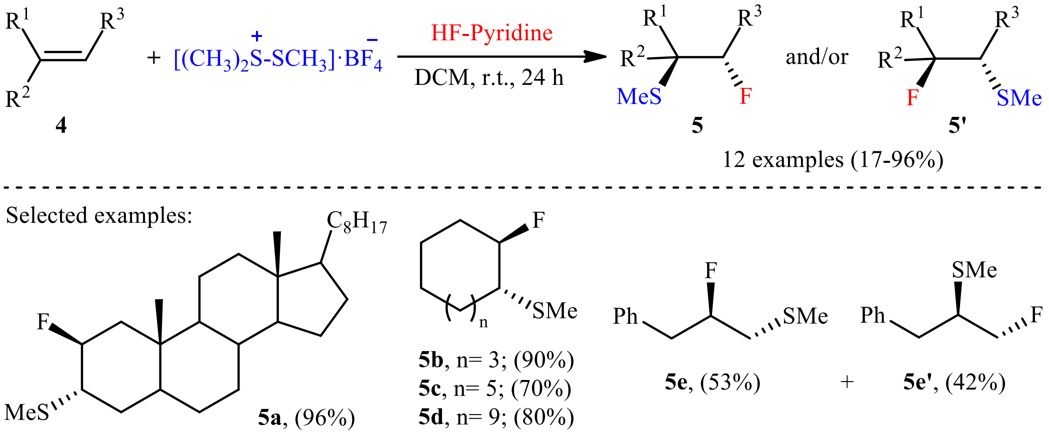
1 **2** **3** **3'**

R^1= ^{n}Bu, CH_2Cl, $C(Me)_2OH$, $^nC_8H_{17}$, Ph
R^2= H, Me
R^3= H
R^1 + R^3= $-(CH_2)_4-$

7 examples (35-70%)

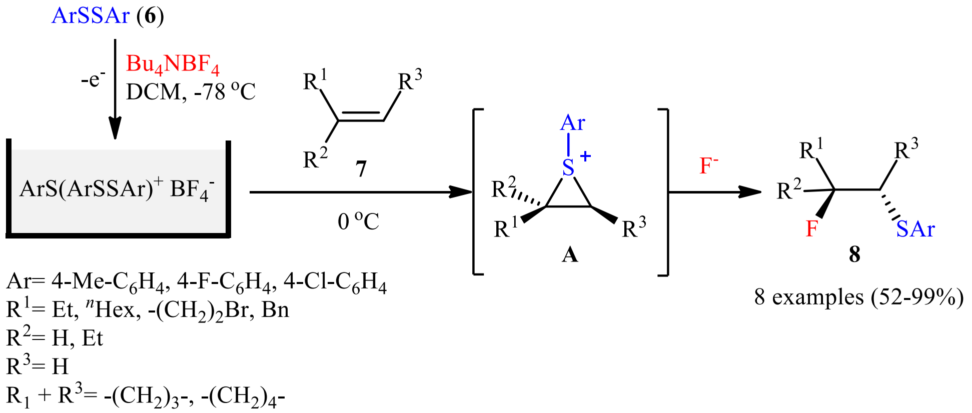
Scheme 1. Purrington-Correa's synthesis of β-fluoro phenyl thioethers **3**.

In 1988, Haufe reported a direct fluoromethane sulfenylation of alkenes **4** using dimethyl(methylthio)sulfonium fluoroborate (DMTSF) and $Et_3N·3HF$ as the sulfenyl and fluoride sources, respectively [40, 41]. The reaction was performed in DCM at room temperature, tolerated various mono-, 1,1-, and 1,2-disubstituted alkenes and provided corresponding β-fluoroalkyl-methylthioethers **5** in excellent yields (Scheme 2). However, this approach is limited to methane sulfenylation and it is relatively difficult to access DMTSF. Shortly afterwards, a similar principle was successfully applied by Benati and Montevecchi to the fluorosulfenylation of alkynes [42]. With unsymmetrical alkynes the addition reaction was found to occur in a highly regioselective fashion, leading exclusively to the Markovnikov products.



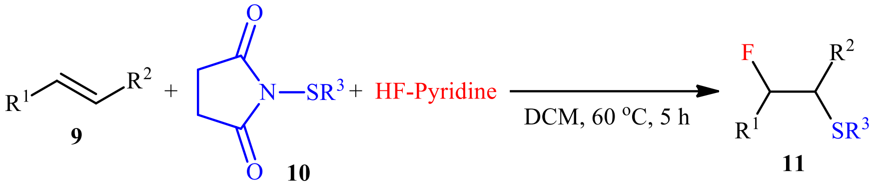
Scheme 2. Haufe's synthesis of β-fluoroalkyl-methylthioethers **5**.

In 2009, Yoshida and co-workers developed an elegant 'cation pool' method for direct fluorosulfenylation of olefinic double bonds, in which highly reactive arylbis(arylsulfanyl) sulfonium tetrafluoroborate $[ArS(ArSSAr)^+BF_4^-]$, were initially generated by the low-temperature (-78 °C) electrochemical oxidation of diaryl disulfides **6** using Bu_4NBF_4 as supporting electrolyte in a divided cell [43]. Subsequently, the resulting reactive cations reacted with alkenes **7** to form the episulfonium ion intermediate **A** that, after quenching with fluoride ions, which are derived from the anionic part of supporting electrolyte (BF_4^-), resulted in the formation of β-fluoro aryl thioethers **8** in moderate to quantitative yields with exclusive Markovnikov selectivity (Scheme 3). Notably, when the same reactions were carried out at -78 °C, the corresponding diarylthio-substituted compounds were obtained as the sole products without any β-fluoro aryl thioether formation.



Scheme 3. Yoshida's synthesis of β-fluoro aryl thioethers **8**.

Following these works, in 2020, Zeng and co-workers developed an efficient and general protocol for direct conversion of various alkenes **9** to the corresponding β-fluorinated thioethers **11**, using readily available *N*-thiosuccinimides **10** as thiolating agent and Olah's reagent (Py-HF) as the source of fluorine under additive-free conditions (Scheme 4) [44]. The reaction was experimentally simple, performed by simple heating of the substrates at 60 °C in DCM, and was applicable to various terminal (aliphatic and aromatic) and internal alkenes, *N*-arylsulfenylsuccinimides as well as *N*-alkylsulfenylsuccinimides with relatively wide functional group compatibility. The results indicated that the aliphatic terminal alkenes gave higher yields compared to the styrene derivatives. In contrary, *N*-arylsulfenylsuccinimides afforded slightly better yields compared to *N*-alkylsulfenylsuccinimides. According to the ^1H NMR analysis of products, the authors found that this transformation proceeded through anti-addition of RS and F to olefinic double bonds. As a result, *Z*-alkenes gave *trans*-β-fluorinated thioethers, while *E*-alkenes gave *cis*-β-fluorinated thioethers. Notably, when α-bromostyrenes were subjected to the same reaction conditions, the corresponding β,β-difluorinated.



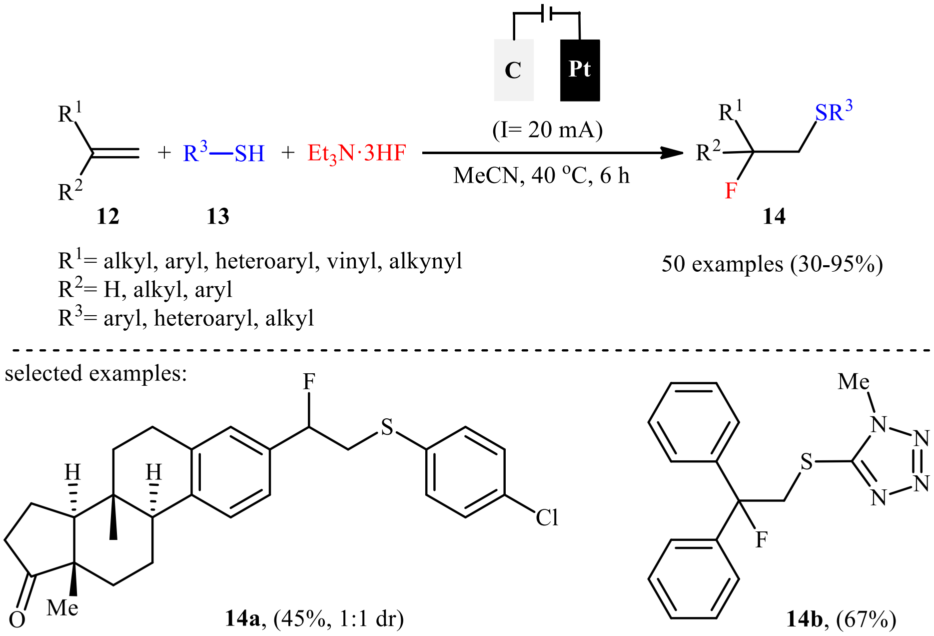
R^1= alkyl, benzyl, aryl
R^2= H, alkyl
R^3= ^{c}Hex, ^{n}Oct, Ph, 4-Me-C_6H_4, 4-OMe-C_6H_4, 4-F-C_6H_4, 4-Cl-C_6H_4, 4-I-C_6H_4, 4-Ac-C_6H_4, 3-Br-C_6H_4, 2-F-C_6H_4

36 examples (32-97%)

Scheme 4. Zeng's synthesis of β-fluorinated thioethers **11**.

thioethers were obtained in moderate yields through a tandem fluorosulfenylation and nucleophilic displacement of the bromide leaving group of resulted β-bromo-β-fluoroalkyl phenyl thioethers by excess hydrofluoride

In 2022, Yuan and Ye along with their co-workers developed an interesting electrochemical approach for regioselective fluorosulfenylation of mono- and 1,1-di-substituted alkenes **12** with thiols **13** and $Et_3N{\cdot}3HF$ under mild conditions [45]. The authors identified carbon and platinum as the optimal anode and cathode, respectively, and $Et_3N{\cdot}3HF$ as the both supporting electrolyte and fluorinating agent. The established electro-fluorosulfenylation was conducted in anhydrous acetonitrile under an inert atmosphere at 40 °C, tolerated a variety of important functional groups (*e.g.*, OMe, F, Cl, Br, CO_2Me, OCOMe, vinyl, alkynyl), and provided corresponding β-fluoro thioethers **14** in moderate to excellent yields as exclusively Markovnikov regioisomers (Scheme 5). According to the authors proposed mechanism, they proposed that this fluorosulfenylation reaction might proceed through a radical pathway *via* an episulfonium ion intermediate **D** (Scheme 6).



R^1= alkyl, aryl, heteroaryl, vinyl, alkynyl
R^2= H, alkyl, aryl
R^3= aryl, heteroaryl, alkyl

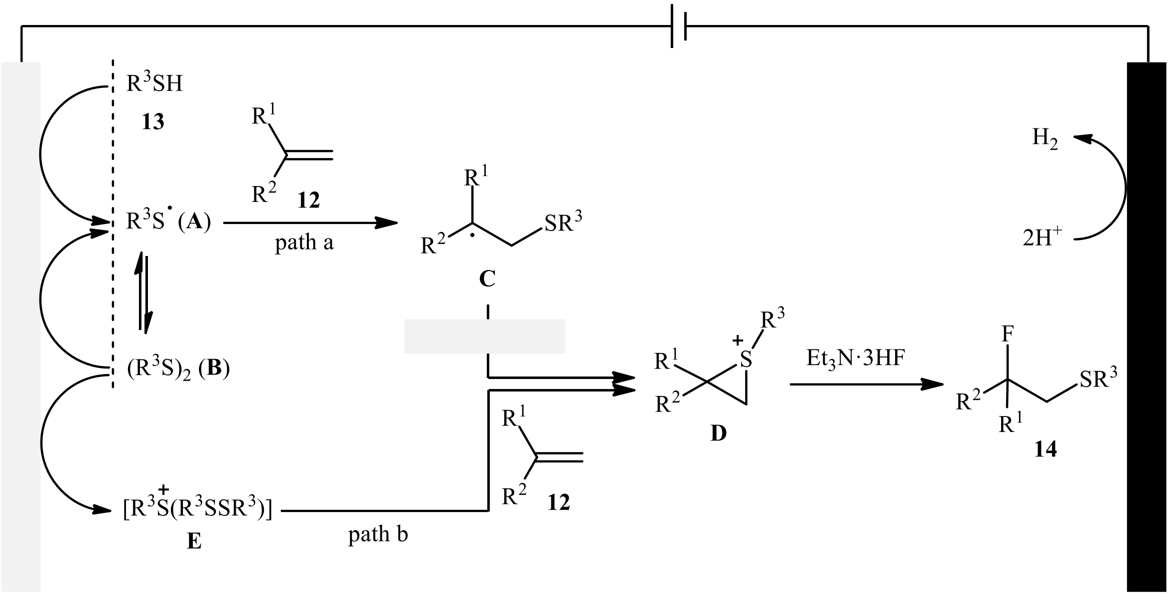
50 examples (30-95%)

selected examples:

14a, (45%, 1:1 dr)

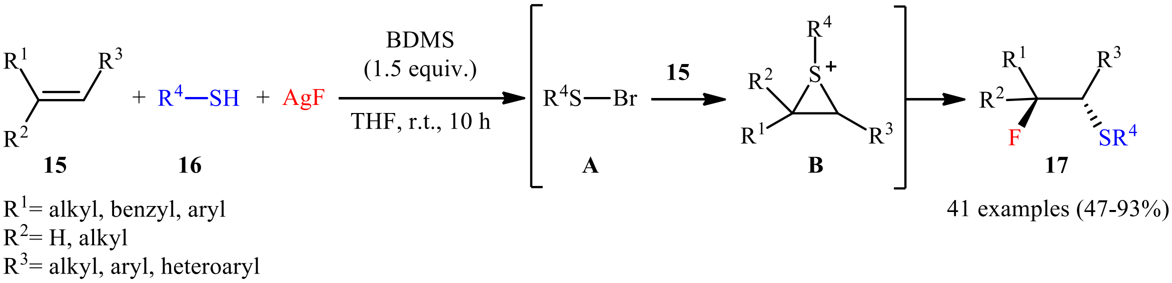
14b, (67%)

Scheme 5. Yuan-Ye's synthesis of β-fluoro thioethers **14**.



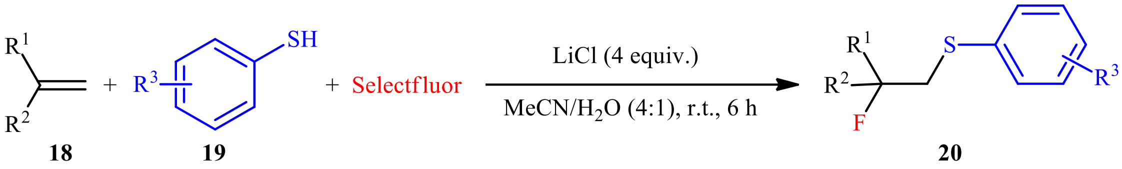
Scheme 6. Proposed mechanism for formation of β-fluoro thioethers **14**.

Based on these developments, recently, Xie and colleagues developed a practical method for bromodimethylsulfonium bromide (BDMS)-mediated fluorosulfenylation of unactivated alkenes **15** using thiols **16** and silver fluoride as the sulfenyl and fluoride sources, respectively [46]. In the presence of 1.5 equiv. of BDMS as bromonating agent, a wide range of terminal and internal alkenes successfully underwent the reaction to generate β-fluorinated thioethers **17** in moderate to high yields with excellent regio- and stereoselectively (Scheme 7). Regarding the regioselectivity of this transformation, in all examples the sulfenyl group selectively attacked to the less substituted carbon atom of the alkene's double bond and fluorine placed on the more substituted carbon atom. A wide range of functionalities both in the alkenes (*e.g.*, F, Cl, Br, I, OMe, CO_2Me, NO_2, OH) and thiols (*e.g.*, F, Cl, Br, OH, CO_2Me, NHBoc) were well tolerated with these reaction conditions. Interestingly, this protocol was also successfully applied to the “late-stage fluorosulfenylation” of natural products and medicinal agents (*e.g.*, vitamin E, cholesterol, triclosan, L-menthol).



Scheme 7. Xie's synthesis of β-fluorinated thioethers **17**.

Very recently, the Niu-Zou group realized that selectfluor could serve as an efficient fluorine source in fluorosulfenylation reactions of alkenes [47]. They showed that three-component reaction between terminal alkenes **18**, aromatic thiols **19**, and selectfluor in the presence of LiCl as an additive formed a large library of corresponding of β-fluoro thioethers **20** in moderate to high yields with outstanding stereo- and regio-selectivities (Scheme 8); in addition, a tolerance for benzyl thiol was also demonstrated. However, aliphatic thiols failed to participate in this transformation. It should be mentioned that the presence of LiCl is crucial for the success of this reaction. No β-fluorinated thioether was observed in the absence of LiCl. Replacing LiCl with some other additives (e.g., NaF, NaBr, NaCl, NaI, KCl, HCl) led to much lower yields or even no product at all. The authors proposed mechanistic pathway for this fluorosulfenylation reaction is depicted in Scheme 9.



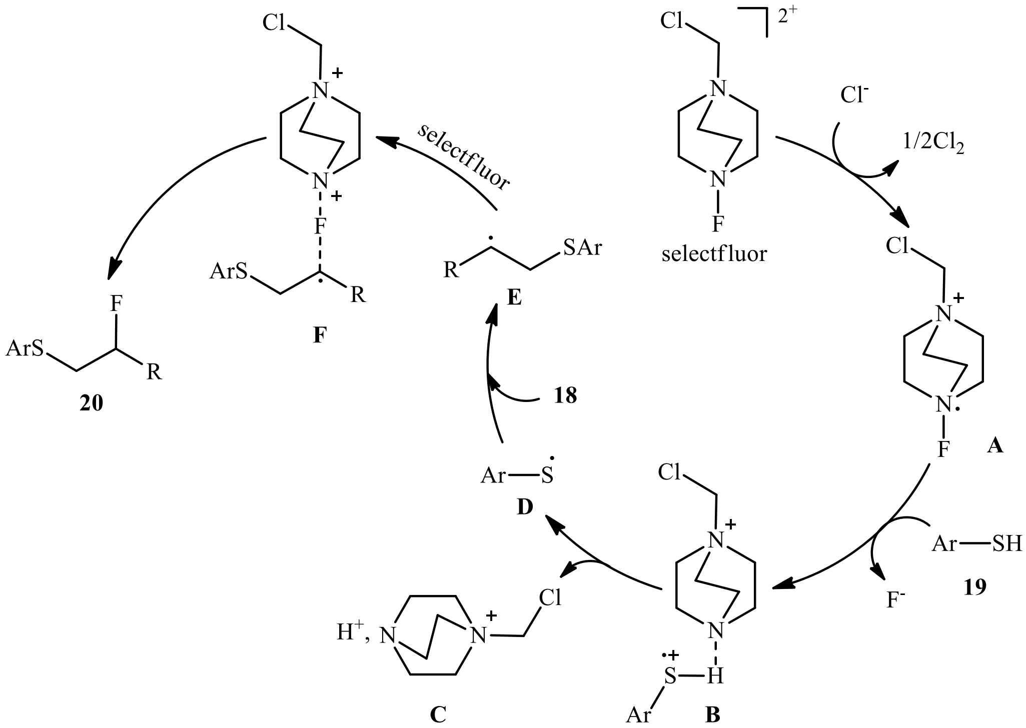
32 examples (49-83%)

R^1= Ph, 4-Me-C_6H_4, 4-^{t}Bu-C_6H_4, 4-Ph-C_6H_4, 4-OMe-C_6H_4, 4-F-C_6H_4, 4-Cl-C_6H_4, 4-Br-C_6H_4, 4-CH_2Cl-C_6H_4, 4-CO_2Me-C_6H_4, 4-NO_2-C_6H_4, 4-CF_3-C_6H_4, 3-Me-C_6H_4, 2-Me-C_6H_4, 2-naphthyl, ^{n}Pr, ^{n}Bu, ^{i}Bu, ^{c}Hex, ^{n}Oct, $(CH_2)_3Br$

R^2= H, Ph

R^3= 4-Me, 4-Et, 4-^{t}Bu, 4-F-, 4-Cl, 4-Br, 4-CF_3, 3-Me, 2-Me, 3,4-$(CH{=}CH)_2$-

Scheme 8. Niu-Zou's synthesis of β-fluoro thioethers **20**.

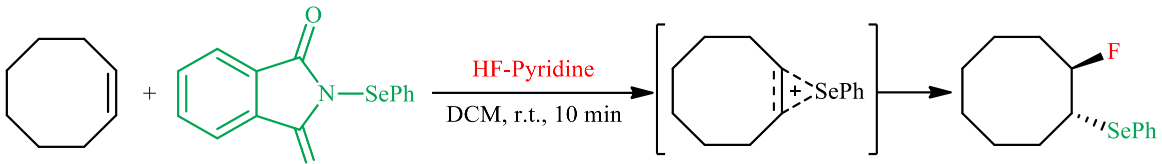


Scheme 9. Mechanistic explanation for the formation of β-fluoro thioethers **20**.

3. Vicinal fluoroselenation of alkenes

One of the earliest reports on the synthesis of β-fluoro selenoethers through 1,2-fluoroselenation of alkenes appeared in 1985 when cyclooctene **21** underwent streoselective phenylselenofluorination using 2-(phenylselanyl)isoindoline-1,3-dione **22** as a commercially available source of PhSe and hydrogen fluoride pyridine complex (HF-pyridine) as a source of nucleophilic fluoride [48]. The reaction was carried out in anhydrous DCM and afforded the corresponding ((1*R*,2*R*)-2-fluorocyclooctyl)(phenyl)selane **23** in high yield of 80% within minutes (Scheme 10). Although only one example was revealed, to the best of our knowledge, this paper represents the first example of fluoroselenation of olefinic C=C double bonds. Not long after this report, Anker's research group reported further examples of β-fluoro selenoethers synthesis under a closely similar condition and by replacing of HF-pyridine with triethylamine trihydrofluoride ($Et_3N{\cdot}3HF$) [49].

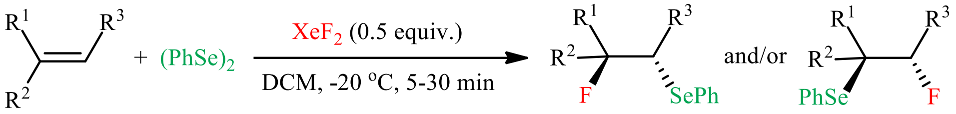
In this context, in 1990, Uneyama and Kanai described phenylselenofluorination of various alkenes **24** using diphenyldiselenide **25** as a stable and easy-handling source of the PhSe unit and XeF_2 as a fluorinating agent [50]. The reaction took place violently at -20 °C, with vigorous gas evolution, and afforded the desired β-fluoro selenoethers **26** in poor to high yields (Scheme 11), along with small amount of hydroxyselenide by-products which were generated through the hydrolysis of fluoroselenide products during chromatographic purification on silica gel.



21 **22** **A** **23**, (80%)

Scheme 10. Nicolaou's synthesis of ((1*R*,2*R*)-2-fluorocyclooctyl)(phenyl)selane **23**.

The reaction exhibited high degree of stereoselectivity, in which the pure *trans* isomers were obtained in all reported examples. However, the regioselectivity of this reaction was erratic. In some cases, the reaction proceeded in a Markovnikov manner and in some other cases in an anti-Makovnikov manner. Based on chemical behavior and spectroscopic observables, it was suggested that phenylselenyl fluoride (PhSeF) was the key intermediate in this transformation. This reagent was thermally unstable, and underwent rapid decomposition at 20 °C.



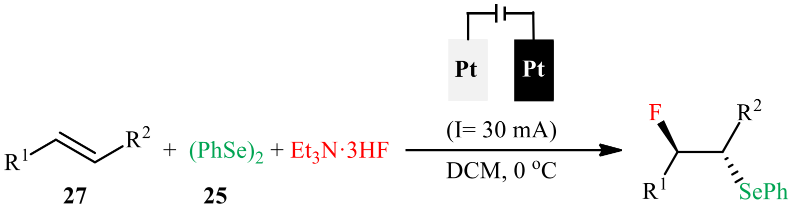
24 **25** **26** **26'**

R^1= ^{n}Hex, CH_2CN, CO_2Me
R^2= H, Me
R^3= H, CH_2CN, CH_2SO_2Ph
R^1 + R^3= -$(CH_2)_4$-, -$CH_2SO_2CH_2$-

8 examples (9-82%)

Scheme 11. Uneyama's synthesis of β-fluoro selenoethers **26**.

Seven years later, electrochemical version of this fluoroselenation reaction was developed by Uneyama and co-workers [51]. They disclosed that the treatment of various terminal and internal alkenes **27** with diphenyldiselenide **25** and $Et_3N\cdot 3HF$ in a divided cell assembled with platinum foils under constant current conditions (I= 30 mA) provided the corresponding β-fluoro selenoethers **28** in moderate to good yields (Scheme 12). According to the authors, initially electrolytic fluorination of diphenyldiselenide **25** in the presence of $Et_3N\cdot 3HF$ leads to the formation of the highly reactive PhSeF intermediate, which subsequently adds to double bonds of alkenes **27** to afford the desired products **28**. Notably, on continuing the oxidation, the initially formed fluoroselenides **28** could be transformed to the corresponding allylfluorides **29** through a selenoxide intermediate (Scheme 13). In this case, the selenenylating reagent could be recycled from the reaction mixture. It should be mentioned that a similar principle was also successfully applied to the fluoroselenation of alkynes.

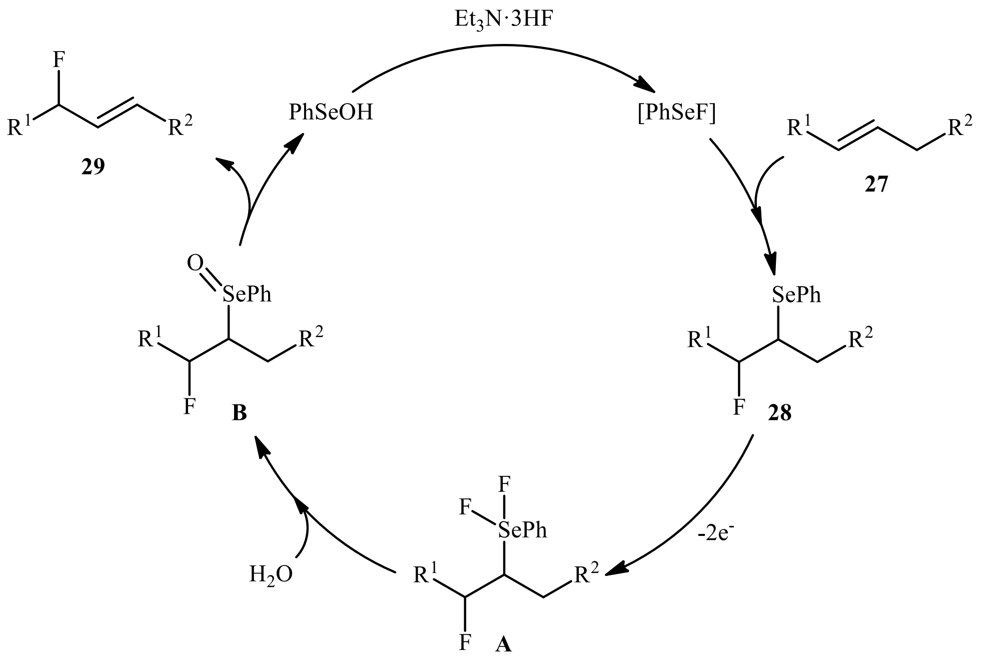


27 **25** **28**

R^1= H
R^2= ^{n}Bu, ^{n}Hex, $^nC_{10}H_{22}$
R^1 + R^2= -$(CH_2)_3$-, -$(CH_2)_4$-, -$(CH_2)_6$-, -$(CH_2)_{10}$-

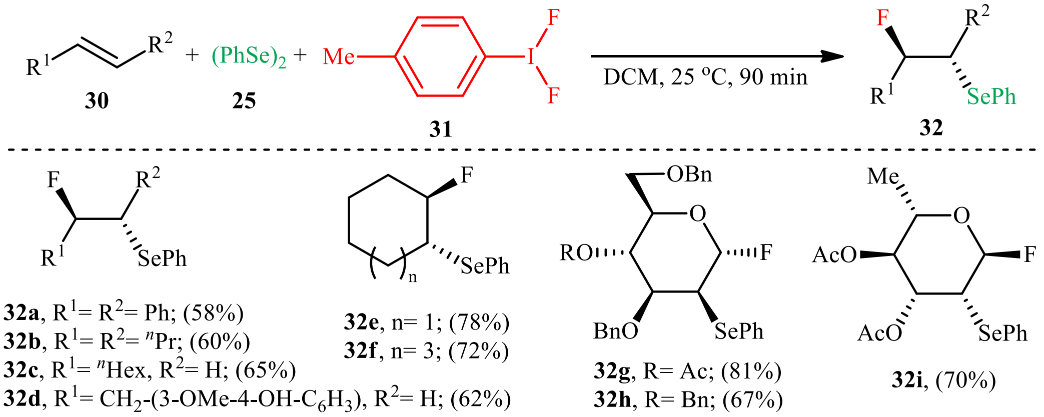
7 examples (47-78%)

Scheme 12. Electrochemical phenylselenofluorination of alkenes **27** with diphenyldiselenide **25** and $Et_3N\cdot 3HF$.



Scheme 13. Electrochemical conversion of β-fluoro selenoethers **28** to allylfluorides **29**.

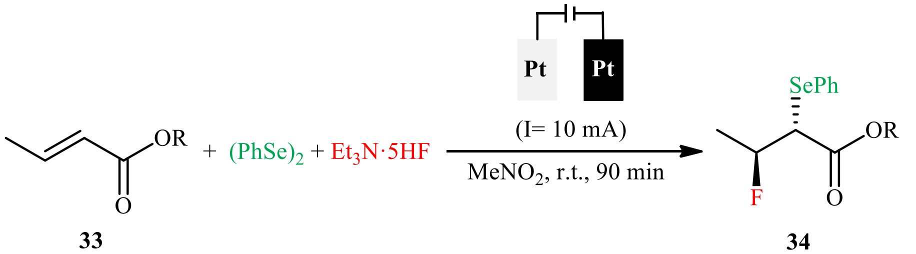
Following these works, Tingoli and co-workers developed an operationally simple method for the direct phenylselenofluorination of alkenes **30** employing diphenyldiselenide **25** and 4-iodotoluene difluoride (DFIT, **31**) as phenylselenating and fluotinating reagents, respectively [52]. Various kinds of aliphatic terminal and 1,2-disubstituted alkenes reacted with these reagents to afford the corresponding phenylseleno-fluorinated products **32** in good to high yields when running the reaction in the presence of in DCM at ambient conditions (Scheme 14). Notably, this reaction proceeded in a Markovnikov fashion and with prevalent *anti*-stereoselectivity *via* the initial addition of the electrophilic phenylselenium species followed by nucleophilic attack of fluorine anion. Interestingly, this phenylselenofluorination chemistry was also successfully extended to internal alkynes.



32a, R^1= R^2= Ph; (58%)
32b, R^1= R^2= ^{n}Pr; (60%)
32c, R^1= ^{n}Hex, R^2= H; (65%)
32d, R^1= CH$_2$-(3-OMe-4-OH-C$_6$H$_3$), R^2= H; (62%)
32e, n= 1; (78%)
32f, n= 3; (72%)
32g, R= Ac; (81%)
32h, R= Bn; (67%)
32i, (70%)

Scheme 14. Tingoli's synthesis of β-fluoro selenoethers **32**.

In 2009, Fuchigami and colleagues investigated electrochemical fluoroselenation of electron-deficient alkenes using the merge of (PhS)$_2$ and Et$_3$N·5HF as a fluoroselenating reagent combination [53]. Platinum plates under a current of 10 mA in MeNO$_2$ were found to be the best reaction conditions, and four alkyl 3-fluoro-2-(phenylselanyl)butanoate derivatives **34** were obtained in good yields from the corresponding crotonic acid esters **33** (Scheme 15). Besides crotonic acid esters, other α,β-unsaturated carbonyl compounds such as acids and amides was also compatible with this scenario. However, when α,β-unsaturated aldehydes and ketones were used as the substrates only trace amount of the products were detected. Along this line, recently, Kiss and co-workers found that a combination of PhSeBr (1 equiv.) and Deoxo-Fluor® (2 equiv.) is a suitable reagent combination for phenylselenofluorination of carbonyl-functionalized cyclic alkenes under additive-free conditions at room temperature [54]. However, only one low-yielding example was described without investigation of the substrate scope. Very recently, the authors applied their methodology in the fluoroselenation of a series of functionalized cyclic alkenes, such as esters, lactams or amino esters as model compounds [55].

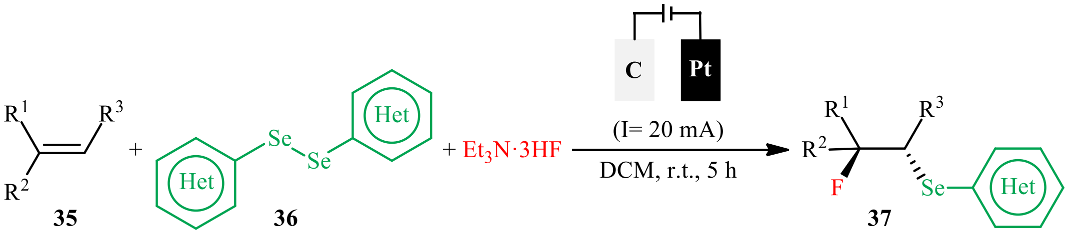


R= Me, Et, ^{i}Pr, $-CH_2$-4-OMe-C_6H_4

4 examples (59-71%)

Scheme 15. Electrochemical fluoroselenation of crotonic acid esters **33**.

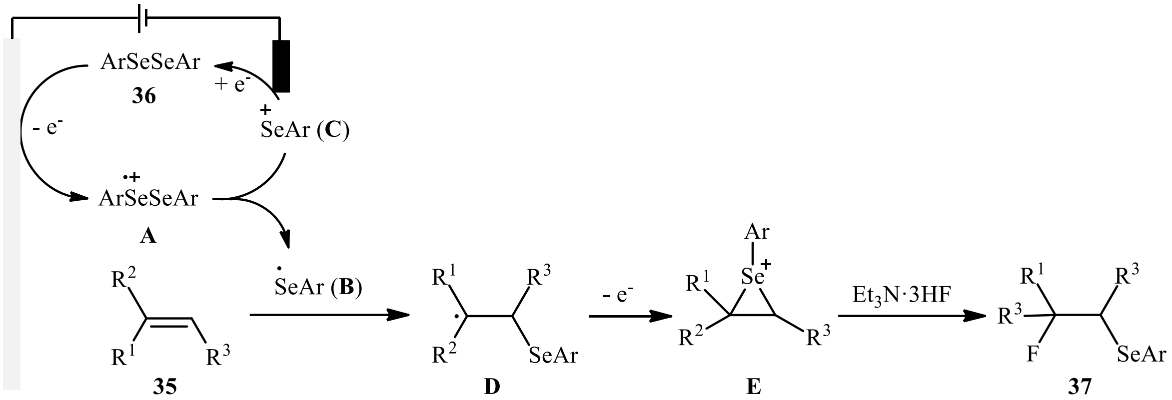
In a significant contribution in this field, Ye and co-workers unraveled an elegant electrochemical fluoroselenation of a diverse array of functionalized alkenes **35** with various commercially available di(hetero)aryl diselenides **36** and $Et_3N\cdot 3HF$ which exhibited considerable better substrate scope compared to all previously reported examples of this chemistry [56]. The reactions were conducted in an undivided cell under a constant current of 20 mA cm^{-2} with a carbon cloth anode and a platinum plate cathode employing DCM as the solvent at room temperature, which afforded the β-fluoro selenoether products **37** in fair to quantitative yields and outstanding regio- and stereo-selectivity (Scheme 16). Both electron-donating and electron-deficient functional groups (*e.g.*, Me, Br, CF_3, CN) on the ring periphery of diselenide substrates were well tolerated by this protocol. Heteroaryl-substituted selenides such as pyridine and thiophene were also compatible substrates in this transformation. Moreover, the scope of alkenes that underwent reaction was broad enough to include terminal, 1,2-disubstituted (cyclic and acyclic), and 1,1-disubstituted alkenes. Notably, the reaction can be easily scaled up without loss of the yields. The mechanism proposed by the authors to explain this electrochemical fluoroselenation reaction starts with the formation of a selenium radical cation **A** *via* oxidation of diaryl diselenide **36** on the surface of carbon cloth anode, which quickly degrades into a radical **B** and a selenium cation **C**. Next, addition of selenium radical **B** across the double bond of alkene **35** gives a nascent carbon-centered radical **D** that, after anodic oxidation forms selenonium intermediate **E**. Finally, nucleophilic attack of the fluoride to the selenonium intermediate **E** affords the observed β-fluoro selenoethers **37** (Scheme 17).



25 examples (33-99%)

R^1= Ph, 4-F-C_6H_4, 4-Cl-C_6H_4, 4-Br-C_6H_4, 4-I-C_6H_4, 4-CN-C_6H_4, 4-CF_3-C_6H_4, 4-OCF_3-C_6H_4, $-CH_2Bn$, Bn, Ad, ^{n}Hex, $^nC_{10}H_{21}$, 2-pyridyl, 2-thiazolyl
R^2= H, Me
R^3= H
$R^1 + R^3$= $-(CH_2)_4-$, $-(CH_2)_5-$, $-CH_2OCH_2-$
(Het)Ar= Ph, 4-Me-C_6H_4, 4-Br-C_6H_4, 4-CF_3-C_6H_4, 4-CN-C_6H_4, 3-thienyl, 5-(2-Cl)-pyridyl

Scheme 16. Ye's synthesis of β-fluoro selenoethers **37**.



Scheme 17. Mechanistic insights on electrochemical fluoroselenation of alkenes **35** with diaryl diselenides **36** and $Et_3N·3HF$.

4. Conclusion

From this review, it is clear that vicinal fluorochalcogenation of alkenes has emerged as a promising synthetic strategy toward synthetically and biologically important β-fluoro thio-/seleno-ethers. Easily available starting material, simplicity of operation, high atom- and step-economy, and high environmental friendliness can be considered as the major advantages of this chemistry. Despite the remarkable accomplishments during the past few years on this chemistry, the fluorinating and chalcogenating agents used in these reactions are limited, and more fluorinating and chalcogenating agents should be investigated or developed in the near future.

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