Letter

Organoselenium-Catalyzed Oxidative Allylic Fluorination with Electrophilic N–F Reagent

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Organoselenium-Catalyzed Oxidative Allylic Fluorination with Electrophilic N–F Reagent

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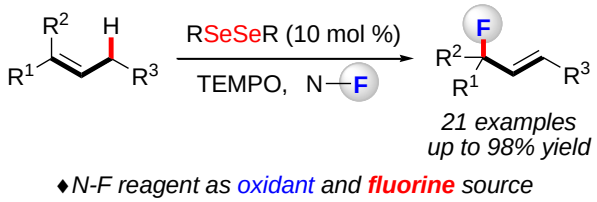
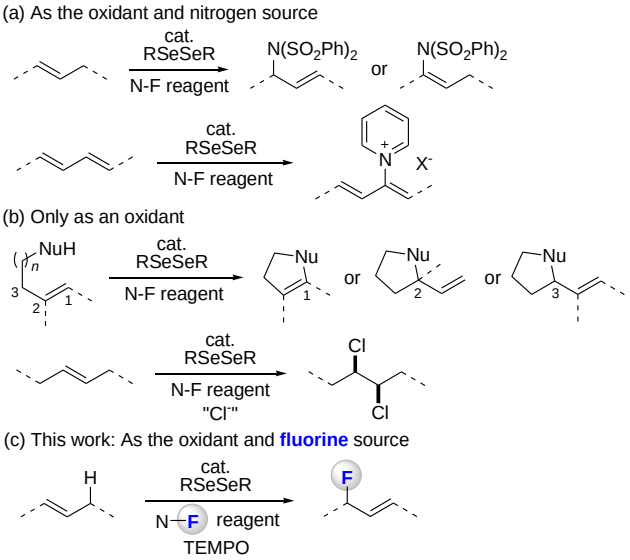
ABSTRACT: An efficient route of organoselenium-catalyzed oxidative allylic fluorination has been developed. In this transformation, bulky electrophilic fluorinating reagent *N*-fluoro-2,4,6-trimethylpyridinium triflate (TMFP-OTf) was employed as the oxidant and fluorine source. Notably, TEMPO as an additive affects the fluorination and leads to better substrate scope and excellent functional group tolerance. By this protocol, a variety of allylic fluorides were synthesized in good to excellent yields. The obtained allylic fluorides could be converted into vinyl fluorides efficiently in the presence of an appropriate base.



KEYWORDS: *selenium catalysis, alkene, electrophilic fluorinating reagents, fluorination, allylic reaction*

Owing to the occurrence of allylic fluoride moiety in pharmaceuticals and agrochemicals, efficient synthesis of allylic fluorides has drawn considerable attention in the past decades.[1,2] In general, these molecules were prepared through allylic substitution of prefunctionalized substrates.[3] Considering step economy, methods for manipulating alkenes to directly construct allylic fluorides via C–H bond cleavage are more attractive.[4,5] In this scenario, a few distinct strategies via transition metal catalysis have been developed recently. For example, Lectka has disclosed a copper catalyzed C–H abstraction/fluorination strategy to prepare allylic fluorides with electrophilic N–F reagent as a fluorine source.[5c] Subsequently, an elegant work of palladium catalyzed allylic C–H fluorination with $Et_3N{\cdot}3HF$ as a nucleophilic fluorinating reagent has been demonstrated by Doyle.[5d] As a supplement, organocatalysis strategy has been utilized in this allylic fluorination as well, but successful examples are rare.[5e-g] Despite these important advances, some drawbacks such as poor operational convenience and narrow substrate scope remain. For the purpose of synthetic divergence, developing new methods that allow efficient allylic fluorination of diversified alkenes in a simple operational way is highly desirable.

Electrophilic selenium catalysis (ESC) through selenenylation-deselenenylation process has emerged as a powerful tool for organic synthesis owing to its unique advantages including simplicity for operation, mild conditions, and excellent regio- and stereoselectivity.[6-9] Particularly, the combination of ESC and electrophilic N–F reagents in selective functionalization of alkenes and dienes has been developed by our group and others in the past few years.[8,9] By this protocol, a variety of valuable compounds such as aminated and pyridinated compounds, N- and O-heterocycles and dichlorides could be efficiently accessed. In these transformations, N–F reagents served as the



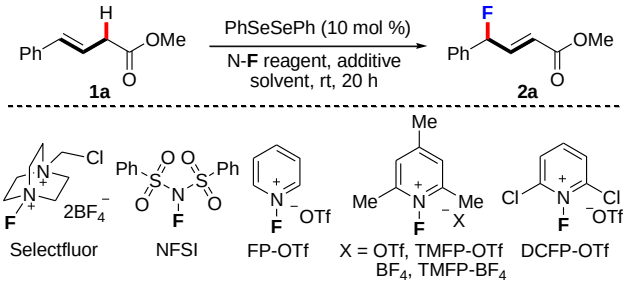
Scheme 1. Application of N–F Reagents in Organoselenium Catalysis

oxidant and nitrogen source (Scheme 1a)[8a,d,9a] or only as an oxidant (Scheme 1b).[8b,c,9b-e] However, the employment of N–F reagents as a fluorinating reagent in selenium catalysis is unprecedented so far. Although selenium-catalyzed fluorination with N–F reagents has been our goal, we have never observed fluorinated products in our previous studies.[8] We believed that it was possible to achieve organoselenium-catalyzed oxidative allylic fluorination using N–F reagents as the oxidant and fluorine source based on the reports in the literature, in which an active species [RSeF] in situ generated was utilized in the

fluoroselenenylation of alkenes,[10,11] and PhSe group could be eliminated under certain oxidative conditions.[12c,e,i]

In light of the literature, the implementation of allylic fluorination through ESC was mainly plagued by three issues: (i) In the stoichiometric fluoroselenenylation, the involved reactive intermediate [RSeF] is unstable and has not been identified yet.[12] (ii) Nitrogen-containing groups from N–F reagents[8d,9a] and trace water[7e,9a] in the reaction are strongly competitive nucleophiles in contrast to F^-. In the literature, high dosage of nucleophilic fluorides had to be employed in order to promote fluorination.[11e,i] If using N–F reagents, the amount of F^- only equivalent to catalyst could be generated and its concentration may be too low to trigger the fluorination. (iii) The nucleophilicity of F^- could be weakened by weak acid or H-bond donor. To overcome these issues, a suitable oxidative system that can not only generate the [RSeF] species smoothly but also ensure the nucleophilicity of fluorine anion is crucial. Very recently, we discovered that *N*-fluoro-2,4,6-trimethylpyridinium salts can efficiently and solely serve as an oxidant for organoselenium-catalyzed regioselective C(sp^2)–H pyridination of 1,3-dienes using exogenous pyridine sources (Scheme 1a).[8d] Inspired by this result, we envisioned that bulky N–F reagent might be an ideal candidate to serve as the oxidant and fluorine source. Herein, we report a strategy to construct allylic fluorides via organoselenium catalyzed oxidative allylic fluorination of alkenes with bulky N–F reagent and TEMPO (Scheme 1c).

Table 1. Condition Evaluation[a]

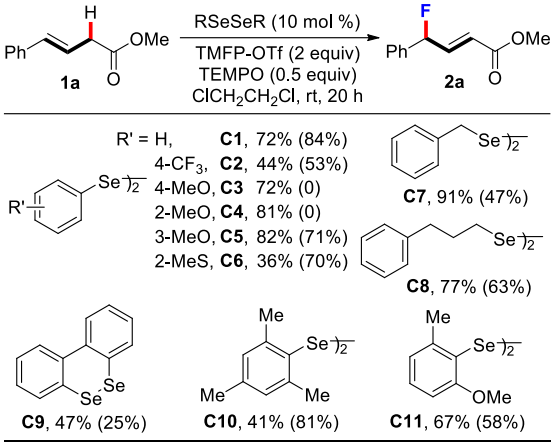


entry	oxidant	additive	solvent	yield (%)[b]
1	Selectfluor	-	CH_2Cl_2	0
2	NFSI	-	CH_2Cl_2	0
3	FP-OTf	-	CH_2Cl_2	0
4	DCFP-OTf	-	CH_2Cl_2	0
5	TMFP-OTf	-	CH_2Cl_2	83
6	TMFP-OTf	-	$ClCH_2CH_2Cl$	84(85)
7	TMFP-OTf	-	$CHCl_3$	59
8	TMFP-OTf	-	MeCN	56
9	TMFP-OTf	-	CH_3NO_2	trace
10	TMFP-BF_4	-	$ClCH_2CH_2Cl$	52
11	TMFP-OTf	$Et_3N{\cdot}3HF$	$ClCH_2CH_2Cl$	47
12	TMFP-OTf	pyridine·HF	$ClCH_2CH_2Cl$	trace
13[c]	TMFP-OTf	-	$ClCH_2CH_2Cl$	66
14[d]	TMFP-OTf	-	$ClCH_2CH_2Cl$	0
15[e]	TMFP-OTf	-	$ClCH_2CH_2Cl$	86
16[f]	TMFP-OTf	-	$ClCH_2CH_2Cl$	22

[a]Conditions: **1a** (0.05 mmol), PhSeSePh (10 mol %), oxidant (0.06 mmol), additive (0.10 mmol), solvent (350 μL), rt, 20 h, under N_2 atmosphere. [b]Determined by ^{19}F NMR with $PhCF_3$ as the internal standard. Isolated yield on 0.1 mmol scale is in the parenthesis. [c]PhSeSePh, 5 mol %. [d]No PhSeSePh. [e]TMFP-OTf, 2 equiv. [f]Under air.

To commence allylic fluorination, (*E*)-methyl 4-phenylbut-3-enoate (**1a**) with ester group which can be further transformed was selected as the model substrate (Table 1). Initially, common N–F reagents such as Selectfluor, NFSI and FP-OTf were tested in the presence of a catalytic amount of PhSeSePh under N_2 atmosphere. Not surprisingly, the desired product was not formed at all (entries 1-3). Instead, some hydroxylated and aminated byproducts were observed.[7e,8d,9a] Other commercial available pyridinium derivatives were further evaluated. However, highly reactive *N*-fluoro-2,6-dichloropyridinium triflate (DCFP-OTf) afforded several unidentified fluorides (entry 4). To our delight, the desired allylic fluoride **2a** was formed in 83% yield when *N*-fluoro-2,4,6-trimethylpyridinium triflate (TMFP-OTf) was utilized as the oxidant (entry 5). This result is in accordance with our assumption that bulky 2,4,6-collidine concomitantly generated in the reaction is a weak nucleophile and base so that the side reactions can be suppressed and the fluorination occurs smoothly. After the suitable oxidant was identified, several polar aprotic solvents were screened to improve the fluorination (entries 6-9). The yield was slightly better when $ClCH_2CH_2Cl$ was used as the solvent (entry 6). Furthermore, TMFP-BF_4 was less effective due to the low solubility of this reagent in $ClCH_2CH_2Cl$ (entry 10). Additional nucleophilic fluorine sources such as $Et_3N{\cdot}3HF$ and pyridine·HF led to lower yields or almost no desired product (entries 11 and 12). When less PhSeSePh was employed, the desired product was decreased (entry 13) and no product was detected in the absence of PhSeSePh (entry 14). More N–F reagent slightly increased the yield (entry 15). It is noteworthy that all the reactions had to be performed under N_2 atmosphere to avoid the formation of hydroxylated byproduct. When the reaction was run under air, the yield dramatically dropped (entry 16).[13] The concentration of reaction is also important for the reactivity of fluorination. Lower concentration resulted in worse reactivity.

Table 2. Effect of TEMPO in Allylic Fluorination[a]

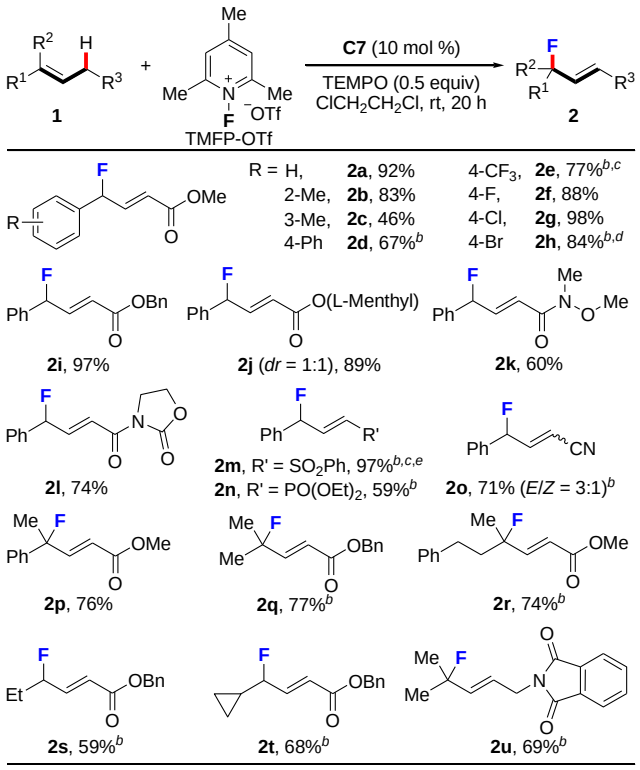


[a]Conditions: **1a** (0.05 mmol), RSeSeR (10 mol %), TMFP-OTf (0.1 mmol), TEMPO (0.025 mmol), $ClCH_2CH_2Cl$ (350 μL), rt, 20 h, under N_2 atmosphere. Yields indicated in the parenthesis were obtained under the similar conditions without TEMPO (0.06 mmol TMFP-OTf was used). Yields were determined by ^{19}F NMR with $PhCF_3$ as the internal standard.

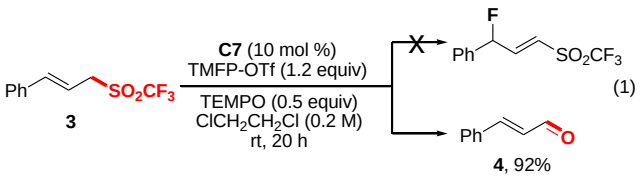
With the above conditions in hand, we attempted to investigate the substrate scope of this fluorination (see Supporting Information). A variety of aryl-substituted olefinic esters were successful to form the corresponding products in good yields ranging from 67-88% under the conditions. However, when the functional group tethering to the double bond on substrates

was changed to the other electron-withdrawing groups such as amide, sulfone, phosphonate and nitrile, the fluorination was ineffective to occur and the desired products were obtained only in trace or moderate yields. We realized that the fluorination of these substrates was suppressed presumably by the inefficiency of turnover-limiting deselenenylation process.[9e] To overcome this issue, various diselenides were evaluated in order to accelerate the oxidation of selenide moiety in intermediate. However, no distinct improvement was afforded (Table 2) and the decomposition of diarylmethyl diselenides into selenium was observed. In order to eliminate catalyst decomposition, several additives were further screened and it was found that allylic fluoride **2a** could be generated in highest yield when BnSeSeBn (**C7**) was combined with TEMPO (0.5 equiv) and TMFP-OTf (2 equiv) (Table 2). Other electron-rich diselenides $(2\text{-MeOC}_6H_4Se)_2$ (**C4**) and $(3\text{-MeOC}_6H_4Se)_2$ (**C5**) were effective under this condition as well (Table 2).

Table 3. Substrate Scope of Allylic Fluorination[a]

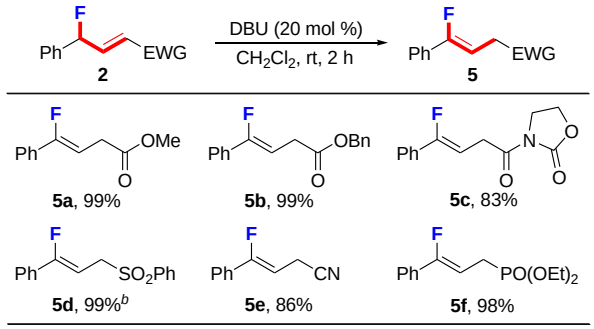


[a]Conditions: **1** (0.1 mmol), **C7** (10 mol %), TMFP-OTf (0.2 mmol), TEMPO (0.05 mmol), $ClCH_2CH_2Cl$ (500 μL), rt, 20 h, under N_2 atmosphere. [b]**C4** (10 mol%) was used. [c]At 40 °C for 48 h. [d]Reaction time, 48 h. [e]TMFP-OTf, 3 equiv.



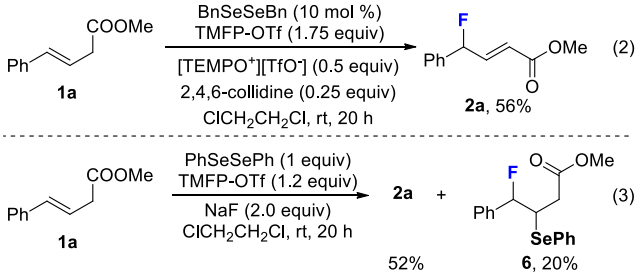
Consequently, the substrate scope was refreshed under the new conditions and became broader (Table 3). The fluorination of aryl-substituted olefinic esters, amides, sulfones, phosphonates and nitriles proceeded smoothly to afford the corresponding products in moderate to excellent yields (**2a-o**, 46-98%). For the formation of some products, electron-rich diselenide catalyst **C4** was used in order to obtain higher yields. Sometimes reaction temperature was raised slightly to consume all the starting materials (**2e** and **2m**). It is noted that fluorination of olefinic nitrile generated *Z*- and *E*-isomer products (**2o**, *E*/*Z* = 3:1), which is different from the cases of other substrates. Furthermore, trisubstituted olefinic esters were compatible with the conditions (**2p-r**, 74-77%). Alkyl-substituted alkenes also underwent fluorination to give products efficiently (**2s-u**, 59-69%).[14] Interestingly, when trifluoromethylsulfone **3** was treated with N–F reagent, cinnamyl aldehyde (**4**) was obtained in excellent yield instead of allylic fluoride (Eq. 1). Currently, the mechanism for the formation of this aldehyde is not so clear.

Table 4. Synthesis of Vinyl Fluorides via Olefin Isomerization[a]



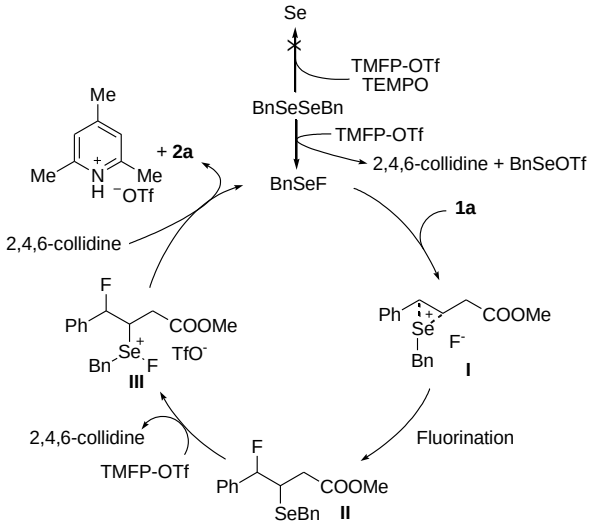
[a]Conditions: **2** (0.08 mmol), DBU (0.016 mmol), CH_2Cl_2 (1.0 mL), rt, 2 h. [b]Triethylamine (1 equiv) was used instead of DBU.

The obtained allylic fluorides are valuable building blocks due to the convenient transformation of their double bond moiety. For example, vinyl fluorides could be efficiently generated via olefin isomerization of the corresponding allylic fluorides in the presence of an appropriate base (Table 4).[15] Various phenyl-substituted vinyl fluorides with different pendent functional groups were synthesized in excellent yields through this process and only *Z*-isomer was observed (**5a-f**, 83-99%).



Then, we turned our attention to elucidating the mechanism. To exclude the possibility that TEMPO was oxidized by N–F reagent to form oxoammonium salt which might serve as a co-oxidant[16,17] to affect the reaction, bench stable [$TEMPO^+$][TfO^-] was tested. The yield of allylic fluoride **2a** was reduced to 56% when it was utilized as an additive instead of TEMPO (Eq. 2). Further analysis of the equimolar mixture of BnSeSeBn and TMFP-OTf was found that BnSeSeBn mainly decomposed into selenium after 1 h and only 36% of BnSeSeBn remained.[18] However, more than twofold BnSeSeBn was detected when the reaction with this mixture was conducted in the presence of TEMPO (see Supporting

Information). These results disclose that free TEMPO as an additive is possible to inhibit the deactivation of BnSeSeBn during the fluorination. Then, we attempted to detect fluoroselenenylated intermediate in order to confirm the generation of [RSeF] species indirectly. Intermediate **6** was observed in 20% NMR yield when PhSeSePh (1.0 equiv), TMFP-OTf (1.2 equiv) and NaF (2 equiv) were added to the reaction (Eq. 3). If NaF was absent, only trace **6** was observed.[19] This evidence shows that diselenide might undergo the Se-Se bond cleavage to form [RSeF] in the initial of reaction.



Scheme 2. Proposed Reaction Mechanism

Based on the mechanistic studies of this and previous works,[8d] a possible mechanism is proposed (Scheme 2). The reaction is initiated by the oxidative cleavage of diselenide to generate electrophilic [BnSeF] and BnSeOTf. The species [BnSeF] reacts with olefinic ester **1a** to form seleniranium ion **I**. After ring-opening by the nucleophilic attack of fluorine anion, fluoroselenenylated intermediate **II** is formed. Then, oxidation of the BnSe group on **II** by TMFP-OTf leads to the formation of intermediate **III**. The desired product **2a** and [BnSeF] are generated after subsequent H-elimination with the assistance of weak base. The role of TEMPO is possible to inhibit the decomposition of BnSeSeBn to selenium that is incompetent to trigger the fluorination. It is noted that the initiation of the reaction via Se(IV) species cannot be ruled out although the fluorination via Se(II) species is more reasonable.

In summary, we have disclosed a new route to synthesize allylic fluorides with bulky electrophilic TMFP-OTf through electrophilic selenium catalysis (ESC). The N–F reagent serves as the oxidant and fluorine source. The combination of electron-rich diselenide with TEMPO improves the reactivity of fluorination, and is crucial for the excellent functional group tolerance and better substrate scope.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: XXX

Experimental details, characterization data, mechanistic studies and NMR spectra of new compounds.

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Notes

The authors declare no competing financial interest.

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