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Electrochemical fluoro-selenenylation of electron-deficient olefins

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ABSTRACT

Electrochemical fluoro-selenenylation of electron-deficient olefins like α,β-unsaturated ester, carboxylic acid, amide, and phosphonate was successfully carried out by the anodic oxidation of diphenyl diselenide in the presence of olefins in $Et_3N{\cdot}5HF/CH_3NO_2$. The anodically generated benzeneselenenyl fluoride [PhSeF] equivalent was stable in the electrolytic solution, which resulted in the efficient fluoro-selenenylation. The fluoro-selenenylation products were shown to be potential useful fluoro-building blocks.

1. Introduction

The efficient methods for preparation of organofluorine compounds are receiving considerable attention because of their unique chemical, physical, and biological properties.[1] We showed that electrochemical fluorination is more elegant and applicable than conventional methods for selective α-fluorination of heteroatom compounds.[2] On the other hand, fluoro-selenenylation of olefins is one of the important methods for preparation of organofluorine compounds since a fluorine atom and a selenenyl group can be introduced into a carbon–carbon double bond at the same time and obtainable fluorinated selenides are expected to be useful fluorine-containing building blocks.[3]

Several fluoro-selenenylation systems such as PhSeNpthalimide-Py·HF/CH_2Cl_2,[4] PhSeNpthalimide-Py·9HF/CH_2Cl_2,[5] ultrasonication in AgF–PhSeBr/CH_2Cl_2,[6] $(PhSe)_2/XeF_2/CH_2Cl_2$,[7] and $(PhSe)_2$/*p*-Tol-IF_2/CH_2Cl_2,[8] which generate benzeneselenenyl fluoride [PhSeF] equivalent[9] in situ have been reported so far. Uneyama et al. also developed electrochemical oxidation of $(PhSe)_2$ in $Et_3N{\cdot}3HF/CH_2Cl_2$.[10] In this system, electrochemical oxidation of diphenyl diselenide generates an electron-deficient selenium species ($PhSe^+$), which is converted into [PhSeF] equivalent in the presence of a fluoride ion without use of any oxidation reagents. However, the electrochemical system cannot be applied to the fluoro-selenenylation of electron-deficient olefins such as methyl acrylate. On the other hand, the reaction of [PhSeF] equivalent with electron-deficient olefins has been successfully demonstrated by using the $(PhSe)_2/XeF_2/CH_2Cl_2$ system. In this system, however, limited conditions like a high concentration of [PhSeF] equivalent, low temperature (−20 °C), and a nitrogen atmosphere are required.[11] Moreover, XeF_2 is very expensive, therefore this method is not suitable for large-scale synthesis. Here, we describe a new efficient system for fluoro-selenenylation of electron-deficient olefins like α,β-unsaturated esters and carboxylic acids by using an electrochemical method, which can be conducted at ambient temperature under mild and safe conditions.

2. Result and discussion

2.1. Electrochemical fluoro-selenenylation of ethyl acrylate under various conditions

First, we investigated the reaction of [PhSeF] equivalent with ethyl acrylate (**1a**) as a model electron-deficient olefin under various conditions as shown in Table 1.

Under the reported electrochemical conditions ($Et_3N{\cdot}3HF/CH_2Cl_2$),[10] the reaction did not proceed at all (Entry 1). On the contrary, when the supporting electrolyte was changed from $Et_3N{\cdot}3HF$ to $Et_3N{\cdot}5HF$, the desired products **2a** and **3a** were formed in 11% and 4%, respectively (Entry 2). This is due to the higher nucleophilicity of fluoride ions of $Et_3N{\cdot}5HF$ compared with that of $Et_3N{\cdot}3HF$. Since the oxidation peak potentials of $(PhSe)_2$ in $Et_3N{\cdot}3HF/CH_2Cl_2$ (1/9) and $Et_3N{\cdot}5HF/CH_2Cl_2$ (1/9) were almost same (1.38 V and 1.39 V vs Fc^+/Fc), the anodically generated species would be the same [PhSeF] equivalent. The electrolysis using an undivided cell at ambient temperature also provided the fluorinated products in almost same yields as Entry 2 (Entry 3). Notably, the use of CH_3NO_2 as the solvent markedly promoted the reaction, and fluorinated products **2a** and **3a** were obtained in 35% and 12% yields, respectively (Entry 4). When $Et_3N{\cdot}3HF/CH_3NO_2$ solution was employed, however, the desired fluoro-selenenylation did not take place (Entry 5). In consideration to the fact that the concentration of [PhSeF] equivalent affects the efficiency of the reaction,[11] current density was changed from 10 mA/cm^2 to 20 mA/cm^2 in an $Et_3N{\cdot}5HF/CH_3NO_2$ solution in order to increase the concentration of [PhSeF] equivalent (Entry 6). However, the products yields were

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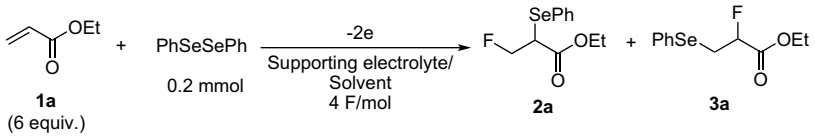
Table 1
Electrochemical fluoro-selenenylation of ethyl acrylate (**1a**) under various conditions



Entry	Cell[a]	Supporting electrolyte/solvent (ml)	Temp	Current density (mA/cm^2)	Yield[b] (%)	
					2a	**3a**
1	D	$Et_3N{\cdot}3HF/CH_2Cl_2$ (1/9)	0 °C	10	0	0
2	D	$Et_3N{\cdot}5HF/CH_2Cl_2$ (1/9)	0 °C	10	11	4
3	UD	$Et_3N{\cdot}5HF/CH_2Cl_2$ (1/9)	rt	10	12	4
4	UD	$Et_3N{\cdot}5HF/CH_3NO_2$ (1/9)	rt	10	35	12
5	UD	$Et_3N{\cdot}3HF/CH_3NO_2$ (1/9)	rt	10	0	0
6	UD	$Et_3N{\cdot}5HF/CH_3NO_2$ (1/9)	rt	20	23	7
7[c]	UD	$Et_3N{\cdot}5HF/CH_3NO_2$ (2/8)	rt	10	73 (54)	18 (14)

[a] D: Divided cell equipped with a sintered glass filter. UD: Undivided cell.
[b] Determined by ^{19}F NMR. Isolated yields are shown in parentheses.
[c] Diphenyl diselenide (0.5 mmol) was used.

decreased due to the over oxidation of the fluorinated products. On the other hand, the concentrations of the supporting electrolyte and diphenyl diselenide were found to affect greatly the efficiency of the reaction. Thus, **2a** and **3a** were obtained in 73% and 18% yields, respectively, by the electrolysis of 0.5 mmol of $(PhSe)_2$ and 3 mmol of ethyl acrylate in an $Et_3N{\cdot}5HF/CH_3NO_2$ (2 ml/8 ml) solution (Entry 7). The use of higher concentrations of $(PhSe)_2$ and olefin should increase the frequency factor in the addition reaction step, therefore, the increased yield is reasonable.

Previously, it was reported that the lifetime of the [PhSeF] equivalent would affect the efficiency of the reaction of [PhSeF] equivalent with electron-deficient olefins.[11] With this in mind, we carried out anodic oxidation of $(PhSe)_2$ in $Et_3N{\cdot}5HF/CH_3NO_2$ using a divided cell equipped with a Nafion membrane in the absence of ethyl acrylate. After 2 F/mol of charge was passed, the electrolysis was stopped, and then the solution was stirred for arbitrary time under air atmosphere at ambient temperature followed by the addition of ethyl acrylate (**1a**) to the anodic compartment. The results are shown in Figure 1.

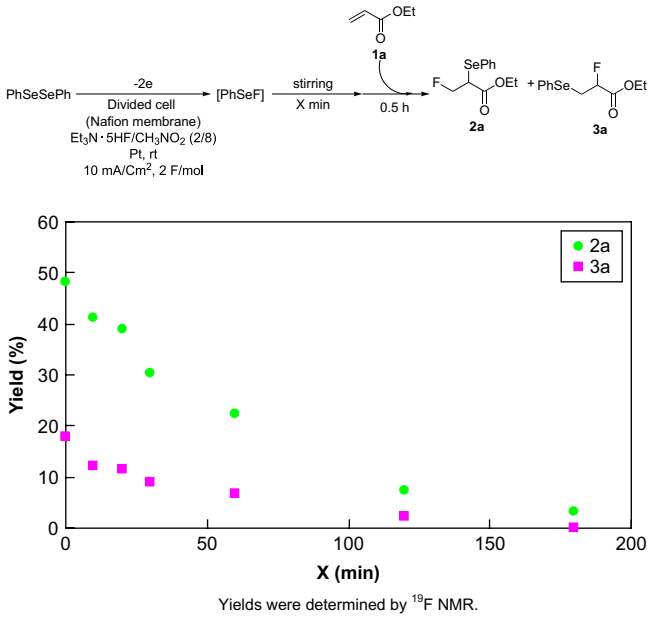


Figure 1. Relationships between yields (**2a** and **3a**) and initiation time of the reaction with **1a** after electrolysis of $(PhSe)_2$.

Immediately after the electrolysis of $(PhSe)_2$, **1a** was added to the electrolytic solution, and the solution was stirred for 0.5 h. In this case, fluorinated products **2a** and **3a** were obtained in 48% and 18% yields, respectively. Both products were isolated in 37% and 15% yields. Moreover, even when the electrolysis was stopped and the resulting electrolytic solution was stirred for 1 h at ambient temperature followed by addition of **1a**, a considerable amount of fluorinated products **2a** and **3a** was detected. These results clearly suggest that electrochemically generated [PhSeF] equivalent is stable in an $Et_3N{\cdot}5HF/CH_3NO_2$ solution. Therefore, it is reasonable that fluoro-selenenylation of ethyl acrylate, which is much less reactive compared with electron-rich olefins, can be successfully carried out since the lifetime of [PhSeF] equivalent is markedly prolonged in this solution.

2.2. Electrochemical fluoro-selenenylation of α,β-unsaturated esters in $Et_3N{\cdot}5HF/CH_3NO_2$ solution

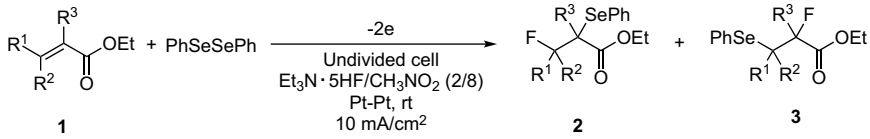
Next, we carried out electrochemical fluoro-selenenylation of various α,β-unsaturated esters like ethyl methacrylate (**1b**), ethyl crotonate (**1c**), ethyl tiglate (**1d**), and ethyl 3-methylcrotonate (**1e**) under the optimized conditions (Table 1, Entry 7). The results are summarized in Table 2.

Desired products were formed in good to excellent yields (Entries 2–5). In the case of reaction with ethyl crotonate, the product was formed as a single diastereomer. Additionally, previous reports on the addition reaction involving electrophilic selenium reagents describe that the reaction affords specifically the trans-addition product.[4–6,8] Therefore, we assume that the reaction of [PhSeF] equivalent with electron-deficient olefins gives the trans-addition products. However, isolated yields were decreased in all cases because of the instability of the products during the separation with a silica gel column chromatography, and the corresponding alcohols were detected by GC–MS. Similar hydrolysis of fluoro-selenenylation products during purification with column chromatography was reported by Uneyama et al. They did not show any isolated yields of fluoro-selenenylation products.[11]

Regioselectivity of the reaction was dependent on the substituent of α,β-unsaturated esters as shown in Scheme 1.

In the case of **1a**, an electrophilic selenenyl group was mainly introduced into the α-position of the ester group since β-selenenylation generates less stable cationic intermediate **A** due to the electron-withdrawing effect of the ester group. On the other hand, an electron-donating methyl group substituent at the β-position of α,β-unsaturated esters should stabilize the cationic intermediate **B**

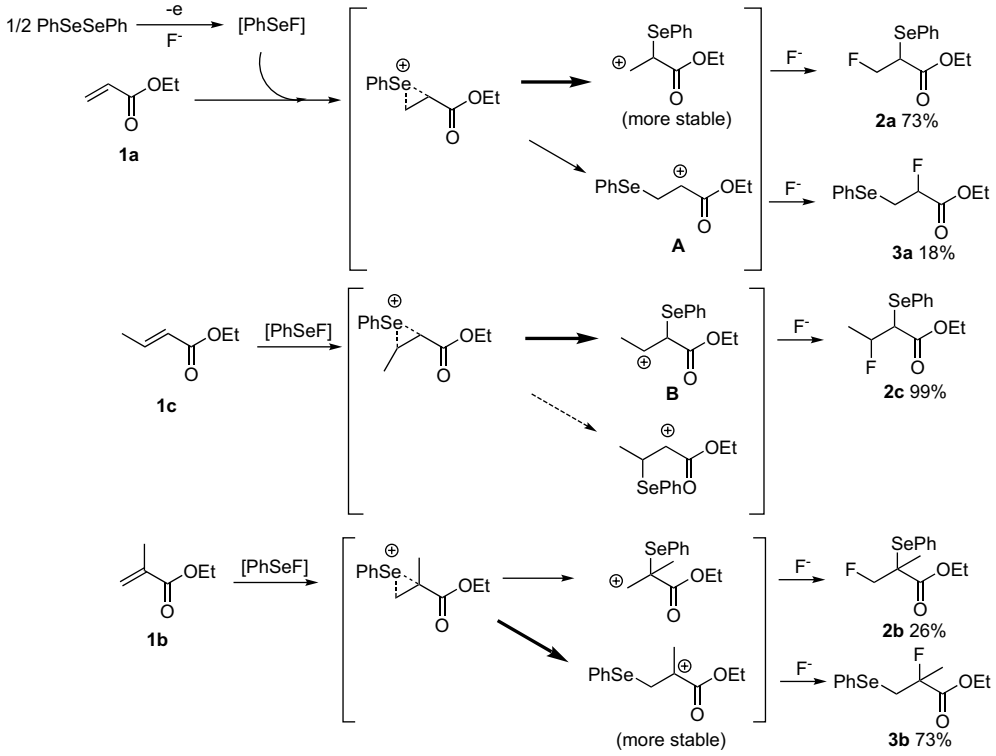
Table 2
Electrochemical fluoro-selenenylation with various α,β-unsaturated esters



1 2 3

Entry	Olefin	R^1	R^2	R^3	Charge passed (F/mol)	Yield[a] (%)			
						2		**3**	
1	**1a**	H	H	H	4	**2a**	73 (54)	**3a**	18 (14)
2	**1b**	H	H	Me	6	**2b**	26 (9)	**3b**	73 (54)
3	**1c**	Me	H	H	4.5	**2c**	99 (71)	**3c**	0
4	**1d**	Me	H	Me	8	**2d**	56 (26)	**3d**	12 (5)
5	**1e**	Me	Me	H	6	**2e**	90 (58)	**3e**	0

[a] Determined by ^{19}F NMR. Isolated yields are shown in parentheses.



Scheme 1.

generated by α-selenenylation. Such stabilization effect seems to result in exclusive selenenylation at the α-position to the carbonyl group. It is reasonable that the substitution of α,β-unsaturated esters with an α-methyl group enhanced β-selenenylation due to its electron-donating and steric effects.

We also conducted the reaction of [PhSeF] equivalent with various kinds of crotonic acid esters (**1f**–**h**) in an $Et_3N{\cdot}5HF/CH_3NO_2$ (2 ml/8 ml) solution. The results are summarized in Table 3.

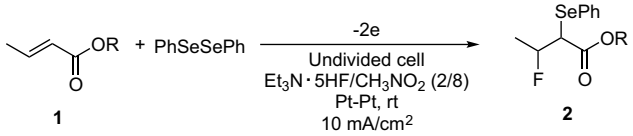
As shown in Table 3, even bulky groups like isopropyl ester group (**1g**) or *p*-methoxybenzyl ester group (**1h**) did not interfere with fluoro-selenenylation, and the desired products **2g** and **2h** were formed in excellent yields.

2.3. Electrochemical fluoro-selenenylation of olefins having various electron-withdrawing group in $Et_3N{\cdot}5HF/CH_3NO_2$ solution

The electrochemical fluoro-selenenylation was also extended to various α,β-unsaturated carbonyl compounds as shown in Table 4.

In the cases of methacrylic acid (**4a**), crotonic acid (**4b**), and methacrylic amide (**4c**), the reactions proceeded smoothly to provide the corresponding fluorinated products in moderate yields (Entries 1–3). On the contrary, the reaction with methyl vinyl

Table 3
Electrochemical fluoro-selenenylation with various crotonates

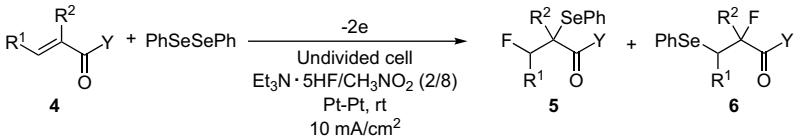


1 2

Entry	Olefin	R	Charge passed (F/mol)	Yield[a] (%)	
1	**1f**	Me	4	**2f**	96 (64)
2	**1c**	Et	4.5	**2c**	99 (71)
3	**1g**	*i*-Pr	4	**2g**	92 (70)
4	**1h**	4-$MeOC_6H_4CH_2$	5	**2h**	99 (59)

[a] Determined by ^{19}F NMR. Isolated yields are shown in parentheses.

Table 4
Electrochemical fluoro-selenenylation with various α,β-unsaturated carbonyl compounds



4 5 6

Entry	Olefin	R^1	R^2	Y	Charge passed (F/mol)	Yield[a] (%)			
						5		**6**	
1	**4a**	H	Me	OH	4.5	**5a**	Trace	**6a**	71 (36)
2	**4b**	Me	H	OH	5	**5b**	59 (20)	**6b**	0
3	**4c**	H	Me	NH_2	4	**5c**	15 (11)	**6c**	50 (45)
4	**4d**	H	H	Me	6	**5d**	21 (14)	**6d**	11 (9)
5	**4e**	H	Me	H	8	**5e**	8 (3)	**6e**	8 (5)

[a] Determined by ^{19}F NMR. Isolated yields are shown in parentheses.

ketone (**4d**) and methacrolein (**4e**) became complicated and the fluorinated products were obtained in low yields (Entries 4 and 5). The fluoro-selenenylation was also successfully extended to acryl and crotyl amides having a chiral oxazolidinone moiety (**4f** and **4g**) and the corresponding fluorinated products were obtained in good to moderate yields as a diastereoisomeric mixture (Scheme 2).

Furthermore, the reactions of olefins having diethyl phosphonate (**7a**), methylsulfonyl (**7b**), and cyano (**7c**) groups were also carried out as shown in Table 5.

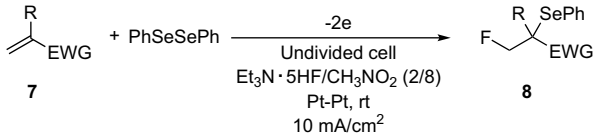
In the case of **7a**, fluorinated product **8a** was formed in moderate yield (Entry 1). On the other hand, the reaction of **7b** provided desired product **8b** in low yield and a considerable amount of starting material was recovered (Entry 2). The stronger electron-withdrawing methylsulfonyl group compared with ester group seems to interfere with the reaction. Moreover, in the case of **7c**, which has much stronger electron-withdrawing cyano group, the reaction did not proceed at all (Entry 3). In this case, the starting material was mostly recovered.

2.4. Transformation of fluoro-selenenylation products

A selenium group of the fluoro-selenenylation products is expected to have versatile functionalities. Therefore, we tried to transform the fluorinated selenides. First, we carried out deselenenylation of **5g** as a model compound with hydrogen peroxide. Deselenenylation proceeded, however, desired olefin **9** was obtained in low yield (Scheme 3). It was determined that compound **9** is *Z*-form on the basis of the coupling constant of olefinic fluorine and proton (ca. 32 Hz). Product **9** is expected to be a good chiral fluorinated Michael acceptor. This is in sharp contrast to the highly effective deselenenylation of α-phenylselenenyl-α-fluoroester derivatives reported previously.[12]

Next, we conducted radical initiated deselenenylation followed by allylation of selenides **2a** and **3a** (Scheme 4). The reaction of **2a** proceeded smoothly and desired product **10** was formed in good

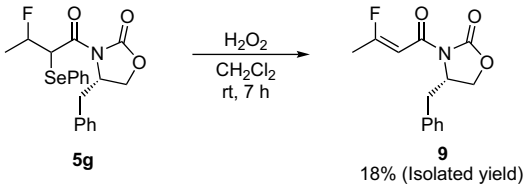
Table 5
Electrochemical fluoro-selenenylation with olefins having various electron-withdrawing groups



7 8

Entry	Olefin	R	EWG	Charge passed (F/mol)	Yield[a] of **8** (%)	
1	**7a**	H	$P(O)(OEt)_2$	6	**8a**	59 (40)
2	**7b**	H	SO_2Me	8	**8b**	19 (19)
3	**7c**	Me	CN	8	**8c**	0

[a] Determined by ^{19}F NMR. Isolated yields are shown in parentheses.

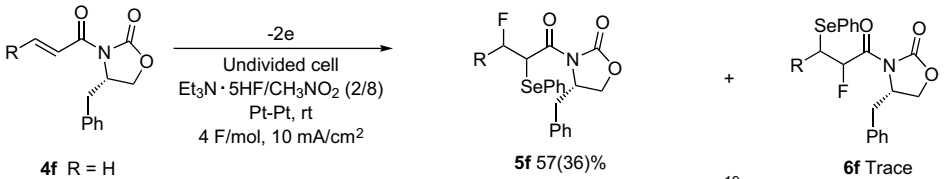


5g **9** 18% (Isolated yield)

Scheme 3.

yield (85%). On the other hand, the reaction of regioisomer **3a** did not proceed at all and 55% of starting material **3a** was recovered. This seems to be due to the instability of the radical intermediate generated by deselenenylation of **3**.

We also conducted the photochemical deselenenylation of **2a** followed by addition reaction onto olefins. The reaction with 1-octen and *n*-butyl vinyl ether provided the desired products in reasonable yields as shown in Scheme 5.



4f R = H
4g R = Me

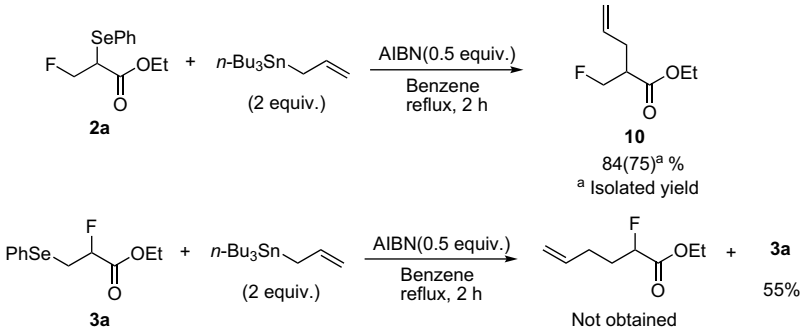
5f 57(36)%
(diastereomeric mixture ca. 1.5:1 determined by ^{19}F NMR)

6f Trace

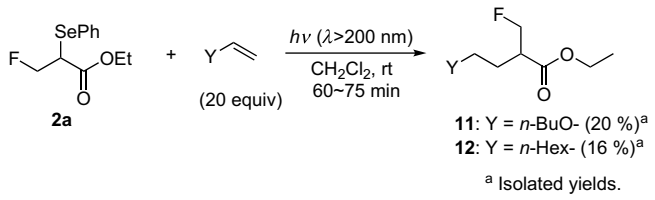
5g 90(56)%
(diastereomeric mixture ca. 1.3:1 determined by ^{19}F NMR)

6g 0%

Scheme 2.



Scheme 4.



Scheme 5.

3. Conclusion

We successfully carried out fluoro-selenenylation of electron-deficient olefins like α,β-unsaturated carbonyl compounds, phosphonate, and sulfonyl compound by using electrochemical oxidation of $(PhSe)_2$ in $Et_3N{\cdot}5HF/CH_3NO_2$. It was demonstrated that the $Et_3N{\cdot}5HF/CH_3NO_2$ solvent system made the lifetime of electrochemically generated [PhSeF] equivalent longer, and consequently this effect resulted in highly effective fluoro-selenenylation of electron-deficient olefins. In sharp contrast to the previous chemical fluoro-selenenylation using expensive XeF_2 under limited conditions like a nitrogen atmosphere and low temperature (−20 °C), this electrochemical method can be readily conducted under an air atmosphere at ambient temperature without any expensive reagents. In addition, we demonstrated the potentiality of the carbon–carbon bond formation of the fluorinated products utilizing their selenenyl groups as the leaving group.

4. Experimental

4.1. General procedure

^1H, ^{13}C, and ^{19}F NMR spectra were recorded at 270, 68, and 254 MHz, respectively, on a JEOL-NM-EX 270 with tetramethylsilane (0.00 ppm) as internal standard. The chemical shifts for ^{19}F are given in δ ppm downfield from internal trifluoroacetic acid. The following abbreviations are used: s, singlet; d, doublet; t, triplet; q, quartet and m, multiplet. High-resolution mass spectra (HRMS) were taken on a JEOL MStation JMS-700 mass spectrometer. Preparative photoreactions were carried out using a low-pressure mercury-vapor lamp UVL6DH-12 (SEN LIGHTS CORP. products). Cyclic voltammetry measurement was carried out with 5 mM of $(PhSe)_2$ and 5 mM of ferrocene (Fc) as a reference in $Et_3N{\cdot}3HF$ or $Et_3N{\cdot}5HF$ (1 ml)/CH_2Cl_2 (9 ml) at a Pt plate electrode (0.5×0.5 cm^2) using a Hokutodenko HA-501 Potentiostat/Galvanostat. Sweep rate was 100 mV/s and Ag wire was used as a pseudo-reference electrode. The oxidation peak potential of $(PhSe)_2$ was shown versus Fc^+/Fc.

4.2. General procedure for electrochemical fluoro-selenenylation

$(PhSe)_2$ (0.5 mmol) and olefins (3 mmol) are dissolved in $Et_3N{\cdot}5HF/CH_3NO_2$ (2 ml/8 ml). Constant current (40 mA) electrolysis of the solution was carried out in an undivided cell equipped with two Pt electrodes (2×2 cm^2) under an air atmosphere at ambient temperature. Other conditions are shown in tables. After $(PhSe)_2$ was mostly consumed (monitored by silica gel TLC), the electrolysis solution was passed through a short column of silica gel ($CHCl_3$ or ethyl acetate). The solvent was then removed by evaporation and the residue was purified by column chromatography on silica gel (hexane/ethyl acetate=10/1–9/1) or by HPLC (Develosil ODS-5, MeCN as eluent) to provide the desired fluorinated products. The yields were calculated based on the theoretical amount of [PhSeF] equivalent.

4.3. Ethyl 3-fluoro-2-(phenylselenyl)propionate (2a)

^1H NMR (270 MHz, $CDCl_3$): δ=7.63–7.59 (m, 2H), 7.38–7.29 (m, 3H), 4.86–4.49 (m, 2H), 4.17 (q, J=7.3 Hz, 2H), 3.85 (m, 1H), 1.24 (t, J=7.3 Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$): δ=170.00 (d, J=2.8 Hz), 135.87, 129.20, 129.09, 126.00, 81.95 (d, J=177.7 Hz), 61.58, 41.61 (d, J=19.6 Hz), 14.01. ^{19}F NMR (254 MHz, $CDCl_3$): δ=−127.85 (td, J=48.1, 11.0 Hz). HRMS (EI): m/z [M^+] calcd for $C_{11}H_{13}FO_2Se$: 276.0065; Found: 276.0063.

4.4. Ethyl 2-fluoro-3-(phenylselenyl)propionate (3a)

^1H NMR (270 MHz, $CDCl_3$): δ=7.60–7.55 (m, 2H), 7.31–7.27 (m, 3H), 5.07 (ddd, J=48.1, 6.6, 4.8 Hz, 1H), 4.25–4.12 (m, 2H), 3.44–3.19 (m, 2H), 1.26 (t, J=7.3 Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$): δ=168.10 (d, J=24.0 Hz), 133.61, 129.12, 128.60, 127.68, 87.96 (d, J=186.7 Hz), 61.89, 28.79 (d, J=22.4 Hz), 14.16. ^{19}F NMR (254 MHz, $CDCl_3$): δ=−107.96 (dt, J=48.1, 22.2 Hz). HRMS (EI): m/z [M^+] calcd for $C_{11}H_{13}FO_2Se$: 276.0065; Found: 276.0068.

4.5. Ethyl 3-fluoro-2-methyl-2-(phenylselenyl)-propionate (2b)

^1H NMR (270 MHz, $CDCl_3$): δ=7.61–7.58 (m, 2H), 7.45–7.29 (m, 3H), 4.75 (dd, J=47.6, 9.1 Hz, 1H), 4.46 (dd, J=47.6, 9.1 Hz, 1H), 4.14–3.98 (m, 2H), 1.58 (s, 3H), 1.16 (t, J=7.1 Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$): δ=171.31 (d, J=2.8 Hz), 138.04, 129.67, 128.88, 125.37, 86.20 (d, J=180.5 Hz), 61.44, 47.91 (d, J=17.3 Hz), 19.77 (d, J=3.4 Hz), 13.96. ^{19}F NMR (254 MHz, $CDCl_3$): δ=−132.60 (t, J=47.6 Hz). HRMS (FAB): m/z [M^+] calcd for $C_{12}H_{15}FO_2Se$: 290.0221; Found: 290.0228.

4.6. Ethyl 2-fluoro-2-methyl-3-(phenylselenyl)-propionate (3b)

^{1}H NMR (270 MHz, $CDCl_3$): δ=7.58–7.55 (m, 2H), 7.32–7.24 (m, 3H), 4.22–4.07 (m, 2H), 3.46–3.31 (m, 2H), 1.66 (d, J=20.9 Hz, 3H), 1.24 (t, J=7.3 Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$): δ=170.34 (d, J=25.2 Hz), 138.01, 133.32, 128.94, 127.35, 94.51 (d, J=185.6 Hz), 61.86, 35.37 (d, J=25.2 Hz), 23.87 (d, J=24.6 Hz), 14.12. ^{19}F NMR (254 MHz, $CDCl_3$): δ=−73.65 to −74.05 (m). HRMS (FAB): m/z [M^+] calcd for $C_{12}H_{15}FO_2Se$: 290.0221; Found: 290.0220.

4.7. Ethyl 3-fluoro-2-(phenylselenyl)butanoate (2c)

^{1}H NMR (270 MHz, $CDCl_3$): δ=7.63–7.60 (m, 2H), 7.39–7.28 (m, 3H), 5.12–4.85 (m, 1H), 4.12 (q, J=7.1 Hz, 2H), 3.65 (dd, J=9.7, 8.4 Hz, 1H), 1.56 (dd, J=30.1, 6.1 Hz, 3H), 1.20 (t, J=7.1 Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$): δ=170.26 (d, J=3.4 Hz), 135.50, 129.16, 128.83, 126.84, 89.91 (d, J=172.1 Hz), 61.32, 48.51 (d, J=21.2 Hz), 19.07 (d, J=22.4 Hz), 14.03. ^{19}F NMR (254 MHz, $CDCl_3$): δ=−87.65 to −88.15 (m). HRMS (FAB): m/z [M^+] calcd for $C_{12}H_{15}FO_2Se$: 290.0221; Found: 290.0220.

4.8. Ethyl 3-fluoro-2-methyl-2-(phenylselenyl)butanoate (2d)

^{1}H NMR (270 MHz, $CDCl_3$): δ=7.60–7.56 (m, 2H), 7.44–7.29 (m, 3H), 5.19 (dq, J=46.0, 6.3 Hz, 1H), 4.10–3.95 (m, 2H), 1.57 (dd, J=24.1, 6.3 Hz, 3H), 1.51 (s, 3H), 1.13 (t, J=7.1 Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$): δ=171.66 (d, J=2.2 Hz), 137.84, 129.55, 128.80, 125.86, 91.77 (d, J=174.9 Hz), 61.28, 51.99 (d, J=19.6 Hz), 16.15 (d, J=2.2 Hz), 15.80 (d, J=23.5 Hz), 13.92. ^{19}F NMR (254 MHz, $CDCl_3$): δ=−94.92 (dq, J=46.0, 24.1 Hz). HRMS (FAB): m/z [M^+] calcd for $C_{13}H_{17}FO_2Se$: 304.0378; Found: 304.0376.

4.9. Ethyl 2-fluoro-2-methyl-3-(phenylselenyl)butanoate (3d)

^{1}H NMR (270 MHz, $CDCl_3$): δ=7.62–7.58 (m, 2H), 7.30–7.27 (m, 3H), 4.20 (qd, J=7.1, 1.6 Hz, 2H), 3.57 (dq, J=24.7, 7.3 Hz, 1H), 1.72 (d, J=21.4 Hz, 3H), 1.50 (d, J=7.3 Hz, 3H), 1.28 (t, J=7.1 Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$): δ=170.39 (d, J=25.2 Hz), 134.99, 128.97, 128.60, 127.85, 97.14 (d, J=187.8 Hz), 61.83, 45.43 (d, J=23.5 Hz), 22.7 (d, J=23.5 Hz), 18.02 (d, J=3.4 Hz), 14.20. ^{19}F NMR (254 MHz, $CDCl_3$): δ=−79.20 to −79.55 (m). HRMS (FAB): m/z [M^+] calcd for $C_{13}H_{17}FO_2Se$: 304.0378; Found: 304.0379.

4.10. Ethyl 3-fluoro-3-methyl-2-(phenylselenyl) butanoate (2e)

^{1}H NMR (270 MHz, $CDCl_3$): δ=7.65–7.62 (m, 2H), 7.33–7.26 (m, 3H), 4.12 (q, J=7.3 Hz, 2H), 3.84 (d, J=10.4 Hz, 1H), 1.62 (d, J=22.1 Hz, 3H), 1.61 (d, J=21.1 Hz, 3H), 1.20 (t, J=7.3 Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$): δ=170.46 (d, J=8.4 Hz), 134.72, 129.10, 128.32, 126.79, 95.35 (d, J=172.7 Hz), 61.19, 54.53 (d, J=25.7 Hz), 25.86 (d, J=23.5 Hz), 25.06 (d, J=24.0 Hz), 14.03. ^{19}F NMR (254 MHz, $CDCl_3$): δ=−56.00 to −56.55 (m). HRMS (FAB): m/z [M^+] calcd for $C_{13}H_{17}FO_2Se$: 304.0378; Found: 304.0373.

4.11. Methyl 3-fluoro-2-(phenylselenyl)butanoate (2f)

^{1}H NMR (270 MHz, $CDCl_3$): δ=7.62–7.59 (m, 2H), 7.37–7.27 (m, 3H), 4.98 (ddq, J=47.2, 9.6, 6.1 Hz, 1H), 3.70–3.63 (m, 1H), 3.66 (s, 3H), 1.56 (dd, J=24.1, 6.1 Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$): δ=170.66 (d, J=3.4 Hz), 135.53, 129.17, 128.91, 126.77, 89.87 (d, J=172.2 Hz), 52.33, 48.31 (d, J=21.2 Hz), 19.03 (d, J=22.4 Hz). ^{19}F NMR (254 MHz, $CDCl_3$): δ=−87.48 to −87.99 (m). HRMS (FAB): m/z [M^+] calcd for $C_{11}H_{13}FO_2Se$: 276.0065; Found: 276.0065.

4.12. Isopropyl 3-fluoro-2-(phenylselenyl)butanoate (2g)

^{1}H NMR (270 MHz, $CDCl_3$): δ=7.63–760 (m, 2H), 7.35–7.27 (m, 3H), 5.11–4.84 (m, 2H), 3.61 (dd, J=9.6, 8.6 Hz, 1H), 1.56 (dd, J=23.9, 6.3 Hz, 3H), 1.22 (d, J=6.3 Hz, 3H), 1.19 (d, J=6.3 Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$): δ=169.87 (d, J=3.4 Hz), 135.33, 129.16, 128.72, 127.07, 90.00 (d, J=172.2 Hz), 68.93, 48.91 (d, J=21.2 Hz), 21.74, 21.63, 19.10 (d, J=22.4 Hz). ^{19}F NMR (254 MHz, $CDCl_3$): δ=−87.89 to −88.39 (m). HRMS (FAB): m/z [M^+] calcd for $C_{13}H_{17}FO_2Se$: 304.0378; Found: 304.0379.

4.13. *p*-Methoxybenzyl 3-fluoro-2-(phenylselenyl)-butanoate (2h)

^{1}H NMR (270 MHz, $CDCl_3$): δ=7.55–7.51 (m, 2H), 7.34–7.22 (m, 5H), 6.89–6.86 (m, 2H), 5.12–4.84 (m, 1H), 5.04 (s, 2H), 3.81 (s, 3H), 3.67 (dd, J=9.6, 8.4 Hz, 1H), 1.56 (dd, J=23.9, 6.3 Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$): δ=170.14 (d, J=3.4 Hz), 159.47, 135.56, 129.94, 129.90, 129.14, 128.83, 127.43, 113.78, 89.81 (d, J=172.7 Hz), 66.84, 55.29, 48.45 (d, J=21.2 Hz), 19.04 (d, J=21.2 Hz). ^{19}F NMR (254 MHz, $CDCl_3$): δ=−87.72 to 88.22 (m). HRMS (EI): m/z [M^+] calcd for $C_{18}H_{19}FO_3Se$: 382.0483; Found: 383.0473.

4.14. 2-Fluoro-2-methyl-3-(phenylselenyl)propionic acid (6a)

^{1}H NMR (270 MHz, $CDCl_3$): δ=9.02 (br s, 1H), 7.64–7.55 (m, 2H), 7.39–7.24 (m, 3H), 3.47–3.32 (m, 2H), 1.71 (d, J=20.8 Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$): δ=175.74 (d, J=26.3 Hz), 137.93, 133.56, 129.33, 129.05, 94.43 (d, J=186.7 Hz), 34.96 (d, J=24.6 Hz), 23.80 (d, J=24.0 Hz). ^{19}F NMR (254 MHz, $CDCl_3$): δ=−74.45 to −74.87 (m). HRMS (FAB): m/z [M+Na^+] calcd for $C_{10}H_{11}FO_2NaSe$: 284.9800; Found: 284.9808.

4.15. 3-Fluoro-2-(phenylselenyl)butanoic acid (5b)

^{1}H NMR (270 MHz, $CDCl_3$): δ=9.64 (br s, 1H), 7.65–7.62 (m, 2H), 7.40–7.28 (m, 3H), 5.09–4.81 (m, 1H), 3.62 (dd, J=9.4, 8.4 Hz, 1H), 1.60 (dd, J=23.9, 6.3 Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$): δ=175.60 (d, J=2.8 Hz), 135.53, 129.35, 129.13, 126.60, 89.65 (d, J=172.2 Hz), 48.07 (d, J=19.6 Hz), 18.98 (d, J=22.9 Hz). ^{19}F NMR (254 MHz, $CDCl_3$): δ=−87.89 to −88.39 (m). HRMS (EI): m/z [M^+] calcd for $C_{10}H_{11}FO_2Se$: 261.9908; Found: 261.9909.

4.16. 3-Fluoro-2-methyl-2-(phenylselenyl)propionamide (5c)

^{1}H NMR (270 MHz, $CDCl_3$): δ=7.66–7.62 (m, 2H), 7.45–7.33 (m, 3H), 6.13 (br s, 1H), 5.64 (br s, 1H), 4.68 (dd, J=47.8, 9.6 Hz, 1H), 4.49 (dd, J=47.8, 9.7 Hz, 1H), 1.56 (s, 3H). ^{13}C NMR (68 MHz, $CDCl_3$): δ=173.65, 137.60, 129.62, 129.12, 127.24, 86.34 (d, J=178.3 Hz), 49.75 (d, J=16.8 Hz), 20.81 (d, J=3.9 Hz). ^{19}F NMR (254 MHz, $CDCl_3$): δ=−133.00 (t, J=47.8 Hz). HRMS (FAB): m/z [M+Na^+] calcd for $C_{10}H_{12}FNONaSe$: 283.9966; Found: 283.9973.

4.17. 2-Fluoro-3-methyl-2-(phenylselenyl)propionamide (6c)

^{1}H NMR (270 MHz, $CDCl_3$): δ=7.57–7.52 (m, 2H), 7.27–7.23 (m, 3H), 6.40 (br s, 1H), 6.29 (br s, 1H), 3.52–3.26 (m, 2H), 1.67 (dd, J=21.8, 1.3 Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$): δ=174.18 (d, J=22.4 Hz), 137.59, 132.85, 128.92, 127.15, 97.21 (d, J=186.1 Hz), 35.05 (d, J=24.0 Hz), 23.93 (d, J=24.0 Hz). ^{19}F NMR (254 MHz, $CDCl_3$): δ=−73.03 to −73.60 (m). HRMS (FAB): m/z [M+Na^+] calcd for $C_{10}H_{12}FNONaSe$: 283.9966; Found: 283.9966.

4.18. 4-Fluoro-3-(phenylselenyl)butan-2-one (5d)

^{1}H NMR (270 MHz, $CDCl_3$): δ=7.56–7.53 (m, 2H), 7.42–7.28 (m, 3H), 4.89–4.48 (m, 2H), 3.97–3.88 (m, 1H), 2.40 (s, 3H). ^{13}C NMR (68 MHz, $CDCl_3$): δ=201.42 (d, J=1.7 Hz), 135.89, 129.34, 129.30, 125.36, 81.14 (d, J=161.5 Hz), 48.67 (d, J=19.6 Hz), 28.59. ^{19}F NMR (254 MHz, $CDCl_3$): δ=−130.51 (td, J=46.2, 9.1 Hz). HRMS (FAB): m/z [M+Na$^+$] calcd for $C_{10}H_{11}FONaSe$: 268.9857; Found: 268.9858.

4.19. 3-Fluoro-4-(phenylselenyl)butan-2-one (6d)

^{1}H NMR (270 MHz, $CDCl_3$): δ=7.57–7.49 (m, 2H), 7.33–7.26 (m, 3H), 4.94 (ddd, J=49.1, 6.8, 4.0 Hz, 1H), 3.41–3.11 (m, 2H), 2.31 (d, J=4.8 Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$): δ=206.64 (d, J=26.3 Hz), 133.33, 129.32, 128.42, 127.60, 94.23 (d, J=186.1 Hz), 28.28 (d, J=22.4 Hz), 26.71. ^{19}F NMR (254 MHz, $CDCl_3$): δ=−107.36 to −107.76 (m). HRMS (FAB): m/z [M+Na$^+$] calcd for $C_{10}H_{11}FONaSe$: 268.9857; Found: 268.9855.

4.20. 3-Fluoro-2-methyl-2-(phenylselenyl)propionaldehyde (5e)

^{1}H NMR (270 MHz, $CDCl_3$): δ=9.32 (d, J=1.6 Hz, 1H), 7.53–7.29 (m, 5H), 4.62 (dd, J=47.4, 9.6 Hz, 1H), 4.53 (dd, J=47.4, 9.6 Hz, 1H), 1.52 (s, 3H). ^{13}C NMR (68 MHz, $CDCl_3$): δ=191.77 (d, J=2.2 Hz), 138.02, 130.00, 129.30, 123.49, 83.46 (d, J=177.7 Hz), 54.57 (d, J=17.8 Hz), 16.06 (d, J=3.4 Hz). ^{19}F NMR (254 MHz, $CDCl_3$): δ=−141.05 (t, J=47.4 Hz). HRMS (FAB): m/z [M+Na$^+$] calcd for $C_{10}H_{11}FONaSe$: 268.9857; Found: 268.9857.

4.21. 2-Fluoro-2-methyl-3-(phenylselenyl)propionaldehyde (6e)

^{1}H NMR (270 MHz, $CDCl_3$): δ=9.74 (d, J=4.5 Hz, 1H), 7.58–7.53 (m, 2H), 7.3–7.25 (m, 3H), 3.30–3.21 (m, 2H), 1.51 (d, J=21.4 Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$): δ=200.39 (d, J=39.7 Hz), 133.30, 129.51, 129.15, 127.6, 98.11 (d, J=178.3 Hz), 33.18 (d, J=24.0 Hz), 21.29 (d, J=23.5 Hz). ^{19}F NMR (254 MHz, $CDCl_3$): δ=−79.66 to −80.11 (m).

4.22. 4-Benzyl-3-[3-fluoro-2-(phenylselenyl)propanoyl]-oxazolidin-2-one (5f)

Diastereomer a (major): ^{1}H NMR (270 MHz, $CDCl_3$): δ=7.66–7.62 (m, 2H), 7.42–7.25 (m, 8H), 5.25 (td, J=10.1, 5.1 Hz, 1H), 4.94–4.51 (m, 3H), 4.26–4.16 (m, 2H), 3.33 (dd, J=13.4, 3.5 Hz, 1H), 2.81 (dd, J=13.4, 9.7 Hz, 1H). ^{13}C NMR (68 MHz, $CDCl_3$): δ=168.94 (d, J=1.7 Hz), 152.82, 136.63, 134.93, 129.44, 129.38, 129.20, 128.93, 127.33, 124.60, 81.58 (d, J=177.2 Hz), 66.19, 55.27, 38.12 (d, J=19.6 Hz), 37.62. ^{19}F NMR (254 MHz, $CDCl_3$): δ=−128.31 (dt, J=46.2, 9.1 Hz). HRMS (FAB): m/z [M+Na$^+$] calcd for $C_{19}H_{18}FNO_3$-NaSe: 430.0334; Found: 430.0343.

Diastereomer b (miner): ^{1}H NMR (270 MHz, $CDCl_3$): δ=7.62–7.59 (m, 2H), 7.43–7.17 (m, 8H), 5.37 (td, J=10.2, 4.8 Hz, 1H), 4.88 (dt, J=47.1, 10.2 Hz, 1H), 4.73–4.51 (m, 2H), 4.27–4.18 (m, 2H), 3.23 (dd, J=13.7, 3.3 Hz, 1H), 2.86 (dd, J=13.7, 9.1 Hz, 1H). ^{13}C NMR (68 MHz, $CDCl_3$): δ=169.07 (d, J=1.7 Hz), 152.74, 136.57, 134.70, 129.45, 129.38, 129.21, 128.87, 127.33, 124.76, 81.64 (d, J=177.2 Hz), 66.15, 55.43, 38.57 (d, J=19.6 Hz), 37.80. ^{19}F NMR (254 MHz, $CDCl_3$): δ=−128.41 (dt, J=47.1, 9.1 Hz). HRMS (FAB): m/z [M+Na$^+$] calcd for $C_{19}H_{18}FNO_3NaSe$: 430.0334; Found: 430.0323.

4.23. 4-Benzyl-3-[3-fluoro-2-(phenylselenyl)butanoyl]-oxazolidin-2-one (5g)

Diastereomer a (major): ^{1}H NMR (270 MHz, $CDCl_3$): δ=7.66–7.62 (m, 2H), 7.37–7.29 (m, 8H), 5.19–4.96 (m, 2H), 4.79–4.70 (m, 1H), 4.29–4.14 (m, 2H), 3.29 (dd, J=13.4, 3.5 Hz, 1H), 2.75 (dd, J=13.4, 9.7 Hz, 1H), 1.60 (dd, J=24.4, 5.8 Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$): δ=169.28 (d, J=1.7 Hz), 152.93, 135.93, 135.01, 129.40, 129.23, 129.13, 128.92, 127.31, 125.57, 90.17 (d, J=171.6 Hz), 66.08, 55.29, 44.25 (d, J=20.1 Hz), 37.54, 18.90 (d, J=22.4 Hz). ^{19}F NMR (254 MHz, $CDCl_3$): δ=−87.65 to −88.15 (m). HRMS (FAB): m/z [M+H$^+$] calcd for $C_{20}H_{21}FNO_3Se$: 422.0671; Found: 422.0663.

Diastereomer b (miner): ^{1}H NMR (270 MHz, $CDCl_3$): δ=7.63–7.60 (m, 2H), 7.40–7.16 (m, 8H), 5.33–5.03 (m, 2H), 4.60–4.52 (m, 1H), 4.16–4.03 (m, 2H), 3.20 (dd, J=13.5, 3.3 Hz, 1H), 2.84 (dd, J=13.5, 8.9 Hz, 1H), 1.59 (dd, J=24.1, 6.1 Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$): δ=169.34 (d, J=2.2 Hz), 152.75, 136.11, 136.04, 134.75, 129.40, 129.16, 128.80, 127.24, 125.55, 90.09 (d, J=171.6 Hz), 65.91, 55.32, 44.35 (d, J=20.1 Hz), 37.73, 18.95 (d, J=22.4 Hz). ^{19}F NMR (254 MHz, $CDCl_3$): δ=−86.65 to −87.14 (m). HRMS (FAB): m/z [M+Na$^+$] calcd for $C_{20}H_{20}FNO_3NaSe$: 444.0490; Found: 444.0498.

4.24. Diethyl [2-fluoro-1-(phenylselenyl)ethyl]-phosphonate (8a)

^{1}H NMR (270 MHz, $CDCl_3$): δ=7.71–7.66 (m, 2H), 7.37–7.28 (m, 3H), 4.96–4.57 (m, 2H), 4.28–4.12 (m, 4H), 3.46–3.28 (m, 1H), 1.38–1.31 (m, 6H). ^{13}C NMR (68 MHz, $CDCl_3$): δ=134.91, 129.23, 128.53, 127.93, 81.81 (d, J=177.7 Hz), 63.19 (dd, J=29.1, 6.7 Hz), 38.28 (dd, J=145.9, 19.6 Hz), 16.51 (dd, J=6.1, 3.4 Hz). ^{19}F NMR (254 MHz, $CDCl_3$): δ=−132.63 to −133.15 (m). HRMS (FAB): m/z [M+Na$^+$] calcd for $C_{12}H_{18}FO_3PNaSe$: 363.0041; Found: 363.0042.

4.25. 2-Fluoro-1-(phenylselenyl)ethyl methyl sulfone (8b)

^{1}H NMR (270 MHz, $CDCl_3$): δ=7.77–7.75 (m, 2H), 7.40–7.31 (m, 3H), 5.24–4.73 (m, 2H), 4.30–4.18 (m, 1H), 3.11 (s, 3H). ^{13}C NMR (68 MHz, $CDCl_3$): δ=135.64, 129.48, 129.47, 125.88, 81.69 (d, J=177.2 Hz), 63.80 (d, J=19.0 Hz), 40.81 (d, J=6.1 Hz). ^{19}F NMR (254 MHz, $CDCl_3$): δ=−133.62 (td, J=48.0, 23.1 Hz). HRMS (FAB): m/z [M+Na$^+$] calcd for $C_9H_{11}FO_2SNaSe$: 304.9527; Found: 304.9525.

4.26. 4-Benzyl-3-(3-fluoro-2-butenoyl)-oxazolidin-2-one (9)

Hydrogen peroxide (35%, ca. 1.2 equiv) was added to a solution of **5g** (87 mg, diastereomixture) in CH_2Cl_2 (3 ml) at ambient temperature. The solution was stirred for 7 h, treated with 1 M aq $Na_2S_2O_3$, and extracted with two portions of CH_2Cl_2. The combined extracts were washed with brine and dried over anhydrous sodium sulfate. After the removal of the solvent by evaporation, the residue was purified by column chromatography on silica gel (hexane/AcOEt=4/1) to provide a pure **9** (10 mg, yield: 18%).

^{1}H NMR (270 MHz, $CDCl_3$): δ=7.37–7.21 (m, 5H), 6.68 (dq, J=32.1, 0.7 Hz, 1H), 4.77–4.68 (m, 1H), 4.20–4.17 (m, 2H), 3.35 (dd, J=13.2, 3.0 Hz, 1H), 2.78 (dd, J=13.2, 9.6 Hz, 1H), 2.14 (dd, J=16.8, 0.7 Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$): δ=170.87 (d, J=290.1 Hz), 161.21 (d, J=1.7 Hz), 153.22, 135.21, 129.34, 128.85, 127.23, 98.22, 66.05, 55.17, 37.94, 19.95 (d, J=25.7 Hz). ^{19}F NMR (254 MHz, $CDCl_3$): δ=6.83 (dq, J=32.1, 16.8 Hz). HRMS (FAB): m/z [M+H$^+$] calcd for $C_{14}H_{15}FNO_3$: 264.1036; Found: 264.1036.

4.27. Ethyl 2-fluoromethyl-4-pentenoate (10)

The solution of AIBN (17 mg) in benzene (1 ml) was added to a solution of **2a** (55 mg) and allyl tri-*n*-butyltin (153 mg) in benzene (4 ml) at ambient temperature, and then the solution was stirred under reflux for 2 h. After the removal of the solvent by evaporation, the residue was purified by column chromatography on silica gel (hexane/AcOEt=20/1) to provide a pure **10** (24 mg, yield: 75%).

^{1}H NMR (270 MHz, $CDCl_3$): δ=5.83–5.68 (m, 1H), 5.15–5.07 (m, 2H), 4.74–4.42 (m, 2H), 4.19 (q, J=7.3 Hz, 2H), 2.91–2.75 (m, 1H),

2.51–2.29 (m, 2H), 1.27 (t, J=7.3 Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$): δ=172.07 (d, J=5.6 Hz), 138.89, 117.72, 82.78 (d, J=170.5 Hz), 60.88, 45.79 (d, J=20.1 Hz), 31.86 (d, J=6.7 Hz), 14.30. ^{19}F NMR (254 MHz, $CDCl_3$): δ=−146.71 (td, J=46.2, 18.5 Hz). HRMS (EI): m/z [M^+] calcd for $C_8H_{13}FO_2$: 160.0900; Found: 160.0895.

4.28. Ethyl 4-butoxy-2-(fluoromethyl)butanoate (11)

A solution of **2a** (27 mg) and *n*-butyl vinyl ether (205 mg) in CH_2Cl_2 (10 ml) was bubbled with N_2 at ambient temperature for 15 min, and then photolyzed for 60 min with 6-W low-pressure mercury-vapor lamp. The reaction was conducted using a quartz vessel. After the photolysis, the resulting solution was evaporated under vacuum and the residue was purified by HPLC (Develosil ODS-5, MeCN as eluent) to provide pure products **11** (4.4 mg, yield: 20%).

^{1}H NMR (270 MHz, $CDCl_3$): δ=4.74–4.63 (m, 1H), 4.57–4.46 (m, 1H), 4.18 (q, J=7.1 Hz, 2H), 3.50–3.36 (m, 4H), 3.00–2.83 (m, 1H), 2.06–1.91 (m, 1H), 1.86–1.72 (m, 1H), 1.59–1.25 (m, 7H), 0.91 (t, J=7.4 Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$): δ=172.65 (d, J=5.0 Hz), 83.56 (d, J=170.5 Hz), 70.81, 67.87, 60.83, 43.61 (d, J=19.7 Hz), 31.81, 27.87 (d, J=5.6 Hz), 19.41, 14.28, 14.00. ^{19}F NMR (254 MHz, $CDCl_3$): δ=−145.03 (td, J=46.0, 20.3 Hz). HRMS (FAB): m/z [M+H^+] calcd for $C_{11}H_{22}FO_3$: 221.1553; Found: 221.1558.

4.29. Ethyl 2-(fluoromethyl)decanoate (12)

A solution of **2a** (27 mg) and 1-octene (230 mg) in CH_2Cl_2 (10 ml) was bubbled with N_2 at ambient temperature for 15 min, and then photolyzed for 75 min with 6-W low-pressure mercury-vapor lamp. The reaction was conducted using a quartz vessel. After the photolysis, the resulting solution was evaporated under vacuum and the residue was purified by HPLC (Develosil ODS-5, MeCN as eluent) to provide pure products **12** (3.8 mg, yield: 16%).

^{1}H NMR (270 MHz, $CDCl_3$): δ=4.73–4.37 (m, 2H), 4.19 (q, J=7.1 Hz, 2H), 2.84–2.67 (m, 1H), 1.67–1.43 (m, 2H), 1.30–1.25 (m, 16H), 0.89 (t, J=6.3 Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$): δ=173.04 (d, J=5.0 Hz), 83.59 (d, J=170.5 Hz), 60.73, 46.34 (d, J=19.6 Hz), 31.88, 29.49, 29.38, 29.26, 27.71 (d, J=6.7 Hz), 27.00, 22.73, 14.31, 14.20. ^{19}F NMR (254 MHz, $CDCl_3$): δ=−144.43 (td, J=46.2, 16.8 Hz). HRMS (FAB): m/z [M+Na^+] calcd for $C_{13}H_{25}FO_2Na$: 255.1736; Found: 255.1734.

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