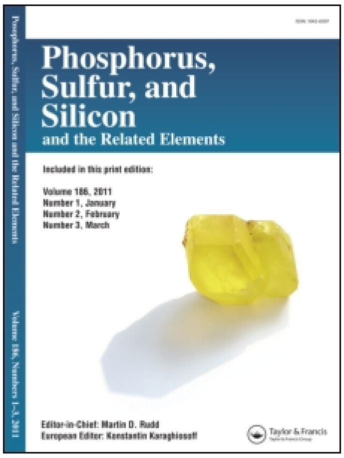

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Electrochemical Fluoro-Chalcogenation

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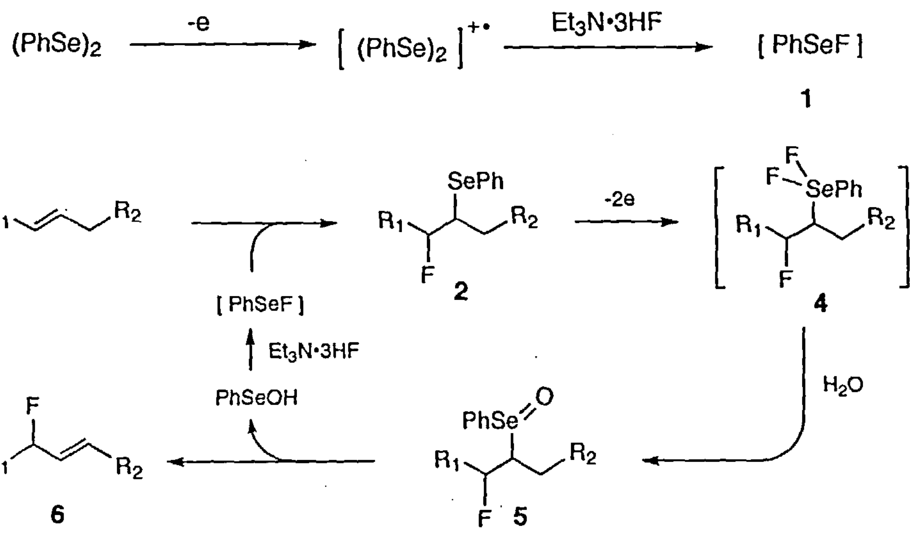
Electrochemical fluoro-chalcogenation (S, Se) of alkenes and alkynes, and recycle use of *in situ* generated PhSeF for allylic fluorination are discussed.

Introduction of fluorine-functionality into organic molecules is a subject of current interests in synthetic fluorine chemistry. Organo-chalcogenes such as sulfur and selenium have potentially versatile reactivities and thus should promote transformations of fluorinated organic molecules. Here, we report a new electrochemical method for introduction of both fluorine and chalcogen functionalities into olefins and further transformations of the products by the use of characteristic reactivities of chalcogene atoms.

Benzene selenenyl and sulfenyl halides (PhMX, M : Se, S, X = Cl, Br) are well known. However, the corresponding fluorides PhSeF or PhSF have not yet been studied in details. In particular, PhSeF must be a very strong selenenylating reagent. Generation of the active reagents has been proposed by several groups, which consists of systems such as AgF-PhSeBr, AgF-R_2NSePh and XeF_2-$(PhSe)_2$.



Electrochemical oxidation of $(PhSe)_2$ can generate an electron-deficient intermediate $[(PhSe)_2]^+$ which reacts with HF leading to [PhSeF]. Likewise, a combination of $(PhS)_2$ and $Et_3N•3HF$ would give [PhSF].

Electrochemical reaction was conducted in a CH_2Cl_2-$Et_3N•3HF$-olefin system in an undivided cell using Pt-Pt ($2 \times 3 cm^2$)as electrodes. A constant current of 0.03A was passed at 0°C until $(PhSe)_2$ was consumed (4 F/mol). The result of the reaction is summarized in Table **1**. The yields were dependent on the types of the substates. For example, both cyclic and cyclic aliphatic olefins reacted smoothly to give **2** in good yields. However, olefins such as ethyl 4-pentenoate and aryl allyl ether provided mainly the corresponding alcohols. Formation of **2** from methyl acrylate was failed because of the less reactivity of the electron-deficient olefin.

The addition of **1** to alkynes also gives the corresponding (E)-olefins **3** exclusively.

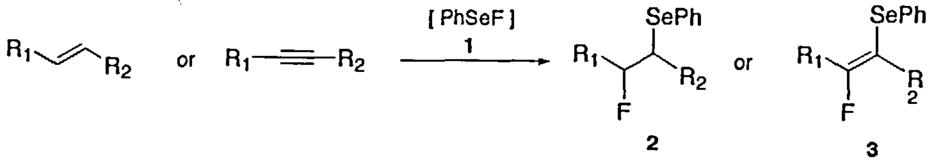


Table 1 Fluoro-selenenylation of alkenes and alkynes

Entry	R_1	R_2	Yield (%) of product[a] 2	Yield (%) of product[a] 3
1	— $(CH_2)_3$ —		60^b	
2	— $(CH_2)_4$ —		54^b	
3	— $(CH_2)_6$ —		$78^{b,c}$	
4	— $(CH_2)_{10}$ —		$47^{b,c}$	
5	H	Bu	$.63^d$	
6	H	$(CH_2)_5CH_3$	65^e	
7	H	$(CH_2)_9CH_3$	50^f	
8	$CH_3(CH_2)_4$	$(CH_2)_4CH_3$		70^b
9	Ph	Bu		51^b
10	Ph	Me		35^b
11	Ph	Ph		10^b
12	Ph	H		10^b

[a] For entries1~6, yields were obtained by ^{19}F NMR. For entries 7~12, isolated yields based on $(PhSe)_2$ [b] *trans*- Isomer was a major product. [c] 6 eq. of olefin was used. [d] Regioisomer (2-F:1-F) = 95:5 [e] Regioisomer (2-F:1-F) = 94:6 [f] Regioisomer (2-F:1-F) = 93:7