PhSeOTf-Et₃N·3HF and PhSeSbF₆-Et₃N·3HF as new PhSe-F equivalents in the fluoroselenenvlation of acetylenes

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The novel reagents PhSeOTf-Et₃N·3HF and PhSeSbF₆-Et₃N·3HF act as PhSe-F equivalents in the fluoroselenenylation of alkynes. Oct-4-yne, cycloundecyne and cyclododecyne, as well as the unsymmetrical alkynes Ph–C=C–Me and Bu–C=C–R (R = Me, Et, 'Pr and 'Bu) give the corresponding (E)-fluoro(phenylseleno)alkenes

in preparative yields. The reagent PhSeOTf-Et, N-3HF gives a similar product composition of regioisomers to $Ph_2Se_2-XeF_2$ in addition reactions to Bu-C=C-R. This is indicative of a similar reaction mechanism of the reagents. Probably a selenirenium ion acts as an intermediate. X-Ray single crystal structure analysis of (E)-1-fluoro-2phenylselenocycloundecene confirms the *trans*-addition of [PhSe–F] to cycloundecyne.

Introduction

Various PhSe-F equivalents have been described for the selective introduction of fluorine via addition reactions to organic substrates, for example, PhSeBr-AgF-ultrasound,^{1,2} PhSeCl-AgF-MeCN,³ N-Phenylselenophthalimide (NPSP)-Py•9HF,⁴⁻⁶ NPSP-Et₃N·3HF,^{6,7} Ph₂Se₂-XeF₂^{8,9} and the electrochemical oxidation of Ph₂Se₂ in the presence of Et₃N·3HF.^{10,11} We have reported an efficient synthesis of (E)-fluoro(organylseleno)alkenes by fluoroselenenylation of alkynes by the RSe-F equivalents $R_2Se_2-XeF_2^{12,13}$ and $RSe-EMe_3-XeF_2^{14}$ (E = Si, Ge, Sn, Pb). The addition of [PhSe-F] to the unsymmetrical alkynes Bu–C=C–R (R = Me, Et, ^{*i*}Pr and ^{*i*}Bu) yields mixtures of regioisomers (Scheme 1). The product composition as a



Scheme 1 Regioisomers from the addition of Ph2Se2-XeF2 to Bu–C≡C–R.

function of the size of R has been interpreted with the assumption of an intermediate selenirenium ion C (Scheme 1) and its nucleophilic ring opening reaction by the fluoride ion.¹²

A selenirenium ion has been characterized by ¹H NMR spectroscopy in the reaction of PhSe⁺ SbF₆⁻ with but-2-yne.¹⁵ If selenirenium ions are indeed intermediates in the fluoroselenenylation reactions of alkynes, ions generated from $PhSe^+ SbF_6^-$ and R-C=C-R should also react with external fluoride forming fluoro(phenylseleno)alkenes. Such a reaction should give, with Bu-C=C-R, a similar product composition of regioisomers as the reaction with Ph₂Se₂-XeF₂. By combination of such strong benzeneselenenylation reagents as PhSeSbF₆,¹⁵ PhSeOTf,¹⁶ or PhSeOTs¹⁷ with suitable fluoride sources, new, highly reactive selenenyl fluoride equivalents should be obtainable which do not need expensive XeF_2 . The investigation of such systems is of mechanistic and preparative interest.

Results and discussion

The reaction of $PhSe^+ X^- (X^- are anions of low nucleophilicity)$ such as SbF_6^- , TfO⁻, BF₄⁻ and TsO⁻) with alkynes in the presence of Et₃N·3HF was investigated. The mild F^- donor Et₃N· 3HF is easy to handle and has already been successfully used in numerous syntheses.18

The seleno electrophiles are generated by bromination of Ph₂Se₂ with Br₂ in CH₂Cl₂, and subsequent reaction of the so obtained PhSeBr with the silver salts $Ag^+ X^- (X^-: SbF_6^-, TfO^-, BF_4^-, TsO^-)$. The thus formed PhSe⁺ X⁻ then reacts at 0 °C in the presence of Et₃N·3HF with oct-4-yne 1 as model alkyne, forming the expected 4-fluoro-5-phenylselenooct-4-ene 9. The relative molar amounts used were PhSe⁺ X⁻:octyne:Et₃N·3HF = 1:1:3, see Scheme 2.¹⁵⁻¹⁷



Scheme 2 Reactions of PhSeX-Et₃N·3HF (X⁻: SbF₆⁻, TfO⁻, BF₄⁻, TsO⁻) with oct-4-yne.

This reaction as a synthetic method is accompanied by some problems. In almost all experiments the undesired by product bromo(phenylseleno)oct-4-ene 10 is detected by ⁷⁷Se NMR spectroscopy ($\delta = 398.2$ ppm): with AgSbF₆ up to 6%, with AgOTf 8-16% and with AgBF₄ and AgOTs even up to 60%, as measured by ⁷⁷Se NMR signal integration. Compound 10 was independently synthesized by addition of PhSeBr to oct-4-yne in CH₂Cl₂ (⁷⁷Se NMR: δ = 398.8 ppm). This method for the preparation of PhSe⁺ X⁻ is probably incomplete due to the low

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solubility of the silver salts in CH_2Cl_2 . Unchanged PhSeBr can then react to give **10**. Yields with AgSbF₆ are moderate, 50–56%, with AgOTf somewhat higher, 64–80%. In other publications ArSeOTf, prepared from ArSeBr + AgOTf in alcohols or MeCN as solvents, is successfully used in reactions with olefins.¹⁹⁻²¹ But these solvents cannot be used for our reaction since they could interfere directly with the reaction. Alkenes undergo oxyselenenylation with alcohols^{19,20} and amidoselenenylation with MeCN.²¹ We obtained a complex mixture without fluoroselenenylation in the reaction of PhSeOTf with Et₃N·3HF and **1** in MeCN.

Bromine and the silver-free preparation of benzeneselenenyl triflate PhSeOTf from benzeneseleninic anhydride (PhSeO)₂O, Ph₂Se₂ and trifluoromethanesulfonic acid anhydride Tf₂O in CH₂Cl₂ according to literature²² is an improvement for our method (Scheme 3). PhSeOTf thus obtained *in situ* and in

 $(PhSeO)_{2}O + 2 Ph_{2}Se_{2} + 3 Tf_{2}O \xrightarrow{CH_{2}Cl_{2}} 6 PhSeOTf$

PhSeOTf, Et₃N·3HF



Scheme 3 Reactions of PhSeOTf-Et₃N·3HF with alkynes.

homogenous solution reacts with oct-4-yne in the presence of $Et_3N\cdot 3HF$ to give fluoro(phenylseleno)octene 9 in good yields and high purity. Thus the PhSeOTf–Et₃N·3HF reagent was reacted with a number of other alkynes: cycloundecyne 2, cyclododecyne 3, unsymmetrical alkynes Ph–C=C–Me 4, and Bu–C=C–R² 5–8 (R² = Me, Et, 'Pr, 'Bu). A 50% excess of the selenium reagent (molar ratio PhSeOTf:alkyne:Et₃N·3HF = 1.5:1:3) was used. In all cases the synthesis of fluoro(phenylseleno)alkenes 9, 13, and 14a/b–17a/b as well as of fluoro-(phenylseleno)cycloalkenes 11 and 12 was successful, Scheme 3.

The PhSeOTf–Et₃N·3HF reagent shows somewhat higher yields and shorter rection times in the fluoroselenenylation of acetylenes than the earlier described reagents PhSeBr–AgF–ultrasound,² NPSP–Et₃N·3HF,^{6,7} and the electrochemical oxidation of Ph₂Se₂ in presence of Et₃N·3HF.^{10,11} The yields of products from individual compounds follow the trend of the Ph₂Se₂–XeF₂ reagent.¹²

High resolution mass spectra proved the assumed elemental composition of the synthesized compounds. NMR spectra of the products agree very well with those obtained from the Ph₂Se₂-XeF₂ and PhSe-EMe₃-XeF₂ reagents.^{12,14} **14a/b**-**17a/b** were analyzed as mixtures. The assignment of the ¹³C, ¹⁹F and ⁷⁷Se NMR spectra have been reported by us before.²³ We can assign the ⁷⁷Se and ¹⁹F signals to the components of mixtures of F/Se-compounds by means of new ⁷⁷Se, ¹⁹F{¹H} HETCOR 2D NMR measurements.²⁴

Of interest is the distribution of regioisomers **A** and **B** in the addition to $Bu-C=C-R^2$ ($R^2 = Me$, Et, 'Pr, 'Bu). The **A:B** ratio is close to 1:1 with 51:49 for Bu/Me and 55:45 for Bu/Et, but increases to 76:24 for Bu/Pr and particularly to 94:6 for Bu/Bu. The **A:B** ratios were measured by ¹⁹F and ⁷⁷Se NMR signal integrations, and both values give the same results. The strong similarity of the **A:B** ratio for both reagents PhSeOTf–Et₃N· 3HF and Ph₂Se₂–XeF₂ shows that the mechanisms of both reactions are closely related. For both reagents one can assume the intermediate formation of a selenirenium ion. Nucleophilic attack of the fluoride ion occurs preferentially at the Bu side in the case of increased steric hindrance by R² and **A** becomes the main isomer (path a of Scheme 3).

X-Ray single crystal structure of 1-fluoro-2phenylselenocycloundecene 11

X-Ray structures of the (E)-cycloundecene ring have been published only for derivatives of cycloundecene-1-carboxylic acid.²⁵ The X-ray crystal structure analysis of fluoro(phenylseleno)cycloundecene 11 is shown in Figure 1. It establishes that the fluoroselenenylation of cycloalkynes is also a transaddition, [dihedral angles F-C17-C7-Se 179.9(4)°, C16-C17-C7–C8 $-177.9(8)^{\circ}$]. We have already reported on the transaddition of [PhSe-F] to acyclic alkynes with Ph2Se2-XeF213 and PhSe-EMe₃-XeF₂¹⁴ (E = Si, Ge, Sn, Pb) and the X-ray structures of the products. C-F, C=C and C-Se bonds in the central F-C=C-Se molecular fragment of 11 are shorter than in acyclic fluoro seleno alkenes.13,14 The large C-C-C angle at the fluorinated C atom [C7-C17-C16 129.5(6)°] and the small F-C-C angle towards the alkyl chain [F-C17-C16 111.1(5)°] are characteristic for such fluoro alkenes.^{13,14} The general feature of this molecule is that the best plane of the $(CH_2)n$ ring is perpendicular to the F–C=C–Se plane. Viewed in the direction of the C-F bond, a triangular form is visible that is only interrupted at the corners by the C8-C9 and C15-C16 bonds. The phenyl ring plane is situated opposite to the eleven-membered ring and also almost perpendicular to the F-C=C-Se plane [C1-Se-C7-C17 88.3(5)°]. In contrast to an acyclic fluoro(arylseleno) alkene¹⁴ the phenyl ring is only slightly torsioned against the Se-C7 bond [C7-Se-C1-C2 9.7(4)°]. The enlargement of almost all bond angles at the sp³-hybridized C atoms of the ring as compared to 109.45° indicates considerable ring strain. The dihedral angles in the ring show six gauche conformations with angles around C17-C16-C15-C14 -57.0(11)°, C15-C16-C17-F -68.5(7)°]. Along two bonds (C10-C11 and C13-C14) an anti conformation with angles about 155° is observed. Finally, along two bonds (C9-C10 and C14-C15) an unfavorable almost eclipsed conformation exists [C8-C9-C10-C11 99.2(10)°, C13-C14-C15-C16 102.2(11)°]. If the elevenmembered ring is viewed from the double bond, the atoms C11, C12 and C13 appear almost linear and parallel to the C=C bond.

The planar-chiral *trans*-cycloalkene 11 is a racemic mixture. The enantiomers crystallize separately. The measured crystal contained the S enantiomer according to the rules of chirality.^{26,27}



Empirical formula Molecular weight	C ₁₇ H ₂₃ FSe 325.32
Temperature	−150 °C
Crystal system	Monoclinic
5	a = 709.9(2) pm
	b = 635.8(1) pm
	c = 1676.6(3) pm
	$\beta = 90.42(1)^{\circ}$
Space group	P2 ₁
Volume	$756.8 \times 10^{6} \text{ pm}^{3}$
Ζ	2
Calculated density	1.428 g cm^{-3}
Absorption coefficient	2.48 mm^{-1}
F(000)	336.0
Crystal size	$0.3 \times 0.3 \times 0.2 \text{ mm}$
Theta range for data collection	1.21-30.93°
Max. and min. transmission	1.000/0.621
Data restraints/parameters	4699/1/175
Goodness-of-fit on F^2	1.070
Final R values $[I \ge 2\sigma(I)]$	0.0646
<i>R</i> indices (all data)	0.0675
Absolute structure parameter	0.1028

 $\delta = 0$), ⁷⁷Se at 76.20 MHz (⁷⁷Se reference: 60 vol% Me₂Se in CDCl₃, $\delta = 0$).

Ph₂Se₂, (PhSeO)₂O, Tf₂O, AgBF₄ (Fluka), Et₃N·3HF, AgSbF₆, AgOTf (Aldrich), AgOTs, **1** (Merck) and **4** (Acros) are commercial products. **5**,²⁸ **6**,²⁹ 7^{30} and **8**³¹ were obtained following literature procedures. Cycloalkynes **2** and **3** were prepared by thermolysis of the corresponding cycloalkeno-1,2,3-selenadiazole over copper powder.³²

X-Ray crystal structure determination

A suitable crystal was mounted on a Bruker SMART CCD 1000 TM diffractometer and cooled to -150 °C. Mo-Ka ($\lambda = 71.1069$ pm) radiation, graphite monochromator, scan width of 0.3° in ω , exposure time of 20 s/frame, and detector crystal distance 40 mm were used. A full shell of data up to $2\theta = 62^{\circ}$ was measured by 1800 frames. Data were reduced to intensities, corrected for background, and a semiempirical absorption correction was applied (SADABS). The structure was solved and refined by use of the SHELXL programs.^{33,34} For experimental details of the crystal structure see Table 1.†

Reactions of 1 with PhSeX [PhSeBr + AgX] and Et₃N·3HF: general procedure

A 50 ml Schlenk vessel containing 2 mmol Ph₂Se₂ (624 mg) was filled with 20 ml dry CH₂Cl₂ on a vacuum line by cooling to -196 °C. Br₂ (2 ml, 1 M in CCl₄, 2 mmol) was injected at room temperature under argon, and the mixture was magnetically stirred for 15 min. The silver salt AgX (4 mmol; X⁻: SbF₆⁻, TfO⁻, BF₄⁻, TsO⁻) was added at 0 °C under exclusion of moisture and the reaction was stirred for 30 min at this temperature. Into this dark green suspension simultaneously 12 mmol Et₃N· 3HF (1.93 g) and 4 mmol oct-4-yne 1 (441 mg) were injected, and the color changed immediately to light yellow. The mixture was further stirred for 1 h at 0 °C and 3 h at room temperature, H₂O (50 ml) was added. AgBr was removed by filtration of the mixture over Celite and washing with 60 ml Et₂O. The aqueous solution was extracted twice with 50 ml Et₂O, and the organic layers were washed consecutively with 50 ml H₂O, 50 ml NaHCO₃ solution, 50 ml H₂O and 50 ml saturated NaCl solution, and dried over Na2SO4. Colorless oils were obtained after removal of the solvent and chromatography through a 10 cm long, 2 cm diameter silica gel column eluting with hexane.



Fig. 1 ORTEP-representation of the molecular structure of (*E*)-1-fluoro-2-phenylselenocycloundecene 11 (thermal ellipsoids of 40% probability, viewed from direction of the phenyl group (above) and along the C–F bond (below). Selected bond lengths/pm and angles/°: Se–C7 190.6(6), Se–C1 190.7(4), F–C17 135.3(7), C7–C17 126.8(9), C7–C8 153.4(11), C16–C17 146.1(12); C7–Se–C1 99.71(19), C7–C17–C16 129.5(6), C17–C7–Se 121.6(6), C17–C7–C8 121.3(6), F–C17–C16 111.1(5); F–C17–C7–Se 179.9(4), C16–C17–C7–C8 –177.9(8), Se–C7–C8–C9 – 68.2(9), C10–C9–C8–C7 – 59.7(11), C8–C9–C10–C11 99.2(10), C12–C11–C10–C9 – 150.0(8), C13–C12–C11–C10 61.6(13), C11–C12–C13–C14 77.9(13), C12–C13–C14 –C15 –159.8(9), C13–C14–C15–C16 102.2(11), C17–C16–C15–C14 –57.0(11), C15–C16–C17–F –68.5(7), C1–Se–C7–C17 88.3(5), C7–Se–C1–C2 9.7(4).

Experimental

Mass EI spectra were measured with a Finnigan MAT 711 instrument at 80 eV electron excitation. High-resolution spectra were measured by the peak-match method using PFK as the reference substance. NMR spectra were measured with a JEOL JNM-LA 400 spectrometer in 5 mm tubes at room temperature: ¹³C at 100.40 MHz (¹³C reference TMS in CDCl₃, $\delta = 0$ ppm), ¹⁹F at 376.00 MHz (¹⁹F reference: external CFCl₃ in CDCl₃,

[†] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. CCDC reference number 184423. See http://www.rsc.org/suppdata/p1/b2/b207886b/ for crystallographic files in .cif or other electronic format.

Reaction with AgSbF₆: yield 9: 0.57-0.64 g (50–56%); sample contained 6% 10. Yield 9 if 1.25 equiv. PhSeSbF₆ used: 0.71 g (62%) with 6% 10.

Reaction with AgOTf: yield 9: 0.73–0.91 g (64–80%); sample contained 8-16% 10.

Reaction with $AgBF_4$: mixture of 9 and 10 with 60% 10. Reaction with AgOTs: mixture of 9 and 10 with 57% 10.

Reaction of alkynes 1–8 with PhSeOTf [(PhSeO)₂O + Ph₂Se₂ + Tf₂O] and Et₃N·3HF: general procedure

A 50 ml Schlenk vessel was filled with 1 mmol (360 mg) (PhSeO)₂O and 2 mmol (624 mg) Ph₂Se₂ under exclusion of moisture. Dry CH₂Cl₂ (20 ml) was condensed in at -196 °C. At 0 °C Tf₂O (3 mmol, 846 mg) was injected under argon, followed by 5 min magnetic stirring. Immediately a deep red color was formed, and the solution became opaque. Alkyne 1-8 (4 mmol) and 12 mmol Et₃N·3HF (1.93 g) were injected simultaneously, and the deep red color changed to light yellow. After 1 h of stirring at 0 °C and 4 h at room temperature (1, 5-7) or 6 h (2-4, 8), H₂O (100 ml) was added, and the aqueous solution was extracted twice with 70 ml Et₂O. The organic layer was washed consecutively with 60 ml H_2O , 60 ml NaHCO₃ solution, 60 ml H₂O, and 60 ml saturated NaCl solution, and dried over Na₂SO₄. A solution of 13 was shaken with 1 g NaBH₄ in 20 ml H₂O until the yellow color disappeared, then washed with twice 100 ml H₂O. Further treatment was similar to that described above.

(*E*)-4-Fluoro-5-phenylselenooct-4-ene 9. Yield (colorless oil): 0.8 g (70%); HR-MS: m/z M⁺: 286.06530 (calculated for C₁₄H₁₉FSe: 286.06359, related to ⁸⁰Se); $\delta_{\rm C}$ (CDCl₃) 13.51 (C-1), 20.42 (C-2), 33.30 (${}^2J_{\rm FC}$ = 28.1 Hz, C-3), 163.34 (${}^1J_{\rm FC}$ = 267.1 Hz, C-4), 109.84 (${}^2J_{\rm FC}$ = 20.7 Hz, C-5), 32.45 (${}^3J_{\rm FC}$ = 5.8 Hz, C-6), 21.79 (${}^4J_{\rm FC}$ = 1.7 Hz, C-7), 13.41 (C-8); Ph: 130.93 (${}^4J_{\rm FC}$ = 1.7 Hz, *i*-C), 130.44 (${}^2J_{\rm Se,C}$ = 11.6 Hz, *o*-C), 129.15 (*m*-C), 126.40 (*p*-C); $\delta_{\rm F}$ -91.84 (t, ${}^3J_{\rm FH}$ = 23.0 Hz); $\delta_{\rm Se}$ 335.1 (${}^3J_{\rm Se,F}$ = 16.6 Hz).

(*E*)-1-Fluoro-2-phenylselenocycloundecene 11. Yield: 0.65 g (50%), colorless crystals, mp 52.5–53.5 °C (MeOH); HR-MS: *m/z* M⁺: 326.09643 (calculated for $C_{17}H_{23}FSe$: 326.09489, related to ⁸⁰Se); $\delta_{\rm C}$ (CDCl₃) 163.28 (${}^{1}J_{\rm FC}$ = 265.3 Hz, C-1), 112.15 (${}^{2}J_{\rm FC}$ = 20.2 Hz, C-2), 31.38 (${}^{3}J_{\rm FC}$ = 5.0 Hz, C-3), 31.43 (${}^{2}J_{\rm FC}$ = 28.9 Hz, C-11), 24.50 ($J_{\rm FC}$ = 1.7 Hz), 24.70, 25.46 ($J_{\rm FC}$ = 2.1 Hz), 25.71, 26.03 ($J_{\rm FC}$ = 2.1 Hz), 26.31, 26.69; Ph: 130.92 (${}^{4}J_{\rm FC}$ = 1.2 Hz, *i*-C), 130.55 (${}^{2}J_{\rm SeC}$ = 12.0 Hz, *o*-C), 129.14 (*m*-C), 126.46 (*p*-C); $\delta_{\rm F}$ – 89.93 (s); $\delta_{\rm Se}$ 337.4 (s).

E)-1-Fluoro-2-phenylselenocyclododecene 12. Yield (colorless oil): 0.96 g (71%); HR-MS: m/z M⁺: 340.11355 (calculated for C₁₈H₂₅FSe: 340.11054, related to ⁸⁰Se); $\delta_{\rm C}$ (CDCl₃) 163.64 (¹J_{F,C} = 265.5 Hz, ²J_{Se,C} = 16.1 Hz, C-1), 110.01 (²J_{F,C} = 20.7 Hz, ¹J_{Se,C} = 99.7 Hz, C-2), 28.46 (³J_{F,C} = 5.0 Hz, C-3), 31.04 (²J_{F,C} = 28.9 Hz, C-12), 23.77, 23.92, 24.47, 25.29 (double intensities), 25.36 (J_{F,C} = 1.7 Hz), 25.73, 26.40; Ph: 130.69 (⁴J_{F,C} = 1.2 Hz, *i*-C), 130.55 (²J_{Se,C} = 11.6 Hz, *o*-C), 129.11 (*m*-C), 126.42 (*p*-C); $\delta_{\rm F}$ -88.32 (d, ³J_{F,H} = 22.0 Hz); $\delta_{\rm Se}$ 325.1 (³J_{Se,F} = 19.4 Hz).

(*E*)-1-Fluoro-1-phenyl-2-phenylselenoprop-1-ene 13. Yield (colorless oil): 0.31 g (27%); HR-MS: *m/z* M⁺: 292.01834 (calculated for C₁₅H₁₃FSe: 292.01665, related to ⁸⁰Se); $\delta_{\rm C}$ (CDCl₃) 157.36 (${}^{1}J_{\rm FC}$ = 258.0 Hz, ${}^{2}J_{\rm se,C}$ = 20.9 Hz, C-1), 106.28 (${}^{2}J_{\rm FC}$ = 24.0 Hz, ${}^{1}J_{\rm se,C}$ = 104.8 Hz, C-2), 18.59 (${}^{3}J_{\rm FC}$ = 7.4 Hz, C-3); Ph: 132.52 (${}^{2}J_{\rm FC}$ = 29.4 Hz, *i*-C), 128.74 (${}^{3}J_{\rm FC}$ = 4.5 Hz, *o*-C), 127.76 (*m*-C),129.29 (${}^{5}J_{\rm FC}$ = 1.2 Hz, *p*-C); SePh: 129.72 (${}^{4}J_{\rm FC}$ = 1.2 Hz, *i*-C), 131.74 (${}^{2}J_{\rm se,C}$ = 11.6 Hz, *o*-C), 129.18 (*m*-C), 127.00 (*p*-C); $\delta_{\rm F}$ -84.41 (${}^{4}J_{\rm F,H}$ = 3.4 Hz); $\delta_{\rm Se}$ 397.7 (${}^{3}J_{\rm Se,F}$ = 33.5 Hz).

(*E*)-3-Fluoro-2-phenylselenohept-2-ene 14a and (*E*)-2-fluoro-3-phenylselenohept-2-ene 14b. Yield (colorless oil): 0.73 g (67%); HR-MS: m/z M⁺: 272.04922 (calculated for C₁₃H₁₇FSe: 272.04794, related to ⁸⁰Se).

14a: $\delta_{\rm C}$ (CDCl₃) 17.75 (${}^{3}J_{\rm F,C} = 7.9$ Hz, C-1), 103.64 (${}^{2}J_{\rm F,C} = 21.5$ Hz C-2), 162.81 (${}^{1}J_{\rm F,C} = 265.9$ Hz, C-3), 30.96 (${}^{2}J_{\rm F,C} = 28.1$ Hz, C-4), 29.08 (${}^{3}J_{\rm F,C} = 0.8$ Hz, C-5), 22.14 (C-6), 13.89, C-7); Ph: 130.38 (${}^{4}J_{\rm F,C} = 2.1$ Hz, *i*-C), 130.76 (${}^{2}J_{\rm Se,C} = 11.6$ Hz, *o*-C), 129.19 (*m*-C), 126.55 (*p*-C); $\delta_{\rm F} -91.83$ (t, ${}^{3}J_{\rm F,H} = 23.1$ Hz, q, ${}^{4}J_{\rm F,H} = 3.3$ Hz); $\delta_{\rm Se}$ 378.4 (${}^{3}J_{\rm Se,F} = 18.7$ Hz).

14b: $\delta_{\rm C}$ 17.72 (${}^{7}J_{\rm F,C}$ = 31.0 Hz, C-1), 160.16 (${}^{1}J_{\rm F,C}$ = 263.8 Hz, C-2), 109.82 (${}^{2}J_{\rm F,C}$ = 20.3 Hz, C-3), 30.46 (${}^{3}J_{\rm F,C}$ = 6.2 Hz, C-4), 30.65 (${}^{4}J_{\rm F,C}$ = 1.7 Hz, C-5), 22.14 (C-6), 13.85 (C-7); Ph: 130.88 (${}^{4}J_{\rm F,C}$ = 2.1 Hz, *i*-C), 130.25 (${}^{2}J_{\rm Se,C}$ = 12.0 Hz, *o*-C), 129.16 (*m*-C), 126.37 (*p*-C); $\delta_{\rm F}$ - 84.03 (q, ${}^{3}J_{\rm F,H}$ = 17.3 Hz, t, ${}^{4}J_{\rm F,H}$ = 2.6 Hz); $\delta_{\rm Se}$ 341.3 (${}^{3}J_{\rm Se,F}$ = 15.8 Hz).

(*E*)-4-Fluoro-3-phenylselenooct-3-ene 15a and (*E*)-3-fluoro-4phenylselenooct-3-ene 15b. Yield (colorless oil): 0.79 g (69%). HR-MS: m/z M⁺: 286.06573 (calculated for C₁₄H₁₉FSe: 286.06359, related to ⁸⁰Se).

15a: $\delta_{\rm C}$ (CDCl₃) 13.63 (${}^{4}J_{\rm F,C}$ = 1.7 Hz, C-1), 24.19 (${}^{3}J_{\rm F,C}$ = 7.0 Hz, C-2), 111.41 (${}^{2}J_{\rm F,C}$ = 20.7 Hz, C-3), 162.98 (${}^{1}J_{\rm F,C}$ = 267.1 Hz, C-4), 31.13 (${}^{2}J_{\rm F,C}$ = 28.1 Hz, C-5), 29.09 (C-6), 22.14 (C-7), 13.92 (C-8); Ph: 130.99 (${}^{4}J_{\rm F,C}$ = 1.7 Hz, *i*-C), 130.40 (*o*-C), 129.15 (*m*-C), 126.38 (*p*-C); $\delta_{\rm F}$ -92.73 (t, ${}^{3}J_{\rm F,H}$ = 23.1 Hz, t, ${}^{4}J_{\rm F,H}$ = 2.5 Hz); $\delta_{\rm Se}$ 331.8 (${}^{3}J_{\rm Se,F}$ = 17.3 Hz).

15b: $\delta_{\rm C}$ 11.62 (C-1), 25.08 (${}^2J_{\rm F,C}$ = 28.9 Hz, C-2), 164.57 (${}^1J_{\rm F,C}$ = 267.1 Hz, C-3), 108.95 (${}^2J_{\rm F,C}$ = 21.1 Hz, C-4), 30.37 (${}^3J_{\rm F,C}$ = 5.8 Hz, C-5), 30.72 (${}^4J_{\rm F,C}$ = 1.7 Hz, C-6), 22.11 (C-7), 13.87 (C-8); Ph: 131.02 (${}^4J_{\rm F,C}$ = 1.7 Hz, *i*-C), 130.33 (*o*-C), 129.14 (*m*-C), 126.38 (*p*-C); $\delta_{\rm F}$ -94.10 (t, ${}^3J_{\rm F,H}$ = 22.7 Hz, t, ${}^4J_{\rm F,H}$ = 2.7 Hz); $\delta_{\rm se}$ 335.6 (${}^3J_{\rm se,F}$ = 15.8 Hz).

(*E*)-4-Fluoro-2-methyl-3-phenylselenooct-3-ene 16a and (*E*)-3-fluoro-2-methyl-4-phenylselenooct-3-ene 16b. Yield (colorless oil): 0.69 g (58%). HR-MS: m/z M⁺: 300.08224 (calculated for C₁₅H₂₁FSe: 300.07924, related to ⁸⁰Se).

16a: $\delta_{\rm C}$ (CDCl₃) 21.89 (${}^4J_{\rm F,C}$ = 2.1 Hz, C-1), 29.41 (${}^3J_{\rm F,C}$ = 7.0 Hz, C-2), 116.39 (${}^2J_{\rm F,C}$ = 18.2 Hz, C-3), 164.07 (${}^1J_{\rm F,C}$ = 268.8 Hz, C-4), 31.56 (${}^2J_{\rm F,C}$ = 28.1 Hz, C-5), 28.87 (C-6), 22.18 (C-7), 13.86 (C-8); Ph: 132.60 (${}^4J_{\rm F,C}$ = 2.1 Hz, *i*-C), 129.17 (*o*-C), 129.02 (*m*-C), 125.90 (*p*-C); $\delta_{\rm F}$ -90.51 (t, ${}^3J_{\rm F,H}$ = 23.1 Hz); $\delta_{\rm Se}$ 276.8 (${}^3J_{\rm Se,F}$ = 13.7 Hz).

16b: $\delta_{\rm C}$ 19.64 (${}^{3}J_{\rm F,C} = 0.8$ Hz, C-1), 30.51 (${}^{2}J_{\rm F,C} = 27.3$ Hz, C-2), 167.04 (${}^{1}J_{\rm F,C} = 271.3$ Hz, C-3), 107.66 (${}^{2}J_{\rm F,C} = 21.5$ Hz, C-4), 30.33 (${}^{3}J_{\rm F,C} = 6.6$ Hz, C-5), 30.72 (${}^{4}J_{\rm F,C} = 1.7$ Hz, C-6), 22.04 (C-7), 13.92 (C-8); Ph: 131.07 (${}^{4}J_{\rm F,C} = 2.1$ Hz, *i*-C), 130.31 (*o*-C), 129.15 (*m*-C), 126.34 (*p*-C); $\delta_{\rm F} -107.73$ (d, ${}^{3}J_{\rm F,H} = 30.6$ Hz, t, ${}^{4}J_{\rm F,H} = 2.7$ Hz); $\delta_{\rm Se}$ 331.1 (${}^{3}J_{\rm Se,F} = 16.6$ Hz).

(*E*)-4-Fluoro-2,2-dimethyl-3-phenylselenooct-3-ene 17a and (*E*)-3-Fluoro-2,2-dimethyl-4-phenylselenooct-3-ene 17b. Yield (colorless oil): 0.31 g (25%). HR-MS: m/z M⁺: 314.09622 (calculated for C₁₆H₂₃FSe: 314.09489, related to ⁸⁰Se).

17a: $\delta_{\rm C}$ (CDCl₃) 31.13 (${}^{4}J_{\rm F,C}$ = 4.5 Hz, C-1), 37.54 (C-2), 117.62 (${}^{2}J_{\rm F,C}$ = 14.1 Hz, ${}^{1}J_{\rm Se,C}$ = 105.7 Hz, C-3), 165.48 (${}^{1}J_{\rm F,C}$ = 275.4 Hz, ${}^{2}J_{\rm Se,C}$ = 17.0 Hz, C-4), 33.59 (${}^{2}J_{\rm F,C}$ = 29.4 Hz, C-5), 29.26 (C-6), 22.15 (C-7), 13.88 (C-8); Ph: 133.53 (${}^{4}J_{\rm F,C}$ = 2.5 Hz, *i*-C), 128.62 (${}^{2}J_{\rm Se,C}$ = 12.0 Hz, *o*-C), 129.07 (*m*-C), 125.67 (*p*-C); $\delta_{\rm F}$ - 78.82 (t, ${}^{3}J_{\rm F,H}$ = 23.4 Hz); $\delta_{\rm Se}$ 341.6 (${}^{3}J_{\rm Se,F}$ = 14.4 Hz).

17b: $\delta_{\rm C}$ 167.75 (¹ $J_{\rm F,C}$ = 270.0 Hz, C-3), 107.85 (² $J_{\rm F,C}$ = 27.7 Hz, C-4); $\delta_{\rm F}$ -84.54 (s); $\delta_{\rm Se}$ 331.1 (³ $J_{\rm Se,F}$ = 20.2 Hz).

(E)-4-Bromo-5-phenylselenooct-4-ene 10

To PhSeBr [prepared from 1 mmol Ph₂Se₂ (312 mg) and 1 mmol Br₂ (1 ml, 1 M in CCl₄)] in 10 ml CH₂Cl₂ at room temperature, oct-4-yne 1 (2 mmol, 220 mg) was added and the mixture was stirred for 2 h at room temperature. After evaporation of the solvent the product was chromatographed through a short silica gel column with hexane. Yield **10** (colorless oil): 0.64 g (92%);

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HR-MS: m/z M⁺: 345.98562 (calculated for C₁₄H₁₉BrSe: 345.98353, related to ^{80}Se and $^{79}Br); \, \delta_{\rm C} \; ({\rm CDCl_3}) \; 13.48 \; ({\rm C-1}),$ 21.30 (C-2), 40.65 (C-3), 129.48 (C-4), 129.21 (C-5), 43.29 (²J_{Se,C} = 9.5 Hz, C-6), 21.87 (C-7), 13.03 (C-8); Ph: 130.59 (i-C), 132.07 $(^{2}J_{\text{Se,C}} = 11.4 \text{ Hz}, o-\text{C}), 129.13 (m-\text{C}), 127.04 (p-\text{C}); \delta_{\text{Se}} 398.8.$

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