PhSeOTf–Et$_3$N·3HF and PhSeSbF$_6$–Et$_3$N·3HF as new PhSe–F equivalents in the fluoroselenenylation of acetylenes

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The novel reagents PhSeOTf–Et$_3$N·3HF and PhSeSbF$_6$–Et$_3$N·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, ^{i}Pr and ^{t}Bu) give the corresponding (*E*)-fluoro(phenylseleno)alkenes in preparative yields. The reagent PhSeOTf–Et$_3$N·3HF gives a similar product composition of regioisomers to Ph$_2$Se$_2$–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-2-phenylselenocycloundecene 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–Et$_3$N·3HF,[6,7] Ph$_2$Se$_2$–XeF$_2$[8,9] and the electrochemical oxidation of Ph$_2$Se$_2$ in the presence of Et$_3$N·3HF.[10,11] We have reported an efficient synthesis of (*E*)-fluoro(organylseleno)-alkenes by fluoroselenenylation of alkynes by the RSe–F equivalents R$_2$Se$_2$–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, ^{t}Bu) yields mixtures of regioisomers (Scheme 1). The product composition as a
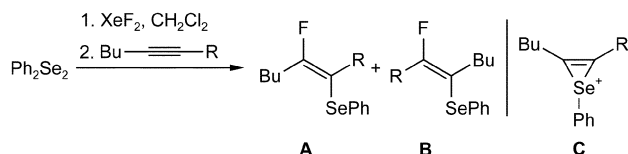
**Scheme 1** Regioisomers from the addition of Ph$_2$Se$_2$–XeF$_2$ to Bu–C≡C–R.

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 ^{1}H NMR spectroscopy in the reaction of PhSe$^+$ SbF$_6^-$ 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 Ph$_2$Se$_2$–XeF$_2$. By combination of such strong benzeneselenenylation reagents as PhSeSbF$_6$,[15] PhSeOTf,[16] or PhSeOTs[17] 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$^-$, BF$_4^-$ and TsO$^-$) with alkynes in the presence of Et$_3$N·3HF was investigated. The mild F$^-$ donor Et$_3$N·3HF is easy to handle and has already been successfully used in numerous syntheses.[18]

The seleno electrophiles are generated by bromination of Ph$_2$Se$_2$ with Br$_2$ in CH$_2$Cl$_2$, 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 Et$_3$N·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:Et$_3$N·3HF = 1:1:3, see Scheme 2.[15–17]
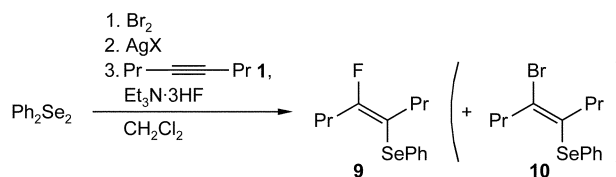

X$^-$	Yield **9** / %	% Bromide **10**
SbF$_6^-$	50-56	up to 6
TfO$^-$	64-80	8-16
BF$_4^-$, TsO$^-$		up to 60

Scheme 2 Reactions of PhSeX–Et$_3$N·3HF (X$^-$: SbF$_6^-$, TfO$^-$, BF$_4^-$, 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 ^{77}Se NMR spectroscopy (δ = 398.2 ppm): with AgSbF$_6$ up to 6%, with AgOTf 8–16% and with AgBF$_4$ and AgOTs even up to 60%, as measured by ^{77}Se NMR signal integration. Compound **10** was independently synthesized by addition of PhSeBr to oct-4-yne in CH$_2$Cl$_2$ (^{77}Se 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 $AgSbF_6$ 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 $Et_3N\cdot 3HF$ and **1** in MeCN.

Bromine and the silver-free preparation of benzeneselenenyl triflate PhSeOTf from benzeneseleninic anhydride $(PhSeO)_2O$, Ph_2Se_2 and trifluoromethanesulfonic acid anhydride Tf_2O in CH_2Cl_2 according to literature[22] is an improvement for our method (Scheme 3). PhSeOTf thus obtained *in situ* and in

Scheme 3   Reactions of PhSeOTf–$Et_3N\cdot 3HF$ with alkynes.
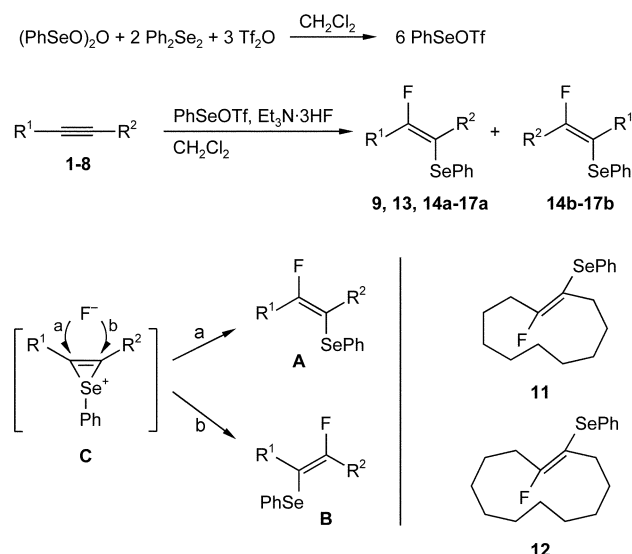
Alkyne	R¹	R²	Fluoride	Yield / %	A : B PhSeOTf/Et₃N·3HF	A : B Ph₂Se₂/XeF₂[12]
1	Pr	Pr	**9**	70		
2	$-(CH_2)_9-$		**11**	50		
3	$-(CH_2)_{10}-$		**12**	71		
4	Ph	Me	**13**	27		
5	Bu	Me	**14a/b**	67	51 : 49	53 : 47
6	Bu	Et	**15a/b**	69	55 : 45	55 : 45
7	Bu	^{i}Pr	**16a/b**	58	76 : 24	80 : 20
8	Bu	^{t}Bu	**17a/b**	25	94 : 6	100 : 0

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–$Et_3N\cdot 3HF$ 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, ^{i}Pr, ^{t}Bu). A 50% excess of the selenium reagent (molar ratio PhSeOTf:alkyne:$Et_3N\cdot 3HF$ = 1.5:1:3) was used. In all cases the synthesis of fluoro(phenyl-seleno)alkenes **9**, **13**, and **14a/b**–**17a/b** as well as of fluoro-(phenylseleno)cycloalkenes **11** and **12** was successful, Scheme 3.

The PhSeOTf–$Et_3N\cdot 3HF$ reagent shows somewhat higher yields and shorter rection times in the fluoroselenenylation of acetylenes than the earlier described reagents PhSeBr–AgF–ultrasound,[2] NPSP–$Et_3N\cdot 3HF$,[6,7] and the electrochemical oxidation of Ph_2Se_2 in presence of $Et_3N\cdot 3HF$.[10,11] The yields of products from individual compounds follow the trend of the Ph_2Se_2–XeF_2 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 Ph_2Se_2–XeF_2 and PhSe–EMe_3–XeF_2 reagents.[12,14] **14a/b**–**17a/b** were analyzed as mixtures. The assignment of the ^{13}C, ^{19}F and ^{77}Se NMR spectra have been reported by us before.[23] We can assign the ^{77}Se and ^{19}F signals to the components of mixtures of F/Se-compounds by means of new ^{77}Se,^{19}F{^{1}H} HETCOR 2D NMR measurements.[24]

Of interest is the distribution of regioisomers **A** and **B** in the addition to Bu–C≡C–R² (R² = Me, Et, ^{i}Pr, ^{t}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/^{i}Pr and particularly to 94:6 for Bu/^{t}Bu. The **A:B** ratios were measured by ^{19}F and ^{77}Se NMR signal integrations, and both values give the same results. The strong similarity of the **A:B** ratio for both reagents PhSeOTf–$Et_3N\cdot 3HF$ and Ph_2Se_2–XeF_2 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). The formation of the **B** isomer is hindered (path b of Scheme 3).

X-Ray single crystal structure of 1-fluoro-2-phenylselenocycloundecene 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(phenyl-seleno)cycloundecene **11** is shown in Figure 1. It establishes that the fluoroselenenylation of cycloalkynes is also a *trans*-addition, [dihedral angles F–C17–C7–Se 179.9(4)°, C16–C17–C7–C8 −177.9(8)°]. We have already reported on the *trans*-addition of [PhSe–F] to acyclic alkynes with Ph_2Se_2–XeF_2[13] and PhSe–EMe_3–XeF_2[14] (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) alkene[14] 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 60° [Se–C7–C8–C9 −68.2(9)°, C10–C9–C8–C7 −59.7(11)°, C13–C12–C11–C10 61.6(13)°, C11–C12–C13–C14 77.9(13)°, 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 eleven-membered 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]
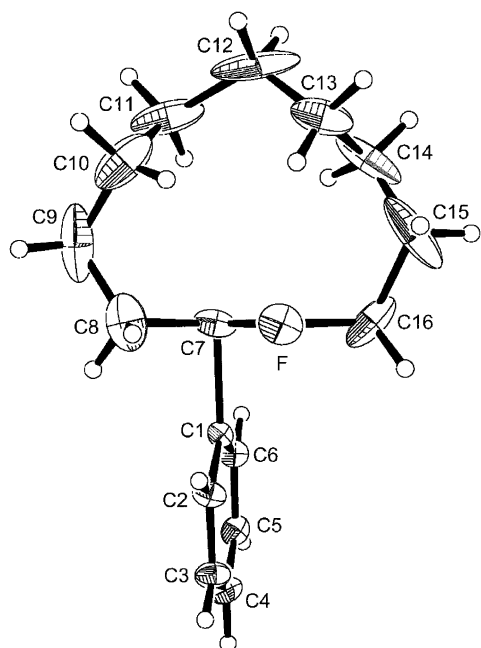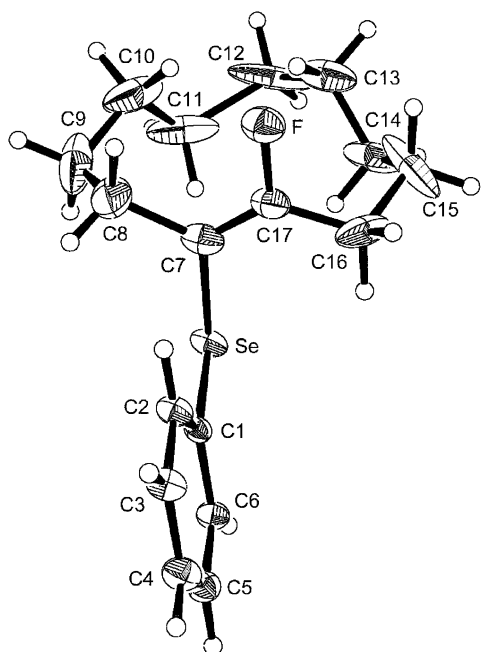
Fig. 1 ORTEP-representation of the molecular structure of (*E*)-1-fluoro-2-phenylselenocycloundecene **11** (thermal ellipsoids of 40% probability, viewed from direction of the phenyl group (above) and along the C–F bond (below). Selected bond lengths/pm and angles/°: Se–C7 190.6(6), Se–C1 190.7(4), 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: ^{13}C at 100.40 MHz (^{13}C reference TMS in CDCl$_3$, δ = 0 ppm), ^{19}F at 376.00 MHz (^{19}F reference: external CFCl$_3$ in CDCl$_3$,

Empirical formula	C$_{17}$H$_{23}$FSe
Molecular weight	325.32
Temperature	−150 °C
Crystal system	Monoclinic
	a = 709.9(2) pm
	b = 635.8(1) pm
	c = 1676.6(3) pm
	β = 90.42(1)°
Space group	$P2_1$
Volume	756.8 × 10^6 pm^3
Z	2
Calculated density	1.428 g cm^{-3}
Absorption coefficient	2.48 mm^{-1}
F(000)	336.0
Crystal size	0.3 × 0.3 × 0.2 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 [$I \geq 2\sigma(I)$]	0.0646
R indices (all data)	0.0675
Absolute structure parameter	0.1028

δ = 0), ^{77}Se at 76.20 MHz (^{77}Se reference: 60 vol% Me$_2$Se in CDCl$_3$, δ = 0).

Ph$_2$Se$_2$, (PhSeO)$_2$O, Tf$_2$O, AgBF$_4$ (Fluka), Et$_3$N·3HF, AgSbF$_6$, 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-Kα (λ = 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 2θ = 62° 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 Et$_3$N·3HF: general procedure

A 50 ml Schlenk vessel containing 2 mmol Ph$_2$Se$_2$ (624 mg) was filled with 20 ml dry CH$_2$Cl$_2$ on a vacuum line by cooling to −196 °C. Br$_2$ (2 ml, 1 M in CCl$_4$, 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$^-$: SbF$_6^-$, TfO$^-$, BF$_4^-$, 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 Et$_3$N·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, H$_2$O (50 ml) was added. AgBr was removed by filtration of the mixture over Celite and washing with 60 ml Et$_2$O. The aqueous solution was extracted twice with 50 ml Et$_2$O, and the organic layers were washed consecutively with 50 ml H$_2$O, 50 ml NaHCO$_3$ solution, 50 ml H$_2$O and 50 ml saturated NaCl solution, and dried over Na$_2$SO$_4$. 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.

Reaction with AgSbF$_6$: yield **9**: 0.57–0.64 g (50–56%); sample contained 6% **10**. Yield **9** if 1.25 equiv. PhSeSbF$_6$ 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)$_2$O + Ph$_2$Se$_2$ +Tf$_2$O] and Et$_3$N·3HF: general procedure

A 50 ml Schlenk vessel was filled with 1 mmol (360 mg) (PhSeO)$_2$O and 2 mmol (624 mg) Ph$_2$Se$_2$ under exclusion of moisture. Dry CH$_2$Cl$_2$ (20 ml) was condensed in at −196 °C. At 0 °C Tf$_2$O (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 Et$_3$N·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**), H$_2$O (100 ml) was added, and the aqueous solution was extracted twice with 70 ml Et$_2$O. The organic layer was washed consecutively with 60 ml H$_2$O, 60 ml NaHCO$_3$ solution, 60 ml H$_2$O, and 60 ml saturated NaCl solution, and dried over Na$_2$SO$_4$. A solution of **13** was shaken with 1 g NaBH$_4$ in 20 ml H$_2$O until the yellow color disappeared, then washed with twice 100 ml H$_2$O. 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 C$_{14}$H$_{19}$FSe: 286.06359, related to ^{80}Se); δ_C (CDCl$_3$) 13.51 (C-1), 20.42 (C-2), 33.30 ($^2J_{F,C}$ = 28.1 Hz, C-3), 163.34 ($^1J_{F,C}$ = 267.1 Hz, C-4), 109.84 ($^2J_{F,C}$ = 20.7 Hz, C-5), 32.45 ($^3J_{F,C}$ = 5.8 Hz, C-6), 21.79 ($^4J_{F,C}$ = 1.7 Hz, C-7), 13.41 (C-8); Ph: 130.93 ($^4J_{F,C}$ = 1.7 Hz, *i*-C), 130.44 ($^2J_{Se,C}$ = 11.6 Hz, *o*-C), 129.15 (*m*-C), 126.40 (*p*-C); δ_F −91.84 (t, $^3J_{F,H}$ = 23.0 Hz); δ_{Se} 335.1 ($^3J_{Se,F}$ = 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 ^{80}Se); δ_C (CDCl$_3$) 163.28 ($^1J_{F,C}$ = 265.3 Hz, C-1), 112.15 ($^2J_{F,C}$ = 20.2 Hz, C-2), 31.38 ($^3J_{F,C}$ = 5.0 Hz, C-3), 31.43 ($^2J_{F,C}$ = 28.9 Hz, C-11), 24.50 ($J_{F,C}$ = 1.7 Hz), 24.70, 25.46 ($J_{F,C}$ = 2.1 Hz), 25.71, 26.03 ($J_{F,C}$ = 2.1 Hz), 26.31, 26.69; Ph: 130.92 ($^4J_{F,C}$ = 1.2 Hz, *i*-C), 130.55 ($^2J_{Se,C}$ = 12.0 Hz, *o*-C), 129.14 (*m*-C), 126.46 (*p*-C); δ_F −89.93 (s); δ_{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 C$_{18}$H$_{25}$FSe: 340.11054, related to ^{80}Se); δ_C (CDCl$_3$) 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); δ_F −88.32 (d, $^3J_{F,H}$ = 22.0 Hz); δ_{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 C$_{15}$H$_{13}$FSe: 292.01665, related to ^{80}Se); δ_C (CDCl$_3$) 157.36 ($^1J_{F,C}$ = 258.0 Hz, $^2J_{Se,C}$ = 20.9 Hz, C-1), 106.28 ($^2J_{F,C}$ = 24.0 Hz, $^1J_{Se,C}$ = 104.8 Hz, C-2), 18.59 ($^3J_{F,C}$ = 7.4 Hz, C-3); Ph: 132.52 ($^2J_{F,C}$ = 29.4 Hz, *i*-C), 128.74 ($^3J_{F,C}$ = 4.5 Hz, *o*-C), 127.76 (*m*-C),129.29 ($^5J_{F,C}$ = 1.2 Hz, *p*-C); SePh: 129.72 ($^4J_{F,C}$ = 1.2 Hz, *i*-C), 131.74 ($^2J_{Se,C}$ = 11.6 Hz, *o*-C), 129.18 (*m*-C), 127.00 (*p*-C); δ_F −84.41 ($^4J_{F,H}$ = 3.4 Hz); δ_{Se} 397.7 ($^3J_{Se,F}$ = 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 C$_{13}$H$_{17}$FSe: 272.04794, related to ^{80}Se).

14a: δ_C (CDCl$_3$) 17.75 ($^3J_{F,C}$ = 7.9 Hz, C-1), 103.64 ($^2J_{F,C}$ = 21.5 Hz C-2), 162.81 ($^1J_{F,C}$ = 265.9 Hz, C-3), 30.96 ($^2J_{F,C}$ = 28.1 Hz, C-4), 29.08 ($^3J_{F,C}$ = 0.8 Hz, C-5), 22.14 (C-6), 13.89, C-7); Ph: 130.38 ($^4J_{F,C}$ = 2.1 Hz, *i*-C), 130.76 ($^2J_{Se,C}$ = 11.6 Hz, *o*-C), 129.19 (*m*-C), 126.55 (*p*-C); δ_F −91.83 (t, $^3J_{F,H}$ = 23.1 Hz, q, $^4J_{F,H}$ = 3.3 Hz); δ_{Se} 378.4 ($^3J_{Se,F}$ = 18.7 Hz).

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

(*E*)-4-Fluoro-3-phenylselenooct-3-ene 15a and (*E*)-3-fluoro-4-phenylselenooct-3-ene 15b. Yield (colorless oil): 0.79 g (69%). HR-MS: *m/z* M$^+$: 286.06573 (calculated for C$_{14}$H$_{19}$FSe: 286.06359, related to ^{80}Se).

15a: δ_C (CDCl$_3$) 13.63 ($^4J_{F,C}$ = 1.7 Hz, C-1), 24.19 ($^3J_{F,C}$ = 7.0 Hz, C-2), 111.41 ($^2J_{F,C}$ = 20.7 Hz, C-3), 162.98 ($^1J_{F,C}$ = 267.1 Hz, C-4), 31.13 ($^2J_{F,C}$ = 28.1 Hz, C-5), 29.09 (C-6), 22.14 (C-7), 13.92 (C-8); Ph: 130.99 ($^4J_{F,C}$ = 1.7 Hz, *i*-C), 130.40 (*o*-C), 129.15 (*m*-C), 126.38 (*p*-C); δ_F −92.73 (t, $^3J_{F,H}$ = 23.1 Hz, t, $^4J_{F,H}$ = 2.5 Hz); δ_{Se} 331.8 ($^3J_{Se,F}$ = 17.3 Hz).

15b: δ_C 11.62 (C-1), 25.08 ($^2J_{F,C}$ = 28.9 Hz, C-2), 164.57 ($^1J_{F,C}$ = 267.1 Hz, C-3), 108.95 ($^2J_{F,C}$ = 21.1 Hz, C-4), 30.37 ($^3J_{F,C}$ = 5.8 Hz, C-5), 30.72 ($^4J_{F,C}$ = 1.7 Hz, C-6), 22.11 (C-7), 13.87 (C-8); Ph: 131.02 ($^4J_{F,C}$ = 1.7 Hz, *i*-C), 130.33 (*o*-C), 129.14 (*m*-C), 126.38 (*p*-C); δ_F −94.10 (t, $^3J_{F,H}$ = 22.7 Hz, t, $^4J_{F,H}$ = 2.7 Hz); δ_{Se} 335.6 ($^3J_{Se,F}$ = 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 C$_{15}$H$_{21}$FSe: 300.07924, related to ^{80}Se).

16a: δ_C (CDCl$_3$) 21.89 ($^4J_{F,C}$ = 2.1 Hz, C-1), 29.41 ($^3J_{F,C}$ = 7.0 Hz, C-2), 116.39 ($^2J_{F,C}$ = 18.2 Hz, C-3), 164.07 ($^1J_{F,C}$ = 268.8 Hz, C-4), 31.56 ($^2J_{F,C}$ = 28.1 Hz, C-5), 28.87 (C-6), 22.18 (C-7), 13.86 (C-8); Ph: 132.60 ($^4J_{F,C}$ = 2.1 Hz, *i*-C), 129.17 (*o*-C), 129.02 (*m*-C), 125.90 (*p*-C); δ_F −90.51 (t, $^3J_{F,H}$ = 23.1 Hz); δ_{Se} 276.8 ($^3J_{Se,F}$ = 13.7 Hz).

16b: δ_C 19.64 ($^3J_{F,C}$ = 0.8 Hz, C-1), 30.51 ($^2J_{F,C}$ = 27.3 Hz, C-2), 167.04 ($^1J_{F,C}$ = 271.3 Hz, C-3), 107.66 ($^2J_{F,C}$ = 21.5 Hz, C-4), 30.33 ($^3J_{F,C}$ = 6.6 Hz, C-5), 30.72 ($^4J_{F,C}$ = 1.7 Hz, C-6), 22.04 (C-7), 13.92 (C-8); Ph: 131.07 ($^4J_{F,C}$ = 2.1 Hz, *i*-C), 130.31 (*o*-C), 129.15 (*m*-C), 126.34 (*p*-C); δ_F −107.73 (d, $^3J_{F,H}$ = 30.6 Hz, t, $^4J_{F,H}$ = 2.7 Hz); δ_{Se} 331.1 ($^3J_{Se,F}$ = 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 C$_{16}$H$_{23}$FSe: 314.09489, related to ^{80}Se).

17a: δ_C (CDCl$_3$) 31.13 ($^4J_{F,C}$ = 4.5 Hz, C-1), 37.54 (C-2), 117.62 ($^2J_{F,C}$ = 14.1 Hz, $^1J_{Se,C}$ = 105.7 Hz, C-3), 165.48 ($^1J_{F,C}$ = 275.4 Hz, $^2J_{Se,C}$ = 17.0 Hz, C-4), 33.59 ($^2J_{F,C}$ = 29.4 Hz, C-5), 29.26 (C-6), 22.15 (C-7), 13.88 (C-8); Ph: 133.53 ($^4J_{F,C}$ = 2.5 Hz, *i*-C), 128.62 ($^2J_{Se,C}$ = 12.0 Hz, *o*-C), 129.07 (*m*-C), 125.67 (*p*-C); δ_F −78.82 (t, $^3J_{F,H}$ = 23.4 Hz); δ_{Se} 341.6 ($^3J_{Se,F}$ = 14.4 Hz).

17b: δ_C 167.75 ($^1J_{F,C}$ = 270.0 Hz, C-3), 107.85 ($^2J_{F,C}$ = 27.7 Hz, C-4); δ_F −84.54 (s); δ_{Se} 331.1 ($^3J_{Se,F}$ = 20.2 Hz).

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

To PhSeBr [prepared from 1 mmol Ph$_2$Se$_2$ (312 mg) and 1 mmol Br$_2$ (1 ml, 1 M in CCl$_4$)] in 10 ml CH$_2$Cl$_2$ 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%);

Acknowledgements

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