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Preparation and Oxidation of α-Phenylselanyl Esters

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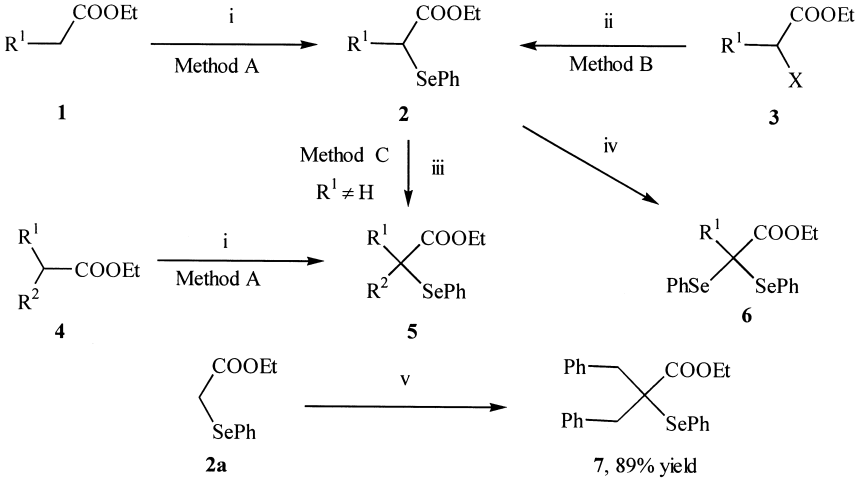
Abstract—Alkylation and selenenylation of selenium-stabilized ester enolates have allowed the preparation of α-phenylselanyl esters **5**, **7**, **8** and of α,α-bis(phenylselanyl)esters **6**, respectively. The competitive selenophilic reaction, leading to an allylic phenylselenide **9**, was avoided in the presence of HMPA. α-phenylselanyl α,β-unsaturated esters **15** were prepared by oxidation of compounds **6** and dehydrohalogenation of β-chloroesters **17**. Some other transformations: oxidation, transesterification and Grignard reaction were also studied. H_2O_2 oxidation of *Z*-esters **15** has led to stable *E*-α-seleninyl esters **20**.

The selenium methodology has now an increasing place in organic synthesis.[1–7] α-Phenylselanyl carbonyl compounds are important bifunctional selenium synthons. α-Phenylselanyl aldehydes and ketones have been extensively studied in our laboratory.[8] We have recently explored the synthetic utility of β-phenylselanyl α-oxoesters as precursors of 2-halo, 2-amino and 2-hydroxy 3-alkylidenesuccinates[9] and alkyl aziridine-2-carboxylates.[10] The use of selenium stabilized enolates, formed by α-deprotonation of α-selanyl carbonyl compounds, is often complicated by competitive nucleophilic attacks on the selenium atom leading to mixture of selenenylated products.[6] We were able, however, to prepare β-phenylselanyl enoxysilanes derived from α-phenylselanyl aldehydes and ketones and to study their reactivity.[11] As a continuation of this work, we were interested with the reactivity of α-phenylselanyl esters. Four methods of preparation were proposed more than twenty years ago but the synthetic use of these esters was not extensively studied.

The two principal routes involve selenenylation of ester enolates[1,12–15] and reaction of a phenylselenolate anion with α-haloesters.[12] Alkylation of α-phenylselanylester enolates constitutes a third way.[12] The last method concerns the reaction of a selenium stabilized carbanion with an alkyl chloroformate.[15] In this paper, we present our observations concerning the methods involving enolates for the preparation of the α-phenylselanyl esters **2**, **5**, **7** (Scheme 1) and **8**



Scheme 1. (i) LDA, THF, −78°C, PhSeCl. (ii) PhSeSePh, EtOH, $NaBH_4$, 0°C. (iii) KH, THF, R^2X (X=I, Br), HMPA, 0°C. (iv) LDA, THF, −78°C, PhSeCl. (v) KH (2 equiv.), THF, −35°C, $PhCH_2Br$ (3 equiv.), HMPA, 0°C.

Keywords: α-phenylselanyl esters; α-β-unsaturated α-phenylselanyl esters; selenoxides; ^{1}H NMR; ^{13}C NMR.

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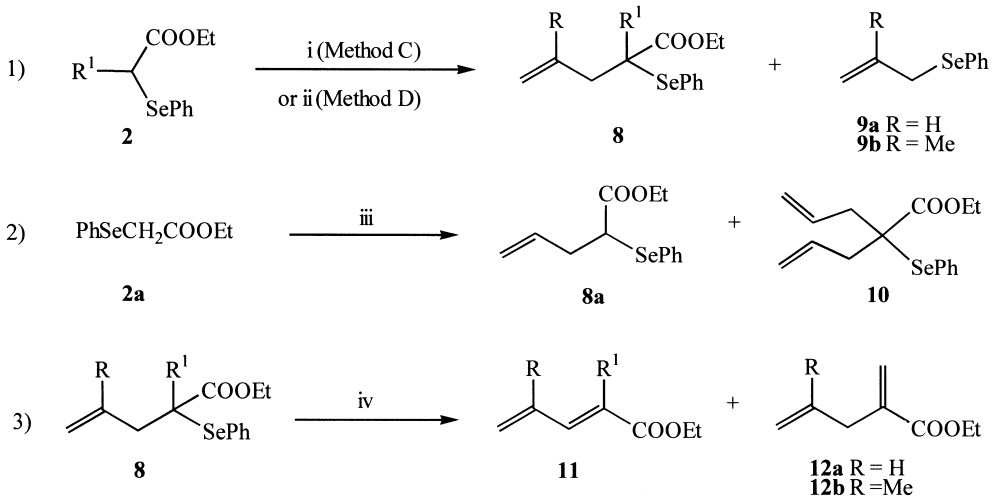


Scheme 2. (i) KH, THF, −35°C; Allyl bromide, HMPA, −35°C. (ii) LDA, THF, −78°C; Allyl bromide or methallyl chloride, HMPA, 0°C. (iii) KH, THF, −35°C, allyl bromide (2 equiv.). **8a**/**10**:84/16. (iv) H_2O_2, pyridine, $CHCl_3$, 0°C.

(Scheme 2) and α,α-bis(phenylselanyl)esters **6**. Two new routes for the preparation of α-phenylselanyl-α,β-unsaturated esters **15**, and some reactions carried out on these esters, are also described. The following paper will be devoted to the formation of dichloro-adducts and to the synthesis of chloroesters.[16]

The preparation of saturated and unsaturated α-selanyl esters was carried out with the goal to study some addition and cyclization reactions involving carbon centered radicals resulting from C–Se bond cleavage and Diels–Alder cycloadditions carried out with the functionalyzed vinylic selenides **15** and selenoxides **20**. Another objective of this work was to find the best method allowing the synthesis of optically active α-phenylselanyl aldehydes and ketones from chiral α-phenylselanyl esters.[17–19]

α-Phenylselanyl esters **2** were essentially prepared by method A (Scheme 1). The enolates, formed by LDA treatment of esters **1**, in THF at −78°C, were treated with PhSeCl (1 equiv.).[12–14] The use of PhSeBr has led to comparable results. No trace of α,α-bis(phenylselanyl)ester **6** was observed with an excess of base. An important dilution was needed to minimize a competitive Claisen condensation. Esters **2a**–**2i** were prepared in good yields (Table 1, entries 1, 3, 5, 7, 9–13). The sodium phenylselenolate treatment of α-haloesters **3** in ethanol has led to esters **2** with excellent yields[12] (Method B, Table 1, entries 2, 4, 6, 8). The use of borane complexed selenolate anions, even in excess, avoids a partial deselenenylation which was observed with free selenolate species.[6,20] The non-enolisable α-phenylselanyl esters **5a** and **5b** were prepared by method A (Table 1, entries 14 and 16) but could also be synthetized by alkylation of the corresponding α-selanyl enolate resulting from KH treatment of α-selanyl esters **2** in the presence of HMPA (Method C, Table 1, entries 15, 17–19). On the contrary to ketones,[6,11] the cleavage of the PhSe group, through a selenophilic attack by the enolate anion was not observed.[14] A double alkylation occurred during benzylation of ester **2a**, with formation of ester **7**

Table 1. α-Phenylselanyl esters **2**, **5** and α,α-bis(phenylselanyl)esters **6**

Entry	Esters **2** and **5**			Method	Yield (%)	Esters **6**	
	No.	R^1	R^2			No.	Yield (%)
1	**2a**	H	H	A	79	**6a**	57
2	**2a**	H	H	B (X=Cl)	87		
3	**2b**	Me	H	A	84		
4	**2b**	Me	H	B (X=Cl)	93		
5	**2c**	Et	H	A	76	**6c**	96
6	**2c**	Et	H	B (X=Br)	96		
7	**2d**	*n*Pr	H	A	78		
8	**2d**	*n*Pr	H	B (X=Br)	95		
9	**2e**	*n*Bu	H	A	74	**6e**	89
10	**2f**	*i*Pr	H	A	76	**6f**	68
11	**2g**	Ph	H	A	60	**6g**	40
12	**2h**	*c*-C_6H_{11}	H	A	75	**6h**	75
13	**2i**	*c*-C_6H_{11}–CH_2	H	A	68		
14	**5a**	Me	Me	A	78		
15	**5a**	Me	Me	C (X=I)	91		
16	**5b**	Me	Et	A	72		
17	**5b**	Me	Et	C (X=I)	71		
18	**5c**	Et	Bn	C (X=Br)	90		
19	**5d**	*n*Bu	Bn	C (X=Br)	87		

Table 2. α-Phenylselanyl γ,δ-unsaturated esters **8** and oxidation products **11** and **12**

Entry	No.	R^1	R	Method	Yield (%)	Oxidation products	
						Yield (%)	**11**/**12**
1	**8a**	H	H	D	96[a]	92	**11a**
2	**8b**	Me	H	C	82	81[b]	**11b**/**12a**:78/22
3	**8b**	Me	H	D	75		
4	**8c**	Et	H	C	75		
5	**8d**	*n*Pr	H	C	76	84	**11c**
6	**8e**	*n*Bu	H	C	76		
7	**8f**	*i*Pr	H	C	70		
8	**8f**	*i*Pr	H	D	68		
9	**8g**	Ph	H	C	81	71	**11d**
10	**8g**	Ph	H	D	72		
11	**8h**	*c*-C_6H_{11}	H	C	85		
12	**8i**	H	Me	D	75		
13	**8j**	Me	Me	C	85	80[b]	**11j**/**12b**:37/63
14	**8j**	Me	Me	D	67		
15	**8k**	*n*Bu	Me	C	72		

[a] Two equivalents of LDA were used.
[b] Overall yield.

(89% yield), when base and benzyl bromide were used in excess (Scheme 1).

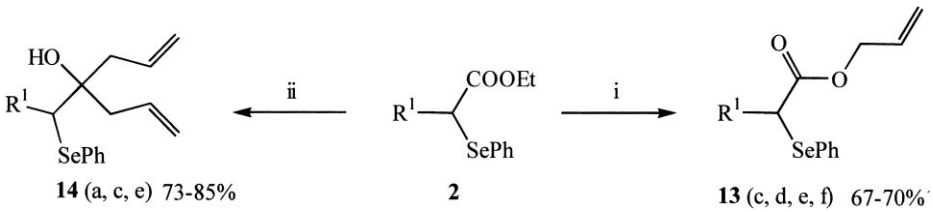
Selenylation of the selenium-stabilized enolates derived from esters **2** was also achieved with success. α,α-Bis-(phenylselanyl)esters **6** were prepared in good yields except **6g** (R^1=Ph, Table 1, entry 11). The first member **6a** of this new family of α-oxoester selenoacetals was previously prepared by selenenylation of ethyl diazoacetate.[21,22]

Allylation of the selenium-stabilized enolates derived from esters **2** was especially studied (Scheme 2 and Table 2). Method C (KH, allyl bromide, THF, HMPA) afforded the expected α-phenylselanyl γ-unsaturated esters **8** but trace amount of allyl phenylselenide **9** (R=H) was also observed as for the allylation of selenium-stabilized ketone enolates.[11b] The formation of this by-product is a consequence of a competitive alkylation of the selenium atom.[23] The amount of selenide **9a** (R=H) increased in the absence of HMPA and **9b** (R=Me) was formed when methallyl chloride was used as reagent. Allylation of lithium enolates has also allowed the preparation of esters **8** without formation of **9** (Method D). Starting from **2a**, the bis-allylated ester **10** did not appear besides **8a**, even in the presence of two molar equivalents of LDA (Table 2, entry 1), but was formed in a minor amount (**8a**/**10**:84/16) using method C (Scheme 2, Reaction 2).

Methods C and D were equally effective for the preparation of the γ-unsaturated esters **8**. These esters were then oxidized by H_2O_2 in the presence of pyridine and 2,4-dienic esters **11** were isolated. When a methyl group was present at the α position, however, the corresponding α-methylenic ester **12** was also formed (Scheme 2, Reaction 3; Table 2, entries 1, 2, 5, 9, 13). The chromatographic separation of **11b** from **12a** and of **11j** from **12b** was unsuccessful. It must be noticed that the deconjugated dienic ester **12** (entry 5, R^1=*n*Pr) was not formed when another alkyl substituent was present on the α carbon in the place of the methyl group.

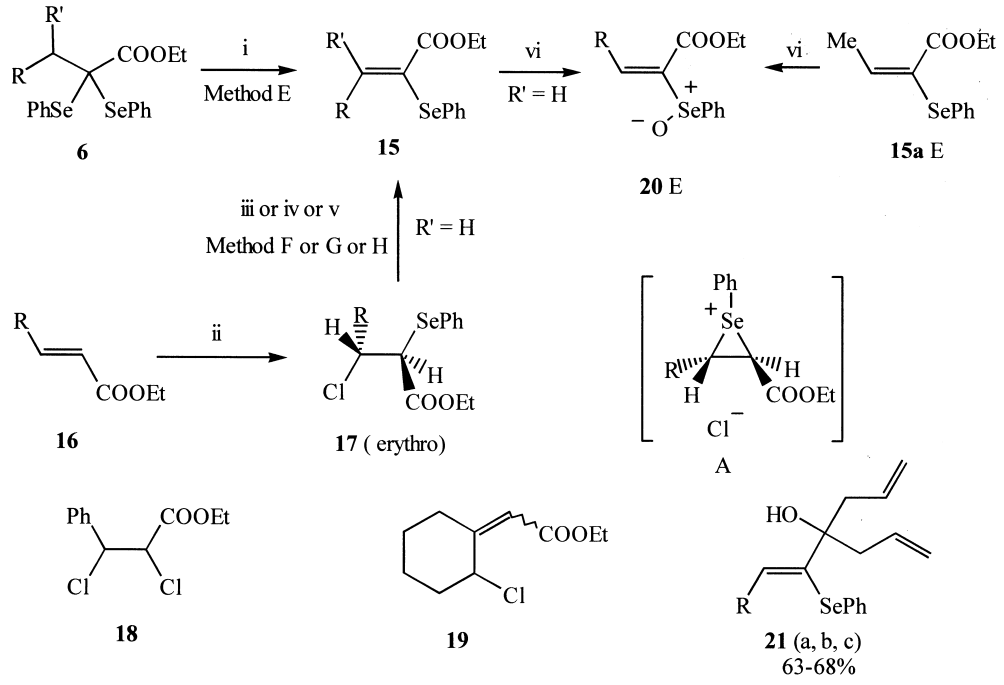
Two other reactions were carried out on α-phenylselanyl esters **2** (Scheme 3). Transesterification into allyl esters **13** was achieved through a probable O-allylation of the intermediate selenium-stabilized enolate. Allyl esters **13c** (R^1=Et), **13d** (R^1=*n*Pr), **13e** (R^1=*n*Bu) and **13f** (R^1=*i*Pr) were prepared with correct yields. Grignard reaction using allylmagnesium chloride provided the dienols **14a**, **14b**, **14c** in good yields. (73–85%). In this reaction, no trace of deselenenylated products was observed.

After several experiments with various oxidizing agents, we have found that sodium periodate treatment of the α,α-bis(phenylselanyl)esters **6** afforded the α-phenylselanyl-α,β-unsaturated esters **15** in very good yields without overoxidation into selenoxides **20** (Scheme 4 and Table 3, entries 1, 6, 11 and 12, Method E). The esters **15a** and **15b** (R′=H) were isolated as mixture of isomers (**15a**: *Z*/*E*=85/15; **15b**: *Z*/*E*=86/14). This reaction constitutes a new preparative method for this class of compounds. The first published one involves conjugated LDA addition to α,β-unsaturated esters, reaction of the intermediate enolate with PhSeBr and diisopropylamine elimination.[24] It was more recently observed that PhSeCl adds stereospecifically to unsaturated esters with formation of β-chloro α-phenyl-



14 (a, c, e) 73-85% **2** **13** (c, d, e, f) 67-70%

Scheme 3. (i) NaH, EtOH, THF, Δ; Allyl bromide, Δ. (ii) Allylmagnesium chloride (2.2 equiv.), THF, −78°C.



Scheme 4. (i) $NaIO_4$, $NaHCO_3$, EtOH, H_2O, 0°C→RT (Method E). (ii) PhSeCl, $ZnCl_2$, CH_2Cl_2, RT. (iii) Et_3N, benzene reflux, 5 h (Method F). (iv) K_2CO_3, acetone reflux, 6 h (Method G). v) DBU, THF, RT, 20 h (Method H). (vi) H_2O_2, pyridine, $CHCl_3$, 0°C→RT.

selanyl esters as thermodynamic addition products.[25,26] With $ZnCl_2$ activation,[26] we have prepared esters **17** (*anti* or *erythro*) from *E*-esters **16**, probably through the seleniranium intermediate A (Scheme 4). Compounds **17a** (R=Me), **17b** (R=*n*Pr) and **17c** (R=*i*Pr) were isolated in 84–94% yields. Ethyl cinnamate, however, has led to ethyl 2,3-dichloro-3-phenylpropanoate **18** and ethyl cyclohexylidenepropenoate to ethyl (2-chlorocyclohexylidene)propenoate **19**. These results could be explained by a selenophilic reaction between the adduct **17** and PhSeCl.[16]

Dehydrochlorination of β-chloroesters **17** was achieved by three different ways (Scheme 4, Table 3). *Z*-Esters **15** (R′=H) were obtained by method F, after a prolonged heating in benzene in the presence of Et_3N. The formation of the kinetic *E*-ester was observed when the reaction was stopped after 3 h (**15a**, *Z*/*E*=94/6, Table 3, entry 2). Method G (K_2CO_3, acetone reflux) provided the *E* isomer as the major product (Table 3, entries 4 and 8). Finally, HCl elimination was achieved by DBU treatment of esters **17a** and **17c** in THF at room temperature (Method H). Esters **15a** (*Z*) and **15c** (*Z*) were isolated in good yields (Table 3, entries 5 and 10). These results show that the two-step sequence: PhSeCl addition–HCl elimination, on α,β-unsaturated esters, is also an efficient route to α-phenylselanyl α,β-unsaturated esters **15** (R′=H). The two methods disclosed here complete those described: reaction of an alkyl chloroformate with α-selanylvinyllithiums,[27] treatment of α-diazoesters with benzeneselenenyl iodide,[28] condensation of aldehydes with ethyl bromo(phenylselanyl)acetate[29] and Wittig-type reaction of α-selanylarsonium ylides with aldehydes.[30] Another method, involving dehydrochlorination of α-chloro-α-phenylselanyl esters was found efficient for the synthesis of esters **15**.[16]

Table 3. α-Phenylselanyl α,β-unsaturated esters **15** and selenoxides **20**

Entry	Substrate			Method	Product			Selenoxide **20** (*Z*)	Yield (%)
	No.	R	R′		No.	Yield (%)	*Z*/*E*		
1	**6c**	Me	H	E	**15a**	85	85/15	**20a**	74
2	**17a**	Me	H	F	**15a**	83	94/6[a]		
3	**17a**	Me	H	F	**15a**	91	100/0		
4	**17a**	Me	H	G	**15a**	92	0/100		
5	**17a**	Me	H	H	**15a**	91	100/0		
6	**6e**	*n*Pr	H	E	**15b**	87	86/14		
7	**17b**	*n*Pr	H	F	**15b**	80	100/0	**20b**	72
8	**17b**	*n*Pr	H	G	**15b**	94	10/90		
9	**17c**	*i*Pr	H	F	**15c**	80	100/0	**20c**	68
10	**17c**	*i*Pr	H	H	**15c**	84	100/0		
11	**6f**	Me	Me	E	**15d**	82	–		
12	**6h**	$-(CH_2)_5-$		E	**15e**	80	–	[b]	

[a] The reaction was stopped after 3 h.
[b] Unidentified products.

H_2O_2 oxidation of *Z*-α-phenylselanyl esters **15** (R′=H), in the presence of pyridine, has provided the vinylselenoxides **20** (*E*) isolated in a pure form. A partial decomposition, however, occurred during the chromatographic purification. Examination of the ^{1}H NMR of **15a** (*Z*) and of the corresponding selenoxide **20a** (δ_{H3}=7.43 ppm for **15a** and δ_{H3}=7.29 ppm for **20a**) led us to assign the *E* stereochemistry for **20a**. The isomerisation could be attributed to a reversible conjugated addition of pyridine. The same *E* stereoisomer was also obtained, using the same experimental conditions, from the kinetic unsaturated α-phenylselanyl ester **15a** (*E*)[16] (85% yield). As shown in Table 3, **20b** (*E*) and **20c** (*E*) were prepared from **15b** (*Z*) and **15c** (*Z*) respectively. $NaIO_4$ oxidation of **15a** (*Z*) was unsuccessful and a partial oxidation was observed using *m*CPBA in CH_2Cl_2. Ethyl cyclohexylidenepropenoate **15e** (R′≠H) has led to a complex mixture which was not studied further. Our unexpected results revealed that the *E* isomers of **20** (R′=H) can only be isolated.

Finally, we have checked that esters **15** reacted with allylmagnesium chloride (2 equiv.) under the same experimental conditions that those used for esters **2**. Phenylselanyl trienols **21** were prepared in 63–68% yields.

In conclusion, we have determined the better experimental conditions for the synthesis of α-alkyl α-phenylselanyl esters **5**, **7**, **8** and α,α-bis(phenylselanyl)esters **6**, respectively, achieved by alkylation and selenenylation of α-selanyl esters enolates. The competitive formation of allylic phenylselenide **9** was avoided during allylation of lithium enolates (Method D) and was reduced by addition of HMPA when potassium enolates were involved (Method C). $NaIO_4$ oxidation of esters **6** constitutes a new method for the synthesis of α-phenylselanyl-α,β-unsaturated esters **15**. *Z*-Esters **15** were oxidized into stable *E*-α-seleninyl esters **20** by H_2O_2 treatment in the presence of pyridine. Transesterification of esters **2** into allyl esters **13** and Grignard reaction achieved on esters **2** and **15** have allowed access to the selenenylated dienols **14** and trienols **21**, respectively.

Experimental

Esters **1**, **3**, **4** and **16** are commercial compounds except **16c** (*E*) and **16h** prepared by Wittig–Horner reaction using triethyl phosphonoacetate, butyllithium and isobutanal or cyclohexanone in 66 and 70% yields respectively. Solvents and eluents were distilled before use. THF was freshly distilled from sodium-benzophenone under argon and light petroleum refers to the fraction with bp 40–60°C. GC/mass spectrometry analysis was performed on a Hewlett–Packard HP5890 with an HP-1 capillary column (25 m, 0.22 mm, He carrier gas) at 70 eV. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Brucker AC200 spectrometer. Infrared spectra were performed on Beckman Acculab 9 and Perkin–Elmer FTIR 1600 spectrometers. C, H Microanalysis was determined with a Carlo–Erba 1106 analyser. The *Z* and *E*-stereochemistry of esters **15** was assigned by comparison of the chemical shift values of the vinylic proton (**15a** *Z*: δH_3=7.43 ppm; **15a** *E*: δH_3=6.33 ppm) with those given in the literature.[29]

Preparation of α-phenylselanyl esters 2

Method A: A solution of *i*Pr_2NH (1.11 g, 11 mmol) in anhydrous THF (20 ml), under argon, was treated with BuLi (4.4 ml, 11 mmol, 2.5 M in hexane) at 0°C for 15 min. Ester **1** (10 mmol) in THF was then added at −78°C. After 20 min at this temperature, a solution of PhSeBr (11 mmol) in THF (4 ml) was added quickly. The mixture was stirred for 15 min at −78°C then quenched with sat. aq. NH_4Cl solution (10 ml) and diluted with ether (50 ml). The organic layer was washed with water (3×10 ml), dried, filtered and evaporated to give a crude product distilled or chromatographed on silica gel (light petroleum/ethyl acetate:5/1).

Method B:[12] To a solution of diphenyldiselenide (5 g, 32 mmol) in EtOH (100 ml), $NaBH_4$ (3 g, 32 mmol) was added with ice-cooling. A solution of ethyl 2-haloester **3** (30 mmol) in EtOH (50 ml) was then introduced. The mixture was stirred at 0°C for 1 h and warmed to room temperature. Water (200 ml) and diethyl ether (500 ml) were added. The organic layer was separated, washed with water (2×50 ml), dried, filtered and concentrated. The crude oil was purified by silica gel chromatography as above.

Ethyl phenylselanylacetate 2a.[13] (79% yield, method A; 87% yield, method B). ^{1}H NMR δ: 7.54–7.60 (2H, m), 7.26 (3H, m), 4.09 (2H, q, *J*=7.0 Hz), 3.48 (2H, s), 1.17 (3H, t, *J*=7.0 Hz).

Ethyl 2-phenylselanylpropanoate 2b.[13] (84% yield, method A; 93% yield, method B). ^{1}H NMR δ: 7.54–7.61 (2H, m), 7.22–7.32 (3H, m), 4.06 (2H, q, *J*=7.0 Hz), 3.74 (1H, q, *J*=7.1 Hz), 1.51 (2H, d, *J*=7.1 Hz), 1.14 (3H, t, *J*=7.0 Hz).

Ethyl 2-phenylselanylbutanoate 2c. (76% yield, method A; 96% yield method B). ^{1}H NMR δ: 7.54–7.60 (2H, m), 7.22–7.29 (3H, m), 4.06 (2H, q, *J*=7.2 Hz), 3.50 (1H, m), 1.65–2.02 (2H, m), 1.13 (2H, t, *J*=7.2 Hz), 0.93 (3H, t, *J*=7.3 Hz). ^{13}C NMR δ: 172.7, 135.5, 128.8, 128.2, 127.9, 60.7, 45.3, 25.1, 13.9, 12.6. IR (cm^{-1}): 1740, 1578. Anal. Calcd for $C_{12}H_{16}O_2Se$: C, 53.14; H, 5.95. Found: C, 53.23; H, 6.13.

Ethyl 2-phenylselanylpentanoate 2d. (95% yield, method B). ^{1}H NMR δ: 7.54–7.60 (2H, m), 7.22–7.30 (3H, m), 4.05 (2H, q, *J*=7.0 Hz), 3.57 (1H, m), 1.80 (2H, m), 1.38 (2H, m), 1.13 (3H, t, *J*=7.0 Hz), 0.88 (3H, t, *J*=7.0 Hz). ^{13}C NMR δ: 172.4, 135.0, 128.4, 127.8, 127.6, 60.2, 42.8, 33.4, 20.9, 13.5, 13.1. IR (cm^{-1}): 1740, 1578. Anal. Calcd for $C_{13}H_{18}O_2Se$: C, 54.74; H, 6.36. Found: C, 54.70; H, 6.34.

Ethyl 2-phenylselanylhexanoate 2e. (74% yield, method A). ^{1}H NMR δ: 7.54–7.60 (2H, m), 7.22–7.30 (3H, m), 4.05 (2H, q, *J*=7.2 Hz), 3.57 (1H, dd, *J*=6.6, 8.7 Hz), 1.63–2.00 (2H, m), 1.15–1.45 (4H, m), 1.13 (3H, t, *J*=7.2 Hz), 0.85 (3H, t, *J*=6.8 Hz). ^{13}C NMR δ: 172.9, 135.5, 128.9, 128.4, 127.8, 60.8, 43.7, 31.5, 30.3, 22.2, 14.0, 13.9. IR (cm^{-1}): 1727, 1578. Anal. Calcd for $C_{14}H_{20}O_2Se$: C, 56.19; H, 6.74. Found: C, 56.15; H, 7.68.

Ethyl 3-methyl-2-phenylselanylbutanoate 2f. (76% yield,

method A). ^{1}H NMR δ: 7.52–7.57 (2H, m), 7.16–7.24 (3H, m), 4.00 (2H, q, J=7.1 Hz), 3.33 (1H, d, J=9.4 Hz), 2.06 (1H, m), 1.09 (3H, d, J=6.6 Hz), 1.08 (3H, t, 7.1 Hz), 0.97 (3H, d, J=6.6 Hz). ^{13}C NMR δ: 172.5, 135.2, 128.8, 128.6, 128.1, 60.5, 53.0, 30.2, 21.0, 20.7, 13.9. IR (cm^{-1}): 1728, 1578. Anal. Calcd for $C_{13}H_{18}O_2Se$: C, 54.74; H, 6.36. Found: C, 54.87; H, 6.42.

Ethyl phenyl(phenylselanyl)acetate 2g. (60% yield, method A). ^{1}H NMR δ: 7.38–7.52 (4H, m), 7.17–7.34 (6H, m), 4.89 (1H, s), 4.09 (2H, q, J=7.1 Hz), 1.15 (3H, d, J=7.1 Hz). ^{13}C NMR δ:170.9, 136.4, 135.6, 129.0, 128.7, 128.6, 128.5, 127.9, 61.4, 48.2, 14.0. IR (cm^{-1}): 1730, 1578. Anal. Calcd for $C_{16}H_{16}O_2Se$: C, 60.19; H, 5.05. Found: C, 60.27; H, 5.09.

Ethyl cyclohexyl(phenylselanyl)acetate 2h. (75% yield, method A). ^{1}H NMR δ: 7.46–7.53 (2H, m), 7.12–7.19 (3H, m), 3.94 (2H, qd, J=1.5, 7.1 Hz), 3.33 (1H, dd, J=1.7, 9.7 Hz), 2.05–2.20 (1H, m), 1.45–1.80 (4H, m), 1.03 (3H, td, J=2.2, 7.1 Hz), 0.80–1.25 (6H, m). ^{13}C NMR δ:171.8, 134.7, 128.4, 127.5, 59.9, 51.5, 38.7, 30.9, 25.6, 25.4, 13.5. IR (cm^{-1}): 1727, 1578. Anal. Calcd for $C_{16}H_{22}O_2Se$: C, 59.08; H, 6.82. Found: C, 58.98; H, 7.16.

Ethyl 3-cyclohexyl-2-phenylselanylpropanoate 2i. (68% yield, method A). ^{1}H NMR δ: 7.53–7.60(2H, m), 7.23–7.30 (3H, m), 4.03 (2H, q, J=7.2 Hz), 3.71 (1H, dd, J=6.6, 9.1 Hz), 1.50–1.90 (7H, m), 1.05–1.45 (6H, m), 1.11 (3H, t, J=7.2 Hz). ^{13}C NMR δ:172.6, 135.0, 128.5, 127.9, 127.7, 60.3, 41.0, 38.7, 35.9, 32.6, 32.4, 26.0, 25.7, 13.6. IR (cm^{-1}): 1728, 1578. Anal. Calcd for $C_{17}H_{24}O_2Se$: C, 60.17; H, 7.13. Found: C, 60.43; H, 7.21.

Preparation of α-phenylselanyl esters 5 and 7

Compounds **5a** and **5b** were also prepared by method A.

Method C: KH (250 mg, 35 wt% dispersion in mineral oil) washed with light petroleum (5×20 ml), dried under argon, was covered with THF (10 ml) and the suspension was slowly added to ester **2** (1 mmol) in THF at −35°C. After stirring for 20 min, alkyl halide (MeI or EtI or BnBr, 3 mmol) in THF (2 ml) and HMPA (0.5 ml) was introduced. The reaction was brought to room temperature and evaporated under reduced pressure. The oily residue was dissolved in light petroleum, washed twice with water (5 ml). The organic layer was concentrated and the crude product was chromatographed on silica gel (light petroleum/CH_2Cl_2:70/30). Dibenzylation of **2a**, leading to ester **7**, was achieved by the same method using a double amount of KH.

Ethyl 2-methyl-2-phenylselanylpropanoate 5a.[13] (78% yield, method A; 91% yield, method C). ^{1}H NMR δ: 7.54–7.60 (2H, m), 7.23–7.38 (3H, m), 4.06 (2H, q, J=7.1 Hz), 1.55 (6H, s), 1.16 (3H, t, J=7.1 Hz). ^{13}C NMR δ: 174.1, 137.7, 129.0, 128.5, 127.7, 60.7, 45.1, 26.2, 13.9. IR (cm^{-1}): 1770, 1578.

Ethyl 2-methyl-2-phenylselanylbutanoate 5b. (72% yield, method A; 71% yield, method C). ^{1}H NMR δ: 7.53–7.59 (2H, m), 7.22–7.38 (3H, m), 4.04 (2H, m), 1.65–2.07 (2H, m), 1.46 (3H, s), 1.15 (3H, td, J=0.5, 7.1 Hz), 0.90 (3H, t, J=7.2 Hz). ^{13}C NMR δ:173.4, 137.8, 128.9, 128.5, 127.3, 60.5, 50.4, 31.3, 22.0, 13.9, 9.8. IR (cm^{-1}): 1710, 1578. Anal. Calcd for $C_{13}H_{18}O_2Se$: C, 54.74; H, 6.36. Found: C, 54.76; H, 6.38.

Ethyl 2-benzyl-2-phenylselanylbutanoate 5c. (90% yield). ^{1}H NMR δ: 7.58–7.64 (2H, m), 7.20–7.40 (8H, m), 4.06 (2H, m), 3.39 (1H, d, J=14.0 Hz), 3.14 (1H, d, J=14.0 Hz), 1.78 (2H, m), 1.16 (3H, t, J=7.0 Hz), 1.09 (3H, t, J=7.0 Hz). ^{13}C NMR δ: 172.9, 137.7, 136.8, 129.9, 129.0, 128.5, 128.2, 127.9, 126.7, 60.7, 56.8, 39.8, 26.0, 13.7, 9.7. IR (cm^{-1}): 1718, 1578. Anal. Calcd for $C_{19}H_{22}O_2Se$: C, 63.15; H, 6.01. Found: C, 62.89; H, 6.31.

Ethyl 2-benzyl-2-phenylselanylhexanoate 5d. (87% yield). ^{1}H NMR δ: 7.58–7.65 (2H, m), 7.15–7.45 (8H, m), 4.04 (2H, qd, J=1.4, 7.1 Hz), 3.38 (1H, d, J=14.2 Hz), 3.15 (1H, d, J=14.2 Hz), 1.15–1.85 (6H, m), 1.15 (3H, t, J=7.1 Hz), 0.88 (3H, t, J=7.3 Hz). ^{13}C NMR δ: 137.7, 136.9, 129.9, 128.9, 128.5, 127.9, 127.2, 126.5, 60.7, 56.0, 40.4, 32.9, 27.3, 22.6, 13.8, 13.7. IR (cm^{-1}): 1718, 1577. Anal. Calcd for $C_{21}H_{26}O_2Se$: C, 64.77; H, 6.73. Found: C, 65.02; H, 6.96.

Ethyl 2-benzyl-3-phenyl-2-phenylselanylpropanoate 7. (89% yield). ^{1}H NMR δ: 7.58–7.65 (2H, m), 7.16–7.42 (13H, m), 4.06 (2H, q, J=7.1 Hz), 3.37 (2H, d, J=14.0 Hz), 3.28 (2H, d, J=14.0 Hz), 1.12 (3H, t, J=7.1 Hz). ^{13}C NMR δ: 172.6, 137.7, 136.7, 129.9, 128.8, 128.3, 127.5, 126.3, 60.7, 54.2, 40.9, 13.4. IR (cm^{-1}): 1715, 1578. Anal. Calcd for $C_{24}H_{24}O_2Se$: C, 68.08; H, 5.71. Found: C, 68.12; H, 5.79.

Preparation of γ,δ-unsaturated esters 8

Esters **8** (except **8a**) were prepared by method C using KH, allyl bromide and HMPA as cosolvent (Table 2). Trace amount of allyl phenylselenide **9a** (R=H) was detected. The selenides **9a** or **9b** (R=Me) were formed using allyl bromide or methallyl bromide in the absence of HMPA (5–10%). A mixture of monoallylated ester **8a** and bis-allylated ester **10** was obtained from **2a** (**8a**/**10**:84/16). Method D was used for the preparation of **8a**, **8b**, **8f**, **8g** and **8j**.

Method D: A solution of ester **2** (1.8 mmol) in THF (3 ml) was added dropwise at −78°C, under stirring, to a solution of LDA (2 mmol) in THF, as for method A. Allyl bromide or methallyl chloride (2 mmol) dissolved in HMPA (0.5 ml) was slowly added. The resulting mixture was brought to 0°C, stirred for 30 min, quenched with sat. aq. NH_4Cl (10 ml) and diluted with ether (10 ml). The organic layer was washed with water (3×10 ml), dried, filtered and evaporated providing an oily product purified by silica gel chromatography (light petroleum/CH_2Cl_2:70/30).

Ethyl 2-phenylselanylpent-4-enoate 8a. (64% yield, method C; 96% yield, method D). ^{1}H NMR δ: 7.54–7.62 (2H, m), 7.20–7.34 (3H, m), 5.76 (1H, m), 5.00–5.15 (2H, m), 4.07 (2H, q, J=7.2 Hz), 3.65 (1H, m), 2.55 (2H, m), 1.14 (3H, t, J=7.0 Hz). ^{13}C NMR δ: 173.2, 135.6, 133.2, 128.9, 128.4, 127.2, 117.5, 60.8, 42.3, 38.4, 35.8, 13.9. IR (cm^{-1}):

1730, 1578. Anal. Calcd for $C_{13}H_{16}O_2Se$: C, 55.13; H, 5.69. Found: C, 55.29; H, 5.82.

Ethyl 2-(prop-2-enyl)-2-phenylselanylpent-4-enoate 10. (10% yield, method C, separated from **8a**). ^{1}H NMR δ: 7.53–7.59 (2H, m), 7.23–7.38 (3H, m), 5.72–5.94 (2H, m), 5.04–5.16 (4H, m), 4.05 (2H, q, J=7.1 Hz), 2.57 (4H, m), 1.15 (3H, t, J=7.1 Hz). ^{13}C NMR δ: 173.0, 137.9, 133.3, 132.0, 129.2, 128.7, 118.8, 60.9, 38.4, 13.9. IR (cm^{-1}): 1720, 1578. Anal. Calcd for $C_{16}H_{20}O_2Se$: C, 59.44; H, 6.24. Found: C, 59.69; H, 6.26.

Ethyl 2-methyl-2-phenylselanylpent-4-enoate 8b. (82% yield, method C; 75% yield, method D). ^{1}H NMR δ: 7.55–7.62 (2H, m), 7.20–7.38 (3H, m), 5.64–5.86 (1H, m), 5.04–5.14 (2H, m), 4.06 (2H, qd, J=2.2, 7.1 Hz), 2.60 (2H, m), 1.49 (3H, s), 1.15 (3H, td, J=2.3, 7.1 Hz). ^{13}C NMR δ: 173.1, 137.8, 133.4, 129.0, 128.5, 127.1, 118.7, 60.7, 48.4, 42.8, 22.5, 13.9. IR (cm^{-1}): 1722, 1578. Anal. Calcd for $C_{14}H_{18}O_2Se$: C, 56.57; H, 6.10. Found: C, 56.55; H, 6.09.

Ethyl 2-ethyl-2-phenylselanylpent-4-enoate 8c. (75% yield, method C). ^{1}H NMR δ: 7.52–7.58 (2H, m), 7.20–7.38 (3H, m), 5.85 (1H, m), 5.06–5.18 (2H, m), 4.06 (2H, q, J=7.2 Hz), 2.54 (2H, m), 1.79 (2H, m), 1.16 (3H, t, J=7.0 Hz), 0.93 (3H, t, J=7.0 Hz). ^{13}C NMR δ: 172.9, 137.7, 133.4, 128.9, 128.5, 126.8, 118.1, 60.6, 54.9, 37.6, 26.8, 13.8, −9.2. IR (cm^{-1}): 1719, 1579. Anal. Calcd for $C_{15}H_{20}O_2Se$: C, 57.88; H, 6.48. Found: C, 57.87; H, 6.51.

Ethyl 2-*n*-propyl-2-phenylselanylpent-4-enoate 8d. (76% yield, method C). ^{1}H NMR δ: 7.52–7.58 (2H, m), 7.22–7.38 (3H, m), 5.86 (1H, m), 5.06–5.16 (2H, m), 4.06 (2H, q, J=7.0 Hz), 2.51–2.58 (2H, m), 1.20–1.85 (4H, m), 1.16 (3H, t, J=7.0 Hz), 0.87 (3H, t, J=7.2 Hz). ^{13}C NMR δ: 173.0, 137.7, 133.5, 129.0, 128.1, 126.9, 118.1, 60.6, 54.2, 38.1, 36.1, 18.1, 14.0, 13.8. IR (cm^{-1}): 1720, 1578. Anal. Calcd for $C_{16}H_{22}O_2Se$: C, 59.07; H, 6.82. Found: C, 59.13; H, 6.85.

Ethyl 2-*n*-butyl-2-phenylselanylpent-4-enoate 8e. (76% yield, method C). ^{1}H NMR δ: 7.50–7.57 (2H, m), 7.22–7.36 (3H, m), 5.85 (1H, m), 5.10 (2H, m), 4.06 (2H, q, J=7.0 Hz), 2.53 (2H, m), 1.60–1.85 (2H, m), 1.15–1.45 (4H, m), 1.15 (3H, t, J=7.0 Hz), 0.86 (3H, t, J=7.0 Hz). ^{13}C NMR δ: 173.0, 137.8, 133.5, 129.0, 128.8, 127.0, 118.2, 60.7, 54.3, 38.1, 33.7, 28.9, 22.7, 13.8. IR (cm^{-1}): 1721, 1578. Anal. Calcd for $C_{17}H_{24}O_2Se$: C, 60.17; H, 7.13. Found: C, 60.05; H, 7.18.

Ethyl 2-isopropyl-2-phenylselanylpent-4-enoate 8f. (70% yield, method C; 68% yield, method D). ^{1}H NMR δ: 7.55–7.60 (2H, m), 7.22–7.35 (3H, m), 6.00 (1H, m), 5.02–5.14 (2H, m), 4.04 (2H, m), 2.55 (2H, m), 2.17 (1H, m), 0.95–1.20 (9H, m). ^{13}C NMR δ: 173.0, 138.0, 135.3, 129.0, 128.5, 117.3, 60.7, 37.2, 32.9, 19.1, 18.2, 13.9. IR (cm^{-1}): 1719, 1578. Anal. Calcd for $C_{16}H_{22}O_2Se$: C, 59.07; H, 6.81. Found: C, 59.09; H, 6.92.

Ethyl 2-phenyl-2-phenylselanylpent-4-enoate 8g. (81% yield, method C; 72% yield, method D). ^{1}H NMR δ: 7.08–7.32 (10H, m), 5.92 (1H, m), 5.02–5.14 (2H, m), 4.16 (2H, m), 2.86 (2H, m), 1.18 (3H, t, J=7.0 Hz). ^{13}C NMR δ: 171.9, 140.2, 137.5, 133.6, 128.7, 128.0, 127.5, 127.2, 126.8, 118.2, 61.3, 40.5, 13.7. IR (cm^{-1}): 1722, 1578. Anal. Calcd for $C_{19}H_{20}O_2Se$: C, 63.51; H, 5.61. Found: C, 63.19; H, 5.36.

Ethyl 2-cyclohexyl-2-phenylselanylpent-4-enoate 8h. (85% yield, method C). ^{1}H NMR δ: 7.53–7.59 (2H, m), 7.20–7.35 (3H, m), 6.02 (1H, m), 5.00–5.15 (2H, m), 4.06 (2H, m), 2.56 (2H, m), 2.00–2.15 (1H, m), 1.00–1.80 (13H, m). ^{13}C NMR δ: 172.8, 137.9, 135.5, 128.9, 128.4, 127.4, 117.1, 60.6, 59.9, 43.4, 37.5, 29.5, 28.3, 26.8, 26.6, 26.3, 13.9. IR (cm^{-1}): 1716, 1578. Anal. Calcd for $C_{19}H_{26}O_2Se$: C, 62.46; H, 7.17. Found: C, 62.65; H, 7.31.

Ethyl 4-methyl-2-phenylselanylpent-4-enoate 8i. (75% yield, method C). ^{1}H NMR δ: 7.56–7.64 (2H, m), 7.22–7.34 (3H, m), 4.75 (2H, m), 4.03 (2H, q, J=7.1 Hz), 3.80 (1H, dd, J=6.1, 9.7 Hz), 2.55 (2H, m), 1.70 (3H, s), 1.12 (3H, t, J=7 Hz). ^{13}C NMR δ: 172.3, 142.0, 135.6, 128.8, 128.4, 127.8, 112.5–60.7, 41.2, 39.7, 22.3, 13.9. IR (cm^{-1}): 1728, 1578. Anal. Calcd for $C_{14}H_{18}O_2Se$: C, 56.57; H, 6.10. Found: C, 56.87; H, 6.31.

Ethyl 2,4-dimethyl-2-phenylselanylpent-4-enoate 8j. (85% yield, method C; 67% yield, method D). ^{1}H NMR δ: 7.54–7.60 (2H, m), 7.15–7.35 (3H, m), 4.80 (1H, m), 4.65 (1H, m), 4.04 (2H, q, J=7.0 Hz), 2.95 (1H, d, J=14.0 Hz), 2.43 (1H, d, J=14.0 Hz), 1.60 (3H, s), 1.46 (3H, s), 1.15 (3H, t, J=7 Hz). ^{13}C NMR δ: 172.0, 141.7, 137.9, 129.2, 128.6, 127.1, 114.9, 60.8, 48.3, 46.6, 23.2, 22.4, 13.8. IR (cm^{-1}): 1719, 1577. Anal. Calcd for $C_{15}H_{20}O_2Se$: C, 57.88; H, 6.48. Found: C, 58.27; H, 6.53.

Ethyl 2-*n*-butyl-4-methyl-2-phenylselanylpent-4-enoate 8k. (72% yield, method C). ^{1}H NMR δ: 7.50–7.60 (2H, m), 7.15–7.40 (3H, m), 4.71 (1H, m), 4.82 (1H, m), 4.02 (2H, q, J=7.0 Hz), 2.76 (1H, d, J=14.1 Hz), 2.54 (1H, d, J=14.1 Hz), 1.05–1.90 (9H, m), 1.14 (3H, t, J=7.1 Hz), 0.87 (3H, m). ^{13}C NMR δ: 173.4, 141.5, 137.8, 129.0, 128.5, 126.0, 114.5, 60.7, 55.3, 42.5, 33.2, 27.0, 23.4, 22.8, 13.8. IR (cm^{-1}): 1720, 1578. Anal. Calcd for $C_{18}H_{26}O_2Se$: C, 61.18; H, 7.42. Found: C, 60.97; H, 7.56.

Allyl phenylselenide 9a.[11c] ^{1}H NMR δ: 7.48 (2H, m), 7.27 (3H, m), 6.04–5.84 (1H, m), 5.01–4.91 (2H, m), 3.51 (2H, m). ^{13}C NMR δ: 134.1, 116.2, 30.3.

2-Methyl-3-prop-2-enyl phenylselenide 9b.[11c] ^{1}H NMR δ: 7.49 (2H, m), 7.27 (3H, m), 4.68 (2H, m), 3.51 (2H, s), 1.85 (3H, s).

Preparation of α,α-bis(phenylselanyl)esters 6

Ester **2** (2 mmol) in THF (1 ml) was added dropwise to a solution of LDA (4.8 mmol) in anhydrous THF (3 ml), at −78°C under argon. The reaction was stirred for 10 min and treated with PhSeCl (932 mg, 4.8 mmol) dissolved in HMPA (2 ml) and THF (6 ml). The mixture was warmed to 0°C, stirred for 30 min, quenched with sat. aq. NH_4Cl. After dilution with ether, the organic layer was washed with water (2×5 ml), dried and concentrated. The crude product

was rectified by Kugelrohr distillation and chromatography on silica gel (light petroleum/ethyl acetate:97/3).

Ethyl bis(phenylselanyl)acetate 6a.[22] (57% yield). ^{1}H NMR δ: 7.55–7.63 (4H, m), 7.22–7.35 (6H, m), 4.78 (1H, s), 4.08 (2H, q, J=7.0 Hz), 1.12 (3H, t, J=7.0 Hz). ^{13}C NMR δ: 169.8, 134.5, 129.0, 128.8, 128.4, 61.5, 38.7, 13.6. IR (cm^{-1}): 1723, 1577.

Ethyl 2,2-bis(phenylselanyl)butanoate 6c. (96% yield). ^{1}H NMR δ: 7.65–7.73 (4H, m), 7.24–7.44 (6H, m), 4.11 (2H, q, J=7.0 Hz), 1.70 (2H, q, J=7.0 Hz), 1.18 (3H, t, J=7.0 Hz), 0.94 (3H, t, J=7.0 Hz). ^{13}C NMR δ: 170.5, 137.5, 129.3, 128.9, 128.4, 61.8, 56.6, 29.4, 13.9. IR (cm^{-1}): 1715, 1576. Anal. Calcd for $C_{18}H_{20}O_2Se_2$: C, 50.72; H, 4.73. Found: C, 51.02; H, 4.68.

Ethyl 2,2-bis(phenylselanyl)hexanoate 6e. (89% yield). ^{1}H NMR δ: 7.65–7.73 (4H, m), 7.24–7.44 (6H, m), 4.09 (2H, q, J=7.0 Hz), 1.64 (2H, m), 1.40 (2H, m), 1.16 (3H, t, J=7.0 Hz), 0.98–1.20 (2H, m), 0.74 (3H, t, J=7.0 Hz). ^{13}C NMR δ: 170.8, 137.5, 129.4, 128.7, 128.5, 61.8, 55.7, 36.0, 28.6, 22.2, 13.9. IR (cm^{-1}): 1718, 1577. Anal. Calcd for $C_{20}H_{24}O_2Se_2$: C, 52.87; H, 5.32. Found: C, 53.12; H, 5.39.

Ethyl 3-methyl-2,2-bis(phenylselanyl)butanoate 6f. (68% yield). ^{1}H NMR δ: 7.68–7.75 (4H, m), 7.22–7.44 (6H, m), 3.92 (2H, q, J=7.0 Hz), 2.34 (1H, m), 1.12 (6H, d, J=6.7 Hz), 1.06 (3H, t, J=7.0 Hz). ^{13}C NMR δ: 170.7, 137.6, 129.1, 128.9, 128.6, 64.0, 61.6, 35.8, 20.1, 13.8. IR (cm^{-1}): 1709, 1577. Anal. Calcd for $C_{19}H_{22}O_2Se_2$: C, 51.83; H, 5.04. Found: C, 52.05; H, 4.96.

Ethyl phenyl[bis(phenylselanyl)]acetate 6g. (40% yield). ^{1}H NMR δ: 7.02–7.40 (15H, m), 4.10 (2H, q, J=7.0 Hz), 1.09 (3H, t, J=7.0 Hz). IR (cm^{-1}): 3056, 3027, 1714, 1578. Anal. Calcd for $C_{22}H_{20}O_2Se_2$: C, 55.71; H, 4.25. Found: C, 56.02; H, 4.32.

Ethyl cyclohexyl[bis(phenylselanyl)]acetate 6h. (75% yield). ^{1}H NMR δ: 7.68–7.75 (4H, m), 7.22–7.40 (6H, m), 3.94 (2H, q, J=7.1 Hz), 1.02–2.02 (11H, m), 1.06 (3H, t, J=7.1 Hz). ^{13}C NMR δ: 170.3, 137.6, 129.1, 128.5, 63.7, 61.4, 45.8, 30.4, 26.7, 26.3, 13.8. IR (cm^{-1}): 1717, 1578. Anal. Calcd for $C_{22}H_{26}O_2Se_2$: C, 55.01; H, 5.46. Found: C, 55.37; H, 5.16.

Oxidation of γ,δ-unsaturated esters 8

A solution of ester **8** (1 mmol) and pyridine (158 mg, 2 mmol) in chloroform (10 ml) was treated dropwise with H_2O_2 (0.7 ml, 8 mmol) at 0°C. The reaction was stirred at the same temperature for 1 h. The solution was washed twice with water, dried and concentrated. The oily product was purified by Kugelrohr distillation.

(*E*)-Ethyl penta-2,4-dienoate 11a.[31] (92% Yield). ^{1}H NMR ($CDCl_3$) δ: 7.16 (1H, dd, J=15.4, 10.8 Hz), 6.35 (1H, dddd, J=16.5, 10.8, 9.9, 0.6 Hz), 5.80 (1H, dd, J=15.4, 0.6 Hz), 5.49 (1H, dd, J=16.5, 0.6 Hz), 5.37 (1H, dt, J=9.9, 0.6 Hz), 4.11 (2H, q, J=7.0 Hz), 1.19 (3H, t, J=7.0 Hz).^{13}C NMR δ: 166.6, 144.5, 134.6, 125.3, 122.1, 60.2, 14.1. IR (cm^{-1}): 1716.

(*E*)-Ethyl 2-methylpenta-2,4-dienoate 11b.[32] (mixture **11b**/**12a**, 81% Yield).^{1}H NMR δ: 7.14 (1H, dd, J=11.3, 0.6 Hz,), 6.63 (1H, dt, J=16.8, 11.3, 10.0 Hz,), 5.54 (1H, dd, J=16.8, 0.9 Hz), 5.43 (1H, dt, J=10.0, 0.6 Hz), 4.19 (2H, q, J=7.0 Hz), 1.93 (3H, s), 1.28 (3H, t, J=7.0 Hz).^{13}C NMR δ: 168.1, 138.0, 132.0, 125.0, 123.8, 60.4, 14.1, 12.4. IR (cm^{-1}): 1709.

Ethyl 2-methylidenepent-4-enoate 12a.[33] ^{1}H NMR δ: 6.15 (1H, d, J=1.0 Hz), 5.65–5.95 (1H, m) 5.52 (1H, m), 5.02–5.10 (2H, m), 4.20 (2H, q, J=7.0 Hz), 3.02 (2H, m), 1.28 (3H, t, J=7.0 Hz). ^{13}C NMR δ: 166.8, 142.6, 138.5, 125.5, 112.2, 60.4, 39.5, 22.0, 13.9. IR (cm^{-1}): 1720,1630.

(*E*)-Ethyl 2-*n*-propylpenta-2,4-dienoate 11c.[34] (84% Yield). ^{1}H NMR δ: 7.15 (1H, d, J=11.4 Hz), 6.62 (1H, ddd, J=16.7, 11.4, 9.9 Hz), 5.54 (1H, dd, J=16.7, 1.6 Hz), 5.42 (1H, dd, J=9.9, 1.6 Hz), 4.19 (2H, q, J=7.0 Hz), 2.37 (2H, t,), 1.44 (2H, m), 1.29 (3H, t, J=7.0 Hz), 0.89 (3H, t). ^{13}C NMR δ: 167.9, 138.3, 132.8, 132.0, 129.9, 60.3, 28.7, 22.7, 14.0, 13.6. IR (cm^{-1}): 1709.

(E)-Ethyl 2-phenylpenta-2,4-dienoate 11d. (71% Yield). ^{1}H NMR δ: 7.43(1H, d, J=11.3 Hz), 7.38–7.15 (5H, m), 6.37(1H, ddd, J=16.9, 11.3, 10.0 Hz), 5.63 (1H, dd, J=16.9, 1.6 Hz), 5.38(1H, dd, J=10.0, 1.6 Hz), 4.23 (2H, q, J=7.1 Hz), 1.27 (3H, t, J=7.1 Hz). ^{13}C NMR δ: 167.2, 140.2, 133.2, 130.0, 127.8, 127.6, 125.4, 118.5, 60.9, 14.2. IR (cm^{-1}): 1712. Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 76.95; H, 6.95.

Ethyl 2,4-dimethylpenta-2,4-dienoate 11e.[35] (mixture **11e**/**12b**, 80% Yield). ^{1}H NMR δ: 7.03 (1H, m), 5.14–5.00 (2H, m), 4.14 (2H, q, J=7.0 Hz), 1.95 (3H, d, J=1.4 Hz), 1.87 (3H, s), 1.24 (3H, t, J=7.0 Hz). ^{13}C NMR δ: 168.5, 140.6, 140.2, 127.4, 119.4, 60.4, 22.6, 14.1, 13.6. IR (cm^{-1}): 1716.

Ethyl 4-methyl-2-methylidenepent-4-enoate 12b.[33] (80% Yield).^{1}H NMR δ: 6.15 (1H, m), 5.48 (1H, m), 4.75–4.66 (2H, m), 4.14 (2H, q, J=7.0 Hz), 2.94 (2H, s), 1.66 (3H, s), 1.23 (3H, t, J=7.0 Hz).^{13}C NMR δ: 166.8, 142.6, 138.5, 125.5, 112.2, 60.4, 39.5, 22.0, 13.9. IR (cm^{-1}): 1716.

Transesterification of esters 2

NaH (100 mg, 4 mmol, 60% dispersion in mineral oil) was added to a solution of ester **2** (1 mmol) in THF (3 ml) and ethanol (0.5 ml). The stirred mixture was heated at reflux for 20 min. Allyl bromide (242 mg, 2 mmol) was then added and the solution was heated at reflux for 16 h. Water (10 ml) was introduced after cooling and the allyl ester **13** was extracted with CH_2Cl_2 (3×5 ml). The organic layer was dried, evaporated and the oily residue was chromatographed on silica gel (light petroleum/CH_2Cl_2: 75/25).

Allyl 2-phenylselanylbutanoate 13c. (68%Yield).^{1}H NMR δ: 7.54–7.60 (2H, m), 7.20–7.35 (3H, m), 5.70–5.95 (1H, m), 5.06–5.85 (2H, m), 4.52 (2H, m), 3.54 (1H, dd, J=6.7, 8.5 Hz), 1.65–2.00 (2H, m), 0.98 (3H, t, J=7.2 Hz). ^{13}C NMR δ: 172.0, 135.4, 128.8, 128.2, 118.1, 65.2, 45.0, 25.0, 12.5. IR (cm^{-1}): 1729, 1578. Anal. Calcd for $C_{13}H_{16}O_2Se$: C, 55.13; H, 5.69. Found: C, 55.02; H, 5.61.

Allyl 2-phenylselanylpentanoate 13d. (67% Yield). ^{1}H NMR δ: 7.54–7.60 (2H, m), 7.20–7.35 (3H, m), 5.70–5.95 (1H, m), 5.10–5.33 (2H, m), 4.51 (2H, m), 3.62 (1H, dd, J=6.6, 8.7 Hz), 1.60–2.00 (2H, m), 1.25–1.55 (2H, m), 0.88 (3H, t, J=7.2 Hz). ^{13}C NMR δ: 172.6, 135.5, 128.8, 128.3, 127.8, 118.1, 65.3, 43.0, 33.7, 18.1, 13.5. IR (cm^{-1}): 1732, 1575. Anal. Calcd for $C_{14}H_{18}O_2Se$: C, 56.57; H, 6.10. Found: C, 56.43; H, 6.19.

Allyl 2-phenylselanylhexanoate 13e. (70% Yield). ^{1}H NMR δ: 7.54–7.60 (2H, m), 7.20–7.35 (3H, m), 5.70–5.95 (1H, m), 5.10–5.32 (2H, m), 4.51 (2H, m), 3.54 (1H, dd, J=6.6, 8.7 Hz), 1.15–1.95 (6H, m), 0.86 (3H, t, J=7.2 Hz). ^{13}C NMR δ: 172.6, 135.5, 131.8, 128.6, 128.3, 127.8, 118.3, 65.3, 43.4, 31.4, 30.1, 22.1, 13.7. IR (cm^{-1}): 1730, 1578. Anal. Calcd for $C_{15}H_{20}O_2Se$: C, 57.88; H, 6.48. Found: C, 57.79; H, 6.39.

Allyl 3-methyl-2-phenylselanylbutanoate 13f. (67% Yield). ^{1}H NMR δ: 7.56–7.61 (2H, m), 7.22–7.30 (3H, m), 5.70–5.90 (1H, m), 5.14–5.31 (2H, m), 4.49 (2H, m), 3.39 (1H, d, J=9.4 Hz), 2.11 (1H, m), 1.14 (3H, d, J=6.7 Hz), 1.01 (3H, t, J=6.6 Hz). ^{13}C NMR δ: 172.2, 135.2, 131.7, 129.0, 128.4, 128.1, 118.2, 65.2, 52.9, 30.1, 20.9, 20.7. IR (cm^{-1}): 1731, 1578. Anal. Calcd for $C_{14}H_{18}O_2Se$: C, 56.57; H, 6.10. Found: C, 56.77; H, 6.24.

Preparation of dienols 14 and trienols 21

Allylmagnesium chloride (2 M solution in THF, 1.1 ml, 2.2 mmol) was added to ester **8** (or **15**) (1 mmol) dissolved in THF (10 ml) at −78°C. The reaction was stirred for 30 min and sat. aq. NH_4Cl (10 ml) was then introduced. The product was extracted with ether (2×10 ml). The organic layer was washed with water, dried and evaporated. The oily residue was chromatographed on silica gel (light petroleum/CH_2Cl_2:75/25).

1-Phenylselanyl-2-(prop-2-enyl)pent-4-en-2-ol 14a. (85% Yield). ^{1}H NMR δ: 7.48–7.56(2H, m), 7.19–7.29 (3H, m),5.68–5.90 (2H, m),5.00–5.15 (4H, m), 3.10 (2H, s) 2.33 (5H, m). ^{13}C NMR δ: 133.0, 132.4, 130.5, 128.8, 126.6, 118.8, 73.1, 43.3, 39.9. IR (cm^{-1}): 3480, 1578. Anal. Calcd for $C_{14}H_{18}O_1Se$: C, 59.43; H, 6.41. Found: C, 59.21; H, 6.33.

3-Phenylselanyl-4-(prop-2-enyl)hepta-6-en-4-ol 14c. (82% Yield). ^{1}H NMR δ: 7.50–7.62 (2H, m), 7.15–7.27 (3H, m), 5.75–6.00 (2H, m), 4.95–5.16 (4H, m), 3.15 (1H, dd, J=12 Hz, J=2 Hz), 2.75 (1H, bs), 2.12–2.60 (4H, m), I.40–2.05 (2H, m), 1.07 (3H, t, J=7.1 Hz). ^{13}C NMR δ: 133.5, 133.2, 133.1, 131.5, 128.8, 126.8, 118.4, 117.7, 75.2, 64.2, 42.4, 41.2, 25.2, 13.4. IR (cm^{-1}): 3479, 1578. Anal. Calcd for $C_{16}H_{22}OSe$: C, 62.13; H, 7.17. Found: C, 62.27; H, 7.20.

5-Phenylselanyl-4-(prop-2-enyl)non-1-en-4-ol 14e. (73% Yield). ^{1}H NMR δ: 7.50–7.60 (2H, m), 7.20–7.26 (3H, m),5.75–6.00 (2H, m),4.95–5.17 (4H, m), 3.23 (1H, dd, J=2.0, 12.0 Hz), 2.76 (1H, s), 2.15–2.60 (4H, m), 1.10–1.93 (6H, m), 0.83 (3H, t, J=7.0 Hz). ^{13}C NMR δ: 133.5, 133.2, 133.2, 131.5, 128.8, 126.9, 118.5, 117.8, 75.2, 62.2, 42.5, 41.1, 31.7, 30.8, 22.1, 13.8. IR (cm^{-1}): 3479, 1578. Anal. Calcd for $C_{16}H_{26}OSe$: C, 64.08; H, 7.77. Found: C, 64.16; H, 7.65.

3-Phenylselanyl-4-(prop-2-enyl)hepta-2, 6-dien-4-ol 21a. (65% yield). ^{1}H NMR δ: 7.10–7.35 (5H, m), 6.43 (1H, q, J=7.0 Hz), 5.60–5.82 (2H, m), 4.95–5.15 (4H, m), 2.25–2.70 (5H, m), 1.82 (3H, d, J=6.8 Hz). ^{13}C NMR δ: 137.7, 133.8, 133.4, 131.1, 129.4, 128.8, 125.8, 118.6, 77.5, 43.8, 18.2. IR (cm^{-1}): 3443, 1578. Anal. Calcd for $C_{16}H_{20}OSe$: C, 62.54; H, 6.56. Found: C, 62.72; H: 6.58.

5-Phenylselanyl-4-(prop-2-enyl)nona-1,5-dien-4-ol 21b. (68% yield). ^{1}H NMR δ: 7.10–7.40 (5H, m), 6.30 (1H, t, J=7.0 Hz),5.73 (2H, m),5.06 (4H, m), 2.15–2.70 (7H, m), 1.37 (2H, m), 0.84 (3H, d, J=7.0 Hz). ^{13}C NMR δ: 139.3, 136.3, 131.4, 129.4, 128.6, 125.7, 118.3, 77.3, 43.8, 34.3, 21.9, 13.5. IR (cm^{-1}): 3508, 1579. Anal. Calcd for $C_{18}H_{24}OSe$: C, 64.47; H, 7.21. Found: C, 64.62; H, 7.42.

7-Methyl-5-phenylselanyl-4-(prop-2-enyl)octa-1,5-dien-4-ol 21c. (63% yield). ^{1}H NMR δ: 7.32–7.40 (2H, m), 7.12–7.22 (3H, m), 6.06 (1H, d, J=10.0 Hz), 5.58–5.80 (2H, m), 4.97–5.12 (4H, m), 2.85 (1H, m), 2.30–2.64 (5H, m), 0.93 (6H, d, J=6.6 Hz). ^{13}C NMR δ: 146.9, 133.6, 133.4, 131.8, 129.9, 128.9, 126.0, 118.6, 77.1, 44.0, 32.3, 22.3. IR (cm^{-1}): 3468, 1578. Anal. Calcd for $C_{18}H_{24}OSe$: C, 64.47; H, 7.21. Found: C, 64.44; H, 7.26.

Preparation of α-phenylselanyl α,β-unsaturated esters 15

*(1) Oxidation of esters **6** (Method E):* $NaIO_4$ (129 mg, 0.6 mmol) was added to a stirred solution of ester **6** (0.5 mmol) in ethanol (10 ml) containing sodium bicarbonate (42 mg, 0.5 mmol) at 0°C. The reaction was stirred for 1.5 h, brought to room temperature, filtered and diluted with CH_2Cl_2 (15 ml). The organic layer was washed twice with water, dried and evaporated. The crude product was purified by silica gel chromatography (light petroleum/CH_2Cl_2:70/30).

*(2) Synthesis of β-chloro-α-phenylselanyl esters **17**:*[26] $ZnCl_2$ (1 M ether solution, 0.1 ml) was added dropwise to a solution of PhSeCl (192 mg, 1 mmol) in CH_2Cl_2 (8 ml) at room temperature. After stirring for 10 min, the unsaturated ester **16** (1 mmol) was slowly added. The resulting mixture was stirred for 30 min and water was added. After dilution with CH_2Cl_2 (10 ml), the organic layer was washed with water, dried, evaporated. The crude product **17** was purified by chromatography as in method A. The formation of the *erythro* isomer was only observed.

***Erythro*-ethyl 3-chloro-2-phenylselanylbutanoate 17a.** (94% yield). ^{1}H NMR δ: 7.56–7.62 (2H, m), 7.22–7.38 (3H, m), 4.32 (1H, dq, J=6.6, 11.0 Hz), 4.11 (2H, q, J=7.0 Hz), 3.68 (1H, d, J=11.0 Hz), 1.72 (3H, d, J=6.6 Hz), 1.19 (3H, t, J=7.0 Hz). ^{13}C NMR δ: 170.1, 135.7, 129.2, 61.2, 56.6, 52.0, 23.2, 15.6, 13.9. IR (cm^{-1}): 1726, 1578. Anal. Calcd for $C_{12}H_{15}O_2ClSe$: C, 47.15; H, 4.95. Found: C, 47.32; H, 5.13.

***Erythro*-ethyl 3-chloro-2-phenylselanylhexanoate 17b.** (92% yield). ^{1}H NMR δ: 7.56–7.62 (2H, m), 7.22–7.35

(3H, m), 4.24 (1H, m), 4.10 (2H, q, *J*=7.1 Hz), 3.75 (1H, d, *J*=11.2 Hz), 2.22 (1H, m), 1.71 (1H, m), 1.46 (2H, m), 1.15 (3H, t, *J*=7.2 Hz), 0.89 (3H, t, *J*=7.2 Hz). ^{13}C NMR δ: 170.1, 135.7, 129.1, 128.9, 127.1, 61.6, 61.0, 50.3, 36.9, 18.8, 13.9, 13.3. IR (cm^{-1}): 1732, 1578. Anal. Calcd for $C_{14}H_{19}O_2ClSe$: C, 50.39; H, 5.74. Found: C, 50.71; H, 5.95.

***Erythro*-ethyl 3-chloro-4-methyl-2-phenylselanylpentanoate 17c.** (84% yield). ^{1}H NMR δ: 7.58–7.64 (2H, m), 7.24–7.40 (3H, m), 4.27 (1H, m), 4.58 (2H, dq, *J*=7.1 Hz), 3.82 (1H, d, *J*=12.0 Hz), 2.50 (1H, m), 1.17 (3H, d, *J*=7.1 Hz), 1.04 (3H, d, *J*=7.0 Hz). 0.77 (3H, d, *J*=7.0 Hz). ^{13}C NMR δ: 170.2, 135.7, 129.0, 128.7, 126.7, 68.2, 61.0, 48.8, 29.4, 20.8, 14.1, 13.7. IR (cm^{-1}): 1735, 1578. Anal. Calcd for $C_{14}H_{19}O_2ClSe$: C, 50.39; H, 5.75. Found: C, 50.35; H, 5.72.

*(3) Dehydrohalogenation of esters **17***

Method F: A solution of β-chloro-α-phenylselanylester **17** (1 mmol), triethylamine (225 mg, 2.5 mmol) in benzene (10 ml) was heated at reflux for 5 h. Water (10 ml) and CH_2Cl_2 (20 ml) were then added. The organic layer was washed with water (3×5 ml), dried and concentrated. The crude product was purified by silica gel chromatography (light petroleum/CH_2Cl_2:70/30).

Method G: A solution of ester **17** (1 mmol) in acetone (10 ml), containing potassium carbonate (0.138 g, 1 mmol), was heated at reflux for 6 h. The mixture was then treated with water and extracted twice with CH_2Cl_2. The organic layer was washed with water, dried and evaporated. The ester **15** was purified as described for method B.

Method H: A solution of ester **17** (1 mmol) and DBU (0.161 g, 1 mmol) in THF (5 ml) was stirred at room temperature for 20 h. After addition of water and extraction with CH_2Cl_2, the organic layer was treated as above.

Ethyl 2-phenylselanylbut-2-enoate 15a. (85% yield, *Z*/*E*: 85/15, method E; 91% yield, *Z*/*E*:100/0, method F; 92% yield, *Z*/*E*:0/100, method G; 91% yield, *Z*/*E*:0/100, method H). ^{1}H NMR δ: *Z* isomer: 7.43 (1H, q, *J*=6.9 Hz), 7.32–7.39 (2H, m), 7.16–7.24 (3H, m), 4.10 (2H, q, *J*=7.1 Hz), 2.03 (3H, d, *J*=6.9 Hz), 1.10 (3H, t, *J*=7.1 Hz). *E* isomer: 7.45–7.52 (2H, m), 7.15–7.35 (3H, m), 6.34 (1H, q, *J*=7.3 Hz), 4.14 (2H, q, *J*=7.0 Hz), 1.99 (3H, d, *J*=7.3 Hz), 1.16 (3H, t, *J*=7.0 Hz). ^{13}C NMR δ: *Z* and *E* isomers: 164.8, 147.8, 130.7, 128.8, 126.4, 125.7, 59.9, 18.4, 13.7. IR (cm^{-1}): *Z* isomer: 1708, 1578. *E* isomer: 1716, 1578. Anal. Calcd for $C_{12}H_{14}O_2Se$: C, 53.53; H, 5.20. Found: C, 53.64; H, 5.52.

Ethyl 2-phenylselanylhex-2-enoate 15b.[29] (87% yield, *Z*/*E*:86/14, method E; 80% yield, *Z*/*E*:100/0, method F; 94% yield, *Z*/*E*:10/90, method G). ^{1}H NMR δ: *Z* isomer: 7.32–7.38 (2H,m), 7.33 (1H, t, *J*=7.3 Hz), 7.15–7.22 (3H, m), 4.08 (2H, q, *J*=7.1 Hz), 2.43 (2H, m), 1.49 (2H, m), 1.08 (3H, t, *J*=7.1 Hz), 0.93 (3H, t, *J*=7.3 Hz). *E* isomer: 7.44–7.52 (2H, m), 7.18–7.30 (3H, m), 6.27 (1H, t, 7.3 Hz), 4.12 (2H, q, 7.0 Hz), 2.42 (2H, m), 1.41 (2H, m), 1.15 (3H, t, *J*=7.0 Hz), 0.87 (3H, t, *J*=7.3 Hz). ^{13}C NMR δ: *Z* and *E* isomers: 165.5, 152.6, 130.9, 128.8, 126.4, 124.7, 61.2, 34.4, 21.5, 13.6. MS: M^+=298. IR (cm^{-1}): *Z* isomer: 1709, 1577. *E* isomer: 1709, 1577.

Ethyl 4-methyl-2-phenylselanylpent-2-enoate 15c.[29] (80% yield, method F; 84% yield, method H, *Z* isomer). ^{1}H NMR δ:7.32–7.39 (2H, m), 7.13–7.26 (3H, m), 7.14 (1H, d, *J*=9.8 Hz), 4.07 (2H, q, *J*=7.1 Hz), 3.06 (1H, m), 1.06 (3H, t, *J*=7.1 Hz), 1.04 (6H, d, *J*=7.0 Hz). ^{13}C NMR δ: 167.1, 158.8, 131.1, 130.9, 128.8, 126.4, 121.8, 61.2, 31.9, 21.5, 13.7. IR (cm^{-1}): 3059, 1709, 1609, 1579.

Ethyl 3-methyl-2-phenylselanylbut-2-enoate 15d.[28] (82% yield, method E). ^{1}H NMR δ: 7.40–7.46 (2H,m), 7.18–7.26 (3H, m), 3.99 (2H, q, *J*=7.2 Hz), 2.06 (3H, s), 2.04 (3H, s), 1.05 (3H, t, *J*=7.2 Hz). ^{13}C NMR δ: 166.1, 148.4, 131.5, 130.2, 128.7, 126.6, 60.7, 24.9, 22.9, 13.6. IR (cm^{-1}): 1718, 1577. Anal. Calcd for $C_{13}H_{16}O_2Se$: C, 55.13; H, 5.69. Found: C, 54.91; H: 5.27.

Ethyl cyclohexylidene(phenylselanyl)acetate 15e. (80% yield, method E). ^{1}H NMR δ: 7.42–7.47 (2H,m), 7.16–7.24 (3H, m), 3.99 (2H, q, *J*=7.1 Hz), 2.53 (2H, m), 2.41 (2H, m), 1.50–1.66 (6H, m), 1.07 (3H, t, *J*=7.1 Hz). ^{13}C NMR δ: 166.1, 154.5, 131.6, 130.7, 128.8, 126.7, 60.7, 34.7, 33.7, 27.9, 27.6, 26.0, 13.8. IR (cm^{-1}): 1715, 1578. Anal. Calcd for $C_{16}H_{20}O_2Se$: C, 59.44; H, 6.24. Found: C, 59.15; H, 6.11.

Oxidation of esters 15

H_2O_2 (0.18 ml, 2 mmol) was added to a solution of α-phenylselanylester **15a** (*Z*) (0.5 mmol) and pyridine (2 mmol, 158 mg) in $CHCl_3$ (5 ml) at 0°C. The mixture was stirred for 1 h at 0°C, diluted with CH_2Cl_2 (10 ml), washed with water (4×1 ml), dried and concentrated. The crude selenoxide **20a** (*E*) was purified by silica gel chromatography (light petroleum/CH_2Cl_2:70/30). By the same procedure, **15a** (*E*)[16] has led to **20a** (*E*) in 85% yield. Selenoxides **20b** (*E*) and **20c** (*E*) were obtained from **15b** (*Z*) and **15c** (*Z*).

***E*-Ethyl 2-phenylseleninylbut-2-enoate 20a.** (74% yield). ^{1}H NMR δ: 7.63–7.70 (2H, m), 7.40–7.45 (3H, m), 7.35 (1H, t, *J*=7.4 Hz), 4.18 (2H, dq, *J*=1.0, 7.1 Hz), 2.22 (3H, d, *J*=7.4 Hz), 1.17 (3H, t, *J*=7.1 Hz). ^{13}C NMR δ: 162.9, 145.5, 142.1, 134.2, 131.1, 129.1, 126.3, 61.4, 15.7, 13.8. IR (cm^{-1}): 1722, 1579. Anal. Calcd for $C_{12}H_{14}O_3Se$: C, 50.53; H, 4.95. Found: C, 50.26; H, 4.86.

***E*-Ethyl 2-phenylseleninylhex-2-enoate 20b.** (72% yield). ^{1}H NMR δ: 7.62–7.69 (2H, m), 7.37–7.44 (3H, m), 7.27 (1H, t, *J*=7.7 Hz), 4.16 (2H, dq, *J*=1.0, 7.1 Hz), 2.71 (2H, m), 1.55 (2H, m), 1.21 (3H, d, *J*=7.1 Hz), 0.91 (3H, t, *J*=7.3 Hz). ^{13}C NMR δ: 162.4, 149.7, 141.8, 133.2, 130.6, 128.7, 126.0, 61.0, 30.9, 21.3, 13.4, 13.2. IR (cm^{-1}): 1722, 1579. Anal. Calcd for $C_{18}H_{14}O_3Se$: C, 53.68; H, 5.79. Found: C, 53.47; H, 6.01.

***E*-Ethyl 4-methyl-2-phenylseleninylpent-2-enoate 20c.** (68% yield). ^{1}H NMR δ: 7.72–7.76 (2H, m), 7.37–7.47 (3H, m), 7.22 (1H, d, *J*=11.1 Hz), 4.03–4.23 (3H, m), 1.18 (3H, t, *J*=7.1 Hz), 1.04 (3H, d, *J*=6.6 Hz) 0.75 (3H, d, *J*=6.6 Hz). ^{13}C NMR δ: 163.1, 131.2, 130.0, 129.8,

126.6, 62.4, 25.1, 22.6, 22.1, 14.4. IR (cm^{-1}): 1726, 1578. Anal. Calcd for $C_{14}H_{18}O_3Se$: C, 53.68; H, 5.79. Found: C, 53.79; H, 5.81.

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