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Selenylated dienes: synthesis, stereochemical studies by ^{77}Se NMR, and transformation into functionalized allenes

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Abstract—2-Phenylselanyl-1,3-dienes **3**–**8** were prepared by a Wittig or Wittig–Horner–Emmons procedure starting from α-phenylselanyl α,β-unsaturated aldehydes. Ratio and configuration of each diene isomers were determined by ^{77}Se and ^{1}H NMR. These dienes were then oxidized into selenoxides, which could be isolated in some cases. In THF, [2,3]-sigmatropic rearrangement of allylic selenoxides, selenimides, and dihalo-selenuranes occurred, yielding allenyl alcohols **12**–**15**, allenyl carbamates **16c**–**19c**, and 1-haloalkyl allenes **20c**–**22c**, respectively.

1. Introduction

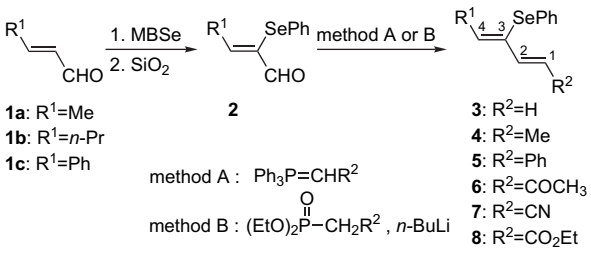
The important place of the 'selenium methodology' in organic synthesis is due to the easy introduction, transformation, and elimination of the selenylated group from organic substrate that allow selective reactions under mild conditions. Selenium reagents are now commonly used[1–4] and extensions to catalysts, ligands, asymmetric synthesis,[5] and radical chemistry[6] were the subject of recent works.

In particular, selenoxides play a pivotal role since the facile oxidation of alkyl phenylselenides allows the preparation of olefinic compounds and allylic alcohols under very mild conditions.[1,2] Our group was mainly involved in the studies of the reactivity of selenylated carbonyl derivatives allowing access to unsaturated, functionalized useful building-blocks[7] and their transformation into allenic alcohols via oxidation of 2-phenylselanyl-1,3-dienes.[8] These interesting selenylated dienes could also act as useful intermediates in organic synthesis, for example, as starting materials in Diels–Alder cycloaddition.[9,10] In the literature, very few preparations of 1-arylselanyl-1,3-butadienes are described: phenylselanyl alkylidene phosphoranes, phenylselanylalkenals[11a] or palladium-catalyzed cross coupling reactions.[11b] A stereoselective synthesis of 1,3-dienyl selenides was reported by reaction of α-arylselanylvinylstannanes with vinyl halides[11c] or by means of α-alkenylzirconium complexes with α-phenylselanylvinyl bromides.[11d]

Herein, we present a general access to 2-phenylselanyl-1,3-dienes along with an unambiguous determination of the stereochemistry by ^{77}Se NMR. Due to both vinylic and allylic position of the selanyl group in 2-phenylselanyl-1,3-dienes, sigmatropic rearrangements of selenoxides, selenimides, and dihalo-selenuranes were also studied, yielding, respectively, allenic alcohols, carbamates, and 1-haloalkyl allenes.

2. Results and discussion

Starting from α,β-unsaturated aldehydes **1**, vinylic (*Z*)-α-phenylselenoaldehydes **2** could be obtained as the unique stereoisomers (except for compound **2c**: *Z*/*E* 87/13) via a selenenylation process using morpholinobenzeneselenamide (MBSe) followed by a silica gel 'trap'.[12] Compounds **2** were then transformed into 3-phenylselanyl-1,3-dienes **3**–**8** via classical Wittig (method A) or Wittig–Horner–Emmons (method B) reactions[8] (**3**–**6** and **7**–**8**, respectively) (Scheme 1). For clarity reasons, the numbering of selenylated dienes will be 3-phenylselanyl-1,3-dienes in the theoretical



Scheme 1. Synthesis of 3-phenylselanyl-1,3-dienes.

Keywords: Selenium; Allenes; Oxidation; Conjugated dienes.
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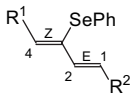
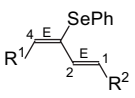
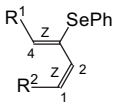
Table 1. Synthesis of conjugated dienes **3**–**8**

Entry	No.	R^1	R^2	Yields (%) (Method A or B)[a]	1*E*,3*Z* 	1*E*,3*E* 	1*Z*,3*Z* 
					Ratio of each diastereomer after chromatography (before chromatography)		
1	**3a**	Me	H	54 (A)	87	13	
2	**3b**	Pr	H	64 (A)	86	14	
3	**3c**	Ph	H	67 (A)	36	64	
4	**4a**	Me	Me	74 (A)	35 (20)	15 (0)	50 (80)
5	**4b**	Pr	Me	69 (A)	48 (20)	8 (0)	44 (80)
6	**4c**	Ph	Me	91 (A)		40[b] (15)	60 (70)[c]
7	**5a**	Me	Ph	88 (A)	70 (10)	20 (20)	10 (70)
8	**5b**	Pr	Ph	82 (A)	70 (10)	20 (20)	10 (70)
9	**5c**	Ph	Ph	94 (A)	55 (34)		45 (66)
10	**6a**	Me	COMe	67 (A)	80	20	
11	**6b**	Pr	COMe	77 (A)	80	20	
12	**6c**	Ph	COMe	88 (A)	55	45	
13	**7a**	Me	CN	61 (B)	68 (68)	10 (10)	20[d] (23)
14	**7b**	Pr	CN	82 (B)	68 (68)	10 (10)	20[d] (23)
15	**7c**	Ph	CN	83 (B)	48[b] (48)	20 (14)	30[d] (38)
16	**8a**	Me	CO_2Et	72 (B)	80	20	
17	**8b**	Pr	CO_2Et	71 (B)	80	20	0
18	**8c**	Ph	CO_2Et	84 (B)	84[b] (54)	16 (46)	

[a] See Scheme 1.
[b] X-ray analysis could be obtained for this isomer.
[c] 15% of 1*Z*,3*E* isomer.
[d] Traces of 1*Z*,3*E* isomer.

part, whereas official numbering will be applied in the experimental part as numbering differs according to substituents.

Only dienes **8** (R^2=CO_2Et) and **5c** (R^1=R^2=Ph) were already synthesized by our group.[8] In this paper, we wanted to extend this methodology to the preparation of various functionalized dienes **6**–**7** and to less stabilized one **3**–**5**. The yields were ranging from 45% to 94% for method A and from 61% to 84% for method B (Table 1). Indeed, the creation of the C1–C2 double bond (see Scheme 1) gave often a mixture of *Z*/*E* diastereomers, some of them were not stable and partial isomerization occurred during column chromatography on silica gel.

Wittig reactions with non-stabilized ylides (R^2=Me) formed predominantly *Z* isomer of the C1–C2 double bond (Table 1, entries 4–6). C1–C2 configurations were easily determined by measurement of $^3J_{H1-H2}$ coupling constant (11.0–12.0 Hz for *Z* and 14.6–15.6 Hz for *E*). With semi-stabilized ylides (R^2=Ph, Table 1, entries 7–9), NMR spectrum of the crude reaction shows three diastereomers, the major one having *Z* configuration at C1–C2 double bond (70% for **5a** and **5b**, 66% for **5c**). In both cases, *Z* configuration for C1–C2 double bond is not stable and isomerization occurred during silica gel chromatography, modifying the diastereomer ratio and rendering their separation difficult. Heating of diastereomeric mixtures led to a complete transformation of the C1–C2 *Z* isomer into the thermodynamically more stable *E* isomer (entry 4: 1*E*,3*Z*/1*E*,3*E*: 70/30; entry 5: 1*E*,3*Z*/1*E*,3*E*: 76/24).

With stabilized ylides, Wittig or Wittig–Horner–Emmons reactions afforded preferentially C1–C2 *E* isomer (**6** R^2=COMe: 100%, **7** R^2=CN: 68–77%, **8** R^2=CO_2Et: 100%). For all the ylides, we observed partial C3–C4 isomerization as starting from *Z* selenylated enal **2**, we always ended up with C3–C4 *E* and *Z* isomers (NMR analysis of crude material).

Due to the complex mixture of diastereomers obtained in the olefination reaction (C1–C2 and C3–C4 isomerizations during the purification steps and the reaction time, respectively), determination of the C3–C4 double bond configuration became quickly a necessity (Table 1). Due to the absence of hydrogen at C3 position and a H4 signal often overlapped on Ar-H signals in ^{1}H NMR spectra, determination of the configurations was very difficult even with NOESY experiment. ^{77}Se NMR appeared to be the easiest and the more reliable method to answer this question. Indeed with a single spectrum, we could determine the ratio and the configuration of each selenylated diene isomers (Table 2). When C1–C2 double bond is *E*, ^{77}Se NMR chemical shift is typical of diene configuration (1*E*,3*E*: $375.8<\delta<423.2$; 1*E*,3*Z*: $251.8<\delta<308.5$). In the same series, chemical shift of H2 in ^{1}H NMR is always 0.3 ppm lower for 3*Z* compared to 3*E* isomer. Configurations 1*E*,3*Z* of dienes **7c** and **8c** and 1*E*,3*E* of **4c** were confirmed by X-ray diffraction.

When C1–C2 double bond configuration is *Z*, the ^{77}Se NMR chemical shift (1*Z*,3*Z*: $348.5<\delta<415.4$) is difficult to compare with C1–C2 *E* series. Indeed in the *Z* series, diene seems to adopt *S*-cis conformation as opposed to the C1–C2 *E* series (*S*-trans). This would be in total accordance with a study of 'Conformational thermodynamic and kinetic parameters of methyl-substituted 1,3-butadienes', which showed the steric interactions in the 1,3-diene framework.[14] Indeed in the C1–C2 *Z* series, strong interaction between SePh and R^2 under *S*-trans conformation forced the dienes

Table 2. ^{77}Se and ^{1}H NMR data (ppm) of dienes **3–8**

Entry	No.	R^1	R^2	1*E*,3*Z*		1*E*,3*E*		1*Z*,3*Z*	
				^{77}Se	^{1}H (H-2)	^{77}Se	^{1}H (H-2)	^{77}Se	^{1}H (H-2)
1	**3a**[a]	Me	H	**251.8**	*6.40*	**387.4**	*6.69*		
2	**3b**	Pr	H	**260.3**	*6.39*	**375.8**	*6.67*		
3	**3c**[a]	Ph	H	**297.1**	*6.51*	**409.2**	*6.83*		
4	**4a**	Me	Me	**265.1**	*6.12*	**399.8**	*6.39*	**362.7**	*5.80*
5	**4b**	Pr	Me	**273.3**	*6.10*	**400.8**	*6.37*	**369.2**	*5.82*
6	**4c**	Ph	Me			**418.5**	*6.56*	**411.0**	*5.86*
7	**5a**	Me	Ph	**261.7**	*7.01*	**396.3**	*7.13*	**368.6**	*6.14*
8	**5b**	Pr	Ph	**269.8**	*6.97*	**397.9**	nd	**374.9**	*6.16*
9	**5c**	Ph	Ph	**304.0**	nd			**415.4**	*6.18*
10	**6a**	Me	COMe	**267.4**	nd	**401.6**	*7.56*		
11	**6b**	Pr	COMe	**275.6**	*7.22*	**403.7**	*7.54*		
12	**6c**	Ph	COMe	**308.5**	nd	**423.2**	*7.61*		
13	**7a**	Me	CN	**252.7**	*7.09*	**385.8**	*7.40*	**348.5**	*6.67*
14	**7b**	Pr	CN	**260.7**	*7.10*	**387.1**	nd	**357.3**	*6.69*
15	**7c**	Ph	CN	**288.2**	nd	**408.6**	nd	**398.4**	*6.75*
16	**8a**[a]	Me	CO_2Et	**263.6**	*7.41*	**399.6**	*7.72*		
17	**8b**	Pr	CO_2Et	**271.5**	*7.41*	**401.1**	*7.70*		
18	**8c**	Ph	CO_2Et	**301.1**	*7.55*	**421.6**	*7.80*		

[a] The only sulfur analogues found in the literature confirm configurations and δ ^{1}H, ^{13}C NMR of dienes **3a**,[13a] **3c**,[13b] and **8a**.[13c]

to adopt a *S*-cis conformation. Unfortunately, due to mixture and whatever the NOESY experimental parameters were, we were unable to prove or disprove this assumption.

The olefination reaction could be resumed as follows (Scheme 2: with non- and semi-stabilized ylides; Scheme 3: with stabilized ylides).

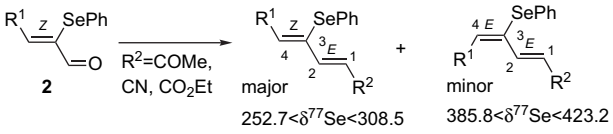
With non- or semi-stabilized ylides, olefination reaction on selenylated enal **2** was stereochemically controlled to yield mainly 1*Z* isomer (Scheme 2). Under the reaction conditions, partial C3–C4 isomerization occurred, delivering 3*E* isomer. Due to structural steric instability (*S*-cis conformation), C1–C2 *Z* isomer isomerized to afford more stable 1*E* isomers (Table 1: entries 4–9).

With stabilized ylides, as it could be predicted, the stereochemistry of the created double bond C1–C2 was *E*: exclusively when R^2=COMe or CO_2Et (Table 1: entries 10–12, 16–18), as the major isomer with R^2=CN (Table 1: entries 13–15). Under the reaction conditions, as for non- or semi-stabilized ylides, partial C3–C4 isomerization occurred, delivering 3*E* isomer (Scheme 2).

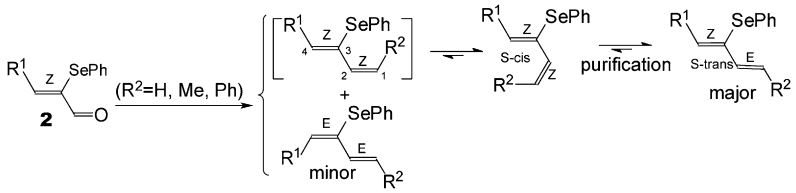
2.1. Allenes formation

Allenic compounds have been the subject of intensive studies.[15] Due to the versatile functionality of 1,2-diene moiety, allenes could serve as either a nucleophile or an electrophile, allowing them to act as precursors for cycloaddition reactions.[16] In particular, palladium-catalyzed reactions of allenes have gained considerable attention in recent years.[17,18] Concerning their formation, allenes are often prepared via addition of organometallic reagents (essentially cuprates) to enynes or to propargylic electrophiles via an S_N2' reaction.[19] Several methods exist to prepare α-hydroxyallenes: addition of lithiated allenes to aldehydes or ketones;[20,21] hydride reduction or Grignard addition onto propargylic oxiranes;[16,22] [2,3]-Wittig rearrangement of propargyl ethers;[23] insertion of alkenylidene carbenes into the α C–H bond of alkoxides.[24]

We present a new and mild method that is compatible with various chemical functionalities to prepare α-hydroxyallenes from selenylated 1,3-dienes after oxidation with hydrogen peroxide. First experiments were performed with stabilized 1,3-dienes **3c–8c** derived from cinnamaldehyde. The selenium atom at allylic position was first oxidized, affording selenoxides, which further rearrange into α-hydroxyallenes **12c–15c** (Table 3). When R^2 is an electron-

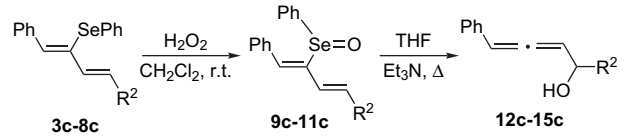


Scheme 3. Olefination reaction with stabilized ylides.



Scheme 2. Olefination reaction with non- and semi-stabilized ylides.

Table 3. α-Hydroxyallenes' synthesis



3c-8c 9c-11c 12c-15c

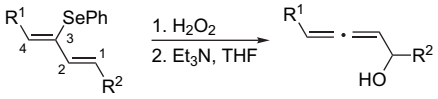
Starting dienes	R^2	Selenoxides (yield %)	Allenes (yield %)
3c	H	—	**12c** (78)
4c	Me	—	**13c** (81)
5c	Ph	—	**14c** (81)
6c	$COCH_3$	**9c** (81)	—
7c	CN	**10c** (63)	—
8c	CO_2Et	**11c** (76)	**15c** (75)

withdrawing group, the moderately stable selenoxides could be isolated as a mixture of diastereomers (Table 3: compounds **9c**, **10c**, and **11c**). The stereochemistry of these selenoxides was impossible to attribute due to complex NMR spectra (as starting dienes were also mixture of isomers, vide supra) and instability of the products.

In all cases, the rearrangement into α-hydroxyallenes was conducted in THF in the presence of triethylamine at room temperature to give compounds **12c**–**15c** in good yields (Table 3). For compound **12c**,[25] only one diastereomer was detected by ^{13}C NMR, but two isomers are present in the case of allenes **13c** (63/37), **14c**[8] (70/30), and **15c**[8] (70/30). Noteworthy the [1,3]-sigmatropic rearrangement of conjugated dienes is specific to selenoxides, no rearrangement occurred with sulfoxides. However, when R^2 was a carbonyl or a nitrile group, the selenoxides **9c** and **10c** decomposed, whatever the conditions, and we were unable to isolate allenes.

After variation of R^2 group, we studied the influence of R^1 group on the transformation of 1,3-dienes into α-hydroxyallenes via [1,3]-sigmatropic rearrangement of allylic selenoxides. For this, our group[8] has already shown that when R^2 is COOEt, the yield was much better when R^1 is an aryl than an alkyl group (Table 4: compounds **15a–c**).

Table 4. α-Hydroxyallenes' synthesis: influence of R^1 group



Starting dienes	R^1	R^2	Allenes (yield %)
4a	Me	Me	**13a**[26] (51)
4b	*n*-Pr	Me	**13b** (63)
4c	Ph	Me	**13c** (81)
5a	Me	Ph	**14a**[27] (38)
5b	*n*-Pr	Ph	**14b** (67)
5c	Ph	Ph	**14c**[8] (81)
8a	Me	CO_2Et	**15a**[8] (30)
8b	*n*-Pr	CO_2Et	**15b**[8] (30)
8c	Ph	CO_2Et	**15c**[8] (75)

Complementary results showed that when R^1 is an alkyl or phenyl group regardless of the nature of R^2: methyl or phenyl, the α-hydroxyallenes **13** and **14** could be obtained with good yields (see Table 4). Furthermore, yields were always higher when R^1 changed by following the order phenyl>propyl>methyl. In all the cases cited above, two diastereomers of allene were detected by ^{13}C NMR. Further studies are still undertaken to try to understand and to explain the stereoselectivity.

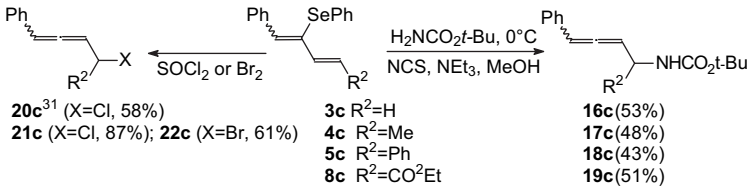
Due to their pharmaceutical interests (anesthetic, hypnotic, enzyme inhibitors[28] or treatment of depression[29]), numerous methods for the preparation of allenic carbamates are described in the literature,[15–18] but none of them have exploited the mildness and the selectivity of organoselenium chemistry.

Hopkins and co-workers[30] studied the [2,3]-sigmatropic rearrangement of allylic selenimides and nitrogen analogues of selenoxides. Thus, *N*-allyl carbamates were prepared by oxidation with anhydrous *N*-chlorosuccinimide (NCS) in methanol in the presence of *tert*-butyl carbamate.

We applied this reaction to dienes **3c**, **4c**, **5c**, and **8c** (Scheme 4). After oxidation by *N*-chlorosuccinimide in the presence of *tert*-butyl carbamate, rearrangement of the selenimide followed by hydrolysis of the intermediate selenamide, we ended up, respectively, with allenic carbamates **16c**, **17c**, **18c**, and **19c** (in 43–53% yields). It is significant to note that traces of water can induce partial hydrolysis of the selenimide, being able to lead to the formation of corresponding hydroxyallene. ^1H and ^{13}C NMR studies showed the presence of only one diastereomer presumably due to an overlap of the chemical shifts of the two expected diastereomers.

Finally, to complete the studies concerning the transformation of easily accessible 3-selenylated-1,3-dienes into various α-functionalized allenes species, chlorination and bromination of selenylated conjugated dienes were undertaken (Scheme 4). Dihalogenated adducts, obtained from halogenation of conjugated dienes, were decomposed in CCl_4 under reflux, yielding α-halogenated allenes. The allenes could be obtained only, if ethylvinylether, a PhSeX trap, is present in the reaction mixture. This additive is necessary to shift the equilibrium to the formation of allenes.

In conclusion, we have developed a general access to 2-phenylselanyl-1,3-dienes and an unambiguous determination



20c[31] (X=Cl, 58%)
21c (X=Cl, 87%); **22c** (X=Br, 61%)

3c R^2=H
4c R^2=Me
5c R^2=Ph
8c R^2=CO^2Et

16c(53%)
17c(48%)
18c(43%)
19c(51%)

Scheme 4. Allenyl carbamates and 1-halogenoalkyl allenes syntheses.[31]

of the stereochemistry of the two double bonds based on ^{77}Se NMR. These dienes, due to both vinylic and allylic position of selanyl group could be transformed via [1,3]-sigmatropic rearrangements into variously functionalized allenes.

This transformation occurred via selenoxide, selenimide or halo-selenurane intermediates under mild and selective conditions that give access to even none stabilized α-hydroxy, α-amino or α-halogenoallenes.

3. Experimental

3.1. General

Solvents were purified by conventional methods prior to use. TLC was performed on Merck 60F-250 silica gel plates and column chromatography over silica gel SI 60 (230–240 mesh). Melting points were taken on a Kofler apparatus and were uncorrected. Elemental analyses were carried out on a Carlo Erba EA 1100 analyzer and mass spectra on a HP5890 (electronic impact 70 eV) using GC–MS coupled with a Jeol AX 500. NMR spectra were recorded on a Bruker DPX 300 spectrometer operating at 300 MHz for proton and 75.4 MHz for carbon. This probe is equipped with pulsed-field (*z*) gradients. ^{77}Se NMR spectra were recorded at 21 °C on a Bruker DPX 400 spectrometer operating at 76.29 MHz for ^{77}Se, using a pulse length of 19 μs (90° pulse=19 μs) and an optimized relaxation delay of 2 s. An average of 1500 scans for ^{77}Se NMR was necessary to have reliable information. Chemical shifts (δ) are expressed in ppm relative to TMS for ^{1}H and ^{13}C nuclei and to Me_2Se for ^{77}Se nuclei; coupling constants (J) are given in Hertz; coupling multiplicities are reported using conventional abbreviations.

3.1.1. Preparation of α-phenylselanyl enals 2. A solution of enal **1** (10 mmol) in anhydrous dichloromethane (50 ml) was added dropwise to the solution of *N*-phenylselanylmorpholine[12a] (1.8 g, 20 mmol), in the same solvent (20 ml). The mixture was stirred for 6 h at room temperature and then hydrolyzed by 1 N HCl solution (15 ml). The aqueous layer was extracted with dichloromethane (3×50 ml) and the organic fractions were dried and concentrated. The α-phenylselanyl enals **2** were purified by chromatography on silica gel (elution with a mixture of petroleum ether/CH_2Cl_2: 85/15).

3.1.1.1. (*Z*)-2-Phenylselanylbut-2-enal 2a. Yield 85%, oil, ^{77}Se δ (ppm) 261.0; ^{1}H NMR δ (ppm) 2.18 (d, 3H, J=6.7 Hz), 7.20–7.27 (m, 3H), 7.32–7.40 (m, 3H), 9.41 (s, 1H, H-1); ^{13}C NMR δ (ppm) 19.1, 127.1, 129.3, 129.5, 129.6, 131.8, 135.3, 137.3 (C-2), 158.0 (C-3), 190.9 (C-1).

3.1.1.2. (*Z*)-2-Phenylselanylhex-2-enal 2b. Yield 83%, oil, ^{77}Se δ (ppm) 268.5; ^{1}H NMR δ (ppm) 0.97 (t, 3H, J=7.4 Hz), 1.55 (m, 2H), 2.60 (q, 2H, J=7.2 Hz), 7.20–7.29 (m, 3H), 7.26 (t, 1H, J=7.2 Hz, H-3), 7.37–7.41 (m, 2H), 9.40 (s, 1H, H-1); ^{13}C NMR δ (ppm) 14.0, 21.7, 34.8, 127.1, 129.3, 129.8, 131.9, 136.1 (C-2), 162.5 (C-3), 191.0 (C-1).

3.1.1.3. 3-Phenyl-2-phenylselanylprop-2-enal 2c. Yield 88%, *Z*/*E* 87/13. (*Z*)-isomer: mp=64 °C, ^{77}Se δ (ppm) 301.1; ^{1}H NMR δ (ppm) 7.18–7.26 (m, 3H), 7.38–7.44 (m, 5H), 7.84–7.88 (m, 2H), 8.01 (s, 1H, H-3), 9.50 (s, 1H, H-1); ^{13}C NMR δ (ppm) 127.4, 128.6, 129.4, 131.0, 131.2, 132.1, 132.5 (C-2), 152.6 (C-3), 191.6 (C-1). (*E*)-isomer: oil, ^{77}Se δ (ppm) 409.5; ^{1}H NMR δ (ppm) 7.18–7.24 (m, 3H), 7.32 (s, 1H, H-3), 7.34–7.42 (m, 5H), 7.64–7.69 (m, 2H), 9.79 (s, 1H, H-1); ^{13}C NMR δ (ppm) 126.6, 128.7, 129.1, 129.4, 129.6, 129.9, 134.8, 136.5, 138.5 (C-2), 145.5 (C-3), 189.1 (C-1).

3.1.2. Preparation of 3-phenylselanyl-1,3-dienes 3. At room temperature, a solution of *n*-BuLi in hexanes (1.6 M, 3.45 ml, 5.5 mmol) was slowly added, under argon, to methyltriphenylphosphonium bromide (1.96 g, 5.5 mmol) in anhydrous THF (30 ml). After stirring for 0.5 h, α-phenylselanyl enal **2** (5 mmol) in THF (5 ml) was added dropwise. The mixture was stirred for 3 h under reflux, quenched with saturated aqueous NH_4Cl, and extracted with diethylether. The organic extracts were dried over magnesium sulfate and concentrated under vacuum. The residue was purified by chromatography on silica gel (light petroleum) and rectified by Kugelrhor distillation.

3.1.2.1. 3-Phenylselanylpent-1,3-diene 3a. Yield 54%, *Z*/*E* 87/13. (*Z*)-isomer: oil, ^{77}Se δ (ppm) 251.8; ^{1}H NMR δ (ppm) 2.00 (d, 3H, J=6.7 Hz, H-5), 5.06 (d, H_{cis}, J=10.2 Hz), 5.59 (d, H_{trans}, J=16.5 Hz), 6.32 (q, 1H, J=6.7 Hz, H-4), 6.40 (dd, 1H, J=10.2, 16.5 Hz, H-2), 7.10–7.32 (m, 5H); ^{13}C NMR δ (ppm) 18.4 (Me), 117.1 (C-1), 125.9, 129.1, 129.3, 129.9, 131.6 (C-3), 138.5 (C-2), 138.8 (C-4). Anal. Calcd for $C_{11}H_{12}Se$: C, 59.20; H, 5.42. Found: C, 58.96; H, 5.37. (*E*)-isomer: oil, ^{77}Se δ (ppm) 387.4; ^{1}H NMR δ (ppm) 1.91 (d, 3H, J=7.2 Hz, H-5), 5.23 (d, H_{cis}, J=10.8 Hz), 5.64 (d, H_{trans}, J=16.7 Hz), 6.02 (q, 1H, J=6.7 Hz, H-4), 6.69 (dd, 1H, J=10.8, 16.7 Hz, H-2), 7.10–7.32 (m, 5H); ^{13}C NMR δ (ppm) 18.0 (Me), 119.9 (C-1), 127.8, 129.1, 129.3, 131.2, 131.6 (C-3), 137.1 (C-2), 137.9 (C-4).

3.1.2.2. 3-Phenylselanylhept-1,3-diene 3b. Yield 64%, *Z*/*E* 86/14. (*Z*)- isomer: oil, ^{77}Se δ (ppm) 260.3; ^{1}H NMR δ (ppm) 0.91 (t, 3H, J=7.4 Hz), 1.45 (m, 2H), 2.45 (q, 2H, J=7.4 Hz), 5.06 (d, H_{cis}, J=10.4 Hz), 5.57 (d, H_{trans}, J=16.6 Hz), 6.26 (t, 1H, J=7.1 Hz, H-4), 6.39 (dd, 1H, J=10.4, 16.6 Hz, H-2), 7.10–7.32 (m, 5H); ^{13}C NMR δ (ppm) 14.0 (Me), 22.6 (C-6), 34.6 (C-5), 117.3 (C-1), 125.9, 127.8, 129.1, 129.3, 131.3 (C-3), 131.6, 138.4 (C-2), 144.3 (C-4). Anal. Calcd for $C_{13}H_{16}Se$: C, 62.15; H, 6.42. Found: C, 62.33; H, 6.26. (*E*)-isomer: oil, ^{77}Se δ (ppm) 375.8; ^{1}H NMR δ (ppm) 1.01 (t, 3H, J=7.4 Hz), 1.55 (m, 2H), 2.45 (q, 2H, J=7.4 Hz), 5.22 (d, H_{cis}, J=10.3 Hz), 5.63 (d, H_{trans}, J=16.6 Hz), 6.03 (t, 1H, J=7.1 Hz, H-4), 6.67 (dd, 1H, J=10.3, 16.6 Hz, H-2), 7.10–7.32 (m, 5H); ^{13}C NMR δ (ppm) 14.0 (Me), 22.7 (C-6), 34.4 (C-5), 120.0 (C-1), 125.9, 127.8, 129.1, 129.3, 131.2 (C-3), 140.9 (C-2), 143.9 (C-4).

3.1.2.3. 1-Phenyl-2-phenylselanylbut-1,3-diene 3c. Yield 67%, *Z*/*E* 36/64. (*Z*)-isomer: oil, ^{77}Se δ (ppm) 297.1; ^{1}H NMR δ (ppm) 5.20 (d, H_{cis}, J=10.2 Hz), 5.70 (d, H_{trans}, J=16.6 Hz), 6.51 (ddd, 1H, J=0.8, 10.2, 16.6 Hz, H-3), 7.15 (s, 1H, H-1), 7.25–7.40 (m, 8H), 7.60 (m, 2H); ^{13}C NMR δ (ppm) 119.2 (C-4), 126.4, 127.3, 127.7, 128.3,

129.3, 129.4, 130.2, 132.7, 139.2 (C-3), 139.5, 140.9 (C-1). (*E*)-isomer: oil, ^{77}Se δ (ppm) 409.2; ^{1}H NMR δ (ppm) 5.34 (dd, H_{cis}, J=1.3, 10.5 Hz), 5.80 (d, H_{trans}, J=16.6 Hz), 6.83 (ddd, 1H, J=1.0, 10.5, 16.6 Hz, H-3), 7.05 (s, 1H, H-1), 7.25–7.40 (m, 8H), 7.50 (m, 2H); ^{13}C NMR δ (ppm) 121.4 (C-4), 126.4, 127.7, 128.1, 128.5, 129.4, 130.1, 130.6, 132.7, 133.2 (C-3), 137.5 (C-1). Anal. Calcd for $C_{16}H_{14}Se$: C, 67.37; H, 4.90. Found: C, 66.97; H, 4.83.

3.1.3. Preparation of selenides 4. The general procedure was used with the following modification. The reaction was carried out with ethyltriphenylphosphonium bromide. The selenide **4** was obtained after chromatography on silica gel (light petroleum) and rectification by Kugelrhor distillation.

3.1.3.1. 3-Phenylselanylhex-2,4-diene 4a. Yield 74%. (2*Z*,4*Z*)-isomer: oil, ^{77}Se δ (ppm) 362.7; ^{1}H NMR δ (ppm) 1.73 (d, 3H, J=6.9 Hz, H-6), 1.96 (d, 3H, J=6.7 Hz, H-1), 5.40 (qd, J=6.9, 11.2 Hz, 1H, H-5), 5.83 (d, 1H, J=11.2 Hz, H-4), 5.97 (q, 1H, J=6.7 Hz, H-2), 7.10–7.25 (m, 5H); ^{13}C NMR δ (ppm) 14.3, 17.8, 125.7, 126.7, 128.9, 129.1, 130.9, 131.6, 132.7, 133.3. Anal. Calcd for $C_{12}H_{14}Se$: C, 60.76; H, 5.95. Found: C, 60.68; H, 5.92. (2*E*,4*Z*)-isomer: oil, ^{77}Se δ (ppm) 335.5; ^{1}H NMR δ (ppm) 1.55 (dd, 3H, J=1.5, 6.9 Hz, H-6), 1.67 (dd, 3H, J=1.3, 6.9 Hz, H-1), 5.51 (m, 1H, H-5), 5.83 (d, 1H, J=13.0 Hz, H-4), 6.17 (m, 1H, H-2), 7.10–7.25 (m, 5H). (2*E*,4*E*)-isomer: oil, ^{77}Se δ (ppm) 399.8; ^{1}H NMR δ (ppm) 1.78 (dd, 3H, J=0.8, 6.7 Hz, H-6), 1.88 (d, 3H, J=7.7 Hz, H-1), 6.10 (m, 1H, H-5), 6.39 (d, 1H, J=15.1 Hz, H-4), 7.10–7.25 (m, 4H), 7.57–7.63 (m, 2H); ^{13}C NMR δ (ppm) 15.3, 18.4, 126.1, 126.3, 128.9, 129.3, 131.0, 132.0, 133.3, 134.7. (2*Z*,4*E*)-isomer: oil, ^{77}Se δ (ppm) 265.1; ^{1}H NMR δ (ppm) 1.72 (d, 3H, J=5.2 Hz, H-6), 1.97 (d, 3H, J=6.9 Hz, H-1), 6.05–6.16 (m, 2H, H-4, H-5), 6.18 (q, 1H, J=6.9 Hz, H-2), 7.10–7.25 (m, 3H), 7.57–7.63 (m, 2H); ^{13}C NMR δ (ppm) 17.9, 18.3, 125.7, 127.8, 129.1, 129.7, 130.9, 131.6, 133.0, 135.5.

3.1.3.2. 4-Phenylselanyloct-2,4-diene 4b. Yield 69%. (2*Z*,4*Z*)-isomer: oil, ^{77}Se δ (ppm) 369.2; ^{1}H NMR δ (ppm) 0.97 (t, 3H, J=7.4 Hz, H-8), 1.51 (m, 2H, H-7), 1.74 (dd, 3H, J=1.8, 6.9 Hz, H-1), 2.37 (m, 2H, H-6), 5.41 (m, 1H, H-2), 5.82 (d, 1H, J=11.5 Hz, H-3), 5.90 (t, 1H, J=7.2 Hz, H-5), 7.10–7.30 (m, 3H), 7.35–7.42 (m, 2H); ^{13}C NMR δ (ppm) 14.0, 14.3 (C-1), 22.7, 34.2, 126.6 (C-2), 127.9, 128.9, 129.3, 131.0 (C-4), 131.6, 131.9 (C-3), 137.85 (C-5). Anal. Calcd for $C_{14}H_{18}Se$: C, 63.39; H, 6.84. Found: C, 63.13; H, 6.94. (2*E*,4*Z*)-isomer: oil, ^{77}Se δ (ppm) 273.3; ^{1}H NMR δ (ppm) 0.90 (t, 3H, J=7.4 Hz), 1.43 (m, 2H), 1.71 (d, 3H, J=5.4 Hz), 2.40 (m, 2H), 6.01–6.17 (m, 3H), 7.10–7.30 (m, 3H), 7.58–7.62 (m, 2H); ^{13}C NMR δ (ppm) 14.0, 18.0 (C-1), 22.6, 34.4, 125.7 (C-3), 128.0, 129.3, 131.6, 133.0 (C-2), 141.1 (C-5). (2*E*,4*E*)-isomer: oil, ^{77}Se δ (ppm) 400.8; ^{1}H NMR δ (ppm) 0.95 (t, 3H, J=7.4 Hz), 1.45 (m, 2H), 1.77 (d, 3H, J=6.4 Hz), 2.29 (m, 2H), 6.02–6.18 (m, 1H), 6.38 (d, 1H, J=14.8 Hz), 7.15–7.30 (m, 4H), 7.58–7.62 (m, 2H).

3.1.3.3. 1-Phenyl-2-phenylselanylpent-1,3-diene 4c. Yield 91%. (1*Z*,3*Z*)-isomer: oil, ^{77}Se δ (ppm) 411.0; ^{1}H NMR δ (ppm) 1.77 (dd, 3H, J=1.5, 6.9 Hz), 5.40 (m, 1H, H-4), 5.79 (d, 1H, J=11.3 Hz, H-3), 6.78 (s, 1H, H-1), 7.18–7.35 (m, 8H), 7.50–7.55 (m, 2H); ^{13}C NMR δ (ppm) 14.5, 127.6 (C-4), 127.8, 128.3, 128.4, 128.9, 129.2, 129.3, 129.9 (C-2), 132.2 (C-3), 132.9 (C-1), 137.4. (1*E*,3*Z*)-isomer: oil, ^{77}Se δ (ppm) 309.0; ^{1}H NMR δ (ppm) 1.38 (dd, 3H, J=1.5, 7.2 Hz), 5.43 (m, 1H, H-4), 6.04 (d, 1H, J=11.3 Hz, H-3), 6.72 (s, 1H, H-1), 7.18–7.35 (m, 8H), 7.50–7.55 (m, 2H). (1*E*,3*E*)-isomer: first eluted, mp=47 °C, ^{77}Se δ (ppm) 418.5; ^{1}H NMR δ (ppm) 1.70 (dd, 3H, J=0.8, 6.7 Hz), 6.25 (m, 1H, H-4), 6.48 (d, 1H, J=14.6 Hz, H-3), 6.77 (s, 1H, H-1), 7.25–7.36 (m, 8H), 7.49–7.54 (m, 2H); ^{13}C NMR δ (ppm) 18.5 (C-5), 126.6, 127.2, 127.8 (C-3), 128.4, 129.2, 129.4, 131.0, 132.3 (C-2), 132.7, 133.9 (C-4), 134.6 (C-1), 137.4. Anal. Calcd for $C_{17}H_{16}Se$: C, 68.23; H, 5.39. Found: C, 68.11; H, 5.35.

3.1.4. Preparation of dienes 5. A solution of *n*-BuLi in hexanes (1.6 M, 3.45 ml, 5.5 mmol) was slowly added, under argon, to benzyltriphenylphosphonium chloride (2.13 g, 5.5 mmol) in anhydrous THF (50 ml). After stirring for 1 h at room temperature, α-phenylselanyl enal **2** (5 mmol) in THF (5 ml) was added dropwise. The mixture was stirred for 3 h at room temperature, quenched with saturated aqueous NH_4Cl, and extracted with diethylether. The organic extracts were dried over magnesium sulfate and concentrated under vacuum. The residue was purified by chromatography on silica gel (light petroleum/CH_2Cl_2: 80/20).

3.1.4.1. 1-Phenyl-3-phenylselanylpent-1,3-diene 5a. Yield 88%. (1*Z*,3*Z*)-isomer: oil, ^{77}Se δ (ppm) 368.6; ^{1}H NMR δ (ppm) 1.79 (dd, 3H, J=1.6, 6.9 Hz), 5.93–6.04 (m, 2H, H-1, H-4), 6.14 (d, 1H, J=12.0 Hz, H-2), 7.10–7.60 (m, 10H); ^{13}C NMR δ (ppm) 17.5, 126.8, 128.6, 128.7, 129.3, 129.8, 131.1 (C-2), 131.8 (C-1), 138.1 (C-3), 138.9 (C-4). (1*E*,3*Z*)-isomer: oil, ^{77}Se δ (ppm) 261.7; ^{1}H NMR δ (ppm) 2.07 (d, 3H, J=6.9 Hz), 6.45 (q, 1H, J=6.9 Hz, H-4), 6.85 (d, 1H, J=15.5 Hz, H-1), 7.01 (d, 1H, J=15.5 Hz, H-2), 7.10–7.45 (m, 10H); ^{13}C NMR δ (ppm) 18.7, 126.8, 128.6, 128.7, 129.3, 129.8, 131.1 (C-2), 131.6 (C-1), 137.4 (C-3), 139.0 (C-4). Anal. Calcd for $C_{17}H_{16}Se$: C, 68.23; H, 5.39. Found: C, 68.54; H, 5.62. (1*E*,3*E*)-isomer: oil, ^{77}Se δ (ppm) 396.6; ^{1}H NMR δ (ppm) 2.02 (d, 3H, J=7.3 Hz), 6.38 (q, 1H, J=7.3 Hz, H-4), 7.03 (d, 1H, J=15.5 Hz, H-1), 7.13 (d, 1H, J=15.5 Hz, H-2), 7.15–7.60 (m, 10H); ^{13}C NMR δ (ppm) 15.7, 126.0, 128.7, 129.3, 129.8, 130.9 (C-2), 131.6, 132.8 (C-1), 137.2 (C-3), 138.2 (C-4).

3.1.4.2. 1-Phenyl-3-phenylselanylhept-1,3-diene 5b. Yield 82%. (1*Z*,3*Z*)-isomer: ^{77}Se δ (ppm) 374.9; ^{1}H NMR δ (ppm) 0.87 (t, 3H, J=7.4 Hz), 1.37 (m, 2H), 2.24 (m, 2H), 5.96 (t, 1H, J=7.2 Hz, H-4), 5.98 (d, 1H, J=12.0 Hz, H-1), 6.16 (d, 1H, J=12.0 Hz, H-2), 7.10–7.60 (m, 10H); ^{13}C NMR δ (ppm) 14.0, 21.9, 33.9, 124.0, 126.7, 128.7, 129.3, 129.8, 130.7, 131.1, 132.2, 137.3 (C-3), 144.5 (C-4). (1*E*,3*Z*)-isomer: ^{77}Se δ (ppm) 269.8; ^{1}H NMR δ (ppm) 0.91 (t, 3H, J=7.4 Hz), 1.44 (m, 2H), 2.47 (m, 2H), 6.35 (t, 1H, J=7.4 Hz, H-4), 6.82 (d, 1H, J=15.4 Hz, H-1), 6.97 (d, 1H, J=15.4 Hz, H-2), 7.10–7.60 (m, 10H); ^{13}C NMR δ (ppm) 14.1, 22.6, 34.8, 124.0, 126.7, 128.7, 129.3, 129.8, 130.7 (C-2), 131.1, 132.2 (C-1), 137.4 (C-3), 144.6 (C-4). Anal. Calcd for $C_{19}H_{20}Se$: C, 69.72; H, 6.16. Found: C, 69.54; H, 5.92. (1*E*,3*E*)-isomer: ^{77}Se δ (ppm)

397.9; ^{1}H NMR δ (ppm) 0.96 (t, 3H, J=7.4 Hz), 1.51 (m, 2H), 2.39 (m, 2H), 6.30 (t, 1H, J=7.4 Hz, H-4), 7.05 (d, 1H, J=15.4 Hz, H-1), 7.10–7.60 (m, 11H); ^{13}C NMR δ (ppm) 14.0, 22.6, 31.9, 124.0, 126.7, 128.7, 129.3, 129.8, 130.8 (C-2), 131.1, 132.2 (C-1), 137.7 (C-3), 144.3 (C-4).

3.1.4.3. 1,4-Diphenyl-2-phenylselanylbut-1,3-diene 5c.[8] Yield 94%. (1*Z*,3*Z*)-isomer: ^{77}Se δ (ppm) 415.4; ^{1}H NMR δ (ppm) 5.98 (dd, 1H, J=1.5, 12.0 Hz, H-4), 6.18 (d, 1H, J=12.0 Hz, H-3), 6.92 (d, 1H, J=1.5 Hz, H-1), 7.15–7.60 (m, 15H); ^{13}C NMR δ (ppm) 126.9, 127.2, 127.7, 128.1, 128.5, 128.7, 128.8, 129.4, 129.5, 130.5 (C-3), 130.9 (C-1), 131.8 (C-4), 133.7, 134.0, 136.0, 137.7 (C-2). (1Z,3*E*)-isomer:[12] ^{77}Se δ (ppm) 304.0; ^{1}H NMR δ (ppm) 7.00 (d, 1H, J=15.4 Hz, H-4), 7.15–7.60 (m, 17H).

3.1.5. Preparation of dienic methylketones 6. A solution of α-phenylselanyl enal **2** (5 mmol) and 1-triphenylphosphoranylidene propanone (1.75 g, 5.5 mmol) in chloroform (30 ml) was stirred at room temperature for 48 h (**6a**) or 60 h (**6c**). After concentration under reduced pressure, the residue was purified by silica gel chromatography (light petroleum/CH_2Cl_2: 70/30).

3.1.5.1. 5-Phenylselanylhepta-3,5-dien-2-one 6a. Yield 67%. (3*E*,5*Z*)-isomer: ^{77}Se δ (ppm) 267.4; ^{1}H NMR δ (ppm) 2.11 (d, 3H, J=6.9 Hz, H-7), 2.23 (s, 3H, H-1), 6.58 (d, 1H, J=15.2 Hz, H-3), 6.75 (q, 1H, J=6.9 Hz, H-6), 7.10–7.30 (m, 6H); ^{13}C NMR δ (ppm) 19.2 (C-7), 28.4 (C-1), 126.8, 129.2, 129.8 (C-3), 131.0, 134.4, 136.9 (C-5), 145.3 (C-4), 148.0 (C-6), 198.3 (C-2). Anal. Calcd for $C_{13}H_{14}OSe$: C, 58.87; H, 5.32. Found: C, 58.51; H, 5.15. (3*E*,5*E*)-isomer: ^{77}Se δ (ppm) 401.6; ^{1}H NMR δ (ppm) 2.04 (d, 3H, J=7.4 Hz, H-7), 2.25 (s, 3H, H-1), 6.59 (d, 1H, J=15.2 Hz, H-3), 6.71 (q, 1H, J=7.4 Hz, H-6), 7.10–7.30 (m, 5H), 7.56 (d, 1H, J=15.2 Hz, H-4).

3.1.5.2. 5-Phenylselanylnona-3,5-dien-2-one 6b. Yield 77%. (3*E*,5*Z*)-isomer: ^{77}Se δ (ppm) 275.6; ^{1}H NMR δ (ppm) 0.93 (t, 3H, J=7.4 Hz, H-9), 1.49 (m, 2H, H-8), 2.23 (s, 3H, H-1), 2.52 (m, 2H, H-7), 6.56 (d, 1H, J=15.1 Hz, H-3), 6.67 (t, 1H, J=7.2 Hz, H-6), 7.10–7.35 (m, 6H, H-4, Ph); ^{13}C NMR δ (ppm) 13.9 (C-9), 22.1 (C-8), 28.5 (C-1), 35.3 (C-7), 126.4, 129.5, 129.9 (C-3), 136.8 (C-5), 145.5 (C-4), 153.5 (C-6), 198.6 (C-2). Anal. Calcd for $C_{15}H_{18}OSe$: C, 61.43; H, 6.19. Found: C, 61.71; H, 6.26. (3*E*,5*E*)-isomer: ^{77}Se δ (ppm) 403.7; ^{1}H NMR δ (ppm) 0.96 (t, 3H, J=7.4 Hz, H-9), 1.48 (m, 2H, H-8), 2.25 (s, 3H, H-1), 2.42 (m, 2H, H-7), 6.56 (d, 1H, J=15.1 Hz, H-3), 6.62 (t, 1H, J=7.2 Hz, H-6), 7.10–7.35 (m, 5H, Ph), 7.54 (d, 1H, J=15.1 Hz, H-4).

3.1.5.3. 6-Phenyl-5-phenylselanylhexa-3,5-dien-2-one 6c. Yield 88%. (3*E*,5*E*)-isomer (cyclohexane/dichloromethane:85/15): ^{77}Se δ (ppm) 423.2; ^{1}H NMR δ (ppm) 2.21 (s, 3H), 6.70 (d, 1H, J=15.4 Hz, H-3), 7.15–7.50 (m, 11H), 7.61 (dd, 1H, J=0.9, 15.4 Hz, H-4); ^{13}C NMR δ (ppm) 27.0 (C-1), 127.7 (C-3), 128.0, 128.2, 128.8, 129.4, 130.4, 131.1, 132.6, 134.4, 136.4 (C-5), 139.5 (C-6), 144.8 (C-4), 198.4 (C-2). (3*E*,5*Z*)-isomer (cyclohexane/dichloromethane: 75/25): mp 45 °C, ^{77}Se δ (ppm) 308.5; ^{1}H NMR δ (ppm) 2.23 (s, 3H), 6.64 (d, 1H, J=15.4 Hz, H-3), 7.10–7.30 (m, 9H), 7.55 (s, 1H, H-6), 7.67–7.71 (m, 2H); ^{13}C NMR δ (ppm) 28.5 (C-1), 126.8 (C-3), 127.9, 128.0, 128.2, 129.4, 130.4, 131.1, 132.6, 134.4, 136.0 (C-5), 146.4 (C-6), 146.8 (C-4), 198.4 (C-2). Anal. Calcd for $C_{18}H_{16}OSe$: C, 66.06; H, 4.93. Found: C, 65.90; H, 4.86.

3.1.6. Preparation of penta-2,4-dienenitriles 7. A solution of *n*-BuLi in hexanes (1.6 M, 3.45 ml, 5.5 mmol) was slowly added, under argon, to cyanomethyldiethylphosphonoacetate (0.97 g, 5.5 mmol) in anhydrous THF (50 ml) at 0 °C. After stirring for 0.5 h at room temperature, the solution was cooled to −78 °C. Then, α-phenylselanyl enal **2** (5 mmol) in THF (5 ml) was added dropwise at this temperature. The mixture was stirred for 2 h at −78 °C for **7a** and **7b** or 12 h for **7c**, quenched with saturated aqueous NH_4Cl, and extracted with diethylether. The organic extracts were dried over magnesium sulfate and concentrated under vacuum. The residue was purified by chromatography on silica gel (light petroleum/CH_2Cl_2: 70/30).

3.1.6.1. 4-Phenylselanylhex-2,4-dienenitrile 7a. Yield 61%. (2*E*,4*Z*)-isomer: ^{77}Se δ (ppm) 252.7; ^{1}H NMR δ (ppm) 2.13 (d, 3H, J=6.9 Hz, H-6), 5.84 (d, 1H, J=15.6 Hz, H-2), 6.69 (q, 1H, J=6.9 Hz, H-5), 7.09 (d, 1H, J=15.7 Hz, H-3), 7.17–7.25 (m, 5H); ^{13}C NMR δ (ppm) 19.3, 99.7 (C-2), 118.3 (C-1), 126.7, 129.4, 129.9, 130.6, 132.0, 148.6 (C-5), 152.1 (C-3). Anal. Calcd for $C_{12}H_{11}NSe$: C, 58.07; H, 4.47. Found: C, 58.13; H, 4.58. (2*E*,4*E*)-isomer: ^{77}Se δ (ppm) 385.8; ^{1}H NMR δ (ppm) 2.04 (d, 3H, J=7.4 Hz, H-6), 5.89 (d, 1H, J=15.6 Hz, H-2), 6.77 (q, 1H, J=7.3 Hz, H-5), 7.42 (d, 1H, J=15.6 Hz, H-3), 7.17–7.25 (m, 5H); ^{13}C NMR δ (ppm) 16.1, 102.4, 118.3, 126.7, 129.3, 129.8, 132.0, 144.4, 151.8. (2*Z*,4*Z*)-isomer: ^{77}Se δ (ppm) 348.5; ^{1}H NMR δ (ppm) 2.10 (dd, 3H, J=0.9, 6.9 Hz, H-6), 5.09 (d, 1H, J=11.4 Hz, H-2), 6.69 (dd, 1H, J=0.9, 11.4 Hz, H-3), 6.76 (qd, 1H, J=0.9, 7.3 Hz, H-5), 7.19–7.25 (m, 3H), 7.38–7.45 (m, 2H); ^{13}C NMR δ (ppm) 18.4, 96.7 (C-2), 116.6 (C-1), 126.4, 127.4, 129.3, 129.7, 140.4, 147.5. (2*Z*,4*E*)-isomer: ^{77}Se δ (ppm) 304.5; ^{1}H NMR δ (ppm) 1.94 (dd, 3H, J=1.0, 7.2 Hz, H-6), 5.25 (d, 1H, J=11.2 Hz, H-2), 6.70 (dd, 1H, J=0.9, 11.2 Hz, H-3), 6.55 (qd, 1H, J=1.0, 7.2 Hz, H-5), 7.19–7.25 (m, 3H), 7.38–7.45 (m, 2H).

3.1.6.2. 4-Phenylselanyloct-2,4-dienenitrile 7b. Yield 82%. (2*E*,4*Z*)-isomer: ^{77}Se δ (ppm) 260.7; ^{1}H NMR δ (ppm) 0.95 (t, 3H, J=7.0 Hz, H-8), 1.50 (m, 2H, H-7), 2.54 (q, 2H, J=7.0 Hz, H-6), 5.83 (d, 1H, J=15.6 Hz, H-2), 6.62 (t, 1H, J=7.4 Hz, H-5), 7.10 (d, 1H, J=15.6 Hz, H-3), 7.12–7.40 (m, 5H); ^{13}C NMR δ (ppm) 13.9, 21.9, 35.2, 99.8 (C-2), 118.2 (C-1), 126.3, 126.7, 128.8 (C-4), 129.2, 129.7, 152.0 (C-3), 153.7 (C-5). Anal. Calcd for $C_{14}H_{15}NSe$: C, 60.87; H, 5.47; N, 5.07. Found: C, 60.63; H, 5.28; N, 4.78. (2*E*,4*E*)-isomer: ^{77}Se δ (ppm) 387.1; ^{1}H NMR δ (ppm) 0.98 (t, 3H, J=7.0 Hz, H-8), 1.52 (m, 2H, H-7), 2.52 (q, 2H, J=7.0 Hz, H-6), 5.90 (d, 1H, J=15.6 Hz, H-2), 6.69 (t, 1H, J=7.1 Hz, H-5), 7.12–7.50 (m, 6H); ^{13}C NMR δ (ppm) 12.7, 22.3, 32.0, 102.4 (C-2), 116.6 (C-1), 125.6, 127.0, 128.8 (C-4), 129.2, 129.7, 144.7 (C-5), 153.8 (C-3). (2*Z*,4*Z*)-isomer: ^{77}Se δ (ppm) 357.3; ^{1}H NMR δ (ppm) 0.97 (t, 3H, J=7.0 Hz, H-8), 1.50 (m, 2H, H-7), 2.39 (q, 2H, J=7.0 Hz, H-6), 5.09 (d, 1H, J=11.5 Hz, H-2), 6.65–6.73 (m, 2H, H-3, H-5), 7.12–7.40 (m, 5H); ^{13}C NMR δ (ppm) 13.7, 22.0, 34.3, 96.9 (C-2),

116.6 (C-1), 125.6, 127.2, 128.8 (C-4), 129.2, 129.7, 145.1 (C-5), 151.1 (C-3).

3.1.6.3. 5-Phenyl-4-phenylselanylpent-2,4-dienenitrile 7c. Yield 83%. (2*E*,4*Z*)-isomer (cyclohexane/dichloromethane: 80/20): mp 92 °C, ^{77}Se δ (ppm) 288.2; ^{1}H NMR δ (ppm) 5.94 (d, 1H, *J*=15.6 Hz, H-2), 7.15–7.35 (m, 9H), 7.47 (s, 1H, H-5), 7.68–7.72 (m, 2H); ^{13}C NMR δ (ppm) 101.3 (C-2), 118.4 (C-1), 126.9, 127.1, 128.4, 129.7, 130.0, 130.2, 130.6, 135.3 (C-4), 147.6 (C-5), 153.0 (C-3). Anal. Calcd for $C_{17}H_{13}NSe$: C, 65.81; H, 4.22; N, 4.51. Found: C, 65.87; H, 3.98; N, 4.38. (2*E*,4*E*)-isomer (cyclohexane/dichloromethane: 90/10): ^{77}Se δ (ppm) 408.6; ^{1}H NMR δ (ppm) 5.99 (d, 1H, *J*=15.8 Hz, H-2), 7.17–7.50 (m, 11H), 7.55 (s, 1H, H-5); ^{13}C NMR δ (ppm) 103.6 (C-2), 117.0 (C-1), 127.6, 128.3, 128.9, 129.4, 129.6, 129.8, 130.0, 131.6, 135.4 (C-4), 146.2 (C-5), 152.8 (C-3).

(2*Z*,4*Z*)-isomer (cyclohexane/dichloromethane: 85/15): ^{77}Se δ (ppm) 398.4; ^{1}H NMR δ (ppm) 5.14 (d, 1H, *J*=11.3 Hz, H-2), 6.75 (dd, 1H, *J*=1.0, 11.3 Hz, H-3), 7.15–7.35 (m, 9H), 7.55–7.60 (m, 2H); ^{13}C NMR δ (ppm) 97.7 (C-2), 116.6 (C-1), 126.6, 128.2, 128.6, 128.9, 129.1, 129.1, 129.3, 133.7, 135.8 (C-4), 138.6 (C-5), 151.8 (C-3).

(2*Z*,4*E*)-isomer (cyclohexane/dichloromethane: 85/15): ^{77}Se δ (ppm); ^{1}H NMR δ (ppm) 5.26 (d, 1H, *J*=11.8 Hz, H-2), 6.99 (dd, 1H, *J*=1.3, 11.8 Hz, H-3), 7.15–7.35 (m, 9H), 7.55–7.60 (m, 2H); ^{13}C NMR δ (ppm) 101.1 (C-2), 116.1 (C-1), 126.6, 128.2, 128.6, 128.9, 129.1, 129.1, 129.3, 133.7, 136.0 (C-4), 142.4 (C-5), 146.9 (C-3).

3.1.7. Preparation of dienic esters 8. A solution of *n*-BuLi in hexanes (1.6 M, 3.45 ml, 5.5 mmol) was slowly added, under argon, to triethylphosphonoacetate (1.2 g, 5.5 mmol) in anhydrous THF (50 ml) at 0 °C. After stirring for 0.5 h at room temperature, α-phenylselanyl enal **2** (5 mmol) in THF (5 ml) was added dropwise. The mixture was stirred for 3 h at room temperature, quenched with saturated aqueous NH_4Cl, and extracted with diethylether. The organic extracts were dried over magnesium sulfate and concentrated under vacuum. The residue was purified by chromatography on silica gel (light petroleum/CH_2Cl_2: 80/20).

3.1.7.1. Ethyl 4-phenylselanylhex-2,4-dienoate 8a.[8] Yield 72%. (2*E*,4*Z*)-isomer: ^{77}Se δ (ppm) 263.6; ^{1}H NMR δ (ppm) 1.27 (t, 3H, *J*=7.1 Hz), 2.09 (d, 3H, *J*=6.9 Hz), 4.17 (q, 2H, *J*=7.1 Hz), 6.30 (dd, 1H, *J*=0.6, 15.1 Hz, H-2), 6.71 (q, 1H, *J*=6.9 Hz, H-5), 7.12–7.32 (m, 5H), 7.41 (d, 1H, *J*=15.1 Hz, H-3); ^{13}C NMR δ (ppm) 14.4, 19.2, 60.5, 121.6 (C-2), 126.3, 129.4, 129.8, 130.4 (C-4), 134.3, 146.9 (C-3), 147.5 (C-5), 167.4 (C-1). (2*E*,4*E*)-isomer: ^{77}Se δ (ppm) 399.6; ^{1}H NMR δ (ppm) 1.26 (t, 3H, *J*=7.1 Hz), 2.04 (d, 3H, *J*=7.4 Hz), 4.17 (q, 2H, *J*=7.1 Hz), 6.33 (d, 1H, *J*=14.8 Hz, H-2), 6.65 (q, 1H, *J*=7.1 Hz, H-5), 7.12–7.30 (m, 5H), 7.72 (d, 1H, *J*=14.8 Hz, H-3); ^{13}C NMR δ (ppm) 13.9, 19.3, 60.4, 122.3 (C-2), 126.8, 129.3, 129.8, 130.4 (C-4), 134.4, 138.9 (C-3), 147.4 (C-5), 167.3 (C-1).

3.1.7.2. Ethyl 4-phenylselanyloct-2,4-dienoate 8b.[8] Yield 71%. (2*E*,4*Z*)-isomer: ^{77}Se δ (ppm) 271.5; ^{1}H NMR δ (ppm) 0.92 (t, 3H, *J*=7.0 Hz), 1.26 (t, 3H, *J*=7.1 Hz), 1.48 (m, 2H), 2.51 (q, 2H, *J*=7.0 Hz), 4.17 (q, 2H, *J*=7.1 Hz), 6.28 (d, 1H, *J*=15.1 Hz, H-2), 6.63 (t, 1H, *J*=7.1 Hz, H-5), 7.12–7.30 (m, 5H), 7.40 (d, 1H, *J*=15.1 Hz, H-3); ^{13}C NMR δ (ppm) 14.0, 14.4, 22.2, 35.2, 60.5, 121.8 (C-2), 126.3, 129.4, 129.8, 130.8, 131.0 (C-4), 150.0 (C-3), 152.9 (C-5), 167.4 (C-1). (2*E*,4*E*)-isomer: ^{77}Se δ (ppm) 401.1; ^{1}H NMR δ (ppm) 0.96 (t, 3H, *J*=7.0 Hz), 1.27 (t, 3H, *J*=7.1 Hz), 1.51 (m, 2H), 2.42 (q, 2H, *J*=7.0 Hz), 4.17 (q, 2H, *J*=7.1 Hz), 6.33 (d, 1H, *J*=15.1 Hz, H-2), 6.59 (t, 1H, *J*=7.1 Hz, H-5), 7.12–7.30 (m, 5H), 7.70 (d, 1H, *J*=15.1 Hz, H-3); ^{13}C NMR δ (ppm) 13.8, 14.4, 22.5, 32.1, 60.6, 124.0 (C-2), 126.7, 129.0, 129.3, 129.8, 131.1 (C-4), 139.3 (C-3), 152.0 (C-5), 167.4 (C-1).

3.1.7.3. Ethyl 5-Phenyl-4-phenylselanylpent-2,4-dienoate 8c.[8] Yield 84%. (2*E*,4*Z*)-isomer: 54%, mp=55 °C; ^{77}Se δ (ppm) 301.1; ^{1}H NMR δ (ppm) 1.28 (t, 3H, *J*=7.2 Hz), 4.16 (q, 2H, *J*=7.2 Hz), 6.38 (d, 1H, *J*=15.1 Hz, H-2), 7.16–7.40 (m, 8H), 7.52 (s, 1H, H-5), 7.55 (d, 1H, *J*=15.1 Hz, H-3), 7.67–7.73 (m, 2H); ^{13}C NMR δ (ppm) 14.4, 60.6, 123.1 (C-2), 126.6, 127.5 (C-4), 128.3, 129.3, 129.4, 130.1, 130.4, 130.7, 136.0, 146.7 (C-3), 147.8 (C-5), 167.1 (C-1). (2*E*,4*E*)-isomer: ^{77}Se δ (ppm) 421.6; ^{1}H NMR δ (ppm) 1.25 (t, 3H, *J*=7.1 Hz), 4.17 (q, 2H, *J*=7.1 Hz), 6.46 (d, 1H, *J*=15.1 Hz, H-2), 7.20–7.42 (m, 9H), 7.45–7.55 (m, 2H), 7.80 (d, 1H, *J*=15.1 Hz, H-3); ^{13}C NMR δ (ppm) 14.3, 60.6, 125.2 (C-2), 127.4, 128.2, 128.7, 129.3 (C-4), 129.5, 129.6, 130.1, 132.4, 136.2, 140.9 (C-3), 144.4 (C-5), 167.1 (C-1).

3.1.8. Preparation of selenoxides 9c–11c. A solution of the diene (1 mmol) in dichloromethane (5 ml) was treated dropwise with H_2O_2 (35% aqueous solution, 0.85 ml). The reaction was stirred at room temperature for 1 h. The solution was washed with water, dried, and concentrated under vacuum. The oily product was washed twice with light petroleum and the crude mixture was used directly in the next step.

3.1.8.1. 6-Phenyl-5-phenylseleninylhex-3,5-dien-2-one 9c. Yield 81%. Major isomer: 60%; ^{1}H NMR ($CDCl_3$, 200 MHz) δ (ppm) 2.28 (s, 3H), 6.53 (d, 1H, *J*=16.5 Hz), 7.88 (s, 1H), 7.15–7.80 (m, 11H). IR (neat): 3057, 2982, 2936, 1715, 1625, 1476, 1438, 1369, 1302, 1263, 1180, 1156, 1022, 737, 690 cm^{-1}. Minor isomer: 40%; ^{1}H NMR ($CDCl_3$, 200 MHz) δ (ppm) 2.24 (s, 3H), 6.67 (d, 1H, *J*=16.2 Hz), 7.15–7.65 (m, 12H).

3.1.8.2. 5-Phenyl-4-phenylseleninylpent-2,4-dienenitrile 10c. Yield 89%. Major isomer: 50%; ^{1}H NMR ($CDCl_3$, 200 MHz) δ (ppm) 6.22 (d, 1H, *J*=16.3 Hz), 7.10–7.72 (m, 12H). Minor isomer: 25%; ^{1}H NMR δ (ppm) 5.45 (d, 1H, *J*=11.9 Hz), 6.81–8.05 (m, 12H). Minor isomer: 25%; ^{1}H NMR δ (ppm) 5.92 (d, 1H, *J*=16.6 Hz), 6.81–7.72 (m, 12H).

3.1.8.3. Ethyl 5-phenyl-4-phenylseleninylpent-2,4-dienoate 11c. Yield 76%. Major isomer 2*E*,4*Z*: 72%; ^{1}H NMR ($CDCl_3$) δ (ppm) 1.25 (t, 3H, *J*=7.1 Hz), 4.16 (m, 2H), 6.51 (d, 1H, *J*=15.7 Hz), 7.40–7.52 (m, 9H), 7.60 (d, 1H, *J*=15.7 Hz), 7.62–7.65 (m, 2H); ^{13}C NMR δ (ppm) 14.1, 60.5, 123.0, 126.3, 128.9, 129.4, 129.7, 129.9, 131.2, 133.6, 137.0, 140.0, 140.6, 141.1, 165.7. IR (neat): 3059,

2981, 2935, 1954, 1887, 1714, 1621, 1576, 1476, 1439, 1368, 1303, 1266, 1176, 1134, 1100, 1022, 738, 690 cm^{-1}. Minor isomer 2*E*,4*E*: 28%; ^1H NMR δ (ppm) 1.30 (t, 3H, *J*=7.1 Hz), 4.22 (m, 2H), 6.25 (d, 1H, *J*=16.2 Hz), 7.40–7.55 (m, 9H), 7.70–7.82 (m, 3H); ^{13}C NMR δ (ppm) 14.1, 60.9, 122.6, 126.6, 128.8, 129.7, 129.9, 130.0, 131.7, 133.7, 136.9, 137.3, 141.3, 165.5.

3.1.9. Preparation of α-hydroxyallenes. A solution of selenoxyde (0.9 mmol) and triethylamine (0.2 g, 2 mmol) in THF (15 ml) was stirred at room temperature for 12 h. After addition of water and extraction with ether, the organic layer was dried over $MgSO_4$ and evaporated. The allene was purified by chromatography on silica gel (light petroleum/ethyl acetate: 95/5).

3.1.9.1. 4-Phenylbuta-2,3-dien-1-ol 12c.[25] Yield 78%. ^1H NMR ($CDCl_3$, 300 MHz) δ (ppm) 1.72 (br s, 1H, OH), 4.26 (m, 2H, H-1), 5.78 (q, 1H, *J*=6.1 Hz, H-2), 6.32 (dt, 1H, *J*=3.0, 6.1 Hz, H-4), 7.19–7.36 (m, 5H, Ph); ^{13}C NMR δ (ppm) 60.5 (C-1), 96.0, 97.3, 127.0, 127.4, 128.8, 133.9, 137.3, 204.4 (C-3).

3.1.9.2. 5-Phenyl penta-3,4-dien-2-ol 13c. Yield 81%, 63/37. ^1H NMR δ (ppm) 1.37 (d, 3H, *J*=6.4 Hz), 1.86 (br s, 1H), 4.47 (m, 1H, H-2), 5.72 (m, 1H, H-3), 6.30 (dd, 1H, *J*=2.3, 6.4 Hz, H-5), 7.18–7.34 (m, 5H); ^{13}C NMR δ (ppm) (22.48, 22.62, C-1), (64.88, 65.19, C-2), (96.19, 96.37, C-5),[32] 99.87 (2C), 125.8, 126.2, 127.4, (132.93, 133.0),[32] (202.21, 202.26, C-4).[32] Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.80; H, 7.72.

3.1.9.3. 1,4-Diphenyl buta-2,3-dien-1-ol 14c.[8] Yield 81%, 70/30. ^1H NMR δ (ppm) 2.16 (d, 1H, *J*=4.1 Hz, O*H*), 5.41 (ddd, 1H, *J*=2.2, 4.1, 6.5 Hz, H-1), 5.88 (dd, 1H, *J*=6.3, 6.5 Hz, H-2), 6.39 (dd, 1H, *J*=2.2, 6.3 Hz, H-4), 7.20–7.50 (m, 10H); ^{13}C NMR δ (ppm) (72.29, 72.49, C-1), (97.72, 98.03),[32] (99.98, 2C), 126.1, 127.0, 127.5, 128.0, 128.7, 128.8, 133.8, 143.0, (203.9, C-3).

3.1.9.4. Ethyl 2-hydroxy-5-phenylpenta-3,4-dienoate 15c.[8] Yield 75%. Major isomer: 70%; ^1H NMR δ (ppm) 1.25 (t, 3H, *J*=7.2 Hz), 2.97 (d, 1H, *J*=7.6 Hz, O*H*), 4.25 (m, 2H), 4.77 (ddd, 1H, *J*=2.8, 6.1, 7.6 Hz, H-2), 5.78 (t, 1H, *J*=6.1 Hz, H-3), 6.41 (dd, 1H, *J*=2.8, 6.1 Hz, H-5), 7.20–7.33 (m, 5H); ^{13}C NMR δ (ppm) 14.2, 62.4, 69.0 (C-2), 95.1 (C-3), 98.6 (C-5), 127.1, 127.6, 128.7, 133.1, 173.2 (C-1), 205.1 (C-4). IR (neat): 3457, 2983, 2937, 1954, 1732, 1454, 1371, 1205, 1095, 1023, 699 cm^{-1}. Minor isomer, ^1H NMR δ (ppm) 1.32 (t, 3H, *J*=7.2 Hz), 3.03 (d, 1H, *J*=6.9 Hz, O*H*), 4.24 (q, 2H, *J*=7.1 Hz), 4.77 (ddd, 1H, *J*=2.6, 6.4, 6.9 Hz, H-2), 5.72 (t, 1H, *J*=6.4 Hz, H-3), 6.40 (dd, 1H, *J*=2.6, 6.4 Hz, H-5), 7.20–7.33 (m, 5H); ^{13}C NMR δ (ppm) 14.2, 62.3, 69.2 (C-2), 95.2 (C-3), 98.4 (C-5), 127.1, 127.7, 128.7, 133.3, 173.1 (C-1), 205.4 (C-4).

3.1.9.5. Hexa-3,4-dien-2-ol 13a. Yield 51%, 60/40. ^1H NMR δ (ppm) 1.28 (d, 3H, *J*=6.3 Hz), 1.69 (dd, 3H, *J*=1.2, 6.9 Hz), 4.32 (m, 1H), 5.21–5.29 (m, 2H); ^{13}C NMR δ (ppm) (14.2, 2C), (23.3, 2C), (66.0, 2C), 88.9, (96.3, 2C), 996.3, 202.4.

3.1.9.6. Octa-3,4-dien-2-ol 13b. Yield 63%, 64/36. ^1H NMR δ (ppm) 0.92 (t, 3H, *J*=7.2 Hz), 1.28 (d, 3H, *J*=6.3 Hz), 1.43 (m, 2H), 1.70 (s, 1H), 1.99 (m, 2H), 4.32 (m, 1H), 5.23–5.31 (m, 2H); ^{13}C NMR δ (ppm) 13.8 (C-8), 22.4 (C-1), 23.6, 30.9, (66.09, 66.29, C-2),[32] (94.31, 94.48), (97.0, 2C), (201.80, 201.94).[32] Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.12. Found: C, 75.92; H, 11.10.

3.1.9.7. 1-Phenyl penta-2,3-dien-1-ol 14a. Yield 38%. Major isomer: 75%; ^1H NMR δ (ppm) 1.70 (dd, 3H, *J*=3.4, 6.6 Hz), 2.11 (d, 1H, *J*=4.1 Hz), 5.24 (m, 1H), 5.37 (m, 2H), 7.25–7.45 (m, 5H); ^{13}C NMR δ (ppm) 14.4, 72.36 (C-1), 89.81 (C-4), 95.66 (C-2), 126.2, 127.8, 128.6, 143.2, 203.13 (C-3). IR (neat): 3390, 3025, 2924, 1969, 1451, 1234, 1196, 1044, 1014, 872, 699 cm^{-1}. Minor isomer: 25%; ^1H NMR δ (ppm) 1.73 (dd, 3H, *J*=3.4, 6.6 Hz), 2.11 (d, 1H, *J*=4.1 Hz), 5.24 (m, 1H), 5.37 (m, 2H), 7.25–7.45 (m, 5H); ^{13}C NMR δ (ppm) 14.5, 72.30 (C-1), 89.93 (C-4), 95.66 (C-2), 126.20, 127.80, 128.6, 143.2, 203.13 (C-3).

3.1.9.8. 1-Phenyl hepta-2,3-dien-1-ol 14b. Yield 67%, 75/25. ^1H NMR δ (ppm) 0.92 (t, 3H, *J*=7.3 Hz, major), 0.94 (t, 3H, *J*=7.3 Hz), 1.44 (m, 2H), 2.01 (m, 1H), 2.13 (d, 1H, *J*=4.0 Hz, O*H*), 5.24 (m, 1H), 5.39 (m, 2H), 7.25–7.42 (m, 5H); ^{13}C NMR δ (ppm) 13.8, 22.4, 30.9, 72.4, (72.32, 72.5, C-1),[32] (94.99, 94.85, C-4),[32] (96.17, 2C), 126.2, 126.3, 127.8, 128.6, 143.3, (202.35, 202.45, C-3).[32] IR (neat): 3386, 2960, 2931, 2872, 1963, 1454, 1233, 1217, 1022, 879, 757, 699. Anal. Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 82.61; H, 8.34.

3.1.9.9. Ethyl-2-hydroxyhexa-3,4-dienoate 15a.[8] Yield 30%, 100/0. ^1H NMR δ (ppm) 1.30 (t, 3H, *J*=7.2 Hz), 1.70 (dd, 3H, *J*=3.1, 7.0 Hz), 2.89 (d, 1H, *J*=6.9 Hz, O*H*), 4.25 (m, 2H), 4.62 (ddd, 1H, *J*=2.7, 6.0, 6.9 Hz, H-2), 5.25 (ddq, 1H, *J*=3.1, 6.0, 7.0 Hz, H-3), 5.35 (ddq, 1H, *J*=2.7, 7.0, 7.2 Hz, H-5); ^{13}C NMR δ (ppm) 14.1, 14.3, 62.0, 69.0 (C-2), 90.4 (C-3), 90.7 (C-5), 173.4 (C-1), 204.4 (C-4). IR (neat): 3473, 2982, 2928, 2855, 1969, 1736, 1445, 1369, 1302, 1262, 1200, 1095, 1023, 868 cm^{-1}.

3.1.9.10. Ethyl 2-hydroxyocta-3,4-dienoate 15b.[8] Yield 30%, 72/28. ^1H NMR δ (ppm) 0.93 (t, 3H, *J*=7.3 Hz), 1.31 (t, 3H, *J*=6.9 Hz), 1.44 (m, 2H), 2.01 (m, 2H), 2.83 (major diast. d, 1H, *J*=7.4 Hz, O*H*), 2.84 (minor diast. d, 1H, *J*=7.3 Hz, O*H*), 4.26 (m, 2H), 4.61 (ddd, 1H, *J*=2.7, 6.0, 7.4 Hz, H-2), 5.30 (ddt, 1H, *J*=3.1, 6.0, 7.1 Hz, H-3), 5.41 (ddt, 1H, *J*=2.7, 6.4, 7.1 Hz, H-5); ^{13}C NMR δ (ppm) 13.7, 14.3, (22.19, 22.26),[32] (30.53, 30.57),[32] 62.0, (69.11, 69.28, C-2),[32] (91.18, 91.23, C-3),[32] (95.52, 95.61, C-5),[32] 173.4 (C-1), 203.6 (C-4). IR (neat): 3473, 2961, 2933, 2874, 1966, 1732, 1464, 1370, 1260, 1197, 1095, 1023, 861 cm^{-1}.

3.1.9.11. Ethyl-2-hydroxy-5-phenylpenta-3,4-dienoate 15c.[8] Yield 75%, 60/40. ^1H NMR δ (ppm) Major isomer: 1.25 (t, 3H, *J*=7.2 Hz), 2.97 (d, 1H, *J*=7.6 Hz, O*H*), 4.25 (m, 2H), 4.77 (ddd, 1H, *J*=2.8, 6.1, 7.6 Hz, H-2), 5.78 (t, 1H, *J*=6.1 Hz, H-3), 6.40 (dd, 1H, *J*=2.8, 6.1 Hz, H-5), 7.17–7.35 (m, 5H); ^{13}C NMR δ (ppm) 14.2, 62.3, 69.0 (C-2), 95.2 (C-3), 98.7 (C-5), 127.1, 127.7, 128.8, 133.1, 173.12 (C-1), 205.07 (C-4). Minor isomer: 1.32 (t, 3H,

J=7.2 Hz), 3.03 (d, 1H, *J*=6.9 Hz, O*H*), 4.25 (m, 2H), 4.77 (ddd, 1H, *J*=2.6, 6.4, 6.9 Hz, H-2), 5.72 (t, 1H, *J*=6.4 Hz, H-3), 6.40 (dd, 1H, *J*=2.6, 6.4 Hz, H-5), 7.17–7.35 (m, 5H); ^{13}C NMR δ (ppm) 14.2, 62.2, 69.0 (C-2), 95.2 (C-3), 98.6 (C-5), 127.1, 127.7, 128.8, 133.1, 173.15 (C-1), 205.43 (C-4). IR (neat): 3457, 2983, 2937, 1954, 1732, 1454, 1371, 1205, 1095, 1025, 862, 770, 699 cm^{-1}.

3.1.10. Preparation of *tert*-butyl-*N*-allenyl carbamates. To a solution of selenide (1 mmol), *tert*-butyl carbamate (0.35 g, 3 mmol), triethylamine (0.8 g, 8 mmol) in methanol (3 ml) and *N*-bromosuccinimide (0.35 g, 3 mmol) were slowly added at 0 °C. The mixture was stirred for 45 min, diluted with ethyl acetate (10 ml), and treated with an aqueous saturated solution of NaCl (10 ml). After extraction and concentration, the oily residue was chromatographed on silica gel (light petroleum/ethyl acetate: 95/5).

3.1.10.1. *tert*-Butyl-*N*-(4-phenylbut-2,3-dien-1-yl)carbamate 16c. Yield 53%. ^{1}H NMR δ (ppm) 1.33 (9H, s), 3.77 (2H, m), 4.66 (1H, br s), 5.57 (1H, q, *J*=5.6 Hz), 6.21 (1H, dt, *J*=3.2, 5.6 Hz), 7.10–7.26 (5H, m); ^{13}C NMR δ (ppm) 28.5, 39.2, 79.7, 93.6, 97.5, 127.0, 127.3, 128.8, 134.0, 155.8, 204.5. Anal. Calcd for $C_{15}H_{19}NO_2$: C, 72.18; H, 7.02; N, 6.11. Found: C, 72.44; H, 7.31; N, 5.81.

3.1.10.2. *tert*-Butyl-*N*-(5-phenylpent-3,4-dien-2-yl)-carbamate 17c. Yield 48%. ^{1}H NMR δ (ppm) 1.30 (3H, d, *J*=6.7 Hz), 1.40 (9H, s), 4.32 (1H, m), 4.52 (1H, br s), 5.65 (1H, t, *J*=5.3 Hz), 6.24 (1H, dd, *J*=3.1, 5.3 Hz), 7.13–7.24 (5H, m); ^{13}C NMR δ (ppm) 21.8, (27.03, 27.48),[32] 39.2, 52.55, 96.9, 98.1, 125.8, 127.2, 128.9, 133.0, 152.0, 202.5. Anal. Calcd for $C_{16}H_{21}NO_2$: C, 74.10; H, 8.16; N, 5.40. Found: C, 74.07; H, 8.32; N, 5.53.

3.1.10.3. *tert*-Butyl-*N*-(1,4-diphenylbuta-2,3-dien-1-yl)-carbamate 18c. Yield 43%. ^{1}H NMR δ (ppm) 1.32 (9H, s), 5.00 (1H, br s), 5.41 (1H, m), 5.82 (1H, t, *J*=5.7 Hz), 6.40 (1H, dd, *J*=3.5, 6.4 Hz), 7.10–7.31 (10H, m); ^{13}C NMR δ (ppm) (28.03, 28.46), 39.3, 53.5, 98.2, 98.9, 127.0, 127.1, 127.6, 127.9, 128.4, 128.5, 134.5, 134.6, 155.0, 203.0. Anal. Calcd for $C_{21}H_{23}NO_2$: C, 78.47; H, 7.21; N, 4.36. Found: C, 78.63; H, 7.19; N, 4.32.

3.1.10.4. Ethyl-2-(*tert*-butoxycarbonylamino)-5-phenylpent-3,4-dienoate 19c. Yield 51%. ^{1}H NMR δ (ppm) 1.16 (3H, t, *J*=7.1 Hz), 1.44 (9H, s), 4.14–4.25 (2H, m), 4.94 (1H, m), 5.21 (1H, br s), 5.81 (1H, m), 6.40 (1H, dd, *J*=3.2, 6.4 Hz), 7.22–7.35 (5H, m); ^{13}C NMR δ (ppm) (14.06,14.45),[32] (28.22, 28.31),[32] 39.2, 52.6, (61.81, 62.91),[32] 93.4, (99.20, 99.43),[32] 127.2, 127.3, 128.8, 133.1, 146.6, 147.7, 155.1, 170.6, 204.3. Anal. Calcd for $C_{18}H_{23}NO_4$: C, 68.11; H, 7.30; N, 4.41. Found: C, 67.88; H, 7.12; N, 4.14.

3.1.11. Preparation of α-halogenoallenes 20–22. A solution of bromine (1.6 ml, 1 mmol) or sulfuryl chloride (1.35 ml, 1 mmol) in hexane was added dropwise to the diene (1 mmol) dissolved in hexane (10 ml) at room temperature. This treatment produces instantaneously a bromo- or chloro-adduct. Their dissolution was carried out in carbon tetrachloride (10 ml) in the presence of a large excess of ethylvinylether (3 mmol). The mixture was stirred for 2 h under reflux and then concentrated under vacuum. The α-halogenoallene was chromatographed on silica gel (light petroleum/CH_2Cl_2: 95/5).

3.1.11.1. 4-Chloro-1-phenylbuta-1,2-diene 20c.[21] Yield 58%. ^{1}H NMR δ (ppm) 4.15 (2H, dd, *J*=7.5, 2.0 Hz), 5.80 (1H, m), 6.34 (1H, dt, *J*=2.0, 6.3 Hz), 7.23–7.34 (5H, m); ^{13}C NMR δ (ppm) 42.4, 93.5, 97.1, 127.2, 127.7, 128.8, 133.5, 206.5.

3.1.11.2. 4-Chloro-1-phenylpenta-1,2-diene 21c. Yield 87%. ^{1}H NMR δ (ppm) 1.68 (3H, d, *J*=6.5 Hz), 4.69 (1H, m, H-4), 5.87 (1H, t, *J*=6.5 Hz, H-3), 6.39 (1H, dd, *J*=2.1, 6.5 Hz, H-1), 7.20–7.35 (5H, m); ^{13}C NMR δ (ppm) 25.1 (C-5), 55.1 (C-4), 98.1, 100.0, 127.1, 127.7, 128.9, 133.5, 204.4 (C-2). Anal. Calcd for $C_{11}H_{11}Cl$: C, 73.94; H, 6.21. Found: C, 74.12; H, 6.13.

3.1.11.3. 4-Bromo-1-phenylpenta-1,2-diene 22c. Yield 61%. ^{1}H NMR δ (ppm) 1.72 (3H, d, *J*=6.7 Hz), 5.25 (1H, m), 5.52 (1H, t, *J*=6.6 Hz), 7.16 (1H, dd, *J*=1.7, 6.6 Hz), 7.14–7.32 (5H, m); ^{13}C NMR δ (ppm) 26.4, 68.2, 100.1, 102.6, 128.6, 129.2, 131.5, 135.9, 208.2. Anal. Calcd for $C_{11}H_{11}Br$: C, 59.22; H, 4.97. Found: C, 59.12; H, 5.21.

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