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Sébastien Redon, Anne-Lise Berthe Berkaoui, Xavier Pannecoucke, Francis Outurquin. Selenylated dienes: synthesis, stereochemical studies by ^{77}Se NMR, and transformation into functionalized allenes. *Tetrahedron*, 2007, 63 (18), pp.3707-3717. 10.1016/j.tet.2007.02.082 . hal-01668240

HAL Id: hal-01668240

<https://hal.science/hal-01668240>

Submitted on 17 Feb 2018

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

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Received 17 January 2007; revised 19 February 2007; accepted 20 February 2007

Available online 23 February 2007

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 ^1H 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 chemistry⁶ 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-blocks⁷ 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, phenylselanylalk-enals^{11a} or palladium-catalyzed cross coupling reactions.^{11b} A stereoselective synthesis of 1,3-dienyl selenides was re-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 morpholinobenzeneselen-amide (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) reactions⁸ (**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 part, whereas official numbering will be applied in the experimental part as numbering differs according to substituents.

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

Table 1. Synthesis of conjugated dienes **3–8**

Entry	No.	R ¹	R ²	Yields (%) (Method A or B) ^a	1 <i>E</i> ,3 <i>Z</i>	1 <i>E</i> ,3 <i>E</i>	1 <i>Z</i> ,3 <i>Z</i>
					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 ₂ Et	72 (B)	80	20	
17	8b	Pr	CO ₂ Et	71 (B)	80	20	0
18	8c	Ph	CO ₂ Et	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.

Only dienes **8** (R²=CO₂Et) and **5c** (R¹=R²=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 (R²=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 (R²=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** R²=COMe: 100%, **7** R²=CN: 68–77%, **8** R²=CO₂Et: 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 ¹H NMR spectra, determination of the configurations was very difficult even with NOESY experiment. ⁷⁷Se NMR appeared to be the easiest and the more reliable method to answer this question. In-deed 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*, ⁷⁷Se NMR chemical shift is typical of diene configuration (1*E*,3*E*: 375.8<δ<423.2; 1*E*,3*Z*: 251.8<δ<308.5). In the same series, chemical shift of H2 in ¹H 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 ⁷⁷Se NMR chemical shift (1*Z*,3*Z*: 348.5<δ< 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 R² under *S*-*trans* conformation forced the dienes 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.

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

Entry	No.	R ¹	R ²	1 <i>E</i> ,3 <i>Z</i>		1 <i>E</i> ,3 <i>E</i>		1 <i>Z</i> ,3 <i>Z</i>
				⁷⁷ Se	¹ H (H-2)		⁷⁷ Se	¹ H (H-2)		⁷⁷ Se
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 ₂ Et	263.6	7.41	399.6	7.72				
17	8b	Pr	CO ₂ Et	271.5	7.41	401.1	7.70				
18	8c	Ph	CO ₂ Et	301.1	7.55	421.6	7.80				

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

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 stereo-chemistry of the created double bond C1–C2 was *E*: exclusively when $R^2 = \text{COMe}$ or CO_2Et (Table 1: entries 10–12, **16–18**), as the major isomer with $R^2 = \text{CN}$ (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).

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

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 cyclo-addition 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 $\text{S}_{\text{N}}2^0$ 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

Table 3. α -Hydroxyallenes' synthesis

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)

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 group⁸ 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 R¹ group

Starting dienes	R ¹	R ²	Allenes (yield %)
4a	Me	Me	13a ²⁶ (51)
4b	<i>n</i> -Pr	Me	13b (63)
4c	Ph	Me	13c (81)
5a	Me	Ph	14a ²⁷ (38)
5b	<i>n</i> -Pr	Ph	14b (67)
5c	Ph	Ph	14c ⁸ (81)
8a	Me	CO ₂ Et	15a ⁸ (30)
8b	<i>n</i> -Pr	CO ₂ Et	15b ⁸ (30)
8c	Ph	CO ₂ Et	15c ⁸ (75)

Complementary results showed that when R¹ is an alkyl or phenyl group regardless of the nature of R²: methyl or phenyl, the α -hydroxyallenes **13** and **14** could be obtained with good yields (see Table 4). Furthermore, yields were always higher when R¹ changed by following the order phenyl>propyl>methyl. In all the cases cited above, two diastereomers of allene were detected by ¹³C NMR. Further studies are still undertaken to try to understand and to explain the stereoselectivity.

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.

Due to their pharmaceutical interests (anesthetic, hypnotic, enzyme inhibitors²⁸ or treatment of depression²⁹), numerous methods for the preparation of allenic carbamates are de-scribed in the literature,^{15–18} but none of them have exploited the mildness and the selectivity of organoselenium chemistry.

Hopkins and co-workers³⁰ studied the [2,3]-sigmatropic re-arrangement 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 selen-imide, being able to lead to the formation of corresponding hydroxyallene. ¹H and ¹³C 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 CCl₄ 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.

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

In conclusion, we have developed a general access to 2-phenylselanyl-1,3-dienes and an unambiguous determination of the stereochemistry of the two double bonds based on ⁷⁷Se 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. ⁷⁷Se NMR spectra were recorded at 21 °C on a Bruker DPX 400 spectrometer operating at 76.29 MHz for ⁷⁷Se, 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 ⁷⁷Se NMR was necessary to have reliable information. Chemical shifts (δ) are expressed in ppm relative to TMS for ¹H and ¹³C nuclei and to Me₂Se for ⁷⁷Se 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*-phenylselanylmor-pholine^{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 x 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/ CH₂Cl₂: 85/15).

3.1.1.1. (Z)-2-Phenylselanylbut-2-enal 2a. Yield 85%, oil, ⁷⁷Se δ (ppm) 261.0; ¹H 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); ¹³C 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, ⁷⁷Se δ (ppm) 268.5; ¹H 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); ¹³C 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, ⁷⁷Se δ (ppm) 301.1; ¹H 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); ¹³C 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, ⁷⁷Se δ (ppm) 409.5; ¹H 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); ¹³C 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-phenyl-selanyl enal **2** (5 mmol) in THF (5 ml) was added dropwise. The mixture was stirred for 3 h under reflux, quenched with saturated aqueous NH₄Cl, 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 Kugelrohr distillation.

3.1.2.1. 3-Phenylselanylpent-1,3-diene 3a. Yield 54%, Z/E 87/13. (Z)-isomer: oil, ⁷⁷Se δ (ppm) 251.8; ¹H 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); ¹³C 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 C₁₁H₁₂Se: C, 59.20; H, 5.42. Found: C, 58.96; H, 5.37. (E)-isomer: oil, ⁷⁷Se δ (ppm) 387.4; ¹H 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); ¹³C 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, ⁷⁷Se δ (ppm) 260.3; ¹H 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); ¹³C 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 C₁₃H₁₆Se: C, 62.15; H, 6.42. Found: C, 62.33; H, 6.26. (E)-isomer: oil, ⁷⁷Se δ (ppm) 375.8; ¹H 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), $7.10\text{--}7.32$ (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 ; ^1H 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), $7.25\text{--}7.40$ (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 ; ^1H 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), $7.25\text{--}7.40$ (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 $\text{C}_{16}\text{H}_{14}\text{Se}$: 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 Kugelrohr distillation.

3.1.3.1. 3-Phenylselanylhexas-2,4-diene **4a**. Yield 74%. ($2Z,4Z$)-isomer: oil, ^{77}Se δ (ppm) 362.7 ; ^1H 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), $7.10\text{--}7.25$ (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 $\text{C}_{12}\text{H}_{14}\text{Se}$: C, 60.76; H, 5.95. Found: C, 60.68; H, 5.92. ($2E,4Z$)-isomer: oil, ^{77}Se δ (ppm) 335.5 ; ^1H 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), $7.10\text{--}7.25$ (m, 5H). ($2E,4E$)-isomer: oil, ^{77}Se δ (ppm) 399.8 ; ^1H 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), $7.10\text{--}7.25$ (m, 4H), $7.57\text{--}7.63$ (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 . ($2Z,4E$)-isomer: oil, ^{77}Se δ (ppm) 265.1 ; ^1H NMR δ (ppm) 1.72 (d, 3H , $J=5.2$ Hz, H-6), 1.97 (d, 3H , $J=6.9$ Hz, H-1), $6.05\text{--}6.16$ (m, 2H, H-4, H-5), 6.18 (q, 1H , $J=6.9$ Hz, H-2), $7.10\text{--}7.25$ (m, 3H), $7.57\text{--}7.63$ (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%. ($2Z,4Z$)-isomer: oil, ^{77}Se δ (ppm) 369.2 ; ^1H 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), $7.10\text{--}7.30$ (m, 3H), $7.35\text{--}7.42$ (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 $\text{C}_{14}\text{H}_{18}\text{Se}$: C, 63.39; H, 6.84. Found: C, 63.13; H, 6.94. ($2E,4Z$)-isomer: oil, ^{77}Se δ (ppm) 273.3 ; ^1H 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), $6.01\text{--}6.17$ (m, 3H), $7.10\text{--}7.30$ (m, 3H), $7.58\text{--}7.62$ (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). ($2E,4E$)-isomer: oil, ^{77}Se δ (ppm) 400.8 ; ^1H 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), $6.02\text{--}6.18$ (m, 1H), 6.38 (d, 1H , $J=14.8$ Hz), $7.15\text{--}7.30$ (m, 4H), $7.58\text{--}7.62$ (m, 2H).

3.1.3.3. 1-Phenyl-2-phenylselanylpent-1,3-diene **4c**. Yield 91%. ($1Z,3Z$)-isomer: oil, ^{77}Se δ (ppm) 411.0 ; ^1H 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), $7.18\text{--}7.35$ (m, 8H), $7.50\text{--}7.55$ (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 . ($1E,3Z$)-isomer: oil, ^{77}Se δ (ppm) 309.0 ; ^1H 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), $7.18\text{--}7.35$ (m, 8H), $7.50\text{--}7.55$ (m, 2H). ($1E,3E$)-isomer: first eluted, mp=47 °C, ^{77}Se δ (ppm) 418.5 ; ^1H 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), $7.25\text{--}7.36$ (m, 8H), $7.49\text{--}7.54$ (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 $\text{C}_{17}\text{H}_{16}\text{Se}$: 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 benzyldiphenylphosphonium 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%. ($1Z,3Z$)-isomer: oil, ^{77}Se δ (ppm) 368.6 ; ^1H NMR δ (ppm) 1.79 (dd, 3H , $J=1.6$, 6.9 Hz), $5.93\text{--}6.04$ (m, 2H , H-1, H-4), 6.14 (d, 1H , $J=12.0$ Hz, H-2), $7.10\text{--}7.60$ (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). ($1E,3Z$)-isomer: oil, ^{77}Se δ

(ppm) 261.7; ^1H 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 $\text{C}_{17}\text{H}_{16}\text{Se}$: C, 68.23; H, 5.39. Found: C, 68.54; H, 5.62. (1E,3E)-isomer: oil, ^{77}Se (ppm) 396.6; ^1H 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%. (1Z,3Z)-isomer: ^{77}Se δ (ppm) 374.9; ^1H 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). (1E,3Z)-isomer: ^{77}Se δ (ppm) 269.8; ^1H NMR (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 $\text{C}_{19}\text{H}_{20}\text{Se}$: C, 69.72; H, 6.16. Found: C, 69.54; H, 5.92. (1E,3E)-isomer: ^{77}Se δ (ppm) 397.9; ^1H 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 d (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%. (1Z,3Z)-isomer: ^{77}Se δ (ppm) 415.4; ^1H 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,3E)-isomer:¹² ^{77}Se δ (ppm) 304.0; ^1H 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%. (3E,5Z)-isomer: ^{77}Se δ (ppm) 267.4; ^1H 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 $\text{C}_{13}\text{H}_{14}\text{OSe}$: C, 58.87; H, 5.32. Found: C, 58.51; H, 5.15. (3E,5E)-isomer: ^{77}Se δ (ppm) 401.6; ^1H NMR d (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%. (3E,5Z)-isomer: ^{77}Se δ (ppm) 275.6; ^1H NMR (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 d (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 $\text{C}_{15}\text{H}_{18}\text{OSe}$: C, 61.43; H, 6.19. Found: C, 61.71; H, 6.26. (3E,5E)-isomer: ^{77}Se δ (ppm) 403.7; ^1H NMR (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-phenylselanylhexas-3,5-dien-2-one **6c**. Yield 88%. (3E,5E)-isomer (cyclohexane/dichloromethane:85/15): ^{77}Se δ (ppm) 423.2; ^1H 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 d (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). (3E,5Z)-isomer (cyclohexane/ dichloromethane: 75/25): mp 45 °C, ^{77}Se δ (ppm) 308.5; ^1H 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 $\text{C}_{18}\text{H}_{16}\text{OSe}$: 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-Phenylselanylhexas-2,4-dienenitrile **7a**. Yield 61%. (2E,4Z)-isomer: ^{77}Se δ (ppm) 252.7; ^1H NMR (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 $\text{C}_{12}\text{H}_{11}\text{NSe}$: C, 58.07; H, 4.47. Found: C, 58.13; H, 4.58. (2E,4E)-isomer: ^{77}Se δ (ppm) 385.8; ^1H 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. (2Z,4Z)-isomer: ^{77}Se δ (ppm) 348.5; ^1H 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. (2Z,4E)-isomer: ^{77}Se δ (ppm) 304.5; ^1H 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%. (2E,4Z)-isomer: ^{77}Se δ (ppm) 260.7; ^1H 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 $\text{C}_{14}\text{H}_{15}\text{NSe}$: C, 60.87; H, 5.47; N, 5.07. Found: C, 60.63; H, 5.28; N, 4.78. (2E,4E)-isomer: ^{77}Se δ (ppm) 387.1; ^1H 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). (2Z,4Z)-isomer: ^{77}Se δ (ppm) 357.3; ^1H 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%. (2E,4Z)-isomer (cyclohexane/dichloro-methane: 80/20): mp 92 °C, ^{77}Se δ (ppm) 288.2; ^1H 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 $\text{C}_{17}\text{H}_{13}\text{NSe}$: C, 65.81; H, 4.22; N, 4.51. Found: C, 65.87; H, 3.98; N, 4.38. (2E,4E)-isomer (cyclohexane/dichloromethane: 90/10): ^{77}Se δ (ppm) 408.6; ^1H 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, H-2), 6.99 (dd, 1H, $J=41.3, 11.8$ 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, 129.6, 129.8, 130.0, 131.6, 135.4 (C-4), 146.2 (C-5), 152.8 (C-3). (2Z,4Z)-isomer (cyclohexane/dichloromethane: 85/15): ^{77}Se δ (ppm) 398.4; ^1H 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), 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-phenylselanylhexas-2,4-dienoate **8a**.⁸ Yield 72%. (2E,4Z)-isomer: ^{77}Se δ (ppm) 263.6; ^1H NMR (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). (2E,4E)-isomer: ^{77}Se δ (ppm) 399.6; ^1H 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%. (2E,4Z)-isomer: ^{77}Se δ (ppm) 271.5; ^1H 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). (2E,4E)-

isomer: ^{77}Se δ (ppm) 401.1; ^1H 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-phenylselenanylpent-2,4-dien-oate **8c**.⁸ Yield 84%. (2E,4Z)-isomer: 54%, mp =55 °C; ^{77}Se δ (ppm) 301.1; ^1H 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). (2E,4E)-isomer: ^{77}Se (ppm) 421.6; ^1H 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%; ^1H 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%; ^1H 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-dien-1-yn-3-ol **10c**. Yield 89%. Major isomer: 50%; ^1H NMR (CDCl_3 , 200 MHz) δ (ppm) 6.22 (d, 1H, $J=16.3$ Hz), 7.10–7.72 (m, 12H). Minor isomer: 25%; ^1H NMR δ (ppm) 5.45 (d, 1H, $J=11.9$ Hz), 6.81–8.05 (m, 12H). Minor isomer: 25%; ^1H NMR δ (ppm) 5.92 (d, 1H, $J=16.6$ Hz), 6.81–7.72 (m, 12H) $J=7.2$ Hz), 3.03 (d, 1H, $J=6.9$ Hz, OH), 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%. ^1H 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 $\text{C}_{15}\text{H}_{19}\text{NO}_2$: 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%. ^1H 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 $\text{C}_{16}\text{H}_{21}\text{NO}_2$: 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%. ^1H 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 $\text{C}_{21}\text{H}_{23}\text{NO}_2$: 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-phenyl-pent-3,4-dienoate **19c**. Yield 51%. ^1H 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 $\text{C}_{18}\text{H}_{23}\text{NO}_4$: 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 sulfonyl 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/CH₂Cl₂: 95/5).

3.1.11.1. 4-Chloro-1-phenylbuta-1,2-diene **20c**.²¹ Yield 58%. ¹H 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); ¹³C 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%. ¹H 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); ¹³C 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 C₁₁H₁₁Cl: 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%. ¹H 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); ¹³C NMR δ (ppm) 26.4, 68.2, 100.1, 102.6, 128.6, 129.2, 131.5, 135.9, 208.2. Anal. Calcd for C₁₁H₁₁Br: C, 59.22; H, 4.97. Found: C, 59.12; H, 5.21.

Acknowledgements

We thank the region Haute-Normandie (doctoral fellowship to S.R.) for financial support of this research.

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