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New synthesis and cyclopropanation of α-phenylselanyl α,β-unsaturated ketones with non-stabilized phosphorus ylides

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ABSTRACT

A general method for the preparation of α-phenylselanyl enones is described. Phosphorus ylides react with these α-phenylselanyl enones in a 1,4-addition, leading to cyclopropanes and/or dihydrofurans, depending on the substitution pattern. This unusual reactivity is due to the phenylselanyl moiety, hindering the carbonyl of the enone and making it less prone to 1,2-additions or promoting conjugate addition by electronic effects.

1. Introduction

Organoselenium compounds are versatile reagents that can either act as nucleophiles or electrophiles and can generate radicals under mild conditions.[1] Indeed, due to the weakness of the carbon–selenium bond, it is easier to introduce, transform, or eliminate than sulfur. Among these compounds, α-selanylated α,β-unsaturated aldehydes have been shown to be good precursors of α-allenols, -allenamines or -allenyl chlorides after formation of the corresponding diene (Wittig) and allylic rearrangement of the selanylated moiety.[2] Following our studies on such compounds, we turned our attention to the preparation of α-selanylated α,β-unsaturated ketones and studied their reactivity toward phosphorus ylides. We now report on the surprising results that were obtained, as cyclopropanes and sometimes dihydrofurans were formed instead of the expected dienes.

Usually, α-phenylselanyl α,β-unsaturated ketones are prepared by α-selenenylation of the corresponding α,β-unsaturated ketones (PhSeX/amine[3] or $PhSeNR_2/SiO_2$[4]), by reaction of α-diazo-ketones with PhSeX,[5] by oxidation of propargylic phenylselenoderivatives,[6] or by trapping allenol- or enol-ethers by PhSeX.[7] Nevertheless, these methods are limited to non-hindered enones or non-aryl-substituted β-positions in order to achieve good yields, or necessitate the preparation of reactive intermediates. We therefore envisioned introducing the selenium moiety at the enal stage and then further converting enals into diverse enones by addition/oxidation sequence (Scheme 1). Due to the high sensitivity of the selenium atom to oxidation, highly chemoselective oxidation methods of allylic alcohols have to be used.

2. Results and discussion

α-Phenylselanyl α,β-unsaturated aldehydes **2** were prepared following our recently published procedure[2] and submitted to diverse alkyllithium reagents. The corresponding allyl alcohols **3–8** were obtained in good yields (57–88%) with methyl-, *n*-butyl-, and aryl-lithium whereas secondary and tertiary alkyllithium reagents (*s*-BuLi, *t*-BuLi) gave rise to lower yields (30–36%), as shown in Table 1. Allyl alcohols were then converted into enones by chemoselective oxidation, without affecting the selanylated moiety, by the mild PhSeSePh/*t*-BuOOH procedure.[8] Enones **9–14** were obtained in good yields, except for those in which R^1=H, due to their relative instability (Table 1). When starting enals were Z, substituted enones were obtained mainly (>95%) as *Z* isomers, as determined by ^{1}H NMR (through NOE experiments when possible) and ^{77}Se NMR spectrometric analyses. Indeed, as previously shown, ^{77}Se NMR is an efficient tool for the determination of the geometry of enals and dienes[2] and we extend this method to enones. Comparison of ^{77}Se chemical shifts (δ ppm) of enones **9–14** with those of the starting *Z*-enals **2b** (^{77}Se 261.0 ppm) and **2c** (^{77}Se 301.1 ppm) indicates that the substitution of the aldehyde hydrogen with R^2=Me, *n*-Bu, *s*-Bu, *t*-Bu, or Ph, respectively, generates a homogeneous deshielding of the Se atom of about 35, 36, 45, 80, or 90 ppm, respectively (Table 2).

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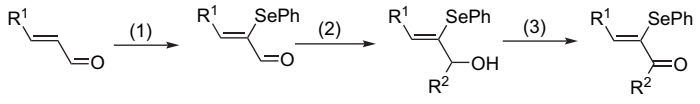


1 | **2** | **3-8** | **9-14**

1a, R^1=H; **1b**, R^1=Me; **1c**, R^1=Ph; **1d**, R^1=*p*-MeO-C_6H_4

2a, R^1=H; **2b**, R^1=Me; **2c**, R^1=Ph; **2d**, R^1=*p*-MeO-C_6H_4

3a-d, R^2=Ph; **4c**, R^2=*p*-MeO-C_6H_4; **5a-d**, R^2=Me; **6a-c**, R^2=*n*-Bu; **7b-c**, R^2=*s*-Bu; **8b-c**, R^2=*t*-Bu

9a-d, R^2=Ph; **10c**, R^2=*p*-MeO-C_6H_4; **11a-d**, R^2=Me; **12a-c**, R^2=*n*-Bu; **13b-c**, R^2=*s*-Bu; **14b-c**, R^2=*t*-Bu

Scheme 1. Synthesis of α-phenylselanylenones **9**–**14**. (1) (a) Morpholinobenzeneselenamide (MBSe), (b) SiO_2; (2) R^2Li, THF, −70 °C; (3) PhSeSePh, *t*-BuOOH, 80 °C.

Table 1
δ^{77}Se of α-phenylselanyl enols **3**–**8** and α-phenylselanyl enones **9**–**14**

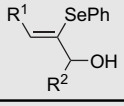
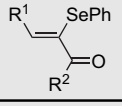
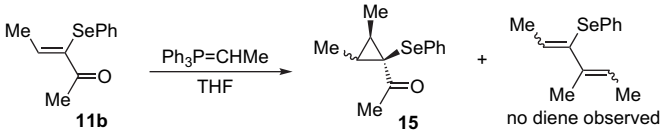
Entry	R^1	R^2						
			No.	Yield (%)	δ^{77}Se	No.	Yield (%)	δ^{77}Se
1	H	Ph	**3a**[9]	60	390.1	**9a**[12]	54	390.8
2	Me	Ph	**3b**	81	269.3	**9b**[4]	88	342.8
3	Ph	Ph	**3c**	88	323.4	**9c**[11,13]	89	404.5
4	*p*-MeO–C_6H_4	Ph	**3d**	85	313.2	**9d**	91	385.4
5	Ph	*p*-MeO–C_6H_4	**4c**	73	327.5	**10c**	80	409.9
6	H	Me	**5a**[9,10]	58	381.0	**11a**[6b,12,14]	54	413.1
7	Me	Me	**5b**	88	254.7	**11b**	85	295.8
8	Ph	Me	**5c**[11]	83	311.3	**11c**[15]	89	337.3
9	*p*-MeO–C_6H_4	Me	**5d**	84	301.4	**11d**	85	325.2
10	H	*n*-Bu	**6a**	57	379.6	**12a**		
11	Me	*n*-Bu	**6b**	75	252.0	**12b**	76	296.9
12	Ph	*n*-Bu	**6c**	66	310.9	**12c**	88	337.4
13	Me	*s*-Bu	**7b**	36	250.9	**13b**	86	304.4
14	Ph	*s*-Bu	**7c**	30	306.9	**13c**	89	349.7
15	Me	*t*-Bu	**8b**	36		**14b**	90	338.0
16	Ph	*t*-Bu	**8c**	31		**14c**	89	388.2

Table 2
δ^{77}Se of α-phenylselanyl enal **2** and α-phenylselanyl enones **9**–**14**

Enal (δ^{77}Se)	Enone (δ^{77}Se)	Δδ (ppm)	Enal (δ^{77}Se)	Enone (δ^{77}Se)	Δδ (ppm)
Z-**2b** (261.0)	**11b** (295.8)	34.8	**Z-2c** (301.1)	**11c** (337.3)	36.2
	12b (297.0)	36		**12c** (337.4)	36.3
	13b (304.4)	43.4		**13c** (349.7)	48.6
	14b (338.0)	77		**14c** (388.2)	87.1
	9b (342.8)	81.8		**9c** (404.5)	103.4

With enones **9**–**14** in hand, we explored their reaction with phosphorus ylides and started with enone **11b** (R^1=Me, R^2=Me) as model substrate. Addition of **11b** to a solution of ethylidenetriphenylphosphorane (R^3=Me, R^4=H) at rt in THF, surprisingly, yielded cyclopropane **15** in 12% yield, 47% of PhSeSePh, and no trace of the desired diene. After a brief survey of the reaction conditions (time and temperature), we found that heating the mixture at 50 °C for 12 h was beneficial, increasing the yield in **15** to 65% (along with 15% of PhSeSePh); again, no diene was observed (Scheme 2).

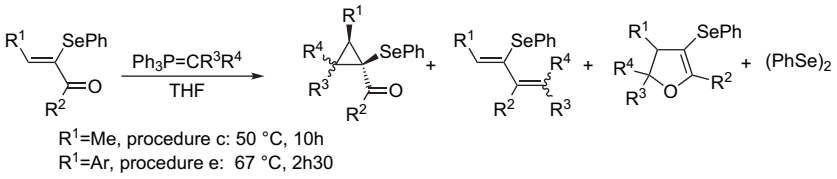
Cyclopropanations via 1,4-addition of phosphorus ylides to enones have been known in the literature for many years, but have never been developed because they generally occur only with highly hindered substrates in which 1,2-additions are not possible or require hard conditions.[16,17] The other methods involving nucleophiles other than phosphorus ylides mainly include sulfur ylides (Corey's ylide), but also ammonium ylides, carbenes, diazomethane, and tellurium derivatives, and have been recently reviewed.[18]



Scheme 2. 1,4-Addition of phosphorus ylide to enone **11b**.

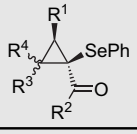
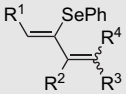
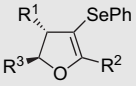
The addition of Corey's ylides to α-phenylthioenones has recently been reported and allows the formation of cyclopropanes or dihydrofurans, depending on both the substituents on the enone and on the oxidation level of the sulfur atom (sulfur, sulfoxide, or sulfone).[19] The advantage of phosphorus ylides lays in the fact that more substituted cyclopropanes can in principle be obtained if alkylphosphorus ylides are used. We thus turned our attention to the cyclopropanation of α-phenylselanyl enones using different phosphorus ylides (Scheme 3, Table 3).

With R^1=Me, cyclopropanes **15**–**20** and **41**–**42** are the exclusive products, regardless of R^2 (Me or Ph), R^3, or R^4 (Me, *n*-Pr, butenyl), in yields ranging between 38 and 65%. The isolated amount of $(PhSe)_2$ ranged between 15 and 26%. The substituted cyclopropanes were isolated as cis and trans mixture at carbons 2 (R^1) and 3 (R^3) from 40/60 to 60/40. When R^2=Me, trans isomer is formed



Scheme 3. Cyclopropanation reactions from enones and phosphorus ylides.

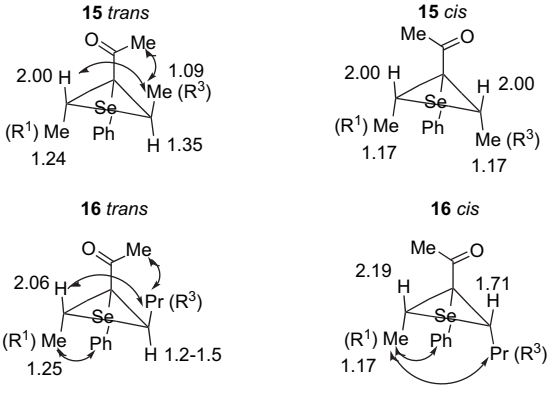
Table 3

Entry	Enone	R^1	R^2	R^3	R^4						$(PhSe)_2$
						Yield[a] (%)	cis/trans[b]	δ^{77}Se ppm	Yield[a] (%)	Yield[a] (%)	Yield[a] (%)
1	**11b**	Me	Me	Me	H	**15**[c] (65)	40/60	276.0/350.6			15
2	**11b**	Me	Me	*n*-Pr	H	**16**[c] (41)	45/55	283.6/352.1			24
3	**11b**	Me	Me	*n*-But-3-enyl	H	**17**[c] (38)	40/60	283.4/352.8			24
4	**9b**	Me	Ph	Me	H	**18**[c] (61)	60/40	309.7/390.9			16
5	**9b**	Me	Ph	*n*-Pr	H	**19**[c] (45)	60/40	318.2/392.3			24
6	**9b**	Me	Ph	*n*-But-3-enyl	H	**20**[c] (45)	52/48	318.4/393.2			26
7	**11c**	Ph	Me	Me	H				**21**[d] (24)		
8	**11c**	Ph	Me	Me	H	**22**[e] (10)	55/45	391.2/421.0		**23** (11) 242.0	
9	**11c**	Ph	Me	*n*-Pr	H	**24**[f] (27)	50/50	389.1/420.7			24
10	**14c**	Ph	*t*-Bu	Me	H	**25**[e] (41)	78/22	300.1/368.0		**26** (16) 262.1	12
11	**9c**	Ph	Ph	Me	H	**27**[e,g] (22)				**28** (47) 266.1	19
12	**9c**	Ph	Ph	*n*-Pr	H	**29**[e] (53)	60/40	329.5/399.2		**30** (7) 266.3	24
13	**9c**	Ph	Ph	*n*-But-3-enyl	H	**31**[e] (32)	56/44	339.6/421.4		**32** (5) 268.1	28
14	**10c**	Ph	Ar[h]	Me	H	**33**[e,g] (25)				**34** (33) 263.7	40
15	**11d**	Ar[h]	Me	Me	H	**35**[e] (13)	70/30		**36** (10) 331.2	**37** (9) 241.4	30
16	**9d**	Ar[h]	Ph	Me	H	**38**[e,g] (13)			**39** (10) 331.0	**40** (35) 266.0	26
17	**11b**	Me	Me	Me	Me	**41**[c] (46)		296.7			22
18	**9b**	Me	Ph	Me	Me	**42**[c] (44)		338.4			16
19	**11c**	Ph	Me	Me	Me	**43**[e] (traces)					22
20	**9c**	Ph	Ph	Me	Me	**44**[e] (traces)					16

[a] Isolated yields.
[b] Determined by ^{77}Se NMR spectrometry on crude mixture.
[c] 50 °C, 10 h.
[d] rt, 3 h.
[e] 67 °C, 2h30.
[f] 50 °C, 2 h.
[g] Deselenenylated cyclopropane.
[h] Ar=*p*-methoxy-phenyl-.

predominantly whereas when R^2=Ph, the cis isomer is the major one. The relationship between R^1 and the selenium group is always cis, as starting enones were of *Z*-configuration. These configurations have been determined by NOE experiments on most of the cyclopropanes. Furthermore, we can also notice that when protons of the cyclopropane ring are cis to the acyl moiety, their chemical shift is always higher than when trans. For example (Scheme 4), in cyclopropanes **15** and **16**, protons cis to the acetyl group have a chemical shift of 2.0–2.2 ppm whereas when they are trans, their chemical shift is lower (1.2–1.5 ppm). These results are consistent with non-selenylated cyclopropanes values.[20] Furthermore, ^{77}Se NMR analysis of cyclopropanes allowed us to correlate the chemical shift to the cis or trans configuration. Thus, for cyclopropanes **15**–**17** (R^1=R^2=Me), we observed 276.0<δ^{77}Se<283.6 for cis configuration and 350.6<δ^{77}Se<352.8 for trans configuration. In a similar manner, for cyclopropanes **18**–**20** (R^1=Me, R^2=Ph), we observed 309.7<δ^{77}Se<318.4 for cis configuration and 390.9<δ^{77}Se<393.2 for trans configuration. These strong differences in chemical shifts in ^{77}Se NMR, in addition to ^{1}H NMR, allowed us to unambiguously attribute either cis or trans configuration to the cyclopropanes.

When we changed R^1 to aryl (Table 3, entries 7–16 and 19–20), the formation of cyclopropane was accompanied with diene and dihydrofuran. Indeed, enones **9c** and **11c** (R^1=Ph) have shown less reactivity toward phosphorus ylides than **9b** and **11b** (R^1=Me) and the formation of cyclopropane is more difficult, necessitating the heating to the reflux of THF but for a shorter time to avoid deselenenylation. Enone **11c** is particularly less reactive and gives rise to low yields in either cyclopropane (27% with butylidenetriphenylphosphorane, entry 9, trace amounts with



Scheme 4. Chemical shifts δ^1H and NOE correlations of cyclopropanes **15** and **16**.

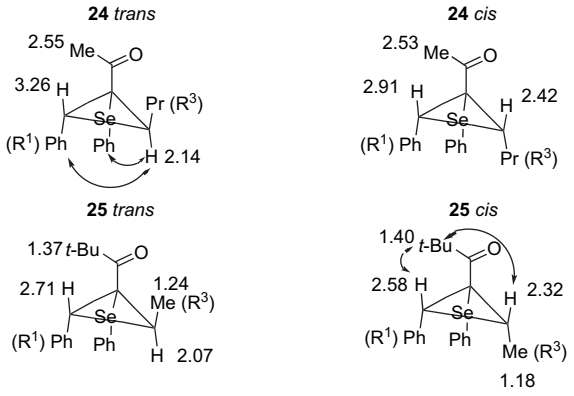
isopropylidenetriphenylphosphorane, entry 19) or dihydrofuran **23** (entry 8). On the contrary, arylenones **9c**, **10c** and **9d** (R^1 and R^2=Ar) are more reactive than **11c** and afford mixtures of cyclopropanes and dihydrofuran in better yields, the latter being sometimes the main product (entries 11, 14, and 16); nevertheless, these enones do not react with hindered ylides (entry 20).

For entries 7 and 8, a dramatic change in the course of the reaction was observed if temperature was changed from rt to reflux: at rt, only diene **21** was isolated in 24% whereas at reflux, only cyclopropane **22** and dihydrofuran **23** were isolated in 10 and 11% yield, respectively. This result emphasizes the versatility of this reaction and shows that optimum temperature and reaction time should be checked for each substrate.

In entries 11, 14, and 16 where R^1 and R^2 are phenyl or aryl and R^3 is methyl, the dihydrofuran was obtained as the major product along with deselenylated cyclopropane and diene (entry 16). In these cases, the formation of deselenylated cyclopropane, instead of the generally observed selenylated one, is not yet understood.

Concerning the relative configuration of the dihydrofurans, NOE experiments show a trans relationship between R^1 and R^3 on dihydrofuran **28**, the same stereochemistry was assigned to other dihydrofurans by analogy. The dienes obtained were isolated as mixtures of stereoisomers.

The cis/trans configuration of the selenylated cyclopropanes **24** and **25** has been determined by NOE experiments and by ^{1}H and ^{77}Se NMR analyses. By analogy, the configuration of cyclopropanes **22**, **29**, **31**, and **35** has also been determined and shows that the cis R^1,R^3 geometry is always the major one (Scheme 5).

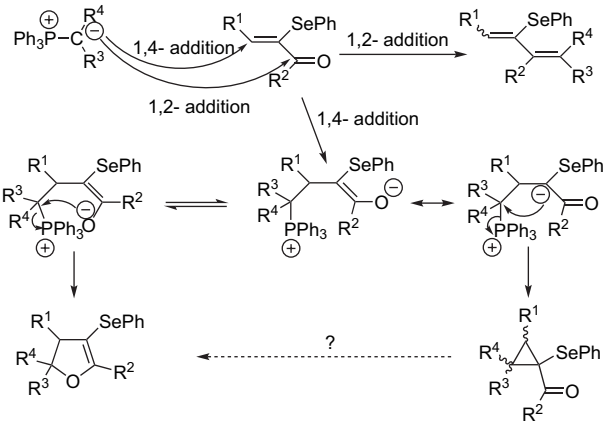


Scheme 5. Chemical shifts δ^1H and NOE correlations of cyclopropanes **24** and **25**.

When a more hindered phosphorus ylide such as isopropylidenetriphenylphosphorane is used (R^3=R^4=Me), the reaction works well when R^1=Me (entries 17 and 18), but failed when R^1=Ph (entries 19 and 20). When semi-stabilized phosphorus ylide is used (R^3=Ph), no cyclopropanation occurred and only diene **45** resulting from Wittig reaction was observed, albeit in low yield (27%, result not shown).

It should also be noted that when a stabilized phosphonate (diethylphosphonoacetate) or the simple methylidenetriphenylphosphorane was used, no reaction occurred at all, whatever the enone was (results not shown).

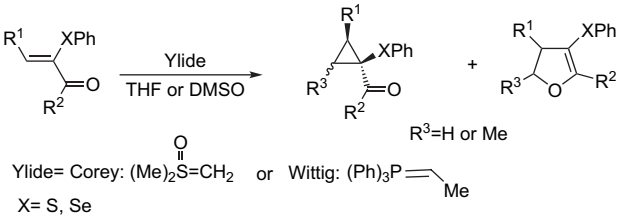
From a mechanistic point of view (Scheme 6), the formation of cyclopropane and dihydrofuran can be explained by 1,4-addition of the ylide onto the enone. The Michael adducts encompassing an enolate and a phosphonium can then transform through two different pathways. In the first one, the carbon of the enolate displaces the phosphonium unit to generate the cyclopropane while in the second one, the oxygen of the enolate substitutes the phosphonium moiety to give the dihydrofuran. The leaving group is triphenylphosphine as determined by ^{31}P NMR of the crude



Scheme 6. Mechanistic considerations.

mixture and recovery of triphenylphosphine after column chromatography. The formation of the diene is the result of the normal Wittig reaction (1,2-addition) while diphenyldiselenide arises from selenophilic reactions on starting enone or reaction intermediates.

Contrary to what was observed by Bernard et al. with α-phenylsulfanylenones[19], the formation of dihydrofuran or cyclopropane is not R^2 but R^1 dependant, as dihydrofuran is only observed when R^1 is an aryl group, regardless of the nature of R^2 (Table 1: alkyl, entries 8 and 10 or aryl, entries 11–14 and 16). This difference may be linked to either the nucleophile nature (sulfur ylide vs phosphorus ylide) or the heteroatom on carbon α to the carbonyl (sulfur vs selenium). Bernard et al. observed also that the oxidation level of the sulfur substituent plays an important role on the course of the reaction as the more electronwithdrawing the substituent was, the more dihydrofuran was isolated. This accounts for a better stabilization of the enolate that drives the equilibrium to the formation of the dihydrofuran. In order to determine whether the difference in reactivity is due to the nucleophile (phosphorus or sulfur ylide) or to the heteroatom (selenium or sulfur), we performed the reaction with Corey's ylide using Bernard's procedure (Scheme 7, Table 4).[19]



Scheme 7. Influence of the ylide on the cyclopropane/dihydrofuran ratio.

From the results obtained in Table 4, it is clear that the cyclopropane/dihydrofuran ratio is more dependent on the nature of the ylide (sulfur or phosphorus) than on the nature of the heteroatom (selenium or sulfur). Indeed, in entries 1 and 3, a dramatic reversal of the cyclopropane/dihydrofuran ratio is observed when the ylide changed from phosphorus to sulfur, keeping the heteroatom (X=Se) unchanged. The result obtained in entry 1 (X=Se, ylide=Corey) is similar to the result obtained by Bernard[19] (entry 2) as the cyclopropane is the major product. The same observation can be made for entries 4–6 where the cyclopropane/dihydrofuran ratios are similar when using Corey's ylide (whatever the heteroatom is) and very different from the ratio obtained when using phosphonium ylide; cyclopropane became almost the unique product with Corey's ylide. For entries 7 and 8, no

Table 4

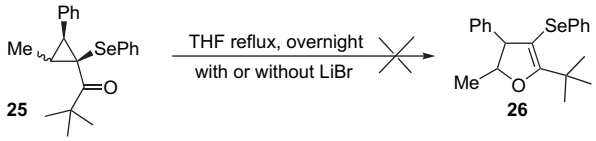
Entry	R^1	R^2	R^3	X	Ylide	Cyclopropane/dihydrofuran	Yield (%)
1	Ph	Ph	H	Se	Corey	**46** (70)/**47** (30)	81
2 (Ref. 20)	*p*-tol	Ph	H	S	Corey	75/25	86
3	Ph	Ph	Me	Se	Wittig	**27** (30)/**28**[a] (70)	69
4	Ph	Me	H	Se	Corey	**48** (90)/**49** (10)	63
5 (Ref. 20)	Ph	Me	H	S	Corey	100/0	68
6	Ph	Me	Me	Se	Wittig	**22** (50)/**23** (50)	22
7	Me	Ph	H	Se	Corey	**50** 100/0	66
8	Me	Ph	Me	Se	Wittig	**18** 100/0	61

[a] : Deselenenylated cyclopropane.

differences were observed and cyclopropane was always the only isolated product.

These results show that the formation of both dihydrofuran and cyclopropane depends on the nature of the ylide and not on the nature of the heteroatom. These two methods are complementary: the use of Corey's ylide leads mainly to the formation of the cyclopropane but is limited to the introduction of a methylene group. On the other hand, the use of a phosphonium ylide gives rise to the formation of both cyclopropane and dihydrofuran, depending on the substitution pattern, and can also generate molecular diversity by changing the functional groups on the ylide.

It is well known that acylcyclopropanes can rearrange to dihydrofuran under thermal,[21] acidic,[19] or Lewis-acidic conditions.[22] Hence, we checked whether the formation of dihydrofuran could arise from rearrangement of the cyclopropane during the reaction and choose to study the rearrangement of cyclopropane **25** formed in a reaction where dihydrofuran was also formed. Cyclopropane **25** was then heated in THF under reflux in the presence or absence of 1 equiv of LiBr (LiBr is present in cyclopropanation reaction as it is formed by reaction of *n*-BuLi with alkylphosphonium bromide). After 16 h of heating, and whatever the conditions were, the cyclopropane was recovered unchanged (Scheme 8). We can therefore postulate that the dihydrofuran does not arise from a rearrangement of the cyclopropane but is formed via an S_N2 reaction of the enolate oxygen site on the phosphonium unit.



Scheme 8. Rearrangement of cyclopropane **25** under the reaction conditions.

The reaction between enone **9b** and phosphorus ylide (R^3=Me) was then monitored by infrared spectroscopy. The spectra were recorded with ReactIR™ 4000 fitted with an immersible DiComp ATR probe (Fig. 1). The reaction was carried out by adding enone **9b** to the phosphorus ylide. Before adding *n*-BuLi, no spectra could be recorded due to the insolubility of phosphonium salt. Then, addition of *n*-BuLi gave a quantitative conversion of phosphonium salt to phosphorus ylide after 6 min of reaction (estimated by the stability of absorption spectra). After addition of enone **9b**, no characteristic absorption of carbonyl group of the enone was observed showing a fast reaction between phosphorus ylide and enone. Indeed, an intermediate species was directly observed with an absorption at 1505 cm^{-1}, characteristic wavenumber of a vibrational C=C bond of an enolate.[23] The appearance of carbonyl group absorption at 1667 cm^{-1} allowed us to follow the kinetics of the formation of the cyclopropane, the absorption band corresponding to the C=C bond of the enolate simultaneously disappearing. The complete reaction was determined from the stable absorption intensity of the carbonyl group, and was estimated to occur

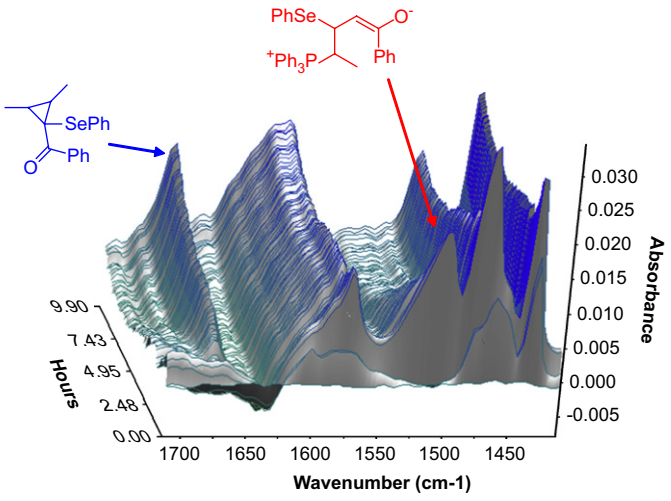


Figure 1. Infrared spectra of cyclopropanation reaction with cyclopropane **18**.

approximately after 10 h (Fig. 2). The red curve shows the instantaneous formation and the progressive disappearance of intermediate enolate with a characteristic band at 1505 cm^{-1}. The blue curve shows the progressive appearance of carbonyl group of cyclopropane **18** with a characteristic band at 1667 cm^{-1}.

3. Conclusion

In conclusion, we have shown that phosphorus ylides react with α-phenylselanyl enones in a 1,4-addition, leading to cyclopropanes and/or dihydrofurans, depending on the substitution pattern. This unusual reactivity is due to the phenylselanyl moiety, hindering the carbonyl of the enone and making it less prone to 1,2-additions or promoting conjugate addition by electronic effects. The geometry of the starting enones and cyclopropanes has been determined by

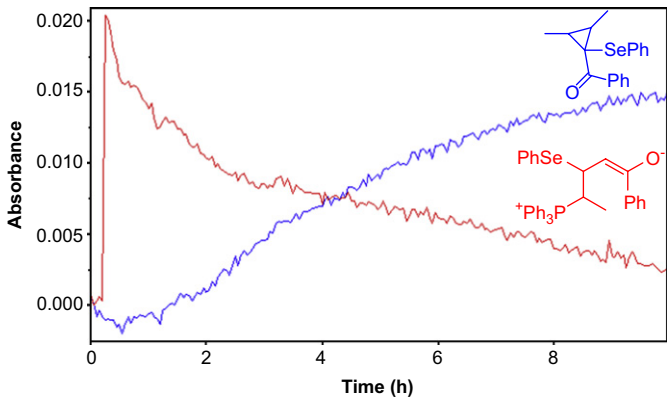


Figure 2. Profile of cyclopropanation reaction with cyclopropane **18**.

the combined use of ^{1}H NMR, NOESY, and ^{77}Se NMR spectra, and the course of the reaction has been followed by in situ IR spectroscopy.

4. Experimental

4.1. General

THF was distilled over sodium/benzophenone. Ether was dried over sodium.

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 parts per million 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. Elemental analyses were obtained on a Carlo–Erba 1106 analyser and mass spectra on an HP5890 (electronic impact 70 eV) using GC–MS coupling with a Jeol AX 500.

4.1.1. 3-(4-Methoxy-phenyl)-2-phenylselanylprop-2-enal **2d**

Compound **2d** was prepared using our reported procedure in Ref. 2a. Yield 84%; yellow solid (mp=72–74 °C); R_f=0.27 (EtOAc/pet. ether: 15/85); ^{77}Se NMR δ (ppm) 289.3; ^{1}H NMR δ (ppm) 3.86 (s, 3H), 6.95 (d, 2H, *J*=9.0 Hz), 7.17–7.20 (m, 3H), 7.35–7.39 (m, 2H), 7.94–7.98 (m, 3H), 9.48 (s, 1H); ^{13}C NMR δ (ppm) 55.5, 114.1, 126.8, 127.0, 128.9, 129.3, 129.8, 131.2, 133.8, 154.0, 162.1, 191.7. IR (neat): 1682, 1603, 1584, 1563, 1508, 1257, 1177, 1123, 1105, 1022, 823, 738 cm^{-1}. Anal. Calcd for $C_{16}H_{14}O_2Se$ (317.23): C, 60.57; H, 4.45. Found: C, 60.81; H, 4.38.

4.2. General procedure for the synthesis of 2-phenylselanyl-2-en-1-ols 3–8

For example, a solution of methyllithium (1.6 M in ether, 1.1 mmol, 0.69 ml) was added dropwise, under nitrogen, at −78 °C, to (*Z*)-2-(phenylselanyl)but-2-enal **2b** (1 mmol, 225 mg) in anhydrous THF (12 ml). The mixture was stirred for 1 h and monitored by TLC. The solution was then quenched with a saturated aqueous NH_4Cl solution (10 ml) and extracted with diethylether (3×12 ml). The organic extracts were dried over magnesium sulfate and concentrated under vacuum. The crude product was then purified by chromatography on silica gel (eluent: EtOAc/pet. ether: 10/90).

4.2.1. 1-Phenyl-2-phenylselanylprop-2-en-1-ol **3a**[9]

Yield 72%; yellow oil; R_f=0.28 (EtOAc/pet. ether: 1/10); ^{77}Se NMR δ (ppm) 390.1; ^{1}H NMR δ (ppm) 2.34 (d, 1H, *J*=4.6 Hz), 5.30 (s, 1H), 5.33 (s, 1H), 5.88 (s, 1H), 7.25–7.43 (m, 8H), 7.50–7.54 (m, 2H); ^{13}C NMR δ (ppm) 77.5, 118.2, 126.8, 128.1, 128.2, 128.5, 128.8, 129.5, 134.8, 141.1, 146.0. IR (neat): 3454, 3058, 2963, 1712, 1673, 1578, 1476, 1438, 1265, 1022, 738, 691 cm^{-1}. Anal. Calcd for $C_{15}H_{14}OSe$ (289.22): C, 62.29; H, 4.88. Found: C, 62.39; H, 5.03.

4.2.2. 1-Phenyl-2-phenylselanylbut-2-en-1-ol **3b**

Yield 83%; red oil; R_f=0.32 (EtOAc/pet. ether: 10/90); ^{77}Se NMR δ (ppm) 269.3; ^{1}H NMR δ (ppm) 1.88 (dd, 3H, *J*=1.0, 6.7 Hz), 2.47 (d, 1H, *J*=5.9 Hz), 5.28 (d, 1H, *J*=5.9 Hz), 6.38 (dq, 1H, *J*=1.0, 6.7 Hz), 7.17–7.35 (m, 5H); ^{13}C NMR δ (ppm) 17.6, 78.2, 126.4, 126.7, 127.6, 128.3, 128.5, 129.2, 130.6, 134.1, 136.5, 141.7. IR (neat): 3390, 3058, 3030, 2909, 1577, 1476, 1438, 1373, 1067, 1022, 735, 691 cm^{-1}. MS (EI): 304.00 (M^+). Anal. Calcd for $C_{16}H_{16}OSe$ (303.25): C, 63.37; H, 5.32. Found: C, 63.39; H, 5.38.

4.2.3. 1,3-Diphenyl-2-phenylselanylprop-2-en-1-ol **3c**

Yield 81%; yellow oil; R_f=0.32 (EtOAc/pet. ether: 1/10); ^{77}Se NMR δ (ppm) 323.4; ^{1}H NMR δ (ppm) 2.45 (d, 1H, *J*=4.5 Hz), 5.32 (d, 1H, *J*=4.5 Hz), 7.14–7.39 (m, 14H), 7.48–7.53 (m, 2H); ^{13}C NMR δ (ppm) 78.0, 127.2, 127.3, 128.1, 128.2, 128.6, 129.3, 129.6, 129.8, 132.5, 134.4, 135.8, 136.5, 141.8. IR (neat): 3394, 3058, 3027, 1576, 1492, 1476, 1438, 1265, 1062, 1022, 737, 694 cm^{-1}. Anal. Calcd for $C_{21}H_{18}OSe$ (365.31): C, 69.04; H, 4.97. Found: C, 69.38; H, 4.92.

4.2.4. 3-(4-Methoxy-phenyl)-1-phenyl-2-phenylselanylprop-2-en-1-ol **3d**

Yield 85%; yellow oil; R_f=0.27 (EtOAc/pet. ether: 15/85); ^{77}Se NMR δ (ppm) 313.2; ^{1}H NMR δ (ppm) 2.54 (d, 1H, *J*=4.8 Hz), 3.86 (s, 3H), 5.39 (d, 1H, *J*=4.8 Hz), 6.89–6.92 (m, 2H), 7.20–7.43 (m, 11H), 7.59–7.62 (m, 2H); ^{13}C NMR δ (ppm) 55.4, 78.4 (C-1), 113.5, 127.0, 128.0, 128.5, 128.9, 129.3, 130.1, 131.1, 131.9, 133.2, 134.7, 141.9, 159.5. IR (neat): 3417, 3059, 3030, 2933, 2836, 1605, 1575, 1512, 1476, 1440, 1304, 1252, 1177, 1065, 1032, 909, 830, 736, 700 cm^{-1}. Anal. Calcd for $C_{22}H_{20}O_2Se$ (395.34): C, 66.83; H, 5.10. Found: C, 66.53; H, 5.31.

4.2.5. 1-(4-Methoxy-phenyl)-3-phenyl-2-phenylselanylprop-2-en-1-ol **4c**

Yield 73%; yellow oil; R_f=0.41 (EtOAc/pet. ether: 1/5); ^{77}Se NMR δ (ppm) 327.5; ^{1}H NMR δ (ppm) 2.38 (d, 1H, *J*=4.9 Hz, O*H*), 3.81 (s, 3H), 5.26 (d, 1H, *J*=4.6 Hz, H-1), 6.85–6.88 (m, 2H), 7.17–7.37 (m, 10H), 7.42 (S, 1H, H-3), 7.51–7.55 (m, 2H); ^{13}C NMR δ (ppm) 55.4, 78.2 (C-1), 113.9, 127.2, 127.9, 128.1, 128.4, 129.2, 129.5, 129.7, 132.5, 133.8 (C-3), 136.0, 136.5, 159.4. IR (neat): 3390, 3055, 2954, 2932, 2835, 1610, 1579, 1513, 1492, 1476, 1440, 1303, 1250, 1173, 1110, 1065, 1034, 832, 737, 692, 591, 562 cm^{-1}. Anal. Calcd for $C_{22}H_{20}O_2Se$ (395.34): C, 66.83; H, 5.10. Found: C, 66.59; H, 5.04.

4.2.6. 3-Phenylselanylbut-3-en-2-ol **5a**[9,10]

Yield 57%; yellow oil; R_f=0.31 (EtOAc/pet. ether: 1/10); ^{77}Se NMR δ (ppm) 381.0; ^{1}H NMR δ (ppm) 1.37 (d, 3H, *J*=6.4 Hz), 1.97 (d, 1H, *J*=6.0 Hz), 3.08 (br s, 1H), 4.37 (q, 1H, *J*=6.0 Hz), 5.11 (s, 1H), 5.76 (s, 1H), 7.20–7.35 (m, 3H), 7.50–7.55 (m, 2H); ^{13}C NMR δ (ppm) 23.1, 71.6, 116.1, 127.2, 128.0, 129.3, 134.6, 148.1. IR (neat): 3388, 3071, 2975, 2926, 1703, 1608, 1578, 1476, 1438, 1368, 1145, 1067, 1022, 739, 691 cm^{-1}. Anal. Calcd for $C_{10}H_{12}OSe$ (227.16): C, 52.87; H, 5.32. Found: C, 52.48; H, 5.16.

4.2.7. 3-Phenylselanylpent-3-en-2-ol **5b**

Yield 88%; yellow oil; R_f=0.30 (EtOAc/pet. ether: 1/10); ^{77}Se NMR δ (ppm) 254.7; ^{1}H NMR δ (ppm) 1.34 (d, 3H, *J*=6.4 Hz), 1.87 (d, 1H, *J*=6.4 Hz), 1.97 (d, 1H, *J*=6.0 Hz), 4.33 (m, 1H), 6.35 (q, 3H, *J*=6.4 Hz), 7.15–7.30 (m, 3H), 7.35–7.40 (m, 2H); ^{13}C NMR δ (ppm) 17.6, 23.0, 72.9, 126.4, 129.4, 130.4, 131.0, 133.0, 138.2. IR (neat): 3382, 3070, 3050, 2972, 2928, 2870, 1577, 1476, 1437, 1372, 1296, 1109, 1000, 984, 735, 691 cm^{-1}. MS (EI): 242.00 (M^+), 205 (M^+−Ph), 197 (M^+−C_5H_9O). Anal. Calcd for $C_{11}H_{14}OSe$ (241.19): C, 54.78; H, 5.85. Found: C, 54.48; H, 5.86.

4.2.8. 4-Phenyl-3-phenylselanylbut-3-en-2-ol **5c**[11]

Yield 88%; yellow oil; R_f=0.26 (EtOAc/pet. ether: 1/10); ^{77}Se NMR δ (ppm) 311.3; ^{1}H NMR δ (ppm) 1.44 (d, 3H, *J*=6.4 Hz), 2.02 (d, 1H, *J*=4. 9 Hz), 4.39 (m, 1H), 7.19–7.34 (m, 7H), 7.38–7.43 (m, 2H), 7.49–7.54 (m, 2H); ^{13}C NMR δ (ppm) 17.7, 78.3, 126.5, 126.7, 128.0, 128.4, 129.3, 130.8, 134.3, 136.6, 141.8. IR (neat): 3325, 3056, 2976, 2928, 1577, 1490, 1476, 1443, 1367, 1265, 1129, 1070, 1045, 1022, 881, 738, 692 cm^{-1}. Anal. Calcd for $C_{16}H_{16}OSe$ (303.25): 63.37; H, 5.32. Found: C, 63.26; H, 5.43.

4.2.9. 4-(4-Methoxy-phenyl)-3-phenylselanylbut-3-en-2-ol ***5d***

Yield 84%; yellow oil; R_f=0.36 (EtOAc/pet. ether: 1/10); ^{77}Se NMR δ (ppm) 301.4; ^{1}H NMR δ (ppm) 1.43 (d, 3H, J=6.3 Hz), 2.09 (d, 1H, J=4.9 Hz), 3.80 (s, 3H), 4.40 (m, 1H), 6.85 (dd, 2H, J=1.9, 6.8 Hz), 7.19–7.28 (m, 4H), 7.39–7.43 (m, 2H), 7.54 (d, 2H, J=8.6 Hz); ^{13}C NMR δ (ppm) 23.4, 55.3, 73.0, 113.5, 126.9, 128.9, 129.3, 130.4, 131.0, 131.5, 133.5, 135.1, 159.4. IR (neat): 3390, 3056, 2971, 2928, 2836, 1605, 1576, 1510, 1476, 1438, 1304, 1251, 1177, 1132, 886, 824, 736, 691 cm^{-1}. Anal. Calcd for $C_{17}H_{18}O_2Se$ (333.27): 61.26; H, 5.44. Found: C, 61.42; H, 5.35.

4.2.10. 2-Phenylselanylhept-1-en-3-ol ***6a***

Yield 57%; yellow oil; R_f=0.33 (EtOAc/pet. ether: 1/10); ^{77}Se NMR δ (ppm) 379.6; ^{1}H NMR δ (ppm) 0.89 (t, 3H, J=6.8 Hz), 1.20–1.32 (m, 4H), 1.63–1.73 (m, 2H), 1.88 (br s, 1H), 4.11 (q, 1H, J=7.2 Hz), 5.12 (s, 1H), 5.75 (s, 1H), 7.25–7.33 (m, 3H), 7.55–7.60 (m, 2H); ^{13}C NMR δ (ppm): 14.1, 22.6, 27.8, 36.1, 76.1, 116.5, 128.1, 128.5, 129.5, 135.0, 147.4. IR (neat): 3386, 3072, 2955, 2931, 2859, 1807, 1578, 1476, 1438, 739 cm^{-1}. Anal. Calcd for $C_{13}H_{18}OSe$ (269.23): C, 57.99; H, 6.74. Found: C, 57.68; H, 7.02.

4.2.11. 3-Phenylselanyloct-2-en-4-ol ***6b***

Yield 75%; yellow oil; R_f=0.36 (EtOAc/pet. ether: 1/10); ^{77}Se NMR δ (ppm) 252.0; ^{1}H NMR δ (ppm) 0.86 (t, 3H, J=6.8 Hz), 1.20–1.32 (m, 4H), 1.55–1.63 (m, 2H), 1.87 (d, 3H, J=6.4 Hz), 1.90 (s, 1H), 4.10 (m, 1H), 6.31 (q, 1H, J=6.4 Hz), 7.18–7.27 (m, 3H), 7.38–7.42 (m, 2H); ^{13}C NMR δ (ppm) 14.1, 17.2, 22.5, 28.0, 36.3, 77.2, 126.2, 129.3, 130.4, 131.1, 133.6, 137.3. IR (neat): 3388, 3070, 2956, 2931, 2858, 1578, 1476, 1438, 739 cm^{-1}. MS (EI): 284.00 (M^+), 205 ($M^+-C_4H_9$), 197 ($M^+-C_5H_9O$). Anal. Calcd for $C_{14}H_{20}OSe$ (283.26): C, 59.36; H, 7.12. Found: C, 59.32; H, 6.95.

4.2.12. 1-Phenyl-2-phenylselanylhept-1-en-3-ol ***6c***

Yield 66%; yellow oil; R_f=0.28 (EtOAc/pet. ether: 1/10); ^{77}Se NMR δ (ppm) 310.9; ^{1}H NMR δ (ppm) 0.87 (t, 3H, J=7.1 Hz), 1.22–1.45 (m, 4H), 1.62–1.84 (m, 2H), 1.94 (d, 1H, J=6.0 Hz), 4.19 (m, 1H), 7.18–7.55 (m, 11H); ^{13}C NMR δ (ppm) 14.2, 22.7, 28.0, 36.7, 76.8, 127.1, 127.9, 128.1, 129.3, 129.4, 130.1, 132.2, 133.8, 136.6, 137.0. IR (neat): 3384, 3057, 2955, 2931, 2858, 1578, 1476, 1438, 1068, 1022, 739 cm^{-1}. Anal. Calcd for $C_{19}H_{22}OSe$ (345.33): C, 66.08; H, 6.42. Found: C, 66.36; H, 6.57.

4.2.13. 5-Methyl-3-phenylselanylhept-2-en-4-ol ***7b***

Yield 36%, two diastereomers 50/50; yellow oil; R_f=0.40 (EtOAc/pet. ether: 1/10); ^{77}Se NMR δ (ppm) 250.9; ^{1}H NMR δ (ppm) 0.78 (m, 3H), 1.10–40 (m, 2H), 1.60–1.80 (m, 4H), 1.85 (d, 3H, J=6.7 Hz), 6.25 (q, 1H, J=6.7 Hz), 7.14–7.37 (m, 6H); ^{13}C NMR δ (ppm): 11.3, 11.6, 13.7, 16.1, 17.6, 24.2 (C-7), 26.6 (C-7), 80.6 (C-3), 82.0 (C-3), 126.3, 126.5, 129.2, 130.5, 130.8, 130.9, 131.1, 134.9 (C-5), 133.8 (C-5), 136.2, 136.4. IR (neat): 3436, 2962, 2931, 2874, 1578, 1476, 1438, 1377, 1022, 735, 690 cm^{-1}. Anal. Calcd for $C_{14}H_{20}OSe$ (283.26): C, 59.36; H, 7.12. Found: C, 58.93; H, 6.96.

4.2.14. 4-Methyl-1-phenyl-2-phenylselanylhex-1-en-3-ol ***7c***

Yield 30%; yellow oil; R_f=0.42 (EtOAc/pet. ether: 1/10); ^{77}Se NMR δ (ppm) 306.9; ^{1}H NMR δ (ppm) 0.76–0.80 (m, 3H), 0.85–0.93 (m, 3H), 1.17–1.43 (m, 2H), 1.65–1.90 (m, 2H), 3.97–4.13 (m, 1H), 7.16–7.52 (m, 11H). IR (neat): 3437, 3057, 2961, 2928, 1682, 1577, 1476, 1438, 1021, 736, 691 cm^{-1}.

4.2.15. 2,2-Dimethyl-4-phenylselanylhex-4-en-3-ol ***8b***

Yield 36%; yellow oil; R_f=0.44 (EtOAc/pet. ether: 1/10); ^{1}H NMR δ (ppm) 0.92 (s, 9H), 1.78 (d, 3H, J=6.7 Hz), 2.41 (d, 1H, J=8.8 Hz), 3.90 (d, 1H, J=8.8 Hz), 6.25 (q, 1H, J=6.7 Hz), 7.14–7.26 (m, 3H), 7.36–7.39 (m, 2H); ^{13}C NMR δ (ppm) 18.2, 26.8, 33.2, 84.1, 126.5, 129.6, 130.2, 136.6. IR (neat): 3484, 2954, 2867, 1578, 1477, 1438, 1464, 1054, 690 cm^{-1}. Anal. Calcd for $C_{14}H_{20}OSe$ (283.26): C, 59.36; H, 7.12. Found: C, 59.61; H, 7.43.

4.2.16. 4,4-Dimethyl-1-phenyl-2-phenylselanylpent-1-en-3-ol ***8c***

Yield 31%; yellow oil; R_f=0.44 (EtOAc/pet. ether: 1/10); ^{1}H NMR δ (ppm) 1.02 (s, 9H), 2.37 (d, 1H, J=7.2 Hz), 4.03 (d, 1H, J=6.6 Hz), 7.08–7.47 (m, 11H); ^{13}C NMR δ (ppm) 26.5, 36.2, 83.8, 126.2, 129.3, 130.0, 132.1, 135.4, 136.3. IR (neat): 3445, 2960, 2867, 1669, 1626, 1578, 1490, 1476, 1069, 1010, 757, 738, 691 cm^{-1}.

4.3. General procedure for the synthesis of α-phenylselanyl enones 9–14

To a solution of diphenyldiselenide (280 mg, 0.9 mmol) in 10 ml cyclohexane was added slowly a solution of *tert*-butyl hydroperoxide 70% in water (180 μl, 1.8 mmol). The mixture was refluxed for 30 min and then was introduced 1-phenyl-2-phenylselanylbut-2-en-1-ol **3b** (454 mg, 1.5 mmol) in cyclohexane (2 ml). The solution was refluxed and monitored by TLC. After completion, the solution was cooled to rt, dried over magnesium sulfate, filtrated, and concentrated under vacuum. The crude product was then purified by chromatography on silica gel (eluent: CH_2Cl_2/pet. ether: 1/5).

4.3.1. 1-Phenyl-2-phenylselanylprop-2-en-1-one ***9a***[12]

Yield 54%; yellow oil; R_f=0.44 (EtOAc/cyclohexane: 1/9); ^{77}Se NMR δ (ppm) 390.8; ^{1}H NMR δ (ppm) 5.71 (s, 1H), 6.20 (s, 1H), 7.25–7.50 (m, 8H), 7.60–7.65 (m, 2H). IR (neat): 1694, 1673, 1597, 1579, 1475, 1448, 1438, 1266, 1174, 1021, 737, 689 cm^{-1}.

4.3.2. 1-Phenyl-2-phenylselanylbut-2-en-1-one ***9b***[4]

Yield 88%; red oil; R_f=0.29 (CH_2Cl_2/pet. ether: 1/5); ^{77}Se NMR δ (ppm) 342.8; ^{1}H NMR δ (ppm) 2.08 (d, 3H, J=6.9 Hz), 6.79 (q, 1H, J=6.9 Hz), 7.16–7.50 (m, 8H), 7.67–7.71 (m, 2H); ^{13}C NMR δ (ppm) 18.5, 127.2, 128.2, 129.2, 129.5, 130.1, 132.4, 132.5, 135.3, 137.2, 144.5, 194.6. IR (neat): 1655, 1596, 1578, 1477, 1447, 1438, 1263, 1063, 1022, 800, 736, 708 cm^{-1}. MS (EI): 302.00 (M^+), 205 ($M^+-C_7H_5O$), 197 ($M^+-C_5H_9O$). Anal. Calcd for $C_{16}H_{14}OSe$ (301.23): C, 63.79; H, 4.68. Found: C, 63.69; H, 4.54.

4.3.3. 1,3-Diphenyl-2-phenylselanylprop-2-en-1-one ***9c***[11,13]

Yield 83%; yellow solid (mp=51–53 °C); R_f=0.32 (CH_2Cl_2/pet. ether: 1/5); ^{77}Se NMR δ (ppm) 404.5; ^{1}H NMR δ (ppm) 7.08–7.17 (m, 3H), 7.31–7.50 (m, 9H), 7.63–7.65 (m, 2H), 7.72–7.74 (m, 2H); ^{13}C NMR δ (ppm) 128.1, 128.2, 128.6, 129.2, 129.7, 129.9, 132.7, 134.5, 135.6, 137.4, 139.0, 194.8. IR (KBr): 1656, 1596, 1579, 1476, 1446, 1244, 1022, 739, 690 cm^{-1}. Anal. Calcd for $C_{21}H_{16}OSe$ (363.30): C, 69.42; H, 4.44. Found: C, 69.67; H, 4.27.

4.3.4. 3-(4-Methoxy-phenyl)-1-phenyl-2-phenylselanylprop-2-en-1-one ***9d***

Yield 91%; yellow oil; R_f=0.37 (EtOAc/pet. ether: 1/9); ^{77}Se NMR δ (ppm) 385.4; ^{1}H NMR δ (ppm) 3.85 (s, 3H), 6.93–6.97 (m, 2H), 7.10–7.17 (m, 3H), 7.33–7.40 (m, 4H), 7.46–7.52 (m, 2H), 7.65–7.75 (m, 4H); ^{13}C NMR δ (ppm) 55.5, 114.0, 127.7, 127.9, 128.2, 129.2, 129.6, 131.2, 132.1, 132.4, 133.6, 137.8, 141.2, 160.7, 195.1. IR (neat): 1657, 1604, 1579, 1509, 1476, 1446, 1439, 1307, 1293, 1253, 1175, 1066, 1024, 909, 828, 735, 706, 690 cm^{-1}. Anal. Calcd for $C_{22}H_{18}O_2Se$ (393.33): C, 67.18; H, 4.61. Found: C, 67.03; H, 4.51.

4.3.5. 1-(4-Methoxy-phenyl)-3-diphenyl-2-phenylselanylprop-2-en-1-one ***10c***

Yield 80%; yellow solid (mp=80–82 °C); R_f=0.30 (EtOAc/cyclohexane: 1/5); ^{77}Se NMR δ (ppm) 409.9; ^{1}H NMR δ (ppm) 3.86 (s, 3H), 6.83–6.86 (m, 2H), 7.07–7.17 (m, 3H), 7.33–7.46 (m, 6H), 7.61–7.65 (m, 2H), 7.76–7.79 (m, 2H); ^{13}C NMR δ (ppm) 55.6, 92.1, 113.5, 128.2, 128.5, 129.0, 129.1, 129.7, 130.0, 132.1, 134.3, 134.7, 135.7, 137.1,

163.4, 193.3. IR (KBr): 1652, 1599, 1574, 1508, 1445, 1313, 1253, 1167, 1023, 840, 770, 738, 690 cm^{-1}. Anal. Calcd for $C_{22}H_{18}O_2Se$ (393.33): C, 67.18; H, 4.61. Found: C, 67.49; H, 4.48.

4.3.6. 3-Phenylselanylbut-3-en-2-one ***11a***[6b,12,14]

Yield 54%; yellow oil; ^{77}Se NMR δ (ppm) 413.1; ^{1}H NMR δ (ppm) 2.44 (s, 3H), 5.49 (s, 1H), 6.46 (s, 1H), 7.37–7.39 (m, 3H), 7.58–7.61 (m, 2H); ^{13}C NMR δ (ppm) 25.6, 124.4, 127.0, 129.1, 137.0, 146.6, 196.6.

4.3.7. 3-Phenylselanylpent-3-en-2-one ***11b***

Yield 85%; yellow oil; R_f=0.30 (CH_2Cl_2/pet. ether: 1/5); ^{77}Se NMR δ (ppm) 295.8; ^{1}H NMR δ (ppm) 2.10 (d, 3H, J=6.8 Hz), 2.37 (s, 3H), 7.19–7.33 (m, 6H); ^{13}C NMR δ (ppm) 19.0, 27.5, 126.6, 129.3, 130.6, 130.7, 135.5, 147.4, 197.2. IR (neat): 1682, 1602, 1577, 1477, 1437, 1355, 1232, 1212, 1069, 1022, 737, 691 cm^{-1}. Anal. Calcd for $C_{11}H_{12}OSe$ (239.17): C, 55.24; H, 5.06. Found: C, 54.98; H, 5.16.

4.3.8. 4-Phenyl-3-phenylselanylbut-3-en-2-one ***11c***[15]

Yield 89%; yellow solid (mp=39–40 °C); R_f=0.30 (CH_2Cl_2/pet. ether: 1/5); ^{77}Se NMR δ (ppm) 337.3; ^{1}H NMR δ (ppm) 2.40 (s, 3H), 7.19–7.42 (m, 8H), 7.66–7.70 (m, 2H), 7.97 (s, 1H); ^{13}C NMR δ (ppm) 28.3, 127.2, 128.3, 129.5, 129.8, 130.4, 130.7, 131.1, 132.8, 135.1, 143.9, 199.1. IR (neat): 1681, 1580, 1476, 1438, 1355, 1223, 1201, 1178, 1069, 1022, 736, 690 cm^{-1}. Anal. Calcd for $C_{16}H_{14}OSe$ (301.24): C, 63.79; H, 4.68. Found: C, 63.58; H, 4.74.

4.3.9. 4-(4-Methoxy-phenyl)-3-phenylselanylbut-3-en-2-one ***11d***

Yield 85%; yellow oil; R_f=0.33 (EtOAc/cyclohexane: 15/85); ^{77}Se NMR δ (ppm) 325.2; ^{1}H NMR δ (ppm) 2.42 (s, 3H), 3.84 (s, 3H), 6.89–6.93 (m, 2H), 7.19–7.35 (m, 5H), 7.78–7.81 (m, 2H), 8.02 (s, 1H); ^{13}C NMR δ (ppm) 28.1, 55.3, 113.8, 126.8, 127.3, 128.8, 129.4, 130.4, 131.1, 132.8, 145.0 (C-4), 161.1, 198.8. IR (neat): 1682, 1603, 1584, 1564, 1506, 1477, 1439, 1309, 1298, 1258, 1177, 1125, 1104, 1024, 829, 737, 690 cm^{-1}. MS (EI): 332 (M^+, 24), 77 (Ph^+, 18), 43 ($MeCO^+$, 100). Anal. Calcd for $C_{17}H_{16}O_2Se$ (331.26): C, 61.63; H, 4.87. Found: C, 61.68; H, 4.65.

4.3.10. 3-Phenylselanyloct-2-en-4-one ***12b***

Yield 76%; yellow oil; R_f=0.28 (CH_2Cl_2/pet. ether: 1/5); ^{77}Se NMR δ (ppm) 296.9; ^{1}H NMR δ (ppm) 0.83 (t, 3H, J=7.4 Hz), 1.17–1.28 (m, 2H), 1.44–1.55 (m, 2H), 2.07 (d, 3H, J=6.9 Hz), 2.70 (t, 2H, J=7.4 Hz), 7.19–7.33 (m, 6H); ^{13}C NMR δ (ppm) 14.0, 19.0, 22.4, 26.8, 39.5, 126.8, 129.4, 130.8, 131.0, 135.5, 146.0, 200.3. IR (neat): 2957, 2931, 2871, 1682, 1596, 1578, 1477, 1438, 736, 690 cm^{-1}. MS (EI): 282.00 (M^+), 205 (M^+-Ph), 197 ($M^+-C_5H_9O$). Anal. Calcd for $C_{14}H_{18}OSe$ (281.24): C, 59.79; H, 6.45. Found: C, 59.88, H, 6.39.

4.3.11. 1-Phenyl-2-phenylselanylhept-1-en-3-one ***12c***

Yield 88%; yellow oil; R_f=0.30 (CH_2Cl_2/pet. ether: 1/5); major *Z*-isomer (65%); ^{77}Se NMR δ (ppm) 337.4; ^{1}H NMR δ (ppm) 0.81 (t, 3H, J=7.4 Hz), 1.12–1.25 (m, 2H), 1.37–1.50 (m, 2H), 2.74 (t, J=7.4 Hz, 2H), 7.15–7.65 (m, 10H), 7.88 (s, 1H); ^{13}C NMR δ (ppm) 14.0, 22.3, 26.8, 40.1, 127.3, 128.4, 128.5, 128.7, 130.4, 133.2, 134.5, 135.4, 142.6, 201.9. *Minor E-isomer*: (35%); ^{1}H NMR δ (ppm) 0.95 (t, 3H, J=7.4 Hz), 1.33–1.45 (m, 2H), 1.67–1.77 (m, 2H), 2.67 (t, J=7.7 Hz, 2H), 7.15–7.65 (m, 11H). IR (neat): 2957, 2931, 2871, 2202, 1676, 1579, 1476, 1444, 1134, 1070, 757; 737, 690 cm^{-1}. Anal. Calcd for $C_{19}H_{20}OSe$ (343.31): C, 66.47; H, 5.87. Found: C, 66.42; H, 6.18.

4.3.12. 5-Methyl-3-phenylselanylhept-2-en-4-one ***13b***

Yield 86%; yellow oil; R_f=0.31 (CH_2Cl_2/pet. ether: 1/5); ^{77}Se NMR δ (ppm) 304.4; ^{1}H NMR δ (ppm) 0.72 (t, 3H, J=7.4 Hz), 0.94 (d, 3H, J=6.9 Hz), 1.23–1.32 (m, 1H), 1.54–1.64 (m, 1H), 2.06 (d, 3H, J=6.9 Hz), 3.18–3.25 (m, 1H), 7.15–7.4 (m, 6H); ^{13}C NMR δ (ppm) 11.7, 16.8, 19.0, 26.6, 43.0, 126.8, 129.4, 130.9, 131.1, 135.7, 145.3, 204.2. IR (neat): 2966, 2932, 1681, 1602, 1578, 1477, 1438, 1070, 1022, 736, 690 cm^{-1}. Anal. Calcd for $C_{14}H_{18}OSe$ (281.24): C, 59.79; H, 6.45. Found: C, 59.68; H, 6.34.

4.3.13. 4-Methyl-1-phenyl-3-phenylselanylhexen-3-one ***13c***

Yield 89%; yellow oil; R_f=0.20 (CH_2Cl_2/pet. ether: 1/5); ^{77}Se NMR δ (ppm) 349.7; ^{1}H NMR δ (ppm) 0.69 (t, 3H, J=7.4 Hz), 0.89 (d, 3H, J=6.9 Hz), 1.23–1.32 (m, 1H), 1.50–1.60 (m, 1H), 3.25–3.32 (m, 1H), 7.15–7.4 (m, 8H), 7.63–7.70 (m, 2H), 7.8 (s, 1H). IR (neat): 2966, 2932, 2874, 1682, 1578, 1476, 1438, 1068, 738, 690 cm^{-1}.

4.3.14. 2,2-Dimethyl-4-phenylselanylhex-4-en-3-one ***14b***

Yield 90%; yellow oil; R_f=0.27 (CH_2Cl_2/pet. ether: 1/5); ^{77}Se NMR δ (ppm) 338.0; ^{1}H NMR δ (ppm) 1.16 (s, 9H), 1.95 (d, 3H, J=6.7 Hz), 6.39 (q, 1H, J=6.7 Hz), 7.20–7.27 (m, 3H), 7.40–7.43 (m, 2H); ^{13}C NMR δ (ppm) 18.0, 26.6, 36.3, 83.8, 126.2, 129.3, 130.0, 132.2, 135.4, 136.2. IR (neat): 2965, 2931, 1677, 1578, 1477, 1438, 1364, 1137, 1098, 1022, 735, 690 cm^{-1}. MS (EI): 282 (M^+), 205 ($M^+-C_4H_9$). Anal. Calcd for $C_{14}H_{18}OSe$ (281.24): C, 59.79; H, 6.45. Found: C, 59, 97; H, 6.54.

4.3.15. 4,4-Dimethyl-1-phenyl-2-phenylselanylpent-1-en-3-one ***14c***

Yield 89%; orange solid (mp=65–68 °C); R_f=0.25 (CH_2Cl_2/pet. ether: 1/5); ^{77}Se NMR δ (ppm) 388.2; ^{1}H NMR δ (ppm) 1.13 (s, 9H), 7.01 (s, 1H), 7.20–7.55 (m, 10H); ^{13}C NMR δ (ppm) 27.9, 44.2, 128.2, 128.4, 128.5, 128.6, 129.2, 129.4, 133.0, 133.1, 134.4, 135.6, 209.0. IR (neat): 2964, 2862, 1682, 1474, 1436, 1116, 1075, 778, 746, 690 cm^{-1}. Anal. Calcd for $C_{19}H_{20}OSe$ (343.31): C, 66.46; H, 5.87. Found: C, 66.05; H, 5.88.

4.4. General procedure for the addition of phosphorus ylides to α-phenylselanyl enones

A solution of *n*-BuLi (1.6 M in hexanes, 0.75 ml, 1.2 mmol) was added slowly, under argon, to ethyltriphenylphosphonium bromide (448 mg, 1.2 mmol) in anhydrous THF (10 ml). After stirring for 5 min at rt, the α-phenylselanyl enone (1 mmol) in THF (2 ml) was added dropwise. The mixture was stirred at reflux or at 50 °C and monitored by TLC. After completion, the solution was cooled to rt, quenched with a saturated aqueous NH_4Cl solution, 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).

4.4.1. 1-(2,3-Dimethyl-1-phenylselanyl-cyclopropyl)-ethanone ***15***

Yield 65%; yellow oil (cis/trans: 40/60). *cis Isomer*: R_f=0.27 (cyclohexane/EtOAc: 97/3); ^{77}Se NMR δ (ppm) 276.0; ^{1}H NMR δ (ppm) 1.17 (d, 6H, J=6.4 Hz), 2.00 (m, 2H), 2.45 (s, 3H), 7.15–7.30 (m, 5H); ^{13}C NMR δ (ppm) 10.7 (2C), 28.6 (2C), 30.8, 43.8, 126.0, 128.5, 129.5, 131.2, 209.0. IR (neat): 2955, 2925, 2852, 1686, 1578, 1478, 1459, 1438, 1385, 1354, 1244, 1209, 1146, 1074, 1022, 997, 734, 690 cm^{-1}. *trans Isomer*: R_f=0.33 (cyclohexane/EtOAc: 97/3), ^{77}Se NMR δ (ppm): 350.6; ^{1}H NMR δ (ppm) 1.09 (d, 3H, J=6.1 Hz), 1.24 (d, 3H, J=6.1 Hz), 1.35 (m, 1H), 2.00 (m, 1H), 2.46 (s, 3H), 7.15–7.35 (m, 5H); ^{13}C NMR δ (ppm) 12.9, 16.0, 26.0, 30.8, 32.2, 43.4, 126.3, 129.3, 129.5, 132.9, 206.5. IR (neat): 3058, 2956, 2927, 1688, 1579, 1478, 1450, 1438, 1381, 1354, 1256, 1191, 1137, 1083, 1071, 1023, 734, 691 cm^{-1}.GC–MS: t_R=9.9 min (cis), 10.3 min (trans). MS (EI, 70 eV) *m*/*z* (relative intensity): 268 (M^+, 26), 266 (14), 225 (M^+-CH_3CO, 6), 188 (35), 187 (34), 157 ($PhSe^+$, 20), 145 (23), 144 (17), 143 (16), 129 (17), 96 (35), 77 (Ph^+, 28), 51 (30), 43 (CH_3CO^+, 100). Anal. Calcd for $C_{13}H_{16}0Se$ (267.22): C, 58.43; H, 6.03. Found: C, 57.78; H, 5.89.

4.4.2. 1-(2-Methyl-1-phenylselanyl-3-propyl-cyclopropyl)-ethanone **16**

Yield 41%; yellow oil (cis/trans: 45/55). *cis Isomer*: R_f=0.36 (cyclohexane/EtOAc: 97/3), ^{77}Se δ (ppm): 283.6; ^{1}H NMR δ (ppm) 0.93 (t, 3H, J=7.3 Hz), 1.18 (d, 3H, J=6.5 Hz), 1.41 (m, 2H), 1.54 (m, 2H), 1.71 (m, 1H), 2.19 (dq, J=6.5, 9.8 Hz, 1H), 2.46 (s, 3H), 7.15–7.30 (m, 5H); ^{13}C NMR δ (ppm) 10.9, 14.1, 22.7, 27.4 (C-2), 28.2, 29.7, 35.1 (C-3), 43.4 (C-1), 126.0, 128.5, 129.45, 134.0, 208.9. IR (neat): 2958, 2926, 1687, 1578, 1478, 1438, 1354, 1138, 1022, 734, 690 cm^{-1}. GC–MS: t_R=10.9 min (trans), 11.2 min (cis). MS (EI, 70 eV) m/z (relative intensity): 296 (M^+, 26), 294 (14), 266 (14), 253 (M^+-CH_3CO, 16), 215 (43), 173 (16), 157 ($PhSe^+$, 25), 124 (19), 96 (88), 95 (75), 77 (Ph^+, 32), 55 (42), 43 (CH_3CO^+, 100). *trans Isomer*: R_f=0.45 (cyclohexane/EtOAc: 97/3); ^{77}Se NMR δ (ppm) 352.1; ^{1}H NMR δ (ppm) 0.90 (t, 3H, J=7.0 Hz), 1.25 (d, 3H, J=6.1 Hz), 1.18–1.48 (m, 5H), 2.06 (dq, J=6.1, 6.5 Hz, 1H), 2.46 (s, 3H), 7.15–7.30 (m, 5H); ^{13}C NMR δ (ppm) 13.9, 16.2, 22.7, 25.5 (C-2), 29.8, 30.8, 38.4 (C-3), 43.2 (C-1), 126.3, 129.2, 129.4, 131.9, 206.6. Anal. Calcd for $C_{15}H_{20}OSe$ (295.28): C, 61.01; H, 6.83. Found: C, 61.08; H, 6.92.

4.4.3. 1-(2-But-3-enyl-3-methyl-1-phenylselanyl-cyclopropyl)-ethanone **17**

Yield 38%; yellow oil (cis/trans: 40/60). *cis Isomer*: R_f=0.36 (cyclohexane/EtOAc: 97/3); ^{77}Se NMR δ (ppm) 283.4; ^{1}H NMR δ (ppm) 1.24 (d, 3H, J=6.5 Hz), 1.60–1.78 (m, 3H), 2.04–2.20 (m, 3H), 2.48 (s, 3H), 4.96–5.06 (m, 2H), 5.73–5.86 (m, 1H), 7.15–7.35 (m, 5H); ^{13}C NMR δ (ppm) 16.1, 25.6, 27.1 (C-2), 29.7, 33.7, 33.7 (C-3), 38.1 (C-1), 115.5, 126.1, 128.5, 129.2, 137.8, 206.5. *trans Isomer*: R_f=0.45 (cyclohexane/EtOAc: 97/3), ^{77}Se NMR δ (ppm) 352.8; ^{1}H NMR δ (ppm) 1.18 (d, 3H, J=6.5 Hz), 1.60–1.76 (m, 3H), 2.04–2.20 (m, 3H), 2.46 (s, 3H), 4.96–5.06 (m, 2H), 5.73–5.86 (m, 1H), 7.15–7.35 (m, 5H); ^{13}C NMR δ (ppm) 10.9, 25.7, 27.3 (C-2), 29.7, 33.6, 34.5 (C-3), 43.3 (C-1), 115.5, 126.1, 128.5, 129.5, 137.9, 208.7. IR (neat): 3074, 2954, 2925, 2360, 1683, 1640, 1579, 1470, 1438, 1354, 1253, 1207, 1147, 1071, 1023, 997, 912, 735, 691, 668 cm^{-1}. MS (EI, 76 eV) m/z (relative intensity): 308 (M^+, 2), 265 (M^+-CH_3CO, 2), 157 ($PhSe^+$, 8), 77 (Ph^+, 10), 43 (CH_3CO^+, 100). Anal. Calcd for $C_{16}H_{20}0Se$ (307.28): C, 62.53; H, 6.56. Found C, 62.35; H, 6.71.

4.4.4. (2,3-Dimethyl-1-phenylselanyl-cyclopropyl)-phenyl-methanone **18**

Yield 61%, yellow oil (cis/trans: 60/40); R_f=0.30 (cyclohexane/EtOAc: 97/3). *cis Isomer*: ^{77}Se NMR δ (ppm) 309.7; ^{1}H NMR δ (ppm) 1.33 (d, 3H, J=4.3 Hz), 1.34 (d, 3H, J=4.3 Hz), 1.86 (m, 2H), 7.15–7.90 (m, 10H); ^{13}C NMR δ (ppm) 10.3, 10.4, 22.3, 40.6, 126.6, 128.7, 129.2, 130.7, 132.0, 132.4, 133.3, 198.3. IR (neat): 3057, 2959, 2927, 2871, 1662, 1596, 1578, 1479, 1438, 1265, 1199, 1071, 1023, 736, 693, 541 cm^{-1}. GC–MS: t_R=13.9 min (cis), 14.6 min (trans). MS (EI, 70 eV) m/z (relative intensity): 330 (M^+, 13), 328 (7), 249 (12), 173 (6), 158 (61), 157 ($PhSe^+$, 25), 129 (16), 105 ($PhCO^+$, 100), 77 (Ph^+, 78), 51 (28). *trans Isomer*: ^{77}Se NMR δ (ppm) 390.9; ^{1}H NMR δ (ppm) 1.11 (d, 3H, J=6.3 Hz), 1.36 (d, 3H, J=6.3 Hz), 1.51 (m, 1H), 1.73 (m, 1H), 7.15–7.95 (m, 10H); ^{13}C NMR δ (ppm) 15.4, 16.1, 24.4, 30.0, 39.4, 126.6, 128.1, 128.5, 129.1, 129.6, 130.7, 132.1, 132.6, 197.2. Anal. Calcd for $C_{18}H_{18}OSe$ (329,29): C, 65.65; H, 5.51. Found: C, 65.41; H, 5.45.

4.4.5. Phenyl-(2-methyl-1-phenylselanyl-3-propyl-cyclopropyl)-methanone **19**

Yield 45%, yellow oil (cis/trans: 60/40). *cis Isomer*: R_f=0.32 (cyclohexane/EtOAc: 97/3); ^{77}Se NMR δ (ppm) 318.2; ^{1}H NMR δ (ppm) 0.98 (t, 3H, J=7.3 Hz), 1.33 (d, 3H, J=6.4 Hz), 1.53 (m, 2H), 1.60–1.82 (m, 3H), 1.965 (dq, 1H, J=6.4, 9.4 Hz), 7.15–7.55 (m, 8H), 7.85–7.90 (m, 2H); ^{13}C NMR δ (ppm) 10.7, 14.3, 22.1 (C-2), 22.7, 28.1, 28.5 (C-3), 40.35 (C-1), 126.6, 128.1, 129.1, 129.2, 129.6, 131.0, 132.4, 136.4, 198.7. IR (neat): 3058, 2958, 2927, 2871, 1666, 1597, 1579, 1479, 1448, 1264, 1231, 1177, 1070, 1023, 735, 691, 657 cm^{-1}. GC–MS: t_R=16.8 min (cis). MS (EI, 70 eV) m/z (relative intensity): 358 (8), 356 (6), 281 (8), 221 (14), 207 (32), 158 (44), 157 (20), 105 ($PhCO^+$, 100), 77 (69), 44 (42). *trans Isomer*: R_f=0.38 (cyclohexane/EtOAc: 97/3); ^{77}Se NMR δ (ppm) 392.3; ^{1}H NMR δ (ppm) 0.87 (t, 3H, J=7.4 Hz), 1.38 (d, 3H, J=6.1 Hz), 1.30–1.50 (m, 5H), 1.73 (dq, 1H, J=6.1, 6.4 Hz), 7.15–7.55 (m, 8H), 7.85–7.90 (m, 2H); ^{13}C NMR δ (ppm) 13.9, 16.5, 22.5, 24.0 (C-2), 32.6, 35.5 (C-3), 39.4 (C-1), 126.7, 128.1, 128.5, 129.1, 129.7, 131.0, 132.6, 136.7, 197.2. Anal. Calcd for $C_{20}H_{22}OSe$ (357.34): C, 67.22; H, 6.20. Found: C, 67.15; H, 6.24.

4.4.6. Phenyl-(2-but-3-enyl-3-methyl-1-phenylselanyl-cyclopropyl)-methanone **20**

Yield 45%, yellow oil (cis/trans: 52/48). *cis Isomer*: R_f=0.32 (cyclohexane/EtOAc: 97/3); ^{77}Se NMR δ (ppm) 318.4; ^{1}H NMR δ (ppm) 1.38 (d, 3H, J=6.15 Hz), 1.70–1.80 (m, 2H), 1.85–1.96 (m, 2H), 2.14–2.24 (m, 2H), 4.96–5.09 (m, 2H), 5.78–5.92 (m, 1H), 7.10–7.55 (m, 8H), 7.82–7.88 (m, 2H). IR (neat): 3059, 2976, 2926, 1666, 1579, 1479, 1448, 1438, 1267, 1233, 1177, 1069, 1023, 999, 736, 691, 657 cm^{-1}; GC–MS: t_R=18.4 min (trans). MS (EI, 70 eV) m/z (relative intensity): 370 (M^+, 4), 213 (21), 184 (22), 158 (34), 157 (23), 105 ($PhCO^+$, 100), 77 (56), 51 (14), 41 (16). *trans Isomer*: R_f=0.38 (cyclohexane/EtOAc: 97/3), ^{77}Se NMR δ (ppm) 393.2; ^{1}H NMR δ (ppm) 1.35 (d, 3H, J=6.4 Hz), 1.70–1.80 (m, 2H), 1.85–1.96 (m, 2H), 2.14–2.24 (m, 2H), 4.96–5.09 (m, 2H), 5.78–5.92 (m, 1H), 7.10–7.55 (m, 8H), 7.82–7.88 (m, 2H); ^{13}C NMR δ (ppm) 10.6, 22.2 (C-3), 25.5, 27.9 (C-2), 33.5, 40.3 (C-1), 115.3, 126.75, 128.1, 129.1, 129.2, 129.7, 131.1, 132.4, 136.3, 138.1, 198.4. Anal. Calcd for $C_{21}H_{22}OSe$ (369.35): C, 68.28; H, 6.00. Found: C, 67.96; H, 5.87.

4.4.7. 1-Phenyl-3-methyl-2-phenylselanylpent-1,3-diene **21**

Yield 24%; yellow oil; R_f=0.68 (cyclohexane/EtOAc: 90/10). *Minor isomer*: ^{1}H NMR δ (ppm) 1.58 (d, 3H, J=6.9 Hz), 1.71 (s, 3H), 5.95 (q, 1H, J=6.7 Hz, H-4), 7.04 (s, 1H, H-1), 7.15–7.36 (m, 8H), 7.49–7.54 (m, 2H); *major isomer*: ^{77}Se NMR δ (ppm) 300.3; ^{1}H NMR δ (ppm) 1.64 (dd, 3H, J=1.3, 6.8 Hz), 1.71 (s, 3H), 5.20 (q, 1H, J=6.8 Hz, H-4), 6.70 (s, 1H, H-1), 7.15–7.36 (m, 8H), 7.49–7.54 (m, 2H); ^{13}C NMR δ (ppm) 15.3, 24.5, 123.8, 127.3, 127.8, 128.2, 128.3, 128.6, 129.1, 129.3, 129.4, 131.6, 135.4, 137.6. IR (neat): 3057, 2924, 2854, 1577, 1475, 1373, 1022, 736, 691 cm^{-1}.

4.4.8. 1-(2-Methyl-3-phenyl-1-phenylselanyl-cyclopropyl)-ethanone **22**

Yield 10%, R_f=0.34 (cyclohexane/EtOAc: 97/3), yellow oil (cis/trans: 55/45). *cis Isomer*: ^{77}Se δ (ppm) 391.2; ^{1}H NMR δ (ppm) 1.31 (d, 3H, J=6.3 Hz), 2.59 (s, 3H), 2.71 (m, 1H, H-2), 2.83 (d, 1H, J=9.8 Hz), 7.15–7.35 (m, 10H); ^{13}C NMR δ (ppm) 12.9, 26.5 (C-2), 29.6, 38.3 (C-3), 43.5 (C-1), 126.1, 127.4, 128.6, 128.7, 129.5, 129.9, 131.6, 135.2, 208.1. IR (neat): 3059, 2958, 2927, 1682, 1578, 1496, 1478, 1446, 1355, 1265, 1215, 1170, 1072, 1055, 1022, 998, 746, 704 cm^{-1}. *trans Isomer*: ^{77}Se NMR δ (ppm) 421.0; ^{1}H NMR δ (ppm) 1.26 (d, 3H, J=5.6 Hz), 2.20 (m, 1H, H-2), 2.54 (s, 3H), 3.21 (d, 1H, J=7.7 Hz), 7.15–7.35 (m, 10H); ^{13}C NMR δ (ppm) 13.4, 22.8 (C-2), 29.8, 36.5 (C-3), 46.0 (C-1), 126.8, 127.8, 129.0, 129.1, 129.6, 130.3, 130.8, 137.2, 205.2. GC–MS: t_R=15.0 min. MS (EI, 70 eV) m/z (relative intensity): 330 (M^+, 6), 328 (4), 221 (12), 207 (12), 158 (12), 157 (7), 129 (20), 115 (15), 91 (10), 77 (12), 51 (14), 44 (21), 43 (100). Anal. Calcd for $C_{18}H_{18}OSe$ (329.29): C, 65.65; H, 5.51. Found: C, 65.32; H, 5.67.

4.4.9. trans-2,5-Dimethyl-3-phenyl-4-phenylselanyl-2,3-dihydrofuran **23**

Yield 11%; yellow oil; R_f=0.47 (cyclohexane/EtOAc: 97/3), ^{77}Se NMR δ (ppm) 242.0; ^{1}H NMR δ (ppm) 1.46 (d, 3H, J=6.3 Hz), 2.14 (d, 3H, J=1.7 Hz), 3.63 (dd, 1H, J=1.7, 6.3 Hz, H-3), 4.60 (m, 1H, H-2), 7.10–7.35 (m, 10H); ^{13}C NMR (δ ppm) 13.7, 21.6, 60.9 (C-3), 85.8 (C-2), 98.2, 126.0, 127.0, 128.0, 128.6, 129.1, 129.6, 132.1, 143.2 (C-4), 162.0 (C-5). IR (neat): 3359, 2970, 2924, 2853, 1578, 1475, 1454,

1438, 1376, 1108, 1073, 1021, 736, 699 cm^{-1}. MS (EI) *m/z* (relative intensity): 330 (M^+, 8), 157 ($PhSe^+$, 8), 77 (Ph^+, 10), 43 (CH_3CO^+, 100). Anal. Calcd for $C_{18}H_{18}OSe$ (329,29): C, 65.65; H, 5.51. Found: C, 65.57; H, 5.61.

4.4.10. 1-(2-Phenyl-1-phenylselanyl-3-propyl-cyclopropyl)-ethanone **24**

Yield 27%; yellow oil, R_f=0.34 (cyclohexane/EtOAc: 97/3) (cis/trans: 50/50). *cis Isomer*: ^{77}Se δ (ppm) 390.1; ^1H NMR δ (ppm) 0.88 (t, 3H, *J*=7.2 Hz), 1.45–1.54 (m, 3H), 1.62–1.74 (m, 1H), 2.42 (m, 1H, H-3), 2.53 (s, 3H), 2.91 (d, 1H, *J*=10.0 Hz), 7.10–7.35 (m, 10H); ^{13}C NMR δ (ppm) 14.3, 23.0, 29.2, 29.6, 32.4 (C-3), 37.4 (C-2), 43.3 (C-1), 126.2, 127.3, 128.5, 128.9, 129.4, 129.9, 131.4, 135.5, 207.8. IR (neat): 3059, 2958, 2925, 2854, 2360, 1684, 1578, 1478, 1438, 1354, 1265, 1211, 1170, 1072, 1022, 736, 699 cm^{-1}. *trans Isomer*: ^{77}Se NMR δ (ppm) 420.7; ^1H NMR δ (ppm) 0.93 (t, 3H, *J*=7.0 Hz), 1.33–1.52 (m, 3H), 1.59–1.69 (m, 1H), 2.10–2.18 (m, 1H, H-3), 2.55 (s, 3H), 3.26 (d, 1H, *J*=7.8 Hz), 7.05–7.35 (m, 10H); ^{13}C NMR δ (ppm) 14.0, 22.7, 30.2, 30.7, 35.6 (C-3), 35.9 (C-2), 45.9 (C-1), 126.8, 126.9, 127.8, 129.0, 129.1, 130.3, 131.0, 137.3, 205.3. MS (EI) *m/z* (relative intensity): 358 (M^+, 4), 315 (M^+-CH_3CO), 157 ($PhSe^+$, 30), 77 (Ph^+, 6), 43 (CH_3CO^+, 100). Anal. Calcd for $C_{20}H_{22}OSe$ (357.34): C, 67.22; H, 6.20. Found: C, 67.28; H, 5.94.

4.4.11. 2,2-Dimethyl-1-(2-methyl-3-phenyl-1-phenylselanyl-cyclopropyl)-propan-1-one **25**

Yield 41%; yellow oil (cis/trans: 78/22); R_f=0.30 (cyclohexane/EtOAc: 98/2). *cis Isomer*: ^{77}Se NMR δ (ppm) 300.1; ^1H NMR δ (ppm) 1.18 (d, 3H, *J*=6.4 Hz), 1.40 (s, 9H), 2.32 (m, 1H, H-2), 2.58 (d, 1H, *J*=10.1 Hz, H-3), 7.08–7.38 (m, 10H); ^{13}C NMR δ (ppm) 12.4, 22.1 (C-2), 29.1, 32.1 (C-3), 39.8, 45.0, 126.1, 126.9, 128.3, 129.0, 129.4, 130.2, 131.0, 135.2, 211.3. IR (neat): 3059, 2966, 2958, 2969, 1677, 1610, 1579, 1497, 1470, 1433, 1393, 1363, 1265, 1118, 1102, 1074, 1023, 735, 699 cm^{-1}. *trans Isomer*: ^{77}Se NMR δ (ppm) 368.0; ^1H NMR δ (ppm) 1.24 (d, 3H, *J*=6.4 Hz), 1.37 (s, 9H), 2.07 (m, 1H, H-2), 2.71 (d, 1H, *J*=7.1 Hz, H-3), 7.08–7.38 (m, 10H); ^{13}C NMR δ (ppm) 16.5, 26.3 (C-2), 27.9, 28.7, 35.0 (C-3), 42.4, 44.4, 126.4, 126.5, 128.2, 128.4, 128.7, 129.0, 136.6, 210.5. MS (EI) *m/z* (relative intensity): 372 (M^+, 36), 157 ($PhSe^+$, 58), 129 ($M^+-PhSe-(CH_3)_3CCO$, 100), 77 (Ph^+, 24). Anal. Calcd for $C_{21}H_{24}OSe$ (372.37): C, 67.92; H, 6.51. Found: C, 68.31; H, 6.40.

4.4.12. trans-5-tert-Butyl-2-methyl-3-phenyl-4-phenylselanyl-2,3-dihydrofuran **26**

Yield 16%; yellow oil; R_f=0.43 (cyclohexane/EtOAc: 98/2); ^{77}Se NMR δ (ppm) 262.1; ^1H NMR δ (ppm) 1.35 (d, 3H, *J*=6.9 Hz), 137 (s, 9H), 3.40 (d, 1H, *J*=4.5 Hz, H-3), 4.48 (m, 1H, H-2), 7.05–7.30 (m, 10H); ^{13}C NMR δ (ppm) 21.6, 29.5, 34.5, 61.9 (C-3), 83.7 (C-2), 94.6, 125.9, 127.0, 127.8, 128.6, 129.1, 129.5, 132.7, 144.1 (C-4), 168.9 (C-5). IR (neat): 3062, 3028, 2967, 2924, 2852, 1603, 1578, 1476, 1455, 1438, 1373, 1360, 1312, 1226, 1133, 1102, 1036, 1022, 969, 734, 699 cm^{-1}. MS (EI) *m/z* (relative intensity): 372 (M^+, 34), 157 ($PhSe^+$, 44), 129 ($M^+-PhSe-(CH_3)_3CCO$, 54), 77 (Ph^+, 22). Anal. Calcd for $C_{21}H_{24}OSe$ (372.37): C, 67.92; H, 6.51. Found: C, 68.20; H, 6.38.

4.4.13. Phenyl-(2-methyl-3-phenyl-cyclopropyl)-methanone **27**[20a,24]

Yield 22%, white solid, mp 42 °C, ^1H NMR δ (ppm) 1.01 (d, 3H, *J*=6.2 Hz), 2.04 (dqd, 1H, *J*=4.6, 6.2, 9.6 Hz, H-2), 2.84 (dd, 1H, *J*=4.6, 4.7 Hz), 3.00 (dd, 1H, *J*=4.7, 9.6 Hz), 7.15–7.55 (m, 8H), 8.02–8.06 (m, 2H); ^{13}C NMR δ (ppm) 13.1, 27.1, 32.0, 35.5, 126.7, 127.7, 128.2, 128.4, 128.7, 129.1, 133.0, 137.0, 199.5. IR (neat): 1665, 1598, 1578, 1448, 1264, 1222, 1023, 737, 696 cm^{-1}.

4.4.14. trans-2-Methyl-3,5-diphenyl-4-phenylselanyl-2,3-dihydrofuran **28**

Yield 47%; yellow oil; R_f=0.64 (cyclohexane/EtOAc: 97/3), ^{77}Se NMR δ (ppm) 266.1; ^1H NMR δ (ppm) 1.43 (d, 3H, *J*=6.3 Hz), 3.62 (d, 1H, *J*=5.8 Hz, H-3) 4.66 (m, 1H, H-2), 7.05–7.35 (m, 15H); ^{13}C NMR δ (ppm) 21.6, 62.2 (C-3), 84.7 (C-2), 99.3, 126.4, 127.2, 128.1, 128.2, 128.3, 128.7, 129.2, 129.6, 130.3, 130.8, 131.4, 143.1 (C-4), 158.4 (C-5). IR (neat): 3059, 3028, 2971, 2925, 2360, 1664, 1597, 1577, 1492, 1476, 1446, 1438, 1266, 1221, 1069, 1022, 909, 736, 692, 668 cm^{-1}. MS (EI) *m/z* (relative intensity): 392 (M^+, 14), 105 ($PhCO^+$, 100), 77 (Ph^+, 34). Anal. Calcd for $C_{23}H_{20}OSe$ (391.35): C, 70.58; H, 5.15. Found: C, 70.48; H, 5.20.

4.4.15. Phenyl-(2-phenyl-1-phenylselanyl-3-propyl-cyclopropyl)-methanone **29**

Yield 53%, yellow oil (cis/trans: 60/40), R_f=0.37 (cyclohexane/EtOAc: 97/3). *cis Isomer*: ^{77}Se NMR δ (ppm) 329.5; ^1H NMR δ (ppm) 0.83 (t, 3H, *J*=7.3 Hz), 1.43 (m, 2H), 1.72 (m, 2H), 2.25 (dt, 1H, *J*=6.8, 10.3 Hz, H-3), 2.81 (d, 1H, *J*=10.3 Hz, H-2), 7.00–7.45 (m, 13H), 7.83–7.85 (m, 2H); ^{13}C NMR δ (ppm) 14.4, 22.7, 29.3 (C-3), 29.4, 33.4 (C-2), 41.5 (C-1), 127.1, 127.2, 128.1, 128.4, 129.0, 129.3, 130.15, 132.2, 133.3, 135.8, 136.4, 198.1. IR (neat): 3059, 2958, 2929, 2871, 2360, 1667, 1598, 1579, 1496, 1479, 1447, 1438, 1258, 1177, 1023, 909, 736, 694, 668 cm^{-1}. MS (EI) *m/z* (relative intensity): 420 (M^+, 8), 157 ($PhSe^+$, 12), 105 ($PhCO^+$, 100), 77 (Ph^+, 46). *trans Isomer*: ^{77}Se NMR δ (ppm) 399.2; ^1H NMR δ (ppm) 0.78 (t, 3H, *J*=7.3 Hz), 1.43 (m, 2H), 1.72 (m, 2H), 2.20 (m, 1H, H-3), 2.79 (d, 1H, *J*=7.0 Hz, H-2), 7.00–7.45 (m, 13H), 7.89–7.92 (m, 2H); ^{13}C NMR δ (ppm): 13.9, 22.5, 32.8 (C-3), 33.0, 34.5 (C-2), 42.6 (C-1), 126.7, 127.3, 127.5, 127.7, 128.3, 128.7, 129.2, 129.9, 132.4, 135.8, 136.3, 196.0. Anal. Calcd for $C_{25}H_{24}OSe$ (419.42): C, 71.59; H, 5.77. Found: C, 71.28; H, 5.94.

4.4.16. trans-3,5-Diphenyl-4-phenylselanyl-2-propyl-2,3-dihydrofuran **30**

Yield 7%; yellow oil; R_f=0.51 (cyclohexane/EtOAc: 97/3), ^{77}Se NMR δ (ppm) 266.3; ^1H NMR δ (ppm) 0.96 (t, 3H, *J*=7.1 Hz), 1.55 (m, 1H), 1.68 (m, 2H), 1.87 (m, 1H), 3.75 (d, 1H, *J*=5.7 Hz, H-3), 4.62 (dt, 1H, *J*=5.3, 5.7 Hz, H-2), 7.12–7.40 (m, 13H), 7.94–7.99 (m, 2H); ^{13}C NMR δ (ppm) 14.2, 18.7, 38.2, 60.7 (C-3), 88.2 (C-2), 99.4, 126.4, 127.1, 128.1, 128.2, 128.7, 129.2, 129.6, 130.4, 130.8, 131.3, 143.5 (C-4), 158.4 (C-5). IR (neat): 3360, 3058, 2958, 2930, 2871, 2359, 1668, 1598, 1576, 1491, 1475, 1455, 1437, 1265, 1183, 1120, 1070, 1022, 736, 694, 539 cm^{-1}. MS (EI) *m/z* (relative intensity): 420 (M^+, 8), 157 ($PhSe^+$, 14), 105 ($PhCO^+$, 100), 77 (Ph^+, 34). Anal. Calcd for $C_{25}H_{24}OSe$ (419.42): C, 71.59; H, 5.77. Found: C, 71.49; H, 5.91.

4.4.17. Phenyl-(2-but-3-enyl-3-phenyl-1-phenylselanyl-cyclopropyl)-methanone **31**

Yield 32%, yellow oil (cis/trans: 56/44). *cis Isomer*: R_f=0.32 (cyclohexane/EtOAc: 97/3), ^{77}Se NMR δ (ppm) 339.6; ^1H NMR δ (ppm) 1.91 (m, 2H), 2.18 (m, 2H), 2.34 (m, 1H), 2.87 (m, 1H), 4.94 (m, 2H), 5.76 (m, 1H), 7.15–7.60 (m, 13H), 7.82–7.95 (m, 2H); ^{13}C NMR δ (ppm) 26.7, 28.7, 33.4 (2C), 41.5, 115.2, 127.7, 128.1, 128.6, 128.7, 129.1, 129.4, 129.6, 130.1, 132.3, 133.6, 134.8, 137.0, 138.1, 197.8. IR (neat): 3060, 2925, 2360, 1661, 1598, 1579, 1496, 1478, 1448, 1224, 1176, 1069, 1022, 911, 737, 691, 668 cm^{-1}. MS (EI) *m/z* (relative intensity): 432 (M^+, 2), 157 ($PhSe^+$, 26), 105 ($PhCO^+$, 100), 77 (Ph^+, 80). *trans Isomer*: R_f=0.38 (cyclohexane/EtOAc: 97/3); ^{77}Se NMR δ (ppm) 421.4; ^1H NMR δ (ppm) 2.05 (m, 2H), 2.20 (m, 2H), 2.34 (m, 1H), 2.98 (m, 1H), 4.95 (m, 2H), 5.76 (m, 1H), 7.05–7.60 (m, 13H), 7.92–7.97 (m, 2H); ^{13}C NMR δ (ppm) 30.5, 32.3 (C-3), 33.4, 34.6 (C-2), 42.7 (C-1), 115.2, 126.7, 127.7, 128.1, 128.3, 128.5, 128.7, 129.2, 129.9, 132.3, 132.9, 133.4, 137.0, 137.7, 195.8.

4.4.18. 2-But-3-enyl-3,5-diphenyl-4-phenylselanyl-2,3-dihydrofuran **32**

Yield 5%; yellow oil; R_f=0.53 (cyclohexane/EtOAc: 97/3), ^{77}Se NMR δ (ppm) 268.1; ^1H NMR δ (ppm) 1.80 (m, 1H), 2.00 (m, 1H), 2.27 (m, 2H), 3.75 (d, 1H, *J*=5.6 Hz, H-3), 4.62 (dt, 1H, *J*=5.3, 5.6 Hz, H-2), 4.94–5.06 (m, 2H), 5.77–5.89 (m, 1H), 7.14–7.40 (m, 13H),

7.94–7.99 (m, 2H); ^{13}C NMR δ (ppm) 29.6, 35.3, 60.7 (C-3), 87.7 (C-2), 99.6, 115.3, 126.5, 127.2, 128.1, 128.2, 128.7, 129.2, 129.6, 130.5, 130.74, 131.2, 132.2, 132.3, 137.8, 143.3 (C-4), 158.3 (C-5). IR (neat): 2925, 2853, 1732, 1641, 1598, 1576, 1490, 1475, 1446, 1070, 1028, 999, 911, 736, 693, 668, 658, 538 cm^{-1}. MS (EI) *m*/*z* (relative intensity): 432 (M^+, 20), 157 ($PhSe^+$, 12), 105 ($PhCO^+$, 100), 77 (Ph^+, 40).

4.4.19. (4-Methoxy-phenyl)-(2-methyl-3-phenyl-cyclopropyl)-methanone **33**

Yield 25%, yellow oil, R_f=0.18 (cyclohexane/EtOAc: 95/5); ^{1}H NMR δ (ppm) 0.94 (d, 3H, *J*=6.4 Hz), 1.94 (dqd, 1H, *J*=4.6, 6.4, 9.4 Hz, H-2), 2.73 (dd, 1H, *J*=4.6, 4.8 Hz), 2.90 (dd, 1H, *J*=4.8, 9.4 Hz), 6.86–6.90 (m, 2H), 7.15–7.25 (m, 5H), 7.94–7.98 (m, 2H); ^{13}C NMR δ (ppm) 13.1, 26.5, 31.5, 35.0, 55.6, 113.9, 126.6, 128.4, 129.2, 130.4, 131.1, 132.1, 137.2, 197.9. IR (neat): 2960, 2991, 1698, 1600, 1575, 1510, 1424, 1311, 1260, 1229, 1168, 1028, 737, 700 cm^{-1}.

4.4.20. trans-2-Methyl-3-phenyl-5-(p-methoxy-phenyl)-4-phenylselanyl-2,3-dihydrofuran **34**

Yield 33%; white solid (mp=75–78 °C); R_f=0.4 (cyclohexane/EtOAc: 95/5); ^{77}Se NMR δ (ppm) 263.7; ^{1}H NMR δ (ppm) 1.42 (d, 3H, *J*=6.3 Hz), 3.62 (d, 1H, *J*=5.8 Hz, H-3), 3.75 (s, 3H), 4.63 (dq, 1H, *J*=6.1, 6.3 Hz, H-2), 6.81–6.85 (m, 2H), 7.05–7.30 (m, 10H), 7.85–7.90 (m, 2H); ^{13}C NMR δ (ppm) 21.6, 55.4 (C-3), 62.3, 84.5 (C-2), 97.2, 113.5, 123.3, 126.2, 127.1, 128.1, 128.6, 129.2, 129.7, 129.9, 131.7, 143.2 (C-4), 158.5 (C-5). IR (neat): 3060, 3028, 2969, 2925, 1608, 1577, 1506, 1476, 1455, 1439, 1254, 1177, 1081, 1030, 832, 737 cm^{-1}. MS (EI) *m*/*z* (relative intensity): 422 (M^+, 8), 135 ($MeO{-}C_6H_4{-}CO^+$, 100), 77 (Ph^+, 18). Anal. Calcd for $C_{24}H_{22}O_2Se$ (421.38): C, 68.40; H, 5.26. Found: C, 68.38, H, 5.22.

4.4.21. 1-[2-(4-Methoxy-phenyl)-3-methyl-1-phenylselanyl-cyclopropyl]-ethanone **35**

Yield 13%, yellow oil (cis/trans: 70/30). *cis Isomer*: R_f=0.32 (cyclohexane/EtOAc: 97/3), ^{1}H NMR δ (ppm) 1.31 (d, 3H, *J*=6.2 Hz), 2.57 (s, 3H), 2.69 (m, 1H, H-2), 2.76 (d, 1H, *J*=9.9 Hz), 3.82 (s, 3H), 6.85–6.90 (m, 2H), 7.15–7.35 (m, 7H); ^{13}C NMR δ (ppm) 12.8, 26.7 (C-2), 29.6, 37.8 (C-3), 43.9 (C-1), 55.35, 114.0, 126.1, 127.2, 128.7, 129.5, 120.2, 131.0, 131.6, 208.1. IR (neat): 2957, 2928, 1682, 1611, 1578, 1514, 1478, 1463, 1455, 1439, 1354, 1291, 1248, 1218, 1175, 1072, 1035, 838, 735, 691 cm^{-1}. *trans Isomer*: R_f=0.34 (cyclohexane/EtOAc: 97/3), ^{1}H NMR δ (ppm) 1.28 (d, 3H, *J*=6.2 Hz), 2.14 (m, 1H, H-2), 2.52 (s, 3H), 3.16 (d, 1H, *J*=8.0 Hz), 3.76 (s, 3H), 6.85–6.90 (m, 2H), 7.15–7.35 (m, 7H); ^{13}C NMR δ (ppm) 13.3, 30.2 (C-2), 30.8, 36.2 (C-3), 46.0 (C-1), 55.35, 113.2, 126.7, 127.2, 129.1, 129.1, 130.0, 130.6, 131.6, 205.5. MS (EI) *m*/*z* (relative intensity): 360 (M^+, 8), 157 ($PhSe^+$, 8), 77 (Ph^+, 10), 43 ($MeCO^+$, 100). Anal. Calcd for $C_{19}H_{20}O_2Se$ (359.31): C, 63.51; H, 5.61. Found: C, 63.62; H, 5.69.

4.4.22. 1-(4-Methoxy-phenyl)-3-methyl-2-phenylselanyl-penta-1,3-diene **36**

Yield 10%, yellow oil; R_f=0.49 (cyclohexane/EtOAc: 95/5). *Major isomer*: ^{1}H NMR δ (ppm) 1.64 (s, 3H, Me-3), 1.82 (d, 3H, *J*=6.6 Hz, H-5), 3.76 (s, 3H, OMe), 5.68 (q, 1H, *J*=6.6 Hz, H-4), 6.70 (s, 1H, H-1), 7.05–7.65 (m, 9H). IR (neat): 2928, 2361, 1605, 1576, 1558, 1507, 1475, 1456, 1438, 1249, 1175, 1119, 1034, 827, 738, 721, 692 cm^{-1}. MS (EI) *m*/*z* (relative intensity): 344 (M^+, 36), 157 ($PhSe^+$, 44), 77 (Ph^+, 56).

4.4.23. trans-2,5-Dimethyl-3-(4-methoxy-phenyl)-4-phenylselanyl-2,3-dihydrofuran **37**

Yield 9%; yellow oil; R_f=0.36 (cyclohexane/EtOAc: 95/5), ^{77}Se NMR δ (ppm) 241.4; ^{1}H NMR δ (ppm) 1.43 (d, 3H, *J*=6.2 Hz), 2.11 (d, 3H, *J*=1.5 Hz), 3.63 (dd, 1H, *J*=1.5, 6.4 Hz, H-3) 4.52 (m, 1H, H-2), 6.78–6.81 (m, 2H), 7.00–7.03 (m, 2H), 7.15–7.26 (m, 10H); ^{13}C NMR δ (ppm) 13.8, 21.5, 55.3, 60.1 (C-3), 86.0 (C-2), 98.6, 114.0, 126.0, 129.0, 129.1, 129.6, 132.2, 135.3, 158.7 (C-4), 161.8 (C-5). IR (neat): 2923, 2854, 1644, 1613, 1578, 1513, 1475, 1454, 1439, 1375, 1302, 1247, 1216, 1175, 1111, 1037, 955, 852, 823, 735, 690 cm^{-1}. MS (EI) *m*/*z* (relative intensity): 360 (M^+, 14), 157 ($PhSe^+$, 26), 77 (Ph^+, 12), 43 (CH_3CO^+, 100). Anal. Calcd for $C_{19}H_{20}O_2Se$ (359.31): C, 63.51; H, 5.61. Found: C, 63.76; H, 5.49.

4.4.24. Phenyl-(2-methyl-3-(p-methoxy-phenyl)-cyclopropyl)-methanone **38**

Yield 13%, yellow oil, R_f=0.13 (cyclohexane/EtOAc: 95/5); ^{1}H NMR δ (ppm) 1.05 (d, 3H, *J*=6.0 Hz), 2.00 (dqd, 1H, *J*=4.8, 6.0, 9.3 Hz, H-2), 2.79 (dd, 1H, *J*=4.6, 4.8 Hz), 2.97 (dd, 1H, *J*=4.6, 9.3 Hz), 3.81 (s, 3H), 6.85 (m, 2H), 7.18 (m, 2H), 7.45–7.58 (m, 3H), 8.02–8.06 (m, 2H); ^{13}C NMR δ (ppm) 13.1, 27.1 (C-2), 32.3 (C-1), 34.9 (C-3), 55.4, 113.8, 128.1, 128.7, 130.2, 131.3, 132.9, 136.8, 138.2, 199.6. IR (neat): 2958, 2991, 1661, 1613, 1580, 1514, 1418, 1327, 1286, 1247, 1221, 1179, 1040, 801, 737, 692 cm^{-1}.

4.4.25. 1-(4-Methoxy-phenyl)-3-phenyl-2-phenylselanyl-penta-1,3-diene **39**

Yield 10%, R_f=0.31 (cyclohexane/EtOAc: 97/3). *Major isomer*: ^{1}H NMR δ (ppm) 2.14 (d, 3H, *J*=7.0 Hz, H-5), 3.83 (s, 3H, OMe), 6.49 (q, 1H, *J*=7.0 Hz, H-4), 6.89 (s, 1H, H-1), 7.00–7.40 (m, 10H), 6.45–7.50 (m, 2H), 7.60–7.70 (m, 2H). IR (neat): 2927, 2854, 2836, 1604, 1508, 1464, 1456, 1440, 1290, 1247, 1172, 1107, 1035, 831, 759, 697 cm^{-1}. MS (EI) *m*/*z* (relative intensity): 406 (M^+, 26), 157 ($PhSe^+$, 36), 77 (Ph^+, 44).

4.4.26. trans-2-Methyl-3-(p-methoxy-phenyl)-5-phenyl-4-phenylselanyl-2,3-dihydrofuran **40**

Yield 35%; yellow oil; R_f=0.26 (cyclohexane/EtOAc: 97/3); ^{77}Se NMR δ (ppm) 266.0; ^{1}H NMR δ (ppm) 1.50 (d, 3H, *J*=6.2 Hz), 3.66 (d, 1H, *J*=5.7 Hz, H-3), 3.80 (s, 3H), 4.70 (m, 1H, H-2), 6.82 (d, 2H, *J*=8.6 Hz), 7.06 (d, 2H, *J*=8.6 Hz), 7.18–7.40 (m, 8H), 7.95–8.00 (m, 2H); ^{13}C NMR δ (ppm) 21.4, 55.2, 61.4 (C-3), 84.7 (C-2), 99.6, 114.0, 126.3, 128.1, 128.2, 129.0, 129.1, 129.5, 130.2, 130.8, 131.3, 135.1, 158.1, 158.7. IR (neat): 3058, 2968, 2925, 2834, 1614, 1674, 1544, 1493, 1476, 1446, 1374, 1337, 1303, 1246, 1175, 1111, 1069, 1033, 954, 865, 826, 769, 735, 691, 650, 560 cm^{-1}. MS (EI) *m*/*z* (relative intensity): 422 (M^+, 8), 135 ($MeOPhCO^+$, 100), 77 (Ph^+, 18). Anal. Calcd for $C_{24}H_{22}O_2Se$ (421.38): C, 68.40; H, 5.26. Found: C, 68.52, H, 5.10.

4.4.27. 1-(2,2,3-Trimethyl-1-phenylselanyl-cyclopropyl)-ethanone **41**

Yield 46%; yellow oil; R_f=0.35 (cyclohexane/EtOAc: 97/3); ^{77}Se NMR δ (ppm) 296.7; ^{1}H NMR δ (ppm) 1.10 (s, 3H), 1.17 (d, 3H, *J*=6.4 Hz), 1.29 (s, 3H), 1.95 (q, 1H, *J*=6.4 Hz), 2.40 (s, 3H), 7.15–7.35 (m, 5H); ^{13}C NMR δ (ppm) 11.64, 18.44, 22.8, 27.0 (C-3), 29.7 (C-2), 30.4, 49.9 (C-1), 126.4, 129.3, 129.8, 132.9, 206.3. IR (neat): 3053, 2956, 2926, 1665, 1575, 1478, 1447, 1248, 1022, 742, 693 cm^{-1}. MS (EI) *m*/*z* (relative intensity): 282 (M^+, 10), 157 ($PhSe^+$, 8), 125 ($M^+{-}PhSe$, 8), 77 (Ph^+, 12), 43 (CH_3CO^+, 100). Anal. Calcd for $C_{14}H_{18}OSe$ (281.24): C, 59.78; H, 6.45. Found: C, 59.71; H, 6.47.

4.4.28. 1-Phenyl-(2,2,3-trimethyl-1-phenylselanyl-cyclopropyl)-methanone **42**

Yield 44%; white solid (mp=136 °C); R_f=0.37 (cyclohexane/EtOAc: 97/3); ^{77}Se NMR δ (ppm) 338.4; ^{1}H NMR δ (ppm) 1.09 (s, 3H), 1.26 (d, 3H, *J*=6.4 Hz), 1.48 (s, 3H), 1.88 (q, 1H, *J*=6.4 Hz), 7.15–7.57 (m, 8H), 7.83–7.86 (m, 2H); ^{13}C NMR δ (ppm) 11.9, 18.2, 24.6 (C-2), 26.6, 28.6 (C-3), 45.6 (C-1), 126.6, 128.1, 129.1, 129.5, 129.6 (Cq.), 131.0, 132.4, 137.0 (Cq.), 197.5 (C=O). IR (neat): 2925, 1664, 1479, 1378, 1244, 1215, 1023, 739, 704 cm^{-1}. MS (EI) *m*/*z* (relative intensity): 344 (M^+, 12), 157 ($PhSe^+$, 14), 105 ($PhCO^+$, 100), 77 (Ph^+,

78). Anal. Calcd for $C_{19}H_{20}OSe$ (343.31): C, 66.46; H, 5.87. Found: C, 66.66; H, 5.92.

4.4.29. 1,4-Diphenyl-3-methyl-2-phenylselanylbuta-1,3-diene ***45***

Yield 27%; yellow oil; ^{1}H NMR δ (ppm) 2.17 (s, 3H), 2.35 (s, 3H), 7.1–8.2 (m, 16H); ^{13}C NMR δ (ppm) 17.0, 77.2, 125.7, 127.3, 132.4, 137.1, 139.2.

4.4.30. Phenyl(2-phenyl-1-(phenylselanyl)cyclopropyl)-methanone ***46***

Yield 57%; yellow oil; R_f=0.45 (cyclohexane/EtOAc: 95/5); ^{1}H NMR δ (ppm) 1.73 (dd, 1H, J=6.0, 7.5 Hz), 2.43 (dd, 1H, J=6.0, 9.4 Hz), 2.81 (dd, 1H, J=7.5, 9.4 Hz), 7.15–7.60 (m, 13H), 7.9 (d, 2H, J=6.0 Hz). ^{13}C NMR δ (ppm) 18.9, 32.1, 38.0, 127.4, 128.2, 128.3, 128.6, 129.0, 129.1, 129.4, 132.5, 132.8, 135.5, 136.1, 197.1. IR: 693, 737, 993, 1023, 1071, 1266, 1447, 1580, 1598, 1652, 2923, 3061 cm^{-1}. MS (EI) m/z (relative intensity): 377 (M^+, 48), 379 ($(M+2)^+$, 100).

4.4.31. 2,3-Dihydro-3,5-diphenyl-4-(phenylselanyl)furan ***47***

Yield 24%; yellow oil; R_f=0.72 (cyclohexane/EtOAc: 95/5); ^{1}H NMR δ (ppm) 4.15 (dd, 1H, J=5.3, 10.2 Hz), 4.52 (dd, 1H, J=5.3, 9.1 Hz), 4.83 (dd, 1H, J=9.1, 10.2 Hz), 7.15–7.40 (m, 13H), 7.94–7.97 (m, 2H). ^{13}C NMR δ (ppm) 54.7, 100.8, 126.6, 127.2, 127.9, 128.2, 128.7, 129.2, 129.6, 130.5, 130.5, 131.2, 143.2, 158.9. MS (EI) m/z (relative intensity): 393 ($(M+O)^+$, 62), 317 ($(M+O+2)^+$, 92).

4.4.32. 1-(2-Phenyl-1-(phenylselanyl)cyclopropyl)ethanone ***48***

Yield 57%; yellow oil; R_f=0.25 (cyclohexane/EtOAc: 95/5); ^{1}H NMR δ (ppm) 1.84 (dd, 1H, J=4.7, 7.7 Hz), 2.50 (dd, 1H, J=4.7, 9.2 Hz), 2.56 (s, 3H), 2.99 (dd, 1H, J=7.7, 9.2 Hz), 7.15–7.40 (m, 10H); ^{13}C NMR δ (ppm) 24.0, 29.5, 35.9, 39.1, 126.7, 127.5, 128.1, 129.2, 129.4, 130.1, 131.0, 136.5, 207.3. MS (EI) m/z (relative intensity): 315 (M^+, 88), 317 ($(M+2)^+$, 100).

4.4.33. 2,3-Dihydro-5-methyl-3-phenyl-4-(phenylselanyl)furan ***49***

Yield 6%; yellow oil; R_f=0.56 (cyclohexane/EtOAc: 95/5); ^{1}H NMR δ (ppm) 2.12 (d, 3H, J=1.5 Hz), 4.06 (dd, 1H, J=5.8, 10.2 Hz), 4.38 (dd, 1H, J=5.8, 9.1 Hz), 4.74 (dd, 1H, J=9.1, 10.2 Hz), 7.10–7.40 (m, 8H), 7.5–7.6 (m, 2H). IR: 689, 733, 1022, 1378, 1455, 1579, 1645, 2853, 2922 cm^{-1}.

4.4.34. (2-Methyl-1-(phenylselanyl)cyclopropyl)(phenyl)-methanone ***50***

Yield 66%; yellow oil; R_f=0.25 (cyclohexane/EtOAc: 95/5); ^{1}H NMR δ (ppm) 1.24 (dd, 1H, J=5.3, 6.0 Hz), 1.53 (d, 3H, J=6.2 Hz), 1.60–1.70 (m, 1H), 1.96 (dd, 1H, J=5.3, 8.8 Hz), 7.15–7.60 (m, 8H), 7.90 (d, 2H, J=6.0 Hz). ^{13}C NMR δ (ppm) 16.2, 21.3, 21.6, 35.2, 127.1, 128.4, 129.2, 130.7, 131.8, 132.7, 135.9, 197.7. IR: 689, 736, 1022, 1066, 1272, 1437, 1477, 1578, 1668, 2925, 3056 cm^{-1}. MS (EI) m/z (relative intensity): 315 (M^+, 60), 317 ($(M+2)^+$, 100).

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