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Synthesis of pyrazolidine, 1-pyrazoline, 2-pyrazoline derivatives by selenium-induced cyclization of homoallylhydrazines

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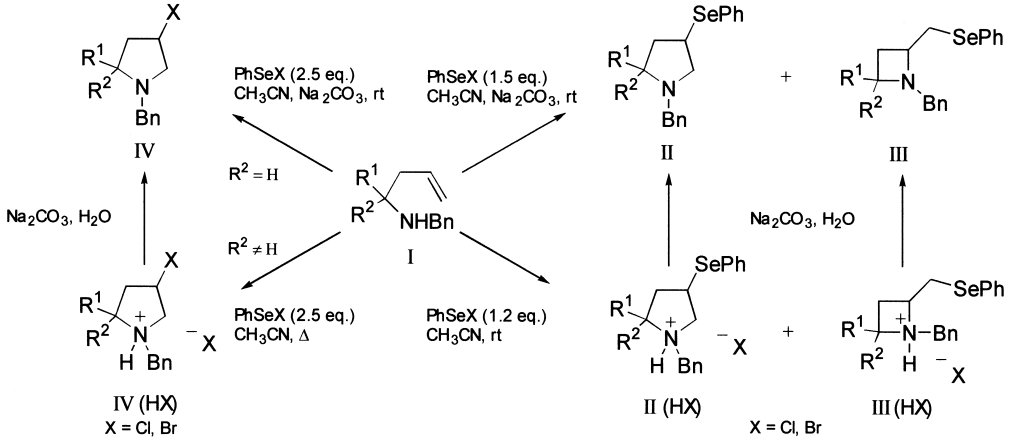
Abstract—The PhSeBr-induced cyclization of *N*′-but-3-en-1-yl ethoxycarbonylhydrazines **1**, phenylhydrazines **2** and dimethylhydrazines **3** has been studied. A 5-*exo-trig* ring closure occurred in each case and phenylselanylmethyl-pyrazolidines **4**, 2-pyrazolines **5** and **10**, 1-pyrazolines **8** and pyrazolidinium bromides **11** were synthesized. Radical deselenenylation has allowed the preparation of 5-methyl-pyrazolidines **12** and 5-methyl-2-pyrazolines **13** and **14**. Decomposition of the dibromoselenuranes derived from 2-pyrazolines **5** and **10** afforded bromomethyl derivatives. With 1-phenyl-2-pyrazolines **10**, an electrophilic *p*-halogenation of the phenyl nucleus was observed.

The selenium-induced cyclofunctionalization of unsaturated alcohols and carboxylic acids is now an efficient method for the synthesis of cyclic ethers and lactones.[1,2] *N*-protected alkenyl amines have been successfully cyclized into aza-heterocycles.[1–3] In these reactions, a seleniranium intermediate is involved and the attack of the internal nucleophile occurs with stereospecific *anti*-addition. According to the Baldwin's rules,[4] the *exo-trig* ring closures are favored, especially with substrates bearing a terminal olefinic bond. In these conditions, 1-alkoxycarbonyl-2-phenylselanylmethyl-pyrrolidines,[2] and -piperidines,[3] have been synthesized. As a consequence of a competitive mono- and di-selenenylation of the amino group,[5] alkenyl primary amines cannot be cyclized, but secondary pent-4-en-1-ylamines afforded, under acidic conditions and with modest yields, 1,2-dialkyl-5-phenylselanylmethylpyrrolidines according to a 5-*exo-trig* ring closure.[6]

In a recent study of the laboratory,[7,8] we observed that competitive 4-*exo-trig* and 5-*endo-trig* processes occurred in the PhSeX-induced cyclization of *N*-benzyl homoallylic amines I (Scheme 1). The reaction was carried out in CH_3CN containing sodium carbonate. Mixtures of phenylselanylpyrrolidines II and phenylselanylmethylazetidines



Scheme 1.

Keywords: pyrazolidine; cyclization; homoallylhydrazines.
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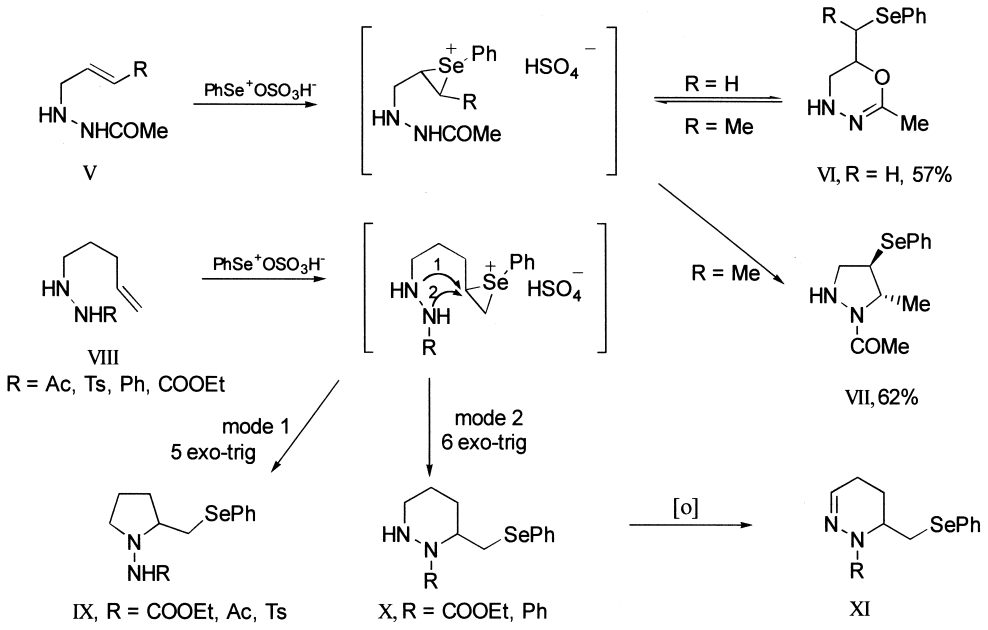
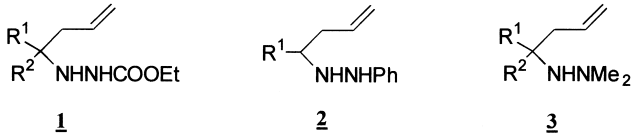


Scheme 2.

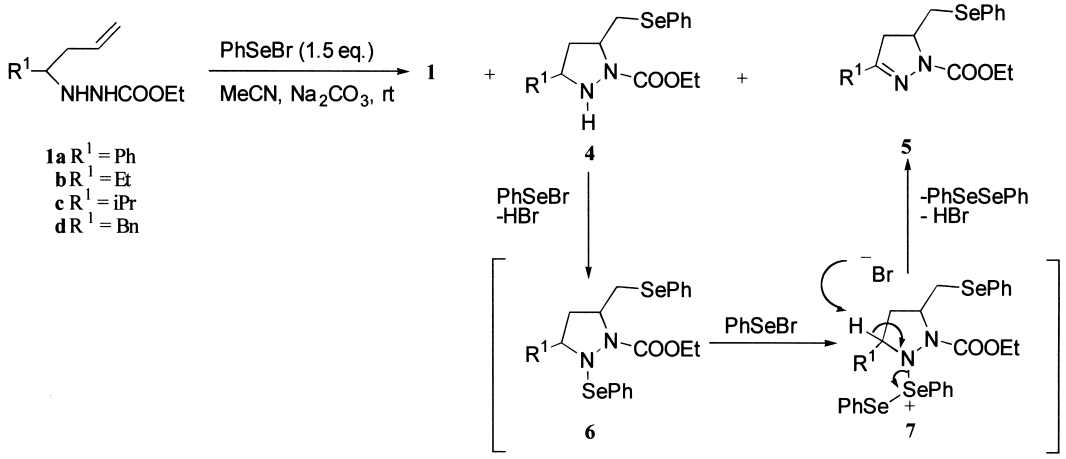
III were obtained as their HX salts in absence of sodium carbonate.[8] The formation of azetidines was observed for the first time by this ring closure process. The ratio of azetidines increased according to the order: PhSeCl<PhSeBr<PhSeI and with the size of the α-substituent (R^2=H). A geminal α-effect ($R^2 \neq H$) led dramatically to the major formation (>80%) of the azetidine derivatives III.[7,8] With an excess of PhSeX (X=Cl, Br), the β-halopyrrolidines IV were isolated with good yields.[7,9]

As an extension of this work, we were then interested in the selenium-induced cyclization of 'homoallyl' or but-3-en-1-ylhydrazine derivatives **1** (NHCOOEt), **2** (NHPh) and **3** (NMe_2).



1 **2** **3**

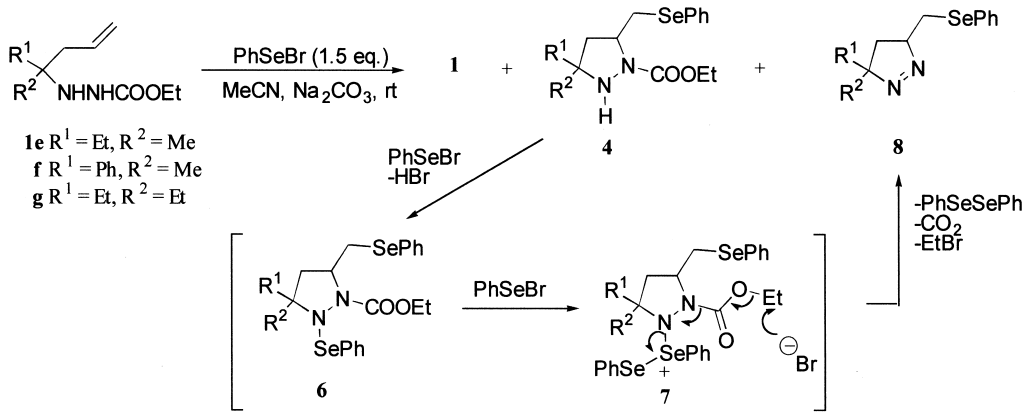
Tiecco et al.[10] have studied the phenylselenenyl sulfate-induced cyclization of *N′*-allylic acetylhydrazines V,



Scheme 3.

Table 1.

Substrate	R^1	Composition (%)			Isolated yield (%)		PhSeBr excess **5** yield (%)
		1	**4**	**5**	**4**	**5**	
1a	Ph	50	–	50	–	42	73
1b	Et	20	40	40	<10	68	82
1c	*i*Pr	20	40	40	<10	67	70
1d	Bn	10	45	45	<10	70	73



Scheme 4.

Table 2.

Substrate	R^1	R^2	Composition (%)			Isolated yield (%)		PhSeBr excess **8** yield (%)
			1	**4**	**8**	**4**	**8**	
1e	Et	Me	10	50	40	49	21	85
1f	Et	Ph	10	75	15	72	<10	64
1g	Et	Et	20	50	30	45	20	76

under acidic conditions (Scheme 2). With the simple allyl substituent, a 1,3,4-oxadiazine VI was formed as a consequence of the ambident nucleophilic nature of the NHCOMe group. When the reaction was carried out on substrates with a more substituted allyl group, the *N*-acetyl pyrazolidine VII was isolated as the thermodynamic product.

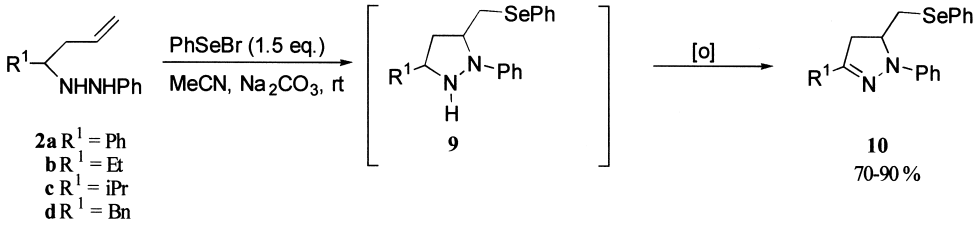
The same group has also investigated the selenium-induced cyclization of *N′*-pent-4-en-1-yl hydrazine derivatives VIII (R=Ph, COOEt, COMe, Ts).[11] As shown in Scheme 2, the nucleophilic center depends on the nature of R. The 5-*exo-trig*. mode was efficient with electron-withdrawing groups (R=COMe, Ts) affording the pyrrolidinamine IX. The 6-*exo-trig* cyclization was favored with R=Ph. The hexahydropyridazine derivatives X were partially oxidized into tetrahydropyridazine derivatives XI during the work-up.

1. Results and discussion

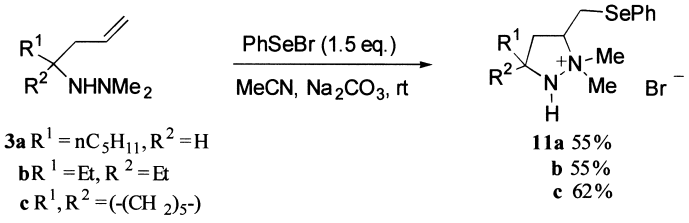
The substrates **1**–**3**, were prepared by reductive allylation (Allylmagnesium chloride, THF, −78°C) of the corresponding hydrazones. They were then treated with PhSeBr (1.5 equiv.) in MeCN, at room temperature, in the presence of sodium carbonate. The same experimental conditions were used for the selenium-induced cyclization of homoallylic amines.[1,2]

The hydrazine derivative **1a** (R^1=Ph, R^2=H) afforded the 2-pyrazoline **5a** in mixture with the substrate. Using an excess of PhSeBr (3 equiv.), **5a** was isolated with 73% yield (Scheme 3, Table 1). The other hydrazine derivatives **1b**–**d** (R^2=H), bearing an α-alkyl group, have led to mixtures of pyrazolidine **4**, 2-pyrazoline **5** and amine **1**. An excess of selenium reagent produced **5** in good yields. As shown in Scheme 3, this result seems to indicate that a selenenamide **6** undergoes a selenophilic reaction with PhSeBr. The presence of the good leaving group in **7** allows the formation of the iminyl double bond. The sequence **4→6→7→5** must occur faster that the cyclization step. Tiecco et al.[11] have observed that hexahydropyridazines are easily oxidized into tetrahydropyridazines during the work-up and the chromatography on silica gel.

The other substrates **1e**–**g** (R^1, R^2≠H) were then considered (Scheme 4, Table 2). Surprisingly, the 1-pyrazine derivatives **8** were obtained beside the pyrazolidine **4**, and unreacted amine **1**. They could be isolated in a pure form. Here, also, an excess of PhSeBr (3 equiv.) gave the 1-pyrazine **8** in a good yield. (Table 2). We suggest that **4** afforded the selenenamide intermediate **6** (R^2≠H) allowing the



Scheme 5.



Scheme 6.

appearance of the selanylselenonium salt **7** ($R^2 \neq H$). The 2-pyrazoline cannot be formed and bromide ion displaces the carboxylate from the ester group. The loss of CO_2 and ethyl bromide allows the formation of the nitrogen–nitrogen double bond (Scheme 4).

The treatment of the phenylhydrazines **2a–d** by PhSeBr (1.5 equiv.), under the same conditions, has led to the isolation of the 1-phenyl-2-pyrazolines **10**, in very good yields (Scheme 5). The corresponding pyrazolidines **9** were not detected and were easily oxidized into 2-pyrazolines **10**. An analogous observation was made by Tiecco et al.[11] during the transformation of *N*-phenyl hexahydropyridazines into tetrahydropyridazines.

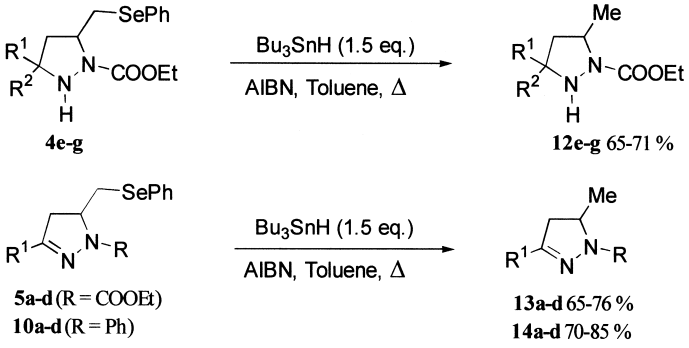
The reaction of the *N,N*-dimethylhydrazines **3a–c**, with PhSeBr, has allowed the formation of the 1,1-dimethylpyrazolidinium bromides **11a–c** in correct yields (Scheme 6). The 5-*exo-trig* mode was still efficient. Starting from substrates **1–3**, the 4-*exo-trig* ring closure was not observed.

The phenylselanylmethyl pyrazolidines **4e–g**, 2-pyrazolines **5a–d** (R=COOEt) and **10a–d** (R=Ph) were then subjected to the radical deselenenylation using a classical route. The 5-methylpyrazolidines **12e–g**, 5-methyl-2-pyrazolidines **13a–d** (R=COOEt) and **14a–d** (R=Ph) were synthesized in good yields (Scheme 7).

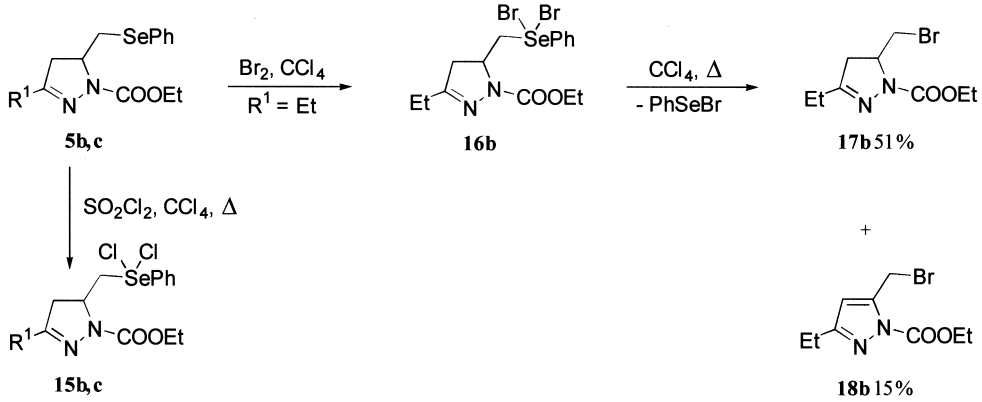
Examination of the literature has shown that the synthesis of pyrazolidines was not extensively studied,[12] if we except the work of Tiecco et al.[10] The same observation can be made for the access to 1-pyrazolines[13] and 2-pyrazolines.[14]

Our interest for the reactivity of Se-dihalo adducts derived from functionalized and unsaturated phenylselenides[15] led us to study the reaction of the 2-pyrazolines **5** (R=COOEt) and **10** (R=Ph) with SO_2Cl_2 or Br_2.

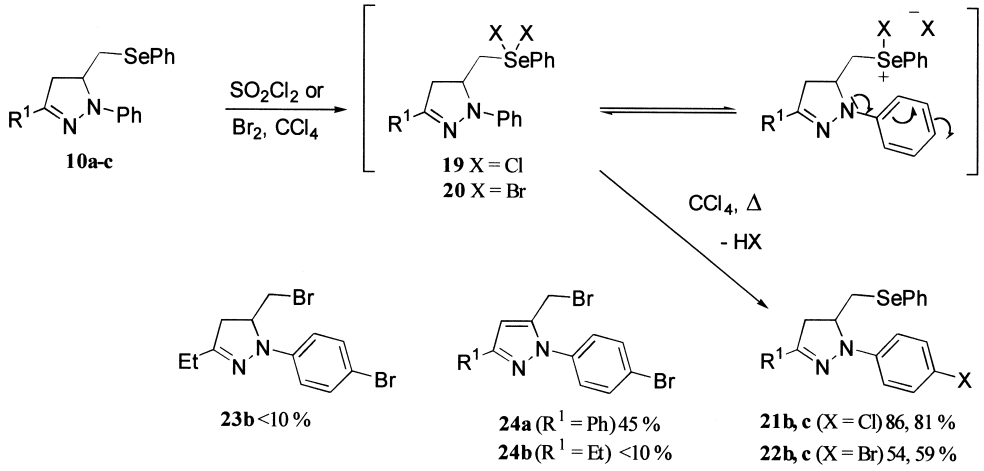
The dichloroselenuranes **15b** (R^1=Et) and **15c** (R^1=*i*Pr) were immediately formed in CCl_4 at room temperature and were not decomposed on heating in the same solvent.



Scheme 7.



Scheme 8.



Scheme 9.

On the contrary, the dibromo adduct **16b** (R^1=Et) afforded the 5-bromomethyl-2-pyrazoline **17b** (51%) and the 5-bromomethylpyrazole **18b** (15%). The pyrazole **18b** must be the oxidation product resulting from the reaction of **17b** with bromine[16] (Scheme 8).

The 1-phenyl-5-phenylselanylmethyl-2-pyrazolines **10a–c** gave unstable dihalo adducts **19** (X=Cl) and **20** (X=Br) which were decomposed on heating. An unexpected *para*-halogenation of the *N*-phenyl nucleus was observed when R^1 was an alkyl group. The 1-*p*-chlorophenyl- and 1-*p*-bromophenyl-5-phenylselanylmethyl-2-pyrazolines **21** and **22** were respectively isolated (Scheme 9). The *p*-bromophenyl derivative **22b** (R^1=Et, 54% yield) was formed along with the 1-*p*-bromophenyl-5-bromomethyl-2-pyrazoline **23b** and the corresponding pyrazole **24b** as minor product. The 5-bromomethyl-1-*p*-bromophenyl-3-phenylpyrazole **24a** was only isolated, in 45% yield, after decomposition of the dibromoselenurane **20a** (R^1=Ph). In these reactions, the dihaloselenurane **19** (or **20**) behaves mainly as a good electrophilic halogenating source, in the reaction with the *N*-activated phenyl group. Compounds **21** and **22** (R^1=alkyl) must be the kinetic products.

The goal of this work was to study the selenium-induced cyclization of homoallylhydrazine derivatives: PhSeBr treatment of the *N′*-but-3-en-1-yl *N*-ethoxycarbonylhydrazines **1**, phenylhydrazines **2** and *N*,*N*-dimethylhydrazines **3** in CH_3CN containing sodium carbonate, has led to the formation of phenylselanylmethylpyrazolidine derivatives. In all cases, a 5-*exo-trig* ring closure was observed. An excess of PhSeBr has led to the oxidation of pyrazolidines **4** (R^2=H) into 2-pyrazolines **5** and of pyrazolidines **4** ($R^2\neq$H) into 1-pyrazolines **8**. Phenylhydrazines **2** afforded directly 1-phenyl-2-pyrazolines **10** and the dimethylhydrazines **3** the 1,1-dimethylpyrazolidinium bromides **11**. Pyrazolidines **4** (R^2=H), 2-pyrazolines **5** (R=COOEt) and **10** (R=Ph) were deselenylated by the classical free-radical method. The action of SO_2Cl_2 or Br_2 on 2-pyrazolines **5** has led to stable Se-dihalo adducts **15** (X=Cl) and **16** (X=Br). The dibromoselenurane **16b** (R^1=Et) was decomposed giving a 51/15 mixture of bromomethyl-2-pyrazoline **17b** and pyrazole **18b**. An unexpected *p*-halogenation of the *N*-phenyl substituent was observed on heating the dihaloadducts **19** (X=Cl) and **20** (X=Br) derived from 1-phenyl-2-pyrazolines **10**. The 5-bromomethyl-1-*p*-bromophenyl pyrazole **24a** and 1-*p*-halophenyl-5-phenylselanylmethyl-2-pyrazolines **21b**,**c** (X=Cl) and **22b**,**c** (X=Br) were the major products formed.

2. Experimental

Ethoxycarbonylhydrazones,[17] phenylhydrazones[18] and dimethylhydrazones[19] were prepared by classical methods. THF was distilled over sodium-benzophenone and MeCN over P_2O_5. The chromatographic separations were achieved on silica gel (0.060–0.200 nm, pore diameter ca. 4 nm) available from ACROS. The ^1H and ^{13}C NMR spectra were recorded on Brucker AC 200 and DPX 300 instruments and carried out in $CDCl_3$ and the MS spectra on a HP 5890 gas chromatograph equipped with an HP 5970 mass selective detector.

2.1. Preparation of homoallyl ethoxycarbonylhydrazines 1

A solution of allylmagnesium chloride solution (2 M in THF) (1.5 equiv., 15 mmol, 7.5 ml when R^2=H (**a**–**d**)) was slowly added, under argon, to the corresponding ethoxycarbonylhydrazone (10 mmol) in THF (40 ml) at −78°C. The reaction mixture was stirred overnight and quenched with aqueous ammonium chloride (10%, 40 ml) at 0°C and extracted with ether (2×20 ml). The combined organic phases were washed with brine (2×20 ml), dried over anhydrous magnesium sulfate and evaporated under reduced pressure. The hydrazine **1** was used without purification for the cyclization step. 3.0 equiv. (30 mmol, 15 ml) of allylmagnesium chloride were used for hydrazones bearing R^1 and $R^2\neq$H.

2.1.1. 1-Ethoxycarbonyl-2-(1-phenylbut-3-en-1-yl)hydrazine 1a. Oil, ^1H NMR, δ: 7.24–7.34 (m, 5H, Ph), 6.1 (s, 1H, NH), 5.67–5.90 (m, 1H, H_3), 5.04–5.17 (m, 2H, H_4), 4.70 (t, 1H, H_1, J=7.0 Hz), 4.20 (s, 1H, NH), 4.12 (q, 2H, H_6, J=7.1 Hz), 2.49 (t, 2H, H_2, J=7.0 Hz), 1.23 (t, 3H, H_7, J=7.1 Hz). ^{13}C NMR, δ: 157.1 (C_5), 134.1 (C_3), 128.0,

126.9, 126.6, 125.5 (Ph), 117.4 (C_4), 63.0 (C_1), 61.0 (C_6), 43.3 (C_2), 14.1 (C_7).

2.1.2. 1-Ethoxycarbonyl-2-(hex-5-en-3-yl)hydrazine 1b. Oil, ^{1}H NMR, δ: 6.25 (s, 1H, NH), 5.66–5.92 (m, 1H, H_5), 4.99–5.14 (m, 2H, H_6), 4.11 (q, 2H, H_8, J=7.1 Hz), 3.4 (s, 1H, NH), 2.75–2.90 (m, 1H, H_3), 1.90–2.25 (m, 2H, H_4), 1.38 (quint, 2H, H_2, J=7.4 Hz), 1.22 (t, 3H, H_9, J=7.1 Hz), 0.87 (t, 3H, H_1, J=7.4 Hz). ^{13}C NMR, δ: 157.4 (C_7), 135.0 (C_6), 117.0 (C_5), 60.9 (C_8), 59.6 (C_3), 36.0 (C_4), 24.3 (C_2), 14.3 (C_9), 9.3 (C_1).

2.1.3. 1-Ethoxycarbonyl-2-(2-methylhex-5-en-3-yl)hydrazine 1c. Oil, ^{1}H NMR, δ: 6.2 (s, 1H, NH), 5.66–5.92 (m, 1H, H_5), 4.99–5.14 (m, 2H, H_6), 4.10 (q, 2H, H_8, J=7.1 Hz), 3.5 (s, 1H, NH), 2.69–2.80 (m, 1H, H_3), 2.13–2.23 (m, 1H, H_2), 1.77–2.02 (m, 2H, H_4), 1.24 (t, 3H, H_9, J=7.1 Hz), 0.88 (d, 6H, H_1, J=6.6 Hz). ^{13}C NMR, δ: 157.2 (C_7), 135.8 (C_6), 117.0 (C_5), 63.2 (C_3), 60.9 (C_8), 32.6 (C_4), 28.2 (C_2), 18.4 (C_1), 14.3 (C_9).

2.1.4. 1-Ethoxycarbonyl-2-(1-phenylpent-4-en-2-yl)hydrazine 1d. Oil, ^{1}H NMR, δ: 7.16–7.28 (m, 5H, Ph), 6.1 (s, 1H, NH), 5.70–5.92 (m, 1H, H_4), 5.06–5.14 (m, 2H, H_5), 4.20 (s, 1H, NH), 4.10 (q, 2H, H_7, J=7.1 Hz), 3.17–3.28 (m, 1H, H_2), 2.69 (t, 2H, H_3), 2.15 (q, 2H, H_1), 1.20 (t, 3H, H_8, J=7.1 Hz). ^{13}C NMR, δ: 157.1 (C_6), 138.2 (Ph), 134.6 (C_4), 128.9, 128.0, 125.9 (Ph), 117.4 (C_5), 60.9 (C_7), 59.4 (C_2), 38.7 (C_3), 36.9 (C_1), 14.2 (C_8).

2.1.5. 1-Ethoxycarbonyl-2-(3-methylhex-5-en-3-yl)hydrazine 1e. Oil, ^{1}H NMR, δ: 5.90 (s, 1H, NH), 5.70–5.89 (m, 1H, H_5), 5.01–5.07 (m, 2H, H_6), 4.10 (q, 2H, H_9, J=7.1 Hz), 3.7 (s, 1H, NH), 2.08 (d, 2H, H_4, J=7.4 Hz), 1.35 (q, 2H, H_2, J=7.5 Hz), 1.21 (t, 3H, H_{10}, J=7.1 Hz), 0.95 (s, 3H, H_7), 0.83 (t, 3H, H_1, J=7.5 Hz). ^{13}C NMR, δ: 157.6 (C_8), 134.0 (C_5), 117.3 (C_6), 60.9 (C_9), 58.6 (C_3), 41.1 (C_4), 29.2 (C_2), 21.6 (C_7), 14.2 (C_{10}), 7.5 (C_1).

2.1.6. 1-Ethoxycarbonyl-2-(3-phenylhex-5-en-3-yl)hydrazine 1f. Oil, ^{1}H NMR, δ: 7.17 (m, 5H, Ph), 5.5–5.8 (m, 2H, NH, H_5), 5.0 (m, 2H, H_6), 4.03 (q, 2H, H_8, J=7.1 Hz), 3.6 (s, 1H, NH), 2.51 (dt, 2H, H_4, J=3.8, 6.6 Hz), 1.67 (q, 2H, H_2, J=7.3 Hz), 1.12 (t, 3H, H_9, J=7.1 Hz), 0.67 (t, 3H, H_1, J=7.3 Hz). ^{13}C NMR, δ: 157.0 (C_7), 142.5 (Ph), 133.8 (C_5), 128.1, 126.6, 126.2 (Ph), 117.6 (C_6), 64.3 (C_3), 61.1 (C_8), 38.9 (C_4), 28.5 (C_2), 14.3 (C_9), 7.5 (C_1).

2.1.7. 1-Ethoxycarbonyl-2-(3-ethylhex-5-en-3-yl)hydrazine 1g. Oil, ^{1}H NMR, δ: 5.9 (s, 1H, NH), 5.71–5.91 (m, 1H, H_5), 5.02–5.10 (m, 2H, H_6), 4.11 (q, 2H, H_8, J=7.1 Hz), 3.4 (s, 1H, NH), 2.05 (dt, 2H, H_4, J=1.1, 7.3 Hz), 1.31 (q, 4H, H_2, J=7.3 Hz), 1.21 (t, 3H, H_9, J=7.1 Hz), 0.81 (t, 6H, H_1, J=7.3 Hz). ^{13}C NMR, δ: 157.4 (C_7), 133.8 (C_5), 117.0 (C_6), 60.7 (C_8), 60.5 (C_3), 38.1 (C_4), 25.7 (C_2), 14.1 (C_9), 7.0 (C_1).

2.2. Preparation of homoallyl phenylhydrazines 2 and dimethylhydrazines 3

The same method was used for phenylhydrazines **2** (allylmagnesium chloride, 3 equiv.) and of dimethylhydrazines **3** (allylmagnesium chloride, 2 equiv.). They were used without purification for the following step.

2.2.1. 1-Phenyl-2-(1-phenylbut-3-en-1-yl)hydrazine 2a.[20] Oil, ^{1}H NMR, δ: 7.31 (m, 7H, Ph), 6.68 (m, 3H, Ph), 5.71 (m, 1H, H_3), 4.8–5.05 (m, 3H, NH, H_4), 3.89 (t, 1H, H_1, J=6.7 Hz), 3.40 (s, 1H, NH), 2.48 (m, 2H, H_2). ^{13}C NMR, δ: 149.8 (Ph), 135.6 (C_3), 129.7, 129.5, 129.2, 129.1, 128.2, 122.9 (Ph), 117.9 (C_4), 113.5 (Ph), 62.9 (C_1), 39.2 (C_2).

2.2.2. 2-(Hex-5-en-3-yl)-1-phenylhydrazine 2b. Oil, ^{1}H NMR, δ: 7.15–7.23 (m, 2H, Ph), 6.87–6.89 (m, 2H, Ph), 6.75–6.79 (m,1H, Ph), 5.70–5.97 (m, 1H, H_5), 5.05–5.19 (m, 2H, H_6), 5.10 (s, 1H, NH), 3.15 (s, 1H, NH), 2.80 (quint, 1H, H_3, J=7.4 Hz), 2.18–2.28 (m, 2H, H_4), 1.47 (quint, 2H, H_2, J=7.4 Hz), 0.95 (t, 3H, H_1, J=7.4 Hz). ^{13}C NMR, δ: 149.6 (Ph), 135.3 (C_5), 128.7, 118.3 (Ph), 117.0 (C_6), 112.5 (Ph), 59.8 (C_3), 36.3 (C_4), 24.6 (C_2), 9.8 (C_1).

2.2.3. 1-(2-Methylhex-5-en-3-yl)-2-phenylhydrazine 2c. Oil, ^{1}H NMR, δ: 7.14–7.22 (m, 2H, Ph), 6.83–6.89 (m, 2H, Ph), 6.71–6.78 (m, 1H, Ph), 5.75–5.98 (m, 1H, H_5), 5.09–5.19 (m, 2H, H_6), 5.05 (s, 1H, NH), 3.30 (s, 1H, NH), 2.67 (dt, 1H, H_3), 1.82–2.35 (m, 3H, H_2, H_4), 0.94 (d, 6H, H_1, J=6.9 Hz). ^{13}C NMR, δ: 150.0 (Ph), 136.5 (C_5), 129.0, 118.6 (Ph), 117.3 (C_6), 112.6 (Ph), 64.2 (C_3), 33.24 (C_4), 28.7 (C_2), 19.0 (C_1).

2.2.4. 1-Phenyl-2-(1-phenylpent-4-en-2-yl)hydrazine 2d. Oil, ^{1}H NMR, δ: 7.09–7.45 (m, 8H, Ph), 6.65–6.76 (m, 2H, Ph), 5.70–5.95 (m, 1H, H_4), 5.09–5.17 (m, 3H, H_5, NH), 3.11 (quint, 2H, NH, H_2, J=6.3 Hz), 2.74 (d, 2H, H_3, J=6.3 Hz), 2.25 (t, 2H, H_1, J=6.3 Hz). ^{13}C NMR, δ: 149.3, 138.9 (Ph), 135.2 (C_4), 129.1, 128.7, 128.2, 126.1, 118.5 (Ph), 117.4 (C_5), 112.4 (Ph), 60.1 (C_2), 38.9 (C_3), 36.9 (C_1).

2.2.5. 1,1-Dimethyl-2-(non-1-en-4-yl)hydrazine 3a. Oil, ^{1}H NMR, δ: 5.8–5.9 (m, 1H, H_2), 5.02 (m, 2H, H_1), 2.65 (quint, 1H, H_4, J=5.3 Hz), 2.33 (s, 6H, H_{10}), 2.00–2.10 (m, 2H, H_3), 1.8 (s, 1H, NH), 1.20–1.40 (m, 8H, H_5, H_6, H_7, H_8), 0.81 (t, 3H, H_9, J=6.3 Hz). ^{13}C NMR, δ: 136.0 (C_2), 117.0 (C_1), 56.3 (C_4), 48.1 (C_{10}), 37.7 (C_3), 33.2 (C_5), 32.1 (C_6), 25.5 (C_7), 22.6 (C_8), 14.0 (C_9).

2.2.6. 2,2-Dimethyl-1-(3-ethylhex-5-en-3-yl)hydrazine 3b. Oil, ^{1}H NMR, δ: 5.8–5.9 (m, 1H, H_5), 4.95 (m, 2H, H_6), 2.35 (s, 6H, H_7), 2.07 (d, 2H, H_4, J=7.1 Hz), 1.8 (s, 1H, NH), 1.28 (q, 4H, H_2, J=7.4 Hz), 0.74 (t, 6H, H_1, J=7.4 Hz). ^{13}C NMR, δ: 135.1 (C_5), 116.3 (C_6), 60.2 (C_3), 50.7 (C_7), 39.1 (C_4), 25.2 (C_2), 7.4 (C_1).

2.2.7. 1-(1-Allylcyclohexyl)-2,2-dimethylhydrazine 3c. Oil, ^{1}H NMR, δ: 5.8–5.9 (m, 1H, H_3), 5.0 (m, 2H, H_4), 2.36 (s, 6H, H_8), 2.09 (d, 2H, H_2, J=7.1 Hz), 1.8 (s, 1H, NH), 1.20–1.4 (m, 10H, H_5, H_6, H_7). ^{13}C NMR, δ: 135.2 (C_3), 117.0 (C_4), 57.6 (C_1), 51.0 (C_8), 40.5 (C_2), 34.2, 25.9, 22.3 (C_2, C_3, C_7).

2.3. Cyclization of the homoallyl ethoxycarbonylhydrazines 1

Method A: PhSeBr (0.708 g, 3 mmol) in anhydrous CH_3CN (20 ml) was added, at room temperature, to the homoallylic

ethoxycarbonylhydrazine **1** (2 mmol) dissolved in the same solvent (10 ml) containing sodium carbonate (400 mg). The mixture was stirred for 16 h and treated with a NaCl aq. solution. After separation, the aqueous layer was extracted with CH_2Cl_2 (2×10 ml). The concentration of the organic layer has led to an oily residue chromatographied on silica gel. PhSeSePh was first separated by cyclohexane elution. From hydrazines **1a–d** (R^2=H), 2-pyrazolines **5** were separated (cyclohexane/ether: 80/20) then the pyrazolidines **4** (cyclohexane/ether: 60/40). From hydrazines **1e–g** ($R^2 \neq$H), the 1-pyrazolines **8** were first eluted (cyclohexane/ether: 90/10) and then the pyrazolidines **4** (cyclohexane/ether: 60/40).

Method B: Using an excess of PhSeBr (3 equiv.), the 2-pyrazolines **5** and the 1-pyrazolines **8** were only formed.

2.3.1. 1-Ethoxycarbonyl-3-phenyl-5-(phenylselanylmethyl)-4,5-dihydro-1*H*-pyrazole 5a. (Method B) mp=43°C, yield=73%, ^{1}H NMR, δ: 7.62–7.66 (m, 2H, Ph), 7.48–7.50 (m, 2H, Ph), 7.31–7.33 (m, 3H, Ph), 7.19–7.21 (m, 3H, Ph), 4.58 (m, 1H, H_5), 4.18 (q, 2H, H_7, J=7.1 Hz), 3.50 (d, 1H, H_9, J=12.2 Hz), 3.33 (dd, 1H, H_4, J=11.0, 17.6 Hz), 3.10 (dd, 1H, H_4, J=4.5, 17.6 Hz), 2.87 (t, 1H, H_9, J=9.8 Hz), 1.29 (t, 3H, H_8, J=7.1 Hz). ^{13}C NMR, δ: 153.7 (C_3), 132.2, 131.0, 130.0, 129.1, 128.5, 128.3, 127.0, 126.5 (Ph), 62.0 (C_7), 57.5 (C_5), 38.4 (C_4), 30.2 (C_9), 14.5 (C_8). Anal. Calcd for $C_{19}H_{20}N_2O_2Se$: C, 58.92; H, 5.20; N, 7.23; found: C, 58.94; H, 5.36; N, 7.32.

2.3.2. 1-Ethoxycarbonyl-3-ethyl-5-(phenylselanylmethyl)-pyrazolidine 4b. (Method A) Oil, yield <10%, ^{1}H NMR, δ: 7.5 (m, 2H, Ph), 7.2 (m, 3H, Ph), 4.25–4.40 (m, 1H, H_5), 4.10 (q, 2H, H_7, J=7.1 Hz), 3.65 (s, 1H, NH), 2.90–3.38 (m, 3H, H_9, H_3), 2.39–2.57 (m, 1H, H_4), 1.66–1.88 (m, 1H, $H_{4'}$), 1.15–1.50 (m, 2H, H_{10}), 1.21 (t, 3H, H_8, J=7.1 Hz), 0.94 (t, 3H, H_{11}, J=7.4 Hz). ^{13}C NMR, δ: 155.2 (C_6), 131.4, 129.1, 128.4, 126.2 (Ph), 61.1 (C_3), 60.9 (C_7), 58.5 (C_5), 40.2 (C_4), 32.1 (C_9), 24.1 (C_{10}), 14.1 (C_8), 10.4 (C_{11}). MS (EI, 70 eV): 342 ($M^{+\cdot}$, 35), 170 (90), 99 (100).

2.3.3. 1-Ethoxycarbonyl-3-ethyl-5-(phenylselanylmethyl)-4,5-dihydro-1*H*-pyrazole 5b. (Method B) Oil, yield=82%, ^{1}H NMR, δ: 7.44–7.51 (m, 2H, Ph), 7.15–7.25 (m, 3H, Ph), 4.35–4.51 (m, 1H, H_5), 4.16 (q, 2H, H_7, J=7.1 Hz), 3.43 (dd, 1H, H_9, J=12.4, 2.6 Hz), 3.05–2.76 (m, 2H, $H_{9'}$,H_4), 2.60–2.72 (dd, 1H, H_4, J=18.1, 4.9 Hz), 2.33 (q, 2H, H_{10}, J=7.5 Hz), 1.24 (t, 3H, H_8, J=7.1 Hz), 1.08 (t, 3H, H_{11}, J=7.5 Hz). ^{13}C NMR, δ: 159.7 (C_3), 132.1, 129.0, 128.6, 126.9 (Ph), 61.7 (C_7), 56.9 (C_5), 40.2 (C_4), 30.1 (C_9), 23.4 (C_{10}), 14.5 (C_8), 10.8 (C_{11}). MS (EI, 70 eV): 340 ($M^{+\cdot}$, 60), 169 (60), 157 (25), 97 (100). Anal. Calcd for $C_{15}H_{20}N_2O_2Se$: C, 53.10; H, 5.94; N, 8.26; found: C, 52.88; H, 6.31; N, 8.18.

2.3.4. 1-Ethoxycarbonyl-3-isopropyl-5-(phenylselanylmethyl)pyrazolidine 4c. (Method A) Oil, yield <10%, ^{1}H NMR, δ: 7.5 (m, 2H, Ph), 7.20 (m, 3H, Ph), 4.42 (m, 1H, H_5), 4.02 (q, 2H, H_7, J=7.1 Hz), 3.70 (s, 1H, NH), 3.28 (dd, 1H, H_9, J=2.9, 12.5 Hz), 3.05 (m, 1H, $H_{9'}$), 2.74 (m, 1H, H_3), 2.33 (m, 1H, H_4), 1.64 (oct, 1H, H_{10}, J=7.0 Hz), 1.45 (m, 1H, $H_{4'}$), 1.16 (t, 3H, H_8, J=7.1 Hz), 0.96 and 0.86 (dd, 6H, H_{11}, J=7.0 Hz). ^{13}C NMR, δ: 155.8 (C_6), 132.1, 123.6, 129.0, 126.77 (Ph), 66.0 (C_3), 61.4 (C_7), 58.9 (C_5), 38.6 (C_4), 32.8 (C_9), 30.3 (C_{10}), 20.6, 18.7 (C_{11}), 14.5 (C_8).

2.3.5. 1-Ethoxycarbonyl-3-isopropyl-5-(phenylselanylmethyl)-4,5-dihydro-1*H*-pyrazole 5c. (Method B) Oil, yield=70%, ^{1}H NMR, δ: 7.48–7.54 (m, 2H, Ph), 7.21–7.27 (m, 3H, Ph), 4.39–4.52 (m, 1H, H_5), 4.17 (q, 2H, H_7, J=7.1 Hz), 3.45 (dd, 1H, H_9, J=12.6, 2.5 Hz), 2.61–3.02 (m, 4H, H_{10}, $H_{9'}$, H_4), 1.25 (t, 3H, H_8, J=7.1 Hz), 1.09 (d, 6H, H_{11}, J=6.9 Hz). ^{13}C NMR, δ: 163.1 (C_3), 153.1 (C_6), 132.2, 129.0, 128.7, 126.9 (Ph), 61.7 (C_7), 56.8 (C_5), 37.5 (C_4), 30.1 (C_9), 29.5 (C_{10}), 20.1, 19.7 (C_{11}), 14.5 (C_8). MS (EI, 70 eV): 354 ($M^{+\cdot}$, 15), 183 (30), 69 (100). Anal. Calcd for $C_{16}H_{22}N_2O_2Se$: C, 54.39; H, 6.28; N, 7.93; found: C, 54.15; H, 6.14; N, 7.82.

2.3.6. 3-Benzyl-1-ethoxycarbonyl-5-(phenylselanylmethyl)-pyrazolidine 4d. (Method A) Oil, yield <10%, ^{1}H NMR, δ: 7.40 (m, 2H, Ph), 7.00–7.30 (m, 8H, Ph), 4.10–4.20 (m, 1H, H_5), 4.01 (q, 2H, H_7, J=7.1 Hz), 3.8 (s, 1H, NH), 3.17 (dd, 2H, H_3, H_9, J=3.1, 12.5 Hz), 3.03 (dd, 2H, $H_{9'}$, H_{10}, J=4.1, 13.0 Hz), 2.47 (dd, 1H, $H_{10'}$, J=8.7, 13.0 Hz), 2.17 (hept, 1H, H_4, J=5.6 Hz), 1.43 (m, 1H, $H_{4'}$), 1.13 (t, 3H, H_8, J=7.1 Hz). ^{13}C NMR, δ: 155.8 (C_6), 137.0, 132.0, 129.6, 128.9, 128.5, 128.1, 126.7, 125.4 (Ph), 61.5 (C_7), 60.8 (C_3), 60.1 (C_5), 40.1 (C_4), 37.2 (C_{10}), 32.5 (C_9), 14.4 (C_8).

2.3.7. 3-Benzyl-1-ethoxycarbonyl-5-(phenylselanylmethyl)-4,5-dihydro-1*H*-pyrazole 5d. (Method B) Oil, yield=73%, ^{1}H NMR, δ: 7.41–7.48 (m, 2H, Ph), 7.16–7.33 (m, 8H, Ph), 4.36–4.48 (m, 1H, H_5), 4.18 (q, 2H, H_7, J=7.1 Hz), 3.67 (s, 2H, H_{10}), 3.36 (dd, 1H, H_9, J=12.7, 2.6 Hz), 2.77–2.91 (m, 2H, $H_{9'}$, H_4), 2.52 (dd, 1H, $H_{4'}$, J=18.2, 5.0 Hz), 1.27 (t, 3H, H_8, J=7.1 Hz). ^{13}C NMR, δ: 156.9 (C_3), 135.3, 132.0, 131.9, 128.8, 128.6, 128.4, 128.2, 126.6 (Ph), 61.5 (C_7), 57.0 (C_5), 39.7 (C_4), 36.4 (C_{10}), 30.1 (C_9), 14.3 (C_8). MS (CI, 200 eV): 403 (MH^+, 100). Anal. Calcd for $C_{20}H_{22}N_2O_2Se$: C, 59.85; H, 5.52; N, 6.98; found: C, 60.25; H, 5.27; N, 6.98.

2.3.8. 1-Ethoxycarbonyl-3-ethyl-3-methyl-5-(phenylselanylmethyl)pyrazolidine 4e. (Method A) Oil, yield=49%, diastereoisomers mixture (1/1), ^{1}H NMR, δ: 7.45 (m, 2H, Ph), 7.25 (m, 3H, Ph), 4.40 (m, 1H, H_5), 4.10 (q, 2H, H_7, J=7.0 Hz), 3.86 (s, 1H, NH), 3.22 (m, 2H, H_9), 2.00–2.30 (m, 1H, H_4), 1.35–1.60 (m, 3H, $H_{4'}$, H_{10}), 1.19 (t, 3H, H_8, J=7.0 Hz), 1.16 and 0.92 (2s, 3H, H_{12}), 0.83, 0.81 (2t, 3H, H_{11}, J=7.4 Hz). ^{13}C NMR, δ: 131.7, 129.6, 128.8, 126.6 (Ph), 61.4 (C_7), 59.0, 58.7 (C_5), 45.1 (C_3), 32.6, 30.9, 29.4 (C_4, C_9, C_{10}), 21.9, 21.2 (C_{12}), 14.4 (C_8), 8.8, 8.6 (C_{11}). MS (EI, 70 eV): 356 ($M^{+\cdot}$, 100), 327 (70), 281 (70), 185 (100). Anal. Calcd for $C_{16}H_{24}N_2O_2Se$: C, 54.08; H, 6.81; N, 7.88; found: C, 53.75; H, 6.85; N, 8.22.

2.3.9. 3-Ethyl-3-methyl-5-(phenylselanylmethyl)-4,5-dihydro-3*H*-pyrazole 8e. (Method B) Oil, yield=85%, diastereoisomers mixture (1/1), ^{1}H NMR, δ: 7.5 (m, 2H, Ph), 7.2 (m, 3H, Ph), 4.56 (m, 1H, H_5), 3.68 and 3.62 (dd, 1H, H_6, J=5.1, 12.3 Hz), 3.05 and 3.02 (dd, 1H, $H_{6'}$, J=8.5, 12.3 Hz), 1.59–1.87 (m, 3H, H_7, H_4), 1.44 and 1.12 (s, 3H, H_9), 1.00 (m, 1H, $H_{4'}$), 0.90 and 0.75 (t, 3H, H_8, J=7.5 Hz). ^{13}C NMR, δ: 132.7, 129.2, 129.0, 127.0 (Ph), 93.1, 92.6 (C_3), 88.3, 87.0 (C_5), 34.5, 34.1, 31.8, 30.9, 30.6, 30.0 (C_4,

C_6, C_7), 25.0, 22.3 (C_9), 8.6, 8.3 (C_8). MS (CI, 200 eV): 283 (MH^+, 100), 125 (20), 97 (20). Anal. Calcd for $C_{13}H_{18}N_2Se$: C, 55.52; H, 6.45; N, 9.96; found: C, 55.36; H, 6.74; N, 10.26.

2.3.10. 1-Ethoxycarbonyl-3-ethyl-3-phenyl-5-(phenylselanylmethyl)pyrazolidine 4f. (Method A) Oil, yield=72%, diastereoisomers mixture (2/1), ^{1}H NMR, δ: 7.50 (m, 2H, Ph), 7.25 (m, 8H, Ph), 3.8–4.2 (m, 4H, NH, H_5, H_7), 3.20 (m, 2H, H_9), 2.83 (dd, 1H, H_4, J=12.5, 7.2 Hz), 1.90 (dd, 1H, H_4, J=12.5, 9.1 Hz), 1.71 (q, 2H, H_{10}, J=7.0 Hz), 1.15 (t, 3H, H_8, J=7.1 Hz), 0.73 (t, 3H, H_{11}, J=7.0 Hz). ^{13}C NMR, δ: 141.5, 132.1, 129.0, 128.2, 128.0, 126.8, 126.5, 126.1 (Ph), 61.3 (C_7), 58.8 (C_5), 33.3 (C_{10}), 31.8, 29.0 (C_4, C_9), 14.1 (C_8), 9.2 (C_{11}). Anal. Calcd for $C_{21}H_{26}N_2O_2Se$: C, 60.43; H, 6.28; N, 6.71; found: C, 60.47; H, 6.03; N, 6.89.

2.3.11. 3-Ethyl-3-phenyl-5-(phenylselanylmethyl)-4,5-dihydro-3*H*-pyrazole 8f. (Method B) Oil, yield=64%, 2/1 diastereoisomers mixture, major diastereoisomer: ^{1}H NMR, δ: 7.10–7.50 (m, 10H, Ph), 4.57 (oct, 1H, H_5, J=5.1 Hz), 3.60 (dd, 1H, H_6, J=5.1, 12.3 Hz), 2.81 (dd, 1H, $H_{6'}$, J=9.0, 12.3 Hz), 2.06 (dd, 1H, H_4, J=8.2, 12.3 Hz), 1.74 (q, 2H, H_7, J=7.4 Hz), 1.44 (1H, $H_{4'}$, J=8.2, 12.8 Hz), 0.66 (t, 3H, H_8, J=7.4 Hz). ^{13}C NMR, δ: Ph, 98.7 (C_3), 88.3 (C_5), 35.4 (C_4), 33.6 (C_7), 30.0 (C_6), 8.8 (C_8). Minor diastereoisomer: ^{1}H NMR, δ: 7.10–7.50 (m, 10H, Ph), 4.36 (oct, 1H, H_5, J=5.1 Hz), 3.65 (dd, 1H, H_6, J=5.1, 12.3 Hz), 3.06 (dd, 1H, $H_{6'}$, J=9.0, 12.3 Hz), 2.15 (dd, 1H, H_4, J=8.2, 12.3 Hz), 1.74 (q, 2H, H_7, J=7.4 Hz), 1.31 (1H, $H_{4'}$, J=8.2, 12.8 Hz), 0.80 (t, 3H, H_8, J=7.4 Hz). ^{13}C NMR, δ: Ph, 98.2 (C_3), 87.8 (C_5), 35.3 (C_4), 34.6 (C_7), 30.0 (C_6), 9.1 (C_8).

2.3.12. 1-Ethoxycarbonyl-3,3-diethyl-5-(phenylselanylmethyl)pyrazolidine 4g. (Method A) Oil, yield=45%, ^{1}H NMR, δ: 7.45 (m, 2H, Ph), 7.25 (m, 3H, Ph), 4.40 (m, 1H, H_5), 4.11 (q, 2H, H_7, J=7.0 Hz), 3.7 (s, 1H, NH), 3.22 (m, 2H, H_9), 2.05–2.15 (m, 1H, H_4), 1.25–1.80 (m, 5H, $H_{4'}$, H_{10}), 1.19 (t, 3H, H_8, J=7.0 Hz), 0.88 and 0.77 (2t, 6H, H_{11}, J=7.4 Hz). ^{13}C NMR, δ: 131.8, 129.7, 128.9, 126.6 (Ph), 61.3 (C_7), 58.7 (C_5), 43.7 (C_3), 32.7, 26.8 (C_4, C_9), 26.2 (C_{10}), 14.6 (C_8), 8.6, 7.8 (C_{11}). MS (EI, 70 eV): 370 ($M^{+\cdot}$, 50), 341 (70), 295 (100), 199 (30). Anal. Calcd for $C_{17}H_{26}N_2O_2Se$: C, 55.28; H, 7.09; N, 7.58; found: C, 55.47; H, 7.02; N, 8.08.

2.3.13. 3,3-Diethyl-5-(phenylselanylmethyl)-4,5-dihydro-3*H*-pyrazole 8g. (Method B) Oil, yield=76%, ^{1}H NMR, δ: 7.5 (m, 2H, Ph), 7.2 (m, 3H, Ph), 4.51 (m, 1H, H_5), 3.66 (dd, 1H, H_6, J=5.1, 12.1 Hz), 2.96 (dd, 1H, $H_{6'}$, J=8.9, 12.1 Hz), 1.83 (q, 2H, H_7, J=7.5 Hz), 1.62 (q, 2H, $H_{7'}$, J=7.5 Hz), 1.60 (hidden, 1H, H_4), 1.03 (dd, 1H, $H_{4'}$, J=8.3, 13.0 Hz), 0.85 and 0.70 (t, 6H, H_8, J=7.5 Hz). ^{13}C NMR, δ: 132.1, 129.4, 129.0, 127.1 (Ph), 96.9 (C_3), 88.3 (C_5), 31.4 (C_7), 30.4 (C_6), 30.2 (C_7), 29.1 (C_4), 8.4, 8.1 (C_8). MS (CI, 200 eV): 297 (MH^+, 100). Anal. Calcd for $C_{14}H_{20}N_2Se$: C, 56.95; H, 6.83; N, 9.49; found: C, 57.26; H, 6.48; N, 9.56.

2.4. Cyclization of the homoallyl phenylhydrazines 2

PhSeBr (0.708 g, 3 mmol) in anhydrous CH_3CN (20 ml) was added, at room temperature, to the homoallylic phenylhydrazine **2** (2 mmol) in the same solvent (10 ml) containing sodium carbonate (400 mg). The mixture was stirred for 16 h and treated with a NaCl aq. solution. After separation, the aqueous layer was extracted with CH_2Cl_2 (2×10 ml). The work-up of the organic phase has led to an oily residue chromatographed on silica gel (cyclohexane/CH_2Cl_2: 80/20).

2.4.1. 1,3-Diphenyl-5-(phenylselanylmethyl)-4,5-dihydro-1*H*-pyrazole 10a. Oil, yield=80%, ^{1}H NMR, δ: 7.57 (d, 2H, Ph), 7.40 (d, 2H, Ph), 7.00–7.30 (m, 9H, Ph), 6.64 (d, 2H, Ph), 4.27 (tt, 1H, H_5, J=3.2, 10.5 Hz), 3.36 (dd, 1H, H_4, J=11.2, 17.6 Hz), 3.11–3.25 (m, 2H, $H_{4'}$, H_6), 2.68 (dd, 1H, $H_{6'}$, J=10.5, 12.5 Hz). ^{13}C NMR, δ: 148.2 (C_3), Ph, 59.3 (C_5), 38.6 (C_4), 29.8 (C_6). MS (CI, 200 eV): 393 (MH^+, 100), 237 (15). Anal. Calcd for $C_{22}H_{20}N_2Se$: C, 67.52; H, 5.15; N, 7.16; found: C, 67.78; H, 5.21; N, 7.26.

2.4.2. 3-Ethyl-1-phenyl-5-(phenylselanylmethyl)-4,5-dihydro-1*H*-pyrazole 10b. Oil, yield=90%, ^{1}H NMR, δ: 7.53–7.59 (m, 2H, Ph), 7.13–7.31 (m, 5H, Ph), 6.64–6.86 (m, 3H, Ph), 4.25 (ddt, 1H, H_5, J=2.6, 4.6, 10.3 Hz), 3.29 (dd, 1H, H_6, J=2.6, 12.4 Hz), 3.05 (dd, 1H, H_4, J=10.3, 17.5 Hz), 2.80–2.69 (m, 2H, $H_{4'}$, $H_{6'}$), 2.38 (q, 2H, H_7, J=7.6 Hz), 1.16 (t, 3H, H_8, J=7.6 Hz). ^{13}C NMR, δ: 153.8 (C_3), 145.0, 133.7, 129.3, 129.2, 128.8, 127.6, 118.6, 113.0 (Ph), 59.4 (C_5), 41.1 (C_4), 30.6 (C_6), 23.8 (C_7), 11.3 (C_8). MS (EI, 70 eV): 344 ($M^{+\cdot}$, 10), 173 (100). Anal. Calcd for $C_{18}H_{20}N_2Se$: C, 62.97; H, 5.87; N, 8.16; found: C, 62.72; H, 6.13; N, 8.38.

2.4.3. 3-Isopropyl-1-phenyl-5-(phenylselanylmethyl)-4,5-dihydro-1*H*-pyrazole 10c. Oil, yield=82%, ^{1}H NMR, δ: 7.59–7.53 (m, 2H, Ph), 7.30–7.13 (m, 5H, Ph), 6.86–6.72 (m, 3H, Ph), 4.27 (ddt, 1H, H_5, J=2.6, 4.5, 10.4 Hz), 3.28 (dd, 1H, H_6, J=2.6, 12.3 Hz), 3.04 (dd, 1H, H_4, J=10.4, 17.3 Hz), 2.81–2.65 (m, 3H, $H_{4'}$, $H_{6'}$, H_7), 1.15 (d, 6H, H_8, J=6.9 Hz). ^{13}C NMR, δ: 157.2 (C_3), 145.0, 133.8, 129.2, 129.1, 128.8, 127.6, 118.6, 113.0 (Ph), 59.4 (C_5), 39.0 (C_4), 30.4 (C_6), 29.8 (C_7), 20.4 (C_8). MS (EI, 70 eV): 358 ($M^{+\cdot}$, 10), 187 (100). Anal. Calcd for $C_{19}H_{22}N_2Se$: C, 63.86; H, 6.20; N, 7.84; found: C, 63.95; H, 6.32; N, 8.16.

2.4.4. 3-Benzyl-1-phenyl-5-(phenylselanylmethyl)-4,5-dihydro-1*H*-pyrazole 10d. Oil, yield=70%, ^{1}H NMR, δ: 7.46–7.51 (m, 2H, Ph), 7.14–7.30 (m, 10H, Ph), 6.78–6.87 (m, 3H, Ph), 4.26 (ddt, 1H, H_5, J=2.6, 4.5, 10.4 Hz), 3.70 (s, 2H, H_7), 3.26 (dd, 1H, H_6, J=2.6, 12.3 Hz), 2.94 (dd, 1H, H_4, J=10.4, 17.3 Hz), 2.65–2.56 (m, 2H, $H_{4'}$, $H_{6'}$). ^{13}C NMR, δ: 150.6 (C_3), 144.9, 137.2, 137.0, 134.1, 133.9, 129.4, 129.1, 128.9, 128.7, 127.7, 119.0, 113.2 (Ph), 59.1 (C_5), 40.2 (C_4), 36.5 (C_7), 30.1 (C_6). MS (EI, 70 eV): 406 ($M^{+\cdot}$, 10), 235 (50), 91 (100). Anal. Calcd for $C_{23}H_{22}N_2Se$: C, 68.14; H, 5.47; N, 6.91; found: C, 68.12; H, 5.28; N, 6.27.

2.5. Cyclization of the homoallyl dimethylhydrazines 3

PhSeBr (0.708 g, 3 mmol) in anhydrous CH_3CN (20 ml) was added, at room temperature, to the homoallylic dimethylhydrazine **3** (2 mmol) in the same solvent (10 ml) containing sodium carbonate (400 mg). The mixture was stirred for 16 h and treated with a NaCl aq. solution. The

aqueous layer was extracted with CH_2Cl_2 (2×10 ml). The white solid obtained, after concentration of the solvent, was recrystallized in a 60/40 pentane/CH_2Cl_2 mixture.

2.5.1. 1,1-Dimethyl-3-pentyl-5-(phenylselanylmethyl)-pyrazolidinium bromide 11a. Mp=123°C, yield=55%, two diastereoisomers are presents (1/1), ^{1}H NMR, δ: 7.50 (m, 2H, Ph), 7.31 (m, 3H, Ph), 4.19 and 4.00 (m, 1H, H_5), 3.60 (m, 1H, H_7), 3.56 and 3.52 (s, 3H, H_6), 3.34 and 3.30 (s, 3H, $H_{6'}$), 3.13 and 2.98 (t, 1H, $H_{7'}$, J=11.3 Hz), 2.82 (quint, 1H, H_3, J=6.7 Hz), 2.50 (s, 1H, NH), 2.34–2.13 and 1.82–1.60 (m, 2H, H_4), 1.20–1.70 (m, 8H, H_8, H_9, H_{10}, H_{11}), 0.85 (t, 3H, H_{12}, J=7.5 Hz). ^{13}C NMR, δ: 133.3, 133.1, 129.5, 129.4, 128.2, 127.8, 127.5, 127.4 (Ph), 78.5, 77.3 (C_5), 56.2, 53.6, 50.4, 46.7 (C_6), 37.5 (C_3), 36.2, 34.8 (C_4), 33.4, 31.2, 26.2 (C_8, C_9, C_{10}), 25.3, 24.5 (C_7), 22.2 (C_{11}), 13.7, 12.7 (C_{12}). MS (FAB+): 341 (M^+−Br, 100). Anal. Calcd for $C_{17}H_{29}N_2BrSe$: C, 48.58; H, 6.95; N, 6.66; found: C, 48.63; H, 6.85; N, 6.74.

2.5.2. 3,3-Diethyl-1,1-dimethyl-5-(phenylselanylmethyl)-pyrazolidinium bromide 11b. Mp 80°C, yield=55%, ^{1}H NMR, δ: 7.55 (m, 2H, Ph), 7.26 (m, 3H, Ph), 3.72 (m, 1H, H_5), 3.55 (d, 1H, H_7, J=11.5 Hz), 3.47, 3.44 (s, 6H, H_6), 2.89 (t, 1H, $H_{7'}$, J=11.5 Hz), 2.6 (s, 1H, NH), 2.44 (dd, 1H, H_4, J=6.2, 14.0 Hz), 1.86 (t, 1H, H_4, J=12.6 Hz), 1.40–1.70 (m, 4H, H_8), 0.81 and 0.74 (t, 6H, H_9, J=7.3 Hz). ^{13}C NMR, δ: 133.0, 129.1, 127.7, 127.1 (Ph), 77.1 (C_5), 63.9 (C_3), 55.2, 50.0 (C_6), 40.1 (C_4), 31.6, 30.3 (C_8), 23.2 (C_7), 8.6, 7.9 (C_9). MS (CI, 200 eV): 327 (MH^+−Br, 15). Anal. Calcd for $C_{16}H_{27}N_2BrSe$: C, 47.30; H, 6.70; N, 6.89; found: C, 47.36; H, 6.99; N, 6.78.

2.5.3. 3,3-Cyclopentylene-1,1-dimethyl-5-(phenylselanylmethyl)pyrazolidinium bromide 11c. Mp>200°C, yield=62%, ^{1}H NMR, δ: 7.55 (m, 2H, Ph), 7.26 (m, 3H, Ph), 3.88 (m, 1H, H_5), 3.62 (d, 1H, H_7, J=12.0 Hz), 3.51 and 3.43 (s, 6H, H_6), 3.01 (t, 1H, $H_{7'}$, J=11.0 Hz), 2.9 (s, 1H, NH), 2.50 (d, 1H, H_4, J=9.0 Hz), 1.90 (t, 1H, $H_{4'}$, J=12.0 Hz), 1.40–1.70 (m, 6H, cycle), 1.10–1.30 (m, 4H, cycle). ^{13}C NMR, δ: 133.5, 129.5, 128.2, 127.6 (Ph), 77.5 (C_5), 61.8 (C_3), 55.4, 50.5 (C_6), 41.0 (C_4), 39.2, 24.5, 23.7, 23.3 (C_7, C_8, C_9, C_{10}). MS (FAB+): 339 (M^+−Br, 100). Anal. Calcd for $C_{17}H_{27}N_2BrSe$: C, 48.88; H, 6.51; N, 6.70; found: C, 49.01; H, 6.82; N, 6.81.

2.6. General procedure for the radical reduction of 4, 5 or 10

A solution of pyrazolidine **4** (or 2-pyrazoline **5** or **10**), Bu_3SnH (0.437 g, 1.5 mmol) and AIBN (0.01 g) in toluene (20 ml) was refluxed for 8 h. The solvent was then evaporated and the residue purified by chromatography on silica gel (cyclohexane/ether: 60/40 for **12**, cyclohexane/ether: 90/10 for **13** and cyclohexane/CH_2Cl_2: 80/20 for **14**)

2.6.1. 1-Ethoxycarbonyl-3-ethyl-3,5-dimethylpyrazolidine 12e. Oil, yield=67%, diastereoisomers mixture (1/1), ^{1}H NMR, δ: 4.12 (q, 2H, H_7, J=7.1 Hz), 4.01–4.10 (m, 1H, H_5), 3.50 (s, 1H, NH), 2.09 (m, 1H, H_4), 1.45–1.69 (m, 1H, $H_{4'}$), 1.08–1.35 (m, 11H, H_8, H_9, H_{10}, H_{12}), 0.89 (dt, 3H, H_{11}, J=7.3 Hz). ^{13}C NMR, δ: 156.8 (C_6), 61.1 (C_7), 55.3, 55.0 (C_5), 47.6, 47.0 (C_3), 31.3 (C_4), 29.1 (C_{10}), 21.7, 21.6 (C_{12}), 20.6 (C_9), 14.6 (C_8), 8.9, 8.5 (C_{11}). MS (EI, 70 eV): 200 ($M^{+\cdot}$, 15), 185 (10), 171 (40), 125 (100). Anal. Calcd for $C_{10}H_{20}N_2O_2$: C, 59.97; H, 10.06; N, 13.99; found: C, 60.24; H, 10.18; N, 14.23.

2.6.2. 1-Ethoxycarbonyl-3-ethyl-5-methyl-3-phenylpyrazolidine 12f. Oil, yield=71%, ^{1}H NMR, δ: 7.2–7.7 (m, 5H, Ph), 4.50 (m, 1H, H_5), 4.25 (q, 2H, H_7, J=7.1 Hz), 3.5 (s, 1H, NH), 3.41 (dd, 1H, H_4, J=11.0, 17.4 Hz), 2.78 (dd, 1H, $H_{4'}$, J=4.6, 17.4 Hz), 1.1–1.6 (m, 8H, H_8, H_9, H_{10}), 0.82 (t, 3H, H_{11}, J=7.5 Hz). ^{13}C NMR, δ: 153.9 (C_6), 131.6, 129.9, 128.5, 126.6 (Ph), 61.9 (C_7), 53.9 (C_5), 27.8 (C_4), 26.9 (C_{10}), 20.6 (C_9), 14.7 (C_8), 13.6 (C_{11}).

2.6.3. 1-Ethoxycarbonyl-3,3-diethyl-5-methylpyrazolidine 12g. Oil, yield=71%, ^{1}H NMR, δ: 4.05–4.25 (m, 1H, H_5), 4.13 (q, 2H, H_7, J=7.1 Hz), 3.25 (s, 1H, NH), 2.11 (dd, 1H, H_4, J=7.8, 12.0 Hz), 1.55–1.75 (m, 1H, $H_{4'}$), 1.17–1.31 (m, 10H, H_8, H_9, H_{10}), 0.87 and 0.80 (dt, 6H, H_{11}, J=7.5 Hz). ^{13}C NMR, δ: 147.8 (C_6), 61.3 (C_7), 54.7 (C_5), 46.0 (C_3), 27.1 (C_4), 25.8 (C_{10}), 20.6 (C_9), 14.4 (C_8), 8.3, 7.8 (C_{11}). MS (EI, 70 eV): 214 ($M^{+\cdot}$, 5), 185 (50), 139 (100), 111 (70). Anal. Calcd for $C_{11}H_{22}N_2O_2$: C, 61.65; H, 10.35; N, 13.07; found: C, 61.67; H, 10.15; N, 13.25.

2.6.4. 1-Ethoxycarbonyl-5-methyl-3-phenyl-4,5-dihydro-1*H*-pyrazole 13a. Oil, yield=76%, ^{1}H NMR, δ: 7.7 (m, 2H, Ph), 7.2 (m, 3H, Ph), 4.46 (m, 1H, H_5), 4.22 (q, 2H, H_7, J=7.1 Hz), 2.36 (dd, 1H, H_4, J=11.0, 17.3 Hz), 2.75 (dd, 1H, $H_{4'}$, J=4.5, 17.3 Hz), 1.31 (d, 3H, H_9, J=6.3 Hz), 1.30 (t, 3H, H_8, J=7.1 Hz). ^{13}C NMR, δ: 153.5, 152.6 (C_3, C_6), 131.2, 129.6, 129.2, 126.3 (Ph), 61.6 (C_7), 53.6 (C_5), 40.6 (C_4), 20.3 (C_9), 14.4 (C_8). MS (CI, 200 eV): 233 (MH^+, 100). Anal. Calcd for $C_{13}H_{16}N_2O_2$: C, 67.22; H, 6.94; N, 12.06; found: C, 67.36; H, 7.16; N, 11.82.

2.6.5. 1-Ethoxycarbonyl-3-ethyl-5-methyl-4,5-dihydro-1*H*-pyrazole 13b. Oil, yield=74%, ^{1}H NMR, δ: 4.15–4.31 (m, 1H, H_5), 4.16 (q, 2H, H_7, J=7.1 Hz), 2.94 (dd, 1H, H_4, J=10.6, 18.1 Hz), 2.22–2.34 (m, 3H, $H_{4'}$, H_{10}), 1.22 (t, 3H, H_8, J=7.1 Hz), 1.19 (d, 3H, H_9, J=6.3 Hz), 1.04 (t, 3H, H_{11}, J=7.6 Hz). ^{13}C NMR, δ: 159.4 (C_3), 152.2 (C_6), 61.0 (C_7), 52.6 (C_5), 41.5 (C_4), 23.1 (C_{10}), 19.8 (C_9), 14.2 (C_8), 10.4 (C_{11}). MS (EI, 70 eV): 184 ($M^{+\cdot}$, 10), 169 (7), 125 (15), 97 (100), 69 (25). Anal. Calcd for $C_9H_{16}N_2O_2$: C, 58.67; H, 8.75; N, 15.21; found: C, 58.42; H, 9.01; N, 15.51.

2.6.6. 1-Ethoxycarbonyl-3-isopropyl-5-methyl-4,5-dihydro-1*H*-pyrazole 13c. Oil, yield=65%, ^{1}H NMR, δ: 4.20–4.40 (m, 1H, H_5), 4.21 (q, 2H, H_7, J=7.1 Hz), 2.95 (dd, 1H, H_4, J=10.6, 17.5 Hz), 2.74 (hept, 1H, H_{10}, J=6.9 Hz), 2.31 (dd, 1H, $H_{4'}$, J=4.3, 17.5 Hz), 1.27 (t, 3H, H_8, J=7.1 Hz), 1.22 (d, 3H, H_9, J=6.9 Hz), 0.87 (dd, 6H, H_{11}, J=6.9 Hz). ^{13}C NMR, δ: 163.1 (C_3), 152.7 (C_6), 61.6 (C_7), 52.8 (C_5), 39.3 (C_4), 29.5 (C_{10}), 20.1 (C_{11}), 19.7 (C_9), 14.5 (C_8). MS (EI, 70 eV): 198 ($M^{+\cdot}$, 30), 183 (10), 139 (30), 111 (95), 97 (70), 69 (100). Anal. Calcd for $C_{10}H_{18}N_2O_2$: C, 60.58; H, 9.15; N, 14.13; found: C, 60.38; H, 9.26; N, 13.88.

2.6.7. 3-Benzyl-1-ethoxycarbonyl-5-methyl-4,5-dihydro-1*H*-pyrazole 13d. Oil, yield=73%, ^{1}H NMR, δ: 7.15–

7.28 (m, 5H, Ph), 4.25–4.39 (m, 1H, H_5), 4.27 (q, 2H, H_7, J=7.1 Hz), 3.68 (d, 2H, H_{10}), 2.86 (dd, 1H, H_4, J=10.8, 17.8 Hz), 2.19 (dd, 1H, $H_{4'}$, J=4.7, 17.8 Hz), 1.31 (t, 3H, H_8, J=7.1 Hz), 1.15 (d, 3H, H_9, J=6.3 Hz). ^{13}C NMR, δ: 157.1 (C_3), 152.6 (C_6), 135.8, 128.6, 128.5, 126.8 (Ph), 61.5 (C_7), 53.3 (C_5), 41.5 (C_4), 36.7 (C_{10}), 20.6 (C_9), 14.6 (C_8). MS (EI, 70 eV): 246 ($M^{+\cdot}$, 40), 231 (10), 159 (30), 91 (100). Anal. Calcd for $C_{14}H_{18}N_2O_2$: C, 68.27; H, 7.37; N, 11.37; found: C, 68.61; H, 7.15; N, 11.65.

2.6.8. 5-Methyl-1,3-diphenyl-4,5-dihydro-1*H*-pyrazole 14a. Solid, yield=85%, ^{1}H NMR, δ: 7.0–7.7 (m, 10H, Ph), 4.43 (m, 1H, H_5), 3.38 (m, 1H, H_4), 2.80 (m, 1H, $H_{4'}$), 1.23 (d, 3H, CH_3, J=6.2 Hz). ^{13}C NMR, δ: 148.1, 136.8, 130.1, 129.0, 128.6, 126.3, 118.8, 114.1, 113.4 (C_3, Ph), 55.3 (C_5), 40.4 (C_4), 19.1 (C_6). Anal. Calcd for $C_{16}H_{16}N_2$: C, 81.32; H, 6.82; N, 11.85, found: C, 80.99; H, 7.01; N, 11.69.

2.6.9. 3-Ethyl-5-methyl-1-phenyl-4,5-dihydro-1*H*-pyrazole 14b. Oil, yield=78%, ^{1}H NMR, δ: 7.20–7.32 (m, 2H, Ph), 7.03–7.07 (m, 2H, Ph), 6.75–6.81 (m, 1H, Ph), 4.12–4.28 (m, 1H, H_5), 2.98–3.12 (m, 1H, H_4), 2.35–2.50 (m, 3H, $H_{4'}$, H_7), 1.23 (d, 3H, H_6, J=6.2 Hz), 1.19 (t, 3H, H_8, J=7.6 Hz). ^{13}C NMR, δ: 153.8 (C_3), 145.5, 128.8, 118.2, 113.1 (Ph), 55.0 (C_5), 42.7 (C_4), 23.7 (C_7), 18.9 (C_6), 11.0 (C_8). MS (EI, 70 eV): 188 ($M^{+\cdot}$, 40), 173 (100), 158 (10), 77 (45). Anal. Calcd for $C_{12}H_{16}N_2$: C, 76.56; H, 8.57; N, 14.88; found: C, 76.23; H, 8.78; N, 14.88.

2.6.10. 3-Isopropyl-5-methyl-1-phenyl-4,5-dihydro-1*H*-pyrazole 14c. Oil, yield=82%, ^{1}H NMR, δ: 7.18–7.27 (m, 2H, Ph), 7.01–7.06 (m, 2H, Ph), 6.72–6.80 (m, 1H, Ph), 4.22 (hept, 1H, H_5, J=6.3 Hz), 3.04 (dd, 1H, H_4, J=10.4, 16.9 Hz), 2.70 (hept, 1H, H_7, J=6.9 Hz), 2.43 (dd, 1H, $H_{4'}$, J=5.1, 16.9 Hz), 1.20 (d, 3H, H_6, J=6.3 Hz), 1.16 (d, 6H, H_8, J=6.9 Hz). ^{13}C NMR, δ: 157.1 (C_3), 145.5, 128.8, 128.1, 113.2 (Ph), 54.9 (C_5), 40.5 (C_4), 29.6 (C_7), 20.2 (C_8), 18.6 (C_6). MS (EI, 70 eV): 202 ($M^{+\cdot}$, 30), 187 (50), 145 (100), 77 (50). Anal. Calcd for $C_{13}H_{18}N_2$: C, 77.18; H, 8.97; N, 13.85; found: C, 76.85; H, 8.98; N, 14.12.

2.6.11. 3-Benzyl-5-methyl-1-phenyl-4,5-dihydro-1*H*-pyrazole 14d. Oil, yield=70%, ^{1}H NMR, δ: 7.28–7.37 (m, 7H, Ph), 7.12–7.16 (m, 2H, Ph), 6.84–6.90 (m, 1H, Ph), 4.26 (hept, 1H, H_5, J=5.5 Hz), 3.78 (s, 2H, H_7), 2.97 (dd, 1H, H_4, J=10.6, 17.1 Hz), 2.35 (dd, 1H, $H_{4'}$, J=5.3, 17.1 Hz), 1.22 (d, 3H, H_6, J=6.2 Hz). ^{13}C NMR, δ: 151.0 (C_3), 144.1, 136.8, 128.8, 128.6, 127.1, 126.5, 118.3, 113.2 (Ph), 55.2 (C_5), 42.1 (C_4), 36.8 (C_7), 18.8 (C_6). MS (EI, 70 eV): 250 ($M^{+\cdot}$, 60), 235 (30), 91 (100). Anal. Calcd for $C_{17}H_{18}N_2$: C, 81.56; H, 7.25; N, 11.19; found: C, 81.67; H, 7.42; N, 11.00.

2.7. Chloration of the 1-ethoxycarbonyl 2-pyrazolines 5

SO_2Cl_2 (134 mg, 1 mmol) in CCl_4 (2 ml) was added dropwise to the pyrazoline **5** (1 mmol), at room temperature, in the same solvent (10 ml). The mixture was stirred for 30 min. The product was filtred and washed with cyclohexane.

2.7.1. (1-Ethoxycarbonyl-3-ethyl-5-(phenylselanylmethyl)-4,5-dihydro-1*H*-pyrazole) dichloro-adduct 15b. White solid, yield=82%, ^{1}H NMR, δ: 7.9 (m, 2H, Ph), 7.45 (m, 3H, Ph), 5.32 (m, 1H, H_5), 4.22–4.46 (m, 3H, H_7, H_9), 4.11 (dd, 1H, $H_{9'}$, J=5.6, 10.5 Hz), 3.23 (dd, 1H, H_4, J=10.5, 18.2 Hz), 2.9 (m, 1H, $H_{4'}$), 2.40 (q, 2H, H_{10}, J=7.5 Hz), 1.33 (t, 3H, H_8, J=7.1 Hz), 1.11 (t, 3H, H_{11}, J=7.5 Hz). ^{13}C NMR, δ: 160.0 (C_3), 153.5 (C_6), 141.0, 131.3, 129.6, 128.9 (Ph), 66.3 (C_9), 62.6 (C_7), 53.6 (C_5), 40.6 (C_4), 23.1 (C_{10}), 14.5 (C_8), 10.6 (C_{11}).

2.7.2. (1-Ethoxycarbonyl-3-isopropyl-5-[(phenylselanylmethyl]-4,5-dihydro-1*H*-pyrazole) dichloro-adduct 15c. White solid, yield=80%, ^{1}H NMR, δ: 7.9 (m, 2H, Ph), 7.5 (m, 3H, Ph), 5.31 (m, 1H, H_5), 4.2–4.5 (m, 3H, H_7, H_9), 4.12 (dd, 1H, $H_{9'}$, J=5.7, 10.3 Hz), 3.21 (m, 1H, H_4, J=5.7, 17.8 Hz), 2.9 (m, 1H, $H_{4'}$), 2.78 (hept, 1H, H_{10}, J=6.9 Hz), 1.32 (t, 3H, H_8, J=7.1 Hz), 1.14 (d, 6H, H_{11}, J=6.9 Hz). ^{13}C NMR, δ: 163.2 (C_3), 153.5 (C_6), 141.1, 131.5, 129.7, 120 (Ph), 66.2 (C_9), 62.7 (C_7), 53.5 (C_5), 38.2 (C_4), 29.5 (C_{10}), 20.1, 19.7 (C_{11}), 14.0 (C_8).

2.8. Bromination of the 1-ethoxycarbonyl-2-pyrazoline 5b

A solution of Br_2 in CCl_4 (C=100 g/l) (1.6 ml, 1 mmol) was slowly added to the pyrazoline **5b** in the same solvent (10 ml). The solid dibromo-adduct **16b** was formed immediately. The mixture was refluxed for 30 min, treated with a sodium thiosulfate aq. solution (10 ml) and then washed with water (10 ml). The organic layer was dried over magnesium sulfate and concentrated. The residue was purified by silica gel chromatography. The pyrazole **18b** was first separated (cyclohexane/ether: 80/20). The bromopyrazoline **17b** was then eluted with the same mixture of solvents.

2.8.1. (1-Ethoxycarbonyl-3-ethyl-5-[(phenylselanylmethyl]-4,5-dihydro-1*H*-pyrazole) dibromo adduct 16b. White solid, ^{1}H NMR, δ: 8.0 (m, 2H, Ph), 7.5 (m, 3H, Ph), 5.39 (m, 1H, H_5), 4.20–4.45 (m, 3H, H_7, H_9), 4.11 (m, 1H, $H_{9'}$), 3.25 (dd, 1H, H_4, J=11.2, 17.9 Hz), 2.9 (m, 1H, $H_{4'}$), 2.40 (q, 2H, H_{10}, J=7.5 Hz), 1.35 (t, 3H, H_8, J=7.1 Hz), 1.12 (t, 3H, H_{11}, J=7.5 Hz). ^{13}C NMR, δ: 151.1 (C_3), 152.1 (C_6), 138.0, 135.0, 129.9, 129.0 (Ph), 63.0 (C_9), 56.9 (C_7), 53.7 (C_5), 41.1 (C_4), 23.1 (C_{10}), 14.5 (C_8), 10.6 (C_{11}).

2.8.2. 5-Bromomethyl-1-ethoxycarbonyl-3-ethyl-4,5-dihydro-1*H*-pyrazole 17b. Oil, yield=51%, ^{1}H NMR, δ: 4.48 (m, 1H, H_5), 4.22 (q, 2H, H_7, J=7.1 Hz), 3.59 (dd, 1H, H_9, J=2.8, 11.0 Hz), 3.5 (m, 1H, $H_{9'}$), 3.00 (dd, 1H, H_4, J=11.0, 18.2 Hz), 2.73 (dd, 1H, $H_{4'}$, J=5.1, 18.2 Hz), 2.37 (q, 2H, H_{10}, J=7.5 Hz), 1.28 (t, 3H, H_8, J=7.1 Hz), 1.10 (t, 3H, H_{11}, J=7.5 Hz). ^{13}C NMR, δ: 159.7 (C_3), 62.2 (C_7), 57.5 (C_5), 39.8 (C_4), 26.9 (C_9), 23.5 (C_{10}), 14.7 (C_8), 10.9 (C_{11}). MS (CI, 200 eV): 263 (MH^+, 100). Anal. Calcd for $C_9H_{15}N_2BrO_2$: C, 41.08; H, 5.75; N, 10.65; found: C, 41.24; H, 5.71; N, 10.33.

2.8.3. 5-Bromomethyl-1-ethoxycarbonyl-3-ethyl-1*H*-pyrazole 18b. Oil, yield=15%, ^{1}H NMR, δ: 6.30 (s, 1H, H_4), 4.70 (s, 2H, H_9), 4.47 (q, 2H, H_7, J=7.1 Hz), 2.60 (q, 2H, H_{10}, J=7.7 Hz), 1.40 (t, 3H, H_8, J=7.1 Hz), 1.17 (t, 3H, H_{11}, J=7.7 Hz). ^{13}C NMR, δ: 158.0 (C_3), 149.8 (C_6), 143.7

(C_5), 111.2 (C_4), 64.6 (C_7), 22.1 (C_9), 21.6 (C_{10}), 14.3 (C_8), 13.1 (C_{11}). MS (EI, 70 eV): 262 ($M^{+\cdot}$, 10), 181 (30), 109 (100).

2.9. Chloration of the 1-phenyl-2-pyrazolines 10

SO_2Cl_2 (134 mg, 1 mmol) in CCl_4 (2 ml) was added dropwise to the pyrazoline **10** (1 mmol), at room temperature, in the same solvent (10 ml). The mixture was refluxed for 30 min. and washed with aq. $NaHCO_3$ solution (2×10 ml). The organic layers were dried over magnesium sulfate and concentrated. The residue was purified by silica gel chromatography (cyclohexane/CH_2Cl_2: 80/20).

2.9.1. 1-(4-Chlorophenyl)-3-ethyl-5-(phenylselanylmethyl)-4,5-dihydro-1*H*-pyrazole 21b. Oil, yield=86%, ^{1}H NMR, δ: 7.5–7.7 (m, 2H, Ph), 6.8–7.4 (m, 7H, Ph), 4.50 (m, 1H, H_5), 3.55 (dd, 1H, H_6, J=3.5, 10.9 Hz), 3.43 (dd, 1H, $H_{6'}$, J=9.1, 10.9 Hz), 3.09 (dd, 1H, H_4, J=10.0, 17.5 Hz), 2.87 (dd, 1H, $H_{4'}$, J=7.5, 17.5 Hz), 2.40 (q, 2H, H_7, J=7.6 Hz), 1.21 (t, 3H, H_8, J=7.6 Hz). ^{13}C NMR, δ: 153.9 (C_3), 144.2, 135.6, 131.0, 129.9, 129.4, 128.1, 127.2, 126.7, 125.0, 120.7 (Ph), 64.0 (C_5), 44.7 (C_4), 40.2 (C_6), 23.6 (C_7), 10.9 (C_8). MS (CI, 200 eV): 379 (MH^+, 100). Anal. Calcd for $C_{18}H_{19}ClN_2Se$: C, 57.23; H, 5.07; N, 7.42; found: C, 57.51; H, 5.21; N, 7.23.

2.9.2. 1-(4-Chlorophenyl)-3-isopropyl-5-(phenylselanylmethyl)-4,5-dihydro-1*H*-pyrazole 21c. Oil, yield=81%, ^{1}H NMR, δ: 7.60 (m, 2H, Ph), 7.20 (m, 3H, Ph), 6.80–7.00 (m, 4H, Ph), 4.43 (m, 1H, H_5), 3.51 (dd, 1H, H_6, J=3.4, 11.0 Hz), 3.40 (dd, 1H, $H_{6'}$, J=9.1, 11.0 Hz), 3.03 (dd, 1H, H_4, J=10.1, 16.9 Hz), 2.83 (dd, 1H, $H_{4'}$, J=7.5, 16.9 Hz), 2.63 (hept, 1H, H_7, J=6.9 Hz), 1.16 (d, 6H, H_8, J=6.9 Hz). ^{13}C NMR, δ: 159.6 (C_3), 144.3, 136.0, 131.2, 130.1, 129.2, 128.2, 126.7, 124.3, 120.3 (Ph), 63.8 (C_5), 44.5 (C_4), 38.3 (C_6), 30.4 (C_7), 20.1 (C_8). MS (CI, 200 eV): 393 (MH^+, 100). Anal. Calcd for $C_{19}H_{21}ClN_2Se$: C, 58.25; H, 5.40; N, 7.15; found: C, 58.63; H, 5.42; N, 7.26.

2.10. Bromination of the 1-phenyl 2-pyrazolines 10

A solution of Br_2 in CCl_4 (C=100 g/l) (1.6 ml, 1 mmol) was slowly added to the pyrazoline in the same solvent (10 ml). The dibromo adduct **20** precipitated immediatly. The suspension was refluxed for 30 min, treated with a sodium thiosulfate aq. solution (10 ml) and then washed with water (10 ml). The organic layer was dried over magnesium sulfate and concentrated. The residue was purified by silica gel chromatography. The pyrazole **24a** and the phenylselanylmethylpyrazoline **22c** were separed by cyclohexane/CH_2Cl_2: (80/20) elution. From **10b**, the bromopyrazoline **23b** was first separated (cyclohexane/CH_2Cl_2: 80/20). The phenylselanylmethylpyrazoline **22b** and then the bromomethylpyrazoline **24b** were then eluted with the same mixture of solvents.

2.10.1. 5-Bromomethyl-1-(4-bromophenyl)-3-phenyl-1*H*-pyrazole 24a. Oil, yield=45%, ^{1}H NMR, δ: 7.75 (d, 2H, Ph, J=7.0 Hz), 7.58 (d, 2H, Ph, J=8.7 Hz), 7.46 (d, 2H, Ph, J=9.0 Hz), 7.20–7.35 (m, 3H, Ph), 6.76 (s, 1H, H_4), 4.40 (s, 2H, H_6). ^{13}C NMR, δ: 152.4, 140.2, 138.1, 132.6, 132.4, 128.8, 128.7, 126.6, 125.8, 122.4 (C_3, C_5, Ph), 106.3 (C_4), 21.0 (C_6). MS (CI, 200 eV): 391 (MH^+, 100), 315 (30), 313 (30). Anal. Calcd for $C_{16}H_{12}N_2Br_2$: C, 49.01; H, 3.08; N, 7.14; found: C, 49.30; H, 3.16; N, 7.20.

2.10.2. 1-(4-Bromophenyl)-3-ethyl-5-[(phenylselanylmethyl]-4,5-dihydro-1*H*-pyrazole 22b. Oil, yield=54%, ^{1}H NMR, δ: 7.5 (m, 2H, Ph), 7.2–7.3 (m, 5H, Ph), 6.57 (d, 2H, Ph), 4.13 (m, 1H, H_5), 3.15 (dd, 1H, H_6, J=2.0, 12.3 Hz), 3.00 (dd, 1H, $H_{6'}$, J=10.7, 17.7 Hz), 2.70 (m, 2H, H_4), 2.30 (q, 2H, H_7, J=7.6 Hz), 1.08 (t, 3H, H_8, J=7.6 Hz). ^{13}C NMR, δ: 153.9 (C_3), 143.1, 134.7, 134.3, 132.7, 132.2, 129.6, 127.2, 114.7 (Ph), 59.6 (C_5), 41.6 (C_4), 30.6 (C_6), 24.1 (C_7), 11.4 (C_8). MS (EI, 70 eV): 422 ($M^{+\cdot}$, 10), 251 (100). Anal. Calcd for $C_{18}H_{19}N_2BrSe$: C, 51.20; H, 4.54; N, 6.63; found: C, 51.36; H, 4.21; N, 6.62.

2.10.3. 5-Bromomethyl-1-(4-bromophenyl)-3-ethyl-4,5-dihydro-1*H*-pyrazole 23b. Oil, yield <10%, ^{1}H NMR, δ: 7.25 (d, 2H, Ph, J=9.0 Hz), 6.81 (d, 2H, Ph, J=9.0 Hz), 4.36 (m, 1H, H_5), 3.49 (dd, 1H, H_6, J=2.8, 10.3 Hz), 3.03–3.17 (m, 2H, H_4, $H_{6'}$), 2.77 (dd, 1H, $H_{4'}$, J=4.6, 17.6 Hz), 2.33 (q, 2H, H_7, J=7.4 Hz), 1.12 (t, 3H, H_8, J=7.4 Hz). ^{13}C NMR, δ: 154.6 (C_3), 143.7, 132.0, 114.3, 111.0 (Ph), 60.1 (C_5), 40.9 (C_6), 33.0 (C_4), 23.6 (C_7), 11.0 (C_8). MS (EI, 70 eV): 346 ($M^{+\cdot}$, 30), 251 (100).

2.10.4. 5-Bromomethyl-1-(4-bromophenyl)-3-ethyl-1*H*-pyrazole 24b. Oil, yield <10%, ^{1}H NMR, δ: 7.53 (d, 2H, Ph), 7.40 (d, 2H, Ph), 6.29 (s, 1H, H_4), 4.36 (s, 2H, H_6), 2.61 (q, 2H, H_7, J=7.5 Hz), 1.21 (t, 3H, H_8, J=7.5 Hz). MS (EI, 70 eV): 344 ($M^{+\cdot}$, 20), 263 (30), 184 (100).

2.10.5. 1-(4-Bromophenyl)-3-isopropyl-5-[(phenylselanylmethyl]-4,5-dihydro-1*H*-pyrazole 22c. Oil, yield=59%, ^{1}H NMR, δ: 7.60 (m, 2H, Ph), 7.20 (m, 5H, Ph), 6.60 (m, 2H, Ph), 4.15 (m, 1H, H_5), 3.12 (dd, 1H, H_6, J=2.6, 12.5 Hz), 2.98 (dd, 1H, $H_{6'}$, J=10.5, 17.3 Hz), 2.55–2.73 (m, 3H, H_4, H_7), 1.08 (d, 6H, H_8, J=6.9 Hz). ^{13}C NMR, δ: 157.8 (C_3), 143.7, 133.9, 131.7, 129.2, 128.6, 127.7, 114.4, 110.3 (Ph), 59.1 (C_5), 39.1 (C_4), 30.1 (C_6), 29.7 (C_7), 20.3 (C_8). MS (CI, 200 eV): 437 (MH^+, 100). Anal. Calcd for $C_{19}H_{21}N_2BrSe$: C, 52.31; H, 4.85; N, 6.42; found: C, 52.61; H, 5.02; N, 6.31.

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