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α-Phenylselanyl imines: preparation of β-phenylselanyl amines and original synthesis of allylaziridines

Catherine Miniejew, Francis Outurquin* and Xavier Pannecoucke*

Université et INSA de Rouen-IRCOF, UMR 6014 CNRS, 1 rue Tesnière, 76821 Mont Saint Aignan, France

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Abstract—Resorting to suitable methods, a wide variety of α-phenylselanyl imines **2–5** were prepared from α-phenylselanyl aldehydes and α-phenylselanyl ketones **1**. These compounds were reduced to afford β-phenylselanyl amines **6–9**. Our experimental conditions have limited the well known deselenenylation side-reaction occurring with most hydrides. On the other hand, the reaction of α-phenylselanyl imines **2** with organometallics led to the expected addition products only in the case of allylated derivatives. Depending on the temperature, either β-phenylselanyl amines **11** or unexpected allylaziridines **12** were recovered.

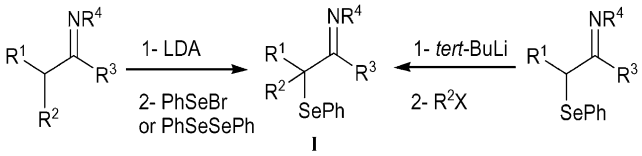
1. Introduction

As illustrated by the large number of organoselenium intermediates involved in natural product synthesis, the selenium methodology offers useful synthetic tools to organic chemists.[1] Our laboratory is especially interested in the applications of α-phenylselanyl carbonyl compounds as valuable bifunctional synthons. During the course of our work, a simple multigram-scale preparation of α-phenylselanyl aldehydes and α-phenylselanyl ketones has been developed.[2a] Obtention and applications of β-phenylselanyl silyl enol ethers have next been reported.[3] α-Phenylselanyl imines are other pivotal targets which give access to interesting nitrogen-containing compounds. However, they seem to have been little studied.[4]

Preliminary studies on the various routes to access α-phenylselanyl imines **I** have been performed, based on the work on α-sulfanyl imines.[5] By analogy with the sulfur series, three methods were assayed to prepare selenenylated imines **I**. Two of them were based on a metallation process (Scheme 1), selenenylation of imines or alkylation of α-phenylselanyl imines. Therefore, using LDA as base, followed by addition of PhSeBr or PhSeSePh, imines deriving from aldehydes or ketones could be transformed into α-phenylselanyl imines **I** but in poor yields varying from 20 (R^4=Bn) to 60% (R^4=*tert*-Bu). The second metallation procedure, based on the alkylation of α-phephenylselanyl imines, revealed to be even more difficult. Indeed, using different bases (best one: *tert*-BuLi), we could not avoid the formation of dialkylated products or diselenenylated imines together with the desired imines **I**. As the selenenylated imines **I** are difficult to purify, these two methods yielded the desired products in rather low yields were abandoned. We then focused our efforts on a third pathway which consists in the synthesis of imines **I** from α-phenylselanyl carbonyl compounds. In this paper, we reported a study on the preparation of selenenylated imines **I** from α-phenylselanyl aldehydes or ketones and their direct transformations via reduction and organometallic additions (Scheme 2), which comes to complete our preliminary observations.[4a]

2. Synthesis of α-phenylselanyl imines

The reactivity of α-phenylselanyl carbonyl compounds is highly variable and depends particularly on the steric hindrance at the α carbon. Thus, in each case, the best and simplest experimental conditions were selected to convert α-phenylselanyl aldehydes or ketones into imines. The condensation of α-phenylselanyl ethanal **1a**[2a] with benzylamine was achieved in ether at −30 °C in the presence of potassium hydroxide. Starting from aldehydes **1b–f**,[2a] better



I

Scheme 1.

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* Corresponding authors. Tel.: +33 2 3552 2402; fax: +33 2 3553 2959; e-mail addresses: francis.outurquin@univ-rouen.fr; xavier.pannecoucke@insa-rouen.fr

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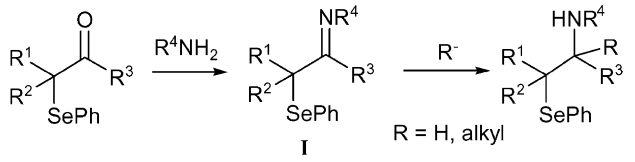
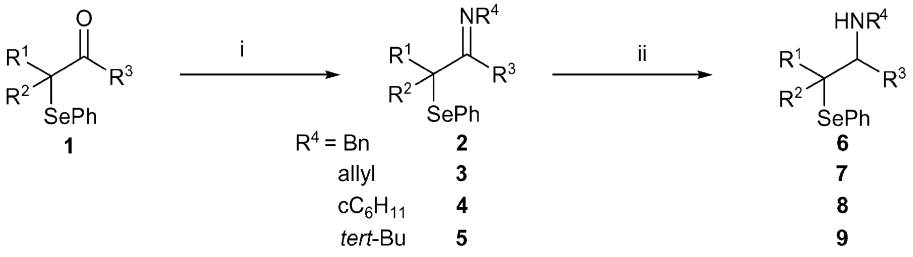


Scheme 2.

results were obtained in dichloromethane at room temperature in the presence of magnesium sulfate. The more hindered aldehydes **1g–i**,[2b] bearing a tertiary α carbon, could also be converted into α-phenylselanyl imines **2g–i** either at reflux of toluene with a Dean–Stark apparatus or in the presence of titanium tetrachloride and 4 equiv of amine.[4] These latter conditions were the sole allowing access to imines **2j–o** from α-phenylselanyl ketones **1j–o**.[2a] The use of benzylamine allows further easy debenzylation to access to primary amines. Nevertheless, our developed methodology can also be transposed to other amines as shown with α-phenylselanyl imines **3c**, **4c** and **5c** resulting from the condensation of α-phenylselanyl butanal **1c** with allylamine, cyclohexylamine or *tert*-butylamine. The stability of the imines increases with the hindrance of the amine or the carbonyl substituents. Thus, α-phenylselanyl imines can be kept at 0 °C under inert atmosphere (a few days for **2g–i**, one day for enolisable imines, while compound **2a** should be prepared just before use), but no purification (distillation, chromatography) could be achieved due to decomposition. However, the crude imines are pure enough for further transformations. The α-phenylselanyl imines **2h–i** are solids which, after rinsing with hexane, gave satisfactory elemental analysis. Only one set of signal in ^{1}H NMR was observed for imines **2a–i** issued from aldehydes. According to literature data,[6] we assumed that the α-phenylselanyl aldimines adopt the *anti* configuration. No tautomery was observed. Nevertheless, the enaminic form of the *N*-*tert*-butyl imine **5c** could be obtained after a prolonged heating in dichloromethane.

3. Reduction of α-phenylselanyl imines

The most important problem known to occur during the reduction of imines **2–5**, is the substrate's deselenenylation leading to the formation of deselenenylated amines. This side-reaction results from a selenophilic attack of the hydride as observed during the reduction of α-phenylselanyl ketones.[7] Indeed, treatment of α-phenylselanyl imines with $LiAlH_4$ led to a complete deselenenylation, even at low temperatures. Among less reactive reducing agents ($NaBH_4$, $Zn(BH_4)_2$, BH_3–THF, BH_3–SMe_2), only $NaBH_4$ afforded the desired β-phenylselanyl amines, but together with the deselenenylated amines (15–20%) (Scheme 3, Table 1).

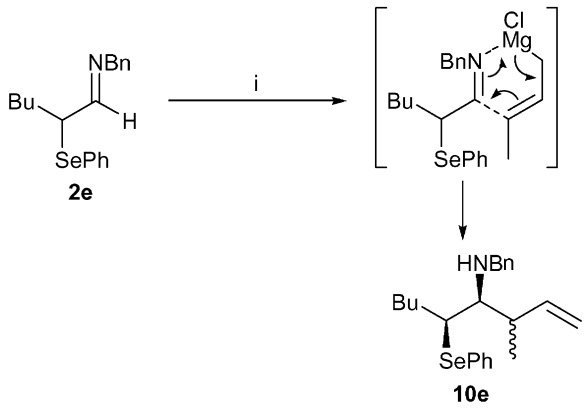


Scheme 3. (i) Method A: R^4NH_2 (1 equiv), KOH, Et_2O, −30 °C, 2 h; Method B: R^4NH_2 (1 equiv), $MgSO_4$, CH_2Cl_2, 20 °C, 4 h; Method C: R^4NH_2 (1 equiv), toluene, reflux, 12 h; Method D, R^4NH_2 (4 equiv), $TiCl_4$, Et_2O, 20 °C, 4 h. (ii) $NaBH_3CN$ (0.5 equiv), AcOH, EtOH, −78 °C, 1 h.

Table 1. Synthesis of β-phenylselanyl amines **6–9** via imines **2–5** (Scheme 3)

Substrates	R^1	R^2	R^3	R^4	Method for imine preparation	Products	Yield[a] (%) (*syn*/*anti*)
1a	H	H	H	Bn	A	**6a**	54
1b	Me	H	H	Bn	B	**6b**	41
1c	Et	H	H	Bn	B	**6c**	72
				Allyl	B	**7c**	64
				cC_6H_{11}	B	**8c**	57
				tert-Bu	B[b]	**9c**	56
1d	*i*Pr	H	H	Bn	B	**6d**	69
1e	Bu	H	H	Bn	B	**6e**	65
1f	Bn	H	H	Bn	B	**6f**	67
1g	Me	Me	H	Bn	C or D	**6g**	64
1h	Ph	Me	H	Bn	C or D	**6h**	59
1i	$-(CH_2)_5-$		H	Bn	C[c] or D	**6i**	51
1j	H	H	Me	Bn	D	**6j**	50
1k	H	H	*tert*-Bu	Bn	D	**6k**	71
1l	H	H	Ph	Bn	D	**6l**	68
1m	Me	H	Et	Bn	D	**6m**	57 (80/20)
1n	Me	H	Ph	Bn	D	**6n**	53 (100/0)
1o	H	$-(CH_2)_4-$		Bn	D	**6o**	57 (80/20)

[a] Estimated from **1**.
[b] 12 h at reflux of CH_2Cl_2.
[c] 48 h at reflux of toluene.



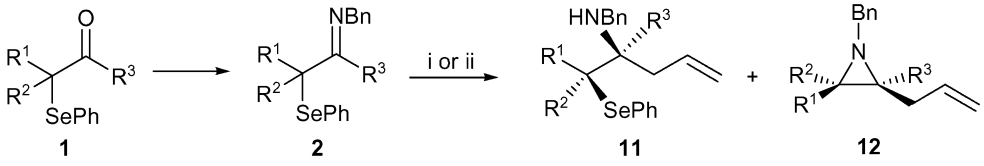
Scheme 4. (i) CrotylMgCl (1.1 equiv), THF, −40→0 °C, 2 h.

The best results were obtained with $NaBH_3CN$ at −78 °C in the presence of acetic acid. These experimental conditions avoided the formation of the deselenenylated amines and afforded the β-phenylselanyl amines **6**–**9** in 41–72% yield. It should be underlined that ketone **1m** led to the β-phenylselanyl amine **6m** in 60% de while substrate **1n** afforded the sole *syn* diastereomer **6n**. The stereochemistry of products **6m**,**n** was assigned after analysis of the corresponding aziridines obtained after an internal S_N2 displacement of the selanyl group.[4a] Such *syn* selectivity has already been observed during the reduction of α-phenylselanyl ketones.[8] It can be rationalized by a Felkin–Ahn-type model with a stereoelectronic controle by the selanyl group.

4. Organometallic additions to α-phenylselanyl imines

In order to access to various other β-phenylselanyl amines, we next studied organometallic additions on imines **2**. After numerous assays with lithium derivatives (MeLi, BuLi), zinc derivatives (Et_2Zn, BuZnCl), a copper derivative (MeCu) and arylated or alkylated grignard reagents (BnMgBr, VinylMgBr, PropylMgBr), only allylated magnesium derivatives led to the expected addition products. The use of crotyl magnesium showed that, in these cases, the reaction proceed through a six-membered cyclic transition state (Scheme 4). The addition of allylmagnesium chloride to imines **2** was first achieved in mild experimental conditions to avoid the substrate's deselenenylation (Scheme 5, Table 2).

At −40 °C, the reaction proceeded cleanly and led to β-phenylselanyl amines **11** in 47–78% yield. However with **2h**, the desired amine **11h** was obtained as a mixture with the unexpected allylaziridine **12h**. Starting from **1m**, the aza-heterocycle **12m** was even the sole product of the reaction, along with diphenyldiselenide, coming from the hydrolysis of PhSeMgBr. Such in situ cyclization has already been observed during reduction or organometallic additions to α-chloro imines.[9] After considering different reaction parameters, we realized that we could favor either one or the other product by controlling the temperature. Indeed, when the allylmagnesium additions were carried out at reflux of THF, the allylaziridines **12** became the sole or the major products of the reaction. Probably because of the substrate's hindrance, no addition product was observed with the pinacolone derivative **1k**. No allylaziridine has been obtained from **1j** even at higher temperature.

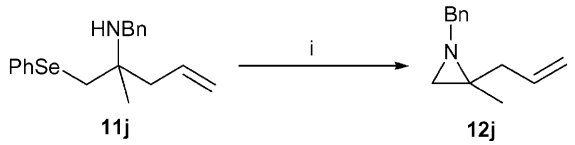


Scheme 5. (i) allylMgCl (1.1 equiv), THF, −40→0 °C, 2 h. (ii) allylMgCl (1.1 equiv), THF, reflux, 2 h.

Table 2. Synthesis of homoallylic β-phenylselanyl amines **11** and allylaziridines **12** via imines **2** (Scheme 5)

Substrates	R^1	R^2	R^3	*T* (°C)	**11** Yield[a] (%) (*syn*/*anti*)	**12** Yield[a] (%) (*cis*/*trans*)
1d	*i*Pr	H	H	−40→0	78 (55/45)	—
				65	—	73 (55/45)
1e	Bu	H	H	−40→0	69 (100/0)	—
				65	—	53 (100/0)
1g	Me	Me	H	−40→0	74	—
				65	11	57
1h	Me	Ph	H	−40→0	47 (100/0)	20 (0/100)
				65	18 (100/0)	41 (0/100)
1j	H	H	Me	−40→0	58	—
				65	52	—
1k	H	H	*t*Bu	−40→0	—[b]	
				65	—[b]	
1l	H	H	Ph	−40→0	65	—
				65	—	61
1m	Me	H	Et	−40→0	—	61 (100/0)
				65	—	57 (100/0)
1n	Me	H	Ph	−40→0	64 (100/0)	—
				65	—	59 (0/100)

[a] Estimated from **1**.
[b] Starting material recovered.



Scheme 6. (i) NBS (1.1 equiv), CH_3CN, 20 °C, 5 min.

Nevertheless, the allylaziridine **12j** could be synthesized after activation of the selanyl group of **11j** with *N*-bromosuccinimide (Scheme 6).[10] When the reaction product exhibits two stereogenic centers, only one diastereomer was obtained either for the β-phenylselanyl amines **11** or for the allylaziridines **12** except for compounds **11d** and **12d** derived from isovaleraldehyde. NOE experiments on allylaziridines **12h**, **12n** and **12m** allowed to assign the *cis* stereochemistry to allylaziridines **12**. We then deduced a *syn* relationship between the amino and the selanyl group of the corresponding β-phenylselanyl amines **11**.

In summary, we report convenient methods to convert α-phenylselanyl aldehydes and ketones into the corresponding α-phenylselanyl imines **2–5**. The reduction of these latter with $NaBH_3CN$ led to β-phenylselanyl amines **6–9** without deselenenylation of the substrates. On the other hand, depending on the temperature, addition of allyl magnesium chloride provided either β-phenylselanyl amines **11** or allylaziridines **12**. To our knowledge, this constitutes the first synthesis of allylaziridines.

5. Experimental

THF was distilled over sodium/benzophenone and dichloromethane over P_2O_5. Ether was dried over sodium.

^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a Brucker DPX 300 instrument and carried out in $CDCl_3$. ^{77}Se NMR spectra were recorded on a Bruker DPX 400 spectrometer operating at 76.29 MHz for ^{77}Se, using as pulsed length 19 μs (90° pulse = 19 μs) and an optimized relaxation delay of 2 s. An average of 1500 scans for ^{77}Se NMR was necessary to have reliable information. Chemical shifts (δ) are expressed in ppm relative to TMS for ^1H 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 analysis were obtained on a Carlo-Erba 1106 analysor and Mass Spectra on a HP5890 (electronic impact 70 eV) using GC–MS coupling with a Jeol AX 500.

5.1. Preparation of α-phenylselanyl imines 2–5

Procedure A: A solution of α-phenylselanyl ethanal **1a** (995 mg, 5 mmol) in ether (5 ml) was added dropwise at −30 °C to the amine (5.5 mmol) in the same solvent (30 ml). The mixture was stirred for 2 h at −30 °C before adding KOH (1 g) and then stirred for 15 h at −5 °C. The solution was filtered and concentrated. This α-phenylselanyl aldimine should be used immediately after its preparation.

Procedure B: Magnesium sulfate (3 g) was added to a solution of α-phenylselanyl aldehydes **1b–f** (5 mmol) in dichloromethane (50 ml). The mixture was stirred for 10 min at −5 °C and the amine (5 mmol) was added dropwise. The whole was then stirred for 3 h at room temperature. The magnesium sulfate was filtered, rinsed with dichloromethane and the organic phase was concentrated. These α-phenylselanyl aldimines could be stored one day at 0 °C under argon.

Procedure C: A solution of α-phenylselanyl aldehydes **1g–i** (5 mmol) and amine (5.25 mmol) in toluene (50 ml) was heated for 12 h under reflux with elimination of water (Dean–Stark). For **2i**, the heating should be continued for 48 h. The solvent was eliminated under vacuo. The imines **2h** and **2i** crystallized slowly and were rinsed with hexane. These α-phenylselanyl aldimines could be stored a few days at 0 °C under argon.

Procedure D: Amine (20 mmol) was added to the α-phenylselanyl carbonyl compounds **1g–n** (5 mmol) in ether (50 ml) at 0 °C, under argon. A solution of titanium tetrachloride (708 mg, 3.75 mmol) in heptane (2 ml) was then slowly introduced. The mixture was stirred for 30 min at 0 °C and then for 3 h at room temperature. The titanium salts were filtered and rinsed with ether.

All the α-phenylselanyl imines **2–5** were isolated but not purified because of decomposition. That is why for most of them we just reported the ^1H NMR spectra. For **2a–g** IR $\nu_{C=N} = 1640–1650\ cm^{-1}$.

5.1.1. Phenyl-*N*-(2-(phenylselanyl)ethylidene)methanamine 2a. ^1H NMR δ: 3.68 (d, 2H, J = 5.7 Hz, H-2), 4.54 (s, 2H, CH_2Ph), 7.05–7.35 (m, 8H, Ph), 7.50–7.55 (m, 2H, Ph), 7.78 (t, 1H, J = 5.7 Hz, H-1).

5.1.2. Phenyl-*N*-(2-(phenylselanyl)propylidene)methanamine 2b. ^1H NMR δ: 1.55 (d, 3H, J = 7.0 Hz, H-3), 3.71–4.20 (m, 1H, H-2), 4.44 (d, 1H, J = 14.0 Hz, CH_2Ph), 4.54 (d, 1H, J = 14.0 Hz, CH_2Ph), 7.0–7.10 (m, 2H, Ph), 7.15–7.35 (m, 6H, Ph), 7.45–7.60 (m, 2H, Ph), 7.71 (d, 1H, J = 6.1 Hz, H-1).

5.1.3. Phenyl-*N*-(2-(phenylselanyl)butylidene)methanamine 2c. ^1H NMR δ: 1.06 (t, 3H, J = 7.3 Hz, H-4), 1.63–2.10 (m, 2H, H-3), 3.84 (dt, 1H, J = 7.1, 7.1 Hz, H-2), 4.42 (d, 1H, J = 14.0 Hz, CH_2Ph), 4.55 (d, 1H, J = 14.0 Hz, CH_2Ph), 7.00–7.05 (m, 2H, Ph), 7.10–7.30 (m, 6H, Ph), 7.45–7.52 (m, 2H, Ph), 7.64 (d, 1H, J = 7.1 Hz, H-1).

5.1.4. Phenyl-*N*-(3-methyl-2-(phenylselanyl)butylidene) methanamine 2d.[4a] ^1H NMR δ: 1.11 (d, 3H, J = 6.7 Hz, H-4), 1.18 (d, 3H, J = 6.7 Hz, H-4), 1.96–2.39 (m, 1H, H-3), 3.82 (dd, 1H, J = 7.8, 8.2 Hz, H-2), 4.40 (d, 1H, J = 13.9 Hz, CH_2Ph), 4.57 (d, 1H, J = 13.9 Hz, CH_2Ph), 7.00–7.06 (m, 2H, Ph), 7.15–7.37 (m, 6H, Ph), 7.48–7.53 (m, 2H, Ph), 7.70 (d, 1H, J = 8.2 Hz, H-1).

5.1.5. Phenyl-*N*-(2-(phenylselanyl)hexylidene)methanamine 2e. ^1H NMR δ: 0.82 (d, 3H, J = 7.2 Hz, H-6), 1.15–1.48 (m, 4H, H-5, H-4), 1.67–1.82 (m, 2H, H-3), 3.80–3.85 (m, 1H, H-2), 4.34 (d, 1H, J = 14.1 Hz, CH_2Ph), 4.47 (d, 1H, J = 14.1 Hz, CH_2Ph), 6.93–7.42 (m, 10H, Ph), 7.54 (d, 1H, J = 7.7 Hz, H-1).

5.1.6. Phenyl-*N*-(3-phenyl-2-(phenylselanyl)propylidene) methanamine 2f. ^{1}H NMR δ: 3.22–3.30 (m, 2H, H-3), 4.24–4.35 (m, 1H, H-2), 4.50 (s, 2H, CH_2Ph), 6.95–7.05 (m, 2H, Ph), 7.20–7.40 (m, 11H, Ph), 7.55–7.60 (m, 2H, Ph), 7.75 (d, 1H, J=6.8 Hz, H-1).

5.1.7. Phenyl-*N*-(2-methyl-2-(phenylselanyl)propylidene) methanamine 2g.[4a] ^{1}H NMR δ: 1.47 (s, 6H, H-3), 4.46 (s, 2H, CH_2Ph), 7.04–7.38 (m, 10H, Ph), 7.69 (s, 1H, H-1).

5.1.8. Phenyl-*N*-(2-phenyl-2-(phenylselanyl)propylidene) methanamine 2h. Mp=35 °C. IR $\nu_{C=N}$=1630 cm^{-1}. ^{1}H NMR δ: 1.87 (s, 3H, H-3), 4.56 (d, 2H, J=14.1 Hz, CH_2Ph), 4.66 (d, 2H, J=14.1 Hz, CH_2Ph), 7.07–7.42 (m, 15H, Ph), 8.16 (s, 1H, H-1). ^{13}C NMR δ: 24.9 (C-3), 55.1 (C-2), 63.8 (*C*H_2Ph), 126.8, 127.1, 127.4, 127.8, 128.4, 128.6, 128.9, 129.1, 138.0, 139.1, 142.2 (Ph), 166.3 (C-1). Anal. Calcd for $C_{22}H_{21}$NSe: C, 69.83; H, 5.59; N, 3.70. Found: C, 69.71; H, 5.39; N, 3.61.

5.1.9. Phenyl-*N*-((1-(phenylselanyl)cyclohexyl)methylidene) methanamine 2i. Mp=43 °C. IR $\nu_{C=N}$= 1625 cm^{-1}. ^{1}H NMR δ: 1.25–2.05 (m, 10H, Cy), 4.53 (s, 2H, CH_2Ph), 7.10–7.50 (m, 10H, Ph), 7.66 (s, 1H, H-1). ^{13}C NMR δ: 23.4, 25.7, 29.4, 34.0 (Cy), 54.8 (*C*-Se), 63.9 (*C*H_2Ph), 126.4, 126.6, 127.7, 128.2, 128.3, 128.4, 128.5, 137.9 (Ph), 166.7 (C-1). Anal. Calcd for $C_{20}H_{23}$NSe: C, 67.40; H, 6.51; N, 3.93. Found: C, 67.34; H, 6.57; N, 3.85.

5.1.10. Phenyl-*N*-(1-(phenylselanyl)propan-2-ylidene)-methan amine 2j.[4a] ^{1}H NMR δ: 1.98 (s, 3H, H-3), 3.69 (s, 2H, H-1), 4.33 (s, 2H, CH_2Ph), 7.04–7.52 (m, 10H, Ph).

5.1.11. Phenyl-*N*-(3,3-dimethyl-1-(phenylselanyl)butan-2-ylidene)methanamine 2k.[4a] *Z*/*E*: 85/15 (non assigned). Major configuration: ^{1}H NMR δ: 1.16 (s, 9H, H-4), 3.64 (s, 2H, H-1), 4.52 (s, 2H, CH_2Ph), 7.14–7.47 (m, 10H, Ph). Minor configuration: ^{1}H NMR δ: 1.17 (s, 9H, H-4), 3.80 (s, 2H, H-1), 4.76 (s, 2H, CH_2Ph), 7.14–7.47 (m, 10H, Ph).

5.1.12. Phenyl-*N*-(1-phenyl-2-(phenylselanyl)ethylidene) methanamine 2l. *Z*/*E*: 60/40 (non assigned). Major configuration: ^{1}H NMR δ: 4.01 (s, 2H, H-2), 4.33 (s, 2H, CH_2Ph), 6.99–7.50 (m, 15H, Ph). Minor configuration: ^{1}H NMR δ: 4.03 (s, 2H, H-2), 4.48 (s, 2H, CH_2Ph), 7.08–7.78 (m, 15H, Ph).

5.1.13. Phenyl-*N*-(2-(phenylselanyl)pentan-3-ylidene) methanamine 2m.[4a] ^{1}H NMR δ: 1.04 (t, 3H, J=7.7 Hz, H-5), 1.56 (d, 3H, J=7.1 Hz, H-1), 2.36–2.50 (m, 2H, H-4), 4.01 (q, 1H, J=7.1 Hz, H-2), 4.44 (s, 2H, CH_2Ph), 7.06–7.47 (m, 10H, Ph).

5.1.14. Phenyl-*N*-(1-phenyl-2-(phenylselanyl)propylidene) methanamine 2n.[4a] ^{1}H NMR δ: 1.54 (d, 3H, J= 7.2 Hz, H-3), 4.22–4.38 (m, 1H, H-2), 4.29 (s, 2H, CH_2Ph), 7.11–7.45 (m, 15H, Ph).

5.1.15. Phenyl-*N*-(2-(phenylselanyl)cyclohexylidene) methanamine 2o.[4a]

^{1}H NMR δ: 1.40–2.40 (m, 8H, Cy), 4.07–4.20 (m, 1H, H-2), 4.43 (s, 2H, CH_2Ph), 7.04–7.24 (m, 8H, Ph) 7.45–7.52 (m, 2H, Ph). ^{13}C NMR δ: 23.2, 26.9, 34.7, 52.2 (C-2), 54.1 (*C*H_2Ph), 126.5, 127.0, 128.4, 129.1, 129.6, 129.8, 134.8.

5.1.16. *N*-(2-(Phenylselanyl)butylidene)allylamine 3c. ^{1}H NMR δ: 1.03 (t, 3H, J=7.3 Hz, H-4), 1.60–2.03 (m, 2H, H-3), 3.76 (dt, 1H, J=7.2, 7.2 Hz, H-2), 3.85–3.95 (m, 2H, CH_2CH=CH$_2$), 4.90–5.05 (m, 2H, CH$_2$CH=CH_2), 5.67–5.75 (m, 1H, CH$_2$C*H*=CH$_2$), 7.20–7.30 (m, 2H, Ph), 7.45–7.65 (m, 4H, Ph, H-1).

5.1.17. *N*-(2-(Phenylselanyl)butylidene)cyclohexylamine 4c. ^{1}H NMR δ: 1.04 (t, 3H, J=7.4 Hz, H-4), 1.05–1.87 (m, 12H, Cy, H-3), 2.79–2.87 (m, 1H, Cy), 3.78 (dt, 1H, J=7.4, 7.4 Hz, H-2), 7.15–7.60 (m, 6H, Ph, H-1).

5.1.18. *N*-(2-(Phenylselanyl)butylidene)*tert*-butylamine 5c. ^{1}H NMR δ: 1.04 (s, 9H, C(CH_3)$_3$), 1.08 (t, 3H, J= 7.4 Hz, H-4), 1.54–2.02 (m, 2H, H-3), 3.85 (dt, 1H, J=7.4, 7.4 Hz, H-2), 7.10–7.55 (m, 6H, Ph, H-1).

5.2. Reduction of α-phenylselanyl imines 2–5

To the α-phenylselanyl imines **2**–**5** (5 mmol) in ethanol (60 ml) at −78 °C, under argon, were added successivelly sodium cyanoborohydride (162 mg, 2.5 mmol) and acetic acid (300 mg, 5 mmol). The reaction mixture was stirred for 1 h at −78 °C and quenched with water (70 ml). After dichloromethane (100 ml) addition, the aqueous phase was separated and washed with dichloromethane (2×80 ml). The combined organic phases were dried over $MgSO_4$ and concentrated. The crude product was purified by silica gel chromatography (cyclohexane/Et_2O: 90/10).

5.2.1. *N*-Benzyl-2-(phenylselanyl)ethan-1-amine 6a. Yield: 54%. ^{1}H NMR δ: 1.80 (sl, 1H, N*H*), 2.88–2.95 (m, 2H, H-2), 3.05–3.12 (m, 2H, H-1), 3.80 (s, 2H, CH_2Ph), 7.22–7.36 (m, 8H, Ph), 7.47–7.55 (m, 2H, Ph). ^{13}C NMR δ: 28.5 (C-2), 48.2 (C-1), 53.3 (*C*H_2Ph), 127.0, 127.7, 128.0, 128.4, 129.0, 131.4, 132.9, 140.1 (Ph). Anal. Calcd for $C_{15}H_{17}$NSe: C, 62.06; H, 5.90; N, 4.82. Found: C, 62.33; H, 6.21; N, 4.59.

5.2.2. *N*-Benzyl-2-(phenylselanyl)propan-1-amine 6b. Yield: 41%. $Bp_{0.05}$: 121–122 °C. ^{1}H NMR δ: 1.52 (d, 3H, J=6.7 Hz, H-3), 1.95 (sl, 1H, N*H*), 2.71–2.97 (m, 2H, H-1), 3.42–3.59 (m, 1H, H-2), 3.90 (s, 2H, CH_2Ph), 7.25–7.45(m, 8H, Ph), 7.60–7.65(m, 2H, Ph). ^{13}C NMR δ: 20.3 (C-3), 40.0 (C-2), 53.3, 54.6 (C-1, *C*H_2Ph), 126.7, 126.9, 127.4, 127.9, 128.2, 128.7, 135.2, 140.1 (Ph). Anal. Calcd for $C_{16}H_{19}$NSe: C, 63.15; H, 6.29; N, 4.60. Found: C, 63.45; H, 6.35; N, 4.34.

5.2.3. *N*-Benzyl-2-(phenylselanyl)butan-1-amine 6c. Yield: 72%. ^{1}H NMR δ: 1.03 (t, 3H, J=7.3 Hz, H-4), 1.60–1.74 (m, 2H, H-3), 1.80 (sl, 1H, N*H*), 2.65–2.82 (m, 2H, H-1), 3.17–3.25 (m, 1H, H-2), 3.75 (d, 1H, J=13.6 Hz, CH$_2$Ph), 3.82 (d, 1H, J=13.6 Hz, CH_2Ph), 7.17–7.32 (m, 8H, Ph), 7.47–7.51 (m, 2H, Ph). ^{13}C NMR δ: 12.6 (C-4), 27.0 (C-3), 49.4 (C-2), 52.8 (C-1), 53.8 (*C*H_2Ph), 126.9, 127.3, 127.7, 128.2, 128.5, 129.0, 135.4, 140.4 (Ph). Anal. Calcd for $C_{17}H_{21}$NSe: C, 64.14; H, 6.65; N, 4.40. Found: C, 64.35; H, 6.72; N, 4.29.

5.2.4. *N*-Benzyl-3-methyl-2-(phenylselanyl)butan-1-amine 6d.[4a] Yield: 69%. ^{1}H NMR δ: 1.01 (d, 3H, J= 6.7 Hz, H-4), 1.05 (d, 3H, J=6.7 Hz, H-4), 2.00–2.06 (m, 1H, H-3), 2.20 (sl, 1H, N*H*), 2.81 (dd, 1H, J=8.4, 12.5 Hz, H-1), 2.91 (dd, 1H, J=5.1, 12.5 Hz, H-1), 3.24–3.29 (m, 1H, H-2), 3.70 (d, 1H, J=13.4 Hz, CH_2Ph), 3.75 (d, 1H, J= 13.4 Hz, CH_2Ph), 7.17–7.33 (m, 8H, Ph), 7.52–7.59 (m, 2H, Ph). ^{13}C NMR δ: 20.1 (C-4), 21.0 (C-4), 31.2 (C-3), 51.7 (C-1), 53.6 (*C*H$_2$Ph), 56.7 (C-2), 126.8, 127.1, 127.4, 128.0, 128.3, 128.9, 134.3, 140.2 (Ph). Anal. Calcd for $C_{18}H_{23}NSe$: C, 65.05; H, 6.98; N, 4.21. Found: C, 64.86; H, 6.71, N, 4.49.

5.2.5. *N*-Benzyl-2-(phenylselanyl)hexan-1-amine 6e. Yield: 65%. ^{1}H NMR δ: 0.87 (t, 3H, J=7.2 Hz, H-6), 1.22–1.55 (m, 4H, H5, H-4), 1.56–1.60 (m, 2H, H-3), 1.80 (sl, 1H, N*H*), 2.67 (dd, 1H, J=7.9, 12.3 Hz, H-1), 2.77 (dd, 1H, J=4.8, 12.3 Hz, H-1), 3.21–3.31(m, 1H, H-2), 3.74 (d, 1H, J=13.4 Hz, CH_2Ph), 3.81 (d, 1H, J=13.4 Hz, CH_2Ph), 7.21–7.34 (m, 8H, Ph), 7.47–7.51 (m, éH, Ph). ^{13}C NMR δ: 14.1 (C-6), 22.6 (C-5), 30.1 (C-4), 33.6 (C-3), 47.5 (C-2), 53.0 (C-1), 53.7 (*C*H$_2$Ph), 127.0, 127.7, 128.2, 128.3, 128.5, 129.0, 135.4, 140.4 (Ph). Anal. Calcd for $C_{19}H_{25}NSe$: C, 65.88; H, 7.27; N, 4.04. Found: C, 66.14; H, 6.95; N, 4.27.

5.2.6. *N*-Benzyl-3-phenyl-2-(phenylselanyl)propan-1-amine 6f. Yield: 67%. ^{1}H NMR δ: 2.67–2.87 (m, 2H, H-1), 2.94–3.14 (m, 2H, H-3), 3.50–3.65 (m, 1H, H-2), 3.71 (d, 1H, J=13.5 Hz, CH_2Ph), 3.81 (d, 1H, J=13.5 Hz, CH_2Ph), 7.15–7.40 (m, 13H, Ph), 7.47–7.53 (m, 2H, Ph). ^{13}C NMR δ: 40.3 (C-3), 47.5 (C-2), 51.7, 53.5 (C-1, *C*H$_2$Ph), 126.9, 127.7, 128.2, 128.4, 129.0, 129.1, 135.3, 139.6 (Ph). Anal. Calcd for $C_{22}H_{23}NSe$: C, 69.46; H, 6.09; N, 3.68. Found: C, 69.30; H, 6.12; N, 3.55.

5.2.7. *N*-Benzyl-2-methyl-2-(phenylselanyl)propan-1-amine 6g.[4a] Yield: 64%. ^{1}H NMR δ: 1.40 (s, 6H, H-3), 1.84 (sl, 1H, N*H*), 2.50 (s, 2H, H-1), 3.86 (s, 2H, CH_2Ph), 7.25–7.40 (m, 8H, Ph), 7.47–7.53 (m, 2H, Ph). ^{13}C NMR δ: 28.4 (C-3), 48.4 (C-2), 54.0 (*C*H$_2$Ph), 59.2 (C-1), 126.8, 127.0, 127.6, 128.1, 128.3, 128.9, 134.2, 141.1 (Ph). Anal. Calcd for $C_{17}H_{21}NSe$: C, 64.14; H, 6.65; N, 4.40. Found: C, 64.45; H, 6.79; N, 4.19.

5.2.8. *N*-Benzyl-2-phenyl-2-(phenylselanyl)propan-1-amine 6h. Yield: 59%. ^{77}Se NMR δ: 564.8. ^{1}H NMR δ: 1.50 (sl, 1H, N*H*), 1.84 (s, 3H, H-3), 3.00 (d, 1H, J= 12.0 Hz, H-1), 3.25 (d, 1H, J=12.0 Hz, H-1), 3.79 (s, 2H, CH_2Ph), 7.10–7.35 (m, 15H, Ph). ^{13}C NMR δ: 26.0 (C-3), 52.7 (C-2), 54.2 (*C*H$_2$Ph), 58.7 (C-1), 126.8, 127.0, 127.4, 127.8, 128.2, 128.3, 128.5, 128.6, 128.7, 137.9, 140.5, 144.1 (Ph). Anal. Calcd for $C_{22}H_{23}NSe$: C, 69.46; H, 6.09; N, 3.68. Found: C, 69.26; H, 5.86; N, 3.98.

5.2.9. Phenyl-*N*-((1-(phenylselanyl)cyclohexyl)methyl) methanamine 6i. Yield: 51%. ^{1}H NMR δ: 0.90–1.90 (m, 11H, Cy, N*H*), 2.47–2.52 (m, 2H, H-1), 3.81 (s, 2H, CH_2Ph), 7.20–7.45 (m, 8H, Ph), 7.57–7.64 (m, 2H, Ph). ^{13}C NMR δ: 26.1, 31.4, 35.5, 53.2, 54.0 56.1 (C-1, *C*H$_2$Ph), 126.7, 128.0, 128.2, 128.5, 129.0, 131.3, 137.9, 140.4 (Ph). Anal. Calcd for $C_{20}H_{25}NSe$: C, 67.02; H, 7.03; N, 3.91. Found: C, 66.73; H, 6.86; N, 3.78.

5.2.10. *N*-Benzyl-1-(phenylselanyl)propan-2-amine 6j.[4a] Yield: 50%. ^{1}H NMR δ: 1.18 (d, 3H, J=6.1 Hz, CH_3), 1.80 (sl, 1H, N*H*), 2.85–3.09 (m, 3H, H-1, H-2), 3.70 (d, 1H, J= 13.1 Hz, CH_2Ph), 3.80 (d, 1H, J=13.1 Hz, CH_2Ph), 7.20–7.35 (m, 8H, Ph), 7.45–7.49(m, 2H, Ph). ^{13}C NMR δ: 20.8 (C-3), 36.3 (C-1), 51.3 (*C*H$_2$Ph), 51.7 (C-2), 127.0, 127.3, 128.2, 128.5, 129.2, 130.4, 133.0, 140.4 (Ph). Anal. Calcd for $C_{16}H_{19}NSe$: C, 63.15; H, 6.30; N, 4.60. Found: C, 63.47; H, 6.39; N, 4.27.

5.2.11. *N*-Benzyl-3,3-dimethyl-1-(phenylselanyl)butan-2-amine 6k.[4a] Yield: 71%. ^{1}H NMR δ: 1.06 (s, 9H, C(CH_3)$_3$), 1.37 (sl, 1H, N*H*), 2.59 (dd, 1H, J=9.0, 3.4 Hz, H-1), 3.00 (dd, 1H, J=12.1, 9.0 Hz, H-2), 3.39 (dd, 1H, J=12.1, 3.4 Hz, H-2), 3.85 (d, J=12.4 Hz, CH_2Ph), 4.06 (d, J= 12.4 Hz, CH_2Ph), 7.28–7.45 (m, 8H, Ph), 7.58–7.62 (m, 2H, Ph). ^{13}C NMR δ: 27.1 (C-4), 32.3 (C-1), 36.4 (C-3), 55.4 (*C*H$_2$Ph), 66.6 (C-2), 126.8, 127.3, 128.0, 128.4, 129.1, 130.0, 133.6, 141.1 (Ph). Anal. Calcd for $C_{19}H_{25}NSe$: C, 65.88; H, 7.28; N, 4.04. Found: C, 66.10; H, 7.31; N, 4.29.

5.2.12. *N*-Benzyl-1-phenyl-2-(phenylselanyl)ethan-1-amine 6l. Yield: 68%. ^{77}Se NMR δ: 268.5. ^{1}H NMR δ: 2.25(sl, 1H, N*H*), 3.06 (dd, 1H, J=9.7, 12.3 Hz, H-2), 3.22 (dd, 1H, J=4.3, 12.3 Hz, H-2), 3.49 (d, 1H, J=13.4 Hz, CH_2Ph), 3.70 (d, 1H, J=13.4 Hz, CH_2Ph), 3.75 (dd, 1H, J=4.3, 9.7 Hz, H-1), 7.20–7.32 (m, 13H, Ph), 7.40–7.44 (m, 2H, Ph). ^{13}C NMR δ: 37.0 (C-2), 51.6 (*C*H$_2$Ph), 61.1 (C-1), 127.0, 127.2, 127.3, 127.7, 128.3, 128.5, 128.8, 129.2, 129.8, 133.2, 140.4, 143.0 (Ph). Anal. Calcd for $C_{21}H_{21}NSe$: C, 68.84; H, 5.78; N, 3.82. Found: C, 68.86; H, 5.96; N, 4.19.

5.2.13. *N*-Benzyl-2-(phenylselanyl)pentan-3-amine 6m.[4a] Yield: 57%, *syn*/*anti*: 80/20. Diastereomer *syn*; ^{1}H NMR δ: 0.89 (t, 3H, J=7.4 Hz, H-5), 1.41 (d, 3H, J=7.1 Hz, H-1), 1.42–1.51 (m, 1H, H-4), 1.66–1.77 (m, 1H, H-4), 2.00 (sl, 1H, N*H*), 2.57 (dt, 1H, J=4.9, 6.6 Hz, H-3), 3.46 (qd, 1H, J=4.9, 7.1 Hz, H-2), 3.74 (d, 1H, J=13.3 Hz, CH_2Ph), 3.79 (d, 1H, J=13.3 Hz, CH_2Ph), 7.15–7.32 (m, 8H, Ph), 7.50–7.54 (m, 2H, Ph). ^{13}C NMR δ: 10.4 (C-5), 18.8 (C-1), 23.9 (C-4), 44.7 (C-2), 51.9 (*C*H$_2$Ph), 62.7 (C-3), 127.0, 127.4 128.3, 128.5, 129.0, 129.4, 134.9, 140.2 (Ph). Diastereomer *anti*; ^{1}H NMR δ: 0.88 (t, 3H, J=7.4 Hz, H-5), 1.39 (d, 3H, J=7.1 Hz, H-1), 1.50–1.60 (m, 1H, H-4), 1.66–1.76 (m, 1H, H-4), 2.00 (sl, 1H, N*H*), 2.52–2.59 (m, 1H, H-3), 3.60–3.65 (m, 1H, H-2), 3.88 (m, 2H, CH_2Ph), 7.15–7.32 (m, 8H, Ph), 7.48–7.52 (m, 2H, Ph). ^{13}C NMR δ: 11.2 (C-5), 17.6 (C-1), 24.7 (C-4), 45.3 (C-2), 51.9 (*C*H$_2$Ph), 62.7 (C-3), 127.8, 128.8, 129.0, 129.9, 130.2, 134.9, 135.3, 139.8 (Ph). Anal. Calcd for $C_{18}H_{23}NSe$: C, 65.05; H, 6.98; N, 4.21. Found: C, 65.36; H, 6.81; N, 4.59.

5.2.14. *syn*-*N*-Benzyl-1-phenyl-2-(phenylselanyl)propan-1-amine 6n.[4a] Yield: 53%. ^{1}H NMR δ: 1.30 (d, 3H, J= 7.1 Hz, H-3), 2.20 (sl, 1H, N*H*), 3.47 (d, 1H, J=13.3 Hz, CH_2Ph), 3.61 (qd, 1H, J=3.5, 7.1 Hz, H-2), 3.76 (d, 1H, J= 13.3 Hz, CH_2Ph), 3.83 (d, 1H, J=3.4 Hz, H-1), 7.20–7.40 (m, 13H, Ph), 7.46–7.50 (m, 2H, Ph). ^{13}C NMR δ: 15.7 (C-3), 47.3 (C-2), 51.7 (*C*H$_2$Ph), 64.3 (C-1), 127.0, 127.4, 127.7, 128.0, 128.3, 128.4, 129.2, 129.4, 129.6, 135.0, 140.5, 141.0 (Ph). Anal. Calcd for $C_{22}H_{23}NSe$: C, 69.47; H, 6.09; N, 3.68. Found: C, 69.82; H, 6.31; N, 3.49.

5.2.15. *N*-Benzyl-2-(phenylselanyl)cyclohexanamine 6o.[4a] Yield: 57%, *syn*/*anti*: 80/20. Diastereomer *syn*; ^{1}H NMR δ: 1.20–2.20 (m, 9H), 2.76 (m, 1H, H-1), 3.74 (s, 2H, CH_2Ph), 3.81 (m, 1H, H-2), 7.20–7.40 (m, 8H, Ph) 7.45–7.49 (m, 2H, Ph). ^{13}C NMR δ: 23.5, 23.8, 30.3, 31.2, 50.7 (*C*H_2Ph), 52.2 (C-2), 57.5 (C-1), 126.9, 127.0, 128.4, 129.1, 129.6, 129.8, 134.9, 141.0 Diastereomer *anti*; ^{1}H NMR δ: 1.20–2.20 (m, 9H), 2.45 (m, 1H, H-1), 3.08 (m, 1H, H-2), 3.71 (d, 1H, J=13.1 Hz, CH_2Ph), 3.93 (d, 1H, J=13.1 Hz, CH_2Ph), 7.15–7.35 (m, 8H, Ph), 7.40–7.43 (m, 2H, Ph). ^{13}C NMR δ: 24.7, 27.4, 32.5, 34.4, 50.9 (C-2), 51.0 (*C*H_2Ph), 59.6 (C-1), 127.0, 128.3, 128.5, 129.1, 129.6, 129.8, 135.1, 140.5 (Ph). Anal. Calcd for $C_{19}H_{23}NSe$: C, 66.27; H, 6.73; N, 4.07. Found: C, 66.17; H, 6.67; N, 4.12.

5.2.16. *N*-Allyl-2-(phenylselanyl)butan-1-amine 7c. Yield: 64%. $bp_{0.05}$: 93 °C. ^{1}H NMR δ: 1.03 (t, 3H, J= 7.2 Hz, H-4), 1.58–1.81 (m, 2H, H-3), 2.10 (sl, 1H, N*H*), 2.63–2.83 (m, 2H, H-1), 3.14–3.28 (m, 3H, H-2, CH_2CH=CH$_2$), 5.02–5.20 (m, 2H, CH$_2$CH=CH_2), 5.77–5.97 (m, 1H, CH$_2$C*H*=CH$_2$), 7.18–7.28 (m, 3H, Ph), 7.50–7.63 (m, 2H, Ph). ^{13}C NMR δ 12.4 (C-4), 26.8 (C-3), 49.2 (C-2), 52.0 (*C*H_2CH=CH$_2$), 52.7 (C-1), 115.9 (CH$_2$CH=H$_2$), 127.5, 127.6, 128.9, 129.1, 131.4, 135.1, 136.7 (Ph, CH$_2$*C*H=CH$_2$). Anal. Calcd for $C_{13}H_{19}NSe$: C, 58.20; H, 7.14; N, 5.22. Found: C, 58.02; H, 7.30; N, 4.94.

5.2.17. *N*-Cyclohexyl-2-(phenylselanyl)butan-1-amine 8c. Yield: 57%. ^{77}Se NMR δ: 332.9. ^{1}H NMR δ: 1.07 (t, 3H, J=7.2 Hz, H-4), 1.10–1.31 (m, 6H, Cy), 1.57–1.85 (m, 7H, Cy, H-3, N*H*), 2.38 (m, 1H, Cy), 2.69 (dd, 1H, J=8.9, 12.5 Hz, H-1), 2.85 (dd, 1H, J=4.8, 12.5 Hz, H-1), 3.16–3.25 (m, 1H, H-2), 7.25–7.40 (m, 3H, Ph), 7.55–7.60 (m, 2H, Ph). ^{13}C NMR δ: 12.5 (C-4), 25.1, 26.2, 27.0 (Cy), 33.8 (C-3), 49.7 (C-2), 50.6 (C-1), 56.6 (Cy), 127.6, 129.0, 128.9, 135.4 (Ph). Anal. Calcd for $C_{16}H_{25}NSe$: C, 61.92; H, 8.12; N, 4.51. Found: C, 61.58; H, 7.87; N, 4.71.

5.2.18. *N*-*tert*-Butyl-2-(phenylselanyl)butan-1-amine 9c. Yield: 56%. ^{1}H NMR δ: 1.07 (t, 3H, J=7.4 Hz, H-4), 1.10 (s, 9H, C(CH_3)$_3$), 1.65–1.81 (m, 2H, H-3), 2.67–2.80 (dd, 1H, J=7.9, 11.8 Hz, H-1), 2.66 (dd, 1H, J=5.1, 11.8 Hz, H-1), 3.11–3.22 (m, 1H, H-2), 7.25–7.30 (m, 3H, Ph), 7.55–7.60 (m, 2H, Ph). ^{13}C NMR δ: 12.5 (C-4), 27.2 (C-3), 29.3 (C(*C*H$_3$)$_3$), 46.4 (C-1), 50.1 (C-2), 50.3 (*C*(CH$_3$)$_3$), 127.6, 128.6, 129.0, 135.3 (Ph). Anal. Calcd for $C_{14}H_{23}NSe$: C, 59.14; H, 8.15; N, 4.93. Found: C, 58.86; H, 7.92; N, 4.65.

5.3. Preparation of β-phenylselanyl amines 10e and 11

A solution of alkylmagnesium chloride 2M in THF (1.1 ml, 2.2 mmol) was slowly added to α-phenylselanyl imines **2** (2 mmol) in THF (30 ml), at −40 °C, under argon. The whole was stirred for 30 min at −40 °C and allowed to reach 0 °C in 2 h. A saturated aqueous solution of ammonium chloride (5 ml) was added, followed by a mixture of water/ether: 1/1 (40 ml). After separation, the aqueous phase was washed with ether (2×50 ml). The combined organic phases were dried over $MgSO_4$ and concentrated. The crude product was purified by column chromatography on silica gel (cyclohexane/Et_2O: 95/5).

5.3.1. *N*-Benzyl-3-methyl-5-(phenylselanyl)non-1-en-4-amine 10e. Yield: 56%, two diastereomers: 70/30. Major diastereomer; ^{1}H NMR δ: 0.86 (t, 3H, J=7.2 Hz, H-9), 1.06 (d, 3H, J=6.6 Hz, CH_3), 1.20–1.50 (m, 4H, H-8, H-7), 1.51 (sl, 1H, N*H*), 1.80–1.98 (m, 2H, H-6), 2.55 (dd, 1H, J=2.4, 7.4 Hz, H-4), 2.58–2.72 (m, 1H, H-3), 3.32 (td, 1H, J=2.4, 7.2 Hz, H-5), 3.83 (s, 2H, CH_2Ph), 5.06–5.16 (m, 2H, H-1), 5.76–5.88 (m, 1H, H-2), 7.25–7.40 (m, 8H, Ph), 7.55–7.58 (m, 2H, Ph). ^{13}C NMR δ: 14.1 (C-9), 18.8 (*C*H$_3$), 22.6 (C-8), 30.6 (C-7), 35.4 (C-6), 42.9 (C-3), 53.4 (C-5), 54.7 (*C*H_2Ph), 64.4 (C-4), 115.6 (C-1), 140.9 (C-2), 126.9, 127.0, 128.4, 128.9, 129.0, 131.7, 134.4, 142.1 (Ph). Minor diastereomer; ^{1}H NMR δ: 0.89 (t, 3H, J=7.0 Hz, H-9), 1.06 (d, 3H, J= 6.7 Hz, CH_3), 1.19–1.99 (m, 7H, H-8, H-7, H-6, N*H*), 2.49–2.61 (m, 1H, H-3), 2.71–2.76 (m, 1H, H-4), 3.43–3.52 (m, 1H, H-5), 3.81 (d, 1H, J=12.3 Hz, CH_2Ph), 3.88 (d, 1H, J= 12.3 Hz, CH_2Ph), 5.00–5.06 (m, 2H, H-1), 5.70–5.83 (m, 1H, H-2), 7.25–7.40 (m, 8H, Ph), 7.55–7.58 (m, 2H, Ph). ^{13}C NMR δ: 14.4 (C-9), 17.6 (*C*H$_3$), 22.9 (C-8), 31.2 (C-7), 31.4 (C-6), 42.2 (C-3), 52.6 (C-5), 54.8 (*C*H_2Ph), 65.7 (C-4), 114.5 (C-1), 142.9 (C-2), 127.3, 127.5, 128.6, 128.7, 129.4, 131.5, 134.5, 143.0 (Ph). Anal. Calcd for $C_{23}H_{31}NSe$: C, 68.98; H, 7.80; N, 3.50. Found: C, 68.62; H, 7.91; N, 3.36.

5.3.2. *N*-Benzyl-6-methyl-5-(phenylselanyl)hept-1-en-4-amine 11d. Yield: 78%, *syn*/*anti*: 55/45. Diastereomer *syn*; ^{1}H NMR δ: 1.02 (d, 3H, J=6.6 Hz, H-7), 1.06 (d, 3H, J=6.6 Hz, H-7), 1.68 (sl, 1H, N*H*), 2.16 (m, 1H, H-6), 2.48 (m, 2H, H-3), 2.88 (m, 1H, H-4), 3.10–3.14 (m, 1H, H-5), 3.74 (d, 1H, J=13.1 Hz, CH_2Ph), 3.89 (d, 1H, J=13.1 Hz, CH_2Ph), 4.93–5.05 (m, 2H, H-1), 5.69–5.79 (m, 1H, H-2), 7.22–7.34 (m, 8H, Ph), 7.55–7.58 (m, 2H, Ph). ^{13}C NMR δ: 21.5 (C-7), 22.1 (C-7), 31.5 (C-6), 37.3 (C-3), 52.0 (*C*H_2Ph), 59.0 (C-4), 62.4 (C-5), 117.4 (C-1), 135.9 (C-2), 126.8, 127.0, 128.3, 128.4, 129.0, 132.1, 133.8, 140.7 (Ph). Diastereomer *anti*; ^{1}H NMR δ: 1.07 (d, 3H, J=6.6 Hz, H-7), 1.15 (d, 3H, J=6.6 Hz, H-7), 1.66 (sl, 1H, N*H*), 2.12–2.20 (m, 1H, H-6), 2.26–2.34 (m, 1H, H-3), 2.44–2.54 (m, 1H, H-3), 2.85–2.95 (m, 1H, H-4), 3.23–3.27 (m, 1H, H-5), 3.68 (s, 2H, CH_2Ph), 4.99–5.10 (m, 2H, H-1), 5.70–5.90 (m, 1H, H-2), 7.22–7.35 (m, 8H, Ph), 7.55–7.60 (m, 2H, Ph). ^{13}C NMR δ: 21.5 (C-7), 22.1 (C-7), 31.0 (C-6), 36.8 (C-3), 51.6 (*C*H_2Ph), 59.2 (C-4), 62.8 (C-5), 116.9 (C-1), 136.3 (C-2), 126.8, 127.0, 128.3, 128.4, 129.0, 132.1, 133.8, 140.7 (Ph). Anal. Calcd for $C_{21}H_{27}NSe$: C, 67.73; H, 7.31; N, 3.76. Found: C, 67.61; H, 7.56; N, 3.59.

5.3.3. *syn*-*N*-Benzyl-5-(phenylselanyl)non-1-en-4-amine 11e. Yield: 69%. ^{1}H NMR δ: 0.87 (t, 3H, J=7.2 Hz, H-9), 1.22–1.35 (m, 3H, H-8, H-7), 1.42–1.63 (m, 3H, H-7, H-6 N*H*), 1.84–1.95 (m, 1H, H-6), 2.20–2.31 (m, 1H, H-3), 2.51–2.62 (m, 1H, H-3), 2.76–2.82 (m, 1H, H-4), 3.24–3.32 (m, 1H, H-5), 3.74 (d, 1H, J=13.4 Hz, CH_2Ph), 3.80 (d, 1H, J=13.4 Hz, CH_2Ph), 4.99–5.07 (m, 2H, H-1), 5.64–5.78 (m, 1H, H-2), 7.22–7.35 (m, 8H, Ph), 7.55–7.60 (m, 2H, Ph). ^{13}C NMR δ: 14.1 (C-9), 22.6 (C-8), 30.7 (C-7), 31.9 (C-6), 36.5 (C-3), 52.0 (*C*H_2Ph), 52.2 (C-5), 59.8 (C-4), 117.5 (C-1), 136.2 (C-2), 127.0, 127.2, 128.3, 128.4, 129.0, 130.8, 134.4, 140.8 (Ph). Anal. Calcd for $C_{22}H_{29}NSe$: C, 68.38; H, 7.56; N, 3.62. Found: C, 68.52; H, 7.91; N, 3.86.

5.3.4. *N*-Benzyl-2-methyl-2-(phenylselanyl)hex-5-en-3-amine 11g. Yield: 74%. ^{1}H NMR δ: 1.38 (s, 3H, H-1),

1.44 (s, 3H, H-1), 1.55 (sl, 1H, N*H*), 2.14–2.25 (m, 1H, H-4), 2.63–2.77 (m, 2H, H-4, H-3), 3.78 (d, 1H, $J=12.6$ Hz, CH_2Ph), 3.92 (d, 1H, $J=12.6$ Hz, CH_2Ph), 5.06–5,16 (m, 2H, H-6), 5.83–5.98 (m, 1H, H-5), 7.25–7.40 (m, 8H, Ph), 7.62–7.65 (m, 2H, Ph). ^{13}C NMR δ: 27.0 (C-1), 27.7 (C-1), 37,0 (C-4), 54.6 (*C*H_2Ph), 65.6 (C-3), 77.36 (C-2), 116.8 (C-6), 137.1 (C-5), 127.0, 127.4, 128.3, 128.4, 128.5, 128.7, 138.5, 140.8 (Ph). Anal. Calcd for $C_{20}H_{25}NSe$: C, 67.03; H, 7.03; N, 3.91. Found: C, 67.31; H, 7.27; N, 3.79.

5.3.5. *syn*-*N*-Benzyl-2-phenyl-2-(phenylselanyl)hex-5-en-3-amine 11h. Yield: 47%. ^{1}H NMR δ: 1.57 (sl, 1H, N*H*), 1.86 (s, 3H, H-1), 1.96–2.06 (m, 1H, H-4), 2.18–2.25 (m, 1H, H-4), 3.62 (dd, 1H, $J=3.2$, 8.3 Hz, H-3), 4.06 (d, 1H, $J=12.3$ Hz, CH_2Ph), 4.13 (d, 1H, $J=12.3$ Hz, CH_2Ph), 4.93–4.99 (m, 2H, H-6), 5.70–5.84 (m, 1H, H-5), 6.99–7.52 (m, 15H, Ph). ^{13}C NMR δ: 21.5 (C-1), 37.7 (C-4), 55.0 (*C*H_2Ph), 61.4 (C-2), 65.7 (C-3), 116.7 (C-6), 136.7 (C-5), 126.3, 127.1, 127.6, 127.8, 128.0, 128.3, 128.5, 128.7, 129.4, 137.6, 140.7, 144.1 (Ph). Anal. Calcd for $C_{25}H_{27}NSe$: C, 71.41; H, 6.47; N, 3.33. Found: C, 71.02; H, 6.19; N, 3.03.

5.3.6. *N*-Benzyl-2-methyl-1-(phenylselanyl)pent-4-en-2-amine 11j. Yield: 58%. ^{1}H NMR δ: 1.26 (s, 3H, CH_3), 1.57 (sl, 1H, N*H*), 2.30–2.51 (m, 2H, H-3), 3.16 (d, 1H, $J=$ 11.8 Hz, H-1), 3.26 (d, 1H, $J=11.8$ Hz, H-1), 3.69 (s, 2H, CH_2Ph), 5.11–5.18 (m, 2H, H-5), 5.81–5.93 (m, 1H, H-4), 7.25–7.38 (m, 8H, Ph), 7.55–7.59 (m, 2H, Ph). ^{13}C NMR δ: 25.0 (*C*H_3), 40.2 (C-1), 43.7 (C-3), 46.5 (*C*H_2Ph), 55.9 (C-2), 118.6 (C-5), 134.2 (C-4), 126.8, 127.0, 128.2, 128.4, 129.2, 131.5, 132.9, 140.9 (Ph). Anal. Calcd for $C_{20}H_{25}NSe$: C, 67.03; H, 7.03; N, 3.91. Found: C, 66.96; H, 6.75; N, 4.02.

5.3.7. *N*-Benzyl-2-phenyl-1-(phenylselanyl)pent-4-en-2-amine 11l. Yield: 65%. ^{1}H NMR δ: 1.88 (sl, 1H, N*H*), 2.65–2.80 (m, 2H, H-3), 3.45 (d, 1H, $J=12.0$ Hz, CH_2Ph), 3.55 (d, 1H, $J=12.0$ Hz, CH_2Ph), 3.62 (s, 2H, H-1), 4.99–5.07 (m, 2H, H-5), 5.43–5.58 (m, 1H, H-4), 7.20–7.60 (m, 15H, Ph). ^{13}C NMR δ: 38.9 (C-1), 44.2 (C-3), 46.7 (*C*H_2Ph), 61.5 (C-2), 118.8 (C-5), 133.5 (C-4), 126.8, 126.9, 127.0, 128.3, 128.4, 128.5, 129.1, 131.2, 133.3, 140.7, 144.0 (Ph). Anal. Calcd for $C_{24}H_{25}NSe$: C, 70.92; H, 6.20; N, 3.44. Found: C, 70.55; H, 6.15; N, 3.22.

5.3.8. *syn*-*N*-Benzyl-3-phenyl-2-(phenylselanyl)hex-5-en-3-amine 11n. Yield: 64%. ^{77}Se NMR δ: 364.0. ^{1}H NMR δ: 1.31 (d, 3H, $J=6.9$ Hz, H-1), 2.33 (sl, 1H, N*H*), 2.88 (dd, 1H, $J=5.3$, 14.8 Hz, H-4), 3.08 (dd, 1H, $J=8.3$, 14.8 Hz, H-4), 3.65 (d, 1H, $J=12.5$ Hz, CH_2Ph), 3.74 (q, 1H, $J=$ 6.9 Hz, H-2), 3.82 (d, 1H, $J=12.5$ Hz, CH_2Ph), 5.15–5.22 (m, 2H, H-6), 5.90–5.98 (m, 1H, H-5), 7.20–7.60 (m, 15H, Ph). ^{13}C NMR δ: 19.0 (C-1), 38.2 (C-4), 46.8 (*C*H_2Ph), 51.6 (C-2), 64.1 (C-3), 118.5 (C-6), 134.0 (C-5), 126.9, 127.1, 127.2, 127.8, 128.0, 128.2, 128,5, 129.0, 130.8, 134.7, 140.9, 141,5 (Ph). Anal. Calcd for $C_{25}H_{27}NSe$: C, 71.41; H, 6.47; N, 3.33. Found: C, 71.12; H, 6.39; N, 3.15.

5.4. Preparation of allylaziridines 12

A solution of allylmagnesium chloride 2M in THF (1.1 ml, 2.2 mmol) was slowly added to α-phenylselanyl imine **2** (2 mmol) in refluxing THF (30 ml), under argon. The whole was stirred for 2 h under reflux. A saturated aqueous solution of ammonium chloride (5 ml) was added, followed by a mixture of water/ether: 1/1 (40 ml). After separation, the aqueous phase was washed with ether (2×50 ml). The combined organic phases were dried over $MgSO_4$ and concentrated. The crude product was purified by column chromatography on silica gel (cyclohexane/Et_2O: 80/20).

5.4.1. 2-Allyl-1-benzyl-3-isopropylaziridine 12d. Yield: 73%, *cis*/*trans*: 55/45. Diastereomer *cis*; ^{1}H NMR δ: 0.84 (d, 3H, $J=6.1$ Hz, CH(CH_3)$_2$), 0.90 (d, 3H, $J=6.7$ Hz, CH(CH_3)$_2$), 1.23 (dd, 1H, $J=6.5$, 9.6 Hz H-3), 1.28–1.38 (m, 1H, C*H*(CH$_3$)$_2$), 1.55–1.63 (m, 1H, H-2), 2.13–2.25 (m, 2H, CH_2CH=CH$_2$), 3.37 (d, 1H, $J=12.6$ Hz, CH_2Ph), 3.49 (d, 1H, $J=12.6$ Hz, CH_2Ph), 4.97–5.11 (m, 2H, CH$_2$CH=CH_2), 5.70–5.87 (m, 1H, CH$_2$C*H*=CH$_2$), 7.26–7.36 (m, 5H, Ph). ^{13}C NMR δ: 20.4 (CH(*C*H$_3$)$_2$), 21.4 (CH(*C*H$_3$)$_2$), 27.7 (*C*H(CH$_3$)$_2$), 32.9 (*C*H$_2$CH=CH$_2$), 44.3 (C-2), 51.5 (C-3), 65.8 (*C*H$_2$Ph), 115.8 (CH$_2$CH=H$_2$), 139.3 (CH$_2$*C*H=CH$_2$), 126.9, 127.2, 128.3, 139.7 (Ph). MS m/z: 215 (M$^+$, 2), 172 (27), 124 (4), 91 (39), 55 (100). Anal. Calcd for $C_{15}H_{21}N$: C, 83.66; H, 9.83; N, 6.50. Found: C, 83.40; H, 9.82; N, 6.61. Diastereomer *trans*; ^{1}H NMR δ: 0.74 (d, 3H, $J=6.4$ Hz, CH(CH_3)$_2$), 0.88 (d, 3H, $J=6.7$ Hz, CH(CH_3)$_2$), 1.14 (dd, 1H, $J=2.3$, 9.2 Hz H-3), 1.19–1.27 (m, 1H, C*H*(CH$_3$)$_2$), 1.87–1.97 (m, 1H, H-2), 2.19–2.36 (m, 1H, CH_2CH=CH$_2$), 2.42–2.54 (m, 1H, CH_2CH=CH$_2$), 3.39 (d, 1H, $J=13.3$ Hz, CH_2Ph), 3.86 (d, 1H, $J=13.3$ Hz, CH_2Ph), 4.97–5.20 (m, 2H, CH$_2$CH=CH_2), 5.82–5.97 (m, 1H, CH$_2$C*H*=CH$_2$), 7.19–7.37 (m, 5H, Ph). ^{13}C NMR δ: 19.9 (CH(*C*H$_3$)$_2$), 20.6 (CH(*C*H$_3$)$_2$), 31.0 (*C*H$_2$CH=CH$_2$), 31.8 (*C*H(CH$_3$)$_2$), 42.0 (C-2), 52.8 (C-3), 56.5 (*C*H$_2$Ph), 116.3 (CH$_2$CH=*C*H$_2$), 136.1 (CH$_2$*C*H=CH$_2$), 126.9, 128.2, 128.4, 140.2 (Ph). MS *m*/*z*: 215 (M$^+$, 2), 172 (27), 124 (4), 91 (38), 55 (100).

5.4.2. *cis*-2-Allyl-1-benzyl-3-butylaziridine 12e. Yield: 53%. ^{1}H NMR δ: 0.85 (t, 3H, $J=6.6$ Hz, CH$_2$CH$_2$CH$_2$CH_3), 1.22–1.43 (m, 6H, CH_2CH_2CH_2CH$_3$), 1.46–1.58 (m, 2H, H-2, H-3), 2.07–2.18 (m, 1H, CH_2CH=CH$_2$), 2.19–2.29 (m, 1H, CH_2CH=CH$_2$), 3.44 (d, 1H, $J=13.3$ Hz, CH_2Ph), 3.50 (d, 1H, $J=13.3$ Hz, CH_2Ph), 4.96–5.10 (m, 2H, CH$_2$CH=CH_2), 5.71–5.83 (m, 1H, CH$_2$C*H*=CH$_2$), 7.22–7.35 (m, 5H, Ph). ^{13}C NMR δ: 14.1 (CH$_2$CH$_2$CH$_2$*C*H$_3$), 22.7 (CH$_2$CH$_2$*C*H$_2$CH$_3$), 27.9 (CH$_2$*C*H$_2$CH$_2$CH$_3$), 30.2 (*C*H$_2$CH$_2$CH$_2$CH$_3$), 32.8 (*C*H$_2$CH=CH$_2$), 43.6 (C-2), 44.2 (C-3), 65.3 (*C*H$_2$Ph), 115.7 (CH$_2$CH=H$_2$), 136.2 (CH$_2$*C*H=CH$_2$), 127.0, 128.2, 128.4, 139.4 (Ph). MS m/z: 229 (M$^+$, 1), 186 (9), 172 (20), 91 (65), 69 (72), 55 (80), 44 (90), 41 (100). Anal. Calcd for $C_{16}H_{23}N$: C, 83.79; H, 10.11; N, 6.11. Found: C, 83.62; H, 10.33; N, 6.05.

5.4.3. 3-Allyl-1-benzyl-2,2-dimethylaziridine 12g. Yield: 57%. ^{1}H NMR δ: 1.20 (s, 3H, CH_3), 1.24 (s, 3H, CH_3), 1.39–1.43 (m, 1H, H-3), 2.06–2.17 (m, 1H, CH_2CH=CH$_2$), 2.27–2.37 (m, 1H, CH_2CH=CH$_2$), 3.67 (s, 2H, CH_2Ph), 4.95–5.08 (m, 2H, CH$_2$CH=CH_2), 5.73–5.83 (m, 1H, CH$_2$C*H*=CH$_2$), 7.18–7.36 (m, 5H, Ph). ^{13}C NMR δ: 18.6 (*C*H$_3$), 22.1 (*C*H$_3$), 34.1 (*C*H$_2$CH=CH$_2$), 40.0 (C-2), 49.9 (C-3), 56.9 (*C*H$_2$Ph), 115.5 (CH$_2$CH=H$_2$), 136.3 (CH$_2$*C*H=CH$_2$), 126.5, 127.6, 128.3, 140.6 (Ph). MS m/z: 201 (M$^+$, 12), 186 (34), 160 (16), 110 (24), 91 (68), 55 (75).

Anal. Calcd for $C_{14}H_{19}N$: C, 83.53; H, 9.51; N, 6.96. Found: C, 83.34; H, 9.61; N, 7.05.

5.4.4. *trans*-3-Allyl-1-benzyl-2-methyl-2-phenylaziridine 12h. Yield: 41%. ^{1}H NMR δ: 1.54 (s, 3H, CH_3), 2.04–2.09 (m, 1H, H-3), 2.22–2.34 (m, 1H, CH_2CH=CH$_2$), 2.39–2.51 (m, 1H, CH_2CH=CH$_2$), 2.78 (d, 1H, J=14.1 Hz, CH_2Ph), 3.54 (d, 1H, J=14.1 Hz, CH_2Ph), 5.01–5.18 (m, 2H, CH$_2$CH=CH_2), 5.75–5.86 (m, 1H, CH$_2$CH=CH$_2$), 7.22–7.37 (m, 10H, Ph). ^{13}C NMR δ: 22.8 (*C*H$_3$), 33.9 (*C*H$_2$CH=CH$_2$), 47.9 (C-3), 48.7 (C-2), 59.0 (*C*H$_2$Ph), 116.2 (CH$_2$CH=H$_2$), 135.9 (CH$_2$*C*H=CH$_2$), 126.7, 127.5, 128.0, 128.2, 128.3, 129.8, 140.1, 140.6 (Ph). Anal. Calcd for $C_{19}H_{21}N$: C, 86.65; H, 8.04; N, 5.32. Found: C, 86.40; H, 8.17; N, 5.42.

5.4.5. 2-Allyl-1-benzyl-2-phenylaziridine 12l. Yield: 61%. ^{1}H NMR δ: 1.88 (s, 1H, H-3), 2.12 (s, 1H, H-3), 2.27 (dd, 1H, J=7.2, 14.1 Hz, CH_2CH=CH$_2$), 2.85 (d, 1H, J=14.1 Hz, CH_2Ph), 2.90 (dd, 1H, J=7.2, 14.1 Hz, CH_2CH=CH$_2$), 3.45 (d, 1H, J=14.1 Hz, CH_2Ph), 4.91–4.99 (m, 2H, CH$_2$CH=CH_2), 5.62–5.76 (m, 1H, CH$_2$CH=CH$_2$), 7.19–7.37 (m, 10H, Ph). ^{13}C NMR δ: 38.0 (C-3), 45.2 (*C*H$_2$CH=CH$_2$), 48.9 (C-2), 58.7 (*C*H$_2$Ph), 117.1 (CH$_2$CH=H$_2$), 134.6 (CH$_2$*C*H=CH$_2$), 126.8, 127.0, 127.2, 127.4, 127.7, 128.2, 137.5, 140.1 (Ph). MS m/z: 249 (M$^+$, 24), 208 (10), 172 (5), 158 (30), 91 (100), 77 (20), 55 (75). Anal. Calcd for $C_{18}H_{19}N$: C, 86.70; H, 7.68; N, 5.62. Found: C, 86.32; H, 7.56; N, 5.32.

5.4.6. *cis*-2-Allyl-1-benzyl-2-ethyl-3-methylaziridine 12m. Yield: 57%. ^{1}H NMR δ: 0.98 (t, 3H, J=7.2 Hz, CH$_2$CH_3), 1.20 (d, J=5.6 Hz, 3H, CH_3), 1.47 (q, 1H, J=5.6 Hz, H-3), 1.52–1.63 (m, 2H, CH_2CH$_3$), 2.16 (dd, 1H, J=7.3, 14.6 Hz, CH_2CH=CH$_2$), 2.28 (dd, 1H, J=7.3, 14.6 Hz, CH_2CH=CH$_2$), 3.59 (d, 1H, J=14.1 Hz, CH_2Ph), 3.83 (d, 1H, J=14.1 Hz, CH_2Ph), 5.02–5,15 (m, 2H, CH$_2$CH=CH_2), 5.70–5.85 (m, 1H, CH$_2$CH=CH$_2$), 7.22–7.39 (m, 5H, Ph). ^{13}C NMR δ: 10.9 (CH$_2$*C*H$_3$), 14.6 (*C*H$_3$), 22.4 (*C*H$_2$CH$_3$), 36.8 (*C*H$_2$CH=CH$_2$), 45.3 (C-3), 47.0 (C-2), 56.5 (*C*H$_2$Ph), 116.7 (CH$_2$CH=H$_2$), 135.8 (CH$_2$*C*H=CH$_2$), 126.7, 127.9, 128.5, 140.7 (Ph). MS m/z: 215 (M$^+$, 1), 200 (25), 186 (13), 124 (15), 91 (72), 69 (85), 56 (40), 41 (100). Anal. Calcd for $C_{15}H_{21}N$: C, 83.67; H, 9.83; N, 6.50. Found: C, 83.77; H, 9.72; N, 6.51.

5.4.7. *trans*-2-Allyl-1-benzyl-3-methyl-2-phenylaziridine 12n. Yield: 41%. ^{1}H NMR δ: 1.38 (d, J=5.6 Hz, 3H, CH_3), 2.12 (q, 1H, J=5.6 Hz, H-3), 2.38 (dd, 1H, J=6.9, 14.6 Hz, CH_2CH=CH$_2$), 2.79 (d, 1H, J=14.3 Hz, CH_2Ph), 2.91 (dd, 1H, J=6.9, 14.6 Hz, CH_2CH=CH$_2$), 3.56 (d, 1H, J=14.3 Hz, CH_2Ph), 4.87–4.93 (m, 2H, CH$_2$CH=CH_2), 5.52–5.66 (m, 1H, CH$_2$CH=CH$_2$), 7.17–7.31 (m, 10H, Ph). ^{13}C NMR δ: 14.6 (*C*H$_3$), 41.1 (*C*H$_2$CH=CH$_2$), 43.9 (C-3), 51.9 (C-2), 58.9 (*C*H$_2$Ph), 116.9 (CH$_2$CH=H$_2$), 134.7 (CH$_2$*C*H=CH$_2$), 126.6, 127.5, 127.7, 128.1, 128.3, 130.6, 138.9, 140.3 (Ph). MS m/z: 263 (M$^+$, 31), 248 (14), 220 (2), 172 (38), 91 (69), 69 (100), 41 (59). Anal. Calcd for $C_{19}H_{21}N$: C, 86.65; H, 8.04; N, 5.32. Found: C, 86.30; H, 8.31; N, 5.37.

5.5. Cyclisation of 11j

To the β-phenylselanyl amine **11j** (1 mmol) in acetonitrile (10 ml) was added NBS (195 mg, 1.1 mmol) at room temperature. After 5 min of stirring, the mixture became red-brown and sodium bicarbonate (212 mg, 2 mmol) was introduced. The mixture turned rapidly yellow. Water (10 ml) was added and the aqueous phase was extracted with dichloromethane (2×10 ml). The combined organic phases were dried over $MgSO_4$ and concentrated. The crude product was purified by column chromatography on silica gel (cyclohexane/Et$_2$O: 80/20) to afford the aziridine **12j**.

5.5.1. 2-Allyl-1-benzyl-2-methylaziridine 12j. Yield: 72%. ^{1}H NMR δ: 1.24 (s, 1H, CH_3), 1.26 (s, 1H, H-3), 1.87 (s, 1H, H-3), 2.04–2.30 (m, 1H, CH_2CH=CH$_2$), 3.65 (s, 2H, CH_2Ph), 5.02–5.13 (m, 2H, CH$_2$CH=CH_2), 5.74–5.88 (m, 1H, CH$_2$CH=CH$_2$), 7.20–7.39 (m, 5H, Ph). ^{13}C NMR δ: 14.9 (*C*H$_3$), 39.9 (C-3), 45.0 (C-2), 45.2 (*C*H$_2$CH=CH$_2$), 57.1 (*C*H$_2$Ph), 117.0 (CH$_2$CH=H$_2$), 135.4 (CH$_2$*C*H=CH$_2$), 126.8, 127.7, 128.5, 140.5 (Ph). MS m/z: 187 (M$^+$, 19), 146 (21), 96 (32), 91 (100), 55 (93). Anal. Calcd for $C_{13}H_{17}N$: C, 83.37; H, 9.15; N, 7.48. Found: C, 83.07; H, 8.94; N, 7.28.

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