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Diastereoselective synthesis of aziridine esters via amino selanyl esters

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Abstract—A synthesis of aziridine esters based on the cyclisation of amino selanyl esters induced by the selanyl group activation was developed with either the Meerwein salt or NBS. Two asymmetric approaches are proposed: the diastereoselective reductions of α-selanyl β-iminoesters derived from α-oxoesters, which lead to cis chiral aziridine esters **6** and **6′**; and the diastereoselective conjugate additions of a chiral amide to α,β-unsaturated esters providing trans chiral aziridine esters **6** and **6″**.

1. Introduction

The aziridine moiety is present in a wide variety of natural biologically active compounds like antitumor and antibiotic agents.[1] Synthetic aziridines exhibit multiple biological properties, such as enzyme inhibitors[2] and DNA alkylation agents since their ring strain. They are, in particular, susceptible for regio- and stereoselective ring opening.[3] Thus, they are useful precursors for diverse nitrogen containing compounds,[4] notably chiral amino acids.[5]

Several reviews have surveyed the asymmetric synthesis of aziridines.[6] One pathway to obtain chiral aziridines consists of the addition of nitrenoid compounds to alkenes,[7] or of carbenes to imines,[8] in presence of asymmetric catalysts. Nonetheless, the conceptually simplest approach relies on the nucleophilic attack of a nitrogen atom on an adjacent carbon atom bearing a leaving group.[9] In this manner, enantiomerically pure starting materials such as amino acids, carbohydrates or hydroxy acids can be used and lead to aziridines after displacement of the hydroxyl group through a S_N2 process.[10] Similarly, aziridine synthesis by derivation of a sulfonium group has been reported.[11]

The selanyl group is known to be easily displaced under mild conditions by nucleophiles when it has an activated IV oxidation state, such as selenone or selenonium salt.[12] Thus, epoxides formation from β-hydroxy selenides through intramolecular substitution is well documented.[13] Our laboratory is interested in selenium methodology, which has provided useful synthetic tools for organic chemists.[14] Previously reported work, bifunctional synthons such as α-selanyl carbonyl derivatives have especially been investigated.[15] We developed specific methods to prepare α-selanyl imines, which after reduction led to the corresponding β-selanyl amines that are potential precursors of aziridines. We first promoted the cyclisation of β-selanyl amines using Meerwein salt, which was subsequently improved using *N*-bromosuccinimide (NBS).[16,17] The synthesis of non-functionalized aziridines from α-selanyl aldehydes and α-selanyl ketones has recently been reported.[17b]

We next focussed our attention on the preparation of chiral aziridine esters. Indeed we had observed a *syn* diastereoselection during the reduction of imines derived from β-selanyl α-oxoesters.[16] Treatment of the *syn* configured β-selanyl α-aminoesters by the Meerwein salt provided corresponding *cis* aziridine esters. In continuation of this work, herein we report a comparison between the Meerwein salt and NBS activation of these substrates, and our attempt to access chiral aziridine esters by introducing an additional asymmetric centre on the amine group (path A, Scheme 1). We also propose a new pathway that would provide aziridine esters via β-amino α-selanylesters prepared from α,β-unsaturated esters (path B, Scheme 1).

2. Results and discussion

β-Selanyl α-oxoesters **1** were first converted into *N*-benzyl imines in presence of titanium tetrachloride (Scheme 2).

Keywords: Selenium activation; Synthetic aziridines; Meerwein salt; N. Bromosuccinimide.
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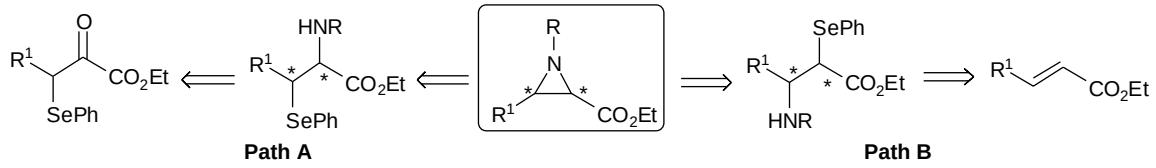
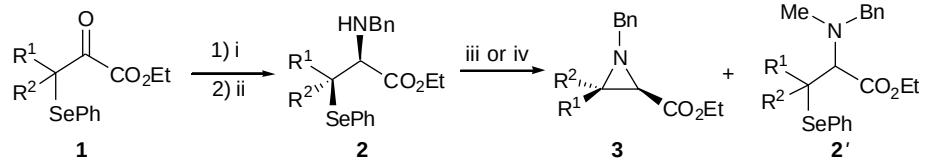


Scheme 1.



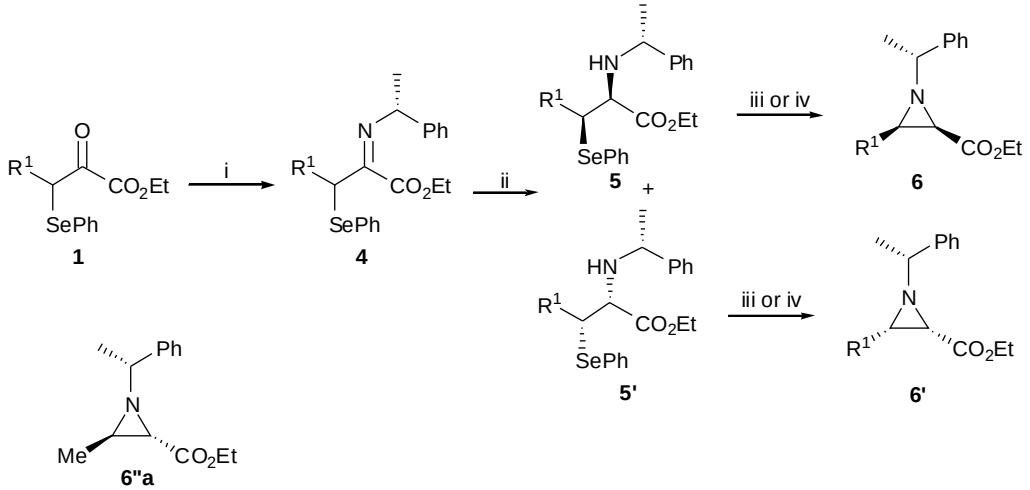
Scheme 2. (i) $BnNH_2$ (4 equiv), $TiCl_4$, Et_2O, 20 °C, 4 h; (ii) $NaBH_3CN$ (0.5 equiv), AcOH, EtOH, 0 °C, 1 h; (iii) Me_3OBF_4 (2 equiv), CH_2Cl_2, 12 h then NaOH aq 1 N; (iv) NBS (1.1 equiv), CH_3CN, 5 min then Na_2CO_3.

Reduction to the amine was performed with sodium cyanoborohydride as it had been shown that this reducing agent limits the deselenenylation of the substrates.[15a] Only one diastereomer was observed in the NMR for the corresponding β-selanyl α-aminoesters **2**. Methylation of the selanyl group with the Meerwein salt and treatment with base led to aziridine esters **3** in 48–61% yields (Table 1). The characteristic aziridine coupling constant J_{H2-H3} allowed us to unambiguously assign the cis stereochemistry of aziridines **3** ($J_{H2-H3}=6.3$–6.8 Hz).[18] Considering that the cyclisation proceeds through an S_N2 mechanism we deduced a *syn* configuration for the β-selanyl α-aminoesters **2**. However, with the hindered substrate **2f**, no aziridine was obtained after the Meerwein salt action. Only a N-methylation reaction was observed yielding **2′f**. This undesired reaction, due to the nature of the activator and which also occurred during the cyclisation of hindered β-selanyl amines derived from α-selanyl aldhehydes, can be suppressed by the use of NBS. Indeed treatment of compound **2f** with this reagent provided the desired aziridine **3f** in 65% yield. In addition, the cyclisation reactions are much faster with NBS than with the Meerwein salt (5 min instead of 12 h) and the aziridine yields are slightly higher.

In order to access chiral aziridine esters, an additional asymmetric centre has been introduced by replacing the benzylamine by the (*R*)-phenylethylamine ((*R*)-PEA). The resulting imines **4** were formed as two diastereomers in equal proportion. Due to their instability, it

Table 1. Synthetic yields of aziridine esters **3** via Scheme 2

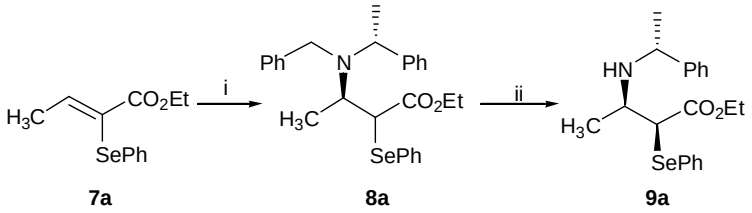
Substrate			**1**→**2** Yield (%)	Cyclisation of **2** products, yield (%)	
No.	R^1	R^2		Via iii	Via iv
1a	Me	H	47	**3a**, 49	**3a**, 45
1b	Et	H	54	**3b**, 57	**3b**, 66
1c	*n*Pr	H	51	**3c**, 61	**3c**, 67
1d	*i*Pr	H	46	**3d**, 54	**3d**, 61
1e	Bn	H	52	**3e**, 48	**3e**, 52
1f	Me	Me	55	**2f***N*-Me, 51	**3f**, 65



Scheme 3. (i) (*R*)-PEA (4 equiv), $TiCl_4$, Et_2O, 20 °C, 4 h; (ii) $NaBH_3CN$ (0.5 equiv), AcOH, EtOH, 0 °C, 1 h; (iii) Me_3OBF_4 (2 equiv), CH_2Cl_2, 12 h then NaOH aq 1 N; (iv) NBS (1.1 equiv), CH_3CN, 5 min then Na_2CO_3.

Table 2. Synthetic yields of aziridine esters **6** and **6′** via Scheme 3

Substrate		**1**→**5**-*syn*/**5′**-*syn* Yield (%), (**5**/**5′**)	Cyclisation of **5** products, yield (%)		Cyclisation of **5′** products, yield (%)	
No.	R^1		Via iii	Via iv	Via iii	Via iv
1a	Me	47, (50/50)	**6a**, 47	**6″a**, 57	**6′a**, 49	**6′a**, 51
1b	Et	53, (50/50)	**6b**, 50	**6b**, 55	**6′b**, 56	**6′b**, 49
1c	*n*Pr	51, (50/50)	**6c**, 55	**6c**, 61	**6′c**, 52	**6′c**, 58
1e	Bn	50, (50/50)	**6e**, 41	**6e**, 48	**6′e**, 44	**6′e**, 52



7a **8a** **9a**

Scheme 4. (i) [(*R*)-BPEA (1.3 equiv), *n*-BuLi (1.3 equiv)], THF, −78 °C, 40 min; (ii) CAN (2.1 equiv), CH_3CN/H_2O, 20 °C, 1 h.

was not possible to separate them and these were reduced as a crude mixture to provide β-selanyl α-aminoesters **5** and **5′** in equal proportion (Scheme 3, Table 2).[†] Substrates **5** and **5′** were separated by silica gel chromatography and subjected to the cyclisation conditions. Activation of the selanyl group of **5a** and **5′a** (R^1=Me) by the Meerwein salt led to the expected formation of *cis* aziridine **6a** and **6′a**, respectively. However, when **5′a** was treated with NBS, **6′a** was obtained, but surprisingly *trans* aziridine **6″a** was exclusively formed from **5a**. This might be explained by an enol equilibrium leading to the more stable aziridine.[19] Considering these results all the cyclisation substrates were then subjected to both activators. Nevertheless, only *cis* aziridine esters were obtained starting from **5b–e** and **5′b–e** no matter what the activation conditions were. This confirmed the *syn* stereochemistry of substrates **5** and **5′**. At this point of our study, we only knew the relative stereochemistry of products **5**, **5′**, **6** and **6′** but could not attribute their absolute configuration.

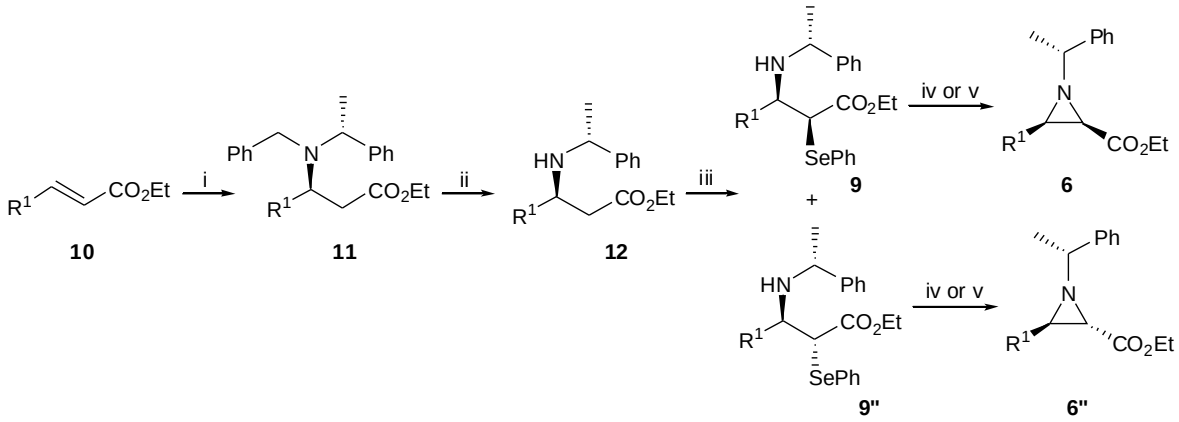
We thus developed another pathway to access similar aziridine esters from α,β-unsaturated esters. Indeed, Davies and co-workers have developed very efficient methods for the diastereoselective conjugate additions of the lithium amide derived from (*R*)-*N*-benzyl-*N*-phenylethylamine ((*R*)-BPEA).[20] Initially addition of this chiral lithium amide to the α-selanyl-α,β-unsaturated ester **7a** gave an unstable adduct **8a**, which decomposed on silica gel or alumina (Scheme 4). Thus **8a** was used without any purification in a debenzylation step with cerium ammonium nitrite (CAN)[21] to provide amine **9a** as a single *syn* diastereomer albeit in 28% yield over two steps, probably due to a competitive retro-Michael reaction. Finally, the selanyl group was introduced at the end of the reaction sequence.

After addition of the chiral lithium amide on α,β-unsaturated esters **10** only one diastereomer (*R*,*R*) was observed in the NMR for products **11**. Based on computational studies, Davies and co-workers have shown that the *Si* face is the most favourable for the amide attack because of the minimisation of steric interactions.[22] The debenzylation with CAN is selective and afforded amines **12** in 48–68% yields. After deprotonation with LDA and addition of benzene selenienyl bromide, β-amino α-selanylesters were obtained as two diastereomers chromatographically separable **9** and **9″** in proportions ranging from 50/50 to 70/30 depending on R^1. The use of camphor selenienyl bromide[23] as a chiral electrophile did not increase the diastereoselectivity. The cyclisation of substrates **9″a–g** by the Meerwein salt provided *trans* aziridine esters **6″a–g** (J_{H2-H3}=2.7–2.8 Hz) which implied an *anti* configuration for precursors **9″**. *cis* Aziridine esters **6a–g** (J_{H2-H3}=6.6–6.9 Hz) were observed from treatment of compounds **9a–g** with the same activator. Similar results were obtained when the cyclisations were carried out with NBS, except with three substrates. Indeed, the activation with this reagent of the selanyl group of compounds **9b** (R^1=Et) led to a mixture of *cis*/*trans* aziridines **6b/6″b** in a ratio 43/57 and compounds **9a**,**g** (R^1=Me, Ph) provided only the *trans* aziridines **6″a**,**g**. As during the cyclisation of β-selanyl α-aminoesters **5a**, these partial or total C2 epimerisations occurred only when the cyclisations were promoted by NBS and not by the Meerwein salt. Considering that the configuration of one of the stereogenic carbons was established by the diastereoselective addition of the chiral amide, we were able to attribute the absolute configuration of aziridines **6**, **6″** and with these results in hand, we deduced the absolute configuration for their precursors **9**, **9″** (Scheme 5, Table 3).

The fact, that *cis* aziridines **6** are the common product of both pathways A and B (Scheme 1), allowed us to distinguish between the two *cis* aziridines **6** and **6′** obtained previously from α-oxo esters **1** (path A) and, as a consequence, to determine the absolute configuration of β-selanyl α-aminoesters **5** and **5′**.

In conclusion, we have developed a synthesis of aziridine esters based on the cyclisation of amino selanyl esters induced by the selanyl group activation with either the Meerwein salt or NBS. Two asymmetric approaches are proposed: the diastereoselective reductions of α-selanyl β-iminoesters derived from α-oxoesters, which lead to *cis*

[†] When R^1=*i*Pr (**1d**), a complex mixture was obtained and no desired amine could be isolated.



Scheme 5. (i) [(*R*)-BPEA (1.3 equiv), *n*-BuLi (1.3 equiv)], THF, −78 °C, 40 min; (ii) CAN (2.1 equiv), CH_3CN/H_2O, 20 °C, 1 h; (iii) LDA (2.1 equiv), THF, −78 °C then PhSeBr (1.3 equiv), −78 °C, 20 min; (iv) Me_3OBF_4 (2 equiv), CH_2Cl_2, 12 h then NaOH aq 1 N; (v) NBS (1.1 equiv), CH_3CN, 5 min then Na_2CO_3.

Table 3. Synthetic yields of aziridines esters **6** and **6″** via Scheme 5

Substrate		**10→11** Yield (%)	**11→12** Yield (%)	**12→9**-*syn*/**9″**-*anti* Yield %, (**9**/**9″**)	Cyclisation of **9** products, yield (%)		Cyclisation of **9″** products, yield (%)	
No.	R^1				Via iv	Via v	Via iv	Via v
10a	Me	79	68	65, (50/50)	**6a**, 51	**6″a**, 58	**6″a**, 53	**6″a**, 59
10b	Et	75	66	59, (50/50)	**6b**, 53	**6b**/**6″b** (43/57), 48	**6″b**, 47	**6″b**, 51
10c	*n*Pr	72	63	56, (50/50)	**6c**, 47	**6c**, 61	**6″c**, 50	**6″c**, 51
10d	*i*Pr	82	53	58, (60/40)	**6d**, 44	**6d**, 49	**6″d**, 48	**6″d**, 53
10e	Bn	78	62	61, (70/30)	**6e**, 42	**6e**, 53	**6″e**, 39	**6″e**, 48
10g	Ph	89	48	57, (70/30)	**6g**, 49	**6″g**, 55	**6″g**, 52	**6″g**, 55

chiral aziridine esters **6** and **6′**; and the diastereoselective conjugate additions of a chiral amide to α,β-unsaturated esters providing trans chiral aziridine esters **6** and **6″**. The comparison of the aziridine esters obtained by these two synthetic ways allowed the attribution of the absolute configuration to all the synthesized compounds.

3. Experimental

THF was distilled over sodium/benzophenone. Ether was dried over sodium. ^{1}H NMR (300 MHz) and ^{13}C NMR (75.4 MHz) spectrum were recorded on a Brucker DPX 300 instrument and carried out in $CDCl_3$. Chemical shifts (δ) were quoted in ppm downfield from tetramethylsilane (TMS). Elemental analyses were obtained on a Carlo-Erba 1106 analyser and Mass Spectra on a HP5890 (electronic impact 70 eV) using GC–MS coupling with a Jeol AX 500.

3.1. Synthesis of α-(phenylselanyl)α-aminoesters 2

Preparation of β-(phenylselanyl)α-iminoesters. Titanium chloride (708 mg, 3.75 mmol, 0.75 equiv) in heptane (2 mL) was slowly added to a solution of β-(phenylselanyl) α-oxoester (5 mmol, 1 equiv) and amine (20 mmol, 4 equiv) in anhydrous ether (70 mL), under argon, at 0 °C. The mixture was stirred 30 min at 0 °C and then 3 h at room temperature. The titanium salts were filtered and rinced with ether. The organic phase was dried over $MgSO_4$ and concentrated to afford the desired β-(phenylselanyl)α-iminoesters.

Reduction of β-(phenylselanyl)α-iminoesters. To the α-(phenylselanyl)α-iminoester (5 mmol) in ethanol (60 mL) at 0 °C, under argon, were added successively sodium cyanoborohydride (314 mg, 5 mmol) and acetic acid (300 mg, 5 mmol). The reaction mixture was stirred for 1 h at 0 °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/ether: 85:15).

3.1.1. *syn*-Ethyl 2-benzylamino-3-(phenylselanyl)-butanoate 2a.[16] Oil, yield=47%. ^{1}H NMR δ: 1.11 (t, 3H, J=7.1 Hz, OCH_2CH_3), 1.37 (d, 3H, J=7.1 Hz, H-4), 2.19 (s, 1H, N*H*), 3.23 (d, 1H, J=5.7 Hz, H-2), 3.53 (qd, 1H, J=5.7, 7.1 Hz, H-3), 3.59 (d, 1H, J=13.2 Hz, CH_2Ph), 3.85 (d, 1H, J=13.2 Hz, CH_2Ph), 3.86 (dq, 1H, J=7.1, 10.8 Hz, OCH_2CH_3), 3.98 (dq, 1H, J=7.1, 10.8 Hz, OCH_2CH_3), 7.17–7.47 (m, 10H, Ph). ^{13}C NMR δ: 14.6 (OCH_2CH_3), 20.6 (C-4), 43.2 (C-3), 52.8 (CH_2Ph), 61.3 (OCH_2CH_3), 65.7 (C-2), 127.5, 128.1, 128.7, 128.8, 129.3, 129.4, 135.7, 140.2 (Ph), 173.6 (C-1).

3.1.2. *syn*-Ethyl 2-benzylamino-3-(phenylselanyl)-pentanoate 2b.[16] Oil, yield=54%. ^{1}H NMR δ: 0.92 (t, 3H, J=7.3 Hz, H-5), 1.03 (t, 3H, J=7.2 Hz, OCH_2CH_3), 1.73 (m, 2H, H-4), 2.10 (s, 1H, N*H*), 3.31 (td, 1H, J=3.9, 7.2 Hz, H-3), 3.35 (d, 1H, J=3.9 Hz, H-2), 3.62 (d, 1H, J=13.3 Hz, CH_2Ph), 3.71 (dq, 1H, J=7.2, 10.8 Hz, OCH_2CH_3), 3.90 (d, 1H, J=13.3 Hz, CH_2Ph), 3.92 (dq, 1H, J=7.2, 10.8 Hz,

OCH_2CH_3), 7.15–7.45 (m, 10H, Ph). ^{13}C NMR δ: 13.1 (OCH_2CH_3), 14.4 (C-5), 27.5 (C-4), 52.8 (C-3), 52.9 (CH_2Ph), 61.2 (OCH_2CH_3), 63.6 (C-2), 126.3, 126.9, 127.3, 127.4, 127.8, 128.8, 133.7, 140.4 (Ph), 173.6 (C-1).

3.1.3. *syn*-Ethyl 2-benzylamino-3-(phenylselanyl)-hexanoate 2c.[16] Oil, yield=51%. ^1H NMR δ: 0.79 (t, 3H, J=7.3 Hz, H-6), 1.02 (t, 3H, J=7.2 Hz, OCH_2CH_3), 1.21–1.31 (m, 1H, H-5), 1.39–1.49 (m, 1H, H-5), 1.66–1.70 (m, 2H, H-4), 2.26 (s, 1H, NH), 3.32 (d, 1H, J=3.9 Hz, H2), 3.39 (td, 1H, J=3.9, 7.2 Hz, H-3), 3.57 (d, 1H, J=13.2 Hz, CH_2Ph), 3.70 (dq, 1H, J=7.2, 10.8 Hz, OCH_2CH_3), 3.89 (d, 1H, J=13.2 Hz, CH_2Ph), 3.91 (dq, 1H, J=7.2, 10.8 Hz, OCH_2CH_3), 7.11–7.45 (m, 10H, Ph). ^{13}C NMR δ: 12.7 (C-6), 13.0 (OCH_2CH_3), 20.1 (C-5), 35.1 (C-4), 49.3 (C-3), 51.4 (CH_2Ph), 59.7 (OCH_2CH_3), 62.3 (C-2), 126.0, 126.3, 127.2, 127.3, 127.8, 128.6, 133.7, 139.0 (Ph), 172.2 (C-1).

3.1.4. *syn*-Ethyl 2-benzylamino-4-methyl-3-(phenylselanyl)pentanoate 2d.[16] Oil, yield=46%. ^1H NMR δ: 0.85 (d, 3H, J=6.7 Hz, H-5), 0.96 (t, 3H, J=7.3 Hz, OCH_2CH_3), 1.09 (d, 3H, J=6.7 Hz, H-5), 1.96–2.04 (m, 1H, H-4), 2.16 (s, 1H, NH), 3.17 (dd, 1H, J=3.8, 7.4 Hz, H-3), 3.50 (d, 1H, J=3.8 Hz, H-2), 3.55 (d, 1H, J=13.3 Hz, CH_2Ph), 3.61 (dq, 1H, J=7.3, 10.7 Hz, OCH_2CH_3), 3.86 (dq, 1H, J=7.2, 10.8 Hz, OCH_2CH_3), 3.87 (d, 1H, J=13.3 Hz, CH_2Ph), 7.09–7.44 (m, 10H, Ph). ^{13}C NMR δ: 15.2 (OCH_2CH_3), 22.4 (C-5), 23.0 (C-5), 33.2 (C-4), 53.7 (CH_2Ph), 61.1 (C-3), 61.9 (OCH_2CH_3), 64.2 (C-2), 128.2, 128.3, 129.5, 129.7, 130.1, 133.3, 135.4, 141.3 (Ph), 174.7 (C-1).

3.1.5. *syn*-Ethyl 2-benzylamino-4-phenyl-3-(phenylselanyl)butanoate 2e.[5b,16] Oil, yield=52%. ^1H NMR δ: 1.00 (t, 3H, J=7.2 Hz, OCH_2CH_3), 2.21 (s, 1H, NH), 3.10 (dd, 1H, J=7.2, 13.9 Hz, H-4), 3.15 (dd, 1H, J=7.3, 13.9 Hz, H-4), 3.29 (d, 1H, J=2.9 Hz, H-2), 3.49 (d, 1H, J=12.8 Hz, CH_2Ph), 3.66 (dt, 1H, J=2.9, 7.2 Hz, H-3), 3.69 (dq, 1H, J=7.2, 10.7 Hz, OCH_2CH_3), 3.86 (dq, 1H, J=7.2, 10.7 Hz, OCH_2CH_3), 3.88 (d, 1H, J=12.8 Hz, CH_2Ph), 7.05–7.43 (m, 15H, Ph). ^{13}C NMR δ: 13.0 (OCH_2CH_3), 39.4 (C-4), 50.6 (C-3), 51.5 (CH_2Ph), 59.8 (OCH_2CH_3), 61.3 (C-2), 125.4, 126.0, 126.5, 127.3, 127.4, 127.8, 128.2, 128.4, 129.1, 133.7, 138.6, 139.1 (Ph), 172.1 (C-1).

3.1.6. Ethyl 2-benzylamino-3-methyl-3-(phenylselanyl)-butanoate 2f.[16] Oil, yield=55%. ^1H NMR δ: 1.15 (t, 3H, J=7.1 Hz, OCH_2CH_3), 1.22 (s, 3H, H-4), 1.35 (s, 3H, H-4), 2.22 (s, 1H, NH), 3.21 (s, 1H, H-2), 3.55 (d, 1H, J=13.1 Hz, CH_2Ph), 3.78 (d, 1H, J=12.8 Hz, CH_2Ph), 4.11 (q, 2H, J=7.1 Hz, OCH_2CH_3), 7.16–7.42 (m, 10H, Ph). ^{13}C NMR δ: 13.3 (OCH_2CH_3), 25.2 (C-4), 26.9 (C-4), 47.6 (C-3), 51.6 (CH_2Ph), 59.6 (OCH_2CH_3), 68.3 (C-2), 126.1, 126.8, 127.0, 127.3, 127.5, 127.6, 137.4, 138.5 (Ph), 172.0 (C-1).

3.2. Cyclisation of β-(phenylselanyl)α-aminoesters 2

Procedure A with Me_3OBF_4. To the β-(phenylselanyl) α-aminoester **2** (1 mmol) in dichloromethane (10 mL) was added Me_3OBF_4 (310 mg, 2.1 mmol) at room temperature. After 12 h of stirring, the mixture was washed with a solution of sodium hydroxide 1 N (10 mL). 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 silica gel chromatography (cyclohexane/ether: 75:25) to afford aziridine **3**.

Procedure B with NBS. To the β-(phenylselanyl) α-aminoester **2** (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 silica gel chromatography (cyclohexane/ether: 75:25) to afford aziridine **3**.

3.2.1. *cis*-Ethyl 1-benzyl-3-methylaziridine-2-carboxylate 3a.[3j,16,18] Oil, yield=49% (A), yield=45% (B). ^1H NMR δ: 1.18 (t, 3H, J=7.2 Hz, OCH_2CH_3), 1.21 (d, 3H, J=5.5 Hz, CH_3), 1.90–1.95 (m, 1H, H-3), 2.13 (d, 1H, J=6.8 Hz, H-2), 3.54 (d, 1H, J=13.9 Hz, CH_2Ph), 3.61 (d, 1H, J=13.9 Hz, CH_2Ph), 4.08 (dq, 1H, J=7.2, 10.7 Hz, OCH_2CH_3), 4.11 (dq, 1H, J=7.2, 10.7 Hz, OCH_2CH_3), 7.13–7.28 (m, 5H, Ph). ^{13}C NMR δ: 13.5 (CH_3), 14.7 (OCH_2CH_3), 42.1 (C-3), 43.1 (C-2), 61.3 (OCH_2CH_3), 64.0 (CH_2Ph), 127.5, 128.1, 128.6, 138.4 (Ph), 170.0 (C=O).

3.2.2. *cis*-Ethyl 1-benzyl-3-ethylaziridine-2-carboxylate 3b.[16] Oil, yield=57% (A), yield=66% (B). ^1H NMR δ: 0.82 (t, 3H, J=7.4 Hz, CH_2CH_3), 1.20 (t, 3H, J=7.1 Hz, OCH_2CH_3), 1.42–1.49 (m, 1H, CH_2CH_3), 1.56–1.63 (m, 1H, CH_2CH_3), 1.81 (q, 1H, J=6.8 Hz, H-3), 2.17 (d, 1H, J=6.8 Hz, H-2), 3.52 (s, 2H, CH_2Ph), 4.13 (q, 2H, J=7.2 Hz, OCH_2CH_3), 7.16–7.28 (m, 5H, Ph). ^{13}C NMR δ: 11.9 (CH_2CH_3), 14.7 (OCH_2CH_3), 21.5 (CH_2CH_3), 43.0 (C-2), 48.5 (C-3), 61.3 (OCH_2CH_3), 64.3 (CH_2Ph), 127.6, 128.5, 128.7, 138.4 (Ph), 170.2 (C=O). Anal. Calcd for $C_{14}H_{19}NO_2$: C, 72.07; H, 8.21; N, 6.00. Found: C, 72.38; H, 8.55; N, 6.19.

3.2.3. *cis*-Ethyl 1-benzyl-3-propylaziridine-2-carboxylate 3c.[16] Oil, yield=61% (A), yield=67% (B). ^1H NMR δ: 0.80 (t, 3H, J=7.2 Hz, $CH_2CH_2CH_3$), 1.19 (t, 3H, J=7.2 Hz, OCH_2CH_3), 1.28–1.63 (m, 4H, $CH_2CH_2CH_3$), 1.85 (q, 1H, J=6.8 Hz, H-3), 2.17 (d, 1H, J=6.8 Hz, H-2), 3.49 (d, 1H, J=13.7 Hz, CH_2Ph), 3.56 (d, 1H, J=13.7 Hz, CH_2Ph), 4.13 (q, 2H, J=7.2 Hz, OCH_2CH_3), 7.19–7.27 (m, 5H, Ph). ^{13}C NMR δ: 12.7 ($CH_2CH_2CH_3$), 13.3 (OCH_2CH_3), 19.6 ($CH_2CH_2CH_3$), 28.7 ($CH_2CH_2CH_3$), 41.6 (C-2), 45.6 (C-3), 59.8 (OCH_2CH_3), 62.9 (CH_2Ph), 126.1, 127.0, 127.3, 136.9 (Ph), 168.8 (C=O). Anal. Calcd for $C_{15}H_{21}NO_2$: C, 72.84; H, 8.56; N, 5.67. Found: C, 72.81; H, 8.66; N, 5.89.

3.2.4. *cis*-Ethyl 1-benzyl-3-*iso*-propylaziridine-2-carboxylate 3d.[16] Oil, yield=54% (A), yield=61% (B). ^1H NMR δ: 0.72 (d, 3H, J=6.2 Hz, $CH(CH_3)_2$), 0.79 (d, 3H, J=6.2 Hz, $CH(CH_3)_2$), 1.15 (t, 3H, J=7.1 Hz, OCH_2CH_3), 1.48–1.53 (m, 2H, H-3, $CH(CH_3)_2$), 2.15 (d, 1H, J=6.3 Hz, H-2), 3.43 (d, 1H, J=13.9 Hz, CH_2Ph), 3.47

(d, 1H, J=13.9 Hz, CH_2Ph), 4.10 (q, 2H, J=7.1 Hz, OCH_2CH$_3$), 7.10–7.25 (m, 5H, Ph). ^{13}C NMR δ: 13.3 (OCH$_2$CH$_3$), 18.6 (CH(CH$_3$)$_2$), 19.9 (CH(CH$_3$)$_2$), 26.2 (CH(CH$_3$)$_2$), 42.0 (C-2), 52.4 (C-3), 59.8 (OCH$_2$CH$_3$), 63.2 (CH$_2$Ph), 127.5, 128.1, 128.6, 138.4 (Ph), 170.0 (C=O). Anal. Calcd for $C_{15}H_{21}NO_2$: C, 72.84; H, 8.56; N, 5.67. Found: C, 73.31; H, 8.99; N, 6.02.

3.2.5. *cis*-Ethyl 1,3-dibenzylaziridine-2-carboxylate 3e.[5b,16] Oil, yield=48% (A), yield=52% (B). ^{1}H NMR δ: 1.18 (t, 3H, J=7.1 Hz, OCH$_2$CH$_3$), 2.10 (q, 1H, J=6.8 Hz, H-3), 2.22 (d, 1H, J=6.8 Hz, H-2), 2.77 (dd, 1H, J=6.8, 14.7 Hz, CH$_2$Ph), 2.98 (dd, 1H, J=5.9, 14.7 Hz, CH$_2$Ph), 3.48 (d, 1H, J=13.7 Hz, CH$_2$Ph), 3.56 (d, 1H, J=13.7 Hz, CH$_2$Ph), 4.14 (q, 2H, J=7.1 Hz, OCH$_2$CH$_3$), 7.07–7.23 (m, 10H, Ph). δ_C (75.4 MHz, CDCl$_3$): 13.3 (OCH$_2$CH$_3$), 33.0 (CH$_2$Ph), 41.4 (C-2), 46.4 (C-3), 60.0 (OCH$_2$CH$_3$), 62.6 (CH$_2$Ph), 125.3, 126.1, 127.0, 127.3, 127.6, 128.4, 136.7, 137.7 (Ph), 168.6 (C=O).

3.2.6. Ethyl 1-benzyl-3,3-dimethylaziridine-2-carboxylate 3f. Oil, yield=65% (B). ^{1}H NMR δ: 1.20 (t, 3H, J=7.2 Hz, OCH$_2$CH$_3$), 1.26 (s, 3H, CH$_3$), 1.28 (s, 3H, CH$_3$), 2.05 (s, 1H, H-2), 3.68 (d, 1H, J=14.8 Hz, CH$_2$Ph), 3.75 (d, 1H, J=14.8 Hz, CH$_2$Ph), 4.14 (q, 2H, J=7.2 Hz, OCH$_2$CH$_3$), 7.15–7.26 (m, 5H, Ph). ^{13}C NMR δ: 14.5 (OCH$_2$CH$_3$), 18.0 (CH$_3$), 21.9 (CH$_3$), 44.8 (C-3), 49.4 (C-2), 56.0 (CH$_2$Ph), 60.9 (OCH$_2$CH$_3$), 126.8, 127.4, 128.4, 139.3 (Ph), 170.4 (C=O). Anal. Calcd for $C_{14}H_{19}NO_2$: C, 72.07; H, 8.21; N, 6.00. Found: C, 72.14; H, 7.79; N, 6.34.

3.3. Synthesis of β-(phenylselanyl)α-aminoesters 5

3.3.1. Preparation of β-(phenylselanyl)α-iminoesters 4. The protocol is the same as the one for the synthesis of α-(phenylselanyl)α-aminoesters **2**. The β-(phenylselanyl) α-iminoesters **4** were isolated but not purified because of decomposition. That is why we just reported their ^{1}H NMR spectrum.

3.3.1.1. Ethyl-2-((*R*)-1-phenylethylimino)-3-(phenylselanyl)butanoate 4a. Oil, two diastereomers: 50/50, conv.=100%. ^{1}H NMR δ: 1.34–1.63 (m, 9H, H-4, CH(Ph)CH$_3$, OCH$_2$CH$_3$), 4.14, 4.16 (2×q, 1H, J=6.9 Hz, H-3), 4.30–4.40 (m, 2H, OCH$_2$CH$_3$), 4.70, 4.73 (2×q, 1H, J=6.4 Hz, CH(Ph)CH$_3$), 7.24–7.65 (m, 10H, Ph).

3.3.1.2. Ethyl 2-((*R*)-1-phenylethylimino)-3-(phenylselanyl)pentanoate 4b. Oil, two diastereomers: 50/50, conv.=100%. ^{1}H NMR δ: 0.98 (t, 3H, J=7.4 Hz, H-5), 1.19–1.31 (m, 6H, CH(Ph)CH$_3$, OCH$_2$CH$_3$), 1.68–1.78 (m, 1H, H-4), 1.90–2.02 (m, 1H, H-4), 3.83, 3.88 (2×t, 1H, J=7.4 Hz, H-3), 4.23, 4.28 (2×q, 2H, J=7.2 Hz, OCH$_2$CH$_3$), 4.60, 4.62 (2×q, 1H, J=6.4 Hz, CH(Ph)CH$_3$), 6.95–7.45 (m, 10H, Ph).

3.3.1.3. Ethyl 2-((*R*)-1-phenylethylimino)-3-(phenylselanyl)hexanoate 4c. Oil, two diastereomers: 50/50, conv.=100%. ^{1}H NMR δ: 0.83, 0.85 (2×t, 3H, J=7.2 Hz, H-6), 1.19–1.31 (m, 6H, CH(Ph)CH$_3$, OCH$_2$CH$_3$), 1.32–1.60 (m, 2H, H-5), 1.62–1.89 (m, 1H, H-4), 1.87–2.03 (m, 1H, H-4), 3.88, 3.93 (2×t, 1H, J=7.9 Hz, H-3), 4.23, 4.28 (2×q, 2H, J=7.2 Hz, OCH$_2$CH$_3$), 4.60, 4.62 (2×q, 1H, J=6.4 Hz, CH(Ph)CH$_3$), 6.95–7.42 (m, 10H, Ph).

3.3.1.4. Ethyl 2-((*R*)-1-phenylethylimino)-4-phenyl-3-(phenylselanyl)butanoate 4e. Oil, two diastereomers: 50/50, conv.=100%. ^{1}H NMR δ: 1.54–1.32 (m, 6H, CH(Ph)CH$_3$, OCH$_2$CH$_3$), 2.98–3.09 (m, 1H, H-4), 3.32–3.45 (m, 1H, H-4), 4.16–4.29 (m, 3H, H-3, OCH$_2$CH$_3$), 4.58–4.69 (m, 1H, CH(Ph)CH$_3$), 7.11–7.45 (m, 15H, Ph).

3.3.2. Reduction of α-(phenylselanyl)α-iminoesters 4. The protocol is the same as the one for the synthesis of α-(phenylselanyl)α-aminoesters **2**.

3.3.2.1. Ethyl 2-((*R*)-1-phenylethylamino)-3-(phenylselanyl)butanoate 5a, 5′a. Oil, **5a/5′a**: 50/50, yield=47%.

(2R,3R)-Ethyl 2-((R)-1-phenylethylamino)-3-(phenylselanyl)butanoate **5′a**. (First eluted). ^{1}H NMR δ: 1.19 (t, 3H, J=7.2 Hz, OCH$_2$CH$_3$), 1.34 (d, 3H, J=6.6 Hz, CH(Ph)CH$_3$), 1.46 (d, 3H, J=6.9 Hz, H-4), 2.37 (s, 1H, NH), 3.36 (d, 1H, J=5.9 Hz, H-2), 3.57 (qd, 1H, J=5.9, 6.9 Hz, H-3), 3.77 (q, 1H, J=6.6 Hz, CH(Ph)CH$_3$), 3.89 (q, 2H, J=7.2 Hz, OCH$_2$CH$_3$), 7.25–7.52 (m, 10H, Ph). ^{13}C NMR δ: 14.2 (OCH$_2$CH$_3$), 20.0 (C-4), 23.3 (CH(Ph)CH$_3$), 43.3 (C-3), 57.5 (CH(Ph)CH$_3$), 61.0 (OCH$_2$CH$_3$), 64.5 (C-2), 127.2, 127.3, 127.7, 128.5, 128.9, 129.1, 135.3, 145.4 (Ph), 173.4 (C-1). $[\alpha]_D^{25}$ +14.8 (c 1.0 in CHCl$_3$).

(2S,3S)-Ethyl 2-((R)-1-phenylethylamino)-3-(phenylselanyl)butanoate **5a**. (Second eluted). ^{1}H NMR δ: 1.14 (t, 3H, J=7.2 Hz, OCH$_2$CH$_3$), 1.37 (d, 3H, J=6.9 Hz, H-4), 1.38 (d, 3H, J=6.4 Hz, CH(Ph)CH$_3$), 2.19 (s, 1H, NH), 3.09 (d, 1H, J=5.1 Hz, H-2), 3.54 (qd, 1H, J=5.1, 6.9 Hz, H-3), 3.73 (q, 1H, J=6.4 Hz, CH(Ph)CH$_3$), 4.01 (dq, 1H, J=7.2, 10.7 Hz, OCH$_2$CH$_3$), 4.18 (dq, 1H, J=7.2, 10.7 Hz, OCH$_2$CH$_3$), 7.23–7.47 (m, 10H, Ph). ^{13}C NMR δ: 14.3 (OCH$_2$CH$_3$), 20.5 (C-4), 25.4 (CH(Ph)CH$_3$), 43.2 (C-3), 57.0 (CH(Ph)CH$_3$), 60.9 (OCH$_2$CH$_3$), 63.9 (C-2), 126.9, 127.2, 127.7, 128.5, 128.9, 129.1, 135.2, 145.4 (Ph), 173.7 (C-1). $[\alpha]_D^{25}$ −17.1 (c 1.0 in CHCl$_3$).

3.3.2.2. Ethyl 2-((*R*)-1-phenylethylamino)-3-(phenylselanyl)pentanoate 5b, 5′b. Oil, **5b/5′b**: 50/50, yield=53%.

(2S,3S)-Ethyl 2-((R)-1-phenylethylamino)-3-(phenylselanyl)pentanoate **5b**. (First eluted). ^{1}H NMR δ: 0.86 (t, 3H, J=7.2 Hz, H-5), 1.08 (t, 3H, J=7.2 Hz, OCH$_2$CH$_3$), 1.40 (d, 3H, J=6.4 Hz, CH(Ph)CH$_3$), 1.64–1.92 (m, 2H, H-4), 2.28 (s, 1H, NH), 3.24 (d, 1H, J=3.3 Hz, H-2), 3.39 (td, 1H, J=3.3, 7.2 Hz, H-3), 3.62–3.78 (m, 2H, OCH$_2$CH$_3$, CH(Ph)CH$_3$), 3.82–2.92 (m, 1H, OCH$_2$CH$_3$), 7.09–7.48 (m, 10H, Ph). ^{13}C NMR δ: 12.8 (C-5), 14.1 (OCH$_2$CH$_3$), 25.3 (CH(Ph)CH$_3$), 27.4 (C-4), 53.1 (C-3), 56.9 (CH(Ph)CH$_3$) 60.7 (OCH$_2$CH$_3$), 61.8 (C-2), 127.2, 127.4, 127.5, 128.4, 128.9, 130.0, 134.7, 145.4 (Ph), 173.7 (C-1). $[\alpha]_D^{25}$ −16.3 (c 1.0, CHCl$_3$).

(2R,3R)-Ethyl 2-((R)-1-phenylethylamino)-3-(phenylselanyl)pentanoate **5′b**. (Second eluted). ^{1}H NMR δ: 1.08 (t, 3H, J=7.2 Hz, OCH$_2$CH$_3$), 1.11 (t, 3H, J=7.2 Hz, H-5), 1.34 (d, 3H, J=6.6 Hz, CH(Ph)CH$_3$), 1.81–1.98 (m, 2H,

H-4), 2.38 (s, 1H, N*H*), 3.41 (ddd, 1H, J=4.1, 6.4, 7.7 Hz, H-3), 3.53 (d, 1H, J=4.1 Hz, H-2), 3.72–3.78 (m, 2H, C*H*(Ph)CH$_3$, OC*H*$_2$CH$_3$), 3.79–3.84 (m, 1H, OC*H*$_2$CH$_3$), 7.24–7.54 (m, 10H, Ph). ^{13}C NMR δ: 12.9 (C-5), 14.1 (OCH$_2$*C*H$_3$), 23.3 (CH(Ph)*C*H$_3$), 37.2 (C-4), 53.3 (C-3), 57.3 (*C*H(Ph)CH$_3$), 60.9 (O*C*H$_2$CH$_3$), 62.2 (C-2), 126.8, 127.2, 127.4, 128.4, 128.9, 134.4, 134.7, 145.6 (Ph), 173.5 (C-1). $[\alpha]_D^{25}$ +12.1 (*c* 1.0, CHCl$_3$).

3.3.2.3. Ethyl 2-((*R*)-1-phenylethylamino)-3-(phenylselanyl)hexanoate 5c, 5′c. Oil, **5c/5′c**: 50/50, yield=51%.

(2S,3S)-Ethyl 2-((R)-1-phenylethylamino)-3-(phenylselanyl)hexanoate **5c**. (First eluted). ^{1}H NMR δ: 0.71 (t, 3H, J=7.2 Hz, H-6), 0.98 (t, 3H, J=7.2 Hz, OCH$_2$C*H*$_3$), 1.18–1.32 (m, 2H, H-5), 1.30 (d, 3H, J=6.4 Hz, CH(Ph)C*H*$_3$), 1.57–1.73 (m, 2H, H-4), 2.16 (s, 1H, N*H*), 3.11 (d, 1H, J=3.3 Hz, H-2), 3.83 (td, 1H, J=3.3, 7.2 Hz, H-3), 3.63 (dq, 1H, J=7.2, 10.7 Hz, OC*H*$_2$CH$_3$), 3.68 (q, 1H, J=6.4 Hz, C*H*(Ph)CH$_3$), 3.86 (dq, 1H, J=7.2, 10.7 Hz, OC*H*$_2$CH$_3$), 7.11–7.41 (m, 10H, Ph). ^{13}C NMR δ: 13.7 (C-6), 14.1 (OCH$_2$*C*H$_3$), 21.2 (C-5), 25.3 (CH(Ph)*C*H$_3$), 36.4 (C-4), 50.7 (C-3), 57.0 (*C*H(Ph)CH$_3$), 60.8 (O*C*H$_2$CH$_3$), 61.9 (C-2), 127.2, 127.4, 127.5, 128.4, 129.0, 130.1, 134.7, 145.5 (Ph), 173.8 (C-1). $[\alpha]_D^{25}$ −14.2 (*c* 1.0 in CHCl$_3$).

(2R,3R)-Ethyl 2-((R)-1-phenylethylamino)-3-(phenylselanyl)hexanoate **5′c**. (Second eluted). ^{1}H NMR δ: 0.84 (t, 3H, J=7.2 Hz, H-6), 0.98 (t, 3H, J=7.2 Hz, OCH$_2$C*H*$_3$), 1.24 (d, 3H, J=6.4 Hz, CH(Ph)C*H*$_3$), 1.31–1.61 (m, 2H, H-5), 1.68–1.85 (m, 2H, H-4), 2.29 (s, 1H, N*H*), 3.36–3.43 (m, 2H, H-2, H-3), 3.67–3.82 (m, 3H, C*H*(Ph)CH$_3$, OC*H*$_2$CH$_3$), 7.15–7.45 (m, 10H, Ph). ^{13}C NMR δ: 13.9 (C-6), 14.1 (OCH$_2$*C*H$_3$), 21.3 (C-5), 23.4 (CH(Ph)*C*H$_3$), 36.3 (C-4), 51.1 (C-3), 57.3 (*C*H(Ph)CH$_3$), 60.9 (O*C*H$_2$CH$_3$), 62.5 (C-2), 126.9, 127.2, 127.3, 127.4, 128.4, 128.5, 134.7, 145.7 (Ph), 173.5 (C-1). $[\alpha]_D^{25}$ +11.7 (*c* 1.0 in CHCl$_3$).

3.3.2.4. Ethyl 2-((*R*)-1-phenylethylamino)-4-phenyl-3-(phenylselanyl)butanoate 5e, 5′e. Oil, **5e/5′e**: 50/50, yield=50%.

(2S,3S)-Ethyl 2-((R)-1-phenylethylamino)-4-phenyl-3-(phenylselanyl)butanoate **5e**. (First eluted). ^{1}H NMR δ: 0.95 (t, 3H, J=7.2 Hz, OCH$_2$C*H*$_3$), 1.35 (d, 3H, J=6.6 Hz, CH(Ph)C*H*$_3$), 2.39 (s, 1H, N*H*), 2.86 (dd, 1H, J=6.9, 14.1 Hz, H-4), 2.99 (dd, 1H, J=7.9, 14.1 Hz, H-4), 3.18 (d, 1H, J=2.8 Hz, H-2), 3.47–3.51 (m, 1H, H-3), 3.65–3.69 (m, 2H, C*H*(Ph)CH$_3$, OC*H*$_2$CH$_3$), 3.84 (dq, 1H, J=7.2, 10.7 Hz, OC*H*$_2$CH$_3$), 6.78–7.22 (m, 15H, Ph). ^{13}C NMR δ: 14.1 (OCH$_2$*C*H$_3$), 25.2 (CH(Ph)*C*H$_3$), 39.8 (C-4), 52.9 (C-3), 57.2 (*C*H(Ph)CH$_3$), 59.9 (O*C*H$_2$CH$_3$), 61.9 (C-2), 126.3, 127.2, 127.3, 127.5, 127.7, 128.3, 128.4, 128.9, 129.4, 134.8, 139.8, 145.4 (Ph), 173.6 (C-1). $[\alpha]_D^{25}$ −15.4 (*c* 1.0 in CHCl$_3$).

(2R,3R)-Ethyl 2-((R)-1-phenylethylamino)-4-phenyl-3-(phenylselanyl)butanoate **5′e**. (Second eluted). ^{1}H NMR δ: 1.04 (t, 3H, J=7.2 Hz, OCH$_2$C*H*$_3$), 1.26 (d, 3H, J=6.4 Hz, CH(Ph)C*H*$_3$), 2.37 (s, 1H, N*H*), 3.21 (dd, 1H, J=7.4, 14.1 Hz, H-4), 3.30 (dd, 1H, J=7.9, 14.1 Hz, H-4), 3.49 (d, 1H, J=3.1 Hz, H-2), 3.73–3.79 (m, 3H, H-3, C*H*(Ph)CH$_3$, OC*H*$_2$CH$_3$), 3.87 (dq, 1H, J=7.2, 10.7 Hz, OC*H*$_2$CH$_3$), 7.15–7.42 (m, 15H, Ph). ^{13}C NMR δ: 14.0 (OCH$_2$*C*H$_3$), 23.0 (CH(Ph)*C*H$_3$), 40.4 (C-4), 51.9 (C-3), 56.9 (*C*H(Ph)CH$_3$), 60.9 (O*C*H$_2$CH$_3$), 61.1 (C-2), 126.5, 126.8, 127.1, 127.4, 127.5, 128.1, 128.3, 128.5, 129.4, 134.8, 139.7, 145.5 (Ph), 173.2 (C-1). $[\alpha]_D^{25}$ +13.6 (*c* 1.0 in CHCl$_3$).

3.4. Cyclisation of β-(phenylselanyl)α-aminoesters 5, 5′

The protocols are the same as for the cyclisation of β-(phenylselanyl)α-aminoesters **2**.

Procedure A with Me$_3$OBF$_4$. β-(Phenylselanyl)α-aminoesters **5** (or **5′**) afforded aziridines **6** (or **6′**).

Procedure B with NBS. β-(Phenylselanyl)α-aminoester **5** (or **5′**) afforded aziridines **6** (or **6′**), except for **5a**, which lead to **6″a**.

3.4.1. (2*R*,3*R*)-Ethyl 3-methyl-1-((*R*)-1-phenylethyl)-aziridine-2-carboxylate 6a.[5b] Oil, yield=47% (A). ^{1}H NMR δ: 1.11 (d, 3H, J=5.6 Hz, C*H*$_3$), 1.23 (t, 3H, J=7.2 Hz, OCH$_2$C*H*$_3$), 1.37 (d, 3H, J=6.4 Hz, CH(Ph)C*H*$_3$), 1.78–1.82 (m, 1H, H-3), 2.15 (d, 1H, J=6.6 Hz, H-2), 2.56 (q, 1H, J=6.4 Hz, C*H*(Ph)CH$_3$), 4.15 (dq, 1H, J=7.2, 10.7 Hz, OC*H*$_2$CH$_3$), 4.17 (dq, 1H, J=7.2, 10.7 Hz, OC*H*$_2$CH$_3$), 7.17–7.33 (m, 5H, Ph). ^{13}C NMR δ: 13.3 (*C*H$_3$), 14.6 (OCH$_2$*C*H$_3$), 23.1 (CH(Ph)*C*H$_3$), 41.3 (C-3), 43.3 (C-2), 61.0 (O*C*H$_2$CH$_3$), 69.8 (*C*H(Ph)CH$_3$), 126.9, 127.2, 128.5, 143.9 (Ph), 170.0 (C=O). MS *m*/*z*: 233 (M$^+$, 2), 128 (68), 105 (100). IR ν_{max} (neat) cm^{-1}: 2967, 1744, 1450, 1186. Anal. Calcd for C$_{14}$H$_{19}$NO$_2$: C, 72.10; H, 8.21; N, 6.00. Found: C, 72.45; H, 8.19; N, 6.33. $[\alpha]_D^{25}$ +57.3 (*c* 1.0 in CH$_2$Cl$_2$).

3.4.2. (2*S*,3*S*)-Ethyl 3-methyl-1-((*R*)-1-phenylethyl)-aziridine-2-carboxylate 6′a.[5b] Oil, yield=49% (A), yield=51% (B). ^{1}H NMR δ: 1.13 (t, 3H, J=7.2 Hz, OCH$_2$C*H*$_3$), 1.28 (d, 3H, J=5.4 Hz, C*H*$_3$), 1.36 (d, 3H, J=6.6 Hz, CH(Ph)C*H*$_3$), 1.94–2.00 (m, 1H, H-3), 2.02 (d, 1H, J=6.9 Hz, H-2), 2.57 (q, 1H, J=6.6 Hz, C*H*(Ph)CH$_3$), 4.06 (dq, 1H, J=7.2, 10.7 Hz, OC*H*$_2$CH$_3$), 4.08 (dq, 1H, J=7.2, 10.7 Hz, OC*H*$_2$CH$_3$), 7.15–7.31 (m, 5H, Ph). ^{13}C NMR δ: 13.8 (*C*H$_3$), 14.5 (OCH$_2$*C*H$_3$), 23.9 (CH(Ph)*C*H$_3$), 42.4 (C-3), 42.7 (C-2), 59.9 (O*C*H$_2$CH$_3$), 69.8 (*C*H(Ph)CH$_3$), 126.7, 127.1, 128.5, 143.3 (Ph), 168.1 (C=O). MS *m*/*z*: 233 (M$^+$, 2), 128 (84), 105 (100). IR ν_{max} (neat) cm^{-1}: 2967, 1744, 1450, 1186. Anal. Calcd for C$_{14}$H$_{19}$NO$_2$: C, 72.10; H, 8.21; N, 6.00. Found: C, 71.81; H, 8.08; N, 6.13. $[\alpha]_D^{25}$ −20.9 (*c* 1.0 in CH$_2$Cl$_2$).

3.4.3. (2*R*,3*R*)-Ethyl 1-((*R*)-1-phenylethyl)-3-ethyl-aziridine-2-carboxylate 6b. Oil, yield=50% (A), yield=55%(B). ^{1}H NMR δ: 0.58 (t, 3H, J=7.4 Hz, CH$_2$C*H*$_3$), 1.25 (t, 3H, J=7.2 Hz, OCH$_2$C*H*$_3$), 1.39 (d, 3H, J=6.6 Hz, CH(Ph)C*H*$_3$), 1.38–1.55 (m, 2H, C*H*$_2$CH$_3$), 1.70 (q, 1H, J=6.6 Hz, H-3), 2.17 (d, 1H, J=6.6 Hz, H-2), 2.53 (q, 1H, J=6.6 Hz, C*H*(Ph)CH$_3$), 4.16 (dq, 2H, J=7.2, 12.3 Hz, OC*H*$_2$CH$_3$), 7.16–7.41 (m, 5H, Ph). ^{13}C NMR δ: 11.4 (CH$_2$*C*H$_3$), 14.4 (OCH$_2$*C*H$_3$), 21.2 (*C*H$_2$CH$_3$), 22.6 (CH(Ph)*C*H$_3$), 43.0 (C-2), 47.7 (C-3), 60.9 (O*C*H$_2$CH$_3$), 70.0 (*C*H(Ph)CH$_3$), 127.2, 127.3, 128.3, 143.6 (Ph), 170.0

(C═O). MS *m/z*: 247 (M^+, 16), 142 (16), 105 (100). IR ν_{max} (neat) cm^{-1}: 2968, 1744, 1451, 1185. Anal. Calcd for $C_{15}H_{21}NO_2$: C, 58.29; H, 8.50; N, 5.66. Found: C, 58.39; H, 8.71; N, 5.48. $[\alpha]_D^{25}$ +56.9 (*c* 1.0, CH_2Cl_2).

3.4.4. (2*S*,3*S*)-Ethyl 1-((*R*)-1-phenylethyl)-3-ethylaziridine-2-carboxylate 6′b. Oil, yield=56% (A), yield=49% (B). ^1H NMR δ: 0.97 (t, 3H, *J*=7.4 Hz, CH_2CH_3), 1.16 (t, 3H, *J*=7.2 Hz, OCH_2CH_3), 1.38 (d, 3H, *J*=6.6 Hz, CH(Ph)CH_3), 1.39–1.73 (m, 2H, CH_2CH_3), 1.84 (dt, 1H, *J*=6.9, 6.1 Hz, H-3), 2.05 (d, 1H, *J*=6.9 Hz, H-2), 2.56 (q, 1H, *J*=6.6 Hz, CH(Ph)CH_3), 4.07 (dq, 1H, *J*=7.2, 10.5 Hz, OCH_2CH_3), 4.09 (dq, 1H, *J*=7.2, 10.5 Hz, OCH_2CH_3), 7.11–7.41 (m, 5H, Ph). ^{13}C NMR δ: 11.9 (CH_2CH_3), 14.3 (OCH_2CH_3), 21.4 (CH_2CH_3), 23.8 (CHαCH_3), 42.5 (C-2), 48.9 (C-3), 60.8 (OCH_2CH_3), 69.5 (CH(Ph)CH_3), 126.6, 127.0, 128.4, 143.8 (Ph), 169.7 (C═O). MS *m/z*: 247 (M^+, 2), 142 (100), 105 (84). IR ν_{max} (neat) cm^{-1}: 2967, 1744, 1450, 1186. Anal. Calcd for $C_{15}H_{21}NO_2$: C, 58.29; H, 8.50; N, 5.66. Found: C, 58.72; H, 8.84; N, 5.27. $[\alpha]_D^{25}$ −19.1 (*c* 1.0, CH_2Cl_2).

3.4.5. (2*R*,3*R*)-Ethyl 1-((*R*)-1-phenylethyl)-3-propylaziridine-2-carboxylate 6c. Oil, yield=55% (A), yield=61% (B). ^1H NMR δ: 0.64 (t, 3H, *J*=7.4 Hz, $CH_2CH_2CH_3$), 0.95–1.08 (m, 2H, $CH_2CH_2CH_3$), 1.21 (t, 3H, *J*=7.2 Hz, OCH_2CH_3), 1.38–1.54 (m, 2H, $CH_2CH_2CH_3$), 1.40 (d, 3H, *J*=6.4 Hz, CH(Ph)CH_3), 1.70–1.76 (m, 1H, H-3), 2.15 (d, 1H, *J*=6.9 Hz, H-2), 2.51 (q, 1H, *J*=6.4 Hz, CH(Ph)CH_3), 4.14 (dq, 1H, *J*=7.2, 10.7 Hz, OCH_2CH_3), 4.16 (dq, 1H, *J*=7.2, 10.7 Hz, OCH_2CH_3), 7.23–7.32 (m, 5H, Ph). ^{13}C NMR δ: 13.7 ($CH_2CH_2CH_3$), 14.4 (OCH_2CH_3), 20.5 ($CH_2CH_2CH_3$), 22.7 (CH(Ph)CH_3), 29.9 ($CH_2CH_2CH_3$), 43.2 (C-2), 46.1 (C-3), 60.9 (OCH_2CH_3), 70.2 (CH(Ph)CH_3), 127.3, 127.4, 128.4, 143.7 (Ph), 170.1 (C═O). MS *m/z*: 261 (M^+, 5), 156 (100), 105 (81), 82 (49). IR ν_{max} (neat) cm^{-1}: 2978, 1744, 1453, 1184. Anal. Calcd for $C_{16}H_{23}NO_2$: C, 73.53; H, 8.87; N, 5.36. Found: C, 73.69; H, 9.07; N, 5.38. $[\alpha]_D^{25}$ +41.2 (*c* 1.0 in CH_2Cl_2).

3.4.6. (2*S*,3*S*)-Ethyl 1-((*R*)-1-phenylethyl)-3-propylaziridine-2-carboxylate 6′c. Oil, yield=52% (A), yield=58% (B). ^1H NMR δ: 0.90 (t, 3H, *J*=7.2 Hz, $CH_2CH_2CH_3$), 1.14 (t, 3H, *J*=7.2 Hz, OCH_2CH_3), 1.18–1.63 (m, 4H, $CH_2CH_2CH_3$), 1.38 (d, 3H, *J*=6.4 Hz, CH(Ph)CH_3), 1.84–1.91 (m, 1H, H-3), 2.05 (d, 1H, *J*=6.9 Hz, H-2), 2.56 (q, 1H, *J*=6.4 Hz, CH(Ph)CH_3), 4.08 (dq, 1H, *J*=7.2, 10.7 Hz, OCH_2CH_3), 4.11 (dq, 1H, *J*=7.2, 10.7 Hz, OCH_2CH_3), 7.16–7.32 (m, 5H, Ph). ^{13}C NMR δ: 14.0 ($CH_2CH_2CH_3$), 14.4 (OCH_2CH_3), 21.0 ($CH_2CH_2CH_3$), 23.8 (CH(Ph)CH_3), 30.2 ($CH_2CH_2CH_3$), 42.5 (C-2), 47.4 (C-3), 60.8 (OCH_2CH_3), 69.7 (CH(Ph)CH_3), 126.7, 127.1, 128.3, 143.9 (Ph), 169.7 (C═O). IR ν_{max} (neat) cm^{-1}: 2978, 1744, 1453, 1184. Anal. Calcd for $C_{16}H_{23}NO_2$: C, 73.53; H, 8.87; N, 5.36. Found: C, 73.85; H, 9.12; N, 5.54. $[\alpha]_D^{25}$ −18.4 (*c* 1.0 in CH_2Cl_2).

3.4.7. (2*R*,3*R*)-Ethyl 3-benzyl-1-((*R*)-1-phenylethyl)-aziridine-2-carboxylate 6e.[5b] Oil, yield=41% (A), yield=48% (B). ^1H NMR δ: 1.20 (t, 3H, *J*=7.2 Hz, OCH_2CH_3), 1.38 (d, 3H, *J*=6.6 Hz, CH(Ph)CH_3), 2.00–2.05 (m, 1H, H-3), 2.22 (d, 1H, *J*=6.4 Hz, H-2), 2.57 (q, 1H, *J*=6.6 Hz, CH(Ph)CH_3), 2.73 (dd, 1H, *J*=7.3, 14.7 Hz, CH_2Ph), 2.85 (dd, 1H, *J*=5.4, 14.7 Hz, CH_2Ph), 4.16 (q, 2H, *J*=7.2 Hz, OCH_2CH_3), 6.88–7.28 (m, 10H, Ph). ^{13}C NMR δ: 14.4 (OCH_2CH_3), 22.7 (CH(Ph)CH_3), 34.2 (CH_2Ph), 42.8 (C-2), 47.1 (C-3), 61.1 (OCH_2CH_3), 70.1 (CH(Ph)CH_3), 126.2, 126.7, 127.2, 127.4, 128.5, 128.7, 138.8, 143.4 (Ph), 170.0 (C═O). MS *m/z*: 309 (M^+, 1), 218 (11), 130 (100), 105 (72). IR ν_{max} (neat) cm^{-1}: 2968, 1743, 1455, 1183. Anal. Calcd for $C_{20}H_{23}NO_2$: C, 77.60; H, 7.49; N, 4.53. Found: C, 77.89; H, 7.53; N, 4.68. $[\alpha]_D^{25}$ +36.1 (*c* 1.0 in CH_2Cl_2).

3.4.8. (2*S*,3*S*)-Ethyl 3-benzyl-1-((*R*)-1-phenylethyl)-aziridine-2-carboxylate 6′e.[5b] Oil, yield=44% (A), yield=52% (B). ^1H NMR δ: 1.13 (t, 3H, *J*=7.2 Hz, OCH_2CH_3), 1.20 (d, 3H, *J*=6.6 Hz, CH(Ph)CH_3), 2.08–2.12 (m, 1H, H-3), 2.10 (d, 1H, *J*=6.6 Hz, H-2), 2.55 (q, 1H, *J*=6.6 Hz, CH(Ph)CH_3), 2.85 (dd, 1H, *J*=4.6, 14.3 Hz, CH_2Ph), 2.99 (dd, 1H, *J*=4.3, 14.3 Hz, CH_2Ph), 4.09 (dq, 1H, *J*=7.2, 10.7 Hz, OCH_2CH_3), 4.12 (dq, 1H, *J*=7.2, 10.7 Hz, OCH_2CH_3), 7.17–7.28 (m, 10H, Ph). ^{13}C NMR δ: 14.4 (OCH_2CH_3), 23.8 (CH(Ph)CH_3), 34.7 (CH_2Ph), 42.5 (C-2), 48.5 (C-3), 59.9 (OCH_2CH_3), 69.6 (CH(Ph)CH_3), 126.6, 126.7, 127.2, 128.5, 128.6, 129.0, 139.1, 139.8 (Ph), 169.6 (C═O). MS *m/z*: 309 (M^+, 1), 218 (11), 130 (100), 105 (72). IR ν_{max} (neat) cm^{-1}: 2968, 1743, 1455, 1183. Anal. Calcd for $C_{20}H_{23}NO_2$: C, 77.60; H, 7.49; N, 4.53. Found: C, 77.92; H, 7.74; N, 4.76. $[\alpha]_D^{25}$ −11.3 (*c* 1.0 in CH_2Cl_2).

3.5. Synthesis of β-aminoesters 11

n-Butyllithium 2.5 M in hexane (5.4 mL, 13 mmol, 1.3 equiv) was added dropwise to a solution of (*R*)-*N*-benzyl-*N*-((*R*)-1-phenylethyl)amine (2.74 g, 13 mmol, 1.3 equiv) in THF (75 mL) at 0 °C under argon. After 15 min at 0 °C, the mixture was cooled to −78 °C. α,β-Unsaturated ester **10** (10 mmol, 1 equiv) in solution in THF (5 mL) was then introduced. After 40 min of stirring at −78 °C, the mixture was quenched with a saturated aqueous solution of ammonium chloride (5 mL) and allowed to reach room temperature. Water (90 mL) and ether (30 mL) were added. The aqueous phase was separated and extracted with ether (2×80 mL). The combined organic phases were washed with an aqueous solution of hydrochloric acid 0.5 N (200 mL) and then with a saturated aqueous solution of sodium chloride (200 mL). After drying over $MgSO_4$ and concentration, the crude product was purified by silica gel chromatography (cyclohexane/ether: 90:10).

3.5.1. (*R*)-Ethyl 3-(*N*-benzyl-*N*-((*R*)-1-phenylethyl)-amino)butanoate 11a.[24] Oil, yield=79%. ^1H NMR δ: 1.18 (d, 3H, *J*=6.6 Hz, H-4), 1.20 (t, 3H, *J*=7.2 Hz, OCH_2CH_3), 1.39 (d, 3H, *J*=6.9 Hz, CH(Ph)CH_3), 2.15 (dd, 1H, *J*=7.9, 14.1 Hz, H-2), 2.40 (dd, 1H, *J*=5.9, 14.1 Hz, H-2), 3.46–3.53 (m, 1H, H-3), 3.73 (d, 1H, *J*=14.6 Hz, CH_2Ph), 3.77 (d, 1H, *J*=14.6 Hz, CH_2Ph), 3.94–4.03 (m, 2H, CH(Ph)CH_3, OCH_2CH_3), 4.08 (dq, 1H, *J*=7.2, 10.8 Hz, OCH_2CH_3), 7.26–7.48 (m, 10H, Ph). ^{13}C NMR δ: 14.2 (OCH_2CH_3), 18.0 (CH(Ph)CH_3), 18.7 (C-4), 39.9 (C2), 49.7 (CH_2Ph), 50.2 (C-3), 57.8 (CH(Ph)CH_3), 60.2 (OCH_2CH_3), 126.7, 126.9, 127.8, 128.1, 128.2, 128.4, 141.9, 144.4 (Ph), 172.5 (C-1). Anal. Calcd for

$C_{21}H_{27}NO_2$: C, 77.50; H, 8.36; N, 4.30. Found: C, 77.72; H, 8.56; N, 4.61. $[\alpha]_D^{25}$ +4.9 (*c* 1.0 in $CHCl_3$).

3.5.2. (*R*)-Ethyl 3-(*N*-benzyl-*N*-((*R*)-1-phenylethyl)-amino)pentanoate 11b. Oil, yield=75%. ^{1}H NMR δ: 0.93 (t, 3H, *J*=7.2 Hz, H-5), 1.11 (t, 3H, *J*=7.2 Hz, OCH_2CH_3), 1.28 (d, 3H, *J*=6.9 Hz, $CH(Ph)CH_3$), 1.40–1.50 (m, 2H, H-4), 1.92 (d, 2H, *J*=6.4 Hz, H-2), 3.12–3.21 (m, 1H, H-3), 3.46 (d, 1H, *J*=14.9 Hz, CH_2Ph), 3.71 (d, 1H, *J*=14.9 Hz, CH_2Ph), 3.76 (q, 1H, *J*=6.9 Hz, $CH(Ph)CH_3$), 3.87–4.00 (m, 2H, OCH_2CH_3), 7.15–7.40 (m, 10H, Ph). ^{13}C NMR δ: 12.1, 14.3 (C-5, OCH_2CH_3), 19.7 ($CH(Ph)CH_3$), 26.4 (C-4), 36.9 (C-2), 50.1 (CH_2Ph), 55.8 (C-3), 57.8 ($CH(Ph)CH_3$), 60.2 (OCH_2CH_3), 126.7, 127.0, 128.1, 128.2, 128.4, 141.8, 143.2 (Ph), 173.1 (C-1). Anal. Calcd for $C_{22}H_{29}NO_2$: C, 77.83; H, 8.61; N, 4.12. Found: C, 77.52; H, 8.46; N, 3.87. $[\alpha]_D^{25}$ +4.3 (*c* 1.0 in $CHCl_3$).

3.5.3. (*R*)-Ethyl 3-(*N*-benzyl-*N*-((*R*)-1-phenylethyl)-amino)hexanoate 11c.[24,25] Oil, yield=72%. ^{1}H NMR δ: 0.79 (t, 3H, *J*=7.2 Hz, H-6), 1.11 (t, 3H, *J*=7.2 Hz, OCH_2CH_3), 1.15–1.21 (m, 1H, H-5), 1.26 (d, 3H, *J*=6.9 Hz, $CH(Ph)CH_3$), 1.47–1.53 (m, 3H, H-4, H-5), 1.90 (dd, 1H, *J*=8.2, 14.6 Hz, H-2), 1.97 (dd, 1H, *J*=4.9, 14.6 Hz, H-2), 3.18–3.31 (m, 1H, H-3), 3.46 (d, 1H, *J*=14.9 Hz, CH_2Ph), 3.71 (d, 1H, *J*=14.9 Hz, CH_2Ph), 3.75 (q, 1H, *J*=6.9 Hz, $CH(Ph)CH_3$), 3.89 (dq, 1H, *J*=7.2, 10.7 Hz, OCH_2CH_3), 3.94 (dq, 1H, *J*=7.2, 10.7 Hz, OCH_2CH_3), 7.15–7.37 (m, 10H, Ph). ^{13}C NMR δ: 14.2, 14.3 (C-6, OCH_2CH_3), 19.9 ($CH(Ph)CH_3$), 20.3 (C-5), 36.0 (C-4), 37.0 (C-2), 50.2 (CH_2Ph), 54.0 (C-3), 58.1 ($CH(Ph)CH_3$), 60.2 (OCH_2CH_3), 126.7, 127.0, 127.4, 128.1, 128.2, 128.4, 142.0, 143.4 (Ph), 173.1 (C-1). $[\alpha]_D^{25}$ +4.1 (*c* 1.0 in $CHCl_3$).

3.5.4. (*R*)-Ethyl 3-(*N*-benzyl-*N*-((*R*)-1-phenylethyl)-amino)-4-methylpentanoate 11d. Oil, yield=82%. ^{1}H NMR δ: 0.85 (d, 3H, *J*=6.6 Hz, H-5), 1.08 (d, 3H, *J*=6.6 Hz, H-5), 1.20 (t, 3H, *J*=7.2 Hz, OCH_2CH_3), 1.37 (d, 3H, *J*=6.9 Hz, $CH(Ph)CH_3$), 1.62–1.79 (m, 1H, H-4), 1.89 (dd, 1H, *J*=2.3, 15.9 Hz, H-2), 2.06 (dd, 1H, *J*=9.2, 15.9 Hz, H-2), 3.17–3.29 (m, 1H, H-3), 3.50 (d, 1H, *J*=14.8 Hz, CH_2Ph), 3.75 (q, 1H, *J*=6.9 Hz, $CH(Ph)CH_3$), 3.78 (d, 1H, *J*=14.8 Hz, CH_2Ph), 4.04 (q, 2H, *J*=7.2 Hz, OCH_2CH_3), 7.18–7.50 (m, 10H, Ph). ^{13}C NMR δ: 14.3 (OCH_2CH_3), 19.7 (C-5), 20.3 ($CH(Ph)CH_3$), 21.1 (C-5), 32.9 (C-4), 35.0 (C-2), 51.4 (CH_2Ph), 58.1 ($CH(Ph)CH_3$), 58.6 (C-3), 60.2 (OCH_2CH_3), 126.1, 126.7, 127.1, 128.7, 141.7, 142.4 (Ph), 173.4 (C-1). Anal. Calcd for $C_{23}H_{31}NO_2$: C, 78.15; H, 8.84; N, 3.96. Found: C, 78.42; H, 9.13; N, 4.22. $[\alpha]_D^{25}$ +5.3 (*c* 1.0 in $CHCl_3$).

3.5.5. (*R*)-Ethyl 3-(*N*-benzyl-*N*-((*R*)-1-phenylethyl)-amino)-4-phenylbutanoate 11e. Oil, yield=78%. ^{1}H NMR δ: 1.09 (t, 3H, *J*=7.2 Hz, OCH_2CH_3), 1.12 (d, 3H, *J*=6.9 Hz, $CH(Ph)CH_3$), 2.03 (d, 2H, *J*=6.9 Hz, H-4), 2.55 (dd, 1H, *J*=6.9, 13.6 Hz, H-2), 2.79 (dd, 1H, *J*=7.0, 13.6 Hz, H-2), 3.54–3.67 (m, 1H, H-3), 3.57 (d, 1H, *J*=14.8 Hz, CH_2Ph), 3.76–3.98 (m, 3H, $CH(Ph)CH_3$, OCH_2CH_3), 3.82 (d, 1H, *J*=14.8 Hz, CH_2Ph), 7.09–7.32 (m, 15H, Ph). ^{13}C NMR δ: 14.2 (OCH_2CH_3), 19.0 ($CH(Ph)CH_3$), 36.9 (C-4), 39.8 (C-2), 50.1 (CH_2Ph), 56.6 (C-3), 57.8 ($CH(Ph)CH_3$), 60.2 (OCH_2CH_3), 126.1, 126.8, 127.0, 128.0, 128.2, 128.3, 128.4, 128.6, 129.6, 140.1, 141.3, 143.2 (Ph), 172.6 (C-1). Anal. Calcd for $C_{27}H_{31}NO_2$: C, 80.76; H, 7.78; N, 3.49. Found: C, 81.02; H, 8.04; N, 3.76. $[\alpha]_D^{25}$ +3.9 (*c* 1.0 in $CHCl_3$).

3.5.6. (*R*)-Ethyl 3-(*N*-benzyl-*N*-((*R*)-1-phenylethyl)-amino)-3-phenylpropanoate 11g. Oil, yield=89%. ^{1}H NMR δ: 0.96 (t, 3H, *J*=6.9 Hz, OCH_2CH_3), 1.15 (d, 3H, *J*=6.7 Hz, $CH(Ph)CH_3$), 2.47 (dd, 1H, *J*=9.4, 14.6 Hz, H-2), 2.58 (dd, 1H, *J*=5.6, 14.6 Hz, H-2), 3.58 (d, 1H, *J*=14.6 Hz, CH_2Ph), 3.66 (d, 1H, *J*=14.6 Hz, CH_2Ph), 3.65 (q, 2H, *J*=6.9 Hz, OCH_2CH_3), 3.93 (q, 1H, *J*=6.7 Hz, $CH(Ph)CH_3$), 4.36 (dd, 1H, *J*=5.6, 9.4 Hz, H-3), 7.17–7.33 (m, 15H, Ph). ^{13}C NMR δ: 14.1 (OCH_2CH_3), 16.0 ($CH(Ph)CH_3$), 37.9 (C-2), 51.0 (CH_2Ph), 57.0 ($CH(Ph)CH_3$), 59.6 (C-3), 60.4 (OCH_2CH_3), 126.7, 126.9, 127.3, 127.9, 128.2, 128.3, 141.6, 141.9, 144.2 (Ph), 171.9 (C-1). Anal. Calcd for $C_{29}H_{25}NO_2$: C, 80.59; H, 7.54; N, 3.61. Found: C, 80.94; H, 7.69; N, 3.87. $[\alpha]_D^{25}$ +6.8 (*c* 1.0 in $CHCl_3$).

3.6. Synthesis of β-aminoesters 12

Cerium and ammonium nitrate (5.74 g, 10.5 mmol, 2.1 equiv) was added to β-amino ester **11** (5 mmol, 1 equiv) in a mixture of acetonitrile/water: 5:1 (50 mL) at 0 °C. After 1 h of stirring at room temperature, a saturated aqueous solution of sodium carbonate (40 mL) was introduced. The solid was filtered and washed with ether (2×25 mL). The aqueous phase was separated and extracted with ether (2×40 mL). The combined organic phases were dried over $MgSO_4$ and concentrated. The crude product was purified by silica gel chromatography (cyclohexane/ether: 70:30).

3.6.1. (*R*)-Ethyl 3-(*N*-((*R*)-1-phenylethyl)amino)butanoate 12a.[26] Oil, yield=68%. ^{1}H NMR δ: 0.97 (d, 3H, *J*=6.6 Hz, H-4), 1.17 (t, 3H, *J*=7.2 Hz, OCH_2CH_3), 1.24 (d, 3H, *J*=6.4 Hz, $CH(Ph)CH_3$), 2.30 (dd, 1H, *J*=6.4, 14.6 Hz, H2), 2.35 (dd, 1H, *J*=5.6, 14.6 Hz, H-2), 2.86–2.94 (m, 1H, H-3), 3.80 (q, 1H, *J*=6.4 Hz, $CH(Ph)CH_3$), 4.05 (q, 2H, *J*=7.2 Hz, OCH_2CH_3), 7.17–7.25 (m, 5H, Ph). ^{13}C NMR δ: 14.4 (OCH_2CH_3), 21.6 (C-4), 24.7 ($CH(Ph)CH_3$), 41.0 (C-2), 47.9 (C-3), 55.1 ($CH(Ph)CH_3$), 60.3 (OCH_2CH_3), 126.6, 127.0, 128.5, 146.2 (Ph), 172.4 (C-1). $[\alpha]_D^{25}$ +31.1 (*c* 1.0, $CHCl_3$).

3.6.2. (*R*)-Ethyl 3-(*N*-((*R*)-1-phenylethyl)amino)-pentanoate 12b. Oil, yield=66%. ^{1}H NMR δ: 0.78 (t, 3H, *J*=7.4 Hz, H-5), 1.18 (t, 3H, *J*=7.1 Hz, OCH_2CH_3), 1.24 (d, 3H, *J*=6.4 Hz, $CH(Ph)CH_3$), 1.31–1.38 (m, 2H, H-4), 1.45 (s, 1H, NH), 2.28 (dd, 1H, *J*=5.6, 14.6 Hz, H-2), 2.38 (dd, 1H, *J*=5.9, 14.6 Hz, H-2), 2.60–2.69 (m, 1H, H-3), 3.81 (q, 1H, *J*=6.4 Hz, $CH(Ph)CH_3$), 4.06 (q, 2H, *J*=7.1 Hz, OCH_2CH_3), 7.14–7.30 (m, 5H, Ph). ^{13}C NMR δ: 10.5 (C-5), 14.4 (OCH_2CH_3), 25.0 ($CH(Ph)CH_3$), 28.1 (C-4), 38.4 (C-2), 53.7 (C-3), 55.2 ($CH(Ph)CH_3$), 60.3 (OCH_2CH_3), 126.8, 127.0, 128.5, 146.2 (Ph), 172.7 (C-1). $[\alpha]_D^{25}$ +29.3 (*c* 1.0, $CHCl_3$).

3.6.3. (*R*)-Ethyl 3-(*N*-((*R*)-1-phenylethyl)amino)-hexanoate 12c.[26b] Oil, yield=63%. ^{1}H NMR δ: 0.72 (t, 3H, *J*=6.9 Hz, H-6), 1.18 (t, 3H, *J*=7.2 Hz, OCH_2CH_3), 1.11–1.29 (m, 10H, H-4, H-5), 1.24 (d, 3H, *J*=6.4 Hz,

CH(Ph)CH_3), 1.46 (s, 1H, N*H*), 2.27 (dd, 1H, J=5.4, 14.6 Hz, H-2), 2.37 (dd, 1H, J=5.6, 14.6 Hz, H-2), 2.67–2.78 (m, 1H, H-3), 3.81 (q, 1H, J=6.4 Hz, C*H*(Ph)CH_3), 4.06 (q, 2H, J=7.2 Hz, OCH_2CH_3), 7.18–7.25 (m, 5H, Ph). ^{13}C NMR δ: 14.2 (C-6), 14.4 (OCH_2*C*H_3), 19.3 (C-5), 25.1 (CH(Ph)*C*H_3), 37.8 (C-4), 38.8 (C-2), 52.0 (C-3), 55.2 (*C*H(Ph)CH_3), 60.3 (O*C*H_2CH_3), 126.9, 127.0, 128.1, 146.2 (Ph), 172.7 (C-1). $[\alpha]_D^{25}$ +28.9 (*c* 1.0, $CHCl_3$).

3.6.4. (*R*)-Ethyl 3-(*N*-((*R*)-1-phenylethyl)amino)-4-methylpentanoate 12d.[26] Oil, yield=53%. ^{1}H NMR δ: 0.79 (d, 3H, J=6.6 Hz, H-5), 0.87 (d, 3H, J=6.9 Hz, H-5), 1.26 (t, 3H, J=7.2 Hz, OCH_2CH_3), 1.31 (d, 3H, J=6.6 Hz, CH(Ph)CH_3), 1.44 (s, 1H, N*H*), 1.62–1.75 (m, 1H, H-4), 2.32 (dd, 1H, J=6.4, 14.6 Hz, H-2), 2.43 (dd, 1H, J=5.4, 14.6 Hz, H-2), 2.61–2.67 (m, 1H, H-3), 3.84 (q, 1H, J=6.6 Hz, C*H*(Ph)CH_3), 4.13 (q, 2H, J=7.2 Hz, OCH_2CH_3), 7.21–7.35 (m, 5H, Ph). ^{13}C NMR δ: 14.4 (OCH_2*C*H_3), 18.5 (C-5), 18.8 (C-5), 24.9 (CH(Ph)*C*H_3), 31.5 (C-4), 36.2 (C-2), 55.6 (*C*H(Ph)CH_3), 57.8 (C-3), 60.3 (O*C*H_2CH_3), 126.9, 127.0, 128.4, 146.4 (Ph), 173.2 (C-1). $[\alpha]_D^{25}$ +25.4 (*c* 1.0, $CHCl_3$).

3.6.5. (*R*)-Ethyl 3-(*N*-((*R*)-1-phenylethyl)amino)-4-phenylbutanoate 12e. Oil, yield=62%. ^{1}H NMR δ: 1.18 (t, 3H, J=7.2 Hz, OCH_2CH_3), 1.20 (d, 3H, J=6.6 Hz, CH(Ph)CH_3), 1.52 (s, 1H, N*H*), 2.32 (d, 2H, J=6.1 Hz, H-4), 2.58 (dd, 1H, J=7.4, 13.6 Hz, H-2), 2.66 (dd, 1H, J=6.4, 13.6 Hz, H-2), 2.92–3.02 (m, 1H, H-3), 3.78 (q, 1H, J=6.6 Hz, C*H*(Ph)CH_3), 4.06 (q, 2H, J=7.2 Hz, OCH_2CH_3), 6.97–7.19 (m, 10H, Ph). ^{13}C NMR δ: 14.4 (OCH_2*C*H_3), 24.8 (CH(Ph)*C*H_3), 38.7 (C-4), 41.6 (C-2), 53.7 (C-3), 55.3 (*C*H(Ph)CH_3), 60.4 (O*C*H_2CH_3), 126.4, 126.6, 126.9, 128.3, 128.4, 129.5, 138.9, 145.7 (Ph), 172.4 (C-1). Anal. Calcd for $C_{20}H_{25}NO_2$: C, 77.14; H, 8.09; N, 4.50. Found: C, 77.36; H, 9.41; N, 4.74. $[\alpha]_D^{25}$ +26.3 (*c* 1.0, $CHCl_3$).

3.6.6. (*R*)-Ethyl 3-(*N*-((*R*)-1-phenylethyl)amino)-3-phenylpropanoate 12g.[26] Oil, yield=48%. ^{1}H NMR δ: 1.10 (t, 3H, J=7.2 Hz, OCH_2*C*H_3), 1.26 (d, 3H, J=6.4 Hz, CHα*C*H_3), 1.77 (s, 1H, N*H*), 2.56 (dd, 1H, J=6.1, 15.1 Hz, H-2), 2.64 (dd, 1H, J=7.7, 15.1 Hz, H-2), 3.58 (q, 1H, J=6.4 Hz, C*H*(Ph)CH_3), 3.99 (q, 2H, J=7.2 Hz, OCH_2CH_3), 4.12 (dd, 1H, J=6.1, 7.7 Hz, H-3), 7.16–7.21 (m, 10H, Ph). ^{13}C NMR δ: 14.3 (OCH_2*C*H_3), 22.4 (CH(Ph)*C*H_3), 43.0 (C-2), 54.7 (*C*H(Ph)CH_3), 57.0 (C-3), 60.6 (O*C*H_2CH_3), 126.7, 126.9, 127.0, 127.1, 128.5, 128.7, 142.9, 146.1 (Ph), 171.9 (C-1). Anal. Calcd for $C_{19}H_{21}NO_2$: C, 76.75; H, 7.80; N, 4.71. Found: C, 76.95; H, 8.13; N, 5.02. $[\alpha]_D^{25}$ +21.7 (*c* 1.0, $CHCl_3$).

3.7. Synthesis of α-(phenylselanyl)β-aminoesters 9, 9″

n-Butyllithium 2.5 M in hexane (1.26 mL, 3.15 mmol, 2.1 equiv) was added dropwise to a solution of diisopropylamine (318 mg, 3.15 mmol, 2.1 equiv) in THF (20 mL) at 0 °C, under argon. After 15 min of stirring at 0 °C, the mixture was cooled to −78 °C and a solution of the β-aminoester **12** (1.5 mmol, 1 equiv) in THF (2 mL) was slowly introduced. After 20 min at −78 °C, a solution of PhSeBr (460 mg, 1.95 mmol, 1.3 equiv) in THF (2 mL) was added. After 20 min of stirring at −78 °C the mixture was quenched with a saturated aqueous solution of ammonium chloride (5 mL) and allowed to reach the room temperature. Water (30 mL) and ether (15 mL) were added. The aqueous phase was separated and extracted with ether (2×30 mL). The combined organic phases were dried over $MgSO_4$ and concentrated. The crude product was purified by silica gel chromatography (cyclohexane/ether: 90:10).

3.7.1. Ethyl 3-((*R*)-1-phenylethylamino)-2-(phenylselanyl)butanoate 9a, 9″a. Oil, **9a/9″a**: 50/50, yield=65%.

3.7.1.1. (2*S*,3*R*)-Ethyl 3-((*R*)-1-phenylethylamino)-2-(phenylselanyl)butanoate 9a. (Second eluted). ^{1}H NMR δ: 1.10 (d, 3H, J=6.4 Hz, H-4), 1.15 (t, 3H, J=7.2 Hz, OCH_2CH_3), 1.31 (d, 3H, J=6.6 Hz, CH(Ph)CH_3), 1.70 (s, 1H, N*H*), 3.11 (quint, 1H, J=6.4 Hz, H-3), 3.83 (d, 1H, J=6.4 Hz, H-2), 3.86 (q, 1H, J=6.6 Hz, C*H*(Ph)CH_3), 4.04–4.10 (m, 2H, OCH_2CH_3), 7.26–7.55 (m, 10H, Ph). ^{13}C NMR δ: 14.2 (OCH_2*C*H_3), 19.3 (C-4), 24.5 (CH(Ph)*C*H_3), 51.4, 52.7 (C-2, C-3), 55.7 (*C*H(Ph)CH_3), 61.1 (O*C*H_2CH_3), 126.7, 126.9, 128.2, 128.5, 129.1, 129.3, 135.2, 146.3 (Ph), 172.1 (C-1). $[\alpha]_D^{25}$ −18.5 (*c* 1.0 in $CHCl_3$).

3.7.1.2. (2*R*,3*R*)-Ethyl 3-((*R*)-1-phenylethylamino)-2-(phenylselanyl)butanoate 9″a. (First eluted). ^{1}H NMR δ: 1.13 (d, 3H, J=6.4 Hz, H-4), 1.16 (t, 3H, J=7.2 Hz, OCH_2CH_3), 1.22 (d, 3H, J=6.4 Hz, CH(Ph)CH_3), 1.64 (s, 1H, N*H*), 3.13 (quint, 1H, J=6.4 Hz, H-3), 3.73 (d, 1H, J=6.4 Hz, H-2), 3.77 (q, 1H, J=6.4 Hz, C*H*(Ph)CH_3), 4.9 (q, 2H, J=7.2 Hz, OCH_2CH_3), 7.24–7.62 (m, 10H, Ph). ^{13}C NMR δ: 14.2 (OCH_2*C*H_3), 19.4 (C-4), 24.0 (CH(Ph)*C*H_3), 52.5, 52.6 (C-2, C-3), 55.8 (*C*H(Ph)CH_3), 61.0 (O*C*H_2CH_3), 126.7, 127.0, 128.1, 128.5, 129.2, 129.7, 134.8, 146.4 (Ph), 172.8 (C-1). $[\alpha]_D^{25}$ −33.4 (*c* 1.0 in $CHCl_3$).

3.7.2. Ethyl 3-((*R*)-1-phenylethylamino)-2-(phenylselanyl)pentanoate 9b, 9″b. Oil, **9b/9″b**: 50/50, yield=59%.

3.7.2.1. (2*S*,3*R*)-Ethyl 3-((*R*)-1-phenylethylamino)-2-(phenylselanyl)pentanoate 9b. (Second eluted). ^{1}H NMR δ: 0.84 (t, 3H, J=7.2 Hz, H-5), 1.19 (t, 3H, J=7.2 Hz, OCH_2CH_3), 1.34 (d, 3H, J=6.6 Hz, CH(Ph)CH_3), 1.66–1.80 (m, 3H, H-4, N*H*), 2.32–2.41 (m, 1H, H-3), 3.87 (q, 1H, J=6.6 Hz, C*H*(Ph)CH_3), 4.01 (d, 1H, J=5.4 Hz, H-2), 4.04–4.19 (m, 2H, OCH_2CH_3), 7.19–7.60 (m, 10H, Ph). ^{13}C NMR δ: 10.5 (C-5), 14.2 (OCH_2*C*H_3), 24.7 (CHα*C*H_3), 25.2 (C-4), 49.9 (C-2), 55.5 (*C*H(Ph)CH_3), 58.4 (C-3), 61.2 (O*C*H_2CH_3), 126.8, 128.1, 128.4, 128.6, 129.1, 129.2, 135.2, 146.1 (Ph), 172.2 (C-1). $[\alpha]_D^{25}$ −17.9 (*c* 1.0, $CHCl_3$).

3.7.2.2. (2*R*,3*R*)-Ethyl 3-((*R*)-1-phenylethylamino)-2-(phenylselanyl)pentanoate 9″b. (First eluted). ^{1}H NMR δ: 0.73 (t, 3H, J=7.2 Hz, H-5), 1.16 (t, 3H, J=7.2 Hz, OCH_2CH_3), 1.21 (d, 3H, J=6.4 Hz, CH(Ph)CH_3), 1.39–1.58 (m, 2H, H-4), 1.73 (s, 1H, N*H*), 2.85–3.91 (m, 1H, H-3), 3.74 (q, 1H, J=6.4 Hz, C*H*(Ph)CH_3), 3.81 (d, 1H, J=5.9 Hz, H2), 3.96–4.13 (m, 2H, OCH_2CH_3), 7.22–7.70 (m, 10H, Ph). ^{13}C NMR δ: 10.1 (C-5), 14.1 (OCH_2*C*H_3), 24.0 (CH(Ph)*C*H_3), 25.4 (C-4), 50.2 (C-2), 55.6 (*C*H(Ph)CH_3), 57.8 (C-3), 61.0 (O*C*H_2CH_3), 126.8, 127.0, 128.0, 128.4, 129.3, 129.4, 134.7, 146.3 (Ph), 172.9 (C1). $[\alpha]_D^{25}$ −30.7 (*c* 1.0, $CHCl_3$).

3.7.3. Ethyl 3-((*R*)-1-phenylethylamino)-2-(phenylselanyl)hexanoate 9c, 9″c. Oil, **9c/9″c**: 50/50, yield=56%.

3.7.3.1. (2*S*,3*R*)-Ethyl 3-((*R*)-1-phenylethylamino)-2-(phenylselanyl)hexanoate 9c. (Second eluted). ^{1}H NMR δ: 0.67 (t, 3H, J=7.2 Hz, H-6), 1.10 (t, 3H, J=7.2 Hz, OCH_2CH_3), 1.21 (d, 3H, J=6.4 Hz, $CH(Ph)CH_3$), 1.15–1.29 (m, 2H, H-5), 1.48–1.42 (m, 2H, H-4), 1.68 (s, 1H, N*H*), 2.75–2.79 (m, 1H, H-3), 3.75 (q, 1H, J=6.4 Hz, $CH(Ph)CH_3$), 3.93 (d, 1H, J=4.8 Hz, H-2), 4.03 (dq, 1H, J=7.2, 10.7 Hz, OCH_2CH_3), 4.06 (dq, 1H, J=7.2, 10.7 Hz, OCH_2CH_3), 7.16–7.45 (m, 10H, Ph). ^{13}C NMR δ: 14.0, 14.2 (C-6, OCH_2CH_3), 19.4 (C-5), 24.8 ($CH(Ph)CH_3$), 34.7 (C-4), 50.0 (C-2), 55.4 ($CH(Ph)CH_3$), 56.7 (C-3), 61.2 (OCH_2CH_3), 126.9, 127.5, 127.9, 128.2, 128.6, 129.2, 135.4, 146.0 (Ph), 172.1 (C-1). $[\alpha]_D^{25}$ −17.4 (*c* 1.0 in $CHCl_3$).

3.7.3.2. (2*R*,3*R*)-Ethyl 3-((*R*)-1-phenylethylamino)-2-(phenylselanyl)hexanoate 9″c. (First eluted). ^{1}H NMR δ: 0.76 (t, 3H, J=7.2 Hz, H-6), 1.15 (t, 3H, J=7.2 Hz, OCH_2CH_3), 1.22 (d, 3H, J=6.4 Hz, $CH(Ph)CH_3$), 1.16–1.34 (m, 2H, H-5), 1.43–1.49 (m, 2H, H-4), 1.68 (s, 1H, N*H*), 2.95–3.01 (m, 1H, H-3), 3.79 (q, 1H, J=6.4 Hz, $CH(Ph)CH_3$), 3.90 (d, 1H, J=5.4 Hz, H-2), 4.01 (q, 2H, J=7.2 Hz, OCH_2CH_3), 7.27–7.63 (m, 10H, Ph). ^{13}C NMR δ: 14.2, 14.3 (C-6, OCH_2CH_3), 19.1 (C-5), 24.2 ($CH(Ph)CH_3$), 35.3 (C-4), 51.0 (C-2), 55.6 ($CH(Ph)CH_3$), 56.4 (C-3), 61.1 (OCH_2CH_3), 127.0, 127.1, 128.1, 128.5, 129.2, 129.5, 134.8, 146.7 (Ph), 172.9 (C-1). $[\alpha]_D^{25}$ −29.8 (*c* 1.0 in $CHCl_3$).

3.7.4. Ethyl 3-((*R*)-1-phenylethylamino)-4-methyl-2-(phenylselanyl)pentanoate 9d, 9″d. Oil, **9d/9″d**: 60/40, yield=58%.

3.7.4.1. (2*S*,3*R*)-Ethyl 3-((*R*)-1-phenylethylamino)-4-methyl-2-(phenylselanyl)pentanoate 9d. (First eluted). ^{1}H NMR δ: 0.78 (d, 3H, J=6.9 Hz, H-5), 0.81 (d, 3H, J=6.9 Hz, H-5), 1.04 (t, 3H, J=7.2 Hz, OCH_2CH_3), 1.38 (d, 3H, J=6.6 Hz, $CH(Ph)CH_3$), 1.55 (s, 1H, N*H*), 1.83 (septd, 1H, J=3.8, 6.9 Hz, H-4), 2.95 (dd, 1H, J=3.8, 6.9 Hz, H-3), 3.89 (q, 1H, J=6.6 Hz, $CH(Ph)CH_3$), 3.91 (dq, 1H, J=7.2, 10.4 Hz, OCH_2CH_3), 3.95 (dq, 1H, J=7.2, 10.4 Hz, OCH_2CH_3), 4.05 (d, 1H, J=6.9 Hz, H-2), 7.26–7.62 (m, 10H, Ph). ^{13}C NMR δ: 14.0 (OCH_2CH_3), 17.9 (C-5), 19.9 (C-5), 24.1 ($CH(Ph)CH_3$), 31.6 (C-4), 51.1 (C-2), 56.8 ($CH(Ph)CH_3$), 59.8 (C-3), 61.1 (OCH_2CH_3), 127.0, 127.1, 128.1, 128.4, 129.0, 130.0, 135.6, 146.2 (Ph), 172.8 (C-1). $[\alpha]_D^{25}$ −19.6 (*c* 1.0 in $CHCl_3$).

3.7.4.2. (2*R*,3*R*)-Ethyl 3-((*R*)-1-phenylethylamino)-4-methyl-2-(phenylselanyl)pentanoate 9″d. (Second eluted). ^{1}H NMR δ: 0.68 (d, 3H, J=6.9 Hz, H-5), 0.79 (d, 3H, J=6.9 Hz, H-5), 1.16 (t, 3H, J=7.2 Hz, OCH_2CH_3), 1.28 (d, 3H, J=6.4 Hz, $CH(Ph)CH_3$), 1.65 (s, 1H, N*H*), 2.01 (septd, 1H, J=4.3, 6.9 Hz, H-4), 2.96 (dd, 1H, J=4.3, 6.9 Hz-3), 3.82 (d, 1H, J=6.9 Hz, H-2), 3.92 (q, 1H, J=6.4 Hz, $CH(Ph)CH_3$), 4.06 (dq, 1H, J=7.2, 10.7 Hz, OCH_2CH_3), 4.09 (dq, 1H, J=7.2, 10.7 Hz, OCH_2CH_3), 7.28–7.63 (m, 10H, Ph). ^{13}C NMR δ: 14.1 (OCH_2CH_3), 17.6 (C-5), 20.1 (C-5), 24.2 ($CH\alpha CH_3$), 31.4 (C-4), 49.9 (C-2), 56.7 ($CH(Ph)CH_3$), 61.0 (OCH_2CH_3), 61.7 (C-3), 127.2, 127.3, 128.3, 128.6, 129.2, 130.0, 135.8, 146.4 (Ph), 173.3 (C-1). $[\alpha]_D^{25}$ −33.5 (*c* 1.0 in $CHCl_3$).

3.7.5. Ethyl 4-phenyl-3-((*R*)-1-phenylethylamino)-2-(phenylselanyl)butanoate 9e, 9″e. Oil, **9e/9″e**: 70/30, yield=61%.

3.7.5.1. (2*S*,3*R*)-Ethyl 4-phenyl-3-((*R*)-1-phenylethylamino)-2-(phenylselanyl)butanoate 9e. (Second eluted). ^{1}H NMR δ: 1.06 (t, 3H, J=7.2 Hz, OCH_2CH_3), 1.19 (d, 3H, J=6.6 Hz, $CH(Ph)CH_3$), 1.67 (s, 1H, N*H*), 2.61 (dd, 1H, J=7.9, 13.7 Hz, H-4), 2.94 (dd, 1H, J=5.1, 13.7 Hz, H-4), 3.09–3.15 (m, 1H, H-3), 3.78 (q, 1H, J=6.6 Hz, $CH(Ph)CH_3$), 3.85 (d, 1H, J=4.9 Hz, H-2), 3.95 (dq, 1H, J=7.2, 10.7 Hz, OCH_2CH_3), 3.97 (dq, 1H, J=7.2, 10.7 Hz, OCH_2CH_3), 6.84–7.07 (m, 15H, Ph). ^{13}C NMR δ: 14.2 (OCH_2CH_3), 24.6 ($CH(Ph)CH_3$), 38.9 (C-4), 49.6 (C-2), 55.6 ($CH(Ph)CH_3$), 58.5 (C-3), 61.1 (OCH_2CH_3), 126.4, 126.6, 126.8, 128.1, 128.3, 128.4, 128.5, 129.1, 129.7, 135.0, 138.7, 145.6 (Ph), 172.3 (C-1). $[\alpha]_D^{25}$ −29.6 (*c* 1.0 in $CHCl_3$).

3.7.5.2. (2*R*,3*R*)-Ethyl 3-((*R*)-1-phenylethylamino)-2-(phenylselanyl)butanoate 9″e. (First eluted). ^{1}H NMR δ: 1.10 (t, 3H, J=7.2 Hz, OCH_2CH_3), 1.16 (d, 3H, J=6.4 Hz, $CH(Ph)CH_3$), 1.87 (s, 1H, N*H*), 2.75 (d, 2H, J=6.6 Hz, H-4), 3.19 (td, 1H, J=5.4, 6.6 Hz, H-3), 3.66 (d, 1H, J=5.4 Hz, H-2), 3.74 (q, 1H, J=6.4 Hz, $CH(Ph)CH_3$), 4.04 (q, 2H, J=7.2 Hz, OCH_2CH_3), 6.94–7.48 (m, 15H, Ph). ^{13}C NMR δ: 14.2 (OCH_2CH_3), 23.9 ($CH(Ph)CH_3$), 39.2 (C-4), 49.6 (C-2), 55.9 ($CH(Ph)CH_3$), 58.3 (C-3), 61.0 (OCH_2CH_3), 126.4, 126.7, 126.9, 128.0, 128.4, 128.5, 129.1, 129.5, 129.9, 134.6, 138.5, 146.0 (Ph), 172.8 (C-1). $[\alpha]_D^{25}$ −16.3 (*c* 1.0 in $CHCl_3$).

3.7.6. Ethyl 3-phenyl-3-((*R*)-1-phenylethylamino)-2-(phenylselanyl)propanoate 9g, 9″g. Oil, **9g/9″g**: 50/50, yield=57%.

3.7.6.1. (2*S*,3*R*)-Ethyl 3-phenyl-3-((*R*)-1-phenylethylamino)-2-(phenylselanyl)propanoate 9g. (First eluted). ^{1}H NMR δ: 0.86 (t, 3H, J=7.2 Hz, OCH_2CH_3), 1.34 (d, 3H, J=6.6 Hz, $CH(Ph)CH_3$), 2.17 (s, 1H, N*H*), 3.56 (q, 1H, J=6.6 Hz, $CH(Ph)CH_3$), 3.73 (dq, 1H, J=7.2, 10.7 Hz, OCH_2CH_3), 3.75 (dq, 1H, J=7.2, 10.7 Hz, OCH_2CH_3), 3.98 (d, 1H, J=9.7 Hz, H-2), 4.25 (d, 1H, J=9.7 Hz, H-3), 7.24–7.62 (m, 15H, Ph). ^{13}C NMR δ: 13.8 (OCH_2CH_3), 21.8 ($CH(Ph)CH_3$), 52.7 (C-2), 54.6 ($CH(Ph)CH_3$), 60.8 (OCH_2CH_3), 60.9 (C-3), 126.7, 126.8, 127.6, 127.8, 128.1, 128.3, 128.4, 128.5, 129.0, 135.9, 140.5, 146.1 (Ph), 171.1 (C-1). $[\alpha]_D^{25}$ −15.7 (*c* 1.0 in $CHCl_3$).

3.7.6.2. (2*R*,3*R*)-Ethyl 3-phenyl-3-((*R*)-1-phenylethylamino)-2-(phenylselanyl)propanoate 9″g. (Second eluted). ^{1}H NMR δ: 1.10 (t, 3H, J=7.2 Hz, OCH_2CH_3), 1.28 (d, 3H, J=6.4 Hz, $CH(Ph)CH_3$), 2.35 (s, 1H, N*H*), 3.61 (q, 1H, J=6.4 Hz, $CH(Ph)CH_3$), 3.89 (d, 1H, J=8.6 Hz, H-2), 4.03 (q, 2H, J=7.2 Hz, OCH_2CH_3), 4.31 (d, 1H, J=8.6 Hz, H-3), 7.18–7.25 (m, 15H, Ph). ^{13}C NMR δ: 14.1 (OCH_2CH_3), 22.1 ($CH(Ph)CH_3$), 51.7 (C-2), 55.1 ($CH(Ph)CH_3$), 61.0 (OCH_2CH_3), 62.0 (C-3), 126.7, 126.8, 127.1, 127.6, 127.7, 128.1, 128.4, 128.5, 128.9, 135.2, 140.4, 146.3 (Ph), 172.2 (C-1). $[\alpha]_D^{25}$ −23.8 (*c* 1.0 in $CHCl_3$).

3.8. Cyclisation of α-(phenylselanyl)β-aminoesters 9, 9″

The protocols are the same as for the cyclisation of β-(phenylselanyl)α-aminoesters **2**.

Procedure A with Me_3OBF_4. α-(Phenylselanyl)β-aminoesters **9** (or **9″**) afforded aziridines **6** (or **6″**).

Procedure B with NBS. α-(Phenylselanyl)β-aminoesters **9** (or **9″**) afforded aziridines **6** (or **6″**), except for **9a** and **9f**, which lead, respectively, to **6″a** and **6″f**.

3.8.1. (2*R*,3*R*)-Ethyl 3-methyl-1-((*R*)-1-phenylethyl)-aziridine-2-carboxylate 6a.[5b] Yield=51% (A).

3.8.2. (2*S*,3*R*)-Ethyl 3-methyl-1-((*R*)-1-phenylethyl)-aziridine-2-carboxylate 6″a. Oil, two invertomers: 60/40, yield=53% (A), yield=59% (B). Major: ^{1}H NMR δ: 1.04 (d, 3H, J=5.4 Hz, CH_3), 1.18 (d, 3H, J=6.6 Hz, CH(Ph)CH_3), 1.26 (t, 3H, J=7.2 Hz, OCH$_2$CH_3), 2.12–2.20 (m, 1H, H-3), 2.44 (d, 1H, J=2.8 Hz, H-2), 3.77 (q, 1H, J=6.6 Hz, CH(Ph)CH$_3$), 4.16 (dq, 1H, J=7.2, 10.7 Hz, OCH_2CH$_3$), 4.19 (dq, 1H, J=7.2, 10.7 Hz, OCH_2CH$_3$), 7.23–7.32 (m, 5H, Ph). ^{13}C NMR δ: 14.5 (OCH$_2$CH_3), 18.0 (CH_3), 23.5 (CH(Ph)CH_3), 41.7 (C-2), 42.1 (C-3), 59.1 (Cα), 61.3 (OCH$_2$CH$_3$), 127.4, 128.7, 128.8, 145.3 (Ph), 170.0 (C=O). Minor: δ_H (300 MHz, CDCl$_3$): 1.14 (d, 3H, J=7.2 Hz, OCH$_2$CH_3), 1.36 (d, 3H, J=6.4 Hz, CHαCH_3), 1.40 (t, 3H, J=6.1 Hz, CH_3), 1.77 (d, 1H, J=2.8 Hz, H-2), 2.56–2.65 (m, 1H, H-3), 3.27 (q, 1H, J=6.4 Hz, CH(Ph)CH$_3$), 4.05 (q, 2H, J=7.2 Hz, OCH_2CH$_3$), 7.23–7.32 (m, 5H, Ph). ^{13}C NMR δ: 10.9 (CH_3), 14.6 (OCH$_2$CH_3), 24.9 (CH(Ph)CH_3), 41.4 (C-3), 43.7 (C-2), 60.4 (CH(Ph)CH$_3$), 61.2 (OCH$_2$CH$_3$), 127.0, 128.7, 128.8, 145.3 (Ph), 170.2 (C=O). MS *m*/*z*: 233 (M$^+$, 2), 128 (77), 105 (100). IR ν_{max} (neat) cm^{-1}: 2979, 1728, 1449, 1190. Anal. Calcd for $C_{14}H_{19}NO_2$: C, 72.10; H, 8.21; N, 6.00. Found: C, 71.87; H, 8.23; N, 5.89. $[\alpha]_D^{25}$ +34.1 (*c* 1.0 in CH_2Cl_2).

3.8.3. (2*R*,3*R*)-Ethyl 1-((*R*)-1-phenylethyl)-3-ethyl-aziridine-2-carboxylate 6b. Yield=53% (A).

3.8.4. (2*S*,3*R*)-Ethyl 1-((*R*)-1-phenylethyl)-3-ethyl-aziridine-2-carboxylate 6″b. Oil, yield=47% (A), yield=51% (B). ^{1}H NMR δ: 0.62 (t, 3H, J=7.4 Hz, CH$_2$CH_3), 1.30 (d, 3H, J=6.6 Hz, CH(Ph)CH_3), 1.37 (t, 3H, J=7.2 Hz, OCH$_2$CH_3), 1.17–1.52 (m, 2H, CH_2CH$_3$), 2.17 (ddd, 1H, J=2.8, 5.4, 6.7 Hz, H-3), 2.56 (d, 1H, J=2.8 Hz, H-2), 3.83 (q, 1H, J=6.6 Hz, CH(Ph)CH$_3$), 4.12–4.22 (m, 2H, OCH_2CH$_3$), 7.22–7.49 (m, 5H, Ph). ^{13}C NMR δ: 11.0 (CH$_2$CH_3), 14.4 (OCH$_2$CH_3), 22.8 (CH(Ph)CH_3), 25.7 (CH_2CH$_3$), 40.7 (C-2), 48.2 (C-3), 59.4 (CH(Ph)CH$_3$), 61.2 (OCH$_2$CH$_3$), 127.3, 127.4, 128.4, 144.7 (Ph), 170.0 (C=O). MS *m*/*z*: 247 (M$^+$, 14), 142 (34), 105 (100). IR ν_{max} (neat) cm^{-1}: 2970, 1728, 1450, 1190. Anal. Calcd for $C_{15}H_{21}NO_2$: C, 58.29; H, 8.50; N, 5.66. Found: C, 58.85; H, 8.67; N, 5.31. $[\alpha]_D^{25}$ +22.6 (*c* 1.0, CH_2Cl_2).

3.8.5. (2*R*,3*R*)-Ethyl 1-((*R*)-1-phenylethyl)-3-propyl-aziridine-2-carboxylate 6c. Yield=47% (A), yield=61% (B).

3.8.6. (2*S*,3*R*)-Ethyl 1-((*R*)-1-phenylethyl)-3-propyl-aziridine-2-carboxylate 6″c. Oil, yield=50% (A), yield=51% (B). ^{1}H NMR δ: 0.69 (t, 3H, J=7.2 Hz, CH$_2$CH$_2$CH_3), 0.98–1.07 (m, 2H, CH$_2$CH_2CH$_3$), 1.24–1.41 (m, 2H, CH_2CH$_2$CH$_3$), 1.30 (d, 3H, J=6.4 Hz, CH(Ph)CH_3), 1.34 (t, 3H, J=7.2 Hz, OCH$_2$CH_3), 2.15–2.23 (m, 1H, H-3), 2.53 (d, 1H, J=2.8 Hz, H-2), 3.80 (q, 1H, J=6.4 Hz, CH(Ph)CH$_3$), 4.23 (dq, 1H, J=7.2, 10.7 Hz, OCH_2CH$_3$), 4.25 (dq, 1H, J=7.2, 10.7 Hz, OCH_2CH$_3$), 7.25–7.41 (m, 5H, Ph). ^{13}C NMR δ: 13.7 (CH_3CH$_2$CH$_2$), 14.4 (OCH$_2$CH_3), 20.1 (CH$_3$CH_2CH$_2$), 22.8 (CH(Ph)CH_3), 34.8 (CH$_3$CH$_2$CH_2), 41.1 (C-2), 46.7 (C-3), 59.5 (CH(Ph)CH$_3$), 61.2 (OCH$_2$CH$_3$), 127.3, 127.5, 128.4, 144.7 (Ph), 170.0 (C=O). MS *m*/*z*: 261 (M$^+$, 1), 156 (91), 105 (100), 82 (69). IR ν_{max} (neat) cm^{-1}: 2968, 1728, 1455, 1189. Anal. Calcd for $C_{16}H_{23}NO_2$: C, 73.53; H, 8.87; N, 5.36. Found: C, 73.75; H, 9.01; N, 5.48. $[\alpha]_D^{25}$ +17.3 (*c* 1.0 in CH_2Cl_2).

3.8.7. (2*R*,3*R*)-Ethyl 1-((*R*)-1-phenylethyl)-3-*iso*-propyl-aziridine-2-carboxylate 6d. Oil, yield=44% (A), yield=49% (B). ^{1}H NMR δ: 0.42 (d, 3H, J=6.4 Hz, CH(CH_3)$_2$), 0.67 (d, 3H, J=6.4 Hz, CH(CH_3)$_2$), 1.22 (t, 3H, J=7.2 Hz, OCH$_2$CH_3), 1.38–1.40 (m, 4H, CH(CH$_3$)$_2$, CH(Ph)CH_3), 1.41–1.48 (m, 1H, H-3), 2.15 (d, 1H, J=6.4 Hz, H-2), 2.45 (q, 1H, J=6.6 Hz, CH(Ph)CH$_3$), 4.15 (q, 2H, J=7.2 Hz, OCH_2CH$_3$), 7.19–7.33 (m, 5H, Ph). ^{13}C NMR δ: 14.4 (OCH$_2$CH_3), 19.8 (CH(CH_3)$_2$), 20.6 (CH(CH_3)$_2$), 22.1 (CH(Ph)CH_3), 27.2 (CH(CH$_3$)$_2$), 43.2 (C-2), 53.2 (C-3), 59.9 (OCH$_2$CH$_3$), 70.4 (CH(Ph)CH$_3$), 127.6, 127.8, 128.4, 143.4 (Ph), 170.2 (C=O). MS *m*/*z*: 261 (M$^+$, 3), 218 (11), 156 (100), 105 (74), 82 (85). IR ν_{max} (neat) cm^{-1}: 2978, 1744, 1453, 1184. Anal. Calcd for $C_{16}H_{23}NO_2$: C, 73.53; H, 8.87; N, 5.36. Found: C, 73.87; H, 9.03; N, 5.16. $[\alpha]_D^{25}$ +48.5 (*c* 1.0 in CH_2Cl_2).

3.8.8. (2*S*,3*R*)-Ethyl 1-((*R*)-1-phenylethyl)-3-*iso*-propyl-aziridine-2-carboxylate 6″d. Oil, yield=48% (A), yield=53% (B). ^{1}H NMR δ: 0.37 (d, 3H, J=6.6 Hz, CH(CH_3)$_2$), 0.71 (d, 3H, J=6.6 Hz, CH(CH_3)$_2$), 1.18–1.20 (m, 1H, CH(CH$_3$)$_2$), 1.21 (d, 3H, J=6.4 Hz, CH(Ph)CH_3), 1.27 (t, 3H, J=7.2 Hz, OCH$_2$CH_3), 1.92 (dd, 1H, J=2.8, 7.7 Hz, H-3), 2.47 (d, 1H, J=2.8 Hz, H-2), 3.69 (q, 1H, J=6.4 Hz, CH(Ph)CH$_3$), 4.12–4.23 (m, 2H, OCH_2CH$_3$), 7.18–7.32 (m, 5H, Ph). ^{13}C NMR δ: 14.4 (OCH$_2$CH_3), 19.5 (CH(CH_3)$_2$), 19.6 (CH(CH_3)$_2$), 22.3 (CH(Ph)CH_3), 31.2 (CH(CH$_3$)$_2$), 39.9 (C-2), 53.5 (C-3), 59.9 (CH(Ph)CH$_3$), 61.2 (OCH$_2$CH$_3$), 127.9, 128.4, 128.6, 144.6 (Ph), 170.1 (C=O). MS *m*/*z*: 261 (M$^+$, 3), 156 (60), 105 (83), 82 (100). IR ν_{max} (neat) cm^{-1}: 2968, 1723, 1449, 1190. Anal. Calcd for $C_{16}H_{23}NO_2$: C, 73.53; H, 8.87; N, 5.36. Found: C, 73.53; H, 8.94; N, 5.28. $[\alpha]_D^{25}$ −22.8 (*c* 1.0 in CH_2Cl_2).

3.8.9. (2*R*,3*R*)-Ethyl 3-benzyl-1-((*R*)-1-phenylethyl)-aziridine-2-carboxylate 6e.[5b] Yield=42% (A), yield=53% (B).

3.8.10. (2*S*,3*R*)-Ethyl 3-benzyl-1-((*R*)-1-phenylethyl)-aziridine-2-carboxylate 6″e. Oil, yield=39% (A), yield=48% (B). ^{1}H NMR δ: 1.19 (d, 3H, J=6.4 Hz, CH(Ph)CH_3), 1.25 (t, 3H, J=6.9 Hz, OCH$_2$CH_3), 2.39 (td, 1H, J=2.8, 5.9 Hz, H-3), 2.53 (dd, 1H, J=5.9, 14.6 Hz, CH_2Ph), 2.58 (d, 1H, J=2.8 Hz, H-2), 2.62 (dd, 1H, J=5.9,

14.6 Hz, CH_2Ph), 3.75 (q, 1H, J=6.4 Hz, CH(Ph)CH_3), 4.12 (dq, 1H, J=6.9, 10.5 Hz, OC$H_2$$CH_3$), 4.16 (dq, 1H, J=6.9, 10.5 Hz, OC$H_2$$CH_3$), 6.86–7.31 (m, 10H, Ph). ^{13}C NMR δ: 14.4 (OCH$_2$$CH_3$), 23.0 (CH(Ph)$CH_3$), 38.8 ($CH_2$Ph), 40.6 (C-2), 47.3 (C-3), 59.4 (CH(Ph)CH_3), 61.3 (O$CH_2$$CH_3$), 126.2, 126.6, 127.2, 127.3, 128.4, 128.6, 138.2, 144.4 (Ph), 169.7 (C=O). IR ν_{max} (neat) cm^{-1}: 2978, 1723, 1449, 1190. Anal. Calcd for $C_{20}H_{23}NO_2$: C, 77.60; H, 7.49; N, 4.53. Found: C, 77.88; H, 7.76; N, 4.69. $[\alpha]_D^{25}$ +13.8 (c 1.0 in CH_2Cl_2).

3.8.11. (2*R*,3*R*)-Ethyl 3-phenyl-1-((*R*)-1-phenylethyl)-aziridine-2-carboxylate 6g.[5b] Oil, yield=49% (A).

3.8.12. (2*S*,3*R*)-Ethyl 3-phenyl-1-((*R*)-1-phenylethyl)-aziridine-2-carboxylate 6″g. Oil, yield=52% (A), yield=55% (B). ^{1}H NMR δ: 1.22–1.31 (m, 6H, CH(Ph)CH_3, OCH$_2$CH_3), 2.75 (d, 1H, J=2.8 Hz, H-2), 3.15 (d, 1H, J=2.8 Hz, H-3), 4.01 (q, 1H, J=6.4 Hz, CH(Ph)CH_3), 4.15 (m, 2H, OC$H_2$$CH_3$), 7.12–7.32 (m, 10H, Ph). ^{13}C NMR δ: 14.2 (OCH$_2$$CH_3$), 23.5 (CH(Ph)$CH_3$), 44.6 (C-2), 47.9 (C-3), 60.6 (CH(Ph)CH_3), 61.2 (O$CH_2$$CH_3$), 126.9, 127.3, 127.8, 128.0, 128.5, 129.1, 135.7, 144.5 (Ph), 167.9 (C=O). M.S. m/z: 295 (M$^+$, 1), 190 (100), 117 (79), 105 (47). IR ν_{max} (neat) cm^{-1}: 2977, 1724, 1455, 1184. Anal. Calcd for $C_{19}H_{21}NO_2$: C, 77.03; H, 7.17; N, 4.74. Found: C, 77.17; H, 7.35; N, 4.93. $[\alpha]_D^{25}$ +22 (c 1.0 in CH_2Cl_2).

References and notes

1. (a) Gerhart, F.; Higgins, W.; Tardif, C.; Ducep, J. *J. Med. Chem.* **1990**, *33*, 2157. (b) Kasai, M.; Kono, M. *Synlett* **1992**, 778. (c) Tanner, M. E.; Miao, S. *Tetrahedron Lett.* **1994**, *35*, 4073. (d) Hodgkinson, T. J.; Shipman, M. *Tetrahedron* **2001**, *57*, 4467.
2. (a) Toda, A.; Aoyama, H.; Mimura, N.; Ohno, H.; Fujii, N.; Ibuka, T. *J. Org. Chem.* **1998**, *63*, 7053. (b) Hwang, G.-I.; Chung, J.-H.; Lee, W. K. *J. Org. Chem.* **1996**, *61*, 6183. (c) Wipf, P.; Uto, Y. *Tetrahedron Lett.* **1999**, *40*, 5165. (d) Cardillo, G.; Gentilucci, L.; Tolomelli, A. *Tetrahedron Lett.* **1999**, *40*, 8261. (e) Park, C. S.; Choi, H. G.; Lee, H.; Lee, W. K.; Ha, H.-J. *Tetrahedron: Asymmetry* **2000**, *11*, 3283. (f) Shin, S.-H.; Han, E. Y.; Park, C. S.; Lee, W. K.; Ha, H.-J. *Tetrahedron: Asymmetry* **2000**, *11*, 3293. (g) Ley, S.; Middleton, B. *J. Chem. Soc.* **1998**, 1995. (h) Ibuka, T.; Mimura, N.; Aoyama, H.; Akaji, M.; Ohno, H.; Miwa, Y.; Taga, T.; Nakai, K.; Tamamura, H.; Fujii, N.; Yamamoto, Y. *J. Org. Chem.* **1997**, *62*, 999.
3. (a) Mc Coull, W.; Davis, F. A. *Synthesis* **2000**, *10*, 1347. (b) Kulkarni, Y. S. *Aldrichim. Acta* **1999**, *32*, 18. (c) Righi, G.; Bonini, C. *Targets Heterocycl. Syst.* **2000**, *4*, 139. (d) Lee, W. K.; Ha, H.-J. *Aldrichim. Acta* **2003**, *36*, 57.
4. (a) Yadav, J. S.; Reddy, B. V. S.; Jyothirmai, B.; Murty, M. S. R. *Synlett* **2002**, 53. Yadav, J. S.; Reddy, B. V. S.; Sadashiv, K.; Harikisham, K. *Tetrahedron Lett.* **2002**, *43*, 2099. (b) Sekar, G.; Singh, V. K. *J. Org. Chem.* **1999**, *64*, 2537. (c) Katagiri, T.; Takahashi, M.; Fujiwara, Y.; Ihara, H.; Uneyama, K. *J. Org. Chem.* **1999**, *64*, 7323. (d) Bae, J. H.; Shin, S.-H.; Park, C. S.; Lee, W. K. *Tetrahedron* **1999**, *55*, 10041. (e) Chuang, T.-H.; Sharpless, K. B. *Org. Lett.* **2000**, *2*, 3555. (f) Wu, J.; Hou, X.-L.; Dai, L.-X. *J. Chem. Soc., Perkin Trans. 1* **2001**, 1314. Hou, X.-L.; Fan, R. H.; Dai, L.-X. *J. Org. Chem.* **2002**, *67*, 5295. (g) Caiazzo, A.; Dalili, S.; Yudin, A. K. *Org. Lett.* **2002**, *4*, 2597. (h) Prévost, N.; Shipman, M. *Tetrahedron* **2002**, *58*, 7165. (i) Sugihara, Y.; Iimura, S.; Nakayama, J. *J. Chem. Soc.* **2002**, 134. (l) Davoli, P.; Moretti, I.; Prati, F.; Apler, H. *J. Org. Chem.* **1999**, *64*, 518.
5. (a) Cardillo, G.; Gentilucci, L.; Tolomelli, A. *Aldrichim. Acta* **2003**, *36*, 39. (b) Lee, K.-D.; Suh, J.-M.; Park, J.-H.; Ha, H.-J.; Choi, H. G.; Park, C. S.; Chang, J. W.; Lee, W. K.; Dong, Y.; Yun, H. *Tetrahedron* **2001**, *57*, 8267.
6. (a) Tanner, D. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 599. (b) Osborn, H. M. I.; Sweeney, J. *Tetrahedron: Asymmetry* **1997**, *8*, 1693. (c) Atkinson, R. S. *Tetrahedron* **1999**, *55*, 1519.
7. (a) Atkinson, R. S. *Tetrahedron* **1999**, *55*, 1519. Atkinson, R. S.; Ayscough, A. P.; Gattrell, W. T.; Raynham, T. M. *J. Chem. Soc., Perkin Trans. 1* **1998**, 2783. Atkinson, R. S.; Meades, C. K. *J. Chem. Soc., Perkin Trans. 1* **2001**, *1*, 1518. Atkinson, R. S.; Draycott, R. D.; Hirst, D. J.; Parratt, M. J.; Raynham, T. M. *Tetrahedron Lett.* **2002**, *43*, 2083. (b) Evans, D. A.; Fault, M. M.; Bilodeau, M. T.; Anderson, B. A.; Barnes, D. M. *J. Am. Chem. Soc.* **1993**, *115*, 5328. (c) Li, Z.; Quan, R. W.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1995**, *117*, 5889. (d) Gillespie, K. M.; Sanders, C. J.; O'Shaughnessy, P.; Westmoreland, I.; Thickitt, C. P.; Scott, P. *J. Org. Chem.* **2002**, *67*, 3450. (e) Quan, R. W.; Li, Z.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1996**, *118*, 8156. (f) Cardillo, G.; Gentilucci, L.; Tomasini, C.; Visa Castejon-Bordas, M. P. *Tetrahedron: Asymmetry* **1996**, *7*, 755. Cardillo, G.; Fabbroni, S.; Gentilucci, L.; Gianotti, M.; Perciaccante, R.; Tolomelli, A. *Tetrahedron: Asymmetry* **2002**, *13*, 1407.
8. (a) Loncaric, C.; Wulff, W. D. *Org. Lett.* **2001**, *3*, 3675. (b) Davis, F. A.; Liu, H.; Zhou, P.; Fang, T.; Reddy, G. V.; Zhang, Y. *J. Org. Chem.* **1999**, *64*, 7559.
9. Galindo, A.; Orea, L.; Gnecco, D.; Enriquez, R. G.; Toscano, A.; Reynolds, W. F. *Tetrahedron: Asymmetry* **1997**, *8*, 2877. Chang, J.-W.; Bae, J. H.; Shin, S.-H.; Park, C. S.; Choi, D.; Lee, W. K. *Tetrahedron Lett.* **1998**, *39*, 9193.
10. (a) Nakajima, K.; Kawai, H.; Takai, M.; Okawa, K. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 917. (b) Olofsson, B.; Wijtmans, R.; Somfai, P. *Tetrahedron* **2002**, *58*, 5979. (c) McCort, I.; Ballereau, S.; Dureault, A.; Depezay, J.-C. *Tetrahedron* **2002**, *58*, 8947.
11. (a) Toshimitsu, A.; Abe, H.; Hirosawa, C.; Tanimoto, S. *J. Chem. Soc., Chem. Commun.* **1992**, 284. (b) Garcia Ruano, J. L.; Lorente, A.; Rodriguez Ramos, J. H. *Tetrahedron Lett.* **1998**, *39*, 9765.
12. Paulmier, C. *Phosphorus, Sulfur and Silicon* **2001**, *172*, 25.
13. (a) Sharpless, K. B.; Gordon, K. M.; Lauer, R. F.; Patrick, D. W.; Singer, S. P.; Young, M. W. *Chem. Scr.* **1975**, *8A*, 9. (b) Krief, A.; Dumont, W.; Van Ende, D.; Halazy, S.; Labar, D.; Laboureur, J. L.; Le, T. Q. *Heterocycles* **1989**, *28*, 1203. (c) Demarcus, M.; Filigheddu, S. N.; Mann, A.; Taddei, M. *Tetrahedron Lett.* **1999**, *40*, 4417. (d) Ward, V. R.; Cooper, M. A.; Ward, D. *J. Chem. Soc., Perkin Trans. 1* **2001**, 944.
14. Paulmier, C. *Selenium Reagents and Intermediates in Organic Synthesis*; Pergamon: Oxford, 1986. Patai, S.; Rappoport, Z. *The Chemistry of Organic Selenium and Tellurium Compounds*; Wiley: New York, 1986. Liotta, D. *Organoselenium Chemistry*; Wiley: New York, 1987. Krief, A.; Hevesi, L. *Organoselenium Chemistry*; Springer: Berlin, 1988. Back, T. G. *Organoselenium Chemistry: a Practical Approach*;

Oxford University Press:: Oxford, 1999. Wirth, T. *Organoselenium Chemistry: Modern Developements in Organic Synthesis*; Springer: Berlin, 2000.

15. (a) Paulmier, C.; Lerouge, P. *Tetrahedron Lett.* **1982**, *23*, 1557. Lerouge, P.; Paulmier, C. *Tetrahedron Lett.* **1984**, *25*, 1983. (b) Houllemare, D.; Ponthieux, S.; Outurquin, F.; Paulmier, C. *Synthesis* **1997**, 10. (c) Ponthieux, S.; Outurquin, F.; Paulmier, C. *Tetrahedron Lett.* **1995**, *36*, 6453. (d) Boivin, S.; Outurquin, F.; Paulmier, C. *Tetrahedron* **1997**, *53*, 16767.
16. Boivin, S.; Outurquin, F.; Paulmier, C. *Tetrahedron Lett.* **2000**, *41*, 663.
17. (a) Miniejew, C.; Outurquin, F.; Pannecoucke, X. *Org. Biomol. Chem.* **2004**, *2*, 1575. (b) Miniejew, C.; Outurquin, F.; Pannecoucke, X. *Tetrahedron* **2005**, *61*, 447.
18. Pierre, J. L.; Baret, P.; Arnaud, P. *Bull. Soc. Chim. Fr.* **1971**, 3619.
19. Cromwell, N. H.; Graff, M. A. *J. Org. Chem.* **1952**, *17*, 414. Mimura, N.; Miwa, Y.; Ibuka, T. *J. Org. Chem.* **2002**, *67*, 5796.
20. Davies, S. G.; Ichihara, O. *Tetrahedron: Asymmetry* **1991**, *2*, 183.
21. Bull, S. D.; Davies, S. G.; Fenton, G.; Mulvaney, A. W.; Prasad, R. S.; Smith, A. D. *J. Chem. Soc., Perkin Trans. 1* **2000**, 3765.
22. Costello, J. F.; Davies, S. G.; Ichihara, O. *Tetrahedron: Asymmetry* **1994**, *5*, 1999.
23. Back, T.; Dyck, B. P.; Parvez, M. *J. Org. Chem.* **1994**, *60*, 703.
24. Monfray, J.; Gelas-Mialhe, Y.; Gramain, J.-C.; Remuson, R. *Tetrahedron: Asymmetry* **2005**, *16*, 1025. Monfray, J.; Gelas-Mialhe, Y.; Gramain, J.-C.; Remuson, R. *Tetrahedron Lett.* **2003**, *44*, 5785.
25. Chalard, P.; Remuson, R.; Gelas-Mialhe, Y.; Gramain, J.-C.; Canet, I. *Tetrahedron Lett.* **1999**, *40*, 1661.
26. (a) Sewald, N.; Hiller, K. D.; Koerner, M.; Findeisen, M. *J. Org. Chem.* **1998**, *63*, 7263. (b) Cimarelli, C.; Palmieri, G. *J. Org. Chem.* **1996**, *61*, 5557.