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Diastereoselective Cyclisation of *N*-Alkenylideneamines into 3,4-Dihydro-2*H*-pyrrol-1-ium Halides

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Dedicated to Prof. Dr. Manfred Christl on the occasion of his 65th birthday

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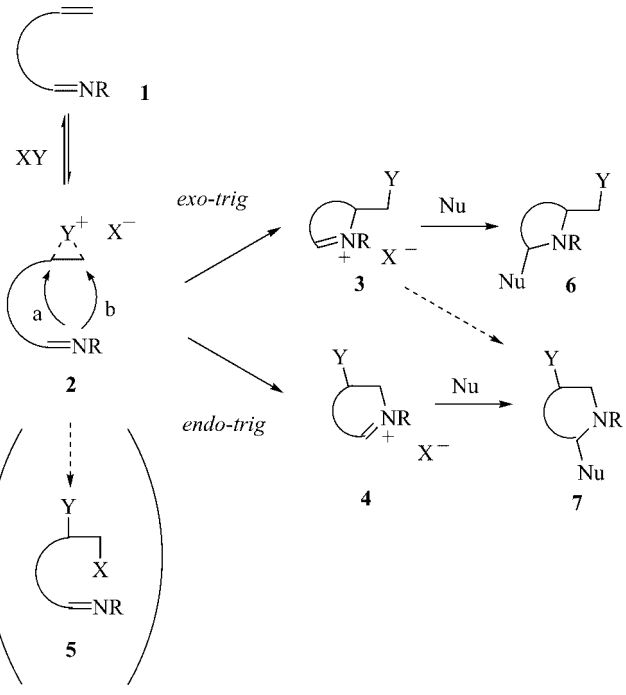
A number of new chiral 2-(α-bromoalkyl)pyrrolinium salts and 2-(α-selenoalkyl)pyrrolidines were synthesized by the halocyclisation and selenocyclisation, respectively, of *N*-(alkenylidene)alkylamines and subsequent reduction. These cyclisations were implemented in a diastereomeric fashion for the first time. Substrate control (starting imines possessing chirality in the *N*-alkyl or the *N*-alkenyl substituent) and reagent control (chiral organoselenenyl bromides) were applied. Asymmetric induction by stereocentres of the alkenylidene or double asymmetric induction by chiral selenenyl bromides on unsaturated imines with a chiral *N*-alkyl group resulted in diatereoselectivities up to 84:16.

Introduction

The asymmetric functionalisation of olefins is an important goal in synthetic organic chemistry. Thus, highly stereoselective epoxidations, dihydroxylations and hydroborations were developed. The addition of electrophiles to C=C bonds can also be combined with an intramolecular nucleophilic attack by ring formation, when alkenes with additional nucleophilic sites (O, S or N) are used as substrates. This electrophile-induced cyclisation is a versatile strategy for the construction of heterocycles. The halolactonisation, where unsaturated carboxylic acids are cyclised by a reaction with halogens to form lactones, is a well-known example of this type of reaction. Other common starting materials are unsaturated carboxylic acid derivatives, imines (Scheme 1), alcohols and amines. Halogens, *N*-halogenated succinimides, mercury(II) acetate, *tert*-butyl hydroperoxide[1] (Sharpless conditions) and organoselenenyl halides[2–5] commonly serve as electrophiles.[6]

The general mechanism of the electrophile-induced cyclisation of unsaturated imines is shown in Scheme 1. Chemo-, regio- and diastereoselectivity are important aspects of such ring formations. Thus, the reaction of the electrophile can give just an addition to the double bond (e.g. to adduct **5**) rather than undergoing a cyclisation to products **6** or **7**. On the other hand, in accordance with the Baldwin rules[7] the cyclisation can follow either the *exo-trig* or the *endo-trig* mode, leading to ring **3** or **4**, respectively. Finally, *cis-trans* isomers can be formed when nucleophiles are added to the primary cyclisation products affording cyclic amine **6** or **7**. A number of studies were devoted to the influence of different electrophiles and reaction conditions on the mode of the cyclisation of alcohols,[2–4,6] thio-



Scheme 1. General mechanism of the electrophile-induced cyclisation of unsaturated imines.

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ethers,[8–12] protected amines[6,13–22] and hydrazines,[23] carbonyl derivatives such as unsaturated oximes,[24–31] hydrazones,[30,32] imines,[33–39] acetals,[40–42] hemiaminals[43,44] and aminals[45] and carboxyl derivatives, such as amides,[46,47] thioamides[48,49] and carboxylic acids.[2–4,6] A comprehensive overview of the whole spectrum of this type of reaction is given in the reviews by Cardillo et al.,[6] Wessjohann et al.,[2] Wirth[3] and Petragnani et al.[4]

Remarkably, there have been no systematic, stereochemical studies on the ring-closing reaction of chiral *N*-(alkenylidene)alkylamines (unsaturated imines) **1**, even though the resulting product **3** or **4** is a suitable candidate for further functionalisation by reaction with nucleophiles at the iminium moiety, giving rise to the formation of interesting heterocycle (pyrrolidine or piperidine) **6** or **7**.

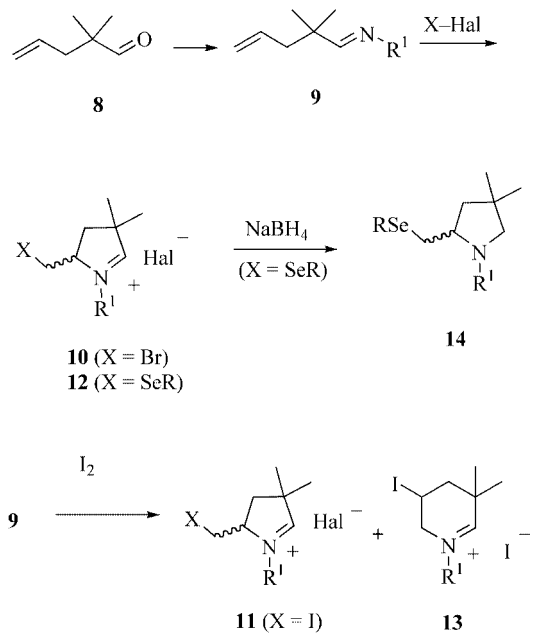
De Kimpe et al.[33,34,36] investigated the reaction of achiral *N*-(alkenylidene)alkylamines with different electrophiles, focusing on its regio- and stereochemistry and the further derivatization of the resulting iminium salts **3** with nucleophiles, such as $LiAlH_4$,[34] alkoxides[36,50] and cyanides.[51] The formation of five-membered, cyclic, iminium salts (pyrrolinium salts) **3** was observed in most cases. However, these pyrrolinium salts **3** can ring expand to six-membered ring products **7** in a subsequent reaction of nucleophiles with the C=N bond. An example of the cyclisation of racemic *N*-(alkenylidene)alkylamines[33] was published, resulting in a diastereomeric ratio (*dr*) of 1:1. The cyclisation of unsaturated optically active oximes[24,28,30,31] leads to cyclic nitrones with *dr* values from 50:50 to 86:14. A 5:1 diastereomeric mixture was obtained by the iodocyclisation of a racemic oxime.[29] Optically active *N*-anilino-2-pyrrolidones were formed by the iodocyclisation of pentose-derived phenylhydrazones in a *dr* of 70:30.[30]

So far, optically active products have not been obtained by the electrophile-induced cyclisation of *N*-(alkenylidene)-alkylamines. Herein, we report three possible approaches to the stereoselective halo- or selenocyclisation of unsaturated imines. Following a substrate control, imines were used with chiral centres in the amine part of the unsaturated imine or in the alkene moiety. Reagent control was attempted by chiral selenyl bromides.

Results

Cyclisation of Chiral *N*-(Alkenylidene)alkylamines with Achiral Reagents

N-(Alkenylidene)alkylamines of the general type **1** are easily accessible by the reaction of an appropriate amine and an aldehyde. 2,2-Dimethylpent-4-enal **8** was chosen as a suitable aldehyde because unwanted enamine tautomerism is excluded, which probably would affect the stereoinduction in the cyclisation of the corresponding imines. Compound **8** was converted into the *N*-(alkenylidene)alkylamines **9** (Scheme 2, Table 1) with various chiral amines as well as achiral or racemic amines at room temperature in dichloromethane in the presence of magnesium sulfate (see the Supporting Information).



Scheme 2. Cyclisation of optically active *N*-(alkenylidene)alkylamines (chiral R^1) with achiral electrophiles.

The electrophile-induced cyclisation of chiral and achiral imines **9** by bromine was carried out in dichloromethane at 0 °C (Table 1, entries 1, 3–7). In all cases, 2-bromomethyl-3,4-dihydro-2*H*-pyrrol-1-ium salts **10** were obtained in a 5-*exo*-*trig* mode. These compounds were isolated in high yields and fully characterized by NMR spectroscopy, showing typical ^1H and ^{13}C chemical shifts for the characteristic functional groups in the products: 8.7–10.5 ppm/186–191 ppm (*CH*=N^+), 3.3–4.4 ppm/32–34 ppm (CH_2Br) and 5.3–6.0 ppm/67–74 ppm ($BrCH_2$–*CH*–N^+). Furthermore, the X-ray analysis of the tribromide of the 5*S* stereoisomer of **10e** (Figure 1) confirmed the proposed structure. The corresponding six-membered 6-*endo*-*trig* product was not observed.

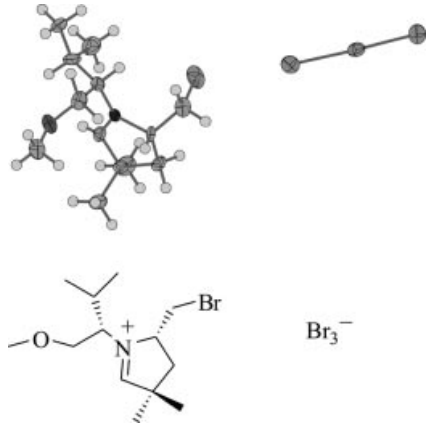
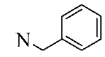
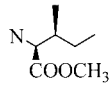
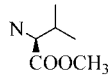
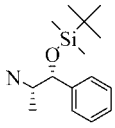
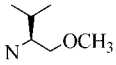
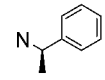
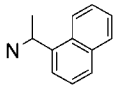
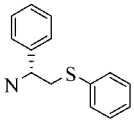
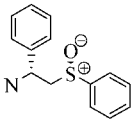
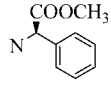
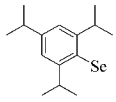


Figure 1. X-ray crystal analysis of the tribromide of the 5*S* stereoisomer of **10e**.

The determination of *dr* values by ^{1}H NMR spectroscopy of the crude products revealed an unsatisfactory stereoselectivity (*dr* = 50:50–42:58) under these conditions. In order to overcome this problem, the reaction temperature was lowered in the cyclisation of compound **9f** from 0 °C to –60 °C or –78 °C (Table 1, entry 7). A modest increase in diastereoselectivity from 45:55 (0 °C) to 35:65 (–75 °C) was observed. Attempts to improve the diastereomeric ratio by the addition of Lewis acids to the reaction mixture were not successful. The addition of $ZnBr_2$ or LiBr did not cause a significant improvement, whereas strong Lewis acids such as $BF_3{\cdot}Et_2O$ or Et_2AlCl prevented the cyclisation (Table 1, entry 6).

Using less reactive iodine in dichloromethane at 0 °C for the cyclisation of the imine **9f** and the achiral *tert*-butyl-substituted **9k** led to mixtures of constitutionally isomeric pyrrolinium salts **11** and tetrahydropyridinium salts **13** as a result of competition between 5-*exo*-*trig* and 6-*endo*-*trig* cyclisation. The latter might occur as a result of thermodynamic control, achieved by iodine, which is less reactive than bromine. Imine **9f** gave rise to a constitutional isomer ratio of 86:14 (*dr* = 63:37 and 69:31, respectively) in favour of the five-membered ring **11a** (Table 1, entry 9), whereas in the case of the *N*-*tert*-butyl substrate **9k**, the pyridinium iodide **13b** was formed as the major isomer of a 19:81 mixture (Table 1, entry 15). Obviously, the bulkiness of the *N*-

Table 1. Synthesis of iminium salts **10**–**13** and pyrrolidines **14**.

Entry	N–R[1]	Imine **9**	X	Hal	Iminium salts **10**–**13**	Yield, *dr*[a] (0 °C)	Pyrrolidines **14**	Yield, *dr*[a] (–78 °C)
1		**9a**	Br	Br	**10a**	96 %[b]		
2			PhSe	Br	**12a**		**14a**	59 %[b]
3		**9b**	Br	Br	**10b**	quant., 44:56		
4		**9c**	Br	Br	**10c**	quant., 46:54		
5		**9d**	Br	Br	**10d**	96 %, 50:50		
6		**9e**	Br	Br	**10e**	93 %, 42:58[c]		
7		**9f**	Br	Br	**10f**	quant., 45:55[d]		
8			PhSe	Br	**12b**		**14b**	62 %, 47:53[e]
9			I	I	**11a** +**13a**	quant.[f]		
10		**9g**[a]	PhSe	Br	**12c**		**14c**	81 %, 48:52
11		**9h**	PhSe	Br	**12d**		**14d**	45 %, 41:59
12		**9i**	PhSe	Br	**12e**		**14e**	75 %, 33:67[e]
13		**9j**	PhSe	Br	**12f**		**14f**	59 %, 35:65[e,g]
14				Br	**12g**		**14g**	61 %, 39:61[d]
15	*t*Bu	**9k**	I	I	**11b** + **13b**	67 %[h]		

[a] Determined by ^{1}H NMR spectroscopy (± 5%). [b] Racemate. [c] Lewis acids were added, and the corresponding values obtained are given in parentheses: $ZnBr_2$ (*dr* = 42:58), LiBr (*dr* = 42:58), $BF_3{\cdot}Et_2O$ (no reaction), Et_2AlCl (no reaction). [d] *dr* = 40:60 at –60 °C, *dr* = 35:65 at –78 °C, *dr* = 36:64 at –90 °C. [e] Separation of diastereomers by column chromatography. [f] A mixture of constitutional isomers was obtained: pyrrolidinium iodide **11a**, 86%, *dr* = 63:37; pyridinium iodide **13a**, 14%, *dr* = 69:31. [g] *dr* = 40:60 at –50 °C in $CHCl_3$. [h] A mixture of constitutional isomers was obtained: pyrrolidinium iodide **11b**/pyridinium iodide **13b** = 19:81.

alkyl substituent governs the regioselectivity in these cases. The products of these iodocyclisations could not be separated but were unambiguously assigned by ^{13}C NMR spectroscopy (e.g. CH_2I (9.7 ppm) and CH–I (12.7 ppm) for **11b** and **13b**, respectively).

Cyclisations of optically active, racemic (**9g**) and achiral (**9a**, **9k**) imines **9** with arylselenyl bromide as the electrophile were carried out at –78 °C in dichloromethane (Table 1). In all cases, the 5-membered-ring iminium salts **12** (X = SePh) formed by the cyclisation were subsequently reduced by sodium borohydride. The resulting pyrrolidines **14** were stable enough for isolation and purification by column chromatography, but the yields were generally lower than those obtained in halocyclisations. This might be an indication that the reduction step from **12** (X = RSe) to pyrrolidines **14** is a low-yielding reaction. NMR spectroscopic studies [2.8–3.2 ppm /33–36 ppm (CH_2–Se), 2.9–3.2 ppm /59–63 ppm ($SeCH_2$–*CH*), 1.4–1.9 ppm/46–47 ppm (CH–CH_2–C_q) and 2.0–2.8 ppm/60–68 ppm (d, N–CH_2–C_q)] and X-ray analysis of the 5*S* stereoisomer (*S*)-**14f** of the pyrrolidine **14** (Figure 2) verified the assigned structure. We determined the *dr* values of these products as ranging from 48:52 to 33:67, which were slightly higher than those obtained in the bromocyclisation. It turned out that *N*-(alkenylidene)alkylamines with an additional heteroatom in the *N*-alkyl substituent gave a somewhat higher induction in selenocyclisations than pure hydrocarbon substituents (Table 1).

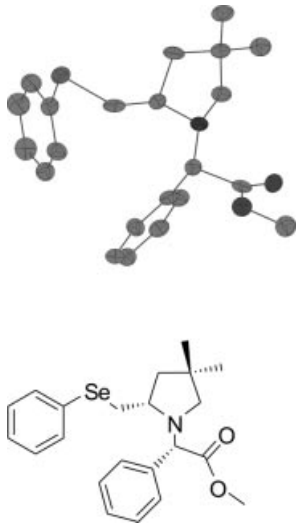
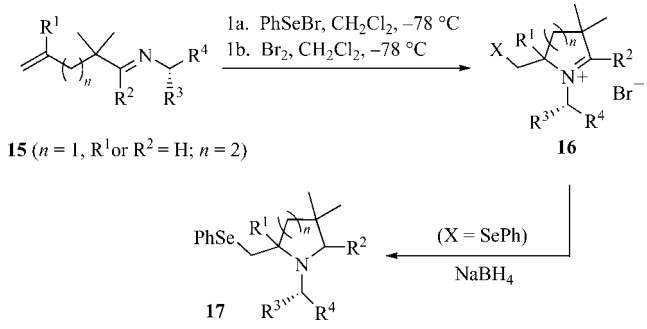


Figure 2. X-ray crystal analysis of the 5*S* stereoisomer of the pyrrolidine **14f** (major isomer).

Sterically hindered organoselenenyl halides were successfully used by Lipshutz et al.[52] to improve the diastereoselectivity of the electrophile-induced cyclisation of alcohols. Interestingly, the application of 2,4,6-(triisopropylphenyl)selenenyl bromide in the cyclisation of the imine **9j** caused the opposite effect; in other words, the diastereoselectivity was slightly lower than that observed with phenylselenyl bromide (Table 1, entries 13 and 14).

We further investigated the effect of introducing substituents into the alkylidene moiety of chiral imines **9** or of chain homologation. Thus, *N*(alkenylidene)alkylamines **15** were cyclised with phenylselenyl bromide, and in the case of **15c**, also with bromine (Scheme 3). Again, the selenocyclisation products **16** (X = SePh) were reduced to the corresponding pyrrolidines **17** by sodium borohydride. The cyclisation of the *N*(hexenylidene)amine **15a** (Table 2, entry 2), which represents a homolog of the imine **9j**, afforded a six-membered ring product by the *exo*-*trig* mode. The *dr* determined for the corresponding piperidine **17a** was lower than that determined in the case of **9j** cyclisation. Thus, this homologation had a disadvantageous effect on the diastereoselectivity (Table 2, entries 1 and 2).



Scheme 3. Cyclisation of optically active *N*-(alkenylidene)alkylamines **15**.

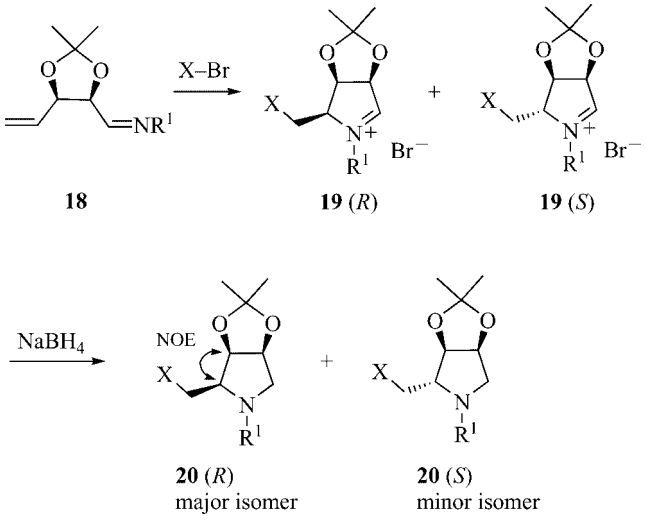
It can be expected that an R^1 methyl substituent shields the C=C bond to a certain extent, and thus, could give rise to an increase in stereoselectivity in electrophile-induced cyclisation. However, the opposite effect was observed (Table 2, compare entry 1 with entry 3 and entry 1 with entry 5). The application of bromine instead of phenylselenyl bromide gave the same unsatisfactory diastereoselectivity (Table 2, entries 1 and 4). Finally, we investigated the effect of a phenyl group at position 1 of the alkylidene moiety of imines **15** (Table 2, entry 6). Selenocyclisation followed by reduction gave rise to a mixture of four diastereomeric products **17d** (*dr* = 13:21:38:28). The cyclisation

Table 2. Syntheses of **14** and **17** and comparison of diastereomeric ratios.

Entry	Imine	Iminium salt	Saturated heterocycle	R^1	R^2	R^3	R^4	*n*	X	*dr*	Yield [%]
1	**9j**	**12f**	**14f**	H	H	$COOCH_3$	Ph	1	PhSe	35:65	58
2	**15a**	**16a**	**17a**	H	H	$COOCH_3$	Ph	2	PhSe	46:54	64
3	**15b**	**16b**	**17b**	Me	H	$COOCH_3$	Ph	1	PhSe	46:54	36
4	**15c**	**16c**	–	Me	H	$COOCH_3$	Ph	1	Br	46:54	quant.
5	**9f**	**12b**	**14b**	H	H	Ph	Me	1	PhSe	47:53	62
6	**15d**	**16d**	**17d**	H	Ph	Ph	Me	1	PhSe	13:21:38:28	57

to **16d** as well as the subsequent reduction to **17d**, where a second stereogenic centre was formed, occurred with unsatisfactory diastereoselectivity. In summary, homologation as well as the introduction of substituents into the alkylidene moiety of chiral imines did not lead to higher stereoselectivities.

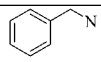
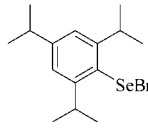
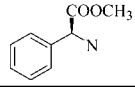
We further approached diastereoselective seleno- or halocyclisation by introducing chirality into the alkenylidene moiety of unsaturated imines. Imines **18** were obtained from a ribose-derived aldehyde (see electronic Supporting Information).[53–55] In the *N*(alkenylidene)alkylamine **18a**, chirality is only found in the alkylidene part, while the other imines **18** are chiral in both the alkylidene and the amine moiety (Scheme 4, Table 3). In all the imines **18**, a chiral centre is near the C=C bond, and thus, a better facial selectivity of the primary electrophilic attack can be expected, which is probably crucial for the overall diastereoselective formation of products **19**. Indeed, an increase in diastereoselectivity to *dr* = 20:80 was observed in the selenocyclisation of **18a** with phenylselenyl bromide. But similar to the other selenocyclisations (vide supra), the product **20a** was formed in low yield. Working at low temperature in $CHCl_3$ had no advantageous effect (Table 3, entry 1, footnote a). Remarkably, the application of the bulkier 2,4,6-(triisopropylphenyl)selenyl bromide gave lower stereoselectivity (38:62) as it did for **9j** (Table 3, entry 3 and Table 2, entry 14). The same stereochemical result was obtained with bromine (Table 3, entry 2), and bromopyrrolinium salt **19b** was obtained in high yield.



Scheme 4. Cyclisation of optically active *N*-(alkenylidene)alkylamines **18** with chiral alkylidene groups with achiral electrophiles.

Epimers **18b** and **18c** appeared as a matched/mismatched pair in the selenocyclisation. We observed *dr* values of 16:84 and 40:60, respectively. Obviously, the chirality in the alkylidene moiety of the unsaturated imine exerts the predominating asymmetric induction. This fact also matches with the very poor stereoselectivities in the cyclisation of imines **9** lacking chirality in the alkylidene part (see Table 1, entry 8). The selenocyclisation of the phenylglycine derivative **18d** gave a marked diastereoselectivity of *dr* = 19:81, but the yields were even lower. NOE investigations of the products **20** and an X-ray crystal analysis of the pyrrolidine **20d** (see Figure 3) revealed that in all cases the *all-cis*-isomer (***R***)-**20** was the major isomer.

Table 3. Synthesis of pyrrolidines **20**.

Entry	R[1]	Imine **18**	X–Br	Salts **19**	**20**	Yield, *dr* (at 0 °C)
1		**18a**	PhSeBr	**19a**	**20a**	42 %, 20:80[a]
2			Br_2	**19b**		quant., 38:62[b]
3				**19c**	**20c**	33 %, 38:62[b]
4		**18b**	PhSeBr	**19d**	**20d**	50 %, 16:84
5		**18c**	PhSeBr	**19e**	**20e**	53 %, 40:60
6		**18d**	PhSeBr	**19f**	**20f**	22 %, 19:81

[a] 38%, *dr* = 75:25 at –50 °C in $CHCl_3$. [b] *cis*/*trans* assignments for the isomers were not possible by NMR spectroscopy.

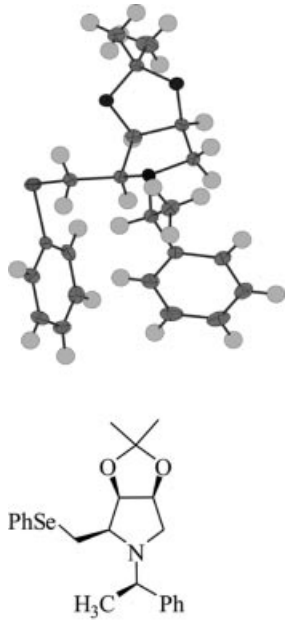
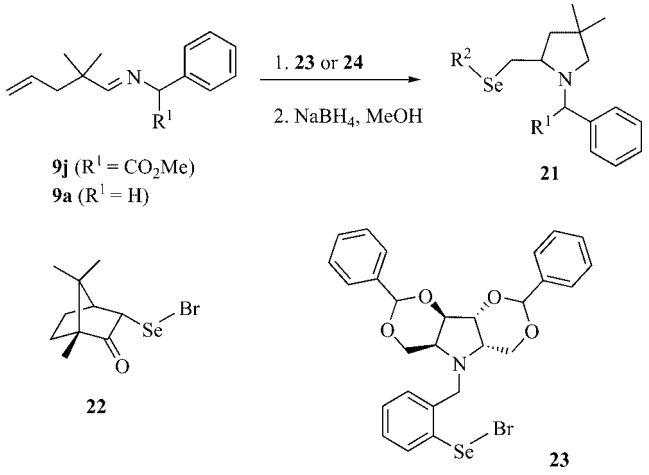


Figure 3. X-ray crystal analysis of the 5*S* stereoisomer of **20d**.

Cyclisation of *N*-(Alkenylidene)alkylamines with Chiral Electrophiles

Inspired by the fact that chiral organoselenenyl halides can stereoselectively react with alkenes on one hand[56,57] and that this methodology has not yet been applied to the

inter- or intramolecular additions of imines to alkenes on the other hand, we tried to apply such chiral selenyl bromides to the selenocyclisation of unsaturated imines. The chiral selenyl bromides **22**[58–67] and **23**,[68–77] generated in situ from the corresponding diselenides and bromine, were applied to the achiral imine **9a** at –78 °C (Scheme 5).



Scheme 5. Cyclisation of *N*-(alkenylidene)alkylamines **9** with chiral selenenyl bromides.

The camphor-derived selenyl bromide **22** gave a slightly higher diastereoselectivity than did **23**, but it was still unsatisfactory (*dr* = 41:59 and 48:52, Table 4, entries 1 and 2, respectively). In a double asymmetric induction[78] approach, selenyl bromide **22** was reacted with the chiral amines **9j** and (*S*)-**9j**. Compound (*S*)-**9j** appeared as a matched case (38:62 and 24:76, Table 4, entries 3 and 4, respectively). Each of the diastereomeric products **21c** exists in two rotameric forms, as proven by temperature-dependent dynamic ^{1}H NMR investigations.

Table 4. Synthesis of pyrrolidines **21**[a].

Entry	R^1	Imine	R^2–SeBr	Pyrrolidines	Yield [%]	*dr*
1	H	**9a**	**22**	**21a**	33	41:59
2	H	**9a**	**23**[b]	**21b**	72	48:52
3	CO_2Me	**9j**	**22**	**21c**	46	38:62[c,d]
4	CO_2Me	(*S*)-**9j**	**22**	**21d**	40	24:76

[a] Reactions were performed at 0 °C. [b] $AgPF_6$ was added. [c] Separation of diastereomers by column chromatography. [d] Diastereomers were isolated as a mixture of rotamers.

Conclusions

In summary, a series of new chiral 2-(α-bromoalkyl)pyrrolinium salts **10**, **16c** and **19b** and 2-(α-selenoalkyl)pyrrolidines **14**, **17**, **20** and **21** were obtained by the halo- or selenocyclisations, respectively, of unsaturated imines (*N*-alkylidene-*N*-alkylamines) and subsequent reduction. Several effects on the stereoselectivity, such as chirality in the amine or the alkylidene substituent, the size of substituents in the alkylidene moiety, the type of electrophile (bromine, iodine, arylselenyl bromides, or chiral organoselenenyl bromides), temperature and the presence of Lewis acids were investigated. As a result, marked diastereoselectivities (up to *dr* = 84:16) were only obtained with a pentose-derived chiral alkylidene substituent and in the case of double asymmetric induction when the imine (*S*)-**9j**, with a chiral *N*-alkyl group (phenylalanine derivative), was cyclised with a camphor-derived selenyl bromide. These are the first cases reported for stereoselective electrophile-induced cyclisations of unsaturated *N*-alkylidene-*N*-alkylamines.

Experimental Section

General Remarks: ^{1}H NMR and ^{13}C NMR spectra were recorded at 300 MHz and 75.5 MHz, respectively, with a Bruker AC 300 spectrometer in $CDCl_3$ with TMS as an internal standard. Diastereomeric ratios were determined by ^{1}H NMR spectroscopy of the crude products. Cyclisation products were obtained as diastereomeric mixtures, and their spectra were recorded from the mixtures, if not otherwise mentioned. Silica gel (0.04–0.063 mm, Merck) was used for preparative column chromatography. Starting materials were purchased from commercial suppliers. All *N*(alkenylidene)alkylamines and 3,4-dihydro-2*H*-pyrrolium bromides decompose easily but can be stored in a freezer (–20 °C) for a few days.

General Procedure for the Synthesis of 3,4-Dihydro-2*H*-pyrrolium Bromides 10: The appropriate *N*(alkenylidene)alkylamine **9** (0.50 mmol) was dissolved in dry CH_2Cl_2 (10 mL) at 0 °C under argon in a flame-dried flask. A solution of bromine in dry CH_2Cl_2 (0.04 M, 0.50 mmol) was added over 30 min, and the temperature was maintained for 2 h at 0 °C. The mixture was warmed slowly to room temperature. The solution was concentrated under vacuum below room temperature, and the remaining product was stored under argon at –20 °C.

***rac*-1-Benzyl-2-bromomethyl-4,4-dimethyl-3,4-dihydro-2*H*-pyrrolium Bromide (10a):** Starting material **9a** (300 mg, 1.49 mmol). Yield: 518 mg (96%), colourless solid, m.p. 60 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.04 (s, 3 H, C*H*$_3$), 1.14 (s, 3 H, C*H*$_3$), 2.04 [dd, *J* = 7.5 Hz, *J* = 13.6 Hz,1 H, C*H*H–C(CH$_3$)$_2$], 2.42 [dd, *J* = 8.7 Hz, *J* = 13.6 Hz, 1 H, C*H*H–C(CH$_3$)$_2$], 3.74 (dd, *J* = 1.9 Hz, *J* = 12.4 Hz, 1 H, CH*H*–Br), 4.12 (dd, *J* = 4.3 Hz, *J* = 12.2 Hz, 1 H, C*H*H–Br), 5.32 (d, *J* = 6.4 Hz 2 H, C*HH*–Ph), 5.44–5.55 (m, 1 H, C*H*–N), 7.37–7.39 (m, 3 H, C*H*$_{ar}$), 7.56–7.59 (m, 2 H, C*H*$_{ar}$), 8.99 (s, 1 H, C*H*=N$^+$) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 24.8 (*C*H$_3$), 25.7 (*C*H$_3$), 32.2 (*C*H$_2$–Br), 39.1 [*C*H$_2$–C(CH$_3$)$_2$], 47.5 [*C*(CH$_3$)$_2$], 55.5 (*C*H$_2$–Ph), 70.5 (*C*H–N), 129.2 (*C*$_{ar}$), 129.8 (2 *C*H$_{ar}$), 130.2 (3 *C*H$_{ar}$), 186.2 (*C*H=N$^+$) ppm. $C_{14}H_{19}Br_2N$ (361.115): calcd. C 46.56, H 5.30, Br 44.25, N 3.88; found C 46.60, H 5.32, Br 43.78, N 3.87.

(2*S*)-2-Bromomethyl-1-[(1*S*,2*S*)-1-methoxycarbonyl-2-methylbutyl]-4,4-dimethyl-3,4-dihydro-2*H*-pyrrolium Bromide and (2*R*)-2-Bromomethyl-1-[(1*S*,2*S*)-1-methoxycarbonyl-2-methylbutyl]-4,4-dimethyl-3,4-dihydro-2*H*-pyrrolium Bromide (10b): Starting material **9b** (60 mg, 0.25 mmol). Diastereomers were not separated. Yield: 100 mg (0.25 mmol, quant.), *dr* = 44:56, yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.78–0.95 (m, 4 H, C*H*–CH$_3$, CH$_2$–C*H*$_3$), 0.98 (s, 3 H, C*H*$_3$), 1.01 (s, 3 H, C*H*$_3$), 1.51, 1.54 (d, *J* = 6.1 Hz, *J* = 7.9 Hz, 3 H, CH–C*H*$_3$), 1.30–1.55 (m, 2 H, C*H*$_2$–CH$_3$), 1.94–2.56 [m, 2 H, C*H*$_2$–C(CH$_3$)$_2$], 3.82–4.41 (m, 2 H, C*H*$_2$–Br), 3.79, 3.84 (s, 3 H, COOC*H*$_3$), 4.88, 4.95 (d, *J* = 9.1 Hz, *J* = 5.6 Hz 1 H, C*H*–COO), 5.59–5.68, 5.89–5.98 (m, 1 H, C*H*–N), 9.38, 9.64 (s, 1 H, C*H*=N$^+$) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 11.3, 11.4

(CH_2–CH_3), 14.8, 15.2 (CH–CH_3), 24.7, 24.9 (C_q–CH_3), 25.8, 26.8 (C_q–CH_3), 25.2, 27.1 (CH_2–CH_3), 33.0, 34.2 (CH_2–Br), 36.6, 40.2 (CH–CH_3), 37.8, 38.4 [CH_2–$C(CH_3)_2$], 48.9, 49.0 [$C(CH_3)_2$], 53.9, 54.2 ($COOCH_3$), 66.7, 67.4 (CH–N), 73.3, 74.6 (CH–COO), 166.8, 167.9 (COO), 189.2, 190.3 ($CH{=}N^+$) ppm. HRMS (EI): calcd. for $C_{14}H_{25}BrNO_2$ 318.1069/320.1048; found 318.1069/320.1049.

(2*S*)-2-Bromomethyl-1-[(1*S*)-1-methoxymethyl-2-methylpropyl]-4,4-dimethyl-3,4-dihydro-2*H*-pyrrolium Bromide and (2*R*)-2-Bromomethyl-1-[(1*S*)-1-methoxymethyl-2-methylpropyl]-4,4-dimethyl-3,4-dihydro-2*H*-pyrrolium Bromide (10e): Starting material **9e** (379 mg, 1.79 mmol). Diastereomers were not separated. Yield: 616 mg (1.66 mmol, 93%), *dr* = 42:58, yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.09 (d, J = 6.4 Hz, 3 H, CH–CH_3), 1.17 (d, J = 6.8 Hz, 3 H, CH–CH_3), 1.52 (s, 3 H, CH_3), 1.61 (s, 3 H, CH_3), 2.16–2.62 [m, 4 H, CH–CH_3, CH–CH_2O, CH_2–$C(CH_3)_2$], 3.43, 3.45 (s, 3 H, OCH_3), 3.70–4.14 (m, 4 H, CH_2–Br, CH_2O), 5.30–5.41 (m, 1 H, CH–N), 8.72, 8.86 (s, 1 H, $CH{=}N^+$) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 18.8, 19.3 (CH–CH_3), 19.5, 20.4 (CH–CH_3), 24.8, 25.0 (C_q–CH_3), 26.0, 26.6 (C_q–CH_3), 27.7, 31.0 (CH–CH_3), 32.2, 33.0 (CH_2–Br), 38.4, 38.5 [CH_2–$C(CH_3)_2$], 48.3, 48.5 [$C(CH_3)_2$], 59.5, 59.6 (OCH_3), 67.8, 68.5 (CH–CH_2O), 68.6, 68.7 (CH_2–O), 71.9, 74.0 (CH–N), 187.3, 187.8 ($CH{=}N^+$) ppm. HRMS (EI): calcd. for $C_{13}H_{25}BrNO$ 290.1120; found 290.1118. Tribromide (*S*)-**10e** was obtained from a $CHCl_3$ solution with excess Br_2 as an orange solid with m.p. 114 °C (CH_2Cl_2/Et_2O).

X-ray Crystal Analysis of the Corresponding Tribromide (*S*)-10e:[79] Empirical formula: $C_{13}H_{25}Br_4NO$, formula weight: 530.98 g/mol, temperature: 180(2) K, wavelength: 0.71073 Å, crystal system: orthorhombic, space group: $P2_121_121$, unit cell dimensions: a = 9.341(3) Å, b = 13.381(4) Å, c = 13.381(4) Å, V = 1928.1(12) Å^3, Z = 4, density (calculated): 1.829 Mg/m^3, absorption coefficient: 8.343 mm^{-1}, $F(000)$ = 1032, crystal size: 0.80 × 0.32 × 0.28 mm, theta range for data collection: 2.01 to 25.90°, limiting indices: $-8 \le h \le 11$, $0 \le k \le 16$, $0 \le l \le 18$; reflections collected: 4078, unique: 3586 [R(int.) = 0.0515], completeness to θ = 25.90 is 99.9%, absorption correction: empirical (psi-scan), max./min. transmission: 0.2035/0.0573, refinement method: full-matrix least-squares on F^2, data/restraints/parameters: 3586–0–189, goodness-of-fit on F^2: 1.112, final R indices [$I > 2\sigma(I)$]: R_1 = 0.0631, wR_2 = 0.1328, R indices (all data): R_1 = 0.1124, wR_2 = 0.1650, absolute structure parameter: 0.03(4), extinction coefficient: 0.0010(4), largest diff. peak and hole: 0.889 and –1.144 e/Å^3.

2-Iodomethyl-4,4-dimethyl-1-[(*R*)-1-phenylethyl]-3,4-dihydro-2*H*-pyrrolium Iodide (11a) and 3-Iodo-5,5-dimethyl-1-[(*R*)-1-phenylethyl]-2,3,4,5-tetrahydropyridinium Iodide (13a): 9f (69 mg, 0.32 mmol) was dissolved in dry CH_2Cl_2 (10 mL) at 0 °C under argon in a flame-dried flask. A solution of iodine (81 mg, 0.32 mmol) in dry CH_2Cl_2 (10 mL) was added over 30 min, and the temperature was maintained for 2 h at 0 °C. The mixture was warmed slowly to room temperature and was concentrated under vacuum below room temperature to give 0.15 g (0.32 mmol, quant. yield) of a yellow oil. Isomers were not separated. **11a**/**13a** = 86:14; *dr* (**11a**) = 37:63; *dr* (**13a**) = 31:69). HRMS (EI): calcd. for $C_{15}H_{21}IN$ 342.0713; found 342.0713. Major isomer **11a**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.46, 1.49 (s, 3 H, CH_3), 1.58, 1.65 (s, 3 H, CH_3), 1.82–1.96 (m, 1 H, CH_2–C_q), 2.03, 2.00 (d, J = 10.0 Hz, 3 H, CH–CH_3), 2.40, 2.57 (dd, J = 8.0 Hz, J = 13.5 Hz, 1 H, CHH–C_q), 3.54–3.62 (m, 1 H, CHH–I), 3.74–3.80 (m, 1 H, CHH–I), 5.07–5.16, 5.33–5.42 (m, 1 H, CH–CH_3), 4.13–4.25, 5.40–5.49 (m, 1 H, CH), 7.32–7.48 (m, 5 H, CH_{ar}), 9.92, 10.10 (s, 1 H, $CH{=}N^+$) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 5.9, 7.8 (CH_2–I), 20.9, 21.6 (CH–CH_3), 24.6, 25.3 (CH_3), 26.1, 26.4 (CH_3), 41.6, 42.0 (CH_2), 47.6 [$C(CH_3)_2$], 62.5, 63.0 (CH–CH_3), 69.1, 72.0 (CH–N), 126.6, 127.7 (2 CH_{ar}), 128.1, 128.8 (CH_{ar}), 130.1, 130.2 (2 CH_{ar}), 134.2, 134.4 (CH–C_{ar}), 185.1, 185.2 ($CH{=}N^+$) ppm. Minor isomer **13a**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.99, 1.10 (s, 3 H, CH_3), 1.53, 1.58 (s, 3 H, CH_3), 2.03–2.00 (m, 4 H, CH–CH_3, CHH–C_q), 2.07–2.30 (m, 1 H, CHH–C_q), 4.61–4.70, 4.92–5.03 (m, 3 H, CH–CH_3, CH_2–N), 4.65–4.74 (m, 1 H, CH–I), 7.32–7.48 (m, 5 H, CH_{ar}), 9.22, 9.56 (s, 1 H, $CH{=}N^+$) ppm.

1-*tert*-Butyl-2-iodomethyl-4,4-dimethyl-3,4-dihydro-2*H*-pyrrolium Iodide (11b) and 1-*tert*-Butyl-3-iodo-5,5-dimethyl-2,3,4,5-tetrahydropyridinium Iodide (13b): 9k (100 mg, 0.598 mmol) was dissolved in dry CH_2Cl_2 (10 mL) at 0 °C under argon in a flame-dried flask. A solution of iodine (152 mg, 0.598 mmol) in dry CH_2Cl_2 (10 mL) was added over 30 min, and the temperature was maintained at 0 °C for 2 h. The mixture was warmed slowly to room temperature and was concentrated under vacuum. The crude product was recrystallized from CH_2Cl_2/Et_2O to give a white solid (170 mg, 0.404 mmol, 67% yield). Isomers (19:81) were not separated, m.p. 214 °C (CH_2Cl_2/Et_2O). HRMS (ESI^+): calcd. for $C_{11}H_{21}IN$ 294.0713; found 294.0710. $C_{11}H_{21}I_2N$ (421.100): calcd. C 31.37, H 5.03, N 3.33; found C 31.52, H 5.30, N 3.40. Major isomer **13b**: ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 1.04 (s, 3 H, CH_3), 1.10 (s, 3 H, CH_3), 1.25 [s, 9 H, $C(CH_3)_3$], 1.93 (m, 1 H, CHH–C_q), 2.07 (m, 1 H, CHH–C_q), 3.75 (m, 1 H, CHH–N), 4.11 (m, 1 H, CHH–N), 4.23–4.36 (m, 1 H, CH–I), 8.54 (s, 1 H, $CH{=}N^+$) ppm. ^{13}C NMR (75.5 MHz, [D$_6$]DMSO): δ = 12.7 (CH–I), 25.0 (CH_3), 25.5 (CH_3), 26.9 [3 C, $C(CH_3)_3$], 46.8 [$C(CH_3)_2$], 42.0 (CH_2), 53.6 (CH_2–N), 69.2 [$C(CH_3)_3$], 178.9 ($CH{=}N^+$) ppm. Minor isomer **11b**: ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 1.17 (s, 3 H, CH_3), 1.25 (s, 3 H, CH_3), 1.32 [s, 9 H, $C(CH_3)_3$], 1.84–1.93 (m, 1 H, CHH–C_q), 2.32–2.43 (m, 1 H, CHH–C_q), 3.59–3.68 (m, 1 H, CHH–I), 3.91–4.02 (m, 1 H, CHH–I), 4.98–5.09 (m, 1 H, CH), 9.25 (s, 1 H, $CH{=}N^+$) ppm. ^{13}C NMR (75.5 MHz, [D$_6$]DMSO): δ = 9.7 (CH_2–I), 19.0 (CH_3), 25.6 (CH_3), 28.8 [3 C, $C(CH_3)_3$], 46.7 [$C(CH_3)_2$], 41.8 (CH_2), 65.2 [$C(CH_3)_3$], 72.6 (CH–N), 187.9 ($CH{=}N^+$) ppm.

General Procedure for the Selenocyclisation and Reduction to Pyrrolidines 14: The appropriate *N*(alkenylidene)alkylamine **9** (0.50 mmol) was dissolved in dry CH_2Cl_2 (10 mL) at –78 °C under argon in a flame-dried flask. A solution of phenylselenyl bromide (0.60 mmol, 1.2 equiv.) in dry CH_2Cl_2 was added over 30 min. After 2 h at –78 °C, MeOH (10 mL) and $NaBH_4$ (0.74 mmol) were added. The mixture was warmed slowly to room temperature. The organic layer was separated and washed with water (10 mL). After separating the layers, the aqueous layer was washed with CH_2Cl_2 (2 × 5 mL). The combined organic layers were dried with $MgSO_4$ and concentrated under vacuum. The remaining yellow oil was purified by column chromatography (40 g silica gel, 2.3 cm column diameter, cyclohexane/EtOAc mixture).

***rac*-1-Benzyl-4,4-dimethyl-2-[(phenylselenyl)methyl]pyrrolidine (14a):** Starting material **9a** (244 mg, 1.21 mmol). Yield: 258 mg (0.719 mmol, 59%), colourless oil, R_f = 0.14 (hexane/EtOAc, 20:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.98 (s, 3 H, C_q–CH_3), 1.10 (s, 3 H, C_q–CH_3), 1.65 (dd, J = 7.9 Hz, J = 12.8 Hz, 1 H, CH–CH′H–C_q), 1.83 (dd, J = 8.1 Hz, J = 12.6 Hz, 1 H, CH–CH′H–C_q), 2.01 (d, J = 9.0 Hz, 1 H, N–CH′H–C_q), 2.65 (d, J = 9.0 Hz, 1 H, N–CH′H–C_q), 2.88 (m, 1 H, CH–CH_2Se), 3.11 (dd, J = 3.1 Hz, J = 11.4 Hz, 1 H, CH′H–Se), 3.15 (dd, J = 4.1 Hz, J = 11.5 Hz, 1 H, CH′H–Se), 3.17 (d, J = 13.2 Hz, 1 H, Ph–CH′H), 4.04 (d, J = 13.2 Hz, 1 H, Ph–CH′H), 7.19–7.48 (m, 10 H, CH_{ar}) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 28.9 (CH_3), 30.1 (CH_3), 33.2 (CH_2Se), 35.9 [$C(CH_3)_2$], 46.5 (CH–CH_2–C_q), 58.3 (CH_2–Ph), 63.6

(*C*H), 68.2 (N–*C*H$_2$–C$_q$), 126.5 (*C*H$_{ar}$), 126.9 (*C*H$_{ar}$), 128.2 (2 *C*H$_{ar}$), 128.7 (2 *C*H$_{ar}$), 129.1 (2 *C*H$_{ar}$), 131.4 (*C*$_{ar}$Se), 132.3 (2 *C*H$_{ar}$), 139.8 (CH–*C*$_{ar}$) ppm. $C_{20}H_{25}NSe$ (358.379): calcd. C 67.03, H 7.03, N 3.91; found C 67.26, H 7.07, N 3.82.

(2*R*)-4,4-Dimethyl-1-[(1*R*)-1-phenylethyl]-2-[(phenylselenyl)methyl]-pyrrolidine and (2*S*)-4,4-Dimethyl-1-[(1*R*)-1-phenylethyl]-2-[(phenylselenyl)methyl]pyrrolidine (14b): Starting material **9f** (82 mg, 0.38 mmol). Diastereomers were separated, *dr* = 47:53. Minor isomer: yield 42 mg (0.11 mmol, 29%), colourless oil, R_f = 0.57 (hexane/EtOAc, 9:1). $[\alpha]_D^{25}$ = –45.9 (*c* = 1.4, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.92 (s, 3 H, C$_q$–C*H*$_3$), 1.06 (s, 3 H, C$_q$–C*H*$_3$), 1.21 (d, *J* = 6.7 Hz, 3 H, CH–C*H*$_3$), 1.54 (dd, *J* = 6.3 Hz, *J* = 12.6 Hz, 1 H, CH–CH′*H*–C$_q$), 1.74 (dd, *J* = 8.3 Hz, *J* = 12.6 Hz, 1 H, CH–C*H*′H–C$_q$), 2.24 (d, *J* = 8.9 Hz, 1 H, N–CH′*H*), 2.44 (d, *J* = 8.9 Hz, 1 H, N–C*H*′H), 2.79–2.82 (m, 2 H, C*H*$_2$Se), 3.06–3.10 (m, 1 H, C*H*–CH$_2$Se), 3.78 (q, *J* = 6.6 Hz, 1 H, C*H*–CH$_3$), 7.10–7.34 (m, 10 H, C*H*$_{ar}$) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 15.1 (CH–*C*H$_3$), 28.3 (C$_q$–*C*H$_3$), 29.0 (C$_q$–*C*H$_3$), 33.3 (*C*H$_2$Se), 35.4 [*C*(CH$_3$)$_2$], 45.8 (CH–*C*H$_2$), 57.8 (*C*H), 60.7 (*C*H), 62.1 (N–*C*H$_2$), 126.0 (*C*H$_{ar}$), 126.3 (*C*H$_{ar}$), 127.2 (2 *C*H$_{ar}$), 127.7 (2 *C*H$_{ar}$), 128.5 (2 *C*H$_{ar}$), 130.6 (*C*$_{ar}$Se), 131.8 (2 *C*H$_{ar}$), 144.9 (CH–*C*$_{ar}$) ppm. HRMS (EI): calcd. for $C_{21}H_{27}NSe$ 373.13087; found 373.13084. Major isomer: yield of 47 mg (0.13 mmol, 33%), colourless oil, R_f = 0.46 (hexane/EtOAc, 9:1). $[\alpha]_D^{25}$ = 142.7 (*c* = 1.1, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.74 (s, 3 H, C$_q$–C*H*$_3$), 1.03 (s, 3 H, C$_q$–C*H*$_3$), 1.30 (d, *J* = 6.9 Hz, 3 H, CH–C*H*$_3$), 1.52 (dd, *J* = 6.5 Hz, *J* = 12.6 Hz, 1 H, CH–CH′*H*–C$_q$), 1.64 (dd, *J* = 8.0 Hz, *J* = 12.6 Hz, 1 H, CH–C*H*′H–C$_q$), 2.15 (d, *J* = 8.9 Hz, 1 H, N–CH′*H*), 2.59 (d, *J* = 8.9 Hz, 1 H, N–C*H*′H), 2.90–2.94 (m, 1 H, C*H*–CH$_2$Se), 3.00–3.13 (m, 2 H, C*H*$_2$Se), 3.75 (q, *J* = 6.8 Hz, 1 H, C*H*–CH$_3$), 7.06–7.41 (m, 10 H, C*H*$_{ar}$) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 21.6 (CH–*C*H$_3$), 28.3 (C$_q$–*C*H$_3$), 29.1 (C$_q$–*C*H$_3$), 34.3 [*C*(CH$_3$)$_2$], 35.9 (*C*H$_2$Se), 46.2 (CH–*C*H$_2$), 59.3 (*C*H), 59.4 (*C*H), 62.9 (N–*C*H$_2$), 126.6 (*C*H$_{ar}$), 126.8 (*C*H$_{ar}$), 127.9 (2 *C*H$_{ar}$), 128.0 (2 *C*H$_{ar}$), 129.0 (2 *C*H$_{ar}$), 131.0 (*C*$_{ar}$Se), 132.7 (2 *C*H$_{ar}$), 142.1 (CH–*C*$_{ar}$) ppm. $C_{21}H_{27}NSe$ (372.406): calcd. C 67.73, H 7.31, N 3.76; found C 67.69, H 7.07, N 3.74.

(*R*)-Methyl 2-[(2*R*)-4,4-Dimethyl-2-(phenylselenylmethyl)pyrrolidin-1-yl]-2-phenylacetate [(*R*)-14f] and (*R*)-Methyl 2-[(2*S*)-4,4-Dimethyl-2-(phenylselenylmethyl)pyrrolidin-1-yl]-2-phenylacetate [(*S*)-14f]: Starting material **9j** (98 mg, 0.38 mmol). Diastereomers were separated. *dr* = 35:65. (*R*)-**14f**: yield of 57 mg (0.14 mmol, 37%), colourless crystals, R_f = 0.26 (hexane/EtOAc, 9:1), m.p. 46–48 °C ($CHCl_3$). $[\alpha]_D^{20}$ = –7.9 (*c* = 1.00, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.72 (s, 3 H, C$_q$–C*H*$_3$), 1.03 (s, 3 H, C$_q$–C*H*$_3$), 1.48 (dd, *J* = 6.4 Hz, *J* = 12.8 Hz, 1 H, CH–CH′*H*–C$_q$), 1.72 (dd, *J* = 8.1 Hz, *J* = 12.6 Hz, 1 H, CH–C*H*′H–C$_q$), 2.20 (d, *J* = 9.0 Hz, 1 H, N–CH′*H*), 2.81 (d, *J* = 9.4 Hz, 1 H, N–CH′*H*), 2.85 (d, *J* = 9.8 Hz, 1 H, SeC*H*′H), 2.98 (dd, *J* = 2.6 Hz, *J* = 11.7 Hz 1 H, SeCH′*H*), 3.02–3.09 (m, 1 H, C*H*–CH$_2$Se), 3.56 (s, 3 H, COOC*H*$_3$), 4.43 (s, 1 H, C*H*–COOCH$_3$), 7.08–7.37 (m, 10 H, C*H*$_{ar}$) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 28.1 (C$_q$–*C*H$_3$), 28.9 (C$_q$–*C*H$_3$), 32.9 (*C*H$_2$Se), 36.0 [*C*(CH$_3$)$_2$], 46.0 (CH–*C*H$_2$), 51.8 (COO*C*H$_3$), 60.5 (*C*H), 63.6 (N–*C*H$_2$), 67.4 (*C*H), 126.7 (*C*H$_{ar}$), 128.0 (*C*H$_{ar}$), 128.3 (2 *C*H$_{ar}$), 129.0 (2 *C*H$_{ar}$), 129.2 (2 *C*H$_{ar}$), 130.5 (*C*$_{ar}$Se), 132.8 (2 *C*H$_{ar}$), 134.9 (*C*$_{ar}$), 172.5 (*C*OO) ppm. HRMS (ESI$^+$): calcd. for $C_{22}H_{27}NO_2Se$ 417.1207; found 417.1207. (*S*)-**14f**: yield of 35 mg (0.084 mmol, 22%), colourless oil, R_f = 0.35 (hexane/EtOAc, 9:1). $[\alpha]_D^{20}$ = 1.2 (*c* = 1.00, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.95 (s, 3 H, C$_q$–C*H*$_3$), 1.00 (s, 3 H, C$_q$–C*H*$_3$), 1.60 (dd, *J* = 7.3 Hz, *J* = 12.6 Hz, 1 H, CH–CH′*H*–C$_q$), 1.79 (dd, *J* = 7.9 Hz, *J* = 12.8 Hz, 1 H, CH–C*H*′H–C$_q$), 2.46 (d, *J* = 9.0 Hz, 1 H, N–CH′*H*), 2.68 (d, *J* = 9.0 Hz, 1 H, N–CH′*H*), 2.91 (dd, *J* = 3.2 Hz, *J* = 11.5 Hz, 1 H, SeC*H*′H), 2.98 (dd, *J* = 7.9 Hz, *J* = 11.7 Hz 1 H, SeCH′*H*), 3.21 (dq, *J* = 3.1 Hz, *J* = 7.7 Hz 1 H, C*H*–CH$_2$Se), 3.61 (s, 3 H, COOC*H*$_3$), 4.65 (s, 1 H, C*H*–COOCH$_3$), 7.13–7.35 (m, 10 H, C*H*$_{ar}$) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 28.5 (C$_q$–*C*H$_3$), 29.2 (C$_q$–*C*H$_3$), 33.0 (*C*H$_2$Se), 35.8 [*C*(CH$_3$)$_2$], 46.3 (CH–*C*H$_2$), 51.3 (COO*C*H$_3$), 60.3 (*C*H), 62.6 (N–*C*H$_2$), 66.1 (*C*H), 126.5 (*C*H$_{ar}$), 127.8 (*C*H$_{ar}$), 128.3 (2 *C*H$_{ar}$), 128.5 (2 *C*H$_{ar}$), 128.9 (2 *C*H$_{ar}$), 130.8 (*C*$_{ar}$Se), 132.2 (2 *C*H$_{ar}$), 137.1 (*C*$_{ar}$), 172.0 (*C*OO) ppm. $C_{22}H_{27}NO_2Se$ (416.415): calcd. C 63.45, H 6.54, N 3.36; found C 63.40, H 6.39, N 3.34.

X-ray Crystal Analysis of (*S*)-14f:[79] Empirical formula: $C_{22}H_{27}NO_2Se$, formula weight: 416.41 g/mol, temperature: 180(2) K, wavelength: 0.71073 Å, crystal system: monoclinic, space group: *P*21, unit cell dimensions: *a* = 6.006(2) Å, *b* = 14.311(3) Å, β = 95.82(4)°, *c* = 11.812(3) Å, *V* = 1009.9(5) Å^3, *Z* = 2, density (calculated): 1.369 Mg/m^3, absorption coefficient: 1.874 mm^{-1}, *F*(000): 432, crystal size: 0.60 × 0.48 × 0.32 mm, theta range for data collection: 2.24 to 25.24°, limiting indices: $-7 \le h \le 7$, $-17 \le k \le 17$, $-14 \le l \le 14$; reflections collected: 6613, unique: 3487 [*R*(int.) = 0.1335], completeness to θ = 25.24 is 96.8%, absorption correction: empirical (psi-scan), max./min. transmission: 0.5854/0.3993, refinement method: full-matrix least-squares on F^2, data/restraints/parameters: 3487/1/239, goodness-of-fit on F^2: 0.960, final *R* indices [$I > 2\sigma(I)$]: R_1 = 0.0867, wR_2 = 0.2052, *R* indices (all data): R_1 = 0.1140, wR_2 = 0.2235, absolute structure parameter: –0.06(3), extinction coefficient: 0.026(6), largest diff. peak and hole: 1.560 and –1.293 e/Å^3.

(*R*)-Methyl 2-{(2*R*)-4,4-Dimethyl-2-[(2,4,6-triisopropylphenylselenyl)methyl]pyrrolidin-1-yl}-2-phenylacetate and (*R*)-Methyl 2-{(2*S*)-4,4-Dimethyl-2-[(2,4,6-triisopropylphenylselenyl)methyl]pyrrolidin-1-yl}-2-phenylacetate (14g): Methyl (*R*)-2-(2,2-dimethylpent-4-enylideneamino)-2-phenylacetate (**9j**) (807 mg, 3.11 mmol) was dissolved in dry CH_2Cl_2 (40 mL) at –78 °C under argon in a flame-dried flask. A solution of (2,4,6triisopropylphenyl)selenyl bromide (5.10 mmol, 1.6 equiv.), generated in situ from bis(2,4,6-triisopropylphenyl) diselenide (1.44 g, 2.55 mmol) and bromine (407 mg, 2.55 mmol) at –78 °C in dry CH_2Cl_2 (30 mL), was added over 30 min. After 2 h at –78 °C, MeOH (10 mL) and $NaBH_4$ (241 mg, 6.37 mmol) were added. The mixture was warmed slowly to room temperature. The organic layer was separated and washed with water (10 mL). The aqueous layer was extracted with CH_2Cl_2 (2 × 5 mL). The combined organic layers were dried with $MgSO_4$ and concentrated under vacuum. The remaining oil was purified by column chromatography (400 mL silica gel, 4.5 cm column diameter, cyclohexane/EtOAc, 9:1). Diastereomers were not separated. *dr* = 61:39. Major isomer: yield of 0.63 g (37%), colourless oil, R_f = 0.70 (hexane/EtOAc, 9:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.96 (s, 3 H, C$_q$–C*H*$_3$), 1.00 (s, 3 H, C$_q$–C*H*$_3$), 1.14 [d, *J* = 6.5 Hz, 6 H, CH(C*H*$_3$)$_2$], 1.15 [d, *J* = 5.3 Hz, 6 H, CH(C*H*$_3$)$_2$], 1.18 [d, *J* = 6.8 Hz, 6 H, CH(C*H*$_3$)$_2$], 1.62 (dd, *J* = 7.2 Hz, *J* = 12.4 Hz, 1 H, CH–CH′*H*–C$_q$), 1.81 (dd, *J* = 7.7 Hz, *J* = 12.6 Hz, 1 H, CH–C*H*′H–C$_q$), 2.40 (d, *J* = 8.7 Hz, 1 H, N–CH′*H*), 2.57 (dd, *J* = 2.6 Hz, *J* = 10.9 Hz, 1 H, SeC*H*′H), 2.70 (d, *J* = 8.7 Hz, 1 H, N–CH′*H*), 2.73–2.82 [m, 2 H, SeCH′*H*, C*H*(CH$_3$)$_2$], 3.17 (dq, *J* = 2.7 Hz, *J* = 7.6 Hz, 1 H, C*H*–CH$_2$Se), 3.54 (s, 3 H, COOC*H*$_3$), 3.83 [q, *J* = 6.9 Hz, 2 H, C*H*(CH$_3$)$_2$], 4.62 (s, 1 H, C*H*–COOCH$_3$), 6.92 (s, 2 H, C*H*$_{ar}$), 7.17–7.28 (m, 5 H, C*H*$_{ar}$) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 24.1 [2 C, CH(*C*H$_3$)$_2$], 27.0 [4 C, 2 CH(*C*H$_3$)$_2$], 28.8 (C$_q$–*C*H$_3$), 29.5 (C$_q$–*C*H$_3$), 34.3 [*C*H(CH$_3$)$_2$], 34.4 [2 C, *C*H(CH$_3$)$_2$], 35.0 (*C*H$_2$Se), 35.9 [*C*(CH$_3$)$_2$], 46.6 (CH–*C*H$_2$), 51.3 (COO*C*H$_3$), 60.9 (*C*H), 62.1 (N–*C*H$_2$), 65.5 (*C*H), 121.7 (2 *C*H$_{ar}$), 127.8 (*C*H$_{ar}$), 128.4 (2 *C*H$_{ar}$), 128.5 (2 *C*H$_{ar}$), 129.3 (*C*$_{ar}$Se), 137.3 (*C*$_{ar}$CH), 149.4 [*C*$_{ar}$CH(CH$_3$)$_2$], 153.2 [2 C, *C*$_{ar}$CH(CH$_3$)$_2$],

172.1 (*C*OO) ppm. Minor isomer: yield of 0.40 g (24%). R_f = 0.60 (hexane/EtOAc, 9:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.67 (s, 3 H, C_q–CH_3), 1.04 (s, 3 H, C_q–CH_3), 1.14 [d, J = 7.2 Hz, 6 H, CH(CH_3)$_2$], 1.16 [d, J = 6.8 Hz, 6 H, CH(CH_3)$_2$], 1.20 [d, J = 6.8 Hz, 6 H, CH(CH_3)$_2$], 1.47 (dd, J = 6.8 Hz, J = 12.4 Hz, 1 H, CH–CH′*H*–C_q), 1.74 (dd, J = 7.9 Hz, J = 12.8 Hz, 1 H, CH–C*H*′H–C_q), 2.17 (d, J = 9.0 Hz, 1 H, N–CH′*H*), 2.63 (d, J = 6.4 Hz, 2 H, SeCH_2), 2.80–2.98 [m, 3 H, N–CH′*H*, C*H*(CH$_3$)$_2$, C*H*–CH$_2$Se], 3.48 (s, 3 H, COOCH_3), 3.83 [q, J = 7.0 Hz, 2 H, C*H*(CH$_3$)$_2$], 4.32 (s, 1 H, C*H*–COOCH$_3$), 6.89–6.92 (m, 2 H, CH_{ar}), 6.96 (s, 2 H, CH_{ar}), 7.14–7.18 (m, 3 H, CH_{ar}) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 24.9 [2 C, CH(*C*H$_3$)$_2$], 27.0 [4 C, 2 CH(*C*H$_3$)$_2$], 28.2 (C_q–*C*H$_3$), 29.1 (C_q–*C*H$_3$), 34.3 [*C*H(CH$_3$)$_2$], 34.4 [2 C, *C*H(CH$_3$)$_2$], 35.3 (*C*H$_2$Se), 36.2 [*C*(CH$_3$)$_2$], 46.3 (CH–*C*H$_2$), 51.8 (COO*C*H$_3$), 60.8 (*C*H), 63.1 (N–*C*H$_2$), 66.9 (*C*H), 121.8 (2 *C*H$_{ar}$), 127.6 (C_{ar}Se), 128.0 (*C*H$_{ar}$), 128.3 (2 *C*H$_{ar}$), 129.3 (2 *C*H$_{ar}$), 134.4 (C_{ar}CH), 149.6 [C_{ar}CH(CH$_3$)$_2$], 153.2 [2 C, C_{ar}CH(CH$_3$)$_2$], 172.6 (*C*OO) ppm. HRMS (ESI$^+$): calcd. for $C_{31}H_{46}NO_2Se$ 544.2688; found 544.2683.

(2*R*)-2-Bromomethyl-1-[(*R*)-(methoxycarbonyl)(phenyl)methyl]-2,4,4-trimethyl-3,4-dihydro-2*H*-pyrrolium Bromide and (2*S*)-2-Bromomethyl-1-[(*R*)-(methoxycarbonyl)(phenyl)methyl]-2,4,4-trimethyl-3,4-dihydro-2*H*-pyrrolium Bromide (16c): Starting material **15c** (240 mg, 0.88 mmol). Yield: 381 mg (0.88 mmol, quant.). Isomers were not separated, *dr* = 46:54, yellow foam. HRMS (ESI$^+$ in MeCN): calcd. for $C_{17}H_{23}BrO_2N$ 352.0907; found 352.0907. Major isomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.48 (s, 3 H, CH_3), 1.66 (s, 3 H, CH_3), 1.94 (s, 3 H, N–C_q–CH_3), 2.23 (d, J = 7.0 Hz, 1 H, C_q–CH′*H*–C_q*x*), 2.53 (d, J = 13.9 Hz, 1 H, C_q–CH′*H*–C_q), 3.82 (d, J = 12.0 Hz, 1 H, Br–C*H*′H), 3.86 (s, 3 H, CH_3), 4.67 (d, J = 12.8 Hz, 1 H, Br–CH′*H*), 6.63 (s, 1 H, C*H*–COOCH$_3$), 7.37–7.78 (m, 5 H, CH_{ar}), 9.41 (s, 1 H, *C*H=N) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 24.7 (N–C_q–*C*H$_3$), 26.6 (*C*H$_3$), 27.8 (*C*H$_3$), 37.5 (*C*H$_2$Br), 48.1 [*C*(CH$_3$)$_2$], 45.9 (*C*H$_2$), 54.9 (COO*C*H$_3$), 63.3 (CH), 83.8 (C_q), 128.4 (2 *C*H$_{ar}$), 130.5 (2 *C*H$_{ar}$), 131.5 (*C*H$_{ar}$), 131.0 (C_{ar}), 166.7 (*C*OO), 189.7 (*C*H=N) ppm. Minor isomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.49 (s, 3 H, CH_3), 1.67 (s, 3 H, CH_3), 1.96 (s, 3 H, N–C_q–CH_3), 2.26 (d, J = 13.9 Hz, 1 H, C_q–CH′*H*–C_q), 2.50 (d, J = 13.8 Hz, 1 H, C_q–CH′*H*–C_q), 3.84 (d, J = 12.7 Hz, 1 H, Br–C*H*′H), 3.90 (s, 3 H, CH_3), 4.93 (d, J = 12.8 Hz, 1 H, Br–CH′*H*), 6.79 (s, 1 H, C*H*–COOCH$_3$), 7.37–7.78 (m, 5 H, CH_{ar}), 8.87 (s, 1 H, *C*H=N) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 25.2 (N–C_q–*C*H$_3$), 25.3 (*C*H$_3$), 27.0 (*C*H$_3$), 38.3 (*C*H$_2$Br), 48.2 [*C*(CH$_3$)$_2$], 45.8 (*C*H$_2$), 55.2 (COO*C*H$_3$), 64.3 (*C*H), 83.1 (C_q), 129.9 (2 *C*H$_{ar}$), 130.2 (2 *C*H$_{ar}$), 131.2 (*C*H$_{ar}$), 130.0 (C_{ar}), 167.6 (*C*OO), 189.7 (*C*H=N) ppm.

(*R*)-Methyl 2-[(2*R*)-5,5-Dimethyl-2-(phenylselenylmethyl)piperidin-1-yl]-2-phenylacetate and (*R*)-Methyl 2-[(2*S*)-5,5-Dimethyl-2-(phenylselenylmethyl)piperidin-1-yl]-2-phenylacetate (17a): Starting material **15a** (0.15 g, 0.55 mmol). Yield: 0.15 g (0.35 mmol, 64%). Isomers were not separated, *dr* = 54:46, colourless oil, R_f = 0.34 and 0.29 (hexane/EtOAc, 8:2). $C_{23}H_{29}NO_2Se$ (430.442): calcd. C 64.18, H 6.79, N 3.25; found C 64.04, H 6.91, N 3.25. Major isomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.91 (s, 3 H, CH_3), 1.00 (s, 3 H, CH_3), 1.10–1.27 (m, 2 H, CH_2), 1.76–1.82 (m, 2 H, CH_2), 1.99 (d, J = 11.6 Hz, 1 H, CH′*H*), 2.56 (d, J = 11.1 Hz, 1 H, C*H*′H), 2.85–2.90 (m, 1 H, C*H*–CH$_2$Se), 2.91–2.96 (m, 1 H, C*H*′H), 3.16–3.24 (m, 1 H, CH′*H*), 3.65 (s, 3 H, CH_3), 4.49 (s, 1 H, C*H*–COOCH$_3$), 7.15–7.52 (m, 10 H, CH_{ar}) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 25.2 (*C*H$_2$Se), 25.5 (*C*H$_3$), 28.1 (CH–*C*H$_2$), 28.4 (*C*H$_3$), 30.7 [*C*(CH$_3$)$_2$], 33.3 (C_q–*C*H$_2$), 51.4 (COO*C*H$_3$), 54.5 (SeCH$_2$–*C*H), 56.7 (N–*C*H$_2$), 69.8 (*C*H–COO), 126.8 (*C*H$_{ar}$), 127.8 (*C*H$_{ar}$), 128.6 (2 *C*H$_{ar}$), 129.0 (2 *C*H$_{ar}$), 129.2 (2 *C*H$_{ar}$), 131.1 (C_{ar}Se), 132.6 (2 *C*H$_{ar}$), 137.1 (C_{ar}), 171.8 (*C*OO) ppm. Minor isomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.78 (s, 3 H, CH_3), 0.84 (s, 3 H, CH_3), 1.23–1.39 (m, 2 H, CH_2), 1.63–1.72 (m, 2 H, CH_2), 2.15–2.20 (m, 1 H, CH′*H*), 2.25 (d, J = 12.1 Hz, 1 H, C*H*′H), 2.98–3.02 (m, 1 H, C*H*–CH$_2$Se), 3.20 (t, J = 12.1 Hz, 1 H, C*H*′H*x*), 3.46 (dd, J = 6.7 Hz, J = 11.7 Hz, 1 H, CH′*H*), 3.69 (s, 3 H, CH_3), 5.06 (s, 1 H, C*H*–COOCH$_3$), 7.15–7.52 (m, 10 H, CH_{ar}) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 24.8 (*C*H$_3$), 27.0 (*C*H$_2$Se), 28.6 (*C*H$_3$), 30.8 [*C*(CH$_3$)$_2$], 31.7 (CH–*C*H$_2$), 36.4 (C_q–*C*H$_2$), 52.0 (COO*C*H$_3$), 56.9 (N–*C*H$_2$), 57.3 (SeCH$_2$–*C*H), 66.1 (*C*H–COO), 126.8 (*C*H$_{ar}$), 128.2 (*C*H$_{ar}$), 128.3 (2 *C*H$_{ar}$), 128.6 (2 *C*H$_{ar}$), 129.1 (2 *C*H$_{ar}$), 130.6 (C_{ar}Se), 132.6 (2 *C*H$_{ar}$), 135.8 (C_{ar}), 173.2 (*C*OO) ppm.

(*R*)-Methyl 2-Phenyl-2-[(2*R*)-2,4,4-trimethyl-2-(phenylselenylmethyl)pyrrolidin-1-yl]acetate and (*R*)-Methyl 2-Phenyl-2-[(2*S*)-2,4,4-trimethyl-2-(phenylselenylmethyl)pyrrolidin-1-yl]acetate (17b): Starting material **15b** (376 mg, 1.38 mmol). Yield: 216 mg (0.502 mmol, 36%). Isomers were not separated, *dr* = 46:54, colourless oil, R_f = 0.36 (hexane/EtOAc, 20:1). $C_{23}H_{29}NO_2Se$ (430.442): calcd. C 64.18, H 6.79, N 3.25; found C 64.03, H 6.54, N 3.09. Minor isomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.98 (s, 3 H, CH_3), 0.99 (s, 3 H, CH_3), 1.13 (s, 3 H, N–C_q–CH_3), 1.41 (d, J = 12.7 Hz, 1 H, C_q–CH′*H*–C_q), 1.90 (d, J = 13.1 Hz, 1 H, C_q–CH′*H*– C_q), 2.33 (d, J = 9.1 Hz, 1 H, N–CH′*H*), 2.95 (d, J = 11.4 Hz, 1 H, Se–C*H*′H), 3.02 (d, J = 9.2 Hz, 1 H, N–C*H*′H), 3.27 (d, J = 11.3 Hz, 1 H, Se–CH′*H*), 3.65 (s, 3 H, CH_3), 4.68 (s, 1 H, C*H*–COOCH$_3$), 7.14–7.43 (m, 10 H, CH_{ar}) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 23.4 (N–C_q–*C*H$_3$), 29.2 (*C*H$_3$), 29.9 (*C*H$_3$), 35.3 [*C*(CH$_3$)$_2$], 40.4 (*C*H$_2$Se), 51.7 (COO*C*H$_3$), 53.0 (*C*H$_2$), 59.6 (*C*H$_2$), 61.7 (*C*H), 64.3 (C_q), 126.6 (*C*H$_{ar}$), 128.6 (*C*H$_{ar}$), 127.7 (2 *C*H$_{ar}$), 128.4 (2 *C*H$_{ar}$), 129.2 (2 *C*H$_{ar}$), 137.9 (C_{ar}Se), 132.2 (2 *C*H$_{ar}$), 138.1 (C_{ar}), 174.1 (*C*OO) ppm. Major isomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.90 (s, 3 H, CH_3), 0.96 (s, 3 H, CH_3), 1.21 (s, 3 H, N–C_q–CH_3), 1.45 (d, J = 12.6 Hz, 1 H, C_q–CH′*H*–C_q), 2.02 (d, J = 13.0 Hz, 1 H, C_q–CH′*H*– C_q), 2.44 (d, J = 9.1 Hz, 1 H, N–CH′*H*), 2.94 (d, J = 11.1 Hz, 1 H, Se–C*H*′H), 2.91 (d, J = 9.2 Hz, 1 H, N–C*H*′H), 3.15 (d, J = 11.1 Hz, 1 H, Se–CH′*H*), 3.63 (s, 3 H, CH_3), 4.64 (s, 1 H, C*H*–COOCH$_3$), 7.14–7.43 (m, 10 H, CH_{ar}) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 25.1 (N–C_q–*C*H$_3$), 28.8 (*C*H$_3$), 29.4 (*C*H$_3$), 34.7 [*C*(CH$_3$)$_2$], 39.8 (*C*H$_2$Se), 51.8 (COO*C*H$_3$), 53.4 (*C*H$_2$), 60.4 (*C*H$_2$), 62.3 (*C*H), 64.7 (C_q), 126.7 (*C*H$_{ar}$), 128.5 (*C*H$_{ar}$), 128.2 (2 *C*H$_{ar}$), 128.4 (2 *C*H$_{ar}$), 129.1 (2 *C*H$_{ar}$), 137.9 (C_{ar}Se), 132.3 (2 *C*H$_{ar}$), 138.4 (C_{ar}), 174.5 (*C*OO) ppm.

3,3-Dimethyl-2-phenyl-1-[(*R*)-1-phenylethyl]-5-(phenylselenylmethyl)pyrrolidine (17d): Starting material **15d** (0.25 g, 0.86 mmol). Yield: 0.22 g (0.49 mmol, 57%). Isomers were not separated, *dr* = 13:21:38:28. After being column chromatographed twice, three of these isomers could be isolated as a mixture, colourless oil, R_f = 0.22 (hexane/EtOAc, 20:1). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 14.6, 18.2, 24.2 (*C*H$_3$), 24.9, 25.7, 26.3 (*C*H$_3$), 28.5, 28.9, 31.0 (*C*H$_3$), 34.6, 34.9, 37.1 (*C*H$_2$Se), 40.3, 40.6, 40.9 [*C*(CH$_3$)$_2$], 44.7, 45.7, 46.6 (CH–*C*H$_2$), 54.8, 55.7, 56.7 (*C*H–CH$_3$), 58.4, 59.4, 60.5 (*C*H–CH$_2$Se), 74.6, 75.2, 78.0 (*C*H–Ph), 125.9–133.0 (15*C*H$_{ar}$), 129.6, 129.8, 130.7 (Se*C*$_{ar}$), 140.7, 142.1, 142.3 (C_{ar}), 143.8, 144.6, 146.7 (C_{ar}) ppm. HRMS (EI): calcd. for $C_{27}H_{31}NSe$ 449.1616; found 449.1612.

(3*aR*,4*R*,6a*S*)-5-Benzyl-4-bromonium-2,2-dimethyl-4,6a-dihydro-3a*H*-[1,3]dioxolo[4,5-*c*]pyrrol-5-ium Bromide and (3*aR*,4*S*,6*aS*)-5-Benzyl-4-bromonium-2,2-dimethyl-4,6a-dihydro-3a*H*-[1,3]dioxolo-[4,5-*c*]pyrrol-5-ium Bromide (19b): *N*-Benzyl[(4*S*,5*R*)-(2,2-dimethyl-5-vinyl[1,3]dioxolane-4-yl)methylene]amine (**18a**) (0.56 g, 2.3 mmol) was dissolved in dry CH_2Cl_2 (20 mL) at –78 °C under argon in a flame-dried flask. A 1.0 M solution of bromine (2.3 mL,

1.0 equiv.) in CH_2Cl_2, which was diluted with dry CH_2Cl_2 (20 mL) was added over 2 h. After 1 h at –78 °C, the mixture was concentrated under vacuum ($T < 30$ °C). Yield: 0.93 g (2.3 mmol, quant.), *dr* = 38:62 (HPLC/MS in MeOH of the crude product), brown foam. HRMS (ESI^+): calcd. for $C_{15}H_{19}BrNO_2$ 324.0599/326.0579; found 324.0601/326.0581.

General Procedure for the Selenocyclisation and Reduction to Tetrahydro[1,3]dioxolo-[4,5-*c*]pyrroles 20: The appropriate *N*(alkenylidene)alkylamine **18** (2.1 mmol) was dissolved in dry CH_2Cl_2 (20 mL) at –78 °C under argon in a flame-dried flask. A solution of the appropriate arylselenyl bromide (1.3 equiv.) in dry CH_2Cl_2 (15 mL) was added over 20 min. After 2.5 h at –78 °C, MeOH (10 mL) and $NaBH_4$ (4.2 mmol) were added. The mixture was warmed slowly to room temperature. The organic layer was separated and washed with water (20 mL). After separating the layers, the aqueous layer was washed with CH_2Cl_2 (2 × 5 mL). The combined organic layers were dried with $MgSO_4$ and concentrated under vacuum. The remaining yellow oil was purified by column chromatography (40 g silica gel, 2.3 cm column diameter, cyclohexane/EtOAc mixture).

(3a*R*,4*R*,6a*S*)-5-Benzyl-tetrahydro-2,2-dimethyl-4-(phenylselenylmethyl)-3a*H*-[1,3]dioxolo[4,5-*c*]pyrrole [(*R*)-20a] and (3a*R*,4*S*,6a*S*)-5-Benzyl-tetrahydro-2,2-dimethyl-4-(phenylselenylmethyl)-3a*H*-[1,3]dioxolo[4,5-*c*]pyrrole [(*S*)-20a]: Starting material **18a** (0.52 g, 2.1 mmol). Diastereomers were not separated. Yield: 0.36 g (0.89 mmol, 42%), *dr* = 20:80, colourless oil, R_f = 0.26 and 0.31 (hexane/EtOAc, 8:2). $C_{21}H_{25}NO_2Se$ (402.389): calcd. C 62.68, H 6.26, N 3.48; found C 62.69, H 6.43, N 3.43. Major isomer (*R*)-**20a**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.33 (s, 3 H, CH_3), 1.55 (s, 3 H, CH_3), 2.06 (dd, *J* = 4.7 Hz, *J* = 11.1 Hz, 1 H, C*H*H), 2.44–2.48 (m, 1 H, C*H*N), 3.06 (d, *J* = 10.9 Hz, 1 H, CH*H*), 3.16 (d, *J* = 14.0 Hz, 1 H, CH*H*–Ph), 3.17 (d, *J* = 9.4 Hz, 2 H, CH_2Se), 3.97 (d, *J* = 13.6 Hz, 1 H, C*H*H–Ph), 4.55 (dd, *J* = 4.5 Hz, *J* = 6.4 Hz, 1 H, CH–C*H*–O), 4.74 (dd, *J* = 4.9 Hz, *J* = 6.4 Hz, 1 H, CH_2C*H*–O), 7.23–7.27 (m, 8 H, CH_{ar}), 7.52–7.55 (m, 2 H, CH_{ar}) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 25.3 (*C*H_2Se), 25.7 (*C*H_3), 26.5 (*C*H_3), 57.0 (*C*H_2Ph), 59.7 (*C*H_2N), 67.9 (*C*HN), 77.6 (*C*HCH$_2$), 81.1 (*C*HCH), 111.5 [*C*(CH$_3$)$_2$], 127.0 (*C*H_{ar}), 127.1 (*C*H_{ar}), 128.4 (2 *C*H_{ar}), 128.7 (2 *C*H_{ar}), 129.2 (2 *C*H_{ar}), 130.9 (*C*$_{ar}$Se), 132.8 (2 *C*H_{ar}), 138.2 (*C*$_{ar}$) ppm. Minor isomer (*S*)-**20a**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.31 (s, 3 H, CH_3), 1.52 (s, 3 H, CH_3), 2.51 (dd, *J* = 4.1 Hz, *J* = 10.5 Hz, 1 H, C*H*H), 3.05–3.16 (m, 4 H), 3.42 (d, *J* = 12.9 Hz, 1 H, CH*H*–Ph), 4.01 (d, *J* = 12.8 Hz, 1 H, C*H*H–Ph), 4.59–4.70 (m, 2 H, C*H*–O), 7.23–7.27 (m, 8 H, CH_{ar}), 7.44–7.48 (m, 2 H, CH_{ar}) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 25.3 (*C*H_3), 27.4 (*C*H_3), 29.2 (*C*H_2Se), 57.1 (*C*H_2Ph), 58.2 (*C*H_2N), 67.7 (*C*HN), 78.0 (*C*HCH$_2$), 84.3 (*C*HCH), 113.0 [*C*(CH$_3$)$_2$], 126.8 (*C*H_{ar}), 127.3 (*C*H_{ar}), 128.4 (2 *C*H_{ar}), 128.8 (2 *C*H_{ar}), 129.2 (2 *C*H_{ar}), 130.9 (*C*$_{ar}$Se), 132.4 (2 *C*H_{ar}), 138.4 (*C*$_{ar}$) ppm.

(3a*R*,4*R*,6a*S*)-Tetrahydro-2,2-dimethyl-5-[(*R*)-1-phenylethyl]-4-(phenylselenylmethyl)-3a*H*-[1,3]dioxolo[4,5-*c*]pyrrole [(*R*)-20d] and (3a*R*,4*S*,6a*S*)-Tetrahydro-2,2-dimethyl-5-[(*R*)-1-phenylethyl]-4-(phenylselenylmethyl)-3a*H*-[1,3]dioxolo[4,5-*c*]pyrrole [(*S*)-20d]: Starting material **18b** (0.52 g, 2.0 mmol) and phenylselenyl bromide (0.65 g, 2.7 mmol). Diastereomers were not separated. Yield: 0.42 g (1.01 mmol, 50%), *dr* = 16:84, white solid, m.p. 117–120 °C, R_f = 0.27 (cyclohexane/EtOAc, 9:1). $C_{22}H_{27}NO_2Se$ (416.415): calcd. C 63.45, H 6.54, N 3.36; found C 63.28, H 6.43, N 3.37. Major isomer (*R*)-**20d**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.32 (s, 3 H, CH_3), 1.43 (d, *J* = 7.2 Hz, 3 H, CH–CH_3), 1.54 (s, 3 H, CH_3), 2.16 (dd, *J* = 4.7 Hz, *J* = 10.3 Hz, 1 H, C*H*H), 2.32–2.38 (m, 1 H, C*H*N), 3.12 (d, *J* = 10.9 Hz, 2 H, CH*H*, CH*H*Se), 3.25 (dd, *J* = 3.4 Hz, *J* = 12.0 Hz, 1 H, C*H*HSe), 3.99 (q, *J* = 7.2 Hz, 1 H, C*H*–Ph), 4.44 (dd, *J* = 4.5 Hz, *J* = 6.4 Hz, 1 H, CH_2C*H*–O), 4.62 (dd, *J* = 4.9 Hz, *J* = 6.4 Hz, 1 H, CH–C*H*–O), 6.89–7.59 (m, 10 H, CH_{ar}) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 19.0 (CH–*C*H$_3$), 25.9 (C$_q$–*C*H$_3$), 26.1 (*C*H_2Se), 26.5 (C$_q$–*C*H$_3$), 52.4 (*C*H_2N), 55.3 (*C*H–Ph), 63.5 (*C*HN), 77.1 (*C*HCH$_2$), 81.0 (*C*HCH), 111.5 [*C*(CH$_3$)$_2$], 127.1 (*C*H_{ar}), 127.3 (*C*H_{ar}), 128.0 (2 *C*H_{ar}), 128.5 (2 *C*H_{ar}), 129.1 (2 *C*H_{ar}), 130.9 (*C*$_{ar}$Se), 134.0 (2 *C*H_{ar}), 137.9 (*C*$_{ar}$) ppm. Minor isomer (*S*)-**20d**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.24 (d, *J* = 6.4 Hz, 3 H, CH–CH_3), 1.31 (s, 3 H, CH_3), 1.55 (s, 3 H, CH_3), 2.84 (dd, *J* = 9.4 Hz, *J* = 12.0 Hz, 1 H, C*H*HSe), 3.04–3.08 (m, 3 H, CH*H*Se, CH_2), 3.41 (dd, *J* = 2.3 Hz, *J* = 8.7 Hz, 1 H, C*H*N), 3.88 (q, *J* = 6.5 Hz, 1 H, C*H*–Ph), 4.54–4.63 (m, 1 H, CH_2C*H*–O), 4.66 (dd, *J* = 1.9 Hz, *J* = 6.4 Hz, 1 H, CH–C*H*–O), 6.89–7.59 (m, 10 H, CH_{ar}) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 18.5 (CH–*C*H$_3$), 25.4 (C$_q$–*C*H$_3$), 27.1 (C$_q$–*C*H$_3$), 27.2 (*C*H_2Se), 53.8 (*C*H_2N), 57.8 (*C*H–Ph), 65.0 (*C*HN), 78.9 (*C*HCH$_2$), 84.4 (*C*HCH), 112.1 [*C*(CH$_3$)$_2$], 127.1 (3 *C*H_{ar}), 127.4 (3 *C*H_{ar}), 128.4 (2 *C*H_{ar}), 129.2 (2 *C*H_{ar}), 133.1 (*C*$_{ar}$Se), 144.8 (*C*$_{ar}$) ppm.

X-ray Crystal Analysis of 20d:[79] Empirical formula: $C_{22}H_{27}NO_2Se$, formula weight: 416.41 g/mol, temperature: 150(2) K, wavelength: 0.71073 Å, crystal system: orthorhombic, space group: P 21 21 21, unit cell dimensions: a = 9.568(4) Å, b = 9.999(3) Å, c = 20.383(3) Å, V = 1950.1(12) Å^3, Z = 4, density (calculated): 1.418 Mg/m^3, absorption coefficient: 1.941 mm^{-1}, F(000): 864, crystal size: 0.80 × 0.80 × 0.60 mm, Theta range for data collection: 2.00 to 27.48 deg, limiting indices: $-12 \le h \le 12$, $-12 \le k \le 12$, $-26 \le l \le 26$; reflections collected: 12622, unique: 4461 [R(int.) = 0.0234], completeness to θ = 27.48 is 99.9%, absorption correction: empirical (psi-scan), max./min. transmission: 0.3888/0.3057, refinement method: full-matrix least-squares on F^2 data/restraints/parameters: 4461/0/344, goodness-of-fit on F^2: 1.067, final R indices [$I > 2\sigma(I)$]: R_1 = 0.0217, wR_2 = 0.0440, R indices (all data): R_1 = 0.0283, wR_2 = 0.0467, absolute structure parameter: –0.011(6), extinction coefficient: 0.0020(3), largest diff. peak and hole: 0.240 and –0.319 e/Å^3.

Methyl (1*S*)-2-Phenyl-2-{(3a*R*,4*R*,6a*S*)-tetrahydro-2,2-dimethyl-4-(phenylselenylmethyl)[1,3]dioxolo[4,5-*c*]pyrrol-5-yl}acetate [(*R*)-20f] and Methyl (1*S*)-2-Phenyl-2-{(3a*R*,4*S*,6a*S*)-tetrahydro-2,2-dimethyl-4-(phenylselenylmethyl)[1,3]dioxolo[4,5-*c*]pyrrol-5-yl}acetate [(*S*)-20f]: Starting material **18d** (0.50 g, 1.6 mmol) and phenylselenyl bromide (0.65 g, 2.7 mmol). Diastereomers were separated, *dr* = 19:81. Major isomer (*R*)-**20f**: yield 0.14 g (0.30 mmol, 18%), colourless oil, R_f = 0.12 (cyclohexane/EtOAc, 9:1). $[a]_D^{23}$ = 201.8 (*c* = 0.82, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.34 (s, 3 H, CH_3), 1.58 (s, 3 H, CH_3), 2.17 (dd, *J* = 4.9 Hz, *J* = 10.9 Hz, 1 H, N–C*H*H), 2.57 (ddd, *J* = 4.1 Hz, *J* = 4.4 Hz, *J* = 10.9 Hz, 1 H, C*H*N), 3.03 (dd, *J* = 3.8 Hz, *J* = 11.9 Hz, 1 H, CH*H*Se), 3.12 (dd, *J* = 10.8 Hz, *J* = 11.9 Hz, 1 H, C*H*HSe), 3.35 (d, *J* = 10.9 Hz, 1 H, N–CH*H*), 3.66 (s, 3 H, COOCH_3), 4.48 (dd, *J* = 4.9 Hz, *J* = 6.4 Hz, 1 H, CH_2C*H*–O), 4.50 (s, 1 H, C*H*–Ph), 4.70 (dd, *J* = 4.9 Hz, *J* = 6.4 Hz, 1 H, CH–C*H*–O), 6.98–7.02 (m, 2 H, CH_{ar}), 7.18–7.32 (m, 6 H, CH_{ar}), 7.55–7.58 (m, 2 H, CH_{ar}) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 25.8 (*C*H_2Se), 26.1 (C$_q$–*C*H$_3$), 26.5 (C$_q$–*C*H$_3$), 52.0 (COO*C*H$_3$), 55.4 (*C*H_2N), 64.9 (*C*HN), 65.7 (*C*H–Ph), 77.1 (*C*HCH$_2$), 80.5 (*C*HCH), 111.8 [(*C*(CH$_3$)$_2$], 127.4 (*C*H_{ar}), 128.2 (*C*H_{ar}), 128.4 (2 *C*H_{ar}), 129.2 (2 *C*H_{ar}), 129.4 (2 *C*H_{ar}), 130.6 (*C*$_{ar}$Se), 133.0 (*C*$_{ar}$), 133.7 (2 *C*H_{ar}), 171.9 (*C*OO) ppm. HRMS (EI): calcd. for $C_{23}H_{27}O_4NSe$ 461.11053; found 461.11055. Minor isomer (*S*)-**20f**: yield of 33 mg (0.072 mmol, 4%), colourless oil, R_f = 0.08 (cyclohexane/EtOAc, 9:1). $[a]_D^{23}$ = –31.7 (*c* = 1.16, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.32 (s, 3 H, CH_3), 1.59 (s, 3 H, CH_3), 2.98–3.04 (m, 3 H, CH_2Se, CH*H*), 3.09 (dd, *J* = 2.9 Hz, *J* =

11.5 Hz, 1 H, N–C*H*H), 3.38 (ddd, *J* = 2.3 Hz, *J* = 3.6 Hz, *J* = 8.2 Hz, 1 H, C*H*N), 3.64 (s, 3 H, COOCH_3), 4.62 (ddd, *J* = 3.0 Hz, *J* = 5.1 Hz, *J* = 6.4 Hz, 1 H, CH_2C*H*–O), 4.68 (dd, *J* = 2.3 Hz, *J* = 6.4 Hz, 1 H, CH–C*H*–O), 4.80 (s, 1 H, C*H*–Ph), 7.19–7.42 (m, 10 H, CH_{ar}) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 25.2 (C_q–CH_3), 27.3 (C_q–CH_3), 28.7 (CH_2Se), 52.0 (COOCH_3), 54.6 (CH_2N), 65.3 (*C*H–Ph), 67.0 (*C*HN), 79.2 (*C*HCH_2), 84.7 (*C*HCH), 112.5 [*C*(CH_3)$_2$], 126.9 (*C*H$_{ar}$), 128.4 (*C*H$_{ar}$), 128.7 (4 *C*H$_{ar}$), 129.2 (2 *C*H$_{ar}$), 132.5 (2 *C*H$_{ar}$), 133.8 (C_{ar}Se), 136.7 (C_{ar}), 171.8 (*C*OO) ppm. HRMS (EI): calcd. for $C_{23}H_{27}O_4NSe$ 461.11053; found 461.11055.

General Procedure for the Selenocyclisation and Reduction to Pyrrolidines 21a, 21c and 21d: The appropriate *N*(alkenylidene)alkylamine **9** (1.64 mmol) was dissolved in dry CH_2Cl_2 (15 mL) at –78 °C under argon in a flame-dried flask. A solution of camphorselenyl bromide **22** (0.96 mmol), generated in situ, in dry CH_2Cl_2 (30 mL) was added over 30 min. After 2 h at –78 °C, MeOH (5 mL) and $NaBH_4$ (73 mg, 1.93 mmol) were added. The mixture was warmed slowly to room temperature. The organic layer was separated and washed with water (10 mL). After separating the layers, the aqueous layer was washed with CH_2Cl_2 (2 × 5 mL). The combined organic layers were dried with $MgSO_4$ and concentrated under vacuum. The remaining yellow oil was purified by column chromatography (40 g of silica gel, 2.3 cm column diameter, cyclohexane/EtOAc mixture).

(4a*R*,4b*R*,8a*S*,9a*S*)-9-{2-[(2*R*)-*N*-Benzyl-4,4-dimethylpyrrolidin-2-ylselenylmethyl]benzyl}-3,6-diphenyl-hexahydro-2,4,5,7-tetraoxa-9-azafluoren and (4a*R*,4b*R*,8a*S*,9a*S*)-9-{2-[(2*S*)-*N*-Benzyl-4,4-dimethylpyrrolidin-2-ylselenylmethyl]benzyl}-3,6-diphenyl-hexahydro-2,4,5,7-tetraoxa-9-azafluoren (21b): The diselenide (0.32 g, 0.32 mmol) was dissolved in dry CH_2Cl_2 (10 mL) at –78 °C under argon in a flame-dried flask. A 0.1 M solution of bromine (0.32 mmol) in dry CH_2Cl_2 was added over 5 min to generate **23**. After 20 min at –78 °C, $AgPF_6$ (0.19 g, 0.75 mmol) was added. The mixture was stirred for 20 min and cooled to –100 °C. *N*-Benzyl(2,2-dimethylpent-4-enylidene)amine (**9a**) (0.36 g, 1.79 mmol) in dry CH_2Cl_2 (5 mL) was added. The mixture was warmed slowly to room temperature. MeOH (5 mL) and sodium borohydride (73 mg, 1.93 mmol) were added, and the mixture was stirred for 1 h. The organic layer was separated and washed with water (10 mL). After separating the layers, the aqueous layer was washed with CH_2Cl_2 (2 × 5 mL). The combined organic layers were dried with $MgSO_4$ and concentrated under vacuum. The remaining oil was purified by column chromatography (40 g silica gel, 2.3 cm column diameter, cyclohexane/EtOAc, 9:1), yielding 0.33 g (0.46 mmol, 72% yield) of a colourless oil. Diastereomers were not separated, *dr* = 48:52, R_f = 0.53 (hexane/EtOAc, 9:1). HRMS (ESI): calcd. for $C_{41}H_{47}O_2N_2Se$ 711.27010; found 711.27013. Major isomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.97 (s, 3 H, CH_3), 1.10 (s, 3 H, CH_3), 1.70 (dd, *J* = 8.3 Hz, *J* = 9.7 Hz, 1 H, C_q–CH*H*–CH), 1.80 (dd, *J* = 3.9 Hz, *J* = 8.3 Hz, 1 H, C_q–CH*H*–CH), 1.99 (d, *J* = 8.8 Hz, 1 H, C_q–CH*H*–N), 2.64 (d, *J* = 9.0 Hz, 1 H, C_q–CH*H*–N), 2.84–2.92 (m, 1 H, C*H*–CH_2–Se), 3.05–3.18 (m, 3 H, Se–CH_2, C*H*), 3.53 (s, 2 H, CH_2–Ar), 3.90–4.17 (m, 6 H, 2 CH_2–O, 2 C*H*), 4.40 (s, 2 H, CH_2–Ph), 4.75 (d, *J* = 15.8 Hz, 1 H, C*H*), 5.49 (s, 2 H, 2O–C*H*–O), 7.11–7.15 (m, 1 H, CH_{ar}), 7.19–7.54 (m, 17 H, CH_{ar}), 7.64 (d, *J* = 7.2 Hz, 1 H, SeC_{ar}–CH_{ar}) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 28.9 (*C*H_3), 30.2 (*C*H_3), 32.6 (*C*H_2Se), 35.9 [*C*(CH_3)$_2$], 46.7 (CH–*C*H_2–C_q), 53.1 (*C*H_2–Ph), 53.8 (*C*H_2–Ar), 58.3 (2 NC*H*–CH_2O), 63.6 (*C*H–CH_2Se), 67.1 (2 *C*H_2–O), 68.3 [N–*C*H_2–C(CH_3)$_2$], 79.7 (2 *C*H–O), 99.9 (2 Ph–*C*H–O), 126.5 (4 *C*H$_{ar}$), 126.7 (*C*H$_{ar}$), 126.8 (*C*H$_{ar}$), 127.4 (*C*H$_{ar}$), 128.2 (4 *C*H$_{ar}$), 128.5 (4 *C*H$_{ar}$), 128.8 (*C*H$_{ar}$), 129.2 (2 *C*H$_{ar}$), 131.3 (SeC_{ar}), 131.8 (*C*H$_{ar}$), 138.5 (2 CH–C_{ar}), 139.9 (CH_2–C_{ar}), 142.5 (CH_2–C_{ar}) ppm. Minor isomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.93 (s, 3 H, CH_3), 1.08, (s, 3 H, CH_3), 1.66 (dd, *J* = 8.1 Hz, *J* = 10.0 Hz, 1 H, C_q–CH*H*–CH), 1.84 (dd, *J* = 3.7 Hz, *J* = 7.9 Hz, 1 H, C_q–CH*H*–CH), 1.99 (d, *J* = 8.8 Hz, 1 H, C_q–CH*H*–N), 2.64 (d, *J* = 9.0 Hz, 1 H, C_q–CH*H*–N), 2.84–2.92 (m, 1 H, C*H*–CH_2–Se), 3.05–3.18 (m, 3 H, Se–CH_2, C*H*), 3.53 (s, 2 H, CH_2–Ar), 3.90–4.17 (m, 6 H, 2 CH_2–O, 2 C*H*), 4.40 (s, 2 H, CH_2–Ph), 4.77 (d, *J* = 16.2 Hz, 1 H, C*H*), 5.50 (s, 2 H, 2O–C*H*–O), 7.11–7.15 (m, 1 H, CH_{ar}), 7.19–7.54 (m, 17 H, CH_{ar}), 7.69 (d, *J* = 7.5 Hz, 1 H, SeC_{ar}–CH_{ar}) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 28.8 (*C*H_3), 30.2 (*C*H_3), 32.5 (*C*H_2Se), 35.9 [*C*(CH_3)$_2$], 46.6 (CH–*C*H_2–C_q), 53.1 (*C*H_2–Ph), 53.8 (*C*H_2–Ar), 58.6 (2 NC*H*–CH_2O), 63.7 (*C*H–CH_2Se), 67.0 (2 *C*H_2–O), 68.3 [N–*C*H_2–C(CH_3)$_2$], 79.7 (2 *C*H–O), 99.9 (2 Ph–*C*H–O), 126.5 (4 *C*H$_{ar}$), 126.6 (*C*H$_{ar}$), 126.8 (*C*H$_{ar}$), 127.3 (*C*H$_{ar}$), 128.2 (4 *C*H$_{ar}$), 128.5 (4 *C*H$_{ar}$), 128.7 (*C*H$_{ar}$), 129.2 (2 *C*H$_{ar}$), 131.6 (SeC_{ar}), 131.8 (*C*H$_{ar}$), 138.5 (2 CH–C_{ar}), 139.9 (CH_2–C_{ar}), 142.6 (CH_2–C_{ar}) ppm.

Methyl (*R*)-2-{(2*R*)-4,4-Dimethyl-2-[(1*R*,2*S*,4*R*)-4,7,7-trimethyl-3-oxobicyclo[2.2.1]hept-2-yl-selenylmethyl]pyrrolidin-1-yl}-2-phenylacetate and Methyl (*R*)-2-{(2*S*)-4,4-Dimethyl-2-[(1*R*,2*S*,4*R*)-4,7,7-trimethyl-3-oxobicyclo[2.2.1]hept-2-yl-selenylmethyl]pyrrolidin-1-yl}-2-phenylacetate (21c): Starting material **9j** (270 mg, 1.04 mmol). Diastereomers were isolated as a mixture of rotamers. *dr* = 38:62. Major isomer: yield of 122 mg (0.25 mmol, 29%), colourless oil, R_f = 0.21 (hexane/EtOAc, 9:1). $[\alpha]_D^{22}$ = –7.4 (*c* = 1.00, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.75, 0.77 (s, 3 H, CH_3), 0.82 (s, 3 H, CH_3), 0.84, 085 (s, 3 H, CH_3), 0.94 (s, 3 H, CH_3), 1.03, 1.04 (s, 3 H, CH_3), 1.32–1.63 (m, 4 H, 2 CH_2), 1.67–1.74 (m, 3 H, CH*H*–N, CH_2), 1.99–2.04 (m, 1 H, SeCH_2–C*H*–N), 2.19, 2.21 (d, *J* = 8.6 Hz, 1 H, C*H*H–N), 2.72–2.83 (m, 2 H, C*H*H–Se, C*H*–CHSe), 2.86–2.92 (m, 1 H, C*H*H–Se), 2.94–3.15 (m, 1 H, C*H*–Se), 3.60, 3.61 (s, 3 H, COOCH_3), 4.51, 4.52 (s, 1 H, C*H*–COO), 7.24–7.29 (m, 5 H, CH_{ar}) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 9.9 (*C*H_3), 19.8 (2 *C*H_3), 23.4, 23.5 (*C*H_2), 28.4, 28.5 (*C*H_3), 29.1, 29.2 (*C*H_3), 29.5, 29.6 (*C*H_2Se), 30.5, 30.6 (*C*H_2), 36.1, 36.2 [*C*(CH_3)$_2$], 46.0, 46.2 (CH–*C*H_2–C_q), 46.6, 46.7 (*C*H–Se), 46.9, 47.0 (C_q–CO), 48.4, 48.5 (*C*H–CHSe), 52.0, 52.1 (COOCH_3), 58.1, 58.2 (C_q–CO), 60.6, 60.9 (*C*H–Ph), 63.7, 63.8 (N–CH_2–C_q), 67.6, 67.8 (*C*H–N), 128.2 (*C*H$_{ar}$), 128.4, 128.5 (2 *C*H$_{ar}$), 129.3, 129.4 (2 *C*H$_{ar}$), 135.2, 135.3 (CH–C_{ar}), 172.7, 172.8 (COO), 218.2, 218.3 (C=O) ppm. HRMS (ESI$^+$) calcd. for $C_{26}H_{37}O_3NSeNa$ 514.1831; found 514.1831. Minor isomer: yield of 74 mg (0.15 mmol, 17%). R_f = 0.26 (hexane/EtOAc, 9:1). $[\alpha]_D^{22}$ = 19.8 (*c* = 1.25, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.80, 0.82 (s, 3 H, CH_3), 0.84 (s, 3 H, CH_3), 0.94, 0.95 (s, 3 H, CH_3), 0.96 (s, 3 H, CH_3), 0.97, 0.98 (s, 3 H, CH_3), 1.32–1.41 (m, 1 H, CH*H*), 1.52–1.64 (m, 3 H, 3 C*H*H), 1.71–1.80 (m, 3 H, 2 CH*H*, CH*H*–N), 2.01–2.11 (m, 1 H, CH*H*–N), 2.41–2.49 (m, 1 H, SeCH_2–C*H*–N), 2.64–2.70 (m, 1 H, C*H*–CHSe), 2.78–2.81 (m, 1 H, C*H*H–Se), 3.17–3.29 (m, 1 H, C*H*H–Se), 3.45, 3.51 (d, *J* = 4.9 Hz, 1 H, CH–Se), 3.65, 3.66 (s, 3 H, COOCH_3), 4.65, 4.70 (s, 1 H, C*H*–COO), 7.19–7.36 (m, 5 H, CH_{ar}) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 9.8 (*C*H_3), 19.8 (2 *C*H_3), 23.4, 23.5 (*C*H_2), 28.7, 28.8 (*C*H_3), 29.4 (*C*H_3), 30.0 (*C*H_2Se), 30.5, 30.6 (*C*H_2), 36.0 [*C*(CH_3)$_2$], 46.3, 46.4 (CH–*C*H_2–C_q), 46.6, 47.7 (*C*H–Se), 46.9 (C_q–CO), 48.4, 48.5 (*C*H–CHSe), 51.5, 51.6 (COOCH_3), 58.1, 58.2 (C_q–CO), 60.6, 60.9 (*C*H–Ph), 62.3, 62.8 (N–CH_2–C_q), 65.7, 66.4 (*C*H–N), 127.8, 127.9 (*C*H$_{ar}$), 128.4 (2 *C*H$_{ar}$), 128.6, 128.7 (2 *C*H$_{ar}$), 137.4 (CH–C_{ar}), 172.2 (COO), 218.3, 218.4 (C=O) ppm. HRMS (ESI$^+$): calcd. for $C_{26}H_{38}O_3NSe$ 492.2011; found 492.2011.

Supporting Information (see also the footnote on the first page of this article): Experimental and spectroscopic data of imines **9**, **10c**, **10d**,**10c**, **14c**, **14d**, **14e**, **15**, **18**, **20c**, **20e**, **21a**, and **21d**.

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