Asymmetric Amidoselenenylation of Alkenes Promoted by Camphorselenenyl Sulfate: A Useful Synthetic Route to Enantiopure Oxazolines

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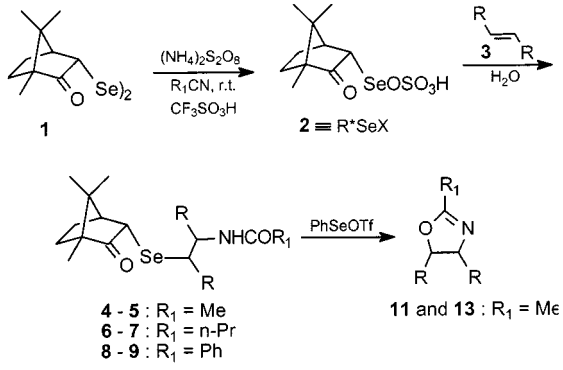
Camphorselenenyl sulfate is an efficient chiral, nonracemic electrophilic reagent which can be produced from the easily available camphor diselenide by treatment with ammonium persulfate. This electrophilic selenium reagent reacts with alkenes, at room temperature in acetonitrile, in the presence of water and trifluoromethanesulfonic acid to afford the amidoselenenylation products with moderate facial selectivity. However, the two diastereomeric addition products can be easily separated. After activation of the selenium moiety with phenylselenenyl triflate or with SO_2Cl_2, these products are deselenenylated stereospecifically by intramolecular substitution and afford enantiomerically pure oxazolines.

Introduction

Several research groups have recently described interesting stereoselective processes promoted by chiral selenium compounds.[1,2] For this purpose a number of chiral diselenides have been prepared and transformed in situ into electrophilic, chiral, nonracemic selenenylating agents which were allowed to react with alkenes in the presence of external or internal nucleophiles.[3−6] With different chiral diselenides, good asymmetric inductions were obtained in the selenomethoxylation and selenohydroxylation, as well as in the selenium-induced cyclofunctionalization of alkenes. Perhaps the most readily available chiral diselenide is the camphor diselenide **1** which was described by Back and coworkers and which can be obtained in a one-pot reaction from (1*R*)-(+)-camphor and elemental selenium.[7,10] The cyclofunctionalization of alkenes promoted by camphorselenenyl chloride proceeds with poor diastereoselectivity. However good results could be obtained at −95 °C with a modified diselenide in which the carbonyl group was converted into a *spiro*-oxazolidinone.[8,10] Good results were also obtained in the selenomethoxylation of alkenes, at −78 °C, with the camphorselenenyl triflate.[9,10] In recent years we have accumulated several examples which demonstrate that the use of the sulfate as the counter ion greatly increases the reactivity of the electrophilic phenylselenenylating agents.[2] On the basis of these observations we have recently investigated some asymmetric syntheses promoted by the camphorselenenyl sulfate **2**, produced in situ by oxidation of **1** with ammonium persulfate (Scheme 1). Indeed, reagent **2** gives rise to the selenomethoxylation[11] of alkenes with a facial selectivity comparable to those obtained with other chiral diselenides,[2] but with the great advantage that the addition reactions can be carried out at room temperature. The reagent **2** was also employed to effect (at 40 °C) the first example of the asymmetric selenohydroxylation[12] of alkenes with moderate to good facial selectivity. With an excess of ammonium persulfate, it was also possible to carry out a one-pot selenenylation-deselenenylation sequence.[2] Thus, starting from the β,γ-unsaturated esters or nitriles, enantiomerically enriched γ-alkoxy or γ-hydroxy α,β-unsaturated derivatives could be prepared directly.[13] We now report that the camphorselenenyl sulfate **2** can also be employed to effect the asymmetric amidoselenenylation of alkenes (Scheme 1). We also report that the two diastereomeric addition products can be separated easily and transformed into enantiomerically pure oxazolines.



Scheme 1. Conversion of alkenes into oxazolines

Results and Discussion

Preliminary experiments were carried out on (*E*)-3-hexene **(3a)** using acetonitrile, butyronitrile or benzonitrile. Ammonium persulfate (0.5 mmol) and trifluoromethanesulfonic acid (1.5 mmol) were added to a solution of the diselenide **1** (0.5 mmol) in MeCN, *n*PrCN or PhCN (2.5 mL) at room temperature. The reaction mixture was stirred for 15 min and then water (5 mmol) and (*E*)-3-hexene (1 mmol) dissolved in the nitrile (2.5 mL) were added. The progress of the reaction was monitored by TLC and GC-MS. The

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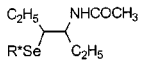
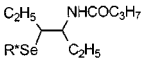
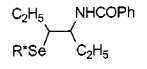
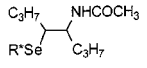
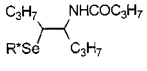
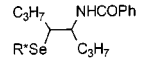
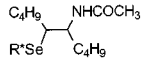
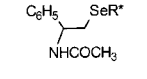
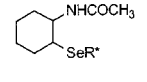
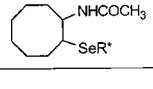
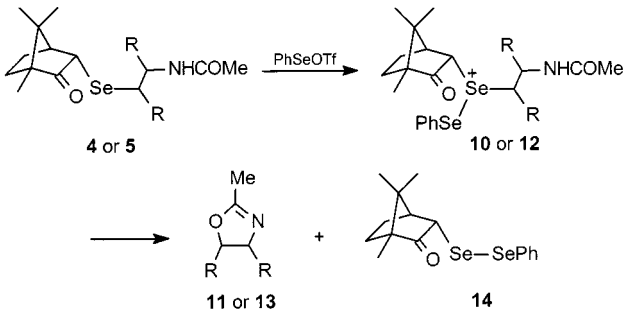
reaction mixture was poured into a sodium hydrogencarbonate solution and then worked up in the usual way. In every case the addition products **4**−**9** were formed as mixtures of two diastereomers deriving from a stereospecific *anti* addition.[2] Reaction times, reaction yields and diastereomeric ratios are reported in Table 1 (entries 1−3). Also reported in Table 1 (entries 4−6) are the results of similar experiments carried out on (*E*)-4-octene **(3b)**. An examination of these data indicates that the reactions in *n*PrCN and in PhCN require considerably longer reaction times and give lower yields than those in MeCN. The diastereomeric excesses were considerably lower in the case of the reactions carried out in benzonitrile. Moreover, the two diastereomers of the acetamido derivatives **4a, 5a** and **4b, 5b** could be readily separated by medium pressure column chromatography, whereas the purification of those deriving from butyronitrile, **6a**, **7a** and **6b**, **7b**, or from benzonitrile, **8a**, **9a** and **8b**, **9b**, was much more difficult. Indeed, in the cases of **6a**, **7a** and **6b**, **7b**, only the major isomers could be isolated as pure enantiomers. On the basis of these observations further experiments starting from other alkenes were therefore carried out in acetonitrile.

Table 1. Amidoselenenylation of alkenes with camphorselenenyl sulfate **2**

Entry	Alkenes 3	Nitrile	Time (h)	Addition Products	Yield (%)	D.r.
1	(*E*)-3-Hexene **3a**	MeCN	23	 **4a+5a**	82	73:27
2	(*E*)-3-Hexene **3a**	*n*-PrCN	48	 **6a+7a**	53	78:22
3	(*E*)-3-Hexene **3a**	PhCN	67	 **8a+9a**	57	61:39
4	(*E*)-4-Octene **3b**	MeCN	24	 **4b+5b**	78	75:25
5	(*E*)-4-Octene **3b**	*n*-PrCN	62	 **6b+7b**	60	78:22
6	(*E*)-4-Octene **3b**	PhCN	63	 **8b+9b**	63	61:39
7	(*E*)-5-Decene **3c**	MeCN	24	 **4c+5c**	80	80:20
8	Styrene **3d**	MeCN	30	 **4d+5d**	50	53:47
9	Cyclohexene **3e**	MeCN	26	 **4e+5e**	61	65:45
10	Cyclooctene **3f**	MeCN	25	 **4f+5f**	86	60:40

The results of these experiments are also collected in Table 1. The diastereomeric ratios were moderate in the 4-acetamido-3-camphorselenenyl hexanes **4a** and **5a**, in the 5-acetamido-4-camphorselenenyl octanes **4b** and **5b** and in the 6-acetamido-5-camphorselenenyl decanes **4c** and **5c**. Poor diastereomeric ratios were observed in the 2-acetamido-1-camphorselenenyl cyclohexanes **4e** and **5e** and in the 2-acetamido-1-camphorselenenyl cyclooctane **4f** and **5f**. The regioselective amidoselenenylation of styrene affords the 2-acetamido-1-camphorselenenyl-2-phenyl ethanes **4d** and **5d** in almost equal amounts. In every case, however, the two diastereomers were separated by medium pressure column chromatography. In this way we obtained both the major, **4a**−**f**, and the minor, **5a**−**f**, stereoisomers in an optically pure form. This is of particular interest since the amido selenides can be deselenenylated in various ways and enantiomerically pure derivatives can thus be obtained. As has been demonstrated in the case of racemic amido selenides,[14] reductive deselenenylation with tin hydrides affords alkyl amides, whereas oxidative deselenenylation gives rise to the elimination products, i.e. allylic amides. Application of these deselenenylation reactions to the amido selenides **4a**−**f** and **5a**−**f** would afford both the enantiomers of the corresponding alkyl amides and allyl amides in an optically pure form.

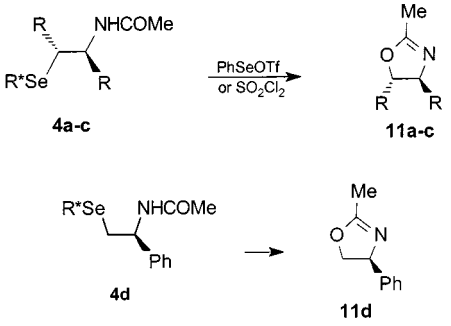
We have recently described a new method of deselenenylation which occurs with substitution. This method consists of the activation of the selenium moiety as a leaving group by transforming the selenides into selenonium ions by treatment with electrophilic selenenylating agents. In this way the selenium moiety of the selenides can be replaced by several nucleophiles.[15] In the case of substrates containing suitably positioned nucleophilic substituents an intramolecular nucleophilic displacement readily takes place and several heterocyclic compounds can be produced.[16] This intramolecular substitution occurs with inversion of configuration at the carbon atom bearing the selenium atom.[16,17] We have applied this simple procedure to the acetamido selenides reported in Table 1 and we have thus obtained both the enantiomers of the corresponding oxazolines in an optically pure form. These conversions are illustrated in Scheme 2.



Scheme 2. Oxazolines from acetamido selenides

The reaction of phenylselenenyl triflate with the optically pure acetamido selenides **4** or **5** gives rise to the selenonium intermediates **10** or **12**, in which an intramolecular substitution takes place to afford the optically pure oxazolines **11** or **13** and the diselenide **14**. The reactions occur at room temperature in diethyl ether and require 7−8 hours. The

diselenide **14** could not be isolated, since during the work up it gives rise to a mixture of the diselenide **1** and of the diphenyl diselenide. The examples reported in Scheme 3 indicate that these conversions are stereospecific and occur with inversion of configuration at the carbon atom holding the camphorseleno group. For the sake of simplicity, the absolute configurations of the oxazolines **11a−d**, as well as those of the major diastereomers **4a−d** obtained from the acetamidoselenenylation reactions of (*E*)-3-hexene, (*E*)-4-octene, (*E*)-5-decene and styrene, are indicated. Obviously, starting from the minor diastereoisomers **5a−d**, the enantiomeric oxazolines **13a−d** were obtained. These absolute configurations have been determined as reported below. The absolute configurations of the stereoisomers deriving from cyclohexene and from cyclooctene, and those of the corresponding two enantiomeric *cis* oxazolines, were not determined. The yields of these cyclization reactions and the optical specific rotations of the oxazolines are collected in Table 2. The stereospecific conversion of the acetamido selenides into oxazolines can also be effected with SO_2Cl_2 in dichloromethane at room temperature. In this case the reactive intermediates are very likely to be the selenium (IV) dichlorides. These reactions are faster (20−30 minutes) than those effected with phenylselenenyl triflate and afford the oxazolines in better yields. The reaction failed in the case of the cyclization of the amido selenides deriving from cyclohexene, Reaction yields are indicated in parentheses in Table 2.



Scheme 3. Stereospecific conversions of acetamido selenides into oxazolines

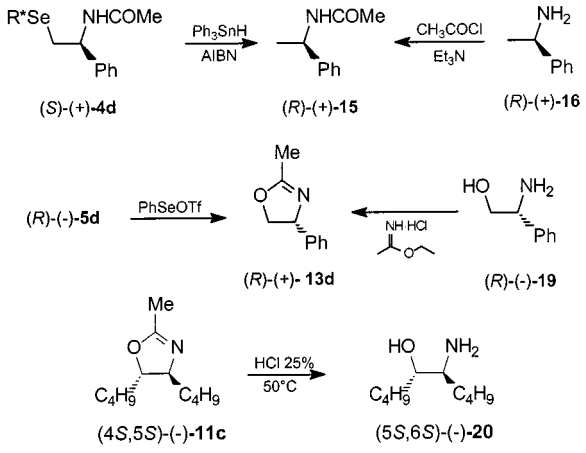
Table 2. Optical specific rotations and yields of oxazolines obtained from acetamido selenides

Acetamido Selenides	Oxazolines	$[\alpha]_D$	Yields %[a]
(3*R*,4*S*)-(−)-**4a**	(4*S*,5*S*)-(−)-**11a**	−49.5	75 (98)
(3*S*,4*R*)-(+)-**5a**	(4*R*,5*R*)-(+)-**13a**	+48.9	84 (95)
(4*R*,5*S*)-(−)-**4b**	(4*S*,5*S*)-(−)-**11b**	−23.7	60 (95)
(4*S*,5*R*)-(+)-**5b**	(4*R*,5*R*)-(+)-**13b**	+24.0	68 (90)
(5*R*,6*S*)-(−)-**4c**	(4*S*,5*S*)-(−)-**11c**	−63.4	72 (93)
(5*S*,6*R*)-(+)-**5c**	(4*R*,5*R*)-(+)-**13c**	+63.5	70 (97)
(2*S*)-(+)-**4d**	(4*S*)-(−)-**11d**	−16.2	70 (85)
(2*R*)-(−)-**5d**	(4*R*)-(+)-**13d**	+16.1	75 (86)
(−)-**4e**	(+)-**11e**	+32.4	55
(−)-**5e**	(−)-**13e**	−32.7	55
(−)-**4f**	(+)-**11f**	+28.1	72 (81)
(−)-**5f**	(−)-**13f**	−28.9	60 (78)

[a] Yields in parentheses refer to the reactions effected with SO_2Cl_2.

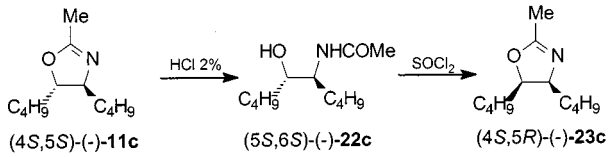
The enantiomeric excess of the final products was calculated by ^1H NMR spectroscopy in $CDCl_3$ in the presence of (*S*)-(+)-1-(9-antryl)2,2,2-trifluoroethanol. In every case the oxazolines were found to be enantiomerically pure (*ee* > 98%).

The absolute configurations of the acetamido selenides formed from styrene were determined by reductive deselenenylation with triphenyltin hydride and AIBN. As indicated in Scheme 4, the major isomer **(+)-4d** afforded the (*R*)-(+)-acetamide **15** which was identical to an authentic sample[18] obtained by acetylation of the commercially available amine **(*R*)-(+)-16**. Isomer **(−)-5d** afforded (*S*)-(−)-acetamide **17** identical to an authentic sample[19] prepared from **(*S*)-(−)-18**. Thus, the absolute configurations of **(+)-4d** and **(−)-5d** are *S* and *R* respectively. Moreover, the configuration of the oxazoline **(*R*)-(+)-13d**, obtained from **(*R*)-(−)-5d**, was confirmed by an independent synthesis consisting of condensation of the commercial (*R*)-(−)-2-amino-2-phenylethan-1-ol **(19)** with ethyl acetimidate hydrochloride.[20] The absolute configuration of the oxazoline **(−)-11c** was determined by treatment with 25% hydrochloric acid at 50 °C. Under these conditions the known (5*S*,6*S*)-(−)-6-aminodecan-5-ol **(20)**[21] was obtained (Scheme 4). Similarly, hydrolysis of **13c** gave the enantiomeric (5*R*,6*R*)-(+)-6-aminodecan-5-ol **(21)**. Thus, compound **11c** is the (4*S*,5*S*)-(−)-4,5-dibutyl-2-methyl oxazoline and compound **13c** is the (4*R*,5*R*)-(+)-4,5-dibutyl-2-methyl oxazoline. Since the conversion of the amido selenides **4** or **5** into the oxazolines **11** or **13** occurs with inversion of configuration at the carbon atom holding the camphorselenenyl group,[16,17] it follows that **11c** is produced from (5*R*,6*S*)-(−)-5-camphorselenenyl-6-acetamido decane **(4c)** and that **13c** is formed from the minor isomer (5*S*,6*R*)-(+)-5-camphorselenenyl-6-acetamido decane **(5c)**. Under the reasonable assumption that the facial selectivity of the acetamidoselenenylation does not change on passing from (*E*)-5-decene to (*E*)-4-octene or (*E*)-3-hexene, it can be suggested that the chiral centers in **4a** and **4b** and in **5a** and **5b** have the same absolute configuration as those of **4c** and **5c**, respectively.



Scheme 4. Determination of the absolute configurations of acetamido selenides and oxazolines

Under milder hydrolytic conditions (2% HCl, room temperature) oxazolines are converted into the corresponding β-hydroxy acetamides in quantitative yields. These compounds can be easily reconverted into oxazoline by simple treatment with thionyl chloride. Interestingly, this reaction occurs with inversion of configuration at the carbon atom holding the oxygen atom.[22] Using these simple reactions it is thus possible to convert the *trans* oxazolines into the corresponding enantiomerically pure *cis* compounds. These conversions are illustrated in Scheme 5. Hydrolysis of **11c** gave the β-hydroxy acetamide **22c**, and further treatment with thionyl chloride gave the *cis* oxazoline **23c**. Similarly, the enantiomeric oxazoline **13c** gave the β-hydroxy acetamide **24c** and then the *cis* oxazoline **25c**. The *cis* relationship between protons H_4 and H_5 in compounds **23c** and **25c** has been confirmed by NOE difference experiments. Irradiation of H_4, in fact, produces a strong enhancement of the H_5 absorption.



Scheme 5. Conversion of *trans* oxazolines into *cis* oxazolines

This procedure has been exemplified only in the case of two oxazolines deriving from (*E*)-5-decene, but it seems reasonable to assume that similar results can also be obtained starting from the other oxazolines described above.

Conclusion

We have described in this paper the first example of the asymmetric amidoselenenylation of alkenes. This process is effected with camphorselenenyl sulfate and occurs with poor to moderate facial selectivity depending on the structure of the alkene employed. However, the reactions carried out in MeCN give rise to two diastereomeric acetamido selenides which can be easily separated and employed for the syntheses of both the enantiomers of several enantiomerically pure derivatives. We have also shown that, starting from acetamido selenides, and using very simple reactions, it is possible to effect the enantiospecific synthesis of all the four 4,5-disubstituted oxazolines.

Experimental Section

New compounds were characterized by mass, ^1H and ^{13}C NMR spectra. GC-MS analyses were carried out with an HP-5890 gas chromatograph (dimethyl silicone column, 12.5 m) equipped with an HP-5971 mass-selective detector. ^1H and ^{13}C NMR spectra were recorded at 400 and 100.62 MHz, respectively, on a Bruker Avance-DRX 400 instrument; unless otherwise specified, $CDCl_3$ was used as the solvent and TMS as internal standard. Optical rotations were measured with a JASCO DIP-1000 digital polarimeter. Elemental analyses were carried out on a Carlo Erba 1106 elemental analyzer.

Amidoselenenylation of Alkenes. General Procedure: Ammonium persulfate (0.5 mmol) and CF_3SO_3H (1.5 mmol) were added to a solution of camphor diselenide **(1)** (0.5 mmol) in CH_3CN, *n*PrCN or PhCN (2.5 mL) and the resulting red solution was stirred at room temperature for 15 minutes. A solution of the alkene **3** (1 mmol) and water (5 mmol) in CH_3CN, *n*PrCN or PhCN (2.5 mL) was then added and the mixture was stirred at room temperature for the times indicated in Table 1. The progress of the reaction was monitored by TLC and GC-MS. The reaction mixture was then poured into aqueous $NaHCO_3$ solution and extracted with diethyl ether. The combined organic extracts were washed with brine, dried over sodium sulfate, filtered and the solvents evaporated. The reaction products were separated by medium pressure chromatography on a silica gel column (Merck, LiChroprep® Si60, 40−63 μm), with a 2:8 mixture of diethyl ether and light petroleum as eluent. The reaction times, the products obtained, the reaction yields and the diastereomeric ratios are reported in Table 1. Physical and spectral data are reported below.

(3*R*,4*S*)-4-Acetamido-3-camphorselenenylhexane (4a): oil, $[\alpha]_D^{23}$ = −61.8 (*c* = 2.6, $CHCl_3$). − ^1H NMR: δ = 7.5 (d, *J* = 9.4 Hz, 1 H), 4.09 (dddd, *J* = 2.7, 5.3, 8.5 and 9.4 Hz, 1 H), 3.51 (dd, *J* = 2.5 and 4.7 Hz, 1 H), 3.02 (ddd, *J* = 2.7, 5.7 and 7.9 Hz, 1 H), 2.3 (dd, *J* = 4.4 and 4.7 Hz, 1 H), 1.99 (s, 3 H), 1.9−1.4 (m, 8 H), 1.11 (t, *J* = 7.3 Hz, 3 H), 1.04 (s, 3 H), 0.98 (t, *J* = 7.4 Hz, 3 H), 0.96 (s, 3 H), 0.89 (s, 3 H). − ^{13}C NMR: δ = 221.3, 170.5, 58.2, 56.6, 53.8, 49.9, 49.5, 46.7, 30.2, 27.8, 23.4, 23.2, 22.9, 19.5, 19.1, 13.0, 10.5, 9.6. − GC-MS: *m*/*z* (%) = 373 (7), 314 (9), 232 (18), 230 (9), 222 (16), 163 (11), 152 (24), 142 (47), 137 (5), 124 (12), 114 (5), 109 (18), 100 (100), 83 (36), 82 (22), 81 (13), 60 (29), 58 (88), 55 (25), 43 (23), 41 (20). − $C_{18}H_{31}NO_2Se$ (372.41): calcd. C 58.06, H 8.39, N 3.76; found C 58.11, H 8.31, N 3.81.

(3*S*,4*R*)-4-Acetamido-3-camphorselenenylhexane (5a): oil, $[\alpha]_D^{23}$ = +51.2 (*c* = 1.0, $CHCl_3$). − ^1H NMR: δ = 5.81 (d, *J* = 8.9 Hz, 1 H), 4.07 (dddd, *J* = 3.6, 7.0, 8.9 and 10.2 Hz, 1 H), 3.75 (dd, *J* = 1.4 and 3.4 Hz, 1 H), 3.12 (ddd, *J* = 3.9, 6.3 and 10.2 Hz, 1 H), 2.1 (dd, *J* = 3.4 and 4.0 Hz, 1 H), 2.03 (s, 3 H), 1.9−1.6 (m, 5 H), 1.45−1.3 (m, 3 H), 1.12 (t, *J* = 7.3 Hz, 3 H), 1.03 (s, 3 H), 0.94 (t, *J* = 7.3 Hz, 3 H), 0.94 (s, 3 H) 0.91 (s, 3 H). − ^{13}C NMR: δ = 217.3, 169.6, 58.1, 53.4, 51.8, 48.7, 48.0, 46.7, 30.3, 27.3, 23.5, 23.4, 23.2, 22.6, 19.5, 13.0, 10.8, 9.6. − GC-MS: *m*/*z* (%) = 373 (6), 314 (7), 232 (13), 222 (15), 163 (10), 152 (21), 142 (70), 124 (11), 114 (11), 109 (17), 100 (100), 83 (35), 82 (17), 81 (14), 60 (39), 58 (75), 55 (23), 43 (20), 41 (17). − $C_{18}H_{31}NO_2Se$ (372.41): calcd. C 58.06, H 8.39, N 3.76; found C 58.09, H 8.42, N 3.70.

(3*R*,4*S*)-4-Butyramido-3-camphorselenenylhexane (6a): oil. − ^1H NMR: δ = 7.4 (d, *J* = 9.4 Hz, 1 H), 4.1 (dddd, *J* = 2.7, 5.7, 7.0 and 9.3 Hz, 1 H), 3.51 (dd, *J* = 2.5 and 4.8 Hz, 1 H), 3.01 (ddd, *J* = 4.2, 7.0 and 13.7 Hz, 1 H), 2.3 (dd, *J* = 4.3 and 4.7 Hz, 1 H), 2.2−2.1 (m, 4 H), 1.8−1.4 (m, 8 H), 1.1 (t, *J* = 7.2 Hz, 3 H), 1.03 (s, 3 H), 0.97 (t, *J* = 7.5 Hz, 3 H), 0.96 (s, 3 H), 0.95 (t, *J* = 7.5 Hz, 3 H), 0.88 (s, 3 H). − ^{13}C NMR: δ = 220.6, 173.1, 58.2, 57.6, 54.1, 50.5, 50.1, 47.2, 38.7, 30.8, 28.4, 24.0, 23.7, 20.0, 19.8, 19.6, 14.2, 13.6, 10.2, 9.5. − GC-MS: *m*/*z* (%) = 401 (9), 250 (21), 232 (21), 170 (35), 152 (19), 128 (32), 109 (13), 100 (23), 88 (22), 83 (29), 71 (12), 58 (100), 43 (28). − $C_{20}H_{35}NO_2Se$ (400.46): calcd. C 59.99, H 8.81, N 3.50; found C 59.09, H 8.42, N 3.70.

(3*S*,4*R*)-4-Butyramido-3-camphorselenenylhexane (7a): GC-MS: *m*/*z* (%) = 401 (22), 314 (18), 250 (47), 232 (36), 180 (12), 170 (100), 163 (15), 152 (36), 142 (18), 128 (56), 123 (16), 109 (26), 100 (38), 88 (46), 71 (14), 58 (84), 55 (26), 43 (22), 41 (19).

(3*R*,4*S*)-4-Benzamido-3-camphorselenenylhexane (8a): oil, $[\alpha]_D^{22}$ = +18.0 (*c* = 1.4, $CHCl_3$). − ^1H NMR: δ = 7.95 (d, *J* = 8.9 Hz, 1

H), 7.8−7.7 (m, 2 H), 7.45−7.35 (m, 3 H), 4.26 (ddt, *J* = 2.7, 8.9 and 11.0 Hz, 1 H), 3.5 (dd, *J* = 2.4 and 4.6 Hz, 1 H), 3.3 (ddd, *J* = 2.7, 5.5 and 9.1 Hz, 1 H), 2.16 (dd, *J* = 4.2 and 4.6 Hz, 1 H), 2.0−1.5 (m, 7 H), 1.3 (ddd, *J* = 5.4, 9.4 and 14.1 Hz, 1 H), 1.16 (t, *J* = 7.3 Hz, 3 H), 1.08 (t, *J* = 7.4 Hz, 3 H), 0.93 (s, 6 H), 0.82 (s, 3 H). − ^{13}C NMR: δ = 221.1, 167.7, 134.6, 131.6, 128.5, 127.9, 58.0, 55.5, 55.0, 49.9, 49.5, 47.0, 30.8, 27.9, 23.7, 23.5, 19.6, 19.3, 13.6, 11.3, 10.0. − GC-MS: *m*/*z* (%) = 435 (1), 350 (1), 314 (3), 284 (8), 232 (8), 204 (15), 162 (29), 122 (11), 105 (100), 83 (14), 77 (20), 41 (5). − $C_{23}H_{33}NO_2Se$ (434.48): calcd. C 63.19, H 7.76, N 3.22; found C 63.87, H 7.99, N 3.90.

(3*S*,4*R*)-4-Benzamido-3-camphorselenenylhexane (9a): oil, $[\alpha]_D^{23}$ = +22.36 (*c* = 0.9, $CHCl_3$). − ^{1}H NMR: δ = 7.8−7.7 (m, 2 H), 7.5−7.3 (m, 3 H), 6.5 (d, *J* = 9.3 Hz, 1 H), 4.3 (ddt, *J* = 9.3, 10.7 and 3.7 Hz, 1 H), 3.7 (dd, *J* = 1.2 and 3.3 Hz, 1 H), 3.26 (ddd, *J* = 3.9, 6.7 and 10.7 Hz, 1 H), 1.99 (dd, *J* = 3.3 and 3.9 Hz, 1 H), 1.8−1.2 (m, 8 H), 1.16 (t, *J* = 7.3 Hz, 3 H), 1.0 (t, *J* = 7.3 Hz, 3 H), 0.91 (s, 3 H), 0.89 (s, 3 H), 0.76 (s, 3 H). − ^{13}C NMR: δ = 217.4, 166.9, 134.7, 131.5, 128.6, 127.4, 58.1, 53.9, 52.6, 48.9, 48.5, 46.7, 30.4, 29.7, 27.6, 23.5, 23.3, 19.5, 13.1, 11.0, 9.7. − GC-MS: *m*/*z* (%) = 435 (1), 284 (11), 204 (23), 162 (29), 122 (17), 105 (100), 83 (12), 77 (20), 41 (5). − $C_{23}H_{33}NO_2Se$ (434.48): calcd. C 63.19, H 7.76, N 3.22; found C 62.56, H 7.42, N 3.31.

(4*R*,5*S*)-5-Acetamido-4-camphorselenenyloctane (4b): oil, $[\alpha]_D^{23}$ = −53.7 (*c* = 2.2, $CHCl_3$). − ^{1}H NMR: δ = 7.57 (d, *J* = 9.5 Hz, 1 H), 4.14 (dddd, *J* = 2.5, 2.6, 8.5 and 9.5 Hz, 1 H), 3.50 (dd, *J* = 2.4 and 4.6 Hz, 1 H), 3.1 (ddd, *J* = 2.6, 5.4 and 8.5 Hz, 1 H), 2.27 (dd, *J* = 4.3 and 4.6 Hz, 1 H), 1.9 (s, 3 H), 1.9−1.2 (m, 12 H), 1.02 (s, 3 H), 0.94 (s, 3 H), 0.93 (t, *J* = 7.0 Hz, 3 H), 0.92 (t, *J* = 7.0 Hz, 3 H), 0.87 (s, 3 H). − ^{13}C NMR: δ = 221.6, 170.4, 59.0, 55.1, 52.5, 50.4, 50.1, 47.2, 37.3, 33.1, 30.8, 23.7, 23.4, 22.0, 20.1, 19.7, 19.6, 14.5, 14.1, 10.2. − GC-MS: *m*/*z* (%) = 401 (4), 342 (6), 250 (13), 232 (12), 191 (12), 170 (41), 152 (17), 128 (28), 126 (10), 114 (84), 110 (52), 81 (11), 72 (100), 69 (27), 60 (25), 55 (23), 43 (22), 41 (17). − $C_{20}H_{35}NO_2Se$ (400.46): calcd. C 59.99, H 8.81, N 3.50; found C 59.88, H 8.89, N 3.47.

(4*S*,5*R*)-5-Acetamido-4-camphorselenenyloctane (5b): oil, $[\alpha]_D^{23}$ = +30.6 (*c* = 0.8, $CHCl_3$). − ^{1}H NMR: δ = 5.77 (d, *J* = 9.2 Hz, 1 H), 4.15 (ddt, *J* = 9.7, 9.2 and 3.5 Hz, 1 H), 3.76 (d, *J* = 4.6 Hz, 1 H), 3.22 (dt, *J* = 3.6 and 7.4 Hz, 1 H), 2.15 (dd, *J* = 4.4 and 4.6 Hz, 1 H), 2.02 (s, 3 H), 1.9−1.2 (m, 12 H), 1.04 (s, 3 H), 0.97 (t, *J* = 7.2 Hz, 3 H), 0.94 (s, 3 H), 0.93 (t, *J* = 7.3 Hz, 3 H), 0.92 (s, 3 H). − ^{13}C NMR: δ = 217.7, 169.7, 58.6, 52.1, 50.3, 49.2, 48.6, 47.2, 36.9, 33.1, 30.8, 24.0, 23.7, 21.8, 20.1, 19.9, 14.3, 10.1. − GC-MS: *m*/*z* (%) = 401 (5), 250 (14), 232 (11), 191 (11), 170 (64), 152 (18), 128 (38), 126 (10), 114 (87), 110 (44), 83 (11), 81 (11), 72 (100), 69 (30), 60 (43), 55 (26), 43 (24), 41 (18). − $C_{20}H_{35}NO_2Se$ (400.46): calcd. C 59.99, H 8.81, N 3.50; found C 59.91, H 8.95, N 3.41.

(4*R*,5*S*)-5-Butyramido-4-camphorselenenyloctane (6b): oil, $[\alpha]_D^{23}$ = −32.0 (*c* = 4, $CHCl_3$). − ^{1}H NMR: δ = 7.45 (d, *J* = 9.5 Hz, 1 H), 4.15 (t, *J* = 9.7 Hz, 1 H), 3.5 (dd, *J* = 2.1 and 4.7 Hz, 1 H), 3.1−3.0 (m, 1 H), 2.26 (dd, *J* = 4.1 and 4.7 Hz, 1 H), 2.2−2.05 (m, 2 H), 1.75−1.0 (m, 14 H), 1.01 (s, 3 H), 0.92 (t, *J* = 7.0 Hz, 3 H), 0.94 (s, 3 H), 0.91 (t, *J* = 7.3 Hz, 6 H), 0.86 (s, 3 H). − ^{13}C NMR: δ = 220.1, 172.9, 58.3, 54.7, 51.8, 50.0, 49.7, 46.7, 38.3, 36.9, 32.7, 30.3, 29.6, 23.3, 21.5, 19.5, 19.4, 19.3, 14.0, 13.7, 13.6, 9.7. − GC-MS: *m*/*z* (%) = 429 (2), 278 (12), 198 (26), 152 (11), 142 (29), 128 (19), 110 (40), 88 (20), 72 (100), 55 (14), 43 (17), 41 (11). − $C_{22}H_{39}NO_2Se$ (428.51): calcd. C 61.67, H 9.17, N 3.27; found C 67.40, H 8.95, N 3.10.

(4*S*,5*R*)-5-Butyramido-4-camphorselenenyloctane (7b): oil. − ^{1}H NMR: δ = 5.7 (d, *J* = 9.2 Hz, 1 H), 4.25−4.1 (m, 1 H), 3.72 (d, *J* = 4.7 Hz, 1 H), 3.20 (dt, *J* = 3.7 and 7.1 Hz, 1 H), 2.2−2.1 (m, 3 H), 2.0−1.0 (m, 14 H), 1.0 (s, 3 H), 0.95−0.9 (m, 9 H), 0.92 (s, 3 H), 0.85 (s, 3 H). − GC-MS *m*/*z* (%) = 429 (2), 278 (13), 208 (5), 154 (16), 142 (32), 110 (31), 96 (15), 88 (35), 72 (100), 69 (22), 55 (18), 43 (23).

(4*R*,5*S*)-5-Benzamido-4-camphorselenenyloctane (8b): oil, $[\alpha]_D^{23}$ = +24.4 (*c* = 2.6, $CHCl_3$). − ^{1}H NMR: δ = 8.01 (d, *J* = 8.7 Hz, 1 H), 7.9−7.7 (m, 2 H), 7.5−7.25 (m, 3 H), 4.33 (ddt, *J* = 11.2, 8.7 and 2.4 Hz, 1 H), 3.52 (dd, *J* = 2.3 and 4.5 Hz, 1 H), 3.41 (ddd, *J* = 2.4, 5.9 and 8.9 Hz, 1 H), 2.14 (dd, *J* = 4.1 and 4.5 Hz, 1 H), 1.9−1.1 (m, 12 H), 1.26 (s, 3 H), 0.98 (t, *J* = 6.8 Hz, 6 H), 0.90 (s, 3 H), 0.8 (s, 3H). − ^{13}C NMR: δ = 221.4, 167.5, 134.4, 131.7, 127.9, 127.2, 58.6, 53.6, 52.8, 49.9, 49.5, 47.1, 36.9, 32.7, 30.8, 23.4, 22.1, 19.9, 19.6, 19.2, 14.6, 14.3, 10.0. − GC-MS: *m*/*z* (%) = 463 (1), 232 (15), 176 (29), 122 (11), 110 (19), 105 (100), 77 (18), 43 (3), 41 (5). − $C_{25}H_{37}NO_2Se$ (462.53): calcd. C 64.93, H 8.06, N 3.03; found C 65.33, H 8.90, N 2.98.

(4*S*,5*R*)-5-Benzamido-4-camphorselenenyloctane (9b): oil, $[\alpha]_D^{23}$ = +6.5 (*c* = 2.0, $CHCl_3$). − ^{1}H NMR: δ = 7.8−7.7 (m, 2 H), 7.5−7.3 (m, 3 H), 6.5 (d, *J* = 9.1 Hz, 1 H), 4.35−4.25 (m, 1 H), 3.72 (d, *J* = 4.5 Hz, 1 H), 3.35 (ddd, *J* = 3.6, 7.1 and 10.6 Hz, 1 H), 2.0 (t, *J*= 4.5 Hz, 1 H), 1.9−1.2 (m, 9 H), 1.25 (s, 3 H), 0.98 (t, *J* = 7.0 Hz, 6 H), 0.91 (s, 3 H), 0.89 (s, 3 H), 0.75 (s, 3 H). − ^{13}C NMR: δ = 217.8, 167.1, 134.9, 131.3, 129.0, 127.3, 58.5, 52.4, 50.9, 49.1, 49.0, 47.0, 37.1, 32.8, 30.8, 30.1, 23.7, 21.8, 19.9, 19.8, 14.4, 14.3, 10.1. − GC-MS: *m*/*z* (%) = 463 (1), 312 (7), 232 (20), 176 (32), 105 (100), 72 (20). − $C_{25}H_{37}NO_2Se$ (462.53): calcd. C 64.93, H 8.06, N 3.03; found C 64.31, H 8.20, N 3.40.

(5*R*,6*S*)-6-Acetamido-5-camphorselenenyldecane (4c): oil, $[\alpha]_D^{23}$ = −16.9 (*c* = 1, $CHCl_3$). − ^{1}H NMR: δ = 7.55 (d, *J* = 9.6 Hz, 1 H), 4.12 (ddt, *J* = 10.6, 9.6 and 2.5 Hz, 1 H), 3.49 (dd, *J* = 2.0 and 4.2 Hz, 1 H), 3.06 (ddd, *J* = 2.5, 4.9 and 9.2 Hz, 1 H), 2.27 (dd, *J* = 4.2 and 4.5 Hz, 1 H), 1.9 (s, 3 H), 1.8−1.2 (m, 16 H), 1.01 (s, 3 H), 0.94 (s, 3 H), 0.9 (t, *J* = 7.1 Hz, 6 H), 0.86 (s, 3 H). − ^{13}C NMR: δ = 221.5, 170.4, 58.8, 55.4, 52.8, 50.4, 50.1, 47.2, 34.9, 30.9, 30.8, 30.7, 30.1, 23.7, 23.4, 23.1, 22.8, 20.0, 19.6, 14.5, 14.4, 10.2. − GC-MS: *m*/*z* (%) = 429 (4), 278 (9), 219 (10), 198 (38), 156 (23), 152 (16), 138 (55), 128 (13), 109 (16), 95 (12), 86 (100), 83 (31), 69 (22), 60 (28), 55 (34), 43 (34), 41 (27). − $C_{22}H_{39}NO_2Se$ (428.51): calcd. C 61.67, H 9.17, N 3.27; found C 61.71, H 9.23, N 3.25.

(5*S*,6*R*)-6-Acetamido-5-camphorselenenyldecane (5c): oil, $[\alpha]_D^{23}$ = +16.7 (*c* = 0.5, $CHCl_3$). − ^{1}H NMR: δ = 5.78 (d, *J* = 9.0 Hz, 1 H), 4.1 (tt, *J* = 3.5 and 9.0 Hz, 1 H), 3.72 (dd, *J* = 1.5 and 4.5 Hz, 1 H), 3.18 (tt, *J* = 3.5 and 7.7 Hz, 1 H), 2.11 (m, 1 H), 1.97 (s, 3 H), 1.8−1.2 (m, 16 H), 1.0 (s, 3 H), 0.9 (s, 3 H), 0.89 (t, *J* = 7.0 Hz, 6 H), 0.88 (s, 3 H). − ^{13}C NMR: δ = 217.5, 169.7, 58.5, 52.3, 50.3, 49.2, 48.3, 47.1, 34.2, 30.8, 30.7, 30.6, 30.0, 28.8, 23.8, 23.7, 23.0, 22.9, 22.8, 20.0, 14.3, 10.0. − GC-MS: *m*/*z* (%) = 429 (1), 278 (11), 232 (10), 219 (13), 198 (76), 152 (19), 138 (39), 128 (81), 109 (20), 95 (26), 86 (100), 83 (38), 60 (46), 55 (58), 43 (60), 41 (49). − $C_{22}H_{39}NO_2Se$ (428.51): calcd. C 61.67, H 9.17, N 3.27; found C 61.66, H 9.21, N 3.33.

(2*S*)-2-Acetamido-2-phenyl-1-camphorselenenylethane (4d): oil, $[\alpha]_D^{19}$ = +24.4 (*c* = 0.1, $CHCl_3$). − ^{1}H NMR: δ = 7.85 (d, *J* = 8.3 Hz, 1 H), 7.4−7.2 (m, 5 H), 5.54 (ddd, *J* = 4.2, 4.5 and 8.3 Hz, 1 H), 3.5 (dd, *J* = 2.2 and 4.7 Hz, 1 H), 3.4 (dd, *J* = 4.2 and 13.3 Hz, 1 H), 3.17 (dd, *J* = 4.5 and 13.3 Hz, 1 H), 2.22 (dd, *J* = 4.3 and 4.7 Hz, 1 H), 2.1 (s, 3 H), 1.8−1.2 (m, 4 H), 1.02 (s, 3 H), 0.96 (s, 3 H), 0.87 (s, 3 H). − ^{13}C NMR: δ = 220.4, 169.7, 140.7, 128.3, 127.2, 126.5, 58.2, 51.7, 49.1, 48.8, 46.8, 34.0, 30.3, 23.2, 23.0, 19.6,

19.1, 9.6. − GC-MS: *m/z* (%) = 393 (4), 334 (29), 162 (31), 148 (40), 106 (100), 79 (10), 43 (14). − $C_{20}H_{27}NO_2Se$ (392.40): calcd. C 61.23, H 6.94, N 3.57; found C 61.10, H 7.01, N 3.65.
By reductive deselenenylation with triphenyltin hydride and AIBN in refluxing benzene for 3 h, this product afforded the (*R*)-(+)-acetamide **15** which was identical to an authentic sample.[18]

(2*R*)-2-Acetamido-2-phenyl-1-camphorselenenylethane (5d): oil, $[\alpha]_D^{23} = -30.0$ (*c* = 1.0, $CHCl_3$). − ^{1}H NMR: δ = 7.4−7.2 (m, 5 H), 6.83 (d, *J* = 7.1 Hz, 1 H), 5.16 (ddd, *J* = 5.8, 7.1 and 8.4 Hz, 1 H), 3.47 (dd, *J* = 1.9 and 4.6 Hz, 1 H), 3.31 (dd, *J* = 5.8 and 12.9 Hz, 1 H), 3.13 (dd, *J* = 8.4 and 12.9 Hz, 1 H), 2.11 (dd, *J* = 4.4 and 4.6 Hz, 1 H), 2.06 (s, 3 H), 1.8−1.2 (m, 4 H), 0.99 (s, 3 H), 0.93 (s, 3 H), 0.80 (s, 3 H). − ^{13}C NMR: δ = 219.3, 169.7, 141.4, 128.6, 127.5, 126.3, 58.2, 53.5, 48.3, 47.0, 46.8, 30.7, 30.5, 23.3, 23.2, 19.5, 19.3, 9.54. − GC-MS: *m/z* (%) = 393 (3), 334 (23), 182 (6), 162 (30), 148 (38), 123 (14), 120 (31), 106 (100), 91 (10), 43 (14). − $C_{20}H_{27}NO_2Se$ (392.40): calcd. C 61.23, H 6.94, N 3.57; found C 61.60, H 6.21, N 3.21.
By reductive deselenenylation with triphenyltin hydride and AIBN, in refluxing benzene for 3 h, this product afforded the (*S*)-(−)-acetamide **17** which was identical to an authentic sample.[19]

2-Acetamido-1-camphorselenenylcyclohexane (4e): oil, $[\alpha]_D^{19} = -7.21$ (*c* = 0.5, $CHCl_3$). − ^{1}H NMR: δ = 6.58 (d, *J* = 7.6 Hz, 1 H), 3.9 (dd, *J* = 1.5 and 4.5 Hz, 1 H), 3.69 (dddd, *J* = 4.1, 7.6, 10.1 and 12.0 Hz, 1 H), 3.05 (dt, *J* = 4.0 and 12.0 Hz, 1 H), 2.01 (dd, *J* = 4.3 and 4.5 Hz, 1 H), 1.9 (s, 3 H), 1.85−1.75 (m, 2 H), 1.7−1.5 (m, 4 H), 1.4−1.2 (m, 6 H), 1.0 (s, 3 H), 0.9 (s, 3 H), 0.88 (s, 3 H). − ^{13}C NMR: δ = 219.2, 170.0, 58.6, 54.6, 49.4, 47.4, 46.4, 46.1, 44.0, 34.4, 33.6, 30.0, 26.8, 24.8, 23.9, 20.1, 20.0, 10.1. − GC-MS: *m/z* (%) = 371 (13), 312 (60), 220 (32), 218 (17), 161 (24), 152 (21), 140 (84), 138 (22), 123 (37), 109 (23), 98 (100), 81 (72), 60 (77), 55 (28), 43 (45). − $C_{18}H_{29}NO_2Se$ (370.39): calcd. C 58.38, H 7.89, N 3.78; found C 57.56, H 7.22, N 4.11.

2-Acetamido-1-camphorselenenylcyclohexane (5e): oil, $[\alpha]_D^{19} = -12.3$ (*c* = 0.5, $CHCl_3$). − ^{1}H NMR: δ = 6.73 (d, *J* = 7.5 Hz, 1 H), 3.6 (ddt, *J* = 4.1, 7.5 and 11.5 Hz, 1 H), 3.57 (dd, *J* = 1.6 and 4.7 Hz, 1 H), 3.01 (dt, *J* = 3.8 and 11.5 Hz, 1 H), 2.35−2.27 (m, 2 H), 2.24 (dd, *J* = 4.4 and 4.7 Hz, 1 H), 1.96 (s, 3 H), 1.8−1.2 (m, 10 H), 1.0 (s, 3 H), 0.92 (s, 3 H), 0.91 (s, 3H). − ^{13}C NMR: δ = 221.3, 170.2, 58.8, 54.0, 49.3, 47.5, 46.7, 46.5, 36.7, 34.6, 30.7, 27.7, 25.0, 24.0, 23.6, 20.1, 19.7, 10.1. − GC-MS: *m/z* (%) = 371 (15), 312 (64), 310 (33), 220 (31), 218 (46), 161 (24), 159 (13), 152 (20), 151 (13), 140 (86), 123 (37), 109 (23), 98 (100), 81 (71), 60 (74), 43 (46). − $C_{18}H_{29}NO_2Se$ (370.39): calcd. C 58.38, H 7.89, N 3.78; found C 58.70, H 7.50, N 3.22.

2-Acetamido-1-camphorselenenylcycloctane (4f): oil, $[\alpha]_D^{17} = -38.06$ (*c* = 3.0, $CHCl_3$). − ^{1}H NMR: δ = 6.8 (d, *J* = 6.1 Hz, 1 H), 3.89 (dddd, *J* = 1.6, 6.1, 6.8 and 11.2 Hz, 1 H), 3.54 (dd, *J* = 1.5 and 4.6 Hz, 1 H), 3.42 (ddd, *J* = 2.3, 6.8 and 9.7 Hz, 1 H), 2.24 (dd, *J* = 4.2 and 4.6 Hz, 1 H), 1.95 (s, 3 H), 1.9−1.2 (m, 16 H), 1.01 (s, 3 H), 0.93 (s, 3 H), 0.92 (s, 3 H). − ^{13}C NMR: δ = 221.6, 169.8, 58.5, 54.5, 48.8, 47.5, 47.1, 46.2, 32.6, 32.0, 30.8, 26.4, 26.0, 25.9, 25.7, 23.8, 23.2, 19.7, 19.3, 9.7. − GC-MS: *m/z* (%) = 399 (3), 248 (23), 232 (11), 206 (12), 189 (18), 168 (26), 152 (12), 151 (11), 126 (56), 124 (24), 109 (100), 81 (20), 67 (35), 60 (35), 55 (24), 43 (32), 41 (18). − $C_{20}H_{33}NO_2Se$ (398.44): calcd. C 60.30, H 8.36, N 3.52; found C 60.50, H 8.66, N 3.63.

2-Acetamido-1-camphorselenenylcyclooctane (5f): oil, $[\alpha]_D^{17} = -17.1$ (*c* = 1.5, $CHCl_3$). − ^{1}H NMR: δ = 6.6 (d, *J* = 6.9 Hz, 1 H), 4.09 (dddd, *J* = 2.7, 6.9, 7.0 and 10.0 Hz, 1 H), 3.95 (dd, *J* = 1.5 and 4.7 Hz, 1 H), 3.4 (ddd, *J* = 2.5, 7.0 and 9.8 Hz, 1 H), 2.16 (t, *J* = 4.7 Hz, 1 H), 1.85 (s, 3 H), 2.0−1.4 (m, 16 H), 1.03 (s, 3 H), 0.94 (s, 3 H), 0.90 (s, 3 H). − ^{13}C NMR: δ = 219.9, 169.6, 58.8, 56.7, 49.2, 47.6, 45.8, 44.6, 32.1, 31.5, 30.7, 27.4, 26.6, 25.9, 25.5, 23.9, 23.6, 20.1, 20.0, 10.1. − GC-MS: *m/z* (%) = 399 (1), 248 (21), 232 (10), 206 (12), 189 (18), 168 (25), 152 (12), 126 (55), 109 (100), 93 (10), 83 (13), 79 (18), 67 (33), 60 (38), 55 (24), 43 (30). − $C_{20}H_{33}NO_2Se$ (398.44): calcd. C 60.30, H 8.36, N 3.52; found C 60.15, H 8.54, N 3.70.

Conversion of Acetamido Selenides 4a−f and 5a−f into Oxazolines 11a−f and 13a−f. Method A: A solution of PhSeOTf in anhydrous diethyl ether (10 mL) was prepared from PhSeBr (1.1 mmol) and AgOTf (1.1 mmol) under N_2 at 0 °C. After 15 minutes the acetamido selenides **4a−f** and **5a−f** (0.5 mmol) were added and the reaction mixtures were stirred for 7−8 h at room temperature. The progress of the reaction was monitored by TLC and GC-MS. The reaction mixture was poured in a 10% aqueous solution of sodium carbonate and extracted with diethyl ether. The organic layer was dried over sodium sulfate and evaporated. The reaction products were separated by medium pressure chromatography on a silica gel column (Merck, LiChroprep® Si60, 40−63 μm) with mixtures of diethyl ether and light petroleum as eluent. Camphor diselenide and phenyl diselenide were also isolated.
Method B: To a solution of the acetamido selenides **4a−f** and **5a−f** (0.5 mmol) in CH_2Cl_2 was added an excess of SO_2Cl_2 at room temperature. After 15 minutes the reaction mixtures were worked up as described above. The aqueous phase was acidified and stirred for 2 h. After the usual work up a quantitative amount of camphor diselenide **1** was obtained. Physical and spectral data of compounds **11a, 13a, 11b, 13b, 11e** and **13e** have already been reported in the literature as racemate.[16,21] Optical rotation values for the two enantiomers are reported in Table 2 together with those of all the other new compounds. Reaction yields are also reported in Table 2.

(4*S*,5*S*)-4,5-Dibutyl-4,5-dihydro-2-methyl-1,3-oxazole (11c): oil, $[\alpha]_D^{26} = -63.4$ (*c* = 2.6, $CHCl_3$). − ^{1}H NMR: δ = 4.02 (dt, *J* = 5.3 and 7.0 Hz, 1 H), 3.54 (qq, *J* = 1.3 and 7.0 Hz, 1 H), 1.94 (d, *J* = 1.3 Hz, 3 H), 1.5−1.2 (m, 12 H), 0.91 (t, *J* = 6.9 Hz, 3 H), 0.89 (t, *J* = 6.9 Hz, 3 H). − ^{13}C NMR: δ = 164.0, 85.5, 72.0, 36.2, 35.5, 28.3, 27.7, 23.1, 22.9, 14.6, 14.4, 14.3. − GC-MS: *m/z* (%) = 197 (3), 154 (9), 140 (100), 112 (19), 99 (14), 96 (15), 83 (30), 68 (44), 55 (15), 43 (41), 41 (15). − $C_{12}H_{23}NO$ (197.32): calcd. C 73.05, H 11.75, N 7.10; found C 72.95, H 11.90, N 7.05.
The reaction of (−)-**11c** with 25% hydrochloric acid at 50 °C for 4 h afforded the (5*S*,6*S*)-(−)-6-aminodecan-5-ol **(20)**.[21]

(4*R*,5*R*)-4,5-Dibutyl-4,5-dihydro-2-methyl-1,3-oxazole (13c): oil, $[\alpha]_D^{27} = +63.5$ (*c* = 2.5, $CHCl_3$). − $C_{12}H_{23}NO$ (197.32): calcd. C 73.05, H 11.75, N 7.10; found C 72.85; H 11.80, N 7.30.
Under conditions identical to those described above for **11c**, the hydrolysis of **13c** gave the (5*R*,6*R*)-(+)-6-aminodecan-5-ol **(21)**.[21]

(4*S*)-4,5-Dihydro-2-methyl-4-phenyl-1,3-oxazole (11d): oil, $[\alpha]_D^{23} = -16.2$ (*c* = 1.0, $CHCl_3$). − ^{1}H NMR: δ = 7.6−7.4 (m, 5 H), 5.2 (ddq, *J* = 8.3, 10.1 and 1.1 Hz, 1 H), 4.6 (dd, *J* = 8.3 and 10.1 Hz, 1 H), 4.09 (t, *J* = 8.3 Hz, 1 H), 2.01 (d, *J* = 1.1 Hz, 3 H). − ^{13}C NMR: δ = 165.9, 142.3, 128.7, 127.5, 126.5, 74.7, 69.6, 13.8. − GC-MS: *m/z* (%) = 161 (54), 130 (100), 119 (17), 104 (13), 91 (24), 90 (56), 51 (17). − C_9H_9NO (147.18): calcd. C 73.45, H 6.16, N 9.52; found C 73.25; H 6.26, N 9.62.

(4*R*)-4,5-Dihydro-2-methyl-4-phenyl-1,3-oxazole (13d) oil, $[\alpha]_D^{23} = +16.1$ (*c* = 1.0, $CHCl_3$). − C_9H_9NO (147.18): calcd. C 73.45, H 6.16, N 9.52; found C 73.50; H 6.11, N 9.60.
This compound was also obtained from the reaction of the commercially available (*R*)-(−)-2-amino-2-phenylethan-1-ol **(19)** with

ethyl acetimidate hydrochloride, according to the general procedure described in the literature.[20]

(+)-3a,4,5,6,7,8,9,9a-Octahydro-2-methylcycloocta[*d*][1,3]oxazole (11f): oil, $[\alpha]_D^{25} = +28.1$ ($c = 0.7$, $CHCl_3$). – ^1H NMR: δ = 4.15 (ddd, $J = 2.1$, 9.5 and 11.5 Hz, 1 H), 4.95–4.85 (m, 1 H), 1.92 (d, $J = 1.4$ Hz, 3 H), 2.0–1.6 (m, 8 H), 1.5–1.3 (m, 4 H). – ^{13}C NMR: δ = 162.9, 84.0, 68.8, 28.3, 27.4, 26.9, 26.6, 25.6, 25.3, 13.7. – GC-MS: *m*/*z* (%) = 167 (7), 152 (14), 138 (21), 124 (37), 108 (54), 96 (59), 83 (53), 68 (100), 60 (69), 55 (81), 42 (46). – $C_{10}H_{17}NO$ (167.25): calcd. C 71.81, H 10.24, N 8.37; found C 70.99, H 10.35, N 8.41. A strong NOE effect was observed between protons H_4 and H_5.

(–)-3a,4,5,6,7,8,9,9a-Octahydro-2-methylcycloocta[*d*][1,3]oxazole (13f): oil, $[\alpha]_D^{25} = -28.9$ ($c = 0.8$, $CHCl_3$). – $C_{10}H_{17}NO$ (167.25): calcd. C 71.81, H 10.24, N 8.37; found C 71.40, H 9.75, N 8.37.

Conversion of the *trans* Oxazolines (–)-11c and (+)-13c into the *cis* Oxazolines (–)-23c and (+)-25c: Compound **(–)-11c** or **(+)-13c** was stirred at room temperature for 12 hours with a 2% solution of HCl. The reaction mixture was extracted with Et_2O and the aqueous layer was treated with 10% $NaHCO_3$ solution. The mixture was extracted with CH_2Cl_2. The organic layer was washed with brine, dried and evaporated. The β-hydroxy acetamido derivatives **(5*S*,6*S*)-(–)-22c** and **(5*R*,6*R*)-(+)-24c** were obtained quantitatively in pure form after column chromatography on silica gel with a mixture of MeOH and CH_2Cl_2 (5%) as eluent.

(5*S*,6*S*)-6-Acetamido-5-hydroxydecane (22c): oil, $[\alpha]_D^{18} = -13.8$ ($c = 0.5$, $CHCl_3$). – ^1H NMR: δ = 5.55 (d, $J = 9.1$ Hz, 1 H), 3.82–3.75 (m, 1 H), 3.56 (ddd, $J = 2.5$, 5.4 and 7.3 Hz, 1 H), 1.9 (s, 3 H), 1.7 (s, 1 H), 1.5–1.2 (m, 12 H), 0.83 (t, $J = 7.0$ Hz, 3 H), 0.82 (t, $J = 7.0$ Hz, 3 H). – ^{13}C NMR: δ = 170.7, 73.6, 53.4, 34.6, 32.8, 28.8, 28.3, 23.8, 23.1, 23.0, 14.4, 14.3. – $C_{12}H_{25}NO_2$ (215.33): calcd. C 66.93, H 11.70, N 6.51; found C 67.05, H 11.66, N 6.34.

(5*R*,6*R*)-6-Acetamido-5-hydroxydecane (24c): oil, $[\alpha]_D^{19} = +13.5$ ($c = 0.4$, $CHCl_3$). – $C_{12}H_{25}NO_2$ (215.33): calcd. C 66.93, H 11.70, N 6.51; found C 66.50, H 11.68, N 6.90.

The β-hydroxy acetamido derivatives **(5*S*,6*S*)-(–)-22c** or **(5*R*,6*R*)-(+)-24c** were treated with $SOCl_2$ at room temperature for 1 hour. The excess of $SOCl_2$ was then removed under vacuum. The crude residue was dissolved in CH_2Cl_2 and washed with a 10% aqueous solution of $NaHCO_3$. The organic layer was dried and evaporated. The residue was chromatographed through a silica gel column with a mixture of diethyl ether and light petroleum (30–70) as eluent. The oxazolines **(4*S*,5*R*)-(–)-23c** and **(4*R*,5*S*)-(+)-25c** were obtained in 95% and 80% yield, respectively. Physical and spectral data are reported below. The *cis* relationship of the substituents in C_4 and C_5 was established on the basis of the strong NOE effect measured between H_4 and H_5.

(4*S*,5*R*)-4,5-Dibutyl-4,5-dihydro-2-methyl-1,3-oxazole (–)-23c: oil, $[\alpha]_D^{18} = -8.4$ ($c = 0.5$, $CHCl_3$). – ^1H NMR: δ = 4.45 (dt, $J = 3.4$ and 9.3 Hz, 1 H), 3.82 (dtq, $J = 4.3$, 9.3 and 1.4 Hz, 1 H), 1.95 (d, $J = 1.4$ Hz, 3 H), 1.6–1.2 (m, 12 H), 0.92 (t, $J = 6.9$ Hz, 3 H), 0.91 (t, $J = 6.9$ Hz, 3 H). – ^{13}C NMR: δ = 165.0, 83.9, 68.6, 31.0, 30.6, 30.4, 30.0, 29.8, 23.7, 23.1, 14.9, 14.8. – GC-MS: *m*/*z* (%) = 197 (5), 154 (23), 140 (100), 126 (12), 112 (32), 99 (27), 83 (52), 68 (70), 55 (19). – $C_{12}H_{23}NO$ (197.32): calcd. C 73.05, H 11.75, N 7.10; found C 73.25, H 11.26, N 7.62.

(4*R*,5*S*)-4,5-Dibutyl-4,5-dihydro-2-methyl-1,3-oxazole (+)-25c: oil, $[\alpha]_D^{21} = +8.3$ ($c = 0.5$, $CHCl_3$). – $C_{12}H_{23}NO$ (197.32): calcd. C 73.05, H 11.75, N 7.10; found C 73.61, H 11.54, N 7.33.

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