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A sulfur-containing diselenide as an efficient chiral reagent in asymmetric selenocyclization reactions

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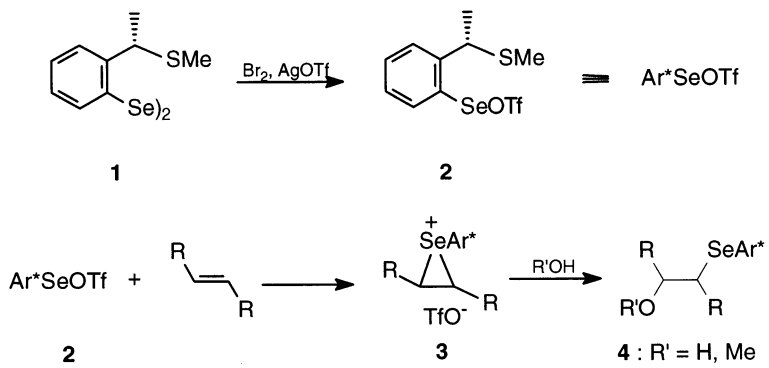
Abstract—Treatment of the di-2-[(1*S*)-1-(methylthio)ethyl]phenyl diselenide with bromine and silver triflate afforded the corresponding selenyl triflate which was used in situ as a strongly electrophilic selenium reagent to effect the asymmetric synthesis of oxygen- or nitrogen-containing heterocycles. Cyclic ethers, lactones, lactams or *N*-protected pyrrolidines have been prepared in good yield with complete regioselectivity and high diastereoselectivity.

1. Introduction

In recent years the introduction of a large number of chiral non-racemic diselenides[1–3] has greatly renewed interest in organoselenium chemistry. Optically active diselenides could in fact be easily converted into electrophilic reagents which were successfully employed to effect efficient asymmetric addition reactions to alkenes. On the basis of much experimental evidence it has been proposed[3–5] that the high stereoselectivity observed with these reagents is due to a non-bonded interaction, which occurs between the selenium atom and an oxygen or nitrogen atom positioned in close proximity. Such an interaction forces the stereogenic center to approach the reaction center during the addition, thus improving the chirality transfer. In an attempt to make this interaction more efficient and hence to increase the diastereoselectivity of the asymmetric addition reactions, we have recently introduced the new diselenide **1**[6] where sulfur takes the place of the oxygen or nitrogen atom (Scheme 1). Treatment of **1** with bromine and silver triflate afforded the corresponding selenyl triflate **2**, which was employed to effect very efficient asymmetric selenomethoxylations and selenohydroxylations of alkenes.[6] The addition of **2** to an alkene gives rise to a mixture of two diastereomeric seleniranium intermediates **3** which are trapped by the nucleophile to afford a mixture of the two enantiomerically pure diastereomeric addition products **4**. The reaction is a stereospecific *anti* addition and the alkoxy- and hydroxy-



Scheme 1.

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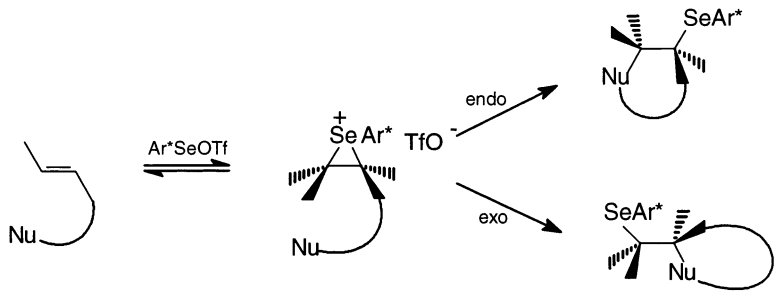
selenides **4** (Scheme 1) are formed in high chemical yields and in diastereomeric ratios which are considerably higher than those observed starting from the corresponding oxygen- and nitrogen-containing diselenides.[1–3]

We report herein that the electrophilic reagent **2** can also be employed with similarly good results to promote the ring closure reactions of alkenes bearing a suitably positioned oxygen- or nitrogen-containing nucleophilic group, according to the general reaction sequence indicated in Scheme 2. This represents a convenient method to produce enantiomerically enriched heterocyclic compounds. Cyclic ethers, lactones, lactams and *N*-protected pyrrolidines can be prepared in good chemical yield, with complete regioselectivity and high diastereoselectivity. As indicated in Scheme 2, depending on the relative positions of the double bond and the nucleophilic group, the reaction products can be the result of an *exo* or an *endo* cyclization reaction.

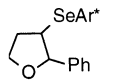
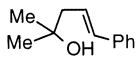
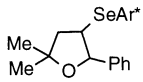
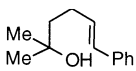
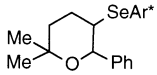
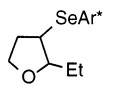
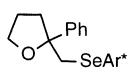
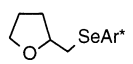
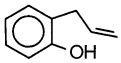
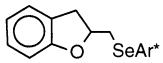
2. Results and discussion

The first experiments were performed starting from the alkenols **5a–g**, which by cyclization afforded the cyclic selenoethers **6a–g**. The selenylating agent **2** was prepared by treating a solution of the diselenide **1** in dichloromethane at −78°C with bromine and then with silver triflate. After 20 min the alkenol was added and the mixture was stirred for 2 h. The reaction temperature was allowed to increase gradually while the progress of the reaction was monitored by TLC and/or



Scheme 2.

Table 1. Cyclization of alkenols **5a–g** promoted by Ar*SeOTf **2** in CH_2Cl_2 at −78°C

Entry	Starting materials		Selenoether products[a]		Time (h.)	Yields (%)	d.r.[b]
a		**5a**		**6a**	5	89	**93:7**
b		**5b**		**6b**	6	88	**93:7**
c		**5c**		**6c**	4	79	**94:6**
d		**5d**		**6d**	3	56	**4:1**
e		**5e**		**6e**	3	73	**92:8**
f		**5f**		**6f**	4	89	**3:1**
g		**5g**		**6g**	4	60	**7:3**

[a] The two diastereoisomers could not be separated.

[b] Diastereomeric ratios were determined by proton NMR.

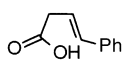
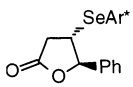
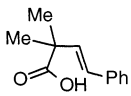
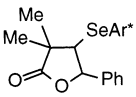
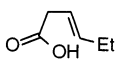
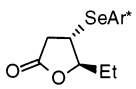
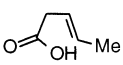
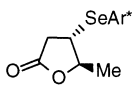
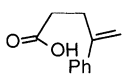
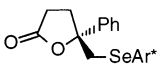
GC–MS. After the usual work-up the crude reaction mixture was examined by proton NMR to determine the diastereomeric ratio. The pure products were obtained after silica gel column chromatography. The diastereomeric ratios measured on the purified products were identical to those observed in the crude mixtures. Reaction times, chemical yields and diastereomeric ratios are reported in Table 1. The cyclizations of the alkenoic acids **7a–e** into the selenolactones **8a–e** were carried out in a very similar way. The only differences were that the selenylating agent **2** was prepared in tetrahydrofuran at −50°C. The alkenoic acids were then added at this temperature. The results of these experiments are collected in Table 2.

Complete regioselectivity and high chemical yields were observed in both types of cyclization reaction. In no case could the two diastereoisomeric selenoethers or selenolactones be separated. Good diastereoselectivities were observed in almost every case. Preliminary experiments indicated that a low initial temperature was necessary to obtain good diastereoselectivities. In the case of the selenoetherification reaction, the 1,1- or 1,2-disubstituted alkenes gave better diastereomeric ratios than the monosubstituted alkenes, particularly if a phenyl group was present.

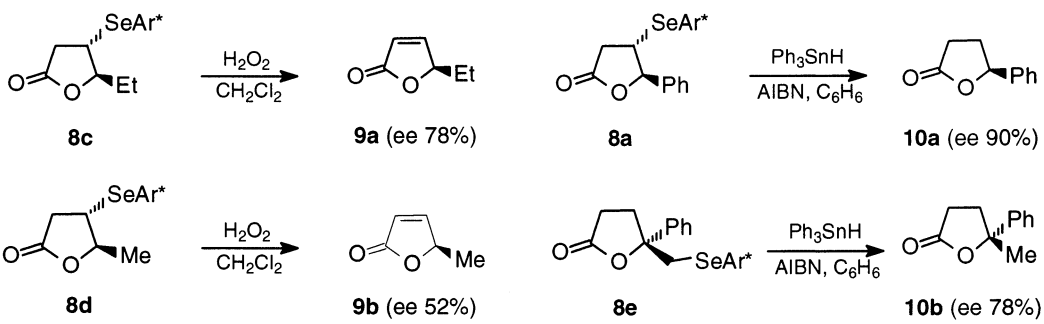
The results confirm the efficiency of the sulfur-containing selenylating agent **2**. The diastereomeric ratios obtained are in fact generally better than those observed with the selenylating agents containing an oxygen or a nitrogen moiety.[1–3] As it has been already pointed out[7] the cyclizations of α,α-disubstituted alkenes, like **5e** and **7e**, are interesting since they give rise to the formation of quaternary stereogenic carbon atoms which are not readily accessible by other methods.

In Table 2 the absolute configurations of the major isomers of the selenolactones **8a**, **8c**, **8d**, **8e** are indicated. These were determined after conversion into the known butenolides **9a** and **9b** or γ-lactones **10a** and **10b** by *syn* elimination of the corresponding selenoxides or by reduction with Ph_3SnH in the presence of catalytic amounts of AIBN, respectively (Scheme 3). The enantiomeric

Table 2. Cyclization of alkenoic acids **7a–e** promoted by Ar*SeOTf **2** in THF at −50°C

Entry	Starting materials		Selenolactone products[a]		Time (h.)	Yields (%)	d.r.[b]
a		**7a**		**8a**	48[c]	75	**19:1**
b		**7b**		**8b**	22	67	**76:24**
c		**7c**		**8c**	6[c]	75	**89:11**
d		**7d**		**8d**	24	87	**76:24**
e		**7e**		**8e**	4	95	**89:11**

[a] The two diastereoisomers could not be separated.
[b] Diastereomeric ratios were determined by proton NMR.
[c] The reaction was carried out in CH_2Cl_2 at −78 °C.



Scheme 3.

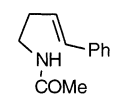
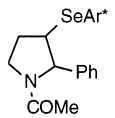
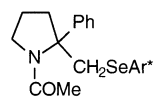
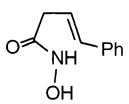
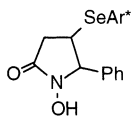
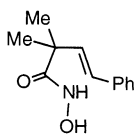
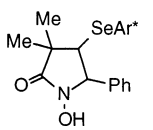
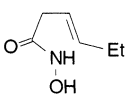
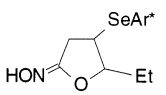
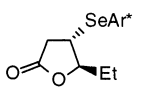
excesses were determined by proton NMR in the presence of a chiral shift reagent and/or by GC–MS using a chiral column and were, as expected, identical to the diastereomeric excesses of the starting products.

We then turned our attention to the selenocyclization reactions leading to nitrogen-containing heterocyclic compounds. These kinds of reaction have recently found wider application[2] since they allow the production of a wide variety of structures starting from alkenes containing internal nitrogen nucleophiles. Despite the numerous examples of cyclization reactions reported in the literature only few asymmetric syntheses of nitrogen-containing heterocyclic compounds from chiral diselenides have been described.[7–11] It therefore seemed of some interest to test the efficiency of the electrophilic reagent **2** to promote such cyclization reactions. We report here the results obtained starting from *N*-alkenyl acetamides **11a** and **11b** or from β,γ-unsaturated hydroxamic acids **13a–c**. Under the reaction conditions described above **11a** and **11b** afforded the *N*-acetyl pyrrolidines **12a** and **12b**, respectively, with good diastereomeric ratios (Table 3).

Interesting results were obtained in the cyclization reactions of the β,γ-unsaturated hydroxamic acids. The results of these experiments are shown in Scheme 4 and collected in Table 3. The γ-phenyl hydroxamic acid **13a** gave the *N*-hydroxy-γ-lactam **15a**, whereas the γ-ethyl hydroxamic acid **13c** afforded the cyclic *N*-hydroxy imidate **16**. During work-up this compound was partially transformed into the corresponding lactone **8c**. Compound **13b**, like **13a**, gave the corresponding *N*-hydroxy-γ-lactam **15b**.

The difference in behavior observed between the phenyl and the ethyl substituted derivatives is due to the bidentate nature of the nucleophilic group of the hydroxamic acids, such that the intramolecular capture of the seleniranium ions **14** can be effected either by the oxygen or by the nitrogen atom. In a previous work,[12] using phenylselenyl sulfate as the electrophilic reagent, we observed that the reaction products can originate under kinetic or thermodynamic control of the reaction. The trapping of the seleniranium intermediate by the oxygen atom, leading to the imidate product, is faster than trapping by nitrogen (which leads to lactam products). However, under the conditions employed, the formation of the cyclic *N*-hydroximidate is reversible and under appropriate reaction conditions *N*-hydroxy-γ-lactams can be separated as the sole reaction prod-

Table 3. Cyclization of *N*-alkenyl acetamides **11a** and **11b** and of β,γ-unsaturated hydroxamic acids **13a–c**

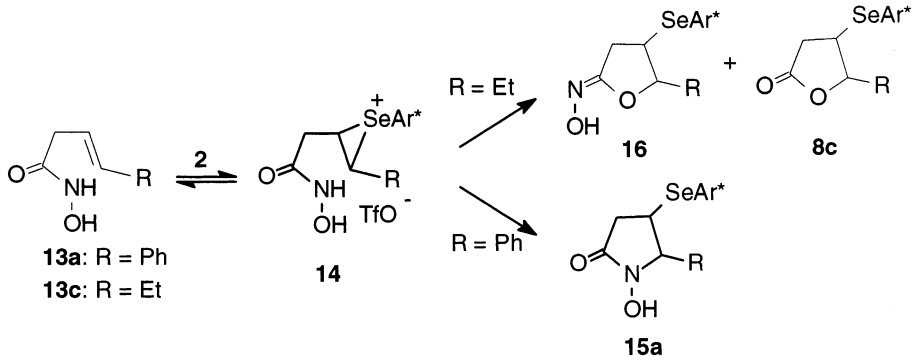
Entry	Starting materials		*N*-heterocycle products[a]		Time (h.)	Yields (%)	d.r.[b]
a		**11a**		**12a**	5[c]	70	**94:6**
b		**11b**		**12b**	3[c]	40	**9:1**
c		**13a**		**15a**	72[d]	70	**91:9**
d		**13b**		**15b**	60[d]	73	**88:12**
c		**13c**		**16**	6[d]	57	**81:19**
				**8c**		25	**81:19**

[a] The two diastereoisomers could not be separated.

[b] Diastereomeric ratios were determined by proton NMR.

[c] The reactions were carried out with Ar*SeOTf **2** in CH_2Cl_2 at –78 °C.

[d] The reactions were carried out with Ar*SeOTf **2** in THF at –50 °C.



Scheme 4.

ucts. It was also observed that the reactions of the γ-phenyl hydroxamic acids are faster than those of γ-alkyl hydroxamic acids. In contrast, under the present reaction conditions, using the electrophilic reagent **2**, the formation of the imidate **16**, deriving from the γ-ethyl hydroxamic acid **13c**, is not reversible. Any attempt to convert **16** into the corresponding lactam, by using longer reaction times or higher temperature, even in the presence of acid, were in fact unsuccessful.

The results of the selenium mediated cyclization reactions reported in this paper confirm that the chiral sulfur-containing diselenide **1** is particularly efficient in promoting asymmetric electrophilic functionalizations. The diastereoselectivities observed are comparable or better than those obtained with the most efficient but less available diselenides which have been described so far in the literature.[7–11,13–15] The asymmetric synthesis of other nitrogen-containing heterocycles promoted by the diselenide **1** is currently under investigation.

3. Experimental

New compounds were characterized by MS, ^{1}H and ^{13}C NMR spectroscopy. GLC analyses and MS spectra were carried out with an HP 6890 gas chromatograph (25 m dimethyl silicone capillary column or 25 m Chirasil-DEX column) equipped with an HP 5973 mass selective detector; for the ions containing selenium only the peaks arising from the selenium-80 isotope are given. ^{1}H and ^{13}C NMR spectra were recorded at 400 and 100.62 MHz, respectively, on a Bruker DRX 400 instrument; unless otherwise specified, $CDCl_3$ was used as solvent and TMS as standard. Optical rotations were measured with a Jasco DIP-1000 digital polarimeter. Elemental analyses were carried out on a Carlo Erba 1106 elemental analyzer.

Compounds **5d**, **5f**, **5g**, **7a**, **7c** and **7d** were commercially available. Alkenols **5a** and **5e**,[7] alkenoic acids **7b**[16] and **7e**[7], alkenamides **11a** and **11b**[7] and hydroxamic acids **13a**–**c**[12] were synthesized according to the procedures reported in the literature.

Compounds **5b** and **5c** were prepared treating the commercially available methyl (3*E*)-4-phenyl-3-butenoate and the 6-phenyl-(5*E*)-hexen-2-one,[17] respectively, with a 3 M solution of MeMgBr in diethyl ether.[18]

Physical and spectral data of **5a**, **5e**, **7b**, **7e** and **11b** are identical to those reported in the literature. Physical and spectral data of all new compounds are reported below. In the cases of hydroxamic acids the NH and OH protons gave exchange with the solvent and were not observed.

3.1. (4*E*)-2-Methyl-5-phenylpent-4-en-2-ol 5b

Oil; ^{1}H NMR: δ 7.5–7.45 (m, 2H), 7.45–7.35 (m, 2H), 7.35–7.2 (m, 1H), 6.50 (dt, 1H, $J=1.2$, 15.8 Hz), 6.34 (dt, 1H, $J=7.5$, 15.8 Hz), 2.42 (dd, 2H, $J=1.2$, 7.5 Hz), 1.8 (br s, 1H), 1.3 (s, 6H); ^{13}C NMR: δ 137.9, 133.9, 129.0 (two carbons), 127.7, 126.6 (two carbons), 126.5, 71.4, 47.9, 29.7 (two carbons). Anal. calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.75; H, 9.18%.

3.2. (5*E*)-2-Methyl-6-phenylhex-5-en-2-ol 5c

Oil; ^{1}H NMR: δ 7.5–7.2 (m, 5H), 6.5 (d, 1H, $J=15.8$ Hz), 6.31 (dt, 1H, $J=6.9$, 15.8 Hz), 2.5–2.3 (m, 2H), 2.0 (br s, 1H), 1.8–1.7 (m, 2H), 1.38 (s, 6H); MS *m*/*z* (rel. int.): 190 (2), 172 (47), 157 (53), 143 (16), 129 (100), 117 (65), 115 (40), 104 (8), 91 (32), 77 (7), 65 (4), 59 (31), 51 (4). Anal. calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 82.26; H, 9.47%.

3.3. *N*-[(3*E*)-4-Phenylbut-3-enyl]acetamide 11a

Oil; ^{1}H NMR: δ 7.4–7.1 (m, 5H), 6.44 (dt, 1H, $J=1.3$, 15.9 Hz), 6.12 (dt, 1H, $J=7.0$, 15.9 Hz), 5.7 (d, 1H, $J=7.0$ Hz), 3.37 (q, 2H, $J=7.0$ Hz), 2.4 (dq, 2H, $J=1.3$, 7.0 Hz), 1.94 (s, 3H); MS *m*/*z* (rel. int.): 189 (5), 130 (100), 115 (36), 91 (10), 72 (7), 65 (2), 51 (2). Anal. calcd for $C_{12}H_{15}NO$: C, 76.16; H, 7.99, N, 7.40. Found: C, 76.23; H, 8.01, N, 7.26%.

3.4. (3*E*)-4-Phenyl-3-butenoic hydroxamic acid 13a

Mp 135–137°C; ^{1}H NMR (CD_3OD): δ 7.4–7.13 (m, 5H), 6.52 (d, 1H, $J=15.8$ Hz), 6.24 (dt, 1H, $J=6.9$, 15.8 Hz), 3.07 (d, 2H, $J=6.9$ Hz); ^{13}C NMR: δ 168.9, 136.5, 133.5, 128.1 (two carbons), 127.1, 125.8 (two carbons), 121.5, 36.7. Anal. calcd for $C_{10}H_{11}NO_2$: C, 67.78; H, 6.26; N, 7.9. Found: C, 67.58; H, 6.12; N, 7.7%.

3.5. (3*E*)-2,2-Dimethyl-4-phenyl-3-butenoic hydroxamic acid 13b

Mp 141–143°C; ^{1}H NMR (CD_3OD): δ 7.42–7.16 (m, 5H), 6.52 (d, 1H, $J=16.3$ Hz), 6.31 (d, 1H, $J=16.3$ Hz), 1.42 (s, 6H); ^{13}C NMR: δ 174.2, 136.2, 132.9, 129.4, 128.4 (two carbons), 127.5, 126.1 (two carbons), 43.1, 24.7 (two carbons). Anal. calcd for $C_{12}H_{15}NO_2$: C, 70.22; H, 7.37; N, 6.82. Found: C, 70.45; H, 7.32; N, 6.89%.

3.6. (3*E*)-3-Hexenoic hydroxamic acid 13c

Mp 75–77°C; ^{1}H NMR (CD_3OD): δ 5.75–5.38 (m, 2H), 2.88 (d, 2H, $J=7.0$ Hz), 1.98 (quint., 2H, $J=7.1$ Hz), 0.9 (t, 3H, $J=7.3$ Hz); ^{13}C NMR: δ 169.7, 137.3, 120.3, 36.8, 25.3, 13.1. Anal. calcd for $C_6H_{11}NO_2$: C, 55.80; H, 8.58; N, 10.84. Found: C, 55.50; H, 8.45; N, 10.67%.

3.7. General procedure for selenocyclization reactions

Ar*SeOTf **2** was prepared at −78°C in dichloromethane or at −50°C in tetrahydrofuran (see Tables 1–3) as indicated below. The diselenide **1** (0.6 mmol), dissolved in dichloromethane or in tetrahydrofuran (3 mL), was treated under nitrogen with a 1 M solution of Br_2 in carbon tetrachloride (0.6 mmol). After 15 min silver trifluoromethanesulfonate (1.3 mmol) was added and the mixture was stirred for 20 min. The alkene (1 mmol) was added and the mixture was stirred for 2 h at the indicated temperature. The reaction temperature was allowed to increase gradually while the progress of the reaction was monitored by TLC and/or GC–MS. Reaction times are reported in Tables 1–3. The reaction mixture was poured into an aqueous solution of 10% $NaHCO_3$ and extracted with dichloromethane. The organic layer was dried over Na_2SO_4, filtered and evaporated. Reaction products were obtained in a pure form after column chromatography of the residue on silica gel. Reaction yields and diastereomeric ratios are reported in Tables 1–3. Physical and spectral data of the reaction products are described below.

3.8. 3-({2-[(1*S*)-1-(Methylthio)ethyl]phenyl}seleno)-2-phenyltetrahydrofuran 6a

Oil; Major diastereoisomer: ^{1}H NMR: δ 7.48 (dd, 1H, $J=1.4$, 7.7 Hz), 7.46 (dd, 1H, $J=1.4$, 7.7 Hz), 7.32–7.22 (m, 6H), 7.06 (dt, 1H, $J=1.4$, 7.7 Hz), 4.86 (d, 1H, $J=6.0$ Hz), 4.56 (q, 1H, $J=7.0$ Hz), 4.18 (ddd, 1H, $J=5.2$, 7.7, 15.6 Hz), 4.12 (dt, 1H, $J=7.2$, 15.6 Hz), 3.58 (ddd, 1H, $J=5.2$, 6.0, 7.7 Hz), 2.50 (ddt, 1H, $J=7.2$, 7.7, 13.0 Hz), 2.13 (ddt, 1H, $J=5.2$, 7.2, 13.0 Hz), 1.93 (s, 3H), 1.51 (d, 3H, $J=7.0$ Hz); ^{13}C NMR: δ 145.7, 141.2, 135.2, 130.3 (three carbons), 128.2, 127.6, 127.3, 127.0, 125.8 (two carbons), 86.2, 67.9, 48.3, 43.9, 34.0, 21.4, 14.0; MS m/z (rel. int.): 378 (1), 231 (43), 183 (91), 147 (100), 115 (14), 105 (40), 104 (12), 103 (11), 102 (10), 91 (39), 77 (24). Anal. calcd for $C_{19}H_{22}OSSe$: C, 60.48; H, 5.88. Found: C, 60.56; H, 5.99%.

Minor diastereoisomer (distinct signals): ^{1}H NMR: δ 4.10 (dt, 1H, $J=7.2$, 15.6 Hz), 3.63 (ddd, 1H, $J=5.2$, 6.0, 7.7 Hz), 1.89 (s, 3H), 1.52 (d, 3H, $J=7.02$ Hz); ^{13}C NMR: δ 20.4, 13.7.

3.9. 2,2-Dimethyl-4-({2-[(1*S*)-1-(methylthio)ethyl]-phenyl}seleno)-5-phenyltetrahydrofuran 6b

Oil; Major diastereoisomer: ^{1}H NMR: δ 7.32–7.22 (m, 3H), 7.19–7.06 (m, 5H), 6.85 (dt, 1H, $J=1.5$, 7.6 Hz), 4.76 (d, 1H, $J=9.5$ Hz), 4.38 (q, 1H, $J=7.0$ Hz), 3.43 (ddd, 1H, $J=8.0$, 9.5, 10.0 Hz), 2.33 (dd, 1H, $J=8.0$, 12.8 Hz), 2.0 (dd, 1H, $J=10.0$, 12.8 Hz), 1.82 (s, 3H), 1.31 (d, 3H, $J=7.0$ Hz), 1.10 (s, 6H); ^{13}C NMR: δ 145.5, 139.9, 138.1, 130.0, 128.3 (two carbons), 128.1, 127.8, 127.1, 126.8, 126.6 (two carbons), 86.1, 80.5, 48.7, 47.9, 43.9, 29.3, 28.7, 21.4, 14.0; MS m/z (rel. int.): 406 (1), 231 (24), 183 (58), 175 (68), 174 (100), 115 (13), 105 (36), 91 (19), 77 (13). Anal. calcd for $C_{21}H_{26}OSSe$: C, 62.22; H, 6.46. Found: C, 62.09; H, 6.59%.

Minor diastereoisomer (distinct signals): ^{1}H NMR: δ 6.86 (dt, 1H, $J=1.5$, 7.6 Hz), 4.79 (d, 1H, $J=9.5$ Hz), 4.40 (q, 1H, $J=7.0$ Hz), 3.51 (ddd, 1H, $J=8.0$, 9.5, 10.0 Hz), 2.27 (dd, 1H, $J=8.0$, 12.8 Hz), 2.01 (dd, 3H, $J=9.5$, 12.4 Hz), 1.75 (s, 3H), 1.40 (d, 3H, $J=7.0$ Hz), 1.29 (s, 3H); ^{13}C NMR: δ 140.2, 85.6, 48.5, 48.3, 44.1, 21.5.

3.10. 2,2-Dimethyl-5-({2-[(1*S*)-1-(methylthio)ethyl]-phenyl}seleno)-6-phenyltetrahydro-2*H*-pyran 6c

Oil; Major diastereoisomer: ^{1}H NMR: δ 7.29–7.25 (m, 3H), 7.24 (dd, 1H, $J=1.3$, 7.7 Hz), 7.19–7.10 (m, 4H), 6.91 (dt, 1H, $J=1.6$, 7.5 Hz), 4.54 (d, 1H, $J=10.8$ Hz), 4.23 (q, 1H, $J=7.0$ Hz), 3.17 (ddd, 1H, $J=4.4$, 10.8, 12.4 Hz), 2.02 (ddt, 1H, $J=3.2$, 4.4, 13.6 Hz), 1.91 (ddt, 1H, $J=4.4$, 12.4, 13.6 Hz), 1.81 (s, 3H), 1.63 (ddd, 1H, $J=4.4$, 12.4, 13.4 Hz), 1.55 (ddd, 1H, $J=3.2$, 4.4, 13.4 Hz), 1.36 (d, 3H, $J=7.0$ Hz), 1.3 (s, 3H), 1.2 (s, 3H); ^{13}C NMR: δ 146.1, 140.8, 136.3, 129.9, 128.1, 128.0 (three carbons), 127.7 (two carbons), 126.8, 126.6, 78.4, 72.5, 47.9, 43.8, 38.1, 31.5, 29.2, 21.7, 21.5, 14.0; MS m/z (rel. int.): 420 (8), 231 (90), 183 (100), 171 (9), 129 (13), 115 (11), 105 (20), 91 (69), 81 (11), 77 (15), 69 (12). Anal. calcd for $C_{22}H_{28}OSSe$: C, 63.00; H, 6.73. Found: C, 63.26; H, 6.85%.

Minor diastereoisomer (distinct signals): ^{1}H NMR: δ 6.97 (dt, 1H, $J=1.6$, 7.5 Hz), 4.47 (q, 1H, $J=7.0$ Hz), 3.23 (dt, 1H, $J=5.4$, 10.7 Hz), 1.82 (s, 3H), 1.45 (d, 3H, $J=7.0$ Hz); ^{13}C NMR: δ 147.0, 141.0, 136.7, 77.6, 72.6, 47.2, 44.2, 14.2.

3.11. 2-Ethyl-3-({2-[(1*S*)-1-(methylthio)ethyl]phenyl}-seleno)tetrahydrofuran 6d

Oil; Major diastereoisomer: ^{1}H NMR: δ 7.51 (dd, 1H, $J=1.3$, 7.8 Hz), 7.44 (dd, 1H, $J=1.4$, 7.8 Hz), 7.22 (dt, 1H, $J=1.4$, 7.8 Hz), 7.06 (dt, 1H, $J=1.3$, 7.8 Hz), 4.52 (q, 1H, $J=7.0$ Hz), 3.86–3.74 (m, 2H), 3.66 (ddd, 1H, $J=4.5$, 6.2, 7.2 Hz), 3.34 (dt, 1H, $J=6.2$, 8.1 Hz), 2.36–2.25 (m, 1H), 1.98–1.90 (m, 1H), 1.81 (s, 3H), 1.52–1.3 (m, 2H), 1.49 (d, 3H, $J=7.0$ Hz), 0.84 (t, 3H,

$J=7.4$ Hz); ^{13}C NMR: δ 145.6, 134.9, 130.4, 128.1, 127.2, 127.0, 86.0, 66.6, 44.3, 43.9, 34.3, 27.2, 21.6, 14.0, 10.1; MS m/z (rel. int.): 330 (5), 231 (68), 183 (100), 135 (3), 104 (10), 99 (9), 91 (8), 77 (7), 57 (9). Anal. calcd for $C_{15}H_{22}OSSe$: C, 54.71; H, 6.73. Found: C, 54.89; H, 6.75%.

Minor diastereoisomer (distinct signals): ^{1}H NMR: δ 7.45 (dd, 1H, $J=1.5$, 7.8 Hz), 3.36 (dt, 1H, $J=6.2$, 8.1 Hz), 1.88 (s, 3H), 1.48 (d, 3H, $J=7.0$ Hz), 0.88 (t, 3H, $J=7.4$ Hz); ^{13}C NMR: δ 135.0, 130.2, 128.2, 85.6, 44.0, 34.5, 27.3, 21.7, 14.1, 10.2.

3.12. 2-[({2-[(1*S*)-1-(Methylthio)ethyl]phenyl}seleno)-methyl]-2-phenyltetrahydrofuran 6e

Oil; Major diastereoisomer: ^{1}H NMR: δ 7.50–7.44 (m, 4H), 7.37–7.32 (m, 2H), 7.29–7.21 (m, 2H), 7.09 (dt, 1H, $J=1.4$, 7.8 Hz), 4.59 (q, 1H, $J=7.0$ Hz), 4.07 (q, 1H, $J=7.6$ Hz), 3.94 (dt, 1H, $J=5.7$, 7.8 Hz), 3.46 (d, 1H, $J=11.8$ Hz), 3.35 (d, 1H, $J=11.8$ Hz), 2.42 (dt, 1H, $J=8.2$, 12.8 Hz), 2.30 (ddd, 1H, $J=5.1$, 7.8, 12.8 Hz), 2.11–2.01 (m, 1H), 1.91 (s, 3H), 1.91–1.8 (m, 1H), 1.56 (d, 3H, $J=7.0$ Hz); ^{13}C NMR: δ 146.2, 145.4, 134.0, 132.8, 128.6 (two carbons), 127.8, 127.7, 127.4, 127.2, 125.6 (two carbons), 86.5, 68.7, 44.3, 42.7, 38.1, 26.4, 22.2, 14.6; MS m/z (rel. int.): 392 (9), 231 (8), 183 (20), 147 (100), 105 (23), 91 (19), 77 (10). Anal. calcd for $C_{20}H_{24}OSSe$: C, 61.38; H, 6.18. Found: C, 61.46; H, 6.36%.

Minor diastereoisomer (distinct signals): ^{1}H NMR: δ 4.54 (q, 1H, $J=7.0$ Hz), 4.08 (q, 1H, $J=7.6$ Hz), 3.95 (dt, 1H, $J=5.7$, 7.8 Hz), 2.43 (dt, 1H, $J=8.2$, 12.8 Hz), 1.95 (s, 3H), 1.52 (d, 3H, $J=7.0$ Hz); ^{13}C NMR: δ 134.3, 132.7, 128.5, 127.9, 127.3, 127.1, 42.9, 38.2, 22.1.

3.13. 2-[({2-[(1*S*)-1-(Methylthio)ethyl]phenyl}seleno)-methyl]tetrahydrofuran 6f

Oil; Major diastereoisomer: ^{1}H NMR: δ 7.46 (dd, 1H, $J=1.3$, 7.8 Hz), 7.4 (dd, 1H, $J=1.5$, 7.8 Hz), 7.16 (dt, 1H, $J=1.3$, 7.8 Hz), 7.03 (dt, 1H, $J=1.5$, 7.8 Hz), 4.5 (q, 1H, $J=7.0$ Hz), 3.98 (quint., 1H, $J=6.7$ Hz), 3.81 (dt, 1H, $J=6.9$, 8.0 Hz), 3.66 (dt, 1H, $J=6.4$, 8.0 Hz), 2.99 (dd, 1H, $J=5.9$, 11.9 Hz), 2.88 (dd, 1H, $J=6.7$, 11.9 Hz), 2.05–1.9 (m, 1H), 1.9–1.78 (m, 2H), 1.86 (s, 3H), 1.6–1.5 (m, 1H), 1.48 (d, 3H, $J=7.0$ Hz); ^{13}C NMR: δ 144.9, 133.2, 131.1, 127.4, 127.3, 126.9, 78.1, 68.2, 43.8, 33.5, 31.5, 25.8, 21.6, 14.1; MS m/z (rel. int.): 316 (22), 231 (59), 183 (100), 157 (3), 135 (3), 116 (3), 115 (3), 104 (11), 103 (11), 102 (12), 91 (11), 77 (8), 61 (4). Anal. calcd for $C_{14}H_{20}OSSe$: C, 53.34; H, 6.39. Found: C, 53.55; H, 6.18%.

Minor diastereoisomer (distinct signals): ^{1}H NMR: δ 4.49 (q, 1H, $J=7.0$ Hz), 3.97 (quint., 1H, $J=6.5$ Hz), 3.01 (dd, 1H, $J=5.8$, 11.8 Hz), 2.86 (dd, 1H, $J=6.8$, 11.8 Hz); ^{13}C NMR: δ 144.8, 133.1, 78.0, 33.4.

3.14. 2-[({2-[(1*S*)-1-(Methylthio)ethyl]phenyl}seleno)-methyl]-2,3-dihydro-1-benzofuran 6g

Oil; Major diastereoisomer: ^{1}H NMR: δ 7.53 (dd, 1H, $J=1.5$, 7.7 Hz), 7.45 (dd, 1H, $J=1.5$, 7.7 Hz), 7.22 (dt, 1H, $J=1.5$, 7.7 Hz), 7.09–7.01 (m, 3H), 6.78 (t, 1H, $J=7.3$ Hz), 6.77 (d, 1H, $J=8.0$ Hz), 4.92–4.82 (m, 1H), 4.53 (q, 1H, $J=7.0$ Hz), 3.30 (dd, 1H, $J=9.0$, 15.7 Hz), 3.23 (dd, 1H, $J=5.6$, 12.3 Hz), 3.07 (dd, 1H, $J=7.4$, 12.3 Hz), 2.98 (dd, 1H, $J=6.8$, 15.7 Hz), 1.9 (s, 3H), 1.52 (d, 3H, $J=7.0$ Hz); ^{13}C NMR: δ 159.0, 145.2, 133.8, 130.3, 127.9, 127.8, 127.4, 127.0, 125.9, 124.8, 120.4, 109.3, 81.5, 43.9, 35.4, 33.2, 21.5, 14.0; MS m/z (rel. int.): 364 (17), 231 (67), 211 (3), 199 (5), 183 (100), 131 (21), 116 (4), 105 (15), 91 (14), 77 (14). Anal. calcd for $C_{18}H_{20}OSSe$: C, 59.51; H, 5.55. Found: C, 59.42; H, 5.39%.

Minor diastereoisomer (distinct signals): ^{1}H NMR: δ 6.69 (d, 1H, $J=8.0$ Hz), 4.54 (q, 1H, $J=7.0$ Hz), 3.28 (dd, 1H, $J=5.5$, 12.3 Hz), 3.02 (dd, 1H, $J=7.8$, 12.3 Hz), 3.0 (dd, 1H, $J=6.7$, 15.7 Hz), 1.53 (d, 3H, $J=7.0$ Hz); ^{13}C NMR: δ 133.7, 130.2, 81.4, 33.1.

3.15. 4-({2-[(1*S*)-1-(Methylthio)ethyl]phenyl}seleno)-5-phenyldihydrofuran-2(3*H*)-one 8a

Oil; Major diastereoisomer: ^{1}H NMR: δ 7.48 (dd, 1H, $J=1.5$, 7.8 Hz), 7.45–7.22 (m, 7H), 7.12 (dt, 1H, $J=1.5$, 7.8 Hz), 5.42 (d, 1H, $J=6.2$ Hz), 4.52 (q, 1H, $J=7.0$ Hz), 3.82 (ddd, 1H, $J=6.2$, 7.4, 8.2 Hz), 3.09 (dd, 1H, $J=8.2$, 18.0 Hz), 2.71 (dd, 1H, $J=7.4$, 18.0 Hz), 1.96 (s, 3H), 1.52 (d, 3H, $J=7.0$ Hz); ^{13}C NMR: δ 174.5, 146.4, 137.2, 136.3, 129.2, 128.7 (two carbons), 128.6, 128.4, 127.6, 127.3 125.5 (two carbons), 86.1, 43.9, 42.9, 35.7, 20.9, 13.8; MS m/z (rel. int.): 392 (1), 231 (72), 183 (100), 160 (14), 131 (3), 115 (16), 105 (16), 91 (20), 77 (23). Anal. calcd for $C_{19}H_{20}O_2SSe$: C, 58.32; H, 5.15. Found: C, 58.55; H, 5.45%.

Minor diastereoisomer (distinct signals): ^{1}H NMR: δ 5.45 (d, 1H, $J=6.2$ Hz), 4.54 (q, 1H, $J=7.0$ Hz), 3.84 (ddd, 1H, $J=6.2$, 7.4, 8.2 Hz), 3.08 (dd, 1H, $J=8.2$, 18.0 Hz), 2.72 (dd, 1H, $J=7.4$, 18.0 Hz), 1.9 (s, 3H), 1.56 (d, 3H, $J=7.0$ Hz); ^{13}C NMR: δ 146.5, 137.4, 136.1, 85.7, 44.1, 42.7, 36.3, 21.2, 14.0.

3.16. 3,3-Dimethyl-4-({2-[(1*S*)-1-(methylthio)ethyl]-phenyl}seleno)-5-phenyldihydrofuran-2(3*H*)-one 8b

Oil; Major diastereoisomer: ^{1}H NMR: δ 7.5–7.25 (m, 6H), 7.16 (dt, 1H, $J=1.2$, 7.7 Hz), 7.10 (dd, 1H, $J=1.2$, 7.7 Hz), 6.87 (dt, 1H, $J=1.2$, 7.7 Hz), 5.31 (d, 1H, $J=10.6$ Hz), 4.28 (q, 1H, $J=7.0$ Hz), 3.48 (d, 1H, $J=10.6$ Hz), 1.89 (s, 3H), 1.42 (s, 3H), 1.39 (s, 3H), 1.32 (d, 3H, $J=7.0$ Hz); ^{13}C NMR: δ 179.0, 145.4, 136.3, 135.8, 129.0, 128.6, 128.3 (two carbons), 127.3, 127.1, 127.0 (two carbons), 126.7, 84.2, 59.8, 43.6, 29.6, 22.9, 21.4, 20.8, 13.6. Anal. calcd for $C_{21}H_{24}O_2SSe$: C, 60.14; H, 5.77. Found: C, 60.36; H, 5.99%.

Minor diastereoisomer (distinct signals): ^{1}H NMR: δ 7.18 (dt, 1H, $J=1.3$, 7.8 Hz), 6.79 (dt, 1H, $J=1.3$, 7.8 Hz), 6.69 (dd, 1H, $J=1.3$, 7.8 Hz), 4.49 (q, 1H, $J=7.0$ Hz), 3.44 (d, 1H, $J=10.6$ Hz), 1.82 (s, 3H), 1.52 (d, 3H, $J=7.0$ Hz); ^{13}C NMR: δ 83.5, 60.1, 43.8, 21.6, 21.1.

3.17. 5-Ethyl-4-({2-[(1*S*)-1-(methylthio)ethyl]phenyl}-seleno)dihydrofuran-2(3*H*)-one 8c

Oil; Major diastereoisomer: ^{1}H NMR: δ 7.58 (dd, 1H, J=1.4, 7.8 Hz), 7.52 (dd, 1H, J=1.4, 7.8 Hz), 7.4 (dt, 1H, J=1.4, 7.8 Hz), 7.19 (dt, 1H, J=1.4, 7.8 Hz), 4.57 (q, 1H, J=6.9 Hz), 4.38 (ddd, 1H, J=4.3, 6.7, 7.7 Hz), 3.63 (ddd, 1H, J=6.7, 8.0, 8.5 Hz), 2.99 (dd, 1H, J=8.5, 18.1 Hz), 2.62 (dd, 1H, J=8.0, 18.1 Hz), 1.99 (s, 3H), 1.8–1.61 (m, 2H), 1.60 (d, 3H, J=6.9 Hz), 0.98 (t, 3H, J=7.4 Hz); ^{13}C NMR: δ 174.6, 146.6, 136.3, 129.4, 128.3, 127.8, 127.5, 87.4, 44.1, 39.2, 36.3, 27.1, 21.3, 14.0, 9.7; MS m/z (rel. int.): 344 (1), 231 (62), 183 (100), 104 (11), 91 (9), 77 (7). Anal. calcd for $C_{15}H_{20}O_2SSe$: C, 52.48; H, 5.87. Found: C, 52.47; H, 5.95%.

Minor diastereoisomer (distinct signals): ^{1}H NMR: δ 7.55 (dd, 1H, J=1.4, 7.8 Hz), 7.53 (dd, 1H, J=1.4, 7.8 Hz), 3.65 (ddd, 1H, J=6.7, 8.0, 8.5 Hz), 2.95 (dd, 1H, J=8.5, 18.1 Hz), 1.59 (d, 3H, J=6.9 Hz), 1.01 (t, 3H, J=7.4 Hz); ^{13}C NMR: δ 86.8, 36.7, 21.4.

3.18. 5-Methyl-4-({2-[(1*S*)-1-(methylthio)ethyl]phenyl}-seleno)dihydrofuran-2(3*H*)-one 8d

Oil; Major diastereoisomer: ^{1}H NMR: δ 7.59 (dd, 1H, J=1.3, 7.7 Hz), 7.52 (dd, 1H, J=1.3, 7.7 Hz), 7.38 (dt, 1H, J=1.3, 7.6 Hz), 7.19 (dt, 1H, J=1.3, 7.6 Hz), 4.6–4.5 (m, 2H), 3.55 (ddd, 1H, J=7.3, 8.3, 9.1 Hz), 3.0 (dd, 1H, J=8.3, 17.9 Hz), 2.61 (dd, 1H, J=9.1, 17.9 Hz), 1.99 (s, 3H), 1.6 (d, 3H, J=7.0 Hz), 1.36 (d, 3H, J=6.3 Hz); ^{13}C NMR: δ 174.5, 146.5, 136.4, 129.4, 128.3, 127.8, 127.5, 82.6, 44.1, 41.5, 36.4, 21.3, 19.6, 14.0; MS m/z (rel. int.): 330 (1), 231 (61), 183 (100), 104 (11), 103 (10), 91 (9), 77 (7). Anal. calcd for $C_{14}H_{18}O_2SSe$: C, 51.07; H, 5.51. Found: C, 49.99; H, 5.41%.

Minor diastereoisomer (distinct signals): ^{1}H NMR: δ 7.58 (dd, 1H, J=1.3, 7.7 Hz), 7.53 (dd, 1H, J=1.4, 7.8 Hz), 3.56 (ddd, 1H, J=7.3, 8.3, 9.1 Hz), 2.95 (dd, 1H, J=8.1, 18.0 Hz), 2.65 (dd, 1H, J=8.9, 18.0), 1.98 (s, 3H), 1.59 (d, 3H, J=7.0 Hz), 1.43 (d, 3H, J=6.3 Hz); ^{13}C NMR: δ 82.0, 36.8, 21.5, 14.1.

3.19. 5-[({2-[(1*S*)-1-(Methylthio)ethyl]phenyl}seleno)-methyl]-5-phenyldihydrofuran-2(3*H*)-one 8e

Oil; Major diastereoisomer: ^{1}H NMR: δ 7.5 (dd, 1H, J=1.3, 7.8 Hz), 7.45 (dd, 1H, J=1.4, 7.8 Hz), 7.44–7.3 (m, 5H), 7.28 (dt, 1H, J=1.3, 7.8 Hz), 7.12 (dt, 1H, J=1.4, 7.8 Hz), 4.53 (q, 1H, J=7.0 Hz), 3.5 (d, 1H, J=12.8 Hz), 3.45 (d, 1H, J=12.8 Hz), 2.75–2.6 (m, 2H), 2.6–2.4 (m, 2H), 1.94 (s, 3H), 1.58 (d, 3H, J=7.0 Hz); ^{13}C NMR: δ 175.7, 145.1, 142.2, 134.1, 131.2, 128.6 (two carbons), 128.2, 128.0, 127.6, 127.0, 124.7 (two carbons), 88.1, 44.0, 41.2, 33.6, 28.9, 21.4, 14.0; MS m/z (rel. int.): 406 (1), 231 (72), 183 (100), 161 (15), 115 (8), 105 (17), 104 (9), 103 (11), 102 (11), 91 (34), 77 (17). Anal. calcd for $C_{20}H_{22}O_2SSe$: C, 59.26; H, 5.47. Found: C, 59.45; H, 5.55%.

Minor diastereoisomer (distinct signals): ^{1}H NMR: δ 7.46 (dd, 1H, J=1.4, 7.8 Hz), 7.27 (dt, 1H, J=1.3, 7.8 Hz), 7.11 (dt, 1H, J=1.4, 7.8 Hz), 4.48 (q, 1H, J=7.0 Hz), 3.51 (d, 1H, J=12.8 Hz), 3.46 (d, 1H, J=12.8 Hz), 1.96 (s, 3H), 1.55 (d, 3H, J=7.0 Hz); ^{13}C NMR: δ 134.3, 128.6, 128.1, 127.9, 127.5, 126.8, 41.4, 33.8, 29.7, 21.3.

3.20. 1-Acetyl-3-({2-[(1*S*)-1-(methylthio)ethyl]phenyl}-seleno)-2-phenylpyrrolidine 12a

Oil; Major diastereoisomer: ^{1}H NMR: δ 7.62 (dd, 1H, J=1.4, 7.7 Hz), 7.54 (dt, 1H, J=1.5, 7.7 Hz), 7.4–7.18 (m, 5H), 7.15–7.0 (m, 2H), 4.43–4.38 (m, 1H), 4.30 (q, 1H, J=7.0 Hz), 4.03–3.77 (m, 3H), 2.4–2.23 (m, 1H), 2.1–1.9 (m, 1H), 1.98 (s, 3H), 1.80 (s, 3H), 1.58 (d, 3H, J=7.0 Hz); ^{13}C NMR: δ 170.6, 146.9, 141.7, 136.3, 130.5, 129.4 (two carbons), 129.0, 128.2, 128.1, 127.8, 125.8 (two carbons), 68.9, 50.5, 46.4, 44.6, 28.5, 22.9, 21.8, 14.5. Anal. calcd for $C_{21}H_{25}NOSSe$: C, 60.29; H, 6.02; N, 3.35. Found: C, 60.15; H, 5.98; N, 3.36%.

Minor diastereoisomer (distinct signals): ^{1}H NMR: δ 5.23–5.19 (m, 1H), 4.31 (q, 1H, J=7.0 Hz), 2.2 (s, 3H), 1.97 (s, 3H); ^{13}C NMR: δ 169.8, 146.6, 141.6, 136.0, 129.2, 127.6, 125.7, 67.0, 48.8, 47.7, 44.5, 29.9, 23.0, 21.9, 14.4.

3.21. 1-Acetyl-2-[({2-[(1*S*)-1-(methylthio)ethyl]phenyl}-seleno)methyl]-2-phenylpyrrolidine 12b

Oil; Major diastereoisomer: ^{1}H NMR: δ 7.58 (dd, 1H, J=1.4, 7.8 Hz), 7.42 (dd, 1H, J=1.6, 7.8 Hz), 7.25–7.08 (m, 6H), 7.06 (dt, 1H, J=1.6, 7.8 Hz), 4.58 (q, 1H, J=7.0 Hz), 4.45 (d, 1H, J=11.4 Hz), 3.73–3.67 (m, 1H), 3.60 (ddd, 1H, J=6.6, 9.9, 10.8 Hz), 3.58 (d, 1H, J=11.4 Hz), 2.50 (dt, 1H, J=6.8, 12.4 Hz), 2.11 (s, 3H), 2.0–1.9 (m, 1H), 1.88 (s, 3H), 1.8–1.6 (m, 2H), 1.51 (d, 3H, J=7.0 Hz); ^{13}C NMR: δ 169.9, 145.7, 144.6, 134.7, 132.3, 128.8 (two carbons), 128.1, 127.9, 127.4, 127.1, 125.6 (two carbons), 71.2, 51.3, 44.4, 40.7, 39.7, 24.5, 22.2, 22.0, 14.6. Anal. calcd for $C_{22}H_{27}NOSSe$: C, 61.11; H, 6.29; N, 3.24. Found: C, 61.23; H, 6.33; N, 3.11%.

Minor diastereoisomer (distinct signals): ^{1}H NMR: δ 7.55 (dd, 1H, J=1.4, 7.8 Hz), 7.43 (dd, 1H, J=1.6, 7.8 Hz), 4.44 (d, 1H, J=11.2 Hz), 3.54 (d, 1H, J=11.2 Hz), 2.57 (dt, 1H, J=6.7, 12.3 Hz), 2.1 (s, 3H), 1.9 (s, 3H), 1.50 (d, 3H, J=7.0 Hz); ^{13}C NMR: δ 144.5, 134.4, 129.2, 128.0, 125.5, 71.0, 50.6, 44.2, 40.8, 39.8, 24.4, 22.3, 22.1.

3.22. 1-Hydroxy-4-({2-[(1*S*)-1-(methylthio)ethyl]phenyl}-seleno)-5-phenylpyrrolidin-2-one 15a

Oil; Major diastereoisomer: ^{1}H NMR: δ 7.48–7.36 (m, 2H), 7.35–7.24 (m, 5H), 7.15–7.0 (m, 3H), 4.73 (d, 1H, J=5.1 Hz), 4.47 (q, 1H, J=7.0 Hz), 3.51 (ddd, 1H, J=5.1, 5.8, 8.7 Hz), 2.98 (dd, 1H, J=8.7, 17.6 Hz), 2.55 (dd, 1H, J=5.8, 17.6 Hz), 1.84 (s, 3H), 1.49 (d, 3H, J=7.0 Hz); ^{13}C NMR: δ 169.4, 146.3, 137.6, 136.1, 129.5, 129.3, 128.8 (two carbons), 128.5, 127.6, 127.3,

126.4 (two carbons), 70.6, 43.9, 39.2, 35.4, 21.2, 13.8. Anal. calcd for $C_{19}H_{21}NO_2SSe$: C, 56.16; H, 5.21; N, 3.45. Found: C, 56.09; H, 5.14; N, 3.31%.

Minor diastereoisomer (distinct signals): ^{1}H NMR: δ 4.77 (d, 1H, $J=5.2$ Hz), 3.55 (ddd, 1H, $J=5.2$, 5.8, 8.7 Hz), 2.53 (dd, 1H, $J=5.8$, 17.6 Hz), 1.82 (s, 3H), 1.46 (d, 3H, $J=7.0$ Hz); ^{13}C NMR: δ 70.2, 44.2, 38.7, 35.5, 21.5, 14.1.

3.23. 1-Hydroxy-3,3-dimethyl-4-({2-[(1*S*)-1-(methylthio)-ethyl]phenyl}seleno)-5-phenylpyrrolidin-2-one 15b

Oil; Major diastereoisomer: ^{1}H NMR: δ 9.5 (br s, 1H), 7.4–7.2 (m, 6H), 7.15 (dt, 1H, $J=1.3$, 7.8 Hz), 7.06 (dd, 1H, $J=1.3$, 7.8 Hz), 6.85 (dt, 1H, $J=1.3$, 7.8 Hz), 4.74 (d, 1H, $J=9.5$ Hz), 4.3 (q, 1H, $J=7.0$ Hz), 3.24 (d, 1H, $J=9.5$ Hz), 1.88 (s, 3H), 1.36 (d, 3H, $J=7.0$ Hz), 1.34 (s, 3H), 1.29 (s, 3H); ^{13}C NMR: δ 174.7, 145.6, 135.9, 135.4, 129.9, 128.7, 128.6, 128.5 (two carbons), 127.6 (two carbons), 127.3, 126.8, 68.9, 58.3, 43.8, 38.5, 23.7, 21.8, 21.2, 13.9. Anal. calcd for $C_{21}H_{25}NO_2SSe$: C, 58.07; H, 5.80; N, 3.22. Found: C, 58.00; H, 5.67; N, 3.02%.

Minor diastereoisomer (distinct signals): ^{1}H NMR: δ 4.75 (d, 1H, $J=9.5$ Hz); ^{13}C NMR: δ 145.3, 136.3, 68.4, 43.2, 21.9, 21.5.

3.24. 5-Ethyl-4-({2-[(1*S*)-1-(methylthio)ethyl]phenyl}-seleno)dihydrofuran-2(3*H*)-one oxime 16

Oil; Major diastereoisomer: ^{1}H NMR: δ 8.5 (br s, 1H), 7.55 (dd, 1H, $J=1.4$, 7.7 Hz), 7.49 (dd, 1H, $J=1.4$, 7.7 Hz), 7.33 (dt, 1H, $J=1.4$, 7.7 Hz), 7.14 (dd, 1H, $J=1.4$, 7.7 Hz), 4.56 (q, 1H, $J=7.0$ Hz), 4.38–4.30 (m, 1H), 3.54–3.46 (m, 1H), 3.08 (dd, 1H, $J=7.9$, 16.7 Hz), 2.69 (dd, 1H, $J=8.2$, 16.7 Hz), 1.9 (s, 3H), 1.85–1.45 (m, 2H), 1.55 (d, 3H, $J=7.0$ Hz), 0.95 (t, 3H, $J=7.4$ Hz); ^{13}C NMR: δ 157.8, 146.4, 136.2, 129.2, 128.9, 127.6, 127.3, 90.3, 44.1, 40.0, 34.2, 26.5, 21.4, 14.0, 9.7. Anal. calcd for $C_{15}H_{21}NO_2SSe$: C, 50.27; H, 5.91; N, 3.91. Found: C, 50.17; H, 5.89; N, 3.90%.

Minor diastereoisomer (distinct signals): ^{1}H NMR: δ 8.1 (br s, 1H), 4.23–4.18 (m, 1H), 3.02 (dd, 1H, $J=7.8$, 16.8 Hz), 2.78 (dd, 1H, $J=8.2$, 16.8 Hz); ^{13}C NMR: δ 146.3, 136.0, 129.1, 128.4, 127.4, 89.8, 34.7, 26.6, 21.5.

3.25. Deselenylation by oxidative elimination of selenolactones 8c and 8d

The selenolactone **8c** or **8d** (0.3 mmol) was treated with an excess of 30% hydrogen peroxide (0.9 mmol) in dichloromethane at room temperature. The progress of the reaction was followed by TLC. After 2 h, the reaction mixture was poured into water and extracted with dichloromethane. The organic layer was dried and evaporated. The reaction product was purified by column chromatography on silica gel using CH_2Cl_2. Physical and spectral data of **9a**[19] and **9b**[20] are in good agreement with those already described in the literature. Specific rotations are reported below.

3.26. (5*R*)-5-Ethylfuran-2(5*H*)-one 9a

E.e. = 78%; $[\alpha]_D^{29} = -70.0$ (c 2.26, CH_2Cl_2).

3.27. (5*R*)-5-Methylfuran-2(5*H*)-one 9b

E.e. = 52%; $[\alpha]_D^{26} = -61.2$ (c 0.7, $CHCl_3$).

3.28. Deselenylation by reductive cleavage of selenolactones 8a and 8e

A catalytic amount of AIBN and triphenyltin hydride (0.9 mmol) were added to a solution of the selenolactone **8a** or **8e** (0.3 mmol) in refluxing benzene under nitrogen. The reaction was stirred under reflux for 2 h and, after removal of the solvent under reduced pressure, the residue was purified by chromatography on silica gel (CH_2Cl_2:petroleum ether = 4:1 for **10a** and CH_2Cl_2 for **10b**). Physical and spectral data of **10a**[8] and **10b**[7,21] are in good agreement with those already described in the literature. Specific rotations are reported below.

3.29. (5*S*)-5-Phenyldihydrofuran-2(3*H*)-one 10a

E.e. = 90%; $[\alpha]_D^{29} = -24.8$ (c 1.0, $CHCl_3$).

3.30. (5*R*)-5-Methylphenyldihydrofuran-2(3*H*)-one 10b

E.e. = 78%; $[\alpha]_D^{29} = +32.4$ (c 0.25, $CHCl_3$).

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