Nucleophile-Selective Selenocyclizations

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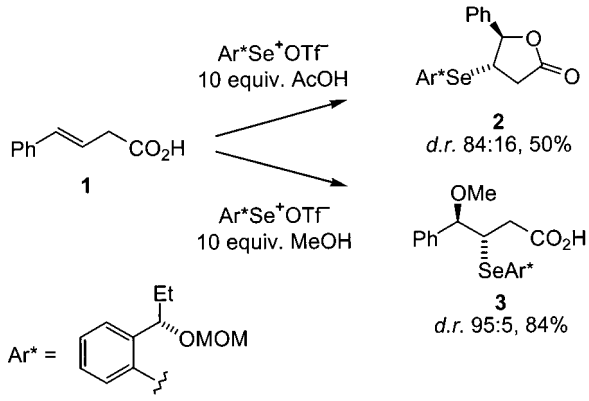
Electrophilic cyclizations are one of the major strategies for cyclofunctionalizations of alkenes. Selective selenocyclizations can be performed by adjusting various factors in such reactions. The nature of the electrophile, the counterion, solvents, and external additives coordinating to the electrophilic species are used to control the course of such cyclizations with high degrees of efficiency. Our investigations have been extended towards stereoselective reactions using chiral selenium electrophiles.

Introduction

Functionalizations of inactivated carbon−carbon double bonds are central transformations and electrophilic selenenylations of alkenes is one important strategy.[1] We and other research groups have shown that this reaction can also be employed in cyclizations for the synthesis of different heterocyclic compounds. Different electrophilic selenium reagents and a variety of reaction conditions have been employed and recent reviews are highlighting the broad scope of this general process.[2] Stereoselective functionalization of alkenes with chiral selenium electrophiles have been performed as well.[3,4] For the elaboration of highly functionalized heterocyclic compounds this methodology continues to receive methodological as well as synthetic attention. Although standard conditions can be used for these cyclizations, the interactions between the selenium electrophile, the counterion, the solvent, and the substrate are not fully understood, and we describe herein our recent investigations towards selective cyclizations.

For example, the addition of external nucleophiles to the reaction can lead to either selenolactonization (addition of 10 equivalents of acetic acid) or to methoxyselenenylation (addition of 10 equivalents of methanol) as shown in Scheme 1.[5] Furthermore, the outcome of this reaction is influenced by the nature of the selenium electrophile used. The interaction between the selenium electrophile and the nucleophile is dependent upon the nature of the nucleophile, and the reactivity of the selenium electrophile also depends on the nature of the counterion. The coordination of the selenium electrophile to a carboxylic acid seems to be stronger than to an alcohol, and therefore in **1**, methoxyselenenylation to **3** is favored over lactonization if methanol



Scheme 1. Selenenylation of **1** under different reaction conditions

is present. An excess of external acetic acid, which then competes in coordinating to the selenium electrophile, leads to the formation of only seleno lactone **2**. As a chiral selenium electrophile has been used in both reactions, the products **2** and **3** are formed in a diastereomeric ratio of 84:16 and 95:5, respectively.

Results and Discussion

Several observations on the effect of counterions in selenenylation reactions have already been reported, but they do not yet allow a conclusive picture.[3c,6] There are also several investigations on the interaction of selenium electrophiles with nearby heteroatoms.[7,8,9] In order to probe in which way different nucleophiles, solvents, and counterions affect selenocyclizations, we synthesized compound **5** containing two different nucleophiles, an alcohol and a carboxylic acid. Alkene **5** was synthesized by the reaction of 3-bromo-2-phenylpropene[10] with the enolate of methyl 3-

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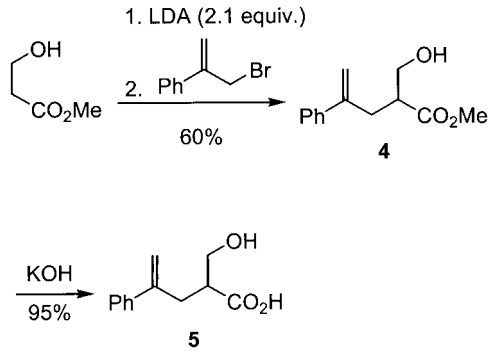
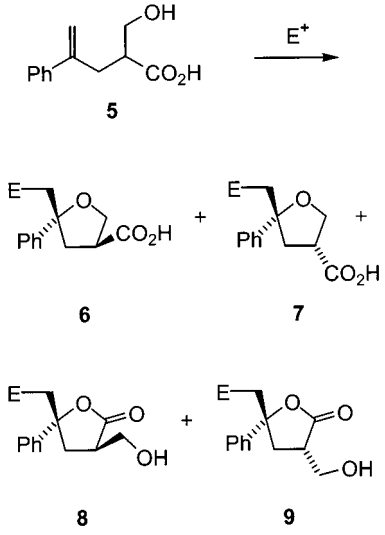
hydroxypropionate[11] and subsequent hydrolysis of ester **4**.



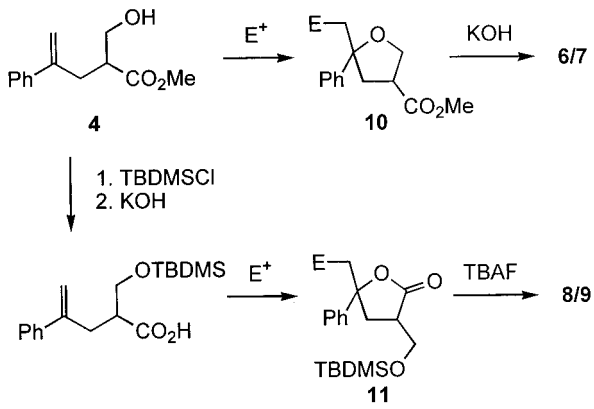
Scheme 2. Synthesis of alkene **5**

Depending on the cyclizing nucleophile, electrophilic 5-*exo*-cyclizations of alkene **5** can then lead to two different heterocycles: tetrahydrofurans or lactones. We have recently reported on the first results of how different interactions with selenium electrophiles can be used to direct cyclizations either towards tetrahydrofurans **6/7** or towards lactones **8/9**.[12] We found that the ratio of tetrahydrofurans to lactones is indeed strongly dependent upon the various factors mentioned above. Unfortunately, NOE experiments could not clarify the relative stereochemistry because of overlapping signals of tetrahydrofurans and lactones, which are both obtained as mixtures of *cis* and *trans* isomers.



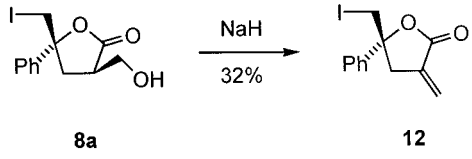
Scheme 3. Electrophilic cyclizations to tetrahydrofurans **6/7** and lactones **8/9** (E = ArSe, I)

The use of **4** in a cyclization reaction to tetrahydrofuran **10** followed by ester hydrolysis allowed the independent synthesis of **6/7**. A sequence of TBDMS-protection and ester hydrolysis precedes the cyclization to lactone **11**, which can be followed by TBAF-deprotection, and leads solely to derivatives **8/9**. But even after the separate synthesis of tetrahydrofurans **6/7** and lactones **8/9**, the stereochemical assignment was impossible.



Scheme 4. Independent synthesis of tetrahydrofurans **6/7** and lactones **8/9** (E = ArSe, I)

However, treatment of **5** with iodine monochloride led only to iodo lactones **8a/9a** (E = I), and no tetrahydrofuran derivatives were detected. The mixture of diastereomers generated in such an iodocyclization could be separated. The major isomer **8a** was recrystallized and X-ray analysis finally allowed an unambiguous assignment of the NMR signals.[13] The tetrahydrofurans **6a** and **7a** (E = I) were only accessible by iodocyclization of **4** to tetrahydrofuran **10a** (93% yield) and subsequent ester hydrolysis to **6a/7a** (94% yield). Interestingly, treatment of **8a** with sodium hydride did not result in a second cyclization, but in an elimination, to generate the α-methylene lactone **12** containing a structural motif found in many natural products.[14] α-Methylene lactones are also valuable building blocks in synthesis.[15]



Scheme 5. Iodo lactone **8a** as the major isomer in an iodocyclization of **5** and subsequent elimination

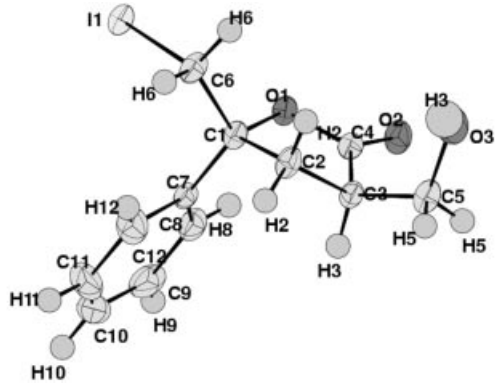
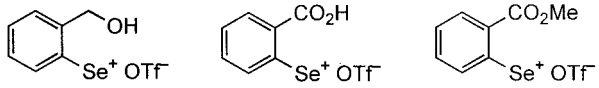


Figure 1. View of the crystal structure of **8a** showing a *cis* relationship between the $-CH_2OH$ and $-CH_2I$ substituents; the ellipsoids represent atomic displacement parameters at the 50% probability level

Compound **5** was treated with the phenylselenenyl electrophile (E = PhSe) using various counterions and different reaction conditions. The products of this cyclization are tetrahydrofurans **6b** and **7b** (E = PhSe) and lactones **8b** and **9b** (E = PhSe). There are two main interactions influencing the cyclization reaction. The selenium electrophile can interact with one of the internal nucleophiles of the unsaturated substrate and there are interactions with an external nucleophile or solvent. Both of these interactions will additionally be influenced by the counterion.

We already know from previous investigations using chiral selenenyl triflates that small amounts of additional solvents (additives) can influence the course of selenenylation reactions dramatically.[16] Addition of alcohols alters the reactivity of the selenium electrophiles, and tetrahydrofurans are the major products. Carboxylic acids, as weakly coordinating additives, lead to a further shift towards tetrahydrofuran products. The addition of 10 equivalents of acetic acid to phenylselenenyl triflate leads to the exclusive formation of **6b** and **7b** (37:63). The ratio indicated that there is almost no interaction between the electrophile and the alcohol/carboxylic acid functionality of the substrate. But if the electrophile−acid coordination is disturbed by additional water, lactones are formed preferentially.

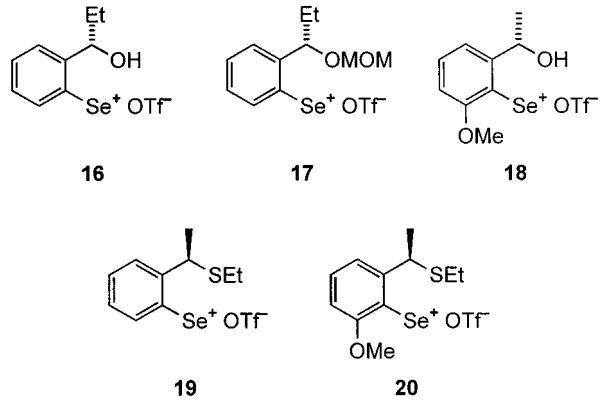
Phenylselenenyl hexafluorophosphate or phenylselenenyl sulfate can be used to synthesize exclusively the lactone **8b/9b** under the standard reaction conditions. The addition of methanol (10 equiv.) in these reactions is important, as its replacement with acetic acid (10 equiv.) leads to the formation of a mixture of all four products in low yields.[12] Irrespective of the additive used, this behavior is also reflected in the ratio of **8b/9b**, as the alcohol moiety of the substrate **5** coordinates to the selenium electrophile during the cyclization, leading to the *cis*-isomer **8b** as the major lactone.



13 **14** **15**

Figure 2. Functionalized selenium electrophiles

We then investigated the internal coordination of an oxygen heteroatom to the selenium electrophile more closely. The selenium electrophiles **13**−**15** (Figure 3), generated from the corresponding diselenides,[17] were employed in the cyclization reaction of **5** under various conditions.



16 **17** **18** **19** **20**

Figure 3. Chiral selenium electrophiles

The additive now seems to have no great influence on the course of the cyclization, because the internal oxygen atom in electrophiles **13**−**15** coordinates to the selenium moiety. Even the *cis*/*trans*-ratio (**8**/**9**) is very similar in these experiments (Table 1, Entries 1−3). Electrophile **13** has a very strong oxygen−selenium interaction, leading to exclusive formation of lactones **8c/9c** irrespective of any additive. Electrophiles **14** and **15** form almost equal mixtures of tetrahydrofurans and lactones with low (tetrahydrofurans) to moderate (lactones) *cis*/*trans* selectivities, and again, no influence of an additive can be observed, as the carboxylic acid/ester moiety coordinates to the selenium electrophile. Due to the high polarity of the tetrahydrofuran products **6d/7d** and **6e/7e**, their purification was impossible. To correctly assign the NMR spectra, ester **4** was subjected to cyclization with electrophiles **14** and **15**. The *cis*/*trans* ratio of about 1:1 in the products **10d** and **10e** is similar to that observed in the reactions mentioned in Table 1. The results of the cyclizations of **4** are summarized in Table 3.

A series of chiral selenium electrophiles **16**−**20** has been investigated in the cyclization reaction. A hydroxy moiety in the chiral side-chain as in compound **16** and even a protected hydroxy moiety in the selenium electrophile **17** is able to coordinate to the selenium moiety efficiently, leading to lactone formation exclusively (Table 2, entries 1 and 2). If a second *ortho*-substituent is introduced, as in selenium electrophile **18**, equal amounts of tetrahydrofuran and lactone

Table 1. Selenocyclizations with different functionalized selenium electrophiles using 10 equivalents of additives (no additive, methanol, acetic acid)

Entry	Electrophile	Products	**6/7**	**8/9**	Tetrahydrofurans/Lactones	Yield [%]
1	**13**	**8c**, **9c**	−	80:20	0:100	40−51[a]
2	**14**	**6d**−**9d**	32:68−52:48	82:18−84:16	46:54−52:48	45−99
3	**15**	**6e**−**9e**	24:76−50:50	81:19−84:16	41:59−50:50	74−91

[a] These reactions were slow, and a considerable amount (24−27%) of diselenide was formed.

Table 2. Selenocyclizations of **5** with different selenium electrophiles with 10 equivalents of methanol as additive

Entry	Electrophile	Products	Solvent	Tetrahydrofurans **6/7/10**	**8/9**	Tetrahydrofurans/ Lactones	Yield [%]
1	**16**	**8f**, **9f**	Et_2O	–	79[b]:21[c]	0:100	40[a]
2	**17**	**8g**, **9g**	Et_2O	–	82[d]:18[e]	0:100	68
3	**18**	**10h**, **8h**, **9h**	Et_2O	30:70[f]	85[g]:15[h]	50:50	77
4	**19**	**6i** –**9i**	THF	38:62	87[i]:13[j]	55:45	55
5	**20**	**6j** –**9j**	THF	41[k]:59[l]	70[m]:30[n]	60:40	48
6	**20**	**10j**	Et_2O	42:58[o]	–	100:0	38

[a] These reactions were slow, and a considerable amount (25%) of diselenide was formed. [b] **21**: 69:31 *e.r.* [c] **22**: 78:22 *e.r.* [d] **21**: 79:21 *e.r.* [e] **22**: 83:17 *e.r.* [f] Methyl ester **10h** was isolated: **10h**-*cis*: 86:14 *d.r.* (NMR); **10h**-*trans*: 82:18 *d.r.* (NMR). [g] **21**: 88:12 *e.r.* [h] **22**: 89:11 *e.r.* [i] **21**: 60:40 *e.r.* [j] **22**: 87:13 *e.r.* [k] 66:34 *d.r.* (NMR). [l] 62:38 *d.r.* (NMR).[m] **21**: 73:27 *e.r.* [n] **22**: 88:12 *e.r.*[o] Methyl ester **10j** was isolated. **10j**-*cis*: 89:11 *d.r.* (NMR); **10j**-*trans*: 72:28 *d.r.* (NMR).

are formed without any preference. The stereoselectivity in the addition reaction to the double bond is, however, improved with this reagent (up to 89:11 *d.r.*), as we have found earlier also with other substrates[5,18] and by calculations.[7] Interestingly, the tetrahydrofuran cyclization product was isolated as the methyl ester **10h** in this reaction. Tiecco at al. have shown that sulfur substituted selenium electrophiles of type **19** and **20** can be added to double bonds with very high selectivities.[19] The diselenides used for the preparation of the electrophiles **19** and **20** were synthesized in analogy to the procedure reported by Tiecco et al. When the cyclization of **5** is performed with these electrophiles using THF as solvent, almost equal amounts of tetrahydrofuran and lactone products are formed (Table 2, entries 4 and 5). When diethyl ether was used as solvent for the reaction, only electrophile **20** gave a clean reaction resulting in the exclusive formation of the corresponding tetrahydrofurans, which were again isolated as the corresponding methyl esters **10j**. This reaction was repeated several times with the same result; obviously an esterification must have taken place during the reaction. The low solubility of electrophile **20** in diethyl ether slows down the reaction, but the reason for the esterification observed with the electrophiles **18** and **20** under these reaction conditions, probably catalyzed by the triflic acid generated during the reaction, remains unclear.

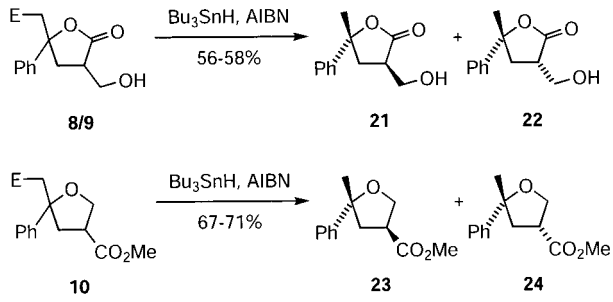
The synthesis of tetrahydrofurans can also be achieved by using ester **4** in the cyclization. We have synthesized a series of tetrahydrofuran cyclization products **10** as outlined in Scheme 4. The results are summarized in Table 3. There is almost no interaction of the electrophile and the ester moiety of **4** as the *cis*- and *trans*-isomers of the tetrahydrofuran cyclization products **10** are formed in almost equal amounts.

The use of chiral selenium electrophiles in the cyclizations allowed us to determine also the enantioselectivity of the addition reaction. A rough estimate can be obtained from the NMR spectroscopic data, but only radical cleavage of the selenium moiety of either the lactones **8/9** or the tetrahydrofurans **10** by tributyltin hydride and subsequent HPLC analysis of the products allows an accurate determination. The enantiomeric ratios of the cleavage products **21**–**24** are included in the footnotes of Tables 2 and 3.

Table 3. Synthesis of tetrahydrofurans **10** from ester **4** and different electrophiles

Entry	Electrophile	Products	*cis*/*trans*	Yield [%]
1	ICl[a]	**10a**	42:58	93
2	PhSeOTf	**10b**	39:61	68
3	**13**	**10c**	48:52	30
4	**14**	**10d**	50:50	79
5	**15**	**10e**	48:52	79
6	**16**	**10f**	30[b]:70[c]	78
7	**17**	**10g**	44[d]:56[e]	41
8	**19**	**10i**	30[f]:70[g]	40

[a] No methanol added as additive. [b] **23**: 76:24 *e.r.* [c] **24**: 71:29 *e.r.* [d] 80:20 *d.r.* (NMR). [e] 83:17 *d.r.* (NMR). [f] 83:17 *d.r.* (NMR). [g] 75:25 *d.r.* (NMR).



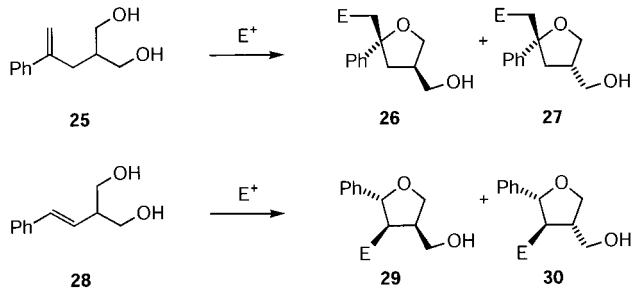
Scheme 6. Radical cleavage of the selenium moiety from the cyclization products (E = ArSe, I)

Because alkene **5** is chiral, we attempted a racemic resolution in reactions using only 0.5 equivalents of electrophile **16**. Depending on the presence of 10 equivalents of methanol as additive, the ratio of tetrahydrofurans to lactones varied slightly, and the remaining starting material was isolated as the methyl ester **4**. But no racemic resolution was observed, and the unchanged alkene was isolated as a racemic mixture.

The comparison of *exo*- and *endo*-cyclizations was made using two different diols, **25** and **28**. While **25** is accessible by reduction of **5** with lithium aluminum hydride in 85% yield, the diol **28** for *endo*-cyclizations was synthesized by complete reduction of the carbon dioxide addition product to the enolate of methyl 5-phenyl-4-pentenoate. The yield

for the reduction to **28** is low (32%) because of the high tendency of the starting material towards decomposition by decarboxylation.

Cyclization of **25** with various electrophiles leads, probably via a coordination of the second hydroxy moiety in **25** to the electrophile, to the formation of **26** as the major isomer. As shown in Table 3, the *cis*/*trans* ratios vary from 59:41 to 81:19. A coordination of the electrophile to the second hydroxy moiety is much stronger and influences cyclizations of **28**, where the major isomer **29** is formed in large excess with ratios (**29/30**) ranging from 86:14 to 94:6. Different electrophiles have been investigated in cyclizations of both substrates and the results are summarized in Table 4.



Scheme 7. Cyclization of diols **25** and **28** (E = ArSe, I)

Table 4. Cyclizations of **25** and **28** with different electrophiles and 10 equivalents of methanol as additive

Entry	Starting material	Electrophile	Products	Ratio	Yield [%]
1	**25**	ICl[a]	**26a**, **27a**	66:34	43
2	**25**	PhSeOTf	**26b**, **27b**	70:30	74
3	**25**	**16**	**26f**[b], **27f**[c]	59:41	28
4	**25**	**19**	**26i**[d], **27i**	81:19	33
5	**28**	ICl[a]	**29a**, **30a**	88:12	79
6	**28**	PhSeOTf	**29b**, **30b**	94:6	50
7	**28**	**16**	**29f**[e], **30f**[f]	93:7	64
8	**28**	**19**	**29i**[g], **30i**[h]	86:14	30

[a] No methanol added as additive. [b] 61:39 *d.r.* (NMR). [c] 59:41 *d.r.* (NMR). [d] 78:22 *d.r.* (NMR). [e] **32**: 77:23 *e.r.* [f] **32**: 72:28 *e.r.* [g] **32**: 77:23 *e.r.* [h] **32**: 88:12 *e.r.*

In order to accurately determine the stereoselectivity in the cyclizations with chiral selenium electrophiles **16** (Table 4, Entries 3 and 7) and **19** (Table 4, Entries 4 and 8), the selenium moiety in the corresponding addition products was cleaved with tributyltin hydride/AIBN as described above. The resulting products, **31** (from **26/27**) and **32** (from **29/30**), were analyzed by HPLC on a chiral stationary phase.

Conclusions

We were able to develop conditions for nucleophile–selective electrophilic cyclizations. The course of the cyclization of the alkene with an alcohol and a carboxylic acid nucleophile can be directed as desired by the choice of the electrophile and the additive used in the reaction. The coordination of the electrophile to the additive and/or to one of the internal nucleophiles influences the stereochemical outcome of the reactions as well. The use of chiral selenium electrophiles led to enantiomerically enriched heterocycles as reaction products.

Experimental Section

General Remarks: All reactions were performed under argon with anhydrous solvents. Melting points are uncorrected. The ^{1}H- and ^{13}C NMR spectra were measured in $CDCl_3$, with TMS as an internal standard. In NMR assignments of type "7a-CH" or "6j-CH_2Se" 7a or 6j, respectively, refer to compound numbers **7a**, **6j** and not to atom position numbers in a molecule.

Cyclization Reaction with Selenium Electrophiles (GP 1):[20] Under an inert atmosphere, the diselenide (0.085 mmol) was dissolved in diethyl ether (3.5 mL), cooled to −78 °C, and treated with bromine (0.085 mmol, 0.085 mL of a 1 M solution in CCl_4). After 10 min a solution of silver triflate (0.24 mmol, 61 mg) in MeOH (2 mmol, 80 μL) (or the corresponding amount of a silver salt dissolved in 10 equivalents of the additive used) was added at −78 °C and stirred for 10 min. The mixture was treated with the substrate (0.17 mmol) and stirred at −78 °C for 3 h, and then at room temperature for 1 h. The mixture was treated with *sym*-collidine (0.13 mmol, 17 μL) followed by water (3 mL). After extraction with *tert*-butyl methyl ether, the organic extracts were combined, dried with $MgSO_4$, and the solvent was evaporated to produce a crude product which was purified by flash chromatography on silica gel.

Deselenenylation by Radical Cleavage of Aryl Selenides (GP 2): AIBN (0.25 mmol, 41 mg) and tributyltin hydride (0.25 mmol, 73 mg) were added to a solution of the substrate (83 μmol) in refluxing toluene (3 mL), and the mixture was refluxed for 45 min. The solvent was evaporated, and the crude product was purified by flash chromatography on silica gel.

Methyl 2-(Hydroxymethyl)-4-phenylpent-4-enoate (4): Lithium diisopropylamide (LDA), prepared from *n*BuLi (21.2 mmol, 8.48 mL, 2.5 M in hexane) and dry diisopropylamine (21.2 mmol, 3 mL) in THF (60 mL), was added at −78 °C to methyl 3-hydroxypropionate[11] (1.0 g, 9.62 mmol) in THF (60 mL) and stirred for 1 h while warming up to room temperature. The reaction mixture was cooled to −78 °C, and 3-bromo-2-phenylpropene[10] (1.90 g, 9.62 mmol) was added dropwise. This mixture was stirred for 4 h at −78 °C and then for 1 h at room temperature. The reaction was quenched with saturated aqueous NH_4Cl and extracted with diethyl ether (3 × 50 mL). The combined organic phases were dried with $MgSO_4$, and after evaporation of the solvent the crude reaction mixture was purified by flash chromatography on silica gel with *tert*-butyl methyl ether/petroleum ether (1:2) as eluent to give a yellow oil in 60% yield (1.27 g, 5.0 mmol). HPLC conditions: Chiracel OD-H, flow rate: 0.5 ml min^{-1}, 2-propanol/*n*-hexane, 10:90, 10 °C, $R_f(1)$ = 17.8 min, $R_f(2)$ = 22.4 min. IR (thin film on NaCl): $\tilde{\nu}$ = 3408, 2952, 1714, 1628, 1495, 1437, 1379, 1170, 1029 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.56–2.67 (m, 2 H, CH_2), 2.80–2.90 (m, 1 H, CH), 3.54 (s, 3 H, CH_3), 3.62 (d, J = 5.2 Hz, 2 H, CH_2OH), 5.04 (d, J = 1.0 Hz, 1 H, =CH_2), 5.23 (d, J = 1.0 Hz, 1 H, =CH_2), 7.15–7.33 (m, 5 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 34.6 (CH_2), 46.4 (CH), 52.2 (OCH_3), 62.8

(CH_2OH), 115.4 (=CH_2), 126.3 (CH-Ar), 126.6 (CH-Ar), 128.2 (CH-Ar), 128.9 (CH-Ar), 140.4 (C), 145.7 (C-Ar), 175.6 (C=O) ppm. MS (EI): *m*/*z* (%) = 221 (100) $[M + H]^+$, 203 (4), 143 (2), 118 (13), 52 (7); HRMS: calcd. for $C_{13}H_{16}O_3$ 221.1177, found 221.1178.

2-(Hydroxymethyl)-4-phenylpent-4-enoic Acid (5): Compound **4** (600 mg, 2.73 mmol) was dissolved in MeOH (25 mL), treated at 0 °C with aqueous KOH (13 mL, 30%), and stirred overnight at room temperature. Water (30 mL) was added, and the solution was washed with diethyl ether (25 mL). The aqueous layer was cooled to 0 °C and CH_2Cl_2 (25 mL) was added followed by 5 N HCl until pH < 5. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 25 mL). The combined organic phases were dried with $MgSO_4$, and the solvent was evaporated. The product was obtained as a yellow solid in 95% yield (534 mg, 2.59 mmol). No further purification was necessary. M.p. 59−61 °C. IR (thin film on NaCl): $\tilde{\nu}$ = 3436, 1704, 1495, 1444, 1207, 1028, 904, 780, 706 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.60−2.72 (m, 2 H, CH_2), 2.93−3.04 (m, 1 H, CH_2), 3.64−3.81 (m, 2 H, CH_2OH), 5.11 (s, 1 H, =CH_2), 5.30 (s, 1 H, =CH_2), 7.20−7.35 (m, 5 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 34.2 (CH_2), 45.9 (CH), 62.4 (CH_2OH), 115.6 (=CH_2), 126.6 (CH-Ar), 128.3 (CH-Ar), 128.9 (CH-Ar), 140.2 (C), 145.3 (C-Ar), 180.2 (C=O) ppm. MS (EI): *m*/*z* (%) = 207 (37) $[M + H]^+$, 191 (100), 173 (65), 159 (58); HRMS: calcd. for $C_{12}H_{14}O_3$ 207.1021, found 207.1019.

5-(Iodomethyl)-5-phenyltetrahydrofuran-3-carboxylic Acid (6a/7a): Compound **10a** (125 mg, 0.36 mmol) was dissolved in MeOH (3 mL) and treated with aqueous KOH (1.5 mL, 30%). The reaction mixture was stirred at room temperature for 6 h and diluted with water (10 mL). Diethyl ether (10 mL) was added, the aqueous layer was acidified by adding 2 N HCl until pH < 4 and extracted with CH_2Cl_2 (3 × 10 mL). The collected organic extracts were dried over $MgSO_4$, and the solvent was evaporated to produce a colorless solid (112 mg, 0.34 mmol) with 94% yield. *d.r.* (**6a/7a**) 43:57; m.p. 108−110 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.63 (dd, *J* = 8.8, 18.8 Hz, 2 H, CH_2), 3.03 (quint, *J* = 8.0 Hz, 1 H, 7a-CH), 3.41 (d, *J* = 10.4 Hz, 1 H, 6a-CH_2I), 3.46 (d, *J* = 10.8 Hz, 1 H, 6a-CH_2I), 3.50 (d, *J* = 10.8 Hz, 1 H, 7a-CH_2I), 3.54 (d, *J* = 10.4 Hz, 1 H, 7a-CH_2I), 3.93 (t, *J* = 8.8 Hz, 1 H, 6a-CH_2O), 4.09 (t, *J* = 8.8 Hz, 1 H, 7a-CH_2O), 4.19 (t, *J* = 8.2 Hz, 1 H, 7a-CH_2O), 4.27 (t, *J* = 8.4 Hz, 1 H, 6a-CH_2O), 7.15−7.40 (m, 5 H, Ar) ppm. **7a:** ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.8 (CH_2), 40.8 (CH_2O), 44.4 (CH), 69.7 (CH_2I), 86.0 (C), 125.7 (CH-Ar), 128.3 (CH-Ar), 128.9 (CH-Ar), 142.5 (C-Ar), 179.4 (C=O) ppm. IR (NaCl): $\tilde{\nu}$ = 3440, 1707, 1447, 1188, 1057, 762, 702 cm^{-1}. MS (EI): *m*/*z* (%) = 350 (3) $[M + NH_4]^+$, 224 (100), 208 (37), 191 (15), 152 (16), 134 (10), 119 (20), 106 (9), 78 (6), 52 (55); HRMS: calcd. for $C_{12}H_{13}O_3I$ 350.0253, found 350.0256.

5-Phenyl-5-(phenylselanylmethyl)tetrahydrofuran-3-carboxylic Acid (6b/7b): Synthesized according to GP 1: yield 75% (192 mg, 0.54 mmol). Synthesized from **10b** (same procedure as described for **6a/7a** from **10a**), product needed no further purification: yield 80% (205 mg, 0.58 mmol); white solid; *d.r.* (**6b/7b**) 37:63; m.p. 52−55 °C. **6b:** ^1H NMR (400 MHz, $CDCl_3$): δ = 2.50−2.70 (m, 2 H, CH_2), 3.18 (d, *J* = 12.4 Hz, 1 H, CH_2Se), 3.30−3.38 (m, 1 H, CH), 3.32 (d, *J* = 11.6 Hz, 1 H, CH_2Se), 3.89 (t, *J* = 8.4 Hz, 1 H, CH_2O), 4.18 (t, *J* = 8.4 Hz, 1 H, CH_2O), 7.00−7.40 (m, 10 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 39.3 (CH_2), 40.7 (CH_2Se), 43.9 (CH), 68.1 (CH_2O), 85.9 (C), 124.1 (CH-Ar), 125.8 (CH-Ar), 126.3 (CH-Ar), 127.3 (CH-Ar), 128.0 (CH-Ar), 129.9 (C-Ar), 131.6 (CH-Ar), 143.8 (C-Ar), 177.7 (C=O) ppm. ^{77}Se NMR (57.3 MHz, $CDCl_3$): δ = 255.3 ppm. **7b:** ^1H NMR (400 MHz, $CDCl_3$): δ = 2.50−2.70 (m, 2 H, CH_2C), 2.97 (quint, *J* = 8.4 Hz, 1 H, CH), 3.29 (d, *J* = 12.0 Hz, 1 H, CH_2Se), 3.39 (d, *J* = 12.0 Hz, 1 H, CH_2Se), 4.02 (t, *J* = 8.4 Hz, 1 H, CH_2O), 4.14 (t, *J* = 7.2 Hz, 1 H, CH_2O), 7.00−7.40 (m, 10 H, 2 × Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 39.5 (CH_2), 39.8 (CH_2 Se), 42.8 (CH), 68.0 (CH_2O), 86.2 (C), 124.1 (CH-Ar), 125.7 (CH-Ar), 126.4 (CH-Ar), 127.4 (CH-Ar), 128.0 (CH-Ar), 130.0 (C-Ar), 131.6 (CH-Ar), 142.7 (CH-Ar), 178.4 (C=O) ppm. ^{77}Se NMR (57.3 MHz, $CDCl_3$): δ = 257.5 ppm. IR (thin film on NaCl): $\tilde{\nu}$ = 3477, 1705, 1643, 1579, 1478, 1437, 1236, 1058, 738, 702 cm^{-1}. MS (EI): *m*/*z* (%) = 362 (2) $[M + H]^+$, 331 (1), 191 (76), 173 (12), 157 (20), 145 (22), 128 (18), 115 (32), 105 (70), 91 (69), 77 (100), 65 (25), 51 (72), 45 (91); HRMS: calcd. for $C_{18}H_{18}O_3Se$ 363.0499, found 363.0495.

5-{2-[(*S*)-1-Hydroxypropyl]phenylselanylmethyl}-5-phenyltetrahydrofuran-3-carboxylic Acid (6f/7f): Synthesized from **10f** (same procedure as described for **6a/7a** from **10a**); colorless oil. Yield 70% (64 mg, 0.2 mmol); *d.r.* (**6f/7f**) 48:52. $[\alpha]_D^{23}$ = +5.04 (*c* = 0.68, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.82 (t, *J* = 6.4 Hz, 3 H, 7f-CH_3), 0.84 (t, *J* = 7.6 Hz, 1 H, 6f-CH_3), 1.53−1.70 (m, 2 H, C$H_2$$CH_3$), 2.48−2.70 (m, 3 H, CH_2, 6f-CH), 2.98 (quint, *J* = 8.4 Hz, 1 H, 7f-CH), 3.26 (d, *J* = 12.4 Hz, 1 H, 6f-CH_2Se), 3.27 (d, *J* = 12.4 Hz, 1 H, 7f-CH_2Se), 3.32 (d, *J* = 13.2 Hz, 1 H, 6f-CH_2Se), 3.34 (d, *J* = 12.4 Hz, 1 H, 7f-CH_2Se), 3.94 (t, *J* = 8.4 Hz, 1 H, 6f-CH_2O), 3.99−4.10 (m, 2 H, 7f-CH_2O), 4.20 (t, *J* = 8.4 Hz, 1 H, 6f-CH_2O), 4.85 (t, *J* = 6.8 Hz, 1 H, 7f-CHOH-Ar), 4.88 (t, *J* = 6.8 Hz, 1 H, 6f-CH_2O), 6.90−7.4 (m, 9 H, Ar) ppm. **7f:** ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.3 (CH_3), 30.1 (CH_2CH_3), 39.9 (CH_2), 40.7 (CH), 43.7 (CH_2Se), 68.1 (CH_2O), 73.3 (CHOH-Ar), 85.8 (C), 124.2 (CH-Ar), 125.2 (CH-Ar), 126.3 (CH-Ar), 126.6 (CH-Ar), 126.9 (CH-Ar), 127.3 (CH-Ar), 128.9 (C-Ar), 133.3 (CH-Ar), 142.9 (C-Ar), 145.0 (C-Ar), 176.6 (C=O) ppm. IR (NaCl): $\tilde{\nu}$ = 3217, 1710, 1447, 1199, 1050, 758, 703 cm^{-1}. MS (EI): *m*/*z* (%) = 402 (100) $[M - H_2O]^+$, 391 (38), 216 (22), 208 (99), 197 (50), 152 (6), 118 (96); HRMS: for $C_{21}H_{24}O_4Se$ calcd. 420.0834, found 420.0834.

5-{[2-[(*R*)-1-(Ethylsulfanyl)ethyl]phenyl]selanylmethyl}-5-phenyltetrahydrofuran-3-carboxylic Acid (6i/7i): Synthesized according to GP 1. Purification by flash chromatography on silica gel with diethyl ether/petroleum ether, 2:1. Yield 28% (19 mg, 0.042 mmol); colorless oil; *d.r.* (**6i/7i**) 38:62. $[\alpha]_D^{23}$ = −18.1 (*c* = 0.21, $CHCl_3$). **7i:** ^1H NMR (400 MHz, $CDCl_3$): δ = 1.06 (t, *J* = 7.2 Hz, 3 H, CH_3), 1.45 (d, *J* = 7.2 Hz, 3 H, CH_3), 2.25 (q, *J* = 7.6 Hz, 2 H, C$H_2$$CH_3$), 2.58 (d, *J* = 7.6 Hz, 1 H, CH_2), 2.62 (d, *J* = 7.6 Hz, 1 H, CH_2), 3.00 (quint, *J* = 8.4 Hz, 1 H, CH), 3.28 (d, *J* = 12.0 Hz, 1 H, CH_2Se), 3.38 (d, *J* = 11.6 Hz, 1 H, CH_2Se), 4.05 (t, *J* = 8.8 Hz, 1 H, CH_2O), 4.18 (t, *J* = 7.2 Hz, 1 H, CH_2O), 4.60 (q, *J* = 7.2 Hz, 1 H, CHS), 6.90−7.48 (m, 9 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.1 (*C*H_3CH_2), 22.8 (*C*H_2CH_3), 25.6 (CH_3), 41.0 (CH-Ar), 41.8 (CH), 42.9 (CH_2), 44.0 (CH_2Se), 69.6 (CH_2O), 87.7 (C), 125.5 (CH-Ar), 127.5 (CH-Ar), 127.8 (CH-Ar), 127.9 (CH-Ar), 128.0 (CH-Ar), 128.8 (CH-Ar), 132.0 (C-Ar), 134.1 (CH-Ar), 144.2 (C-Ar), 146.0 (C-Ar), 178.5 (C=O) ppm. IR (NaCl): $\tilde{\nu}$ = 3367, 3046, 2956, 2915, 1725, 1711, 1594, 1489, 1464, 1448, 1368, 1333, 1263, 1217, 1157, 1101, 1049, 1027, 761, 700, 650 cm^{-1}. MS (EI): *m*/*z* (%) = 398 (2) $[M + NH_4]^+$, 468 (100), 451 (33), 433 (9), 422 (38); HRMS calcd. for $C_{22}H_{26}O_3SSe$ 468.1106, found 468.1109.

5-{[2-[(*R*)-1-(Ethylsulfanyl)ethyl]-6-methoxyphenyl]selanylmethyl}-5-phenyltetrahydrofuran-3-carboxylic Acid (6j/7j): Synthesized according to GP 1. Purification by flash chromatography on silica gel with diethyl ether/petroleum ether, 2:1. Yield 23% (17 mg, 0.035 mmol), colorless oil, *d.r.* (**6j/7j**) 47:53. $[\alpha]_D^{23}$ = −26.96 (*c* = 0.46, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.05 (t, *J* =

7.6 Hz, 3 H, 6j-CH_3), 1.08 (t, J = 7.6 Hz, 3 H, 7j-CH_3), 1.34 (d, J = 7.2 Hz, 3 H, 6j-CH_3), 1.44 (d, J = 7.2 Hz, 3 H, 7j-CH_3), 2.25 (q, J = 7.2 Hz, 2 H, 6j-C$H_2$$CH_3$), 2.29 (q, J = 8.4 Hz, 2 H, 7j-C$H_2$$CH_3$), 2.49−2.57 (m, 1 H, CH_2), 2.70−2.90 (m, 1 H, CH_2), 2.98 (quint, J = 8.4 Hz, 1 H, 9j-CH), 3.21 (d, J = 11.6 Hz, 1 H, 6j-CH_2Se), 3.23 (d, J = 12.0 Hz, 1 H, 7j-CH_2Se), 3.38−3.45 (m, 1 H, 6j-CH), 3.76 (s, 3 H, 7j-OCH_3), 3.79 (s, 3 H, 6j-OCH_3), 3.88 (t, J = 8.8 Hz, 1 H, 6j-CH_2O), 4.04 (t, J = 8.4 Hz, 1 H, 7j-CH_2O), 4.13 (t, J = 8.4 Hz, 1 H, 7j-CH_2O), 4.21 (t, J = 8.4 Hz, 1 H, 6j-CH_2O), 4.76 (q, J = 6.8 Hz, 1 H, 7j-CH-Ar), 4.89 (q, J = 7.2 Hz, 1 H, 6j-CH-Ar), 6.60−7.40 (m, 9 H, Ar) ppm. **7j:** ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.1 ($CH_3$$CH_2$), 22.9 ($CH_2$$CH_3$), 25.6 ($CH_3$), 40.6 (CH), 41.3 ($CH_2$), 44.0 (CH-Ar), 45.4 ($CH_2$Se), 56.4 ($OCH_3$), 69.5 ($CH_2$O), 87.9 (C), 109.3 (CH-Ar), 120.0 (CH-Ar), 127.7 (CH-Ar), 128.6 (CH-Ar), 129.7 (CH-Ar), 144.5 (C-Ar), 146.1 (C-Ar), 150.1 (C-Ar), 159.7 (C-Ar), 178.3 (C=O) ppm. IR (NaCl): $\tilde{\nu}$ = 3364, 2962, 2922, 2360, 1707, 1569, 1463, 1423, 1260, 1057, 771, 695 cm^{-1}. MS (EI): m/z (%) = 398 (2) [M + NH_4]$^+$, 503 (1), 275 (22), 245 (16), 213 (42), 183 (100), 145 (23), 102 (36); HRMS: calcd. for $C_{23}H_{28}O_4SSe$ 503.0766, found 503.0763.

3-(Hydroxymethyl)-5-(iodomethyl)-5-phenyldihydro-3*H*-furan-2-one (8a/9a): Compound **5** (50 mg, 0.24 mmol) was dissolved in CH_2Cl_2 (8 mL), iodine monochloride (0.39 mmol, 1 M solution in CH_2Cl_2) was added, and the reaction mixture was stirred at room temperature for 15 min. The reaction was quenched with saturated aqueous $Na_2S_2O_3$ and extracted with CH_2Cl_2. The combined organic extracts were dried over $MgSO_4$, the solvent was evaporated, and the crude product was purified by flash chromatography on silica gel using *tert*-butyl methyl ether/petroleum ether (1:1) as eluent. Yield 74% (63 mg, 0.18 mmol); colorless white solid; m.p. 108−110 °C; *d.r.* (**8a/9a**) 76:24. The mixture was further purified by flash chromatography on silica gel using *tert*-butyl methyl ether/petroleum ether (1:1) as eluent to yield 56% (45 mg, 0.134 mmol) of the *cis* isomer (**8a**) and 18% (15 mg, 0.045 mmol) of a mixture of **8a** and **9a**. The X-ray structure of the isomer **8a** clarified the stereochemistry.[13] M.p. 108−110 °C; **8a:** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.56−2.77 (m, 3 H, CH_2C, CH), 3.58 (d, J = 11.2 Hz, 1 H, CH_2I), 3.63 (d, J = 11.2 Hz, 1 H, CH_2I), 3.77 (dd, J = 4.8, 11.2 Hz, 1 H, CH_2OH), 3.92 (dd, J = 4.0, 11.2 Hz, 1 H, CH_2OH), 7.25−7.40 (m, 5 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.1 (CH_2I), 37.1 (CH_2C), 43.3 (CH); 61.1 (CH_2OH), 85.1 (C), 125.4 (CH-Ar), 129.2 (CH-Ar), 129.3 (CH-Ar), 140.0 (C-Ar), 176.9 (C=O) ppm. **9a:** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.48−2.55 (m, 1 H, CH_2), 2.80−2.89 (m, 1 H, CH_2), 3.53−3.65 (m, 2 H, CH_2Se), 3.65 (dd, J = 5.6, 10.8 Hz, 1 H, CH_2OH), 3.83 (dd, J = 4.8, 11.2 Hz, 1 H, CH_2OH), 7.20−7.45 (m, 5 H, Ar) ppm. IR (thin film on NaCl): $\tilde{\nu}$ = 3437, 1768, 1644, 1448, 1152, 699, 650 cm^{-1}. MS (EI): m/z (%) = 350 (27) [M + NH_4]$^+$, 332 (11), 302 (3), 258 (3), 224 (75), 206 (100), 178 (26), 161 (16), 145 (13), 119 (11), 91 (5); HRMS: calcd. for $C_{12}H_{13}O_3I$ 350.0253, found 350.0250.

3-(Hydroxymethyl)-5-phenyl-5-(phenylselanylmethyl)dihydro-3*H*-furan-2-one (8b/9b): Synthesized according to GP 1. Purification by flash chromatography on silica gel with *tert*-butyl methyl ether/petroleum ether, 1:1. Yield 60% (52 mg, 0.144 mmol), white solid; m.p. 50−52 °C; *d.r.* (**8b/9b**) 83:17; **8b:** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.54−2.71 (m, 3 H, CH_2, CH), 3.35 (d, J = 13.2 Hz, 1 H, CH_2Se), 3.48 (d, J = 13.2 Hz, 1 H, CH_2Se), 3.75 (dd, J = 5.2, 11.2 Hz, 1 H, CH_2OH), 3.88 (dd, J = 4.0, 11.2 Hz, 1 H, CH_2OH), 7.10−7.40 (m, 10 H, 2 × Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 35.3 (CH_2), 40.0 (CH_2Se), 41.5 (CH), 59.8 (CH_2OH), 85.9 (C), 123.8 (CH-Ar), 126.4 (CH-Ar), 127.3 (CH-Ar), 128.1 (CH-Ar), 128.3 (CH-Ar), 129.1 (C-Ar), 132.2 (CH-Ar), 140.4 (C-Ar), 176.1 (C=O) ppm. ^{77}Se NMR (57.3 MHz, $CDCl_3$): δ = 259.7 ppm. **9b:** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.33−2.41 (m, 1 H, CH_2), 2.71−2.80 (m, 1 H, CH), 3.17 (quint, J = 5.6 Hz, 1 H, CH), 3.34 (d, J = 13.6 Hz, 1 H, CH_2Se), 3.38 (d, J = 13.2 Hz, 1 H, CH_2Se), 3.62 (dd, J = 6.0, 11.2 Hz, 1 H, CH_2OH), 3.78 (dd, J = 5.2, 11.6 Hz, 1 H, CH_2OH), 7.10−7.40 (m, 10 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 34.9 (CH_2), 40.3 (CH_2Se); 42.5 (CH), 60.5 (CH_2OH), 86.0 (C), 123.6 (CH-Ar), 126.5 (CH-Ar), 127.1 (CH-Ar), 127.6 (CH-Ar), 128.3 (CH-Ar), 128.9 (C-Ar), 132.0 (C-Ar), 142.2 (CH-Ar), 176.0 (C=O) ppm. ^{77}Se NMR (57.3 MHz, $CDCl_3$): δ = 258.5 ppm. IR (thin film on NaCl): $\tilde{\nu}$ = 3426, 3068, 2932, 1771, 1579, 1478, 1448, 1314, 1155, 1022, 969, 738, 701 cm^{-1}. MS (EI): m/z (%) = 380 (12) [M + NH_4]$^+$, 362 (13), 224 (81), 206 (100), 194 (32), 178 (37), 161 (28), 119 (35), 96 (20), 78 (20); HRMS: calcd. for $C_{18}H_{18}O_3Se$ 380.0765, found 380.0766.

3-(Hydroxymethyl)-5-{[2-(hydroxymethyl)phenyl]selanylmethyl}-5-phenyldihydro-3*H*-furan-2-one (8c/9c): Synthesized according to GP 1. Purification by flash chromatography on silica gel with ethyl acetate/petroleum ether, 2:1. Yield 51% (30 mg, 0.077 mmol); colorless oil; *d.r.* (**8c/9c**) 80:20. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.50−2.80 (m, 2 H, CH_2), 3.35 (d, J = 13.2 Hz, 1 H, CH_2Se), 3.50 (d, J = 13.2 Hz, 1 H, CH_2Se), 3.68 (dd, J = 4.4, 11.2 Hz, 1 H, 8c-CH_2OH), 3.76 (dd, J = 5.2, 11.2 Hz, 1 H, 9c-CH_2OH), 3.92 (dd, J = 3.6, 11.2 Hz, 1 H, 8c-CH_2OH), 4.05 (q, J = 12.4 Hz, 2 H, 9c-CH_2OH), 4.66 (q, J = 12.8 Hz, 2 H, 8c-CH_2OH-Ar), 7.05−7.58 (m, 9 H, 2 × Ar) ppm. **8c:** ^{13}C NMR (100 MHz, $CDCl_3$): δ = 36.6 (CH_2), 41.7 (CH_2Se), 43.1 (CH), 60.7 (CH_2OH), 65.7 (*C*H_2OH-Ar), 87.2 (C), 125.0 (C-Ar), 125.2 (CH-Ar), 128.6 (CH-Ar), 128.7 (CH-Ar), 129.0 (CH-Ar), 129.2 (CH-Ar), 130.6 (C-Ar), 135.2 (CH-Ar), 141.9 (CH-Ar), 143.1 (C-Ar), 177.5 (C=O) ppm. IR (NaCl): $\tilde{\nu}$ = 3376, 2359, 1758, 1643, 1446, 1236, 1145, 952, 766, 700 cm^{-1}. MS (EI): m/z (%) = 410 (2) [M + NH_4]$^+$, 166 (9), 128 (30), 105 (49), 91 (73), 79 (31), 42 (47); HRMS: calcd. for $C_{19}H_{20}O_4Se$ 410.0865, found 410.0866.

2-{[4-(Hydroxymethyl)-5-oxo-2-phenyltetrahydrofuran-2-yl]methylselanyl}benzoic Acid (8d/9d): Synthesized according to GP 1. Purification by flash chromatography on silica gel with ethyl acetate/petroleum ether, 1:1. Yield 23% (9 mg, 0.022 mmol), colorless oil; *d.r.* (**8d/9d**) 80:20. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.40−2.98 (m, 1 H, CH_2), 3.27 (quint, J = 4.8 Hz, 1 H, 8d-CH), 3.66 (d, J = 11.2 Hz, 1 H, 8d-CH_2Se), 3.73 (d, J = 11.2 Hz, 1 H, 8d-CH_2Se), 3.79 (dd, J = 4.4, 11.6 Hz, 1 H, 8d-CH_2OH), 3.86 (dd, J = 4.8, 11.2 Hz, 1 H, 9d-CH_2OH), 3.92 (dd, J = 4.0, 11.6 Hz, 1 H, 8d-CH_2OH), 7.22−8.10 (m, 9 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 35.3 (*C*H_2), 40.4 (CH_2Se), 42.9 (CH), 61.1 (CH_2OH), 85.6 (*C*), 125.5 (CH-Ar), 128.9 (CH-Ar), 129.1 (C-Ar), 129.2 (CH-Ar), 129.3 (CH-Ar), 129.4 (CH-Ar), 129.7 (CH-Ar), 130.6 (CH-Ar), 134.2 (C-Ar), 140.0 (CH-Ar), 172.0 (O=CAr), 177.1 (C=O) ppm. IR (NaCl): $\tilde{\nu}$ = 3428, 1770, 1688, 1599, 1579, 1453, 1423, 1328, 1292, 1157, 1097, 1067, 1032, 926, 766, 706 cm^{-1}.

Methyl 2-{[4-(Hydroxymethyl)-5-oxo-2-phenyltetrahydrofuran-2-yl]-methylselanyl}benzoate (8e/9e): Synthesized according to GP 1. Purification by flash chromatography on silica gel with ethyl acetate/petroleum ether, 1:2. Yield 31% (22 mg, 0.052 mmol); colorless oil; *d.r.* (**8e/9e**) 84:16; m.p. 140−142 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.40−2.59 (m, 1 H, 9e-CH_2), 2.59−2.76 (m, 3 H, 8e-CH_2, CH), 2.88−2.98 (m, 1 H, 9e-CH_2), 3.22 (quint, J = 8.4 Hz, 1 H, 9e-CH), 3.38 (d, J = 12.4 Hz, 1 H, CH_2Se), 3.47 (d, J = 12.4 Hz, 1 H, CH_2Se), 3.64 (dd, J = 4.9, 11.6 Hz, 1 H, 9e-CH_2OH), 3.75 (dd, J = 5.2, 11.2 Hz, 1 H, 8e-CH_2OH), 3.84 (s, 3 H, 8e-OCH_3), 3.85 (s, 3 H, 9e-OCH_3), 3.87 (dd, J = 3.9, 11.4 Hz, 1 H, 8e-CH_2OH), 7.10−7.95 (m, 9 H, Ar) ppm. **8e:** ^{13}C NMR (100 MHz,

$CDCl_3$): δ = 37.0 (CH_2), 38.2 (CH_2Se), 43.0 (CH), 52.8 (OCH_3), 61.2 (CH_2OH), 87.2 (C), 125.3 (CH-Ar), 125.5 (CH-Ar), 128.9 (CH-Ar), 129.0 (CH-Ar), 129.2 (CH-Ar), 131.8 (CH-Ar), 133.1 (C-Ar), 136.9 (C-Ar), 141.9 (C-Ar), 167.7 (C=O-Ar), 177.5 (C=O) ppm. IR (NaCl): $\tilde{\nu}$ = 3458, 2925, 1767, 1708, 1579, 1433, 1303, 1273, 1256, 1147, 1097, 1032, 750, 698 cm^{-1}. MS (EI): *m/z* (%) = 421 (9) $[M + H]^+$, 288 (9), 215 (100), 191 (12), 159 (6), 143 (6), 100 (5); HRMS: for $C_{20}H_{20}O_5Se$ calcd. 421.0549, found 421.0546.

3-(Hydroxymethyl)-5-{2-[(*R*)-(1-hydroxypropyl)phenyl]selanylmethyl}-5-phenyldihydro-3*H*-furan-2-one (8f/9f): Synthesized according to GP 1. Purification by flash chromatography on silica gel with *tert*-butyl methyl ether/petroleum ether, 2:1. Yield 40% (27 mg, 0.064 mmol); colorless oil; *d.r.* (**8f/9f**) 79:21. $[\alpha]_D^{22}$ = −8.0 (*c* = 0.40, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.84 (t, *J* = 7.6 Hz, 3 H, 9f-CH_3), 0.85 (t, *J* = 7.6 Hz, 3 H, 8f-CH_3), 1.49−1.76 (m, 2 H, CH_2CH_3), 2.35−2.67 (m, 2 H, 9f-CH_2), 2.57 (t, *J* = 11.6 Hz, 1 H, 8f-CH_2O), 2.85 (t, *J* = 11.6 Hz, 1 H, 8f-CH_2O), 2.58−2.67 (m, 1 H, CH), 3.32 (d, *J* = 13.6 Hz, 1 H, 9f-CH_2Se), 3.35 (d, *J* = 13.6 Hz, 1 H, 8f-CH_2Se), 3.45 (d, *J* = 14.0 Hz, 1 H, 8f-CH_2Se), 3.51 (d, *J* = 13.2 Hz, 1 H, 9f-CH_2Se), 3.62 (dd, *J* = 3.6, 11.6 Hz, 1 H, 9f-CH_2OH), 3.73 (dd, *J* = 4.8, 11.6 Hz, 1 H, 8f-CH_2OH), 3.92 (dd, *J* = 5.2, 11.6 Hz, 1 H, 9f-CH_2OH), 3.96 (dd, *J* = 4.0, 11.6 Hz, 1 H, 8f-CH_2OH), 4.98 (dd, *J* = 6.0, 13.2 Hz, 1 H, 8f-ArCHOH), 5.18 (t, *J* = 5.6 Hz, 1 H, 9f-ArCHOH), 7.05−7.55 (m, 9 H, Ar) ppm. **8f:** ^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.7 (CH_3), 32.2 (CH_2CH_3), 36.5 (CH_2), 42.6 (CH_2Se), 43.1 (CH), 60.7 (CH_2OH), 74.6 (CHOH), 87.5 (C), 125.1 (CH-Ar), 126.7 (CH-Ar), 128.5 (CH-Ar), 128.7 (CH-Ar), 129.1 (CH-Ar), 129.2 (CH-Ar), 129.8 (C-Ar), 135.3 (CH-Ar), 142.1 (C-Ar), 147.5 (C-Ar), 178.0 (C=O) ppm. IR (NaCl): $\tilde{\nu}$ = 3390, 3055, 2928, 1770, 1448, 1315, 1260, 1159, 1029, 970, 759, 701 cm^{-1}. MS (EI): *m/z* (%) = 420 (9) $[M]^+$, 403 (2), 224 (100), 206 (26), 136 (53); HRMS: calcd. for $C_{21}H_{34}O_4Se$ 420.0834, found 420.0838.

3-(Hydroxymethyl)-5-{[2-[(*S*)-1-(methoxymethoxy)propyl]phenyl]selanylmethyl}-5-phenyldihydrofuran-2-one (8g/9g): Synthesized according to GP 1. Purification by flash chromatography on silica gel with *tert*-butyl methyl ether/petroleum ether, 2:1. Yield 68% (47 mg, 0.101 mmol); colorless oil; *d.r.* (**8g/9g**) 85:15. $[\alpha]_D^{21}$ = −49.2 (*c* = 0.065, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 7.6 Hz, 3 H, 9 g-CH_3), 0.91 (t, *J* = 7.2 Hz, 3 H, 8 g-CH_3), 1.49−1.72 (m, 2 H, CH_2CH_3), 2.30−2.94 (m, 2 H, CH_2), 3.05−3.16 (m, 1 H, 9 g-CH), 3.30 (s, 3 H, 9 g-OCH_3), 3.31 (d, *J* = 11.2 Hz, 1 H, 9 g-CH_2Se), 3.36 (s, 3 H, 8 g-OCH_3), 3.53 (d, *J* = 13.2 Hz, 1 H, 9 g-CH_2Se), 3.63 (dd, *J* = 4.4, 12.8 Hz, 1 H, 8 g-CH_2OH), 3.73 (dd, *J* = 4.8, 11.2 Hz, 1 H, 9 g-CH_2OH), 4.48 (dd, *J* = 6.8, 10.0 Hz, 2 H, 8 g-OCH_2O), 4.99 (dd, *J* = 4.8, 8.0 Hz, 1 H, 8 g-CHO), 5.07 (dd, *J* = 4.8, 8.0 Hz, 1 H, 9 g-CH_2OH), 7.05−7.42 (m, 9 H, Ar) ppm. **8g:** ^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.9 (CH_3), 31.8 (CH_2CH_3), 35.5 (CH_2), 41.1 (CH_2Se), 43.3 (CH), 56.0 (OCH_3), 60.3 (CH_2OH), 78.3 (CHO), 86.9 (C), 94.7 (OCH_2O), 125.1 (CH-Ar), 125.2 (CH-Ar), 127.1 (CH-Ar), 128.4 (C-Ar), 128.5 (CH-Ar), 129.0 (CH-Ar), 130.2 (CH-Ar), 133.8 (CH-Ar), 142.4 (C-Ar), 144.4 (C-Ar), 177.2 (C=O) ppm. IR (NaCl): $\tilde{\nu}$ = 3472, 2922, 1770, 1644, 1448, 1158, 1104, 1029, 916, 756, 701 cm^{-1}. MS (EI): *m/z* (%) = 482 (55) $[M + NH_4]^+$, 464 (21), 456(29), 433 (91), 420 (55), 403 (68), 391 (100), 377 (26), 359 (47); HRMS: calcd. for $C_{23}H_{28}O_5Se$ 482.1440, found 482.1438.

5-{[2-[(*S*)-1-Hydroxyethyl]-6-methoxyphenyl]selanylmethyl}-3-(hydroxymethyl)-5-phenyldihydro-3*H*-furan-2-one (8h/9h): Synthesized according to GP 1. Purification by flash chromatography on silica gel with ethyl acetate/petroleum ether, 1:1. Yield 35% (23 mg, 0.053 mmol); colorless oil; *d.r.* (**8h/9h**) 85:15. $[\alpha]_D^{22}$ = −62.2 (*c* = 0.45, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.26 (d, *J* = 6.8 Hz, 3 H, 8 h-CH_3), 1.30 (d, *J* = 6.8 Hz, 3 H, 9 h-CH_3), 2.30−2.52 (m, 1 H, CH_2CH_3), 2.56−2.65 (m, 1 H, 9 h-CH), 2.82−3.00 (m, 1 H, CH_2), 3.18 (d, *J* = 14.0 Hz, 1 H, 8 h-CH_2Se), 3.35 (d, *J* = 14.0 Hz, 1 H, 9 h-CH_2Se), 3.43 (d, *J* = 14.0 Hz, 1 H, 9 h-CH_2Se), 3.58 (d, *J* = 14.0 Hz, 1 H, 8 h-CH_2Se), 3.70 (dd, *J* = 4.8, 11.6 Hz, 1 H, 8 h-CH_2OH), 3.80 (s, 3 H, 8 h-OCH_3), 3.82 (s, 3 H, 9 h-OCH_3), 3.93 (dd, *J* = 3.6, 11.6 Hz, 1 H, 9 h-CH_2OH), 3.95 (dd, *J* = 4.0, 11.6 Hz, 1 H, 8 h-CH_2OH), 5.36 (q, *J* = 6.4 Hz, 1 H, 8 h-CHOH-Ar), 5.56 (q, *J* = 6.4 Hz, 1 H, 9 h-CHOH-Ar), 6.70−7.40 (m, 8 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.4 (CH_3), 36.5 (CH_2), 39.3 (CH_2Se), 43.2 (CH), 56.5 (OCH_3), 60.4 (CH_2OH), 69.7 (CHOH-Ar), 87.8 (*C*), 109.9 (CH-Ar), 116.7 (C-Ar), 118.5 (CH-Ar), 125.1 (CH-Ar), 128.6 (CH-Ar), 128.9 (CH-Ar), 142.4 (C-Ar), 151.1 (C-Ar), 159.3 (C-Ar), 178.2 (C=O) ppm. IR (NaCl): $\tilde{\nu}$ = 3447, 2937, 1760, 1637, 1564, 1464, 1261, 1157, 1054, 916, 846, 786, 705 cm^{-1}. MS (EI): *m/z* (%) = 454 (12) $[M + NH_4]^+$, 436 (15), 419 (23), 312 (6), 286 (12), 260 (12), 254 (27), 246 (36); HRMS: calcd. for $C_{21}H_{24}O_5Se$ 454.1127, found 454.1131.

5-{[2-[(*R*)-1-(Ethylsulfanyl)ethyl]phenyl]selanylmethyl}-3-(hydroxymethyl)-5-phenyldihydro-3*H*-furan-2-one (8i/9i): Synthesized according to GP 1. Purification by flash chromatography on silica gel with diethyl ether/petroleum ether, 2:1. Yield 28% (19 mg, 0.042 mmol); colorless oil; d.r. (*cis*/*trans*) = 85:15. $[\alpha]_D^{21}$ = −11.7 (*c* = 0.29, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.09 (t, *J* = 7.2 Hz, 3 H, 8i-CH_3), 1.10 (t, *J* = 7.2 Hz, 3 H, 9i-CH_3), 1.44 (d, *J* = 7.2 Hz, 3 H, 9i-CH_3), 1.48 (d, *J* = 7.2 Hz, 3 H, 8i-CH_3), 2.31 (q, *J* = 7.6 Hz, 2 H, CH_2CH_3), 2.56−2.70 (m, 2 H, CH_2), 3.38 (d, *J* = 12.4 Hz, 1 H, 8i-CH_2Se), 3.48 (d, *J* = 12.8 Hz, 1 H, 8i-CH_2Se), 3.49 (d, *J* = 13.2 Hz, 1 H, 9i-CH_2Se), 3.65 (dd, *J* = 4.8, 12.0 Hz, 1 H, 9i-CH_2OH), 3.73 (dd, *J* = 4.8, 11.6 Hz, 1 H, 8i-CH_2OH), 3.79 (dd, *J* = 4.0, 12.0 Hz, 1 H, 9i-CH_2OH), 3.88 (dd, *J* = 3.6, 11.6 Hz, 1 H, 8i-CH_2OH), 4.48 (q, *J* = 6.8 Hz, 1 H, 9i-CH), 4.57 (q, *J* = 6.8 Hz, 1 H, 8i-CH), 7.00−7.50 (m, 9 H, Ar) ppm. **8i:** ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.0 (CH_3CH_2), 22.6 (CH_2CH_3), 25.6 (CH_3), 30.7 (CH), 41.5 (CH), 43.0 (CH_2Se), 61.2 (CH_2OH), 87.2 (C), 125.3 (CH-Ar), 127.7 (CH-Ar), 128.0 (CH-Ar), 128.6 (CH-Ar), 129.0 (CH-Ar), 131.2 (C-Ar), 134.8 (C-Ar), 141.8 (C-Ar), 146.2 (C-Ar), 177.5 (C=O) ppm. IR (NaCl): $\tilde{\nu}$ = 3453, 2961, 2915, 1776, 1464, 1442, 1261, 1157, 1025, 762, 701, 650 cm^{-1}. MS (EI): *m/z* (%) = 468 (4) $[M + NH_4]^+$, 245 (64), 206 (83), 194 (32), 180 (47), 167 (100), 145 (38), 136 (42), 119 (98), 108 (39), 78 (36); HRMS calcd. for $C_{22}H_{26}O_3SSe$ 468.1106, found 468.1104.

5-{[2-[(*R*)-1-(Ethylsulfanyl)ethyl]-6-methoxyphenyl]selanylmethyl}-3-(hydroxymethyl)-5-phenyldihydro-*3H*-furan-2-one (8j/9j): Synthesized according to GP 1. Purification by flash chromatography on silica gel with diethyl ether/petroleum ether, 2:1. Yield 21% (15 mg, 0.031 mmol); colorless oil; *d.r.* (**8j/9j**) 82:18. $[\alpha]_D^{23}$ = −49.2 (*c* = 0.59, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.08 (t, *J* = 7.6 Hz, 3 H, 9j-CH_3), 1.12 (t, *J* = 7.2 Hz, 3 H, 8j-CH_3), 1.39 (d, *J* = 7.2 Hz, 3 H, 8j-CH_3), 1.59 (d, *J* = 7.2 Hz, 3 H, 9j-CH_3), 2.19−2.37 (m, 2 H, CH_2CH_3), 2.49−2.62 (m, 2 H, CH_2), 2.98 (quintet, *J* = 8.4 Hz, 1 H, 9j-CH), 3.10 (dd, *J* = 3.2, 11.6 Hz, 1 H, 9j-CH_2OH), 3.23 (d, *J* = 12.4 Hz, 1 H, CH_2Se), 3.26 (d, *J* = 12.0 Hz, 1 H, CH_2Se), 3.30 (dd, *J* = 4.0, 12.0 Hz, 8j-CH_2OH), 3.77 (s, 3 H, 8j-OCH_3), 3.78 (dd, *J* = 4.0, 9.2 Hz, 1 H, 8j-CH_2OH) 3.79 (s, 3 H, 9j-OCH_3), 3.97 (dd, *J* = 4.0, 9.2 Hz, 1 H, 9j-CH_2OH), 4.56 (q, *J* = 6.8 Hz, 1 H, 9j-CH-Ar), 4.73 (q, *J* = 8.4 Hz, 1 H, 8j-CH-Ar), 6.60−7.40 (m, 9 H, Ar) ppm. **8j:** ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.7 (CH_3CH_2), 22.9 (CH_2S), 23.2 (CH_3), 40.4 (CH-Ar), 40.8 (CH_2), 48.0 (CH), 48.4 (CH_2Se), 53.7 (OCH_3), 60.9 (CH_2OH), 85.2 (C), 106.7 (CH-Ar), 117.3 (CH-Ar), 124.9 (CH-

Ar), 125.8 (CH-Ar), 126.0 (CH-Ar), 126.4 (CH-Ar), 127.1 (CH-Ar), 130.5 (CH-Ar), 137.6 (CH-Ar), 142.0 (C-Ar), 144.0 (C-Ar), 157.1 (C-Ar), 177.8 (C=O) ppm. IR (NaCl): $\tilde{\nu}$ = 3427, 2966, 2915, 2363, 1734, 1564, 1464, 1373, 1261, 1047, 1032, 755, 695, 650 cm^{-1}. MS (EI): *m/z* (%) = 398 (2) $[M + NH_4]^+$, 503 (23), 275 (38), 245 (16), 213 (100), 159 (26); HRMS calcd. for $C_{23}H_{28}O_4SSe$ 503.0766, found 503.0767.

Methyl 5-(Iodomethyl)-5-phenyltetrahydrofuran-3-carboxylate (10a): Synthesized according to the procedure for the synthesis of **8a/9a** using substrate **4**. Purification by flash chromatography on silica gel with *tert*-butyl methyl ether/petroleum ether, 1:2. Yield 93% (236 mg, 0.68 mmol); white solid; m.p. 69−71 °C; *d.r.* (*cis*/*trans*) 42:58. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.58 (d, *J* = 8.8 Hz, 1 H, CH_2C), 2.63 (d, *J* = 8.6 Hz, 1 H, CH_2C), 3.00 (quint, *J* = 8.4 Hz, 1 H, *cis*-CH), 3.35 (quint, *J* = 8.4 Hz, 1 H, *trans*-CH), 3.40 (d, *J* = 10.8 Hz, 1 H, *cis*-CH_2I), 3.45 (d, *J* = 11.2 Hz, 1 H, *cis*-CH_2I), 3.47 (s, 3 H, *cis*-OCH_3), 3.49 (d, *J* = 10.8 Hz, 1 H, *trans*-CH_2I), 3.55 (d, *J* = 10.8 Hz, 1 H, *trans*-CH_2I), 3.64 (s, 3 H, *trans*-OCH_3), 3.93 (t, *J* = 8.4 Hz, 1 H, *cis*-CH_2O), 4.08 (t, *J* = 8.4 Hz, 1 H, *trans*-CH_2O), 4.16 (t, *J* = 8.4 Hz, 1 H, *trans*-CH_2O), 4.24 (t, *J* = 8.4 Hz, 1 H, *cis*-CH_2O), 7.15−7.45 (m, 5 H, Ar) ppm. *trans*-**10a:** ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.6 (CH_2), 39.6 (CH_2O), 43.0 (OCH_3), 51.2 (CH), 68.5 (CH_2I), 84.4 (C), 124.2 (CH-Ar), 126.6 (CH-Ar), 127.4 (CH-Ar), 141.4 (C-Ar), 171.4 (C=O) ppm. IR (NaCl): $\tilde{\nu}$ = 3449, 2952, 1735, 1447, 1200, 1027, 763, 702 cm^{-1}. MS (EI): MS: *m/z* (%) = 364 (28) $[M + NH_4]^+$, 347 (5), 238 (100), 221 (56), 205 (29), 152 (14), 136 (10), 119 (21), 110 (10), 98 (13), 90 (18), 52 (60), 44 (65); HRMS: calcd. for $C_{13}H_{15}O_3I$ 364.0410, found 364.0414.

Methyl 5-Phenyl-5-(phenylselanylmethyl)tetrahydrofuran-3-carboxylate (10b): Synthesized according to GP 1. Purification by flash chromatography on silica gel with *tert*-butyl methyl ether/petroleum ether, 1:10. Yield 68% (318 mg, 085 mmol); white solid; m.p. 44−46 °C; *d.r.* (*cis*/*trans*) 39:61. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.49−2.70 (m, 3 H, CH_2C, *cis*-CH), 2.96 (quint, *J* = 8.4 Hz, 1 H, *trans*-CH), 3.20 (d, *J* = 12.4 Hz, 1 H, *cis*-CH_2Se), 3.31 (d, *J* = 12.0 Hz, 1 H, *trans*-CH_2Se), 3.34 (d, *J* = 12.4 Hz, 1 H, *cis*-CH_2Se), 3.40 (d, *J* = 12.0 Hz, 1 H, *trans*-CH_2Se), 3.47 (s, 3 H, *cis*-OCH_3), 3.62 (s, 3 H, *trans*-OCH_3), 3.91 (t, *J* = 8.4 Hz, 1 H, *cis*-CH_2O), 4.04 (t, *J* = 8.4 Hz, 1 H, *trans*-CH_2O), 4.13 (t, *J* = 8.4 Hz, 1 H, *trans*-CH_2O), 4.18 (t, *J* = 8.4 Hz, 1 H, *cis*-CH_2O), 7.00−7.40 (m, 10 H, Ar) ppm. *trans*-**10b:** ^{13}C NMR (100 MHz, $CDCl_3$): δ = 41.3 (CH_2), 42.3 (CH_2 Se), 44.2 (CH), 52.6 (OCH_3), 69.8 (CH_2O), 87.5 (C), 125.6 (CH-Ar), 127.1 (CH-Ar), 127.8 (CH-Ar), 128.8 (CH-Ar), 129.3 (CH-Ar), 131.6 (C-Ar), 133.1 (CH-Ar), 144.5 (C-Ar), 173.8 (C=O) ppm. IR (thin film on NaCl): $\tilde{\nu}$ = 3440, 1735, 1644, 1578, 1478, 1436, 1200, 1061, 1022, 737, 703 cm^{-1}. MS (EI): *m/z* (%) = 377 (56) $[M + H]^+$, 238 (56), 221 (37), 205 (63), 52 (39); HRMS: calcd. for $C_{19}H_{20}O_3Se$ 377.0656, found 377.0660.

Methyl 5-{[2-(Hydroxymethyl)phenyl]selanylmethyl}-5-phenyltetrahydrofuran-3-carboxylate (10c): Synthesized according to GP 1. Purification by flash chromatography on silica gel with diethyl ether/petroleum ether, 1:4. Yield 30% (11 mg, 0.027 mmol); colorless oil; *d.r.* (*cis*/*trans*) 48:52. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.52 (dd, *J* = 8.4 Hz, 2 H, *cis*-CH_2), 2.58 (d, *J* = 8.4 Hz, 2 H, *trans*-CH_2), 2.97 (q, *J* = 8.4 Hz, 1 H, *cis*-CH), 3.21 (d, *J* = 12.4 Hz, 1 H, *trans*-CH_2Se), 3.31 (d, *J* = 10.8 Hz, 1 H, *cis*-CH_2Se), 3.36 (d, *J* = 10.8 Hz, *trans*-CH_2Se), 3.39 (d, *J* = 12.4 Hz, 1 H, *cis*-CH_2Se), 3.46 (s, 3 H, *trans*-OCH_3), 3.62 (s, 3 H, *cis*-OCH_3), 3.95 (t, *J* = 8.8 Hz, 1 H, *cis*-CH_2O), 4.06 (t, *J* = 8.0 Hz, 1 H, *trans*-CH_2O), 4.08 (t, *J* = 8.0 Hz, 1 H, *trans*-CH_2O), 4.10 (t, *J* = 8.4 Hz, 1 H, *cis*-CH_2O), 4.58 (d, *J* = 12.4 Hz, 1 H, *cis*-CH_2OH-Ar), 4.59 (d, *J* = 12.4 Hz, 1 H, *trans*-CH_2OH-Ar), 4.66 (d, *J* = 12.4 Hz, 1 H, *trans*-CH_2OH-Ar), 4.69 (d, *J* = 12.4 Hz, 1 H, *cis*-CH_2OH-Ar) ppm. *trans*-**10c:** ^{13}C NMR (100 MHz, $CDCl_3$): δ = 41.6 (CH_2), 42.9 (CH_2Se), 45.2 (CH), 52.4 (CH_2O), 66.2 (CH_2OH-Ar), 69.8 (OCH_3), 87.2 (C), 125.5 (CH-Ar), 127.7 (CH-Ar), 127.9 (CH-Ar), 128.3 (CH-Ar), 128.7 (CH-Ar), 129.0 (CH-Ar), 129.2 (CH-Ar), 131.3 (C-Ar), 135.5 (CH-Ar), 143.2 (C-Ar), 144.2 (C-Ar), 145.0 (C-Ar), 173.0 (C=O) ppm. IR (NaCl): $\tilde{\nu}$ = 3430, 3056, 2946, 1732, 1584, 1446, 1373, 1333, 1273, 1200, 1122, 1027, 931, 755, 704 cm^{-1}. MS (EI): *m/z* (%) = 424 (2) $[M + NH_4]^+$, 389 (5), 238 (100), 221 (74), 205 (20), 143 (11), 108 (20); HRMS: calcd. for $C_{20}H_{22}O_4Se$ 424.1022, found 424.1020.

Methyl 5-[(2-Carboxyphenyl)selanylmethyl]-5-phenyltetrahydrofuran-3-carboxylate (10d): Synthesized according to GP 1. Purification by flash chromatography on silica gel with ethyl acetate/petroleum ether, 1:1. Yield 79% (30 mg, 0.072 mmol); white solid; m.p. 146−148 °C; *d.r.* (*cis*/*trans*) 50:50. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.62−2.78 (m, 2 H, CH_2), 2.98 (quint, *J* = 7.6 Hz, 1 H, *trans*-CH), 3.21 (d, *J* = 12.0 Hz, 1 H, *cis*-CH_2Se), 3.31 (d, *J* = 12.0 Hz, 1 H, *cis*-CH_2Se), 3.33 (d, *J* = 12.0 Hz, 1 H, *trans*-CH_2Se), 3.37 (d, *J* = 11.6 Hz, 1 H, *trans*-CH_2Se), 3.46 (s, 3 H, *cis*-OCH_3), 3.63 (s, 3 H, *trans*-OCH_3), 3.94 (t, *J* = 8.4 Hz, 1 H, *cis*-CH_2O), 4.05 (t, *J* = 8.4 Hz, 1 H, *trans*-CH_2O), 4.17 (t, *J* = 7.6 Hz, 1 H, *trans*-CH_2O), 4.22 (t, *J* = 8.4 Hz, 1 H, *cis*-CH_2O), 7.10−8.10 (m, 9 H, Ar) ppm. *trans*-**10d:** ^{13}C NMR (100 MHz, $CDCl_3$): δ = 36.9 (CH_2), 39.8 (CH_2Se), 42.8 (CH), 50.9 (OCH_3), 68.4 (CH_2O), 85.9 (C), 123.7 (CH-Ar), 124.0 (CH-Ar), 126.3 (CH-Ar), 126.6 (CH-Ar), 127.4 (CH-Ar), 131.4 (CH-Ar), 132.1 (CH-Ar), 137.9 (C-Ar), 143.1 (C-Ar), 144.3 (C-Ar), 170.4 (O=CAr), 171.8 (C=O) ppm. IR (NaCl): $\tilde{\nu}$ = 2946, 1732, 1584, 1558, 1462, 1428, 1373, 1256, 1207, 1142, 1033, 741, 703 cm^{-1}. MS (EI): *m/z* (%) = 438 (19) $[M + NH_4]^+$, 318 (19), 238 (100), 221 (74), 205 (18), 143 (8), 105 (6), 78 (5); HRMS: calcd. for $C_{20}H_{20}O_5Se$ 438.0814, found 438.0815.

Methyl 5-{[2-(Methoxycarbonyl)phenyl]selanylmethyl}-5-phenyltetrahydrofuran-3-carboxylate (10e): Synthesized according to GP 1. Purification by flash chromatography on silica gel with ethyl acetate/petroleum ether, 1:2. Yield 79% (31 mg, 0.072 mmol); white solid; m.p. 140−142 °C; *d.r.* (*cis*/*trans*) 48:52. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.60−2.80 (m, 2 H, CH_2), 2.97 (quint, *J* = 7.6 Hz, 1 H, *trans*-CH), 3.19 (d, *J* = 11.6 Hz, 1 H, *cis*-CH_2Se), 3.29 (d, *J* = 12.0 Hz, 1 H, *cis*-CH_2Se), 3.30 (d, *J* = 11.6 Hz, 1 H, *trans*-CH_2Se), 3.34 (d, *J* = 11.6 Hz, 1 H, *trans*-CH_2Se), 3.46 (s, 3 H, *cis*-OCH_3), 3.62 (s, 3 H, *trans*-OCH_3), 3.83 (s, 3 H, *cis*-OCH_3-Ar), 3.85 (s, 3 H, *trans*-OCH_3-Ar), 3.92 (t, *J* = 8.4 Hz, 1 H, *cis*-CH_2O), 4.05 (t, *J* = 8.4 Hz, 1 H, *trans*-CH_2O), 4.15 (t, *J* = 7.6 Hz, 1 H, *trans*-CH_2O), 4.20 (t, *J* = 8.4 Hz, 1 H, *cis*-CH_2O), 7.05−7.95 (m, 9 H, Ar) ppm. *trans*-**10e:** ^{13}C NMR (100 MHz, $CDCl_3$): δ = 38.2 (CH_2), 39.3 (CH_2Se), 41.5 (CH), 44.1 (OCH_3-Ar), 52.7 (OCH_3), 69.7 (CH_2O), 86.9 (C), 125.0 (CH-Ar), 125.5 (CH-Ar), 127.8 (CH-Ar), 128.9 (CH-Ar), 131.8 (CH-Ar), 132.9 (CH-Ar), 138.5 (C-Ar), 144.6 (C-Ar), 145.9 (C-Ar), 167.7 (O=CAr), 173.2 (C=O) ppm. IR (NaCl): $\tilde{\nu}$ = 3428, 2946, 1735, 1710, 1579, 1458, 1434, 1273, 1253, 1202, 1052, 1027, 740 cm^{-1}. MS (EI): *m/z* (%) = 452 (100) $[M + NH_4]^+$, 435 (30), 403 (3), 391 (5); HRMS: calcd. for $C_{21}H_{22}O_5Se$ 452.0971, found 452.0971.

Methyl 5-{[2-[(*S*)-1-Hydroxypropyl]phenyl]selanylmethyl}-5-phenyltetrahydrofuran-3-carboxylate (10f): Synthesized according to GP 1. Purification by flash chromatography on silica gel with *tert*-butyl methyl ether/petroleum ether, 1:2. Yield 78% (37 mg, 0.11 mmol); colorless oil; *d.r.* (*cis*/*trans*) 30:70. $[\alpha]_D^{23}$ = −6.71 (*c* = 0.69, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.85 (t, *J* = 7.2 Hz, 3 H, *trans*-CH_3), 0.83 (t, *J* = 7.2 Hz, 3 H, *cis*-CH_3), 1.55−1.70 (m, 2 H,

CH_2CH_3), 2.35−2.41 (m, 1 H, *trans*-CH_2), 2.47−2.66 (m, 4 H, *cis*-CH_2, *cis*-CH, *trans*-CH_2), 2.86−3.02 (quint, J = 8.4 Hz, 1 H, *trans*-CH), 3.25 (d, J = 12.4 Hz, 1 H, *trans*-CH_2Se), 3.29 (d, J = 12.4 Hz, 1 H, *trans*-CH_2Se), 3.32 (d, J = 12.4 Hz, 1 H, *cis*-CH_2Se), 3.38 (d, J = 12.0 Hz, 1 H, *cis*-CH_2Se), 3.46 (s, 3 H, *trans*-OCH_3), 3.62 (s, 3 H, *cis*-OCH_3), 3.90 (t, J = 8.4 Hz, 1 H, *cis*-CH_2O), 4.00−4.11 (m, 2 H, *trans*-CH_2O), 4.19 (t, J = 8.0 Hz, 1 H, *cis*-CH_2O), 6.95−7.40 (m, 9 H, Ar) ppm. *trans*-**10f:** ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.33 (CH_3), 30.2 (CH_2CH_3), 40.1 (CH_2), 42.8 (CH), 43.9 (CH_2Se), 51.2 (OCH_3), 68.4 (CH_2O), 73.1 (CHOH-Ar), 85.7 (C), 124.2 (CH-Ar), 125.1 (CH-Ar), 126.2 (CH-Ar), 126.8 (CH-Ar), 127.2 (CH-Ar), 127.3 (CH-Ar), 129.0 (C-Ar), 133.1 (CH-Ar), 143.8 (C-Ar), 145.2 (C-Ar), 171.6 (C=O) ppm. IR (NaCl): $\tilde{\nu}$ = 3478, 2958, 2876, 1736, 1585, 1446, 1200, 1052, 1027, 977, 756, 703 cm^{-1}. MS (EI): *m*/*z* (%) = 433 (1) $[M]^+$, 416 (67), 391 (2), 222 (100), 198 (35); HRMS: calcd. for $C_{22}H_{26}O_4Se$ 434.0991, found 434.0999.

Methyl 5-{(2-[(*S*)-1-(Methoxymethoxy)propyl]phenyl)selanylmethyl}-5-phenyltetrahydrofuran-3-carboxylate (10g): Synthesized according to GP 1. Purification by flash chromatography on silica gel with ethyl acetate/petroleum ether, 1:1. Yield 41% (18 mg, 0.038 mmol); colorless oil; *d.r.* (*cis*/*trans*) 44:56. $[\alpha]_D^{21}$ = −81.8 (c = 0.34, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, J = 7.6 Hz, 3 H, CH_3), 1.55−1.70 (m, 2 H, CH_2CH_3), 2.53−2.73 (m, 2 H, CH_2), 2.97 (quint, J = 7.6 Hz, 1 H, CH), 3.18 (d, J = 12.0 Hz, 1 H, *cis*-CH_2Se), 3.29 (d, J = 12.0 Hz, 1 H, *trans*-CH_2Se), 3.32 (d, J = 12.4 Hz, 1 H, *trans*-CH_2Se), 3.40 (d, J = 12.0 Hz, 1 H, *cis*-CH_2Se), 3.48 (s, 3 H, *cis*-OCH_3), 3.62 (s, 3 H, *trans*-OCH_3), 3.92 (t, J = 8.4 Hz, 1 H, *cis*-CH_2O), 4.05 (t, J = 8.4 Hz, 1 H, *trans*-CH_2O), 4.11 (t, J = 8.0 Hz, 1 H, *trans*-CH_2O), 4.17 (t, J = 8.4 Hz, 1 H, *cis*-CH_2O), 4.38 (dd, J = 3.6, 6.4 Hz, 1 H, OCH_2O), 4.45 (dd, J = 3.6, 6.8 Hz, 1 H, OCH_2O), 4.90 (t, J = 7.6 Hz, 1 H, *cis*-ArCHOH), 4.92 (t, J = 7.6 Hz, 1 H, *trans*-ArCHOH), 7.00−7.40 (m, 9 H, Ar) ppm. *trans*-**10g:** ^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.9 (CH_3), 31.0 (CH_2CH_3), 41.1 (CH_2), 41.6 (CH_2Se), 45.3 (CH), 52.3 (OCH_3), 56.0 (OCH_3-Ar), 69.7 (CH_2O), 78.6 (ArCHOH), 87.1 (C), 95.0 (OCH_2O), 125.6 (CH-Ar), 126.9 (CH-Ar), 127.6 (CH-Ar), 127.8 (CH-Ar), 127.9 (CH-Ar), 128.2(C-Ar), 128.7 (CH-Ar), 130.9 (CH-Ar), 134.1 (C-Ar), 144.5 (C-Ar), 173.2 (C=O) ppm. IR (NaCl): $\tilde{\nu}$ = 3377, 2948, 2360, 1737, 1567, 1501, 1439, 1404, 1346, 1240, 1201, 1175, 1102, 1032, 958, 911, 807 cm^{-1}. MS (EI): *m*/*z* (%) = 496 (100) $[M + NH_4]^+$, 447 (55), 417 (86), 358 (91), 340 (32), 312 (26); HRMS: calcd. for $C_{24}H_{30}O_5SSe$ 496.1597, found 496.1599.

5-{[2-((*S*)-1-Hydroxyethyl)-6-methoxyphenyl]selanylmethyl}-5-phenyltetrahydrofuran-3-carboxylic Acid (10h): Synthesized according to GP 1. Purification by flash chromatography on silica gel with ethyl acetate/petroleum ether, 1:1. Yield 38% (21 mg, 0.047 mmol); colorless oil; *d.r.* (*cis*/*trans*) 30:70. $[\alpha]_D^{23}$ = +55 (c = 0.04, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.28 (d, J = 6.8 Hz, 3 H, *cis*-CH_3), 1.30 (d, J = 6.8 Hz, 3 H, *trans*-CH_3), 2.30−2.72 (m, 2 H, CH_2C), 2.94 (quint, J = 6.8 Hz, 1 H, *trans*-CH), 3.29 (d, J = 12.4 Hz, 1 H, *cis*-CH_2Se), 3.35 (d, J = 12.8 Hz, 1 H, *cis*-CH_2Se), 3.48 (s, 3 H, *cis*-OCH_3), 3.62 (s, 3 H, *trans*-OCH_3), 3.80 (s, 3 H, *trans*-$ArOCH_3$), 3.81 (s, 3 H, *cis*-$ArOCH_3$), 3.96 (t, J = 8.4 Hz, 1 H, *cis*-CH_2O), 3.98 (t, J = 8.0 Hz, 1 H, *trans*-CH_2O), 4.04 (t, J = 8.0 Hz, 1 H, *trans*-CH_2O), 4.21 (t, J = 8.4 Hz, 1 H, *cis*-CH_2O), 5.18 (d, J = 6.4 Hz, 1 H, *trans*-ArCHOH), 5.22 (d, J = 6.8 Hz, 1 H, *cis*-ArCHOH), 6.60−7.30 (m, 8 H, Ar) ppm. *trans*-**10h:** ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.6 (CH_3), 40.0 (CH_2C), 41.8 (CH_2Se), 44.1 (CH), 52.6 (OCH_3), 56.4 (CHOH), 69.7 (CH_2O), 88.0 (CCH_2Se), 109.8 (CH-Ar), 118.3 (C-Ar), 125.5 (CH-Ar), 127.4 (CH-Ar), 128.5 (CH-Ar), 129.9 (CH-Ar), 145.4 (C-Ar), 150.6 (C-Ar), 159.7 (C-Ar), 174.0 (C=O) ppm. IR (NaCl): $\tilde{\nu}$ = 3440, 1730, 1644, 1463, 1260, 1057 cm^{-1}. MS (EI): *m*/*z* (%) = 446 (27) $[M]^+$, 432 (20), 246 (74), 228 (100); HRMS: calcd. for $C_{22}H_{26}O_5Se$ 446.0967, found 446.0956.

Methyl 5-{[2-[(*R*)-1-(Ethylsulfanyl)ethyl]phenyl]selanylmethyl}-5-phenyltetrahydrofuran-3-carboxylate (10i): Synthesized according to GP 1. Purification by flash chromatography on silica gel with diethyl ether/petroleum ether, 1:2. Yield 40% (26 mg, 0.056 mmol); colorless oil; *d.r.* (*cis*/*trans*) 33:67. $[\alpha]_D^{23}$ = −8.08 (c = 1.04, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.06 (t, J = 7.2 Hz, 3 H, *trans*-CH_3), 1.07 (t, J = 7.2 Hz, 3 H, *cis*-CH_3), 1.40 (d, J = 7.2 Hz, 3 H, *cis*-CH_3),1.45 (d, J = 7.2 Hz, 3 H, *trans*-CH_3), 1.47 (t, J = 7.2 Hz, 3 H, *trans*-CH_3), 1.59 (t, J = 7.2 Hz, 3 H, *cis*-CH_3), 2.27 (m, 1 H, *cis*-CH), 2.50−2.71 (m, 2 H, CH_2), 2.97 (m, 1 H, *trans*-CH), 3.20 (d, J = 12.0 Hz, 1 H, *cis*-CH_2Se), 3.31 (d, J = 12.0 Hz, 1 H, *trans*-CH_2Se), 3.32 (d, J = 12.0 Hz, 1 H, *trans*-CH_2Se), 3.37 (d, J = 12.0 Hz, 1 H, *cis*-CH_2Se), 3.48 (s, 3 H, *cis*-OCH_3), 3.63 (s, 3 H, *trans*-OCH_3), 3.92 (t, J = 8.8 Hz, 1 H, *cis*-CH_2O), 4.05 (t, J = 8.8 Hz, 1 H, *trans*-CH_2O), 4.13 (t, J = 8.0 Hz, 1 H, *trans*-CH_2O), 4.17 (t, J = 8.4 Hz, 1 H, *cis*-CH_2O), 4.52 (q, J = 6.8 Hz, 1 H, *cis*-ArCH), 4.59 (q, J = 6.8 Hz, 1 H, *trans*-ArCH), 6.90−7.40 (m, 9 H, Ar) ppm. *trans*-**10i:** ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.7 (CH_3CH_2), 21.4 (CH_2CH_3), 24.2 (CH_3), 28.7 (ArCH), 40.4 (CH_2), 42.8 (CH_2Se), 44.0 (CH), 51.1 (OCH_3), 68.4 (CH_2O), 86.1 (C), 124.1 (CH-Ar), 126.0 (CH-Ar), 126.3 (CH-Ar), 126.6 (CH-Ar), 127.3 (CH-Ar), 130.6 (CH-Ar), 132.6 (C-Ar), 143.0 (C-Ar), 144.0 (CH-Ar), 144.5 (C-Ar), 172.4 (C=O) ppm. IR (NaCl): $\tilde{\nu}$ = 3046, 2966, 2925, 2865, 1737, 1584, 1494, 1446, 1368, 1268, 1199, 1057, 1022, 761, 705 cm^{-1}. MS (EI): *m*/*z* (%) = 482 (18) $[M + NH_4]^+$, 403 (58), 238 (100), 221 (68), 205 (27), 167 (11), 122 (8); HRMS: calcd. for $C_{23}H_{28}O_3SSe$ 482.1263, found 482.1270.

Methyl 5-{[2-[(*R*)-1-(Ethylsulfanyl)ethyl]-6-methoxyphenyl]selanylmethyl}-5-phenyltetrahydrofuran-3-carboxylate (10j): Synthesized according to GP 1. Purification by flash chromatography on silica gel with diethyl ether/petroleum ether, 1:1. Yield 38% (24 mg, 0.046 mmol); colorless oil; *d.r.* (*cis*/*trans*) 42:58. $[\alpha]_D^{23}$ = −9.56 (c = 0.126, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.06 (t, J = 7.6 Hz, 3 H, *cis*-CH_3), 1.10 (t, J = 7.6 Hz, 3 H, *trans*-CH_3), 1.36 (d, J = 6.4 Hz, 3 H, CH_3), 1.42 (q, J = 6.8 Hz, 2 H, CH_2CH_3), 2.47−2.57 (m, 1 H, CH_2), 2.67−2.74 (m, 1 H, CH_2), 2.95 (quint, J = 8.4 Hz, 1 H, *cis*-CH), 3.76 (d, J = 12.0 Hz, 1 H, CH_2Se), 3.80 (d, J = 12.8 Hz, 1 H, CH_2Se), 3.77 (s, 3 H, *trans*-OCH_3), 3.80 (s, 3 H, *cis*-OCH_3), 3.91 (t, J = 8.4 Hz, 1 H, *cis*-CH_2O), 4.03 (t, J = 8.4 Hz, 1 H, *trans*-CH_2O), 4.11 (t, J = 8.0 Hz, 1 H, *trans*-CH_2O), 4.20 (t, J = 8.0 Hz, 1 H, *cis*-CH_2O), 4.87 (q, J = 6.8 Hz, 1 H, ArCH), 6.60−7.40 (m, 9 H, Ar) ppm. *trans*-**10j:** ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.1 (CH_3CH_2), 23.1 (CH_3) 25.6 (CH_2), 40.9 (ArCH), 43.4 (CH_2C), 44.1 (CH), 45.6 (CH_2Se), 52.5 (OCH_3), 56.4 ($ArOCH_3$), 69.7 (CH_2O), 87.3 (C), 109.3 (CH-Ar), 119.9 (C-Ar), 125.5 (CH-Ar), 127.6 (CH-Ar), 128.6 (CH-Ar), 128.7 (CH-Ar), 129.8 (CH-Ar), 144.2 (C-Ar), 146.5 (C-Ar), 159.1 (C-Ar), 173.8 (C=O) ppm. IR (NaCl): $\tilde{\nu}$ = 3418, 2950, 1736, 1568, 1464, 1373, 1261, 1202, 1050, 1022, 786, 761, 730, 704 cm^{-1}. MS (EI): *m*/*z* (%) = 511 (15) $[M + NH_4]^+$, 433 (34), 275 (23), 238 (100), 221 (71), 205 (30), 152 (18); HRMS: calcd. for $C_{24}H_{30}O_4SSe$ 511.1030, found 511.1053.

Methyl 2-[(*tert*-Butyldimethylsilanyl)oxymethyl]-4-phenylpent-4-enoate: Compound **5** (250 mg, 1.14 mmol) was dissolved in DMF (6.5 mL), treated with *tert*-butyldimethylsilyl chloride (196 mg, 1.3 mmol) and imidazole (176 mg, 2.6 mmol), and stirred at room temperature overnight. The mixture was diluted with diethyl ether (25 mL) and washed with saturated aqueous NaCl. The organic

layer was dried with $MgSO_4$, and after evaporation of the solvent the crude product was purified by flash chromatography on silica gel using *tert*-butyl methyl ether/petroleum ether (1:4) as eluent. The product (yellow oil) was isolated in 89% yield (340 mg, 1.02 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.00 [s, 6 H, $Si(CH_3)_2$], 0.85 [s, 9 H, $C(CH_3)_3$], 2.65−2.75 (m, 1 H, CH), 2.75−2.88 (m, 2 H, CH_2), 3.60 (s, 3 H, OCH_3), 3.64−3.78 (m, 2 H, CH_2O), 5.03 (d, J = 1.2 Hz, 1 H, $=CH_2$), 5.22 (d, J = 0.8 Hz, 1 H, $=CH_2$), 7.23−7.40 (m, 5 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = −0.50 ($SiMe_2$), 18.6 (CMe_3), 26.1 [$C(CH_3)_3$], 34.3 (CH_2), 47.4 (CH), 51.8 (OCH_3), 63.7 (CH_2O), 114.9 ($=CH_2$), 126.6 (CH-Ar), 128.0 (CH-Ar), 128.8 (CH-Ar), 140.7 (C), 146.0 (C-Ar), 174.9 (C=O) ppm. IR (thin film on NaCl): $\tilde{\nu}$ = 3420, 2954, 2857, 1739, 1629, 1495, 1472, 1435, 1387, 1361, 1256, 1205, 1169, 1106, 1006, 901, 837, 777, 707 cm^{-1}. MS (EI): *m*/*z* (%) = 335 (100) [M + H]$^+$, 277 (11), 245 (4), 220 (3), 203 (9), 159 (2), 132 (2), 106 (3), 91 (3), 76 (2), 58 (2), 52 (19), 44 (2); HRMS: calcd. for $C_{19}H_{30}O_3Si$ 335.2042, found 335.2040.

2-[(*tert*-Butyldimethylsilanyl)oxymethyl]-4-phenylpent-4-enoic Acid: Methyl 2-[(*tert*-butyldimethylsilanyl)oxymethyl]-4-phenylpent-4-enoate (268 mg, 0.8 mmol) was dissolved in methanol (7.5 mL), treated at 0 °C with aqueous KOH (3.5 mL, 30%), and stirred at room temperature overnight. Water (15 mL) was added, and the solution was washed with diethyl ether (15 mL). The aqueous layer was cooled to 0 °C, and CH_2Cl_2 (15 mL) was added followed by 5 N HCl until pH < 5. The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 15 mL). The combined organic phases were dried with $MgSO_4$, the solvent was evaporated, and the crude product was purified by flash chromatography on silica gel using *tert*-butyl methyl ether/petroleum ether (1:4) as eluent. The product was obtained as a yellow solid in 59% yield (150 mg, 0.47 mmol) together with **5** (30%, 49 mg, 0.24 mmol). M.p. 46−48 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.00 [s, 6 H, $Si(CH_3)_2$], 0.85 [s, 9 H, $C(CH_3)_3$], 2.62−2.79 (m, 2 H, CH_2), 2.91 (dd, J = 7.0, 14.4 Hz, 1 H, CH), 3.75 (d, J = 5.6 Hz, 2 H, CH_2O), 5.13 (s, 1 H, $=CH_2$), 5.32 (s, 1 H, $=CH_2$), 7.22−7.42 (m, 5 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.1 [$C(CH_3)_3$], 24.7 [$C(CH_3)_3$], 32.5 (CH_2), 45.4 (CH), 61.8 (CH_2O), 113.7 ($C=CH_2$), 125.2 (CH-Ar), 126.7 (CH-Ar), 127.4 (CH-Ar), 139.1 ($C=CH_2$), 144.2 (C-Ar), 178.7 (C=O) ppm. IR (thin film on NaCl): $\tilde{\nu}$ = 3386, 2955, 1709, 1638, 1470, 1256, 1110, 835, 777 cm^{-1}. MS (EI): *m*/*z* (%) = 321 (58) [M + H]$^+$, 263 (30), 245 (4), 224 (5), 189 (3), 171 (2), 143 (3), 118 (2), 91 (5), 75 (2); HRMS: calcd. for $C_{18}H_{28}O_3Si$ 321.1886, found 321.1882.

3-[(*tert*-Butyldimethylsilanyl)oxymethyl]-5-phenyl-5-(phenylselanylmethyl)dihydrofuran-2-one (11b): Synthesized according to GP1. Purification by flash chromatography on silica gel with *tert*-butyl methyl ether/petroleum ether, 1:4. Yield 24%, (18 mg, 0.04 mmol); white solid; m.p. 41−43 °C; *d.r.* (*cis*/*trans*) 68:32. ^{1}H NMR (400 MHz, $CDCl_3$): δ = −0.85 [d, J = 3.2 Hz, 6 H, *trans*-$Si(CH_3)_2$], 0.00 [d, J = 3.2 Hz, 6 H, *cis*-$Si(CH_3)_2$], 0.60 [s, 9 H, *trans*-$C(CH_3)_3$], 0.80 [s, 9 H, *cis*-$C(CH_3)_3$], 2.52−2.75 (m, 3 H, CH_2C, *cis*-CH), 3.05−3.13 (m, 1 H, *trans*-CH), 3.37 (d, J = 12.8 Hz, 1 H, CH_2Se), 3.46 (d, J = 12.8 Hz, 1H CH_2Se), 3.63 (dd, J = 3.2, 10.0 Hz, 1 H, *trans*-CH_2OSi), 3.72 (dd, J = 3.2, 10.4 Hz, 1 H, *cis*-CH_2OSi), 3.80 (dd, J = 4.8, 10.0 Hz, 1 H, *trans*-CH_2OSi), 3.91 (dd, J = 4.4, 10.0 Hz, 1 H, *cis*-CH_2OSi), 7.10−7.50 (m, 10 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.3 [$C(CH_3)_3$], 24.8 [$C(CH_3)_3$], 35.7 (CH_2), 40.1 (CH_2Se), 42.1 (CH), 59.8 (CH_2OSi), 85.2 (C), 123.6 (CH-Ar), 124.0 (CH-Ar), 126.2 (CH-Ar), 127.1 (CH-Ar), 127.5 (CH-Ar), 128.2 (CH-Ar), 132.2 (CH-Ar), 141.1 (C-Ar), 175.0 (C=O) ppm. IR (thin film on NaCl): $\tilde{\nu}$ = 3443, 2976, 2855, 1778, 1649, 1463, 1258, 1112, 740 cm^{-1}. MS (EI): *m*/*z* (%) = 477 (35) [M + H]$^+$, 419 (7), 338 (84), 321 (100), 263 (23), 222 (36), 206 (23), 164 (15), 132 (44), 119 (37), 91 (22), 78 (13); HRMS: calcd. for $C_{24}H_{32}O_3SeSi$ 477.1364, found 477.1365.

5-(Iodomethyl)-3-methylene-5-phenyldihydrofuran-2-one (12): Sodium hydride (18.6 mg, 0.15 mmol) was suspended in THF (5 mL), and **8a** (0.056 mmol, 18.6 mg) was added. This reaction mixture was stirred at room temperature for 5 h, quenched with water, and extracted with diethyl ether (3 × 10 mL). The combined organic extracts were dried over $MgSO_4$, and the solvent was evaporated to produce a pale yellow solid, which was purified by flash chromatography on silica gel with ethyl acetate/ petroleum ether, 1:2 to produce a pale yellow solid in 32% yield (16 mg, 0.018 mmol). M.p. 66−68 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.03 (tt, J = 2.8, 2.8 Hz, 1 H, CH_2), 3.47 (tt, J = 2.8, 2.8 Hz, 1 H, CH_2), 3.66 (dd, J = 7.2, 12.0 Hz, 1 H, CH_2I), 3.81 (dd, J = 3.6, 12.4 Hz, 1 H, CH_2I), 5.59 (t, J = 2.8 Hz, 1 H, $=CH_2$), 6.18 (t, J = 2.8 Hz, 1 H, $=CH_2$), 7.22−7.38 (m, 5 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 37.0 (CH_2), 69.7 (CH_2I), 86.5 (C), 122.9 ($HC=CH_2$), 125.3 (CH-Ar), 128.7 (CH-Ar), 129.2 (CH-Ar), 135.0 ($CH=CH_2$), 140.9 (C-Ar), 170.1 (C=O) ppm. IR (NaCl): $\tilde{\nu}$ = 2931, 2853, 1767, 1456, 1270, 1116, 1011, 808 cm^{-1}. MS (EI): *m*/*z* (%) = 315 (35) [M]$^+$, 187 (34), 173 (100), 141 (21), 128 (12), 115 (19), 105 (60), 91 (25), 77 (14), 51 (17), 40 (25); HRMS: calcd. for $C_{12}H_{11}O_2I$ 332.0142, found 332.0147.

Electrophile 13: Synthesized from 2,2′-diselenobis(benzyl alcohol).[17a]

Electrophile 14: Synthesized from 2,2′-diselenobis(benzoic acid).[17b]

Electrophile 15: Synthesized from 2,2′-diselenobis(benzoic acid methyl ester).[17c]

Electrophile 16: Synthesized from (*S*,*S*)-bis{[2-(1-hydroxypropyl)phenyl] diselenide}.[21]

Electrophile 17: Synthesized from (*S*,*S*)-bis{[2-[1-(methoxymethoxy)propyl]phenyl] diselenide}.[5]

Electrophile 18: Synthesized from (*S*,*S*)-bis{[2-(1-hydroxyethyl)-6-methoxyphenyl] diselenide}.[5]

Electrophile 19: Synthesized from (*R*,*R*)-bis{[2-[1-(ethylsulfanyl)-ethyl]phenyl] diselenide}.

(*R*)-1-Bromo-2-[1-(ethylsulfanyl)ethyl]benzene: In a dry flask at −20 °C (*S*)-2-(2-bromophenyl)-ethanol[22] (2.0 g, 9.95 mmol), potassium hydroxide (1.11 g, 19.7 mmol), and *p*-toluenesulfonyl chloride (2.15 g, 11 mmol) were dissolved in diethyl ether/THF (1:1) (40 mL), and the reaction mixture was stirred at −20 °C for 24 h. At −20 °C sodium ethanethiolate (1.04 g, 12.4 mmol) was added, and the reaction mixture was warmed up to room temperature and stirred for an additional 14 h. The reaction was quenched with water (25 mL) and extracted with diethyl ether (3 × 25 mL). The collected organic extracts were dried over $MgSO_4$, and the solvent was evaporated to produce a yellow oil, which was further purified by flash chromatography on silica gel with petroleum ether to obtain a colorless oil. Yield 65% (1.59 g, 6.46 mmol). HPLC conditions: Chiracel OD-H, flow rate: 0.5 ml min^{-1}, 2-propanol/*n*-hexane, 2:98, 15 °C, R_f(*R*) = 8.2 min, R_f(*S*) = 9.3 min; *e.r.* 96:4. $[\alpha]_D^{20}$ = −54.7 (*c* = 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.12 (t, J = 7.4 Hz, 3 H, CH_3), 1.43 (d, J = 7.2 Hz, 3 H, CH_3), 2.20−2.38 (m, 2 H, SCH_2), 4.49 (q, J = 7.2 Hz, 1 H, CH), 6.98 (t, J = 8.0 Hz, 1 H, Ar), 7.24 (t, J = 8.0 Hz, 1 H, Ar), 7.42 (d, J = 8.0 Hz, 1 H, Ar), 7.55 (d, J = 8.0 Hz, 1 H, Ar) ppm. ^{13}C NMR (100 MHz,

$CDCl_3$): δ = 15.0 (CH_3CH_2), 22.6 (CH_3), 25.7 (CH_2), 42.5 (CH), 124.2 (Ar), 128.3 (Ar), 128.7 (Ar), 129.1 (Ar), 132.9 (Ar), 143.6 (Ar) ppm. IR (NaCl): $\tilde{\nu}$ = 2970, 2924, 2360, 1467, 1438, 1372, 1263, 1021, 755, 726, 658 cm^{-1}. MS (EI): *m/z* (%) = 245 (51) [M + NH_4]$^+$, 183 (87), 165 (23), 135 (12), 104 (100), 77 (30), 59 (7); HRMS: calcd. for $C_{10}H_{13}BrS$ 243.9916, found 243.9912.

(*R*,*R*)-Bis{2-[1-(ethylsulfanyl)ethyl]phenyl} Diselenide: Tiecco′s procedure was followed.[19e] Under Ar at −78 °C (*R*)-1-Bromo-2-[1-(ethylsulfanyl)ethyl]benzene (100 mg, 0.41 mmol) in Et_2O (3 mL) was slowly treated with *t*BuLi (0.82 mmol, 0.54 mL, 1.5 M in pentane). The reaction mixture was stirred at −78 °C for 15 min, warmed up to room temperature, and stirred for 30 min. After cooling to −78 °C selenium powder (32 mg, 0.41 mmol) was added. The reaction mixture was allowed to warm up to room temperature and stirred for 4 h. The reaction was quenched with aqueous HCl (1 N) and extracted with Et_2O (3 × 5 mL). The combined organic extracts were dried over $MgSO_4$, and after evaporation of the solvent the deep red oil was purified by flash chromatography on silica gel (diethyl ether/petroleum ether, 1:10). Yield 60 mg (0.12 mmol, 60%); red oil. $[\alpha]_D^{21}$ = −18.0 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.10 (t, *J* = 7.6 Hz, 6 H, CH_3), 1.46 (d, *J* = 6.8 Hz, 6 H, CH_3), 2.31 (q, *J* = 7.2 Hz, 2 H, SCH_2), 2.32 (q, *J* = 7.2 Hz, 2 H, SCH_2), 4.37 (q, *J* = 7.2 Hz, 2 H, CH), 7.04 (dt, *J* = 7.6, 1.2 Hz, 2 H, Ar), 7.17 (dt, *J* = 7.6, 1.2 Hz, 2 H, Ar), 7.35 (dd, *J* = 8.0, 1.2 Hz, 2 H, Ar), 7.68 (dd, *J* = 8.0, 1.2 Hz, 2 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.0 (CH_3CH_2), 22.0 (CH_2), 25.7 (CH_3), 43.7 (CH), 127.4 (CH-Ar), 128.2 (CH-Ar), 128.6 (CH-Ar), 132.4 (C-Ar), 134.5 (CH-Ar), 145.0 (C-Ar) ppm. ^{77}Se NMR (57.3 MHz, $CDCl_3$): δ = 430.3 ppm. IR (NaCl): $\tilde{\nu}$ = 3056, 2965, 2915, 1719, 1579, 1463, 1373, 1262, 1021, 755, 730 cm^{-1}.

Electrophile 20: Synthesized from (*R*,*R*)-bis{2-[1-(ethylsulfanyl)-ethyl]-6-methoxyphenyl} diselenide.

(*R*)-1-[1-(Ethylsulfanyl)ethyl]-3-methoxybenzene: (*S*)-1-(3-Methoxyphenyl)ethanol[5] (1.5 g, 9.86 mmol) was dissolved in diethyl ether/THF (1:1) (40 mL) at −20 °C, KOH (19.7 mmol, 1.104 g) and tosyl chloride (10.8 mmol, 2.12 g) were added, and the reaction mixture was stirred at −20 °C for 24 h. Sodium ethanethiolate (19.7 mmol, 1.66 g) was added, the mixture was allowed to warm up to room temperature, and stirred for an additional 14 h. The reaction was quenched with water (50 mL) and extracted with diethyl ether (3 × 25 mL). The combined organic extracts were dried over $MgSO_4$, and after evaporation of the solvent the yellow oil was purified by flash chromatography on silica gel using ethyl acetate/petroleum ether, 1:4 as eluent. A side product, bis[1-(3-methoxyphenyl)ethyl] ether, was isolated in 16% yield as a colorless oil. Yield 28% (542 mg, 2.76 mmol); colorless oil. HPLC conditions: Chiracel OD-H, flow rate: 0.5 ml min^{-1}, 2-propanol/*n*-hexane, 1:99, 25 °C, R_f(*R*) = 11.2 min, R_f(*S*) = 12.9 min; *e.r.* 96:4. $[\alpha]_D^{21}$ = −84.8 (*c* = 0.125, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.18 (t, *J* = 7.6 Hz, 3 H, CH_3), 1.58 (d, *J* = 7.2 Hz, 3 H, CH_3), 2.37 (q, *J* = 5.2 Hz, 2 H, CH_2), 3.84 (s, 3 H, OCH_3), 3.99 (q, *J* = 7.2 Hz, 1 H, CH), 6.78 (d, *J* = 8.0 Hz, 1 H, Ar), 6.95 (d, *J* = 10.4 Hz, 2 H, Ar), 7.24(dd, *J* = 8.0 Hz, 1 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.9 (CH_3CH_2), 23.0 (CH_3), 25.6 (CH_2), 44.1 (CH), 55.6 (OCH_3), 112.6 (CH-Ar), 113.2 (CH-Ar), 120.1 (CH-Ar), 129.8 (CH-Ar), 146.3 (C-Ar), 160.1 (C-Ar) ppm. IR (NaCl): $\tilde{\nu}$ = 2967, 2917, 1600, 1485, 1454, 1369, 1318, 1259, 1203, 1154, 1044, 874, 781, 701 cm^{-1}. MS (EI): *m/z* (%) = 197 (56) [M]$^+$, 152 (100), 135 (25), 72 (12); HRMS: calcd. for $C_{11}H_{16}OS$ 197.0995, found 197.0994.

Bis[1-(3-methoxyphenyl)ethyl] Ether: $[\alpha]_D^{23}$ = +44.63 (*c* = 2.16, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.43 (d, *J* = 6.4 Hz, 3 H, CH_3), 1.51 (d, *J* = 6.4 Hz, 3 H, CH_3), 3.78 (s, 3 H, OCH_3), 3.86 (s, 3 H, OCH_3), 4.28 (q, *J* = 6.4 Hz, 1 H, CH), 4.56 (q, *J* = 6.4 Hz, 1 H, CH), 6.78−6.93 (m, 6 H, Ar), 7.21−7.35 (m, 2 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.4 (CH_3), 25.1 (CH_3) 55.6 (CH), 75.0 (OCH_3), 111.7 (CH-Ar), 112.8 (CH-Ar), 119.0 (CH-Ar), 129.9 (CH-Ar), 146.4 (C-Ar), 160.2 (C-Ar) ppm. IR (NaCl): $\tilde{\nu}$ = 2972, 2925, 2825, 1723, 1601, 1579, 1486, 1455, 1433, 1368, 1317, 1282, 1257, 1158, 1093, 1047, 956, 874, 782, 700 cm^{-1}. MS (EI): *m/z* (%) = 304 (49) [M + NH_4]$^+$, 286 (9), 269 (12), 168 (8), 152 (100), 136 (18), 74 (11); HRMS: calcd. for $C_{18}H_{22}O_3$ 304.1907, found 304.1903.

(*R*,*R*)-Bis{2-[1-(Ethylsulfanyl)ethyl]-6-methoxyphenyl} Diselenide: Tiecco′s procedure was followed.[19e] Under Ar at −78 °C (*R*)-1-[1-(ethylsulfanyl)ethyl]-3-methoxybenzene (130 mg, 0.66 mmol) was slowly treated with *t*BuLi (1 mmol, 0.66 mL, 1.5 M in pentane). The reaction mixture was stirred at −78 °C for 15 min, warmed up to room temperature, and stirred for 30 min. After cooling to −78 °C and addition of THF (1 mL), selenium powder (1.32 mmol, 104 mg) was added. The reaction mixture was allowed to warm up to room temperature and stirred for 24 h. The reaction was quenched with aqueous HCl (1M) and extracted with diethyl ether (3 × 5 mL). The combined organic extracts were dried over $MgSO_4$, and after evaporation of the solvent the deep red oil was purified by flash chromatography on silica gel (diethyl ether/petroleum ether, 1:10). Yield 62 mg (0.112 mmol, 34%); yellow oil. $[\alpha]_D^{21}$ = −173.8 (*c* = 0.97, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.04 (t, *J* = 7.6 Hz, 6 H, CH_3), 1.22 (d, *J* = 6.8 Hz, 6 H, CH_3), 2.23 (q, *J* = 7.2 Hz, 4 H, CH_2), 3.65 (s, 6 H, OCH_3), 4.52 (q, *J* = 6.8 Hz, 2 H, CH), 6.67 (d, *J* = 8.0 Hz, 2 H, Ar), 7.01 (d, *J* = 7.6 Hz, 2 H, Ar) 7.18 (dd, *J* = 8.0, 10.4 Hz, 2 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.8 (CH_3CH_2), 20.9 (CH_2), 24.1 (CH_3), 42.0 (CH), 55.0 (OCH_3), 108.0 (CH-Ar), 118.0 (CH-Ar), 120.6 (CH-Ar), 129.4 (C-Ar), 148.0 (C-Ar), 159.0 (C-Ar) ppm. IR (NaCl): $\tilde{\nu}$ = 3427, 2970, 2920, 1562, 1462, 1262, 1045, 781, 650 cm^{-1}. MS (EI): *m/z* (%) = 573 (7) [M + NH_4]$^+$, 275 (58), 213 (100), 181 (10), 151 (20), 135 (17), 119 (8), 100 (15); HRMS: calcd. for $C_{22}H_{30}O_2S_2Se_2$ 572.9910, found 572.9905.

3-(Hydroxymethyl)-5-methyl-5-phenyldihydrofuran-2-one (21/22): Synthesized according to GP 2. Purification by flash chromatography on silica gel with ethyl acetate/ petroleum ether, 2:1. Yield 56% (10 mg, 0.049 mmol); colorless oil; **21:** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.70 (s, 3 H, CH_3), 2.29 (t, *J* = 11.2 Hz, 1 H, CH_2), 2.59 (t, *J* = 11.2 Hz, 1 H, CH_2), 2.59−2.69 (m, 1 H, CH), 3.69 (dd, *J* = 5.2, 11.2 Hz, 1 H, CH_2OH), 3.89 (dd, *J* = 4.0, 11.2 Hz, 1 H, CH_2OH), 7.20−7.40 (m, 5 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 30.6 (CH_3), 39.4 (CH_2), 43.1 (CH), 61.2 (CH_2OH), 86.1 (C), 124.6 (CH-Ar), 128.2 (CH-Ar), 129.1 (CH-Ar), 144.1 (C-Ar), 178.4 (C=O) ppm. HPLC conditions: Chiracel OD-H, flow rate: 0.5 ml min^{-1}, 2-propanol/*n*-hexane, 3:97, 10 °C, R_f(1) = 68.0 min, R_f(2) = 81.4 min. **22:** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.65 (s, 3 H, CH_3), 2.51−2.65 (m, 2 H, CH_2), 3.02−3.12 (m, 1 H, CH), 3.72 (dd, *J* = 6.0, 10.8 Hz, 1 H, CH_2OH), 3.88 (dd, *J* = 5.2, 11.2 Hz, 1 H, CH_2OH), 7.10−7.30 (m, 5 H, Ar) ppm. HPLC conditions: Chiracel OD-H, flow rate: 0.5 ml min^{-1}, 2-propanol/*n*-hexane, 3:97, 10 °C, R_f(1) = 98.2 min, R_f(2) = 190.9 min. IR (NaCl): $\tilde{\nu}$ = 3394, 2359, 1758, 1643, 1446, 1236, 1145 cm^{-1}. MS (EI): *m/z* (%) = 207 (100) [M + H]$^+$, 190 (46), 160 (7), 147 (22), 124 (13), 113 (14), 91 (66); HRMS: calcd. for $C_{12}H_{14}O_3$ 207.1016, found 207.1013.

Methyl 5-Methyl-5-phenyltetrahydrofuran-3-carboxylate (23/24): Synthesized according to GP 2. Purification by flash chromatography on silica gel with ethyl acetate/petroleum ether, 1:10. Yield 68% (28.8 mg, 0.13 mmol). **23:** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.42 (s, 3 H, CH_3), 2.35 (dd, J = 8.9, 12.6 Hz, 1 H, CH_2), 2.50 (dd, J = 8.1, 12.6 Hz, 1 H, CH_2), 3.28 (quint, J = 8.1 Hz, 1 H, CH), 3.50 (s, 3 H, OCH_3), 4.00 (t, J = 8.5 Hz, 1 H, CH_2O), 4.20 (t, J = 8.4 Hz, 1 H, CH_2O), 7.10−7.35 (m, 5 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 30.2 (CH_3), 42.9 (CH_2), 44.9 (CH), 52.3 (OCH_3), 69.4 (CH_2O), 85.3 (C), 125.0 (CH-Ar), 127.0 (CH-Ar), 128.6 (CH-Ar), 147.5 (C-Ar), 173.6 (C=O) ppm. GC conditions: Chirasil-Dex CB (25 m), 75−110 °C at 0.5 °C min^{-1}, R_f(major) = 54.9 min, R_f(minor) = 56.0 min. **24:** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.50 (s, 3 H, CH_3), 2.27 (dd, J = 9.4, 12.3 Hz, 1 H, CH_2), 2.53 (dd, J = 8.1, 12.4 Hz, 1 H, CH_2), 2.96 (quint, J = 8.2 Hz, 1 H, CH), 3.62 (s, 3 H, OCH_3), 4.02 (t, J = 8.7 Hz, 1 H, CH_2O), 4.11 (t, J = 8.7 Hz, 1 H, CH_2O), 7.12−7.32 (m, 5 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 30.1 (CH_3), 43.1 (CH_2), 44.3 (CH), 52.5 (OCH_3), 69.5 (CH_2O), 85.8 (C), 124.9 (CH-Ar), 127.2 (CH-Ar), 128.7 (CH-Ar), 146.9 (C-Ar), 174.4 (C=O) ppm. HPLC conditions: Chiracel OD-H, flow rate: 0.5 ml min^{-1}, 2-propanol/*n*-hexane, 3:97, 10 °C, R_f(minor) = 17.5 min, R_f(major) = 19.7 min. IR (thin film on NaCl): $\tilde{\nu}$ = 3466, 2966, 1736, 1629, 1489, 1445, 1373, 1328, 1268, 1199, 1167, 1062, 1022, 761, 702 cm^{-1}. MS (EI): *m*/*z* (%) = 221 (11) $[M]^+$, 205 (100), 173 (10), 159 (4), 145 (49), 131 (6), 117 (16), 105 (36), 91 (7), 77 (11), 65 (4), 51 (8), 43 (12); HRMS: calcd. for $C_{13}H_{16}O_3 + NH_4^+$ 238.1438, found 238.1438.

2-(2-Phenylallyl)propane-1,3-diol (25): Lithium aluminum hydride (17 mg, 0.44 mmol) was dissolved in dry THF (5 mL). Compound **5** (180 mg, 0.88 mmol) was dissolved in THF (5 mL), added in and stirred at room temperature overnight. The reaction was quenched at 0 °C with diluted H_2SO_4, extracted with diethyl ether, dried over $MgSO_4$, and the solvent was evaporated to produce a colorless solid which was further purified by flash chromatography on silica gel with *tert*-butyl methyl ether. Yield 85% (144 mg, 0.75 mmol); m.p. 55−56 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.75−1.85 (m, 1 H, CH), 2.47 (d, J = 7.6 Hz, 2 H, CH_2), 3.58 (dd, J = 7.2, 10.8 Hz, 2 H, CH_2OH), 3.72 (dd, J = 3.6, 10.4 Hz, 1 H, CH_2OH), 5.04 (d, J = 0.8 Hz, 1 H, =CH_2), 5.26 (d, J = 1.2 Hz, 1 H, =CH_2), 7.15−7.45 (m, 5 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 34.3 (CH_2), 40.5 (CH), 66.2 (CH_2OH), 114.8 (=CH_2), 126.6 (CH-Ar), 128.1 (CH-Ar), 128.9 (CH-Ar), 140.9 (C=), 146.6 (C-Ar) ppm. IR (NaCl): $\tilde{\nu}$ = 3374, 2927, 2882, 1626, 1494, 1444, 1092, 1028, 971, 898, 779, 709 cm^{-1}. MS (EI): *m*/*z* (%) = 192 (10), 174 (31), 157 (76), 150 (23), 143 (30), 128 (27), 117 (100), 103 (17), 91 (10); HRMS calcd. for $C_{12}H_{16}O_2$ 193.1223, found 193.1222.

[5-(Iodomethyl)-5-phenyltetrahydrofuran-3-yl]methanol (26a/27a): Synthesized according to the procedure for the synthesis of **8a/9a** using substrate **25**. Purification by flash chromatography on silica gel with ethyl acetate/petroleum ether, 1:1. Yield 43% (29 mg, 0.091 mmol); colorless oil; *d.r.* (**26a/27a**) 70:30. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.95−2.15 (m, 1 H, CH_2), 2.30−2.58 (m, 3 H, CH_2, 26a-CH), 2.70 (quint, J = 7.6 Hz, 1 H, 27a-CH), 3.42 (d, J = 10.4 Hz, 1 H, 27a-CH_2I), 3.47 (t, J = 10.4 Hz, 1 H, 27a-CH_2I), 3.49 (d, J = 10.4 Hz, 1 H, 26a-CH_2I), 3.50 (d, J = 10.4 Hz, 1 H, 26a-CH_2I), 3.63 (d, J = 6.4 Hz, 2 H, CH_2O), 3.80 (t, J = 8.0 Hz, 1 H, 26a-CH_2OH), 3.97 (t, J = 8.0 Hz, 1 H, 26a-CH_2OH), 4.04 (t, J = 7.2 Hz, 1 H, 27a-CH_2OH), 4.18 (t, J = 8.4 Hz, 1 H, 27a-CH_2OH), 7.10−7.45 (m, 5 H, Ar) ppm. **26a:** ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.3 (CH_2), 40.9 (CH_2O), 42.2 (CH), 64.8 (CH_2OH), 70.9 (CH_2I), 85.5 (C), 125.8 (CH-Ar), 127.9 (CH-Ar), 128.8 (CH-Ar), 143.3 (C-Ar) ppm. IR (NaCl): $\tilde{\nu}$ = 3438, 2931, 2875, 1644, 1446, 1188, 1048, 763, 702 cm^{-1}. MS (EI): *m*/*z* (%) = 319 (6) $[M + H]^+$, 301 (100), 283 (5), 206 (14), 192 (23), 174 (4), 156 (6); HRMS calcd. for $C_{12}H_{15}O_2I$ 336.0455, found 336.0456.

[5-Phenyl-5-(phenylselanylmethyl)tetrahydrofuran-3-yl]methanol (26b/27b): Synthesized according to GP 1. Purification by flash chromatography on silica gel with ethyl acetate/petroleum ether, 1:2. Yield 74% (46 mg, 0.13 mmol); colorless oil; *d.r.* (**26b/27b**) 66:34. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.01 (dd, J = 6.8, 12.8 Hz, 1 H, 27b-CH_2), 2.08 (dd, J = 8.4, 11.6 Hz, 1 H, 26b-CH_2), 2.33 (quint, J = 7.2 Hz, 1 H, 26b-CH), 2.38−2.44 (m, 1 H, 26b-CH_2), 2.52 (dd, J = 8.8, 12.8 Hz, 1 H, 27b-CH_2), 2.67 (quint, J = 7.2 Hz, 1 H, 27b-CH), 3.25 (d, J = 12.0 Hz, 1 H, 27b-CH_2Se), 3.26 (d, J = 12.0 Hz, 1 H, 26b-CH_2Se), 3.33 (d, J = 12.0 Hz, 1 H, 27b-CH_2Se), 3.42 (d, J = 12.4 Hz, 1 H, 26b-CH_2Se), 3.60 (d, J = 6.8 Hz, 2 H, CH_2O), 3.76 (dd, J = 6.4, 8.8 Hz, 1 H, 26b-CH_2OH), 3.94 (t, J = 8.4 Hz, 1 H, 26b-CH_2OH), 4.04 (t, J = 7.2 Hz, 1 H, 27b-CH_2OH), 4.12 (t, J = 7.2 Hz, 1 H, 27b-CH_2OH), 7.01−7.40 (m, 10 H, Ar) ppm. **26b:** ^{13}C NMR (100 MHz, $CDCl_3$): δ = 39.3 (CH_2), 40.6 (CH_2Se); 41.9 (CH), 63.6 (CH_2OH), 69.3 (CH_2O), 85.7 (C), 124.2 (CH-Ar), 125.6 (CH-Ar), 126.1 (CH-Ar), 127.3 (CH-Ar), 127.9 (CH-Ar), 130.3 (C-Ar), 131.4 (CH-Ar), 143.9 (C-Ar) ppm. IR (NaCl): $\tilde{\nu}$ = 3414, 3060, 2930, 2876, 1642, 1579, 1478, 1446, 1202, 1049, 1022, 764, 737, 703 cm^{-1}. MS (EI): *m*/*z* (%) = 349 $[M]^+$ (17), 331 (29), 220 (7), 192 (100), 178 (22), 174 (7), 144 (8), 108 (20), 84 (7); HRMS calcd. for $C_{18}H_{20}O_2Se$ 366.0967, found 366.0962.

1-{2-[[(*S*)-4-(Hydroxymethyl)-2-phenyltetrahydrofuran-2-yl]methylselanyl]phenyl}propan-1-ol (26f/27f): Synthesized according to GP 1. Purification by flash chromatography on silica gel with ethyl acetate/petroleum ether, 1:2. Yield 28% (20 mg, 0.05 mmol); colorless oil; *d.r.* (**26f/27f**) 59:41. $[\alpha]_D^{22}$ = +8.0 (c = 0.075, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.84 (t, J = 7.2 Hz, 1 H, 27f-CH_3), 0.86 (t, J = 7.6 Hz, 1 H, 26f-CH_3), 1.53−1.74 (m, 2 H, C$H_2$$CH_3$), 1.92−2.15 (m, 1 H, CH_2), 2.30 (quint, J = 6.8 Hz, 1 H, 26f-CH), 2.35−2.52 (m, 1 H, CH_2), 2.66 (quint, J = 7.2 Hz, 1 H, 27f-CH), 3.23 (d, J = 12.0 Hz, 1 H, 27f-CH_2Se), 3.30 (d, J = 12.0 Hz, 1 H, 26f-CH_2Se), 3.35 (d, J = 12.4 Hz, 1 H, 26f-CH_2Se), 3.36 (d, J = 11.2 Hz, 1 H, 27f-CH_2Se), 3.60 (d, J = 9.6 Hz, 2 H, CH_2O), 3.76 (dd, J = 6.4 Hz, 1 H, 26f-CH_2OH), 3.96 (t, J = 8.0 Hz, 1 H, 26f-CH_2OH), 4.05 (t, J = 7.2 Hz, 1 H, 27f-CH_2OH), 4.13 (t, J = 7.2 Hz, 1 H, 27f-CH_2OH), 4.86 (q, J = 6.8 Hz, 1 H, 26f-CH-Ar), 5.02−5.10 (m, 1 H, CH-Ar), 6.90−7.44 (m, 9 H, Ar) ppm. **26f:** ^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.8 (CH_3), 31.4 (*C*H_2CH_3), 41.2 (CH), 41.9 (CH_2Se), 43.2 (CH_2), 64.8 (CH_2OH), 70.6 (CH_2O), 74.8 (CH-Ar), 87.3 (C), 125.7 (CH-Ar), 126.5 (CH-Ar), 127.3 (CH-Ar), 127.6 (CH-Ar), 128.3 (CH-Ar), 128.4 (CH-Ar), 130.7 (C-Ar), 134.8 (CH-Ar), 146.6 (C-Ar) ppm. IR (NaCl): $\tilde{\nu}$ = 3418, 2928, 2865, 1632, 1446, 1268, 1197, 1047, 753, 703 cm^{-1}. MS: *m*/*z* (%) = 389 (43) $[M - H_2O]^+$, 371 (22), 197 (31), 176 (36), 158 (36), 108 (100), 100 (7); HRMS calcd. for $C_{21}H_{26}O_3Se + NH_4^+$ 424.1385, found 424.1389.

{5-[2-[(*R*)-1-(Ethylsulfanyl)ethyl]phenylselanylmethyl]-5-phenyltetrahydrofuran-3-yl}methanol (26i/27i): Synthesized according to GP 1. Purification by flash chromatography on silica gel with ethyl acetate/petroleum ether, 1:2. Yield 33% (28 mg, 0.06 mmol); colorless oil; *d.r.* (**26i/27i**) 81:19. $[\alpha]_D^{22}$ = −7.71 (c = 1.4, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.07 (t, J = 7.2 Hz, 3 H, 26i-CH_3), 1.10 (t, J = 7.6 Hz, 3 H, 27i-CH_3), 1.41 (d, J = 7.2 Hz, 3 H, 27i-CH_3), 1.45 (d, J = 7.2 Hz, 3 H, 26i-CH_3), 2.06−2.14 (m, 1 H, CH_2), 2.24−2.45 (m, 4 H, CH_2S, CH_2, CH), 2.50−2.56 (m, 1 H, 27i-CH_2), 2.68 (quint, J = 7.6 Hz, 1 H, 27i-CH), 3.24 (d, J = 12.0 Hz, 1 H, 26i-CH_2Se), 3.27 (d, J = 12.0 Hz, 1 H, 27i-CH_2Se), 3.36 (d, J = 12.0 Hz, 1 H, 27i-CH_2Se), 3.38 (d, J = 12.0 Hz, 1 H, 26i-CH_2Se),

3.62 (d, J = 6.8 Hz, 2 H, 26i-CH_2O), 3.63 (d, J = 6.4 Hz, 1 H, 27i-CH_2O), 3.77 (t, J = 8.4 Hz, 1 H, 26i-CH_2OH), 3.78 (t, J = 6.8 Hz, 1 H, 27i-CH_2OH), 3.95 (t, J = 8.0 Hz, 1 H, 26i-CH_2OH), 4.54 (q, J = 6.8 Hz, 1 H, 27i-CH-Ar), 4.58 (q, J = 6.8 Hz, 1 H, 26i-CH-Ar), 6.90−7.40 (m, 9 H, Ar) ppm. **26i:** ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.1 (CH_3), 23.0 (CH_3CH), 25.6 (CH_2S), 40.8 (CH_2), 42.0 (CH), 42.6 (CH_2Se), 42.9 (CH-Ar), 65.1 (CH_2O), 70.7 (CH_2OH), 87.2 (C), 125.6 (CH-Ar), 127.5 (CH-Ar), 127.9 (CH-Ar), 128.0 (CH-Ar), 128.7 (CH-Ar), 132.1 (C-Ar), 133.9 (CH-Ar), 145.4 (C-Ar), 145.9 (C-Ar) ppm. IR (NaCl): $\tilde{\nu}$ = 3396, 3056, 2928, 2869, 1599, 1584, 1494, 1464, 1446, 1378, 1262, 1202, 1047, 806, 763, 730, 704 cm^{-1}. MS (EI): m/z (%) = 436 (100) $[M]^+$, 407 (24); HRMS calcd. for $C_{22}H_{28}O_2SSe$ 436.0970, found 436.0975.

2-Styrylpropane-1,3-diol (28): Lithium aluminum hydride (417 mg, 11 mmol) was dissolved in dry THF (10 mL). (*E*)-2-(Methoxycarbonyl)-4-phenylbut-3-enoic acid[23] (1.00 g, 4.55 mmol) dissolved in THF (5 mL) was added to this mixture at 0 °C and stirred at room temperature overnight. The reaction was quenched at 0 °C with ethanol (20 mL), and the solvents were evaporated. The solid was dissolved in water (15 mL), extracted with diethyl ether (3 × 15 mL), the combined organic phases were dried over $MgSO_4$, the solvent was evaporated, and the residual yellow oil was further purified by flash chromatography on silica gel with diethyl ether to give a pale yellow solid in 32% yield (260 mg, 1.46 mmol); m.p. 76−78 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.51−2.54 (m, 1 H, CH), 3.77 (d, J = 6.0 Hz, 4 H, CH_2OH), 6.03 (dd, J = 8.4, 16.0 Hz, 1 H, =CH), 6.50 (d, J = 16.0 Hz, 1 H, =CH), 7.12−7.35 (m, 5 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 47.6 (CH), 65.5 (CH_2OH), 126.6 (CH-Ar), 127.2 (=CH), 128.0 (CH-Ar), 129.0 (CH-Ar), 133.6 (CH=), 137.2 (C-Ar) ppm. IR (NaCl): $\tilde{\nu}$ = 3408, 2925, 2885, 1647, 1494, 1449, 1031, 967, 748, 694 cm^{-1}. MS (EI): m/z (%) = 196 (100) $[M + NH_4]^+$, 178 (8), 161 (16), 130 (24); HRMS calcd. for $C_{11}H_{14}O_2$ 196.1332, found 196.1333.

(4-Iodo-5-phenyltetrahydrofuran-3-yl)methanol (29a/30a): Synthesized according to the procedure for the synthesis of **8a/9a** using substrate **28**. Purification by flash chromatography on silica gel with *tert*-butyl methyl ether/petroleum ether, 1:2. Yield 79% (34 mg, 0.11 mmol);, colorless oil; *d.r.* (**29a/30a**) 88:12. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.73−2.83 (m, 1 H, CH), 3.69 (dd, J = 6.4, 10.8 Hz, 1 H, CH_2O), 3.71 (t, J = 8.8 Hz, 1 H, CHI), 3.84 (t, J = 8.4 Hz, 1 H, 30a-CHI), 3.98 (dd, J = 6.8, 8.8 Hz, 1 H, CH_2OH), 4.07 (t, J = 8.8 Hz, CH_2OH), 4.26 (dd, J = 6.8, 9.2 Hz, 1 H, 30a-CH_2OH), 4.94 (d, J = 8.8 Hz, 1 H, 29a-OCH), 5.28 (d, J = 5.2 Hz, 1 H, 30a-OCH), 7.18−7.42 (m, 5 H, Ar) ppm. **29a:** ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.8 (CH), 52.0 (CHI), 60.8 (CH_2OH), 68.6 (CH_2), 88.6 (OCH), 124.8 (C-Ar), 125.6 (CH-Ar), 127.5 (CH-Ar), 137.1 (CH-Ar) ppm. IR (NaCl): $\tilde{\nu}$ = 3364, 3032, 2938, 1602, 1494, 1454, 1377, 1312, 1216, 1150, 1052, 966, 914, 759 cm^{-1}. MS (EI): m/z (%) = 305 (33) $[M + H]^+$, 178 (13), 151 (15), 117 (100), 99 (14), 85 (44), 79 (11), 60 (42); HRMS calcd. for $C_{11}H_{13}O_2I + NH_4$+ 322.0298, found 322.0301.

[5-Phenyl-4-(phenylselanyl)tetrahydrofuran-3-yl]methanol (29b/30b): Synthesized according to GP 1. Purification by flash chromatography on silica gel with ethyl acetate/petroleum ether, 1:4. Yield 50% (30 mg, 0.091 mmol); colorless oil; *d.r.* (**29b/30b**) 94:6. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.45−2.56 (m, 1 H, CH), 3.10 (t, J = 7.6 Hz, 1 H, CHSe), 3.58−3.72 (m, 2 H, CH_2), 3.93 (dd, J = 2.8, 5.6 Hz, 2 H, CH_2OH), 4.24 (dd, J = 4.3, 6.0 Hz, 1 H, 30b-CH_2OH), 4.67 (d, J = 8.8 Hz, 1 H, OCH), 4.86 (d, J = 6.8 Hz, 1 H, OCH), 7.05−7.44 (m, 10 H, Ar) ppm. **29b:** ^{13}C NMR (100 MHz, $CDCl_3$): δ = 48.3 (CHSe), 48.8 (CH), 62.3 (CH_2OH), 69.0 (CH_2OH), 85.8 (OCH), 125.4 (CH-Ar), 126.4 (CH-Ar), 126.7 (CH-Ar), 127.0 (CH-Ar), 127.4 (CH-Ar), 128.1 (CH-Ar), 132.8 (CH-Ar), 134.4 (C-Ar), 138.9 (C-Ar) ppm. IR (NaCl): $\tilde{\nu}$ = 3405, 3059, 2869, 1732, 1578, 1494, 1476, 1437, 1376, 1302, 1176, 1048, 1023, 739, 697 cm^{-1}. MS (EI): m/z (%) = 335 (100) $[M + H]^+$, 317 (22), 178 (100), 160 (12); HRMS calcd. for $C_{17}H_{18}O_2Se$ 335.0545, found 335.0552.

(1*S*)-1-{2-[4-(Hydroxymethyl)-2-phenyltetrahydrofuran-3-yl]phenylselanyl}propan-1-ol (29f/30f): Synthesized according to GP 1. Purification by flash chromatography on silica gel with *tert*-butyl methyl ether/petroleum ether, 2:1. Yield 64% (35 mg, 0.11 mmol); colorless oil; *d.r.* (**29f/30f**) 93:7. $[\alpha]_D^{22}$ = +70.6 (c = 0.60, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.82 (t, J = 7.6 Hz, 3 H, CH_3), 152−1.72 (m, 2 H, CH_2), 2.48−2.62 (m, 1 H, CH), 3.17 (dd, J = 6.8, 8.4 Hz, 1 H, CHSe), 3.43 (dd, J = 6.0, 10.8 Hz, 1 H, CH_2O), 3.58 (dd, J = 6.4, 10.8 Hz, 1 H, CH_2O), 3.89 (dd, J = 4.8, 9.2 Hz, 1 H, CH_2OH), 3.97 (dd, J = 7.6, 8.8 Hz, 1 H, CH_2OH), 4.68 (d, J = 8.8 Hz, 1 H, 29f-OCH), 4.87 (d, J = 8.8 Hz, OCH), 5.98 (q, J = 6.0 Hz, 1 H, 29f-ArCHOH), 5.09 (q, J = 6.0 Hz, 1 H, 29f-ArCHOH), 6.80−7.44 (m, 9 H, Ar) ppm. **29f:** ^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.7 (CH_3), 31.7 (CH_2), 51.0 (CHSe), 51.5 (CH), 63.3 (CH_2OH), 67.5 (CH_2O), 71.0 (ArCHOH), 87.5 (OCH), 121.8 (C-Ar), 128.2 (CH-Ar), 128.3 (CH-Ar), 128.5 (CH-Ar), 128.8 (CH-Ar), 129.2 (CH-Ar), 131.8 (CH-Ar), 136.8 (CH-Ar), 140.2 (C-Ar), 147.4 (C-Ar) ppm. IR (NaCl): $\tilde{\nu}$ = 3358, 3056, 2962, 2880, 1615, 1456, 1378, 1263, 1192, 1048, 972, 911, 754, 699 cm^{-1}. MS (EI): m/z (%) = 392 (36) $[M]^+$, 187 (11), 149 (10), 122 (12), 107 (100), 85 (48), 61 (15); HRMS calcd. for $C_{20}H_{24}O_3Se$ 392.0885, found 392.0887.

{4-[2-[(*R*)-2-(Ethylsulfanyl)ethyl]phenylselanyl]-5-phenyltetrahydrofuran-3-yl}methanol (29i/30i): Synthesized according to GP 1. Purification by flash chromatography on silica gel with diethyl ether/petroleum ether, 2:1. Yield 30% (14 mg, 0.032 mmol); colorless oil;, *d.r.* (**29i/30i**) 86:14. $[\alpha]_D^{23}$ = −30.5 (c = 0.57, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.05 (t, J = 7.6 Hz, 3 H, 30i-CH_3), 1.11 (t, J = 7.6 Hz, 3 H, 29i-CH_3), 1.39 (d, J = 6.8 Hz, 3 H, 29i-CH_3), 1.43 (d, J = 6.8 Hz, 3 H, 30i-CH_3), 2.32 (q, J = 7.6 Hz, 2 H, SCH_2), 2.48−2.62 (m, 1 H, CH), 3.20 (dd, J = 6.8, 8.4 Hz, 1 H, 29i-CH_2O), 3.29 (dd, J = 6.4, 9.2 Hz, 1 H, 30i-CH_2O), 3.52−3.66 (m, 1 H, CH_2O), 3.97 (dd, J = 5.2, 8.8 Hz, 1 H, CH_2OH), 4.03 (dd, J = 7.6, 8.8 Hz, 1 H, 29i-CH_2OH), 4.26 (dd, J = 7.6, 8.4 Hz, 1 H, 30i-CH_2OH) 4.43 (q, J = 6.8 Hz, 1 H, 30i-SCH), 4.56 (q, J = 6.8 Hz, 1 H, 29i-SCH), 4.72 (d, J = 8.4 Hz, 1 H, 29i-OCH), 4.82 (d, J = 7.2 Hz, 1 H, 30i-OCH), 6.75−7.44 (m, 9 H, Ar) ppm. **29i:** ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.1 (CH_3), 22.6 (CH_2), 25.6 (CH_3), 43.0 (CHS), 50.7 (CH), 51.1 (CH-Se), 63.6 (CH_2OH), 70.4 (CH_2O), 87.8 (C), 126.8 (CH-Ar), 127.8 (CH-Ar), 128.8 (CH-Ar), 129.1 (CH-Ar), 129.6 (CH-Ar), 136.6 (C-Ar), 140.3 (C-Ar), 146.8 (C-Ar) ppm. IR (NaCl): $\tilde{\nu}$ = 3428, 3056, 2956, 2915, 2855, 1589, 1494, 1454, 1373, 1263, 1212, 1157, 1041, 1027, 754, 699, 650 cm^{-1}. MS (EI): m/z (%) = 398 (2) $[M + NH_4]^+$, 440 (8), 391 (15), 376 (25), 363 (100), 344 (12), 335 (8); HRMS calcd. for $C_{21}H_{26}O_2SSe$ 440.1157, found 440.1161.

(5-Methyl-5-phenyltetrahydrofuran-3-yl)methanol (31): Synthesized according to GP 2. Purification by flash chromatography on silica gel with ethyl acetate/petroleum ether, 1:2. Yield 61% (7 mg, 0.039 mmol); colorless oil; *d.r.* (*cis*/*trans*) 80:20. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.44 (s, 3 H, *trans*-CH_3), 1.49 (s, 3 H, *cis*-CH_3), 1.70 (dd, J = 8.8, 12.0 Hz, 1 H, *cis*-CH_2), 1.89 (dd, J = 7.2, 12.4 Hz, 1 H, *trans*-CH_2), 2.22 (dd, J = 8.4, 12.8 Hz, 1 H, *trans*-CH_2), 2.30 (quint, J = 8.0 Hz, 1 H, *cis*-CH), 2.41 (dd, J = 7.6, 12.0 Hz, 1 H, *cis*-CH_2), 2.63 (quint, J = 7.6 Hz, 1 H, *trans*-CH), 3.38 (dd, J = 7.6, 10.8 Hz, 1 H, *trans*-CH_2O), 3.44 (dd, J = 6.4,

10.4 Hz, 1 H, *trans*-CH_2O), 3.59 (dd, J = 2.4, 6.8 Hz, 2 H, *cis*-CH_2O), 3.73 (dd, J = 6.4, 8.8 Hz, 1 H, *cis*-CH_2OH), 3.92 (t, J = 8.8 Hz, 1 H, *cis*-CH_2OH), 4.20 (t, J = 7.6 Hz, 1 H, *trans*-CH_2OH), 7.10−7.35 (m, 5 H, Ar) ppm. ***cis*-isomer:** ^{13}C NMR (100 MHz, $CDCl_3$): δ = 29.4 (CH_3), 40.8 (CH), 41.5 (CH_2), 64.1 (CH_2OH), 68.7 (CH_2O), 84.0 (C), 123.6 (CH-Ar), 125.5 (CH-Ar), 127.2 (CH-Ar), 146.4 (C-Ar) ppm. IR (NaCl): $\tilde{\nu}$ = 3397, 2976, 2925, 2875, 1489, 1446, 1373, 1263, 1127, 1097, 1037, 906, 850, 801, 761, 700 cm^{-1}. MS (EI): *m*/*z* (%) = 210 (100) $[M + NH_4]^+$, 193 (16), 177 (8), 136 (8), 115 (7), 74 (10); HRMS: calcd. for $C_{12}H_{16}O_2$ 210.1489, found 210.1490.

(5-Phenyltetrahydrofuran-3-yl)methanol (32): Synthesized according to GP 2. Purification by flash chromatography on silica gel with ethyl acetate/petroleum ether, 1:2. Yield 73% (3 mg, 0.02 mmol); colorless oil; *d.r.* (*trans*/*cis*) 92:8. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.42−1.51 (m, 2 H, CH_2), 2.41 (dd, J = 6.4, 12.4 Hz, 1 H, CH_2O), 2.58 (quint, J = 7.2 Hz, 1 H, CH), 3.59 (dd, J = 2.4, 6.4 Hz, 1 H, CH_2O), 3.87 (dd, J = 5.6, 8.8 Hz, 1 H, CH_2OH), 3.95 (t, J = 8.8 Hz, 1 H, CH_2OH), 4.79 (dd, J = 6.4, 9.6 Hz, 1 H, *trans*-CHO), 4.92 (t, J = 7.6 Hz, 1 H, *cis*-CHO), 7.15−7.35 (m, 5 H, Ar) ppm. ***trans*-isomer:** ^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.7 (CH_2), 41.3 (CH), 64.3 (CH_2OH), 70.0 (CH_2O), 80.2 (OCH), 124.7 (CH-Ar), 126.4 (CH-Ar), 127.4 (CH-Ar), 141.3 (C-Ar) ppm. IR (NaCl): $\tilde{\nu}$ = 3428, 3016, 2918, 2845, 1652, 1453, 1373, 1265, 1217, 1053, 909, 758, 700 cm^{-1}. MS (EI): *m*/*z* (%) = 196 (100) $[M + NH_4]^+$, 179 (8); HRMS: calcd. for $C_{11}H_{14}O_2$ 196.1332, found 196.1331. HPLC conditions: Chiracel OD-H, flow rate: 0.5 ml min^{-1}, 2-propanol/*n*-hexane, 3:97, 10 °C, R_f(*cis-1*) = 91.4 min, R_f(*cis-2*) = 99.0 min, R_f(*trans-1*) = 112.3 min, R_f(*trans-2*) = 126.1 min.

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