Asymmetric Addition Reactions with Optimized Selenium Electrophiles

Thomas Wirth* and Gianfranco Fragale

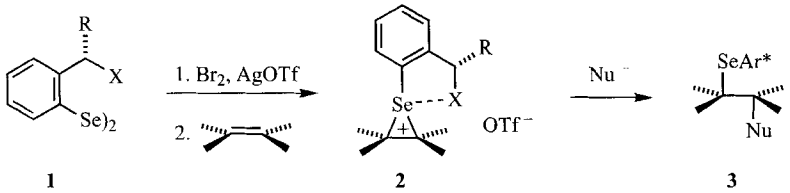
Abstract: The synthesis of various nonracemic diselenides by different methods is described. These diselenides are precursors for optically active selenium electrophiles. Their facial selectivity upon addition to styrene was investigated with respect to the chiral moiety neighboring the selenium. Diselenides **1i**, **1n**, and **1v** yielded addition products **7** with diastereomeric excesses up to 95%. Some diselenides, intermediates, and products of the addition reaction were investigated by ^{77}Se NMR spectroscopy.

Keywords
asymmetric synthesis · chirality · diselenides · selenium

Introduction

The stereoselective functionalization of nonactivated C=C double bonds is still a challenge in organic chemistry. Efficient methods are available for asymmetric epoxidation[1] or dihydroxylation[2] of unfunctionalized alkenes; however, stoichiometric addition reactions of chiral reagents to unfunctionalized alkenes deserve further investigation. Adducts formed using this method could provide access to highly desirable building blocks in further syntheses.

Recently, we showed that optically active diselenides of type **1** are easily accessible.[3] After conversion to the corresponding selenium electrophiles these compounds can add to alkenes in the presence of a nucleophile (Scheme 1). A seleniranium ion **2** is formed and trapped from the *anti* side by either an external or internal nucleophile. The addition products **3** are obtained in good yields and with high diastereoselectivities. Because they still contain the selenium functionality they are versatile starting materials for subsequent reactions:[4] 1. The homolytic cleavage of the carbon–selenium bond generates radicals and thus provides an entry into radical chemistry. 2. By oxidation of the selenium to the selenoxide, β-hydride elimination can occur. Further oxidation to the selenone generates an excellent leaving group. 3. Deprotonation in the α position is possible, as well as a selenium–metal exchange which opens up the broad field of carbanionic chemistry.



Scheme 1. Optically active diselenides **1** are converted to the corresponding selenium electrophiles, which then add to alkenes in the presence of a nucleophile.

Herein we report the synthesis of various optically active diselenides of type **1** and their addition to styrene. We and other research groups have already reported that unsaturated carboxylic acids or unsaturated alcohols can undergo intramolecular selenoetherification or selenolactonization reactions.[3, 5] We applied such an addition reaction followed by intramolecular radical cyclization to the synthesis of furofuran lignans.[6] Here we investigate the development of efficient and easily accessible selenium electrophiles that can participate in addition reactions. As a test reaction we studied the addition of selenium cations to styrene using methanol as nucleophile. A wide range of alkenes can be employed in these addition reactions; however, sometimes higher diastereoselectivities are obtained with *trans*-disubstituted alkenes than with styrene.

Results and Discussion

Different research groups have employed optically active selenium compounds in asymmetric addition reactions. Most of these compounds have an asymmetric moiety with a heteroatom in close proximity to the selenium atom. Because of the facile synthesis of diselenides **1a–k** with X = OR′ we were able to vary the substituents R and R′ and to investigate their influence upon the addition reaction. Several methods are known for the synthesis of diselenides.[7] The reaction of aryllithium compounds (generated either by halogen–lithium exchange or by *ortho* deprotonation) with elemental selenium produces selenols, which are subsequently oxidized by air to diselenides. If halogenated precursors are available, the reaction of these substrates with sodium diselenide may be an alternative for the synthesis of

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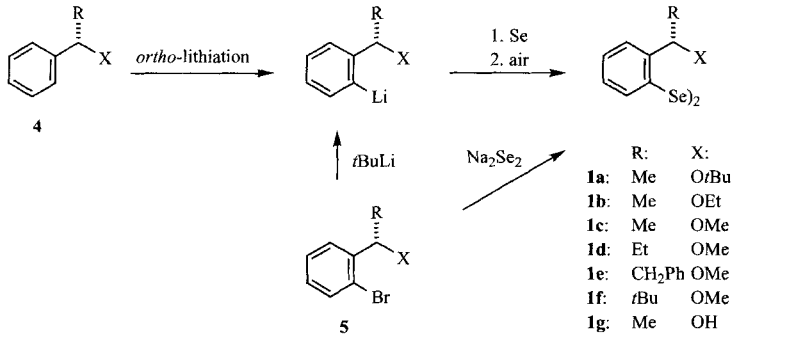
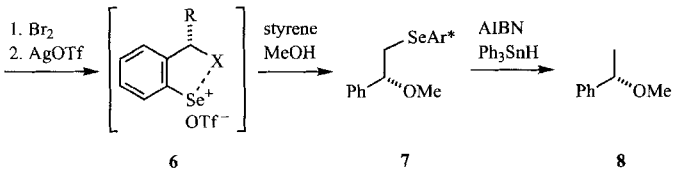
diselenides, especially if functional groups in the molecule do not tolerate the use of butyllithium. The method of diselenide synthesis did not affect the optical purity of the asymmetric center. The enantiomeric excess of optically enriched starting material can be correlated within experimental error to the diastereomeric excess in the resulting diselenide, which can be determined by NMR spectroscopy. The same diselenide (e.g., **1i**, Scheme 2) prepared in different ways had equal optical rotations, showing again the stereochemical integrity of the chiral center during diselenide formation.



Scheme 2. Different synthetic routes to diselenides **1**.

The selenium electrophile **6** is generated from diselenides **1** via the selenenyl bromide and exchange of the bromine with the less nucleophilic triflate. Addition to styrene in the presence of methanol yields the addition products **7** (Scheme 3). For the comparison, only the reactions with styrene are described. Different counterions as well as different solvents were screened. We obtained the highest diastereoselectivities with the selenenyl



Scheme 3. Generation of selenium electrophile **6** from diselenide **1** via selenenyl bromide. Addition of **6** to styrene in the presence of methanol yields **7**, which is cleaved to give **8**.

Abstract in German: *Es wird die Synthese nichtracemischer Diselenide mit Hilfe verschiedener Methoden beschrieben. Diese Diselenide sind Vorläufer für optisch aktive Selenelektrophile. Die Seitenselektivität bei der Addition der Selenelektrophile an Styrol wurde besonders im Hinblick auf die chirale Einheit neben dem Selenatom untersucht. Die Diselenide* **1i**, **1n** *und* **1v** *lieferten die Additionsprodukte* **7** *mit Diastereomerenüberschüssen bis zu 95%. Einige Diselenide, Intermediate und Produkte der Additionsreaktionen wurden zusätzlich mit* ^{77}*Se-NMR Spektroskopie untersucht.*

triflates in diethyl ether, and these conditions were used in all experiments (see experimental section, GP4).

We first investigated diselenides of type **1** with an oxygen atom (X = OR′) in the chiral side chain. It turned out that an intramolecular oxygen–selenium interaction is necessary for high diastereoselectivity. The smaller the residue R′ on the oxygen, the better is the interaction with the selenium and the transfer of chirality to the newly generated stereocenter. This means that diselenides **1** with a free hydroxy group (X = OH) give the highest diastereoselectivities (Table 1). The diastereomeric excesses of the addition products **7** were determined by NMR spectroscopy as well as by GC analysis of the cleavage product **8**. The configuration of the newly generated stereocenter was determined by an independent synthesis of **8**.

Diselenide **1l** shows greater conformational flexibility because the interaction of the oxygen and the selenium lead not to a five-membered but to a six-membered ring. The diastereomeric excess decreases to approximately 4:1 (60% *de*). Selenocyanates can also serve as precursors for selenium cations. In compound **1m** the oxygen atom is adjacent to a chiral center and again a five-membered heterocycle is formed by interaction of selenium with oxygen; however, the much greater flexibility of this system leads to an addition product with 0% *de*. Therefore we synthesized diselenides **1n** and **1o**, in which the conformational flexibility is reduced by the annulation of a second ring. They are accessible from the optically active alcohols[8] by the *ortho*-lithiation route.[9] The addition products were obtained with diastereomeric excesses of 93% ($n = 1$) and 85% ($n = 2$), respectively.[10] We then examined diselenides bearing chiral side chains with two heteroatoms. The isoxazoline-derived diselenide **1p** did not react in the addition reaction. Neither diselenide **1q**, with an acetal moiety, nor diselenide **1h**, with an ethoxymethoxy substituent, were more effi-

Table 1. Reactions of diselenides with styrene and methanol to give addition products **7**.

1	R	X	*T* [°C]	Yield **7** [%]	*de* [a] **7** [%]
1a	Me	O*t*Bu	−78	68	36
1b	Me	OEt	−78	58	74
1c	Me	OMe	−78	63	74
1d	Et	OMe	−78	51	69
1e	CH_2Ph	OMe	−78	75	32
1f [b]	*t*Bu	OMe	−78	45	72
1g	Me	OH	−78	70	77
1g	Me	OH	−100	67	83
1h	Et	$O(CH_2)_2OMe$	−78	54	70
1i	Et	OH	−100	81	89
1i	Et	OH	−114	46	92
1j	*n*Pr	OH	−100	54	87
1k [b]	*t*Bu	OH	−100	33	35
1l			−78	63	60
1m			−78 → 20	26	0
1n			−100	28	93
1o			−100	46	85
1q			−78 → 20	56	0

[a] The *de* values of **7** differ only slightly (±3%) from the *ee* values of the corresponding cleavage product **8**. [b] Diselenides **1f** and **1k** were employed as racemates.

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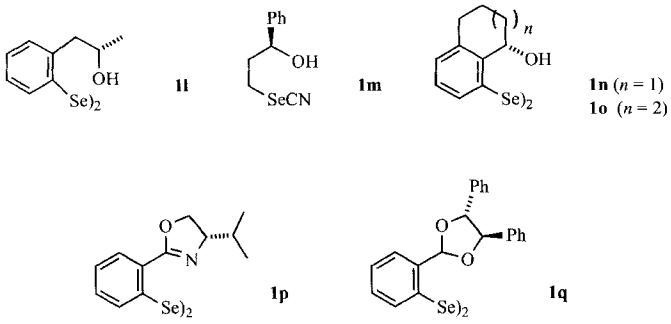


cient in the addition reaction than the diselenides with a free hydroxy group. This indicates that a strong oxygen–selenium interaction is necessary to obtain high diastereoselectivities in the addition reaction.

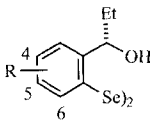
Following on from these results, we varied the electronic properties of diselenide **1i**. Attachment of substituents at the aromatic ring should change the electrophilicity of the selenium cations and therefore have an influence upon their reactivity as well as upon the diastereoselectivity of the addition reaction. Additional substituents at the second *ortho* position to the selenium do indeed have a dramatic influence. These diselenides have a low reactivity towards alkenes and the addition products are formed with low yields and diastereoselectivities (results listed in Table 2). A methyl substituent (**1r**) is not tolerated, and

Table 2. Reactions of further diselenides with styrene and methanol to give addition products **7**.

Diselenide		*T* [°C]	Yield **7** [%]	*de* [a] **7** [%]
1s	R = 6-CF_3	−78 → 20	38	21
1u	R = 5-*t*Bu	−100	33	53
1v	R = 4-NO_2	−100	72	93
1v	R = 4-NO_2	−114	37	95
1w	X = NMe_2	0	64	10
1x	X = pyrrolidin-1-yl	−78 → 20	55	0
1y		−78 → 20	40	6

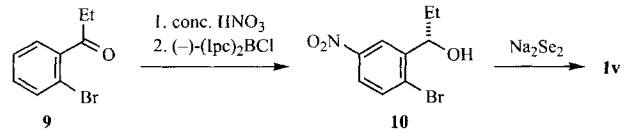
[a] See Table 1.

with a trifluoromethyl (**1s**) group only about 20% *de* was obtained in the addition product. Even a *tert*-butyl group in position 5 (**1u**) decreases the diastereomeric excess to 53%. By connecting a second chiral side chain at position 6 identical to that at position 2, a C_2-symmetrical diselenide (**1t**) is generated. Because the selenium cation is now stabilized by two hydroxy groups, we found it to be completely unreactive towards alkenes.[11] The diselenides **1s** and **1u** could be obtained by the *ortho*-lithiation route; this was not possible in the synthesis of **1r** and **1t**, where the optically active brominated precursors were synthesized. They were lithiated by a bromium–lithium exchange and treated with elemental selenium to yield the diselenides after oxidative workup.



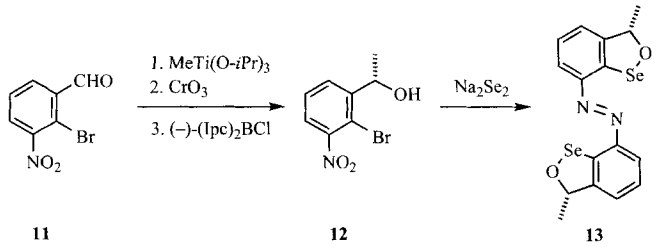
1i: R = H
1r: R = 6 - CH_3
1s: R = 6 - CF_3
1t: R = 6 - (*S*)-CH(OH)Et
1u: R = 5 - *t*Bu
1v: R = 4 - NO_2

Electron-withdrawing substituents in position 4, however, do enhance the electrophilicity of the selenium species. Diselenide **1v**, with a nitro group in the *para* position to the selenium, adds to styrene with a diastereoselectivity of 95%. The nitro-substituted precursor **10** was synthesized from bromopropiophenone (**9**). Compound **10** could not be lithiated without decomposition and was therefore transformed to the diselenide **1v** by treatment with sodium diselenide,[7h] as shown in Scheme 4.



Scheme 4. Diselenide **1v** was obtained from **9** via **10**, which could not be lithiated without decomposition and was therefore treated with sodium diselenide.

The precursor **12** necessary for the synthesis of a diselenide with a nitro group in the *ortho* position to selenium was synthesized from 2-bromo-3-nitrobenzaldehyde (**11**)[12] by a sequence of alkylation,[13] oxidation, and asymmetric reduction (Scheme 5), but the diselenide synthesis failed. A different product, the diazo compound **13**, was isolated from the reaction



Scheme 5. The precursor **12** was synthesized from **11** by a sequence of alkylation, oxidation, and asymmetric reduction, but the diselenide synthesis gave the unexpected product **13**.

mixture and its structure determined by X-ray analysis.[14] It is known that nitro compounds can be coupled to symmetrical diazo compounds with reducing agents,[15] but a benzannulated selenooxole moiety has, to our knowledge, not been described till now.

We also synthesized a variety of diselenides **1** with nitrogen instead of oxygen as the heteroatom coordinated to selenium. For example, the diselenides **1w** and **1x** can be easily prepared

1w: X = NMe_2
1x: X = pyrrolidin-1-yl
1y

from commercially available optically active phenylethylamine. We were able to show that these diselenides are excellent procatalysts for the diethylzinc addition to aldehydes.[16] But, in contrast to other nitrogen-containing diselenides,[5a, e] they add only slowly and with low diastereoselectivites to styrene, as shown in Table 2.

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The addition products from pyridinium-based selenium cations are known to be more reactive precursors for a β-hydride elimination than the benzene counterparts.[17] For this reason diselenide **1y** was prepared, but the diastereomeric excess of the addition product is very low (6% *de*). Compound **1y** was the only diselenide from which crystals suitable for an X-ray analysis could be obtained. The X-ray structure of **1y**[18] indicates small oxygen–selenium distances of about 2.90 Å even in the solid state. It has been observed several times that divalent selenium can interact with nearby heteroatoms in solution as well as in the solid state.[19]

We also analyzed the addition reaction of **1i** to styrene by ^{77}Se NMR. The chemical shift of diselenide **1i** ($\delta = 456$) is within the range of the diselenides synthesized ($\delta = 414–475$, except **1r**: $\delta = 368$). After addition of bromine the selenenyl bromide is generated with a resonance at $\delta = 872$. This value is almost unchanged by the addition of silver triflate to generate **6i** ($\delta = 882$) or the corresponding hexafluoroantimonate with $\delta = 895$. Compared with the literature value for phenylselenenyl bromide ($\delta = 867$) or with the selenenyl bromide generated from **1b** ($\delta = 880$) this indicates only a small influence of the coordinating oxygen on the resonance in the ^{77}Se NMR spectrum. The coordination of a nitrogen has a much greater influence on the chemical shift of the ^{77}Se nucleus. The chemical shifts of the selenenyl bromides generated from **1w** and **1x** are observed at $\delta = 995$ and 974, respectively. The corresponding selenenyl triflates **6w** ($\delta = 1409$, or 1382 in the presence of methanol) and **6x** ($\delta = 1263$) are more markedly influenced by the counterion. This was also observed by other research groups.[20] The selenium cations were generated at $-40\,^{\circ}C$ because decomposition was observed at room temperature. After addition of styrene to the selenenyl bromide generated from **1i**, a signal at $\delta = 1005$ was observed which may correspond to the seleniranium ion **2**. When the selenenyl triflate **6i** was used, no signal was observed in the ^{77}Se spectrum. However, quenching this reaction mixture with methanol at $-40\,^{\circ}C$ apparently resulted in a reaction to the desired product **7i** because a signal at $\delta = 237$ appeared. Compound **7i** was also isolated from the reaction mixture in the NMR tube after aqueous workup.

Conclusion

A series of new optically active diselenides has been synthesized. Many of them are easily accessible in a short synthetic sequence. The diselenides of type **1** bearing a free hydroxy group were found to give the highest diastereoselectivities in the addition reactions to styrene. Structural as well as electronical aspects of these compounds were studied, leading to the production of optimized diselenides like **1i**, **1n**, and **1v**. Diastereomeric excesses of up to 95% were found in the addition products of the selenium cations generated from these diselenides. Although slightly enhanced diastereoselectivities were found with diselenides **1n** and **1v**, we use the diselenide **1i** in synthetic applications because of the low-cost accessibility of gram quantities of this reagent.[6] The ^{77}Se NMR spectra of the diselenides **1**, of the products **7** and of some intermediates of the addition reaction support the findings described.

Experimental Section

General: All reactions were performed under argon with anhydrous solvents. ^{1}H and ^{13}C NMR spectra were recorded with a Varian Gemini 300 spectrometer (solvent: $CDCl_3$), chemical shifts are reported relative to tetramethyl silane as internal standard, coupling constants in Hz. Multiplicities in the ^{13}C NMR spectra were determined by the APT pulse sequence. ^{77}Se NMR spectra were recorded with a Varian Gemini 400 spectrometer (solvent: $CDCl_3$) with diphenyl diselenide ($\delta = 475$) as external standard. IR spectra were measured with a Perkin–Elmer 781 spectrophotometer. MS spectra were recorded with a Finnigan MAT 312 apparatus. Optical rotations were measured with a Perkin–Elmer 141 polarimeter.

General procedure for the synthesis of diselenides from the bromo precursors by bromine–lithium exchange (GP1): The bromo precursor (2 mmol) was dissolved in dry THF (20 mL) under argon, cooled to $-78\,^{\circ}C$ and treated slowly with *t*BuLi (6 mmol). After warming up and stirring for 30 min at $0\,^{\circ}C$, selenium powder (2.2 mmol) was added. The mixture was allowed to warm up to room temperature and stirred for an additional 3 h, then 1 N HCl (20 mL) was added. After extraction of the resulting mixture with *tert*-butyl methyl ether (3×25 mL) and drying of the combined organic phases with $MgSO_4$, powdered KOH (100 mg) was added. The solvent was removed under vacuum and the residue purified by flash chromatography on silica gel. The diselenides were obtained as yellow oils.

General procedure for the synthesis of diselenides from the bromo precursors with sodium diselenide (GP2): Sodium diselenide (4 mmol) was prepared from sodium and selenium in dry THF (10 mL).[7h] The bromo precursor (2 mmol) was dissolved in dry THF (3 mL) and added to the solution. After refluxing for a further 4 h the mixture was cooled to room temperature and water (20 mL) was added. After extraction of the resulting mixture with *tert*-butyl methyl ether (3×20 mL) the combined organic phases were dried with $MgSO_4$. The solvent was removed under vacuum and the residue purified by flash chromatography on silica gel. The diselenides were obtained as yellow oils.

General procedure for the synthesis of diselenides via *ortho* deprotonation (GP3): The precursor (5 mmol) and TMEDA (10 mmol, 1.16 g) were dissolved in dry pentane (10 mL) under argon, cooled to $0\,^{\circ}C$ and treated slowly with *n*BuLi (10.5 mmol, solution in hexane). The mixture was refluxed for 14 h. After cooling to $0\,^{\circ}C$, selenium powder (5 mmol, 395 mg) was added. The mixture was allowed to warm up to room temerature and stirred for an additional 5 h, then 1 N HCl (20 mL) was added. After extraction of the resulting mixture with *tert*-butyl methyl ether (3×50 mL) and drying of the combined organic phases with $MgSO_4$, powdered KOH (100 mg) was added. The solvent was removed under vacuum and the residue purified by flash chromatography on silica gel. The diselenides were obtained as yellow oils.

General procedure for the addition of selenium cations to styrene (GP4): The diselenide (0.1 mmol) was dissolved in dry diethyl ether (4 mL) under argon, cooled to $-78\,^{\circ}C$ and treated with bromine (0.11 mmol, 0.11 mL of a 1 M solution in CCl_4). After 10 min a solution of silver triflate (72 mg, 0.28 mmol) in methanol (0.1 mL) was added and stirred for 10 min at $-78\,^{\circ}C$. The reaction mixture was cooled to $-100\,^{\circ}C$ and treated with styrene (0.4 mmol, 0.046 mL). After 3–4 h of stirring at $-100\,^{\circ}C$, *sym*-collidine (0.3 mmol, 0.04 mL) was added, followed by water (4 mL). After extraction of the reaction mixture with *tert*-butyl methyl ether (3×10 mL), drying of the combined organic phases with $MgSO_4$ and removal of the solvent under reduced pressure the residue was purified by flash chromatography on silica gel, yielding the addition products as colorless oils. The diastereomers could not be separated by flash chromatography and enrichment was excluded by comparison with the diastereomeric excess of the crude reaction mixtures. Spectroscopic data are given only for the major diastereomers of **7**.

The starting materials for the synthesis of the diselenides were prepared by chiral reduction[21] of the corresponding ketones and subsequent alkylation (if necessary) of the hydroxy group by standard procedures: **1a**, **1b**, **1c**, and **1g**: 2-bromoacetophenone yielded (*S*)-1-(2-bromophenyl)ethan-1-ol (96% *ee*),[22] **1d** and **1h**: 1-(2-bromophenyl)propan-1-one[23] yielded (*S*)-1-(2-bromophenyl)propan-1-ol (93% *ee*),[22] **1e**: 1-(2-bromophenyl)-2-phenylethanone[24] yielded (*S*)-1-(2-bromophenyl)-2-phenylethan-1-ol (92% *ee*),[22] **1j**: 1-(2-bromophenyl)butan-1-one[25] yielded (*S*)-1-(2-bromophenyl)butan-

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1-ol (96% *ee*),[26] **1l**: 1-(2-bromophenyl)propan-2-one[27] yielded (*S*)-1-(2-bromophenyl)propan-2-ol (74% *ee*),[28] **1m**: 3-bromo-1-phenylpropan-1-one[29] yielded (*S*)-3-bromo-1-phenylpropan-1-ol (enantiomeric excess determined after reduction to 1-phenylpropan-1-ol with $LiAlH_4$: 97% *ee*[26]), **1y**: 1-(2-bromopyridin-3-yl)ethanone[30] yielded (*S*)-1-(2-bromopyridin-3-yl)ethan-1-ol (94% *ee*).[31] Because it was not possible to perform a chiral reduction with 1-(2-bromophenyl)-2,2-dimethylpropan-1-one, the corresponding alcohol[32] was employed as a racemate for the synthesis of **1f** and **1k**. The precursors for the synthesis of other diselenides are described elsewhere: **1n** and **1o**: ref. [8]; **1p**: ref. [33]; (*S*)-(+)-valinol is commercially available; **1q**: from 2-bromobenzaldehyde according to ref. [34]; (*R*,*R*)-1,2-diphenylethane-1,2-diol is commercially available; **1r**, **1s** and **1u**: ref. [16a], determination of *ee* described therein; **1t**: ref. [35], determination of *ee* described therein.

(*S*,*S*)-Bis{2-[1-(1,1-dimethylethoxy)ethyl]phenyl} diselenide (1a): GP1, purification: *tert*-butyl methyl ether/pentane 1:25, yellow oil, yield: 39%. $[\alpha]_D^{25} = +88.5$ ($c = 1.0$ in $CHCl_3$); ^1H NMR: $\delta = 1.15$ (s, 18H), 1.42 (d, $J = 6.5$ Hz, 6H), 5.04 (q, $J = 6.5$ Hz, 2H), 7.11 (dd, $J = 7.5$ Hz, $J = 7.5$ Hz, 2H), 7.23 (dd, $J = 7.5$ Hz, $J = 7.5$ Hz, 2H), 7.45 (d, $J = 6.5$ Hz, 2H), 7.75 (d, $J = 7.5$ Hz, 2H); ^{13}C NMR: $\delta = 25.6$, 28.5, 70.0, 74.8, 126.5, 127.6, 127.7, 132.8, 134.4, 147.8; ^{77}Se NMR: $\delta = 414.3$; IR ($CHCl_3$): $\tilde{\nu} = 2976$, 2359, 1462, 1367, 1212, 1190, 1083 cm^{-1}; UV (MeOH): $\lambda_{max} = 241$ nm; MS (70 eV, EI): *m*/*z* (%) = 514 (15) [M^+], 201 (23), 183 (36), 104 (9), 91 (8), 77 (8), 57 (100); $C_{24}H_{34}O_2Se_2$ (512.34): calcd C 56.26, H 6.69; found C 56.18, H 6.60.

(*S*,*S*)-Bis[2-(1-ethoxyethyl)phenyl] diselenide (1b): GP1, purification: *tert*-butyl methyl ether/pentane 1:10, yellow oil, yield: 58%. $[\alpha]_D^{25} = +70.5$ ($c = 1.0$ in $CHCl_3$); ^1H NMR: $\delta = 1.20$ (t, $J = 7$ Hz, 6H), 1.46 (d, $J = 6.5$ Hz, 6H), 3.33 (q, $J = 7$ Hz, 4H), 4.82 (q, $J = 6.5$ Hz, 2H), 7.14 (dd, $J = 7.5$ Hz, $J = 7.5$ Hz, 2H), 7.25 (dd, $J = 7.5$ Hz, $J = 7.5$ Hz, 2H), 7.35 (d, $J = 7.5$ Hz, 2H), 7.73 (d, $J = 7.5$ Hz, 2H); ^{13}C NMR: $\delta = 15.5$, 22.7, 64.2, 77.2, 126.3, 128.0, 128.2, 128.8, 133.1, 144.3; ^{77}Se NMR: $\delta = 424.8$; IR ($CHCl_3$): $\tilde{\nu} = 2978$, 2871, 2359, 1464, 1437, 1210, 1097 cm^{-1}; UV (MeOH): $\lambda_{max} = 242$, 205 nm; MS (70 eV, EI): *m*/*z* (%) = 458 (24) [M^+], 229 (22), 199 (26), 183 (100), 157 (12), 104 (36), 91 (32), 77 (34); HRMS calcd for $C_{20}H_{26}O_2Se_2$ [M^+]: 458.0262, found 458.0269.

(*S*,*S*)-Bis[2-(1-methoxyethyl)phenyl] diselenide (1c): GP1, purification: *tert*-butyl methyl ether/pentane 1:10, yellow oil, yield: 58%. $[\alpha]_D^{25} = +54.8$ ($c = 1.0$ in $CHCl_3$); ^1H NMR: $\delta = 1.45$ (d, $J = 6.5$ Hz, 6H), 3.21 (s, 6H), 4.73 (q, $J = 6.5$ Hz, 2H), 7.15 (dd, $J = 7.5$ Hz, $J = 7.5$ Hz, 2H), 7.27 (dd, $J = 7.5$ Hz, $J = 7.5$ Hz, 2H), 7.34 (d, $J = 6.5$ Hz, 2H), 7.73 (d, $J = 7.5$ Hz, 2H); ^{13}C NMR: $\delta = 22.5$, 56.5, 79.0, 126.3, 128.1, 128.3, 129.6, 133.3, 143.8; ^{77}Se NMR: $\delta = 427.5$; IR ($CHCl_3$): $\tilde{\nu} = 3011$, 2931, 2825, 2358, 1586, 1463, 1372, 1212, 1109 cm^{-1}; UV (MeOH): $\lambda_{max} = 242$, 204 nm; MS (70 eV, EI): *m*/*z* (%) = 430 (29) [M^+], 215 (35), 183 (100), 157 (7), 102 (21), 91 (29), 77 (18); $C_{18}H_{22}O_2Se_2$ (428.17): calcd C 50.49, H 5.18; found C 50.91, H 5.19.

(*S*,*S*)-Bis[2-(1-methoxypropyl)phenyl] diselenide (1d): GP1, purification: *tert*-butyl methyl ether/pentane 1:50, yellow oil, yield: 81%. $[\alpha]_D^{25} = +98.6$ ($c = 1.0$ in $CHCl_3$); ^1H NMR: $\delta = 0.93$ (t, $J = 7.5$ Hz, 6H), 1.65–1.85 (m, 4H), 3.16 (s, 6H), 4.48 (dd, $J = 7.4$ Hz, $J = 5.7$ Hz, 2H), 7.14 (dd, $J = 7.5$ Hz, $J = 7.5$ Hz, 2H), 7.21–7.30 (m, 4H), 7.73 (d, $J = 7.5$ Hz, 2H); ^{13}C NMR: $\delta = 10.4$, 30.0, 56.9, 84.7, 126.9, 127.8, 128.2, 129.9, 133.1, 142.5; ^{77}Se NMR: $\delta = 427.1$; IR ($CHCl_3$): $\tilde{\nu} = 3009$, 2934, 2826, 2359, 1586, 1462, 1356, 1118, 1078 cm^{-1}; UV (MeOH): $\lambda_{max} = 242$, 204 nm; MS (70 eV, EI): *m*/*z* (%) = 458 (39) [M^+], 229 (23), 197 (100), 182 (29), 157 (13), 116 (63), 91 (25), 77 (19); $C_{20}H_{26}O_2Se_2$ (456.23): calcd C 52.65, H 5.74; found C 52.68, H 5.80.

(*S*,*S*)-Bis[2-(1-methoxy-2-phenylethyl)phenyl] diselenide (1e): GP1, purification: *tert*-butyl methyl ether/pentane 1:20, yellow oil, yield: 48%. $[\alpha]_D^{25} = +179.0$ ($c = 1.0$ in $CHCl_3$); ^1H NMR: $\delta = 2.96$ (dd, $J = 13.5$ Hz, $J = 5.5$ Hz, 2H), 3.08 (s, 6H), 3.10 (dd, $J = 13.5$ Hz, $J = 7.7$ Hz, 2H), 4.80 (dd, $J = 7.7$ Hz, $J = 5.5$ Hz, 2H), 7.10–7.30 (m, 16H), 7.69 (d, $J = 8$ Hz, 2H); ^{13}C NMR: $\delta = 43.8$, 57.0, 84.3, 126.4, 127.0, 128.2, 128.3, 128.5, 129.7, 130.3, 133.7, 138.3, 142.2; ^{77}Se NMR: $\delta = 432.7$; IR ($CHCl_3$): $\tilde{\nu} = 3010$, 2932, 2359, 1496, 1454, 1217, 1096 cm^{-1}; UV (MeOH): $\lambda_{max} = 242$, 204 nm; MS (70 eV, EI): *m*/*z* (%) = 582 (16) [M^+], 491 (7), 459 (6), 259 (95), 231 (33), 201 (32), 178 (79), 157 (22), 121 (28), 91 (100), 77 (27), 57 (25); HRMS calcd for $C_{30}H_{30}O_2Se_2$ [M^+]: 582.0575, found: 582.0580.

(*RS*,*RS*)-Bis[2-(2,2-dimethyl-1-methoxypropyl)phenyl] diselenide (1f): GP1, purification: *tert*-butyl methyl ether/pentane 1:50, yellow oil, yield: 61%. ^1H NMR: $\delta = 1.00$ (s, 18H), 3.00 (s, 3H), 3.20 (s, 3H), 4.42 (s, 1H), 4.50 (s, 1H), 7.12–7.44 (m, 6H), 7.77 (d, $J = 7.5$ Hz, 1H), 7.91 (d, $J = 7.5$ Hz, 1H); ^{13}C NMR: $\delta = 26.5$, 36.6, 57.3, 57.5, 89.5, 127.2, 127.3, 127.5, 128.0, 128.1, 128.3, 128.5, 133.6, 140.3; ^{77}Se NMR: $\delta = \approx 445$ (br); IR ($CHCl_3$): $\tilde{\nu} = 2977$, 2869, 2358, 1480, 1462, 1362, 1210, 1096 cm^{-1}; MS (70 eV, EI): *m*/*z* (%) = 514 (14) [M^+], 457 (9), 231 (42), 225 (100), 210 (24), 199 (10), 185 (17), 157 (13), 129 (15), 91 (22), 77 (16), 57 (35); HRMS calcd for $C_{24}H_{34}O_2Se_2$ [M^+]: 514.0888, found: 514.0892.

(*S*,*S*)-Bis[2-(1-hydroxyethyl)phenyl] diselenide (1g): GP1, purification: *tert*-butyl methyl ether/pentane 1:2, yellow oil, yield: 48%. $[\alpha]_D^{25} = +246.5$ ($c = 1.0$ in $CHCl_3$). ^1H NMR: $\delta = 1.38$ (d, $J = 6.5$ Hz, 6H), 2.18 (s, 2H), 5.06 (q, $J = 6.5$ Hz, 2H), 7.20 (dd, $J = 7.5$ Hz, $J = 7.5$ Hz, 2H), 7.34 (dd, $J = 7.5$ Hz, $J = 7.5$ Hz, 2H), 7.51 (d, $J = 7.5$, 2H), 7.74 (d, $J = 7.5$, 2H); ^{13}C NMR: $\delta = 24.4$, 69.4, 125.8, 128.4, 129.1, 129.3, 135.2, 147.3; ^{77}Se NMR: $\delta = 445.9$; IR ($CHCl_3$): $\tilde{\nu} = 3599$, 3416, 3010, 2976, 1586, 1464, 1434, 1369, 1254, 1210, 1087, 1002 cm^{-1}; UV (MeOH): $\lambda_{max} = 240$, 205 nm. MS (70 eV, EI): *m*/*z* (%) = 402 (21) [M^+], 199 (34), 183 (100), 157 (15), 104 (25), 91 (34), 77 (38), 51 (16), 43 (95); $C_{16}H_{18}O_2Se_2$ (400.24): calcd C 48.02, H 4.53; found C 48.26, H 4.61.

(*S*,*S*)-Bis{2-[1-(2-methoxyethoxy)propyl]phenyl} diselenide (1h): GP1, purification: *tert*-butyl methyl ether/pentane 1:2, yellow oil, yield: 81%. $[\alpha]_D^{25} = +94.5$ ($c = 1.0$ in $CHCl_3$); ^1H NMR: $\delta = 0.94$ (t, $J = 7.5$ Hz, 6H), 1.62–1.93 (m, 4H), 3.30–3.45 (m, 4H), 3.36 (s, 6H), 3.50 (dd, $J = 5.0$ Hz, $J = 4.3$ Hz, 4H), 4.62 (dd, $J = 7.5$ Hz, $J = 5.5$ Hz, 2H), 7.14 (dd, $J = 7.5$ Hz, $J = 7.5$ Hz, 2H), 7.25 (dd, $J = 7.5$ Hz, $J = 7.5$ Hz, 2H), 7.34 (d, $J = 7.5$, 2H), 7.71 (d, $J = 7.5$, 2H); ^{13}C NMR: $\delta = 10.5$, 30.2, 59.0, 68.3, 72.0, 83.3, 127.0, 128.0, 128.2, 129.8, 133.4, 143.0; ^{77}Se NMR: $\delta = 428.6$; IR ($CHCl_3$): $\tilde{\nu} = 3018$, 2878, 2359, 1462, 1214, 1081 cm^{-1}; UV (MeOH): $\lambda_{max} = 242$, 205 nm; MS (70 eV, EI): *m*/*z* (%) = 546 (12) [M^+], 213 (9), 197 (28), 183 (10), 116 (15), 91 (8), 77 (4), 59 (100), 45 (19); $C_{24}H_{34}O_4Se_2$ (544.34): calcd C 52.96, H 6.30; found C 52.96, H 6.28.

(*S*,*S*)-Bis[2-(1-hydroxypropyl)phenyl] diselenide (1i): Preparation and characterization see ref. [6a].

(*S*,*S*)-Bis[2-(1-hydroxybutyl)phenyl] diselenide (1j): GP1, purification: *tert*-butyl methyl ether/pentane 1:2, yellow oil, yield: 80%. $[\alpha]_D^{25} = +241.0$ ($c = 1.0$ in $CHCl_3$). ^1H NMR: $\delta = 0.84$ (t, $J = 7.4$ Hz, 6H), 1.17–1.38 (m, 4H), 1.55–1.65 (m, 4H), 2.59 (s, 2H), 4.84 (dd, $J = 7.7$ Hz, $J = 5.2$ Hz, 2H), 7.16 (dd, $J = 7.5$ Hz, $J = 7.5$ Hz, 2H), 7.31 (dd, $J = 7.5$ Hz, $J = 7.5$ Hz, 2H), 7.44 (d, $J = 7.5$, 2H), 7.74 (d, $J = 7.5$, 2H); ^{13}C NMR: $\delta = 13.9$, 19.1, 40.6, 73.1, 126.3, 128.3, 129.2, 129.8, 135.6, 147.0; ^{77}Se NMR: $\delta = 455.9$; IR ($CHCl_3$): $\tilde{\nu} = 3604$, 3063, 2961, 2934, 1601, 1463, 1266, 1134, 1049, 1016 cm^{-1}; MS (70 eV, EI): *m*/*z* (%) = 458 (16) [M^+], 227 (20), 211 (34), 183 (100), 157 (28), 130 (69), 115 (45), 102 (26), 91 (51), 78 (76); HRMS calcd for $C_{20}H_{26}O_2Se_2$ [M^+]: 458.0262, found: 458.0272.

(*RS*,*RS*)-Bis[2-(2,2-dimethyl-1-hydroxypropyl)phenyl] diselenide (1k): GP1, purification: *tert*-butyl methyl ether/pentane 1:5, yellow oil, yield: 18%; ^1H NMR: $\delta = 0.77$ (s, 18H), 2.38 (s, 2H), 4.46 (s, 2H), 7.10–7.36 (m, 6H), 7.89 (d, $J = 7.7$ Hz, 2H); ^{13}C NMR: $\delta = 25.9$, 36.1, 79.5, 128.1, 128.3, 128.7, 134.3, 136.9, 145.0; IR ($CHCl_3$): $\tilde{\nu} = 3606$, 3433, 2956, 2870, 2359, 1479, 1463, 1364, 1004 cm^{-1}; MS (70 eV, EI): *m*/*z* (%) = 486 (8) [M^+], 411 (6), 241 (6), 225 (43), 211 (17), 185 (100), 157 (15), 144 (8), 129 (10), 104 (10), 78 (43), 57 (57); HRMS calcd for $C_{22}H_{30}O_2Se_2$ [M^+]: 486.0575, found: 486.0558.

(*S*,*S*)-Bis[2-(2-hydroxypropyl)phenyl] diselenide (1l): GP1, purification: *tert*-butyl methyl ether/pentane 1:1, yellow oil, yield: 52%. $[\alpha]_D^{25} = -67.0$ ($c = 1.0$ in $CHCl_3$); ^1H NMR: $\delta = 1.19$ (d, $J = 6.2$ Hz, 6H), 1.59 (s, 2H), 2.76–2.97 (m, 4H), 3.87 (m, 2H), 7.10–7.26 (m, 6H), 7.70 (d, $J = 7.7$ Hz, 2H); ^{13}C NMR: $\delta = 23.1$, 45.7, 68.3, 127.7, 128.5, 130.6, 132.2, 134.7, 140.1; ^{77}Se NMR: $\delta = 448.5$; IR ($CHCl_3$): $\tilde{\nu} = 3600$, 3442, 3062, 3010, 2930, 2359, 1586, 1464, 1378, 1256, 1116, 1041, 933 cm^{-1}; MS (70 eV, EI): *m*/*z* (%) = 430 (18) [M^+], 214 (8), 197 (40), 183 (12), 170 (21), 116 (21), 91 (100), 77 (9), 65 (11); HRMS calcd for $C_{18}H_{22}O_2Se_2$ [M^+]: 429.9949, found: 429.9940.

(*S*)-1-Phenyl-3-selenocyanatopropan-1-ol (1m): (*S*)-3-Bromo-1-phenylpropan-1-ol (1 mmol, 215 mg) was treated with potassium selenocyanate

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(1 mmol, 144 mg) in DMF (2 mL) at 60 °C for 2 h. After addition of water (10 mL) and extraction with *tert*-butyl methyl ether (3 × 10 mL) the combined organic phases were washed with water (4 × 5 mL) and dried with $MgSO_4$. The solvent was removed under vacuum and the residue purified by flash chromatography (*tert*-butyl methyl ether/pentane 1:3) on silica gel. Compound **1m** was obtained as a white solid in 73% yield (175 mg). M.p.: 51–53 °C; ^{1}H NMR: δ = 2.05 (s, 1H), 2.31 (m, 2H), 3.22 (dt, J = 4.8 Hz, J = 6.7 Hz, 2H), 4.89 (m, 1H), 7.30–7.42 (m, 5H); ^{13}C NMR: δ = 25.8 (t), 38.9 (t), 73.0 (d), 103.0 (s), 125.5 (d, 2C), 127.9 (d), 128.5 (d, 2C), 142.8 (s); ^{77}Se NMR: δ = 523.1; IR ($CHCl_3$): $\tilde{\nu}$ = 3604, 3064, 2919, 2359, 2153, 1602, 1496, 1455, 1398, 1266, 1335, 1050, 1016 cm^{-1}; MS (70 eV, EI): m/z (%) = 241 (1) [M^+], 213 (3), 133 (3), 117 (9), 107 (100), 79 (52), 77 (28), 51 (9); $C_{10}H_{11}NOSe$ (240.17).

(*S,S*)-Bis[1-(8-hydroxy-5,6,7,8-tetrahydronaphthyl)] diselenide (1n): GP3, purification: *tert*-butyl methyl ether/pentane 1:2, yellow solid, m.p.: 54–57 °C, yield: 36%. $[\alpha]_D^{25}$ = − 88.8 (c = 1.02 in $CHCl_3$); ^{1}H NMR ([D$_6$]benzene): δ = 1.65–2.08 (m, 8H), 2.37 (s, 2H), 2.60–2.85 (m, 4H), 5.02 (m, 2H), 7.10 (dd, J = 7.5 Hz, J = 7.5 Hz, 2H), 7.08 (d, J = 7.5 Hz, 2H), 7.63 (d, J = 7.5 Hz, 2H); ^{13}C NMR: δ = 18.1 (t), 30.2 (t), 32.6 (t), 66.8 (d), 128.5 (d), 128.8 (d), 129.5 (s), 131.2 (d), 134.9 (s), 138.4 (s); ^{77}Se NMR: δ = 436.2; IR ($CHCl_3$): $\tilde{\nu}$ = 3591, 3406, 3006, 2942, 2869, 1562, 1457, 1440, 1378, 1074, 1005, 962 cm^{-1}; MS (70 eV, EI): m/z (%) = 454 (15) [M^+], 226 (51), 211 (24), 147 (31), 129 (100), 115 (45), 91 (53), 77 (17), 65 (12), 51 (12); HRMS calcd for $C_{20}H_{22}O_2Se_2$ [M^+]: 453.9949, found: 453.9970.

(*S,S*)-Bis[1-(5*H*-6,7,8,9-tetrahydrobenzocyclohepten-9-ol)] diselenide (1o): GP3, purification: *tert*-butyl methyl ether/pentane 1:2, yellow solid, m.p.: 56–59 °C, yield: 75%. $[\alpha]_D^{25}$ = + 327.4 (c = 0.85 in $CHCl_3$); ^{1}H NMR: δ = 1.31–2.16 (m, 10H), 2.61 (d, J = 7.0 Hz, 4H), 3.33 (t, J = 7.0 Hz, 4H), 5.51 (d, J = 7.0 Hz, 2H), 6.95–7.12 (m, 4H), 7.67 (d, J = 7.5 Hz, 2H); ^{13}C NMR: δ = 24.8 (t), 28.2 (t), 32.8 (t), 35.7 (t), 73.5 (d), 128.4 (d), 131.4 (d), 131.7 (s), 133.4 (d), 144.3 (s), 144.4 (s); ^{77}Se NMR: δ = 482.8; IR ($CHCl_3$): $\tilde{\nu}$ = 3596, 3419, 3005, 2932, 2856, 1445, 1073, 993 cm^{-1}; MS (70 eV, EI): m/z (%) = 482 (20) [M^+], 239 (68), 224 (71), 209 (8), 195 (27), 183 (10), 169 (16), 143 (100), 129 (74), 115 (80), 104 (22), 91 (72), 77 (26), 63 (13), 51 (12); HRMS calcd for $C_{22}H_{26}O_2Se_2$ [M^+]: 482.0262, found: 482.0220.

(*S,S*)-Bis{2-[4,5-dihydro-4-(1-methylethyl)oxazol-2-yl]phenyl} diselenide (1p): GP3, purification: *tert*-butyl methyl ether/pentane 1:10, pale yellow crystals, m.p. 187–189 °C, yield: 23%. $[\alpha]_D^{25}$ = −138.0 (c = 1.0 in $CHCl_3$); ^{1}H NMR: δ = 1.03 (d, J = 6.8 Hz, 6H), 1.13 (d, J = 6.8 Hz, 6H), 1.87 (sept, J = 6.8 Hz, 2H), 4.14–4.30 (m, 4H), 4.48 (dd, J = 9.0 Hz, J = 7.7 Hz, 2H), 7.22–7.28 (m, 4H), 7.81–7.88 (m, 4H); ^{13}C NMR: δ = 19.0, 33.4, 70.7, 73.4, 125.6, 126.1, 129.5, 130.6, 131.4, 133.7, 163.0; ^{77}Se NMR: δ = 473.1; IR ($CHCl_3$): $\tilde{\nu}$ = 2961, 1646, 1464, 1359, 1210, 1208, 1134, 1081, 1024, 963 cm^{-1}; UV (MeOH): λ_{max} = 314, 204 nm; MS (70 eV, CI[NH_3]): m/z (%) = 537 (2) [M^+ + H], 457 (4), 270 (100), 228 (4), 190 (90), 146 (4), 104 (2); $C_{24}H_{28}N_2O_2Se_2$ (534.30): calcd C 53.95, H 5.28, N 5.24, O 5.99; found C 53.18, H 5.17, N 5.14, O 6.17.

(*R,R*)-Bis{2-[4,5-diphenyl-1,3-dioxolan-2-yl]phenyl} diselenide (1q): GP1, purification: *tert*-butyl methyl ether/pentane 1:10, yellow oil, yield: 29%. $[\alpha]_D^{25}$ = − 23.1 (c = 0.74 in $CHCl_3$); ^{1}H NMR: δ = 4.96 (d, J = 8.1 Hz, 2H), 5.04 (d, J = 8.1 Hz, 2H), 6.62 (s, 2H), 7.30–7.37 (m, 24H), 7.74 (dd, J = 7.2 Hz, J = 2.1 Hz, 2H), 7.91 (dd, J = 7.3 Hz, J = 1.8 Hz, 2H); ^{13}C NMR: δ = 85.1 (d, 2C), 87.5 (d, 2C), 104.2 (d, 2C), 126.3 (d, 4C), 127.1 (d, 6C), 127.5 (d, 2C), 128.2 (d, 2C), 128.5 (d, 10C), 130.3 (d, 2C), 130.8 (s, 2C), 133.1 (d, 2C), 136.2 (s, 2C), 137.0 (s, 2C), 138.2 (s, 2C); ^{77}Se NMR: δ = 431.7; IR ($CHCl_3$): $\tilde{\nu}$ = 3066, 2916, 1588, 1496, 1454, 1360, 1126, 1088, 1025 cm^{-1}; MS (70 eV, EI): m/z (%) = 762 (2) [M^+], 471 (2), 380 (4), 275 (10), 180 (61), 165 (42), 91 (100), 77 (42); $C_{42}H_{34}O_4Se_2$ (760.53): calcd C 66.33, H 4.51; found C 66.35, H 4.70.

(*S,S*)-Bis[2-(1-hydroxypropyl)-6-methylphenyl] diselenide (1r): GP1, purification: *tert*-butyl methyl ether/pentane 1:2, yellow solid, m.p.: 57–59 °C, yield: 34%. $[\alpha]_D^{25}$ = − 46.4 (c = 1.15 in $CHCl_3$); ^{1}H NMR: δ = 0.71 (t, J = 7.4 Hz, 6H), 1.44 (m, 4H), 1.63 (s, 2H), 2.64 (s, 6H), 4.48 (t, J = 6.2 Hz, 2H), 5.04 (d, J = 8.1 Hz, 2H), 7.26–7.33 (m, 6H); ^{13}C NMR: δ = 10.2 (q), 24.6 (q), 31.6 (t), 74.6 (d), 123.7 (d), 129.2 (d), 129.5 (s), 129.9 (d), 143.6 (s), 150.0 (s); ^{77}Se NMR: δ = 367.8; IR ($CHCl_3$): $\tilde{\nu}$ = 3564, 3063, 3005, 2965, 2932, 1602, 1460, 1378, 1266, 1178, 1135, 1049, 1016, 973, 813 cm^{-1}; MS (70 eV, EI): m/z (%) = 458 (47) [M^+], 228 (62), 212 (100), 199 (69), 130 (35), 115 (21), 91 (58), 71 (16), 57 (32); HRMS calcd for $C_{20}H_{26}O_2Se_2$ [M^+]: 458.0262, found: 458.0269.

(*S,S*)-Bis[2-(1-hydroxypropyl)-6-trifluoromethylphenyl] diselenide (1s): GP3, purification: *tert*-butyl methyl ether/pentane 1:4, yellow oil, yield: 14%. $[\alpha]_D^{25}$ = + 217.4 (c = 0.61 in $CHCl_3$); ^{1}H NMR: δ = 0.70 (t, J = 7.4 Hz, 6H), 1.40–1.60 (m, 4H), 2.75 (s, 2H), 4.67 (t, J = 6.1 Hz, 2H), 7.53 (m, 2H), 7.74 (d, J = 7.7 Hz, 2H), 7.79 (d, J = 7.7 Hz, 2H); ^{13}C NMR: δ = 9.9 (q), 32.2 (t), 74.5 (d), 123.7 (s, $^1J_{C,F}$ = − 264 Hz), 126.4 (s), 126.6 (d), 129.8 (d), 130.3 (d), 135.0 (s, $^2J_{C,F}$ = − 27 Hz), 151.8 (s); ^{77}Se NMR: δ = 433.7; IR ($CHCl_3$): $\tilde{\nu}$ = 3604, 3419, 2967, 2932, 2877, 1462, 1418, 1313, 1136, 1093, 1048, 997 cm^{-1}; MS (70 eV, EI): m/z (%) = 566 (37) [M^+], 282 (76), 266 (68), 253 (100), 184 (29), 145 (22), 115 (27), 57 (24); HRMS calcd for $C_{20}H_{20}F_6O_2Se_2$ [M^+]: 565.9697, found: 565.9698.

(*S,S*)-Bis[2,6-bis-(1-hydroxypropyl)phenyl] diselenide (1t): GP1, purification: *tert*-butyl methyl ether/pentane 1:1, yellow oil, yield: 46%. $[\alpha]_D^{25}$ = + 322.6 (c = 0.96 in MeOH); ^{1}H NMR: δ = 0.85 (m, 12H), 1.50–1.85 (m, 8H), 3.50 (s, 4H), 5.00 (m, 4H), 7.20–7.55 (m, 6H); ^{13}C NMR: δ = 10.1 (q), 31.6 (t), 74.7 (d), 125.0 (s), 125.7 (d), 130.5 (d), 149.2 (d); IR (KBr): $\tilde{\nu}$ = 3363, 2963, 2930, 2498, 1458, 1170, 1047, 979 cm^{-1}; MS (70 eV, EI): m/z (%) = 546 (0.4) [M^+], 300 (18), 272 (100), 255 (37), 243 (97), 223 (37), 209 (52), 197 (46), 182 (29), 156 (25), 142 (20), 129 (22), 115 (54), 102 (14), 91 (38), 77 (31); $C_{24}H_{34}O_4Se_2$ 544.46.

(*S,S*)-Bis[5-(1,1-dimethylethyl)-2-(1-hydroxypropyl)-phenyl] diselenide (1u): GP3, purification: *tert*-butyl methyl ether/pentane 4:1, yellow oil, yield: 42%. $[\alpha]_D^{25}$ = + 465.6 (c = 1.05 in $CHCl_3$); ^{1}H NMR: δ = 0.81 (t, J = 7.4 Hz, 6H), 1.27 (s, 18H), 1.62 (m, 4H), 2.05 (s, 2H), 4.69 (t, J = 6.6 Hz, 2H), 7.34 (s, 4H), 7.78 (s, 2H); ^{13}C NMR: δ = 10.4 (q), 31.1 (t), 31.2 (q), 34.7 (s), 74.4 (d), 125.7 (d), 126.3 (d), 129.5 (s), 132.8 (d), 143.9 (s), 151.3 (s); ^{77}Se NMR: δ = 461.7; IR ($CHCl_3$): $\tilde{\nu}$ = 3599, 3426, 2966, 2875, 1596, 1481, 1463, 1383, 1263, 1115, 1041, 971 cm^{-1}; MS (70 eV, EI): m/z (%) = 542 (10) [M^+], 269 (22), 254 (27), 239 (42), 197 (18), 117 (12), 91 (11), 77 (5), 57 (100); HRMS calcd for $C_{26}H_{38}O_2Se_2$ [M^+]: 542.1201, found: 542.1215.

(*S,S*)-Bis[2-(1-hydroxypropyl)-4-nitrophenyl] diselenide (1v): GP2, purification: *tert*-butyl methyl ether/pentane 1:2, yellow oil, yield: 45%. $[\alpha]_D^{25}$ = + 132.3 (c = 0.31 in $CHCl_3$); ^{1}H NMR: δ = 1.03 (t, J = 7.5 Hz, 6H), 1.90 (m, 4H), 2.32 (s, 2H), 4.99 (t, J = 6.5 Hz, 2H), 7.84 (d, J = 8.7 Hz, 2H), 7.99 (dd, J = 8.7 Hz, J = 2.5 Hz, 2H), 8.27 (d, J = 2.5 Hz, 2H); ^{13}C NMR: δ = 10.1 (q), 30.3 (t), 74.7 (d), 121.1 (d), 122.6 (d), 132.0 (d), 137.6 (s), 145.3 (s), 147.2 (s); ^{77}Se NMR: δ = 441.5; IR ($CHCl_3$): $\tilde{\nu}$ = 3596, 2967, 1571, 1522, 1456, 1345, 1204, 1134, 1048, 1016, 813 cm^{-1}; MS (70 eV, EI): m/z (%) = 520 (8) [M^+], 440 (11), 405 (10), 259 (37), 243 (40), 230 (100), 196 (24), 182 (30), 156 (18), 115 (53), 77 (24), 57 (36); HRMS calcd for $C_{18}H_{20}N_2O_6Se_2$ [M^+]: 519.9651, found: 519.9654.

(*R,R*)-Bis{2-[1-(dimethylamino)ethyl]phenyl} diselenide (1w): Preparation and characterization see ref. [16a].

(*R,R*)-Bis{2-[1-(pyrrolidin-1-yl)ethyl]phenyl} diselenide (1x): Preparation and characterization see ref. [16a].

(*S,S*)-Bis[3-(1-ethoxyethyl)pyridin-2-yl] diselenide (1y): GP1, purification: *tert*-butyl methyl ether/pentane 1:2, yellow solid, yield: 26%. $[\alpha]_D^{25}$ = 96.3 (c = 0.54 in $CHCl_3$); ^{1}H NMR: δ = 1.20 (d, J = 6.9 Hz, 6H), 1.48 (d, J = 6.5 Hz, 6H), 3.38 (q, J = 6.9 Hz, 4H), 4.80 (q, J = 6.5 Hz, 2H), 7.10 (dd, J = 7.6 Hz, J = 4.7 Hz, 2H), 7.55 (dd, J = 7.6 Hz, J = 1.6 Hz, 2H), 8.33 (d, J = 4.7 Hz, J = 1.6 Hz, 2H); ^{13}C NMR: δ = 15.5 (q), 22.4 (q), 64.5 (t), 75.9 (d), 122.1 (d), 133.4 (d), 140.1 (s), 149.2 (d), 152.5 (s); ^{77}Se NMR: δ = 474.8; IR ($CHCl_3$): $\tilde{\nu}$ = 3019, 1574, 1396, 1214, 1102, 760; MS (70 eV, EI): m/z (%) = 460 (15) [M^+], 379 (11), 333 (6), 231 (15), 200 (61), 184 (100), 122 (10), 104 (56), 92 (13), 78 (51), 65 (8), 51 (25); $C_{18}H_{24}N_2O_2Se_2$ (458.20): calcd C 47.18, H 5.28, N 6.11; found C 47.17, H 5.17, N 6.11.

1-[(*S*)-1-(1,1-Dimethylethoxy)ethyl]-2-[(*R*)-(2-methoxy-2-phenyl)ethyl]selenobenzene (7a): GP4, purification: *tert*-butyl methyl ether/pentane 1:50, colorless oil, yield: 68%. ^{1}H NMR: δ = 1.15 (s, 9H), 1.33 (t, J = 5.8 Hz, 3H), 3.12 (dd, J = 12 Hz, J = 5.3 Hz, 1H), 3.28 (s, 3H), 3.36 (dd, J = 12 Hz, J = 7.6 Hz, 1H), 4.43 (m, 1H), 5.08 (m, 1H), 7.12 (t, J = 7.2 Hz, 1H), 7.24

(t, $J = 7.5$ Hz, 1H), 7.36 (m, 7H), 7.60 (d, $J = 7.4$ Hz, 1H); ^{13}C NMR: $\delta = 25.8$, 28.6, 35.1, 57.1, 68.8, 74.3, 83.2, 126.6, 126.7, 127.0, 127.2, 127.9, 128.2, 128.6, 131.8, 140.9, 148.9; IR ($CHCl_3$): $\tilde{\nu} = 2976$, 2932, 2358, 1454, 1367, 1234, 1192, 1134, 1083, 1050, 1016, 956, 813 cm^{-1}; MS (70 eV, EI): m/z (%) = 392 (19) [M^+], 199 (59), 183 (24), 135 (14), 121 (100), 103 (20), 91 (24), 77 (20); HRMS calcd for $C_{21}H_{28}O_2Se$ [M^+]: 392.1254, found 392.1244.

1-[(*S*)-1-Ethoxyethyl]-2-[(*R*)-(2-methoxy-2-phenyl)ethyl]selenobenzene (7b): GP4, purification: *tert*-butyl methyl ether/pentane 1:50, yellow oil, yield: 27%. ^{1}H NMR: $\delta = 1.17$ (t, $J = 7$ Hz, 3H), 1.40 (d, $J = 6.4$ Hz, 3H), 3.05 (dd, $J = 12$ Hz, $J = 5$ Hz, 1H), 3.24 (s, 3H), 3.33 (m, 3H), 4.36 (dd, $J = 8.5$ Hz, $J = 5.1$ Hz, 1H), 4.88 (q, $J = 6.5$ Hz, 1H), 7.13 (td, $J = 7.5$ Hz, $J = 2.5$ Hz, 1H), 7.22–7.52 (m, 8H); ^{13}C NMR: $\delta = 15.5$, 23.3, 35.3, 57.1, 64.0, 76.3, 83.1, 125.9, 126.7, 127.4, 127.5, 127.8, 128.2, 128.6, 132.6, 140.9, 145.5; IR ($CHCl_3$): $\tilde{\nu} = 2978$, 2929, 2872, 1601, 1454, 1398, 1266, 1135, 1108, 1050, 1016 cm^{-1}; MS (70 eV, EI): m/z (%) = 364 (17) [M^+], 228 (18), 199 (12), 183 (16), 149 (14), 135 (11), 121 (100), 103 (17), 91 (20), 77 (20); HRMS calcd for $C_{19}H_{24}O_2Se$ [M^+]: 364.0941, found: 364.0958.

1-[(*S*)-1-Methoxypropyl]-2-[(*R*)-(2-methoxy-2-phenyl)ethyl]selenobenzene (7d): GP4, purification: *tert*-butyl methyl ether/pentane 1:50, yellow oil, yield: 51%. ^{1}H NMR: $\delta = 0.95$ (t, $J = 7.3$ Hz, 3H), 1.71 (m, 2H), 3.08 (dd, $J = 12$ Hz, $J = 5$ Hz, 1H), 3.22 (s, 3H), 3.26 (s, 3H), 3.32 (dd, $J = 12$ Hz, $J = 8.4$ Hz, 1H), 4.39 (dd, $J = 8.3$ Hz, $J = 5$ Hz, 1H), 4.61 (t, $J = 6.6$ Hz, 1H), 7.16 (td, $J = 7.6$ Hz, $J = 1.7$ Hz, 1H), 7.23–7.42 (m, 7H), 7.47 (dd, $J = 7.7$ Hz, $J = 1.3$ Hz, 1H); ^{13}C NMR: $\delta = 10.3$, 30.4, 35.5, 56.8, 57.0, 83.1, 83.5, 126.4, 126.7, 127.2, 127.8, 128.2, 128.6, 130.6, 132.6, 140.9, 143.6; IR ($CHCl_3$): $\tilde{\nu} = 3008$, 2934, 2826, 1463, 1234, 1210, 1134, 1106, 1050, 1016, 813 cm^{-1}; MS (70 eV, EI): m/z (%) = 364 (20) [M^+], 228 (14), 197 (9), 183 (7), 149 (9), 135 (11), 121 (100), 103 (16), 91 (21), 77 (19); HRMS calcd for $C_{19}H_{24}O_2Se$ [M^+]: 364.0941, found: 364.0945.

1-[(*S*)-1-Methoxy-2-phenylethyl]-2-[(*R*)-(2-methoxy-2-phenyl)ethyl]selenobenzene (7e): GP4, purification: *tert*-butyl methyl ether/pentane 1:10, yellow oil, yield: 75%. ^{1}H NMR: $\delta = 2.90$–3.10 (m, 3H), 3.15 (s, 3H), 3.23 (s, 3H), 3.25–3.36 (m, 1H), 4.35 (m, 1H), 4.92 (m, 1H), 7.10–7.40 (m, 14H); ^{13}C NMR: $\delta = 35.7$, 44.1, 57.1, 83.1, 83.4, 126.5, 126.6, 126.7, 127.3, 127.4, 128.0, 128.1, 128.2 128.7, 129.6, 133.0, 138.9, 140.9, 143.3; IR ($CHCl_3$): $\tilde{\nu} = 3005$, 2935, 2826, 1602, 1495, 1454, 1366, 1102, 1050, 909 cm^{-1}; MS (70 eV, EI): m/z (%) = 426 (8) [M^+], 335 (35), 259 (9), 231 (47), 199 (10), 178 (19), 157 (8), 135 (13), 121 (100), 103 (23), 91 (43), 77 (25); HRMS calcd for $C_{24}H_{26}O_2Se$ [M^+]: 426.1097, found: 426.1102.

1-[(*S)-2,2-Dimethyl-1-methoxypropyl]-2-[(*R**)-(2-methoxy-2-phenyl)ethyl]selenobenzene (7f)**: GP4, purification: *tert*-butyl methyl ether/pentane 1:50, yellow oil, yield: 45%; ^{1}H NMR: $\delta = 0.92$ (s, 9H), 3.04 (dd, $J = 12.1$ Hz, $J = 5.2$ Hz, 1H), 3.11 (s, 3H), 3.25 (s, 3H), 3.32 (dd, $J = 12.1$ Hz, $J = 8.2$ Hz, 1H), 4.40 (dd, $J = 8.2$ Hz, $J = 5.2$ Hz, 1H), 4.51 (s, 1H), 7.16 (td, $J = 7.7$ Hz, $J = 1.7$ Hz, 1H), 7.20–7.41 (m, 7H), 7.50 (d, $J = 7.7$ Hz, 1H); ^{13}C NMR: $\delta = 26.3$ (3C), 36.4 (2C), 57.0, 57.2, 83.2, 88.6, 126.4, 126.5, 126.7, 127.7, 128.1, 128.3, 128.6, 132.6, 140.9, 141.4; IR ($CHCl_3$): $\tilde{\nu} = 3008$, 2955, 2870, 1462, 1362, 1097 cm^{-1}; MS (70 eV, EI): m/z (%) = 392 (4) [M^+], 335 (16), 231 (31), 199 (6), 135 (8), 121 (100), 103 (10), 91 (18), 77 (12), 57 (6); HRMS calcd for $C_{21}H_{28}O_2Se$ [M^+]: 392.1254, found: 392.1256.

(*S*)-1-(2-{[(*R*)-(2-Methoxy-2-phenyl)ethyl]seleno}phenyl)ethanol (7g): GP4, purification: *tert*-butyl methyl ether/pentane 1:2, yellow oil, yield: 67%. ^{1}H NMR: $\delta = 1.47$ (d, $J = 6.5$ Hz, 3H), 2.56 (s, 1H), 3.10 (dd, $J = 12.2$ Hz, $J = 4.8$ Hz, 1H), 3.22 (s, 3H), 3.24 (dd, $J = 12.2$ Hz, $J = 8.6$ Hz, 1H), 4.34 (dd, $J = 8.6$ Hz, $J = 4.8$ Hz, 1H), 5.28 (q, $J = 6.5$ Hz, 1H), 7.14 (td, $J = 7.5$ Hz, $J = 1.5$ Hz, 1H), 7.22–7.35 (m, 6H), 7.48 (m, 2H); ^{13}C NMR: $\delta = 24.1$, 36.1, 57.0, 69.2, 83.1, 125.7, 126.7 (2C), 127.8, 128.1, 128.2, 128.5, 128.6 (2C), 133.8, 140.8, 147.0; IR ($CHCl_3$): $\tilde{\nu} = 3603$, 3437, 3064, 3006, 2933, 1601, 1494, 1454, 1266, 1135, 1104, 1050, 1016, 813 cm^{-1}; MS (70 eV, EI): m/z (%) = 336 (13) [M^+], 200 (22), 183 (12), 135 (10), 121 (100), 103 (18), 91 (23), 87 (14), 77 (26); HRMS calcd for $C_{17}H_{20}O_2Se$ [M^+]: 336.0628, found: 336.0622.

1-[(*S*)-1-(2-Methoxyethoxy)propyl]-2-[(*R*)-(2-methoxy-2-phenyl)ethyl]selenobenzene (7h): GP4, purification: *tert*-butyl methyl ether/pentane 1:5, yellow oil, yield: 54%. ^{1}H NMR: $\delta = 0.97$ (t, $J = 7.4$ Hz, 3H), 1.74 (m, 2H), 3.08 (dd, $J = 12.1$ Hz, $J = 5.1$ Hz, 1H), 3.26 (s, 3H), 3.37 (s, 3H), 3.26–3.55 (m, 5H), 4.39 (dd, $J = 8.2$ Hz, $J = 4.9$ Hz, 1H), 4.72 (m, 1H), 7.14 (t, $J = 7.6$ Hz, 1H), 7.23–7.38 (m, 6H), 7.45 (d, $J = 7.7$ Hz, 2H); ^{13}C NMR: $\delta = 10.5$, 30.6, 35.5, 57.0, 59.0, 68.2, 72.0, 82.3, 83.1, 126.6, 126.7 (2C), 127.3, 127.8, 128.2, 128.6 (2C), 130.5, 132.4, 140.9, 143.9; IR ($CHCl_3$): $\tilde{\nu} = 3005$, 2933, 2877, 1455, 1134, 1104, 1084, 1050, 1016 cm^{-1}; MS (70 eV, EI): m/z (%) = 408 (6) [M^+], 213 (4), 197 (8), 183 (6), 135 (7), 121 (100), 103 (11), 91 (16), 77 (12), 73 (19), 59 (39); HRMS calcd for $C_{21}H_{28}O_3Se$ [M^+]: 408.1203, found: 408.1223.

(*S*)-1-(2-{[(*R*)-(2-Methoxy-2-phenyl)ethyl]seleno}phenyl)propanol (7i): GP4, purification: *tert*-butyl methyl ether/pentane 1:4, colorless oil, yield: 81%. ^{1}H NMR: $\delta = 0.98$ (t, $J = 7.4$ Hz, 3H), 1.79 (quint, $J = 7.3$ Hz, 2H), 2.41 (s, 1H), 3.12 (dd, $J = 12.2$ Hz, $J = 4.8$ Hz, 1H), 3.24 (s, 3H), 3.27 (dd, $J = 12.2$ Hz, $J = 8.5$ Hz, 1H), 4.36 (dd, $J = 8.5$ Hz, $J = 4.9$ Hz, 1H), 5.04 (m, 1H), 7.13–7.51 (m, 9H); ^{13}C NMR: $\delta = 10.4$, 31.2, 36.2, 57.0, 74.7, 83.0, 126.4, 126.7 (2C), 127.6, 128.0, 128.2, 128.6 (2C), 129.7, 133.7, 140.8, 146.0; ^{77}Se NMR: $\delta = 267$; IR ($CHCl_3$): $\tilde{\nu} = 3604$, 3442, 3064, 3005, 2935, 2877, 1601, 1455, 1266, 1135, 1105, 1049, 1016 cm^{-1}; MS (70 eV, EI): m/z (%) = 350 (3) [M^+], 214 (8), 185 (7), 157 (4), 135 (6), 121 (100), 115 (6), 103 (9), 91 (14), 77 (18), 73 (23), 51 (5), 43 (6); HRMS calcd for $C_{18}H_{22}O_2Se$ [M^+]: 350.0784, found: 350.0793.

(*S*)-1-(2-{[(*R*)-(2-Methoxy-2-phenyl)ethyl]seleno}phenyl)butanol (7j): GP4, purification: *tert*-butyl methyl ether/pentane 1:3, colorless oil, yield: 54%. ^{1}H NMR: $\delta = 0.96$ (t, $J = 7.3$ Hz, 3H), 1.30–1.82 (m, 4H), 2.42 (d, $J = 4.2$ Hz, 1H), 3.12 (dd, $J = 12.2$ Hz, $J = 4.9$ Hz, 1H), 3.25 (s, 3H), 3.27 (dd, $J = 12.2$ Hz, $J = 8.5$ Hz, 1H), 4.36 (dd, $J = 8.5$ Hz, $J = 4.9$ Hz, 1H), 5.13 (m, 1H), 7.16 (td, $J = 7.7$ Hz, $J = 1.6$ Hz, 1H), 7.25–7.41 (m, 6H), 7.47 (m, 2H); ^{13}C NMR: $\delta = 14.1$, 19.3, 36.2, 40.5, 57.0, 73.2, 83.1, 126.4, 126.7 (2C), 127.6, 128.0, 128.2, 128.6 (2C), 129.5, 133.7, 140.8, 146.4; IR ($CHCl_3$): $\tilde{\nu} = 3603$, 3444, 3064, 3006, 2934, 2876, 1494, 1455, 1135, 1105, 1050, 1016, 957 cm^{-1}; MS (70 eV, EI): m/z (%) = 364 (12) [M^+], 228 (20), 185 (14), 149 (10), 135 (11), 121 (100), 103 (15), 91 (20), 77 (22); HRMS calcd for $C_{19}H_{24}O_2Se$ [M^+]: 364.0941, found: 364.0944.

(*S*)-2,2-Dimethyl-1-(2-{[(*R*)-(2-methoxy-2-phenyl)ethyl]seleno}phenyl)propanol (7k): GP4, purification: *tert*-butyl methyl ether/pentane 1:5, colorless oil, yield: 33%. ^{1}H NMR: $\delta = 0.95$ (s, 9H), 2.03 (s, 1H), 3.10 (dd, $J = 12.1$ Hz, $J = 5.2$ Hz, 1H), 3.26 (s, 3H), 3.28–3.35 (m, 1H), 4.36 (dd, $J = 8.2$ Hz, $J = 5.2$ Hz, 1H), 5.03 (s, 1H), 7.15–7.54 (m, 9H); ^{13}C NMR: $\delta = 26.1$ (3C), 36.9, 37.0, 57.0, 79.5, 83.3, 126.6, 126.7 (2C), 126.8, 127.9, 128.1, 128.4, 128.5 (2C), 133.3, 140.5, 142.0; IR ($CHCl_3$): $\tilde{\nu} = 3605$, 3064, 2955, 2870, 1601, 1480, 1464, 1395, 1364, 1266, 1135, 1105, 1049, 1016, 1002 cm^{-1}; MS (70 eV, EI): m/z (%) = 378 (14) [M^+], 289 (23), 185 (100), 157 (16), 135 (9), 121 (63), 103 (21), 91 (24), 77 (30); HRMS calcd for $C_{20}H_{26}O_2Se$ [M^+]: 378.1097, found: 378.1098.

(*S*)-1-(2-{[(*R*)-(2-Methoxy-2-phenyl)ethyl]seleno}phenyl)propan-2-ol (7l): GP4, purification: *tert*-butyl methyl ether/pentane 1:4, colorless oil, yield: 81%. ^{1}H NMR: $\delta = 1.25$ (d, $J = 6.2$ Hz, 3H), 1.64 (s, 1H), 2.81–3.00 (m, 2H), 3.08 (dd, $J = 12.2$ Hz, $J = 4.8$ Hz, 1H), 3.24 (s, 3H), 3.29 (dd, $J = 12.2$ Hz, $J = 8.6$ Hz, 1H), 4.04 (m, 1H), 4.34 (dd, $J = 8.5$ Hz, $J = 4.9$ Hz, 1H), 7.05–7.38 (m, 8H), 7.48 (d, $J = 7.8$ Hz, 1H); ^{13}C NMR: $\delta = 23.0$, 35.6, 45.8, 57.1, 68.4, 83.1, 126.7 (2C), 127.1, 127.4, 128.2, 128.6 (2C), 130.6, 132.2, 133.1, 140.3, 140.9; IR ($CHCl_3$): $\tilde{\nu} = 3596$, 3064, 3006, 2932, 1601, 1494, 1454, 1377, 1135, 1106, 1049, 1016 cm^{-1}; MS (70 eV, EI): m/z (%) = 350 (15) [M^+], 274 (8), 170 (8), 135 (14), 121 (100), 103 (15), 91 (28), 87 (17), 77 (17); HRMS calcd for $C_{18}H_{22}O_2Se$ [M^+]: 350.0784, found: 350.0789.

3-{[(*R*,*S*)-(2-Methoxy-2-phenyl)ethyl]seleno}-1-phenylpropan-1-ol (7m): ^{1}H NMR: $\delta = 1.80$–2.12 (m, 2H), 2.16 (d, $J = 3.5$ Hz, 1H), 2.58 (m, 2H), 2.76 (ddd, $J = 9.1$ Hz, $J = 5.3$ Hz, $J = 3.8$ Hz, 1H), 2.97 (ddd, $J = 12.5$ Hz, $J = 7.9$ Hz, $J = 4.6$ Hz, 1H), 3.23 (s, 3H), 4.32 (m, 1H), 4.78 (m, 1H), 7.26–7.38 (m, 10H). ^{13}C NMR: $\delta = 21.0$ (t), 31.3 (t), 39.5 (t), 57.0 (q), 73.9 (d), 84.4 (d), 125.9 (d, 2C), 126.7 (d, 2C), 127.7 (d), 128.1 (d), 128.5 (d, 4C), 141.2 (s), 144.2 (s); IR ($CHCl_3$): $\tilde{\nu} = 3604$, 3436, 3065, 3006, 2933, 2826, 1602, 1493, 1454, 1135, 1106, 1049, 1016 cm^{-1}; MS (70 eV, EI): m/z (%) = 350 (8) [M^+], 214 (29), 183 (6), 133 (21), 121 (100), 105 (13), 91 (18), 77 (23); HRMS calcd for $C_{18}H_{22}O_2Se$ [M^+]: 350.0784, found: 350.0789.

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1-{[(*R*)-(2-Methoxy-2-phenyl)ethyl]seleno}-(*S*)-5,6,7,8-tetrahydronaphth-8-ol (7n): GP4, purification: *tert*-butyl methyl ether/pentane 1:4, yellowish oil, yield: 28%. $[\alpha]_D^{25} = -69.5$ ($c = 0.45$ in $CHCl_3$); ^1H NMR: $\delta = 1.79$ (m, 3H), 2.00 (m, 1H), 2.18 (m, 1H), 2.82 (m, 2H), 3.23 (d, $J = 7.0$ Hz, 2H), 3.26 (s, 3H), 4.38 (t, $J = 7.0$ Hz, 1H), 5.12 (d, $J = 3.2$ Hz, 1H), 6.97–7.39 (m, 8H); ^{13}C NMR: $\delta = 17.6$ (t), 30.1 (t), 31.3 (t), 36.5 (t), 57.0 (q), 66.1 (d), 83.5 (d), 126.6 (d, 2C), 128.17 (d), 128.22 (d), 128.7 (d, 2C), 128.8 (d), 132.0 (d), 133.5 (s), 138.4 (s), 139.8 (s), 140.8 (s); ^{77}Se NMR: $\delta = 231.8$; IR ($CHCl_3$): $\tilde{\nu} = 3595$, 3423, 3003, 2981, 2831, 1469, 1388, 1366, 1078, 1020, 908, 849 cm^{-1}; MS (70 eV, EI): m/z (%) = 362 (6) [M^+], 226 (11), 147 (8), 121 (100), 103 (6), 91(10), 77 (9); HRMS calcd for $C_{19}H_{22}O_2Se$ [M^+]: 362.0784, found: 362.0784.

1-{[(*R*)-(2-Methoxy-2-phenyl)ethyl]seleno}-(*S*)-(5*H*-6,7,8,9-tetrahydro)benzocyclohepten-9-ol (7o): GP4, purification: *tert*-butyl methyl ether/pentane 1:4, yellowish oil, yield: 46%. ^1H NMR: $\delta = 1.41$ (m, 1H), 1.72 (m, 2H), 1.97 (m, 1H), 2.20 (m, 3H), 2.62 (dd, $J = 14.0$ Hz, $J = 6.6$ Hz, 1H), 3.10 (dd, $J = 12.2$ Hz, $J = 4.9$ Hz, 1H), 3.20 (m, 1H), 3.24 (s, 3H), 3.39 (t, $J = 12.4$ Hz, 1H), 4.37 (t, $J = 5$ Hz, 1H), 5.81 (d, $J = 6$ Hz, 1H), 7.02 (m, 2H), 7.27–7.43 (m, 6H); ^{13}C NMR: $\delta = 24.5$ (t), 28.2 (t), 32.8 (t), 35.7 (t), 36.5 (t), 57.0 (q), 73.3 (d), 83.2 (d), 126.6 (d, 2C), 128.0 (d), 128.1 (d), 128.7 (d, 2C), 130.6 (d), 131.6 (s), 132.5 (s), 140.9 (s), 144.3 (s), 146.0 (s); ^{77}Se NMR: $\delta = 248.6$; IR ($CHCl_3$): $\tilde{\nu} = 3600$, 3442, 3005, 2933, 1857, 1453, 1354, 1103, 1073, 993, 909; MS (70 eV, EI): m/z (%) = 376 (17) [M^+], 240 (39), 161 (22), 121 (100), 103 (17), 91 (24), 77 (19); HRMS calcd for $C_{20}H_{24}O_2Se$ [M^+]: 376.0941, found: 376.0955.

2-(*R*,*R*)-[4,5-Diphenyl-1,3-dioxolan-2-yl]-1-{[(*R*,*S*)-(2-methoxy-2-phenyl)ethyl]seleno}benzene (7q): GP4, purification: *tert*-butyl methyl ether/pentane 1:50, colorless oil, yield: 56%. ^1H NMR: $\delta = 3.16$ (dd, $J = 8.6$ Hz, $J = 4.9$ Hz, 1H), 3.22 (s, 3H), 3.29 (dd, $J = 10.2$ Hz, $J = 8.7$ Hz, 1H), 4.34 (m, 1H), 4.97 (s, 2H), 6.78 (s, 1H), 7.20–7.38 (m, 17H), 7.62 (d, $J = 7.4$ Hz, 1H), 7.84 (m, 1H); ^{13}C NMR: $\delta = 36.3$, 57.0, 83.0, 85.3, 87.3, 104.1, 126.3–128.6, 129.7, 134.5, 136.6, 138.5, 139.2, 140.9; IR ($CHCl_3$): $\tilde{\nu} = 3065$, 3006, 2919, 1698, 1601, 1496, 1455, 1398, 1267, 1135, 1091, 1049, 1016 cm^{-1}; MS (70 eV, EI): m/z (%) = 516 (1) [M^+], 410 (5), 381 (7), 301 (29), 275 (24), 215 (12), 196 (17), 185 (39), 167 (12), 135 (11), 121 (100), 105 (34), 91 (70), 77 (19); $C_{30}H_{28}O_3Se$ 515.52.

(*S*)-1-(2-{[(*R*)-(2-Methoxy-2-phenyl)ethyl]seleno}-6-[trifluoromethyl]phenyl)propanol (7s): GP4, purification: *tert*-butyl methyl ether/pentane 1:4, colorless oil, yield: 38%. $[\alpha]_D^{25} = -38.5$ ($c = 0.80$ in $CHCl_3$); ^1H NMR: $\delta = 1.00$ (t, $J = 7.4$ Hz, 3H), 1.77 (quint, $J = 7.4$ Hz, 2H), 2.68 (s, 1H), 2.80–3.20 (m, 2H), 3.26 (s, 3H), 4.35–4.50 (m, 1H), 5.47 (t, $J = 6.3$ Hz, 1H), 7.20–7.35 (m, 5H), 7.45 (td, $J = 8.0$ Hz, $J = 3.0$ Hz, 1H), 7.64 (m, 1H), 7.71 (d, $J = 7.6$ Hz, 1H); ^{13}C NMR: $\delta = 10.5$ (q), 31.4 (t), 38.6 (t), 56.9 (q), 74.7 (d), 83.4 (d), 124.0 (s, $J_{C,F} = -274$ Hz), 126.4 (d, 2C), 126.5 (s), 128.1 (d), 128.6 (d, 2C), 129.18 (d), 129.22 (d), 130.1 (d), 135.0 (s, $J_{C,F} = -27$ Hz), 140.7 (s), 151.3 (s); ^{77}Se NMR: $\delta = 196.2$; IR ($CHCl_3$): $\tilde{\nu} = 3672$, 3417, 3006, 2935, 1455, 1312, 1161, 1134, 1101, 836 cm^{-1}; MS (70 eV, EI): m/z (%) = 418 (6) [M^+], 282 (12), 135 (11), 121 (100), 103 (10), 91 (10), 77 (11), 43 (6); HRMS calcd for $C_{19}H_{21}F_3O_2Se$ [M^+]: 418.0658, found: 418.0652.

(*S*)-1-(2-{[(*R*)-(2-Methoxy-2-phenyl)ethyl]seleno}-5-[(2,2-dimethylethyl]-phenyl)propanol (7u): GP4, purification: *tert*-butyl methyl ether/pentane 1:4, colorless oil, yield: 33%. ^1H NMR: $\delta = 0.98$ (t, $J = 7.4$ Hz, 3H), 1.31 (s, 9H), 1.79 (m, 2H), 2.34 (d, $J = 4.5$ Hz, 1H), 3.12 (dd, $J = 12.3$ Hz, $J = 4.9$ Hz, 1H), 3.24 (s, 3H), 3.25 (dd, $J = 12.3$ Hz, $J = 8.4$ Hz, 1H), 4.34 (dd, $J = 8.4$ Hz, $J = 4.9$ Hz, 1H), 5.01 (m, 1H), 7.26–7.38 (m, 7H), 7.58 (d, $J = 1.7$ Hz, 1H); ^{13}C NMR: $\delta = 10.5$ (q), 31.1 (t), 31.3 (q, 3C), 34.6 (s), 36.3 (t), 57.0 (q), 74.6 (d), 83.0 (d), 124.9 (d), 126.0 (d), 126.6 (d, 2C), 128.1 (d), 128.5 (d, 2C), 129.1 (s), 131.3 (d), 140.8 (s), 143.2 (s), 150.9 (s); IR ($CHCl_3$): $\tilde{\nu} = 3603$, 3440, 3005, 2967, 2875, 1597, 1482, 1454, 1382, 1265, 1135, 1104, 1049, 1016, 965 cm^{-1}; MS (70 eV, EI): m/z (%) = 406 (15) [M^+], 270 (23), 241 (21), 191 (21), 135 (13), 121 (100), 103 (13), 91 (14), 77 (13); HRMS calcd for $C_{22}H_{30}O_2Se$ [M^+]: 406.1410, found: 406.1420.

(*S*)-1-(2-{[(*R*)-(2-Methoxy-2-phenyl)ethyl]seleno}-4-nitrophenyl)propanol (7v): GP4, purification: *tert*-butyl methyl ether/pentane 1:4, colorless oil, yield: 44%. $[\alpha]_D^{25} = +48.2$ ($c = 0.35$ in $CHCl_3$); ^1H NMR: $\delta = 1.02$ (t, $J = 7.4$ Hz, 3H), 1.79 (m, 2H), 2.37 (s, 1H), 3.20–3.40 (m, 2H), 3.26 (s, 3H), 4.44 (m, 1H), 4.98 (t, $J = 6.3$ Hz, 1H), 7.30–7.42 (m, 5H), 7.45 (d, $J = 8.6$ Hz, 1H), 7.94 (dd, $J = 8.6$ Hz, $J = 2.6$ Hz, 1H), 8.32 (d, $J = 2.6$ Hz, 1H); ^{13}C NMR: $\delta = 10.2$ (q), 30.7 (t), 35.4 (t), 57.1 (q), 73.4 (d), 82.7 (d), 120.9 (d), 122.2 (d), 126.6 (d, 2C), 128.5 (d), 128.8 (d, 2C), 130.6 (d), 140.2 (s), 140.3 (s), 146.3 (s), 146.6 (s); ^{77}Se NMR: $\delta = 265.1$; IR ($CHCl_3$): $\tilde{\nu} = 3604$, 3436, 2934, 2877, 1600, 1574, 1520, 1455, 1342, 1135, 1107, 1016, 976 cm^{-1}; MS (70 eV, EI): m/z (%) = 395 (6) [M^+], 259 (5), 121 (100), 103 (10), 91 (12), 77 (14); HRMS calcd for $C_{18}H_{21}NO_4Se$ [M^+]: 395.0635, found: 395.0635.

2-[(*R*)-1-(Dimethylamino)ethyl]-1-{[(*R*,*S*)-(2-methoxy-2-phenyl)ethyl]seleno}-benzene (7w): GP4, purification: *tert*-butyl methyl ether/pentane 1:2, colorless oil, yield: 64%. ^1H NMR: $\delta = 1.31$ (d, $J = 6.6$ Hz, 3H), 2.20 (s, 6H), 3.06 (m, 1H), 3.25 (s, 3H), 3.28 (m, 1H), 3.80 (m, 1H), 4.37 (m, 1H), 7.08–7.46 (m, 9H); ^{13}C NMR: $\delta = 16.4$ (q), 34.8 (t), 41.9 (q, 2C), 57.0 (q), 63.4 (d), 83.2 (d), 126.4 (d), 126.6 (d, 2C), 126.9 (d), 127.2 (d), 128.0 (d), 128.5 (d, 2C), 131.5 (d), 132.7 (s), 141.2 (s), 145.4 (s); IR ($CHCl_3$): $\tilde{\nu} = 2987$, 2937, 2862, 2824, 1586, 1455, 1178, 1104, 952 cm^{-1}; MS (70 eV, EI): m/z (%) = 363 (20) [M^+], 348 (58), 332 (9), 228 (100), 212 (35), 183 (53), 147 (36), 121 (41), 104 (52), 91 (58), 72 (86); HRMS calcd for $C_{19}H_{25}NOSe$ [M^+]: 363.1101, found: 363.1101.

1-{[(*R*,*S*)-(2-Methoxy-2-phenyl)ethyl]seleno}-2-[(*R*)-1-(pyrrolidin-1-yl)ethyl]-benzene (7x): GP4, purification: *tert*-butyl methyl ether/pentane 1:2, colorless oil, yield: 55%. ^1H NMR: $\delta = 1.35$ (d, $J = 6.5$ Hz, 3H), 1.76 (m, 4H), 2.45 (m, 2H), 2.56 (m, 2H), 3.05 (dt, $J = 12.0$ Hz, $J = 4.7$ Hz, 1H), 3.25 (s, 3H), 3.27 (m, 1H), 3.78 (q, $J = 6.5$ Hz, 1H), 4.37 (dd, $J = 8.6$ Hz, $J = 5.1$ Hz, 1H), 7.09 (td, $J = 7.5$ Hz, $J = 1.7$ Hz, 1H), 7.20 (t, $J = 7.1$ Hz, 1H), 7.29–7.42 (m, 6H), 7.50 (d, $J = 7.7$ Hz, 1H); ^{13}C NMR: $\delta = 21.8$ (q), 23.6 (t, 2C), 34.9 (t), 52.3 (t, 2C), 57.0 (q), 63.5 (d), 83.0 (d), 126.6 (d, 2C), 126.8 (d), 127.1 (d), 127.5 (d), 128.0 (d), 128.5 (d, 2C), 130.5 (s), 131.5 (d), 141.2 (s), 146.5 (s); IR ($CHCl_3$): $\tilde{\nu} = 2977$, 1711, 1366, 1178, 1078, 848 cm^{-1}; MS (70 eV, EI): m/z (%) = 389 (23) [M^+], 374 (52), 254 (100), 240 (10), 183 (29), 174 (16), 121 (21), 104 (36), 98 (60), 91 (36), 70 (59); HRMS calcd for $C_{21}H_{27}NOSe$ [M^+]: 389.1257, found: 389.1259.

3-[(*S*)-1-Ethoxyethyl]-2-[(*R*,*S*)-(2-methoxy-2-phenyl)ethyl]selenopyridine (7y): GP4, purification: *tert*-butyl methyl ether/pentane 1:10, yellow oil, yield: 40%. ^1H NMR: $\delta = 1.21$ (t, $J = 7.1$ Hz, 3H), 1.43 (d, $J = 6.4$ Hz, 3H), 3.30 (s, 3H), 3.30–3.52 (m, 3H), 3.71 (ddd, $J = 12.5$ Hz, $J = 4.5$ Hz, $J = 2.6$ Hz, 1H), 4.47 (dt, $J = 8.8$ Hz, $J = 5.0$ Hz, 1H), 4.61 (q, $J = 6.5$ Hz, 1H), 7.07 (dd, $J = 7.4$ Hz, $J = 4.7$ Hz, 1H), 7.25–7.43 (m, 5H), 7.59 (d, $J = 6.7$ Hz, 1H), 8.34 (dd, $J = 4.7$ Hz, $J = 1.7$ Hz, 1H); ^{13}C NMR: $\delta = 15.4$, 22.5, 32.8, 57.2, 64.3, 74.4, 83.5, 120.4, 126.8 (2C), 127.9, 128.5 (2C), 132.7, 139.6, 141.5, 148.5, 153.5; ^{77}Se NMR: $\delta = 303.8$; $C_{18}H_{23}NO_2Se$ 364.35.

(*S*)-1-Methoxy-1-phenylethane (8): Selenide **7** (0.5 mmol), triphenyltin hydride (0.75 mmol, except for **7v**: 7.5 mmol) and AIBN (10 mg) were dissolved in toluene (0.5 mL) and heated under reflux for 1 hour.[36] Flash chromatography of the reaction mixture (*tert*-butyl methyl ether/pentane 1:50) yielded **7**. The enantiomeric excess was determined by GC (Chrompack, β-CD-permethylated, 25 m, 40 °C).

(*S*)-1-[2-(1-Bromo-4-nitrophenyl)]propan-1-ol (10): 2-Bromo-propiophenone **9**[37] was nitrated[38] to give 2-bromo-5-nitropropiophenone, which was then reduced with (−)-*B*-chlorodiisopinocampheylborane[21] and **10** was obtained. Yield: 68% after recrystallization from hexane, >99% *ee*;[39] m.p.: 74–75 °C, $[\alpha]_D^{25} = -43.6$ ($c = 1.01$ in $CHCl_3$); ^1H NMR: $\delta = 1.05$ (t, $J = 7.4$ Hz, 3H), 1.63–1.95 (m, 2H), 2.1 (d, $J = 3.8$ Hz, 1H), 5.05 (dt, $J = 3.8$ Hz, $J = 7.4$ Hz, 2H), 7.70 (d, $J = 8.7$ Hz, 1H), 7.97 (dd, $J = 8.7$ Hz, $J = 2.8$ Hz, 1H), 8.45 (d, $J = 2.8$ Hz, 1H); ^{13}C NMR: $\delta = 9.8$ (q), 30.4 (t), 73.5 (d), 122.4 (d), 123.0 (d), 128.7 (s), 133.5 (d), 145.9 (s), 147.4 (s); IR (KBr): $\tilde{\nu} = 3304$, 2970, 2932, 1607, 1574, 1527, 1455, 1340, 1274, 1192, 1108, 1028, 982, 879, 833, 813 cm^{-1}; MS (70 eV, EI): m/z (%) = 261/259 (9/9) [M^+], 232/230 (99/100), 185/183 (12/11), 156 (4), 77 (8); $C_9H_{10}BrNO_3$ (260.09): calcd C 41.56, H 3.88, N 5.39; found C 41.45, H 3.90, N 5.37.

2-Bromo-3-nitroacetophenone: Prepared by oxidation of (*RS*)-1-[2-(1-bromo-2-nitrophenyl)]ethan-1-ol with chromium(VI) oxide. Yield: 99%. ^1H NMR: $\delta = 2.65$ (s, 3H), 7.54 (s, 1H), 7.55 (d, $J = 2.1$ Hz, 1H), 7.78 (m, 1H); ^{13}C NMR: $\delta = 30.5$ (q), 110.0 (s), 126.0 (d), 128.6 (d), 130.5 (d), 145.0 (s), 151.1 (s), 200.1 (s); IR ($CHCl_3$): $\tilde{\nu} = 3028$, 1710, 1592, 1541, 1418, 1356, 1266, 1203, 1134, 1049 cm^{-1}; MS (70 eV, EI): m/z (%) = 245/243 (37/36) [M^+], 230/228

(99/100), 184/182 (38/39), 156/154 (9/9), 118 (6), 103 (13), 103 (13), 89 (10), 75 (59), 63 (14), 43 (99). $C_8H_6BrNO_3$ (244.05).

(*S*)-1-[2-(1-Bromo-2-nitrophenyl)]ethan-1-ol (12): Prepared by reduction of 2-bromo-3-nitroacetophenone with (−)-*B*-chlorodiisopinocampheylborane.[21] Yield: 99%, 94% *ee*.[40] $[\alpha]_D^{25} = -66.2$ ($c = 1.42$ in $CHCl_3$); ^{1}H NMR: $\delta = 1.50$ (d, $J = 6.3$ Hz, 3H), 2.10 (s, 1H), 5.35 (q, $J = 6.0$ Hz, 1H), 7.48 (t, $J = 7.7$ Hz, 1H), 7.59 (dd, $J = 7.8$ Hz, $J = 1.7$ Hz, 1H), 7.59 (dd, $J = 7.8$ Hz, $J = 1.4$ Hz, 1H); ^{13}C NMR: $\delta = 23.8$ (q), 69.2 (d), 112.3 (s), 124.0 (d), 128.5 (d), 129.8 (d), 148.0 (s), 151.0 (s); IR ($CHCl_3$): $\tilde{\nu} = 3604$, 1538, 1365, 1211, 1110, 921 cm^{-1}; MS (70 eV, EI): *m/z* (%) = 247/245 (8/9) [M^+], 232/230 (95/100), 185 (10), 157/155 (7/8), 120 (5), 105 (11), 91 (14), 75 (31), 65 (10), 43 (34); $C_8H_8NO_3Br$ (246.06): calcd C 39.05, H 3.28, N 5.69, O 19.51; found C 39.23, H 3.27, N 5.51, O 19.39.

Bis-(3-methyl-2-oxa-1-selenaindan-7-yl)diazene (13): GP2, purification: *tert*-butyl methyl ether: pentane 2:1, then $CHCl_3$, black crystals, m.p. >280 °C, yield: 31%. ^{1}H NMR: $\delta = 1.57$ (d, $J = 6.3$ Hz, 6H), 5.60 (q, $J = 6.3$ Hz, 2H), 7.21 (d, $J = 7.3$ Hz, 2H), 7.48 (dd, $J = 8.1$ Hz, $J = 7.3$ Hz, 2H), 8.17 (d, $J = 8.1$ Hz, 2H); ^{13}C NMR: $\delta = 23.4$ (q), 78.6 (d), 123.7 (d), 124.0 (d), 126.3 (s), 128.1 (d), 144.7 (s), 145.0 (s); IR (KBr): $\tilde{\nu} = 3430$, 2924, 1655, 1575, 1416, 1340, 1276, 1046, 953, 875, 782, 722 cm^{-1}; UV (MeOH): λ_{max} (ε) = 593 (14300), 359 (9900), 269 (12100) nm; MS (70 eV, EI): *m/z* (%) = 426 (24) [M^+], 409 (100), 292 (10), 232 (16), 213 (8), 197 (38), 181 (12), 169 (19), 156 (14), 135 (10), 119 (27), 102 (12), 89 (25), 75 (34), 63 (26), 43 (53); $C_{16}H_{14}N_2O_2Se_2$ (424.10): calcd C 45.31, H 3.33, N 6.61; found C 44.71, H 3.43, N 6.35.

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