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Synthesis of New Sulfoxide-Containing Diselenides and Unexpected Cyclization Reactions to 2,3-Dihydro-1,4-benzoselenothiine 1-Oxides

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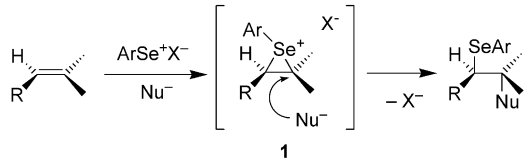
New chiral sulfoxide-containing diselenides were prepared and their corresponding selenium electrophiles were used for the stereoselective functionalization of alkenes. The influence of solvents and different nucleophiles on the outcome of the selenenylation reaction was studied. Besides the successful selenenylation reactions, one selenium electrophile showed an unexpected reactivity in forming a six-membered heterocyclic system upon reaction with alkenes. A mechanism for the formation of these 2,3-dihydro-1,4-benzoselenothiine 1-oxides is proposed.

Introduction

The functionalization of activated C=C bonds with electrophilic organoselenium compounds has been successfully applied in various cases.[1] Furthermore, we and other research groups have investigated stereoselective reactions of alkenes with chiral selenium electrophiles.[2,3] Optically active diselenides bearing a sulfoxide moiety as chiral centre are easily accessible and the selenium electrophiles generated from these diselenides can add to alkenes with high selectivities. A variety of nucleophiles have been used to open the seleniranium intermediates **1** and the addition products gave rise to many subsequent reactions (Scheme 1).



Scheme 1. Selenenylation of alkenes.

Herein we report the synthesis of new optical active sulfoxide-containing diselenides and the addition reactions of their corresponding selenium electrophiles to alkenes. Additionally, we present the formation of a six-membered heterocyclic ring system (2,3-dihydro-1,4-benzoselenothiine 1-oxides) via a new cyclization reaction and an interesting dimerization product.

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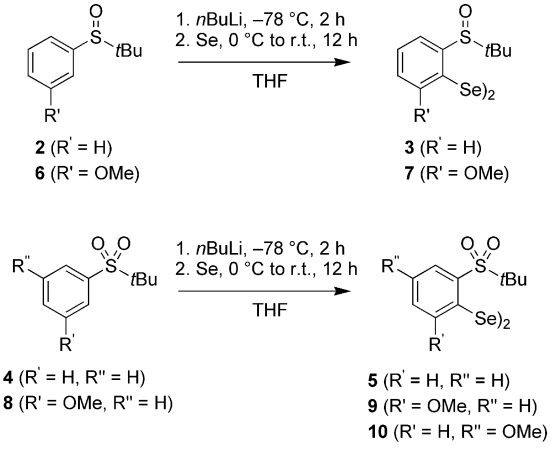
Results and Discussion

The racemic bis[2-(*tert*-butylsulfinyl)phenyl] diselenide (**3**) was synthesized from sulfoxide **2**, after oxidation of the corresponding sulfide with sodium periodate. We found that the most effective method for the synthesis of *tert*-butyl phenyl sulfide, described by Breau et al., was the use of *tert*-butyl alcohol together with acetic acid, acetic anhydride and perchloric acid.[4] The following oxidation to the sulfoxide **2** produced also the sulfone **6** as a side product and 6% of starting material were reisolated.[5] Diselenide **3** was then synthesized by a standard procedure via *ortho*-lithiation and addition of elemental selenium in tetrahydrofuran followed by oxidative workup, in 39% yield.[6] Additionally, bis[2-(*tert*-butylsulfonyl)phenyl] diselenide (**5**) was prepared from *tert*-butyl phenyl sulfone (**4**) using the same reaction conditions as mentioned above in 28% yield as shown in Scheme 2.



Scheme 2. Synthesis of racemic bis[2-(*tert*-butylsulfinyl)phenyl] diselenides and bis[2-(*tert*-butylsulfonyl)phenyl] diselenides.

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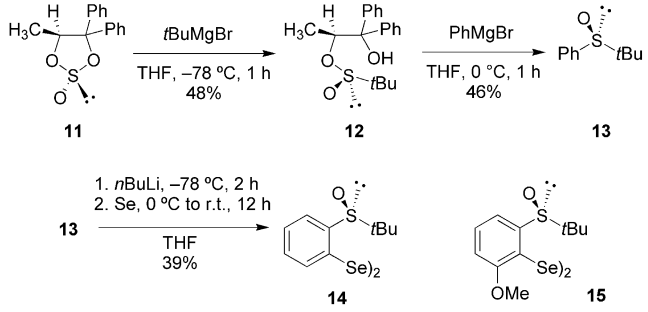
The stereoselective oxidation of *tert*-butyl phenyl sulfide what was attempted via modified Sharpless procedures for the asymmetric oxidation of sulfides to sulfoxides. A method by Kagan et al.[7] described the use of Ti(O-*i*Pr)$_4$, diethyl tartrate, water and *tert*-butyl hydroperoxide in dichloromethane. Whereas the procedure is suitable for small substituents on the phenyl sulfide moiety, it was not possible to achieve a selective oxidation with *tert*-butyl phenyl sulfide as starting material. A similar method published by Jia et al. with (*S*)-BINOL as a ligand and toluene as suitable solvent was not selective.[8] Using Kagan's conditions and (*R*)-TRIP [(*R*)-3,3′-bis(2,4,6-triisopropylphenyl)-2,2′-dihydroxy-1,1′-dinaphthyl] as ligand did also not afford an enantio-enriched sulfoxide.

However, enantiomerically pure sulfoxides can be obtained from the cyclic chiral sulfite **11**, which can be synthesized in two steps from (*S*)-ethyl lactate.[9] (*S*)-*tert*-Butyl phenyl sulfoxide (**13**) was *ortho*-lithiated with *n*-butyllithium in THF and treated with selenium to afford the diselenide **14** in 39% yield after oxidative workup (Scheme 3).



Scheme 3. Synthesis of (*S*)-bis[2-(*tert*-butylsulfinyl)phenyl] diselenide.

It was possible to obtain X-ray structural analyzes of **14** and **5**. The synthesis of enantiomerically enriched diselenide **15** was attempted analog to the preparation of diselenide **14**. The coordinating and directing effect of the methoxy group in hydroxy diselenide **16** had a positive effect in the stereoselective outcome in the methoxyselenenylation of alkenes.[10] The properties of the corresponding methoxy-substituted sulfinyl compound could be interesting. However, the route used for diselenide **14** proved to be not suitable for its synthesis as the reaction of **12** with (3-methoxyphenyl)-magnesium bromide led to a complex reaction mixture.

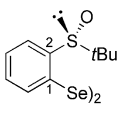
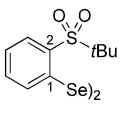
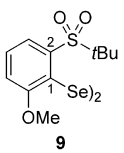
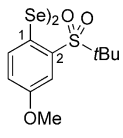
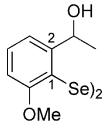
Nevertheless it was possible to obtain racemic **7** in 24% yield via the corresponding sulfoxide, obtained by oxidation of *tert*-butyl 3-methoxyphenyl sulfide. However, it was not possible to obtain crystals from this compound suitable for X-ray crystal structure determination.

Therefore, the sulfone analog **9** of the diselenide was synthesized albeit with very low yields (3%) and crystallized.[11] During this reaction another diselenide **10** was formed through lithiation in *p*-position to the methoxy substituent in 8% yield, which could be separated and crystallized as well.[11]

We compared these crystal structures[11] with the structural data of diselenide **16**, which has been synthesized in our group earlier and results in a high degree of stereoselectivity (up to 99:1 *dr*) in the addition reaction to alkenes (Table 1).[12]

Direct comparison between diselenide **14** and **16** reveals that the oxygen attached to the chiral center has *no* interaction with the selenium atoms in the solid state. The Se–Se distance is almost identical for both compounds. The dihedral angle C^1–C^2–SO in **14** is slightly larger than the C^1–C^2–CO angle of **16** which is an effect of the bulkier *tert*-butyl group. For the same reason, the C–Se–Se–C angle seems to be larger. The downfield shift of 70 ppm observed in the ^{77}Se NMR can be assigned to the different electronical effects of the sulfur substituent. This can be backed up, taking into account the chemical shifts of the sulfone-substituted diselenides, which are shifted downfield by about 100 ppm in comparison to the alcohol-substituted diselenide **16**. Although the Se–Se distance in all these diselenides is almost identical, there is a huge difference in the C–Se–Se–C dihedral angles. Remarkably, this angle is almost identical for diselenides **10** and **16**, but slightly forced open in diselenide **5**. Again, out of steric effects it can be presumed that this angle is even wider in diselenide **9**. The same reason seems to account for the dihedral angles of C^{1}C^{2}SO in the sulfone-containing diselenides. In the three diselenides, **5**, **9**, and **10**, one oxygen of the sulfone moieties is in coordinating distance to the adjacent selenium atom and in case of **9** even at the same distance than the methoxy group. The second sulfoxide oxygen however

Table 1. Comparison of crystal structures of diselenides.

	 **14**	 **5**	 **9**	 **10**	 **16**
Se–O distance	4.65 Å	2.79 Å 4.73 Å	2.96 Å, 4.81 Å, 2.99 Å (OMe) 2.97 Å (OMe)	2.78 Å, 4.72 Å	4.42 Å (OH), 2.97 Å (OMe)
Se–Se bond length	2.31 Å	2.32 Å	2.35 Å	2.23 Å	2.33 Å
Dihedral angle C^{1}C^{2}XO	147° (CCSO)	152.5°, 24.7° (CCSO)	156.2°, 27.8° (CCSO)	148.8°, 20.2° (CCSO)	131° (CCCO)
CSeSeC dihedral angle	89.5°	96.2°	113.7°, 112.5°	78.9°	77.5°
^{77}Se NMR	436 ppm	476 ppm	465 ppm	467 ppm	366 ppm

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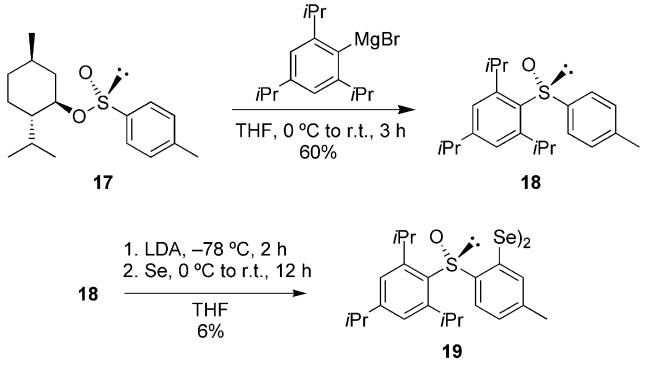
is in a similar distance as the oxygen atoms in diselenides **14** and **16**.

Another chiral sulfoxide **19** (Scheme 4) was synthesized by using the commercially available (–)-(1*R*)-menthyl (*S*)-*p*-toluenesulfinate (**17**). The substitution of the menthyl group can be performed with any Grignard reagent, but it has to be taken into account that the next step requires a lithium base for the *ortho*-deprotonation preventing the use of any moieties with acidic protons. An ideal choice seemed to be a (2,4,6-triisopropyl)phenyl group which can only be *ortho*-lithiated at the desired position and only provides slightly acidic protons. (*R*)-4-Methyl-1-[(2,4,6-triisopropylphenyl)-sulfinyl]benzene (**18**) was obtained in 60% yield. The following *ortho*-lithiation was challenging. Using lithium diisopropylamide or LiTMP at –78 °C in tetrahydrofuran led to the isolation of **19** in 6% yield (LiTMP 4% yield) and a large amount of unidentified side products. Variation of the reaction temperature (–78 °C, 0 °C, room temp., 40 °C), a change of the lithium base (LDA, *n*BuLi, LiTMP) or the use of different solvents (THF, cyclopentyl methyl ether) led to complex reaction mixtures and did not enhance the yield.



Scheme 4. Synthesis of the chiral diselenide **19**.

As the product was isolated in a very low yield, the following methoxyselenenylation reactions were carried out only with diselenides **3** and **7**. A typical reaction proceeds via the generation of selenenyl bromide by addition of elemental bromine to the diselenide, exchange of the bromine counter-anion with the less nucleophilic triflate and addition of the selenenyl cation onto the carbon–carbon double bond. Attack of a nucleophile, in this case methanol, led to product formation. The diastereomeric ratio of the products derived from the racemic selenium electrophiles **20** and **21** determined by NMR indicates a reasonably stereocontrol, which can be assumed as a synergetic effect of sulfoxide and the *tert*-butyl group (Table 2).

Table 2. Selectivities of the methoxyselenenylation of 2′-chlorostyrene with **20** in several solvents affording product **22a**.

Entry	Solvent	**22a**, yield [%]	**22a**, *dr*[a]
1	THF	29	4:1
2	CPME[b]	29	4:1
3	Et_2O	36	5:1
4	Et_2O/CH_2Cl_2 (4:1)	41	5:1
5	CH_2Cl_2	41	11:1
6	$CHCl_3$[c]	48	7:1

[a] Determined by ^{1}H NMR spectroscopy. [b] CPME: cyclopentyl methyl ether. [c] Reaction was carried out at –50 °C.

The influence of the solvent on the methoxyselenenylation was tested with 2′-chlorostyrene and racemic **20** and **21**. The reactions were carried out at –78 °C and stopped after 2 h. Interestingly, the colour of the selenium electrophile **21** is depending on the solvent (colour of RSeBr in all solvents: orange; RSeOTf in THF: purple, in cyclopentyl methyl ether (CPME): red and in CH_2Cl_2: green) and can also be used as an indicator for the progress of the reaction. This is not the case with **21** which always gives yellow mixtures. The best selectivity with **20** was found using dichloromethane. When the reactions were carried out in polar ethers like tetrahydrofuran and cyclopentyl methyl ether (CPME) the selectivities dropped significantly. The observed diastereomeric ratio was decreased in chloroform, however, this reaction showed the highest yield.

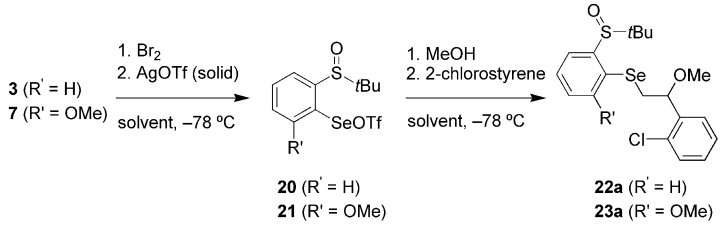
Surprisingly, **21** is less reactive and less selective in the same reaction (Table 3). The highest diatereomeric ratio was observed in tetrahydrofuran (3:1), but with low yield. In chloroform the yield was better however, the diasteromeric ratio decreased to 2:1.

Table 3. Selectivities of the methoxyselenenylation of 2′-chlorostyrene with **21** in several solvents affording product **23a**.

Entry	Solvent	**23a**, yield [%]	**23a**, *dr*[a]
1	THF	18	3:1
2	CPME[b]	30	1:1
3	Et_2O	10	1:1
4	acetonitrile[c]	23	1:1
5	CH_2Cl_2	20	1:1
6	$CHCl_3$[d]	40	2:1

[a] Determined by ^{1}H NMR spectroscopy. [b] CPME: cyclopentyl methyl ether. [c] Reaction was carried out at –40 °C. [d] Reaction was carried out at –50 °C.

Then the reactivity towards different substrates was investigated initially with diselenide **3**. Monosubstituted double bonds (Table 4 entry 1 and 2) showed reasonable selectivities with a diastereomeric ratio of up to 6:1. But



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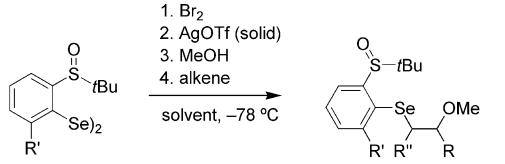
only styrene gave a good yield in tetrahydrofuran. Methyl cinnamate and 3-nitrostyrene seem to be not reactive enough for the conditions of the methoxyselenenylation reaction. Substituents in the 2′-position of the aromatic system seem to enhance the selectivity and led to reasonable yields. More bulk on the double bond system leads to lower yields, however the β-substitution enhances the selectivity.

Table 4. Reactivity of **21** towards different substrates.

Entry	Alkene	Product	Solvent	Yield [%]	*dr*[a]
1	styrene	**22b**	THF	52	6:1
2	2-vinylnaphthalene	**22c**	THF	32	5:1
3	methylcinnamate	–	THF	0	–
4	3-nitrostyrene	–	THF	0	–
5	2-chlorostyrene	**22a**	CH_2Cl_2	41	11:1
6	α-methylstyrene	**22d**	CH_2Cl_2	38	4:1
7	β-methylstyrene	**22e**	CH_2Cl_2	30	11:1
8	1-phenyl-1-cyclohexene	**22f**	CH_2Cl_2	30	9:1

[a] Determined by ^{1}H NMR spectroscopy.



3 (R′ = H)
7 (R' = OMe)

22a–f (R′ = H)
23a–c (R' = OMe)

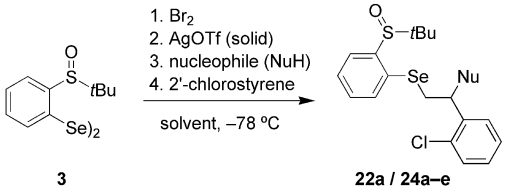
As was already observed during the solvent screening with diselenide **7**, the yields and selectivities are lower with styrene leading to product **23b** in 24% yield; *dr* 2:1 and with β-methylstyrene resulting in **23c** in 22% yield; *dr* 1:1.

In reactions of selenium electrophiles generated from diselenide **3** we could also show that the diastereomeric ratio of the products decreases with the size of the nucleophile, at comparable yields (Table 5).

Table 5. Reactivity of **3** with 2-chlorostyrene and different nucleophiles.

Entry	Nucleophile	Product	Solvent	Yield [%]	*dr*[a]
1	methanol	**22a**	CH_2Cl_2	41	11:1
2	ethanol	**24a**	CH_2Cl_2	47	8:1
3	2-propanol	**24b**	CH_2Cl_2	47	8:1
4	*tert*-butyl alcohol	**24c**	CH_2Cl_2	30	6:1
5	benzyl alcohol	**24d**	CH_2Cl_2	30	3.5:1
6	benzoic acid	–	CH_2Cl_2	traces	–
7	$TMSN_3$	**24e**	CH_2Cl_2	35	6:1
8	NaN_3	–	acetonitrile[b]	0	–

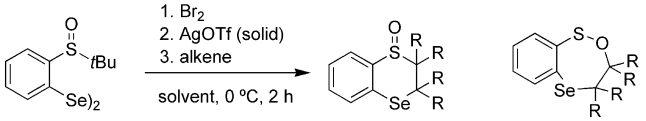
[a] Determined by ^{1}H NMR spectroscopy. [b] Reaction was carried out at –40 °C.



3

22a / 24a–e

If the reaction of the selenium electrophile and the alkene is carried out in the absence of an external nucleophile, the formation of different products was observed. For this reaction it is crucial that the temperature is increased to 0 °C. To the best of our knowledge this is the first time that such a reactivity has been observed (Scheme 5).



3 **25** **26**

Scheme 5. Alkene addition to selenium electrophiles.

In these cases the sulfoxide moiety seems to react as an internal nucleophile. However, it was only possible to isolate products with α-substituted double bonds. β-Substitution in this reaction seems to result in to much strain during the cyclization step (Table 6).

Table 6. Cyclization reaction with different substrates.

Alkene	Product	Solvent	Yield [%]
Styrene	**25a**	THF	10
2-Vinylnaphthalene	**25b**	THF	16
Methyl cinnamate	–	THF	–
2-Chlorostyrene	**25c**	Et_2O	9
α-Methylstyrene	**25d**	CH_2Cl_2	12
β-Methylstyrene	–	THF	–
1-Methyl-1-cyclohexene	–	THF	–

The products obtained in this reaction could have different structures as NMR and mass spetrometric data cannot distinguish between compounds **25** and **26**. Without reference spectra, the IR vibrations for both structures can not be distinguished, as the S–O and the S=O absorbances are in the same region according to literature.[13] Fortunately, the X-ray structural analysis of **25b** (Figure 1) proved the presence of structures **25**. According to the X-ray crystal structure, the oxygen atom and the naphthyl ring system are *cis* to each other, which indicates that the cleavage of the *tert*-butyl group has occurred after the sulfur–carbon bond formation.

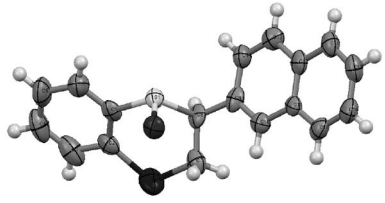


Figure 1. Crystal structure of 2-naphthyl-2,3-dihydro-1,4-benzoselenothiine 1-oxide (**25b**).

The mechanistic pathway outlined in Scheme 6 is suggested for the product formation. After the formation of the seleniranium cation the sulfur attacks the electrophilic benzylic carbon atom in **27** to form intermediate **28**. The newly formed six membered ring system gets stabilized upon cleavage of the *tert*-butyl group. Calculations of similar structures (R = H, *tert*-butyl replaced by methyl) have shown that an oxygen involvement as shown in **29** is less likely, as the energy of this structure is above the energy of **28**.[14,15]

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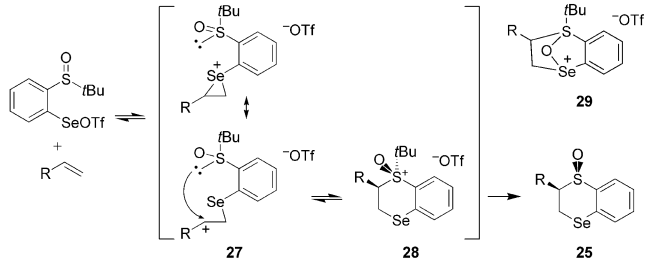
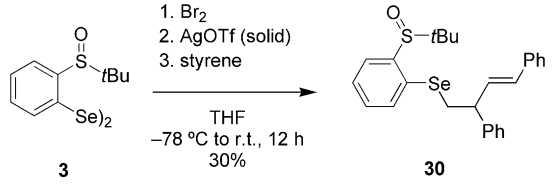


Scheme 6. Proposed mechanistic pathway.

Another reactivity was observed when the reaction mixture was warmed to room temperature overnight instead of warming it to 0 °C immediately and if the alkene was present in excess. The observed dimer **30** formed in a 1:1 diasteromeric mixture in 30% yield via a cationic dimerization and regenerates the double bond by deprotonation during the workup. (Scheme 7).



Scheme 7. Styrene as nucleophile.

Conclusions

Six new diselenides could be synthesized with either a sulfone or sulfoxide moiety as a side chain. Crystal structure comparison and methoxyselenenylation reactions show that the obtained diselenides can be easily converted into selenium electrophiles. The sulfoxide-containing diselenide shows, depending on the solvent, good diastereoselective induction in the methoxyselenenylation of activated alkenes. Additionally the new diselenides can be used to easily form interesting six-membered heterocyclic ring systems (2,3-dihydro-1,4-benzoselenothiine 1-oxides). The formation of these heterocycles seems to be a very selective process, with oxygen and the aryl ring system on the same side. A possible mechanism for the product formation could be proposed, according to the obtained crystal structure. Further investigations in this research are under way.

Experimental Section

General: Melting points were obtained in open capillary tubes. ^{1}H NMR and ^{13}C NMR spectra were recorded on a AV-400 Bruker using the solvents indicated with 400 and 100 MHz, respectively, also a DRX-500 Bruker was used in the some cases for ^{1}H (500 MHz) and ^{13}C (125 MHz). Mass spectra (*m*/*z*) and HRMS were recorded under the conditions of electron impact (EI) and electrospray (ES) and chemical ionization (CI). All reactions were monitored by thin-layer chromatography that was performed on precoated sheets of silica gel 60, and flash column chromatography was performed with silica gel 60 (Merck, 230–400 mesh). Eluting solvents are indicated in the text. All experiments were performed under an inert atmosphere of argon. THF and diethyl ether were dried with sodium, dichloromethane was dried with CaH, cyclopentyl methyl ether, chloroform, methanol, ethanol, 2-propanol and *tert*-butyl alcohol were dried with molecular sieves (4 Å). All other purchased chemicals were used without further purification. Isomers in NMR spectroscopic data are shown with an asterisk. For the low resolution mass data only the main isotope peak of the usual selenium isotope pattern is given.

GP 1. General Procedure for the Addition of Selenium Electrophiles to Styrene: Bis[2-(*tert*-butylsulfinyl)phenyl] diselenide (**3**) (0.1 mmol) was dissolved in dry solvent (4 mL) under argon, cooled to –78 °C, and treated with bromine (0.1 mmol, 0.1 mL of a 1 M solution in CCl_4). After 20 min silver triflate (solid) (54 mg, 0.21 mmol) was added and the mixture was stirred for 25 min at –78 °C. The reaction mixture was treated with MeOH (0.10 mL) and subsequently with the alkene (0.22 mmol). After the mixture had been stirred for 2 h at –78 °C, it was warmed to 0 °C and further stirred for 30 min. Then 2,4,6-collidine (0.10 mL) was added, followed by water (4 mL). After extraction of the reaction mixture with dichloromethane (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 column chromatography on silica gel, yielding the addition products as colourless oils. The diastereomers could not be separated by column chromatography (ethyl acetate/hexane, 5:1).

GB 2. General Procedure for the Synthesis of 1,4-Benzselenathiine 1-Oxides: Bis[2-(*tert*-butylsulfinyl)phenyl] diselenide (0.1 mmol) was dissolved in dry tetrahydrofuran (4 mL) under argon, cooled to –78 °C, and treated with bromine (0.1 mmol, 0.1 mL of a 1 M solution in CCl_4). After 20 min silver triflate (solid) (54 mg, 0.21 mmol) was added and the mixture was stirred for 25 min at –78 °C. The reaction mixture was treated with the alkene (0.22 mmol). After the mixture had been stirred for 5 min at –78 °C, it was immediately warmed to 0 °C and further stirred for 60 min. Then MeOH (0.10 mL) was added and the mixture was stirred for additional 10 min at 0 °C. Then 2,4,6-collidine (0.10 mL) was added, followed by water (4 mL). After extraction of the reaction mixture with dichloromethane (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 column chromatography (ethyl acetate/hexanes, 1:5) on neutral Al_2O_3, yielding the addition products as pale yellow oils.

Bis[2-(*tert*-Butylsulfinyl)phenyl] Diselenide (3): To a solution of *tert*-butyl phenyl sulfoxide (13 mmol, 2.37 g) in 130 mL dry THF was added slowly *n*-butyllithium (2.5 M solution in hexane, 14.3 mmol, 5.72 mL) at –78 °C. The mixture was stirred for 1.5 h at this temperature. Then selenium (14.3 mmol, 1.13 g) was added with vigorous stirring at 0 °C. After 15 h stirring at room temperature the mixture was quenched with 100 mL water and extracted with dichloromethane (3 × 100 mL). The combined organic phases were dried with $MgSO_4$ and the solvent was removed in vacuo. After column chromatography (hexane/ethyl acetate, 4:1, 1:4) diselenide **3** was isolated with 39% yield (2.64 g) as yellow oil which crystallized from diethyl ether upon standing. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67–7.58 (t, *J* = 12 Hz, 4 H, ArH), 7.36–7.25 (d, *J* = 8 Hz, 4 H, ArH), 1.20 [d, *J* = 5.4 Hz, 18 H, $C(CH_3)_3$] ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 140.8 (C), 140.8* (C), 132.7 (CH), 132.4 (CH), 132.2 (C), 132.2* (C), 127.7 (CH), 127.7* (CH), 127.5 (CH), 127.5* (CH), 58.6 [$C(CH_3)_3$], 58.6* [$C(CH_3)_3$], 23.3 [$C(CH_3)_3$] ppm. ^{77}Se NMR (57 MHz, $CDCl_3$): δ = 438, 440 ppm. IR (film): $\tilde{\nu}$ = 2962, 2925, 2235, 1569, 1471, 1455, 1439, 1362, 1168, 1127,

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1045, 1018, 921, 755, 731 cm^{-1}. MS (ES+): *m*/*z* (%) = [M + H]$^+$: 544 (15), 523 (100), 497 (43), 462 (23), 449 (30), 423 (15), 391 (17), 279 (22), 260 (47), 235 (22), 205 (30), 187 (13). HRMS (ES+): [M + H]$^+$ $C_{20}H_{27}O_2S_2{}^{76}Se_2$ calcd. 514.9831; found 514.9829; m.p. 115–116 °C (crystals from diethyl ether).

Bis[2-(*tert*-Butylsulfonyl)phenyl] Diselenide (5): To a solution of *tert*-butyl phenyl sulfone (2.55 mmol, 505 mg) in 25 mL dry THF was added slowly *n*-butyllithium (2.5 M solution in hexane, 2.8 mmol, 1.12 mL) at –78 °C. The mixture was stirred for 1.5 h at this temperature. Then selenium (2.8 mmol, 221 mg) was added with vigorous stirring at 0 °C. After 15 h stirring at room temperature the mixture was quenched with 25 mL water and extracted with dichloromethane (3 × 25 mL). The combined organic phases were dried with $MgSO_4$ and the solvent was removed in vacuo. After column chromatography (hexane/ethyl acetate, 4:1, 1:4) the diselenide **5** was isolated with 28% yield (395 mg) as yellow oil which crystallized from diethyl ether upon standing. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.76 (ddd, *J* = 1.7, *J* = 7.5, *J* = 18.5 Hz, 4 H, ArH), 7.33 (dt, *J* = 1.7, *J* = 7.5, *J* = 18.5 Hz, 1 H, 4 H, ArH), 1.38 [s, 18 H, $C(CH_3)_3$] ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 134.3 (CH), 133.9 (C), 133.7 (CH), 132.9 (C), 131.6 (CH), 126.8 (CH), 62.6 [$C(CH_3)_3$], 23.8 [$C(CH_3)_3$] ppm. ^{77}Se NMR (57 MHz, $CDCl_3$): δ = 477 ppm. IR (film): $\tilde{\nu}$ = 2985, 1573, 1559, 1476, 1440, 1421, 1395, 1364, 1293, 1278, 1252, 1193, 1139, 1114, 1086, 1039, 1021, 799, 761, 736, 707, 649, 634, 570 cm^{-1}. MS (ES+): *m*/*z* (%) = [M + NH_4]$^+$: 576 (8), 574 (11), 573 (37), 571 (100), 569 (89), 567 (50), 565 (14), 565 (4), 482 (2), 480 (5), 476 (3). HRMS: (ES+): [M + NH_4]$^+$ calcd. for $C_{20}H_{30}O_4S_2{}^{74}Se^{76}SeN$: 512.9864; found 512.9864; m.p. 204–206 °C (crystals from diethyl ether).

Bis[2-(*tert*-Butylsulfinyl)-6-methoxyphenyl] Diselenide (7): To a solution of *tert*-butyl 3-methoxyphenyl sulfoxide (2.80 mmol, 600 mg) in 20 mL dry THF was added slowly *n*-butyllithium (2.5 M solution in hexane, 3.20 mmol, 1.28 mL) at –78 °C. The mixture was stirred for 1.5 h at this temperature. Then selenium (2.85 mmol, 225 mg) was added with vigorous stirring at 0 °C. After 15 h stirring at room temperature the mixture was quenched with 20 mL water and extracted with dichloromethane (3 × 20 mL). The combined organic phases were dried with $MgSO_4$ and the solvent was removed in vacuo. After column chromatography (hexane/ethyl acetate, 4:1, 1:1, then 1:2) the diselenide **7** was isolated with 24% yield (391 mg) as yellow foam. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51 (t, *J* = 7.8 Hz, 2 H, ArH), 7.49 (t, *J* = 7.8 Hz, 2 H, ArH)*, 7.43 (dd, *J* = 1.1, *J* = 7.8 Hz, 2 H, ArH), 7.40 (dd, *J* = 1.1, *J* = 7.8 Hz, 2 H, ArH)*, 7.01 (dd, *J* = 1.0, *J* = 8.1 Hz, 2 H, ArH), 6.98 (dd, *J* = 0.94, *J* = 8.1 Hz, 2 H, ArH)*, 3.71 (s, 6 H, OMe), 3.70 (s, 6 H, OMe)*, 1.19 [s, 18 H, $C(CH_3)_3$], 1.12 [s, 18 H, $C(CH_3)_3$]* ppm. ^{13}C NMR (500 MHz, $CDCl_3$): δ = 159.9* (C), 159.7 (C), 146.4* (C), 146.1 (C), 130.7* (CH), 130.5 (CH), 120.3 (C), 119.1* (CH), 119.0 (CH), 113.1* (CH), 113.0 (CH), 58.3*, 57.8, 56.5*, 56.4, 23.5* [$C(CH_3)_3$], 23.3 [$C(CH_3)_3$] ppm. ^{77}Se NMR (57 MHz, $CDCl_3$): δ = 378 ppm. IR (film): $\tilde{\nu}$ = 2965, 2934, 1699, 1567, 1456, 1429, 1263, 1181, 1160, 1040, 785, 725 cm^{-1}. MS (ES+): *m*/*z* (%) = [M + H]$^+$: 1180 (17), 583 (100), 503 (15), 291 (58), 235 (38). HRMS (ES+): [M + H]$^+$ calcd. for $C_{22}H_{31}S_2O_4{}^{74}Se$ ^{76}Se: 573.0075; found 573.0078.

Bis[2-(*tert*-Butylsulfonyl)-6-methoxyphenyl] Diselenide (9) and Bis[2-(*tert*-Butylsulfonyl)-4-methoxyphenyl] Diselenide (10): To a solution of *tert*-butyl 3-methoxyphenyl sulfone (8.8 mmol, 2.0 g) in 90 mL dry THF was added slowly *n*-butyllithium (2.5 M solution in hexane, 9.6 mmol, 3.84 mL) at –78 °C. The mixture was stirred for 1.5 h at this temperature. Then selenium (9.6 mmol, 758 mg) was added with vigorous stirring at 0 °C. After 15 h stirring at room temperature the mixture was quenched with 90 mL water and extracted with dichloromethane (3 × 90 mL). The combined organic phases were dried with $MgSO_4$ and the solvent was removed in vacuo. After column chromatography (hexane/ethyl acetate, 4:1, 1:1) the products **9** and **10** were isolated as yellow amorphous solids which were recrystallized from chloroform.

Bis[2-(*tert*-Butylsulfonyl)-6-methoxyphenyl] Diselenide (9): Yield 3% (162 mg); yellow crystals. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52 (dd, ^4J = 1.1, ^3J = 7.9 Hz, 2 H, ArH), 7.38 (t, ^3J = 8.1 Hz, 2 H, ArH), 7.10 (dd, ^4J = 0.9, ^3J = 8.2 Hz, 2 H, ArH), 3.92 (s, 6 H, OMe), 1.19 [s, 18 H, $C(CH_3)_3$] ppm. ^{13}C NMR (500 MHz, $CDCl_3$): δ = 160.4 (C), 139.1 (C), 128.8 (CH), 125.4 (CH), 124.0 (C), 115.6 (CH), 61.4, 56.8, 24.0 [$C(CH_3)_3$] ppm. ^{77}Se NMR (57 MHz, $CDCl_3$): δ = 465 ppm. IR (film): $\tilde{\nu}$ = 2972, 2926, 1570, 1458, 1432, 1286, 1260, 1183, 1156, 1106, 1029, 841, 790, 723, 656 cm^{-1}. MS (ES+): *m*/*z* (%) = [M + H]$^+$: 614 (80), 556 (10), 534 (10), 438 (8), 372 (3), 356 (7), 292 (13), 251 (100), 234 (55), 186 (25), 172 (10), 57 (65). HRMS (ES+): [M + H]$^+$ calcd. for $C_{22}H_{30}O_6S_2{}^{76}Se_2$: 605.9863; found 605.9866; m.p. (crystals from $CHCl_3$): 253–256 °C.

Bis[2-(*tert*-Butylsulfonyl)-4-methoxyphenyl] Diselenide (10): Yield 8% (431 mg); yellow crystals. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69 (d, ^3J = 8.9 Hz, 2 H, ArH), 7.38 (d, ^4J = 2.8 Hz, 2 H, ArH), 6.99 (dd, ^4J = 2.9, ^3J = 8.9 Hz, 2 H, ArH), 3.82 (s, 6 H, OMe), 1.45 [s, 18 H, $C(CH_3)_3$] ppm. ^{13}C NMR (500 MHz, $CDCl_3$): δ = 159.0 (C), 134.5 (C), 133.3 (CH), 123.0 (C), 121.2 (CH), 118.8 (CH), 63.1, 56.3, 24.3 [$C(CH_3)_3$] ppm. ^{77}Se NMR (57 MHz, $CDCl_3$): δ = 467 ppm. IR (film): $\tilde{\nu}$ = 2971, 1591, 1465, 1435, 1291, 1259, 1230, 1145, 1037, 707, 653 cm^{-1}. MS (ES+): *m*/*z* (%) = [M + H]$^+$: 614 (80), 556 (15), 438 (12), 372 (5), 308 (10), 292 (17), 251 (100), 234 (60), 186 (30), 171 (11), 77 (6), 57 (81). HRMS (ES+): [M + H]$^+$ calcd. for $C_{22}H_{30}O_6S_2{}^{76}Se_2$: 605.9863; found 605.9866; m.p. (foam): 85 °C; m.p. (crystals from $CHCl_3$): 193–196 °C.

(*S*)-Bis[2-(*tert*-Butylsulfinyl)phenyl] Diselenide (14): To a solution of (–)-(*S*)-*tert*-butyl phenyl sulfoxide (1.21 mmol, 220 mg) in 12 mL dry THF was added slowly *n*-butyllithium (2.5 M solution in hexane, 1.24 mmol, 0.496 mL) at –78 °C. The mixture was stirred for 1.5 h at this temperature. Then selenium (1.24 mmol, 98.0 mg) was added with vigorous stirring at 0 °C. After 15 h stirring at room temperature the mixture was quenched with 10 mL water and extracted with dichloromethane (3 × 10 mL). The combined organic phases were dried with $MgSO_4$ and the solvent was removed in vacuo. After column chromatography (hexane/ethyl acetate, 4:1, 1:4) the diselenide **14** was isolated with 39% yield (245 mg) as yellow oil which crystallized from diethyl ether upon standing. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.64 (dd, ^4J = 1.3, ^3J = 7.7 Hz, 2 H, ArH), 7.61 (dd, ^4J = 1.6, ^3J = 7.5 Hz, 2 H, ArH), 7.32 (dt, ^4J = 1.4, ^3J = 7.5 Hz, 2 H, ArH), 7.28 (dt, ^4J = 1.7, ^3J = 7.5 Hz, 1 H, 2 H, ArH), 1.20 [s, 9 H, $C(CH_3)_3$] ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 140.9 (C), 132.4 (CH), 132.2 (CH), 131.3 (C), 127.7 (CH), 127.5 (CH), 58.6 [$C(CH_3)_3$], 23.3 [$C(CH_3)_3$] ppm. ^{77}Se NMR (57 MHz, $CDCl_3$): δ = 436 ppm. IR (KBr): $\tilde{\nu}$ = 2960, 1568, 1440, 1362, 1167, 1081, 1047, 1018, 756 cm^{-1}. MS (ES+): *m*/*z* (%) = [M + H]$^+$: 526 (30), 523 (100), 519 (50), 515 (3), 263 (17), 261 (100), 259 (44), 257 (17), 207 (17), 205 (95), 203 (42), 201 (17). HRMS (ES+): [M + H]$^+$ calcd. for $C_{20}H_{27}O_2S_2{}^{74}Se^{76}Se$: 512.9864; found 512.9864. $[\alpha]_D^{20}$ = –65.45 (*c* = 0.1, $CHCl_2$); m.p. 118.5–119.5 °C (crystals from diethyl ether).

(*R*)-4-Methyl-1-[(2,4,6-triisopropylphenyl)sulfinyl]benzene (18): To a solution of (–)-(1*R*)-menthyl (*S*)-toluenesulfinate (1 mmol, 294 mg) in 5 mL dry THF was added slowly (2,4,6-triisopropylphenyl)magnesium bromide (1.5 mmol) at 0 °C. The mixture was stirred at 0 °C for 3 h, quenched with 5 mL water and extracted with diethyl ether

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(3 × 10 mL). The combined organic phases were dried with Na_2SO_4 and the solvent was removed in vacuo. After column chromatography (petroleum ether/diethyl ether, 10:1) the product was isolated with 60% yield (205 mg) as white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.21 (m, 2 H, ArH), 7.15 (m, 2 H, ArH), 7.01 (s, 2 H, ArH), 3.68 [m, 2 H, C*H*(CH_3)$_3$], 2.81 [m, 1 H, C*H*(CH_3)$_3$], 2.29 (s, 3 H, ArCH_3), 1.19 [m, 36 H, CH(C*H*$_3$)$_3$] ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.2, 151.2, 143.2, 139.3, 135.7, 129.5, 124.6, 123.4, 34.4, 24.7, 23.7 ppm. IR (KBr): $\tilde{\nu}$ = 2956, 1598, 1560, 1492, 1458, 1423, 1382, 1362, 1301, 1083, 1042, 1025, 809 cm^{-1}. MS (ES+): *m*/*z* (%) = [M + H]$^+$: 343 (100), 327 (83), 312 (3), 285.3 (2), 250 (3), 233 (5), 189 (8), 161 (5), 140 (18), 124 (10), 108 (15), 98 (6), 91 (10), 84 (10), 72 (10), 58 (10), 44 (10). HRMS (ES+): [M + H$^+$] calcd. for $C_{22}H_{30}OS$: 343.2090; found 343.2091.

Bis{5-methyl-2-[(2,4,6-triisopropylphenyl)sulfinyl]phenyl} Diselenide (19): To a solution of diisopropylamine (2.58 mmol, 362 μL) in dry THF (8 mL) under argon was added *n*-butyllithium (2.40 mmol, 960 μL, 2.5 M solution in hexane) at 0 °C. After 15 min the solution was cooled to –78 °C and (*R*)-4-methyl-1-(2,4,6-triisopropylphenylsulfinyl)benzene (0.86 mmol, 292 mg) in dry THF (3 mL) was added. This mixture was stirred at –78 °C for 90 min and then warmed to 0 °C. After 10 min selenium was added with vigorous stirring and the mixture was warmed to room temperature overnight. To this mixture was added 1 M hydrochloric acid (15 mL) and the layers were separated. The aqueous layer was washed 3 x with 10 mL diethyl ether and the combined organic layers were treated with 100 mg potassium hydroxide and dried with Na_2SO_4. After the solvent was removed in vacuo and column chromatography (petroleum ether/diethyl ether, 2:1) diselenide **19** was obtained with 6% yield (43 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54 (br. s, 2 H, ArH), 7.14 (d, *J* = 8 Hz, 2 H, ArH), 7.02 (m, 6 H, ArH), 3.72 [m, 4 H, C*H*(CH_3)$_3$], 2.83 [sep, *J* = 7 Hz, 2 H, C*H*(CH_3)$_3$], 2.27 (s, 6 H, ArCH_3), 1.18 [d, *J* = 7 Hz, 18 H, CH(C*H*$_3$)$_3$], 1.13 [d, *J* = 7 Hz, 18 H, CH(C*H*$_3$)$_3$] ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.8, 151.5, 142.7, 141.2, 134.8, 134.5, 129.9, 128.3, 126.1, 123.3, 34.4, 29.2, 24.1, 23.7, 21.1 ppm. IR (film): $\tilde{\nu}$ = 2961, 2926, 2868, 1595, 1456, 1384, 1363, 1045, 1018, 909, 732 cm^{-1}. ^{77}Se NMR (500 MHz, $CDCl_3$): δ = 452.1 ppm. MS (NES+): *m*/*z* (%) = [M + H]$^+$: 921 (8), 843 (100), 523 (5), 391 (4). HRMS (NES+): [M + H$^+$] calcd. for $C_{44}H_{59}O_2S_2{}^{76}Se_2$: 835.2335; found 835.2336.

Sulfoxide 22a: Synthesized according to GB 1; yield 41% (35 mg), mixture of diastereomers 11:1 (solvent: CH_2Cl_2). MS (ES+): *m*/*z* (%) = [M + H]$^+$: 861 (5), 431 (100), 342 (23), 204 (14). HRMS (ES+): calcd. for $C_{19}H_{24}O_2ClS^{74}Se$: 425.0405; found 425.0410. IR (film): $\tilde{\nu}$ = 3055, 2929, 2824, 1571, 1471, 1444, 1360, 1227, 1167, 1105, 1047, 1022, 965, 757, 705, 666 cm^{-1} Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73 (dd, *J* = 7.83, 1.46 Hz, 1 H, ArH), 7.57 (dd, *J* = 7.63, 0.97 Hz, 1 H, ArH), 7.35–7.46 (m, 2 H, ArH), 7.22–7.33 (m, 2 H, ArH) 7.17 (d, *J* = 1.65 Hz, 1 H, ArH), 7.15 (d, *J* = 1.45 Hz, 1 H, ArH), 4.83 (dd, *J* = 8.41, 3.77 Hz, 1 H, C*H*OCH_3), 3.24 (s, 3 H, OCH_3), 3.10–3.23 (m, 2 H, SeC*H*$_2$CH), 1.19 [s, 9 H, C(C*H*$_3$)$_3$] ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.5 (C), 138.1 (C), 134.1 (CH), 132.8 (C), 131.7 (C), 131.3 (CH), 129.5 (CH), 129.0 (CH), 127.4 (CH), 127.4 (CH), 127.3 (CH), 127.1 (CH), 79.3 (*C*HOCH$_3$), 58.2 [*C*(CH$_3$)$_3$], 57.4 (O*C*H$_3$), 35.6 (Se*C*H$_2$CH), 23.3 [C(*C*H$_3$)$_3$] ppm. Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77 (dd, *J* = 7.86, 1.43 Hz, 1 H, ArH), 7.53 (dd, *J* = 7.78, 0.95 Hz, 1 H, ArH), 7.35–7.46 (m, 2 H, ArH), 7.22–7.33 (m, 2 H, ArH), 7.19 (d, *J* = 3.77 Hz, 1 H, ArH), 7.13 (d, *J* = 1.67 Hz, 1 H, ArH), 4.68 (dd, *J* = 9.33, 3.26 Hz, 1 H, C*H*OCH_3), 3.24 (s, 3 H, OCH_3), 3.10–3.23 (m, 1 H, SeC*H*$_2$CH), 3.02 (dd, *J* = 12.40, 9.33 Hz, 1 H, SeC*H*$_2$CH), 1.19 [s, 9 H, C(C*H*$_3$)$_3$] ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.7 (C), 138.1 (C), 134.1 (CH), 132.9 (C), 131.6 (C), 131.3 (CH), 129.6 (CH), 129.0 (CH), 127.4 (CH), 127.4 (CH), 127.2 (CH), 127.1 (CH), 78.8 (*C*HOCH$_3$), 58.1 [*C*(CH$_3$)$_3$], 57.6 (O*C*H$_3$), 35.8 (Se*C*H$_2$CH), 23.3 [C(*C*H$_3$)$_3$] ppm.

Sulfoxide 22b: Synthesized according to GB 1; yield 51% (40 mg); yellow foam; mixture of diastereomers 6:1 (solvent: THF). IR (film): $\tilde{\nu}$ = 3056, 2934, 1643, 1570, 1443, 1267, 1151, 1102, 1030, 958, 851, 738, 703, 640, 591 cm^{-1}. MS (ES+): *m*/*z* (%) = [M + NH$_4$]$^+$: 815 (20), 793 (25), 752 (3), 664 (5), 455 (13), 419 (19), 397 (100), 309 (14), 261 (10), 216 (18). HRMS (ES+): [M + NH$_4$]$^+$: calcd. for $C_{19}H_{25}O_2S^{74}Se$: 391.0795; found 391.0800. $[a]_D^{20}$ = –127.7 (*c* = 0.44, $CHCl_2$). Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 (dd, *J* = 7.8, 1.4 Hz, 1 H, ArH), 7.48 (dd, *J* = 7.7, 1.0 Hz, 1 H, ArH), 7.36 (dt, *J* = 7.8, 7.6, 1.3 Hz, 1 H, ArH), 7.26 (m, 6 H, ArH), 4.28 (dd, *J* = 8.3, 5.1 Hz, 1 H, C*H*OCH_3), 3.29 (dd, *J* = 12.1, 8.3 Hz, 1 H, SeC*H*$_2$CH), 3.14 (s, 3 H, OCH_3), 3.01 (dd, *J* = 12.2, 5.0 Hz, 1 H, SeC*H*$_2$CH), 1.15 [s, 9 H, C(C*H*$_3$)$_3$] ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 142.4 (C), 139.4 (C), 132.9 (CH), 130.5 (CH), 127.6 (2CH), 127.2 (CH), 126.5 (2CH), 125.6 (2CH), 123.4 (C), 81.8 (*C*HOCH$_3$), 57.2 [*C*(CH$_3$)$_3$], 55.1 (O*C*H$_3$), 36.2 (Se*C*H$_2$CH), 22.3 [C(*C*H$_3$)$_3$] ppm. Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 (dd, *J* = 7.8, 1.4 Hz, 1 H, ArH), 7.43 (dd, *J* = 7.8, 1.0 Hz, 1 H, ArH), 7.36 (dt, *J* = 7.8, 7.6, 1.3 Hz, 1 H, ArH), 7.26 (m, 6 H, ArH), 4.26 (m, 1 H, C*H*OCH_3), 3.22 (dd, *J* = 12.1, 9.2 Hz, 1 H, SeC*H*$_2$CH), 3.17 (s, 3 H, OCH_3), 3.04 (m, 1 H, SeC*H*$_2$CH), 1.15 [s, 9 H, C(C*H*$_3$)$_3$] ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 142.5 (C), 139.5 (C), 132.9 (CH), 130.6 (CH), 127.6 (2CH), 127.3 (CH), 126.6 (2CH), 125.6 (2CH), 123.4 (C), 81.8 (*C*HOCH$_3$), 57.3 [*C*(CH$_3$)$_3$], 55.1 (O*C*H$_3$), 36.2 (Se*C*H$_2$CH), 22.3 [C(*C*H$_3$)$_3$] ppm.

Sulfoxide 22c: Synthesized according to GB 1; yield 32% (28 mg), mixture of diastereomers 5:1 (solvent: THF). IR (film): $\tilde{\nu}$ = 2928, 1711, 1598, 1445, 1366, 1262, 1153, 1095, 1045, 753 cm^{-1}. MS (ES+): *m*/*z* (%) = [M + H]$^+$: 893 (34), 796 (4), 469 (5), 447 (100), 359 (12), 260 (7). HRMS (ES+): calcd. for $C_{23}H_{27}O_2S^{80}Se$: 447.0891; found 447.0886. Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88–7.69 (m, 5 H, ArH), 7.57 (dd, *J* = 7.7, 1.1 Hz, 1 H, ArH), 7.53–7.46 (m, 2 H, ArH), 7.46–7.37 (m, 2 H, ArH), 7.37–7.27 (m, 1 H, ArH), 4.50 (dd, *J* = 7.9, 5.5 Hz, 1 H, C*H*OCH_3), 3.45 (dd, *J* = 12.22, 8.01 Hz, 1 H, SeC*H*$_2$CH), 3.25 (s, 3 H, OCH_3), 3.15 (dd, *J* = 12.21, 5.46 Hz, 1 H, SeC*H*$_2$CH), 1.21 [s, 9 H, C(C*H*$_3$)$_3$] ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.6 (C), 137.8 (C), 133.9 (CH), 133.3 (C), 133.1 (CH), 131.6 (CH), 131.4 (CH), 128.6 (CH), 127.9 (CH), 127.7 (CH), 127.5 (CH), 127.5 (CH), 126.3 (2CH), 126.1 (CH), 123.9 (CH), 83.1 (*C*HOCH$_3$), 58.2 [*C*(CH$_3$)$_3$], 57.2 (O*C*H$_3$), 36.8 (Se*C*H$_2$CH), 23.3 [C(*C*H$_3$)$_3$] ppm. Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88–7.69 (m, 5 H, ArH), 7.57 (dd, *J* = 7.7, 1.1 Hz, 1 H, ArH), 7.53–7.46 (m, 2 H, ArH), 7.46–7.37 (m, 2 H, ArH), 7.37–7.27 (m, 1.2 H, ArH), 4.50 (m, 1 H, C*H*OCH_3), 3.39 (dd, *J* = 12.15, 9.17 Hz, 1 H, SeC*H*$_2$CH), 3.29 (s, 3 H, OCH_3), 3.18 (m, 1 H, SeC*H*$_2$CH), 1.23 [s, 9 H, C(C*H*$_3$)$_3$] ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.4 (C), 137.9 (C), 133.9 (CH), 133.5 (C), 133.2 (CH), 132.1 (CH), 131.3 (CH), 128.5 (CH), 127.9 (CH), 127.7 (CH), 127.4 (CH), 127.2 (CH), 126.3 (2× CH), 125.9 (CH), 123.9 (CH), 83.0 (*C*HOCH$_3$), 58.2 [*C*(CH$_3$)$_3$], 57.0 (O*C*H$_3$), 37.3 (Se*C*H$_2$CH), 23.3 [C(*C*H$_3$)$_3$] ppm.

Sulfoxide 22d: Synthesized according to GB 1; yield 38% (31 mg); mixture of diastereomers 4:1 (solvent: CH_2Cl_2). MS (ES+): *m*/*z* (%) = [M + H]$^+$: 821 (50), 433 (6), 411 (100), 379 (22), 323 (12), 260 (29), 204 (6). HRMS (ES+): $C_{23}H_{27}O_2S^{80}Se$: calcd. 411.0891; found 411.0889. IR (film): $\tilde{\nu}$ = 3054, 2976, 2824, 1571, 1492, 1445, 1422,

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1362, 166, 1073, 1046, 1022, 868, 763, 701 cm^{-1} Major isomer: ^1H NMR (400 MHz, $CDCl_3$): δ = 7.72 (dd, J = 7.76, 0.97 Hz, 1 H, ArH), 7.44 (d, J = 7.72 Hz, 1 H, ArH), 7.20–7.40 (m, 7 H, ArH), 3.43 (d, J = 11.56 Hz, 1 H, SeCH_2CH), 3.17 (d, J = 11.54 Hz, 1 H, SeCH_2CH), 3.07 (s, 3 H, OCH_3), 1.68 (s, 3 H, CH_3), 1.16 [s, 9 H, C(CH_3)$_3$] ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 157.3 (C), 143.3 (C), 134.2 (CH), 132.3 (C), 131.4 (CH), 128.4 (2CH), 127.4 (CH), 127.2 (CH), 126.2 (2CH), 121.3 (CH), 78.9 (*C*OCH$_3$), 58.2 [*C*(CH$_3$)$_3$], 51.1 (O*C*H$_3$), 44.2 (Se*C*H$_2$CH), 24.2 (C*C*H$_3$), 23.4 [C(*C*H$_3$)$_3$] ppm; Minor Isomer: ^1H NMR (500 MHz, $CDCl_3$): δ = 7.72 (dd, J = 7.76, 0.97 Hz, 1 H, ArH), 7.20–7.40 (m, 8 H, ArH), 3.37 (d, J = 11.61 Hz, 1 H, SeCH_2CH), 3.19 (d, J = 11.63 Hz, 1 H, SeCH_2CH), 3.09 (s, 3 H, OCH_3), 1.68 (s, 3 H, CH_3), 1.17 [s, 9 H, C(CH_3)$_3$] ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 157.3 (C), 143.7 (C), 134.0 (CH), 132.6 (C), 131.3 (CH), 128.4 (2CH), 127.5 (CH), 127.2 (CH), 126.1 (2CH), 121.3 (CH), 78.9 (*C*OCH$_3$), 58.1 [*C*(CH$_3$)$_3$], 51.1 (O*C*H$_3$), 44.2 (Se*C*H$_2$CH), 24.2 (C*C*H$_3$), 23.5 [C(*C*H$_3$)$_3$] ppm.

Sulfoxide 22e: Synthesized according to GB 1; yield 30% (27 mg); mixture of diastereomers 11:1 (solvent: CH_2Cl_2). MS (ES+): *m*/*z* (%) = $[M + H]^+$: 821 (2), 411 (100), 323 (25), 204 (16). HRMS: calcd. for $C_{20}H_{27}O_2S^{74}Se$ 405.0951; found 405.0960. IR (film): $\tilde{\nu}$ = 2975, 2927, 1445, 1125, 1080, 1045, 1022, 755, 702 cm^{-1} Minor isomer is indicated by:*. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.84 (dd, J = 1.4, J = 7.9 Hz, 1 H, ArH), 7.81 (dd, J = 1.4, J = 7.9 Hz, 1 H, ArH)*, 7.61 (m, 1 H, ArH)*, 7.59 (dd, J = 1.1, J = 7.7 Hz, 1 H, ArH), 7.47 (dt, J = 1.3, J = 7.6 Hz, 1 H, ArH), 7.36 (m, 3 H, ArH), 7.29 (m, 3 H, ArH), 4.41 (d, J = 4.7 Hz, 1 H, SeCHC*H*), 4.32 (d, J = 4.3 Hz, 1 H, SeCHC*H*)*, 3.52 (dq, J = 4.7, J = 7.0 Hz, 1 H, 1 H, SeC*H*CH), 3.29 (s, 3 H, OCH_3)*, 3.28 (s, 3 H, OCH_3), 1.31 (d, J = 7.0 Hz, 3 H, CH_3), 1.21 [s, 9 H, C(CH_3)$_3$]*, 1.21 [s, 9 H, C(CH_3)$_3$] ppm. ^{13}C NMR (500 MHz, $CDCl_3$): δ = 144.8 (C), 139.1 (C), 135.5 (CH), 135.5* (CH), 131.2 (C), 131.0* (C), 128.3 (2CH), 128.2* (2CH), 127.9 (CH), 127.8 (CH), 127.6 (CH), 127.0 (2CH), 126.9* (2CH), 86.2 (*C*OCH$_3$), 58.3 [*C*(CH$_3$)$_3$], 57.4 (O*C*H$_3$), 48.6 (Se*C*HCH) 23.4 [C(*C*H$_3$)$_3$], 16.6 (SeCH*C*H$_3$) ppm.

Sulfoxide 22f: Synthesized according to GB 1; yield 30% (27 mg); mixture of diastereomers 9:1 (solvent: CH_2Cl_2). MS: *m*/*z* (%) = (ES^+) *m*/*z* (%) $[M + H]^+$: 901 (50), 580 (16), 451 (100), 419 (66), 363 (14), 260 (7). HRMS: calcd. for $C_{20}H_{27}O_2S^{80}Se$: 451.1204; found 451.1197. IR (film): $\tilde{\nu}$ = 2935, 2857, 1445, 1361, 1209, 1151, 1065, 1047, 1020, 880, 758, 699 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.72 (dd, J = 1.4, J = 7.9 Hz, 1 H, ArH), 7.33 (m, 6 H, ArH), 7.40–7.29 (m, 6 H, ArH)*, 7.12 (dt, J = 1.5, J = 7.5 Hz, 1 H, ArH), 6.85 (dd, J = 1.0, J = 7.8 Hz, 1 H, ArH), 3.66 (s, 1 H, ArSeC*H*), 3.60 (s, 1 H, ArSeC*H*)*, 2.88 (s, 3 H, OCH_3), 2.86 (s, 3 H, OCH_3)*, 2.16 (dd, J = 3.4, J = 9.6 Hz, 2 H), 1.73–1.66 (m, 3 H)*, 1.69 (m, 3 H), 1.60 (m, 3 H), 1.12 [s, 9 H, C(CH_3)$_3$] ppm. ^{13}C NMR (500 MHz, $CDCl_3$): δ = 144.7 (C), 143.7 (C), 135.8 (CH), 131.0 (CH), 130.9 (CH), 128.1 (2CH), 127.6 (CH), 127.5 (CH), 127.2 (CH), 126.8 (2CH), 79.1 (*C*OCH$_3$), 58.5 [*C*(CH$_3$)$_3$], 58.3 (O*C*H$_3$), 50.1 (ArSe*C*H), 27.9 (CH_2), 26.0 (CH_2), 23.5 [C(*C*H$_3$)$_3$], 21.3 (CH_2), 20.7 (CH_2) ppm.

2-(*tert*-Butylsulfinyl)-6-methoxyphenyl 2-(2-Chlorophenyl)-2-methoxyethyl Selenide (23a): Synthesized according to GB 1; yield 40% (37 mg); mixture of diastereomers 2:1 (solvent: chloroform, –50 °C). MS (ES+): *m*/*z* (%) = 524 (100) [[M + MeCNNa]$^+$], 483 (68) [M + Na]$^+$. HRMS: calcd. $C_{20}H_{26}O_3{}^{35}ClS^{80}Se$: 461.0456 found 461.0468. IR: $\tilde{\nu}$ = 2934, 1568, 1455, 1428, 1361, 1285, 1260, 1169, 1149, 1104, 1040, 1026, 834, 786, 759, 732, 706 cm^{-1} Isomer A: ^1H NMR (250 MHz, $CDCl_3$): δ = 7.40 (m, 3 H, ArH), 7.22 (m, 1 H, ArH), 7.18 (m, 1 H, ArH), 7.10 (m, 1 H, ArH) 6.87 (m, 1 H, ArH), 4.88 (dd, J = 3.5, J = 9.1 Hz, 1 H, C*H*OCH$_3$), 3.86 (s, 3 H, OCH_3), 3.20 (m, 4 H, OCH_3 and Se*C*H$_2$CH), 2.96 (dd, J = 3.5, J = 12.2 Hz, 1 H, 1 H, Se*C*H$_2$CH), 1.15 [s, 9 H, C(CH_3)$_3$] ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 159.2 (C), 146.8 (C), 138.2 (C), 132.7 (C), 129.5 (CH), 129.3 (CH), 128.9 (CH), 127.4 (CH), 127.2 (CH), 119.6 (2CH), 112.5 (CH), 79.9 (*C*OCH$_3$), 58.3 [*C*(CH$_3$)$_3$], 57.5 (O*C*H$_3$), 56.3 (O*C*H$_3$), 34.3 (ArSe*C*H), 23.6 [C(*C*H$_3$)$_3$] ppm; Isomer B: ^1H NMR (400 MHz, $CDCl_3$): δ = 7.51 (d, J = 8.5 Hz, 1 H, ArH), 7.38 (dd, J = 1.7, J = 8.0 Hz, 1 H, ArH), 7.23 (m, 3 H, ArH), 7.13 (m, 1 H, ArH), 6.85 (dd, J = 2.9, J = 8.5 Hz, 1 H, ArH), 4.76 (dd, J = 3.6, J = 8.8 Hz, 1 H, C*H*OCH$_3$), 3.78 (s, 3 H, OCH_3), 3.22 (s, 3 H, OCH_3), 3.07 (dd, J = 8.8, J = 12.5 Hz, 1 H, Se*C*H$_2$CH), 2.99 (dd, J = 3.6, J = 12.5 Hz, 1 H, Se*C*H$_2$CH), 1.17 [s, 9 H, C(CH_3)$_3$] ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.9 (C), 146.8 (C), 138.0 (C), 137.3 (C), 132.9 (CH), 129.6 (CH), 128.0 (CH), 127.3 (CH), 127.1 (CH), 118.8 (2CH), 111.6 (CH), 79.4 (*C*OCH$_3$), 58.5 [*C*(CH$_3$)$_3$], 57.4 (O*C*H$_3$), 55.7 (O*C*H$_3$), 36.2 (ArSe*C*H), 23.5 [C(*C*H$_3$)$_3$] ppm.

2-(*tert*-Butylsulfinyl)-6-methoxyphenyl 2-Methoxy-2-phenylethyl Selenide (23b): Synthesized according to GB 1; yield 24% (20 mg), mixture of diastereomers 2:1 (solvent: chloroform, –50 °C). MS (ES+): *m*/*z* (%) = $[M + H]^+$: 490 (100) [M + Na + acetonitrile$^+$], 449 (80) [M + Na$^+$], 427 (75), 425 (40), 380 (15), 339 (30), 276 (35), 130 (25), 85 (38). HRMS: $[M + H]^+$ $C_{20}H_{27}O_3S$ ^{80}Se calcd. 427.0846; found 427.0865. IR: $\tilde{\nu}$ = 2936, 1568, 1492, 1455, 1429, 1360, 1286, 1260, 1169, 1149, 1104, 1040, 1026, 957, 833, 786, 768, 702 cm^{-1} Isomer is indicated by:*. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.47 (m, 2 H, ArH), 7.35 (m, 1 H, ArH), 7.28 (m, 3 H, ArH), 7.22 (m, 1 H, ArH) 6.97 (dd, J = 2.6, J = 6.7 Hz, 1 H, ArH), 6.94 (dd, J = 3.0, J = 6.2 Hz, 1 H, ArH)*, 4.39 (dd, J = 5.3, J = 8.3 Hz, 1 H, C*H*OCH$_3$), 4.18 (dd, J = 4.2, J = 9.4 Hz, 1 H, C*H*OCH$_3$)*, 3.95 (s, 3 H, OCH_3), 3.88 (s, 3 H, OCH_3)*, 3.32 (dd, J = 8.4, J = 12.0 Hz, 1 H, SeCH_2CH), 3.22 (s, 3 H, OCH_3)*, 3.19 (s, 3 H, OCH_3), 3.13 (dd, J = 4.6, J = 7.6 Hz, 1 H, SeCH_2CH)*, 3.04 (dd, J = 4.2, J = 12.2 Hz, 1 H, 1 H, SeCH_2CH)*, 2.89 (dd, J = 5.3, J = 12.0 Hz, 1 H, SeCH_2CH), 1.22 [s, 9 H, C(CH_3)$_3$]*, 1.20 [s, 9 H, C(CH_3)$_3$] ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 159.1 (C), 140.8 (C), 129.4 (2CH), 128.5 (CH), 128.1 (CH), 127.9* (CH), 126.6 (CH), 126.4 (CH), 119.6 (C), 112.6 (CH), 112.5* (CH), 83.8 (*C*HOCH$_3$), 58.2 [*C*(CH$_3$)$_3$], 57.1* (O*C*H$_3$), 56.9 (O*C*H$_3$), 56.2 (O*C*H$_3$), 56.2* (O*C*H$_3$), 36.0 (Se*C*H$_2$CH), 23.5 [C(*C*H$_3$)$_3$] ppm.

2-(*tert*-Butylsulfinyl)-6-methoxyphenyl 2-Methoxy-2-phenylpropyl Selenide (23c): Synthesized according to GB 1; yield 22% (19 mg); mixture of diastereomers 1:1 (solvent: chloroform, –50 °C). MS (ES+): *m*/*z* (%) = $[M + H]^+$: 504 (12), 463 (100) $[M + Na]^+$, 449 (5), 415 (10). HRMS: $[M + Na]^+$ calcd. $C_{21}H_{28}O_3SNa^{80}Se$: 463.0822 found 463.0831. IR: $\tilde{\nu}$ = 3059, 1568, 1493, 1455, 1429, 1362, 1286, 1261, 1167, 1149, 1092, 1072, 1040, 1026, 911, 834, 786, 766, 701 cm^{-1} Isomer is indicated by:*. ^1H NMR (250 MHz, $CDCl_3$): δ = 7.20–7.50 (m, 7 H, ArH), 6.94 (dd, J = 2.6, J = 6.8 Hz, 1 H, ArH), 6.87 (dd, J = 2.7, J = 6.7 Hz, 1 H, ArH)*, 3.91 (s, 3 H, OCH_3), 3.84 (s, 3 H, OCH_3)*, 3.45 (d, J = 11.0 Hz, 1 H, SeC*H*CH)*, 3.32 (d, J = 11.5 Hz, 1 H, SeC*H*CH), 3.20 (d, J = 11.5 Hz, 1 H, SeCHC*H*), 3.13 (m, 1 H, SeCHC*H*)*, 3.11 (s, 3 H, OCH_3)*, 3.07 (s, 3 H, OCH_3), 1.72 (s, 3 H, CH_3), 1.72 (s, 3 H, CH_3)*, 1.19 [s, 9 H, C(CH_3)$_3$]*, 1.18 [s, 9 H, C(CH_3)$_3$] ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 159.1, 143.5, 143.5, 129.4, 129.2, 128.2, 128.2, 127.3, 127.3, 126.1, 126.0, 119.6, 119.5, 112.5, 112.4, 79.0, 79.0, 58.2, 56.2, 56.1, 50.9, 42.5, 42.0, 30.3, 23.5, 23.4 ppm.

Sulfoxide 24a: Synthesized according to GB 1; yield 47% (45 mg); mixture of diastereomers 8:1 (solvent: CH_2Cl_2). MS (ES+): *m*/*z* (%) = $[M + H]^+$: 445 (100), 391 (28), 343 (25), 261 (8), 204 (16). HRMS:

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calcd. for $C_{20}H_{26}O_2ClS^{74}Se$ 439.0561; found 439.0569. IR (film): $\tilde{\nu}$ = 2973, 2926, 1572, 1471, 1442, 1362, 1168, 1119, 1096, 1048, 1023, 908, 756, 733, 591 cm^{-1} Minor isomer is indicated by:*. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.81 (dd, J = 1.4, J = 7.9 Hz, 1 H, ArH)*, 7.77 (dd, J = 1.5, J = 7.8 Hz, 1 H, ArH), 7.62 (dd, J = 1.2, J = 7.7 Hz, 1 H, ArH), 7.58 (dd, J = 1.1, J = 7.8 Hz, 1 H, ArH)*, 7.51 (m, 1 H, ArH)*, 7.49 (dd, J = 1.6, J = 8.0 Hz, 1 H, ArH), 7.41 (dt, J = 1.3, J = 7.6 Hz, 1 H, ArH), 7.34 (dt, J = 1.5, J = 7.5 Hz, 1 H, ArH), 7.28 (m, 2 H, ArH), 7.19 (m, 1 H, ArH), 4.97 (dd, J = 3.6, J = 8.7 Hz, 1 H, C*H*OCH_3), 4.84 (dd, J = 3.3, J = 9.3 Hz, 1 H, C*H*OCH_3)*, 3.41 (m, 2 H, CH_2CH_3), 3.23 (m, 1 H, SeCH_2CH), 3.15 (dd, J = 3.7, J = 12.5 Hz, 1 H, SeCH_2CH), 3.08 (dd, J = 9.3, J = 12.4 Hz, 1 H, SeCH_2CH)*, 1.23 [s, 9 H, C(CH_3)$_3$], 1.18 (t, J = 7.0 Hz, 1 H, CH_2CH_3) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 143.2 (C), 138.6 (C), 134.0 (CH), 132.6 (C), 131.9 (C), 131.9* (C), 131.2 (CH), 129.5* (CH), 129.4 (CH), 128.9 (CH), 127.4 (CH), 127.3 (CH), 127.3* (CH), 127.2 (CH), 127.2 (CH), 77.5 (SeCH$_2$*C*H), 65.3* (O*C*H$_2$CH$_3$), 65.1 (O*C*H$_2$CH$_3$), 58.2 [*C*(CH$_3$)$_3$], 35.9* (ArSe*C*H), 35.7 (ArSe*C*H), 23.3 [C(*C*H$_3$)$_3$], 23.2* [C(*C*H$_3$)$_3$], 15.2* (OCH$_2$*C*H$_3$), 15.1 (OCH$_2$*C*H$_3$) ppm.

Sulfoxide 24b: Synthesized according to GB 1; yield 47% (46 mg); mixture of diastereomers 8:1 (solvent: CH_2Cl_2). MS (ES+): *m*/*z* (%) = [M + H]$^+$: 481 (7), 459 (100), 391 (28), 343 (13), 199 (14). HRMS: calcd. for $C_{21}H_{28}O_2ClS^{74}Se$ 453.0718; found 453.0722. IR (film): $\tilde{\nu}$ = 2971, 2928, 1572, 1470, 1443, 1378, 1363, 1329, 1166, 1120, 1087, 1048, 1023, 941, 756, 705 cm^{-1} Minor isomer is indicated by:*. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.80 (dd, J = 1.5, J = 7.9 Hz, 1 H, ArH)*, 7.77 (dd, J = 1.5, J = 7.8 Hz, 1 H, ArH), 7.62 (dd, J = 1.2, J = 7.7 Hz, 1 H, ArH), 7.58 (dd, J = 1.2, J = 7.8 Hz, 1 H, ArH)*, 7.54 (dd, J = 1.6, J = 8.1 Hz, 1 H, ArH), 7.40 (dt, J = 1.3, J = 7.6 Hz, 1 H, ArH), 7.33 (dt, J = 1.5, J = 7.5 Hz, 1 H, ArH), 7.28 (m, 2 H, ArH), 7.19 (m, 1 H, ArH), 5.11 (dd, J = 3.4, J = 9.0 Hz, 1 H, SeCH$_2$C*H*), 5.00 (m, 1 H, SeCH$_2$C*H*)*, 3.51 [sept., J = 6.1 Hz, 1 H, CHOC*H*(CH$_3$)$_2$], 3.24 (dd, J = 9.1, J = 12.4 Hz, 1 H, SeCH_2CH), 3.24 (dd, J = 9.1, J = 12.4 Hz, 1 H, SeCH_2CH)*, 3.10 (dd, J = 3.5, J = 12.3 Hz, 1 H, SeCH_2CH), 1.23 [s, 9 H, C(CH_3)$_3$], 1.23 [s, 9 H, C(CH_3)$_3$]*, 1.19 [d, J = 6.3 Hz, 1 H, CHOCH-(CH_3)$_2$], 1.08 [d, J = 6.4 Hz, 1 H, CHOCH(CH_3)$_2$]*, 1.07 [d, J = 6.2 Hz, 1 H, CHOCH(CH_3)$_2$] ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 143.4 (C), 140.0 (C), 134.2 (CH), 134.0* (CH), 132.8 (C), 132.8 (C), 131.7 (CH), 129.8 (CH), 129.3 (CH), 128.0 (CH), 127.8 (CH), 127.7 (CH), 127.6 (CH), 127.6* (CH), 75.4 (SeCH$_2$*C*H), 71.2* [O*C*H(CH$_3$)$_2$], 70.9 [O*C*H(CH$_3$)$_2$], 58.7 [*C*(CH$_3$)$_3$], 36.6 (ArSe*C*H), 23.8 [C(*C*H$_3$)$_3$], 23.6* [C(*C*H$_3$)$_3$], 22.0* [OCH(*C*H$_3$)$_2$], 21.9 [OCH(*C*H$_3$)$_2$] ppm.

Sulfoxide 24c: Synthesized according to GB 1; yield 30% (30 mg); mixture of diastereomers 6:1 (solvent: CH_2Cl_2). MS (ES+): *m*/*z* (%) = [M + H]$^+$: 945 (38), 495 (7), 473 (100), 417 (44), 343 (21), 260 (16), 205 (12). HRMS: calcd. for $C_{22}H_{30}O_2ClS^{74}Se$ 467.0874; found 467.0877. IR (film): $\tilde{\nu}$ = 2972, 1470, 1443, 1365, 1187, 1082, 1047, 1022, 755 cm^{-1} Minor isomer is indicated by:*. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.79 (dd, J = 1.5, J = 7.9 Hz, 1 H, ArH)*, 7.76 (m, 2 H, ArH), 7.63 (m, 2 H, ArH), 7.58 (dd, J = 1.2, J = 7.7 Hz, 1 H, ArH)*, 7.39 (dt, J = 1.4, J = 7.6 Hz, 1 H, ArH), 7.33 (dt, J = 1.5, J = 7.5 Hz, 1 H, ArH), 7.27 (m, 2 H, ArH), 7.16 (m, 1 H, ArH), 5.21 (dd, J = 3.5, J = 8.9 Hz, 1 H, C*H*OCH_3), 5.14 (dd, J = 3.3, J = 9.1 Hz, 1 H, C*H*OCH_3)*, 3.24 (dd, J = 8.9, J = 12.3 Hz, 1 H, SeCH_2CH), 3.19 (m, 1 H, SeCH_2CH)*, 3.03 (dd, J = 3.6, J = 12.3 Hz, 1 H, SeCH_2CH), 1.23 [s, 9 H, C(CH_3)$_3$], 1.12 [s, 9 H, C(CH_3)$_3$] ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 142.5 (C), 133.7 (CH), 133.4 (C), 133.3 (C), 131.7 (CH), 131.5 (C), 129.6 (CH), 129.0 (CH), 128.7 (CH), 127.8 (CH), 127.5 (CH), 127.4 (CH), 75.6 [O*C*(CH$_3$)$_3$], 70.6 (SeCH$_2$*C*H), 58.7 [*C*(CH$_3$)$_3$], 37.6 (ArSe*C*H), 29.0 [OC(*C*H$_3$)$_3$], 23.8 [C(*C*H$_3$)$_3$] ppm.

Sulfoxide 24d: Synthesized according to GB 1: Reaction in dry dichloromethane at –78 °C; yield 30% (32 mg); dr: 3.5:1. MS (ES+): *m*/*z* (%) = [M + H]$^+$: 1013 (15), 507 (100), 391 (12), 342 (22), 204 (13). HRMS: calcd. for $C_{25}H_{28}O_2ClS^{74}Se$ 425.0418; found 501.0717. IR: $\tilde{\nu}$ = 3060, 3029, 2973, 2925, 2864, 1570, 1471, 1441, 1361, 1167, 1089, 1047, 1024, 755 cm^{-1} Minor isomer is indicated by:*. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.72 (dd, J = 1.3, J = 7.9 Hz, 1 H, ArH)*, 7.67 (dd, J = 1.4, J = 7.8 Hz, 1 H, ArH), 7.50 (td, J = 2.6, J = 8.4 Hz, 1 H, ArH), 7.46 (dd, J = 1.1, J = 7.8 Hz, 1 H, ArH)*, 7.42 (dd, J = 1.1, J = 7.8 Hz, 1 H, ArH), 7.36 (m, 1 H, ArH)*, 7.31 (m, 1 H, ArH), 7.20 (m, 8 H, ArH), 5.00 (dd, J = 3.5, J = 8.7 Hz, 1 H, C*H*OCH_2Ar), 4.96 (m, 1 H, C*H*OCH_2Ar)*, 4.34 (m, 2H CHOCH_2Ar), 3.22 (dd, J = 8.7, J = 12.6 Hz, 1 H, SeCH_2CH), 3.08 (dd, J = 3.6, J = 12.6 Hz, 1 H, SeCH_2CH), 1.14 {s, 9 H, [C(CH_3)$_3$]} ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 143.2, 138.0, 137.5, 134.0, 132.8, 131.7, 131.3*, 131.2, 129.6*, 129.6, 129.1, 128.3, 128.0, 127.9, 127.9*, 127.8, 127.7*, 127.4, 127.4, 127.3, 127.3*, 127.3*, 71.6, 71.3, 58.2, 35.9*, 35.5, 23.3 ppm.

2-Azido-2-(2-chlorophenyl)ethyl 2-(*tert*-Butylsulfinyl)phenyl Selenide (24e): Synthesized according to GB 1; yield 35% (33 mg); mixture of diastereomers 6:1 (solvent: CH_2Cl_2). MS (ES+): *m*/*z* (%) = [M + H]$^+$: 442 (100), 368 (20), 343 (40), 261 (2), 205 (21). HRMS: calcd. for $C_{18}H_{21}ClN_3OS^{76}Se$ 438.0281; found 438.0281. IR: $\tilde{\nu}$ = 2963, 2925, 2107, 1472, 1443, 1249, 1046, 1021, 756 cm^{-1} Minor isomer is indicated by:*. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.82 (dd, J = 1.4, J = 7.9 Hz, 1 H, ArH)*, 7.79 (dd, J = 1.4, J = 7.8 Hz, 1 H, ArH), 7.61 (dd, J = 1.1, J = 7.7 Hz, 1 H, ArH), 7.57 (dd, J = 1.1, J = 7.7 Hz, 1 H, ArH)*, 7.46 (tt, J = 1.9, J = 3.4 Hz, 2 H, ArH), 7.38 (dd, J = 1.4, J = 7.5 Hz, 1 H, ArH), 7.30 (m, 2 H, ArH), 7.23 (dd, J = 1.7, J = 7.6 Hz, 1 H, ArH), 7.21 (m, 1 H, ArH)*, 5.22 (dd, J = 4.6, J = 8.5 Hz, 1 H, C*H*N_3), 3.31 (dd, J = 4.6, J = 12.7 Hz, 1 H, SeCH_2CH)*, 3.25 (dd, J = 4.6, J = 12.8 Hz, 1 H, SeCH_2CH), 3.18 (dd, J = 8.5, J = 12.8 Hz, 1 H, SeCH_2CH), 3.09 (dd, J = 9.1, J = 12.6 Hz, 1 H, SeCH_2CH)*, 1.22 [s, 9 H, C(CH_3)$_3$] ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 136.1 (C), 134.6 (C), 134.3 (C), 132.5 (CH), 131.5, 130.1 (C), 129.9 (CH), 129.7 (CH), 128.1 (CH), 127.8 (CH), 127.6 (CH), 127.5 (CH), 62.1 (SeCH$_2$*C*HN$_3$), 58.4 [*C*(CH$_3$)$_3$], 34.3 (ArSe*C*H$_2$), 23.3 [C(*C*H$_3$)$_3$] ppm.

Selenathiine 1-Oxide 25a: Synthesized according to GB 2; yield 10% (6 mg). MS (ES+): *m*/*z* (%) = [M + H]$^+$: 617 (10), 421 (10), 331 (15), 309 (100), 205 (6). HRMS: calcd. for $C_{14}H_{13}OS^{76}Se$ 304.9874, found 304.9880. $[\alpha]_D^{20}$ = +48.0 (c = 0.1, CH_2Cl_2). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.57 (dd, J = 7.8, 0.9 Hz, 1 H, ArH), 7.47 (dd, J = 7.7, 1.4 Hz, 1 H, ArH), 7.37 (dt, J = 7.7, 7.6, 1.5 Hz, 1 H, ArH), 7.29–7.23 (m, 4 H, ArH), 7.09 (dd, J = 7.6, 1.8 Hz, 2 H, ArH), 4.51 (dd, J = 8.1, 6.2 Hz, 1 H, SeCH$_2$C*H*S), 3.88 (dd, J = 11.7, 8.2 Hz, 1 H, SeCH_2CHS), 3.33 (dd, J = 11.7, 6.1 Hz, 1 H, SeCH_2CHS) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 139.5 (C), 134.7 (CH), 131.6 (CH), 131.1 (CH), 130.1 (CH), 128.6 (CH), 128.4 (CH and C), 128.2 (2CH), 127.2 (C), 126.7 (CH), 61.3 (SeCH$_2$*C*HS), 16.7 (Se*C*H$_2$CHS) ppm. IR (film): $\tilde{\nu}$ = 3057, 2928, 1575, 1494, 1452, 1425, 1251, 1093, 1063, 1049, 1030, 754, 728, 698 cm^{-1}.

Selenathiine Oxide 25b: Synthesized according to GB 2; yield 16% (11 mg). MS (ES+): *m*/*z* (%) = [M + H]$^+$: 717 (55), 471 (10), 380 (10), 359 (100). HRMS: calcd. for $C_{18}H_{15}OClS^{80}Se$ 359.0003; found 359.0001. IR (film): $\tilde{\nu}$ = 3055, 2926, 1443, 1425, 1051, 1031, 909, 856, 819, 751, 728 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.73–7.63 (m, 3 H, ArH), 7.55–7.50 (m, 2 H, ArH), 7.41–7.37 (m, 2 H,

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ArH), 7.30 (t, J = 7.8, 1.3 Hz, 1 H, ArH), 7.20–7.18 (m, 1 H, ArH), 7.18–7.13 (m, 1 H, ArH), 7.12–7.09 (m, 1 H, ArH), 4.61–4.56 (m, 1 H, SeCH$_2$C*H*S), 3.92 (dd, J = 11.7, 8.4 Hz, 1 H, SeC*H*$_2$CHS), 3.31 (dd, J = 11.7, 6.03 Hz, 1 H, SeC*H*$_2$CHS) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 139.6 (C), 133.1 (C), 133.0 (CH), 132.3 (CH), 131.7 (CH), 131.1 (CH), 130.3 (CH), 128.2 (CH), 128.1 (CH), 127.7 (CH), 127.6 (CH), 127.3 (C), 126.7 (CH), 126.5 (CH), 126.4 (CH), 125.7 (CH), 61.5 (SeCH$_2$*C*HS), 16.8 (Se*C*H$_2$CHS) ppm. ^{77}Se NMR (57 MHz, $CDCl_3$): δ = 244 ppm.

Selenathiine Oxide 25c: Synthesized according to GB 2; yield 9% (6 mg). MS (ES+): m/z (%) = $[M + H]^+$: 717 (55), 471 (10), 380 (10), 359 (100). HRMS: calcd. for $C_{14}H_{11}O^{35}ClS^{78}Se$ 339.9392; found 339.9400. IR (film): $\tilde{\nu}$ = 3375, 3056, 2972, 2928, 1571, 1471, 1441, 1363, 1164, 1092, 1047, 755 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.60 (dd, J = 1.5, J = 7.7 Hz, 1 H, ArH), 7.49 (ddd, J = 5.1, J = 6.2, J = 16.7 Hz, 1 H, ArH), 7.38 (dd, J = 1.5, J = 6.8 Hz, 1 H, ArH), 7.34 (dd, J = 1.5, J = 7.7 Hz, 1 H, ArH), 7.25 (dd, J = 2.3, J = 3.0 Hz, 1 H, ArH), 7.23 (m, 1 H, ArH), 4.79 (dd, J = 3.7, J = 11.9 Hz, 1 H, SeCH$_2$C*H*S), 4.03 (t, J = 11.9 Hz, 1 H, SeC*H*$_2$CHS), 3.04 (dd, J = 3.8, J = 11.7 Hz, 1 H, SeC*H*$_2$CHS) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 138.8 (C), 134.1 (C), 132.7 (2CH), 132.6 (CH), 130.8 (CH), 129.8 (C), 129.7 (CH), 128.8 (CH), 127.5 (CH), 127.3 (C), 126.0 (CH), 56.2 (SeCH$_2$*C*HS), 13.9 (Se*C*H$_2$CHS) ppm.

Selenathiine Oxide 25d: Synthesized according to GB 2; yield 12% (8 mg). IR (film): $\tilde{\nu}$ = 3389, 2926, 1571, 1494, 1444, 1094, 1060, 755, 697 cm^{-1}. MS (ES+): m/z (%) = $[M + H]^+$: 645 (25), 490 (8), 338 (7), 323 (100). HRMS: calcd. for $C_{15}H_{15}OS^{80}Se$ 323.0003; found 323.0002. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 (dd, J = 7.7, 1.5 Hz, 1 H, ArH), 7.69–7.65 (m, 2 H, ArH), 7.59 (dd, J = 7.6, 1.1 Hz, 1 H, ArH), 7.51–7.29 (m, 5 H, ArH), 3.58 (d, J = 12.3 Hz, 1 H, SeC*H*$_2$CHS), 3.17 (d, J = 12.3 Hz, 1 H, SeC*H*$_2$CHS), 1.46 (s, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 141.2 (C), 131.7 (CH), 130.5 (CH), 128.9 (2CH), 128.4 (CH), 128.1 (CH), 127.6 (C), 127.5 (CH), 126.7 (C), 126.5 (2CH), 64.2 (SeCH$_2$*C*S), 30.6 (CH_3), 20.1 (Se*C*H$_2$CS) ppm.

2-(*tert*-Butylsulfinyl)phenyl (*E*)-2,4-diphenylbut-3-enyl Selenide (30): Bis[2-(*tert*-butylsulfinyl)phenyl] diselenide (1 mmol) was dissolved in dry tetrahydrofuran (40 mL) under argon, cooled to –78 °C, and treated with bromine (1 mmol, 1 mL of a 1 M solution in CCl_4). After 20 min silver triflate (solid) (540 mg, 2.1 mmol) was added and the mixture was stirred for 25 min at –78 °C. The reaction mixture was treated with the alkene (2.2 mmol). The mixture was further stirred at –78 °C and warmed to –10 °C overnight. Then MeOH (1 mL) was added and the mixture was stirred for additional 60 min at 0 °C. Then 2,4,6-collidine (1 mL) was added, followed by water (40 mL). After extraction of the reaction mixture with dichloromethane (3 × 50 mL), drying of the combined organic phases with $MgSO_4$ and removal of the solvent under reduced pressure, the residue was purified by flash column chromatography on silica gel, yielding the addition products as pale yellow oils. The diastereomers could not be separated by flash chromatography (ethyl acetate/hexanes, 1:5); yield 30% (309 mg), pale yellow grease. MS (ES+): m/z (%) = $[M + H]^+$: 969 (5), 937 (15), 501 (22), 469 (100), 413 (27), 365 (5), 309 (7), 251 (7), 207 (20). HRMS: calcd. for $C_{26}H_{29}OS^{74}Se$ 463.1158; found 463.1163. IR (film): $\tilde{\nu}$ = 3057, 3026, 2966, 2926, 1599, 1569, 1494, 1443, 1426, 1362, 1326, 1217, 1148, 1091, 965, 749, 699 cm^{-1}. Mixture of diastereomers (1:1): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.73 (ddd, J = 1.4, J = 3.7, J = 7.8 Hz, 1 H, ArH), 7.45 (td, J = 1.2, J = 7.6 Hz, 1 H, ArH), 7.35 (m, 1 H, ArH), 7.20 (m, 11 H, ArH), 6.37 (dd, J = 15.9, J = 20.4 Hz, 1 H, SeCH$_2$CHCHC*H*Ar), 6.27 (ddd, J = 1.9, J = 7.6, J = 15.8 Hz, 1 H, SeCH$_2$CHC*H*CHAr), 3.69 (p, J = 7.4 Hz, 1 H, SeCH$_2$C*H*CHCHAr), 3.30 (m, 2 H, SeC*H*$_2$CHC*H*CHAr), 1.12 [s, 9 H, C(C*H*$_3$)$_3$] ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.4 (C), 143.4* (C), 142.7 (C), 142.6* (C), 136.9 (C), 136.8* (C), 133.7, 133.6*, 131.8, 131.8*, 131.7, 131.4, 131.4*, 131.1, 130.9, 128.7, 128.7*, 128.4, 127.6, 127.6*, 127.5, 127.4*, 127.0, 126.9*, 126.3, 126.3*, 122.5, 58.2 [*C*(CH$_3$)$_3$], 58.1* [*C*(CH$_3$)$_3$], 49.1 (SeCH$_2$C*H*), 49.0* (SeCH$_2$C*H*), 35.9 (SeC*H*$_2$CH), 35.8* (SeC*H*$_2$CH), 23.3 [C(*C*H$_3$)$_3$] ppm.

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