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Terpenyl Selenides: Synthesis and Application in Asymmetric Epoxidation

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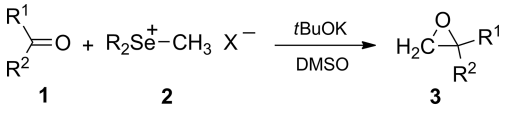
Synthesis of terpenyl selenides derived from limonene, menthol, caranol, and myrtanol is described. Three methodologies for the synthesis of terpenyl selenonium salts are compared. The results of selenium-mediated epoxidation through the use of isoselenocineole derived from limonene and methyl terpenyl, phenyl terpenyl, diterpenyl selenides, and selenonium salts are presented. The influence of solvent, counteranion, and diastereomeric purity of selenonium salt on the enantioselectivity of the epoxidation reaction is discussed.

Introduction

Phosphonium ylides are very important intermediates in modern organic chemistry, especially because of their use in the formation of C=C bonds in Wittig-type reactions. Another important group are sulfonium ylides, which are used for the synthesis of epoxides, substituted aziridines, and cyclopropanes.[1] Chiral sulfonium ylides have been applied in asymmetric synthesis with good yield, and high diastereo- and enantioselectivities.[2] Selenonium ylides are less common and, until now, only a few examples of their applications have been reported.[3] They have similar reactivity to sulfonium analogues and can be easily formed by the reaction of selenonium salts with bases. For example, nonenolizable carbonyl compounds **1** were used for selenium-mediated epoxidation by the reaction of selenonium salts **2** and *t*BuOK (Scheme 1).[4]



Entry	R	X	R^1	R^2	Yield (%)
1	Me	BF_4	H	Ph	90
2	Ph	BF_4	H	Ph	90
3	Ph	BF_4	Ph	Ph	90

Scheme 1. Application of selenonium salts in epoxidation reactions.

Selenonium ylides were also used for the synthesis of cyclopropane derivatives. They were generated by the reaction of selenonium salt with sodium hydroxide[5] or selenide with carbene.[6] The first example of the use of chiral selenonium ylides for asymmetric epoxidation was described quite recently. (2*R*,5*R*)-2,5-Dimethyltetrahydroselenophene (**4**) was used as an efficient catalyst (0.2 equiv.) for the benzylidenation of aromatic aldehydes with high enantiomeric excess (> 90%*ee*).[7] Recently, *exo*-α-methylseleno-iso borneol (**5**), and *exo*-α-phenylseleno-isoborneol (**6**) were converted into the corresponding selenonium salts by reaction with benzyl bromide and silver tetrafluoroborate, which were used for asymmetric synthesis of chiral epoxides with good yields and good stereoselectivities (50–81%*ee*).[8] Selenides **4**–**5** and **7**–**8** were the first chiral selenides applied in the asymmetric cyclopropanation with good yields, excellent diastereoselectivities, and high enantioselectivities, up to 99%*ee*[9] (Figure 1).

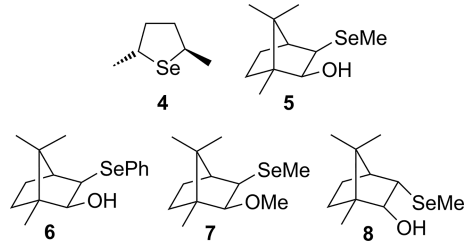


Figure 1. Chiral selenides used for asymmetric epoxidation and cyclopropanation.

Well-known sulfonium ylides have found interesting applications in asymmetric synthesis. For example, isothiocineole **9** (Figure 2), derived from limonene, was used for asymmetric epoxidation and aziridination with high enantio- and diastereoselectivities,[2] and it was used in the key step of the quinine and quinidine synthesis.[10]

Here, we report the synthesis of the selenium analogue **10** of sulfide **9** (Figure 2), and compare their reactivity in sulfur- and selenium-mediated asymmetric epoxidation.

Recently, we presented our results on asymmetric epoxidation through the use of methyl terpenyl, phenyl terpenyl, and diterpenyl sulfides derived from monoterpenes from *p*-

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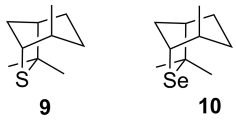
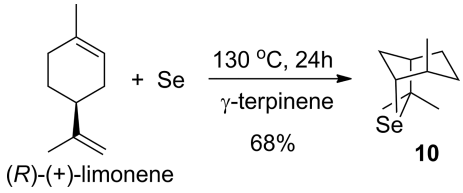


Figure 2. Structures of isothiocineole **9** and isoselenocineole **10**.

menthane, carane, and pinane group.[11] We therefore decided to prepare the selenium analogues and to compare their reactivity in selenium-mediated asymmetric epoxidation.

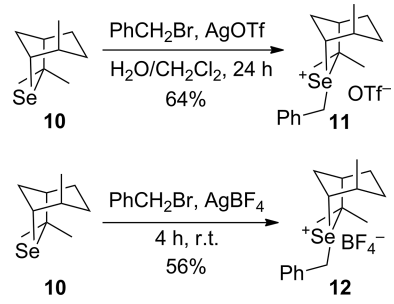
Results and Discussion

The first goal of our investigation was the synthesis of the selenium analogue of isothiocineole **9**. Selenide **10** has been prepared by a methodology similar to that of its sulfur analogue (Scheme 2).[2] The reaction of limonene with selenium in the presence of γ-terpinene at 130 °C gave isoselenocineole **10** with 68% yield.



Scheme 2. Synthesis of isoselenocineole **10**.

Selenide **10** was used for the synthesis of triflane salt **11** by application of Aggarwal's methodology,[2] and tetrafluoroborate salt **12** was prepared by stirring selenide **10** with benzyl bromide in the presence of $AgBF_4$ (Scheme 3). The structure of selenonium salt **12** was confirmed by X-ray analysis (Figure 3). The asymmetric part of the crystal structure (ASU) contains a selenonium cation and a BF_4^- anion. The absolute configuration (1*R*,4*R*,5*R*,6*R*) was determined by the Flack method.[12] A tetrahedral geometry around Se atom was found, with the Se distance between the plane defined by three C atoms being 0.955(3) Å. The observed Se6–C7 and Se6–C12 distances (2.038(5) and 1.956(5) Å), are approximately 0.15–0.2 Å longer than those of S–C bonds in similar compounds as verified with CSD.[13] The C12–Se6–C7 angle was 104.8(2)°, and the C10–C7–Se6–C12 torsion angle was –8.2(5)°. Although the accessible surface of C12 is limited by the C10 methyl, the phenyl ring, as well as a fragment of the terpenyl moiety, electrophilic attack on C12 in the ylide should be easier than for the sulfur analogue.[2]



Scheme 3. Synthesis of selenonium salts **11** and **12**.

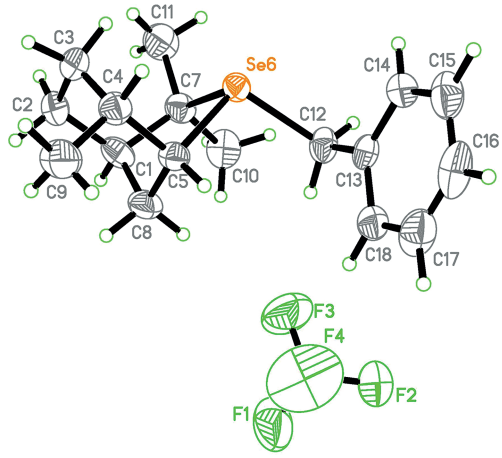
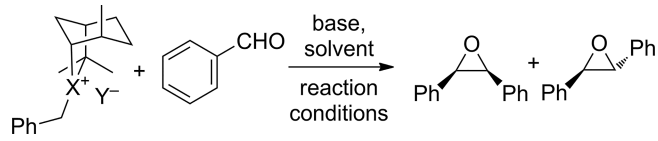


Figure 3. X-ray structure of selenonium salt **12**. The BF_4^- anion reveals significant rotational disorder in the crystal lattice.

Selenonium salts **11** and **12** were used for the asymmetric synthesis of epoxystilbene (Table 1). Aggarwal obtained the triflate sulfonium salt from isothiocineole, benzyl bromide, and AgOTf, and they used it to synthesize *trans*-epoxystilbene with good yield with high diastereoselectivity and enantioselectivity (entry 1).[2] Under the same reaction conditions, triflate selenonium salt **11** gave the product with

Table 1. Asymmetric epoxidation with isothiocineole and isoselenocineole salts.

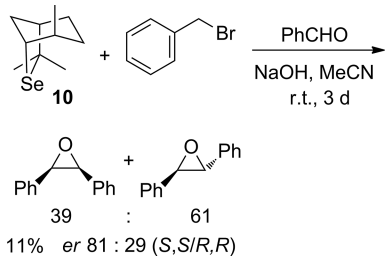


Entry	X	Y^-	Base	Solvent	Reaction conditions	Yield [%]	*cis*/*trans*[a]	*er* (*SS*/*RR*)[b]
1	S	OTf^-	KOH	MeCN/H_2O (9:1)	24 h, 0 °C	77	5:95	99:1
2	Se	OTf^-	KOH	MeCN/H_2O (9:1)	24 h, 0 °C	11	71:29	52:48
3	Se	OTf^-	NaOH	MeCN	3 d, room temp.	31	40:60	84:16
4	Se	BF_4^-	NaOH	MeCN	3 d, room temp.	45	38:62	84:16

[a] Determined on the basis of ^1H NMR spectroscopy. [b] Determined on the basis of HPLC analysis using a Chiralcel Daicel OD-H column.

only 11% yield, and the major product was the *cis*-compound. Lack of enantioselectivity for the *trans* product was observed (entry 2). Under anhydrous conditions, used for sulfur compounds in our previous work (entries 3 and 4),[11] an increase in the diastereoselectivity and enantioselectivity was observed. The best yield was obtained when BF_4^- counteranion was chosen.

We also assessed the use of isoselenocineole **10** for the one-pot synthesis of epoxy stilbene without isolating the selenonium salt (Scheme 4). Similar diastereoselectivity and enantioselectivity were obtained, but a decrease in the yield was observed.



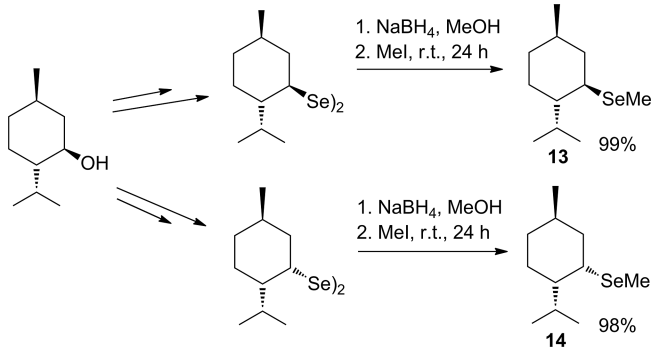
Scheme 4. One-pot synthesis of epoxy stilbene.

In the second step of our investigation, we prepared a series of methyl terpenyl **13**–**19**, benzyl terpenyl **20**, **21**, phenyl terpenyl **22**–**28**, and diterpenyl selenides **29**–**34**. Representative examples of the synthesis of the *p*-menthane group are presented in Scheme 5.

Methyl and benzyl terpenyl selenides were prepared in the reaction of terpenyl selenols with sodium hydride and methyl iodide or benzyl bromide (Scheme 5, Path a, Method a).

Phenyl terpenyl selenides were prepared by using sodium phenyl selenolate with terpenyl tosylates, chlorides, or epoxides (Scheme 5, Path b). Diterpenyl selenides were obtained in the reaction of terpenylsodium selenolates with terpenyl tosylates or in the reaction of sodium diselenide with epoxides (Scheme 5, Path c).

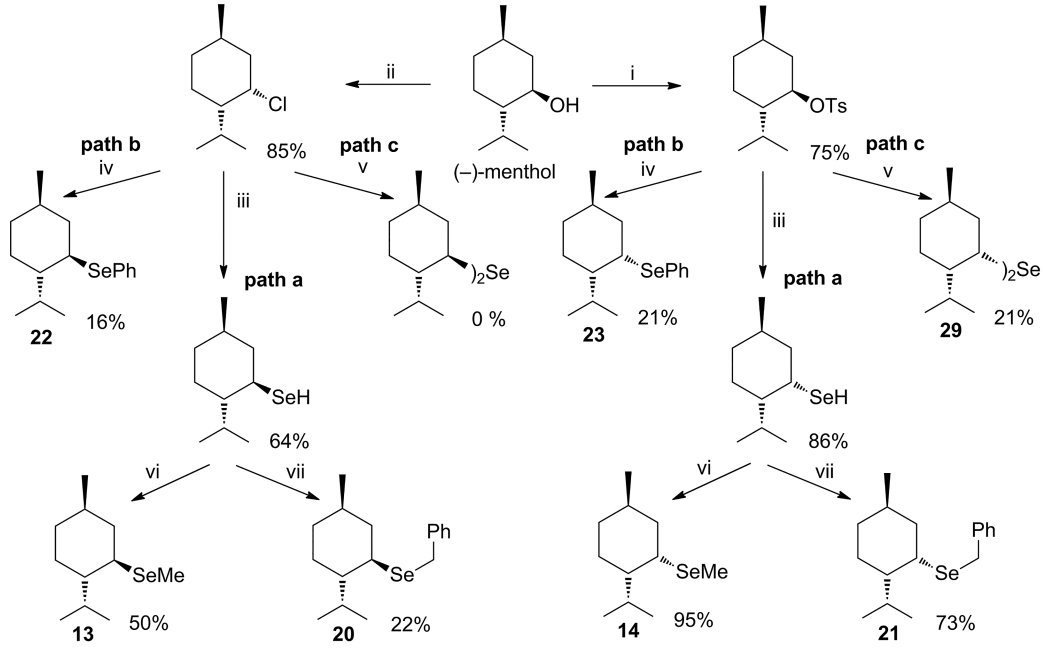
Alternatively, methyl terpenyl selenides were synthesized in the one-pot reaction of diselenides with $NaBH_4$ and methyl iodide (Scheme 6, Method b).



Scheme 6. One-pot synthesis of methyl terpenyl selenides.

Terpenyl tosylates, chlorides, and epoxides have been prepared according to methodologies described in our previous works.[14] Using these paths, we have also prepared selenides from carane and pinane systems (Figure 4).

Encouraged by the asymmetric epoxidation with isoselenocineole salts, we prepared benzyl methyl menthyl and



Reagents and reaction conditions: i) TsCl, Py, 0 °C, 24 h; ii) Ph_3P, CCl_4, reflux, 20 h; iii) 1. Se, NaOH, N_2H_4, DMF, 100 °C, 2 h; 2. $NaBH_4$, MeOH, HCl:H_2O (1:1), 0 °C; iv) Ph_2Se_2, $NaBH_4$, MeOH, 50 °C, 24 h; v) Se, $NaBH_4$, DMF/EtOH, 50 °C, 24 h; vi) NaH, MeI, PE, r.t., 24h; vii) NaH, BnBr, PE, r.t., 3.5 h.

Scheme 5. Synthesis of methyl terpenyl **13**, **14**, benzyl terpenyl **20**, **21**, phenyl terpenyl **22**, **23**, and diterpenyl selenides **29**.

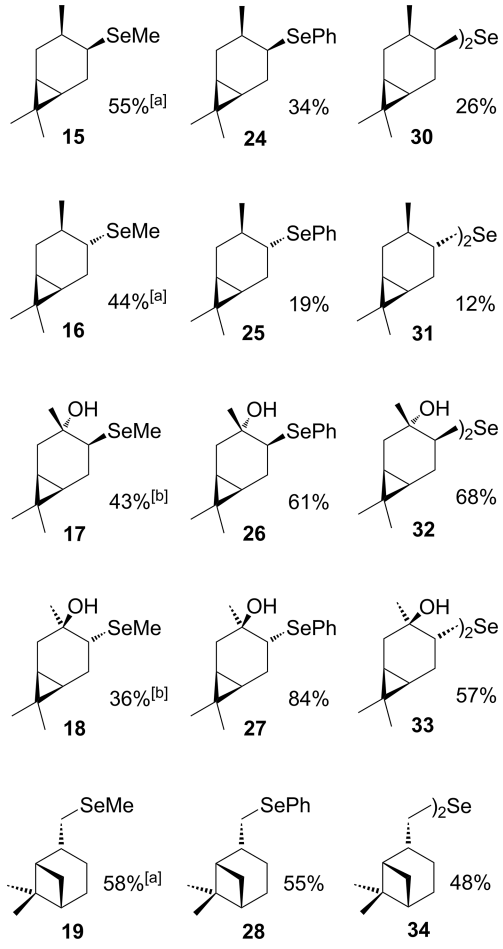
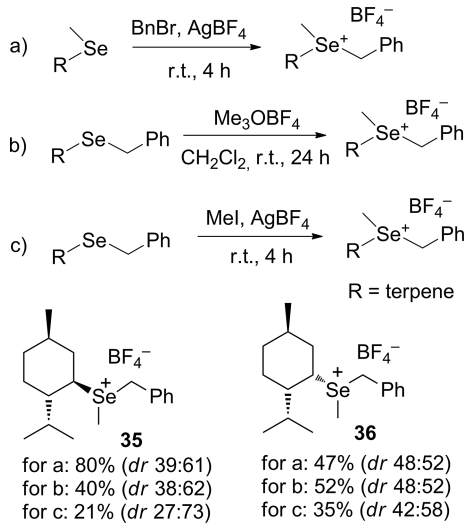


Figure 4. Selenides from carane and pinane groups. [a] Prepared by Method a. [b] Prepared by Method b.

benzyl methyl neomenthyl selenonium salts **35** and **36**. We tested three methodologies for their synthesis: (a) the reaction of methyl menthyl selenide with benzyl bromide in the presence of $AgBF_4$; (b) the reaction of benzyl menthyl selenide with Meerwein's reagent, and (c) the reaction of benzyl menthyl selenide with methyl iodide in the presence of $AgBF_4$. The results are presented in Scheme 7. In the case of **36**, the product was an almost equimolar mixture of two diastereoisomers. The selenonium salt **35** was obtained as an approximate 70:30 mixture of two diastereoisomers. The main diastereoisomer was isolated by column chromatography (silica gel; CH_2Cl_2/MeOH, 90:10). However, attempts at crystallization from CH_2Cl_2/heptane at room temperature led back to the initial mixture.

Selenonium salts **35** and **36** were used for the asymmetric epoxidation by reaction with benzaldehyde and sodium hydroxide (Table 2, entries 1 and 2); however, a lack of diastereoselectivity and enantioselectivity was observed. Significant increase of enantioselectivity was observed when one isolated diastereomer of **35** was used (entry 3).

The use of selenides **13**–**19** and **22**–**34** for the one-pot synthesis of epoxystilbene without isolation of the selenonium salt resulted in higher diastereo- and enantioselectivities (Table 2, entry 3–22). Among methyl terpenyl



Scheme 7. Synthesis of selenonium salts **35** and **36**.

Table 2. Results of the epoxidation reactions.

Entry[a]	Salt/selenide	Yield [%]	Ratio *cis*/*trans*[a]	Ratio *trans* (*SS*/*RR*)[b]
1	**35**	89	45:55	53:47
2	**36**	32	50:50	52:48
3	**35**	85	43:57	77:23
4	**13**	22	55:45	44:56
5	**14**	70	58:42	64:36
6	**15**	8	54:46	58:42
7	**16**	6	70:30	58:42
8	**17**	10	51:49	58:42
9	**18**	12	60:40	65:35
10	**19**	56	54:46	58:42
11	**22**	20	58:42	**11:89**
12	**23**	55	**4:96**	53:47
13	**24**	10	36:64	50:50
14	**25**	12	36:64	30:70
15	**26**	0	–	–
16	**27**	0	–	–
17	**28**	13	38:62	42:58
18	**29**	7	16:84	51:49
19	**30**	10	52:48	59:41
20	**31**	10	33:67	60:40
21	**32**	11	58:42	**13:87**
22	**33**	12	50:50	61:49
23	**34**	40	53:47	45:55

[a] Determined on the basis of ^{1}H NMR spectroscopy. [b] Determined on the basis of HPLC analysis using a Chiralcel Daicel OD-H column.

selenides **13**–**19** (entries 4–10), the best diastereoselectivity was observed for methyl isocaranyl selenide **16** (entry 7). Introduction of a hydroxyl group into this system (selenide **18**) led to an increase in enantioselectivity and gave the best result (entry 9). Similar enantioselectivity was observed for methyl neomenthyl selenide **14** with the dominating *S*,*S*-enantiomer (entry 5).

Interestingly, the epimeric methyl menthyl selenide **13** gave the opposite enantiomer predominantly (Table 2, entry 4). A similar dependence for phenyl neomenthyl **23** and phenyl menthyl selenides **22** was observed (entries 11 and 12). Among all tested compounds, selenide **23** gave the highest diastereoselectivity 96:4 (*trans*/*cis*), whereas selenide

22 gave the best enantioselectivity (11:89). Very high enantioselectivity was also observed for symmetric selenides **32** from the carane group, containing a hydroxyl group (entry 21). For selenides **26** and **27** we could not isolate the product (entries 15 and 16). Comparison of the diastereoselectivity and enantioselectivity of the epoxidation reaction of terpenyl sulfides obtained in our previous work[11] with these terpenyl selenides, reveal that sulfides in general led to high diastereoselectivities but low enantioselectivities, whereas terpenyl selenides gave low to moderate diastereoselectivities but, in some cases, very good enantioselectivities. Introduction of the phenyl group instead of the methyl group led to higher enantioselectivities for both sulfides and selenides.

Conclusions

Convenient methodologies for the synthesis of selenides and selenonium salts derived from *p*-menthane, carane, and pinane groups have been proposed. Both selenides and selenonium salts were successfully used for selenium-mediated asymmetric epoxidation. Comparison of results of epoxidation obtained through the use of cyclic sulfide and selenide – isothiocineole and isoselenocineole, revealed better diastereo- and enantioselectivities for the sulfide. Our results reveal that the nature of the solvent (more polar solvents decrease stereoselectivity of reaction) and counteranion are important factors affecting the yield, diastereoselectivity, and enantioselectivity. Furthermore, the use of selenonium salt with a significant excess of one diastereoisomer resulted in better enantioselectivity of the epoxidation reaction. The use of pure diastereoisomer provided higher enantioselectivity. On the other hand, probable isomerization during the epoxidation can decrease the enantioselectivity of the reaction.

Experimental Section

General: Melting points were measured with a Büchi Tottoli SPM-20 heating unit and are uncorrected. NMR spectra were recorded with a Bruker Avance III (400 MHz) or Bruker Avance III (700 MHz) for ^{1}H and 176.1 MHz or 100.6 MHz for ^{13}C. Chemical shifts are expressed in parts per million (ppm) relative to TMS. ^{77}Se NMR spectra were recorded with a Bruker Avance III/ 400 or Bruker Avance III/ 700 with diphenyl diselenide as an external standard. Elemental analyses were performed with a Vario MACRO CHN analyzer. TLC was conducted on precoated silica gel plates (Merck 60F254) and the spots were visualized under UV light. Column chromatography was carried out with column using Silica Gel 60 Merck (70–230 mesh). All reactions requiring anhydrous conditions were conducted in flame-dried apparatus.

Isoselenocineole (10): Selenium was added to a mixture of limonene (20 mL, 124.0 mmol) and γ-terpinene (19.85 mL, 124.0 mmol), and the reaction mixture was stirred and heated at 130 °C for 8 h. An additional portion of selenium (7.777 g, 99.2 mmol) and γ-terpinene (21.85 mL, 136.0 mmol) was added and the solution was stirred for 16 h at 130 °C. The solution was cooled and the product was isolated by distillation under reduced pressure and purified by distillation (60–62 °C/0.5 Torr), yield 18.268 g (68%); yellow liquid; $[\alpha]_D^{22}$ = +55.51 (*c* = 0.41, $CHCl_3$). ^{1}H NMR (700 MHz, $CDCl_3$): δ = 1.14 (d, *J* = 7.7 Hz, 3 H, CH_3), 1.23 (dq, *J* = 1.4, 14.0 Hz, 1 H), 1.53–1.57 (m, 1 H), 1.58 (s, 3 H, CH_3), 1.64–1.67 (m, 1 H), 1.68 (s, 3 H, CH_3), 1.83 (d, *J* = 2.8 Hz, 1 H), 1.99–2.05 (m, 1 H), 2.15 (dq, *J* = 2.8, 13.3 Hz, 1 H), 2.37 (dt, *J* = 1.4, 12.6 Hz, 1 H), 2.43–2.50 (m, 1 H), 3.72 (s, 1 H) ppm. ^{13}C NMR (100.6, $CDCl_3$): δ = 18.7 (CH_3), 23.7 (CH_2), 24.5 (CH_2), 27.0 (CH_3), 35.4 (CH), 35.6 (CH_3), 36.1 (CH_2), 48.8 (CH), 49.9 (CH), 50.2 (C) ppm. ^{77}Se NMR (76.3 MHz, $CDCl_3$): δ = 481.70 ppm. IR (film): $\tilde{\nu}$ = 2937, 1457, 1379, 1130, 1083, 1037 cm^{-1}. $C_{10}H_{18}Se$ (217.21): calcd. C 55.30, H 8.35; found C 55.54, H 8.27.

Synthesis of Methyl Terpenyl Selenides; General Procedure (Method a): A solution of selenol (2.5 mmol) in anhydrous petroleum ether (5 mL) was carefully added to a suspension of NaH (0.121 g, 5.0 mmol) in anhydrous petroleum ether (5 mL). The mixture was kept for 0.5 h at ambient temperature under an argon atmosphere. Methyl iodide (160 μL, 2.6 mmol) was added and the mixture was stirred for 24 h, then poured into water (75 mL) and extracted with diethyl ether (3 × 50 mL). The combined ethereal layers were dried with anhydrous $MgSO_4$, and the solvent was evaporated. A crude product was purified by the column chromatography (petroleum ether) to give the pure methyl terpenyl selenide.

Method b: $NaBH_4$ (0.40 g, 10.7 mmol) was carefully added to the diselenide (1.64 mmol) in methanol (15 mL) under an argon atmosphere. Methyl iodide (1.15 g, 8.1 mmol) was added and the mixture was stirred for 24 h. The solution was poured into water (8 mL) and extracted with diethyl ether (3 × 5 mL). The combined ethereal layers were dried with anhydrous $MgSO_4$, and the solvent was evaporated. The crude product was purified by column chromatography to give pure methyl terpenyl selenide.

(1*R*,2*S*,5*R*)-(–)-Menthyl Methyl Selenide (13): Purification by column chromatography on silica gel (PE), yield 0.292 g (50%; Method a), 0.756 g (99%, Method b); yellow liquid; $[\alpha]_D^{26}$ = –72.26 (*c* = 0.91, $CHCl_3$). ^{1}H NMR (700 MHz, $CDCl_3$): δ = 0.75 (d, *J* = 6.3 Hz, 3 H, CH_3), 0.88 (d, *J* = 6.3 Hz, 3 H, CH_3), 0.90 (d, *J* = 7.0 Hz, 3 H, CH_3), 1.03 (ddd, *J* = 3.5, 12.6, 21.7 Hz, 1 H), 1.18–1.28 (m, 2 H), 1.33–1.41 (m, 1 H), 1.69 (dq, *J* = 3.5, 13.3 Hz, 1 H), 1.72–1.76 (m, 1 H), 1.91 (s, 3 H, CH_3), 2.16 (dq, *J* = 2.1, 12.6 Hz, 1 H), 2.27–2.32 (m, 1 H), 2.67 (dt, *J* = 4.2, 11.9 Hz, 1 H) ppm. ^{13}C NMR (176.1, $CDCl_3$): δ = 2.7 (CH_3), 16.5 (CH_3), 22.9 (CH_3), 23.6 (CH_3), 26.2 (CH_2), 30.3 (CH), 35.6 (CH), 36.2 (CH_2), 44.6 (CH), 45.6 (CH_2), 48.7 (CH) ppm. ^{77}Se NMR (76.3 MHz, $CDCl_3$): δ = 148.76 ppm. IR (film): $\tilde{\nu}$ = 2925, 1455, 1385, 1368, 1180, 897 cm^{-1}. $C_{11}H_{22}Se$ (233.25): calcd. C 56.64, H 9.51; found C 56.38, H 9.58.

(1*S*,2*S*,5*R*)-(+)-Methyl Neomenthyl Selenide (14): Purification by the column chromatography on silica gel (PE), yield 0.554 g (95%; Method a), 0.749 g (98%; Method b); yellow liquid; $[\alpha]_D^{23}$ = +94.47 (*c* = 0.48, $CHCl_3$). ^{1}H NMR (700 MHz, $CDCl_3$): δ = 0.89 (d, *J* = 7.0 Hz, 3 H, CH_3), 0.91 (d, *J* = 6.3 Hz, 3 H, CH_3), 0.94 (d, *J* = 6.3 Hz, 3 H, CH_3), 1.05–1.12 (m, 1 H), 1.30 (ddd, *J* = 2.8, 11.2, 13.3 Hz, 1 H), 1.56–1.62 (m, 1 H), 1.70–1.76 (m, 2 H), 1.85–1.94 (m, 1 H), 1.95 (s, 3 H, CH_3), 2.00 (dq, *J* = 2.1, 13.3 Hz, 1 H), 3.26 (t, *J* = 2.5 Hz, 1 H) ppm. ^{13}C NMR (176.1, $CDCl_3$): δ = 5.4 (CH_3), 22.2 (CH_3), 22.4 (CH_3), 23.5 (CH_3), 28.3 (CH_2), 29.1 (CH), 32.7 (CH), 36.7 (CH_2), 42.7 (CH_2), 48.2 (CH), 50.8 (CH) ppm. ^{77}Se NMR (76.3 MHz, $CDCl_3$): δ = 64.67 ppm. IR (film): $\tilde{\nu}$ = 2920, 1474, 1455, 1383, 1272, 1230, 1184, 891 cm^{-1}. $C_{11}H_{22}Se$ (233.25): calcd. C 56.64, H 9.51; found C 56.88, H 9.47.

(1*S*,3*R*,4*S*,6*R*)-(+)-4-Caranyl Methyl Selenide (15): Purification by the column chromatography on silica gel (PE), yield 0.318 g (55%;

Method a); yellow liquid; $[\alpha]_D^{23}$ = +18.78 (*c* = 1.45, $CHCl_3$). ^1H NMR (700 MHz, $CDCl_3$): δ = 0.55 (ddd, *J* = 5.6, 8.4, 8.4 Hz, 1 H), 0.65 (ddd, *J* = 6.3, 8.4, 8.4 Hz, 1 H), 0.80–0.86 (m, 1 H), 0.93 (d, *J* = 7.0 Hz, 3 H, CH_3), 0.96 (s, 3 H, CH_3), 0.97 (s, 3 H, CH_3), 1.41 (ddd, *J* = 6.3, 8.4, 14.7 Hz, 1 H), 1.78–1.88 (m, 2 H), 1.94 (s, 3 H, CH_3), 2.26 (ddd, *J* = 7.0, 9.1, 15.4 Hz, 1 H), 3.03 (q, *J* = 8.4 Hz, 1 H) ppm. ^{13}C NMR (176.1, $CDCl_3$): δ = 6.0 (CH_3), 17.2 (CH_3), 19.0 (C), 21.5 (CH_3), 22.8 (CH), 22.8 (CH), 27.0 (CH_2), 29.9 (CH_3), 31.1 (CH_2), 32.6 (CH), 45.5 (CH) ppm. ^{77}Se NMR (76.3 MHz, $CDCl_3$): δ = 123.66 ppm. IR (film): $\tilde{\nu}$ = 2924, 2863, 1455, 1375, 1273, 1195, 1129, 898 cm^{-1}. $C_{11}H_{20}Se$ (231.24): calcd. C 57.14, H 8.72; found C 57.51, H 8.61.

(1*S*,3*R*,4*R*,6*R*)-(+)-4-Isocaranyl Methyl Selenide (16): Purification by the column chromatography on silica gel (PE), yield 0.254 g (44%; Method a); yellow liquid; $[\alpha]_D^{23}$ = –60.48 (*c* = 1.45, $CHCl_3$). ^1H NMR (700 MHz, $CDCl_3$): δ = 0.57 (ddd, *J* = 2.1, 8.4, 9.8 Hz, 1 H), 0.75 (ddd, *J* = 4.9, 9.8, 9.8 Hz, 1 H), 0.83 (ddd, *J* = 5.6, 11.9, 14.7 Hz, 1 H), 0.95 (s, 3 H, CH_3), 0.96 (s, 3 H, CH_3), 1.00 (d, *J* = 7.0 Hz, 3 H, CH_3), 1.29–1.37 (m, 1 H), 1.92 (s, 3 H, CH_3), 1.97–2.02 (m, 2 H), 2.15 (ddd, *J* = 1.4, 6.3, 14.7 Hz, 1 H), 2.24 (dt, *J* = 6.3, 10.5 Hz, 1 H) ppm. ^{13}C NMR (176.1, $CDCl_3$): δ = 2.2 (CH_3), 15.6 (CH_3), 17.5 (C), 20.6 (CH), 20.7 (CH), 21.6 (CH_3), 28.9 (CH_3), 29.2 (CH_2), 29.4 (CH_2), 34.5 (CH), 44.5 (CH) ppm. ^{77}Se NMR (76.3 MHz, $CDCl_3$): δ = 175.85 ppm. IR (film): $\tilde{\nu}$ = 2924, 2864, 1455, 1375, 898 cm^{-1}. $C_{11}H_{20}Se$ (231.24): calcd. C 57.14, H 8.72; found C 56.92, H 8.77.

(1*S*,3*R*)-(–)-*trans*-3-Hydroxy-4-caranyl Methyl Selenide (17): Purification by the column chromatography on silica gel (dichloromethane/ethyl acetate, 80:20), yield 0.292 g (36%; Method b); yellow liquid; $[\alpha]_D^{20}$ = –70.80 (*c* = 1.50, $CHCl_3$). ^1H NMR (700 MHz, $CDCl_3$): δ = 0.53 (t, *J* = 9.1 Hz, 1 H), 0.77 (ddd, *J* = 4.9, 9.1, 9.8 Hz, 1 H), 0.95 (s, 3 H, CH_3), 0.98 (s, 3 H, CH_3), 1.19 (s, 3 H, CH_3), 1.27 (ddd, *J* = 1.4, 4.9, 14.7 Hz, 1 H), 2.00 (s, 3 H, CH_3), 2.01–2.09 (m, 2 H), 2.28 (dd, *J* = 7.7, 15.4 Hz, 1 H), 2.53 (dd, *J* = 7.0, 12.6 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 5.5 (CH_3), 15.3 (CH_3), 17.7 (C), 20.3 (CH), 20.5 (CH), 23.1 (CH_3), 28.8 (CH_3), 29.0 (CH_2), 33.4 (CH_2), 53.7 (CH), 71.9 (C) ppm. ^{77}Se NMR (76.3 MHz, $CDCl_3$): δ = 91.07 ppm. IR (film): $\tilde{\nu}$ = 3391, 2925, 2349, 1454, 1372, 1130, 922 cm^{-1}. $C_{11}H_{20}OSe$ (247.24): calcd. C 53.44, H 8.15; found C 53.38, H 8.23.

(1*S*,3*S*)-(+)-*cis*-3-Hydroxy-4-isocaranyl Methyl Selenide (18): Purification by the column chromatography on silica gel (dichloromethane/ethyl acetate, 95:5), yield 0.349 g (43%; Method b); yellow liquid; $[\alpha]_D^{22}$ = +57.10 (*c* = 1.41, $CHCl_3$). ^1H NMR (700 MHz, $CDCl_3$): δ = 0.67–0.77 (m, 2 H), 0.94 (s, 3 H, CH_3), 0.97 (s, 3 H, CH_3), 1.22 (s, 3 H, CH_3), 1.28 (dd, *J* = 7.0, 16.1 Hz, 1 H), 1.94 (dd, *J* = 8.4, 15.4 Hz, 1 H), 1.98 (s, 3 H, CH_3), 2.29 (ddd, *J* = 5.6, 8.4, 14.7 Hz, 2 H), 2.85 (q, *J* = 5.6 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 6.4 (CH_3), 16.8 (CH_3), 19.9 (CH), 20.0 (C), 24.3 (CH), 27.7 (CH_2), 29.6 (CH_3), 29.7 (CH_3), 34.1 (CH_2), 52.2 (CH), 74.1 (C) ppm. ^{77}Se NMR (76.3 MHz, $CDCl_3$): δ = 124.66 ppm. IR (film): $\tilde{\nu}$ = 3429, 2926, 2864, 2359, 1456, 1375, 1131, 919 cm^{-1}. $C_{11}H_{20}OSe$ (247.24): calcd. C 53.44, H 8.15; found C 53.51, H 8.13.

(1*S*,2*R*,5*S*)-(–)-Methyl Myrtanyl Selenide (19): Purification by the column chromatography on silica gel (PE), yield 0.335 g (58%; Method a); yellow liquid; $[\alpha]_D^{25}$ = –36.01 (*c* = 1.55, $CHCl_3$). ^1H NMR (700 MHz, $CDCl_3$): δ = 0.87 (d, *J* = 9.8 Hz, 1 H, CH), 0.98 (s, 3 H, CH_3), 1.17 (s, 3 H, CH_3), 1.47–1.52 (m, 1 H), 1.81–1.86 (m, 1 H), 1.86–1.89 (m, 1 H), 1.90–1.94 (m, 1 H), 1.94 (s, 3 H, CH_3), 1.99–2.04 (m, 2 H), 2.22–2.27 (m, 1 H), 2.31–2.35 (m, 1 H), 2.62 (ddd, *J* = 7.7, 11.9, 26.6 Hz, 2 H) ppm. ^{13}C NMR (176.1, $CDCl_3$): δ = 4.1 (CH_3), 23.0 (CH_2), 23.3 (CH_3), 26.2 (CH_2), 28.0 (CH_3), 33.4 (CH_2), 33.7 (CH_2), 38.6 (C), 41.3 (CH), 41.6 (CH), 46.3 (CH) ppm. ^{77}Se NMR (133.6 MHz, $CDCl_3$): δ = 62.23 ppm. IR (film): $\tilde{\nu}$ = 2919, 1467, 1422, 1383, 1366, 1274, 1210 cm^{-1}. $C_{11}H_{20}Se$ (231.24): calcd. C 57.14, H 8.72; found C 57.37, H 8.65.

Synthesis of Benzyl Terpenyl Selenides; General Procedure: A solution of selenol (4.6 mmol) in anhydrous petroleum ether (3 mL) was carefully added to a suspension of NaH (0.250 g, 10.4 mmol) in anhydrous petroleum ether (3 mL). The mixture was kept for 0.5 h at ambient temperature under an argon atmosphere. Benzyl bromide (0.750 g, 4.4 mmol) was added and the mixture was stirred for 3 h. The solution was poured into water (30 mL) and extracted with diethyl ether (3 × 30 mL). The combined ethereal layers were dried with anhydrous $MgSO_4$, and the solvent was evaporated. A crude product was purified by the column chromatography to give pure benzyl terpenyl selenide.

(1*R*,2*S*,5*R*)-(–)-Benzyl Menthyl Selenide (20): Purification by the column chromatography on silica gel (PE/EtOAc, 90:10), yield 0.299 g (22%); yellow liquid; $[\alpha]_D^{25}$ = –69.52 (*c* = 1.66, $CHCl_3$). ^1H NMR (700 MHz, $CDCl_3$): δ = 0.66 (d, *J* = 6.8 Hz, 3 H, CH_3), 0.89 (d, *J* = 7.2 Hz, 3 H, CH_3), 0.92 (d, *J* = 6.4 Hz, 3 H, CH_3), 1.23–1.33 (m, 3 H), 1.33–1.41 (m, 2 H), 1.67–1.79 (m, 2 H), 2.24 (dq, *J* = 2.0, 9.2 Hz, 1 H), 2.27–2.36 (m, 1 H), 2.71 (ddd, *J* = 4.0, 12.0, 12.0 Hz, 1 H), 3.82 (s, 2 H, CH_2), 7.18–7.24 (m, 1 H, ArH), 7.27–7.36 (m, 4 H, ArH) ppm. ^{13}C NMR (176.1, $CDCl_3$): δ = 15.0 (CH_3), 21.5 (CH_3), 22.3 (CH_3), 25.0 (CH_2), 25.5 (CH_2), 29.0 (CH), 34.3 (CH), 34.9 (CH_2), 44.0 (CH), 45.2 (CH_2), 47.5 (CH), 126.5 (CH_{Ar}), 128.4 (2 × CH_{Ar}), 129.0 (2 × CH_{Ar}), 140.0 (C_{Ar}) ppm. ^{77}Se NMR (133.5 MHz, $CDCl_3$): δ = 519.33 ppm. IR (film): $\tilde{\nu}$ = 2929, 1676, 1487, 1455, 1246, 1181, 1022, 736 cm^{-1}. $C_{17}H_{26}Se$ (309.35): calcd. C 66.00, H 8.47; found C 66.17, H 8.40.

(1*S*,2*S*,5*R*)-(+)-Benzyl Neomenthyl Selenide (21): Purification by the column chromatography on silica gel (PE/EtOAc, 90:10), yield 1.010 g (73%); yellow liquid; $[\alpha]_D^{23}$ = +114.51 (*c* = 0.55, $CHCl_3$). ^1H NMR (700 MHz, $CDCl_3$): δ = 0.72 (d, *J* = 7.0 Hz, 3 H, CH_3), 0.87 (d, *J* = 6.3 Hz, 3 H, CH_3), 0.89 (d, *J* = 6.3 Hz, 3 H, CH_3), 1.01–1.05 (m, 1 H), 1.26–1.32 (m, 2 H), 1.52–1.57 (m, 1 H), 1.70–1.77 (m, 2 H), 1.90–1.95 (m, 2 H), 3.27 (t, *J* = 2.1 Hz, 1 H), 3.73 (d, *J* = 11.9 Hz, 1 H), 3.78 (d, *J* = 11.9 Hz, 1 H), 7.17–7.20 (m, 1 H, ArH), 7.22–7.28 (m, 2 H, ArH), 7.28–7.33 (m, 2 H, ArH) ppm. ^{13}C NMR (176.1, $CDCl_3$): δ = 20.6 (CH_3), 21.2 (CH_3), 22.4 (CH_3), 27.0 (CH_2), 27.6 (CH), 28.1 (CH_2), 31.3 (CH), 35.5 (CH_2), 42.0 (CH_2), 45.3 (CH), 49.6 (CH), 126.7 (CH_{Ar}),128.5 (2 × CH_{Ar}), 129.1 (2 × CH_{Ar}), 140.0 (C_{Ar}) ppm. ^{77}Se NMR (76.3 MHz, $CDCl_3$): δ = 243.07 ppm. IR (film): $\tilde{\nu}$ = 3070, 2933, 1576, 1465, 1448, 1376, 1234, 1022, 856, 739 cm^{-1}. $C_{17}H_{26}Se$ (309.35): calcd. C 66.00, H 8.47; found C 66.15, H 8.41.

Synthesis of Phenyl Terpenyl Selenides; General Procedure: $NaBH_4$ (0.3 g, 8.0 mmol) was carefully added to a solution of diphenyl diselenide (0.605 g, 1.9 mmol) in methanol (30 mL) under an argon atmosphere. Tosylate (3.9 mmol) in methanol (20 mL) was added and the mixture was stirred for 24 h at 50 °C. Methanol was evaporated, water (100 mL) was added, and the product was extracted with petroleum ether (3 × 100 mL). The combined ethereal layers were dried with anhydrous $MgSO_4$, and the solvent was evaporated. A crude product was purified by column chromatography (petroleum ether) to give pure phenyl terpenyl selenide.

(1*R*,2*S*,5*R*)-(–)-Menthyl Phenyl Selenide (22): Purification by column chromatography on silica gel (PE), yield 0.067 g (6%); yellow liquid; $[\alpha]_D^{25}$ = –62.59 (*c* = 0.95, $CHCl_3$). ^1H NMR (700 MHz, $CDCl_3$): δ = 0.80 (d, *J* = 6.3 Hz, 3 H, CH_3), 0.85 (d, *J* = 6.3 Hz, 3 H, CH_3), 0.88–0.94 (m, 1 H), 0.95 (d, *J* = 7.0 Hz, 3 H, CH_3), 1.06–1.12 (m, 1 H), 1.25–1.37 (m, 3 H), 1.72–1.78 (m, 2 H), 2.10 (dq, *J*

= 2.1, 13.3 Hz, 1 H), 2.41–2.49 (m, 1 H), 3.10 (dt, *J* = 7.0, 11.9 Hz, 1 H), 7.28–7.32 (m, 3 H, ArH), 7.57–7.61 (m, 2 H, ArH) ppm. ^{13}C NMR (176.1 MHz, $CDCl_3$): δ = 16.1 (CH_3), 22.4 (CH_3), 23.1 (CH_3), 26.0 (CH_2), 30.1 (CH), 35.3 (CH), 35.7 (CH_2), 45.9 (CH_2), 48.7 (CH), 49.4 (CH), 128.3 (CH_{Ar}), 129.8 (2 × CH_{Ar}), 130.0 (C_{Ar}), 136.5 (2 × CH_{Ar}) ppm. ^{77}Se NMR (76.3 MHz, $CDCl_3$): δ = 377.33 ppm. IR (film): $\tilde{\nu}$ = 2925, 1653, 1540, 1507, 1457, 1178, 1022, 735 cm^{-1}. $C_{16}H_{24}Se$ (295.32): calcd. C 65.07, H 8.19; found C 64.91, H 8.25.

(1*S*,2*S*,5*R*)-(+)-Neomenthyl Phenyl Selenide (23): Purification by the column chromatography on silica gel (PE), yield 0.236 g (21%); yellow liquid; $[\alpha]_D^{25}$ = +100.04 (*c* = 0.65, $CHCl_3$). ^{1}H NMR (700 MHz, $CDCl_3$): δ = 0.85 (d, *J* = 7.0 Hz, 3 H, CH_3), 0.87 (d, *J* = 7.0 Hz, 3 H, CH_3), 0.87–0.90 (m, 1 H), 0.91 (d, *J* = 7.0 Hz, 3 H, CH_3), 0.99–1.02 (m, 1 H), 1.12 (ddd, *J* = 3.5, 12.6, 25.2 Hz, 1 H), 1.30 (ddd, *J* = 3.5, 12.6, 14.7 Hz, 1 H), 1.63–1.69 (m, 1 H), 1.73–1.77 (m, 1 H), 1.77–1.81 (m, 1 H), 1.94–1.99 (m, 2 H), 3.69 (t, *J* = 2.8 Hz, 1 H), 7.21–7.24 (m, 3 H, ArH), 7.53–7.54 (m, 2 H, ArH) ppm. ^{13}C NMR (176.1, $CDCl_3$): δ = 20.7 (CH_3), 21.0 (CH_3), 22.1 (CH_3), 27.2 (CH_2), 27.8 (CH), 31.4 (CH), 35.3 (CH_2), 41.9 (CH_2), 49.6 (CH), 50.5 (CH), 126.9 (CH_{Ar}),128.9 (2 × CH_{Ar}), 130.8 (C_{Ar}), 134.2 (2 × CH_{Ar}) ppm. ^{77}Se NMR (133.5 MHz, $CDCl_3$): δ = 288.89 ppm. IR (film): $\tilde{\nu}$ = 3071, 2922, 1580, 1476, 1455, 1384, 1278, 1230, 1182, 1022, 857, 738 cm^{-1}. $C_{16}H_{24}Se$ (295.32): calcd. C 65.07, H 8.19; found C 65.28, H 8.05.

(1*S*,3*R*,4*S*,6*R*)-(+)-4-Caranyl Phenyl Selenide (24): Purification by the column chromatography on silica gel (PE), yield 0.379 g (34%); yellow liquid; $[\alpha]_D^{23}$ = +49.09 (*c* = 1.65, $CHCl_3$). ^{1}H NMR (700 MHz, $CDCl_3$): δ = 0.55 (ddd, *J* = 6.3, 9.1, 9.1 Hz, 1 H), 0.67 (ddd, *J* = 7.0, 9.1, 9.1 Hz, 1 H), 0.89 (ddd, *J* = 7.0, 9.8, 14.7 Hz, 1 H), 0.97 (s, 3 H, CH_3), 0.98 (d, *J* = 7.0 Hz, 3 H, CH_3), 1.02 (s, 3 H, CH_3), 1.50 (ddd, *J* = 6.3, 8.4, 15.4 Hz, 1 H), 1.87 (ddd, *J* = 5.6, 8.4, 14.7 Hz, 1 H), 1.95–1.99 (m, 1 H), 2.22 (ddd, *J* = 7.0, 9.1, 15.4 Hz, 1 H), 3.58 (dt, *J* = 6.3, 8.4 Hz, 1 H), 7.23–7.26 (m, 3 H, ArH), 7.52–7.55 (m, 2 H, ArH) ppm. ^{13}C NMR (176.1, $CDCl_3$): δ = 15.9 (CH_3), 17.8 (C), 20.4 (CH_3), 21.3 (CH), 21.6 (CH), 25.7 (CH_2), 26.0 (CH_2), 28.5 (CH_3), 31.0 (CH), 47.2 (CH), 126.8 (CH_{Ar}), 128.9 (2 × CH_{Ar}), 131.2 (C_{Ar}), 133.8 (2 × CH_{Ar}) ppm. ^{77}Se NMR (76.3 MHz, $CDCl_3$): δ = 343.72 ppm. IR (film): $\tilde{\nu}$ = 3070, 2925, 2863, 1579, 1477, 1454, 1437, 1376, 1023, 738 cm^{-1}. $C_{16}H_{22}Se$ (293.31): calcd. C 65.52, H 7.56; found C 65.78, H 7.50.

(1*S*,3*R*,4*R*,6*R*)-(+)-4-Isocaranyl Phenyl Selenide (25): Purification by the column chromatography on silica gel (PE), yield 0.212 g (19%); yellow liquid; $[\alpha]_D^{20}$ = –102.72 (*c* = 0.69, $CHCl_3$). ^{1}H NMR (700 MHz, $CDCl_3$): δ = 0.55–0.58 (m, 1 H), 0.74 (ddd, *J* = 4.9, 9.1, 9.1 Hz, 1 H), 0.85 (ddd, *J* = 5.6, 12.6, 15.4 Hz, 1 H), 0.95 (s, 6 H, 2 × CH_3), 1.03 (d, *J* = 6.3 Hz, 3 H), 1.40–1.47 (m, 1 H), 1.98–2.04 (m, 3 H), 2.75 (dt, *J* = 7.7, 10.5 Hz, 1 H), 7.24–7.27 (m, 3 H, ArH), 7.52–7.55 (m, 2 H, ArH) ppm. ^{13}C NMR (176.1, $CDCl_3$): δ = 15.6 (CH_3), 17.5 (C), 20.6 (CH), 20.7 (CH), 21.8 (CH_3), 28.8 (CH_3), 29.3 (CH_2), 29.5 (CH_2), 34.7 (CH), 49.1 (CH), 127.2 (CH_{Ar}), 128.8 (2 × CH_{Ar}), 129.7 (C_{Ar}), 134.9 (2 × CH_{Ar}) ppm. ^{77}Se NMR (76.3 MHz, $CDCl_3$): δ = 397.57 ppm. IR (film): $\tilde{\nu}$ = 3070, 2923, 1579, 1476, 1437, 1375, 1022, 738 cm^{-1}. $C_{16}H_{22}Se$ (293.31): calcd. C 65.52, H 7.56; found C 65.40, H 7.64.

(1*S*,3*S*)-(+)-(*trans*)-3-Hydroxy-4-caranyl Phenyl Selenide (26): Purification by the column chromatography on silica gel (PE), yield 1.010 g (86%); yellow liquid; $[\alpha]_D^{20}$ = +82.86 (*c* = 0.85, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.73–0.79 (m, 2 H), 1.02 (s, 6 H, 2 × CH_3), 1.32 (s, 3 H, CH_3), 1.33–1.40 (m, 2 H), 2.00–2.09 (m, 1 H), 2.27–2.36 (m, 2 H), 3.42 (dd, *J* = 5.6, 10.4 Hz, 1 H), 7.27–7.30 (m, 3 H, ArH), 7.57–7.62 (m, 2 H, ArH) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 15.4 (CH_3), 18.3 (CH), 18.8 (C), 22.8 (CH), 26.6 (CH_2), 28.3 (CH_3), 28.6 (CH_3), 33.0 (CH_2), 54.2 (CH), 72.7 (CH), 127.3 (CH_{Ar}), 129.1 (2 × CH_{Ar}), 130.3 (C_{Ar}), 134.0 (2 × CH_{Ar}) ppm. ^{77}Se NMR (76.3 MHz, $CDCl_3$): δ = 342.42 (Se) ppm. IR (film): $\tilde{\nu}$ = 3435, 2942, 2346, 1579, 1477, 1437, 1375, 1130, 920, 870, 836 cm^{-1}. $C_{16}H_{22}OSe$ (309.31): calcd. C 62.13, H 7.17; found C 62.34, H 7.11.

(1*S*,3*R*)-(–)-(*cis*)-3-Hydroxy-4-isocaranyl Phenyl Selenide (27): Purification by the column chromatography on silica gel (PE), yield 0.693 g (59%); yellow liquid; $[\alpha]_D^{20}$ = –80.96 (*c* = 0.52, $CHCl_3$). ^{1}H NMR (700 MHz, $CDCl_3$): δ = 0.63 (t, *J* = 8.4 Hz, 1 H), 0.85 (ddd, *J* = 4.9, 9.8, 9.8 Hz, 1 H), 1.00 (s, 3 H, CH_3), 1.01 (s, 3 H, CH_3), 1.32 (s, 3 H, CH_3), 1.38 (ddd, *J* = 4.2, 4.9, 13.3 Hz, 1 H), 2.17 (dd, *J* = 10.5, 14.7 Hz, 1 H), 2.25 (ddd, *J* = 4.9, 6.3, 14.7 Hz, 1 H), 2.42 (dd, *J* = 7.0, 14.7 Hz, 1 H), 3.08 (dd, *J* = 7.7, 12.6 Hz, 1 H), 7.27–7.30 (m, 3 H, ArH), 7.58–7.60 (m, 2 H, ArH) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 16.4 (CH_3), 18.8 (C), 21.4 (CH), 21.7 (CH), 24.5 (CH_3), 29.7 (CH_3), 30.9 (CH_2), 34.5 (CH_2), 59.0 (CH), 72.7 (CH), 128.3 (CH_{Ar}), 130.2 (2 × CH_{Ar}), 131.3 (C_{Ar}), 134.6 (2 × CH_{Ar}) ppm. ^{77}Se NMR (76.3 MHz, $CDCl_3$): δ = 316.10 (Se) ppm. IR (film): $\tilde{\nu}$ = 3448, 2937, 2864, 2346, 1578, 1477, 1438, 1375, 1217, 1114, 927, 756 cm^{-1}. $C_{16}H_{22}OSe$ (309.31): calcd. C 62.13, H 7.17; found C 61.97, H 7.20.

(1*S*,2*R*,5*S*)-(–)-Myrtanyl Phenyl Selenide (28): Purification by the column chromatography on silica gel (PE), yield 0.613 g (55%); yellow liquid; $[\alpha]_D^{23}$ = –40.69 (*c* = 1.76, $CHCl_3$). ^{1}H NMR (700 MHz, $CDCl_3$): δ = 0.86 (d, *J* = 9.8 Hz, 1 H), 1.00 (s, 3 H, CH_3), 1.16 (s, 3 H, CH_3), 1.52–1.58 (m, 1 H), 1.81–1.93 (m, 3 H), 2.01–2.07 (m, 1 H), 2.28–2.34 (m, 2 H), 2.98 (dd, *J* = 8.4, 11.9 Hz, 1 H), 3.05 (dd, *J* = 7.0, 11.9 Hz, 1 H), 7.19–7.21 (m, 1 H, ArH), 7.22–7.25 (m, 2 H, ArH), 7.45–7.48 (m, 2 H, ArH) ppm. ^{13}C NMR (176.1, $CDCl_3$): δ = 23.0 (CH_2), 23.3 (CH_3), 26.2 (CH_2), 28.0 (CH_3), 33.4 (CH_2), 35.9 (CH_2), 38.7 (C), 41.3 (CH), 41.5 (CH), 46.3 (CH), 126.5 (CH_{Ar}), 129.0 (2 × CH_{Ar}), 131.0 (C_{Ar}), 132.4 (2 × CH_{Ar}) ppm. ^{77}Se NMR (133.5 MHz, $CDCl_3$): δ = 276.17 ppm. IR (film): $\tilde{\nu}$ = 2918, 1580, 1477, 1437, 1382, 1023, 733 cm^{-1}. $C_{16}H_{22}Se$ (293.31): calcd. C 65.52, H 7.56; found C 65.36, H 7.62.

Synthesis of Diterpene Selenides; General Procedure: To a mixture of $NaBH_4$ (0.132 g, 3.5 mmol) and selenium (0.131 g, 1.7 mmol), anhydrous ethanol (5 mL) was carefully added at ambient temperature under an argon atmosphere. Anhydrous DMF (5 mL) was added and the mixture was warmed to 60 °C for 10 min. The dark brownish solution was decolorized, the reaction mixture was then cooled to ca. 20 °C and tosylate (3.3 mmol) in DMF (2 mL) was added. The reaction mixture was stirred and kept at 50 °C for 3 d. The solution was poured into water (100 mL) and extracted with petroleum ether (3× 75 mL). The combined ethereal layers were washed with water (50 mL), brine (50 mL), dried with anhydrous $MgSO_4$, and the solvent was evaporated. The crude product was purified by the column chromatography (petroleum ether) to give pure diterpene selenide.

(1*S*,2*S*,5*R*)-(+)-Dineomenthyl Selenide (29): Purification by column chromatography on silica gel (PE), yield 0.123 g (21%); yellow liquid; $[\alpha]_D^{24}$ = +106.96 (*c* = 0.48, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (d, *J* = 6.4 Hz, 6 H, 2 × CH_3), 0.92 (d, *J* = 6.8 Hz, 6 H, 2 × CH_3), 0.94 (d, *J* = 6.8 Hz, 6 H, 2 × CH_3), 0.95–1.00 (m, 4 H), 1.07–1.17 (m, 2 H), 1.23–1.31 (m, 2 H), 1.61–1.70 (m, 2 H), 1.70–1.78 (m, 4 H), 1.99 (dq, *J* = 2.4, 13.6 Hz, 2 H), 2.02–2.12 (m, 2 H), 3.28 (t, *J* = 2.8 Hz, 2 H) ppm. ^{13}C NMR (100.6, $CDCl_3$): δ = 20.4 (2 × CH_3), 21.1 (2 × CH_3), 22.1 (2 × CH_3), 27.3 (2 × CH_2), 27.7 (2 × CH), 31.0 (2 × CH), 35.5 (2 × CH_2), 41.6 (2 × CH_2), 43.3 (2 × CH), 49.6 (2 × CH) ppm; ^{77}Se NMR (76.3 MHz, $CDCl_3$): δ =

128.90 ppm. IR (film): ṽ = 2921, 1455, 1366, 1277, 1229, 1178, 761 cm^{-1}. $C_{20}H_{36}Se$ (355.46): calcd. C 67.58, H 10.21; found C 67.49, H 10.20.

(1*S*,3*R*,4*S*,6*R*)-(+)-Bis(4-caranyl) Selenide (30): Purification by column chromatography on silica gel (PE), yield 0.152 g (26%); yellow liquid; $[\alpha]_D^{23}$ = +69.73 (*c* = 1.50, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.60 (ddd, *J* = 5.6, 8.4, 8.4 Hz, 2 H), 0.67 (ddd, *J* = 6.8, 8.8, 8.8 Hz, 2 H), 0.82–0.91 (m, 2 H), 0.98 (d, *J* = 6.8 Hz, 6 H, 2 × CH_3), 1.00 (s, 6 H, 2 × CH_3), 1.02 (s, 6 H, 2 × CH_3), 1.52 (ddd, *J* = 5.6, 8.0, 15.2 Hz, 2 H), 1.82–1.89 (m, 4 H), 2.30 (ddd, *J* = 6.8, 8.4, 15.2 Hz, 2 H), 3.03 (dt, *J* = 6.3, 7.7 Hz, 2 H) ppm. ^{13}C NMR (100.6, $CDCl_3$): δ = 16.0 (2 × CH_3), 17.6 (2 × C), 20.4 (2 × CH_3), 21.3 (2 × CH), 21.8 (2 × CH), 25.8 (2 × CH_2), 26.4 (2 × CH_2), 28.6 (2 × CH_3), 31.2 (2 × CH), 42.4 (2 × CH) ppm. ^{77}Se NMR (133.5 MHz, $CDCl_3$): δ = 268.00 ppm. IR (film): ṽ = 2924, 2863, 1454, 1376, 1330, 1129 cm^{-1}. $C_{20}H_{34}Se$ (353.44): calcd. C 67.96, H 9.70; found C 68.15, H 9.63.

(1*S*,3*R*,4*R*,6*R*)-(+)-Bis(4-isocaranyl) Selenide (31): Purification by the column chromatography on silica gel (PE), yield 0.070 g (12%); yellow liquid; $[\alpha]_D^{23}$ = –103.92 (*c* = 0.54, $CHCl_3$). ^{1}H NMR (700 MHz, $CDCl_3$): δ = 0.54 (ddd, *J* = 1.4, 7.7, 9.1 Hz, 2 H), 0.73 (ddd, *J* = 5.6, 9.8, 9.8 Hz, 2 H), 0.77–0.86 (m, 4 H), 0.93 (s, 6 H, 2 × CH_3), 0.94 (s, 6 H, 2 × CH_3), 0.97 (d, *J* = 7.0 Hz, 6 H, 2 × CH_3), 1.29–1.36 (m, 2 H), 1.91–2.00 (m, 4 H), 2.14 (ddd, *J* = 2.1, 6.3, 15.4 Hz, 2 H), 2.33 (ddd, *J* = 6.3, 10.5, 10.5 Hz, 2 H) ppm. ^{13}C NMR (176.1, $CDCl_3$): δ = 15.5 (2 × CH_3), 17.5 (2 × C), 20.5 (2 × CH), 20.7 (2 × CH), 21.6 (2 × CH_3), 28.9 (2 × CH_3), 29.7 (2 × CH_2), 29.9 (2 × CH_2), 35.6 (2 × CH), 43.9 (2 × CH) ppm. ^{77}Se NMR (76.3 MHz, $CDCl_3$): δ = 377.98 ppm. IR (film): ṽ = 2924, 1455, 1374, 1224, 1167, 814 cm^{-1}. $C_{20}H_{34}Se$ (353.44): calcd. C 67.96, H 9.70; found C 68.24, H 9.62.

(1*S*,3*S*)-(+)-(*trans*)-Bis(3-hydroxy-4-caranyl) Selenide (32): Purification by the column chromatography on silica gel (dichloromethane/EtOAc, 90:10), yield 0.433 g (68%); yellow solid; m.p. 97–98 °C; $[\alpha]_D^{23}$ = +117.32 (*c* = 1.50, $CHCl_3$). ^{1}H NMR (700 MHz, $CDCl_3$): δ = 0.76–0.79 (m, 2 H), 0.84–0.90 (m, 2 H), 1.01 (s, 6 H, 2 × CH_3), 1.05 (s, 6 H, 2 × CH_3), 1.28 (s, 6 H, 2 × CH_3), 1.29–1.40 (m, 4 H), 2.07 (dd, *J* = 9.0, 15.6, Hz, 2 H), 2.36–2.43 (m, 2 H), 2.96 (dd, *J* = 4.8, 10.8 Hz, 2 H) ppm. IR (film): ṽ = 3441, 2935, 1456, 1373, 1227, 1172, 796 cm^{-1}. $C_{20}H_{34}O_2Se$ (385.44): calcd. C 62.32, H 8.89; found C 62.41, H 8.98.

(1*S*,3*R*)-(–)-(*cis*)-Bis(3-hydroxy-4-isocaranyl) Selenide (33): Purification by the column chromatography on silica gel (dichloromethane/EtOAc, 90:10), yield 0.439 g (69%); yellow solid; m.p. 99–101 °C; $[\alpha]_D^{23}$ = –129.42 (*c* = 0.48, $CHCl_3$). ^{1}H NMR (700 MHz, $CDCl_3$): δ = 0.56 (t, *J* = 8.4 Hz, 2 H), 0.81 (ddd, *J* = 5.2, 10.0, 10.0 Hz, 2 H), 0.98 (s, 6 H, 2 × CH_3), 1.03 (s, 6 H, 2 × CH_3), 1.24 (s, 6 H, 2 × CH_3), 1.30 (ddd, *J* = 1.2, 5.2, 14.0 Hz, 2 H), 2.01–2.15 (m, 4 H), 2.35 (dd, *J* = 7.2, 14.8 Hz, 2 H), 2.74 (ddd, *J* = 7.2, 12.4 Hz, 2 H) ppm. ^{13}C NMR (100.6, $CDCl_3$): δ = 1.0 (2 × CH_3), 15.3 (2 × CH_3), 17.8 (2 × C), 20.4 (2 × CH), 20.5 (2 × CH), 23.1 (2 × CH_3), 28.8 (2 × CH_3), 30.1 (2 × CH_2), 33.4 (2 × CH_2), 55.2 (2 × CH), 71.4 (2 × C) ppm. ^{77}Se NMR (76.3 MHz, $CDCl_3$): δ = 206.17 ppm. IR (film): ṽ = 3448, 2938, 2243, 1448, 1375, 1113, 909, 733 cm^{-1}. $C_{20}H_{34}O_2Se$ (385.44): calcd. C 62.32, H 8.89; found C 62.44, H 8.79.

(1*S*,2*R*,5*S*)-(–)-Dimyrtanyl Selenide (34): Purification by the column chromatography on silica gel (PE), yield 0.280 g (48%); yellow liquid; $[\alpha]_D^{22}$ = –62.33 (*c* = 1.25, $CHCl_3$). ^{1}H NMR (700 MHz, $CDCl_3$): δ = 0.86 (d, *J* = 9.1 Hz, 2 H), 0.98 (s, 6 H, 2 × CH_3), 1.16 (s, 6 H, 2 × CH_3), 1.46–1.51 (m, 2 H), 1.79–1.84 (m, 2 H), 1.85–1.88 (m, 2 H), 1.89–1.94 (m, 2 H), 1.98–2.03 (m, 4 H), 2.18–2.24 (m, 2 H), 2.30–2.34 (m, 2 H), 2.60 (ddd, *J* = 7.0, 9.8, 25.2 Hz, 4 H) ppm. ^{13}C NMR (176.1, $CDCl_3$): δ = 23.1 (2 × CH_2), 23.3 (2 × CH_3), 26.2 (2 × CH_2), 28.1 (2 × CH_3), 32.1 (2 × CH_2), 33.5 (2 × CH_2), 38.6 (2 × C), 41.3 (2 × CH), 42.1 (2 × CH), 46.4 (2 × CH) ppm. ^{77}Se NMR (76.3 MHz, $CDCl_3$): δ = 129.97 ppm. IR (film): ṽ = 2913, 1466, 1382, 1365, 1232, 1201 cm^{-1}. $C_{20}H_{34}Se$ (353.44): calcd. C 67.96, H 9.70; found C 67.92, H 9.71.

Synthesis of Selenonium Salts; Method a: The selenide (2.23 mmol) was dissolved in dichloromethane (1 mL), then benzyl bromide (0.763 g, 4.46 mmol) and a solution of silver triflate (0.572 g, 2.23 mmol) in water (2 mL) were added. The resulting biphasic mixture was stirred at room temp. for 1 d. Water (5 mL) and dichloromethane (5 mL) were added and the layers were separated. The aqueous organic layer was extracted with dichloromethane (3 × 3 mL). The combined organic layers were dried with $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was dissolved in the minimal amount of dichloromethane and added dropwise to rapidly stirred diethyl ether (10 mL). The precipitate was filtered and washed several times with diethyl ether.

Method b: $AgBF_4$ (0.443 g, 2.27 mmol) was carefully added to a mixture of selenide (2.26 mmol) and benzyl bromide (0.963 g, 5.63 mmol) at 0 °C, under an argon atmosphere. The resulting mixture was stirred at room temp. for 4 h. The crude product was dissolved in dichloromethane (10 mL) and filtered through Celite. The solvent was removed under reduced pressure, diethyl ether (10 mL) was added and the mixture was decanted. The precipitate was washed several times with diethyl ether.

Method c: Meerwein reagent (0.09 g, 0.64 mmol) was added to the solution of selenide (0.32 mmol) in dichloromethane (3 mL) under an argon atmosphere. The mixture was stirred at room temp. for 1 d. The crude product was dissolved in dichloromethane (5 mL) and filtered. The solvent was removed under reduced pressure, diethyl ether (5 mL) was added and the mixture was decanted. The precipitate was washed several times with diethyl ether.

Method d: $AgBF_4$ (0.127 g, 0.65 mmol) was carefully added to the selenide (0.64 mmol) and methyl iodide (0.230 g, 1.62 mmol) at 0 °C under an argon atmosphere. The resulting mixture was stirred at room temp. for 4 h. The crude product was dissolved in dichloromethane (5 mL) and filtered through Celite. The solvent was removed under the reduced pressure, diethyl ether (5 mL) was added and the mixture was decanted. The precipitate was washed several times with diethyl ether.

(1*R*,4*R*,5*R*,6*R*)-6-Benzyl-4,7,7-trimethyl-6-seleniabicyclo[3.2.1]octane Trifluoromethanesulfonate (11): Purification by precipitate, yield 0.653 g (64%; method a); white solid; m.p. 113–114 °C; $[\alpha]_D^{22}$ = –215.50 (*c* = 1.20, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.14 (d, *J* = 7.2 Hz, 3 H, CH_3), 1.22–1.36 (m, 1 H), 1.60–1.64 (m, 2 H), 1.72–1.79 (m, 1 H), 1.82 (s, 3 H, CH_3), 1.92 (s, 3 H, CH_3), 2.15–2.25 (m, 1 H), 2.41 (s, 1 H), 2.50–2.59 (m, 1 H), 2.67 (d, *J* = 13.6 Hz, 1 H), 3.98 (s, 1 H), 4.32 (d, *J* = 11.2 Hz, 1 H), 5.06 (d, *J* = 11.2 Hz, 1 H), 7.35–7.42 (m, 3 H, ArH), 7.52–7.61 (m, 2 H, ArH) ppm. ^{13}C NMR (100.6, $CDCl_3$): δ = 17.8 (CH_3), 22.7 (CH_2), 23.7 (CH_3), 26.1 (CH_2), 26.3 (CH_3), 31.6 (CH), 33.6 (CH_2), 41.4 (CH_2), 50.8 (CH), 64.5 (CH), 76.5 (C), 129.5 (CH_{Ar}), 129.7 (2 × CH_{Ar}), 130.3 (C_{Ar}), 130.5 (2 × CH_{Ar}) ppm; ^{77}Se NMR (76.3 MHz, $CDCl_3$): δ = 564.13 ppm. IR (film): ṽ = 2923, 2854, 1462, 1377, 1256, 1150, 1029 cm^{-1}. $C_{18}H_{25}F_3O_3SSe$ (457.41): calcd. C 47.27, H 5.51; found C 47.58, H 5.43.

(1*R*,4*R*,5*R*,6*R*)-6-Benzyl-4,7,7-trimethyl-6-seleniabicyclo[3.2.1]octane Tetrafluoroborate (12): Purification by precipitate, yield 0.500 g (56%; Method b); white solid; m.p. 136–138 °C; $[\alpha]_D^{23}$ = –292.89 (*c*

= 0.45, acetone). ^{1}H NMR (700 MHz, $CDCl_3$): δ = 1.17 (dd, J = 4.9, 6.3 Hz, 3 H, CH_3), 1.60 (s, 2 H), 1.65 (s, 1 H), 1.78 (s, 1 H), 1.83 (s, 3 H, CH_3), 1.93 (s, 3 H, CH_3), 2.25 (s, 1 H), 2.43 (s, 1 H), 2.56 (s, 1 H), 2.70 (d, J = 10.5 Hz, 1 H), 4.03 (s, 1 H), 4.29 (s, 1 H), 4.97 (s, 1 H), 7.35–7.42 (m, 3 H, ArH), 7.52–7.61 (m, 2 H, ArH) ppm. ^{13}C NMR (100.6, $CDCl_3$): δ = 17.9 (CH_3), 22.1 (CH_2), 23.8 (CH_3), 26.1 (CH_2), 26.4 (CH_3), 31.6 (CH), 33.7 (CH_2), 41.4 (CH_2), 50.8 (CH), 64.7 (CH), 76.7 (C), 129.6 (CH_{Ar}), 129.8 ($2\times CH_{Ar}$), 130.1 (C_{Ar}), 130.6 ($2\times CH_{Ar}$) ppm. ^{77}Se NMR (76.3 MHz, $CDCl_3$): δ = 564.99 ppm. IR (film): $\tilde{\nu}$ = 2923, 2853, 1462, 1377 cm^{-1}. $C_{17}H_{25}BF_4Se$ (395.14): calcd. C 51.67, H 6.38; found C 51.36, H 6.45.

(1*S*,2*S*,5*R*)-Benzyl Methyl Mentyl Selenonium Tetrafluoroborate (35): Purification by the column chromatography on silica gel (dichloromethane/methanol, 90:10), yield 0.715 g (80%; Method b), 0.051 g (40%; Method c), 0.053 g (21%; Method d); white solid; $[a]_D^{22}$ = –76.85 (c = 1.05, $CHCl_3$). ^{1}H NMR (700 MHz, $CDCl_3$): δ = 0.59 (d, J = 6.3 Hz, 3 H, CH_3), 0.71–0.87 (m, 1 H), 0.90 (d, J = 6.3 Hz, 3 H, CH_3), 0.93–0.97 (m, 1 H), 0.99 (d, J = 7.0 Hz, 3 H, CH_3), 1.29–1.39 (m, 1 H), 1.52–1.82 (m, 6 H), 2.17 (d, J = 12.6 Hz, 1 H), 2.54 (s, 3 H, CH_3), 4.62 (d, J = 3.5 Hz, 2 H), 7.28–7.38 (m, 3 H, ArH), 7.42–7.50 (m, 2 H, ArH) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 13.9 (CH_3), 15.9 (CH_3), 22.4 (CH_3), 23.3 (CH_3), 26.5 (CH_2), 31.0 (CH), 34.8 (CH_2), 35.2 (CH), 36.9 (CH_2), 43.3 (CH_2), 46.6 (CH), 58.2 (CH), 130.6 (C_{Ar}), 131.0 (CH_{Ar}), 131.1 (CH_{Ar}),131.2 (CH_{Ar}), 131.6 (CH_{Ar}),131.7 (CH_{Ar}) ppm. ^{77}Se NMR ($CDCl_3$): δ = 372. 46 ppm. $C_{18}H_{29}BF_4Se$ (411.19): calcd. C 52.58, H 7.11; found C 52.97, H 7.08.

(1*S*,2*S*,5*R*)-Benzyl Methyl Neomentyl Selenonium Tetrafluoroborate (36): Method b: mix of salts (48:52); yield: 0.420 g (47%). Method c: mix of salts (48:52); yield: 0.066 g (52%); Method d: mix of salts (42:58); yield: 0.089 g (35%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90–0.93 (m, 2 H), 0.97 (d, J = 6.8 Hz, 3 H, CH_3), 0.99 (d, J = 7.2 Hz, 3 H, CH_3), 1.05 (d, J = 6.4 Hz, 3 H, CH_3), 1.06 (d, J = 6.4 Hz, 3 H, CH_3), 1.07–1.15 (m, 4 H), 1.22–1.33 (m, 4 H), 1.38–1.53 (m, 4 H), 1.68–1.81 (m, 4 H), 1.88–1.97 (m, 2 H), 2.01–2.12 (m, 2 H), 2.41 (d, J = 15.2 Hz, 1 H), 2.52 (d, J = 16.0 Hz, 1 H), 2.59 (s, 3 H, CH_3), 2.76 (s, 3 H, CH_3), 4.54 (d, J = 10.8 Hz, 1 H), 4.62 (d, J = 11.2 Hz, 1 H), 4.82–4.96 (m, 2 H, CH_2), 5.01–5.09 (m, 2 H, CH_2), 7.39–7.48 (m, 2×3 H, ArH), 7.49–7.58 (m, 2×2 H, ArH) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.2 (CH_3), 19.3 (CH_3), 20.7 (CH_3), 20.8 (CH_3), 21.2 (CH_3), 21.3 (CH_3), 21.6 (CH_3), 21.7 (CH_3), 26.5 (CH_2), 26.7 (CH_2), 29.5 (CH), 29.7 (CH), 31.1 (CH), 31.4 (CH), 34.1 (CH_2), 34.3 (CH_2), 37.0 (CH_2), 37.2 (CH_2), 41.2 (CH_2), 44.7 (CH_2), 48.3 (CH), 49.1 (CH), 63.4 (CH), 66.1 (CH), 129.0 (C_{Ar}), 129.3 (C_{Ar}), 129.6 ($2\times CH_{Ar}$), 129.7 ($2\times CH_{Ar}$),129.8 (CH_{Ar}), 130.1 (CH_{Ar}), 130.6 ($2\times CH_{Ar}$), 130.7 ($2\times CH_{Ar}$) ppm. ^{77}Se NMR (76.3 MHz, $CDCl_3$): δ = 337. 76 (Se), 345.40 (Se) ppm.

Epoxidation: A mixture of selenide (2.18 mmol), benzyl bromide (0.749 g, 4.38 mmol), sodium hydroxide (0.088 g, 2.20 mmol) and benzaldehyde (0.231 g, 2.18 mmol) in acetonitrile (10 mL) was stirred for 3 d. Acetonitrile was evaporated and water (80 mL) was added. The mixture was extracted with petroleum ether ($3\times$ 75 mL) and the combined ethereal layers were dried with anhydrous magnesium sulfate. The solvent was evaporated, and a crude product was purified by column chromatography (petroleum ether/EtOAc, 95:5) to give the pure *trans*-stilbene oxide.

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