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# Synthesis and reactions of enantiomerically pure dialkyl diselenides from the *p*-menthane group

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ABSTRACT

A convenient route for the synthesis of optically active dialkyl diselenides from the *p*-menthane system utilizing a reaction of alkyl tosylates and chlorides with sodium diselenide is reported. The diselenides obtained have been used for asymmetric methoxyselenenylation of styrene. Quantum chemical calculations of the chair conformers stability of the terpeneselenenyl bromides from the *p*-menthane group have also been carried out using density functional theory (DFT, at the B3LYP/6-311G(d) level). The influence of the diselenides structure on the stereoselectivity in the methoxyselenenylation reaction is also discussed.



## 1. Introduction

In recent years, organoselenium compounds have played an important role in organic synthesis. The discovery of the selenoxide elimination in early 1970s was a major breakthrough for the development of organoselenium chemistry.[1–3] Oxidation of selenides to the corresponding selenoxides or selenones and subsequent elimination or substitution, reductive deselenenylation, transformations into carboanions, and participation in radical coupling processes make the organoselenium derivatives versatile building blocks.[4–7] In 1958 it was discovered that electrophilic selenium compounds can add stereospecifically to alkenes.[8] In this context chiral organic selenium compounds, particulary optically active diselenides, are frequently used as convenient reagents for introducing various asymmetric functional groups to carbon–carbon double bonds and for constructing heterocyclic compounds via ring-closure processes.[9–13] Organoselenium compounds frequently posseses unique biological activities.[14–16]

In previous papers, we have described a convenient method for the synthesis of optically active terpene alkyl diselenides. As a result of the reaction between sodium diselenide with the respective tosylates or chlorides, we obtained dialkyl diselenides derived from (−)-menthol, (−)-*trans*-4-caranol, (−)-isopinocampheol, (−)-myrtanol, and (−)-borneol.[17,18] The resulting diselenides has been employed in the asymmetric selenenylation of olefins,[18] and selenocyclization of the unsaturated alcohols and carboxylic acids.[19] The investigation concerning the helicity of the diselenide chromofore via the use of the above diselenides have also been described.[20]

Herein, we report the results of our investigations concerning the synthesis of the dialkyl diselenides from the *p*-menthane group as well as the results of the asymmetric methoxyselenenylation of styrene with their use. Our attention was focused on determining the influence of the structure of the obtained diselenides on their stereoselectivity in the addition reactions to a carbon–carbon bond.

Herein, we report a synthesis of two diselenides from the *p*-menthane group, namely (+)-dineomenthyl diselenide **3** and (−)-dimenthyl diselenide **5**, which we obtained as a result of the reaction of menthyl tosylate **2** and neomenthyl chloride **4** with sodium diselenide (Scheme 1).[18] The tosylate **2** and chloride **4** were obtained from the commercially available (−)-menthol **1**.

We decided to use this methodology for the synthesis of the epimeric diselenides derived from (+)-isomenthol **6**, (+)-carvomenthol **13**, and (−)-neoisocarvomenthol **14**.

## 2. Result and discussion

We started our investigations with the synthesis of diselenides derived from (+)-isomenthol **6**. We obtained (+)-isomenthyl tosylate **7** from the commercially available (+)-isomenthol **6** via reaction with tosyl chloride in pyridine. The subsequent reaction with carbon tetrachloride and triphenylphosphine led to (+)-neoisomenthyl chloride **9**. Under the influence of sodium diselenide generated in situ (Se, NaOH, $N_2H_4 \times H_2O$)[18] on tosylate **7** and chloride **9**, we received (−)-dineoisomenthyl diselenide **8** and (−)-diisomenthyl diselenide **10**, respectively. The reaction with sodium diselenide was carried out at 100 °C in DMF for 1 h for the tosylate and 2 h for the chloride (Scheme 2).

Further investigations regarding the synthesis of diselenides derived from (+)-carvomenthol **13** and (−)-neoisocarvomenthol **14**

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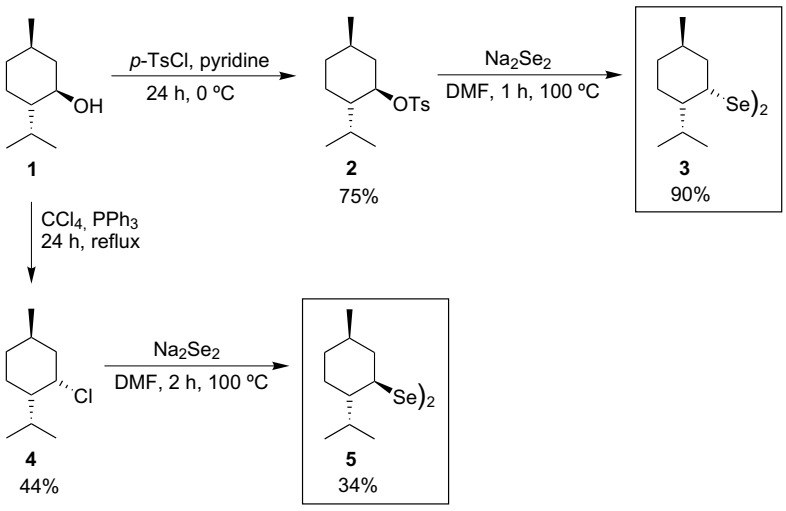
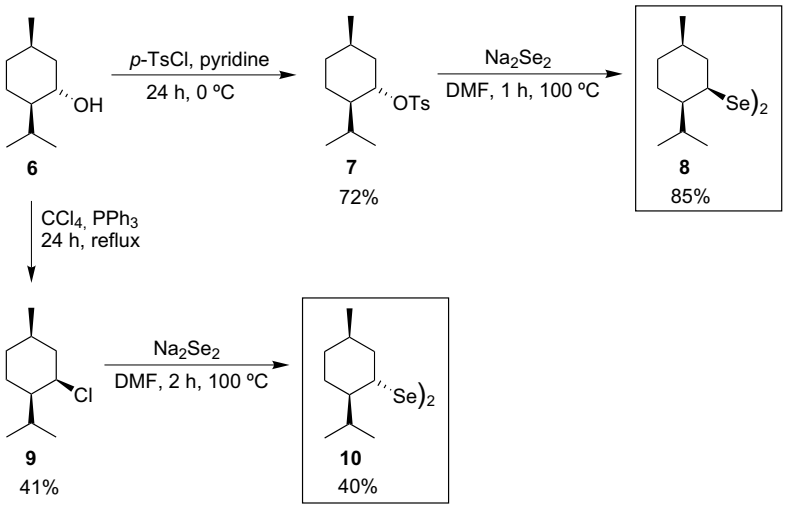



**Scheme 1.** Synthesis of (+)-dineomenthyl diselenide **3** and (−)-dimenthyl diselenide **5**.




**Scheme 2.** Synthesis of (−)-dineoisomenthyl diselenide **8** and (+)-diisomenthyl diselenide **10**.

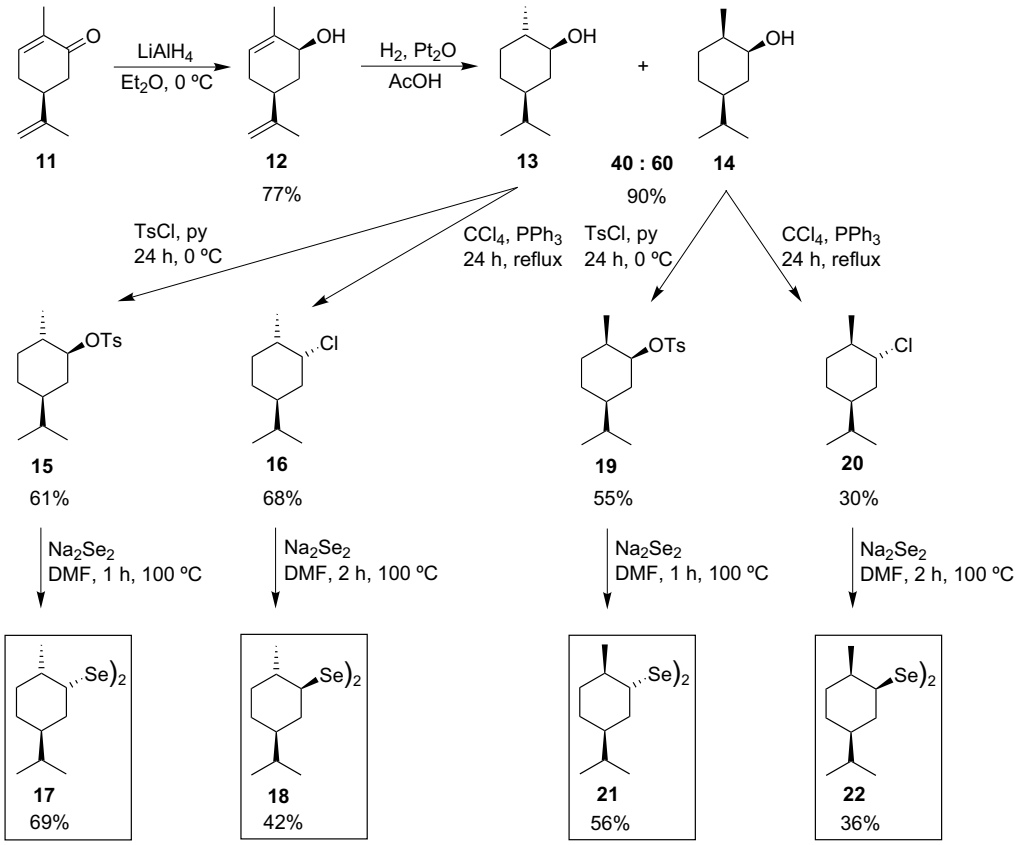
were carried out. We obtained a mixture of alcohols **13** and **14** in a 40:60 ratio from (+)-carvone **11** after reduction with $LiAlH_4$ to give (+)-*cis*-carveol **12**, and then hydrogenation on the platinum catalyst. The enantiomerically pure (+)-carvomenthol **13** and (−)-neoisocarvomenthol **14** were separated by means of the fractional distillation using Fisher® Spaltrohr concentric tube column (90 theoretical plates) and then used for the synthesis of carvomenthyl **15** and neoisocarvomenthyl **19** tosylates as well as neocarvomenthyl **16** and isocarvomenthyl **20** chlorides. The obtained tosylates **15** and **19** and chlorides **16** and **20** in the reaction with sodium diselenide gave (−)-dineocarvomenthyl diselenide **17**, (+)-dicarvomenthyl diselenide **18**, (−)-diisocarvomenthyl diselenide **21** and (+)-dineoisocarvomenthyl diselenide **22** (Scheme 3).

The enantiomerically pure diselenides were used for the asymmetric methoxyselenenylation of styrene (Scheme 4), to give the following bromides: neomenthylselenenyl **3a**, menthylselenenyl **5a**, neoisomenthylselenenyl **8a**, isomenthylselenenyl **10a**, neocarvomenthylselenenyl **17a**, carvomenthylselenenyl **18a**, isocarvomenthylselenenyl **21a**, and neoisocarvomenthylselenenyl **22a**, after the addition of bromine to diselenides **3**, **5**, **8**, **10**, **17**, **18**, **21**, and **22**. The reaction was then treated with silver triflate in methanol followed by styrene to give the methoxyselenenylation products **23**–**30**.

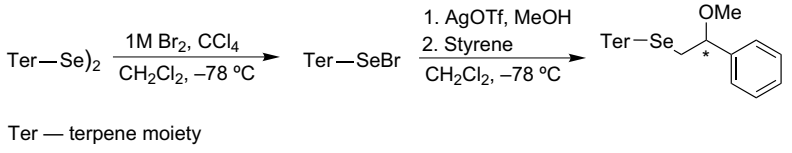
The yields of the methoxyselenenylation reaction and the diastereomeric ratio of adducts are presented in Table 1. The best results (70:30) were obtained for (+)-dineomenthyl diselenide **3** and (−)-diisomenthyl diselenide **10**.

In order to determine the influence of the structure of the diselenides on the diastereoselectivity in the methoxyselenenylation reactions, we conducted the optimization of the chair conformers geometry of the terpeneselenenyl bromides from the *p*-menthyl group at the B3LYP/6-311G(d) level. The optimized structures of the chair conformers of terpeneselenenyl bromides and their differences in energy have been presented in Figure 1.

On the basis of the optimized structures of terpeneselenenyl bromides and the results of the addition reaction from Table 1, it can be concluded that in the case of bromides **3a**, **5a**, **8a**, and **10a** derived from (−)-menthol **1** and (+)-isomenthol **6**, the stabilization of the structure via an equatorial position of the isopropyl group favors an increase in the diastereoselectivity. For bromide **8a**, the very low degree of selectivity can be explained by the axial position of the isopropyl group in the dominating chair conformation what arouse from the calculations. The position of the isopropyl group for the neoisomenthyl structure was also postulated by Härtner et al.[21] and Senda et al.[22] We assume that for bromides **17a**, **18a**, **21a** and **22a** derived from (+)-carvomenthol and (−)-neo-




**Scheme 3.** Synthesis of diselenides derived from (+)-carvomenthol **13** and (−)-neoisocarvomenthol **14**.




**Scheme 4.** Asymmetric methoxyselenenylation reaction with the use of diselenides from the *p*-menthane group.

isocarvomenthol, the position of the group with selenium in the vicinity of a methyl group but not the isopropyl one, causes a decrease in the stereoselectivity of the addition products. Better diastereomeric ratios have been observed for bromides **17a** and **18a**, whose structures are stabilized by the diequatorial position of the alkyl groups. By comparing the calculated energies of the more stable conformers for terpeneselenenyl bromides **5a** and **8a** ($\Delta$ = 16.57 kJ/mol), **17a** and **21a** ($\Delta$ = 1.31 kJ/mol) as well as **18a** and **22a** ($\Delta$ = 4.16 kJ/mol), which differed only by the stereochemistry of the isopropyl or methyl group, we were able to demonstrate that the bromides **5a**, **17a**, and **18a** are more energetically stable. In all cases, a greater stability of the compared bromides correlated with an increase of a stereoselectivity of the selenenylation products of styrene. For bromides **3a** and **10a** ($\Delta$ = 5.27 kJ/mol) in spite of the greater stability of the bromide **10a** no addition to styrene was observed, probably due to an increase in stereoselectivity caused by an isopropyl group at the equatorial position as evidenced on the basis of calculations, thus can influence the structures of the selenenyl bromides **3a** and **10a**.

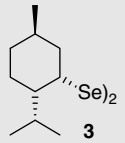
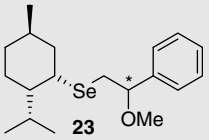
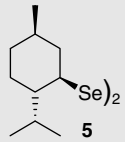
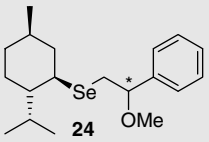
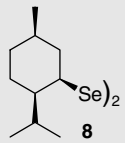
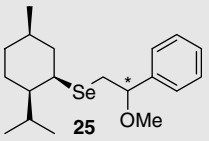
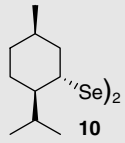
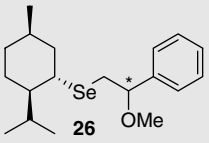
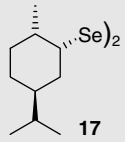
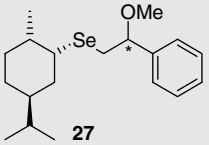
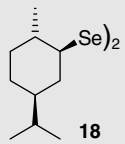
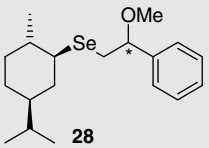
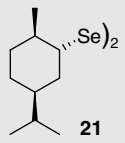
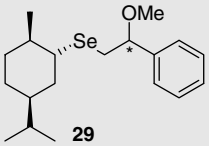
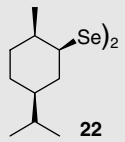
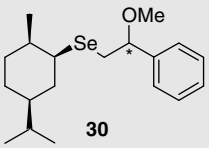
## 3. Conclusions

It has been demonstrated that the reaction of sodium diselenide with alkyl tosylates and chlorides is a convenient method for the synthesis of the dialkyl diselenide from *p*-menthane group. The best diastereomeric ratio for methoxyselenenylation of styrene was obtained for (+)-dineomenthyl diselenide **3** and (−)-diisomenthyl diselenide **10**, when the reaction was carried out at −78 °C. On the basis of the experimental results of the methoxyselenenylation reaction and theoretical calculations by the DFT method of the stability of the selenenyl electrophiles conformers from the *p*-menthane system, we assume that the stiffering of the selenium electrophile structure by an equatorial arrangement of the alkyl groups can considerably influence the diastereomeric ratio of the methoxyselenenylation products.

## 4. Experimental

Melting points were measured with a Büchi Tottoli SPM-20 heating unit and are uncorrected. NMR spectra were recorded on Bruker AM-300 at 300 MHz or Varian 200 at 200 MHz for $^{1}$H and 75.5 MHz or 50.3 MHz for $^{13}$C. Chemical shifts are expressed in parts per million (ppm) relative to TMS. $^{77}$Se NMR spectra were recorded on Varian 200 with diphenyl diselenide as an external standard. Elemental analyses were performed on a Vario MACRO CHN analyzer. TLC was conducted on precoated silica gel plates (Merck 60$F_{254}$) and the spots were visualized under UV light. Column chromatography was carried out on column using Silica

**Table 1**
Methoxyselenenylation of styrene with the use of diselenides from the *p*-menthane group

| Entry | Diselenide | Product | dr[a] | Yield (%) |
|---|---|---|---|---|
| 1 |  **3** |  **23** | **70:30**[b] | 86[b] |
| 2 |  **5** |  **24** | 62:38[b] | 79[b] |
| 3 |  **8** |  **25** | 52:48 | 42 |
| 4 |  **10** |  **26** | **70:30** | 72 |
| 5 |  **17** |  **27** | 64:36 | 79 |
| 6 |  **18** |  **28** | 65:35 | 75 |
| 7 |  **21** |  **29** | 52:48 | 51 |
| 8 |  **22** |  **30** | 56:44 | 41 |

[a] Diastereomeric ratios were established on the basis of $^{1}H$ and $^{77}Se$ NMR spectra.
[b] Ref. 10.

Gel 60 Merck (70–230 mesh). Methanol was distilled from magnesium turnings. Dichloromethane was distilled from calcium hydride and restored under molecular sieves 4 Å. All reactions requiring anhydrous conditions were conducted in flame-dried apparatus.

### 4.1. (+)-*cis*-Carveol 12

The product was isolated by the distillation under reduced pressure 65–66 °C/0.4 mmHg. Yield 77%; colorless liquid; $[\alpha]_D^{23} = +44.1$ (*c* 5.14, $CHCl_3$); $^{1}H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 1.43–1.46 (m, 1H), 1.50 (dt, $J_{H,H}$ = 12.0, 9.6 Hz, 1H), 1.73–1.79 (m, 6H), 1.89–2.01 (m, 1H), 2.03–2.08 (m, 1H), 2.10–2.20 (m, 1H), 2.22–2.32 (m, 1H), 4.15–4.25 (m, 1H), 4.73 (m, 2H), 5.50 (m, 1H) ppm; $^{13}C$ NMR (50.3 MHz, $CDCl_3$): $\delta$ = 18.9 ($CH_3$), 20.6 ($CH_3$), 31.0 ($CH_2$), 38.0 ($CH_2$), 40.4 (CH), 70.8 (CH), 109.1 (=$CH_2$), 123.8 (=CH), 136.2 (C=), 148.9 (C=) ppm. Elemental Anal. Calcd for $C_{10}H_{16}O$ (152.23): C, 78.90; H, 10.59. Found: C, 78.88; H, 10.34.

### 4.2. (+)-(1*S*,2*S*,5*S*)-Carvomenthol 13

Yield 58%; colorless oil; $[\alpha]_D^{20} = +25.6$ (*c* 5.36, $CHCl_3$); $^{1}H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 0.86 (s, 3H; $CH_3$), 0.88 (s, 3H; $CH_3$), 0.90–0.99 (m, 2H), 1.00 (d, $J_{H,H}$ = 6.6 Hz, 3H; $CH_3$), 1.08–1.28 (m, 3H), 1.38–1.51 (m, 2H), 1.57–1.64 (m, 1H), 1.69–1.76 (m, 1H), 1.91–1.98 (m, 1H), 3.08–3.16 (m, 1H) ppm; $^{13}C$ NMR (75.5 MHz, $CDCl_3$): $\delta$ = 18.3 ($CH_3$), 19.7 ($CH_3$), 19.8 ($CH_3$), 29.0 ($CH_2$), 32.5 (CH), 33.2 ($CH_2$), 38.8 ($CH_2$), 40.2 (CH), 43.1 (CH), 76.6 (CH) ppm. Elemental Anal. Calcd for $C_{10}H_{20}O$ (156.27): C, 76.86; H, 12.90. Found: C, 76.80; H, 12.78.

### 4.3. (−)-(1*S*,2*R*,5*S*)-Neoisocarvomenthol 14

Yield 70%; colorless oil; $[\alpha]_D^{24} = -37.3$ (*c* 15.7, $CHCl_3$); $^{1}H$ NMR (200 MHz, $CDCl_3$): $\delta$ = 0.86 (s, 3H; $CH_3$), 0.88 (s, 3H; $CH_3$), 0.90 (d, $J_{H,H}$ = 7.0 Hz, 3H; $CH_3$), 1.06–1.28 (m, 4H), 1.31–1.54 (m, 3H), 1.60–1.69 (m, 2H), 2.02–2.08 (m, 1H), 3.74 (m, 1H) ppm; $^{13}C$ NMR (50.3 MHz, $CDCl_3$): $\delta$ = 10.5 ($CH_3$), 19.7 ($CH_3$), 19.8 ($CH_3$), 22.5 ($CH_2$), 30.6 ($CH_2$), 32.3 ($CH_2$), 32.6 (CH), 33.8 (CH), 43.1 (CH), 72.9 (CH) ppm. Elemental Anal. Calcd for $C_{10}H_{20}O$ (156.27): C, 76.86; H, 12.90. Found: C, 76.85; H, 12.93.

### 4.4. Preparation of tosylates: general procedure

Tosyl chloride (110 mmol) was added in one portion to a solution of the terpene alcohol (100 mmol) in pyridine (125 mL) at 0 °C. The reaction mixture was stirred for 1 h at the same temperature and then for 24 h at room temperature, after which it was poured to water (100 mL). The resulting precipitate was filtered off and dried under vacuum. The crude product was purified by the crystallization from petroleum ether.

#### 4.4.1. (+)-(1*S*,2*R*,5*R*)-Isomenthyl tosylate 7

Yield 72%; white crystals; mp 83–84 °C; $[\alpha]_D^{25} = +10.1$ (*c* 10.90, $CHCl_3$); $^{1}H$ NMR (200 MHz, $CDCl_3$): $\delta$ = 0.75 (d, $J_{H,H}$ = 6.8 Hz, 3H; $CH_3$), 0.79 (d, $J_{H,H}$ = 6.8 Hz, 3H; $CH_3$), 0.85 (d, $J_{H,H}$ = 6.8 Hz, 3H; $CH_3$), 0.99–1.77 (m, 8H), 1.78–1.96 (m, 1H), 2.48 (s, 3H; $CH_3$), 4.71 (dt, $J_{H,H}$ = 5.8, 3.2 Hz, 1H; CH), 7.34 (d, $J_{H,\ H}$ = 7.8 Hz, 2H; 2 × $CH_{ar}$), 7.78 (d, $J_{H,H}$ = 7.8 Hz, 2H; 2 × $CH_{ar}$) ppm; $^{13}C$ NMR (50.3 MHz, $CDCl_3$): $\delta$ = 19.1 ($CH_3$), 20.7 ($CH_2$), 20.8 (2 × $CH_3$), 21.5 ($CH_3$), 25.9 (CH), 27.0 (CH), 29.2 ($CH_2$), 36.1 ($CH_2$), 45.7 (CH), 81.9 (CH), 127.7 (2 × $CH_{ar}$), 129.6 (2 × $CH_{ar}$), 134.8 ($C_{ar}$), 144.2 ($C_{ar}$) ppm. Elemental Anal. Calcd for $C_{17}H_{26}O_3S$ (310.45): C, 65.77; H, 8.44. Found: C, 65.66; H, 8.32.

#### 4.4.2. (+)-(1*S*,2*S*,5*S*)-Carvomenthyl tosylate 15

Yield 61%; white crystals; mp 55–56 °C; $[\alpha]_D^{26} = +48.5$ (*c* 10.11, $CHCl_3$); $^{1}H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 0.76 (d, $J_{H,H}$ = 6.8 Hz, 3H; $CH_3$), 0.77 (d, $J_{H,H}$ = 6.8 Hz, 3H; $CH_3$), 0.80 (d, $J_{H,H}$ = 6.6 Hz, 3H; $CH_3$), 0.84–1.22 (m, 3H), 1.36–1.63 (m, 4H), 1.70–1.81 (m, 1H), 1.93–2.01 (m, 1H), 2.43 (s, 3H; $CH_3$), 4.11 (m, 1H), 7.33 (d, $J_{H,H}$ = 8.2 Hz, 2H; 2 × $CH_{ar}$), 7.79 (d, $J_{H,H}$ = 8.2 Hz, 2H; 2 × $CH_{ar}$) ppm; $^{13}C$ NMR (75.5 MHz, $CDCl_3$): $\delta$ = 18.3 ($CH_3$), 19.5 ($CH_3$), 19.6 ($CH_3$), 21.6 ($CH_3$), 28.2 ($CH_2$), 32.2 (CH), 33.1 ($CH_2$), 36.4 ($CH_2$), 37.7 (CH), 42.9 (CH), 88.5 (CH), 127.7 (2 × $CH_{ar}$), 129.8 (2 × $CH_{ar}$),

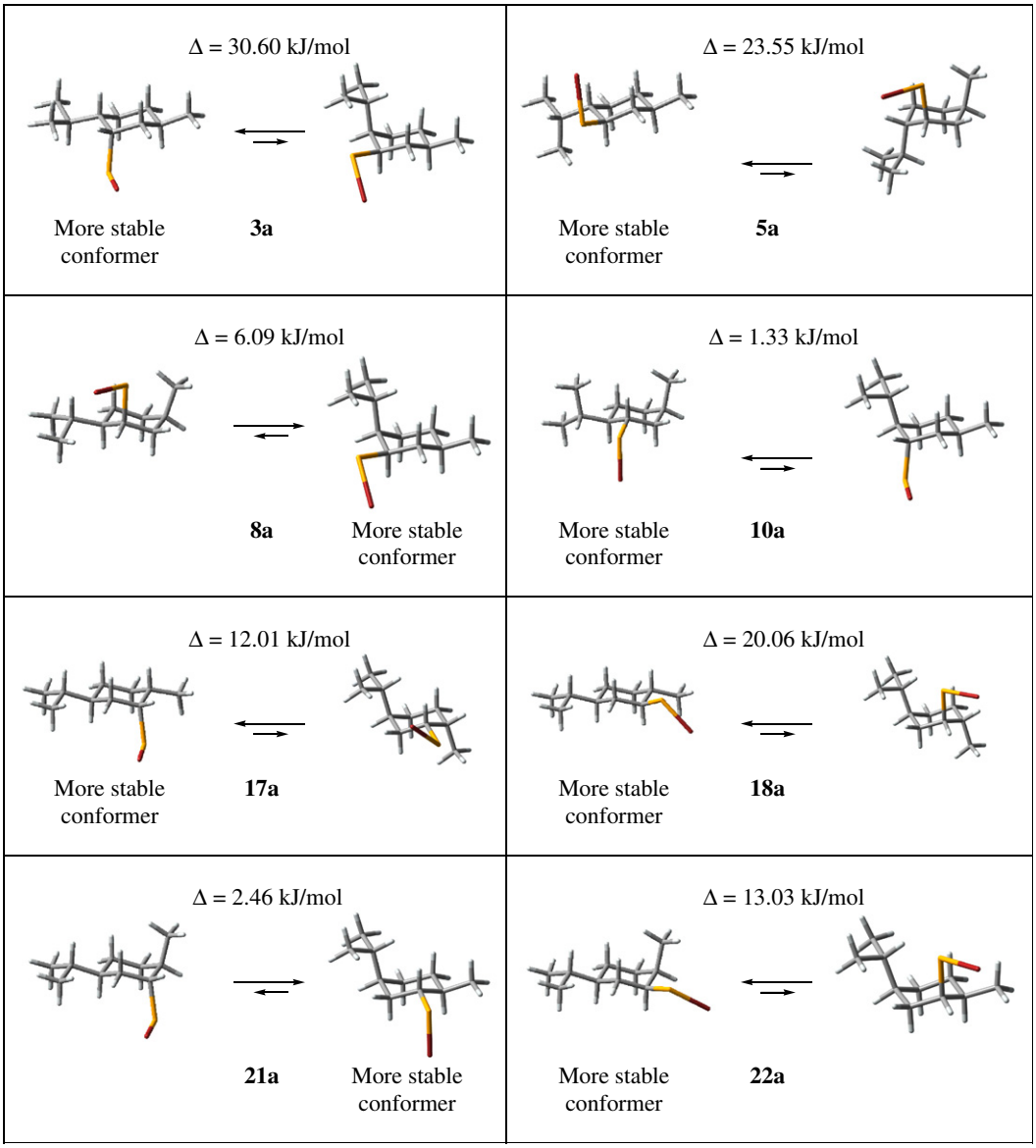



**Figure 1.** Optimized structures of the terpeneselenenyl bromides from *p*-menthane group.

134.8 ($C_{ar}$), 144.3 ($C_{ar}$) ppm. Elemental Anal. Calcd for $C_{17}H_{26}O_3S$ (310.45): C, 65.77; H, 8.44. Found: C, 65.70; H, 8.35.

#### 4.4.3. (−)-(1*S*,2*R*,5*S*)-Neoisocarvomenthyl tosylate 19

Yield 55%; white crystals; mp 62–63 °C; $[\alpha]_D^{26} = -5.5$ (*c* 4.90, $CHCl_3$); $^1H$ NMR (200 MHz, $CDCl_3$): $\delta = 0.80$ (d, $J_{H,H} = 6.8$ Hz, 3H; $CH_3$), 0.82 (d, $J_{H,H} = 6.8$ Hz, 3H; $CH_3$), 0.90 (d, $J_{H,H} = 7.0$ Hz, 3H; $CH_3$), 1.00–1.18 (m, 2H), 1.21–1.70 (m, 6H), 2.01–2.19 (m, 1H), 2.44 (s, 3H; $CH_3$), 4.58 (dt, $J_{H,H} = 11.4$, 4.8 Hz, 1H; CH), 7.32 (d, $J_{H,H} = 8.4$ Hz, 2H; 2 × $CH_{ar}$), 7.80 (d, $J_{H,H} = 8.4$ Hz, 2H; 2 × $CH_{ar}$) ppm; $^{13}C$ NMR (50.3 MHz, $CDCl_3$): $\delta = 11.2$ ($CH_3$), 19.6 (2 × $CH_3$), 21.5 ($CH_2$), 21.9 ($CH_3$), 29.9 ($CH_2$), 30.3 ($CH_2$), 32.1 (CH), 32.3 (CH), 43.1 (CH), 85.0 (CH), 127.5 (2 × $CH_{ar}$), 129.6 (2 × $CH_{ar}$), 135.0 ($C_{ar}$), 144.2 ($C_{ar}$) ppm. Elemental Anal. Calcd for $C_{17}H_{26}O_3S$ (310.45): C, 65.77; H, 8.44. Found: C, 65.70; H, 8.37.

### 4.5. Preparation of chlorides: general procedure

A solution of the terpene alcohol (100 mmol) and triphenylphosphine (110 mmol) in carbon tetrachloride (240 mL) was refluxed for 24 h, after which it was cooled and petroleum ether (300 mL) was added. The precipitate formed was filtered off under vacuum, and the filtrate was concentrated and evaporated by means of a rotary evaporator.

#### 4.5.1. (+)-(1*R*,2*R*,4*R*)-Neoisomenthyl chloride 9

Purification by the crystallization from petroleum ether. Yield 41%; white crystals; mp 81–82 °C; $[\alpha]_D^{25} = +23.9$ (*c* 5.10, $CHCl_3$); $^1H$ NMR (200 MHz, $CDCl_3$): $\delta = 0.85$ (d, $J_{H,H} = 7.0$ Hz, 3H; $CH_3$), 0.90 (s, 3H; $CH_3$), 0.94 (s, 3H; $CH_3$), 1.08–1.64 (m, 7H) 1.86–2.03 (m, 2H), 3.77 (dt, $J_{H,H} = 7.8$, 4.0 Hz, 1H; CH) ppm; $^{13}C$ NMR (50.3 MHz, $CDCl_3$): $\delta = 18.1$ ($CH_3$), 19.6 ($CH_2$), 19.9 ($CH_3$), 21.0 ($CH_3$), 26.0 (CH), 27.5 (CH), 30.5 ($CH_2$), 40.0 ($CH_2$), 49.6 (CH), 67.8 (CH) ppm. Elemental Anal. Calcd for $C_{10}H_{19}Cl$ (174.71): C, 68.75; H, 10.96. Found: C, 68.70; H, 10.92.

#### 4.5.2. (−)-(1*S*,2*R*,4*S*)-Neocarvomenthyl chloride 16

Purification by column chromatography on silica gel with petroleum ether/ethyl acetate, 95:5. Yield 68%; colorless liquid; $[\alpha]_D^{25} = -38.1$ (*c* 5.70, $CHCl_3$); $^1H$ NMR (200 MHz, $CDCl_3$): $\delta = 0.86$ (d, $J_{H,H} = 6.6$ Hz, 3H; $CH_3$), 0.87 (d, $J_{H,H} = 6.6$ Hz, 3H; $CH_3$), 0.99 (d, $J_{H,H} = 6.6$ Hz, 3H; $CH_3$), 1.02–1.15 (m, 1H), 1.38–1.79 (m, 7H),

2.02–2.13 (m, 1H), 4.36 (m, 1H) ppm; $^{13}$C NMR (50.3 MHz, $CDCl_3$): $\delta$ = 19.5 ($CH_3$), 19.7 ($CH_3$), 19.8 ($CH_3$), 28.0 ($CH_2$), 28.9 ($CH_2$), 32.1 (CH), 36.2 (CH), 37.2 (CH), 38.1 ($CH_2$), 67.2 (CH) ppm. Elemental Anal. Calcd for $C_{10}H_{19}Cl$ (174.71): C, 68.75; H, 10.96. Found: C, 68.62; H, 10.78.

#### 4.5.3. (−)-(1*R*,2*R*,4*S*)-Isocarvomenthyl chloride 20

The product was isolated by the distillation under reduced pressure 30–31 °C/0.1 mmHg. Yield 30%; colorless liquid; $[\alpha]_D^{22} = -43.8$ (*c* 3.15, $CHCl_3$); $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 0.86 (d, $J_{H,H}$ = 6.0 Hz, 3H; $CH_3$), 0.89 (d, $J_{H,H}$ = 6.0 Hz, 3H; $CH_3$), 1.04 (d, $J_{H,H}$ = 7.4 Hz, 3H; $CH_3$), 1.20–1.39 (m, 1H), 1.40–1.57 (m, 4H), 1.68–2.03 (m, 4H), 3.95–4.03 (m, 1H) ppm; $^{13}$C NMR (50.3 MHz, $CDCl_3$): $\delta$ = 18.8 ($CH_3$), 20.2 ($CH_3$), 20.4 ($CH_3$), 24.9 ($CH_2$), 27.6 ($CH_2$), 29.6 (CH), 35.4 ($CH_2$), 38.2 (CH), 39.4 (CH), 64.9 (CH) ppm. Elemental Anal. Calcd for $C_{10}H_{19}Cl$ (174.71): C, 68.75; H, 10.96. Found: C, 68.72; H, 10.92.

### 4.6. Preparation of diselenides: general procedure

The standard synthesis of diselenides was conducted under argon, by dropping hydrazine hydrate (0.6 mL) into a mixture of selenium (22 mmol) and sodium hydroxide (33 mmol) in DMF (20 mL). After heating at 100 °C for 15 min, the reaction mixture was cooled to ambient temperature and the respective tosylate (22 mmol) or chloride (22 mmol) was added. The solution was heated again at 100 °C for 1 h (2 h for chlorides). The reaction mixture was cooled, poured into water (100 mL), and extracted with petroleum ether (3 × 100 mL). The combined ether layers were washed with water (100 mL), dried over anhydrous $MgSO_4$, and evaporated. The product was purified by column chromatography (petroleum ether, silica gel).

#### 4.6.1. (−)-(1*R*,2*R*,5*R*,1′*R*,2′*R*,5′*R*)-Dineoisomenthyl diselenide 8

Yield 85%; yellow liquid; $[\alpha]_D^{25} = -232.5$ (*c* 6.70, $CHCl_3$); $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 0.95 (d, $J_{H,H}$ = 6.6 Hz, 3H; $CH_3$), 1.00 (d, $J_{H,H}$ = 6.6 Hz, 3H; $CH_3$), 1.03 (d, $J_{H,H}$ = 6.6 Hz, 3H; $CH_3$), 1.17–1.35 (m, 1H), 1.40–1.58 (m, 3H), 1.60–1.98 (m, 4H), 2.05–2.18 (m, 1H), 3.47–3.56 (m, 1H) ppm; $^{13}$C NMR (50.3 MHz, $CDCl_3$): $\delta$ = 21.7 ($CH_3$), 22.1 ($CH_3$), 22.9 ($CH_3$), 26.8 ($CH_2$), 28.7 (CH), 30.7 ($CH_2$), 32.4 (CH), 39.3 ($CH_2$), 46.8 (CH), 52.0 (CH) ppm; $^{77}$Se NMR (38.1 MHz, $CDCl_3$): $\delta$ = 395.8 ppm. Elemental Anal. Calcd for $C_{20}H_{38}Se_2$ (436.44): C, 55.04; H, 8.77. Found: C, 54.92; H, 8.89.

#### 4.6.2. (+)-(1*S*,2*R*,5*R*,1′*S*,2′*R*,5′*R*)-Diisomenthyl diselenide 10

Yield 40%; yellow liquid; $[\alpha]_D^{22} = +27.6$ (*c* 0.90, $CHCl_3$); $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 0.88 (d, $J_{H,H}$ = 6.6 Hz, 3H; $CH_3$), 0.90 (d, $J_{H,H}$ = 6.6 Hz, 3H; $CH_3$), 0.92 (d, $J_{H,H}$ = 6.6 Hz, 3H; $CH_3$), 1.08–1.33 (m, 3H), 1.38–2.06 (m, 6H), 3.47–3.54 (m, 1H) ppm; $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ = 19.3 ($CH_3$), 20.8 ($CH_3$), 21.2 ($CH_3$), 22.1 ($CH_2$), 27.8 (CH), 28.6 (CH), 30.4 ($CH_2$), 38.0 ($CH_2$), 46.8 (CH), 47.2 (CH) ppm; $^{77}$Se NMR (38.1 MHz, $CDCl_3$): $\delta$ = 375.4 ppm. Elemental Anal. Calcd for $C_{20}H_{38}Se_2$ (436.44): C 55.04, H 8.77; found: C, 54.83; H, 8.53.

#### 4.6.3. (−)-(1*R*,2*S*,5*S*,1′*R*,2′*S*,5′*S*)-Dineocarvomenthyl diselenide 17

Yield 69%; yellow oil; $[\alpha]_D^{20} = -195.5$ (*c* 3.36, $CHCl_3$); $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 0.86 (d, $J_{H,H}$ = 6.4 Hz, 3H; $CH_3$), 0.87 (d, $J_{H,H}$ = 6.4 Hz, 3H; $CH_3$), 1.04 (d, $J_{H,H}$ = 6.6 Hz, 3H; $CH_3$), 1.16–1.40 (m, 2H), 1.41–1.60 (m, 5H), 1.64–1.74 (m, 1H), 2.26–2.34 (m, 1H), 3.55 (m, 1H) ppm; $^{13}$C NMR (50.3 MHz, $CDCl_3$): $\delta$ = 19.7 ($CH_3$), 19.9 ($CH_3$), 21.9 ($CH_3$), 29.4 ($CH_2$), 30.9 ($CH_2$), 32.4 (CH), 37.3 ($CH_2$), 37.4 (CH), 38.6 (CH), 57.6 (CH) ppm; $^{77}$Se NMR (38.1 MHz, $CDCl_3$): $\delta$ = 306.1 ppm. Elemental Anal. Calcd for $C_{20}H_{38}Se_2$ (436.44): C, 55.04; H, 8.77. Found: C, 55.08; H, 8.82.

#### 4.6.4. (+)-(1*S*,2*S*,5*S*,1′*S*,2′*S*,5′*S*)-Dicarvomenthyl diselenide 18

Yield 42%; yellow oil; $[\alpha]_D^{20} = +256.7$ (*c* 0.60, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 0.88 (d, $J_{H,H}$ = 6.8 Hz, 3H; $CH_3$), 0.87 (d, $J_{H,H}$ = 6.8 Hz, 3H; $CH_3$), 0.94–1.18 (m, 3H), 1.09 (d, $J_{H,H}$ = 6.6 Hz, 3H; $CH_3$), 1.23–1.53 (m, 3H), 1.64–1.73 (m, 1H), 1.78–1.88 (m, 1H), 2.16–2.28 (m, 1H), 2.51–2.67 (m, 1H) ppm; $^{13}$C NMR (50.3 MHz, $CDCl_3$): $\delta$ = 19.7 ($CH_3$), 19.8 ($CH_3$), 22.2 ($CH_3$), 29.3 ($CH_2$), 32.7 (CH), 36.0 ($CH_2$), 38.6 (CH), 39.8 ($CH_2$), 45.5 (CH), 52.2 (CH) ppm; $^{77}$Se NMR (38.1 MHz, $CDCl_3$): $\delta$ = 352.2 ppm. Elemental Anal. Calcd for $C_{20}H_{38}Se_2$ (436.44): C, 55.04; H, 8.77. Found: C, 54.94; H, 8.75.

#### 4.6.5. (−)-(1*R*,2*R*,5*S*,1′*S*,2′*R*,5′*S*)-Diisocarvomenthyl diselenide 21

Yield 56%; yellow oil; $[\alpha]_D^{20} = -66.6$ (*c* 10.64, $CHCl_3$); $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 0.87 (d, $J_{H,H}$ = 6.6 Hz, 3H; $CH_3$), 0.88 (d, $J_{H,H}$ = 6.6 Hz, 3H; $CH_3$), 1.06 (d, $J_{H,H}$ = 6.8 Hz, 3H; $CH_3$), 1.22–1.59 (m, 6H), 1.69–2.00 (m, 3H), 3.14 (m, 1H) ppm; $^{13}$C NMR (50.3 MHz, $CDCl_3$,): $\delta$ = 20.2 ($CH_3$), 20.3 ($CH_3$), 20.4 ($CH_3$), 25.3 ($CH_2$), 28.7 ($CH_2$), 29.9 (CH), 33.2 ($CH_2$), 35.3 (CH), 40.4 (CH), 49.6 (CH) ppm; $^{77}$Se NMR (38.1 MHz, $CDCl_3$): $\delta$ = 366.1 ppm. Elemental Anal. Calcd for $C_{20}H_{38}Se_2$ (436.44): C, 55.04; H, 8.77. Found: C, 55.01; H, 8.72.

#### 4.6.6. (+)-(1*S*,2*R*,5*S*,1′*S*,2′*R*,5′*S*)-Dineoisocarvomenthyl diselenide 22

Yield 36%; yellow oil; $[\alpha]_D^{25} = +80.4$ (*c* 0.95, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 0.88 (d, $J_{H,H}$ = 6.9 Hz, 3H; $CH_3$), 0.87 (d, $J_{H,H}$ = 6.9 Hz, 3H; $CH_3$), 0.97 (d, $J_{H,H}$ = 7.2 Hz, 3H; $CH_3$), 1.09–1.26 (m, 3H), 1.36–1.52 (m, 3H), 1.68–1.76 (m, 1H), 1.92–2.00 (m, 1H), 2.20–2.34 (m, 1H), 3.32 (dt, $J_{H,H}$ = 13.2, 3.9 Hz, 1H) ppm; $^{13}$C NMR (50.3 MHz, $CDCl_3$): $\delta$ = 13.2 ($CH_3$), 19.7 (2 × $CH_3$), 22.6 ($CH_2$), 31.9 ($CH_2$), 32.7 (CH), 32.9 (CH), 33.4 ($CH_2$), 46.1 (CH), 50.7 (CH) ppm; $^{77}$Se NMR (38.1 MHz, $CDCl_3$): $\delta$ = 353.8 ppm. Elemental Anal. Calcd for $C_{20}H_{38}Se_2$ (436.44): C, 55.04; H, 8.77. Found: C, 55.00; H, 8.56.

### 4.7. General procedure for asymmetric methoxyselenenylation

A typical experimental procedure for the asymmetric methoxyselenenylation of styrene is as follows. To a $CH_2Cl_2$ solution (14.0 mL) of diselenide (210 mg, 0.48 mmol) at −78 °C was slowly added a $CCl_4$ (0.48 mL) solution of bromine (77 mg, 0.48 mmol) under an argon atmosphere. After 15 min, a solution of silver triflate (270 mg, 1.05 mmol) in methanol (0.74 mL) was added. The resulting heterogeneous mixture was stirred at −78 °C for 20 min. Next styrene (250 mg, 2.40 mmol) was added to the solution and stirred for 2 h at the same temperature. The mixture was treated with an aqueous solution of 10% $NaHCO_3$, extracted with $CH_2Cl_2$ (3 × 20 mL), after which the combined organic phases were dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue was purified by chromatography on silica gel, yielding the addition products as yellow oils. The diastereomeric excess was determined by $^1$H and $^{77}$Se NMR spectra.

#### 4.7.1. ((1*R*,2*R*,5*R*)-2-Isopropyl-5-methylcyclohexyl)(2-methoxy-2-phenylethyl)selane 25

Purification by column chromatography on silica gel with petroleum ether/ethyl acetate, 95:5. Yield 42%; yellowish oil; $^1$H NMR (300 MHz, $CDCl_3$): major diastereomer $\delta$ = 0.82–1.04 (m, 10H), 1.12–1.98 (m, 9H), 2.73 (dd, $J_{H,H}$ = 12.2, 5.4 Hz, 1H; C*H*$_2$Se), 2.99 (dd, $J_{H,H}$ = 12.2, 8.4 Hz, 1H; C*H*$_2$Se), 3.24 (s, 3H; $OCH_3$), 4.33 (dd, $J_{H,H}$ = 8.4, 5.4 Hz, 1H; CH), 7.34 (m, 5H; 5 × $CH_{ar}$) ppm; minor diastereomer—only separated signals: 2.68 (dd, $J_{H,H}$ = 12.2, 5.4 Hz, 1H; C*H*$_2$Se) ppm; $^{13}$C NMR (50.3 MHz, $CDCl_3$): major diastereomer $\delta$ = 21.7 ($CH_3$), 22.0 ($CH_3$), 22.9 ($CH_3$), 27.0 ($CH_2$), 28.5 (CH), 30.6

($CH_2$), 32.1 ($CH_2$), 32.7 (CH), 39.1 ($CH_2$), 44.9 (CH), 45.7 (CH), 56.8 ($OCH_3$), 84.5 (CH), 126.6 (2 × $CH_{ar}$), 127.8 ($CH_{ar}$), 128.3 (2 × $CH_{ar}$), 141.5 ($C_{ar}$) ppm; minor diastereomer—only separated signals: 27.2 ($CH_2$), 28.3 (CH), 30.5 ($CH_2$), 32.0 ($CH_2$), 32.5 (CH), 56.7 ($OCH_3$), 126.7 (2 × $CH_{ar}$) ppm; $^{77}$Se NMR (38.1 MHz, $CDCl_3$): major diastereomer $\delta$ = 231.1 ppm; minor diastereomer: 233.1 ppm. Elemental Anal. Calcd for $C_{19}H_{30}OSe$ (353.4): C, 64.57; H, 8.56. Found: C, 64.40; H, 8.52.

#### 4.7.2. ((1*S*,2*R*,5*R*)-2-Isopropyl-5-methylcyclohexyl)(2-methoxy-2-phenylethyl)selane 26

Purification by column chromatography on silica gel with petroleum ether/ethyl acetate, 95:5. Yield 72%; yellowish oil; $^1$H NMR (300 MHz, $CDCl_3$): major diastereomer $\delta$ = 0.80–0.94 (m, 9H), 1.04–1.94 (m, 10H), 2.70 (dd, $J_{H,H}$ = 12.4, 5.6 Hz, 1H; C*H*$_2$Se), 2.97 (dd, $J_{H,H}$ = 12.4, 8.0 Hz, 1H; C*H*$_2$Se), 3.24 (s, 3H; $OCH_3$), 4.32 (dd, $J_{H,H}$ = 8.0, 5.6 Hz, 1H; CH), 7.34 (m, 5H; 5 × $CH_{ar}$) ppm; minor diastereomer—only separated signals: 2.65 (dd, $J_{H,H}$ = 12.4, 5.6 Hz, 1H; C*H*$_2$Se) ppm; $^{13}$C NMR (50.3 MHz, $CDCl_3$): major diastereomer $\delta$ = 19.5 ($CH_3$), 21.0 ($CH_3$), 21.3 ($CH_3$), 22.4 ($CH_2$), 27.5 (CH), 28.7 (CH), 30.2 ($CH_2$), 31.0 ($CH_2$), 37.9 ($CH_2$), 42.0 (CH), 47.2 (CH), 56.9 ($OCH_3$), 84.7 (CH), 126.7 (2 × $CH_{ar}$), 127.9 ($CH_{ar}$), 128.4 (2 × $CH_{ar}$), 141.5 ($C_{ar}$) ppm; minor diastereomer—only separated signals: 19.4 ($CH_3$), 20.9 ($CH_3$), 22.3 ($CH_2$), 41.8 (CH), 84.4 (CH) ppm; $^{77}$Se NMR (38.1 MHz, $CDCl_3$): $\delta$ = 238.2 ppm. Elemental Anal. Calcd for $C_{19}H_{30}OSe$ (353.4): C, 64.32; H, 8.56. Found: C, 64.40; H, 8.35.

#### 4.7.3. ((1*R*,2*S*,5*S*)-5-Isopropyl-2-methylcyclohexyl)(2-methoxy-2-phenylethyl)selane 27

Purification by column chromatography on silica gel with petroleum ether/ethyl acetate, 95:5. Yield 79%; yellowish oil; $^1$H NMR (300 MHz, $CDCl_3$): major diastereomer $\delta$ = 0.84 (d, $J_{H,H}$ = 6.6 Hz, 3H; $CH_3$), 0.85 (d, $J_{H,H}$ = 6.6 Hz, 3H; $CH_3$), 0.97 (d, $J_{H,H}$ = 6.6 Hz, 3H; $CH_3$), 1.17–1.56 (m, 7H), 1.61–1.67 (m, 1H), 1.96–2.08 (m, 1H), 2.68 (dd, $J_{H,H}$ = 12.0, 5.4 Hz, 1H; C*H*$_2$Se), 2.99 (dd, $J_{H,H}$ = 12.0, 8.4 Hz, 1H; C*H*$_2$Se), 3.08–3.18 (m, 1H), 3.24 (s, 3H; $OCH_3$), 4.32 (dd, $J_{H,H}$ = 8.4, 5.4 Hz, 1H; CH), 7.34 (m, 5H; 5 × $CH_{ar}$) ppm; minor diastereomer—only separated signals: 2.72 (dd, $J_{H,H}$ = 12.0, 5.4 Hz, 1H; C*H*$_2$Se), 2.95 (dd, $J_{H,H}$ = 12.0, 8.4 Hz, 1H; C*H*$_2$Se), 4.35 (dd, $J_{H,H}$ = 8.4, 5.4 Hz, 1H; CH) ppm; $^{13}$C NMR (50.3 MHz, $CDCl_3$): major diastereomer $\delta$ = 19.6 ($CH_3$), 19.9 ($CH_3$), 21.6 ($CH_3$), 29.2 ($CH_2$), 30.8 ($CH_2$), 32.2 ($CH_2$), 32.4 (CH), 37.4 (CH), 37.6 ($CH_2$), 38.9 (CH), 50.8 (CH), 56.8 ($OCH_3$), 84.8 (CH), 126.7 (2 × $CH_{ar}$), 127.8 ($CH_{ar}$), 128.5 (2 × $CH_{ar}$), 141.5 ($C_{ar}$) ppm; minor diastereomer—only separated signals: 21.5 ($CH_3$), 32.0 ($CH_2$), 84.6 (CH) ppm; $^{77}$Se NMR (38.1 MHz, $CDCl_3$): major diastereomer $\delta$ = 146.9 ppm; minor diastereomer: 146.0 ppm. Elemental Anal. Calcd for $C_{19}H_{30}OSe$ (353.4): C, 64.57; H, 8.56. Found: C, 64.60; H, 8.59.

#### 4.7.4. ((1*S*,2*S*,5*S*)-5-Isopropyl-2-methylcyclohexyl)(2-methoxy-2-phenylethyl)selane 28

Purification by column chromatography on silica gel with petroleum ether/ethyl acetate, 95:5. Yield 75%; yellowish oil; $^1$H NMR (200 MHz, $CDCl_3$): major diastereomer $\delta$ = 0.84 (d, $J_{H,H}$ = 6.6 Hz, 3H; $CH_3$), 0.85 (d, $J_{H,H}$ = 6.6 Hz, 3H; $CH_3$), 0.97 (d, $J_{H,H}$ = 7.0 Hz, 3H; $CH_3$), 1.01–1.12 (m, 4H), 1.15–1.47 (m, 2H), 1.55–1.92 (m, 2H), 2.02–2.41 (m, 2H) 2.79 (dd, $J_{H,H}$ = 12.2, 5.4 Hz, 1H; C*H*$_2$Se), 3.00 (dd, $J_{H,H}$ = 12.2, 8.0 Hz, 1H; C*H*$_2$Se), 3.24 (s, 3H; $OCH_3$), 4.32 (dd, $J_{H,H}$ = 8.0, 5.4 Hz, 1H; CH), 7.34 (m, 5H; 5 × $CH_{ar}$) ppm; minor diastereomer—only separated signals: 2.75 (dd, $J_{H,H}$ = 12.2, 5.4 Hz, 1H; C*H*$_2$Se), 2.93 (dd, $J_{H,H}$ = 12.2, 8.0 Hz, 1H; C*H*$_2$Se), 3.25 (s, 3H; $OCH_3$), 4.30 (dd, $J_{H,H}$ = 8.0, 5.4 Hz, 1H; CH) ppm; $^{13}$C NMR (75.5 MHz, $CDCl_3$): major diastereomer $\delta$ = 19.6 ($CH_3$), 19.8 ($CH_3$), 22.1 ($CH_3$), 29.2 ($CH_2$), 29.6 ($CH_2$), 32.6 (CH), 35.9 ($CH_2$), 38.8 (CH), 39.4 ($CH_2$), 45.4 (CH), 48.1 (CH), 56.9 ($OCH_3$), 84.6 (CH), 126.7 (2 × $CH_{ar}$), 127.9 ($CH_{ar}$), 128.4 (2 × $CH_{ar}$), 141.4 ($C_{ar}$) ppm; minor diastereomer—only separated signals: 22.0 ($CH_3$), 29.3 ($CH_2$), 38.6 (CH), 39.3 ($CH_2$), 45.3 (CH), 84.5 (CH), 126.8 (2 × $CH_{ar}$) ppm; $^{77}$Se NMR (38.1 MHz, $CDCl_3$): major diastereomer $\delta$ = 212.4 ppm; minor diastereomer: 214.2 ppm. Elemental Anal. Calcd for $C_{19}H_{30}OSe$ (353.4): C, 64.57; H, 8.56. Found: C, 64.48; H, 8.49.

#### 4.7.5. ((1*R*,2*R*,5*S*)-5-Isopropyl-2-methylcyclohexyl)(2-methoxy-2-phenylethyl)selane 29

Purification by column chromatography on silica gel with petroleum ether/ethyl acetate, 95:5. Yield 51%; yellowish oil; $^1$H NMR (300 MHz, $CDCl_3$): major diastereomer $\delta$ = 0.83 (d, $J_{H,H}$ = 6.6 Hz, 3H; $CH_3$), 0.86 (d, $J_{H,H}$ = 6.6 Hz, 3H; $CH_3$), 0.99 (d, $J_{H,H}$ = 7.0 Hz, 3H; $CH_3$), 1.22–1.48 (m, 5H), 1.54–1.92 (m, 4H), 2.75 (dd, $J_{H,H}$ = 12.3, 5.8 Hz, 1H; C*H*$_2$Se), 2.80–2.90 (m, 1H), 2.98 (dd, $J_{H,H}$ = 12.3, 7.8 Hz, 1H; C*H*$_2$Se), 3.24 (s, 3H; $OCH_3$), 4.32 (dd, $J_{H,H}$ = 7.8, 5.8 Hz, 1H; CH), 7.34 (m, 5H; 5 × $CH_{ar}$) ppm; minor diastereomer—only separated signals: 0.84 (d, $J_{H,H}$ = 6.6 Hz, 3H; $CH_3$), 0.87 (d, $J_{H,H}$ = 6.6 Hz, 3H; $CH_3$), 1.01 (d, $J_{H,H}$ = 7.0 Hz, 3H; $CH_3$), 4.30 (dd, $J_{H,H}$ = 7.8, 5.8 Hz, 1H; CH) ppm; $^{13}$C NMR (75.5 MHz, $CDCl_3$): major diastereomer $\delta$ = 19.9 ($CH_3$), 20.1 ($CH_3$), 20.3 ($CH_3$), 24.9 ($CH_2$), 28.7 ($CH_2$), 30.2 (CH), 30.9 ($CH_2$), 32.8 ($CH_2$), 35.5 (CH), 40.3 (CH), 45.2 (CH), 56.9 ($OCH_3$), 84.5 (CH), 126.6 (2 × $CH_{ar}$), 127.9 ($CH_{ar}$), 128.4 (2 × $CH_{ar}$), 141.4 ($C_{ar}$) ppm; minor diastereomer—only separated signals: 20.0 ($CH_3$), 20.2 ($CH_3$), 28.6 ($CH_3$), 30.1 (CH), 32.7 ($CH_2$), 35.4 (CH), 40.4 (CH), 45.1 (CH), 128.5 (2 × $CH_{ar}$) ppm; $^{77}$Se NMR (38.1 MHz, $CDCl_3$): major diastereomer $\delta$ = 238.3 ppm; minor diastereomer: 238.7 ppm. Elemental Anal. Calcd for $C_{19}H_{30}OSe$ (353.4): C, 64.57; H, 8.56. Found: C, 64.41; H, 8.52.

#### 4.7.6. ((1*S*,2*R*,5*S*)-5-Isopropyl-2-methylcyclohexyl)(2-methoxy-2-phenylethyl)selane 30

Purification by column chromatography on silica gel with petroleum ether/ethyl acetate, 95:5. Yield 41%; yellowish oil; $^1$H NMR (200 MHz, $CDCl_3$): major diastereomer $\delta$ = 0.82 (d, $J_{H,H}$ = 6.6 Hz, 3H; $CH_3$), 0.86 (d, $J_{H,H}$ = 6.6 Hz, 3H; $CH_3$), 1.22 (d, $J_{H,H}$ = 7.0 Hz, 3H; $CH_3$), 1.23–1.62 (m, 6H), 1.63–1.76 (m, 2H), 1.80–2.20 (m, 2H), 2.76 (dd, $J_{H,H}$ = 12.0, 5.8 Hz, 1H; C*H*$_2$Se), 2.97 (dd, $J_{H,H}$ = 12.0, 8.4 Hz, 1H; C*H*$_2$Se), 3.24 (s, 3H; $OCH_3$), 4.33 (dd, $J_{H,H}$ = 8.4, 5.8 Hz, 1H; CH), 7.34 (m, 5H; 5 × $CH_{ar}$) ppm; minor diastereomer—only separated signals: 2.72 (dd, $J_{H,H}$ = 12.0, 5.8 Hz, 1H; C*H*$_2$Se), 2.92 (dd, $J_{H,H}$ = 12.0, 8.4 Hz, 1H; C*H*$_2$Se), 4.30 (dd, $J_{H,H}$ = 8.4, 5.8 Hz, 1H; CH) ppm; $^{13}$C NMR (50.3 MHz, $CDCl_3$): major diastereomer $\delta$ = 19.8 ($CH_3$), 21.1 ($CH_3$), 22.6 ($CH_3$), 24.4 ($CH_2$), 28.8 ($CH_2$), 30.7 (CH), 31.9 ($CH_2$), 34.1 ($CH_2$), 36.6 (CH), 42.2 (CH), 46.0 (CH), 56.7 ($OCH_3$), 84.4 (CH), 126.7 (2 × $CH_{ar}$), 127.9 ($CH_{ar}$), 128.4 (2 × $CH_{ar}$), 143.2 ($C_{ar}$) ppm; minor diastereomer—only separated signals: 19.7 ($CH_3$), 22.5 ($CH_3$), 24.3 ($CH_2$), 28.7 ($CH_2$), 31.8 ($CH_2$), 42.1 (CH), 45.9 (CH), 56.6 ($OCH_3$), 84.3 (CH) ppm; $^{77}$Se NMR (38.1 MHz, $CDCl_3$): major diastereomer $\delta$ = 226.1 ppm; minor diastereomer: 229.3 ppm. Elemental Anal. Calcd for $C_{19}H_{30}OSe$ (353.4): C, 64.57; H, 8.56. Found: C, 64.45; H, 8.42.

### 4.8. Computational methods

All theoretical calculations were carried out by using the GAUSSIAN 03 program.[23] The hybrid Berke 3-Lee–Yang–Parr (B3LYP) exchange–correlation functional[24,25] was applied to DFT calculations. Geometries were fully optimized at the B3LYP/6-311G(d) level of theory. For all stable conformers, the nature as a potential energy minimum was established at the B3LYP/6-311G(d) level by verifying that all vibrations frequencies were real.

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