DOI: 10.1002/ejoc.200600044

Syntheses and Reactions of New Optically Active Terpene Dialkyl Diselenides

Jacek Ścianowski,*[a] Zbigniew Rafiński,[a] and Andrzej Wojtczak[a]

Keywords: Terpenoids / Selenium / Electrophilic addition / Asymmetric synthesis

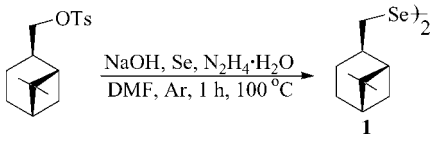
The reaction of sodium diselenide with optically active alkyl tosylates or chlorides is found to be a useful method for the synthesis of optically active dialkyl diselenides. Optically active monoterpene diselenides derived from menthane, carane, pinane, and bornane systems have been obtained. The influence of the terpene fragment of the obtained diselenides on the diastereomeric excess of the methoxyselenylation products has been investigated. The best result for methoxyselenylation was observed for (–)-diisopinocamphyl diselenide.

Introduction

In recent years the synthetic[1] and pharmacological[2] role of organoselenium compounds has been increasingly appreciated. This great interest in organoselenium chemistry, especially in the reactions of optically active diselenides,[3] prompted us to search for a useful method for the synthesis of optically active terpene dialkyl diselenides.

The only terpenes extensively studied so far are optically active diselenides that are camphor derivatives. These diselenides were obtained either by oxidation of the reaction products of organometallic compounds with selenium,[4] the reaction of selenocyanates with samarium iodide,[5] or the reaction of bromides with sodium diselenide.[6] Optically active diselenides derived from camphor have been used, for example, in methoxy- and hydroxyselenylation reactions and in selenocyclizations, amongst others.[4–6]

In a previous paper we proposed a new method for the synthesis of dialkyl diselenides based on the reaction of alkyl tosylates with sodium diselenide, and we successfully employed this method for the synthesis of optically active bis(*cis*-myrtanyl) diselenide (**1**; Scheme 1).[7]



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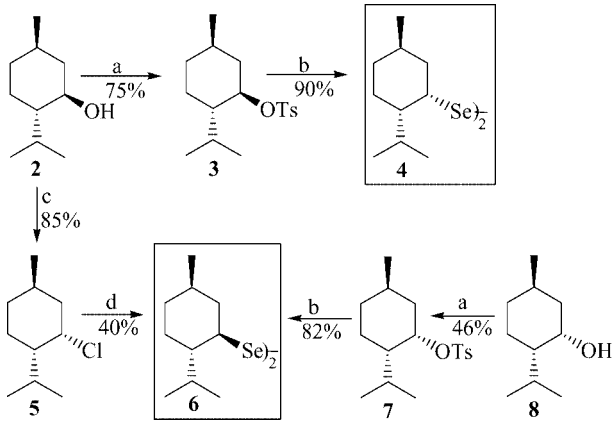
Scheme 1. Synthesis of bis(*cis*-myrtanyl) diselenide (**1**).

We present here a synthesis of optically active diselenides derived from menthane, carane, pinane, and bornane systems based on the reaction of sodium diselenide with alkyl tosylates or chlorides. The resulting diselenides have been investigated in the methoxyselenylation reaction.

[a] Department of Chemistry, Nicolaus Copernicus University, 7 Gagarin Street, 87-100 Torun, Poland,
E-mail: jsch@chem.uni.torun.pl

Results and Discussion

This research began with the synthesis of menthane diselenides. The reactions were conducted as a one-step version.[7] Treatment of (–)-menthol (**2**) with tosyl chloride in pyridine[8] led to (–)-menthyl tosylate (**3**), which gave (+)-dineomenthyl diselenide (**4**) upon treatment with sodium diselenide (Scheme 2).



Scheme 2. Synthesis of (+)-dineomenthyl diselenide (**4**) and (–)-dimenthyl diselenide (**6**). Reagents and conditions: a) TsCl, pyridine, 24 h, 0 °C; b) NaOH, Se, $N_2H_4·H_2O$, DMF, Ar, 1 h, 100 °C; c) CCl_4, PPh_3, 24 h, reflux; d) NaOH, Se, $N_2H_4·H_2O$, DMF, Ar, 2 h, 100 °C.

The structure of **4** (Figure 1) was confirmed by an X-ray crystallographic analysis.[9]

The absolute configurations at C-1 and C-1′ were established as *S*,*S*, which confirms the S_N2 substitution mechanism of the toluenesulfonyl group by sodium diselenide. The diselenide bridge torsion angle C(1)–Se(1)–Se(2)–C(1′) is –112.1(4)°. The cyclohexyl rings in both neomentyl moieties have a chair conformation.

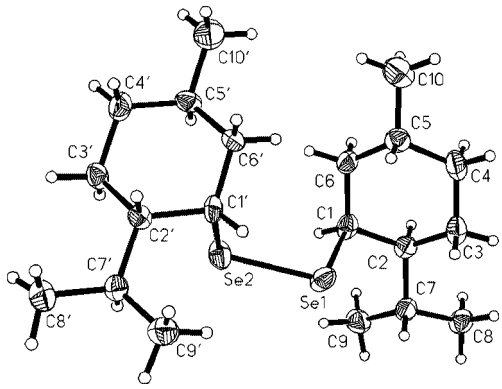


Figure 1. X-ray structure of (+)-dineomenthyl diselenide (**4**). Selected bond lengths [Å] and angles [°]: Se(1)–Se(2) 2.3182(11), Se(1)–C(1) 2.008(8), Se(2)–C(1′) 1.990(7); C(1)–Se(1)–Se(2) 100.6(2) C(1′)–Se(2)–Se(1) 100.05(18).

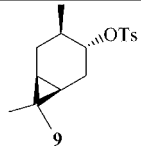
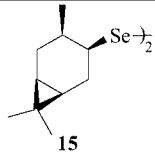
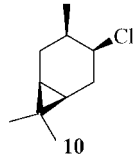
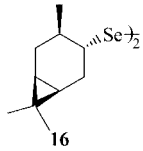
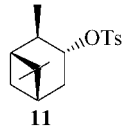
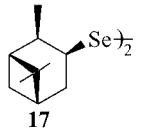
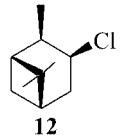
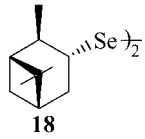
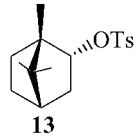
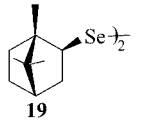
(+)-Neomenthyl chloride (**5**) was obtained as a result of the reaction of (–)-menthol with CCl_4 and PPh_3.[10] When treated with sodium diselenide, chloride **5** gave (–)-dimenthyl diselenide (**6**). Diselenide **6** could also be obtained from the reaction of sodium diselenide with (+)-neomenthyl tosylate (**7**), which was itself formed from (+)-neomenthol (**8**; Scheme 2). Analogous reactions were conducted with (+)-menthol to give (–)-dineomenthyl and (+)-dimenthyl diselenides, respectively.

Subsequent studies on the synthesis of optically active diselenides were carried out on the bicyclic terpene systems using (–)-*trans*-4-caranol,[11] (–)-isopinocampheol,[12] and (–)-borneol. The respective tosylates **9**, **11**, and **13**, and the chlorides **10** and **12** were obtained by the methods described above.[8,10] Because of the instability of the bicyclic terpene tosylates, which undergo spontaneous decomposition even at room temperature, the diselenides were obtained in a two-step procedure. The respective tosylate or chloride was added to the sodium diselenide prepared in the first step (NaOH, Se, $N_2H_4{\cdot}H_2O$, DMF, Ar, 100 °C, 15 minutes). The syntheses of (+)-bis(*cis*-4-caranyl) diselenide (**15**), (–)-bis(*trans*-4-caranyl) diselenide (**16**), (+)-dipinocamphyl diselenide (**17**), (–)-diisopinocamphyl diselenide (**18**), and (–)-diisobornyl diselenides (**19**) are presented in Table 1. The structures of all diselenides obtained were established on the basis of their ^1H, ^{13}C, and ^{77}Se NMR spectra.

(–)-Dipinocamphyl and (+)-diisopinocamphyl diselenides were also obtained from (+)-isopinocampheol. The synthesis of diselenide from isobornyl chloride failed.

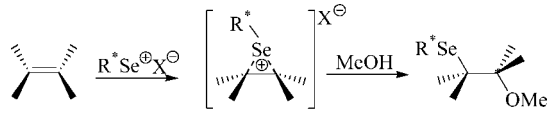
The optically active terpene diselenides were used for the asymmetric electrophilic methoxyselenylation. All chiral diselenides used in the methoxyselenylation reactions described so far have contained heteroatoms, which control the diastereomeric excess of the resulting products. There is much theoretical and experimental evidence concerning the influence of heteroatoms in the literature.[3,4] So, for comparison, we decided to investigate the influence of the structure of the unfunctionalized terpene diselenides on the diastereomeric excess of the formed adducts in the methoxyselenylation.

Table 1. Synthesis of diselenides **15**–**19**.

Entry	Tosylate[a] /chloride[b]	Diselenide	Yield (%)	^{77}Se NMR
1	 **9**	 **15**	95	351.1
2	 **10**	 **16**	70	366.9
3	 **11**	 **17**	64	353.2
4	 **12**	 **18**	32	444.1
5	 **13**	 **19**	33	464.4

[a] See ref.[8] [b] See ref.[10]

The addition of the selenic electrophile to a double bond, conducted in methanol, proceeds as a two-stage process, namely formation of a seleniranic ion and subsequent reaction with a nucleophile (Scheme 3).



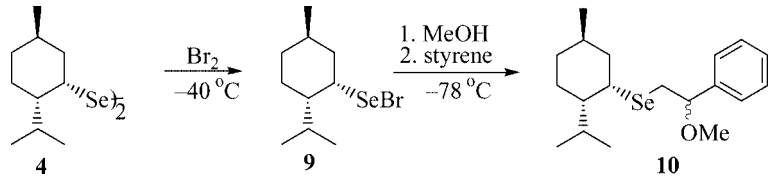
$X^{\ominus}$ = $Br^{\ominus}$, $Cl^{\ominus}$, $OSO_3H^{\ominus}$, $OTf^{\ominus}$

$R^*Se^{\oplus}X^{\ominus}$ = optically active selenic electrophile

Scheme 3. Mechanism of methoxyselenylation.

The optically active selenic electrophiles hitherto obtained were synthesized in the process of reaction of selenides with bromine,[4d] sulfuryl chloride,[4a–4d,4f,4j,4l] or ammonium persulfate.[4d,4g,4h] A bromide is usually changed for a triflate anion by treatment with silver triflate.[4d,4e,4i,4f] PF_6^- and BF_4^- have also been used as counterions.[4f]

The preliminary studies on the choice of the reaction conditions were conducted with (+)-dineomenthyl diselenide (**4**; Scheme 4). We investigated the influence of the solvent, the temperature, and the kind of counterion on the yield and the diastereomeric excess for the addition to styrene.



4 9 10

Scheme 4. Addition of bromide **9** to styrene in the presence of methanol.

For this purpose, we used THF, *tert*-butyl methyl ether, and dichloromethane as solvents (Table 2). The best results were obtained for dichloromethane. In the case of *tert*-butyl methyl ether, the process was conducted at 0 °C because at lower temperatures the reaction failed.

Table 2. Influence of solvent on the diastereomeric excess of the methoxyselenylation with (+)-dineomenthyl diselenide.

Solvent	Temp. [°C]	Time [h]	Yield [%]	*dr*[a]
THF	–78	6	62	50:50
*t*BuOMe	–78	6	0	–
	0	6	72	52:48
CH_2Cl_2	–78	2	93	70:30

[a] Estimated on the basis of ^{1}H NMR spectroscopy.

The investigation of the influence of the temperature and counterion on the ratio of the produced diastereomers for the reaction conducted in dichloromethane was the subsequent step of our study (Table 3). The best diastereomeric excesses were obtained at –78 °C both for a bromide ion and a triflate. The lowering of the reaction temperature in the case of the bromide ion to –95 °C diminished the product yield. A similar drop in yield was observed for the triflate ion. A lowering of the diastereomeric excess was also observed in both cases with a decrease of temperature. The use of sulfuryl chloride and ammonium persulfate was unsuccessful.

Table 3. Influence of temperature and counterion on the methoxyselenylation with (+)-dineomenthyl diselenide (**4**).

Counterion	Temp. [°C]	Time [h]	Yield [%]	*dr*[a]
Br^-	–95	3	43	60:40
	–78	2	93	70:30
OTf^-	–95	3	48	60:40
	–78	2	86	70:30
Cl^-	–78	2	no reaction	–
HSO_4^- [b]	25	24	no reaction	–
	40	6	no reaction	–

[a] Estimated on the basis of ^{1}H NMR spectroscopy. [b] The reactions were carried out with the addition of trifluoromethanesulfonic acid.

For comparison, we also investigated the influence of counterion and temperature for (–)-dimenthyl diselenide (**6**) (Table 4). The position of a diselenide group in a *trans* relation to an isopropyl group exerts a radical influence on the reaction rate. In the case of bromide ion for the reaction conducted at –78 °C we observed mainly the bromoselenylation product, whereas for the triflate ion the methoxyselenylation product dominated. A change of temperature did not influence the diastereomeric excess.

Table 4. Influence of temperature and counterion on the methoxyselenylation with (–)-dimenthyl diselenide (**6**).

Counterion	Temp. [°C]	Time [h]	Yield [%]	*dr*[a]
Br^-	–78	2	11	56:44
OTf^-	–95	3	90	65:35
	–78	2	80	62:38

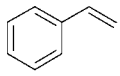
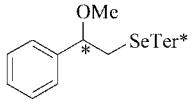
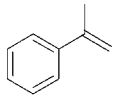
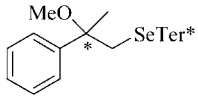
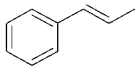
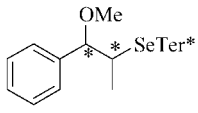
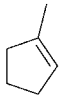
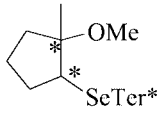
[a] Estimated on the basis of ^{1}H NMR spectroscopy.

On the basis of the obtained results we conducted subsequent methoxyselenylation reactions in dichloromethane at –78 °C using the triflate anion as a counterion. For these methoxyselenylations we used diselenides derived from menthane (**4** and **6**), carane (**15** and **16**), and pinane (**17** and **18**), as well as bis(*cis*-myrtanyl) diselenide (**1**). Styrene, α-methylstyrene, β-*trans*-methylstyrene, and 1-methylcyclopentene served as alkenes (Table 5). The methoxyselenylation products **20**–**47** were isolated by column chromatography and their diastereomeric excess was estimated by means of ^{1}H NMR spectroscopy. The pure compounds were isolated in all cases except for the reaction of *cis*-caranyl and pinocamphyl diselenides with β-*trans*-methylstyrene **37** and **40** (Table 5), whose purification by means of chromatographic techniques led to partial decomposition. In this case the diastereomeric excess was established from the ^{1}H NMR spectrum of the crude mixtures. The best diastereomeric excess was obtained for the menthyl and pinane diselenides. Much worse results were observed for *cis*-caranyl, *trans*-caranyl, and myrtanyl diselenides. The studies with the (+)-diisobornyl diselenide (**19**) failed because of its instability under the reaction conditions and spontaneous decomposition.

Conclusions

A series of new, optically active dialkyl diselenides have been obtained by treatment of optically active alkyl tosylates and chlorides derived from mono- and bicyclic terpenes with sodium diselenide. The obtained diselenides have been used with success as selenic electrophiles for asymmetric methoxyselenylation. The best results were observed for (–)-diisopinocamphyl diselenide (**18**), which shows that the structure of the diselenides has a strong influence on the diastereomeric excess of the formed adducts. Further investigation of the functionalization of these terpene diselenides and the influence on the diastereomeric excess of the resulting products is in progress.

Table 5. Asymmetric methoxyselenylation of olefins with menthyl, pinanyl, and caranyl diselenides.

Entry	Alkene	Diselenide	Structure[a]	Product	*dr* [b]	Yield (%)
1		**1**		**20**	51:49	64
		4		**21**	70:30	86
		6		**22**	62:38	79
		15		**23**	52:48	78
		16		**24**	53:47	81
		17		**25**	52:48	48
		18		**26**	82:18	57
2		**1**		**27**	52:48	50
		4		**28**	62:38	33
		6		**29**	72:28	55
		15		**30**	52:48	94
		16		**31**	52:48	89
		17		**32**	61:39	65
		18		**33**	66:34	76
3		**1**		**34**	52:48	86
		4		**35**	54:46	27
		6		**36**	52:48	62
		15		**37**	52:48[c]	60
		16		**38**	58:42	81
		17		**39**	62:38	60
		18		**40**	65:35[c]	48
4		**1**		**41**	52:48	18
		4		**42**	78:22	33
		6		**43**	75:25	84
		15		**44**	65:35	18
		16		**45**	70:30	33
		17		**46**	70:30	32
		18		**47**	72:28	44

[a] Ter*: terpene fragment. [b] Estimated on the basis of ^{1}H and ^{77}Se NMR spectroscopy. [c] Estimated on the basis of ^{1}H NMR spectroscopy of the crude product.

Experimental Section

General: ^{1}H and ^{13}C NMR spectra were recorded with Bruker Avance 300 or Varian Gemini 200 spectrometers at 300, 200, 75, and 50.3 MHz, respectively (*J* values are given in Hz). ^{77}Se NMR spectra were recorded with a Varian Gemini 200 instrument at 38 MHz. Optical rotations were measured in 50-mm cells with a polAAr 3000 polarimeter. All melting points are uncorrected. Elemental analysis was carried out with a vario MACRO elemental analyzer. Column chromatography was performed with Merck silica gel 60 (70–230 mesh) or basic alumina. Methanol and dichloromethane were distilled from calcium hydride. Commercial grade *N*,*N*-dimethylformamide was used without purification. All methoxyselenylation reactions were carried out under an argon atmosphere. The same general procedure as given for entries 2 and 3 of Table 5 below was employed for all reactions in Tables 2–4, using styrene, with the variations indicated in these tables. Diastereomeric excesses were measured by integration of the ^{1}H NMR signals of the methoxy groups, which were generally well-separated for the two diastereomers, or by integration of the ^{77}Se NMR signals.

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). The reaction mixture was stirred for 1 h at the same temperature. It was then poured into water (100 mL) and the resulting precipitate was filtered off and dried under vacuum. The crude product was used without further purification.

(–)-Menthyl Tosylate (3): Yield: 25.6 g (75%), white solid; m.p. 95–97 °C. $[\alpha]_D^{20}$ = –72.79 (*c* = 6.04, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 7.80 (d, $^{3}J_{H,H}$ = 8.0 Hz, 2 H, 2×CH), 7.32 (d, $^{3}J_{H,H}$ = 8.0 Hz, 2 H, CH), 4.40 (dt, $^{3}J_{H,H}$ = 10.6 and 4.4 Hz, 1 H, CH), 2.44 (s, 3 H, CH_3), 2.15 (m, 1 H, CH), 1.89 (m, 1 H, CH), 1.69–0.93 (m, 7 H), 0.87 (d, $^{3}J_{H,H}$ = 6.2 Hz, 3 H, CH_3), 0.83 (d, $^{3}J_{H,H}$ = 7.0 Hz, 3 H, CH_3), 0.52 (d, $^{3}J_{H,H}$ = 7.0 Hz, 3 H, CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ = 144.2, 134.8, 129.6 (2 C), 127.7 (2 C), 83.6, 47.6, 41.9, 33.7, 31.6, 25.4, 22.9, 21.8, 21.5, 20.8, 15.2 ppm.

(+)-Neomentyl Tosylate (7): Yield: 15.7 g (46%), white solid; m.p. 59–62 °C. $[\alpha]_D^{20}$ = –25.10 (*c* = 3.20, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 7.82 (d, $^{3}J_{H,H}$ = 8.0 Hz, 2 H, 2×CH), 7.31 (d, $^{3}J_{H,H}$ = 8.0 Hz, 2 H, CH), 5.01 (m, 1 H), 2.44 (s, 3 H, CH_3), 1.75 (m, 9 H), 0.83 (d, $^{3}J_{H,H}$ = 6.6 Hz, 3 H, CH_3), 0.78 (d, $^{3}J_{H,H}$ = 6.6 Hz, 3 H, CH_3), 0.75 (d, $^{3}J_{H,H}$ = 7.0 Hz, 3 H, CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ = 144.1, 135.3, 129.5 (2 C), 127.5

(2 C), 81.6, 47.8, 39.6, 34.4, 28.5, 25.8, 24.1, 21.8, 21.5, 20.6, 20.5 ppm.

(–)-*trans*-4-Caranyl Tosylate (9): Yield: 29.4 g (86%), white solid; m.p. 42–43 °C. $[\alpha]_D^{20}$ = –46.17 (*c* = 8.65, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.77 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H, 2×CH), 7.32 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H, 2×CH), 4.10–3.97 (m, 1 H), 2.44 (s, 3 H, CH_3), 2.19–1.34 (m, 5 H), 0.93 (s, 3 H, CH_3), 0.88 (s, 3 H, CH_3), 0.84–0.79 (m, 1 H), 0.74 (d, $^3J_{H,H}$ = 6.4 Hz, 3 H, CH_3), 0.70–0.61 (m, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ = 144.3, 134.8, 129.6 (2 C), 127.7 (2 C), 87.5, 34.0, 28.4, 28.2, 27.8, 21.6, 21.4, 19.7, 17.8, 17.7, 15.8 ppm.

(–)-Isopinocamphyl Tosylate (11): Yield: 22.2 g (65%), white solid; m.p. 58–60 °C. $[\alpha]_D^{20}$ = –36.50 (*c* = 7.80, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.82 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H, 2×CH), 7.34 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H, 2×CH), 4.81–4.71 (m, 1 H, CH), 2.44 (s, 3 H, CH_3), 2.40–2.11 (m, 3 H), 1.98–1.74 (m, 3 H), 1.18 (s, 3 H, CH_3), 1.05 (d, $^3J_{H,H}$ = 10.0 Hz, 1 H, CH), 0.89 (d, $^3J_{H,H}$ = 7.4 Hz, 3 H, CH_3), 0.85 (s, 3 H, CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ = 144.4, 134.5, 129.7 (2 C), 127.8 (2 C), 83.0, 47.5, 44.0, 42.6, 38.2, 41.3, 35.8, 32.2, 23.9, 21.6, 19.6 ppm.

(–)-Bornyl Tosylate (13): Yield: 23.5 g (69%), white solid; m.p. 74–76 °C. $[\alpha]_D^{20}$ = –11.24 (*c* = 10.05, $CHCl_3$). ^1H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 7.78 (d, $^3J_{H,H}$ = 8.2 Hz, 2 H, 2×CH), 7.32 (d, $^3J_{H,H}$ = 8.2 Hz, 2 H, 2×CH), 4.60 (m, 1 H, CH), 2.44 (s, 3 H, CH_3), 2.20–2.02 (m, 1 H, CH), 1.98–1.58 (m, 3 H), 1.34–1.21 (m, 2 H), 1.18 (dd, $^2J_{H,H}$ = 9.8, $^3J_{H,H}$ = 3.2 Hz, 2 H, CH_2), 0.82 (s, 3 H, CH_3), 0.80 (s, 3 H, CH_3), 0.71 (s, 3 H, CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ = 144.3, 134.3, 129.6 (2 C), 127.7 (2 C), 87.9, 49.5, 47.5, 44.6, 36.0, 27.7, 26.5, 21.5, 19.6, 18.6, 12.8 ppm.

Preparation of Chlorides. General Procedure: A solution of the terpene alcohol (100 mmol) and triphenylphosphane (200 mmol) in carbon tetrachloride (240 mL) was refluxed for 24 h. It was then cooled and petroleum ether (300 mL) was added. The formed precipitate was filtered off under vacuum, concentrated, and evaporated by means of a rotary evaporator. The product was isolated by distillation under reduced pressure.

(+)-Neomenthyl Chloride (5): Yield: 14.8 g (85%), colorless liquid. $[\alpha]_D^{20}$ = +53.03 (*c* = 9.05, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 4.52 (m, 1 H), 2.08–2.03 (m, 1 H), 1.98–1.86 (m, 1 H), 1.77–1.69 (m, 2 H), 1.59–1.51 (m, 2 H), 1.42–1.30 (m, 2 H), 1.08–1.00 (m, 1 H) 0.93 (d, $^3J_{H,H}$ = 6.6 Hz, 3 H, CH_3), 0.91 (d, $^3J_{H,H}$ = 6.6 Hz, 3 H, CH_3), 0.88 (d, $^3J_{H,H}$ = 6.6 Hz, 3 H, CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ = 63.3, 48.9, 43.2, 34.8, 30.0, 25.8, 24.2, 21.8, 20.7, 20.1 ppm.

(+)-*cis*-4-Caranyl Chloride (10): Yield: 11.3 g (66%), colorless liquid. $[\alpha]_D^{20}$ = +26.76 (*c* = 12.45, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 4.32–4.24 (m, 1 H), 2.63–2.46 (m, 1 H), 1.90 (dt, $^3J_{H,H}$ = 16.8 and 3.0 Hz, 1 H, CH), 1.72–1.56 (m, 2 H), 1.08 (s, 3 H, CH_3), 0.97 (d, $^3J_{H,H}$ = 6.4 Hz, 3 H, CH_3), 1.07–0.76 (m, 2 H), 0.41 (dt, $^3J_{H,H}$ = 9.2 and 3.0 Hz, 1 H, CH) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ = 63.6, 34.0, 29.2, 28.7, 23.0, 22.1, 19.0, 17.8, 17.6, 15.9 ppm.

(+)-Pinocamphyl Chloride (12): Yield: 7.7 g (45%), colorless liquid. $[\alpha]_D^{20}$ = +24.66 (*c* = 20.00, EtOH). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 4.71 (dt, $^3J_{H,H}$ = 9.9 and 7.8 Hz, 1 H, CH), 2.71–2.57 (m, 2 H), 2.25–2.17 (m, 2 H), 2.00–1.86 (m, 2 H), 1.25 (d, $^3J_{H,H}$ = 7.2 Hz, 1 H, CH), 1.21 (d, $^3J_{H,H}$ = 7.8 Hz, 3 H, CH_3), 1.20 (s, 3 H, CH_3), 1.06 (s, 3 H, CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ = 55.8, 48.4, 41.5, 39.6, 39.4, 38.7, 28.5, 27.3, 23.1, 18.3 ppm.

Preparation of Diselenides. General Procedure: The standard synthesis of diselenides was conducted under argon, by adding hydrazine hydrate (0.6 mL) dropwise to 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 ethereal layers were washed with water (100 mL), dried with anhydrous $MgSO_4$, and the solvents evaporated. The product was purified by column chromatography (petroleum ether, silica gel). The structures of all diselenides obtained were established on the basis of their ^1H, ^{13}C, and ^{77}Se NMR spectra.

(+)-Dineomenthyl Diselenide (4): Yield: 4.3 g (90%), yellow crystals; m.p. 57–59 °C. $[\alpha]_D^{20}$ = +302.15 (*c* = 5.58, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 3.64 (m, 2 H, 2×CH), 2.32 (m, 2 H, 2×CH), 2.02–1.55 (m, 10 H), 1.40–1.04 (m, 6 H), 0.97 (d, $^3J_{H,H}$ = 6.4 Hz, 6 H, 2×CH_3), 0.91 (d, $^3J_{H,H}$ = 6.6 Hz, 6 H, 2×CH_3), 0.90 (d, $^3J_{H,H}$ = 6.4 Hz, 6 H, 2×CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ = 51.7 (2 C), 49.6 (2 C), 41.9 (2 C), 35.4 (2 C), 31.3 (2 C), 27.4 (2 C), 26.7 (2 C), 22.1 (2 C), 21.0 (2 C), 20.8 (2 C) ppm. ^{77}Se NMR (38 MHz, $CDCl_3$, 25 °C): δ = 290.4 ppm. $C_{20}H_{38}Se_2$ (436.44): calcd. C 55.04, H 8.77; found C 55.08, H 8.82.

(–)-Dimenthyl Diselenide (6): Yield: 1.9 g (40%), yellow oil. $[\alpha]_D^{20}$ = –306.27 (*c* = 5.10, $CHCl_3$). ^1H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 2.85 (dt, $^3J_{H,H}$ = 11.2 and 3.8 Hz, 2 H, 2×CH), 2.42–2.22 (m, 4 H), 1.73–0.98 (m, 14 H), 0.91 (d, $^3J_{H,H}$ = 7.2 Hz, 6 H, 2×CH_3), 0.90 (d, $^3J_{H,H}$ = 6.2 Hz, 6 H, 2×CH_3), 0.77 (d, $^3J_{H,H}$ = 7.2 Hz, 6 H, 2×CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ = 47.9 (2 C), 47.7 (2 C), 45.4 (2 C), 34.8 (2 C), 34.4 (2 C), 29.1 (2 C), 24.9 (2 C), 22.2 (2 C), 21.4 (2 C), 15.3 (2 C) ppm. ^{77}Se NMR (38 MHz, $CDCl_3$, 25 °C): δ = 336.3 ppm. $C_{20}H_{38}Se_2$ (436.44): calcd. C 55.04, H 8.77; found C 55.04, H 8.85.

(+)-Bis(*cis*-4-caranyl) Diselenide (15): Yield: 4.6 g (95%), yellow oil. $[\alpha]_D^{20}$ = +140.95 (*c* = 10.85, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 3.39–3.46 (m, 2 H), 2.34–2.44 (m, 2 H), 1.77–1.91 (m, 4 H), 1.50–1.60 (m, 2 H), 1.00 (s, 6 H, CH_3), 0.99 (s, 6 H, 2×CH_3), 0.96 (d, $^3J_{H,H}$ = 7.2 Hz, 6 H, 2×CH_3), 0.77–0.90 (m, 2 H), 0.56–0.71 (m, 4 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ = 49.5 (2 C), 31.4 (2 C), 28.5 (2 C), 26.4 (2 C), 25.8 (2 C), 21.5 (2 C), 21.4 (2 C), 20.1 (2 C), 17.8 (2 C), 15.9 (2 C) ppm. ^{77}Se NMR (38 MHz, $CDCl_3$, 25 °C): δ = 351.1 ppm. $C_{20}H_{34}Se_2$ (432.40): calcd. C 55.55, H, 7.92; found C 55.56, H 7.86.

(–)-Bis(*trans*-4-caranyl) Diselenide (16): Yield: 3.4 g (70%), yellow oil. $[\alpha]_D^{20}$ = –140.95 (*c* = 7.85, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.54 (m, 2 H), 2.05 (m, 6 H), 1.32 (m, 2 H), 1.02 (d, $^3J_{H,H}$ = 6.3 Hz, 6 H, 2×CH_3), 0.97 (s, 6 H, 2×CH_3), 0.95 (s, 6 H, 2×CH_3), 0.74 (m, 6 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ = 49.8 (2 C), 34.9 (2 C), 29.9 (2 C), 29.5 (2 C), 28.9 (2 C), 21.9 (2 C), 21.1 (2 C), 20.7 (2 C), 17.6 (2 C), 15.6 (2 C) ppm. ^{77}Se NMR (38 MHz, $CDCl_3$, 25 °C): δ = 366.9 ppm. $C_{20}H_{34}Se_2$ (432.40): calcd. C 55.55, H 7.92; found C 55.52, H 7.90.

(–)-Dipinocamphyl Diselenide (17): Yield: 3.1 g (64%), yellow oil. $[\alpha]_D^{20}$ = –9.69 (*c* = 52.04, $CHCl_3$). ^1H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 4.03–4.19 (m, 2 H), 2.49–2.75 (m, 4 H), 1.90–2.44(m, 8 H), 1.34 (d, $^3J_{H,H}$ = 10.0 Hz, 2 H, 2×CH), 1.22 (d, $^3J_{H,H}$ = 7.8 Hz, 6 H, 2×CH_3), 1.19 (s, 6 H, 2×CH_3), 1.01 (s, 6 H, 2×CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ = 48.9 (2 C), 42.1 (2 C), 40.6 (2 C), 39.6 (2 C), 38.6 (2 C), 36.8 (2 C), 28.2 (2 C), 27.6 (2 C), 23.4 (2 C), 19.8 (2 C) ppm. ^{77}Se NMR (38 MHz, $CDCl_3$, 25 °C): δ = 352.2 ppm. $C_{20}H_{34}Se_2$ (432.40): calcd. C 55.55, H 7.92; found C 55.35, H 8.10.

(+)-Diisopinocamphyl Diselenide (18): Yield: 1.5 g (32%), yellow oil. $[\alpha]_D^{20}$ = +98.11 (*c* = 7.95, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 3.45 (m, 2 H), 2.55 (m, 2 H), 1.92 (m, 12 H), 1.20 (s, 6 H, 2×CH_3), 1.15 (d, $^3J_{H,H}$ = 7.2 Hz, 6 H, 2×CH_3), 1.02 (s, 6 H, 2×CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ = 48.4 (2 C), 46.6 (2 C), 42.4 (2 C), 42.2 (2 C), 38.8 (2 C), 38.7 (2 C), 33.6 (2 C), 27.9 (2 C), 23.2 (2 C), 21.9 (2 C) ppm. ^{77}Se NMR (38 MHz, $CDCl_3$, 25 °C): δ = 444.4 ppm. $C_{20}H_{34}Se_2$ (432.40): calcd. C 55.55, H 7.92; found C 55.01, H 8.21.

(+)-Diisobornyl Diselenide (19): Yield: 1.6 g (33%), yellow solid; m.p. 170–171 °C. $[\alpha]_D^{20}$ = +7.04 (*c* = 7.19, $CHCl_3$). ^1H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 3.41 (t, $^3J_{H,H}$ = 6.4 Hz, 2 H, 2×CH), 2.12–1.94 (m, 4 H), 1.81–1.61 (m, 6 H), 1.33–1.11 (m, 4 H), 1.05 (s, 6 H, 2×CH_3), 0.92 (s, 6 H, 2×CH_3), 0.82 (s, 6 H, 2×CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ = 59.3 (2 C), 50.0 (2 C), 47.2 (2 C), 46.5 (2 C), 41.9 (2 C), 38.4 (2 C), 27.4 (2 C), 20.6 (2 C), 19.9 (2 C), 15.6 (2 C) ppm. ^{77}Se NMR (38 MHz, $CDCl_3$, 25 °C): δ = 464.41 ppm. $C_{20}H_{34}Se_2$ (432.40): calcd. C 55.55, H 7.92; found C 55.52, H 8.14.

General Procedure for the Asymmetric Methoxyselenylation: The diselenide (250 mg, 0.58 mmol) was dissolved in dry dichloromethane (8 mL) under argon. A 1 M solution of bromine (0.58 mL, 0.58 mmol) in tetrachloromethane was added dropwise at –78 °C. After 15 min, a 0.70 M methanol solution of silver triflate (320 mg, 1.80 mL) was added at –78 °C and stirred for another 15 min. The mixture was treated with the substrate (2.9 mmol) and stirred at the same temperature for between 2 and 5 h. The reaction was quenched with aqueous $NaHCO_3$ solution, diluted with 50 mL of dichloromethane, washed with water and brine, dried, filtered, and concentrated in vacuo. The crude product was purified by chromatography on silica gel or basic alumina.

(1*S*,2*R*,5*S*)-2-(2-Methoxy-2-phenylethylselanylmethyl)-6,6-dimethylbicyclo[3.1.1]heptane (20): Purification by column chromatography on silica gel with petroleum ether/ethyl acetate (95:5). Yield: 270 mg (64%), yellow oil; *dr* 51:49. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): major diastereomer: δ = 7.34 (m, 5 H, Ph), 4.32 (dd, $^3J_{H,H}$ = 7.8 and 5.4 Hz, 1 H, CH), 3.24 (s, 3 H, OCH_3), 2.96 (dd, $^2J_{H,H}$ = 12.6, $^3J_{H,H}$ = 7.8 Hz, 1 H, CH_2Se), 2.71 (dd, $^2J_{H,H}$ = 12.6, $^3J_{H,H}$ = 5.4 Hz, 1 H, CH_2Se), 2.64–2.49 (m, 2 H), 2.36–2.28 (m, 1 H), 2.24–2.14 (m, 1 H), 2.05–1.78 (m, 4 H), 1.52–1.39 (m, 1 H), 1.18 (s, 3 H, CH_3), 0.96 (s, 3 H, CH_3), 0.86 (d, $^3J_{H,H}$ = 9.4 Hz, 1 H, CH) ppm; minor diastereomer: δ = 2.95 (dd, $^2J_{H,H}$ = 12.6, $^3J_{H,H}$ = 7.8 Hz, 1 H, CH_2Se), 2.70 (dd, $^2J_{H,H}$ = 12.6, $^3J_{H,H}$ = 5.4 Hz, 1 H, CH_2Se), 1.17 (s, 3 H, CH_3), 0.97 (s, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): major diastereomer: δ = 141.2, 128.3 (2 C), 127.8, 126.6 (2 C), 84.4, 56.8, 46.1, 41.8, 41.2, 38.5, 33.3, 32.8, 31.0, 27.9, 26.0, 23.1, 22.8 ppm; minor diastereomer: δ = 84.3, 46.2, 41.7, 32.7, 31.1, 22.7 ppm. ^{77}Se NMR (38 MHz, $CDCl_3$, 25 °C): δ = 202.7 ppm. $C_{19}H_{28}OSe$ (351.39): calcd. C 64.94, H 8.03; found C 64.93, H 7.98.

{2-[(1*S*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexylselanyl]-1-methoxyethyl}benzene (21): Purification by column chromatography on silica gel with petroleum ether/ethyl acetate (95:5). Yield: 350 mg (86%), yellow oil; *dr* 70:30. ^1H NMR (200 MHz, $CDCl_3$, 25 °C): major diastereomer: δ = 7.34 (m, 5 H, Ph), 4.31 (dd, $^3J_{H,H}$ = 8.2, $^3J_{H,H}$ = 5.4 Hz, 1 H, CH), 3.36 (m, 1 H, CH), 3.24 (s, 3 H, OCH_3), 2.97 (dd, $^2J_{H,H}$ = 12.4, $^3J_{H,H}$ = 8.2 Hz, 1 H, CH_2Se), 2.70 (dd, $^2J_{H,H}$ = 12.4, $^3J_{H,H}$ = 5.4 Hz, 1 H, CH_2Se), 2.05–0.98 (m, 9 H), 0.93 (d, $^3J_{H,H}$ = 6.4 Hz, 3 H, CH_3), 0.89 (d, $^3J_{H,H}$ = 6.4 Hz, 3 H, CH_3), 0.87 (d, $^3J_{H,H}$ = 6.4 Hz, 3 H, CH_3) ppm; minor diastereomer: δ = 3.25 (s, 3 H, OCH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): major diastereomer: δ = 141.5, 128.4 (2 C), 127.9, 126.6 (2 C), 85.0, 56.8, 46.0, 42.1, 35.4, 31.1, 30.9, 27.6, 26.8, 22.2, 21.0, 20.9 ppm; minor diastereomer: δ = 84.4, 45.9, 42.0, 30.8 ppm. ^{77}Se NMR (38 MHz, $CDCl_3$, 25 °C): major diastereomer: δ = 148.9 ppm; minor diastereomer: δ = 146.2 ppm. $C_{19}H_{30}OSe$ (353.40): calcd. C 64.57, H 8.56; found C 64.52, H 8.48.

{2-[(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexylselanyl]-1-methoxyethyl}benzene (22): Purification by column chromatography on silica gel with petroleum ether/ethyl acetate (95:5). Yield: 330 mg (79%), yellow oil; *dr* 62:38. ^1H NMR (200 MHz, $CDCl_3$, 25 °C): major diastereomer: δ = (m, 5 H, Ph), 4.32 (dd, $^3J_{H,H}$ = 8.0 and 5.8 Hz, 1 H, CH), 3.24 (s, 3 H, OCH_3), 2.95 (dd, $^2J_{H,H}$ = 12.2, $^3J_{H,H}$ = 8.0 Hz, 1 H, CH_2Se), 2.75 (dd, $^2J_{H,H}$ = 12.2, $^3J_{H,H}$ = 5.8 Hz, 1 H, CH_2Se), 2.35–2.06 (m, 3 H), 2.80–2.55 (m, 1 H), 1.74–1.64 (m, 2 H), 1.28–0.95 (m, 4 H), 0.88 (d, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH_3), 0.86 (d, $^3J_{H,H}$ = 6.2 Hz, 3 H, CH_3), 0.72 (d, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH_3) ppm; minor diastereomer: δ = 0.74 (d, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): major diastereomer: δ = 141.2, 128.14 (2 C), 127.6, 126.5 (2 C), 84.2, 56.6, 47.5, 44.6, 43.3, 34.5, 33.9, 28.6, 28.4, 24.6, 21.9, 21.2, 14.9 ppm; minor diastereomer: δ = 126.4 (2 C), 84.5, 44.8, 43.5, 34.0 ppm. ^{77}Se NMR (38 MHz, $CDCl_3$, 25 °C): major diastereomer: δ = 230.0 ppm; minor diastereomer: δ = 227.0 ppm. $C_{19}H_{30}OSe$ (353.40): calcd. C 64.57, H 8.56; found C 64.45, H 8.42.

(1*R*,3*S*,4*R*,6*S*)-3-(Methoxyphenylmethylselanyl)-4,7,7-trimethylbicyclo[4.1.0]heptane (23): Purification by column chromatography on silica gel with petroleum ether/ethyl acetate (95:5). Yield: 325 mg (78%), yellow oil; *dr* 52:48. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): major diastereomer: δ = 7.36 (m, 5 H, Ph), 4.32 (dd, $^3J_{H,H}$ = 8.4 and 5.4 Hz, 1 H, CH), 3.24 (s, 3 H, OCH_3), 3.03 (m, 1 H), 2.95 (dd, $^2J_{H,H}$ = 12.6, $^3J_{H,H}$ = 8.4 Hz, 1 H, CH_2Se), 2.72 (dd, $^2J_{H,H}$ = 12.3, $^3J_{H,H}$ = 5.4 Hz, 1 H, CH_2Se), 2.27–2.17 (m, 1 H), 1.84–1.74 (m, 2 H), 1.49–1.38 (m, 1 H), 0.97 (s, 3 H, CH_3), 0.91 (d, $^3J_{H,H}$ = 6.6 Hz, 1 H, CH), 0.85–0.76 (m, 1 H), 0.68–0.50 (m, 2 H) ppm; minor diastereomer: δ = 3.22 (s, 3 H, OCH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): major diastereomer: δ = 141.3, 128.2 (2 C), 127.7, 126.4 (2 C), 84.4, 56.7, 43.1, 31.3, 30.9, 28.4, 26.1, 25.3, 21.2, 21.1, 20.1, 17.4, 15.7 ppm; minor diastereomer: δ = 84.2, 43.2, 31.6, 25.4, 20.0 ppm. ^{77}Se NMR (38 MHz, $CDCl_3$, 25 °C): δ = 203.7 ppm. $C_{19}H_{28}OSe$ (351.39): calcd. C 64.94, H 8.03; found C 64.90, H 8.01.

(1*R*,3*R*,4*R*,6*S*)-3-(Methoxyphenylmethylselanyl)-4,7,7-trimethylbicyclo[4.1.0]heptane (24): Purification by column chromatography on silica gel with petroleum ether/ethyl acetate (95:5). Yield: 340 mg (81%), yellow oil; *dr* 53:47. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): major diastereomer: δ = 7.36 (m, 5 H, Ph), 4.32 (dd, $^3J_{H,H}$ = 8.1 and 5.4 Hz, 1 H, CH), 3.24 (s, 3 H, OCH_3), 2.94 (dd, $^2J_{H,H}$ = 12.3, $^3J_{H,H}$ = 8.1 Hz, 1 H, CH_2Se), 2.72 (dd, $^2J_{H,H}$ = 12.3, $^3J_{H,H}$ = 5.4 Hz, 1 H, CH_2Se), 2.30–2.20 (m, 1 H), 2.15–2.10 (m, 1 H), 2.01–1.87 (m, 2 H), 1.35–1.25 (m, 1 H), 0.97 (d, $^3J_{H,H}$ = 6.6 Hz, 3 H, CH_3), 0.95 (s, 3 H, CH_3), 0.89 (s, 3 H, CH_3), 0.57–0.51 (m, 1 H) ppm; minor diastereomer: δ = 3.23 (s, 3 H, OCH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): major diastereomer: δ = 141.4, 128.2 (2 C), 127.7, 126.5 (2 C), 84.5, 56.7, 44.6, 34.8, 29.8, 29.6, 29.3, 28.7, 21.5, 20.4, 17.2, 15.5 ppm; minor diastereomer: δ = 84.6, 56.6, 44.5, 35.0 ppm. ^{77}Se NMR (38 MHz, $CDCl_3$, 25 °C): major diastereomer: δ = 256.3 ppm; minor diastereomer: δ = 255.7 ppm. $C_{19}H_{28}OSe$ (351.39): calcd. C 64.94, H 8.03; found C 64.88, H 7.95.

(1*R*,2*R*,3*S*,5*S*)-3-(Methoxyphenylmethylselanyl)-2,6,6-trimethylbicyclo[3.1.1]heptane (25): Purification by column chromatography on silica gel with petroleum ether/ethyl acetate (95:5). Yield: 200 mg (48%), yellow oil; *dr* 52:48. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): major diastereomer: δ = 7.35 (m, 5 H, Ph), 4.38 (dd, $^3J_{H,H}$ = 7.8

and 5.4 Hz, 1 H, CH), 3.65 (q, $^3J_{H,H}$ = 9.6 Hz, 1 H, CH), 3.25 (s, 3 H, OCH_3), 2.99 (dd, $^2J_{H,H}$ = 12.3, $^3J_{H,H}$ = 7.8 Hz, 1 H, CH_2Se), 2.75 (dd, $^2J_{H,H}$ = 12.3, $^3J_{H,H}$ = 5.4 Hz, 1 H, CH_2Se), 2.52–1.84 (m, 7 H), 1.23 (d, $^3J_{H,H}$ = 9.9 Hz, 1 H, CH), 1.20–1.18 (m, 6 H, CH_3), 1.00 (s, 3 H, CH_3), 0.99–0.83 (m, 1 H) ppm; minor diastereomer: δ = 3.24 (s, 3 H, OCH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): major diastereomer: δ = 141.4, 128.2 (2 C), 127.9, 126.6 (2 C), 84.4, 56.8, 48.8, 41.9, 39.4, 37.9, 36.2, 34.0, 30.5, 27.8, 27.5, 23.4, 19.5 ppm; minor diastereomer: δ = 84.1, 36.3, 33.8, 30.3, 19.4 ppm. ^{77}Se NMR (38 MHz, $CDCl_3$, 25 °C): δ = 206.4 ppm. $C_{19}H_{28}OSe$ (351.39): calcd. C 64.94, H 8.03; found C 64.84, H 7.96.

(1*R*,2*R*,3*R*,5*S*)-3-(Methoxyphenylmethylselanyl)-2,6,6-trimethylbicyclo[3.1.1]heptane (26): Purification by column chromatography on silica gel with petroleum ether/ethyl acetate (95:5). Yield: 230 mg (57%), yellow oil; *dr* 82:18. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): major diastereomer: δ = 7.35 (m, 5 H, Ph), 4.37 (m, 1 H), 3.25 (s, 3 H, OCH_3), 3.10–2.75 (m, 2 H), 2.44–2.29 (m, 2 H), 2.17–1.73 (m, 4 H), 1.16 (s, 3 H, CH_3), 1.02 (d, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH_3), 0.89 (s, 3 H, CH_3) ppm; minor diastereomer: δ = 3.27 (s, 3 H, OCH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): major diastereomer: δ = 141.4, 128.4 (2 C), 127.9, 126.9 (2 C), 84.5, 56.7, 48.4, 45.2, 42.5, 38.6, 38.3, 36.6, 33.8, 29.9, 27.9, 23.1, 21.4 ppm; minor diastereomer: δ = 126.6 (2 C), 45.6, 41.9, 37.0, 30.4 ppm. ^{77}Se NMR (38 MHz, $CDCl_3$, 25 °C): δ = 309.5 ppm. $C_{19}H_{28}OSe$ (351.39): calcd. C 64.94, H 8.03; found C 64.86, H 8.05.

(1*S*,2*R*,5*S*)-2-(2-Methoxy-2-phenylpropylselanylmethyl)-6,6-dimethylbicyclo[3.1.1]heptane (27): Purification by column chromatography on basic alumina with petroleum ether/ethyl acetate (95:5). Yield: 210 mg (50%), yellow oil; *dr* 52:48. ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): major diastereomer: δ = 7.38 (m, 5 H, Ph), 3.10 (s, 3 H, OCH_3), 3.07–2.81 (m, 2 H), 2.43–1.72 (m, 9 H), 1.69 (s, 3 H, CH_3), 1.50–1.18 (m, 1 H), 1.15 (s, 3 H, CH_3), 0.92 (s, 3 H, CH_3), 0.82 (d, $^3J_{H,H}$ = 9.4 Hz, 1 H) ppm; minor diastereomer: δ = 0.90 (s, 3 H, CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): major diastereomer: δ = 143.8, 128.0 (2 C), 127.1, 126.3, (2 C), 79.3, 50.8, 46.3, 41.8, 41.2, 38.5, 38.4, 33.3, 33.2, 27.9, 26.0, 23.1, 22.8, 22.5 ppm; minor diastereomer: δ = 144.7, 79.2, 46.2, 41.7, 23.0, 22.7, 22.4 ppm. ^{77}Se NMR (38 MHz, $CDCl_3$, 25 °C): major diastereomer: δ = 115.2 ppm; minor diastereomer: δ = 114.9 ppm. $C_{20}H_{30}OSe$ (365.41): calcd. C 65.73, H 8.27; found C 65.77, H 8.31.

[2-[(1*S*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexylselanyl]-1-methoxy-1-methylethyl]benzene (28): Purification by column chromatography on silica gel with petroleum ether/ethyl acetate (95:5). Yield: 140 mg (33%), yellow oil; *dr* 62:38. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): major diastereomer: δ = 7.43–7.22 (m, 5 H, Ph), 3.14 (m, 1 H, CHSe), 3.10 (s, 3 H, OCH_3), 3.00 (d, $^2J_{H,H}$ = 11.7 Hz, 1 H, CH_2), 2.88 (d, $^2J_{H,H}$ = 11.7 Hz, 1 H, CH_2), 1.95–1.75 (m, 2 H), 1.71 (s, 3 H, CH_3), 1.70–1.50 (m, 3 H), 1.33–0.91 (m, 5 H), 0.90 (d, $^3J_{H,H}$ = 6.6 Hz, 3 H, CH_3), 0.87 (d, $^3J_{H,H}$ = 6.3 Hz, 3 H, CH_3), 0.84 (d, $^3J_{H,H}$ = 6.6 Hz, 3 H, CH_3) ppm; minor diastereomer: δ = 3.08 (s, 3 H, OCH_3), 1.69 (s, 3 H, CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): major diastereomer: δ = 144.1, 128.1 (2 C), 127.1, 126.3 (2 C), 79.2, 50.8, 49.6, 46.2, 41.9, 38.1, 35.3, 31.0, 27.5, 26.8, 23.0, 22.1, 20.9 ppm; minor diastereomer: δ = 128.4 (2 C), 127.8, 126.4 (2 C), 79.4, 46.4, 38.2, 27.6, 22.8, 20.8 ppm. ^{77}Se NMR (38 MHz, $CDCl_3$, 25 °C): major diastereomer: δ = 118.4 ppm; minor diastereomer: δ = 120.6 ppm. $C_{20}H_{32}OSe$ (367.43): calcd. C 65.37, H 8.78; found C 65.23, H 8.66.

[2-[(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexylselanyl]-1-methoxy-1-methylethyl]benzene (29): Purification by column chromatography on basic alumina with petroleum ether/ethyl acetate (95:5). Yield: 220 mg (55%), yellow oil; *dr* 72:28. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): major diastereomer: δ = 7.44–7.26 (m, 5 H, Ph), 3.10 (s, 3 H, OCH_3), 2.98 (d, $^2J_{H,H}$ = 11.7 Hz, 1 H, CH_2), 2.88 (d, $^2J_{H,H}$ = 11.7 Hz, 1 H, CH_2), 2.56–2.15 (m, 2 H), 2.04–2.00 (m, 1 H), 1.70 (s, 3 H, CH_3), 1.66–1.56 (m, 2 H), 1.49–0.95 (m, 5 H), 0.86 (d, $^3J_{H,H}$ = 6.9 Hz, 3 H, CH_3), 0.83 (d, $^3J_{H,H}$ = 6.3 Hz, 3 H, CH_3), 0.67 (d, $^3J_{H,H}$ = 6.9 Hz, 3 H, CH_3) ppm; minor diastereomer: δ = 3.11 (s, 3 H, OCH_3), 1.70 (s, 3 H, CH_3), 0.70 (d, $^3J_{H,H}$ = 6.9 Hz, 3 H, CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): major diastereomer: δ = 143.9, 128.0 (2 C), 127.1, 126.3 (2 C), 79.2, 50.8, 47.7, 44.7, 43.4, 35.3, 34.7, 34.1, 28.7, 24.8, 22.7, 22.1, 21.4, 15.1 ppm; minor diastereomer: δ = 79.3, 47.8, 44.9, 35.8, 34.2, 28.8, 22.9, 15.2 ppm. ^{77}Se NMR (38 MHz, $CDCl_3$, 25 °C): δ = 201.2 ppm. $C_{20}H_{32}OSe$ (367.43): calcd. C 65.37, H 8.78; found C 65.25, H 8.70.

(1*R*,3*S*,4*R*,6*S*)-3-(2-Methoxy-2-phenylpropylselanyl)-4,7,7-trimethylbicyclo[4.1.0]heptane (30): Purification by column chromatography on basic alumina with petroleum ether/ethyl acetate (95:5). Yield: 390 mg (94%), yellow oil; *dr* 52:48. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): major diastereomer: δ = 7.44–7.22 (m, 5 H, Ph), 3.10 (s, 3 H, OCH_3), 3.04–2.62 (m, 3 H), 2.20–1.98 (m, 1 H), 1.84–1.70 (m, 2 H), 1.69 (s, 3 H, CH_3), 1.44–1.28 (m, 1 H), 0.95 (s, 3 H, CH_3), 0.89 (d, $^3J_{H,H}$ = 6.6 Hz, 3 H, CH_3), 0.87 (d, $^3J_{H,H}$ = 6.6 Hz, 3 H, CH_3), 0.85–0.52 (m, 3 H) ppm; minor diastereomer: δ = 3.12 (s, 3 H, OCH_3), 0.89 (d, $^3J_{H,H}$ = 6.6 Hz, 3 H, CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): major diastereomer: δ = 144.0, 127.9 (2 C), 126.9, 126.1 (2 C), 79.1, 50.7, 43.0, 38.2, 30.8, 28.4, 25.8, 25.3, 22.6, 21.5, 21.2, 19.9, 17.3, 15.7 ppm; minor diastereomer: δ = 143.9, 79.0, 43.3, 38.5, 31.0, 26.0, 25.4, 21.3, 20.0 ppm. ^{77}Se NMR (38 MHz, $CDCl_3$, 25 °C): major diastereomer: δ = 181.3 ppm; minor diastereomer: δ = 180.5 ppm. $C_{20}H_{30}OSe$ (365.41): calcd. C 65.73, H 8.27; found C 65.65, H 8.30.

(1*R*,3*R*,4*R*,6*S*)-3-(2-Methoxy-2-phenylpropylselanyl)-4,7,7-trimethylbicyclo[4.1.0]heptane (31): Purification by column chromatography on basic alumina with petroleum ether/ethyl acetate (95:5). Yield: 370 mg (89%), yellow oil; *dr* 52:48. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): major diastereomer: δ = 7.43–7.20 (m, 5 H, Ph), 3.10 (s, 3 H, OCH_3), 2.96 (d, $^2J_{H,H}$ = 12.0 Hz, 1 H, CH_2), 2.89 (d, $^2J_{H,H}$ = 12.0 Hz, 1 H, CH_2), 2.08–1.82 (m, 4 H), 1.69 (s, 3 H, CH_3), 1.27 (m, 1 H), 0.93 (s, 3 H, CH_3), 0.91 (d, $^3J_{H,H}$ = 6.6 Hz, 3 H, CH_3), 0.85 (s, 3 H, CH_3), 0.77–0.64 (m, 2 H), 0.54–0.47 (m, 1 H); minor diastereomer: δ = 3.10 (s, 3 H, OCH_3), 1.68 (s, 3 H, CH_3), 0.84 (s, 3 H, CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): major diastereomer: δ = 143.9, 128.0 (2 C), 127.1, 126.3 (2 C), 79.3, 50.9, 44.6, 36.6, 34.8, 29.6, 29.3, 28.7, 22.6, 21.6, 20.5, 17.3, 15.5 ppm; minor diastereomer: δ = 44.9, 37.0, 35.2, 29.5, 22.5 ppm. ^{77}Se NMR (38 MHz, $CDCl_3$, 25 °C): major diastereomer: δ = 233.7 ppm; minor diastereomer: δ = 231.7 ppm. $C_{20}H_{30}OSe$ (365.41): calcd. C 65.73, H 8.27; found C 65.61, H 8.15.

(1*R*,2*R*,3*S*,5*S*)-3-(2-Methoxy-2-phenylpropylselanyl)-2,6,6-trimethylbicyclo[3.1.1]heptane (32): Purification by column chromatography on basic alumina with petroleum ether/ethyl acetate (95:5). Yield: 270 mg (65%), yellow oil; *dr* 61:39. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): major diastereomer: δ = 7.46–7.22 (m, 5 H, Ph), 3.35 (m, 1 H), 3.12 (s, 3 H, OCH_3), 3.00 (d, $^2J_{H,H}$ = 12.0 Hz, 1 H, CH_2Se), 2.90 (d, $^2J_{H,H}$ = 12.0 Hz, 1 H, CH_2Se), 2.45–2.08 (m, 3 H), 2.05–1.77 (m, 3 H), 1.73 (s, 3 H, CH_3), 1.21–1.11 (m, 6 H, CH_3), 0.94 (s, 3 H, CH_3), 0.82 (m, 1 H) ppm; minor diastereomer: δ = 3.13 (s, 3 H, OCH_3), 1.74 (s, 3 H, CH_3), 0.95 (s, 3 H, CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): major diastereomer: δ = 144.0, 128.1 (2 C), 127.2, 126.3 (2 C), 79.2, 50.9, 48.8, 41.8, 39.4, 37.7, 37.4, 35.8, 33.9, 27.7, 27.5, 23.4, 22.6, 19.5 ppm; minor diastereomer: δ = 41.9, 37.8, 36.1, 33.8, 22.7, 19.3 ppm. ^{77}Se NMR

(38 MHz, $CDCl_3$, 25 °C): major diastereomer: δ = 183.0 ppm; minor diastereomer: δ = 187.2 ppm. $C_{20}H_{30}OSe$ (365.41): calcd. C 65.73, H 8.27; found C 65.75, H 8.42.

(1*R*,2*R*,3*R*,5*S*)-3-(2-Methoxy-2-phenylpropylselanyl)-2,6,6-trimethylbicyclo[3.1.1]heptane (33): Purification by column chromatography on basic alumina with petroleum ether/ethyl acetate (95:5). Yield: 320 mg (76%), yellow oil; *dr* 66:34. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): major diastereomer: δ = 7.45–7.21 (m, 5 H, Ph), 3.11 (s, 3 H, OCH_3), 3.08–2.84 (m, 2 H), 2.51–2.26 (m, 2 H), 2.10–1.81 (m, 3 H), 1.73 (s, 3 H, CH_3), 1.78–1.69 (m, 1 H), 1.39–1.32 (m, 1 H), 1.14 (s, 3 H, CH_3), 1.04 (d, $^3J_{H,H}$ = 7.2 Hz, 1 H, CH), 0.94 (d, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH_3), 0.82 (s, 3 H, CH_3) ppm; minor diastereomer: δ = 3.12 (s, 3 H, OCH_3), 1.71 (s, 3 H, CH_3), 1.16 (s, 3 H, CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): major diastereomer: δ = 143.8, 128.1 (2 C), 127.2, 126.6 (2 C), 79.5, 51.0, 48.3, 45.0, 42.4, 38.6, 38.1, 36.9, 36.3, 33.7, 27.8, 23.0, 22.4, 21.3 ppm; minor diastereomer: δ = 144.1, 127.1, 126.3 (2 C), 79.1, 50.8, 48.4, 45.6, 38.2, 33.9, 27.9, 23.1, 21.5 ppm. ^{77}Se NMR (38 MHz, $CDCl_3$, 25 °C): major diastereomer: δ = 294.7 ppm; minor diastereomer: δ = 290.0 ppm. $C_{20}H_{30}OSe$ (365.41): calcd. C 65.73, H 8.27; found C 65.65, H 8.18.

(1*S*,2*R*,5*S*)-2-(2-Methoxy-1-methyl-2-phenylethylselanylmethyl)-6,6-dimethylbicyclo[3.1.1]heptane (34): Purification by column chromatography on basic alumina with petroleum ether/ethyl acetate (95:5). Yield: 363 mg (86%), yellow oil; *dr* 52:48. ^1H NMR (200 MHz, $CDCl_3$, 25 °C): major diastereomer: δ = 7.36 (m, 5 H, Ph), 4.24 (d, $^3J_{H,H}$ = 5.8 Hz, 1 H, CH), 3.26 (s, 3 H, OCH_3), 3.16–2.98 (m, 1 H), 2.56–2.42 (m, 2 H), 2.40–2.03 (m, 3 H), 2.02–1.73 (m, 4 H), 1.49–1.32 (m, 1 H), 1.40 (d, $^3J_{H,H}$ = 7.0 Hz, 3 H, CH_3), 1.16 (s, 3 H, CH_3), 0.94 (s, 3 H, CH_3), 0.84 (d, $^3J_{H,H}$ = 9.4 Hz, 1 H, CH) ppm; minor diastereomer: δ = 4.21 (d, $^3J_{H,H}$ = 5.8 Hz, 1 H, CH), 3.27 (s, 3 H, OCH_3), 1.39 (d, $^3J_{H,H}$ = 7.0 Hz, 3 H, CH_3), 1.15 (s, 3 H, CH_3), 0.92 (s, 3 H, CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): major diastereomer: δ = 140.0, 127.9 (2 C), 127.5, 127.2 (2 C), 88.0, 57.1, 46.3, 41.9, 41.1, 40.4, 38.4, 33.3, 31.6, 27.9, 26.0, 23.1, 22.8, 17.6 ppm; minor diastereomer: δ = 87.9, 46.2, 41.8, 31.4, 22.7, 17.5 ppm. ^{77}Se NMR (38 MHz, $CDCl_3$, 25 °C): major diastereomer: δ = 246.9 ppm; minor diastereomer: δ = 248.7 ppm. $C_{20}H_{30}OSe$ (365.41): calcd. C 65.73, H 8.27; found C 65.68, H 8.36.

[2-[(1*S*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexylselanyl]-1-methoxypropyl]benzene (35): Purification by column chromatography on basic alumina with petroleum ether/ethyl acetate (95:5). Yield: 114 mg (27%), yellow oil; *dr* 54:46. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): major diastereomer: δ = 7.39–7.24 (m, 5 H, Ph), 4.27 (d, $^3J_{H,H}$ = 5.7 Hz, 1 H, CH), 3.27 (s, 3 H, OCH_3), 3.06 (m, 1 H), 2.05–1.45 (m, 5 H), 1.40 (d, $^3J_{H,H}$ = 6.9 Hz, 3 H, CH_3), 1.35–0.97 (m, 2 H), 0.91 (d, $^3J_{H,H}$ = 6.6 Hz, 3 H, CH_3), 0.88 (d, $^3J_{H,H}$ = 6.6 Hz, 3 H, CH_3), 0.83 (d, $^3J_{H,H}$ = 6.3 Hz, 3 H, CH_3) ppm; minor diastereomer: δ = 3.28 (s, 3 H, OCH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): major diastereomer: δ = 140.4, 128.1 (2 C), 127.5, 127.3 (2 C), 87.9, 57.4, 49.5, 45.0, 42.2, 42.9, 35.3, 30.8, 27.6, 26.9, 22.2, 21.0, 20.9, 17.9 ppm; minor diastereomer: δ = 140.2, 87.5, 42.7, 40.5, 20.8, 17.8 ppm. ^{77}Se NMR (38 MHz, $CDCl_3$, 25 °C): δ = 261.7 ppm; minor diastereomer: δ = 261.0 ppm. $C_{20}H_{32}OSe$ (367.43): calcd. C 65.37, H 8.78; found C 65.31, H 8.74.

[2-[(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexylselanyl]-1-methoxypropyl]benzene (36): Purification by column chromatography on basic alumina with petroleum ether/ethyl acetate (95:5). Yield: 260 mg (62%), yellow oil; *dr* 52:48. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): major diastereomer: δ = 7.43 (m, 5 H, Ph), 4.28 (d, $^3J_{H,H}$ = 5.7 Hz, 1 H, CH), 3.26 (s, 3 H, OCH_3), 3.18–3.09 (m, 1 H), 2.55–2.16 (m, 2 H), 2.06–1.87 (m, 1 H), 1.71–1.52 (m, 4 H), 1.42 (d, $^3J_{H,H}$ = 6.9 Hz, 3 H, CH_3), 1.25–0.90 (m, 6 H), 0.87 (d, $^3J_{H,H}$ = 6.9 Hz, 3 H, CH_3), 0.84 (d, $^3J_{H,H}$ = 6.9 Hz, 3 H, CH_3), 0.72 (d, $^3J_{H,H}$ = 6.9 Hz, 3 H, CH_3) ppm; minor diastereomer: δ = 4.23 (d, $^3J_{H,H}$ = 5.7 Hz, 1 H, CH), 3.25 (s, 3 H, OCH_3), 1.41 (d, $^3J_{H,H}$ = 6.9 Hz, 3 H, CH_3), 0.71 (d, $^3J_{H,H}$ = 6.9 Hz, 3 H, CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): major diastereomer: δ = 140.3, 127.9 (2 C), 127.5, 127.2 (2 C), 88.4, 57.3, 48.1, 45.2, 43.3, 39.3, 38.2, 34.7, 34.2, 28.7, 24.9, 22.2, 21.4, 18.2, 15.2 ppm; minor diastereomer: δ = 140.2, 88.2, 45.1, 43.5, 34.0, 28.6, 24.8, 22.1, 21.3, 18.1 ppm. ^{77}Se NMR (38 MHz, $CDCl_3$, 25 °C): major diastereomer: δ = 350.8 ppm; minor diastereomer: δ = 343.3 ppm. $C_{20}H_{32}OSe$ (367.43): calcd. C 65.37, H 8.78; found C 65.29, H 8.71.

(1*R*,3*R*,4*R*,6*S*)-3-(2-Methoxy-1-methyl-2-phenylethylselanyl)-4,7,7-trimethylbicyclo[4.1.0]heptane (38): Purification by column chromatography on basic alumina with petroleum ether/ethyl acetate (95:5). Yield: 340 mg (81%), yellow oil; *dr* 58:42. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): major diastereomer: δ = 7.32 (m, 5 H, Ph), 4.21 (d, $^3J_{H,H}$ = 6.2 Hz, 1 H, CH), 3.23 (s, 3 H, OCH_3), 3.15–3.04 (m, 1 H, CH), 2.10–1.80 (m, 4 H), 1.41 (d, $^3J_{H,H}$ = 7.0 Hz, 3 H, CH_3), 1.38–1.16 (m, 2 H), 0.95 (d, $^3J_{H,H}$ = 7.0 Hz, 3 H, CH_3), 0.87 (s, 3 H, CH_3), 0.81 (s, 3 H, CH_3), 0.80–0.43 ppm (m, 2 H); minor diastereomer: δ = 4.23 (d, $^3J_{H,H}$ = 6.2 Hz, 1 H, CH), 3.26 (s, 3 H, OCH_3), 1.40 (d, $^3J_{H,H}$ = 7.0 Hz, 3 H, CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): major diastereomer: δ = 140.3, 128.0 (2 C), 127.7, 127.5 (2 C), 88.5, 57.3, 44.6, 40.4, 35.6, 30.3, 29.5, 28.8, 21.7, 20.7, 18.0, 17.4, 15.8 ppm; minor diastereomer: δ = 140.4, 88.4, 57.4, 44.1, 39.5, 18.3, 15.7 ppm. ^{77}Se NMR (38 MHz, $CDCl_3$, 25 °C): major diastereomer: δ = 371.2 ppm; minor diastereomer: δ = 380.4 ppm. $C_{20}H_{30}OSe$ (365.41): calcd. C 65.73, H 8.27; found C 65.75, H 8.42.

(1*R*,2*R*,3*S*,5*S*)-3-(2-Methoxy-1-methyl-2-phenylethylselanyl)-2,6,6-trimethylbicyclo[3.1.1]heptane (39): Purification by column chromatography on basic alumina with petroleum ether/ethyl acetate (95:5). Yield: 250 mg (60%), yellow oil; *dr* 62:38. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): major diastereomer: δ = 7.36 (m, 5 H, Ph), 4.21 (d, $^3J_{H,H}$ = 3.8 Hz, 1 H, CH), 3.27 (s, 3 H, OCH_3), 3.29–3.21 (m, 1 H), 3.15–3.02 (m, 1 H), 2.44–2.24 (m, 2 H), 2.18–2.07 (m, 2 H), 1.94–1.79 (m, 3 H), 1.42 (d, $^3J_{H,H}$ = 4.8 Hz, 3 H, CH_3), 1.38–1.26 (m, 1 H), 1.18 (d, $^3J_{H,H}$ = 7.8 Hz, 3 H, CH_3), 1.16–1.14 (m, 1 H), 0.96 (s, 3 H, CH_3), 0.85 (m, 1 H) ppm; minor diastereomer: δ = 4.27 (d, $^3J_{H,H}$ = 5.7 Hz, 1 H, CH), 1.43 (d, $^3J_{H,H}$ = 6.9 Hz, 3 H, CH_3), 0.98 (s, 3 H, CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): major diastereomer: δ = 140.4, 127.9 (2 C), 127.5, 127.2 (2 C), 88.2, 57.2, 48.9, 41.9, 39.6, 39.3, 37.9, 35.9, 32.8, 27.7, 27.5, 20.4, 19.9, 17.3 ppm; minor diastereomer: δ = 140.3, 88.1, 41.9, 38.1, 36.6, 27.6, 19.5, 17.8 ppm. ^{77}Se NMR (38 MHz, $CDCl_3$, 25 °C): major diastereomer: δ = 256.4 ppm; minor diastereomer: δ = 257.6 ppm. $C_{20}H_{30}OSe$ (365.41): calcd. C 65.73, H 8.27; found C 65.85, H 8.46.

(1*S*,2*R*,5*S*)-2-(2-Methoxy-2-methylcyclopentylselanylmethyl)-6,6-dimethylbicyclo[3.1.1]heptane (41): Purification by column chromatography on basic alumina with petroleum ether/ethyl acetate (95:5). Yield: 70 mg (18%), yellow oil; *dr* 52:48. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): major diastereomer: δ = 3.49–3.25 (m, 1 H), 3.23 (s, 3 H, OCH_3), 2.71 (m, 1 H), 2.45–2.15 (m, 3 H), 2.10–1.32 (m, 14 H), 1.31 (s, 3 H, CH_3), 1.18 (s, 3 H, CH_3), 1.00 (s, 3 H, CH_3), 0.88 (d, $^3J_{H,H}$ = 9.4 Hz, 1 H, CH) ppm; minor diastereomer: δ = 3.22 (s, 3 H, OCH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C) major diastereomer: δ = 85.8, 50.2, 47.4, 46.2, 41.9, 41.2, 38.5, 35.5, 33.3, 32.4, 32.1, 27.8, 26.0, 23.0, 22.8, 21.2, 20.4 ppm; minor diastereomer: δ = 47.2, 41.8, 35.8, 22.7 ppm. ^{77}Se NMR (38 MHz, $CDCl_3$, 25 °C): major diastereomer: δ =

184.7 ppm; minor diastereomer: δ = 186.2 ppm. $C_{17}H_{30}OSe$ (329.38): calcd. C 61.98, H 9.18; found C 61.92, H 9.14.

(1*S*,2*S*,4*R*)-1-Isopropyl-2-(2-methoxy-2-methylcyclopentylselanyl)-4-methylcyclohexane (42): Purification by column chromatography on silica gel with petroleum ether/ethyl acetate (95:5). Yield: 140 mg (33%), yellow oil; *dr* 78:22. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): major diastereomer: δ = 3.43 (m, 1 H, CHSe), 3.24 (s, 3 H, OCH_3), 2.36–1.36 (m, 14 H), 1.34 (s, 3 H, CH_3), 1.31–1.02 (m, 2 H), 0.94 (d, $^3J_{H,H}$ = 6.6 Hz, 3 H, CH_3), 0.89 (d, $^3J_{H,H}$ = 6.6 Hz, 3 H, CH_3), 0.88 (d, $^3J_{H,H}$ = 6.6 Hz, 3 H, CH_3) ppm; minor diastereomer: δ = 3.22 (s, 3 H, OCH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): major diastereomer: δ = 85.6, 50.2, 49.5, 47.0, 44.9, 41.9, 35.8, 35.4, 32.9, 31.0, 27.6, 26.9, 22.2, 21.4, 20.9, 20.8 ppm; minor diastereomer: δ = 85.7, 49.6, 47.1, 45.0, 42.4, 31.1 ppm. ^{77}Se NMR (38 MHz, $CDCl_3$, 25 °C): δ = 292.2 ppm. $C_{17}H_{32}OSe$ (331.40): calcd. C 61.60, H 9.73; found C 61.58, H 9.74.

(1*S*,2*R*,4*R*)-1-Isopropyl-2-(2-methoxy-2-methylcyclopentylselanyl)-4-methylcyclohexane (43): Purification by column chromatography on silica gel with petroleum ether/ethyl acetate (95:5). Yield: 380 mg (84%), yellow oil; *dr* 75:25. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): major diastereomer: δ = 3.23 (s, 3 H, OCH_3), 2.93–2.67 (m, 1 H), 2.43–2.17 (m, 3 H), 1.83–1.59 (m, 8 H), 1.31 (s, 3 H, CH_3), 1.30–1.15 (m, 3 H), 1.11–0.90 (m, 2 H), 0.89 (d, $^3J_{H,H}$ = 6.9 Hz, 3 H, CH_3), 0.88 (d, $^3J_{H,H}$ = 6.0 Hz, 3 H, CH_3), 0.76 (d, $^3J_{H,H}$ = 6.9 Hz, 3 H, CH_3) ppm; minor diastereomer: δ = 3.25 (s, 3 H, OCH_3), 1.29 (s, 3 H, CH_3), 0.73 (d, $^3J_{H,H}$ = 6.9 Hz, 3 H, CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): major diastereomer: δ = 86.0, 50.3, 48.1, 45.7, 45.6, 43.8, 35.3, 34.8, 34.3, 33.2, 28.9, 25.0, 22.2, 21.5, 21.3, 20.7, 15.2 ppm; minor diastereomer: δ = 85.6, 47.7, 45.4, 33.4, 28.7, 20.8, 15.0 ppm. ^{77}Se NMR (38 MHz, $CDCl_3$, 25 °C): major diastereomer: δ = 205.1 ppm; minor diastereomer: δ = 206.3 ppm. $C_{17}H_{32}OSe$ (331.40): calcd. C 61.60, H 9.73; found C 61.52, H 9.67.

(1*R*,3*S*,4*R*,6*S*)-3-(2-Methoxy-2-methylcyclopentylselanyl)-4,7,7-trimethylbicyclo[4.1.0]heptane (44): Purification by column chromatography on basic alumina with petroleum ether/ethyl acetate (95:5). Yield: 70 mg (18%), yellow oil; *dr* 65:35. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): major diastereomer: δ = 3.24 (s, 3 H, OCH_3), 3.22–3.15 (m, 1 H), 2.42–2.15 (m, 2 H), 1.92–1.62 (m, 7 H), 1.54–1.32 (m, 2 H), 1.30 (s, 3 H, CH_3), 0.98 (s, 3 H, CH_3), 0.97 (s, 3 H, CH_3), 0.94 (d, $^3J_{H,H}$ = 6.9 Hz, 3 H, CH_3), 0.90–0.53 (m, 3 H) ppm; minor diastereomer: δ = 3.22 (s, 3 H, OCH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): major diastereomer: δ = 85.7, 50.3, 47.4, 42.4, 35.7, 32.7, 30.8, 28.5, 26.2, 25.7, 21.9, 21.3, 20.9, 20.7, 21.1, 17.5, 15.8 ppm; minor diastereomer: δ = 85.9, 47.5, 42.5, 35.6, 32.6, 30.7, 28.4, 21.8 ppm. ^{77}Se NMR (38 MHz, $CDCl_3$, 25 °C): major diastereomer: δ = 320.2 ppm; minor diastereomer: δ = 324.6 ppm. $C_{17}H_{30}OSe$ (329.38): calcd. C 61.98, H 9.18; found C 62.02, H 9.20.

(1*R*,3*R*,4*R*,6*S*)-3-(2-Methoxy-2-methylcyclopentylselanyl)-4,7,7-trimethylbicyclo[4.1.0]heptane (45): Purification by column chromatography on basic alumina with petroleum ether/ethyl acetate (95:5). Yield: 125 mg (33%), yellow oil; *dr* 70:30.^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): major diastereomer: δ = 3.31 (m, 1 H), 3.23 (s, 3 H, OCH_3), 2.53–2.44 (m, 1 H), 2.28–1.94 (m, 5 H), 1.84–1.60 (m, 7 H), 1.40–1.31 (m, 1 H), 1.29 (s, 3 H, CH_3), 1.02 (d, $^3J_{H,H}$ = 6.6 Hz, 3 H, CH_3), 0.95 (s, 3 H, CH_3), 0.87–0.70 (m, 2 H), 0.61–0.54 (m, 1 H) ppm; minor diastereomer: δ = 3.21 (s, 3 H, OCH_3), 1.28 (s, 3 H, CH_3), 0.94 (s, 3 H, CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): major diastereomer: δ = 86.0, 50.3, 46.5, 45.9, 44.1, 35.6, 35.1, 32.5, 30.1, 29.5, 28.8, 21.7, 21.4, 20.7, 20.6, 17.4, 15.4 ppm; minor diastereomer: δ = 85.9, 46.4, 44.0, 35.0, 21.6, 15.3 ppm. ^{77}Se NMR (38 MHz, $CDCl_3$, 25 °C) major diastereomer: δ = 312.0 ppm; minor diastereomer: δ = 308.1 ppm. $C_{17}H_{30}OSe$ (329.38): calcd. C 61.98, H 9.18; found C 62.00, H 9.15.

(1*R*,2*R*,3*S*,5*S*)-3-(2-Methoxy-2-methylcyclopentylselanyl)-2,6,6-trimethylbicyclo[3.1.1]heptane (46): Purification by column chromatography on basic alumina with petroleum ether/ethyl acetate (95:5). Yield: 121 mg (32%), yellow oil; *dr* 70:30. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): major diastereomer: δ = 3.85 (m, 1 H), 3.52–3.25 (m, 1 H), 3.24 (s, 3 H, OCH_3), 2.55–2.04 (m, 5 H), 1.96–1.60 (m, 8 H), 1.32 (s, 3 H, CH_3), 1.20 (d, $^3J_{H,H}$ = 7.8 Hz, 3 H, CH_3), 1.17 (s, 3 H, CH_3), 1.00 (s, 3 H, CH_3) ppm; minor diastereomer: δ = 1.30 (s, 3 H, CH_3), 1.17 (d, $^3J_{H,H}$ = 7.8 Hz, 3 H, CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): major diastereomer: δ = 85.9, 50.4, 49.0, 46.2, 42.0, 39.6, 38.2, 36.5, 36.0, 33.2, 32.6, 27.9, 27.6, 23.6, 21.5, 20.7, 19.9 ppm; minor diastereomer: δ = 85.7, 48.8, 41.9, 36.4, 32.5, 27.5, 21.4, 20.6 ppm. ^{77}Se NMR (38 MHz, $CDCl_3$, 25 °C): major diastereomer: δ = 263.1 ppm. $C_{17}H_{30}OSe$ (329.38): calcd. C 61.98, H 9.18; found C 61.90, H 9.19.

(1*R*,2*R*,3*R*,5*S*)-3-(2-Methoxy-2-methylcyclopentylselanyl)-2,6,6-trimethylbicyclo[3.1.1]heptane (47): Purification by column chromatography on basic alumina with petroleum ether/ethyl acetate (95:5). Yield: 180 mg (44%), yellow oil; *dr* 72:28. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): major diastereomer: δ = 3.42–3.25 (m, 1 H), 3.24 (s, 3 H, OCH_3), 3.22–3.10 (m, 1 H), 2.64–2.52 (m, 1 H), 2.41–2.18 (m, 2 H), 2.10–1.89 (m, 3 H), 1.82–1.60 (m, 6 H), 1.32 (s, 3 H, CH_3), 1.18 (s, 3 H, CH_3), 1.13 (d, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH_3), 1.04 (d, $^3J_{H,H}$ = 9.6 Hz, 1 H, CH), 1.01 (s, 3 H, CH_3) ppm; minor diastereomer: δ = 1.30 (s, 3 H, CH_3), 1.11 (d, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): major diastereomer: δ = 86.1, 50.4, 48.5, 47.0, 45.8, 42.6, 39.2, 38.6, 36.8, 35.6, 34.0, 33.1, 27.9, 23.2, 21.5, 21.3, 20.6 ppm; minor diastereomer: δ = 85.7, 49.9, 45.5, 38.9, 35.9, 33.2, 21.2, 20.8 ppm. ^{77}Se NMR (38 MHz, $CDCl_3$, 25 °C): δ = 372.1 ppm.$C_{17}H_{30}OSe$ (329.38): calcd. C 61.98, H 9.18; found C 62.11, H 9.29.

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Received: January 19, 2006
Published Online: May 22, 2006

