Reactivity of dipinanyl diselenides functionalized at the C-10-position with $-\text{CH}_2\text{O}(\text{Se})\text{Ph}$, $-\text{OH}$ and $-\text{OCPh}_3$ substituents

Jacek Ścianowski,* Jakub Szumera, Agata J. Pacuła and Zbigniew Rafiński

*Department of Organic Chemistry, Faculty of Chemistry, Nicolaus Copernicus University in Torun,
7 Gagarin Street, 87-100 Torun, Poland*

E-mail: jsch@chem.umk.pl

Dedicated to Prof. Jacek Młochowski on the occasion of his 80th anniversary

Received 06-24-2016

Accepted 09-09-2016

Published on line 09-25-2016

Abstract

Terpenyl alcohols, (-)-nopol and (-)-myrtenol were efficiently applied in the synthesis of new diselenides. The pinane skeleton, as the core of the structure, was decorated at the C-10 position by hydroxyl and O-trityl groups, and also OPh and SePh substituents connected to the C-10 carbon by $-\text{CH}_2-$ linker. The diselenides were transformed to electrophilic selenium reagents and tested in asymmetric methoxyselenenylation of styrene, and selenocyclization of *o*-allylphenol.

Keywords: Diselenides, terpenes, asymmetric selenenylation, selenocyclization, Se-heteroatom interactions

Introduction

One advantage of organoselenium compounds is their broad applicability. They have been successfully used as reagents in the formation of new carbon-carbon and carbon-heteroatom bonds and as catalysts in asymmetric synthesis, for example in asymmetric epoxidation, cyclopropanation and aziridination reactions.¹⁻² This field of research is constantly expanding as Se-containing molecules are powerful reagents that can provide good chemo-, regio- and stereoselectivity. Diselenides especially can be acclaimed as one of the most useful classes of organoselenium compounds. These derivatives can be easily transformed into nucleophilic, electrophilic and radical reagents providing highly efficient precursors for new bond formation.³⁻⁸ Looking for new selenium derivatives is also interesting due to their biological and pharmacological functions.⁹⁻¹⁵

Addition to double bonds is one of the most common chemical transformations. Formation of the addition products by organoselenium electrophiles **1** proceeds by a two-step mechanism. Initial formation of a seleniranium ion **2** is followed by *anti*-addition of an internal **3** or external nucleophile **4**. When addition is an intramolecular process, a cyclization takes place. Depending on the regioselectivity of the reaction, *endo* **6** or *exo* **7** cyclization products are observed (Scheme 1).¹⁶⁻¹⁷

Scheme 1. Mechanism of selenenylation and selenocyclization reactions.

The selectivity of the reaction can be influenced by the type of alkene, since the selenium reagent attacks the nucleophile from the less hindered side, and also by the structure of electrophilic selenium reagent (RSeX). The intramolecular nonbonding interactions between selenium and other heteroatoms are highly interesting and can influence the stereoselectivity of the performed reactions. These interactions, engaging the free electron pair of the heteroatom and the selenium σ^* orbital, stabilize the required structure of the reagent, thus improving the stereoselectivity.¹⁸ The type of heteroatom and its placement in the structure of the molecule, particularly its distance from the selenium atom, can significantly influence the reactivity of the compound.

Previously, our research group has synthesised several examples of terpenyl diselenides, bearing an additional heteroatom, and transformed them into corresponding electrophiles and used these as reagents in the asymmetric selenenylation of olefins and selenocyclization of unsaturated alcohols and acids.¹⁹⁻²⁶ Application of dipinocamphyl diselenides **8** and **9** substituted with phenylselenenyl and pentafluorophenoxy groups resulted in good diastereomeric ratios with moderate yields. For diselenide **10**, bearing a hydroxyl group, the diastereomeric excess was minimal. In this paper we have changed the stereochemistry of the C3 carbon of compound **10** and evaluated the influence of this property on the formation of the diastereomers.

The stereoselectivity of methoxyselenenylation performed with diisopinocampyl diselenide **11** and myrtanyl diselenide **12** was comparable.²³⁻²⁴ The best diastereoselectivity for terpenyl diselenides, *dr* 90:10, was observed for bis(*cis*-3-hydroxyisocaranyl) diselenide **13** (Figure 1).²⁵

Figure 1. Results for the selenenylation and selenocyclization reaction performed with diselenides **8-13**.

The goal of this project was to synthesize dipinanyl diselenides with the selenium reactive center separated from the heteroatom by four carbon atoms and investigate their reactivity in additions to double bonds and selenocyclization reactions. The aim was also the synthesis of highly hindered derivatives substituted with a trityl group.

Results and Discussion

In the first part of the investigation we have used commercially available (-)-nopol **14** as a precursor to synthesize pinane derived diselenides. Substrate **14** was converted to corresponding chloride **15** and tosylate **16** by standard procedures described in previous papers.²⁰ Next step involved the hydroboration oxidation of chloride **15** to alcohol **17** and further reaction with sodium diselenide yielding the final product **18**. Tosylate **16** was transformed to ether **19** and selenide **20** via treatment with sodium phenolate or sodium phenyl selenolate respectively. Obtained derivatives **19** and **20** were next converted to alcohols **21** and **22** (Scheme 2).

Scheme 2. Synthesis of bis(3-hydroxynopyl) diselenide **18**, and alcohols **21** and **22**.

Alcohols **21** and **22** were then treated with tosyl chloride yielding tosylate **23** and with triphenylphosphine/carbon tetrachloride to form corresponding chlorides **24** and **25**. Further reaction of obtained tosylate and chlorides with sodium diselenide enabled to obtain diselenides **26** and **27** (Scheme 3)

Scheme 3. Synthesis of diselenides **26** and **27**.

In the next step, (-)-myrtenol **28** was converted into myrtenyl trityl ether **29**. Hydroboration oxidation to alcohol **30**, followed by mesylation and nucleophilic substitution with sodium diselenide yielded diselenide **32**. The product was further hydrolyzed to bis(10-hydroxypinocampyl) diselenide **33** (Scheme 4).

Scheme 4. Synthesis of pinocampyl diselenides **32** and **33**.

The reactivity of diselenides obtained was tested in the methoxyselenenylation of styrene (Table 1).

Table 1. Results for the asymmetric methoxyselenenylation of styrene.

Diselenide	Product	<i>dr</i>	Yield [%]
18	34	63:37	20
26	35	52:48	40
33	36	72:28	65

The best diastereoselectivity was obtained with diselenide **33**. Inversion of configuration at the C3 carbon of compound **33** resulted in an improvement of stereoselectivity in comparison to diselenide **10**, *dr* 52:48. Elongation of the C2 linker, from one $-\text{CH}_2-$ group (compound **11**) to $-\text{CH}_2\text{CH}_2-$ for diselenide **26** resulted in lower diastereoselectivity (Figure 1). In the case of trityl derivative **32**, hydrolysis of the trityl moiety was observed in the addition reaction conditions, and the electrophilic reagent from diselenide **32** could not be generated. For compound **27** no addition product was observed.

Diselenides **18** and **26** were also used in selenocyclization of *o*-allylphenol (Table 2).

Cyclization performed with electrophiles formed from diselenides **18** and **26** resulted in moderate diastereoselectivity. The results showed that elongation of the carbon chain placed at the C2 position in the pinane skeleton decreases the selectivity of the Se-electrophile.

Table 2. Results for the asymmetric selenocyclization of *o*-allylphenol.

Diselenide	Product	<i>dr</i>	Yield [%]
18	37	60:40	80
26	38	56:44	62

Conclusion

We have reported an efficient methodology for the synthesis of new chiral diselenides with a pinane system. Hydroxy, phenoxy, phenylselenenyl and trithyl groups were attached to the pinane skeleton at C10 and C11 positions. The derivatives were converted into corresponding electrophilic reagents and tested in the asymmetric selenenylation and selenocyclization reactions. The best diastereoselectivity was observed for 10-hydroxypinacamphyl diselenide, *dr* 72:28.

Experimental Section

General. ^1H NMR spectra were obtained at 200, 300 or 700 MHz and chemical shifts were recorded relative to SiMe_4 (δ 0.00) or solvent resonance (CDCl_3 δ 7.26). Multiplicities were given as: s (singlet), d (doublet), dd (double doublet), ddd (double double doublet), t (triplet), dt (double triplet), td (triple doublet) and m (multiplet). The number of protons (*n*) for a given resonance was indicated by *n*H. Coupling constants are reported as a *J* value in Hz. ^{13}C NMR spectra were acquired at 50.3 Hz and chemical shifts were recorded relative to solvent resonance (CDCl_3 δ 77.25). Commercially available solvents THF, DMF, methanol, diethyl and petroleum ether (Aldrich) and chemicals were used without further purification. Column chromatography was performed using Merck Kieselgel 60 (0.06-0.2 mm).

General procedure for the synthesis of terpene chlorides **15, **24** and **25**.** A mixture of terpene alcohol **14**, **21** or **22** (100 mmol) and triphenylphosphine (200 mmol) in CCl_4 (240 mL) was refluxed for 24 h. The solution was cooled and petroleum ether (300 mL) was added. The precipitate formed was filtered off and the solution was concentrated under reduced pressure. Product **15** was isolated by vacuum distillation, and chlorides **24** and **25** by column chromatography (petroleum ether/ CHCl_3 90:10).

(1R)-(-)-nopyl chloride (15**).** 82%, $[\alpha]_D^{20} = -35.8$ (*c* 2.36, CHCl_3). ^1H NMR (200 MHz, CDCl_3): δ_{H} 0.83 (s, 3H, CH_3), 1.18 (d, *J* 9.9 Hz, 1H), 1.28 (s, 3H, CH_3), 1.98-2.15 (m, 2H), 2.20-2.29 (m, 2H), 2.32-2.46 (m, 3H), 3.46-3.54 (m, 2H), 5.30-5.34 (m, 1H). ^{13}C NMR (CDCl_3 , 75.5 MHz): δ_{C} 21.2 (CH_3), 26.2 (CH_3), 31.3 (CH_2), 31.6 (CH_2), 38.0 (C), 40.1 (CH_2), 40.7 (CH), 42.4 (CH_2), 44.5 (CH), 116.2 (CH), 144.4 (C). Anal. calcd for $\text{C}_{11}\text{H}_{17}\text{Cl}$ (184.71): C, 71.53; H, 9.28 Found: C, 71.45; H, 9.20.

(1S)-(-)-10-Phenoxymethylpinocamphyl chloride (24**).** 29%, $[\alpha]_D^{20} = -30.7$ (*c* 1.85, CHCl_3). ^1H NMR (300 MHz, CDCl_3): δ = 1.07 (s, 3H), 1.22 (s, 3H), 1.27 (d, *J* 10.2 Hz, 1H), 1.87-1.98 (m, 2H), 2.14 (dt, *J* 6.3, 3.6 Hz, 1H), 2.21-

2.29 (m, 2H), 2.45-2.56 (m, 1H), 2.64 (ddd, J 14.4, 9.6, 4.8 Hz, 1H), 2.67-2.74 (m, 1H), 3.94 (ddd, J 9.3, 7.2, 6.3 Hz, 1H), 4.06 (ddd, J 9.3, 6.3, 6.3 Hz, 1H), 4.82 (ddd, J 9.9, 9.9, 8.4 Hz, 1H), 6.75-6.94 (m, 3H; $3\times\text{CH}$), 7.26-7.33 (m, 2H; $2\times\text{CH}$); ^{13}C NMR (75.5 MHz, CDCl_3): δ = 23.1 (CH_3), 27.0 (CH_3), 27.7 (CH_2), 31.8 (CH_2), 38.6 (CH_2), 39.3 (C), 41.2 ($2\times\text{CH}$), 46.9 (CH), 55.4 (CH), 67.5 (CH_2), 114.4 ($2\times\text{CH}$), 120.5 (CH), 129.4 ($2\times\text{CH}$), 160.0 (C). Anal. calcd for $\text{C}_{17}\text{H}_{23}\text{ClO}$ (278.82): C, 73.23; H, 8.31 Found: C, 73.20; H, 8.25.

(1S)-(+)-10-Phenylselanylmethylpinocampyl chloride (25). 34%, $[\alpha]_D^{20} = +29.2$ (c 1.25, CHCl_3). ^1H NMR (300 MHz, CDCl_3): δ = 0.82 (s, 3H), 1.07 (d, J 9.6 Hz, 1H), 1.19 (s, 3H), 1.71 (ddd, J 14.1, 4.2, 2.7 Hz, 1H), 1.78-2.05 (m, 6H), 2.24-2.42 (m, 1H), 2.45-2.55 (m, 1H), 2.93-3.01 (m, 2H), 4.06 (ddd, J 14.1, 9.0, 4.5 Hz, 1H), 7.22-7.30 (m, 3H), 7.45-7.52 (m, 2H). ^{13}C NMR (50.3 MHz, CDCl_3): δ = 23.6 (CH_3), 26.5 (CH_2), 27.4 (CH_3), 32.5 (CH_2), 35.9 (CH_2), 37.9 (C), 39.1 (CH_2), 41.5 (CH), 45.4 (CH), 53.1 (CH), 70.0 (CH), 126.7 (CH), 129.0 ($2\times\text{CH}$), 130.3 (C), 132.4 ($2\times\text{CH}$). ^{77}Se NMR (38.1 MHz, CDCl_3): δ = 288.5 (SePh). Anal. calcd for $\text{C}_{17}\text{H}_{23}\text{ClSe}$ (341.78): C, 59.74; H, 6.78 Found: C, 59.87; H, 6.69.

General procedure for the synthesis of terpene tosylates 16 and 23. Tosyl chloride (110 mmol) was added to a solution of terpene alcohol **14** or **21** (100 mmol) in dry pyridine (125 mL), cooled to 0 °C. The mixture was stirred at rt for 24 h, water (100 mL) was added and the resulting precipitate was filtered off, dried and used without further purification.

(1R)-(-)-Nopyl tosylate (16). 65%, $[\alpha]_D^{20} = -27.5$ (c 13.90, CHCl_3). ^1H NMR (200 MHz, CDCl_3): δ_{H} 0.76 (s, 3H, CH_3), 1.08 (d, J 9.6 Hz, 1H), 1.23 (s, 3H, CH_3), 1.90-1.97 (m, 1H), 2.00-2.13 (m, 1H), 2.17-2.39 (m, 5H), 2.45 (s, 3H, CH_3), 4.02 (t, J 7.0 Hz, 2H), 5.22 (m, 1H), 7.33 (d, J 8.2 Hz, 2H), 7.78 (d, J 8.2 Hz, 2H). ^{13}C NMR (CDCl_3 , 50 MHz): δ_{C} 21.0 (CH_3), 21.5 (CH_3), 26.1 (CH_3), 31.2 (CH_2), 31.4 (CH_2), 36.0 (CH_2), 37.9 (C), 40.5 (CH), 45.4 (CH), 68.5 (CH_2), 114.2 (CH), 127.8 ($2\times\text{CH}$), 129.7 ($2\times\text{CH}$), 133.2 (C), 142.6 (C), 144.6 (C). Anal. calcd for $\text{C}_{18}\text{H}_{24}\text{O}_3\text{S}$ (320.45): C, 67.47; H, 7.55 Found: C, 67.57; H, 7.61.

(1S)-(+)-10-Phenoxymethylisopinocampyl tosylate (23). 63%, $[\alpha]_D^{20} = +5.49$ (c 2.04, CHCl_3). ^1H NMR (200 MHz, CDCl_3): δ_{H} 0.57-0.79 (m, 2H), 1.00 (s, 3H, CH_3), 1.03 (d, J 7.0 Hz, 3H, CH_3), 1.06 (s, 3H, CH_3), 1.25-1.46 (m, 2H), 1.82-2.28 (m, 3H), 3.44-3.58 (dd, J 8.2, 6.2 Hz, 1H), 6.97-7.05 (m, 1H), 7.20-7.38 (m, 2H), 7.52-7.57 (dd, J 7.8, 1.0 Hz, 1H). ^{13}C NMR (CDCl_3 , 50 MHz): δ_{C} 15.7 (CH_3), 17.8 (C), 18.7 (CH_3), 21.0 (CH), 21.2 (CH), 24.6 (CH_2), 25.5 (CH_2), 28.4 (CH_3), 30.5 (CH), 45.9 (CH), 124.9 (C), 126.5 (CH), 127.5 (CH), 130.1 (CH), 133.0 (CH), 138.5 (C). Anal. calcd for $\text{C}_{24}\text{H}_{30}\text{O}_4\text{S}$ (414.56): C, 69.53; H, 7.29 Found: C, 69.50; H, 7.22.

General procedure for the synthesis of terpene alcohols 17, 21, 22 and 30. To a solution of olefin **15**, **19**, **20** or **29** (51.5 mmol) in dry THF (75 mL) cooled to 0 °C, borane–dimethyl sulfide complex (5.2 mL, 10 M, 51.5 mmol) was added dropwise. The reaction was stirred at 0 °C for 1 h and at rt overnight. Water was added to the reaction mixture and solvent was evaporated. To the residue THF (75 mL), 3M NaOH (50 mL) and 30% H_2O_2 (20 mL) were added. The reaction mixture was stirred at 50 °C for 2 h, THF was evaporated and the water layer was washed with Et_2O . The combined organic layers were dried over MgSO_4 in the presence of MnO_2 , solvent was evaporated and the crude product was purified by column chromatography (silica gel, CHCl_3).

(1S)-(+)-10-Chloromethylisopinocampheol (17). 75%, $[\alpha]_D^{20} = +16.5$ (c 2.79, CHCl_3). ^1H NMR (300 MHz, CDCl_3): δ_{H} 0.88 (s, 3H, CH_3), 1.08 (d, J 9.9 Hz, 1H), 1.21 (s, 3H, CH_3), 1.73 (ddd, J 14.1, 4.2, 2.4 Hz, 1H), 1.75 (bs, 1H, OH), 1.86-2.09 (m, 5H), 2.35-2.43 (m, 1H), 2.49-2.58 (m, 1H), 3.59-3.69 (m, 2H), 4.07-4.12 (m, 1H). ^{13}C NMR (CDCl_3 , 50 MHz): δ_{C} 23.7 (CH_3), 27.4 (CH_3), 33.6 (CH_2), 37.9 (C), 38.5 (CH_2), 39.8 (CH_2), 41.5 (CH), 44.0 (CH_2), 45.6 (CH), 50.4 (CH), 70.0 (CH). Anal. calcd for $\text{C}_{11}\text{H}_{19}\text{ClO}$ (202.72): C, 65.17; H, 9.45 Found: C, 65.06; H, 9.38.

(1S)-(+)-10-Phenoxymethylisopinocampheol (21). 59%, $[\alpha]_D^{20} = +5.93$ (c 1.58, CHCl_3). ^1H NMR (200 MHz, CDCl_3): δ_{H} 0.96 (s, 3H, CH_3), 1.16 (d, J 9.6 Hz, 1H), 1.22 (s, 3H, CH_3), 1.67-2.17 (m, 6H), 2.26-2.61 (m, 3H), 4.01-

4.30 (m, 3H), 6.88–6.99 (m, 3H), 7.21–7.35 (m, 2H). ^{13}C NMR (CDCl_3 , 50 MHz): δ_{C} 23.7 (CH_3), 27.5 (CH_3), 33.7 (CH_2), 35.7 (CH_2), 37.9 (C), 38.3 (CH_2), 41.5 (CH), 47.0 (CH), 51.0 (CH), 67.5 (CH_2), 70.2 (CH_2), 114.5 ($2\times\text{CH}$), 120.9 (CH), 129.5 ($2\times\text{CH}$), 159.6 (C). Anal. calcd for $\text{C}_{17}\text{H}_{24}\text{O}_2$ (260.37): C, 78.42; H, 9.29 Found: C, 78.38; H, 9.33.

(1S)-(+)-10-Phenylselanylmethylisopinocampheol (22). 34%, $[\alpha]_{\text{D}}^{20} = +29.2$ (c 1.25, CHCl_3). ^1H NMR (200 MHz, CDCl_3): δ_{H} 0.82 (s, 3H, CH_3), 1.07 (d, J 9.6 Hz, 1H), 1.19 (s, 3H, CH_3), 1.71 (ddd, J 14.1, 4.2, 2.7 Hz, 1H), 1.78–2.05 (m, 6H), 2.24–2.42 (m, 1H), 2.45–2.55 (m, 1H), 2.93–3.01 (m, 2H), 4.06 (ddd, J 14.1, 9.0, 4.5 Hz, 1H), 7.22–7.30 (m, 3H), 7.45–7.52 (m, 2H). ^{13}C NMR (CDCl_3 , 50 MHz): δ_{C} 23.6 (CH_3), 26.5 (CH_2), 27.4 (CH_3), 32.5 (CH_2), 35.9 (CH_2), 37.9 (C), 39.1 (CH_2), 41.5 (CH), 45.4 (CH), 53.1 (CH), 70.0 (CH), 126.7 (CH), 129.0 ($2\times\text{CH}$), 130.3 (C), 132.4 ($2\times\text{CH}$). ^{77}Se NMR (38 MHz, CDCl_3): δ_{Se} 288.5. Anal. calcd for $\text{C}_{17}\text{H}_{24}\text{OSe}$ (323.33): C, 63.15; H, 7.48 Found: C, 63.06; H, 7.63.

(1S)-(+)-10-(Triphenylmethoxy)isopinocampheol (30). 94%, $[\alpha]_{\text{D}}^{20} = -29.90$ (1.06, CHCl_3). ^1H NMR (700 MHz, CDCl_3): δ_{H} 0.581 (s, 3H, CH_3), 1.165 (s, 3H, CH_3), 1.14–1.20 (m, 1H), 1.79 (ddd, J 14.0, 4.9, 2.1 Hz, 1H), 1.88 (t, J 5.6 Hz, 1H), 1.95–1.98 (m, 1H), 2.33–2.39 (m, 1H), 2.41–2.49 (m, 1H), 2.54 (s, 1H, OH), 3.15–3.19 (m, 1H), 3.32 (dd, J 8.4, 5.6 Hz, 1H), 4.18 (dt, J 9.8, 4.9 Hz, 1H), 7.23–7.31 (m, 3H), 7.32–7.39 (m, 6H), 7.47–7.54 (m, 6H). ^{13}C NMR (CDCl_3 , 50 MHz): δ_{C} 23.1 (CH_3), 27.5 (CH_3), 34.4 (CH_2), 36.9 (CH_2), 37.9 (C), 41.8 (CH), 43.5 (CH), 53.3 (CH), 67.4 (CH_2), 68.0 (CH), 87.0 (CH), 127.1 ($3\times\text{CH}$), 127.9 ($6\times\text{CH}$), 128.7 ($6\times\text{CH}$), 144.0 ($3\times\text{C}$). Anal. calcd for $\text{C}_{29}\text{H}_{32}\text{O}_2$ (412.56): C, 84.43; H, 7.82 Found: C, 84.70; H, 7.90.

General procedure for the synthesis of compounds 19 and 20. To a solution of diphenyl diselenide (7.3 g, 23.39 mmol), or phenol (46.80 mmol) for compound **19**, in MeOH (45 mL), under argon and at 0 °C, sodium borohydride (1.77 g, 46.78 mmol) was added and the mixture was stirred for 10 min. A solution of (1R)-(-)-nopyl tosylate **16** (15.00 g, 46.80 mmol) in MeOH (45 mL) was added and the mixture was stirred for 24 h at rt. The solution was poured on water and extracted with petroleum ether (3 x 100 mL). The combined organic layers were washed with brine, dried over anhydrous MgSO_4 and evaporated. The crude product was purified using column chromatography (silica gel, **19**: PE/AcOEt 95:5, **20**: hexane).

(1R)-(-)-Nopyl phenyl ether (19). 70%, $[\alpha]_{\text{D}}^{20} = -27.2$ (c 3.99, CHCl_3). ^1H NMR (300 MHz, CDCl_3): δ_{H} 0.84 (s, 3H, CH_3), 1.21 (d, J 8.4 Hz, 1H), 1.25 (s, 3H, CH_3), 2.08–2.11 (m, 2H), 2.22–2.26 (m, 2H), 2.38 (ddd, J 8.4, 8.4, 5.4 Hz, 1H), 2.43–2.48 (m, 2H), 3.97 (t, J 7.5 Hz, 2H), 5.35–5.39 (m, 1H), 6.84–6.98 (m, 3H), 7.22–7.36 (m, 2H). ^{13}C NMR (CDCl_3 , 50 MHz): δ_{C} 21.2 (CH_3), 26.3 (CH_3), 31.4 (CH_2), 31.7 (CH_2), 36.6 (CH_2), 38.1 (C), 40.8 (CH), 46.0 (CH), 66.3 (CH_2), 114.6 ($2\times\text{CH}$), 118.5 (CH), 120.5 (CH), 129.4 ($2\times\text{CH}$), 144.6 (C), 158.9 (CH). Anal. calcd for $\text{C}_{17}\text{H}_{22}\text{O}$ (242.36): C, 84.25; H, 9.15 Found: C, 84.22; H, 9.11.

(1R)-(-)-Nopyl phenyl selenide (20). 88%, $[\alpha]_{\text{D}}^{20} = -18.9$ (c 3.85, CHCl_3). ^1H NMR (300 MHz, CDCl_3): δ_{H} 0.85 (s, 3H, CH_3), 1.08 (d, J 8.4 Hz, 1H), 1.28 (s, 3H, CH_3), 2.02 (dt, J 7.2, 1.5 Hz, 1H), 2.07–2.25 (m, 3H), 2.31–2.36 (m, 3H), 2.85–3.00 (m, 2H), 5.27 (m, 1H), 7.20–7.30 (m, 3H), 7.46–7.52 (m, 2H). ^{13}C NMR (CDCl_3 , 50 MHz): δ_{C} 21.2 (CH_3), 25.4 (CH_2), 26.3 (CH_3), 31.2 (CH_2), 31.7 (CH_2), 37.6 (CH_2), 38.0 (C), 40.8 (CH), 45.7 (CH), 117.4 (CH), 126.6 (CH), 129.0 ($2\times\text{CH}$), 132.4 ($2\times\text{CH}$), 133.0 (C), 147.1 (C). ^{77}Se NMR (38 MHz, CDCl_3): δ_{Se} 303.0. Anal. calcd for $\text{C}_{17}\text{H}_{22}\text{Se}$ (305.32): C, 66.88; H, 7.26 Found: C, 66.86; H, 7.23.

General procedure for the synthesis of diselenides 18, 26, 27 and 32. To a suspension of selenium (3.95 g, 50 mmol) and NaOH (3.00 g, 75.0 mmol) in dry DMF (100 mL) hydrazine hydrate (1.21 mL, 25.0 mmol) was added dropwise and the mixture was heated at 100 °C for 15 min. The reaction mixture was cooled to ambient temperature and the appropriate tosylate **23** (50.0 mmol), mesylate **31** (50.0 mmol) or chloride **17**, **25** (50.0

mmol) dissolved in DMF (50 mL) was added. The mixture was stirred at 50 °C (rt for compound **32**) for 24 h. The solution was poured on water (250 mL) and extracted with petroleum ether (4 x 100 mL). The combined organic layers were washed with water, brine, dried over anhydrous MgSO_4 and evaporated. The crude product was purified using column chromatography (silica gel, **18**: $\text{CH}_2\text{Cl}_2/\text{AcOEt}$ 80:20, **26**, **27**: hexane, **32**: CHCl_3).

(1S,1'S)-(-)-Bis(3-hydroxynopyl) diselenide (18). 52%, $[\alpha]_D^{20} = -11.6$ (c 1.60, CHCl_3). ^1H NMR (200 MHz, CDCl_3): δ_{H} 0.91 (s, 6H, CH_3), 1.08 (d, J 9.9 Hz, 2H), 1.21 (s, 6H, CH_3), 1.67-2.08 (m, 12H), 2.14-2.22 (m, 2H), 2.32-2.61 (m, 4H), 2.97-3.08 (m, 4H), 4.03-4.14 (m, 2H). ^{13}C NMR (CDCl_3 , 50 MHz): δ_{C} 23.8 ($2\times\text{CH}_3$), 27.4 ($2\times\text{CH}_3$), 28.5 ($2\times\text{CH}_2$), 33.7 ($2\times\text{CH}_2$), 36.3 ($2\times\text{CH}_2$), 38.0 ($2\times\text{C}$), 39.2 ($2\times\text{CH}_2$), 41.6 ($2\times\text{CH}$), 45.4 ($2\times\text{CH}$), 52.7 ($2\times\text{CH}$), 70.1 ($2\times\text{CH}$). ^{77}Se NMR (38 MHz, CDCl_3): δ_{Se} 306.8. Anal. calcd for $\text{C}_{22}\text{H}_{38}\text{O}_2\text{Se}_2$ (492.46): C, 53.66; H, 7.78 Found: C, 53.59; H, 7.70.

(1S,1'S)-(+)-Bis(10-phenoxyethylpinocampyl) diselenide (26). 32%, $[\alpha]_D^{20} = +44.4$ (c 1.05, CHCl_3). ^1H NMR (200 MHz, CDCl_3): δ_{H} 0.81-0.99 (m, 2H), 1.03 (s, 6H, CH_3), 1.20 (s, 6H, CH_3), 1.22-1.62 (m, 6H), 1.78-2.80 (m, 16H), 3.83-4.06 (m, 4H), 4.18 (q, J 8.4 Hz, 2H), 6.81-6.95 (m, 6H), 7.20-7.35 (m, 4H). ^{13}C NMR (CDCl_3 , 50 MHz): δ_{C} 23.2 ($2\times\text{CH}_3$), 27.3 ($2\times\text{CH}_3$), 27.3 ($2\times\text{CH}_2$), 33.0 ($2\times\text{CH}_2$), 36.7 ($2\times\text{CH}_2$), 39.3 ($2\times\text{C}$), 40.6 ($2\times\text{CH}$), 40.9 ($2\times\text{CH}$), 41.8 ($2\times\text{CH}$), 46.1 ($2\times\text{CH}$), 67.6 ($2\times\text{CH}_2$), 114.4 ($4\times\text{CH}$), 120.4 ($2\times\text{CH}$), 129.3 ($4\times\text{CH}$), 158.9 ($2\times\text{C}$). ^{77}Se NMR (38 MHz, CDCl_3): δ_{Se} 356.3. Anal. calcd for $\text{C}_{34}\text{H}_{46}\text{O}_2\text{Se}_2$ (644.65): C, 63.35; H, 7.19 Found: C, 63.42; H, 7.32.

(1S,1'S)-(+)-Bis(10-phenylselenanylmethylisopinocampyl) diselenide (27). 28%, $[\alpha]_D^{20} = +62.5$ (c 1.11, CHCl_3). ^1H NMR (200 MHz, CDCl_3): δ_{H} 0.94 (s, 6H, CH_3), 1.18 (d, J 9.4 Hz, 2H), 1.20 (s, 6H, CH_3), 1.74-2.60 (m, 16H), 2.82-3.07 (m, 4H), 3.36-3.44 (m, 2H), 7.18-7.32 (m, 6H), 7.43-7.53 (m, 4H). ^{13}C NMR (CDCl_3 , 50 MHz): δ_{C} 23.2 ($2\times\text{CH}_3$), 26.0 ($2\times\text{CH}_2$), 27.6 ($2\times\text{CH}_3$), 32.6 ($2\times\text{CH}_2$), 35.9 ($2\times\text{CH}_2$), 38.5 ($2\times\text{C}$), 38.8 ($2\times\text{CH}_2$), 40.1 ($2\times\text{CH}$), 42.2 ($2\times\text{CH}$), 44.8 ($2\times\text{CH}$), 51.8 ($2\times\text{CH}$), 126.6 ($2\times\text{CH}$), 129.0 ($4\times\text{CH}$), 130.5 ($2\times\text{C}$), 132.3 ($4\times\text{CH}$). ^{77}Se NMR (38 MHz, CDCl_3): δ_{Se} 297.5, 463.4. Anal. calcd for $\text{C}_{34}\text{H}_{46}\text{Se}_4$ (770.57): C, 53.00; H, 6.02 Found: C, 52.93; H, 6.13.

(1S,1'S)-(+)-Bis[10-(triphenylmethoxy)pinocampyl] diselenide (32). 61%, $[\alpha]_D^{20} = 154.11$ (2.65, CHCl_3). ^1H NMR (700 MHz, CDCl_3): δ_{H} 0.60 (s, 6H, CH_3), 1.17 (s, 6H, CH_3), 1.30 (d, J 10.5 Hz, 2H), 1.87-1.93 (m, 4H), 2.25 (dt, J 9.8, 4.9 Hz, 2H), 2.38-2.45 (m, 4H), 2.78-2.84 (m, 2H), 3.19 (t, J 9.1 Hz, 2H), 3.44 (dd, J 9.1, 5.6 Hz, 2H), 3.95-4.01 (m, 2H), 7.21-7.24 (m, 6H), 7.28-7.31 (m, 12H), 7.45-7.48 (m, 12H). ^{13}C NMR (CDCl_3 , 50 MHz): δ_{C} 22.4 ($2\times\text{CH}_3$), 27.2 ($2\times\text{CH}_3$), 27.4 ($2\times\text{CH}_2$), 36.5 ($2\times\text{CH}_2$), 36.9 ($2\times\text{CH}$), 39.2 ($2\times\text{C}$), 41.8 ($2\times\text{CH}$), 44.0 ($2\times\text{CH}$), 44.2 ($2\times\text{CH}$), 66.1 ($2\times\text{CH}_2$), 86.4 ($2\times\text{C}$), 126.8 ($6\times\text{CH}$), 127.6 ($12\times\text{CH}$), 128.8 ($12\times\text{CH}$), 144.4 ($6\times\text{C}$). ^{77}Se NMR (38 MHz, CDCl_3): δ_{Se} 366.95. Anal. calcd for $\text{C}_{58}\text{H}_{62}\text{O}_2\text{Se}_2$ (949.03): C, 73.40; H, 6.58 Found: C, 73.37; H, 6.48.

(1S)-(-)-6,6-Dimethyl-2-((trityloxy)methyl)bicyclo[3.1.1]hept-2-ene (29). To a solution of (1R)-(-)-myrtenol (10.0 g, 65.7 mmol) in pyridine (5.3 g, 65.7 mmol) and CH_2Cl_2 (130 mL) trityl chloride (18.3 g, 65.7 mmol) was added and the mixture was stirred for 24 h at rt. The solution was poured into water (100 mL) and extracted with CH_2Cl_2 (2 x 20 mL). The combined organic layers were dried over anhydrous MgSO_4 and evaporated. The crude product was purified by crystallization ($\text{Et}_2\text{O}/\text{MeOH}$). 78%, $[\alpha]_D^{20} = -16.12$ (1.46, CHCl_3). ^1H NMR (700 MHz, CDCl_3): δ_{H} 0.93 (s, 3H, CH_3), 1.22 (d, J 8.4 Hz, 1H), 1.29 (s, 3H, CH_3), 1.97 (td, J 5.6, 1.4 Hz, 1H), 2.13-2.16 (m, 1H), 2.31-2.41 (m, 3H), 3.44-3.49 (m, 2H), 5.72-5.74 (m, 1H), 7.24-7.27 (m, 3H), 7.28-7.33 (m, 6H), 7.48-7.51 (m, 6H). ^{13}C NMR (CDCl_3 , 50 MHz): δ_{C} 21.1 (CH_3), 26.2 (CH_3), 31.3 (CH_2), 31.5 (CH_2), 38.0 (C), 41.1 (CH), 43.6 (CH), 66.5 (CH_2), 86.5 (C), 117.1 (CH), 126.8 ($3\times\text{CH}$), 127.7 ($6\times\text{CH}$), 128.6 ($6\times\text{CH}$), 144.4 ($3\times\text{C}$), 145.5 (C). Anal. calcd for $\text{C}_{29}\text{H}_{30}\text{O}$ (394.55): C 88.28; H 7.66 Found: C 88.03; H 7.72.

(1R)-(+)-6,6-Dimethyl-2-((trityloxy)methyl)bicyclo[3.1.1]heptan-3-yl methanesulfonate (31). To a solution of 10-(triphenylmethoxy)-isopinocampheol (6.2 g, 15 mmol) in dry Et_2O (100 mL) cooled to -30 °C, under argon atmosphere, Et_3N (6.3 mL, 45 mmol) was added dropwise followed by the addition of mesyl chloride (3.5 g, 30 mmol). The mixture was stirred for 1.5 h at rt. The solution was poured into water (100 mL) and extracted with

CH₂Cl₂ (2 x 20 mL). The combined organic layers were dried over anhydrous MgSO₄ and evaporated. The crude product was purified by crystallization (Et₂O/hexane). 69%, $[\alpha]_D^{20} = +23.86$ (1.38, CHCl₃). ¹H NMR (700 MHz, CDCl₃): δ_H 0.58 (s, 3H, CH₃), 1.20 (s, 3H, CH₃), 1.21 (d, *J* 10.5 Hz, 1H), 1.94-1.99 (m, 1H), 2.15 (dt, *J* 14.7, 3.5 Hz, 1H), 2.29 (td, *J* 5.6, 1.4 Hz, 1H), 2.46-2.51 (m, 1H), 2.55-2.60 (m, 2H), 2.84 (s, 3H, CH₃), 3.20 (t, *J* 8.4 Hz, 1H), 3.24 (dd, *J* 9.1, 5.6 Hz, 1H), 4.78-4.83 (m, 1H), 7.24-7.29 (m, 3H), 7.31-7.35 (m, 6H), 7.45-7.48 (m, 6H). ¹³C NMR (CDCl₃, 50 MHz): δ_C 23.5 (CH₃), 26.9 (CH₃), 32.7 (CH₂), 36.6 (CH₂), 37.8 (C), 38.6 (CH₃), 41.2 (CH), 42.8 (CH), 49.7 (CH), 65.0 (CH₂), 78.1 (CH), 86.7 (C), 127.0 (3×CH), 127.8 (6×CH), 128.7 (6×CH), 143.9 (3×C). Anal. calcd for C₃₀H₃₄O₄S (490.65): C 73.44; H 6.98 Found: C 73.68; H 7.14.

((1R)-(-)-6,6-Dimethyl-3-(methylselenanyl)bicyclo[3.1.1]heptan-2-yl)methanol (33). To a solution of diselenide **31** (2 g, 2.1 mmol) in CH₂Cl₂ (20 mL), HCl_{aq} (37%, 0.5 mL) was added. The mixture was stirred for 1 h at rt and washed with water until pH=7. The organic layer was dried over anhydrous MgSO₄ and evaporated. The crude product was purified by column chromatography (CHCl₃). 30%, $[\alpha]_D^{20} = -9.19$ (1.45, CHCl₃). ¹H NMR (700 MHz, CDCl₃): δ_H 0.93 (s, 6H, CH₃), 1.21 (s, 6H, CH₃), 1.39 (d, *J* 9.8 Hz, 2H), 1.94-1.98 (m, 2H), 2.15 (dd, *J* 14, 9.1 Hz, 2H), 2.18-2.21 (m, 2H), 2.24-2.29 (m, 2H), 2.13-2.30 (bs, 1H, OH), 2.56 (ddd, *J* 14.0, 9.8, 4.9 Hz, 2H), 2.64-2.69 (m, 2H), 3.60 (dd, *J* 11.9, 4.9 Hz, 2H), 4.11-4.16 (m, 2H), 4.18 (dd, *J* 11.2, 7.7 Hz, 2H). ¹³C NMR (CDCl₃, 50 MHz): δ_C 23.2 (2×CH₃), 27.1 (2×CH₃), 27.5 (2×CH₂), 36.7 (2×CH₂), 39.0 (2×C), 39.9 (2×CH), 41.7 (2×CH), 46.0 (2×CH), 48.4 (2×CH), 66.3 (2×CH₂). ⁷⁷Se NMR (38 MHz, CDCl₃): δ_{Se} 365.92. Anal. calcd for C₂₀H₃₄O₂Se₂ (464.40): C 51.73; H 7.38 Found: C 51.62; H 7.45.

General procedure for the methoxyselenenylation of styrene. To a solution of diselenide (0.58 mmol) dissolved in dry CH₂Cl₂ (8 mL), cooled to -78 °C, a solution of bromine in CCl₄ (0.58 mL, 1M, 0.58 mmol) was added dropwise. After 15 min, a 0.70 M MeOH solution of silver triflate (320 mg, 1.80 mL) was added at -78 °C and the mixture stirred for another 15 min. Styrene (2.9 mmol) was added and the mixture was stirred at the same temperature for 2 h. The reaction mixture was poured on 10% NaHCO₃ solution, diluted with 50 mL of CH₂Cl₂, washed with water and brine, dried over MgSO₄ and concentrated in vacuo. The crude product was purified by column chromatography (silica gel, petroleum ether/EgtOAc 95:5).

(1S)-3-Hydroxynopyl-(2-methoxy-2-phenylethyl) selenide (34). 20%, *dr* 63:37. ¹H NMR (200 MHz, CDCl₃): δ_H main diastereoisomer δ = 0.85 (s, 3H, CH₃), 1.08 (d, *J* 9.6 Hz, 1H), 1.19 (s, 3H, CH₃), 1.62-2.06 (m, 7H), 2.29-2.61 (m, 4H), 2.76 (dd, *J* 12.6, 5.6 Hz, 1H), 2.98 (dd, *J* 12.6, 8.0 Hz, 1H), 3.24 (s, 3H, OCH₃), 4.01 (m, 1H), 4.32 (ddd, *J* 8.2, 5.6, 3.0 Hz, 1H), 7.22-7.40 (m, 5H) ppm; minor diastereoisomer – only separated signals: 2.73 (dd, *J* 12.6, 5.6 Hz, 1H), 2.96 (dd, *J* 12.6, 8.0 Hz, 1H). ¹³C NMR (CDCl₃, 50 MHz): δ_C main diastereoisomer δ = 23.6 (CH₃), 23.7 (CH₂), 27.4 (CH₃), 31.0 (CH₂), 33.4 (CH₂), 36.1 (CH₂), 37.9 (C), 38.9 (CH₂), 41.5 (CH), 45.7 (CH), 53.2 (CH), 56.8 (OCH₃), 69.9 (CH), 84.3 (CH), 126.6 (2×CH), 127.9 (CH), 128.4 (2×CH), 141.3 (C) ppm; minor diastereoisomer – only separated signals: 30.9 (CH₂), 36.2 (CH₂), 45.6 (CH), 84.4 (CH). ⁷⁷Se NMR (38 MHz, CDCl₃): δ_{Se} main diastereoisomer δ = 147.2 (Se) ppm; minor diastereoisomer: 148.4 Anal. calcd for C₂₀H₃₀O₂Se (381.41): C, 62.98; H, 7.93 Found: C, 62.80; H, 7.90.

(1S)-10-Phoxymethylpinocampyl-(2-methoxy-2-phenylethyl) selenide (35). 40%, *dr* 61:39. ¹H NMR (200 MHz, CDCl₃): δ_H main diastereoisomer δ = 0.98 (s, 3H, CH₃), 1.18 (s, 3H, CH₃), 1.21-1.34 (m, 2H), 1.82-2.19 (m, 4H), 2.22-2.56 (m, 3H), 2.78 (dd, *J* 12.0, 5.2 Hz, 1H), 3.03 (dd, *J* 12.0, 7.8 Hz, 1H), 3.25 (s, 3H, OCH₃), 3.58-3.74 (m, 1H), 3.90-4.00 (m, 2H), 4.37 (dd, *J* 7.8, 5.2 Hz, 1H), 6.80-6.97 (m, 3H), 7.20-7.38 (m, 7H) ppm; minor diastereoisomer – only separated signals: 2.76 (dd, *J* 12.0, 5.2 Hz, 1H), 3.06 (dd, *J* 12.0, 7.8 Hz, 1H), 3.26 (s, 3H, OCH₃) ppm. ¹³C NMR (CDCl₃, 50 MHz): δ_C main diastereoisomer δ = 23.4 (CH₃), 27.1 (CH₂), 27.3 (CH₃), 30.9 (CH₂), 32.9 (CH₂), 34.1 (CH), 36.1 (CH₂), 39.3 (C), 39.9 (CH), 41.7 (CH), 45.9 (CH), 56.9 (OCH₃), 67.5 (CH₂), 84.4 (CH), 114.4 (2×CH), 120.3 (CH), 126.7 (2×CH), 127.9 (CH), 128.4 (2×CH), 129.3 (2×CH), 141.3 (C), 159.0 (C) ppm;

minor diastereoisomer – only separated signals: 30.7 (CH₂), 32.8 (CH₂), 33.9 (CH), 36.3 (CH₂), 46.0 (CH), 84.1 (CH), 141.2 (C). ⁷⁷Se NMR (38 MHz, CDCl₃): δ_{Se} main diastereoisomer δ = 203.5 (Se) ppm; minor diastereoisomer: 204.4. Anal. calcd for C₂₆H₃₄O₂Se (457.51): C, 67.71; H, 7.27 Found: C, 67.72; H, 7.17.

((1R)-3-Hydroxymyrtilanyl-(2-methoxy-2-phenylethyl) selenide (36). 65%, *dr* 72:28. ¹H NMR (700 MHz, CDCl₃): δ_H main diastereoisomer δ=0.86 (s, 3H, CH₃), 1.17 (s, 3H, CH₃), 1.29 (d, *J* 10.5 Hz, 1H), 1.85-1.91 (m, 1H), 2.07-2.14 (m, 2H), 2.16-2.22 (m, 1H), 2.36-2.44 (m, 1H), 2.44-2.52 (m, 1H), 2.90 (dd, *J* 12.6, 4.9 Hz, 1H), 2.93-3.04 (m, 1H), 3.11 (dd, *J* 12.6, 7.7 Hz, 1H), 3.26 (s, 3H, CH₃), 3.45-3.51 (m, 1H), 3.51-3.61 (m, 1H), 4.10-4.18 (m, 1H), 4.38 (dd, *J* 7.7, 4.9 Hz, 1H), 7.28-7.40 (m, 5H); minor diastereoisomer – only separated signals δ=3.26 (s, 3H, CH₃), 4.32 (dd, *J* 7.7, 4.9 Hz, 1H). ¹³C NMR (CDCl₃, 50 MHz): δ_C main diastereoisomer δ=23.45 (CH₃), 27.18 (CH₃), 27.42 (CH₂), 32.55 (CH₂), 33.45 (CH), 36.75 (CH₂), 38.86 (C), 41.68 (CH), 46.72 (CH), 48.68 (CH), 56.87 (CH₃), 66.74 (CH₂), 83.55 (CH), 126.62 (2×CH), 128.11 (CH), 128.57 (2×CH), 140.90 (C); minor diastereoisomer – only separated signals δ=23.42 (CH₃), 27.38 (CH₂), 32.41 (CH₂), 33.84 (CH), 36.53 (CH₂), 41.64 (CH), 48.40 (CH), 56.98 (CH₃), 66.83 (CH₂), 84.08 (CH), 126.59 (2×CH), 128.58 (2×CH). ⁷⁷Se NMR (38 MHz, CDCl₃): δ_{Se} main diastereoisomer: 188.66; minor diastereoisomer: 191.73. Anal. calcd for C₁₉H₂₈O₂Se (367.38): C 62.12; H 7.68 Found: C 62.47; H 7.56.

General procedure for the selenocyclization of *o*-allylphenol. To a solution of diselenide (1.0 mmol) dissolved in dry CH₂Cl₂ (39.5 mL), cooled to -78 °C, under argon atmosphere, solution of bromine in CCl₄ (1.0 mL, 1.0 mmol) was added dropwise. After 15 min, a MeOH (1.8 mL) solution of silver triflate (320 mg) was added at -78 °C and the mixture stirred for another 15 min. *o*-Allylphenol (0.38 μL, 2.9 mmol) was added and the mixture was stirred at the same temperature for 2 h. The reaction mixture was poured into 10% NaHCO₃ (75 mL) solution, diluted with 75 mL of CH₂Cl₂, washed with water and brine, dried over MgSO₄ and concentrated in vacuo. The crude product was purified by column chromatography (silica gel, petroleum ether/EtOAc 95:5).

2-[[[(1S)-3-Hydroxynopylselenanyl]methyl]-2,3-dihydrobenzofuran (37). 88%, *dr* 60:40. ¹H NMR (300 MHz, CDCl₃): δ_H main diastereoisomer δ = 0.88 (s, 3H, CH₃), 1.06 (d, *J* 9.8 Hz, 1H), 1.21 (s, 3H, CH₃), 1.66–1.98 (m, 7H), 2.30–2.59 (m, 2H), 2.73–3.08 (m, 5H), 3.38 (dd, *J* 15.8, 9.0 Hz, 1H), 4.04–4.14 (m, 1H), 4.92–5.03 (m, 1H), 6.75 (d, *J* 7.8 Hz, 1H), 6.84 (t, *J* 7.4 Hz, 1H), 7.06-7.18 (m, 2H) ppm; minor diastereoisomer – only separated signals: 1.22 (s, 3H, CH₃), 6.85 (t, *J* 7.4 Hz, 1H). ¹³C NMR (CDCl₃, 50 MHz): δ_C main diastereoisomer δ = 23.5 (CH₂), 23.6 (CH₃), 27.3 (CH₃), 28.6 (CH₂), 33.4 (CH₂), 35.6 (CH₂), 36.2 (CH₂), 37.8 (C), 39.0 (CH₂), 41.0 (CH), 45.5 (CH), 52.9 (CH), 69.8 (CH), 82.6 (CH), 109.2 (CH), 120.4 (CH), 124.8 (CH), 126.2 (C), 127.9 (CH), 159.0 (C) ppm; minor diastereoisomer – only separated signals: 36.3 (CH₂), 53.1 (CH), 82.5 (CH). ⁷⁷Se NMR (38 MHz, CDCl₃): δ_{Se} 139.9. Anal. calcd for C₂₀H₂₈O₂Se (379.40): C, 63.31; H, 7.44 Found: C, 63.42; H, 7.40.

2-[[[(1S)-10-Phenoxymethylpinocampylselenanyl]methyl]-2,3-dihydrobenzofuran (38). 62%, *dr* 56:44. ¹H NMR (200 MHz, CDCl₃): δ_H 1.01 (s, 3H, CH₃), 1.22 (s, 3H, CH₃), 1.23-1.86 (m, 6H), 1.90–2.71 (m, 6H), 2.78-3.14 (m, 3H), 3.38 (dd, *J* 15.9, 9.0 Hz, 1H), 3.91-4.09 (m, 2H), 4.85-5.03 (m, 1H), 6.76-6.98 (m, 4H), 7.03-7.36 (m, 5H). ¹³C NMR (CDCl₃, 50 MHz): δ_C main diastereoisomer δ = 23.5 (CH₃), 27.2 (CH₂), 27.3 (CH₃), 28.7 (CH₂), 33.0 (CH₂), 34.7 (CH), 35.8 (CH₂), 36.6 (CH₂), 39.4 (C), 40.1 (CH), 41.9 (CH), 46.1 (CH), 67.5 (CH₂), 82.6 (CH), 109.4 (CH), 114.5 (2×CH), 120.5 (2×CH), 125.0 (CH), 126.4 (C), 128.0 (CH), 129.4 (2×CH), 159.0 (C), 159.3 (C) ppm; minor diastereoisomer – only separated signals: 28.4 (CH₂), 46.0 (CH), 82.7 (CH), 109.4 (CH). ⁷⁷Se NMR (38 MHz, CDCl₃): δ_{Se} main diastereoisomer: 190.9; minor diastereoisomer: 196.4. Anal. calcd for C₂₆H₃₂O₂Se (455.49): C, 68.56; H, 7.08 Found: C, 68.66; H, 7.19.

Acknowledgements

This work was supported by the PhD grant of Faculty of Chemistry, Nicolaus Copernicus University in Toruń.

References

1. McGarrigle, E. M.; Myers, E. L.; Illa, O.; Shaw, M. A.; Riches, S. L.; Aggarwal, V. K. *Chem. Rev.* **107**, **2007**, 5841.
<http://dx.doi.org/10.1021/cr068402y>
2. Ścianowski, J.; Rafiński, Z. Electrophilic selenium reagents: Addition reactions to double bonds and selenocyclizations. In: *Organoselenium Chemistry: Between Synthesis and Biochemistry*; Santi, C., Ed.; Bentham, 2014; pp 8-60.
<http://dx.doi.org/10.2174/9781608058389114010005>
3. Back, T.G., Ed. *Organoselenium Chemistry: A Practical Approach*, Oxford University Press: Oxford, 1999.
4. Wirth, T., Ed. *Organoselenium Chemistry, Top. Curr. Chem.* **2000**.
5. Wirth, T., Ed. *Organoselenium Chemistry: Synthesis and Reactions*, Wiley-VCH: Weinheim, 2012.
6. Santi, C., Ed. *Organoselenium Chemistry: Between Synthesis and Biochemistry*: Bentham, 2014.
7. Santi, C.; Santoro, S. Electrophilic selenium reagents. In: *Organoselenium Chemistry: Synthesis and Reactions*; Wirth, T., Ed.; Wiley-VCH, 2012; pp 1-51.
8. Sancineto, L.; Palomba, M.; Bagnoli, L.; Marini, F.; Santi, C. *Curr. Org. Chem.* **2015**, *20*, 122.
<http://dx.doi.org/10.2174/1385272819666150724233204>
9. Młochowski, J.; Kloc, K.; Lisiak, R.; Potaczek, P.; Wójtowicz, H. *Arkivoc* **2007**, *vi*, 14.
<http://dx.doi.org/10.3998/ark.5550190.0008.603>
10. Bhuyan, B.J.; Mugesh G. Biological and Biochemical Aspects of Selenium Compounds. In: *Organoselenium Chemistry: Synthesis and Reactions*; Wirth, T. Ed.; Wiley-VCH: Weinheim, 2012; pp 361–396.
11. Santi, C.; Tidei, C.; Scalera, C.; Piroddi, M.; Galli, F. *Curr. Chem. Biol.* **2013**, *7*, 25.
<http://dx.doi.org/10.2174/2212796811307010003>
12. Pacuła, A. J.; Ścianowski, J.; Aleksandrak, K. B. *RSC Adv.* **2014**, *4*, 48959.
<http://dx.doi.org/10.1039/C4RA08631G>
13. Iwaoka, M. Antioxidant Organoselenium Molecules in Organoselenium Chemistry: Between Synthesis and Biochemistry. In: Santi, C., Ed.; Bentham Books, 2014; pp 361-378.
14. Wirth, T. *Angew. Chem. Int. Ed.* **2015**, *54*, 10074.
<http://dx.doi.org/10.1002/anie.201505056>
15. Pacuła, A. J.; Mangiavacchi, F.; Sancineto, L.; Lenardão, E. J.; Ścianowski, J.; Santi, C. *Curr. Chem. Biol.* **2015**, *9*, 97.
<http://dx.doi.org/10.2174/2212796810666160120220725>
16. Ścianowski, J.; Rafiński, Z. Electrophilic selenium reagents: Addition reactions to double bonds and selenocyclizations. In: *Organoselenium Chemistry: Between Synthesis and Biochemistry*; Santi, C., Ed.; Bentham, 2014; pp 8-60.
<http://dx.doi.org/10.2174/9781608058389114010005>
17. Sancineto, L.; Palomba, M.; Bagnoli, L.; Marini, F.; Santi C. *Curr. Org. Chem.* **2016**, *20*, 122.
<http://dx.doi.org/10.2174/1385272819666150724233204>

18. Coles, M. P. *Curr. Org. Chem.* **2006**, *10*, 1993.
<http://dx.doi.org/10.2174/138527206778521222>
19. Ścianowski, J. *Tetrahedron Lett.* **2005**, *46*, 3331.
<http://dx.doi.org/10.1016/j.tetlet.2005.03.073>
20. Ścianowski, J.; Rafiński, Z.; Wojtczak, A. *Eur. J. Org. Chem.* **2006**, 3216.
<http://dx.doi.org/10.1002/ejoc.200600044>
21. Rafiński, Z.; Ścianowski, J.; Wojtczak, A. *Tetrahedron : Asymmetry* **2008**, *19*, 223.
<http://dx.doi.org/10.1016/j.tetasy.2007.11.032>
22. Rafiński, Z.; Ścianowski, J. *Tetrahedron: Asymmetry* **2008**, *19*, 1237.
<http://dx.doi.org/10.1016/j.tetasy.2008.04.027>
23. Rafiński, Z.; Ścianowski, J.; Wojtczak, A. *Lett. Org. Chem.* **2009**, *6*, 321.
<http://dx.doi.org/10.2174/157017809788489846>
24. Ścianowski, J.; Rafiński, Z.; Szuniewicz, A.; Wojtczak, A. *Tetrahedron* **2009**, *65*, 10162.
<http://dx.doi.org/10.1016/j.tet.2009.10.005>
25. Ścianowski, J.; Rafiński, Z.; Wojtczak, A.; Burczyński, K. *Tetrahedron: Asymmetry* **2009**, *20*, 2871.
<http://dx.doi.org/10.1016/j.tetasy.2009.12.001>
26. Ścianowski, J.; Rafalski, J.; Banach, A.; Czaplewska, J.; Komoszyńska, A. *Tetrahedron: Asymmetry* **2013**, *24*, 1089.
<http://dx.doi.org/10.1016/j.tetasy.2013.07.018>