Synthesis and Reactions of the Optically Active Dialkyl Diselenides from the Pinane Group

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Abstract: A convenient method of synthesis of the optically active dialkyl diselenides from the pinane group is described. The 3-hydroxy and 3-alkoxy derivatives of bis(*cis*-myrtanyl) diselenide have been obtained. The influence of a structure of the resulting diselenides on the diastereomeric excess of the methoxyselenenylation reaction and the selenocyclization have been investigated.

Keywords: Asymmetric synthesis, Diselenides, Selenium, Terpenoids.

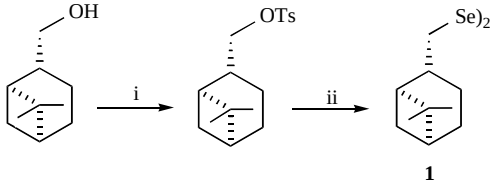
INTRODUCTION

Diselenides are a class of organic compounds with a great synthetic importance. Depending on the reaction conditions they can be employed both as precursors for synthesis of nucleophilic, radical or electrophilic reagents [1]. Diselenides are also investigated because of their biological and pharmacological functions. Especially interesting are results concerning antioxidizing, antimicrobial, antiviral, and antitumor properties [2].

In recent years, diselenides are frequently employed as precursors for an asymmetric synthesis. For example the optically active diselenides have been used in synthesis in the new asymmetric carbon-carbon and carbon-heteroatom coupling [3]. The investigation on the use of the optically active diselenides as catalysts in asymmetric reactions was also conducted [4].

Recently, we have described a method for the preparation of terpene-derived dialkyl diselenides, which was based on a reaction of sodium diselenide with alkyl tosylates and chlorides [5,6].

We have obtained non-functionalized diselenides from *p*-menthane, pinane, carane and bornane groups [5-7]. For example, we have obtained bis(*cis*-myrtanyl) diselenide **1** in a reaction of sodium diselenide with *cis*-myrtanyl tosylate (Scheme **1**) [5]. The obtained diselenide has been employed in the asymmetric methoxyselenenylation [6] and selenocyclization [8].



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Scheme 1. *Reagents and conditions:* i) TsCl, pyridine, 0 °C, 30 min, then RT, 24 h, 87%; ii) Se, NaOH, $N_2H_4 \times H_2O$, 100 °C, 1 h, 91%.

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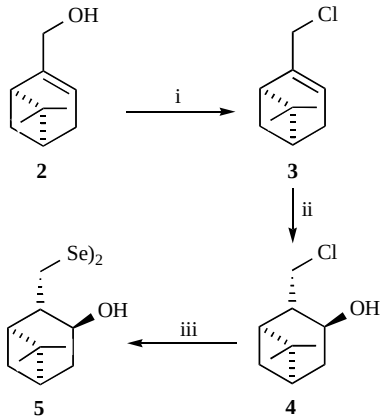
Hitherto, only the functionalized terpene diselenides being derivatives of camphor have been described [9].

In the present paper we describe our investigations concerning the synthesis of the dialkyl diselenides from the pinane group functionalized with hydroxy or alkoxy groups, derivatives of bis(*cis*-myrtanyl) diselenide **1**. The use of the obtained diselenides in the methoxyselenenylation reaction of styrene and selenocyclization with the use of *o*-allylphenol is also reported.

RESULTS AND DISCUSSION

We started our investigations on the functionalized optically active diselenides from pinane group with the synthesis of the bis(3-*trans*-hydroxy-*cis*-myrtanyl) diselenide **5** (Scheme **2**). Myrtenyl chloride **3** was obtained in a reaction of (-)-myrtenol **2** with triphenylphosphine in carbon tetrachloride [10]. It was subsequently transformed into 10-chloroisopinocampheol **4** by the hydroboration oxidation reaction [11]. Diselenide **5** was obtained in a reaction of chloride **4** with sodium diselenide generated *in situ* (Se, NaOH, $N_2H_4 \times H_2O$).



2 **3** **5** **4**

Scheme 2. *Reagents and conditions:* i) PPh_3, CCl_4, reflux, 24 h, 80%; ii) BMS, H_2O_2/NaOH, 65%; iii) Se, NaOH, $N_2H_4 \times H_2O$, 50 °C, 20 h, 54%.

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The structure of obtained diselenide **5** was confirmed by ^{1}H, ^{13}C, ^{77}Se NMR and X-ray analyses.

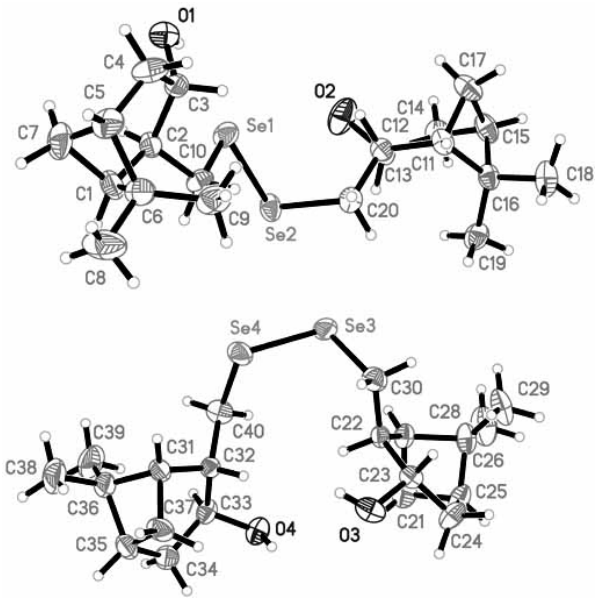
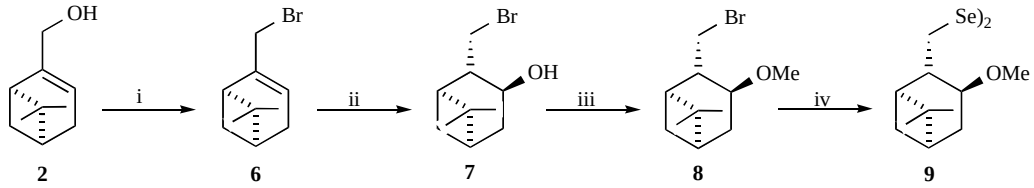


Fig. (1). X-ray structure of diselenide **5**.

The structure of **5** contains two diselenide molecules in the asymmetric unit Fig. (**1**) [12-14]. The geometry of *cis*-pinane moieties is typical for that ring system. The Se-Se distances are 2.3140(9) and 2.2978(9) Å for Se1-Se2 and Se3-Se4, respectively, and are similar to that of 2.3182(11) reported for dineomenthyl diselenide [6]. The C-Se distances vary between 1.941(8) and 1.984(7) Å and are similar to those reported for other terpene selenides [6,8]. The C-Se-Se angles range from 99.3(2)° for C10-Se1-Se2 to 102.7(2)° for C40-Se4-Se3. Two molecules reveal significant differences in the diselenide bridge conformation. The C-Se-Se-C torsion angles for the diselenide bridges are -90.9(3)° and -87.5(3)° for C10-Se1-Se2-C20 and C30-Se3-Se4-C40, respectively. These values are significantly lower than that of -112.1(4)°, reported for (+)-dineomenthyl diselenide [6]. The orientation of pinane moieties relative to the diselenide bridges, described with the C-C-Se-Se torsion angles, reveal even larger differences between two molecules. In molecule 1 the C2-C10 Se1-Se2 and Se1-Se2-C20-C12 torsion angles are -163.5(4)° and -76.2(5)°, while in the second molecule the equivalent torsion angles are C22-C30-Se3-Se4 83.6(5)° and Se3-Se4-C40-C32 118.2(5)°. The absolute configuration of the chiral centers in all *cis*-pinane moieties is 1*S*,2*S*,3*S*,5*R*. Analysis of the intermolecular interactions revealed the network of H-bonds involving three out of four hydroxyl groups, with the O···O distances being O1-H1O···O3 [x+1, y-1, z] 2.630 Å, O3-H3O···O4 [x+1, y, z] 2.636 Å and O4-H4O···O1 [x-1, y+1, z] 2.727 Å. The O2-H group is buried between the pinane moieties and does not form any H-bond.

We have also synthesized the diselenides containing the alkoxy groups. We obtained (+)-bis(*trans*-3-methoxy-*cis*-



Scheme 3. *Reagents and conditions*: i) PBr_3, hexane, -20 °C, 30 min, then RT, 5 h, 59%; ii) BMS, H_2O_2/NaOH, 46%; iii) 60% NaH, MeI, RT, 24 h, 92%; iv) Se, NaOH, $N_2H_4 \times H_2O$, 50 °C, 20 h, 76%.

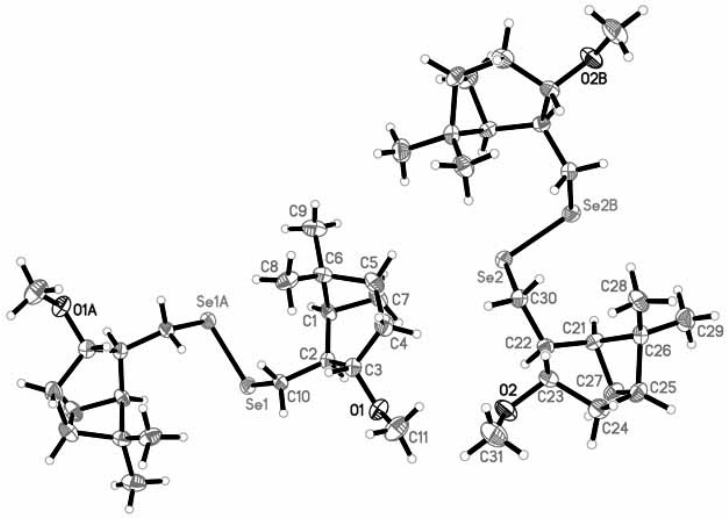
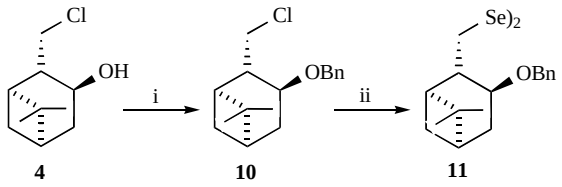


Fig. (2). X-ray structure of diselenide **9**.



Scheme 4. *Reagents and conditions:* i) 60% NaH, BnCl, RT, 48 h, 66%; ii) Se, NaOH, $N_2H_4 \times H_2O$, 50 °C, 20 h, 42%.

myrtanyl) diselenide **9** as a result of the hydroboration oxidation of the myrtenyl bromide **6**, subsequent protection of the hydroxy group in the resulted 10-bromoisopinocampheol **7** with the methyl group and final reaction of 10-bromoisopinocampheyl methyl ether **8** with sodium diselenide (Scheme **3**).

The structure of the obtained diselenide was confirmed by the X-ray analysis Fig. (**2**) [12-14].

Structure **9** is formed by the two halves of different diselenide molecules positioned in the asymmetric unit. The two-fold axis parallel to crystallographic *z* dissects the diselenide bonds of the two molecules, relating each half of the diselenide to its symmetry equivalent counterpart. The Se-Se bond distances are Se1-Se1 [-x, -y, z] 2.3229(7) Å and Se2-Se2 [-x+1, -y, z] 2.3205(8) Å, and are significantly longer than those reported for the 3-hydroxy compound **5**. The C10-Se1 and C30-Se2 distances of 1.955(3) and 1.958(3) Å, as well as the C-Se-Se angles are mimilar to those found in **5** or dineomenthyl diselenide [6]. However, the angles C2-C10-Se1 117.1(2) deg and C22-C30-Se2 117.4(2) deg are larger than the corresponding angles reported for **5**.

Conformation of the diselenide bridges described with the torsion angles C10-Se1-Se1 [-x, -y, z]-C10 [-x, -y, z] -64.3(2)° and C30-Se2-Se2 [-x+1, -y, z]-C30 [-x+1, -y, z] -66.3(2)° is similar in both molecules, although the difference close to 10σ is statistically significant. The observed value is different from that of -90 deg reported for **5**. Also the orientation of the pinane moiety relative to the diselenide bridge in **9** is different from that found in **5**. The torsion angles C2-C10-Se1-Se1 [-x, -y, z] -92.3(2) and C22-C30-Se2-Se2 [-x+1, -y, z] -89.5(3)° have either the opposite sign or have a much smaller absolute value than those reported for **5**.

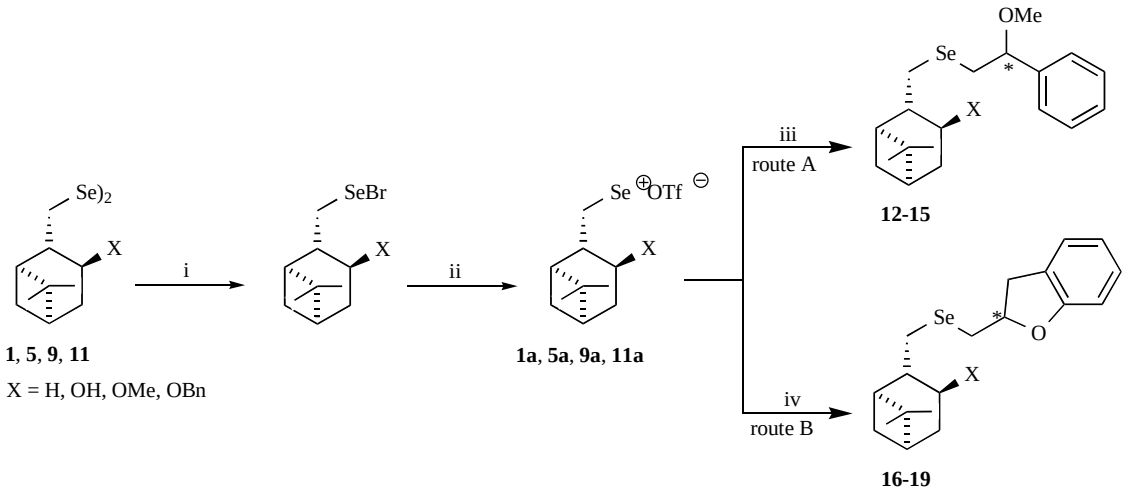
The methoxy groups are buried between the methoxy groups and *gem*-dimethyl groups of the pinane moieties of the surrounding diselenide molecules. Their conformation is *trans* with the torsion angles being C(2)-C(3)-O(1)-C(11) -165.0(3)° and C(22)-C(23)-O(2)-C(31) -163.3(3)°. The absolute configuration of the chiral centers in all *cis*-pinane moieties is 1*S*,2*S*,3*S*,5*R*.

The diselenide **11** containing a benzyloxy groups has been obtained in a reaction of sodium diselenide with the chloride **10**, formed as a result of a reaction of 10-chloroisopinocampheol **4** with sodium hydride and benzyl chloride (Scheme **4**).

Many literature reports concerning an influence of heteroatoms in diselenide molecules on the increase of the diastereomeric excesses in the methoxyselenenylation reaction and selenocyclization [3] prompted us to the use of obtained diselenides in the methoxyselenenylation of styrene (route A) and selenocyclization with the use of *o*-allylphenol (route B) (Scheme **5**). Treatment of diselenides **1**, **5**, **9** and **11** with 1M solution of bromine and then silver triflate gave the corresponding triflate precursors. The resulting salts **1a**, **5a**, **9a**, **11a**, have not been isolated from the reaction mixture but used directly in a reaction with styrene [6] or *o*-allylphenol [8] to give the respective methoxy selenides **12**-**15** and selenides being derivatives of dihydrobenzofuran **16**-**19**.

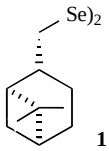
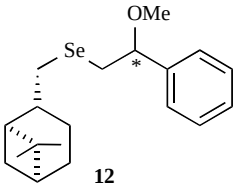
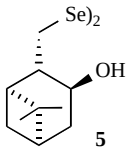
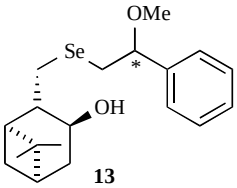
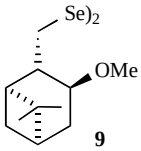
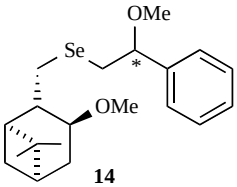
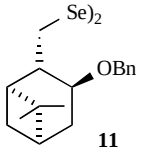
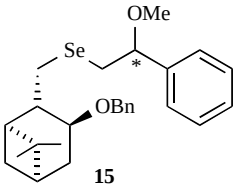
The yields and the diastereomeric ratios have been presented in Tables **1** and **2**. The diastereomeric ratios for the addition and selenocyclization products were similar both for non-functionalized diselenide **1** and the functionalized diselenides **5**, **9**, **11**. The slight increase of the diastereomeric ratio has been observed for the diselenide **9** containing the methoxy groups.

In conclusion, the new unknown functionalized diselenides from the pinane group have been obtained. It has been demonstrated that the elaborated methodology of synthesis of the optically active dialkyl diselenides based on



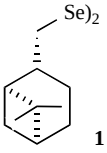
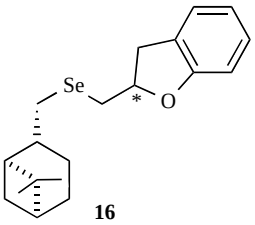
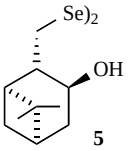
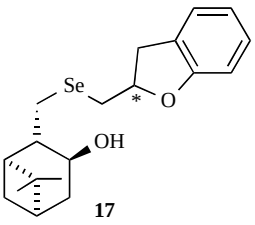
Scheme 5. *Reagents and conditions:* i) 1M Br_2 in CCl_4, -78 °C, 15 min; ii) AgOTf in MeOH, -78 °C, 15 min; iii) styrene, -78 °C, 5 h; iv) *o*-allylphenol, -78 °C, 5 h.

Table 1. Metoxyselenenylation of Styrene Prompted by the Monoterpene Diselenides

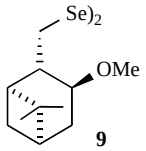
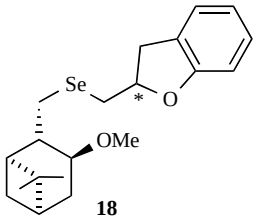
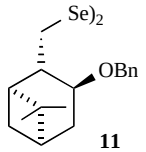
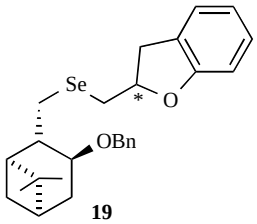
Entry	Diselenide	Product	*D.r.*[a]	Isolated Yield (%)
1	 **1**	 **12**	51:49[b]	64[b]
2	 **5**	 **13**	52:48	20
3	 **9**	 **14**	64:36	58
4	 **11**	 **15**	52:48	82

[a]Diastereomeric ratios were established on the basis of ^{1}H NMR and ^{77}Se NMR spectra.
[b]Lit. [6a].

Table 2. Cyclization of *o*-allylphenol with Use of Monoterpene Diselenides

Entry	Diselenide	Product	*D.r.*[a]	Isolated Yield (%)
1	 **1**	 **16**	52:48[b]	83[b]
2	 **5**	 **17**	52:48	74

(Table 2). Contd…..

Entry	Diselenide	Product	*D.r.*[a]	Isolated Yield (%)
3	 **9**	 **18**	62:38	31
4	 **11**	 **19**	57:43	38

[a]Diastereomeric ratios were established on the basis of ^{1}H NMR and ^{77}Se NMR spectra.
[b]Lit. [7].

a reaction of alkyl halides with sodium diselenide can be an efficient method for the functionalized dialkyl diselenides. The obtained functionalized diselenides have been successfully used in reactions of addition to the double bonds and selenocyclization. The best diastereoselection has been observed for a diselenide containing a methoxy groups. The developed methodology can be considered as a good base for further research on a synthesis and use of the functionalized optically active diselenides.

EXPERIMENTAL

General

(1*R*)-(-)-Myrtenol (95%, 94 *ee*) was purchased from Aldrich. Dichloromethane and *N*,*N*-dimethylformamide were distilled from CaH_2 and stored over molecular sieves 4Å. Methanol was distilled from magnesium turns and stored over molecular sieves 4Å. ^{1}H, ^{13}C and ^{77}Se NMR spectra were measured in $CDCl_3$ on a Bruker AM-300 or Varian Gemini 200 spectrometer (300 MHz or 200 MHz for ^{1}H and 75.5 MHz or 50.3 MHz for ^{13}C). Chemical shifts (δ) are given in ppm relative to TMS and coupling constants (*J*) are given in Hz. ^{77}Se NMR spectra were recorded on Varian Gemini 200, with diphenyl diselenide as the internal standard. Elemental analyses were performed on a Vario MACRO CHN analyzer. Column chromatography was carried out using MERCK Silica gel 60 (70-230 mesh) with the indicated solvents (petroleum ether (Pet ether): 40-60 °C). All reaction requiring anhydrous conditions were conducted in a flame-dried apparatus.

(-)-Myrtenyl Chloride (3)

The solution of (-)-myrtenol (30.4 g, 200 mmol) and triphenylphosphine (57.7 g, 220 mmol) in carbon tetrachloride (500 mL) was refluxed for 24 h. Then it was cooled and petroleum ether (600 mL) was added. The formed precipitate was filtered off under vacuum, and the filtrate was concentrated by means of a rotary evaporator. The product was isolated by the distillation under reduced pressure.

Yield: 80%. Colorless liquid. B.p. 44-46 °C (0.15 Torr). $[\alpha]_D^{19}$ -42.0 (*c* 10.46, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$): 0.83 (s, 3H, CH_3), 1.18 (d, *J*=9.9 Hz, 1H, CH*H*), 1.31 (s, 3H, CH_3), 2.06-2.17 (m, 1H), 2.21-2.33 (m, 3H), 2.38-2.47 (m, 1H), 3.94-4.05 (m, 2H), 5.56-5.64 (m, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): 21.1 (CH_3), 26.0 (CH_3), 31.2 (CH_2), 31.5 (CH_2), 38.0 (C), 40.4 (CH), 44.2 (CH), 48.6 (CH_2), 122.4 (CH=), 144.1 (C=). Anal. Calcd for $C_{10}H_{15}Cl$: C, 70.37; H, 8.86. Found: C, 70.32; H, 8.81

(-)-Myrtenyl Bromide (6)

To a solution of (-)-myrtenol (30.4 g, 200 mmol) in hexane (60 mL) PBr_3 (21.6 g, 80 mmol) was added at -20 °C, and the mixture was stirred for 30 min and then at r.t. for 5 h. Saturated aqueous $NaHCO_3$ was added and the product extracted with diethyl ether. The extracts were washed with brine, dried ($MgSO_4$), and evaporated. The crude product was purified by the distillation under reduced pressure.

Yield: 59%. Colorless liquid. B.p. 48-50 °C (0.15 Torr). $[\alpha]_D^{24}$ -22.0 (*c* 14.88, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$): 0.83 (s, 3H, CH_3), 1.18 (d, *J*=9.9 Hz, 1H, CH*H*), 1.31 (s, 3H, CH_3), 2.06-2.17 (m, 1H), 2.21-2.33 (m, 3H), 2.38-2.47 (m, 1H), 4.00 (m, 2H), 5.63-5.70 (m, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): 21.1 (CH_3), 26.0 (CH_3), 31.3 (CH_2), 31.5 (CH_2), 37.0 (CH_2), 37.9 (C), 40.3 (CH), 44.8 (CH), 123.1 (CH=), 144.1 (C=). Anal. Calcd for $C_{10}H_{15}Br$: C, 55.83; H, 7.03. Found: C, 55.68; H, 6.92.

(-)-10-Chloroisopinocampheol (4)

Yield: 65%. Colorless oil. B.p. 60–62 °C (0.15 Torr). $[\alpha]_D^{20}$ -55.8 (*c* 9.35, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): 0.88 (s, 3H, CH_3), 1.14 (d, *J*=9.9 Hz, 1H, CH*H*), 1.22 (s, 3H, CH_3), 1.78 (ddd, *J*=14.1, 4.2, 2.4 Hz, 1H, CH), 1.94-2.02 (m, 2H), 2.10 (bs, 1H, OH), 2.23-2.31 (m, 1H), 2.39-2.58 (m, 2H), 3.54 (dd, *J*=10.5, 6.3 Hz, 1H, CH*H*), 3.65 (dd, *J*=10.5, 10.5 Hz, 1 H, CH*H*), 4.27 (qui, *J*=4.8 Hz, 1H, CH). ^{13}C

NMR (50 MHz, $CDCl_3$): 23.8 (CH_3), 27.1 (CH_3), 33.1 (CH_2), 37.5 (CH_2), 37.8 (C), 41.4 (CH), 44.5 (CH), 48.6 (CH_2), 55.6 (CH), 68.1 (CH). Anal. Calcd for $C_{10}H_{17}ClO$: C, 63.65; H, 9.08. Found: C, 63.58; H, 8.98.

(-)-10-Bromoisopinocampheol (7)

Yield: 46%. Colorless oil. B.p. 92-94 °C (0.8 Torr); $[\alpha]_D^{21}$ -21.6 (*c* 3.18, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$): 0.88 (s, 3H, CH_3), 1.17 (d, *J*=9.9 Hz, 1H, CH*H*), 1.22 (s, 3H, CH_3), 1.80 (ddd, *J*=14.2, 4.6, 2.4 Hz, 1H), 1.90–2.07 (m, 2H), 2.21 (bs, 1H, OH), 2.28–2.62 (m, 3H), 3.42 (dd, *J*=14.9, 9.6 Hz, 1H, CH*H*), 3.53 (dd, *J*=15.9, 14.9 Hz, 1H, CH*H*), 4.25 (qui, *J*=6.9 Hz, 1H, CH). ^{13}C NMR (50 MHz, $CDCl_3$): 23.7 (CH_3), 27.0 (CH_3), 33.0 (CH_2), 37.4 (CH_2), 37.6 (CH_2), 37.7 (C), 41.4 (CH), 45.4 (CH), 55.5 (CH), 68.7 (CH). Anal. Calcd for $C_{10}H_{17}BrO$: C, 51.52; H, 7.35. Found: C, 51.61; H, 7.28.

Synthesis of Compounds (8, 10); General Procedure

NaH (60% in mineral oil, 11 mmol) was added to a solution of monoterpene alcohol (10 mmol) in dry THF (10 mL). The suspension was stirred at room temperature for 20 min, and then alkyl iodide (30 mmol) was added, and the mixture was stirred at room temperature from 24 h to 48 h. The reaction mixture was poured onto ice and extracted with ether; the combined ethereal layers were washed with saturated aqueous sodium chloride, dried over anhydrous magnesium sulfate, and evaporated. The crude product was purified by the column chromatography or by distillation under reduced pressure.

(+)-10-Bromoisopinocampheyl Methyl Ether (8)

Yield: 92%. Colorless oil. Column chromatography (70-230 mesh silica gel, Pet ether/EtOAc, 95:5). $[\alpha]_D^{20}$ +14.2 (*c* 6.02, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$): 0.87 (s, 3H, CH_3), 0.88-0.98 (m, 1H), 1.08 (d, *J*=9.6 Hz, 1H, CH*H*), 1.24 (s, 3H, CH_3), 1.68-1.80 (m, 1H), 1.81-2.00 (m, 1H), 2.17-2.47 (m, 4H), 3.34 (s, 3H, CH_3), 3.39-3.60 (m, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): 23.5 (CH_3), 27.1 (CH_3), 32.2 (CH_2), 34.8 (CH_2), 36.9 (CH_2), 38.1 (C), 41.1 (CH), 43.4 (CH), 52.6 (CH), 56.3 (OCH_3), 77.5 (CH). Anal. Calcd for $C_{11}H_{19}BrO$: C, 53.45; H, 7.75. Found: C, 53.38; H, 7.74.

(+)-Benzyl 10-chloroisopinocampheyl Ether (10)

Yield: 66%. Colorless oil. B.p. 107–109 °C (0.15 Torr). $[\alpha]_D^{21}$ +38.8 (*c* 4.37, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): 0.86 (s, 3H, CH_3), 1.17 (d, *J* =9.9 Hz, 1H, CH*H*), 1.24 (s, 3H, CH_3), 1.87-2.05 (m, 2H), 2.20-2.25 (m, 1H), 2.35-2.50 (m, 3H), 3.46 (dd, *J*=10.5, 9.6 Hz, 1H, CH*H*), 3.62 (dd, *J*=10.5, 6.3 Hz, 1H, CH*H*), 3.68-3.76 (m, 1H), 4.45 (d, *J*=11.4 Hz, 1H, CH*H*), 4.62 (d, *J*=11.4 Hz, 1H, CH*H*), 7.29-7.39 (m, 5H, 5×CH). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 23.5 (CH_3), 27.2 (CH_3), 32.2 (CH_2), 35.2 (CH_2), 38.2 (C), 41.4 (CH), 42.7 (CH), 47.6 (CH_2), 52.7 (CH), 70.6 (CH_2), 74.3 (CH), 127.5 (CH), 127.8 (2×CH), 128.3 (2×CH), 138.5 (C). Anal. Calcd for $C_{17}H_{23}ClO$: C, 73.23; H, 8.31. Found: C, 73.30; H, 8.34.

General Procedure for the Synthesis of Diselenides

Sodium diselenide (10 mmol) was prepared from sodium hydroxide, hydrazine hydrate and elemental selenium in dry DMF [6]. The bromo or chloro precursor (5 mmol) was dissolved in dry DMF (5 mL) under argon and added to the solution. The mixture was heated at 50 °C for 20 h. The reaction mixture was cooled, poured into water (30 mL), and extracted with diethyl ether (3×20 mL). The combined ethereal layers were washed with water (2×20 mL), dried with anhydrous $MgSO_4$, and the solvent was evaporated. Crude product was purified by chromatography on a silica gel column. The diselenides were obtained as yellow solids.

(-)-Bis(trans-3-hydroxy-cis-myrtanyl) Diselenide (5)

Yield: 54%. Yellow crystals. M.p. 127-128 °C. Column chromatography (70-230 mesh silica gel, CH_2Cl_2/EtOAc, 80:20). $[\alpha]_D^{22}$ -38.4 (*c* 1.98, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (s, 3H, CH_3), 1.17 (d, *J*= 9.9 Hz, 1H, CH*H*), 1.22 (s, 3H, CH_3), 1.76 (ddd, *J*=14.1, 4.2, 2.7 Hz, 1H, CH), 1.93-2.04 (m, 2H), 2.22-2.30 (m, 1H), 2.37-2.43 (m, 2H), 2.47-2.54 (m, 1H), 2.99 (dd, *J*=12.0, 6.9 Hz, 1H, CH*H*), 3.16 (dd, *J*=12.0, 9.0 Hz, 1 H, CH*H*), 4.15-4.23 (m, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 23.8 (CH_3), 27.3 (CH_3), 33.4 (CH_2), 35.8 (CH_2), 38.0 (CH_2), 38.1 (C), 41.5 (CH), 46.2 (CH), 53.6 (CH), 69.9 (CH). ^{77}Se NMR (38 MHz, $CDCl_3$): δ = 303.0. Anal. Calcd for $C_{20}H_{34}O_2Se_2$: C, 51.73; H, 7.38. Found: C, 51.65; H, 7.34.

(+)-Bis(trans-3-methoxy-cis-myrtanyl) Diselenide (9)

Yield: 76%. Yellow crystals. M.p. 47-49 °C. Column chromatography (70-230 mesh silica gel, Pet ether/EtOAc, 95:5). $[\alpha]_D^{22}$ +40.7 (*c* 3.28, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.89 (s, 3H, CH_3), 1.05 (d, *J*=9.6 Hz, 1H, CH*H*), 1.21 (s, 3H, CH_3), 1.72-1.84 (m, 1H), 1.90-1.98 (m, 1H), 2.08-2.24 (m, 2H), 2.28-2.47 (m, 2H), 3.11 (dd, *J*=10.2, 8.8 Hz, 1H, CH*H*), 3.17 (dd, *J*=10.2, 7.2 Hz, 1H, CH*H*), 3.32 (s, 3H, CH_3), 3.56 (m, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 23.7 (CH_3), 27.2 (CH_3), 32.6 (CH_2), 35.0 (CH_2), 36.0 (CH_2), 38.2 (C), 41.3 (CH), 44.7 (CH), 50.7 (CH), 56.1 (OCH_3), 78.8 (CH). ^{77}Se NMR (38 MHz, $CDCl_3$): δ = 300.5. Anal. Calcd for $C_{22}H_{38}O_2Se_2$: C, 53.66; H, 7.78. Found: C, 53.70; H, 7.74.

(+)-Bis(trans-3-benzyloxy-cis-myrtanyl) Diselenide (11)

Yield: 42%. Yellow solid. M.p. 51-53 °C. Column chromatography (70-230 mesh silica gel, Pet ether/CH_2Cl_2/EtOAc, 68:31:1). $[\alpha]_D^{22}$ +51.2 (*c* 2.33, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.89 (s, 3H, CH_3), 1.18 (d, *J*=9.9 Hz, 1H, CH*H*), 1.22 (s, 3H, CH_3), 1.82-2.03 (m, 2H), 2.08-2.18 (m, 1H), 2.25-2.58 (m, 3H), 3.06 (dd, *J*=10.5, 9.6 Hz, 1H, CH*H*), 3.20 (dd, *J*=10.5, 6.3 Hz, 1H, CH*H*), 3.75-3.84 (m, 1H), 4.42-4.50 (m, 2H), 7.21-7.40 (m, 5H, 5×CH). ^{13}C NMR (50 MHz, $CDCl_3$): δ =23.7 (CH_3), 27.2 (CH_3), 32.6 (CH_2), 35.4 (CH_2), 35.8 (CH_2), 38.2 (C), 41.3 (CH), 44.8 (CH), 50.8 (CH), 70.4 (CH_2), 76.8 (CH), 127.3 (CH), 127.7 (2×CH), 128.2 (2×CH), 138.7 (C). ^{77}Se NMR (38 MHz, $CDCl_3$): δ = 303.5. Anal. Calcd for $C_{34}H_{46}O_2Se_2$: C, 63.35; H, 7.19. Found: C, 63.24; H, 7.11.

(1S,2S,3S,5R)-2-[(2-Methoxy-2-phenylethylselanyl) methyl]-6,6-dimethylbicyclo[3.1.1]heptan-3-ol (13)

Yield: 20%. Light yellow oil. *D.r.* 52:48. Column chromatography (70-230 mesh silica gel, CH_2Cl_2/EtOAc, 95:5). ^{1}H NMR (200 MHz, $CDCl_3$): major diastereomer δ = 0.86 (s, 3H, CH_3), 1.10 (d, *J*=9.8 Hz, 1H, CH*H*), 1.20 (s, 3H, CH_3), 1.60-2.16 (m, 5H), 2.31–2.62 (m, 4H), 2.65–3.05 (m, 3H),

3.24 (s, 3H; OCH_3), 3.65–3.74 (m, 1H), 4.10-4.21 (m, 1H), 4.36 (dd, *J*=8.0, 5.0 Hz, 1H, CH), 7.35 (m, 5H, 5×CH); minor diastereomer (distinct signals) δ = 0.85 (s, 3H, CH_3), 1.08 (d, *J*=9.8 Hz, 1H, CH*H*), 3.25 (s, 3H, OCH_3), 4.32 (dd, *J*=8.0, 5.0 Hz, 1H, CH). ^{13}C NMR (50 MHz, $CDCl_3$): major diastereomer δ = 23.8 (CH_3), 27.3 (CH_3), 30.5 (CH_2), 30.9 (CH_2), 33.6 (CH_2), 37.2 (CH_2), 38.0 (C), 41.5 (CH), 47.0 (CH), 52.8 (CH), 56.8 (OCH_3), 69.9 (CH), 84.1 (CH), 126.6 (2×CH), 128.1 (CH), 128.6 (2×CH), 141.0 (C); minor diastereomer (distinct signals) δ = 27.4 (CH_3), 30.7 (CH_2), 31.3 (CH_2), 33.7 (CH_2), 37.3 (CH_2), 53.1 (CH), 70.0 (CH_2), 84.0 (CH), 128.0 (CH), 128.5 (2×CH). ^{77}Se NMR (38 MHz, $CDCl_3$): major diastereomer δ = 134.7; minor diastereomer δ = 131.3. Anal. Calcd for $C_{19}H_{28}O_2Se$: C, 62.12; H, 7.68. Found: C, 62.10; H, 7.55.

(2-Methoxy-2-phenylethyl){[(1S,2S,3S,5R)-3-methoxy-6,6-dimethylbicyclo[3.1.1]heptan-2-yl]methyl}selane (14)

Yield: 58%. Light yellow oil. *D.r*. 64:36. Column chromatography (70-230 mesh silica gel, Pet ether/EtOAc, 95:5). ^{1}H NMR (200 MHz, $CDCl_3$): major diastereomer δ = 0.85 (s, 3H, CH_3), 1.02 (d, *J*=9.8 Hz, 1H, CH*H*), 1.20 (s, 3H, CH_3), 1.71-1.83 (m, 1H), 1.86–2.12 (m, 3H), 2.27–2.45 (m, 2H), 2.50–2.78 (m, 3H), 2.95 (dd, *J*=12.2, 8.0 Hz, 1H, CH*H*), 3.25 (s, 3H, OCH_3), 3.31 (s, 3H, OCH_3), 3.42–3.59 (m, 1H), 4.28-4.39 (m, 1H), 7.35 (m, 5H, 5×CH); minor diastereomer (distinct signals) δ = 0.84 (s, 3H, CH_3), 3.24 (s, 3H, OCH_3), 3.30 (s, 3H, OCH_3). ^{13}C NMR (50 MHz, $CDCl_3$): major diastereomer δ = 23.6 (CH_3), 27.3 (CH_3), 30.4 (CH_2), 31.2 (CH_2), 32.8 (CH_2), 35.0 (CH_2), 38.2 (C), 41.3 (CH), 44.9 (CH), 50.3 (CH), 56.1 (OCH_3), 56.8 (OCH_3), 79.0 (CH), 84.3 (CH), 126.6 (2×CH), 127.8 (CH), 128.4 (2×CH), 141.3 (C); minor diastereomer (distinct signals) δ = 30.6 (CH_2), 32.7 (CH_2), 44.9 (CH), 50.4 (CH), 84.4 (CH), 126.7 (2×CH). ^{77}Se NMR (38 MHz, $CDCl_3$): major diastereomer δ = 139.3; minor diastereomer δ = 137.5. Anal. Calcd for $C_{20}H_{30}O_2Se$: C, 62.98; H, 7.93. Found: C, 63.92; H, 7.77.

{[(1S,2S,3S,5R)-3-(Benzyloxy)-6,6-dimethylbicyclo[3.1.1]heptan-2-yl]methyl}(2-methoxy-2-phenylethyl)selane (15)

Yield: 82%. Light yellow oil. *D.r*. 52:48. Column chromatography (70-230 mesh silica gel, Pet ether/EtOAc, 95:5). ^{1}H NMR (200 MHz, $CDCl_3$): major diastereomer δ = 0.87 (s, 3H, CH_3), 1.12 (d, *J*=9.8 Hz, 1H, CH*H*), 1.22 (s, 3H, CH_3), 1.84-2.03 (m, 2H), 2.04–2.24 (m, 2H), 2.27–2.78 (m, 5H), 2.95 (dd, *J*=12.2, 8.0 Hz, 1H, CH*H*), 3.24 (s, 3H, OCH_3), 3.70–3.82 (m, 1H), 4.35 (dd, *J*=8.0, 5.0 Hz, 1H, CH), 4.42-4.63 (m, 2H), 7.21-7.42 (m, 10H; 10×CH); minor diastereomer (distinct signal) δ = 0.84 (s, 3H, CH_3). ^{13}C NMR (50 MHz, $CDCl_3$): major diastereomer δ = 23.7 (CH_3), 27.3 (CH_3), 30.5 (CH_2), 31.3 (CH_2), 32.8 (CH_2), 35.4 (CH_2), 38.3 (C), 41.5 (CH), 45.0 (CH), 50.5 (CH), 56.9 (OCH_3), 70.6 (CH), 77.1 (CH_2), 84.5 (CH), 126.7 (CH), 127.4 (CH), 127.8 (2×CH), 127.9 (2×CH), 128.3 (2×CH), 128.4 (2×CH), 138.9 (C), 141.3 (C); minor diastereomer (distinct signals) δ = 30.4 (CH_2), 44.9 (CH), 50.4 (CH), 84.2 (CH), 126.6 (CH). ^{77}Se NMR (38 MHz, $CDCl_3$): major diastereomer δ = 140.6; minor diastereomer δ = 140.1. Anal. Calcd for $C_{26}H_{34}O_2Se$: C, 68.26; H, 7.49. Found: C, 68.15; H, 7.33.

(1S,2S,3S,5R)-2-{[(2,3-Dihydrobenzofuran-2-yl)methylselanyl]methyl}-6,6-dimethylbicyclo[3.1.1]heptan-3-ol (17)

Yield: 74%. Light yellow oil. *D.r*. 52:48. Column chromatography (70-230 mesh silica gel, CH_2Cl_2/EtOAc, 90:10). ^{1}H NMR (200 MHz, $CDCl_3$): major diastereomer δ = 0.90 (s, 3H, CH_3), 1.17 (d, *J*=9.9 Hz, 1H, CH*H*), 1.23 (s, 3H, CH_3), 1.76 (ddd, *J*=13.8, 4.6, 2.4 Hz, 1H), 1.89–2.00 (m, 2H), 2.08–2.14 (m, 1H), 2.36–2.60 (m, 3H), 2.71–3.08 (m, 6H), 3.37 (dd, *J*=15.6, 9.0 Hz; 1H), 4.14–4.26 (m, 1H), 4.93–5.04 (m, 1H), 6.74-6.86 (m, 2H, 2×CH), 7.08-7.18 (m, 2H, 2×CH); minor diastereomer (distinct signal) δ = 0.89 (s, 3H, CH_3). ^{13}C NMR (50 MHz, $CDCl_3$): major diastereomer δ = 23.8 (CH_3), 27.4 (CH_3), 29.1 (CH_2), 30.8 (CH_2), 33.6 (CH_2), 35.7 (CH_2), 37.5 (CH_2), 38.0 (C), 41.5 (CH), 46.9 (CH), 53.2 (CH), 70.0 (CH), 82.4 (CH), 109.4 (CH), 120.6 (CH), 125.0 (CH), 126.2 (C), 128.1 (CH), 159.1 (C); minor diastereomer (distinct signals) δ = 28.6 (CH_2), 30.5 (CH_2), 33.7 (CH_2), 35.9 (CH_2), 53.1 (CH), 70.1 (CH), 82.6 (CH), 126.1 (CH). ^{77}Se NMR (38 MHz, $CDCl_3$): major diastereomer δ = 116.9; minor diastereomer δ = 118.5. Anal. Calcd for $C_{19}H_{26}O_2Se$: C, 62.46; H, 7.17. Found: C, 62.40; H, 7.08.

2-({[(1S,2S,3S,5R)-3-Methoxy-6,6-dimethylbicyclo[3.1.1]heptan-2-yl]methylselanyl}methyl)-2,3-dihydrobenzofuran (18)

Yield: 31%. Light yellow oil. *D.r*. 62:38. Column chromatography (70-230 mesh silica gel, Pet ether/EtOAc, 95:5). ^{1}H NMR (300 MHz, $CDCl_3$): major diastereomer δ = 0.90 (s, 3H, CH_3), 1.05 (d, *J*=9.9 Hz, 1H, CH*H*), 1.23 (s, 3H, CH_3), 1.76–1.83 (m, 1H), 1.93–1.99 (m, 1H), 2.08–2.14 (m, 2H), 2.33–2.46 (m, 2H), 2.72–3.08 (m, 5H), 3.30 (s, 3H, CH_3), 3.38 (dd, *J*=15.6, 9.0 Hz, 1H), 3.52–3.62 (m, 1H), 4.92–5.03 (m, 1H), 7.5 (d, *J*=7.5 Hz, 1H, CH), 6.84 (dt, *J*=7.5, 0.9 Hz, 1H, CH), 7.10 (dt, *J*=7.5, 0.9 Hz, 1H, CH), 7.15 (d, *J*=7.5 Hz, 1H, CH); minor diastereomer (distinct signals) δ = 1.22 (s, 3H, CH_3), 3.34 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): major diastereomer δ = 23.6 (CH_3), 27.2 (CH_3), 28.8 (CH_2), 30.6 (CH_2), 32.7 (CH_2), 34.9 (CH_2), 35.6 (CH_2), 38.2 (C), 41.3 (CH), 45.0 (CH), 50.2 (CH), 56.0 (CH_3), 78.8 (CH), 82.6 (CH), 109.2 (CH), 120.4 (CH), 124.9 (CH), 126.3 (C), 127.8 (CH), 159.2 (C); minor diastereomer (distinct signals) δ = 28.7 (CH_3), 30.5 (CH_3), 32.8 (CH_2), 35.7 (CH_2), 38.1 (C), 44.9 (CH), 50.3 (CH), 56.1 (CH_3), 78.9 (CH), 82.7 (CH), 109.3 (CH), 126.3 (CH), 127.9 (CH), 159.1 (C). ^{77}Se NMR (38 MHz, $CDCl_3$): major diastereomer δ = 116.1; minor diastereomer δ = 119.1. Anal. Calcd for $C_{20}H_{28}O_2Se$: C, 63.31; H, 7.44. Found: C, 63.22; H, 7.35.

2-({[(1S,2S,3S,5R)-3-(Benzyloxy)-6,6-dimethylbicyclo[3.1.1]heptan-2-yl]methylselanyl}methyl)-2,3-dihydrobenzofuran (19)

Yield: 39%. Light yellow oil. *D.r*. 57:43. Column chromatography (70-230 mesh silica gel, Pet ether/EtOAc, 90:10). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.90 (s, 3H, CH_3), 1.18 (d, *J*=9.9 Hz, 1H, CH*H*), 1.24 (s, 3H, CH_3), 1.84-2.06 (m, 2H), 2.08–2.56 (m, 4H), 2.65–3.11 (m, 5H), 3.38 (dd, *J*=15.6, 9.0 Hz, 1H), 3.65–3.74 (m, 1H), 4.39-4.63 (m, 2H), 4.93–5.04 (m, 1H), 6.78 (d, *J*=7.5 Hz, 1H, CH), 7.82 (t, *J*=7.5, 1H, CH), 7.05-7.18 (m, 2H, 2×CH), 7.22-7.40 (m, 5H, 5×CH). ^{13}C NMR (50 MHz, $CDCl_3$): major diastereomer δ =

23.8 (CH_3), 27.3 (CH_3), 28.9 (CH_2), 30.5 (CH_2), 32.8 (CH_2), 35.4 (CH_2), 35.8 (CH_2), 38.3 (C), 41.5 (CH), 45.1 (CH), 50.4 (CH), 70.5 (CH), 77.0 (CH_2), 82.6 (CH), 109.4 (CH), 120.4 (CH), 124.9 (CH), 126.4 (C), 127.4 (CH), 127.8 (2×CH), 128.0 (CH), 128.3 (2×CH), 138.8 (C), 159.1 (C); minor diastereomer (distinct signals) δ = 28.8 (CH_2), 30.3 (CH_2), 35.7 (CH_2), 82.7 (CH). ^{77}Se NMR (38 MHz, $CDCl_3$): major diastereomer δ = 118.4; minor diastereomer δ = 121.7. Anal. Calcd for $C_{26}H_{32}O_2Se$: C, 68.56; H, 7.08. Found: C, 68.39; H, 7.02.

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[12] Crystals of **5** and **9** have been obtained from the n-heptane solution. The diffraction experiments were performed for 0.63×0.33×0.20 mm yellow crystal of **5** and for 0.41×0.21×0.10 mm yellow crystal of **9**. The X-ray data were collected at 291(2) K with an Oxford Sapphire CCD diffractometer using MoKα radiation λ =0.71073 Å by ω-2θ method. The numerical absorption correction was applied (CrysAlis171 package of programs, Oxford Diffraction, 2000) with the maximum and minimum transmissions of 0.5524 and 0.2203 for **5** and 0.7465 and 0.3503 for **9**. The structure of **5** was solved in the triclinic P1 space group and structure of **9** was determined in the orthorhombic P2(1)2(1)2 space group. The structures were solved with direct methods and refined with the full-matrix least-squares method on F2 with the use of SHELX-97 program package [13]. The hydrogen atoms have been located from the difference electron density maps and constrained during refinement. The absolute structure has been determined with the Flack method [14], the Flack x value being -0.008(13) for **5** and -0.014(11) for **9**. The structural data have been deposited with Cambridge Crystallographic Data Centre, the CCDC numbers 689256 and 689255, respectively.

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