Tetrahedron 65 (2009) 10162–10174

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

New chiral selenium electrophiles derived from functionalized terpenes

Jacek Ścianowski [a,*], Zbigniew Rafiński [a], Aleksandra Szuniewicz [a], Andrzej Wojtczak [b]

[a] Department of Organic Chemistry, Nicolaus Copernicus University, Gagarina 7, 87-100 Torun, Poland
[b] Department of Crystallochemistry and Biocrystallography, Nicolaus Copernicus University, Gagarina 7, 87-100 Torun, Poland

ARTICLE INFO

Article history:
Received 30 June 2009
Received in revised form
16 September 2009
Accepted 2 October 2009
Available online 7 October 2009

Dedicated to Professor Marek Zaidlewicz on the occasion of his 70th birthday

Keywords:
Terpenoids
Diselenides
Asymmetric synthesis
Selenenylation reaction

ABSTRACT

A convenient method for the synthesis *of optically* active dialkyl diselenides derived from bicyclic terpenes functionalized with hydroxy, etheral, sulfide, and selenide groups is described. The diselenides were used for a synthesis of chiral electrophilic selenium reagents, then in the asymmetric selenenylation of styrene and selenocyclization with *o*-allylphenol. The influence of nonbonding selenium-heteroatom interactions in the generated organoselenium electrophiles on the stereoselectivity of an addition reaction has been investigated. Calculations by a DFT method on a B3LYP (6–311G (*d*)) level, confirmed the existence of nonbonded selenium–heteroatom interactions in the investigated systems.

1. Introduction

Diselenides are important reagents in modern organic synthesis and have been very often used as the key substrates in multistep syntheses. The major advantage of diselenides is the ease of their transformation into nucleophilic, radical, and electrophilic reagents, as well as their air, acid, base, and temperature stability.[1] Diselenides are also used in asymmetric synthesis, for example, as ligands in the addition of diethylzinc to aldehydes.[2]

The search for a useful method of a diselenide synthesis has also great importance because of their physiological and pharmacological role, in particular their antioxidant, antiviral, and antitumor activity.[3]

Our previous research has focused on the synthesis of nonracemic monoterpene dialkyl diselenides, the precursors for a synthesis of chiral electrophilic selenium reagents. Recently, we have described a convenient methodology for epimeric dialkyl diselenides synthesis, based on the reaction of alkyl tosylates or chlorides with disodium diselenide generated in situ (Se, NaOH, $N_2H_4 \times H_2O$). The obtained nonracemic diselenides derived from *p*-menthane, pinane, carane or bornane groups[4–7] have been converted to triflate salts and used for a stereoselective selenenylation of olefins, [5–7] as well as selenocyclization of unsaturated alcohols and carboxylic acids.[8] Until now, the best stereoselectivity in the methoxyselenenylation of styrene with the electrophile **1a** containing a isopinocampheyl group in its molecule (dr 82:18) has been observed.[5] On the other hand the best results for the selenocyclization of *o*-allylphenol have been achieved with the triflate salt **3a** generated from (+)-neomenthyl diselenide **3** (dr 70:30) (Scheme 1). The diastereomeric mixture of dihydrobenzofuran derivatives **4** was separated by crystallization from *n*-pentane and the structure of the major stereoisomer confirmed by X-ray crystal structure determination.[8]

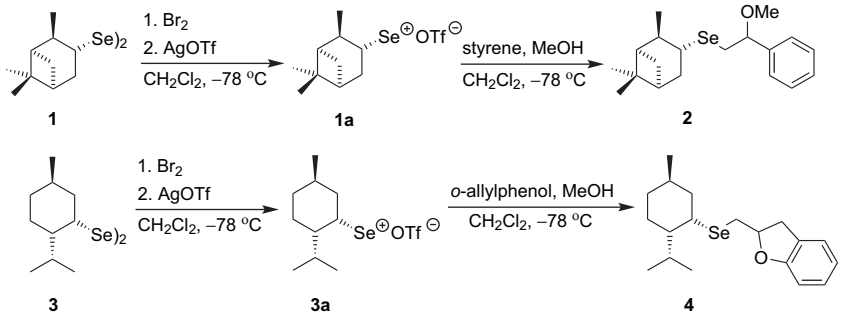
Stereoselective selenenylation is a matter of permanent interest for numerous scientific groups, and highly selective electrophilic reagents are known. Inspite of numerous papers describing an influence of a heteroatom on the asymmetric induction in addition,[9] the lack of experimental examples showing a difference in stereoselection between unsubstituted alkyl electrophiles and their analogs containing functional groups with different heteroatoms is evident.

Among the functionalized terpene diselenides used so far in the asymmetric synthesis, a bornane system and its derivatives were the only chiral source.[10]

Furthermore, to date, no comparative analysis of the influence of the structure, or the range of functional group or heteroatom, on the stereoselectivity of selenenylation has been reported for unfunctionalized and functionalized alkyl electrophiles. Therefore the aim of the reported research was to investigate the syntheses and reactions of functionalized dialkyl diselenides containing

* Corresponding author. Department of Chemistry, Nicolaus Copernicus University, 7 Gagarin street, 87-100 Torun, Poland. Tel.: +48 56 611 4532; fax: +48 56 654 2477.
E-mail address: jsch@chem.uni.torun.pl (J. Ścianowski).

0040-4020/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2009.10.005



Scheme 1. Asymmetric selenenylation of olefins.

hydroxy, etheral, sulfide, and selenide groups. The other goal was to conduct the methoxyselenenylation of styrene and selenocyclization of *o*-allylphenol with the use of the respective triflate salts generated from diselenides. The final goal was to explain the influence of selenium–heteroatom interaction on the stereoselectivity of addition and to compare the results with those obtained for electrophiles generated from diselenides not having any functional groups.

2. Results and discussion

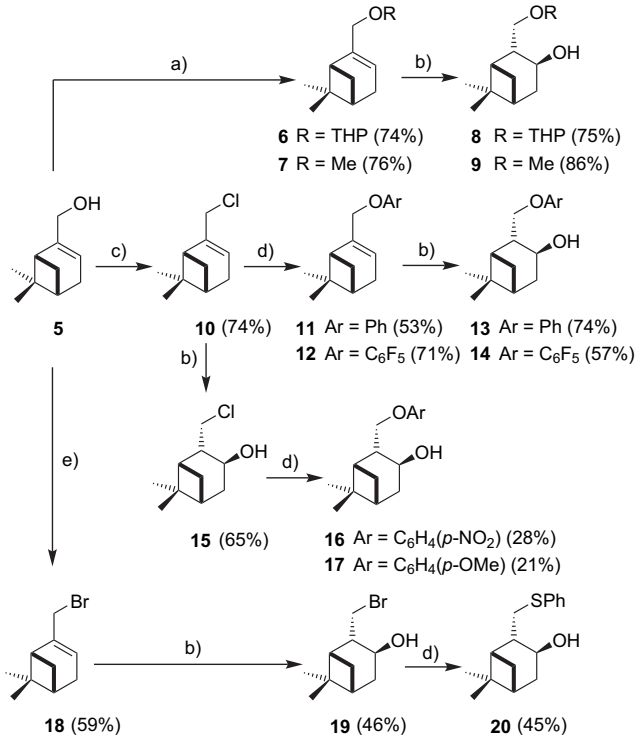
The first step of our investigation was the synthesis of terpene alcohols containing functional groups at the C-10-position, to obtain precursors for a synthesis of functionalized nonracemic diselenides. The commercially available (1*R*)-(-)-myrtenol **5** was used as a substrate for most of the obtained alcohols. Alcohols **8** and **9**, with hydroxy groups protected with tetrahydropyranyl and methoxy groups, were obtained directly from myrtenol **5** in a reaction with dihydropyran in the presence of catalytic amounts of *p*-toluenesulfonic acid or sodium hydride and methyl iodide, followed by hydroboration-oxidation.[7] Aryl ethers **11** and **12** were obtained by chlorination of myrtenol **5** by means of carbon tetrachloride in the presence of triphenylphosphine[7] and subsequent substitution with sodium phenolate or sodium pentafluorophenolate. Hydroboration of the resulting ethers gave chiral alcohols **13** and **14** (Scheme 2).

Alcohol **16** was synthesized by inserting a *p*-nitrophenoxy group to a pinane system after hydroboration-oxidation of myrtanyl chloride **10**. Alcohol **17** was obtained analogously. Because of the higher reactivity of allylic bromides, myrtanyl bromide **18** was used for the reaction with sodium benzenethiolate. ^{1}H NMR spectroscopic analysis showed the presence of two products **21** and **22**, indicating that under the reaction conditions the product of rearrangement is also formed (Scheme 3).

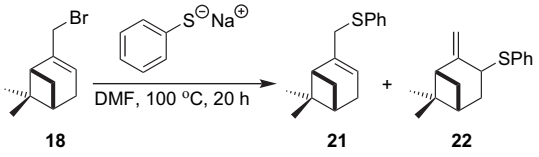
The hydroboration-oxidation of myrtanyl bromide **18** and substitution of bromoalcohol **19** by means of sodium benzenethiolate gave the isopinocampheyl derivative **20** with a sulfide substituent (Scheme 2).

We also tried to synthesis a ethers containing the bulky *tert*-butyl groups in the *ortho*-position of a phenyl ring. Instead, the reaction of myrtanyl chloride **10** with 2,6-di-*tert*-butyl phenolate gave **23**, a product of substitution in *para*-position relative to hydroxyl. The similar substitution in the *para*-position in relation to the hydroxyl group was observed, for example, by Hayakawa and co-workers.[11] Hydroboration-oxidation gave alcohol **24** (Scheme 4).

10-Phenylselanylisopinocampheol **29**, was obtained from 10-phenylselanyl-2-pinene **27** via chlorination of *β*-pinene **25** with *N*-chlorosuccinimide[12] and substitution by means of sodium benzeneselenolate[13] (Scheme 5).

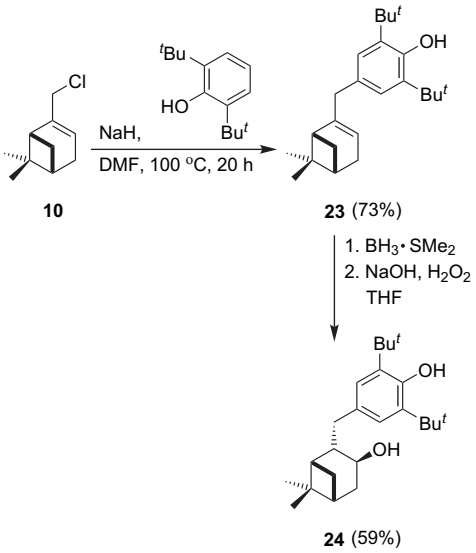


Scheme 2. Synthesis of functionalized alcohols from the pinane system. Reagents and conditions: (a) dihydropyrane, TsOH/CH_2Cl_2, RT, 18 h; or NaH, MeI, RT, 20 h; (b) (i) $BH_3{\cdot}SMe_2$, THF, 0 °C→RT, 18 h; (ii) NaOH, 30% H_2O_2, RT→60 °C, 5.5 h (two steps); (c) CCl_4, PPh_3, reflux, 20 h; (d) NaXAr (X=O, S), DMF, 100 °C, 20 h; (e) PBr_3, hexane, −20 °C→RT, 18.5 h.

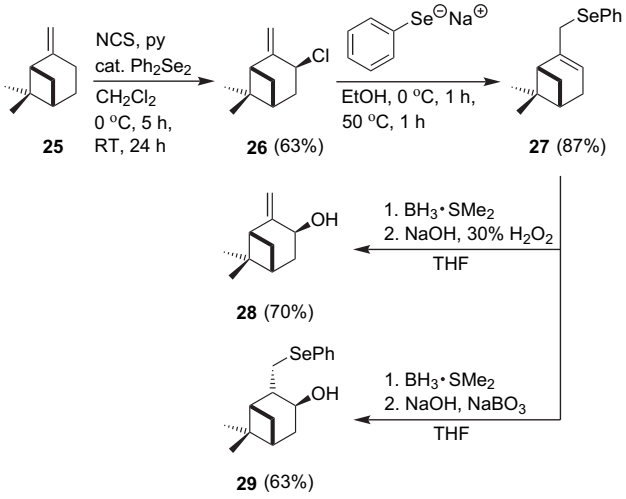


Scheme 3. Reaction of (−)-myrtenyl bromide with sodium benzenethiolate.

It is generally known that under oxidation conditions the SePh group can easily undergo the *syn*-elimination to olefins. Hydrogen peroxide usually used in hydroboration–oxidation is also commonly employed for elimination of a phenylselanyl group (SePh).[1] The use of the standard conditions (30% hydrogen peroxide) in the oxidation step gave allylic alcohol **28**. An alternative oxidation with sodium perborate ($NaBO_3$) under alkaline conditions gave selectively 10-phenylselanylisopinocampheol **29** without elimination of the SePh group. To the best of our knowledge this is the first

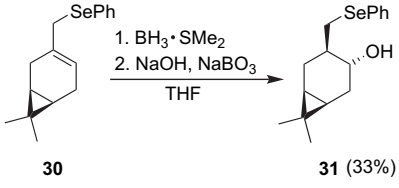


Scheme 4. Synthesis of alcohol **24**.



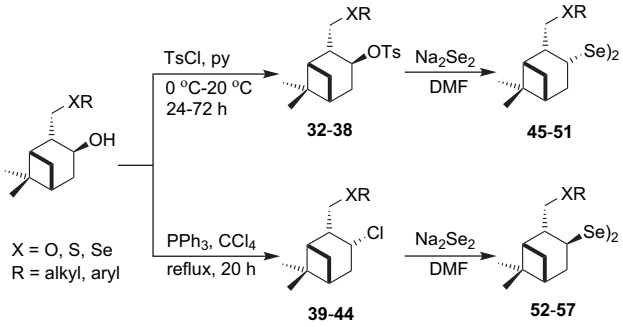
Scheme 5. Synthesis of 10-phenylselanylisopinocampheol **29**.

example of hydroboration–oxidation in the presence of SePh leading to formation of hydroxyphenylselenides. To confirm the universal character of the described oxidation methodology we also obtained the respective 10-phenylselanyl-4-isocaranol **31**, which was formed from 10-phenylselanyl-3-carene **30**[14] by hydroboration with the adduct of borane-dimethyl sulfide and subsequent oxidation with sodium perborate (Scheme 6).



Scheme 6. Synthesis of 10-phenylselanyl-4-isocaranol **31**.

The terpene alcohols obtained using the previously developed methodology based on a reaction of alkyl tosylates and halides with generated in situ disodium diselenide[5] (Scheme 7), were used in the synthesis of chiral tosylates and chlorides leading to the respective diselenides.



Scheme 7. Syntheses of functionalized diselenides.

A route through tosylates **32**–**38** led via a single inversion of configuration and gave diselenides **45**–**51**. Alternatively, when chlorides **39**–**44** were employed, double inversion was observed during transformation of alcohols to the corresponding chlorides. Reaction of these chlorides with disodium diselenide gave epimeric diselenides **52**–**57**. The yields of the syntheses of tosylates, chlorides, and diselenides are presented in Table 1.

The reaction of alcohol **8** with tosyl chloride in pyridine or carbon tetrachloride in the presence of triphenylphosphine gave the respective tosylate **58** and chloride **59** (Scheme 8). An attempt at deprotection of the tosylate **58** THP group to a hydroxyl group failed. As a result of the reaction of chloride **59** with catalytic amounts of *p*-toluenesulphonic acid in methanol, the respective hydroxychloride **39** was obtained, which was used for the synthesis of diselenide **52** (Table 1).

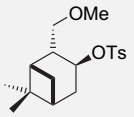
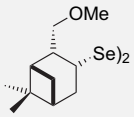
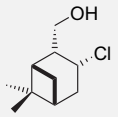
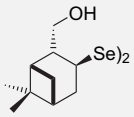
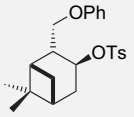
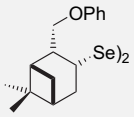
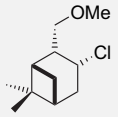
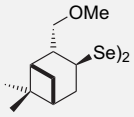
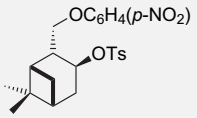
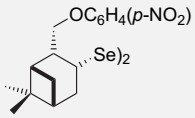
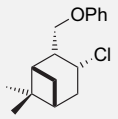
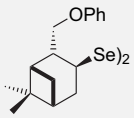
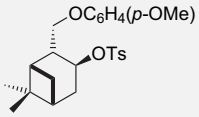
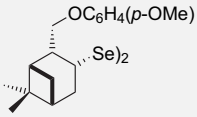
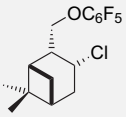
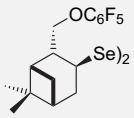
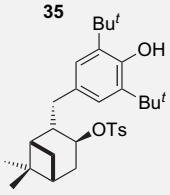
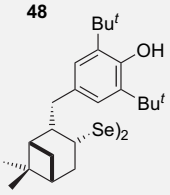
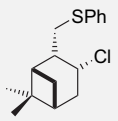
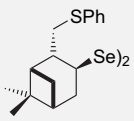
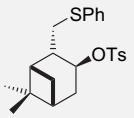
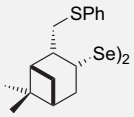
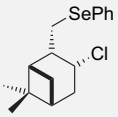
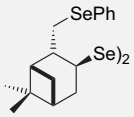
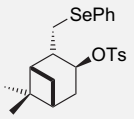
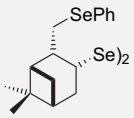
Tosylate **60** with pentafluorinated phenoxy group at the C-10-position proved to be unreactive in a reaction with disodium diselenide at room temperature, as well as when heated to 50 °C for 24 h. When this reaction was conducted at 100 °C a reaction product was obtained, being a result of intramolecular substitution of the pentafluorophenoxyl group to give unsymmetric cyclic diselenide **61** in 11% yield (Scheme 9). The same product was also obtained conducting a reaction of tosylate **38** with a disodium diselenide at 100 °C.

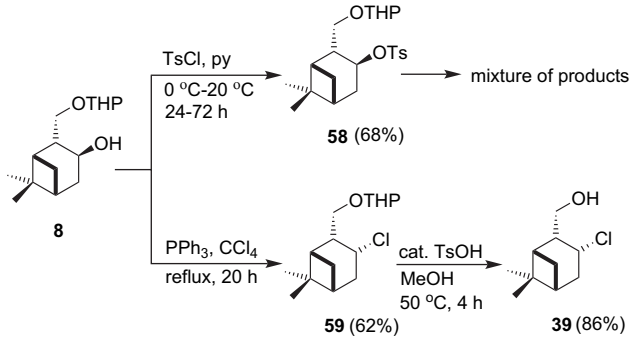
When analogous conditions were employed for chloride **44**, only a mixture of undefined products was observed. The lowering of the reaction temperature to 20 °C allowed us to obtain diselenides bis(10-phenylselanylpinocampheyl) **51** and bis(10-phenylselanylisopinocampheyl) **57** in good yields. There is only one literature example of the synthesis of a chiral aryl diselenide with a selenide substituent (SeMe).[15] The structure of diselenide **51** was confirmed by X-ray analysis (Fig. 1).

We used the obtained diselenides for asymmetric methoxyselenenylation of styrene. The diselenides **45**–**51** and **52**–**57** were treated with a 1 M solution of bromine and then with silver triflate to obtain the corresponding triflate salts **46a**–**57a**, which in turn were used for the addition to styrene in the presence of methanol as a nucleophile. Stereoselectivities and yields of methoxyselenenylation of styrene for products **63**–**75** are presented in Table 2.

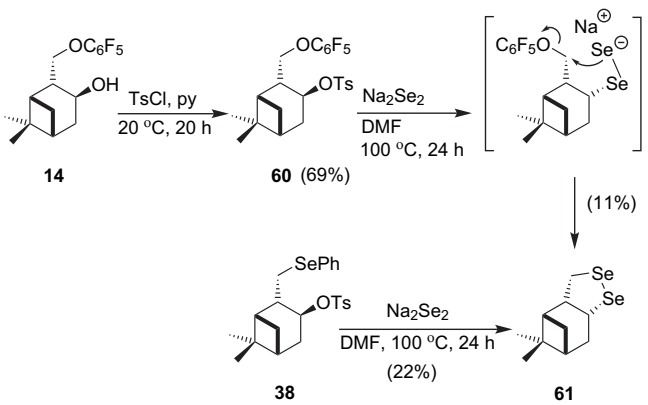
Attempts to isolate the methoxyselenenylation derivatives of diselenides **45** and **49** failed. For electrophiles **46a**–**51a** having a selenenyl group (SeOTf) in the *cis* position relative to the group bound to C-2, we observed the stereoselection to be higher than that found with the use of electrophile **62**, which has no functional group (dr 52:48). That might be caused by a selenium–heteroatom interaction in the transition state of the methoxyselenenylation reaction. It has been found that for electrophiles **46a**–**51a** the best stereoselectivity can be obtained for electrophile **46a** with a phenoxy group (dr 70:30). Introduction of an electron-acceptor ($-NO_2$)

Table 1
Syntheses of functionalized tosylates, chlorides and diselenides

Tosylate	Yield [%]	Diselenide	Yield [%]	Chloride	Yield [%]	Diselenide	Yield [%]
 **32**	67	 **45**	81	 **39**	62	 **52**	55
 **33**	69	 **46**	30	 **40**	69	 **53**	45
 **34**	91	 **47**	27	 **41**	43	 **54**	19
 **35**	83	 **48**	25	 **42**	72	 **55**	33
 **36**	70	 **49**	8	 **43**	41	 **56**	23
 **37**	79	 **50**	15	 **44**	73	 **57**	47
 **38**	88	 **51**	68				



Scheme 8. Synthesis of 10-hydroxyisopinocampheyl chloride **39**.



Scheme 9. Formation of cyclic diselenide **61**.

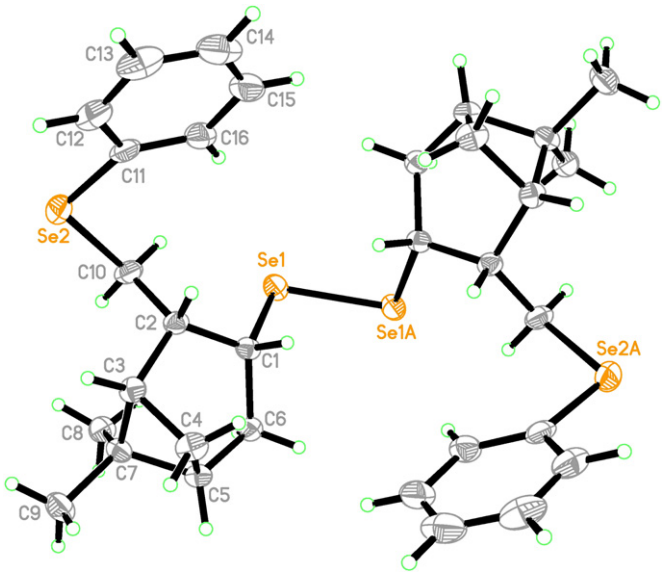
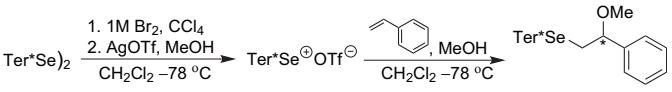


Figure 1. Crystal structure of **51** with the thermal ellipsoids plotted at 30% probability.

or electron-donor (–OMe) substituents reduced the stereoselectivity of the reaction. Replacement of the etheral group of electrophile **46a** with a sulfide or a selenide group (electrophiles **50a** and **51a**) resulted in a considerable drop in the stereoselectivity. So far, the literature reports for chiral aryl electrophilic reagents demonstrated a dependence in which the increase of a stereoselection correlated with ability of heteroatoms to donate electrons into the sigma-* orbital of the selenium atom in the N<O<S series.[16] In the reported research we have observed the opposite tendency for electrophiles **46a**, **50a** or **51a** with OPh, SPh, and SePh groups (O>S≈Se).

Among the selenium electrophiles **52a**–**57a** with the selenenyl group (SeOTf) positioned *trans* relative to the group bound to C-2, the best results have been obtained for triflate **55a** with a pentafluorophenoxy group (OC_6F_5, dr 84:16) and **57a** with a selenide group (SePh, dr 72:28). Comparison with electrophiles **46a** and **54a** with the opposite configuration at C-3, showed a decrease in stereoselection for electrophile **54a**, which seems to be caused by a lack of Se···O interaction. Our results revealed that in methoxyselenenylation with electrophiles **54a**, **56a**, and **57a** containing the OPh, SPh or SePh groups, the stereoselectivity increases with the atomic mass and the size of a heteroatom in the Se>S>O series. Such a dependence of stereoselection on the size of a heteroatom suggests that in these cases the effects connected with a steric hindrance of the functional group has a predominant influence on the asymmetric induction. The role of the substituents in the pinane ring can be determined by comparison of a stereoselection of nonfunctionalized electrophilic reagents **62** and **1a** with functionalized compounds **46a**, and **52a**–**57a**. Data for the pair of electrophiles **62** and **46a** suggest, that the increased selectivity found for electrophile **46a** when compared to unsubstituted **62**, can be caused by the Se···O interaction between the phenoxy group oxygen and selenium atom. For triflates **52a**–**54a** the presence of a hydroxy, methoxy or phenoxy group in the C-10-position of pinane reduces the stereoselectivity with respect to electrophile **1a**. On the other hand, an increase in asymmetric induction has been

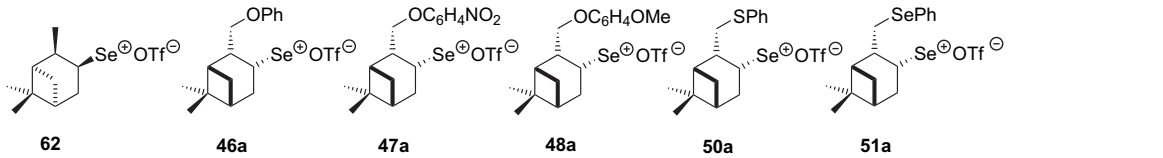
Table 2
Methoxyselenenylation of the styrene with the use of functionalized selenium electrophiles



63-75

Entry	Alkene	Electrophile	Product	Dr	Yield [%]
1		**62**	**63**	52:48	48
2		**46a**	**64**	70:30	70
3		**47a**	**65**	65:35	40
4		**48a**	**66**	61:39	65
5		**50a**	**67**	52:48	82
6		**51a**	**68**	56:44	14
7[a]		**1a**	**69**	82:18	57
8		**52a**	**70**	52:48	61
9		**53a**	**71**	52:48	80
10		**54a**	**72**	52:48	73
11		**55a**	**73**	86:14	56
12		**56a**	**74**	56:44	63
13		**57a**	**75**	72:28	28

[a] See ref 5.



62 **46a** **47a** **48a** **50a** **51a**

1a **52a** **53a** **54a** **55a** **56a** **57a**

observed for the bulky aryl group $-OC_6F_5$ of electrophile **55a** and phenylselanyl group –SePh in **57a**, suggesting a dependence of the stereoselection on steric effects.

To confirm the hypothesis concerning the role of the selenium–heteroatom interactions in the *cis*-pinane system, the molecular modeling was performed with density functional theory (DFT) using the B3LYP method[17] and a 6–311G(*d*) functional base, as implemented in GAUSSIAN 03.[18] The aim was an optimization of geometric parameters for the selected selenium electrophiles and to check if a linear arrangement of heteroatom with a selenenyl group is possible. Calculations have been conducted for selenenyl bromides containing phenoxy **76**, *p*-nitrophenoxy **77**, *p*-methoxyphenoxy **78**, phenylsulphanyl **79**, and phenylselanyl **80** groups. The optimized structures are presented in Figure 2.

On the basis of the calcd structural parameters (Table 3) it can be established that atomic distances ($r_{Se\cdots X}$) between the selenium atom (SeBr) and heteroatoms (O, S, Se) are significantly smaller then the sum of the van der Waals radii (Se···O, 3.40 Å Se···S, 3.68 Å Se···Se, 3.76 Å).[19]

Furthermore, a near linear arrangement of X···Se–Br with angles close to 180° ($O_{X\cdots Se-Br}$) revealed the presence of selenium-heteroatom interactions for the model compounds.

The selenocyclization of *o*-allylphenol with electrophiles generated from functionalized diselenides **46**–**57** was also investigated. The resulting diselenides were transformed to the respective triflate salts **46a**–**57a** and converted to the dihydrobenzofuran derivatives **81**–**91** in the reaction with *o*-allylphenol. The highest stereoselectivity of selenocyclization was obtained for electrophile **55a** with a OC_6F_5 group (dr 77:23) and for electrophile **57a** with a –SePh (Table 4).

We also conducted the syntheses of diselenides from the carane system starting from alcohol **31** and used them in methoxyselenenylation and selenocyclization (Scheme 10).

The reaction of alcohol **31** with tosyl chloride in pyridine or with carbon tetrachloride in the presence of triphenylphosphine gave tosylate **92** and chloride **96**, respectively, that were further transformed to diselenides **93** and **97** with the use of disodium diselenide. During the reaction of diselenides with bromine and silver triflate in situ, the triflate salts **93a** and **97a** were obtained. These salts reacted with styrene and methanol giving the methoxyselenenylation products **94** and **98**, whereas reaction with

Table 3
Selected structural parameters for bromides **76**–**80**

Entry	Electrophile	$r_{Se\cdots X}$[a], [Å]	$\theta_{X\cdots Se-Br}$[b], [deg]
1	**76**	2.66	172.0
2	**77**	2.67	169.6
3	**78**	2.56	170.6
4	**79**	2.88	173.9
5	**80**	2.90	176.0

[a] Distance between selenium atom of SeBr and heteroatom.
[b] Angle between bromine atom and heteroatom in X···Se–Br.

o-allylphenol led to dihydrobenzofuran derivatives **95** and **99**. The diastereomeric ratio was estimated on the basis of the ^1H NMR and ^{77}Se NMR spectroscopic analyses. A small increase in diastereoselection was observed for methoxyselenenylation with diselenide **93**, in which the groups in positions 3 and 4 are in a *cis*-relationship, compared to diselenide **97** in which these groups are positioned *trans*. No differences were observed in the diastereoselection for the selenocyclization reaction.

3. Conclusion

The developed methodology was used to synthesize a series of optically active dialkyl diselenides, derivatives of monoterpenes from the pinane and carane systems and functionalized with hydroxy, methoxy, phenoxy, phenylsulfanyl and phenylselanyl groups. We have developed a convenient method of oxidation of products of the hydroboration reaction in the presence of a phenylselanyl group with the use of $NaBO_3$. It has been demonstrated that when in the pinane system the functional group bound to C-2 is in a *cis*-relationship to the selenide group at the C-3-position, the stereoselectivity of methoxyselenenylation of styrene is increased relative to the nonfunctionalized pinocampheyl electrophile. DFT calculations on model selenenyl bromides have confirmed that the stereoselectivity may be coupled to the interaction between a heteroatom and selenium atom in the transition state of the addition reaction. For compounds having substituents in the C-2 and C-3 positions in the *cis* stereochemistry, it is evident that the highest stereoselectivity of methoxyselenenylation can be achieved for a substituent with an oxygen atom and it decreases with a size of the heteroatom (S and Se). For

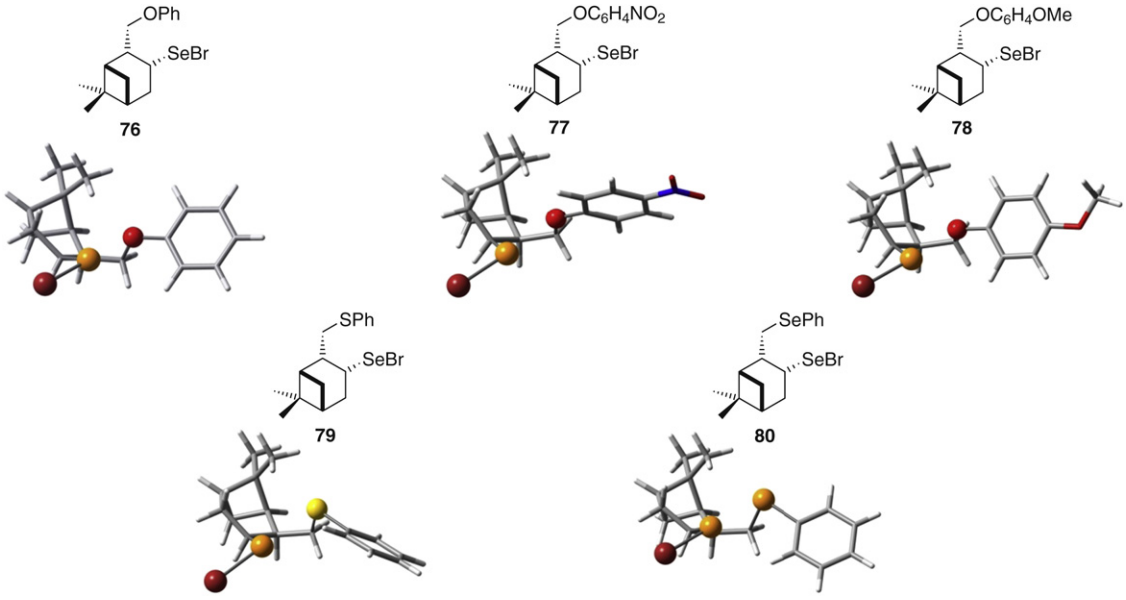
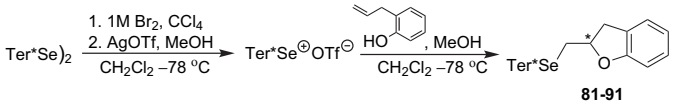
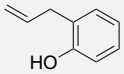
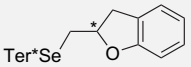


Figure 2. Structures of **76**–**80** optimized with the DFT method. Heteroatoms are color-coded: nitrogen blue, oxygen red, sulfur yellow, selenium orange, bromine brown.

Table 4
Asymmetric selenocyclization of *o*-allylphenol



Entry	Alkene	Electrophile	Product	Dr[a]	Yield [%]
1		**46a**	**81**	63:37	23
2		**47a**	**82**	63:37	28
3		**48a**	**83**	61:39	34
4		**50a**	**84**	61:39	60
5		**51a**	**85**	56:44	57
6		**52a**	**86**	—	—
7[a]		**53a** 	**87**	57:43	60
8		**54a**	**88**	52:48	57
9		**55a**	**89**	77:23	49
10		**56a**	**90**	52:48	62
13		**57a**	**91**	72:28	23

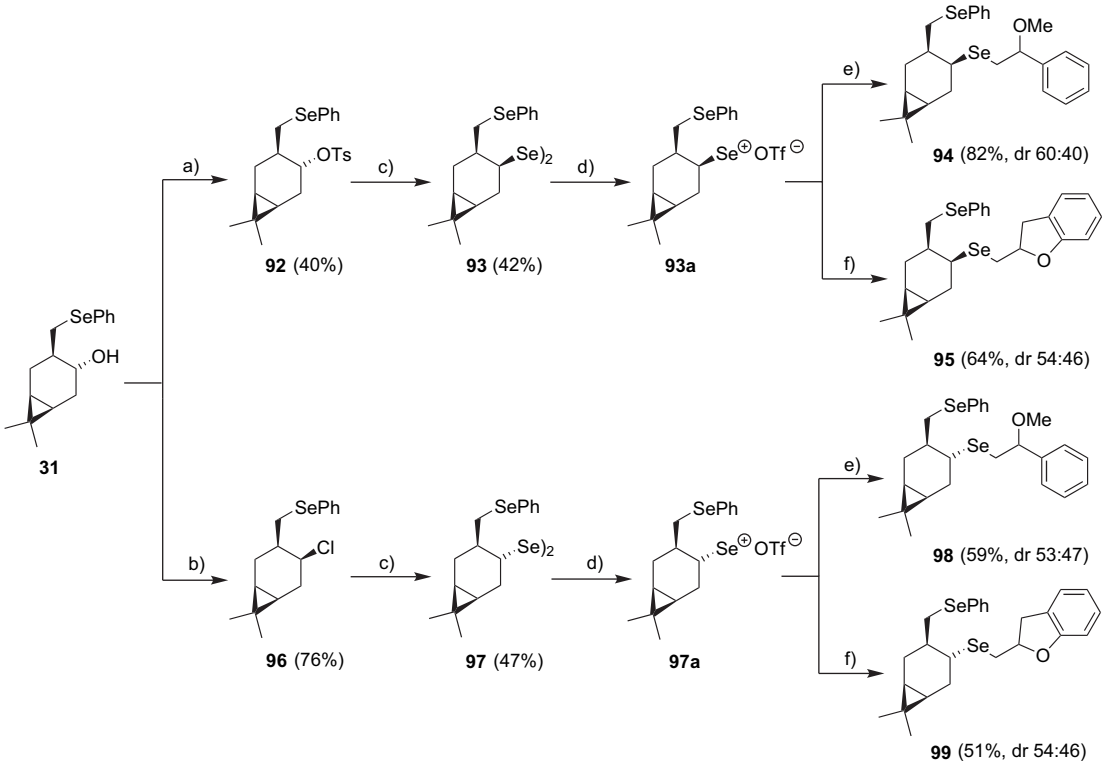
[a] Dr estimated on the basis of ^{1}H NMR and ^{77}Se NMR.

compounds with these substituents at the C-2 positioned *trans* relative to the selenide group at position C-3, the presence of substituents with heteroatoms decreased the diastereomeric excesses in selenenylation when compared to a non-substituted system. In these cases the increase in size of the heteroatoms or the introduction of bulky groups improves the stereoselection of addition and the effects connected with a steric hindrance of the functional group have a dominating influence on the asymmetric induction. The best results have been observed for $-OC_6F_5$ and –SePh substituents. We demonstrated that the stereoselection of selenocyclization is lower than the stereoselection of methoxyselenenylation in the investigated systems. The use of electrophiles from the carane system in methoxyselenenylation of styrene and selenocyclization of *o*-allylphenol has not revealed any significant improvement in the stereoselection. Until now the results of addition and cyclization reactions with the use of terpene selenium electrophiles are lower than presented for aryl selenium electrophiles, inspite searching for new electrophiles derived from natural products seems to be interesting course of research.

4. Experimental section

4.1. General

Unless otherwise stated, all manipulations were performed in dried glassware under argon atmosphere using dried solvents. The ^{1}H, ^{13}C, and ^{77}Se NMR spectra were measured in $CDCl_3$ with



Scheme 10. Synthesis of the functionalized diselenides from carane systems and selenenylation reaction. Reagents and conditions: (a) TsCl, py, 0 °C→RT, 20 h; (b) CCl_4, PPh_3, reflux, 20 h; (c) (i) Se, NaOH, $N_2H_4\times H_2O$, 100 °C, 15 min; (ii) terpene chloride or tosylate, RT, 20 h (two steps); (d) (i) 1 M Br_2/CCl_4, −78 °C, 15 min; (ii) AgOTf/MeOH, −78 °C, 15 min (two steps); e) styrene, −78 °C, 5 h; f) *o*-allylphenol, −78 °C, 5 h.

TMS as an internal standard. All melting points are uncorrected. Elemental analyses were carried out by the Instrumental Analyses Laboratory. All alcohols, chlorides, tosylates and diselenides were obtained according to procedures described in the literature.[5,6] The methoxyselenenylation and selenocyclization reactions were carried out according to the protocols described in the literature.[5,8]

4.2. Synthesis of ethers and alcohols

*4.2.1. (1R)-Myrtenyl tetrahydro-2H-pyrane ether (**6**).* A solution of myrtenol (10.0 g, 65.7 mmol), dihydropyran (9.5 g, 112.7 mmol) and *p*-TSA (130 mg) in CH_2Cl_2 (130 mL) was stirred at room temperature for 18 h. The reaction mixture was washed with the saturated Na_2CO_3 solution, water, brine and dried over anhydrous $MgSO_4$. The solvent was evaporated, and the residue was purified by distillation to afford the desired ether **6** (11.5 g, 74%) as a colorless oil; bp 84–86 °C/0.15 Torr; ^{1}H NMR (300 MHz, $CDCl_3$): mixture of diastereomers δ=0.84 (s, 3H; CH_3), 1.18 (d, *J*=8.7 Hz, 1H, CH*H*), 1.28 (s, 3H, CH_3), 1.46–1.90 (m, 6H), 2.06–2.20 (m, 2H), 2.23–2.33 (m, 2H), 2.35–2.44 (m, 1H), 3.46–3.55 (m, 1H), 3.84–3.93 (m, 2H), 3.99–4.09 (m, 1H), 4.62 (m, 1H), 5.45–5.52 (m, 1H); ^{13}C NMR (50.3 MHz, $CDCl_3$): mixture of diastereomers δ=19.3 (CH_2), 19.4 (CH_2), 20.9 (CH_3), 21.0 (CH_3), 25.4 (CH_2), 25.5 (CH_2), 26.0 (CH_3), 26.1 (CH_3), 30.5 (CH_2), 30.6 (CH_2), 31.0 (CH_2), 31.2 (CH_2), 31.3 (CH_2), 31.5 (CH_2), 37.9 (C), 38.0 (C), 40.8 (CH), 40.9 (CH), 43.3 (CH), 43.6 (CH), 61.9 (CH_2), 62.0 (CH_2), 69.4 (CH_2), 69.5 (CH_2), 97.1 (CH), 97.4 (CH), 118.9 (CH), 119.4 (CH) ppm; elemental analysis calcd (%) for $C_{15}H_{24}O_2$ (236.35): C 76.23, H 10.24; found: C 76.02, H 10.17.

*4.2.2. (R)-(-)-Methyl myrtenyl ether (**7**).* To a solution of sodium hydride (4.7 g, 197.1 mmol) in dry THF (110 mL), the THF (100 mL) solution of myrtenol (15.0 g, 98.5 mmol) was slowly added at room temperature. After stirring for 20 min, methyl iodide (12.3 mL, 197.1 mmol) was added dropwise. The resulting solution was stirred at 20 °C for 24 h. The reaction was quenched by addition of water, then the volatiles were removed under reduced pressure. Subsequently ethyl acetate (100 mL) was added and the mixture was washed sequentially with water, saturated aq $Na_2S_2O_3$ and brine. The organic phase was dried over magnesium sulfate, filtered, and the solvent was removed under vacuum. The crude product was purified by the distillation under reduced pressure to afford ether **7** (12.5 g, 76%) as a colorless liquid; bp 36–38 °C/0.6 Torr; $[\alpha]_D^{20}$=−32.6 (*c* 8.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.84 (s, 3H, CH_3), 1.17 (d, 1H, *J*=9.9 Hz, CH*H*), 1.29 (s, 3H, CH_3), 2.08–2.14 (m, 1H), 2.16 (dt, 1H, *J*=5.7 Hz, *J*=1.5 Hz), 2.25–2.30 (m, 2H), 2.40 (dt, 1H, *J*=8.7 Hz, *J*=5.7 Hz), 3.29 (s, 3H, OCH_3), 3.76–3.79 (m, 2H), 5.48–5.51 (m, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=21.0 (CH_3), 26.1 (CH_3), 31.2 (CH_2), 31.5 (CH_2), 37.9 (C), 40.9 (CH), 43.3 (CH), 57.7 (OCH_3), 75.5 (CH_2), 119.9 (CH=), 145.3 (C=) ppm; elemental analysis calcd (%) for $C_{11}H_{18}O$ (166.26): C 79.46, H 10.91; found: C 79.40, H 10.88.

*4.2.3. (1S)-10-(Tetrahydro-2H-pyran-2-yloxy)isopinocampheol (**8**).* Yield: 9.0 g, (75%), colorless oil; bp 120–122 °C/0.2 Torr; ^{1}H NMR (200 MHz, $CDCl_3$): mixture of diastereomers δ=0.90 (s, 3H, CH_3), 1.12 (d, *J*=9.8 Hz, 1H CH*H*), 1.20 (s, 3H, CH_3), 1.47–1.68 (m, 4H), 1.70–2.03 (m, 5H), 2.16–2.60 (m, 4H), 3.34–3.58 (m, 2H), 3.62–3.93 (m, 2H), 4.36–4.44 (m, 1H), 4.62 (m, 1H); ^{13}C NMR (50.3 MHz, $CDCl_3$): mixture of diastereomers δ=19.3 (CH_2), 19.5 (CH_2), 23.6 (CH_3), 23.7 (CH_3), 25.0 (CH_2), 25.1 (CH_2), 27.2 (CH_3), 27.3 (CH_3), 30.4 (CH_2), 30.5 (CH_2), 33.9 (CH_2), 34.1 (CH_2), 36.5 (CH_2), 36.6 (CH_2), 37.8 (C), 41.6 (CH), 43.1 (CH), 43.4 (CH), 52.8 (CH), 61.9 (CH_2), 62.4 (CH_2), 67.5 (CH), 68.1 (CH), 71.7 (CH_2), 72.0 (CH_2), 98.6 (CH), 99.4 (CH) ppm; elemental analysis calcd (%) for $C_{15}H_{26}O_3$ (254.37): C 70.83, H 10.30; found: C 70.98, H 10.44.

*4.2.4. (1S)-(+)-10-Methoxyisopinocampheol (**9**).* Yield: 11.5 g (86%), colorless oil; bp 72–74 °C/0.6 Torr; $[\alpha]_D^{19}$=+4.8 (*c* 5.4, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ=0.90 (s, 3H, CH_3), 1.12 (d, 1H, *J*=9.9 Hz, CH*H*), 1.20 (s, 3H, CH_3), 1.68–2.04 (m, 3H), 2.12–2.25 (m, 1H) 2.31 (bs, 1H, OH), 2.35–2.58 (m, 2H), 3.36 (s, 3H, OCH_3), 3.38–3.43 (m, 2H), 4.23–4.34 (m, 1H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ=23.8 (CH_3), 27.5 (CH_3), 34.3 (CH_2), 36.9 (CH_2), 38.0 (C), 41.8 (CH), 43.4 (CH), 53.1 (CH), 55.5 (OCH_3), 68.3 (CH), 77.5 (CH_2) ppm; elemental analysis calcd (%) for $C_{11}H_{20}O_2$ (184.28): C 71.70, H 10.94; found: C 71.62, H 10.73.

*4.2.5. (1S)-(+)-10-Phenoxyisopinocampheol (**13**).* Yield: 3.2 g (74%), colorless oil; $[\alpha]_D^{17}$=+0.7 (*c* 4.12, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ=0.94 (s, 3H, CH_3), 1.19 (d, 1H, *J*=9.6 Hz, CH*H*), 1.25 (s, 3H, CH_3), 1.82 (dd, 1H, *J*=13.5 Hz, *J*=4.5 Hz), 2.01 (d, 2H, *J*=6.1 Hz, CH_2), 2.28 (d, 1H, *J*=2.7 Hz), 2.41–2.59 (m, 3H), 3.94–4.05 (m, 2H), 4.33–4.44 (m, 1H), 6.90–6.99 (m, 3H, arom. H), 7.27–7.33 (m, 2H, arom. H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ=23.9 (CH_3), 27.3 (CH_3), 34.0 (CH_2), 37.1 (CH_2), 38.0 (C), 41.7 (CH), 43.3 (CH), 52.7 (CH), 67.8 (CH), 71.8 (CH_2), 114.4 (2×CH), 120.8 (CH), 129.4 (2×CH), 158.7 (C) ppm; elemental analysis calcd (%) for $C_{16}H_{22}O_2$ (246.34): C 78.01, H 9.00; found: C 77.95, H 8.91.

*4.2.6. (1S)-(-)-10-Pentafluorophenoxyisopinocampheol (**14**).* Yield: 1.8 g, (57%); colorless oil; $[\alpha]_D^{20}$=−0.2 (*c* 2.09, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ=0.88 (s, 3H, CH_3), 1.20 (d, 1H, *J*=9.6 Hz, CH*H*), 1.23 (s, 3H, CH_3), 1.76–1.88 (m, 1H), 1.97–2.06 (m, 2H), 2.18 (m, 1H), 2.21–2.63 (m, 3H), 4.19 (d, 2H, *J*=7.8 Hz, CH_2), 4.34–4.46 (m, 1H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ=23.7 (CH_3), 27.1 (CH_3), 33.4 (CH_2), 37.2 (CH_2), 37.8 (C), 41.4 (CH), 42.8 (CH), 53.2 (CH), 67.4 (CH), 79.6 (t, *J*=3.4 Hz, CH_2) ppm; elemental analysis calcd (%) for $C_{16}H_{17}F_5O_2$ (336.30): C 57.14, H 5.10; found: C 57.10, H 5.08.

*4.2.7. (1S)-(-)-10-(3,5-Di-tert-butyl-4-hydroxyphenyl)isopinocampheol (**24**).* Yield: 1.6 g (59%), colorless oil; $[\alpha]_D^{20}$=−15.3 (*c* 3.59, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ=1.04 (s, 3H, CH_3), 1.19 (d, 1H, *J*=9.9 Hz, CH*H*), 1.24 (s, 3H, CH_3), 1.44 (s, 18H, 6×CH_3), 1.67 (ddd, 1H, *J*=14.0 Hz, *J*=4.6 Hz, 2.0 Hz), 1.90–1.99 (m, 3H), 2.03–2.17 (m, 1H), 2.30–2.58 (m, 2H), 2.64–2.70 (m, 2H), 4.16–4.27 (m, 1H), 5.07 (s, 1H, OH), 7.00 (s, 2H, arom. H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ=24.0 (CH_3), 27.6 (CH_3), 30.3 (6×CH_3), 34.0 (2×C), 34.2 (CH_2), 37.9 (C), 38.0 (CH_2), 41.4 (CH), 41.6 (CH_2), 45.1 (CH), 55.3 (CH), 69.6 (CH), 125.3 (2×CH_{ar}), 131.4 (C_{ar}), 136.0 (2×C_{ar}), 151.9 (C_{ar}) ppm; elemental analysis calcd (%) for $C_{24}H_{38}O_2$ (358.56): C 80.39, H 10.68; found: C 80.37, H 10.64.

*4.2.8. General procedure for a preparation of aryl ethers **11**, **12**, **16**, **17**, **20**, and **23**.* To a stirred solution of sodium hydride (33.0 mmol) in DMF (20 mL) under Argon, a DMF (10 mL) solution of phenol (33.0 mmol) was slowly added at room temperature. The reaction mixture was stirred for 20 min, then a solution of terpene chloride (30.0 mmol) in DMF (10 mL) was added and the mixture was stirred at 100 °C for 20 h. After quenching with water, the mixture was extracted with Et_2O (3×40 mL), and the combined organic phases were washed with a 1.5 M solution of NaOH, water, brine, and dried over anhydrous $MgSO_4$. The solvent was removed under vacuum, and the crude product was purified by silica gel column chromatography.

*4.2.8.1. (1R)-Myrtenyl phenyl ether (**11**).* Yield: 3.6 g (53%), colorless oil; $[\alpha]_D^{20}$=−12.6 (*c* 2.92, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.84 (s, 3H, CH_3), 1.20 (d, 1H, *J*=8.4 Hz, CH*H*), 1.30 (s, 3H, CH_3), 2.09–2.15 (m, 1H), 2.20 (dt, 1H, *J*=5.4 Hz, *J*=1.2 Hz), 2.27–2.32 (m,

2H), 2.42 (dt, 1H, J=8.7 Hz, J=5.4 Hz), 4.34–4.44 (m, 2H, CH_2), 5.58–5.62 (m, 1H, CH=), 6.88–6.96 (m, 3H, arom. H), 7.25–7.38 (m, 2H, arom. H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=21.0 (CH_3), 26.2 (CH_3), 31.2 (CH_2), 31.5 (CH_2), 38.1 (C), 40.8 (CH), 43.2 (CH), 70.5 (CH_2), 114.8 (2×CH), 120.1 (CH), 120.5 (CH), 129.2 (2×CH), 144.0 (C=), 159.0 (CH) ppm; elemental analysis calcd (%) for $C_{16}H_{20}O$ (228.33): C 84.16, H 8.83; found: C 84.06, H 8.76.

*4.2.8.2. (1R)-(+)-Myrtenyl pentafluorophenyl ether (**12**).* Yield: 6.8 g (71%), colorless oil; $[\alpha]_D^{22}$=+8.9 (*c* 3.33, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ=0.78 (s, 3H, CH_3), 0.98 (d, 1H, J=9.6 Hz, CH*H*), 1.31 (s, 3H, CH_3), 2.04–2.13 (m, 1H), 2.24–2.45 (m, 4H), 4.51–4.63 (m, 2H), 5.60–5.68 (m, 1H, CH=); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ=20.9 (CH_3), 26.0 (CH_3), 31.4 (CH_2), 31.5 (CH_2), 38.0 (C), 40.5 (CH), 43.3 (CH), 77.7 (t, J=3.4 Hz, CH_2), 124.4 (CH=), 143.5 (C=) ppm; elemental analysis calcd (%) for $C_{16}H_{15}F_5O$ (318.28): C 60.38, H 4.75; found: C 60.26, H 4.71.

*4.2.8.3. (1S)-(+)-10-(4-Nitrophenoxy)isopinocampheol (**16**).* Yield: 2.4 g (28%), white solid; mp 95–98 °C; $[\alpha]_D^{24}$=+5.6 (*c* 1.43, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.94 (s, 3H, CH_3), 1.19 (d, 1H, J=9.9 Hz, CH*H*), 1.26 (s, 3H, CH_3), 1.82 (ddd, 1H, J=14.1 Hz, J=4.8 Hz, 2.4 Hz), 1.97 (bs, 1H, OH), 2.00–2.09 (m, 2H), 2.43–2.62 (m, 3H), 4.05 (dd, 1H, J=8.7 Hz, J=6.6 Hz, CH*H*), 4.14 (dd, 1H, J=8.7 Hz, J=8.7 Hz, CH*H*), 4.30–4.39 (m, 1H), 6.97 (d, 2H, J=9.6 Hz, arom. H), 8.20 (d, 2H, J=9.6 Hz, arom. H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ=24.0 (CH_3), 27.3 (CH_3), 33.8 (CH_2), 37.7 (CH_2), 38.0 (C), 41.6 (CH), 43.1 (CH), 52.4 (CH), 67.4 (CH), 72.5 (CH_2), 114.5 (2×CH), 126.0 (2×CH), 141.6 (C), 163.8 (C) ppm; elemental analysis calcd (%) for $C_{16}H_{21}NO_4$ (291.34): C 65.96, H 7.27; found: C 65.87, H 7.20.

*4.2.8.4. (1S)-(+)-10-(4-Methoxyphenoxy)isopinocampheol (**17**).* Yield: 1.7 g (21%), colorless oil; $[\alpha]_D^{24}$=+1.9 (*c* 2.27, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.93 (s, 3H, CH_3), 1.18 (d, 1H, J=9.9 Hz, CH*H*), 1.24 (s, 3H, CH_3), 1.80 (ddd, 1H, J=13.8 Hz, 5.1 Hz, 1.8 Hz), 1.96–2.04 (m, 2H), 2.26 (bs, 1H, OH), 2.36–2.58 (m, 3H), 3.77 (s, 3H, CH_3), 3.89–3.99 (m, 2H, CH_2), 4.36–4.42 (m, 1H, CH), 6.84 (s, 2H, arom. H), 6.85 (s, 2H, arom. H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=23.8 (CH_3), 27.3 (CH_3), 33.9 (CH_2), 37.1 (CH_2), 38.4 (C), 41.6 (CH), 43.1 (CH), 52.7 (CH), 55.5 (CH_3), 67.5 (CH), 72.5 (CH_2), 114.4 (2×CH), 115.3 (2×CH), 152.8 (C), 153.8 (C) ppm; elemental analysis calcd (%) for $C_{17}H_{24}O_3$ (276.37): C 73.88, H 8.75; found: C 73.77, H 8.64.

*4.2.8.5. (1S)-(-)-10-Phenylsulfanylisopinocampheol (**20**).* Yield: 2.0 g (45%), yellow oil; $[\alpha]_D^{22}$=−11.9 (*c* 6.15, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.92 (s, 3H, CH_3), 1.18 (d, J=9.9 Hz, 1H, CH*H*), 1.22 (s, 3H, CH_3), 1.74 (ddd, 1H, J=14.2 Hz, J=4.6 Hz, J=2.4 Hz), 1.90–2.02 (m, 2H), 2.08–2.19 (m, 1H), 2.23 (bs, 1H, OH), 2.32–2.61 (m, 2H), 3.03 (d, J=8.0 Hz, 2H, CH_2), 4.28 (qui, 1H, J=4.8 Hz, CH), 7.16–7.38 (m, 5H, arom. H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ=23.8 (CH_3), 27.4 (CH_3), 33.6 (CH_2), 37.8 (CH_2), 38.0 (C), 39.1 (CH_2), 41.5 (CH), 45.8 (CH), 52.2 (CH), 69.6 (CH), 126.1 (CH), 129.0 (2×CH), 129.1 (2×CH), 136.1 (C) ppm; elemental analysis calcd (%) for $C_{16}H_{22}OS$ (262.41): C 73.23, H 8.45; found: C 73.16, H 8.38.

*4.2.8.6. (1R)-(-)-10-(3,5-Di-tert-butyl-4-hydroxyphenyl)-2-pinene (**23**).* Yield: 7.5 g (73%), colorless oil; $[\alpha]_D^{22}$=−4.5 (*c* 2.34, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ=0.76 (s, 3H, CH_3), 1.11 (s, 3H, CH_3), 1.37 (d, 1H, J=9.9 Hz, C*H*$_2$), 1.43 (s, 18H, 6×CH_3), 1.97–2.42 (m, 5H), 3.18–3.27 (m, 2H), 5.03 (s, 1H, OH), 5.25 (m, 1H), 6.98 (s, 2H, arom. H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ=21.0 (CH_3), 26.2 (CH_3), 30.3 (6×CH_3), 31.4 (CH_2), 31.9 (CH_2), 34.2 (2×C), 37.8 (C), 40.6 (CH), 43.3 (CH_2), 45.4 (CH), 117.3 (CH=), 125.4 (2×CH), 129.9 (C), 135.4 (2×C), 147.6 (C=), 151.8 (C) ppm; elemental analysis calcd (%) for $C_{24}H_{36}O$ (340.54): C 84.65, H 10.66; found: C 84.71, H 10.74.

*4.2.9. General procedure for the preparation of alcohols **29** and **31**.* To a solution of olefin (15.0 g, 51.5 mmol) in dry THF (75 mL), borane–dimethyl sulfide complex (5.2 mL, 10 M, 51.5 mmol) was added dropwise at 0 °C and stirred for 20 h at room temperature. The reaction mixture was carefully quenched by addition of water and stirred at room temperature until hydrogen was no longer evolved. The volatiles were pumped off, then THF (75 mL) was added. The reaction mixture was immersed in an ice-water bath, then 3 M sodium hydroxide (8.6 mL, 25.8 mmol) and sodium perborate (7.9 g, 51.5 mmol) was added. The reaction mixture was stirred at 0 °C for 4 h, then at room temperature overnight. After quenching with sodium chloride, the organic phase was separated and dried over anhydrous $MgSO_4$ in a presence of MnO_2. The solvent was removed under vacuum, and the crude product was purified by column chromatography (silica gel, chloroform as an eluent) to give the terpene alcohols with the phenylselenide group as a yellow oils.

*4.2.9.1. (1S)-(-)-10-Phenylselanylisopinocampheol (**29**).* Yield: 10.0 g (63%), yellow oil, $[\alpha]_D^{17}$=−35.5 (*c* 5.18, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ=0.90 (s, 3H, CH_3), 1.06 (d, 1H, J=9.0 Hz, CH*H*), 1.20 (s, 3H, CH_3), 1.70–1.78 (m, 1H), 1.92–2.03 (m, 2H), 2.11–2.22 (m, 1H), 2.34–2.43 (m, 2H), 2.47–2.55 (m, 1H), 3.15 (d, 2H, J=8.1 Hz, CH_2), 4.20–4.28 (m, 1H), 7.24–7.31 (m, 3H, arom. H), 7.48–7.53 (m, 2H, arom. H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ=23.6 (CH_3), 27.1 (CH_3), 33.4 (CH_2), 33.6 (CH_2), 37.6 (CH_2), 37.8 (C), 41.3 (CH), 46.4 (CH), 52.8 (CH), 69.9 (CH), 126.7 (CH), 129.0 (2×CH), 129.9 (C), 132.2 (2×CH); ^{77}Se NMR (38.1 MHz, $CDCl_3$): δ=277.1 (Se) ppm; elemental analysis calcd (%) for $C_{16}H_{22}OSe$ (309.31): C 62.13, H 7.17; found: C 62.11, H 7.22.

*4.2.9.2. (1S)-(-)-10-Phenylselanyl-4-isocaranol (**31**).* Yield: 5.3 g (33%), yellow oil; $[\alpha]_D^{21}$=−63.4 (*c* 1.58, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.62 (m, 2H), 0.85–0.88 (m, 1H), 0.92 (s, 3H, CH_3), 0.97 (s, 3H, CH_3), 1.45–1.67 (m, 3H), 2.06 (dd, 1H, J=14.4 Hz, J=6.9 Hz), 2.13–2.27 (m, 1H), 2.85 (dd, 1H, J=12.0 Hz, J=7.5 Hz, CH*H*), 3.25 (dd, 1H, J=12.0 Hz, 3.9 Hz, CH*H*), 3.32–3.42 (m, 1H, CH), 7.19–7.38 (m, 3H, arom. H), 7.45–7.55 (m, 2H, arom. H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ=15.8 (CH_3), 17.8 (C), 20.0 (CH), 21.4 (CH), 26.1 (CH_2), 28.7 (CH_3), 30.7 (CH_2), 32.0 (CH_2), 42.3 (CH), 72.7 (CH), 126.6 (CH), 129.1 (2×CH), 131.1 (C), 132.2 (2×CH) ppm; elemental analysis calcd (%) for $C_{16}H_{22}OSe$ (309.31): C 62.13, H 7.17; found: C 62.32, H 7.45.

4.3. Synthesis of tosylates

*4.3.1. (1S)-(+)-10-Methoxyisopinocampheyl tosylate (**32**).* Yield: 3.60 g (67%), colorless oil; $[\alpha]_D^{24}$=+36.1 (*c* 7.4, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ=0.83 (s, 3H, CH_3), 1.14 (d, 1H, J=9.6 Hz, CH*H*), 1.19 (s, 3H, CH_3), 1.85–1.99 (m, 2H), 2.03–2.14 (m, 2H), 2.32–2.42 (m, 2H), 2.44 (s, 3H, CH_3), 3.14 (s, 3H, OCH_3), 3.16–3.22 (m, 2H), 4.80 (ddd, 1H, J=9.6 Hz, J=5.4 Hz, J=4.2 Hz, CH), 7.26–7.36 (m, 2H, arom. H), 7.78–7.84 (m, 2H, arom. H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ=21.5 (CH_3), 24.0 (CH_3), 27.0 (CH_3), 32.9 (CH_2), 36.1 (CH_2), 38.0 (C), 41.3 (CH), 42.6 (CH), 49.1 (CH), 58.4 (OCH_3), 74.1 (CH_2), 77.9 (CH), 127.8 (2×CH), 129.6 (2×CH), 134.6 (C), 144.4 (C) ppm; elemental analysis calcd (%) for $C_{18}H_{26}O_4S$ (338.46): C 63.88, H 7.74; found: C 63.97, H 7.93.

*4.3.2. (1S)-(+)-10-Phenoxyisopinocampheyl tosylate (**33**).* Yield: 2.08 g, (69%), white solid; mp 92–94 °C; $[\alpha]_D^{19}$=+41.2 (*c* 2.32, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ=0.90 (s, 3H, CH_3), 1.14 (d, 1H, J=9.9 Hz, CH*H*), 1.21 (s, 3H, CH_3), 1.91–2.15 (m, 2H), 2.18–2.26 (m, 1H), 2.36 (s, 3H, CH_3), 2.37–2.62 (m, 3H), 3.69 (d, 2H, J=7.0 Hz, CH_2), 4.91–5.01 (m, 1H), 6.72 (d, 2H, J=8.2 Hz, arom. H). 6.89–6.97 (m, 1H, arom. H), 7.22–7.29 (m, 4H, arom. H), 7.82 (d, 2H, J=8.2 Hz, arom. H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=21.6 (CH_3), 24.2 (CH_3), 27.0

(CH_3), 33.6 (CH_2), 36.1 (CH_2), 38.1 (C), 41.3 (CH), 42.9 (CH), 48.9 (CH), 68.5 (CH_2), 77.2 (CH), 114.4 (2×CH), 120.7 (CH), 127.8 (2×CH), 129.3 (2×CH), 129.8 (2×CH), 134.2 (C), 144.6 (C), 158.5 (C) ppm; elemental analysis calcd (%) for $C_{23}H_{28}O_4S$ (400.53): C 68.97, H 7.05; found: C 68.85, H 7.01.

*4.3.3. (1S)-(+)-10-(4-Nitrophenoxy)isopinocampheyl tosylate (**34**).* Yield: 1.80 g (91%), white solid; mp 98–99 °C; $[\alpha]_D^{23}$=+23.8 (*c* 1.63, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ=0.92 (s, 3H, CH_3), 1.18 (d, 1H, *J*=9.9 Hz, CH*H*), 1.23 (s, 3H, CH_3), 1.90–2.08 (m, 2H), 2.15–2.24 (m, 1H), 2.40 (s, 3H, CH_3), 2.41–2.58 (m, 2H), 2.60–2.71 (m, 1H), 3.81–4.00 (m, 2H, CH_2), 4.96–5.05 (m, 1H), 6.83 (d, 2H, *J*=7.8 Hz, arom. H), 7.28 (d, 2H, *J*=7.8 Hz, arom. H), 7.82 (d, 2H, *J*=7.8 Hz, arom. H), 8.18 (d, 2H, *J*=7.8 Hz, arom. H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=21.6 (CH_3), 24.2 (CH_3), 27.0 (CH_3), 33.3 (CH_2), 35.8 (CH_2), 38.1 (C), 41.3 (CH), 42.9 (CH), 48.9 (CH), 69.6 (CH_2), 76.7 (CH), 114.4 (2×CH), 125.8 (2×CH), 127.7 (2×CH), 129.8 (2×CH), 134.4 (C), 141.6 (C), 144.8 (C), 163.6 (C) ppm; elemental analysis calcd (%) for $C_{23}H_{27}NO_6S$ (445.53): C 62.00, H 6.11; found: C 61.98, H 6.06.

*4.3.4. (1S)-(+)-10-(4-Methoxyphenoxy)isopinocampheyl tosylate (**35**).* Yield: 1.32 g (83%), white solid; mp 73–76 °C; $[\alpha]_D^{21}$=+39.6 (*c* 4.03, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ=0.89 (s, 3H, CH_3), 1.17 (d, 1H, *J*=9.9 Hz, CH*H*), 1.21 (s, 3H, CH_3), 1.84–2.12 (m, 3H), 2.18–2.24 (m, 1H), 2.38 (s, 3H, CH_3), 2.40–2.62 (m, 2H), 3.65 (d, 2H, *J*=7.2 Hz, CH_2), 3.77 (s, 3H, OCH_3), 4.91–5.01 (m, 1H), 6.60–6.68 (m, 2H, arom. H), 6.77–6.89 (m, 2H, arom. H), 7.26–7.36 (m, 2H, arom. H), 7.76–7.84 (m, 2H, arom. H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=21.5 (CH_3), 24.1 (CH_3), 27.0 (CH_3), 33.2 (CH_2), 36.0 (CH_2), 38.0 (C), 41.3 (CH), 42.9 (CH), 49.0 (CH), 55.6 (OCH_3), 69.3 (CH_2), 77.2 (CH), 114.4 (2×CH), 115.2 (2×CH), 127.7 (2×CH), 129.7 (2×CH), 134.2 (C), 144.5 (C), 152.6 (C), 153.7 (C) ppm; elemental analysis calcd (%) for $C_{24}H_{30}O_5S$ (430.56): C 66.95, H 7.02; found: C 66.92; H 6.93.

*4.3.5. (1S)-(+)-10-Phenylsulphanylisopinocampheyl tosylate (**37**).* Yield: 2.50 g (79%), yellow solid; mp 95–96 °C; $[\alpha]_D^{20}$=+19.2 (*c* 1.88, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ=0.87 (s, 3H, CH_3), 1.03 (d, 1H, *J*=9.9 Hz, CH*H*), 1.18 (s, 3H, CH_3), 1.82–2.05 (m, 2H), 2.22–2.41 (m, 4H), 2.43 (s, 3H, CH_3), 2.76 (dd, 1H, *J*=10.5, *J*=9.9 Hz, CH*H*), 2.98 (dd, 1H, *J*=10.5 Hz, *J*=3.8 Hz, CH*H*), 4.82–4.94 (m, 1H), 7.16–7.26 (m, 5H, arom. H), 7.34 (d, 2H, *J*=7.8 Hz, arom. H), 7.80 (d, 2H, *J*=7.8 Hz, arom. H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ=21.6 (CH_3), 23.8 (CH_3), 27.0 (CH_3), 33.0 (CH_2), 36.2 (CH_2), 36.6 (CH_2), 38.1 (C), 41.2 (CH), 43.1 (CH), 48.8 (CH), 80.5 (CH), 125.9 (CH), 127.8 (2×CH), 128.8 (4×CH), 129.8 (2×CH), 134.3 (C), 136.1 (C), 144.7 (C) ppm; elemental analysis calcd (%) for $C_{23}H_{28}O_3S_2$ (416.60): C 66.31, H 6.77; found: C 66.39, H 6.70.

*4.3.6. (1S)-(+)-10-(Phenylselanyl)isopinocampheyl tosylate (**38**).* Yield: 4.61 g (88%), white solid; mp 67–69 °C $[\alpha]_D^{22}$=+5.7 (*c* 7.60, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.84 (s, 3H, CH_3), 1.01 (d, 1H, *J*=9.9 Hz, CH*H*), 1.14 (s, 3H, CH_3), 1.86–2.00 (m, 2H), 2.24–2.42 (m, 4H), 2.43 (s, 3H, CH_3), 2.77 (dd, 1H, *J*=12.3 Hz, *J*=12.3 Hz, CH*H*), 2.93 (dd, 1H, *J*=12.3 Hz, *J*=4.2 Hz, CH*H*), 4.75 (ddd, 1H, *J*=9.6 Hz, *J*=5.4 Hz, *J*=4.2 Hz, CH), 7.21–7.26 (m, 3H, arom. H), 7.31 (d, 2H, *J*=8.4 Hz, arom. H), 7.36–7.41 (m, 2H, arom. H), 7.79 (d, 2H, *J*=8.4 Hz, 2×CH); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ=21.6 (CH_3), 23.7 (CH_3), 26.9 (CH_3), 31.0 (CH_2), 33.0 (CH_2), 36.1 (CH_2), 38.0 (C), 41.2 (CH), 43.7 (CH), 49.8 (CH), 81.1 (CH), 126.7 (CH), 127.7 (2×CH), 129.0 (2×CH), 129.7 (2×CH), 130.2 (C), 132.2 (2×CH), 134.2 (C), 144.6 (C); ^{77}Se NMR (38.1 MHz, $CDCl_3$): δ=280.8 (Se) ppm; elemental analysis calcd (%) for $C_{23}H_{28}O_3SSe$ (463.49): C 59.60, H 6.09; found: C 59.64, H 6.16.

*4.3.7. (1S)-10-(Tetrahydro-2H-pyran-2-yloxy)isopinocampheyl tosylate (**58**).* Yield: 4.9 g (68), colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): mixture of diastereomers δ=0.85 (s, 3H, CH_3), 1.11–1.16 (m, 1H), 1.20 (s, 3H, CH_3), 1.42–1.65 (m, 5H), 1.68–2.19 (m, 5H), 2.34 (m, 2H), 2.44 (s, 3H, CH_3), 3.16–3.22 (m, 1H), 3.42–3.65 (m, 2H), 3.72–3.84 (m, 1H), 4.40–4.46 (m, 1H), 4.80–4.95 (m, 1H), 7.35 (m, 2H, arom. H), 7.81 (m, 2H, arom. H); ^{13}C NMR (50.3 MHz, $CDCl_3$): mixture of diastereomers δ=19.2 (CH_2), 19.3 (CH_2), 21.6 (2×CH_3), 24.0 (CH_3), 24.2 (CH_3), 25.3 (CH_2), 25.4 (CH_2), 27.0 (CH_3), 27.1 (CH_3), 30.3 (CH_2), 30.4 (CH_2), 32.9 (CH_2), 33.4 (CH_2), 36.0 (CH_2), 36.1 (CH_2), 38.0 (C), 38.1 (C), 41.3 (CH), 41.4 (CH), 42.8 (CH), 43.4 (CH), 49.4 (CH), 49.5 (CH), 61.8 (2×CH_2), 68.6 (CH_2), 68.8 (CH_2), 77.7 (CH), 77.9 (CH), 98.5 (CH), 98.9 (CH), 127.7 (2×CH), 129.9 (2×CH), 134.7 (C), 144.4 (C) ppm; elemental analysis calcd (%) for $C_{23}H_{34}O_5S$ (422.58): C 65.37, H 8.11; found: C 65.53, H 8.23.

*4.3.8. (1S)-(+)-10-Pentafluorophenoxyisopinocampheyl tosylate (**60**).* Yield: 1.80 g (69%), white solid; mp 90–92 °C; $[\alpha]_D^{19}$=+33.4 (*c* 1.64, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ=0.83 (s, 3H, CH_3), 1.17 (d, 1H, *J*=9.9 Hz, CH*H*), 1.21 (s, 3H, CH_3), 1.82–2.17 (m, 2H), 2.21–2.32 (m, 1H), 2.43 (s, 3H, CH_3), 2.45–2.70 (m, 3H), 3.88 (d, 2H, *J*=7.4 Hz, CH_2), 4.77–4.87 (m, 1H, CHSe), 7.28 (d, 2H, *J*=7.8 Hz, arom. H), 7.78 (d, 2H, *J*=7.8 Hz, arom. H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ=21.4 (CH_3), 23.9 (CH_3), 26.9 (CH_3), 32.7 (CH_2), 36.1 (CH_2), 38.0 (C), 41.2 (CH), 42.3 (CH), 49.6 (CH), 76.1 (CH), 76.2 (CH_2), 127.8 (2×CH), 129.6 (2×CH), 134.2 (C), 144.6 (C) ppm; elemental analysis calcd (%) for $C_{23}H_{23}F_5O_4S$ (490.48): C 56.32, H 4.73; found: C 56.23, H 4.70.

*4.3.9. (1S)-(-)-10-Phenylselanyl-4-isocaranyl tosylate (**92**).* Yield: 2.42 g (40%), yellow oil; $[\alpha]_D^{20}$=−36.6 (*c* 4.40, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ=0.63–0.83 (m, 2H), 0.86 (s, 3H, CH_3), 0.96 (s, 3H, CH_3), 1.64–1.89 (m, 3H), 2.20–2.36 (m, 2H), 2.40 (dd, 1H, *J*=12.2 Hz, *J*=9.8 Hz, CH*H*), 2.43 (s, 3H, CH_3), 3.10 (dd, 1H, *J*=12.2 Hz, *J*=3.4 Hz, CH*H*), 4.28 (dt, 1H, *J*=9.8 Hz, *J*=7.2 Hz, CH), 7.19–7.42 (m, 7H, arom. H), 7.77 (d, 2H, *J*=8.4 Hz, arom. H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ=15.6 (CH_3), 17.9 (C), 19.7 (CH), 20.6 (CH), 21.6 (CH_3), 25.4 (CH_2), 27.7 (CH_2), 28.2 (CH_3), 30.6 (CH_2), 39.9 (CH), 85.1 (CH), 126.5 (CH), 127.6 (2×CH), 129.0 (2×CH), 129.7 (2×CH), 130.6 (C), 131.9 (2×CH), 134.4 (C), 144.5 (C) ppm; elemental analysis calcd (%) for $C_{23}H_{28}O_3SSe$ (463.49): C 59.60, H 6.09; found: C 59.52, H 6.01.

4.4. Synthesis of chlorides

*4.4.1. (1S)-(-)-10-Hydroxypinocampheyl chloride (**39**).* A mixture of (1*S*)-10-(tetrahydro-2*H*-pyran-2-yloxy)pinocampheyl chloride (2.0 g, 7.3 mmol) and *p*-toluenesulfonic (100 mg) acid in methanol (50 mL) was stirred at 50 °C for 4 h. The resulting mixture was allowed to stir at room temperature, then a saturated solution of sodium hydrogen carbonate (10 mL) was added and stirring was continued for another 30 min. The organic phase was separated, and the aqueous layer was extracted with ethyl acetate (2×50 mL). The combined organic phases were washed with water and brine, dried over $MgSO_4$, filtered and the solvent was removed under vacuum. The crude product was purified by column chromatography (silica gel, petroleum ether/chloroform/ethyl acetate=15/7/1 as an eluent) to afford deprotected alcohol **39** (1.20 g, 86%) as a colorless oil. $[\alpha]_D^{21}$=−18.0 (*c* 3.9, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ=0.88 (s, 3H; CH_3), 1.12 (d, *J*=9.8 Hz, 1H, CH*H*), 1.22 (s, 3H, CH_3), 1.75–1.84 (m, 1H), 1.93–2.02 (m, 2H), 2.08 (bs, 1H, OH), 2.20–2.35 (m, 1H), 2.38–2.62 (m, 2H), 3.54 (dd, *J*=10.4, *J*=6.2 Hz, 1H, CH*H*), 3.54 (dd, *J*=10.4, *J*=10.4 Hz, 1H, CH*H*), 4.28 (qui, *J*=5.4, 1H, CHSe); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ=23.6 (CH_3), 27.0 (CH_3), 33.0 (CH_2), 37.3 (CH_2), 37.6 (C), 41.3 (CH), 44.4 (CH), 48.5 (CH_2), 55.5 (CH), 67.9 (CH) ppm; elemental analysis calcd (%) for $C_{10}H_{17}ClO$ (188.69): C 63.35, H 9.08; found: C 66.31, H 9.04.

*4.4.2. (1S)-(-)-10-Methoxypinocampheyl chloride (**40**).* Yield: 4.60 g (69%), colorless oil; bp 54–56 °C/0.3 Torr; $[\alpha]_D^{24}$=−24.2 (*c* 5.9,

$CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$): δ=0.98 (s, 3H, CH_3), 1.20 (s, 3H, CH_3), 1.24 (d, 1H, J=9.8 Hz, CH*H*), 1.85–1.96 (m, 1H), 2.14–2.28 (m, 3H), 2.56–2.79 (m, 2H), 3.33 (s, 3H, OCH_3), 3.44 (dd, 1H, J=10.2 Hz, J=5.8, Hz, CH*H*), 3.86 (dd, 1H, J=10.2 Hz, J=8.6 Hz, CH*H*), 4.73 (dt, 1H, J=8.6 Hz, J=6.0 Hz, CH); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ=22.8 (CH_3), 26.8 (CH_3), 27.7 (CH_2), 38.6 (CH_2), 39.0 (C), 41.2 (CH), 45.3 (CH), 45.4 (CH), 53.5 (CH), 58.2 (OCH_3), 74.3 (CH_2) ppm; elemental analysis calcd (%) for $C_{11}H_{19}ClO$ (202.74): C 65.17, H 9.45; found: C 65.34, H 9.61.

*4.4.3. (1S)-(-)-10-Phenoxypinocampheyl chloride (**41**).* Yield: 1.71 g (43%), colorless liquid; $[\alpha]_D^{20}$=−23.3 (*c* 2.06, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ=1.06 (s, 3H, CH_3), 1.23 (s, 3H, CH_3), 1.25 (d, 1H, J=9.9 Hz, CH*H*), 1.93–1.99 (m, 1H), 2.24–2.39 (m, 3H), 2.69 (ddd, 1H, J=14.4 Hz, J=9.9 Hz, J=4.8 Hz), 3.02 (dddd, 1H, J=10.2 Hz, J=10.2 Hz, J=6.9 Hz, J=3.3 Hz), 4.05 (dd, 1H, J=9.9 Hz, J=6.9 Hz, CH*H*), 4.50 (dd, 1H, J=9.9 Hz, J=6.3 Hz, CH*H*), 4.82 (ddd, 1H, J=10.2 Hz, J=10.2 Hz, J=7.2 Hz, CH), 6.68–6.98 (m, 2H, arom. H), 7.23–7.37 (m, 3H, arom. H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=22.8 (CH_3), 26.9 (CH_3), 27.7 (CH_2), 38.6 (CH_2), 39.1 (C), 41.1 (CH), 44.5 (CH), 44.8 (CH), 53.1 (CH), 69.2 (CH_2), 114.7 (2×CH), 120.6 (CH), 129.4 (2×CH), 158.8 (C) ppm; elemental analysis calcd (%) for $C_{16}H_{21}ClO$ (264.79): C 72.57, H 7.99; found: C 72.54, H 7.98.

*4.4.4. (1S)-(-)-10-Pentafluorophenoxypinocampheyl chloride (**42**).* Yield: 3.70 g (72%), colorless oil; $[\alpha]_D^{22}$=−35.6 (*c* 4.10, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ=1.01 (s, 3H, CH_3), 1.24 (s, 3H, CH_3), 1.28 (d, 1H, J=9.9 Hz, CH*H*), 1.90–1.99 (m, 1H), 2.25 (ddt, 1H, J=14.4 Hz, J=7.5 Hz, J=1.5 Hz), 2.31–2.41 (m, 2H), 2.68 (ddd, 1H, J=14.4 Hz, J=9.9 Hz, J=4.8 Hz), 3.02 (dddd, 1H, J=9.9 Hz, J=9.9 Hz, J=6.6 Hz, J=3.0 Hz), 4.28 (dd, 1H, J=9.6 Hz, J=7.2 Hz, CH*H*), 4.64 (dd, 1H, J=9.6 Hz, J=6.6 Hz, CH*H*), 4.77 (ddd, 1H, J=9.9 Hz, J=9.9 Hz, J=7.2 Hz, CHSe); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=22.7 (CH_3), 26.7 (CH_3), 27.6 (CH_2), 38.6 (CH_2), 39.0 (C), 41.0 (CH), 44.6 (CH), 45.4 (CH), 52.3 (CH), 77.0 (t, J=2.9 Hz, CH_2) ppm; elemental analysis calcd (%) for $C_{16}H_{16}ClF_5O$ (354.74): C 54.17, H 4.55; found: C 54.16, H 4.52.

*4.4.5. (1S)-(-)-10-Phenylsulfanylpinocampheyl chloride (**43**).* Yield: 1.30 g (41%), colorless liquid; $[\alpha]_D^{20}$=−32.2 (*c* 4.90, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ=1.08 (s, 3H, CH_3), 1.18 (d, 1H, J=10.2 Hz, CH*H*), 1.21 (s, 3H, CH_3), 1.90–1.96 (m, 1H), 2.20–2.42 (m, 3H), 2.66 (ddd, 1H J=14.7 Hz, J=9.9 Hz, J=5.1 Hz), 2.70–2.79 (m, 1H), 3.12 (dd, 1H, J=13.5 Hz, J=9.3 Hz, CH*H*), 3.58 (dd, 1H, J=13.5 Hz, J=6.0 Hz, CH*H*), 4.77 (ddd, 1H, J=9.9 Hz, J=9.9 Hz, J=7.8 Hz, CH), 7.22–7.36 (m, 5H, arom. H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=22.8 (CH_3), 26.8 (CH_3), 27.9 (CH_2), 35.9 (CH_2), 38.7 (CH_2), 39.2 (C), 41.2 (CH), 44.4 (CH), 45.0 (CH), 54.7 (CH), 125.7 (CH), 128.8 (2×CH), 128.9 (2×CH), 136.9 (C) ppm; elemental analysis calcd (%) for $C_{16}H_{21}ClS$ (280.86): C 68.42; H 7.54%. found: C 68.65, H 7.83.

*4.4.6. (1S)-(-)-10-Phenylselanylpinocampheyl chloride (**44**).* Yield: 3.10 g (73%), yellow oil; $[\alpha]_D^{21}$=−47.5 (*c* 10.54, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ=1.05 (s, 3H, CH_3), 1.17 (s, 3H, CH_3), 1.19 (d, 1H, J=9.6 Hz, CH*H*), 1.89–1.95 (m, 1H), 2.17–2.40 (m, 3H), 2.65 (ddd, 1H, J=14.4 Hz, J=9.6 Hz, J=4.5 Hz), 2.83 (dddd, 1H, J=9.6 Hz, J=9.6 Hz, J=6.3 Hz, J=3.3 Hz), 3.11 (dd, 1H, J=12.3 Hz, J=9.6 Hz, CH*H*), 3.57 (dd, 1H, J=12.3 Hz, J=6.3 Hz, CH*H*), 4.75 (dt, 1H, J=9.9 Hz, J=7.5 Hz, CH), 7.20–7.31 (m, 3H, arom. H), 7.46–7.54 (m, 2H, arom. H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ=22.7 (CH_3), 26.8 (CH_3), 28.0 (CH_2), 31.0 (CH_2), 38.6 (CH_2), 39.0 (C), 41.2 (CH), 45.6 (CH), 45.8 (CH), 55.1 (CH), 126.5 (CH), 128.9 (2×CH), 131.0 (C), 132.3 (2×CH); ^{77}Se NMR (38.1 MHz, $CDCl_3$): δ=299.8 (Se) ppm; elemental analysis calcd (%) for $C_{16}H_{21}ClSe$ (327.75): C 58.63, H 6.46; found: C 58.77, H 6.59.

*4.4.7. (1S)-10-(Tetrahydro-2H-pyran-2-yloxy)pinocampheyl chloride (**59**).* Yield: 3.0 g (62%), colorless oil; bp 80–82 °C/0.4 mmHg; ^1H NMR (300 MHz, $CDCl_3$): mixture of diastereomers δ=0.88 (s, 3H, CH_3), 1.10 (d, J=9.6 Hz, 1H, CH*H*), 1.24 (s, 3H, CH_3), 1.50–1.60 (m, 2H), 1.68–2.03 (m, 5H), 2.16–2.54 (m, 4H), 3.47–3.54 (m, 2H), 3.64 (dd, J=10.5, J=6.6 Hz, 1H, CH*H*), 3.80 (dd, J=10.5, J=4.5 Hz, 1H CH*H*), 3.86 (m, 2H), 4.68–4.78 (m, 1H); ^{13}C NMR (50.3 MHz, $CDCl_3$): mixture of diastereomers δ=19.4 (CH_2), 20.0 (CH_2), 23.4 (CH_3), 23.6 (CH_3), 25.5 (CH_2), 25.6 (CH_2), 27.1 (CH_3), 27.2 (CH_3), 31.2 (CH_2), 32.2 (CH_2), 32.5 (CH_2), 35.1 (CH_2), 36.9 (CH_2), 38.0 (C), 38.3 (C), 41.3 (CH), 41.5 (CH), 41.9 (CH), 43.1 (CH), 47.4 (CH_2), 48.0 (CH_2), 52.7 (CH), 53.2 (CH), 62.5 (CH_2), 63.1 (CH_2), 70.5 (CH), 73.3 (CH), 96.0 (CH), 99.3 (CH) ppm; elemental analysis calcd (%) for $C_{15}H_{25}ClO_2$ (272.81): C 66.04, H 9.24; found: C 66.31, H 9.54.

*4.4.8. (1S)-(+)-10-Phenylselanyl-4-caranyl chloride (**96**).* Yield: 2.80 g (76%), yellow oil; $[\alpha]_D^{20}$=+83.6 (*c* 4.26, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ=0.38 (dt, 1H, J=9.3 Hz), 0.83–0.97 (m, 2H), 0.99 (s, 3H, CH_3), 1.09 (s, 3H, CH_3), 1.64–1.74 (m, 1H), 1.78–1.87 (m, 1H), 1.98 (dt, 1H, J=17.1 Hz, J=2.4 Hz), 2.59 (dt, 1H, J=17.1 Hz, J=9.0 Hz), 2.87 (dd, 1H, J=12.6 Hz, J=6.6 Hz, CH*H*), 2.87 (dd, 1H, J=12.6 Hz, J=8.1 Hz, CH*H*), 4.56–4.63 (m, 1H, CH), 7.21–7.31 (m, 3H, arom. H), 7.45–7.53 (m, 2H, arom. H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=15.9 (CH_3), 17.4 (CH), 18.0 (C), 20.7 (CH_2), 23.4 (CH), 28.6 (CH_3), 29.2 (CH_2), 32.0 (CH_2), 40.0 (CH), 61.3 (CH), 126.8 (CH), 129.0 (2×CH), 130.3 (C), 132.5 (2×CH); ^{77}Se NMR (38.1 MHz, $CDCl_3$): δ=266.7 (Se); elemental analysis calcd (%) for $C_{16}H_{21}ClSe$ (327.75): C 58.63, H 6.46; found: C 58.76, H 6.57.

4.5. Synthesis of diselenides

*4.5.1. (1S,1′S)-(+)-Bis(10-methoxypinocampheyl) diselenide (**45**).* Yield: 2.10 g (81%), yellow oil; $[\alpha]_D^{30}$=+44.2 (*c* 3.6, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$): δ=0.92 (s, 6H, CH_3), 1.19 (s, 6H, CH_3), 1.37 (d, 2H, J=9.3 Hz, CH*H*), 1.90–1.95 (m, 2H), 2.06 (dd, 2H, J=14.1 Hz, J=9.3 Hz), 2.14–2.24 (m, 4H), 2.52 (ddd, 2H, J=14.1 Hz, J=9.3 Hz, J=4.8 Hz), 2.64–2.70 (m, 2H), 3.32 (s, 6H, OCH_3), 3.43 (dd, 2H, J=9.3 Hz, J=6.0 Hz, CH*H*), 3.79 (dd, 2H, J=9.3 Hz, J=7.2 Hz, CH*H*), 4.11 (q, 2H, J=9.6 Hz, CH); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ=23.0 (2×CH_3), 27.1 (2×CH_3), 27.2 (2×CH_2), 36.4 (2×CH_2), 37.5 (2×CH), 39.2 (2×C), 41.8 (2×CH), 44.4 (2×CH), 45.6 (2×CH), 58.2 (2×OCH_3), 76.2 (2×CH_2); ^{77}Se NMR (38.1 MHz, $CDCl_3$): δ=366.5 ppm; elemental analysis calcd (%) for $C_{22}H_{38}Se_2$ (492.46): C 53.66, H 7.78; found: C 53.81, H 7.94.

*4.5.2. (1S,1′S)-(+)-Bis(10-phenoxypinocampheyl) diselenide (**46**).* Yield: 170 mg (30%), yellow oil; $[\alpha]_D^{18}$=+131.8 (*c* 6.23, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ=1.00 (s, 6H, CH_3), 1.23 (s, 6H, CH_3), 1.42 (d, 2H, J=10.2 Hz, CH*H*), 1.97 (q, 2H, J=4.8 Hz,), 2.06 (dd, 2H, J=13.8 Hz, J=9.3 Hz,), 2.23–2.38 (m, 4H), 2.56 (ddd, 2H, J=13.8 Hz, J=9.6 Hz, J=4.8 Hz), 2.95 (dddd, 2H, J=10.5 Hz, J=10.5 Hz, J=6.9 Hz, J=3.6 Hz), 4.04 (dd, 2H, J=9.6 Hz, J=6.9 Hz, CH*H*), 4.20 (q, 2H, J=9.9 Hz, CHSe), 4.46 (dd, 2H, J=9.6 Hz, J=6.9 Hz, CH*H*), 6.90–6.97 (m, 6H, arom. H), 7.23–7.32 (m, 4H, arom. H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ=23.0 (2×CH_3), 27.2 (2×CH_3), 27.3 (2×CH_2), 36.2 (2×CH_2), 37.4 (2×CH), 39.2 (2×C), 41.7 (2×CH), 43.4 (2×CH), 45.1 (2×CH), 71.0 (2×CH_2), 114.7 (4×CH), 120.5 (2×CH), 129.3 (4×CH), 158.6 (2×C); ^{77}Se NMR (38.1 MHz, $CDCl_3$): δ=364.7 (Se_2) ppm; elemental analysis calcd (%) for $C_{32}H_{42}O_2Se_2$ (616.59): C 62.33, H 6.8; found: C 62.21; H 6.84.

*4.5.3. (1S,1′S)-(+)-Bis[10-(4-nitrophenoxy)pinocampheyl] diselenide (**47**).* Yield: 320 mg (27%), yellow solid; mp 43–45 °C; $[\alpha]_D^{21}$=+170.1 (*c* 1.82, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$): δ=0.97 (s, 6H, CH_3), 1.23 (s, 6H, CH_3), 1.42 (d, 2H, J=9.9 Hz, CH*H*), 1.94–2.10 (m, 4H), 2.22–2.38 (m, 4H), 2.52 (ddd, 2H, J=14.1 Hz, J=6.9 Hz, J=4.2 Hz), 2.86–2.97 (m, 2H), 4.11 (dd, 2H, J=9.6 Hz, J=6.6 Hz, CH*H*), 4.18 (q, 2H, J=9.6 Hz, CHSe), 4.55 (dd, 2H,

J=9.6 Hz, *J*=6.9 Hz, CH*H*), 6.92 (d, 4H, *J*=9.2 Hz, arom. H), 8.16 (d, 4H, *J*=9.2 Hz, arom. H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=23.0 (2×CH_3), 27.0 (2×CH_3), 27.1 (2×CH_2), 35.7 (2×CH_2), 37.5 (2×CH), 39.0 (2×C), 41.4 (2×CH), 43.0 (2×CH), 45.0 (2×CH), 72.2 (2×CH_2), 114.5 (4×CH), 125.8 (4×CH), 141.3 (2×C), 144.8 (2×C), 163.6 (2×C); ^{77}Se NMR (38.1 MHz, $CDCl_3$): δ=361.4 (Se_2) ppm; elemental analysis calcd (%) for $C_{32}H_{40}N_2O_6Se_2$ (706.59): C 54.39, H 5.71; found: C 54.29, H 5.70.

*4.5.4. (1S,1′S)-(+)-Bis[10-(4-methoxyphenoxy)pinocampheyl] diselenide (**48**).* Yield: 250 mg (25%), yellow oil; $[\alpha]_D^{23}$=+135.3 (*c* 5.24, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.97 (s, 6H, CH_3), 1.21 (s, 6H, CH_3), 1.39 (d, 2H, *J*=9.9 Hz, CH*H*), 1.93–1.98 (m, 2H), 2.07 (dd, 2H, *J*=14.1 Hz, *J*=9.6 Hz), 2.12–2.34 (m, 4H), 2.54 (ddd, 2H, *J*=14.1 Hz, *J*=9.9 Hz, *J*=4.8 Hz), 2.90 (dddd, 2H, *J*=10.2 Hz, *J*=10.2 Hz, *J*=6.6 Hz, *J*=3.6 Hz), 3.76 (s, 6H, OCH_3), 3.97 (dd, 2H, *J*=9.6 Hz, *J*=6.6 Hz, CH*H*), 4.17 (q, 2H, *J*=9.6 Hz, CHSe), 4.38 (dd, 2H, *J*=9.6 Hz, *J*=6.9 Hz, CH*H*), 6.78–6.86 (m, 8H, arom. H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=23.0 (2×CH_3), 27.2 (2×CH_3), 27.3 (2×CH_2), 36.2 (2×CH_2), 37.4 (2×CH), 39.2 (2×C), 41.8 (2×CH), 43.6 (2×CH), 45.2 (2×CH), 55.7 (2×OCH_3), 71.9 (2×CH_2), 114.6 (4×CH), 115.7 (4×CH), 152.9 (2×C), 153.8 (2×C); ^{77}Se NMR (38.1 MHz, $CDCl_3$): δ=364.9 (Se_2) ppm; elemental analysis calcd (%) for $C_{34}H_{46}O_4Se_2$ (676.65): C 60.35, H 6.85; found: C 60.30, H 6.81.

*4.5.5. (1S,1′S)-(-)-Bis[10-(3,5-di-tert-butyl-4 hydroxyphenyl)pinocampheyl] diselenide (**49**).* Yield: 59.0 mg, (8%), yellow solid; mp 173–175 °C; $[\alpha]_D^{22}$=−11.9 (*c* 1.08, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.20 (s, 6H, CH_3), 1.24 (s, 6H, CH_3), 1.29 (d, 2H, *J*=10.2 Hz, CH*H*), 1.44 (s, 36H, CH_3), 1.89–1.98 (m, 4H), 2.12–2.33 (m, 4H), 2.59–2.69 (m, 4H), 2.80 (dd, 2H, *J*=12.9 Hz, *J*=12.9 Hz), 3.15 (dd, 2H, *J*=12.9 Hz, *J*=4.5 Hz), 4.33 (q, 2H, *J*=9.9 Hz, CH), 5.02 (s, 2H, OH), 6.95 (s, 4H, arom. H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ=24.1 (2×CH_3), 27.5 (2×CH_3), 27.9 (2×CH_2), 30.4 (12×CH_3), 34.3 (4×C), 37.3 (2×C), 39.1 (2×CH_2), 39.3 (2×CH), 40.4 (2×CH_2), 42.1 (2×CH), 43.9 (2×CH), 46.6 (2×CH), 125.8 (4×CH_{ar}), 132.5 (2×C_{ar}), 135.5 (4×C_{ar}), 151.6 (2×C_{ar}); ^{77}Se NMR (38.1 MHz, $CDCl_3$): δ=362.0 (Se_2) ppm; elemental analysis calcd (%) for $C_{48}H_{74}O_2Se_2$ (841.02): C 68.55, H 8.87; found: C 68.49, H 8.95.

*4.5.6. (1S,1′S)-(+)-Bis(10-phenylsulfanylpinocampheyl) diselenide (**50**).* Yield: 120 mg, (15%), yellow oil; $[\alpha]_D^{22}$=+121.6 (*c* 0.65, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ=1.01 (s, 6H, CH_3), 1.20 (s, 6H, CH_3), 1.33 (d, 2H, *J*=9.9 Hz, CH*H*), 1.86–1.99 (m, 2H), 2.11 (dd, 2H, *J*=13.8 Hz, *J*=9.3 Hz), 2.18–2.28 (m, 2H), 2.37–3.77 (m, 6H), 3.18 (dd, 2H, *J*=10.2 Hz, *J*=9.6 Hz, CH*H*), 3.56 (dd, 2H, *J*=10.2 Hz, *J*=4.2 Hz, CH*H*), 4.19 (q, 2H, *J*=10.2 Hz, CHSe), 7.10–7.37 (m, 10H, arom. H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ=22.9 (2×CH_3), 27.2 (2×CH_3), 27.5 (2×CH_2), 36.4 (2×CH_2), 38.2 (2×CH), 39.3 (2×C), 40.1 (2×CH), 41.8 (2×CH), 43.0 (2×CH), 45.0 (2×CH), 125.6 (2×CH), 128.8 (4×CH), 128.9 (4×CH), 137.0 (2×C); ^{77}Se NMR (38.1 MHz, $CDCl_3$): δ=360.0 (Se_2) ppm; elemental analysis calcd (%) for $C_{32}H_{42}S_2Se_2$ (648.73): C 59.25, H 6.53; found: C 59.20, H 6.39.

*4.5.7. (1S,1′S)-(+)-Bis(10-Phenylselanylpinocampheyl) diselenide (**51**).* Yield: 1.09 g (68%), yellow solid; mp 90–92 °C; $[\alpha]_D^{20}$=+115.5 (*c* 1.90, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.00 (s, 6H, CH_3), 1.17 (s, 6H, CH_3), 1.31 (d, 2H, *J*=9.9 Hz, CH*H*), 1.88–1.98 (m, 2H), 2.03–2.11 (m, 2H), 2.18–2.29 (m, 2H), 2.35–2.43 (m, 2H), 2.54 (ddd, 2H, *J*=14.1 Hz, *J*=9.6 Hz, *J*=4.1 Hz,), 2.72–2.85 (m, 2H), 3.21 (dd, 2H, *J*=12.0 Hz, *J*=10.5 Hz, CH*H*), 3.54 (dd, 2H, *J*=12.0 Hz, *J*=6.0 Hz, CH*H*), 4.15 (q, 2H, *J*=9.6 Hz, CH), 7.16–7.32 (m, 6H, arom. H), 7.41–7.53 (m, 4H, arom. H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ=22.8 (2×CH_3), 27.1 (2×CH_3), 27.7 (2×CH_2), 33.4 (2×CH_2), 36.4 (2×CH_2), 39.2 (2×CH), 40.7 (2×CH), 41.8 (2×C), 44.2 (2×CH), 45.6 (2×CH), 126.6 (2×CH), 128.9 (4×CH), 131.1 (2×C), 132.4 (4×CH); ^{77}Se NMR (38.1 MHz, $CDCl_3$): δ=295.0 (Se), 360.2 (Se_2) ppm; elemental analysis calcd (%) for $C_{32}H_{42}Se_4$ (742.52): C 51.76, H 5.70; found: C 51.79, H 5.75.

*4.5.8. (1S,1′S)-(+)-Bis(10-methoxyisopinocampheyl) diselenide (**53**).* Yield: 1.80 g (45%), yellow oil; $[\alpha]_D^{30}$=+166.2 (*c* 4.1, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ=0.99 (s, 6H, CH_3), 1.19 (d, 2H, *J*=9.6 Hz, CH*H*), 1.21 (s, 6H, CH_3), 1.90–2.01 (m, 2H), 2.10–2.27 (m, 4H), 2.33–2.64 (m, 6H), 3.33 (s, 6H, CH_3), 3.38–3.54 (m, 6H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ=23.2 (2×CH_3), 27.5 (2×CH_3), 32.5 (2×CH_2), 35.8 (2×CH), 38.2 (2×CH_2), 38.5 (2×C), 42.3 (2×CH), 43.3 (2×CH), 51.5 (2×CH), 58.6 (2×OCH_3), 75.6 (2×CH_2); ^{77}Se NMR (38.1 MHz, $CDCl_3$): δ=462.8 ppm; elemental analysis calcd (%) for $C_{22}H_{38}Se_2$ (492.46): C 53.66, H 7.78; found: C 53.63, H 7.80.

*4.5.9. (1S,1′S)-(+)-Bis(10-phenoxyisopinocampheyl) diselenide (**54**).* Yield: 308 mg (19%), yellow oil; $[\alpha]_D^{20}$=+62.6 (*c* 1.27, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ=1.01 (s, 6H, CH_3), 1.08 (d, 2H, *J*=9.6 Hz, CH*H*), 1.22 (s, 6H, CH_3), 1.93–2.08 (m, 2H), 2.18–2.38 (m, 4H), 2.39–2.72 (m, 8H), 3.50–3.62 (m, 2H), 3.87–4.17 (m, 2H), 6.81–7.00 (m, 6H, arom. H), 7.19–7.36 (m, 4H, arom. H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ=23.3 (2×CH_3), 27.5 (2×CH_3), 32.7 (2×CH_2), 35.4 (2×CH), 38.1 (2×CH_2), 38.5 (2×C), 42.3 (2×CH), 43.4 (2×CH), 51.4 (2×CH), 70.0 (2×CH_2), 114.4 (4×CH), 120.5 (2×CH), 129.4 (4×CH), 158.8 (2×C); ^{77}Se NMR (38.1 MHz, $CDCl_3$): δ=461.0 (Se_2) ppm; elemental analysis calcd (%) for $C_{32}H_{42}O_2Se_2$ (616.59): C 62.33, H 6.87; found: C 62.45, H 6.98.

*4.5.10. (1S,1′S)-(-)-Bis(10-pentafluorophenoxyisopinocampheyl) diselenide (**55**).* Yield: 1.10 g, (33%), yellow oil; $[\alpha]_D^{22}$=−12.3 (*c* 13.36, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.03 (s, 6H, CH_3), 1.24 (s, 6H, CH_3), 1.26 (d, 2H, *J*=9.6 Hz, CH*H*), 1.94–2.05 (m, 2H), 2.17–2.48 (m, 6H), 2.67 (ddd, 2H, *J*=14.4 Hz, *J*=9.9 Hz, *J*=4.8 Hz), 3.05 (dddd, 2H, *J*=9.9 Hz, *J*=9.9 Hz, *J*=6.1 Hz, *J*=3.0 Hz,), 4.36–4.44 (m, 2H), 4.74–4.84 (m, 4H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=22.7 (2×CH_3), 26.7 (2×CH_3), 27.5 (2×CH_2), 38.5 (2×CH_2), 39.0 (2×C), 41.0 (2×CH), 44.6 (2×CH), 45.4 (2×CH), 52.2 (2×CH), 76.5 (t, *J*=3.8 Hz, 2×CH_2); ^{77}Se NMR (38.1 MHz, $CDCl_3$): δ=383.5 (Se_2) ppm; elemental analysis calcd (%) for $C_{32}H_{32}F_{10}O_2Se_2$ (796.50): C 48.25, H 4.05; found: C 48.44, H 4.21.

*4.5.11. (1S,1′S)-(+)-Bis(10-phenylsulfanylisopinocampheyl) diselenide (**56**).* Yield: 350 mg (23%), yellow oil; $[\alpha]_D^{20}$=+108.7 (*c* 2.14, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ=1.01 (s, 6H, CH_3), 1.14 (d, 2H, *J*=9.6 Hz, CH*H*), 1.19 (s, 6H, CH_3), 1.92–2.01 (m, 2H), 2.16–2.48 (m, 8H), 2.50–2.66 (m, 2H), 2.94 (dd, 2H, *J*=12.8 Hz, *J*=10.4 Hz, CH*H*), 3.18 (dd, 2H, *J*=12.8 Hz, *J*=4.2 Hz, CH*H*), 3.44–3.62 (m, 2H, CHSe), 7.11–7.37 (m, 10H, arom. H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ=23.2 (2×CH_3), 27.5 (2×CH_3), 32.8 (2×CH_2), 38.3 (2×CH_2), 38.5 (2×CH), 38.6 (2×C), 39.9 (2×CH), 42.3 (2×CH), 44.2 (2×CH), 51.2 (2×CH), 125.7 (2×CH), 128.7 (4×CH), 128.9 (4×CH), 136.8 (2×C); ^{77}Se NMR (38.1 MHz, $CDCl_3$): δ=458.6 (Se_2) ppm; elemental analysis calcd (%) for $C_{32}H_{42}S_2Se_2$ (648.73): C 59.25, H 6.53; found: C 59.24, H 6.50.

*4.5.12. (1S,1′S)-(+)-Bis(10-phenylselanylisopinocampheyl) diselenide (**57**).* Yield: 311 mg (35%), yellow oil; $[\alpha]_D^{20}$=+64.0 (*c* 1.00, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.00 (s, 6H, CH_3), 1.15 (d, 2H, *J*=9.9 Hz, CH*H*), 1.16 (s, 6H, CH_3), 1.93–1.98 (m, 2H), 2.18–2.47 (m, 8H), 2.50–2.61 (m, 2H), 2.99 (dd, 2H, *J*=12.0 Hz, *J*=10.5 Hz, CH*H*), 3.54 (dd, 2H, *J*=12.0 Hz, *J*=4.8 Hz, CH*H*), 4.15 (m, 2H, CH), 7.18–7.32 (m, 6H, arom. H), 7.43–7.53 (m, 4H, arom. H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ=23.1 (2×CH_3), 27.4 (2×CH_3), 32.7 (2×CH_2), 33.3 (2×CH_2), 38.5 (2×CH_2), 38.6 (2×C), 40.5 (2×CH), 42.2 (2×CH), 44.9 (2×CH), 52.2 (2×CH), 126.6 (2×CH), 129.0 (4×CH), 130.9 (2×C), 132.2 (4×CH); ^{77}Se NMR (38.1 MHz, $CDCl_3$): δ=297.3 (Se), 461.2 (Se_2) ppm; elemental

analysis calcd (%) for $C_{32}H_{42}Se_4$ (742.52): C 51.76, H 5.70; found: C 51.85, H 5.68.

*4.5.13. (1S,2R,3R,5S)-(-)-3,10-Pinane diselenide (**61**).* Yield: 0.56 g (22%), red oil; $[\alpha]_D^{22}=-258.1$ (*c* 4.68, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ=1.12 (s, 3H, CH_3), 1.20 (d, 1H, *J*=9.6 Hz, CH*H*), 1.22 (s, 3H, CH_3), 1.88–1.99 (m, 2H), 2.21–2.33 (m, 2H), 2.39–2.48 (m, 1H), 2.84 (dddd, 1H, *J*=13.8 Hz, *J*=11.1 Hz, *J*=5.7 Hz, *J*=3.0 Hz), 3.34 (dd, 1H, *J*=11.1 Hz, *J*=5.7 Hz, CH*H*), 3.68 (dd, 1H, *J*=12.9 Hz, *J*=11.1 Hz, CH*H*), 4.49 (dt, 1H, *J*=10.5 Hz, *J*=6.6 Hz, CHSe); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=24.9 (CH_3), 27.0 (CH_3), 29.1 (CH_2), 33.9 (CH_2), 39.1 (C), 39.2 (CH_2), 40.3 (CH), 41.1 (CH), 46.3 (CH), 56.9 (CH); ^{77}Se NMR (38.1 MHz, $CDCl_3$): δ=342.3 (Se), 435.2 (Se) ppm; elemental analysis calcd (%) for $C_{10}H_{16}Se_2$ (294.15): C 40.83, H 5.48; found C 40.87, H 5.54.

*4.5.14. (1S,1′S)-(+)-Bis(10-phenylselanyl-4-caranyl) diselenide (**93**).* Yield: 490 mg (42%), yellow oil; $[\alpha]_D^{20}=+140.0$ (*c* 0.50, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$): δ=0.53 (dt, 2H, *J*=9.0 Hz, *J*=4.6 Hz), 0.72–0.95 (m, 4H), 0.98 (s, 6H, CH_3), 1.03 (s, 6H, CH_3), 1.77–2.03 (m, 6H), 2.50 (dt, 2H, *J*=16.2 Hz, *J*=8.6 Hz), 2.88 (dd, 2H, *J*=12.2 Hz, *J*=7.6 Hz, CH*H*), 3.17 (dd, 2H, *J*=12.2 Hz, *J*=6.8 Hz, CH*H*), 3.75 (m, 2H, CHSe), 7.19–7.30 (m, 6H, arom. H), 7.43–7.57 (m, 4H, arom. H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ=16.3 (2×CH_3), 18.2 (2×C), 19.6 (2×CH), 22.8 (2×CH), 23.6 (2×CH_2), 27.7 (2×CH_2), 28.5 (2×CH_3), 34.4 (2×CH_2), 38.9 (2×CH), 48.5 (2×CH), 126.6 (2×CH), 128.9 (4×CH), 131.0 (2×C), 132.3 (4×CH); ^{77}Se NMR (38.1 MHz, $CDCl_3$): δ=275.4 (Se_2), 368.6 (Se) ppm; elemental analysis calcd (%) for $C_{32}H_{42}Se_4$ (742.52): C 51.76, H 5.70; found: C 51.74, H 5.66.

*4.5.15. (1S,1′S)-(-)-Bis(10-phenylselanyl-4-isocaranyl) diselenide (**97**).* Yield: 530 mg (47%), yellow oil; $[\alpha]_D^{20}=-108.0$ (*c* 0.50, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ=0.55–0.78 (m, 4H), 0.93 (m, 2H), 0.99 (s, 12H, CH_3), 1.55–1.78 (m, 2H), 2.00 (ddd, 2H, *J*=15.0 Hz, *J*=6.3 Hz, *J*=3.3 Hz), 2.15–2.27 (m, 4H), 2.87 (m, 2H), 2.90 (dd, 2H, *J*=12.0 Hz, *J*=7.8 Hz, CH*H*), 3.36 (dd, 2H, *J*=12.0 Hz, *J*=3.9 Hz, CH*H*), 7.18–7.30 (m, 6H, arom. H), 7.45–7.55 (m, 4H, arom. H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ=15.6 (2×CH_3), 17.9 (2×C), 20.5 (2×CH), 20.6 (2×CH), 26.6 (2×CH_2), 28.6 (2×CH_3), 28.9 (2×CH_2), 35.3 (2×CH_2), 40.2 (2×CH), 47.2 (2×CH), 126.5 (2×CH), 129.0 (4×CH), 131.1 (2×C), 132.2 (4×CH); ^{77}Se NMR (38.1 MHz, $CDCl_3$): δ=255.4 (Se_2), 368.7 (Se) ppm; elemental analysis calcd (%) for $C_{32}H_{42}Se_4$ (742.52): C 51.76, H 5.70; found: C 51.71, H 5.65.

Acknowledgements

This work was financially supported by the Nicolaus Copernicus University under Grant 377-Ch and the European Social Fund and state budget under the project of Self-government of the Voivodeship ‘Step in the future’ -scholarship for PhD students.

Supplementary data

Characterization data of all methoxyselenenylation and selenocyclization products are provided. Crystallographic data of **51** is included in Supplementary data. Supplementary data associated with this article can be found in online version, at doi:10.1016/j.tet.2009.10.005.

References and notes

1. (a) Paulmier, C. *Selenium Reagents and Intermediates in Organic Synthesis*; Pergamon: Oxford, 1985; (b) *Chemistry of Organoselenium and Tellurium Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: New York, NY, 1987; (c) *Organoselenium Chemistry: A Practical Approach*; Back, T. G., Ed.; Oxford University: Oxford, 1999; (d) *Topics in Current Chemistry*; Wirth, T., Ed.; Springer: Heidelberg, 2000; Vol. 208.
2. (a) Wirth, T. *Tetrahedron Lett.* **1995**, *36*, 7849; (b) Wirth, T.; Kulicke, K. J.; Fragale, G. *Helv. Chim. Acta* **1996**, *79*, 1957; (c) Braga, A. L.; Paixão, M. W.; Lüdtke, D. S.; Silveira, C. C.; Rodrigues, O. E. D. *Org. Lett.* **2003**, *5*, 2635.
3. (a) Mugesh, G.; Singh, H. B. *Chem. Soc. Rev.* **2000**, *29*, 347; (b) Mugesh, G.; du Mont, W.-W.; Sies, H. *Chem. Rev.* **2001**, *101*, 2125; (c) Malmstrom, J.; Jonsson, M.; Cotgreave, I. A.; Hammarstrom, L.; Sjodin, M.; Engman, L. *J. Am. Chem. Soc.* **2001**, *123*, 3434; (d) Back, T. G.; Moussa, Z. *J. Am. Chem. Soc.* **2003**, *125*, 13455; (e) Wójtowicz, H.; Chojnacka, M.; Młochowski, J.; Palus, J.; Syper, L.; Hudecowa, D.; Uher, M.; Piasecki, E.; Rybka, M. *Il Farmaco* **2003**, *58*, 1235; (f) Meotti, F. C.; Stangherlin, G. Z.; Nogueira, C. W.; Rocha, J. B. T. *Environ. Res.* **2004**, *94*, 276; (g) Schrauzer, G.N. Patent US, 6,867,238, 2005.
4. Ścianowski, J. *Tetrahedron Lett.* **2005**, *46*, 3331.
5. Ścianowski, J.; Rafiński, Z.; Wojtczak, A. *Eur. J. Org. Chem.* **2006**, *14*, 3216.
6. Rafiński, Z.; Ścianowski, J. *Tetrahedron: Asymmetry* **2008**, *19*, 1237.
7. Rafiński, Z.; Ścianowski, J.; Wojtczak, A. *Lett. Org. Chem.* **2009**, *6*, 321.
8. Rafiński, Z.; Ścianowski, J.; Wojtczak, A. *Tetrahedron: Asymmetry* **2008**, *19*, 223.
9. (a) Browne, D. M.; Wirth, T. *Curr. Org. Chem.* **2006**, *10*, 1893; (b) Tiecco, M.; Testaferri, L.; Bagnoli, L.; Marini, F.; Santi, C.; Temperini, A.; Scarponi, C.; Sternativo, S.; Terlizzi, R.; Tomassini, C. *ARKIVOC* **2006**, 186; (c) Zhu, C.; Huang, Y. *Curr. Org. Chem.* **2006**, *10*, 1905; (d) Coles, M. P. *Curr. Org. Chem.* **2006**, *10*, 1993.
10. (a) Back, T. G.; Dyck, B. P. *Chem. Commun.* **1996**, 2567; (b) Back, T. G.; Nan, S. *J. Chem. Soc., Perkin Trans. 1* **1998**, 3123; (c) Back, T. G.; Dyck, B. P.; Nan, S. *Tetrahedron* **1999**, *55*, 3191; (d) Back, T. G.; Moussa, Z. *Org. Lett.* **2000**, *19*, 3007.
11. Le Noble, W. J.; Hayakawa, T.; Sen, A. K.; Tatsukami, Y. *J. Org. Chem.* **1971**, *36*, 193.
12. Hori, T.; Sharpless, K. B. *J. Org. Chem.* **1979**, *44*, 4204.
13. Uzarewicz, A.; Ścianowski, J.; Bąkowska-Janiszewska, J. *Pol. J. Chem.* **1999**, *73*, 1791.
14. Uzarewicz, A.; Ścianowski, J.; Bąkowska–Janiszewska, J. *Pol. J. Chem.* **2000**, *74*, 1079.
15. Cox, M.; Wirth, T. *Phosphorus Sulfur* **2005**, *180*, 659.
16. (a) Wirth, T. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1726; (b) Wirth, T.; Fragale, G. *Chem.—Eur. J.* **1997**, *3*, 1894; (c) Tiecco, M.; Testaferri, L.; Santi, C.; Tomassini, C.; Marini, F.; Bagnoli, L.; Temperini, A. *Tetrahedron: Asymmetry* **2000**, *11*, 4645; (d) Wirth, T. *Liebigs Ann./Recueil* **1997**, 2189; (e) Wirth, T. *Tetrahedron* **1999**, *55*, 1; (f) Tiecco, M.; Testaferri, L.; Bagnoli, L.; Marini, F.; Temperini, A.; Tomassini, C.; Santi, C. *Tetrahedron Lett.* **2000**, *41*, 3241; (g) Tiecco, M.; Testaferri, L.; Santi, C.; Tomassini, C.; Marini, F.; Bagnoli, L.; Temperini, A. *Chem.—Eur. J.* **2002**, *8*, 1118.
17. (a) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B.* **1988**, *37*, 785; (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
18. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M. W.; Gill, P. M.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03, Revision B.01*; Gaussian: Pittsburgh PA, 2003.
19. Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.