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New diphenyl diselenides *o*-substituted by O(S, Se)-caranyl skeleton – synthesis and application in asymmetric reactions

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Abstract: An efficient methodology for the synthesis of diphenyl diselenides *o*-substituted by O(S, Se)-caranyl moieties has been presented. 4-Caranyl and 4-isocaranyl groups have been connected to the phenyl ring by oxygen, sulfur or selenium atom. The influence of the selenium-heteroatom interactions on the diastereoselectivity of the methoxyselenenylation of styrene has been evaluated. The best result was obtained for diselenide with O-caranyl group substituted in *ortho*-position. X-ray crystal structure of this compound was determined and the observed intramolecular interactions were discussed. Additionally diselenides bearing a sulfur atom were transformed to corresponding methyl *o*-(S-caranyl) and *o*-(S-isocaranyl)-substituted phenyl selenides, and were tested as catalysts in the Tsuji-Trost allylic alkylation and Henry reaction.

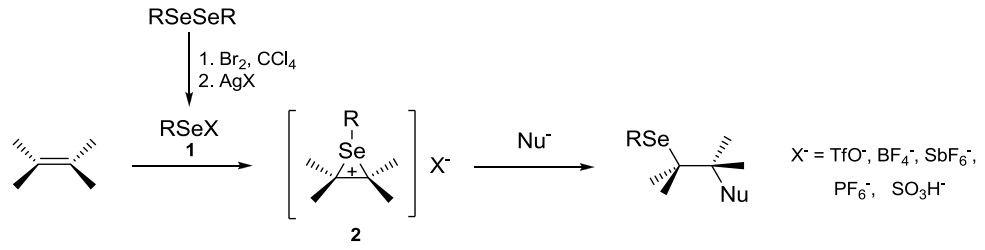
Key words: diselenides, terpenes, methoxyselenenylation reaction, allylic alkylation, Henry reaction, selenium-heteroatom interactions

Introduction

Organoselenium compounds have been broadly applied in organic synthesis as reagents and catalysts enabling a wide range of transformations. Se-derivatives can be used as electrophilic, nucleophilic and radical species with broad application potential providing simple and efficient methods for generating new carbon-carbon, carbon-nitrogen, carbon-oxygen and carbon-halogen bonds [1-5]. Due to the unique properties of the selenium atom, selenofunctionalization can proceed with good chemo- and regioselectivity [6].

Chiral diselenides are efficient precursors of electrophilic reagents commonly applied in the asymmetric selenenylation of olefins. In the reaction of a selenium electrophile **1** with the

unsaturated substrate, the formation of a seleniranium ion **2** is observed, followed by a stereospecific *anti*-addition of the present nucleophile (Scheme 1) [7-9].



Scheme 1. Selenenylation of a double bond.

Stereoselectivity of the reaction can be influenced by several factors: structure of the substrate and organoselenium reagent, type of the counteranion and non-bonding interactions between selenium and other heteroatoms. These interactions can be divided into two types. When the bonding atom acts as a weak electrophile, pulling closer the electron density of the selenium lone electron pair, it is a Type 1 bonding. Type 2 is observed when the approaching heteroatom is a weak nucleophile in relation to the antibonding σ^* selenium orbital [10] (Figure 1).

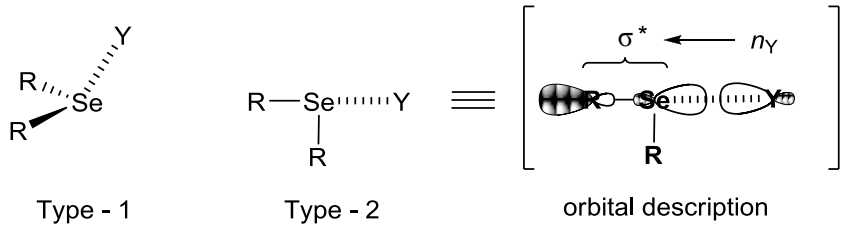


Figure 1. Schematic representation of different types of Se···Y nonbonded interaction [10].

When a chiral center with a heteroatom is in close proximity to selenium, the exhibited non-bonding interaction stabilizes the structure and shortens the distance between the chiral moiety and the reactive center improving the selectivity of the reaction. Examples of derivatives possessing a chiral moiety in proximity to a heteroatom are showed in Figure 2 [11-13].

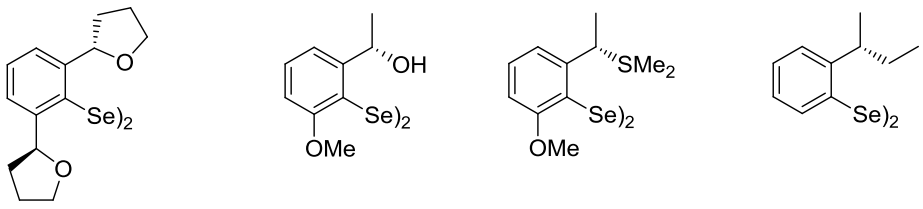


Figure 2. Examples of chiral diselenides applied in methoxyselenenylation of styrene.

Compounds **3**-**5** provided high diastereomeric excess for the asymmetric methoxyselenenylation of styrene. The results clearly demonstrate the importance of the non-bonding Se-heteroatom interaction on the selectivity of the addition reaction. This conclusion is also supported by the result for compound **6** where the absence of a heteroatom in the side chain resulted in *de* 0%.

Recently, several papers and reviews have reported the synthesis and utilization of terpenyl diselenides in which the selenium atom was directly connected to the chiral moiety [14-22]. However, terpenes have not yet been implemented as chirality sources in the structure of diaryl diselenides. In this work we present the synthesis and application routes for new diphenyl diselenides substituted in the *ortho* position by chiral caranyl and isocaranyl moieties connected to the aromatic ring through oxygen, sulfur or selenium atom (Figure 3). The influence of the terpenyl moieties and the type of heteroatom on the diastereoselectivity of the applied electrophiles in methoxyselenenylation reaction of styrene has been evaluated.

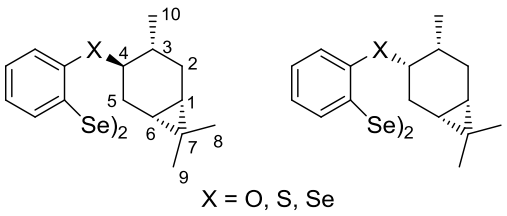
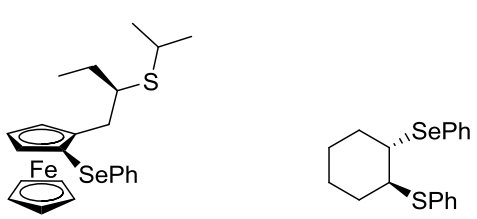


Figure 3. Structure of the synthetized diaryl diselenides.

Additionally derivatives bearing a sulfur atom were transformed to methyl o-substituted phenyl selenides and used in the allylic alkylation and Henry reaction. Hitherto, only few examples of S,Se-donating ligands used in the Pd-catalyzed allylic substitution were reported so far. The bis(chalcogen) ligands **7** and **8** effectively catalyze the asymmetric allylic alkylation with enantioselectivities of 44% and 34% *ee* respectively (Figure 4) [23-24]. The results of these reactions are also demonstrated.



7, yield: 65%, *ee* 44% (*R*) **8**, yield: 90%, *ee* 34% (*R*)

Figure 4. Selenides applied in the Tsuji-Trost reaction.

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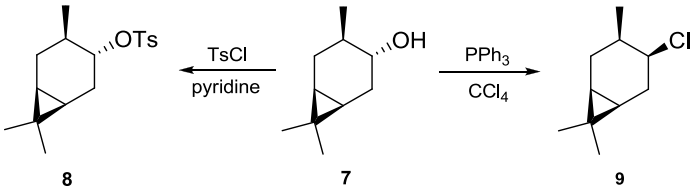
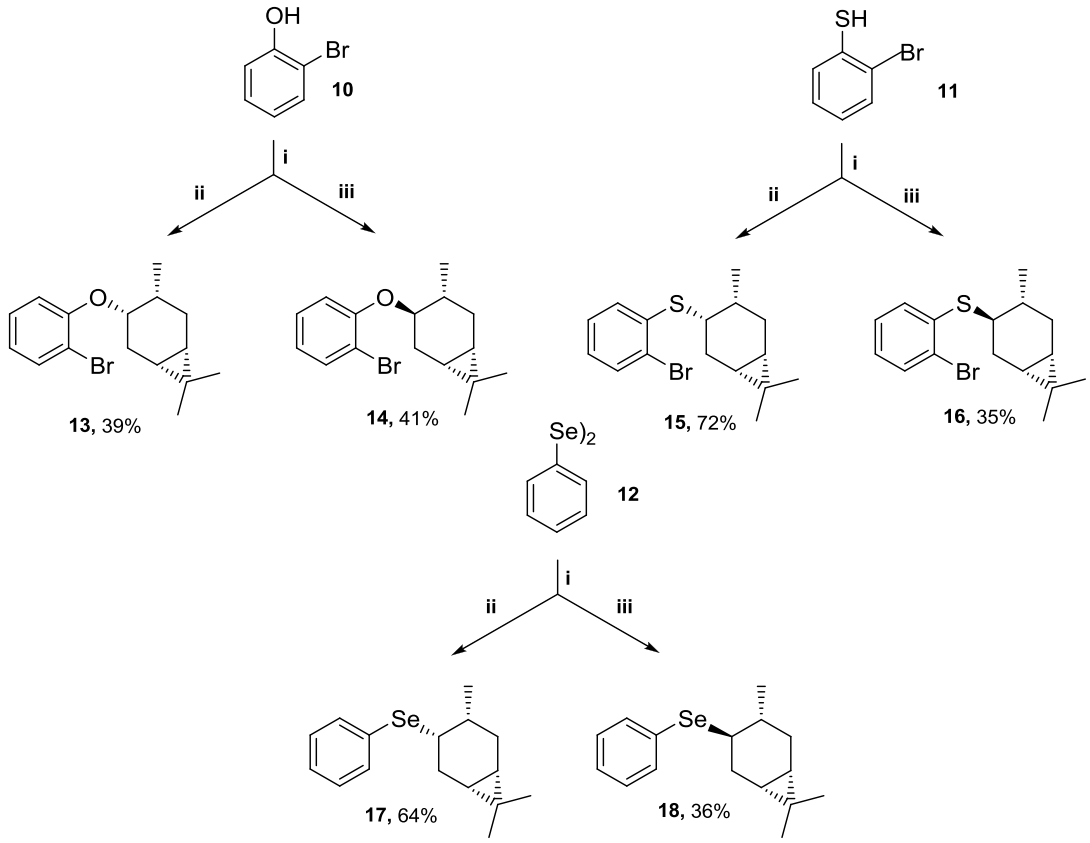
Results and discussion

First step of our research included the synthesis of (–)-4-isocaranyl tosylate **8** and (+)-4-caranyl chloride **9** from (–)-4-isocaranol **7** according to the previously reported methodology (Scheme 2) [16].



Scheme 2. Synthesis of isocaranyl tosylate and caranyl chloride.

Substrates for the synthesis of diselenides, phenyl-caranyl *o*-bromo ethers **13**, **14**, sulphides **15**, **16** and phenyl-caranyl selenides **17**, **18** were obtained in the reaction of isocaranyl tosylate and caranyl chloride with *o*-bromo phenol **10**, *o*-bromo thiophenol **11** and diphenyl diselenide **12** previously treated with sodium hydride (Scheme 3).



Scheme 3. Synthesis of compounds **13-18**.

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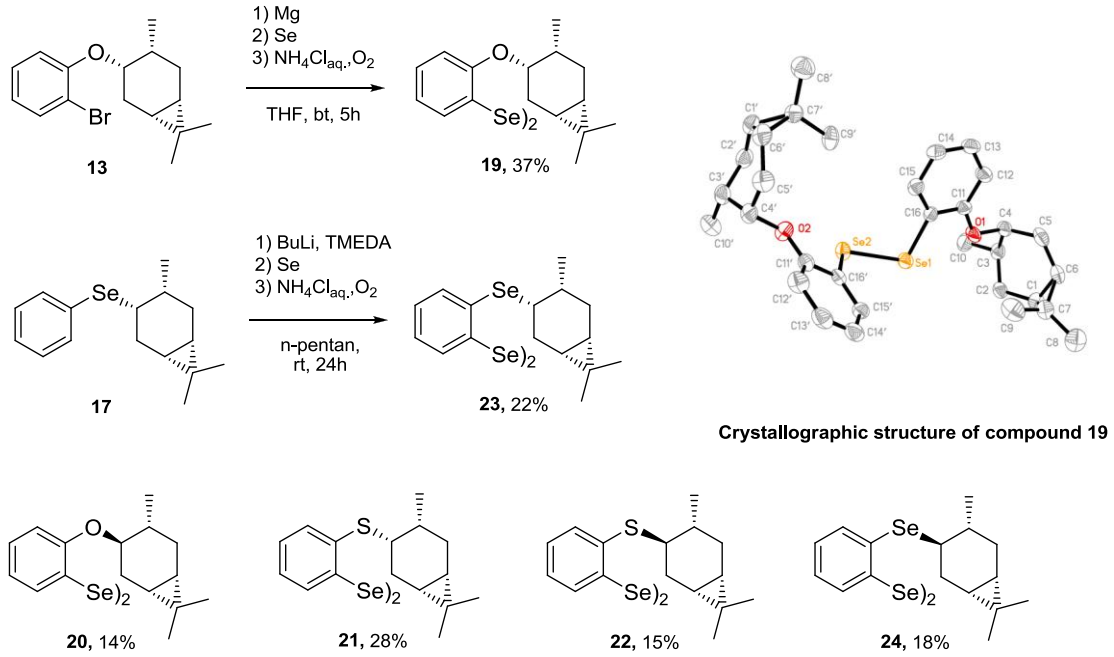
Diselenides **19-24** were synthetized by two methods. For substrates **13-16** possessing bromium in the aromatic ring magnesium and selenium powders were used to form selenolate, subsequently hydrolyzed with ammonium chloride and oxidized to diselenides **19-22**. In case of diselenides **23** and **24,** in the first step of synthesis metalation with butyl lithium was performed (Scheme 4).



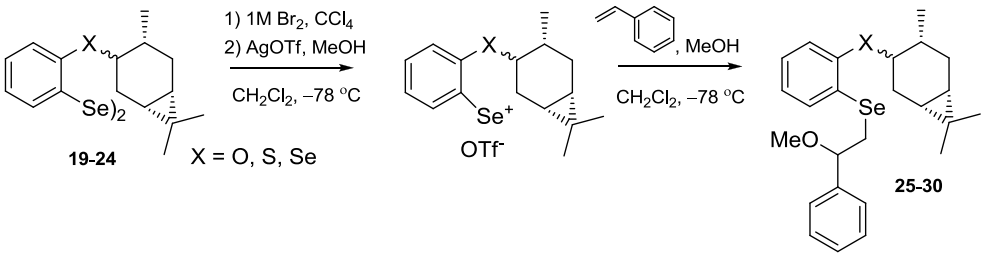
Scheme 4. Synthesis of diselenides **19-24**.

Crystallographic analysis was made for diselenide **19**. The asymmetric part of the structure consists of a single molecule. Two *o*-phenyl-O-caranyl fragments are connected by the diselenide bridge (Scheme 4). The *1S,3R,4S,6R* configuration was found for the first caranyl moiety and identical 1'*S*,3'*R*,4'*S*,6'*R* for the second moiety, consistent with the substrate configuration. The Se1-C16 and Se2-C16' distances of 1.936(7) and 1.930(7) Å are typical for such bonds. The C16-Se1-Se2 and C16'-Se2-Se1 angles are 102.6(2) and 103.5(2)º, respectively. Conformation of the diselenide bridge is anticlinal with the C16-Se1-Se2-C16' torsion angle of -95.2(3)º. Orientation of two phenyl rings relative to the diselenide bridge is different, with the torsion angles C11-C16-Se1-Se2 of -162.1(5) and Se1-Se2-C16'-C11' of 156.0(5)º. In such conformation, the dihedral angle between the phenyl ring planes is 71.6(4)º. Orientation of the caranyl moieties relative to the neighboring phenyl ring is similar, with torsion angles C11-O1-C4-C3 and C11'-O2-C4'-C3' being -157.1(7) and -156.9(7)º. The non-bonded interactions in the organoselenium compounds have been reviewed in the literature [10]. The structural data reported here revealed the presence of intramolecular

contacts Se1…O1 and Se2…O2 of 2.854(6) and 2.877(5) Å, respectively, shorter by 0.5 Å than the sum of vdW radii. Since the distance between the O atoms and the adjacent C-Se1-Se2 planes are 0.708 and -0.980Å for O1 and O2, respectively, and the Se…O interactions are approximately co-linear with the Se1-Se2 bond, they fulfill the criterion of Type 2 interactions between selenium and the nucleophile. Analysis also revealed the intramolecular interactions Se1...H15'-C15' and Se2...H15a-C15 involving the phenyl C-H groups, with the Se…H distances being 3.04 and 2.87 Å, respectively. These interactions correspond to the interactions considered as Se…H-C hydrogen bonds. Since distances of H15 and H15' from the C-Se-Se plane are -2.689 and 2.526 Å, respectively, these interactions fulfill the criterion of Type 1 interactions with the weak electrophile interacting with electrons of the selenium lone-pair. Also the intermolecular Se1…H14'-C14'[-x,-1/2+y,1-z], Se2…H6A'-C6'[-x,-1/2+y,-z], Se2…H5A'-C5'[-x,-1/2+y,-z] and Se2…H6A'-C6'[-x,-1/2+y,-z] are found, with the Se…H distances of 3.29, 3.28, 3.12 and 2.84 Å, respectively.

In the next part of our research diselenides were applied in the methoxyselenenylation of styrene. Compounds **19**-**24** were transformed to electrophilic reagents by treatment with 1M solution of bromine and silver triflate. In the presence of methanol as an external nucleophile the addition products **25**-**30** were obtained. Results are presented in Table 1. The best diastereoselectivity was obtained for diselenide bearing an oxygen atom **25**.

Table 1. Results for the asymmetric methoxyselenenylation of styrene.



Diselenide	Product	*dr*	Yield [%]
19	**25**	68:32	78
20	**26**	61:39	14
21	**27**	63:37	47
22	**28**	52:48	11
23	**29**	53:47	66
24	**30**	56:44	19

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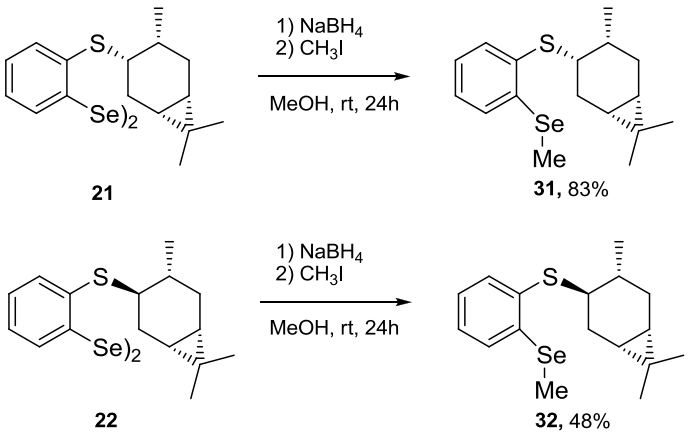
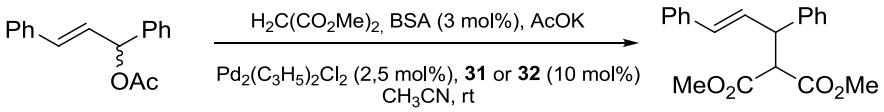
Diselenides **21** and **22** were additionally transformed to methyl selenides **31** and **32** using sodium borohydride and methyl iodide (Scheme 5).



Scheme 5. Synthesis of methyl selenides **31** and **32**.

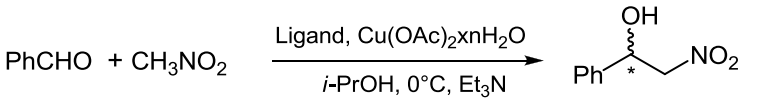
Catalytic efficiency of compounds **31** and **32** was also tested. Tsuji-Trost reaction of dimethyl malonate with *rac*-1,3-diphenyl-2-propenyl acetate, was performed using 3 mol% of *N*,*O*-bis(trimethylsilyl)acetamide-potassium acetate as a base, 2.5 mol% of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$, and 10 mol% of tested chiral ligand in acetonitrile solution. Dimethyl(1,3-diphenyl-2-propen-1-yl)malonate was obtained in high yield and moderate enatioselectivity (Scheme 6).



	Yield	*ee* [%]
31	94	44 (*R*)
32	74	16 (*S*)

Scheme 6. Pd-Catalyzed alkylation of *rac*-1,3-diphenyl-2-propenyl acetate with dimethyl malonate.

Derivatives **31** and **32** were also tested in the copper-catalyzed Henry reaction (Scheme 7).



	Yield	*ee* [%]
31	77	11 (*S*)
32	50	0

Scheme 7. Nitroaldol reaction catalyzed by Ligand/$Cu(OAc)_2$.

In case of compound **31** addition of benzaldehyde to nitromethane proceeds with good yield but low enantioselectivity. For selenide **32** no enatiomeric excess was observed. The reaction was run in the presence of base additive such as Et_3N to accelerate the reaction.

Conclusions

In this paper we have presented an efficient methodology for the synthesis of diphenyl diselenides *o*-substituted with caranyl and isocaranyl moieties connected to the atromatic ring by oxygen, sulfur or selenium atom. Diselenides were applied as reagents in methoxyselenenylation of styrene. The best result was obtained for diselenide bearing O-caranyl substituent. Crystallographic structure of the most efficient reagent was presented and the evaluated intramolecular nonbonding Se-H and Se-O interactions were discussed. Diselenides bearing a sulfur atom were also transformed to corresponding methyl selenides. These derivatives were applied as ligands in Pd-catalyzed alkylation (Tsuji-Trost reaction) and Henry reaction with good yield and low to moderate enantioselectivities.

Experimental

General. 1H NMR spectra were obtained at 200 or 300 MHz and chemical shifts were recorded relative to $SiMe_4$ (δ 0.00) or solvent resonance ($CDCl_3$ δ7.26). Multiplicities were given as: s (singlet), d (doublet), dd (double doublet), ddd (double double doublet), t (triplet), dt (double triplet), td (triple doublet) and m (multiplet). The number of protons (n) for a given resonance was indicated by nH. Coupling constants were reported as a J value in Hz. 13C NMR spectra were acquired at 50.3Hz and chemical shifts were recorded relative to solvent resonance ($CDCl_3$ δ77.25). Commercially available solvents THF, DMF, methanol, diethyl and petroleum ether (Aldrich) and chemicals were used without further purification. Column chromatography was performed using Merck Kieselgel 60 (0.06-0.2mm). The enantiomeric composition of nitroaldols was determined by HPLC analysis using a chiral stationary phase (Chiracel OD-H or Daicel Chiralpak AD-H). The absolute configuration was assigned by comparison of the retention time and the sign of the specific rotation with literature data.

General procedure for the synthesis of phenyl-terpenyl o-bromoethers 13,14, sulphides 15,16 and selenides 17,18.

To a solution of 60% sodium hydride (dispersion in mineral oil) (0.5g, 12.5 mmol) in DMSO (10 ml) substrate **10**, **11**, or **12** (10 mmol) was added. The mixture was stirred for 1h under argon atmosphere at room temperature (at 50^{o}C for diphenyl diselenide **12**). Tosylate **8** or

chloride **9** (10 mmol) dissolved in DMSO (10 ml) was added and the mixture was stirred for 5h at 100°C (4 days at room temperature for compounds **14** and **16**). Mixture was poured on 3 M sodium hydroxide solution (100 ml), extracted with diethyl ether (3x50 ml), washed with water, 3 M sodium hydroxide and water. Combined organic layers were dried with anhydrous magnesium sulphate and evaporated. Crude product was purified using column chromathography (silica gel, hexane).

(1*S*,3*R*,4*S*,6*R*)-4-(2-Bromophenoxy)-3,7,7-trimethylbicyclo[4.1.0]heptane (13).

Yield 39%, $[\alpha]_D^{20}$ = +64.89 (c 1.78, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$): δ_H 0.47 (dt, 1H, *J* = 1.22, 6.22 Hz), 0.83-0.91 (m, 1H), 0.98 (s, 3H, CH_3), 1.00 (s, 3H, CH_3), 1.10 (d, 3H, CH_3, *J* = 3.42 Hz), 1.25-1.85 (m, 4H), 2.23 (ddd, 1H, *J* = 4.92, 6.18, 10,88 Hz), 4.26 (dd, 1H, J =1.76, 4.82 Hz), 6.73-6.78 (m, 2H), 7.18-7.26 (m, 1H), 7.49-7.52 (dd, 1H, *J* = 1.14, 5.5 Hz). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ_C 15.1 (CH_3), 16.9 (CH), 17.6 (C), 17.8 (CH_3), 21.7 (CH_2), 22.0 (CH), 24.1 (CH_2), 28.9 (CH_3), 33.4 (CH), 74.9 (CH), 112.6 (C), 113.1 (CH), 120.7 (CH), 128.1 (CH), 133.5 (CH), 154.4 (C). Anal. calcd for $C_{16}H_{21}BrO$ (309.24): C, 62.14; H, 6.84 Found: C, 62.23; H, 6.87.

(1*S*,3*R*,4*R*,6*R*)-4-(2-Bromophenoxy)-3,7,7-trimethylbicyclo[4.1.0]heptane (14).

Yield 41%, $[\alpha]_D^{20}$ = -6.18 (c 1.40, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$): δ_H 0.78-0.98 (m, 2H), 0.98 (d, 3H, CH_3, *J* = 2.84 Hz), 0.99 (s, 3H, CH_3), 1.01 (s, 3H, CH_3), 1.65-1.78 (m, 2H), 1.79-1.90 (m, 1H), 2.05-2.12 (m, 1H), 2.15-2.25 (m, 1H), 3.70-3.83 (m, 1H), 6.74-6.85 (m, 2H), 7.17-7.26 (m, 1H), 7.50-7.54 (dd, 1H, *J* = 1.64, 6.48 Hz). ^{13}C NMR ($CDCl_3$, 50 MHz): δ_C 16.1 (CH_3), 17.7 (C), 18.4 (CH_3), 20.2 (CH), 21.4 (CH), 27.0 (CH_2), 28.4 (CH_2), 28.6 (CH_3), 34.7 (CH), 82.9 (CH), 113.0 (C), 114.5 (CH), 121.3 (CH), 128.2 (CH), 133.5 (CH), 155.1 (C). Anal. calcd for $C_{16}H_{21}BrO$ (309.24): C, 62.14; H, 6.84 Found: C, 62.10; H, 6.88.

(1*S*,3*R*,4*S*,6*R*)-4-(2-Bromophenylthio)-3,7,7-trimethylbicyclo[4.1.0]heptane (15).

Yield 71%, $[\alpha]_D^{20}$ = +38.52 (c 1.42, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$): δ_H 0.57-0.79 (m, 2H), 1.00 (s, 3H, CH_3), 1.03 (d, 3H, CH_3, *J* = 7.0 Hz), 1.06 (s, 3H, CH_3), 1.25-1.46 (m, 2H), 1.82-2.28 (m, 3H), 3.44-3.58 (dd, 1H, J = 6.2, 8.2 Hz), 6.97-7.05 (m, 1H), 7.20-7.38 (m, 2H), 7.52-7.57 (dd, 1H, J = 1.0, 7.8 Hz). ^{13}C NMR ($CDCl_3$, 50 MHz): δ_C 15.7 (CH_3), 17.8 (C), 18.8 (CH_3), 21.0 (CH), 21.2 (CH), 24.6 (CH_2), 25.6 (CH_2), 28.5 (CH_3), 30.6 (CH), 45.9 (CH), 124.9 (C), 126.6 (CH), 127.5 (CH), 130.1 (CH), 133.1 (CH), 138.5 (C). Anal. calcd for $C_{16}H_{21}BrS$ (325.31): C, 59.07; H, 6.51 Found: C, 58.89; H, 6.57.

(1*S*,3*R*,4*R*,6*R*)-4-(2-Bromophenylthio)-3,7,7-trimethylbicyclo[4.1.0]heptane (16). Yield 35%, $[\alpha]_D^{20}$ = –123.20 (c 1.69, $CHCl_3$). ^1H NMR (200 MHz, $CDCl_3$): δ_H 0.61-0.92 (m, 2H), 0.97 (s, 3H, CH_3), 0.98 (s, 3H, CH_3), 1.03 (d, 3H, CH_3, *J* = 6.29 Hz), 1.25-2.16 (m, 5H), 2.81-2.89 (m, 1H), 7.01-7.11 (m, 1H), 7.20-7.30 (m, 1H), 7.37 (dd, 1H, *J* = 1.49, 6.18 Hz), 7.56 (dd, 1H, J= 1.4, 8.0 Hz). ^{13}C NMR ($CDCl_3$, 50 MHz): δ_C 15.6 (CH_3), 17.6 (C), 19.7 (CH), 20.6 (CH_3), 20.7 (CH), 27.8 (CH_2), 28.7 (CH_3), 29.3 (CH_2), 34.6 (CH), 50.6 (CH), 126.1 (C), 127.2 (CH), 127.4 (CH), 131.8 (CH), 133.1 (CH), 137.4 (C). Anal. calcd for $C_{16}H_{21}BrS$ (325.31): C, 59.07; H, 6.51 Found: C, 59.28; H, 6.47.

(1*S*,3*R*,4*S*,6*R*)-4-(Phenylseleno)-3,7,7-trimethylbicyclo[4.1.0]heptane (17). Yield 64%, $[\alpha]_D^{20}$ = +44.16 (c 1.1, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ_H 0.51-0.59 (m, 1H), 0.64-0.72 (m, 1H), 0.97 (s, 3H, CH_3), 0.98 (d, 3H, CH_3, *J* = 7.05 Hz), 1.02 (s, 3H, CH_3), 1.26-1.55 (m, 2H), 1.82-2.02 (m, 2H), 2.17-2.27 (m, 1H), 3.58 (dt, 1H, *J* = 6.66, 8.43 Hz), 7.22- 7.29 (m, 3H), 7.50-7.56 (m, 2H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ_C 15.8 (CH_3), 17.7 (C), 20.3 (CH_3), 21.3 (CH), 21.4 (CH), 25.7 (CH_2), 25.9 (CH_2), 28.5 (CH_3), 31.0 (CH), 47.0 (CH), 126.7 (CH), 128.8 (2 x CH), 131.1 (C), 133.8 (2 x CH). ^{77}Se NMR (38 MHz, CDCl3): δ_{Se} 346.33. Anal. calcd for $C_{16}H_{22}Se$ (293.31): C, 65.52; H, 7.56 Found: C, 65.42 H, 7.59.

(1*S*,3*R*,4*R*,6*R*)-4-(Phenylseleno)-3,7,7-trimethylbicyclo[4.1.0]heptane (18). Yield 36%, $[\alpha]_D^{20}$ = -102.72 (c 1.88, $CHCl_3$). ^1H NMR (200 MHz, $CDCl_3$): δ_H 0.50-0.62 (m, 1H), 0.68-0.87 (m, 1H), 0.93 (s, 3H, CH_3), 0.97 (s, 3H, CH_3), 1.03 (d, 3H, CH_3, *J* = 6.80 Hz), 1.24-2.08 (m, 5H), 2.68-2.83 (dt, 1H, *J* = 8.4, 16.4 Hz), 7.22-7.33 (m, 3H), 7.45-7.64 (m, 2H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ_C 15.6 (CH_3), 17.5 (C), 20.6 (CH), 20.7 (CH), 21.8 (CH_3), 28.8 (CH_3), 29.7 (CH_2), 29.5 (CH_2), 34.7 (CH), 48.9 (CH), 127.1 (CH), 128.8 (2 x CH), 129.1 (C), 134.9 (2 x CH). ^{77}Se NMR (38 MHz, CDCl3): δ_{Se} 403.61. Anal. calcd for $C_{16}H_{22}Se$ (293.31): C, 65.52; H, 7.56 Found: C, 65.62; H, 7.54.

General procedure for the synthesis of diselenides 19-22.

To a suspension of magnesium (0.12g, 5.0 mmol) in THF (20 ml) compound **13**, **14**, **15** or **16** (5.0 mmol) dissolved in THF (10ml) was added. Mixture was stirred in reflux for 3h. Selenium (0.39g, 5.0 mmol) was added and the reaction was stirred in reflux for additional 2h. Mixture was poured on a saturated solution of ammonium chloride (15ml) and oxidized with air for 3h. Decantated solution was extracted with diethyl ether (3x50ml). Combined organic layers were washed with water, dried over anhydrous magnesium sulfate and evaporated. Crude product was purified using column chromatography (silica gel, hexane).

bis(2-((1*S*,3*R*,4*S*,6*R*)-3,7,7-Trimethyl-bicyclo[4.1.0]heptan-4-yloxy)phenyl)diselenide (19)

Yield 74%, $[\alpha]_D^{20}$ = +36.05 (c 1.43, $CHCl_3$). ^1H NMR (200 MHz, $CDCl_3$): δ_H 0.46 (dt, 1H, *J* = 1.86, 9.33 Hz), 0.80-0.97 (m, 1H), 1.01 (s, 3H, CH_3), 1.05 (d, 3H, CH_3, *J* = 6.67 Hz), 1.07 (s, 3H, CH_3), 1.17-2.00 (m, 4H), 2.16-2.38 (m, 1H), 4.33 (dd, 1H, *J* = 2.52, 6.84 Hz), 6.63- 6.70 (m, 1H), 6.78 (dt, 1H, *J* = 1.14, 7.53 Hz), 7.09-7.18 (m, 1H), 7.41 (dd, 1H, *J* = 1.56, 7.74 Hz). ^{13}C NMR ($CDCl_3$, 50 MHz): δ_C 15.1 (CH_3), 16.9 (CH), 17.6 (C), 17.7 (CH_3), 21.8 (CH_2), 22.1 (CH), 24.1 (CH_2), 28.9 (CH_3), 33.4 (CH), 75.1 (CH), 112.6 (C), 113.1 (CH), 120.7 (CH), 128.1 (CH), 133.6 (CH), 154.4 (C). ^{77}Se NMR (38 MHz, CDCl3): δ_{Se} 316.82. Anal. calcd for $C_{32}H_{42}O_2Se_2$ (616.59): C, 62.33; H, 6.87 Found: C, 62.53; H, 6.82.

bis(2-((1*S*,3*R*,4*R*,6*R*)-3,7,7-Trimethyl-bicyclo[4.1.0]heptan-4-yloxy)phenyl)diselenide (20)

Yield 28%, $[\alpha]_D^{20}$ = –104.83 (c 1.78, $CHCl_3$). ^1H NMR (200 MHz, $CDCl_3$): δ_H 0.75-1.00 (m ,2H), 1.01 (s, 3H, CH_3), 1.03 (s, 3H, CH_3), 1.04 (d, 3H, CH_3, *J* = 9.8 Hz), 1.53-2.29 (m, 4H), 2.95-2.99 (m, 1H), 3.79-3.91 (m, 1H), 6.71-6.77 (m, 1H), 6.78-6.85 (m, 1H), 7.09-7.19 (m, 1H), 7.49 (dd, 1H, *J* = 1.6, 7,8 Hz). ^{13}C NMR ($CDCl_3$, 50 MHz): δ_C 16.1 (CH_3), 17.7 (C), 18.8 (CH_3), 20.2 (CH), 21.3 (CH), 27.1 (CH_2), 28.3 (CH_2), 28.6 (CH_3), 34.6 (CH), 82.3 (CH), 112.1 (CH), 119.8 (C), 121.5 (CH), 127.6 (CH), 130.0 (CH), 155.6 (C). ^{77}Se NMR (38 MHz, CDCl3): δ_{Se} 326.7. Anal. calcd for $C_{32}H_{42}O_2Se_2$ (616.59): C, 62.33; H, 6.87 Found: C, 62.28; H, 6.86.

bis(2-((1*S*,3*R*,4*S*,6*R*)-3,7,7-Trimethyl-bicyclo[4.1.0]heptan-4-ylthio)phenyl)diselenide (21).

Yield 56%, $[\alpha]_D^{20}$ = +81.05 (c 1.68, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ_H 0.45-0.59 (m, 1H), 0.63-0.74 (m, 1H), 0.99 (s, 3H, CH_3), 1.09 (d, 3H, CH_3, *J* = 7.22 Hz), 1.10 (s, 3H, CH_3), 1.41-1.60 (m, 2H), 1.79-2.23 (m, 3H), 3.40-3.51 (m, 1H), 7.05-7.20 (m, 2H), 7.33-7.47 (m, 1H), 7.52-7.64 (m, 1H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ_C 15.9 (CH_3), 17.9 (C), 18.9 (CH_3), 20.9 (CH_2), 21.2 (CH_2), 25.0 (CH), 25.6 (CH), 28.5 (CH_3), 31.0 (CH), 51.1 (CH), 127.2 (CH), 128.8 (CH), 128.9 (CH), 134.4 (CH), 134.5 (C), 136.6 (C). ^{77}Se NMR (38 MHz, CDCl3): δ_{Se} 397.14. Anal. calcd for $C_{32}H_{42}S_2Se_2$ (648.73): C, 59.25; H, 6.53 Found: C, 59.16; H, 6.48.

bis(2-((1S,3R,4R,6R)-3,7,7-Trimethyl-bicyclo[4.1.0]heptan-4-ylthio)phenyl)diselenide (22).

Yield 30%, $[\alpha]_D^{20}$ = -86.09 (c 1.72, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ_H 0.63-0.90 (m, 2H), 0.93 (s, 3H, CH_3), 0.97 (s, 3H, CH_3), 1.11 (d, 3H, CH_3, *J* = 6.56 Hz), 1.40-1.59 (m, 2H), 1.82-2.07 (m, 3H), 2.75-2.86 (m, 1H), 7.09-7.19 (m, 2H), 7.33-7.44 (m, 1H), 7.54-7.61 (m,

1H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ_C 15.6 (CH_3), 17.6 (CH_3), 20.1 (CH), 20.7 (CH), 20.7 (C), 28.1 (CH_2), 28.8 (CH_3), 29.4 (CH_2), 34.7 (CH), 53.4 (CH), 126.7 (CH), 128.5 (CH), 129.3 (CH), 133.0 (C), 135.4 (CH), 137.2 (C). ^{77}Se NMR (38 MHz, CDCl3): δ_{Se} 392.92. Anal. calcd for $C_{32}H_{42}S_2Se_2$ (648.73): C, 59.25; H, 6.53 Found: C, 59.17; H, 6.46.

General procedure for the synthesis of diselenides 23 and 24.

To a solution of selenide **17** or **18** (5.0 mmol) in penthane (8 ml), under argon atmosphere, TMEDA (5.5 mmol) was added, followed by addition of 2.5M solution of *n*-buthyllithium (2.1ml, 5.25mmol). Mixture was stirred at 0^{o}C for 0.5h and at room temperature for 8h. Selenium (0.39g, 5.0 mmol) was added and the reaction was stirred at room temperature for additional 12h. Mixture was poured on a saturated solution of ammonium chloride (15ml) and oxidized with air for 3h. Decantated solution was extracted with diethyl ether (3x50ml). Combined organic layers were washed with water, dried over anhydrous magnesium sulfate and evaporated. Crude product was purified using column chromatography (silica gel, hexane:ethyl acetate 95:5).

bis(2-((1*S*,3*R*,4*S*,6*R*)-3,7,7-Trimethyl-bicyclo[4.1.0]heptan-4-ylseleno)phenyl)diselenide (23).

Yield 44%, $[\alpha]_D^{20}$ = +55.39 (c 1.65, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$): δ_H 0.47-0.80 (m, 2H), 0.99 (s, 3H, CH_3), 1.04 (d, 3H, CH_3, *J* = 7.00 Hz), 1.07 (s, 3H, CH_3), 1.52-1.73 (m, 4H), 2.17- 2.38 (m, 1H), 3.58-3.75 (m, 1H), 7.03-7.22 (m, 2H), 7.48-7.65 (m, 2H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ_C 16.0 (CH_3), 17.9 (C), 20.3 (CH_3), 21.5 (2 x CH), 25.9 (CH_2), 26.1 (CH_2), 28.5 (CH_3), 31.4 (CH), 50.1 (CH), 126.8 (CH), 128.6 (CH), 129.4 (CH), 129.6 (C), 136.7 (CH), 138.1 (C). ^{77}Se NMR (38 MHz, CDCl3): δ_{Se} 324.18, 421.35. Anal. calcd for $C_{32}H_{42}Se_4$ (742.52): C, 51.76; H, 5.70 Found: C, 51.58; H, 5.76.

bis(2-((1*S*,3*R*,4*R*,6*R*)-3,7,7-Trimethyl-bicyclo[4.1.0]heptan-4-ylseleno)phenyl)diselenide (24).

Yield 36%, $[\alpha]_D^{20}$ = –91.48 (c 1.59, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$): δ_H 0.53-0.90 (m, 2H), 0.95 (s, 3H, CH_3), 0.96 (s, 3H, CH_3), 1.08 (d, 3H, CH_3, *J* = 6.67 Hz), 1.45-1.70 (m, 2H), 1.90-2.20 (m, 3H), 2.90-3.09 (m, 1H), 7.00-7.25 (m, 2H), 7.47-7.63 (m, 2H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ_C 15.7 (CH_3), 17.6 (C), 20.7 (2 x CH), 21.6 (CH_3), 28.8 (CH_3), 29.0 (CH_2), 29.6 (CH_2), 35.1 (CH), 50.9 (CH), 126.6 (CH), 128.3 (CH), 129. (C), 129.7 (CH), 137.4 (CH), 138.5 (C). ^{77}Se NMR (38 MHz, CDCl3): δ_{Se} 372.29, 419.11. Anal. calcd for $C_{32}H_{42}Se_4$ (742.52): C, 51.76; H, 5.70 Found: C, 51.57; H, 5.64.

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General procedure for the synthesis of methyl selenides 31 and 32.

To a solution of selenide **21** or **22** (0.6 mmol) in methanol (10 ml) and diethyl ether (10ml), under argon atmosphere, sodium borohydride (0,6g, 15 mmol) was added. Mixture was stirred at room temperature until decoloration. Methyl iodide (5.0g, 35mmol) was added and stirring was continued for 2 days. Solvent was evaporated under reduce pressure, water (50ml) was added and the obtained mixture was extracted with diethyl ether (3x50ml). Combined organic layers were dried over anhydrous magnesium sulfate and evaporated. Crude product was purified using column chromatography (silica gel, hexane).

(1*S*,3*R*,4*S*,6*R*)-4-(2-(methylseleno)phenylthio)(3,7,7-trimethylbicyclo[4.1.0]heptan) (31). 83%, $[\alpha]_D^{20}$ = +59.96 (c 2.55, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 0.51-0.72 (m, 2H), 0.87-0.96 (m, 1H), 0.97 (s, 3H, CH_3), 1.04 (d, 3H, CH_3, *J*=6.90 MHz), 1.08 (s, 3H, CH_3), 1.37-1.47 (m, 1H), 1.84-1.95 (m, 1H), 1.97-2.18 (m, 2H), 2.27 (s, 3H, CH_3), 3.32- 3.50 (dt, 1H, J = 6.3, 8.1 Hz), 7.13-7.25 (m, 3H), 7.36-7.41 (m, 1H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ_C 6.4 (CH_3), 15.9 (CH_3), 17.7 (C), 18.8 (CH_3), 20.9 (CH), 21.1 (CH), 24.8 (CH_2), 25.5 (CH_2), 28.5 (CH_3), 30.8 (CH), 49.0 (CH), 125.4 (CH), 127.3 (CH), 127.6 (CH), 133.0 (CH), 135.9 (C), 138.1 (C). ^{77}Se NMR (38 MHz, CDCl3): δ_{Se} 200.14. Anal. calcd for $C_{17}H_{24}SSe$ (339.40): C, 60.16; H, 7.13 Found: C, 60.06; H, 7.21.

(1*S*,3*R*,4*R*,6*R*)-4-(2-(methylseleno)phenylthio)-3,7,7-trimethylbicyclo[4.1.0]heptan (32). Yield 48%, $[\alpha]_D^{20}$ = –125.75 (c 1.21, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$): δ_H 0.52-0.93 (m, 2H), 0.92 (s, 3H, CH_3), 0.96 (s, 3H, CH_3), 1.07 (d, 3H, CH_3, *J*=6.60 Hz), 1.38-1.58 (m, 2H), 1.86-2.08 (m, 3H), 2.27 (s, 3H, CH_3), 2.71-2.92 (m, 1H), 7.12-7.29 (m, 3H), 7.57-7.64 (m, 1H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ_C 6.4 (CH_3), 15.6 (CH_3), 17.5 (C), 19.9 (CH), 20.7 (CH_3), 20.7 (CH), 27.8 (CH_2), 28.7 (CH_3), 29.3 (CH_2), 34.7 (CH), 51.9 (CH), 125.2 (CH), 127.1 (CH), 128.0 (CH), 134.2 (CH), 134.6 (C), 139.2 (C). ^{77}Se NMR (38 MHz, CDCl3): δ_{Se} 200.83. Anal. calcd for $C_{17}H_{24}SSe$ (339.397): C, 60.16; H, 7.13 Found: C, 60.12; H, 7.15.

General procedure for the methoxyselenenylation of styrene.

To a solution of diselenide (0.58mmol) dissolved in dry dichloromethane (8ml), cooled to -78^{o}C, solution of bromine in tetrachloromethane (0.58ml, 1M, 0.58mmol) was added dropwise. After 15 min, a 0.70M methanol solution of silver triflate (320 mg, 1.80 mL) was added at –78 °C and stirred for another 15 min. Styrene (2.9 mmol) was added and the mixture was stirred at the same temperature for 2h. The reaction was poured on 10% NaHCO3 solution, diluted with 50 ml of dichloromethane, washed with water and brine, dried

over magnesium sulfate and concentrated in vacuum. The crude product was purified by column chromatography (silica gel, petroleum ether: ethyl acetate 95:5).

(1*S*,3*R*,4*S*,6*R*-)-4-(2-(2-Methoxy-2-phenylethylseleno)phenoxy)-3,7,7-trimethylbicyclo[4.1.0]heptan (25).

Yield 78%, *dr* 68:32. ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 0.43 (dt, 2H, J = 2.1, 9.3 Hz), 0.81-0.93 (m, 4H), 0.96 (d, 6H, 2 x CH_3, J = 7.5 Hz), 0.98 (s, 6H, 2 x CH_3), 0.99 (s, 6H, 2 x CH_3), 1.24-1.43 (m, 4H), 1.51-1.88 (m, 4H), 2.18-2.30 (m, 2H), 2.98-3.06 (m, 2H), 3.25 (s, 6H, 2 x CH_3), 4.23-4.30 (m, 2H), 4.33-4.41 (m, 2H), 6.65-6.67 (m, 2H), 6.78-6.85 (m, 2H), 7.08-7.16 (m, 2H), 7.21-7.28 (m, 2H), 7.29-7.42 (m, 10H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ_C 15.4 (2 x C), 17.0 (2 x CH_3), 17.5 (2 x CH), 17.8 (2 x CH_3), 21.9 (2 x CH_2), 22.1 (2 x CH), 24.2 (2 x CH_2), 28.8 (2 x CH_3), 31.9 (2 x CH_2), 33.4 (2 x CH), 57.0 (2 x CH_3),74.7 (2 x CH), 83.2 (2 x CH), 111.3 (2 x CH),120.5 (2 x CH), 121.4 (2 x C), 126.6 (2 x CH), 126.6 (4 x CH), 127.9 (2 x CH), 128.4 (4 x CH), 129.6 (2 x CH), 141.3 (2 x C), 155.6 (2 x C). ^{77}Se NMR (38 MHz, CDCl3): δ_{Se} 223.96. Anal. calcd for $C_{25}H_{32}O_2Se$ (443.480): C, 67.71; H, 7.27 Found: C, 67.58; H, 7.25.

(1*S*,3*R*,4*R*,6*R*)-4-(2-(2-Methoxy-2-phenylethylseleno)phenoxy)-3,7,7-trimethylbicyclo[4.1.0]heptan (26).

Yield 14%, *dr* 61:39. ^{1}H NMR (200 MHz, $CDCl_3$): δ_H 0.67-0.96 (m, 6H), 0.96-1.02 (m, 12H, 4 x CH_3), 0.99 (s, 6H, 2 x CH_3), 1.23-1.46 (m, 6H), 1.98- 2.30 (m, 4H), 3.00-3.12 (m, 2H), 3.24 (s, 6H, 2 x CH_3), 3.71-3.74 (m,2H), 4.30-4.45 (m, 2H), 6.70-6.89 (m, 6H), 7.06-7.38 (m, 10H), 7.40-7.50 (m, 2H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ_C 16.1 (2 x CH_3), 17.6 (2 x C), 18.6 (2 x CH_3), 20.2 (2 x CH), 21.3 (2 x CH), 26.9 (2 x CH_2), 28.3 (2 x CH_2), 28.6 (2 x CH_3), 32.1 (2 x CH_2), 34.7 (2 x CH), 57.0 (2 x CH_3), 81.5 (2 x CH), 83.2 (2 x CH), 112.4 (2 x CH), 120.9 (2 x CH), 121.4 (2 x C), 126.7 (4 x CH), 127.9 (2 x CH), 128.5 (4 x CH), 130.3 (2 x CH), 130.4 (2 x CH), 141.3 (2 x C), 156.4 (2 x C). ^{77}Se NMR (38 MHz, CDCl3): δ_{Se} 272.13, 328.68. Anal. calcd for $C_{25}H_{32}O_2Se$ (443.48): C, 67.71; H, 7.27 Found: C, 67.52; H, 7.23.

(1*S*,3*R*,4*S*,6*R*-)-4-(2-(2-methoxy-2-phenylethylseleno)phenylthio)-3,7,7-trimethylbicyclo[4.1.0]heptan (27).

Yield 47%, *dr* 63:37. ^{1}H NMR (200 MHz, $CDCl_3$): δ_H 0.50-0.77 (m, 4H), 0.99 (d, 6H, 2 x CH_3, J = 6.0 Hz), 0.99 (s, 6H, 2 x CH_3), 1.02 (s, 6H, 2 x CH_3), 1.25-1.48 (m, 4H), 1.80-2.22 (m, 6H), 3.03-3.14 (m, 2H,), 3.27 (s, 6H, 2 x CH_3), 3.30-3.49 (m, 4H), 4.25 (ddd, 2H, J = 0.8, 5.0, 8.6 Hz), 7.04-7.19 (m, 4H), 7.23-7.43 (m, 14H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ_C 15.8 (2 x CH_3), 17.8 (2 x C), 18.8 (2 x CH_3), 21.1 (2 x CH), 24.7 (2 x CH_2), 25.6 (2 x CH_2), 28.5 (2 x

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CH_3), 30.6 (2 x CH), 33.9 (2 x CH_2), 48.3 (2 x CH), 48.4 (2 x CH), 57.0 (2 x CH_3), 82.9 (2 x CH), 126.2 (2 x CH), 126.6 (4 x CH), 126.8 (2 x CH), 128.0 (2 x CH), 128.5 (4 x CH), 130.1 (2 x CH), 131.7 (2 x CH), 135.7 (2 x C), 137.7 (2 x C), 141.1 (2 x C). ^{77}Se NMR (38 MHz, CDCl3): δ_{Se} 275.76, 275.55. Anal. calcd for $C_{25}H_{32}OSSe$ (459.55): C, 65.64; H, 7.02 Found: C, 65.33; H, 7.08.

(1*S*,3*R*,4*R*,6*R*-)-4-(2-(2-methoxy-2-phenylethylseleno)phenylthio)-3,7,7-trimethylbicyclo[4.1.0]heptan (28).

Yield 11%, *dr* 52:48. ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 0.69-0.91 (m, 4H), 0.94 (s, 6H, 2 x CH_3), 0.96 (s, 6H, 2 x CH_3), 1.05 (dd, 6H, 2 x CH_3, *J* = 4.96 Hz, *J* = 1.30 Hz), 1.10-1.36 (m, 4H), 1.37-1.51 (m, 2H), 1.83-2.07 (m, 6H), 2.73-2.85 (m, 2H), 3.06 (d, 1H, *J* = 5.1 Hz), 3.09 (d, 1H, *J* = 4.8 Hz), 3.26 (s, 6H, 2 x CH_3), 4.38-4.46 (m, 2H), 7.07-7.18 (m, 4H), 7.25- 7.40 (m, 14H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ_C 15.6 (2 x CH_3), 17.5 (2 x C), 19.9 (2 x CH_3), 20.8 (4 x CH), 27.8 (2 x CH_2), 28.7 (2 x CH_3), 29.3 (2 x CH_2), 33.9 (2 x CH_2), 34.7 (2 x CH), 51.6 (2 x CH), 57.0 (2 x CH_3), 83.0 (2 x CH), 125.9 (2 x CH), 126.6 (4 x CH) 127.4 (2 x CH), 127.5 (2 x C), 128.1 (2 x CH), 128.6 (4 x CH), 129.7 (2 x CH), 133.2 (2 x CH), 137.2 (2 x C), 141.2 (2 x C). ^{77}Se NMR (38 MHz, CDCl3): δ_{Se} 268.42, 268.83. Anal. calcd for $C_{25}H_{32}OSSe$ (459.55): C, 65.34; H, 7.02 Found: C, 65.22; H, 6.97.

(1*S*,3*R*,4*S*,6*R*-)-4-(2-(2-methoxy-2-phenylethylseleno)phenylseleno)-3,7,7-trimethylbicyclo[4.1.0]heptan (29).

Yield 66%, *dr* 53:47. ^{1}H NMR (200 MHz, $CDCl_3$): δ_H 0.49-0.78 (m, 4H), 0.98 (s, 6H, 2 x CH_3), 1.00 (d, 6H, 2 x CH_3, *J* = 6.0 Hz), 1.04 (s, 6H, 2 x CH_3), 1.23-1.62 (m, 6H), 1.80-2.09 (m, 4H), 2.13-2.33 (m, 2H), 3.00-3.14 (m, 2H), 3.26 (s, 6H, 2 x CH_3), 3.55-3.68 (m, 2H), 4.38-4.48 (m, 2H), 7.04-7.19 (m, 2H), 7.20-7.54 (m, 16H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ_C 15.8 (2 x C), 17.7 (2 x CH_3), 20.3 (2 x CH_3), 21.3 (2 x CH), 21.6 (2 x CH), 25.6 (2 x CH_2), 26.1 (2 x CH_2), 28.4 (2 x CH_3), 30.9 (2 x CH), 34.8 (2 x CH_2), 47.1 (2 x CH), 56.9 (2 x CH_3), 82.9 (2 x CH), 126.4 (2 x CH), 126.6 (4 x CH), 127.4 (2 x CH), 127.9 (2 x CH), 128.5 (4 x CH), 130.3 (2 x CH), 133.8 (2 x C), 133.9 (2 x CH), 137.4 (2 x C), 141.1 (2 x C). ^{77}Se NMR (38 MHz, CDCl3): δ_{Se} 282.77, 283.14, 338.95, 339.45. Anal. calcd for $C_{25}H_{32}OSe_2$ (506.44): C, 59.29; H, 6.37 Found: C, 59.18; H, 6.38.

(1*S*,3*R*,4*S*,6*R*-)-4-(2-(2-methoxy-2-phenylethylseleno)phenylseleno)-3,7,7-trimethylbicyclo[4.1.0]heptan (30).

Yield 19%, *dr* 56:44. ^{1}H NMR (200 MHz, $CDCl_3$): δ_H 0.55-0.92 (m, 6H), 0.96 (s, 12H, 4 x CH_3), 1.03-1.05 (m, 6H, 2 x CH_3), 1.22-1.63 (m, 6H), 1.90-2.09 (m, 6H), 3.00-3.15 (m, 2H),

3.26 (s, 6H , 2 x CH_3), 4.38-4.47 (m, 2H), 7.00-7.20 (m, 4H), 7.21-7.40 (m, 12H), 7.40-7.50 (m, 2H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ_C 15.6 (2 x CH_3), 17.5 (2 x C), 20.5 (2 x CH_3), 20.8 (2 x CH), 21.5 (2 x CH), 28.6 (2 x CH_2), 28.8 (2 x CH_3), 29.5 (2 x CH_2), 34.7 (2 x CH_2), 35.0 (2 x CH), 48.9 (2 x CH), 57.0 (2 x CH_3), 83.0 (2 x CH), 126.1 (2 x CH), 126.6 (4 x CH), 127.8 (2 x CH), 128.1 (2 x CH), 128.5 (4 x CH), 129.8 (2 x CH), 132.7 (2 x C), 135.1 (2 x CH), 138.2 (2 x C), 141.2 (2 x C). ^{77}Se NMR (38 MHz, CDCl3): δ_{Se} 285.16, 285.52, 389.53, 390.86. Anal. calcd for $C_{25}H_{32}OSe_2$ (506.44): C, 59.29; H, 6.37 Found: C, 59.37; H, 6.31.

General procedure for palladium-catalyzed allylic alkylation.

The Pd-catalyzed allylic substitution reaction (Trost-Tsuji reaction) of dimethyl malonate with *rac*-1,3-diphenyl-2-propenyl acetate, was performed using 3 mol% of *N*,*O*-bis(trimethylsilyl)acetamide-potassium acetate as a base, 2.5 mol% of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$, and 10 mol% of tested chiral ligand in acetonitrile solution. The product (dimethyl(1,3-diphenyl-2-propen-1-yl)malonate) was purified by column chromatography (*n*-hexane/ethyl acetate, 5:1), analyzed by ^{1}H NMR, and specific rotation in CH_2Cl_2 ware measured. Stereochemical effect of the catalytic reaction was determined by HPLC (Chiracel AD-H), *n*-hexane/*i*-PrOH, 95:5, flow rate: 1.0 mL/min, λ=225 nm, enantiomer (*R*) t_r = 16.3 min, enantiomer (*S*) t_r = 23.7 min. The absolute configuration was assigned by comparison of the retention times in HPLC and optical rotation signs with literature data [25-26].

General procedure for copper-catalyzed Henry reaction.

Ligand (0.06 mmol, 12 mol%) and $Cu(OAc)_2{\cdot}H_2O$ (10.0 mg, 0.05 mmol, 10 mol%) were dissolved in *i*-PrOH (1 mL) and the mixture was stirred for 3 h at rt to give a blue or dark green solution. Then benzaldehyde (0.5 mmol, 1 eq), nitromethane (5.0 mmol, 10 eq) and Et_3N (1.0 mol%) were added with additional 1 mL of *i*-PrOH. The reaction mixture was cooled to 0 °C. After 3 days, the crude product was isolated by column chromatography (hexane/AcOEt 6:1) to give β-nitroalcohol (2-nitro-1-phenylethan-1-ol) as a mixture of diastereomers. Product was analyzed by ^{1}H NMR, and the enantiomeric excess was determined using chiral HPLC (Chiracel OD-H), *n*-hexane/*i*-PrOH, 90:10, flow rate: 1.0 mL/min, λ=254 nm, enantiomer (*R*) t_r = 13.2 min, enantiomer (*S*) t_r = 16.3 min). The absolute configuration was assigned by comparison of the retention times in HPLC and optical rotation signs with literature data [27-29].

Crystallographic data for bis(2-((1*S*,3*R*,4*S*,6*R*)-3,7,7-Trimethyl-bicyclo[4.1.0]heptan-4-yloxy)phenyl)diselenide (19).

Crystals of diselenide **19** were grown from the methanol solution. The X-ray intensities were collected with an Oxford Sapphire CCD diffractometer using MoKα radiation λ =0.71073 Å, at 292(2) K, by ω-2θ method. Structure was solved by direct methods and refined with the full-matrix least-squares method on F^2 with the use of SHELX97 and SHELX2014 program packages [30]. Analytical absorption corrections were applied (RED171 package of programs [31] Oxford Diffraction, 2000), the maximum and minimum transmission of 0.2026 and 0.4609. Hydrogen atoms were located from the electron density maps and their positions were constrained in the refinement. The absolute structure was determined with the Flack method [32], the Flack x being -0.045(17). The structural data have been deposited with Cambridge Crystallographic Data Centre, the CCDC number 1453055.

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Convenient methodology for the synthesis of optically active diselenides and selenides functionalized with terpenyl moieties and their applications in selenenylation of alkenes, and Tsuji-Trost, and Henry reactions are presented.