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Asymmetric alkene cycloalumination by $AlEt_3$, catalyzed with neomenthylindenyl zirconium η^5-complexes

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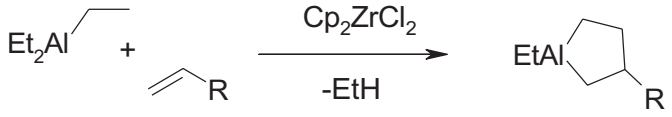
ABSTRACT

The paper is devoted to a study of the reaction of terminal alkene cycloalumination by $AlEt_3$ catalyzed with neomenthylindenyl zirconium complexes (p-*S*)(p-*S*)-*bis*[η^5-[1-[(1*S*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl]indenyl]]zirconium dichloride (**1**) or (p-*S*)-(η^5-cyclopentadienyl)[η^5-[1-[(1*S*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl]indenyl]]zirconium dichloride (**2**). It was shown that alkene and catalyst structures, as well as solvent, affect the overall yield and enantiomeric excess of the reaction product - 3-alkylsubstituted aluminacyclopentanes. The reaction of terminal alkenes with $AlEt_3$, catalyzed by complex **1**, in hydrocarbon solvents gives predominantly S-enantiomers of cyclic organoaluminum compounds with enantiomeric excess up to 37%. Complex **2** shows smaller stereoinduction effect and provides *R*-enantiomers of aluminacyclopentanes with 6–26%ee.

The effectiveness of selenium-containing derivatizing reagent (*R*)-2-phenylselenopropanoic acid for the enantiomeric excess estimation in β-alkyl-1,4-butanediols obtained from cyclic organoaluminum compounds was shown.

1. Introduction

The reaction of $AlEt_3$ with terminal alkenes in the presence of Cp_2ZrCl_2, according to the Dzhemilev procedure [1], provides cyclic organoaluminum compounds (OAC) – aluminacyclopentanes, which possess immense synthetic potential due to their reactivity with various electrophilic and nucleophilic reagents providing wide range of products, for example, 1,4-butanediols, halogen substituted derivatives, carbo- and hetero-(O, N, S, Se, Si, P) cycles, etc. [2].



Asymmetric induction in catalytic alkene cycloalumination could result in effective methods for the enantioselective synthesis of practically important β-substituted metallacyclopentanes and their derivatives.

Earlier, there were attempts to involve enantiopure Ti and Zr complexes of C_1- and C_2-symmetry in alkene cycloalumination [3,4]. Our investigations concerning the reaction of 1-hexene with $AlEt_3$ in the presence of neomenthyl zirconocene complexes demonstrated that the enantioselectivity depends on the catalyst structure and the reaction conditions [4]. The present work is devoted to a detailed study of asymmetric alkene cycloalumination, mainly of the substrate structure effect on the chemo- and enantioselectivity of the reaction. Moreover, a new derivatizing reagent (*R*)-2-phenylselenopropanoic acid (*R*-PSPA) has been tested for the estimation of the enantiomeric excess of β-substituted 1,4-butanediols obtained after the oxidation and hydrolysis of the cyclic OAC.

2. Results and discussion

The reaction of $AlEt_3$ with terminal alkenes **3a**–**g** in the presence of 8 mol% of catalysts **1** or **2** at room temperature in hydrocarbon solvents (hexane, cyclohexane, benzene) provides aluminacyclopentanes **4a**–**g** (Scheme 1, Table 1). Carbo- (**5a**–**g**) and hydroalumination products (**6a**–**g**) were identified as well.

The absolute configuration of β-stereogenic centers in aluminacyclopentanes **4a**–**g** and the enantiomeric excess were established by the analysis of the oxidation and hydrolysis products – β-

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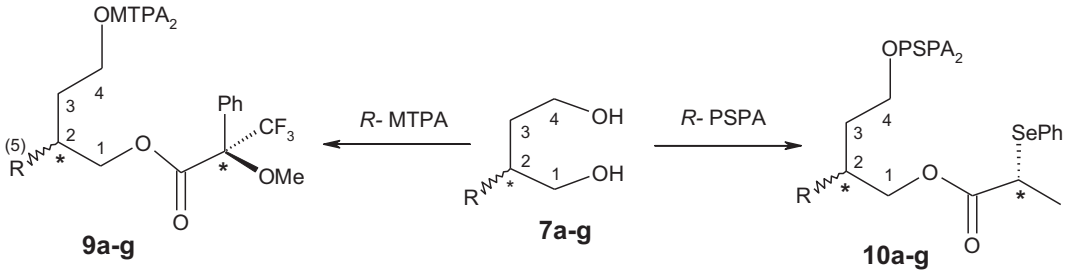
alkyl-1,4-butanediols **7a**–**g** (Table 1). They were involved in the reaction with *R*-MTPA (*S*-MTPA-Cl) [6] and (*R*)-2-phenylseleno propanoic acid [7] (*R*-PSPA) to yield the corresponding esters **9a**–**g** and **10a**–**g**.



^{13}C NMR spectra of esters **9b**–**e**, substituted with linear alkyl groups exhibit a double set of signals for C_2, C_3 and C_5 carbon atoms. More bulky isobutyl (**9g**) and cyclohexyl (**9f**) substituents provide additional diastereomeric signal splitting for C_4, C_6 and C_1 atoms. The signal splitting for characteristic C_2 and C_5 in **9b**–**g** is in full agreement with the diastereomeric effects in MTPA ester of β-butyl-1,4-butanediol (**9a**) [4]; this leads to conclusions about the absolute configuration of β-stereogenic centers in **7b**–**g.**

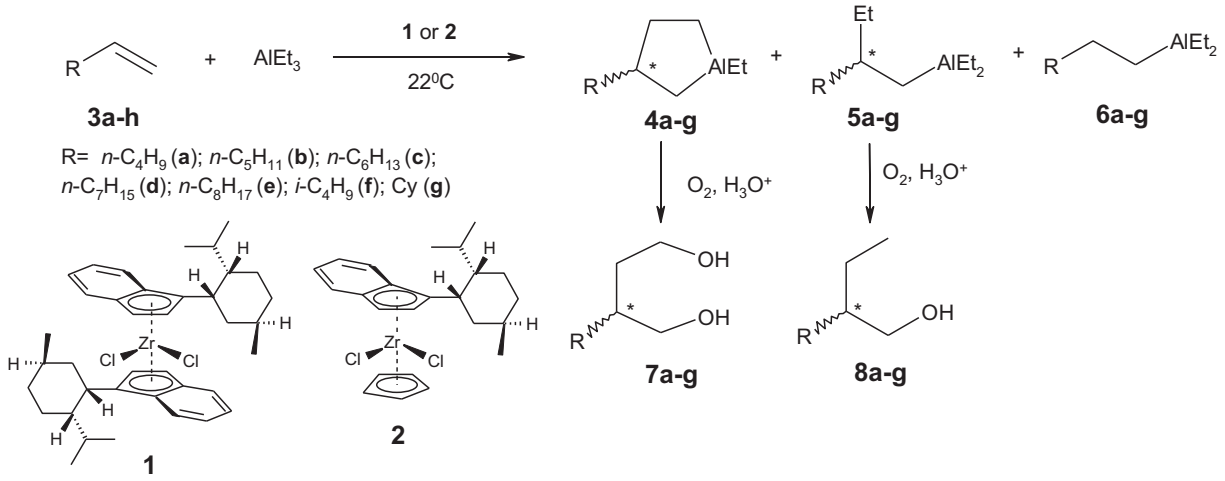
In ^{77}Se NMR spectra of (*R*)-phenylselenopropanoic acid esters of (*2R,S*)-alkyl-1,4-butanediols (**10a**–**g**) two pairs of signals of *RRR*- and *RRS*-diastereomers with $\Delta\delta_{Se} \approx 0.1$–$0.3$ ppm in the range of 452–454 ppm were observed. The diastereomeric ratios of **10a**–**g** obtained from ^{77}Se NMR spectra coincided with the ratio of the corresponding diastereomeric R-MTPA esters **9a**–**g** determined from the ^{13}C NMR spectra. It should be noted that R-PSPA was more useful and convenient for the enantiomeric excess elucidation, because it readily reacted with β-substituted 1,4-butanediols, compared to R-MTPA, in addition to a time-saving during the measurement of ^{77}Se NMR spectra. In contrast to R-PSPA, the reaction of *S*-MTPA-Cl with **7a**–**g** proceeds for ~8 h and the yield of the esters largely depends on the dryness of the initial alcohols. Moreover, longer accumulation of ^{13}C NMR spectra is required.

As follows from Table 1, the catalyst and substrate structure, as well as solvent, remarkably affect the alkene conversion and the reaction chemo- and enantioselectivity. Thus, complex **1** shows higher activity in the absence or in the reduced amount of the solvent (for example, entries 3, 4, 7, 10, 12, 15, 20, 22) and reaction runs with 70–99% alkene conversion; however, the cycloalumination enantioselectivity is low and does not exceed 17%ee. The dilution of the reaction media with hydrocarbons dramatically reduces the alkene conversion to 11–42%; nevertheless, it increases the enantiomeric excess of cycloalumination product **4a**–**g** up to 37%ee (for example, entries 1, 2, 5, 8, 11, 13, 14, 18, 21). The reaction catalyzed with complex **2** runs with decreased alkene conversion and enantioselectivity of 6–26%ee, which are less sensitive to the solvent effect.

The aluminacyclopentanes obtained in the reaction of alkenes **3a**–**g** with $AlEt_3$ in the presence of catalyst **1** were enriched with *S*-enantiomers, while the catalysis by complex **2** predominantly gave *R*-enantiomers of cyclic OAC. The substituent seniority order changes in cyclohexyl substituted aluminacyclopentaine **4g**, therefore, the product has the opposite descriptor of the absolute configuration, however, arrangement of the related atomic groups at β-stereogenic center remains the same as in **4a**–**f**.

The length increase for the alkyl chain in the linear alkenes, for example, using of 1-nonene (**3d**) or 1-decene (**3e**) in the reaction, catalyzed with complex **1**, decreases the cycloalumination enantioselectivity to 23–26%ee (entries 11, 13, 14). Moreover, the involvement of sterically hindered alkenes 4-methylpentene-1 (**3f**) or vinylcyclohexane (**3g**) in the reaction provides cyclic OACs with reduced enantiomeric excess of 24–25%ee (entries 18, 21). In the case of catalyst **2** the same effects were observed.

Therefore, the enantioselectivity of the alkene cycloalumination by $AlEt_3$, catalyzed with neomenthyl zirconocene complexes, is mainly determined by the catalyst structure, the substrate bulkiness and the solvent nature. In order to explain the observed effects, a probable mechanism of the process should be considered. As it was shown previously [8–11], the key



Scheme 1.

Table 1
Reaction of alkenes **3a**–**g** with $AlEt_3$, catalyzed by complexes **1** or **2** (mole ratio [Zr]: alkene: $AlEt_3$ = 4:50:60, reaction time 24 h, 20 °C).

Entry	Alkene	Solvent	Alkene conversion, %	Product ratio,[c] % (ee%, *R*/*S*)			$[\alpha]_D^{25}$ (**7**) (CH_2Cl_2)
				4	**5**	**6**	
Catalyst **1**							
1	1-Hexene (**3a**)	C_6H_{12}	79	76 (34, *S*)	10	11	+3.3 (c = 0.4) [4]
2		C_6H_{14}	65	86 (36, *S*)	14 (8, *S*)	–	
3		–[a]	99	81 (6, *S*)	9	10	
4		–	99	45 (<1, *S*)	30	25	
5	1-Heptene (**3b**)	C_6H_{12}	42	66 (37, *S*)	24	8	+1.5 (c = 2.3)
6		C_6H_{14}	13	47 (24, *S*)	53	–	
7		C_6H_6[b]	90	68 (17, *S*)	20	2	
8	1-Octene (**3c**)	C_6H_{12}	11	24 (35, *S*)	26	50	+2.5 (c = 1.0)
9		C_6H_{14}[b]	61	35 (12, *S*)	10	16	
10		C_6H_6[b]	98	51 (10, *S*)	35	11	
11	1-Nonene (**3d**)	C_6H_{12}	23	50 (23, *S*)	18	33	+1.1 (c = 0.5)
12		C_6H_6[b]	70	44 (13, *S*)	20	6	
13	1-Decene (**3e**)	C_6H_{12}	18	50 (24, *S*)	38	11	+2.4 (c = 1.3)
14		C_6H_{14}	42	55 (26, *S*)	37	8	+1.3 (c = 2.7)
15		C_6H_6[b]	94	57 (2, *S*)	23	14	
16		–[a]	55	29 (14, *S*)	51	20	
17		–	56 (15 h)	34 (20, *S*)	46	20	
18	4-Methyl-1-pentene (**3f**)	C_6H_{12}	53	55 (25, *S*)	45	–	+1.4 (c = 1.4)
19		C_6H_6[b]	95	75 (15, *S*)	10	10	
20		–	91	55 (10, *S*)	37	8	
21	Vinylcyclohexane	C_6H_6	30	77 (24, *R*)	13	10	+4.8 (c = 0.9)[d]
22	(**3g**)	–	74	70 (6, *R*)	7	23	+1.2 (c = 3.3)
Catalyst **2**							
23	**3a**	C_6H_{14}	78	67 (26, *R*)	24	9	−3.5 (c = 1.3) [4],[e]
24	**3e**	C_6H_{14}	65	66 (10, *R*)	18	16	−0.6 (c = 1.6)
25		C_6H_{12}	58	66 (7, *R*)	17	17	
26		–	77	59 (9, *R*)	19	22	
27	**3f**	C_6H_6	40	60 (12, *R*)	40	-	−1.0 (c = 2.3)
28	**3g**	–	66	79 (6, *S*)	16	5	−1.0 (c = 2.1)

[a] 2 mol% [Zr].
[b] Solvent volume is reduced to 10 times.
[c] Determined by GC-MS of deuterolysis products.
[d] Lit. data for (2*S*)-cyclohexylbutane-l,4-diol: $[\alpha]_D^{25} = -17.5$ (c = 0.49, EtOH) [5a].
[e] Lit. data for (2*R*)-butyl-1,4-butanediol: $[\alpha]_D^{25} = -1$ (c = 1.5, EtOH) [5b].

intermediate of the cycloalumination reaction is five-membered complex **12** [12], which is formed from the alkylchloride **11**, responsible for the carboalumination pathway (Scheme 2). It is also known that stereoselectivity of zirconocene complexes in alkene polymerization may depend on the conformational behavior of the substituted η^5- ligands [13,14]. Apparently, the reaction of Zr complexes with $AlEt_3$ gives the definite rotamers of Zr,Al-complex **12** (Scheme 2), which populations and effective concentration change with the reaction conditions (solvent, temperature, reagent ratio).

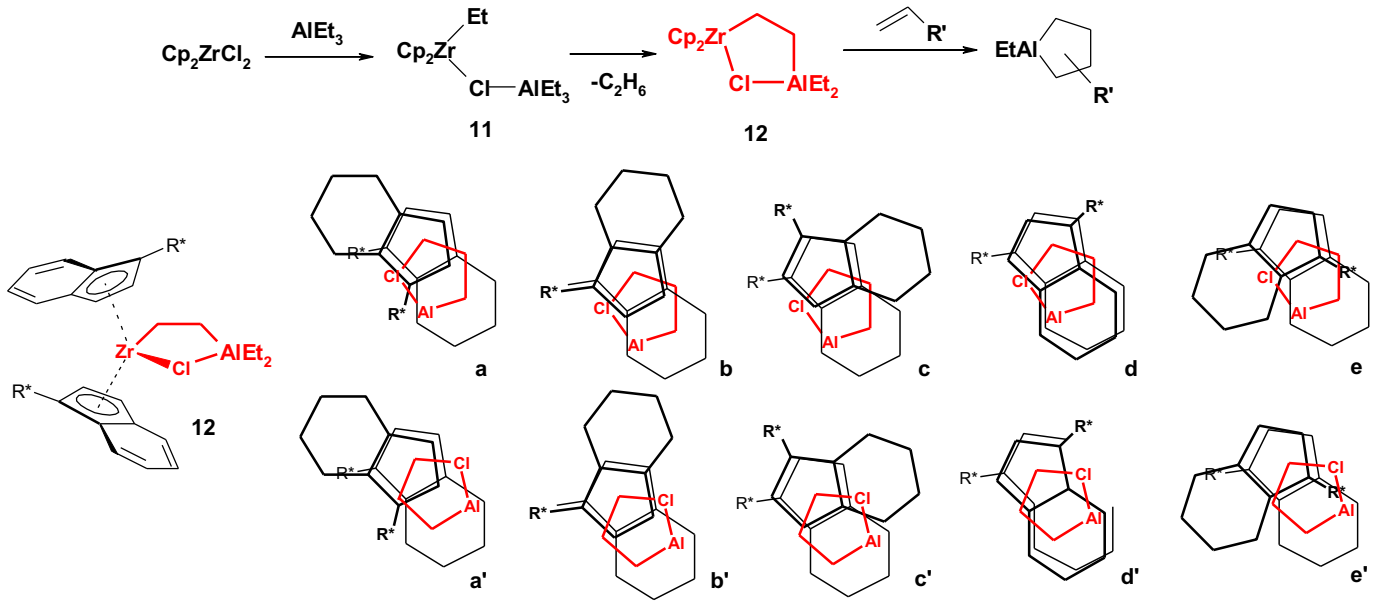
The analysis of complex **12** possible conformers shows that a large number of rotamers could exist (incidentally, the number of rotamers can be much greater than indicated in Scheme 2). Nevertheless, only a few conformers, for example, **12a**–**c,e**, has Zr–C bond accessible for alkene coordination. Thus, the cycloalumination reaction runs under a kinetic control, where the steric factor prevails, and the maximum reaction rate is achieved for the less constrained conformers.

Moreover, the kinetic control is confirmed by the fact that the increasing size of the alkene substituent decreases the substrate conversion and enantiomeric excess of the cyclic OAC. Probably, alkenes, substituted with bulky *i*-butyl-, and cyclohexyl-groups, have to "find" the least sterically hindered conformers, thereby decreasing the rate and the enantioselectivity of the reaction. As a result, the "Key–Lock" principle is realized here, while a high reaction enantioselectivity is achieved due to the perfect fit between the geometry of Zr,Al-complex as the catalytically active center and the substrate.

3. Conclusions

It was shown that the enantioselectivity of the catalytic alkene cycloalumination depends on the catalyst and the alkene structure, as well as on the solvent nature. The reaction of the terminal alkenes with $AlEt_3$, catalyzed with complex **1**, in hydrocarbon solvents gives predominantly *S*-enantiomers of 3-alkylsubstituted aluminacyclopentanes with 24–37%ee. Complex **2** shows smaller stereoinduction effect and provides *R*-enantiomers of aluminacyclopentanes with 6–26%ee.

Also, it was shown that MTPA and (*R*)-2-phenylselenopropanoic acid appears to be effective for enantiomeric excess estimation of β-alkyl-1,4-butanediols obtained from aluminacyclopentanes.



Scheme 2.

4. Experimental section

4.1. General

All operations with organometallic compounds were carried out under argon using Schlenk techniques. Solvents (benzene, hexane, cyclohexane) were dried by refluxing over i-Bu_2AlH and freshly distilled prior to use. Methylene chloride was dried over P_2O_5. THF was freshly distilled from sodium/benzophenone. Commercially available 98% $AlEt_3$ were involved in the reactions. Catalysts **1, 2** were prepared from (+)-3-[(1′*S*,2′*S*,5′*R*)-2′-isopropyl-5′-methylcyclohexyl]indene (3-neomenthylindene) and $ZrCl_4$ [(99.5%, Aldrich) or $CpZrCl_3$ using the standard techniques [6,13]. Complex **2** is unstable in air and light, especially in solution, therefore, it was synthesized immediately prior to use. (*R*)-Phenylselenopropanoic acid was synthesized according to the procedure described in Ref. [7].

The ^1H and ^{13}C NMR spectra were recorded on a Bruker AVANCE-400 spectrometer (400.13 MHz (^1H), 100.62 MHz (^{13}C), 76.35 MHz (^{77}Se)). Benzene-d_6, toluene-d_8 and $CDCl_3$ were used as solvents. The samples were prepared in standard tubes of 5 mm diameter. Chemical shifts are internally referenced to the TMS signal. NMR ^{77}Se shifts are given relative to the Me_2Se. Two-dimensional NMR spectra (COSY, HSQC, HMBC) were measured with standard pulse sequences.

The hydrolysis products of the reaction mixture were analyzed on a Carlo Erba gas chromatograph (He, column 50,000 × 0.32 mm, fixed phase 'Ultra-1', flame-ionization detector). Mass spectra were obtained on MD 800, TRIO 1000 VG Masslab (Great Britain) spectrometer.

The enantioselectivity of the carbo- and cyclometallation reactions was determined from the enantiomeric purity of corresponding alcohols, which were derived after the oxidation and hydrolysis of a reaction media. The alcohols were derivatised with (*S*)-(+)-α-methoxy-α-trifluoromethylphenylacetyl chloride [(*S*)-MTPA-Cl] or (*R*)-phenylselenopropanoic acid [(*R*)-PSPA], and the obtained diastereomeric esters analyzed by ^1H and ^{13}C NMR spectroscopy. Analysis of the (*R,R*)- and (*R,S*)-diastereomers of the MTPA esters of the β-substituted 1,4-butanediols **7a**–**g** was carried out using ^{13}C NMR spectra obtained as a result of long-term accumulation (~30,000 sc). Optical rotation angles $[\alpha]_D$ were determined on a Perkin Elmer-341 polarimeter.

5. Synthesis of (+)-3-[(1′*S*,2′*S*,5′*R*)-2′-Isopropyl-5′-methylcyclohexyl]indene (3-neomenthylindene) (improved)

Indene (80 mmol, 9.4 ml) was added dropwise to a suspension of 80 mmol of NaH (3.2 g of 60% NaH in paraffin) in 150 ml of THF. The mixture was stirred at room temperature to complete NaH dissolution. To this mixture a solution of 19.4 g (62.5 mmol) of (−)-menthyl tosylate in 100 ml of THF was added dropwise at 0 °C. The mixture was stirred for 1 h at room temperature and then refluxed for 72 h. The mixture was hydrolyzed with water (100 ml). The organic phase was separated and the aqueous phase was extracted twice with ether (50-ml portions). The combined organic layers were dried over Na_2SO_4. The solvent was evaporated in vacuum and the remaining residue was separated by column chromatography on silica gel (hexane/$CHCl_3$ 7:1). 3-Neomenthylindene (7 g, 44 %) was obtained by vacuum distillation (110 °C, 10 mm Hg) of the first fractions of column chromatography. Physical chemistry constants and NMR characteristics of obtained 3-neomenthylindene were identical to the literature data [13].

5.1. Reaction of terminal alkenes with $AlEt_3$ in the presence of complexes *1* or *2*

A 10 ml flask equipped with a magnetic stirrer and filled with argon was loaded with 0.02–0.075 mmol of complexes **1** or **2**, 3 ml of a solvent (benzene, hexane, cyclohexane), 1 mmol of alkenes (**3a**–**g**) and 1.2 mmol of $AlEt_3$. The reaction mixture was stirred for 24 h at 22 °C. Then, a part of the reaction mixture was decomposed with 10% HCl or DCl at 0 °C. The products were extracted with benzene; further, the organic layer was dried over Na_2SO_4 and analyzed by GC or GC-MS. Another part of the reaction mixture was cooled to 0 °C and a dry oxygen was passed through for 2 h. The resultant mixture was further stirred under oxygen atmosphere for 24 h, and then treated with 10% HCl and extracted with Et_2O. The organic layer was dried over Na_2SO_4, filtered, and concentrated. Alcohols **7a**–**g** were separated by column chromatography. The chromatography of the mixture **7** + **8** on silica gel (hexane/Et_2O

4:1) provided compound **8**; then the column was washed with acetone to give **7a**–**g** as a colorless oils. The organic fractions were concentrated and dried over Na_2SO_4. MTPA esters of **7a**–**g** were prepared as described in Ref. [6] PSPA esters of **7a**–**g** were prepared according to Ref. [7].

*5.1.1. (2R,S)-pentyl-1,4-butanediol (**7b**)*

^{1}H NMR ($CDCl_3$) δ_H 0.89 (3H, t, $^3J_{HH}$ = 6.4 Hz, CH_3), 1.17–1.40 (8H, m, CH_2), 1.52–1.76 (3H, m, C*H*C*H*$_2$CH$_2$OH), 3.47 (1H, dd, $^2J_{HH}$ = 10.8 Hz, $^3J_{HH}$ = 6.8 Hz, CHCH*H*OH), 3.59–3.70 (1H, m, CHC*H*HOH) 3.64–3.72 (1H, m, CH$_2$CHHOH), 3.74–3.84 (1H, m, CH$_2$C*H*HOH). ^{13}C NMR ($CDCl_3$) δ_C 14.1 (C_9), 22.6 (C_8), 26.8 (C_6), 32.1 (C_7), 31.7 (C_5), 35.8 (C_3), 39.4 (C_2), 61.2 (C_4), 66.4 (C_1).

*5.1.2. (2R,S)-hexyl-1,4-butanediol (**7c**)*

n_D^{22} = 1.4555, IR (KBr, cm^{-1}): 3341, 2926, 1465, 1045. ^{1}H NMR (400.13 MHz, $CDCl_3$) δ_H 0.89 (3H, t, $^3J_{HH}$ = 6.9 Hz, CH_3), 1.17–1.38 (10H, m, CH_2), 1.53–1.77 (2H, m, CHC*H*$_2$CH$_2$OH), 1.59–1.72 (2H, m, C*H*CH$_2$OH), 3.50 (1H, dd, $^2J_{HH}$ = 10.4 Hz, $^3J_{HH}$ = 7.2 Hz, CHCH*H*OH), 3.63–3.72 (1H, m, CHC*H*HOH) 3.62–3.72 (m, 1H, CH$_2$CHHOH), 3.75–3.84 (m, 1H, CH$_2$C*H*HOH). ^{13}C NMR ($CDCl_3$) δ_C 14.1 (C_{10}), 22.6 (C_9), 27.1 (C_6), 29.6 (C_7), 31.8 (C_5), 31.8 (C_8), 35.8 (C_3), 39.4 (C_2), 61.2 (C_4), 66.4 (C_1).

*5.1.3. (2R,S)-heptyl-1,4-butanediol (**7d**)*

^{1}H NMR ($CDCl_3$) δ_H 0.90 (3H, t, $^3J_{HH}$ = 7.04 Hz, CH_3), 1.20–1.40 (m, 12H, CH_2), 1.52–1.78 (3H, m, C*H*C*H*$_2$CH$_2$OH), 3.52 (1H, dd, $^2J_{HH}$ = 10.7 Hz, $^3J_{HH}$ = 6.8 Hz, CHCH*H*OH), 3.62–3.73 (1H, m, CHC*H*HOH) 3.62–3.73 (1H, m, CH$_2$CHHOH), 3.77–3.85 (1H, m, CH$_2$C*H*HOH). ^{13}C NMR ($CDCl_3$) δ_C 14.1 (C_{11}), 22.7 (C_{10}), 27.1 (C_6) 29.3 (C_8), 29.9 (C_7), 31.7 (C_5), 31.9 (C_9), 35.8 (C_3), 39.3 (C_2), 61.3 (C_4), 66.4 (C_1).

*5.1.4. (2R,S)-octyl-1,4-butanediol (**7e**)*

n_D^{22} = 1.4565, IR (KBr, cm^{-1}): 3329, 2925, 1465, 1046. ^{1}H NMR ($CDCl_3$) δ_H 0.86 (3H, t, $^3J_{HH}$ = 6.4 Hz, CH_3), 1.13–1.37 (14H, m, CH_2), 1.50–1.69 (3H, m, C*H*C*H*$_2$CH$_2$OH), 3.40 (1H, dd, $^2J_{HH}$ = 10.8 Hz, $^3J_{HH}$ = 6.8 Hz, CHCH*H*OH), 3.56–3.63 (1H, m, CHC*H*HOH) 3.56–3.59 (1H, m, CH$_2$CHHOH), 3.69–3.75 (1H, m, CH$_2$C*H*HOH). ^{13}C NMR ($CDCl_3$) δ_C 14.1 (C_{12}), 22.7 (C_{11}), 27.1 (C_6) 29.3 (C_9), 29.6 (C_8), 29.9 (C_7), 31.7 (C_5), 31.9 (C_{10}), 35.9 (C_3), 39.4 (C_2), 61.2 (C_4), 66.5 (C_1).

*5.1.5. (2R,S)-isobutyl-1,4-butanediol (**7f**)*

n_D^{22} = 1.4520, IR (KBr, cm^{-1}): 3329, 2955, 1468, 1040. ^{1}H NMR ($CDCl_3$) δ_H 0.88 (6H, d, J_{HH} = 6.0 Hz, CH_3), 0.90 (6H, d, J_{HH} = 6.4 Hz, CH_3), 1.04–1.22 (2H, m, CH_2), 1.57–1.68 (1H, m, CH), 1.49–1.62 (1H, m, CH*H*CH$_2$OH), 1.64–1.74 (1H, m, C*H*HCH$_2$OH), 1.67–1.78 (1H, m, C*H*CH$_2$OH), 3.43 (1H, dd, $^2J_{HH}$ = 10.8 Hz, $^3J_{HH}$ = 7. Hz, CHCHHOH), 3.64 (1H, dd, $^2J_{HH}$ = 10.8 Hz, $^3J_{HH}$ = 4.0 Hz, CHC*H*HOH) 3.60–3.68 (1H, m, CH$_2$CHHOH), 3.76 (1H, ddd, $^2J_{HH}$ = 10.4 Hz, $^3J_{HH}$ = 6.4 Hz, $^3J_{HH}$ = 4.4 Hz, CH$_2$C*H*HOH). ^{13}C NMR ($CDCl_3$) δ_C 22.7, 22.9 (C_7, C_8), 25.2 (C_6), 36.0 (C_3), 37.1 (C_2), 41.1 (C_5), 61.1 (C_4), 66.5 (C_1).

*5.1.6. (2R,S)-cyclohexyl-1,4-butanediol (**7g**)*

n_D^{22} = 1.4910, IR (KBr, cm^{-1}): 3329, 2923, 1449, 1043. ^{1}H NMR ($CDCl_3$) δ_H 0.95–1.12 (2H$_{ax}$, m, Cy), 1.57–1.72 (2H$_{eq}$, m, Cy), 1.13–1.31 (2H$_{ax}$, m, Cy), 1.71–1.80 (2H$_{eq}$, m, Cy), 1.015–1.2 (1H$_{ax}$, m, Cy), 1.61–1.71 (1H$_{eq}$, m, Cy), 1.34–1.44 (1H, m, C*H*CHCH$_2$OH), 1.45–1.53 (1H, m, CHC*H*CH$_2$OH), 1.54–1.66 (1H, m, CHC*H*HCH$_2$OH), 1.68–1.78 (1H, m, CHCH*H*CH$_2$OH), 3.58 (1H, dd, $^2J_{HH}$ = 10.6 Hz, $^3J_{HH}$ = 7.8 Hz, CHCHHOH), 3.71 (1H, dd, $^2J_{HH}$ = 10.8 Hz, $^3J_{HH}$ = 3.6 Hz, CHC*H*HOH), 3.64 (1H, ddd, $^2J_{HH}$ = 10.8 Hz, $^3J_{HH}$ = 8.0 Hz , $^3J_{HH}$ = 4.4 Hz, CH$_2$CHHOH), 3.81 (1H, ddd, $^2J_{HH}$ = 10.8 Hz, $^3J_{HH}$ = 6.4 Hz , $^3J_{HH}$ = 4.4 Hz, CH$_2$C*H*HOH). ^{13}C NMR ($CDCl_3$) δ_C 26.6, 26.7, 26.8 (C_7, C_8, C_9), 30.1, 30.2 (C_6, C_{10}), 33.4 (C_3), 40.2 (C_5), 45.0 (C_2), 61.9 (C_4), 64.9 (C_1).

*5.1.7. (R)-MTPA ester of (2R,S)-pentyl-1,4-butanediol (**9b**)*

^{1}H NMR (C_7D_8) δ_H 0.85 (3H, t, $^3J_{HH}$ = 7.1 Hz, CH_3), 0.95–1.25 (6H, m, CH$_2$(C*H*$_2$)$_3$CH$_3$), 1.25–1.49 (2H, m, C*H*$_2$CH$_2$OH), 1.42–1.56 (1H, m, CH), 1.51–1.72 (2H, m, C*H*$_2$CHCH$_2$OH), 3.88 (1H, dd, $^2J_{HH}$ = 11.1 Hz, $^3J_{HH}$ = 5.1 Hz, CHCH*H*OH), 3.94–4.08 (1H, m, CHC*H*HOH), 3.94–4.13 (2H, m, CH$_2$C*H*$_2$OH), 3.40 (6H, s, OCH_3), 6.85–7.35 (4H, m, Ph), 7.52–7.92 (6H, m, Ph). ^{13}C NMR (C_7D_8) δ_C 13.7 (C_9), 22.3 (C_8), 25.9 (C_6), 29.66 (*RRR*), 29.84 (*SRR*) (C_3), 30.36 (*SRR*), 30.44 (*RRR*) (C_5), 31.7 (C_7), 33.92 (*RRR*), 34.02 (*SRR*) (C_2), 54.8 (OCH_3), 63.5 (C_4), 67.5 (C_1), 123.7 (q, J_{C-F} = 287 Hz, CF_3), 125.2, 127.3, 127.6, 127.8, 132.4, 133.8 (Ph), 166.0, 168.9 (C=O).

*5.1.8. (R)-MTPA ester of (2R,S)-hexyl-1,4-butanediol (**9c**)*

^{1}H NMR (C_7D_8) δ_H 0.97 (3H, t, $^3J_{HH}$ = 7.3 Hz, CH_3), 1.06–1.24 (10H, m, CH(C*H*$_2$)$_5$CH$_3$), 1.41–1.51 (2H, m, C*H*$_2$CH$_2$OH), 1.50–1.58 (1H, m, C*H*CH$_2$OH), 3.94 (1H, dd, $^2J_{HH}$ = 11.1 Hz, $^3J_{HH}$ = 5.1 Hz, CHCH*H*OH), 4.01–4.17 (3H, m, CHC*H*HOH, CH$_2$C*H*$_2$OH), 3.47 (6H, s, OCH_3), 6.91–7.10 (4H, m, Ph), 7.62–8.05 (6H, m, Ph). ^{13}C NMR (C_7D_8) δ_C 14.0 (C_{10}), 22.7 (C_9), 26.5 (C_6), 29.3 (C_7), 29.77 (*RRR*), 29.94 (*SRR*) (C_3), 30.52 (*SRR*), 31.50 (*RRR*) (C_5), 31.6 (C_8), 34.03 (*RRR*), 34.13 (*SRR*) (C_2), 54.9 (OCH_3), 63.5 (C_4), 67.5 (C_1), 84.7 (q, J = 27.6 Hz, CH_3OC), 124.3 (q, J_{C-F} = 286 Hz, CF_3), 127.2–130.2 (Ph), 166.0 (C=O).

*5.1.9. (R)-MTPA ester of (2R,S)-heptyl-1,4-butanediol (**9d**)*

^{1}H NMR (C_7D_8) δ_H 0.91 (3H, t, $^3J_{HH}$ = 7.1 Hz, CH_3), 1.02–1.26 (12H, m, CH(C*H*$_2$)$_6$CH$_3$), 1.36–1.52 (2H, m, C*H*$_2$CH$_2$OH), 1.55–1.64 (1H, m, C*H*CH$_2$OH), 3.90 (1H, dd, $^2J_{HH}$ = 11.1 Hz, $^3J_{HH}$ = 5.3 Hz, CHCH*H*OH), 3.96–4.18 (3H, m, CHC*H*HOH, CH$_2$C*H*$_2$OH), 3.45 (6H, s, OCH_3), 6.77–7.35 (4H, m, Ph), 7.50–7.93 (6H, m, Ph). ^{13}C NMR (C_7D_8) δ_C 14.0 (C_{11}), 22.7 (C_{10}), 26.4 (C_6), 29.2 (C_8), 29.7 (C_7), 29.83 (*RRR*), 29.98 (*SRR*) (C_3), 30.48 (*SRR*), 30.58 (*RRR*) (C_5), 31.6 (C_9), 34.09 (*RRR*), 34.20 (*SRR*) (C_2), 54.9 (OCH_3), 63.6 (C_4), 67.6 (C_1), 84.7 (q, J = 27.8 Hz, CH_3OC), 123.7 (q, J_{C-F} = 288 Hz, CF_3), 127.2–130.2 (Ph), 166.1, 166.2 (C=O).

*5.1.10. (R)-MTPA ester of (2R,S)-octyl-1,4-butanediol (**9e**)*

^{1}H NMR (C_7D_8) δ_H 0.90 (3H, t, $^3J_{HH}$ = 6.8 Hz, CH_3), 0.97–1.12 (12H, m, CH(C*H*$_2$)$_6$CH$_2$CH$_3$), 1.12–1.21 (2H, m, C*H*$_2$CH$_3$), 1.41–1.50 (2H, m, C*H*$_2$CH$_2$OH), 1.50–1.59 (1H, m, CH), 3.85 (1H, dd, $^2J_{HH}$ = 11.2 Hz, $^3J_{HH}$ = 6.4 Hz, CHCH*H*OH), 3.94–4.18 (3H, m, CHC*H*HOH, CH$_2$C*H*$_2$OH), 3.48 (6H, s, OCH_3), 7.05–7.14 (4H, m, Ph), 7.51–7.89 (6H, m, Ph). ^{13}C NMR (C_7D_8) δ_C 14.0 (C_{12}), 22.6 (C_{11}), 26.5 (C_6), 29.3 (C_9), 29.5 (C_8), 29.7 (C_7) 29.73 (*RRR*), 29.79 (*SRR*) (C_3), 30.57 (*SRR*), 30.65 (*RRR*) (C_5), 31.9 (C_{10}) 34.06 (*RRR*), 34.17 (*SRR*) (C_2), 54.96 (OCH_3), 63.7 (C_4), 67.7 (C_1), 84.8 (q, J = 27.0 Hz, CH_3OC), 123.0 (q, J_{C-F} = 288 Hz, CF_3), 127.3–130.2 (Ph), 166.1 (C=O).

*5.1.11. (R)-MTPA ester of (2R,S)-isobutyl-1,4-butanediol (**9f**)*

^{1}H NMR (C_7D_8) δ_H 0.67 (3H, d, ^3J = 6.0 Hz, CH_3), 0.68 (3H, d, ^3J = 6.0 Hz, CH_3), 0.76–0.82 (1H, m, (CH$_3$)$_2$CHCH*H*), 0.89–1.0 (1H, m, (CH$_3$)$_2$CHC*H*H), 1.25–1.49 (2H, m, C*H*$_2$CH$_2$OH), 1.27–1.36 (1H, m, (CH$_3$)$_2$C*H*), 1.54–1.68 (1H, m, C*H*CH$_2$OH), 3.83–3.91 (1H, m, CHCH*H*OH), 3.95–4.03 (1H, m, CHC*H*HOH), 3.95–4.10 (2H, m, CH$_2$C*H*$_2$OH), 3.40 (6H, s, OCH_3), 6.74–7.33, 7.48–7.90 (10H, Ph). ^{13}C NMR (C_7D_8) δ_C 21.8 (C_8), 24.77 (*SRR*), 24.82 (*RRR*) (C_6), 22.5 (C_7), 30.21 (*RRR*), 30.38 (*SRR*) (C_3), 31.64 (*RRR*), 31.78 (*SRR*) (C_2), 39.82 (*SRR*), 40.00 (*RRR*) (C_5), 63.48 (*RRR*), 63.56 (*SRR*) (C_4), 67.7 (C_1), 54.93 (OCH3), 84.7 (q, J = 26.2 Hz), 123.1 (q, J_{C-F} = 287 Hz), 127.3–130.2 (Ph), 166.1, 166.2 (C=O).

*5.1.12. (R)-MTPA ester of (2R,S)-cyclohexyl-1,4-butanediol (**9g**)*

^{1}H NMR (C_7D_8) δ_H 0.58–0.75 (2H, m, C*H*$_{ax}$HCH (Cy)), 1.22–1.39 (2H, m, CH*H*$_{eq}$CH (Cy)), 0.89–1.11 (3H, m, C*H*$_{ax}$HCH$_2$ (Cy)), 1.48–

1.62 (3H, m, CH$H_{eq}$$CH_2$ (Cy)), 1.00–1.13 (1H, m, $CH$$CHCH_2OH$), 1.29–1.39 (1H, m, $CH$$CH_2OH$), 1.26–1.36 (1H, m, $CH$$HCH_2OH$), 1.44–1.54 (1H, m, $CH$$HCH_2OH$), 3.91 (1H, dd, ^2J = 11.6 Hz, ^3J = 5.7 Hz, $CH_2CH$$HOH$) (*SRR*), 3.95–4.04 (1H, m, $CH_2CH$$HOH$) (*RRR*), 4.07–4.15 (1H, m, $CH_2CH$$HOH$) (*SRR*, *RRR*), 3.93–4.15 (2H, m, $CHCH_2OH$), 3.41 (6H, s, OCH_3), 6.75–7.58 (10H, Ph). ^{13}C NMR (C_7D_8) δ_C 26.16, 26.30, 26.32 (C_8, C_9, C_{10}, (Cy)), 29.3, 29.4 (C_6, C_7, (Cy)), 27.12 (*SRR*), 27.23 (*RRR*) (C_3), 38.39 (*RRR*), 38.47 (*SRR*) (C_5), 39.15 (C_2), 64.11 (C_4), 66.24 (*SRR*), 66.28 (*RRR*) (C_1), 54.9 (OCH_3), 84.5 (q, J = 26.4 Hz, $COCH_3$), 123.5 (q, J_{C-F} = 288 Hz), 127.3–130.2 (Ph), 166.0 (C=O).

5.1.13. (R)-phenylselenopropanoic acid ester of (2R,S)-butyl-1,4-butanediol (**10a**)

^{1}H NMR ($CDCl_3$) δ_H 0.89 (3H, t, CH_3CH_2, ^3J = 6.8 Hz), 1.20–1.29 (4H, m, $(CH_2)_2$), 1.22–1.31 (2H, m, CH_3CH_2), 1.54 (3H, d, CH_3CH, ^3J = 7.2 Hz), 1.55 (3H, d, CH_3CH, ^3J = 7.2 Hz), 1.51 (2H, pent, $CHCH_2CH_2O$, ^3J = 6.8 Hz), 1.58–1.67 (1H, m, CH_2CHCH_2O), 3.73–3.83 (2H, m, CH_3CH), 3.91 (1H, dd, $CHCHHO$, ^2J = 11.2 Hz, ^3J = 5.6 Hz), 3.97 (1H, dd, $CHCHHO$, ^2J = 11.2 Hz, ^3J = 5.6 Hz), 3.98–4.09 (2H, m, CH_2CH_2O), 7.25–7.35 (6H, m, Ph), 7.55–7.62 (4H, m, Ph). ^{13}C NMR ($CDCl_3$) δ_C 14.0 (C_8), 17.65, 17.70, 17.73 (CH_3CH), 22.8 (C_7), 28.8 (C_6), 30.7 (C_5), 30.10 (*RRR*), 30.17 (*SRR*) (C_3), 34.39 (*RRR*), 34.42 (*SRR*) (C_2), 37.6 (SeCH), 63.0 (C_4), 67.13 (*RRR*), 67.16 (*SRR*) (C_1), 173.4, 173.5 (C=O), 127.90, 127.94, 127.99, 128.42, 128.45, 129.00, 129.02, 135.4, 135.6, 135.97 (Ph). ^{77}Se NMR ($CDCl_3$) δ_{Se} 453.50 (*RRR*), 453.89 (*RRR*), 454.08 (*SRR*), 454.25 (*SRR*).

5.1.14. (R)-phenylselenopropanoic acid ester of (2R,S)-pentyl-1,4-butanediol (**10b**)

^{1}H NMR ($CDCl_3$) δ_H 0.90 (3H, t, CH_3CH_2, ^3J = 6.9 Hz), 1.19–1.39 (8H, m, $(CH_2)_4$), 1.557 (3H, d, CH_3CH, ^3J = 7.0 Hz), 1.564 (3H, d, CH_3CH, ^3J = 7.1 Hz), 1.51 (2H, pent, $CHCH_2CH_2O$, ^3J = 6.8 Hz), 1.59–1.69 (1H, m, CH_2CHCH_2O), 3.74–3.85 (2H, m, CH_3CH), 3.93 (1H, dd, $CHCHHO$, ^2J = 11.1 Hz, ^3J = 5.6 Hz), 3.98 (1H, dd, $CHCHHO$, ^2J = 11.1 Hz, ^3J = 5.3 Hz), 4.00–4.15 (2H, m, CH_2CH_2O), 7.24–7.39 (6H, m, Ph), 7.56–7.65 (4H, m, Ph). ^{13}C NMR ($CDCl_3$) δ_C 14.1 (C_9), 17.67, 17.71, 17.75 (CH_3CH), 22.6 (C_8), 26.3 (C_6), 32.0 (C_7), 30.12 (*SRR*), 30.14 (*RRR*) (C_3), 30.9 (C_5), 34.42 (*RRR*), 34.46 (*SRR*) (C_2), 37.3 (SeCH), 63.0 (C_4), 67.15 (*RRR*), 67.18 (*SRR*) (C_1), 173.4, 173.5 (C=O), 127.7, 128.43, 128.46, 129.01, 129.04, 135.4, 135.5 (Ph). ^{77}Se NMR ($CDCl_3$) δ_{Se} 453.36 (*RRR*), 453.78 (*RRR*), 453.98 (*SRR*), 454.16 (*SRR*).

5.1.15. (R)-phenylselenopropanoic acid ester of (2R,S)-Hexyl-1,4-butanediol (**10c**)

^{1}H NMR ($CDCl_3$) δ_H 0.90 (3H, t, CH_3CH_2, ^3J = 6.3 Hz), 1.21–1.38 (10H, m, $(CH_2)_5$), 1.50 (2H, pent, $CHCH_2CH_2O$, ^3J = 6.2 Hz), 1.58 (6H, d, CH_3CH, ^3J = 6.9 Hz), 1.61–1.69 (1H, m, CH_2CHCH_2O), 3.73–3.87 (2H, m, CH_3CH), 3.92 (1H, dd, ^3J = 5.3 Hz, ^2J = 10.9 Hz, $CHCHHO$), 3.98 (1H, dd, ^3J = 6.0 Hz, ^2J = 10.9 Hz, $CHCHHO$), 3.99–4.11 (2H, m, CH_2CH_2O), 7.17–7.39 (6H, m, Ph), 7.53–7.69 (4H, m, Ph). ^{13}C NMR ($CDCl_3$) δ_C 14.1 (C_{10}), 17.67, 17.71, 17.75 (CH_3CH), 22.6 (C_9), 26.6 (C_6), 29.9 (C_7), 30.11 (*SRR*), 30.16 (*RRR*) (C_3), 30.9 (C_5), 31.8 (C_8), 34.41 (*RRR*), 34.45 (*SRR*) (C_2), 37.3 (SeCH), 63.1 (C_4), 67.18 (*RRR*), 67.21 (*SRR*) (C_1), 127.7, 128.45, 128.49, 128.99, 135.4, 135.6 (Ph), 173.5, 173.6 (C=O). ^{77}Se NMR ($CDCl_3$) δ_{Se} 453.58 (*RRR*), 454.04 (*RRR*), 454.23 (*SRR*), 454.43 (*SRR*).

5.1.16. (R)-phenylselenopropanoic acid ester of (2R,S)-heptyl-1,4-butanediol (**10d**)

^{1}H NMR ($CDCl_3$) δ_H 0.90 (3H, t, CH_3CH_2, ^3J = 6.8 Hz), 1.20–1.34 (12H, m, $(CH_2)_6$), 1.51 (2H, pent, $CHCH_2CH_2O$, ^3J = 6.8 Hz), 1.55 (3H, d, CH_3CH, ^3J = 7.2 Hz), 1.56 (3H, d, CH_3CH, ^3J = 6.8 Hz), 1.60–1.67 (1H, m, CH_2CHCH_2O), 3.73–3.84 (2H, m, CH_3CH), 3.92 (1H, dd, ^3J = 5.7 Hz, ^2J = 11.1 Hz, $CHCHHO$), 3.98 (1H, dd, ^3J = 5.7 Hz, ^2J = 11.1 Hz, $CHCHHO$), 3.98–4.09 (2H, m, CH_2CH_2O), 7.24–7.42 (6H, m, Ph), 7.55–7.65 (4H, m, Ph). ^{13}C NMR ($CDCl_3$) δ_C 14.1 (C_{11}), 17.67, 17.70, 17.74 (CH_3CH), 22.7 (C_{10}), 26.7 (C_6), 29.2 (C_8), 29.9 (C_7), 30.11 (*SRR*), 30.17 (*RRR*) (C_3), 31.0 (C_5), 31.9 (C_9), 34.42 (*RRR*), 34.46 (*SRR*) (C_2), 37.3 (SeCH), 63.1 (C_4), 67.17 (*RRR*), 67.20 (*SRR*) (C_1), 127.7, 128.0, 128.9, 129.04, 129.2, 135.4, 135.6 (Ph), 173.5, 173.6 (C=O). ^{77}Se NMR ($CDCl_3$) δ_{Se} 453.40 (*RRR*), 453.82 (*RRR*), 454.02 (*SRR*), 454.21 (*SRR*).

5.1.17. (R)-phenylselenopropanoic acid ester of (2R,S)-octyl-1,4-butanediol (**10e**)

^{1}H NMR ($CDCl_3$) δ_H 0.87 (3H, t, CH_3CH_2, ^3J = 6.5 Hz), 1.20–1.30 (6H, m, $(CH_2)_3$), 1.50 (2H, pent, $CHCH_2CH_2O$, ^3J = 6.8 Hz), 1.45–1.56 (1H, m, CH_2CHCH_2O), 1.54 (3H, d, CH_3CH, ^3J = 7.1 Hz), 1.55 (3H, d, CH_3CH, ^3J = 7.0 Hz), 3.70–3.84 (2H, m, CH_3CH), 3.87–4.01 (2H, m, $CHCH_2HO$), 3.98–4.08 (2H, m, CH_2CH_2O), 7.22–7.39 (6H, m, Ph), 7.52–7.64 (4H, m, Ph). ^{13}C NMR ($CDCl_3$) δ_C 14.1 (C_{12}), 17.66, 17.70, 17.75 (CH_3CH), 26.6 (C_9), 29.3 (C_8), 29.5 (C_7), 29.9 (C_6), 31.0 (C_5), 30.09 (*SRR*), 30.15 (*RRR*) (C_3), 31.9 (C_{10}), 34.40 (*RRR*), 34.44 (*SRR*) (C_2), 37.3 (SeCH), 63.0 (C_4), 67.13 (*RRR*), 67.15 (*SRR*) (C_1), 127.1, 127.7, 128.42, 128.46, 129.0, 129.04, 135.4, 135.6 (Ph), 173.4, 173.5 (C=O). ^{77}Se NMR ($CDCl_3$) δ_{Se} 453.44 (*RRR*), 453.87 (*RRR*), 454.06 (*SRR*), 454.27 (*SRR*).

5.1.18. (R)-phenylselenopropanoic acid ester of (2R,S)-isobutyl-1,4-butanediol (**10f**)

^{1}H NMR ($CDCl_3$) δ_H 0.83–0.92 (6H, m, CH_3), 0.99–1.22 (2H, m, $CHCH_2CH$), 1.44–1.52 (2H, m, $CHCH_2CH_2O$), 1.45–1.52 (1H, m, CH_2CHCH_2O), 1.53–1.60 (6H, m, CH_3CH), 1.54–1.66 (1H, m, CH_3CHCH_3), 3.74–3.86 (2H, m, CH_3CH), 3.86–4.03 (2H, m, $CHCH_2O$), 3.99–4.08 (2H, m, CH_2CH_2O), 7.23–7.37 (6H, m, Ph), 7.56–7.64 (4H, m, Ph). ^{13}C NMR ($CDCl_3$) δ_C 17.7 (CH_3CH), 23.7 (C_7), 23.8 (C_8), 25.16 (C_6), 30.47 (*RRR*), 30.56 (*SRR*) (C_3), 32.21 (*RRR*), 32.27 (*SRR*) (C_2), 37.34, 37.38 (SeCH), 40,51 (*RRR*), 40.54 (*SRR*) (C_5), 62.96 (*RRR*), 63.0 (*SRR*) (C_4), 67.4 (C_1), 127.22, 127.72, 128.44, 128.47, 129.01, 129.04, 135.40, 135.57, 135.60 (Ph), 173.4, 173.5 (C=O). ^{77}Se NMR ($CDCl_3$) δ_{Se} 453.32 (*RRR*), 454.13 (*RRR*), 454.37 (*SRR*), 454.42 (*SRR*).

5.1.19. (R)-phenylselenopropanoic acid ester of (2R,S)-cyclohexyl-1,4-butanediol (**10g**)

^{1}H NMR (C_7D_8) δ_H 0.92–1.04 (2H, m, CH_{ax}HCH (Cy)), 1.54–1.63 (2H, m, CHH_{eq}CH (Cy)), 1.11–1.23 (3H, m, $CH_{ax}HCH_2$ (Cy)), 1.57–1.67 (3H, m, CH$H_{eq}CH_2$ (Cy)), 1.28–1.39 (1H, m, $CHCHCH_2O$, Cy), 1.56 (6H, d, CH_3CH, ^3J = 7.4 Hz), 1.54–1.63 (2H, m, CH_2CH_2O), 1.58–1.67 (1H, m, $CHCH_2O$), 3.72–3.84 (2H, m, $CHCH_3$), 3.97–4.11 (2H, m, CH_2CH_2O), 3.90–3.98 (1H, m, $CHCHHO$), 4.02–4.10 (1H, m, $CHCHHO$), 7.22–7.41 (6H, m, Ph), 7.55–7.69 (4H, m, Ph). ^{13}C NMR ($CDCl_3$) δ_C 17.70 (CH_3CH), 26.6, 26.7, 29.99, 30.01 (Cy), 29.74 (*SRR*), 29.77 (*RRR*) (C_3), 37.4 (SeCH), 38.96 (*RRR*), 39.04 (*SRR*) (C_5, Cy), 39.6 (C_2), 63.8 (C_4), 65.8 (C_1), 127.6, 127.7, 128.4, 128.9, 129.00, 129.03, 134.8, 135.4, 135.6, 135.9, (Ph), 173.1 (C=O). ^{77}Se NMR ($CDCl_3$) δ_{Se} 453.39 (*SRR*), 453.88 (*SRR*), 453.64 (*RRR*), 454.22 (*RRR*).

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Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2012.10.021.

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