Monatsh Chem (2013) 144:183–190
DOI 10.1007/s00706-012-0792-7

ORIGINAL PAPER

Asymmetric synthesis of new chiral 1,2- and 1,3-diols

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Received: 4 November 2011 / Accepted: 8 May 2012 / Published online: 12 June 2012

Abstract Seven chiral 1,2-diols and six chiral 1,3-diols were synthesized by the asymmetric reduction of the corresponding 1,2-diketones and 1,3-diketones using oxazaborolidine–BH_3 catalyst. The 13 corresponding racemic 1,2- and 1,3-diols were synthesized by reducing the diketones with $NaBH_4$ and they were used for determining the ee values through their chiral resolution on HPLC and GC. Five starting diketones, four racemic 1,2-diols, five chiral 1,2-diols, and two chiral 1,3-diols are novel compounds. The new chiral compounds were characterized by IR, ^1H and ^{13}C NMR, MS, and elemental analysis. The asymmetric reduction method, oxazaborolidine–BH_3, was applied to these diketones for the first time in this study. The relationship between the structure of the diketone and the yield, diastereoselectivity, and enantiomeric excess was discussed.

Keywords Asymmetric synthesis · Chiral 1,2-diol · Chiral 1,3-diol · Diketone · Reduction

Introduction

Chiral diols are structural motifs often found in various important natural products and have also been proven valuable as chiral ligands and auxiliaries in stereoselective organic syntheses. The enantioselective synthesis of chiral diols is still a stimulating subject. One of the most successful methods is the enantioselective reduction of prochiral diketones by chiral catalysts and reagents. During the past few years, a large number of reducing agents and chiral catalysts have been developed that facilitate the reduction reaction under a wide range of conditions [1–3]. Although hydrogenation in the presence of diphosphine–Ru (or Rh) complexes [4, 5] and hydride reduction promoted by chiral organoboranes [6–8] have been reported to be very effective on a broad range of ketones, only a limited number of examples have been applied for the enantio- and diastereoselective reduction of diketones of different structure. Amongst them the development of methods for the diastereoselective reduction of carbonyl groups continues to be of interest in organic chemistry [9, 10]. In particular, chemical routes towards *vicinal* diols in terms of stereospecificity and enantioselectivity include the catalytic *cis*-dihydroxylation of olefins with OsO_4 [11, 12] and the catalytic asymmetric transfer hydrogenation of diketones [13]. Biocatalytic methods for the synthesis of diols are the kinetic resolution of racemic diols achieved by enzymatic oxidation [14] and the enzymatic and microbial reduction of diketones [15, 16].

The oxazaborolidine-mediated enantioselective reduction of ketones with borane is a well-established methodology. Since the famous CBS (Corey–Bakshi–Shibata) oxazaborolidine catalyst was obtained by Corey et al. [17, 18] from (*R*)- or (*S*)-proline, a number of new chiral oxazaborolidines have been synthesized and used widely in asymmetric reductions. Among the characteristics of the CBS-catalyzed enantioselective reduction of prochiral ketones are its high reaction rate and high enantioselectivity. Recently, we successfully reported the asymmetric reduction of prochiral monoketones by (*R*)-(+)-2-methyl-CBS-oxazaborolidine (*R*-Me-CBS) [19]. The *R*-Me-CBS reduction was applied to biphenyl alkyl diketones (lignin models) [20], 1,3-ferrocenyldiketones [21], and tetralin-

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1,4-dione [22]. Additionally, some C_2-symmetric diketones were reduced with *erythro*-diphenyl oxazaborolidine [23].

In this study we applied this stereoselective (*R*)-oxazaborolidine–borane reduction to 1,2-diketones **1a**–**1g** and 1,3-diketones **1h**–**1p**, in order to prepare chiral 1,2-diols **2a**–**2g** and 1,3-diols **2h**–**2p**, and $NaBH_4$ for the synthesis of racemic 1,2- and 1,3-diols. **2b**, **2c**, **2d**, and **2e** are new racemic diols. Amongst the chiral 1,2-diols the five chiral 1,2-diols **2a**–**2e** and two chiral 1,3-diols **2m** and **2n** are novel.

Results and discussion

Thirteen chiral diols **2a**–**2p** with alkyl and aryl, substituted aryl, hetero aryl, and biaryl groups were synthesized for the first time in this study by asymmetric CBS–BH_3 reduction of the corresponding diketones **1a**–**1p**. The five new 1,2-diketones **1a**–**1e** were synthesized by oxidation of their corresponding alkenes using $KMnO_4$ and a phase transfer agent (Scheme 1) [24].

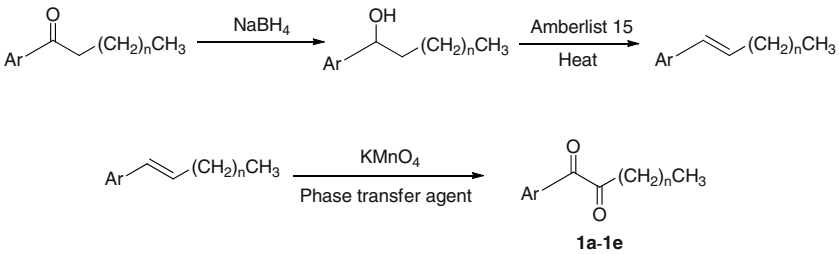
In the literature survey *R*-Me-CBS was the best reducing catalyst [9] exposing very high ee values for the ketones. The (*S*) enantiomers of some aryl–alkyl substituted secondary carbinols were synthesized with excellent ee values by us via asymmetric reduction method with *R*-Me-CBS [19]. In this study, the five new 1,2-diketones **1a**–**1e**, two commercially available 1,2-diketones **1f**, **1g**, and all six purchased 1,3-diketones **1h**–**1p** of different structure were reduced to the corresponding diols **2a**–**2p** using *R*-Me-CBS for the first time. When diketones **1a**–**1p** were treated with $BH_3{\cdot}Me_2S$ (1:2 diketone/borane ratio) in the presence of 60 mol% of *R*-Me-CBS in THF at 0 °C to rt, the reduction was completed within 1 h according to the known stereochemical course of CBS-catalyzed reduction of ketones [17]. In order to compare and determine the ee values of the chiral diols, the corresponding diketones were reduced by $NaBH_4$ to racemic diols that were resolved on chiral HPLC or GC. Newly synthesized 1,2- and 1,3-diols were characterized according to their ^{1}H NMR and HPLC or GC spectra.

The *syn* and *anti* diastereoisomers of the diols and their diastereomeric ratios were defined by ^{1}H NMR (Table 1). The HPLC traces of the racemic diols contained four peaks and those of meso diols three peaks. The retention times of the *syn* and *anti* enantiomers, which were resolved on chiral HPLC, are given in the "Experimental" section. Since no similar standards were available for **2a**–**2e**, **2g**, and **2k**–**2p**, the absolute configurations of these compounds could not be determined. The configurations of the diols **2f**, **2h**, and **2j** were established via literature data. The reduction with $NaBH_4$ gave the racemic diols in high yields by slightly favoring the *syn* diastereoisomer as shown in Table 2.

The influence of substrate structure on the stereoselectivity of the reaction was examined using the catalyst *R*-Me-CBS. Unsymmetrical 1,2-diols with different aromatic groups showed similar stereoselectivity. The best results were obtained for **2d** with a dr ratio of 84:16 (Table 1, entry 4). Amongst 1,3-diols the best dr ratio was obtain for **2m** (dr = 92:8) (Table 1, entry 11).

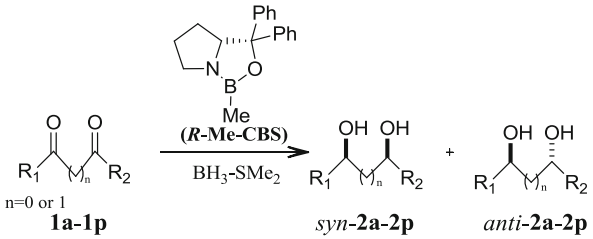
The 1,2-diketones **1a**–**1g** and 1,3-diketones **1k**–**1p**, which have no rotation between the two carbonyl groups, exhibited *syn* diastereoselectivity. The 1,3-diketones with

Scheme 1



Diketone	Diol	Ar	n
1a	**2a**	Ph	15
1b	**2b**	*p*-MeC_6H_4	10
1c	**2c**	*p*-$MeOC_6H_4$	11
1d	**2d**	2-Thienyl	13
1e	**2e**	2-Naphthyl	10

Table 1 Asymmetric reduction of prochiral diketones with *R*-Me-CBS



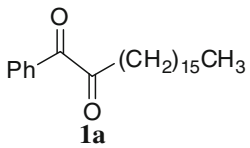
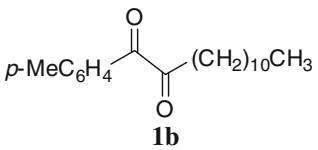
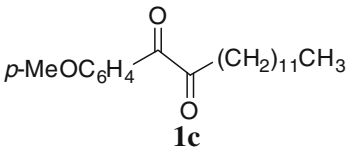
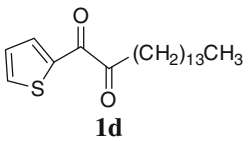
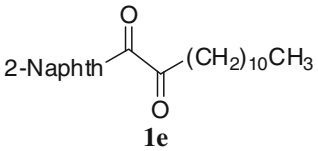
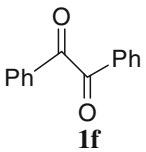
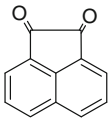
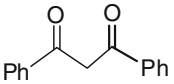
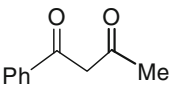
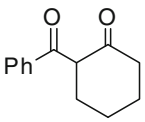
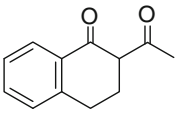
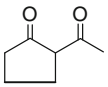
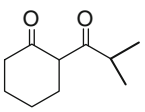
Entry	Substrate	Yield[a]/%	dr[b] (*syn/anti*)	ee[c] (*syn/anti*)	Conf.[d] (*syn/anti*)
1	 **1a**	50	72/28	n.d./50	n.d.
2	 **1b**	40	78/22	54/60	n.d.
3	 **1c**	70	75/25	62/54	n.d.
4	 **1d**	25	84/16	70/42	n.d.
5	 **1e**	64	72/28	68/54	n.d.
6	 **1f**	95	100/0	0	*meso*

Table 1 continued

Entry	Substrate	Yield[a]/%	dr[b] (*syn/anti*)	ee[c] (*syn/anti*)	Conf.[d] (*syn/anti*)
7	 **1g**	83	75/25	22/n.d.	n.d.
8	 **1h**	22	17/83	0/66	*meso*/(*S*,*S*)
9	 **1j**	20	30/70	20/87	(*S*,*S*)/(*R*,*S*)
10	 **1k**	20	68/32	>99/>99	n.d.
11	 **1m**	21	92/8	72/>99	n.d.
12	 **1n**	40	77/23	85/12	n.d.
13	 **1p**	60	64/36	>99/83	n.d.

[a] Isolated yield of products

[b] The dr was determined by ^{1}H NMR

[c] The ee was determined by HPLC or GC analysis

[d] Absolute configurations could not be determined (n.d.) except of **2f**, **2h**, and **2j**

Table 2 Comparison of dr rates in the racemic and asymmetric reductions

Entry	Substrate	Racemic reduction dr (*syn/anti*)	Asymmetric reduction dr (*syn/anti*)	Asymmetric reduction ee (*syn/anti*)
1	**1a**	58/42	72/28	n.d./50
2	**1b**	60/40	78/22	54/60
3	**1c**	65/35	75/25	62/54
4	**1d**	60/40	84/16	70/42
5	**1e**	55/45	72/28	68/54
6	**1f**	66/34	100/0	0
7	**1g**	57/53	75/25	2/n.d.
8	**1h**	46/54	17/83	0/66
9	**1j**	47/53	30/70	20/87
10	**1k**	54/46	68/32	>99/>99
11	**1m**	50/50	92/8	72/>99
12	**1n**	58/42	77/23	85/12
13	**1p**	50/50	64/36	>99/83

free rotation **1h** and **1j**, which have one methylene group between the two carbonyl groups, exhibited *anti* diastereoselectivity. In this work all substrates **1a**–**1p** have two prochiral centers. The absolute configurations of the chiral diols **2a**–**2p** could not be determined in this study because of the lack of the similar diols with fixed configuration.

Conclusion

The synthesized chiral 1,2-diols **2a**–**2g** and 1,3-diols **2h**–**2p** are new compounds and they are valuable intermediates in the preparation of new ligands and in the synthesis of several natural molecules. These chiral diols were obtained by the diastereoriched reduction of 13 prochiral diketones of different structure via the *R*-Me-CBS catalyst. According to the literature survey, this catalyst has not previously been applied to the asymmetric reduction of the 1,2 and 1,3-diketones achieved in this study. The diastereomeric ratios of the new chiral diols were determined by chiral HPLC or GC and their structures were analyzed by IR, ^{1}H and ^{13}C NMR, MS, and elemental analysis. The five new 1,2-diketones **1a**–**1e** were synthesized for the first time in this study by oxidation of the corresponding alkenes (Scheme 1) [24].

Experimental

The majority of the chemicals used in this work were commercially available from Merck or Aldrich. The alkenes used for the synthesis of diketones were obtained from the corresponding alcohols by elimination of water using known methods. The racemic diols were prepared by the reduction of the corresponding diketones with $NaBH_4$ in methanol/THF. The reactions were monitored by TLC using silica gel plates and the products were purified by flash column chromatography on silica gel (Merck, 230–400 mesh) with hexane/ethyl acetate. NMR spectra were recorded at 500 MHz for ^{1}H and 125 MHz for ^{13}C using Me_4Si as the internal standard in $CDCl_3$. GC–MS spectra were recorded on a Shimadzu QP2010 Plus. IR spectra were recorded on a Mattson 1000. Melting points were determined with a Büchi Melting Point B-540. Enantiomeric excess (ee) of the chiral alcohols was determined with a Shimadzu DGU-20A_5 HPLC apparatus fitted with a 25 cm Chiralcel OD chiral column. The enantiomeric excess of diols **2n** and **2p** was determined by GC on a 25 m × 0.25 mm CP Cyclodex B 236M column.

*General procedure for synthesis of diketones **1a–1e***

Alkene (10 mmol) was dissolved in 25 cm^3 of methylene chloride and 5 cm^3 of acetic acid in a three-necked, round-bottomed flask equipped with a mechanical stirrer. About 0.5 g of phase transfer agent (benzyl triethyl ammonium chloride was used in this study, different from the literature [24]) dissolved in 20 cm^3 of methylene chloride was added, followed by powdered potassium permanganate (30 mmol) in small portions over 2 h. An ice bath was used to maintain the temperature below 30 °C. The mixture was then stirred vigorously overnight, cooled, and treated with 20 cm^3 of water and 1 g of sodium bisulfite to reduce any excess oxidant. After 20 min the solution was acidified with concentrated HCl and the excess potassium permanganate was reduced by addition, in small portions, of the required amount of sodium bisulfide. Any solid carboxylic acids which precipitated were collected by filtration, and the organic layer was separated. The aqueous layer was saturated with sodium chloride and extracted with ether (2 × 30 cm^3) and the aqueous layer was separated. The ether layers were combined, washed once with 30 cm^3 of 5 % NaOH solution and water, then dried over anhydrous Na_2SO_4. Evaporation was carried out under reduced pressure after filtration. The crude yellow product was purified by column chromatography (*n*-hexane/EtOAc 8:2).

1-Phenyl-1,2-octadecanedione (**1a**, $C_{24}H_{38}O_2$)
M.p.: 31.2–32.4 °C; 25 % yield; IR (KBr): $\bar{\nu}$ = 3,082, 2,953, 2,860, 1,715, 1,700, 1,607, 1,456, 1,407, 1,302, 1,153, 1,078, 708, 698 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.80 (t, 3H, J = 7.3 Hz), 1.12–1.62 (m, 28H), 2.79 (t, 2H, J = 7.3 Hz), 7.20–7.90 (m, 5H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.60, 22.11, 24.57, 26.85, 28.34, 29.63, 36.85, 37.51, 128.51, 129.10, 132.58, 132.70,

190.71, 202.78 ppm; MS: m/z = 43, 57, 77, 97, 108, 117, 134, 254, 282, 328, 358 (M^+).

1-(4-Methylphenyl)-1,2-tridecanedione (**1b**, $C_{20}H_{30}O_2$)
M.p.: 24.3–25.5 °C; 16 % yield; IR (KBr): $\bar{\nu}$ = 3,038, 2,938, 2,853, 1,746, 1,700, 1,615, 1,461, 1,384, 1,238, 1,053, 830, 738 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 0.80 (t, 3H, J = 6.8 Hz), 1.18–1.79 (m, 18H), 2.08 (t, 2H, J = 3.9 Hz), 2.30 (s, 3H), 7.20 (d, 2H, J = 7.8 Hz), 7.80 (d, 2H, J = 8.3 Hz) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.14, 21.49, 23.26, 24.57, 26.96, 28.02, 29.62, 37.51, 130.39, 130.49, 132.44, 146.19, 190.71, 202.75 ppm; MS: m/z = 41, 57, 77, 97, 107, 118, 122, 134, 145, 183, 223, 237, 288, 302 (M^+).

1-(4-Methoxyphenyl)-1,2-tetradecanedione (**1c**, $C_{21}H_{32}O_3$)
M.p.: 35.4–36.7 °C; 20 % yield; IR (KBr): $\bar{\nu}$ = 3,038, 2,923, 2,861, 1,715, 1,669, 1,615, 1,469, 1,438, 1,323, 1,269, 1,184, 869, 723 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 0.80 (t, 3H, J = 7.3 Hz), 1.10–1.70 (m, 22H), 2.78 (t, 2H, J = 7.8 Hz), 3.80 (s, 3H), 6.90 (d, 2H, J = 9.2 Hz), 7.90 (d, 2H, J = 9.2 Hz) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.96, 22.44, 24.57, 26.85, 28.02, 29.63, 37.51, 55.30, 130.00, 131.40, 162.94, 190.71, 202.78 ppm; MS: m/z = 41, 57, 77, 97, 107, 108, 122, 136, 145, 164, 223, 226, 302, 318, 332 (M^+).

1-(2-Thienyl)-1,2-hexadecanedione (**1d**, $C_{20}H_{32}O_2S$)
M.p.: 28.3–29.1 °C; 15 % yield; IR (KBr): $\bar{\nu}$ = 3,100, 2,930, 2,853, 1,715, 1,638, 1,461, 1,415, 1,362, 1,261, 1,046, 753, 698 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 0.80 (t, 3H, J = 6.8 Hz), 1.14–1.38 (m, 22H), 1.68 (pent, 2H, J = 7.3 Hz), 2.82 (t, 2H, J = 7.8 Hz), 7.05 (dd, 1H, J_1 = 3.9 Hz, J_2 = 4.8 Hz), 7.52 (dd, 1H, J_1 = 0.9 Hz, J_2 = 4.8 Hz), 7.62 (dd, 1H, J_1 = 0.9 Hz, J_2 = 3.9 Hz) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.60, 22.11, 24.20, 26.85, 28.02, 29.63, 30.85, 37.58, 129.61, 131.70, 132.33, 145.74, 186.09, 201.87 ppm; MS: m/z = 43, 57, 69, 85, 108, 112, 136, 140, 154, 223, 254, 302, 322, 336 (M^+).

1-(2-Naphthyl)-1,2-tridecanedione (**1e**, $C_{23}H_{30}O_2$)
M.p.: 19.2–20.1 °C; 30 % yield; IR (KBr): $\bar{\nu}$ = 3,053, 2,930, 2,860, 1,711, 1,680, 1,600, 1,507, 1,300, 1,287, 1,248, 1,040, 793, 746 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 0.80 (t, 3H, J = 6.9 Hz), 1.10–1.70 (m, 18H), 2.90 (t, 2H, J = 7.8 Hz), 7.40–8.90 (m, 7H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.14, 23.26, 24.60, 26.96, 28.02, 29.61, 32.40, 37.51, 125.10, 128.00, 130.80, 132.52, 133.72, 134.35, 190.71, 202.77 ppm; MS: m/z = 44, 57, 69, 82, 96, 129, 156, 165, 184, 212, 281, 308, 338 (M^+).

General procedure for reduction of prochiral diketones by (R)-(+)-2-methyl-CBS-oxazaborolidine (R-Me-CBS)

In a typical procedure, to a solution of *R*-Me-CBS (0.36 mmol, 0.36 cm^3 of 1 M solution in toluene) was added $BH_3{\cdot}Me_2S$ (2 M in THF, 1.5 mmol, 0.75 cm^3) and the mixture was stirred under nitrogen atmosphere, then cooled to 0 °C. After 10 min of stirring, a solution of diketone (0.6 mmol) in 5 cm^3 of THF was added within 40 min at 0 °C. The reaction mixture was maintained at rt for 1 h and then quenched with 2 M HCl. The solution was extracted with 30 cm^3 ether. The aqueous layer was separated and was extracted once more with 80 cm^3 ether. The ether layers were combined, washed once with water, and dried over anhydrous Na_2SO_4. Evaporation was carried out under reduced pressure after filtration. The residue was purified by column chromatography (*n*-hexane/EtOAc).

1-Phenyl-1,2-octadecanediol (**2a**, $C_{24}H_{42}O_2$)
M.p.: 72.2–73.2 °C; 50 % yield; ee not determined for *syn*, 50 % ee for *anti*, *syn*/*anti* = 72:28; HPLC analysis: Chiralcel OD chiral column, mobile phase *i*-PrOH/hexane 5:95, flow rate 0.5 cm^3/min, wavelength 210 nm; t_R: t_{anti} (major) = 16.249 min, t_{anti} (minor) = 17.049 min, t_{syn} (major + minor) = 18.611 min; IR (KBr): $\bar{\nu}$ = 3,353, 3,069, 2,915, 2,861, 1,500, 1,476, 1,376, 1,246, 1,084, 1,061, 769, 707 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 0.82 (t, 3H, J = 6.8 Hz), 1.12–1.42 (m, 32H), 3.75 (m, 1H), 4.60 (d, 1H, J = 4.3 Hz), 7.22–7.32 (m, 5H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.10, 21.60, 24.60, 24.80, 28.20, 30.01, 30.60, 31.00, 31.60, 74.20, 76.00, 125.80, 126.80, 127.40, 139.50 ppm; MS: m/z = 43, 57, 77, 97, 108, 117, 131, 207, 253, 328, 341 (M^+-H_2O).

1-(4-Methylphenyl)-1,2-tridecanediol (**2b**, $C_{20}H_{34}O_2$)
M.p.: 31.3–32.6 °C; 40 % yield; 54 % ee for *syn*, 60 % ee for *anti*, *syn*/*anti* = 78:22; HPLC analysis: Chiralcel OD chiral column, mobile phase *i*-PrOH/hexane 7:93, flow rate 0.8 cm^3/min, wavelength 210 nm; t_R: t_{anti} (major) = 16.162 min, t_{anti} (minor) = 17.316 min, t_{syn} (minor) = 18.160 min, t_{syn} (major) = 18.847 min; IR (KBr): $\bar{\nu}$ = 3,423, 3,292, 3,023, 2,930, 2,846, 1,538, 1,469, 1,269, 1,107, 1,046, 807, 730 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 0.82 (t, 3H, J = 6.3 Hz), 1.12–1.32 (m, 18H), 1.48–1.52 (m, 4H), 2.30 (s, 3H), 3.75 (m, 1H), 4.60 (d, 1H, J = 4.3 Hz), 7.08–7.22 (m, 4H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.09, 21.30, 21.69, 23.91, 23.94, 28.14, 28.69, 30.93, 33.12, 33.17, 63.31, 63.37, 125.80, 128.13, 168.05, 173.31 ppm; MS: m/z = 43, 57, 77, 97, 107, 117, 122, 131, 145, 183, 207, 272 (M^+-H_2O).

1-(4-Methoxyphenyl)-1,2-tetradecanediol (**2c**, $C_{21}H_{36}O_3$)
M.p.: 72.5–73.2 °C; 70 % yield; 62 % ee for *syn*, 54 % ee for *anti*, *syn*/*anti* = 75:25; HPLC analysis: Chiralcel OD chiral column, mobile phase *i*-PrOH/hexane 7:93, flow rate 1 cm^3/min, wavelength 210 nm; t_R: t_{anti} (minor) = 21.317 min, t_{anti} (major) = 22.742 min, t_{syn} (minor) = 24.185 min, t_{syn} (major) = 25.199 min; IR (KBr): $\bar{\nu}$ = 3,273, 3,195, 3,008, 2,914, 2,848, 1,614, 1,470, 1,284, 1,176, 1,106, 1,028, 827, 718 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.81 (t, 3H, J = 6.8 Hz), 1.11–1.45 (m, 22H), 1.50 (s, 1H), 1.70 (s, 1H), 3.50 (m, 1H), 3.71 (s, 3H), 4.54 (d, 1H, J = 3.5 Hz), 6.71–7.42 (m, 4H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.19, 23.01, 24.60, 29.20, 30.01, 32.00, 32.50, 55.52, 75.00, 78.00, 114.01, 128.02, 133.00, 160.05 ppm; MS: m/z = 43, 57, 69, 77, 121, 137, 147, 161, 302, 318 (M^+-H_2O).

1-(2-Thienyl)-1,2-hexadecanediol (**2d**, $C_{20}H_{36}O_2S$)
M.p.: 55.2–56.9 °C; 25 % yield; 70 % ee for *syn*, 42 % ee for *anti*, *syn*/*anti* = 84:16; HPLC analysis: Chiralcel OD chiral column, mobile phase *i*-PrOH/hexane 7:93, flow rate 1 cm^3/min, wavelength 210 nm; t_R: t_{anti} (minor) = 12.299 min, t_{anti} (major) = 15.317 min, t_{syn} (minor) = 16.852 min, t_{syn} (major) = 19.086 min; IR (KBr): $\bar{\nu}$ = 3,200, 3,195, 3,047, 2,914, 2,847, 1,671, 1,511, 1,299, 1,176, 1,135, 1,061, 771, 690 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.81 (t, 3H, J = 6.3 Hz), 1.13–1.52 (m, 28H), 3.70 (m, 1H), 4.81 (d, 1H, J = 3.9 Hz), 6.81–7.42 (m, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.31, 22.89, 25.97, 29.29, 29.90, 32.13, 32.56, 73.71, 74.98, 124.70, 125.85, 126.74, 143.38 ppm; MS: m/z = 43, 57, 69, 85, 97, 114, 225, 267, 306, 322, 341 (M^+).

1-(2-Naphthyl)-1,2-tridecanediol (**2e**, $C_{23}H_{34}O_2$)
M.p.: 78–79.3 °C; 64 % yield; 68 % ee for *syn*, 54 % ee for *anti*, *syn*/*anti* = 72:28; HPLC analysis: Chiralcel OD chiral column, mobile phase *i*-PrOH/hexane 10:90, flow rate 1 cm^3/min, wavelength 210 nm; t_R: t_{syn} (minor) = 6.518 min, t_{syn} (major) = 9.431 min, t_{anti} (major) = 12.063 min, t_{anti} (minor) = 21.389 min; IR (KBr): $\bar{\nu}$ = 3,353, 3,276, 3,052, 2,912, 2,847, 1,616, 1,456, 1,232, 1,164, 1,099, 1,059, 778, 735 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.81 (t, 3H, J = 6.8 Hz), 1.12–1.60 (m, 20H), 1.80 (br s, 1H), 2.70 (br s, 1H), 4.01 (m, 1H), 5.52 (d, 1H, J = 4.3 Hz), 7.38–8.43 (m, 7H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.10, 22.01, 25.60, 28.20, 29.01, 30.00, 31.00, 32.40, 73.00, 75.00, 122.00, 128.00, 129.80, 132.70, 135.50 ppm; MS: m/z = 44, 57, 69, 82, 96, 129, 158, 167, 207, 281, 308, 341 (M^+).

meso-1,2-Diphenylethane-1,2-diol (**2f**)
M.p.: 145.3–146 °C (Ref. [25] 142–144 °C); 95 % yield; 0 % ee for *meso*, *syn*/*anti* = 100:0; HPLC analysis: Chiralcel OD chiral column, mobile phase *i*-PrOH/hexane 1:99, flow rate 1 cm^3/min, wavelength 210 nm; t_R: t_{anti} = 20.480 and 21.070 min (not observed), t_{syn} (meso) = 22.380 min.

1,2-Dihydro-1,2-acenaphthylenediol (**2g**)
M.p.: 207.2–209.4 °C (Ref. [26] 208.5–209.5 °C); 83 % yield; 22 % ee for *syn*, not determined for *anti*, *syn*/*anti* = 75:25; HPLC analysis: the enantiomeric excess was determined by HPLC analysis using a chiral column after derivatization to the corresponding diacetate, Chiralcel OD chiral column, mobile phase *i*-PrOH/hexane 1:99, flow rate 1 cm^3/min, wavelength 210 nm; t_R: t_{anti} (minor) = 10.848 min, t_{anti} (major) = 11.728 min, t_{syn} (major + minor) = 16.627 min.

1,3-Diphenylpropane-1,3-diol (**2h**)
M.p.: 148.8–149.9 °C (Ref. [25] 160–161 °C); 22 % yield; 0 % ee for *meso*, 66 % ee (*S*,*S*) for *anti*, *syn*/*anti* = 17:83; HPLC analysis: Chiralcel OD chiral column, mobile phase *i*-PrOH/hexane 10:90, flow rate 1 cm^3/min, wavelength 210 nm; t_R: t_{anti} (major) = 10.767 min for (*S*,*S*)-isomer, t_{anti} (minor) = 12.370 min for (*R*,*R*)-isomer, t_{syn} (meso) = 14.771 min.

1-Phenyl-1,3-butanediol (**2j**)
M.p.: 64.2–65.5 °C (Ref. [27] 65 °C); 20 % yield; 20 % ee for *syn*, 87 % ee for *anti*, *syn*/*anti* = 30:70; HPLC analysis: Chiralcel OD chiral column, mobile phase *i*-PrOH/hexane 5:95, flow rate 1 cm^3/min, wavelength 210 nm; t_R: t_{anti} (minor) = 15.417 min for (*S*,*R*)-isomer, t_{anti} (major) = 16.913 min for (*R*,*S*)-isomer, t_{syn} (major) = 17.974 min for (*S*,*S*)-isomer, t_{syn} (minor) = 24.189 min for (*R*,*R*)-isomer.

α-(2-Hydroxycyclohexyl)benzenemethanol (**2k**, $C_{13}H_{18}O_2$)
M.p.: 89.2–90.5 °C; 20 % yield; >99 % ee for *syn*, >99 % ee for *anti*, *syn*/*anti* = 68:32; HPLC analysis: Chiralcel OD chiral column, mobile phase *i*-PrOH/hexane 5:95, flow rate 1 cm^3/min, wavelength 210 nm; t_R: t_{syn} (minor) = 12.859 min (not observed), t_{syn} (major) = 13.596 min, t_{anti} (minor) = 15.099 min (not observed), t_{anti} (major) = 31.282 min; IR (KBr): $\bar{\nu}$ = 3,346, 3,061, 3,030, 2,930, 2,853, 1,453, 1,415, 1,330, 1,192, 1,076, 761, 707 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.98–1.80 (m, 10H), 3.39–3.43 (m, 1H), 4.11 (br s, 1H), 4.91 (d, 1H, J = 4.1 Hz), 7.15–7.35 (m, 5H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 18.71, 19.91, 25.87, 34.20, 48.15, 71.63, 78.17, 126.11, 127.27, 128.33, 143.44 ppm; MS: m/z = 41, 51, 54, 67, 79, 107, 117, 125, 170, 188, 207 (M^+).

1,2,3,4-Tetrahydro-2-(1-hydroxyethyl)-1-naphthalenol (**2m**, $C_{12}H_{16}O_2$)
n_D^{20} = 1.580; 21 % yield; 72 % ee for *syn*, >99 % ee for *anti*, *syn*/*anti* = 92:8; HPLC analysis: Chiralcel OD chiral column, mobile phase *i*-PrOH/hexane 10:90, flow rate 1 cm^3/min, wavelength 210 nm; t_R: t_{syn} (major) = 8.015 min, t_{syn}

(minor) = 10.031 min, t_{anti} (minor) = 10.776 min, t_{anti} (major) = 12.820 min; IR (KBr): $\bar{\nu}$ = 3,429, 3,062, 3,022, 2,970, 2,928, 1,469, 1,455, 1,397, 1,297, 1,136, 1,062, 740, 662 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 1.22 (d, 3H, J = 23.9 Hz), 1.24–1.30 (m, 3H), 1.82 (br s, 2H), 2.80 (m, 2H), 4.10 (m, 1H), 4.62 (d, 1H, J = 7.1 Hz), 7.01–7.52 (m, 4H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.95, 22.93, 28.21, 48.32, 68.92, 73.06, 125.32, 127.37, 135.38, 138.39 ppm; MS: m/z = 43, 45, 55, 65, 77, 91, 119, 129, 145, 159, 174, 192 (M^+).

2-(1-Hydroxyethyl)cyclopentanol (**2n**, $C_7H_{14}O_2$)
n_D^{20} = 1.507; 40 % yield; 85 % ee for *syn*, 12 % ee for *anti*, *syn*/*anti* = 77:23; GC analysis: the enantiomeric excess was determined after derivatization to the corresponding diacetate by GC analysis using a chiral column CP Cyclodex B 236 M capillary column (25 m × 0.25 mm), at 70 °C then 5 °C/min to 150 °C for 30 min; t_R: t_{anti} (major) = 22.833 min, t_{anti} (minor) = 23.191 min, t_{syn} (major) = 25.332 min, t_{syn} (minor) = 25.700 min; IR (KBr): $\bar{\nu}$ = 3,376, 2,961, 2,876, 1,423, 1,415, 1,330, 1,130, 1,053, 792, 661 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 1.14 (d, 3H, J = 6.3 Hz), 1.24–1.40 (m, 8H), 1.50–1.64 (m, 1H), 4.24 (m, 1H), 4.25–4.46 (m, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.90, 28.02, 32.04, 36.15, 44.00, 68.24, 76.16 ppm; MS: m/z = 41, 45, 53, 55, 65, 68, 71, 79, 84, 94, 112 ($M^+ - H_2O$).

2-(1-Hydroxy-2-methylpropyl)cyclohexanol
(**2p**, $C_{10}H_{20}O_2$)
M.p.: 104.2–105.6 °C; 60 % yield; >99 % ee for *syn*, 83 % ee for *anti*, *syn*/*anti* = 64:36; GC analysis: the enantiomeric excess was determined after derivatization to the corresponding diacetate by GC analysis using a chiral column CP Cyclodex B 236M capillary column (25 m × 0.25 mm), at 70 °C then 5 °C/min to 150 °C for 30 min; t_R: t_{anti} (minor) = 13.023 min, t_{anti} (major) = 13.428 min, t_{syn} (minor) = 14.623 min (not observed), t_{syn} (major) = 14.988 min; IR (KBr): $\bar{\nu}$ = 3,353, 2,930, 2,861, 1,415, 1,330, 1,138, 1,084, 915, 738 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 0.87 (d, 6H, J = 6.3 Hz), 1.24–1.45 (m, 11H), 1.50–1.82 (m, 1H), 3.31 (m, 1H), 3.45 (m, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 18.35, 20.05, 25.22, 26.08, 31.11, 34.20, 42.39, 72.69, 82.63 ppm; MS: m/z = 43, 55, 67, 83, 93, 111, 129, 136, 154, 171 (M^+).

Acknowledgments This study was supported by the Istanbul University Department of Scientific Research Projects (İ.Ü. Bilimsel Araştırma Projeleri Birimi) with Project Number 3099.

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