ISSN 1070-4280, Russian Journal of Organic Chemistry, 2015, Vol. 51, No. 2, pp. 202–209. © Pleiades Publishing, Ltd., 2015.
Original Russian Text © R.R. Fayzullin, O.A. Antonovich, D.V. Zakharychev, Z.A. Bredikhina, A.V. Kurenkov, A.A. Bredikhin, 2015, published in Zhurnal Organicheskoi Khimii, 2015, Vol. 51, No. 2, pp. 214–221.

Synthesis and Some Features of Phase Behavior of Chiral *p*-Alkoxyphenyl Glycerol Ethers

R. R. Fayzullin, O. A. Antonovich, D. V. Zakharychev, Z. A. Bredikhina, A. V. Kurenkov, and A. A. Bredikhin

Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Center, Russian Academy of Sciences, ul. Academika Arbuzova 8, Kazan, Tatarstan, 420088 Russia
e-mail: robert.fayzullin@gmail.com

Received September 24, 2014

Abstract—A series of (*S*)-3-(4-alkoxyphenoxy)propane-1,2-diols was prepared with the enantiomeric excess 86–92% by Sharpless asymmetric dihydroxylation of 1-alkoxy-4-allyloxybenzenes with an AD-mix-β mixture. *R*-Enantiomers with enantiomeric excess 97–99% and racemic samples were obtained by reaction of sodium *p*-substituted phenolates with (*R*)- and *rac*-3-chloropropane-1,2-diol. The phase behavior of racemates and scalemates in the produced homolog series of glycerol aryl ethers with hydrocarbon substituents of various length was examined by means of thermomicroscopy. The higher memberes of the homolog series of both racemic and scalemic diols undergo at heating an enantiotropic phase transition to a smectic liquid crystal phase.

DOI: 10.1134/S1070428015020116

Terminal ethers of glycerol are lipid-like compounds of a special interest for physical and organic chemistry owing to the molecular anisotropy and the capability to form versatile supramolecular systems linked with hydrogen bonds [1]. The presence of an asymmetric center in the hydrophilic fragment of these molecules may cause a chiral-dependent character of their phase behavior, namely, of crystallization [1], formation of mesophase [2–4] and supramolecular gels [5–7].

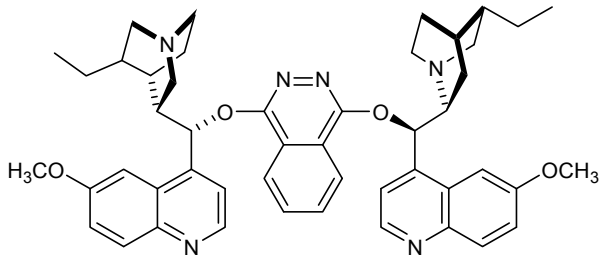
The interest to the series of 3-(4-alkoxyphenoxy)-propane-1,2-diols is due to several reasons. Some racemic specimens of this series are lyotropic and thermotropic liquid crystals [8]. Non-racemic analogs have not been studied from this viewpoint. We formerly investigated the related homolog series of racemic and enantiomeric 3-(4-alkylphenoxy)propane-1,2-diols where chiral-dependent low-molecular gelation agents and thermally induced mesogens were found [9–11]. It was established in [11] that 3-(4-propylphenoxy)propane-1,2-diol crystallized in the form of racemic conglomerate, i.e., it suffered a rare phenomenon of the spontaneous resolution of the racemate at crystallization. Some racemic 3-(4-alkoxyphenoxy)propane-1,2-diols exhibit a moderate antiviral action [12].

In this study a synthesis is described of a series of scalemic (non-racemic, enantiomerically enriched) and racemic *p*-alkoxysubstituted 3-phenoxypropane-1,2-diols and preliminary data are obtained on the features of their chiral-dependent phase behavior, in particular, the dependence of the formation of thermotropic liquid crystal phases on the enantiomeric composition of the samples and the capability of these compounds to supramolecular gel formation has been explored.

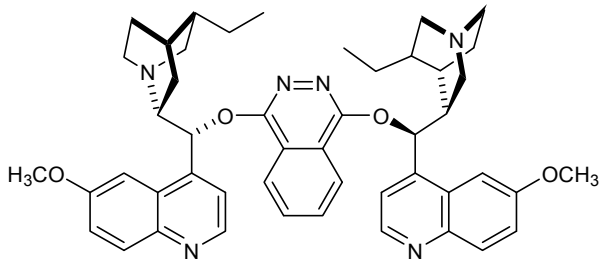
Asymmetric Sharpless dihydroxylation catalyzed with coordination compounds of OsO_4 with some chiral amines is a synthetically powerful, useful, and popular oxidation procedure for substituted olefins. This method is widely utilized now in the organic chemistry [13, 14]. In the most known version derivatives of quinine and quinidine $(DHQ)_2$-PHAL or $(DHQD)_2$-PHAL are used as ligands (Scheme 1) that are contained in commercial reagents AD-mix-α and AD-mix-β respectively.

In this study we applied Sharpless reaction to the preparation of non-racemic diols **1a**–**1g**. In the first stage from the corresponding phenols **3a**–**3g** and allyl bromide in the presence of a base K_2CO_3 the homolog series of *p*-alkoxy-substituted phenylallyl ethers **2a**–**2g** was obtained in moderate yields (~65–70%). Compounds

Scheme 1.



$(DHQ)_2$-PHAL

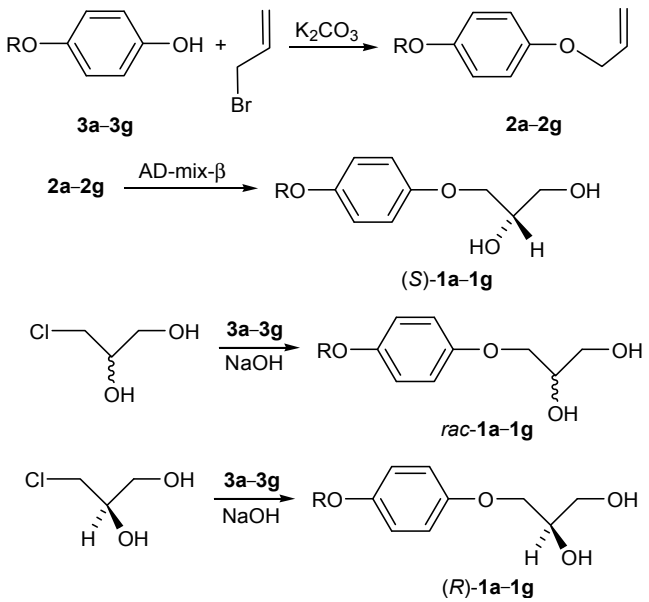


$(DHQD)_2$-PHAL

2 were oxidized by a standard procedure using the mixture AD-mix-β to obtain the target compounds. Diols *rac*-**1a**–**1g** were obtained by the reaction of *rac*-3-chloropropane-1,2-diol with the corresponding phenols **3a**–**3g** in the presence of NaOH (Scheme 2).

The stereoselectivity of the Sharpless oxidation of aryl allyl ethers **2a**–**2g** was examined by HPLC using a chiral stationary phase. According to HPLC data the dihydroxylation afforded the corresponding scalemic diols *scal*-**1a**–**1g** with a moderate enantiomer excess (*ee* 86–92%). The length of the alkoxy substituent in aryl allyl ethers **2a**–**2g** located far from the prochiral double bond virtually did not affect the enantioselectivity of the reaction.

Scheme 2.



R = Me (**a**), Et (**b**), Pr (**c**), Bu (**d**), Pentyl (**e**), Hexyl (**f**), Heptyl (**g**).

The attempts to increase the enantiomeric purity of diols *scal*-**1a**–**1g** by recrystallization failed, the *ee* values remained virtually unchanged. This may be attributed to the accidental coincidence of eutectic composition of each diol **1a**–**1g** with the enantiomeric composition of the oxidation products, but this assumption looks improbable. We believe that more probably on the phase diagrams of diols **1a**–**1g** exist prolonged practically linear fragments corresponding to solid solutions of enantiomers. This is indicated by the close values of melting points of racemic and non-racemic samples in the whole series of diols **1a**–**1g**. Testing of this hypothesis will be the subject of our further studies.

Since the enantiomeric purity of obtained diols *scal*-**1a**–**1g** was not sufficient for physicochemical investigations and also aiming at the reliable establishing of the configuration of the Sharpless oxidation products we synthesized a series of diols (*R*)-**1a**–**1g** (*ee* ≥ 97%) from (*R*)-3-chloropropane-1,2-diol (*ee* 98%) and the corresponding phenols **3a**–**3g** (Scheme 2). This reaction occurs without racemization and inversion of the asymmetric center [1, 15].

The dihydroxylation of olefins like allyl ethers **2a**–**2g** with AD-mix-β mixture leads commonly to the formation of non-racemic diols of predominantly *S*-configuration at the chiral atom C^2. The oxidation of studied aryl allyl ethers occurred along the common rule [11, 16], but an exclusion was observed for 1-allyloxy-2-nitrobenzene: the product of its reaction with AD-mix-β turned out to be enriched with the *R*-enantiomer [17].

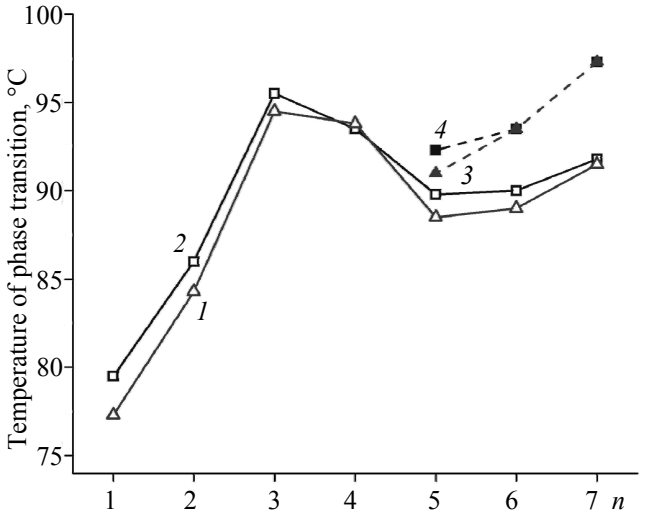
In order to determine the absolute configuration of glycerol ethers obtained by the stereoselective dihydroxylation we compared the values of their specific rotation with those of the reference samples (*R*)-**1a**–**1g**. All diols (*R*)-**1a**–**1g** have a negative sign of the specific rotation of the plane-polarized light in anhydrous methanol, whereas the dihydroxylation products in the same conditions possess a positive sign. According to HPLC data, the predominant enantiomer in the samples synthesized from (*R*)-3-chloropropane-1,2-diol has a shorter retention time,

whereas for the diols obtained from aryl allyl ethers, the enantiomer with the longer retention time prevailed. Therefore, undoubtedly the products of ethers **2** dihydroxylation with AD-mix-β are *S*-diols **1**.

Some aspects of the phase behavior of racemic glycerol ethers *rac*-**1d**–**1g** were studied in [8]. At heating in ethers *rac*-**1e**–**1g** a smectic liquid crystal phase SmA was observed. Yet, to our best knowledge, no publications exist on the phase behavior of non-racemic diols *scal*-**1a**–**1g** and racemic diols *rac*-**1a**–**1c**.

To the study of the phase behavior of compounds **1a**–**1g** we applied the method of optical polarization microscopy at a controlled heating of the sample. The data on the temperatures of the phase transitions for racemic and scalemic samples of diols *rac*- and (*R*)-**1a**–**1g** are presented in the figure. It is clearly seen that in all compounds series the temperatures of the phase transitions of the racemic and enantiomeric samples have close values. The plot of the dependence of these values on the length of the alkoxy substituent (see the figure) may be tentatively divided in two parts with the node point corresponding to diol **1d** whose melting points of racemate and scalemate are virtually identic.

In a series of ethers **1a**–**1c** the crystalline phase at melting transforms in an isotropic liquid (melt), and the temperatures of this transition considerably grow with the lengthening of the hydrocarbon substituent. In the series of compounds **1e**–**1g** the melting is accompanied with the formation of the liquid crystal phase, and the melting points and the point of the mesophase transition to the isotropic liquid monotonically grow.



Plot of temperatures of phase transitions in glycerol ethers **1a**–**1g** as a function of the number of carbon atoms (*n*) in the linear hydrocarbon substituent R. Melting points: (*1*) scalemic samples (*ee* ≥ 97%); (*2*) racemates; temperature of transition to isotropic state: (*3*) scalemic samples; (*4*) racemates.

In the other words, in compounds *rac*- and *scal*-**1e**–**1g** the transformation of a crystal into a common liquid phase is preceded by the transition into a turbid, more viscous anisotropic mesophase. The latter is easily identified by characteristic colored textures observed in microscope under a polarized light [18].

At the formation of a liquid crystal from a melt in all cases an appearance and growth was observed of seeds characteristic of smectic phase, the so-called *bâtonnets*; growing in size and combining they generated the confocal liquid-crystalline texture with large isotropic zones. The behavior and textures of racemic and scalemic samples were similar.

In contrast to analogs with alkyl substituents [10, 11] diols **1a**–**1g** are not prone to the formation of metastable (supercooled) liquid crystalline phases. A fast crystallization starts at small decrease in the temperature below the boarder of the phase transition.

A specific feature of 3-(4-alkylphenoxy)propane-1,2-diols consists in their capability to act as low-molecular gelation agents [9–11]. Such gelation agents owing to noncovalent interactions form in the solvent environment stable networks which immobilize the amount of solvent of a many times larger mass [19]. Unlike the alkyl analogs neither of diols **1a**–**1g** both in racemic and enantiomerically pure state possessed gelating properties with respect to hydrocarbon solvents. For the formation of supramolecular gels the solubility of the gelation agent is known to correspond to strict demands. On the one hand, it should not be too high in order to prevent a fast crystallization on cooling the solution. On the other hand, it should not be too low in order to ensure sufficient strength to the supramolecular network penetrating the environment to be gellated [19]. The studied *p*-alkoxy-substituted phenyl ethers of glycerol **1a**–**1g** are not sufficiently soluble in hydrocarbons at room temparature. We believe that it is just the reason of their incapability to gel formation. Another reason may originate from the crystal packing of diols **1a**–**1g** unfavorable for the formation of network or fibrillary structures.

Thus for the higher members of the series both of racemic and scalemic diols *rac*- and *scal*-**1e**–**1g** we found an existence of enantiotropic thermally induced transition into a smectic liquid crystalline phase,

whereas in the total series of compounds **1a**–**1d** the formation of metastable mesophases was not observed due to the inclination to spontaneous crystallization of a slightly supercooled melt. The behavior of racemic and scalemic samples at heating and the appearance of the liquid crystal structures proved to be similar. No one of the studied samples of ethers **1a**–**1d** exhibited an ability of supramolecular gelation of hydrocarbon solvents.

EXPERIMENTAL

NMR spectra were registered on a spectrometer Bruker Avance-500 [500.13 (^{1}H), 125.76 (^{13}C) MHz] in $CDCl_3$. Chemical shifts in the NMR spectra were measured with respect to the residual signals of solvents. IR spectra were recorded on a spectrophotometer Bruker Tensor 27. Mass spectra (EI, 70 eV) were taken on an instrument DFS Thermo Electron Corporation. Elemental analysis was carried out on a CHN-analyzer EuroVector EA3000. HPLC analysis was performed on a chromatograph Shimadzu LC-20AD equipped with UV (λ 275 nm) detector, column Chiralcel OD (0.46 × 25 cm), 20°C, flow rate 1 mL/min, eluent *i*-PrOH–hexane, 1 : 9 (**1b**–**1g**), 2 : 8 (**1a**). Optical rotation was measured on a polarimeter Perkin Elmer 341 ([α], 10^{-1}·deg·cm^2·g^{-1}; *c*, g/100 mL). Melting points and temperature of transition to isotropic state (transition point, tp) was determined on Boëtius heating block and was reported without corrections. The thermotropic phase behavior of diols **1a**–**1g** was examined by thermomicroscopy using a polarization optical microscope Polam P-312. The stage was heated with a ceramic heating element, the heating rate was determined by the voltage controlled with laboratory autotransformer. The sample temperature was controlled by electronic thermometer with a thermocouple K contacting the stage just near the sample. TLC was carried out on Silufol UV-254 (254 nm) plates, development under UV irradiation or in iodine vapor.

In the study commercial reagents were used: 4-methoxyphenol (99%) from Acros Organics; 4-ethoxyphenol (99%), 4-propoxyphenol (98%), 4-butoxyphenol (98%), 4-hexyloxyphenol (98%), racemic 3-chloropropane-1,2-diol (98%), (*R*)-3-chloropropane-1,2-diol (97%, *ee* 98%), and allyl bromide (99%) from Alfa Aesar; 4-heptyloxyphenol (97%) and AD-mix-β from Aldrich.

4-Pentyloxyphenol (3e) was obtained by a slightly modified procedure [20]. To a solution of 11.01 g (100 mmol) of 1,4-hydroquinone in 130 mL of DMSO under an argon atmosphere was added at vigorous stirring 6.17 g (110 mmol) of powdered KOH. The reaction mixture turned yellow, and thereto was added dropwise a solution of 15.1 g (100 mmol) of 1-bromopentane in 30 mL of DMSO within 0.5 h. The reaction mixture was stirred for 3 h at 40°C (TLC monitoring; R_f of the reaction product ~0.58, eluent hexane–EtOAc, 6 : 4). Then the reaction mixture was poured in 400 mL of cold water, acidified to pH 1 with dilute hydrochloric acid. The precipitate was filtered off and washed with cold water, then it was subjected to column chromatography on silica gel (eluent hexane–CH_2Cl_2, 9 : 1–4 : 6). The obtained oily substance was crystallized from hexane at cooling. Yield 36%, white needle crystals, mp 46.5–47°C (hexane). ^{1}H NMR spectrum, δ, ppm: 0.93 t (3H, CH_3, *J* 7.2 Hz), 1.33–1.47 m [4H, $CH_2(C\underline{H}_2)_2CH_3$], 1.76 quintet (2H, $CH_2C\underline{H}_2CH_2$, *J* 7.0 Hz), 3.90 t (2H, CH_2, *J* 6.6 Hz), 4.20 br.s (1H, OH), 6.73–6.81 m (4H$_{arom}$). Mass spectrum, *m/z* (I_{rel}, %): 180 (11) $[M]^+$, 144 (4), 110 (100), 81 (8), 65 (5), 53 (5), 43 (18).

Aryl allyl ethers (2a–2g). General procedure [11]. A slurry of 6 mmol of an appropriate phenol **3a**–**3g**, 0.8 g (6.6 mmol) of allyl bromide, and 0.91 g (6.6 mmol) of crushed calcined K_2CO_3 in 10 mL of anhydrous acetone was boiled at stirring for 10–12 h. The reaction was monitored by TLC (R_f of reaction products ~0.7, eluent hexane–EtOAc, 9 : 1). Then the reaction mixture was diluted with water (30 mL), the reaction products were extracted with Et_2O (3 × 40 mL). The combined extracts were washed with 1 M water solution of NaOH (15 mL) and dried with $MgSO_4$. The solvent was removed at a reduced pressure. The obtained low melting crystals **2b**, **2c**, and **2g** or oily substances **2a** and **2d**–**2f** were purified by column chromatography on silica gel, eluent hexane–EtOAc, 9 : 1–8 : 2.

1-(Allyloxy)-4-methoxybenzene (2a). Yield 65%, light yellow oily substance, bp 73–75°C (10 mmHg), n_D^{22} 1.5271 {bp 76–76.5°C (1.5 mmHg), n_D^{25} 1.5265 [21]}. IR spectrum (film), cm^{-1}: 1508, 1462, 1231, 1039, 928, 825, 522. ^{1}H NMR spectrum, δ, ppm: 3.77 s (3H, CH_3), 4.49 d.d.d (2H, CH_2O, *J* 1.5, 5.3 Hz), 5.27 d.d.t (1H, CH_2, *J* 1.5, 1.5, 10.5 Hz), 5.41 d.d.t (1H, CH_2, *J* 1.5, 1.5, 17.2 Hz), 6.06 d.d.t (1H, CH, *J* 5.3, 10.5, 17.2 Hz), 6.81–6.89 m (4H$_{Ar}$). Mass spectrum, *m/z* (I_{rel}, %): 164 (15) $[M]^+$, 123 (100), 95 (28), 63 (7), 52 (8), 41 (24).

1-(Allyloxy)-4-ethoxybenzene (2b). Yield 67%, colorless crystals, mp 44.5–45°C (mp 42.2–45°C [22]).

IR spectrum (mineral oil), cm^{-1}: 1510, 1454, 1238, 1048, 922, 821, 533. ^1H NMR spectrum, δ, ppm: 1.39 t (3H, CH_3, *J* 7.0 Hz), 3.98 q (2H, CH_2, *J* 7.0 Hz), 4.49 d.d.d (2H, CH_2O, *J* 1.5, 5.3 Hz), 5.27 d.d.t (1H, CH_2, *J* 1.5, 1.5, 10.4 Hz), 5.40 d.d.t (1H, CH_2, *J* 1.5, 1.5, 17.3 Hz), 6.05 d.d.t (1H, CH, *J* 5.3, 10.4, 17.3 Hz), 6.80–6.88 m ($4H_{Ar}$). Mass spectrum, *m/z* (I_{rel}, %): 178 (11) $[M]^+$, 137 (27), 109 (100), 81 (21), 63 (5), 53 (8), 41 (18).

1-(Allyloxy)-4-propoxybenzene (2c). Yield 69%, colorless crystals, mp 40–41°C. IR spectrum (mineral oil), cm^{-1}: 1508, 1463, 1229, 1027, 924, 825, 530. ^1H NMR spectrum, δ, ppm: 1.02 t (3H, CH_3, *J* 7.4 Hz), 1.78 sextet (2H, CH_2, *J* 7.1 Hz), 3.87 t (2H, CH_2O, *J* 6.6 Hz), 4.48 d.d.d (2H, CH_2O, *J* 1.5, 5.3 Hz), 5.26 d.d.t (1H, CH_2, *J* 1.5, 1.5, 10.5 Hz), 5.39 d.d.t (1H, CH_2, *J* 1.5, 1.5, 17.2 Hz), 6.05 d.d.t (1H, CH, *J* 5.3, 10.5, 17.2 Hz), 6.81–6.88 m ($4H_{Ar}$). Mass spectrum, *m/z* (I_{rel}, %): 192 (10) $[M]^+$, 151 (10), 109 (100), 81 (10), 64 (4), 53 (4), 43 (41).

1-(Allyloxy)-4-butoxybenzene (2d). Yield 65%, colorless oily substance, n_D^{22} 1.5020. IR spectrum (film), cm^{-1}: 1508, 1474, 1230, 1030, 926, 824, 523. ^1H NMR spectrum, δ, ppm: 0.97 t (3H, CH_3, *J* 7.4 Hz), 1.48 sextet (2H, $C\underline{H}_2CH_3$, *J* 7.4 Hz), 1.74 quintet (2H, $CH_2C\underline{H}_2CH_2O$, *J* 7.0 Hz), 3.91 t (2H, CH_2O, *J* 6.5 Hz), 4.48 d.d.d (2H, CH_2O, *J* 1.5, 5.3 Hz), 5.26 d.d.t (1H, CH_2, *J* 1.5, 1.5, 10.5 Hz), 5.39 d.d.t (1H, CH_2, *J* 1.5, 1.5, 17.2 Hz), 6.05 d.d.t (1H, CH, *J* 5.3, 10.5, 17.2 Hz), 6.79–6.88 m ($4H_{Ar}$). Mass spectrum, *m/z* (I_{rel}, %): 206 (9) $[M]^+$, 165 (4), 109 (100), 81 (8), 57 (28), 41 (42).

1-(Allyloxy)-4-pentyloxybenzene (2e). Yield 70%, colorless oily substance, n_D^{22} 1.5025. IR spectrum (film), cm^{-1}: 1508, 1470, 1229, 1032, 924, 824, 522. ^1H NMR spectrum, δ, ppm: 0.93 t (3H, CH_3, *J* 7.1 Hz), 1.37–1.47 m [4H, $CH_2(C\underline{H}_2)_2CH_3$], 1.76 quintet (2H, $CH_2C\underline{H}_2CH_2O$, *J* 6.9 Hz), 3.90 t (2H, CH_2O, *J* 6.6 Hz), 4.49 d.d.d (2H, CH_2O, *J* 1.5, 5.3 Hz), 5.27 d.d.t (1H, CH_2, *J* 1.5, 1.5, 10.3 Hz), 5.40 d.d.t (1H, CH_2, *J* 1.5, 1.5, 17.2 Hz), 6.05 d.d.t (1H, CH, *J* 5.3, 10.3, 17.2 Hz), 6.80–6.88 m ($4H_{Ar}$). Mass spectrum, *m/z* (I_{rel}, %): 220 (10) $[M]^+$, 179 (4), 150 (6), 109 (100), 81 (5), 71 (13), 55 (6), 43 (66).

1-(Allyloxy)-4-hexyloxybenzene (2f). Yield 66%, colorless oily substance, n_D^{22} 1.5058. IR spectrum (film), cm^{-1}: 1508, 1469, 1229, 1033, 926, 824. ^1H NMR spectrum, δ, ppm: 0.93 t (3H, CH_3, *J* 6.5 Hz), 1.32–1.41 m [4H, $CH_2(C\underline{H}_2)_2CH_3$], 1.47 quintet (2H, $CH_2C\underline{H}_2CH_2$, *J* 7.0 Hz), 1.77 quintet (2H, $CH_2C\underline{H}_2$·CH_2O, *J* 7.1 Hz), 3.91 t (2H, CH_2O, *J* 6.6 Hz), 4.49 d.d.d (2H, CH_2O, *J* 1.5, 5.3 Hz), 5.28 d.d.t (1H, CH_2, *J* 1.5, 1.5, 10.5 Hz), 5.41 d.d.t (1H, CH_2, *J* 1.5, 1.5, 17.3 Hz), 6.06 d.d.t (1H, CH, *J* 5.3, 10.5, 17.3 Hz), 6.81–6.89 m ($4H_{Ar}$). Mass spectrum, *m/z* (I_{rel}, %): 234 (9) $[M]^+$, 150 (7), 109 (100), 85 (12), 57 (10), 43 (96).

1-(Allyloxy)-4-heptyloxybenzene (2g). Yield 68%, colorless crystals, mp 32.5–33°C. IR spectrum (mineral oil), cm^{-1}: 1508, 1466, 1229, 1024, 931, 825, 533. ^1H NMR spectrum, δ, ppm: 0.89 t (3H, CH_3, *J* 6.9 Hz), 1.25–1.39 m [6H, $CH_2(C\underline{H}_2)_3CH_3$], 1.44 quintet (2H, $CH_2C\underline{H}_2CH_2$, *J* 7.1 Hz), 1.77 quintet (2H, $CH_2C\underline{H}_2$·CH_2O, *J* 7.0 Hz), 3.90 t (2H, CH_2O, *J* 6.6 Hz), 4.48 d.d.d (2H, CH_2O, *J* 1.5, 5.3 Hz), 5.26 d.d.t (1H, CH_2, *J* 1.5, 1.5, 10.5 Hz), 5.39 d.d.t (1H, CH_2, *J* 1.5, 1.5, 17.3 Hz), 6.05 d.d.t (1H, CH, *J* 5.3, 10.5, 17.3 Hz), 6.80–6.87 m ($4H_{Ar}$). Mass spectrum, *m/z* (I_{rel}, %): 248 (9) $[M]^+$, 150 (9), 109 (100), 81 (5), 57 (95), 41 (53).

Racemic and enantiomeric 3-(4-alkoxyphenoxy) propane-1,2-diols (1a–1g). General procedure [11]. To a solution of 15 mmol of an appropriate phenol **3a**–**3g** in 9 mL of EtOH was added at stirring a solution of 0.72 g (18 mmol) of NaOH in 3 mL of water. The mixture was boiled at stirring for 2 h, cooled to 50°C, and was added by portions a solution of 1.95 g (17.6 mmol) of *rac*- or (*R*)-3-chloropropane-1,2-diol in 3 mL of EtOH. The mixture was boiled at stirring for ~15 h. The reaction completion was fixed by TLC (R_f of reaction products ~0.2, eluent hexane–EtOAc, 6 : 4). On cooling the reaction mixture was diluted with water (70 mL), the reaction products were extracted with Et_2O (3 × 60 mL). The combined extracts were washed with 1 M water solution of NaOH (15 mL) to remove phenol residues and dried with $MgSO_4$. The solvent was removed in a vacuum. The crystalline residue was purified by column chromatography on silica gel (eluent hexane–EtOAc, 8 : 2–4 : 6). The recrystallization was done from a mixture hexane–EtOAc, 5 : 1. NMR spectra of obtained diols (*R*)-**1a**–**1g** are identical to the spectra of racemic analogs.

3-(4-Methoxyphenoxy)propane-1,2-diol (1a).

***rac*-(1a)**. Yield 75%, colorless plate crystals, mp 79.5°C. ^1H NMR spectrum, δ, ppm: 2.01 t (1H, $CH_2O\underline{H}$, *J* 6.1 Hz), 2.59 d (1H, $CHO\underline{H}$, *J* 4.8 Hz), 3.75 d.d.d (1H, $C\underline{H}_2OH$, *J* 5.6, 11.4 Hz), 3.77 s (3H, CH_3O), 3.83 d.d.d (1H, $C\underline{H}_2OH$, *J* 4.0, 6.5, 11.4 Hz), 4.00 d.d (1H, CH_2O, *J* 9.5, 14.3 Hz), 4.01 d.d (1H, CH_2O, *J* 9.5, 12.2 Hz), 4.06–4.11 m (1H, $C\underline{H}OH$), 6.82–6.87 m ($4H_{Ar}$). ^{13}C NMR spectrum, δ, ppm: 56.1, 64.1, 70.4,

70.8, 115.1, 116.0, 152.9, 154.7. Found, %: C 60.51; H 7.18. $C_{10}H_{14}O_4$. Calculated, %: C 60.59; H 7.12.

(*R*)-(1a). Yield 77%, colorless plate crystals, mp 77.3°C, $[\alpha]_D^{20}$ –7.6 (*c* 1, MeOH), $[\alpha]_{365}^{20}$ –26.7 (*c* 1, MeOH), *ee* 98.8% [HPLC, chiral column, t_R, min: 7.1 (major), 10.7 (minor)].

3-(4-Ethoxyphenoxy)propane-1,2-diol (1b).

***rac*-(1b)**. Yield 69%, colorless plate crystals, mp 86°C. ^{1}H NMR spectrum, δ, ppm: 1.39 t (3H, CH_3, *J* 7.0 Hz), 2.15 br.s (2H, OH), 3.74 d.d (1H, C$\underline{H}_2$OH, *J* 5.3, 11.4 Hz), 3.83 d.d (1H, C$\underline{H}_2$OH, *J* 3.6, 11.4 Hz), 3.94–4.02 m (4H, CH_2O, $CH_3C\underline{H}_2O$), 4.05–4.12 m (1H, C$\underline{H}$OH), 6.79–6.89 m (4H_{Ar}). ^{13}C NMR spectrum, δ, ppm: 15.2, 64.1, 64.4, 70.4, 70.8, 115.87, 115.93, 152.9, 154.0. Found, %: C 62.19; H 7.52. $C_{11}H_{16}O_4$. Calculated, %: C 62.25; H 7.60.

(*R*)-(1b). Yield 70%, colorless plate crystals, mp 84.3°C, $[\alpha]_D^{20}$ –7.1 (*c* 1.0, MeOH), $[\alpha]_{365}^{20}$ –25.1 (*c* 1, MeOH), *ee* 97.2% [HPLC, chiral column, t_R, min: 19.2 (major), 27.0 (minor)].

3-(4-Propoxyphenoxy)propane-1,2-diol (1c).

***rac*-(1c)**. Yield 62%, colorless plate crystals, mp 95.5°C. ^{1}H NMR spectrum, δ, ppm: 1.02 t (3H, CH_3, *J* 7.5 Hz), 1.78 sextet (2H, CH_2, *J* 7.1 Hz), 2.38 br.s (2H, OH), 3.74 d.d (1H, C$\underline{H}_2$OH, *J* 5.3, 11.4 Hz), 3.83 d.d (1H, C$\underline{H}_2$OH, *J* 3.7, 11.4 Hz), 2.87 t (2H, CH_2O, *J* 6.6 Hz), 3.99 d.d (1H, CH_2O, *J* 9.5, 12.6 Hz), 4.00 d.d (1H, CH_2O, *J* 9.5, 10.0 Hz), 4.04–4.11 m (1H, C$\underline{H}$OH), 6.80–6.87 m (4H_{Ar}). ^{13}C NMR spectrum, δ, ppm: 10.8, 23.0, 64.1, 70.4, 70.6, 70.8, 115.88, 115.93, 152.8, 154.2. Found, %: C 63.76; H 8.05. $C_{12}H_{18}O_4$. Calculated, %: C 63.70; H 8.02.

(*R*)-(1c). Yield 62%, colorless plate crystals, mp 94.5°C, $[\alpha]_D^{20}$ –7.6 (*c* 1.0, MeOH), $[\alpha]_{365}^{20}$ –24.0 (*c* 1, MeOH), *ee* 98.6% [HPLC, chiral column, t_R, min: 18.0 (major), 23.8 (minor)].

3-(4-Butoxyphenoxy)propane-1,2-diol (1d).

***rac*-(1d)**. Yield 65%, colorless plate crystals, mp 93.5°C (mp 96.5°C [8]). ^{1}H NMR spectrum, δ, ppm: 0.97 t (3H, CH_3, *J* 7.4 Hz), 1.48 sextet (2H, C$\underline{H}_2CH_3$, *J* 7.4 Hz), 1.74 quintet (2H, $CH_2C\underline{H}_2CH_2O$, *J* 7.0 Hz), 2.49 br.s (2H, OH), 3.73 d.d (1H, C$\underline{H}_2$OH, *J* 5.4, 11.4 Hz), 3.83 d.d (1H, C$\underline{H}_2$OH, *J* 3.7, 11.4 Hz), 3.91 t (2H, CH_2O, *J* 6.6 Hz), 3.98 d.d (1H, CH_2O, *J* 9.5, 12.2 Hz), 3.99 d.d (1H, CH_2O, *J* 9.5, 10.1 Hz), 4.04–4.11 m (1H, C$\underline{H}$OH), 6.79–6.88 m (4H_{Ar}). ^{13}C NMR spectrum, δ, ppm: 14.1, 19.5, 31.7, 64.1, 68.7, 70.3, 70.9, 115.8, 115.9, 152.8, 154.1. Found, %: C 65.04; H 8.33. $C_{13}H_{20}O_4$. Calculated, %: C 64.98; H 8.39.

(*R*)-(1d). Yield 69%, colorless plate crystals, mp 93.8°C, $[\alpha]_D^{20}$ –6.1 (*c* 1.0, MeOH), $[\alpha]_{365}^{20}$ –20.9 (*c* 1, MeOH), *ee* 98.9% [HPLC, chiral column, t_R, min: 15.9 (major), 21.5 (minor)].

3-(4-Pentyloxyphenoxy)propane-1,2-diol (1e).

***rac*-(1e)**. Yield 63%, colorless needle crystals, mp 89.8°C, tp 92.3°C (mp 92°C, tp 92°C [8]). ^{1}H NMR spectrum, δ, ppm: 0.93 t (3H, CH_3, *J* 7.1 Hz), 1.33–1.47 m [4H, $CH_2(C\underline{H}_2)_2CH_3$], 1.76 quintet (2H, $CH_2C\underline{H}_2CH_2O$, *J* 7.0 Hz), 3.08 br.s (2H, OH), 3.76 d.d (1H, C$\underline{H}_2$OH, *J* 5.6, 11.5 Hz), 3.81 d.d (1H, C$\underline{H}_2$OH, *J* 3.6, 11.5 Hz), 3.89 t (2H, CH_2O, *J* 6.6 Hz), 3.99 d.d (1H, CH_2O, *J* 9.5, 12.2 Hz), 4.00 d.d (1H, CH_2O, *J* 9.5, 10.2 Hz), 4.04–4.11 m (1H, C$\underline{H}$OH), 6.77–6.85 m (4H_{Ar}). ^{13}C NMR spectrum, δ, ppm: 14.3, 22.8, 28.5, 29.4, 64.1, 69.0, 70.3, 70.9, 115.8, 115.9, 152.8, 154.2. Found, %: C 66.05; H 8.76. $C_{14}H_{22}O_4$. Calculated, %: C 66.12; H 8.72.

(*R*)-(1e). Yield 70%, colorless plate crystals, mp 88.5°C, tp 91°C, $[\alpha]_D^{20}$ –6.2 (*c* 1.0, MeOH), $[\alpha]_{365}^{20}$ –20.6 (*c* 1, MeOH), *ee* 97.7% [HPLC, chiral column, t_R, min: 17.4 (major), 21.8 (minor)].

3-(4-Hexyloxyphenoxy)propane-1,2-diol (1f).

***rac*-(1f)**. Yield 65%, colorless plate crystals, mp 90°C, tp 93.5°C (mp 91°C, tp 97°C [8]). ^{1}H NMR spectrum, δ, ppm: 0.90 t (3H, CH_3, *J* 7.0 Hz), 1.30–1.39 m [4H, $CH_2(C\underline{H}_2)_2CH_3$], 1.41–1.48 m (2H, $CH_2C\underline{H}_2CH_2$), 1.75 quintet (2H, $CH_2C\underline{H}_2CH_2O$, *J* 7.0 Hz), 2.44 br.s (2H, OH), 3.73 d.d (1H, C$\underline{H}_2$OH, *J* 5.4, 11.5 Hz), 3.82 d.d (1H, C$\underline{H}_2$OH, *J* 3.7, 11.5 Hz), 3.90 t (2H, OCH_2, *J* 6.6 Hz), 3.98 d.d (1H, CH_2O, *J* 9.6, 12.3 Hz), 4.00 d.d (1H, CH_2O, *J* 9.6, 10.2 Hz), 4.05–4.10 m (1H, C$\underline{H}$OH), 6.78–6.87 m (4H_{Ar}). ^{13}C NMR spectrum, δ, ppm: 14.4, 22.9, 26.1, 29.7, 31.9, 64.1, 69.0, 70.4, 70.8, 115.87, 115.93, 152.8, 154.2. Found, %: C 67.09; H 9.07. $C_{15}H_{24}O_4$. Calculated, %: C 67.14; H 9.01.

(*R*)-(1f). Yield 69%, colorless plate crystals, mp 89°C, tp 93.5°C, $[\alpha]_D^{20}$ –5.4 (*c* 1.0, MeOH), $[\alpha]_{365}^{20}$ –18.9 (*c* 1, MeOH), *ee* 97.1% [HPLC, chiral column, t_R, min: 16.5 (major), 21.1 (minor)].

3-(4-Heptyloxyphenoxy)propane-1,2-diol (1g).

***rac*-(1g)**. Yield 64%, colorless plate crystals, mp 91.8°C, tp 97.3°C (mp 96°C, tp 103°C [8]). ^{1}H NMR

spectrum, δ, ppm: 0.89 t (3H, CH_3, *J* 6.9 Hz), 1.25–1.39 m [6H, $CH_2(C\underline{H}_2)_3CH_3$], 1.40–1.78 m (2H, $CH_2\cdot C\underline{H}_2CH_2$), 1.75 quintet (2H, $CH_2C\underline{H}_2CH_2O$, *J* 7 Hz), 2.32 br.s (2H, OH), 3.74 d.d (1H, $C\underline{H}_2OH$, *J* 5.5, 11.4 Hz), 3.82 d.d (1H, $C\underline{H}_2OH$, *J* 3.8, 11.4 Hz), 3.90 t (2H, OCH_2, *J* 6.6 Hz), 3.99 d.d (1H, CH_2O, *J* 9.5, 12.8 Hz), 4.00 d.d (1H, CH_2O, *J* 9.5, 10.7 Hz), 4.06–4.10 m (1H, C<u>H</u>OH), 6.81–6.85 m ($4H_{Ar}$). ^{13}C NMR spectrum, δ, ppm: 14.4, 22.9, 26.4, 29.4, 29.7, 32.1, 64.1, 69.0, 70.4, 70.8, 115.87, 115.93, 152.8, 154.2. Found, %: C 68.11; H 9.29. $C_{16}H_{26}O_4$. Calculated, %: C 68.06; H 9.28.

(*R*)-(1g). Yield 68%, colorless plate crystals, mp 91.5°C, tp 97.3°C, $[\alpha]_D^{20}$ –5.3 (*c* 1.0, MeOH), $[\alpha]_{365}^{20}$ –18.2° (*c* 1, MeOH), *ee* 97.1% [HPLC, chiral column, t_R, min: 15.2 (major), 19.2 (minor)].

Asymmetric Sharpless dihydroxylation. General procedure [11, 16]. A slurry of 1.4 g of AD-mix-β in 5 mL of *t*-BuOH and 5 mL of water was cooled at stirring to 0°C. To the slurry 1 mmol of an appropriate aryl allyl ether **2a**–**2g** was added, the reacton mixture was vigorously stirred at 0°C for 20 h. Then 1.5 g of Na_2SO_3 was added to the mixture, and the reaction mixture was stirred at room temperature for 30 min. The organic layer was separated, the reaction products were extracted from water layer with EtOAc (3 × 30 mL). The combined organic solutions were washed with brine (20 mL) and dried with $MgSO_4$. The solvent was removed at a reduced pressure. The crude product when necessary was purified by column chromatography on silica gel (eluent hexane–EtOAc, 8 : 2–4 : 6). At the application of AD-mix-β the *S*-enantiomer prevailed in the product. The spectra of diols (*S*)-**1a**–**1g** obtained by this procedure are identic to the spectra of racemic analogs.

(*S*)-3-(4-Methoxyphenoxy)propane-1,2-diol (*S*)-(1a). Yield 78%, colorless plate crystals, mp 77.3°C, $[\alpha]_D^{20}$ +6.6 (*c* 1, MeOH), *ee* 86.1% [HPLC, chiral column, t_R, min: 7.0 (minor), 10.3 (major)].

(*S*)-3-(4-Ethoxyphenoxy)propane-1,2-diol (*S*)-(1b). Yield 59%, colorless plate crystals, mp 84.3°C, $[\alpha]_D^{20}$ +6.4 (*c* 1.0, MeOH), *ee* 86.4% [HPLC, chiral column, t_R, min: 19.7 (minor), 27.1 (major)].

(*S*)-3-(4-Propoxyphenoxy)propane-1,2-diol (*S*)-(1c). Yield 62%, colorless plate crystals, mp 94.5°C, $[\alpha]_D^{20}$ +6.0 (*c* 1.0, MeOH), *ee* 89.7% [HPLC, chiral column, t_R, min: 18.0 (minor), 23.8 (major)].

(*S*)-3-(4-Butoxyphenoxy)propane-1,2-diol (*S*)-(1d). Yield 69%, colorless plate crystals, mp 94°C, $[\alpha]_D^{20}$ +5.7 (*c* 1.0, MeOH), *ee* 92.3% [HPLC, chiral column, t_R, min: 16.6 (minor), 21.9 (major)].

(*S*)-3-(4-Pentyloxyphenoxy)propane-1,2-diol (*S*)-(1e). Yield 76%, colorless plate crystals, mp 88.5°C, tp 91°C, $[\alpha]_D^{20}$ +5.7 (*c* 1.0, MeOH), *ee* 89.6% [HPLC, chiral column, t_R, min: 17.3 (minor), 21.7 (major)].

(*S*)-3-(4-Hexyloxyphenoxy)propane-1,2-diol (*S*)-(1f). Yield 70%, colorless plate crystals, mp 89°C, tp 93.5°C, $[\alpha]_D^{20}$ +5.0 (*c* 1.0, MeOH), *ee* 90.5% [HPLC, chiral column, t_R, min: 16.3 (minor), 20.6 (major)].

(*S*)-3-(4-Heptyloxyphenoxy)propane-1,2-diol (*S*)-(1g). Yield 74%, colorless plate crystals, mp 91.5°C, tp 97.3°C, $[\alpha]_D^{20}$ +5.0 (*c* 1.0, MeOH), *ee* 90.4% [HPLC, chiral column, t_R, min: 15.5 (minor), 19.2 (major)].

REFERENCES

1. Bredikhin, A.A., Bredikhina, Z.A., and Zakharychev, D.V., *Mendeleev Commun*., 2012, vol. 22, p. 171.
2. Tschierske, C., *Chirality at the Nanoscale: Nanoparticles, Surfaces, Materials and More*, Amabilino, D.B., Ed., Weinheim: Wiley-VCH, 2009.
3. Reddy, R.A. and Tschierske, C., *J. Mater. Chem*., 2006, vol. 16, p. 907.
4. Goodby, J.W., *J. Mater. Chem*., 1991, vol. 1, p. 307.
5. Malik, S., Fujita, N., and Shinkai, S., *Chirality at the Nanoscale: Nanoparticles, Surfaces, Materials and More*, Amabilino, D.B., Ed., Weinheim: Wiley-VCH, 2009.
6. Smith, D.K., *Chem. Soc. Rev*., 2009, vol. 38, p. 684.
7. Brizard, A., Oda, R., and Huc, I., *Top. Curr. Chem*., 2005, vol. 256, p. 167.
8. Tschierske, C., Hentrich, F., Joachimi, D., Agert, O., and Zaschke, H., *Liq. Cryst*., 1991, vol. 9, p. 571.
9. Bredikhin, A.A., Bredikhina, Z.A., Akhatova, F.S., and Gubaidullin, A.T., *Chem. Commun*., 2010, vol. 46, p. 3523.
10. Bredikhin, A.A., Zakharychev, D.V., Bredikhina, Z.A., Gubaidullin, A.T., and Fayzullin, R.R., *CrystEngComm*., 2012, vol. 14, p. 211.
11. Bredikhin, A.A., Zakharychev, D.V., Fayzullin, R.R., Antonovich, O.A., Pashagin, A.V., and Bredikhina, Z.A., *Tetrahedron: Asymmetry*, 2013, vol. 24, p. 807.
12. Ueda, T., Toyoshima, S., Takahashi, K., Muraoka, M., Koibuchi, H., and Seto, Y., *Chem. Pharm. Bull*., 1960, vol. 8, p. 921.

13. Kolb, H.C., VanNieuwenhze, M.S., and Sharpless, K.B., *Chem. Rev*., 1994, vol. 94, p. 2483.
14. Zaitsev, A.B. and Adolfsson, H., *Synthesis*., 2006, vol. 11, p. 1725.
15. Bredikhin, A.A., Gubaidullin, A.T., Bredikhina, Z.A., Fayzullin, R.R., Samigullina, A.I., and Zakharychev, D.V., *J. Mol. Struct*., 2013, vol. 1045, p. 104.
16. Wang, Z.-M., Zhang, X.-L., and Sharpless, K.B., *Tetrahedron Lett*., 1993, vol. 34, p. 2267.
17. Bredikhina, Z.A., Kurenkov, A.V., Antonovich, O.A., Pashagin, A.V., and Bredikhin, A.A., *Tetrahedron: Asymmetry*, 2014, vol. 25, p. 1015.
18. Dierking, I., *Textures of Liquid Crystals*, Weinheim: Wiley-VCH, 2009.
19. *Molecular Gels: Materials with Self-assembled Fibrillar Networks*, Weiss, R.G. and Terech, P., Eds., Dordrecht: Springer, Nether-lands, 2006.
20. Liu, L.-M., Liu, K.-P., Dong, Y.-P., Chen, E.-Q., and Tang, B.Z., *Macromolecules*, 2010, vol. 43, p. 6014.
21. White, W.N. and Norcross, B.E., *J. Am. Chem. Soc*., 1961, vol. 83, p. 3265.
22. Goering, H.L. and Jacobson, R.R., *J. Am. Chem. Soc*., 1958, vol. 80, p. 3277.