

Synthesis of New Liquid Crystalline Compounds with Side Chains Containing Hydroxy Groups or Chlorine Atom

V. N. Kovganko and N. N. Kovganko

Sevchenko Institute of Applied Physical Problems, Byelorussian State University,
ul. Kurchatova 7, Minsk, 220064 Belarus
e-mail: kauhanka@bsu.by

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Abstract—Catalytic hydrogenation of the oxo group in 3-hydroxy-1-(4-hydroxyphenyl)octan-1-one gave 1-(4-hydroxyphenyl)octane-1,3-diol and 1-(4-hydroxyphenyl)octan-3-ol which were converted into the corresponding benzyl ethers containing a hydroxy group, 1,3-diol fragment, or chlorine atom in the side chain. The products were shown to possess liquid crystalline properties.

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Mesomorphic compounds whose molecules possess various groups in the rigid central part or flexible side chain have found increasing application in the design of new liquid crystalline data imaging systems [1, 2]. Therefore, development of new procedures for the preparation of such compounds can be regarded as an important problem of organic synthesis.

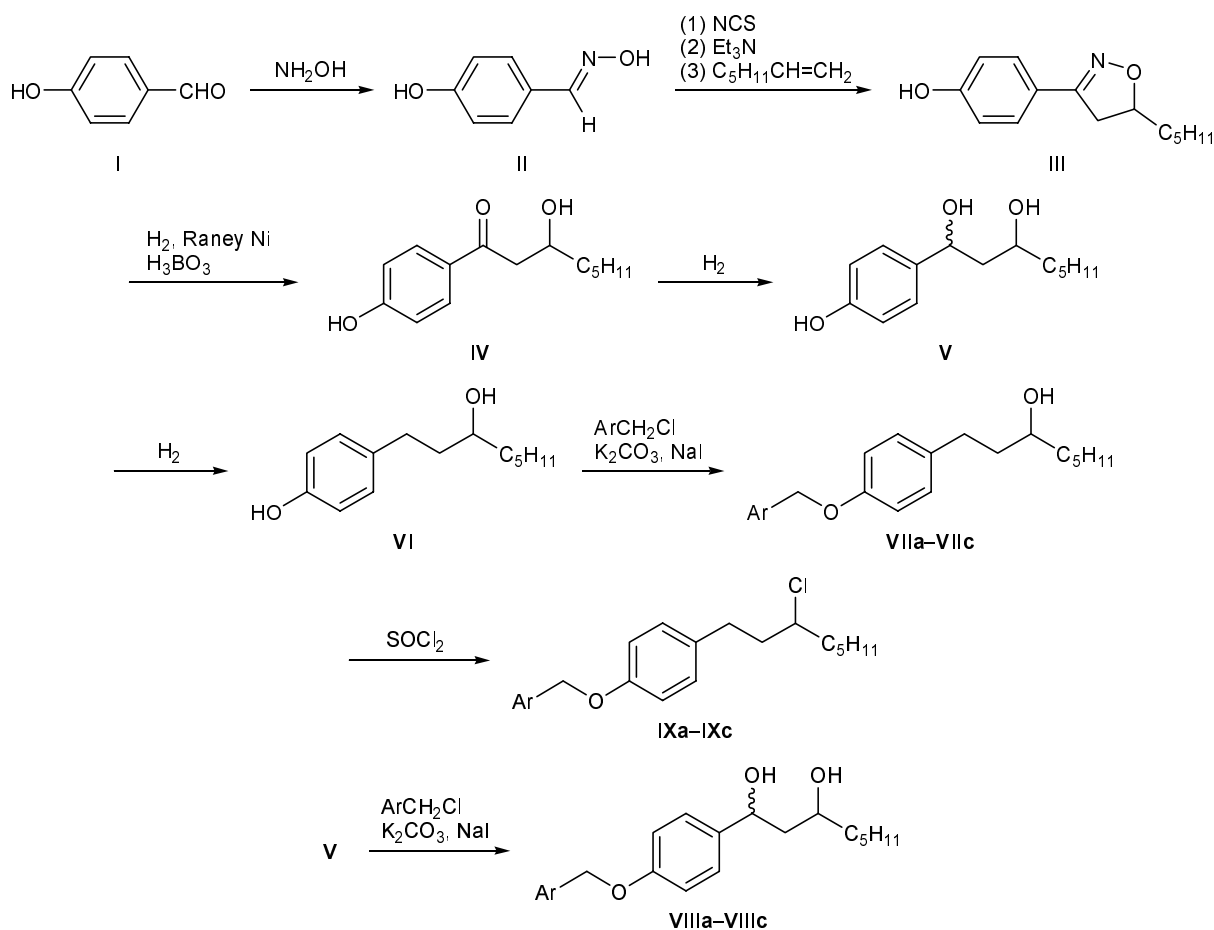
A number of liquid crystalline compounds containing various functional groups in the side chain were previously synthesized on the basis of products obtained by transformation of 4,5-dihydroisoxazole derivatives [3–5]. For example, this approach was utilized in the synthesis of mesogenic compounds having a β -hydroxy ketone, β -chloro ketone, or enone fragment in the side chain.

The present communication describes the results of our studies on the application of 4,5-dihydroisoxazoles for the preparation of liquid crystalline compounds with functionalized side chains, in particular of those containing a 1,3-diol fragment, hydroxy group, or chlorine atom in the side chain. It should be noted that compounds containing hydroxy and 1,3-diol moieties have already been proposed as components of liquid crystalline compositions for ferroelectric displays [6–8]. Replacement of hydroxy groups in mesomorphic compounds by chlorine and fluorine atoms is widely used in the chemistry of liquid crystals to obtain new substances possessing practically important physical properties [9–11]. As a result, the application of halogen-containing liquid crystalline compounds as components of smectic and nematic compositions continuously extends [6, 9–14].

The schemes developed previously [3–5] for the synthesis of liquid crystalline compounds with functionalized side chains on the basis of 4,5-dihydroisoxazoles involved β -hydroxy ketone **IV** as key intermediate product. Compound **IV** was synthesized in three steps which included transformation of initial *p*-hydroxybenzaldehyde (**I**) into oxime **II**, treatment of **II** in succession with *N*-chlorosuccinimide (NCS) and triethylamine to generate the corresponding nitrile oxide, 1,3-dipolar cycloaddition of the latter to hept-1-ene with formation of 4,5-dihydroisoxazole derivative **III**, and reductive cleavage of the heteroring in **III** with hydrogen over Raney nickel in the presence of boric acid (Scheme 1). We presumed that reduction of the ketone carbonyl group in **IV** could give rise to intermediate products which can be used in the synthesis of liquid crystalline compounds having a 1,3-diol fragment, hydroxy group, or chlorine atom in the side chain. Therefore, in the first step we examined catalytic hydrogenation of hydroxy ketone **IV**.

By hydrogenation of compound **IV** over Raney nickel we obtained 1,3-diol **V** and alcohol **VI**, the latter resulting from the subsequent reduction of the benzylic hydroxy group in **V** to methylene. Compounds **V** and **VI** were isolated by chromatography in 82 and 17% yield, respectively. According to the ^1H NMR data, compound **V** was a mixture of two diastereoisomers. The reduction of the benzylic hydroxy group in **V** to produce alcohol **VI** is a fairly fast process (TLC data). Compound **VI** was formed immediately after the hydrogenation started, though the reaction mixture still contained initial β -hydroxy ketone

Scheme 1.



IV. The hydrogenation of 4,5-dihydroisoxazole **III** over Raney nickel in the presence of boric acid gave β -hydroxy ketone **IV** as the major product and 1,3-diol **V**, but the latter was formed in a small amount even on prolonged keeping of the reaction mixture under hydrogen. Presumably, boric acid inhibits subsequent catalytic hydrogenation of the carbonyl group in **IV**.

By hydrogenation of β -hydroxy ketone **IV** over Pd/C (which is a more active catalyst than Raney nickel) we obtained 95% of alcohol **VI** as the only product. In this case, the reduction of initially formed 1,3-diol **V** occurred at a much higher rate than in the presence of Raney nickel, and compound **VI** was the major product present in the reaction mixture during the entire process.

The structure of compounds was proved by the IR and ¹H NMR spectra. In the IR spectra of **V** and **VI** we observed no absorption in the region 1700–1650 cm⁻¹ typical of carbonyl group. The hydroxy protons in **V** appeared in the ¹H NMR spectra as broadened singlets

at δ 6.17 and 7.05 ppm (major diastereoisomer) and δ 6.08 and 6.87 ppm (minor diastereoisomer). The signal from the phenolic hydroxy proton was located in a much weaker field, at δ 11.44 ppm. The major diastereoisomer of diol **V** showed in the ¹H NMR spectrum a broadened doublet of doublets at δ 5.39 ppm due to 1-H and a multiplet at δ 4.14–4.20 ppm due to 3-H. The corresponding signals of the minor diastereoisomer appeared at δ 5.60 (br.d.d, 1-H) and 4.45–4.52 ppm (m, 3-H). The observed chemical shifts are typical of 1,3-diols [15, 16]. The signal from 1-H is displaced appreciably downfield (relative to that from 3-H) due to effect of the aromatic fragment. The C²H₂ methylene group in **V** gives rise to one-proton multiplets in the region δ 2.10–2.36 ppm.

The ¹H NMR spectrum of alcohol **VI** contained only one broadened singlet at δ 5.76 ppm from the hydroxy proton (this assignment was confirmed by H–D exchange experiments). The C¹H₂ benzylic protons gave two multiplets at δ 2.82 and 2.98 ppm (1H each).

Compound **VI** was characterized by upfield shift of the multiplet signals from 3-H and C²H₂ (δ 3.80 and 1.84–1.98 ppm, respectively) relative to the corresponding signals in the spectrum of diol **V**.

With a view to obtain liquid crystalline compounds with side-chain hydroxy group and 1,3-diol moiety, alcohols **V** and **VI** were subjected to benzylation at the phenolic hydroxy group with substituted benzyl chlorides. We thus built up the central polycyclic part of liquid crystalline compounds with bridging OCH₂ moiety. Treatment of phenol **V** with substituted benzyl chlorides in the presence of potassium carbonate and sodium iodide led to formation of the corresponding benzyl ethers **VIIIa–VIIIc** with a side-chain 1,3-diol moiety in high preparative yields. Under the given conditions, only the phenolic hydroxy group was involved in etherification, while the alcoholic hydroxy groups remained intact. Likewise, from phenol **VI** we obtained 88–92% of benzyl ethers **VIIa–VIIc** containing one hydroxy group in the side chain.

The structure of benzyl ethers **VIIa–VIIc** and **VIIIa–VIIIc** was confirmed by IR and ¹H NMR spectroscopy. The ¹H NMR spectra of **VIIa–VIIc** and **VIIIa–VIIIc** contained a singlet at δ 5.09–5.17 ppm, belonging to the benzylic CH₂O group. The position and multiplicity of signals from protons in the side chain of these compounds were almost the same as in the spectra of parent phenols **VI** and **V**.

Benzyl ethers **VIIa–VIIc** were treated with thionyl chloride to obtain new liquid crystalline compounds having a chlorine atom in the side chain. As a result, compounds **IXa–IXc** were isolated in 69–80% yield. The IR spectra of **IXa–IXc** lacked OH stretching

vibration bands in the region 3600–3200 cm⁻¹, and no OH proton signals were observed in their ¹H NMR spectra. The 3-H signals in the ¹H NMR spectra of **IXa–IXc** appeared ~0.1 ppm downfield relative to the corresponding signals of alcohols **VIIa–VIIc**. The observed variation of the chemical shift is typical of replacement of hydroxy group by chlorine atom. In addition, signals from the C¹H₂ benzylic protons changed their multiplicity and position by 0.15–0.17 ppm upfield.

Phase transition study showed that all benzyl ethers **VII–IX** exhibit mesomorphic properties and give rise to smectic mesophase (see table). Among these, only compound **VIIIa** formed monotropic smectic phase, while the other compounds formed enantiotropic liquid crystalline phase. Hydroxy- and chloro-substituted ethers **VIIa–VIIc** and **IXa–IXc** gave smectic phase *C* in a fairly broad temperature range. In addition, compounds **VIIb**, **VIIc**, and **IXa–IXc** formed smectic phase *A*. As follows from the data in table, replacement of the hydroxy group in **VII** by chlorine atom not only reduces the temperature of formation of smectic phase but also extends its temperature range.

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EXPERIMENTAL

The IR spectra were measured from solutions in chloroform on a Specord 75IR spectrometer. The UV spectra were recorded from solutions in ethanol on a Specord M-40 spectrophotometer. The ¹H NMR spectra were obtained on a Bruker Avance 400 instrument (400 MHz) using pyridine-*d*₅ as solvent and HMDS as internal reference. The progress of reactions was monitored, and the purity of products was checked, by thin-layer chromatography on Kieselgel 60 F₂₅₄ plates (Merck). The melting points and phase transition temperatures were determined using a melting point apparatus coupled with a polarizing microscope. Mesophases were identified by comparing the observed texture with the corresponding standards [17]. The phase transition temperatures of compounds **VII–IX** are given in table.

1-(4-Hydroxyphenyl)octane-1,3-diol (V). A suspension of 1 g of Raney nickel in 20 ml of methanol was saturated with hydrogen over a period of 1 h under stirring. Ketone **IV**, 2.43 g (10.3 mmol) [4] and 20 ml of methanol were added, and the mixture was stirred for 8.5 h in a hydrogen atmosphere, additional portions

Phase transition temperatures of compounds **VII–IX**^a

Comp. no.	mp, °C	Smectic phase C (SmC)	T _{tr} , °C	Smectic phase A (SmA)	T _{cl} , °C
VIIa	119	●	–	–	128
VIIb	128	●	139	●	142.5
VIIc	118	●	145	●	147
VIIIa	125.5	● (SmX)	–	–	–
VIIIb	146	–	–	●	147.5
VIIIc	146.5	–	–	●	151
IXa	56	●	102	●	109
IXb	104	●	132	●	138
IXc	91	●	134	●	143.5

^a T_{tr} is transition temperature, T_{cl} is clarification temperature, and SmX is indefinite monotropic smectic phase; diastereoisomer ratios in analytical samples of diols **VIII**: 7:4 (a), 8:1 (b), 5:1 (c).

of Raney nickel being added (2 g after 1 h, 2 g after 2 h, and 1 g after 3 h). The catalyst was filtered off and washed with 40 ml of methanol on a filter. The solvent was distilled off from the filtrate under reduced pressure, the residue was applied to a column charged with silica gel, and the column was eluted with ethyl acetate–petroleum ether (1:4 to 1:1, gradient elution) to isolate 0.39 g (17%) of alcohol **VI** and 2 g (82%) of oily 1,3-diol **V** (a mixture of two diastereoisomers at a ratio of 1:0.7). UV spectrum: λ_{\max} 277 nm. IR spectrum, ν , cm^{-1} : 3585, 3540–3100 (OH); 3000 (C–H_{arom}); 2950, 2925, 2850 (C–H_{alk}); 1610, 1590, 1505 (C=C_{arom}). ¹H NMR spectrum, δ , ppm: major diastereoisomer: 0.82 t (3H, C⁸H₃, $J = 7$ Hz), 1.18–1.34 m (4H, C⁷H₂, C⁶H₂), 1.42–1.57 m (2H), 1.57–1.74 m (2H, C⁵H₂, C⁴H₂), 2.10 d.d.d (1H, $J_1 = 3$, $J_2 = 5$, $J_3 = 14$ Hz), 2.36 t.d (1H, $J_1 = 9$, $J_2 = 14$ Hz) (C²H₂), 4.14–4.20 m (1H, 3-H), 5.39 d.d (1H, 1-H, $J_1 = 5$, $J_2 = 9$ Hz), 6.17 br.s (1H, OH), 7.05 br.s (1H, OH), 7.27 d (2H, H_{arom}, $J = 8.5$ Hz), 7.68 d (2H, H_{arom}, $J = 8.5$ Hz), 11.44 br.s (1H, OH, phenol); minor diastereoisomer: 0.81 t (3H, C⁸H₃, $J = 7$ Hz), 1.18–1.34 m (4H, C⁷H₂, C⁶H₂), 1.57–1.84 m (4H, C⁵H₂, C⁴H₂), 2.18 d.d.d (1H, $J_1 = 3$, $J_2 = 9$, $J_3 = 13.5$ Hz) and 2.29 d.d.d (1H, $J_1 = 3$, $J_2 = 9.5$, $J_3 = 13.5$ Hz) (C²H₂), 4.45–4.52 m (1H, 3-H), 5.60 d.d (1H, 1-H, $J_1 = 3$, $J_2 = 9$ Hz), 6.08 br.s (1H, OH), 6.87 br.s (1H, OH), 7.26 d (2H, H_{arom}, $J = 8.5$ Hz), 7.68 d (2H, H_{arom}, $J = 8.5$ Hz), 11.44 br.s (1H, OH, phenol).

1-(4-Hydroxyphenyl)octan-3-ol (VI). β -Hydroxy ketone **IV**, 0.306 g (1.3 mmol), was hydrogenated in 10 ml of methanol in the presence of 0.036 g of 10% Pd/C until the initial compound disappeared (2 h). The catalyst was filtered off and washed with 30 ml of methanol on a filter, the solvent was distilled off from the filtrate under reduced pressure, and the residue was applied to a column charged with silica gel. The column was eluted with ethyl acetate–cyclohexane (1:2) to isolate 0.273 g (95%) of compound **VI** with mp 65.5–67°C (from toluene–petroleum ether). UV spectrum: λ_{\max} 278 nm. IR spectrum, ν , cm^{-1} : 3600, 3550–3100 (OH); 3010 (C–H_{arom}); 2955, 2930, 2860 (C–H_{alk}); 1610, 1590, 1510 (C=C_{arom}). ¹H NMR spectrum, δ , ppm: 0.76 t (3H, C⁸H₃, $J = 7$ Hz), 1.12–1.27 m (4H, C⁶H₂, C⁷H₂), 1.35–1.47 m (1H) and 1.48–1.65 m (3H) (C⁴H₂, C⁵H₂), 1.84–1.98 m (2H, C²H₂), 2.82 d.d.d (1H, $J_1 = 7$, $J_2 = 9$, $J_3 = 14$ Hz) and 2.98 d.d.d (1H, $J_1 = 6$, $J_2 = 9.5$, $J_3 = 14$ Hz) (C¹H₂), 3.80 m (1H, 3-H), 5.76 br.s (1H, OH, exchanges with D₂O), 7.12 d (2H, H_{arom}, $J = 8.4$ Hz), 7.23 d (2H, H_{arom}, $J = 8.4$ Hz), 11.19 br.s (1H, OH, phenol, exchanges with D₂O).

1-[4-(4'-Pentylbiphenyl-4-ylmethoxy)phenyl]octan-3-ol (VIIa). Sodium iodide, 0.3 g (2 mmol), and potassium carbonate, 0.7 g (5 mmol), were added to a solution of 0.2 g (0.9 mmol) of phenol **VI** and 0.27 g (0.99 mmol) of 4-(4-pentylphenyl)benzyl chloride in 10 ml of acetone. The mixture was refluxed for 5 h under stirring and diluted with 40 ml of water. The precipitate was filtered off and washed in succession with water (100 ml) and cold petroleum ether. Yield 0.38 g (92%). An analytical sample was obtained by double recrystallization from propan-2-ol. UV spectrum: λ_{\max} 260 nm. IR spectrum, ν , cm^{-1} : 3600, 3550–3150 (OH); 3025, 3005, 3000 (C–H_{arom}); 2950, 2925, 2855 (C–H_{alk}); 1605, 1575, 1500 (C=C_{arom}). ¹H NMR spectrum, δ , ppm: 0.75 t (3H, CH₃, $J = 7$ Hz), 0.76 t (3H, C⁸H₃, $J = 7$ Hz), 1.10–1.28 m (8H, CH₂), 1.32–1.66 m (6H, CH₂), 1.82–1.96 m (2H, C²H₂), 2.52 t (2H, CH₂C₆H₄, $J = 8$ Hz), 2.82 d.d.d (1H, $J_1 = 7$, $J_2 = 9$, $J_3 = 14$ Hz) and 2.99 d.d.d (1H, $J_1 = 6$, $J_2 = 10$, $J_3 = 14$ Hz) (C¹H₂), 3.75–3.84 m (1H, 3-H), 5.09 s (2H, CH₂O), 5.79 br.d (1H, OH, $J = 2$ Hz), 7.07 d (2H, H_{arom}, $J = 9$ Hz), 7.24 d (2H, H_{arom}, $J = 9$ Hz), 7.25 d (2H, H_{arom}, $J = 8$ Hz), 7.54 d (2H, H_{arom}, $J = 8$ Hz), 7.60 d (2H, H_{arom}, $J = 8$ Hz), 7.66 d (2H, H_{arom}, $J = 8$ Hz).

Compounds **VIIb**, **VIIc**, and **VIIIa–VIIIc** were synthesized in a similar way.

1-[4-(4'-Propoxybiphenyl-4-ylmethoxy)phenyl]octan-3-ol (VIIb). Yield 91%. UV spectrum: λ_{\max} 269 nm. IR spectrum, ν , cm^{-1} : 3600, 3540–3200 (OH); 3000 (C–H_{arom}); 2950, 2925, 2865, 2850 (C–H_{alk}); 1600, 1500, 1495 (C=C_{arom}). ¹H NMR spectrum, δ , ppm: 0.76 t (3H, C⁸H₃, $J = 7$ Hz), 0.87 t (3H, CH₃, $J = 7$ Hz), 1.12–1.30 m (4H, CH₂), 1.36–1.70 m (4H, CH₂), 1.64 sext (2H, CH₃CH₂CH₂O, $J = 7$ Hz), 1.81–1.96 m (2H, C²H₂), 2.83 d.d.d (1H, $J_1 = 7$, $J_2 = 9$, $J_3 = 14$ Hz) and 2.99 d.d.d (1H, $J_1 = 6$, $J_2 = 9.5$, $J_3 = 14$ Hz) (C¹H₂), 3.74–3.88 m (1H, 3-H), 3.80 t (2H, CH₂CH₂O, $J = 7$ Hz), 5.09 s (2H, CH₂O), 5.80 d (1H, OH, $J = 5$ Hz), 7.05 d (2H, H_{arom}, $J = 9$ Hz), 7.08 d (2H, H_{arom}, $J = 8$ Hz), 7.25 d (2H, H_{arom}, $J = 8$ Hz), 7.53 d (2H, H_{arom}, $J = 8$ Hz), 7.60 d (2H, H_{arom}, $J = 9$ Hz), 7.63 d (2H, H_{arom}, $J = 8$ Hz).

1-[4-(4'-Butoxybiphenyl-4-ylmethoxy)phenyl]octan-3-ol (VIIc). Yield 88%. UV spectrum: λ_{\max} 269 nm. IR spectrum, ν , cm^{-1} : 3600, 3540–3150 (OH); 3025, 3015, 3000 (C–H_{arom}); 2950, 2930, 2865 (C–H_{alk}); 1600, 1575, 1500, 1490 (C=C_{arom}). ¹H NMR spectrum, δ , ppm: 0.76 t (3H, C⁸H₃, $J = 7$ Hz), 0.79 t (3H, CH₃, $J = 7.5$ Hz), 1.14–1.26 m (4H, C⁶H₂, C⁷H₂),

1.34 sext (2H, CH₃CH₂CH₂CH₂O, $J = 7.5$ Hz), 1.36–1.45 m (1H) and 1.48–1.65 m (5H) (CH₂), 1.82–1.96 m (2H, C²H₂), 2.82 d.d.d (1H, $J_1 = 7$, $J_2 = 9.5$, $J_3 = 14$ Hz) and 2.99 d.d.d (1H, $J_1 = 5.5$, $J_2 = 9$, $J_3 = 14$ Hz) (C¹H₂), 3.75–3.84 m (1H, 3-H), 3.86 t (2H, CH₂CH₂O, $J = 6.5$ Hz), 5.09 s (2H, CH₂O), 5.80 br.s (1H, OH), 7.06 d (2H, H_{arom}, $J = 9$ Hz), 7.08 d (2H, H_{arom}, $J = 8$ Hz), 7.25 d (2H, H_{arom}, $J = 8$ Hz), 7.53 d (2H, H_{arom}, $J = 8$ Hz), 7.61 d (2H, H_{arom}, $J = 9$ Hz), 7.63 d (2H, H_{arom}, $J = 8$ Hz).

1-[4-(4'-Pentylbiphenyl-4-ylmethoxy)phenyl]octane-1,3-diol (VIIIa). Yield 76%. UV spectrum: λ_{\max} 259 nm. IR spectrum, ν , cm⁻¹: 3590, 3545–3150 (OH); 2955 (C–H_{arom}); 2945, 2915, 2850 (C–H_{alk}); 1600, 1575, 1500 (C=C_{arom}). ¹H NMR spectrum, δ , ppm: major diastereoisomer: 0.70–0.79 m (6H, CH₃); 1.12–1.22 m, 1.30–1.45 m, 1.45–1.62 m, and 1.62–1.76 m (CH₂); 1.97–2.08 m (1H) and 2.21–2.30 m (1H, C²H₂); 2.52 t (2H, CH₂C₆H₄, $J = 8$ Hz); 4.03–4.14 m (1H, 3-H); 5.11 s (2H, CH₂O); 5.28–5.34 m (1H, 1-H); 6.10–6.15 m (1H, OH); 6.98–7.03 m (1H, OH); 7.14–7.18 m (2H, H_{arom}); 7.25 d (2H, H_{arom}, $J = 8$ Hz); 7.54 d (2H, H_{arom}, $J = 8$ Hz); 7.60 d (2H, H_{arom}, $J = 8$ Hz); 7.62–7.65 m (2H, H_{arom}); 7.66 d (2H, H_{arom}, $J = 8$ Hz); minor diastereoisomer: 2.05–2.10 m (1H), 2.13–2.21 m (1H, C²H₂), 4.35–4.45 m (1H, 3-H), 5.10 s (2H, CH₂O), 5.50–5.56 m (1H, 1-H), 6.00–6.05 m (1H, OH), 6.83–6.87 m (1H, OH), 7.14–7.18 m (2H, H_{arom}), 7.62–7.65 m (2H, H_{arom}).

1-[4-(4'-Propoxybiphenyl-4-ylmethoxy)phenyl]octane-1,3-diol (VIIIb). Yield 97%. UV spectrum: λ_{\max} 267 nm. IR spectrum, ν , cm⁻¹: 3590, 3550–3200 (OH); 3000 (C–H_{arom}); 2950, 2925, 2865, 2850 (C–H_{alk}); 1600, 1575, 1490 (C=C_{arom}). ¹H NMR spectrum, δ , ppm: major diastereoisomer: 0.82 m (3H, C⁸H₃); 0.95 t (3H, CH₃, $J = 7$ Hz); 1.20–1.32 m (4H), 1.42–1.52 m (1H), 1.58–1.67 m (2H), and 1.68–1.76 m (1H) (CH₂); 1.72 sext (2H, CH₃CH₂CH₂O, $J = 7$ Hz); 2.04–2.10 m and 2.26–2.36 m (1H each, C²H₂); 3.88 t (2H, CH₂CH₂O, $J = 7$ Hz); 4.11–4.18 m (1H, 3-H); 5.17 s (2H, CH₂O); 5.34–5.40 m (1H, 1-H); 6.17 br.s (1H, OH); 7.05 br.s (1H, OH); 7.12 d (2H, H_{arom}, $J = 9$ Hz); 7.22 d (2H, H_{arom}, $J = 8.5$ Hz); 7.60 d (2H, H_{arom}, $J = 8.5$ Hz); 7.65–7.74 m (6H, H_{arom}); minor diastereoisomer: 2.12–2.16 m and 2.20–2.25 m (1H each, C²H₂), 4.42–4.49 m (1H, 3-H), 5.48–5.62 m (1H, 1-H), 6.06 m (1H, OH), 6.89 m (1H, OH).

1-[4-(4'-Butoxybiphenyl-4-ylmethoxy)phenyl]octane-1,3-diol (VIIIc). Yield 92%. UV spectrum: λ_{\max} 267 nm. IR spectrum, ν , cm⁻¹: 3590, 3550–3150

(OH); 2995 (C–H_{arom}); 2950, 2925, 2865 (C–H_{alk}); 1600, 1575, 1490 (C=C_{arom}). ¹H NMR spectrum, δ , ppm: major diastereoisomer: 0.74 t (3H, C⁸H₃, $J = 7$ Hz); 0.79 t (3H, CH₃, $J = 7$ Hz); 1.10–1.26 m (4H), 1.32–1.46 m (1H), and 1.48–1.72 m (3H) (CH₂); 1.34 sext (2H, CH₃CH₂CH₂, $J = 7$ Hz); 1.62 quint (2H, CH₂CH₂CH₂O, $J = 7$ Hz); 1.96–2.04 m and 2.19–2.30 m (1H each, C²H₂); 3.86 t (2H, CH₂CH₂O, $J = 7$ Hz); 4.02–4.12 m (1H, 3-H); 5.10 s (2H, CH₂O); 5.30 d.d (1H, 1-H, $J_1 = 5$, $J_2 = 8$ Hz); 6.00–6.20 m (OH); 7.06 d (2H, H_{arom}, $J = 8.5$ Hz); 7.15 d (2H, H_{arom}, $J = 8.5$ Hz); 7.52 d (2H, H_{arom}, $J = 8.5$ Hz); 7.57–7.68 m (6H, H_{arom}); minor diastereoisomer: 2.04–2.10 m and 2.12–2.18 m (1H each, C²H₂), 4.35–4.43 m (1H, 3-H), 5.52 d.d (1H, 1-H, $J_1 = 3$, $J_2 = 9$ Hz).

3-Chloro-1-[4-(4'-pentylbiphenyl-4-ylmethoxy)phenyl]octane (IXa). Benzyl ether VIIa, 0.126 g (0.275 mmol), was dissolved in 6 ml of methylene chloride, and 2 ml of thionyl chloride and one drop of dimethylformamide were added. The mixture was kept for 2 h at 20°C, and the solvent and excess thionyl chloride were distilled off under atmospheric pressure. The residue was dissolved in 10 ml of methylene chloride, and the solvent was distilled off under reduced pressure to remove excess thionyl chloride more completely. The residue was recrystallized from 2-propanol. Yield 0.105 g (80%). UV spectrum: λ_{\max} 258 nm. IR spectrum, ν , cm⁻¹: 3005 (C–H_{arom}); 2950, 2925, 2855 (C–H_{alk}); 1610, 1575, 1500 (C=C_{arom}). ¹H NMR spectrum, δ , ppm: 0.74 t (3H, $J = 7$ Hz) and 0.75 t (3H, $J = 7$ Hz) (CH₃), 1.00–1.31 m (9H) and 1.34–1.46 m (1H) (CH₂), 1.51 quint (2H, CH₂, $J = 7.5$ Hz), 1.56–1.64 m (2H, C⁴H₂), 1.86–2.01 m (2H, C²H₂), 2.52 t (2H, CH₂, $J = 7.5$ Hz), 2.69 t.d (1H, $J_1 = 8$, $J_2 = 14$ Hz) and 2.82 d.d.d (1H, $J_1 = 6$, $J_2 = 8.5$, $J_3 = 14$ Hz) (C¹H₂), 3.89 m (1H, 3-H), 5.10 s (2H, CH₂O), 7.09 d (2H, H_{arom}, $J = 8.5$ Hz), 7.19 d (2H, H_{arom}, $J = 8.5$ Hz), 7.25 d (2H, H_{arom}, $J = 8.5$ Hz), 7.55 d (2H, H_{arom}, $J = 8.5$ Hz), 7.60 d (2H, H_{arom}, $J = 8.5$ Hz), 7.67 d (2H, H_{arom}, $J = 8.5$ Hz).

Compounds IXb and IXc were synthesized in a similar way.

3-Chloro-1-[4-(4'-propoxybiphenyl-4-ylmethoxy)phenyl]octane (IXb). Yield 69%. UV spectrum: λ_{\max} 268 nm. IR spectrum, ν , cm⁻¹: 3000 (C–H_{arom}); 2925, 2855 (C–H_{alk}); 1605, 1575, 1495 (C=C_{arom}). ¹H NMR spectrum, δ , ppm: 0.74 t (3H, C⁸H₃, $J = 7$ Hz); 0.87 t (3H, CH₃, $J = 7$ Hz); 1.00–1.18 m (4H), 1.20–1.31 m (1H), 1.35–1.47 m (1H), and 1.54–1.68 m (2H) (CH₂); 1.64 sext (2H, CH₃CH₂CH₂O, $J = 7$ Hz); 1.85–2.01 m (2H, C²H₂); 2.68 t.d (1H, $J_1 = 8.5$, $J_2 =$

14 Hz) and 2.82 d.d.d (1H, $J_1 = 6$, $J_2 = 8.5$, $J_3 = 14$ Hz) (C^1H_2); 3.80 t (2H, CH_2CH_2O , $J = 7$ Hz); 3.88 m (1H, 3-H); 5.10 s (2H, CH_2O); 7.05 d (2H, H_{arom} , $J = 8.5$ Hz); 7.09 d (2H, H_{arom} , $J = 8.5$ Hz); 7.19 d (2H, H_{arom} , $J = 8.5$ Hz); 7.54 d (2H, H_{arom} , $J = 8.5$ Hz); 7.61 d (2H, H_{arom} , $J = 8.5$ Hz); 7.64 d (2H, H_{arom} , $J = 8.5$ Hz).

1-[4-(4'-Butoxybiphenyl-4-ylmethoxy)phenyl]-3-chlorooctane (IXc). Yield 78%. UV spectrum: λ_{max} 269 nm. IR spectrum, ν , cm^{-1} : 3010 ($C-H_{arom}$); 2955, 2930, 2870 ($C-H_{alk}$); 1605, 1500, 1490 ($C=C_{arom}$). 1H NMR spectrum, δ , ppm: 0.74 t (3H, C^8H_3 , $J = 7$ Hz), 0.79 t (3H, CH_3 , $J = 7.5$ Hz), 0.98–1.47 m (6H, CH_2), 1.34 sext (2H, $CH_3CH_2CH_2$, $J = 7.5$ Hz), 1.52–1.66 m (4H, $CH_3CH_2CH_2$, C^4H_2), 1.86–1.99 m (2H, C^2H_2), 2.68 t.d (1H, $J_1 = 9$, $J_2 = 13$ Hz) and 2.82 d.d.d (1H, $J_1 = 6$, $J_2 = 8$, $J_3 = 13$ Hz) (C^1H_2), 3.86 t (2H, CH_2CH_2O , $J = 7$ Hz), 3.84–3.92 m (1H, 3-H), 5.10 s (2H, CH_2O), 7.06 d (2H, H_{arom} , $J = 9$ Hz), 7.09 d (2H, H_{arom} , $J = 9$ Hz), 7.19 d (2H, H_{arom} , $J = 9$ Hz), 7.52 d (2H, H_{arom} , $J = 9$ Hz), 7.61 d (2H, H_{arom} , $J = 9$ Hz), 7.64 d (2H, H_{arom} , $J = 9$ Hz).

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