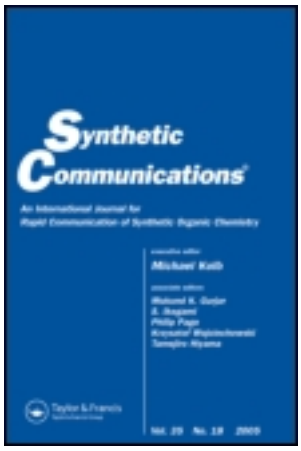

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An Efficient Strategy for the Synthesis of Chiral Liquid Crystals Using Evans' Methodology

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ABSTRACT

The synthesis of liquid crystal compound **2** was achieved using Evans' methodology. The strategy was based on three key synthetic reactions: alkylation of chiral amide enolates, Mitsunobu and, finally, esterification. The final compound presents a stable smectic A phase.

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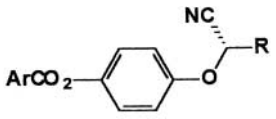
The design and synthesis of new materials with liquid-crystalline properties and technological application derived from chiral starting reagents constitute a permanent challenge to the synthetic organic chemist. In the literature, there are several synthetic methodologies, which have been reported that are related to the synthesis of chiral liquid crystals (CLCs). Most of them start from chiral reagents with adequate functionalities. (*S*)-(−)-Ethyl lactate,[1] (*S*)-(−)-2-methyl-1-butanol,[2] (*R*)-(−)-2-octanol[3] and α-aminoacids[4] are the most relevant reagents used in the field of the synthesis of chiral liquid crystals. The reagents above are extensively used due to their availability in high optical purity, low cost and commercial accessibility.

Few examples are found in the literature using stereogenic synthesis methodology in the preparation of chiral materials with liquid-crystalline properties.[5] Walba and co-workers[6] reported the first synthesis of chiral aryl cyanohydrin ether **1** from chiral oxazolidinone template. The key step in their synthesis work was the diastereoselective hydroxylation of chiral imide enolates with oxaziridine oxidants (Fig. 1).

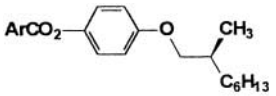
The enantiomerically pure 2-oxazolidinone system is an excellent chiral auxiliary and is one of the most popular tools for the synthesis of chiral α-alkylcarbonyl derivatives. Evans and co-workers[7] were the pioneers in the development of that synthesis methodology. This chiral agent—known as Evans' oxazolidinone—reveals to be effective in the aspect of the stereochemical control of new C–C bonds, which are made in the alkylation reaction of chiral amide enolates.[8]

Based upon the considerations discussed above, we report here preliminary results using chiral oxazolidinone as powerful tool in chiral enolate alkylation reaction and the synthesis of chiral liquid crystals using the methodology of Evans. We used this approach to construct either alcohol β-methyl-**8** and phenol **12**. The general chemical structure of the chiral liquid crystal **2** prepared in this work is shown in the Fig. 2.



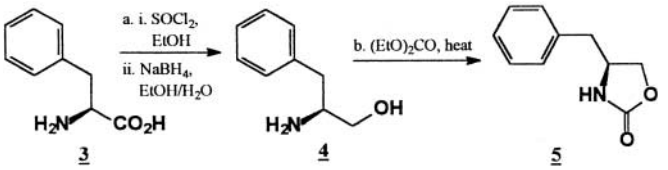
1 Ar = *p*-$C_{10}H_{21}OC_6H_4$
R = -C_5H_6

Figure 1. Chiral aryl cyanohydrin **1** from Walba's Approach.



2 Ar = *p*-$C_{10}H_{21}OC_6H_4$

Figure 2. Chemical structure of chiral liquid crystal **2**

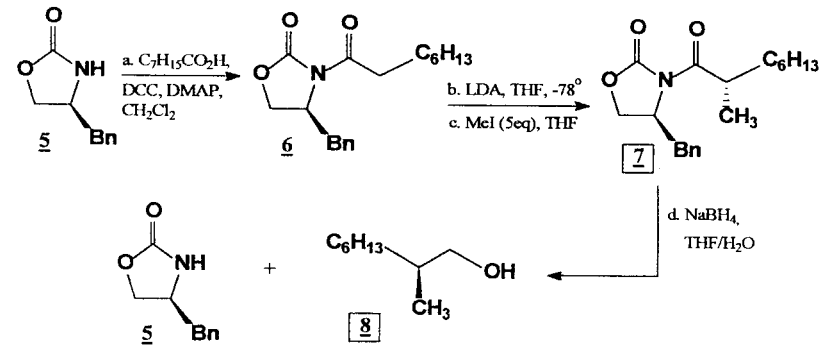


Scheme 1.

Synthesis of the chiral auxiliaries (*S*)-4-benzyl-2-oxazolidinone (5). The synthesis of the final compound **2** was carried out as described in Schs. 1–4. The chiral auxiliary **5** (Sch. 1) was obtained from L-phenylalanine (**3**) in three steps: esterification reaction ($SOCl_2$, EtOH) followed by in situ reduction ($NaBH_4$, EtOH/NaOH) to afford the intermediate (*S*)-2-amino-3-phenylpropan-1-ol (**4**) in 67% yield and $[\alpha]_D = -24$ (1.03; EtOH).[9] Condensation reaction with diethylcarbonate gives the desired chiral auxiliary (*S*)-4-benzyl-2-oxazolidinone (**5**) in 62% yield {$[\alpha]_D = +5$ (1.10; EtOH)}.[10]

Alkylation reaction of the chiral amide enolate from 6. The (*S*)-*N*-acyloxazolidinone **6** was readily accessible[11] by reaction of caprylic acid with the auxiliary **5** for 48 h at room temperature with 1,3-dicyclohexylcarbodiimide (DCC) as dehydrating agent and catalytic quantities of 4-(*N,N*-dimethylamino)pyridine (DMAP) in 65% yield and $[\alpha]_D = +95$ (1.2; EtOH). The key step in our synthetic planning is the diastereoselective alkylation reaction of amide enolate[12] under kinetic conditions from (*S*)-*N*-acyl-4-benzyl-2-oxazolidinone **(6)**. The alkylation reaction of the lithium enolate of **6**, prepared with LDA (1.5 Eq.) at -78°C for 1 h, followed by addition of alkylating agent (CH_3I, 5 Eq.) for 12 h ($-78^\circ \rightarrow 25^\circ$C) gives the alkylated product **7** as a colorless oil in 68% yield {$[\alpha]_D = +92^\circ$(1,55, EtOH)} after column chromatography on silica gel with hexane-ethylacetate as eluent (9/1) (Sch. 2, Fig. 3) and with excellent levels of asymmetric induction.[13]

The reductive removal of the chiral auxiliary ($NaBH_4$, THF:water) [14] furnishes the chiral 2-methylalkanol **8** in 65% yield and $[\alpha]_D = -21$ (0.875; CH_2Cl_2). The chiral auxiliary **5** was recovered stereochemically



Scheme 2.

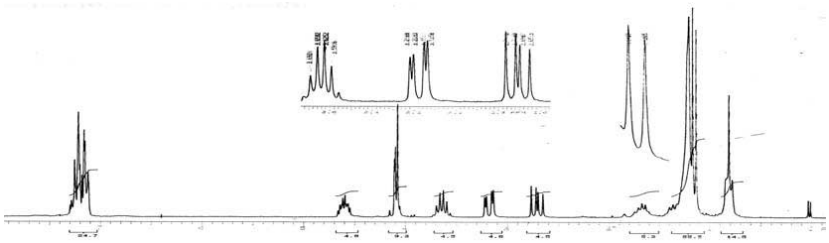
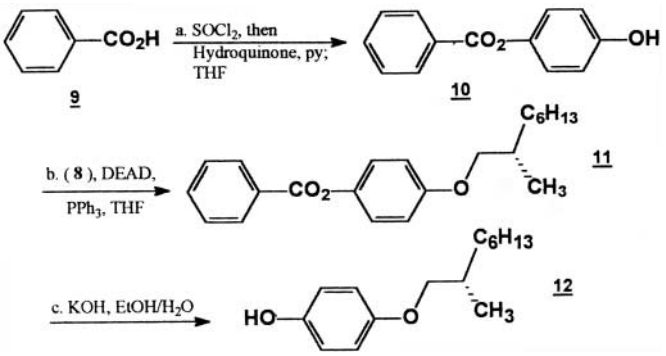


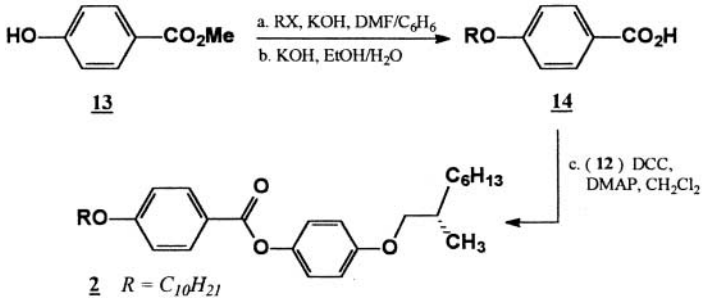
Figure 3. ^{1}H-NMR spectrum (200 MHz, $CDCl_3$) of the compound **7** obtained after column chromatography.

unchanged {$[\alpha]_D = +5$ (1.10; EtOH)}.[10] The diastereomeric excess of the crude mixture could not be estimated by ^{1}H-NMR and was assumed to be $>95\%$.

Synthesis of the chiral phenol 12 by Mitsunobu reaction. The synthesis of the key intermediate **12** outlined in Sch. 3 was achieved by Mitsunobu reaction[15] starting from hydroquinone monobenzoate[16] **10** and the chiral alcohol **8**. Compound **10** was synthesized in 63% yield by conversion of acid **9** to the acyl chloride followed by reaction with hydroquinone in pyridine. The correspondent diester-$PhCO_2C_6H_4O_2CPh$ was obtained in 16% yields as by-product. We have optimized the reaction conditions in the Mitsunobu reaction and obtained compound **11** in 57% yield. The choice of the solvent is critical due to low solubility of the compound **10**. In CH_2Cl_2, the reaction yields the desired product **11**, but all attempts to repeat that reaction, however, gave only poor yields (15–25% yield) or failed.[17]



Scheme 3.



Scheme 4.

The best reaction conditions use THF as solvent and addition of a THF solution of **8** and diethyl azodicarboxylate within 1 h to the solution of **10** and PPh_3 at $0^{\circ}C \rightarrow 25^{\circ}C$ for 48 h. Alkaline hydrolysis afforded (*S*)-(+)-4-[1-(2-methyl)octyloxy] phenol (**12**) in 73% yield and $[\alpha]_D = +47$ (1.44; CH_2Cl_2).

Convergent synthesis of the chiral liquid crystal 2. With compound **12** available, we started to prepare the acid portion **14** outlined in Sch. 4. Alkylation of methyl *p*-hydroxybenzoate (**13**) with alkyl bromides followed by hydrolysis afforded the *p*-*n*-alkoxybenzoic acid (**14**) in 80% yield.[18] Our convergent synthesis finishes with esterification of phenol **12** using dicyclohexylcarbodiimide (DCC) as dehydrating agent and DMAP as catalyst to give the target molecule **2** in 63% yield.

The thermal transitions and the mesomorphic textures were determined using a Leitz Ortholux polarizing microscope in conjunction with a

Mettler FP-52 heating stage. The texture of the mesophase[19] was identified by microscopy studies. The thermal transitions for **2** are: **K** 39.5 $\mathbf{S_A}$ 55.5 **I**. When the sample is cooled from its isotropic phase, the smectic A phase appears, which exhibited focal-conic texture. The stable enantiotropic smectic A phase was found. On heating, the sample enters into the smectic A phase at 39.5°C and finally melts to an isotropic liquid at 55.5°C. The range of temperature for the mesophase is 16°C. The two peaks observed at 39.5°C and 55.5°C were associated with $\mathbf{K} \rightarrow \mathbf{S_A}$ and $\mathbf{S_A} \rightarrow \mathbf{N}$ transitions, respectively, during the microscopy studies.

In conclusion, we have presented an efficient and practical synthesis of the chiral liquid crystal **2** using Evans' methodology.

EXPERIMENTAL SECTION

^{1}H NMR and ^{13}C NMR spectra in $CDCl_3$ were obtained using Varian-200 and 300 MHz spectrometers using TMS as the internal standard. IR Spectra were recorded in Nujol on a 3000 Galaxy Series spectrometer. Optical rotations were recorded on a Perkin-Elmer 341 polarimeter at the sodium D line. The thermal transitions and the mesomorphic textures were determined using a Leitz Ortholux polarizing microscope in conjunction with a Mettler FP-52 heating stage. Mass spectra were recorded on a GC–MS Shimadzu QP-5050 (EI, 70 eV). Purification by column chromatography was carried out on 70–230 mesh Merck silica gel 60. L-Phenylalanine, *p*-hydroxy methylbenzoate, 4-(*N,N*-dimethylamino)-pyridine (DMAP), 1,3-dicyclohexylcarbodiimide (DCC), diethylazodicarboxilate (DEAD), butyllithium (2.1 M), sodiumborohydride, diisopropylamine and triphenyl phosphine (PPh_3) were purchased from Aldrich, and used as received unless otherwise specified. Chemicals were used without further purification. THF was distilled over sodium-benzophenone. Dichloromethane (CH_2Cl_2) was distilled over calcium hydride (CaH_2) under argon immediately before use. Analytical thin-layer chromatography (TLC) was conducted on Merck aluminum plates with 0.2 mm of silica gel 60F-254. Anhydrous sodium sulfate was used to dry all organic extracts.

(*S*)-2-Amino-3-phenylpropan-1-ol (4). The compound **4** was synthesized according to Ref.[9]. White solid; M.p.: 89–91°C; Yield: 67%; $[\alpha]_D = -24$ (1.03; EtOH). **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 1.90 (broad, 3H, NH_2, OH), 2.52 (dd, 1H, C$\underline{H}$CHPh, $^2J_{gem} = 13.5$, $^3J_{trans} = 8.4$ Hz), 2.80 (dd, 1H, CHC$\underline{H}$Ph, $^2J_{gem} = 13.6$, $^3J_{cis} = 4.9$ Hz), 3.10 (m, 1H, C$\underline{H}$N), 3.39 (dd, 1H, C$\underline{H}$HO, $^3J_{trans} = 7.2$,

$^2J_{gem} = 10.5$ Hz), 3.64 (dd, 1H, C<u>H</u>HO, $^3J_{cis} = 3.8$, $^2J_{gem} = 10.7$ Hz), 7.20 (m, 5H Ar). **^{13}C NMR** ($CDCl_3$, 50 MHz): δ 40.5, 54.5, 63.2, 127.1, 128.5, 129.3, 139.0.

(*S*)-4-Benzyl-2-oxazolidinone (5). The compound **5** was prepared according to Ref.[10] White solid; M.p.: 89°C; Yield: 62%; $[\alpha]_D = +5$ (1.10; EtOH); **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 2.90 (m, 2H, CH_2Ph), 4.10 (m, 2H, CH_2O), 4.40 (m, 1H, CHN), 6.10 (broad, 1H, NH) 7.30 (m, 5H, Ar). **^{13}C NMR** ($CDCl_3$, 50 MHz): δ 40.9, 52.0, 69.8, 127.0, 128.8, 128.9, 135.8, 159.5.

(*S*)-*N*-Octanoyl-4-benzyl-2-oxazolidinone (6). (*S*)-4-Benzyl-2-oxazolidinone (**5**) (7.15 g, 40.0 mmol) and caprylic acid (5.0 g, 34.0 mmol), were added in dry CH_2Cl_2 (30 mL) under argon and the solution was stirred at room temperature for 10 min. DCC (7.6 g, 37 mmol) and DMAP (0.410 g, 0.37 mmol) were then added. The solution was stirred for 48 h at room temperature. The solution was filtered off and the solvent evaporated. The crude product was purified by column chromatography (silica gel, diethyl ether/hexane = 1:9) to yield 6.7 g (65%) of **6** as colorless oil. $[\alpha]_D = +45$ (1.12; EtOH). **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 0.90 (t, 3H, CH_3), 1.40 (m, 8H, CH_2), 1.70 (m, 2H, C<u>H</u>$_2$CH$_2$CO), 2.70–3.10 (m, 3H, CHPh, CH_2CO), 3.30 (dd, 1H, CHPh), 4.20 (m, 2H, CH_2O), 4.60 (m, 1H, CHN), 7.30 (m, 5H, Ar).

(*S*)-*N*-[(*S*)-(2-Methyl)octanoyl]-4-benzyl-2-oxazolidinone (7). To a solution of 15.4 mmol of LDA at −78°C (prepared from diisopropylamine (1.55 g) and *n*-BuLi 1.3 M (12.0 mL) in 16 mL of anhydrous THF was added dropwise a solution of 10.2 mmol (3.10 g) of (*S*)-*N*-octanoyl-4-benzyl-2-oxazolidinone (**6**) in 20 mL of THF. After the reaction mixture was stirred at −78°C for 1.5 h, 7.25 g (51.0 mmol, 3.17 mL) of MeI in 7 mL of THF at −78°C was added slowly. The solution was stirred for 4 h at −78°C, left at room temperature for 8 h and then quenched by the addition of 20 mL of aqueous saturated ammonium chloride solution. The solvent and the volatile components were removed by rotary evaporation, and the resultant yellow slurry was extracted with dichloromethane (3 × 75 mL). The organic layers were combined and washed with 5% $NaHCO_3$ solution (2 × 25 mL) and water (2 × 25 mL), and dried over anhydrous sodium sulfate, and concentrated to give a yellow oil. The alkylated product **7** was obtained as a colorless oil in 68% yield {$[\alpha]_D = +92°$(1.55, EtOH)} after column chromatography on silica gel with hexane-ethylacetate as eluent (9/1). Analysis by CG (SPB-5, 23 psi, 30 m × 0.25 m) showed a single peak with *Rf* 19.33. The minor isomer was not detected in this experiment. **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 0.80 (t, 3H, CH_3CH_2), 1.15 (d, 3H, CH_3CH, $J = 6.9$ Hz), 1.20 (m, 9H, CH_2, CH), 1.70 (m, 1H, CHCO), 2.50 (dd, 1H, C<u>H</u>HPh,

$^2J_{gem} = 13.3$, $^3J_{trans} = 9.40$ Hz), 3.18 (dd, 1H, CHHPh, $^2J_{gem} = 13.4$, $^3J_{cis} = 3.20$ Hz), 3.63 (sext., 1H, $CHCH_3$, $J = 6.7$ Hz), 4.10 (m, 2H, CH_2O), 4.60 (m, 1H, CH–N), 7.20 (m, 5H, Ar). **^{13}C NMR** ($CDCl_3$, 50 MHz): δ 14.6, 17.9, 23.1, 27.7, 29.8, 32.2, 33.9, 38.2, 38.4, 55.7, 66.5, 127.7, 129.3, 129.9, 135.8, 152.5, 177.7.

(*S*)-2-Methyloctanol (8). This compound was prepared according to Ref.[14] To a mixture of the **7** (6.50 mmol) in THF (12.5 mL) was added a solution of sodium borohydride (26.0 mmol, 0.97 g) in water (4 mL) at 20–25°C. The mixture was stirred at room temperature for overnight. To the reaction mixture was added 2 N HCl (24 mL) at 20–25°C. The reaction mixture was extracted with ethyl acetate (3×50 mL). The organic phase were washed with brine (2×50 mL) and concentrated. The solid residue was washed with cold hexane and the chiral auxiliary was easily separated from the solution by simple filtration. The yellow oil residue was purified by silica gel chromatography with hexane-ethyl ether as eluent (9/1) to give compound **(8)** in 65% yield. $[\alpha]_D = -21$ (0.875; CH_2Cl_2). **^{1}H NMR** ($CDCl_3$, 300 MHz): δ 0.85 (t, 3H, CH_3CH_2), 0.90 (d, 3H, CH_3CH, $J = 6.7$ Hz), 1.15 (m, 9H, CH_2, CH), 1.60 (m, 2H, CH_2), 1.80 (broad, 1H, OH), 3.40 (dd, 1H, CHHO, $^2J_{gem} = 10.3$, $^3J_{trans} = 6.60$ Hz), 3.50 (dd, 1H, CHHO, $^2J_{gem} = 13.4$, $^3J_{cis} = 5.80$ Hz). **^{13}C NMR** ($CDCl_3$, 50 MHz): δ 14.0, 16.5, 22.6, 26.9, 29.6, 31.8, 33.2, 35.7, 68.3. **IR** ν_{max}/cm^{-1} 3360, 2910, 2856, 1640, 1460, 1370, 1034 (film).

4-Hydroxyphenyl benzoate (10). The compound **10** was synthesized following the procedure reported by Helgee and co-workers.[16] Data: yield 63%; M.p.: 172°C; **^{1}H NMR** ($CDCl_3$/DMSO, 200 MHz): δ 6.90 (dd, 4H, Ar), 7.52 (m, 3H, Ar), 8.10 (d, 2H, Ar). **I.R.** $\nu_{máx}/cm^{-1}$: 3368, 2928, 1515, 1463, 1377, 1242, 1105, 770, 722.

(*S*)-(+)-4-[1-(2-methyl)octyloxy]phenyl benzoate (11). The solution of diethylazodicarboxylate (DEAD, 0.87 g, 5 mmol) and (*S*)-2-methyloctanol **(8)** (0.490 g, 3.4 mmol) in THF (5 mL) was added dropwise to a cold stirred solution of 4-hydroxyphenyl benzoate (0.73 g, 3.4 mmol), triphenylphosphine (1.31 g, 5 mmol) and THF (30 mL) for 1 h. The mixture was stirred at room temperature for 48 h and the solvent was evaporated from the reaction mixture. The resulting oil was dissolved in ethylacetate and on addition four times the volume of light petroleum. Triphenylphosphine oxide was precipitated. The solid was filtered off and the solution was evaporated to dryness. The material obtained was purified by column chromatography on silica gel with hexane-ethylacetate as eluent (9/1) in 57% (0.66 g) yield of yellow oil. **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 0.90 (m, 3H, CH_3), 1.0 (d, 3H, CH_3, $J = 6.65$ Hz), 1.30 (m, 11H, CH_2, CH), 3.70 (dd, 1H, CHHO, $^2J_{gem} = 8.90$, $^3J_{trans} = 6.70$ Hz), 3.80 (dd, 1H, CHHO,

$^2J_{gem} = 8.90$, $^3J_{cis} = 5.80$ Hz), 6.90 (d, 2H, Ar, $J = 9.20$ Hz), 7.10 (d, 2H, Ar, $J = 9.10$ Hz), 7.40–7.70 (m, 3H, Ar), 8.20 (d, 2H, Ar, $J = 7.50$ Hz).

(*S*)-(+)-4-[1-(2-methyl)octyloxy]phenol (12). To 0.66 g (1.94 mmol) of (*S*)-(+)-4-[1-(2-methyl)octyloxy]phenyl benzoate (**11**) in the mixture ethanol/water (20 mL), 0.26 g (4.8 mmol) of potassium hydroxide was added. The mixture was stirred overnight at room temperature. The ethanol was evaporated and the product was extracted from diethyl ether and washed with water (2×25 mL) and dried over Na_2SO_4 and purified on silica gel using ethyl acetate/hexane (1:9) to yield 0.34 g (73%) as pale oil. $[\alpha]_D = +47$ (1.44; CH_2Cl_2); **^{1}H NMR** ($CDCl_3$, 300 MHz): δ 0.90 (m, 3H, CH_3), 0.95 (d, 3H, CH_3, $J = 6.60$ Hz), 1.15 (m, 11H, CH_2, CH), 3.60–3.90 (m, 2H, CH_2O), 6.80 (m, 4H, Ar). **^{13}C NMR** ($CDCl_3$, 50 MHz): δ 14.0, 17.0, 22.6, 26.8, 29.5, 31.8, 33.2, 33.5, 74.1, 115.6, 115.9, 149.4, 153.3. **IR** ν_{max}/cm^{-1} 3360, 2920, 2855, 1600, 1510, 1228, 1100, 1030, 824, 770 (nujol).

(*S*)-4′-[1-(2-methyl)octyloxy]phenyl 4-*n*-decyloxybenzoate (2). (*S*)-(+)-4-[1-(2-methyl)octyloxy]phenol (**12**) (70.8 mg, 0.30 mmol) and 4-*n*-decyloxybenzoic acid (**14**) (83.4 mg, 0.30 mmol), were added in dry CH_2Cl_2 (10 mL) under argon and the solution was stirred at room temperature for 10 min. 1,3-Dicyclohexylcarbodiimide (DCC) (74.0 mg, 0.36 mmol) and 4-(*N,N*-dimethylamino)pyridine (DMAP) (0.036 mmol) were then added. The solution was stirred for 24 h at room temperature. The solution was filtered and the solvent evaporated. The crude product was purified by column chromatography (silica gel, acetate/hexane = 1:9) to yield 93.0 mg (63%) of **2** as white solid. Thermal transitions for **2** are: **K** 39.5 **S_A** 55.5 **I**. **^{1}H NMR** ($CDCl_3$, 300 MHz): δ 0.90 (m, 6H, CH_3), 1.00 (d, 3H, CH_3), 1.20–1.90 (m, 27H, CH_2, CH), 3.80 (m, 2H, OCH_2CH), 4.00 (t, 2H, CH_2O), 6.90 (m, 4H, Ar), 7.10 (d, 2H, Ar, $J = 8.6$ Hz), 8.10 (d, 2H, Ar, $J = 9.0$ Hz). **^{13}C NMR** ($CDCl_3$, 50 MHz): δ 14.09, 17.02, 22.65, 25.95, 26.88, 29.08, 29.19, 29.23, 29.30, 29.34, 29.53, 29.55, 31.80, 31.84, 31.87, 33.13, 33.48, 68.26, 73.60, 114.20, 115.03, 121.66, 122.41, 132.17, 144, 30, 156.93, 163.40, 165.32.

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