

Electronic supplementary information

3-Hydroxycinnamic acid - a new central core for the design of bent-shaped liquid crystals

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S1. Synthesis

S1.1 General

Structures of intermediates and final products were confirmed by ¹H NMR spectroscopy (Varian Gemini 300 HC instrument), deuteriochloroform was used as solvent and signals of the solvent served as internal standard, *J* values are given in Hz. Elemental analyses were carried out on a Perkin-Elmer 2400 instrument. Purity of all final compounds was confirmed by HPLC analysis (Tessek C18 25x4.5 RP column) and found >99.8%. Column chromatography was carried out using Merck Kieselgel 60 (60-100 μm). The experimental part summarizes general synthetic procedures for the preparation of intermediates **1** and **3-5** and the target compounds of the series **I**, **II** and **III**.

S1.2 Synthesis of intermediates

3-*tert*-Butyl(dimethyl)silyloxycinnamic acid (**1**)

To a solution of 3-hydroxycinnamic acid (4.0 g; 24.4 mmol) and imidazole (3.4 g; 48.8 mmol) in dry DMF (45 ml), a solution of *tert*-butyl(dimethyl)silyl chloride in dry DMF (12 ml) was added dropwise. The reaction mixture was stirred at 60 °C for 9 h and then poured in cold aq. 1 M HCl (100 ml). The solution was extracted with ethyl acetate (3 × 75 ml), the combined organic solution was washed with aq. 6 M HCl (3 × 60 ml), water (2 × 60 ml) and dried with anhydrous magnesium sulphate. The solvent was evaporated and the crude product was crystallized from toluene to yield 5.3 g (78%) of acid **1**, m.p. 114-117 °C. ¹H NMR (DMSO-*d*₆): 0.18 (s, 6 H, (CH₃)₂Si), 0.94 (s, 9 H, (CH₃)₃SiC), 6.48 (d, 1 H, *J* = 15.8, CH=CHCOO), 6.88 (m, 1 H, H-4), 7.12 (s, 1 H, H-2), 7.27 (m, 2 H, H-5, H-6), 7.52 (d, 1 H, *J* = 15.8,

CH=CH-COO), 12.37 (bs, 1 H, COOH). Elemental analysis: for C₁₅H₂₂O₃Si (278.43), calculated C 64.71, H 7.96; found C 64.65, H 8.02%.

4-Alkyloxyphenyl 4-[(3-(tert-butyl(dimethyl)silyloxy)cinnamoyl)oxy]benzoate (3A-D)

To a solution of acid **1** (1.50 mmol), hydroxy ester **2A-D** (1.53 mmol) and catalytic amount of DMAP (0.05 g) in dry dichloromethane (30 ml), DCC (0.32 g; 1.56 mmol) was added in one portion and the reaction mixture was stirred in the argon atmosphere for 3 h. The precipitate was filtered and the filtrate evaporated. The crude product was purified by column chromatography (hexane/ethyl acetate, 8/1).

4-Octyloxyphenyl 4-[(3-(tert-butyl(dimethyl)silyloxy)cinnamoyl)oxy]benzoate (3A). Yield 91%, m.p. 78-79.5 °C. ¹H NMR: 0.23 (s, 6 H, (CH₃)₂Si), 0.91 (t, 3 H, *J* = 6.9, CH₃), 1.01 (s, 9 H, (CH₃)₃Si), 1.22-1.40 (m, 8 H, (CH₂)₄), 1.46 (m, 2 H, CH₂), 1.79 (m, 2 H, CH₂), 3.96 (t, 3 H, *J* = 6.7, OCH₂), 6.59 (d, 1 H, *J* = 16.1, CH=CHCOO), 6.93 (m, 3 H, 2 H, H-4), 7.06 (t, 1 H, *J* = 2.1, H-2), 7.11 (d, 2 H, *J* = 9.1), 7.20 (d, 1 H, *J* = 7.9, H-6), 7.30 (d, 1 H, *J* = 7.9, H-5), 7.32 (d, 2 H, *J* = 8.8), 7.53 (d, 1 H, *J* = 16.1, CH=CHCOO), 8.26 (d, 2 H, *J* = 8.8). Elemental analysis: for C₃₆H₄₆O₆Si (602.85), calculated C 71.73, H 7.69; found C 71.73, H 7.64%.

4-Decyloxyphenyl 4-[(3-(tert-butyl(dimethyl)silyloxy)cinnamoyl)oxy]benzoate (3B) (R = C₁₀H₂₁, yield 91%, m.p. 79-80 °C), *4-dodecyloxyphenyl 4-[(3-(tert-butyl(dimethyl)silyloxy)cinnamoyl)oxy]benzoate (3C)* (R = C₁₂H₂₅, yield 90%, m.p. 71-72 °C), and *4-tetradecyloxyphenyl 4-[(3-(tert-butyl(dimethyl)silyloxy)cinnamoyl)oxy]benzoate (3D)* (R = C₁₄H₂₉, yield 89%, m.p. 60-61 °C) were obtained by the same procedure.

In the same way, the reaction of acid **1** with hydroxy ester **2E** gave rise to ester **3E** with inversed orientation of the linking carboxylic group. *4-[(3-(tert-Butyl(dimethyl)silyloxy)cinnamoyl)oxy]phenyl 4-octyloxybenzoate (3E)*, yield 84%, m.p. 98 °C. ¹H NMR: 0.23 (s, 6 H, (CH₃)₂Si), 0.89 (t, 3 H, *J* = 6.9, CH₃), 1.00 (s, 9 H, (CH₃)₃Si), 1.24-1.40 (m, 8 H, (CH₂)₄), 1.48 (m, 2 H, CH₂), 1.83 (m, 2 H, CH₂), 4.04 (t, 2 H, *J* = 6.5), 6.59 (d, 1 H, *J* = 16.1, CH=CHCOO), 6.91 (ddd, 1 H, ³*J* = 7.9, ⁴*J*_{H-4,H-2} = 2.3, ⁴*J*_{H-4,H-6} = 2.5, H-4), 6.97 (d, 2 H, *J* = 8.8), 7.06 (t, 1 H, *J* = 2.3, H-2), 7.19 (m, 1 H, H-6), 7.23 (d, 4 H, *J* = 1.8), 7.29 (t, 1 H, *J* = 7.9, H-6), 7.82 (d, 1 H, *J* = 16.1, CH=CHCOO), 8.14 (d, 2 H, *J* = 8.8). Elemental analysis: for C₃₆H₄₆O₆Si (602.85), calculated C 71.73, H 7.69; found C 71.68, H 7.69%.

4-Dodecyloxyphenyl 4-[(3-(tert-butyl(dimethyl)silyloxy)cinnamoyl)oxy]benzoate (3F) (R = C₁₀H₂₁, yield 91%, m.p. 78 °C), *4-dodecyloxyphenyl 4-[(3-(tert-butyl(dimethyl)silyloxy)cinnamoyl)oxy]benzoate (3G)* (R = C₁₂H₂₅, yield 84%, m.p. 62 °C), and *4-tetradecyloxyphenyl 4-[(3-(tert-butyl(dimethyl)silyloxy)cinnamoyl)oxy]benzoate (3H)* (R = C₁₄H₂₉, yield 78%, m.p. 63 °C) were prepared by the above procedure.

In the same way, acylation of hydroxy esters **2I** with acid **1** afforded ester **3I** with an additional ester group in the terminal chain. *Octyl 4-{4-[(3-(tert-butyl(dimethyl)silyloxy)cinnamoyl)oxy]benzoyl}oxy}benzoate (3I)* was purified by column chromatography (hexane/ethyl acetate 10/1), yield 70 %, m.p. 58-59 °C. ¹H NMR: 0.32 (s, 6 H, (CH₃)₂Si), 0.89 (t, 3 H, *J* = 6.9, CH₃), 1.01 (s, 9 H, (CH₃)₃Si), 1.20-1.52 (m, 10 H, (CH₂)₅), 1.78 (m, 2 H, CH₂), 4.33 (t, 2 H, *J* = 6.7, COOCH₂), 6.60 (d, 1 H, *J* = 16.1, CH=CHCOO), 6.93 (dd, 1 H, ³*J* = 7.9, ⁴*J* = 1.8, H-4), 7.07 (bs, 1 H, H-2), 7.20 (d, 1 H, *J* = 7.9, H-6), 7.30 (dd, 1 H, ³*J* = 7.9, ⁴*J* = 2.0, H-5), 7.31 (d, 2 H, *J* = 8.5, 2 H), 7.35 (d, 2 H, *J* =

8.5), 7.85 (d, 1 H, $J = 16.1$, $\text{CH}=\underline{\text{CH}}\text{COO}$), 8.13 (d, 2 H, $J = 8.5$), 8.27 (d, 2 H, $J = 8.5$). Elemental analysis: for $\text{C}_{37}\text{H}_{46}\text{O}_7\text{Si}$ (630.86), calculated C 70.45, H 7.35; found C 70.43, H 7.38%.

Decyl 4-{4-([3-(tert-butyl(dimethyl)silyloxy)cinnamoyl]oxy)benzoyl}oxy}benzoate (3J) ($\text{R} = \text{C}_{10}\text{H}_{21}$, yield 87%, m. p. 52.5-53.5 °C), *dodecyl 4-{4-([3-(tert-butyl(dimethyl)silyloxy)cinnamoyl]oxy)benzoyl}oxy}benzoate (3K)* ($\text{R} = \text{C}_{12}\text{H}_{25}$, yield 72%, m.p. 53-56 °C), and *tetradecyl 4-{4-([3-(tert-butyl(dimethyl)silyloxy)cinnamoyl]oxy)benzoyl}oxy}benzoate (3L)* ($\text{R} = \text{C}_{14}\text{H}_{29}$, yield 76%, m.p. 67-69 °C) were synthesized analogously.

4-Alkyloxyphenyl 4-[(3-hydroxycinnamoyl)oxy]benzoate (4A-D)

To a solution of **3A-D** (1.00 mmol) in wet THF (30 ml, 1% H_2O), tetrabutylammonium fluoride (0.08 g; 0.25 mmol) was added and the reaction mixture was stirred at room temperature for 1 h. Then it was poured into water (50 ml) and washed with ethyl acetate (2×50 ml). The collected organic solution was washed with water (20 ml), saturated solution of NaCl (20 ml) and dried with anhydrous magnesium sulphate. The solvent was removed and the crude product was purified by column chromatography (hexane/ethyl acetate, 4/1) and crystallization from ethanol.

4-Octyloxyphenyl 4-[(3-hydroxycinnamoyl)oxy]benzoate (4A), yield 74%, m.p. 134-137 °C. ^1H NMR: 0.89 (t, 3 H, $J = 6.9$, CH_3), 1.25-1.39 (m, 8 H, $(\text{CH}_2)_4$), 1.47 (m, 2 H, CH_2), 1.79 (m, 2 H, CH_2), 3.96 (t, 2 H, $J = 6.6$, OCH_2), 4.84 (s, 1 H, OH), 6.61 (d, 1 H, $J = 16.1$, $\text{CH}=\underline{\text{CH}}\text{COO}$), 6.92 (m, 3 H, 2H + H-4), 7.07 (t, 1 H, $J = 2.1$, H-2), 7.11 (d, 2 H, $J = 9.1$), 7.18 (m, 1 H, H-6), 7.31 (t, 1 H, $J = 7.9$, H-5), 7.32 (d, 2 H, $J = 8.8$), 7.84 (d, 1 H, $J = 16.1$, $\text{CH}=\underline{\text{CH}}\text{COO}$), 8.26 (d, 2 H, $J = 8.8$). Elemental analysis: for $\text{C}_{30}\text{H}_{32}\text{O}_6$ (488.59), calculated C 73.75, H 6.60; found C 73.79, H 6.56%.

In the same way, *4-decyloxyphenyl 4-[(3-hydroxycinnamoyl)oxy]benzoate (4B)* ($\text{R} = \text{C}_{10}\text{H}_{21}$, yield 59%, m.p. 131-134 °C), *4-dodecyloxyphenyl 4-[(3-hydroxycinnamoyl)oxy]benzoate (4C)* ($\text{R} = \text{C}_{12}\text{H}_{25}$, yield 61%, m.p. 121-125 °C), and *4-tetradecyloxyphenyl 4-[(3-hydroxycinnamoyl)oxy]benzoate (4D)* ($\text{R} = \text{C}_{14}\text{H}_{29}$, yield 58%, m.p. 120-124 °C) were prepared.

Deprotection of silyl derivatives **3E-H** yielded the corresponding hydroxy esters **4E-H**.

4-[(3-Hydroxycinnamoyl)oxy]phenyl 4-octyloxybenzoate (4E), yield 90%, m.p. 122 °C. ^1H NMR: 0.90 (t, 3 H, $J = 6.9$, CH_3), 1.25-1.40 (m, 8 H, $(\text{CH}_2)_4$), 1.48 (m, 2 H, CH_2), 1.83 (m, 2 H, CH_2), 4.05 (t, 2 H, $J = 6.6$, OCH_2), 4.94 (s, 1 H, OH), 6.59 (d, 1 H, $J = 16.1$, $\text{CH}=\underline{\text{CH}}\text{COO}$), 6.90 (dd, 1 H, $^3J = 7.9$, $^4J = 2.5$, H-4), 6.97 (d, 2 H, $J = 8.8$), 7.05 (bs, 1 H, H-2), 7.17 (d, 1 H, $J = 7.9$, H-6), 7.23 (d, 4 H, $J = 1.2$), 7.30 (t, 1 H, $J = 7.9$, H-5), 7.81 (d, 1 H, $J = 16.1$, $\text{CH}=\underline{\text{CH}}\text{COO}$), 8.14 (d, 2 H, $J = 8.8$). Elemental analysis: for $\text{C}_{30}\text{H}_{32}\text{O}_6$ (488.59), calculated C 73.75, H 6.60; found C 73.74, H 6.54%.

4-[(3-Hydroxycinnamoyl)oxy]phenyl 4-decyloxybenzoate (4F) ($\text{R} = \text{C}_{10}\text{H}_{21}$, yield 82%, m.p. 121 °C), *4-[(3-hydroxycinnamoyl)oxy]phenyl 4-dodecyloxybenzoate (4G)* ($\text{R} = \text{C}_{12}\text{H}_{25}$, yield 86%, m.p. 122 °C), and *4-[(3-hydroxycinnamoyl)oxy]phenyl 4-tetradecyloxybenzoate (4H)* ($\text{R} = \text{C}_{14}\text{H}_{29}$, yield 76%, m.p. 121 °C) were also prepared by the same procedure.

Alkyl 4-{4-[[[(3-hydroxycinnamoyl)oxy]benzoyl]oxy]benzoate (4I-L)

To a solution of **3I-L** (1.12 mmol) in a mixture of THF (140 ml) and H₂O (35 ml), tetrabutylammonium fluoride (0.09 g; 0.28 mmol) was added and the reaction mixture was stirred at room temperature for 24 h. Then it was poured into water (200 ml) and washed with ethyl acetate (3 × 100 ml). The collected organic solution was washed with water (120 ml), saturated solution of NaCl (120 ml) and dried with anhydrous magnesium sulphate. The solvent was removed and the crude product was purified by column chromatography (toluene/*tert*-butyl methyl ether, 12/1).

Octyl 4-{4-[[[(3-hydroxycinnamoyl)oxy]benzoyl]oxy]benzoate (4I), yield 58%, m.p. 127 °C. ¹H NMR: 0.89 (t, 3 H, *J* = 6.9, CH₃), 1.24-1.53 (m, 10 H, (CH₂)₅), 1.78 (m, 2 H, CH₂), 4.33 (t, 2 H, *J* = 6.7, OCH₂), 5.08 (s, 1 H, OH), 6.60 (d, 1 H, *J* = 16.1, CH=CHCOO), 6.92 (dd, 1 H, ³*J* = 7.9, ⁴*J* = 2.6, H-4), 7.07 (bs, 1 H, H-2), 7.18 (d, 1 H, *J* = 8.2, H-6), 7.30 (d, 2 H, *J* = 8.5, 2 H), 7.31 (dd, 1 H, ³*J* = 7.9, ⁴*J* = 2.6, H-5), 7.35 (d, 2 H, *J* = 8.5), 7.85 (d, 1 H, *J* = 16.1, CH=CHCOO), 8.14 (d, 2 H, *J* = 8.5), 8.27 (d, 2 H, *J*=8.5). Elemental analysis: for C₃₁H₃₂O₇ (516.60), calculated C 72.08, H 6.24; found C 71.99, H 6.23%.

Analogously, *decyl 4-{4-[[[(3-hydroxycinnamoyl)oxy]benzoyl]oxy]benzoate (4J)* (R = C₁₀H₂₁, yield 59%, m. p. 130 °C), *dodecyl 4-{4-[[[(3-hydroxycinnamoyl)oxy]benzoyl]oxy]benzoate (4K)* (R = C₁₂H₂₅, yield 51%, m.p. 123 °C), and *tetradecyl 4-{4-[[[(3-hydroxycinnamoyl)oxy]benzoyl]oxy]benzoate (4L)* (R = C₁₄H₂₉, yield 76%, m.p. 124 °C) were prepared.

S1.3 Synthesis of the target materials I-III

4-Octyloxyphenyl 4-{(3-[4-(((4-octyloxybenzoyl)oxy)benzoyl]oxy)cinnamoyl)oxy}-benzoate (Ia)

The acid chloride **5A** was prepared from the corresponding 4-[(4-octyloxybenzoyl)oxy]benzoic acid (0.10 g; 0.27 mmol), thionyl chloride (0.2 ml; 2.8 mmol) and pyridine (0.25 ml; 3.1 mmol) in dry toluene (15 ml). The reaction mixture was stirred and heated to boiling for 2 h. The solvent and unreacted thionyl chloride were evaporated and the residue dried at reduced pressure. The crude acid chloride was dissolved in dry dichloromethane (5 ml) and added to a solution of hydroxy ester **4A** (0.12 g; 0.25 mmol) and DMAP (0.04 g; 0.33 mmol) in dry dichloromethane (20 ml). The reaction mixture was stirred at room temperature for 0.5 h and then decomposed with 1% aq. HCl (50 ml). Layers were separated and the aqueous layer was washed with dichloromethane (2 × 30 ml). The collected organic solution was washed with water (20 ml), saturated solution of NaCl (20 ml) and dried with anhydrous magnesium sulphate. The solvent was removed and the crude product was purified by column chromatography (1% methanol in chloroform). 0.16 g (76%) of **Ia** was obtained. ¹H NMR: 0.89 (t, 6 H, *J* = 6.9, 2 × CH₃), 1.30 (m, 16 H, 2 × (CH₂)₄), 1.46 (m, 4 H, 2 × CH₂), 1.81 (m, 4 H, 2 × CH₂), 3.96 (t, 2 H, *J* = 6.7, OCH₂), 4.06 (t, 2 H, *J* = 6.5, CH₂O), 6.67 (d, 1 H, *J* = 16.1, CH=CHCOO), 6.93 (d, 2 H, *J* = 9.1), 6.99 (d, 2 H, *J* = 8.8), 7.11 (d, 2 H, *J* = 9.1), 7.33 (m, 3 H, 2 H + H-4), 7.40 (d, 2 H, *J* = 8.8), 7.51 (m, 3 H, H-2, H-5, H-6), 7.91 (d, 1 H, *J* = 16.1, CH=CHCOO), 8.16 (d, 2 H, *J* = 8.8, 2 H), 8.26 (d, 2 H, *J* = 8.8, 2 H), 8.30 (d, 2 H, *J* = 8.8, 2 H). Elemental analysis: for C₅₂H₅₆O₁₀ (841.02), calculated C 74.26, H 6.71; found C 74.43, H 6.67%.

Employing the same synthetic strategy, the other compounds of series **I** were prepared.

4-Decyloxyphenyl 4-[(3-[4-(((4-decyloxybenzoyl)oxy)benzoyl)oxy]cinnamoyl)oxy]benzoate (Ib). Yield 74%. ¹H NMR: 0.89 (t, 6 H, *J* = 6.9, 2 × CH₃), 1.28 (m, 24 H, 2 × (CH₂)₆), 1.46 (m, 4 H, 2 × CH₂), 1.81 (m, 4 H, 2 × CH₂), 3.96 (t, 2 H, *J* = 6.7, OCH₂), 4.06 (t, 2 H, *J* = 6.5, CH₂O), 6.67 (d, 1 H, *J* = 16.1, CH=CHCOO), 6.93 (d, 2 H, *J* = 9.1), 6.99 (d, 2 H, *J* = 8.8), 7.11 (d, 2 H, *J* = 9.1), 7.33 (m, 3 H, 2 H + H-4), 7.40 (d, 2 H, *J* = 8.8), 7.51 (m, 3 H, H-2,H-5,H-6), 7.91 (d, 1 H, *J* = 16.1, CH=CHCOO), 8.16 (d, 2 H, *J* = 8.8), 8.26 (d, 2 H, *J* = 8.8), 8.30 (d, 2 H, *J* = 8.8). Elemental analysis: for C₅₆H₆₄O₁₀ (897.13), calculated C 74.98, H 7.19; found C 75.05, H 7.11%.

4-Dodecyloxyphenyl 4-[(3-[4-(((4-dodecyloxybenzoyl)oxy)benzoyl)oxy]cinnamoyl)oxy]benzoate (Ic). Yield 65%. ¹H NMR: 0.89 (t, 6 H, *J* = 6.9, 2 × CH₃), 1.29 (m, 32 H, 2 × (CH₂)₈), 1.46 (m, 4 H, 2 × CH₂), 1.81 (m, 4 H, 2 × CH₂), 3.96 (t, 2 H, *J* = 6.7, OCH₂), 4.06 (t, 2 H, *J* = 6.5, CH₂O), 6.67 (d, 1 H, *J* = 16.1, CH=CHCOO), 6.93 (d, 2 H, *J* = 9.1), 6.99 (d, 2 H, *J* = 8.8), 7.11 (d, 2 H, *J* = 9.1), 7.33 (m, 3 H, 2 H + H-4), 7.40 (d, 2 H, *J* = 8.8), 7.51 (m, 3 H, H-2,H-5,H-6), 7.91 (d, 1 H, *J* = 16.1, CH=CHCOO), 8.16 (d, 2 H, *J* = 8.8), 8.26 (d, 2 H, *J* = 8.8), 8.30 (d, 2 H, *J* = 8.8). Elemental analysis: for C₆₀H₇₂O₁₀ (953.24), calculated C 75.60, H 7.61; found C 75.58, H 7.66%.

4-Tetradecyloxyphenyl 4-[(3-[4-(((4-tetradecyloxybenzoyl)oxy)benzoyl)oxy]cinnamoyl)oxy]benzoate (Id). Yield 70%. ¹H NMR: 0.88 (t, 6 H, *J* = 6.9, 2 × CH₃), 1.27 (m, 40 H, 2 × (CH₂)₁₀), 1.46 (m, 4 H, 2 × CH₂), 1.81 (m, 4 H, 2 × CH₂), 3.96 (t, 2 H, *J* = 6.7, OCH₂), 4.06 (t, 2 H, *J* = 6.5, CH₂O), 6.67 (d, 1 H, *J* = 16.1, CH=CHCOO), 6.93 (d, 2 H, *J* = 9.1), 6.99 (d, 2 H, *J* = 8.8), 7.11 (d, 2 H, *J* = 9.1), 7.33 (m, 3 H, 2 H + H-4), 7.40 (d, 2 H, *J* = 8.8), 7.51 (m, 3 H, H-2,H-5,H-6), 7.91 (d, 1 H, *J* = 16.1, CH=CHCOO), 8.16 (d, 2 H, *J* = 8.8), 8.26 (d, 2 H, *J* = 8.8), 8.30 (d, 2 H, *J* = 8.8). Elemental analysis: for C₆₄H₈₀O₁₀ (1009.35), calculated C 76.16, H 7.99; found C 76.10, H 7.97%.

4-[3-(4-(4-Alkyloxybenzoyloxy)benzoyloxy)cinnamoyloxy]phenyl 4-alkyloxybenzoate (IIa-d)

By the same procedure as for **Ia-d**, acylation of hydroxy esters **4E-H** with acid chlorides **5A-D** yielded crude compounds **IIa-IId**, which were purified by column chromatography (1% methanol in CHCl₃) and subsequent crystallization.

4-[(3-[4-((4-Octyloxybenzoyl)oxy)benzoyl)oxy]cinnamoyl)oxy]phenyl 4-octyloxybenzoate (IIa). Yield 50%. ¹H NMR: 0.89 (t, 6 H, *J* = 6.9, 2 × CH₃), 1.25-1.42 (m, 16 H, 2 × (CH₂)₄), 1.46 (m, 4 H, 2 × CH₂), 1.81 (m, 4 H, 2 × CH₂), 4.08 (m, 4 H, 2 × CH₂O), 6.67 (d, 1 H, *J* = 16.1, CH=CHCOO), 6.97 (d, 2 H, *J* = 8.8), 6.99 (d, 2 H, *J* = 9.1), 7.24 (bs, 4 H), 7.31 (m, 1 H, H-4), 7.39 (d, 2 H, *J* = 8.8), 7.50 (m, 3 H, H-2,H-5,H-6), 7.89 (d, 1 H, *J* = 16.1, CH=CHCOO), 8.14 (d, 2 H, *J* = 8.8), 8.16 (d, 2 H, *J* = 8.8), 8.29 (d, 2 H, *J* = 8.8). Elemental analysis: for C₅₂H₅₆O₁₀ (841.02), calculated C 74.26, H 6.71; found C 74.32, H 6.73%.

4-[(3-[4-((4-Decyloxybenzoyl)oxy)benzoyl)oxy]cinnamoyl)oxy]phenyl 4-decyloxybenzoate (IIb). Yield 78%. ¹H NMR: 0.89 (t, 6 H, *J* = 6.9, 2 × CH₃), 1.23-1.41 (m, 24 H, 2 × (CH₂)₆), 1.48 (m, 4 H, 2 × CH₂), 1.83 (m, 4 H, 2 × CH₂), 4.06 (m, 4 H, 2 × CH₂O), 6.67 (d, 1 H, *J* = 16.1, CH=CHCOO), 6.97 (d, 2 H, *J* = 8.8), 6.99 (d, 2 H, *J* = 8.8), 7.24 (bs, 4 H), 7.31 (m, 1 H, H-4), 7.39 (d, 2 H, *J* = 8.8), 7.50 (m, 3 H, H-2,H-5,H-6), 7.89 (d, 1 H, *J* = 16.1,

CH=CHCOO), 8.14 (d, 2 H, $J = 8.8$), 8.16 (d, 2 H, $J = 8.8$), 8.29 (d, 2 H, $J = 8.8$). Elemental analysis: for C₅₆H₆₄O₁₀ (897.13), calculated C 74.98, H 7.19; found C 74.93, H 7.16%.

4-[(3-[(4-((4-Dodecyloxybenzoyl)oxy)benzoyl)oxy]cinnamoyl)oxy]phenyl 4-dodecyloxybenzoate (IIc). Yield 59%. ¹H NMR: 0.89 (t, 6 H, $J = 6.9$, 2 × CH₃), 1.28 (m, 32 H, 2 × (CH₂)₈), 1.48 (m, 4 H, 2 × CH₂), 1.83 (m, 4 H, 2 × CH₂), 4.06 (m, 4 H, 2 × CH₂O), 6.67 (d, 1 H, $J = 16.1$, CH=CHCOO), 6.97 (d, 2 H, $J = 8.8$), 6.99 (d, 2 H, $J = 8.8$), 7.24 (bs, 4 H), 7.31 (m, 1 H, H-4), 7.39 (d, 2 H, $J = 8.8$), 7.50 (m, 3 H, H-2,H-5,H-6), 7.89 (d, 1 H, $J = 16.1$, CH=CHCOO), 8.14 (d, 2 H, $J = 8.8$), 8.16 (d, 2 H, $J = 8.8$), 8.29 (d, 2 H, $J = 8.8$). Elemental analysis: for C₆₀H₇₂O₁₀ (953.24), calculated C 75.60, H 7.61; found C 75.66, H 7.57%.

4-[(3-[(4-((4-Tetradecyloxybenzoyl)oxy)benzoyl)oxy]cinnamoyl)oxy]phenyl 4-tetradecyloxybenzoate (IId). Yield 73%. ¹H NMR: 0.88 (t, 6 H, $J = 6.9$, 2 × CH₃), 1.30 (m, 40 H, 2 × (CH₂)₁₀), 1.48 (m, 4 H, 2 × CH₂), 1.83 (m, 4 H, 2 × CH₂), 4.06 (m, 4 H, 2 × CH₂O), 6.67 (d, 1 H, $J = 16.1$, CH=CHCOO), 6.97 (d, 2 H, $J = 8.8$), 6.99 (d, 2 H, $J = 8.8$), 7.24 (bs, 4 H), 7.31 (m, 1 H, H-4), 7.39 (d, 2 H, $J = 8.8$), 7.50 (m, 3 H, H-2,H-5,H-6), 7.89 (d, 1 H, $J = 16.1$, CH=CHCOO), 8.14 (d, 2 H, $J = 8.8$), 8.16 (d, 2 H, $J = 8.8$), 8.29 (d, 2 H, $J = 8.8$). Elemental analysis: for C₆₄H₈₀O₁₀ (1009.35), calculated C 76.16, H 7.99; found C 76.13, H 8.01%.

Octyl 4-{4-(3-[4-(4-octyloxybenzoyloxy)benzoyloxy]cinnamoyloxy)benzoyloxy}benzoate (IIIa)

The acid chloride **5A** was prepared from the corresponding 4-[(4-octyloxybenzoyl)oxy]benzoic acid (0.20 g; 0.54 mmol), thionyl chloride (0.2 ml; 2.8 mmol) and pyridine (0.25 ml; 3.1 mmol) in dry toluene (20 ml). The reaction mixture was stirred and heated to boiling for 2 h. The solvent and unreacted thionyl chloride were evaporated and the residue dried at reduced pressure. The crude acid chloride was dissolved in dry toluene (5 ml) and added to a solution of hydroxy ester **4I** (0.12 g; 0.22 mmol) and DMAP (0.06 g; 0.51 mmol) in dry hot toluene (20 ml) under stirring. After cooling to room temperature, the mixture was decomposed with water (30 ml). Layers were separated and the aqueous layer was washed with chloroform (3×25 ml). The collected organic solution was washed with water (40 ml) and dried with anhydrous magnesium sulphate. The solvent was removed and the crude product was purified by column chromatography (toluene/*tert*-butyl methyl ether, 18/1). 0.13 g (69%) of **IIIa** was obtained. ¹H NMR: 0.90 (t, 6 H, $J = 6.9$, 2 × CH₃), 1.23-1.54 (m, 20 H, 2 × (CH₂)₅), 1.81 (m, 4 H, 2 × CH₂), 4.06 (t, 2 H, $J = 6.7$, CH₂O), 4.33 (t, 2 H, $J = 6.7$, COOCH₂), 6.67 (d, 1 H, $J = 15.8$, CH=CHCOO), 6.99 (d, 2 H, $J = 8.8$), 7.32 (m, 3 H, Ar-H, H-4), 7.36 (d, 2 H, $J = 8.8$), 7.39 (d, 2 H, $J = 8.8$), 7.51 (m, 3 H, H-2,H-5,H-6), 7.92 (d, 1 H, $J = 16.1$, CH=CHCOO), 8.13 (d, 2 H, $J = 8.8$), 8.16 (d, 2 H, $J = 8.8$), 8.27 (d, 2 H, $J = 8.8$), 8.30 (d, 2 H, $J = 8.8$). Elemental analysis: for C₅₃H₅₆O₁₁ (869.03), calculated C 73.25, H 6.50; found C 73.26, H 6.46%.

Analogously, the other compounds of the series **III** were prepared.

Decyl 4-{4-(3-[4-(4-decyloxybenzoyloxy)benzoyloxy]cinnamoyloxy)benzoyloxy}benzoate (IIIf). Yield 47%. ¹H NMR: 0.89 (t, 6 H, $J = 6.9$, 2 × CH₃), 1.18-1.51 (m, 28 H, 2 × (CH₂)₇), 1.81 (m, 4 H, 2 × CH₂), 4.06 (t, 2 H, $J = 6.7$, CH₂O), 4.33 (t, 2 H, $J = 6.7$, COOCH₂), 6.67 (d, 1 H, $J = 15.8$, CH=CHCOO), 6.99 (d, 2 H, $J = 8.8$), 7.31 (m, 3 H, Ar-H, H-4), 7.36 (d, 2 H, J

= 8.8), 7.39 (d, 2 H, $J = 8.8$), 7.51 (m, 3 H, H-2,H-5,H-6), 7.92 (d, 1 H, $J = 16.1$, CH=CHCOO), 8.14 (d, 2 H, $J = 8.8$), 8.16 (d, 2 H, $J = 8.8$), 8.27 (d, 2 H, $J = 8.8$), 8.29 (d, 2 H, $J = 8.8$). Elemental analysis: for $C_{57}H_{64}O_{11}$ (925.14), calculated C 74.00, H 6.97; found C 73.95, H 7.00%.

Dodecyl 4-{4-(3-[4-(4-dodecyloxybenzoyloxy)benzoyloxy]cinnamoyloxy)benzoyloxy}-benzoate (IIIc). Yield 48%. 1H NMR: 0.88 (t, 6 H, $J = 6.9$, $2 \times CH_3$), 1.19-1.52 (m, 36 H, $2 \times (CH_2)_9$), 1.80 (m, 4 H, $2 \times CH_2$), 4.06 (t, 2 H, $J = 6.7$, CH_2O), 4.33 (t, 2 H, $J = 6.7$, $COOCH_2$), 6.67 (d, 1 H, $J = 15.8$, CH=CHCOO), 6.99 (d, 2 H, $J = 8.8$), 7.32 (m, 3 H, Ar-H, H-4), 7.36 (d, 2 H, $J = 8.8$), 7.39 (d, 2 H, $J = 9.1$), 7.51 (m, 3 H, H-2,H-5,H-6), 7.92 (d, 1 H, $J = 16.1$, CH=CHCOO), 8.13 (d, 2 H, $J = 8.8$), 8.16 (d, 2 H, $J = 8.8$), 8.27 (d, 2 H, $J = 8.8$), 8.30 (d, 2 H, $J = 8.8$). Elemental analysis: for $C_{61}H_{72}O_{11}$ (981.25), calculated C 74.67, H 7.40; found C 74.70, H 7.40%.

Tetradecyl 4-{4-(3-[4-(4-tetradecyloxybenzoyloxy)benzoyloxy]cinnamoyloxy)benzoyloxy}benzoate (IIIId). Yield 46%. 1H NMR: 0.88 (t, 6 H, $J = 6.9$, $2 \times CH_3$), 1.22-1.52 (m, 44 H, $2 \times (CH_2)_{11}$), 1.81 (m, 4 H, $2 \times CH_2$), 4.06 (t, 2 H, $J = 6.7$, CH_2O), 4.33 (t, 2 H, $J = 6.7$, $COOCH_2$), 6.67 (d, 1 H, $J = 15.8$, CH=CHCOO), 6.99 (d, 2 H, $J = 8.8$), 7.32 (m, 3 H, Ar-H, H-4), 7.36 (d, 2 H, $J = 8.8$), 7.40 (d, 2 H, $J = 8.8$), 7.51 (m, 3 H, H-2,H-5,H-6), 7.92 (d, 1 H, $J = 16.1$, CH=CHCOO), 8.14 (d, 2 H, $J = 8.8$), 8.16 (d, 2 H, $J = 8.8$), 8.27 (d, 2 H, $J = 8.8$), 8.30 (d, 2 H, $J = 8.8$). Elemental analysis: for $C_{65}H_{80}O_{11}$ (1037.36), calculated C 75.26, H 7.77; found C 75.27, H 7.75%.

S2. Experimental results

S2.1 Mesomorphic properties of intermediates

We have found some intermediates exhibit mesomorphic properties. Namely, we characterized silyl derivatives **3E-3H** and hydroxy derivatives **4E-4L**, which exhibit calamitic mesophases. For the mostly observed nematic phase (N) typical mosaic or schlieren-like textures were observed in the polarizing microscope. In the smectic phases fan-type textures have been found. Temperatures were detected by DSC measurements and are summarized with corresponding enthalpy changes at phase transitions in Table S1. The planar texture of **3G** is presented in Fig. S1.

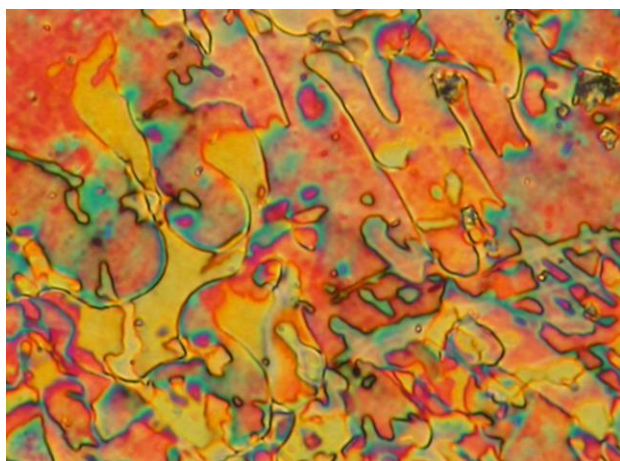


Fig.S1

The planar texture of **3G** in the nematic phase. Width of the figure corresponds to 150 μm .

Table S1

For intermediates the phase transition temperatures, T_{tr} , melting points, m.p., and corresponding enthalpies, ΔH , indicated on second heating and cooling runs at a rate 5K/min. Enthalpies are presented in brackets in kJ/mol. Observed mesophases are indicated.

Comp.	R	m. p. (ΔH)	T_{cr} (ΔH)	SmC	T_{tr} (ΔH)	SmA	T_{tr} (ΔH)	N	T_{tr} (ΔH)	Iso
3E	C_8H_{17}	98 (+27.2)	60 (-26.5)	-		-		•	68 (-0.53)	•
3F	$\text{C}_{10}\text{H}_{21}$	78 (+32.3)	50 (-24.8)	-		-		•	69 (-0.57)	•
3G	$\text{C}_{12}\text{H}_{25}$	62 (+26.0)	49 (-23.0)	-		-		•	61 (-0.61)	•
3H	$\text{C}_{14}\text{H}_{29}$	63 (+37.8)	22 (-10.6)	•	47 (-2.5)	-		•	60 (-0.82)	•
4E	C_8H_{17}	122 (+28.5)	88 (-23.8)	-		-		•	167 (-1.30)	•
4F	$\text{C}_{10}\text{H}_{21}$	121 (+28.0)	102 (-27.4)	-		-		•	161 (-1.45)	•
4G	$\text{C}_{12}\text{H}_{25}$	122 (+25.7)	101 (-25.2)	-		-		•	159 (-1.44)	•
4H	$\text{C}_{14}\text{H}_{29}$	121 (+34.3)	109 (-32.3)	•	140 (-0.29)	-		•	156 (-2.02)	•
4I	C_8H_{17}	127 (+34.9)	100 (-34.5)	-		-		•	118 (-0.29)	•
4J	$\text{C}_{10}\text{H}_{21}$	130 (+46.1)	109 (-46.9)	-		-		•	119 (-0.48)	•
4K	$\text{C}_{12}\text{H}_{25}$	123 (+47.5)	97 (-38.9)	-		•	120 (-1.8)	-		•
4L	$\text{C}_{14}\text{H}_{29}$	124 (+45.6)	102 (-41.7)	-		•	120 (-1.9)	-		•

S2.1 Dielectric spectroscopy measurements

Dielectric properties were studied using Schlumberger 1260 impedance analyser. The frequency dispersions were measured on cooling at a rate of about 0.2 K/min, keeping the temperature of the sample stable during the frequency sweeps in the range of 10 Hz ÷ 10 MHz. The frequency dispersion data were analyzed using the Cole-Cole formula (1) in a generalized form. For the frequency dependent complex permittivity $\varepsilon^*(f) = \varepsilon' - i\varepsilon''$ we have utilized:

$$\varepsilon^* - \varepsilon_\infty = \frac{\Delta\varepsilon}{1 + (if/f_r)^{(1-\alpha)}} - i\left(\frac{\sigma}{2\pi\varepsilon_0 f^n} + Af^m\right) \quad (1),$$

where f_r is the relaxation frequency, $\Delta\varepsilon$ is the dielectric strength, α is the distribution parameter of the relaxation, ε_0 is the permittivity of a vacuum, ε_∞ is the high frequency permittivity and n, m, A are the parameters of fitting. The second and the third terms in the equation are used to eliminate a low frequency contribution from d.c. conductivity σ and a high frequency contribution due to the resistance of the electrodes, respectively. Due to the gold electrodes the contribution of the third term was negligible for the frequencies up to 1 MHz. Measured values of real, ε' , and imaginary, ε'' , parts of the dielectric permittivity $\varepsilon^*(f) = \varepsilon' - i\varepsilon''$ were simultaneously fitted to formula (1). The results of the fitting procedure for **IId** are shown in Fig. S2, where the temperature dependences of $\Delta\varepsilon$ and f_r are presented in the temperature ranges of both mesophases.

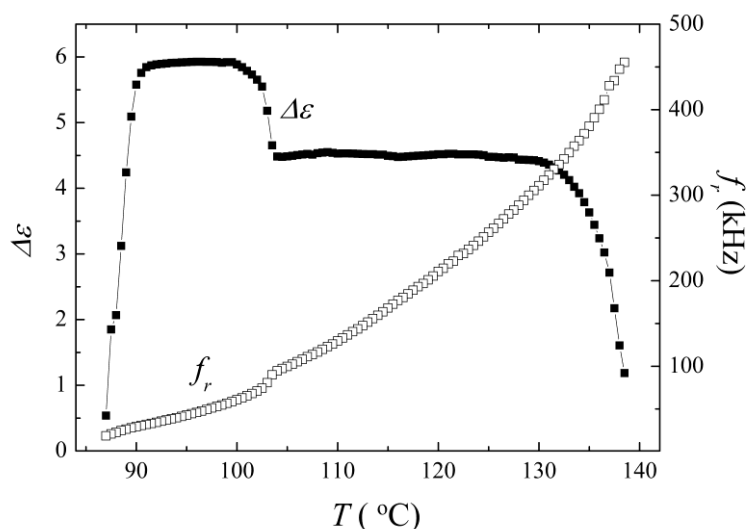


Fig. S2

Temperature dependence for the fitted values of the relaxation frequency, f_r , and the dielectric strength, $\Delta\varepsilon$, for **IId**.

S2.3. X-ray analysis

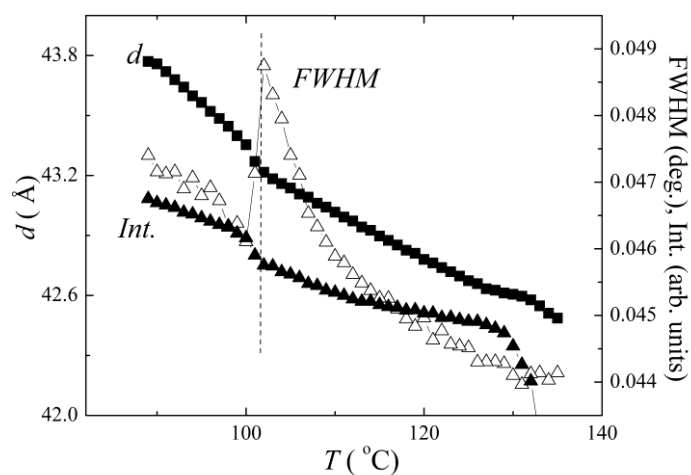


Fig. S3

For **IIId** the temperature dependence of the layer spacing, d , in the B_2 and B_5 mesophases taken on cooling from the isotropic phase. The B_2 - B_5 phase transition is marked by the dashed line. From the right side the intensity, *Int.*, and the full-width at a half maximum, *FWHM*, of the x-ray signal is presented.

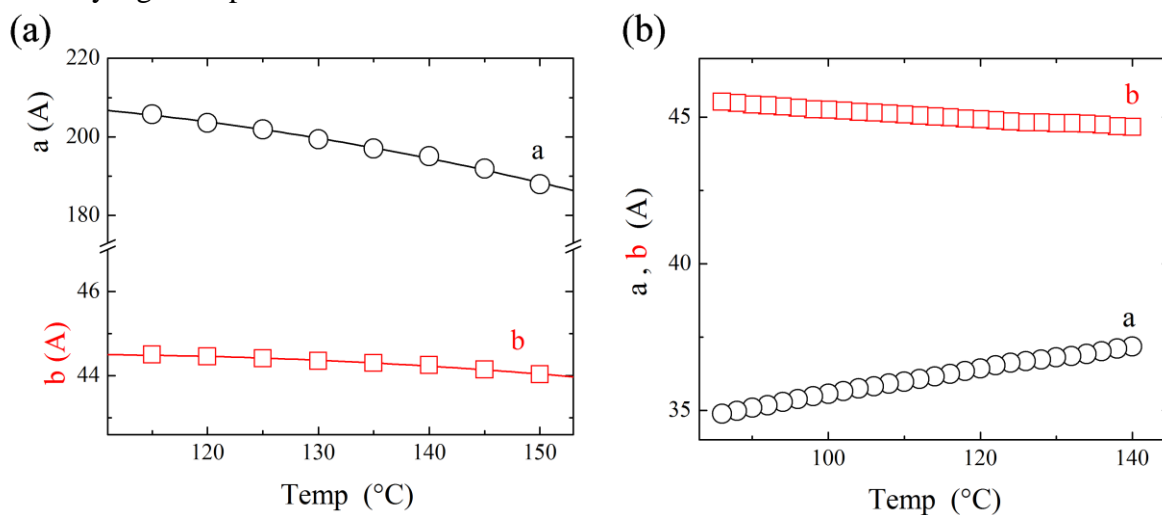


Fig. S4

Temperature evolution of the unit cell dimensions (a is the molecular block width and b is the layer fragment thickness) for compounds (a) **Ia** in the B_{1Rev} phase and (b) **IIa** in the B_1 phase.