Electronic supplementary information

Bent-core liquid crystals based on 6-substituted 3-hydroxybenzoic acid: the role of substitution and linkage group orientation on mesomorphic properties

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Contents

1. Experimental procedures

1.1. Characterization

The structures of intermediates and products were confirmed by ^{1}H NMR and ^{1}H-^{1}H correlation spectroscopy (Varian Gemini 300 HC instrument), deuteriochloroform and acetone-d_6 were used as solvents and the signals of the solvent served as internal standard, *J* values are given in Hz. The spectra of protected as well as deprotected intermediates of a homologue with the shortest aliphatic chain are presented. The spectra of other homologues within the same series differ only in integral intensities of the signals of $(CH_2)_n$ groups of the terminal aliphatic chains. Elemental analyses were carried out on Perkin-Elmer 2400 instrument. The purity of all final compounds was confirmed by HPLC analysis (Luna Silica 150 × 4.6 mm ID, 5 μm column) and found >99.7%. Column chromatography was carried out using Merck Kieselgel 60 (60-100 μm). The experimental part summarizes procedures for the synthesis of the representative intermediates and the compounds of the series **I**–**III**.

1.2. Synthesis of central cores

6-Fluoro-3-methoxybenzoic acid (7). Potassium permanganate (79.0 g, 500.0 mmol) was added portion wise to a vigorously stirred suspension of 4-fluoro-3-methylanisole (**4**) (20.0 g, 143.0 mmol) in water (150 ml) and pyridine (55 ml) at 60ºC. The suspension was stirred for 8 h at 60ºC and at room temperature for 3 days. Precipitated manganese dioxide was filtered off, then repeatedly suspended in hot water (500 ml) and filtered. The combined aqueous filtrate was stirred with 10% aq. sodium sulphite till clarification, filtered, and extracted with diethyl ether (100 ml) to remove the unreacted anisole. The aq. solution was acidified with aq. H_2SO_4 (1/1) to pH = 1, the precipitated product was filtered and dried under reduced pressure. After crystallisation from toluene, 5.40 g (22%) of acid **1** were obtained, m. p. 141–143ºC (ref. [28] 142–143ºC). ^{1}H NMR (acetone-d_6): 3.84 (s, 3 H, OCH_3), 7.17-7.20 (m, 2 H, 2 × CH, H-4, H-5), 7.44 (m, 1 H, CH, H-2).

6-Fluoro-3-hydroxybenzoic acid (9). BBr_3 (7.6 ml, 79.3 mmol) was slowly added to a mixture of acid **1** (5.40 g, 31.7 mmol) in dry dichloromethane (180 ml) at 0ºC. The temperature was allowed to rise to room temperature and the reaction mixture was stirred for 24 h. After cooling to 0ºC, the mixture was decomposed with water (120 ml), the crude product was filtered off and washed with water (100 ml). The filtrate was extracted with

dichloromethane (3 × 50 ml), the combined organic solution was washed with water (50 ml) and the aqueous layer was evaporated to yield the second crop of the product. The collected solids were suspended in boiling dichloromethane (100 ml) and cooled to room temperature, the product was filtered, washed with ice-cold water, and dried under reduced pressure to yield 4.60 g (93%) of hydroxy acid **9**, m. p. 197–199ºC (ref. [29] 198.5–200ºC). ^{1}H NMR (acetone-d_6): 7.06-7.10 (m, 2 H, 2 × CH, H-4, H-5), 7.38 (m, 1 H, CH, H-2), 8.65 (br s, 1 H, OH).

3-Benzyloxy-6-fluorobenzoic acid (1). Benzyl bromide (9.4 ml, 79.3 mmol) was added drop wise to acid **9** (4.60 g, 29.5 mmol) and K_2CO_3 (8.2 g, 47.6 mmol) in acetone (150 ml). The mixture was stirred and heated to boiling for 48 h. After cooling, it was diluted with water (120 ml) and extracted with chloroform (3 × 70 ml). The combined organic solution was dried with anhydrous magnesium sulphate and the solvent was evaporated. The residue was dissolved in a mixture of ethanol (50 ml) and dioxane (40 ml), 25% aq. sodium hydroxide (15 ml) was added and the solution was heated to boiling for 1 h. After cooling to room temperature, water (100 ml) was added, the mixture was acidified with 25% aq. sulfuric acid to pH = 1, cooled to 0°C, and stirred for 0.5 h. The precipitated solid was filtered, washed with hexane and crystallised from toluene to yield 3.91 g (54%) of the protected acid **1**, m.p. 144.0–144.5ºC. ^{1}H NMR ($CDCl_3$): 5.08 (s, 2 H, $PhCH_2$), 7.09 (dd, 1 H, ^3J = 8.8, ^3J = 9.7, CH, H-5), 7.18 (ddd, 1 H, ^3J = 8.8, ^4J = 2.9, ^4J = 4.1, H-4), 7.31-7.46 (m, 5 H, 5 x CH), 7.59 (dd, 1H, ^4J = 2.9, ^4J = 5.6, CH, H-2).

6-Chloro-3-methoxybenzoic acid (8) has been obtained by oxidation of anisole **5** (21.3 g, 136.0 mmol) with potassium permanganate (75.0 g, 474.6 mmol) in the same manner as for acid **7**. Yield 9.20 g (36%), m.p. 173–175ºC (ref. [30] 174–175ºC). ^{1}H NMR (acetone-d_6): 3.86 (s, 3 H, OCH_3), 7.12 (dd, 1 H, ^3J = 8.8, ^4J = 2.9, CH, H-4), 7.40 (d, 1 H, ^4J = 2.9, CH, H-2), 7.44 (d, 1 H, ^3J = 8.8, CH, H-5).

6-Chloro-3-hydroxybenzoic acid (10) has been prepared by deprotection of acid **8** (6.40 g, 34.3 mmol) by the means of BBr_3 (6.5 ml, 67.7 mmol) as for acid **9**. Yield 5.0 g (85%), m.p. 176–178ºC (ref. [S1] 169–170ºC). ^{1}H NMR (acetone-d_6): 7.00 (dd, 1 H, ^3J = 8.8, ^4J = 2.9, CH, H-4), 7.33 (d, 1 H, ^3J = 8.8, CH, H-5), 7.34 (d, 1 H, ^4J = 2.9, CH, H-2), 9.27 (s, 1 H, OH).

3-tert-Butyl(dimethyl)silyloxy-6-chlorobenzoic acid (2). A solution of *tert*-butyl(dimethyl)silyl chloride (10.9 g, 72.3 mmol) in dry *N*,*N*´-dimethylformamide (DMF) (30 ml) was added drop wise to a solution of acid **9** (5.0 g, 29.0 mmol) and imidazole (5.0 g, 73.4 mmol) in dry DMF (60 ml). The solution was stirred at room temperature for 8 h and then decomposed by the addition of 4% aq. hydrochloric acid (100 ml). The product was extracted with ethyl acetate (3 × 60 ml), the combined organic solution was washed with 4% aq. hydrochloric acid (3 × 40 ml), evaporated and the crude product was purified by column chromatography (toluene/*tert*-butyl methyl ether, 8/1) and crystallisation from toluene to yield 6.0 g (72%) of the protected acid **2**, m.p. 91–92ºC. ^{1}H NMR ($CDCl_3$): 0.22 (s, 6 H, 2 × CH_3), 0.98 (s, 9 H, $C(CH_3)_3$), 6.95 (dd, 1 H, ^3J = 8.8, ^4J = 2.9, CH, H-4), 7.33 (d, 1 H, ^3J = 8.8, CH, H-5), 7.34 (d, 1 H, ^4J = 2.9, CH, H-2).

3-Benzyloxy-6-methylbenzoic acid (3)

Benzylation was performed in the same way as for acid **1** starting from acid **6** (4.95 g, 32.5 mmol) and benzyl bromide (11.5 ml, 96.8 mmol). The product was crystallised from hexane, yield 6.03 g (76%), m.p. 139–141.5°C. ^{1}H NMR (acetone-d_6): 2.41 (s, 3 H, CH_3), 5.10 (s, 2 H, $PhCH_2$), 7.08 (dd, 1 H, ^3J = 8.8, ^4J = 2.9, CH, H-4), 7.19 (d, 1 H, ^3J = 8.8, CH, H-5), 7.27-7.45 (m, 6 H, 6 x CH, C_6H_5, H-2).

1.3. Synthesis of intermediates

4-[(3-Benzyloxy-6-fluorobenzoyl)oxy]phenyl 4-octyloxybenzoate (15a)

A catalytic amount of DMAP (10 mg) was added to a solution of acid **1** (300 mg; 1.22 mmol), phenol **11a** (400 mg; 1.17 mmol), and DCC (252 mg; 1.22 mmol) in dry dichloromethane (20 ml). The reaction mixture was stirred at room temperature for 4 h. The precipitated *N*,*N*´-dicyclohexylurea was filtered off and washed with dichloromethane (2 × 5 ml). The filtrate was evaporated and the product was purified by crystallisation from ethanol to yield 500 mg (76%) of **15a**, m.p. 118–119.5ºC. ^{1}H NMR ($CDCl_3$): 0.90 (t, 3 H, J = 6.7, CH_3), 1.25-1.58 (m, 10 H, $(CH_2)_5$), 1.82 (m, 2 H, CH_2), 4.05 (t, 2 H, J = 6.7, OCH_2), 5.11 (s, 2 H, $PhCH_2$), 6.97 (d, 2 H, J = 8.8, 2 × CH), 7.13 (dd, 1 H, ^3J = 8.8, ^3J = 9.7, CH), 7.18 (ddd, 1 H, ^3J = 8.8 Hz, ^4J = 3.2, ^4J = 4.1, CH), 7.25-7.29 (m, 4 H, 4 × CH), 7.32-7.47 (m, 5 H, 5 × CH), 7.65 (dd, 1 H, ^4J = 3.2, ^4J = 5.6, CH), 8.14 (d, 2 H, J = 8.8, 2 × CH). Elemental analysis: for $C_{35}H_{35}FO_6$ (570.66): calculated C 73.67, H 6.18, F 3.33; found C 73.44, H 6.07, F 3.45%.

Intermediates **15b** (R = $C_{10}H_{21}$, yield 73%, m.p. 89–90°C), **15c** (R = $C_{12}H_{25}$, yield 74%, m.p. 99.5–105.5°C) and **15d** (R = $C_{14}H_{29}$, yield 74%, m.p. 99–100°C) were prepared by the same procedure.

4-{[6-Chloro-3-tert-butyl(dimethyl)silyloxybenzoyl]oxy}phenyl 4-octyloxybenzoate (16a) was obtained by the same method as for **15a** by the reaction of acid **2** with phenol **11a**. Purification was achieved by column chromatography (toluene/*tert*-butyl methyl ether, 12/1) yielding 450 mg (63%) of **16a**, white solid, m. p. 44–46°C. ^{1}H NMR ($CDCl_3$): 0.24 (s, 6 H, 2 × CH_3), 0.89 (t, 3 H, *J* = 6.7, CH_3), 1.00 (s, 9 H, $C(CH_3)_3$), 1.26-1.56 (m, 10 H, $(CH_2)_5$), 1.82 (m, 2 H, CH_2), 4.05 (t, 2 H, *J* = 6.7, OCH_2), 6.95-6.99 (m, 3 H, 3 × CH), 7.25-7.29 (m, 4 H, 4 × CH), 7.36 (d, 1 H, ^3J = 8.8, CH), 7.48 (d, 1 H, ^4J = 2.9, CH), 8.14 (d, 2 H, *J* = 8.8, 2 × CH). Elemental analysis: for $C_{34}H_{43}ClO_6Si$ (611.26): calculated C 66.81, H 7.09, Cl 5.80; found C 66.75, H 7.13, Cl 5.83%.

Intermediates **16b** (R = $C_{10}H_{21}$, yield 87%, m.p. 39.5–42°C), **16c** (R = $C_{12}H_{25}$, yield 83%, m.p. 44–47°C) and **16d** (R = $C_{14}H_{29}$, yield 65%, m.p. 46.5–49.5°C) were prepared in the same way.

4-[(3-Benzyloxy-6-methylbenzoyl)oxy]phenyl 4-octyloxybenzoate (17a) was prepared by the acylation of phenol **11a** with acid **3** as above. Yield 92%, m.p. 117–119ºC. ^{1}H NMR ($CDCl_3$): 0.88 (t, 3 H, *J* = 6.7, CH_3), 1.23-1.55 (m, 10 H, $(CH_2)_5$), 1.83 (m, 2 H, CH_2), 2.60 (s, 3 H, CH_3), 4.05 (t, 2 H, *J* = 6.7, OCH_2), 5.12 (s, 2 H, $PhCH_2$), 6.98 (d, 2 H, *J* = 8.8, 2 × CH), 7.11 (dd, 1 H, ^3J = 8.8, ^4J = 2.9, CH), 7.22 (d, 1 H, ^3J = 8.8, CH), 7.25-7.29 (m, 4 H, 4 × CH), 7.33-7.48 (m, 5 H, 5 × CH), 7.78 (d, 1 H, ^4J = 2.9, CH), 8.15 (d, 2 H, *J* = 8.8, 2 × CH). Elemental analysis: for $C_{36}H_{38}O_6$ (566.70): calculated C 76.30, H 6.76; found C 76.15, H 6.85%.

Intermediates **17b** (R = $C_{10}H_{21}$, yield 87%, m.p. 110–113°C), **17c** (R = $C_{12}H_{25}$, yield 87%, m.p. 98–99.5°C) and **17d** (R = $C_{14}H_{29}$, yield 95%, m.p. 99.5–101°C) were prepared analogously.

4-Octyloxyphenyl 4-[(3-benzyloxy-6-fluorobenzoyl)oxy]benzoate (21a) was prepared as above by the acylation of phenol **12a** with acid **1**. Subsequent purification via crystallisation from ethanol afforded **21a**, yield 77%, m.p. 79–81ºC. ^{1}H NMR ($CDCl_3$): 0.89 (t, 3 H, *J* = 6.7, CH_3), 1.25-1.54 (m, 10 H, $(CH_2)_5$), 1.79 (m, 2 H, CH_2), 3.96 (t, 2 H, *J* = 6.7, OCH_2), 5.11 (s, 2

H, $PhCH_2$), 6.93 (d, 2 H, *J* = 8.8, 2 × CH), 7.10-7.15 (m, 3 H, 3 × CH), 7.19 (ddd, 1 H, ^3J = 8.8, ^4J = 3.2, ^4J = 4.1, CH), 7.34-7.47 (m, 7 H, 7 × CH), 7.65 (dd, 1 H, ^4J = 3.2, ^4J = 5.6, CH), 8.28 (d, 2 H, *J* = 8.8, 2 × CH). Elemental analysis: for $C_{35}H_{35}FO_6$ (570.66): calculated C 73.67, H 6.18, F 3.33; found C 73.84, H 6.09, F 3.40%.

Compounds **21b** (R = $C_{10}H_{21}$, yield 69%, m.p. 78–80°C), **21c** (R = $C_{12}H_{25}$, yield 50%, m.p. 81.5–83°C) and **21d** (R = $C_{14}H_{29}$, yield 66%, m.p. 82–85°C) were prepared in the same way.

4-Octyloxyphenyl 4-{[6-chloro-3-tert-butyl(dimethyl)silyloxybenzoyl]oxy}benzoate (22a) was prepared as for **15a** by the reaction of phenol **12**a with acid **2**. The product was purified by column chromatography (toluene/*tert*-butyl methyl ether, 12/1), yield 88%, m.p. 43.5–45ºC. ^{1}H NMR ($CDCl_3$): 0.24 (s, 6 H, 2 × CH_3), 0.89 (t, 3 H, *J* = 6.7, CH_3), 1.00 (s, 9 H, $C(CH_3)_3$), 1.27-1.55 (m, 10 H, $(CH_2)_5$), 1.79 (m, 2 H, CH_2), 3.96 (t, 2 H, *J* = 6.7, OCH_2), 6.93 (d, 2 H, *J* = 8.8, 2 × CH), 6.99 (dd, 1 H, ^3J = 8.8, ^4J = 2.9, CH), 7.12 (d, 2 H, *J* = 8.8, 2 × CH), 7.38 (d, 1 H, ^3J = 8.8, CH), 7.40 (d, 2 H, *J* = 8.8, 2 × CH), 7.50 (d, 1 H, ^4J = 2.9, CH), 8.28 (d, 2 H, *J* = 8.8, 2 × CH). Elemental analysis: for $C_{34}H_{43}ClO_6Si$ (611.26): calculated C 66.81, H 7.09, Cl 5.80; found C 66.64, H 7.17, Cl 5.85%.

Intermediates **22b** (R = $C_{10}H_{21}$, yield 82%, m.p. 47–49°C), **22c** (R = $C_{12}H_{25}$, yield 90%, m.p. 53–55°C) and **22d** (R = $C_{14}H_{29}$, yield 89%, m.p. 58.5–60.5°C) were prepared by the same method.

4-Octyloxyphenyl 4-[(3-benzyloxy-6-methylbenzoyl)oxy]benzoate (23a) was obtained by the acylation of phenol **12a** with acid **3** and purified by crystallisation from ethanol. Yield 75%, m.p. 82–84ºC. ^{1}H NMR ($CDCl_3$): 0.88 (t, 3 H, *J* = 6.7, CH_3), 1.22-1.51 (m, 10 H, $(CH_2)_5$), 1.79 (m, 2 H, CH_2), 2.61 (s, 3 H, CH_3), 3.96 (t, 2 H, *J* = 6.7, OCH_2), 5.13 (s, 2 H, $PhCH_2$), 6.93 (d, 2 H, *J* = 8.8, 2 × CH), 7.09-7.15 (m, 3 H, 3 × CH), 7.24 (d, 1 H, ^3J = 8.8, CH), 7.33-7.48 (m, 7 H, 7 × CH), 7.79 (d, 1 H, ^4J = 2.9, CH), 8.28 (d, 2 H, *J* = 8.8, 2 × CH). Elemental analysis: for $C_{36}H_{38}O_6$ (566.70): calculated C 76.30, H 6.76; found C 76.17, H 6.82%.

Intermediates **23b** (R = $C_{10}H_{21}$, yield 75%, m.p. 62–65°C), **23c** (R = $C_{12}H_{25}$, yield 64%, m.p. 87–88°C) and **23d** (R = $C_{14}H_{29}$, yield 81%, m.p. 75–77°C) were prepared in the same way.

Octyl 4-{{4-[(3-benzyloxy-6-fluorobenzoyl)oxy]benzoyl}oxy}benzoate (24a) was synthesised by the reaction of phenol **13a** with acid **1** and purified by crystallisation from ethanol. Yield 66%, m.p. 86–87.5ºC. ^{1}H NMR ($CDCl_3$): 0.89 (t, 3 H, *J* = 6.7, CH_3), 1.25-1.54 (m, 10 H,

(CH_2)$_5$), 1.78 (m, 2 H, CH_2), 4.33 (t, 2 H, *J* = 6.7, OCH_2), 5.11 (s, 2 H, $PhCH_2$), 7.15 (dd, 1 H, ^3J = 8.8, ^3J = 9.7, CH), 7.21 (ddd, 1 H, ^3J = 8.8, ^4J = 3.2, ^4J = 4.1, CH), 7.31 (d, 2 H, *J* = 8.8, 2 × CH), 7.35-7.47 (m, 7 H, 7 × CH), 7.66 (dd, 1 H, ^4J = 3.2, ^4J = 5.6, CH), 8.14 (d, 2 H, *J* = 8.8, 2 × CH), 8.29 (d, 2 H, *J* = 8.8, 2 × CH). Elemental analysis: for $C_{36}H_{35}FO_7$ (598.67): calculated C 72.23, H 5.89, F 3.17; found C 72.49, H 5.88, F 3.24%.

Intermediates **24b** (R = $C_{10}H_{21}$, yield 78%, m.p. 87.5–88.5°C), **24c** (R = $C_{12}H_{25}$, yield 69%, m.p. 87–87.5°C) and **24d** (R = $C_{14}H_{29}$, yield 75%, m.p. 88.5–90°C) were prepared analogously.

Octyl 4-{{4-{[6-chloro-3-tert-butyl(dimethyl)silyloxybenzoyl]oxy}benzoyl}oxy}benzoate (25a). Acylation of phenol **13a** with acid **2** was performed by the same method as for **15a**. The product was purified by column chromatography (toluene/*tert*-butyl methyl ether, 12/1), yield 83%, viscous oil. ^{1}H NMR ($CDCl_3$): 0.24 (s, 6 H, 2 × CH_3), 0.89 (t, 3 H, *J* = 6.7, CH_3), 1.00 (s, 9 H, C(CH_3)$_3$), 1.24-1.52 (m, 10 H, (CH_2)$_5$), 1.78 (m, 2 H, CH_2), 4.33 (t, 2 H, *J* = 6.7, OCH_2), 7.00 (dd, 1 H, ^3J = 8.8, ^4J = 2.9, CH), 7.31 (d, 2 H, *J* = 8.8, 2 × CH), 7.39 (d, 1 H, ^3J = 8.8, CH), 7.42 (d, 2 H, *J* = 8.8, 2 × CH), 7.50 (d, 1 H, ^4J = 2.9, CH), 8.14 (d, 2 H, *J* = 8.8, 2 × CH), 8.29 (d, 2 H, *J* = 8.8, 2 × CH). Elemental analysis: for $C_{35}H_{43}ClO_7Si$ (639.27): calculated C 65.76, H 6.78, Cl 5.55; found C 65.57, H 6.64, Cl 5.50%.

Intermediates **25b** (R = $C_{10}H_{21}$, yield 75%, m.p. 36–38.5°C), **25c** (R = $C_{12}H_{25}$, yield 85%, m.p. 44–46°C) and **25d** (R = $C_{14}H_{29}$, yield 89%, m.p. 52–54.5°C) were prepared by the same procedure.

Octyl 4-{{4-[(3-benzyloxy-6-methylbenzoyl)oxy]benzoyl}oxy}benzoate (26a) was prepared by the reaction of phenol **13a** with acid **3** and purified by crystallisation from ethanol. Yield 85%, m.p. 78.5–80.5ºC. ^{1}H NMR ($CDCl_3$): 0.88 (t, 3 H, *J* = 6.7, CH_3), 1.23-1.50 (m, 10 H, (CH_2)$_5$), 1.78 (m, 2 H, CH_2), 2.61 (s, 3 H, CH_3), 4.33 (t, 2 H, *J* = 6.7, OCH_2), 5.13 (s, 2 H, $PhCH_2$), 7.14 (dd, 1 H, ^3J = 8.8, ^4J = 2.9, CH), 7.25 (d, 1 H, ^3J = 8.8, CH), 7.31 (d, 2 H, *J* = 8.8, 2 × CH), 7.34-7.48 (m, 7 H, 7 × CH), 7.80 (d, 1 H, ^4J = 2.9, CH), 8.14 (d, 2 H, *J* = 8.8, 2 × CH), 8.29 (d, 2 H, *J* = 8.8, 2 × CH). Elemental analysis: for $C_{37}H_{38}O_7$ (594.71): calculated C 74.73, H 6.44; found C 74.90, H 6.46%.

Compounds **26b** (R = $C_{10}H_{21}$, yield 76%, m.p. 72–74°C), **26c** (R = $C_{12}H_{25}$, yield 80%, m.p. 75.5–78.5°C) and **26d** (R = $C_{14}H_{29}$, yield 91%, m.p. 79–80°C) were prepared by the same procedure.

4-[(6-Fluoro-3-hydroxybenzoyl)oxy]phenyl 4-octyloxybenzoate (18a)

Ammonium formate (221 mg; 3.51 mmol) was added to a suspension of benzyl derivative **15a** (500 mg, 0.88 mmol) and 10% Pd/C (50 mg). The reaction mixture was stirred and heated to boiling for 3 h in an argon atmosphere, filtered while hot; the catalyst was washed with acetone (15 ml) and the filtrate was evaporated. The product was purified by column chromatography (toluene/*tert*-butyl methyl ether, 8/1) and crystallisation from toluene. Yield 74%, m.p. 140–140.5ºC. ^{1}H NMR ($CDCl_3$): 0.89 (t, 3 H, *J* = 6.7), 1.25-1.53 (m, 10 H, $(CH_2)_5$), 1.83 (m, 2 H, CH_2), 4.05 (t, 2 H, *J* = 6.7, OCH_2), 5.03 (s, 1 H, OH), 6.97 (d, 2 H, *J* = 8.8, 2 × CH), 7.06-7.14 (m, 2 H, 2 × CH), 7.25-7.29 (m, 4 H, 4 × CH), 7.51 (dd, 1 H, ^4J = 3.2, ^4J = 5.6, CH), 8.14 (d, 2 H, *J* = 8.8, 2 × CH). Elemental analysis: for $C_{28}H_{29}FO_6$ (480.54): calculated C 69.99, H 6.08, F 3.95; found C 69.78, H 5.97, F 4.02%.

Intermediates **18b** (R = $C_{10}H_{21}$, yield 79%, m.p. 141–142°C), **18c** (R = $C_{12}H_{25}$, yield 82%, m.p. 137–138°C) and **18d** (R = $C_{14}H_{29}$, yield 76%, m.p. 137.5–138°C) were prepared by the same method.

4-[(3-Hydroxy-6-methylbenzoyl)oxy]phenyl 4-octyloxybenzoate (20a) was prepared by debenzylation of **17a** by the method as for **18a**. Purification was achieved by column chromatography (toluene/acetone, 14/1) and crystallisation from toluene, yield 77%, m.p. 99.5–101ºC. ^{1}H NMR ($CDCl_3$): 0.88 (t, 3 H, *J* = 6.7, CH_3), 1.23-1.53 (m, 10 H, $(CH_2)_5$), 1.83 (m, 2 H, CH_2), 2.59 (s, 3 H, CH_3), 4.05 (t, 2 H, *J* = 6.7, OCH_2), 4.87 (s, 1 H, OH), 6.95-7.01 (m, 3 H, 3 × CH), 7.18 (d, 1 H, ^3J = 8.8, CH), 7.25-7.30 (m, 4 H, 4 × CH), 7.62 (d, 1 H, ^4J = 2.9, CH), 8.14 (d, 2 H, *J* = 8.8, 2 × CH). Elemental analysis: for $C_{29}H_{32}O_6$ (476.57): calculated C 73.09, H 6.77; found C 73.01, H 6.69%.

Homologues **20b** (R = $C_{10}H_{21}$, yield 79%, m.p. 99.5–101°C), **20c** (R = $C_{12}H_{25}$, yield 82%, m.p. 104–104.5°C) and **20d** (R = $C_{14}H_{29}$, yield 76%, m.p. 101.5–103°C) were prepared by the same procedure.

4-Octyloxyphenyl 4-[(6-fluoro-3-hydroxybenzoyl)oxy]benzoate (27a) was synthesised by debenzylation of **21a**. The product was purified by column chromatography (toluene/*tert*-butyl methyl ether, 8/1) and crystallisation from toluene. Yield 45%, m.p. 134–136.5ºC. ^{1}H NMR ($CDCl_3$): 0.89 (t, 3 H, *J* = 6.7, CH_3), 1.23-1.52 (m, 10 H, $(CH_2)_5$), 1.79 (m, 2 H, CH_2), 3.96 (t, 2 H, *J* = 6.7, OCH_2), 5.05 (s, 1 H, OH), 6.93 (d, 2 H, *J* = 8.8, 2 × CH), 7.08-7.13 (m, 4

H, 4 × CH), 7.37 (d, 2 H, *J* = 8.8, 2 × CH), 7.53 (dd, 1 H, ^4J = 3.2, ^4J = 5.6, CH), 8.28 (d, 2 H, *J* = 8.8, 2 × CH). Elemental analysis: for $C_{28}H_{29}FO_6$ (480.54): calculated C 69.99, H 6.08, F 3.95; found C 69.87, H 5.92, F 3.91%.

Compounds **27b** (R = $C_{10}H_{21}$, yield 48%, m.p. 134–137°C), **27c** (R = $C_{12}H_{25}$, yield 61%, m.p. 130–132°C) and **27d** (R = $C_{14}H_{29}$, yield 71%, m.p. 128.5–131.5°C) were prepared by the same procedure.

4-Octyloxyphenyl 4-[(3-hydroxy-6-methylbenzoyl)oxy]benzoate (29a). Debenzylation of **23a** was followed by column chromatography (toluene/acetone, 14/1) and crystallisation from toluene, yield 70%, m.p. 116–118ºC. ^{1}H NMR ($CDCl_3$): 0.88 (t, 3 H, *J* = 6.7, CH_3), 1.20-1.51 (m, 10 H, $(CH_2)_5$), 1.79 (m, 2 H, CH_2), 2.59 (s, 3 H, CH_3), 3.95 (t, 2 H, *J* = 6.7, OCH_2), 5.19 (s, 1 H, OH), 6.93 (d, 2 H, *J* = 8.8, 2 × CH), 6.98 (dd, 1 H, ^3J = 8.8, ^4J = 2.9, CH), 7.11 (d, 2 H, *J* = 8.8, 2 × CH), 7.19 (d, 1 H, ^3J = 8.8, CH), 7.33 (d, 2 H, *J* = 8.8, 2 × CH), 7.64 (d, 1 H, ^4J = 2.9, CH), 8.27 (d, 2 H, *J* = 8.8, 2 × CH). Elemental analysis: for $C_{29}H_{32}O_6$ (476.57): calculated C 73.09, H 6.77; found C 73.13, H 6.72%.

Intermediates **29b** (R = $C_{10}H_{21}$, yield 67%, m.p. 100–103°C), **29c** (R = $C_{12}H_{25}$, yield 80%, m.p. 98–99°C) and **29d** (R = $C_{14}H_{29}$, yield 72%, m.p. 102–103.5°C) were prepared by the same procedure.

Octyl 4-{{4-[(6-fluoro-3-hydroxybenzoyl)oxy]benzoyl}oxy}benzoate (30a). Deprotection of **24a** was achieved as for **18a** and the product was purified by column chromatography (toluene/*tert*-butyl methyl ether 8/1) and crystallisation from toluene, yield 57%, m.p. 113–114ºC. ^{1}H NMR ($CDCl_3$): 0.89 (t, 3 H, *J* = 6.7, CH_3), 1.23-1.51 (m, 10 H, $(CH_2)_5$), 1.78 (m, 2 H, CH_2), 4.33 (t, 2 H, *J* = 6.7, OCH_2), 5.19 (s, 1 H, OH), 7.09-7.13 (m, 2 H, 2 × CH), 7.30 (d, 2 H, *J* = 8.8, 2 × CH), 7.40 (d, 2 H, *J* = 8.8, 2 × CH), 7.54 (dd, 1 H, ^4J = 3.2, ^4J = 5.6, CH), 8.14 (d, 2 H, *J* = 8.8, 2 × CH), 8.29 (d, 2 H, *J* = 8.8, 2 × CH). Elemental analysis: for $C_{29}H_{29}FO_7$ (508.55), calculated C 68.49, H 5.75, F 3.74; found C 68.66, H 5.76, F 3.68%.

Intermediates **30b** (R = $C_{10}H_{21}$, yield 49%, m.p. 111–113°C), **30c** (R = $C_{12}H_{25}$, yield 56%, m.p. 108–110°C) and **30d** (R = $C_{14}H_{29}$, yield 52%, m.p. 113–118°C) were prepared by the same procedure.

Octyl 4-{{4-[(3-hydroxy-6-methylbenzoyl)oxy]benzoyl}oxy}benzoate (32a) was obtained by deprotection of **26a**. The product was purified by column chromatography (toluene/acetone,

14/1) and crystallisation from toluene. Yield 80%, m.p. 115–118ºC. ^{1}H NMR ($CDCl_3$): 0.88 (t, 3 H, J = 6.7, CH_3), 1.21-1.50 (m, 10 H, $(CH_2)_5$), 1.78 (m, 2 H, CH_2), 2.60 (s, 3 H, CH_3), 4.33 (t, 2 H, J = 6.7, OCH_2), 4.85 (s, 1 H, OH), 7.01 (dd, 1 H, ^3J = 8.8, ^4J = 2.9, CH), 7.21 (d, 1 H, ^3J = 8.8, CH), 7.30 (d, 2 H, J = 8.8, 2 × CH), 7.37 (d, 2 H, J = 8.8, 2 × CH), 7.66 (d, 1 H, ^4J = 2.9, CH), 8.14 (d, 2 H, J = 8.8, 2 × CH), 8.29 (d, 2 H, J = 8.8, 2 × CH). Elemental analysis: for $C_{30}H_{32}O_7$ (504.59): calculated C 71.41, H 6.39; found C 71.24, H 6.45%.

Intermediates **32b** (R = $C_{10}H_{21}$, yield 78%, m.p. 106–109°C), **32c** (R = $C_{12}H_{25}$, yield 86%, m.p. 115–118°C) and **32d** (R = $C_{14}H_{29}$, yield 78%, m.p. 110.5–114°C) were prepared by the same procedure.

4-[(6-Chloro-3-hydroxybenzoyl)oxy]phenyl 4-octyloxybenzoate (19a)

TBAF·$3H_2O$ (60 mg; 0.190 mmol) was added to a solution of *tert*-butyl(dimethyl)silyl-protected ester **16a (**450 mg; 0.736 mmol) in a mixture of tetrahydrofuran (50 ml) and water (12 ml). The mixture was stirred at room temperature for 5 h, diluted with water (100 ml) and extracted with ethyl acetate (3 × 80 ml). The combined organic solution was washed with water (100 ml) and brine (100 ml), dried with anhydrous magnesium sulphate and evaporated. The crude product was purified by column chromatography (hexane/ethyl acetate, 3/1) and crystallisation from toluene. Yield 71%, m. p. 105–110°C. ^{1}H NMR ($CDCl_3$): 0.89 (t, 3 H, J = 6.7, CH_3), 1.25-1.56 (m, 10 H, $(CH_2)_5$), 1.83 (m, 2 H, CH_2), 4.05 (t, 2 H, J = 6.7, OCH_2), 5.36 (s, 1 H, OH), 6.96-7.00 (m, 3 H, 3 × CH), 7.25-7.28 (m, 4 H, 4 × CH), 7.38 (d, 1 H, ^3J = 8.8, CH), 7.50 (d, 1 H, ^4J = 2.9, CH), 8.14 (d, 2 H, J = 8.8, 2 × CH). Elemental analysis for: $C_{28}H_{29}ClO_6$ (496.99): calculated C 67.67, H 5.88, Cl 7.13; found C 67.59, H 5.96, Cl 7.08%.

Homologous derivatives **19b** (R = $C_{10}H_{21}$, yield 65%, m.p. 104–107°C), **19c** (R = $C_{12}H_{25}$, yield 82%, m.p. 103–106°C), and **19d** (R = $C_{14}H_{29}$, yield 84%, m.p. 104-105°C) were prepared by the same procedure.

4-Octyloxyphenyl 4-[(6-chloro-3-hydroxybenzoyl)oxy]benzoate (28a) was prepared using the method described above by deprotection of **22a**. Yield 44%, m.p. 106–107.5°C. ^{1}H NMR ($CDCl_3$): 0.82 (t, 3 H, J = 6.7, CH_3), 1.19-1.46 (m, 10 H, $(CH_2)_5$), 1.72 (m, 2 H, CH_2), 3.89 (t, 2 H, J = 6.7, OCH_2), 5.42 (s, 1 H, OH), 6.86 (d, 2 H, J = 8.8, 2 × CH), 6.94 (dd, 1 H, ^3J = 8.8, ^4J = 2.9, CH), 7.05 (d, 2 H, J = 8.8, 2 × CH), 7.31 (d, 2 H, J = 8.8, 2 × CH), 7.32 (d, 1 H, ^3J = 8.8, CH), 7.47 (d, 1 H, ^4J = 2.9, CH), 8.21 (d, 2 H, J = 8.8, 2 × CH). Elemental analysis: for $C_{28}H_{29}ClO_6$ (496.99): calculated C 67.67, H 5.88, Cl 7.13; found C 67.77, H 6.23, Cl 7.02%.

Intermediates **28b** (R = $C_{10}H_{21}$, yield 69%, m.p. 99–102.5°C), **28c** (R = $C_{12}H_{25}$, yield 73%, m.p. 108–111°C), and **28d** (R = $C_{14}H_{29}$, yield 70%, m.p. 113–115°C) were prepared by the same procedure.

Octyl 4-{{4-[(6-chloro-3-hydroxybenzoyl)oxy]benzoyl}oxy}benzoate (31a). Deprotection of **25a** was performed as for **19a**, yield 57%, m.p. 118.5–121.5°C. ^{1}H NMR ($CDCl_3$): 0.89 (t, 3 H, *J* = 6.7, CH_3), 1.21-1.52 (m, 10 H, $(CH_2)_5$), 1.78 (m, 2 H, CH_2), 4.34 (t, 2 H, *J* = 6.7, OCH_2), 5.79 (s, 1 H, OH), 7.02 (dd, 1 H, ^3J = 8.8, ^4J = 2.9, CH), 7.27 (d, 2 H, *J* = 8.8, 2 × CH), 7.39 (m, 3 H, 3 × CH), 7.58 (d, 1 H, ^4J = 2.9, CH), 8.14 (d, 2 H, *J* = 8.8, 2 × CH), 8.29 (d, 2 H, *J* = 8.8, 2 × CH). Elemental analysis: for $C_{29}H_{29}ClO_7$ (525.00): calculated C 66.35, H 5.57, Cl 6.75; found C 66.59, H 5.48, Cl 6.67%.

Intermediates **31b** (R = $C_{10}H_{21}$, yield 44%, m.p. 115–118°C), **31c** (R = $C_{12}H_{25}$, yield 52%, m.p. 107–119°C) and **31d** (R = $C_{14}H_{29}$, yield 61%, m.p. 114–117.5°C) were prepared by the same procedure.

1.4. Synthesis of the target compounds

4-[6-Fluoro-3-(4-(4-octyloxybenzoyloxy)benzoyloxy)benzoyloxy]phenyl 4-octyloxybenzoate (Ia/F)

DMAP (76 mg, 0.625 mmol) was added to a solution of hydroxy ester **18a** (150 mg, 0.312 mmol), in toluene (12 ml) at 100 °C in an argon atmosphere. Then a solution of acid chloride **14a** (243 mg, 0.625 mmol) in toluene (5 ml) was added via a syringe. The reaction mixture was stirred for 5 minutes, then cooled down to room temperature and decomposed with cold water (30 ml). Layers were separated and the aqueous layer was extracted with chloroform (3 × 30 ml). The combined organic solution was washed with water (50 ml) and dried with anhydrous magnesium sulphate. The solvent was removed under reduced pressure and the product was purified by column chromatography (toluene/*tert*-butyl methyl ether, 18/1) and by crystallisation from an ethyl acetate/ethanol mixture. Yield 180 mg (69%). ^{1}H NMR ($CDCl_3$): 0.89 (m, 6 H, 2 × CH_3), 1.24-1.53 (m, 20 H, 2 × $(CH_2)_5$), 1.82 (m, 4 H, 2 × CH_2), 4.05 (m, 4 H, 2 × OCH_2), 6.97 (d, 2 H, *J* = 8.8, 2 × CH), 6.99 (d, 2 H, *J* = 8.8, 2 × CH), 7.26-7.33 (m, 5 H, 5 × CH), 7.39 (d, 2 H, *J* = 8.8, 2 × CH), 7.49 (ddd, 1 H, ^3J = 8.8, ^4J = 3.2, ^4J = 4.1, CH), 7.97 (dd, 1 H, ^4J = 3.2, ^4J = 5.8, CH), 8.14 (d, 2 H, *J* = 8.8, 2 × CH), 8.15 (d, 2 H, *J* = 8.8, 2 × CH), 8.28 (d, 2 H, *J* = 8.8, 2 × CH). Elemental analysis: for $C_{50}H_{53}FO_{10}$ (832.97): calculated C 72.10, H 6.41, F 2.28; found C 71.91, H 6.32, F 2.34%.

By the same way, all compounds of the series **Ib-d/X**, **IIa-d/X**, and **IIIa-d/X** have been synthesised.

4-[3-(4-(4-Decyloxybenzoyloxy)benzoyloxy)-6-fluorobenzoyloxy]phenyl 4-octyloxybenzoate (Ib/F). Yield 59%. ^{1}H NMR ($CDCl_3$): 0.89 (m, 6 H, 2 × CH_3), 1.23-1.53 (m, 28 H, 2 × $(CH_2)_7$), 1.82 (m, 4 H, 2 × CH_2), 4.05 (m, 4 H, 2 × OCH_2), 6.97 (d, 2 H, J = 8.8, 2 × CH), 6.99 (d, 2 H, J = 8.8, 2 × CH), 7.26-7.33 (m, 5 H, 5 × CH), 7.39 (d, 2 H, J = 8.8, 2 × CH), 7.49 (ddd, 1 H, ^3J = 8.8, ^4J = 3.2, ^4J = 4.1, CH), 7.97 (dd, 1 H, ^4J = 3.2, ^4J = 5.8, CH), 8.14 (d, 2 H, J = 8.8, 2 × CH), 8.15 (d, 2 H, J = 8.8, 2 × CH), 8.28 (d, 2 H, J = 8.8, 2 × CH). Elemental analysis: for $C_{54}H_{61}FO_{10}$ (889.08): calculated C 72.95, H 6.92, F 2.13; found C 72.84, H 6.86, F 2.15%.

4-[3-(4-(4-Dodecyloxybenzoyloxy)benzoyloxy)-6-fluorobenzoyloxy]phenyl 4-octyloxybenzoate (Ic/F). Yield 71%. ^{1}H NMR ($CDCl_3$): 0.89 (m, 6 H, 2 × CH_3), 1.22-1.54 (m, 36 H, 2 × $(CH_2)_9$), 1.82 (m, 4 H, 2 × CH_2), 4.05 (m, 4 H, 2 × OCH_2), 6.97 (d, 2 H, J = 8.8, 2 × CH), 6.99 (d, 2 H, J = 8.8, 2 × CH), 7.26-7.33 (m, 5 H, 5 × CH), 7.39 (d, 2 H, J = 8.8, 2 × CH), 7.49 (ddd, 1 H, ^3J = 8.8, ^4J = 3.2, ^4J = 4.1, CH), 7.97 (dd, 1 H, ^4J = 3.2, ^4J = 5.8, CH), 8.14 (d, 2 H, J = 8.8, 2 × CH), 8.15 (d, 2 H, J = 8.8, 2 × CH), 8.28 (d, 2 H, J = 8.8, 2 × CH). Elemental analysis: for $C_{58}H_{69}FO_{10}$ (945.19): calculated C 73.70, H 7.36, F 2.01; found C 73.76, H 7.37, F 1.99%.

4-[6-Fluoro-3-(4-(4-tetradecyloxybenzoyloxy)benzoyloxy)benzoyloxy]phenyl 4-octyloxybenzoate (Id/F). Yield 82%. ^{1}H NMR ($CDCl_3$): 0.89 (m, 6 H, 2 × CH_3), 1.22-1.54 (m, 44 H, 2 × $(CH_2)_{11}$), 1.82 (m, 4 H, 2 × CH_2), 4.05 (m, 4 H, 2 × OCH_2), 6.97 (d, 2 H, J = 8.8, 2 × CH), 6.99 (d, 2 H, J = 8.8, 2 × CH), 7.26-7.33 (m, 5 H, 5 × CH), 7.39 (d, 2 H, J = 8.8, 2 × CH), 7.49 (ddd, 1 H, ^3J = 8.8, ^4J = 3.2, ^4J = 4.1, CH), 7.97 (dd, 1 H, ^4J = 3.2, ^4J = 5.8, CH), 8.14 (d, 2 H, J = 8.8, 2 × CH), 8.15 (d, 2 H, J = 8.8, 2 × CH), 8.28 (d, 2 H, J = 8.8, 2 × CH). Elemental analysis: for $C_{62}H_{77}FO_{10}$ (1001.30): calculated C 74.37, H 7.75, F 1.90; found C 74.28, H 7.72, F 1.84%.

4-[6-Chloro-3-(4-(4-octyloxybenzoyloxy)benzoyloxy)benzoyloxy]phenyl 4-octyloxybenzoate (Ia/Cl) was prepared as above by acylation of **19a** with acid chloride **14a**. Yield 71%. ^{1}H NMR ($CDCl_3$): 0.90 (m, 6 H, 2 × CH_3), 1.24-1.55 (m, 20 H, 2 × $(CH_2)_5$), 1.83 (m, 4 H, 2 ×

CH_2), 4.05 (m, 4 H, 2 × OCH_2), 6.97 (d, 2 H, *J* = 8.8, 2 × CH), 6.99 (d, 2 H, *J* = 8.8, 2 × CH), 7.26-7.30 (m, 4 H, 4 × CH), 7.38-7.44 (m, 3 H, 3 × CH), 7.60 (d, 1 H, ^3J = 8.8, CH), 7.96 (d, 1 H, ^4J = 2.9, CH), 8.14 (d, 2 H, *J* = 8.8, 2 × CH), 8.15 (d, 2 H, *J* = 8.8, 2 × CH), 8.29 (d, 2 H, *J* = 8.8, 2 × CH). Elemental analysis: for $C_{50}H_{53}ClO_{10}$ (849.43): calculated C 70.70, H 6.29, Cl 4.17; found C 70.52 H 6.30, Cl 4.17%.

4-[6-Chloro-3-(4-(4-decyloxybenzoyloxy)benzoyloxy)benzoyloxy]phenyl 4-octyloxybenzoate (Ib/Cl). Yield 58%. ^{1}H NMR ($CDCl_3$): 0.90 (m, 6 H, 2 × CH_3), 1.24-1.54 (m, 28 H, 2 × $(CH_2)_7$), 1.83 (m, 4 H, 2 × CH_2), 4.05 (m, 4 H, 2 × OCH_2), 6.97 (d, 2 H, *J* = 8.8, 2 × CH), 6.99 (d, 2 H, *J* = 8.8, 2 × CH), 7.26-7.30 (m, 4 H, 4 × CH), 7.38-7.44 (m, 3 H, 3 × CH), 7.60 (d, 1 H, ^3J = 8.8, CH), 7.96 (d, 1 H, ^4J = 2.9, CH), 8.14 (d, 2 H, *J* = 8.8, 2 × CH), 8.15 (d, 2 H, *J* = 8.8, 2 × CH), 8.29 (d, 2 H, *J* = 8.8, 2 × CH). Elemental analysis: for $C_{54}H_{61}ClO_{10}$ (905.54): calculated C 71.63, H 6.79, Cl 3.92; found C 71.48, H 6.67, Cl 3.99%.

4-[6-Chloro-3-(4-(4-dodecyloxybenzoyloxy)benzoyloxy)benzoyloxy]phenyl 4-octyloxybenzoate (Ic/Cl). Yield 68%. ^{1}H NMR ($CDCl_3$): 0.90 (m, 6 H, 2 × CH_3), 1.23-1.54 (m, 36 H, 2 × $(CH_2)_9$), 1.83 (m, 4 H, 2 × CH_2), 4.05 (m, 4 H, 2 × OCH_2), 6.97 (d, 2 H, *J* = 8.8, 2 × CH), 6.99 (d, 2 H, *J* = 8.8, 2 × CH), 7.26-7.30 (m, 4 H, 4 × CH), 7.38-7.44 (m, 3 H, 3 × CH), 7.60 (d, 1 H, ^3J = 8.8, CH), 7.96 (d, 1 H, ^4J = 2.9, CH), 8.14 (d, 2 H, *J* = 8.8, 2 × CH), 8.15 (d, 2 H, *J* = 8.8, 2 × CH), 8.29 (d, 2 H, *J* = 8.8, 2 × CH). Elemental analysis: for $C_{58}H_{69}ClO_{10}$ (961.64): calculated C 72.44, H 7.23, Cl 3.69; found C 72.31, H 7.19, Cl 3.74%.

4-[6-Chloro-3-(4-(4-tetradecyloxybenzoyloxy)benzoyloxy)benzoyloxy]phenyl 4-octyloxybenzoate (Id/Cl). Yield 89%. ^{1}H NMR ($CDCl_3$): 0.90 (m, 6 H, 2 × CH_3), 1.23-1.55 (m, 44 H, 2 × $(CH_2)_{11}$), 1.83 (m, 4 H, 2 × CH_2), 4.05 (m, 4 H, 2 × OCH_2), 6.97 (d, 2 H, *J* = 8.8, 2 × CH), 6.99 (d, 2 H, *J* = 8.8, 2 × CH), 7.26-7.30 (m, 4 H, 4 × CH), 7.38-7.44 (m, 3 H, 3 × CH), 7.60 (d, 1 H, ^3J = 8.8, CH), 7.96 (d, 1 H, ^4J = 2.9, CH), 8.14 (d, 2 H, *J* = 8.8, 2 × CH), 8.15 (d, 2 H, *J* = 8.8, 2 × CH), 8.29 (d, 2 H, *J* = 8.8, 2 × CH). Elemental analysis: for $C_{62}H_{77}ClO_{10}$ (1017.75): calculated C 73.17, H 7.63, Cl 3.48; found C 73.01, H 7.69, Cl 3.46%.

4-[6-Methyl-3-(4-(4-octyloxybenzoyloxy)benzoyloxy)benzoyloxy]phenyl 4-octyloxybenzoate (Ia/CH$_3$) was synthesised by acylation of **20a** with acid chloride **14a**, yield 69%. ^{1}H NMR ($CDCl_3$): 0.89 (m, 6 H, 2 × CH_3), 1.22-1.55 (m, 20 H, 2 × $(CH_2)_5$), 1.82 (m, 4 H, 2 × CH_2),

2.70 (s, 3 H, CH_3), 4.05 (m, 4 H, 2 × OCH_2), 6.97 (d, 2 H, *J* = 8.8, 2 × CH), 6.99 (d, 2 H, *J* = 8.8, 2 × CH), 7.24-7.29 (m, 4 H, 4 × CH), 7.36-7.42 (m, 4 H, 4 × CH), 8.04 (d, 1 H, ^4J = 2.9, CH), 8.14 (d, 2 H, *J* = 8.8, 2 × CH), 8.15 (d, 2 H, *J* = 8.8, 2 × CH), 8.29 (d, 2 H, 2 × CH). Elemental analysis: for $C_{51}H_{56}O_{10}$ (829.01): calculated C 73.89, H 6.81; found C 73.82, H 6.74.

4-[3-(4-(4-Decyloxybenzoyloxy)benzoyloxy)-6-methylbenzoyloxy]phenyl 4-octyloxybenzoate (Ib/CH₃). Yield 78%. ^{1}H NMR ($CDCl_3$): 0.89 (m, 6 H, 2 × CH_3), 1.22-1.54 (m, 28 H, 2 × $(CH_2)_7$), 1.82 (m, 4 H, 2 × CH_2), 2.70 (s, 3 H, CH_3), 4.05 (m, 4 H, 2 × OCH_2), 6.97 (d, 2 H, *J* = 8.8, 2 × CH), 6.99 (d, 2 H, *J* = 8.8, 2 × CH), 7.24-7.29 (m, 4 H, 4 × CH), 7.36-7.42 (m, 4 H, 4 × CH), 8.04 (d, 1 H, ^4J = 2.9, CH), 8.14 (d, 2 H, *J* = 8.8, 2 × CH), 8.15 (d, 2 H, *J* = 8.8, 2 × CH), 8.29 (d, 2 H, 2 × CH). Elemental analysis for $C_{55}H_{64}O_{10}$ (885.12): calculated 74.64% C, 7.29% H; found 74.61% C, 7.40% H.

4-[3-(4-(4-Dodecyloxybenzoyloxy)benzoyloxy)-6-methylbenzoyloxy]phenyl 4-octyloxybenzoate (Ic/CH₃). Yield 56%. ^{1}H NMR ($CDCl_3$): 0.89 (m, 6 H, 2 × CH_3), 1.23-1.55 (m, 36 H, 2 × $(CH_2)_9$), 1.82 (m, 4 H, 2 × CH_2), 2.70 (s, 3 H, CH_3), 4.05 (m, 4 H, 2 × OCH_2), 6.97 (d, 2 H, *J* = 8.8, 2 × CH), 6.99 (d, 2 H, *J* = 8.8, 2 × CH), 7.24-7.29 (m, 4 H, 4 × CH), 7.36-7.42 (m, 4 H, 4 × CH), 8.04 (d, 1 H, ^4J = 2.9, CH), 8.14 (d, 2 H, *J* = 8.8, 2 × CH), 8.15 (d, 2 H, *J* = 8.8, 2 × CH), 8.29 (d, 2 H, 2 × CH). Elemental analysis for $C_{63}H_{80}O_{10}$ (997.33): calculated 75.87% C, 8.09% H; found 75.69% C, 7.98% H.

4-[6-Methyl-3-(4-(4-tetradecyloxybenzoyloxy)benzoyloxy)benzoyloxy]phenyl 4-octyloxybenzoate (Id/CH₃). Yield 74%. ^{1}H NMR ($CDCl_3$): 0.89 (m, 6 H, 2 × CH_3), 1.22-1.55 (m, 44 H, 2 × $(CH_2)_{11}$), 1.82 (m, 4 H, 2 × CH_2), 2.70 (s, 3 H, CH_3), 4.05 (m, 4 H, 2 × OCH_2), 6.97 (d, 2 H, *J* = 8.8, 2 × CH), 6.99 (d, 2 H, *J* = 8.8, 2 × CH), 7.24-7.29 (m, 4 H, 4 × CH), 7.36-7.42 (m, 4 H, 4 × CH), 8.04 (d, 1 H, ^4J = 2.9, CH), 8.14 (d, 2 H, *J* = 8.8, 2 × CH), 8.15 (d, 2 H, *J* = 8.8, 2 × CH), 8.29 (d, 2 H, 2 × CH). Elemental analysis for $C_{63}H_{80}O_{10}$ (997.33): calculated 75.87% C, 8.09% H; found 75.75% C, 8.06% H.

4-Octyloxyphenyl 4-{6-fluoro-3-[4-(4-octyloxybenzoyloxy)]benzoyloxy]benzoyloxy}benzoate (IIa/F). Reaction of **27a** with acid chloride **14a** yielded the compound **IIa/F**, yield 65%. ^{1}H NMR ($CDCl_3$): 0.90 (m, 6 H, 2 × CH_3), 1.24-1.54 (m, 20 H, 2 × $(CH_2)_5$), 1.81 (m, 4 H, 2 × CH_2), 3.96 (t, 2 H, *J* = 6.7, OCH_2), 4.05 (t, 2 H, *J* = 6.7, OCH_2), 6.93 (d, 2 H, *J* = 8.8, 2 ×

CH), 6.99 (d, 2 H, J = 8.8, 2 × CH), 7.12 (d, 2 H, J = 8.8, 2 × CH), 7.31 (dd, 1 H, ^3J = 8.8, ^3J = 9.7, CH), 7.37-7.41 (m, 4 H, 4 × CH), 7.51 (ddd, 1 H, ^3J = 8.8, ^4J = 3.2, ^4J = 4.1, CH), 7.99 (dd, 1 H, ^4J = 3.2, ^4J = 5.8, CH), 8.15 (d, 2 H, J = 8.8, 2 × CH), 8.28 (m, 4 H, 4 × CH). Elemental analysis: for $C_{50}H_{53}FO_{10}$ (832.97): calculated C 72.10, H 6.41, F 2.28; found C 71.98, H 6.37, F 2.30%.

4-Decyloxyphenyl 4-{3-[4-(4-decyloxybenzoyloxy)]benzoyloxy]-6-fluorobenzoyloxy}benzoate (IIb/F). Yield 72%. ^{1}H NMR ($CDCl_3$): 0.90 (m, 6 H, 2 × CH_3), 1.24-1.53 (m, 28 H, 2 × $(CH_2)_7$), 1.81 (m, 4 H, 2 × CH_2), 3.96 (t, 2 H, J = 6.7, OCH_2), 4.05 (t, 2 H, J = 6.7, OCH_2), 6.93 (d, 2 H, J = 8.8, 2 × CH), 6.99 (d, 2 H, J = 8.8, 2 × CH), 7.12 (d, 2 H, J = 8.8, 2 × CH), 7.31 (dd, 1 H, ^3J = 8.8, ^3J = 9.7, CH), 7.37-7.41 (m, 4 H, 4 × CH), 7.51 (ddd, 1 H, ^3J = 8.8, ^4J = 3.2, ^4J = 4.1, CH), 7.99 (dd, 1 H, ^4J = 3.2, ^4J = 5.8, CH), 8.15 (d, 2 H, J = 8.8, 2 × CH), 8.28 (m, 4 H, 4 × CH). Elemental analysis: for $C_{54}H_{61}FO_{10}$ (889.08): calculated C 72.95, H 6.92, F 2.13; found C 72.78, H 6.87, F 2.18%.

4-Dodecyloxyphenyl 4-{3-[4-(4-dodecyloxybenzoyloxy)]benzoyloxy]-6-fluorobenzoyloxy}benzoate (IIc/F). Yield 74%. ^{1}H NMR ($CDCl_3$): 0.90 (m, 6 H, 2 × CH_3), 1.24-1.54 (m, 36 H, 2 × $(CH_2)_9$), 1.81 (m, 4 H, 2 × CH_2), 3.96 (t, 2 H, J = 6.7, OCH_2), 4.05 (t, 2 H, J = 6.7, OCH_2), 6.93 (d, 2 H, J = 8.8, 2 × CH), 6.99 (d, 2 H, J = 8.8, 2 × CH), 7.12 (d, 2 H, J = 8.8, 2 × CH), 7.31 (dd, 1 H, ^3J = 8.8, ^3J = 9.7, CH), 7.37-7.41 (m, 4 H, 4 × CH), 7.51 (ddd, 1 H, ^3J = 8.8, ^4J = 3.2, ^4J = 4.1, CH), 7.99 (dd, 1 H, ^4J = 3.2, ^4J = 5.8, CH), 8.15 (d, 2 H, J = 8.8, 2 × CH), 8.28 (m, 4 H, 4 × CH). Elemental analysis: for $C_{58}H_{69}FO_{10}$ (945.19): calculated C 73.70, H 7.36, F 2.01; found C 73.63, H 7.32, F 1.95%.

4-Tetradecyloxyphenyl 4-{6-fluoro-3-[4-(4-tetradecyloxybenzoyloxy)]benzoyloxy]benzoyloxy}benzoate (IId/F). Yield 51%. ^{1}H NMR ($CDCl_3$): 0.90 (m, 6 H, 2 × CH_3), 1.23-1.54 (m, 44 H, 2 × $(CH_2)_{11}$), 1.81 (m, 4 H, 2 × CH_2), 3.96 (t, 2 H, J = 6.7, OCH_2), 4.05 (t, 2 H, J = 6.7, OCH_2), 6.93 (d, 2 H, J = 8.8, 2 × CH), 6.99 (d, 2 H, J = 8.8, 2 × CH), 7.12 (d, 2 H, J = 8.8, 2 × CH), 7.31 (dd, 1 H, ^3J = 8.8, ^3J = 9.7, CH), 7.37-7.41 (m, 4 H, 4 × CH), 7.51 (ddd, 1 H, ^3J = 8.8, ^4J = 3.2, ^4J = 4.1, CH), 7.99 (dd, 1 H, ^4J = 3.2, ^4J = 5.8, CH), 8.15 (d, 2 H, J = 8.8, 2 × CH), 8.28 (m, 4 H, 4 × CH). Elemental analysis: for $C_{62}H_{77}FO_{10}$ (1001.30): calculated C 74.37, H 7.75, F 1.90; found C 74.25, H 7.90, F 1.81%.

4-Octyloxyphenyl 4-{6-chloro-3-[4-(4-octyloxybenzoyloxy)]benzoyloxy]benzoyloxy}benzoate (IIa/Cl) has been prepared from intermediate **28a** and acid chloride **14a**, yield 82%. ^{1}H NMR ($CDCl_3$): 0.89 (m, 6 H, 2 × CH_3), 1.23-1.53 (m, 20 H, 2 × $(CH_2)_5$), 1.81 (m, 4 H, 2 × CH_2), 3.96 (t, 2 H, *J* = 6.7. OCH_2), 4.06 (t, 2 H, *J* = 6.7, OCH_2), 6.93 (d, 2 H, *J* = 8.8, 2 × CH), 6.99 (d, 2 H, *J* = 8.8, 2 × CH), 7.12 (d, 2 H, *J* = 8.8, 2 × CH), 7.38-7.46 (m, 5 H, 5 × CH), 7.62 (d, 1 H, ^{3}J = 8.8, CH), 8.00 (d, 1 H, ^{4}J = 2.9, CH), 8.15 (d, 2 H, *J* = 8.8, 2 × CH), 8.29 (m, 4 H, 4 × CH). Elemental analysis: for $C_{50}H_{53}ClO_{10}$ (849.43): calculated C 70.70, H 6.29, Cl 4.17; found C 70.60, H 6.26, Cl 4.18%.

4-Decyloxyphenyl 4-{6-chloro-3-[4-(4-decyloxybenzoyloxy)]benzoyloxy]benzoyloxy}benzoate (IIb/Cl). Yield 75%. ^{1}H NMR ($CDCl_3$): 0.89 (m, 6 H, 2 × CH_3), 1.23-1.53 (m, 28 H, 2 × $(CH_2)_7$), 1.81 (m, 4 H, 2 × CH_2), 3.96 (t, 2 H, *J* = 6.7. OCH_2), 4.06 (t, 2 H, *J* = 6.7, OCH_2), 6.93 (d, 2 H, *J* = 8.8, 2 × CH), 6.99 (d, 2 H, *J* = 8.8, 2 × CH), 7.12 (d, 2 H, *J* = 8.8, 2 × CH), 7.38-7.46 (m, 5 H, 5 × CH), 7.62 (d, 1 H, ^{3}J = 8.8, CH), 8.00 (d, 1 H, ^{4}J = 2.9, CH), 8.15 (d, 2 H, *J* = 8.8, 2 × CH), 8.29 (m, 4 H, 4 × CH). Elemental analysis: for $C_{54}H_{61}ClO_{10}$ (905.54): calculated C 71.63, H 6.79, Cl 3.92; found C 71.44, H 6.77, Cl 4.00%.

4-Dodecyloxyphenyl 4-{6-chloro-3-[4-(4-dodecyloxybenzoyloxy)]benzoyloxy]benzoyloxy}benzoate (IIc/Cl). Yield 75%. ^{1}H NMR ($CDCl_3$): 0.89 (m, 6 H, 2 × CH_3), 1.23-1.54 (m, 36 H, 2 × $(CH_2)_9$), 1.81 (m, 4 H, 2 × CH_2), 3.96 (t, 2 H, *J* = 6.7. OCH_2), 4.06 (t, 2 H, *J* = 6.7, OCH_2), 6.93 (d, 2 H, *J* = 8.8, 2 × CH), 6.99 (d, 2 H, *J* = 8.8, 2 × CH), 7.12 (d, 2 H, *J* = 8.8, 2 × CH), 7.38-7.46 (m, 5 H, 5 × CH), 7.62 (d, 1 H, ^{3}J = 8.8, CH), 8.00 (d, 1 H, ^{4}J = 2.9, CH), 8.15 (d, 2 H, *J* = 8.8, 2 × CH), 8.29 (m, 4 H, 4 × CH). Elemental analysis: for $C_{58}H_{69}ClO_{10}$ (961.64): calculated C 72.44, H 7.23, Cl 3.69; found C 72.28, H 7.18, Cl 3.60%.

4-Tetradecyloxyphenyl 4-{6-chloro-3-[4-(4-tetradecyloxybenzoyloxy)]benzoyloxy]benzoyloxy}benzoate (IId/Cl). Yield 83%. ^{1}H NMR ($CDCl_3$): 0.89 (m, 6 H, 2 × CH_3), 1.22-1.54 (m, 44 H, 2 × $(CH_2)_{11}$), 1.81 (m, 4 H, 2 × CH_2), 3.96 (t, 2 H, *J* = 6.7. OCH_2), 4.06 (t, 2 H, *J* = 6.7, OCH_2), 6.93 (d, 2 H, *J* = 8.8, 2 × CH), 6.99 (d, 2 H, *J* = 8.8, 2 × CH), 7.12 (d, 2 H, *J* = 8.8, 2 × CH), 7.38-7.46 (m, 5 H, 5 × CH), 7.62 (d, 1 H, ^{3}J = 8.8, CH), 8.00 (d, 1 H, ^{4}J = 2.9, CH), 8.15 (d, 2 H, *J* = 8.8, 2 × CH), 8.29 (m, 4 H, 4

× CH). Elemental analysis: for $C_{62}H_{77}ClO_{10}$ (1017.75): calculated C 73.17, H 7.63, Cl 3.48; found C 73.09, H 7.59, Cl 3.39%.

4-Octyloxyphenyl 4-{6-methyl-3-[4-(4-octyloxybenzoyloxy)]benzoyloxy]benzoyloxy}benzoate (IIa/CH₃). Compound **29a** (120 mg; 0.252 mmol) was acylated with acid chloride **14a**. Yield 73%. ^{1}H NMR ($CDCl_3$): 0.88 (m, 6 H, 2 × CH_3); 1.20-1.52 (m, 20 H, 2 × $(CH_2)_5$), 1.80 (m, 4 H, 2 × CH_2), 2.71 (s, 3 H, CH_3), 3.96 (t, 2 H, *J* = 6.7, OCH_2), 4.05 (t, 2 H, *J* = 6.7, OCH_2), 6.93 (d, 2 H, *J* = 8.8, 2 × CH), 6.99 (d, 2 H, *J* = 8.8, 2 × CH), 7.12 (d, 2 H, *J* = 8.8, 2 × CH), 7.32-7.43 (m, 6 H, 6 × CH), 8.07 (d, 1 H, ^4J = 2.9, CH), 8.15 (d, 2 H, *J* = 8.8, 2 × CH), 8.28 (d, 2 H, *J* = 8.8, 2 × CH), 8.29 (d, 2 H, *J* = 8.8, 2 × CH). Elemental analysis: for $C_{51}H_{56}O_{10}$ (829.01): calculated C 73.89, H 6.81; found C 73.79, H 6.72%.

4-Decyloxyphenyl 4-{3-[4-(4-decyloxybenzoyloxy)]benzoyloxy]-6-methylbenzoyloxy}benzoate (IIb/CH₃). Yield 65%. ^{1}H NMR ($CDCl_3$): 0.88 (m, 6 H, 2 × CH_3); 1.21-1.52 (m, 28 H, 2 × $(CH_2)_7$), 1.80 (m, 4 H, 2 × CH_2), 2.71 (s, 3 H, CH_3), 3.96 (t, 2 H, *J* = 6.7, OCH_2), 4.05 (t, 2 H, *J* = 6.7, OCH_2), 6.93 (d, 2 H, *J* = 8.8, 2 × CH), 6.99 (d, 2 H, *J* = 8.8, 2 × CH), 7.12 (d, 2 H, *J* = 8.8, 2 × CH), 7.32-7.43 (m, 6 H, 6 × CH), 8.07 (d, 1 H, ^4J = 2.9, CH), 8.15 (d, 2 H, *J* = 8.8, 2 × CH), 8.28 (d, 2 H, *J* = 8.8, 2 × CH), 8.29 (d, 2 H, *J* = 8.8, 2 × CH). Elemental analysis: for $C_{55}H_{64}O_{10}$ (885.12): calculated C 74.64, H 7.29; found C 74.68, H 7.42%.

4-Dodecyloxyphenyl 4-{3-[4-(4-dodecyloxybenzoyloxy)]benzoyloxy]-6-methylbenzoyloxy}benzoate (IIc/CH₃). Yield 74%. ^{1}H NMR ($CDCl_3$): 0.88 (m, 6 H, 2 × CH_3); 1.20-1.51 (m, 36 H, 2 × $(CH_2)_9$), 1.80 (m, 4 H, 2 × CH_2), 2.71 (s, 3 H, CH_3), 3.96 (t, 2 H, *J* = 6.7, OCH_2), 4.05 (t, 2 H, *J* = 6.7, OCH_2), 6.93 (d, 2 H, *J* = 8.8, 2 × CH), 6.99 (d, 2 H, *J* = 8.8, 2 × CH), 7.12 (d, 2 H, *J* = 8.8, 2 × CH), 7.32-7.43 (m, 6 H, 6 × CH), 8.07 (d, 1 H, ^4J = 2.9, CH), 8.15 (d, 2 H, *J* = 8.8, 2 × CH), 8.28 (d, 2 H, *J* = 8.8, 2 × CH), 8.29 (d, 2 H, *J* = 8.8, 2 × CH). Elemental analysis: for $C_{59}H_{72}O_{10}$ (941.23): calculated C 75.29, H 7.71; found C 75.11, H 7.69%.

4-Tetradecyloxyphenyl 4-{6-methyl-3-[4-(4-tetradecyloxybenzoyloxy)]benzoyloxy]benzoyloxy}benzoate (IId/CH₃). Yield 60%. ^{1}H NMR ($CDCl_3$): 0.88 (m, 6 H, 2 × CH_3); 1.20-1.52 (m, 44 H, 2 × $(CH_2)_{11}$), 1.80 (m, 4 H, 2 × CH_2), 2.71 (s, 3 H, CH_3), 3.96 (t, 2 H, *J* = 6.7, OCH_2), 4.05 (t, 2 H, *J* = 6.7, OCH_2), 6.93 (d, 2 H, *J* =

8.8, 2 × CH), 6.99 (d, 2 H, *J* = 8.8, 2 × CH), 7.12 (d, 2 H, *J* = 8.8, 2 × CH), 7.32-7.43 (m, 6 H, 6 × CH), 8.07 (d, 1 H, ^4J = 2.9, CH), 8.15 (d, 2 H, *J* = 8.8, 2 × CH), 8.28 (d, 2 H, *J* = 8.8, 2 × CH), 8.29 (d, 2 H, *J* = 8.8, 2 × CH). Elemental analysis for: $C_{63}H_{80}O_{10}$ (997.33): calculated C 75.87, H 8.09; found C 75.74, H 8.00%.

***Octyl 4-{4-{6-fluoro-3-[4-(4-octyloxybenzoyloxy)benzoyloxy]benzoyloxy}benzoyloxy}benzoate (IIIa/F*)** was obtained by the reaction of **30a** with acid chloride **14a**, yield 31%. ^{1}H NMR ($CDCl_3$): 0.89 (m, 6 H, 2 × CH_3), 1.25-1.54 (m, 20 H, 2 × $(CH_2)_5$), 1.80 (m, 4 H, 2 × CH_2), 4.06 (t, 2 H, *J* = 6.7, OCH_2), 4.33 (t, 2 H, *J* = 6.7, OCH_2), 6.99 (d, 2 H, *J* = 8.8, 2 × CH), 7.31 (d, 2 H, *J* = 8.8, 2 × CH), 7.32 (dd, 1 H, ^3J = 8.8, ^3J = 9.7, CH), 7.40 (d, 2 H, *J* = 8.8, 2 × CH), 7.42 (d, 2 H, *J* = 8.8, 2 × CH), 7.52 (ddd, 1 H, ^3J = 8.8, ^4J = 3.2, ^4J = 4.1, CH), 7.99 (dd, 1 H, ^4J = 3.2, ^4J = 5.8, CH), 8.14 (d, 2 H, *J* = 8.8, 2 × CH), 8.15 (d, 2 H, *J* = 8.8, 2 × CH), 8.28 (d, 2 H, *J* = 8.8, 2 × CH), 8.30 (d, 2 H, *J* = 8.8, 2 × CH). Elemental analysis: for $C_{51}H_{53}FO_{11}$ (860.98): calculated C 71.15, H 6.20, F 2.21; found C 71.01, H 6.14, F 2.17%.

Decyl 4-{4-{3-[4-(4-decyloxybenzoyloxy)benzoyloxy]-6-fluorobenzoyloxy}benzoyloxy}benzoate (IIIa/F). Yield 56%. ^{1}H NMR ($CDCl_3$): 0.89 (m, 6 H, 2 × CH_3), 1.25-1.54 (m, 28 H, 2 × $(CH_2)_7$), 1.80 (m, 4 H, 2 × CH_2), 4.06 (t, 2 H, *J* = 6.7, OCH_2), 4.33 (t, 2 H, *J* = 6.7, OCH_2), 6.99 (d, 2 H, *J* = 8.8, 2 × CH), 7.31 (d, 2 H, *J* = 8.8, 2 × CH), 7.32 (dd, 1 H, ^3J = 8.8, ^3J = 9.7, CH), 7.40 (d, 2 H, *J* = 8.8, 2 × CH), 7.42 (d, 2 H, *J* = 8.8, 2 × CH), 7.52 (ddd, 1 H, ^3J = 8.8, ^4J = 3.2, ^4J = 4.1, CH), 7.99 (dd, 1 H, ^4J = 3.2, ^4J = 5.8, CH), 8.14 (d, 2 H, *J* = 8.8, 2 × CH), 8.15 (d, 2 H, *J* = 8.8, 2 × CH), 8.28 (d, 2 H, *J* = 8.8, 2 × CH), 8.30 (d, 2 H, *J* = 8.8, 2 × CH). Elemental analysis for $C_{55}H_{61}FO_{11}$ (917.09): calculated C 72.03, H 6.70, F 2.07; found C 71.85, H 6.76, F 2.02%.

Dodecyl 4-{4-{3-[4-(4-dodecyloxybenzoyloxy)benzoyloxy]-6-fluorobenzoyloxy}benzoyloxy}benzoate (IIIc/F). Yield 67%. ^{1}H NMR ($CDCl_3$): 0.89 (m, 6 H, 2 × CH_3), 1.25-1.53 (m, 36 H, 2 × $(CH_2)_9$), 1.80 (m, 4 H, 2 × CH_2), 4.06 (t, 2 H, *J* = 6.7, OCH_2), 4.33 (t, 2 H, *J* = 6.7, OCH_2), 6.99 (d, 2 H, *J* = 8.8, 2 × CH), 7.31 (d, 2 H, *J* = 8.8, 2 × CH), 7.32 (dd, 1 H, ^3J = 8.8, ^3J = 9.7, CH), 7.40 (d, 2 H, *J* = 8.8, 2 × CH), 7.42 (d, 2 H, *J* = 8.8, 2 × CH), 7.52 (ddd, 1 H, ^3J = 8.8, ^4J = 3.2, ^4J = 4.1, CH), 7.99 (dd, 1 H, ^4J = 3.2, ^4J = 5.8, CH), 8.14 (d, 2 H, *J* = 8.8, 2 × CH), 8.15 (d, 2 H, *J* = 8.8, 2 × CH), 8.28 (d, 2 H, *J* = 8.8, 2 ×

CH), 8.30 (d, 2 H, *J* = 8.8, 2 × CH). Elemental analysis for $C_{59}H_{69}FO_{11}$ (973.20): calculated C 72.82, H 7.15, F 1.95; found C 72.67, H 7.21, F 1.93%.

Tetradecyl 4-{4-{6-fluoro-3-[4-(4-tetradecyloxybenzoyloxy)benzoyloxy]benzoyloxy}benzoyloxy}benzoate (IIId/F). Yield 83%. ^{1}H NMR ($CDCl_3$): 0.89 (m, 6 H, 2 × CH_3), 1.24-1.54 (m, 44 H, 2 × $(CH_2)_{11}$), 1.80 (m, 4 H, 2 × CH_2), 4.06 (t, 2 H, *J* = 6.7, OCH_2), 4.33 (t, 2 H, *J* = 6.7, OCH_2), 6.99 (d, 2 H, *J* = 8.8, 2 × CH), 7.31 (d, 2 H, *J* = 8.8, 2 × CH), 7.32 (dd, 1 H, ^3J = 8.8, ^3J = 9.7, CH), 7.40 (d, 2 H, *J* = 8.8, 2 × CH), 7.42 (d, 2 H, *J* = 8.8, 2 × CH), 7.52 (ddd, 1 H, ^3J = 8.8, ^4J = 3.2, ^4J = 4.1, CH), 7.99 (dd, 1 H, ^4J = 3.2, ^4J = 5.8, CH), 8.14 (d, 2 H, *J* = 8.8, 2 × CH), 8.15 (d, 2 H, *J* = 8.8, 2 × CH), 8.28 (d, 2 H, *J* = 8.8, 2 × CH), 8.30 (d, 2 H, *J* = 8.8, 2 × CH). Elemental analysis for $C_{63}H_{77}FO_{11}$ (1029.31): calculated C 73.52, H 7.54, F 1.85; found C 73.43, H 7.50, F 1.90%.

Octyl 4-{4-{6-chloro-3-[4-(4-octyloxybenzoyloxy)benzoyloxy]benzoyloxy}benzoyloxy}benzoate (IIIa/Cl) has been prepared by acylation of **31a** with acid chloride **14a**, yield 74%. ^{1}H NMR ($CDCl_3$): 0.89 (m, 6 H, 2 × CH_3), 1.24-1.55 (m, 20 H, 2 × $(CH_2)_5$), 1.80 (m, 4 H, 2 × CH_2), 4.06 (t, 2 H, *J* = 6.7, OCH_2), 4.33 (t, 2 H, *J* = 6.7, OCH_2), 6.99 (d, 2 H, *J* = 8.8, 2 × CH), 7.31 (d, 2 H, *J* = 8.8, 2 × CH), 7.38-7.47 (m, 5 H, 5 × CH), 7.63 (d, 1 H, ^3J = 8.8, CH), 8.00 (d, 1 H, ^4J = 2.9, CH), 8.14 (d, 2 H, *J* = 8.8, 2 × CH), 8.15 (d, 2 H, *J* = 8.8, 2 × CH), 8.29 (d, 2 H, *J* = 8.8, 2 × CH), 8.30 (d, 2 H, *J* = 8.8, 2 × CH). Elemental analysis: for $C_{51}H_{53}ClO_{11}$ (877.44): calculated C 69.81, H 6.09, Cl 4.04; found C 69.57, H 6.13, Cl 4.01%.

Decyl 4-{4-{6-chloro-3-[4-(4-decyloxybenzoyloxy)benzoyloxy]benzoyloxy}benzoyloxy}benzoate (IIIb/Cl). Yield 70%. ^{1}H NMR ($CDCl_3$): 0.89 (m, 6 H, 2 × CH_3), 1.23-1.55 (m, 28 H, 2 × $(CH_2)_7$), 1.80 (m, 4 H, 2 × CH_2), 4.06 (t, 2 H, *J* = 6.7, OCH_2), 4.33 (t, 2 H, *J* = 6.7, OCH_2), 6.99 (d, 2 H, *J* = 8.8, 2 × CH), 7.31 (d, 2 H, *J* = 8.8, 2 × CH), 7.38-7.47 (m, 5 H, 5 × CH), 7.63 (d, 1 H, ^3J = 8.8, CH), 8.00 (d, 1 H, ^4J = 2.9, CH), 8.14 (d, 2 H, *J* = 8.8, 2 × CH), 8.15 (d, 2 H, *J* = 8.8, 2 × CH), 8.29 (d, 2 H, *J* = 8.8, 2 × CH), 8.30 (d, 2 H, *J* = 8.8, 2 × CH). Elemental analysis: for $C_{55}H_{61}ClO_{11}$ (933.55): calculated C 70.76, H 6.59, Cl 3.80; found C 70.56, H 6.53, Cl 3.87%.

Dodecyl 4-{4-{6-chloro-3-[4-(4-dodecyloxybenzoyloxy)benzoyloxy]benzoyloxy}benzoyloxy}benzoate (IIIc/Cl). Yield 81%.

^{1}H NMR ($CDCl_3$): 0.89 (m, 6 H, 2 × CH_3), 1.24-1.55 (m, 36 H, 2 × $(CH_2)_9$), 1.80 (m, 4 H, 2 × CH_2), 4.06 (t, 2 H, *J* = 6.7, OCH_2), 4.33 (t, 2 H, *J* = 6.7, OCH_2), 6.99 (d, 2 H, *J* = 8.8, 2 × CH), 7.31 (d, 2 H, *J* = 8.8, 2 × CH), 7.38-7.47 (m, 5 H, 5 × CH), 7.63 (d, 1 H, ^3J = 8.8, CH), 8.00 (d, 1 H, ^4J = 2.9, CH), 8.14 (d, 2 H, *J* = 8.8, 2 × CH), 8.15 (d, 2 H, *J* = 8.8, 2 × CH), 8.29 (d, 2 H, *J* = 8.8, 2 × CH), 8.30 (d, 2 H, *J* = 8.8, 2 × CH). Elemental analysis: for $C_{59}H_{69}ClO_{11}$ (989.65): calculated C 71.61, H 7.03, Cl 3.58; found C 71.51, H 7.09, Cl 3.62%.

Tetradecyl 4-{4-{6-chloro-3-[4-(4-tetradecyloxybenzoyloxy)benzoyloxy]benzoyloxy}benzoyloxy}benzoate (IIId/Cl). Yield 80%. ^{1}H NMR ($CDCl_3$): 0.89 (m, 6 H, 2 × CH_3), 1.24-1.56 (m, 44 H, 2 × $(CH_2)_{11}$), 1.80 (m, 4 H, 2 × CH_2), 4.06 (t, 2 H, *J* = 6.7, OCH_2), 4.33 (t, 2 H, *J* = 6.7, OCH_2), 6.99 (d, 2 H, *J* = 8.8, 2 × CH), 7.31 (d, 2 H, *J* = 8.8, 2 × CH), 7.38-7.47 (m, 5 H, 5 × CH), 7.63 (d, 1 H, ^3J = 8.8, CH), 8.00 (d, 1 H, ^4J = 2.9, CH), 8.14 (d, 2 H, *J* = 8.8, 2 × CH), 8.15 (d, 2 H, *J* = 8.8, 2 × CH), 8.29 (d, 2 H, *J* = 8.8, 2 × CH), 8.30 (d, 2 H, *J* = 8.8, 2 × CH). Elemental analysis: for $C_{63}H_{77}ClO_{11}$ (1045.76): calculated C 72.36, H 7.42, Cl 3.39; found C 72.22, H 7.37, Cl 3.43%.

Octyl 4-{4-{6-methyl-3-[4-(4-octyloxybenzoyloxy)benzoyloxy]benzoyloxy}benzoyloxy}benzoate (IIIa/CH$_3$). Acylation of **32a** with acid chloride **14a** provided the target product **IIIa/CH$_3$** in 71% yield. ^{1}H NMR ($CDCl_3$): 0.88 (m, 6 H, 2 × CH_3), 1.18-1.53 (m, 20 H, 2 × $(CH_2)_5$), 1.80 (m, 4 H, 2 × CH_2), 2.71 (s, 3 H, CH_3), 4.05 (t, 2 H, *J* = 6.7, OCH_2), 4.32 (t, 2 H, *J* = 6.7, OCH_2), 6.99 (d, 2 H, *J* = 8.8, 2 × CH), 7.31 (d, 2 H, *J* = 8.8, 2 × CH), 7.35-7.44 (m, 6 H, 6 × CH), 8.07 (d, 1 H, ^4J = 2.9, CH), 8.13 (d, 2 H, *J* = 8.8, 2 × CH), 8.15 (d, 2 H, *J* = 8.8, 2 × CH), 8.29 (m, 4 H, 4 × CH). Elemental analysis: for $C_{52}H_{56}O_{11}$ (857.02): calculated C 72.88, H 6.59; found C 72.71, H 6.64%.

Decyl 4-{4-{3-[4-(4-decyloxybenzoyloxy)benzoyloxy]-6-methylbenzoyloxy}benzoyloxy}benzoate (IIIb/CH$_3$). Yield 65%. ^{1}H NMR ($CDCl_3$): 0.88 (m, 6 H, 2 × CH_3), 1.20-1.53 (m, 28 H, 2 × $(CH_2)_7$), 1.80 (m, 4 H, 2 × CH_2), 2.71 (s, 3 H, CH_3), 4.05 (t, 2 H, *J* = 6.7, OCH_2), 4.32 (t, 2 H, *J* = 6.7, OCH_2), 6.99 (d, 2 H, *J* = 8.8, 2 × CH), 7.31 (d, 2 H, *J* = 8.8, 2 × CH), 7.35-7.44 (m, 6 H, 6 × CH), 8.07 (d, 1 H, ^4J = 2.9, CH), 8.13 (d, 2 H, *J* = 8.8, 2 × CH), 8.15 (d, 2 H, *J* = 8.8, 2 × CH), 8.29 (m, 4 H, 4 × CH). Elemental analysis: for $C_{56}H_{64}O_{11}$ (913.13): calculated C 73.66, H 7.06; found C 73.45, H 7.21%.

Dodecyl 4-{4-{3-[4-(4-dodecyloxybenzoyloxy)benzoyloxy]-6-methylbenzoyloxy}benzoyloxy}benzoate (IIIc/CH_3). Yield 69%. ^{1}H NMR ($CDCl_3$): 0.88 (m, 6 H, 2 × CH_3), 1.21-1.54 (m, 36 H, 2 × $(CH_2)_9$), 1.80 (m, 4 H, 2 × CH_2), 2.71 (s, 3 H, CH_3), 4.05 (t, 2 H, *J* = 6.7, OCH_2), 4.32 (t, 2 H, *J* = 6.7, OCH_2), 6.99 (d, 2 H, *J* = 8.8, 2 × CH), 7.31 (d, 2 H, *J* = 8.8, 2 × CH), 7.35-7.44 (m, 6 H, 6 × CH), 8.07 (d, 1 H, ^4J = 2.9, CH), 8.13 (d, 2 H, *J* = 8.8, 2 × CH), 8.15 (d, 2 H, *J* = 8.8, 2 × CH), 8.29 (m, 4 H, 4 × CH). Elemental analysis: for $C_{60}H_{72}O_{11}$ (969.24): calculated C 74.35, H 7.49; found C 74.28, H 7.39%.

Tetradecyl 4-{4-{6-methyl-3-[4-(4-tetradecyloxybenzoyloxy)benzoyloxy]benzoyloxy}benzoyloxy}benzoate (IIId/CH_3). Yield 80%. ^{1}H NMR ($CDCl_3$): 0.88 (m, 6 H, 2 × CH_3), 1.19-1.53 (m, 44 H, 2 × $(CH_2)_{11}$), 1.80 (m, 4 H, 2 × CH_2), 2.71 (s, 3 H, CH_3), 4.05 (t, 2 H, *J* = 6.7, OCH_2), 4.32 (t, 2 H, *J* = 6.7, OCH_2), 6.99 (d, 2 H, *J* = 8.8, 2 × CH), 7.31 (d, 2 H, *J* = 8.8, 2 × CH), 7.35-7.44 (m, 6 H, 6 × CH), 8.07 (d, 1 H, ^4J = 2.9, CH), 8.13 (d, 2 H, *J* = 8.8, 2 × CH), 8.15 (d, 2 H, *J* = 8.8, 2 × CH), 8.29 (m, 4 H, 4 × CH). Elemental analysis: for $C_{64}H_{80}O_{11}$ (1025.34): calculated C 74.79, H 7.86; found C 74.60, H 7.74%.

2. Mesomorphic properties

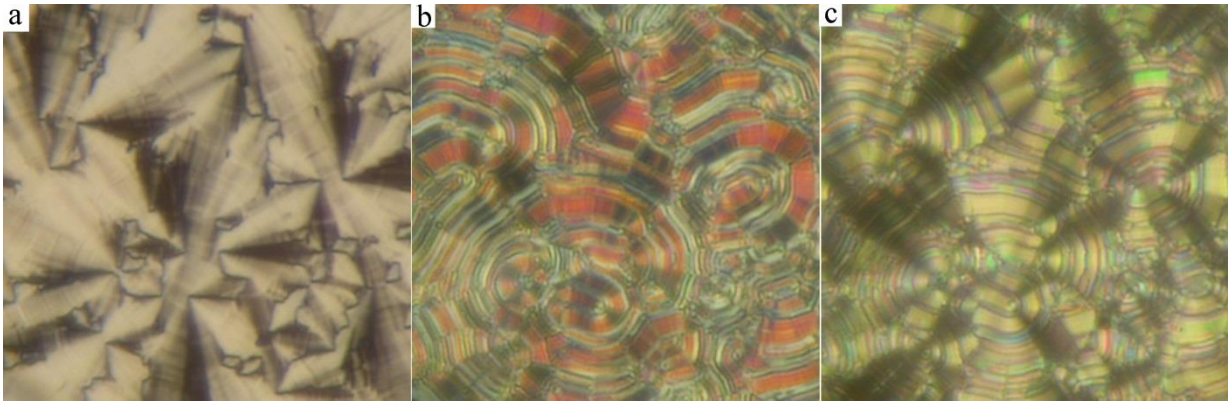

Figure S1

Planar texture of **Id/F** at T=110°C a) after the field application, b) at intermediate field of about 10 V/μm and c) at field of about 20 V/μm.

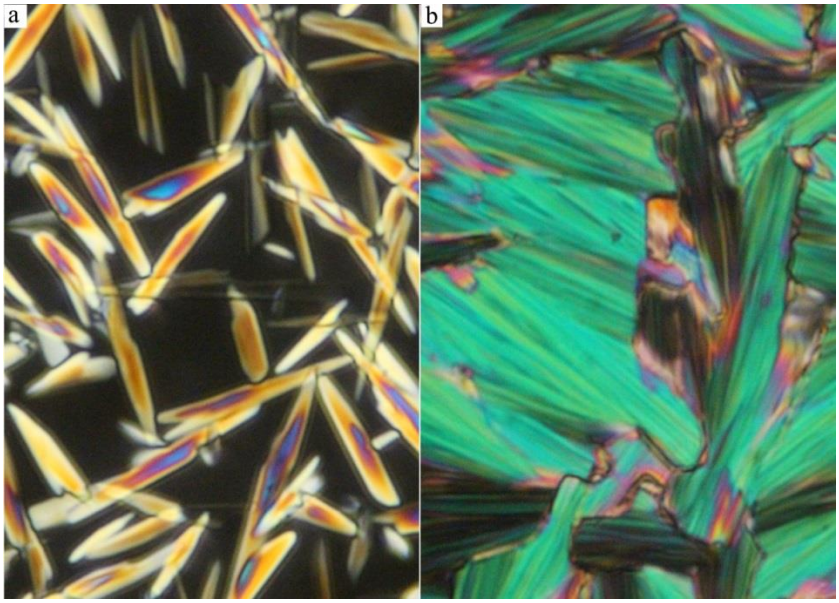

Figure S2

Planar texture for **IIId/F** on cooling from the isotropic phase (Iso), a) at the Iso- B_{1Rev} phase transition and b) in B_{1Rev} phase at T=125°C.

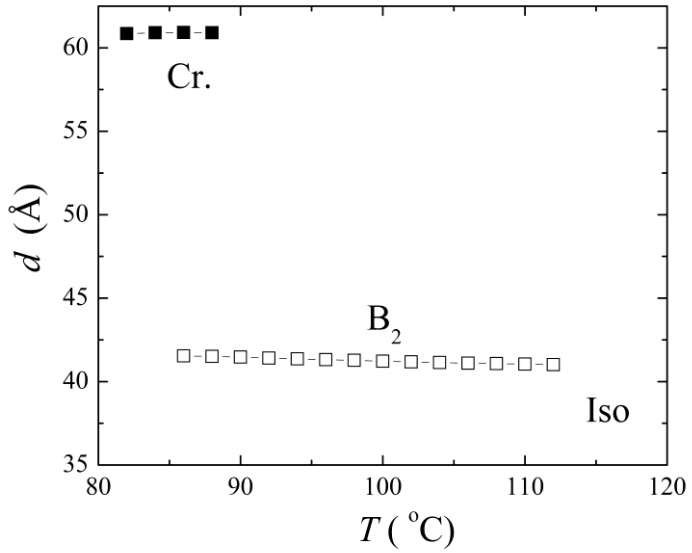

Figure S3
Temperature dependences of the layer spacing, *d*, in the SmC_AP_A phase for compound **Id/F**.

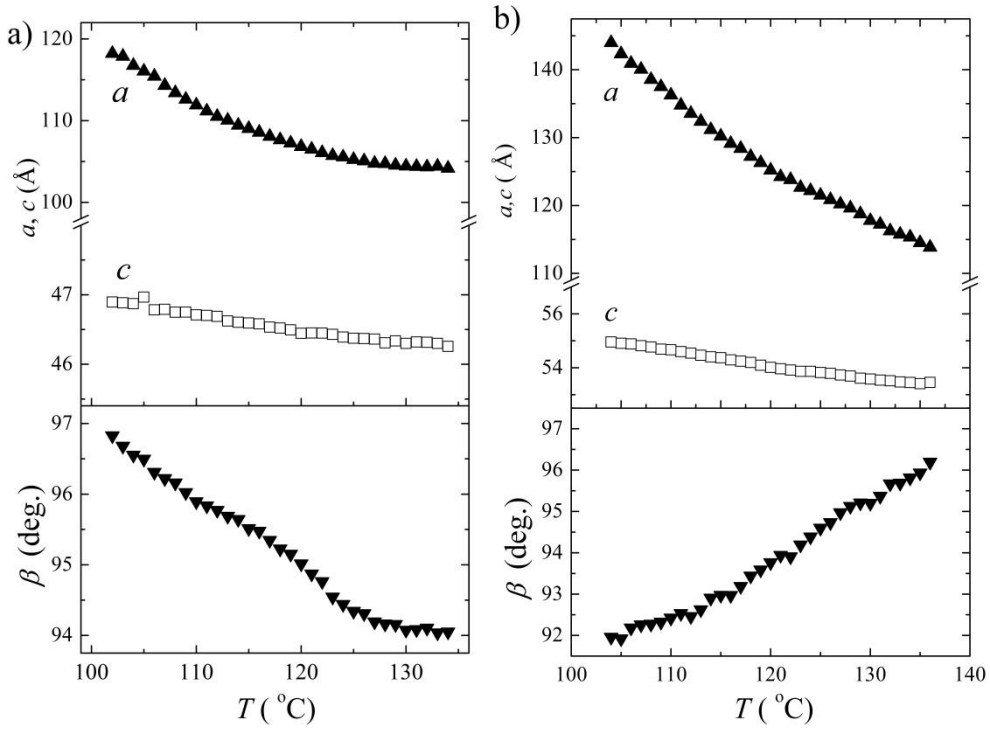

Figure S4
Temperature dependences of the cell parameters for a) **IIb/F** and b) **IIId/F**.

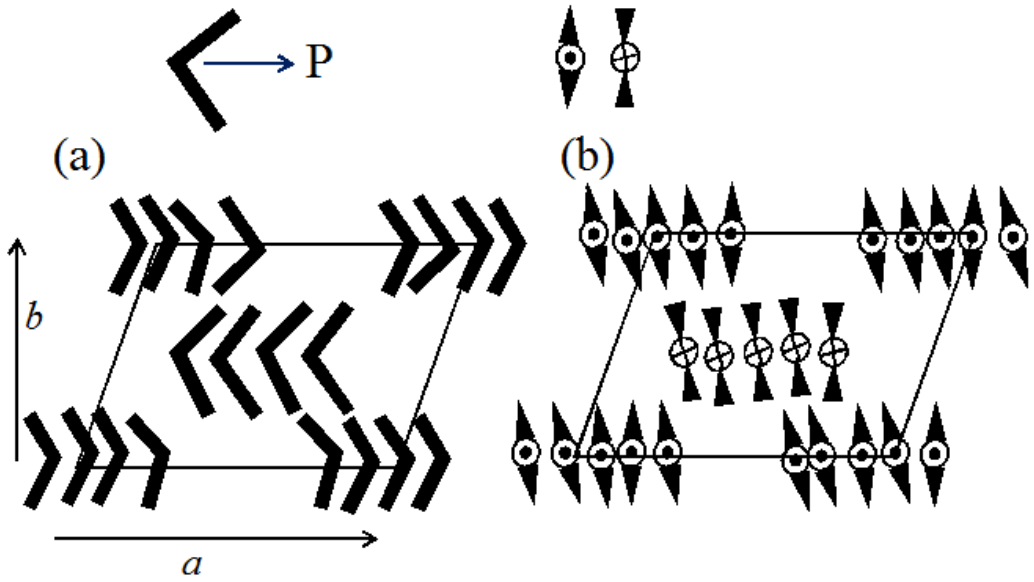

Figure S5
Schematic picture of the molecular arrangements in the columnar a) B_1 and b) B_{1Rev} phase.

3. *Ab-initio* calculations

In this section, the optimization of side arms of the target materials is described in detail. All calculations were performed in Gaussian 03W®, initial geometries were designed and results visualized in GaussView 3.0®.

3.1 *Optimization of lengthening arms*

Prior to the optimization of the target materials, a thorough conformational analysis of lengthening arms (**Figure S6**) was performed. We assumed that the energy barrier of the rotation of one dihedral angle is almost independent on the conformation of the others. This assumption allowed us to perform the relaxed scan optimization of the selected molecules with a 15 degrees step. It has already been described [S2] that the carbonyl group connected to an aromatic ring lies within the layer of this unit, whereas the second aromatic ring connected to the oxygen atom of the ester linkage is rotated with respect to this layer. Since the free rotation of terminal functional groups (alkoxy chain, carboxylic group and hydroxy group) has negligible contribution to the total free energy of the molecule, only torsion angle δ (see **Figure S6**) remains the key free energy-determining parameter.

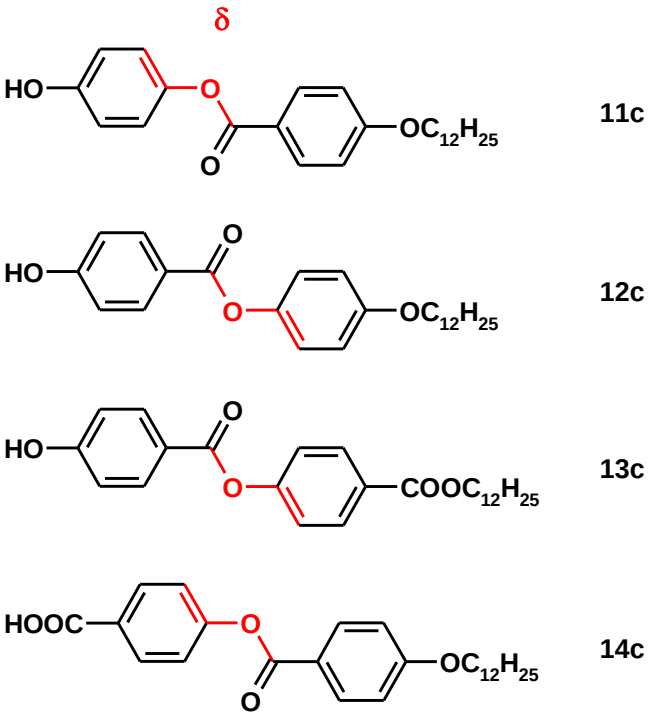

Figure S6 Structures of the studied lengthening arms. The torsion angle δ of the connecting ester linkage is marked in red colour. (Colour version available online)

The computations were performed on HF/6-31g(d) level to save calculation time. Since the calculation error given by HF method could be considered the same in each case, it was subtracted in the process of determining differences in energies (**Δ*E***) of given conformers (**Figures S7-10**). The conformers with minimum energy found with HF/6-31g(d) method were further optimized with released coordinates of torsion angle ***δ*** on DFT level (B3LYP/6-31g(d)) to possible global energetic minimum (**Figures S11-14**).

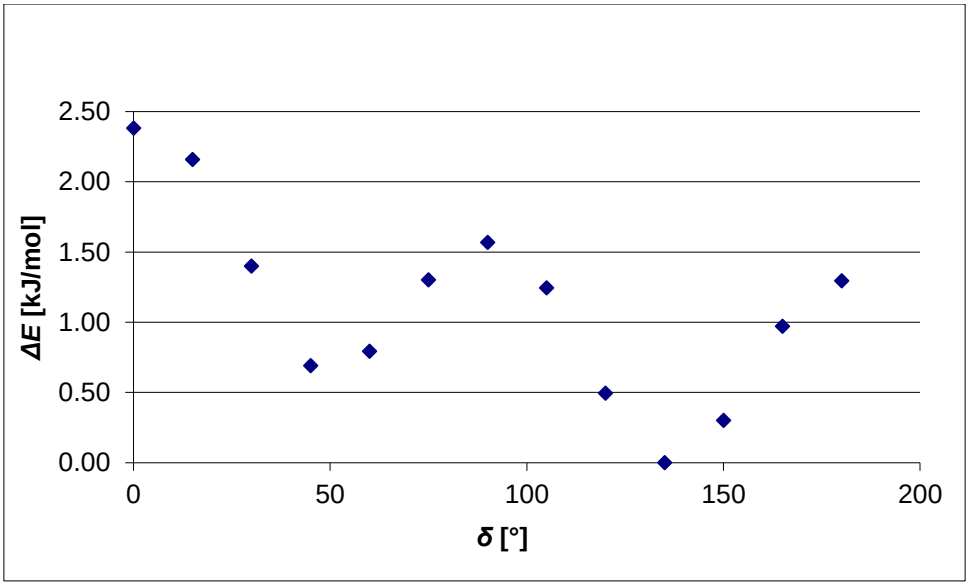

Figure S7: Conformational analysis of **11c**: values of **Δ*E*** versus torsion angle ***δ***; figure denotes only angles between 0°-180° for clarity, the profile between 180°-360° is symmetrical.

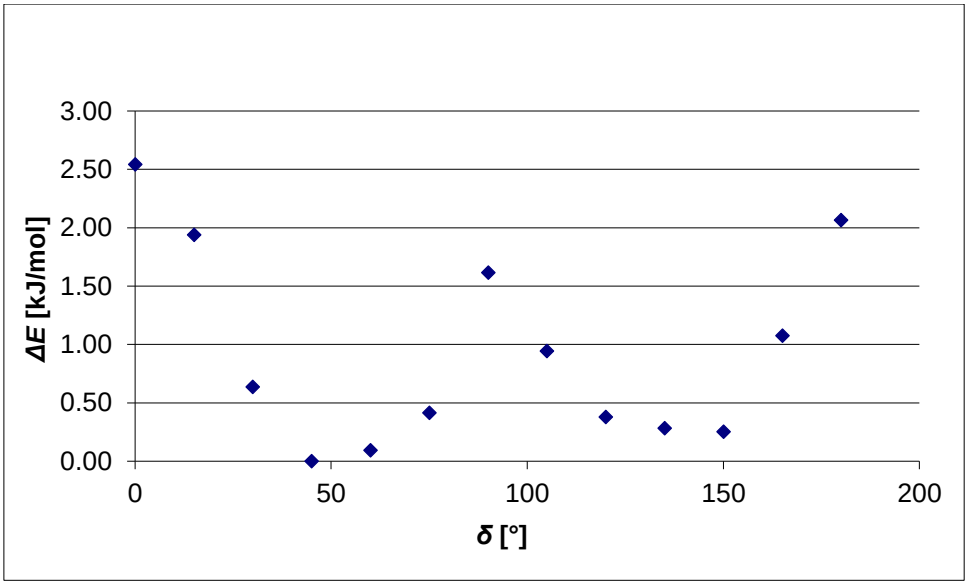

Figure S8: Conformational analysis of **12c**: values of **Δ*E*** versus torsion angle ***δ***; figure denotes only angles between 0°-180° for clarity, the profile between 180°-360° is symmetrical.

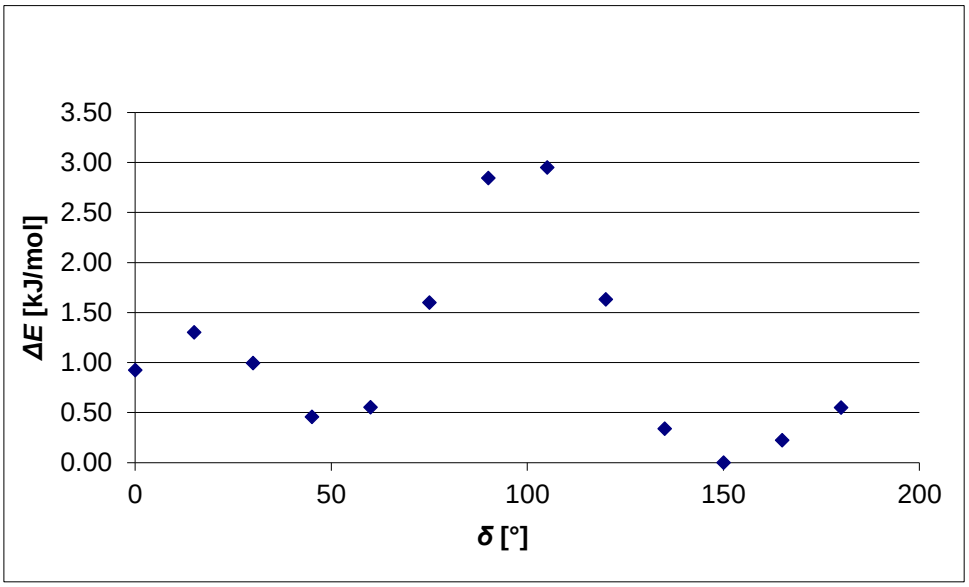

Figure S9: Conformational analysis of **13c**: values of **Δ*E*** versus torsion angle ***δ***; figure denotes only angles between 0°-180° for clarity, the profile between 180°-360° is symmetrical.

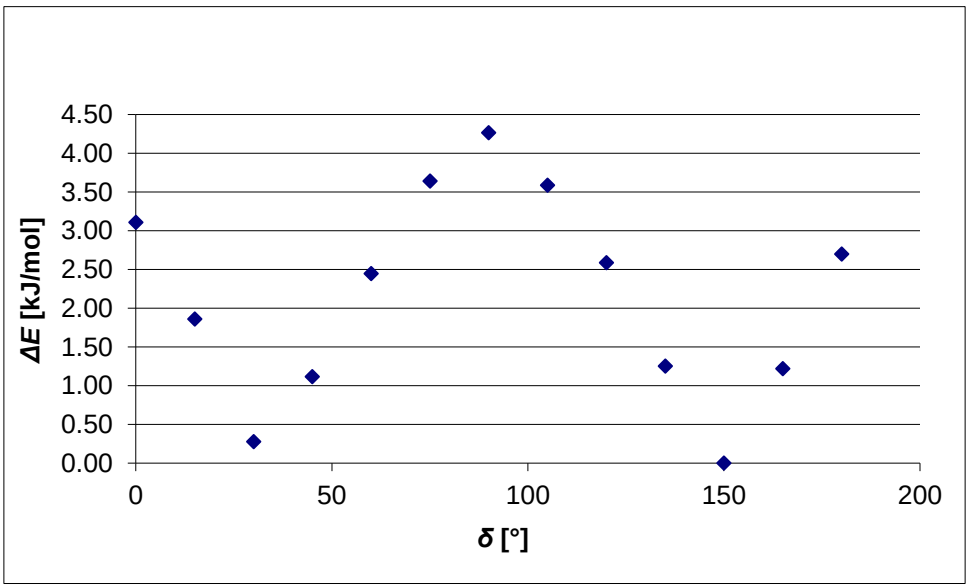

Figure S10: Conformational analysis of **14c**: values of **Δ*E*** versus torsion angle ***δ***; figure denotes only angles between 0°-180° for clarity, the profile between 180°-360° is symmetrical.

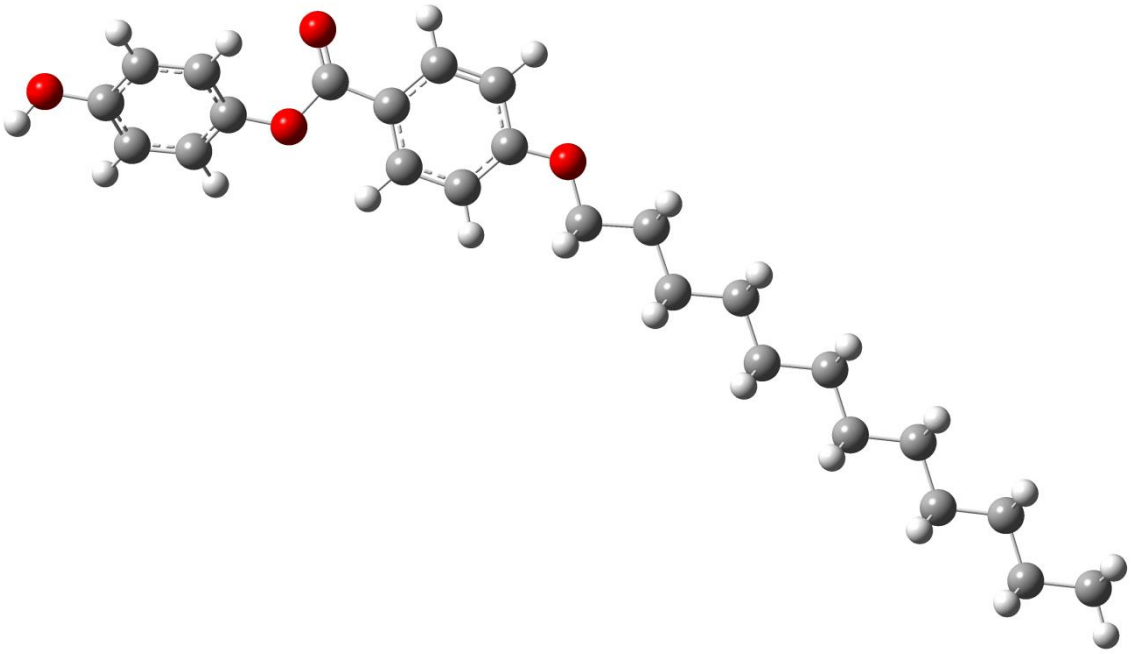

Figure S11: Conformational analysis of **11c**: geometry of found global minimum of energy.

Figure S12: Conformational analysis of **12c**: geometry of found global minimum of energy.

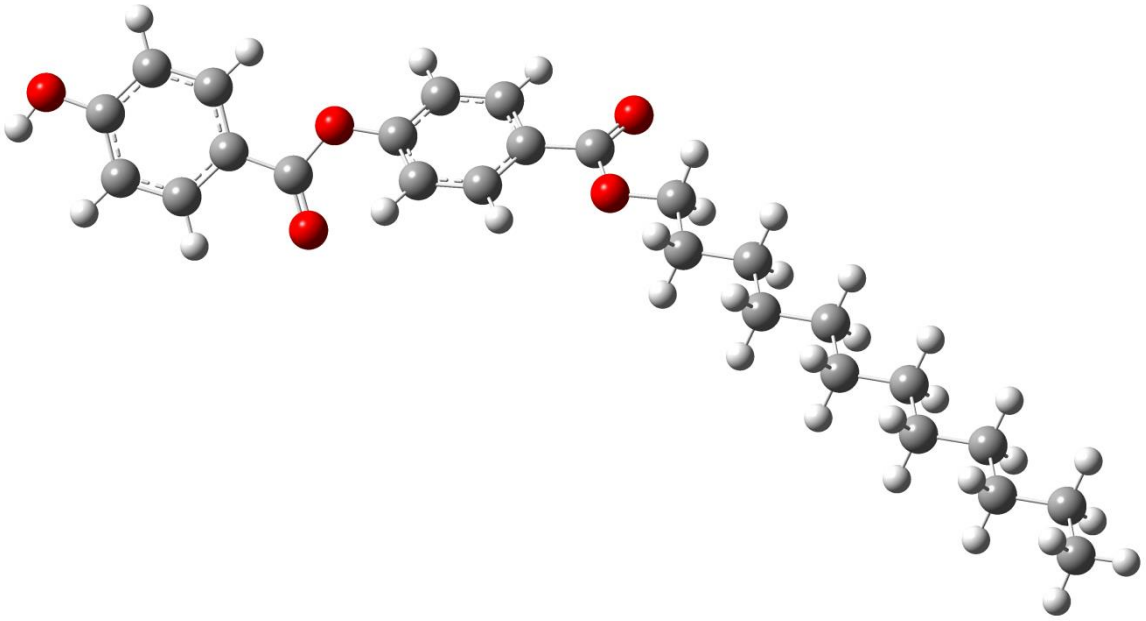

Figure S13: Conformational analysis of **13c**: geometry of found global minimum of energy.

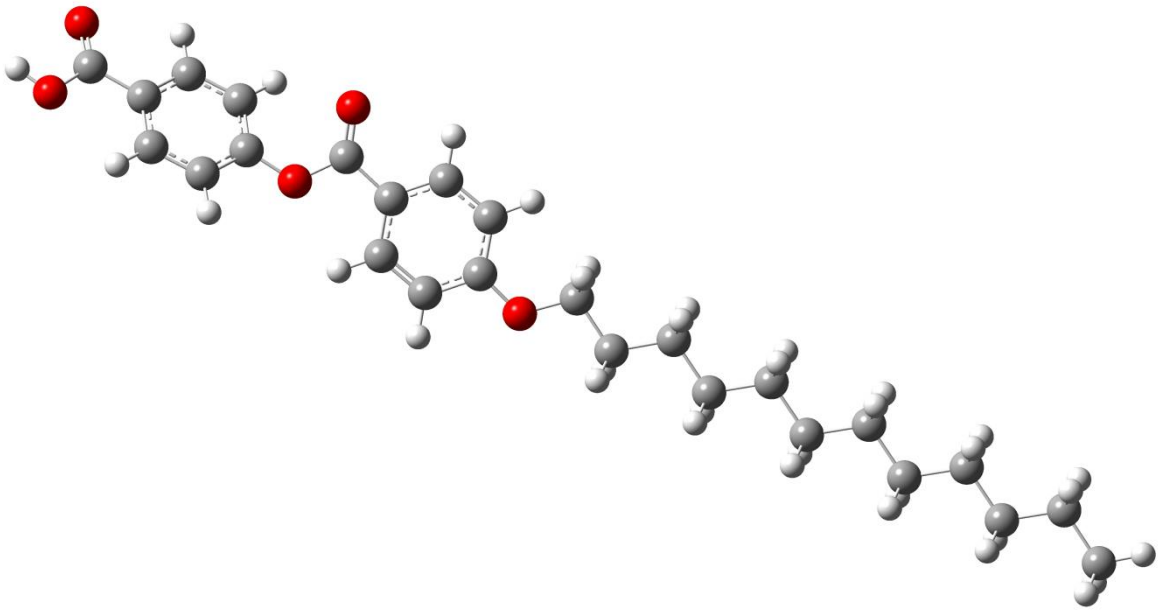

Figure S14: Conformational analysis of **14c**: geometry of found global minimum of energy.

3.2 *Optimization of hydroxy ester intermediates*

Central cores (laterally substituted 3-hydroxybenzoic acids) were connected to the optimized lengthening arms **11c, 12c,** or **13c**. Based on previously reported calculations [S1], only the angle of 180° between the core itself and its carboxylic function connecting the lengthening

arm to the core, was considered as the starting geometry in each calculation (**Figure S15**). Resulting structures were optimized on DFT level (B3LYP/6-31g(d)) to minimum.

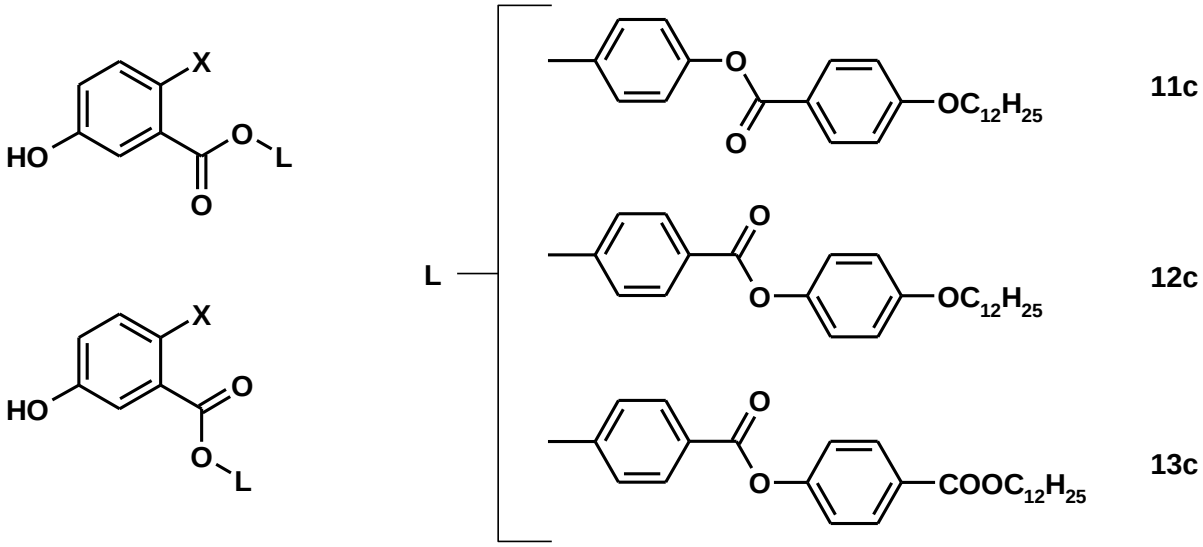

Figure S15: Model of the starting geometries for the optimization of hydroxy ester intermediates.

The most pronounced influence of the molecular structure on the observed mesomorphic behaviour was found for materials of series **III** (compare Tables 1-3 in the main document). Thus, in the following we focused of the hydroxy esters **30c**-**32c** from this series. The resulting conformers with minimum energy have already documented the influence of lateral substituent. The respective visualizations (**Figure S16-S18**) depict the steric influence imposed by chlorine and methyl and the resulting tilting of the first aromatic core of the elongating side arm, which is not present for fluoro substituted compound.

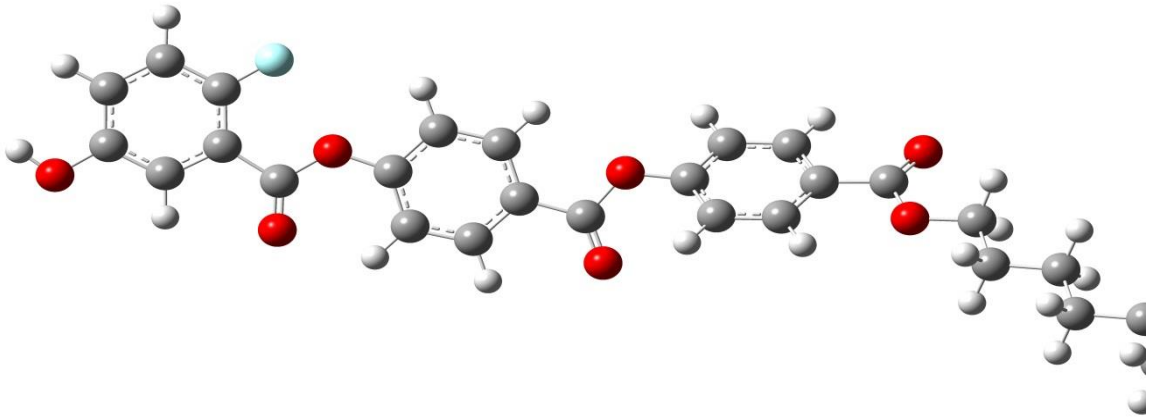

Figure S16 Conformer with minimum energy of compound **30c**. Due to the size of the molecule, the main part of the aliphatic chain was omitted in the figure.

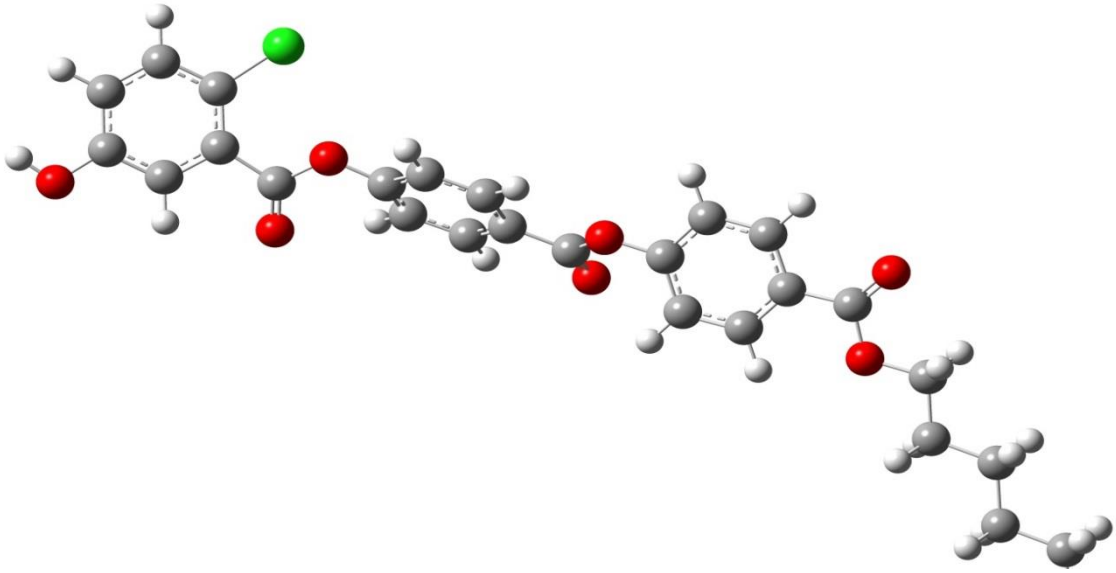

Figure S17 Conformer with minimum energy of compound **31c**. Due to the size of the molecule, the main part of the aliphatic chain was omitted in the figure.

Figure S18 Conformer with minimum energy of compound **32c**. Due to the size of the molecule, the main part of the aliphatic chain was omitted in the figure.

3.3. *Optimization of the target materials*

Similarly to the hydroxy ester intermediates discussed in the previous section, the second elongating arm **14c** was connected under the angle of 180°, and both starting conformations were optimized to minimum on DFT level (B3LYP/6-31g(d)). The obtained conformers with minimum energy of series **III** serve as the basis for discussion provided in the main document.

Conformers with minimum energy for series **I** and **II** (**Figure S19** and **Figure S20**) show features similar to materials of series **III**. As can be seen, the reorientation of the ester linkage in series **I** (marked with an arrow) supports the co-planar alignment of the outer phenyl ring with the central core. We assume, that this change could support the self-assembly of the materials that, in consequence, led to the formation of monotropic mesophases.

The change of the dipole moment and overall electrostatic potential distribution will be discussed in our follow up quantum chemical calculation study.

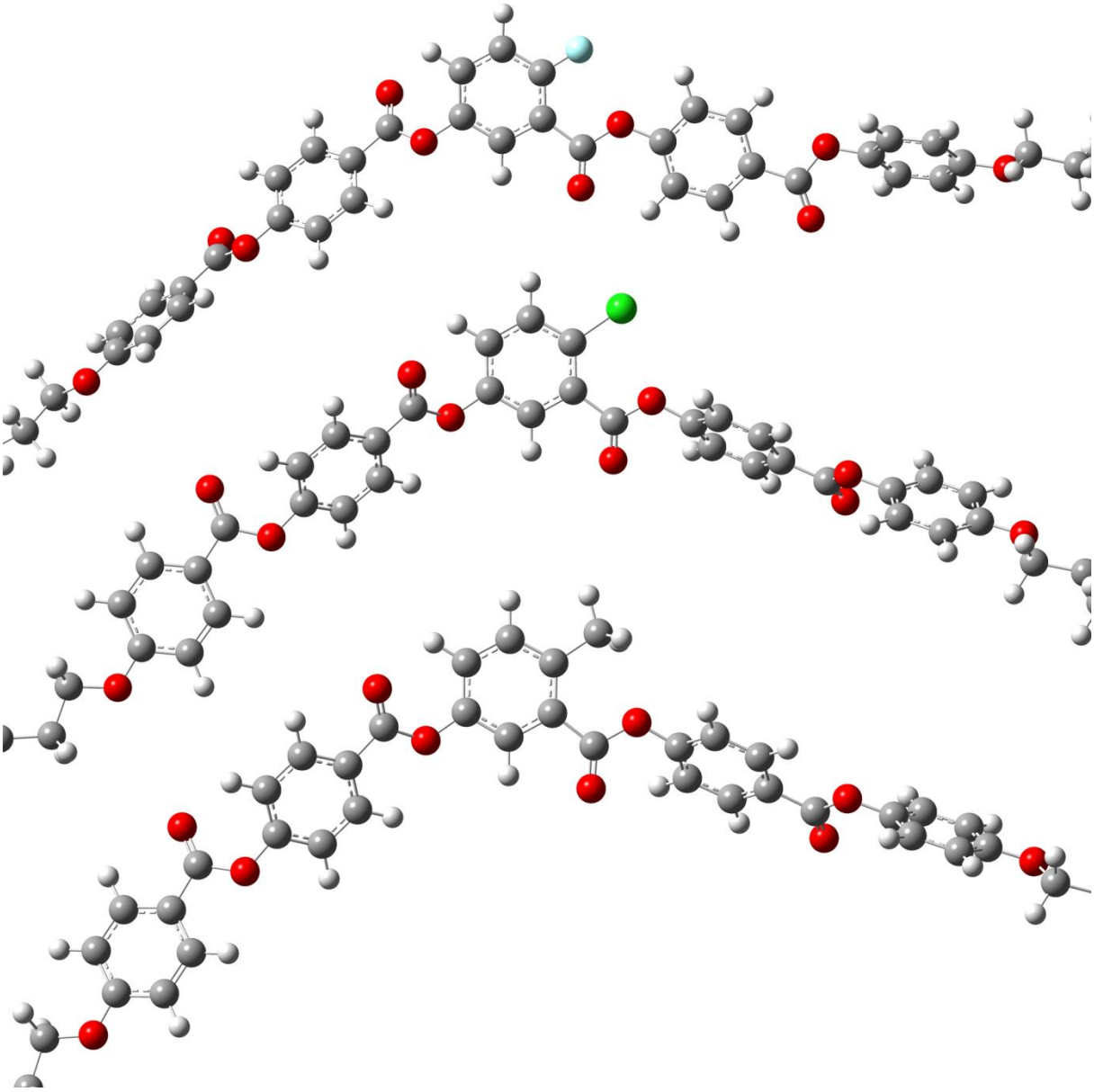

Figure S19 Conformers with minimum energy of materials **IIc/F**, **IIc/Cl** and **IIc/CH$_3$**.

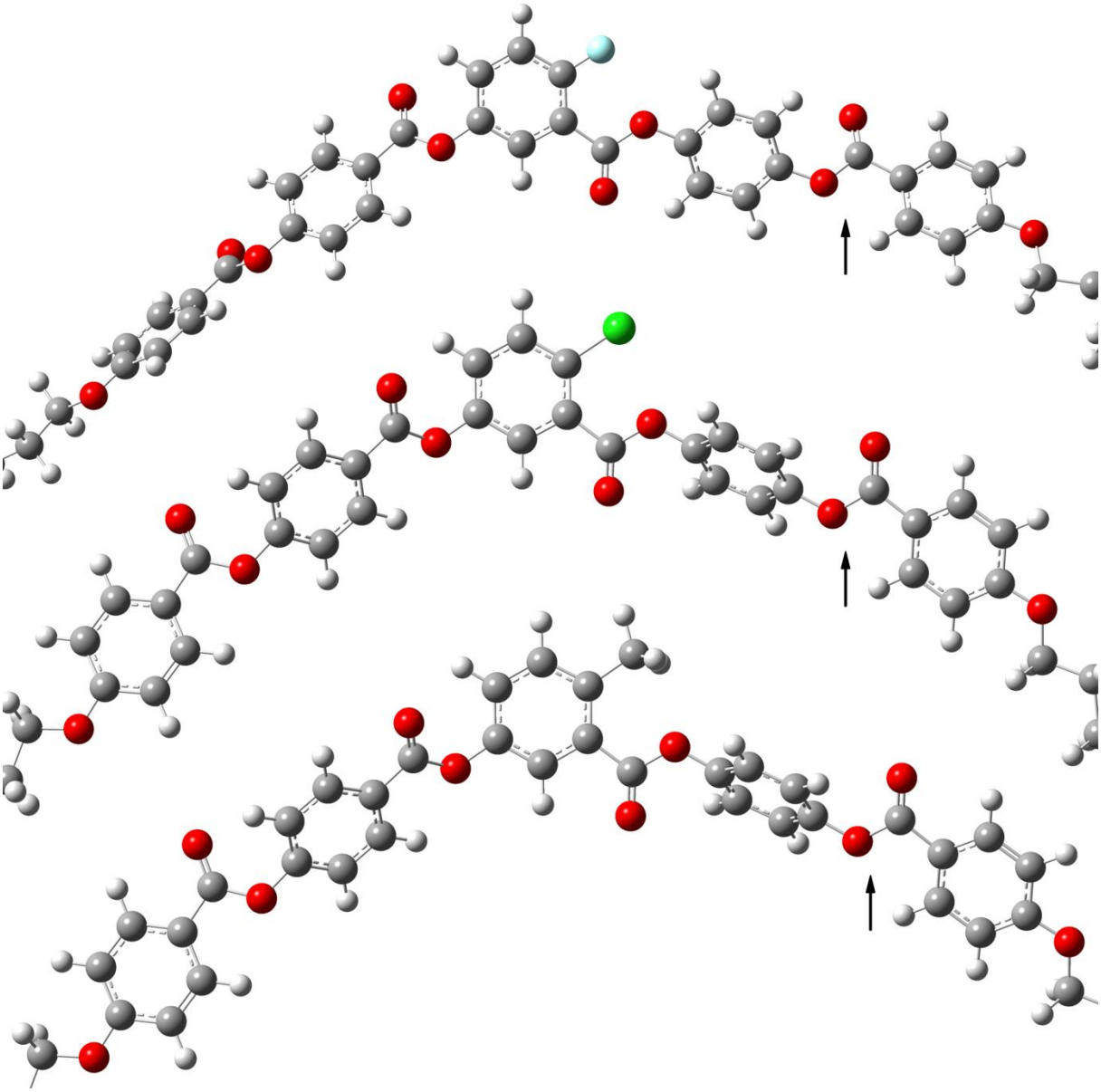

Figure S20 Conformers with minimum energy of materials **Ic/F**, **Ic/Cl** and **Ic/CH$_3$**. The arrow marks the inversed ester linkage.

4. References

S1. Gunosewoyo H, Guo JL, Bennett MR, Coster MJ, Kassiou M. Cubyl amides: novel P2X$_7$ receptor antagonists. Bioorg Med Chem Lett. 2008;18:3720–3723.

S2. Krishnan SAR, Weissflog W, Pelzl G, Diele S, Kresse H, Vakhovskaya Z, Friedemann R. DFT and MD studies on the influence of the orientation of ester linkage groups in banana-shaped mesogens. Phys Chem Chem Phys. 2006;8:1170–1177.