Electronic Supplementary Information

Structures of intermediates and products were confirmed by $^1$H NMR spectroscopy (Varian Gemini 300 HC instrument), deuteriochloroform was used as solvent and signals of the solvent served as an 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 checked 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 procedures for the synthesis of representative intermediates and target compounds of series I.

Benzyl 7-benzyloxynaphthalene-2-carboxylate (6)

To a slurry of acid 1 (2.0 g; 10.6 mmol) and potassium carbonate (5.1 g; 37.1 mmol) in acetone (30 ml), benzyl bromide (4.4 g; 25.7 mmol) was added and the reaction mixture was stirred and heated at reflux for 6 h. After cooling to room temperature, the mixture was diluted with water (150 ml) and extracted with ethyl acetate (3x50 ml). The combined organic solution was washed with water (30 ml), and dried with anhydrous magnesium sulfate. The solvent was evaporated and the crude product was purified by column chromatography (silica gel, eluent toluene) to afford 3.3 g (88%) of ester 6, m. p. 103-104.5 °C. $^1$H NMR: 5.19 s, 2 H (OCH$_2$); 5.42 s, 2 H (COOCH$_2$); 7.22-7.60 m, 12 H (H-6, H-8, Ph); 7.80 m, 2 H (H-4, H-5); 7.97 dd, 1 H, $^3J = 8.5$, $^4J = 1.1$ (H-3); 8.52 s, 1 H (H-1). Elemental analysis for C$_{25}$H$_{20}$O$_3$ (368.44) calcd C 81.50, H 5.47; found C 81.29, H 5.39.
7-Benzzyloxynaphthalene-2-carboxylic acid (7)
To a solution of ester 6 (3.0 g; 8.14 mmol) in ethanol (25 ml), a solution of sodium hydroxide (1.5 g; 37.5 mmol) in water (20 ml) was added. The reaction mixture was heated at reflux for 5 h, after cooling to room temperature it was acidified with 5% aq. hydrochloric acid (100 ml). The precipitate was filtered off, washed with water (2x20 ml) and dried. 2.2 g (96 %) of acid 7 was obtained, m. p. 222-223 °C. $^1$H NMR: 5.22 s, 2 H (OCH$_2$); 7.30-7.45 m, 4 H (H-6, Ph); 7.51 d, 2 H, $J = 8.5$ (Ph); 7.62 d, 1 H, (H-8); 7.80 dd, $^3J = 8.5$, $^4J = 1.8$ (H-3); 7.91 d, 2 H, $J = 8.2$ (H-4, H-5); 8.46 s, 1 H (H-1). Elemental analysis for C$_{25}$H$_{20}$O$_3$ (278.31) calcd C 77.68, H 5.07; found C 77.55, H 5.11.

Methyl 7-hydroxynaphthalene-2-carboxylate (8)
Into an ice cold solution of acid 1 (2.0 g; 10.6 mmol) in methanol (100 ml), gaseous hydrogen chloride was introduced for 1 h. Then the reaction mixture was stirred at room temperature for 12 h, diluted with CH$_2$Cl$_2$ (50 ml) and water (50 ml) and layers were separated. The water layer was extracted with CH$_2$Cl$_2$ (3x30 ml). The combined organic solution was washed with water (2x50 ml), and dried with anhydrous MgSO$_4$. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica gel, eluent toluene) to afford 1.56 g (73 %) of ester 8, m. p. 157-158 °C. $^1$H NMR: 3.98 s, 3 H (OCH$_3$); 5.17 s, 1 H (OH); 7.22 dd, 1 H, $^3J = 8.8$, $^4J = 2.4$ (H-6); 7.27 d, 1 H (H-8); 7.79 d, 1 H (H-5); 7.81 d, 1 H, $J = 8.5$ (H-4); 7.91 dd, 1 H, $^3J = 8.5$, $^4J = 1.2$ (H-3); 8.45 s, 1 H (H-1). Elemental analysis for C$_{12}$H$_{10}$O$_3$ (202.21) calcd C 71.28, H 4.98; found C 71.11, H 4.88.

Methyl 8-chloro-7-hydroxynaphthalene-2-carboxylate (9)
To a solution of ester 8 (1.0 g; 4.95 mmol) in pyridine (15 ml), N-chlorosuccinimide (0.73 g; 5.47 mmol) in pyridine (5 ml) was added dropwise in argon atmosphere. The reaction mixture was stirred at room temperature for 16 h and then poured on a mixture of 15% hydrochloric acid (100 ml) and ice (100 g). The mixture was extracted with CHCl$_3$ (8x50 ml), the combined organic solution was washed with water (50 ml) and dried with anhydrous magnesium sulfate. The solvent was evaporated and the crude product was purified by column chromatography (silica gel, eluent chloroform) and crystallized from toluene. 0.79 g (67 %) of chloro derivative 9 was obtained, m. p. 165.5-166.5°C. $^1$H NMR: 4.02 s, 3 H (OCH$_3$); 5.95 s, 1 H (OH); 7.36 d, 1 H, $J = 8.8$ (H-6); 7.75 d, 1 H (H-5);
Elemental analysis for C_{12}H_{9}ClO_{3} (236.66) calcd C 60.90; H 3.83, Cl 14.98; found C 60.75, H 3.71, Cl 14.79.

8-Chloro-7-hydroxynaphthalene-2-carboxylic acid (2)

Chloro ester 9 (1.81 g; 7.65 mmol) was added to a solution of sodium hydroxide (0.91 g; 22.8 mmol) in ethanol (120 ml) and water (30 ml), and the mixture was heated at reflux for 6 h. Then it was acidified with 5% aq. solution of HCl (300 ml), and the precipitate was filtered off, washed with water (30 ml) and dried. 1.6 g (94%) of acid 2 was obtained, m. p. 280-282 °C. \(^{1}H\) NMR (DMSO-\(d_{6}\)): 7.39 d, 1 H, \(J = 9.1\) (H-6); 7.84 m, 2 H (H-4, H-5); 7.95 d, 1 H, \(J = 8.0\) (H-3); 8.66 s, 1 H (H-1). Elemental analysis for C_{11}H_{7}ClO_{3} (222.63) calcd C 59.35, H 3.17; Cl 15.92; found C 59.26, H 3.36, Cl 15.76.

7-(tert-Butyldimethylsilyloxy)-8-chloronaphthalene-2-carboxylic acid (10)

To a solution of acid 2 (1.5 g; 6.62 mmol) and imidazole (1.83 g; 26.88 mmol) in dry DMF (75 ml), TBDMS chloride (2.34 g; 15.52 mmol) in DMF (15 ml) was added dropwise and the reaction mixture was stirred at 60 °C for 6 h. It was diluted with water (50 ml) and EtOAc (30 ml). Layers were separated and the water layer was extracted with EtOAc (3x30 ml). The combined organic solution was washed with water (2x30 ml) and dried with anhydrous magnesium sulfate. The solvent was evaporated and the crude product was crystallized from toluene. Yield: 1.86 g (82%) of acid 10, m. p. 196.5-198.4 °C. \(^{1}H\) NMR: 0.28 s, 6 H ((CH_{3})_{2}); 1.09 s, 9 H ((CH_{3})_{3}C); 7.26 d, 1 H, \(J = 9.1\) (H-6); 7.72 d, 1 H (H-5); 7.86 d, 1 H, \(J = 8.8\) (H-4); 8.04 dd, 1 H, \(J = 8.5, 4J = 1.8\) (H-3); 9.06 s, 1 H (H-1). Elemental analysis for C_{17}H_{21}ClO_{3}Si (336.89) calcd C 60.61, H 6.28, Cl 10.52; found C 60.49, H 6.34, Cl 10.37.

7-Bromo-2-methoxynaphthalene (11)

To a mixture of bromo derivative 4 (15.0 g; 67.2 mmol) and potassium carbonate (28 g; 202 mmol) in acetone (120 ml), iodomethane (8.4 ml; 135 mmol) was added under stirring and then heated to boiling for 4 h. After cooling it was decomposed with water (200 ml) and extracted with ethyl acetate (4x75 ml). The combined organic solution was washed with water (50 ml), and dried with anhydrous magnesium sulfate. The solvent was evaporated and the crude product was crystallized from ethanol to afford 14.0 g (88%) of naphthalene 11, m. p. 97.5-98 °C. \(^{1}H\) NMR: 3.91 s, 3 H (OCH_{3}); 7.03 d, 1 H, \(J = 2.4\) (H-
7-Bromo-2-methoxynaphthalene-1-carboxaldehyde (12)

To a solution of N-phenyl-N-methylformamide (12 ml; 97.5 mmol) in dry 1,2-dichloroethane (20 ml), POCl₃ (8.6 ml; 97.5 mmol) was added dropwise at 0 °C in argon atmosphere, and the mixture was stirred for 0.5 h. Then methoxy derivative 11 (5.8 g; 24.4 mmol) in 1,2-dichloroethane (17 ml) was added and the reaction mixture was stirred at 0 °C for 15 min and at 40 °C for 72 h. The mixture was decomposed with 2% aq. hydrochloric acid (150 ml), the organic layer was separated and the water layer was extracted with dichloromethane (3x50 ml). The combined organic solution was washed with 5% aq. hydrochloric acid (35 ml), water (2x30 ml), and dried with anhydrous magnesium sulfate. The solvent was evaporated and the crude product was crystallized from toluene. Yield: 4.2 g (65 %) of aldehyde 12, m. p. 151-152 °C. ¹H NMR: 4.05 s, 3 H (OCH₃); 7.28 d, 1 H, ³J = 9.1 (H-6); 7.48 dd, 1 H, ³J = 8.5, ⁴J = 1.9 (H-3); 7.60 d, 1 H, ⁴J = 8.5 (H-4); 7.99 d, 1 H (H-5); 9.50 d, 1 H (H-1); 10.80 s, 1 H (CHO). Elemental analysis for C₁₂H₉BrO₂ (265.11) calcd C 54.37, H 3.42, Br 30.14; found C 54.20, H 3.40, Br 30.03.

7-Bromo-2-methoxy-1-methylnaphthalene (13)

To an ice cold solution of aldehyde 12 (2.25 g; 8.5 mmol) in trifluoroacetic acid (6.5 ml), triethylsilane (4.1 ml; 25.5 mmol) was added dropwise in argon atmosphere. The cooling bath was removed and the reaction mixture was stirred for 15 min. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica gel, eluent toluene/tert-butyl methyl ether 20/1) followed by crystallization from toluene. Yield: 1.83 g (86 %) of 13, m. p. 225-227 °C. ¹H NMR: 2.50 s, 3 H (CH₃); 3.95 s, 3 H (OCH₃); 7.26 d, 1 H, ⁴J = 8.8 (H-6); 7.40 dd, 1 H, ³J = 8.7, ⁴J = 1.9 (H-3); 7.63 d, 1 H (H-5); 7.67 d, 1 H (H-4); 8.10 d, 1 H (H-1). Elemental analysis for C₁₂H₁₁BrO (251.12) calcd C 57.40, H 4.42, Br 31.82; found C 57.33, H 4.40, Br 31.63.

7-Methoxy-8-methylnaphthalene-2-carbonitrile (14)

A mixture of 13 (4.6 g; 18.3 mmol), cuprous cyanide (2.3 g; 25.6 mmol) and DMF (65 ml) was stirred and heated to boiling for 18 h. After cooling the solvent was removed under reduced pressure. The residue was diluted with CHCl₃ (100 ml) and filtered, the filtrate
was evaporated and the crude product was purified by column chromatography (silica gel, eluent toluene). 3.3 g (91 %) of nitrile 14 was isolated, m. p. 98-101 °C. \(^1\)H NMR: 2.54 s, 3 H (CH\(_3\)); 3.97 s, 3 H (OCH\(_3\)); 7.40 d, 1 H, \(J = 9.1\) (H-6); 7.45 dd, 1 H, \(^3\)J = 8.5, \(^4\)J = 1.4 (H-3); 7.75 d, 1 H (H-5); 7.83 d, 1 H (H-4); 8.33 d, 1 H (H-1). Elemental analysis for C\(_{13}\)H\(_{11}\)NO (197.24) calcd C 79.17, H 5.62, N 8.11; found C 79.02, H 5.48, N 8.06.

7-Methoxy-8-methylnaphthalene-2-carboxylic acid (15)
A mixture of nitrile 14 (1.75 g; 9.1 mmol) and sodium hydroxide (1.82 g; 45.5 mmol) in 50% aq. ethanol (60 ml) was heated to boiling for 72 h, the solution was filtered while hot (charcoal) and the filtrate was acidified with 15% aq. hydrochloric acid to pH~1. The deposited solid was filtered, washed with water (2x20 ml), and dried. Yield: 1.81 g (94 %) of acid 15, m. p. 225-227 °C. \(^1\)H NMR (DMSO-d\(_6\)): 2.49 s, 3 H (CH\(_3\)); 3.90 s, 3 H (OCH\(_3\)); 7.53 d, 1 H, \(J = 9.1\) (H-6); 7.80 d, 1 H, \(J = 8.5\) (H-3); 7.87 d, 1 H (H-5); 7.92 d, 1 H (H-4); 8.57 s, 1 H (H-1). Elemental analysis for C\(_{13}\)H\(_{12}\)O\(_3\) (216.24) calcd C 72.21, H 5.59; found C 72.01, H 5.60.

7-Hydroxy-8-methylnaphthalene-2-carboxylic acid (3)
To a slurry of acid 15 (1.8 g; 8.3 mmol) in dichloromethane (20 ml), BBr\(_3\) (3.2 ml; 33.3 mmol) was added dropwise at -78 °C in argon atmosphere. The reaction mixture was stirred at -78 °C for 1.5 h, then the cooling bath was removed and stirring continued at room temperature for 4 h. The reaction mixture was then poured on icy water (200 ml), the precipitate was filtered, washed with water (2x10 ml) and dried to afford 1.5 g (90 %) of acid 3, m. p. 242-243 °C. \(^1\)H NMR (DMSO-d\(_6\)): 2.45 s, 3 H (CH\(_3\)); 7.27 d, 1 H, \(J = 8.5\) (H-6); 7.68 d, 1 H (H-5); 7.73 d, 1 H, \(J = 8.5\) (H-4); 7.83 d, 1 H, \(J = 8.5\) (H-3); 8.51 s, 1 H (H-1); 9.73 s, 1 H (OH). Elemental analysis for C\(_{12}\)H\(_{10}\)O\(_3\) (202.21) calcd C 71.28, H 4.98; found C 71.11, H 4.87.

Benzyl 7-benzyloxy-8-methylnaphthalene-2-carboxylate (16)
A mixture of acid 3 (1.5 g; 7.5 mmol), potassium carbonate (2.1 g; 15.1 mmol), benzyl bromide (3.6 g; 21.0 mmol) and acetone (30 ml) was stirred and heated at reflux for 6 h. After cooling to room temperature it was diluted with water (50 ml) and extracted with ethyl acetate (3x40 ml). The combined organic solution was washed with water (50 ml) and dried with anhydrous magnesium sulfate. The solvent was evaporated and the crude product was crystallized from an ethanol/ethyl acetate mixture. 2.58 g (90 %) of ester 16.
Supplementary Material (ESI) for Journal of Materials Chemistry
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was obtained, m. p. 101-102.5 °C. $^1$H NMR: 2.66 s, 3 H (CH$_3$); 5.22 s, 2 H (OCH$_2$); 5.44 s, 2 H (COOCH$_2$); 7.39 m, 7 H (Ph, H-6); 7.49 m, 4 H (Ph); 7.71 d, 1 H, $^3$J = 9.1 (H-5); 7.80 d, 1 H, $^3$J = 8.5 (H-4); 7.96 dd, 1 H, $^3$J = 8.5, $^4$J = 1.5 (H-3); 8.80 s, 1 H (H-1). Elemental analysis for C$_{26}$H$_{22}$O$_3$ (382.46) calcd C 81.65, H 5.80; found C 81.55, H 5.70.

7-Benzylxoy-8-methylnaphthalene-2-carboxylic acid (17)
To a solution of ester 16 (2.58 g; 6.7 mmol) in ethanol (30 ml), sodium hydroxide (1.5 g; 37.5 mmol) in water (15 ml) was added and the reaction mixture was stirred and heated at reflux for 2.5 h. The solvent was partly removed under reduced pressure and the residue was diluted with water (50 ml) and acidified with 10% hydrochloric acid to pH~1. The deposited solid was filtered, washed with water (2x15 ml) and dried to afford 1.91 g (97%) of acid 17, m. p. 222-223 °C. $^1$H NMR: 2.69 s, 3 H (CH$_3$); 5.23 s, 2 H (OCH$_2$); 7.33-7.52 m, 6 H (H-6, Ph); 7.74 d, 1 H, $^3$J = 9.1 (H-5); 7.85 d, 1 H, $^3$J = 8.5 (H-4); 7.98 dd, 1 H, $^3$J = 8.5, $^4$J = 1.6 (H-3); 8.85 s, 1 H (H-1). Elemental analysis for C$_{19}$H$_{16}$O$_3$ (292.34) calcd C 78.06, H 5.52; found C 77.99, H 5.54.

4-(Tetrahydropyranyloxy)phenyl 4-octyloxybenzoate (20a)
A mixture of monoprotected hydroquinone 19 (4.3 g; 22 mmol), 4-octyloxybenzoic acid (18a) (5.0 g; 20 mmol), DCC (4.54 g; 20 mmol) and catalytic amount of DMAP in dry dichloromethane (100 ml) was stirred at room temperature for 2.5 h. The reaction mixture was decomposed with water (0.5 ml), filtered and the filtrate was evaporated. The crude product was crystallized from an ethanol/ethyl acetate mixture. Yield: 7.0 g (82%) of ester 20a, m. p. 74-75 °C. $^1$H NMR: 0.88 t, 3 H; 1.30 bs, 8 H; 1.47 bs, 2 H; 1.67 m, 3 H; 1.83 m, 4 H; 2.00 m, 1 H; 3.62 m, 1 H; 3.92 m, 1 H; 4.04 t, 2 H (OCH$_2$); 5.39 t, 1 H (OCHO); 6.96 d, 2 H, $^3$J = 9.1; 7.09 s, 4 H; 8.12 d, 2 H. Elemental analysis for C$_{26}$H$_{34}$O$_5$ (426.56) calcd C 73.21, H 8.03; found C 73.14, H 7.89.

In the same way esters 20b (R = C$_{10}$H$_{21}$, yield 79%, m.p. 77.5-79 °C), 20d (R = C$_{11}$H$_{23}$, yield 85%, m.p. 78-80 °C), 20e (R = C$_{12}$H$_{25}$, yield 74%, m.p. 80-81 °C), and 20f (R = C$_{14}$H$_{29}$, yield 76%, m.p. 79-81 °C) were obtained.

4-Hydroxyphenyl 4-octyloxybenzoate (21a)
Ester 20a (4.5 g; 10.6 mmol) was dissolved in 30% aq. THF (60 ml), and acetic acid (20 ml) was added. The mixture was heated to boiling for 2 h, cooled to room temperature, and diluted with water (50 ml) and ethyl acetate (75 ml). The organic layer was separated...
and the water layer was washed with ethyl acetate (2x40 ml). The combined organic solution was washed with water (30 ml), and dried with anhydrous magnesium sulfate. The solvent was removed under reduced pressure and the crude product was crystallized from an ethanol/ethyl acetate mixture. Yield: 2.9 g (80 %) of hydroxyphenyl ester 21a, m. p. 106.5-108.5 °C, 1H NMR: 0.88 t, 3 H; 1.27 bs, 8 H; 1.47 m, 2 H; 1.82 m, 2 H; 4.04 t, 2 H (OCH₂); 5.19 s, 1 H (OH); 6.80 d, 2 H, J = 8.8; 6.96 d, 2 H, J = 8.8; 7.03 d, 2 H, J = 9.1; 8.13 d, 2 H, J = 8.8. Elemental analysis for C₂₁H₂₆O₄ (426.56) calcd C 73.66, H 7.65; found C 73.39, H 7.55.

Analogously, esters 21b (R = C₁₀H₂₁, yield 88%, m. p. 106.5-108.5 °C, m.p. 111 °C), 21d (R = C₁₁H₂₃, yield 87%, m. p. 109.5-110 °C, m.p. 112 °C), 21e (R = C₁₂H₂₅, yield 83%, m. p. 108-110 °C, m.p. 113 °C) and 21f (R = C₁₄H₂₉, yield 86%, m. p. 113.5-114.5°C, m.p. 115 °C) were obtained.

(4-(7-Benzyloxynaphthalene-2-carbonyl)oxy)phenyl 4-(octyloxy)benzoate (24a)

To a solution of acid 7 (0.3 g; 1.08 mmol) and hydroxy ester 21a (0.39 g; 1.14 mmol) in dry dichloromethane (30 ml), DCC (0.24 g; 1.14 mmol) and catalytic amount of DMAP (20 mg) were added and the mixture was stirred at room temperature for 3 h. Then it was decomposed with water (0.2 ml), filtered and the filtrate evaporated. The crude product was purified by column chromatography (silica gel, eluent toluene/tert-butyl methyl ether, 20/1), 0.55 g (85 %) of ester 24a was isolated, m. p. 159-160.5 °C. 1H NMR: 0.90 t, 3 H (CH₃); 1.32 m, 8 H ((CH₂)₄); 1.48 m, 2 H (CH₂); 1.83 m, 2 H (CH₂); 4.05 t, 2 H (CH₂O); 5.22 s, 2 H (CH₂O); 6.98 d, 2 H, J = 8.8; 7.30 d, 4 H, J = 2.8; 7.35-7.54 m, 7 H (Ph, H-6, H-8); 7.84 d, 1 H, J = 9.1 (H-5); 7.88 d, 1 H, J = 8.5 (H-4); 8.07 dd, 1 H, 3J = 8.5, 4J = 1.6 (H-3); 8.15 d, 2 H, J = 8.8; 8.67 s, 1 H (H-1). Elemental analysis for C₃₉H₃₈O₆ (602.73) calcd C 77.72, H 6.35; found C 77.53, H 6.31.

In the same way derivatives 24b (R¹ = C₁₀H₂₁, yield 79%, m.p. 137 °C), 24d (R¹ = C₁₁H₂₃, yield 78%, m.p. 129 °C), 24e (R¹ = C₁₂H₂₅, yield 83%, m. p. 128 °C) and 24f (R¹ = C₁₄H₂₉, yield 79%, m.p. 128 °C) were obtained. For 24b C₄₁H₄₂O₆ (630.79) calcd C 78.07, H 6.71; found C 77.88, H 6.49; 24d C₄₂H₄₄O₆ (644.82) calcd C 78.23, H 6.88; found C 78.19, H 6.75; 24e C₄₃H₄₆O₆ (658.84) calcd C 78.39, H 7.04; found C 78.11, H 6.96; 24f C₄₅H₅₀O₆ (686.90) calcd C 78.69, H 7.34; found C 78.44, H 7.27.

(4-(7-Hydroxynaphthalene-2-carbonyl)oxy)phenyl 4-(octyloxy)benzoate (25a)

To a solution of benzyl derivative 24a (0.42 g; 0.70 mmol) in acetone (40 ml), 10% Pd/C
(42 mg) was added, followed by ammonium formate (0.18 g; 2.85 mmol). The reaction mixture was heated to boiling for 10 h. The hot mixture was filtered and the filtrate was evaporated. The crude product was purified by column chromatography (silica gel, eluent toluene/tert-butyl methyl ether, 20/1), 0.33 g (91 %) of ester 25a was obtained. $^1$H NMR: 0.90 t, 3 H; 1.31 m, 8 H; 1.48 m, 2 H; 1.83 m, 2 H; 4.05 t, 2 H (CH$_2$O); 5.23 s, 1 H (OH); 6.98 d, 2 H, $J = 8.8$; 7.30 m, 6 H (Ph, H-6,H-8); 7.84 d, 1 H, $J = 8.8$ (H-5); 7.88 d, 1 H (H-4); 8.05 dd, 1 H, $^3J = 8.5$, $^4J = 1.5$ (H-3); 8.15 d, 2 H, $J = 9.1$; 8.62 s, 1 H (H-1). Elemental analysis for C$_{32}$H$_{32}$O$_6$ (512.61) calcd C 74.98, H 6.29; found C 75.12, H 6.26. By the same procedure compounds 25b (R$^1$ = C$_{10}$H$_{21}$, yield 85%), 25d (R$^1$ = C$_{11}$H$_{23}$, yield 84%), 25e (R$^1$ = C$_{12}$H$_{25}$, yield 95%), and 25f (R$^1$ = C$_{14}$H$_{29}$, yield 94%) were prepared. For 25b C$_{34}$H$_{36}$O$_6$ (540.66) calcd C 75.53, H 6.71; found C 75.37, H 6.66; 25d C$_{35}$H$_{38}$O$_6$ (554.69) calcd C 75.79, H 6.91; found C 75.58, H 6.90; 25e C$_{36}$H$_{40}$O$_6$ (568.72) calcd C 76.03, H 7.09; found C 75.85, H 6.98; 25f C$_{38}$H$_{44}$O$_6$ (596.77) calcd C 76.48, H 7.43; found C 76.33, H 7.32.

(4-{(7-(4-{[(4-Octyloxybenzoyl)oxy]benzoyl)}oxy)naphthalene-2-carbonyl)}oxy)phenyl 4-(octyloxy)benzoate (Ia)

A mixture of acid 23a (0.26 g; 0.77 mmol), SOCl$_2$ (0.2 ml; 2.8 mmol) and pyridine (0.25 ml; 3.1 mmol) in dry toluene (15 ml) was stirred and heated to boiling for 2 h. The solvent and unreacted SOCl$_2$ were evaporated and the residue dried at reduced pressure. The crude acid chloride was dissolved in dry toluene (10 ml) and added to a hot solution of hydroxy ester 25a (0.3 g; 0.59 mmol) and DMAP (0.1 g; 0.82 mmol) in toluene (40 ml). After cooling to room temperature the reaction mixture was diluted with 5% hydrochloric acid (50 ml) and chloroform (80 ml). Layers were separated and the aqueous layer was washed with chloroform (2x15 ml). The combined organic solution was washed with water (2x25 ml), saturated solution of NaCl (30 ml), and dried with anhydrous MgSO$_4$. The solvent was evaporated and the crude product was purified by column chromatography (silica gel, eluent dichloromethane). Yield: 0.43 g (85 %) of Ia. $^1$H NMR: 0.90 t, 6 H; 1.31 m, 16 H; 1.49 m, 4 H; 1.83 m, 4 H; 4.05 m, 4 H; 6.98 d, 2 H; 7.00 d, 2 H; 7.32 d, 4 H; 7.41 d, 2 H, $J = 8.8$; 7.54 dd, 1 H, $^3J = 8.8$, $^4J = 2.4$ (H-6); 7.88 d, 1 H, $J = 2.1$ (H-8); 8.00 d, 2 H, $J = 8.8$ (H-4, H-5); 8.16 d, 2 H; 8.17 d, 2 H; 8.22 dd, 1 H, $^3J = 8.5$, $^4J = 1.5$ (H-3); 8.34 d, 2 H; 8.79 s, 1 H (H-1). Elemental analysis for C$_{54}$H$_{56}$O$_{10}$ (865.04) calcd C 74.98, H 6.53; found C 74.79, H 6.55. Materials Ib (R$^1$ = R$^2$ = C$_{10}$H$_{21}$, yield 89%), Ic (R$^1$ = C$_{11}$H$_{23}$, R$^2$ = C$_{11}$H$_{21}$, yield 78%), Id
(R² = C₃₈H₄₅ClO₆Si (661.32) calcd C 69.02, H 6.86, Cl 5.36; found C 69.23, H 6.70, Cl 5.39.

Analogously, esters 24h (R¹ = C₁₀H₂₁, yield 62%, m.p. 159.5-161.5 °C), 24i (R¹ = C₁₁H₂₃, yield 60%, m.p. 146-149 °C), 24j (R¹ = C₁₂H₂₅, yield 59%, m.p. 139-140 °C), and 24k (R¹ = C₁₄H₂₉, yield 58%, m.p. 134-135 °C) were obtained. For 24h C₄₀H₄₉ClO₆Si (689.37) calcd C 69.69, H 7.16, Cl 5.14; found C 69.40, H 6.98, Cl 5.01; 24i C₄₁H₅₁ClO₆Si (703.40) calcd C 70.01, H 7.31, Cl 5.04; found C 69.88, H 7.20, Cl 4.92; 24j C₄₂H₅₃ClO₆Si (717.43) calcd C 70.32, H 7.45, Cl 4.94; found C 70.13, H 7.28, Cl 4.77; 24k C₄₄H₅₇ClO₆Si (745.48) calcd C 70.89, H 7.71, Cl 4.76; found C 70.60, H 7.54, Cl 4.54.

(4-(8-Chloro-7-hydroxynaphthalene-2-carbonyl)oxy)phenyl 4-(octyloxy)benzoate (25g)
The solution of silyl derivative 24g (0.19 g; 0.29 mmol) in THF (30 ml), TBAF (25 mg; 0.08 mmol) was added. The reaction mixture was stirred at room temperature for 1.5 h and then diluted with water (30 ml) and ethyl acetate (25 ml). The organic layer was separated and the water layer was washed with ethyl acetate (2x20 ml). The combined organic solution was washed with water (30 ml), and dried with anhydrous magnesium sulfate.
The solvent was removed at reduced pressure and the crude product was purified by column chromatography (silica gel, eluent toluene/tert-butyl methyl ether, 20/1). 0.14 g (88%) of ester 25g was isolated. 1H NMR: 0.88 t, 3 H; 1.21-1.40 bs, 8 H; 1.48 m, 2 H; 1.83 m, 2 H; 4.05 t, 2 H; 6.00 s, 1 H (OH); 6.98 d, 2 H, J = 9.1; 7.32 d, 4 H, J = 4.7; 7.41 d, 1 H, J = 8.8 (H-6); 7.80 1 H, J = 8.8 (H-5); 7.92 d, 1 H, J = 8.8 (H-4); 8.14 m, 3 H (2xCH, H-3); 8.99 d, 1 H, J = 1.8 (H-1). Elemental analysis for C_{32}H_{31}ClO_{6} (547.05) calcd C 70.26, H 5.71, Cl 6.48; found C 70.51, H 5.57, Cl 6.39.

By the same procedure compounds 25h (R¹ = C_{10}H_{21}, yield 88%), 25i (R¹ = C_{11}H_{23}, yield 86%), 25j (R¹ = C_{12}H_{25}, yield 88%), and 25k (R¹ = C_{14}H_{29}, yield 94%) were prepared. For 25h C_{34}H_{35}ClO_{6} (575.11) calcd C 71.01, H 6.13, Cl 6.16; found C 70.93, H 6.00, Cl 6.05; 25i C_{35}H_{37}ClO_{6} (589.13) calcd C 71.36, H 6.33, Cl 6.02; found C 71.19, H 6.20, Cl 5.84; 25j C_{36}H_{39}ClO_{6} (603.16) calcd C 71.69, H 6.52, Cl 5.88; found C 71.43, H 6.38, Cl 5.70; 25k C_{38}H_{43}ClO_{6} (631.22) calcd C 72.31, H 6.87, Cl 5.62; found C 72.16, H 6.69, Cl 5.50.

(4-{8-Chloro-(7-(4-{[4-octyloxybenzoyl]oxy}benzoyl)oxy)naphthalene-2-carbonyl}-oxy)phenyl 4-(octyloxy)benzoate (IIa)

According the same procedure as for Ia, hydroxy ester 25g (0.13 g; 0.24 mmol) was acylated with chloride of acid 23a (0.10 g; 0.26 mmol) in the presence of DMAP (0.03 g; 0.26 mmol) in toluene (40 ml). After column chromatography (silica gel, eluent dichloromethane) of the crude product, 0.17 g (81%) of IIa was obtained. 1H NMR: 0.90 t, 3 H; 1.33 m, 16 H; 1.49 m, 4 H; 1.83 m, 4 H; 4.06 m, 4 H; 6.98 d, 2 H, J = 8.8; 7.00 d, 2 H, J = 8.8; 7.33 d, 4 H, J = 6.7; 7.43 d, 2 H, J = 8.8; 7.58 d, 1 H, J = 8.8 (H-6); 7.94 d, 1 H, J = 8.8 (H-5); 8.03 d, 1 H, J = 8.8 (H-4); 8.16 d, 2 H, J = 8.8; 8.17 d, 2 H, J = 8.8; 8.29 dd, 1 H, 3J = 8.5, 4J = 1.6 (H-3); 8.39 d, 2 H, J = 8.8; 9.23 s, 1 H (H-1). Elemental analysis for C_{54}H_{55}ClO_{10} (899.49) calcd C 72.11, H 6.16, Cl 3.94; found C 72.34, H 5.93, Cl 4.05.

Materials IIb (R¹ = R² = C_{10}H_{21}, yield 95%), IIc (R¹ = C_{11}H_{21}, R² = C_{11}H_{23}, yield 91%), IId (R¹ = R² = C_{12}H_{25}, yield 89%), and IIe (R¹ = R² = C_{14}H_{29}, yield 96%) were obtained by the same way. For IIb C_{58}H_{63}ClO_{10} (955.60) calcd C 72.90, H 6.65, Cl 3.71; found C 72.80, H 6.51, Cl 3.54; IIc C_{60}H_{65}ClO_{10} (981.63) calcd C 73.42, H 6.67, Cl 3.61; found C 73.33, H 6.50, Cl 3.49; IId C_{62}H_{71}ClO_{10} (1011.70) calcd C 73.61, H 7.07, Cl 3.50; found C 73.44, H 6.85, Cl 3.30; IIe C_{66}H_{70}ClO_{10} (1067.81) calcd C 74.24, H 7.46, Cl 3.32; found C 74.29, H 7.22, Cl 3.09.
(4-(7-Benzzyloxy-8-methylnaphthalene-2-carbonyl)oxy)phenyl 4-(octyloxy)benzoate (24l)

By the same way as for 24a, reaction of acid 17 (0.25 g; 0.86 mmol) with hydroxy ester 21a (0.33 g; 0.95 mmol), DCC (0.2 g; 0.95 mmol) and catalytic amount of DMAP (0.02 g) in dry dichloromethane (30 ml) for 5 h afforded the crude product which was purified by crystallization from an ethanol/ethyl acetate mixture. Yield: 0.42 g (80 %) of ester 24l. 1H NMR: 0.89 t, 3 H; 1.21-1.40 bs, 8 H; 1.48 m, 2 H; 1.83 m, 2 H; 2.64 s, 3 H (CH3); 4.05 t, 2 H; 5.24 s, 2 H (OCH2Ph); 6.98 d, 2 H, J = 8.8; 7.31 d, 4 H, J = 4.4; 7.33-7.51 m, 5 H (Ph, H-6); 7.76 d, 1 H, J = 8.8 (H-5); 7.88 d, 1 H, J = 8.5 (H-4); 8.07 dd, 1 H, 3J = 8.5, 4J = 1.5 (H-3); 8.16 d, 2 H, J = 8.8; 8.99 s, 1 H (H-1). Elemental analysis for C40H40O6 (616.76) calcd C 77.90, H 6.54; found C 78.12, H 6.32.

By the same procedure also compounds 24m (R1 = C10H21, yield 80%), 24n (R1 = C11H23, yield 69%), 24o (R1 = C12H25, yield 83%), and 24p (R1 = C14H29, yield 77%) were synthesized. For 24m C42H44O6 (644.82) calcd C 78.23, H 6.88; found C 78.09, H 6.80; 24n C43H46O6 (658.84) calcd C 78.39, H 7.04; found C 78.30, H 6.94; 24o C44H48O6 (672.87) calcd C 78.54, H 7.19; found C 78.36, H 6.99; 24p C46H52O6 (700.92) calcd C 78.83, H 7.48; found C 78.59, H 7.41.

(4-(7-Hydroxy-8-methylnaphthalene-2-carbonyl)oxy)phenyl 4-(octyloxy)benzoate (25l)

To a solution of benzyl derivative 24l (0.42 g; 0.68 mmol) in acetone (50 ml), 10% Pd/C (42 mg) and then ammonium formate (0.18 g; 2.85 mmol) were added. The reaction mixture was heated to boiling 4 h. After the same procedure as for 25a and column chromatography (silica gel, eluent toluene/tert-butyl methyl ether, 20/1), 0.32 g (89 %) of 25l was obtained. 1H NMR: 0.89 t, 3 H; 1.22-1.40 bs, 8 H; 1.45 m, 2 H; 1.83 m, 2 H; 2.64 s, 3 H (CH3); 4.05 t, 2 H; 5.07 s, 1 H (OH); 6.98 d, 2 H, J = 8.8; 7.22 d, 1 H, J = 8.8 (H-6); 7.31 d, 4 H, J = 3.8; 7.70 d, 1 H, J = 8.8 (H-5); 7.88 d, 1 H, J = 8.5 (H-4); 8.06 dd, 1 H, 3J = 8.5, 4J = 1.8 (H-3); 8.16 d, 2 H, J = 8.8; 8.88 s, 1 H (H-1). Elemental analysis for C33H34O6 (526.64) calcd C 75.26, H 6.51; found C 75.02, H 6.75.

Analogously, esters 25m (R1 = C10H21, yield 87%), 25n (R1 = C11H23, yield 88%), 25o (R1 = C12H25, yield 84%), and 25p (R1 = C14H29, yield 88%) were obtained. For 25m C35H38O6 (554.69) calcd C 75.26, H 6.51; found C 75.55, H 6.76; 25n C36H40O6 (568.72) calcd C 76.03, H 7.09; found C 75.97, H 6.99; 25o C37H42O6 (582.74) calcd C 76.26, H 7.26; found C 76.23, H 7.33; 25p C39H46O6 (610.80) calcd C 76.69, H 7.59; found C
(4-{8-Methyl-(7-(4-[(4-octyloxybenzoyl)oxy]benzoyl)oxy)naphthalene-2-carbonyl}-oxy)phenyl 4-(octyloxy)benzoate (IIIa)

According the same procedure as for Ia, hydroxy ester 25l (0.29 g; 0.55 mmol) was acylated with chloride of acid 23a (0.26 g; 0.67 mmol) in the presence of DMAP (0.08 g; 0.67 mmol) in toluene (40 ml). After column chromatography (silica gel, eluent dichloromethane) of the crude product, 0.42 g (88 %) of IIIa was isolated. $^1$H NMR: 0.90 t, 6 H; 1.31 m, 16 H; 1.45 m, 4 H; 1.83 m, 4 H; 2.67 s, 3 H (CH$_3$); 4.06 m, 4 H; 6.98 d, 2 H, $J$ = 9.1; 7.00 d, 2 H, $J$ = 9.1; 7.33 d, 4 H, $J$ = 5.3; 7.42 d, 2 H, $J$ = 8.8; 7.46 d, 1 H, $J$ = 8.8 (H-6); 7.86 d, 1 H, $J$ = 8.8 (H-5); 8.00 d, 1 H, $J$ = 8.8 (H-4); 8.16 d, 2 H, $J$ = 8.8; 8.17 d, 2 H, $J$ = 9.1; 8.23 dd, 1 H, $^3J$ = 8.8, $^4J$ = 1.6 (H-3); 8.37 d, 2 H, $J$ = 8.8; 9.00 d, 1 H, $J$ = 1.6 (H-1). Elemental analysis for C$_{55}$H$_{58}$O$_{10}$ (879.07) calcd C 75.15, H 6.65; found C 75.47, H 6.39.

Materials IIIb (($R^1 = R^2 = C_{10}H_{21}$, yield 86%), IIIc ($R^1 = C_{11}H_{21}$, $R^2 = C_{11}H_{23}$, yield 68%), IIId (($R^1 = R^2 = C_{12}H_{25}$, yield 90%) and IIIe (($R^1 = R^2 = C_{14}H_{29}$, yield 81%) were obtained by the same way. For IIIb C$_{59}$H$_{66}$O$_{10}$ (935.18) calcd C 75.78, H 7.11; found C 75.58, H 7.02; IIIc C$_{61}$H$_{68}$O$_{10}$ (961.22) calcd C 76.22, H 7.13; found C 76.14, H 6.97; IIId C$_{63}$H$_{74}$O$_{10}$ (991.29) calcd C 76.34, H 7.52; found C 76.28, H 7.29; IIIe C$_{67}$H$_{82}$O$_{10}$ (1047.39) calcd C 76.83, H 7.89; found C 76.55, H 7.70.
Table S1: Intermediates 25: melting point, m.p., detected on second heating, the phase transition temperature, $T_{tr}$, and the temperature of crystallization, $T_{cr}$, detected on the second cooling at a rate of 5 K min$^{-1}$ are presented in °C and corresponding enthalpies, $\Delta H$, are in kJ mol$^{-1}$.

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<th>$T_{cr}$ [(\Delta H)]</th>
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Figure S1  Schematic drawing of the a) B1, b) B1Rev, c) comparison B1Rev and B1RevTilted phase. $a$ and $b$ are dimensions of the crystallographic cell (Ref. 4).

References