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Nematic-polar columnar phase sequence in new bent-shaped liquid crystals based on 7-hydroxynaphthalene-2-carboxylic acid core

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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-Benzyloxynaphthalene-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_2Cl_2 (50 ml) and water (50 ml) and layers were separated. The water layer was extracted with CH_2Cl_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);

7.84 d, 1 H, J = 8.5 (H-4); 7.99 dd, 1 H, ^3J = 8.5, ^4J = 1.8 (H-3); 8.81 s, 1 H (H-1). Elemental analysis for $C_{12}H_9ClO_3$ (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 $C_{11}H_7ClO_3$ (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 ($(CH_3)_3C$); 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, ^3J = 8.5, ^4J = 1.8 (H-3); 9.06 s, 1 H (H-1). Elemental analysis for $C_{17}H_{21}ClO_3Si$ (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-

8); 7.14 dd, 1 H, ^3J = 9.1, ^4J = 2.4 (H-6); 7.40 dd, 1 H, ^3J = 8.8, ^4J = 2.1 (H-3); 7.62 d, 1 H, J = 9.1 (H-4); 7.69 d, 1 H, J = 8.8 (H-5); 7.89 d, 1 H (H-1). Elemental analysis for $C_{11}H_9BrO$ (237.10) calcd C 55.72, H 3.83, Br 33.70; found C 55.60, H 3.78, Br 33.59.

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), $POCl_3$ (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. ^{1}H NMR: 4.05 s, 3 H (OCH_3); 7.28 d, 1 H, J = 9.1 (H-6); 7.48 dd, 1 H, ^3J = 8.5, ^4J = 1.9 (H-3); 7.60 d, 1 H, J = 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 $C_{12}H_9BrO_2$ (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. ^{1}H NMR: 2.50 s, 3 H (CH_3); 3.95 s, 3 H (OCH_3); 7.26 d, 1 H, J = 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 $C_{12}H_{11}BrO$ (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 $CHCl_3$ (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, ^3J = 8.5, ^4J = 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**

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, J = 9.1 (H-5); 7.80 d, 1 H, J = 8.5 (H-4); 7.96 dd, 1 H, ^3J = 8.5, ^4J = 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-Benzyloxy-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, J = 9.1 (H-5); 7.85 d, 1 H, J = 8.5 (H-4); 7.98 dd, 1 H, ^3J = 8.5, ^4J = 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, 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,[1] m.p. 111 °C. ^{1}H 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 (OCH_2); 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 $C_{21}H_{26}O_4$ (426.56) calcd C 73.66, H 7.65; found C 73.39, H 7.55.

Analogously, esters **21b** (R = $C_{10}H_{21}$, yield 88%, m.p. 106.5-108.5 °C, m.p. 111 °C),[2] **21d** (R = $C_{11}H_{23}$, yield 87%, m.p. 109.5-110 °C,[29] m.p. 112 °C), **21e** (R = $C_{12}H_{25}$, yield 83%, m.p. 108-110 °C,[3] m.p. 113 °C) and **21f** (R = $C_{14}H_{29}$, yield 86%, m.p. 113.5-114.5°C,[29] 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. ^{1}H NMR: 0.90 t, 3 H (CH_3); 1.32 m, 8 H ($(CH_2)_4$); 1.48 m, 2 H (CH_2); 1.83 m, 2 H (CH_2); 4.05 t, 2 H (CH_2O); 5.22 s, 2 H (CH_2O); 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 $C_{39}H_{38}O_6$ (602.73) calcd C 77.72, H 6.35; found C 77.53, H 6.31.

In the same way derivatives **24b** (R^1 = $C_{10}H_{21}$, yield 79%, m.p. 137 °C), **24d** (R^1 = $C_{11}H_{23}$, yield 78%, m.p. 129 °C), **24e** (R^1 = $C_{12}H_{25}$, yield 83%, m.p. 128 °C), and **24f** (R^1 = $C_{14}H_{29}$, yield 79%, m.p. 128 °C) were obtained. For **24b** $C_{41}H_{42}O_6$ (630.79) calcd C 78.07, H 6.71; found C 77.88, H 6.49; **24d** $C_{42}H_{44}O_6$ (644.82) calcd C 78.23, H 6.88; found C 78.19, H 6.75; **24e** $C_{43}H_{46}O_6$ (658.84) calcd C 78.39, H 7.04; found C 78.11, H 6.96; **24f** $C_{45}H_{50}O_6$ (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_2O); 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**

($R^1 = R^2 = C_{12}H_{25}$, yield 90%), and **Ie** ($R^1 = R^2 = C_{14}H_{29}$, yield 81%) were obtained by the same way. For **Ib** $C_{58}H_{64}O_{10}$ (921.15) calcd C 75.63, H 7.00; found C 75.60, H 6.91; **Ic** $C_{60}H_{66}O_{10}$ (947.19) calcd C 76.09, H 7.02; found C 75.92, H 6.90; **Id** $C_{62}H_{72}O_{10}$ (977.26) calcd C 76.20, H 7.43; found C 76.11, H 7.36; **Ie** $C_{66}H_{80}O_{10}$ (1033.37) calcd C 76.71, H 7.80; found C 76.70, H 7.58.

(4-(8-Chloro-7-(*tert*-butyldimethylsilyloxy)naphthalene-2-carbonyl)oxy)phenyl 4(-octyloxy)benzoate (24g)

Analogously as for **24a**, acid **10** (0.2 g; 0.59 mmol) was reacted with hydroxy ester **21a** (0.22 g; 0.64 mmol) in the presence of DCC (0.13 g; 0.63 mmol) and catalytic amount of DMAP (30 mg) in dry CH_2Cl_2 (35 ml). Purification by column chromatography (silica gel, eluent hexane/ethyl acetate, 4:1) afforded 0.2 g (51 %) of silyl derivative **24g**, m. p. 163-165 °C. ^{1}H NMR: 0.29 s, 6H ($(CH_3)_2Si$); 0.89 t, 3 H (CH_3); 1.09 s, 9 H ($(CH_3)_3Si$); 1.25-1.42 bs, 8 H ($(CH_2)_4$); 1.48 m, 2 H (CH_2); 1.83 m, 2 H (CH_2); 4.05 t, 2 H (CH_2O); 6.98 d, 2 H, *J* = 8.8; 7.31 d, 1 H, *J* = 8.8 (H-6); 7.32 d, 4 H, *J* = 5.6; 7.74 d, 1 H, *J* = 9.1 (H-5); 7.90 d, 1 H, *J* = 8.5 (H-4); 8.14 m, 3 H (Ph, H-3); 9. 14 d, 1 H, *J* = 1.5 (H-1). Elemental analysis for $C_{38}H_{45}ClO_6Si$ (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** ($R^1 = C_{10}H_{21}$, yield 62%, m.p. 159.5-161.5 °C), **24i** ($R^1 = C_{11}H_{23}$, yield 60%, m.p. 146-149 °C), **24j** ($R^1 = C_{12}H_{25}$, yield 59%, m.p. 139-140 °C), and **24k** ($R^1 = C_{14}H_{29}$, yield 58%, m.p. 134-135 °C) were obtained. For **24h** $C_{40}H_{49}ClO_6Si$ (689.37) calcd C 69.69, H 7.16, Cl 5.14; found C 69.40, H 6.98, Cl 5.01; **24i** $C_{41}H_{51}ClO_6Si$ (703.40) calcd C 70.01, H 7.31, Cl 5.04; found C 69.88, H 7.20, Cl 4.92; **24j** $C_{42}H_{53}ClO_6Si$ (717.43) calcd C 70.32, H 7.45, Cl 4.94; found C 70.13, H 7.28, Cl 4.77; **24k** $C_{44}H_{57}ClO_6Si$ (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)

To a 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. ^{1}H 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** ($R^1 = C_{10}H_{21}$, yield 88%), **25i** ($R^1 = C_{11}H_{23}$, yield 86%), **25j** ($R^1 = C_{12}H_{25}$, yield 88%), and **25k** ($R^1 = C_{14}H_{29}$, 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. ^{1}H 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** ($R^1 = R^2 = C_{10}H_{21}$, yield 95%), **IIc** ($R^1 = C_{11}H_{21}$, $R^2 = C_{11}H_{23}$, yield 91%), **IId** ($R^1 = R^2 = C_{12}H_{25}$, yield 89%), and **IIe** ($R^1 = R^2 = C_{14}H_{29}$, 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** $C_{66}H_{79}ClO_{10}$ (1067.81) calcd C 74.24, H 7.46, Cl 3.32; found C 74.29, H 7.22, Cl 3.09.

(4-(7-Benzyloxy-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**. ^{1}H 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 (CH_3); 4.05 t, 2 H; 5.24 s, 2 H (O$\underline{CH_2}$Ph); 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 $C_{40}H_{40}O_6$ (616.76) calcd C 77.90, H 6.54; found C 78.12, H 6.32.

By the same procedure also compounds **24m** (R^1 = $C_{10}H_{21}$, yield 80%), **24n** (R^1 = $C_{11}H_{23}$, yield 69%), **24o** (R^1 = $C_{12}H_{25}$, yield 83%), and **24p** (R^1 = $C_{14}H_{29}$, yield 77%) were synthesized. For **24m** $C_{42}H_{44}O_6$ (644.82) calcd C 78.23, H 6.88; found C 78.09, H 6.80; **24n** $C_{43}H_{46}O_6$ (658.84) calcd C 78.39, H 7.04; found C 78.30, H 6.94; **24o** $C_{44}H_{48}O_6$ (672.87) calcd C 78.54, H 7.19; found C 78.36, H 6.99; **24p** $C_{46}H_{52}O_6$ (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. ^{1}H 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 (CH_3); 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 $C_{33}H_{34}O_6$ (526.64) calcd C 75.26, H 6.51; found C 75.02, H 6.75.

Analogously, esters **25m** (R^1 = $C_{10}H_{21}$, yield 87%), **25n** (R^1 = $C_{11}H_{23}$, yield 88%), **25o** (R^1 = $C_{12}H_{25}$, yield 84%), and **25p** (R^1 = $C_{14}H_{29}$, yield 88%) were obtained. For **25m** $C_{35}H_{38}O_6$ (554.69) calcd C 75.79, H 6.91; found C 75.55, H 6.76; **25n** $C_{36}H_{40}O_6$ (568.72) calcd C 76.03, H 7.09; found C 75.97, H 6.99; **25o** $C_{37}H_{42}O_6$ (582.74) calcd C 76.26, H 7.26; found C 76.23, H 7.33; **25p** $C_{39}H_{46}O_6$ (610.80) calcd C 76.69, H 7.59; found C

76.46, H 7.58.

(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 ºC and corresponding enthalpies, ΔH, are in kJ mol^{-1}.

	R^1	m.p. [ΔH]	T_{cr} [ΔH]	**N**	T_{tr} [ΔH]	Iso
25a	C_8H_{17}	184 [+41.1]	142 [-24.2]	●	202 [-0.1]	●
25b	$C_{10}H_{21}$	184 [+39.4]	153 [-18.3]	●	197 [-0.7]	●
25d	$C_{11}H_{23}$	180 [+48.8]	154 [-32.4]	●	193 [-1.1]	●
25e	$C_{12}H_{25}$	171 [+34.5]	156 [-21.1]	●	189 [-0.9]	●
25f	$C_{14}H_{29}$	160 [+18.2]	156 [-20.8]	●	179 [-1.5]	●
25g	C_8H_{17}	141 [+19.9]	116 [-19.8]	●	140 [-0.2]	●
25h	$C_{10}H_{21}$	142 [+24.2]	117 [-25.5]	●	147 [-0.5]	●
25i	$C_{11}H_{23}$	152 [+27.0]	132 [-11.7]	●	148 [-0.6]	●
25j	$C_{12}H_{25}$	157 [+32.2]	131 [-32.0]	●	150 [-0.8]	●
25k	$C_{14}H_{29}$	154 [+20.8]	132 [-20.1]	●	138 [-0.4]	●
25l	C_8H_{17}	146 [+41.7]	107 [-6.5]	●	150 [-0.6]	●
25m	$C_{10}H_{21}$	151 [+32.8]	106 [-19.2]	●	134 [-0.7]	●
25n	$C_{11}H_{23}$	147 [+23.2]	103 [-17.5]	●	132 [-0.6]	●
25o	$C_{12}H_{25}$	144 [+38.3]	113 [-22.8]	●	137 [-0.7]	●
25p	$C_{14}H_{29}$	141 [+36.9]	105 [-21.2]	●	130 [-0.8]	●

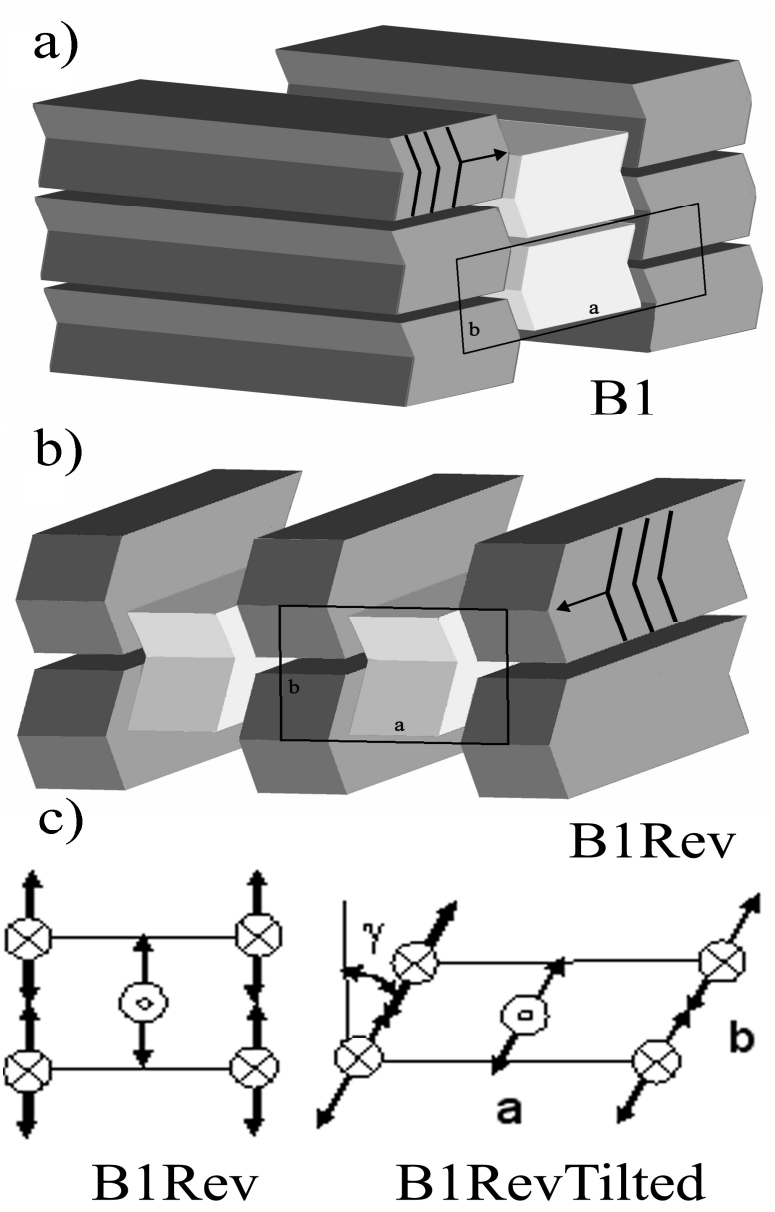

Figure S1 Schematic drawing of the a) B_1, b) B_{1Rev}, c) comparison B_{1Rev} and $B_{1RevTilted}$ phase. *a* and *b* are dimensions of the crystallographic cell (Ref. 4).

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