**Supplemental information**

**The role of lateral substitution on mesomorphic properties of achiral analogues of MHOPBC**

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**1. Synthesis**

General chemical formula of studied compounds is presented in Figure S1.



Figure S1 General chemical formula of studied compounds.

**1.1. Characterisation**

Structures of intermediates and products were confirmed by 1H and 13C NMR spectroscopy (Varian Gemini 300 HC instrument), deuteriochloroform a dimethylsulfoxide-*d*6 were used as solvents and signals of the solvents served as internal standard, *J* values are given in Hz. Assignment of the signals of 1H and 13C NMR spectra follows the models, numbering of which is shown in Figure S2.



Figure S2 Numbering of the model structures of compounds **I/n-IX/n**

Elemental analyses were carried out on a Perkin-Elmer 2400 instrument. Purity of all final compounds was confirmed by HPLC analysis (Tessek C18 25x4.5 RP column) and found >99.8%. Preparative column chromatography was carried out using Merck Kieselgel 60 (60-100 μm). The experimental part summarizes procedures for the synthesis of new compounds, representative intermediates and target compounds of series **I/n-IX/n**.

**1.2. Synthesis of the biphenylcarboxylic acids 1/n-4/n**

The structures of key intermediates and the synthetic scheme are shown in Scheme S1. Non-substituted 4´-alkoxy-1,1´-biphenyl-4-carboxylic acids (**1/n**) (alkyl=CnH2n+1,n=6,8,10,12) were prepared by alkylation of 4´-hydroxy-1,1´-biphenyl-4-carboxylic acid [S1]. In the key step of the synthesis of fluoro and chloro substituted acids **2/n-5/n**, we utilized the Suzuki coupling reaction of the corresponding arylboronic acids **6/n** and **7** with halobenzoate esters **8** and **9**, resp. The corresponding 4-alkoxyphenylboronic acids **6/n** (n = 6, 8, 10, 12) were obtained by the known method [S2]. Synthesis of the fluoro substituted boronic acid **7a** started with substituted aniline **14a** [S3], which was first transformed to fluoro derivative **15** utilizing the Schiemann reaction (Scheme 1). Compound **15** was subsequently lithiated with *n*-butyllithium(BuLi) and the formed lithium salt was trapped with trimethyl borate to yield the boronic acid **7a**. Boronic acid **7b** was synthesized analogously starting from aniline **14b**. [S4]

The further reaction partners represented esters **8** and **9** (Scheme 1). While the compounds **8a** and **8b** were obtained by the esterification of commercially available acids, esters **9a** and **9b** were synthesized by the Schiemann and Sandmeyer reaction from the known amino ester **16**, respectively [S6,S7]



Scheme S1 Synthesis of biphenylcarboxylic acids **1/n-5/n** and their precursors.

The coupling reaction of boronic acids **6/n** and **7** with esters **8** and **9** was performed by a modified procedure [S8] via a Pd(0)-catalysed reaction in the presence of a 2 M aq. potassium carbonate solution in methanol. The esters **10/n** and **11/n** were finally hydrolysed to acids **2/n** and **3/n**, resp. To obtain the alkoxy substituted acids **4/n** and **5/n**, the methoxy group of esters **12** and **13** was cleaved by heating with aq. hydrobromic acid in acetic acid (AcOH) and the formed hydroxy acids were alkylated with the corresponding 1-bromoalkane under standard basic reaction conditions to yield acids **4/n** and **5/n**.

**1.3. Synthesis of the lengthening units**

The 4-(alkoxy)phenols **17/n-19/n** (n=6,8,10,12) (Scheme S2) represent the phenol intermediates for the synthesis of the target series of compounds **I-IX**. 4-(Alkoxy)phenols **17/n** were prepared by monoalkylation of hydroquinone according to [S9]. Synthesis of 4‑alkoxy-2-halophenols **18/n** and **19/n** started with the corresponding alkoxyacetophenones **20/n** and **21/n**, resp.,available by the reported procedure [S10]. They were subjected to a Baeyer-Villiger oxidation with *m*-chloroperoxybenzoic acid (MCPBA) and subsequent hydrolysis to phenols **18/n** and **19/n**.



Scheme S2 Synthesis of the lengthening units **17/n-19/n**.

**1.4. Synthesis of the compounds I/n-IX/n**

The series of materials **I-IX/n** were obtained by a standard *N,N*´-dicyclohexylcarbodiimide (DCC) mediated esterification of acids **1/n-5/n** with phenols **17/n-19/n** catalysed with 4-(*N*,*N*-dimethylamino)pyridine (DMAP) in dichloromethane (Scheme S3).



Scheme S3 Synthesis of the target materials **I-IX/n**.

**1.5. Experimental procedures**

***1.5.1. 4-Bromo-2-fluoroanisole (15a)***

A solution of sodium nitrite (9.0 g; 130 mmol) in water (20 mL) was added to the mixture of **14** [3] (25.0 g; 120 mmol), conc. HCl (22 mL, 35%) and water (70 mL) keeping the reaction temperature below 3 °C. The resulting mixture was stirred at the same temperature for 15 min and then an ice-cold solution of sodium tetrafluoroborate (27.0 g; 245 mmol) in water (55 mL) was added. The deposited solid was filtered off, washed with ice-cold water (20 mL), ethanol (30 mL), and diethyl ether (50 mL), and dried under reduced pressure. The tetrafluoroborate (32.0 g, 86 %) was mixed with sand (80 g) and decomposed by heating to 160-170 °C for 1 h. After cooling the residue was extracted with hot hexane (3 × 100 mL), the combined hexane solutions were washed with 10% aq. hydroxide (50 mL), water (70 mL) and dried with anhydrous sodium sulfate. After removing the solvent, the crude product was purified by distillation. Yield 9.90 g (40 %) of a colourless liquid, b.p. 105‑107°C/2.26 kPa. 1H NMR (CDCl3): 3.78 (s, 3 H, OCH3), 6.60 (dd, 1 H, *J*(6,5) = 9.1, *J*(6,2) = 3.0, H-6), 6.69 (dd, 1 H, *J*(2,F) = 10.4, *J*(2,6) = 3.0, H-2), 7.40 (dd, 1 H, *J*(5,6) = 9.1, *J*(5,F) = 8.0, H-5). Elemental analysis: for C7H6BrFO (205.03): calcd C 41.01, H 2.95; found C 40.88, H 2.80%.

***1.5.2. 3-Chloro-4-iodoanisole (15b)***

A solution of *n-*butyl nitrite (6.5 g; 63 mmol) was added drop-wise to the mixture of **14** [S3] (15.0 g; 60 mmol), conc. HCl (5.5 mL, 63 mmol, 35%) in ethanol (80 mL) keeping the reaction temperature below  °C. The resulting mixture was stirred at the same temperature for 15 min and then added to the solution of HgCl2 (24.5 g, 90 mmol) in diethylether (400 mL). The precipitated solid was filtered off, washed with diethylether (50 mL) and dried under reduced pressure yielding 32 g (95 %) of white solid. Then it was mixed with ammonium chloride (70 g) and decomposed by heating to ca. 160-170 °C for 1 h. After cooling the residue was extracted with hot hexane (3 × 70 mL), the combined hexane solutions were washed with 10% aq. sodium hydroxide (70 mL), water (70 mL) and dried with anhydrous magnesium sulphate. After removal of the solvent, the oily residue was purified by distillation under reduced pressure yielding 8.3 g (50 %) of 3-chloro-4-iodoanisole (**15b**), b.p. 147-150°C/1.33-1.73kPa ([S11] 127-130°C/0.80-0.93kPa). 1H NMR (CDCl3): 3.78 (s, 3H, OCH3), 6.56 (dd, 1H, *J*(6,5) = 8.8, *J*(6,2) = 2.7, H-6), 7.02 (d, 1H, *J*(2,6) = 2.7, H-2), 7.68 (d, 1H, *J*(5,6) = 8.8, H-5).

***1.5.3. 2-Fluoro-4-methoxyphenylboronic acid (7a)***

A solution of **15a** (10.0 g, 49 mmol) in dry diethyl ether (80 mL) was cooled to 78 °C in an nitrogen atmosphere and a solution of *n*-butyllithium (20.5 mL of a 2.5 M solution in hexanes, 52  mmol) was added drop wise. The mixture was stirred at 78 °C for 30 min and then trimethyl borate (16.2 mL, 150 mmol) was added. The reaction mixture was allowed to warm to room temperature, acidified with 10% aq. HCl (50 mL) and stirred for 30 min. The organic layer was separated and the aqueous layer was extracted with diethyl ether (2 × 70 mL). The combined organic solutions were washed with brine (50 mL) and dried with anhydrous sodium sulfate. The solvent was evaporated and the residue was crystallized from methanol to yield 7.12 g (85 %) of **7a**, m.p. 125 °C. 1H NMR (CDCl3): 3.83 (s, 3H; OCH3); 5.11 (d, 2H, *J*(H,F) = 6.6 ; B(OH)2); 6.58 (dd, 1H, *J*(3,2-F) = 12.9, *J*(3,5) = 2.5; H-3); 6.75 (dd, 1H, *J*(5,6) = 8.2, *J*(5,3) = 2.5; H-5); 7.74 (dd, 1H, *J*(6,5) = 8.2, *J*(6,2-F) = 8.2; H-6).

***1.5.4. 2-Chloro-4-methoxyphenylboronic acid (7b)***

Using the same protocol as for boronic acid **7a**: From **15b** (7.0 g, 26 mmol) in dry diethyl ether (40 mL), *n*-butyllithium (11.5 mL of a 2.5 M solution in hexanes, 29  mmol) and trimethyl borate (8.1 mL, 78 mmol) yielded 2.92 g (60 %) of boronic acid **7b**. 1H NMR (CDCl3): 3.87 (s, 3 H, OCH3), 5.21 (bs, 2 H, B(OH)2), 6.85 (dd, 1 H, *J*(5,6) = 8.4, *J*(5,3) = 2.4, H-5), 7.00 (d, 1 H, *J*(3,5) = 2.4, H-3), 7.88 (d, 1 H, *J*(6,5) = 8.4, H-6).

***1.5.5. Methyl 3-fluoro-4-iodobenzoate (9a)***

A solution of sodium nitrite (5.50 g, 79 mmol) in water (10 mL) was slowly added to the mixture of **16** [6] (20.0 g, 72 mmol), conc. HCl (15 mL, 35%) and water (40 mL) at 0 °C. The resulting solution was stirred for 30 min and then an ice-cold solution of sodium tetrafluoroborate (15.80 g, 140 mmol) in water (32 mL) was added. The precipitate was filtered off, washed with ice-cold water (10 mL), ethanol (20 mL), diethyl ether (50 mL), and dried under reduced pressure. The diazonium tetrafluoroborate (20.50 g, 76 %) was mixed with sand (50 g) and the mixture was heated to 160 °C for 1 h. After cooling, then residue was extracted with hot hexane (3 × 100 mL), the combined hexane solutions were washed with 5% aq. sodium hydroxide (50 mL), water (50 mL), and dried with anhydrous sodium sulphate. After evaporation of the solvent, the crude product was purified by column chromatography (hexane/diethyl ether 10/2). Yield 7.82 g (39 %) of ester **10**, m.p. 69‑72 °C. 1H NMR (CDCl3): 3.92 (s, 3 H, OCH3), 7.56 (dd, 1 H, *J*(6,5) = 8.2, *J*(6,2) = 1.9, H-6), 7.68 (dd, 1 H, *J*(2,F) = 8.2, *J*(2,6) = 1.9, H-2), 7.85 (dd, 1 H, *J*(5,6) = 8.2, *J*(5,F) = 8.2, H-5). Elemental analysis: for C8H6FIO2 (280.04): calcd C 34.31, H 2.16, found C 34.20, H 2.08%.

***1.5.6. Methyl 3-chloro-4-iodobenzoate (9a)***

Using the same diazotization protocol as described in the case of **9a**: **16** [6] (12.0 g, 43 mmol) was diazotized with sodium nitrite (3.10 g, 45 mmol) in water (10 mL) in conc. HCl (13 mL, 35%) and water (10 mL). Filtered solution of diazonium salt was poured into the stirred mixture of conc. HCl (23 mL, 35%) and cuprous chloride prepared from cupric sulphate pentahydrate (15.0 g, 60 mmol), sodium bisulfite (4.30 g, 41 mmol) and sodium chloride (5.40 g, 92.5 mmol). Resulting dark brown solution was heated to 60 °C and strirred for 30 min. After cooling the product was isolated by extraction with dichloromethane (3 × 20 mL). Combined organic layers were washed with NaOH solution (20 mL, 5%), then with water and the separated organic layer dried over anhydrous magnesium sulphate. After removal of the solvent, the crude product was purified by column chromatography (hexane/diethyl ether, 5/1) and further crystallized from hexane giving 8.80 g (68 %) of benzoate **9a**, m.p. 67-69 °C. 1H NMR (CDCl3): 3.91 (s, 3H; OCH3); 7.57 (dd, 1H, *J*(6,5) = 8.2, *J*(6,2) = 1.9; H-6); 7.95 (d, 1H, *J*(5,6) = 8.2; H-5); 8.1 (d, 1H, *J*(2,6) = 1.9; H-2).

***1.5.7. Methyl 2,2'-difluoro-4'-methoxy-1,1'-biphenyl-4-carboxylate (12)***

Triphenylphosphine (33 mg, 0.13 mmol) was added to a mixture of **9** (4.70 g, 16.7 mmol) and boronic acid **6** (3.00 g, 17.6 mmol) in degassed methanol (80 mL) and stirred in an nitrogen atmosphere for 10 min. 10% aq. PdCl2 (80 μL) and aq. sodium carbonate (9.0 mL of a 2M solution) were added and the reaction mixture was heated to boiling for 3 h. After cooling, the mixture was poured into 5% aq. HCl (50 mL) and extracted with diethyl ether (3 × 40 mL). The combined organic solution was washed with brine and dried with anhydrous sodium sulfate. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (dichloromethane/methanol 100/2). Yield 3.21 g (70 %), m.p. 208 °C. 1H NMR (CDCl3): 3.85 (s, 3 H, OCH3), 3.94 (s, 3 H, OCH3), 6.74 (d, 1 H, *J*(3´,F) = 11.8, H-3´), 6.79 (d, 1H, *J*(5´,6´) = 9.1, H-5´), 7.31 (m, 1H, H-6´), 7.44 (m, 1H, H-6), 7.82 (d, 1H, *J*(3,F) = 10.1, H-3), 7.87 (d, 1H, *J*(5,6) = 8.0, H-5). Elemental analysis: for C15H12F2O3 (278.26): calcd C 64.75, H 4.35, found C 64.66, H 4.30%.

In this way, ester **13** and analogously esters **10/n**, **11/n** were synthesised by the reaction of esters **8** with boronic acids **6/n**.

***Methyl 2,2'-dichloro-4'-methoxy-1,1'-biphenyl-4-carboxylate (13)***

1H NMR (CDCl3): 3.85 (s, 3H; OCH3); 3.95 (s, 3H; OCH3); 6.89 (dd, 1H, *J*(5´,6´) = 8.5, *J*(5´,3´) = 2.8; H-5´); 7.04 (d, 1H, *J*(3´,5´) = 2.8; H-3´); 7.16 (d, 1H, *J*(6´,5´) = 8.5; H-6´); 7.35 (d, 1H *J*(5,6) = 8.0; H-5); 7.97 (dd, 1H, *J*(6,5) = 8.0, *J*(6,2) = 1.7; H-6); 8.14 (d, 1H, *J*(2,6) = 1.7; H-2). Elemental analysis: for C15H12Cl2O3 (311.16): calcd C 57.90, H 3.89, found C 57.78, H 3.73 %.

***Methyl 3-fluoro-4´-hexyloxy-1,1´-biphenyl-4-carboxylate (10/6)****.* Yield 80 %, m.p. 105-106 °C. 1H NMR (CDCl3):0.90 (t, 3 H, *J* = 6.7, CH3), 1.20-1.55 (m, 6 H, (CH2)3), 1.75-1.85 (m, 2 H, OCH2C**H**2), 3.94 (s, OCH3), 4.00 (t, 2 H, *J* = 6.7, OCH2), 6.99 (d, 2 H, *J*(3´,2´)= *J*(5´,6´)*=* 8.8, H-3´, H-5´), 7.36 (dd, 1 H, , *J*­HF= 12.3, *J*(6,2)=1.8, H-6), 7.43 (dd, 1 H, *J*HF= 8.2, *J*(2,6) =1.8, H-2), 7.56 (d, 2 H, *J*(2´,3´)= *J*(6´,5´)*=* 8.8, H-2´, H-6´), 8.06 (dd, 1 H, *J*(5,6) *= J*HF= 7.90, H-5). Elemental analysis: for C20H23FO3 (330.40): calcd C 72.71, H 7.02, found C 72.59, H 6.88%.

***Methyl 3-fluoro-4´-octyloxy-1,1´-biphenyl-4-carboxylate (10/8)****.* Yield 61 %, m.p. 84-85 °C.***Methyl 3-fluoro-4´-decyloxy-1,1´-biphenyl-4-carboxylate (10/10)****.* Yield 69 %, m.p. 72-73 °C.

***Methyl 3-fluoro-4´-dodecyloxy-1,1´-biphenyl-4-carboxylate (10/12)****.*Yield 88 %, m.p. 63 °C.

***Methyl 3-chloro-4´-hexyloxy-1,1´-biphenyl-4-carboxylate (11/6)****.* Yield 67 %, m.p. 70-72 °C. 1H NMR (CDCl3):0.90 (t, *J* = 6.7, 3 H, CH3), 1.25-1.55 (m, 6 H, (CH2)3), 1.75-1.85 (m, 2 H, OCH2C**H**2), 3.94 (s, OCH3), 4.00 (t, 2 H, *J* = 6.7, OCH2), 6.99 (d, 2 H, *J*(3´,2´)= *J*(5´,6´)*=* 8.8, H-3´, H-5´), 7.50-7.58 (m, 3 H, H-6, H-2´, H-6´), 7.68 (d, 1 H, *J =* 1.8, H-2), 8.09 (d, 1 h, *J*(5,6)= 8.2, H-5). Elemental analysis: for C20H23ClO3 (346.86): calcd C 69.26, H 6.68, found C 69.13, H 6.62%.

***Methyl 3-chloro-4´-octyloxy-1,1´-biphenyl-4-carboxylate (11/8)****.* Yield 76 %, m.p. 69 °C.***Methyl 3-chloro-4´-decyloxy-1,1´-biphenyl-4-carboxylate (11/10)****.* Yield 67 %, m.p. 44-45 °C.

***Methyl 3-chloro-4´-dodecyloxy-1,1´-biphenyl-4-carboxylate (11/12)****.* Yield 89 %, m.p. 39-40 °C.

***1.5.8. General procedure for the preparation of acids 2/n and 3/n***

Ester **10/n**, **11/n** (1 mmol) was dissolved in ethanol (15 mL), a saturated solution of potassium hydroxide in ethanol (5 mL) was added and the resulting mixture was heated to boiling for 2 h. After cooling, the precipitated sodium salt of acid **2/n**,**3/n** was filtered off and then stirred in a 1/1 mixture of conc. HCl and water (10 ml). The product was filtered off, washed with water (10 mL), dried, and crystallised from acetone.

***3-Fluoro-4´-hexyloxy-1,1´-biphenyl-4-carboxylic acid (2/6)****.* Yield 88 %, m.p. 176-177 °C. 1H NMR (CDCl3):0.90 (t, 3 H, *J* = 6.7, CH3), 1.20-1.55 (m, 6 H, (CH2)3), 1.75-1.85 (m, 2 H, OCH2C**H**2), 4.00 (t, 2 H, *J* = 6.7, OCH2), 6.99 (d, 2 H, *J*(3´,2´)= *J*(5´,6´)*=* 8.8, H-3´, H-5´), 7.36 (dd, 1 H, , *J*­HF= 12.3, *J*(6,2)=1.8, H-6), 7.43 (dd, 1 H, *J*HF= 8.2, *J*(2,6) =1.8, H-2), 7.56 (d, 2 H, *J*(2´,3´)= *J*(6´,5´)*=* 8.8, H-2´, H-6´), 8.06 (dd, 1 H, *J*(5,6) *= J*HF= 7.90, H-5). Elemental analysis: for C19H21FO3 (316.38): calcd C 72.13, H 6.69, found C 72.10, H 6.55%.

***3-Fluoro-4´-octyloxy-1,1´-biphenyl-4-carboxylic acid (2/8)****,* Yield 86 %, m.p. 145-146 °C.

***4´-Decyloxy-3-fluoro-1,1´-biphenyl-4-carboxylic acid (2/10)****.* Yield 88 %, m.p. 133-135 °C.

***4´-Dodecyloxy-3-fluoro-1,1´-biphenyl-4-carboxylic acid (2/12)****.* Yield 84 %, m. p. 119 °C.

***3-Chloro-4´-hexyloxy-1,1´-biphenyl-4-carboxylic acid (3/6)****.* Yield 85 %, m.p. 143‑145 °C. 1H NMR (CDCl3):0.90 (t, *J* = 6.7, 3 H, CH3), 1.25-1.55 (m, 6 H, (CH2)3), 1.75-1.85 (m, 2 H, OCH2C**H**2), 4.00 (t, 2 H, *J* = 6.7, OCH2), 6.99 (d, 2 H, *J*(3´,2´)= *J*(5´,6´)*=* 8.8, H-3´, H-5´), 7.50-7.58 (m, 3 H, H-6, H-2´, H-6´), 7.68 (d, 1 H, *J =* 1.8, H-2), 8.09 (d, 1 h, *J*(5,6)= 8.2, H-5). Elemental analysis: for C19H21ClO3 (332.83): calcd C 68.57, H 6.36, found C 68.42, H 6.22%.

***3-Chloro-4´-octyloxy-1,1´-biphenyl-4-carboxylic acid (3/8)****.* Yield 85 %, m.p. 126-128 °C.

***3-Chloro-4´-decyloxy-1,1´-biphenyl-4-carboxylic acid (3/10)****.* Yield 82 %, m.p. 88 °C.

***3-Chloro-4´-dodecyloxy-1,1´-biphenyl-4-carboxylic acid (3/12)****.* Yield 89 %, m.p. 90‑93 °C.

***1.5.9. 2,2´-Difluoro-4´-hydroxy-1,1´-biphenyl-4-carboxylic acid (4/0)***

A mixture of ester **12** (1.00 g 3.59 mmol) and 48% aq. hydrobromic acid (30 mL) in acetic acid (20 mL) was refluxed for 6 h. After cooling, the mixture was poured into water (500 mL) and extracted with diethyl ether (3 × 80 mL). The organic solution was washed with water (20 mL) and dried with anhydrous sodium sulfate. The crude product was purified by column chromatography (dichloromethane/methanol 10/1), yield 0.81 g (90 %), m.p. 305 °C. 1H NMR (DMSO-*d*6): 6.74 (d, 1 H, *J*(3´,F) = 11.8, H-3´), 6.79 (d, 1 H, *J*(5´,6´) = 9.1, H-5´), 7.31 (m, 1 H, H-6´), 7.44 (m, 1 H, H-6), 7.82 (d, 1 H, *J*(3,F) = 10.1, H-3), 8.87 (d, 1 H, *J*(5,6) = 8.0, H-5). Elemental analysis: for C13H8F2O3 (250.20): calcd C 62.41, H 3.22, found C 62.26, H 3.09%.

***1.5.10. 2,2´-Difluoro-4´-hexyloxy-1,1´-biphenyl-4-carboxylic acid (4/6)***

A solution of 1-bromohexane (0.41 g, 2.48 mmol) in DMF (10 mL) was added to a boiling mixture of acid **4/0** (0.19 g, 0.76 mmol) and potassium carbonate (1.04 g, 7.5 mmol) in DMF (15 mL) and heated to boiling for further 10 h. The mixture was filtered while hot, and the solvent was removed under reduced pressure. The residue was dissolved in ethanol (15 mL), a saturated solution of potassium hydroxide in ethanol (5 mL) was added, and the resulting mixture was heated to boiling for 2 h. The precipitated sodium salt of **4/6** was filtered off and washed with conc. HCl and water. After crystallization from acetic acid, 0.22 g (85 %) of **4/6** was obtained. 1H NMR (DMSO-*d*6): 0.82 (t, 3 H, *J* = 6.7, CH3), 1.20-1.50 (m, 6 H, (CH2)3), 1.70 (m, 2 H, OCH2C**H**2), 3.99 (t, 2 H, *J* = 6.5, OCH2), 6.88 (d, 1 H, *J*(3´,F) = 11.8, H-3´), 6.93 (d, 1 H, *J*(5´,6´) = 9.1, H-5´), 7.38 (m, 1 H, H-6´), 7.47 (m, 1 H, H-6), 7.83 (d, 1 H, *J*(3,F) = 10.1, H-3), 8.88 (d, 1 H, *J*(5,6) = 8.0, H-5). Elemental analysis: for C19H20F2O3 (334.37): calcd C 68.25, H 6.03, found C 68.18, H 5. 94%.

In the same way, acids **4/n** and **5/n** were prepared.

***2,2´-Difluoro-4´-octyloxy-1,1´-biphenyl-4-carboxylic acid*** *(****4/8)****.* Yield 83 %.

***4´-Decyloxy-2,2´-difluoro-1,1´-biphenyl-4-carboxylic acid (4/10)****.* Yield 80 %.

***4´-Dodecyloxy-2,2´-difluoro-1,1´-biphenyl-4-carboxylic acid (4/12)****.* Yield 81 %.

***2,2´-Dichloro-4´-hexyloxy-1,1´-biphenyl-4-carboxylic acid (5/6)****.* Yield 89 %.

***2,2´-Dchloro-4´-octyloxy-1,1´-biphenyl-4-carboxylic acid*** *(****5/8)****.* Yield 84 %.

***4´-Decyloxy-2,2´-dichloro-1,1´-biphenyl-4-carboxylic acid (5/10)****.* Yield 84 %.

***4´-Dodecyloxy-2,2´-dichloro-1,1´-biphenyl-4-carboxylic acid (5/12)****.* Yield 80 %.

***1.5.11. General procedure for the oxidation of acetophenones 20/n and 21/n to phenols 18/n and 19/n, resp.***

A mixture of 4-alkoxy-2-haloacetophenone **20/n**,**21/n** [S10] (10.0 mmol) anhydrous magnesium sulfate (3.20 g, 26.6 mmol), and MCPBA (3.20 g, 18.6 mmol) in chloroform (20 mL) was stirred at room temperature for 5 days. The resulting slurry was filtered and the filtrate washed with 5% aq. sodium hydroxide (3 × 10 mL) and water (20 mL). The organic solution was evaporated and the residue was dissolved in methanol (30 mL). 25% aq. ammonia (30 mL) was added and the mixture was stirred for 1 h, diluted with ethyl acetate (40 mL), washed with 5% aq. sodium hydrogencarbonate (30 mL), and dried with anhydrous sodium sulfate. The solvent was removed and the crude product was purified by column chromatography (dichloromethane/hexane, 4/1).

***2-Fluoro-4-(hexyloxy)phenol (18/6)****.* Yield 69%, colourless oil. 1H NMR (CDCl3): 0.90 (t, 3 H, *J* = 6.7, CH3), 1.20-1.55 (m, 6 H, (CH2)3), 1.74 (m, 2 H, OCH2C**H**2), 3.87 (t, 2 H, *J*  = 6.7, OCH2), 4.70 (s, 1 H, OH), 6.57 (ddd, 1 H, *J*(5,6) = 8.8, *J*(5,3) = 2.9, *J*HF *=*1.5, H-5), 6.66 (dd, 1 H, *J*HF *=*12.0, *J*(3,5) = 2.9, H-3), 7.89 (dd, 1 H, *J*HF = *J*(6,5) = 8.8, H-6). ). Elemental analysis: for C12H17FO2 (212.27): calcd C 67.90, H 8.07, found C 67.69, H 8.11%.

***2-Fluoro-4-(octyloxy)phenol (18/8)****.* Yield 77 %, m.p. 31.5-32 °C.

***4-Decyloxy-2-fluorophenol (18/10)****.* Yield 86%, m.p. 35.5-37.5 °C.

***4-Dodecyloxy-2-fluorophenol (18/12)****.* Yield 79%, m.p. 48‑51 °C.

***2-Chloro-4-(hexyloxy)phenol (19/6)****.* Yield 87 %, colourless oil. 1H NMR (CDCl3): 0.90 (t, 3 H, *J*  = 6.7, CH3), 1.20-1.55 (m, 6 H, (CH2)3), 1.74 (m, 2 H, OCH2C**H**2), 3.87 (t, 2 H, *J*  = 6.7, OCH2), 5.14 (s, 1 H, OH), 6.74 (dd, 1 H, *J*(5,6) = 8.8, *J*(5,3) = 2.9, H-5), 6.87 (d, 1 H, *J*(3,5) = 2.9, H-3), 6.92 (d, 1 H, *J*(6,5) = 8.8, H-6). Elemental analysis: for C12H17ClO2 (228.72): calcd C 63.02, H 7.49, found C 62.87, H 7.59%.

***2-Chloro-4-(octyloxy)phenol (19/8)****.* Yield 85 %, colourless oil.

***2-Chloro-4-(decyloxy)phenol (19/10)****.* Yield 82 %, colourless oil.

***2-Chloro-4-(dodecyloxy)phenol (19/12)****.* Yield 87 %, m.p. 25‑27 °C.

**1.6. Target compound synthesis and characterisation**

General procedure: *N,N*´-Dicyclohexylcarbodiimide (DCC) (1.2 mmol) was added to a mixture of acid **1/n-4/n** (1.0 mmol), phenol **17/n-19/n** (1.0 mmol), resp., and 4-dimethylaminopyridine (DMAP) (1.1 mmol) in dry dichloromethane (20 mL). The reaction mixture was stirred at room temperature for 12 h and filtered through a Celite pad. The filtrate was evaporated and the crude product was purified by column chromatography (dichloromethane/hexane) and crystallization from a hexane/ethanol mixture.

***4-(Hexyloxy)phenyl 4´-hexyloxy-1,1´-biphenyl-4-carboxylate (I/6)****.* Yield 75 %. 1H NMR (CDCl3): 0.89 (t, 6 H, *J* = 6.3, 2 × CH3), 1.30-1.55 (m, 12 H, 2 ×  (CH2)3), 1.79 (m, 4 H, 2 × OCH2C**H**2), 3.96 (t, 2 H, *J* = 6.6, OCH2, 4.02 (t, 2 H, *J=* 6.6, OCH2), 6.93 (d, 2 H, *J* = 9.0, H-3´´,H-5´´), 7.00 (d, 2 H, *J* = 8.7, H-3´,H-5´), 7.13 (d, 2 H, *J* = 9.0, H-2´´,H-6´´), 7.59 (d, 2 H, *J* = 8.7, H-2´,H-6´), 7.68 (d, 2 H, *J* = 8.4, H-3,H-5), 8.22 (d, 2 H, *J* = 8.4 H-2,H-6). 13C NMR (CDCl3): 14.4 (2 × CH3), 22.9 (2 × **C**H2CH3), 26.3 (2 × **C**H2CH2CH2O), 30.0 (2 × **C**H2CH2O), 32.1 (2 × **C**H2CH2CH3), 68.4 (CH2O), 68.7 (CH2O), 114.8 (C-3´´,C-5´´), 115.1 (C-3´,C-5´), 122.5 (C-2´´,C-6´´), 128.1 (C-3,C-5,C-2´,C-6´), 128.9 (C-1), 129.8 (C-2,C-6), 132.2 (C-1´), 144.7 (C-1´´), 147.0 (C-4), 155.8 (C-4´´), 159.4 (C-4´), 163.8 (**C**OO). Elemental analysis: for C31H38O4 (474.65): calcd C 78.45, H 8.07, found C 78.37, H 8.11%.

***4-(Octyloxy)phenyl 4´-octyloxy-1,1´-biphenyl-4-carboxylate (I/8)****.* Yield 91 %. 1H NMR (CDCl3): 0.89 (t, 6 H, *J* = 6.3, 2 × CH3), 1.30-1.55 (m, 20 H, 2 × (CH2)5), 1.79 (m, 4 H, 2 × OCH2C**H**2), 3.96 (t, 2 H, *J* = 6.6, OCH2, 4.02 (t, 2 H, *J=* 6.6, OCH2), 6.93 (d, 2 H, *J* = 9.0, H-3´´,H-5´´), 7.00 (d, 2 H, *J* = 8.7, H-3´,H-5´), 7.13 (d, 2 H, *J* = 9.0, H-2´´,H-6´´), 7.59 (d, 2 H, *J* = 8.7, H-2´,H-6´), 7.68 (d, 2 H, *J* = 8.4, H-3,H-5), 8.22 (d, 2 H, *J* = 8.4 H-2,H-6). 13C NMR (CDCl3): 14.4 (2 × CH3), 22.9 (2 × **C**H2CH3), 26.3 (2 × **C**H2CH2CH2O), 30.0 (2 × **C**H2CH2O), 32.1 (2 × **C**H2CH2CH3), 68.4 (CH2O), 68.7 (CH2O), 114.8 (C-3´´,C-5´´), 115.1 (C-3´,C-5´), 122.5 (C-2´´,C-6´´), 128.1 (C-3,C-5,C-2´,C-6´), 128.9 (C-1), 129.8 (C-2,C-6), 132.2 (C-1´), 144.7 (C-1´´), 147.0 (C-4), 155.8 (C-4´´), 159.4 (C-4´), 163.8 (**C**OO). Elemental analysis: for C35H46O4 (530.75): calcd C 79.21, H 8.74, found C 79.13, H 8.70%.

***4-(Decyloxy)phenyl 4´-decyloxy-1,1´-biphenyl-4-carboxylate (I/10)****.* Yield 80 %. 1H NMR (CDCl3): 0.89 (t, 6 H, *J* = 6.3, 2 × CH3), 1.30-1.55 (m, 28 H, 2 × (CH2)7), 1.79 (m, 4 H, 2 × OCH2C**H**2), 3.96 (t, 2 H, *J* = 6.6, OCH2, 4.02 (t, 2 H, *J=* 6.6, OCH2), 6.93 (d, 2 H, *J* = 9.0, H-3´´,H-5´´), 7.00 (d, 2 H, *J* = 8.7, H-3´,H-5´), 7.13 (d, 2 H, *J* = 9.0, H-2´´,H-6´´), 7.59 (d, 2 H, *J* = 8.7, H-2´,H-6´), 7.68 (d, 2 H, *J* = 8.4, H-3,H-5), 8.22 (d, 2 H, *J* = 8.4 H-2,H-6). 13C NMR (CDCl3): 14.4 (2 × CH3), 22.9 (2 × **C**H2CH3), 26.3 (2 × **C**H2CH2CH2O), 30.0 (2 × **C**H2CH2O), 32.1 (2 × **C**H2CH2CH3), 68.4 (CH2O), 68.7 (CH2O), 114.8 (C-3´´,C-5´´), 115.1 (C-3´,C-5´), 122.5 (C-2´´,C-6´´), 128.1(C-3,C-5,C-2´,C-6´), 128.9 (C-1), 129.8 (C-2,C-6), 132.2 (C-1´), 144.7 (C-1´´), 147.0 (C-4), 155.8 (C-4´´), 159.4 (C-4´), 163.8 (**C**OO). Elemental analysis: for C39H54O4 (586.86): calcd C 79.82, H 9.27, found C 79.70, H 9.31%.

***4-(Dodecyloxy)phenyl 4´-dodecyloxy-1,1´-biphenyl-4-carboxylate (I/12)****.* Yield 80 %. 1H NMR (CDCl3): 0.89 (t, 6 H, *J* = 6.3, 2 × CH3), 1.30-1.55 (m, 36 H, 2 × (CH2)9), 1.79 (m, 4 H, 2 × OCH2C**H**2), 3.96 (t, 2 H, *J* = 6.6, OCH2, 4.02 (t, 2 H, *J=* 6.6, OCH2), 6.93 (d, 2 H, *J* = 9.0, H-3´´,H-5´´), 7.00 (d, 2 H, *J* = 8.7, H-3´,H-5´), 7.13 (d, 2 H, *J* = 9.0, H-2´´,H-6´´), 7.59 (d, 2 H, *J* = 8.7, H-2´,H-6´), 7.68 (d, 2 H, *J* = 8.4, H-3,H-5), 8.22 (d, 2 H, *J* = 8.4 H-2,H-6). 13C NMR (CDCl3): 14.4 (2 × CH3), 22.9 (2 × **C**H2CH3), 26.3 (2 × **C**H2CH2CH2O), 30.0 (2 × **C**H2CH2O), 32.1 (2 × **C**H2CH2CH3), 68.4 (CH2O), 68.7 (CH2O), 114.8 (C-3´´,C-5´´), 115.1 (C-3´,C-5´), 122.5 (C-2´´,C-6´´), 128.1 (C-3,C-5,C-2´,C-6´), 128.9 (C-1), 129.8 (C-2,C-6), 132.2 (C-1´), 144.7 (C-1´´), 147.0 (C-4), 155.8 (C-4´´), 159.4 (C-4´), 163.8 (**C**OO). Elemental analysis: for C43H62O4 (642.97): calcd C 80.33, H 9.72, found C 80.22, H 9.70%.

***4-(Hexyloxy)phenyl 4´-hexyloxy-3-fluoro-1,1´-biphenyl-4-carboxylate (II/6)****.* Yield 85%. 1H NMR (CDCl3): 0.89 (t, 6 H, *J* = 6.7, 2 × CH3), 1.20-1.55 (m, 12 H, 2 × (CH2)3), 1.80 (m, 4 H, 2 × OCH2C**H**2), 3.96 (t, 2 H, *J* = 6.7, OCH2), 4.01 (t, 2 H, *J* = 6.7, OCH2), 6.93 (d, 2 H, *J*(3´´,2´´) = *J*(5´´,6´´) = 9.1, H-3´´,H-5´´), 7.00 (d, 2 H, *J*(3´,2´) = *J*(5´,6´) = 8.8, H-3´,H-5´), 7.14 (d, 2 H, *J*(2´´,3´´) = *J*(6´´,5´´) = 9.1, H-2´´,H-6´´), 7.38 (dd, 1 H, *J*HF = 12.3, *J*(2,6) = 1.8, H-2), 7.45 (d, 1 H, *J* = 8.2, H-6), 7.57 (d, 2 H, *J*(2´,3´) = *J*(6´,5´) = 8.8, H-2´,H-6´), 8.11 (dd, 1 H, *J*(5,6) = *J*HF = 8.2, H-5). 13C NMR (CDCl3): 14.4 (2 × CH3), 22.9 (2 × **C**H2CH3), 26.3 (2 × **C**H2CH2CH2O), 29.8 (2 × **C**H2CH2O), 32.1 (2 × **C**H2CH2CH3), 68.4 (CH2O), 68.7 (CH2O), 114.9 (d, *J*CF = 23.2, C-2), 115.3 (C-3´,C-5´,C-3´´,C-5´´), 115.9 (d, *J*CF = 9.4, C-4), 122.2 (d, *J*CF= 9.4, C-6), 122.6 (C-2´´,C-6´´), 128.6 (C-2´,C-6´), 130.8 (C-1´), 133.2 (C-5), 144.2 (C-1´´), 148.3 (d, *J*CF= 8.9, C-1), 157.2 (C-4´´), 160.2 (C-4´), 162.9 (d, *J*CF= 260.4, C-3), 163.4 (d, *J*CF= 0.1, CO). Elemental analysis: for C31H37FO4 (492.64): calcd C 75.58, H 7.57, found C 75.50, H 7.49%.

***4-(Octyloxy)phenyl 3-fluoro-4´-octyloxy-1,1´-biphenyl-4-carboxylate (II/8)****.* Yield 83 %. 1H NMR (CDCl3): 0.89 (t, 6 H, *J* = 6.7, 2 × CH3), 1.20-1.55 (m, 20 H, 2 × (CH2)3), 1.80 (m, 4 H, 2 × OCH2C**H**2), 3.96 (t, 2 H, *J* = 6.7, OCH2), 4.01 (t, 2 H, *J* = 6.7, OCH2), 6.93 (d, 2 H, *J*(3´´,2´´) = *J*(5´´,6´´) = 9.1, H-3´´,H-5´´), 7.00 (d, 2 H, *J*(3´,2´) = *J*(5´,6´) = 8.8, H-3´,H-5´), 7.14 (d, 2 H, *J*(2´´,3´´) = *J*(6´´,5´´) = 9.1, H-2´´,H-6´´), 7.38 (dd, 1 H, *J*HF = 12.3, *J*(2,6) = 1.8, H-2), 7.45 (d, 1 H, *J* = 8.2, H-6), 7.57 (d, 2 H, *J*(2´,3´) = *J*(6´,5´) = 8.8, H-2´,H-6´), 8.11 (dd, 1 H, *J*(5,6) = *J*HF = 8.2, H-5). 13C NMR (CDCl3): 14.4 (2 × CH3), 22.9 (2 × **C**H2CH3), 26.3 (2 × **C**H2CH2CH2O), 29.6-29.8, (2 × (CH2)2), 2 × **C**H2CH2O), 32.1 (2 × **C**H2CH2CH3), 68.4 (CH2O), 68.7 (CH2O), 114.9 (d, *J*CF = 23.2, C-2), 115.3 (C-3´,C-5´,C-3´´,C-5´´), 115.9 (d, *J*CF= 9.4, C-4), 122.2 (d, *J*CF= 9.4, C-6), 122.6 (C-2´´,C-6´´), 128.6 (C-2´,C-6´),130.8 (C-1´), 133.2 (C-5), 144.2 (C-1´´), 148.3 (d, *J*CF= 8.9, C-1), 157.2 (C-4´´), 160.2 (C-4´), 162.9 (d, *J*CF= 260.4, C-3), 163.4 (d, *J*CF= 0.1, CO). Elemental analysis: for C35H45FO4 (548.74): calcd C 76.61, H 8.27, found C 76.49, H 8.20%.

***4-(Decyloxy)phenyl 4´-decyloxy-3-fluoro-1,1´-biphenyl-4-carboxylate (II/10)****.* Yield 61 %. 1H NMR (CDCl3): 0.89 (t, 6 H, *J* = 6.7, 2 × CH3), 1.20-1.55 (m, 28 H, 2 × (**C**H2)7), 1.80 (m, 4 H, 2 × OCH2C**H**2), 3.96 (t, 2 H, *J* = 6.7, OCH2), 4.01 (t, 2 H, *J* = 6.7, OCH2), 6.93 (d, 2 H, *J*(3´´,2´´) = *J*(5´´,6´´) = 9.1, H-3´´,H-5´´), 7.00 (d, 2 H, *J*(3´,2´) = *J*(5´,6´) = 8.8, H-3´,H-5´), 7.14 (d, 2 H, *J*(2´´,3´´) = *J*(6´´,5´´) = 9.1, H-2´´,H-6´´), 7.38 (dd, 1 H, *J*HF = 12.3, *J*(2,6) = 1.8, H-2), 7.45 (d, 1 H, *J* = 8.2, H-6), 7.57 (d, 2 H, *J*(2´,3´) = *J*(6´,5´) = 8.8, H-2´,H-6´), 8.11 (dd, 1 H, *J*(5,6) = *J*HF = 8.2, H-5). 13C NMR (CDCl3): 14.4 (2 × CH3), 22.9 (2 × **C**H2CH3), 26.3 (2 × **C**H2CH2CH2O), 29.6-29.8 (2 × (CH2)4), 2 × CH2CH2O), 32.1 (2 × **C**H2CH2CH3), 68.4 (CH2O), 68.7 (CH2O), 114.9 (d, *J*CF = 23.2, C-2), 115.3 (C-3´, C-5´, C-3´´, C-5´´), 115.9 (d, *J*CF= 9.4, C-4), 122.2 (d, *J*CF= 9.4, C-6), 122.6 (C-2´´, C-6´´), 128.6 (C-2´, C-6´), 130.8 (C-1´), 133.2 (C-5), 144.2 (C-1´´), 148.3 (d, *J*CF= 8.9, C-1), 157.2 (C-4´´), 160.2 (C-4´), 162.9 (d, *J*CF= 260.4, C-3), 163.4 (d, *J*CF= 0.1, CO). Elemental analysis: for C39H53FO4 (604.85): calcd C 77.45, H 8.83, found C 77.37, H 8.72%.

***4-(Dodecyloxy)phenyl 4´-dodecyloxy-3-fluoro-1,1´-biphenyl-4-carboxylate (II/12)****.* Yield 89 %. 1H NMR (CDCl3): 0.89 (t, 6 H, *J* = 6.7, 2 × CH3), 1.20-1.55 (m, 36 H, 2 × (CH2)9), 1.80 (m, 4 H, 2 × OCH2C**H**2), 3.96 (t, 2 H, *J* = 6.7, OCH2), 4.01 (t, 2 H, *J* = 6.7, OCH2), 6.93 (d, 2 H, *J*(3´´,2´´) = *J*(5´´,6´´) = 9.1, H-3´´,H-5´´), 7.00 (d, 2 H, *J*(3´,2´) = *J*(5´,6´) = 8.8, H-3´,H-5´), 7.14 (d, 2 H, *J*(2´´,3´´) = *J*(6´´,5´´) = 9.1, H-2´´,H-6´´), 7.38 (dd, 1 H, *J*HF = 12.3, *J*(2,6) = 1.8, H-2), 7.45 (d, 1 H, *J* = 8.2, H-6), 7.57 (d, 2 H, *J*(2´,3´) = *J*(6´,5´) = 8.8, H-2´, H-6´), 8.11 (dd, 1 H, *J*(5,6) = *J*HF = 8.2, H-5). 13C NMR (CDCl3): 14.4 (2 × CH3), 22.9 (2 × **C**H2CH3), 26.3 (2 × **C**H2CH2CH2O), 29.6-29.8 (2 × (CH2)6), 2 × **C**H2CH2O), 32.1 (2 × **C**H2CH2CH3), 68.4 (CH2O), 68.7 (CH2O), 114.9 (d, *J*CF = 23.2, C-2), 115.3 (C-3´, C-5´, C-3´´, C-5´´), 115.9 (d, *J*CF= 9.4, C-4), 122.2 (d, *J*CF= 9.4, C-6), 122.6 (C-2´´, C-6´´), 128.6 (C-2´, C-6´),130.8 (C-1´), 133.2 (C-5), 144.2 (C-1´´), 148.3 (d, *J*CF= 8.9, C-1), 157.2 (C-4´´), 160.2 (C-4´), 162.9 (d, *J*CF= 260.4, C-3), 163.4 (d, *J*CF= 0.1, CO). Elemental analysis: for C43H61FO4 (660.96): calcd C 78.14, H 9.30, found C 78.10, H 9.21%.

***4-(Hexyloxy)phenyl 3-chloro-4´-hexyloxy-1,1´-biphenyl-4-carboxylate (III/6)****.* Yield 85 %. 1H NMR (CDCl3):0.92 (t, 6 H, *J* = 6.7, 2 × CH3), 1.20-1.55 (m, 12 H, 2 × (CH2)3), 1.80 (m, 4 H, (2xOCH2C**H**2), 3.95 (t, 2 H, *J*= 6.7, OCH2), 4.01 (t, 2 H, *J* = 6.7, OCH2), 6.93 (d, 2 H, *J*(3´´,2´´) = *J*(5´´,6´´) = 9.1, H-3´´,H-5´´), 7.00 (d, 2 H, *J*(3´,2´)= *J*(5´,6´)*=* 8.8, H-3´,H-5´), 7.16 (d, 2 H, *J*(2´´,3´´) = *J*(6´´,5´´) = 9.1, H-2´´,H-6´´), 7.50-7.62 (m, 3 H, H-6,H-2´,H-6´), 7.70 (d, 1 H, *J*(5,6) *=* 1.5, H-2), 8.10 (d, 1 H, *J*(5,6) = 8.2, H-5). 13C NMR (CDCl3): 14.4 (2 × CH3), 22.9 (2 × **C**H2CH3), 26.3 (2 × **C**H2CH2CH2O), 29.8 (2 × **C**H2CH2O), 32.1 (2 × **C**H2CH2CH3), 68.4 (CH2O), 68.7 (CH2O), 115.3 (C-3´,C-5´,C-3´´,C-5´´), 122.6 (C-2´´,C-6´´), 124.8 (C-6), 126.8 (C-4), 128.6 (C-2´´,C-6´´), 129.4 (C-2), 130.7 (C-1´), 132.8 (C-5), 135.3 (C-3), 144.3 (C-1´´), 146.2 (C-1), 157.2 (C-4´´), 160.1 (C-4´), 164.5 (CO). Elemental analysis: for C31H37ClO4 (509.09): calcd C 73.17, H 7.33, found C 73.06, H 7.22%.

***4-(Octyloxy)phenyl 3-chloro-4´-octyloxy-1,1´-biphenyl-4-carboxylate (III/8)****.* Yield 72 %. 1H NMR (CDCl3):0.92 (t, 6 H, *J* = 6.7, 2 × CH3), 1.20-1.55 (m, 20 H, 2 × (CH2)5), 1.80 (m, 4 H, (2 × OCH2C**H**2), 3.95 (t, 2 H, *J*= 6.7, OCH2), 4.01 (t, 2 H, *J* = 6.7, OCH2), 6.93 (d, 2 H, *J*(3´´,2´´) = *J*(5´´,6´´) = 9.1, H-3´´,H-5´´), 7.00 (d, 2 H, *J*(3´,2´)= *J*(5´,6´)*=* 8.8, H-3´,H-5´), 7.16 (d, 2 H, *J*(2´´,3´´) = *J*(6´´,5´´) = 9.1, H-2´´,H-6´´), 7.50-7.62 (m, 3 H, H-6,H-2´,H-6´), 7.70 (d, 1 H, *J*(5,6) *=* 1.5, H-2), 8.10 (d, 1 H, *J*(5,6) = 8.2, H-5). 13C NMR (CDCl3): 14.4 (2 × CH3), 22.9 (2 × **C**H2CH3), 26.3 (2 × **C**H2CH2CH2O), 29.6-29.8 (2 × (CH2)2, 2 × **C**H2CH2O), 32.1 (2 × **C**H2CH2CH3), 68.4 (CH2O), 68.7 (CH2O), 115.3 (C-3´,C-5´,C-3´´,C-5´´), 122.6 (C-2´´,C-6´´), 124.8 (C-6), 126.8 (C-4), 128.6 (C-2´´,C-6´´), 129.4 (C-2), 130.7 (C-1´), 132.8 (C-5), 135.3 (C-3), 144.3 (C-1´´), 146.2 (C-1), 157.2 (C-4´´), 160.1 (C-4´), 164.5 (CO). Elemental analysis: for C35H45ClO4 (565.20): calcd C 74.38, H 8.03, found C 74.31, H 8.00%.

***4-(Decyloxy)phenyl 3-chloro-4´-decyloxy-1,1´-biphenyl-4-carboxylate*** *(****III/10)****.* Yield 73 %. 1H NMR (CDCl3):0.92 (t, 6 H, *J* = 6.7, 2 ×CH3), 1.20-1.55 (m, 28 H, 2 × (CH2)7), 1.80 (m, 4 H, (2 × OCH2C**H**2), 3.95 (t, 2 H, *J*= 6.7, OCH2), 4.01 (t, 2 H, *J* = 6.7, OCH2), 6.93 (d, 2 H, *J*(3´´,2´´) = *J*(5´´,6´´) = 9.1, H-3´´,H-5´´), 7.00 (d, 2 H, *J*(3´,2´)= *J*(5´,6´)*=* 8.8, H-3´,H-5´), 7.16 (d, 2 H, *J*(2´´,3´´) = *J*(6´´,5´´) = 9.1, H-2´´,H-6´´), 7.50-7.62 (m, 3 H, H-6,H-2´,H-6´), 7.70 (d, 1 H, *J*(5,6) *=* 1.5, H-2), 8.10 (d, 1 H, *J*(5,6) = 8.2, H-5). 13C NMR (CDCl3): 14.4 (2 × CH3), 22.9 (2 × **C**H2CH3), 26.3 (2 × **C**H2CH2CH2O), 29.6-29.8 (2 × (CH2)4, 2 × **C**H2CH2O), 32.1 (2 × **C**H2CH2CH3), 68.4 (CH2O), 68.7 (CH2O), 115.3 (C-3´,C-5´,C-3´´,C-5´´), 122.6 (C-2´´,C-6´´), 124.8 (C-6), 126.8 (C-4), 128.6 (C-2´´,C-6´´), 129.4 (C-2), 130.7 (C-1´), 132.8 (C-5), 135.3 (C-3), 144.3 (C-1´´), 146.2 (C-1), 157.2 (C-4´´), 160.1 (C-4´), 164.5 (CO). Elemental analysis: for C39H53ClO4 (621.31): calcd C 75.39, H 8.60, found C 75.25, H 8.44%.

***4-(Dodecyloxy)phenyl 3-chloro-4´-dodecyloxy-1,1´-biphenyl-4-carboxylate (III/12)****.* Yield 77 %. 1H NMR (CDCl3):0.92 (t, 6 H, *J* = 6.7, (2 × CH3), 1.20-1.55 (m, 36 H, 2 × (CH2)9), 1.80 (m, 4 H, 2 × OCH2C**H**2), 3.95 (t, 2 H, *J*= 6.7, OCH2), 4.01 (t, 2 H, *J*= 6.7, OCH2), 6.93 (d, 2 H, *J*(3´´,2´´) = *J*(5´´,6´´) = 9.1, H-3´´,H-5´´), 7.00 (d, 2 H, *J*(3´,2´)= *J*(5´,6´)*=* 8.8, H-3´,H-5´), 7.16 (d, 2 H, *J*(2´´,3´´) = *J*(6´´,5´´) = 9.1, H-2´´,H-6´´), 7.50-7.62 (m, 3 H, H-6,H-2´,H-6´), 7.70 (d, 1 H, *J*(5,6) *=* 1.5, H-2), 8.10 (d, 1 H, *J*(5,6) = 8.2, H-5). 13C NMR (CDCl3): 14.4 (2 × CH3), 22.9 (2 × **C**H2CH3), 26.3 (2 × **C**H2CH2CH2O), 29.6-29.8 (2 × (CH2)6, 2 × CH2CH2O), 32.1 (2 × **C**H2CH2CH3), 68.4 (CH2O), 68.7 (CH2O), 115.3 (C-3´,C-5´,C-3´´,C-5´´), 122.6 (C-2´´,C-6´´), 124.8 (C-6), 126.8 (C-4), 128.6 (C-2´´,C-6´´), 129.4 (C-2), 130.7 (C-1´), 132.8 (C-5), 135.3 (C-3), 144.3 (C-1´´), 146.2 (C-1), 157.2 (C-4´´), 160.1 (C-4´), 164.5 (CO). Elemental analysis: for C43H61ClO4 (677.42): calcd C 76.24, H 9.08, found C 76.10, H 8.99%.

***2-Fluoro-4-(hexyloxy)phenyl 4´-hexyloxy-1,1´-biphenyl-4-carboxylate (IV/6)****.* Yield 78 %. 1H NMR (CDCl3): 0.88 (t, 6 H, *J* = 6.7, 2 × CH3), 1.20-1.55 (m, 12 H, 2 × (CH2)3), 1.80 (m, 4 H, 2 × OCH2C**H**2), 3.94 (t, 2 H, *J* = 6.7, OCH2), 4.01 (t, 2 H, *J* = 6.7, OCH2), 6.85 (ddd, 1 H, *J*(5´´,6´´) = 8.8, *J*(5´´,3´´) = 2.9, *J*HF *=*1.2, H-5´´), 6.66 (dd, 1 H, *J*HF *=*11.7, *J*(3´´,5´´) = 2.9, H-3´´), 7.00 (d, 2 H, *J*(3´,2´) = *J*(5´,6´) = 8.8, H-3´, H-5´), 7.13 (dd, 1 H, *J*HF = *J*(6´´,5´´) = 8.8, H-6´´), 7.59 (d, 2 H, *J*(2´,3´) = *J*(6´,5´) = 8.8, H-2´,H-6´), 7.69 (d, 2 H, *J*(2,3) = *J*(6,5) = 8.5, H-2,H-6), 8.23 (d, 2 H, *J*(3,2) = *J*(5,6) = 8.5, H-3,H-5). 13C NMR (CDCl3): 14.4 (2 × CH3), 22.9 (2 × **C**H2CH3), 26.2 (**C**H2CH2CH2O), 26.3 (**C**H2CH2CH2O), 29.8 (2 × **C**H2CH2O), 32.2 (2 × **C**H2CH2CH3), 68.4 (CH2O), 68.9 (CH2O), 103.6 (d, *J*HF = 21.5, C-3´´), 110.4 (d, *J*HF = 3.3, C-5´´), 115.2 (C-3´,C-5´), 124.1 (C-6´´), 126.8 (C-2,C-6), 128.6 (C-2´,C-6´), 131.1 (C-3,C-5), 131.7 (C-4), 132.0 (d, *J*HF = 21.6, C-1´´), 132.2 (C-1´), 146.4 (C-1), 154.7 (d, *J*HF = 248.3, C-2´´), 158.0 (d, *J*HF = 9.4, C-4´´), 159.8 (C-4´), 164.8 (CO). Elemental analysis: for C31H37FO4 (492.64): calcd C 75.58, H 7.57, found C 75.47, H 7.43%.

***2-Fluoro-4-(octyloxy)phenyl 4´-octyloxy-1,1´-biphenyl-4-carboxylate (IV/8)****.* Yield 75 %. 1H NMR (CDCl3): 0.88 (t, 6 H, *J* = 6.7, 2 × CH3), 1.20-1.55 (m, 20 H, 2 × (CH2)5), 1.80 (m, 4 H, (2 × OCH2C**H**2), 3.94 (t, 2 H, *J* = 6.7, OCH2), 4.01 (t, 2 H, *J* = 6.7, OCH2), 6.85 (ddd, 1 H, *J*(5´´,6´´) = 8.8, *J*(5´´,3´´) = 2.9, *J*HF *=*1.2, H-5´´), 6.66 (dd, 1 H, *J*HF *=*11.7, *J*(3´´,5´´) = 2.9, H-3´´), 7.00 (d, 2 H, *J*(3´,2´) = *J*(5´,6´) = 8.8, H-3´,H-5´), 7.13 (dd, 1 H, *J*HF = *J*(6´´,5´´) = 8.8, H-6´´), 7.59 (d, 2 H, *J*(2´,3´) = *J*(6´,5´) = 8.8, H-2´,H-6´), 7.69 (d, 2 H, *J*(2,3) = *J*(6,5) = 8.5, H-2,H-6), 8.23 (d, 2 H, *J*(3,2) = *J*(5,6) = 8.5, H-3,H-5). 13C NMR (CDCl3): 14.4 (2 × CH3), 22.9 (2 × CH2**C**H3), 26.2 (**C**H2CH2CH2O), 26.3 (**C**H2CH2CH2O), 29.6-29.9 (2 × (**C**H2)2, 2 × **C**H2CH2O), 32.2 (2 × **C**H2CH2CH3), 68.4 (CH2O), 68.9 (CH2O), 103.6 (d, *J*HF = 21.5, C-3´´), 110.4 (d, *J*HF = 3.3, C-5´´), 115.2 (C-3´,C-5´), 124.1 (C-6´´), 126.8 (C-2,C-6), 128.6 (C-2´,C-6´), 131.1 (C-3,C-5), 131.7 (C-4), 132.0 (d, *J*HF = 21.6, C-1´´), 132.2 (C-1´), 146.4 (C-1), 154.7 (d, *J*HF = 248.3, C-2´´), 158.0 (d, *J*HF = 9.4, C-4´´), 159.8 (C-4´), 164.8 (CO). Elemental analysis: for C35H45FO4 (548.74): calcd C 76.61, H 8.27, found C 76.50, H 8.23%.

***4-Decyloxy-2-fluorophenyl 4´-decyloxy-1,1´-biphenyl-4-carboxylate (IV/10)****.* Yield 83 %. 1H NMR (CDCl3): 0.88 (t, 6 H, *J* = 6.7, 2 × CH3), 1.20-1.55 (m, 28 H, 2 × (CH2)7), 1.80 (m, 4 H, (2 × OCH2C**H**2), 3.94 (t, 2 H, *J* = 6.7, OCH2), 4.01 (t, 2 H, *J* = 6.7, OCH2), 6.85 (ddd, 1 H, *J*(5´´,6´´) = 8.8, *J*(5´´,3´´) = 2.9, *J*HF *=*1.2, H-5´´), 6.66 (dd, 1 H, *J*HF *=*11.7, *J*(3´´,5´´) = 2.9, H-3´´), 7.00 (d, 2 H, *J*(3´,2´) = *J*(5´,6´) = 8.8, H-3´,H-5´), 7.13 (dd, 1 H, *J*HF = *J*(6´´,5´´) = 8.8, H-6´´), 7.59 (d, 2 H, *J*(2´,3´) = *J*(6´,5´) = 8.8, H-2´,H-6´), 7.69 (d, 2 H, *J*(2,3) = *J*(6,5) = 8.5, H-2,H-6), 8.23 (d, 2 H, *J*(3,2) = *J*(5,6) = 8.5, H-3,H-5). 13C NMR (CDCl3): 14.4 (2 × CH3), 22.9 (2 × **C**H2CH3), 26.2 (**C**H2CH2CH2O), 26.3 (**C**H2CH2CH2O), 29.6-29.9 (2 × (**C**H2)4, 2 × **C**H2CH2O), 32.2 (2 × **C**H2CH2CH3), 68.4 (CH2O), 68.9 (CH2O), 103.6 (d, *J*HF = 21.5, C-3´´), 110.4 (d, *J*HF = 3.3, C-5´´), 115.2 (s, C-3´,C-5´), 124.1 (C-6´´), 126.8 (C-2,C-6), 128.6 (C-2´,C-6´), 131.1 (C-3,C-5), 131.7 (C-4), 132.0 (d, *J*HF = 21.6, C-1´´), 132.2 (C-1´), 146.4 (C-1), 154.7 (d, *J*HF = 248.3, C-2´´), 158.0 (d, *J*HF = 9.43, C-4´´), 159.8 (C-4´), 164.8 (CO). Elemental analysis: for C39H53FO4 (604.85): calcd C 77.45, H 8.83, found C 77.30, H 8.84%.

***4-Dodecyloxy-2-fluorophenyl 4´-dodecyloxy-1,1´-biphenyl-4-carboxylate (IV/12)****.* Yield 82 %. 1H NMR (CDCl3): 0.88 (t, 6 H, *J* = 6.7, 2 × CH3), 1.20-1.55 (m, 36 H, 2 × (CH2)9), 1.80 (m, 4 H, (2 × OCH2C**H**2), 3.94 (t, 2 H, *J* = 6.7, OCH2), 4.01 (t, 2 H, *J* = 6.7, OCH2), 6.85 (ddd, 1 H, *J*(5´´,6´´) = 8.8, *J*(5´´,3´´) = 2.9, *J*HF *=*1.2, H-5´´), 6.66 (dd, 1 H, *J*HF *=*11.7, *J*(3´´,5´´) = 2.9, H-3´´), 7.00 (d, 2 H, *J*(3´,2´) = *J*(5´,6´) = 8.8, H-3´,H-5´), 7.13 (dd, 1 H, *J*HF = *J*(6´´,5´´) = 8.8, H-6´´), 7.59 (d, 2 H, *J*(2´,3´) = *J*(6´,5´) = 8.8, H-2´,H-6´), 7.69 (d, 2 H, *J*(2,3) = *J*(6,5) = 8.5, H-2,H-6), 8.23 (d, 2 H, *J*(3,2) = *J*(5,6) = 8.5, H-3,H-5). 13C NMR (CDCl3): 14.4 (2 × CH3), 22.9 (2 × **C**H2CH3), 26.2 (**C**H2CH2CH2O), 26.3 (**C**H2CH2CH2O), 29.6-29.9 (2 × (**C**H2)6, 2 × **C**H2CH2O), 32.2 (2 × **C**H2CH2CH3), 68.4 (CH2O), 68.9 (CH2O), 103.6 (d, *J*HF = 21.5, C-3´´), 110.4 (d, *J*HF = 3.3, C-5´´), 115.2 (s, C-3´,C-5´), 124.1 (C-6´´), 126.8 (C-2,C-6), 128.6 (C-2´,C-6´), 131.1 (C-3,C-5), 131.7 (C-4), 132.0 (d, *J*HF = 21.6, C-1´´), 132.2 (C-1´), 146.4 (C-1), 154.7 (d, *J*HF = 248.3, C-2´´), 158.0 (d, *J*HF = 9.43, C-4´´), 159.8 (C-4´), 164.8 (CO). Elemental analysis: for C43H61FO4 (660.96): calcd C 78.14, H 9.30, found C 78.03, H 9.16%.

***2-Chloro-4-(hexyloxy)phenyl 4´-hexyloxy-1,1´-biphenyl-4-carboxylate (V/6)****.* Yield 93 %. 1H NMR (CDCl3): 0.89 (t, 6 H, *J* = 6.7, 2 × CH3), 1.20-1.55 (m, 12 H, 2 × (CH2)3), 1.80 (m, 4 H, 2 × OCH2C**H**2), 3.95 (t, 2 H, *J* = 6.7, OCH2), 4.01 (t, 2 H, *J* = 6.7, OCH2), 6.85 dd, 1 H, *J*(5´´,6´´) = 9.1, *J*(5´´,3´´) = 2.3, H-5´´), 6.95-7.05 (m, 3 H, H-3´,H‑5´,H-3´´), 7.17 (d, 1 H, *J*(6´´,5´´) = 9.1, H-6´´), 7.59 (d, 2 H, *J*(2´,3´) = *J*(6´,5´) = 8.8, H-2´,H-6´), 7.69 (d, 2 H, *J*(2,3) = *J*(6,5) = 8.5, H-2,H-6), 8.26 (d, 2 H, *J*(3,2) = *J*(5,6) = 8.5, H-3,H-5). 13C NMR (CDCl3): 14.4 (2 × CH3), 22.9 (2 × **C**H2CH3), 26.2 (**C**H2CH2CH2O), 26.3 (**C**H2CH2CH2O), 29.8 (2 × **C**H2CH2O), 32.2 (2 × **C**H2CH2CH3), 68.4 (CH2O), 68.9 (CH2O), 114.2 (C-5´´), 115.2 (C-3´, C-5´), 116.1 (C-3´´), 124.3 (C-6´´), 126.9 (C-2,C-6), 127.2 (C-2´´), 128.6 (C-2´,C-6´), 131.1 (C-3,C-5), 132.2 (C-1´), 140.8 (C1´´), 146.4 (C-1), 157.6 (C-4´´), 159.8 (C-4´), 164.9 (CO). Elemental analysis: for C31H37ClO4 (509.09): calcd C 73.17, H 7.33, found C 73.02, H 7.29%.

***2-Chloro-4-(octyloxy)phenyl 4´-octyloxy-1,1´-biphenyl-4-carboxylate (V/8)****.* Yield 78 %. 1H NMR (CDCl3): 0.89 (t, 6 H, *J* = 6.7, 2 × CH3), 1.20-1.55 (m, 20 H, 2 × (CH2)5), 1.80 (m, 4 H, (2 × OCH2C**H**2), 3.95 (t, 2 H, *J* = 6.7, OCH2), 4.01 (t, 2 H, *J* = 6.7, OCH2), 6.85 (dd, 1 H, *J*(5´´,6´´) = 9.1, *J*(5´´,3´´) = 2.3, H-5´´), 6.95-7.05 (m, 3 H, H-3´,H-5,H-3´´), 7.17 (d, 1 H, *J*(6´´,5´´) = 9.1, H-6´´), 7.59 (d, 2 H, *J*(2´,3´) = *J*(6´,5´) = 8.8, H-2´,H-6´), 7.69 (d, 2 H, *J*(2,3) = *J*(6,5) = 8.5, H-2,H-6), 8.26 (d, 2 H, *J*(3,2) = *J*(5,6) = 8.5, H-3,H-5). 13C NMR (CDCl3): 14.4 (2 × CH3), 22.9 (2 × **C**H2CH3), 26.2 (**C**H2CH2CH2O), 26.3 (**C**H2CH2CH2O), 29.6-29.9 (2 × (**C**H2)2, 2 × **C**H2CH2O), 32.2 (2 × **C**H2CH2CH3), 68.4 (CH2O), 68.9 (CH2O), 114.2 (C-5´´), 115.2 (C-3´,C-5´), 116.1 (C-3´´), 124.3 (C-6´´), 126.9 (C-2,C-6), 127.2 (C-2´´), 128.6 (C-2´,C-6´), 131.1 (C-3,C-5), 132.2 (C-1´), 140.8 (**C**1´´), 146.4 (C-1), 157. 6 (C-4´´), 159.8 (C-4´), 164.9 (CO). Elemental analysis: for C35H45ClO4 (565.20): calcd C 74.38, H 8.03, found C 74.24, H 8.11%.

***2-Chloro-4-(decyloxy)phenyl 4´-decyloxy-1,1´-biphenyl-4-carboxylate (V/10)****.* Yield 69 %. 1H NMR (CDCl3): 0.89 (t, 6 H, *J* = 6.7, 2 × CH3), 1.20-1.55 (m, 28 H, 2 × (CH2)7), 1.80 (m, 4 H, (2 × OCH2C**H**2), 3.95 (t, 2 H, *J* = 6.7, OCH2), 4.01 (t, 2 H, *J* = 6.7, OCH2), 6.85 (dd, 1 H, *J*(5´´,6´´) = 9.1, *J*(5´´,3´´) = 2.3, H-5´´), 6.95-7.05 (m, 3 H, H-3´,H-5´,H-3´´), 7.17 (d, 1 H, *J*(6´´,5´´) = 9.1, H-6´´), 7.59 (d, 2 H, *J*(2´,3´) = *J*(6´,5´) = 8.8, H-2´,H-6´), 7.69 (d, 2 H, *J*(2,3) = *J*(6,5) = 8.5, H-2,H-6), 8.26 (d, 2 H, *J*(3,2) = *J*(5,6) = 8.5, H-3,H-5). 13C NMR (CDCl3): 14.4 (2 × CH3), 22.9 (2 × **C**H2CH3), 26.2 (**C**H2CH2CH2O), 26.3 (**C**H2CH2CH2O), 29.6-29.9 (2 × (**C**H2)4, 2 × **C**H2CH2O), 32.2 (2 × **C**H2CH2CH3), 68.4 (CH2O), 68.9 (CH2O), 114.2 (C-5´´), 115.2 (C-3´,C-5´), 116.1 (C-3´´), 124.3 (C-6´´), 126.9 (C-2,C-6), 127.2 (C-2´´), 128.6 (C-2´,C-6´), 131.1 (C-3,C-5), 132.2 (C-1´), 140.8 (C1´´), 146.4 (C-1), 157.6 (C-4´´), 159.8 (C-4´), 164.9 (CO). Elemental analysis: for C39H53ClO4 (621.31): calcd C 75.39, H 8.60, found C 75.33, H 8.56%.

***2-Chloro-4-(dodecyloxy)phenyl 4´-dodecyloxy-1,1´-biphenyl-4-carboxylate (V/12)****.* Yield 77 %. 1H NMR (CDCl3): 0.89 (t, 6 H, *J* = 6.7, 2 × CH3), 1.20-1.55 (m, 36 H, 2 × (CH2)9), 1.80 (m, 4 H, (2 × OCH2C**H**2), 3.95 (t, 2 H, *J* = 6.7, OCH2), 4.01 (t, 2 H, *J* = 6.7, OCH2), 6.85 (dd, 1 H, *J*(5´´,6´´) = 9.1, *J*(5´´,3´´) = 2.3, H-5´´), 6.95-7.05 (m, 3 H, H-3´,H-5,H-3´´), 7.17 (d, 1 H, *J*(6´´,5´´) = 9.1, H-6´´), 7.59 (d, 2 H, *J*(2´,3´) = *J*(6´,5´) = 8.8, H-2´,H-6´), 7.69 (d, 2 H, *J*(2,3) = *J*(6,5) = 8.5, H-2,H-6), 8.26 (d, 2 H, *J*(3,2) = *J*(5,6) = 8.5, H-3,H-5). 13C NMR (CDCl3): 14.4 (2 × CH3), 22.9 (2 × **C**H2CH3), 26.2 (**C**H2CH2CH2O), 26.3 (**C**H2CH2CH2O), 29.6-29.9 (2 × (**C**H2)6, 2 × **C**H2CH2O), 32.2 (2 × **C**H2CH2CH3), 68.4 (CH2O), 68.9 (CH2O), 114.2 (C-5´´), 115.2 (C-3´,C-5´), 116.1 (C-3´´), 124.3 (C-6´´), 126.9 (C-2,C-6), 127.2 (C-2´´), 128.6 (C-2´,C-6´), 131.1 (C-3,C-5), 132.2 (C-1´), 140.8 (C1´´), 146.4 (C-1), 157.6 (C-4´´), 159.8 (C-4´), 164.9 (CO). Elemental analysis: for C43H61ClO4 (677.42): calcd C 76.24, H 9.08, found C 76.18, H 9.12%.

***2-Fluoro-4-(hexyloxy)phenyl 3-fluoro-4´-hexyloxy-1,1´-biphenyl-4-carboxylate (VI/6)****.* Yield 84 %. 1H NMR (CDCl3): 0.88 (t, 6 H, *J* = 6.7, 2 × CH3), 1.20-1.55 (m, 12 H, 2 × (CH2)6), 1.80 (m, 4 H, (2 × OCH2C**H**2), 3.94 (t, 2 H, *J* = 6.7, OCH2), 4.01 (t, 2 H, *J* = 6.7, OCH2), 6.64-6.82 (m, 2 H, (H-3´´,H-5´´), 7.00 (d, 2 H, *J*(3´,2´) = *J*(5´,6´) = 8.8, H-3´,H-5´), 7.15 (dd, 1 H, *J*HF = *J*(6´´,5´´) = 8.8, H-6´´), 7.38 (dd, 1 H, *J*HF = 12.3, *J*(2,6) = 1.8, H-2), 7.46 (dd, 1 H, *J*(6,5) = 8.2, *J*(6,2) = 1.8, H­-6), 7.57 (d, 2 H, *J*(2´,3´) = *J*(6´,5´) = 8.8, H-2´,H-6´), 8.14 (dd, 1 H, *J*(5,6) = *J*HF = 7.9, H-5). 13C NMR (CDCl3): 14.4 (2 × CH3), 22.9 (2 × **C**H2CH3), 26.2 (**C**H2CH2CH2O), 26.3 (**C**H2CH2CH2O), 29.8 (2 × **C**H2CH2O), 32.2 (2 × **C**H2CH2CH3), 68.4 (CH2O), 68.9 (CH2O), 103.6 (d, *J*CF = 21.6, C-3´´), 110.4 (d, *J*CF = 3.3, C-5´´), 115.0 (d, *J*CF = 22.6, C-2), 115.3-115.4 (C-4,C-3´,C-5´), 122.2 (d, *J*CF =  3.3, C-6), 124.1 (d, *J*CF = 2.2, C-6´´), 130.8 (C-1´), 131.5 (d, *J*CF = 13.3, C-1´´), 133.3 (C-5), 148.6 (d, *J*CF = 9.4, C-1), 154.6 (d, *J*CF = 248.9, C-2´´), 158.1 (d, *J*CF = 10.0, C-4´´), 160.3 (C-4´), 162.3 (d, *J*CF= 4.5, CO), 163.1 (d, *J*CF = 261.46, C-3). Elemental analysis: for C31H36F2O4 (510.63): calcd C 72.92, H 7.11, found C 72.79, H 7.03%.

***2-Fluoro-4-(octyloxy)phenyl 3-fluoro-4´-octyloxy-1,1´-biphenyl-4-carboxylate (VI/8)****.* Yield 78 %. 1H NMR (CDCl3): 0.88 (t, 6 H, *J* = 6.7, 2 × CH3), 1.20-1.55 (m, 20 H, 2 × (CH2)5), 1.80 (m, 4 H, 2 × OCH2C**H**2), 3.94 (t, 2 H, *J* = 6.7, OCH2), 4.01 (t, 2 H, *J* = 6.7, OCH2), 6.64-6.82 (m, 2 H, (H-3´´,H-5´´), 7.00 (d, 2 H, *J*(3´,2´) = *J*(5´,6´) = 8.8, H-3´,H-5´), 7.15 (dd, 1 H, *J*HF = *J*(6´´,5´´) = 8.8, H-6´´), 7.38 (dd, 1 H, *J*HF = 12.3, *J*(2,6) = 1.8, H-2), 7.46 (dd, 1 H, *J*(6,5) = 8.2, *J*(6,2) = 1.8, H­-6), 7.57 (d, 2 H, *J*(2´,3´) = *J*(6´,5´) = 8.8, H-2´,H-6´), 8.14 (dd, 1 H, *J*(5,6) = *J*HF = 7.9, H-5). 13C NMR (CDCl3): 14.4 (2 × CH3), 22.9 (2 × **C**H2CH3), 26.2 (**C**H2CH2CH2O), 26.3 (**C**H2CH2CH2O), 29.6-29.9 (2 × (**C**H2)2, 2 × **C**H2CH2O), 32.2 (2 × **C**H2CH2CH3), 68.4 (CH2O), 68.9 (CH2O), 103.6 (d, *J*CF = 21.6, C-3´´), 110.4 (d, *J*CF = 3.3, C-5´´), 115.0 (d, *J*CF = 22.6, C-2), 115.3-115.4 (C-4,C-3´,C-5´), 122.2 (d, *J*CF =  3.3, C-6), 124.1 (d, *J*CF = 2.2, C-6´´), 130.8 (C-1´), 131.5 (d, *J*CF = 13.3, C-1´´), 133.3 (C-5), 148.6 (d, *J*CF = 9.4, C-1), 154.6 (d, *J*CF = 248.9, C-2´´), 158.1 (d, *J*CF = 10.0, C-4´´), 160.3 (C-4´), 162.3 (d, *J*CF= 4.5, CO), 163.1 (d, *J*CF = 261.46, C-3). Elemental analysis: for C35H44F2O4 (566.74): calcd C 74.18, H 7.83, found C 74.12, H 7.69%.

***4-Decyloxy-2-fluorophenyl 4´-decyloxy-3-fluoro-1,1´-biphenyl-4-carboxylate (VI/10)****.* Yield 85 %. 1H NMR (CDCl3): 0.88 (t, 6 H, *J* = 6.7, 2 × CH3), 1.20-1.55 (m, 28 H, 2 × (CH2)7), 1.80 (m, 4 H, (2 × OCH2C**H**2), 3.94 (t, 2 H, *J* = 6.7, OCH2), 4.01 (t, 2 H, *J* = 6.7, OCH2), 6.64‑6.82 (m, 2 H, (H-3´´,H-5´´), 7.00 (d, 2 H, *J*(3´,2´) = *J*(5´,6´) = 8.8, H-3´,H-5´), 7.15 (dd, 1 H, *J*HF = *J*(6´´,5´´) = 8.8, H-6´´), 7.38 (dd, 1 H, *J*HF = 12.3, *J*(2,6) = 1.8, H-2), 7.46 (dd, 1 H, *J*(6,5) = 8.2, *J*(6,2) = 1.8, H­-6), 7.57 (d, 2 H, *J*(2´,3´) = *J*(6´,5´) = 8.8, H-2´,H-6´), 8.14 (dd, 1 H, *J*(5,6) = *J*HF = 7.9, H-5). 13C NMR (CDCl3): 14.4 (2 × CH3), 22.9 (2 × **C**H2CH3), 26.2 (**C**H2CH2CH2O), 26.3 (**C**H2CH2CH2O), 29.6-29.9 (2 × (**C**H2)4, 2 × **C**H2CH2O), 32.2 (2 × **C**H2CH2CH3), 68.4 (CH2O), 68.9 (CH2O), 103.6 (d, *J*CF = 21.6, C-3´´), 110.4 (d, *J*CF = 3.3, C-5´´), 115.0 (d, *J*CF = 22.6, C-2), 115.3-115.4 (C-4,C-3´,C-5´), 122.2 (d, *J*CF =  3.3, C-6), 124.1 (d, *J*CF = 2.2, C-6´´), 130.8 (C-1´), 131.5 (d, *J*CF = 13.3, C-1´´), 133.3 (C-5), 148.6 (d, *J*CF = 9.4, C-1), 154.6 (d, *J*CF = 248.9, C-2´´), 158.1 (d, *J*CF = 10.0, C-4´´), 160.3 (C-4´), 162.3 (d, *J*CF= 4.5, CO), 163.1 (d, *J*CF = 261.46, C-3). Elemental analysis: for C39H52F2O4 (622.84): calcd C 75.21, H 8.42, found C 75.10, H 8.37%.

***4-Dodecyloxy-2-fluorophenyl 4´-dodecyloxy-3-fluoro-1,1´-biphenyl-4-carboxylate (VI/12)****.* Yield 94 %. 1H NMR (CDCl3): 0.88 (t, 6 H, *J* = 6.7, 2 × CH3), 1.20-1.55 (m, 36 H, 2 × (**C**H2)9), 1.80 (m, 4 H, (2 × OCH2C**H**2), 3.94 (t, 2 H, *J* = 6.7, OCH2), 4.01 (t, 2 H, *J* = 6.7, OCH2), 6.64-6.82 (m, 2 H, (H-3´´,H-5´´), 7.00 (d, 2 H, *J*(3´,2´) = *J*(5´,6´) = 8.8, H-3´,H-5´), 7.15 (dd, 1 H, *J*HF = *J*(6´´,5´´) = 8.8, H-6´´), 7.38 (dd, 1 H, *J*HF = 12.3, *J*(2,6) = 1.8, H-2), 7.46 (dd, 1 H, *J*(6,5) = 8.2, *J*(6,2) = 1.8, H­-6), 7.57 (d, 2 H, *J*(2´,3´) = *J*(6´,5´) = 8.8, H-2´, H‑6´), 8.14 (dd, 1 H, *J*(5,6) = *J*HF = 7.9, H-5). 13C NMR (CDCl3): 14.4 (2 × CH3), 22.9 (2 × **C**H2CH3), 26.2 (**C**H2CH2CH2O), 26.3 (**C**H2CH2CH2O), 29.6-29.9 (2 × (**C**H2)6, 2 × **C**H2CH2O), 32.2 (2 × **C**H2CH2CH3), 68.4 (CH2O), 68.9 (CH2O), 103.6 (d, *J*CF = 21.6, C-3´´), 110.4 (d, *J*CF = 3.3, C-5´´), 115.0 (d, *J*CF = 22.6, C-2), 115.3-115.4 (C-4,C-3´,C-5´), 122.2 (d, *J*CF =  3.3, C-6), 124.1 (d, *J*CF = 2.2, C-6´´), 130.8 (C-1´), 131.5 (d, *J*CF = 13.3, C-1´´), 133.3 (C-5), 148.6 (d, *J*CF = 9.4, C-1), 154.6 (d, *J*CF = 248.9, C-2´´), 158.1 (d, *J*CF = 10.0, C-4´´), 160.3 (C-4´), 162.3 (d, *J*CF= 4.5, CO), 163.1 (d, *J*CF = 261.46, C-3). Elemental analysis: for C43H60F2O4 (678.95): calcd C 76.07, H 8.91, found C 75.92, H 8.83%.

***2-Chloro-4-(hexyloxy)phenyl 3-chloro-4´-hexyloxy-1,1´-biphenyl-4-carboxylate (VII/6)****.* Yield 80 %. 1H NMR (CDCl3): 0.88 (t, 6 H, *J* = 6.7, 2 × CH3), 1.20-1.55 (m, 12 H, 2 × (CH2)3), 1.80 (m, 4 H, (2 × OCH2C**H**2), 3.95 (t, 2 H, *J* = 6.7, OCH2), 4.01 (t, 2 H, *J* = 6.7, OCH2), 6.85 (dd, 1 H, *J*(5´´,6´´) = 8.8, *J*(5´´,3´´) = 2.9, H-5´´), 6.95-7.05 (m, 3 H, H-3´,H-5´,H-3´´), 7.19 (d, 1 H, *J*(6´´,5´´) = 8.8, H-6´´), 7.52-7.62 (m, 3 H, H-6,H-2´,H-6´), 7.71 (d, 1 H, *J*(5,6) *=* 1.8, H-2), 8.21 (d, 1 H, *J*(5,6) = 8.2, H-5). 13C NMR (CDCl3): 14.3 (2 × CH3), 22.9 (2 × **C**H2CH3), 26.2 (**C**H2CH2CH2O), 26.3 (**C**H2CH2CH2O), 29.6 (2 × **C**H2CH2O), 32.0 (2 × **C**H2CH2CH3), 68.4 (CH2O), 68.9 (CH2O), 114.2 (C-5´´), 115.3 (C-3´,C-5´), 116.1 (C-3´´), 124.3 (C-6´´), 126.9 (C-6), 126.0 (C-2), 127.4 (C-2´´), 128.6 (C-2´,C-6´), 129.5 (C-5), 130.7 (C-4), 133.1 (C-3), 135.7 (C-1´), 146.5 (C-1), 157.7 (C-4´´), 160.2 (C-4´), 163.3 (CO). Elemental analysis: for C31H36Cl2O4 (543.54): calcd C 68.50, H 6.68, found C 68.38, H 6.55%.

***2-Chloro-4-(octyloxy)phenyl 3-chloro-4´-octyloxy-1,1´-biphenyl-4-carboxylate (VII/8)****.* Yield 64 %. 1H NMR (CDCl3): 0.88 (t, 6 H, *J* = 6.7, 2 × CH3), 1.20-1.55 (m, 20 H, 2 × (CH2)5), 1.80 (m, 4 H, (2 × OCH2C**H**2), 3.95 (t, 2 H, *J*) = 6.7, OCH2), 4.01 (t, 2 H, *J* = 6.7, OCH2), 6.85 (dd, 1 H, *J*(5´´,6´´) = 8.8, *J*(5´´,3´´) = 2.9, H-5´´), 6.95-7.05 (m, 3 H, H-3´,H-5´,H-3´´), 7.19 (d, 1 H, *J*(6´´,5´´) = 8.8, H-6´´), 7.52-7.62 (m, 3 H, H-6, H-2´,H-6´), 7.71 (d, 1 H, *J*(5,6) *=* 1.8, H-2), 8.21 (d, 1 H, *J*(5,6) = 8.2, H-5). 13C NMR (CDCl3): 14.3 (2 × CH3), 22.9 (2 × **C**H2CH3), 26.2 (**C**H2CH2CH2O), 26.3 (**C**H2CH2CH2O), 29.4-29.6 (2 × (**C**H2)2, 2 × **C**H2CH2O), 32.0 (2 × **C**H2CH2CH3), 68.4 (CH2O), 68.9 (CH2O), 114.2 (C-5´´), 115.3 (C-3´,C-5´), 116.1 (C-3´´), 124.3 (C-6´´), 126.9 (C-6), 126.0 (C-2), 127.4 (C-2´´), 128.6 (C-2´,C-6´), 129.5 (C-5), 130.7 (C-4), 133.1 (C-3), 135.7 (C-1´), 146.5 (C-1), 157.7 (C-4´´), 160.2 (C-4´), 163.3 (CO). Elemental analysis: for C35H44Cl2O4 (599.64): calcd C 70.11, H 7.40, found C 70.01, H 7.29%.

***2-Chloro-4-(decyloxy)phenyl 3-chloro-4´-decyloxy-1,1´-biphenyl-4-carboxylate (VII/10)****.* Yield 95 %. 1H NMR (CDCl3): 0.88 (t, 6 H, *J* = 6.7, 2 × CH3), 1.20-1.55 (m, 28 H, 2 × (CH2)7), 1.80 (m, 4 H, 2 × OCH2C**H**2), 3.95 (t, 2 H, *J* = 6.7, OCH2), 4.01 (t, 2 H, *J* = 6.7, OCH2), 6.85 (dd, 1 H, *J*(5´´,6´´) = 8.8, *J*(5´´,3´´) = 2.9, H-5´´), 6.95-7.05 (m, 3 H, H-3´,H-5´,H-3´´), 7.19 (d, 1 H, *J*(6´´,5´´) = 8.8, H-6´´), 7.52-7.62 (m, 3 H, H-6,H-2´,H-6´), 7.71 (d, 1 H, *J*(5,6) *=* 1.8, H-2), 8.21 (d, 1 H, *J*(5,6) = 8.2, H-5). 13C NMR (CDCl3): 14.3 (2 × CH3), 22.9 (2 × **C**H2CH3), 26.2 (**C**H2CH2CH2O), 26.3 (**C**H2CH2CH2O), 29.4-29.6 (2 × (**C**H2)4, 2 × **C**H2CH2O), 32.0 (2 × **C**H2CH2CH3), 68.4 (CH2O), 68.9 (CH2O), 114.2 (C-5´´), 115.3 (C-3´,C-5´), 116.1 (C-3´´), 124.3 (C-6´´), 126.9 (C-6), 126.0 (C-2), 127.4 (C-2´´), 128.6 (C-2´,C-6´), 129.5 (C-5), 130.7 (C-4), 133.1 (C-3), 135.7 (C-1´), 146.5 (C-1), 157.7 (C-4´´), 160.2 (C-4´), 163.3 (CO). Elemental analysis: for C39H52Cl2O4 (655.74): calcd C 71.44, H 7.99, found C 71.30, H 8.03%.

***2-Chloro-4-(dodecyloxy)phenyl 3-chloro-4´-dodecyloxy-1,1´-biphenyl-4-carboxylate (VII/12)****.* Yield 91 %. 1H NMR (CDCl3): 0.88 (t, 6 H, *J* = 6.7, 2 × CH3), 1.20-1.55 (m, 36 H, 2 × (CH2)9), 1.80 (m, 4 H, (2 × OCH2C**H**2), 3.95 (t, 2 H, *J* = 6.7, OCH2), 4.01 (t, 2 H, *J* = 6.7, OCH2), 6.85 (dd, 1 H, *J*(5´´,6´´) = 8.8, *J*(5´´,3´´) = 2.9, H-5´´), 6.95-7.05 (m, 3 H, H-3´,H-5´,H-3´´), 7.19 (d, 1 H, *J*(6´´,5´´) = 8.8, H-6´´), 7.52-7.62 (m, 3 H, H-6,H-2´,H-6´), 7.71 (d, 1 H, *J*(5,6) *=* 1.8, H-2), 8.21 (d, 1 H, *J*(5,6) = 8.2, H-5). 13C NMR (CDCl3): 14.3 (2 × CH3), 22.9 (2 × **C**H2CH3), 26.2 (**C**H2CH2CH2O), 26.3 (**C**H2CH2CH2O), 29.4-29.6 (2 × (**C**H2)6, 2 × **C**H2CH2O), 32.0 (2 × **C**H2CH2CH3), 68.4 (CH2O), 68.9 (CH2O), 114.2 (C-5´´), 115.3 (C-3´,C-5´), 116.1 (C-3´´), 124.3 (C-6´´), 126.9 (C-6), 126.0 (C-2), 127.4 (C-2´´), 128.6 (C-2´,C-6´), 129.5 (C-5), 130.7 (C-4), 133.1 (C-3), 135.7 (C-1´), 146.5 (C-1), 157.7 (C-4´´), 160.2 (C-4´), 163.3 (CO). Elemental analysis: for C43H60Cl2O4 (711.86): calcd C 72.55, H 8.50, found C 72.49, H 8.45%.

***4-(Hexyloxy)phenyl 2,2´-difluoro-4´-hexyloxy-1,1´-biphenyl-4-carboxylate (VIII/6)****.* Yield 40 %. 1H NMR (CDCl3): 0.89 (t, 6 H, *J* = 6.6, 2 × CH3), 1.20-1.55 (m, 12 H, 2 × (CH2)3), 1.78 (q, 2 H, *J* = 6.6, OCH2C**H**2), 1.81 (q, 2 H, *J* = 6.6, OCH2C**H**2), 3.96 (t, 2 H, *J* = 6.3, OCH2), 3.99 (t, 2 H, *J* = 6.3, OCH2), 6.74 (dd, 1 H, *J*(3´,2´-F) = 11.8, *J*(3´,5´) = 2.5, H-3´), 6.80 (dd, 1 H, *J*(5´,6´) = 8.5, *J*(5´,3´) = 2.5, H-5´), 6.93 (d, 2 H, *J*(3´´,2´´) = *J*(5´´,6´´) = 9.1, H-3´´, H-5´´), 7.12 (d, 2 H, *J*(2´´,3´´) = *J*(6´´,5´´) = 9.1, H-2´´,H-6´´), 7.32 (m, 1 H, H-6´), 7.51 (m, 1 H, H-6), 7.95 (dd, 1 H, *J*(3,F) = 10.4, *J*(3,5) = 1.7, H-3), 8.02 (dd, 1 H, *J*(5,6) = 8.2, *J*(5,3) = 1.7, H-5). 13C NMR (CDCl3): 14.4 (CH3), 22.9 (**C**H2CH3), 26.3 (**C**H2CH2CH2O), 30.0 (**C**H2CH2O), 32.1 (**C**H2CH2CH3), 68.4 (CH2O), 68.7 (CH2O), 105.0 (C-3´), 111.8 (C-5´), 114.8 (C-3´´,C-5´´), 115.7 (C-3), 121.9 (C- 1´), 122.5 (C-2´´,C-6´´), 124.6 (C-6´), 127.0 (C-6), 128.1 (C-5), 130.0 (C-1), 130.5 (C- 4), 144.7 (C-1´´), 156.4 (C-4´´), 158.8 (C-2´), 160.0 (C-4´), 162.2 (C-2), 163.4 (CO). Elemental analysis: for C31H36F2O4 (510.63): calcd C 72.92, H 7.11, found C 72.84, H 7.13%.

***4-(Octyloxy)phenyl 2,2´-difluoro-4´-octyloxy-1,1´-biphenyl-4-carboxylate (VIII/8)****.* Yield 41 %. 1H NMR (CDCl3): 0.88 (t, 6 H, *J* = 6.6, 2 × CH3), 1.20-1.55 (m, 20 H, 2 × (CH2)5), 1.78 (q, 2 H, *J* = 6.6, OCH2C**H**2), 1.81 (q, 2 H, *J* = 6.6, OCH2C**H**2), 3.96 (t, 2 H, *J* = 6.3, OCH2), 3.99 (t, 2 H, *J* = 6.3, OCH2), 6.74 (dd, 1 H, *J*(3´,2´-F) = 11.8, *J*(3´,5´) = 2.5, H-3´), 6.80 (dd, 1 H, *J*(5´,6´) = 8.5, *J*(5´,3´) = 2.5, H-5´), 6.93 (d, 2 H, *J*(3´´,2´´) = *J*(5´´,6´´) = 9.1, H-3´´,H-5´´), 7.12 (d, 2 H, *J*(2´´,3´´) = *J*(6´´,5´´) = 9.1, H-2´´,H-6´´), 7.32 (m, 1 H, H-6´), 7.51 (m, 1 H, H-6), 7.95 (dd, 1 H, *J*(3,F) = 10.4, *J*(3,5) = 1.7, H-3), 8.02 (dd, 1 H, *J*(5,6) = 8.2, *J*(5,3) = 1.7, H-5). 13C NMR (CDCl3): 14.4 (CH3), 22.9 (**C**H2CH3), 26.3 (**C**H2CH2CH2O), 30.0 (**C**H2CH2O), 32.1 (**C**H2CH2CH3), 68.4 (CH2O), 68.7 (CH2O), 105.0 (C-3´), 111.8 (C-5´), 114.8 (C-3´´,C-5´´), 115.7 (C-3), 121.9 (C- 1´), 122.5 (C-2´´,C-6´´), 124.6 (C-6´), 127.0 (C-6), 128.1 (C-5), 130.0 (C-1), 130.5 (C-4), 144.7 (C-1´´), 156.4 (C-4´´), 158.8 (C-2´), 160.0 (C-4´), 162.2 (C-2), 163.4 (CO). Elemental analysis: for C35H44F2O4 (566.74): calcd C 74.18, H 7.83, found C 74.09, H 7.78%.

***4-(Decyloxy)phenyl 4´-decyloxy-2,2´-difluoro-1,1´-biphenyl-4-carboxylate (VIII/10)****.* Yield 40 %. 1H NMR (CDCl3): 0.87 (t, 6 H, *J* = 6.6, 2 ×CH3), 1.20-1.55 (m, 28 H, 2 × (CH2)7), 1.78 (q, 2 H, *J* = 6.6, OCH2C**H**2), 1.81 (q, 2 H, *J* = 6.6, OCH2C**H**2), 3.96 (t, 2 H, *J* = 6.3, OCH2), 3.99 (t, 2 H, *J* = 6.3, OCH2), 6.74 (dd, 1 H, *J*(3´,2´-F) = 11.8, *J*(3´,5´) = 2.5, H-3´), 6.80 (dd, 1 H, *J*(5´,6´) = 8.5, *J*(5´,3´) = 2.5, H-5´), 6.93 (d, 2 H, *J*(3´´,2´´) = *J*(5´´,6´´) = 9.1, H-3´´,H-5´´), 7.12 (d, 2 H, *J*(2´´,3´´) = *J*(6´´,5´´) = 9.1, H-2´´,H-6´´), 7.32 (m, 1 H, H-6´), 7.51 (m, 1 H, H-6), 7.95 (dd, 1 H, *J*(3,F) = 10.4, *J*(3,5) = 1.7, H-3), 8.02 (dd, 1 H, *J*(5,6) = 8.2, *J*(5,3) = 1.7, H-5). 13C NMR (CDCl3): 14.4 (CH3), 22.9 (**C**H2CH3), 26.3 (**C**H2CH2CH2O), 30.0 (**C**H2CH2O), 32.1 (**C**H2CH2CH3), 68.4 (CH2O), 68.7 (CH2O), 105.0 (C-3´), 111.8 (C-5´), 114.8 (C-3´´,C-5´´), 115.7 (C-3), 121.9 (C- 1´), 122.5 (C-2´´,C-6´´), 124.6 (C-6´), 127.0 (C-6), 128.1 (C-5), 130.0 (C-1), 130.5 (C- 4), 144.7 (C-1´´), 156.4 (C-4´´), 158.8 (C-2´), 160.0 (C-4´), 162.2 (C-2), 163.4 (CO). Elemental analysis: for C39H52F2O4 (622.84): calcd C 75.21, H 8.42, found C 75.12, H 8.33%.

***4-(Dodecyloxy)phenyl 4´-dodecyloxy-2,2´-difluoro-1,1´-biphenyl-4-carboxylate (VIII/12)****.* Yield 45 %. 1H NMR (CDCl3): 0.87 (t, 6 H, *J* = 6.6, 2 × CH3), 1.20-1.55 (m, 36 H, 2 × (CH2)9), 1.78 (q, 2 H, *J* = 6.6, OCH2C**H**2), 1.81 (q, 2 H, *J* = 6.6, OCH2C**H**2), 3.96 (t, 2 H, *J* = 6.3, OCH2), 3.99 (t, 2 H, *J* = 6.3, OCH2), 6.74 (dd, 1 H, *J*(3´,2´-F) = 11.8, *J*(3´,5´) = 2.5, H-3´), 6.80 (dd, 1 H, *J*(5´,6´) = 8.5, *J*(5´,3´) = 2.5, H-5´), 6.93 (d, 2 H, *J*(3´´,2´´) = *J*(5´´,6´´) = 9.1, H-3´´,H-5´´), 7.12 (d, 2 H, *J*(2´´,3´´) = *J*(6´´,5´´) = 9.1, H-2´´,H-6´´), 7.32 (m, 1 H, H-6´), 7.51 (m, 1 H, H-6), 7.95 (dd, 1 H, *J*(3,F) = 10.4, *J*(3,5) = 1.7, H-3), 8.02 (dd, 1 H, *J*(5,6) = 8.2, *J*(5,3) = 1.7, H-5). 13C NMR (CDCl3): 14.4 (CH3), 22.9 (**C**H2CH3), 26.3 (**C**H2CH2CH2O), 29.4-29.6 ((**C**H2)6, **C**H2CH2O), 32.1 (**C**H2CH2CH3), 68.4 (CH2O), 68.7 (CH2O), 105.0 (C-3´), 111.8 (C-5´), 114.8 (C-3´´,C-5´´), 115.7 (C-3), 121.9 (C- 1´), 122.5 (C-2´´,C-6´´), 124.6 (C-6´), 127.0 (C-6), 128.1 (C-5), 130.0 (C-1), 130.5 (C- 4), 144.7 (C-1´´), 156.4 (C-4´´), 158.8 (C-2´), 160.0 (C-4´), 162.2 (C-2), 163.4 (CO). Elemental analysis: for C43H60F2O4 (678.95): calcd C 76.07, H 8.91, found C 75.97, H 8.80%.

***4-(Hexyloxy)phenyl 2,2´-dichloro-4´-hexyloxy-1,1´-biphenyl-4-carboxylate (IX/6)****.* Yield 23 %. 1H NMR (CDCl3): 0.89 (t, 6H, *J*(6a,5a) = 6.6; 2 × CH3); 1.22-1.55 (m, 12H; 2 × (CH2)3); 1.80 (m, 4H; 2 × OCH2CH2); 3.96 (t, 2H, *J*(1a,2a)= 6.6; OCH2); 3.99 (t, 2H, *J*(1a,2a) = 6.6; OCH2); 6.89 (dd, 1H, *J*(5´,6´) = 8.5, *J*(5´,3´) = 2.5; H-5´); 6.98 (d, 2H, *J*(3´´,2´´) = *J*(5´´,6´´) = 9.1; H-3´´, H-5´´); 7.04 (d, 1H, *J*(3´,5´) = 2.5; H-3´); 7.12 (d, 2H, *J*(2´´,3´´) = *J*(6´´,5´´) = 9.1; H-2´´, H-6´´); 7.17 (d, 1H, *J*(6´,5´) = 8.5; H-6´); 7.42 (d, 1H, *J*(5,6) = 8.0; H-5); 8.11 (dd, 1H, *J*(6,5) = 8.0, *J*(6,2) = 1.7; H-6); 8.30 (d, 1H, *J*(2,6) = 1.7; H-2). 13C NMR (CDCl3): 14.4 (CH3); 22.9 (CH2CH3); 26.3 (CH2CH2CH2O); 30.0 (CH2CH2O); 32.1 (CH2CH2CH3); 68.4 (CH2O); 68.7 (CH2O); 114.8 (C-3´´, C-5´´); 122.4 (C-2´´, C-6´´); 128.9 (C-5); 129.2 (C-6´); 129.6 (C-2); 130.0 (C-6); 130.4 (C-1); 131.9 (C-1´); 133.1 (C-3, C-2´); 139.8 (C-4); 144.9 (C-1´´); 153.0 (C-4´); 156.7 (C-4´´); 162.2 (COO). Elemental analysis: for C31H36Cl2O4 (543.53): calcd C 68.50, H 6.68, found C 68.31, H 6.53%.

***4-(Octyloxy)phenyl 2,2´-dichloro-4´-octyloxy-1,1´-biphenyl-4-carboxylate (IX/8)****.* Yield 32 %. 1H NMR (CDCl3): 0.88 (t, 6H, *J*(6a,5a) = 6.6; 2 × CH3); 1.22-1.55 (m, 20H; 2 × (CH2)5); 1.80 (m, 4H; 2 × OCH2CH2); 3.96 (t, 2H, *J*(1a,2a)= 6.6; OCH2); 3.99 (t, 2H, *J*(1a,2a) = 6.6; OCH2); 6.89 (dd, 1H, *J*(5´,6´) = 8.5, *J*(5´,3´) = 2.5; H-5´); 6.98 (d, 2H, *J*(3´´,2´´) = *J*(5´´,6´´) = 9.1; H-3´´, H-5´´); 7.04 (d, 1H, *J*(3´,5´) = 2.5; H-3´); 7.12 (d, 2H, *J*(2´´,3´´) = *J*(6´´,5´´) = 9.1; H-2´´, H-6´´); 7.17 (d, 1H, *J*(6´,5´) = 8.5; H-6´); 7.41 (d, 1H, *J*(5,6) = 8.0; H-5); 8.12 (dd, 1H, *J*(6,5) = 8.0, *J*(6,2) = 1.7; H-6); 8.30 (d, 1H, *J*(2,6) = 1.7; H-2). 13C NMR (CDCl3): 14.4 (CH3); 22.9 (CH2CH3); 26.3 (CH2CH2CH2O); 29.6 ((CH2)2); 30.0 (CH2CH2O); 32.1 (CH2CH2CH3); 68.4 (CH2O); 68.7 (CH2O); 114.8 (C-3´´, C-5´´); 122.4 (C-2´´, C-6´´); 128.9 (C-5); 129.2 (C-6´); 129.6 (C-2); 130.0 (C-6); 130.4 (C-1); 131.9 (C-1´); 133.1 (C-3, C-2´); 139.8 (C-4); 144.9 (C-1´´); 153.0 (C-4´); 156.7 (C-4´´); 162.2 (COO). Elemental analysis: for C35H44Cl2O4 (599.64): calcd C 70.11, H 7.40, found C 70.09, H 7.33%.

***4-(Decyloxy)phenyl 2,2´-dichloro-4´-decyloxy-1,1´-biphenyl-4-carboxylate (IX/10)****.* Yield 36 %. 1H NMR (CDCl3): 0.87 (t, 6H, *J*(6a,5a) = 6.6; 2 × CH3); 1.22-1.55 (m, 28H; 2 × (CH2)7); 1.80 (m, 4H; 2 × OCH2CH2); 3.96 (t, 2H, *J*(1a,2a)= 6.6; OCH2); 3.99 (t, 2H, *J*(1a,2a) = 6.6; OCH2); 6.89 (dd, 1H, *J*(5´,6´) = 8.5, *J*(5´,3´) = 2.5; H-5´); 6.98 (d, 2H, *J*(3´´,2´´) = *J*(5´´,6´´) = 9.1; H-3´´, H-5´´); 7.04 (d, 1H, *J*(3´,5´) = 2.5; H-3´); 7.12 (d, 2H, *J*(2´´,3´´) = *J*(6´´,5´´) = 9.1; H-2´´, H-6´´); 7.17 (d, 1H, *J*(6´,5´) = 8.5; H-6´); 7.42 (d, 1H, *J*(5,6) = 8.0; H-5); 8.11 (dd, 1H, *J*(6,5) = 8.0, *J*(6,2) = 1.7; H-6); 8.30 (d, 1H, *J*(2,6) = 1.7; H-2). 13C NMR (CDCl3): 14.4 (CH3); 22.9 (CH2CH3); 26.3 (CH2CH2CH2O); 29.6 ((CH2)4); 30.0 (CH2CH2O); 32.1 (CH2CH2CH3); 68.4 (CH2O); 68.7 (CH2O); 114.8 (C-3´´, C-5´´); 122.4 (C-2´´, C-6´´); 128.9 (C-5); 129.2 (C-6´); 129.6 (C-2); 130.0 (C-6); 130.4 (C-1); 131.9 (C-1´); 133.1 (C-3, C-2´); 139.8 (C-4); 144.9 (C-1´´); 153.0 (C-4´); 156.7 (C-4´´); 162.2 (COO). Elemental analysis: for C39H52Cl2O4 (655.74): calcd C 71.44, H 7.99, found C 71.32, H 8.01%.

**2. Results**

Textures were observed under a polarizing microscope on cooling from the isotropic phase. Photos of the LC phases are presented in Figures S3-S7 for the selected compounds.

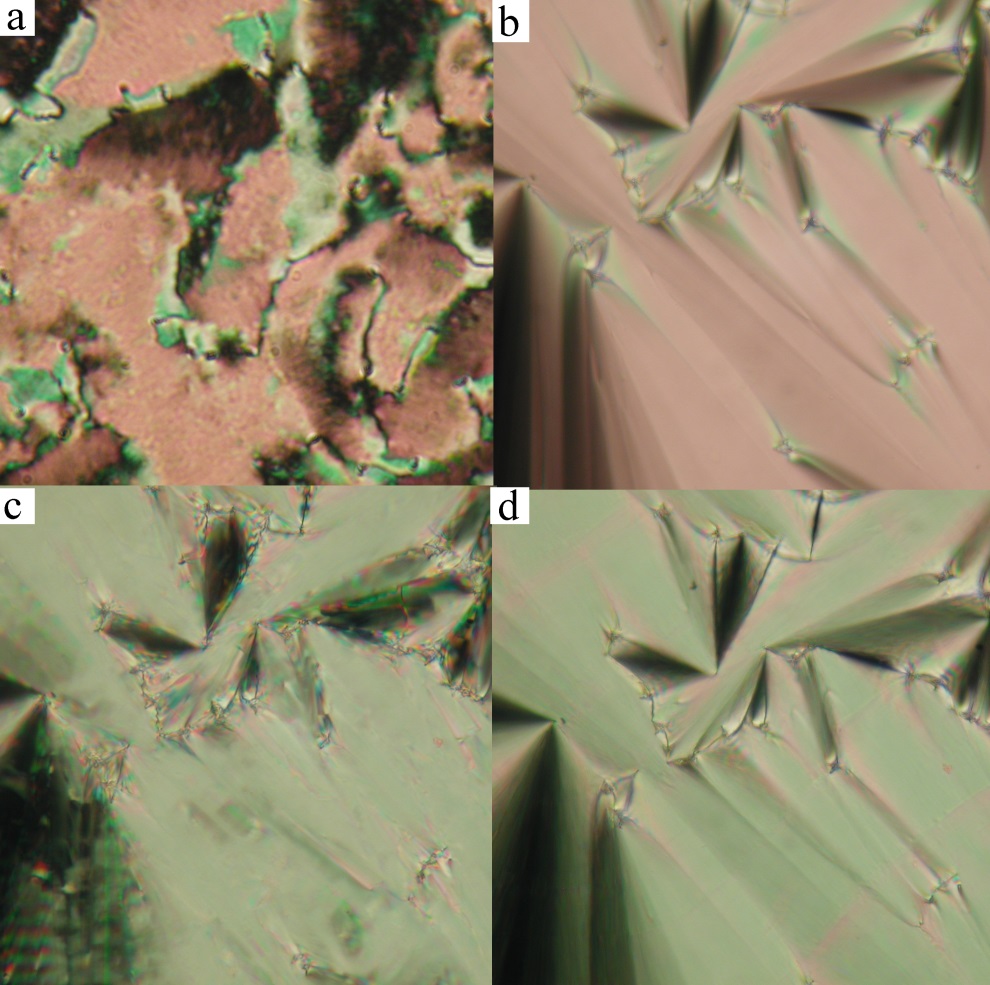


Figure S3 Planar textures of **I/8** in a) nematic phase, b) SmA phase, c) SmC phase, and d) SmB phases.



Figure S4 Planar textures of **II/8** compound in: a) nematic, b) SmA, and c) SmC phases.

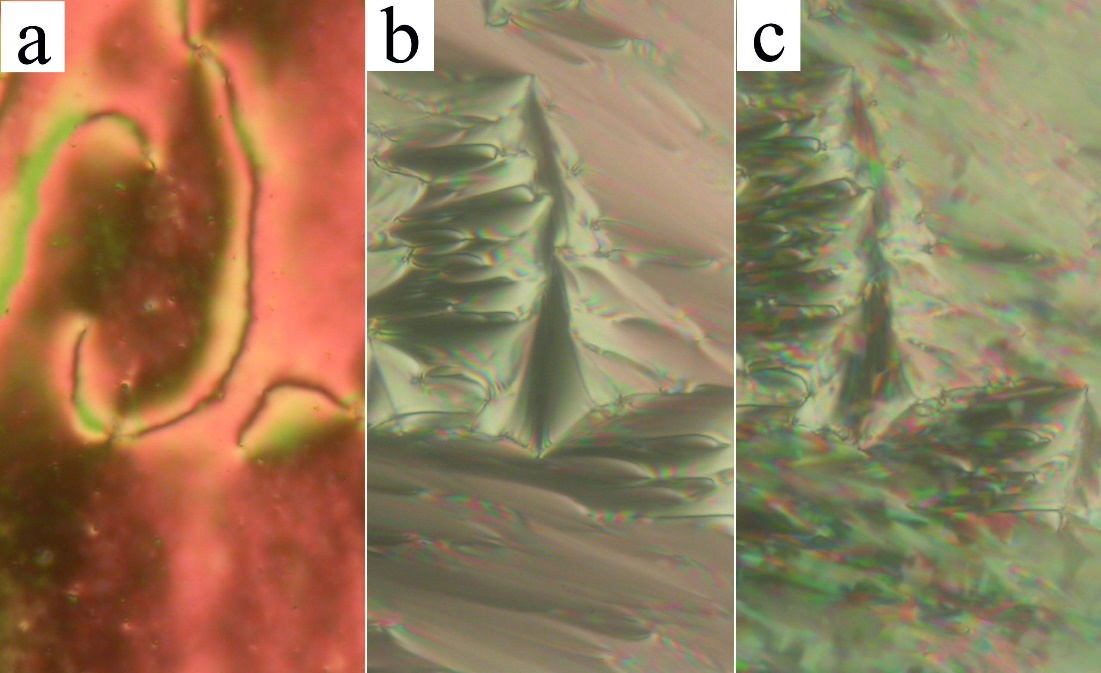


Figure S5 Planar textures of **III/10** compound in a) nematic, b) SmA, and c) SmC phases.

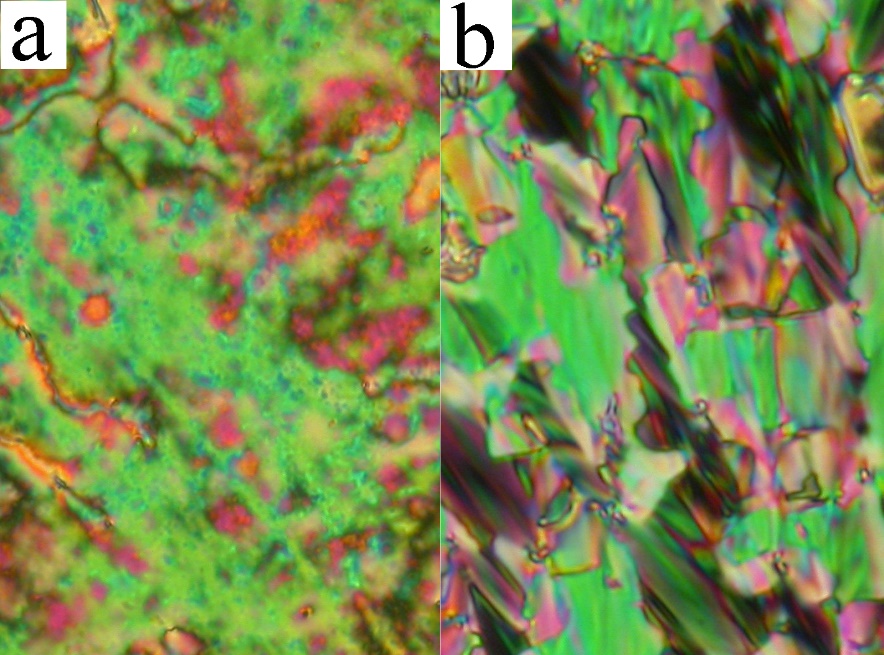


Figure S6 Planar textures of **IV/12** compound in a) nematic, and b) SmC phases.

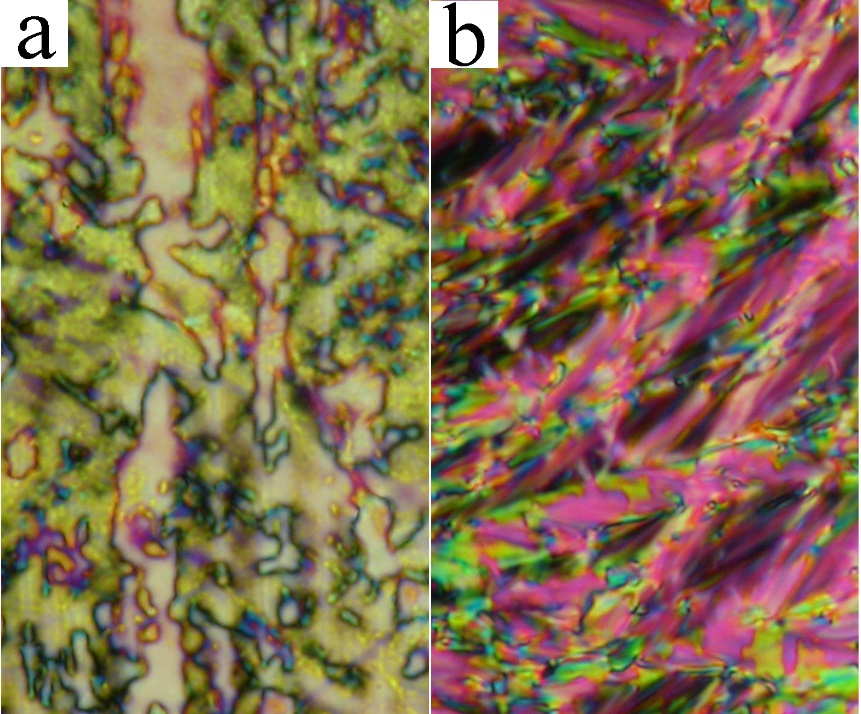


Figure S7 Planar texture of **V/10** compound in a) nematic, and b) SmC phases.

Temperature dependence of the layer spacing values were obtained from the X-ray diffraction data and are presented in Figures S8-S10 for the selected representatives of the studied series.



Figure S8 Temperature dependence of the layer spacing for the selected compound of **II/n** and **III/n** series.



Figure S9 Temperature dependence of the layer spacing for the selected representatives of **IV/n** and **V/n** series.



Figure S10 Temperature dependence of the layer spacing for the longest representatives of **VI/n** and **VII/n** series.

Table S1 Thermal expansion coefficient, α (Å/K), in the SmA phase for the selected compounds**.**

|  |  |
| --- | --- |
| Material | α (Å/K) |
| **II/8** | ‒0.010 |
| **II/12** | ‒0.036 |
| **III/8** | ‒0.008 |
| **III/10** | ‒0.02 |
| **III/12** | ‒0.039 |

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