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Electronic Supplementary Information

Photosensitive chiral self-assembling materials: significant effects of small lateral substituents

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1. General

^{1}H NMR spectra were recorded on Varian Gemini 300 HC instrument; deuteriochloroform ($CDCl_3$) and hexadeuteriodimethyl sulfoxide (DMSO-d_6) were used as solvents and signals of the solvent served as internal standard. Chemical shifts (δ) are given in ppm and *J* values are given in Hz. Numbering of aromatic protons and carbons in materials of series **I** is shown in figure S1 and the signals were identified by APT, gCOSY and gHMBC experiments. For all azo compounds, only spectra of *E*-isomer are given.

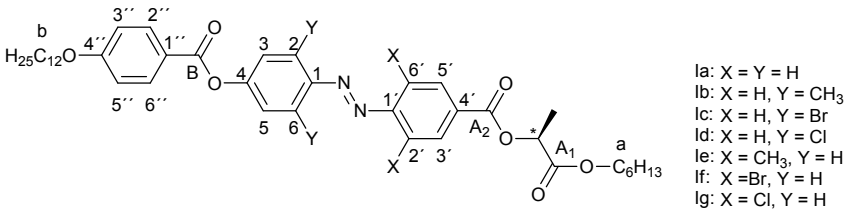


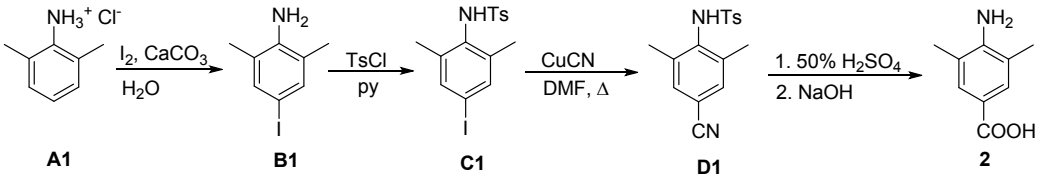
Fig. **S1** Chemical structure of the studied compounds including numbering of atoms.

Elemental analyses were carried out on Elementar vario EL III instrument. The purity of all final compounds was checked by HPLC analysis (high-pressure pump ECOM Alpha; column WATREX Biospher Si 100, 250 × 4 mm, 5 μm; detector WATREX UVD 250) and were found to be >99.8 %. Column chromatography was carried out using Merck Kieselgel 60 (60–100 μm). Enantiomeric purity of chiral compounds was confirmed by chiral HPLC system (chiral column: Daicel Chiralpak AD-3, 150 × 4.6 mm I.D., 3 μm).
4-Amino-3,5-dibromobenzoic acid (**2**), 4-amino-3,5-dichlorobenzoic acid (**3**),
3,5-dichlorophenol (**9**) and the compound **Ia** were obtained by the reported procedures.[S1-S4]

2. Synthesis

2.1. Synthesis of intermediates 2, 5 and 8

4-Amino-3,5-dimethylbenzoic acid (2)
4-Amino-3,5-dimethylbenzoic acid (**2**) was synthesized by a four-step procedure shown in scheme S2. First the 2,6-dimethylanilinium chloride (**A1**) was iodinated in the presence of calcium carbonate and the amino group in the formed iodo aniline **B1** was subsequently protected by a standard tosylation to yield **C1**. Radical cyanation of with copper(I) cyanide afforded the protected nitrile **D1**, hydrolysis of which with sulphuric acid yielded acid **5** in the final step.



Scheme S2 Synthesis of 4-Amino-3,5-dimethylbenzoic acid (**2**)

N-(4-Iodo-2,6-dimethylphenyl) p-toluenesulfonamide (B1)
A mixture of powdered iodine (105.0 g; 0.41 mol) and calcium carbonate (104.40 g; 1.04 mol) was added portion wise to the solution of 2,6-dimethylanilinium chloride (65.0 g; 0.41 mol) in water (350 mL) under vigorous shaking. Then the mixture was allowed to stand for 45 min with occasional agitation, then heated to 60 °C for 5 min, and finally cooled to room temperature. The resulting mixture was extracted with diethyl ether (3 × 150 mL) and dried with anhydrous sodium sulphate. Recrystallization from hexane yielded 4-iodo-2,6-dimethylaniline (**B1**) (93.70 g, 92 %); m.p. 55-56 °C (ref.[S6] 52-53 °C). ^{1}H NMR ($CDCl_3$): 7.24 (2 H, s, H-3, H-5), 3.52 (2 H, br. s. NH), 2.13 (6 H, s, $Ar(CH_3)_2$).

N-(4-Iodo-2,6-dimethylphenyl) p-toluenesulfonamide (C1)
Tosyl chloride (38.80 g; 0.17 mol) was added portion wise to the stirred solution of 4-iodo-2,6-dimethylaniline (45.6 g; 0.19 mol) in pyridine (250 mL) at 0 °C. The mixture was stirred

for 2 h and then the most of the solvent was removed under reduced pressure. The residue was diluted with ethyl acetate (300 mL) and washed with aq. hydrochloric acid (1 : 16, 2 × 100 mL) and water (100 mL). Organic layer was dried with anhydrous magnesium sulphate, the solvent was removed and crystallization from methanol yielded the sulfonamide **C2** (77.20 g, 95 %), m.p 148-150°C. ^{1}H NMR ($CDCl_3$): 7.59 (2 H, d, J = 8.2, Ar-H), 7.37 (2 H, s, Ar-H), 7.26 (2 H, d, J = 8.2, Ar-H), 5.93 (1 H, s, NH), 2.43 (3 H, s, CH_3), 1.98 (6 H, s, 2 × CH_3).

3,5-Dimethyl-4-(p-toluenesulfonamido)benzonitrile (D1)

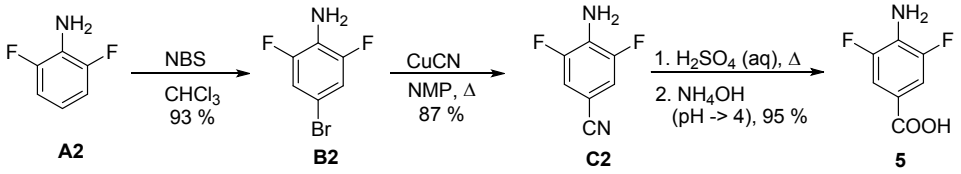
A mixture of sulfonamide **C1** (48.70 g; 0.12 mol) and copper(I) cyanide (17.50 g; 0.20 mol) in DMF (500 mL) was refluxed for 18 h in an argon atmosphere. After cooling, the resulting mixture was filtered and the filtrate poured into water (2000 mL). The white precipitate was filtered off and recrystallized from methanol to yield nitrile **D1** (31.80 g, 91 %), m.p 169-171 °C. ^{1}H NMR ($CDCl_3$): 7.59 (2 H, d, J = 8.2, Ar-H), 7.32 (2 H, s, Ar-H), 7.28 (2 H, d, J = 7.9, Ar-H), 6.16 (1 H, s, NH), 2.44 (3 H, s, CH_3), 2.08 (6 H, s, 2 × CH_3).

4-Amino-3,5-dimethylbenzoic acid (2)

Nitrile **D1** (41.60 g, 0.14 mol) was suspended in 50% aq. sulphuric acid (200 mL). The reaction mixture was heated to 80 °C and vigorously stirred for 2 h. After cooling to room temperature, the mixture was carefully neutralized with 30% aq. sodium hydroxide and the white precipitate was filtered off. Recrystallization from ethanol yielded acid **2** (19.20 g, 83 %). M.p. 250-251°C. ^{1}H NMR (DMSO-d_6): 7.42 (2 H, s, H-3, H-5), 5.31 (2 H, bs, NH_2), 2.08 (6 H, s, 2 × CH_3).

4-Amino-3,5-difluorobenzoic acid (5)

4-Amino-3,5-difluorobenzoic acid (**5**) was synthesized analogously like acid **2** by a three-step procedure shown in scheme S1. First the 2,6-difluoroaniline (**A2**) was brominated by *N*-bromosuccinimide in chloroform yielding aniline **B2**. Radical cyanation of **B2** with copper(I) cyanide afforded the nitrile **C2**. In the final step, hydrolysis of **C2** with sulphuric acid yielded acid **5**.



Scheme S2 Snythesis of 4-Amino-3,5-difluorobenzoic acid (**5**).

4-Bromo-2,6-difluoroaniline (B2)

N-bromosuccinimide (88.50 g, 0.49 mol) was added portion-wise to the solution of 2,6-difluoraniline (**A2**) (54.90 g, 0.41 mol) in chloroform (500 mL) with vigorous stirring at room temperature. Reaction mixture was stirred overnight and the the solid was filtered off. Filtrate was washed with solution of sodium metabisulphite (150 mL, 5%), saturated solution of sodium bicarbonate (200 mL) and brine (200 mL). After drying with anhydrous magnesium sulphate the solvent was evaporated and the crude product purified by flash chromatography on silica using dichloromethane as eluent. Final recrystallization from heptane yielded 79.6 g (93 %) of 4-bromo-2,6-difluoroaniline. m.p. 65-67 °C (ref.[S5] 64-66 °C).^{1}H NMR ($CDCl_3$): 6.99 (2 H, m, H-3, H-5), 3.75 (2 H, bs, NH_2).

4-Amino-3,5-difluoorbenzonitrile (C2)

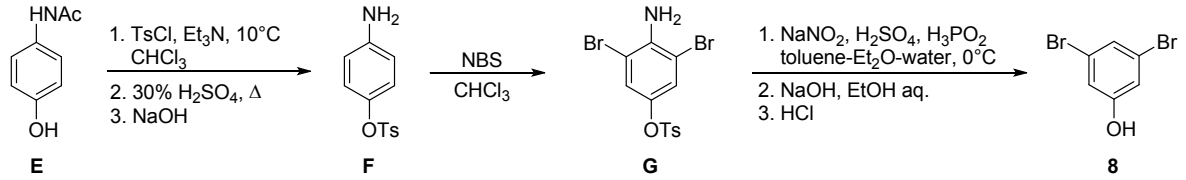
A mixture of copper(I) cyanide (58.5 g, 0.65 mol) and 4-bromo-2,6-difluoroaniline (**B2**) (79 g, 0,38 mol) in *N*-methylpyrolidone (250 mL) was refluxed under anhydrous conditions for 1.5 h. After cooling to room temperature the resulting mixture was filtered and the first portion of product was isolated by maceration of the solid with ethanol (2 × 300 mL). The filtrate was poured into the solution of sodium chloride (700 mL, 30%) with Siegnette's salt (20.0 g) and carefully basified with aqueous ammonia until a white precipitate was formed. White solid product was filtered off and washed with water. Combined portions of crude product were dissolved in dichloromethane and purified by adsorption filtration through a small column of silica. Further recrystallization from ethanol yielded 51.2 g (87 %) 4-Amino-3,5-difluorobenzonitrile. M.p. 110-112 °C (ref[S5] 110-111 °C). ^{1}H NMR ($CDCl_3$): 7.15 (2 H, m, H-2, H-6), 4.28 (2 H, bs, NH_2).

4-Amino-3,5-difluorobenzoic acid (5)

Nitrile **C2** (37.0 g, 0.24 mol) was suspended in 50% aq. sulphuric acid (200 mL). The reaction mixture was heated to 80 °C and vigorously stirred for 2 h. After cooling to room temperature, the mixture was carefully neutralized with 30% aq. sodium hydroxide and the white precipitate was filtered off. Recrystallization from ethanol yielded acid **5** 39.4 g (95 %). M.p. 174-176 °C. ^{1}H NMR (DMSO-d_6): 7.39 (2 H, m, H-2, H-6), 6.08 (2 H, br. s., NH_2).

3,5-Dibromophenol (8)

3,5-Dibromophenol (**8**) was obtained by the synthetic procedure shown in scheme S3. The synthesis started with 4-acetamidophenol (**E**), hydroxyl group of which was first protected by tosylation and the amino group was then released by acid-catalyzed hydrolysis to yield the aniline **F**. Dibromination of **F** with NBS left the bromo aniline **G**. The amino group was removed in a two-step process of diazotation/reduction with H_3PO_2 and finally, hydrolysis of the intermediate tosylate afforded the phenol **8**.



Scheme S3 Synthesis of 3,5-Dibromophenol (**8**).

(4-Aminophenyl) p-toluenesulfonate (F)

A solution of TsCl (19.80 g; 0.10 mol) in dichloromethane (50 mL) was added drop wise to the mixture of 4-acetamidophenol (**E**) (15.0 g; 0.10 mol) and pyridine (15 mL) in dichloromethane (100 mL) at room temperature. The resulting mixture was stirred overnight and then washed with water (100 mL). The solvent was evaporated under reduced pressure and the residue transferred to 30% aq. sulphuric acid (200 mL). The mixture was heated to boiling with stirring until the suspension turned into a clear solution. The mixture was then poured into crushed ice (300 g) and neutralized with aq. sodium hydroxide (10%). The precipitated solid was filtered off and washed with cold water (100 mL) and dried. Yield: 24.50 g (95 %), m.p 146-148°C. ^{1}H NMR ($CDCl_3$): 7.68 (2 H, d, J = 8.2, Ar-H), 7.29 (2 H, d, J = 8.5, Ar-H), 6.73 (2 H, d, J = 8.8, Ar-H), 6.52 (2 H, d, J=8.8, Ar-H), 3.65 (2 H, br. s., NH_2), 2.44 (3 H, s, CH_3).

3,5-Dibromo-4-aminophenyl) p-toluenesulfonate (G)

N-bromosuccinimide (12.80 g; 71.90 mmol) was added portionwise to the solution of aniline **F** (8.6 g; 32.66 mmol) in chloroform (250 mL) and the temperature of the mixture was kept below 35 °C by cold water. The resulting mixture was stirred at room temperature for 19 h and filtered. The filtrate was washed with water (100 mL), 5% aq. sodium sulphite (25 mL), and dried with anhydrous magnesium sulphate. After evaporation of the solvent, the crude product was purified by column chromatography (eluent dichloromethane) and crystallization from hexane. Yield: 13.20 g (96 %), m.p 139-141°C. ^{1}H NMR ($CDCl_3$): 7.70 (2 H, d, J = 8.5, Ar-H), 7.34 (2 H, d, J = 7.9, Ar-H), 7.04 (2 H, s, H-3, H-5), 4.55 (2 H, bs), 2.46 (3 H, s, CH_3).

3,5-Dibromophenol (8)

Aniline **G** (25.40 g; 60.32 mmol) was dissolved in a mixture of toluene (400 mL) and diethyl ether (100 mL) and cooled to 0 °C. A solution of hypophosphoric acid was prepared by mixing sodium hypophosphite monohydrate (32.0 g; 0.30 mol) and sulphuric acid (21.1 mL, 96%) in water (100 mL) and added to the solution of aniline **F**. A solution of sodium nitrite (9.0 g; 0.13 mol) in water (50 mL) was added drop wise under stirring during 1 h. On completion of the addition, the resulting mixture was stirred at 0 °C for 3 h and then allowed to warm to room temperature overnight and extracted with diethyl ether (2 × 100 mL). The combined organic layers were washed with water (50 mL). The solvent was evaporated and the residue dissolved in a mixture of ethanol (150 mL) and aq. sodium hydroxide (4.0 g, 0.1 mol) in water (5 mL). The mixture was stirred at 45 °C for 1 h and then diluted with water (500 mL). The aq. solution was acidified with hydrochloric acid to pH ~ 3, and the phenol **6** was extracted with diethyl ether (3 × 100 mL). The combined organic layers were washed with water (50 mL) and brine (50 mL), and dried with anhydrous magnesium sulphate. The crude product was purified by column chromatography (eluent dichloromethane : acetone, 99.5 : 0.5), and crystallized from hexane to yield 12.50 g (82 %) of **8,** m.p 87-89 °C. ^{1}H NMR ($CDCl_3$): 7.23 (1 H, t, J = 1.6, H-4), 6.96 (2 H, d, J = 1.5, H-2, H-4).

2.2. Synthesis of azo carboxylic acids 11 (see Scheme 1)

4-Hydroxy-2,6-dimethylazobenzene-4'-carboxylic acid (11a)

A solution of ethyl 4-aminobenzoate (**1**) (16.50 g; 100 mmol) in a mixture of conc. H_2SO_4 (14 mL) and acetic acid (100 mL) was diazotized with a solution of sodium nitrite (10 g, 0.14 mol) in water (20 mL) keeping the temperature below 5 °C. The diazonium salt solution was stirred for 30 min and then added in small portions to a solution of 3,5-dimethylphenol (**5**) (12.50 g; 102 mmol) dissolved in the solution of NaOH (84 g, 2.10 mol) in a minimum amount of water at 5 °C. The precipitate was filtered off, stirred with conc. HCl and then filtered again and washed with ice-cold water (50 mL) and dried. The product was purified by crystallization from ethanol to yield 25.60 g (95 %) of acid **11b**, m.p. 233 °C. ^{1}H NMR (DMSO-d_6): 8.08 (2 H, d, J = 8.5, H-2′, H-6′), 7.81 (2 H, d, J = 8.5, H-3′, H-5′), 6.61 (2 H, s, H-3, H-5), 2.43 (6 H, s, 2 × CH_3).

2,6-Dibromo-4-hydroxyazobenzene-4'-carboxylic acid (11b). By the method as for **11a**, diazotation reaction of ethyl 4-aminobenzoate (13.0 g; 78.70 mmol), followed by coupling 3,5-dibromophenol (20.0 g; 79.4 mmol) yielded 28.40 g (90 %) of **11b**, m.p. 252 °C. ^{1}H NMR (DMSO-d_6): 8.16 (2 H, d, J = 8.2, H-2′, H-6′), 7.93 (2 H, d, J = 8.2, H-3′, H-5′), 7.22 (2 H, s, H-3, H-5).

2,6-Dichloro-4-hydroxyazobenzene-4'-carboxylic acid (11c). Diazotation of ethyl 4-aminobenzoate (9.40 g; 56.9 mmol) and coupling 3,5-dichlorophenol (10.20 g; 62.60 mmol) was performed as for **11a**. 13.50 g (70 %) of acid **11c** was isolated, m.p. 229-231 °C. ^{1}H

NMR (DMSO-d_6): 8.14 (2 H, d, J = 8.2, H-2′, H-6′), 7.91 (2 H, d, J = 8.2, H-3′, H-5′), 7.00 (2 H, s, H-3, H-5)

2,6-Difluoro-4-hydroxyazobenzene-4'-carboxylic acid (11d).
Analogously like for **11a**. Diazotation of ethyl4-aminobenzoate (12.70 g; 76.88 mmol) followed by azo coupling with 3,5-difluorophenol (10.0 g; 76.87 mmol) yielded 19.67 g (92 %) of acid **11d**, M.p. 267-270 °C ^{1}H NMR (DMSO-d_6): 8.11 (2 H, d, J = 8.2, H-2, H-6), 7.84 (2 H, d, J = 8.2, H-3, H-5), 6.69 (2 H, d, J = 11.7, H-3′, H-5′). ^{13}C NMR (DMSO-d_6): 166.82 (COO), 162.23 (t, J = 15.2, C-4′), 157.29 (dd, J = 257.4, 7.7, C-2′, C-6′), 155.30 (C-4), 132.59 (C-1), 130.71 (C-2, C-6), 123.42 (t, J = 9.4, C-1′), 122.09 (C-3, C-5), 100.53 (dd, J = 22.5, 2.2, C-3′, C-5′).

4-Hydroxy-2',6'-dimethylazobenzene-4'-carboxylic acid (11e). A solution of 4-amino-3,5-dimethylbenzoic acid (**2**) (7.0 g; 42.37 mmol) and conc. H_2SO_4 (6 mL) in acetic acid (40 mL) was diazotized with a solution of sodium nitrite (3.20 g, 47.83 mmol) in water (5 mL) keeping the temperature below 5 °C The diazonium salt solution was stirred for 30 min and added in small portions to a solution of phenol (4.19 g; 44.5 mmol) dissolved in the solution of NaOH (55.0 g; 1.38 mol) in water (50 mL) at 5 °C. The precipitate was filtered off, stirred with conc. HCl and then filtered again and washed with ice-cold water and dried. Crystallization from ethanol gave rise acid **11e** (8.93 g; 78 %), m.p. 215 °C.^{1}H NMR (DMSO-d_6): 7.74 (2 H, d, J = 8.5, H-2, H-6), 6.64 (2 H, s, H-3′, H-5′), 6.96 (2 H, d, J = 8.5, H-3, H-5).

2',6'-Dibromo-4-hydroxyazobenzene-4'-carboxylic acid (11f). Preparation of acid **11f** was analogous to the preparation of acid **11e**. Starting from acid **3** (10.0 g; 33.90 mmol) and phenol (3.40 g; 36.10 mmol), 9.10 g (67 %) of **11f** was obtained, m.p. 241 °C. ^{1}H NMR (DMSO-d_6): 8.18 (2 H, s, H-3′, H-5′), 7.85 (2 H, d, J = 8.8, H-2, H-6), 6.98 (2 H, d, J = 8.8, H-3, H-5).

2',6'-Dichloro-4-hydroxyazobenzene-4'-carboxylic acid (11g). Acid **11g** was prepared by the same method as for **11e** from acid **4** (16.20 g; 78.60 mmol) and phenol (7.70 g; 81.8 mmol). Yield 20.10 g (82 %) of acid **11g**, m.p. 235 °C. ^{1}H NMR (DMSO-d_6): 8.01 (2 H, s, H-3′, H-5′), 7.84 (2 H, d, J = 8.7, H-2, H-6), 6.98 (2 H, d, J = 8.7, H-3, H-5).

2',6'-Difluoro-4-hydroxyazobenzene-4'-carboxylic acid (11h). Acid **11h** was prepared by the analogous method as **11e** from acid **5** (10.0 g; 57.76 mmol) and phenol (6.0 g; 63.76 mmol). Yield 11.02 g (69 %) of acid **11h**, m.p. 238 °C. ^{1}H NMR (DMSO-d_6): 7.82 (2 H, d, J = 8.8, H-3′, H-5′), 7.72 (2 H, d, J = 8.8, H-2, H-6), 6.98 (2 H, d, J = 8.8, H-3′, H-5′). ^{13}C NMR (DMSO-d_6): 170.07 (COO), 167.83 (C-4′), 159.42 (dd, J_{CF} = 254.4, 4.7, C-3, C-5), 151.21 (C-1′), 138.76 (t, J_{CF} = 11.1, C-4), 137.34 (t, J_{CF} = 7.4, C-1), 130.77 (C-3′, C-5′), 121.41 (C-2′, C-6′), 118.77 (d, J_{CF} = 24.5, C-2, C-6).

2.3. Protection of acids 11

4-(Methoxycarbonyloxy)-2,6-dimethylazobenzene-4'-carboxylic acid (12a).
Acid **11a** (20.0 g; 90.0 mmol) was dissolved in a solution of NaOH (9.0 g; 0.23 mol) in water (150 mL), cooled to 0 °C, and methyl chloroformate (13.90 g; 0.15 mol) was added drop wise under stirring and keeping the temperature below 0 °C. The resulting mixture was left for 2 h at 5 °C, and poured on crushed ice. After acidification with conc. HCl to pH=2, the precipitate was filtered and washed with cold water (20 mL). Crystallization from ethanol yielded 25.1 g (85%) of acid **12a**, m.p. 179 °C. ^{1}H NMR (DMSO-d_6): 8.11 (2 H, d, J = 8.2, H-3′, H-5′), 7.87

(2 H, d, *J* = 8.2, H-2′, H-6′), 7.11 (2 H, s, H-3, H-5), 3.85 (3 H, s, OCH_3), 2.35 (6 H, s, 2 × CH_3).

2,6-Dibromo-4-(methoxycarbonyloxy)azobenzene-4'-carboxylic acid (12b). Analogously as above starting with acid **11a** (6.0 g; 15.0 mmol), 6.39 g (93 %) of acid **12b** was obtained, m.p. 221 °C. ^{1}H NMR (DMSO-d_6): 8.20 (2 H, d, *J* = 8.2, H-3′, H-5′), 8.01 (2 H, d, *J* = 8.2, H-2′, H-6′), 7.91 (2 H, s, H-3, H-5), 3.87 (3 H, s, OCH_3).

2,6-Dichloro-4-(methoxycarbonyloxy)azobenzene-4'-carboxylic acid (12c). In the same way, protection of acid **11a** (2.70 g; 8.80 mmol) yielded 3.0 g (92 %) of **12c**, m.p. 202-204 °C. ^{1}H NMR (DMSO-d_6): 8.19 (2 H, d, *J* = 8.2, H-3′, H-5′), 7.98 (2 H, d, *J* = 8.2, H-2′, H-6′), 7.76 (2 H, s, H-3, H-5), 3.88 (3 H, s, OCH_3).

2,6-Difluoro-4-(methoxycarbonyloxy)azobenzene-4'-carboxylic acid (12d). Following the same procedure as for acid **12a**, starting from acid **11d** (2.0 g, 7.19 mmol), 2.30 g (95 %) of **12d** was obtained. M.p. 226-227 °C. ^{1}H NMR (DMSO-d_6): 8.16 (2 H, d, *J* = 8.2, H-2, H-6), 7.95 (2 H, d, *J* = 8.2, H-3, H-5), 7.50 (2 H, d, *J* = 10.9, H-3′, H-5′), 3.89 (3 H, s, OCH_3). ^{13}C NMR (DMSO-d_6): 166.75 (COO), 155.32 (dd, *J* = 257.04, 6.1, C-2′, C-6′), 154.74 (C-4), 152.47 (t, *J* = 14.6, C-4′), 152.42 (OCOO), 133.75 (C-1), 130.81 (C-2, C-6), 128,39 (t, *J* = 9.6, C-1′), 122.64 (C-3, C-5), 107.58 (dd, *J* = 24.0, 3.6, C-3′, C-5′), 55.51 (OCH_3).

4-(Methoxycarbonyloxy)-2',6'-dimethylazobenzene-4'-carboxylic acid (12e). Preparation of acid **12e** was analogous: protection of acid **11a** (5.70 g; 21.08 mmol) gave rise to 6.0 g (87 %) of **12e**, m.p. 198-199 °C. ^{1}H NMR (DMSO-d_6): 7.97 (2 H, d, *J* = 8.5, H-2, H-6), 7.76 (2 H, s, H-3′, H-5′), 7.51 (2 H, d, *J* = 8.5, H-3, H-5), 3.87 (3 H, s, OCH_3), 2.27 (6 H, s, 2 × CH_3).

2',6'-Dibromo-4-(methoxycarbonyloxy)azobenzene-4'-carboxylic acid (12f). Starting with acid **11f** (23.50 g; 58.75 mmol), 25.0 g (93 %) of acid **12f** was isolated, m.p. 217 °C. ^{1}H NMR (DMSO-d_6): 8.19 (2 H, s, H-3′, H-5′), 8.03 (2 H, d, *J* = 9.0, H-2, H-6), 7.55 (3 H, d, *J* = 9.0, H-3, H-5), 3.86 (3 H, s, OCH_3).

2',6'-Dichloro-4-(methoxycarbonyloxy)azobenzene-4'-carboxylic acid (12g). Finally, acid **11g** (6.70 g; 21.53 mmol) yielded 7.70 g (96 %) of **12g**, m.p. 210-211 °C. ^{1}H NMR (DMSO-d_6): 7.94-8.09 (4 H, m, H-3′, H-5′, H-2, H-6), 7.54 (2 H, d, *J* = 9.1, H-3, H-5), 3.86 (3 H, s, OCH_3).

2.4. Introduction of the chiral terminal chain to compound 12a-g

(S)-1-(Hexyloxy)-1-oxopropan-2-yl 4-((4-((methoxycarbonyl)oxy)-2,6-dimethylphenyl)diazenyl)benzoate (13a) A solution of acid **12a** (25.10 g; 76.45 mmol) in thionyl chloride (200 mL) was heated to boiling for 10 h After the thionyl chloride was distilled off, the residue was diluted once with toluene (100 mL) and evaporated. Yield 24.12 g of the crude acid chloride of **12a**, which was used in the next step without further purification. ^{1}H NMR ($CDCl_3$): 8.28 (2 H, d, *J* = 8.5, H-3′, H-5′), 7.94 (2 H, d, *J* = 8.5, H-2′, H-6′), 7.00 (2 H, s, H-3, H-5), 3.93 (3 H, s, OCH_3), 2.47 (6 H, s, 2 × CH_3).
To a solution of hexyl lactate (14.6 g; 80 mmol) in dry dichloromethane (150 mL) and pyridine (7 mL) cooled to -20 °C, a solution of the acid chloride in dry dichloromethane (250 mL) was added drop wise to the cooled mixture and stirred for additional 3 h. Then the reaction mixture was refluxed for 3 h and then poured int 5% aq. HCl (200 mL). The organic layer was separated and washed with water, and dried with anhydrous magnesium sulphate. The solvent was removed under reduced pressure and the resulting viscous red oil of **13a**

(30.34 g, 90 %) was used in the next step without further purification. ^{1}H NMR ($CDCl_3$): 8.24 (2 H, d, *J* = 8.2, H-3′, H-5′), 7.91 (2 H, d, *J* = 8.2, H-2′, H-6′), 6.98 (2 H, s, H-3, H-5), 5.36 (1 H, q, *J* = 7.0, C*H), 4.14-4.21 (2 H, m, C*HCOOC**H**$_2$), 3.93 (3 H, s, OCH_3), 2.44 (6 H, s, 2 × Ar–CH_3), 1.48-1.72 (5 H, m, $COOCH_2C$**H**$_2$, C*C**H**$_3$), 1.15-1.44 (6 H, m, $(CH_2)_3$), 0.89 (3 H, t, *J* = 6.7, CH_2C**H**$_3$).

(S)-1-(Hexyloxy)-1-oxopropan-2-yl 4-((2,6-dibromo-4-((methoxycarbonyl)oxy)phenyl)diazenyl)benzoate (13b) Preparation of ester **13b** was analogous to the preparation of ester **13a**. From 6.39 g (13.95 mmol) of acid **12c** and 50 mL of thionyl chloride 7.10 g (14.90 mmol) of acid chloride was obtained. ^{1}H NMR ($CDCl_3$): 8.00 (2 H, d, *J* = 8.8), 7.73 (2 H, d, *J* = 8.8, H-2′, H-6′),), 7.52 (2 H, s, H-3, H-5), 3.97 (3 H, s, OCH_3). Acid chloride of **12b** (7.10 g, 14.90 mmol), hexyl lactate (3.0 g, 17.20 mmol) and pyridine (14 mL) in dry dichloromethane (100 mL) yielded 9.0 g (98 %) of **13b**. ^{1}H NMR ($CDCl_3$): 8.27 (2 H, d, *J* = 8.8, H-3′, H-5′), 8.03 (2 H, d, *J* = 8.8, H-2′, H-6′), 7.55 (2 H, s, H-3, H-5), 5.36 (1 H, q, *J* = 6.95, C*H), 4.14 - 4.21 (2 H, m, C*HCOOC**H**$_2$), 3.93 (3 H, s, OCH_3), 1.48 - 1.72 (5 H, m, $COOCH_2C$**H**$_2$, C*C**H**$_3$), 1.15 - 1.44 (6 H, m, $(CH_2)_3$), 0.89 (3 H, t, *J* = 6.7, CH_2C**H**$_3$).

(S)-1-(Hexyloxy)-1-oxopropan-2-yl 4-((2,6-dichloro-4-((methoxycarbonyl)oxy)phenyl)diazenyl)benzoate (13c). Preparation of ester **13c** was analogous to the preparation of ester **13a**. From **12c** (3.0 g, 8.13 mmol) and thionyl chloride (50 mL) 3.10 g of acid chloride was obtained. ^{1}H NMR ($CDCl_3$): 8.32 (2 H, d, *J* = 9.0, H-3′, H-5′), 8.04 (2 H, d, *J* = 9.0, H-2′, H-6′), 7.36 (2 H, s, H-3, H-5), 3.96 (3 H, s, OCH_3). Acid chloride of **12c** (3.1 g, 8.0 mmol), hexyl lactate (1.50 g, 8.60 mmol) and pyridine (0.7 mL) in dry dichloromethane (50 mL) yielded 4.0 g (95 %) of **13c**. ^{1}H NMR ($CDCl_3$)*:* 8.27 (2 H, d, *J* = 8.4, H-3′, H-5′), 7.99 (2 H, d, *J* = 8.4, H-2′, H-6′), 7.35 (2 H, s, H-3, H-5), 5.36 (1 H, q, *J* = 6.95, C*H), 4.14 - 4.21 (2 H, m, C*HCOOC**H**$_2$), 3.93 (3 H, s, OCH_3), 1.48 - 1.72 (5 H, m, $COOCH_2C$**H**$_2$, C*C**H**$_3$), 1.15 - 1.44 (6 H, m, $(CH_2)_3$), 0.89 (3 H, t, *J* = 6.7, CH_2C**H**$_3$).

(S)-1-(Hexyloxy)-1-oxopropan-2-yl 4-((2,6-difluoro-4-((methoxycarbonyl)oxy)phenyl)diazenyl)benzoate (13d). Preparation of ester **13d** was analogous to the preparation of ester **13a**. From **12d** (1.60 g, 4.76 mmol) and thionyl chloride (30 mL) 1.51 g of acid chloride was obtained. Acid chloride of **12d** (1.51 g, 4.26 mmol), hexyl lactate (0.92 g, 5.27 mmol) and pyridine (1.0 mL) in dry dichloromethane (100 mL) yielded 2.0 g (87 %) of **13d**. ^{1}H NMR ($CDCl_3$): 8.24 (2 H, d, *J* = 8.5, H-2, H-6), 7.96 (2 H, d, *J* = 8.5, H-3, H-5), 7.02 (2 H, d, *J* = 9.4, H-3′, H-5′), 5.35 (1 H, q, *J* = 7.0, CH*), 4.10 – 4.26 (2 H, m, CH*COOC**H**$_2$), 3.96 (3 H, s, OCH_3), 1.65 (5 H, m, $COOCH_2C$**H**$_2$, CH*C**H**$_3$), 1.24 – 1.40 (6 H, m, $(CH_2)_3$), 0.87 (3 H, t, *J* = 6.7, CH_2C**H**$_3$). ^{13}C NMR ($CDCl_3$): 170.69 (C-A1), 165.21 (C-A2), 155.69 (C-4), 156.16 (dd, *J* = 240.0, 6.0, C-2′, C-6′), 152.81 (OCOO), 152.15 (t, *J* = 13.8, C-4′), 131.97 (C-1), 130.89 (C-2, C-6), 129.08 (t, *J* = 9.7, C-1′), 122.73 (C-3, C-5), 106.32 (dd, *J* = 24.0, 3.8, C-3′, C-5′), 69.53 (CH*), 65.61 (OCH_2), 55.95 (OCH_3), 31.31 (**C**$H_2CH_2CH_3$), 28.42 (**C**H_2CH_2O), 25.41 (**C**$H_2CH_2CH_2O$), 22.48 (**C**H_2CH_3), 17.11 (**C**H_3CH*), 13.95 (**C**H_3CH_2).

(S)-1-(Hexyloxy)-1-oxopropan-2-yl 4-((4-((methoxycarbonyl)oxy)phenyl)diazenyl)-3,5-dimethylbenzoate (13e). Preparation of ester **13e** was analogous to the preparation of ester **13a**. From **12e** (6.0 g, 18.27 mmol) and thionyl chloride (50 mL) 6.10 g of acid chloride was obtained. ^{1}H NMR ($CDCl_3$): 7.98 (2 H, d, *J* = 8.8, H-2, H-6), 7.89 (2 H, s, H-3′, H-5′), 7.38 (2 H, d, *J* = 8.8, H-3, H-5), 3.96 (3 H, s, OCH_3), 2.30 (6 H, s, 2xCH_3). Acid chloride of **12e** (6.1 g, 17.59 mmol), hexyl lactate (3.2 g, 18.37 mmol) and pyridine (6 mL) in dry

dichloromethane (50 mL) yielded 8.20 g (93 %) of **13e**. ^{1}H NMR ($CDCl_3$): 7.96 (2 H, d, *J* = 8.7, H-2, H-6), 7.85 (2 H, s, H-3′, H-5′), 7.37 (2 H, d, *J* = 8.7, H-3, H-5), 5.36 (1 H, q, *J* = 6.95, C*H), 4.06 - 4.27 (2 H, m, C*HCOOC**H**$_2$), 3.95 (3 H, s, OCH_3), 2.31 (6 H, s, 2xAr-CH_3), 1.59 - 1.73 (5 H, m, $COOCH_2CH_2$, C*C**H**$_3$), 1.14 - 1.45 (6 H, m, $(CH_2)_3$), 0.90 (3 H, t, *J* = 6.7, CH_2CH_3)

(S)-1-(Hexyloxy)-1-oxopropan-2-yl 3,5-dibromo-4-((4-((methoxycarbonyl)oxy)phenyl)diazenyl)benzoate (13f). Preparation of ester **13f** was analogous to the preparation of ester **13a**. From **12f** (15.0 g, 32.74 mmol) and thionyl chloride (200 mL) 14.40 g of acid chloride was obtained. ^{1}H NMR ($CDCl_3$): 8.29 (2 H, s, H-3′, H-5′), 8.04 (2 H, d, *J* = 8.8, H-2, H-6), 7.31 (2 H, d, *J* = 8.8, H-3, H-5), 3.91 (3 H, s, OCH_3). Acid chloride of **12f** (14.4 g, 30.13 mmol), hexyl lactate (6.0 g, 34.43 mmol) and pyridine (2.8 mL) in dry dichloromethane (250 mL) yielded 15.0 g (81 %) of **13f**. ^{1}H NMR ($CDCl_3$): 8.31 (2 H, s, H-3′, H-5′), 8.02 (2 H, d, *J* = 8.7, H-2, H-6), 7.38 (2 H, d, *J* = 8.7, H-3, H-5), 5.36 (1 H, q, *J* = 6.95, C*H), 4.14 - 4.21 (2 H, m, C*H–COOC**H**$_2$), 3.93 (3 H, s, OCH_3), 1.48 - 1.72 (5 H, m, $COOCH_2CH_2$, C*C**H**$_3$), 1.15 - 1.44 (6 H, m, $(CH_2)_3$), 0.89 (3 H, t, *J* = 6.7, CH_2CH_3).

(S)-1-(Hexyloxy)-1-oxopropan-2-yl 3,5-dichloro-4-((4-((methoxycarbonyl)oxy)phenyl)diazenyl)benzoate (13g). Preparation of ester **13g** was analogous to the preparation of ester **13a**. From **12g** (7.70 g, 20.85 mmol) and thionyl chloride (100 mL) 7.91 g of acid chloride was obtained. ^{1}H NMR (DMSO-d_6): 8.05 (2 H, s, H-3′, H-5′), 8.03 (2 H, d, *J* = 8.8, H-2, H-6), 7.55 (3 H, d, *J* = 8.8, H-3, H-5), 3.86 (3 H, s, OCH_3). Acid chloride of **12g** (7.91 g, 20.41 mmol), hexyl lactate (4.4 g, 25.25 mmol) and pyridine (2.1 mL) in dry dichloromethane (100 mL) yielded 9.53 g (89 %) of **13g**. ^{1}H NMR ($CDCl_3$): 8.11 (2 H, s, H-3′, H-5′), 8.03 (2 H, d, *J* = 8.9, H-2, H-6), 7.39 (2 H, d, *J* = 8.9, H-3, H-5), 5.37 (1 H, q, *J* = 7.0, C*H), 4.14 - 4.21 (2 H, m, C*H–COOC**H**$_2$), 3.95 (3 H, s, OCH_3), 1.48 - 1.72 (5 H, m, $COOCH_2CH_2$, C*C**H**$_3$), 1.15 - 1.44 (6 H, m, $(CH_2)_3$), 0.89 (3 H, t, *J* = 6.7, CH_2CH_3).

2.5. Deprotection of compounds 13a-g

(S)-1-(Hexyloxy)-1-oxopropan-2-yl 4-((4-hydroxy-2,6-dimethylphenyl)diazenyl)benzoate (14a)

To a solution of ester **14a** (30.34 g; 62.6 mmol) in THF (250 mL), cooled to -20 °C, 25% aq. ammonia (50 mL) was added in small portions with stirring. The reaction progress was monitored by TLC. After 40 min, chloroform was added (500 mL) and the mixture was poured into water (200 mL) and acidified with 5% aq. HCl to pH = 3. The organic layer was separated, washed with water (100 mL) and dried with anhydrous sodium sulphate. The solvent was evaporated and the residue was rapidly stirred with hexane for 15 min and left in the refrigerator at -20 °C to crystalize. The deposited crystals were rapidly filtered off and dried at reduced pressure to yield 22.12 g (83 %) of **14a** as a viscous liquid. ^{1}H NMR ($CDCl_3$): 8.18 (2 H, d, *J* = 8.5, H-3′, H-5′), 7.80 (2 H, d, *J* = 8.5, H-2′, H-6′), 6.59 (2 H, s, H-3, H-5), 5.32 (1 H, q, *J* = 7.0, C*H), 4.14-4.21 (2 H, m, C*HCOOC**H**$_2$), 2.52 (6 H, s, 2 × Ar-CH_3), 1.48-1.72 (5 H, m, $COOCH_2CH_2$, C*C**H**$_3$), 1.15-1.44 (6 H, m, $(CH_2)_3$), 0.89 (3 H, t, *J* = 6.7, CH_2CH_3).

(S)-1-(Hexyloxy)-1-oxopropan-2-yl 4-((2,6-dibromo-4-hydroxyphenyl)diazenyl)benzoate (14b). Preparation of ester **14b** was analogous to the preparation of phenol **14a**. Hydrolysis of **13b** (9.0 g, 14.65 mmol) with aqueous ammonia (4.8 ml, 25%) in THF (150 mL)-chloroform (150 mL) mixture yielded 5.63 g (69 %). ^{1}H NMR ($CDCl_3$): 8.25 (2 H, d, *J* = 8.7), 7.94 (2 H, d, *J* = 8.7), 7.15 (2 H, s), 5.37 (1 H, q, *J* = 6.95, C*H), 4.14 - 4.21 (2 H, m, C*HCOOC**H**$_2$),

1.48 - 1.72 (5 H, m, $COOCH_2C\mathbf{H}_2$, C*$C\mathbf{H}_3$), 1.15 - 1.44 (6 H, m, $(CH_2)_3$), 0.89 (3 H, t, J = 6.7, $CH_2C\mathbf{H}_3$).

(S)-1-(Hexyloxy)-1-oxopropan-2-yl 4-((2,6-dichloro-4-hydroxyphenyl)diazenyl)benzoate (14c). Preparation of ester **14c** was analogous to the preparation of phenol **14a**. Hydrolysis of **13c** (4.0 g, 7.61 mmol) with aqueous ammonia (3.0 ml, 25%) in a THF (100 mL)-chloroform (100 mL) mixture yielded 2.50 g (70 %). ^{1}H NMR ($CDCl_3$): 8.23 (2 H, d, J = 8.5), 7.95 (2 H, d, J = 8.5), 6.94 (2 H, s), 5.38 (1 H, q, J = 6.95, C*H), 4.14 - 4.21 (2 H, m, C*$HCOOC\mathbf{H}_2$), 1.48 - 1.72 (5 H, m, $COOCH_2C\mathbf{H}_2$, C*$C\mathbf{H}_3$), 1.15 - 1.44 (6 H, m, $(CH_2)_3$), 0.89 (3 H, t, J = 6.7, $CH_2C\mathbf{H}_3$).

(S)-1-(Hexyloxy)-1-oxopropan-2-yl 4-((2,6-difluoro-4-hydroxyphenyl)diazenyl)benzoate (14d). Preparation of ester **14d** was analogous to the preparation of phenol **14a**. Hydrolysis of **13d** (2.0 g, 4.06 mmol) with aqueous ammonia (1.6 ml, 25%) in a THF 50 mL)-chloroform (100 mL) mixture yielded 1.26 g (71 %). M.p. 81-83 °C. ^{1}H NMR ($CDCl_3$): 8.13 (2 H, d, J = 8.8, H-2, H-6, 7.83 (2 H, d, J = 8.8, H-3, H-5), 7.11 (1 H, br. s, OH), 6.45 (2 H, d, J = 10.6, H-3′, H-5′), 5.34 (1 H, q, J = 7.4, CH*), 4.22 (2 H, m, CH*$COOC\mathbf{H}_2$), 1.69 (5 H, m, $COOCH_2C\mathbf{H}_2$, CH*$C\mathbf{H}_3$), 1.22 – 1.44 (6 H, m, $(CH_2)_3$), 0.88 (3 H, t, J = 6.7, $CH_2C\mathbf{H}_3$). ^{13}C NMR ($CDCl_3$): 171.81 (C-A1), 165.46 (C-A2), 159.51 (t, J = 15.0, C-4′), 157.62 (dd, J = 261.0, 7.5, C-2′, C-6′), 156.09 (C-4), 130.73 (C-2, C-6), 130.69 (C-1), 125.04 (t, J = 9.4, C-1′), 122.31 (C-3, C-5), 100.50 (dd, J = 23.3, 3.8, C-3′, C-5′), 69.42 (CH*), 66.01 ($COO\mathbf{C}H_2$), 31.31 ($\mathbf{C}H_2CH_2CH_3$), 28.40 ($\mathbf{C}H_2CH_2O$), 25.41 ($\mathbf{C}H_2CH_2CH_2O$), 22.49 ($\mathbf{C}H_2CH_3$), 17.09 (CH*$\mathbf{C}H_3$), 13.96 ($CH_2\mathbf{C}H_3$).

(S)-1-(Hexyloxy)-1-oxopropan-2-yl 4-((4-hydroxyphenyl)diazenyl)-3,5-dimethylbenzoate (14e). Preparation of ester **14e** was analogous to the preparation of phenol **14a**. Hydrolysis of **13e**(4.10 g, 8.46 mmol) with aqueous ammonia (2.8 ml, 25%) in a THF (100 mL)-chloroform (150 mL) mixture yielded 2.74 g (76 %). ^{1}H NMR (CDCl3): 7.81 (2 H, s, H-3′, H-5′), 7.71 (2 H, d, J = 8.8, H-2, H-6), 6.89 (2 H, d, J = 8.8, H-3, H-5), 6.51 (1 H, s, OH), 5.34 (1 H, q, J = 7.0, C*H), 4.10 - 4.29 (2 H, m, C*$HCOOC\mathbf{H}_2$), 2.24 (6 H, s, 2x Ar-CH_3), 1.56 - 1.73 (5 H, m, $COOCH_2C\mathbf{H}_2$, C*$C\mathbf{H}_3$), 1.14 - 1.45 (6 H, m, $(CH_2)_3$), 0.90 (3 H, t, J = 6.7, $CH_2C\mathbf{H}_3$).

(S)-1-(Hexyloxy)-1-oxopropan-2-yl 3,5-dibromo-4-((4-hydroxyphenyl)diazenyl)benzoate (14f). Preparation of ester **14f** was analogous to the preparation of phenol **14a**. Hydrolysis of **13f** (15.0 g, 24.41 mmol) with aqueous ammonia (16.5 ml, 25%) in a THF (200 mL)-chloroform (500 mL) mixture yielded 10.18 g (75 %). ^{1}H NMR ($CDCl_3$): 8.28 (2 H, s, H-3′, H-5′), 7.94 (2 H, d, J = 8.7, H-2, H-6), 6.97 (2 H, d, J = 8.7, H-3, H-5), 5.36 (1 H, q, J = 6.95, C*H), 4.14 - 4.21 (2 H, m, C*$HCOOC\mathbf{H}_2$), 1.48 - 1.72 (5 H, m, $COOCH_2C\mathbf{H}_2$, C*$C\mathbf{H}_3$), 1.15 - 1.44 (6 H, m, $(CH_2)_3$), 0.89 (3 H, t, J = 6.7, $CH_2C\mathbf{H}_3$).

(S)-1-(Hexyloxy)-1-oxopropan-2-yl 3,5-dichloro-4-((4-hydroxyphenyl)diazenyl)benzoate (14g). Preparation of ester **14g** was analogous to the preparation of phenol **14a**. Hydrolysis of **13g** (9.53 g, 18.14 mmol) with aqueous ammonia (10.5 ml, 25%) in a THF (150 mL)-chloroform (200 mL) mixture yielded 5.92 g (70 %). ^{1}H NMR ($CDCl_3$): 8.09 (2 H, s, H-3′, H-5′), 7.92 (2 H, d, J = 8.8, H-2, H-6), 6.98 (2 H, d, J = 8.8, H-3, H-5), 5.37 (1 H, q, J = 6.95, C*H), 4.14 - 4.21 (2 H, m, C*$HCOOC\mathbf{H}_2$), 1.48 - 1.72 (5 H, m, $COOCH_2C\mathbf{H}_2$, C*$C\mathbf{H}_3$), 1.15 - 1.44 (6 H, m, $(CH_2)_3$), 0.89 (3 H, t, J = 6.7, $CH_2C\mathbf{H}_3$).

2.6. Synthesis of the target compounds Ib-h

(S)-1-(Hexyloxy)-1-oxopropan-2-yl 4-((4-((4-(dodecyloxy)benzoyl)oxy)-2,6-dimethylphenyl)diazenyl)benzoate (Ib).

The ester **14a** (8.0 g; 18.8 mmol) and 4-(dodecyloxy)benzoic acid (9.2 g; 30.0 mmol) were dissolved in dry dichloromethane (150 mL), and *N,N′*-dicyclohexylcarbodiimide (DCC) (6.5 g; 31.50 mmol) and 4-(*N,N*-dimethylamino)pyridine (DMAP) (0.2 g; 2 mmol) were added. The mixture was stirred at room temperature for 24 h and then filtered. The filtrate was evaporated and the residue purified by column chromatography (silica gel, dichloromethane – acetone, 99.5 : 0.5) to get 13.0 g (91 %) of **Ib**. ^{1}H NMR ($CDCl_3$): 8.22 (2H, d, *J* =8.4, H-3′, H-5′), 8.17 (2H, d, *J* = 8.8, H-2′′, H-6′′), 7.84 (2H, d, *J* = 8.4, H-2′, H-6′), 7.00 (4H, m, H-3′′, H-5′′, H-3, H-5), 5.32 (1H, q, *J* = 6.9, C*H), 4.20 (2H, t, *J* = 6.8, C*H–COOC**H**$_2$), 4.05 (2H, t, *J* = 6.4, CH_2OAr), 2.53 (6H, s, 2 × Ar-CH_3), 1.85 (2H, quint., C**H**$_2CH_2OAr$), 1.65 (3H, d, *J* = 7.0, C*CH_3), 1.20-1.50 (20 H, m, 10 × CH_2), 0.90 (6H, m 2 × CH_2C**H**$_3$). ^{13}C NMR ($CDCl_3$): 170.77 (CO-A1), 165.40 (CO-A2), 164.88 (CO-B), 163.59 (C-4′′), 155.48 (C-1′), 151.06 (C-4), 148.11 (C-1), 134.10 (C-4′), 132.29 (C-3′, C-5′), 131.03 (C-2′′, C-6′′), 130.91 (C-2′, C-6′), 122.41 (C-3, C-5), 122.28 (C-2, C-6′), 121.28 (C-1′′), 114.29 (C-3′′, C-5′′), 69.45 (C*), 68.32 (CH_2O-b), 65.59 (CH_2O-a), 32.1 (**C**$H_2CH_2CH_3$), 29.2–29.6 (2 × $(CH_2)_2$, 2 × **C**H_2CH_2O), 26.3 (**C**$H_2CH_2CH_2$O-b), 26.1 (**C**$H_2CH_2CH_2$O-a), 22.9 (2 × **C**H_2CH_3), 17.39 (C***C**H_3), 14.3 (2 × CH_3). Elemental Analysis for $C_{43}H_{58}N_2O_7$ (714.93): calcd C 72.24, H 8.18, N 3.92; found C 72.03, H 8.11, N 3.90 %.

(S)-3,5-Dibromo-4-((4-(((1-(hexyloxy)-1-oxopropan-2-yl)oxy)carbonyl)phenyl)diazenyl)phenyl 4-(dodecyloxy)benzoate Ic. Preparation of compound **Ic** was analogous to the preparation of compound **Ib**. Reaction of ester **14b** (0.60 g, 1.08 mmol) with 4-(dodecyloxy)benzoic acid (0.36 g, 1.19 mmol) in dry dichloromethane (50 mL) in the presence of dicyclohexylcarbodiimide (0.24 g, 1.16 mmol) and DMAP (0.01 g, 0.08 mmol) yielded 0.72 g (75 %). ^{1}H NMR ($CDCl_3$): 8.28 (2 H, d, *J* = 8.5, H-3′, H-5′), 8.12 (2 H, d, *J* = 9.10, H-2′′, H-6′′), 8.03 (2 H, d, *J* = 8.5, H-2′, H-6′), 7.61 (2 H, s, H-3, H-5), 6.99 (2 H, d, *J* = 8.8, H-3′′, H-5′′), 5.37 (1 H, q, *J* = 7.0, C*H), 4.12 - 4.26 (2 H, m, C*H–COOC**H**$_2$), 4.05 (2 H, t, *J* = 6.6, CH_2OAr), 1.85 (2H, quint., C**H**$_2CH_2OAr$), 1.67 (3 H, d, *J* = 7.0, C*CH_3), 1.14 - 1.54 (20 H, m, 10xCH_2), 0.90 (6H, m 2x CH_2C**H**$_3$). ^{13}C NMR ($CDCl_3$): 170.66 (COO-A1), 165.17 (COO-A2), 164.09 (COO-B), 163.99 (C-4′′), 154.44 (C-4), 150.45 (C-1′), 147.45 (C-4′), 132.47 (C-2′′, C-6′′), 132.41 (C-1), 130.99 (C-2, C-6), 126.64 (C-3, C-5), 122.93 (C-2′, C-6′), 120.28 (C-1′′), 115.28 (C-3′, C-5′), 114.48, (C-3′′, C-5′′), 69.59(C*), 68.40 (CH_2O-b), 65.65 (CH_2O-a), 31.91 (**C**$H_2CH_2CH_3$-b), 31.32 (**C**$H_2CH_2CH_3$-a), 28.44 – 29.58 ($(CH_2)_6$, **C**H_2CH_2O-b), 28.42 (**C**H_2CH_2O-a), 25.96 (**C**$H_2CH_2CH_2$O-b), 25.43 (**C**$H_2CH_2CH_2$O-a), 22.69 (**C**H_2CH_3-b), 22.49 (**C**H_2CH_3-a), 17.11 (C***C**H_3), 14.13 (CH_2**C**H_3-b), 13.97 (CH_2**C**H_3-a). Elemental Analysis for $C_{41}H_{52}Br_2N_2O_7$ (844.67): calcd C 58.30, H 6.21, N 3.32; found C 58.21, H 6.30, N 3.30 %.

(S)-3,5-Dichloro-4-((4-(((1-(hexyloxy)-1-oxopropan-2-yl)oxy)carbonyl)phenyl)diazenyl)phenyl 4-(dodecyloxy)benzoate Id. Preparation of compound **Id** was analogous to the preparation of compound **Ib**. Reaction of ester **14c** (1.90 g, 4.07 mmol) with 4-(dodecyloxy)benzoic acid (1.40 g, 4.57 mmol) in dry dichloromethane (50 mL) in the presence of dicyclohexylcarbodiimide (0.94 g, 4.56 mmol) and DMAP (0.05 g, 0.41 mmol) yielded 2.78 g (85 %). ^{1}H NMR ($CDCl_3$): 8.28 (2 H, d, *J* = 8.51, H-3′, H-5′), 8.12 (2 H, d, *J* = 8.8 H-2′′, H-6′′), 8.01 (2 H, d, *J* = 8.5, H-2′, H-6′), 7.38 (2 H, s, , H-3, H-5), 6.99 (2 H, d, *J* = 8.8, H-3′′, H-5′′), 5.37 (1 H, q, *J* = 6.9, C*H), 4.11 - 4.27 (2 H, m, C*H–COOC**H**$_2$), 4.05 (2 H, t, *J* = 6.3, CH_2OAr), 1.85 (2H, quint., C**H**$_2CH_2OAr$), 1.67 (3 H, d, *J* = 7.0, C*CH_3), 1.19 - 1.51 (20 H, m, 10xCH_2), 0.90 (6H, m 2x CH_2C**H**$_3$). ^{13}C NMR ($CDCl_3$): 170.65 (COO-A1), 165.16 (COO-A2), 164.02 (COO-B), 164.0 (C-4′′), 154.83 (C-1′), 150.21 (C-1), 145.50 (C-4), 132.48 (C-3′, C-5′), 132.37 (C-4′), 130.97 (C-2′′, C-6′′), 127.67 (C-2, C-6), 123.05 (C-3, C-5), 122.88 (C-2′, C-6′), 120.28 (C-1′′),

114.48 (C-3′′, C-5′′), 69.58 (C*), 68.41 (CH_2O-b), 65.63 (CH_2O-a), 31.91 (**C**$H_2CH_2CH_3$), 31.32 (**C**$H_2CH_2CH_3$), 28.44 – 29.58 (2x$(CH_2)_2$, 2x**C**H_2CH_2O), 25.96 (**C**$H_2CH_2CH_2O$-a), 25.43 (**C**$H_2CH_2CH_2O$-b), 22.69 (**C**H_2CH_3), 22.49 (**C**H_2CH_3), 17.11 (C***C**H_3), 14.13 (CH_2**C**H_3), 13.96 (CH_2**C**H_3) Elemental analysis: for $C_{41}H_{52}Cl_2N_2O_7$ (755.77): calcd C 65.16, H 6.94, N 3.71; found C 65.73, H 7.03, N 3.74 %.

(S)-3,5-difluoro-4-((4-(((1-(hexyloxy)-1-oxopropan-2-yl)oxy)carbonyl)phenyl)diazenyl)phenyl 4-(dodecyloxy)benzoate Ie.
Preparation of compound **Ie** was analogous to the preparation of compound **Ib**. Reaction of ester **14d** (0.80 g, 1.84 mmol) with 4-(dodecyloxy)benzoic acid (0.60 g, 1.98 mmol) in dry dichloromethane (50 mL) in the presence of dicyclohexylcarbodiimide (0.40 g, 1.94 mmol) and 4-(*N,N*-dimethylamino)-pyridine (0.02 g, 0.2 mmol) yielded 1.28 g (96 %). ^{1}H NMR ($CDCl_3$) 8.25 (2 H, d, *J* = 8.5, H-2, H-6), 8.12 (2 H, d, *J* = 8.8, H-2′′, H-6′′), 7.98 (2 H, d, *J* = 8.5, H-3, H-5), 7.05 (2 H, d, *J* = 9.4, H-2′, H-6′), 6.99 (2 H, d, *J* = 8.8, H-3′′, H-5′′), 5.36 (1 H, q, *J* = 7.0, CH*), 4.18 (3 H, m, CH*COOC**H**$_2$), 4.06 (2 H, t, *J* = 6.6, $ArOCH_2$), 1.83 (2 H, quint., C**H**$_2CH_2O$-b), 1.65 (5 H, m, C**H**$_3$CH*, C**H**$_2CH_2O$-a), 1.17 - 1.52 (24 H, m, 12 × CH_2), 0.87 (6 H, m, 2 × CH_2C**H**$_3$). ^{13}C NMR ($CDCl_3$) 170.70 (C-A1), 165.25 (C-A2), 164.08 (C-4′′), 163.68 (C-B), 155.79 (C-4), 156.30 (dd, *J* = 253.4, 6.5, C-3′, C-5′), 152.73 (t, *J* = 14.0, C-4′), 132.52 (C-2′′, C-6′′), 131.83 (C-1), 130.89 (C-2, C-6), 128.80 (t, *J* = 9.5, C-1′), 122.70 (C-3, C-5), 120.17 (C-1′′), 114.51 (C-3′′, C-5′′), 107.17 (dd, *J* = 24.0, 3.7, C-2′, C-6′), 69.52 (C*), 68.42 (CH_2O-b), 65.61 (CH_2O-a), 31.90 (**C**$H_2CH_2CH_3$-b), 31.31 (**C**$H_2CH_2CH_3$-a), 29.04 – 29,64 ($(CH_2)_6$, **C**H_2CH_2O-b), 28.42 (**C**H_2CH_2O-a), 25.95 (**C**$H_2CH_2CH_2O$-b), 25.41 (**C**$H_2CH_2CH_2O$-a), 22.68 (**C**H_2CH_3-b), 22.48 (**C**H_2CH_3-a), 17.11 (CH***C**H_3), 14.12 (**C**H_3CH_2-b), 13.95 (**C**H_3CH_2-a). Elemental analysis: for $C_{41}H_{52}F_2N_2O_7$ (755.77): calcd C 68.12, H 7.25, N 3.88; found C 67.99, H 7.34, N 3.81 %.

(S)-1-(Hexyloxy)-1-oxopropan-2-yl 4-((4-((4-(dodecyloxy)benzoyl)oxy)phenyl)diazenyl)-3,5-dimethylbenzoate If. Preparation of compound **If** was analogous to the preparation of compound **Ib**. Reaction of ester **14e** (1.60 g, 3.75 mmol) with 4-(dodecyloxy)benzoic acid (1.30 g, 4.12 mmol) in dry dichloromethane (50 mL) in the presence of dicyclohexylcarbodiimide (0.85 g, 4.12 mmol) and 4-(*N,N*-dimethylamino)-pyridine (0.05 g, 0.41 mmol) yielded 2.52 g (88 %). ^{1}H NMR ($CDCl_3$): 8.17 (2 H, d, *J* = 9.1, H-2, H-6), 8.00 (2 H, d, *J* = 8.8, H-2′′, H-6′′), 7.86 (2 H, s, H-3′, H-5′), 7.39 (2 H, d, *J* = 8.8, H-3, H-5), 6.99 (2 H, d, *J* = 8.8, H-3′′, H-5′′), 5.34 (1 H, q, *J* = 7.2, C*H), 4.11 - 4.25 (2 H, m, C*H–COOC**H**$_2$), 4.06 (2 H, t, *J* = 6.5, CH_2OAr), 2.32 (6 H, s, 2xAr-CH_3), 1.85 (2H, quint., C**H**$_2CH_2OAr$), 1.65 (3 H, d, *J* = 7.0, C*CH_3), 1.15 - 1.55 (20 H, m, 10xCH_2), 0.90 (6H, m 2x CH_2C**H**$_3$). ^{13}C NMR ($CDCl_3$) 170.92 (COO-A1), 165.71 (COO-A2), 164.64 (COO-B), 163.77 (C-4′′), 155.25 (C-1′), 153.73 (C-4), 150.07 (C-1), 132.40 (C-2′′, C-6′′), 130.52 (C3′, C-5′), 130.13 (C-4′), 128.13 (C-2′, C-6′), 124.00 (C-2, C-6), 122.64 (C-3, C-5), 121.01 (C-1′′), 114.37 (C-3′′, C-5′′), 69.23(C*), 68.37 (CH_2O-b), 65.53 (CH_2O-a), 31.91 (**C**$H_2CH_2CH_3$), 31.34 (**C**$H_2CH_2CH_3$), 28.44 – 29.58 (2x$(CH_2)_2$, 2x**C**H_2CH_2O), 25.97 (**C**$H_2CH_2CH_2O$-a), 25.44 (**C**$H_2CH_2CH_2O$-b), 22.69 (**C**H_2CH_3), 22.49 (**C**H_2CH_3), 18.41 (2xAr-CH_3), 17.13 (C***C**H_3), 14.13 (CH_2**C**H_3), 13.97 (CH_2**C**H_3). Elemental Analysis for $C_{43}H_{58}N_2O_7$ (714.93): calcd C 72.24, H 8.18, N 3.92; found C 72.14, H 8.15, N 3.89 %.

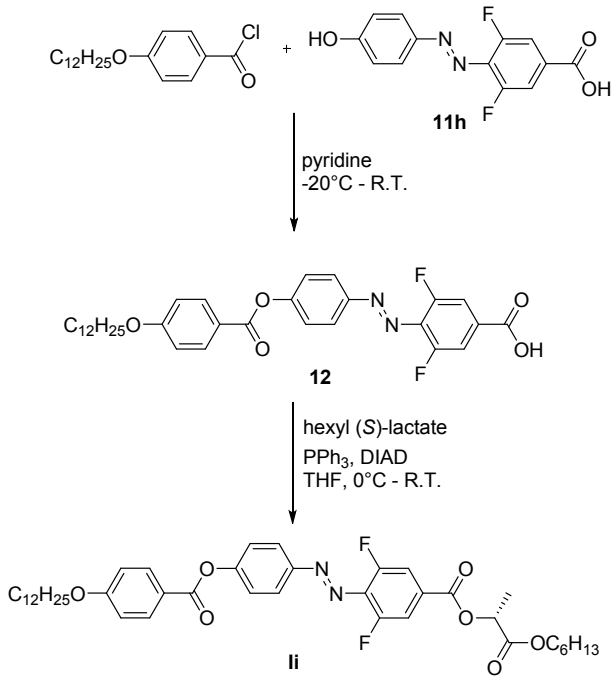
(S)-1-(Hexyloxy)-1-oxopropan-2-yl 3,5-dibromo-4-((4-((4-(dodecyloxy)benzoyl)oxy)phenyl)diazenyl)benzoate Ig. Preparation of compound **Ig** was analogous to the preparation of compound **Ib**. Reaction of ester **14f** (1.90 g, 3.42 mmol) with 4-(dodecyloxy)benzoic acid (1.10 g, 3.59 mmol) in dry dichloromethane (50 mL) in the presence of dicyclohexylcarbodiimide (0.74 g, 3.59 mmol) and 4-(*N,N*-dimethylamino)-

pyridine (0.04 g, 0.33 mmol) yielded 2.60 g (85 %). ^{1}H NMR ($CDCl_3$): 8.34 (2 H, s, H-3′, H-5′), 8.17 (2 H, d, *J* = 8.8, H-2, H-6), 8.08 (2 H, d, *J* = 8.8, H-2′′, H-6′′), 7.43 (2 H, d, *J* = 8.5, H-3, H-5), 7.00 (2 H, d, *J* = 8.8, H-3′′, H-5′′), 5.34 (1 H, q, *J* = 7.0, C*H), 4.14 - 4.24 (2 H, m, C*H–COOC**H**$_2$), 4.06 (2 H, t, *J* = 6.5, CH_2OAr), 1.84 (2H, quint., C**H**$_2$$CH_2$OAr), 1.67 (3 H, d, *J* = 7.0, C*CH_3), 1.13 - 1.56 (20 H, m, 10xCH_2), 0.90 (6H, m 2x CH_2C**H**$_3$). ^{13}C NMR (75 MHz, ($CDCl_3$): 170.30 (COO-A1), 164.45 (COO-A2), 163.86 (COO-B), 163.17 (C-4′′), 154.77 (C-1′), 154.00 (C-4), 149.46 (C-1), 134.08 (C3′, C-5′), 132.44 (C-2′′, C-6′′), 130.28 (C-4′), 124.74 (C-2, C-6), 122.78 (C-3, C-5), 121.00 (C-1′′), 114.85 (C-2′, C-6′), 114.45 (C-3′′, C-5′′), 69.97(C*), 68.42 (CH_2O-b), 65.75 (CH_2O-a), 31.92 (**C**$H_2CH_2CH_3$), 31.33 (**C**$H_2CH_2CH_3$), 28.47 – 29.58 (2x$(CH_2)_2$, 2x**C**H_2CH_2O), 25.98 (**C**$H_2CH_2CH_2$O-a), 25.45 (**C**$H_2CH_2CH_2$O-b), 22.69 (**C**H_2CH_3), 22.50 (**C**H_2CH_3), 17.13 (C***C**H_3), 14.10 (CH_2**C**H_3), 13.95 (CH_2**C**H_3). Elemental Analysis for $C_{41}H_{52}Br_2N_2O_7$ (844.67): calcd C 58.30, H 6.21, N 3.32; found C 58.20, H 6.25, N 3.29 %.

(S)-1-(Hexyloxy)-1-oxopropan-2-yl 3,5-dichloro-4-((4-((4-(dodecyloxy)benzoyl)oxy)phenyl)diazenyl)benzoate Ih. Preparation of compound **Ih** was analogous to the preparation of compound **Ib**. Reaction of ester **14g** (3.67 g, 7.85 mmol) with 4-(dodecyloxy)benzoic acid (2.89 g, 9.42 mmol) in dry dichloromethane (100 mL) in the presence of dicyclohexylcarbodiimide (1.78 g, 8.64 mmol) and 4-(*N,N*-dimethylamino)-pyridine (0.10 g, 0.82 mmol) yielded 5.50 g (87 %). ^{1}H NMR ($CDCl_3$): 8.19 (2 H, d, *J* = 8.8, H-2, H-6), 8.14 (2 H, s, H-3′, H-5′), 8.08 (2 H, d, *J* = 8.8, H-2′′, H-6′′), 7.45 (2 H, d, *J* = 8.8, H-3, H-5), 7.02 (2 H, d, *J* = 8.8, H-3′′, H-5′′), 5.38 (1 H, q, *J* = 7.2, C*H), 4.14 - 4.26 (2 H, m, C*H–COOC**H**$_2$), 4.09 (2 H, t, *J* = 6.6, CH_2OAr), 1.86 (2H, quint., C**H**$_2$$CH_2$OAr), 1.68 (3 H, d, *J* = 7.0, C*CH_3), 1.19 - 1.52 (20 H, m, 10xCH_2), 0.90 (6H, m 2x CH_2C**H**$_3$). ^{13}C NMR (75 MHz, ($CDCl_3$): 170.30 (COO-A1), 164.35 (COO-A2), 163.86 (COO-B), 163.41 (C-4′′), 154.77 (C-1′), 152.00 (C-4), 149.82 (C-1), 132.45 (C-2′′, C-6′′), 130.34 (C-3′, C-5′), 129.68 (C-4′), 126.93 (C-2′, C-6′), 124.71 (C-2, C-6), 122.76 (C-3, C-5), 121.01 (C-1′′), 114.45 (C-3′′, C-5′′), 69.97(C*), 68.43 (CH_2O-b), 65.78 (CH_2O-a), 31.92 (**C**$H_2CH_2CH_3$), 31.33 (**C**$H_2CH_2CH_3$), 28.47 – 29.65 (2x$(CH_2)_2$, 2x**C**H_2CH_2O), 25.99 (**C**$H_2CH_2CH_2$O-a), 25.45 (**C**$H_2CH_2CH_2$O-b), 22.69 (**C**H_2CH_3), 22.50 (**C**H_2CH_3), 18.41 (2xAr-CH_3), 17.06 (C***C**H_3), 14.10 (CH_2**C**H_3), 13.94 (CH_2**C**H_3). Elemental analysis: for $C_{41}H_{52}Cl_2N_2O_7$ (755.77): calcd C 61.20, H 4.63, N 3.48; found C 65.02, H 6.81, N 3.68 %.

2.7. Synthesis of Ii

Synthetic route to compound **Ii** was different from the synthesis of the rest of studied compounds and it is shown in scheme S4. Acid **11i** was directly acylated by (4-dodecyloxy)benzoylchloride and then the chiral sidechain was introduced via Mitsunobu reaction with hexyl lactate.



Scheme S4 Synthesis of **Ii**

4-((4′-((4′′-(dodecyloxy)benzoyl)oxy)phenyl)diazenyl)-3,5-difluorobenzoic acid (12i)

Oxalylchloride (1.5 ml, 17.37 mmol) was added dropwise to the suspension of 4-(dodecyloxy)benzoic acid (2.80g, 9.14 mmol) in dry dichloromethane with catalytic amount of *N*,*N*-dimethylformamide. Reaction mixture was stirred until a clear solution was obtained (ca. 30 min). Resulting solution was filtered and the solvent evaporated. Oily residue was dissolved in dichloromethane, cooled to -20 °C and added dropwise to the solution of acid **11i** (2.30 g, 8.27 mmol) in pyridine (100 mL) at -20 °C. The mixture was allowed to warm to room temperature and further stirred for 50 min. The resulting mixture was poured into a mixture of crushed ice (300 g) and concentrated hydrochloric acid (100 mL). The precipitade solid was filtered off, washed with water and dried in vacuum dryer. Dried solid was boiled with dichloromethane (150 mL) and filtered. Filtrate was evaporated, boiled with hexane (150 mL) and the solid product filtered off. Yield 3.10 g (66 %). m.p. 138 °C-LC-161 °C-Iso. ^{1}H NMR ($CDCl_3$) δ ppm 8.17 (2 H, d, *J* = 8.8, H-2′′, H-6′′), 8.07 (2 H, d, *J* = 8.8, H-2′, H-6′), 7.80 (2 H, d, *J* = 8.5, H-2, H-6), 7.42 (2 H, d, *J* = 8.8, H-3′, H-5′), 7.00 (2 H, d, *J* = 8.8, H-3′′, H-5′′), 4.07 (2 H, t, *J* = 6.5, OCH_2), 1.84 (2 H, quin. *J* = 7.1, C**H**$_2$CH$_2$O), 1.14 – 1.59 (18 H, m, $(CH_2)_9$), 0.89 (3 H, t, *J* = 6.6, CH_2C**H**$_3$). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 167.42 (C-A2), 164.46 (C-B), 163.79 (C-4′′), 154.58 (C-4′), 155.05 (dd, *J* = 258.8, 4.4, C-3, C-5), 150.62 (C-1), 134.92 (t, *J* = 10.7, C-1), 132.31 (C-2′′, C-6′′), 130.46 (t, *J* = 9.0, C-4), 124.68 (C-2′, C-6′), 122.70 (C-3′, C-5′), 120.91 (C-1′′), 114.39 (m, C-2, C-6, C-3′′, C-5′′), 68.38 (OCH_2), 31.91 (**C**$H_2$$CH_2$$CH_3$), 29.07 - 29.91 (m, $(CH_2)_6$, **C**$H_2$$CH_2$O), 25.96 (**C**$H_2$$CH_2$$CH_2$O), 22.69 (**C**$H_2$$CH_3$), 14.13 ($CH_2$**C**$H_3$).

(R)-1-(Hexyloxy)-1-oxopropan-2-yl 4-((4-((4-(dodecyloxy)benzoyl)oxy)phenyl)diazenyl)-3,5-difluorobenzoate Ii.

Triphenylphosphine (0.82 g, 3.85 mmol) was dissolved in tetrahydrofurane (THF) (30 mL) and after cooling to 0 °C diisopropyl azodicarboxylate (1.0 g, 3.81 mmol) was added with stirring. After 10 minutes the solution of acid **12i** (1.33 g, 2.35 mmol) and hexyl lactate (0.32 g, 1.84 mmol) in THF (100 mL) was added and the reaction mixture was stirred for 30 min at 0 °C. The cooling bath was removed and the reaction mixture was further stirred at

room temperature for 1 h. The solvent was evaporated and the oily residue was stirred with hexane (20 mL) for 30 min. Precipitated solid was filtered off and purified by column chromatography on silica (eluent: dichlormethane-acetone 97.5 : 2.5). Further crystalization from ethanol and hexane yielded 1.45 g (86 %) of **Ii**. ^{1}H NMR ($CDCl_3$): 8.16 (2 H, d, J = 8.8. H-2´´, H-6´´), 8.05 (2 H, d, J = 8.8, H-2´, H-6´), 7.77 (2 H, d, J = 8.5, H-2, H-6), 7.41 (2 H, d, J = 8.8, H-3´, H-5´), 6.99 (2 H, d, J = 8.8, H-3´´, H-5´´), 5.34 (1 H, q, J = 7.0, CH*), 4.19 (2 H, m, CH*COOC**H**$_2$), 4.06 (2 H, t, J = 6.5, CH_2OAr), 1.83 (2 H, 2 H, quin., C**H**$_2$$CH_2$OAr), 1.65 (5 H, m, C**H**$_3$CH*, C**H**$_2$$CH_2$O-a), 1.19 – 1.52 (24 H, m, 12 × CH_2), 0.88 (4 H, t, J = 6.6, 2 × CH_2C**H**$_3$). ^{13}C NMR ($CDCl_3$) 170.28 (C-A1), 164.42 (C-A2), 163.78 (C-B), 163.37 (C-4´´), 155.08 (dd, J = 258.5, 4.4, C-3, C-5), 154.52 (C-4´), 150.64 (C-1´), 134.57 (t, J = 10.9, C-4), 132.41 (C-2´´, C-6´´), 130.86 (t, J = 9.1, C-1), 124.64 (C-2´, C-6´), 122.67 (C-3´, C-5´), 120.94 (C-1´´), 114.38 (C-3´´, C-5´´), 114.06 (d, J = 26.0, C-2, C-6), 70.00 (CH*), 68.37 (CH_2O-b), 65.76 (CH_2O-a), 31.91 (**C**$H_2CH_2CH_3$-b), 31.30 (**C**$H_2CH_2CH_3$-a), 29.55 – 29,65 ((CH_2)$_6$, **C**H_2CH_2O-b), 28.42 (**C**H_2CH_2O-a), 25.96 (**C**$H_2CH_2CH_2$O-b), 25.41 (**C**$H_2CH_2CH_2$O-a), 22.69 (**C**H_2CH_3-b), 22.49 (**C**H_2CH_3-a), 17.03 (CH***C**H_3), 14.14 (CH_2**C**H_3-b), 13.95 (CH_2**C**H_3-a). Elemental analysis: for $C_{41}H_{52}F_2N_2O_7$ (722.86): calcd C 68.12, H 7.25, N 3.88; found C 67.86, H 7.31, N 3.85 %.

3. Examples of changes in ^{1}H-NMR spectra of Ia and Id induced by UV light.

^{1}H-NMR spectra were measured using Varian Gemini 300 HC instrument at 300 MHz. TMS was used as internal standard Illumination was performed on 10 mM solutions of the studied compounds in $CDCl_3$ in glass NMR cuvettes at 20 °C with a low-pressure mercury lamp (8 W sterilair BLB-8, 366 nm) equipped with filter. Since the NMR cuvettes are made of borosilicate glass, the transmittance at 366 nm ca. 90 %. For practical reasons, only the part of the NMR spectra where substantial changes occur upon exposure to light is shown. Prior to irradiation, as shown in Figure S2(a), the NMR spectrum consists of seven signals corresponding to the seven sets of protons in the *E*-form of **Ia**. After illumination by 366 nm a new set of signals, corresponding to *Z*-isomer emerged as shown in Figure S2(b) and a substantial drop of *E*-isomer signals' intensity is observed. After the heat treatment, the spectra recover to its initial state before exposure to light which confirms the reversible *E-Z* isomerization process. The spectra of **Id** have shown analogous changes as seen in Figure S3. The composition of the photostationary state mixture can be calculated from the integral intensities of signals belonging to each isomer. The changes of these intensities in time were used for the kinetics measurement of thermal Z-E isomerization.

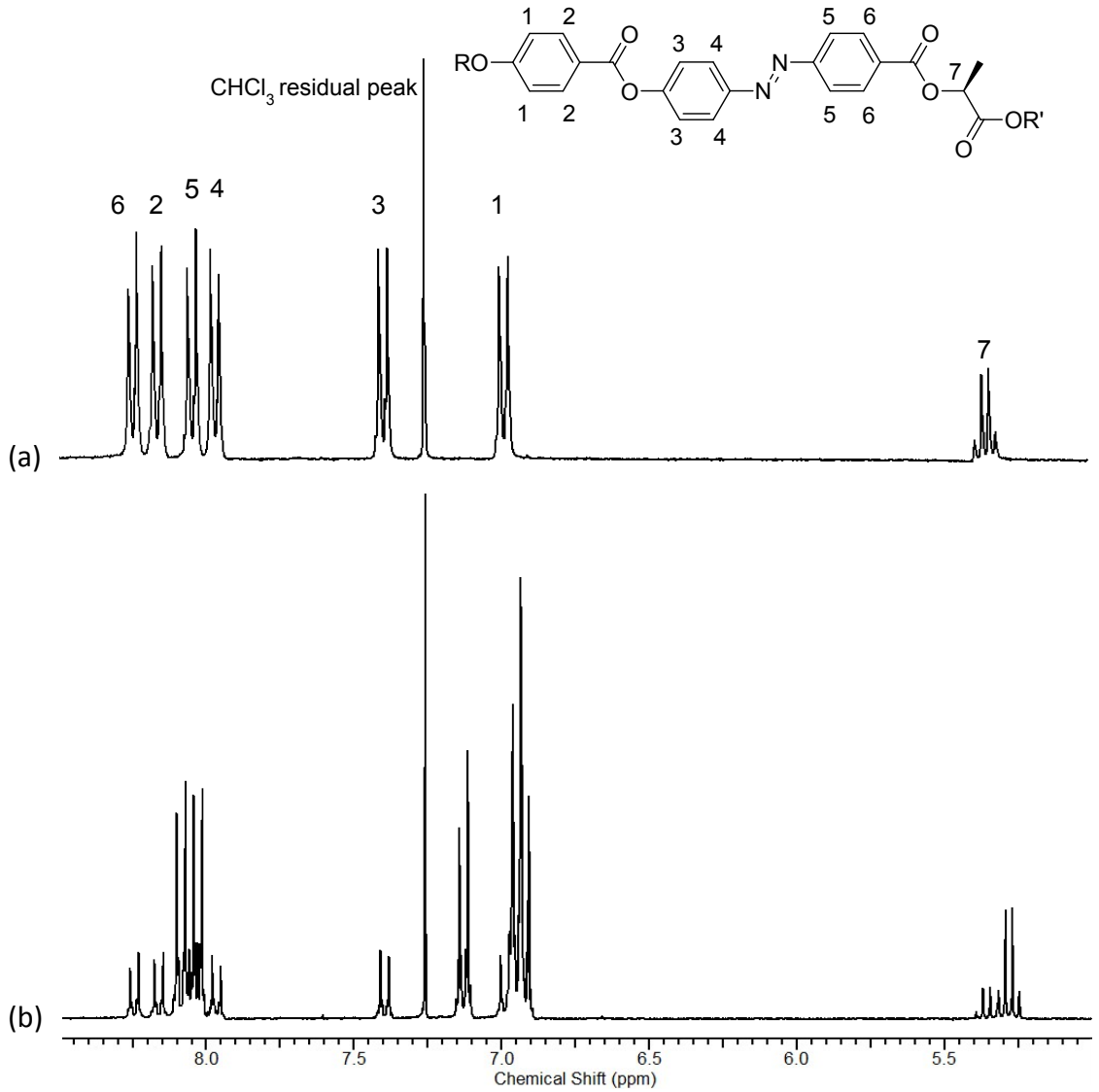


Fig. S2. ^{1}H NMR spectra of **Ia** in $CDCl_3$ (a) prior to irradiation (b) after irradiation by UV light (366 nm).

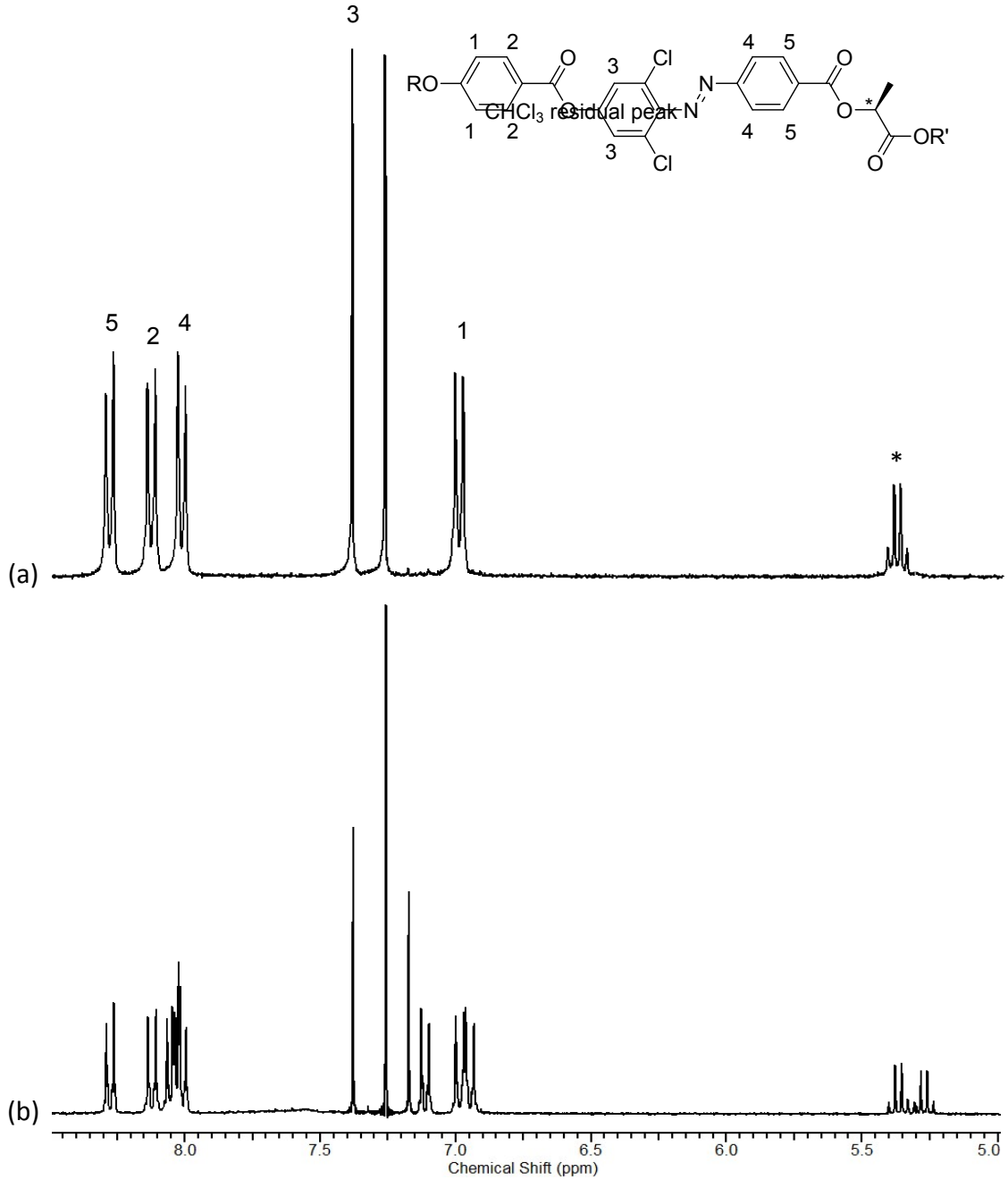


Fig. S3. ^{1}H NMR spectra of **Id** in $CDCl_3$ (a) prior to irradiation (b) after irradiation by UV light (366 nm).

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