

## Supporting Information for “Novel Liquid Crystalline Mesogens and Main-Chain Chiral Smectic Thiol-ene Polymers based on Trifluoromethylphenyl Moieties”

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### Supporting Information

**General considerations.** For the mesogenic materials, liquid crystal phases and phase transition temperatures were determined by polarized light microscopy using a Nikon-HCS400 microscope with an Instec-STC200 temperature controlled stage or a Leitz Ortholux microscope equipped with a Mettler FP 82 hot stage. X-ray diffraction experiments were performed with a rotating anode generator operated with a small-size focus (copper anode, wavelength  $\lambda = 0.15418$ , focus size:  $0.2 \times 0.2 \text{ mm}^2$ , power: 50 kV, 20 mA). The optics

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consisted of two parabolic multilayer graded mirrors at right angles. It delivered a well-defined and intense parallel monochromatic beam. The sample was on a rotation stage and the diffraction patterns were recorded onto photo-stimulable plates. Vacuum pipes were inserted between the sample and the imaging plate to reduce air scattering. We presently used grazing incidence geometry and the sample was allowed to oscillate by a few degrees during exposure.

New compounds in the synthetic route were routinely characterized by NMR spectroscopy.  $^1\text{H}$  NMR spectra were recorded at 500MHz, 400MHz or 300MHz, using  $\text{CDCl}_3$  (internal reference 7.26 ppm) as solvent.  $^{13}\text{C}$  NMR spectra were obtained at 100MHz or 75MHz using  $\text{CDCl}_3$  (internal reference 77.23ppm) as solvent. All non-aqueous reactions were conducted in oven-dried glassware, under a dry argon atmosphere.  $\text{CH}_2\text{Cl}_2$  was distilled from  $\text{CaH}_2$  under argon. THF was distilled from sodium-benzophenone ketyl under argon. A Sigma 2K15 centrifuge was used for isolation of the polymers after precipitation. All flash chromatographies were performed using Sorbent Technologies 60 Å silica gel (32-63  $\mu\text{m}$ ).

**4-Nitro-2-trifluoromethyl-phenol (5).** 1-Methoxy-4-nitro-2-trifluoromethyl-benzene (**4**, 15.0 g, 68.0 mmol) was dissolved in 250 mL of DMF. To the resulting solution was added LiCl (11.5 g, 272 mmol). The reaction mixture was refluxed in DMF for 3 hours and then concentrated in a high vacuum rotary evaporator to remove all the solvents. The organic residues were separated from inorganic salts in 500 mL ethyl acetate and 200 mL water (pH=3 by concentrated HCl), and the aqueous layer was further extracted with ethyl acetate (3 x 200 mL). The combined organic layers were dried over anhydrous  $\text{MgSO}_4$ , filtered, and then concentrated at reduced pressure to give a black oil. Purification of this crude product by flash chromatography (3:2 hexanes - ethylacetate) gave the desired phenol **5** (13.8 g, 98%) as a white solid;  $\delta_{\text{H}}$  (500 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 8.46 (d, 1H,  $J=2.75$  Hz), 8.30 (dd, 1H,  $J=2.53$ , 9.12 Hz), 7.53 (br s, 1H), 7.08 (d, 1H,  $J=9.01$  Hz).

**1-(1-S-Methyl-heptyloxy)-4-nitro-2-trifluoromethyl-benzene (7).** DEAD (2.65 mL, 16.33 mmol) was added via syringe with stirring and under argon to a solution of a mixture of compound **5** (2.94 g, 14.2 mmol) and commercially available alcohol **6** (1.87 g, 14.2 mmol) and triphenylphosphine (4.33g, 16.33 mmol) in 120 mL dry THF. The reaction mixture was allowed to stir for 12 hours at 25 °C, and was then concentrated by rotary evaporation to give an orange oil which was directly subjected to purification by flash chromatography (10:1 hexanes - ethylacetate) to provide desired compound **7** (3.85 g, 82%) as an orange oil;  $\delta_{\text{H}}$  (500 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 8.45 (d, 1H, J=2.74 Hz), 8.36 (dd, 1H, J=2.84, 9.25 Hz), 7.05 (d, 1H, J=9.25 Hz), 4.59 (m, 1H), 1.77 (m, 1H), 1.65 (m, 1H), 1.33 (m, 11H), 0.85 (t, 3H, J=6.96 Hz);  $\delta_{\text{C}}$  (100 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 161.5, 140.0, 129.3, 124.2.0, 124.1, 124.0, 121.3, 113.4, 76.8, 36.2, 31.9, 31.8, 29.3, 25.2, 22.7, 19.4, 14.2.

**4-(1-S-Methyl-heptyloxy)-2-trifluoromethyl-phenylamine (8).** To a pressure bottle, compound **7** (3.85 g, 12.05 mmol) and 10% wt. Pd/C (385mg) were added in 30 mL ethanol. The pressure bottle was set in a hydrogenation apparatus and the H<sub>2</sub> pressure was set to 30atm pressure. The reaction was allowed to stir at room temperature for 2 days. The reaction solution was filtered to remove all the Pd/C catalyst, and was then concentrated by rotary evaporation to give a dark oil which was directly subjected to purification by flash chromatography (1:1 hexanes - ethylacetate) to provide desired amine **8** (2.97 g, 85%) as a yellow oil;  $\delta_{\text{H}}$  (500 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 6.87 (d, 1H, J=2.84 Hz), 6.77 (m, 2H), 4.29 (m, 1H), 3.49 (br s, 2H), 1.69 (m, 1H), 1.53 (m, 1H), 1.31 (m, 11H), 0.86 (t, 3H, J=6.87 Hz);  $\delta_{\text{C}}$  (100 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 149.1, 139.4, 119.6, 116.4, 114.2, 114.1, 75.6, 60.7, 32.0, 29.5, 25.5, 22.8, 19.7, 14.4, 14.3.

**4-Iodo-1-(1-S-methyl-heptyloxy)-2-trifluoromethyl-benzene (9).** In a 500 mL round bottom flask equipped with a mechanical stirrer, amine **8** (2.97 g, 10.25 mmol) was added to a solution made of 90 mL DMSO and 90 mL 30% H<sub>2</sub>SO<sub>4</sub>. A solution of NaNO<sub>2</sub> (1.06 g, 15.38

mmol) in 10 mL H<sub>2</sub>O was added drop wise into the reaction flask cooled at 0 °C in an ice bath. The reaction mixture was kept at 0 °C for one hour and then a solution of NaI (4.61 g, 30.75 mmol) in 10 mL H<sub>2</sub>O was added. After 20 minutes at 0 °C, the reaction mixture was allowed to stir at room temperature for another 40 minutes. Another batch of NaI (4.61 g, 30.75 mmol) in 10 mL H<sub>2</sub>O was then added into the reaction flask and stirred at room temperature for another one hour. The reaction mixture was quenched by saturated NaHSO<sub>3</sub> solution and then was extracted by 300 mL ethyl acetate (each for three times). Combined organic phases were washed with 150 mL saturated NaHCO<sub>3</sub>, 100 mL H<sub>2</sub>O and 100 mL brine respectively. The reaction mixture was then concentrated as an oil which was directly subjected to purification by flash chromatography (10:1 hexanes - ethylacetate) to provide compound **9** (3.45 g, 84%) as a yellow oil;  $\delta_{\text{H}}$  (500 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 7.80 (d, 1H, J=2.20 Hz), 7.70 (dd, 1H, J=2.56, 8.79 Hz) 6.73 (d, 1H, J=8.79 Hz), 4.41 (m, 1H), 1.73 (m, 1H), 1.58 (m, 1H), 1.26 (m, 11H), 0.86 (t, 3H, J=6.87 Hz);  $\delta_{\text{C}}$  (100 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 156.4, 141.9, 136.1, 136.0, 136.0, 116.1, 80.6, 75.3, 36.4, 32.0, 31.9, 29.4, 25.4, 22.8, 19.5, 14.3.

**[4-(1-S-Methyl-heptyloxy)-2,3-bis-trifluoromethyl-phenyl]-carbamic acid tert-butyl ester (14)**. DEAD (0.64 mL, 3.95 mmol) was added via syringe with stirring and under argon to a solution of phenol **13**<sup>15</sup> (1.05 g, 3.04 mmol), alcohol **6** (400 mg, 3.04 mmol) and triphenylphosphine (1.05 g, 3.95 mmol) in 30 mL dry THF. The reaction mixture was stirred overnight for 12 hours at 25 °C and then concentrated as an oil which was directly subjected to purification by flash chromatography (15:1 hexanes - ethylacetate) to provide ester **14** (1.22 g, 88%) as a white solid;  $\delta_{\text{H}}$  (500 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 7.88 (d, 1H, J=8.57 Hz), 7.19 (d, 1H, J=9.34 Hz), 6.56 (br s, 1H), 4.49 (m, 1H), 1.77 (m, 1H), 1.62 (m, 1H), 1.37 (m, 11H), 0.92 (t, 3H, J=6.98 Hz);  $\delta_{\text{C}}$  (100 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 174.0, 155.1, 153.7, 131.2, 129.7, 118.9, 81.6, 76.3, 68.2, 36.4, 32.0, 29.4, 28.4, 25.4, 22.8, 19.4, 14.3.

**4-(1-S-Methyl-heptyloxy)-2,3-bis-trifluoromethyl-phenylamine (15).** To a solution of compound **14** (1.72 g, 3.77 mmol) in 10 mL CH<sub>2</sub>Cl<sub>2</sub> was added TFA (3 mL) via syringe. The reaction mixture was stirred at 25 °C for 12 hours and then washed by saturated Na<sub>2</sub>CO<sub>3</sub> aqueous solution and brine. The residue was concentrated as oil which was not subject to any further purification to provide amine **15** (1.46 g);  $\delta_{\text{H}}$  (500 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 7.04 (d, 1H, J=9.16 Hz), 6.86 (d, 1H, J=9.16 Hz), 4.31 (m, 1H), 1.70 (m, 1H), 1.56 (m, 1H), 1.32 (m, 11H), 0.89 (t, 3H, J=6.91 Hz).

**1-Iodo-4-(1-S-methyl-heptyloxy)-2,3-bis-trifluoromethyl-benzene (16).** In a 500 mL round bottom flask with a mechanical stir apparatus, amine **15** (1.40 g, 3.77 mmol) was added in a solution mixture made of 20 mL DMSO and 20 mL 30% H<sub>2</sub>SO<sub>4</sub>. A solution of NaNO<sub>2</sub> (390 mg, 5.66 mmol) in 3 mL H<sub>2</sub>O was added drop wise into the reaction flask at 0 °C. The reaction mixture was kept at 0 °C for one hour and then a solution of NaI (1.70 g, 11.31 mmol) in 3 mL H<sub>2</sub>O was added. After 20 minutes at 0 °C, the reaction mixture was allowed to stir at room temperature for another 40 minutes. Another batch of NaI (1.70 g, 11.31 mmol) in 10 mL H<sub>2</sub>O was then added into the reaction flask and stirred at room temperature for another one hour. The reaction mixture was quenched by saturated NaHSO<sub>3</sub> solution and the aqueous layer was extracted by 100 mL ethylacetate (each for three times). Organic phases were washed with 50 mL saturated NaHCO<sub>3</sub>, 50 mL H<sub>2</sub>O and 50 mL brine. The reaction mixture was then concentrated as an oil which was directly subjected to purification by flash chromatography (10:1 hexanes - ethylacetate) to provide compound **16** (1.17 g, 68%) as a yellow oil;  $\delta_{\text{H}}$  (400 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 8.06 (d, 1H, J=8.98 Hz), 6.84 (d, 1H, J=8.97 Hz), 4.48 (m, 1H), 1.75 (m, 1H), 1.62 (m, 1H), 1.35 (m, 11H), 0.88 (t, 3H, J=6.42 Hz);  $\delta_{\text{C}}$  (100 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 157.9, 146.1, 132.7, 118.8, 79.5, 76.4, 68.2, 36.4, 36.3, 32.0, 29.4, 25.4, 22.8, 19.4, 14.3.

**4-(1-S-Methyl-heptyloxy)-3-trifluoromethyl-phenol (17).** *Tert*-Butyl Lithium (1.7 M in hexanes) solution (6.89 mL, 11.7 mmol) was added into 60 mL of dry THF in a 250 mL round bottom flask under Ar at  $-78^{\circ}\text{C}$ . To this stirred solution, compound **9** (2.23 g, 5.57 mmol) in 10 mL of dry THF solution was added dropwise via a canula. The reaction mixture was stirred at  $-78^{\circ}\text{C}$  for 30 minutes. Trimethyl borate (696  $\mu\text{L}$ , 6.13 mmol) was added to the reaction mixture via syringe at  $-78^{\circ}\text{C}$ . The reaction mixture was stirred at  $-78^{\circ}\text{C}$  for another 20 minutes. Then, it was slowly warmed to room temperature and stirred for another one hour. A solution of 10% HCl was added slowly to bring the pH of the solution to acidic. The reaction mixture was cooled down to  $0^{\circ}\text{C}$  and 10% sodium hydroxide solution was added to turn the reaction mixture to basic. Then 30% hydrogen peroxide solution (1.07 mL, 11.14 mmol) was added dropwise. The reaction mixture was warmed to room temperature and stirred for another one hour. A solution of 10% HCl was used to bring the pH of the solution back to acid again. Saturated sodium bisulfite solution was used to destroy the remaining  $\text{H}_2\text{O}_2$  and iodine. Most of THF was removed by rotatory evaporation and the aqueous phase was extracted by three times of 150 mL methylene chloride. The combined extracts were washed by saturated sodium bicarbonate solution, brine and dried over  $\text{MgSO}_4$ . Solvent was removed and the crude product was purified via flash chromatography (10:1 hexanes - ethylacetate) to provided desired phenol **17** (1.40 g, 86.5%) as a colorless liquid;  $\delta_{\text{H}}$  (500 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 7.02 (d, 1H,  $J=3.08$  Hz), 6.88 (m, 2H), 4.79 (br s, 1H), 4.33 (m, 1H), 1.70 (m, 1H), 1.54 (m, 1H), 1.31 (m, 11H), 0.86 (t, 3H,  $J=6.87$  Hz);  $\delta_{\text{C}}$  (100 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 148.5, 119.7, 116.1, 114.5, 114.4, 75.7, 36.6, 32.0, 29.5, 25.5, 22.8, 19.6, 14.3.

**4-(1-S-Methyl-heptyloxy)-2,3-bis-trifluoromethyl-phenol (18).** *Tert*-Butyl Lithium (1.7 M in hexanes) solution (0.59 mL, 1.00 mmol) was added into 10 mL of dry THF in a 50 mL round bottom flask under Ar at  $-78^{\circ}\text{C}$ . To this stirring solution, compound **16** (223 mg, 0.48 mmol) in 10 mL of dry THF solution was added dropwise via a cannula. The reaction mixture

was stirred at  $-78\text{ }^{\circ}\text{C}$  for 30 minutes. A solution of trimethyl borate (60  $\mu\text{L}$ , 0.52 mmol) was added to the reaction mixture via syringe at  $-78\text{ }^{\circ}\text{C}$ . The reaction mixture was stirred at  $-78\text{ }^{\circ}\text{C}$  for another 20 minutes. Then, it was slowly warmed to room temperature and stirred for another one hour. A solution of 10% HCl was added slowly to bring the pH of the solution to acid. The reaction mixture was cooled down to  $0\text{ }^{\circ}\text{C}$  and 10% sodium hydroxide solution was added to turn the reaction mixture to basic. Then 30% hydrogen peroxide solution (95  $\mu\text{L}$ , 1.00 mmol) was added dropwise. The reaction mixture was warmed to room temperature and stirred for another one hour. A solution of 10% HCl was used to bring the pH of the solution back to acid again. Saturated sodium bisulfite solution was used to destroy the remaining  $\text{H}_2\text{O}_2$  and iodine. Most of THF was removed by rotatory evaporator and the aqueous phase was extracted by three times of 50 mL methylene chloride. The combined extraction was washed by saturated sodium bicarbonate solution, brine and dried over  $\text{MgSO}_4$ . Solvent was removed and the crude product was purified via flash chromatography (5:1 hexanes - ethylacetate) to provided desired phenol **18** (141 mg, 83%) as a colorless liquid;  $\delta_{\text{H}}$  (500 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 7.14 (AA'BB', 2H), 5.95 (m, 1H), 4.39 (m, 1H), 1.73, (m, 1H), 1.58 (m, 1H), 1.35 (m, 11H), 0.88 (t, 3H,  $J=6.82\text{ Hz}$ );  $\delta_{\text{C}}$  (100 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 152.1, 148.6, 148.5, 125.6, 124.3, 124.0, 122.9, 121.5, 76.7, 68.2, 36.5, 32.0, 29.4, 25.5, 22.8, 19.4, 14.3.

**4-(1-S-Methyl-heptyloxy)-3-trifluoromethyl-benzoic acid (19)**. To a solution of iodo-compound **9** (6.3 g, 15.7 mmol) in 100 mL dry THF was added n-BuLi/hexanes (1.6 M) (11.8 mL, 18.8 mmol) dropwise at  $-78\text{ }^{\circ}\text{C}$ . The reaction mixture was stirred at  $-78\text{ }^{\circ}\text{C}$  for another one hour. Several clean pieces of solid  $\text{CO}_2$  were added into the reaction mixture. The reaction mixture was stirred at  $-78\text{ }^{\circ}\text{C}$  for another one hour and then allowed to warm to room temperature slowly. After 3 hours stirring at room temperature, the reaction was quenched by 10% HCl, and extracted by 300 mL EtOAc. The organic solution was then concentrated by rotary evaporation to give crude product as a dark oil, which was directly subjected to

purification by flash chromatography (5:1 hexanes - ethylacetate) to provide acid **19** (4.3 g, 86%) as an oil;  $\delta_{\text{H}}$  (500 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 8.30 (d, 1H,  $J=2.09$  Hz), 8.19 (dd, 1H,  $J=2.09$ , 8.79 Hz), 7.00 (d, 1H,  $J=8.90$  Hz), 4.55 (m, 1H), 1.76 (m, 1H), 1.62 (m, 1H), 1.42 (m, 1H), 1.33 (m, 10H), 0.85 (t, 3H,  $J=6.92$  Hz).

**4'-(1-S-Methyl-heptyloxy)-3'-trifluoromethyl-biphenyl-4-ol (21)**. A pressure tube was charged with **9** (238 mg, 0.59 mmol),  $\text{Pd}_2(\text{dba})_3$  (27.2 mg, 0.03 mmol), 2-dicyclohexylphosphanyl-2'-dimethylaminobiphenyl (23.4 mg, 0.06 mmol), 4-hydroxyphenylboronic acid **20** (163.8 mg, 1.19 mmol) and  $\text{K}_3\text{PO}_4$  (252.2 mg, 1.19 mmol), and was purged with Ar. Anhydrous dichloromethane (6 mL) was then added. The reaction mixture was purged with Ar again, capped and was heated at 80 °C for 3 hours. After cooled to room temperature, the mixture was partitioned between brine and EtOAc. The organic layer was washed with water, dried over  $\text{MgSO}_4$ , and concentrated. The residual oil was purified by flash chromatography (5:1 hexanes - ethylacetate) to provided desired phenol **21** (89 mg, 41%) as a colorless oil;  $\delta_{\text{H}}$  (500 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 7.70 (d, 1H,  $J=2.38$  Hz), 7.58 (dd, 1H,  $J=2.56$ , 7.60 Hz), 7.40 (AA'BB', 2H), 7.00 (d, 1H,  $J=8.70$  Hz), 6.88 (AA'BB', 2H), 4.48 (m, 1H), 1.77 (m, 1H), 1.61 (m, 1H), 1.36 (m, 11H), 0.87 (t, 3H,  $J=6.91$  Hz);  $\delta_{\text{C}}$  (100 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 155.2, 132.8, 132.6, 131.2, 128.2, 125.7, 125.6, 116.0, 114.4, 75.1, 36.6, 32.0, 29.5, 25.5, 19.7, 14.3.

**4'-(1-S-Methyl-heptyloxy)-2',3'-bis-trifluoromethyl-biphenyl-4-ol (22)**. A pressure tube was charged with **16** (1.18 g, 2.51 mmol),  $\text{Pd}_2(\text{dba})_3$  (115 mg, 0.13 mmol), 2-dicyclohexylphosphanyl-2'-dimethylaminobiphenyl (98.8 mg, 0.25 mmol), 4-hydroxyphenylboronic acid **20** (692 mg, 5.0 mmol) and  $\text{K}_3\text{PO}_4$  (1.07 g, 5.0 mmol), and was purged with Ar. Anhydrous DME (15 mL) was then added. The reaction mixture was purged with Ar again, capped and was heated at 80 °C for 3 hours. After cooling to room temperature, the mixture was partitioned between brine and EtOAc. The organic layer was



washed with water, dried over  $\text{MgSO}_4$ , and concentrated. The residual oil was purified by flash chromatography (5:1 hexanes - ethylacetate) to provide desired phenol **22** (665 mg, 61%) as a colorless oil;  $\delta_{\text{H}}$  (400 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 7.39 (d, 1H,  $J=8.79$  Hz), 7.18 (m, 3H), 6.87 (AA'BB', 2H), 4.93 (s, 1H), 4.53 (m, 1H), 1.80 (m, 1H), 1.66 (m, 1H), 1.37 (m, 11H), 0.88 (t, 2H,  $J=6.92$  Hz);  $\delta_{\text{C}}$  (100 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 157.1, 155.3, 136.3, 134.9, 133.8, 130.2, 117.3, 115.3, 76.0, 68.2, 36.5, 32.0, 29.4, 25.5, 22.8, 19.5, 14.3.

**4-(1-S-methyl-heptyloxy)-3-trifluoromethyl-phenyl 4'-(7,7,8,8,9,9,10,10,10-Nonafluoro-decyloxy)-biphenyl-4-carboxylate (W530, 3).** 90 mL oxalyl chloride was added into acid **23** (1.96 g, 3.79 mmol) in a 250 mL round bottom flask equipped with a magnetic spin bar under dry Ar. Stirring at room temperature, a drop of dry DMF was added. The reaction mixture was stirred for 4 hours. It hardly became a clear solution. The solvent oxalyl chloride was removed and the residue was dried under high vacuum. Then it was dissolved in 40 mL dry THF. To this solution, triethylamine (1 mL, 7.6 mmol) and phenol **17** (1.1 g, 3.79 mmol) in 10 mL dry THF were added respectively. The reaction mixture was stirred at room temperature for 12 hours. Few drops of water were added to quench the reaction. The reaction mixture was then concentrated as a solid which was absorbed in silica gel and directly subjected to purification by flash chromatography (10:1 hexanes - ethylacetate) to provide compound **3** (2.32 g, 76%) as a white solid. Further purification was carried out by recrystallization from ethanol (acetonitrile did not give good results) to provide **W530** (1.5 g, 50.2%) as a white crystal;  $\delta_{\text{H}}$  (400 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 8.20 (AA'BB', 2H), 7.67 (AA'BB', 2H), 7.58 (AA'BB', 2H), 7.41 (d, 1H,  $J=2.45$  Hz), 7.32 (AA'BB', 1H), 7.00 (m, 3H), 4.43 (m, 1H), 4.01 (t, 2H,  $J=6.36$  Hz), 2.07 (m, 2H), 1.81 (m, 3H), 1.69 (m, 3H), 1.61 (m, 5H), 1.37 (m, 10H), 0.87 (t, 3H,  $J=6.91$  Hz);  $\delta_{\text{C}}$  (100 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 178.1, 165.5, 159.7, 146.3, 143.2, 139.7, 132.2, 131.0, 128.7, 127.3, 126.9, 126.4, 121.1, 115.2, 114.7, 75.5, 68.0, 36.5, 32.0, 30.9, 29.4, 29.2, 29.1,

26.0, 25.4, 22.8, 20.3, 19.6, 17.5, 14.3. Phase transitions: SmC\* - 40 °C – SmA\* - 98 °C – I.  
(on cooling, determined by microscope observation).

**4-(1-S-methyl-heptyloxy)-2,3-bis-trifluoromethyl-phenyl 4'-Decyloxy-biphenyl-4-carboxylate (W557, 27).** A solution of DCC (70 mg, 0.34 mmol) in 3 mL dry CH<sub>2</sub>Cl<sub>2</sub> was added via canula with stirring and under argon to a solution of phenol **18** (101 mg, 0.28 mmol), acid **24** (110 mg, 0.31 mmol) and DMAP (7 mg, 0.06 mmol) in 5 mL dry CH<sub>2</sub>Cl<sub>2</sub>. The reaction mixture was allowed to stir for 12 hours at 25 °C, and then concentrated by rotary evaporation to give crude product as a dark oil, which was directly subjected to purification by flash chromatography (10:1 hexanes - ethylacetate) to provide **W557** (145 mg, 74%) as a white solid (Found: C, 72.63; H, 7.97; F, 8.94. C<sub>38</sub>H<sub>49</sub>F<sub>3</sub>O<sub>4</sub> requires C, 72.82; H, 7.88; F, 9.09);  $\delta_{\text{H}}$  (500 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 8.25 (AA'BB', 2H), 7.74 (AA'BB', 2H), 7.62 (AA'BB', 2H), 7.41 (d, 1H, J=9.23 Hz), 7.28 (d, 1H, J=9.34 Hz), 7.04 (AA'BB', 2H), 4.54 (m, 1H), 4.05 (t, 2H, J=6.60 Hz), 1.85 (m, 3H), 1.66 (m, 1H), 1.42 (m, 25H), 0.90 (m, 6H);  $\delta_{\text{C}}$  (100 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 165.1, 159.9, 146.8, 132.0, 131.2, 131.1, 129.3, 129.0, 128.6, 127.0, 126.6, 119.0, 115.2, 76.6, 68.4, 38.9, 36.4, 32.1, 32.0, 30.6, 29.8, 29.6, 29.6, 29.5, 29.4, 29.2, 26.3, 25.5, 24.0, 23.2, 22.9, 22.8, 19.5, 14.4, 14.3, 11.2. Phase transitions: Crystal – 33 °C - I (on cooling, determined by microscope observation), Crystal – 65 °C - I (on heating, determined by microscope observation).

**4'-(1-S-methyl-heptyloxy)-3'-trifluoromethyl-biphenyl-4-yl 4-Decyloxy-benzoate (W558, 28).** Same DCC coupling protocol applied as described above gave a white wax-like solid (Found: C, 72.50; H, 8.12; F, 8.84. C<sub>38</sub>H<sub>49</sub>F<sub>3</sub>O<sub>4</sub> requires C, 72.82; H, 7.88; F, 9.09);  $\delta_{\text{H}}$  (400 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 8.15 (AA'BB', 2H), 7.76 (d, 1H, J=2.29 Hz), 7.64 (dd, 1H, J=2.29, 8.61 Hz), 7.56 (AA'BB', 2H), 7.25 (AA'BB', 2H), 7.03 (d, 1H, J=8.70 Hz), 6.97 (AA'BB', 2H), 4.50 (m, 1H), 4.03 (t, 2H, J=6.55 Hz), 1.80 (m, 3H), 1.64 (m, 1H), 1.35 (m, 25H), 0.87(m, 6H);  $\delta_{\text{C}}$  (100 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 165.2, 163.8, 155.9, 150.7, 137.6, 132.7, 132.6,

132.2, 131.7, 128.0, 126.1, 122.5, 121.6, 114.5, 114.3, 75.1, 68.6, 36.6, 32.1, 32.0, 29.8, 29.6, 29.6, 29.5, 29.3, 26.2, 25.5, 22.9, 22.8, 19.7, 14.4, 14.3. Phase transitions: SmA\* – 49 °C - I (on cooling, determined by microscope observation).

**4'-(1-S-methyl-heptyloxy)-2',3'-bis-trifluoromethyl-biphenyl-4-yl 4-Decyloxy-benzolate (W555, 29).** Same DCC coupling protocol applied as described above gave a white solid (Found: C, 67.03; H, 7.27; F, 16.04. C<sub>38</sub>H<sub>48</sub>F<sub>6</sub>O<sub>4</sub> requires C, 67.42; H, 6.96; F, 16.41);  $\delta_{\text{H}}$  (400 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 8.16 (AA'BB', 2H), 7.44 (d, 1H, J=15.82 Hz), 7.34 (AA'BB', 2H), 7.23 (m, 3H), 6.97 (AA'BB', 2H), 4.55 (m, 1H), 4.05 (t, 2H, J=6.48 Hz), 1.82 (m, 3H), 1.66 (m, 1H), 1.37 (m, 25H), 0.88 (m, 6H). Phase transitions: Crystal – 14 °C - I (on cooling, determined by microscope observation), Crystal – 55 °C - I (on heating, determined by microscope observation).

**4'-decyloxy-biphenyl-4-yl 4-(1-Methyl-heptyloxy)-3-trifluoromethyl-benzolate (W551, 30).** Same DCC coupling protocol applied as described above gave a white wax-like solid (Found: C, 72.92; H, 8.19; F, 8.76; C<sub>38</sub>H<sub>49</sub>F<sub>3</sub>O<sub>4</sub> requires C, 72.82; H, 7.88; F, 9.09);  $\delta_{\text{H}}$  (500 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 8.45 (d, 1H, J=2.20 Hz), 8.32 (dd, 1H, J=2.20, 8.79 Hz), 7.59 (AA'BB', 2H), 7.51 (AA'BB', 2H), 7.25 (AA'BB', 2H), 7.06 (d, 1H, J=9.01 Hz), 6.98 (AA'BB, 2H), 4.60 (m, 1H), 3.99 (t, 2H, J=6.59 Hz), 1.81 (m, 3H), 1.68 (m, 1H), 1.66 (m, 1H), 1.45 (m, 3H), 1.32 (m, 22H), 0.90 (m, 6H);  $\delta_{\text{C}}$  (100 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 164.3, 160.8, 159.1, 150.0, 139.0, 135.8, 132.9, 130.2, 130.1, 128.3, 128.0, 124.8, 122.1, 120.9, 120.1, 119.8, 115.1, 115.0, 113.4, 75.8, 68.3, 36.4, 32.2, 32.0, 29.9, 29.9, 29.7, 29.6, 29.6, 29.4, 26.3, 25.3, 23.0, 22.8, 19.5, 14.4, 14.3. Phase transitions: SmC\* – 55 °C – I (on cooling, determined by microscope observation).

**4'-(1-S-methyl-heptyloxy)-2',3'-bis-trifluoromethyl-biphenyl-4-yl 4'-Decyloxy-biphenyl-4-carboxylate (W556, 31).** Same DCC coupling protocol applied as described above gave a white solid (Found: C, 70.22; H, 6.99; F, 14.51. C<sub>45</sub>H<sub>52</sub>F<sub>6</sub>O<sub>4</sub> requires C, 70.11;

H, 6.80; F, 14.79);  $\delta_{\text{H}}$  (500 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 8.24 (AA'BB', 2H), 7.69 (AA'BB', 2H), 7.59 (AA'BB', 2H), 7.43 (d, 1H,  $J=8.70$  Hz), 7.26 (AA'BB', 2H), 7.19 (d, 1H,  $J=8.88$  Hz), 6.99 (AA'BB', 2H), 4.53 (m, 1H), 4.00 (t, 2H,  $J=6.55$  Hz), 1.80 (m, 3H), 1.64 (m, 1H), 1.37 (m, 25H), 0.88 (m, 6H);  $\delta_{\text{C}}$  (100 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 174.0, 165.4, 159.8, 150.7, 146.3, 136.3, 132.1, 131.0, 130.0, 128.6, 127.6, 126.9, 121.8, 117.3, 115.2, 76.1, 68.4, 68.2, 36.5, 32.1, 32.0, 29.8, 29.6, 29.6, 29.5, 29.4, 26.3, 25.5, 22.9, 22.8, 19.5, 14.4, 14.4. Phase transitions: Crystal – 49 °C - I (on cooling, determined by microscope observation), Crystal – 78 °C - I (on heating, determined by microscope observation).

**3-trifluoromethyl-biphenyl-4,4'-diol (38)**. A pressure tube was charged with **33** (synthetic procedure in ref. **20**; 1.45 g, 6.02 mmol),  $\text{Pd}_2(\text{dba})_3$  (275 mg, 0.30 mmol), 2-dicyclohexylphosphanyl-2'-dimethylaminobiphenyl (236 mg, 0.60 mmol), 4-hydroxyphenylboronic acid **20** (1.66 g, 12.0 mmol) and  $\text{K}_3\text{PO}_4$  (2.55 g, 12.0 mmol), and was purged with Ar. Anhydrous DME (25 mL) was then added. The reaction mixture was purged with Ar again, capped and was heated at 80 °C for 17 hours. After cooling to room temperature, the mixture was partitioned between brine and EtOAc. The organic layer was washed with water, dried over  $\text{MgSO}_4$ , and concentrated. The residual oil was purified by flash chromatography (5:1 hexanes - ethylacetate) to provided desired phenol **38** (1.51 g) as a brown red solid which contained some palladium impurities but could be used in the subsequent reaction without further purification;  $\delta_{\text{H}}$  (300 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 7.65 (d, 1H,  $J=1.76$  Hz), 7.58 (dd, 1H,  $J=1.83, 8.52$  Hz), 7.41 (d, 2H,  $J=8.62$  Hz), 7.01 (d, 1H,  $J=8.48$  Hz), 6.90 (d, 1H,  $J=8.61$  Hz), 5.63 (s, 1H), 4.96 (s, 1H).

**(R)-4'-(1-Methyl-hept-6-enyloxy)-3'-trifluoromethyl-biphenyl-4-ol (36)**

Diethylazodicarboxylate (DEAD) (1.06 mL, 6.57 mmol) was added via syringe with stirring and under argon to a solution of 3-trifluoromethyl-biphenyl-4,4'-diol (**38**) prepared as described above (1.51 g, 5.97 mmol), (S)-oct-7-en-2-ol (**34**) (764 mg, 5.97 mmol) and

triphenyl phosphine (TPP) (1.69 g, 6.45 mmol) in 40 mL dry THF. The reaction mixture was allowed to stir for 12 hours at 25° C, and was then concentrated by rotary evaporation to give an orange oil which was directly subjected to purification by flash chromatography (20:1 hexanes - ethylacetate) to provide (R)-4'-(1-methyl-hept-6-enyloxy)-3'-trifluoromethyl-biphenyl-4-ol (**36**) (1.17 g, 52.8% over two steps) as a colorless oil;  $\delta_{\text{H}}$  (300 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 7.71 (d, 1H, J=2.03 Hz), 7.59 (dd, 1H, J=2.19, 8.49 Hz), 7.41 (d, 2H, J=8.58 Hz), 7.01 (d, 1H, J=8.67 Hz), 6.90 (d, 1H, J=8.57 Hz), 5.80 (m, 1H), 4.96 (m, 2H), 4.80 (s, 1H), 4.49 (m, 1H), 2.06 (m, 2H), 1.79 (m, 1H), 1.65 (m, 1H), 1.42 (m, 4H), 1.33 (d, 3H, J=6.05 Hz);  $\delta_{\text{C}}$  (75 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 155.1, 155.1, 138.8, 132.5, 132.4, 131.0, 128.0, 125.5, 125.4, 115.8, 114.4, 114.1, 74.7, 36.2, 33.7, 28.8, 24.7, 19.4.

**4-(9-Bromo-nonyloxy)-benzoic acid (41).** A 100 mL round bottom flask was charged with 4-hydroxy-benzoic acid ethyl ester (**39**) (6.00 g, 35.7 mmol), 1,9-dibromononane (**40**) (10.54 g, 35.7 mmol) and K<sub>2</sub>CO<sub>3</sub> (7.40 g, 53.5 mmol) in 25 mL 2-butanone. The reaction mixture was stirred for 18 hours at 80 °C and then filtered. The resulting solution was concentrated to an oil, which was directly subjected to purification by flash chromatography (25:1 hexanes - ethylacetate) to provide 4-(9-Bromo-nonyloxy)-benzoic acid ethyl ester (4.85 g, 13.1 mmol) as a white solid. A 250 mL round bottom flask was charged with 4-(9-Bromo-nonyloxy)-benzoic acid ethyl ester (4.85 g, 13.1 mmol), 24 mL 40% hydrobromic acid aqueous solution, 60 mL acetic acid and 12 mL ethanol. The reaction mixture was kept refluxing for 18 hours and then cooled in an ice/water bath until solid appeared. The solid was filtered, washed by water and dried under high vacuum to give pure 4-(9-Bromo-nonyloxy)-benzoic acid (3.37 g, 27.6% over two steps) as a white solid; mp 136 °C;  $\delta_{\text{H}}$  (300 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 8.04 (AA'BB', 2H), 6.93 (AA'BB', 2H), 4.02 (t, 2H, J=6.49 Hz), 3.41 (t, 2H, J=6.84 Hz), 1.83 (m, 4H), 1.39, (m, 10H);  $\delta_{\text{C}}$  (75 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 171.5, 163.6, 132.3, 121.3, 114.2, 68.2, 34.0, 32.8, 29.3, 29.2, 29.1, 28.7, 28.1, 25.9.

**4-(9-Bromo-nonyloxy)-benzoic acid 4'-(1-methyl-hept-6-enyloxy)-3'-trifluoromethyl -biphenyl-4-yl ester (42)**. Same DCC coupling protocol applied as described above gave a white wax-like solid;  $\delta_{\text{H}}$  (300 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 8.16 (AA'BB', 2H), 7.77 (d, 1H,  $J=1.92$  Hz), 7.66 (dd, 1H,  $J=1.88, 8.45$  Hz), 7.57 (AA'BB', 2H), 7.27 (AA'BB', 2H), 7.05 (d, 1H,  $J=8.73$  Hz), 6.98 (AA'BB', 2H), 5.81 (m, 1H), 4.96 (m, 2H), 4.51 (m, 1H), 4.05 (t, 2H,  $J=6.43$  Hz), 3.42 (t, 2H,  $J=6.82$  Hz), 2.07 (m, 2H), 1.85 (m, 5H), 1.66 (m, 1H), 1.40 (m, 14H), 1.35 (d, 3H,  $J=5.70$  Hz);  $\delta_{\text{C}}$  (75 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 165.0, 163.6, 155.6, 150.4, 138.8, 137.4, 132.3, 132.0, 131.4, 127.8, 125.9, 122.2, 122.0, 121.4, 114.4, 114.3, 114.1, 74.8, 68.3, 36.2, 34.1, 33.7, 32.8, 29.3, 29.2, 29.1, 28.8, 28.7, 28.1, 26.0, 24.7, 19.5. Phase sequence and transition temperatures: SmA\* – 44 °C – I (on cooling, determined by microscope observation).

**4-(9-Mercapto-nonyloxy)-benzoic acid 4'-(1-methyl-hept-6-enyloxy)-3'-trifluoromethyl -biphenyl-4-yl ester (43)**. A solution of 4-(9-Bromo-nonyloxy)-benzoic acid 4'-(1-methyl-hept-6-enyloxy)-3'-trifluoromethyl-biphenyl-4-yl ester (**42**) (1.56 g, 2.27 mmol) in 70 mL dry THF was cooled to -10 °C under argon. Bis(trimethylsilyl)thiane (0.57 mL, 2.72 mmol) and TBAF (1M solution in THF, 2.50 mL, 2.50 mmol) were added via syringe respectively. The reaction mixture was allowed to stir for 10 minutes at -10 °C, and then quickly poured into a saturated ammonium chloride solution. The resulting solution was extracted by ethyl acetate (200 mL, three times). The combined organic phases were washed by brine, dried over sodium sulfate and then concentrated by rotary evaporation to give crude product as an oil, which was directly subjected to purification by flash chromatography (20:1 hexanes – ethyl acetate) to provide 4-(9-Mercapto-nonyloxy)-benzoic acid 4'-(1-methyl-hept-6-enyloxy)-3'-trifluoromethyl-biphenyl-4-yl ester (**43**) (1.35 g, 92.8%) as a white wax-like solid;  $\delta_{\text{H}}$  (300 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 8.16 (AA'BB', 2H), 7.77 (d, 1H,  $J=1.90$  Hz), 7.66 (dd, 1H,  $J=1.86, 8.66$  Hz), 7.57 (AA'BB', 2H), 7.27 (AA'BB', 2H), 7.05 (d, 1H,  $J=8.73$  Hz), 6.98 (AA'BB', 2H),

5.79 (m, 1H), 4.96 (m, 2H), 4.51 (m, 1H), 4.05 (t, 2H, J=6.48 Hz), 2.53 (q, 2H, J=7.22, 7.40 Hz), 2.06 (m, 2H), 1.83 (m, 3H), 1.62 (m, 3H), 1.46 (m, 14H), 1.35 (d, 3H, J=5.70 Hz);  $\delta_c$  (75 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 165.0, 163.6, 155.6, 150.4, 138.8, 137.4, 132.3, 132.0, 131.4, 127.8, 125.9, 122.2, 121.4, 120.1, 120.0, 114.4, 114.3, 114.1, 74.8, 68.3, 36.2, 34.0, 33.7, 29.4, 29.3, 29.1, 29.0, 28.8, 28.3, 26.0, 24.7, 24.6, 19.4. Phase sequence and transition temperatures: SmA\* – 37 °C – I (on cooling, determined by microscope observation).