Supplementary Information

The dramatic influence of the location of bend and of lateral fluoro substitution on the mesomorphic properties of angular chiral esters based on a 1,3-disubstituted benzene ring

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Experimental

Structural information of materials was obtained by ^{1}H and ^{13}C NMR spectroscopy (JEOL Eclipse 400 spectrometer), by mass spectrometry (Finnigan-MAT 1020 spectrometer), and by elemental analysis (Fisons EA1108 CHN). Specific optical rotation, $[\alpha]_D$, for the final compounds (**1** to **11**) was determined at 26 °C in chloroform using a Bendix-NPL Automatic Polarimeter Type 143A. The purity of all final compounds (**1** to **11**) was checked by HPLC analysis (Merck-Hitachi with Merck RP 18 column, Cat. No. 16 051) and were all found to be >99.9% pure. The progress of some reactions and the purity of some intermediates were analyzed by Gas Liquid Chromatography (GLC) using a Varian CP3380 gas chromatograph with a 10 m, 0.25 mm internal diameter, 0.12 mm fused silica capillary column. All melting points, transition temperatures and mesophase morphologies were determined using an Olympus BH-2 polarizing microscope in conjunction with a Mettler FP52 heating stage and FP5 temperature controller, and these values were confirmed using differential scanning calorimetry (Perkin-Elmer DSC-7 and Mettler-Toledo DSC822e). The spontaneous polarization values and tilt angles were evaluated as a function of temperature in electrooptical cells (5 μm thickness with antiparallel rubbed polyimide alignment layers) using equipment purchased from Instec Inc. (USA), employing a triangular wave of 10 V μm^{-1} at a frequency of 30 Hz.

Compounds **13**, **15**, **19**, **26**, **29**, **33**, **39** and **40**, and other simple starting materials and solvents are commercially-available. Compounds **22**,[1] **23H**,[2] and **36**,[3] were prepared as described previously.

1-Benzyloxy-2,3,4-trifluorobenzene (**14**)

A stirred mixture of compound **13** (22.00 g, 0.149 mol), benzyl chloride (16.92 g, 0.134 mol) and potassium carbonate (62 g, 0.45 mol) in butanone (200 ml) was heated under reflux for 16 h. The mixture was cooled and the potassium carbonate was filtered off. The solvent was removed *in vacuo*, and the crude product was purified by column chromatography (silica gel / hexane with the gradual introduction of DCM) to give a colourless solid.

Yield 31.0 g (97%). mp 58 °C. ^{1}H NMR (400 MHz, $CDCl_3$) 5.04(2H, s), 6.61(1H, m), 6.77(1H, m), 7.26-7.37(5H, m). MS m/z 238 (M^+).

3-Benyloxybenzoic acid (**16H**)

Benzyl chloride (144.00 g, 1.12 mol) was added dropwise to a refluxing solution of compound **15** (70.00 g, 0.51 mol), NaOH (40.00 g, 1.0 mol), ethanol (200 ml) and H_2O (100 ml). The mixture was heated under reflux for 16 h, cooled, and the ethanol was removed *in vacuo*. Sodium hydroxide (40 g, 1 mol) and water (200 ml) were added and the mixture was heated under reflux for 2 hours. The mixture was poured onto crushed ice and HCl (36%), and the crude product was filtered off and recrystallized from ethanol to yield a colourless powder.

Yield 72.34 g (62%). mp 133 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.38(1H, ddd, J = 7.9 Hz, J = 1.8 Hz, J = 1.2 Hz), 6.48-6.58(4H, m), 6.63(2H, dd, J = 8.7 Hz, J = 1.5 Hz), 6.76(2H, m). MS *m/z* 228(M^+).

5-Benzyloxy-2,3,4-trifluorobenzoic acid (**16F**)

n-Butyllithium (25.2 ml, 2.5 M, 0.063 mol) was added dropwise to a cooled (-78 °C), stirred solution of compound **14** (15.00 g, 0.063 mol) in dry THF (300 ml) under dry nitrogen. The resulting solution was stirred for one hour, poured onto solid carbon dioxide, and allowed to warm to room temperature overnight. The reaction mixture was acidified with 10% HCl (100 ml), the product was extracted into ether (x2), and the combined ethereal extracts were washed with water and dried ($MgSO_4$). The solvent removed *in vacuo* to yield an off-white solid, which was recrystallized from ethanol to yield colourless crystals.

Yield 7.88 g (44%). mp 175 °C. ^{1}H NMR (400 MHz, D6-DMSO) δ 5.17(2H, s), 7.24-7.44(6H, m). MS *m/z* 282 (M^+).

(*S*)-1-Methylheptyl 3-benzyloxybenzoate (**17H**)

DCC (8.61 g, 0.042 mol) was added all at once to a stirred mixture of compound **16H** (8.50 g, 0.037 mol), (*S*)-2-octanol (5.00 g, 0.038 mol) and DMAP (1.39 g, 0.011 mol) in dry DCM (200 ml) at room temperature. The mixture was stirred at room temperature overnight (TLC analysis revealed a complete reaction), the DCU was filtered off and the solvent was removed *in vacuo*. The crude product was purified by column chromatography (silica gel / hexane with the gradual introduction of DCM) to give a colourless oil.

Yield 10.40 g (83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87(3H, t), 1.22-1.40(11H, m, including 3H, d), 1.60(1H, m), 1.75(1H, m), 5.09(2H, s), 5.15(1H, sext), 7.14(1H, ddd, J = 7.9 Hz, J = 1.8 Hz, J = 1.2 Hz), 7.30-7.40(4H, m), 7.44(2H, dd, J = 8.7 Hz, J = 1.5 Hz), 7.54(2H, m). MS *m/z* 340(M^+).

(*S*)-1-Methylheptyl 5-benzyloxy-2,3,4-trifluorobenzoate (**17F**)

Quantities: Compound **16F** (6.28 g, 0.022 mol), (*S*)-2-octanol (2.95 g, 0.023 mol), DCC (5.21 g, 0.025 mol), DMAP (0.84 g, 0.0069 mol). The experimental procedure was as described in the preparation of compound **17H**, to yield a colourless oil.

Yield 6.96 g (80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.80(3H, t), 1.20-1.40(11H, m, including 3H, d), 1.52(1H, m), 1.64(1H, m), 5.06(2H, s), 5.06(1H, sext), 7.24-7.38(6H, m). MS m/z 394(M^+).

(*S*)-1-Methylheptyl 3-hydroxybenzoate (**18H**)

A mixture of compound **17H** (10.40 g, 0.031 mol) and 10% palladium-on-carbon (1.50 g) in ethyl acetate (250 ml) was hydrogenated at 35 psi for 16 hours. The mixture was filtered through hyflo supercell, and the solvent was removed *in vacuo* to give a colourless oil.

Yield 7.33 g (95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.86(3H, t), 1.20-1.40(11H, m, including 3H, d), 1.60(1H, m), 1.72(1H, m), 5.15(1H, sextet), 6.82(1H, s), 7.09(1H, ddd, J = 7.9 Hz, J = 1.8 Hz, J = 1.2 Hz), 7.30(1H, dd, J = 7.9 Hz, J = 7.9 Hz), 7.59(1H, ddd, J = 7.9 Hz, J = 1.2 Hz, J = 1.2 Hz), 7.66(1H, dd, J = 1.8 Hz, J = 1.2 Hz). MS *m/z* 250(M^+).

(*S*)-1-Methylheptyl 5-hydroxy-2,3,4-trifluorobenzoate (**18F**)

Quantities: Compound **17F** (6.96 g, 0.018 mol), 10% palladium-on-carbon (1.00 g). The experimental procedure was as described in the preparation of compound **18H** to yield a colourless solid.

Yield 5.38 g (98%). mp 54 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87(3H, t), 1.22-1.42(11H, m, including 3H, d), 1.59(1H, m), 1.70(1H, m), 5.15(1H, sext), 5.50(1H, d, *J* = 2.7 Hz), 7.37(1H, ddd, *J* = 8.6 Hz, *J* = 6.2 Hz, *J* = 2.5 Hz). MS *m/z* 304(M^+).

(*S*)-1-Methylheptyl 3-(4-benzyloxyphenylcarbonyloxy)benzoate (**20H**)

Quantities: Compound **19** (2.87 g, 0.013 mol), compound **18H** (3.0 g, 0.012 mol), DCC (2.72 g, 0.0132 mol), DMAP (0.44 g, 3.6 mmol). The experimental procedure was as described in the preparation of compound **17H**, to yield a colourless oil.

Yield 5.18 g (92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87(3H, t), 1.22-1.40(11H, m, including 3H, d), 1.60(1H, m), 1.73(1H, m), 5.12(2H, s), 5.15(1H, sext), 7.08(2H, d, *J* = 8.7 Hz), 7.34-7.48(6H, m), 7.50(1H, dd, *J* = 7.9 Hz, *J* = 7.9 Hz), 7.85(1H, dd, *J* = 1.8 Hz, *J* = 1.2 Hz), 7.95(1H, ddd, *J* = 7.9 Hz, *J* = 1.2 Hz, *J* = 1.2 Hz), 8.17(2H, d, *J* = 8.7 Hz). MS *m/z* 460(M^+).

(*S*)-1-Methylheptyl 5-(4-benzyloxyphenylcarbonyloxy)-2,3,4-trifluorobenzoate (**20F**)

Quantities: Compound **19** (1.46 g, 0.0064 mol), compound **18F** (2.00 g, 0.0066 mol), DCC (1.50 g, 0.0073 mol), DMAP (0.24 g, 0.0020 mol). The experimental procedure was as described in the preparation of compound **17H** to yield a colourless oil.

Yield 2.96 g (90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (3H, t), 1.22-1.44 (11H, m, including 3H, d), 1.60 (1H, m), 1.72 (1H, m), 5.16 (1H, sext), 5.17 (2H, s), 7.08 (2H, d, *J* = 8.7 Hz), 7.33-7.47 (5H, m), 7.65 (1H, ddd, *J* = 7.8 Hz, *J* = 5.9 Hz, *J* = 2.0 Hz), 8.14 (2H, d, *J* = 8.7 Hz). MS *m/z* 514(M^+).

(*S*)-1-Methylheptyl 3-(4-hydroxyphenylcarbonyloxy)benzoate (**21H**)

Quantities: compound **20H** (5.18 g, 0.011 mol), 10% palladium-on-carbon (2 g). The experimental procedure was as described for the preparation of compound **18H** to give a colourless solid.

Yield 3.54 g (87%). mp 75 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85(3H, t), 1.22-1.40(11H, m, including 3H, d), 1.60(1H, m), 1.71(1H, m), 5.15(1H, sext), 6.47(1H, s), 6.93(2H, d, *J* = 8.7 Hz),

7.41(1H, ddd, *J* = 7.9 Hz, *J* = 1.8 Hz, *J* = 1.2 Hz), 7.50(1H, dd, *J* = 7.9 Hz, *J* = 7.9 Hz), 7.85(1H, dd, *J* = 1.8 H, *J* = 1.2 Hz), 7.94(1H, ddd, *J* = 7.9 Hz, *J* = 1.2 Hz, *J* = 1.2 Hz), 8.10(2H, d, *J* = 8.7 Hz). MS *m/z* 370(M^+).

(*S*)-1-Methylheptyl 2,3,4-trifluoro-5-(4-hydroxyphenylcarbonyloxy)benzoate (**21F**)

Quantities: Compound **20F** (2.81 g, 0.0055 mol), 10% palladium-on-carbon (0.50 g). The experimental procedure was as described in the preparation of compound **18H**, except that the product was purified *via* column chromatography (silica gel, DCM / Hexane, 1:1), to yield a colourless solid.

Yield 2.07 g (89%). mp 103 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87(3H, t), 1.23-1.42(11H, m, includes 3H, d), 1.6 (1H, m), 1.73(1H, m), 5.17(1H, sext), 6.11(1H, s, broad), 6.94(2H, d, *J* = 8.7 Hz), 7.65(1H, ddd, *J* = 8.1 Hz, *J* = 6.6 Hz, *J* = 2.6 Hz), 8.10(2H, d, *J* = 8.7 Hz). MS m/z 424 (M^+).

(*S*)-(+)-1-Methylheptyl 3-[4-(4'-dodecyloxybiphenyl-4-ylcarbonyloxy)phenylcarbonyloxy]benzoate (**1H**)

DCC (0.77 g, 3.7 mmol) was added all at once to a stirred mixture of compound **21H** (1.50 g, 4.1 mmol), compound **22** (1.30 g, 3.4 mmol) and DMAP (0.15 g, 1.2 mmol) in dry DCM (100 ml) at room temperature. The mixture was stirred at room temperature overnight (TLC analysis revealed a complete reaction), the DCU was filtered off and the solvent was removed *in vacuo*. The crude product was purified by column chromatography (silica gel / hexane with the gradual introduction of DCM) to give a colourless solid, which was recrystallized from ethanol-ethyl acetate (5:1) to yield colourless crystals.

Yield 1.20 g (48%). Transitions (°C) Cryst 37.9 SmC*ferro 143.5 SmA*helical 156.5 Iso. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87(6H, 2xt), 1.22-1.40(27H, m, including 3H, d), 1.47(2H, quint), 1.60(1H, m), 1.74(1H, m), 1.81(2H, quint), 4.00(2H, t), 5.17(1H, sext), 7.00(2H, d, *J* = 8.7 Hz), 7.39(2H, d, *J* = 8.7 Hz), 7.43(1H, ddd, *J* = 7.9 Hz, *J* = 1.8 Hz, *J* = 1.2 Hz), 7.50(1H, dd, *J* = 7.9 Hz, *J* = 7.9 Hz), 7.59(2H, d, *J* = 8.7 Hz), 7.70(2H, d, *J* = 8.7 Hz), 7.89(1H, dd, *J* = 1.8 Hz, *J* = 1.2 Hz), 7.98(1H, ddd, *J* = 7.9 Hz, *J* = 1.2, *J* = 1.2 Hz), 8.24(2H, d, *J* = 8.7 Hz), 8.30(2H, d, *J* = 8.7 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.02, 14.09, 20.00, 22.55, 22.65, 25.36, 26.00, 29.10, 29.20, 29.32, 29.36, 29.54, 29.57, 29.60, 29.63, 31.68, 31.87, 35.96, 68.08, 72.15, (alkyl carbons,

20 required, 20 found), 114.94, 122.08, 122.78, 126.18, 126.59, 126.65, 126.79, 127.09, 128.34, 129.37, 130.77, 131.67, 131.85, 132.56, 146.29, 150.74, 155.35, 159.63, (aromatic carbons, 18 required, 18 found), 164.22, 164.43, 165.18, (carbonyl carbons, 3 required, 3 found). MS *m/z* 734(M^+). Elemental analysis: calc. for $C_{47}H_{58}O_7$: C 76.81, H 7.95; found: C 76.74, H 7.91. $[\alpha]_D$ = +15.05°.

(*S*)-1-Methylheptyl 5-[4-(4'-dodecyloxybiphenyl-4-ylcarbonyloxy)phenylcarbonyloxy]-2,3,4-trifluorobenzoate (**1F**)

Quantities: Compound **22** (0.97 g, 0.0025 mol), compound **21F** (1.09 g, 0.0026 mol), DCC (0.59 g, 0.0029 mol), DMAP (0.10 g, 0.00078 mol). The experimental procedure was as described in the preparation of compound **1H** to yield colourless crystals.

Yield 0.81 g (41%). Transitions (°C): Cr 70.0 SmC* 137.9 SmA* 165.3 I. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88(6H, 2xt), 1.22-1.42(27H, m, including 3H, d), 1.48(2H, quint), 1.61(1H, m), 1.73 (1H, m), 1.82(2H, quint), 4.02(2H, t), 5.17(1H, sext), 7.01(2H, d, *J* = 8.7 Hz), 7.43(2H, d), 7.61(2H, d, *J* = 8.7 Hz), 7.68(1H, ddd, *J* = 7.9 Hz, *J* = 6.4 Hz, *J* = 2.4 Hz), 7.72(2H, d, *J* = 8.7 Hz), 8.25(2H, d, *J* = 8.7 Hz), 8.29(2H, d, *J* = 8.7 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) 17.57, 17.64, 23.44, 26.09, 26.21, 28.79, 29.56, 32.60, 32.76, 32.88, 32.92, 33.10, 33.13, 33.17, 33.19, 35.21, 35.44, 39.37, 71.68, 77.00 (alkyl carbons, 20 required, 20 found); 118.53, 119.51(dd, *J* = 8.5 Hz, *J* = 3.8 Hz), 123.53, 125.88, 128.70, 130.20, 130.24, 131.92, 134.36, 135.23, 135.75, 138.16(dd, *J* = 10.8 Hz, *J* = 3.8 Hz), 144.50(ddd, *J* = 253.7 Hz, *J* = 16.9 Hz, *J* = 13.1 Hz), 149.96, 150.40(ddd, *J* = 258.5 Hz, *J* = 11.5 Hz, *J* = 2.3 Hz), 153.10(ddd, *J* = 261.4 Hz, *J* = 11.5 Hz, *J* = 2.3 Hz), 159.41, 163.23 (aromatic carbons, 18 required, 18 found), 165.39, 166.40, 167.95 (carbonyl carbons, 3 required, 3 found). MS m/z 788 (M^+). Elemental analysis: $C_{47}H_{55}O_7F_3$ requires C 71.55 %, H 7.03 %; found C 71.79 %, H 7.09 %. $[\alpha]_D$ = +13.85°.

(*S*)-1-Methylheptyl 4-(3-benzyloxyphenylcarbonyloxy)benzoate (**24H**)

Quantities: Compound **23H** (0.95 g, 3.8 mmol), compound **16H** (0.91 g, 4.0 mmol), DCC (0.86 g, 4.2 mmol), and DMAP (0.14 g, 1.1 mmol). The experimental procedure was as described for the preparation of compound **17H** to yield a colourless oil.

Yield 1.74 g (99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88(3H, t), 1.25-1.45(11H, m, including 3H, d), 1.61 (1H, m), 1.75 (1H, m), 5.12(2H, s), 5.15(1H, sext), 7.25-7.31(3H, m), 7.34-7.47(6H,

m), 7.80(1H, dd, *J* = 1.8 Hz, *J* = 1.8 Hz), 7.82(1H, ddd, *J* = 7.9 Hz, *J* = 1.8 Hz, *J* = 1.2 Hz), 8.13 (2H, d, *J* = 8.7 Hz). MS *m/z* 460(M^+).

(*S*)-1-Methylheptyl 4-(5-benzyloxy-2,3,4-trifluorophenylcarbonyloxy)benzoate (**24F**)

Quantities: Compound **23H** (1.4 g, 5.60 mmol), compound **16F** (1.50 g, 5.32 mmol), DCC (1.20 g, 5.83 mmol), and DMAP (0.21 g, 1.72 mmol). The experimental procedure was as described for the preparation of compound **17H** to yield a colourless oil.

Yield 2.43 g (89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87(3H, t), 1.22-1.45(11H, m, including 3H, d), 1.64(1H, m), 1.74 (1H, m), 5.17(1H, sext), 5.27(2H, s), 7.26(2H, d, *J* = 8.7 Hz), 7.30-7.38(6H, m), 8.05 (2H, d, *J* = 8.7 Hz). MS *m/z* 514(M^+).

(*S*)-1-Methylheptyl 4-(3-hydroxyphenylcarbonyloxy)benzoate (**25H**)

Quantities: Compound **24H** (1.74 g, 3.8 mmol), 10% palladium-on-carbon (0.20 g). The experimental procedure was as described for the preparation of compound **18H** to yield a colourless solid.

Yield 1.50 g (100%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85(3H, t), 1.22-1.40(11H, m, including 3H, d), 1.60(1H, m), 1.71(1H, m), 5.15(1H, sext), 6.73(1H, s), 7.06(1H, ddd, *J* = 7.9 Hz, *J* = 1.8 Hz, *J* = 1.2 Hz), 7.18(2H, d, *J* = 8.7 Hz), 7.29(1H, dd, *J* = 7.9 Hz, *J* = 7.9 Hz), 7.59(1H, dd, *J* = 1.8 Hz, *J* = 1.2 Hz) 7.67(1H, ddd, *J* = 7.9 H, *J* = 1.8 Hz, *J* = 1.2 Hz), 8.05(2H, d, *J* = 8.7 Hz). MS *m/z* 370(M^+).

(*S*)-1-Methylheptyl 4-(2,3,4-trifluoro-5-hydroxyphenylcarbonyloxy)benzoate (**25F**)

Quantities: Compound **24F** (2.43 g, 4.73 mmol), 10% palladium-on-carbon (0.50 g). The experimental procedure was as described for the preparation of compound **18H** to yield a colourless solid.

Yield 2.01 g (100%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85(3H, t), 1.22-1.42(11H, m, including 3H, d), 1.59(1H, m), 1.70(1H, m), 5.15(1H, sext), 6.25(1H, s), 7.22(2H, d, *J* = 8.7 Hz), 7.34(1H, ddd, *J* = 8.6 Hz, *J* = 6.2 Hz, *J* = 2.5 Hz), 8.00(2H, d, *J* = 8.7 Hz). MS *m/z* 424(M^+).

(*S*)-1-Methylheptyl 4-[3-(4'-dodecyloxybiphenyl-4-ylcarbonyloxy)phenylcarbonyloxy]benzoate (**2H**)

Quantities: Compound **25H** (1.50 g, 4.1 mmol), compound **22** (1.32 g, 3.4 mmol), DCC (0.78 g, 3.8 mmol), and DMAP (0.13 g, 1.0 mmol). The experimental procedure was as described for the preparation of compound **1H** to yield colourless crystals.

Yield 0.63 g (25%). Transitions (°C) Cryst 81.5 Iso. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87(6H, 2xt), 1.22-1.40(27H, m, including 3H, d), 1.47(2H, quint), 1.60(1H, m), 1.74(1H, m), 1.81(2H, quint), 4.00(2H, t), 5.17(1H, sext), 7.01(2H, d, *J* = 8.7 Hz), 7.30(2H, d, *J* = 8.7 Hz), 7.55(1H, ddd, *J* = 7.9 Hz, *J* = 1.8 Hz, *J* = 1.2 Hz), 7.58-7.62(3H, m), 7.72(2H, d, *J* = 8.7 Hz), 8.08(1H, dd, *J* = 1.8 Hz, *J* = 1.2 Hz), 8.11-8.16(3H, m), 8.26(2H, d, *J* = 8.7 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.06, 14.11, 20.08, 22.55, 22.68, 25.39, 26.00, 29.10, 29.20, 29.34, 29.36, 29.54, 29.57, 29.62, 29.65, 31.71, 31.90, 36.10, 68.15, 71.96, (alkyl carbons, 20 required, 20 found), 114.99, 121.61, 122.78, 126.18, 126.59, 126.66, 126.79, 127.09, 128.39, 129.37, 130.78, 131.18, 131.85, 132.56, 146.31, 151.04, 154.15, 159.23, (aromatic carbons, 18 required, 18 found), 164.25, 164.52, 165.26, (carbonyl carbons, 3 required, 3 found). MS *m/z* 734(M^+). Elemental analysis: calc. for $C_{47}H_{58}O_7$: C 76.81, H 7.95; found: C 76.71, H 7.88. $[\alpha]_D$ = +14.03°.

(*S*)-1-Methylheptyl 4-[2,3,4-trifluoro-5-(4'-dodecyloxybiphenyl-4-ylcarbonyloxy)phenylcarbonyloxy]benzoate (**2F**)

Quantities: Compound **25F** (2.01 g, 4.74 mmol), compound **22** (1.72 g, 4.50 mmol), DCC (1.08 g, 5.24 mmol), and DMAP (0.20 g, 1.64 mmol). The experimental procedure was as described for the preparation of compound **1H**.

Yield 1.42 g (38%). Transitions (°C) Cryst 38.0 (SmC* 34.5) SmA* 49.8 Iso. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88(6H, 2xt), 1.22-1.40(27H, m, including 3H, d), 1.46(2H, quint), 1.62(1H, m), 1.74(1H, m), 1.81(2H, quint), 4.01(2H, t), 5.15(1H, sext), 7.00(2H, d, *J* = 8.7 Hz), 7.30(2H, d, *J* = 8.7 Hz), 7.59(2H, d, *J* = 8.7 Hz), 7.71(2H, d, *J* = 8.7 Hz), 7.87(1H, ddd, *J* = 7.2 Hz, *J* = 7.2 Hz, *J* = 2.0 Hz), 8.13(2H, d, *J* = 8.7 Hz), 8.23(2H, d, *J* = 8.7 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.04, 14.11, 20.06, 22.57, 22.68, 25.39, 26.02, 29.13, 29.22, 29.34, 29.38, 29.57, 29.59, 29.63, 29.65, 31.72, 31.91, 36.03, 68.17, 72.09, (alkyl carbons, 20 required, 20 found), 114.2(dd, *J* = 7.6, *J* = 3.5), 115.00, 120.73, 121.36, 125.39, 126.71, 128.37, 129.05, 131.04, 131.19, 131.48, 135.19(dd, *J* = 11.42 Hz, *J* = 5.71 Hz), 141.33(ddd, *J* = 254.10 Hz, *J* = 17.13 Hz, *J* = 13.70 Hz), 146.89. 147.81(ddd, *J* = 260.48 Hz, *J* = 11.10 Hz, *J* = 2.96 Hz), 149.83(ddd, *J* = 264.92 Hz, *J* = 10.66 Hz, *J* = 2.37 Hz), 153.57, 159.7 (aromatic carbons, 18 required, 18 found), 160.11, 163.46,

165.23 (carbonyl carbons, 3 required, 3 found). MS *m/z* 788(M^+). Elemental analysis: calc. for $C_{47}H_{55}O_7F_3$: C 77.55, H 7.03; found: C 77.71, H 7.09. $[\alpha]_D$ = +12.15°.

1-Benzyloxy-3-bromobenzene (**27**)

Quantities: compound **26** (50.00 g, 0.289 mol), benzyl chloride (32.8 g, 0.260 mol). The experimental procedure was as described for the preparation of compound **14**, except that the crude product was purified using a short column of silica gel, and eluting with hexane to yield a colourless oil.

Yield 63.58 g (93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.05(2H, s), 6.91(1H, ddd, *J* = 7.9 Hz, *J* = 2.6 Hz, *J* = 1.3 Hz), 7.15(1H, dd, *J* = 7.9 Hz, *J* = 7.9 Hz), 7.17(1H, dd, *J* = 1.3 Hz, *J* = 1.3 Hz), 7.33-7.44(5H, m). MS *m/z* 264(M^+), 262(M^+).

3-Benzyloxyphenylboronic acid (**28H**)

n-Butyllithium (40.7 ml, 2.5 M in hexane, 0.101 mol) was added dropwise to a cooled (-78 °C), stirred solution of compound **27** (23.00 g, 0.088 mol) in dry THF (500 ml) under dry nitrogen. The solution was stirred at -78 °C for one hour and trimethyl borate (18.72 g, 0.180 mol) was added dropwise at -78 °C. The stirred mixture was allowed to warm to room temperature overnight, and 10% hydrochloric acid was added. The product was extracted into ether (x2), and the combined ethereal extracts were washed with water, and dried ($MgSO_4$). The solvent was removed *in vacuo*, and the crude solid product was stirred in hexane give a colourless powder.

Yield 13.23 g (66%). ^{1}H NMR (400 MHz, D6-DMSO) δ 5.09(2H, s), 6.96(1H, ddd, *J* = 8.4 Hz, *J* = 2.5 Hz, *J* = 1.2 Hz), 7.17(1H, dd, *J* = 8.4 Hz, *J* = 8.4 Hz), 7.22-7.40(7H, m). MS *m/z* 228(M^+).

5-Benzyloxy-2,3,4-trifluorophenylboronic acid (**28F**)

Quantities: Compound **14** (31.5 g, 0.13 mol), *n*-butyllithium (60.0 ml, 2.5 M, 0.15 mol), trimethyl borate (32.0 g, 0.31 mol). The experimental procedure was as described in the preparation of compound **28H**, to yield a colourless powder.

Yield 34.3 g (94%). ^{1}H NMR (400 MHz, D6-DMSO) δ 5.19(2H, s), 7.2 (1H, ddd, *J* = 8.9, *J* = 4.4, *J* = 2.2), 7.23-7.41(5H, m), 8.48 (2H, s). MS *m/z* 282 (M^+).

(*S*)-1-Methylheptyl 4-bromobenzoate (**30**)

Quantities: compound **29** (6.42 g, 0.032 mol), (*S*)-2-octanol (4.24 g, 0.033 mol), DCC (7.48 g, 0.036 mol), DMAP (1.20 g, 0.010 mol). The experimental procedure was as described for the preparation of compound **17H** to yield a colourless oil.

Yield 9.16 g (92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89(3H, t), 1.22-1.40(11H, m, including 3H, d), 1.60(1H, m), 1.72(1H, m), 5.14(1H, sext), 7.58(2H, d, *J* = 8.6 Hz), 7.90(2H, d, *J* = 8.6 Hz). MS *m/z* 314(M^+), 312(M^+).

(*S*)-1-Methylheptyl 3-benzyloxybiphenyl-4'-carboxylate (**31H**)

Compound **28H** (3.88 g, 0.017 mol) was added to a stirred mixture of compound **30** (4.50 g, 0.014 mol), sodium carbonate (1.80 g, 0.017 mol), tetrakis(triphenylphosphine)palladium(0) (0.46 g, 0.0004 mol) in DME (100 ml and water (20 ml) under nitrogen. The stirred mixture was heated under reflux overnight. Water was added to the mixture, and the product was extracted into ether (x2). The combined ethereal extracts were washed with brine, and dried ($MgSO_4$). The solvent was removed *in vacuo* and the crude product was purified by column chromatography (silica gel / hexane with the gradual introduction of dichloromethane) to give a colourless oil.

Yield 5.35 g (92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90(3H, t), 1.25-1.45(11H, m, including 3H, d), 1.65(1H, m), 1.78(1H, m), 5.14(2H, s), 5.21(1H, sext), 7.03(1H, ddd, *J* = 9.0 Hz, *J* = 2.4 Hz, *J* = 1.2 Hz), 7.23-7.26(2H, m), 7.33-7.45(4H, m), 7.48(2H, dd, *J* = 8.5 Hz, *J* = 1.5 Hz), 7.66(2H, d, *J* = 8.7 Hz), 8.14(2H, d, *J* = 8.7 Hz). MS *m/z* 416(M^+).

(*S*)-1-Methylheptyl 5-benzyloxy-2,3,4-trifluorobiphenylbiphenyl-4'-carboxylate (**31F**)

Quantities: Compound **30** (4.50 g, 0.014 mol), compound **28F** (4.87 g, 0.017 mol). The experimental procedure was as described in the preparation of compound **31H** to yield a colourless oil.

Yield 6.43 g (98%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90(3H, t), 1.22-1.45(11H, m, including 3H, d), 1.65(1H, m), 1.78(1H, m), 5.19(2H, s), 5.19(1H, sext), 6.84(1H, ddd, *J* = 8.7 Hz, *J* = 7.0 Hz, *J* = 2.8 Hz), 7.34-7.48(5H, m), 7.52(2H, dd = 8.7 Hz, *J* = 1.5 Hz), 8.13(2H, d, *J* = 8.7 Hz). MS *m/z* 470(M^+).

(*S*)-1-Methylheptyl 3-hydroxybiphenyl-4'-carboxylate (**32H**)

Quantities: compound **31H** (5.35 g, 0.013 mol), 10% palladium on carbon (1.00 g). The experimental procedure was as described for the preparation of compound **18H**, except that due to incomplete hydrogenolysis, the crude product was purified by column chromatography (silica gel / hexane with the gradual introduction of dichloromethane) to give a colourless oil.

Yield 2.46 g (58%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88(3H, t), 1.23-1.42(11H, m, including 3H, d), 1.64(1H, m), 1.76(1H, m), 5.20(1H, sext), 6.91(1H, ddd, *J* = 8.9 Hz, *J* = 2.4 Hz, *J* = 1.2 Hz), 7.13(1H, dd, *J* = 2.4 Hz, *J* = 2.4 Hz), 7.19(1H, ddd, *J* = 8.9 Hz, *J* = 2.4 Hz, *J* = 1.2 Hz), 7.34(1H, dd, *J* = 8.9 Hz, *J* = 8.9 Hz), 7.63(2H, d, *J* = 8.7 Hz), 8.11(2H, d, *J* = 8.7 Hz). MS *m/z* 326(M^+).

(*S*)-1-Methylheptyl 5-hydroxy-2,3,4-trifluorobiphenyl-4'-biphenylcarboxylate (**32F**)

Quantities: Compound **31F** (6.43 g, 0.014 mol), 10% palladium-on-carbon (1.00 g). The experimental procedure was as described in the preparation of compound **18H** to yield a colourless solid.

Yield 4.02 g (76%). mp 97 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.86(3H, t), 1.22-1.42(11H, m, including 3H, d), 1.65(1H, m), 1.75(1H, m), 5.19(1H, sext), 5.52(1H, d, *J* = 3.0), 6.88(1H, ddd, *J* = 8.9, *J* = 6.7, *J* = 2.4), 7.55(2H, dd, *J* = 8.6, *J* = 1.5), 8.11(2H, d, *J* = 8.6). MS m/z 380 (M^+).

(*S*)-1-Methylheptyl 3-(4'-dodecyloxybiphenyl-4-ylcarbonyloxy)biphenyl-4'-carboxylate (**3H**)

Quantities: compound **22** (1.00 g, 2.6 mmol), compound **32H** (0.88 g, 2.7 mmol), DCC (0.61 g, 3.0 mmol), DMAP (0.10 g, 0.8 mmol). The experimental procedure was as described for the preparation of compound **1H** to yield colourless crystals.

Yield: 1.04 g (58%). Transitions (°C) Cryst 88.0 Iso. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87(6H, 2xt), 1.22-1.40(27H, m, including 3H, d), 1.47(2H, quint), 1.62(1H, m), 1.74(1H, m), 1.80(2H, quint), 4.01(2H, t), 5.17(1H, sext), 7.01(2H, d, *J* = 8.7 Hz), 7.28(1H, ddd, *J* = 8.4 Hz, *J* = 2.2 Hz, *J* = 1.2 Hz), 7.50(1H, dd, *J* = 1.2 Hz, *J* = 1.2 Hz), 7.52-7.57(2H, m), 7.61(2H, d, *J* = 8.7 Hz), 7.68(2H, d, *J* = 8.7 Hz), 7.73(2H, d, *J* = 8.7 Hz), 8.11(2H, d, *J* = 8.7 Hz), 8.26(2H, d, *J* = 8.7 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.07, 14.12, 20.09, 22.56, 22.68, 25.41, 26.03, 29.16, 29.19, 29.34, 29.36, 29.58, 29.59, 29.63, 29.65, 31.73, 31.90, 36.05, 68.13, 71.84, (alkyl carbons, 20

required, 20 found), 114.96, 120.67, 121.40, 124.75, 126.61, 127.05, 127.27, 128.37, 129.95, 130.06, 130.74, 131.86, 131.87, 141.74, 144.34, 146.09, 151.47, 159.59, (aromatic carbons, 18 required, 18 found), 165.13, 166.01, (carbonyl carbons, 2 required, 2 found). MS *m/z* 690(M^+). Elemental analysis: calc. for $C_{46}H_{58}O_5$: C 79.96, H 8.46; found: C 80.04, H 8.46. $[\alpha]_D$ = +18.94°.

(*S*)-1-Methylheptyl 5-(4'-dodecyloxybiphenyl-4-carbonyloxy)-2,3,4-trifluorobiphenyl-4'-carboxylate (**3F**)

Quantities: Compound **22** (0.92 g, 0.0024 mol), compound **32F** (0.93 g, 0.0025 mol), DCC (0.57 g, 0.0028 mol), DMAP (0.09 g, 0.00075 mol). The experimental procedure was as described in the preparation of compound **1H**, to yield colourless crystals.

Yield 1.12 g (63%). Transitions (°C): Cr 48.7 (SmC* 28.9 SmA* 31.9) I. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (6H, 2 x t), 1.23-1.42 (27H, m, includes 3H, d), 1.48 (2H, quint), 1.62 (1H, m), 1.74 (1H, m), 1.82 (2H, quint), 4.02 (2H, t), 5.18 (1H, sext), 7.01 (2H, d, *J* = 8.7 Hz), 7.19 (1H, ddd, *J* = 7.2 Hz, *J* = 7.2 Hz, *J* = 1.9 Hz), 7.60 (2H, d, *J* = 8.7 Hz), 7.72 (2H, d, *J* = 8.7 Hz), 8.13 (2H, d, *J* = 8.7 Hz), 8.24 (2H, d, *J* = 8.7 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) 14.09, 14.15, 20.08, 22.63, 22.73, 25.45, 26.08, 29.20, 29.28, 29.40, 29.44, 29.63, 29.66, 29.69, 29.71, 31.77, 31.96, 36.08, 68.17, 72.09 (alkyl carbons, 20 required, 20 found); 115.04, 118.24, 124.67(dd, *J* = 11.9 Hz, *J* = 3.9 Hz), 125.78, 126.72, 128.41, 128.81, 128.84, 129.94, 130.98, 131.04, 131.63, 135.41(dd, *J* = 10.6 Hz, *J* = 3.6 Hz), 137.55, 141.15(ddd, *J* = 249.6 Hz, *J* = 14.4 Hz, *J* = 1.6 Hz), 143.82(ddd, *J* = 252.8 Hz, *J* = 11.2 Hz, *J* = 3.2 Hz), 146.58(ddd, *J* = 246.4 Hz. *J* = 11.2 Hz, *J* = 2.6 Hz), 146.73, 159.80 (aromatic carbons, 18 required, 18 found); 163.77, 165.67 (carbonyl carbons, 2 required, 2 found). MS m/z 744 (M^+). Elemental analysis: $C_{46}H_{55}O_5F_3$ requires C 74.17%, H 7.44%; found C 74.41%, H 7.76%. $[\alpha]_D$ = +18.40°.

5-Bromo-2,3,4-trifluorobenzoic acid (**34**)

n-Butyllithium (4.48 g, 0.070 mol, 28 ml, 2.5M) was added dropwise to a stirred, cooled (-78 °C) solution of diisopropylamine (7.90 g, 0.078 mol) in THF (200 ml) under an atmosphere of nitrogen. The resulting solution was allowed to stir for 30 minutes and compound **33** (15.00 g, 0.071 mol) in THF (20 ml) added dropwise at -78 °C. After 45 minutes the reaction mixture was poured onto solid carbon dioxide and allowed to warm to room temperature overnight. The

product was extracted as the lithium salt into 10% sodium hydroxide and washed with diethyl ether (two portions). The diethyl ether washings were back-washed with fresh sodium hydroxide solution and the combined basic extracts acidified with 36% HCl. The product was then extracted into ether (x2), the combined ethereal extracts were washed with water and dried ($MgSO_4$). The solvent removed *in vacuo* to yield a colourless solid, which was recrystallized from ethanol / hexane (1:3) to yield colourless crystals.

Yield 8.42 g (47%). ^{1}H NMR (400 MHz, D6-DMSO) δ 7.96 (1H, ddd, J = 7.4 Hz, J = 7.4 Hz, J = 2.6 Hz). MS m/z 254 (M^+), 256 (M^+).

Ethyl 5-bromo-2,3,4-trifluorobenzoate (**35F**)

A stirred mixture of compound **34** (8.42 g, 0.033 mol), ethanol (200 ml) and sulphuric acid (0.5 ml) was heated under reflux overnight. The cooled reaction mixture was poured into water (300 ml) and the product extracted into ether (x2). The combined ethereal extracts were washed successively with sodium hydrogen carbonate solution and brine, and dried ($MgSO_4$). The solvent was removed *in vacuo* to yield a colourless oil.

Yield 2.82 g (30%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32(3H, t), 4.32 (2H, quart), 7.87(1H, ddd, J = 6.1 Hz, J = 6.1 Hz, J = 2.0 Hz). MS m/z 282 (M^+), 284 (M^+).

Ethyl 4"-dodecyl-[1,1':4',1"]-terphenyl-3-carboxylate (**37H**)

Quantities: compound **35H** (1.31 g, 5.7 mmol), compound **36** (2.73 g, 7.1 mmol). The experimental procedure was as described for the preparation of compound **31H** to yield a colourless solid.

Yield: 1.72 g (62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89(3H, t), 1.22-1.38(16H, m), 1.41 (3H, t), 1.48(2H, quint), 1.83(2H, quint), 4.02(2H, t), 4.43(2H, q), 7.00(2H, d, J = 8.9 Hz), 7.53(1H, dd, J = 7.4 Hz, J = 7.4 Hz), 7.58(2H, d, J = 8.9 Hz), 7.65(2H, d, J = 8.9 Hz), 7.69(2H, d, J = 8.9 Hz), 7.83(1H, ddd, J = 7.4 Hz, J = 1.8 Hz, J = 1.8 Hz), 8.04(1H, ddd, J = 7.4 Hz, J = 1.8 Hz, J = 1.8 Hz), 8.34(1H, dd, J = 1.8 Hz, J = 1.8 Hz). MS *m/z* 486(M^+).

Ethyl 4"-Dodecyloxy-2,3,4-trifluoro-[1,1':4',1"]-5-terphenylcarboxyate (**37F**)

Quantities: Compound **35F** (2.82 g, 0.010 mol), compound **36** (4.75 g, 0.012 mol). The experimental procedure was as described for the preparation of compound **31H**. However, the

crude product was suspected to be a mixture of the desired ester (**37F**) and the free acid (**38F**), and hence was used directly in the next step.

4"-Dodecyloxy-[1,1':4',1"]-terphenyl-3-carboxylic acid (**38H**)

A stirred mixture of compound **37H** (1.72 g, 3.5 mmol) and potassium hydroxide (0.40 g, 7.1 mmol) in ethanol (80 ml) and water (20 ml) was heated under reflux for 16 h. The mixture was poured on to ice and 36% hydrochloric acid and cooled. The resulting white precipitate was filtered off, washed with lots of water, and recrystallized from ethanol / ethyl acetate (1:1) to yield colourless crystals.

Yield 1.41 g (88%). ^{1}H NMR (400 MHz, D6-DMSO) δ 0.87(3H, t), 1.20-1.38(16H, m), 1.44 (2H, quint), 1.75(2H, quint), 4.03(2H, t), 7.04(2H, d, *J* = 8.9 Hz), 7.51(1H, dd, *J* = 7.4 Hz, *J* = 7.4 Hz), 7.67(2H, d, *J* = 8.9 Hz), 7.73(2H, d, *J* = 8.9 Hz), 7.77(2H, d, *J* = 8.9 Hz), 7.82(1H, ddd, *J* = 7.4 Hz, *J* = 1.8 Hz, *J* = 1.8 Hz), 7.90(1H, ddd, *J* = 7.4 Hz, *J* = 1.8 Hz, *J* = 1.8 Hz), 8.21(1H, dd, *J* = 1.8 Hz, *J* = 1.8 Hz). MS *m/z* 458(M^+).

4"-Dodecyloxy-2,3,4-trifluoro-[1,1':4',1"]-terphenyl-5-carboxylic acid (**38F**)

Compound **37F** was used directly using the method as described for the preparation of compound **38H** to yield colourless crystals.

Yield 1.88 g (37%). mp 217 °C. ^{1}H NMR (400 MHz, D6-DMSO) δ 0.73(3H, t), 1.06-1.26(16H, m), 1.33(2H, quint), 1.66(2H, quint), 3.86(2H, t), 6.84(2H, d, *J* = 8.7 Hz), 7.38-7.42(4H, m), 7.51(2H, d, *J* = 8.7 Hz), 7.77(1H, ddd, *J* = 7.1 Hz, *J* = 7.1 Hz, *J* = 2.0 Hz). MS m/z 512 (M^+)

(*S*)-1-Methylheptyl 4-(4"-dodecyloxy-[1,1':4',1"]-terphenyl-3-ylcarbonyloxy)benzoate (**4H**)

Quantities: compound **23** (0.67 g, 2.7 mmol), compound **38H** (1.20, 2.6 mmol), DCC (0.61 g, 3.0 mmol), DMAP (0.1 g, 0.8 mmol). The experimental procedure was as described for the preparation of compound **1H** to yield colourless crystals.

Yield 0.42 g (24%). Transitions (°C) Cryst 109.8 Iso. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87(6H, 2xt), 1.20-1.40(27H, m, including 3H, d), 1.46(2H, quint), 1.61(1H, m), 1.74(1H, m), 1.81(2H, quint), 3.99(2H, t), 5.16(1H, sext), 6.98(2H, d, *J* = 8.8 Hz), 7.31(2H, d, *J* = 8.8 Hz), 7.56(2H, d, *J* = 8.8 Hz), 7.60(1H, dd, *J* = 7.6 Hz, *J* = 7.6 Hz), 7.66(2H, d, *J* = 8.8 Hz), 7.01(2H, d, *J* = 8.8 Hz), 7.91(1H, ddd, *J* = 7.6 Hz, *J* = 1.8 Hz, *J* = 1.2 Hz), 8.13(2H, d, *J* = 8.8 Hz), 8.17(1H, ddd, *J* = 7.6

Hz, *J* = 1.8 Hz, *J* = 1.2 Hz), 8.46(1H, dd, *J* = 1.8 Hz, *J* = 1.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.10, 14.11, 20.13, 22.63, 22.73, 25.45, 26.11, 29.11, 29.22, 29.34, 29.40, 29.58, 29.59, 29.63, 29.66, 31.78, 31.96, 36.12, 68.18, 72.01, (alkyl carbons, 20 required, 20 found), 114.93, 121.75, 127.24, 127.54, 128.08, 128.72, 128.95, 129.23, 129.72, 131.22, 132.30, 132.77, 137.35, 138.01, 140.58, 141.49, 154.40, 158.96, (aromatic carbons, 18 required, 18 found), 164.81, 165.54, (carbonyl carbons, 2 required, 2 found). MS *m/z* 690(M^+). Elemental analysis: calc. for $C_{46}H_{58}O_5$: C 79.96, H 8.46; found: C 80.06, H 8.52. $[\alpha]_D$ = +15.23°.

(*S*)-1-Methylheptyl 4-(4"-dodecyloxy-2,3,4-trifluoro-[1,1':4',1"]-terphenyl-5-yl)benzoate (**4F**)
Quantities: Compound **38F** (0.96 g, 0.0019 mol), compound **23** (0.48 g, 0.0019 mol), DCC (0.43 g, 0.0021 mol), DMAP (0.10 g, 0.00057 mol). The experimental procedure was as described for the preparation of compound **1H**, to yield colourless crystals.
Yield 0.87 g (62 %). Transitions (°C): Cr 84.6 I. ^{1}H NMR (400 MHz, $CDCl_3$) 0.81 (6H, 2 x t), 1.15-1.33 (27H, m, including 3H, d), 1.41 (2H, quint), 1.56 (1H, m), 1.67 (1H, m), 1.74 (1H, m), 3.94 (2H, t), 5.09 (1H, sext), 6.92 (2H, d, *J* = 8.7 Hz), 7.25 (2H, d, *J* = 8.7 Hz), 7.49 (2H, d, *J* = 8.7 Hz), 7.53 (2H, dd, *J* = 8.7 Hz, *J* = 1.5 Hz), 7.61 (2H, d, *J* = 8.7 Hz), 7.97 (1H, ddd, *J* = 7.6 Hz, *J* = 7.6 Hz, *J* = 2.2 Hz), 8.07 (2H, d, *J* = 8.7 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) 14.04, 14.10, 20.02, 22.57, 22.67, 25.38, 26.03, 29.13, 29.24, 29.33, 29.39, 29.57, 29.59, 29.62, 29.65, 31.71, 31.89, 36.01, 68.05, 72.01 (alkyl carbons, 20 required, 20 found); 114.84, 121.43, 126.43(dd, *J* = 10.8, *J* = 3.8), 126.85, 126.98, 128.03, 128.96, 129.08, 129.10, 130.79, 131.18, 132.20, 140.94(ddd, *J* = 253.7, *J* = 15.4, *J* = 15.4), 141.39, 150.75(ddd, *J* = 266.7, *J* = 11.5, *J* = 3.1), 152.20(ddd, *J* = 258.3, *J* = 10.8, *J* = 2.3), 153.68, 159.12 (aromatic carbons, 18 required, 18 found); 160.81, 165.24 (carbonyl carbons, 2 required, 2 found). MS m/z 744 (M^+). Elemental analysis: $C_{46}H_{55}O_5F_3$ requires C 74.17 %, H 7.44 %; found C 74.42 %, H 7.70 %. $[\alpha]_D$ = +13.55°.

(*S*)-1-Methylhepyl 3-(4'-dodecyloxybiphenyl-4-ylcarbonyloxy)benzoate (**5H**)
Quantities: compound **18H** (0.74 g, 3.0 mmol), compound **22** (1.12 g, 2.9 mmol), DCC (0.68 g, 3.3 mmol, DMAP (0.11 g, 0.9 mmol). The experimental procedure was as described for the preparation of compound **1H** to yield colourless crystals.

Yield 1.12 g (63%). Transitions (°C) Cryst 44.8 SmC* 45.4 SmA* 55.2 Iso. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87(6H, 2xt), 1.22-1.40(27H, m, including 3H, d), 1.48(2H, quint), 1.62(1H, m), 1.74(1H, m), 1.82(2H, quint), 4.02(2H, t), 5.17(1H, sext), 7.01(2H, d, *J* = 8.8 Hz), 7.43(1H, ddd, *J* = 7.9 Hz, *J* = 1.8 Hz, *J* = 1.2 Hz), 7.51(1H, dd, *J* = 7.9 Hz, *J* = 7.9 Hz), 7.60(2H, d, *J* = 8.8 Hz), 7.71(2H, d, *J* = 8.8 Hz), 7.88(1H, dd, *J* = 1.8 Hz, *J* = 1.2 Hz), 7.97(1H, ddd, *J* = 7.9 Hz, *J* = 1.2, *J* = 1.2 Hz), 8.24(2H, d, *J* = 8.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.06, 14.12, 20.05, 22.58, 22.68, 25.40, 26.03, 29.13, 29.22, 29.35, 29.39, 29.58, 29.60, 29.63, 29.66, 31.71, 31.91, 36.00, 68.14, 72.16, (alkyl carbons, 20 required, 20 found), 114.97, 122.87, 126.29, 126.62, 127.03, 127.09, 128.38, 129.38, 130.76, 131.85, 132.55, 146.16, 150.90, 159.61, (aromatic carbons, 14 required, 14 found), 164.99, 165.30, (carbonyl carbons, 2 required, 2 found). MS *m/z* 614(M^+). Elemental analysis: calc. for $C_{40}H_{54}O_5$: C 78.14, H 8.85; found: C 78.20, H 8.89. $[\alpha]_D$ = +17.16°.

(*S*)-1-Methylheptyl 5-(4'-dodecyloxybiphenyl-4-ylcarbonyloxy)-2,3,4-trifluorobenzoate (**5F**)
Quantities: Compound **22** (1.14 g, 0.0030 mol), compound **18F** (0.94 g, 0.0031 mol), DCC (0.70 g, 0.0034 mol), DMAP (0.11 g, 0.00093 mol). The experimental procedure was as described in the preparation of compound **1H**, except that only ethanol was used for the recrystallization, to yield colourless crystals.
Yield 1.39 g (69%). Transitions (°C): Cr 40.6 (SmC* 30.6) SmA* 64.2 I. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (6H, 2xt), 1.22-1.42 (27H, m, including 3H, d), 1.48 (2H, quint), 1.61 (1H, m), 1.72 (1H, m), 1.82 (2H, quint), 4.02 (2H, t), 5.18 (1H, sext), 7.01 (2H, d, *J* = 8.7 Hz), 7.60 (2H, d, *J* = 8.7 Hz), 7.68 (1H, ddd, *J* = 7.7 Hz, 6.5 Hz, 2.6 Hz), 7.71 (2H, d, *J* = 8.7 Hz), 8.22 (2H, d, *J* = 8.7 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) 14.02, 14.10, 19.89, 22.55, 22.68, 25.24, 26.02, 29.06, 29.22, 29.34, 29.38, 29.57, 29.59, 29.62, 29.65, 31.67, 31.91, 35.83, 68.12, 73.41 (alkyl carbons, 20 required, 20 found); 114.99, 115.88(dd, *J* = 8.7 Hz, *J* = 3.7 Hz), 120.08, 125.51, 126.72, 128.39, 131.03, 131.58, 134.72(dd, *J* = 10.0 Hz, *J* = 3.8 Hz), 141.05(ddd, *J* = 257.5 Hz, *J* = 16.9 Hz, *J* = 13.8 Hz), 146.60(ddd *J* = 244.5 Hz, *J* = 12.9 Hz, *J* = 4.3 Hz) 146.78, 149.50(ddd, *J* = 248.8 Hz, 12.0 Hz, *J* = 2.6 Hz), 159.74 (aromatic carbons, 14 required, 14 found), 161.89, 163.54 (carbonyl carbons, 2 required, 2 found). MS m/z 668(M^+). Elemental analysis: $C_{40}H_{51}O_5F_3$ requires C 71.83%, H 7.69%; found C 72.15 %, H 7.90 %. $[\alpha]_D$ = +13.2°.

Benzyl 4-(4-dodecyloxyphenylcarbonyloxy)benzoate (**41**)

Quantities: compound **39** (15.00 g, 0.049 mol), compound **40** (11.40 g, 0.050 mol), DCC (11.33 g, 0.055 mol), DMAP (1.83 g, 0.015 mol). The experimental procedure was as described for the preparation of compound **17H** to yield a colourless solid.

Yield 23.52 g (93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88(3H, t), 1.22-1.40(16H, m), 1.46(2H, quint), 1.82(2H, quint), 4.04(2H, t), 5.38(2H, s), 6.98(2H, d. *J* = 8.8 Hz), 7.29(2H, d, *J* = 8.8 Hz), 7.32-7.42(3H, m), 7.46(2H, dd, *J* = 7.2 Hz, *J* = 1.8 Hz), 8.12(2H, d, *J* = 8.8 Hz), 8.16(2H, d, *J* = 8.8 Hz). MS *m/z* 516(M^+).

4-(4-Dodecyloxyphenylcarbonyloxy)benzoic acid (**42**)

Quantities: compound **41** (23.52 g, 0.046 mol), 10% palladium on carbon (2 g). The experimental procedure was as described for the preparation of compound **18H** to yield a colourless solid.

Yield 15.28 g (78%). ^{1}H NMR (400 MHz, D6-DMSO) δ 0.81(3H, t), 1.14-1.30(16H, m), 1.36(2H, quint), 1.70(2H, quint), 4.04(2H, t), 7.07(2H, d. *J* = 8.4 Hz), 7.35(2H, d, *J* = 8.4 Hz), 7.98(2H, d, *J* = 8.4 Hz), 8.04(2H, d, *J* = 8.4 Hz). MS *m/z* 426(M^+).

(*S*)-1-Methylheptyl 4-[4-(4-dodecyloxyphenylcarbonyloxy)phenylcarbonyloxy]benzoate (**6H**)

Quantities: compound **18H** (0.77 g, 3.1 mmol), compound **42** (1.29 g, 3.0 mmol), DCC (0.70 g, 3.4 mmol), DMAP (0.12 g, 1.0 mmol). The experimental procedure was as described for the preparation of compound **1H** to yield colourless crystals.

Yield 1.12 g (63%). Transitions (°C) Cryst 48.0 (SmC* 47.1) SmA* 52.5 Iso. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87(6H, 2xt), 1.22-1.40(27H, m, including 3H, d), 1.48(2H, quint), 1.60(1H, m), 1.73(1H, m), 1.83(2H, quint), 4.05(2H, t), 5.16(1H, sext), 6.99(2H, d, *J* = 8.7 Hz), 7.38(2H, d, *J* = 8.7 Hz), 7.43(1H, ddd, *J* = 7.9 Hz, *J* = 1.8 Hz, *J* = 1.2 Hz), 7.52(1H, dd, *J* = 7.9 Hz, *J* = 7.9 Hz), 7.87(1H, dd, *J* = 1.8 Hz, *J* = 1.2 Hz), 7.98(1H, ddd, *J* = 7.9 Hz, *J* = 1.2, *J* = 1.2 Hz), 8.15(2H, d, *J* = 8.8 Hz), 8.29(2H, d, *J* = 8.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.04, 14.11, 20.03, 22.57, 22.68, 25.39, 25.95, 29.06, 29.12, 29.33, 29.35, 29.54, 29.56, 29.61, 29.64, 31.70, 31.89, 35.98, 68.36, 72.19, (alkyl carbons, 20 required, 20 found), 114.39, 120.85, 122.16, 122.81, 126.22, 126.51, 127.12, 129.41, 131.85, 132.41, 132.58, 150.76, 155.49, 163.82, (aromatic carbons, 14 required, 14 found), 164.29, 164.32, 165.24, (carbonyl carbons, 3 required,

3 found). MS *m/z* 614(M^+). Elemental analysis: calc. for $C_{41}H_{54}O_7$: C 74.74, H 8.26; found: C 74.81, H 8.29. $[\alpha]_D$ = +15.61°.

(*S*)-1-Methylheptyl 5-[4-(4-dodecyloxyphenylcarbonyloxy)phenylcarbonyloxy]-2,3,4-trifluorobenzoate (**6F**)

Quantities: Compound **42** (1.07 g, 0.0025 mol), compound **18F** (0.79 g, 0.0026 mol), DCC (0.59 g, 0.0029 mol), DMAP (0.10 g, 0.00078 mol). The experimental procedure was as described in the preparation of compound **1H**, to yield a colourless solid.

Yield 0.81 g (46%). Transitions (°C): Cr 42.4 (SmC* 32.5) SmA* 58.5 I. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88(3H, t), 0.89(3H, t), 1.22-1.42(27H, m, including 3H, d), 1.48(2H, quint), 1.61(1H, m), 1.72(1H, m), 1.83(2H, quint), 4.06 (2H, t), 5.17(1H, sext), 6.98(2H, d, *J* = 8.7 Hz), 7.40(2H, d, *J* = 8.7 Hz), 7.67(1H, ddd, *J* = 8.1 Hz, *J* = 6.5 Hz, *J* = 2.3 Hz), 8.15(2H, d, *J* = 8.7 Hz), 8.28(2H, d, *J* = 8.7 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) 14.01, 14.08, 19.88, 22.54, 22.66, 25.24, 25.95, 29.06(x2), 29.33(x2), 29.53, 29.56, 29.61, 29.63, 31.66, 31.89, 35.83, 68.37, 73.43 (alkyl carbons, 20 required, 20 found); 114.40, 115.94(dd, *J* = 8.4 Hz, *J* = 3.6 Hz), 120.01, 120.74, 122.35, 124.97, 132.13, 132.41, 134.66(dd, *J* = 10.8 Hz, *J* = 3.7 Hz), 141.15(ddd, *J* = 252.0 Hz, *J* = 14.7 Hz, *J* = 2.5 Hz), 146.86(ddd, *J* = 260.4 Hz, *J* = 12.6 Hz, *J* = 4.2 Hz), 149.45(ddd, *J* = 264.6 Hz, *J* = 12.6, *J* = 2.5 Hz), 156.00, 162.87 (aromatic carbons, 14 required, 9 found); 161.81, 163.87, 164.14 (carbonyl carbons, 3 required, 3 found). MS m/z 712(M^+). Elemental analysis: $C_{41}H_{51}O_7F_3$ requires C 69.08 %, H 7.21 %; found C 69.30%, H 7.52%. $[\alpha]_D$ = + 11.90°.

(*S*)-1-Methylheptyl 4-(4-benzyloxyphenylcarbonyloxy)benzoate (**43H**)

Quantities: Compound **19** (1.34 g, 5.9 mmol), compound **23H** (1.4 g, 5.6 mmol), DCC (1.27 g, 6.2 mmol), DMAP (0.21 g, 1.7 mmol). The experimental procedure was followed as described in the preparation of compound **17H** to yield a colourless oil.

Yield 2.0 g (78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88(3H, t), 1.25-1.45(11H, m, including 3H, d), 1.61(1H, m), 1.75(1H, m), 5.13(2H, s), 5.17(1H, sext), 7.07(2H, d, *J* = 8.7 Hz), 7.28(2H, d, *J* = 8.7 Hz), 7.34-7.46 (5H, m), 8.11(2H, d, *J* = 8.7 Hz), 8.17(2H, d, *J* = 8.7 Hz). MS *m/z* 460(M^+).

(*S*)-1-Methylheptyl 4-(4-benzyloxyphenylcarbonyloxy)-2,3-difluorobenzoate (**43F**)

Quantities: compound **19** (2.30 g, 0.010 mol), compound **23F** (3.15 g, 0.011 mol), DCC (2.50 g, 0.012 mol), DMAP (0.44 g, 3.61 mmol). The experimental procedure was as described for the preparation of compound **17H** to yield a colourless solid.

Yield 4.56 g (92%). mp 64 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88(3H, t), 1.22-1.45(11H, m, including 3H, d), 1.62(1H, m), 1.74(1H, m), 5.16(2H, s), 5.18(1H, sext), 7.07(2H, d, *J* = 8.7 Hz), 7.12(1H, ddd, *J* = 7.9 Hz, *J* = 7.8 Hz, *J* = 2.8 Hz), 7.33-7.47(5H, m), 7.76(1H, ddd, *J* = 7.9 Hz, *J* = 7.8 Hz, *J* = 2.8 Hz), 8.15(2H, d, *J* = 8.7 Hz). MS *m/z* 496(M^+).

(*S*)-1-Methylheptyl 4-(4-hydroxyphenylcarbonyloxy)benzoate (**44H**)

Quantities: Compound **43H** (2.0 g, 4.0 mmol), 10% palladium-on-carbon (0.20 g). The experimental procedure was as described for the preparation of compound **18H** to yield a colourless oil.

Yield 1.5 g (100%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87(3H, t), 1.22-1.40(11H, m, including 3H, d), 1.60(1H, m), 1.71(1H, m), 5.15(1H, sext), 6.92(2H, d, *J* = 8.7 Hz), 7.28(2H, d, *J* = 8.7 Hz), 8.08(2H, d, *J* = 8.7 Hz), 8.12(2H, *J* = 8.7 Hz). MS *m/z* 370(M^+).

(*S*)-1-Methylheptyl 4-(4-hydroxyphenylcarbonyloxy)-2,3-difluorobenzoate (**44F**)

Quantities: compound **43F** (4.50 g, 9.07 mmol), 10% palladium-on-carbon (0.5 g). The experimental procedure was as described for the preparation of compound **18H** to yield a colourless oil.

Yield: 4.29 g (100%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87(3H, t), 1.22-1.42(11H, m, including 3H, d), 1.62(1H, m), 1.74(1H, m), 5.19(1H, sext), 6.94(2H, d, *J* = 8.7 Hz), 7.12(1H, ddd, *J* = 7.9 Hz, *J* = 7.8 Hz, *J* = 2.8 Hz), 7.76(1H, ddd, *J* = 7.9 Hz, *J* = 7.8 Hz, *J* = 2.8 Hz), 8.10(2H, *J* = 8.7 Hz). MS *m/z* 406(M^+).

(*S*)-(+)-1-Methylheptyl 4-[4-(4'-dodecyloxybiphenyl-4-ylcarbonyloxy)phenylcarbonyloxy]benzoate (**7H**)

Quantities: compound **22** (2.95 g, 7.72 mmol), compound **44H** (3.00 g, 8.11 mmol), DCC (1.91 g, 9.27 mmol), DMAP (0.32 g, 2.62 mmol). The experimental procedure was as described for the preparation of compound **1H**, except that ethyl acetate was used in the recrystallization to yield colourless crystals.

Yield 4.15 g (73%). Transitions (°C) Cryst 105.0 SmC*anti 165.8 SmC*ferri 167.0 SmC*ferro 209.5 SmA* 237.5 Iso. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88(6H, 2xt), 1.22-1.40(27H, m, including 3H, d), 1.48(2H, quint), 1.62(1H, m), 1.74(1H, m), 1.82(2H, quint), 4.02(2H, t), 5.16(1H, sext), 7.01(2H, d, *J* = 8.7 Hz), 7.31(2H, d, *J* = 8.7 Hz), 7.42(2H, d, *J* = 8.7 Hz), 7.61(2H, d, *J* = 8.7 Hz), 7.72(2H, d, *J* = 8.7 Hz), 8.13(2H, d, *J* = 8.7 Hz), 8.26(2H, d, *J* = 8.7 Hz), 8.30(2H, d, *J* = 8.7 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.07, 14.12, 20.09, 22.59, 22.68, 25.40, 26.03, 29.16, 29.23, 29.35, 29.39, 29.58, 29.60, 29.63, 29.66, 31.73, 31.91, 36.05, 68.16, 71.97, (alkyl carbons, 20 required, 20 found), 115.01, 121.66, 122.16, 126.60, 126.68, 126.82, 128.40, 128.63, 130.83, 131.17, 131.75, 131.94, 146.39, 154.34, 155.45, 159.68, (aromatic carbons, 16 required, 16 found), 163.96, 164.42, 165.38, (carbonyl carbons, 3 required, 3 found). MS *m/z* 734(M^+). Elemental analysis: calc. for $C_{47}H_{58}O_7$: C 76.81, H 7.95; found: C 76.86, H 7.95. $[\alpha]_D$ = +15.15°.

(*S*)-(+)-1-Methylheptyl 4-[4-(4'-dodecyloxybiphenyl-4-ylcarbonyloxy)phenylcarbonyloxy]-2,3-difluorobenzoate (**7F**)

Quantities: compound **22** (3.20 g, 8.38 mmol), compound **44F** (3.75 g, 9.23 mmol), DCC (2.10 g, 0.010 mol), DMAP (0.37 g, 3.03 mmol). The experimental procedure was as described for the preparation of compound **1H** to yield colourless crystals.

Yield 1.20 g (19%). Transitions (°C) Cryst 82.4 SmC*anti 159.5 SmC*ferri 163.2 SmC*ferro 182.5 SmA* 219.4 Iso. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88(6H, 2xt), 1.22-1.40(27H, m, including 3H, d), 1.47(2H, quint), 1.62(1H, m), 1.74(1H, m), 1.82(2H, quint), 4.02(2H, t), 5.18(1H, sext), 7.02(2H, d, *J* = 8.7 Hz), 7.15(1H, ddd, *J* = 9.1 Hz, *J* = 6.3 Hz, *J* = 2.0 Hz), 7.43(2H, d, *J* = 8.7 Hz), 7.61(2H, d, *J* = 8.7 Hz), 7.71(2H, d, *J* = 8.7 Hz), 7.78(1H, ddd, *J* = 9.1 Hz, *J* = 6.5 Hz, *J* = 2.0 Hz), 8.24(2H, d, *J* = 8.7 Hz), 8.31(2H, d, *J* = 8.7 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.04, 14.10, 19.94, 22.55, 22.67, 25.26, 26.01, 29.09, 29.22, 29.33, 29.38, 29.56, 29.58, 29.61, 29.64, 31.69, 31.90, 35.89, 68.14, 72.99 (alkyl carbons, 20 required, 20 found), 115.00, 118.23(d, *J* = 4.2 Hz), 118.91(d, *J* = 7.4 Hz), 122.30, 125.39, 125.85(d, *J* = 3.7 Hz), 126.66, 126.72, 128.38, 130.82, 131.71, 132.22, 142.81(dd, *J* = 12.1 Hz, *J* = 2.0 Hz), 143,71(dd, *J* = 249.7 Hz, *J* = 19.8 Hz), 146.41, 151.29(dd, *J* = 263.2 Hz, *J* = 11.6 Hz), 155.80, 159.69 (aromatic carbons, 18 required, 18 found), 162.57, 162.75, 164.42 (carbonyl carbons, 3 required, 3 found). MS *m/z* 770(M^+). Elemental analysis: calc. for $C_{47}H_{56}F_2O_7$: C 73.22, H 7.32; found: C 73.11, H 7.46. $[\alpha]_D$ = +11.54°.

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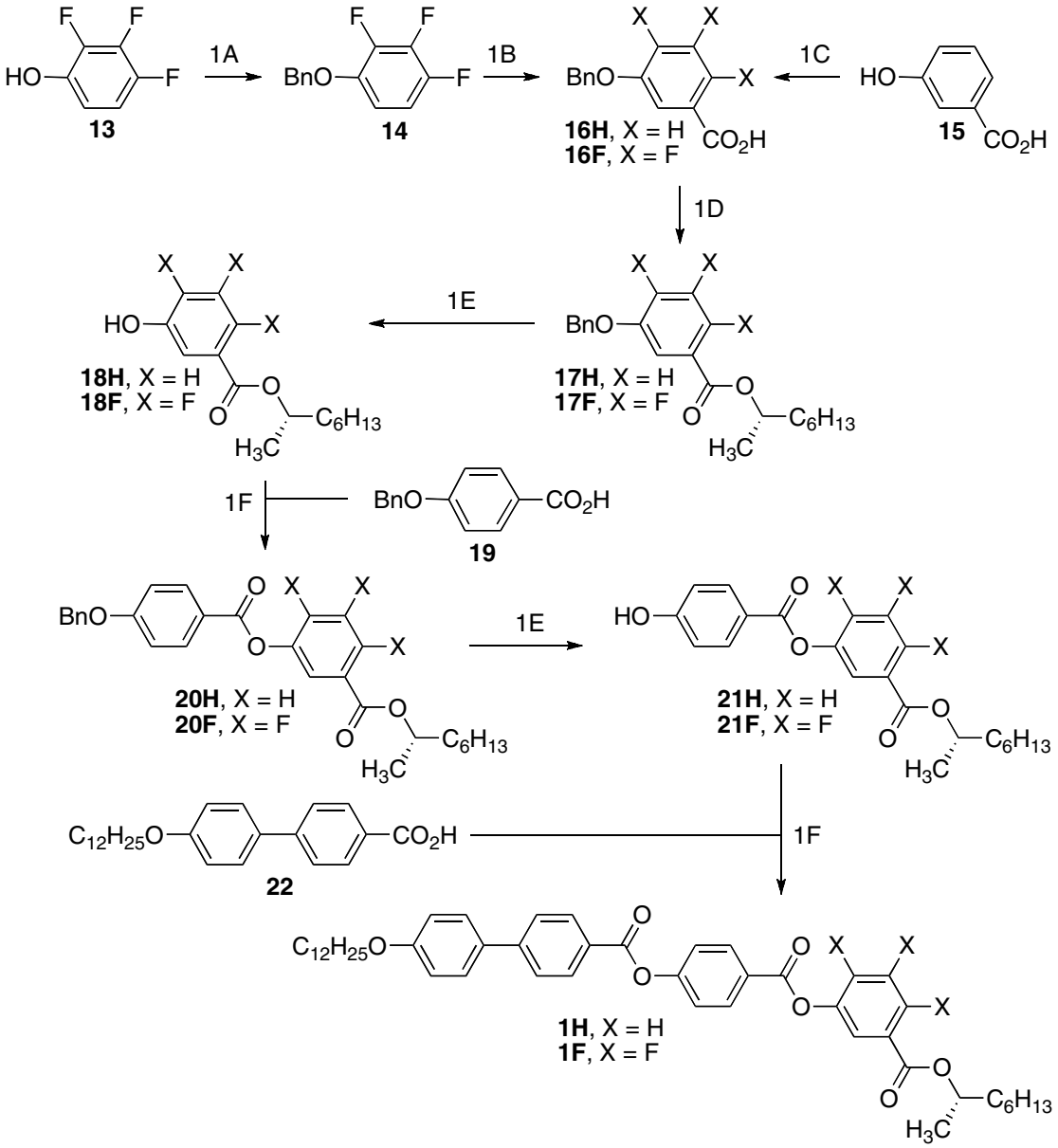
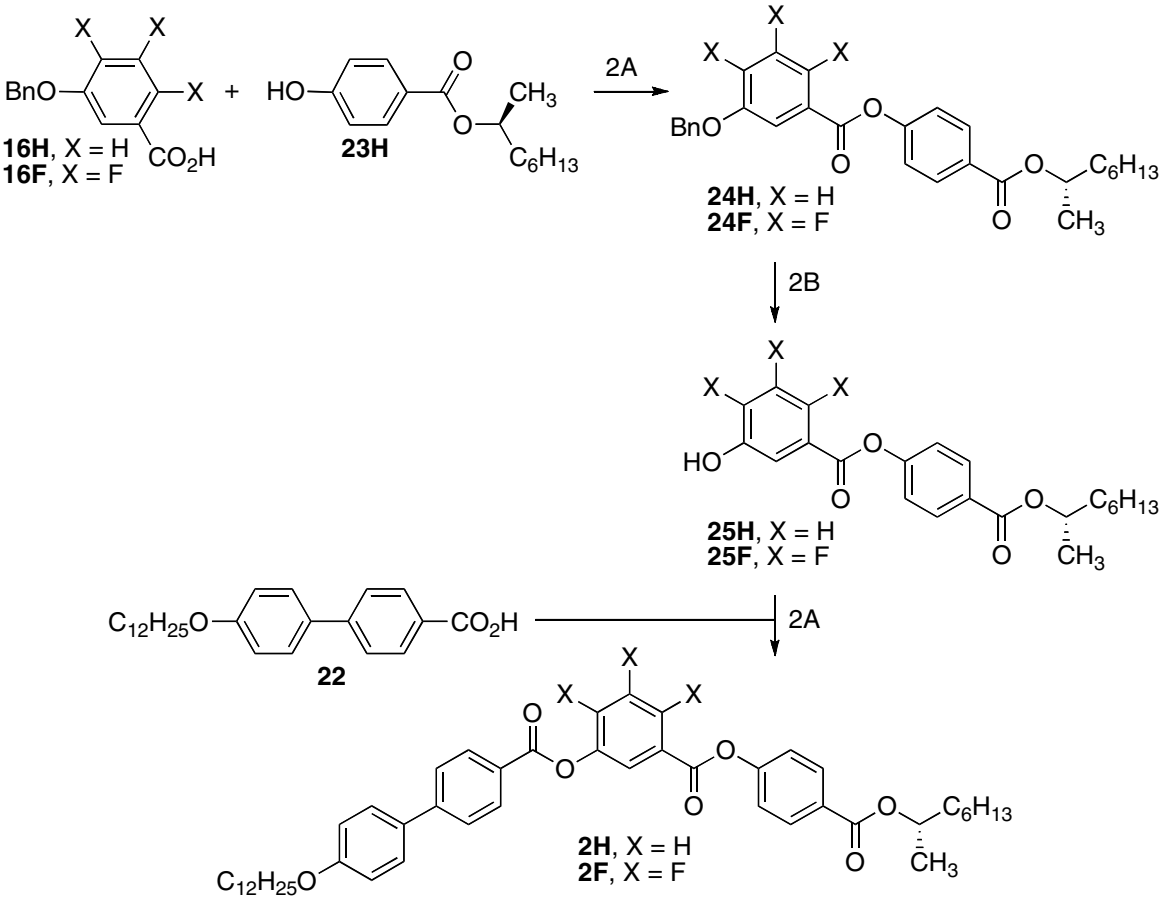
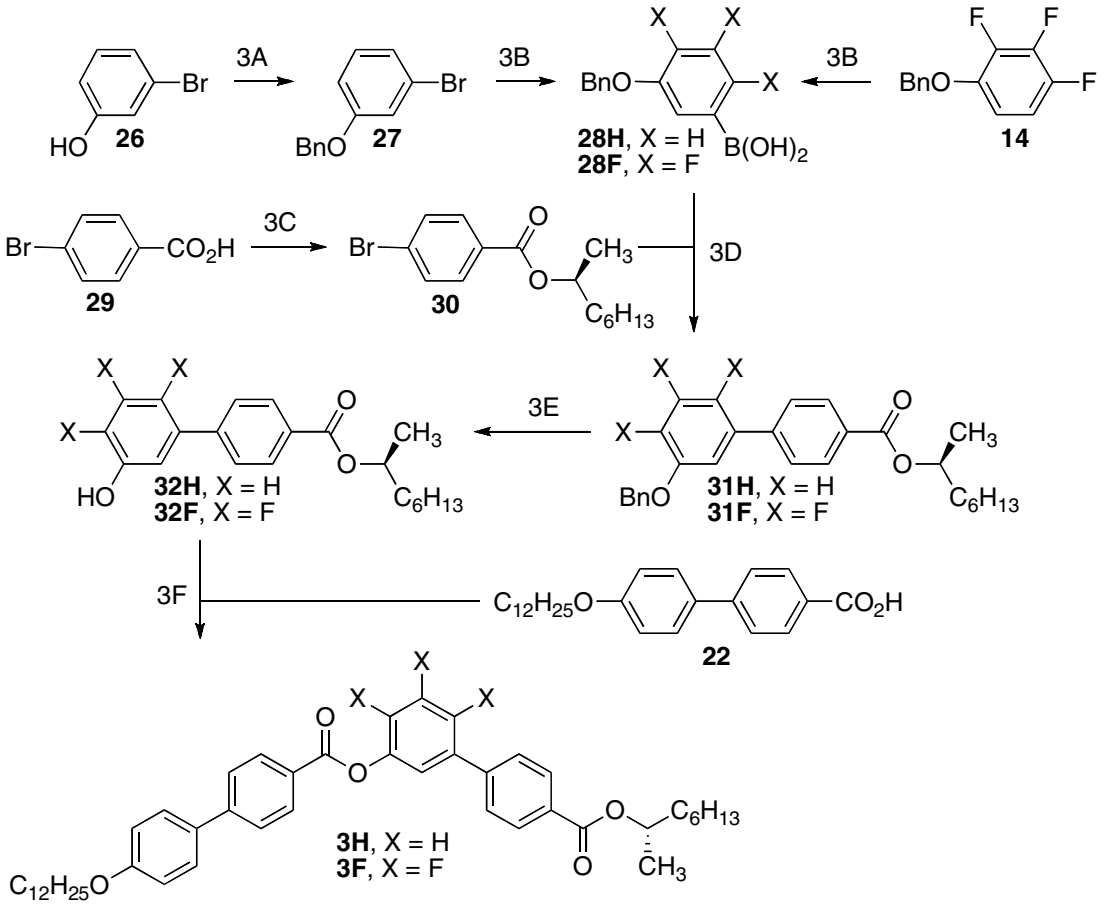


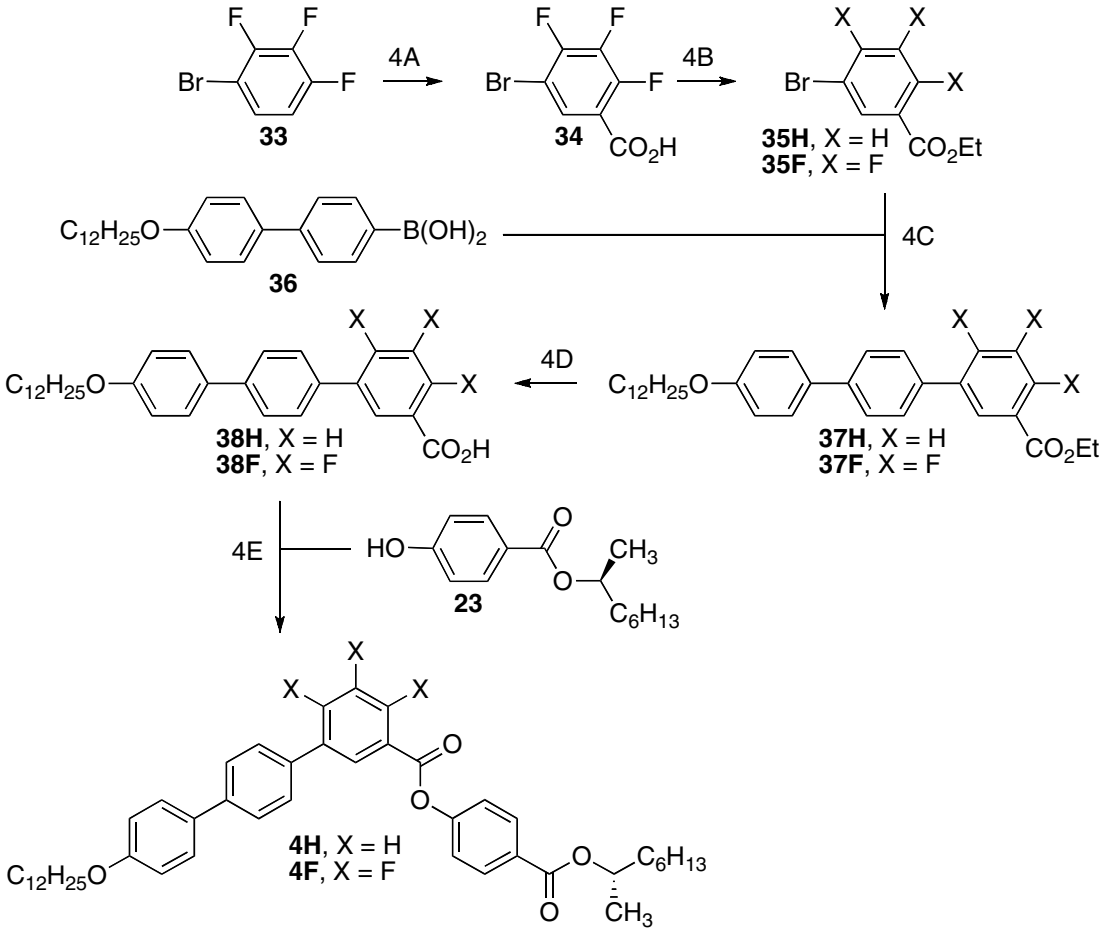
Scheme 1: 1A: BnCl, K_2CO_3, butanone; 1B: (i) n-BuLi, THF; (ii) $(MeO)_3B$; (iii) 10% HCl; 1C: BnCl, NaOH, EtOH, H_2O; 1D: (*S*)-2-octanol, DCC, DMAP, DCM; 1E: H_2, 10% Pd/C, EtOAc; 1F: DCC, DMAP, DCM.



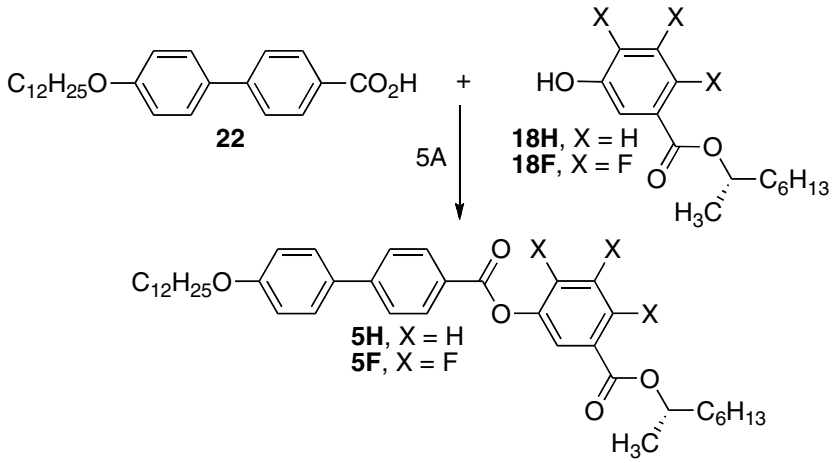
Scheme 2: 2A: DCC, DMAP, DCM; 2B: H_2, 10% Pd/C, EtOAc.



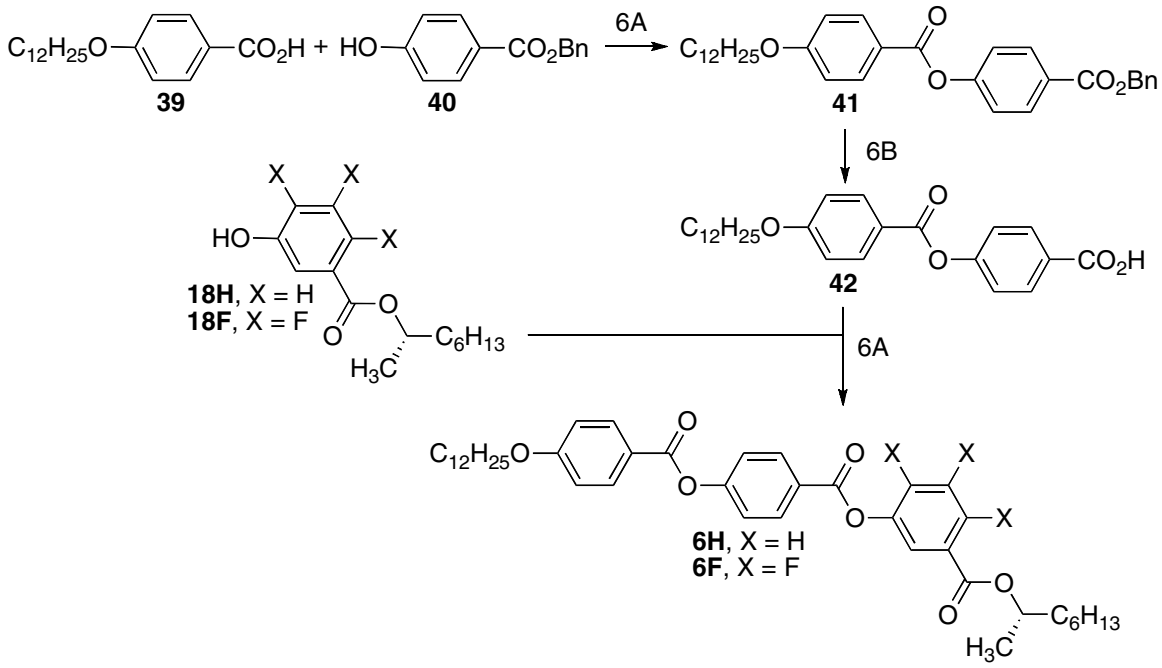
Scheme 3: 3A: BnCl, K_2CO_3, butanone; 3B: (i) n-BuLi, THF; (ii) $(MeO)_3B$; (iii) 10% HCl; 3C: (*S*)-2-octanol, DCC, DMAP, DCM; 3D: $Pd(PPh_3)_4$, Na_2CO_3, DME, H_2O; 3E: H_2, 10% Pd/C, EtOAc; 3F: DCC, DMAP, DCM.



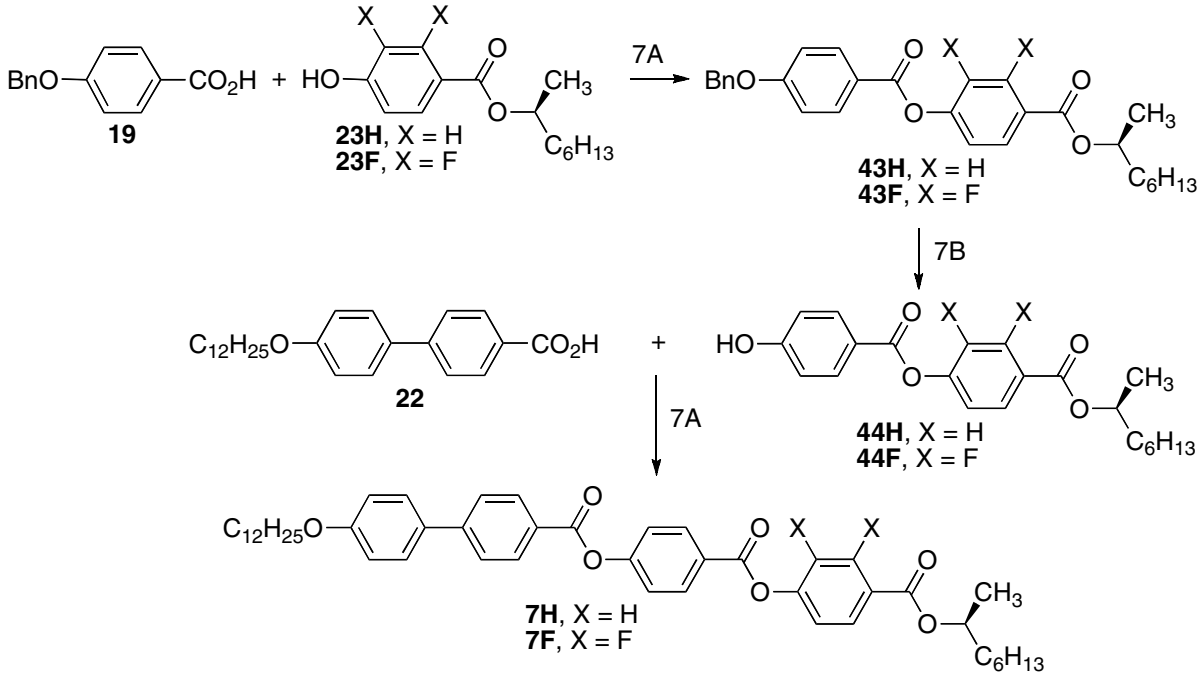
Scheme 4: 4A: (i) LDA, THF; (ii) CO_2, THF; (iii) 10% HCl; 4B, EtOH, H_2SO_4; 4C: $Pd(PPh_3)_4$, Na_2CO_3, DME, H_2O; 4D: (i) KOH, EtOH, H_2O; (ii) 36% HCl; 4E: DCC, DMAP, DCM.



Scheme 5: 5A: DCC, DMAP, DCM.



Scheme 6: 6A: DCC, DMAP, DCM; 6B: H_2, 10% Pd/C, EtOAc.



Scheme 7: 7A: DCC, DMAP, DCM; 7B H_2, 10% Pd/C, EtOAc.