

Supplementary

4-Cyano-4'-(11-hydroxyundecyloxy)biphenyl 2

4-Cyano-4'-hydroxybiphenyl (8.22 g; 0.042 mol), **1**, 11-bromo-1-undecanol (10.0 g; 0.040 mol) and potassium carbonate (23.0 g; 0.170 mol) were heated under reflux in dry butanone (125 ml) for 15 h. The solids were removed by filtration and washed with acetone (2 x 50 ml). The combined solvents were removed *in vacuo* to give a white solid which was recrystallised from acetonitrile. Yield 14.31 g (93%)

¹H nmr (CDCl₃): δ 1.30 (12H, m), 1.50 (5H, m), 1.80 (2H, quint), 3.64 (2H, t), 4.00 (2H, t), 6.90 (2H, d), 7.52 (2H, d), 7.66 (4H, q) ppm.

4'-(11-Hydroxyundecyloxy)biphenyl-4-carboxylic acid 3

Compound **2** (5.00 g; 0.0137 mol) was heated under reflux in a mixture of sodium hydroxide (2.0 g; 0.05 mol) in ethanol (100 ml) and water (50 ml) for 18 h. Upon completion, to the cooled reaction mixture (ice bath) c. hydrochloric acid was added (until pH 1) and the reaction mixture was stirred for a further 1h and then filtered. The retained solid was washed with ethanol (60 ml) and then air dried to give a white powdery solid. Yield 5.14 g (98%)

¹H nmr (DMSO): δ 1.24 (18H, m), 1.70 (2H, quint), 3.99 (2H, t), 4.36 (1H, broad s), 7.02 (2H, d), 7.66 (2H, d), 7.73 (2H, d), 7.98 (2H, d), 12.90 (1H, broad s) ppm. IR (KBr) ν_{\max} 1202, 1256, 1293, 1604, 1686, 2500-3500 cm⁻¹. MS (m/z) 384 (M⁺), 214, 197.

(R)-(-)-4-(1-Methylheptyloxycarbonyl)phenyl 4'-(11-hydroxyundecyloxy)biphenyl-4-carboxylate 8

Compound **3** (1.0 g; 2.6 mmol), compound **7** (0.65 g; 2.6 mmol), 1-(3-dimethylaminopropyl)-3-ethyl carbodiimide.HCl (0.50 g; 2.6 mol) and 4-(dimethylamino)pyridine (0.20 g) were stirred together at room temperature in a mixture of dimethylformamide and dichloromethane (30 ml; 3:1) for 4h. Upon completion, the solvent was removed *in vacuo* and the product purified by column chromatography over

silica (dichloromethane as eluent) and recrystallised from acetonitrile to give a white powder. Yield 1.17 g (73%)

¹H nmr (CDCl₃): δ 0.88(3H, t), 1.20-1.40 (22H, m), 1.47-1.70 (7H, m), 1.75-1.90 (3H, m), 3.64 (2H, t), 4.02 (2H, t), 5.16 (1H, sext), 7.01 (2H, d), 7.31 (2H, d), 7.60 (2H, d), 7.70 (2H, d), 8.13 (2H, d), 8.23 (2H, d) ppm. IR (KBr) ν_{\max} 1290, 1603, 1714, 1732, 2851, 2919, 3200-3600 cm⁻¹. MS (m/z) 616 (M⁺), 540. OR: $[\alpha]_{\text{D}}^{20} = -15.94^{\circ}$; 0.004352 g ml⁻¹ in CHCl₃

(R)-(-)- 1-Methylheptyloxycarbonylphenyl 4'-[11-(2,2,3,3,4,4,5,5-octafluoropentanoyloxy)undecyloxy]biphenyl-4-carboxylate 15

Compound **8** (0.25 g; 0.41 mmol), 2,2,3,3,4,4,5,5-octafluoropentanoic acid (0.096 g; 0.41 mmol), 1-(3-dimethylaminopropyl)-3-ethyl carbodiimide.HCl (0.079 g; 0.41 mmol) and 4-(dimethylamino)pyridine (0.05 g) were stirred together at room temperature in dichloromethane (25 ml) for 24 h. Upon completion, the solvent was removed *in vacuo* and the product purified by column chromatography over silica (dichloromethane as eluent). The product was isolated as a room temperature liquid crystal. Yield 0.25 g (71%).

¹H nmr (CDCl₃): δ 0.88(3H, t), 1.20-1.50 (23H, m), 1.55-1.85 (8H, m), 4.02 (2H, t), 4.37 (2H, t), 5.16 (1H, sext), 6.06 (1H, tt), 7.00 (2H, d), 7.31 (2H, d), 7.60 (2H, d), 7.70 (2H, d), 8.13 (2H, d), 8.23 (2H, d) ppm. ¹⁹F nmr (CDCl₃): δ -120.12 (2F, t), -125.94 (2F, t), -130.90 (2F, m), -138.31 (1F, m), -138.52 (1F, m) ppm. IR (neat) ν_{\max} 1191, 1275, 1604, 1713, 1736, 1780, 2855, 2930 cm⁻¹. MS (m/z) 845 (M⁺), 595. Elemental Analysis (C₄₄H₅₂F₈O₇): Expected % C 62.53; H 6.20; Calculated % C 62.39; H 6.34.

4-(3-Hydroxy)propyloxybenzoic acid 22

Methyl 4-hydroxybenzoic acid, **21** (5.00 g; 0.030 mol), 3-bromopropan-1-ol (4.18 g; 0.030 mol) and potassium carbonate (16.60 g; 0.120 mol) were heated together under reflux in butanone (75 ml) overnight. Upon completion, the inorganic solids were filtered off and the solvent removed *in vacuo* to give a crude solid which was hydrolysed by heating under reflux with potassium hydroxide in an ethanol/water solution followed by

acidification with hydrochloric acid. The carboxylic acid was isolated by filtration and purified by recrystallisation from acetonitrile. Yield 5.29 g (90%).

¹H nmr (DMSO): δ 1.87 (2H, quint), 3.55 (2H, t), 4.10 (2H, t), 4.57 (1H, broad S), 7.00 (2H, d), 7.87 (2H, d), 12.60 (1H, broad S) ppm. IR (KBr disc) ν_{\max} 1171, 1252, 1289, 1428, 1607, 1675, 2875, 2956, 3293 cm^{-1} . MS (m/z) 196 (M^+), 138, 121.

(R)-(-)-1-Methylheptyl 4'-[4-(3-hydroxypropyloxy)benzoyloxy]biphenyl-4-carboxylate **25**
Compound **22** (2.00 g; 0.010 mol), compound **24** (3.31 g; 0.010 mol), 1-(3-dimethylaminopropyl)-3-ethyl carbodiimide.HCl (1.92 g; 0.010 mol) and 4-(dimethylamino)pyridine (0.50 g) were stirred together at room temperature in dimethylformamide (40 ml) for 24 h. Upon completion, the solvent was removed *in vacuo* and the product purified by column chromatography over silica (dichloromethane as eluent) and recrystallised from acetonitrile:dichloromethane (5:1). Yield 4.87 g (96%).
K 84.2 SmA 111.7 Iso Liq °C.

¹H nmr (CDCl_3): δ 0.88 (3H, t), 1.24-1.46 (11H, m), 1.58-1.80 (3H, m), 2.10 (2H, quint), 3.89 (2H, t), 4.22 (2H, t), 5.18 (1H, sext), 7.01 (2H, d), 7.31 (2H, d), 7.65 (2H, d), 7.66 (2H, d), 8.10 (2H, d), 8.17 (2H, d) ppm. IR (KBr disc) ν_{\max} 1067, 1184, 1275, 1603, 1713, 1745, 2851, 2920, 3400 cm^{-1} . MS (m/z) 504 (M^+).

(R)-(-)-1-Methylheptyl 4'-{4-[3-(2,2,3,3,4,4,5,5-octafluoropentanoyloxy)propyloxy]benzoyloxy}biphenyl-4-carboxylate **26**

Compound **25** (0.250 g; 0.50 mmol), 2,2,3,3,4,4,5,5-octafluoropentanoic acid (0.122 g; 0.50 mmol), 1-(3-dimethylaminopropyl)-3-ethyl carbodiimide.HCl (0.096 g; 0.50 mmol) and 4-(dimethylamino)pyridine (0.050 g) were stirred together at room temperature in dichloromethane (20 ml) for 24 h. Upon completion, the solvent was removed *in vacuo* and the product purified by column chromatography over silica (dichloromethane as eluent) and recrystallised from acetonitrile. Yield 0.25 g (69%).

¹H nmr (CDCl_3): δ 0.88 (3H, t), 1.23-1.46 (11H, m), 1.60-1.80 (2H, m), 2.29 (2H, quint), 4.16 (2H, t), 4.62 (2H, t), 5.18 (1H, sext), 6.04 (1H, tt), 7.01 (2H, d), 7.30 (2H, d), 7.66 (2H, d), 7.67 (2H, d), 8.11 (2H, d), 8.18 (2H, d) ppm. ¹⁹F nmr (CDCl_3): δ -120.05 (2F, t),

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-125.86 (2F, t), -130.71 (2H, m), -138.21 (1F, m), -138.42 (1F, m) ppm. IR (KBr disc)
 ν_{\max} 1169, 1607, 1707, 1733, 1780, 2937 cm^{-1} . MS (m/z) 732 (M^+). Elemental Analysis
($\text{C}_{36}\text{H}_{36}\text{F}_8\text{O}_7$), expected % C 58.33, H 5.03; calculated % C 58.11, H 4.99.