

## Supplementary Information

### ***Methyl 4'-pentadecyloxybiphenyl-4-carboxylate (2a)***

1-Bromopentadecane (6.67 g, 23.0 mmol), compound **1** (5.00 g, 23.0 mmol), potassium carbonate (3.45 g, 25.0 mmol) were dissolved in butanone (150 ml) and heated under reflux overnight until the reaction was complete (analysis by TLC); the solution was then cooled to room temperature, poured into water (250 ml) and stirred for 2 h. The organic solution was separated and dried (MgSO<sub>4</sub>). The drying agent was filtered off and the solvent removed *in vacuo* to yield a colourless solid which was purified by column chromatography (dichloromethane on silica), recrystallised (ethanol) and dried *in vacuo* (P<sub>2</sub>O<sub>5</sub>). Yield 7.09 g (70%), mp 123.6-124.8 °C. δ<sub>H</sub>: 0.81 (3H, t), 1.12-1.31 (22H, m), 1.32-1.44 (2H, m), 1.74 (2H, quint), 3.86 (3H, s), 3.94 (2H, t), 6.91 (2H, d), 7.50 (2H, d), 7.55 (2H, d), 8.01 (2H, d); ν<sub>max</sub> (KBr disc)/cm<sup>-1</sup> 770, 830, 960, 1030, 1110, 1200, 1290, 1400, 1440, 1465, 1500, 1530, 1600, 1720, 2840, 2910; *m/z* 438 (M<sup>+</sup>), 228, 197, 69, 57, 43 (100%).

### ***Methyl 4'-hexadecyloxybiphenyl-4-carboxylate (2b)***

The experimental procedure followed was the same as for the preparation of compound **2a**. The following quantities were used: 1-Bromohexadecane 6.73 g, 22.0 mmol; compound **1** 5.04 g, 22.0 mmol; potassium carbonate 3.34 g, 24.0 mmol; butanone 400 ml. Yield 8.50 g (85%), mp 122.3-123.7 °C. δ<sub>H</sub>: 0.81 (3H, t), 1.12-1.31 (24H, m), 1.32-1.44 (2H, m), 1.75 (2H, quint), 3.87 (3H, s), 3.94 (2H, t), 6.91 (2H, d), 7.50 (2H, d), 7.55 (2H, d), 8.01 (2H, d); ν<sub>max</sub> (KBr disc)/cm<sup>-1</sup> 775, 830, 960, 1105, 1200, 1290, 1430, 1460, 1500, 1525, 1600, 1720, 2840, 2920; *m/z* 452 (M<sup>+</sup>), 228 (100%), 197, 168, 139.

***4'-Pentadecyloxybiphenyl-4-carboxylic acid (3a)***

10M Sodium hydroxide (15 ml) was added to a solution of compound **2a** (5.30 g, 12.0 mmol) in ethanol (600 ml) and the mixture was heated under reflux for 2 h. The reaction mixture was cooled to room temperature and acidified with 2M hydrochloric acid until pH 3 and left to stir for 1 h. The colourless solid formed was filtered off, washed with copious amounts of water until the washings were neutral, recrystallised (glacial acetic acid) and dried in an oven for 48 h. Yield 3.92 g (77%), K 158.0 N 240.8 Iso °C.  $\delta_{\text{H}}$ : 0.86 (3H, t), 1.17-1.40 (22H, m), 1.42-1.53 (2H, m), 1.81 (2H, quint), 4.00 (2H, t), 6.98 (2H, d), 7.57 (2H, d), 7.62 (2H, d), 8.08 (2H, d), acidic proton not observed;  $\nu_{\text{max}}$  (KBr disc)/ $\text{cm}^{-1}$  700, 760, 820, 900, 1020, 1120, 1190, 1240, 1280, 1420, 1460, 1520, 1590, 1680, 2820, 2900, 3000;  $m/z$  424 ( $\text{M}^+$ , 100%), 380, 315, 270, 214, 197.

***4'-Hexadecyloxybiphenyl-4-carboxylic acid (3b)***

The experimental procedure followed was the same as for the preparation of compound **3a**. The following quantities were used: Compound **2b** 8.40 g, 19.0 mmol; 10M sodium hydroxide 20 ml; ethanol 700 ml. Yield 6.59 g (79%), K 156.1 N 239.5 Iso °C.  $\delta_{\text{H}}$ : 0.80 (3H, t), 1.12-1.32 (24H, m), 1.34-1.44 (2H, m), 1.74 (2H, quint), 3.97 (2H, t), 6.92 (2H, d), 7.51 (2H, d), 7.58 (2H, d), 8.02 (2H, d), acidic proton not observed;  $\nu_{\text{max}}$  (KBr disc)/ $\text{cm}^{-1}$  700, 760, 820, 900, 1020, 1120, 1190, 1240, 1280, 1420, 1460, 1520, 1590, 1680, 2820, 2900, 3000;  $m/z$  438 ( $\text{M}^+$ ), 424, 214 (100%), 197, 169, 139, 91, 55.

***(S)-(+)-4-(2-Methylbutyloxycarbonyl)phenyl 4'-pentadecyloxybiphenyl-4-carboxylate (1.1)***

*N,N'*-Dicyclohexylcarbodiimide (0.44 g, 2.12 mmol) and 4-(dimethylamino)pyridine (0.10 g, 0.10 mmol) were added to a stirred solution of compound **3a** (0.90 g, 2.12 mmol) and compound **4a** (0.44 g, 2.12 mmol) in THF (100 ml). The mixture was left stirring at room temperature for 24 h until the reaction was complete. The dicyclohexylurea formed was filtered off and the solvent removed *in vacuo* to yield a viscous colourless oil which was purified by column chromatography (petrol:ethyl acetate 7:1 on silica). The colourless solid was recrystallised (ethanol) and dried *in vacuo* (P<sub>2</sub>O<sub>5</sub>). Yield 0.40 g (31%),  $[\alpha]_{\text{D}}^{24} = +3.4^{\circ}$ , CHCl<sub>3</sub>, 0.00352 g ml<sup>-1</sup>. Elemental analysis for C<sub>40</sub>H<sub>54</sub>O<sub>5</sub>: calculated C 78.14%; H 8.85%; found C 77.78%; H 8.68%.

$\delta_{\text{H}}$ : 0.87 (3H, t), 0.96 (3H, t), 1.02 (3H, d), 1.20-1.38 (24H, m), 1.42-1.52 (2H, m), 1.82 (3H, quint and oct), 4.01 (2H, t), 4.20 (2H, m), 7.01 (2H, d), 7.32 (2H, d), 7.61 (2H, d), 7.71 (2H, d), 8.14 (2H, d), 8.24 (2H, d);  $\nu_{\text{max}}$  (KBr disc)/cm<sup>-1</sup> 680, 720, 760, 825, 880, 1020, 1080, 1110, 1160, 1210, 1260, 1470, 1500, 1600, 1720, 1740, 2840, 2930;  $m/z$  614 (M<sup>+</sup>), 407 (100%), 197, 168, 141, 57.

***(S)-(+)-4-(2-Methylbutyloxycarbonyl)-3-fluorophenyl 4'-pentadecyloxybiphenyl-4-carboxylate (1.2)***

The experimental procedure followed was the same as for the preparation of **1.1**. The following quantities were used: Compound **3a** 0.90 g, 2.12 mmol; compound **4b** 0.48 g, 2.12 mmol; *N,N'*-dicyclohexylcarbodiimide 0.44 g, 2.12 mmol; 4-(dimethylamino)pyridine 0.10 g, 0.10 mmol; THF 150 ml. Yield 0.32 g (24%),  $[\alpha]_{\text{D}}^{24}$

= +1.4°, CHCl<sub>3</sub>, c. 0.00876 g ml<sup>-1</sup>. Elemental analysis for C<sub>40</sub>H<sub>53</sub>F<sub>1</sub>O<sub>5</sub>: calculated C 75.92%; H 8.44%; found C 76.29%; H 8.57%.

δ<sub>H</sub>: 0.87 (3H, t), 0.98 (3H, t), 1.02 (3H, d), 1.21-1.40 (24H, m), 1.42-1.54 (2H, m), 1.82 (3H, quint and oct), 4.02 (2H, t), 4.21 (2H, m), 7.01 (2H,d), 7.09-7.14 (2H, m), 7.61 (2H, d), 7.72 (2H, d), 8.05 (1H, t), 8.21 (2H, d); ν<sub>max</sub> (KBr disc)/cm<sup>-1</sup> 680, 720, 750, 800, 820, 880, 960, 1055, 1100, 1180, 1250, 1280, 1420, 1460, 1500, 1590, 1710, 1740, 2840, 2900; m/z 632 (M<sup>+</sup>), 407 (100%), 251, 197, 168, 139, 57.

***(S)-(+)-4-(2-Methylbutyloxycarbonyl)-2-fluorophenyl 4'-pentadecyloxybiphenyl-4-carboxylate (1.3)***

The experimental procedure followed was the same as for the preparation of **1.1**. The following quantities were used: Compound **3a** 0.90 g, 2.12 mmol; compound **4c** 0.48 g, 2.12 mmol; *N,N'*-dicyclohexylcarbodiimide 0.44 g, 2.12 mmol; 4-(dimethylamino)pyridine 0.10 g, 0.10 mmol; THF 150 ml. Yield 0.43 g (32%), [α]<sub>D</sub><sup>24</sup> = +1.4°, CHCl<sub>3</sub>, c. 0.00830 g ml<sup>-1</sup>. Elemental analysis for C<sub>40</sub>H<sub>53</sub>F<sub>1</sub>O<sub>5</sub>: calculated C 75.92%; H 8.44%; found C 76.18%; H 8.53%.

δ<sub>H</sub> (CD<sub>2</sub>Cl<sub>2</sub>): 0.88 (3H, t), 0.97 (3H, t), 1.02 (3H, d), 1.20-1.42 (22H, m), 1.44-1.56 (4H, m), 1.80 (2H, quint), 1.88 (1H, oct), 4.02 (2H, t), 4.18 (2H, m), 7.01 (2H, d), 7.40 (1H, t), 7.62 (2H, d), 7.74 (2H, d), 7.87-7.92 (2H, m), 8.23 (2H, d); ν<sub>max</sub> (KBr disc)/cm<sup>-1</sup> 680, 720, 750, 800, 820, 880, 960, 1055, 1100, 1180, 1255, 1280, 1420, 1460, 1500, 1600, 1710, 1740, 2840, 2900; m/z 632 (M<sup>+</sup>), 407 (100%), 252, 197, 141, 55.

***(S)-(+)-4-(2-Methylbutyloxycarbonyl)phenyl 4'-hexadecyloxybiphenyl-4-carboxylate (1.4)***

The experimental procedure followed was the same as for the preparation of **1.1**. The following quantities were used: Compound **3b** 0.90 g, 2.05 mmol; compound **4a** 0.43 g, 2.05 mmol; *N,N'*-dicyclohexylcarbodiimide 0.42 g, 2.05 mmol; 4-(dimethylamino)pyridine 0.10 g, 0.10 mmol; THF 150 ml. Yield 0.40 g (31%),  $[\alpha]_D^{24} = +3.4^\circ$ ,  $\text{CHCl}_3$ , c. 0.00707 g ml<sup>-1</sup>. Elemental analysis for C<sub>41</sub>H<sub>56</sub>O<sub>5</sub>: calculated C 78.30%; H 8.98%; found C 78.30%; H 9.22%.

$\delta_{\text{H}}$  (CD<sub>2</sub>Cl<sub>2</sub>): 0.88 (3H, t), 0.97 (3H, t), 1.02 (3H, d), 1.20-1.42 (24H, m), 1.44-1.60 (4H, m), 1.81 (2H, quint), 1.87 (1H, oct), 4.02 (2H, t), 4.17 (2H, m), 7.00 (2H, d), 7.33 (2H, d), 7.64 (2H, d), 7.73 (2H, d), 8.12 (2H, d), 8.22 (2H, d);  $\nu_{\text{max}}$  (KBr disc)/cm<sup>-1</sup> 680, 720, 750, 820, 880, 1070, 1140, 1190, 1280, 1460, 1490, 1590, 1710, 1730, 2820, 2900; *m/z* 628 (M<sup>+</sup>), 541, 421 (100%), 197, 57.

***(S)-(+)-4-(2-Methylbutyloxycarbonyl)-3-fluorophenyl 4'-hexadecyloxybiphenyl-4-carboxylate (1.5)***

The experimental procedure followed was the same as for the preparation of compound **86**. The following quantities were used: Compound **3b** 0.90 g, 2.05 mmol; compound **4b** 0.46 g, 2.05 mmol; *N,N'*-dicyclohexylcarbodiimide 0.42 g, 2.05 mmol; 4-(dimethylamino)pyridine 0.10 g, 0.10 mmol; THF 150 ml. Yield 0.48 g (36%),  $[\alpha]_D^{24} = +3.4^\circ$ ,  $\text{CHCl}_3$ , c. 0.00787 g ml<sup>-1</sup>. Elemental analysis for C<sub>41</sub>H<sub>55</sub>F<sub>1</sub>O<sub>5</sub>: calculated C 76.13%; H 8.57%; found C 75.85%; H 8.57%.

Table 1

$\delta_{\text{H}}$  ( $\text{CD}_2\text{Cl}_2$ ): 0.88 (3H, t), 0.96 (3H, t), 1.02 (3H, d), 1.18-1.40 (24H, m), 1.44-1.54 (4H, m), 1.81 (2H, quint), 1.85 (1H, oct), 4.02 (2H, t), 4.18 (2H, m), 7.00 (2H, d), 7.12-7.17 (2H, m), 7.62 (2H, d), 7.74 (2H, d), 8.03 (1H, t), 8.21 (2H, d);  $\nu_{\text{max}}$  (KBr disc)/ $\text{cm}^{-1}$  680, 710, 750, 820, 880, 1060, 1120, 1180, 1240, 1280, 1420, 1460, 1480, 1590, 1710, 1730, 2820, 2900;  $m/z$  646 ( $\text{M}^+$ ), 421 (100%), 363, 197.

***(S)-(+)-4-(2-Methylbutyloxycarbonyl)-2-fluorophenyl 4'-hexadecyloxybiphenyl-4-carboxylate (1.6)***

The experimental procedure followed was the same as for the preparation of **1.1**. The following quantities were used: Compound **3b** 0.90 g, 2.05 mmol; compound **4c** 0.46 g, 2.05 mmol; *N,N'*-dicyclohexylcarbodiimide 0.42 g, 2.05 mmol; 4-(dimethylamino)pyridine 0.10 g, 0.10 mmol; THF 150 ml. Yield 0.46 g (35%),  $[\alpha]_{\text{D}}^{24} = +1.5^\circ$ ,  $\text{CHCl}_3$ , c. 0.00353 g  $\text{ml}^{-1}$ . Elemental analysis for  $\text{C}_{41}\text{H}_{55}\text{F}_1\text{O}_5$ : calculated C 76.13%; H 8.57%; found C 76.34%; H 8.68%.

$\delta_{\text{H}}$  ( $\text{CD}_2\text{Cl}_2$ ): 0.88 (3H, t), 0.97 (3H, t), 1.02 (3H, d), 1.20-1.42 (24H, m), 1.45-1.58 (4H, m), 1.81 (2H, quint), 1.85 (1H, oct), 4.02 (2H, t), 4.18 (2H, m), 7.01 (2H, d), 7.39 (1H, t), 7.62 (2H, d), 7.74 (2H, d), 7.87-7.92 (2H, m), 8.23 (2H, d);  $\nu_{\text{max}}$  (KBr disc)/ $\text{cm}^{-1}$  680, 700, 750, 820, 880, 1060, 1100, 1180, 1280, 1420, 1460, 1500, 1590, 1710, 1740, 2840, 2900;  $m/z$  646 ( $\text{M}^+$ ), 421 (100%), 307, 252, 197, 141.

***1-Methylcyclobutanecarboxylic acid (6)***

Butyllithium (240 ml, 0.60 mol, 2.5M in hexanes) was added to a stirred solution of diisopropylamine (60.6 g, 0.60 mol) in THF (750 ml) maintained at 0 °C. This was stirred for 15 minutes and then cyclobutanecarboxylic acid (**5**) (25.0, 0.25 mol) in THF (100 ml) was added dropwise keeping the temperature below 5 °C. The reaction

solution was stirred at 5 °C for another 15 min and then iodomethane (35.5 g, 0.25 mol) in THF (100 ml) was added dropwise and the reaction solution was left to stir at room temperature overnight. The reaction was then cooled to 0 °C and acidified with 10% hydrochloric acid (150 ml) to pH 3. The product was then extracted with ether (3 x 400 ml) and the combined ethereal extracts were washed with brine (500 ml) and dried (Na<sub>2</sub>SO<sub>4</sub>). The drying agent was filtered off and the solvent removed *in vacuo* to yield a crude yellow-coloured oil which was purified by distillation to give a colourless oil. Yield 27.0 g (95%), bp 150-160 °C.  $\delta_{\text{H}}$ : 1.40 (3H, s), 1.79-2.00 (4H, m), 2.45-2.55 (2H, m), 10.70-11.90 (1H br s);  $\nu_{\text{max}}$  (film)/cm<sup>-1</sup> 940, 1160, 1220, 1240, 1310, 1410, 1460, 1700, 2700, 2970, 3120;  $m/z$  114 (M<sup>+</sup>), 99, 86, 69, 58 (100%).

***(1-Methylcyclobutyl)methanol (7)***

A solution of compound **6** (27.0 g, 0.24 mol) in ether (100 ml) was added dropwise to a stirred suspension of lithium aluminium hydride (11.4 g, 0.30 mol) in ether (350 ml). The reaction mixture was heated under reflux for 3 h and then cooled in an ice bath to below room temperature. A saturated solution of sodium sulphate (100 ml) was added dropwise to destroy any of the unreacted lithium aluminium hydride. The resulting precipitate was filtered off and washed with ether; the combined filtrates were dried (MgSO<sub>4</sub>). The drying agent was filtered off and the solvent removed *in vacuo* to yield a colourless oil which was purified by distillation. Yield 20.1 g (85%), bp 100-110 °C.  $\delta_{\text{H}}$ : 1.13 (3H, s), 1.62-1.70 (2H, m), 1.82-1.94 (4H, m), 2.02 (1H, s), 3.46 (2H, s);  $\nu_{\text{max}}$  (film)/cm<sup>-1</sup> 1010, 1040, 1440, 2840, 2920, 3330;  $m/z$  99, 82, 70, 67, 57 (100%), 54, M<sup>+</sup> not observed.

***1-(10-Bromodecyloxymethyl)-1-methylcyclobutane (9a)***

A 50% aqueous sodium hydroxide solution (100.0 g), tetrabutylammonium bromide (1.53 g, 4.75 mmol) and hexane (400 ml) were cooled with stirring in an ice bath. Compound **7** (9.50 g, 95 mmol) and 1,10-dibromodecane (71.2 g, 238 mmol) were added and the reaction was left stirring until it reached room temperature; the reaction mixture was then heated under reflux for 3 h and then cooled to below 5 °C. Water (300 ml) was added and the organic layer was retained and dried (Na<sub>2</sub>SO<sub>4</sub>). The drying agent was filtered off and the solvent was removed *in vacuo*. The resulting oil was purified by column chromatography [dichloromethane:hexane (1:6), to remove the excess of 1,10-dibromodecane; dichloromethane, to isolate the product, and then ethyl acetate to obtain the product arising from double alkylation, on silica). Yield 6.66 g (22%).  $\delta_{\text{H}}$ : 1.13 (3H, s), 1.23-1.48 (12H, m), 1.49-1.60 (2H, m), 1.61-1.67 (2H, m), 1.78-1.95 (6H, m), 3.23 (2H, s), 3.41 (2H, t), 3.43 (2H, t);  $\nu_{\text{max}}$  (film)/cm<sup>-1</sup> 1100, 1360, 1450, 2840, 2900;  $m/z$  320,318 (M<sup>+</sup>), 247, 162, 137,135, 100, 82 (100%), 71.

***1-(11-Bromoundecyloxymethyl)-1-methylcyclobutane (9b)***

The experimental procedure followed was the same as for the preparation of compound **9a**. The following quantities were used: Compound **7** 9.50 g, 95 mmol; 1,11-dibromoundecane 74.7 g, 0.24 mol; 50% aqueous sodium hydroxide solution 100.0 g; hexane 400 ml; tetrabutylammonium bromide 1.53 g, 4.75 mmol. Yield 9.26 g (29%).  $\delta_{\text{H}}$ : 1.12 (3H, s), 1.24-1.32 (12H, m), 1.34-1.45 (2H, m), 1.57 (2H, quint), 1.61-1.68 (2H, m), 1.77-1.95 (6H, m), 3.22 (2H, s), 3.40 (2H, t), 3.42 (2H, t);  $\nu_{\text{max}}$



Table 1

(film)/cm<sup>-1</sup> 1118, 1371, 1468, 2861, 2933; *m/z* 334,332 (M<sup>+</sup>), 292,290, 164, 134, 99, 81 (100%), 54.

***3-(10-Bromodecyloxymethyl)-3-methyloxetane (10a)***

The experimental procedure followed was the same as for the preparation of compound **9a**. The following quantities were used: 3-(hydroxymethyl)-3-methyloxetane (**8**) 19.1 g, 0.19 mol; 1,10-Dibromodecane 113.9 g, 0.39 mol; 50% aqueous sodium hydroxide solution 260.00 g; hexane 400 ml; tetrabutylammonium bromide 3.04 g, 9.50 mmol. Yield 32.3 g (55%), bp 170 °C at 0.5 mmHg.  $\delta_{\text{H}}$ : 1.25-1.48 (12H, m), 1.35 (3H, s), 1.57 (2H, quint), 1.85 (2H, quint), 3.41 (2H, t), 3.46 (2H, t), 3.47 (2H, s), 4.36 (2H, d), 4.51 (2H, d);  $\nu_{\text{max}}$  (film)/cm<sup>-1</sup> 830, 980, 1110, 2850, 2920; *m/z* 304, 263, 177, 163, 83, 72 (100%), M<sup>+</sup> not observed.

***3-(11-Bromoundecyloxymethyl)-3-methyloxetane (10b)***

The experimental procedure followed was the same as for the preparation of compound **9a**. The following quantities were used: compound **8** 13.8 g, 0.13 mol; 1,11-Dibromoundecane (**37**) 100.0 g, 0.32 mol; 50% aqueous sodium hydroxide solution 195.0 g; hexane 300 ml; tetra-butylammonium bromide 2.08 g, 9.50 mmol. Yield 55.4 g (81%), bp 175 °C at 0.5 mmHg.  $\delta_{\text{H}}$ : 1.24-1.48 (14H, m), 1.31 (3H, s), 1.55 (2H, quint), 1.85 (2H, quint), 3.41 (2H, t), 3.47 (2H, t), 3.49 (2H, s), 4.36 (2H, d), 4.52 (2H, d);  $\nu_{\text{max}}$  (film)/cm<sup>-1</sup> 830, 980, 1110, 2850, 2920; *m/z* 290, 137, 97, 72, 55 (100%), M<sup>+</sup> not observed.

***Methyl 4'-[10-(1-methylcyclobutan-1-ylmethoxy)decyloxy]biphenyl-4-carboxylate (11a)***

The experimental procedure followed was the same as for the preparation of compound **2a**. The following quantities were used: Compound **9a** 6.45 g, 20.0 mmol; compound **1** 4.56 g, 20.0 mmol; potassium carbonate 3.31 g, 24.0 mmol; butanone 250 ml. Yield 6.79 g (73%), mp 103.6-104.2 °C.  $\delta_{\text{H}}$ : 1.21 (3H, s), 1.27-1.35 (10H, m), 1.47 (2H, quint), 1.56 (2H, quint), 1.62-1.68 (2H, m), 1.77-1.94 (6H, m), 3.22 (2H, s), 3.42 (2H, t), 3.93 (3H, s), 4.00 (2H, t), 6.98 (2H, d), 7.56 (2H, d), 7.61 (2H, d), 8.07 (2H, d);  $\nu_{\text{max}}$  (KBr disc)/ $\text{cm}^{-1}$  723, 771, 834, 960, 1111, 1200, 1293, 1439, 1502, 1606, 1727, 2858, 2932;  $m/z$  466 ( $\text{M}^+$ ), 365, 228 (100%), 197, 152, 69, 55.

***Methyl 4'-[11-(1-methylcyclobutan-1-ylmethoxy)undecyloxy]biphenyl-4-carboxylate (11b)***

The experimental procedure followed was the same as for the preparation of compound **2a**. The following quantities were used: Compound **9b** 9.00 g, 27.0 mmol; compound **1** 6.18 g, 27.0 mmol; potassium carbonate 4.49 g, 33.0 mmol; butanone 500 ml. Yield 9.39 g (73%), mp 100.9-102.1 °C.  $\delta_{\text{H}}$ : 1.23 (3H, s), 1.24-1.40 (12H, m), 1.47 (2H, quint), 1.57 (2H, quint), 1.62-1.68 (2H, m), 1.76-1.94 (6H, m), 3.23 (2H, s), 3.42 (2H, t), 3.93 (3H, s), 4.00 (2H, t), 6.98 (2H, d), 7.56 (2H, d), 7.61 (2H, d), 8.07 (2H, d);  $\nu_{\text{max}}$  (KBr disc)/ $\text{cm}^{-1}$  720, 774, 833, 1035, 1116, 1197, 1249, 1292, 1431, 1497, 1607, 1680, 2856, 2927;  $m/z$  480 ( $\text{M}^+$ ), 452, 365, 228 (100%), 197, 83, 55.

***Methyl 4'-[10-(3-methyloxetan-3-ylmethoxy)decyloxy]biphenyl-4-carboxylate (12a)***

The experimental procedure followed was the same as for the preparation of compound **2a**. The following quantities were used: Compound **10a** 32.3 g, 0.10 mol;

compound **1** 22.9 g, 0.10 mol; potassium carbonate 27.6 g, 0.20 mol; potassium iodide 3.32 g, 20 mmol; butanone 600 ml. Yield 34.63 g (74%), mp 89.1 °C.  $\delta_{\text{H}}$ : 1.23-1.40 (13H, m), 1.40- 1.60 (4H, m and quint), 1.80 (2H, quint), 3.45 (4H, t and s), 3.94 (3H, s), 4.01 (2H, t), 4.35 (2H, d), 4.51 (2H, d), 6.99 (2H, d), 7.57 (2H, d), 7.62 (2H, d), 8.05 (2H, d);  $\nu_{\text{max}}$  (KBr disc)/ $\text{cm}^{-1}$  830, 1110, 1190, 1250, 1290, 1490, 1520, 1600, 1720, 2850, 2920, 3440;  $m/z$  468 ( $\text{M}^+$ ), 384, 228 (100%), 197, 152, 139.

***Methyl 4'-[11-(3-methyloxetan-3-ylmethoxy)undecyloxy]biphenyl-4-carboxylate***

**(12b)**

The experimental procedure followed was the same as for the preparation of compound **2a**. The following quantities were used: Compound **10b** 35.3 g, 0.11 mol; compound **1** 23.9 g, 0.11 mol; potassium carbonate 30.4 g, 0.22 mol; potassium iodide 3.65 g, 22 mmol; butanone 700 ml. Yield 47.7 g (90%), mp 83.3-85.4 °C.  $\delta_{\text{H}}$ : 1.24-1.51 (17H, m), 1.58 (2H, quint), 1.81 (2H, quint), 3.45 (2H, t), 3.47 (2H, s), 3.93 (3H, s), 4.01 (2H, t), 4.36 (2H, d), 4.51 (2H, d), 6.99 (2H, d), 7.56 (2H, d), 7.61 (2H, d), 8.08 (2H, d);  $\nu_{\text{max}}$  (KBr disc)/ $\text{cm}^{-1}$  830, 1110, 1190, 1250, 1285, 1430, 1525, 1600, 1720, 2840, 2920, 3400;  $m/z$  482 ( $\text{M}^+$ ), 256, 228 (100%), 197, 169, 69, 55.

***4'-[10-(1-Methylcyclobutan-1-ylmethoxy)decyloxy]biphenyl-4-carboxylic acid (13a)***

The experimental procedure followed was the same as for the preparation of compound **3a**. The following quantities were used: Compound **11a** 6.30 g, 14.0 mmol; 10M Sodium hydroxide 15 ml; ethanol 500ml. Yield 5.40 g (85%), K 147.3 N 221.6 Iso °C.  $\delta_{\text{H}}$ : 1.23 (3H, s), 1.24-1.40 (10H, m), 1.47 (2H, quint), 1.55 (2H, quint), 1.62-1.68 (2H, m), 1.77-1.94 (6H, m), 3.23 (2H, s), 3.43 (2H, t), 4.01 (2H, t), 6.98 (2H, d), 7.57 (2H, d), 7.65 (2H, d), 8.15 (2H, d), acidic proton not observed;  $\nu_{\text{max}}$

(KBr disc)/cm<sup>-1</sup> 723, 772, 834, 958, 1031, 1113, 1199, 1291, 1437, 1497, 1606, 1726, 2856, 2937, 3408; *m/z* 452 (M<sup>+</sup>), 424, 390, 214 (100%), 121, 110.

***4'-[11-(1-Methylcyclobutan-1-ylmethoxy)undecyloxy]biphenyl-4-carboxylic acid (13b)***

The experimental procedure followed was the same as for the preparation of compound **3a**. The following quantities were used: Compound **11b** 9.00 g, 19.0 mmol; 10M sodium hydroxide 20 ml; ethanol 500 ml. Yield 7.85 g (89%), K 147.6 N 219.6 Iso °C. δ<sub>H</sub>: 1.05 (3H, s), 1.23-1.36 (12H, m), 1.49 (2H, quint), 1.51 (2H, quint), 1.55-1.61 (2H, m), 1.71-1.90 (6H, m), 3.21 (2H, s), 3.36 (2H, t), 3.97 (2H, t), 6.94 (2H, d), 7.55 (2H, d), 7.59 (2H, d), 8.04 (2H, d), acidic proton not observed; ν<sub>max</sub> (KBr disc)/cm<sup>-1</sup> 720, 775, 834, 1031, 1118, 1195, 1249, 1430, 1499, 1606, 1682, 2856, 2932, 3420; *m/z* 466 (M<sup>+</sup>), 365, 214 (100%), 197, 83, 55.

***4'-[10-(3-Methyloxetan-3-ylmethoxy)decyloxy]biphenyl-4-carboxylic acid (14a)***

The experimental procedure followed was the same as for the preparation of compound **3a**. The following quantities were used: Compound **12a** 32.0 g, 0.070 mol; 10M sodium hydroxide 30 ml; ethanol and water (1:5) 1.5 l. Yield 24.2 g (76%), K 173.9 N 185.4 Iso °C. δ<sub>H</sub>: 1.23-1.51 (15H, m), 1.56 (2H, quint), 1.72 (2H, quint), 3.38 (4H, s and t), 3.91 (2H, t), 4.24 (2H, d), 4.40 (2H, d), 6.90 (2H, d), 7.48 (2H, d), 7.54 (2H, d), 8.00 (2H, d), acid proton not observed; ν<sub>max</sub> (KBr disc)/cm<sup>-1</sup> 830, 1110, 1190, 1250, 1290, 1490, 1520, 1600, 1670, 2850, 2920, 3450; *m/z* 454 (M<sup>+</sup>), 370, 228, 214 (100%), 197, 83.

***4'-[11-(3-Methyloxetan-3-ylmethoxy)undecyloxy]biphenyl-4-carboxylic acid (14b)***

The experimental procedure followed was the same as for the preparation of compound **3a**. The following quantities were used: Compound **12b** 47.7 g, 0.10 mol; 10M sodium hydroxide 30ml; ethanol and water (1:5) 1.5 l. Yield 42.1 g (90%), K 150.4 N 186.5 Iso °C.  $\delta_{\text{H}}$ : 1.20-1.51 (17H, m), 1.57 (2H, quint), 1.81 (2H, quint), 3.46 (2H, t), 3.48 (2H, s), 4.01 (2H, t), 4.36 (2H, d), 4.51 (2H, d), 6.99 (2H, d), 7.56 (2H, d), 7.61 (2H, d), 8.08 (2H, d), acidic proton not observed;  $\nu_{\text{max}}$  (KBr disc)/ $\text{cm}^{-1}$  830, 1110, 1190, 1250, 1290, 1430, 1490, 1520, 1600, 1720, 2850, 2920, 3450;  $m/z$  468 ( $\text{M}^+$ ), 386, 214 (100%), 197, 69, 55.

***(S)-(+)-4-(2-Methylbutyloxycarbonyl)phenyl 4'-[10-(1-methylcyclobutan-1-ylmethoxy)decyloxy]biphenyl-4-carboxylate (2.1)***

The experimental procedure followed was the same as for the preparation of **1.1**. The following quantities were used: Compound **13a** 0.90 g, 1.99 mmol; compound **4a** 0.41 g, 1.99 mmol; *N,N'*-dicyclohexylcarbodiimide 0.41 g, 1.99 mmol; 4-(dimethylamino)pyridine 0.10 g, 0.10 mmol; dichloromethane 100 ml. Yield 0.86 g (67%),  $[\alpha]_{\text{D}}^{24} = +1.7^\circ$ ,  $\text{CHCl}_3$ , 0.00680 g  $\text{ml}^{-1}$ . Elemental analysis for  $\text{C}_{41}\text{H}_{54}\text{O}_6$ : calculated C 76.60%; H 8.47%; found C 76.87%; H 8.70%.

$\delta_{\text{H}}$  ( $\text{CD}_2\text{Cl}_2$ ): 0.97 (3H, t), 1.02 (3H, d), 1.10 (3H, s), 1.26-1.41 (13H, m), 1.47 (2H, quint), 1.51-1.58 (2H, m), 1.59-1.66 (2H, m), 1.76-1.93 (6H, m), 3.21 (2H, s), 3.40 (2H, t), 4.01 (2H, t), 4.17 (2H, m), 7.00 (2H, d), 7.33 (2H, d), 7.62 (2H, d), 7.73 (2H, d), 8.12 (2H, d), 8.22 (2H, d);  $\nu_{\text{max}}$  (KBr disc)/ $\text{cm}^{-1}$  693, 726, 767, 830, 889, 1069, 1115, 1195, 1274, 1467, 1504, 1607, 1720, 1736, 2860, 2935;  $m/z$  642 ( $\text{M}^+$ ), 435, 335, 214, 196, 168, 97, 83 (100%).

***(S)-(+)-4-(2-Methylbutyloxycarbonyl)-3-fluorophenyl 4'-[10-(1-methylcyclobutan-1-ylmethoxy)decyloxy]biphenyl-4-carboxylate (2.2)***

The experimental procedure followed was the same as for the preparation of **1.1**. The following quantities were used: Compound **13a** 0.90 g, 1.99 mmol; compound **4b** 0.45 g, 1.99 mmol; *N,N'*-dicyclohexylcarbodiimide 0.41 g, 1.99 mmol; 4-(dimethylamino)pyridine 0.10 g, 0.10 mmol; dichloromethane 100 ml. Yield 0.86 g (65%),  $[\alpha]_D^{24} = +1.7^\circ$ ,  $\text{CHCl}_3$ , c. 0.01377 g ml<sup>-1</sup>. Elemental analysis for C<sub>41</sub>H<sub>53</sub>F<sub>1</sub>O<sub>6</sub>: calculated C 74.52%; H 8.08%; found C 74.36%; H 8.32%.

$\delta_{\text{H}}$  (CD<sub>2</sub>Cl<sub>2</sub>): 0.96 (3H, t), 1.02 (3H, d), 1.10 (3H, s), 1.26-1.42 (13H, m), 1.45 (2H, quint), 1.50-1.58 (2H, m), 1.60-1.66 (2H, m), 1.76-1.93 (6H, m), 3.21 (2H, s), 3.40 (2H, t), 4.02 (2H, t), 4.18 (2H, m), 7.00 (2H, d), 7.12-7.17 (2H, m), 7.62 (2H, d), 7.74 (2H, d), 8.02 (1H, t), 8.21 (2H, d);  $\nu_{\text{max}}$  (KBr disc)/cm<sup>-1</sup> 691, 724, 768, 829, 895, 1061, 1130, 1191, 1251, 1280, 1434, 1501, 1610, 1710, 1737, 2860, 2936; *m/z* 660 (M<sup>+</sup>), 435, 335, 214, 196, 168, 139, 97, 83 (100%).

***(S)-(+)-4-(2-Methylbutyloxycarbonyl)-2-fluorophenyl 4'-[10-(1-methylcyclobutan-1-ylmethoxy)decyloxy]biphenyl-4-carboxylate (2.3)***

The experimental procedure followed was the same as for the preparation of **1.1**. The following quantities were used: Compound **13a** 0.90 g, 1.99 mmol; compound **4c** 0.45 g, 1.99 mmol; *N,N'*-dicyclohexylcarbodiimide 0.41 g, 1.99 mmol; 4-(dimethylamino)pyridine 0.10 g, 0.10 mmol; dichloromethane 100 ml. Yield 0.91 g (69%),  $[\alpha]_D^{24} = +2.0^\circ$ ,  $\text{CHCl}_3$ , c. 0.00598 g ml<sup>-1</sup>. Elemental analysis for C<sub>41</sub>H<sub>53</sub>F<sub>1</sub>O<sub>6</sub>: calculated C 74.52%; H 8.08%; found C 74.51%; H 8.37%.

Table 1

$\delta_{\text{H}}$ : 0.96 (3H, t), 1.02 (3H, d), 1.10 (3H, s), 1.26-1.42 (13H, m), 1.47 (2H, quint), 1.51-1.58 (2H, m), 1.60-1.66 (2H, m), 1.76-1.94 (6H, m), 3.21 (2H, s), 3.40 (2H, t), 4.01 (2H, t), 4.18 (2H, m), 7.00 (2H, d), 7.39 (1H, t), 7.62 (2H, d), 7.74 (2H, d), 7.87-7.92 (2H, m), 8.23 (2H, d);  $\nu_{\text{max}}$  (film)/ $\text{cm}^{-1}$  693, 762, 829, 894, 1061, 1115, 1185, 1259, 1299, 1398, 1509, 1604, 1723, 1752, 2856, 2936;  $m/z$  660 ( $\text{M}^+$ ), 466, 435, 335, 214 (100%), 197, 139, 83.

***(S)-(+)-4-(2-Methylbutyloxycarbonyl)phenyl 4'-[11-(1-methylcyclobutan-1-ylmethoxy)undecyloxy]biphenyl-4-carboxylate (2.4)***

The experimental procedure followed was the same as for the preparation of **1.1**. The following quantities were used: Compound **13b** 0.90 g, 1.93 mmol; compound **4a** 0.40 g, 1.93 mmol; *N,N'*-dicyclohexylcarbodiimide 0.40 g, 1.93 mmol; 4-(dimethylamino)pyridine 0.10 g, 0.10 mmol; dichloromethane 100 ml. Yield 0.90 g (71%),  $[\alpha]_{\text{D}}^{24} = +1.9^\circ$ ,  $\text{CHCl}_3$ , c. 0.00624 g  $\text{ml}^{-1}$ . Elemental analysis for  $\text{C}_{42}\text{H}_{56}\text{O}_6$ : calculated C 76.79%; H 8.59%; found C 76.74%; H 8.87%.

$\delta_{\text{H}}$ : 0.97 (3H, t), 1.02 (3H, d), 1.12 (3H, s), 1.26-1.41 (15H, m), 1.48 (2H, quint), 1.54 (2H, quint), 1.60-1.66 (2H, m), 1.76-1.93 (6H, m), 3.23 (2H, s), 3.42 (2H, t), 4.01 (2H, t), 4.18 (2H, m), 7.00 (2H, d), 7.32 (2H, d), 7.59 (2H, d), 7.70 (2H, d), 8.13 (2H, d), 8.23 (2H, d);  $\nu_{\text{max}}$  (KBr disc)/ $\text{cm}^{-1}$  689, 731, 765, 831, 886, 1014, 1073, 1117, 1198, 1269, 1471, 1503, 1604, 1710, 1740, 2856, 2927;  $m/z$  656 ( $\text{M}^+$ ), 471, 350, 215, 196, 97, 83, 55 (100%).

***(S)-(+)-4-(2-Methylbutyloxycarbonyl)-3-fluorophenyl 4'-[11-(1-methylcyclobutan-1-ylmethoxy)undecyloxy]biphenyl-4-carboxylate (2.5)***

The experimental procedure followed was the same as for the preparation of **1.1**. The following quantities were used: Compound **13b** 0.90 g, 1.93 mmol; compound **4b** 0.44 g, 1.93 mmol; *N,N'*-dicyclohexylcarbodiimide 0.40 g, 1.93 mmol; 4-(dimethylamino)pyridine 0.10 g, 0.10 mmol; dichloromethane 100 ml. Yield 1.00 g (77%),  $[\alpha]_D^{24} = +1.8^\circ$ ,  $\text{CHCl}_3$ , c. 0.00653 g ml<sup>-1</sup>. Elemental analysis for C<sub>42</sub>H<sub>55</sub>F<sub>1</sub>O<sub>6</sub>: calculated C 74.75%; H 8.21%; found C 74.46%; H 8.43%.

$\delta_{\text{H}}$ : 0.96 (3H, t), 1.02 (3H, d), 1.12 (3H, s), 1.26-4.42 (15H, m), 1.47 (2H, quint), 1.57 (2H, quint), 1.60-1.66 (2H, m), 1.76-1.94 (6H, m), 3.23 (2H, s), 3.42 (2H, t), 4.01 (2H, t), 4.20 (2H, m), 7.00 (2H, d), 7.10-7.15 (2H, m), 7.59 (2H, d), 7.70 (2H, d), 8.04 (1H, t), 8.21 (2H, d);  $\nu_{\text{max}}$  (KBr disc)/cm<sup>-1</sup> 691, 724, 768, 829, 895, 1061, 1130, 1191, 1251, 1280, 1434, 1501, 1610, 1710, 1737, 2860, 2936; *m/z* 674 (M<sup>+</sup>), 421, 350, 196 (100%), 139, 97.

***(S)-(+)-4-(2-Methylbutyloxycarbonyl)-2-fluorophenyl 4'-[11-(3-methylcyclobutan-1-ylmethoxy)undecyloxy]biphenyl-4-carboxylate (2.6)***

The experimental procedure followed was the same as for the preparation of **1.1**. The following quantities were used: Compound **13b** 0.90 g, 1.93 mmol; compound **4c** 0.44 g, 1.93 mmol; *N,N'*-dicyclohexylcarbodiimide 0.40 g, 1.93 mmol; 4-(dimethylamino)pyridine 0.10 g, 0.10 mmol; dichloromethane 100 ml. Yield 0.99 g (76%),  $[\alpha]_D^{24} = +2.1^\circ$ ,  $\text{CHCl}_3$ , c. 0.00573 g ml<sup>-1</sup>. Elemental analysis for C<sub>42</sub>H<sub>55</sub>F<sub>1</sub>O<sub>6</sub>: calculated C 74.75%; H 8.21%; found C 74.70%; H 8.46%.



Table 1

$\delta_{\text{H}}$ : 0.97 (3H, t), 1.02 (3H, d), 1.10 (3H, s), 1.26-1.42 (15H, m), 1.46 (2H, quint), 1.51-1.58 (2H, m), 1.60-1.66 (2H, m), 1.76-1.94 (6H, m), 3.21 (2H, s), 3.40 (2H, t), 4.02 (2H, t), 4.18 (2H, m), 7.01 (2H, d), 7.40 (1H, t), 7.63 (2H, d), 7.74 (2H, d), 7.88-7.93 (2H, m), 8.23 (2H, d);  $\nu_{\text{max}}$  (film)/ $\text{cm}^{-1}$  721, 763, 830, 1062, 1114, 1187, 1262, 1295, 1473, 1509, 1605, 1723, 1753, 2857, 2925;  $m/z$  674 ( $\text{M}^+$ ), 421, 367, 214, 197, 83, 55 (100%).

**(S)-(+)-4-(2-Methylbutyloxycarbonyl)phenyl 4'-[10-(3-methyloxetan-3-ylmethoxy)decyloxy]biphenyl-4-carboxylate (3.1)**

The experimental procedure followed was the same as for the preparation of **1.1**. The following quantities were used: Compound **14a** 1.40 g, 3.10 mmol; compound **4a** 0.64 g, 3.10 mmol; *N,N'*-dicyclohexylcarbodiimide 0.64 g, 3.10 mmol; 4-(dimethylamino)pyridine 0.10 g, 0.10 mmol; dichloromethane 50 ml. Yield 1.35 g (68%),  $[\alpha]_{\text{D}}^{24} = +2.2^\circ$ ,  $\text{CHCl}_3$ , c. 0.02719 g  $\text{ml}^{-1}$ . Elemental analysis for  $\text{C}_{40}\text{H}_{52}\text{O}_7$ : calculated C 74.50%; H 8.13%; found C 74.73%; H 8.03%.

$\delta_{\text{H}}$ : 0.98 (3H, t), 1.05 (3H, d), 1.27-1.40 (13H, m), 1.44-1.61 (6H, m), 1.82 (2H, quint), 1.87 (1H, oct), 3.47 (2H, s), 3.48 (2H, t), 4.03 (2H, t), 4.19 (2H, m), 4.35 (2H, d), 4.51 (2H, d), 7.00 (2H, d), 7.32 (2H, d), 7.60 (2H, d), 7.70 (2H, d), 8.14 (2H, d), 8.24 (2H, d);  $\nu_{\text{max}}$  (film)/ $\text{cm}^{-1}$  760, 830, 980, 1010, 1060, 1110, 1160, 1190, 1270, 1460, 1500, 1600, 1710, 1730, 2850, 2920;  $m/z$  644 ( $\text{M}^+$ ), 437, 335, 197 (100%), 121, 43.

***(S)-(+)-4-(2-Methylbutyloxycarbonyl)-3-fluorophenyl 4'-[10-(3-methyloxetan-3-ylmethoxy)decyloxy]biphenyl-4-carboxylate (3.2)***

The experimental procedure followed was the same as for the preparation of **1.1**. The following quantities were used: Compound **14a** 1.37 g, 3.00 mmol; compound **4b** 0.68 g, 3.00 mmol; *N,N'*-dicyclohexylcarbodiimide 0.62 g, 3.00 mmol; 4-(dimethylamino)pyridine 0.10 g, 0.10 mmol; dichloromethane 50 ml. Yield 1.60 g (80%),  $[\alpha]_D^{24} = +2.0^\circ$ ,  $\text{CHCl}_3$ , c. 0.04240 g ml<sup>-1</sup>. Elemental analysis for C<sub>40</sub>H<sub>51</sub>F<sub>1</sub>O<sub>7</sub>: calculated C 72.48%; H 7.76%; found C 73.03%; H 7.93%.

$\delta_{\text{H}}$ : 0.96 (3H, t), 1.02 (3H, d), 1.26-1.36 (14H, m), 1.44-1.52 (2H, m), 1.54-1.62 (3H, m), 1.81 (3H, quint and oct), 3.46 (2H, t), 3.47 (2H, s), 4.01 (2H, t), 4.20 (2H, m), 4.36 (2H, d), 4.51 (2H, d), 7.01 (2H, d), 7.10-7.15 (2H, m), 7.60 (2H, d), 7.70 (2H, d), 8.05 (1H, t), 8.21 (2H, d);  $\nu_{\text{max}}$  (film)/cm<sup>-1</sup> 700, 730, 770, 830, 900, 980, 1020, 1060, 1130, 1190, 1255, 1280, 1300, 1435, 1500, 1530, 1605, 1710, 1730, 2860, 2930; *m/z* 662 (M<sup>+</sup>), 437, 335, 196, 139, 55 (100%).

***(S)-(+)-4-(2-Methylbutyloxycarbonyl)-2-fluorophenyl 4'-[10-(3-methyloxetan-3-ylmethoxy)decyloxy]biphenyl-4-carboxylate (3.3)***

The experimental procedure followed was the same as for the preparation of **1.1**. The following quantities were used: Compound **14a** 1.37 g, 3.00 mmol; compound **4c** 0.68 g, 3.00 mmol; *N,N'*-dicyclohexylcarbodiimide 0.62 g, 3.00 mmol; 4-(dimethylamino)pyridine 0.10 g, 0.10 mmol; dichloromethane 50 ml. Yield 1.25 g (63%),  $[\alpha]_D^{25} = +1.0^\circ$ ,  $\text{CHCl}_3$ , c. 0.01227 g ml<sup>-1</sup>. Elemental analysis for C<sub>40</sub>H<sub>51</sub>F<sub>1</sub>O<sub>7</sub>: calculated C 72.48%; H 7.76%; found C 72.75%; H 7.79%.

Table 1

$\delta_{\text{H}}$ : 0.97 (3H, t), 1.02 (3H, d), 1.27 (3H, s), 1.26-1.42 (10H, m), 1.45-1.62 (6H, m), 1.80 (2H, sext), 1.87 (1H, oct), 3.43 (2H, s), 3.45 (2H, t), 4.02 (2H, t), 4.18 (2H, m), 4.28 (2H, d), 4.45 (2H, d), 7.01 (2H, d), 7.40 (1H, t), 7.63 (2H, d), 7.75 (2H, d), 7.87-7.94 (2H, m), 8.23 (2H, d);  $\nu_{\text{max}}$  (film)/ $\text{cm}^{-1}$  760, 830, 890, 980, 1015, 1060, 1110, 1180, 1260, 1300, 1430, 1460, 1510, 1600, 1720, 1750, 2860, 2930;  $m/z$  662 ( $\text{M}^+$ ), 438 (100%), 335, 197, 139, 83.

***(S)-(+)-4-(2-Methylbutyloxycarbonyl)phenyl 4'-[11-(3-methyloxetan-3-ylmethoxy)undecyloxy]biphenyl-4-carboxylate (3.4)***

The experimental procedure followed was the same as for the preparation of **1.1**. The following quantities were used: Compound **14b** 1.64 g, 3.50 mmol; compound **4a** 0.73 g, 3.50 mmol; *N,N'*-dicyclohexylcarbodiimide 0.72 g, 3.50 mmol; 4-(dimethylamino)pyridine 0.10 g, 0.10 mmol; dichloromethane 50 ml. Yield 1.28 g (56%),  $[\alpha]_{\text{D}}^{25} = +6.7^\circ$ ,  $\text{CHCl}_3$ , c. 0.00893 g  $\text{ml}^{-1}$ . Elemental analysis for  $\text{C}_{41}\text{H}_{54}\text{O}_7$ : calculated C 74.74%; H 8.26%; found C 74.53%; H 8.35%.

$\delta_{\text{H}}$ : 0.97 (3H, t), 1.02 (3H, d), 1.25-1.40 (15H, m), 1.42-1.61 (6H, m), 1.74-1.94 (3H, m), 3.47 (2H, t), 3.48 (2H, s), 4.01 (2H, t), 4.19 (2H, m), 4.37 (2H, d), 4.51 (2H, d), 7.00 (2H, d), 7.31 (2H, d), 7.59 (2H, d), 7.69 (2H, d), 8.13 (2H, d), 8.24 (2H, d);  $\nu_{\text{max}}$  (film)/ $\text{cm}^{-1}$  830, 1010, 1070, 1110, 1160, 1195, 1260, 1490, 1525, 1595, 1710, 1730, 2850, 2920;  $m/z$  658 ( $\text{M}^+$ ), 451, 196, 138, 121 (100%), 93.

***(S)-(+)-4-(2-Methylbutyloxycarbonyl)-3-fluorophenyl 4'-[11-(3-methyloxetan-3-ylmethoxy)undecyloxy]biphenyl-4-carboxylate (3.5)***

The experimental procedure followed was the same as for the preparation of **1.1**. The following quantities were used: Compound **14b** 1.39 g, 3.00 mmol; compound **4b**

Table 1

0.67 g, 3.00 mmol; *N,N'*-dicyclohexylcarbodiimide 0.61 g, 3.00 mmol; 4-(dimethylamino)pyridine 0.10 g, 0.10 mmol; dichloromethane 50 ml. Yield 1.41 g (70%),  $[\alpha]_D^{24} = +3.3^\circ$ ,  $\text{CHCl}_3$ , c. 0.02183 g ml<sup>-1</sup>. Elemental analysis for C<sub>41</sub>H<sub>53</sub>F<sub>1</sub>O<sub>7</sub>: calculated C 72.75%; H 7.89%; found C 72.51%; H 8.13%.

$\delta_{\text{H}}$ : 0.96 (3H, t), 1.03 (3H, d), 1.24-1.40 (19H, m), 1.44-1.62 (2H, m), 1.80 (2H, quint), 1.85 (1H, oct), 3.46 (2H, t), 3.48 (2H, s), 4.02 (2H, t), 4.20 (2H, m), 4.36 (2H, d), 4.51 (2H, d), 7.00 (2H, d), 7.08-7.15 (2H, m), 7.60 (2H, d), 7.70 (2H, d), 8.03 (1H, t), 8.22 (2H, d);  $\nu_{\text{max}}$  (film)/cm<sup>-1</sup> 700, 725, 770, 830, 900, 1020, 1060, 1130, 1190, 1250, 1280, 1435, 1500, 1610, 1710, 1730, 2860, 2930;  $m/z$  676 (M<sup>+</sup>), 451, 367, 196, 139, 55 (100%).

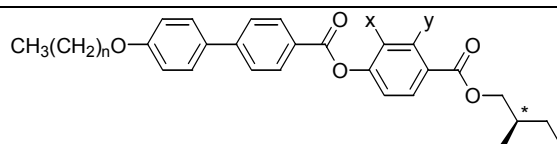
***(S)-(+)-4-(2-Methylbutyloxycarbonyl)-2-fluorophenyl 4'-[11-(3-methyloxetan-3-ylmethoxy)undecyloxy]biphenyl-4-carboxylate (3.6)***

The experimental procedure followed was the same as for the preparation of **1.1**. The following quantities were used: Compound **14b** 1.16 g, 3.00 mmol; compound **4c** 0.67 g, 3.00 mmol; *N,N'*-dicyclohexylcarbodiimide 0.61 g, 3.00 mmol; 4-(dimethylamino)pyridine 0.10 g, 0.10 mmol; dichloromethane 50 ml. Yield 1.30 g (65%),  $[\alpha]_D^{25} = +1.7^\circ$ ,  $\text{CHCl}_3$ , c. 0.01431 g ml<sup>-1</sup>. Elemental analysis for C<sub>41</sub>H<sub>53</sub>F<sub>1</sub>O<sub>7</sub>: calculated C 72.75%; H 7.89%; found C 72.50%; H 7.91%.

$\delta_{\text{H}}$ : 0.96 (3H, t), 1.01 (3H, d), 1.27 (3H, s), 1.26-1.42 (12H, m), 1.43-1.61 (6H, m), 1.80 (2H, quint), 1.86 (1H, oct), 3.43 (2H, s), 3.44 (2H, t), 4.02 (2H, t), 4.17 (2H, m), 4.27 (2H, d), 4.44 (2H, d), 7.00 (2H, d), 7.39 (1H, t), 7.63 (2H, d), 7.74 (2H, d), 7.87-7.94 (2H, m), 8.23 (2H, d);  $\nu_{\text{max}}$  (film)/cm<sup>-1</sup> 760, 830, 900, 1010, 1060, 1110, 1190,

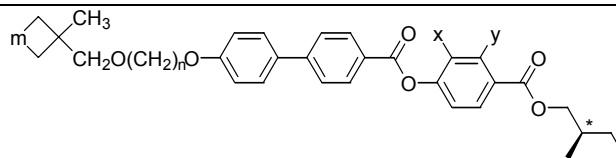
Table 1

1260, 1300, 1430, 1470, 1510, 1600, 1720, 1750, 2860, 2920;  $m/z$  676 ( $M^+$ ), 451, 367,  
349, 197, 156, 139 (100%).



Compound Number	n	x	y	Mp <sup>a</sup> (°C) ( $\Delta H_{\text{transition}}/\text{J g}^{-1}$ )	Transition Temperatures (°C)					
					Iso liq.	SmA*	SmC*	Recryst <sup>a</sup>		
<b>1.1</b>	14	H	H	82.2 (85.3)	•	168.2 (11.5)	•	127.4 (0.1)	•	53.2 (68.8)
<b>1.2</b>	14	H	F	60.7 (81.0)	•	165.8 (11.1)	•	123.7 (0.1)	•	44.0 (67.6)
<b>1.3</b>	14	F	H	72.7 (72.5)	•	139.3 (10.0)	•	99.9 (0.1)	•	47.4 (50.2)
<b>1.4</b>	15	H	H	73.7 (88.8)	•	167.3 (11.4)	•	127.6 (0.1)	•	55.8 (69.5)
<b>1.5</b>	15	H	F	53.1 (83.0)	•	164.8 (11.5)	•	122.5 (0.1)	•	45.4 (69.8)
<b>1.6</b>	15	F	H	71.0 (51.0)	•	138.5 (9.5)	•	98.1 (<0.1)	•	48.2 (66.4)

<sup>a</sup> The melting point and recrystallisation temperature were determined by DSC.



Compound Number	m	n	x	y	Mp <sup>a</sup> (°C) ( $\Delta H_{\text{transition}}/\text{J g}^{-1}$ )	Transition temperatures (°C)					Recryst <sup>a</sup>				
						Iso Liq.	BP		SmA*	SmC*		SmC <sub>A</sub> *			
<b>2.1</b>	CH <sub>2</sub>	10	H	H	32.4 (31.6)	•	146.7 (8.8)	—	—	•	125.7 (0.4)	•	—	—	-9.4 (3.7)
<b>2.2</b>	CH <sub>2</sub>	10	H	F	41.8 (24.6)	•	147.6 (8.9)	—	—	•	123.9 (0.4)	•	—	—	-19.6 (2.5)
<b>2.3</b>	CH <sub>2</sub>	10	F	H	36.1 (36.6)	•	115.7 (7.4)	—	—	•	101.5 (0.4)	•	—	—	-6.2 (7.9)
<b>2.4</b>	CH <sub>2</sub>	11	H	H	59.4 (46.8)	•	146.8 (9.3)	—	—	•	124.0 (0.4)	•	88.9 (<0.05)	•	10.6 (19.9)
<b>2.5</b>	CH <sub>2</sub>	11	H	F	38.2 (35.8)	•	145.7 (9.7)	—	—	•	119.3 (0.4)	•	89.8 (<0.05)	•	-11.9 (7.2)
<b>2.6</b>	CH <sub>2</sub>	11	F	H	68.1 (47.8)	•	117.1 (7.3)	—	—	•	101.2 (0.3)	•	—	—	32.8 (33.9)
<b>3.1</b>	O	10	H	H	-5.6 (4.1)	•	135.3 (4.4)	—	—	•	101.3 (0.1)	•	—	—	-14.0 (3.7)
<b>3.2</b>	O	10	H	F	-20.1 (2.9)	•	143.7 (6.6)	—	—	•	98.9 (0.2)	•	—	—	-21.4 (2.0)
<b>3.3</b>	O	10	F	H	31.3 (13.1)	•	111.2 <sup>b</sup> (1.5)	•	108.0 <sup>b</sup> (1.5)	•	54.7 (<0.1)	•	—	—	<-70
<b>3.4</b>	O	11	H	H	52.0 (46.8)	•	130.5 (7.2)	—	—	•	104.5 (0.1)	•	70.0 (<0.05)	•	3.9 (13.7)
<b>3.5</b>	O	11	H	F	32.4	•	124.9	—	—	•	112.3	•	65.0	•	-10.0

					(20.7)		(6.1)		(0.2)		(0.1)		(6.5)
<b>3.6</b>	O	11	F	H	73.4	•	102.6	—	—	•	74.8	•	14.2
					(30.6)		(6.3)				(0.2)		(3.1)

<sup>a</sup> The melting point and recrystallisation temperature were determined by DSC. <sup>b</sup> The enthalpy values are combined due to overlapping peaks on the DSC.