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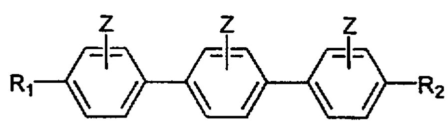
None

(58) Field of Search
Online: CAS ONLINE

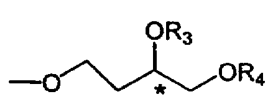
(54) Abstract Title
Liquid crystalline optionally laterally fluorinated terphenyl with chiral 3,4-di[(un)saturated-alkoxy]butoxy or 1,4-di[(un)saturated-alkoxy]but-2-oxyterminus

(57) The invention relates to terphenyl compounds having the general formula [1]:-

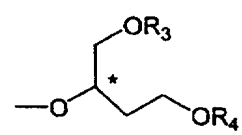


[1]

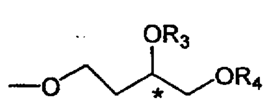
where each of R_1 and R_2 is the same or different and is selected from the group consisting of:- alkyl, alkyloxy, alkylthio, alkenyl, alkenyloxy, alkenylthio, alkynyl, alkynyloxy, alkynylthio,



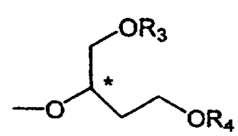
and



where * indicates an asymmetric carbon atom,
provided that at least one of R_1 and R_2 is



or



and where each of R_3 and R_4 is the same or different and is an alkyl, alkenyl or alkynyl group; and Z is independently selected from hydrogen and fluorine at each of the four lateral terphenyl carbons in each ring. The compounds are suitable for use in liquid crystal compositions.

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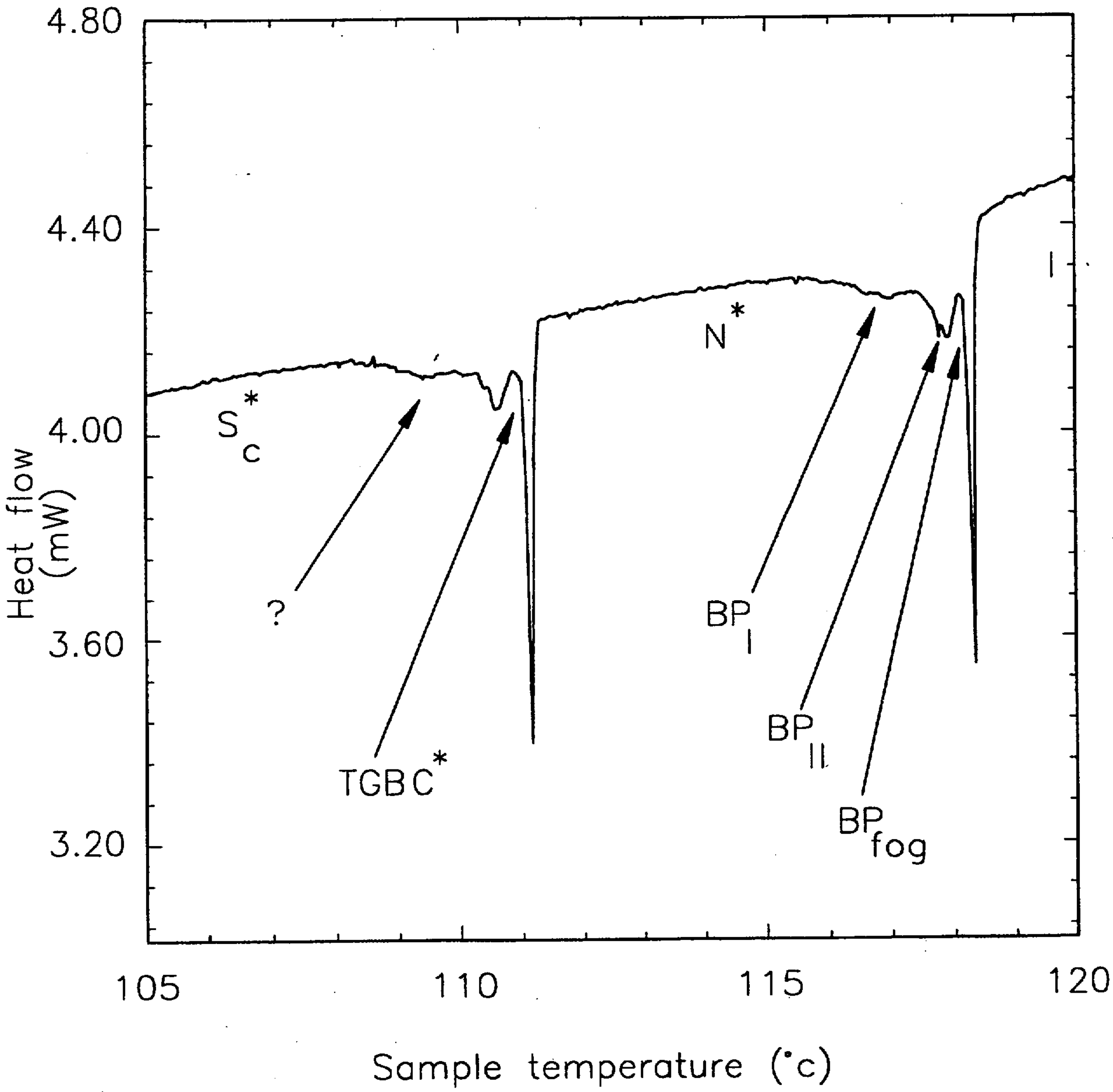
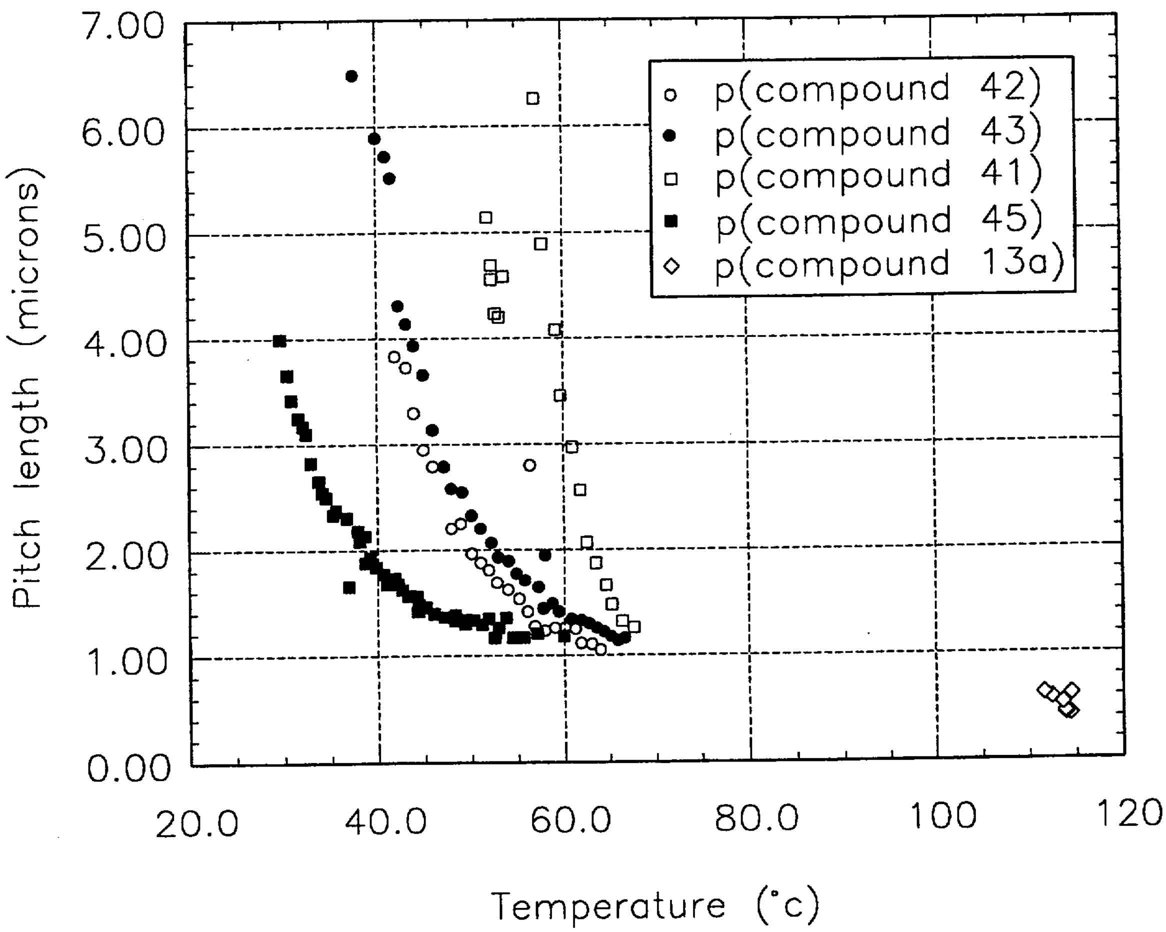
At least one drawing originally filed was informal and the print reproduced here is taken from a later filed formal copy.



Cooling DSC Scan at 1°C min^{-1}
of compound 13a showing phase detail

FIG 1



Pitch length–temperature dependence of chiral nematic phases

FIG 2

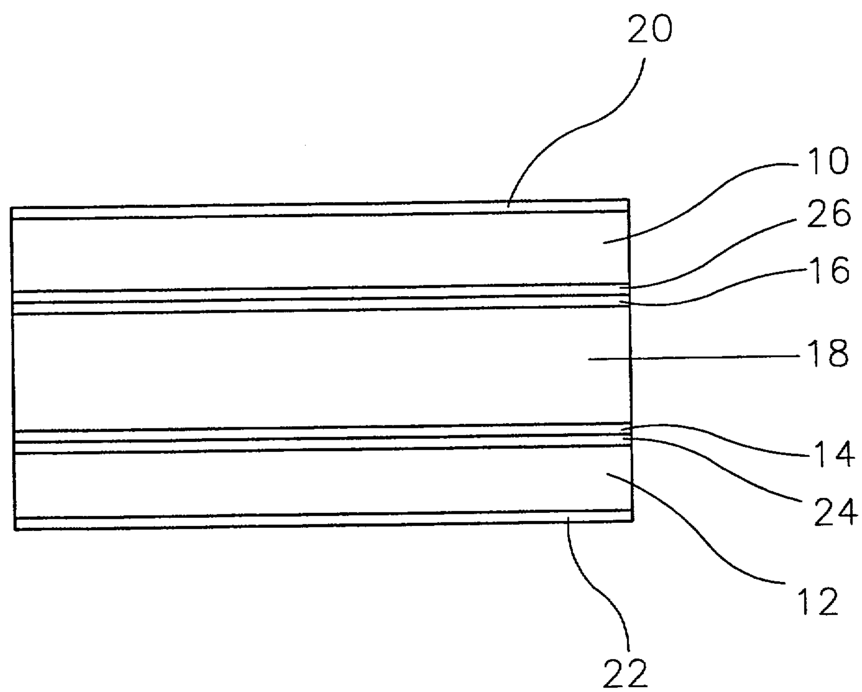


FIG 3

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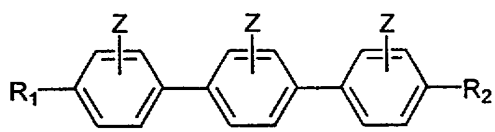
NOVEL TERPHENYL COMPOUNDS

This invention relates to novel terphenyl compounds and is more particularly concerned with novel terphenyl compounds which have useful chiral liquid crystalline properties.

Terphenyls and latterly fluoro-substituted terphenyls are known to be effective smectic C materials and are therefore useful components in ferroelectric liquid crystal mixtures.

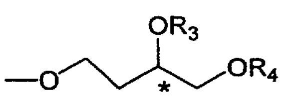
It is an object of the present invention to provide novel terphenyl compounds which preferably have useful chiral liquid crystalline properties.

According to the present invention there is provided a terphenyl compound having the general formula [1]:-

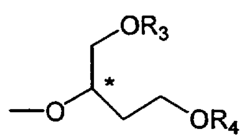


[1]

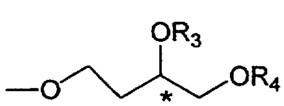
where each of R_1 and R_2 is the same or different and is selected from the group consisting of:- alkyl, alkyloxy, alkenyl, alkenyloxy, alkynyl, alkynyloxy, alkylthio, alkenylthio and alkynylthio



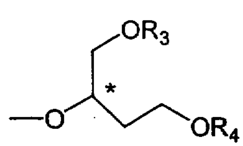
and



where * indicates an asymmetric carbon atom,
provided that at least one of R_1 and R_2 is



or

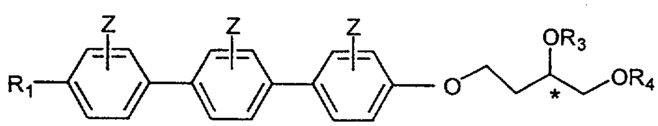


and where each of R_3 and R_4 is the same or different and is an alkyl, alkenyl or alkynyl group; and Z is independently selected from hydrogen and fluorine at each terphenyl carbon.

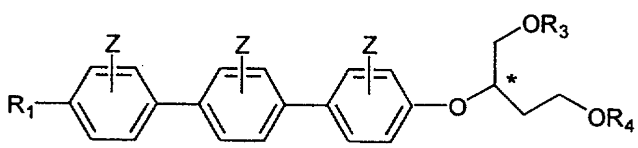
The group represented by R_1 or R_2 may be a C_1- to C_{16}-alkyl or alkyloxy group or a C_2- to C_{16}-alkenyl, alkynyl, alkenyloxy or alkynyloxy group, preferably a C_1- to C_{16} n-alkyl group, more preferably a C_7- to C_{12} n-alkyl group.

The group represented by R_3 or R_4 may be a C_1- to C_{16}-alkyl group or a C_2- to C_{16}-alkenyl or alkynyl group, and is preferably a C_1- to C_{16} n-alkyl group, more preferably a C_1- to C_5 n-alkyl group.

Preferably, said compound has the general formula [2] or the general formula [3]:-



[2]

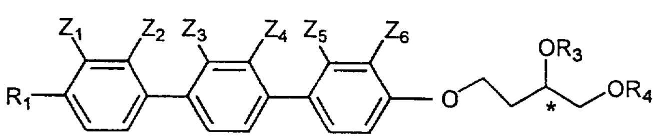


[3]

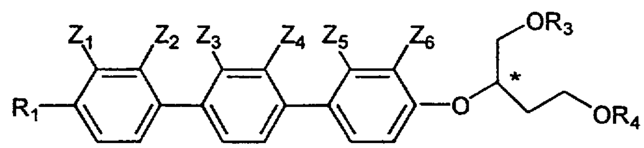
wherein R_1, R_3, R_4 and Z are as defined above.

It will be understood that each of the three aromatic rings of the terphenyl moiety may be independently unsubstituted, mono-, di-, tri- or tetra-fluoro substituted. Preferably, each of the three aromatic rings is independently mono-fluoro substituted or unsubstituted.

Preferably, the compound has the general formula [4] or the general formula [5]:-



[4]



[5]

wherein R_1, R_3 and R_4 are as defined above, and
one of Z_1 to Z_6 is F, the remaining Z_1 to Z_6 being H.

In particularly preferred examples of the compound, R_1 is n-octyl and R_3 and R_4 are independently selected from methyl and n-pentyl.

According to a second aspect of the present invention, there is provided a liquid crystal composition containing a compound according to said first aspect of the present invention.

According to a third aspect of the present invention, there is provided an electro-optical liquid crystal device including a liquid crystal cell have a layer of a liquid crystal composition according to said second aspect of the present invention, and means for applying an electrical field across said layer.

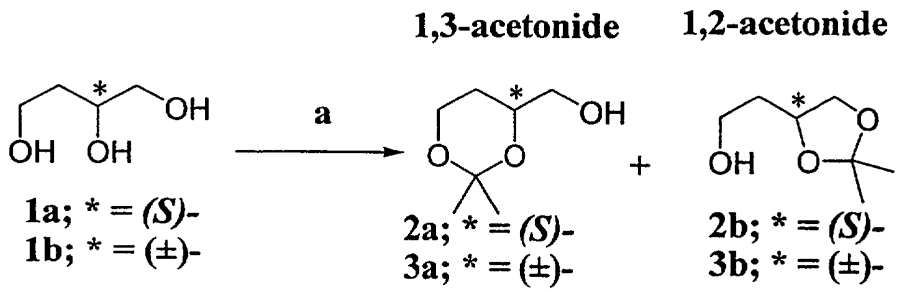
Examples

***(S)*-1,2,4-butanetriol as starting material**

Successful manipulation of the triols **1a** and **b** involves the use of a suitable protection (and deprotection) step which masks two of the hydroxy groups and thereby allows selective reaction of the remaining unprotected hydroxy moiety. This may be achieved using the acetonide (or isopropylidene ketal) protection group, although this leads to the possibility of two isomeric acetonides being formed, namely the 1,2- (5-membered ring) or 1,3- (6-membered ring), as is shown in **scheme 1.** It is normally the case that the 1,2- acetonide is favoured over the 1,3-acetonide (kinetic and thermodynamic control). Treatment by a known method (H. Hayashi et. al., **J. Am. Chem. Soc.**, 1973, **95**, 8749) of *(S)*-1,2,4-butanetriol (**1a**) with anhydrous acetone in the presence of p-toluene sulphonic acid (p-TSA) gave a mixture of the 1,2- (**2b**) and 1,3-acetonide (**2a**) in good yield (73%). Analysis by ^{1}H NMR revealed a ratio of 96:4 of (**2b**) to

(**2a**) by integration of the $(CH_3)_2C$ signals. A similar result was obtained for the racemate (**3a** and **b**). The presence of the 1,3-acetonide proved to be no hindrance as it was easily removed by recrystallisation or column chromatography of later derivatives. Isolation of pure *(S)*-1,2-isopropylidene-1,2,4-butanetriol was not necessary.

Scheme 1: Manipulation of *(S)*- or *(±)*-1,2,4-butanetriol (1a and 1b)



a. Anhydrous acetone, p-TSA, 1.5 hr, RT.

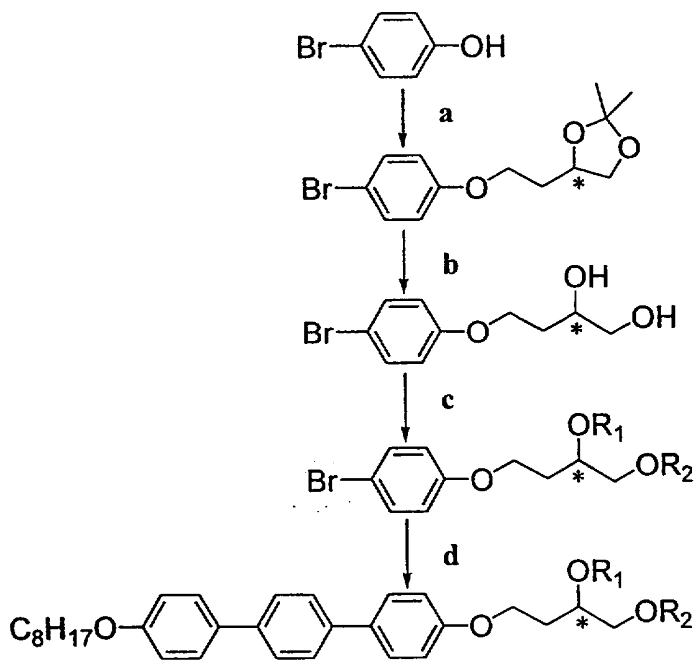
A. 1,*(S)*-2-(4''-Octyloxyterphenyl-4-oxy)dialkoxy-butanes (Examples 1 to 3)

Summary

The route employed is outlined in **scheme 2.** Here 4-bromophenol (**4**) was alkylated with acetonide **2a/b** or **3a/b** using the Mitsunobu reaction (O. Mitsunobu, **Synthesis**, 1981, 1) to give compound **5a** or **b** in 74 % yield (purification by flash chromatography removed all trace of the six membered ring side product). Deprotection of **5a** or **b** using p-TSA in methanol at room temperature gave 4-bromo-1-(1,2-dihydroxybutoxy)benzenes **6a** or **b** in 87 % yield. Compound **6a or b** was then alkylated with methyl iodide or 1-bromopentane and excess sodium hydride (D.M. Walba et. al., **J. Am. Chem. Soc.**, 1986, **108**, 5211) to give compounds **7**, **8a**, **8b**, **9** and **10** in yields of between 62-88%. Compound **10** was synthesised from the monopentylated side product (**9**) of the reaction of compounds **6a** to **8a** (showing the greater reactivity of the 1° alcohol site over the 2° alcohol). The final step involved the Suzuki coupling of compounds **7**, **8a, 8b** and **10** with 4-(4-octyloxyphenyl)phenylboronic acid (**11**) using palladium(0) *tetrakis*(triphenylphosphine) catalyst, 2M sodium carbonate and 1,2-dimethoxyethane (R.B. Miller et. al., **Organometallics**, 1984, **3**, 1261; M. Hird et. al., **Mol. Cryst. Liq. Cryst.**, 1991, 206, 187; L.K.M. Chan et. al., **Mol.Cryst. Liq. Cryst.**, 1985, **123**, 185; L.K.M. Chan et. al.,

Mol. Cryst. Liq. Cryst., 1987, **150B**, 335 and **Mol. Cryst. Liq. Cryst.**, 1988, **158B**, 209). Compounds **12 (Example 1)**, **13a (Example 2)**, **13b** and **14 (Example 3)** were obtained in 20 - 55 % yields after rigorous flash chromatography and repeated recrystallisation.

Scheme 2 : Route to 1,*(S)*-2-(4"-Octyloxyterphenyl-4-oxy)dialkoxybutanes (12, 13 and 14)



4

5a..* = ***(S)*-;**
5b..* = ***(±)*-.**

6a..* = ***(S)*-;**
6b..* = ***(±)*-.**

7..* = ***(S)*-, $R_1 = CH_3$ & $R_2 = CH_3$;**
8a..* = ***(S)*-, R_1 & $R_2 = C_5H_{11}$;**
8b..* = ***(±)*-, R_1 & $R_2 = C_5H_{11}$;**
9..* = ***(S)*-, $R_1 = OH$ & $R_2 = C_5H_{11}$;**
10..* = ***(S)*-, $R_1 = CH_3$ & $R_2 = C_5H_{11}$;**

12..* = ***(S)*-, $R_1 = CH_3$ & $R_2 = CH_3$;**
13a..* = ***(S)*-, R_1 & $R_2 = C_5H_{11}$;**
13b..* = ***(±)*-, R_1 & $R_2 = C_5H_{11}$;**
14..* = ***(S)*-, $R_1 = CH_3$ & $R_2 = C_5H_{11}$.**

a..compound **2a/b** or **3a/b**, DEAD, TPP, THF, N_2, RT;
b.. p-TSA, MeOH, RT.
c..(i) NaH, DMF, (ii) RBr, DMF, N_2, RT.
d..4-(4-Octyloxyphenyl)phenylboronic acid (**11**), $Pd(PPh_3)_4$, Na_2CO_3,1,2-dimethoxyethane, reflux, N_2.

Experimental details

The structures and purities of all intermediates and final products were confirmed by a combination of NMR spectroscopy (^1H, ^{13}C, ^{13}C DEPT, ^{19}F NMR, 2D COSY, CHCORR), FT-IR spectroscopy (ATR or DRIFT sampling), UV-Vis spectroscopy (5-10 mg of sample is dissolved in 50 cm^3 of solvent (e.g. $CHCl_3$), a 1 ml aliquot is then removed and made up to 10 ml), gas chromatography and high performance liquid chromatography. The transition temperatures and associated enthalpies were determined using a combination of optical microscopy and differential scanning calorimetry.

(S)-1,2,4-Butanetriol **(1a)** ^{1}H NMR (300MHz; acetone, TMS) δ: 1.66 (2H,m, C$\underline{H}_2$CH$_2$OH), 3.47 (2H,m, diastereotopic protons), 3.72 (2H,m, C$\underline{H}_2$OH), 3.80 (1H,m, C*$\underline{H}$), 4.12 (3H,m, O$\underline{H}$); ^{13}C NMR (75MHz; acetone, TMS) δ: 36.92 ($\underline{C}$H$_2$CH$_2$OH, -ve DEPT), 59.95 ($\underline{C}$H$_2$OH, -ve DEPT), 67.34 ($\underline{C}$H$_2$C*H, -ve DEPT), 70.96 ($\underline{C}$*H, +ve DEPT); GC analysis (det 300°C, inj 280 °C, oven 80 °C 5 min 10 °C/min to 280 °C hold 1 min): 98.94% (R_T = 10.90 min).

(S)-1,2-Isopropylidene-1,2,4-butanetriol **(2a/b)** *(S)*-1,2,4-Butanetriol (1) (9.02 g, 85.1 mmol) was stirred in acetone (500 ml) with *p*-toluenesulfonic acid (400 mg) for 1½ hours at room temperature. Sodium bicarbonate was added to the mixture and stirred for a further 10 minutes. Acetone was removed by evaporation under reduced pressure. Ethyl acetate (100 ml) was added to the residue, and then the mixture was washed with aqueous sodium bicarbonate (50 ml) and aqueous sodium chloride (50 ml). The mixture was then dried with anhydrous magnesium sulphate, filtered and the solvent removed by evaporation. Kugelrohr distillation (90 °C, 1 mbar) yielded a colourless liquid. Yield = 6.84 g (55%); ^{1}H NMR (300MHz; CDCl$_3$, TMS) δ: 1.37 (3H,s, C$\underline{H}_3$), 1.43 (3H,s, C$\underline{H}_3$), 1.83 (2H,q, C$\underline{H}_2$CH$_2$OH), 2.68 (1H,br t, O$\underline{H}$), 3.60 (1H,pseudo t, diastereotopic proton), 3.80 (2H,q, C$\underline{H}_2$OH), 4.09 (1H,dd, diastereotopic proton), 4.27 (1H,quintet, C*$\underline{H}$) Analysis of peak heights from ^{1}H NMR showed that the product contained 96% (S)-1,2-isopropylidene-1,2,4-butanetriol and 4% *(S)*-2,4-isopropylidene-1,2,4-butanetriol; ^{13}C NMR (75MHz; CDCl$_3$, TMS) δ: 25.69 ($\underline{C}$H$_3$, +ve DEPT), 26.89 ($\underline{C}$H$_3$, +ve DEPT), 35.65 ($\underline{C}$H$_2$CH$_2$OH, -ve DEPT), 60.48 ($\underline{C}$H$_2$C*H, -ve DEPT), 69.46 ($\underline{C}$H$_2$OH, -ve DEPT), 75.03 ($\underline{C}$*H, +ve DEPT), 109.08 ($\underline{C}$(CH$_3$)$_2$, no DEPT); FT-IR (film; ATR/ZnSe) ν_{max}: 3417, 2992, 2939, 2873, 1381, 1209, 1156, 1050, 871cm^{-1}.

(±)-1,2-Isopropylidene-1,2,4-butanetriol (3a/b) Was obtained in exactly the same way as **2a/b** using (±)-1,2,4-butanetriol **1b** as starting material. Yield = 9.08 g (73%); ^{1}H NMR (300MHz; CDCl$_3$, TMS) δ: 1.36 (3H,s, C$\underline{H}_3$), 1.42 (3H,s, C$\underline{H}_3$), 1.81 (2H,q, C$\underline{H}_2$CH$_2$OH), 2.94 (1H,br t, O$\underline{H}$), 3.59 (1H,pseudo t, diastereotopic proton), 3.76 (2H,q, C$\underline{H}_2$OH), 4.09 (1H,dd, diastereotopic proton), 4.26 (1H,quintet, C$\underline{H}$) Analysis of peak heights from ^{1}H NMR showed that the product contained 96% (±)-1,2-isopropylidene-1,2,4-butanetriol and 4% (±)-2,4-isopropylidene-1,2,4-butanetriol; FT-IR (film; ATR/ZnSe) ν_{max}: 3423, 2985, 2938, 2878, 1370, 1244, 1214, 1157, 1052, 854 cm^{-1}.

1-{(2,2-Dimethyl)-1,(S)-2-dioxolan-4-yl}ethoxy-4-bromobenzene **(5a)** Compound **2a/b** (9.07 g, 62.1 mmol), triphenylphoshine (10.83 g, 41.3 mmol) and dry tetrahydrofuran (100 ml) was added to a stirred mixture of 4-bromophenol (**4**) (7.16 g, 41.3 mmol), diethylazodicarboxylate (7.20 g, 41.3 mmol) and dry tetrahydrofuran (45 ml) at RT under dry nitrogen, stirred for 18 h, before being diluted with diethyl ether (150 ml) and then washed with brine (50 ml). The organic phase was dried ($MgSO_4$), filtered and evaporated to give a colourless oil. Purification by flash chromatography [fine mesh silica gel: 8% ethyl acetate in hexanes] gave a colourless oil. Yield = 9.27 g (74%); ^{1}H NMR (300MHz; $CDCl_3$, TMS) δ: 1.36 (3H,s. $C\underline{H}_3CH$), 1.42 (3H,s, $C\underline{H}_3CH$), 2.03 (2H,m, $OCH_2C\underline{H}_2CH$), 3.64 (1H,dd, $CHC\underline{H}_2O$), 4.05 (2H,m, $OC\underline{H}_2CH_2$), 4.11 (1H,dd, $CHC\underline{H}_2O$), 4.28 (1H,quint, $CH_2C^*\underline{H}CH_2$), 6.77 (2H,d, Ar-$\underline{H}_2$, $^3J_{HH}$ = 9.05 Hz), 7.36 (2H, d, Ar-$\underline{H}_3$, $^3J_{HH}$ = 7.36 Hz); ^{13}C NMR (75MHz; $CDCl_3$, TMS) δ: 25.70, 26.95 ($\underline{C}H_3CH$, +ve DEPT), 33.38 ($OCH_2\underline{C}H_2CH$, -ve DEPT), 64.85 ($O\underline{C}H_2CH_2CH$, -ve DEPT), 69.48 ($CH\underline{C}H_2O$, -ve DEPT), 73.27 ($\underline{C}^*HCH_2O$, +ve DEPT), 108.83 ($(CH_3)_2\underline{C}$, no DEPT), 112.87 (Ar-$\underline{C}_4$, no DEPT), 116.20 (Ar-$\underline{C}_2$, +ve DEPT), 132.22 (Ar-$\underline{C}_3$, +ve DEPT), 157.83 (Ar-$\underline{C}_1$, no DEPT); FT-IR (film; ATR/ZnSe) ν_{max}: 2986, 2939, 2873, 1488, 1472, 1369, 1240, 1171, 1064, 820 cm^{-1}. GC Analysis (inj 250 °C; det 300 °C; oven 80 °C hold 1 min, 30 °C/min to 280 °C hold 2 min) R_T = 7.21 (99.75 %) min.

1-{(2,2-Dimethyl)-1,(R,S)-2-dioxolan-4-yl}ethoxy-4-bromobenzene (5b) A similar procedure to that used for compound **5a** was used. Quantities used: compound **3a/b** (9.00 g, 61.6 mmol), triphenylphosphine (10.78 g, 41.4 mmol), 4-bromophenol (**4**) (7.11 g, 41.4 mmol), diethylazodicarboxylate (7.16 g, 41.4 mmol) and tetrahydrofuran (160 ml). Purification by flash chromatography [fine mesh silica gel: 8% ethyl acetate in hexane] gave a colourless oil which was dried *in vacuo* (P_2O_5, 0.5 mbar, RT, 16 h). Yield = 4.55 g (37%); ^{1}H NMR (300MHz, $CDCl_3$, TMS) δ: 1.36 (3H, s, $O_2CC\underline{H}_3$), 1.42 (3H, s, $O_2CC\underline{H}_3$), 2.03 (2H, dd, $ArOCH_2C\underline{H}_2{}^{(\pm)}CH$), 3.63 (1H, t, $^{(\pm)}CHC\underline{H}_2OC$), 4.03 (2H, m, $ArOC\underline{H}_2CH_2{}^{(\pm)}CH$), 4.11 (1H, dd, $^{(\pm)}CHC\underline{H}_2OC$), 4.28 (1H, q, $ArOCH_2CH_2{}^{(\pm)}C\underline{H}$), 6.76 (2H, dd, Ar$\underline{H}_2$/$\underline{H}_6$, $^3J_{HH}$ = 6.80 Hz), 7.35 (2H, dd, Ar$\underline{H}_3$/$\underline{H}_5$, $^3J_{HH}$ = 6.76 Hz). ^{13}C NMR (75MHz, $CDCl_3$, TMS) δ: 25.8 ($O_2C\underline{C}H_3$, +ve DEPT), 27.0 ($O_2C\underline{C}H_3$, +ve DEPT), 33.4 ($ArOCH_2\underline{C}H_2{}^{(\pm)}CH$, -ve DEPT), 64.9 ($ArO\underline{C}H_2CH_2{}^{(\pm)}CH$, -ve DEPT), 69.5 ($^{(\pm)}CH\underline{C}H_2OC$, -ve DEPT), 73.3 ($ArOCH_2CH_2{}^{(\pm)}\underline{C}H$, +ve DEPT), 108.8 ($O_2\underline{C}(CH_3)_2$, no DEPT), 112.9 (Ar-$\underline{C}_4$, no DEPT), 116.3 (Ar-$\underline{C}_2$/$\underline{C}_6$, no DEPT), 132.3 (Ar-$\underline{C}_3$/$\underline{C}_5$, no DEPT), 157.8 (Ar-$\underline{C}_1$, no DEPT). FT/IR (film/ATR/ZnSe) μ_{max}: 2984, 2933, 2877, 1488, 1472, 1369, 1285, 1240, 1171, 1158, 1059, 1002, 820 cm^{-1}.

4-Bromo-1-(1,(S)-2-dihydroxybutoxy)benzene (6a) p-Toluenesulfonic acid (500 mg) was added to a stirred solution of compound **5a** (9.16 g, 30.4 mmol) in methanol (460 ml) and left to stir for 18 h at room temperature. The reaction was quenched by addition of sodium bicarbonate (3.00 g) and stirred for a further 10 mins. The methanol was removed by evaporation under reduced pressure and the residue redissolved in ethyl acetate (200 ml). The organic solution was then washed with water (50 ml), dried ($MgSO_4$), filtered and evaporated to give a colourless solid, recrystallised (ethanol) and dried *in vacuo* (P_2O_5, 20 mbar, 50 °C, 18 h). Yield = 6.88 g (87 %). ^{1}H NMR (300MHz; $CDCl_3$, TMS) *δ*: 1.92 (2H,m, $OCH_2C\underline{H_2}CH$), 2.47 (1H,s broad, $CHCH_2O\underline{H}$), 2.88 (1H,s broad, $CH_2CH(O\underline{H})CH_2$), 3.53 (1H,dd, $CHC\underline{H_2}OH$, J = 11.15 and 7.10 Hz), 3.71 (1H,dd, $CHC\underline{H_2}OH$, J = 11.15 and 2,72 Hz), 3.99 (1H,m $CH_2C^*\underline{H}CH_2$), 4.09 (2H,m, $OC\underline{H_2}CH_2CH$), 6.78 (2H,d, Ar-$\underline{H_2}$, $^3J_{HH}$ = 9.05 Hz), 7.37 (2H,d, Ar-$\underline{H_3}$, $^3J_{HH}$ = 8.98 Hz). ^{13}C NMR (75MHz; $CDCl_3$, TMS) *δ*: 32.41 ($OCH_2\underline{C}H_2CH$, -ve DEPT), 65.22 ($O\underline{C}H_2CH_2CH$, -ve DEPT), 66.69 ($CH\underline{C}H_2OH$, -ve DEPT), 69.93 ($CH_2\underline{C}^*HCH_2$, +ve DEPT), 113.14 (Ar-$\underline{C_4}$, no DEPT), 116.25 (Ar-$\underline{C_2}$, +ve DEPT), 132.31 (Ar-$\underline{C_3}$, +ve DEPT), 157.66 (Ar-$\underline{C_1}$, no DEPT). FT-IR (KBr/DRIFT) ν_{max}: 3390, 3304, 2959, 2926, 2873, 1490, 1458, 1289, 1248, 1239, 1121, 1060, 971, 822 cm^{-1}.

4-Bromo-1-(1,(R,S)-2-dihydroxybutoxy)benzene (6b) This compound was prepared in a manner similar to compound **6a**. Quantities used: p-toluenesulfonic acid (500 mg), compound **5b** (4.30 g, 14.3 mmol), in methanol (460 ml). Purified by flash chromatography [fine mesh silica gel: dichloromethane (initially) then 1:1 dichloromethane to ethyl acetate]. Dried *in vacuo* (P_2O_5, 0.5 mbar, RT, 16 h), to give a white crystalline solid. Yield = 2.75 g (74%); ^{1}H NMR (300MHz, $CDCl_3$, TMS) δ: 1.87 (2H, m, $ArOCH_2C\underline{H_2}^{(\pm)}CH$), 3.01 (1H, broad s, $CHO\underline{H}$), 3.31 (1H, broad s, $CHCH_2O\underline{H}$), 3.5 (1H, t, $^{(\pm)}CHC\underline{H_2}OH$), 3.63 (1H, d, $^{(\pm)}CHC\underline{H_2}OH$), 3.96 (1H, m, $ArOCH_2CH_2^{(\pm)}C\underline{H}$), 4.06 (2H, m, $ArOC\underline{H_2}CH_2^{(\pm)}CH$), 6.76 (2H, dd, Ar$\underline{H_2}$/$\underline{H_6}$, $^3J_{HH}$ = 6.74 Hz), 7.35 (2H, dd, Ar$\underline{H_3}$/$\underline{H_5}$, $^3J_{HH}$ = 6.9 Hz). FT/IR (KBr/Drift) μ_{max}: 3277, 2939, 2880, 1593, 1492, 1471, 1291, 1249, 1102, 1079, 1052, 984, 971, 827, 812, 647cm^{-1}.

4-Bromo-1-(1,(S)-2-dimethoxybutoxy)benzene (7) A solution of methyl iodide (3.21 g, 22.6 mmol) in dry DMF (5 ml) was added dropwise to a stirred mixture of compound **6a** (2.03 g, 7.8 mmol), sodium hydride (1.19 g, *ca.* 29 mmol of a 60% dispersion in mineral oil) and dry DMF (20 ml) at room temperature under dry nitrogen. After a slight exotherm had subsided, the reaction was left to stir at RT for a further 18 h, after which TLC showed no starting material to have remained. The excess sodium hydride was destroyed by the cautious dropwise addition of water (50 ml). The product was then extracted using diethyl ether (5 x 50 ml). The combined ether extracts were then washed successively with sat. sodium bicarbonate (50 ml), 10 % v/v hydrochloric acid (50 ml) and water (50 ml) before being dried ($MgSO_4$), filtered and evaporated to give a colourless oil. Purification by flash chromatography [fine mesh silica gel: dichloromethane] gave a colourless oil which was dried *in vacuo* (P_2O_5, 10 mbar, RT, 18h), Yield = 1.97 g (88%). ^{1}H NMR (300MHz; $CDCl_3$, TMS) *δ*: 1.98 (2H,m, $OCH_2C\underline{H_2}CH$), 3.39

(3H,s, $CH_2OC\underline{H}_3$), 3.41 (3H,s, $CHOC\underline{H}_3$), 3.47 (2H,m, $CHC\underline{H}_2OCH_3$), 3.57 (1H,m, C*$\underline{H}$), 4.02 (2H,m, $OC\underline{H}_2CH_2CH$), 6.78 (2H,d, Ar-$\underline{H}_2$, $^3J_{HH}$ = 8.96 Hz), 7.36 (2H,d, Ar-$\underline{H}_3$, $^3J_{HH}$ = 8.88 Hz). ^{13}C NMR (75MHz; $CDCl_3$, TMS) *δ*: 31.26 ($OCH_2\underline{C}H_2CH$, -ve DEPT), 57.79 ($CH_2O\underline{C}H_3$, +ve DEPT), 59.29 ($CHO\underline{C}H_3$, +ve DEPT), 64.47 ($O\underline{C}H_2CH_2CH$, -ve DEPT), 74.28 ($\underline{C}H_2OCH_3$, -ve DEPT), 76.76 ($\underline{C}$*H, +ve DEPT), 112.72 (Ar-$\underline{C}_4$, no DEPT), 116.28 (Ar-$\underline{C}_2$, +ve DEPT), 132.21 (Ar-$\underline{C}_3$, +ve DEPT), 158.01 (Ar-$\underline{C}_1$, no DEPT). FT-IR (film; ZnSe/ATR) ν_{max}: 2927, 2879, 2833, 1488, 1473, 1240, 1131, 1101, 1071, 1044, 1001, 820 cm^{-1}. GC Analysis (inj 250 °C; det 300 °; oven 80 °C hold 1 min, 30 °C min^{-1} to 280 °C hold 2 min) R_T = 6.85 (100 %) min.

4-Bromo-1-(1,(S)-2-dipentoxybutoxy)benzene (8a) A similar procedure to that employed for compound **7** was used. Quantities used: compound **6a** (2.01 g, 7.7 mmol), 1-bromopentane (3.42 g, 22.6 mmol), sodium hydride (1.36 g, *ca.* 34 mmol of 60 % dispersion in oil) and dry DMF (25 ml). Worked up reaction mixture was purified by flash chromatography [fine mesh silica gel: dichloromethane] to give two fractions as colourless oils. **8a** (R_f CH_2Cl_2 = 0.64) Yield = 1.90 g (62%) and **9** (R_f CH_2Cl_2 = 0.19) Yield = 0.50 g. Both dried *in vacuo* (P_2O_5, 10 mbar, 20 °C, 12 h). Compound **8a** ^{1}H NMR (300MHz; $CDCl_3$, TMS) *δ*: 0.85-0.89 (6H,t overlapping, $C\underline{H}_3C_4O$), 1.29 (8H,m, $CH_3C\underline{H}_2C\underline{H}_2C_2O$), 1.55 (4H,m , $C_3C\underline{H}_2CH_2O$), 1.96 (2H,m, $OCH_2C\underline{H}_2CH$), 3.41 (1H,m, $CHC\underline{H}_2OC_5$), 3.46 (4H,m, $OC\underline{H}_2C_4$), 3.64 (2H,m, CH_2C*$\underline{H}CH_2$ & $CHC\underline{H}_2O$), 4.05 (2H,m, $ArOC\underline{H}_2CH_2$), 6.78 (2H,d, Ar-$\underline{H}_2$, $^3J_{HH}$ = 9.07 Hz), 7.36 (2H, d, Ar-$\underline{H}_3$, $^3J_{HH}$ = 8.93 Hz). ^{13}C NMR (75MHz; $CDCl_3$, TMS) *δ*: 14.03 ($\underline{C}H_3C_4OCH_2$, +ve DEPT), 14.07 ($\underline{C}H_3C_4OCH$, +ve DEPT), 22.49, 22.53 ($CH_3\underline{C}H_2C_3O$, -ve DEPT), 28.32, 29.37, 29.80 ($\underline{C}H_2$'s, -ve DEPT), 31.94 ($OCH_2\underline{C}H_2CH$, -ve DEPT), 64.59 ($O\underline{C}H_2CH_2CH$, -ve DEPT), 70.45, $CH\underline{C}H_2OC_5$, -ve DEPT), 71.68 ($CHCH_2O\underline{C}H_2C_4$, -ve DEPT), 73.12 ($CHO\underline{C}H_2C_4$, -ve DEPT), 75.11 ($\underline{C}$*H, +ve DEPT), 112.61 (Ar-$\underline{C}_4$, no DEPT), 116.26 (Ar-$\underline{C}_2$, +ve DEPT), 132.18 (Ar-$\underline{C}_3$, +ve DEPT), 158.11 (Ar-$\underline{C}_1$, no DEPT). FT-IR (film; ZnSe/ATR) ν_{max}: 2954, 2929, 2858, 1489, 1467, 1243, 1109, 1102, 820 cm^{-1}. GC Analysis (inj 250 °C; det 300 °C; oven 80 °C hold 1 min, 30 °C min^{-1} to 280 °C hold 5 min) R_T = 9.60 (99.42 %) min. ***4-Bromo-1-(1-pentoxy-(S)-2-hydroxybutoxy)benzene (9)*** ^{1}H NMR (300MHz; $CDCl_3$, TMS) *δ*: 0.90 (3H,t, $C\underline{H}_3C_4O$), 1.32 (4H,m, $CH_3C\underline{H}_2C\underline{H}_2C_2O$), 1.59 (2H,m, $OCH_2C\underline{H}_2C_3$), 1.90 (2H,m, $OCH_2C\underline{H}_2CH$), 2.56 (1H,s broad, $CH_2CH(O\underline{H})CH_2$), 3.34 (1H,m, $CHC\underline{H}_2OC_5$), 3.49 (3H,m, $CHC\underline{H}_2OC_5$), 4.06 (1H,m, C*$\underline{H}$OH), 4.09 (2H,m, $OC\underline{H}_2CH_2CH$), 6.79 (2H,d, Ar-$\underline{H}_2$, $^3J_{HH}$ = 8.91 Hz), 7.36 (2H,d, Ar-$\underline{H}_3$, $^3J_{HH}$ = 8.98 Hz). ^{13}C NMR (75MHz; $CDCl_3$, TMS) *δ*: 14.05 ($\underline{C}H_3C_4O$, +ve DEPT), 22.52, 28.28 ($CH_3\underline{C}H_2\underline{C}H_2$, -ve DEPT), 29.32 ($CH_3CH_2CH_2\underline{C}H_2$, -ve DEPT), 32.70 ($OCH_2\underline{C}H_2CH$, -ve DEPT), 64.94 ($O\underline{C}H_2CH_2CH$, -ve DEPT), 67.69 ($\underline{C}$*HOH, +ve DEPT), 71.57 ($CH_2O\underline{C}H_2C_4$, -ve DEPT), 74.78 ($\underline{C}H_2OC_5$, -ve DEPT), 112.83 (Ar-$\underline{C}_4$, no DEPT), 116.27 (Ar-$\underline{C}_2$, +ve DEPT), 132.27 (Ar-$\underline{C}_3$, +ve DEPT), 157.90 (Ar-$\underline{C}_1$, no DEPT). FT-IR (film; ZnSe/ATR) ν_{max}: 3430, 2954, 2930, 2868, 2861, 1488, 1473, 1241, 1112, 1102, 1071, 1003, 820 cm^{-1}. GC Analysis (inj 250 °C; det 300 °C; oven 80 °C hold 1 min, 30 °C min^{-1} to 280 °C hold 5 min) R_T = 8.46 (100 %) min.

4-Bromo-1-(1,(R,S)-2-dipentoxybutoxy)benzene (8b) This compound was prepared in a manner similar to compound **8a**. Quantities used: 1-bromopentane (4.34 g, 9.6 mmol), compound **7b** (2.50 g, 9.6 mmol), sodium hydride (1.92 g, 60% dispersion in oil, *ca.*, 48 mmol) and dimethylformamide (40 ml). This was purified by flash chromatography [fine mesh silica gel: dichloromethane] to give a colourless oil. Dried *in vacuo* (P_2O_5, 0.6 mbar, RT, 16 h). Yield = 2.35 g (61%); ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ: 0.87 (6H, m, $OC_4C\underline{H}_3$'s), 1.30 (8H, m, $OC_2C\underline{H}_2C\underline{H}_2CH_3$'s), 1.55 (4H, m, $OCH_2C\underline{H}_2C_3$'s), 1.90 (1H, m, $ArOCH_2C\underline{H}_2{}^{(\pm)}CH$), 1.99 (1H, m, $ArOCH_2C\underline{H}_2{}^{(\pm)}CH$), 3.44 (4H + 1H, m, $OC\underline{H}_2C_4$'s + $^{(\pm)}CHC\underline{H}_2O$), 3.63 (1H + 1H, m, $ArOCH_2CH_2{}^{(\pm)}C\underline{H}$ + $^{(\pm)}CHC\underline{H}_2O$), 4.05 (2H, m, $ArOC\underline{H}_2CH_2{}^{(\pm)}CH$), 6.78 (2H, dd, ArH_2/H_6, $^3J_{HH}$ = 6.78 Hz), 7.36 (2H, dd, ArH_3/H_5, $^3J_{HH}$ = 6.8 Hz). FT/IR (film/ATR/ZnSe) μ_{max}: 2954, 2929, 2858, 1591, 1489, 1467, 1285, 1243, 1171, 1105, 1072, 1002, 820 cm^{-1}.

4-Bromo-1-(1-pentoxy-(S)-2-methoxybutoxy)benzene (10) A similar procedure to that employed in the preparation of compound **7** was used. Quantities used: compound **6a** (0.44 g, 1.33 mmol), methyl iodide (1.14 g, 8.1 mmol), sodium hydride (0.24 g, *ca.* 6 mmol of a 60 % dispersion in oil) and dry DMF (10 ml). The crude product was purified by flash chromatography [fine mesh silica gel: dichloromethane] to give a colourless oil which was dried *in vacuo* (P_2O_5, 10 mbar, RT, 18h). Yield = 0.38 g (83%). ^{1}H NMR (300MHz; $CDCl_3$, TMS) δ: 0.89 (3H,t, $C\underline{H}_3C_4O$), 1.31 (4H,m, $CH_3C\underline{H}_2C\underline{H}_2C_2O$), 1.58 (2H,m, $C_3C\underline{H}_2CH_2O$), 1.97 (2H,m, $OCH_2C\underline{H}_2CH$), 3.41 (3H,s, $OC\underline{H}_3$), 3.47 (4H,m, $C\underline{H}_2OCH_2C_4$), 3.56 (1H,m, $C^*\underline{H}$), 4.02 (2H,m, $OC\underline{H}_2CH_2CH$), 6.79 (2H,d, Ar-$\underline{H}_2$, $^3J_{HH}$ = 8.96 Hz), 7.36 (2H,d, Ar-$\underline{H}_3$, $^3J_{HH}$ = 8.99 Hz). ^{13}C NMR (75MHz; $CDCl_3$, TMS) δ: 14.06 ($\underline{C}H_3C_4O$, +ve DEPT), 22.53, 28.30, 29.34 ($\underline{C}H_2$'s, -ve DEPT), 31.50 ($OCH_2\underline{C}H_2CH$, -ve DEPT), 57.90 ($\underline{C}H_3O$, +ve DEPT), 64.57 ($O\underline{C}H_2CH_2CH$, -ve DEPT), 71.74. 72.54 ($\underline{C}H_2O\underline{C}H_2C_4$, -ve DEPT), 76.61 ($\underline{C}$*H, +ve DEPT), 112.69 (Ar-$\underline{C}_4$, no DEPT), 116.30 (Ar-$\underline{C}_2$, +ve DEPT), 132.21 (Ar-$\underline{C}_3$, +ve DEPT), 158.05 (Ar-$\underline{C}_1$, no DEPT). FT-IR (film; ZnSe/ATR) ν_{max}: 2954, 2930, 2861, 1488, 1473, 1466, 1242, 1101, 1072, 820 cm^{-1}. GC Analysis (inj 250 °C; det 300 °C; oven 80 °C hold 1 min, 30 °C min^{-1} to 280 °C hold 5 min) R_T = 8.26 (100 %) min.

EXAMPLE 1

1,2-(S)-dimethoxy-(4''-Octyloxyterphenyl-4-oxy)butane (12) 4-(4-Octyloxyphenyl)phenylboronic acid (**11**) (1.47 g, 4.5 mmol) was added to a stirred mixture of compound **7** (1.00 g, 3.5 mmol), palladium(0) *tetrakis*(triphenylphosphine) (0.12 g, 0.1 mmol), 2M sodium carbonate (25 ml) and 1,2-dimethoxyethane (25 ml). The reaction was then heated under gentle reflux for 6 h under a stream of dry nitrogen gas. The cooled reaction mixture was then poured onto water (150 ml) and the products extracted using diethyl ether (4 x 70 ml). The combined ether extracts were then washed with brine (50 ml), dried ($MgSO_4$), filtered and evaporated to give a dark solid. This was then absorbed on silica gel and passed through a short silica gel column using 4:1 dichloromethane-ethyl acetate to remove front and baseline material. The colourless solid obtained was then purified rigorously by flash chromatography [fine mesh silica gel: dichloromethane] and repeated recrystallisation (toluene x 5). The colourless solid was dried *in vacuo* (P_2O_5, 10 mbar, 50 °C, 8 h). Yield = 0.33 g (15%). ^{1}H NMR (300MHz; $CDCl_3$, TMS) δ: 0.89 (3H,t, $C\underline{H}_3C_7O$), 1.32 (8H,m $C\underline{H}_2$'s), 1.48 (2H,m, $C\underline{H}_2CH_2CH_2O$), 1.81 (2H,m, $C\underline{H}_2CH_2O$), 2.03 (2H,m, $OCH_2C\underline{H}_2CH$), 3.41 (3H,s, $C\underline{H}_3O$), 3.44 (3H,s, $CH_2OC\underline{H}_3$), 3.50 (2H,m, $C\underline{H}_2OCH_3$), 3.63 (1H,m, C*$\underline{H}$), 4.00 (2H,t, $OC\underline{H}_2C_7$), 4.11 (2H,m, $OC\underline{H}_2CH_2CH$), 6.98, 6.99 (4H,d, Ar-$\underline{H}_{3' \text{ or } 3''}$, $^3J_{HH}$ = 8.75 and 8.79 Hz), 7.55, 7.56 (4H,2d, Ar-$\underline{H}_{2' \text{ or } 2''}$, $^3J_{HH}$ = 8.74 Hz and 8.72 Hz), 7.60 (4H,s, Ar-$\underline{H}_{2/3}$). ^{13}C NMR (75MHz; $CDCl_3$, TMS) δ: 14.13 ($\underline{C}H_3C_7O$, +ve DEPT), 22.68, 26.08, 29.27, 29.30, 29.38, ($\underline{C}H_2$'s, -ve DEPT), 31.36 ($OCH_2\underline{C}H_2CH$, -ve DEPT), 31.83 ($\underline{C}H_2$, -ve DEPT), 57.83 ($\underline{C}H_3OCH$, +ve DEPT), 59.31 ($\underline{C}H_3OCH_2$, +ve DEPT), 64.31 ($O\underline{C}H_2CH_2CH$, -ve DEPT), 68.10 ($C_7\underline{C}H_2O$, -ve DEPT), 74.40 ($\underline{C}H_2OCH_3$, -ve DEPT), 76.91 ($\underline{C}$*H, +ve DEPT), 114.81 (d, Ar-$\underline{C}_{3' \text{ or } 3''}$, +ve DEPT), 126.97 (s, Ar-$\underline{C}_{2/3}$, +ve DEPT), 127.94, 127.98 (Ar-$\underline{C}_{2' \text{or } 2''}$, +ve DEPT), 133.04, 133.27 (Ar-$\underline{C}_{1' \text{ or } 1''}$, no DEPT), 139.05, 139.17 (Ar-$\underline{C}_{1 \text{ or } 4}$, no dept), 158.47, 158.72 (Ar-$\underline{C}_{4'}$ or $_{4''}$, no DEPT). FT-IR (KBr/DRIFT) ν_{max}: 2926, 2860, 1605, 1493, 1468, 1288, 1249, 1186, 1139, 1113, 970, 819, 809, 506 cm^{-1}. UV-Vis (6.43 mg, $CHCl_3$) λ_{max}: 294.00 (1.1201) nm. HPLC analysis (C18 column; 1 ml min^{-1} 99.5:0.5 acetonitrile-tetrahydrofuran) RT = 10.05 (99.78%) min.

EXAMPLE 2

1,2-(S)-dipentoxy(4''-Octyloxyterphenyl-4-oxy)butane (13a) A similar method to that employed for compound **12** was used. Quantities used: compound **11** (1.49 g, 4.6 mmol), compound **8a** (1.40 g, 3.5 mmol), palladium(0) *tetrakis*(triphenylphosphine) (0.18 g, 0.18 mmol), 2M sodium carbonate (30 ml) and 1,2-dimethoxyethane (30 ml). Crude product was first passed through a short column [silica gel: 9:1 dichloromethane-ethyl acetate], before being purified by flash chromatography (twice) [fine mesh silica gel: 1:1 dichloromethane-hexanes] to give a colourless solid which was recrystallised (toluene x 3). Dried *in vacuo* (P_2O_5, 10 mbar, 50 °C, 6 h). Yield = 0.56 g (27%). ^{1}H NMR (300MHz; $CDCl_3$, TMS) δ: 0.88 (9H,m, C$\underline{H}_3$'s), 1.31 (16H,m, C$\underline{H}_2$'s), 1.47 (2H,m, $C_5C\underline{H}_2CH_2CH_2O$), 1.55 (4H,m, $OCH_2C\underline{H}_2C_3$), 1.81 (2H,m, $OCH_2C\underline{H}_2C_6$), 2.00 (2H,m, $OCH_2C\underline{H}_2CH$), 3.43 (1H,m, $CHC\underline{H}_2O$), 3.49 (4H,m, $OC\underline{H}_2C_4$), 3.65 (1H,m, $CHC\underline{H}_2O$), 3.71 (1H,m, C*$\underline{H}$), 3.99 (2H,t, $ArOC\underline{H}_2C_7$), 4.12 (2H,m, OCH_2CH_2CH), 6.98 (2H,d, Ar-$\underline{H}_{3'/3''}$, $^3J_{HH}$ = 8.78 Hz), 6.99 (2H,d, Ar-$\underline{H}_{3'/3''}$, $^3J_{HH}$ = 8.77 Hz), 7.55 (4H,d, Ar-$\underline{H}_{2'/2''}$, $^3J_{HH}$ = 8.75 Hz), 7.60 (4H,s, Ar-$\underline{H}_{2/3}$). ^{13}C NMR (75MHz; $CDCl_3$, TMS) δ: 14.08, 14.06 ($\underline{C}H_3C_4O$, +ve DEPT), 14.13 ($\underline{C}H_3C_7O$, +ve DEPT), 22.52, 22.67 ($\underline{C}H_2$'s, -ve DEPT), 26.07 ($ArOCH_2CH_2\underline{C}H_2C_5$, -ve DEPT), 28.34, 29.27, 29.30, 29.39, 29.84, 31.83, 32.05 ($\underline{C}H_2$'s, -ve DEPT), 64.43 ($O\underline{C}H_2CH_2CH$, -ve DEPT), 68.08 ($ArO\underline{C}H_2C_7$, -ve DEPT), 70.49 ($\underline{C}H_2OC_5$, -ve DEPT), 71.67, 73.22 ($O\underline{C}H_2C_4$, -ve DEPT), 75.25 ($\underline{C}$*H, +ve DEPT), 114.79 (Ar-$\underline{C}_{3'/3''}$, +ve DEPT), 126.96 (Ar-$\underline{C}_{2/3}$, +ve DEPT), 127.93 (Ar-$\underline{C}_{2'/2''}$, +ve DEPT), 133.04, 133.13 (Ar-$\underline{C}_{1'/1''}$, no DEPT), 139.10 (Ar-$\underline{C}_{1/4}$, no DEPT), 158.58, 158.70 (Ar-$\underline{C}_{4'/4''}$, no DEPT). FT-IR (KBr/DRIFT) ν_{max}: 2955, 2934, 2856, 1607, 1494, 1475, 1468, 1293, 1261, 1252, 1188, 1117, 1096, 998, 822, 813, 503 cm^{-1}. UV-Vis (7.34 mg, $CHCl_3$) λ_{max}: 290.50 (1.0240) nm. HPLC analysis (C_{18} column; 1 ml min^{-1} 90:10 acetonitrile-tetrahydrofuran) R_T = 19.27 (99.84%) min.

***1,2-(R,S)-dipentoxy(4''-Octyloxyterphenyl-4-oxy)butane* (*13b*)** A similar method to that employed for compound **12** was used. Quantities used: compound **11** (2.00 g, 6.1 mmol), compound **8b** (1.64 g, 4.09 mmol), palladium(0) *tetrakis*(triphenylphosphine) (0.16 g, 0.14 mmol), 2M sodium carbonate (20 ml) and 1,2-dimethoxyethane (30 ml). Yield = 0.56 g (27%). ^{1}H NMR (300MHz; $CDCl_3$, TMS) δ: 0.88 (9H,m, C$\underline{H}_3$'s), 1.31 (16H,m, C$\underline{H}_2$'s), 1.46 (2H,m, $C_5C\underline{H}_2CH_2CH_2O$), 1.57 (4H,m, $OCH_2C\underline{H}_2C_3$), 1.80 (2H,m, $OCH_2C\underline{H}_2C_6$), 1.95, 2.03 (2H,m, $OCH_2C\underline{H}_2CH$), 3.46 (1H,m, $CHC\underline{H}_2O$), 3.46 (4H,m, $OC\underline{H}_2C_4$), 3.64 (1H,m, $CHC\underline{H}_2O$), 3.70 (1H,m, C*$\underline{H}$), 3.99 (2H,t, $ArOC\underline{H}_2C_7$), 4.14 (2H,m, OCH_2CH_2CH), 6.97 (2H,d, Ar-$\underline{H}_{3'/3''}$, $^3J_{HH}$ = 8.79 Hz), 6.98 (2H,d, Ar-$\underline{H}_{3'/3''}$, $^3J_{HH}$ = 8.78 Hz), 7.55 (4H,d, Ar-$\underline{H}_{2'/2''}$, $^3J_{HH}$ = 8.74 Hz), 7.59 (4H,s, Ar-$\underline{H}_{2/3}$). ^{13}C NMR (75MHz; $CDCl_3$, TMS) δ: 14.05, 14.07 ($\underline{C}H_3C_4O$, +ve DEPT), 14.12 ($\underline{C}H_3C_7O$, +ve DEPT), 22.52, 22.55, 22.68 ($\underline{C}H_2$'s, -ve DEPT), 26.08 ($ArOCH_2CH_2\underline{C}H_2C_5$, -ve DEPT), 28.34, 28.35, 29.27, 29.31, 29.39, 29.85, 31.83, 32.06 ($\underline{C}H_2$'s, -ve DEPT), 64.44 ($O\underline{C}H_2CH_2CH$, -ve DEPT), 68.08 ($ArO\underline{C}H_2C_7$, -ve DEPT), 70.48 ($\underline{C}H_2OC_5$, -ve DEPT), 71.68 ($O\underline{C}H_2C_4$, -ve DEPT), 75.26 ($\underline{C}$*H, +ve DEPT), 114.80 (Ar-$\underline{C}_{3'/3''}$, +ve DEPT), 126.95 (Ar-$\underline{C}_{2/3}$, +ve DEPT), 127.93 (Ar-$\underline{C}_{2'/2''}$, +ve DEPT), 133.04, 133.14 (Ar-$\underline{C}_{1'/1''}$, no DEPT), 139.10 (Ar-$\underline{C}_{1/4}$, no DEPT), 158.58, 158.71 (Ar-$\underline{C}_{4'/4''}$, no DEPT). FT-IR (KBr/DRIFT) ν_{max}: 3039, 2955, 2933, 2858, 1607, 1491, 1473, 1468, 1292, 1252, 1186, 1116, 821, 811, 738, 672, 505 cm^{-1}. UV-Vis (5.00 mg, $CHCl_3$) λ_{max}: 294.50 (0.7719) nm. HPLC analysis (C_{18} column; 1 ml min^{-1} 90:10 acetonitrile-tetrahydrofuran) R_T = 18.75 (99.86%) min.

EXAMPLE 3

1-Pentoxy-2-(S)-methoxy-(4''-Octyloxyterphenyl-4-oxy)butane (14) A similar method to that employed for compound **12** was used. Quantities used: compound **11** (0.45g, 1.4 mmol), compound **10** (0.34 g, 1.0 mmol), palladium(0) *tetrakis*(triphenylphosphine) (0.04 g, 0.03 mmol), 2M sodium carbonate (10 ml) and 1,2-dimethoxyethane (10 ml). The crude product was passed through a short column [silica gel: dichloromethane] before being purified by flash chromatography [fine mesh silica gel: 7:3 dichloromethane-hexanes] to give a colourless solid which was recrystallised (toluene x 2) and dried *in vacuo* (P_2O_5, 10 mbar, 50 °C, 6 h). Yield = 0.30 g (55 %). ^{1}H NMR (300MHz; $CDCl_3$, TMS) δ: 0.89 (3H,m, C$\underline{H}_3$), 0.90 (3H,m, C$\underline{H3}$), 1.33 (12H,m, C$\underline{H}_2$'s), 1.48 (2H,m, $C_5C\underline{H}_2CH_2CH_2O$), 1.60 (2H,m, $OCH_2C\underline{H}_2C_3$), 1.81 (2H,m, $OCH_2C\underline{H}_2C_6$), 2.02 (2H,m, $OCH_2C\underline{H}_2CH$), 3.44 (3H,s, $C\underline{H}_3O$), 3.53 (4H,m, $C\underline{H}_2OC\underline{H}_2C_4$), 3.62 (1H,m, $CH_2C\underline{H}CH_2O$), 4.00 (2H,t, $OC\underline{H}_2C_7$), 4.12 (2H,m, $OC\underline{H}_2CH_2CH$), 6.98, 6.99 (4H,dd, Ar-$\underline{H}_{3'/3''}$, $^3J_{HH}$ = 8.77 and 8.85 Hz), 7.55, 7.57 (4H,dd, Ar-$\underline{H}_{2'/2''}$, $^3J_{HH}$ = 8.78 and 8.78 Hz), 7.60 (4H,s, Ar-$\underline{H}_{2/3}$). ^{13}C NMR (75MHz; $CDCl_3$, TMS) δ: 14.07 ($\underline{C}H_3C_4O$, +ve DEPT), 14.13 ($\underline{C}H_3C_7O$, +ve DEPT), 22.54, 22.68 ($\underline{C}H_2$'s, -ve DEPT), 26.07 ($\underline{C}H_2$, -ve DEPT), 28.31, 29.26, 29.30, 29.36, 29.34 ($\underline{C}H_2$'s, -ve DEPT), 31.59 ($OCH_2\underline{C}H_2CH$, -ve DEPT), 31.83 ($\underline{C}H_2$, -ve DEPT), 57.95 ($\underline{C}H_3O$, +ve DEPT), 64.39 ($O\underline{C}H_2CH_2CH$, -ve DEPT), 68.09 ($ArO\underline{C}H_2C_7$, -ve DEPT), 71.74 ($O\underline{C}H_2C_4$, -ve DEPT), 72.63 ($\underline{C}H_2OC_5$, -ve DEPT), 77.02 ($\underline{C}$*H, +ve DEPT), 114.79, 114.81 (Ar-$\underline{C}_{3'/3''}$, +ve DEPT), 126.96 (Ar-$\underline{C}_{2/3}$, +ve DEPT), 127.93, 127.95 (Ar-$\underline{C}_{2'/2''}$, +ve DEPT), 133.03, 133.21 (Ar-$\underline{C}_{1/4}$, no DEPT), 139.05, 139.14 (Ar-$\underline{C}_{1'/1''}$, no DEPT), 158.51 (Ar-$\underline{C}_{4''}$, no DEPT), 158.71 (Ar-$\underline{C}_{4'}$, no DEPT). FT-IR (KBr/DRIFT) ν_{max}: 2966, 2926, 2860, 1613, 1493, 1288, 1250, 1186, 1115, 819, 667, 505 cm^{-1}. UV-Vis (4.89 mg, $CHCl_3$) λ_{max}: 295.50 (0.7500) nm. HPLC analysis (C18 column; 1 ml min^{-1} 90:10 acetonitrile-tetrahydrofuran) R_T = 10.02 (100%) min.

B. 1,*(S)*-2-(4''-Octyloxy-mono-fluoro-terphenyl-4-oxy)dialkoxy-butanes (Examples 4 to 9)

Summary

Data generated from Examples 1 to 3 (see below) showed that the 1,*(S)*-2-dialkyloxybutane terminal unit was capable of generating an interesting mixture of novel chiral phases (N^*, TGB A^* and TGB C^*) as well as ferroelectric phases ($S_C{}^*$), albeit at relatively high melting (65-162 °C) and thermal stabilities (118-180 °C). It was hoped that fluorine substitution on the terphenyl moiety would lower the thermal stability of the various phases as well as the melting point, while maintaining the interesting phase behaviour.

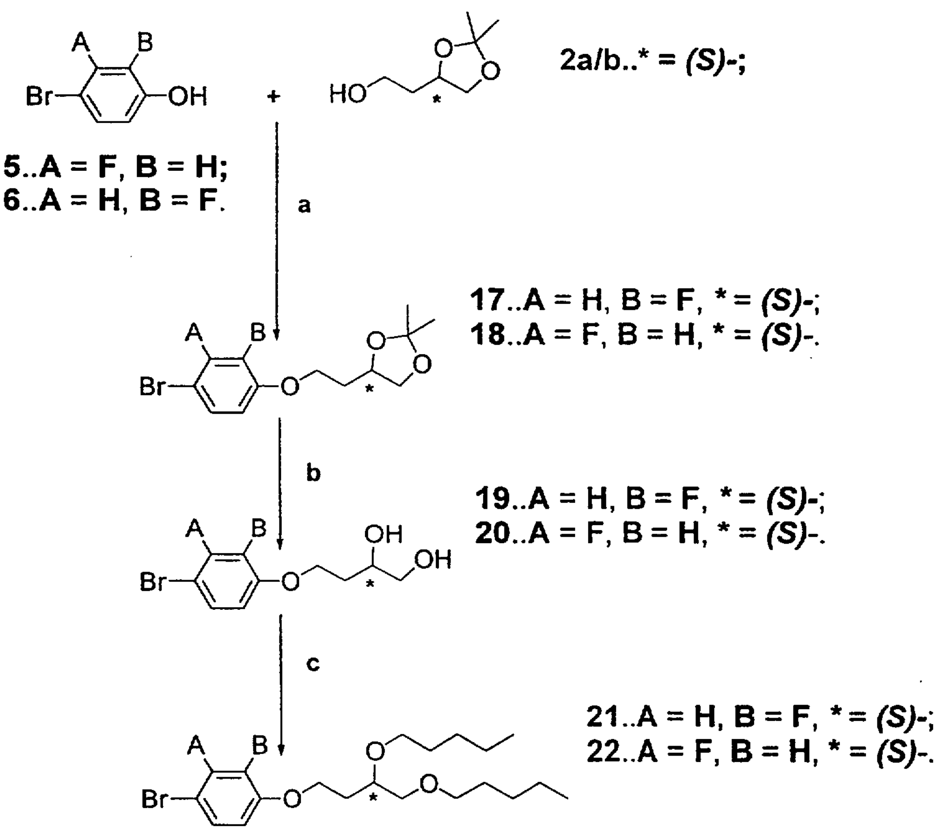
The routes employed are shown in schemes 3 to 6. **Scheme 3** charts the route used to synthesise mono-fluoro-4-bromo-1-(1-pentoxy-2-pentoxybutoxy)benzenes (**21** and **22**) and is essentially synthetically identical to that described in first three steps of scheme 2. Schemes 4 and 5 describe the routes to various phenyl, biphenylene and mono-fluorobiphenylene units which are used in the final steps of synthesis (Scheme 6). **Scheme 4** shows the routes used for the synthesis of 4-(2'- or 3'-fluoro-4'-octyloxyphenyl)phenylboronic acids **30** and **31**. Here the appropriately substituted bromophenols **15** or **16** were alkylated using 1-bromooctane and potassium carbonate in butanone to give compounds **23** and **24** as colourless liquids in quantitative yields. These were then converted to their respective boronic acids **25** and **26** using butyllithium and trimethyl borate at -78 °C. Compounds **25** and **26** then underwent Suzuki cross-coupling with 1-bromo-4-iodobenzene (**27**) using palladium(0) *tetrakis*(triphenyl-phosphine) catalyst to give the biphenyls **28** and **29** in low to moderate yields (26-51%) (R.B. Miller et. al., *supra*; M. Hird et. al., *supra*; L.K.M. Chan et. al., *supra*; L.K.M. Chan et. al., *supra*). Compounds **28** and **29** were then converted to 4-(2'-fluoro-4'-octyloxyphenyl)phenyl boronic acid **30** and 4-(3'-fluoro-4'-octyloxyphenyl)phenyl boronic acid **31** respectively in high yields. **Scheme 5** outlines the three step route to 4-(4'-octyloxyphenyl-2-fluorophenylboronic acid (**36**) and 4-(4'-Octyloxyphenyl)-3-fluorophenylboronic acid (**39**) starting from 1-bromo-4-octyloxybenzene (**32**) using and identical synthetic approach to scheme 4.

Finally, the relevant fragments drawn from schemes 3, 4 to 5 were brought together in **scheme 6** which illustrates the final steps in the synthesis of the target materials **40, 41, 42, 43,** and **45**. All compounds were simply formed in one step reaction from the chiral ethers **13a, 21** and **22** with the appropriate boronic acids **11, 30, 31, 36** and **39** and palladium(0) *tetrakis*(triphenyl-phosphine) under Suzuki cross-couplings.

All final materials were purified rigorously by flash chromatography (often repeatedly) and by repeated recrystallisation until HPLC analysis revealed purities in excess of at least 99.8%. This route failed for the synthesis of 1,2-(S)-dipentoxy-(3'-fluoro-4"-octyloxyterphenyl-4-oxy)butane, only starting material **13a** and the hydrodeboronated 3-fluorobiphenyl being recovered.

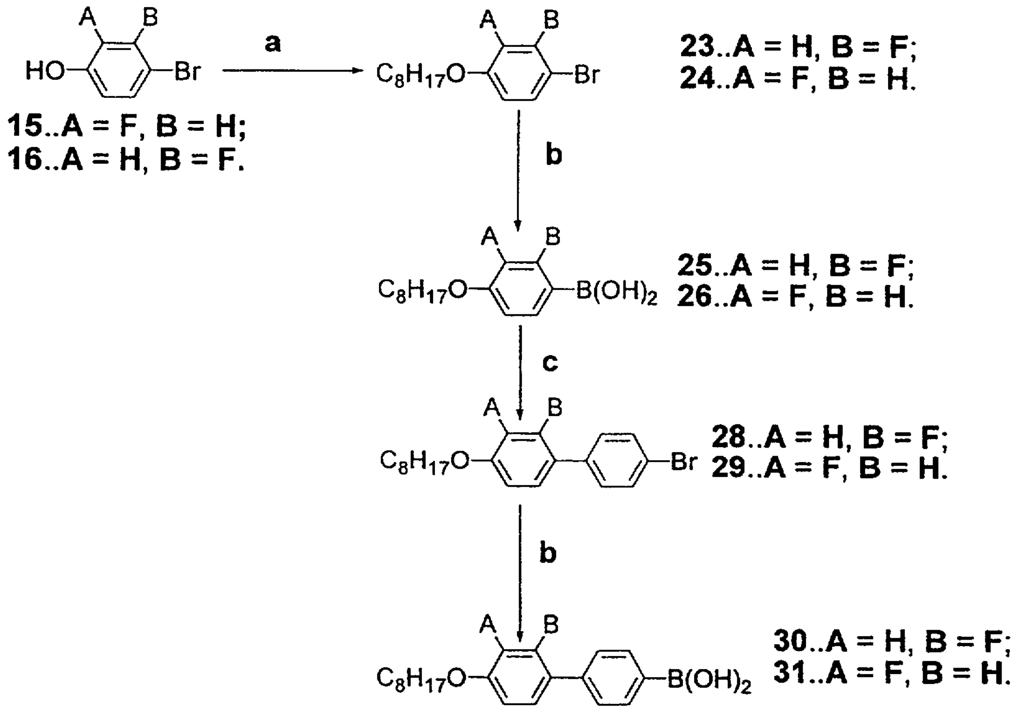
Presumably, the α-fluoro substituent of compound (39) causing activation of the boronic acid which results in facile hydro-deboronation.

Scheme 3 : Synthetic Route to 2- or 3-mono-fluoro-4-Bromo-1-(1-Pentoxy-2-Pentoxybutoxy)benzenes (21 and 22)



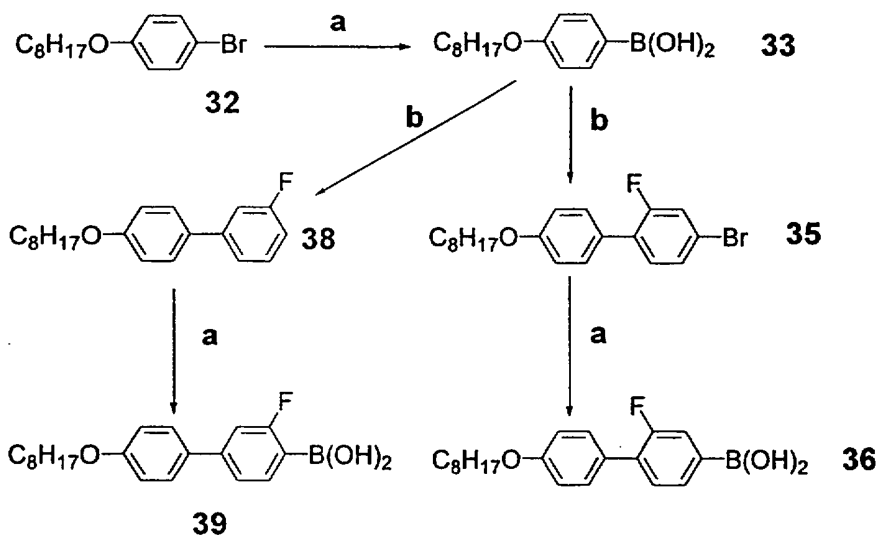
(a)..Diethyl azodicarboxylate, PPh_3, THF, N_2, RT;
(b)..4-Toluenesulfonic acid, MeOH, RT;
(c)..(i) NaH, DMF, N_2, RT;
(ii) $C_5H_{11}Br$, DMF, N_2, RT;
(iii) H^+, H_20;

Scheme 4: Synthetic Route to 4-(2' or 3'-fluoro-4-octyloxyphenyl)phenylboronic Acids (30) and (31)



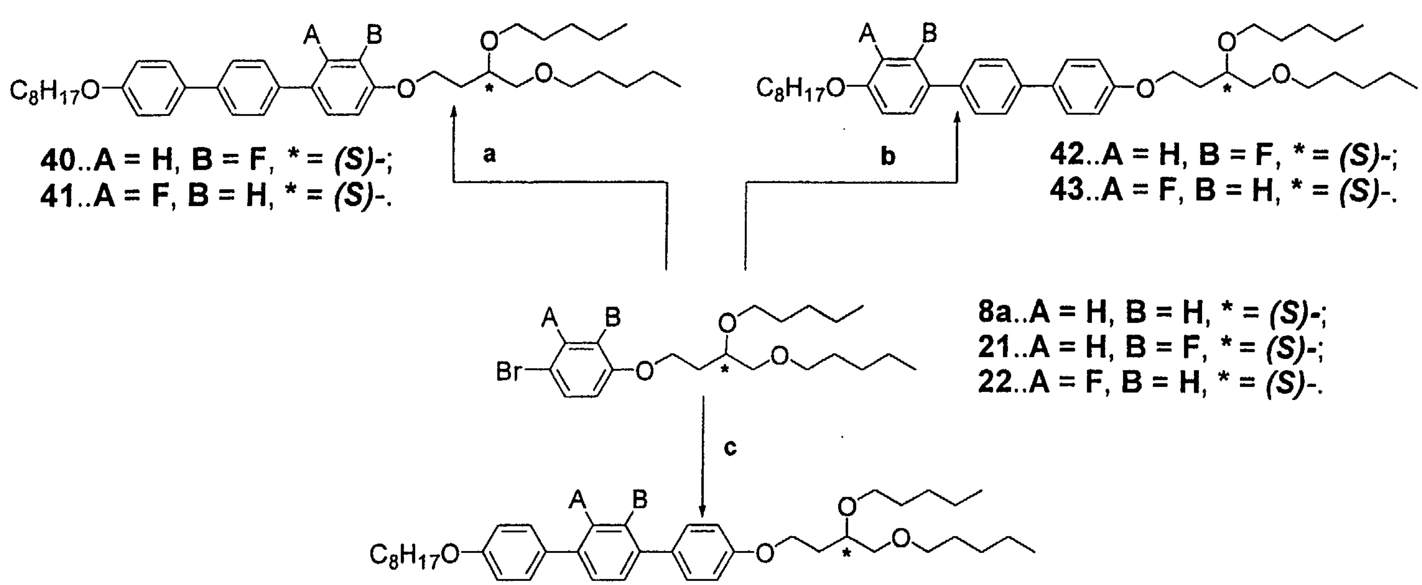
(a)..$C_8H_{17}Br$, K_2CO_3, butanone, reflux;
(b) ..(i) BuLi, THF, -78 °C, N_2;
(ii) $B(OMe)_3$, THF, -78 °C to RT, N_2;
(iii) H^+, H_20.
(c)..1-bromo-4-iodobenzene (27), $Pd(PPh_3)_4$, 2M Na_2CO_3, 1,2-dimethoxyethane, N_2, reflux.

Scheme 5 : Synthetic Route to 4-(4'-Octyloxyphenyl)-2-fluorophenyl boronic Acid (36) And 4-(4'-Octyloxyphenyl)-3-fluorophenylboronic Acid (39)



(a) ..(i) BuLi, THF, -78 °C, N_2;
(ii) $B(OMe)_3$, THF, -78 °C to RT, N_2;
(iii) H^+, H_20.
(b)..1-bromo-3-fluoro-4-iodobenzene (**34**) or 1-fluoro-3-iodobenzene (**37**), $Pd(PPh_3)_4$, 2M Na_2CO_3, 1,2-dimethoxyethane, N_2, reflux.

Scheme 6 : Final Steps to the 1,*(S)*-2-(4''-Octyloxy-mono-fluoro-terphenyl-4-oxy)dipentoxybutanes (40, 41, 42, 43, 44 and 45)



40..A = H, B = F, * = *(S)*-;
41..A = F, B = H, * = *(S)*-.

42..A = H, B = F, * = *(S)*-;
43..A = F, B = H, * = *(S)*-.

8a..A = H, B = H, * = *(S)*-;
21..A = H, B = F, * = *(S)*-;
22..A = F, B = H, * = *(S)*-.

44..A = H, B = F, * = *(S)*-;
45..A = F, B = H, * = *(S)*-.

a..Compound **11**, $Pd(PPh_3)_4$, 2M Na_2CO_3, 1,2-dimethoxyethane, reflux, N_2.
b..Compounds **30** or **31**, $Pd(PPh_3)_4$, 2M Na_2CO_3, 1,2-dimethoxyethane, reflux, N_2.
c..Compounds **36** or **39**, $Pd(PPh_3)_4$, 2M Na_2CO_3, 1,2-dimethoxyethane, reflux, N_2.

Experimental details

1-{(2,2-Dimethyl)-1,(S)-2-dioxolan-4-yl}ethoxy-4-bromo-2-fluorobenzene (17) A similar procedure to that used for compound **5a** was used. Quantities used: compound **2a/b** (9.00 g, 61.6 mmol), triphenylphosphine (10.78 g, 41.1 mmol), 2-fluoro-4-bromophenol **(16)** (7.85 g, 41.1 mmol), diethylazodicarboxylate (7.16 g, 41.1 mmol) and tetrahydrofuran (150 ml). Purified by flash chromatography [fine mesh silica gel: 10% ethyl acetate in hexane] to give a colourless oil. Dried *in vacuo* (P_2O_5, RT, 5.0 mbar, 36 h). Yield = 8.59 g (66%). ^{1}H NMR (300MHz, $CDCl_3$, TMS) δ: 1.36 (3H, s, $CC\underline{H}_3$), 1.42 (3H, s, $CC\underline{H}_3$), 2.06 (2H, dd, $OCH_2C\underline{H}_2CH^*$), 3.65 (1H, t, $^*CHC\underline{H}_2O$), 4.01 (2H + 1H, m, $OC\underline{H}_2CH_2CH^*$ + $^*CHC\underline{H}_2O$), 4.30 (1H, q, $OCH_2CH_2C\underline{H}^*$), 6.83 (1H, t, Ar-$\underline{H}_5$, $^3J_{HH}$ = 8.73 Hz), 7.16 (1H, m, Ar-$\underline{H}_6$, $^3J_{HH}$ = 8.65 Hz), 7.21 (1H, m, Ar-$\underline{H}_3$, $^3J_{HF}$ = 10.46 Hz). ^{13}C NMR (75MHz, $CDCl_3$, TMS) δ: 26.29 ($C\underline{C}H_3$, +ve DEPT), 33.39 ($OCH_2\underline{C}H_2CH^*$, -ve DEPT), 66.24 ($O\underline{C}H_2CH_2CH^*$, -ve DEPT), 69.45 ($^*CH\underline{C}H_2O$, -ve DEPT) 73.16 ($OCH_2CH_2\underline{C}H^*$, +ve DEPT), 103.86 ($\underline{C}CH_3$, no DEPT), 112.11 (Ar-$\underline{C}_4$, d, J_{CF} = 8.164 Hz, no DEPT), 115.82 (Ar-$\underline{C}_6$, d, J_{CF} = 2.123 Hz, +ve DEPT), 119.67 (Ar$\underline{C}_3$, d, J_{CF} = 21.35 Hz, +ve DEPT), 127.17 (Ar-$\underline{C}_5$, d, J_{CF} = 4.12 Hz, +ve DEPT), 146.25 (Ar-$\underline{C}_1$, d, J_{CF} = 10.41 Hz, no DEPT), 152.4 (Ar-$\underline{C}_2$, d, J_{CF} = 250.9 Hz, no DEPT). ^{19}F NMR (282MHz, $CDCl_3$, TMS) δ: -131.589 (1F, t, ArC_2-$\underline{F}$, $^3J_{HF}$ = 9.5 Hz, collapses to singlet at -131.59 ppm on decoupling). FT/IR (film/ATR/ZnSe) μ_{max}: - 2988, 2945, 2871, 1498, 1372, 1264, 1204, 1144, 1059, 866, 810 cm^{-1}.

1-{(2,2-Dimethyl)-1,(S)-2-dioxolan-4-yl}ethoxy-4-bromo-3-fluorobenzene (18) A similar procedure to that used for compound **5a** was used. Quantities used: compound **2a/b** (8.80 g, 60.3 mmol), triphenylphosphine (10.54 g, 40.1 mmol), 3-fluoro-4-bromophenol **(15)** (7.67 g, 40.1 mmol), diethylazodicarboxylate (7.00 g, 40.1 mmol) and tetrahydrofuran (145 ml). Purified by flash chromatography [fine mesh silica gel: 10% ethyl acetate in hexane] to give a colourless oil. Dried *in vacuo* (P_2O_5, RT, 0.5 mbar, 18h). Yield = 6.81 g (53%); ^{1}H NMR (300MHz, $CDCl_3$, TMS) δ: 1.36 (3H, s, $O_2CC\underline{H}_3$), 1.42 (3H, s, $O_2CC\underline{H}_3$), 2.04 (2H, q, $OCH_2C\underline{H}_2CH$), 3.64 (1H, q, $CHC\underline{H}_2O$), 4.04 (1H, t, $OC\underline{H}_2CH_2CH$), 4.11(1H, m, $CHC\underline{H}_2O$), 4.28 (1H, q, $OCH_2CH_2C\underline{H}$), 6.63 (1H, m, Ar-$\underline{H}_6$, $^3J_{HH}$ = 8.88 Hz), 6.71 (1H, m, Ar-$\underline{H}_5$, $^3J_{HH}$ = 10.41 Hz), 7.39 (1H, m, Ar-$\underline{H}_2$, $^3J_{HF}$ = 8.81 Hz). ^{13}C NMR (75MHz, $CDCl_3$, TMS) δ: 25.70 ($O_2C\underline{C}H_3$, +ve DEPT), 26.98 ($O_2C\underline{C}H_3$, +ve DEPT), 33.33 ($OCH_2\underline{C}H_2CH$, -ve DEPT), 65.32 ($O\underline{C}H_2CH_2CH$, -ve DEPT), 69.45 ($CH\underline{C}H_2O$, -ve DEPT), 73.11 ($OCH_2CH_2\underline{C}H$, +ve DEPT), 99.3 (Ar-$\underline{C}_4$, d, J_{CF} = 21.2 Hz, no DEPT), 102.37 (Ar-$\underline{C}_2$, d, J_{CF} = 25.5 Hz, +ve DEPT), 108.97 (O_2-$\underline{C}$-$(CH_3)_2$, no DEPT), 111.81 (Ar-$\underline{C}_6$, d, J_{CF} = 3.00 Hz, +ve DEPT), 133.34 (Ar-$\underline{C}_5$, d, J_{CF} = 2.0 Hz, +ve DEPT), 159.37 (Ar-$\underline{C}_1$, d, J_{CF} = 10 Hz, no DEPT), 159.48 (Ar-$\underline{C}_3$, d, J_{CF} = 246 Hz, no DEPT). ^{19}F NMR (282MHz, $CDCl_3$, TMS) δ: –105.65 (1F, t, ArC_3-$\underline{F}$, $^3J_{HF}$ = 9.24 Hz, collapses to singlet at –105 ppm on decoupling). FT/IR (film/ATR/ZnSe) μ_{max}: 2985, 2933, 2871, 1603, 1583, 1488, 1470, 1379, 1321, 1291, 1259, 1239, 1165, 1059, 982, 833 cm^{-1}.

4-Bromo-2-fluoro-1-(1,(S)-2-dihydroxybutoxy)benzene (19) This compound was prepared in a manner similar to compound **6a**. Quantities used: p-toluenesulfonic acid (500 mg), compound **17** (8.00 g, 25.0 mmol) and methanol (460 ml). Purified by flash chromatography [fine mesh silica gel: dichloromethane (initially) then 1:1 dichloromethane: ethyl acetate (finally)]. Dried *in vacuo* (P_2O_5, 10 mbar, RT, 60 h). Yield = 5.25g (75%). ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ : 1.91 (2H, m, $OCH_2C\underline{H}_2$*CH), 3.13 (1H, broad s, *$CHCH_2O\underline{H}$), 3.43 (1H, broad s, *CHO$\underline{H}$), 3.52 (1H, t, *$CHC\underline{H}_2OH$), 3.70 (1H, s, *$CHC\underline{H}_2OH$), 3.98 (1H, s, OCH_2CH_2*C$\underline{H}$), 4.15 (2H, m, $OC\underline{H}_2CH_2$-*CH), 6.83 (1H, t, Ar-$\underline{H}_6$, $^3J_{HH}$ = 9.25 Hz), 7.16 (1H, m, Ar-$\underline{H}_5$, $^3J_{HH}$ = 8.12 Hz), 7.21 (1H, dd, Ar-$\underline{H}_3$, $^3J_{HF}$ = 13.22 Hz). ^{13}C NMR (75MHz, $CDCl_3$, TMS) δ: 32.33 ($OCH_2\underline{C}H_2$*CH, -ve DEPT), 66.53 (*$CH\underline{C}H_2OH$, -ve DEPT), 66.63 ($O\underline{C}H_2CH_2$*CH, -ve DEPT), 69.60 (OCH_2CH_2*$\underline{C}$H, -ve DEPT), 112.33 (Ar-$\underline{C}_4$, d, J_{CF} = 8.818 Hz, no DEPT), 115.88 (Ar-$\underline{C}_6$, d, J_{CF} = 2.05 Hz, +ve DEPT), 119.67 (Ar-$\underline{C}_3$, d, J_{CF} = 21.19 Hz, +ve DEPT), 127.29 (Ar-$\underline{C}_5$, d, J_{CF} = 4.037 Hz, +ve DEPT), 146.01 (Ar-$\underline{C}_1$, d, J_{CF} = 10.69 Hz, no DEPT), 152.38 (Ar-$\underline{C}_2$, d, J_{CF} = 250.41 Hz, no DEPT). ^{19}F NMR (282 MHz, $CDCl_3$, TMS) δ: –131.90 (1F, t, ArC_2-F, J_{HF} = 9.44 Hz, collapses to a singlet at -131.90 ppm on decoupling). FT/IR (KBr/Drift) μ_{max}: 3251, 1508, 1466, 1306, 1269, 1213, 1130, 1079, 968, 869, 804 cm^{-1}.

4-Bromo-3-fluoro-1-(1,(S)-2-dihydroxybutoxy)benzene (20) This compound was prepared in a manner similar to compound **6a**. Quantities used: p-toluene sulphonic acid (500 mg), compound **18** (6.00 g, 18.8 mmol) in methanol (460 ml). Dried *in vacuo* (P_2O_5, 0.4 mbar, RT, 18 h). Yield = 4.94 g (94%). ^{1}H NMR (300MHz, $CDCl_3$, TMS) δ: 1.91(2H, m, $OCH_2C\underline{H}_2CH$), 2.49 (1H, Broad, s, CHO$\underline{H}$), 2.85 (1H, Broad, s, $CHCH_2O\underline{H}$), 3.52 (1H, dd, $CHC\underline{H}_2OH$), 3.71 (1H, dd, $CHC\underline{H}_2OH$), 3.98 (1H, q, $OCH_2CH_2C\underline{H}$), 4.10 (2H, m, $OC\underline{H}_2CH_2CH$), 6.60 (1H, m, Ar-$\underline{H}_6$, $^3J_{HH}$ = 8.85 Hz), 6.69 (1H, dd, Ar-$\underline{H}_2$, $^3J_{HF}$ = 10.3 Hz), 7.40 (1H, t, Ar-$\underline{H}_5$, $^3J_{HH}$ = 8.44 Hz). ^{13}C NMR (75MHz, $CDCl_3$, TMS) δ: 32.70 ($OCH_2\underline{C}H_2CH$, -ve DEPT), 65.83 ($O\underline{C}H_2CH_2CH$, -ve DEPT), 69.92 ($OCH_2CH_2\underline{C}H$, +ve DEPT), 99.94 (Ar-$\underline{C}_4$, d, J_{CF} = 21.1 Hz, no DEPT), 103.78 (Ar-$\underline{C}_2$, d, J_{CF} = 25.5 Hz, +ve DEPT), 112.18 (Ar-$\underline{C}_6$, d, J_{CF} = 2.882 Hz, +ve DEPT), 133.78 (Ar-$\underline{C}_5$, d, J_{CF} = 2.165 Hz, +ve DEPT), 159.58 (Ar-$\underline{C}_1$, d, J_{CF} = 9.45 Hz, no DEPT), 159.85 (Ar-$\underline{C}_3$, d, J_{CF} = 247.2 Hz, no DEPT). ^{19}F NMR (282 MHz, $CDCl_3$, TMS) δ: -105.46 (1F, t, ArC_3-$\underline{F}$, $^3J_{HF}$ = 9.2 Hz, collapses to singlet at -105.46 ppm on decoupling). FT/IR (KBr/Drift) μ_{max}: 3244, 2939, 2906, 2880, 2833, 1613, 1593, 1487, 1463, 1321, 1263, 1237, 1171, 1130, 1075, 985, 961, 919, 824 cm^{-1}.

4-Bromo-2-fluoro-1-(1,(S)-2-dipentoxybutoxy)benzene (21) This compound was prepared in a manner similar to compound **8a**. Quantities used: 1-bromopentane (7.31g, 48.4 mmol), compound **19** (4.50 g, 16.1 mmol), sodium hydride (2.58 g, 60% dispersion in oil *ca.*, 64 mmol) and dimethylformamide (50 ml). Purified by flash chromatography [fine mesh silica gel: dichloromethane] to give a colourless oil. Dried *in vacuo* (P_2O_5, 10 mbar, RT, 24 h). Yield = 3.43 g (51%). ^{1}H NMR (300MHz; $CDCl_3$, TMS) δ: 0.87 (6H, m, $OC_4C\underline{H}_3$'s), 1.30 (8H, m, $OCH_2CH_2C\underline{H}_2C\underline{H}_2CH_3$), 1.55 (4H, m, $OCH_2C\underline{H}_2C_3$), 1.93 (1H, m, $ArOCH_2C\underline{H}_2{*}CH$), 2.04 (1H, m, $ArOCH_2C\underline{H}_2{*}CH$), 3.44 (4H + 1H, m, O-$C\underline{H}_2C_4$ + $ArOCH_2CH_2{*}C\underline{H}$), 3.65 (2H, m, $*CHC\underline{H}_2OC_5$), 4.13 (2H, m, $ArOC\underline{H}_2CH_2{*}CH$), 6.85 (1H, t, Ar-$\underline{H}_6$, $^3J_{HH}$ = 8.70 Hz), 7.16 (1H, dd, Ar-$\underline{H}_5$, $^3J_{HH}$ = 9.71 Hz), 7.21 (1H, dd, Ar-$\underline{H}_3$, $^3J_{HH}$ = 10.47 Hz). ^{13}C NMR (75MHz, $CDCl_3$, TMS) δ: 14.41 ($OC_4\underline{C}H_3$'s, +ve DEPT), 22.88 ($OC_3\underline{C}H_2CH_3$, -ve DEPT), 28.71 ($ArOCH_2\underline{C}H_2{*}CH$, -ve DEPT), 29.75 ($OC_2\underline{C}H_2C_2$, -ve DEPT), 31.19 ($OCH_2\underline{C}H_2C_3$, -ve DEPT), 66.37 ($ArO\underline{C}H_2CH_2{*}CH$ /-ve), 71.38 ($O\underline{C}H_2C_4$, -ve DEPT), 73.39 ($*CH\underline{C}H_2OC_5$, -ve DEPT), 75.31 ($ArOCH_2CH_2{*}\underline{C}H$, +ve DEPT), 112.17 (Ar-$\underline{C}_4$, d, J_{CF} = 8.2 Hz, no DEPT), 116.26 (Ar-$\underline{C}_6$, d, J_{CF} = 2.2 Hz, +ve DEPT), 120.0 (Ar-$\underline{C}_3$, d, J_{CF} = 21.2 Hz, +ve DEPT), 127.5 (Ar-C_5, d, J_{CF} = 4.1 Hz, +ve DEPT), 146.9 (Ar-$\underline{C}_1$, d, J_{CF} = 10.7 Hz, no DEPT), 152.9 (Ar-$\underline{C}_2$, d, J_{CF} = 250.7 Hz, no DEPT). ^{19}F NMR (282 MHz, $CDCl_3$, TMS) δ: -131.69 (1F, t, ArC_2-$\underline{F}$, J_{HF} = 9.59 Hz, collapses to singlet at -131.69 on decoupling). FT/IR (film/ATR/ZnSe) μ_{max}: - 2955, 2930, 2859, 1501, 1304, 1264, 1206, 1116, 1107, 872, 810 cm^{-1}.

4-Bromo-3-fluoro-1-(1,(S)-2-dipentoxybutoxy)benzene (22) This compound was prepared in a manner similar to compound **8a**. Quantities used: 1-bromopentane (6.49 g, 43 mmol), compound **20** (4.00 g, 14.3 mmol), sodium hydride (2.29 g, 60% dispersion in oil, *ca.*, 57 mmol) and dimethylformamide (50 ml). This was purified by flash chromatography [fine mesh silica gel: 10% ethyl acetate in hexane] to give a colourless oil. Dried *in vacuo* (P_2O_5, 0.8 mbar, RT, 16 h). Yield = 3.60 g (60%). ^{1}H NMR (300MHz, $CDCl_3$, TMS) δ : 0.87 (6H, m, $OC_4C\underline{H}_3$), 1.30 (8H, m, $OC_2C\underline{H}_2C\underline{H}_2CH_3$), 1.55 (4H, m, $OCH_2C\underline{H}_2CH_3$), 1.96 (2H, m, $OCH_2C\underline{H}_2{*}CH$), 3.43 (4H + 1H, m, $OC\underline{H}_2C_4$ + $*CHC\underline{H}_2OC_5$), 3.63 (1H + 1H, m, $OC\underline{H}_2CH_2{*}CH$ + $CHC\underline{H}_2OC_5$), 4.05 (2H, m, $OC\underline{H}_2CH_2{*}CH$), 6.60 (1H, ddd, Ar-$\underline{H}_6$, $^3J_{HH}$ = 8.8 Hz), 6.70 (1H, dd, Ar-$\underline{H}_2$, $^3J_{HF}$ = 10.49 Hz), 7.38 (1H, t, Ar-$\underline{H}_5$, $^3J_{HH}$ = 8.69 Hz). ^{13}C NMR (75MHz, $CDCl_3$, TMS) δ: 14.4 ($OC_4\underline{C}H_3$, +ve DEPT), 22.9 ($OC_3\underline{C}H_2CH_3$, -ve DEPT), 28.71 ($OCH_2\underline{C}H_2{*}CH$, -ve DEPT), 29.96 ($OCH_2CH_2\underline{C}H_2CH_2CH_3$, -ve DEPT), 32.25 ($OCH_2\underline{C}H_2C_3$, -ve DEPT), 65.22 ($O\underline{C}H_2CH_2{*}CH$, -ve DEPT), 71.44 ($*CH\underline{C}H_2OC_5$, -ve DEPT), 73.46 ($O\underline{C}H_2C_4$, -ve DEPT), 75.45 ($OCH_2CH_2{*}\underline{C}H$, +ve DEPT), 99.4 (Ar-$\underline{C}_4$, d, J_{CF} = 21.42 Hz, no DEPT), 103.71 (Ar-$\underline{C}_2$, d, J_{CF} = 25.45 Hz, +ve DEPT), 112.21 (Ar-$\underline{C}_6$, d, J_{CF} = 3.24 Hz, +ve DEPT), 133.63 (Ar-$\underline{C}_5$, d, J_{CF} = 1.90 Hz, +ve DEPT), 159.84 (Ar-$\underline{C}_3$, d, J_{CF} = 246.25 Hz, no DEPT), 160.02 (Ar-$\underline{C}_1$, d, J_{CF} = 9.927

Hz, no DEPT). ^{19}F NMR (282 MHz, $CDCl_3$, TMS) δ: –105.86 (1F, t, ArC_3-F, J_{HF} = 8.65 Hz, collapses to a singlet at –105.86 ppm on decoupling). FT/IR (Film/ATR/ZnSe) μ_{max}: 2955, 2930, 2859, 1604, 1583, 1489, 1466, 1321, 1291, 1167, 1141, 1120, 1109 cm^{-1}.

1-Bromo-3-fluoro-4-octyloxybenzene (23) Bromooctane (9.93 g, 51.44 mmol) in acetone (50 ml) was added dropwise to a stirred, refluxing solution of compound **15** (6.55 g, 34.29 mmol), potassium carbonate (9.47 g, 68.58 mmol) and acetone (50 ml). The solution was then allowed to reflux for 5 h. TLC analysis showed some starting material present, so a small amount of potassium carbonate and bromooctane were added. The solution was then allowed to reflux for a further 10 h. TLC analysis showed no starting material left, so the mixture was allowed to cool to room temperature overnight. The solution was then filtered, and the solid residue washed with dichloromethane. The filtrate was then evaporated to a colourless oil which was redissolved in dichloromethane (200 ml). This solution was washed with water (50 ml), 10% (v/v) sodium hydroxide (50 ml) and finally water (50 ml). This was then dried ($MgSO_4$), filtered, evaporated to a colourless oil and purified by flash chromatography [coarse silica gel: dichloromethane]. Dried *in vacuo* (P_2O_5, 0.1mbar, RT, 18 h) to give a colourless oil. Yield = 10.73 g (>100%); ^{1}H NMR (300MHz, $CDCl_3$, TMS) δ: 0.88 (3H, t, $ArOC_7C\underline{H}_3$), 1.35 (10H, m, $ArOC_2C\underline{H}_2C\underline{H}_2C\underline{H}_2C\underline{H}_2C\underline{H}_2CH_3$), 1.81 (2H, m, $ArOCH_2C\underline{H}_2C_6$), 3.91 (2H, t, $ArOC\underline{H}_2C_7$), 6.59 (1H, ddd, $Ar\underline{H}_6$, $^3J_{HH}$ = 6.84 Hz), 6.67 (1H, dd, $Ar\underline{H}_2$, $^3J_{HF}$ = 10.52 Hz), 7.39 (1H, t, $Ar\underline{H}_5$, $^3J_{HH}$ = 8.44 Hz). FT/IR (film/ATR/ZnSe) μ_{max}: 2955, 2924, 2854, 2869, 1604, 1583, 1488, 1467, 1321, 1291, 1166, 1143 cm^{-1}.

1-Bromo-2-fluoro-4-Octyloxybenzene (24) Prepared using a similar procedure to compound **23**. Quantities used: 1-bromooctane (7.58 g, 39.3 mmol), compound **16** (5.00 g, 26.2 mmol), potassium carbonate (7.24 g, 52.4 mmol) and butanone (160 ml). Purified by flash chromatography [fine mesh silica gel: dichloromethane] and then dried *in vacuo* (P_2O_5, 0.2 mbar, RT, 18 hrs) Yield = 9.18 g (>100%); ^{1}H NMR (300MHz, $CDCl_3$, TMS) δ: 0.88 (3H, t, $C\underline{H}_3C_7O$), 1.30 (8H, m, $CH_3C\underline{H}_2C\underline{H}_2C\underline{H}_2C\underline{H}_2C_3O$), 1.42 (2H, m, $C_5C\underline{H}_2CH_2CH_2O$), 1.75 (2H, q, $C_6C\underline{H}_2CH_2O$), 3.89 (2H, t, $C_7C\underline{H}_2O$), 6.58 (1H, ddd, ArC_5-$\underline{H}$, $^3J_{HH}$ = 8.86 Hz), 6.67 (1H, dd, ArC_3-$\underline{H}$, $^3J_{HF}$ = 10.53 Hz), 7.37 (1H, t, ArC_6-$\underline{H}$, $^3J_{HH}$ = 8.46 Hz). ^{13}C NMR (300MHz, $CDCl_3$, TMS) δ: 14.49 ($\underline{C}H_3C_7O$, +ve DEPT), 23.06 ($CH_3\underline{C}H_2C_6O$, -ve DEPT), 29.42 ($C_3\underline{C}H_2C_4O$, -ve DEPT), 29.62 ($C_4\underline{C}H_2C_3O$, -ve DEPT), 29.71 ($C_6\underline{C}H_2CH_2O$, -ve DEPT), 32.20 ($CH_3CH_2\underline{C}H_2C_5O$, -ve DEPT), 68.98 ($C_7\underline{C}H_2O$, -ve DEPT), 99.28 (Ar-$\underline{C}_1$, $\underline{d}$, J_{CF} = 21.5 Hz, no DEPT), 103.64 (Ar-$\underline{C}_3$, $\underline{d}$, J_{CF} = 25.4 Hz, +ve DEPT), 112.28 (Ar-$\underline{C}_5$, $\underline{d}$, J_{CF} = 3.00 Hz, +ve DEPT), 133.60 (Ar-$\underline{C}_6$, $\underline{d}$, J_{CF} = 1.91 Hz, +ve DEPT), 159.84 (Ar-$\underline{C}_2$, $\underline{d}$, J_{CF} = 246.14 Hz, no DEPT), 160.16 (Ar-$\underline{C}_4$, $\underline{d}$, J_{CF} = 9.92 Hz, no DEPT). ^{19}F NMR (282MHz, $CDCl_3$, TMS) δ: -

105.89 (1F, t, ArC_2-F, J_{HF} = 9.30 Hz, collapses to a singlet at -105.89 on decoupling). FT/IR (film/ATR/ZnSe) μ_{max}: - 3383, 3198, 2954, 2856, 1607, 1471, 1397, 1341, 1287, 1267, 1162, 1124 cm^{-1}.

2-Fluoro-4-octyloxyphenylboronic acid (25) Butyllithium (8.0 ml, 2.5 M in hexanes, 20 mmol) was added dropwise *via* syringe and septum to a stirred solution of compound **23** (5.00 g, 16.5 mmol) in dry tetrahydrofuran (150 ml) at –78°C under a dry nitrogen atmosphere. Once this addition had occurred the solution was allowed to stir at this cooled temperature for a further 2 h. To this, trimethylborate (3.58 g, 34.5 mmol) in dry tetrahydrofuran (20ml) was added dropwise ensuring that the temperature did not exotherm over -70°C. The solution was allowed to stir at this cooled temperature for a further hour before being allowed to warm to room temperature overnight. To this now warmed solution 10% (v/v) hydrogen chloride solution (50 ml) was added dropwise and the solution allowed to stir for a further 30 min. The product was extracted by washing with diethyl ether (3 x 75 ml). These extracts were combined, dried ($MgSO_4$), filtered and evaporated to give a brown oil. Dried *in vacuo* (P_2O_5, 0.1mbar, RT, 60 h) to form a brown solid. Yield = 3.99 g (90%); FT/IR (KBr/Drift) μ_{max}: 3509, 3344, 3218, 2943, 2866, 1618, 1573, 1431, 1375, 1289, 1135, 1036, 1003, 851, 791, 659 cm^{-1}.

3-Fluoro-4-octyloxyphenylboronic acid (26) Prepared using a similar procedure to compound **25**. Quantities used: Butyllithium (2 ml, 10.0 M in hexanes, 20 mmol), compound **24** (5.00 g, 16.5 mmol) and dry tetrahydrofuran (150 ml). Dried *in vacuo* (P_2O_5, 0.7mbar, RT, 72 h) to give a brown oil. Yield = 4.82 g (>100%); FT/IR (film/ATR/ZnSe) μ_{max}: 3204, 2925, 2852, 2359, 2334, 1616, 1456, 1430, 1420, 1352, 1323, 1292, 1230, 1125 cm^{-1}.

4-(2'-Fluoro-4'-octyloxyphenyl)-4-bromobenzene (28) This compound was prepared in a manner similar to compound **12**. Quantities used: compound **25** (3.50 g, 13.1 mmol), compound **27** (2.95 g, 10.5 mmol), palladium(0) *tetrakis*(triphenylphosphine) (0.43 g, 0.37 mmol), 2M sodium carbonate (45 ml), and 1,2-dimethoxyethane (70 ml). Purified by flash chromatography [fine mesh silica gel: 5% dichloromethane in hexane] to give a pale oil. Dried *in vacuo* (P_2O_5, 0.1mbar, RT, 72 h) to give a white crystalline solid. Yield = 2.00 g (51%); ^{1}H NMR (300MHz, $CDCl_3$, TMS) δ: 0.89 (3H, t, $C\underline{H}_3C_7O$), 1.33 (8H, m, $CH_3C\underline{H}_2C\underline{H}_2C\underline{H}_2C\underline{H}_2C_3O$), 1.45 (2H, m, $C_5C\underline{H}_2CH_2CH_2O$), 1.78 (2H, q, $C_6C\underline{H}_2CH_2O$), 3.95 (2H, t, $C_7C\underline{H}_2O$), 6.69 (1H, dd, Ar'$C_3\underline{H}$, $^3J_{HF}$ = 12.58 Hz), 6.74 (1H, dd, Ar'$C_5\underline{H}$, $^3J_{HH}$ = 8.58 Hz), 7.28 (1H, t, Ar'$C_6\underline{H}$, $^3J_{HH}$ = 8.8 Hz), 7.37 (2H, dd, $Ar\underline{H}_2/\underline{H}_6$, $^3J_{HH}$ = 8.52 Hz), 7.53 (2H, dd, $Ar\underline{H}_3/\underline{H}_5$, $^3J_{HH}$ = 6.6 Hz). ^{13}C NMR (75MHz, $CDCl_3$, TMS) δ: 14.53 ($\underline{C}H_3C_7O$, +ve DEPT), 23.08 ($CH_3\underline{C}H_2C_6O$, -ve DEPT), 26.41 ($C_5\underline{C}H_2CH_2CH_2O$, -ve DEPT), 29.51 ($C_3\underline{C}H_2C_4O$, -ve

DEPT), 29.65 ($C_4\underline{C}H_2C_3O$, -ve DEPT), 29.74 ($C_6\underline{C}H_2CH_2O$, -ve DEPT), 68.86 ($C_7\underline{C}H_2O$, -ve DEPT), 102.94 (Ar'$\underline{C}_3$, $\underline{d}$, J_{CF} = 26.2 Hz, +ve DEPT), 111.36 (Ar'$\underline{C}_5$, $\underline{d}$, J_{CF} = 3.1 Hz, +ve DEPT), 120.26 (Ar'$\underline{C}_1$, $\underline{d}$, J_{CF} = 13.4 Hz, no DEPT), 121.61 (Ar$\underline{C}_4$, no DEPT), 130.72 (Ar$\underline{C}_2$/$\underline{C}_6$, +ve DEPT) 130.76 (Ar$\underline{C}_2$/$\underline{C}_6$, +ve DEPT), 131.05 (Ar'$\underline{C}_6$, $\underline{d}$, J_{CF} = 4.3 Hz, +ve DEPT), 131.92 (Ar$\underline{C}_3$/$\underline{C}_5$, +ve DEPT), 135.13 (Ar$\underline{C}_1$, $\underline{d}$, J_{CF} = 1.2 Hz, no DEPT), 160.48 (Ar'$\underline{C}_4$, $\underline{d}$, J_{CF} = 10.9 Hz, no DEPT), 160.54 (Ar'$\underline{C}_2$, $\underline{d}$, J_{CF} = 247.9 Hz, no DEPT). ^{19}F NMR (282MHz, $CDCl_3$, TMS) δ: -116.013 (1F, t, Ar'C_2-$\underline{F}$, $^3J_{HF}$ = 9.67 Hz, collapses to singlet at -116.013 on decoupling). FT/IR (KBr/Drift) μ_{max}: 2925, 2860, 1620, 1473, 1460, 1327, 1235, 1129, 1030, 957, 840, 816, 725, 515, 462 cm^{-1}.

4-(3'-Fluoro-4'-octyloxyphenyl)-4-bromobenzene (29) This compound was prepared in a similar manner to compound **12**. Quantities used: compound **26** (4.70 g, 17.5 mmol), compound **27** (3.96 g, 14.0 mmol), palladium(0) *tetrakis*(triphenylphosphine) (0.48 g, 0.42 mmol), 2M sodium carbonate (45 ml) and 1,2-dimethoxyethane (70 ml). Purified using flash chromatography [fine mesh silica gel: hexanes] to give a white solid and recrystallised using hexane. Dried *in vacuo* (P_2O_5, 0.1mbar, RT, 16 h). Yield = 1.39 g (26.2%); ^1H NMR (300MHz, $CDCl_3$, TMS) δ: 0.89 (3H, m, $C\underline{H}_3C_7O$), 1.34 (8H, m, $CH_3C\underline{H}_2C\underline{H}_2C\underline{H}_2C\underline{H}_2C_3O$), 1.45 (2H, m, $C_5C\underline{H}_2CH_2CH_2O$), 1.79 (2H, q, $CH_6C\underline{H}_2CH_2O$), 3.93 (2H, t, $CH_7C\underline{H}_2O$), 6.69 (1H, dd, Ar'C_3-$\underline{H}$, $^3J_{HF}$ = 12.58 Hz), 6.75 (1H, dd, Ar'C_5-$\underline{H}$, $^3J_{HH}$ = 8.37 Hz), 7.27 (1H, t, Ar'C_6-$\underline{H}$, $^3J_{HH}$ = 8.82 Hz), 7.37 (2H, dd, Ar$C_{2/6}$-$\underline{H}$, $^3J_{HH}$ = 6.77 Hz), 7.53 (2H, dd, Ar$C_{3/5}$-$\underline{H}$, $^3J_{HH}$ = 7.53 Hz). ^{13}C NMR (75MHz, $CDCl_3$, TMS) δ: 14.51 ($\underline{C}H_3C_7O$, +ve DEPT), 23.06 ($CH_3\underline{C}H_2C_6O$, -ve DEPT), 26.39 ($C_5\underline{C}H_2CH_2CH_2O$, -ve DEPT), 29.49 ($C_3\underline{C}H_2C_4O$, -ve DEPT), 29.72 ($C_6\underline{C}H_2CH_2O$, -ve DEPT), 32.20 ($CH_3CH_2\underline{C}H_2CH_5O$, -ve DEPT), 68.86 ($C_7\underline{C}H_2O$, -ve DEPT), 102.93 (Ar'-$\underline{C}_3$, $\underline{d}$, J_{CF} = 26.23 Hz, +ve DEPT), 111.36 (Ar'-$\underline{C}_6$, $\underline{d}$, J_{CF} = 3.01 Hz, +ve DEPT), 120.26 (Ar'-$\underline{C}_4$, $\underline{d}$, J_{CF} = 13.55 Hz, no DEPT), 121.59 (Ar-$\underline{C}_4$, no DEPT), 130.72 (Ar-$\underline{C}_2$, +ve DEPT), 130.76 (Ar-$\underline{C}_6$, +ve DEPT), 131.05 (Ar'-$\underline{C}_5$, $\underline{d}$, J_{CF} = 5.35 Hz, +ve DEPT), 131.92 (Ar-$\underline{C}_{3/5}$, +ve DEPT), 135.11 (Ar-$\underline{C}_1$, no DEPT), 160.48 (Ar'-$\underline{C}_1$, $\underline{d}$, J_{CF} = 11 Hz, no DEPT), 160.54 (Ar'-$\underline{C}_2$, $\underline{d}$, J_{CF} = 247.94 Hz, no DEPT). ^{19}F NMR (282MHz, $CDCl_3$, TMS) δ: -116.05 (1F, t, Ar'C_2-$\underline{F}$, $^3J_{HF}$ = 10.2 Hz, collapses to a singlet at -116.05 on decoupling). FT/IR (KBr/Drift) μ_{max}: 2924, 2856, 1619, 1486, 1467, 1327, 1305, 1269, 1234, 1172, 1028, 999, 957, 841, 833, 816 cm^{-1}. GC Analysis (inj = 300 °C, det = 300 °C, Oven = 120 °C hold 0.5min, then 40 °C min^{-1} to 300 °C hold 4min) R_T = 7.02 (97.61 %) min.

4-(2'-Fluoro-4-octyloxyphenyl)phenylboronic acid (30) Prepared using a similar procedure to compound **25**. Quantities used: Butyllithium (2 ml, 2.5 M in hexanes, 5 mmol), compound **28** (1.75 g, 4.62 mmol) and tetrahydrofuran (50 ml). Dried *in vacuo* (P_2O_5, 0.3mbar, RT, 16h) to give a viscous oil. Yield = 1.8 g (>100%); FT/IR (film/ATR/ZnSe) μ_{max}: 3205, 2924, 2855, 1607, 1532, 1477, 1398, 1340, 1309, 1286, 1230, 1161, 1123 cm^{-1}.

4-(3'-Fluoro-4'-octyloxyphenyl)phenylboronic acid (31) Prepared using a similar procedure to compound **25**. Quantities used: Butyllithium (0.5 ml, 10.0 M in hexanes, 5 mmol), compound **29** (1.20 g, 3.17 mmol) and dry tetrahydrofuran (40 ml). Dried *in vacuo* (P_2O_5, 2.0 mbar, RT, 18 h) to give a viscous oil. Yield = 0.83 g (76%) FT/IR (film/ATR/ZnSe) μ_{max}: 3383, 3198, 2954, 2925, 2856, 1607, 1471, 1397, 1341, 1287, 1267, 1162, 1124 cm^{-1}.

4-Octyloxyphenylboronic acid (33) Prepared using a similar procedure to compound **25**. Quantities used: Butyllithium (14.2 ml, 35.5 mmol), compound **32** (10.0 g, 35.1 mmol) and tetrahydrofuran (130ml). Dried *in vacuo* (P_2O_5, RT, 0.5mbar, 16 h).Yield = 8.89 g (>100%); FT/IR (KBr/Drift) μ_{max}: 3204, 3039, 2927, 2854, 1602, 1413, 1368, 1363, 1352, 1306, 1292, 1246, 1171, 838, 745, 688 cm^{-1}.

4-(4'-Octyloxyphenyl)-bromo-2-fluorobenzene (35) This compound was prepared in a manner similar to compound **12**. Quantities used: compound **32** (4.00 g, 16 mmol), compound **34** (4.51 g, 15 mmol), palladium(0) *tetrakis*(triphenylphosphine) (0.58 g, 0.50 mmol), 2M sodium carbonate (50 ml) and 1,2-dimethoxyether (75 ml). Purified by flash chromatography [fine mesh silica gel: hexane] to give a white solid. GC analysis revealed a slight impurity which was removed by flash chromatography [fine mesh silica gel: hexane] to give a white crystalline solid. Dried *in vacuo* (P_2O_5, 0.5mbar, RT, 18 h). Yield = 1.52 g (27%); ^1H NMR (300MHz, $CDCl_3$, TMS) δ: 0.90 (3H, t, $OC_7\underline{CH_3}$), 1.34 (8H, m, $OC_3\underline{CH_2}\underline{CH_2}\underline{CH_2}\underline{CH_2}CH_3$), 1.46 (2H, q, $OC_2\underline{CH_2}C_5$), 1.80 (2H, q, $OCH_2\underline{CH_2}C_6$), 3.99 (2H, t, $O\underline{CH_2}C_7$), 6.96 (2H, dd, Ar'$\underline{H_3}$/$\underline{H_5}$, $^3J_{HH}$ = 6.7 Hz), 7.26 (1H, m, Ar$\underline{H_3}$), 7.32 (2H, m, Ar$\underline{H_5}$/$\underline{H_6}$), 7.43 (2H, dd, Ar'$\underline{H_2}$/$\underline{H_6}$, $^3J_{HH}$ = 8.7 Hz). ^{13}C NMR (75MHz, CDCl3, TMS) δ: 14.12 ($OC_7\underline{C}H_3$, +ve DEPT), 22.67 ($OC_6\underline{C}H_2CH_3$, -ve DEPT), 26.05 ($OC_2\underline{C}H_2C_5$, -ve DEPT), 29.25 ($OC_3\underline{C}H_2\underline{C}H_2C_3$, -ve DEPT), 29.37 ($OCH_2\underline{C}H_2C_6$, -ve DEPT), 31.82 ($OC_5\underline{C}H_2C_2$, -ve DEPT), 68.06 ($O\underline{C}H_2C_7$, -ve DEPT), 114.6 (Ar'-$\underline{C_3}$/$\underline{C_5}$, +ve DEPT), 119.6 (Ar-$\underline{C_3}$, $\underline{d}$, J_{CF} = 26.4 Hz, +ve DEPT), 120.5 (Ar-$\underline{C_1}$, $\underline{d}$, J_{CF} = 9.48 Hz, no DEPT), 126.8 (Ar'-$\underline{C_1}$, $\underline{d}$, J_{CF} = 1.4 Hz, no DEPT), 127.6 (Ar-$\underline{C_5}$, $\underline{d}$, J_{CF} = 3.72 Hz, +ve DEPT), 127.9 (Ar-$\underline{C_4}$, $\underline{d}$, J_{CF} = 4.17 Hz, no DEPT), 129.92 (Ar'-$\underline{C_2}$/$\underline{C_6}$, $\underline{d}$, indistinguishable, +ve DEPT), 131.41 (Ar-$\underline{C_6}$, $\underline{d}$, J_{CF} = 4.17 Hz, +ve DEPT), 159.05 (Ar'-$\underline{C_4}$, no DEPT), 159.43 (Ar-$\underline{C_2}$, $\underline{d}$, J_{CF} = 251.6 Hz, no DEPT). ^{19}F NMR (282MHz, $CDCl_3$, TMS) δ: -115.684 (1F, t, ArC_2-$\underline{F}$, $^3J_{HF}$ = 8.9 Hz, collapses to singlet at -115.684 on decoupling). FT/IR (KBr/Drift) μ_{max}: 3078, 3045, 2925, 2860, 1558, 1527, 1474, 1391, 1250, 1123, 1036, 1010, 863, 821, 738, 572 cm^{-1}.

4-(4'Octyloxyphenyl)-2-fluorophenyl boronic acid (36) Prepared using a similar procedure to compound **25**. Quantities used: Butyllithium (1.38 ml, 2.5M in hexanes, *ca.*, 3.45 mmol), compound **35** (1.30 g, 3.40 mmol) and tetrahydrofuran (100 ml). Dried *in vacuo* (P_2O_5, 0.5 mbar, RT, 18 h), to give a red wax. Yield = 1.12g (95%). FT/IR (KBr/Drift) μ_{max}: 3350, 3204, 2924, 2853, 1607, 1522, 1398, 1374, 1363, 1347, 1253, 1182, 1036, 904, 819, 758, 678 cm^{-1}.

4-(4'-Octyloxyphenyl)-3-fluorobenzene (38) This compound was prepared in a manner similar to compound **12**. Quantities used: compound **33** (4.2 g, 16.8 mmol), compound **37** (2.48 g, 11.2 mmol), palladium(0) *tetrakis*(triphenylphosphine) (0.43 g, 0.37 mmol), 2M sodium carbonate (50 ml) and 1,2-dimethoxyethane (75 ml). Purified by flash chromatography [fine mesh silica gel: hexanes] to give a colourless solid. Recrystallised (hexanes), filtered and dried *in vacuo* (P_2O_5, 0.4 mbar, RT, 5 h). Yield = 1.77 g (53%). ^{1}H NMR (300MHz, $CDCl_3$, TMS) δ: 0.89 (3H, t, $\underline{CH_3}C_7OAr$), 1.30 (8H, m, $\underline{CH_2}$'s), 1.45 (2H, m, $\underline{CH_2}$), 1.80 (2H, q, $\underline{CH_2}$), 3.98 ($ArOC\underline{H_2}C_7$), 6.96 (3H, dd, Ar-$\underline{H}_{2/6}$ and Ar-$\underline{H}_{2'}$, $^3J_{HH}$ 6.85 Hz), 7.24 (1H, dd, Ar-$\underline{H}_{4'}$, $^3J_{HF}$ 10.20 Hz), 7.33 (2H, m, Ar-$\underline{H}_{5'/6'}$), 7.48 (2H, dd, Ar-$\underline{H}_{3/5}$, $^3J_{HH}$ 6.65 Hz). ^{13}C NMR (75MHz, $CDCl_3$, TMS) δ: 14.18 ($ArOC_7\underline{C}H_3$), 22.73 ($ArOC_6\underline{C}H_2CH_3$, -ve DEPT), 26.12, 29.32, 29.43 ($\underline{CH_2}$'s, -ve DEPT), 31.89 ($ArOCH_2\underline{C}H_2C_6$, -ve DEPT), 68.14 ($ArO\underline{C}H_2C_7$, -ve DEPT), 113.34, 113.50 (Ar-$\underline{C}_{2'}$ or $\underline{C}_4$, d, J_{CF} 21.14 Hz and 21.93 Hz, +ve DEPT), 114.88 (Ar-$\underline{C}_{3/5}$, +ve DEPT), 122.28 (Ar-$\underline{C}_{6'}$, d, J_{CF} 2.72 Hz, +ve DEPT), 128.12 (Ar-$\underline{C}_{2/6}$, +ve DEPT), 130.16 (Ar-$\underline{C}_{5'}$, d, J_{CF} 8.36 Hz, +ve DEPT), 132.20 (Ar-$\underline{C}_1$, d, J_{CF} 2.18 Hz, no DEPT), 143.21 (Ar-$\underline{C}_{1'}$, J_{CF} 7.59 Hz, no DEPT), 159.18 (Ar-$\underline{C}_4$, no DEPT), 163.26 (Ar-$\underline{C}_3$, d, J_{CF} 245.20 Hz, no DEPT). ^{19}F NMR (282MHz, $CDCl_3$, TMS) δ: -113.66 (1F, dt, $^3J_{HF}$ 9.51 Hz, collapses to a singlet at -113.66 on decoupling). FT/IR (KBr/Drift) μ_{max}: 3072, 3039, 2954, 2933, 2856, 1590, 1521, 1473, 1291, 1265, 1188, 1123, 1036, 884, 835, 785, 692, 612, 533 cm^{-1}.

4-(4-Octyloxyphenyl)-3-fluorophenylboronic Acid (39) Prepared using a similar procedure to compound **25**. Quantities used: Butyllithium 2.02 ml, 2.5 M in hexanes, *ca.* 5.05 mmol), compound **38** (1.5 g, 5.00 mmol), trimethyl borate (1.04 g, 10.0 mmol) and dry tetrahydrofuran (115 ml). Dried *in vacuo* (P_2O_5, 0.6 mbar, RT, 18 h) to give a colourless solid. Yield = 1.61 g (94%). FT/IR (KBr/Drift) μ_{max}: 3211, 2955, 2922, 2857, 1590, 1522, 1488, 1473, 1447, 1394, 1291, 1265, 1191, 1123, 1030, 835, 785 cm^{-1}.

EXAMPLE 4

1,2-(S)-Dipentoxy-(4''-octyloxyterphenyl-3-fluoro-4-oxy)butane (40) This compound was prepared in a manner similar to compound **12**. Quantities used: Compound **11** (2.50 g, 7.7 mmol), compound **21** (2.14 g, 5.1 mmol), palladium(0) *tetrakis*(triphenylphosphine) (0.20 g, 0.17mmol), 2M sodium carbonate (25 ml) and 1,2-dimethoxyethane (35 ml). Purified by flash chromatography [fine mesh silica gel: 1:1 hexanes-dichloromethane] to give a v pale yellow solid. This was further purified [fine mesh silica gel: 5% ethyl acetate in hexanes] to give a white crystalline solid. This was further purified by flash chromatography [fine mesh silica gel: 4% ethyl acetate in hexane], then again [fine mesh silica gel: 4% ethyl acetate in hexanes] to give a white solid. This was further purified by recrystallisation, (hexanes x 4). Dried *in vacuo* (P_2O_5, RT, 0.1 mbar, 18 h). Yield = 0.25g, (8%). ^{1}H NMR (300MHz, $CDCl_3$, TMS) δ: 0.87 (9H, m, $OC_4C\underline{H}_3$'s + $ArOC_7C\underline{H}_3$), 1.31 (16H, m, $OC_2C\underline{H}_2C\underline{H}_2CH_3$'s + $ArOC_3C\underline{H}_2C\underline{H}_2C\underline{H}_2C\underline{H}_2CH_3$), 1.46 (2H, m, $ArOC_2C\underline{H}_2C_5$), 1.58 (4H, m, $OCH_2C\underline{H}_2C_3$'s), 1.81 (2H, q, $ArOCH_2C\underline{H}_2C_6$), 1.98 (1H, m, $ArOCH_2C\underline{H}_2{}^*CH$), 2.08 (1H, m, $ArOCH_2C\underline{H}_2{}^*CH$), 3.44 (4H, m, $OC\underline{H}_2C_4$'s), 3.50 (1H, m, $^*CHC\underline{H}_2OC_5$), 3.66 (1H, m, $^*CHC\underline{H}_2OC_5$), 3.73 (1H, m, $ArOCH_2CH_2{}^*C\underline{H}$), 3.99 (2H, t, $ArOC\underline{H}_2C_7$), 4.21 (2H, m, $ArOC\underline{H}_2CH_2{}^*CH$), 6.98 (2H, d, Ar'-$\underline{H}_3/\underline{H}_5$, $^3J_{HH}$ = 8.74 Hz), 7.05 (1H, t, Ar''-$\underline{H}_5$, $^3J_{HH}$ = 8.5 Hz), 7.35 (2H, dd, Ar''-$\underline{H}_2/\underline{H}_6$, $^3J_{HF}$ = 10.70 Hz), 7.55 (2H, m, Ar'-H_2/H_6, $^3J_{HH}$ = 8.68 Hz), 7.60 (4H, m, Ar-$\underline{H}_2/\underline{H}_3/\underline{H}_5/\underline{H}_6$). ^{13}C NMR (75MHZ, $CDCl_3$, TMS) δ: 14.09 ($OC_4\underline{C}H_3$'s + $ArOC_7\underline{C}H_3$, +ve DEPT), 22.59 ($OC_3\underline{C}H_2CH_3$'s + $ArOC_6\underline{C}H_2CH_3$, -ve DEPT), 26.07 ($ArOC_2\underline{C}H_2C_5$, -ve DEPT), 28.32 → 29.38 ($\underline{C}H_2$'s, -ve DEPT), 29.81 ($OCH_2\underline{C}H_2C_3$'s, -ve DEPT), 31.83 ($ArOCH_2\underline{C}H_2C_6$, -ve DEPT), 31.93 ($ArOCH_2\underline{C}H_2{}^*CH$, -ve DEPT), 65.85 ($ArO\underline{C}H_2CH_2{}^*CH$, -ve DEPT), 68.07 ($ArO\underline{C}H_2C_7$, -ve DEPT), 70.43 ($O\underline{C}H_2C_4$'s, -ve DEPT), 72.38 ($^*CH\underline{C}H_2OC_5$, -ve DEPT), 75.04 ($ArOCH_2CH_2{}^*\underline{C}H$, +ve DEPT), 114.57 (Ar''-$\underline{C}_2$, $\underline{d}$, J_{CF} = 19.16 Hz, +ve DEPT), 114.80 (Ar'-$\underline{C}_2/\underline{C}_5$, +ve DEPT), 114.94 (Ar''-$\underline{C}_5$, $\underline{d}$, J_{CF} = 2.03 Hz, +ve DEPT), 122.40 (Ar''-$\underline{C}_6$, $\underline{d}$, J_{CF} = 3.18 Hz, +ve DEPT), 126.97 (Ar'-$\underline{C}_2/\underline{C}_6$, +ve DEPT), 127.94 (Ar-$\underline{C}_2/\underline{C}_3/\underline{C}_5/\underline{C}_6$, +ve DEPT), 132.97 (Ar'-$\underline{C}_1$, no DEPT), 133.87 (Ar''-$\underline{C}_1$, $\underline{d}$, J_{CF} = 6.48 Hz, no DEPT), 137.93 (Ar-$\underline{C}_1$, no DEPT), 139.66 (Ar-$\underline{C}_4$, no DEPT), 146.4 (Ar''-$\underline{C}_4$, $\underline{d}$, J_{CF} = 10.86 Hz, no DEPT), 152.80 (Ar''-$\underline{C}_3$, $\underline{d}$, J_{CF} = 245.4 Hz, no DEPT), 158.8 (Ar'-$\underline{C}_4$, no DEPT). ^{19}F NMR (282MHz, CDCl3, TMS) δ: -134.71 (1F, t, Ar''C_3-$\underline{F}$, $^3J_{HF}$ = 8.54 Hz, collapses to singlet at –134.71 on decoupling). FT/IR (KBr/Drift) μ_{max}: 2955, 2928, 2860, 1506, 1497, 1466, 1300, 1273, 1244, 1135, 1118, 831, 806cm^{-1}. UV/Vis (0.005g, $CHCl_3$) λ_{max}: 292 (0.8486) nm. HPLC analysis (C18 column; 1 ml min^{-1} 95:5 acetonitrile-tetrahydrofuran) R_T = 26.93 (98.83%) min.

EXAMPLE 5

1,2-(S)-Dipentoxy-(4''-octyloxyterphenyl-2-fluoro-4-oxy)butane (41) This compound was prepared in a manner similar to compound **12**. Quantities used: compound **11** (2.34 g, 7.2 mmol), compound **22** (2.00 g, 4.7 mmol), palladium(0) *tetrakis*(triphenylphosphine) (0.17 g, 0.14 mmol), 2M sodium carbonate (20 ml) and 1,2-dimethoxyethane (30 ml). Purified by flash chromatography [fine mesh silica gel, 1:1 hexanes-chloromethane then to give a pale yellow oil, which was further purified by flash chromatography [fine mesh silica gel: % ethyl acetate in hexanes] to give a viscous colourless fluid. Purified again [fine mesh silica gel: 1:1 hexanes-chloromethane] to give a viscous colourless fluid. Dried *in vacuo* (P_2O_5, RT, 0.1 mbar, 18 h). Yield = 1.06g (36%). ^{1}H NMR (300MHz, $CDCl_3$, TMS) δ: 0.88 (9H, m, $OC_7C\underline{H}_3$ + $OC_4C\underline{H}_3$), 1.45 (22H, m, $OCH_2C\underline{H}_2C\underline{H}_2C\underline{H}_2CH_3$ + $OCH_2CH_2C\underline{H}_2C\underline{H}_2C\underline{H}_2C\underline{H}_2C\underline{H}_2CH_3$), 1.81 (2H, q, $OCH_2C\underline{H}_2C_6$), 2.03 (2H, m, $OCH_2C\underline{H}_2CH^*$), 3.47 (4H + 1H, m, $^*CHC\underline{H}_2OC_5$ + $OC\underline{H}_2C_4$), 3.66 (1H + 1H, $OCH_2CH_2C\underline{H}^*$ + $^*CHC\underline{H}_2OC_5$), 4.00 (2H, t, $OC\underline{H}_2C_7$), 4.12 (2H, m, $OC\underline{H}_2CH_2CH^*$), 6.75 (2H, m, Ar''$H_5/H_6$), 6.98 (2H, m, Ar H_3/H_5), 7.38 (1H, t, Ar''H_3), 7.58 (6H, m, Ar H_2/H_6 + Ar'$H_2/H_3/H_5/H_6$). ^{13}C NMR (75MHz, $CDCl_3$, TMS) δ: 14.42, 14.45, 14.50 ($OC_7\underline{C}H_3$,+ve DEPT + $OC_4\underline{C}H_3$, +ve DEPT) 22.90, 22.92, 23.06 ($OC_6\underline{C}H_2CH_3$, -ve DEPT + $OC_3\underline{C}H_2CH_3$, -ve DEPT), 26.46→32.33 (CH_2's, -ve DEPT), 30.22 ($OCH_2\underline{C}H_2CH^*$, -ve DEPT), 65.21 ($O\underline{C}H_2CH_2CH^*$, -ve DEPT), 68.48 ($O\underline{C}H_2C_7$, -ve DEPT), 70.87 ($^*CH\underline{C}H_2OC_5$, -ve DEPT), 72.09, 73.52 ($O\underline{C}H_2C_4$, -ve DEPT), 75.51 ($OCH_2CH_2\underline{C}H^*$, +ve DEPT), 102.96 (Ar-$\underline{C}_3$'', d, J_{CF} = 25 Hz, +ve DEPT), 111.21 (Ar-$\underline{C}_5$'', d, J_{CF} = 3.6 Hz, +ve DEPT), 115.9 (Ar-$\underline{C}_3$'/$\underline{C}_5$', +ve DEPT), 121.25 (Ar-$\underline{C}_1$'', d, J_{CF} = 13.1 Hz, no DEPT), 127.05 (Ar-$\underline{C}_2/\underline{C}_3/\underline{C}_5/\underline{C}_6$, +ve DEPT), 128.40 (Ar-$\underline{C}_2$'/$\underline{C}_6$', +ve DEPT), 129.45 (Ar-$\underline{C}_6$'', d, J_{CF} = 3 Hz, +ve DEPT), 131.20 (Ar-$\underline{C}_4$, no DEPT), 134.47 (Ar-$\underline{C}_1$', no DEPT), 134.97 (Ar-$\underline{C}_1$, no DEPT), 159.17 (Ar-$\underline{C}_4$', no DEPT), 160.01 (Ar C_4'', d, J_{CF} = 10 Hz, no DEPT), 160.72 (Ar C_2'', d, J_{CF} = 245.4 Hz, no DEPT). ^{19}F NMR (282 MHz, $CDCl_3$, TMS) δ: 115.99 (1F, t, Ar C_2''-$\underline{F}$, J_{HF} = 10.71 Hz, collapses to singlet at -115.99 on decoupling). FT/IR (Film/ATR/ZnSe) μ_{max}: -3853, 3744, 3648, 2954, 2929, 2857, 2361, 2336, 1666, 1560, 1491, 1295, 1249, 1123, 831, 818 cm^{-1}. UV/Vis (0.005g, $CHCl_3$) λ_{max}: 291.00 (1.1738) nm. HPLC analysis (C18 column; 1 ml min^{-1} 95:5 acetonitrile-tetrahydrofuran) R_T = 26.09 (99.95%) min.

EXAMPLE 6

1,2-(S)-Dipentoxy-(2''-fluoro-4''-octyloxyterphenyl-4-oxy)butane (42) This compound was prepared in a manner similar to compound **12**. Quantities used: compound **30** (1.60 g, 4.65 mmol), compound **8a** (1.49 g, 3.72 mmol), palladium(0) *tetrakis*(triphenylphosphine) (0.18 g, 0.15 mmol), 2M sodium carbonate (25 ml) and 1,2-dimethoxyethane (30 ml). Purified by flash chromatography [fine mesh silica gel: 1:1 hexanes:dichloromethane] to give a pale yellow solid. Further purification [fine mesh silica gel: 10% ethyl acetate in hexanes] (twice) gave a white crystalline solid which was recrystallised (ethanol x 2) and dried *in vacuo* (P_2O_5, 0.3 mbar, 40°C, 16 h) to give a white crystalline solid. Yield = 0.56 g, (24%). ^{1}H NMR (300MHz, $CDCl_3$, TMS) δ: 0.88 (9H, m, $OC_4C\underline{H}_3$'s + $ArOC_7C\underline{H}_3$), 1.31 (16H, m, $OC_2C\underline{H}_2C\underline{H}_2CH_3$'s + $ArOC_3C\underline{H}_2C\underline{H}_2C\underline{H}_2C\underline{H}_2CH_3$), 1.46 (2H, m, $ArOC_2C\underline{H}_2C_5$), 1.59 (4H, m, $OCH_2C\underline{H}_2C_3$'s), 1.80 (2H, q, $ArOCH_2C\underline{H}_2C_6$), 1.95 (1H, m, $ArOCH_2C\underline{H}_2{}^*CH$), 2.04 (1H, m, $ArOCH_2C\underline{H}_2{}^*CH$), 3.47

(4H + 1H, m, $OC\underline{H}_2C_4$'s + $*CHC\underline{H}_2OC_5$), 3.64 (1H, m, $*CHC\underline{H}_2OC_5$), 3.70 (1H, m, $ArOCH_2CH_2*C\underline{H}$), 3.97 (2H, t, $ArOC\underline{H}_2C_7$), 4.14 (2H, m, $ArOC\underline{H}_2CH_2*CH$), 6.72 (1H, dd, Ar'$H_3$, $^3J_{HF}$ = 12.54 Hz), 6.77 (1H, dd, Ar'H_5, $^3J_{HH}$ = 8.47 Hz), 6.99 (2H, dd, Ar''H_3/H_5, $^3J_{HH}$ = 6.96 Hz), 7.38 (1H, t, Ar'H_6, $^3J_{HH}$ = 8.8 Hz), 7.58 (4H + 2H, m, $ArH_2/H_3/H_5/H_6$ + Ar''H_2/H_6). ^{13}C NMR (75MHz CDCl3, TMS) δ: 14.09($OC_4\underline{C}H_3$'s + $ArOC_7\underline{C}H_3$, +ve DEPT), 22.59 ($OC_3\underline{C}H_2CH_3$'s + $ArOC_6\underline{C}H_2CH_3$, -ve DEPT), 26.01 ($ArOC_2\underline{C}H_2C_5$, -ve DEPT), 28.34 ($\underline{C}H_2$'s, -ve DEPT), 29.13 ($ArOCH_2\underline{C}H_2C_6$, -ve DEPT), 29.32 ($\underline{C}H_2$'s, -ve DEPT), 29.84 ($OCH_2\underline{C}H_2C_3$'s, -ve DEPT), 31.82 ($\underline{C}H_2$'s, -ve DEPT), 32.04 ($ArOCH_2\underline{C}H_2*CH$, -ve DEPT), 64.6 ($ArO\underline{C}H_2CH_2*CH$, -ve DEPT), 68.4 ($ArO\underline{C}H_2C_7$, -ve DEPT), 70.5 ($*CH\underline{C}H_2OC_5$, -ve DEPT), 72.44 ($O\underline{C}H_2C_4$'s, -ve DEPT), 75.23 ($ArOCH_2CH_2*\underline{C}H$, +ve DEPT), 102.49 (Ar'-$\underline{C}_3$, d, J_{CF} = 26.52 Hz, +ve DEPT), 110.84 (Ar'-$\underline{C}_5$, d, J_{CF} = 3.01 Hz, +ve DEPT), 114.78 (Ar''-$\underline{C}_3/\underline{C}_5$, +ve DEPT), 120.72 (Ar'-$\underline{C}_1$, d, J_{CF} = 13.65 Hz, no DEPT), 126.65 (Ar-$\underline{C}_3/\underline{C}_5$, +ve DEPT), 128.01 (Ar''-$\underline{C}_2/\underline{C}_6$, +ve DEPT), 129.06 (Ar-$\underline{C}_2/\underline{C}_6$, d, indistinguishable, +ve DEPT), 130.79 (Ar'-$\underline{C}_6$, d, J_{CF} = 5.44 Hz, +ve DEPT), 133.09 (Ar''-$\underline{C}_1$, no DEPT), 134.1 (Ar-$\underline{C}_1$, d, J_{CF} = 1.5 Hz, no DEPT), 139.54 (Ar-$\underline{C}_4$, no DEPT), 158.63 (Ar''-$\underline{C}_4$, no DEPT), 159.74 (Ar'-$\underline{C}_4$, d, J_{CF} = 10.91 Hz, no DEPT), 160.32 (Ar'-$\underline{C}_2$, d, J_{CF} = 247.38 Hz, no DEPT). ^{19}F NMR (282MHz, CDCl3, TMS) δ: -116.00 (1F, t, Ar'C_2-$\underline{F}$, $^3J_{CF}$ = 10.73 Hz, collapses to a singlet at –116.00 on decoupling). FT/IR (KBr/Drift) μ_{max}: 2932, 2867, 1625, 1494, 1474, 1329, 1292, 1251, 1181, 1115, 841, 812 cm^{-1}. UV/Vis (0.005g, $CHCl_3$) λ_{max}: 291.5 (0.9197) nm. HPLC analysis (C18 column; 1 ml min^{-1} 95:5 acetonitrile-tetrahydrofuran) R_T = 29.77 (99.66%) min.

EXAMPLE 7

1,2-(S)-Dipentoxy-(3''-fluoro-4''-octyloxyterphenyl-4-oxy)butane (43) This compound was prepared in a manner similar to compound **12**. Quantities used: compound **31** (0.75 g, 2.20 mmol), compound **8a** (0.70 g, 1.74 mmol), palladium(0) *tetrakis*(triphenylphosphine) (0.09 g, 0.07 mmol), 2M Sodium Carbonate (15ml) and 1,2-dimethoxyethane (20 ml). Purified by flash chromatography [Fine mesh silica gel: 6:4 hexane-dichloromethane] to give a pale oil. This was further purified by flash chromatography [fine mesh silica gel: 5% ethyl acetate in hexane] to give a white crystalline solid. This was further purified by repeated flash chromatography [fine mesh silica gel: 5% ethyl acetate in hexane] to give a viscous white liquid, then fine mesh silica gel: 6:4 hexane-dichloromethane and finally fine mesh silica gel: 12.5% diethyl ether in hexane. The resultant solid was then purified by repeated recrystallisation (ethanol x 3) to give a white crystalline solid. Dried *in vacuo* (P_2O_5, 0.2mbar, RT, 48 h). Yield = 0.10g (10%). ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ: 0.87 (9H, m, $OC_4C\underline{H}_3$ + $OC_7C\underline{H}_3$), 1.29 (16H, m, $OC_2C\underline{H}_2C\underline{H}_2CH_3$ + $OC_3C\underline{H}_2C\underline{H}_2C\underline{H}_2C\underline{H}_2CH_3$), 1.52 (6H, m, $OC_2C\underline{H}_2C_5$ + $OCH_2C\underline{H}_2C_3$), 1.80 (2H, q, $OCH_2C\underline{H}_2C_6$), 1.95 (1H, m, $ArOCH_2C\underline{H}_2*CH$), 2.05 (1H, m, $ArOCH_2C\underline{H}_2*CH$), 3.46 (4H + 1H, m, $O\underline{CH_2}C_4$ + *$CHC\underline{H_2}OC_5$), 3.67 (1H + 1H, m, $ArOCH_2CH_2$*$C\underline{H}$ + *$CHC\underline{H_2}OC_5$), 3.98 (2H, t, $OC\underline{H_2}C_7$), 4.14 (2H, m, $ArOC\underline{H_2}CH_2$*CH), 6.72 (1H, dd, Ar'-$\underline{H}_2$, $^3J_{HF}$ = 12.56 Hz), 6.77 (1H, dd, Ar'-$\underline{H}_5$, $^3J_{HH}$ = 8.49 Hz), 6.99 (2H, m, Ar''-$\underline{H}_3$/$\underline{H}_5$, $^3J_{HH}$ = 8.77 Hz), 7.38 (1H, t, Ar'-$\underline{H}_6$, $^3J_{HH}$ = 8.82 Hz), 7.58 (6H, m, Ar-$\underline{H}_2$,/$\underline{H}_3$/$\underline{H}_5$/$\underline{H}_6$, + Ar''-$\underline{H}_2$/$\underline{H}_6$, $^3J_{HH}$ = 8.84 Hz). 13C NMR (75 MHz, $CDCl_3$, TMS) δ: 14.48 ($OC_4\underline{C}H_3$ + $OC_7\underline{C}H_3$, +ve DEPT), 22.98 ($\underline{C}H_2$'s, -ve DEPT), 26.41 ($OCH_2CH_2\underline{C}H_2C_5$, -ve DEPT), 28.74 ($\underline{C}H_2$'s, -ve DEPT), 29.53 ($OCH_2\underline{C}H_2C_5$, -ve DEPT), 29.71 ($\underline{C}H_2$'s, -ve DEPT), 30.24 ($OCH_2\underline{C}H_2C_3$, -ve DEPT), 32.21 ($ArOCH_2\underline{C}H_2$*CH, -ve DEPT), 64.83 ($ArO\underline{C}H_2CH_2$*CH, -ve DEPT), 68.83 ($O\underline{C}H_2C_7$, -ve DEPT), 70.88 (*$CH\underline{C}H_2OC_5$, -ve DEPT), 72.85 ($O\underline{C}H_2C_4$, -ve DEPT), 75.65 ($ArOCH_2CH_2$*$\underline{C}H$, +ve DEPT), 102.91 (Ar'-$\underline{C}_2$, $\underline{d}$, J_{CF} = 26.34 Hz, +ve DEPT), 111.25 (Ar'-$\underline{C}_5$, $\underline{d}$, J_{CF} = 3.00 Hz, +ve DEPT), 115.19 (Ar''-$\underline{C}_5$, +ve DEPT), 121.14 (Ar'-$\underline{C}_1$, $\underline{d}$, J_{CF} = 13.67 Hz, no DEPT), 127.05 (Ar-$\underline{C}_2$/$\underline{C}_5$, +ve DEPT), 128.41 (Ar''-$\underline{C}_2$/$\underline{C}_6$, +ve DEPT), 129.46 (Ar-$\underline{C}_2$/$\underline{C}_6$, +ve DEPT), 131.19 (Ar'-$\underline{C}_6$, $\underline{d}$, J_{CF} = 5.16 Hz, +ve DEPT), 134.5 (Ar''-$\underline{C}_1$, no DEPT), 139.9 (Ar-$\underline{C}_1$, no DEPT), 159.03 (Ar''-$\underline{C}_4$, no DEPT), 160.15 (Ar'-$\underline{C}_3$, $\underline{d}$, J_{CF} = 247.1 Hz, no DEPT), 160.73 (Ar'-$\underline{C}_4$, $\underline{d}$, J_{CF} = 10.91 Hz, no DEPT). ^{19}F NMR (282MHz, $CDCl_3$, TMS) δ: –116.02 (1F, t, Ar'C_3-$\underline{F}$, $^3J_{HF}$ = 10.8 Hz, collapses to singlet at –116.02 ppm on decoupling). FT/IR (KBr/Drift) μ_{max}: 2951, 2858, 1633, 1494, 1475, 1466, 1288, 1251, 1116, 838, 812 cm^{-1}. UV/Vis (0.005g, $CHCl_3$) λ_{max}: 291.50 (0.5916) nm. HPLC analysis (C18 column; 1 ml min^{-1} 95:5 acetonitrile-tetrahydrofuran) R_T = 28.29 (100%) min.

EXAMPLE 8

1,2-(S)-Dipentoxy-(2'-fluoro-4''-octyloxyterphenyl-4-oxy)butane (45) This compound was prepared in a manner similar to compound **12**. Quantities used: compound **36** (1.0 g, 3.00 mmol), compound **8a** (0.8 g, 2.00 mmol), palladium(0) *tetrakis*(triphenylphosphine) (0.08 g, 0.07 mmol), 2M sodium carbonate (20 ml) and 1,2-dimethoxyethane (30 ml) under a dry nitrogen atmosphere. This was purified by flash chromatography [fine mesh silica gel, 1:1 hexane to dichloromethane] to give a pale yellow oil. A further column was then run [fine mesh silica gel, 1:1 hexane to dichloromethane to give a pale oil. This was further purified [fine mesh silica gel, 25% hexane in dichloromethane] to give a colourless oil. This was further purified by [fine mesh silica gel, 5% ethyl acetate in hexane] to give a white liquid crystal. Recrystallised [ethanol x 2, -78 °C] and then dried *in vacuo* (P_2O_5, 0.3 mbar, RT, 16 h). Yield = 0.07 g (6%). ^1H NMR (300 MHz, $CDCl_3$, TMS) δ: 0.88 (9H, m, $ArOC_7C\underline{H_3}$ + $OC_4C\underline{H_3}$'s), 1.30 (16H, m, $ArOC_3C\underline{H_2}C\underline{H_2}C\underline{H_2}C\underline{H_2}CH_3$ + $OC_2C\underline{H_2}C\underline{H_2}CH_3$'s), 1.47 (2H, m, $ArOC_2C\underline{H_2}C_5$), 1.57 (4H, m, $OCH_2C\underline{H_2}C_3$'s), 1.81 (2H, q, $ArOCH_2C\underline{H_2}C_6$), 1.95 (1H, m, $ArOCH_2C\underline{H_2}$*CH), 2.05 (1H, m, $ArOCH_2C\underline{H_2}$*CH), 3.46 (4H + 1H, m, $OC\underline{H_2}C_4$'s + *$CHC\underline{H_2}OC_5$), 3.68 (1H + 1H, m, *$CHC\underline{H_2}OC_5$ + $ArOCH_2CH_2$*$C\underline{H}$), 4.00 (2H, t, $ArOC\underline{H_2}C_7$), 4.14 (2H, m, $ArOC\underline{H_2}CH_2$*CH), 6.98 (2H, d, Ar$\underline{H}_3$/$\underline{H}_5$ + Ar''$\underline{H}_3$/$\underline{H}_5$, $^3J_{HH}$ = 8.82 Hz), 6.99 (2H, d, Ar$\underline{H}_3$/$\underline{H}_5$ + Ar''$\underline{H}_3$/$\underline{H}_5$, $^3J_{HH}$ = 8.78 Hz), 7.33 (1H, dd, Ar'$\underline{H}_3$, $^3J_{HF}$ = 12.21 Hz), 7.38 (1H, dd, Ar'$\underline{H}_5$, $^3J_{HH}$ = 8.01 Hz), 7.45 (1H, t, Ar'$\underline{H}_6$, $^3J_{HH}$ = 8.05 Hz), 7.52 (2H, dd, Ar''$\underline{H}_2$/$\underline{H}_6$), 7.54 (2H, dd, Ar$\underline{H}_2$/$\underline{H}_6$). ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ: 14.05, 14.07, 14.13, (ArOC$_7\underline{C}H_3$ + OC$_4\underline{C}H_3$'s, +ve DEPT), 22.51, 22.54, 22.67 (ArOC$_6\underline{C}H_2CH_3$ + OC$_3\underline{C}H_2CH_3$, -ve DEPT), 26.07, 28.34, 29.27, 29.38, 29.84, 31.83 ($\underline{C}H_2$'s, -ve DEPT), 32.03 (ArOCH$_2\underline{C}H_2$*CH, -ve DEPT), 64.46 (ArO$\underline{C}H_2CH_2$*CH, -ve DEPT), 68.04 (ArO$\underline{C}H_2C_7$, -ve DEPT), 70.49, 71.68 (O$\underline{C}H_2C_4$, -ve DEPT), 73.19 (*CH$\underline{C}H_2OC_5$, -ve DEPT), 75.21 (ArOCH$_2CH_2$*$\underline{C}$H, +ve DEPT), 113.98 (Ar'C_3, d, J_{CF} = 23.86 Hz, +ve DEPT), 114.49, 114.80 (Ar$\underline{C}_3$/$\underline{C}_5$ + Ar''$\underline{C}_3$/$\underline{C}_5$, indistinguishable doublet), 122.32 (Ar'C_5, d, J_{CF} = 2.9 Hz, +ve DEPT), 126.7 (Ar'C_1, d, J_{CF} = 13.26 Hz, no DEPT), 127.69 (Ar''C_1, broad singlet, no DEPT), 127.91 (ArC_2/C_6, +ve DEPT), 129.99 (Ar''C_2/C_6, indistinguishable doublet, J_{CF} = 2.96 Hz, +ve DEPT), 130.59 (Ar'C_6, d, J_{CF} = 4.21 Hz, +ve DEPT), 131.93 (ArC_1, no DEPT), 141.34 (Ar'C_4, d, J_{CF} = 8.1 Hz, no DEPT), 158.75, 158.96 (Ar''C_4/ArC_4, indistinguishable doublet, no DEPT), 159.99 (Ar'C_2, d, J_{CF} = 246.4 Hz, no DEPT). ^{19}F NMR (282 MHz, $CDCl_3$, TMS) δ: -118.62 (1F, dd, Ar'C_2-$\underline{F}$, $^3J_{HF}$ = 11.83 Hz, collapses to a singlet at –118.62 on decoupling). FT/IR (film/ATR/ZnSe) μ_{max}: 2954, 2927, 2856, 1609, 1545, 1487, 1468, 1292, 1247, 1180, 1111, 1045, 817 cm^{-1}. UV/Vis (0.005 g, $CHCl_3$) λ_{max}: 294.0 (0.4512) nm. HPLC analysis (C18 column; 1 ml min^{-1} 95:5 acetonitrile-tetrahydrofuran) RT = 29.01 (99.02%) min.

The present invention will now be described in further detail and with reference to the accompanying drawings in which:-

Figure 1 is a cooling DSC scan for compound 13a,

Figure 2 is a pitch length – temperature dependence graph for compounds 13a, 41, 42, 43 and 45, and

Figure 3 is a schematic section through an electro-optical liquid crystal device according to the present invention.

Liquid Crystal Behaviour

A. 1,*(S)*-2-(4"-Octyloxyterphenyl-4-oxy)dialkoxybutanes (Examples 1 to 3)

All three of compounds **12**, **13a**, and **14** showed complicated and unique liquid-crystalline behaviour and were characterised by optical microscopy and differential scanning calorimetry, the results are listed in table 1 below. Although all the materials show enantiotropic liquid-crystalline phase behaviour, the phase behaviour of the three Examples is best described on cooling from the isotropic liquid:-

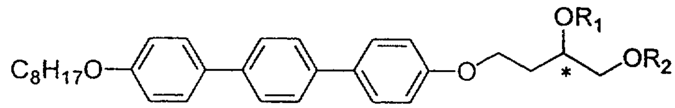
Example 1: Cooling compound **12** from the isotropic liquid results in the formation of shimmering grey focal-conic fans which rapidly give way to homeotropic black texture *via* a highly mobile filaments (vermis-like), the appearance of which suggests a transition sequence of I-TGB A^*-$S_A{}^*$. On continued cooling of the homeotropic texture to 176.5 °C, highly mobile, grey circular domains appear which quickly coalesce to form a conventional *schlieren* $S_C{}^*$ texture containing 4-brush singularities. The sample crystallises at 161.1 °C. DSC analysis of this material confirms the presence of these events which are clearly resolved during a cooling scan rate of 1 °C min^{-1}. This material is believed to show a I-TGB A^*-S_A-TGB C^*-$S_C{}^*$-K phase sequence, which has been observed previously in a number of other unrelated chiral materials (A. Bouchta et. al., **Liquid Crystals**, 1992, **12(4)**, 575; H.T. Nguyen et al. **J. Phys. II France,** 1992, **2**, 1889; L. Navailles et. al., **Liquid Crystals**, 1993, **15(4)**, 479; N. Isaert et. al., **J. Phys. II France**, 1994, 4, 1501; and A. Bouchta at al., **J. Mater. Chem.**, 1995, **5(2)**, 2079). The presence of the two TGB phases is confirmation of the highly twisting nature of this material.

Example 2: Cooling compound **13a** from the isotropic liquid gives way to the formation of blue-green platelets at 118.4 °C which rapidly give way to a *pseudo*-focal conic texture. If the cover slip is mechanically disturbed the material briefly adopts a planar *Grandjean* type texture before reverting to the undisturbed form, clearly confirming this as a nematic phase. Further cooling to around 111.2 °C results in the formation of a highly coloured planar texture of a smectic C^* phase. If the hot stage is held just on the transition then fine filaments (or vermis) are seen penetrating the $S_C{}^*$ texture from the undisturbed N^* state. This is believed to be a TGB C^* phase and exists only for a range of approximately 0.4 °C. Further cooling of the $S_C{}^*$ phase results in the formation of a higher order smectic phase (denoted $S_X{}^*$) before crystallisation occurs. Surprisingly, all of these phase transitions are observed during DSC analysis (Fig 1); at a cooling scan rate of 1 °C min^{-1}, the BP "event" is resolved in three transitions, presumably Iso-BP_{fog}-BP_{II}-BP_I. Furthermore, the N^*-TGB C^*-$S_C{}^*$ is also clearly resolved (this also shows an unidentified change in heat capacity (labelled as ? in figure 2) at *ca* 109 °C . The $S_C{}^*$-$S_X{}^*$ transition is a weakly first order, its enthalpy change is *ca.*, 0.21 kJ mol^{-1}.

Compound **13a**'s racemate, compound **13b**, as might be expected gave a far simpler phase sequence. Cooling from the isotropic liquid results in the formation of N droplets, which coalesce to give areas of *schlieren* texture (containing 2- and 4-brush singularities) interspersed with homeotropically aligned material. The homeotropic regions seem to predominate until at 108.9 °C they give way to a bright S_C *schlieren* texture containing 4-brush singularities only. Further cooling to this achiral S_C phase results in the formation of an unidentified higher order smectic phase (S_X^*). This transition is somewhat difficult to observe (the texture appears to become feathery) and is best observed by DSC. Further cooling of compound **13b** results only in crystallisation.

Example 3: Cooling compound **14** slowly (0.5 °C min^{-1}) from the isotropic liquid causes the formation of droplets which develop a grey *Grandjean* texture with highly mobile pitch lines (rotation of the microscope's upper polariser gives a red dispersion in an anticlockwise rotation *i.e.*, right handed twist sense). Further cooling of this texture results in a blue planar texture (with slowly moving domains) which slowly sweeps across the field of view. This is believed to be a S_C^* phase (with identical twist sense to the N^* phase). Further cooling results only in recrystallisation of the sample at around 140.6 °C. These events are confirmed by DSC studies, particularly at low cooling scan rates (0.5 °C min^{-1}) when the I-N^*-S_C^* appears slightly better resolved.

Table 1 : Transition Temperatures and Enthalpies of 1,*(S)*-2-(4"-Octyloxyterphenyl-4-oxy)dialkoxybutanes (12, 13a, 13b and 14)

Number	R_1	R_2	mp [a]	Transition Temperatures (°C) [a]
				
12	CH_3	CH_3	162.1	**I** 179.6 **TGB A*** 179.1 S_A 176.5 **TGB C*** 175.0 $S_C{}^*$ 161.1 **K**
				[4.81] [b] [1.66] [b] [8.72]
13a	C_5H_{11}	C_5H_{11}	64.7	**I** 118.4 **BP** [c] 115.1 **N*** 111.2 **TGB C*** 111.1 $S_C{}^*$ 72.3 $S_X{}^*$ 63.2 **K**
				[1.81] [d] [0.93] [d] [0.21] [e] [4.23]
13b	C_5H_{11}	C_5H_{11}	66.6	**I** 117.9 **N** 108.9 S_C 74.6 S_X 63.4 **K**
				[1.59] [1.15] [0.25] [4.34]
14	CH_3	C_5H_{11}	141.31	**I** 156.6 **N*** 156.1 $S_C{}^*$ 140.1 **K**
				[7.92] [f] [10.12]

[a]..taken from DSC studies at heating and cooling rates of 5 °C min^{-1}; enthalpies given in parenthesis [ ] in kJ mol^{-1}. [b]..combined I-TGB A*-S_A and S^A-TGB C*-$S_C{}^*$ enthalpies, complete resolution is not obtained at 5 °C min^{-1}. [c]..3-Events noted in DSC run at cooling rate of 1 °C min^{-1}, only 1 by optical microscopy. Presumably I-BP_{fog}-BP_{II}-BP_I-N*, [d]..combined I-BP-N* and N*-TGB C*-$S_C{}^*$ enthalpies, complete resolution not achieved although events are clearly visible. [e]..weakly first order transition. [f]..combined I-N*-$S_C{}^*$ enthalpy, complete resolution not achieved.

B. The Mono-Fluoro-Substituted 1,*(S)*-2-(4"-Octyloxyterphenyl-4-oxy)dialkoxy-butanes (Examples 4 to 8)

All five materials synthesised showed enantiotropic liquid crystalline behaviour, showing N* or $S_C{}^*$ phases with relatively low melting and clearing temperatures, which are listed in table 2 below. However, the optical microscopy of the individual compounds revealed a number of unexpected facts about the phase behaviour that was not at all apparent from the DSC studies.

Example 4: Compound **40** has a moderately low melting point (51 °C). Cooling from the isotropic liquid resulted in the formation of a S_A phase characterised by the presence of regions of broken focal-conic fan and darker homeotropic regions, the focal-conic regions gradually becoming homeotropic as the temperature dropped. At around 84 °C, this mixed texture gave way to a greyish *schlieren* texture which contained small regions of focal-conics. Analysis of the *schlieren* domains revealed the presence of 4-brush singularities, meaning that this phase could be assigned as S_C^* (rotation of the microscope's upper polariser resulted in an anticlockwise colour dispersion). At around 46 °C, the focal-conic regions became 'feathery' in appearance. DSC confirmed this as another phase transition and is probably a higher order phase S_X^*.

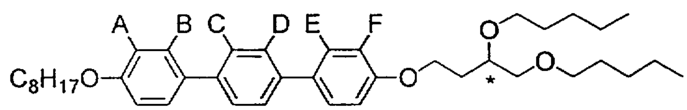
Example 5: Compound **41** proved remarkably different to compound **40.** Here the influence of the 2-fluoro-substituent in the inter annular position drastically reduces the melting point to ca. 28 °C and the clearing point to 73 °C, corresponding to depressions of 36 and 45 °C respectively over its parent compound **13a.** Cooling compound **41** from its isotropic liquid resulted in a N^* phase with of a blue *Grandjean* texture (rotation of the microscope's upper polariser gives an anticlockwise colour dispersion). Continued cooling causes the texture to become highly mobile, rippled and then *schlieren*-like. At a temperature of 58.3 °C, the texture appears to be completely *schlieren* (Brownian motion and shimmering in the texture is clearly visible). If cooling is continued, this *schlieren* texture appears to reform into a *Grandjean* texture at approximately 56.6 °C. This phenomenon is a twist inversion: the chiral nematic phase is experiencing a N^*-N^*_∞-N^* sequence in which the pitch unwinds to infinite pitch and then rewinds. The handedness of the helix is opposite above and below the unwound N^*_∞ state as shown by rotation of the microscope's upper polariser; it is anticlockwise above and clockwise below. If cooling is continued the N^* phase undergoes a transition to a S_C^* phase at 48.4 °C. DSC analysis showed this phase transition to be 1st order in nature ($\Delta H = 1.13$ kJ mol^{-1}). This material eventually crystallises at 4 °C, indicating potential use in formulating room temperature mixtures.

Example 6: Compound **42** shows some similarities in both structure and behaviour to compound **41.** Like compound **41**, the 2''-fluoro-substituent results in dramatic depression of the melting point and clearing point when compared to the parent compound **13a.** Compound **42** forms a blue *Grandjean* textured N^* phase on cooling from the isotropic liquid, further cooling results in the steady unwinding of the phases helix until a shimmering, *schlieren* texture is observed at 35.1 °C (the N^*_∞). This never actually rewinds because the phase undergoes a transition to an S_C^* phase at 30.5 °C, before crystallising at 14.4 °C.

Example 7: Compound **43**, has similar properties to both **41** and **42**, having a similar low melting point of 34 °C. It forms a N^* phase on cooling from the isotropic liquid at 70.9 °C. Just like compound **41**, the blue *Grandjean* texture gradually gives way to an unwound N^*_∞ state at *ca.*, 36.3-34.7 °C before the *Grandjean* texture reforms at 30.7 °C. Once again the handedness of the helix above and below the twist inversion was checked by rotating the microscope's upper polariser and observing the colour dispersion; anticlockwise above the N^*_∞ state and clockwise below the N^*_∞ state. The N^* eventually gives way to a S_C^* phase before recrystallising at 14.8 °C.

Example 8: Compound **45**, with its interannular fluorosubstituent might be expected to give both low thermal stability and melting point and this is indeed the case. This material has a melting point (as determined by DSC) of 2.6 °C some 62 °C lower than its non fluoro-substituted parent compound **13a**. Cooling compound **45** from the isotropic liquid results in the formation of a *Grandjean* texture characteristic of a N^* phase. As the temperature is cooled to around 26.2 °C, the texture shows every indication of unwinding and the texture becomes *schlieren*-like in nature. Unlike compounds **41** and **43** no inversion is observed because at 25.6 °C the texture undergoes a transition to a planar S_C^* phase. Crystallisation was not observed by microscopy or by DSC, but does occur after standing at -30 °C for 5 mins.

Table 2 : Transition Temperatures and Associated Enthalpies of 1,*(S)*-2-(4''-Octyloxy-mono-fluoro-terphenyl-4-oxy)dialkoxybutanes (40, 41, 42, 43 and 45)



Compound Number	A B C D E F	Transition Temperatures (°C)[a] and Enthalpies (kJ mol^{-1}) mp	I	N^*	S_A	S_C^*	S_X^*	K_2	K_1
40	H H H H H F	51.2	•103.4		• 84.5	• 48.4	• 38.3	• 34.0	•
		[18.54]	[2.99]		[0.16]	[0.29]	[5.76]	[8.02]	
41	H H H H F H	27.7	• 73.4	• 48.4		• 4.1		•	
		[18.05]	[0.53]	[1.13]		[15.51]			
42	H F H H H H	34.1	• 71.2	• 30.8		• 14.4		•	
		[28.29]	[0.47]	[0.32]		[25.49]			
43	F H H H H H	33.8	• 71.5	• 31.5		• 14.8		•	
		[28.28]	[0.54]	[0.29]		[27.34]			
45	H H F H H H	2.6	• 65.4	• 25.6		• > -30.0 [b]		•	
		[16.36]	[0.45]	[0.66]		[-] [b]			

[a]..taken from DSC heating and cooling scans at 5 °C min^{-1}; [b]..crystallisation not observed above -30 °C, therefore no enthalpy determined.

Helical Pitch Measurements of Chiral Nematic Phases

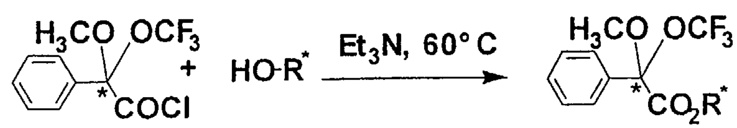
These were performed using the Cano wedge method (M.F. Grandjean, **C.R. Acad. Sci.**, 1921, 172, 71; and R.R. Cano, **Bull. Soc. Miner. Cryst.**, 1968, 91, 20) using prefabricated EHC wedge cells (average wedge angle of 0.47 degrees), the distance between the disclination lines being measured using a calibrated graticule and eyepiece. The results are plotted in figure 2 as a function of temperature.

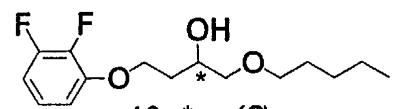
All the monofluoro-substituted materials (compounds **41**, **42**, **43**, and **45**) show pitch lengths which vary between 1.06 to 6.48 microns (the plotted curves do not necessarily show the pitch over the full chiral nematic range, as the disclination lines could not always be observed). Of the two twist inverting materials **41** and **43**, only compound **41** shows the inversion phenomenon clearly. Here the pitch tends to infinity at *ca* 58 °C before dropping to pitch length of between 4 and 5 microns before entering the underlying S_C^* phase. Materials **42**, **43** and **45** all show similarly shaped curves which tend to infinity (an unwound state) before reaching their underlying S_C^* phases. Interestingly, the parent compound **13a**, shows a much shorter pitch, *ca* 0.49 - 0.62 microns which probably explains why the material shows both Blue Phases and the TGB C* phases only observed in highly chiral compounds.

Optical Purity

Although twist inversion phenomena in liquid crystals are now relatively well known, examples of materials which show this behaviour with one chiral centre are rare (A.J. Slaney et. al., **J. Mater. Chem.**, 1992, **2**, 805 and C. Loubser et. al., **J. Mater. Chem.**, 1994, **4**, 71). As the materials **41** and **43** fall into both these categories, it became imperative that their optical purity be determined or in some way estimated so that the possibility of an opposite enantiomer present as an undetectable 'impurity' causing a compensation of helical twist can be discounted. The starting butanetriol (purchased from Fluka) is claimed to have an *ee* of >96%, so in order to determine this, and to discount racemisation of the chiral centre during the synthetic route (schemes 2 and 3) a series of Mosher's esters were prepared from various intermediates (**2a/b, 3a/b** and **6a**) using *(R)*-(-)-α-methoxy-(trifluoromethyl)phenylacetylchloride (MTPACl), as outlined in table 3 below. The resulting diastereoisomeric Mosher's esters were then analysed by $^{19}F-\{^1H\}$ NMR (J.A. Dale et. al., **J. Org. Chem.**, 1969, **34**, 2543).

Table 3 : Results of Determination of Optical Purities of Various Mosher's Esters





46; * = (*S*)-

Alcohol Number	R*OH Config.	MTPA-Cl Config.	Observation in ^{19}F-{^{1}H} Spectrum ($CDCl_3$, TMS)
2a/b	*(S)*-	*(R)*-	Two signals at -71.98 and -72.17 ppm. Corresponds to the *(R)(S)*- and *(R)(S)*-diastereoisomeric pairs of the 1,2- and 1,3-acetonide systems. Integration *ca* 93:7 1,2- to 1,3-acetonide system.
3a/b	*(R,S)*-	*(R)*-	Four signals at -71.97/-71.97 ppm and -72.15/72.17 ppm. Corresponds to the *(R)(R)*- and *(R)(S)*- diastereoisomeric pairs of the 1,2 and 1,3-acetonide ester systems Integration *ca* 92:8 1,2 to 1,3-acetonide.
6a	*(S)*-	*(R)*-	Only mono-ester formed. Two signals at -71.89 and -72.04 ppm. Opposite enantiomer or chemical impurity? Proved to be the Ethyl mosher's ester.
46	*(S)*-	*(R)*-	One signal at -71.99 ppm. Therefore this materials has an *ee* of 99%+
Methanol	-	*(R)*-	One signal at -72.14 ppm.
Ethanol	-	*(R)*-	One signal at -72.04 ppm.

The method was first tested using the racemic acetonide **3a/b**, here four signals were observed corresponding to the *(R)(R)*- and *(R)(S)*-diastereoisomeric pairs of both the 1,2-acetonide (5-membered ring) and 1,3-acetonide (6-membered ring) at -71.97, -71.97 ppm and -72.15, -72.17 ppm . Integration of the signals revealed a ratio of 92:8 1,2- to 1,3- which corresponds well with the result determined by ^{1}H NMR. This was repeated for the optically active variant **2a/b** and two signals at -71.98 and -72.17 ppm observed, again corresponding to a 93:7 ratio of *(R)(S)*-1,2-acetonide and *(R)(S)*-1,3-acetonide. The lack of any other signals indicates that no racemization takes place during the formation of the acetonide, which is in accordance with the published literature.

However, it was a concern that racemization might occur during the deprotection step using p-toluenesulfonic acid in methanol, so the Mosher's ester of compound **6a** was prepared. Here the position was clouded by the observation of two peaks at -71.89 and -72.04 ppm. The former peak was undoubtedly the *(R)(S)*-diastereoisomer but the second peak could be the *(R)(R)*-diastereoisomer indicating a lower optical purity of **6a** or an impurity peak such as the Mosher's acid anhydride (unlikely) or a reaction product of MTPACl and methanol or ethanol impurity in the triethylamine. To test this, the methyl and ethyl esters of MTPACl were prepared; the ^{19}F-{^{1}H} NMR spectra of these show peaks at -72.14 and -72.04 ppm respectively. A sample of the ethyl Mosher's ester was 'spiked' into an NMR sample of the Mosher's ester of **6a**. The ^{19}H-{^{1}H} NMR spectrum showed the 'impurity' peak to increase in height over the *(R)(S)*-diastereoisomer peak at -72.04 ppm. This conclusively proves that the 'impurity' in the **6a** Mosher's ester is the ethyl Mosher's ester, meaning that compound **6a** is essentially optically pure and that no racemization occurs during the deprotection reaction using p-toluenesulfonic acid in methanol.

This result was finally checked by preparing the Mosher's ester 2,3-difluoro-1-(1-pentoxy-*(S)*-2-hydroxybutoxy)benzene (synthesised from 2,3-difluorophenol in three steps using similar methods to those used in the preparation of compound **5a** in scheme 2), the extraction being performed with freshly distilled and dried triethylamine. The ^{19}F-{^{1}H} NMR spectra showed one peak at -72.04 ppm corresponding to the *(R)(S)*-diastereoisomer only, indicating that the product is essentially optically pure (*ee* >99%). From this it can reasonably be assumed that the final targets are all enantiopure (possibly enriched due to the further purification in later synthetic steps) and that the twist inversion phenomenon that occurs in compound **41** and **43** is not due to a compensation due to the opposite enantiomer.

Referring now to Fig 3, the device illustrated therein comprises first and second spaced glass substrates 10 and 12 between which is defined a liquid crystal cell. The mutually facing surfaces of the substrates 10 and 12 are provided with respective rubbed alignment layers 14 and 16 between and in contact with which is disposed a layer 18 of a liquid crystal composition including compound 13a.

Linear polarisers 20 and 22 are provided on the outer surfaces of the substrate 10 and the substrate 12, respectively. The polariser 20 has its polarisation axis aligned with the rubbing directions of the alignment layers 14 and 16 which are mutually parallel, whilst the linear polariser 22 has its polarisation axis perpendicular to that of the polariser 20 and the rubbing directions of the alignment layers 14 and 16. The liquid crystal molecules in the chiral smectic phase within the liquid crystal composition in the layer 18 are sensitive to changes in electrical field applied across the layer 18 via the electrodes 24 and 26. Thus, in a manner known per se, the layer 18 can be switched such that light transmission through the device is enabled at one voltage and prevented at another voltage so that the device can act as a fast-operating optical shutter.

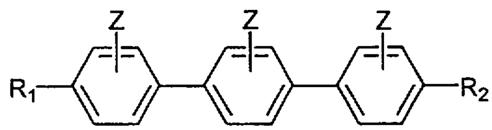
The following are given as some representative examples of possible industrial applications for the compounds of the present invention:-

1. Compensating dopants which utilise the twist inversion phenomenon.
2. Components in ferroelectric mixtures, since the Examples have room temperature S_c^* phase ranges.
3. S_A-suppressing dopants for ferroelectric mixtures.

4. Twist compensating dopants for use in ferroelectric mixtures. Unwinding a preceding nematic phase can improve the subsequent alignment of the underlying S_c^* phase.
5. High twist dopants (low melting point).

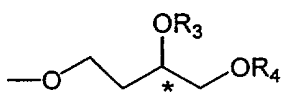
CLAIMS

1. A terphenyl compound having the general formula [1]:-

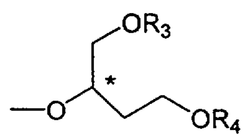


[1]

where each of R_1 and R_2 is the same or different and is selected from the group consisting of:- alkyl, alkyloxy, alkenyl, alkenyloxy, alkynyl, alkynyloxy, alkylthio, alkenylthio and alkynylthio

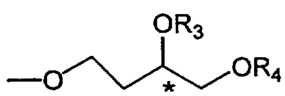


and

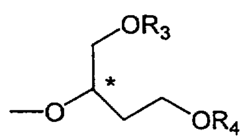


where * indicates an asymmetric carbon atom,

provided that at least one of R_1 and R_2 is



or



and where each of R_3 and R_4 is the same or different and is an alkyl, alkenyl or alkynyl group; and Z is independently selected from hydrogen and fluorine at each terphenyl carbon.

2. A compound as claimed in claim 1, wherein the group represented by R_1 or R_2 is a C_1- to C_{16}-alkyl or alkyloxy group or a C_2- to C_{16}-alkenyl, alkynyl, alkenyloxy or alkynyloxy group.

3. A compound as claimed in claim 2, wherein the group represented by R_1 or R_2 is a C_1- to C_{16} n-alkyl group.

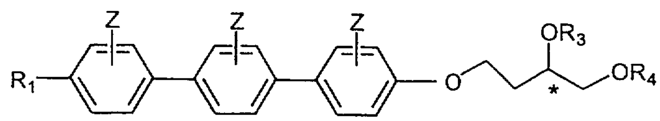
4. A compound as claimed in claim 3, wherein the group represented by R_1 or R_2 is a C_7- to C_{12} n-alkyl group.

5. A compound as claimed in any preceding claim, wherein the group represented by R_3 or R_4 is a C_1- to C_{16}-alkyl group or a C_2- to C_{16}-alkenyl or alkynyl group.

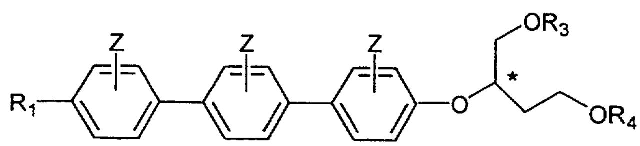
6. A compound as claimed in claim 5, wherein the group represented by R_3 or R_4 is a C_1- to C_{16} n-alkyl group.

7. A compound as claimed in claim 6, wherein the group represented by R_3 or R_4 is a C_1- to C_5 n-alkyl group.

8. A compound as claimed in any preceding claim having the general formula [2] or the general formula [3]:-



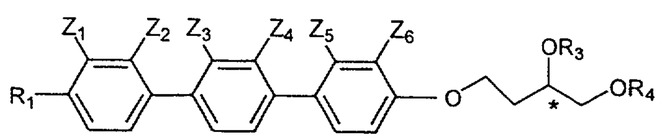
[2]



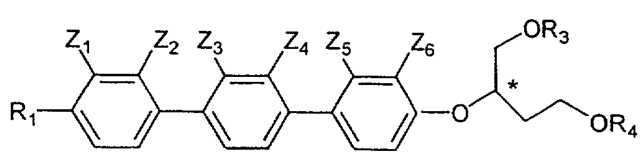
[3]

wherein R_1, R_3, R_4 and Z are as defined above.

9. A compound as claimed in claim 8 having the general formula [4] or the general formula [5]:-



[4]



[5]

wherein R_1, R_3 and R_4 are as defined above, and one of Z_1 to Z_6 is F, the remaining Z_1 to Z_6 being H.

10. A compound as claimed in any preceding claim, wherein R_1 is n-octyl.

11. A compound as claimed in any preceding claim wherein R_3 and R_4 are independently selected from methyl and n-pentyl.

12. A compound substantially as hereinbefore described with reference to any one of Examples 1 to 8.

13. A liquid crystal composition containing at least one compound according to any one of claims 1 to 12.

14. An electro-optical liquid crystal device including a liquid crystal cell having a layer of a liquid crystal composition according to claim 13, and means for applying an electrical field across said layer.

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Application No:	GB 0013312.4	**Examiner:**	Stephen Quick
Claims searched:	1-14	**Date of search:**	22 August 2000

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Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

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Category	Identity of document and relevant passage	Relevant to claims
	No documents of relevance found	

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