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An investigation into the effect of lateral fluoro substitution in the molecular core on the spontaneous polarization of chiral cyclohexanes

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A range of chiral biphenylcyclohexanes of high enantiomeric excess has been prepared by asymmetric synthesis. These materials were designed as chiral dopants for ferroelectric mixtures based on fluoro-substituted host materials. Accordingly, fluoro substituents were strategically incorporated into the aromatic core of the chiral biphenylcyclohexanes in order to determine their effect on the spontaneous polarization of the ferroelectric mixtures. Chiral hydroboration was used to generate the chiral cyclohexane units which were attached to the core by using palladium-catalysed cross-coupling reactions with arylboronic acids; the synthetic methods used are discussed. The spontaneous polarization of the chiral materials was evaluated in H1 host mixture and the results are reported and discussed in comparison with the non-fluoro-substituted analogues.

1. Introduction

Ferroelectric liquid crystal light shutter devices, such as displays and spatial light modulators, offer extremely short switching times and considerable research effort continues in order to optimize ferroelectric technology to enable rewarding commercial exploitation [1–3]. It is now well recognized that the best way of formulating ferroelectric mixtures is to use an achiral smectic C host mixture and to add a chiral dopant (usually 5–10%) to confer ferroelectric properties on the mixture [2, 4–7]. Much attention has been paid to optimizing the properties of the achiral host materials for ferroelectric mixtures in terms of mesomorphic properties, low viscosity, high dielectric biaxiality and chemical and photochemical stability [5, 8–11]. However, despite the fact that chiral materials are essential components in fast-switching ferroelectric mixtures, it is often assumed that because only a small amount of chiral material is included in a ferroelectric mixture that the structure and properties of the material are of little importance, except for the ability to confer a high spontaneous polarization (P_S). The properties of chiral dopants have been widely evaluated and optimized, and it is well recognized that the generation of a high P_S necessitates the use of a polar unit (*e.g.* fluoro or cyano) at the chiral centre and the restriction of rotation about the chiral centre [12]. However, the nature of the core structure is less well understood; for example, the effect of lateral fluoro substitution in the core has not been widely investigated in terms of P_S values, and little is known about the importance of matching the core structure of the chiral dopant to that of the host materials. Fluoro-substitution in liquid crystals and materials for liquid crystal mixtures has been widely studied because of the beneficial effects on important physical properties arising from the small size and high electronegativity of fluorine [4, 5, 8, 13]. Currently, all the best ferroelectric host mixtures are composed of materials with one or more lateral fluoro substituent in the aromatic core. Accordingly, the aim of this work was to determine the effect of lateral fluoro substituents in the core of chiral dopants on the mesomorphic properties and spontaneous polarization of ferroelectric mixtures.

Chiral compounds of structure **I** were prepared with one and two fluoro substituents in various positions on the biphenyl core. These core-lateral fluoro-substituted chiral dopants were added to H1 host material. The mesomorphic behaviour was examined and the spontaneous polarization of the resulting ferroelectric mixtures was evaluated as a function of temperature and concentration of chiral dopant. The spontaneous polarization values of the fluoro-substituted materials were then compared with the value for the unfluorinated analogue. The analogous unfluorinated chiral cyclohexanes have already been evaluated for spontaneous polarization and their values were disappointingly low [14]. The low spontaneous polarization values obtained for these compounds were attributed to the compensation effects of

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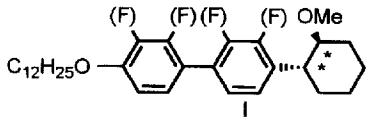
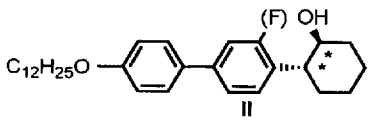
the two chiral centres within the cyclohexane ring. However, lateral fluoro substituents within the core, not necessarily close to the chiral units, may significantly change the spontaneous polarization depending upon the packing arrangements within the phase structure.



I

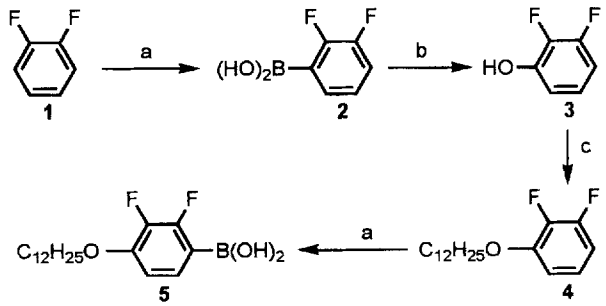


II

Core fluoro-substituted compounds of structure **II** were prepared for two reasons: (a) to determine the effect on mesomorphic properties and spontaneous polarization of the hydroxyl unit at the chiral centre when compared with the chiral methoxy-substituted analogues, and (b) to determine the effect of lateral fluoro substitution in the core, since intramolecular hydrogen bonding might be expected to occur between the outer edge lateral fluoro substituent and the hydroxyl hydrogen which may enhance spontaneous polarization due to the coupling of two polar units.

2. Synthesis

The synthesis of liquid crystal materials with lateral fluoro substituents in the aromatic core has been greatly facilitated by the development of palladium-catalysed cross-coupling reactions involving arylboronic acids and aryl bromides, iodides and trifluoromethanesulfonates [5, 15–17]. For materials with the core-lateral fluoro substituents in the far ring from the chiral cyclohexane, appropriate fluoro-substituted arylboronic acids were prepared. An acidic proton of 1,2-difluorobenzene (**1**) was removed (scheme 1) using *n*-butyllithium at −78°C and the resulting anion was quenched with trimethyl borate to generate a boronic ester which was hydrolysed *in situ* to generate boronic acid **2**. The very low temperature prevents the elimination of lithium fluoride which would generate a benzyne derivative [5]. Oxidation of **2** with hydrogen peroxide provided phenol **3** in good yield. A simple *O*-alkylation involving dodecyl bromide and potassium carbonate was used to introduce a long terminal alkoxy chain (compound **4**). The exploitation of the remaining acidic proton enabled the fluoro-substituted boronic acid **5** to be produced for use in palladium-catalysed cross-coupling reactions. For the analogous arylboronic acids with only one fluoro substituent (schemes 2 and 3), the lack of symmetry dictated

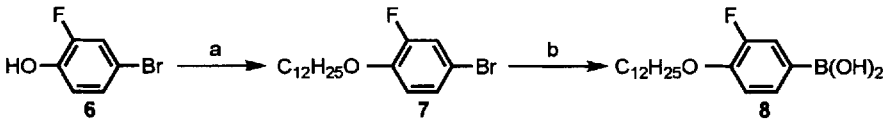


a ..... (i) n-BuLi, THF; (ii) $B(OMe)_3$, THF; (iii) 10% HCl.
b ..... H_2O_2, THF.
c ..... $C_{12}H_{25}Br$, K_2CO_3, acetone.

Scheme 1

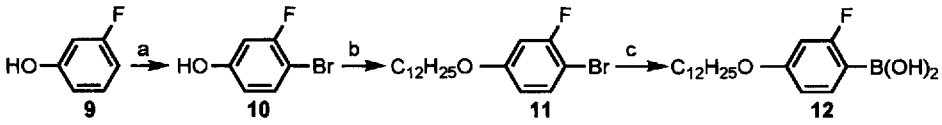
that the boronic acid unit be generated through an aryl bromide. Phenol **6**, with the fluoro substituent next to the hydroxyl group, is commercially available (scheme 2) and was *O*-alkylated as described above to introduce a long terminal chain. An arylboronic acid was also generated as described above, except that the bromo substituent of compound **7** provided the lithiation site. The appropriate phenol (**10**), with the fluoro substituent away from the hydroxyl unit, is not readily available, but can be prepared by the bromination of phenol **9** (scheme 3). Subsequently, the synthesis of boronic acid **12** was carried out as described above for scheme 2. However, the location of the lithiation site *ortho* to the lateral fluoro substituent (compound **12**) does necessitate a very low temperature (−78°C) to prevent the formation of a benzyne derivative through the elimination of lithium fluoride. The bromo-substituted chiral cyclohexane (**13**) was prepared by using Brown's chiral hydroboration procedure [18] and the synthesis is described in the publication reporting the synthesis of the parent compounds [14]. The bromo substituent of compound **13** was exploited in palladium-catalysed cross-coupling reactions (scheme 4) with the appropriate fluoro-substituted arylboronic acids (**5**, **8** and **12**) to provide good yields of the desired fluoro-substituted chiral cyclohexanes with lateral fluoro substitution in the core (**14**–**16**).

Those materials with lateral fluoro substituents in the aromatic ring next to the chiral cyclohexane required the separate preparation of lateral fluoro-substituted phenyl chiral cyclohexanes (schemes 5 and 6). The versatility of the 1,2-difluorobenzene unit in synthetic organic chemistry is again illustrated in scheme 5. The anion created by the removal of an acidic proton with *n*-butyllithium was quenched with cyclohexanone. The resulting benzylic alcohol was dehydrated to generate the substituted prochiral cyclohexene unit (**17**). Brown's chiral hydroboration procedure was then applied which



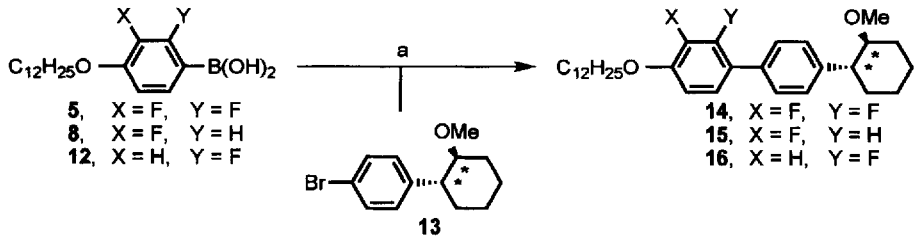
a ..... $C_{12}H_{25}Br$, K_2CO_3, acetone.
b ..... (i) n-BuLi, THF; (ii) $B(OMe)_3$, THF; (iii) 10% HCl.

Scheme 2



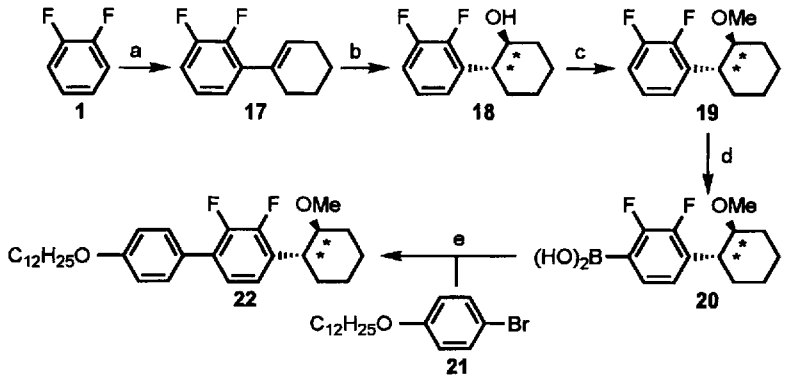
a ..... Bromine, glacial acetic acid.
b ..... $C_{12}H_{25}Br$, K_2CO_3, acetone.
c ..... (i) n-BuLi, THF; (ii) $B(OMe)_3$, THF; (iii) 10% HCl.

Scheme 3



a ..... $Pd(PPh_3)_4$, 1,2-dimethoxyethane, 2M-Na_2CO_3.

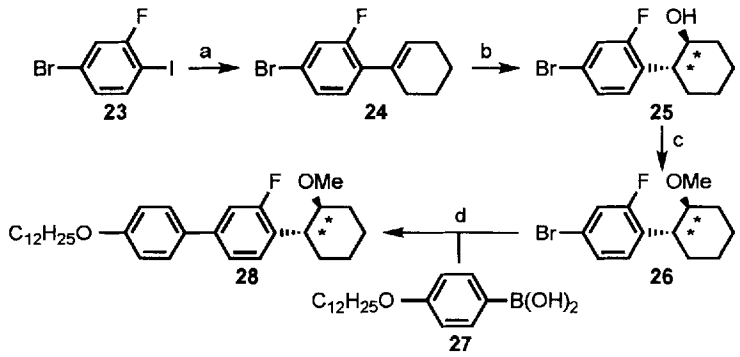
Scheme 4



a ..... (i) n-BuLi, THF; (ii) cyclohexanone; (iii) PTSA, toluene.
b ..... (i) *(R)*-Alpine-boramine™, $BF_3{\cdot}OEt_2$, THF; (ii) 3M-NaOH, 30% H_2O_2.
c ..... NaH, MeI, DMF.
d ..... (i) n-BuLi, THF; (ii) $B(OMe)_3$, THF; (ii) 10% HCl.
e ..... $Pd(PPh_3)_4$, 1,2-dimethoxyethane, 2M-Na_2CO_3.

Scheme 5

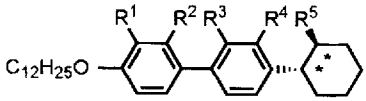
resulted in the generation of the chiral cyclohexanol **18** which was methylated to give the desired chiral methoxycyclohexane unit. Exploitation of the second acidic proton provided the boronic acid (**20**) which was then coupled to a standard alkoxybromoaryl unit to give the desired chiral cyclohexane (**22**) with a difluorophenyl unit. Similarly (scheme 6), a monofluoro-substituted prochiral arylcyclohexene (**24**) was prepared from the anion generated from the iodo site of 4-bromo-2-fluoro-1-iodobenzene (**23**). Brown's chiral hydro-



a ..... (i) n-BuLi, THF; (ii) cyclohexanone; (iii) PTSA, toluene.
b ..... (i) *(R)*-Alpine-boramine™, BF_3•OEt_2, THF; (ii) 3M-NaOH, 30% H_2O_2.
c ..... NaH, MeI, DMF.
d ..... $Pd(PPh_3)_4$, 1,2-dimethoxyethane, 2M-Na_2CO_3.

Scheme 6

Table 1. Transition temperatures for mixtures of compounds **32**[14], **14–16**, **22**, **28**, **30** and **31** (9 mass %) in H1† host.



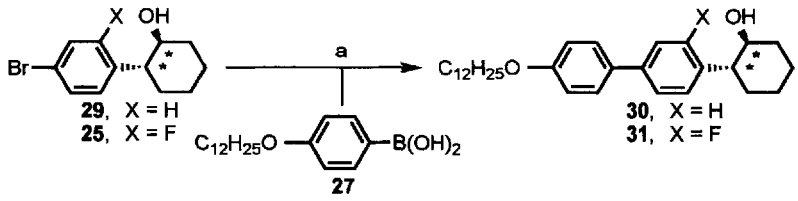
Compound	R^1	R^2	R^3	R^4	R^5	Transition temperatures/°C
32[14]	H	H	H	H	OMe	I 141·5 N* 92·4 S_A* 87·6 S_C*
14	F	F	H	H	OMe	I 139·6 N* 78·5 S_C*
15	F	H	H	H	OMe	I 140·4 N* 80·0 S_C*
16	H	F	H	H	OMe	I 140·8 N* 86·6 S_C*
22	H	H	F	F	OMe	I 140·5 N* 83·5 S_C*
28	H	H	H	F	OMe	I 140·6 N* 93·5 S_A* 87·5 S_C*
30	H	H	H	H	OH	I 146·4 N* 112·8 S_A* 95·8 S_C*
31	H	H	H	F	OH	I 145·2 N* 109·6 S_A* 97·3 S_C*

† Transition temperatures of H1 host are I 152·0 N 113·0 S_A 107·0 S_C 28·0 S_I/°C.

boration again gave the chiral cyclohexanol **25** which was methylated. The bromo substituent of compound **26** was coupled to a standard alkoxyarylboronic acid to give compound **28** with a laterally fluoro-substituted phenyl ring next to the chiral unit. The synthesis of the chiral hydroxy-substituted chiral dopants (**30** and **31**) simply involved the palladium-catalysed cross-coupling of the chiral cyclohexanol units (**29** and **25**, respectively) to arylboronic acid **27** (scheme 7).

3. Results and discussion

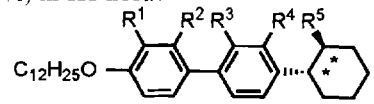
As expected, on the basis of the results for the parent systems [14], all the chiral dopants were non-mesomorphic and were accordingly evaluated for their mesogenic behaviour in the standard host material (H1) which was used in the previous publication for the evaluation of the analogous parent systems. Table 1 shows the transition temperatures and liquid crystal phase morphology of ferroelectric mixtures based on 9 mass % of each chiral material in H1 host. Lateral fluoro substituents add to the molecular breadth and in the inner core positions they also cause inter-annular twisting which reduces polarizability; both factors usually cause a significant reduction in the melting point and liquid crystal phase stabilities, especially those of smectic phases where the increased molecular breadth particularly disrupts lamellar packing. Where a fluoro substituent occupies an outer-edge position no inter-annular twisting occurs and so liquid crystal phase stabilities are not so dramatically affected. The filling of free space at the outer-edge position [19] of the biphenyl core, by the polar fluoro substituent tends partially to counter the disruption to lamellar packing caused by the increased molecular breadth. However, in the case of the ferroelectric mixtures reported here, only 9 mass % of each lateral fluoro-substituted chiral material is involved and so such differences in transition temperatures are minimal. In all cases of the methoxy compounds (dopants **14–16**, **22** and **28**), one and two lateral fluoro substituents have little effect on the T^2_{N-I} values



a ..... $Pd(PPh_3)_4$, 1,2-dimethoxyethane, 2M-Na_2CO_3.

Scheme 7

Table 2. Spontaneous polarizations (P_S) and tilt angles (θ) for mixtures of compounds **32**[14], **14–16**, **22**, **28**, **30** and **31** (9 mass %) in H1 host.†



Compound	R^1	R^2	R^3	R^4	R^5	P_S/nC cm^{-2}	θ/°
32[14]	H	H	H	H	OMe	3·4	29
14	F	F	H	H	OMe	2·1	27
15	F	H	H	H	OMe	2·9	28
16	H	F	H	H	OMe	2·8	27
22	H	H	F	F	OMe	3·4	30
28	H	H	H	F	OMe	3·7	28
30	H	H	H	H	OH	4·4	29
31	H	H	H	F	OH	2·2	25

† All values were recorded at 40°C below the Curie temperature.

of the mixtures when compared with dopant **32** [14]. The effect of fluoro-substitution on the smectic phases is more interesting and the most significant factor is that the S_A^2 phase has been eliminated in mixtures based on dopants **14–16** and **22**. The fact that the only smectic character exhibited is as the tilted chiral smectic C phase is not surprising because the increased molecular breadth will disrupt lamellar packing, but the increased lateral polarity will facilitate molecular tilting. It is rather strange that the chiral smectic C phase stability of the ferroelectric mixture based on chiral dopant **15** (outer-edge fluoro substituent) is significantly lower than that for chiral dopant **16** (fluoro substituent occupying an inner-core position). This unusual trend was also seen for other homologues prepared and was repeatable with different mass % mixtures involving the same chiral dopants (not reported here). The position of the fluoro substituent in dopant **16** must greatly facilitate packing within the structure of the host material when compared with that of dopant **15**. Further explanation for this unusual occurrence is difficult to provide, but this case emphasises the difference in trends which can be seen in the mesomorphic behaviour of mixtures when compared with those of pure compounds. Where the lateral fluoro substituent is at an outer-edge position, adjacent to the chiral cyclohexane core (**28**), the transition temperatures are nearly identical to those for the parent system; in fact the smectic A phase stability is actually higher. This result is reasonably explained in terms of the shielding effect afforded to the lateral fluoro substituent by the bulky methoxy group at a chiral centre. The same feature explains the difference between the values for the two difluoro-substituted chiral dopants, where dopant **22** supports higher chiral smectic C phase stability than dopant **14**.

The parent system with the hydroxyl group at a chiral centre (**30**) generates the same liquid crystal phase morphology as the parent methoxy analogue (**32**). However, the phase stabilities are higher in each case because of the smaller size of the hydroxyl group. The smectic A phase stability is especially high for the mixture based on dopant **30** because intermolecular hydrogen bonding enhances lamellar attractions. The introduction of a lateral fluoro substituent adjacent to the chiral cyclohexanol unit leaves the phase morphology unchanged. However, the chiral smectic C phase stability is slightly increased, despite an overall reduction in the smectic phase stability.

The spontaneous polarization (P_S) values (table 2) were obtained for 9 mass % mixtures of each chiral material in H1 host and each value was recorded at 40°C below the Curie point. Despite the lack of a smectic A phase in mixtures based on chiral dopants **14–16** and **22** no alignment problems were encountered. The P_S of the mixture based on the methoxy parent system (**32**) [14] is rather low and the values for mixtures based on fluoro-substituted chiral dopants (**14–16**, **22** and **28**) are not much different from those of the parent system. However, once again, the trends were repeated for other homologues and for other mass % mixtures (not reported here). The P_S value is lowest for the difluoro-substituted dopant (**14**) where the fluoro substituents are in the far ring from the chiral cyclohexane. Both monofluoro-substituted chiral dopants (**15** and **16**), where the fluoro substituents are away from the chiral unit, have P_S values intermediate between the parent system and the difluoro-substituted analogue. Where the fluoro substituents are close to the chiral

cyclohexane (**22** and **28**) the P_S values are much higher, although the difluoro unit (**22**) just maintains the same level as the parent system. The chiral dopant with just one fluoro substituent next to the chiral unit produces a slightly higher P_S value than the parent system.

The parent system with the hydroxyl group at a chiral centre produces a much higher P_S than the methoxy-substituted analogue. However, in contrast to the results for the fluoro-substituted methoxy systems discussed above, the monofluoro-substituted chiral dopant (**31**) generates a much lower P_S value. This result is surprising and disappointing because it was expected that attraction between the lateral fluoro substituent and the hydroxyl hydrogen would generate a particularly high P_S value. A plausible explanation for the reduced value of P_S may be that the attractive forces between the dopant molecules and the molecules of the host material are dominant and prevent any coupling between the lateral fluoro substituent and the hydroxyl unit. In fact such intermolecular attractions would then cause the fluoro substituent to detract from the polarity of the hydroxyl unit rather than augment it.

As for the parent systems, the tilt angle of each mixture was measured at 40°C below the Curie temperature and all were found to be very similar which indicates that the structure of the dopant has a minor effect on tilt angle. The tilt angle measured for the mixture containing dopant **31** is lower than for the others and this parallels the recorded P_S value.

4. Conclusions

(1) Fluoro-substitution in the aryl core positions of the chiral dopants affects the mesomorphic behaviour of ferroelectric mixtures. In most cases, the smectic A phase is eliminated from the phase sequences of the ferroelectric mixtures.

(2) The position of the fluoro substituent within the core affects the P_S values of ferroelectric mixtures. In the systems reported here, fluoro substitution generally reduces P_S values. However, the location of a fluoro substituent close to the chiral centre enhances P_S value.

(3) The hydroxyl group at a chiral centre generates a higher P_S than the analogous methoxy unit.

(4) Fluoro substitution in the aryl core of a chiral dopant improves the solubility of the dopant in the host material.

5. Experimental

5.1. *General*

Confirmation of the structures of intermediates and products was obtained by ^{1}H NMR spectroscopy (JEOL JNM-GX270 spectrometer), infrared spectroscopy (Perkin-Elmer 783 spectrophotometer) and mass spectrometry (Finnigan-MAT 1020 GC/MS spectrometer). Elemental analysis (Fisons EA1108 CHN) was obtained for each final compound prepared (**14**–**16**, **22**, **28**, **30** and **31**). Optical rotations were determined using $CHCl_3$ as solvent for each final compound prepared, using a Bendix-NLP automated polarimeter. The progress of reactions was monitored frequently using a Perkin-Elmer 8320 capillary gas chromatograph fitted with a 12 m QC2/BP1–1·0 SGE column. Transition temperatures, spontaneous polarizations (P_S) and tilt angles (θ) involved the use of a Mettler FP5 hot stage and control unit in conjunction with an Olympus BH2 polarising microscope. Transition temperatures were confirmed using differential scanning calorimetry (DSC; Perkin-Elmer DSC-7 and IBM data station). Spontaneous polarizations were measured using a Diamant bridge. The purities of intermediates were checked by GLC analysis (see above) and the purity of each final compound was checked by HPLC analysis (Microsorb C18 80-215-C5 RP column) and the compounds were found to be >99% pure in each case.

The enantiomeric excesses of alcohols **5**, **18** and **25** were determined by the preparation of the diastereomeric Mosher esters using *R*-(+)-α-methoxy-(trifluoromethyl)-phenylacetic acid chloride (Mosher acid chloride) and were found to be 99% [20]. The enantiomeric excess values of the subsequent chiral materials were assumed to be 99%.

Tetrakis(triphenylphosphine)palladium(0) was prepared according to the literature procedure [21]. Compounds **1**, **6**, **9**, and **23** were purchased from Fluorochem. H1 host material was purchased from Merck Limited (Poole, UK) and compounds **13**, **21**, **27** and **29** had been made previously [14].

5.2. *2,3-Difluorophenylboronic acid (***2***)*

n-Butyllithium (53 ml, 2.5 M in hexane, 0·133 mol) was added dropwise to a stirred, cooled (−78°C) solution of compound **1** (15 g, 0·132 mol) in dry THF (140 ml) under dry nitrogen. The reaction mixture was maintained under these conditions for 2·5 h and a solution of trimethyl borate (27·4 g, 0·264 mol) in dry THF (50 ml) was added dropwise at −78°C. The reaction mixture was allowed to warm to room temperature overnight and stirred for 1 h with 10% hydrochloric acid (120 ml). The product was extracted into ether (twice), and the combined ethereal extracts were washed with water and dried ($MgSO_4$). The solvent was removed *in vacuo* to yield a white solid. Yield 18·3 g (88%); ^{1}H NMR ($CDCl_3$) δ 7·10 (1H, q), 7·15 (1H, t), 7·50 (2H, s, broad), 7·65 (1H, t); IR (KCl) ν_{max} 3700–3000, 1625, 1470, 1360, 1270, 1045, 905 cm^{-1}; MS *m/z* 158 (M^+), 140, 125, 114.

5.3. *2,3-Difluorophenol (**3**)*

10% Hydrogen peroxide (135 ml, 0·396 mol) was added dropwise to a stirred refluxing solution of compound **2** (19·8 g, 0·126 mol) in ether. The stirred mixture was heated under reflux for 2·5 h and cooled. The ether layer was separated and the aqueous layer washed with ether. The combined ethereal extracts were washed with 10% sodium hydroxide (× 3) and the combined aqueous extracts were acidified with 36% hydrochloric acid. The product was extracted into ether (× 2), and the combined ethereal extracts were washed with water and dried ($MgSO_4$). The solvent was removed *in vacuo*. This crude product was recrystallized from petroleum spirit (40–60°C) to give an off-white solid. Yield 9·84 g (60%); m.p. 29·5–31·5°C; ^{1}H NMR ($CDCl_3$) δ 5·35 (1H, s), 6·65–6·80 (2H, m), 6·95 (1H, q); IR (KCl) ν_{max} 3700–3000, 1630, 1540, 1515, 1490, 1480, 1350, 1310, 1250, 1190, 1020 cm^{-1}; MS *m/z* 130 (M^+), 110, 101.

5.4. *1-Dodecyloxy-2,3-difluorobenzene (**4**)*

Quantities: compound **3** (7·00 g, 0·054 mol) in acetone (150 ml), 1-bromododecane (13·43 g, 0·054 mol) in acetone (20 ml) and potassium carbonate (22·73 g, 0·165 mol). The experimental procedure was as described in a previous publication [14]. The crude product was purified by column chromatography (silica gel/dichloromethane) to give a colourless solid. Yield 15·24 g (95%); m.p. 19–20°C; ^{1}H NMR ($CDCl_3$) δ 0·85 (3H, t), 1·30 (18H, m), 1·75 (2H, quint), 4·00 (2H, t), 6·70 (2H, m), 6·95 (1H, m); IR (KCl) ν_{max} 2920, 2850, 1620, 1510, 1480, 1460, 1390, 1310, 1295, 1250, 1210, 1170, 1090 cm^{-1}; MS *m/z* 298 (M^+), 168, 140, 130, 125, 111, 97, 83.

5.5. *4-Dodecyloxy-2,3-difluorophenylboronic acid (**5**)*

Quantities: compound **4** (13·33 g, 0·0447 mol) in anhydrous THF (150 ml), *n*-butyllithium (25 ml, 2·5 M in hexane, 0·0625 mol) and trimethyl borate (9·33 g, 0·09 mol) in anhydrous THF (25 ml). The experimental procedure was as described for the preparation of compound **2**. Yield 16·44 g (108%); ^{1}H NMR ($CDCl_3$) δ 0·85, (3H, t), 1·30 (18H, m), 1·70 (2H, quint), 4·05 (2H, t), 6·95 (1H, m), 7·30 (1H, m), 8·15 (2H, broad s); IR (KCl) ν_{max} 3100–3600, 2990, 2960, 2915, 2880, 1620, 1505, 1500, 1465, 1355, 1300, 1210, 1125, 1085, 1060, 1025 cm^{-1}; MS *m/z* 342 (M^+), 315, 147, 130, 112, 98, 84.

5.6. *1-Bromo-3-fluoro-4-dodecyloxybenzene (**7**)*

Quantities: compound **6** (20·80 g, 0·109 mol) in acetone (300 ml), 1-bromododecane (27·17 g, 0·109 mol) in acetone (30 ml) and potassium carbonate (46 g, 0·33 mol). The experimental procedure was as described for the preparation of compound **4**. Yield 38·02 g (97%); b.p. 176–178°C at 1·1 mmHg; ^{1}H NMR ($CDCl_3$) δ 0·85 (3H, t), 1·30 (18H, m), 1·80 (2H, quint), 4·00 (2H, t), 6·80 (1H, t), 7·20 (2H, m); IR (KCl) ν_{max} 2920, 2850, 1580, 1495, 1460, 1410, 1390, 1310, 1280, 1260, 1240, 1205, 1130, 1070, 1020 cm^{-1}; MS *m/z* 360 (M^+), 358 (M^+), 190, 111, 97, 83, 69, 63, 55.

5.7. *4-Dodecyloxy-3-fluorophenylboronic acid (**8**)*

Quantities: compound **7** (10·00 g, 0·039 mol) in anhydrous THF (150 ml), *n*-butyllithium (17 ml, 2·5 M in hexane, 0·0425 mol) and trimethyl borate (8·12 g, 0·078 mol) in anhydrous THF (50 ml). The experimental procedure was as described for the preparation of compound **2**. Yield 9·64 g (107%); ^{1}H NMR ($CDCl_3$) δ 0·90 (3H, t), 1·30 (18H, m), 1·80 (2H, quint), 4·00 (2H, t), 7·00 (2H, m), 7·80 (1H, m), no obvious OH absorption; IR (KCl) ν_{max} 3100–3600, 2920, 2850, 1605, 1500, 1455, 1410, 1350, 1305, 1270, 1220, 1130, 1090, 1020 cm^{-1}; MS *m/z* 324 (M^+), 138, 128, 112, 97, 83, 69.

5.8. *4-Bromo-2-fluorophenol (**10**)*

Bromine (72·12 g, 0·45 mol) in glacial acetic acid (40 ml) was added to a stirred solution of compound **9** (50·02 g, 0·45 mol) in glacial acetic acid (200 ml) over 5 min at 5°C. The mixture was stirred for 5 min and poured into water (1000 ml). The product was extracted into dichloromethane (twice), and the combined dichloromethane extracts were washed with brine (300 ml) and water (300 ml) and dried ($MgSO_4$). The solvent was removed *in vacuo* to yield a crude product which was recrystallized from petroleum spirit (40–60°C) at 0°C to give an off-white solid. Yield 64·4 g (75%); m.p. 32·5–33·5°C; ^{1}H NMR ($CDCl_3$) δ 6·00 (1H, broad s), 6·60 (2H, m), 6·85 (1H, t); IR (KCl) ν_{max} 3000–3500, 1605, 1595, 1495, 1455, 1380, 1350, 1295, 1250, 1225, 1155, 1120, 1040 cm^{-1}; MS *m/z* 192 (M^+), 190 (M^+), 111, 95, 83.

5.9. *1-Bromo-4-dodecyloxy-2-fluorobenzene (**11**)*

Quantities: compound **10** (15·00 g, 0·078 mol) in acetone (215 ml), 1-bromododecane (19·56 g, 0·079 mol) in acetone (20 ml) and potassium carbonate (33·16 g, 0·204 mol). The experimental procedure was as described for the preparation of compound **4**. Yield 24·77 g (89%); b.p. 180–182°C at 1·2 mmHg; ^{1}H NMR ($CDCl_3$) δ 0·85 (3H, t), 1·30 (18H, m), 1·75 (2H, quint), 3·90 (2H, t), 6·65 (2H, m), 7·40 (1H, t); IR (KCl) ν_{max} 2920, 2850, 1600, 1580, 1485, 1460, 1430, 1420, 1380, 1320, 1290, 1260, 1240, 1165, 1140, 1120, 1050, 1015 cm^{-1}; MS *m/z* 360 (M^+), 358 (M^+), 190, 111, 97, 83, 69, 63, 57.

5.10. *4-Dodecyloxy-2-fluorophenylboronic acid (**12**)*

Quantities: compound **11** (8·00 g, 0·022 mol) in anhydrous THF (92 ml), *n*-butyllithium (10 ml, 2·5 M in hexane, 0·025 mol) and trimethyl borate (4·79 g,

0·045 mol) in anhydrous THF (35 ml). The experimental procedure was as described for the preparation of compound **2**. Yield 7·69 g (106%); ^{1}H NMR ($CDCl_3$) δ 0·85 (3H, t), 1·30 (18H, m), 1·70 (2H, quint), 4·00 (2H, t), 6·70 (2H, m), 7·50 (1H, t), 7·85 (2H, broad s); IR (KCl) ν_{max} 3100–3700, 2920, 2850, 1615, 1560, 1465, 1425, 1380, 1345, 1290, 1230, 1145, 1110, 1025, 1005 cm^{-1}; MS *m/z* 324 (M^+), 296, 196, 156, 128, 112, 97, 83, 69, 57.

5.11. *trans-(1R, 2S)-(+)-1-(2,3-Difluoro-4-dodecyloxybiphenyl-4'-yl)-2-methoxycyclohexane* (**14**)

Quantities: compound **13** (0·76 g, 0·0028 mol) in 1,2-dimethoxyethane (3 ml), aqueous sodium hydrogen carbonate (7 ml, 2M), tetrakis(triphenylphosphine)palladium(0) (0·15 g, 0·12 mmol) and compound **5** (1·20 g, 0·0035 mol) in 1,2-dimethoxyethane (3 ml). The experimental procedure was as described in a previous publication [14]. The crude product was purified by column chromatography (silica gel/dichloromethane) and recrystallized from ethanol to yield a white solid. Yield 0·60 g (44%); m.p. 39–40°C; $[\alpha]_D$ + 2·3° (0·0205 g ml^{-1}, 27°C); ^{1}H NMR ($CDCl_3$) δ 0·90 (3H, t), 1·20–1·60 (22H, m), 1·70–1·90 (5H, m), 2·30 (1H, m), 2·55 (1H, m), 3·15 (3H, s), 3·30 (1H, m), 4·05 (2H, t), 6·80 (1H, m), 7·10 (1H, m), 7·30 (2H, m), 7·45 (2H, m); IR (KCl) ν_{max} 2920, 2850, 1625, 1500, 1470, 1410, 1400, 1315, 1295, 1195, 1130, 1095, 1075 cm^{-1}; MS *m/z* 486 (M^+), 318, 286, 258, 245, 232, 219, 203, 183, 170, 151, 143, 128, 115, 91, 83, 71; CHN analysis requires: C 76·54%, H 9·11%; found: C 76·14%, H 9·25%.

5.12. *trans-(1R, 2S)-(+)-1-(4-Dodecyloxy-3-fluorobiphenyl-4'-yl)-2-methoxycyclohexane* (**15**)

Quantities: compound **13** (0·76 g, 0·0028 mol) in 1,2-dimethoxyethane (3 ml), aqueous solution of sodium hydrogen carbonate (7 ml, 2M), tetrakis(triphenylphosphine)palladium(0) (0·15 g, 0·12 mmol) and compound **8** (1·22 g, 0·0035 mol) in 1,2-dimethoxyethane (4 ml). The experimental procedure was as described for the preparation of compound **14**. Yield 0·53 g (41%); m.p. 50–51°C; $[\alpha]_D$ + 7·1° (0·0203 g ml, 25°C); ^{1}H NMR ($CDCl_3$) δ 0·90 (3H, t), 1·20–1·60 (22H, m), 1·70–1·90 (5H, m), 2·30 (1H, m), 2·55 (1H, m), 3·15 (3H, s), 3·30 (1H, m), 4·05 (2H, t), 7·00 (1H, t), 7·30 (4H, m), 7·50 (2H, d); IR (KCl) ν_{max} 2920, 2860, 1615, 1580, 1560, 1530, 1500, 1485, 1465, 1450, 1400, 1310, 1290, 1270, 1260, 1245, 1210, 1190, 1130, 1105, 1095, 1070, 1040, 1020 cm^{-1}; MS *m/z* 468 (M^+), 300, 268, 240, 227, 214, 201, 150, 125, 97, 83, 71; CHN analysis requires: C 79·44%, H 9·68%; found: C 79·14%, H 9·84%.

5.13. *trans-(1R, 2S)-(+)-1-(4-Dodecyloxy-2-fluorobiphenyl-4'-yl)-2-methoxycyclohexane* (**16**)

Quantities: compound **13** (0·76 g, 0·0028 mol) in 1,2-dimethoxyethane (3 ml), aqueous solution of sodium hydrogen carbonate (7 ml, 2M), tetrakis(triphenylphosphine)palladium(0) (0·15 g, 0·12 mmol) and compound **12** (1·13 g, 0·0035 mol) in 1,2-dimethoxyethane (3 ml). The experimental procedure was as described for the preparation of compound **14**. Yield 0·30 g (23%); m.p. 47–48°C; $[\alpha]_D$ + 8·4° (0·0172 g ml^{-1}, 27°C); ^{1}H NMR ($CDCl_3$) δ 0·90 (3H, t), 1·20–1·60 (18H, m), 1·70–1·90 (5H, m), 2·30 (1H, m), 2·55 (1H, m), 3·15 (3H, s), 3·30 (1H, m), 3·95 (2H, t), 6·70 (2H, m), 7·25–7·50 (5H, m); IR (KCl) ν_{max} 2920, 2850, 1620, 1575, 1520, 1495, 1470, 1405, 1395, 1355, 1315, 1285, 1230, 1190, 1165, 1125, 1095, 1040, 1000 cm^{-1}; MS *m/z* 468 (M^+), 300, 268, 240, 227, 214, 201, 183, 150, 125, 115, 97, 83, 71; CHN analysis requires: C 79·44%, H 9·68%; found: C 79·39%, H 9·78%.

5.14. *1-(2,3-Difluorophenyl)cyclohex-1-ene* (**17**)

n-Butyllithium (68 ml, 2·5 M in hexane, 0·170 mol) was added dropwise to a stirred, cooled (−78°C) solution of compound **1** (17·5 g, 0·154 mol) in dry THF (280 ml) under dry nitrogen. The reaction mixture was maintained under these conditions for 2·5 h and then a solution of cyclohexanone (14·72 g, 0·154 mol) in dry THF (40 ml) was added dropwise at −78°C. The reaction mixture was allowed to warm to room temperature overnight and then washed with saturated ammonium chloride solution (600 ml). The product was extracted into ether (twice) and the combined ethereal extracts were washed with water and dried ($MgSO_4$). The solvent was removed *in vacuo* to yield an orange liquid. The crude intermediate, toluene (300 ml) and toluene-4-sulfonic acid (5·20 g, 0·0273 mol) were heated under reflux in a Dean–Stark apparatus for 1·5 h. The resulting solution was allowed to cool and was washed with a saturated solution of sodium hydrogen carbonate (300 ml); the product was diluted with ether. The organic layer was washed with water and dried ($MgSO_4$). The solvent was removed *in vacuo* to yield a colourless liquid which was purified by column chromatography (silica gel/dichloromethane) and distillation. Yield 17·6 g (59%); b.p. 84–86°C at 0·9 mmHg; ^{1}H NMR ($CDCl_3$) δ 1·70 (4H, m), 2·20 (2H, m), 2·40 (2H, t), 5·95 (1H, t), 6·95 (3H, m); IR (KCl) ν_{max} 2950, 2850, 1620, 1585, 1485, 1470, 1440, 1385, 1330, 1260, 1250, 1220, 1160, 1085, 1065, 1040, 1030 cm^{-1}; MS *m/z* 194 (M^+), 179, 165, 151, 146, 140, 133, 127, 119, 115, 107, 101, 94, 88, 67, 51.

5.15. *trans-(1S, 2R)-(+)-2-(2,3-Difluorophenyl)cyclohexan-1-ol* (**18**)

Boron trifluoride diethyl etherate (6·0 ml, 0·0423 mol) was added dropwise over 2 min to a solution of (*R*)-

Alpine-boramine® (9·43 g, 0·0226 mol) in anhydrous THF (20 ml) under dry nitrogen. This mixture was stirred under dry nitrogen for 2 h at room temperature, cooled to 0°C and a solution of compound **17** (7·5 g, 0·0386 mol) in anhydrous THF (20 ml) was added. The mixture was then allowed to warm to room temperature overnight and stirred for a further 5 days. Any solid then present was removed by filtration. The filtrate was heated to reflux and aqueous sodium hydroxide (16 ml, 10%) followed by aqueous hydrogen peroxide (13·5 ml, 30%) was added. This mixture was heated under reflux for 1 h and then allowed to cool to room temperature. The solution was saturated with potassium carbonate and the product was extracted into ether (twice). The combined ethereal extracts were washed with water and dried ($MgSO_4$). The solvent was removed *in vacuo* to yield a colourless liquid. This crude product was purified by column chromatography (silica gel/dichloromethane) to give a white solid. Yield 5·48 g (67%); b.p. 108–110°C at 2·4 mmHg; $[\alpha]_D + 9{\cdot}0°$ (0·024 g ml^{-1}, 26°C); ^{1}H NMR ($CDCl_3$) δ 1·40–1·60 (5H, m), 1·80 (3H, m), 2·20 (1H, m), 2·80 (1H, m), 3·75 (1H, m), 7·00 (3H, m); IR (KCl) ν_{max} 3100–3600, 2915, 2855, 1700, 1620, 1590, 1480, 1445, 1405, 1345, 1310, 1280, 1235, 1195, 1160, 1070, 1055, 1020 cm^{-1}; MS *m/z* 212 (M^+), 194, 179, 174, 169, 156, 153, 146, 140, 133, 127, 119, 113, 107, 101, 98, 95, 91, 75, 67, 63.

5.16. *trans-(1R, 2S)-(+)-1-(2,3-Difluorophenyl)-2-methoxycyclohexane* (**19**)

Compound **18** (5·00 g, 0·0236 mol) was added to a solution of sodium hydride (1·42 g, 80%, 0·047 mol) in DMF (15 ml) under dry nitrogen. This mixture was stirred for 15 min and a solution of methyl iodide (3·40 g, 0·02365 mol) in DMF (15 ml) was added. The reaction mixture was stirred for 12 h at room temperature and water (20 ml) was added slowly. The product was extracted with ether (twice). The combined ethereal extracts were washed with water and dried ($MgSO_4$). The solvent was removed *in vacuo* to yield a colourless liquid. The crude product was purified by column chromatography (silica gel/dichloromethane) to give a colourless liquid. Yield 3·16 g (59%); b.p. (short path) 140–142°C at 1·0 mmHg; $[\alpha]_D + 20{\cdot}4°$ (0·032 g ml^{-1}, 25°C); ^{1}H NMR ($CDCl_3$) δ 1·20–1·60 (4H, m), 1·70–2·00 (3H, m), 2·25 (1H, m), 2·90 (1H, m), 3·18 (3H, s), 3·35 (1H, m), 7·00 (3H, m); IR (KCl) ν_{max} 2915, 2855, 2820, 1620, 1590, 1480, 1445, 1375, 1355, 1345, 1320, 1275, 1255, 1235, 1210, 1190, 1160, 1120, 1100, 1060, 1045, 1020 cm^{-1}; MS *m/z* 226 (M^+), 194, 166, 127, 71, 67, 58, 45.

5.17. *2,3-Difluoro-4-[trans-(1R, 2S)-(+)-2-methoxycyclohexyl]phenylboronic acid* (**20**)

Quantities: compound **19** (4·5 g, 0·02 mol) in anhydrous THF (100 ml), *n*-butyllithium (9 ml, 2·5 M in hexane, 0·0225 mol) and trimethyl borate (4·30 g, 0·041 mol) in anhydrous THF (30 ml). The experimental procedure was as described for the preparation of compound **2**. Yield 5·71 g (106%); $[\alpha]_D + 16{\cdot}6°$ (0·020 g ml^{-1}, 25°C); ^{1}H NMR ($CDCl_3$) δ 0·80–1·80 (7H, m), 2·20 (1H, m), 2·80 (1H, m), 3·10 (3H, s), 3·35 (1H, m), 7·20 (2H, m), 8·25 (2H, broad s); IR (KCl) ν_{max} 3100–3600, 2915, 2855, 2820, 1625, 1495, 1450, 1380, 1345, 1345, 1290, 1270, 1250, 1235, 1220, 1190, 1160, 1140, 1120, 1100, 1070, 1020 cm^{-1}; MS *m/z* 270 (M^+), 226, 194, 166, 140, 127, 98, 85, 77, 71, 67, 63.

5.18. *trans-(1R, 2S)-(+)-1-(2,3-Difluoro-4'-dodecyloxybiphenyl-4-yl)-2-methoxycyclohexane* (**22**)

Quantities: compound **20** (1·20 g, 0·0049 mol) in 1,2-dimethoxyethane (7 ml), aqueous solution of sodium hydrogen carbonate (7 ml, 2M), tetrakis(triphenylphosphine)palladium(0) (0·30 g, 0·24 mmol) and compound **21** (0·95 g, 0·0028 mol) in 1,2-dimethoxyethane (2·5 ml). The experimental procedure was as described for the preparation of compound **14**. Yield 1·02 g (75%); m.p. 42–43°C; $[\alpha]_D + 18{\cdot}1°$ (0·0264 g ml^{-1}, 27°C); ^{1}H NMR ($CDCl_3$) δ 0·90 (3H, t), 1·20–1·60 (22H, m), 1·70–1·90 (5H, m), 2·30 (1H, m), 2·90 (1H, m), 3·20 (3H, s), 3·40 (1H, m), 4·00 (2H, t), 6·95–7·15 (4H, m), 7·45 (2H, m); IR (KCl) ν_{max} 2920, 2850, 1610, 1580, 1520, 1490, 1460, 1410, 1370, 1360, 1310, 1285, 1250, 1190, 1180, 1125, 1100, 1050, 1025 cm^{-1}; MS *m/z* 486 (M^+), 318, 286, 245, 232, 219, 214, 201, 197, 188, 177, 169, 159, 152, 143, 123, 111, 97, 91, 83, 71; CHN analysis requires: C 76·25%, H 9·14%; found: C 76·25%, H 9·14%.

5.19. *1-(4-Bromo-2-fluorophenyl)cyclohex-1-ene* (**24**)

Quantities: compound **23** (12·00 g, 0·040 mol) in dry THF (80 ml), *n*-butyllithium (16 ml, 2·5 M in hexane, 0·040 mol), cyclohexanone (3·92 g, 0·040 mol) in dry THF (20 ml) and toluene-4-sulfonic acid (1·00 g, 0·0053 mol). The experimental procedure was as described for the preparation of compound **17**. Yield 9·48 g (93%); b.p. 106–108°C at 1·7 mmHg; ^{1}H NMR ($CDCl_3$) δ 1·70 (4H, m), 2·20 (2H, m), 2·40 (2H, t), 5·95 (1H, t), 7·20 (3H, m); IR (KCl) ν_{max} 2920, 2860, 2830, 1630, 1595, 1555, 1480, 1445, 1430, 1400, 1270, 1240, 1205, 1135, 1120, 1000 cm^{-1}; MS *m/z* 254 (M^+), 239, 226, 213, 200, 175, 160, 147, 133, 127, 119, 109, 99, 94, 87, 79, 73, 67.

5.20. *trans-(1S, 2R)-(+)-2-(4-Bromo-2-fluorophenyl)cyclohexan-1-ol* (**25**)

Quantities: boron trifluoride diethyl etherate (13 ml, 0·0916 mol), (*R*)-Alpine-boramine® (20·15 g, 0·0483 mol)

in anhydrous THF (50 ml), compound **24** (21·00 g, 0·077 mol), aqueous sodium hydroxide (36·5 ml, 10%) followed by aqueous hydrogen peroxide (78 ml, 12%). The experimental procedure was as described for the preparation of compound **18**. Yield 11·50 g (55%); m.p. 64·5–65·5°C; $[\alpha]_D + 17·36°$ (0·029 g ml^{-1}, 27°C); ^{1}H NMR ($CDCl_3$) δ 1·40–1·60 (5H, m), 1·80 (3H, m), 2·20 (1H, m), 2·80 (1H, m), 3·70 (1H, m), 7·25 (3H, m); IR (KCl) ν_{max} 3100–3600, 2915, 1700, 1600, 1570, 1480, 1445, 1405, 1260, 1210, 1130, 1060 cm^{-1}; MS *m/z* 272 (M^+), 254, 228, 215, 202, 189, 175, 160, 147, 134, 121, 109, 98, 82, 75, 71, 66, 62, 56.

5.21. *trans-(1R, 2S)-(+)-1-(4-Bromo-2-fluorophenyl)-2-methoxycyclohexane* (**26**)

Quantities: compound **25** (5·00 g, 0·0196 mol), sodium hydride (1·18 g, 80%, 0·039 mol) in DMF (20 ml), methyl iodide (2·79 g, 0·0196 mol) in DMF (20 ml). The experimental procedure was as described for the preparation of compound **19**. Yield 3·56 g (47%); b.p. (short path) 186–187°C at 0·45 mmHg; $[\alpha]_D + 14·8°$ (0·154 g ml^{-1}, 23°C); ^{1}H NMR ($CDCl_3$) δ 1·20–1·60 (4H, m), 1·70–1·90 (3H, m), 2·30 (1H, m), 2·85 (1H, m), 3·15 (3H, s), 3·30 (1H, m), 7·20 (3H, m); IR (KCl) ν_{max} 2915, 2850, 2820, 1600, 1570, 1480, 1445, 1405, 1375, 1355, 1340, 1325, 1260, 1230, 1210, 1170, 1130, 1100, 1070, 1040, 1010 cm^{-1}; MS *m/z* 286 (M^+), 256, 226, 202, 187, 175, 160, 147, 133, 120, 101, 81, 71, 58, 42.

5.22. *trans-(1R, 2S)-(+)-1-(4'-Dodecyloxy-3-fluorobiphenyl-4-yl)-2-methoxycyclohexane* (**28**)

Quantities: compound **26** (0·81 g, 0·003 mol) in 1,2-dimethoxyethane (3 ml), aqueous solution of sodium hydrogen carbonate (7 ml, 2M), tetrakis(triphenylphosphine)palladium(0) (0·25 g, 0·21 mmol) and compound **27** (1·25 g, 0·0053 mol) in 1,2-dimethoxyethane (4 ml). The experimental procedure was as described for the preparation of compound **14**. Yield 0·78 g (56%); m.p. 58–59°C; $[\alpha]_D + 4·7°$ (0·0202 g ml^{-1} at 22°C); ^{1}H NMR ($CDCl_3$) δ 0·90 (3H, t), 1·20–1·60 (22H, m), 1·70–1·90 (5H, m), 2·30 (1H, m), 2·85 (1H, m), 3·20 (3H, s), 3·40 (1H, m), 4·00 (2H, t), 6·95 (2H, d), 7·25 (3H, m), 7·5 (2H, d); IR (KCl) ν_{max} 2920, 2850, 1605, 1580, 1555, 1520, 1495, 1470, 1450, 1390, 1350, 1285, 1265, 1245, 1210, 1185, 1170, 1125, 1100, 1095, 1040, 1020 cm^{-1}; MS *m/z* 468 (M^+), 369, 300, 253, 239, 234, 227, 220, 214, 201, 183, 172, 159, 146, 133, 121, 107, 97, 91, 83, 71; CHN analysis requires: C 79·44%, H 9·68%; found: C 79·29%, H 9·90%.

5.23. *trans-(1S, 2R)-(+)-2-(4'-Dodecyloxybiphenyl-4-yl)cyclohexan-1-ol* (**30**)

Quantities: compound **29** (0·77 g, 0·003 mol) in 1,2-dimethoxyethane (3 ml), aqueous solution of sodium hydrogen carbonate (7 ml, 2 M), tetrakis(triphenylphosphine)palladium(0) (0·25 g, 0·20 mmol) and compound **27** (1·15 g, 0·0038 mol) in 1,2-dimethoxyethane (16 ml). The experimental procedure was as described for the preparation of compound **14**. Yield 0·75 g (57%); m.p. 90–91°C; $[\alpha]_D + 5·8°$ (0·0247 g ml^{-1}, 22°C); ^{1}H NMR ($CDCl_3$) δ 0·90 (3H, t), 1·20–1·60 (23H, m), 1·70–1·90 (5H, m), 2·15 (1H, m), 2·50 (1H, m), 3·70 (1H, m), 4·00 (2H, t), 6·95 (2H, d), 7·30 (2H, d), 7·50 (4H, m); IR (KCl) ν_{max} 3100–3700, 2920, 2850, 1605, 1580, 1525, 1495, 1465, 1390, 1280, 1250, 1180, 1130, 1110, 1100, 1060, 1040, 1000 cm^{-1}; MS *m/z* 436 (M^+), 420, 351, 268, 221, 209, 196, 183, 165, 153, 141, 128, 107, 97, 77, 69; CHN analysis requires: C 81·86%, H 10·88%; found: C 81·55%, H 10·32%.

5.24. *trans-(1S, 2R)-(+)-2-(4'-Dodecyloxy-3-fluorobiphenyl-4-yl)cyclohexan-1-ol* (**31**)

Quantities: compound **25** (0·76 g, 0·003 mol) in 1,2-dimethoxyethane (3 ml), aqueous solution sodium hydrogen carbonate (7 ml, 2 M), tetrakis(triphenylphosphine)palladium(0) (0·25 g, 0·20 mmol) and compound **27** (1·15 g, 0·0038 mol) in 1,2-dimethoxyethane (16 ml). The experimental procedure was as described for the preparation of compound **14**. Yield 0·57 g (42%); m.p. 94–95°C; $[\alpha]_D + 11·7°$ (0·0205 g ml^{-1}, 27°C); ^{1}H NMR ($CDCl_3$) δ 0·90 (3H, t), 1·20–1·60 (23H, m), 1·70–1·90 (5H, m), 2·15 (1H, m), 2·85 (1H, m), 3·80 (1H, m), 4·00 (2H, t), 6·95 (2H, d), 7·30 (3H, m), 7·50 (2H, d); IR (KCl) ν_{max} 3100–3700, 2920, 2850, 1605, 1580, 1555, 1525, 1495, 1465, 1430, 1395, 1280, 1250, 1225, 1210, 1200, 1185, 1170, 1135, 1125, 1110, 1100, 1080, 1060, 1045, 1035, 1020, 1005 cm^{-1}; MS *m/z* 454 (M^+), 286, 267, 240, 227, 214, 201, 183, 171, 133, 97, 83, 69; CHN analysis requires: C 78·66%, H 10·21%; found: C 78·45%, H 9·76%.

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