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The relationship between molecular structure and mesomorphic properties of 2,2′- and 3,2′-difluoroterphenyls synthesized by palladium-catalysed cross-couplings

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Several homologues of two structurally different types of mesogenic difluoroterphenyls have been prepared. One set of compounds contains two inner-core fluoro-substituents and the other set possesses both an inner-core and an outer-core fluoro-substituent. The use of various types of palladium-catalysed cross-coupling reactions was invaluable in the synthesis (for example, selective couplings, and couplings to trifluoromethanesulphonate derivatives). Additionally, a novel selective lithiation is reported. The mesogenic materials are all low melting and the types of mesophase generated are considerably structure dependent. However, most of the materials support the tilted S_C phase which is required of ferroelectric host materials. The mesomorphic behaviour of these novel materials is discussed in terms of the molecular structure and the structure/property relationships are compared with those for difluoroterphenyls with different arrangements of lateral fluoro-substitution.

1. Introduction

Typical models depict calamitic liquid crystals as rods, each consisting of a rigid core which has two flexible terminal chains [1]. The core provides the anisotropy necessary to give mesomorphic behaviour and the terminal chains serve to reduce the melting point so that mesophases can be exhibited. These types of structure are excellent for generating mesomorphism, but they do not take account of the other factors that are of equal importance when considering materials for specific applications. In these cases, specific functional moieties need to be present in the structure to provide the necessary physical properties. The generation of the S_C phase [2–6], for example, requires a particularly subtle blend of a correctly positioned lateral dipolar group and an optimum compromise of terminal chain length. If the S_C phase is to be exhibited across a useful temperature range, then the melting point must be low, which is not always easy to achieve. Quite apart from the mesomorphic considerations, there are different optimum electronic and optical properties that are required for different applications; additionally, other factors such as viscosity, elastic constants and material stability and compatibility must be considered [7].

Lateral substituents have long been used to modify the mesomorphism of compounds and some remarkable materials have been produced [4–6, 8–16]. Lateral fluoro-substitution in mesogenic materials, reported for the first time in 1954 [17], is of great importance in mesogenic materials because of its unique combination of small size and high electronegativity. The first significant use of lateral fluoro-substituents was in the generation of nematic materials [8–13]. The steric effects caused by the protrusion of the fluoro-substituent tend to disrupt the side-to-side intermolecular forces of attraction which reduce the melting point and the tendency to form smectic mesophases (steric effects), whilst being less destructive towards the non-lamellar nematic phase [8–13].

Another remarkable feature of lateral fluoro-substitution is its ability to confer tilted smectic mesomorphism upon many of its compounds [5, 6, 13–16]. The lateral dipole of the fluoro-substituent provides the driving force for the tilt, which, if correctly combined with other dipolar groups (for example, esters or ethers) and/or the correct sizes of terminal chains, results in wide S_C ranges [5, 6, 13–16]. Significant additional benefits of lateral fluoro-substitution have been found that result from combinations of both steric and electronic effects [16].

In terphenyl systems there are two different positions for the fluoro-substituent. Firstly, within the molecular

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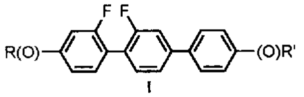
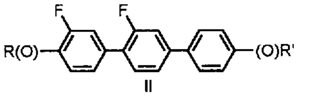
core which results in an inter-annular bond twist which partially disrupts the conjugation, and secondly, on the outer-edge of the molecular core where no inter-annular twisting, due to the fluoro-substituent, is possible [4, 5, 9, 15, 16]. The position of the lateral fluoro-substituent on the molecular core is of fundamental importance to mesomorphic behaviour [4, 5, 9, 15, 16] and also to certain other important physical properties, such as dielectric anisotropy and viscosity [7]. The *ortho-* (i.e. 2,3- and 2′,3′-) difluoroterphenyls [5, 6] have a strong lateral dipole because the two fluoro-substituents are fixed on one side of the molecules. This aids tilting and generates materials with low melting points and very wide $\mathrm{S_C}$ ranges that make excellent host materials for ferroelectric ($\mathrm{S_C^*}$) mixtures [5–7].



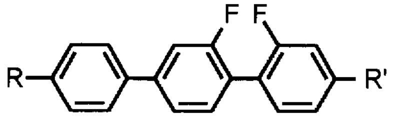
I



II

This paper is concerned with difluoroterphenyls where the two fluoro-substituents are in different rings (structures **I** and **II**). These materials were prepared in order to rationalize further our understanding of the steric and the dipolar effects of lateral fluoro-substituents on mesomorphic properties using model terphenyl materials, with a view to their potential use as host materials for ferroelectric ($\mathrm{S_C^*}$) mixtures for display devices and spatial light modulators. The use of two lateral fluoro-substituents should enable the mesomorphic and other physical properties to be fine-tuned by their appropriate relative positioning. The 2,2′-difluoroterphenyls (structure **I**), shown in table 1, have only one inter-annular twist, albeit one that is caused by two substituents. Both the steric and the polar effects would suggest that the two fluoro-substituents would prefer to be as far apart as possible, therefore broadening the molecules and generating nematogens. However, previous studies have shown that in 2,2′-dihalogenobiphenyls the halogeno-substituents tend to attract each other to achieve a van der Waals minimum bond distance [18]. Other studies [19] have shown that 1,2-dicyanoethane and 1,2-dimethoxyethane, for example, prefer the *gauche* conformation. In fact, esters based on a 2,2′-difluorobiphenyl core have previously been reported to have negative dielectric anisotropy which suggests that the two fluoro-substituents may be acting additively [20]. If this were the case, then the molecular breadth would be minimized and the dipoles of the fluoro-substituents would be mainly additive, perhaps allowing the generation of a $\mathrm{S_C}$ phase. The 3,2′-difluoroterphenyls (structure **II**), shown in table 2, again only have one inter-annular twist; however only one fluoro-substituent is involved in this case and so this 'sub-unit' would be expected to produce a similar effect to that in monofluoroterphenyls. Most significantly, the 3,2′-difluoroterphenyls have the second fluoro-substituent on the outer edge of the core [4, 5, 9, 15, 16]. In this position the fluoro-substituent cannot disrupt the polarizability of the molecular core through inter-annular twisting and so is less disruptive to mesomorphism than a fluoro-substituent located within the core. Such an arrangement should therefore allow the exhibition of the $\mathrm{S_C}$ phase if the other dipoles are correctly positioned in the molecular structure.

Table 1. Transition temperatures for the 2,2′-difluoroterphenyls (**5**, **9** and **10**).



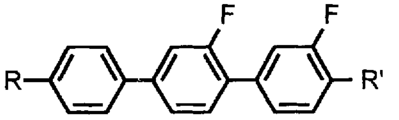
Compound			Transition temperatures/°C						
No.	*R*	*R′*	C		$\mathrm{S_C}$		N		I
5	$C_6H_{13}O$	C_5H_{11}	●	52·0	(●	41·5)	●	122·0	●
9	C_5H_{11}	$C_6H_{13}O$	●	31·5	—		●	114·0	●
10	C_5H_{11}	C_5H_{11}	●	43·5	—		●	85·0	●

A 2,3″-difluoroterphenyl (compound **27**) was also prepared in order to complete the set of analogous compounds [16] shown in table 4. This enables a full and thorough discussion involving two different sets of internally substituted difluoroterphenyls and two different sets of difluoroterphenyls with an outer edge substituent.

2. Synthesis

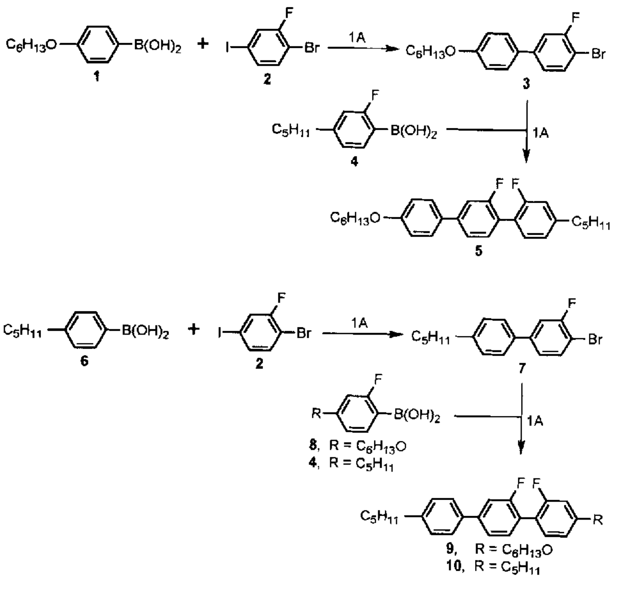
In recent years, the synthesis of new mesogenic materials has increased dramatically in an attempt to satisfy the growing range of applications. Many devices, such as those based on ferroelectric technology, are close to being a commercial success. However, there is still a need for faster, lower viscosity ferroelectric ($\mathrm{S_C^*}$) mixtures that also have the many other necessary characteristics such as stability, high dielectric biaxiality with a net negative dielectric anisotropy, good alignment, low birefringence and good addressing capability [21]. In order to help satisfy all of these requirements, the structural features of materials are often complex when compared to more traditional mesogenic materials. The development of palladium-catalysed cross-coupling procedures for synthesis [22–25] has been of significant benefit to the liquid crystal field. Such methodology allows the construction of materials with synthetically difficult substitution patterns via the synthesis of smaller, more easily managed sub-units that are then coupled together. The various types of coupling reaction and their merits have been discussed previously and the best method available for the preparation of multi-aryl mesogens such

Table 2. Transition temperatures for the 3,2''-difluoroterphenyls (**15**, **23** and **24**).



Compound			Transition temperatures/°C								
No.	*R*	*R'*	C		S_C		S_A		N		I
15	$C_6H_{13}O$	C_5H_{11}	●	45·0	●	64·0	●	156·0	—		●
23	C_5H_{11}	$C_6H_{13}O$	●	41·0	●	72·0	●	131·0	●	140·0	●
24	C_5H_{11}	C_5H_{11}	●	34·0	—		●	115·0	●	116·5	●

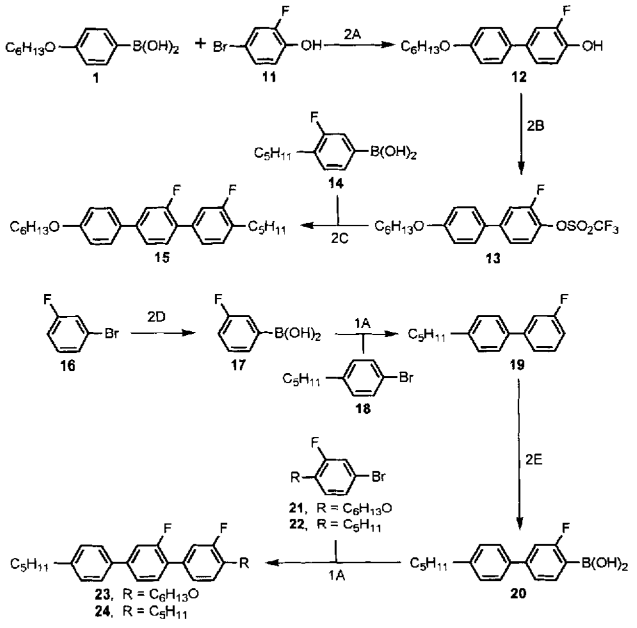
as terphenyls involves arylboronic acids (or their ester derivatives) with aryl halides or trifluoromethanesulphonates (triflates) [24]. Therefore palladium-catalysed cross-couplings involving arylboronic acids have been used in the synthesis of the materials shown in schemes 1 and 2. However, for these terphenyl materials, two coupling reactions were necessary; this means that some form of selectivity was required and this was achieved in three different ways. Scheme 1 shows the use of arylboronic acids (**1** and **6**) in selective coupling reactions with 1-bromo-2-fluoro-4-iodobenzene (compound **2**). The iodo-substituent is the more reactive site (better leaving group) and good yields of materials **3** and **7** were obtained. The selective coupling reactions were continually monitored by GLC analysis to provide optimum yields of the desired product, whilst minimizing the amount of double-coupled material in the crude mixture. Subsequently, the bromo-site was exploited in other, separate cross-coupling reactions to give unsymmetrical terphenyl materials (compounds **5**, **9** and **10**) in excellent overall yields.



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

Scheme 1. The synthetic routes to the 2,2'-difluoroterphenyls.

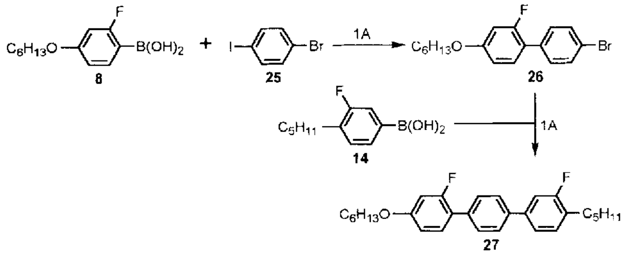
Scheme 2 illustrates the next two different approaches, neither of which involved any real selectivity issues, but for which the overall result was identical to that achieved via the route utilizing selective couplings. The use of a mild base (caesium carbonate) [26] enabled the successful coupling of bromophenol **11** with boronic acid **1** to provide a biphenol compound (**12**). The use of conventional base (aqueous sodium carbonate) in the presence of such phenolic materials results in very low yields (< 10 per cent). The conversion of the biphenol (**12**) into



2A: $Pd(PPh_3)_4$, 1,2-dimethoxyethane, Cs_2CO_3, water.
2B: Trifluoromethanesulphonic anhydride, pyridine.
2C: $Pd(PPh_3)_4$, 1,2-dimethoxyethane, 2 M Na_2CO_3, LiCl.
2D: (i) *n*BuLi, THF; (ii) $(MeO)_3B$, THF, (iii) 10 per cent HCl.
2E: (i) *sec*BuLi, THF, (ii) $(MeO)_3B$, THF, (iii) 10 per cent HCl.

Scheme 2. The synthetic routes to the 3,2'-difluoroterphenyls.

a triflate derivative occurred in unusually low yield (33 per cent), but sufficient material was isolated to enable a coupling reaction with a different arylboronic acid (**14**); this provided the liquid crystalline terphenyl **15** in good yield. The approach that provided compounds **23** and **24** is similar to that used for the synthesis of some 2′,3′-difluoroterphenyls [5], but here there are two different acidic protons in compound **19**. In some previous work [25], several attempts were made to lithiate next to a fluoro-substituent at an internal site, but these failed. This lack of reactivity at the 2-position allowed the prospect of selective lithiation at the less hindered site (4-position) of compound **19**. Compound **19** was prepared by an unambiguous coupling reaction between bromide **18** and the fluoro-substituted boronic acid **17** prepared from 1-bromo-2-fluorobenzene (**16**). Lithiation of compound **19** was initially attempted using *n*-butyllithium, but this resulted in an incomplete reaction. The use of *sec*-butyllithium resulted in the quantitative preparation of the desired boronic acid **20**, which was then coupled with aryl bromides **21** and **22** to provide compounds **23** and **24**, respectively. This novel selective lithiation was thought to be of little use for the analogous alkyloxy-substituted system, because protons next to ether substituents are also labile to butyllithium; this has yet to be attempted, and if successful it could be used in a more efficient preparation of compound **15**. Of course, the methods shown in scheme 1 and scheme 2 are interchangeable, and overall there is little to choose between them, but the selective coupling methodology of scheme 1 is neater and more general. Where possible, it is advisable to avoid the use of boronic acids with an *ortho*-fluoro substituent (for example, as in compounds **4**, **8** and **20**), because the electron-withdrawing nature of the fluoro-substituent facilitates the hydrodeboronation process which prevents coupling [24]. If the coupling reaction is slow (for example, from steric hindrance) then the hydrodeboronation process will occur faster than coupling and poor yields will result [24]. However, methods involving anhydrous conditions have recently been developed that circumvent this problem (for a review see [24]). In the case of compounds **5**, **9** and **10**, the yields are very high, and this is because the coupling procedures are accelerated by the presence of the *ortho*-fluoro-substituent in the coupling bromide compound (for example, **3** and **7**) and the boronic acid was present in sufficient excess (around 20 per cent excess). In the preparation of compounds **23** and **24**, the use of an excess of boronic acid ensured quite good isolated yields (50 per cent). However, the fluoro-substituent of the bromo-substituted species (compounds **21** and **22**) is in the *meta* position, which does not accelerate coupling as in the above cases; this allowed considerable hydrodeboronation to occur before coupling was complete which led to reduced yields.



Scheme 3. The synthetic route to a 2,3″-difluoroterphenyl.

Scheme 3 again illustrates the use of a selective coupling procedure on a bromo-iodo-substituted aryl compound. The desired bromo-substituted compound (**26**) was obtained in good yield and was easily purified. A subsequent coupling with the different arylboronic acid (**14**) provided the desired terphenyl material (compound **27**) in good yield.

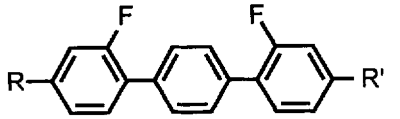
Overall, the lithiation procedures that provide the appropriate arylboronic acids and the subsequent palladium-catalysed cross-coupling reactions constitute a highly efficient methodology in the synthesis of liquid crystal materials of general substitution patterns.

3. Discussion of transition temperatures

The use of a lateral fluoro-substituent in the modification of transition temperatures and other physical properties has been reported for many different types of core system [4–6, 8–16]. Almost always, lateral fluoro-substitution causes a reduction in the overall mesomorphic thermal stability of the materials, although the effect on the melting point is often more variable. The more detailed effect of the lateral fluoro-substituent on melting points, mesophase types and their thermal stabilities is extremely structure dependent. The use of two lateral fluoro-substituents has been recently reported and the largest, but still incomplete, study has been based on 4-alkoxy-4″-alkyl- or 4,4″-dialkyl-1,1′:4′,1″-terphenyls [5, 16]. When using two lateral fluoro-substituents in such systems there are many more structural isomers for each homologue than when monofluoro-substitution is being considered. However, the use of two fluoro-substituents in terphenyl systems is advantageous is providing two broad categories of material that have, in most cases, low melting points. Firstly, certain structural permutations provide materials with wide S_C ranges with narrow S_A and N ranges at higher temperatures [5, 6, 16]; secondly, purely nematogenic materials can be generated by using alternative structural arrangements [16].

Of the many difluoroterphenyls so far reported, [5, 16], compound **5** is the only one to exhibit a S_C phase where the fluoro-substituents are not *ortho* to each other in the same ring or where one of the fluoro-substituents does not occupy an outer edge position; this may be the result of the

Table 3. Transition temperatures for the 2,2″-difluoroterphenyls (**28** and **29**) [16].



Compound			Transition temperature/°C				
No.	*R*	*R′*	C		N		I
28	$C_6H_{13}O$	C_5H_{11}	•	45·0	•	131·0	•
29	C_5H_{11}	C_5H_{11}	•	58·5	•	92·0	•

two fluoro-substituents being attracted to each other (see Introduction). The 2,2′-substitution pattern is quite special, because although both fluoro-substituents are internally positioned in different rings, only one inter-annular bond is affected. Compound **28** (see table 3) [16] also has two internally positioned fluoro-substituents in different rings; however, here there are two inter-annular bonds affected. From the point of view of the inter-annular twists caused by the lateral fluoro-substituents, the $T_{N\text{-}I}$ value of compound **28** should be lower than that for both compounds **5** and **9**. However, the $T_{N\text{-}I}$ value for compound **28** is a significant 9°C higher than that of compound **5**, which suggests that two interannular twists are less destructive of mesomorphism than a single twist caused by two fluoro-substituents. However, compound **5** exhibits a S_C phase, whereas compound **28** supercools to 19°C in the nematic phase, making the S_C phase stability of compound **28** at least 22·5°C lower than that of compound **5**. Additionally, the $T_{N\text{-}I}$ value of compound **9** is 17°C lower than that of compound **28**. Perhaps in the higher temperature nematic phase, with greater thermal energy, the two fluoro-substituents of the 2,2′-difluoro-compounds (**5** and **9**) are less attracted to each other than they appear to be in the S_C phase, so generating broader molecules which reduce the $T_{N\text{-}I}$ value. Similarly the $T_{N\text{-}I}$ value of compound **10** is lower than for its analogue, compound **29** [16]. The enhanced smectic tendency of compound **5**, when compared with the analogous compound **9** is due to the greater polarizability conferred by the fact that the untwisted biphenyl moiety is alkoxy-substituted rather than alkyl-substituted (see later). The S_C phase of compound **5** arises because of the combined dipole moments of the two fluoro-substituents that are tending to act in the same direction, which provides a large enough driving force for molecular tilting to occur when this structural feature is combined with the possibility of an oppositely acting dipole moment from the ether oxygen at the other end of the molecule. This structural arrangement allows a strong lateral dipole at one end of the molecule and a weaker, but significant, dipole at the other end of the molecule to be opposed and ensures the optimum S_C phase stability for a fixed arrangement of fluoro-substituents, often to the point of excluding the S_A phase. On the other hand, compound **9** has all of the dipoles at one end of the molecule and they are not strong enough to provide the extra drive to tilt the molecules with the dipolar combination. The dialkyl compound (**10**), like compound **9**, shows no smectic tendency, and both materials could be useful nematogens. The melting point of the dialkyl-compound (**10**) is higher than that of the alkoxy-compound (**9**) because the alkyl chains are the same length; other, unsymmetrically substituted dialkyl-systems would be expected to have considerably lower melting points. This expectation is substantiated by comparing analogous compounds **33** and **34** (see table 5).

Moving the position of the fluoro-substituent in the outer ring to the outer edge position (see table 2) considerably changes the mesomorphic nature of the compounds. Compound **15** has an untwisted alkoxy-substituted biphenyl section and in combination with the outer-edge fluoro-substituent has conferred significant smectic character upon the material. In fact, the S_A phase stability is so high that the nematic phase is not revealed. The dipoles present in compounds **15** and **23** are from the two fluoro-substituents and the ether moiety; appropriate relative positioning of these groups allows tilting and the S_C phase is exhibited up to quite a high temperature. Compound **23** does not benefit from the enhanced polarizability of the untwisted alkoxy-substituted biphenyl section (see later) and so the S_A phase stability is considerably reduced, and this allows the nematic phase to be exhibited. Of greater importance is that the S_C phase stability of compound **23** is higher than that of compound **15**, despite the lower overall smectic tendency and despite the accumulation of dipolar units at one end of the molecule. This is conveniently explained by considering the different relative dipole positions. Compound **23** has the ether oxygen in mesomeric combination with the outer edge fluoro-substituent which confers a particularly strong dipole (as measured by the magnitude of the negative $\Delta\varepsilon$ in the 2,3-difluoroterphenyls) [7]. Although the other dipolar fluoro-substituent is rather close, the strength of the outer-most dipole is sufficient to confer a strong tilting tendency. So the overall smectic tendency depends on the molecular polarizability and the S_C phase stability, and additionally, it depends upon the relative positions and magnitudes of the molecular dipoles. Compounds **15** and **23** are shown in figure 1 to illustrate the way in which the relative stabilities of the S_C and S_A phases can be controlled by varying the positions of the fluoro-substituents. It should be noted that the levels of mesomorphic character shown in figure 1 are relative to each other and are not absolute, because the combination for compound **24** of the 'poor S_C unit' with the 'poor general smectic unit'

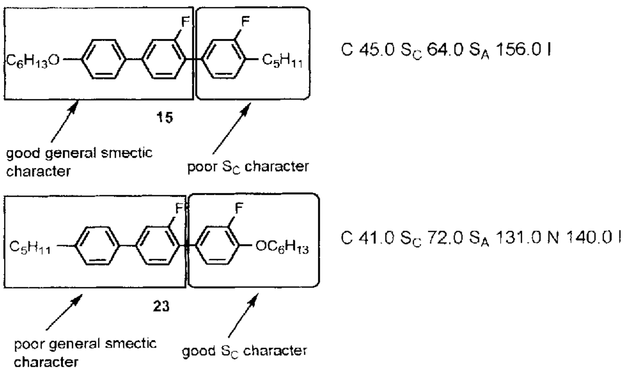


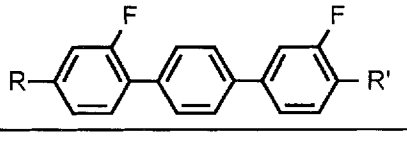
Figure 1. The effect of the position of the fluoro-substituents on the relative stabilities of the S_C and S_A phases.

gives high S_A phase stability, but an S_C phase is not seen even though the material supercooled to − 10°C. The other combination would give a dialkoxy-substituted compound which, although likely to improve the S_C phase stability, would probably lead to a high melting point. The lateral dipoles in compound **24** are sufficient to confer a good degree of lamellar attraction, but the magnitudes and relative positions do not confer tilting, because the two dipoles (only from fluoro-substituents) are too close together and neither is strong enough to induce molecular pivoting. Perhaps the most remarkable feature of the compounds shown in table 2 is their very low melting points. In the case of compounds **15** and **23**, this enables the generation of useful S_C ranges for application as ferroelectric host materials. Materials with outer edge fluoro-substituents that have previously been reported [16] all have considerably higher melting points which can be disadvantageous in applications as ferroelectric host materials.

Table 4 shows the more typical effect of the outer-edge fluoro-substituent on melting point. Compounds **30** and **31** have previously be reported [16] and compound **27** is a novel material to complete this structural set. Compounds **27**, **30** and **31** (see table 4) differ only slightly in structure to compounds **15**, **23** and **24**, but the difference in mesomorphic behaviour is of significant interest. The compounds shown in table 4 (compounds **27**, **30** and **31**) have higher melting points, higher S_C phase stability and lower S_A phase stability than those analogues shown in table 2 (compounds **15**, **23** and **24**), but the T_{N-I} values are similar. The compounds shown in table 4 have higher S_C phase stability because the dipoles are more separated, which gives a more efficient tilting mechanism. Compound **30**, like compound **23**, has the dipole of the ether oxygen interacting mesomerically with the outer-edge fluoro-substituent which provides a strong outboard dipole moment. The dipole moment from the other fluoro-substituent is at the other end of the molecule for compound **30**, and this facilitates tilting to such an extent that the high S_C phase stability is sufficient to eliminate the S_A phase. Compound **27** has two, more closely-matched dipoles but tilting is still favourable, because they are well separated. Compound **27** has a lower S_C phase stability which, based on dipole strengths and positions is fully expected. However, the higher S_A phase stability of compound **27**, based on the previous argument that the compound with the alkoxy-substituted untwisted biphenyl section has the higher S_A phase stability, is an unexpected result. This reasoning is still correct in the majority of cases, but it does not, by itself, cover all situations. In compounds **27** and **30**, the dipole strengths and their positions strongly favour molecular tilting and these factors eclipse the orthogonal molecular requirements of the S_A phase. In fact the sets of alkyl-alkoxy-substituted compounds in tables 2 and 4 show increased S_C and decreased S_A phase stability with strengthening dipoles that facilitate molecular tilting.

The terminal dialkyl-substituted terphenyls (compounds **24** and **31**) provide a good opportunity to analyse the dipolar effect of differently positioned lateral fluoro-substituents on the S_C phase stability without the complication of the presence of a dipolar alkyloxy-group. The first point to note is that the S_C phase is very rare in compounds without dipolar units such as ester or ether moieties. The ease of molecular tilting is illustrated in

Table 4. Transition temperatures for the 2,3″-difluoroterphenyls (**27**, **30** [16] and **31** [16]).



Compound			Transition temperatures/°C								
No.	*R*	*R'*	C		S_C		S_A		N		I
27	$C_6H_{13}O$	C_5H_{11}	●	75·5	●	92·5	●	124·5	●	139·0	●
30	C_5H_{11}	$C_6H_{13}O$	●	90·0	●	105·5	—		●	139·0	●
31	C_5H_{11}	C_5H_{11}	●	69·5	(●	67·0)	●	83·0	●	111·5	●

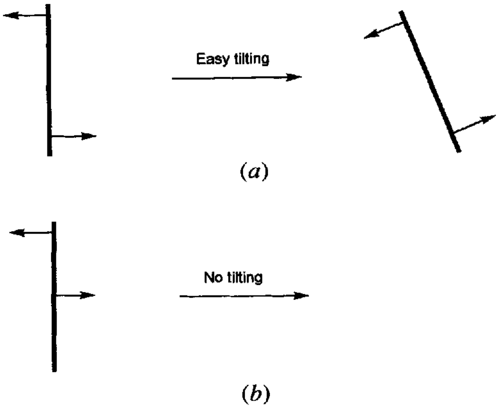
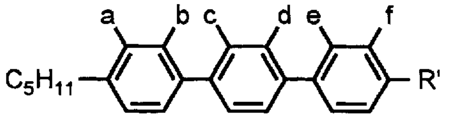


Figure 2. The ease of molecular tilting as a function of lateral dipole separation. (*a*) Lateral dipole positions as in compound 31. (*b*) Lateral dipole positions as in compound 24.

figure 2 for compounds **31** and **24** as a function of their dipole positions. The fact that the dialkyl-compound (**31**) exhibits the S_C phase illustrates that the optimum fluoro-substituent positioning for molecular tilting is when their separation is large (see figure 2 (*a*)). Where one of the fluoro-substituents is moved towards the centre of the molecules (compound **24**)m the S_C phase is not seen even when the compound is cooled to − 10°C (see figure 2 (*b*)). However, the S_A phase stability of compound **24** is considerably higher than that of compound **31**. This is because compound **24** has a terminal benzene ring without lateral substitution which provides a greater lamellar contact area than is possible for compound **31**.

Table 5 (compounds **32–37**) [5] is presented to illustrate the optimum conditions required to generate materials with very high S_C phase stabilities. These materials have the two fluoro-substituents fixed on one side of the molecule, which minimizes molecular breath and maximizes the lateral dipole. Where the two fluoro-substituents are internally positioned, but are fixed on one side of the molecule (compound **32**, table 5), the dipoles of the fluoro-substituents obviously reinforce and provide a strong driving force for molecular tilt. Therefore, even with two inter-annular twists, and hence no untwisted biphenyl section, compound **32** exhibits a S_C phase of quite high thermal stability aided by the narrow molecules. Since there are no other structural moieties that are conducive to smectic phase generation, compound **32** does not exhibit a S_A phase. Even longer chain dialkyl-substituted analogues of compound **32** (for example, compound **34**) exhibit the S_C phase at surprisingly high temperatures because the only source of a lateral dipole is centrally located within the molecule; this illustrates the importance of a strong lateral dipole generated by the two *ortho*-fluoro-substituents. The fact that compound **34** (dialkyl-substituted) exhibits the S_C phase up to a similar temperature to that of the alkyl-alkoxy-substituted compound (**32**) is because of the increase in length on one of the terminal chains and the imbalance in the molecular structure that is created by the use of two unequal terminal chains. This unsymmetrical arrangement of the terminal substituents is responsible for the much lower melting point of compound **34** when compared to that of compound **33**, and in combination with the strong centrally located lateral dipole, facilitates molecular tilting. The relatively high T_{N-I} value of compound **32**, when compared with compounds **5** and **9**, reflects the narrower molecules generated by the use of the *ortho*-difluorophenyl moiety. Those *ortho*-difluoroterphenyls with an outer-edge fluoro-substituent (compounds **35–37**) have a completely unfluorinated biphenyl section which allows for efficient lamellar packing of the molecules. The arrangement of dipole moments in compound **35** is such that the tilt-inducing, strong, lateral dipole from the *ortho*-difluorophenyl unit is reinforced by the ether oxygen at the other end of the molecule to generate an extremely high S_C phase stability. The presence of the

Table 5. Transition temperatures for the 2,3- and 2′,3′-difluoroterphenyls (**32–37**) [5].



Compound								Transition temperatures/°C								
No.	*R*	*a*	*b*	*c*	*d*	*e*	*f*	C		S_C		S_A		N		I
32	$C_6H_{13}O$	H	H	F	F	H	H	●	54·0	●	67·0	—		●	149·0	●
33	C_5H_{11}	H	H	F	F	H	H	●	60·0	—		—		●	120·0	●
34	C_9H_{19}	H	H	F	F	H	H	●	42·5	●	66·0	—		●	110·0	●
35	$C_6H_{13}O$	F	F	H	H	H	H	●	101·5	●	156·5	●	167·0	●	171·5	●
36	$C_6H_{13}O$	H	H	H	H	F	F	●	97·5	●	145·5	—		●	166·0	●
37	C_5H_{11}	F	F	H	H	H	H	●	81·0	●	115·5	●	131·5	●	142·0	●

untwisted alkoxy-substituted biphenyl section aids mesomorphic properties and enables an S_A phase to be revealed. On the other hand, the isomeric compound (**36**) has a very strong lateral dipole at one end of the molecule (the ether oxygen is acting mesomerically with the *ortho*-fluoro-substituent) which induces tilt, but the untwisted biphenyl section is alkyl-substituted in this case, and so mesomorphic properties are reduced. The overall effect of this structural combination is to lower the smectic phase stability to the extent that the S_C phase is generated with a slightly lower phase stability than that of compound **35**, but that the S_A phase is eliminated. The strong lateral dipole from the fluoro-substituents (especially strong when acting mesomerically with an ether oxygen) ensures extremely high S_C phase stability. Even when the sole source of a lateral dipole is from the difluoro-unit (compounds **34** and **37**), the S_C phase stability is still remarkably high.

4. Conclusions

(*a*) Palladium-catalysed cross-coupling reactions enable the efficient synthesis of a general range of lateral fluoro-substituted terphenyls. The selective lithiation of compound **19** to give a boronic acid **20** is particularly useful.

(*b*) The mesomorphic behaviour and hence the suitability for applications of difluoroterphenyl materials depends strongly on the relative positions of the two fluoro-substituents. The combination of an outer-edge fluoro-substituent and an inner-core fluoro-substituent can generate ferroelectric host materials that have low melting points and reasonably high S_C phase stability.

(*c*) The S_C phase stability of compound **5** suggests that the two fluoro-substituents are attracting each other, but the T_{N-I} values of compounds **5**, **9** and **10** in comparison with those of compounds **28** and **29** suggest that in the nematic phase the attraction is less.

(*d*) Compounds **15** and **23** could be very useful materials in ferroelectric (S_C^*) host mixtures because of their very low melting points and reasonably high S_C phase stability. Although compound **27** has a considerably higher melting point, the S_C phase stability is similarly higher and therefore this material could also be useful in ferroelectric mixtures.

5. Experimental

5.1. *Analysis*

Confirmation of the structures of intermediates and products was obtained by ^{1}H NMR spectroscopy (JEOL JNM-GX270 spectrometer), infrared spectroscopy (Perkin–Elmer 457 grating spectrophotometer) and mass spectrometry (Finnigan-MAT 1020 GC/MS spectrometer). The progress of reactions was frequently monitored using a Perkin–Elmer 8320 capillary gas chromatograph fitted with a 12 m QC2/BP1–1·0 SGE column. Transition temperatures were measured using a Mettler FP5 hot-stage and control unit in conjunction with an Olympus BH 2 polarizing microscope and were confirmed using differential scanning calorimetry (Perkin–Elmer DSC-7 and IBM data station). The purities of intermediates **3**, **7**, **13**, **19** and **26** and the final compounds **5**, **9** and **10** (see table 1), **15**, **23** and **24** (see table 2) and **27** (see table 4) were checked by GLC analysis (see above) and by HPLC analysis (Microsorb C18 80-215-C5 RP column) and were found to be >99 per cent pure.

The preparations of intermediates **1** [15], **2** [16], **4** [16], **6** [15], **8** [16], **14** [15], **18** [5], **21** [15], and **22** [15] have been previously reported. Tetrakis(triphenylphosphine)palladium(0) [27] was prepared according to the literature procedure. Compounds **11**, **16** and **25** were purchased from the Aldrich Chemical Co.

5.1.1, *4-Bromo-3-fluoro-4′-hexyloxybiphenyl* (**3**)

Tetrakis(triphenylphosphine)palladium(0) (0·22 g, 0·19 mmol) and compound **1** (1·60, 7·21 mmol) were sequentially added to a stirred mixture of compound **2** (1·80 g, 5·98 mmol) in 1,2-dimethoxyethane (35 ml) and 10 per cent (wt/vol) aqueous sodium carbonate (35 ml) under nitrogen. The stirred mixture was heated under reflux for 3 h (carefully monitored by GLC analysis until the reaction was complete). The mixture was cooled and water was added. The product was extracted into ether ($\times 2$) and the combined ethereal extracts were washed with brine and dried ($MgSO_4$). The solvent was removed *in vacuo* and the crude product was purified by column chromatography (silica gel/petroleum fraction (b.p. 40–60°C)–dichloromethane, 10:1) to give a colourless solid which has heated at 0·1 mmHg in a Kugelrohr apparatus (oven temperature 150°C) to remove any volatile materials.

Yield 1·86 g (89 per cent); m.p. 48–49°C; ^{1}H NMR ($CDCl_3$) δ 0·90 (3 H, t), 1·35 (4 H, m), 1·45 (2 H, quint), 1·80 (2 H, quint), 4·00 (2 H, t), 6·95 (2 H, d), 7·20 (1 H, dd), 7·29 (1 H, dd), 7·46 (2 H, d), 7·55 (1 H, dd); IR (KBr) ν_{max} 2960, 2940, 2860, 1610, 1520, 1475, 1395, 1250, 1185, 1030, 840, 820 cm^{-1}; MS *m/z* 352 (M^+), 350 (M^+), 268, 266.

5.1.2. *2,2′-Difluoro-4″-hexyloxy-4-pentylterphenyl* (**5**)

Quantities: compound **3** (1·66 g, 4·73 mmol), compound **4** (1·19 g, 5·67 mmol), tetrakis(triphenylphosphine)palladium(0) (0·17 g 0·15 mmol).

The experimental procedure was as described for the preparation of compound **3**, except that the reaction mixture was heated under reflux for 16 h (overnight for convenience). The crude product was purified by column chromatography (silica gel/petroleum fraction (b.p. 40–60°C)-dichloromethane, 10:1) to give a colourless solid which was recrystallized from ethanol–ethyl acetate (20:1) to yield colourless cystals.

Yield 1·50 g (73 per cent); transitions (°C) C 52·0 (S_C 41·5) N 122·0 I; ^{1}H NMR ($CDCl_3$) δ 0·90 (6 H, 2 × t), 1·35 (8 H, m), 1·45 (2 H, quint), 1·65 (2 H, quint), 1·80 (2 H, quint), 2·65 (2 H, t), 4·00 (2 H, t), 6·97 (2 H, d), 7·00 (1 H, dd), 7·04 (1 H, dd), 7·30 (1 H, dd), 7·32 (1 H, dd), 7·39 (1 H, dd), 7·42 (1 H, dd), 7·55 (2 H, d); IR (KBr) ν_{max} 2960, 2940, 2860, 1610, 1490, 1400, 1255, 1185, 1120, 1025, 895, 875, 850, 815 cm^{-1}; MS *m/z* 436 (M^+), 421, 407, 393, 379, 365, 352, 295.

5.1.3. *4-Bromo-3-fluoro-4′-pentylbiphenyl* (**7**)

Quantities: compound **2** (2·00 g, 6·64 mmol), compound **6** (1·53 g, 7·97 mmol), tetrakis(triphenylphosphine)palladium(0) (0·25 g, 0·22 mmol).

The experimental procedure was as described for the preparation of compound **3**. The crude product was purified by column chromatography (silica gel/petroleum fraction (b.p. 40–60°C) to give a colourless oil which was heated at 0·1 mmHg in a Kugelrohr apparatus (oven temperature 150°C) to remove any volatile materials.

Yield 1·79 g, (84 per cent), ^{1}H NMR ($CDCl_3$) δ 0·90 (3 H, t), 1·35 (4 H, m), 1·65 (2 H, quint), 2·65 (2 H, t), 7·21 (1 H, dd), 7·24 (2 H, d), 7·32 (1 H, dd), 7·44 (2 H, d), 7·55 (1 H, dd); IR (film) ν_{max} 2960, 2940, 2860, 1480, 1395, 1310, 1200, 1060, 1030, 900, 880, 840, 810 cm^{-1}; MS *m/z* 322 (M^+), 320 (M^+), 265, 263.

5.1.4. *2,2′-Difluoro-4-hexyloxy-4″-pentylterphenyl* (**9**)

Quantities: compound **7** (0·75 g, 2·34 mmol), compound **8** (0·64g, 2·67 mmol), tetrakis(triphenylphosphine)palladium(0) (0·10 g, 0·09 mmol).

The experimental procedure was as described for the preparation of compound **5** and yielded colourless crystals.

Yield 0·87 g (85 per cent); transitions (°C) C 31·5 N 114·0 I; ^{1}H NMR ($CDCl_3$) δ 0·90 (6 H, 2 × t), 1·35 (8 H, m), 1·45 (2 H, quint), 1·65 (2 H, quint), 1·80 (2 H, quint), 2·65 (2 H, t), 4·00 (2 H, t), 6·73 (1 H, dd), 6·78 (1 H, dd), 7·27 (2 H, d), 7·33 (1 H, dd), 7·37 (1 H, dd), 7·40 (2 H, m), 7·53 (2 H, d); IR (film ν_{max} 2960, 2940, 2860, 1620, 1490, 1470, 1400, 1290, 1165, 1120, 890, 830, 805 cm^{-1}; MS *m/z* 436(M^+), 379, 352, 295.

5.1.5 *2,2′-Difluoro-4,4″-dipentylterphenyl* (**10**)

Quantities: compound **7** (0·75 g, 2·34 mmol), compound **4** (0·56 g, 2·67 mmol), tetrakis(triphenylphosphine)palladium(0) (0·10 g, 0·09 mmol).

The experimental procedure was as described for the preparation of compound **5**. The crude product was purified by column chromatography (silica gel/petroleum fraction (b.p. 40–60°C) to give a colourless solid which was recrystallized from ethanol–ethyl acetate (20:1) to yield colourless crystals.

Yield 0·60 g (63 per cent); transitions (°C) C 43·5 N 85·0 I; ^{1}H NMR ($CDCl_3$) δ 0·90 (6 H, 2 × t), 1·40 (8 H, m), 1·65 (4 H, quint), 2·65 (4 H, t), 7·00 (1 H, dd), 7·04 (1 H, dd), 7·27 (2 H, d), 7·34 (1 H, dd), 7·38 (1 H, dd). 7·43 (2 H, m), 7·53 (2 H, d); IR (KBr) ν_{max} 2960, 2940, 2860, 1630, 1555, 1490, 1400, 1190, 1125, 895, 870, 810 cm^{-1}; MS *m/z* 406 (M^+), 349, 292.

5.1.6. *3-Fluoro-4′-hexyloxy-4-hydroxybiphenyl* (**12**)

Caesium carbonate (7·70 g, 0·024 mol) and tetrakis-(triphenylphosphine)palladium(0) (0·56 g, 0·48 mmol) were sequentially added to a stirred mixture of compound **11** (3·00 g, 0·016 mol) and compound **1** (4·30 g, 0·019 mol) in 1,2-dimethoxyethane (30 ml) and water (30 ml) under nitrogen. The mixture was heated under reflux for 15 h (GLC analysis revealed a complete reaction) and cooled. Water was added and the product was extracted into ether (× 2) and the combined ethereal extracts were washed with brine and dried ($MgSO_4$). The solvent was removed *in vacuo* and a small sample of the crude product was recrystallized from 2 per cent ether–hexane to yield a colourless powder.

Crude yield 4·60 g (100 per cent); m.p. 113–114°C; ^{1}H NMR ($CDCl_3$) δ 0·90 (3 H, t), 1·35 (4 H, m), 1·45 (2 H, quint), 1·80 (2 H, quint), 3·95 (2 H, t)., 5·15 (1 H, s), 6·94 (2 H, d), 7·03 (1 H, dd), 7·22 (1 H, ddd), 7·25 (1 H, dd), 7·43 (2 H, d); IR (KBr) ν_{max} 3600–3100, 2960, 2940, 2860, 1600, 1500, 1200, 820 cm^{-1}; MS *m/z* 288 (M^+, 230, 217, 204.

5.1.7. *3-Fluoro-4′-hexyloxybiphenyl-4-yl trifluoromethanesulphonate* (**13**)

Trifluoromethanesulphonic anhydride (5·20 g, 0·018 mol) was added dropwise to a stirred, cooled (0°C) solution of compound **12** (4·60 g, 0·016 mol) in dry pyridine (45 ml) under dry nitrogen. The stirred solution was allowed to warm to room temperature and stirred overnight (TLC and GLC analysis revealed a complete reaction) and the mixture was poured into water. The product was extracted into ether (× 2) and the combined ethereal extracts were washed sequentially with 10 per cent hydrochloric acid, water and brine and dried ($MgSO_4$). The solvent was removed *in vacuo* and the crude product was purified by column chromatography (silica gel/petroleum fraction (b.p. 40–60°C) with the gradual introduction of dichloromethane) to give a colourless solid.

Yield 2·20 g (33 per cent); m.p. 46–47°C; ^{1}H NMR $CDCl_3$) δ 0·90 (3 H, t), 1·35 (4 H, m), 1·50 (2 H, quint), 1·80 (2 H, quint), 4·00 (2 H, t), 6·98 (2 H, d), 7·34–7·44

(3 H, m). 7·47 (2 H, d); IR (KBr) ν_{max} 2960, 2940, 2860, 1605, 1495, 1430, 1215, 1190, 950 cm^{-1}; MS *m/z* 420 (M$^+$), 336, 287, 271, 203.

5.1.8. *3,2′-Difluoro-4″-hexyloxy-4-pentylterphenyl* (15)

Quantities: compound **13** (0·95 g, 2·26 mmol), compound **14** (0·60 g, 2·86 mmol), tetrakis(triphenylphosphine)palladium(0) (0·15 g, 0·13 mmol).

The experimental procedure was as described for the preparation of compound **5**. The crude product was purified by column chromatography (silica gel/petroleum fraction (b.p. 40–60°C)–dichloromethane 10:1) to give a colourless solid which was crystallized from ethanol–ethyl acetate (20:1) to yield colourless crystals.

Yield 0·62 g (63 per cent); transitions (°C) C 45·0 S$_C$ 64·0 S$_A$156·0 I; ^{1}H NMR (CDCl$_3$) δ 0·90 (6 H, 2 × t), 1·35 (8 H, m). 1·45 (2 H, quint), 1·65 (2 H, quint), 1·80 (2 H, quint), 2·65 (2 H, t), 4·00 (2 H, t), 6·98 (2 H, d), 7·25–7·50 (6 H, m), 7·55 (2 H, d); IR (KBr) ν_{max} 2980, 2960, 2860, 1605, 1575, 1475, 1390, 1250, 1175, 1130, 1030, 910, 810 cm^{-1}; MS *m/z* 436 (M$^+$), 379, 352, 295.

5.1.9. *3-Fluorophenylboronic acid* (17)

n-Butyllithium (9·00 ml, 10·0 M in hexanes, 0·090 mol) was added slowly dropwise to a stirred, cooled (− 78°C) solution of compound **16** (15·00 g, 0·086 mol) in dry THF (120 ml) under dry nitrogen. The mixture was stirred at − 78°C for 30 min and a solution of trimethyl borate (18·00 g, 0·173 mol) in dry THF (20 ml) was added dropwise at − 78°C and the mixture was allowed to warm to room temperature overnight. 10 per cent hydrochloric acid was added and the mixture was stirred at room temperature for 1 h. 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* to give a colourless solid.

Yield 9·03 g (75 per cent); ^{1}H NMR (DMSO) δ 7·10–7·20 (1 H, m), 7·40 (1 H, m), 7·45 (1 H, m), 7·55 (1 H, m), 7·90–8·40 (2 H, s); IR (KBr) ν_{max} 3700–3000, 1440, 1410,–1250, 1200, 740 cm^{-1}; MS *m/z* 438, 421, 406, 393, 378, 366, 364, 244.

5.1.10 *3-Fluoro-4′-pentylbiphenyl* (19)

Quantities: compound **18** (4·70 g, 0·021 mol), compound **17** (3·48 g, 0·025 mol), tetrakis(triphenylphosphine)palladium(0) (0·73 g, 0·63 mol).

The experimental procedure was as described for the preparation of compound **5**. The crude product was purified by column chromatography (silica gel/petroleum fraction (b.p. 40–60°C) to give a colourless oil.

Yield 4·07 g, (80 per cent); ^{1}H NMR (CDCl$_3$) δ 0·90 (3 H, t), 1·35 (4 H, m), 1·65 (2 H, quint), 2·65 (2 H, t), 6·95–7·05 (2 H, m), 7·24 (2 H, d), 7·34 (2 H, m), 7·48 (2 H, d); IR (film) ν_{max} 2960, 2940, 2860, 1620, 1595, 1490, 1190, 1160, 885, 790, 695 cm^{-1}; MS *m/z* 242 (M$^+$), 185.

5.1.11. *3-Fluoro-4′-pentylbiphenyl-4-ylboronic acid* (20)

Quantities: compound **19** (3·85 g, 0·016 mol), *sec*-butyllithium (13·00 ml, 1·3 M in hexanes, 0·017 mol), trimethyl borate (3·35 g, 0·032 mol).

The experimental procedure was similar to that described for the preparation of compound **17**, except that the lithium salt was left to stir at − 78°C for 2 h and not 30 min.

Yield 4·50 g, (98 per cent); ^{1}H NMR (DMSO) δ 0·90 (3 H, t), 1·35 (4 H, m), 1·60 (2 H, quint), 2·60 (2 H, t), 7·25 (2 H, d), 7·35 (1 H, dd), 7·45 (1 H, dd), 7·50 (1 H, t), 7·65 (2 H, d), 8·20 (2 H, s); IR (KBr) ν_{max} 3700–3000, 2960, 2940, 2840, 1620, 1550, 1490–1300 cm^{-1}; MS *m/z* 286(M$^+$), 258, 242, 229, 201, 185.

5.1.12. *3,2′-Difluoro-4-hexyloxy-4″-pentylterphenyl* (23)

Quantities: compound **21** (0·80 g, 2·91 mmol), compound **20** (1·10 g, 3·85 mmol), tetrakis(triphenylphosphine)palladium(0) (0·15 g, 0·13 mmol).

The experimental procedure was as described for the preparation of compound **15**.

Yield 0·61 g (48 per cent); transitions (°C) C 41·0 S$_C$ 72·0 S$_A$ 131·0 N 140·0 I; ^{1}H NMR (CDCl$_3$) δ 0·90 (6 H, t), 1·35 (8 H, m), 1·45 (2 H, quint), 1·65 (2 H, quint), 1·80 (2 H, quint), 2·65 (2 H, t), 4·05 (2 H, t), 7·03 (1 H, dd), 7·26 (2 H, d), 7·30 (2 H, m), 7·41 (2 H, m), 7·45 (1 H, dd), 7·54 (2 H, d); IR (KBr) ν_{max} 2960, 2940, 2860, 1615, 1485, 1390, 1305, 1275, 1250, 1125, 800 cm^{-1}; MS *m/z* 436(M$^+$), 379, 352, 295.

5.1.13. *3,2′-Difluoro-4,4″-dipentylterphenyl* (24)

Quantities: compound **22** (0·80 g, 3·27 mmol), compound **20** (1·15 g, 4·02 mmol), tetrakis(triphenylphosphine)palladium(0) (0·13 g, 0·11 mmol).

The experimental procedure was as described for the preparation of compound **10**.

Yield 0·68 g (51 per cent); transitions (°C) C 34·0 S$_A$ 115·0 N 116·5 I; ^{1}H NMR (CDCl$_3$) δ 0·90 (6 H, t), 1·35 (8 H, m), 1·65 (4 H, quint), 2·65 (4 H, 2 × t), 7·22–7·32 (6 H, m), 7·35–7·49 (2 H, m), 7·54 (2 H, d); IR (KBr) ν_{max} 2960, 2940, 2860, 1615, 1570, 1475, 1390, 1175, 1125, 910, 875, 810 cm^{-1}; MS *m/z* 406(M$^+$), 363, 349.

5.1.14. *4′-Bromo-2-fluoro-4-hexyloxybiphenyl* (26)

Quantities: compound **25** (2·00 g, 7·07 mmol), compound **8** (2·10 g, 8·75 mmol), tetrakis(triphenylphosphine)palladium(0) (0·25 g, 0·22 mmol).

The experimental procedure was as described for the preparation of compound **3**, except that the reaction was complete after 1·75 h. The crude product was purified by column chromatography (silica gel/petroleum fraction (b.p. 40–60°C) with the introduction of a small amount of dichloromethane) to give a colourless oil which distilled at 0·1 mmHg in a Kugelrohr apparatus (oven temperature 180°C) to yield a colourless solid.

Yield 1·60 g (64 per cent); m.p. 58–59°C; ^{1}H NMR ($CDCl_3$) δ 0·90 (3 H, t), 1·35 (4 H, m), 1·45 (2 H, quint), 1·80 (2 H, quint), 4·00 (2 H, t), 6·69 (1 H, dd), 6·76 (1 H, dd), 7·29 (1H, dd), 7·37 (2 H, dd), 7·53 (2 H, d); IR (KBr) ν_{max} 2960, 2940, 2860, 1610, 1575, 1465, 1390, 1295, 1235, 1160, 1120, 1040, 805 cm^{-1}; MS m/z 352 (M^+), 350 (M^+), 268, 266.

5.2.15. *2,3''-Difluoro-4-hexyloxy-4''-pentylterphenyl* (**27**)

Quantities: compound **26** (0·95 g, 2·71 mmol), compound **14** (0·70 g, 3·33 mmol), tetrakis(triphenylphosphine)palladium(0) (0·10 g, 0·09 mmol).

The experimental procedure was as described for the preparation of compound **5**. The crude product was purified by column chromatography (silica gel/petroleum fraction (b.p. 40–60°C)–dichloromethane, 10 : 1) to give a colourless solid which was recrystallized from ethanol to yield colourless crystals.

Yield 0·76 g (64 per cent); transitions (°C) C 75·5 S_C 92·5 S_A 124·5 N 139·0 I; ^{1}H NMR ($CDCl_3$) δ 0·90 (6 H, 2 × t), 1·35 (8 H, m), 1·45 (2 H, quint), 1·65 (2 H, quint), 1·80 (2 H, quint), 2·65 (2 H, t), 4·00 (2 H, t), 6·72 (1 H, dd), 6·78 (1 H, dd). 7·24 (1 H, dd), 7·29 (1 H, dd), 7·33 (1 H, dd), 7·38 (1 H, dd), 7·58 (2 H, dd), 7·63 (2 H, d); IR (KBr) ν_{max} 2960, 2940, 2860, 1615, 1575, 1490, 1315, 1280, 1235, 1170, 1115, 1030, 765 cm^{-1}; MS m/z 436 (M^+), 379, 352, 295.

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