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The Synthesis of Several Lateral Difluoro-substituted 4,4″-Dialkyl- and 4,4″-Alkoxyalkyl-Terphenyls and a Rationalisation of the Effect of Such Substitution on Mesophase Type and Transition Temperatures†

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In recent years we have prepared a large number of mono-fluoro- and *ortho*-difluoro-substituted 4,4″-dialkyl- and 4,4″-alkoxyalkyl-terphenyls. The synthesis and transition temperatures of a variety of related difluoro compounds is presented here so that it is now possible to identify (i) broadening of the molecule, (ii) twisting about an inter-annular bond, and (iii) the presence of an 'inner' (2-, 2′-, 3′- or 2″-substituent) or an 'outer' (3- or 3″-substituent) fluorine, as being the major factors which influence the type and the thermal stability of the mesophases obtained.

Keywords: fluoro-substitution, terphenyls, structure-property relationships

Biphenyls and terphenyls are excellent core systems for generating liquid crystals,[1,2] either independently[3–8] or in conjunction with other good units such as cyclohexane,[9,10] and fluoro-substitution is one of the most useful ways of modifying an aromatic core unit.

Fluorine's value as a lateral substituent lies in the fact that it is of small size and high electronegativity and these two characteristic properties lead to a subtle modification of physical properties, often reducing melting point without totally eliminating liquid crystal phases. The following examples illustrate the valuable effects which appropriate fluoro-substitution is able to achieve;

(a) increase $\varepsilon_\perp$, which reduces $\Delta\varepsilon/\Delta\varepsilon_\perp$,[11]
(b) increase the width-to-length ratio which reduces k_{33}/k_{11}[12] and also, in some instances, increases k_{33}/k_{11},[13]
(c) reduce smectic phase thermal stability more than nematic and reveal wide-

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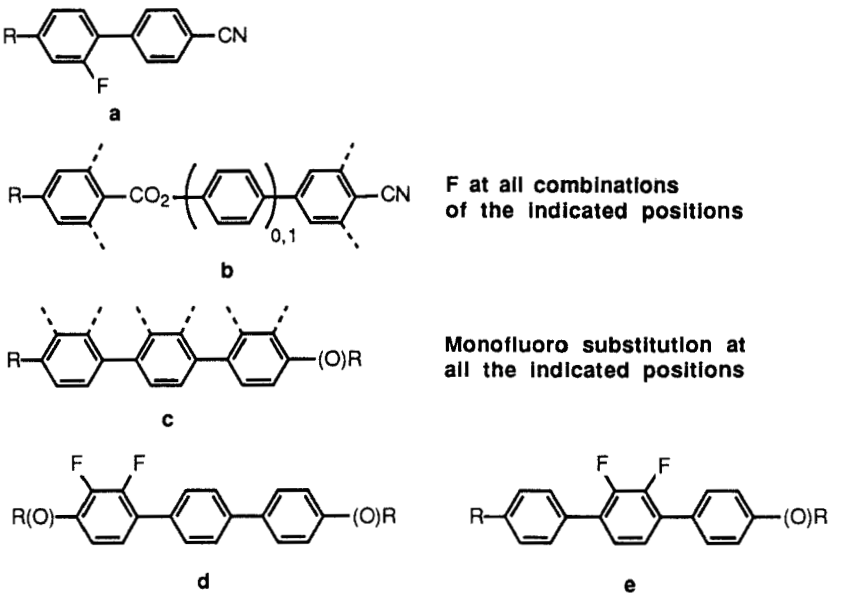
range nematic systems (but in certain situations it can increase smectic tendencies),[10]

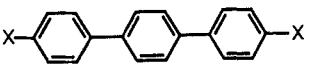
(d) disrupt anti-parallel correlations in terminal cyano-substituted systems to give higher $+\Delta\varepsilon$ materials,[14–18]

(e) give systems of negative dielectric anisotropy, which are useful both as hosts for ferroelectric mixtures and in ECB mixtures, [two lateral fluorines *ortho* to each other (2,3-disubstitution)[19–22] or two fluorines adjacent to an inter-annular bond (2,2′-disubstitution)[13] can achieve this effect].

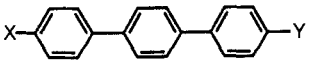
In recent years we have looked in some detail at fluoro-substitution (mainly mono[6,23–28] and di-[19,20]) in a variety of terpenyls and biphenyls (see structures **a-e**) where most of the systems and positions of substitution were chosen with the object of achieving a particular physical property (e.g. $+\Delta\varepsilon$, $-\Delta\varepsilon$ character). In this paper we present a related aspect of this work, which is designed not to produce materials for any obvious physical application but is part of a systematic study of the effect of two fluoro-substituents at all possible positions of simple dialkyl- and alkylalkoxy-terphenyls. We believe that this analysis allows us to identify several characteristic ways in which fluoro-substitution affects the thermal stabilities and types of the mesophases produced.

With a symmetrically 4,4″-disubstituted terphenyl, three mono-fluoro- and fourteen difluoro-substituted terphenyls are possible and for the unsymmetrical 4,4″-disubstituted terphenyls there are six mono-fluoro- and tweny four di-fluoro-substituted compounds. Not all of these compounds have been prepared for this work but a sufficient number are now available for us to be able to illustrate the main trends in melting points, mesophase type and transition temperatures produced by different positions of substitution. Since for most difluoroterphenyls there are two mono-fluoro-terphenyls with which they could be compared, even with the limited





3 mono- and 14 di-fluoro- derivatives



6 mono- and 24 di-fluoro- derivatives

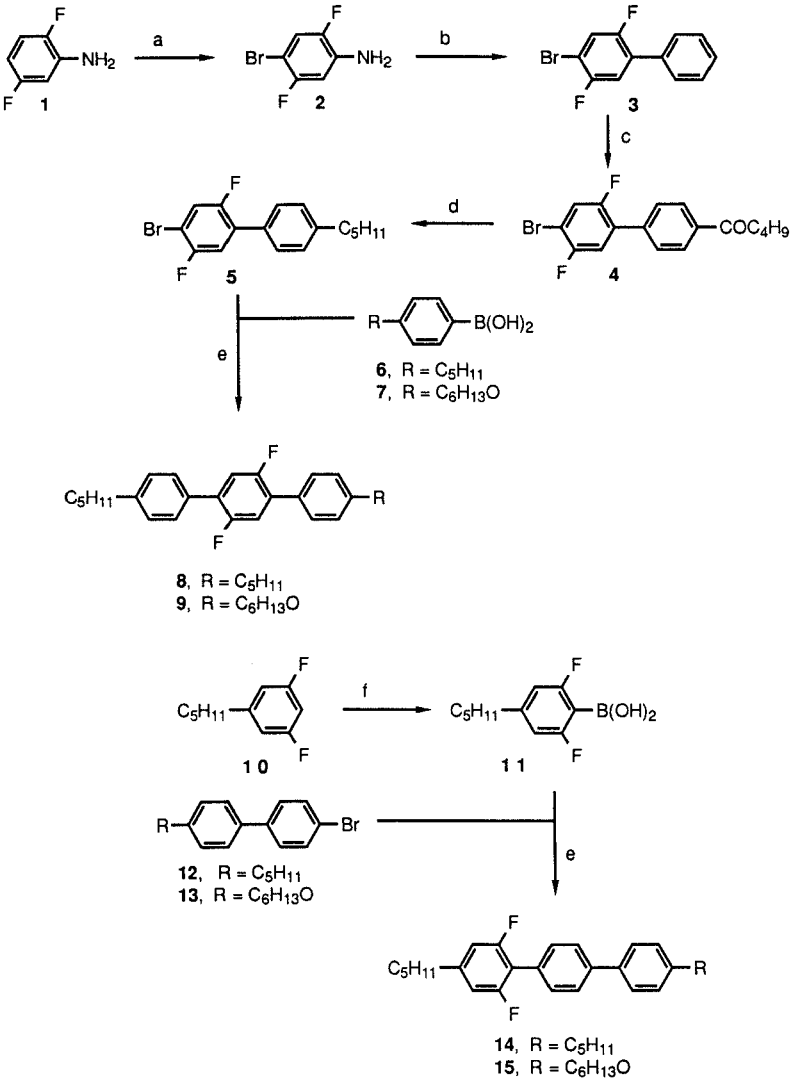
number of compounds we present here, there are an immense number of comparisons which can be made for the effect of the second fluoro-substituent and, to avoid repetitive comparisons, only the major issues are highlighted. The main comparisons relate to 4-hexoxy-4″-pentylterphenyl but a few examples are given for 4,4″-dipentylterphenyl derivatives and for 4-octoxy-4″-pentylterphenyl derivatives.

Until a few years ago, an efficient synthesis of many of the monofluoro compounds and of most of the difluoro derivatives was impossible by conventional processes which involve the introduction and modification of a functional group. The reason is that in a terphenyl (or biphenyl) molecule which is terminally substituted, all the lateral positions are hindered and substitution at the positions *ortho* to the inter-annular bonds is particularly difficult for steric reasons even assuming the correct directing nature of the terminal substituents. However, the recent developments of metal-catalysed cross-coupling reactions of organozincs[29] and of arylboronic acids[30] with aryl halides have revolutionised the synthesis of such liquid crystals and have now made possible the efficient synthesis from benzene or biphenyl units of terphenyls with any substitution pattern.[19,20,27,28,31]

In particular we would like to draw attention to the following practical advantages of arylboronic acids in coupling reactions; (a) the boronic acids can be prepared separately, kept indefinitely, and then used in various couplings, (b) aqueous conditions are used in the coupling reactions, (c) *ortho*-fluoro-arylboronic acids can be prepared at low temperature without benzyne formation occurring. The preparation of the *ortho*-difluoro-substituted terphenyls has been reported previously[19] and the preparation of the non-*ortho*-difluoro-substituted compounds is shown in Schemes I to III.

All the difluoro-substituted terphenyls were prepared by the excellent palladium-catalysed cross-coupling procedure involving arylboronic acids and aryl bromides (or iodides). This procedure is very convenient and provides high yields of easily purified materials. The arylboronic acids were prepared *via* the appropriate lithium or Grignard reagent; in the case of *ortho* fluoro-substituted boronic acids the lithium derivative had to be formed and used at low temperature ($< -65°C$) to avoid benzyne formation by the loss of LiF. The need for such a low temperature excludes the use of arylzinc reagents because their formation requires a higher temperature.

The preparation of compound **5** by the route shown in Scheme I was successful but only a very low yield was obtained. Recently we have had great success in the selective coupling of arylboronic acids at the iodo site of an aryl iodo-bromo unit.[19,20,31] Therefore we recommend the preparation of compound **5** *via* the diazotisation/



a ..... NBS, CH_2Cl_2.

b ..... Isopentyl nitrite, benzene.

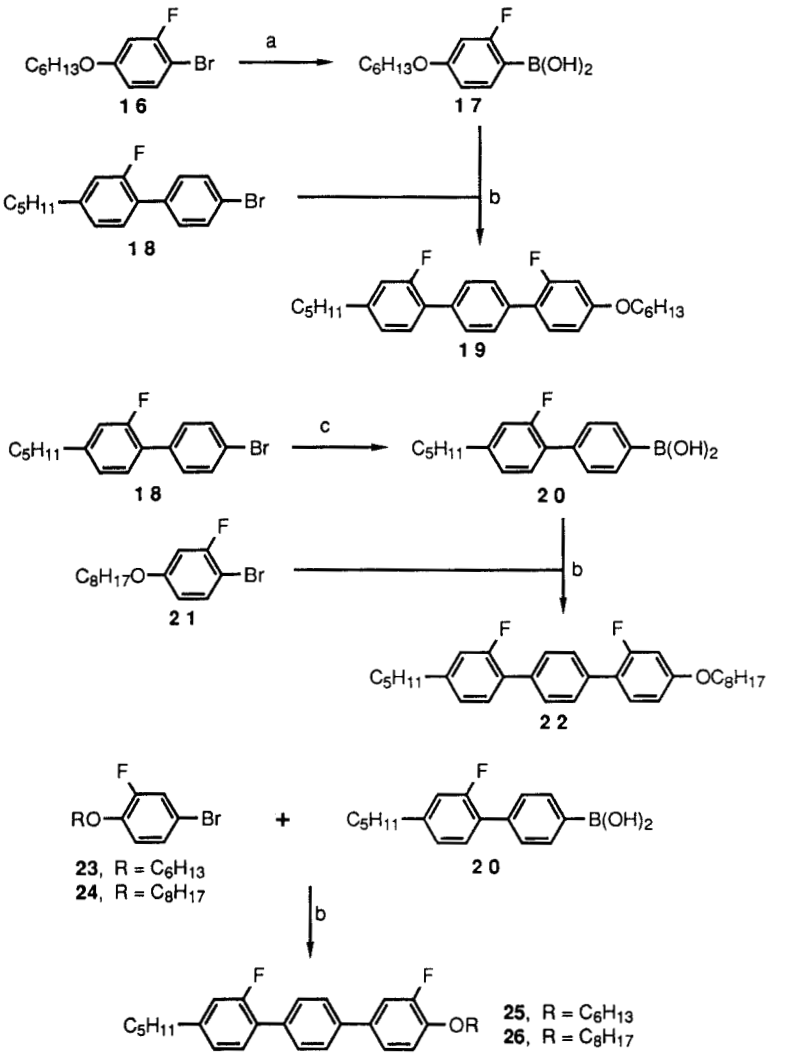
c ..... C_4H_9COCl, aluminium chloride, CH_2Cl_2.

d ..... Et_3SiH, CF_3CO_2H.

e ..... $Pd(PPh_3)_4$, benzene, EtOH, 2M-Na_2CO_3.

f ..... (i) nBuLi, THF; (ii) $(^iPrO)_3B$, THF; (iii) 10% HCl.

SCHEME I



a ..... (i) nBuLi, THF; (ii) $(^{i}PrO)_3B$, THF; (iii) 10% HCl.

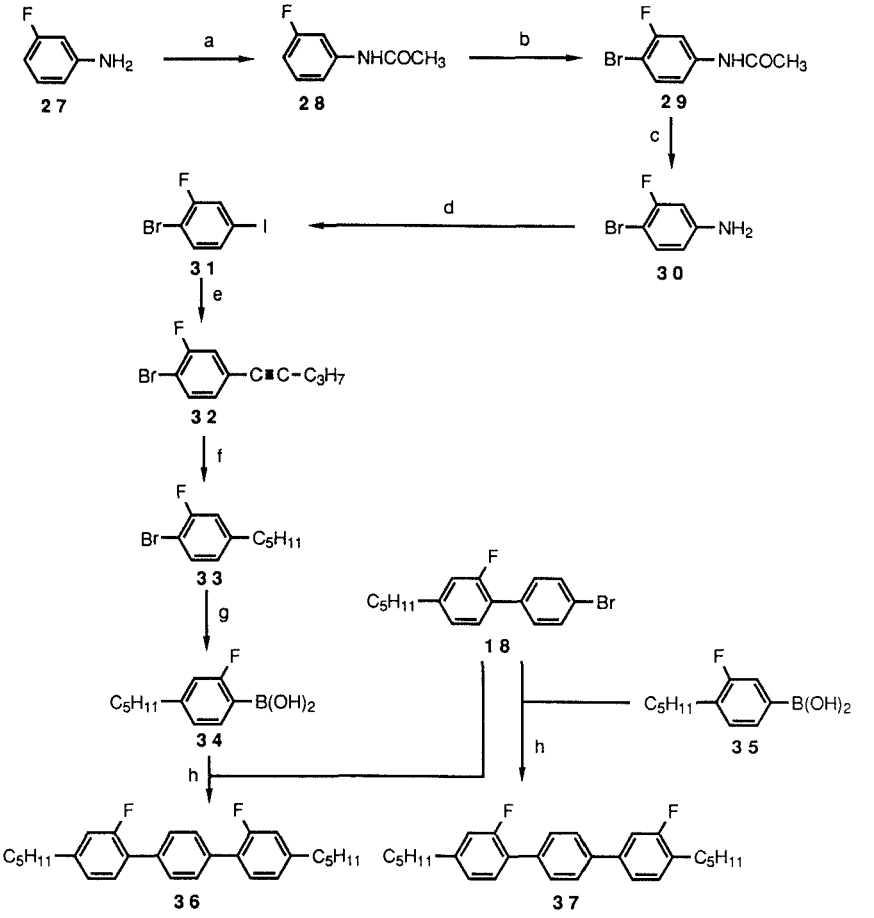
b ..... $Pd(PPh_3)_4$, benzene, EtOH, 2M-Na_2CO_3.

c ..... (i) Mg, THF; (ii) $(^{i}PrO)_3B$, THF; (iii) 10% HCl.

SCHEME II

iodination (see compound **31**) of compound **2** followed by a selective coupling with compound **6**.

Terphenyls **14** and **15** were obtained in very low yields due to substantial hydrodeboronation[32] of boronic acid **11**. This is due to the electron-withdrawing effect of the two *ortho* fluoro-substituents which make the boron atom susceptible to nucleophilic attack from the aqueous base. This combines with a slow trans-



a ..... Acetic anhydride, glacial acetic acid.

b ..... NBS, dichloromethane.

c ..... 36% HCl, ethanol.

d ..... 36% HCl, $NaNO_2$, water; (ii) KI, water.

e ..... (i) Pent-1-yne, nBuLi, THF; (ii) $ZnCl_2$, THF; (iii) compound **31**, $Pd(PPh_3)_4$, THF.

f ..... PtO_2, ethanol, H_2.

g ..... (i) nBuLi, THF; (ii) $(MeO)_3B$, THF; (iii) 10% HCl.

h ..... $Pd(PPh_3)_4$, DME, 2M-Na_2CO_3.

SCHEME III

metallation step, caused by slight steric hindrance due to the two *ortho* fluoro-substituents, to give low yields of the desired terphenyls. Although hydrodeboronation does occur to a small extent where there is only one fluoro-substituent *ortho* to the boronic acid moiety, this does not prevent high yields of the desired product being obtained. This indicates either that the rate of hydrodeboronation

is slower for one fluoro-subtituent *ortho* to the boronic acid moiety or the rate of coupling is faster, or a combination of both these factors.

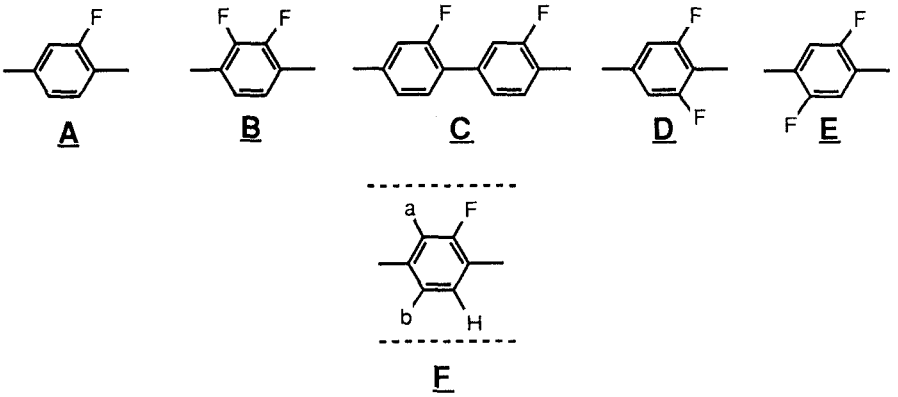
The different approach to the preparation of homologues **19** and **22** illustrates the possibility of a 'reverse' synthesis.

The treatment of compound **27** with *N*-bromosuccinimide (NBS) gave a mixture of two products (in contrast to the treatment of 2-fluoroaniline with NBS[27]). However, the rate-moderating and steric hindering effect of the acetanilide moiety provides greater selectivity to give compound **29**. Total selectivity is afforded by the room-temperature palladium-catalysed cross-coupling[29] of pent-1-ynylzinc chloride to give compound **32**. The seven-step synthesis of compound **34** appears long, but the route is straightforward and produces an excellent overall yield.

Before the effect of the fluoro-substituents is discussed for specific examples, several general points are presented so that these ideas can be used to rationalise some of the changes in transition temperatures and mesophase types.

(a) *Broadening of the molecule.* Irrespective of its position, a lateral fluoro-substituent will broaden the molecule but a gradation in the magnitude of this effect occurs in the following way. Compounds which contain the partial system **A** will inevitably be broader than the parent molecule (van der Waals radius for hydrogen and for fluorine is 1.20 and 1.47 Å respectively[33]), but **B** will give about the same breadth as **A**, since the second fluorine does not protrude any further from the molecule than the first fluorine (see also Reference 34 for a similar situation with lateral cyano groups). With **C**, the molecule will be somewhat broader because rotation about the inter-annular bonds means that for part of the time two fluoro-substituents can be on either side of the molecule and for **D** and **E** the molecules will be the broadest because the two fluorines are fixed on either side of the ring.

It may appear that by discussing the breadth of the molecules in this way we are considering the phases as being composed of static molecules. In reality, the molecules would rotate about their long molecular axis and to an approximation all the difluoro systems would then rotate within the boundaries of the same cylinder of rotation, e.g., in **F**, the system with a = F, b = H and that with a = H, b = F fit within the same limits on rotation. The fact that we detect broadening of the molecule to be a major factor would imply that the molecules undergo a mutually



co-operative rotation so as to maintain as close a contact with each other as possible; an individual cylinder of rotation for a molecule would effectively leave free-space for part of the rotation, if this occurred independently of other molecules.

(b) *Twisting about the inter-annular bond* (see Reference 33).

(i) Partial structures such as **G**, **H** and **I** have fluoro-substituents which cause an increased twisting about both inter-annular bonds and therefore disrupt the mechanism by which the polarisability of the molecule operates giving separate phenyl units. Molecules containing structures such as **J** and **K** only twist about one inter-annular bond and a normal biphenyl region remains.

(ii) A secondary issue is that when one inter-annular twist occurs, the biphenyl unit remaining may have an alkyl or an alkoxy terminal group (the latter giving higher transition temperatures) and the biphenyl unit may have none, one or two fluoro-substituents on it.

(c) *Position of fluorine on an 'outer' or 'inner' edge.* A fluoro-substituent *ortho*- to a terminal group appears to more effectively fill space and often leads to no significant reduction in smectic phase thermal stability.[10]

Fluorine is a highly electronegative substituent to introduce into a molecule and for this reason it may have been expected that di-fluoro substitution would reveal unusual differences in mesophase type and their thermal stabilities depending upon the resultant dipole of the two fluorines. The position of the dipole within the molecule and its direction with respect to the long molecular axis could affect the ability of the molecule to generate tilted phases as discussed by McMillan[35] since the C—F bond dipoles may be opposed (e.g., as in **E**), give a resultant dipole along the molecular axis (e.g., as in **D**), or a resultant dipole across the molecule (e.g., as in **B**), with additional effects arising depending upon whether the substituents were in the centre or an end ring. Certainly, mono-fluoro terphenyls do give rise to tilted phases and examples of S_K, S_G, S_J, S_I and S_C mesophases are seen for compounds in Tables I to III.[23–26,28] However, in the complexity of the substitution patterns which exist for the di-fluoro compounds it is not possible to identify a major effect arising from the direction of the resultant dipole because any comparison of two isomeric di-fluoro compounds inevitably means that one is dealing with a different combination of the three effects outlined above. It would therefore appear from our results that, as noted by Osman in his survey of lateral substituent effects,[11] the decrease in T_{N-I} values is because of the van der Waals volume of

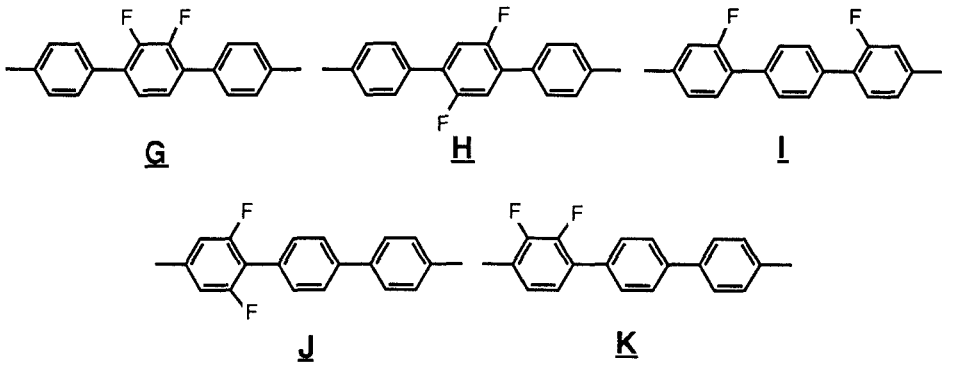
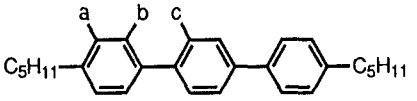


TABLE I

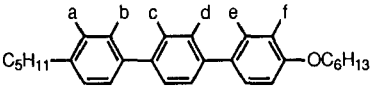
Transition temperatures (°C) for 4,4″-dipentylterphenyl (**38**) and its monofluoro-substituted derivatives (**39–41**)



	Compound			Transition Temperatures (°C)						
No.	a	b	c	K	S_G	S_B	S_C	S_A	N	I
38	H	H	H	* 192.0	----------	----------	----------	* 213.0	----------	*
39	F	H	H	*	* 156.5	----------	----------	* 185.5	----------	*
40	H	F	H	* 72.5	----------	----------	* 80.0	----------	* 136.0	*
41	H	H	F	* 51.5	----------	* 62.0	----------	* 109.5	* 136.5	*

TABLE II

Transition temperatures (°C) for 4-hexoxy-4″-pentylterphenyl (**42**) and its monofluoro-substituted derivatives (**43–48**)



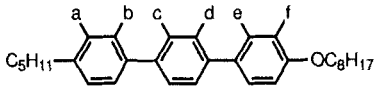
	Compound						Transition Temperatures (°C)								
No.	a	b	c	d	e	f	K	S_K	S_G	S_J	S_B	S_I	S_C	S_A	N	I
42	H	H	H	H	H	H	* 205.0	----------	----------	----------	* 216.0	----------	----------	* 228.5	----------	*
43	F	H	H	H	H	H	*	----------	* 176.0	----------	----------	----------	----------	* 210.0	----------	*
44	H	F	H	H	H	H	* 115.0	----------	----------	----------	----------	----------	* 131.5	----------	* 166.5	*
45	H	H	F	H	H	H	* 70.0	----------	* 78.0	----------	* 92.0	* 93.0	* 118.0	* 155.0	* 166.5	*
46	H	H	H	F	H	H	* 62.5	----------	(* 47.5	----------	* 50.0)	* 113.5	----------	* 162.5	*	
47	H	H	H	H	F	H	* 83.5	(* 48.5	----------	* 62.0)	----------	* 105.0	----------	* 166.0	*	
48	H	H	H	H	H	F	*	----------	* 160.0	----------	----------	----------	* 162.0	* 201.0	----------	*

the lateral fluoro substituent and is independent of the dipole moment, i.e. dipole attractive or repulsive forces play a minor role compared to that of the dispersive forces.

Tables I to III give the transition temperatures for the parent 4,4″-dipentylterphenyl and mono-fluoro derivatives, for the parent 4-hexoxy-4″-pentylterphenyl and mono-fluoro derivatives and for the parent 4-octoxy-4″-pentylterphenyl and

TABLE III

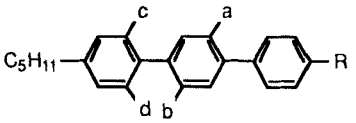
Transition temperatures (°C) for 4-octoxy-4″-pentylterphenyl (**49**) and its monofluoro-substituted derivatives (**50–55**)



Compound							Transition Temperatures (°C)									
No.	a	b	c	d	e	f	K	S_K	S_G	S_J	S_B	S_I	S_C	S_A	N	I
49	H	H	H	H	H	H	* 194.5	----------	----------	----------	* 211.0	----------	----------	* 221.5	----------	*
50	F	H	H	H	H	H	*	----------	* 170.5	----------	----------	----------	* 176.5	* 202.5	----------	*
51	H	F	H	H	H	H	* 102.0	----------	----------	----------	----------	(* 99.5)	* 137.5	----------	* 160.0	*
52	H	H	F	H	H	H	* 69.0	----------	* 83.0	----------	* 100.5	----------	* 124.0	* 158.0	* 161.0	*
53	H	H	H	F	H	H	* 47.0	----------	----------	(* 40.0)	----------	* 53.5	* 116.5	* 130.0	* 155.0	*
54	H	H	H	H	F	H	* 69.0	(* 25.0	----------	* 43.5)	----------	----------	* 119.0	----------	* 158.0	*
55	H	H	H	H	H	F	*	----------	* 146.0	----------	* 158.0	----------	----------	* 195.0	----------	*

TABLE IV

Transition temperatures (°C) for 4-pentyl- or 4-hexoxy-4″-pentyl-2′,5′-difluoroterphenyls (**8** and **9**) and 4-pentyl-4″-pentyl- or 4″-hexoxy-2,6-difluoroterphenyls (**14** and **15**)

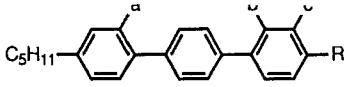


Compound						Transition Temperatures (°C)				
No.	R	a	b	c	d	K		N		I
8	C_5H_{11}	F	F	H	H	*	63.0	*	85.5	*
9	$C_6H_{13}O$	F	F	H	H	*	51.0	*	117.0	*
14	C_5H_{11}	H	H	F	F	*	50.0	*	82.0	*
15	$C_6H_{13}O$	H	H	F	F	*	61.0	*	122.5	*

mono-fluoro derivatives respectively;[1,2,23–26,28] Tables IV and V give the transition temperatures for compounds with two fluorines in one ring and two fluorines in separate rings respectively; Table VI gives the transition temperatures for some *ortho* difluoro-substituted terphenyls.[19,20] Each of the effects we have outlined above will be illustrated independently or in conjunction with each other as we

TABLE V

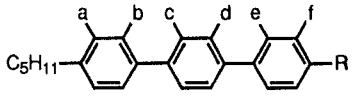
Transition temperatures (°C) for 4-alkoxy-4″-pentyl- and 4,4″-dipentyl-2,2″-difluoro-terphenyls (**19**, **22** and **36**) and 4″-alkoxy-4-pentyl- and 4,4″-dipentyl-2,3″-difluoroterphenyls (**25**, **26** and **37**)



Compound					Transition Temperatures (°C)								
No.	R	a	b	c	K		S_C		S_A		N		I
19	$C_6H_{13}O$	F	F	H	*	45.0	----------				*	131.0	*
22	$C_8H_{17}O$	F	F	H	*	42.5	----------				*	121.5	*
25	$C_6H_{13}O$	F	H	F	*	90.0	*	105.5	----------		*	139.0	*
26	$C_8H_{17}O$	F	H	F	*	75.5	*	107.0	----------		*	132.0	*
37	C_5H_{11}	F	H	F	*	69.5	(*	67.0)	*	83.0	*	111.5	*
36	C_5H_{11}	F	F	H	*	58.5	----------				*	92.0	*

TABLE VI

Transition temperatures (°C) for some *ortho*-difluoro-substituted terphenyls (**56–60**)



Compound								Transition Temperatures (°C)								
No.	R	a	b	c	d	e	f	K		S_C		S_A		N		I
56	C_5H_{11}	H	H	F	F	H	H	*	60.0	----------				*	120.0	*
57	$C_6H_{13}O$	H	H	F	F	H	H	*	54.0	*	67.0	----------		*	149.0	*
58	C_5H_{11}	F	F	H	H	H	H	*	81.0	*	115.5	*	131.5	*	142.0	*
59	$C_6H_{13}O$	F	F	H	H	H	H	*	101.5	*	156.5	*	167.0	*	171.5	*
60	$C_6H_{13}O$	H	H	H	H	F	F	*	97.5	*	145.5	----------		*	166.0	*

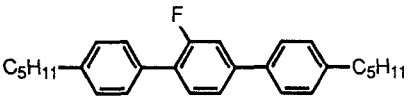
discuss and rationalise the changes in the types of mesophase and in their thermal stabilities.

Table I shows how mono-fluoro substitution dramatically depresses melting points (the peculiarity of the K-S_G transition for compounds **39**, **43**, **48**, etc. will be discussed elsewhere) and shows the combined effect of broadening the molecule and twisting about an inter-annular bond (compounds **40** and **41**) or of broadening

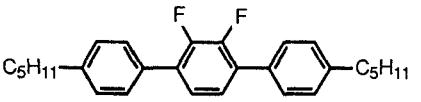
and the 'outer edge' effect (compound **39**). Compound **39** still has an untwisted terphenyl unit and although somewhat broader, the fluorine in the 3-position fills space reasonably effectively and smectic thermal stability is well maintained. Compounds **40** and **41** have a similar breadth to each other and the single, increased inter-annular twist[33,36] in each has caused a significant and almost identical depression of the clearing point. Smectic character is much depressed by the twisting, as expected, and compound **41** with the fluoro-substituted biphenyl unit and a more central lateral group has the greater smectic character whereas compound **40** with the lateral group in an end ring shows a tilted phase (see also compound **39**).

Similar comments are also capable of rationalising the values shown in Table II, and in this case more different positions for substitution provide a greater number of comparisons. In a condensed form we draw attention to the following points which have been discussed more fully above. (a) The pronounced depression of melting point in all mono-fluoro systems; (b) the moderate depression caused by broadening at an 'outer edge' and the high thermal stability of a tilted phase (compounds **43** and **48**) and (c) compounds **44–47** all have a fluoro-substituent which gives one increased inter-annular twist giving closely similar clearing points (see the comments above for the dipentyl systems); when the fluorine is at positions b or c (compounds **44** and **45** respectively) an alkoxybiphenyl portion is created and these compounds have a higher smectic thermal stability than when the fluorine is at position d or e (compounds **46** and **47** respectively) and an alkylbiphenyl portion is obtained. Additionally, for each of these pairs of compounds, the isomer with the fluoro substituent in the biphenyl region (i.e. compounds **45** and **46**) has greater smectic character than the compound with the fluoro-substituent in the phenyl unit (i.e. compounds **44** and **47** respectively; see also compounds **40** and **41**) and all of them show an S_C and sometimes other tilted mesophases. Very similar comments apply to the compounds shown in Table III.

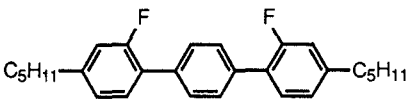
When the difluoro compounds are considered it is possible to see the effect of a second inter-annular increased twisting and of an increasing breadth of the molecule. The comparison of compound **41** with compound **56** shows that although the molecule is not broadened by the second *ortho*-fluorine, the clearing point is depressed by 16.5°C, which we attribute to a further disruption of the molecular polarisability. The compounds **56**, **36**, and **8** have two increased inter-annular twists,



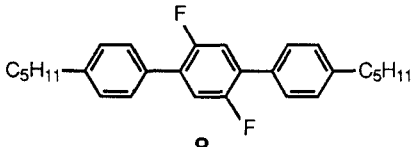
41



56



36



8

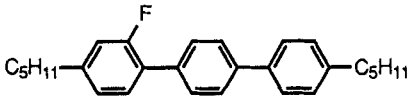
created in different ways by the presence of a single fluorine atom near the inter-ring bonds and all of these compounds have lost their smectic character completely. There is also a clear gradation in the decrease in T_{N-I} values (120.0, 92.0, 85.5°C) as the molecules become progressively wider in the sequence **56**, **36**, **8**. (The last compound has fluorine permanently positioned to give maximum width and compound **36** is intermediate because of independent rotation of the two fluoro-substituted rings).

Once again a very similar picture emerges for the hexoxy/pentyl system were the equivalent comparisons are between compounds **57**, **19**, and **9** in relation to the mono-fluoro systems **45** or **46**. An S_C phase is still present in compound **57** and its thermal stability has been reduced by 51°C, much less than the reduction (at least 88°C) in the S_A thermal stability of compound **45**.

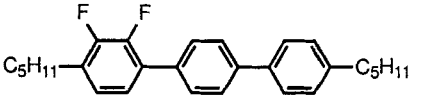
It was mentioned earlier that the 'outer edge' substituent has a relatively small effect on clearing points (see compounds **39**, **43**, **48**, **50**, and **55**). In all these cases two structural changes have been made at the same time, i.e. an 'outer edge' fluorine has been introduced and the molecule has been made broader and it is not possible to disentangle the two effects. A better way of illustrating the 'outer edge' effect of a fluoro-substituent is to compare compounds such as **40** and **58**, because in this comparison the second fluorine does not introduce any extra twisting nor does it have a major broadening effect. Such a comparison of the mesophase thermal stabilities for **40** and **58** shows that the S_C thermal stability increases by 35.5°C, nematic by 6.0°C and S_A, which is not present in compound **40**, by at least 51.5°C. Two similar comparisons are again possible for the hexoxy/pentyl compounds, for the fluorine substituents in the pentyl- (compounds **44** and **59**) or the hexoxy-ring (compounds **47** and **60**). In the former comparison, S_C, S_A, and N thermal stabilities are increased in a parallel fashion to the **40/58** comparison and for the latter pair, T_{N-I} values are identical but S_C character is strongly promoted.

The behaviour of the non-S_C exhibiting compound **9** was examined by mixing small amounts of the compound (~5–15%) with two of Chan's monofluoroterphenyls.[23–26] The work revealed that these small amounts totally eliminated the ordered smectic phases below the S_C phase whilst only slightly depressing the thermal stabilities of the S_C, S_A and nematic phases (see Table VII). The values given in brackets for the mixtures are the temperatures at which recrystallisation occurred on cooling. Similar mixture work was carried out on some of the other non-S_C exhibiting compounds with similar results which confirms that these materials are capable of eliminating ordered smectic mesophases from host materials and have a much higher S_C tendency than their transition temperatures suggest.

This work was substantiated by subsequent work carried out by our collaborators at R.S.R.E. (Malvern).



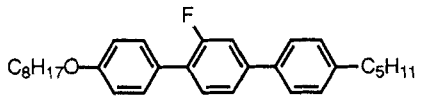
40



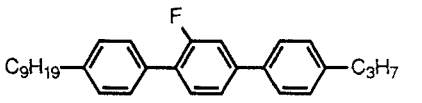
58

TABLE VII

Transition temperatures (°C) for mixtures of compound **9** in host materials **53** and **61**



53



61

Composition	K	S_J	S_I	S_C	S_A	N	I
100% **53**	* 47.0	(* 40.0)	* 53.5	* 116.5	* 130.0	* 155.0	*
94% **53** 6% **9**	* 50.0 (27.5)	----------		* 113.0	* 122.0	* 152.5	*
90% **53** 10% **9**	* 48.0 (23.0)	----------		* 109.5	* 113.0	* 150.5	*
Composition	K	S_B		S_C	S_A	N	I
100% **61**	* 46.0	(* 35.0)		* 52.0	* 89.0	* 126.5	*
95% **61** 5% **9**	* 43.5 (8.0)	----------		* 50.0	* 72.0	* 125.0	*
84% **61** 16% **9**	* 41.0 (8.0)	----------		* 48.0	* 60.0	* 125.0	*

EXPERIMENTAL

Confirmation of the structures of intermediates and products was obtained by ^1H 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 BH2 polarising microscope and these were confirmed using differential scanning calorimetry (Perkin-Elmer DSC-2C and data station). The purity of each of the final liquid crystalline compounds was checked by glc analysis (see above) and by hplc analysis (Microsorb C18 80-215-C5 RP column) and all compounds were >99.9% pure.

Compounds **12**, **13** and **18** were kindly supplied by our collaborators at BDH Limited, Poole, Dorset. Compounds **6**, **7**, **16**, **21**, **23**, **24** and **35** were prepared as described in Reference 28 and compound **10** was prepared as described in Reference 27.

4-Bromo-2,5-difluoroaniline (**2**). *Quantities*: compound **1** (31.0 g, 0.24 mol), *N*-

bromosuccinimide (42.0 g, 0.24 mol). The experimental procedure was as described in a previous publication.[30]

Yield 47.4 g (95%); mp 74–75°C; ^{1}H nmr ($CDCl_3$)δ 3.80 (2H, *s*), 6.55 (1H, *q*), 7.10 (1H, *q*); ir (KCl) ν_{max} 3415, 3340, 1630, 1500, 1420, 1230, 1190, 1170, 870, 800, 740 cm^{-1}; ms *m/z* 209 (M^+), 207 (M^+), 127, 108, 101.

4-Bromo-2,5-difluorobiphenyl (**3**). A solution of compound **2** (47.4 g, 0.23 mol) in dry benzene (200 ml) was added dropwise over 1.5 h to a stirred, cooled (0°C) solution of isopentyl nitrite (33.6 g, 0.29 mol) in dry benzene (200 ml). The mixture was heated under reflux for 1.5 h and cooled. Ether was added and the organic phase was washed with water, aqueous sodium hydrogen carbonate, 10% hydrochloric acid and water, and dried ($MgSO_4$). The solvent was removed *in vacuo* and the crude product was steam distilled to give a brown-black solid. This was further purified by column chromatography (silica gel/dichloromethane) to give a dark brown low-melting solid.

Yield 13.20 g (22%); 1H nmr ($CDCl_3$) unresolved multiplet at δ 7.00–7.80; ir (KCl) ν_{max} 3100, 2920, 1610, 1480, 1390, 1340, 1270, 1180, 880, 850, 790, 600 cm^{-1}; ms *m/z* 298, 283, 270 (M^+), 268 (M^+), 201, 188, 168.

4-Bromo-2,5-difluoro-4'-pentanoylbiphenyl (**4**). Aluminum chloride (25.40 g, 0.190 mol) was ground and added to a stirred, cooled (0°C) solution of pentanoyl chloride (34.9 g, 0.29 mol) in dry dichloromethane (120 ml). A solution of compound **3** (13.20 g, 0.049 mol) in dry dichloromethane (120 ml) was added dropwise over 2 h at 0°C. The mixture was stirred at room temperature for 48 h and poured onto crushed ice/36% hydrochloric acid. The separated aqueous phase was washed with dichloromethane (twice); the combined organic layers were washed with water, aqueous sodium hydrogen carbonate and water, and dried ($MgSO_4$). The solvent was removed *in vacuo* to afford a dark brown oil which was distilled under reduced pressure (0.1 mmHg, temperature not recorded) and was further purified by column chromatography (silica gel/dichloromethane) to give a low-melting brown solid.

Yield 8.00 g (46%); ^{1}H nmr ($CDCl_3$)δ 1.00 (3H, *t*), 1.40 (2H, *m*), 1.70 (2H, *m*), 3.00 (2H, *t*), 7.25 (1H, *q*), 7.40 (1H, *q*), 7.60 (2H, *q*), 8.00 (2H, *q*); ir (KCl) ν_{max} 2900, 1680, 1610, 1480, 1390, 1180, 860, 780 cm^{-1}; ms *m/z* 310, 297, 188.

4-Bromo-2,5-difluoro-4'-pentylbiphenyl (**5**). Triethylsilane (7.00 g, 0.06 mol) was added dropwise over 2 h to a stirred, cooled (0°C) solution of compound **4** (8.00 g, 0.023 mol) in trifluoroacetic acid (40 ml). The reaction mixture was stirred at room temperature overnight and poured into aqueous sodium hydrogen carbonate. 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* and the residue was distilled to give a red oil.

Yield 5.50 g (70%); bp (short path), 110–120°C at 0.1 mmHg; ^{1}H nmr ($CDCl_3$)δ 0.80 (3H, *t*), 1.30 (4H, *m*), 1.60 (2H, *m*), 2.70 (2H, *t*), 7.00–7.40 (6H, *m*); ms *m/z* 340 (M^+), 338 (M^+), 283, 201.

2',5'-Difluoro-4,4''-dipentylterphenyl (**8**). A solution of compound **6** (0.8604 g, 4.48 mmol) in ethanol (15 ml) was added to a stirred mixture of compound **5** (1.25 g, 3.69 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.1404 g, 0.122 mmol) in benzene (30 ml) and 2M sodium carbonate (30 ml) at room temperature under dry nitrogen. The stirred mixture was heated under reflux (~100°C) for 16 h (glc analysis revealed a complete reaction). 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 the residue was purified by column chromatography [silica gel/petroleum fraction (bp 40–60°C)-dichloromethane, 1:1] to give a colourless solid which was recrystallised from ethanol to yield colourless crystals.

Yield 0.56 g (37%); transitions (°C) K 63.0 N 85.5 I; ^{1}H nmr ($CDCl_3$)δ 0.90 (6H, *t*), 1.40 (8H, *m*), 1.65 (4H, quint), 2.65 (4H, *t*), 7.20 (2H, *q*), 7.25 (4H, *d*), 7.50 (4H, *d*); ir (KCl) ν_{max} 2960, 2920, 2860, 1630, 1480, 1390, 1270, 1170, 1120, 1020, 880 cm^{-1}; ms *m/z* 406 (M^+), 349, 292, 203.

2',5'-Difluoro-4-hexoxy-4''-pentylterphenyl (**9**). *Quantities:* compound **5** (1.25 g, 3.69 mmol), compound **7** (0.9806 g, 4.42 mmol), tetrakis(triphenylphosphine)-palladium (0) (0.1392 g, 0.121 mmol).

The experimental procedure was as described for the preparation of compound **8**. The crude product was purified by column chromatography [silica gel/petroleum fraction (bp 40–60°C)-dichloromethane, 3:1] to give a colourless solid which was recrystallised from ethanol to yield colourless crystals.

Yield 0.72 g (45%); transitions (°C) K 51.0 N 117.0 I; ^{1}H nmr ($CDCl_3$)δ 0.90 (6H, 2xt), 1.35 (8H, *m*), 1.45 (2H, quint), 1.65 (2H, quint), 1.80 (2H, quint), 2.65 (2H, *t*), 4.00 (2H, *t*), 7.00 (2H, *d*), 7.18 (1H, *q*), 7.23 (1H, *q*), 7.27 (2H, *d*), 7.48 (2H, *q*), 7.53 (2H, *q*); ir (KCl) ν_{max} 2960, 2940, 2870, 2860, 1610, 1530, 1490, 1390, 1260, 1170, 1030, 890 cm^{-1}; ms *m/z* 436 (M^+), 397, 379, 366, 352, 295, 282.

2,6-Difluoro-4-pentylphenylboronic acid (**11**). *n*-Butyllithium (2.70 ml, 10.4M in hexane, 0.028 mol) was added dropwise to a stirred, cooled (−78°C) solution of compound **10** (5.00 g, 0.027 mol) in dry THF (60 ml) under dry nitrogen. The reaction mixture was maintained under these conditions for 2.5 h and then a previously cooled solution of tri-isopropyl borate (10.22 g, 0.054 mol) in dry THF (50 ml) was added dropwise at −78°C. The reaction mixture was allowed to warm to room temperature overnight and then stirred for 1 h with 10% hydrochloric acid (30 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 colourless solid.

Yield 7.00 g (100%); ^{1}H nmr ($CDCl_3$)δ 0.90 (3H, *t*), 1.35 (4H, *m*), 1.60 (2H, *m*), 2.60 (2H, *t*), 5.45 (2H, *t*), 6.65 (2H, *d*); ir (KCl) ν_{max} 3350, 2960, 2940, 2850, 1640, 1555, 1440, 1330, 1200, 1130, 1010, 1000, 860, 810 cm^{-1}; ms *m/z* 228 (M^+), 211, 200, 185, 171, 153, 143, 128, 108.

2,6-Difluoro-4,4''-dipentylterphenyl (**14**). *Quantities:* compound **12** (1.40 g, 4.62

mmol), compound **11** (1.37 g, 6.00 mmol), tetrakis(triphenylphosphine)palladium (0) (0.2614 g, 0.226 mmol).

The experimental procedure was as described for the preparation of compound **8**. The crude product was purified by column chromatography [silica gel/petroleum fraction (bp 40–60°C)-dichloromethane, 1:1] to give a colourless liquid which contained a solid. The solid was filtered off and washed with petroleum fraction (bp 40–60°C). The solvent was removed from the filtrate and washings *in vacuo* to give a colourless liquid; two impurities were removed using a Kugelrohr distillation apparatus (0.1 mmHg) to leave a colourless solid which was recrystallised from ethanol to yield colourless crystals.

Yield 0.19 g (10%); transitions (°C) K 50.0 N 82.0 I; ^{1}H nmr ($CDCl_3$)δ 0.90 (6H, 2xt), 1.35 (8H, *m*), 1.65 (4H, *m*), 2.60 (4H, 2xt), 6.80 (2H, *d*), 7.25 (2H, *d*), 7.50 (2H, *d*), 7.55 (2H, *d*), 7.65 (2H, *d*); ir (KCl) ν_{max} 2980, 2950, 2880, 1640, 1580, 1480, 1430, 1400, 1200, 1020, 1010, 860 cm^{-1}; ms *m/z* 406 (M^+), 349, 292.

2,6-Difluoro-4″-hexoxy-4-pentylterphenyl (**15**). *Quantities:* compound **13** (1.30 g, 3.90 mmol), compound **11** (1.10 g, 4.82 mmol), tetrakis(triphenylphosphine)palladium(0) (0.1579 g, 0.137 mmol).

The experimental procedure was as described for the preparation of compound **8**. The crude product was purified by column chromatography [basic alumina/petroleum fraction (bp 40–60°C) with the gradual addition of dichloromethane] to give a colourless solid which was recrystallised from ethanol to give colourless crystals.

Yield 0.20 g (20%); transitions (°C) K 61.0 N 122.5 I; ^{1}H nmr ($CDCl_3$)δ 0.95 (6H, 2xt), 1.35 (8H, *m*), 1.50 (2H, quint), 1.65 (2H, quint), 1.80 (2H, quint), 2.60 (2H, *t*), 4.00 (2H, *t*), 6.80 (2H, *d*), 6.95 (2H, *d*), 7.50 (2H, *d*), 7.55 (2H, *d*), 7.65 (2H, *d*); ir (KCl) ν_{max} 2950, 2860, 1640, 1610, 1580, 1510, 1490, 1290, 1250, 1210, 1020, 820 cm^{-1}; ms *m/z* 436 (M^+), 352, 295.

2-Fluoro-4-hexoxyphenylboronic acid (**17**). *Quantities:* compound **16** (9.00 g, 0.033 mol), *n*-butyllithium (3.30 ml, 10.0M in hexane, 0.033 mol), tri-isopropyl borate (11.28 g, 0.060 mol).

The experimental procedure was as described for the preparation of compound **11**.

Yield 7.80 g (99%); ^{1}H nmr ($CDCl_3$)δ 0.90 (3H, *t*), 1.35 (4H, *m*), 1.45 (2 H, quint), 1.80 (2H, quint), 3.95 (2H, *t*), 5.00 (<2H, *d*), 6.55 (1H, *q*), 6.75 (1H, *q*), 7.70 (1H, *t*); ir (KCl) ν_{max} 3350, 2950, 2880, 1630, 1570, 1430, 1380, 1340, 1320, 1270, 1160, 1010, 1000 cm^{-1}; ms *m/z* 240 (M^+), 233, 225, 128, 112.

2,2″-Difluoro-4-hexoxy-4″-pentylterphenyl (**19**). *Quantities:* compound **18** (1.45 g, 4.50 mmol), compound **17** (1.30 g, 5.42 mmol), tetrakis(triphenylphosphine)palladium(0) (0.1691 g, 0.146 mmol).

The experimental procedure was as described for the preparation of compound **8**. The crude product was purified by column chromatography [silica gel/petroleum

fraction (bp 40–60°C)-dichloromethane, 3:1] to give a colourless solid which was recrystallised from ethanol to yield colourless crystals.

Yield 0.31 g (16%); transitions (°C) K 45.0 N 131.0 I; ^{1}H nmr ($CDCl_3$)δ 0.90 (6H, 2xt), 1.40 (8H, *m*), 1.45 (2H, quint), 1.65 (2H, quint), 1.80 (2H, quint), 2.65 (2H, *t*), 4.00 (2H, *t*), 6.72 (1H, *q*), 6.78 (1H, *q*), 6.99 (1H, *q*), 7.04 (1H, *q*), 7.38 (2H, 2xt), 7.60 (4H, *s*); ir (KCl) ν_{max} 2960, 2940, 2860, 1620, 1490, 1390, 1310, 1250, 1230, 1160, 1020 cm^{-1}; ms *m/z* 436 (M^+), 352, 295, 266, 185.

2-Fluoro-4-pentylbiphenyl-4'-ylboronic acid (**20**). *Quantities:* compound **18** (9.90 g, 0.031 mol), magnesium (0.8710 g, 0.036 mol), tri-isopropyl borate (11.66 g, 0.062 mol).

The experimental procedure was as described in a previous publication.[30]

Yield 8.85 g (100%); ^{1}H nmr ($CDCl_3$)δ 0.90 (3H, *t*), 1.30 (4H, *m*), 1.60 (2H, quint), 2.60 (2H, *t*), 7.00 (2H, *d*), 7.35 (2H, *m*), 7.50 (1H, *d*), 7.60–7.80 (2H, *m*), no obvious OH absorption; ir (KCl) ν_{max} 3600-3200, 2980, 2960, 2860, 1640, 1620, 1580, 1535, 1405, 1390-1320, 1140, 840 cm^{-1}; ms *m/z* 368, 356, 320, 311, 299, 286 (M^+), 285, 272, 262, 258, 252, 237.

2,2''-Difluoro-4-octoxy-4''-pentylterphenyl (**22**). *Quantities:* compound **21** (1.45 g, 4.79 mmol), compound **20** (1.75 g, 6.12 mmol), tetrakis(triphenylphosphine)palladium(0) (0.2979 g, 0.26 mmol).

The experimental procedure was as described for the preparation of compound **8**. The crude product was purified by column chromatography [silica gel/petroleum fraction (bp 40–60°C)-dichloromethane, 6:1] to give a colourless solid which was recrystallised from ethanol to yield colourless crystals.

Yield 1.57 g (55%); transitions (°C) K 42.5 N 121.5 I; ^{1}H nmr ($CDCl_3$)δ 0.90 (6H, 2xt), 1.35 (12H, *m*), 1.45 (2H, quint), 1.65 (2H, quint), 1.80 (2H, quint), 2.65 (2H, *t*), 4.00 (2H, *t*), 6.72 (1H, *q*), 6.78 (1H, *q*), 6.99 (1H, *q*), 7.04 (1H, *q*), 7.38 (2H, 2xt), 7.60 (4H, *s*); ir (KCl) ν_{max} 2940, 2860, 1630, 1495, 1480, 1405, 1325, 1315, 1170 cm^{-1}; ms *m/z* 464 (M^+), 351, 335, 320, 306, 294.

2,3''-Difluoro-4''-hexoxy-4-pentylterphenyl (**25**). *Quantities:* compound **23** (1.35 g, 4.91 mmol), compound **20** (1.77 g, 6.19 mmol), tetrakis(triphenylphosphine)palladium(0) (0.2991 g, 0.26 mmol).

The experimental procedure was as described for the preparation of compound **8**.The crude product was purified by column chromatography [silica gel/petroleum fraction (bp 40–60°C)-dichloromethane, 6:1] to give a colourless solid which was recrystallised from ethanol-ethyl acetate (10:1) to yield colourless crystals.

Yield 1.10 g (51%); transitions (°C) K 96.0 S_C 105.5 N 139.0 I; ^{1}H nmr ($CDCl_3$)δ 0.90 (6H, 2xt), 1.35 (8H, *m*), 1.50 (2H, quint), 1.65 (2H, quint), 1.85 (2H, quint), 2.65 (2H, *t*), 4.05 (2H, *t*), 7.00 (3H, *m*), 7.35 (3H, *m*), 7.60 (4H, *s*); ir (KCl) ν_{max} 2970, 2940, 2880, 1625, 1590, 1520, 1470, 1405, 1305, 1140, 810 cm^{-1}; ms *m/z* 436 (M^+), 379, 352, 295.

2,3''-Difluoro-4''-octoxy-4-pentylterphenyl (**26**). *Quantities:* compound **24** (0.80 g,

2.64 mmol), compound **20** (1.00 g, 3.50 mmol), tetrakis(triphenylphosphine)palladium(0) (0.1621 g, 0.14 mmol).

The experimental procedure was as described for the preparation of compound **8**. The crude product was purified by column chromatography [silica gel/petroleum fraction (bp 40–60°C)-dichloromethane, 5:1] to give a colourless solid which was recrystallised from ethanol-ethyl acetate (5:1) to yield colourless crystals.

Yield 0.96 g (78%); transitions (°C) K 75.5 S_C 107.0 N 132.0 I; ^{1}H nmr ($CDCl_3$)δ 0.90 (6H, 2xt), 1.35 (12H, *m*), 1.50 (2H, quint), 1.65 (2H, quint), 1.80 (2H, quint), 2.65 (2H, *t*), 4.05 (2H, *t*), 7.00 (3H, *m*), 7.35 (3H, *m*), 7.60 (4H, *s*); ir (KCl) ν_{max} 2960, 2940, 2860, 1620, 1520, 1500, 1570, 1400, 1300, 1275, 1245, 1190, 1140, 870, 805 cm^{-1}; ms *m/z* 464 (M^+), 407, 352.

N-(3-Fluorophenyl)ethanamide (**28**). A solution of acetic anhydride (30.30 g, 0.297 mol) in glacial acetic acid (30 ml) was added to stirred 3-fluoroaniline (30.00 g, 0.270 mol). The resulting stirred mixture was heated under reflux for 20 min. and poured into cold water. 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* and the residue was recrystallised from aqueous glacial acetic acid to yield colourless crystals.

Yield 28.90 g (70%); mp 89–90°C; ^{1}H nmr ($CDCl_3$)δ 2.15 (3H, *s*), 6.79 (1H, *t*), 7.14–7.27 (2H, *m*), 7.48 (1H, sext), 8.20 (1H, *s*); ir (KBr) ν_{max} 3300, 3260, 3210, 3150, 3090, 1670, 1615, 1555, 1475, 1445, 1370, 1325, 1290, 1265, 1140, 1020, 960, 870, 790, 770, 690 cm^{-1}; ms *m/z* 153 (M^+), 111.

N-(4-Bromo-3-fluorophenyl)ethanamide (**29**). A stirred solution of compound **28** (13.50 g, 0.088 mol) and *N*-bromosuccinimide (15.73 g, 0.088 mol) in dry dichloromethane (120 ml) was heated under reflux for 5 h and left at room temperature for 16 h (glc analysis revealed a complete reaction with only one product present). The mixture was washed with water (×2) and dried ($MgSO_4$). The solvent was removed *in vacuo* to yield an off-white solid.

Yield 20.40 g (100%); mp 151–152°C; ^{1}H nmr ($CDCl_3$)δ 2.20 (3H, *s*), 7.04 (1H, *q*), 7.30 (1H, *s*), 7.44 (1H, *t*), 7.59 (1H, *q*); ir (KBr) ν_{max} 3320, 3280, 3220, 1680, 1605, 1545, 1420, 1320, 1260, 860 cm^{-1}; ms *m/z* 233 (M^+), 231 (M^+), 191, 189.

4-Bromo-3-fluoroaniline (**30**). 36% Hydrochloric acid (25 ml) was added dropwise to a stirred, refluxing solution of compound **29** (19.75 g, 0.085 mol) in ethanol (50 ml). The stirred solution was heated under reflux for 2 h (glc analysis revealed a complete reaction) and water (150 ml) was added. The mixture was distilled to remove ethyl acetate, water and ethanol and 5% sodium hydroxide solution was added to the residue until just alkaline. The product was extracted into dichloromethane (×2) and the combined organic extracts were washed with water and dried ($MgSO_4$). The solvent was removed *in vacuo* to give an off-white solid.

Yield 15.95 g (99%); mp 63–65°C; ^{1}H nmr ($CDCl_3$)δ 3.80 (2H, *s*), 6.35 (1H, oct), 6.45 (1H, *q*), 7.24 (1H, *q*); ir (KBr) ν_{max} 3450, 3340, 3220, 1630, 1610, 1490, 1445, 1320, 1180, 1040, 960, 845, 800, 605 cm^{-1}; ms *m/z* 191 (M^+), 189 (M^+).

1-Bromo-2-fluoro-4-iodobenzene (**31**). A stirred mixture of compound **30** (13.68 g, 0.072 mol), 36% hydrochloric acid (100 ml) and water (40 ml) was heated to a solution and then cooled (−5°C) as a suspension. A solution of sodium nitrite (5.47 g, 0.079 mol) in water (30 ml) was added dropwise and the resultant clear solution was stirred at 0°C for 20 min. A solution of potassium iodide (24.00 g, 0.145 mol) in water (40 ml) was added dropwise followed by cyclohexane (50 ml). The mixture was stirred at room temperature for 16 h. Water and ether were added and the separated aqueous layer was washed with ether. The combined ethereal extracts were washed successively with water, sodium metabisulphite solution, water, 10% sodium hydroxide solution, water and dried ($MgSO_4$). The solvent was removed *in vacuo* and the residue was distilled to give a colourless solid.

Yield 16.65 g (77%); bp 118–120°C at 15 mmHg; mp 36–37°C; ^{1}H nmr ($CDCl_3$)δ 7.25 (1H, *q*), 7.35 (1H, oct), 7.45 (1H, *q*); ir (KBr) ν_{max} 1570, 1470, 1390, 1220, 1070, 1040, 860, 805 cm^{-1}; ms *m/z* 302 (M^+), 300 (M^+), 175, 173.

1-Bromo-2-fluoro-4-pent-1-ynylbenzene (**32**). *Quantities:* pent-1-yne (4.02 g, 0.059 mol), *n*-butyllithium (6.00 ml, 10.0M in hexane, 0.060 mol), zinc chloride (8.16 g, 0.060 mol), compound **31** (15.50 g, 0.051 mol), tetrakis(triphenylphosphine)palladium(0) (2.95 g, 2.55 mmol).

The experimental procedure was as described in a previous publication.[30] The crude product was distilled to yield a colourless liquid.

Yield 11.31 g (92%); bp 132–134°C at 15 mmHg; ^{1}H nmr ($CDCl_3$)δ 1.05 (3H, *t*), 1.65 (2H, sext), 2.35 (2H, *t*), 7.03 (1H, oct), 7.13 (1H, *q*), 7.43 (1H, *q*); ir (film) ν_{max} 2980, 2940, 2880, 2240, 1560, 1480, 1410, 1300, 1185, 1050, 875, 820 cm^{-1}; ms *m/z* 242 (M^+), 240 (M^+), 213, 211.

1-Bromo-2-fluoro-4-pentylbenzene (**33**). A stirred mixture of compound **32** (10.95 g, 0.045 mol) and platinum(IV) oxide (0.25 g) in ethanol (150 ml) was hydrogenated at room temperature and atmospheric pressure for 2 h (glc analysis revealed a complete reaction). The solvent was removed *in vacuo* and the residue was distilled to yield a colourless liquid.

Yield 10.58 g (96%); bp 128–130°C at 15 mmHg; ^{1}H nmr ($CDCl_3$)δ 0.90 (3H, *t*), 1.30 (4H, *m*), 1.60 (2H, quint), 2.55 (2H, *t*), 6.83 (1H, oct), 6.93 (1H, *q*), 7.40 (1H, *q*); ir (film) ν_{max} 2980, 2940, 2860, 1580, 1490, 1420, 1245, 1160, 1045, 875, 815 cm^{-1}; ms *m/z* 246 (M^+), 244 (M^+), 189, 187.

2-Fluoro-4-pentylphenylboronic acid (**34**). *Quantities:* compound **33** (9.92 g, 0.040 mol), *n*-butyllithium (4.00 ml, 10.0M in hexane, 0.040 mol), trimethyl borate (8.35 g, 0.80 mol).

The experimental procedure was as described for the preparation of compound **11**, except that glc analysis revealed complete lithiation after 10 min.

Yield 8.28 g (99%); ^{1}H nmr ($CDCl_3$)δ 0.90 (3H, *t*), 1.35 (4H, *m*), 1.65 (2H, quint), 2.65 (2H, *t*), 6.92 (1H, *d*), 7.05 (1H, *q*), 8.02 (1H, *t*), no obvious OH absorption;

ir (KBr) ν_{max} 3700–3100, 2960, 2840, 1630, 1560, 1420, 1400–1300, 1140, 1035, 870, 820, 660 cm^{-1}; ms *m/z* 210 (M^+), 153, 110.

2,2''-Difluoro-4,4''-dipentylterphenyl (**36**). *Quantities:* compound **18** (1.10 g, 3.43 mmol), compound **34** (0.88 g, 4.19 mmol), tetrakis(triphenylphosphine)palladium (0) (0.15 g, 0.13 mmol).

The experimental procedure was as described for the preparation of compound **8** except that 1,2-dimethoxyethane was used in place of benzene and ethanol. The crude product was purified by column chromatography [silica gel/petroleum fraction (bp 40–60°C)-dichloromethane, 20:1 to give a colourless solid which was recrystallised from ethanol to yield colourless crystals.

Yield 1.20 g (86%); transitions (°C) K 58.5 N 92.0 I; ^1H nmr ($CDCl_3$)δ 0.90 (6H, *t*), 1.35 (8H, *m*), 1.65 (4H, quint), 2.65 (4H, *t*), 6.99 (2H, *q*), 7.04 (2H, *q*), 7.38 (2H, *t*), 7.61 (4H, *s*); ir (KBr) ν_{max} 2960, 2940, 2860, 1625, 1570, 1490, 1400, 1265, 1140, 1120, 1010, 955, 870, 815 cm^{-1}; ms *m/z* 406 (M^+), 349, 292.

2,3''-Difluoro-4,4''-dipentylterphenyl (**37**). *Quantities:* compound **18** (1.10 g, 3.43 mmol), compound **35** (0.90 g, 4.29 mmol), tetrakis(triphenylphosphine)palladium (0) (0.15 g, 0.13 mmol).

The experimental procedure was as described for the preparation of compound **36**. The crude product was purified by column chromatography [silica gel/petroleum fraction (bp 40–60°C)-dichloromethane, 49:1] to give a colourless solid which was recrystallised from ethanol to yield colourless crystals.

Yield 0.96 g (69%); transitions (°C) K 69.5 (S_C 67.0) S_A 83.0 N 111.5 I; ^1H nmr ($CDCl_3$)δ 0.90 (6H, 2xt), 1.35 (8H, *m*), 1.65 (4H, *m*), 2.65 (4H, 2xt), 6.99 (1H, *q*), 7.04 (1H, *q*), 7.25 (1H, *t*), 7.29 (1H, *q*), 7.34 (1H, *q*), 7.38 (1H, *t*), 7.62 (4H, *s*); ir (KBr) ν_{max} 2960, 2940, 2860, 1625, 1580, 1550, 1490, 1395, 1260, 1170, 1140, 870, 810 cm^{-1}; ms *m/z* 406 (M^+), 349, 292.

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