The Synthesis and Transition Temperatures of Some 4,4″-Dialkyl- and 4,4″-Alkoxyalkyl-1,1′:4′,1″-terphenyls with 2,3- or 2′,3′-Difluoro Substituents and of their Biphenyl Analogues

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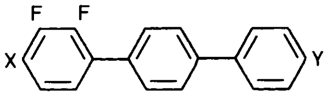
The tetrakis(triphenylphosphine)palladium(0)-catalysed coupling of arylboronic acids with aryl halides is used to prepare several 4,4″-dialkyl- and 4,4″-alkoxyalkyl-1,1′:4′,1″-terphenyls with 2,3- or 2′,3′-difluoro substituents and their related biphenyl systems. Lithiation *ortho* to a 1,2-difluoroaromatic unit provides the route to the 2,3-difluoroarylboronic acids.

The 2,3-difluoro substituted terphenyls are low-melting liquid crystals with wide-range S_C phases and no underlying smectic phase; these compounds are excellent hosts for ferroelectric systems. The compounds with widest S_C ranges are those with the difluoro substituents in an end ring and the compounds with difluoro substituents in the central ring show more nematic character and so are useful for ECB devices.

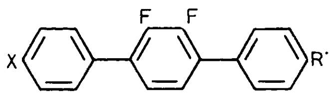
Much interest surrounds the laterally monofluoro-substituted terphenyls which we have reported in recent years [1–4] and one particular area of current interest concerns their use as host materials to give S_C^* systems for ferroelectric display devices. The earlier work revealed that a lateral fluoro-substituent in terphenyls offers two distinct advantages for devising ferroelectric host materials; firstly, it reduces the melting point of the parent system and suppresses the more ordered smectic phases and, secondly, it generates compounds with a tendency to form tilted smectic phases such as S_C, S_I, and S_F.

The disadvantages in the use of these compounds as ferroelectric hosts are that they are of moderately high birefringence, they have weakly positive values of dielectric anisotropy and, almost always, ordered smectic phases are still present as enantiotropic or monotropic phases. It was clear that further improvements needed to be made in the physical properties of these compounds before they can be regarded as viable host materials for S_C^* mixtures.

We report here the synthesis and transition temperatures of some laterally *o*-difluoro-substituted terphenyls **(I)** and **(II)** which show much improved physical properties. These compounds are excellent hosts for ferroelectric systems as shown by work carried out by our collaborators at RSRE (Malvern) which will be mentioned later.



(I)



(II)

X = R, RO; Y = R′, R′O

Positioning of the fluoro substituents in this way means they are inherently fixed on one side of the molecule (in another paper we will discuss the results for other difluoroterphenyls with their substituents in a variety of positions in the same or different rings). This 2,3-difluoro relationship offers the advantage of narrow molecules which are no broader than monofluoroterphenyls and so they retain similar liquid crystal thermal stabilities. However, the most essential advantage is that these molecules have significantly lower dielectric anisotropies (negative $\Delta\varepsilon$). The extra fluorine eliminates all ordered smectic phases except for compounds **(48)** and **(51)**, and melting points are still reasonably low (lower than for monofluoroterphenyls in some cases).

Some difluorobiphenyls have also been prepared in the expectation that such compounds would have lower birefringence and viscosity. Also, in order to determine the effect of even further lateral fluoro-substitution, a tri- and a tetrafluoroterphenyl have been made.

The crucial part of the synthesis for all of the compounds is the ability to lithiate a position *ortho* to an aryl fluorine atom.[5–8] We have previously used lithiation between two aryl fluorine atoms in the production of some fluorinated esters.[9] The *ortho*-lithiation procedure thus enables a wide range of functional groups to be obtained *ortho* to a fluorine atom in 1,2-difluorobenzenes [*e.g.* $-CO_2H(-CN)$, $-B(OH)_2(-OH)$, $-CH(OH)R$].

We have therefore developed a general method of synthesising *o*-difluoro-terphenyls and -biphenyls which involves starting with 1,2-difluorobenzene. The biphenyl and terphenyl units can then be made by a coupling reaction [9–11] which we have optimised to give excellent yields. The basis behind this method is the preparation of a boronic acid *via* lithiation *ortho* to a fluorine atom, and the boronic acid† is then coupled with an aryl bromide or iodide (Scheme 2) using tetrakis(triphenylphosphine)palladium(0) as a catalyst.[12] Subsequent lithiation *ortho* to the other fluorine gives a biphenyl boronic acid which can similarly be coupled with the same or a different aryl bromide or iodide (*e.g.*, Schemes 2 and 3). The boronic acid **(12)**

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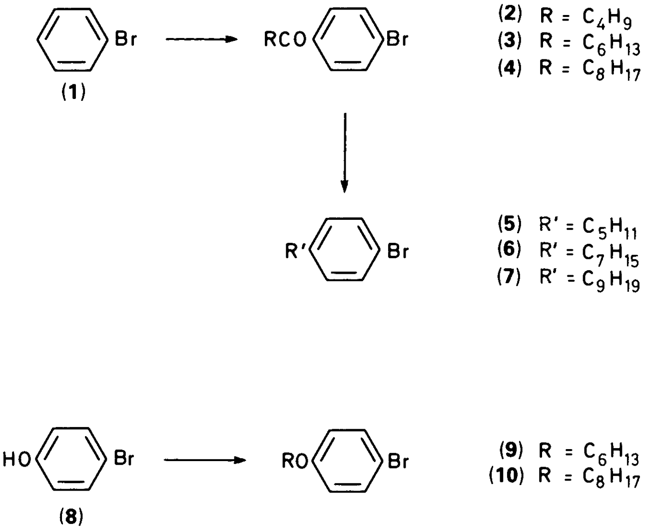
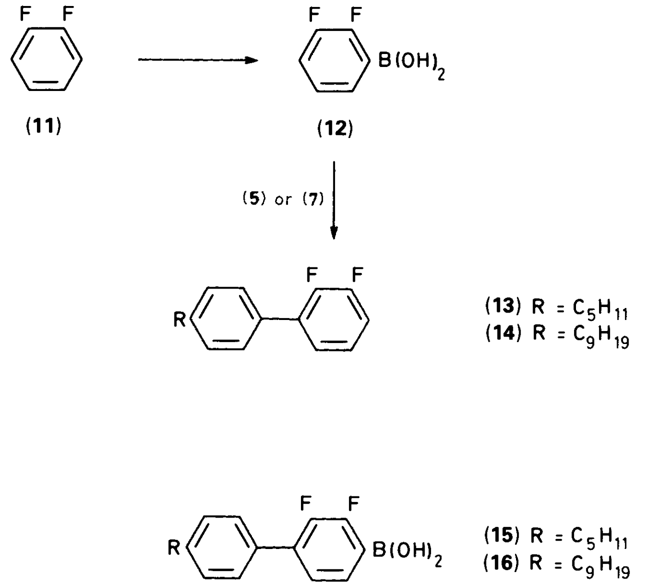
† The ^1H n.m.r. spectra for products from the boronic acid preparations frequently gave no evidence for OH groups and the mass spectra gave peaks ranging from the mass ion of the boronic acid to the mass ion for the trimeric anhydride; these products, which may therefore be mixtures of boronic acids and anhydrides, were not carefully purified since the basic conditions used in the subsequent coupling reactions permit the use of either.



Scheme 1.



Scheme 2.

can also be converted into a phenol on oxidation with hydrogen peroxide[13,14] and subsequent alkylation gives alkoxydifluoro systems. A second lithiation, formation of boronic acid, and coupling gives a variety of terphenyls or biphenyls (Schemes 4, 6, 7, and 8).

When 2,3-difluorophenyl-lithium is treated with an aldehyde, an alcohol is formed which is easily and efficiently converted into an alkyl chain. Alkyldifluorobenzenes can be treated in the same manner as the alkoxy-2,3-difluorobenzenes to give either biphenyls or terphenyls (Schemes 5–8).

The use of boronic acids in these coupling reactions to obtain biphenyl and terphenyl units offers the following advantages over other methods:[15–17] (*a*) the boronic acids can be prepared and stored indefinitely enabling them to be used as required; (*b*) the coupling reaction offers good yields without homocoupling products and the crude product is easily purified by column chromatography and recrystallisation (or distillation); (*c*) anhydrous conditions are not necessary; (*d*) *o*-fluoro-substituted boronic acids can be formed at low temperature by reaction of the *o*-lithiated aryl fluoride with a trialkyl borate but at higher temperatures (approximately greater than −50 °C, *e.g.*, in forming arylzincs) *o*-fluoroaryl-lithiums are unstable.

Discussion and Comparison of the Transition Temperatures of the Difluoroterphenyls (*see Tables* 1 *and* 2).—The 1,2-difluoroterphenyls reported are dialkyl and alkyl,alkoxy systems with the two *ortho*-fluorines in the middle ring or in either end ring. The compounds containing the two fluorines in the centre ring have much lower melting points and lower phase-transition temperatures than their analogues with fluorines in either end ring. In particular, the S_A and S_C phases are strongly promoted by the two fluorines being in either end ring and large S_C ranges are found in these compounds.

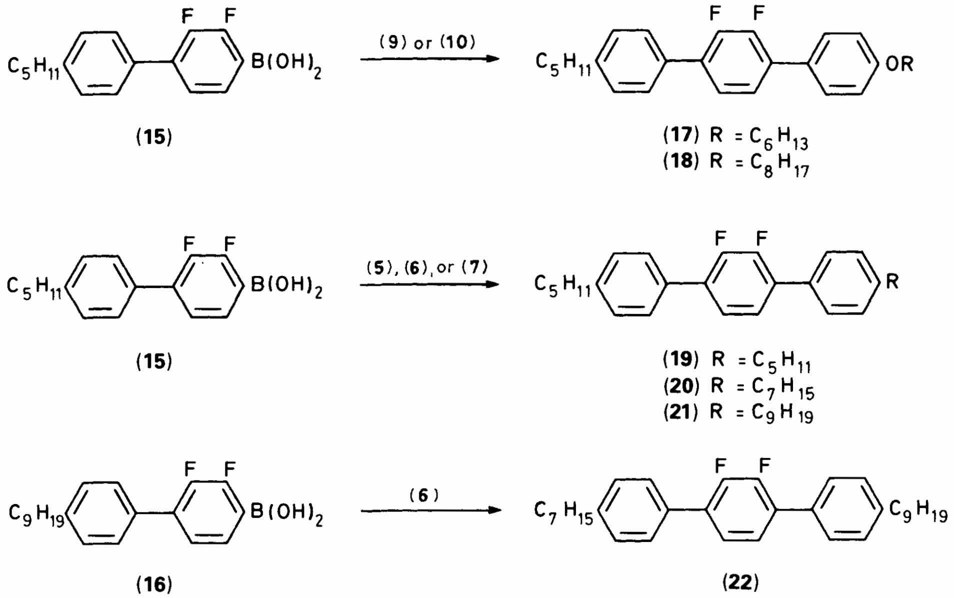
The dialkyl compound (**19**) is solely nematic and because it is symmetrical it has a high melting point (60.0 °C), whereas compounds (**17**) and (**18**), which are alkyl,alkoxy systems have lower melting points (54.0 and 48.5 °C, respectively), and they also exhibit both an S_C phase, which has a moderate range, and a larger-range nematic phase. The unsymmetrical dialkyl compounds (**20**)–(**22**) show much lower melting points (36.5, 42.5, and 49.0 °C, respectively) than compound (**19**) and the larger size of the alkyl groups encourages S_C character, with some S_A tendency as shown in compound (**22**). This increase in smectic tendency is at the expense of the nematic-phase stability, as the clearing points (T_{N-I} values) are *ca.* 10.0 °C lower than for compound (**19**). The octyloxy group of compound (**18**) lowers the melting point, raises the T_{S_C-N} value and lowers the T_{N-I} value as compared to the hexyloxy compound (**17**). Other examples of this lowering of melting point and raising of smectic tendency in moving from hexyloxy to octyloxy will be seen later.

Moving on to the higher-melting difluoroterphenyls with fluorines in the outer rings, it can be seen that, in general, they have much greater smectic tendencies (particularly S_C, with large ranges) and smaller nematic ranges than those compounds with fluorines in the centre ring. Compound (**19**) with fluorines in the centre ring has no smectic phases, but a 60 °C nematic range, whereas compound (**45**) has S_C and S_A phases with only a 10.5 °C nematic range. The position is clearer when we compare compounds (**17**) and (**18**) with compounds (**30**) and (**31**), respectively and with compounds (**46**) and (**47**), respectively. When the two fluorines are in an alkoxy-substituted end ring [with an alkyl substituent in the other end ring; compounds (**30**) and (**31**)] then the S_C thermal stability is increased by 78.5 °C [compound (**30**)] and by 49.0 °C [compound (**31**)], but nematic thermal stability is increased by only 17.0 and 17.5 °C, respectively.

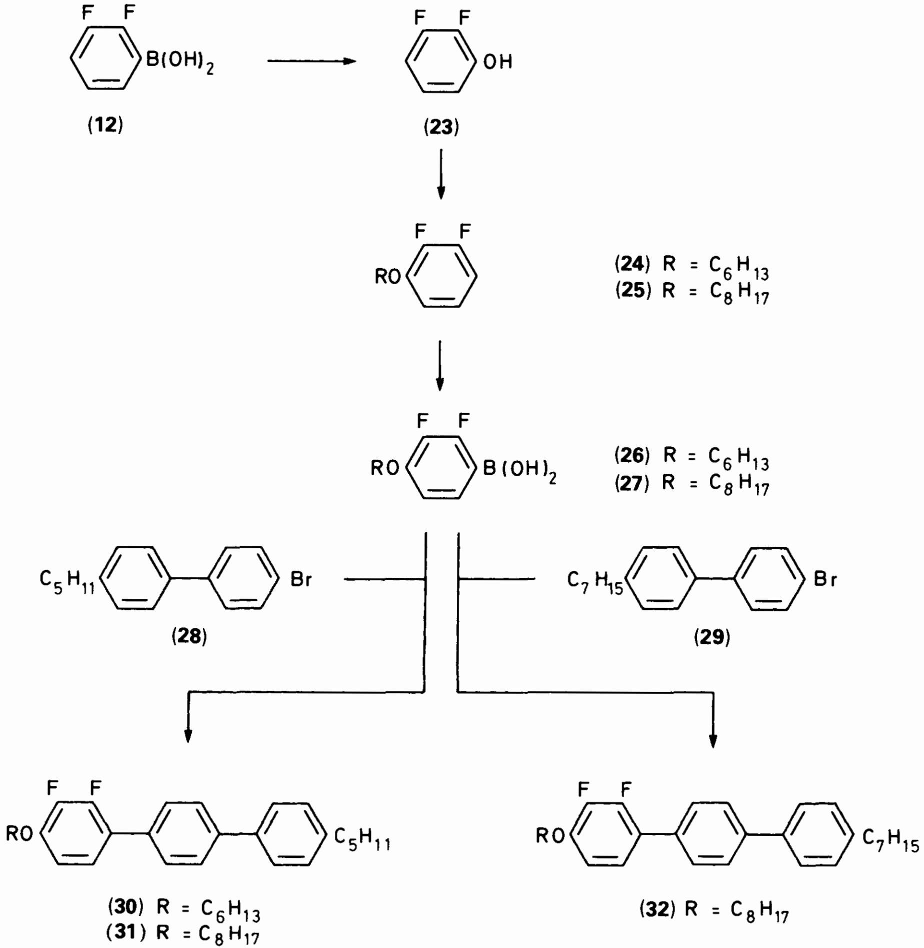
When the two fluorines are in the alkyl-substituted end ring [with an alkoxy substituent in the other end ring; compounds (**46**) and (**47**)] the smectic phases have even greater thermal stability, with an S_A phase beginning to appear (ranges *ca.* 10 °C). The S_C thermal stabilities are increased by 89.5 °C [compound (**46**)] and by 60.5 °C [compound (**47**)], but the increases in nematic thermal stabilities are less at 22.5 and 24.5 °C, respectively.

Liquid crystal phase stabilities are higher for compounds (**46**) and (**47**) when compared with compounds (**30**) and (**31**) because the first two compounds have an unsubstituted, less twisted *alkoxy*biphenyl unit which allows greater molecular polarisability whereas compounds (**30**) and (**31**) just have an *alkyl*-biphenyl unit. Since the melting points for these compounds are similar (within the range 89.0 to 101.5 °C) then compounds (**46**) and (**47**) have very large S_C ranges.

Dialkyldifluoroterphenyls [compounds (**45**), (**48**)–(**51**)] with the two fluorines in an end ring, as expected, have reasonably low-melting points. The highest melting point (81.0 °C) is for compound (**45**) and is accounted for by the alkyl chains being identical; compound (**48**) with unsymmetrical terminal groups, melts 15.5 °C lower. The $T_{S_C-S_A}$ value of compound (**48**)



Scheme 3.

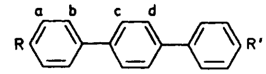


Scheme 4.

has increased by 3.0 °C, the T_{S_A-N} value has increased by 3.5 °C and the T_{N-I} value has decreased by 5.0 °C. Compound (**49**) melts even lower but the S_C tendency is also lowered [the T_{N-I} value however is similar to compound (**48**)]. Compound (**50**) has a long and a short alkyl chain which reduces the compound's smectic thermal stability more than its melting point when compared with compound (**45**). These compounds generally give a good compromise of low melting points and high $T_{S_C-S_A/N}$ values, but compound (**21**) with a C_9 alkyl group and with the two fluorines in the centre ring also has a very low melting point (42.5 °C) and a respectable T_{S_C-N} value of 66.0 °C.

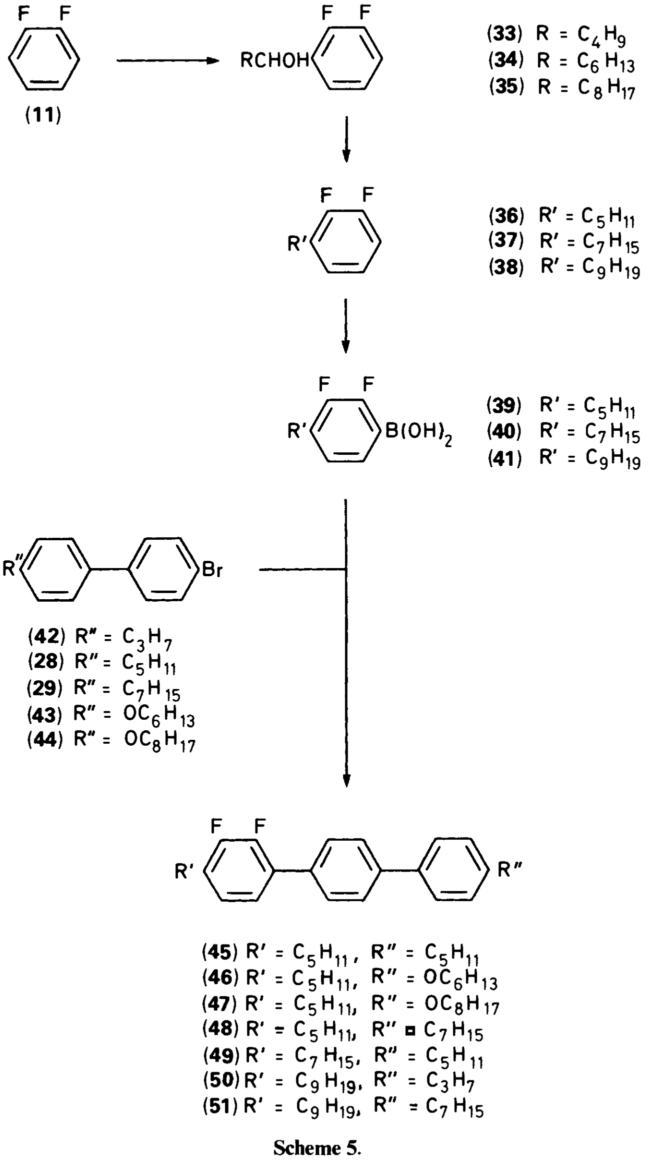
In an effort to reduce melting points further without any loss

Table 1. Transition temperatures/°C for several difluoro-substituted 4,4″-dialkylterphenyls.



Compd. No.	R	R′	a	b	c	d	K		S_I		S_C		S_A		N		I
(19)	C_5H_{11}	C_5H_{11}	H	H	F	F	*	60.0	—	—	—	—	—	—	*	120.0	*
(45)	C_5H_{11}	C_5H_{11}	F	F	H	H	*	81.0	—	—	*	115.5	*	131.5	*	142.0	*
(20)	C_5H_{11}	C_7H_{15}	H	H	F	F	*	36.5	—	—	(*	24.0)	—	—	*	111.5	*
(48)	C_5H_{11}	C_7H_{15}	F	F	H	H	*	65.5	*	74.5	*	118.5	*	135.0	*	137.0	*
(49)	C_7H_{15}	C_5H_{11}	F	F	H	H	*	56.0	—	—	*	105.5	*	131.0	*	136.0	*
(21)	C_5H_{11}	C_9H_{19}	H	H	F	F	*	42.5	—	—	*	66.0	—	—	*	110.0	*
(22)	C_7H_{15}	C_9H_{19}	H	H	F	F	*	49.0	—	—	*	77.0	*	93.0	*	108.5	*
(50)	C_9H_{19}	C_3H_7	F	F	H	H	*	63.0	—	—	*	84.5	*	117.0	*	131.5	*
								80.0									
(51)	C_9H_{19}	C_7H_{15}	F	F	H	H	*	44.0	*	55.0	*	105.0	*	127.0	—	—	*
(56)	C_5H_{11}	4MH[a]	F	F	H	H	*	64.0	—	—	*	86.0	—	—	*	100.5	*

[a] (±)-4-Methylhexyl.



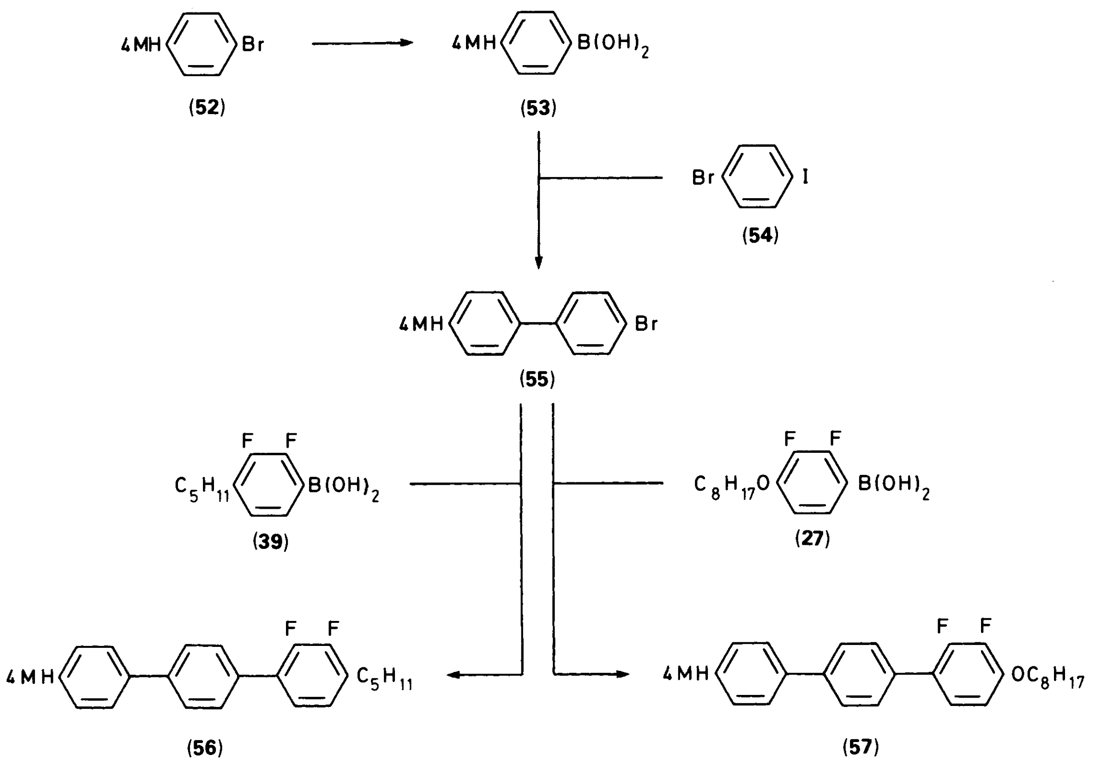
Scheme 5.

of S_C character, two compounds (**56**) and (**57**) with a (±)-4-methylhexyl (4MH) substituent were prepared. However, if the values for compound (**56**) are compared with those for compound (**48**) it is clear that this approach was not successful. A small fall in melting point (1.5 °C) was achieved, but S_C thermal stability was greatly reduced (32.5 °C), and the S_A phase was lost, giving a larger nematic range but a reduced T_{N-I} value (by 36.5 °C). Compound (**57**) can be compared to compound (**31**) [a slightly different structural comparison than for compounds (**56**) and (**48**)] and the reduction in melting point of 21.5 °C is comparable to the reduction of S_C character by 24.0 °C; again the S_A phase was lost to create a larger nematic range with a 31.0 °C lower T_{N-I} value.

Compounds (**64**) and (**66**) are a trifluoroterphenyl and a tetrafluoroterphenyl respectively (see Table 3) and can be compared with compound (**31**) and with each other to see the effect of additional fluoro-substitution; compound (**66**) can also be compared with compound (**47**). The additional fluorine of compound (**64**) compared to compound (**31**) reduced the melting point by 35.5 °C, but S_C character was affected much more markedly and was lowered by 82.5 °C. The loss of the S_A phase has given a compound of large nematic range (58.0 °C) with a T_{N-I} value reduced by 39.5 °C. The tetrafluoroterphenyl (**66**) has a much increased melting point over compound (**64**) (three fluorines) but this is not much higher than that for either of the difluoro compounds [(**31**) and (**47**)]. The T_{N-I} value is much the same as for the trifluoro compound (**64**) which is as expected, since the fourth fluorine is on the end position of the core. The S_C phase has disappeared altogether, but this has probably been masked by the high melting point.

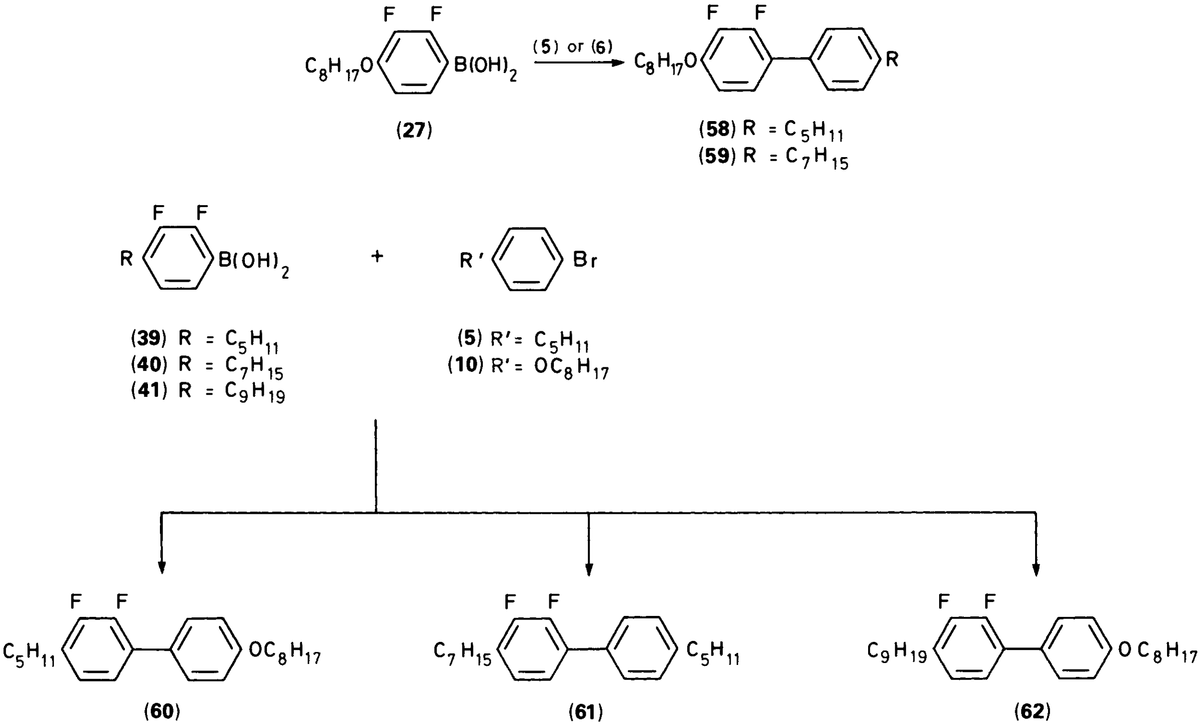
The fact that the T_{N-I} value of compound (**64**) is not decreased, but increased very slightly (1 °C) by the introduction of the fourth fluorine provides another instance, substantiating several earlier observations, that substituents exerting no additional broadening or twisting effects simply fill up space and can enhance nematic thermal stability.[18]

A most interesting feature of this set of compounds is the appearance of a more ordered smectic phase (S_I) in compounds (**48**) and (**51**). The reason for this appears to be the presence of the long (C_7H_{15}) alkyl chain in the unsubstituted, less twisted biphenyl unit of the molecule, so enhancing the smectic order. For both compounds (**48**) and (**51**) this ordered smectic phase was revealed by DSC analysis and identified by optical microscopy (free-standing film) as an S_I phase. It is particularly interesting that this more ordered, tilted smectic phase has been found in two dialkyl compounds and yet it does not appear in any alkyl,alkoxy compounds where it might have been more expected [compounds (**30**)–(**32**), (**46**), and (**47**)] since the greater polarity/polarisability of an alkoxy substituent is well known to



4MH = (±)-4-Methylhexyl

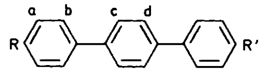
Scheme 6.



Scheme 7.

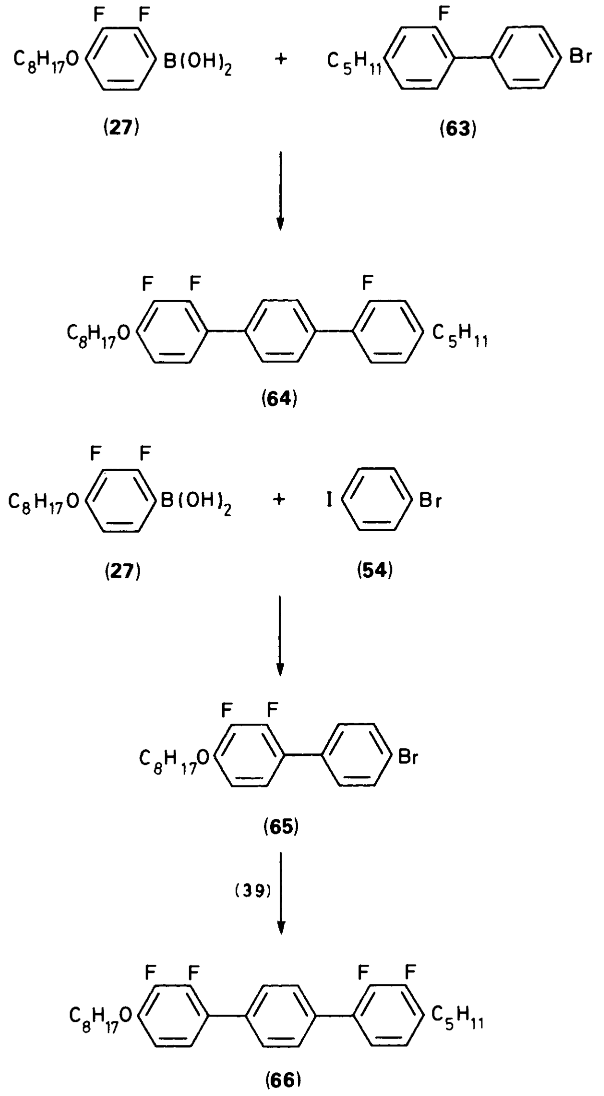
favour smectic phases of the tilted type. The higher melting points of these alkyl,alkoxy compounds could however simply be masking the S_I phase. However, if compound (**48**) is compared with compound (**32**), the melting point of compound (**32**) is only 24.0 °C higher and its S_C thermal stability is 29.5 °C higher. The S_I phase thermal stability would only have to be 15.0 °C higher than that for compound (**48**) for the S_I phase to be seen in compound (**32**). It could be that the lone pairs on the oxygen atom of the alkoxy chain cause intermolecular repulsion preventing the ordering required for the formation of an S_I

Table 2. Transition temperatures/°C for several difluoro-substituted 4-alkoxy-4″-alkyl-*p*-terphenyls.



Compd. No.	R	R′	a	b	c	d	K		S_C		S_A		N		I
(17)	$C_6H_{13}O$	C_5H_{11}	H	H	F	F	*	54.0	*	67.0	—		*	149.0	*
(18)	$C_8H_{17}O$	C_5H_{11}	H	H	F	F	*	48.5	*	95.0	—		*	141.5	*
(30)	$C_6H_{13}O$	C_5H_{11}	F	F	H	H	*	97.5	*	145.5	—		*	166.0	*
(31)	$C_8H_{17}O$	C_5H_{11}	F	F	H	H	*	93.5	*	144.0	*	148.0	*	159.0	*
(32)	$C_8H_{17}O$	C_7H_{15}	F	F	H	H	*	89.5	*	148.0	*	151.5	*	154.0	*
(36)	C_5H_{11}	$C_6H_{13}O$	F	F	H	H	*	101.5	*	156.5	*	167.0	*	171.5	*
(47)	C_5H_{11}	$C_8H_{17}O$	F	F	H	H	*	89.0	*	155.5	*	165.0	*	166.0	*
(57)	$C_8H_{17}O$	4MH[a]	F	F	H	H	*	72.0	*	120.0	—		*	128.0	*

[a] (±)-4-Methylhexyl.



Scheme 8.

phase yet making little difference to the more stable crystal state. This prevention of ordering, making no difference to the thermal stability of the less ordered phases (S_C, S_A, N), may outweigh any enhancement of phase stability caused by increased polarity/polarisability.

Summary for Difluoro-substituted Terphenyls.—(*a*) Compounds with identical alkyl chains [compounds (**19**) and (**45**)] have higher melting points than some alkoxy,alkyl compounds.

(*b*) Alkyl,alkoxy compounds generally have higher melting points and higher phase-transition temperatures than dialkyl systems.

(*c*) Compounds with the two fluorines in the end rings rather than in the centre ring have higher melting points and higher phase-transition temperatures, with greater smectic tendencies.

(*d*) Compounds with the two fluorines in the centre ring tend to be more nematic in character, although alkyl,alkoxy compounds of this type do have reasonable S_C thermal stabilities. S_C character is introduced into dialkyl compounds of this type by unsymmetrical alkyl chains; an S_A phase is introduced by long alkyl chains.

(*e*) An octyloxy group reduces melting point, increases S_C character and reduces nematic character when compared to a hexyloxy group.

(*f*) A third fluorine seems to lower melting point, but S_C and nematic thermal stabilities are reduced by a similar magnitude and the S_A phase is removed.

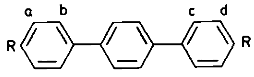
(*g*) A fourth fluoro-substituent raises the melting point significantly and eradicates the smectic phases. The T_{N-I} value is little affected by the substitution of the fourth fluorine.

Discussion and Comparison of the Transition Temperatures of the Difluorobiphenyls (*see Table* 4).—A small selection of *o*-difluorobiphenyls was prepared in the hope of producing compounds of low melting point, lower birefringence, lower viscosity, and perhaps more negative $\Delta\varepsilon$ than the terphenyls. In the biphenyls the *o*-fluoro substituents obviously have to be in an end ring. As for the terphenyls, where the unfluorinated section contains an alkoxy group the phase-transition temperatures are higher and the compounds have greater smectic tendency. The melting point of compound (**60**) is lower than that of compound (**58**) and its S_A and nematic phases are enantiotropic, whereas compound (**58**) just shows a monotropic nematic phase.

A longer alkyl chain in conjunction with an octyloxy group greatly enhances phase transition temperatures although melting points are also increased. Compounds (**62**) and (**59**) have similar melting points and both show S_C, S_A, and nematic phases but the thermal stabilities of each of these phases is greater in compound (**62**) which has the octyloxy group in an unsubstituted ring. As expected, the dialkyl compound (**61**) does not show any phases at all.

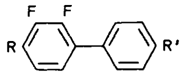
Compared with the terphenyls, these biphenyls have lower melting points and greatly reduced liquid-crystal thermal stabilities, but the five compounds in Table 4 do constitute a most interesting group of very low-melting mesogens, two of which show enantiotropic mesophases.

Table 3. Transition temperatures/°C for a trifluoro- and a tetrafluoro-substituted 4-alkoxy-4″-alkyl-*p*-terphenyl.



Compd. No.	R	R′	a	b	c	d	K		S_C		N		I
(64)	$C_8H_{17}O$	C_5H_{11}	F	F	F	H	*	58.0	*	61.5	*	119.5	*
(66)	$C_8H_{17}O$	C_5H_{11}	F	F	F	F	*	111.5	—	—	*	120.5	*

Table 4. Transition temperatures/°C for several difluoro-substituted 4-alkoxy-4′-alkyl- and 4,4′-dialkyl-biphenyls.



Compd. No.	R	R′	K		S_C		S_A		N		I
(60)	C_5H_{11}	$C_8H_{17}O$	*	8.0	—	—	*	12.0	*	18.0	*
(61)	C_7H_{15}	C_5H_{11}	*	0.5	—	—	—	—	—	—	*
(62)	C_9H_{19}	$C_8H_{17}O$	*	25.0	(*	11.5)	*	33.0	*	34.0	*
(58)	$C_8H_{17}O$	C_5H_{11}	*	14.0	—	—	—	—	(*	13.5)	*
(59)	$C_8H_{17}O$	C_7H_{15}	*	24.0	(*	6.0	*	13.0	*	23.0)	*

The only biphenyl exhibiting an S_C phase which can be directly compared to a terphenyl is compound (**59**), which has a 65.5 °C lower melting point than compound (**32**), but much larger reductions in liquid crystal thermal stabilities are seen; down by 142.0, 138.5, and 131.0 °C for S_C, S_A, and nematic respectively. Similar reductions on going from a terphenyl to a biphenyl are seen in other comparisons [*e.g.* compound (**60**) with compound (**47**) and compound (**58**) with compound (**31**)].

Summary for Difluoro-substituted Biphenyls.—(*a*) All such systems have low melting points (much lower than for terphenyls).

(*b*) Monotropic S_C, enantiotropic S_A, and nematic phases are seen for certain compounds, but the thermal stabilities of these phases are very much lower than for the terphenyls.

(*c*) Higher liquid-crystal thermal stabilities with little change in melting point are seen for biphenyls with an alkoxy group in the unfluorinated ring (*cf.* the same trend seen in the terphenyls).

These difluoro-terphenyls and -biphenyls allow mixtures to be formulated which have wide-range S_C phases without an underlying smectic phase and mixtures can be produced which have the correct phase sequence (S_C–S_A–N–Isotropic) required for giving good alignment in a ferroelectric cell.[19] The physical properties of these materials are being studied more extensively at RSRE (Malvern) as single compounds and as a variety of mixtures designed to optimise those properties required for host materials for ferroelectric systems. These results will be published in detail later and will describe excellent host mixtures which have many outstanding physical properties. However, one interesting property to emerge from work at RSRE (Malvern) is that the dielectric anisotropies of compounds with an alkoxy-difluoro end-group are much more negative than those values for compounds with an alkyl-difluoro end-group or with the difluoro unit in the centre of the molecule. The reason for this marked effect is probably because of mesomeric involvement of a terminal alkoxy group with the two electron-attracting lateral fluoro-substituents.

Some of these compounds which have wide-range nematic phases can also be used in ECB (electrically controlled birefringence) devices.

Experimental

Confirmation of the structures of intermediates and products was obtained by ^{1}H n.m.r. 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 compounds in Tables 1–4 was checked by g.l.c. (see above) and h.p.l.c. (Microsorb C18 80-215-C5 RP column) and all compounds were >99.9% pure.

1-*Bromo*-4-*pentanoylbenzene* (**2**).—Pentanoyl chloride (50.0 g, 0.41 mol) was added dropwise to a stirred, cooled (0 °C) mixture of compound (**1**) (150 cm^3) and aluminium chloride (62.0 g, 0.46 mol). The mixture was stirred at 0 °C for 1 h, heated at 80 °C for 2 h, cooled, and poured into 18% hydrochloric acid. The product was extracted into chloroform (twice), and the combined organic extracts were washed with water and steam distilled to remove chloroform and the excess of bromobenzene. The product was extracted into chloroform (twice), and the combined organic extracts were washed with water and dried ($MgSO_4$). The solvent was removed *in vacuo* and the residue was distilled to yield a colourless solid (78.1 g, 78%); b.p. 180–184 °C at 20 mmHg; $\delta(CDCl_3)$ 0.90 (3 H, t), 1.60 (4 H, m), 3.00 (2 H, t), 7.80 (2 H, d), and 8.00 (2 H, d); ν_{max}(KCl) 2 960, 2 880, 1 685, 1 585, 1 400, 1 070, 1 010, and 980 cm^{-1}; *m*/*z* 242 (M^+), 240 (M^+), 213, 198, and 185.

1-*Bromo*-4-*heptanoylbenzene* (**3**).—Quantities: heptanoyl chloride (60.0 g, 0.40 mol), compound (**1**) (150 cm^3), aluminium chloride (62.0 g, 0.46 mol). The experimental procedure was as described for the preparation of compound (**2**). Yield 107 g (99%); b.p. 130–135 °C at 0.1 mmHg; $\delta(CDCl_3)$ 0.90 (3 H, t), 1.35 (6 H, m), 1.75 (2 H, quintet), 2.95 (2 H, t), 7.60 (2 H, d), and 7.85 (2 H, d); ν_{max}(KCl) 2 980, 2 950, 2 910, 2 880, 1 680, 1 590, 1 470, 1 400, 1 200, 1 070, 1 010, 980, 840, 800, and 730 cm^{-1}; *m*/*z* 270 (M^+), 268 (M^+), 213, 200, 183, 157, and 132.

1-*Bromo*-4-*nonanoylbenzene* (**4**).—Quantities: nonanoyl chloride (13.90 g, 0.079 mol), compound (**1**) (55 cm^3), aluminium chloride (12.10 g, 0.091 mol). The experimental procedure was as described for the preparation of compound (**2**). Yield 23.0 g (98%); b.p. 138–140 °C at 0.1 mmHg; δ(CDCl$_3$) 0.85 (3 H, t), 1.30 (10 H, m), 1.70 (2 H, quintet), 2.90 (2 H, t), 7.60 (2 H, d), and 7.80 (2 H, d); ν_{max}(KCl) 2 940, 2 860, 1 690, 1 590, 1 470, 1 380, 1 070, 1 005, and 810 cm^{-1}; *m/z* 298 (M^+), 296 (M^+), 200, 198, 185, 183, 157, and 155.

1-*Bromo*-4-*pentylbenzene* (**5**).—A mixture of compound (**2**) (77.1 g, 0.32 mol), hydrazine hydrate (46.4 g, 0.93 mol), and potassium hydroxide (59.0 g, 1.05 mol) in diethylene glycol (250 cm^3) was heated at 130 °C for 2 h, the excess of hydrazine hydrate was distilled off and the temperature was raised to 200 °C for 2 h. The cooled mixture was poured into 18% hydrochloric acid, 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 yield a colourless liquid (58.1 g, 80%); b.p. 145–148 °C at 20 mmHg; δ(CDCl$_3$) 0.90 (3 H, t), 1.30 (4 H, m), 1.60 (2 H, quintet), 2.60 (2 H, t), 7.10 (2 H, d), and 7.50 (2 H, d); ν_{max}(KCl) 2 960, 2 930, 2 880, 1 490, 1 410, 1 075, 1 015, and 830 cm^{-1}; *m/z* 228 (M^+), 226 (M^+), 195, 185, and 171.

1-*Bromo*-4-*heptylbenzene* (**6**).—Quantities: compound (**3**) (106.0 g, 0.39 mol), hydrazine hydrate (56.50 cm^3, 58.20 g, 1.16 mol), potassium hydroxide (74 g). The experimental procedure was as described for the preparation of compound (**5**). Yield 59.0 g (58%); b.p. 105–115 °C at 0.1 mmHg; δ(CDCl$_3$) 0.90 (3 H, t), 1.25 (8 H, m), 1.55 (2 H, quintet), 2.50 (2 H, t), 7.00 (2 H, d), and 7.35 (2 H, d); ν_{max}(film) 2 950, 2 860, 1 490, 1 410, 1 075, 1 015, and 800 cm^{-1}; *m/z* 256 (M^+), 254 (M^+), 169, 103, and 91.

1-*Bromo*-4-*nonylbenzene* (**7**).—Quantities: compound (**4**) (22.00 g, 0.0074 mol), hydrazine hydrate (10.70 cm^3, 11.00 g, 0.22 mol), potassium hydroxide (13.70 g). The experimental procedure was as described for the preparation of compound (**5**). Yield 8.38 g (40%); b.p. 124–126 °C at 0.1 mmHg; δ(CDCl$_3$) 0.90 (3 H, t), 1.25 (12 H, s), 1.55 (2 H, quintet), 2.55 (2 H, t), 7.03 (2 H, d), 7.38 (2 H, d); ν_{max}(film) 2 960, 2 940, 2 860, 1 595, 1 490, 1 470, 1 405, 1 250, 1 075, 1 015, 820, and 800 cm^{-1}; *m/z* 284 (M^+), 282 (M^+), 171, and 169.

1-*Bromo*-4-*hexyloxybenzene* (**9**).—A solution of 1-bromohexane (60.0 g, 0.36 mol) in acetone (150 cm^3) was added dropwise to a stirred mixture of compound (**8**) (71.0 g, 0.41 mol) and potassium carbonate (120.0 g, 0.87 mol) in acetone (600 cm^3) at room temperature. The stirred mixture was heated under reflux for 43 h (*i.e.*, until g.l.c. analysis revealed a complete reaction). The product was extracted into ether (twice), and the combined ethereal extracts were washed consecutively with water, 5% sodium hydroxide, and water, and dried (MgSO$_4$). The solvent was removed *in vacuo* and the residue was distilled to yield a colourless liquid (79.4 g, 86%); b.p. 100–110 °C at 0.1 mmHg; δ(CDCl$_3$) 0.90 (3 H, t), 1.50 (6 H, m), 1.80 (2 H, quintet), 4.00 (2 H, t), 7.00 (2 H, d), and 7.70 (2 H, d); ν_{max}(film) 2 960, 2 940, 2 880, 1 590, 1 490, 1 290, 1 250, 1 170, 1 070, 1 000, and 820 cm^{-1}; *m/z* 258 (M^+), 256 (M^+), 174, and 172.

1-*Bromo*-4-*octyloxybenzene* (**10**).—Quantities: compound (**8**) (64.5 g, 0.37 mol), 1-bromo-octane (60.0 g, 0.31 mol), potassium carbonate (103.5 g, 0.75 mol). The experimental procedure was as described for the preparation of compound (**9**). Yield 86.5 g (98%); b.p. 145 °C at 0.1 mmHg; δ(CDCl$_3$) 0.90 (3 H, t), 1.30 (8 H, m), 1.40 (2 H, quintet), 1.75 (2 H, quintet), 3.95 (2 H, t), 6.75 (2 H, d), and 7.35 (2 H, d); ν_{max}(KCl) 2 950, 2 860, 1 600, 1 585, 1 495, 1 475, 1 290, 1 250, 1 175, 1 080, 1 005, and 835 cm^{-1}; *m/z* 286 (M^+), 284 (M^+), 174 and 172.

2,3-*Difluorophenylboronic acid* (**12**).—Butyl-lithium (10.0 mol dm^{-3} in hexane; 6.60 cm^3; 0.066 mol) was added dropwise to a stirred, cooled (−78 °C) solution of compound (**11**) (7.50 g, 0.066 mol) in dry THF (80 cm^3) 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 (24.82 g, 1.32 mol) in dry THF (50 cm^3) 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 (60 cm^3). 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 colourless crystals (9.80 g, 94%); m.p. 234–237 °C; δ(CDCl$_3$) 7.10 (1 H, q), 7.15 (1 H, t), 7.50 (1 H, br s), and 7.65 (1 H, t); ν_{max}(KCl) 3 700–3 000, 1 625, 1 470, 1 360, 1 270, 1 045, and 905 cm^{-1}; *m/z* 158 (M^+), 140, 125, and 114.

2,3-*Difluoro*-4′-*pentylbiphenyl* (**13**).—A solution of compound (**12**) (3.50 g, 0.022 mol) in ethanol (15 cm^3) was added to a stirred mixture of compound (**5**) (3.80 g, 0.017 mol) and tetrakis(triphenylphosphine)palladium(0) (0.6510 g, 0.56 mmol) in benzene (30 cm^3) and aqueous sodium carbonate (2 mol dm^{-3}; 30 cm^3) at room temperature under dry nitrogen. The stirred mixture was heated under reflux (*ca.* 95 °C) for 23 h (*i.e.*, until g.l.c/t.l.c. analysis revealed a complete reaction). The product was extracted into ether (twice) 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 (b.p. 40–60 °C)–dichloromethane 3:1] to yield a colourless liquid (4.30 g, 99%); δ(CDCl$_3$) 0.90 (3 H, t), 1.35 (4 H, m), 1.65 (2 H, quintet), 2.60 (2 H, t), 7.05–7.15 (3 H, m), 7.25 (2 H, d), and 7.45 (2 H, q); ν_{max}(KCl) 2 960, 2 940, 2 860, 1 480, 1 265, 1 100, 895, and 780 cm^{-1}; *m/z* 260 (M^+), 203.

2,3-*Difluoro*-4′-*nonylbiphenyl* (**14**).—Quantities: compound (**7**) (3.50 g, 0.0124 mol), compound (**12**) (2.35 g, 0.015 mol), tetrakis(triphenylphosphine)palladium(0) (0.72 g, 0.62 mmol). The experimental procedure was as described for the preparation of compound (**13**). The crude product was purified by column chromatography [silica gel; petroleum fraction (b.p. 40–60 °C)–dichloromethane 5:1] to give a colourless liquid. Yield 2.93 g (77%); δ(CDCl$_3$) 0.85 (3 H, t), 1.25 (12 H, s), 1.60 (2 H, t), 2.60 (2 H, t), 7.06–7.18 (3 H, m), 7.27 (2 H, d), and 7.46 (2 H, q); ν_{max}(film) 2 960, 2 860, 1 630, 1 595, 1 520, 1 485, 1 410, 1 315, 1 265, 1 225, 1 100, 900, and 780 cm^{-1}; *m/z* 316 (M^+), 203, and 183.

2,3-*Difluoro*-4′-*pentylbiphenyl*-4-*ylboronic acid* (**15**).—Quantities: compound (**13**) (4.00 g, 0.015 mol), butyl-lithium (1.50 cm^3; 10.0 mol dm^{-3} in hexane, 0.015 mol), tri-isopropyl borate (5.70 g, 0.030 mol). The experimental procedure was as described for the preparation of compound (**12**). Yield 4.50 g (99%); δ(CDCl$_3$) 0.90 (3 H, t), 1.30 (4 H, m), 1.65 (2 H, t), 2.65 (2 H, t), 5.20 (2 H, d), 7.25–7.35 (3 H, m), 7.50 (2 H, q), and 7.60 (1 H, sextet); ν_{max}(KCl) 3 600–3 000, 2 960, 2 940, 2 860, 1 625, 1 520, 1 450, 1 355, 1 220, and 915 cm^{-1}; *m/z* 304 (M^+), 260, and 203.

2,3-*Difluoro*-4′-*nonylbiphenyl*-4-*ylboronic acid* (**16**).—Quantities: compound (**14**) (2.71 g, 8.58 mmol), butyl-lithium (3.44 cm^3; 2.5 mol dm^{-3} in hexane, 8.60 mmol), tri-isopropyl borate (3.30 g, 0.018 mol). The experimental procedure was as described for the preparation of compound (**12**). Yield 3.10 g (100%); δ(CDCl$_3$) 0.85 (3 H, t), 1.30 (12 H, m), 1.60 (2 H, quintet), 2.65 (2 H, t), 7.20 (2 H, m), 7.27 (2 H, d), and 7.47 (2 H, q), no obvious OH absorption; ν_{max}(KCl) 3 700–3 100, 2 960, 2 940, 2 860, 1 630, 1 525, 1 455, 1 420–1 300, 1 225, 1 165, 1 100, 1 035, 915, 895, 830, 810, and 755 cm^{-1}; *m/z* 332, 316, 307, 280, and 203.

2′,3′-*Difluoro*-4-*hexyloxy*-4″-*pentyl*-p-*terphenyl* (**17**).—Quantities: compound (**9**) (1.30 g, 5.06 mmol), compound (**15**) (2.00 g, 6.58 mmol), tetrakis(triphenylphosphine)palladium(0) (0.3121 g, 0.27 mmol). The experimental procedure was as described for the preparation of compound (**13**).

The crude product was purified by column chromatography [silica gel; petroleum fraction (b.p. 40–60 °C)–dichloromethane 6:1] to give a colourless solid which was recrystallised from ethanol to yield colourless crystals. Yield 1.10 g (50%); transitions/°C K 54.0 S_C 67.0 N 149.0 I; $\delta(CDCl_3)$ 0.90 (6 H, 2 × t), 1.30 (8 H, m), 1.45 (2 H, quintet), 1.65 (2 H, quintet), 1.80 (2 H, quintet), 2.65 (2 H, t), 4.00 (2 H, t), 7.00 (2 H, d), 7.25 (2 H, d), 7.30 (2 H, d), 7.50 (2 H, q), and 7.52 (2 H, q): ν_{max}(KCl) 2 960, 2 930, 2 855, 1 605, 1 480, 1 460, 1 405, 1 250, and 1 105 cm^{-1}; *m/z* 436 (M^+), 379, 352, and 295.

2′,3′-*Difluoro*-4-*octyloxy*-4″-*pentyl*-p-*terphenyl* (**18**).—Quantities: compound (**10**) (1.40 g, 4.91 mmol), compound (**15**) (1.90 g, 6.25 mmol), tetrakis(triphenylphosphine)palladium(0) (0.3102 g, 0.27 mmol). The experimental procedure was as described for the preparation of compound (**13**). The crude product was purified by column chromatography [silica gel; petroleum fraction (b.p. 40–60 °C)–dichloromethane 5:1] to give a colourless solid which was recrystallised from ethanol–ethyl acetate (4:1) to yield colourless crystals. Yield 1.75 g (77%); transitions/°C K 48.5 S_C 95.0 N 141.5 I; $\delta(CDCl_3)$ 0.90 (6 H, 2 × t), 1.30 (12 H, m), 1.45 (2 H, quintet), 1.65 (2 H, quintet), 1.80 (2 H, quintet), 2.65 (2 H, t), 4.00 (2 H, t), 7.00 (2 H, d), 7.22 (2 H, d), 7.28 (2 H, d), 7.50 (2 H, q), and 7.53 (2 H, q); ν_{max}(KCl) 2 980, 2 940, 2 880, 1 625, 1 540, 1 500, 1 470, 1 420, 1 260, 1 190, 1 115, 915, and 810 cm^{-1}; *m/z* 464 (M^+), 407, 394, and 352.

2′,3′-*Difluoro*-4,4″-*dipentyl*-p-*terphenyl* (**19**).—Quantities: compound (**5**) (1.30 g, 5.73 mmol), compound (**15**) (2.10 g, 6.90 mmol), tetrakis(triphenylphosphine)palladium(0) (0.3267 g, 6.90 mmol). The experimental procedure was as described for the preparation of compound (**13**).

The crude product was purified by column chromatography [silica gel; petroleum fraction (b.p. 40–60 °C)–dichloromethane 5:1] to yield a colourless solid which was recrystallised from ethanol to give colourless crystals. Yield 1.27 g (55%); transitions/°C K 60.0 N 120.0 I; $\delta(CDCl_3)$ 0.90 (6 H, 2 × t), 1.35 (8 H, m), 1.65 (4 H, quintet), 2.65 (4 H, t), 7.22 (2 H, d), 7.28 (4 H, d), and 7.50 (4 H, d); ν_{max}(KCl) 2 960, 2 930, 2 855, 1 480, 1 460, 1 405, and 1 105 cm^{-1}; *m/z* 406 (M^+) and 349.

2′,3′-*Difluoro*-4-*heptyl*-4″-*pentyl*-p-*terphenyl* (**20**).—Quantities: compound (**6**) (1.27 g, 4.98 mmol), compound (**15**) (1.82, 5.99 mmol), tetrakis(triphenylphosphine)palladium(0) (0.3069 g, 0.266 mmol). The experimental procedure was as described for the preparation of compound (**13**).

The crude product was purified by column chromatography [silica gel/petroleum fraction (b.p. 40–60 °C)–dichloromethane 20:1] to give a colourless solid which was recrystallised from ethanol to yield colourless crystals. Yield 0.86 g (40%); transitions/°C K 36.5 (S_C 24.0) N 111.5 I; $\delta(CDCl_3)$ 0.90 (6 H, 2 × t), 1.30 (12 H, m), 1.65 (4 H, quintet), 2.65 (4 H, t), 7.24 (2 H, m), 7.28 (4 H, d), and 7.52 (4 H, d); ν_{max}(KCl) 2 960, 2 940, 2 860, 1 490, 1 410, 1 205, 1 020, 910, 895, and 795 cm^{-1}; *m/z* 434 (M^+), 377, 363, 349, and 292.

2′,3′-*Difluoro*-4-*nonyl*-4″-*pentyl*-p-*terphenyl* (**21**).—Quantities: compound (**7**) (3.10 g, 0.011 mol), compound (**15**) (4.25 g, 0.014 mol), tetrakis(triphenylphosphine)palladium(0) (0.5118 g, 0.44 mmol). The experimental procedure was as described for the preparation of compound (**13**).

The crude product was purified by column chromatography [silica gel; petroleum fraction (b.p. 40–60 °C)–dichloromethane 2:1] to give a colourless solid which was recrystallised from ethanol (+5 drops of ethyl acetate) to yield colourless crystals. Yield 1.86 g (37%); transitions/°C K 42.5 S_C 66.0 N 110.0 I; $\delta(CDCl_3)$ 0.90 (6 H, 2 × t), 1.35 (16 H, m), 1.65 (4 H, quintet), 2.65 (4 H, t), 7.24 (2 H, m), 7.28 (4 H, d), and 7.50 (4 H, d); ν_{max}(KCl) 2 960, 2 940, 2 860, 1 490, 1 465, 1 410, 1 320, 1 205, 1 105, 910, 895, and 800 cm^{-1}; *m/z* 426 (M^+), 405, 349, and 292.

2′,3′-*Difluoro*-4-*hetpyl*-4″-*nonyl*-p-*terphenyl* (**22**).—Quantities: compound (**6**) (1.00 g, 3.92 mmol), compound (**16**) (1.65 g, 4.58 mmol), tetrakis(triphenylphosphine)palladium(0) (0.2398 g, 0.208 mmol). The experimental procedure was as described for the preparation of compound (**13**). 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 recrystallised from ethanol–ethyl acetate (10:1) to yield colourless crystals. Yield 0.71 g (37%); transitions/°C K 49.0 S_C 77.0 S_A 93.0 N 108.5 I; $\delta(CDCl_3)$ 0.85 (6 H, 2 × t), 1.30 (20 H, m), 1.65 (4 H, quintet), 2.65 (4 H, t), 7.24 (2 H, m), 7.28 (4 H, d), and 7.52 (4 H, d); ν_{max}(KCl) 2 960, 2 940, 2 860, 1 490, 1 410, 1 205, 1 105, 1 020, 910, 895, and 800 cm^{-1}; *m/z* 490 (M^+), 446, 405, 392, 377, 316, and 292.

2,3-*Difluorophenol* (**23**).—10% Hydrogen peroxide (30 cm^3, 0.088 mol) was added dropwise to a stirred solution of compound (**12**) (4.40 g, 0.028 mol) in ether (30 cm^3) heated under reflux. The stirred mixture was heated under reflux for 2.5 h and cooled. The ether layer was separated and the aqueous layer was washed with ether. The combined ethereal layers were washed with 10% sodium hydroxide and the separated aqueous layer was acidified with 36% hydrochloric acid. 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 give an off-white solid (2.90 g, 80%); m.p. 34–36 °C; $\delta(CDCl_3)$ 5.35 (1 H, s), 6.65–6.80 (2 H, m), and 6.95 (1 H, q); ν_{max}(KCl) 3 700–3 000, 1 630, 1 540, 1 515, 1 490, 1 480, 1 350, 1 310, 1 250, 1 190, and 1 020 cm^{-1}; *m/z* 130 (M^+), 110, and 101.

1,2-*Difluoro*-3-*hexyloxybenzene* (**24**).—Quantities: compound (**23**) (7.00 g, 0.054 mol), 1-bromohexane (10.72 g, 0.065 mol), potassium carbonate (17.40 g, 0.126 mol). The experimental procedure was as described for the preparation of compound (**9**). Yield 11.10 g (96%); b.p. 122 °C at 15 mmHg; $\delta(CDCl_3)$ 0.90 (3 H, t), 1.30 (4 H, m), 1.40 (2 H, quintet), 1.80 (2 H, quintet), 4.00 (2 H, t), 6.75 (2 H, m), and 6.95 (1 H, m); ν_{max}(KCl) 2 980, 2 940, 2 880, 1 635, 1 525, 1 495, 1 325, 1 300, 1 265, and 1 090 cm^{-1}; *m/z* 214 (M^+) and 130.

1,2-*Difluoro*-3-*octyloxybenzene* (**25**).—Quantities: compound (**23**) (7.00 g, 0.054 mol), 1-bromo-octane (12.55 g, 0.065 mol), potassium carbonate (17.40 g, 0.126 mol). The experimental procedure was as described for the preparation of compound (**9**). Yield 8.90 g (68%); b.p. 150 °C at 15 mmHg; $\delta(CDCl_3)$ 0.85 (3 H, t), 1.25 (8 H, m), 1.45 (2 H, quintet), 1.80 (2 H, quintet), 4.00 (2 H, t), 6.75 (2 H, m), and 6.95 (1 H, m); ν_{max}(KCl) 2 950, 2 880, 1 630, 1 525, 1 490, 1 485, 1 325, 1 300, 1 265, and 1 090 cm^{-1}; *m/z* 242 (M^+), 171, 156, and 130.

2,3-*Difluoro*-4-*hexyloxyphenylboronic acid* (**26**).—Quantities: compound (**24**) (10.00 g, 0.047 mol), butyl-lithium (4.70 cm^{-3}; 10.0 mol dm^{-3} in hexane, 0.047 mol), tri-isopropylborate (17.70 g, 0.094 mol). The experimental procedure was as described for the preparation of compound (**12**). Yield 12.10 g (100%); $\delta(CDCl_3)$ 0.90 (3 H, t), 1.30 (4 H, m), 1.45 (2 H, quintet), 1.80 (2 H, quintet), 4.00 (2 H, t), 6.70 (1 H, t), and 7.55 (1 H, t); no obvious OH absorption; ν_{max}(KCl) 3 650–3 100, 2 960, 2 940, 2 860, 1 630, 1 525, 1 470, 1 360, 1 310, 1 225, and 1 035 cm^{-1}; *m/z* 258 (M^+) and 174.

2,3-*Difluoro*-4-*octyloxyphenylboronic acid* (**27**).—Quantities: compound (**25**) (7.50 g, 0.031 mol), butyl-lithium (3.10 cm^3; 10.0 mol dm^{-3} in hexane, 0.031 mol), tri-isopropyl borate (11.66 g, 0.062 mol). The experimental procedure was as described for the preparation of compound (**12**). Yield 9.00 g (100%); δ(CDCl$_3$) 0.90 (3 H, t), 1.30 (8 H, m), 1.45 (2 H, quintet), 1.80 (2 H, quintet), 4.05 (2 H, t), 6.80 (1 H, t), and 7.80 (1 H, t); no obvious OH absorption; ν_{max}(KCl) 3 600–3 100, 2 980, 2 940, 2 880, 1 635, 1 530, 1 475, 1 365, 1 315, 1 230, 1 090, and 1 035 cm^{-1}; *m*/*z* 286 (M^+), 271, 258, and 241.

2,3-*Difluoro*-4-*hexyloxy*-4″-*pentyl*-p-*terphenyl* (**30**).—Quantities: compound (**28**) (1.40 g, 4.62 mmol), compound (**26**) 1.50 g, 5.81 mmol), tetrakis(triphenylphosphine)palladium(0) (0.2868 g, 0.248 mmol). The experimental procedure was as described for the preparation of compound (**13**).

The crude product was purified by column chromatography [silica gel; petroleum fraction (b.p. 40–60 °C)–dichloromethane 3:1] to give a colourless solid which was recrystallised from ethanol–ethyl acetate (10:1) to yield colourless crystals. Yield 1.65 g (82%); transitions/°C K 97.5 S$_C$ 145.5 N 166.0 I; δ(CDCl$_3$) 0.90 (6 H, t), 1.35 (8 H, m), 1.45 (2 H, quintet), 1.65 (2 H, quintet), 1.85 (2 H, quintet), 2.65 (2 H, t), 4.05 (2 H, t), 6.80 (1 H, sextet), 7.15 (1 H, sextet), 7.25 (2 H, d), 7.54 (2 H, d), 7.57 (2 H, q), and 7.65 (2 H, d); ν_{max}(KCl) 2 990, 2 960, 2 880, 1 645, 1 525, 1 505, 1 475, 1 405, 1 310, 1 205, 1 120, 1 090, and 805 cm^{-1}; *m*/*z* 436 (M^+), 351, 334, 322, 306, and 294.

2,3-*Difluoro*-4-*octyloxy*-4″-*pentyl*-p-*terphenyl* (**31**).—Quantities: compound (**28**) (1.54 g, 5.08 mmol), compound (**27**) (1.75 g, 6.12 mmol), tetrakis(triphenylphosphine)palladium(0) (0.3090 g, 0.268 mmol). The experimental procedure was as described for the preparation of compound (**13**).

The crude product was purified by column chromatography [silica gel; petroleum fraction (b.p. 40–60 °C)–dichloromethane 3:1] to give a colourless solid which was recrystallised from ethanol–ethyl acetate (4:1) to yield colourless crystals. Yield 1.97 g (84%); transitions/°C K 93.5 S$_C$ 144.0 S$_A$ 148.0 N 159.0 I; δ(CDCl$_3$) 0.90 (6 H, 2 × t), 1.30 (12 H, m), 1.45 (2 H, quintet), 1.65 (2 H, quintet), 1.80 (2 H, t), 2.65 (2 H, t), 4.05 (2 H, t), 6.80 (1 H, sextet), 7.15 (1 H, sextet), 7.25 (2 H, d), 7.54 (2 H, d), 7.57 (2 H, q), and 7.65 (2 H, d); ν_{max}(KCl) 2 980, 2 940, 2 880, 1 645, 1 525, 1 505, 1 475, 1 405, 1 310, and 1 090 cm^{-1}; *m*/*z* 464 (M^+), 351, 321, 307, and 294.

2,3-*Difluoro*-4-*octyloxy*-4″-*heptyl*-p-*terphenyl* (**32**).—Quantities: compound (**29**) (1.54 g, 4.65 mmol), compound (**27**) (1.80 g, 6.29 mmol), tetrakis(triphenylphosphine)palladium(0) 0.2717 g, 0.23 mmol). The experimental procedure was as described for the preparation of compound (**13**).

The crude product was purified by column chromatography [silica gel; petroleum fraction (b.p. 40–60 °C)–dichloromethane 3:1] to give a colourless solid which was recrystallised from ethanol–ethyl acetate (4:1) to yield colourless crystals. Yield 1.72 g (75%); transitions/°C K 89.5 S$_C$ 148.0 S$_A$ 151.5 N 154.0 I; δ(CDCl$_3$) 0.90 (6 H, 2 × t), 1.30 (16 H, m), 1.45 (2 H, quintet), 1.65 (2 H, quintet), 1.85 (2 H, quintet), 2.65 (2 H, t), 4.05 (2 H, t), 6.81 (1 H, sextet), 7.13 (1 H, sextet), 7.27 (2 H, d), 7.54 (2 H, d), 7.57 (2 H, q), and 7.65 (2 H, d); ν_{max}(KCl) 2 960, 2 940, 2 860, 1 635, 1 505, 1 470, 1 400, 1 305, 1 200, 1 120, 1 085, 900, and 805 cm^{-1}; *m*/*z* 492 (M^+), 435, 408, 380, and 295.

1-(2,3-*Difluorophenyl*)*pentan*-1-*ol* (**33**).—Butyl-lithium (10.50 cm^{-3}; 10.0 mol dm^{-3} in hexane; 0.105 mol) was added dropwise to a stirred, cooled (−78 °C) solution of compound (**11**) (12.00 g, 0.105 mol) in dry THF (80 cm^3) under dry nitrogen. The mixture was maintained under these conditions for 2.5 h and a solution of pentanal (9.03 g, 0.105 mol) in dry THF (50 cm^3) was added dropwise at −78 °C. The mixture was allowed to warm slowly to room temperature overnight. Ammonium chloride solution was added and the product was extracted into ether (twice), the combined ethereal extracts were washed with water and dried (MgSO$_4$). The solvent was removed *in vacuo* and the residue was distilled to yield a colourless oil (18.25 g, 87%); b.p. 182–184 °C at 0.1 mmHg; δ(CDCl$_3$) 0.85 (3 H, t), 1.30 (4 H, m), 1.75 (2 H, m), 2.80 (1 H, s), 4.95 (1 H, t), 7.05 (2 H, m), and 7.18 (1 H, m); ν_{max}(KCl) 3 500–3 100, 2 960, 2 940, 2 860, 1 630, 1 600, 1 485, 1 275, 1 205, and 830 cm^{-1}; *m*/*z* 200 (M^+), 149, 143, 127, and 115.

1-(2,3-*Difluorophenyl*)*heptan*-1-*ol* (**34**).—Quantities: compound (**11**) (12.00 g, 0.105 mol), butyl-lithium (42.00 cm^3; 2.5 mol dm^{-3} in hexane, 0.105 mol), heptanal (11.97 g, 0.105 mol). The experimental procedure was as described for the preparation of compound (**33**). Yield 20.70 g (86%), b.p. 106–108 °C at 0.1 mmHg; δ(CDCl$_3$) 0.90 (3 H, t), 1.30 (8 H, m), 1.75 (2 H, m), 2.45 (1 H, s), 5.00 (1 H, t), 7.02–7.08 (2 H, m), and 7.16–7.22 (1 H, m); ν_{max}(KCl) 3 600–3 100, 2 960, 2 940, 2 860, 1 630, 1 600, 1 485, 1 280, 1 205, 1 065, 935, 835, 790, and 730 cm^{-1}; *m*/*z* 228 (M^+).

1-(2,3-*Difluorophenyl*)*nonan*-1-*ol* (**35**).—Quantities: compound (**11**) (12.00 g, 0.105 mol), butyl-lithium (10.50 cm^3; 10.0 mol dm^{-3} in hexane; 0.105 mol), nonanal (14.91 g, 0.105 mol). The experimental procedure was as described for the preparation of compound (**33**). Yield 19.61 g (73%); b.p. 118–122 °C at 0.1 mmHg; δ(CDCl$_3$) 0.85 (3 H, t), 1.25 (12 H, m), 1.75 (2 H, m), 2.95 (1 H, s), 5.00 (1 H, t), 7.05 (2 H, m), and 7.18 (1 H, m); ν_{max}(KCl) 3 600–3 100, 2 940, 2 860, 1 630, 1 600, 1 485, 1 275, 1 205, 1 060, 825, and 785 cm^{-1}; *m*/*z* 256 (M^+), 238, 216, 203, and 142.

1,2-*Difluoro*-3-*pentylbenzene* (**36**).—Phosphorus pentaoxide (34.10 g, 0.24 mol) was added to a stirred solution of compound (**33**) (16.00 g, 0.08 mol) in pentane (100 cm^3). The mixture was stirred at room temperature overnight (g.l.c. analysis revealed a complete reaction) and the mixture was filtered. 5% Palladium-on-charcoal (1.85 g) was added to the filtrate and the stirred mixture was hydrogenated for 4 h at room temperature and pressure (g.l.c. analysis revealed a complete reaction). The palladium-on-charcoal was filtered off, the pentane was distilled off, and the product was distilled to yield a colourless liquid (10.45 g, 71%); b.p. 206–208 °C; δ(CDCl$_3$) 0.90 (3 H, t), 1.35 (4 H, m), 1.60 (2 H, quintet), 2.65 (2 H, t), and 6.90–7.00 (3 H, m); ν_{max}(KCl) 2 960, 2 940, 2 860, 1 630, 1 600, 1 490, 1 285, 1 210, 1 110, 1 060, 995, 835, 780, and 730 cm^{-1}; *m*/*z* 184 (M^+), 143, 127, 115, and 101.

1,2-*Difluoro*-3-*heptylbenzene* (**37**).—Quantities: compound (**34**) (19.70 g, 0.086 mol), phosphorus pentaoxide (37.0 g, 0.26 mol), 5% Pd/C (2.00 g). The experimental procedure was as described for the preparation of compound (**36**). Yield 10.72 g (59%); b.p. 124–126 °C at 15 mmHg; δ(CDCl$_3$) 0.90 (3 H, t), 1.30 (8 H, m), 1.60 (2 H, quintet), 2.65 (2 H, t), and 6.92–7.00 (3 H, m); ν_{max}(KCl) 2 960, 2 940, 2 860, 1 630, 1 600, 1 490, 1 285, 1 210, 980, 825, 780, and 730 cm^{-1}; *m*/*z* 212 (M^+), 169, 153, 143, and 128.

1,2-*Difluoro*-3-*nonylbenzene* (**38**).—Quantities: compound (**35**) (18.50 g, 0.072 mol), phosphorus pentaoxide (32 g, 0.225 mol), 5% Pd/C (2.00 g). The experimental procedure was as described from the preparation of compound (**36**). Yield 11.16 g (65%); b.p. 146–148 °C at 15 mmHg; δ(CDCl$_3$) 0.90 (3 H, t), 1.60 (12 H, m), 1.60 (2 H, quintet), 2.65 (2 H, t), 6.92–7.00 (3 H, m); ν_{max}(film) 2 980, 2 960, 2 860, 1 630, 1 600, 1 490, 1 285, 1 210, 1 040, 995, 825, 780, and 730 cm^{-1}; *m*/*z* 240 (M^+), 197, and 182.

2,3-*Difluoro*-4-*pentylphenylboronic acid* (**39**).—Quantities: compound (**36**) (9.85 g, 0.054 mol), butyl-lithium (5.40 cm^3; 10.0 mol dm^{-3} in hexane; 0.054 mol), tri-isopropyl borate (21.0 g, 0.11 mol). The experimental procedure was as described for the preparation of compound (**12**). Yield 12.30 g (100%); δ(CDCl$_3$) 0.90 (3 H, t), 1.30 (4 H, m), 1.60 (2 H, quintet), 2.65 (2 H, t), 6.95 (1 H, m), and 7.45 (1 H, m); no obvious OH absorption; ν_{max}(film) 3 600–3 100, 2 980, 2 940, 2 860, 1 640, 1 460, 1 400–1 280, 1 220, 1 140, 1 000, and 960 cm^{-1}; *m/z* 228 (M^+), 211, 205, 197, 193, 184, 171, 153, 149, and 143.

2,3-*Difluoro*-4-*heptylphenylboronic acid* (**40**).—Quantities: compound (**37**) (9.80 g, 0.046 mol), butyl-lithium (4.60 cm^3; 10.0 mol dm^{-3} in hexane; 0.046 mol), tri-isopropyl borate (18.0 g, 0.096 mol). The experimental procedure was as described for the preparation of compound (**12**). Yield 11.75 g (100%); δ(CDCl$_3$) 0.90 (3 H, t), 1.25 (8 H, m), 1.60 (2 H, quintet), 2.65 (2 H, t), 6.96 (1 H, m), and 7.40 (1 H, m); no obvious OH absorption; ν_{max}(KCl) 3 600–3 100, 2 960, 2 940, 2 860, 1 635, 1 455, 1 435–1 250, 1 220, 1 135, and 670 cm^{-1}; *m/z* 298, 270, 256 (M^+), 239, 228, 220, 212, 199, 185, 171, 155, 142, and 127.

2,3-*Difluoro*-4-*nonylphenylboronic acid* (**41**).—Quantities: compound (**38**) (10.15 g, 0.042 mol), butyl-lithium (4.20 cm^3; 10.0 mol dm^{-3} in hexane; 0.042 mol), tri-isopropyl borate (16.0 g, 0.085 mol). The experimental procedure was as described for the preparation of compound (**12**). Yield 11.90 g (100%); δ(CDCl$_3$) 0.90 (3 H, t), 1.30 (12 H, m), 1.60 (2 H, m), 2.65 (2 H, t), 7.00 (1 H, m), and 7.40 (1 H, t); no obvious OH absorption; ν_{max}(KCl) 3 600–3 200, 2 960, 2 940, 2 860, 1 635, 1 460, 1 400–1 335, 1 320, and 1 135 cm^{-1}; *m/z* 284 (M^+), 267, 256, 213, 199, 184, and 172.

2,3-*Difluoro*-4,4″-*dipentyl*-p-*terphenyl* (**45**).—Quantities: compound (**28**) (1.60 g, 5.28 mmol), compound (**39**) (1.45 g, 6.36 mmol), tetrakis(triphenylphosphine)palladium(0) (0.3767 g, 0.326 mmol). The experimental procedure was as described for the preparation of compound (**13**). The crude product was purified by column chromatography [silica gel; petroleum fraction (b.p. 40–60 °C)–dichloromethane 4:1] to give a colourless solid which was recrystallised from ethanol–ethyl acetate (10:1) to yield colourless crystals. Yield 1.70 g (79%); transitions/°C K 81.0 S$_C$ 115.5 S$_A$ 131.5 N 142.0 I; δ(CDCl$_3$) 0.90 (6 H, t), 1.35 (8 H, m), 1.65 (4 H, quintet), 2.65 (4 H, 2 × t), 7.00 (1 H, sextet), 7.15 (1 H, sextet), 7.28 (2 H, d), 7.56 (2 H, d), 7.60 (2 H, q), and 7.68 (2 H, d); ν_{max}(KCl) 2 960, 2 940, 2 860, 1 490, 1 465, 1 400, 900, and 805 cm^{-1}; *m/z* 406 (M^+), 361, 349, 337, 305, and 292.

2,3-*Difluoro*-4″-*hexyloxy*-4-*pentyl*-p-*terphenyl* (**46**).—Quantities: compound (**43**) (1.67 g, 5.02 mmol), compound (**39**) (1.40 g, 6.14 mmol), tetrakis(triphenylphosphine)palladium(0) (0.3420 g, 0.296 mmol). The experimental procedure was as described for the preparation of compound (**13**). The crude product was purified by column chromatography [silica gel; petroleum fraction (b.p. 40–60 °C)–dichloromethane 3:1] to give a colourless solid which was recrystallised from ethanol–ethyl acetate to yield colourless crystals. Yield 1.30 g (59%); transitions/°C K 101.5 S$_C$ 156.5 S$_A$ 167.0 N 171.5 I; δ(CDCl$_3$) 0.90 (6 H, 2 × t), 1.35 (8 H, m), 1.45 (2 H, quintet), 1.65 (2 H, quintet), 1.80 (2 H, quintet), 2.65 (2 H, t), 4.00 (2 H, t), 6.98 (2 H, d), 7.00 (1 H, sextet), 7.14 (1 H, sextet), 7.56 (2 H, d), 7.59 (2 H, q), and 7.63 (2 H, d); ν_{max}(KCl) 2 960, 2 940, 2 860, 1 605, 1 510, 1 490, 1 465, 1 290, 1 255, 1 185, 1 120, 900, 835, and 805 cm^{-1}; *m/z* 464 (M^+), 435, 420, 408, 390, 379, 366, and 352.

2,3-*Difluoro*-4″-*octyloxy*-4-*pentyl*-p-*terphenyl* (**47**).—Quantities: compound (**44**) (1.70 g, 4.71 mmol), compound (**39**) (1.30 g, 5.70 mmol), tetrakis(triphenylphosphine)palladium(0) (0.3127 g, 0.271 mmol). The experimental procedure was as described for the preparation of compound (**13**). The crude product was purified by column chromatography [silica gel; petroleum fraction (b.p. 40–60 °C)–dichloromethane 3:1] to give a colourless solid which was recrystallised from ethanol–ethyl acetate (3:1) to yield colourless crystals. Yield 1.60 g (73%); transitions/°C K 89.0 S$_C$ 155.5 S$_A$ 165.0 N 166.0 I; δ(CDCl$_3$) 0.90 (6 H, 2 × t), 1.30 (12 H, m), 1.45 (2 H, quintet), 1.65 (2 H, quintet), 1.80 (2 H, quintet), 2.65 (2 H, t), 4.00 (2 H, t), 6.98 (2 H, d), 7.00 (1 H, sextet), 7.14 (1 H, sextet), 7.57 (2 H, d), 7.60 (2 H, q), and 7.64 (2 H, d); ν_{max}(KCl) 2 960, 2 940, 2 860, 1 610, 1 510, 1 490, 1 400, 1 290, 1 255, 1 185, 920, 900, 830, and 810 cm^{-1}; *m/z* 464 (M^+), 435, 420, 408, 390, 379, 366, and 352.

2,3-*Difluoro*-4″-*heptyl*-4-*pentyl*-p-*terphenyl* (**48**).—Quantities: compound (**29**) (1.64 g, 4.95 mmol), compound (**39**) (1.35 g, 5.92 mmol), tetrakis(triphenylphosphine)palladium(0) (0.3211 g, 0.278 mmol). The experimental procedure was as described for the preparation of compound (**13**). The crude product was purified by column chromatography [silica gel; petroleum fraction (b.p. 40–60 °C)–dichloromethane 5:1] to give a colourless solid which was recrystallised from ethanol–ethyl acetate (10:1) to yield colourless crystals. Yield 1.52 g (71%); transitions/°C K 65.5 S$_I$ 74.5 S$_C$ 118.5 S$_A$ 135.0 N 137.0 I; δ(CDCl$_3$) 0.90 (6 H, 2 × t), 1.35 (12 H, m), 1.65 (4 H, quintet), 2.65 (4 H, 2 × t), 7.00 (1 H, sextet), 7.15 (1 H, sextet), 7.28 (2 H, d), 7.56 (2 H, d), 7.60 (2 H, q), and 7.67 (2 H, d); ν_{max}(KCl) 2 960, 2 940, 2 860, 1 490, 1 465, 1 400, 1 315, 1 120, 895, and 805 cm^{-1}; *m/z* 434 (M^+), 421, 391, 377, 362, 349, and 336.

2,3-*Difluoro*-4-*heptyl*-4″-*pentyl*-p-*terphenyl* (**49**).—Quantities: compound (**28**) (1.50 g, 4.95 mmol), compound (**40**) (1.52 g, 5.94 mmol), tetrakis(triphenylphosphine)palladium(0) (0.3421 g, 0.296 mmol). The experimental procedure was as described for the preparation of compound (**13**). The crude product was purified by column chromatography [silica gel; petroleum fraction (b.p. 40–60 °C)–dichloromethane 5:1] to give a colourless solid which was recrystallised from ethanol–ethyl acetate (10:1) to yield colourless crystals. Yield 1.54 g (72%); transitions/°C K 56.0 S$_C$ 105.5 S$_A$ 131.0 N 136.5 I; δ(CDCl$_3$) 0.90 (6 H, 2 × t), 1.35 (12 H, m), 1.65 (4 H, quintet), 2.65 (4 H, 2 × t), 7.00 (1 H, sextet), 7.15 (1 H, sextet), 7.28 (2 H, d), 7.56 (2 H, d), 7.60 (2 H, q), and 7.68 (2 H, d); ν_{max}(KCl) 2 960, 2 940, 2 860, 1 490, 1 465, 1 400, 1 220, 1 185, 1 125, 900, and 810 cm^{-1}; *m/z* 434 (M^+), 420, 405, 390, 377, 363, and 349.

2,3-*Difluoro*-4-*nonyl*-4″-*propyl*-p-*terphenyl* (**50**).—Quantities: compound (**42**) (1.37 g, 4.98 mmol), compound (**41**) (1.75 g, 6.16 mmol), tetrakis(triphenylphosphine)palladium(0) (0.3167 g, 0.274 mmol). The experimental procedure was as described for the preparation of compound (**13**).

The crude product was purified by column chromatography [silica gel; petroleum fraction (b.p. 40–60 °C)–dichloromethane 5:1] to give a colourless solid which was recrystallised from ethanol–ethyl acetate (10:1) to yield colourless crystals. Yield 1.78 g (82%); transitions/°C K 63.0/80.0 S$_C$ 84.5 S$_A$ 117.0 N 131.5 I; δ(CDCl$_3$) 0.85 (3 H, t), 0.95 (3 H, t), 1.30 (12 H, m), 1.65 (4 H, quintet), 2.65 (4 H, 2 × t), 7.00 (1 H, sextet), 7.16 (1 H, sextet), 7.28 (2 H, d), 7.56 (2 H, d), 7.60 (2 H, q), and 7.66 (2 H, d); ν_{max}(KCl) 2 960, 2 940, 2 860, 1 490, 1 465, 1 400, 1 120, 900, and 805 cm^{-1}; *m/z* 434 (M^+), 405, 334, 321, 305, and 292.

2,3-*Difluoro*-4-*nonyl*-4″-*heptyl*-p-*terphenyl* (**51**).—Quantities: compound (**29**) (1.53 g, 4.62 mmol), compound (**41**) (1.80 g, 6.34 mmol), tetrakis(triphenylphosphine)palladium(0) (0.2696 g, 0.23 mmol). The experimental procedure was as described for the preparation of compound (**13**).

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 recrystallised from ethanol–ethyl acetate to yield colourless crystals. Yield 2.00 g (88%); transitions/°C K 44.0 S$_\text{I}$ 55.0 S$_\text{C}$ 105.0 S$_\text{A}$ 127.0 I; δ(CDCl$_3$) 0.90 (6 H, 2 × t), 1.35 (20 H, m), 1.65 (4 H, quintet), 2.65 (4 H, 2 × t), 6.99 (1 H, sextet), 7.15 (1 H, sextet), 7.27 (2 H, d), 7.55 (2 H, d), 7.59 (2 H, q), and 7.67 (2 H, d); ν_max(KCl) 2 960, 2 940, 2 860, 1 490, 1 465, 1 400, 1 125, 1 010, 900, and 805 cm^{-1}; m/z 490 (M^+), 405, 377, and 292.

4-(4-*Methylhexyl)phenylboronic acid* (**53**).—Quantities: compound (**52**) (7.90 g, 0.031 mol), butyl-lithium (3.10 cm^3; 10.0 mol dm^{-3} in hexane, 0.031 mol), tri-isopropyl borate (12.00 g, 0.064 mol). The experimental procedure was as described for the preparation of compound (**12**). Yield 6.80 g (100%); δ(CDCl$_3$) 0.85 (7 H, m), 1.15 (2 H, m), 1.35 (2 H, m), 1.65 (2 H, quintet), 2.65 (2 H, t), 7.30 (2 H, d), and 8.10 (2 H, d); no obvious OH absorption; ν_max(film) 2 960, 2 940, 2 880, 1 615, 1 565, 1 520, 1500–1 270, 1 185, and 1 025 cm^{-1}; m/z 221, 219, 205, 192, 185, 176, 165, 149, 135, 131, 125, and 107.

4-*Bromo*-4′-(4-*methylhexyl)biphenyl* (**55**).—Quantities: compound (**53**) (3.30 g, 0.015 mol), compound (**54**) (3.50 g, 0.012 mol), tetrakis(triphenylphosphine)palladium(0) (0.70 g, 0.61 mmol). The experimental procedure was as described for the preparation of compound (**13**) except that the reaction was carefully monitored by g.l.c. and t.l.c. analysis and heated under reflux for 1.5 h. The crude product was purified by column chromatography [silica gel; petroleum fraction (b.p. 40–60 °C)–dichloromethane 5:1] to give a colourless solid. Yield 3.75 g (94%); m.p. *ca.* 25 °C; δ(CDCl$_3$) 0.85 (7 H, m), 1.15 (2 H, m), 1.35 (2 H, quintet), 1.60 (2 H, quintet), 2.60 (2 H, t), 7.25 (2 H, d), 7.43 (2 H, d), 7.47 (2 H, d), and 7.54 (2 H, d); ν_max(KCl) 2 960, 2 940, 2 880, 2 860, 1 485, 1 465, 1 390, 1 380, 1 080, and 810 cm^{-1}; m/z 332 (M^+), 330 (M^+), 247, 245, 232, 198, 167, and 165.

2,3-*Difluoro*-4″-(4-*methylhexyl*)-4-*pentyl*-p-*terphenyl* (**56**).—Quantities: compound (**55**) (1.15 g, 3.47 mmol), compound (**39**) (0.96 g, 4.21 mmol), tetrakis(triphenylphosphine)palladium(0) (0.2117 g, 0.183 mmol). The experimental procedure was as described for the preparation of compound (**13**).

The crude product was purified by column chromatography [silica gel; petroleum fraction (b.p. 40–60 °C)–dichloromethane 5:1] to give a colourless solid which was recrystallised from ethanol–ethyl acetate (10:1) to yield colourless crystals. Yield 0.90 g (60%); transitions/°C K 64.0 S$_\text{C}$ 86.0 N 100.5 I; δ(CDCl$_3$) 0.90 (9 H, m), 1.20 (2 H, septet), 1.35 (7 H, m), 1.65 (4 H, quintet), 2.70 (4 H, 2 × t), 7.00 (1 H, sextet), 7.15 (1 H, sextet), 7.28 (2 H, d), 7.56 (2 H, d), 7.60 (2 H, q), and 7.67 (2 H, d); ν_max(KCl) 2 960, 2 940, 2 860, 1 490, 1 465, 1 400, 1 315, 1 220, 1 185, 1 120, 900, and 805 cm^{-1}; m/z 434 (M^+), 377, 362, and 349.

2,3-*Difluoro*-4″-(4-*methylhexyl*)-4-*octyloxy*-p-*terphenyl* (**57**).—Quantities: compound (**55**) (1.49 g, 4.23 mmol), compound (**27**) (1.46 g, 5.10 mmol), tetrakis(triphenylphosphine)palladium(0) (0.2618 g, 0.227 mmol). The experimental procedure was as described for the preparation of compound (**13**).

The crude product was purified by column chromatography [silica gel; petroleum fraction (b.p. 40–60 °C)–dichloromethane 5:1] to give a colourless solid which was recrystallised from ethanol–ethyl acetate (10:1) to yield colourless crystals. Yield 1.16 g (56%); transitions/°C K 72.0 S$_\text{C}$ 120.0 N 128.0 I; δ(CDCl$_3$) 0.85 (9 H, m), 1.15 (2 H, septet), 1.30 (11 H, m), 1.45 (2 H, quintet), 1.65 (2 H, quintet), 1.85 (2 H, quintet), 2.65 (2 H, t), 4.05 (2 H, t), 6.81 (1 H, sextet), 7.14 (1 H, sextet), 7.28 (2 H, d), 7.54 (2 H, d), 7.57 (2 H, q), and 7.66 (2 H, d); ν_max(KCl) 2 960, 2 940, 2 880, 1 630, 1 500, 1 470, 1 300, 1 200, 1 110, 1 085, 900, and 795 cm^{-1}; m/z 492 (M^+), 446, 421, 407, 380, and 295.

2,3-*Difluoro*-4-*octyloxy*-4′-*pentylbiphenyl* (**58**).—Quantities: compound (**5**) (1.25 g, 5.51 mmol), compound (**27**) (1.90 g, 6.64 mmol), tetrakis(triphenylphosphine)palladium(0) (0.3424 g, 0.296 mmol). The experimental procedure was as described for the preparation of compound (**13**).

The crude product was purified by column chromatography [silica gel; petroleum fraction (b.p. 40–60 °C)–dichloromethane 6:1] to give a colourless liquid which was distilled [Kugelrohr, 210 °C (maximum) at 0.1 mmHg] to yield a colourless liquid. Yield 1.20 g, (56%); transitions/°C K 14.0 (N 13.5) I; δ(CDCl$_3$) 0.90 (6 H, 2 × t), 1.30 (12 H, m), 1.45 (2 H, quintet), 1.65 (2 H, quintet), 1.80 (2 H, quintet), 2.60 (2 H, t), 4.00 (2 H, t), 6.76 (1 H, sextet), 7.08 (1 H, sextet), 7.24 (2 H, d), and 7.40 (2 H, q); ν_max(film) 2 960, 2 940, 2 860, 1 635, 1 505, 1 470, 1 315, 1 295, 1 200, 1 110, 1 080, 900, and 800 cm^{-1}; m/z 388 (M^+), 360, 345, 331, 318, and 276.

2,3-*Difluoro*-4′-*heptyl*-4-*octyloxybiphenyl* (**59**).—Quantities: compound (**6**) (1.32 g, 5.18 mmol), compound (**27**) (1.78 g, 6.22 mmol), tetrakis(triphenylphosphine)palladium(0) (0.3217 g, 0.279 mmol). The experimental procedure was as described for the preparation of compound (**13**).

The crude product was purified by column chromatography [silica gel; petroleum fraction (b.p. 40–60 °C)–dichloromethane 6:1] to give a colourless liquid which was distilled [Kugelrohr, 230 °C (maximum) at 0.1 mmHg] to yield a colourless liquid. Yield 1.10 g (51%); transitions/°C K 24.0 (S$_\text{C}$ 6.0 S$_\text{A}$ 13.0 N 23.0) I; δ(CDCl$_3$) 0.90 (6 H, 2 × t), 1.35 (16 H, m), 1.45 (2 H, quintet), 1.60 (2 H, quintet), 1.80 (2 H, quintet), 2.60 (2 H, t), 4.05 (2 H, t), 6.77 (1 H, sextet), 7.07 (1 H, sextet), 7.23 (2 H, d), and 7.41 (2 H, q); ν_max(film) 2 960, 2 940, 2 860, 1 635, 1 505, 1 470, 1 315, 1 295, 1 200, 1 110, 1 080, 900, and 800 cm^{-1}; m/z 416 (M^+), 398, 381, 364, 354, 346, and 331.

2,3-*Difluoro*-4′-*octyloxy*-4-*pentylbiphenyl* (**60**).—Quantities: compound (**10**) (1.58 g, 5.54 mmol), compound (**39**) (1.55 g, 6.80 mmol), tetrakis(triphenylphosphine)palladium(0) (0.3761 g, 0.326 mmol). The experimental procedure was as described for the preparation of compound (**13**).

The crude product was purified by column chromatography [silica gel; petroleum fraction (b.p. 40–60 °C)–dichloromethane 6:1] to give a colourless liquid which was distilled [Kugelrohr, 240 °C (maximum) at 0.1 mmHg] to yield a colourless liquid. Yield 1.69 g (79%); transitions/°C K 8.0 S$_\text{A}$ 12.0 N 18.0 I; δ(CDCl$_3$) 0.90 (6 H, 2 × t), 1.30 (12 H, m), 1.45 (2 H, quintet), 1.65 (2 H, quintet), 1.80 (2 H, quintet), 2.65 (2 H, t), 4.00 (2 H, t), 6.94 (1 H, sextet), 6.97 (2 H, d), 7.05 (1 H, sextet), and 7.46 (2 H, q); ν_max(film) 2 960, 2 940, 2 860, 1 615, 1 525, 1 495, 1 465, 1 415, 1 250, 1 175, 1 115, 895, 840, and 815 cm^{-1}; m/z 388 (M^+), 366, 358, 331, and 309.

2,3-*Difluoro*-4-*heptyl*-4′-*pentylbiphenyl* (**61**).—Quantities: compound (**5**) (1.35 g, 5.95 mmol), compound (**40**) (1.85 g, 7.23 mmol), tetrakis(triphenylphosphine)palladium(0) (0.3721 g, 0.322 mmol). The experimental procedure was as described for the preparation of compound (**13**).

The crude product was purified by column chromatography [silica gel; petroleum fraction (b.p. 40–60 °C)–dichloromethane 10:1] to give a colourless liquid which was distilled [Kugelrohr, 210 °C (maximum) at 0.1 mmHg] to yield a colourless liquid. Yield 1.70 g (80%); transitions/°C K 0.5 I; δ(CDCl$_3$) 0.90 (6 H, 2 × t), 1.35 (12 H, m), 1.65 (4 H, m), 2.65 (4 H, 2 × t), 6.96 (1 H, sextet), 7.08 (1 H, sextet), 7.24 (2 H, d), and 7.44 (2 H, q); ν_max(film) 2 960, 2 940, 2 860, 1 490, 1 465, 1 410, 1 315, 1 290, 1 220, 1 180, 1 120, and 895 cm^{-1}; m/z 358 (M^+), 344, 330, 316, and 301.

2,3-*Difluoro*-4-*nonyl*-4′-*octyloxybiphenyl* (**62**).—Quantities: compound (**10**) (1.40 g, 4.91 mmol), compound (**41**) (1.67 g, 5.88 mmol), tetrakis(triphenylphosphine)palladium(0) (0.2992 g, 0.259 mmol). The experimental procedure was as described for the preparation of compound (**13**).

The crude product was purified by column chromatography [silica gel; petroleum fraction (b.p. 40–60 °C)–dichloromethane 6:1] to give a colourless liquid which was distilled [Kugelrohr, 230 °C (maximum) at 0.1 mmHg] to yield a colourless liquid. Yield 0.97 g (37%); transitions/°C K 25.0 (S_C 11.5) S_A 33.0 N 34.0 I; δ(CDCl$_3$) 0.90 (6 H, 2 × t), 1.30 (20 H, m), 1.45 (2 H, quintet), 1.60 (2 H, quintet), 1.80 (2 H, quintet), 2.65 (2 H, t), 4.00 (2 H, t), 6.94 (1 H, sextet), 6.97 (2 H, d), 7.06 (1 H, sextet), and 7.46 (2 H, q); ν_{max}(film) 2 960, 2 940, 2 860, 1 610, 1 525, 1 490, 1 465, 1 250, 1 180, 895, and 815 cm^{-1}; *m*/*z* 444 (M^+), 434, 405, 332, 321, and 307.

2,2″,3-*Trifluoro*-4-*octyloxy*-4″-*pentyl*-p-*terphenyl* (**64**).—Quantities: compound (**63**) (1.40 g, 4.36 mmol), compound (**27**) (1.50 g, 5.24 mmol), tetrakis(triphenylphosphine)palladium(0) (0.2717 g, 0.235 mmol). The experimental procedure was as described for the preparation of compound (**13**). The crude product was purified by column chromatography [silica gel; petroleum fraction (b.p. 40–60 °C)–dichloromethane 3:1] to give a colourless solid which was recrystallised from ethanol–ethyl acetate (10:1) to yield colourless crystals. Yield 1.60 g (76%); transitions/°C K 58.0 S_C 61.5 N 119.5 I; δ(CDCl$_3$) 0.90 (6 H, 2 × t), 1.30 (12 H, m), 1.45 (2 H, quintet), 1.65 (2 H, quintet), 1.85 (2 H, quintet), 2.65 (2 H, t), 4.05 (2 H, t), 6.82 (1 H, sextet), 7.00 (1 H, q), 7.04 (1 H, q), 7.14 (1 H, sextet), 7.38 (1 H, t), 7.57 (2 H, q), and 7.63 (2 H, q); ν_{max}(KCl) 2 960, 2 940, 2 860, 1 635, 1 515, 1 500, 1 470, 1 400, 1 300, 1 195, 1 130, 1 110, 1 090, 900, and 805 cm^{-1}; *m*/*z* 482 (M^+), 425, 370, and 313.

4′-*Bromo*-2,3-*difluoro*-4-*octyloxybiphenyl* (**65**).—Quantities: compound (**54**) (3.50 g, 0.012 mol), compound (**27**) (4.30 g, 0.015 mol), tetrakis(triphenylphosphine)palladium(0) (0.70 g, 0.61 mmol). The experimental procedure was as described for the preparation of compound (**13**) except that the reaction mixture was carefully monitored by g.l.c. and t.l.c. analysis and was heated under reflux for 2.25 h. The crude product was purified by column chromatography [silica gel; petroleum fraction (b.p. 40–60 °C)–dichloromethane 5:1] to yield a colourless solid. Yield 4.00 g (84%); m.p. *ca.* 30 °C; δ(CDCl$_3$) 0.90 (3 H, t), 1.30 (8 H, quintet), 1.45 (2 H, quintet), 1.80 (2 H, quintet), 4.05 (2 H, t), 6.76 (1 H, sextet), 7.02 (1 H, sextet), 7.36 (2 H, q), and 7.53 (2 H, d); ν_{max}(KCl) 2 960, 2 940, 2 860, 1 635, 1 520, 1 495, 1 470, 1 395, 1 315, 1 300, 1 205, 1 075, 1 015, 1 005, 900, 835, and 800 cm^{-1}; *m*/*z* 398 (M^+) and 396 (M^+).

2,2″,3,3″-*Tetrafluoro*-4-*octyloxy*-4″-*pentyl*-p-*terphenyl* (**66**).—Quantities: compound (**65**) (1.70 g, 4.28 mmol), compound (**39**) (1.35 g, 5.92 mmol), tetrakis(triphenylphosphine)palladium(0) (0.2671 g, 0.23 mmol). The experimental procedure was as described for the preparation of compound (**13**). The crude product was purified by column chromatography [silica gel; petroleum fraction (b.p. 40–60 °C)–dichloromethane 5:1] to give a colourless solid which was recrystallised from ethyl acetate to yield colourless crystals. Yield 1.10 g (51%); transitions/°C K 111.5 N 120.5 I; δ(CDCl$_3$) 0.90 (6 H, 2 × t), 1.30 (12 H, m), 1.50 (2 H, quintet), 1.65 (2 H, quintet), 1.85 (2 H, quintet), 2.70 (2 H, t), 4.10 (2 H, t), 6.84 (1 H, sextet), 7.02 (1 H, sextet), 7.15 (2 H, 2 × sextet), and 7.60 (4 H, s); ν_{max}(KCl) 2 960, 2 940, 2 860, 1 630, 1 520, 1 470, 1 405, 1 305, 1 200, 1 130, 980, 895, and 805 cm^{-1}; *m*/*z* 500 (M^+), 443, and 388.

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