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The synthesis and mesomorphic properties of liquid crystals with bulky terminal groups designed for bookshelf geometry ferroelectric mixtures

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The synthesis and mesomorphic properties of a systematic range of *ortho* difluoroterphenyls with a bulky terminal chain are detailed. The bulky terminal chain consists of either a tertiarybutyl group or a trimethylsilyl unit, each separated from the core by a short (dimethylene) chain, with the other terminal chain being either octyloxy or heptyl. The synthesis of the materials was affected efficiently using a combination of low temperature lithiations and palladium-catalysed cross-coupling reactions. Unusually for liquid crystals with bulky terminal chains, the smectic phase stability (particularly smectic C) is upheld by more than the nematic phase stability, and in most cases the smectic C phase stability is actually higher than comparable analogues with conventional unbranched terminal chains. It is postulated that the surprisingly high smectic C phase stability results from a phase separation effect due to the incompatibility of the spherical bulky group and the conventional unbranched terminal chain, hence implying that the smectic 'layers' are well defined, and such definition of the layers bodes well for bookshelf geometry in ferroelectric mixtures.

1. Introduction

It was way back in 1975 that the chiral smectic C (SmC*) phase was shown to be ferroelectric when confined in a thin cell (*1*), and in 1980 that the concept of a surface-stabilised ferroelectric display was reported (*2*). Display devices based on ferroelectric technology offer huge advantages over the conventional nematic displays in terms of very fast (microsecond) switching times, bistability, high resolution and wide angles of view, and hence prompted intense research into the synthesis and properties of new materials and into device engineering (*3–8*). However, ferroelectric technology is not as straightforward as nematic technology, and problems in developing materials with the vast array of appropriate properties and in generating and maintaining the necessary molecular alignment have slowed progress significantly. Hence, nematic technology has developed much faster, and generated some excellent, high-quality displays, especially in terms of vertically-aligned and in-plane switching formats (*9*). Nevertheless, the advantages of ferroelectric technology still make it commercially attractive, not just for display devices, but also for spatial light modulators (SLMs) and telecommunications switches. Indeed, ferroelectric technology is commercially successful with the joint venture of Displaytech and Miyota producing four million displays per year of the liquid crystal on silicon (LCOS) microdisplay variety. At the recent International Liquid Crystal conference in Korea it was made clear that nematic technology is reaching limitations, and hence ferroelectric liquid crystals should be developed to provide for future fast-switching, high resolution displays (*10*).

One important issue is the control of alignment of ferroelectric liquid crystal materials. Usually, the material possesses a cooling phase sequence of nematic, smectic A, smectic C, with the theory that the fluid nematic phase aligns molecules homogeneously, the molecules then order in the usual smectic layers of the smectic A phase, and on further cooling the molecules tilt within the layers to generate the necessary smectic C phase (*3, 4, 6, 8, 11, 12*). Unfortunately, the process of tilting causes a layer shrinkage, which tends to cause the layers to buckle in order to fill free space created; such a buckling causes chevrons (*3, 8, 13–16*) rather than a perfect bookshelf geometry. Such chevrons are detrimental to the appearance of the display by introducing a visible defect (zigzag defect) at the point of layer kinking, which reduces contrast. The generation of suitable chiral smectic C mixtures which do not give a layer shrinkage on cooling would eliminate the chevron formation and generate the desired bookshelf geometry, thus enhancing the scope and value of ferroelectric liquid crystals technology in commercial device applications, particularly for microdisplays for projection displays where defects in alignment are more detrimental.

It is now well established that the only viable way of generating appropriate ferroelectric liquid crystal mixtures is to use achiral host materials to fine tune

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the essential properties such as mesomorphism, birefringence, and viscosity. An optimised achiral host mixture is then doped with a suitable chiral material to introduce the essential reduced symmetry properties to the mixture (*3, 4, 8, 11, 17*). The *ortho*-difluoroterphenyl materials are well established as excellent host materials for ferroelectric mixtures. Both dialkyl and alkyl-alkoxy analogues tend to give low melting points, generate the SmC phase over a wide temperature range, confer a low viscosity (particularly the dialkyl analogues), show an optical anisotropy appropriate for small cell spacings, and they are of high resistivity (*6, 11, 17*). This research is aimed at maintaining the desirable properties of the difluoroterphenyl compounds, and hence the core unit has been retained, but one of the terminal chains has been replaced with a short, bulky unit.

Two bulky units were chosen, a tertiary butyl group and the slightly larger trimethylsilyl group, which are located very close to the core in order to affect the maximum influence on the molecular properties. It is expected that the bulky terminal chain will be incompatible with the conventional unbranched terminal chain, causing phase separation, thus making the smectic layers more distinct, less inter-dependent and be conducive towards a bookshelf phase structure. As shown in Figure 1, all three possible *ortho*-difluoroterphenyl cores (**1**, **2** and **3**) have been investigated, in combination with the two conventional terminal chains, octyloxy (**a**) and heptyl (**b**), and the two bulky terminal units of tertiarybutyl (**C**) and trimethylsilyl (**Si**). Such systematic combinations provide for a total of 12 novel liquid crystals, and enable a comprehensive investigation of initial melting point, mesophase morphology and transition temperatures in comparison with the known analogues with conventional terminal chains. On-going work involves the formulation of achiral host mixtures and ferroelectric mixtures, and the evaluation of their physical properties, and these extensive results will be published later.

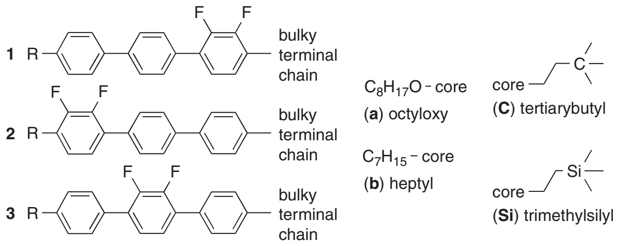
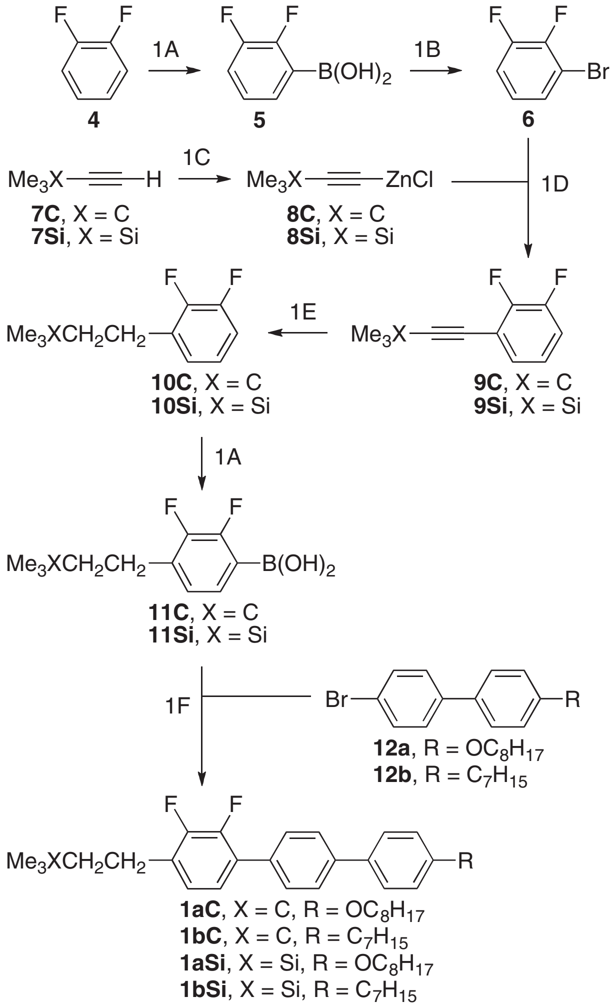


Figure 1. The general molecular architectures of the targeted novel materials.

2. Discussion of synthesis

The introduction of the desired bulky terminal units was facilitated by the commercial availability of both the tertiarybutylethyne (**7C**) and the trimethylsilylethyne (**7Si**). In all cases these alkynes were converted into their zinc chloride derivatives (**8C** and **8Si**, respectively), and coupled to an aryl unit in the presence of a palladium-catalyst through the method of Negishi (*18*).

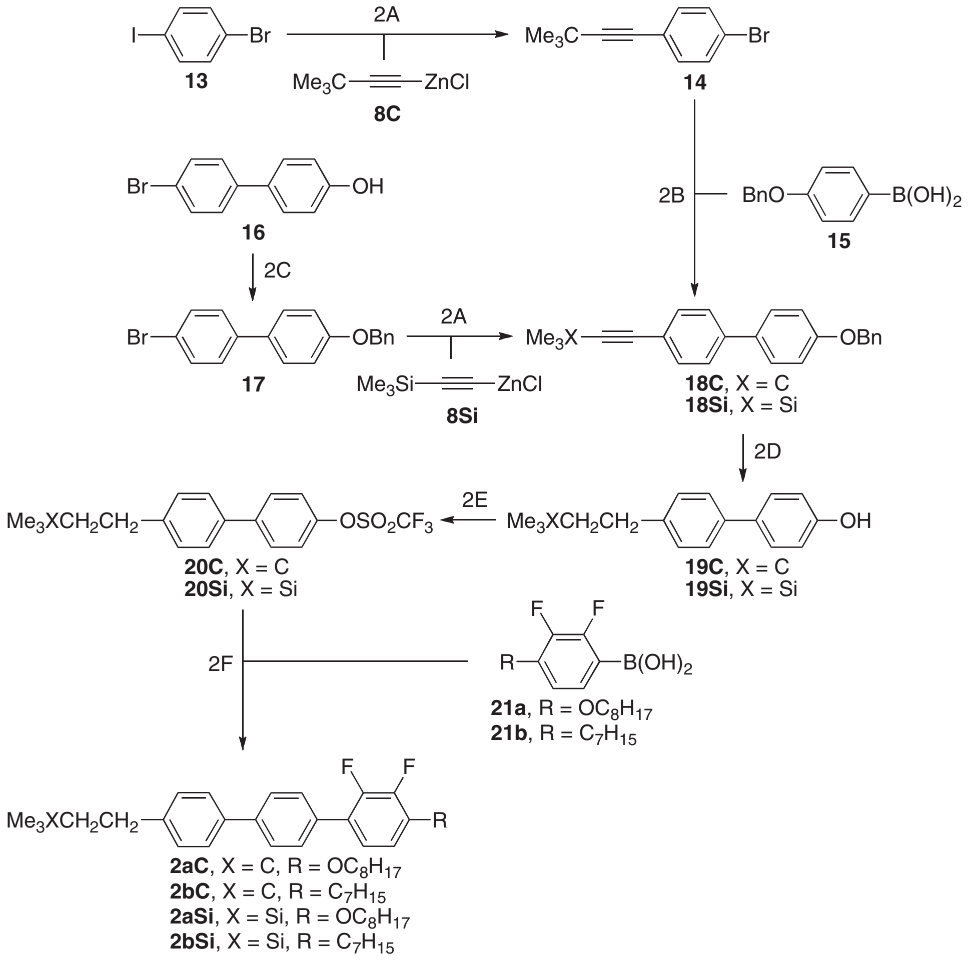
Scheme 1 outlines the synthesis of materials with the two fluoro substituents in the same end ring as the bulky terminal unit. Both the bulky terminal units (tertiarybutyl and trimethylsilyl) were introduced into the difluorinated benzene ring in the same manner. The direct electrophilic bromination of 1,2-difluorobenzene (**4**) would place the bromine in the 4-position. Accordingly, the acidic proton of



Scheme 1. 1A: (i) *n*-BuLi, THF; (ii) $(MeO)_3B$; (iii) 10% HCl; 1B: NBS, CH_3CN; 1C: (i) *n*-BuLi, THF; (ii) $ZnCl_2$; 1D: $Pd(PPh_3)_4$, THF; 1E: H_2, 10% Pd/C, EtOH; 1F: $Pd(PPh_3)_4$, DME, Na_2CO_3, H_2O.

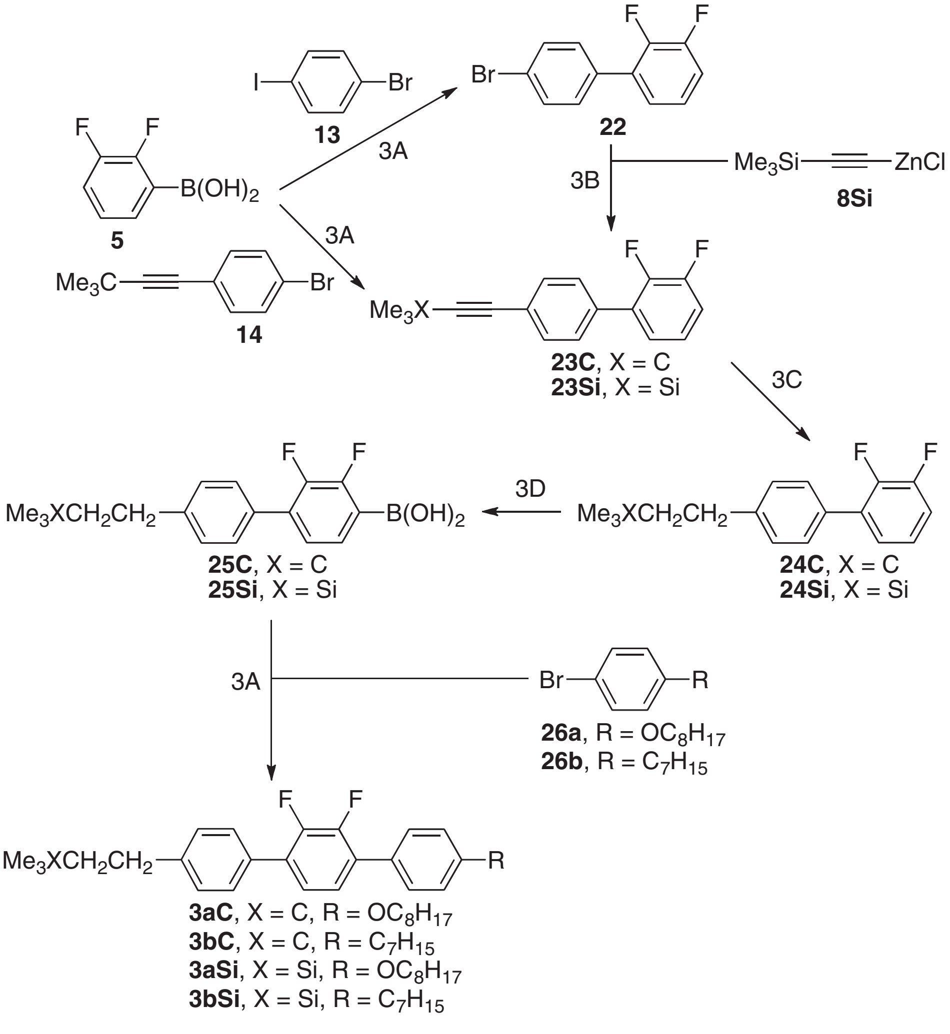
1,2-difluorobenzene (**4**) was exploited with butyllithium; a subsequent quenching with trimethyl borate followed by acidification gave the desired arylboronic acid (**5**) (*17*). The boronic acid moiety of compound **5** was replaced with bromide using NBS in acetonitrile (*19*) to generate the desired bromo-difluorobenzene unit (**6**), which was then coupled to the bulky alkynylzinc chlorides (**8C** and **8Si**) to give difluorophenylalkynes **9C** and **9Si**. Subsequent hydrogenation generated the desired difluorophenyl unit with the bulky terminal units linked by a dimethylene chain (**10C** and **10Si**). Exploitation of the acidic proton in compounds **10C** and **10Si** with butyllithium at low temperature furnished boronic acids **11C** and **11Si**, which were then coupled to the appropriate bromobiphenyls (**12a** and **12b**) using Suzuki methodology (*17, 20*) to generate the four final products (**1aC**, **1bC**, **1aSi** and **1bSi**).

Scheme 2 shows the synthesis of the isomeric materials to those shown in Scheme 1, with the two fluoro substituents in the same end ring as the conventional linear terminal chain. Here the tertiarybutyl unit was introduced through a selective coupling to generate compound **14**, which was then coupled to the benzyl-protected arylboronic acid **15** to provide the required biphenyl unit **18C**. A different strategy was followed for the trimethylsilyl moiety, which was introduced directly into a benzyl-protected biphenyl unit (compound **17**) through a zinc chloride coupling to generate the required acetylenic biphenyl unit (**18Si**). Both strategies have their merits of flexibility, but here the latter strategy is the more efficient. Treatment of both **18C** and **18Si** with hydrogen in the presence of a palladium catalyst served to hydrogenate the triple bond and hydrogenolyse the protecting group in the one efficient step. The resulting phenols (**19C** and **19Si**) were then converted into the respective triflates (**20C** and **20Si**), which make excellent leaving groups in Suzuki coupling reactions (*21–23*) and allowed the generation of the four final products (**2aC**, **2bC**, **2aSi** and **2bSi**).



Scheme 2. 2A: $Pd(PPh_3)_4$, THF; 2B: $Pd(PPh_3)_4$, DME, Na_2CO_3; H_2O; 2C: BnCl, K_2CO_3, MEK; 2D: H_2, 10% Pd/C, EtOH; 2E: $(CF_3SO_2)_2O$, pyridine; 2F: $Pd(PPh_3)_4$, DME, Na_2CO_3, LiCl, H_2O.

Scheme 3 concerns the synthesis of further isomeric materials to those shown in Schemes 1 and 2, with two the fluoro substituents in the centre ring. Here a selective coupling was employed to generate the required biphenyl unit possessing the bulky terminal chain (compounds **23C** and **23Si**). However, a slightly different strategy was employed for each bulky terminal unit, which illustrates the versatility of the coupling reaction methodology. The tertiarybutyl unit was introduced through a selective Negishi alkynylzinc chloride coupling (*18, 23–25*) at the initial one ring stage (compound **14**), and a subsequent Suzuki coupling (*17, 20*) with the difluorophenylboronic acid **5** generated the desired difluorobiphenyl unit (**23C**). The analogous trimethylsilyl-containing difluorobiphenyl unit (**23Si**) was generated through an alkynylzinc chloride coupling reaction with bromobiphenyl **22** (generated through a selective Suzuki coupling (*17, 20*) between boronic acid **5** and bromoiodobenzene **13**). Both strategies are equally viable, with the former being the more general and the latter being slightly more efficient. Hydrogenation of the two acetylenic biphenyls (**23C** and **23Si**) furnished the dimethylene-linked bulky units in the biphenyls (**24C** and **24Si**), which were converted into the boronic acid derivatives (**25C** and **25Si**) through the exploitation of the acid proton in the manner discussed earlier for Scheme 1. These boronic acids were then coupled sequentially, through the usual Suzuki methodology (*17, 20*), with the appropriate aryl bromides (**26a** and **26b**) containing the conventional unbranched terminal chains, to generate the four final products (**3aC**, **3bC**, **3aSi** and **3bSi**).



Scheme 3. 3A: $Pd(PPh_3)_4$, DME, Na_2CO_3, H_2O; 3B: $Pd(PPh_3)_4$, THF; 3C: H_2, 10% Pd/C, EtOH; 3D: (i) *n*-BuLi, THF; (ii) $(MeO)_3B$; (iii) 10% HCl.

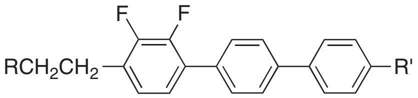
3. Discussion of mesomorphic properties

The melting points, transition temperatures and mesophase morphologies of the novel compounds are presented systematically in Tables 1, 2 and 3. Discussion will involve comparison of the different classes of novel compounds, and also some comparisons will be drawn with known materials of identical core structure (series **K**) (*17*).

All of the novel compounds exhibit the smectic C phase, but the smectic A phase, and particularly the nematic phase, so prominent in the parent difluoroterphenyls (**K**) (*17*), do not generally feature; nevertheless, these mesophase headings have been included in all of the tables for this very emphasis. The dominance of the smectic C phase results from the molecular phase separation due to the bulky end-groups, as mentioned in the aims, and the strong tendency to molecular tilting because of the strong lateral dipole of the *ortho*-difluorophenyl moiety, particularly when an alkoxy terminal chain is also present (**a**). Since carbon (**C**) is a smaller atom than silicon (**Si**), less disruption of the intermolecular forces of attraction confers higher melting points and higher transition temperatures on the '**C**' series of compounds (tertiarybutyl terminal chain) when compared with the '**Si**' series of compounds (trimethylsilyl terminal chain). Also, as is usual with liquid crystals, those compounds with a terminal alkoxy chain (**a**) have higher transition temperatures, and usually higher melting points, than analogous compounds with a terminal alkyl chain (**b**).

Compound **1aC** (Table 1) has the highest mesophase stability of the novel compounds, which is in

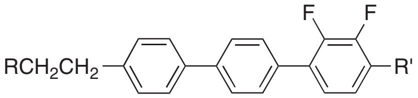
Table 1. The mesomorphism of those compounds with the fluoro substituents in the end ring containing the bulky terminal unit, and known compounds for comparison.



Compound			Transition temperatures (°C)								
No.	R	R′	Cryst		SmC		SmA		N		Iso
1aC	Me_3C	**a**	•	95.0	•	156.0	—	—	—	—	•
1bC	Me_3C	**b**	•	86.0	•	125.0	•	129.6	—	—	•
1aSi	Me_3Si	**a**	•	81.0	•	141.5	—	—	—	—	•
1bSi	Me_3Si	**b**	•	57.5	•	106.1	•	119.5	—	—	•
1aK	C_3H_7	**a**	•	89.0	•	155.5	•	165.0	•	166.0	•
1bK	C_3H_7	**b**	•	65.5	•	118.5	•	135.0	•	137.0	•

a = $C_8H_{17}O$, **b** = C_7H_{15}.
Except where indicated, all alkyl chains are unbranched.

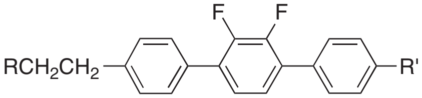
Table 2. The mesomorphism of those compounds with the fluoro substituents in the end ring containing the linear terminal unit, and known compounds for comparison.



Compound			Transition temperatures (°C)								
No.	R	R′	Cryst		SmC		SmA		N		Iso
2aC	Me_3C	**a**	•	81.3	•	131.0	—	—	—	—	•
2bC	Me_3C	**b**	•	71.0	•	101.0	—	—	—	—	•
2aSi	Me_3Si	**a**	•	78.8	•	118.6	—	—	—	—	•
2bSi	Me_3Si	**b**	•	66.7	•	78.9	—	—	—	—	•
2aK	C_3H_7	**a**	•	93.5	•	144.0	•	148.0	•	159.0	•
2bK	C_3H_7	**b**	•	56.0	•	105.5	•	131.0	•	136.0	•

a = $C_8H_{17}O$, **b** = C_7H_{15}.
Except where indicated, all alkyl chains are unbranched.

Table 3. The mesomorphism of those compounds with the fluoro substituents in the centre ring, and known compounds for comparison.



Compound			Transition temperatures (°C)								
No.	R	R′	Cryst		SmC		SmA		N		Iso
3aC	Me_3C	**a**	•	89.0	•	106.9	—	—	•	114.4	•
3bC	Me_3C	**b**	•	60.0	•	76.0	—	—	•	77.7	•
3aSi	Me_3Si	**a**	•	56.1	•	101.9	—	—	—	—	•
3bSi	Me_3Si	**b**	•	58.9	•	61.7	—	—	—	—	•
3aK	C_3H_7	**a**	•	48.5	•	95.0	—	—	•	141.5	•
3bK	C_3H_7	**b**	•	36.5	•	24.0	—	—	•	111.5	•

a = $C_8H_{17}O$, **b** = C_7H_{15}.
Except where indicated, all alkyl chains are unbranched.

keeping with the parent system (compound **1aK**) (*17*), and is due to the outer-ring location of the lateral fluoro substituents and the alkoxy chain being part of the untwisted biphenyl section of the terphenyl core. Unfortunately, the same attributes confer a high melting point (95°C), particularly high no doubt because of the conformationally, stiff short bulky terminal chain. The bulky tertiarybutyl group as part of the terminal chain in compound **1aC** has depressed the overall liquid crystallinity when compared with the parent system (compound **1aK**) (*17*), which is to be expected considering the steric bulk. However, the nematic and smectic A phase stabilities have been reduced to the point of elimination, and the smectic C phase stability (156.0°C) is virtually identical to that of the parent system (155.5°C), hence indicating that the bulky tertiarybutyl group can be better accommodated with the molecules being tilted than when they are orthogonal within the smectic phase. The alkyl analogue (**1bC**) has similar attributes, but the lower polarisability confers reduced mesophase stability and a slightly lower melting point. The lack of an ether oxygen means a lower tendency towards molecular tilting, and the smectic C phase stability is lower (by 31°C) than for compound **1aC**, which allows a smectic A phase to be exhibited. Despite this lower smectic C phase stability compared with compound **1aC**, the smectic C phase stability of compound **1bC** is actually 7.5°C higher than that of the comparable parent system (compound **1bK**) (*17*), which emphasises the remarkable ability of the short bulky terminal chain to maximise the tendency towards molecular tilting. A similar pattern is seen for the trimethylsilyl compounds (**1aSi** and **1bSi**), except of course the larger silicon atom confers lower temperatures throughout. In the alkoxy compounds **1a**, the larger silicon atom reduces the smectic C phase stability by 14°C, yet in the alkyl compounds **1b** it is reduced by 19°C; however, for the latter compounds (**1b**) the smectic A phase stability is reduced by just 10°C. These lower temperatures caused by the larger silicon atom are also translated to the melting points, and the lack of an ether oxygen in compound **1bSi** ensures a significantly lower melting point, yet the smectic C phase stability is still usefully high to make this compound a particularly promising candidate for ferroelectric mixtures.

Table 2 shows materials isomeric to those of Table 1 with the two fluoro substituents in the end ring with the conventional unbranched chain. Compound **2aC** has the same mesophase morphology as the isomeric compound (**1aC**), but the smectic C phase stability is 25°C lower. This lower clearing point is caused by an alkyl chain, rather than an alkoxy chain, now being part of the untwisted biphenyl section of the terphenyl core. For the same reason, the melting point of compound **2aC** (81.3°C) is significantly lower than that of compound **1aC** (95°C). In the dialkyl compound (**2bC**) the smectic A phase stability has been reduced by more than the smectic C phase stability, causing it to be eliminated, which again emphasises the strong tendency of the short bulky terminal group to support the smectic C phase. However, unlike the isomeric compounds (**1ac** and **1bC**) shown in Table 1 where the bulky tertiarybutyl group conferred a higher smectic C phase stability in comparison with the parent systems (**1aK** and **1bK**) (*17*), in compounds **2aC** and **2bC**, it is slightly lower than that seen in the parent systems (**2aK** and **2bK**) (*17*), which is due to the more disadvantageous structural feature of an alkyl chain as part of the untwisted biphenyl section of the terphenyl core. As seen for the isomeric compounds in Table 1, the trimethylsilyl compounds (**2aSi** and **2bSi**) have lower transition temperatures than the tertiarybutyl analogues because of the larger size of silicon in comparison with carbon.

Table 3 shows materials isomeric to those shown in Tables 1 and 2, here with the two fluoro substituents in the centre ring. Lateral fluoro substituents in the centre ring cause two interannular twistings, which reduces polarisability, and hence liquid crystal phase stability is reduced. Additionally, the increase in breadth being in the centre of the molecule tends to disrupt smectic phase stability by significantly more than nematic phase stability. The same reasoning also tends to confer low melting points for compounds with this location of lateral fluoro substituents. Compare the parent compounds **3aK** and **3bK** (Table 3) with their isomeric analogues (**1aK**, **1bK**, **2aK** and **2bK**) with fluoro substituents in an outer ring (Tables 1 and 2) for clarification of this general tendency (*17*). Hence, it is somewhat amazing to see the melting points, mesophase morphology and transition temperature of the novel compounds (**3aC**, **3bC**, **3aSi**, **3bSi**) shown in Table 3, particularly the latter two compounds, which contain the more bulky trimethylsilyl group at the terminus. Compound **3aC** has a melting point comparable to those compounds where the lateral fluoro substituents occupy outer-ring positions (compounds **1aC** and **2aC**), and 40°C higher than the comparable parent system (compound **3aK**) (*17*), which is rather unfortunate. However, the smectic C phase stability is remarkably high, 12°C higher than that of the parent system with the unbranched terminal chains (compound **3aK**) (*17*), but the nematic phase stability is 27°C lower. This class of compound with a core that is least supportive towards liquid crystal phase stability, and particularly unsupportive towards the smectic C phase, actually gains most from a bulky terminal chain. For the dialkyl analogue (compound **3bC**), the disruption to the nematic phase stability is 34°C, yet the smectic C phase stability has increased by a massive 52°C in comparison with the parent system with the unbranched chains (compound **3bK**) (*17*). Indeed, the larger trimethylsilyl unit, whist not enhancing the smectic C phase stability, certainly does not cause much of a further reduction as was seen for the other two classes of compound shown in Tables 1 and 2. However, the nematic phase is eliminated, showing a much greater support for the smectic C phase stability in comparison with the nematic phase stability, a completely anomalous situation to that seen for the parent systems (compounds **2aK** and **3bK**) (*17*).

4. Summary

The introduction of short, bulky terminal groups into difluoroterphenyl core structures has caused a significant change to mesomorphic properties when compared with the parent compounds possessing conventional unbranched terminal chains. In general the smectic C phase stability has been maintained, and in some cases actually enhanced, by the use of bulky groups, at the expense of the smectic A and nematic phases, which in most cases have been eliminated to leave the smectic C phase as the sole liquid crystal phase.

The results for those materials where the two lateral fluoro substituents are in the centre ring (Table 3) are particularly significant because the parent systems, especially the dialkyl variants, show relatively low smectic C tendency. However, the inclusion of the short, bulky terminal units has markedly enhanced the stability of the smectic C phase, and since it is this class of compound which shows by far the lowest viscosity then this class of novel materials are excellent candidates for ferroelectric mixtures.

5. Experimental

Structural information of materials was obtained by ^{1}H and ^{13}C NMR spectroscopy (JEOL Eclipse 400 spectrometer), by mass spectrometry (Finnigan-MAT 1020 spectrometer), and by elemental analysis (Fisons EA1108 CHN). The purity of all final compounds (series **1** to **3**) was checked by HPLC analysis (Gilson 233XL autosampler, 321 binary solvent pump, a Hewlett Packard 1100 series diode array detector and a Luna C18(2) column) and found to be >99.9% pure in each case. The progress of some reactions and the purity of some intermediates were analysed by Gas Liquid Chromatography (GLC) using a Varian CP3380 gas chromatograph with a 10 m, 0.25 mm internal diameter, 0.12 mm fused silica capillary column. All melting points, transition temperatures and mesophase morphologies were determined using an Olympus BH-2 polarising microscope in conjunction with a Mettler FP52 heating stage and FP5 temperature controller, and these values were confirmed using differential scanning calorimetry (Mettler-Toledo DSC822e).

Compounds **4**, **7C**, **7Si**, **13**, **15** and **16**, and other simple starting materials and solvents are commercially available. Compounds **12a**, **12b**, **21a**, **21b**, **26a** and **26b** were all prepared as described previously (*17*).

5.1 2,3-Difluorophenylboronic acid (5)

A solution of *n*-butyllithium (176 ml, 2.5M in hexanes, 0.44 mol) was added dropwise to a stirred, cooled (–78°C) solution of compound **4** (50.00 g, 0.439 mol) in anhydrous THF (400 ml) under dry nitrogen. The reaction mixture was stirred at –78°C for 1 h and trimethyl borate (91.00 g, 0.875 mol) was added dropwise, and the reaction mixture was allowed to warm to room temperature overnight. 10% Hydrochloric acid (400 ml) was added and the mixture was stirred at room temperature for 1 h. The product was extracted into ether (×2), and the combined ethereal extracts were washed with brine and dried ($MgSO_4$). The solvent was removed *in vacuo* and the solid residue was stirred in hexane, filtered, and air dried under suction to yield a colourless powder.

Yield 28.0 g (40%). ^{1}H NMR (400 MHz, D6-DMSO), δ 7.13(1H, dddd), 7.29(1H, dddd), 7.38(1H, dddd), 8.38(2H, s). MS *m*/*z* 158(M^+).

5.2 1-Bromo-2,3-difluorobenzene (6)

N-bromosuccinimide (78.30 g, 0.440 mol) was added to a stirred suspension of compound **5** (35.00 g, 0.222 mol) in acetonitrile (300 ml) under dry nitrogen. The stirred mixture was heated under reflux for 16 h (GLC and TLC analysis revealed a complete reaction) and poured into water. The product was extracted into hexane (×2), and the combined organic extracts were washed successively with sodium bisulphite and sodium bicarbonate and dried ($MgSO_4$). The solvent was distilled off at atmosphere pressure (68°C) and the product was distilled at atmospheric pressure.

Yield 30.0 g (70%). bp 158°C. ^{1}H NMR (400 MHz, $CDCl_3$), δ 6.98(1H, dddd), 7.11(1H, dddd), 7.29(1H, dddd). MS *m*/*z* 194(M^+), 192(M^+).

5.3 1,2-Difluoro-3-(3,3-dimethylbut-1-ynyl) benzene (9C)

A solution of *n*-butyllithium (78 ml, 2.5M in hexanes, 0.195 mol) was added dropwise to a stirred, cooled (–5°C) solution of compound **7C** (19.20 g, 0.234 mol) in anhydrous THF (150 ml) under dry nitrogen. The mixture was stirred at –5°C for 10 min and zinc chloride (31.80 g, 0.234 mol) was added, and the mixture was stirred at room temperature for 15 min. A solution of compound **6** (30.00 g, 0.155 mol) in anhydrous THF (80 ml) was added followed by tetrakis(triphenylphosphine)palladium(0) (8.00 g, 0.0069 mol), and the stirred mixture was heated under reflux overnight (GLC analysis revealed a complete reaction). The cooled mixture was poured into 10% hydrochloric acid and the product was extracted into ether (×2). The combined ethereal extracts were washed successively with water and sodium bicarbonate and dried ($MgSO_4$). The solvent was removed *in vacuo* and the crude product was purified by column chromatography to yield a colourless oil.

Yield 28.0 g (93%). ^{1}H NMR (400 MHz, $CDCl_3$), δ 1.33(9H, s), 6.96(1H, dddd), 7.05(1H, dddd), 7.12(1H, dddd). MS *m*/*z* 194(M^+).

5.4 1,2-Difluoro-3-(trimethylsilylethynyl)benzene (9Si)

Quantities: compound **7Si** (22.90 g, 0.234 mol), *n*-butyllithium (78 ml, 2.5M in hexanes, 0.195 mol), zinc chloride (31.80 g, 0.234 mol), compound **6** (30.00 g, 0.155 mol). The experimental procedure was as described for the preparation of compound **9C** to yield a colourless oil.

Yield 30.0 g (92%). ^{1}H NMR (400 MHz, $CDCl_3$), δ 0.26(9H, s), 6.98(1H, dddd), 7.10(1H, dddd), 7.18(1H, dddd). MS *m*/*z* 210(M^+).

5.6 1,2-Difluoro-3-(3,3-dimethylbutyl)benzene (10C)

A mixture of compound **9C** (27.00 g, 0.139 mol) and 10% palladium-on-carbon (5 g) in ethanol (500 ml) was hydrogenated at 30 psi overnight (GLC analysis revealed a complete reaction). The catalyst was filtered off and the solvent was removed *in vacuo* to yield a colourless oil.

Yield 21.0 g (76%). ^{1}H NMR (400 MHz, $CDCl_3$), δ 0.96(9H, s), 1.48(2H, m), 2.62(2H, m), 6.89–6.97(3H, m). MS *m*/*z* 198(M^+).

5.7 1,2-Difluoro-3-(trimethylsilylethyl)benzene (10Si)

Quantities: compound **9Si** (29.00 g, 0.138 mol), 10% palladium-on-carbon (5 g). The experimental procedure was as described for the preparation of compound **10C** to yield a colourless oil.

Yield 21.2 g (71%). ^{1}H NMR (400 MHz, $CDCl_3$), δ 0.07(9H, s), 0.87(2H, m), 2.71(2H, m), 6.98–7.10(3H, m). MS *m*/*z* 218(M^+).

5.8 2,3-Difluoro-4-(3,3-dimethylbutyl) phenylboronic acid (11C)

Quantities: compound **10C** (20.00 g, 0.101 mol), *n*-butyllithium (40 ml, 2.5M in hexanes, 0.100 mol), trimethyl borate (20.78 g, 0.200 mol). The experimental procedure was as described for the preparation of compound **5** to yield a colourless powder.

Yield 15.0 g (62%). ^{1}H NMR (400 MHz, D6-DMSO), δ 0.81(9H, s), 1.32(2H, m), 2.41(2H, m), 6.95(1H, ddd), 7.16(1H, ddd), 8.38(2H, s). MS *m*/*z* 242(M^+).

5.9 2,3-Difluoro-4-(trimethylsilylethyl)phenylboronic acid (11Si)

Quantities: compound **10Si** (20.00 g, 0.093 mol), *n*-butyllithium (38 ml, 2.5M in hexanes, 0.095 mol), trimethyl borate (19.50 g, 0.188 mol). The experimental procedure was as described for the preparation of compound **5** to yield a colourless powder.

Yield 18.0 g (75%). ^{1}H NMR (400 MHz, D6-DMSO), δ 0.15(9H, s), 0.99(2H, m), 2.78(2H, m), 7.21(1H, ddd), 7.39(1H, ddd), 8.38(2H, s). MS *m*/*z* 258(M$^+$).

5.10 2,3-Difluoro-4-(3,3-diemthylbutyl)-4″-octyloxy-[4,4′:1′,4″]-terphenyl (1aC)

Compound **11C** (1.82 g, 7.53 mmol) was added to a stirred mixture of compound **12a** (2.27 g, 6.28 mmol), sodium carbonate (7.42 g, 0.070 mol) and tetrakis(triphenylphosphine)palladium(0) (0.15 g, 0.13 mmol) in water (35 ml) and 1,2-dimethoxyethane (35 ml) under nitrogen. The stirred mixture was heated under reflux overnight (GLC and TLC revealed a complete reaction) and poured into water. 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 crude product was purified by column chromatography (silica gel/hexane) to yield a colourless solid which was recrystallised from ethanol to yield colourless crystals.

Yield 2.10 g (58%). Transitions (°C) Cryst 95.0 SmC 156.0 Iso. ^{1}H NMR (400 MHz, CDCl$_3$), δ 0.91(3H, t), 1.00(9H, s), 1.28–1.40(8H, m), 1.45–1.56(4H, m). 1.82(2H, quint), 2.67(2H, m), 4.01(2H, t), 6.99(2H, d, J = 8.72 Hz), 7.02(1H, ddd, J = 7.36 Hz, J = 7.36 Hz, J = 1.84 Hz), 7.15(1H, ddd, J = 7.36 Hz, J = 7.36 Hz, J = 1.84 Hz), 7.75(2H, d, J = 8.72 Hz), 7.59(2H, dd, J = 8.72 Hz, J = 1.20 Hz), 7.64(2H, d, J = 8.72 Hz). ^{13}C NMR (100 MHz, CDCl$_3$), δ 14.10, 22.66, 24.26, 26.07, 29.17, 29.26, 29.30, 29.38, 30.61, 31.82, 44.56, 68.07 (alkyl chains, 12 required, 12 found), 114.82, 124.18(dd, J = 3.07 Hz, J = 3.07 Hz), 124.54(dd, J = 3.84 Hz, J = 3.84 Hz), 126.70, 127.90(dd, J = 8.10, J = 1.90), 128.02, 129.14(d, J = 1.53 Hz), 131.50(dd, J = 8.03 Hz, J = 5.35 Hz), 132.76, 133.20, 140.33, 148.12(dd, J = 251.37 Hz, J = 16.14 Hz), 149.50(dd, J = 247.52 Hz, J = 15.37 Hz), 158.92 (aromatic carbons, 14 required, 14 found). MS *m*/*z* 478(M$^+$). Elemental analysis: $C_{32}H_{40}F_2O$ requires C 80.30%, H 8.42%; found C 80.36%, H 8.41%.

5.11 2,3-Difluoro-4″-heptyl-4-(3,3-dimethylbutyl)-[4,4′:1′,4″]-terphenyl (1bC)

Quantities: compound **12b** (2.28 g, 6.60 mmol), compound **11C** (1.90 g, 8.03 mmol). The experimental procedure was as described for the preparation of compound **1aC** to yield colourless crystals.

Yield 2.30 g (63%). Transitions (°C) Cryst 86.0 SmC 125.0 SmA 129.0 Iso. ^{1}H NMR (400 MHz, CDCl$_3$), δ 0.91(3H, t), 0.98(9H, s), 1.34(8H, m), 1.56(2H, m), 1.70(2H, quint), 2.67(2H, t), 2.69(2H, m), 7.03(1H, ddd, J = 7.36 Hz, J = 7.36 Hz, J = 1.84 Hz), 7.17(1H, ddd, J = 7.36 Hz, J = 7.36 Hz, J = 1.84 Hz), 7.29(2H, d, J = 8.72 Hz), 7.57(2H, d, J = 8.72 Hz), 7.62(2H, dd, J = 8.72, J = 1.20), 7.61(2H, d, J = 8.72 Hz). ^{13}C NMR (100 MHz, CDCl$_3$), δ 14.11, 22.69, 24.28, 29.16, 29.22, 29.37, 30.59, 31.49, 31.85, 35.64, 44.55 (alkyl chains, 11 required, 11 found), 124.21(dd, J = 3.07 Hz, J = 3.07 Hz), 124.55(dd, J = 3.84 Hz, J = 3.84 Hz), 126.87, 127.00, 127.92(dd, J = 6.92 Hz, J = 3.07 Hz), 128.86, 129.12, 131.51(dd, J = 8.46 Hz, J = 5.38 Hz), 133.57, 137.80, 140.62, 142.34, 148.13(dd, J = 250.61 Hz, J = 115.37 Hz), 149.51(dd, J = 246.75 Hz, J = 14.61 Hz) (aromatic carbons, 14 required, 14 found). MS *m*/*z* 448(M$^+$). Elemental analysis: $C_{31}H_{38}F_2$ requires C 82.99%, H 8.54%; found C 82.87%, H 8.50%.

5.12 2,3-Difluoro-4-(trimethylsilylethyl)-4″-oxtyloxy-[4,4′:1′,4″]-terphenyl (1aSi)

Quantities: compound **12a** (1.43 g, 3.96 mmol), compound **11Si** (1.23 g, 4.75 mmol). The experimental procedure was as described for the preparation of compound **1aC** to yield colourless crystals.

Yield 0.85 g (44%). Transitions (°C) Cryst 81.0 SmC 141.5 Iso. ^{1}H NMR (400 MHz, CDCl$_3$), δ 0.09(9H, s), 0.92(5H, m), 1.28–1.43(8H, m), 1.52(2H, quint), 1.84(2H, quintet), 2.78(2H, m), 4.02(2H, t), 7.00(2H, d, J = 8.72 Hz), 7.05(1H, ddd, J = 7.36 Hz, J = 7.36, J = 1.84 Hz), 7.17(1H, ddd, J = 7.36 Hz, J = 7.36 Hz, J = 1.84 Hz), 7.58(2H, d, J = 8.72 Hz), 7.61(2H, dd, J = 8.72 Hz, J = 1.20 Hz), 7.63(2H, d, J = 8.72 Hz). ^{13}C NMR (100 MHz, CDCl$_3$), δ –1.84, 14.10, 17.35, 22.66, 23.08, 26.07, 29.28(x2), 29.38, 31.83, 68.07 (alkyl chains, 11 required, 11 found); 114.82, 123.94(dd, J = 4.61, J = 4.61), 124.16(dd, J = 3.07 Hz, J = 3.07 Hz), 126.71, 127.83 (dd, J = 12.34 Hz, J = 1.56 Hz), 128.03, 129.14(d, J = 2.29 Hz), 132.78, 133.24, 133.29(dd, J = 12.30 Hz, J = 2.31 Hz), 140.33, 147.91(dd, J = 251.37 Hz, J = 16.14 Hz), 149.32(dd, J = 247.52 Hz, J = 15.37 Hz), 158.92 (aromatic carbons, 14 required, 14 found). MS *m*/*z* 494(M$^+$). Elemental analysis: $C_{31}H_{40}F_2OSi$ requires C 75.26%, H 8.15%; found C 75.36%, H 8.21%.

5.13 2,3-Difluoro-4″-heptyl-4-(trimethylsilylethyl)-[4,4′:1′,4″]-terphenyl (1bSi)

Quantities: compound **12b** (1.43 g, 4.32 mmol), compound **11Si** (1.23 g, 4.75 mmol). The experimental procedure was as described for the preparation of compound **1aC** to yield colourless crystals.

Yield 0.77 g (39%). Transitions (°C) Cryst 57.5 SmC 106.1 SmA 119.5 Iso. ^{1}H NMR (400 MHz, $CDCl_3$), δ 0.09 (9H, s), 0.92(5H, m), 1.28–1.43(8H, m), 1.69(2H, quint), 2.68(2H, t), 2.74(2H, m), 7.05(1H, ddd, J = 7.36 Hz, J = 7.36 Hz, J = 1.84 Hz), 7.17 (1H, ddd, J = 7.36 Hz, J = 7.36 Hz, J = 1.84 Hz), 7.30 (2H, d, J = 8.72 Hz), 7.58(2H, d, J = 8.72 Hz), 7.62(2H, dd, J = 8.72 Hz, J = 1.20 Hz), 7.69(2H, d, J = 8.72 Hz). ^{13}C NMR (100 MHz, $CDCl_3$), δ −1.84, 14.11, 17.35, 22.68, 23.08, 29.20, 29.35, 31.50, 31.83, 35.63 (alkyl chains, 10 required, 10 found); 123.93(dd, J = 4.61 Hz, J = 4.61 Hz), 124.17(dd, J = 3.07 Hz, J = 3.07 Hz), 126.89, 127.03, 127.82(dd, J = 9.18 Hz, J = 1.20 Hz), 128.88, 129.14(d, J = 2.31 Hz), 133.36(dd, J = 10.76 Hz, J = 2.31 Hz), 133.62, 137.83, 140.63, 142.37, 147.92(dd, J = 250.60 Hz, J = 15.37 Hz), 149.29(dd, J = 246.75 Hz, J = 14.61 Hz) (aromatic carbons, 14 required, 14 found). MS *m/z* 464(M^+). Elemental analysis: $C_{30}H_{38}F_2Si$ requires C 77.54%, H 8.24%; found C 77.51%, H 8.17%.

5.14 1-Bromo-4-(3,3-dimethylbut-1-ynyl)benzene (14)

Quantities: compound **7C** (12.30 g, 0.150 mol), *n*-butyllithium (60 ml, 2.5M in hexanes, 0.150 mol), zinc chloride (25.00 g, 0.184 mol), compound **13** (30.00 g, 0.106 mol). The experimental procedure was as described for the preparation of compound **9C**, except that the reaction mixture was stirred at room temperature overnight, rather than heated under reflux, to yield a colourless solid.

Yield 10.4 g (44%). mp 51.7°C. ^{1}H NMR (400 MHz, $CDCl_3$), δ 1.30(9H, s), 7.22(2H, d), 7.37(2H, d). MS *m/z* 238(M^+), 236(M^+).

5.15 4-Benzyloxy-4′-bromobiphenyl (17)

A stirred mixture of compound **16** (40.00 g, 0.161 mol), benzyl chloride (25.20 g, 0.199 mol) and potassium carbonate (48.00 g, 0.348 mol) in butanone (300 ml) was heated under reflux overnight (GLC analysis revealed a complete reaction). The potassium carbonate was filtered off and the solvent was removed *in vacuo*. The crude product was recrystallised from ethanol to yield colourless crystals.

Yield 25.0 g (44%). mp 152.0°C. ^{1}H NMR (400 MHz, $CDCl_3$), δ 5.10(2H, s), 7.03(2H, d), 7.35(1H, tt), 7.41(4H, m), 7.45(2H, dd), 7.48(2H, d), 7.53(2H, d). MS *m/z* 340(M^+), 338(M^+).

5.16 4-Benzyloxy-4′-(3,3-dimethylbut-1-ynyl)biphenyl (18C)

Quantities: compound **14** (5.00 g, 0.021 mol), compound **15** (7.18 g, 0.031 mol). The experimental procedure was as described for the preparation of compound **1aC** to yield colourless crystals.

Yield 6.83 g (95%). mp 211.0°C. ^{1}H NMR (400 MHz, $CDCl_3$), δ 1.32(9H, s), 5.11(2H, s), 7.04(2H, d), 7.34(1H, d), 7.35–7.48(8H, m), 7.52(2H, d). MS *m/z* 340(M^+).

5.17 4-Benzyloxy-4′-(trimethylsilylethynyl)biphenyl (18Si)

Quantities: compound **7Si** (8.67 g, 0.088 mol), *n*-butyllithium (35 ml, 2.5M in hexanes, 0.088 mol), zinc chloride (15.00 g, 0.110 mol), compound **17** (25.00 g, 0.074 mol). The experimental procedure was as described for the preparation of compound **9C** to yield a colourless solid.

Yield: 18.50 g (70%). mp 159.0°C. ^{1}H NMR (400 MHz, $CDCl_3$), δ 0.27(9H, s), 5.13(2H, s), 7.06(2H, d), 7.35–7.48(5H, m), 7.51(4H, 2×d), 7.53(2H, d). MS *m/z* 356(M^+).

5.18 4-Hydroxy-4′-(3,3-dimethylbutyl)biphenyl (19C)

Quantities: compound **18C** (6.80 g, 0.020 mol), 10% palladium-on-carbon (1.00 g). The experimental procedure was as described for the preparation of compound **10C** to yield a colourless solid.

Yield 5.00 g (98%). mp 144.5°C. ^{1}H NMR (400 MHz, $CDCl_3$), δ 0.97(9H, s), 1.53(2H, m), 2.59(2H, m), 6.88(2H, d), 7.23(2H, d), 7.43–7.48(4H, 2×d). MS *m/z* 254(M^+).

5.19 4-Hydroxy-4′-(trimethylsilylethyl)biphenyl (19Si)

Quantities: compound **18Si** (18.30 g, 0.051 mol), 10% palladium-on-carbon (3.00 g). The experimental procedure was as described for the preparation of compound **10C** to yield a colourless solid.

Yield 10.70 g (78%). mp 112.4°C. ^{1}H NMR (400 MHz, $CDCl_3$), δ 0.03(9H, s), 0.91(2H, m), 2.65(2H, m), 6.89(2H, d), 7.26(2H, d), 7.45(2H, d), 7.47(2H, d). MS *m/z* 270(M^+).

5.20 4′-(3,3-Dimethylbutyl)biphenyl-4-yl triflate (20C)

Triflic anhydride (5.31 g, 0.019 mol) was added dropwise to a stirred, cooled (0°C) solution of compound **19C** (4.00 g, 0.016 mol) in anhydrous pyridine (80 ml) under dry nitrogen. The mixture was stirred at room temperature overnight and poured into water. The product was extracted into ether (×2). The combined ethereal extracts were washed successively with water, 10% hydrochloric acid (×2) and water and dried ($MgSO_4$). The solvent was removed *in vacuo* and the crude product was purified by column chromatography (silica gel/hexane with the gradual introduction of dichloromethane) to yield a colourless solid.

Yield 5.40 g (89%). mp 48.4°C. ^{1}H NMR (400 MHz, $CDCl_3$), δ 0.97(9H, s), 1.53(2H, m), 2.59(2H, m), 7.20(2H, d), 7.24(2H, d), 7.38(2H, d), 7.54(2H, d). MS *m*/*z* 386(M^+).

5.21 4′-(Trimethylsilylethyl)biphenyl-4-yl triflate (20Si)

Quantities: compound **19Si** (5.00 g, 0.018 mol), triflic anhydride (6.26 g, 0.022 mol). The experimental procedure was as described for the preparation of compound **20C** to yield a colourless oil.

Yield 6.80 g (91%). ^{1}H NMR (400 MHz, $CDCl_3$), δ 0.04 (9H, s), 0.90 (2H, m), 2.67 (2H, m), 7.27 (2H, d), 7.29 (2H, d), 7.44 (2H, d), 7.59 (2H, d). MS *m*/*z* 402(M^+).

5.22 2,3-Difluoro-4″-(3,3-dimethylbutyl)-4-octyloxy-[4,4′:1′,4″]-terphenyl (2aC)

Quantities: compound **20C** (1.17 g, 3.04 mmol), compound **21a** (0.95 g, 3.64 mmol). The experimental procedure was as described for the preparation of compound **1aC**, except that lithium chloride (0.40 g, 9.10 mmol) was added, to yield colourless crystals.

Yield: 0.80 g (55%). Transitions (°C) Cryst 81.3 SmC 131.0 Iso. ^{1}H NMR (400 MHz, $CDCl_3$), δ 0.89(3H, t), 0.98(9H, s), 1.33–1.40(8H, m), 1.55(4H, m), 1.84(2H, quint), 2.62(2H, m), 4.08(2H, t), 6.81(1H, ddd, $J = 7.36$ Hz, $J = 7.36$ Hz, $J = 1.84$ Hz), 7.14(1H, ddd, $J = 7.36$ Hz, $J = 7.36$ Hz, $J = 1.84$ Hz), 7.27(2H, d, $J = 8.72$ Hz), 7.55(2H, d, $J = 8.72$ Hz), 7.57(2H, dd, $J = 8.72$ Hz, $J = 1.20$ Hz), 7.65(2H, d, $J = 8.72$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$), δ 14.09, 22.65, 25.88, 29.18(×2), 29.31(×2), 30.56, 30.90, 31.80, 46.38, 69.84 (alkyl chains, 12 required, 12 found), 109.52(d, $J = 2.31$ Hz), 122.53(dd, $J = 10.76$ Hz, $J = 0.77$ Hz), 123.43(dd, $J = 4.61$ Hz, $J = 4.61$ Hz), 126.93, 127.02, 128.74, 129.00(d, $J = 3.07$ Hz), 133.53, 137.79, 140.34, 141.88(dd, $J = 246.75$ Hz, $J = 16.14$ Hz), 142.95, 147.88(dd, $J = 8.46$ Hz, $J = 3.07$ Hz), 148.96(dd, $J = 249.06$ Hz, $J = 11.53$ Hz) (aromatic carbons, 14 required, 14 found). MS *m*/*z* 478(M^+). Elemental analysis: $C_{32}H_{40}F_2O$ requires C 80.30%, H 8.42%; found C 80.22%, H 8.37%.

5.23 2,3-Difluoro-4-heptyl-4″-(3,3-dimethylbutyl)-[4,4′:1′,4″]-terphenyl (2bC)

Quantities: compound **20C** (1.70 g, 4.46 mmol), compound **21b** (1.40 g, 5.36 mmol). The experimental procedure was as described for the preparation of compound **1aC**, except that lithium chloride (0.57 g, 13.4 mmol) was added, to yield colourless crystals.

Yield 1.45 g (73%). Transitions (°C) Cryst 71.0 SmC 101.0 Iso. ^{1}H NMR (400 MHz, $CDCl_3$), δ 0.89(3H, t), 0.98(9H, s), 1.26–1.42(8H, m), 1.54(2H, m), 1.63(2H, quint), 2.66(2H, m), 2.67(2H, t), 7.00(1H, ddd, $J = 7.36$ Hz, $J = 7.36$ Hz, $J = 1.84$ Hz), 7.14(1H, ddd, $J = 7.36$ Hz, $J = 7.36$ Hz, $J = 1.84$ Hz), 7.28(2H, d, $J = 8.72$ Hz), 7.56(2H, d, $J = 8.72$ Hz), 7.60(2H, dd, $J = 8.72$ Hz, $J = 1.20$ Hz), 7.67(2H, d, $J = 8.72$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$), δ 14.10, 22.66, 28.79, 29.10, 29.28, 29.34, 30.05, 30.57, 30.92, 31.79, 46.39 (alkyl chains, 11 required, 11 found), 124.14(dd, $J = 3.07$ Hz, $J = 3.07$ Hz), 124.72(dd, $J = 3.84$ Hz, $J = 3.84$ Hz), 126.97, 127.03, 128.01(dd, $J = 9.99$ Hz, $J = 0.77$ Hz), 128.79, 129.14(d, $J = 3.07$ Hz), 130.87(dd, $J = 13.07$ Hz, $J = 0.77$ Hz), 133.60, 137.80, 140.63, 143.00, 148.11(dd, $J = 248.29$ Hz, $J= 13.07$ Hz), 149.54(dd, $J = 239.07$ Hz, $J = 6.15$ Hz) (aromatic carbons, 14 required, 14 found). MS *m*/*z* 448(M^+). Elemental analysis: $C_{31}H_{38}F_2$ requires C 82.99%, H 8.54%; found C 83.13%, H 8.40%.

5.24 2,3-Difluoro-4″-(trimethylsilyl)-4′-octyloxy-[4.4′:1′,4″]-terphenyl (2aSi)

Quantities: compound **20Si** (1.63 g, 4.05 mmol), compound **21a** (1.40 g, 4.86 mmol). The experimental procedure was as described for the preparation of compound **1aC**, except that lithium chloride (0.55 g, 12.9 mmol) was added, to yield colourless crystals.

Yield 0.60 g (30%). Transitions (°C) Cryst 78.8 SmC 118.6 Iso. ^{1}H NMR (400 MHz, $CDCl_3$), δ 0.06(9H, s), 0.91(3H, t), 0.94(2H, m), 1.33–1.40(8H, m), 1.51(2H, quint), 1.86(2H, quint), 2.70(2H, m), 4.08(2H, t), 6.82(1H, ddd, $J = 7.36$ Hz, $J = 7.36$ Hz, $J = 1.84$ Hz), 7.14(1H, ddd, $J = 7.36$ Hz, $J = 7.36$ Hz, $J = 1.84$ Hz), 7.31(2H, d, $J = 8.72$ Hz), 7.56(2H, d, $J = 8.72$ Hz), 7.58(2H, dd, $J = 8.72$ Hz, $J = 1.20$ Hz), 7.68(2H, d, $J = 8.72$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$), δ –1.74, 14.08, 18.67, 22.64, 25.88, 29.18(x2), 29.29, 29.70, 31.79, 69.88 (alkyl chains, 11 required, 11 found), 109.50(d, $J = 3.84$ Hz), 122.58(dd, $J = 10.76$ Hz, $J = 0.77$ Hz), 123.44(dd, $J = 3.84$ Hz, $J = 3.84$ Hz), 126.91, 127.03, 128.26, 129.00(d, $J = 3.07$ Hz), 133.53, 137.76, 140.38, 141.91(dd, $J = 246.75$ Hz, $J = 14.61$ Hz), 144.72, 147.87(dd, $J = 8.46$ Hz, J= 3.07 Hz), 148.97(dd, $J = 249.06$ Hz, J = 11.53 Hz) (aromatic carbons, 14 required, 14 found). MS *m*/*z* 494(M^+). Elemental analysis: $C_{31}H_{40}F_2OSi$ requires C 75.26%, H 8.15%; found C 75.33%, H 8.24%.

5.25 2,3-Difluoro-4-heptyl-4′′-(trimethylsilyl)-[4,4′:1′,4′′]-terphenyl (2bSi)

Quantities: compound **20Si** (1.73 g, 4.31 mmol), compound **21b** (1.43 g, 5.60 mmol). The experimental procedure was as described for the preparation of compound **1aC**, except that lithium chloride (0.55 g, 12.9 mmol) was added, to yield colourless crystals.

Yield 0.90 g (45%). Transitions (°C) Cryst 66.7 SmC 78.9 Iso. ^{1}H NMR (400 MHz, $CDCl_3$), δ 0.05(9H, s), 0.91(3H, t), 0.93(2H, m), 1.26–1.37(8H, m), 1.67(2H, quint), 2.66–2.72(4H, m), 7.02(1H, ddd, $J = 7.36$ Hz, $J = 7.36$ Hz, $J = 1.84$ Hz), 7.16(1H, ddd, $J = 7.36$ Hz, $J = 7.36$ Hz, $J = 1.84$ Hz), 7.30(2H, d, $J = 8.72$ Hz), 7.51(2H, d, $J = 8.72$ Hz), 7.56(2H, dd, $J = 8.72$ Hz, $J = 1.20$ Hz), 7.63(2H, d, $J = 8.72$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$), δ –1.75, 14.09, 18.68, 22.66, 28.79, 29.09, 29.27, 29.71, 30.05, 31.79 (alkyl chains, 10 required, 10 found); 124.13(dd, $J = 3.07$ Hz, $J = 3.07$ Hz), 124.73(dd, $J = 4.61$ Hz, $J = 4.61$ Hz), 126.94, 127.03, 127.97(dd, $J = 10.70$ Hz, $J = 0.80$ Hz), 128.28, 129.14(d, $J = 3.07$ Hz), 130.90(dd, $J = 13.00$ Hz, $J = 0.70$ Hz), 133.60, 137.75, 140.66, 144.77, 148.01(dd, $J = 247.52$ Hz, $J = 12.30$ Hz), 149.54(dd, $J = 239.84$ Hz, $J = 6.92$ Hz) (aromatic carbons, 14 required, 14 found). MS *m/z* 464(M$^+$). Elemental analysis: $C_{30}H_{38}F_2Si$ requires C 77.54%, H 8.24%; found C 77.58%, H 8.22%.

5.26 4′-Bromo-2,3-difluorobiphenyl (22)

Quantities: compound **13** (35.00 g, 0.124 mol), compound **5** (23.44 g, 0.148 mol). The experimental procedure was as described for the preparation of compound **1aC**, except that the crude product was distilled to yield a colourless oil.

Yield 19.00 g (57%). ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.15(3H, m), 7.41(2H, dd), 7.59(2H, d). MS *m/z* 270(M$^+$), 268(M$^+$).

5.27 2,3-Difluoro-4′-(3,3-dimethylbut-1-ynyl)biphenyl (23C)

Quantities: compound **14** (5.00 g, 0.021 mol), compound **5** (5.00 g, 0.032 mol). The experimental procedure was as described for the preparation of compound **1aC** to yield colourless crystals.

Yield 5.35 g (94%). mp 57.8°C. ^{1}H NMR (400 MHz, $CDCl_3$), δ 1.31(9H, s), 7.08–7.18(3H, m), 7.37(4H, m). MS *m/z* 270(M$^+$).

5.28 2,3-Difluoro-4′-(trimethylsilylethynyl)biphenyl (23Si)

Quantities: compound **7Si** (7.00 g, 0.071 mol), *n*-butyllithium (28 ml, 2.5M in hexanes, 0.070 mol), zinc chloride (11.50 g, 0.085 mol), compound **22** (16.00 g, 0.059 mol). The experimental procedure was as described for the preparation of compound **9C** to yield a colourless oil.

Yield: 12.00 g (71%). ^{1}H NMR (400 MHz, $CDCl_3$), δ 0.20(9H, s), 7.04–7.14(3H, m), 7.39(2H, dd), 7.46(2H, d). MS *m/z* 286(M$^+$).

5.29 2,3-Difluoro-4′-(3,3-dimethylbutyl)biphenyl (24C)

Quantities: compound **23C** (5.00 g, 0.0185 mol), 10% palladium-on-carbon (1.00 g). The experimental procedure was as described for the preparation of compound **10C** to yield a colourless oil.

Yield 5.00 g (98%). ^{1}H NMR (400 MHz, $CDCl_3$), δ 0.98(9H, s), 1.53(2H, m), 2.61(2H, m), 7.08(2H, m), 7.16(1H, m), 7.25(2H, d), 7.43(2H, dd). MS *m/z* 274(M$^+$).

5.30 2,3-Difluoro-4′-(trimethylsilylethyl)biphenyl (24Si)

Quantities: compound **23Si** (13.00 g, 0.045 mol), 10% palladium-on-carbon (2.00 g). The experimental procedure was as described for the preparation of compound **10C** to yield a colourless oil.

Yield 12.00 g (92%). ^{1}H NMR (400 MHz, $CDCl_3$), δ 0.04(9H, s), 0.90(2H, m), 2.67(2H, m), 7.10(2H, m), 7.18(1H, m), 7.29(2H, d), 7.46(2H, dd). MS *m/z* 290(M$^+$).

5.31 2,3-Difluoro-4′-(3,3-dimethylbutyl)biphenyl-4-ylboronic acid (25C)

Quantities: compound **24C** (4.95 g, 0.018 mol), *n*-butyllithium (7.3 ml, 2.5M in hexanes, 0.018 mol), trimethyl borate (3.74 g, 0.036 mol). The experimental procedure was as described for the preparation of compound **5** to yield a colourless powder.

Yield 3.00 g (52%). ^{1}H NMR (400 MHz, D6-DMSO), δ 0.86(9H, s), 1.39(2H, m), 2.41(2H, m), 7.18(1H, ddd), 7.23(2H, d), 7.31(1H, ddd), 7.39(2H, dd). MS *m/z* 318(M$^+$).

5.32 2,3-Difluoro-4′-(trimethylsilyl)biphenyl-4-ylboronic acid (25Si)

Quantities: compound **24Si** (7.00 g, 0.024 mol), *n*-butyllithium (9.7 ml, 2.5M in hexanes, 0.024 mol), trimethyl borate (5.01 g, 0.048 mol). The experimental procedure was as described for the preparation of compound **5** to yield a colourless powder.

Yield 3.21 g (40%). ^{1}H NMR (400 MHz, D6-DMSO), δ 0.03(9H, s), 0.89(2H, m), 2.66(2H, m), 7.29(1H, ddd), 7.33(2H, d), 7.41(1H, ddd), 7.49(2H, dd). MS *m/z* 334(M$^+$).

5.33 2′,3′-Difluoro-4-(3,3-dimethylbutyl)-4″-octyloxy-[4.4′:1′,4″]-terphenyl (3aC)

Quantities: compound **26a** (1.30 g, 3.35 mmol), compound **25C** (1.30 g, 4.02 mmol). The experimental procedure was as described for the preparation of compound **1aC** to yield colourless crystals.

Yield 1.13 g (75%). Transitions (°C) Cryst 89.0 SmC 106.9 N 114.4 Iso. ^{1}H NMR (400 MHz, CDCl$_3$), δ 0.89(3H, t), 0.98(9H, s), 1.32(8H, m), 1.47(2H, m), 1.54(2H, t), 1.57(2H, m), 1.81(2H, quint), 2.63(2H, m), 4.01(2H, t), 6.99(2H, d, $J = 8.86$ Hz), 7.19–7.24(2H, m), 7.29(2H, d, $J = 8.86$ Hz), 7.49(2H, dd, $J = 8.86$ Hz, $J = 1.80$ Hz), 7.52(2H, dd, $J = 8.86$ Hz, $J = 1.80$ Hz). ^{13}C NMR (100 MHz, CDCl$_3$), δ 14.10, 22.66, 26.06, 29.26, 29.32(x2), 29.37, 30.56, 31.01, 31.82, 46.29, 68.04 (alkyl chains, 12 required, 12 found); 114.59, 124.29 (dd, $J = 3.84$ Hz, $J = 3.84$ Hz), 124.49 (dd, $J = 3.84$ Hz, $J = 3.84$ Hz), 126.78, 128.56, 128.73 (d, $J = 3.07$ Hz), 129.20 (2×dd, $J = 9.99$ Hz, $J = 9.99$ Hz), 129.94 (d, $J = 3.07$ Hz), 131.95, 143.64, 148.44 (dd, $J = 250.6$ Hz, $J = 11.53$ Hz), 148.60 (dd, $J = 251.37$ Hz, $J = 9.99$ Hz), 159.15 (aromatic carbons, 14 required, 14 found). MS *m*/*z* 478(M$^+$). Elemental analysis: C$_{32}$H$_{40}$F$_2$O requires C 80.30%, H 8.42%; found C 80.37%, H 8.52%.

5.34 2′,3′-Difluoro-4-heptyl-4″-(3,3-dimethylethyl)-[4.4′:1′,4″]-terphenyl (3bC)

Quantities: compound **26b** (0.82 g, 3.22 mmol), compound **25C** (1.20 g, 3.84 mmol). The experimental procedure was as described for the preparation of compound **1aC** to yield colourless crystals.

Yield 0.30 g (21%). Transitions (°C) Cryst 60.0 SmC 76.0 N 77.7 Iso. ^{1}H NMR (400 MHz, CDCl$_3$), δ 0.89(3H, t), 0.98(9H, s), 1.25–1.38(8H, m), 1.55(2H, m), 1.66(2H, quint), 2.63(4H, m), 7.19–7.24(2H, m), 7.26–7.31(4H, m), 7.47–7.52(4H, m). ^{13}C NMR (100 MHz, CDCl$_3$), δ 14.10, 22.68, 29.19, 29.32, 29.35, 30.57, 31.01, 31.41, 31.82, 35.72, 46.30, (alkyl chains, 11 required, 11 found); 124.52(2×dd, $J = 3.84$ Hz, $J = 3.07$ Hz), 128.57, 128.65, 128.69, 128.77, 129.47 (2×dd, $J = 6.92$ Hz, $J = 6.92$ Hz), 131.92, 131.96, 143.06, 143.70, 149.74 (2×dd, $J = 250.60$ Hz, $J = 15.37$ Hz) (aromatic carbons, 14 required, 14 found). MS *m*/*z* 448(M$^+$). Elemental analysis: C$_{31}$H$_{38}$F$_2$ requires C 82.99%, H 8.54%; found C 82.89%, H 8.57%.

5.35 2′,3′-Difluoro-4-(trimethylsilylethyl)-4″-octyloxy-[4.4′:1′,4″]-terphenyl (3aSi)

Quantities: compound **26a** (1.15 g, 4.04 mmol), compound **25Si** (1.60 g, 4.79 mmol). The experimental procedure was as described for the preparation of compound **1aC** to yield colourless crystals.

Yield 0.74 g (37%). Transitions (°C) Cryst 56.1 SmC 101.9 Iso. ^{1}H NMR (400 MHz, CDCl$_3$), δ 0.05 (9H, s), 0.89(2H, t), 0.92(2H, m), 1.27–1.35(9H, m), 1.47(2H, quint), 1.81(2H, t), 2.68(2H, m), 4.01(2H, t), 6.99(2H, d, $J = 8.86$ Hz), 7.19–7.24(2H, m), 7.31(2H, d, $J = 8.86$ Hz), 7.49(2H, dd, $J = 8.86$ Hz, $J = 1.47$ Hz), 7.52(2H, dd, $J = 8.86$ Hz, $J = 1.47$ Hz). ^{13}C NMR (100 MHz, CDCl$_3$), δ –1.75, 14.09, 18.61, 22.66, 26.05, 29.25(x2), 29.36, 29.81, 31.82, 68.07, (alkyl chains, 11 required, 11 found); 114.60, 124.30(dd, $J = 3.84$ Hz, $J = 3.84$ Hz), 124.50(dd, $J = 3.84$ Hz, $J = 3.84$ Hz), 126.81, 128.03, 128.73(d, $J = 3.07$ Hz), 129.20(2×dd, $J = 9.99$ Hz, $J = 3.84$ Hz), 129.96(d, $J = 3.07$ Hz), 131.91, 145.41, 148.44(dd, $J = 250.50$ Hz, J= 13.84 Hz), 148.60(dd, $J = 250.50$ Hz, $J = 8.46$ Hz), 159.15 (aromatic carbons, 14 required, 14 found). MS *m*/*z* 494(M$^+$). Elemental analysis: C$_{31}$H$_{40}$F$_2$OSi requires C 75.26%, H 8.15%; found C 75.23%, H 8.18%.

5.36 2′,3′-Difluoro-4-heptyl-4″-(triemethylsilylethyl)-[4,4′:1′,4″]-terphenyl (3bSi)

Quantities: compound **26b** (1.09 g, 4.27 mmol), compound **21b** (1.73 g, 5.18 mmol). The experimental procedure was as described for the preparation of compound **1aC** to yield colourless crystals.

Yield 1.20 g (60%). Transitions (°C) Cryst 58.9 SmC 61.7 Iso. ^{1}H NMR (100 MHz, CDCl$_3$), δ 0.04(9H, s), 0.89(3H, t), 0.92(2H, m), 1.25–1.38(8H, m), 1.66(2H, quint), 2.65(2H, t), 2.69(2H, m), 7.19–7.24(2H, m), 77.26–7.31(4H, m), 7.47–7.52(4H, m). ^{13}C NMR (400 MHz, CDCl$_3$), δ –1.75, 14.10, 18.61, 22.68, 29.19, 29.35, 29.81, 31.4, 31.82, 35.72, (alkyl chains, 10 required, 10 found); 124.51(2×dd, $J = 3.84$ Hz, $J = 3.84$ Hz), 128.04, 128.65, 128.72(2×dd, $J = 7.69$ Hz, $J = 1.54$ Hz), 129.43, 129.51, 131.88, 131.97, 143.05, 145.44, 148.52(2×dd, $J = 250.50$ Hz, $J = 15.40$ Hz) (aromatic carbons, 14 required, 14 found). MS *m*/*z* 464(M$^+$). Elemental analysis: C$_{30}$H$_{38}$F$_2$Si requires C 77.54%, H 8.24%; found C 77.53%, H 8.28%.

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References

(1) Meyer, R.B.; Liebert, L.; Strzelecki, L.; Keller, P. *J. Phys. Lett.* **1975**, *36*, L69–L71.

(2) Clark, N.A.; Lagerwall, S.T. *Appl. Phys. Lett.* **1980**, *36*, 899–901.

(3) Lagerwall, S.T. *Ferroelectric and Antiferroelectric Liquid Crystals*; Wiley-VCH: Weinheim, 1999.

(4) Wand, M.D.; Thurmes, W.N.; Vohra, R.T. *Ferroelectrics* **2000**, *246*, 1061–1068.

(5) Wilkinson, T.D.; Crossland, W.A.; Davey, A.B. *Ferroelectrics* **2002**, *278*, 799–804.

(6) Slaney, A.J.; Minter, V.; Jones, J.C. *Ferroelectrics*, **1996**, *178*, 65–74.

(7) Finkenzeller, U.; Pausch, A.E.; Poetsch; E.; Suermann, J. *Kontakte (Darmstadt)* **1993**, 3–14.

(8) Lagerwall, S.T. *Ferroelectrics* **2004**, *301*, 15–45.

(9) Pauluth, D.; Tarumi, K. *J. Mater. Chem.* **2004**, *14*, 1219–1227.

(10) Souk, J.H. *Keynote Lecture 2*, 22nd International Liquid Crystal Conference, Korea, July **2008**.

(11) Hird, M.; Goodby, J.W.; Hindmarsh, P.; Lewis, R.A.; Toyne, K.J. *Ferroelectrics* **2002**, *276*, 219–237.

(12) Bradshaw, M.J.; Brimmell, V.; Raynes, E.P. *Liq. Cryst.* **1987**, *2*, 107–110.

(13) Clark, N.A.; Rieker, T.P. *Appl. Phys. Rev. A* **1988**, *37*, 1053–1056.

(14) Elston, S.J. *J. Mod. Opt.* **1995**, *42*, 19–95.

(15) Rieker, T.P.; Clark, N.A.; Smith, G.S.; Parmar, D.S.; Sirota, E.B.; Safinya, C.R. *Phys. Rev. Lett.* **1987**, *59*, 2658–2661.

(16) Dierking, I.; Komitov, L.; Lagerwall, S.T. *Liquid Crystals* **1998**, *24*, 769–774.

(17) Gray, G.W.; Hird, M.; Lacey, D.; Toyne, K.J. *J. Chem. Soc., Perkin Trans.* **1989**, *2*, 2041–2053.

(18) King, A.O.; Negishi, E.; Villani, F.J.; Silveira, A. *J. Org. Chem.* **1978**, *43*, 358–360.

(19) Thiebes, C.; Prakash, G.K.S.; Petasis, S.; O.G.A., *Synlett.* **1998**, 141–142.

(20) Miyaura, N.; Yanagi, T.; Suzuki, A. *Synth. Commun.* **1981**, *11*, 513–519.

(21) Huth, A.; Beetz, I.; Schumann, I. *Tetrahedron* **1989**, *45*, 6679–6682.

(22) Fu, J.-M.; Snieckus, V. *Tetrahedron Lett.* **1990**, *31*, 1665–1668.

(23) Hird, M.; Toyne, K.J.; Gray, G.W. *Liq. Cryst.* **1993**, *14*, 741–761.

(24) Hird, M.; Toyne, K.J.; Gray, G.W.; Day, S.E.; McDonnell, D.G. *Liq. Cryst.* **1993**, *15*, 123–150.

(25) Hird, M.; Toyne, K.J.; Goodby, J.W.; Gray, G.W.; Minter, V.; Tuffin, R.P.; McDonnell, D.G. *J. Mater. Chem.* **2004**, *14*, 1731–1743.