PERKIN 2

The synthesis and mesomorphic properties of 4,4″-dialkyl-2,2′,3- and 2,2′,3′-trifluoro-1,1′:4′,1″-terphenyls for high dielectric biaxiality ferroelectric liquid crystal mixtures

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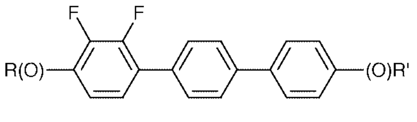
Two series of liquid crystalline terphenyls with terminal alkyl chains have been synthesised with three lateral fluoro substituents in close proximity to each other. Two terminal alkyl chains were employed to minimise viscosity, maximise solubility and generate low melting points. The first series of materials employs fluoro substituents at an outer-edge position to maximise the smectic phase C phase stability, whereas the second series has the fluoro substituents in the centre of the molecule in an attempt to minimise melting points, but surprisingly the melting points of the former compounds are much lower. The synthetic routes to all of the materials involved low-temperature lithiations to generate arylboronic acids which were then involved in sequential, selective palladium-catalysed cross-coupling reactions. Many of the materials produced have extremely low melting points and some exhibit the smectic C phase at room temperature. In general, the 2,2′,3- and 2,2′,3′-patterns of lateral fluoro substitution in 1,1′:4′,1″-terphenyls generate materials of low viscosity and high lateral dipole. In particular, many materials from the first series have low melting points and exhibit the smectic C phase, hence they show great promise for the formulation of ferroelectric mixtures with a high dielectric biaxiality which is very important in τV minimum driving schemes; whereas the materials from the second series are nematogens and hence could be useful for vertically aligned nematic devices.

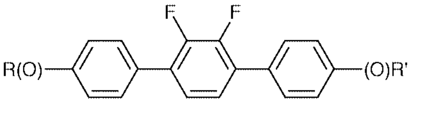
Introduction

Ferroelectric mixtures for fast-switching displays are composed of achiral host materials which enables the fine-tuning of the mesomorphic behaviour, and allows the tailoring of many important physical properties, such as birefringence and particularly the requirement for a low viscosity.[1–6] Such achiral host mixtures need to be doped with a chiral material which then confers chirality on the whole mixture; removal of the macroscopic helical structure then generates the required ferroelectric properties. Ideally, the quantity of the required chiral material should be as low as possible so as to minimise the viscosity, but must be sufficiently high to provide the necessary spontaneous polarisation.[6] Ferroelectric mixtures for displays that operate in the τV_{min} mode are additionally required to have a high dielectric biaxiality, which is achieved through the use of components with a large lateral dipole.[3–5] Lateral fluoro substituents have long been used to generate a lateral dipole because their small size and high electronegativity serve to minimise any reduction in liquid crystal phase stability and to minimise viscosity.[1,6]

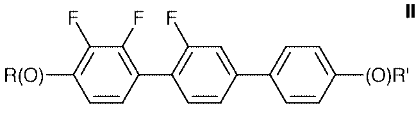
The *ortho*-difluoroterphenyls (**I** and **II**) make excellent host materials for ferroelectric mixtures; they have low melting points, wide smectic C phase temperature ranges and a low viscosity, they also have a high lateral dipole due to the two fluoro substituents that are fixed on the same side of the molecule.[1] In order to enhance the lateral dipole, recent work has concentrated on locating a third fluoro substituent next to the existing two fluoro substituents so as to create a 2,2′-difluoro substitution pattern within a trifluoroterphenyl structure (**III** and **IV**). It is known from many different sources that the 2,2′-difluoro substituents in a biphenyl moiety tend to attract each other to their van der Waals minimum so providing a high lateral dipole.[7–9] Another important molecular structural feature that considerably increases the lateral dipole is the special relationship between an ether oxygen of the terminal alkoxy chain and the adjacent fluoro substituent in a phenyl ring; it is thought that in this case there is a mesomeric effect from the oxygen which enhances the polarity of the fluoro substituent.[1,10]



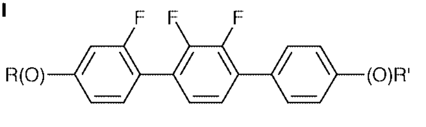
I



II



III



IV

Recently, we have reported on a series of trifluoroterphenyls of types **III** and **IV** where at least one of the terminal chains is alkoxy, thus combining the useful structural combinations mentioned above.[6] These materials showed particularly high lateral dipole moments and enhanced the dielectric biaxiality of ferroelectric mixtures. However, the viscosity of the alkoxy-alkyl-difluoroterphenyls is considerably higher than for the dialkyl analogues.[1,10] Hence, the aim of this work was to synthesise a series of analogous trifluoroterphenyls (**III** and **IV**), but with two alkyl terminal chains in order to minimise viscosity. Melting points of dialkyl compounds are nearly always lower than for the analogous alkoxy-alkyl systems due to the reduced polarity.[1,11] Provided melting points are low, the dialkyl compounds of type **III** will certainly exhibit the smectic C phase (the outer-edge fluoro substituent enhances lamellar attractions

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and the lateral polarity from the fluoro substituents promotes molecular tilting),[1,11] albeit to lower temperature than for the alkoxy-alkyl systems where the ether oxygen enhances polarisability and lateral dipole. The dialkyl compounds of type **IV** will have particularly low viscosity because the fluoro substituents are away from the outer edge of the core, but the lack of an outer-edge fluoro substituent combined with more interannular twisting means that they will most certainly not exhibit smectic phases and hence be nematogens.[1,11] Despite the obvious expected disadvantages in terms of mesophase morphology and transition temperatures, the expected low melting points and low viscosity will ensure some considerable potential as additives to enhance the dielectric biaxiality of ferroelectric mixtures for $\tau V_{\min}$ applications. Those materials that are nematogenic will possibly be useful for vertically aligned nematic (VAN) devices[12–14] where a negative dielectric anisotropy and a low viscosity are required.

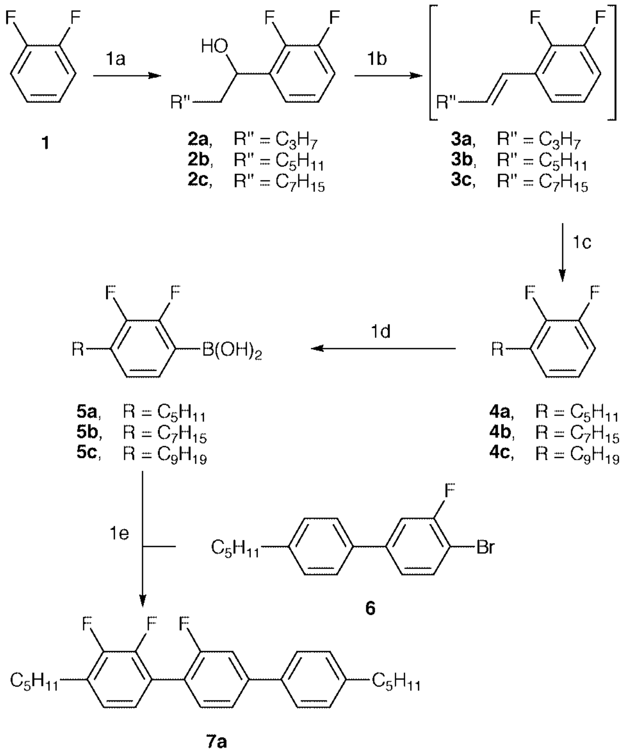
A wide range of homologues of types **III** and **IV** of the dialkyltrifluoroterphenyls has been synthesised in order to (a) fully evaluate the effect of a third lateral fluoro substituent on melting points, transition temperatures and mesophase morphology, and (b) find the optimum combination of terminal chain lengths that generates a material with as low a melting point as possible and that exhibits a smectic C phase over as wide a temperature range as possible.

Synthesis of materials

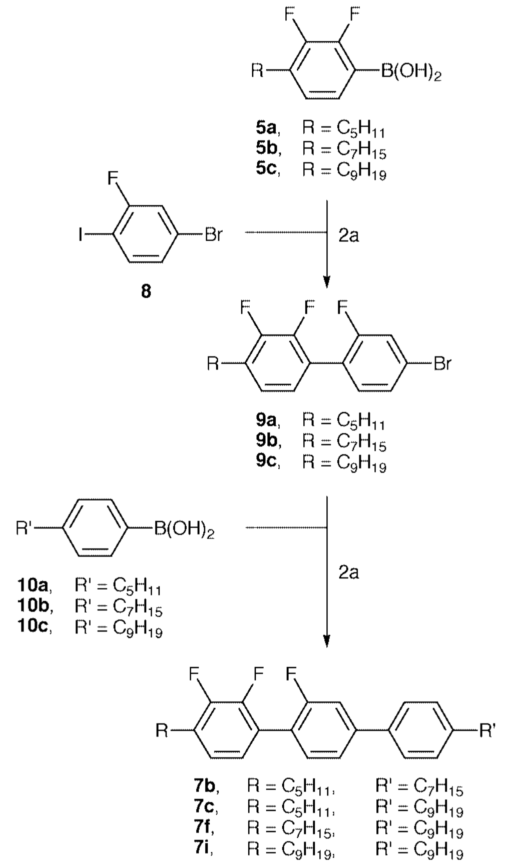
Palladium-catalysed cross-coupling reactions are virtually essential in the efficient synthesis of novel liquid crystals designed to meet the very exacting requirements for future advanced technology. Palladium-catalysed cross-coupling reactions are very efficient and general in the synthesis of multi-aryl materials because they allow the individual construction of aromatic rings of the desired substitution pattern; they thus facilitate the synthesis of materials that are virtually impossible to generate through other methods. Those cross-coupling reactions involving boronic acids offer particular advantages in terms of tolerance towards other functional groups, selectivity and provide high yields of easily-purified multi-aryl materials.[1,6,15–18]

The requirement for fluoro substituents in these novel liquid crystals (and many reported previously) actually facilitates the synthesis. The electron-withdrawing effect of the two fluoro substituents renders adjacent protons acidic, and such sites were exploited sequentially by a strong base at low temperature and then functionalised, firstly to introduce the desired alkyl chain, and finally to provide substituted difluorophenylboronic acids **5a–c** (Scheme 1). Subsequent palladium-catalysed cross-coupling with the substituted aryl bromide **6** (itself prepared through a selective cross-coupling) provided **7a** as an example of a dialkyl liquid crystalline trifluoroterphenyl. However, this particular cross-coupling involving a combination of boronic acid and bromide is disadvantaged by the slight steric hindrance due to the fluoro substituents and the tendency of *ortho*-fluoroarylboronic acids (*e.g.*, **5a–c**) to undergo hydrodeboronation.

Scheme 2 shows the alternative approach of a selective coupling reaction involving the alkyldifluorophenylboronic acids **5a–c** and the commercially available 4-bromo-2-fluoro-1-iodobenzene (**8**) to provide a range of bromo-substituted alkyl-trifluorobiphenyls. The final coupling reactions are now particularly efficient because the boronic acids **10a–c** are not prone to hydrodeboronation and there is less steric hindrance. Overall, this approach is better than that shown in Scheme 1 because of the commercial availability of compound **8** and the activation of the iodo leaving group due to the *ortho* fluoro substituent which facilitates good selectivity in the first coupling reaction.

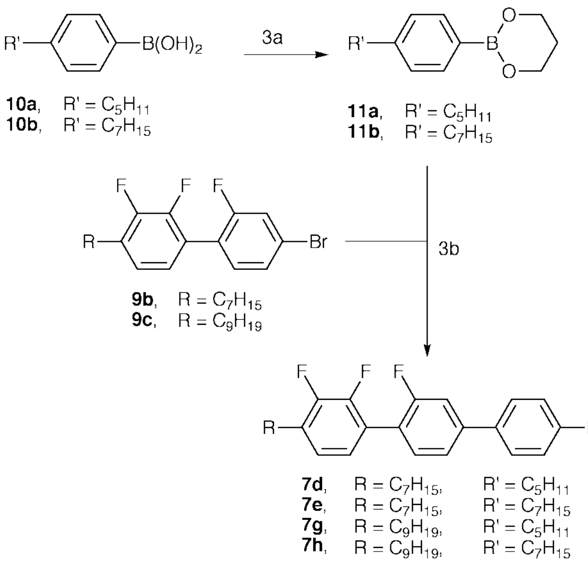


Scheme 1 1a ... (i) *n*-BuLi, THF; (ii) R″CH_2CHO, THF; (iii) NH_4Cl, H_2O; 1b ... P_2O_5, pentane or PTSA, toluene; 1c ... H_2, Pd/C, ethanol–THF; 1d ... (i) *n*-BuLi, THF; (ii) $(MeO)_3B$, THF; (iii) 10% HCl; 1e ... $Pd(PPh_3)_4$, 2 M Na_2CO_3, DME.



Scheme 2 2a ... $Pd(PPh_3)_4$, 2 M Na_2CO_3, DME.

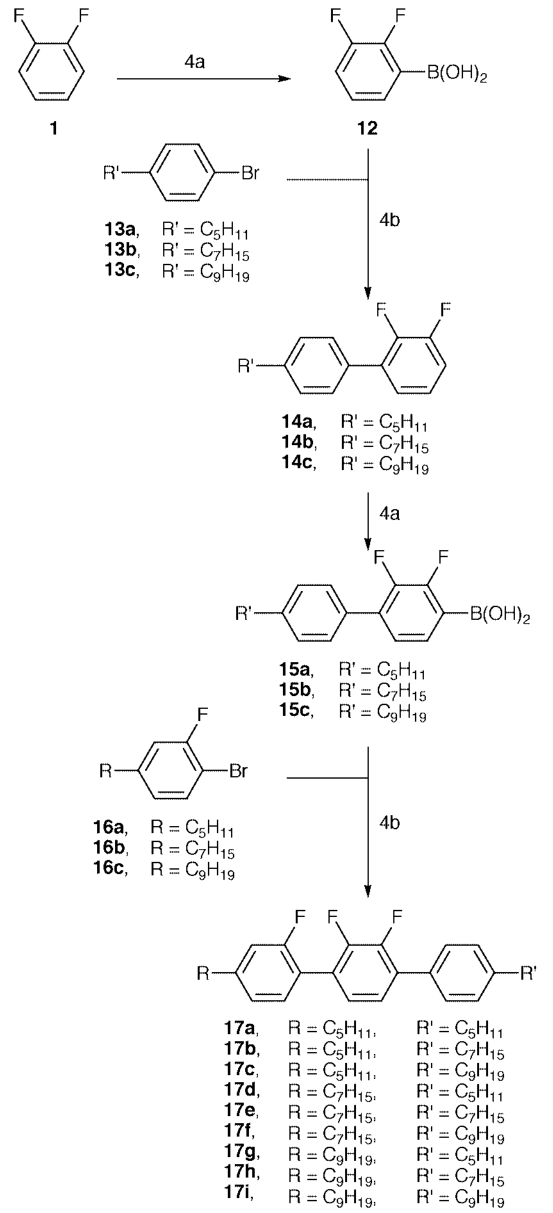
As part of a long and on-going investigation into the scope and limitations of palladium-catalysed cross-coupling reactions in the synthesis of multi-aryl materials, two arylboronic esters (**11a** and **11b**) were prepared from their parent arylboronic acids (**10a** and **10b**). Arylboronic acids are very difficult to



Scheme 3 3a ... Propane-1,3-diol, hexane; 3b ... Pd(PPh_3)$_4$, K_3PO_4, DMF.

purify and characterise because of their tendency to exist as mixtures of the boronic acid and the trimeric anhydride, whereas the analogous esters can be purified and characterised easily. Another reported advantage of the boronic esters is their reduced tendency towards hydrodeboronation[19] in palladium-catalysed cross-coupling reactions when used in anhydrous conditions, a point not relevant here because boronic acids **10a** and **10b** are not prone to hydrodeboronation. Boronic esters can also be used with the same aqueous base conditions as boronic acids, in which case hydrolysis to the boronic acid occurs. For the purposes of cross-coupling reactions there is usually no point in preparing the boronic esters, except where hydrodeboronation is a problem, as the boronic acids are perfectly satisfactory, a point shown by the close similarity (around 80%) of yields (before recrystallisation) of materials from Schemes 2 and 3.

Scheme 4 shows the synthesis of those trifluoroterphenyls (**17a–i**) with the fluoro substituents in the centre of the molecule. Once again palladium-catalysed cross-coupling reactions are essential for such syntheses. The exploitation of an acidic proton in compound **1** at low temperature generated the required arylboronic acid (**12**) which was then involved in a palladium-catalysed cross-coupling reaction to yield difluorobiphenyls **14a–c**. The other acidic proton was exploited to generate difluorobiarylboronic acids **15a–c** which were then coupled to the appropriate fluoro-substituted aryl bromides to generate the required liquid crystals in reasonably good yields.



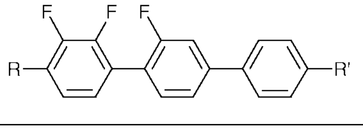
Scheme 4 4a ... (i) *n*-BuLi, THF; (ii) (MeO)$_3$B, THF; (iii) 10% HCl; 4b ... Pd(PPh_3)$_4$, 2 M Na_2CO_3, DME.

Discussion of mesophase morphology and transition temperatures

Table 1 shows the transition temperatures of a series of nine homologous dialkyl trifluoroterphenyls with the fluoro substituents at the outermost positions of the core and a typical alkoxy-alkyl analogue (**18**)[6] for comparison with compound **7f**. In terms of expectation, the outer-edge position tends to fill space at the site of the terminal chain which enhances lateral inter-molecular attractions and hence offers scope for the generation of smectic phases, in particular the tilted smectic C phase due to the strong lateral dipole. However, two of the fluoro substituents are at an inter-annular position and the one in the centre ring will cause additional broadening of the molecules, hence tending to depress smectic phase stability and leave nematogens. With three lateral fluoro substituents the polarity is high and hence the usual influence of a lateral fluoro substituent in reducing melting point may not be expected to hold. However, the melting points of the compounds in Table 1 are remarkably low considering the location of a fluoro substituent at an outer-edge position; compound **7b** in particular exhibits a smectic C phase at room temperature and does not crystallise down to −100 °C. Such low melting points are of obvious benefit in compounds where the thermal stabilities of the smectic C phase are moderate at best.

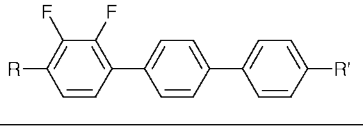
The lack of an ether oxygen is particularly detrimental towards the smectic C phase stability of compounds **7a–i** where in most cases the smectic phase stability continues way beyond the tilted smectic C through the exhibition of a smectic A phase. Interestingly, where the smectic phase stability is weak (*e.g.*, the short-chain homologues, **7a** and **7d**) it is the smectic C phase and not the smectic A phase that is exhibited; in fact **7g** is nematogenic. Where the terminal chains are long (particularly R′) the smectic A phase is particularly dominant; *e.g.*, compare compounds **7a–c** where the smectic A phase thermal stability increases more dramatically than that of the smectic C phase. The alkoxy-alkyl analogues did not generally generate a smectic A phase and the whole smectic tendency was exhibited as the tilted smectic C phase because of the additional polarity from the ether oxygen. It is particularly interesting to compare compound **7f** with the analogous alkoxy-alkyl system (**18**);[6] for **7f**

Table 1 Transition temperatures for 4,4″-dialkyl-2,2′,3-trifluoroterphenyls (**7a**–**i**) and compound **18**

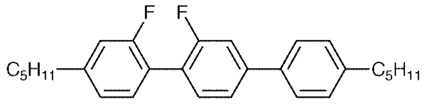


Compound			Transition temperatures/°C								
No.	R	R′	Cryst		S_C		S_A		N		Iso
7a	C_5H_{11}	C_5H_{11}	•	31.8	•	(20.3)	—	—	•	81.5	•
7b	C_5H_{11}	C_7H_{15}	•	?	•	37.2	•	51.7	•	75.0	•
7c	C_5H_{11}	C_9H_{19}	•	30.8	•	49.2	•	78.6	•	83.1	•
7d	C_7H_{15}	C_5H_{11}	•	22.7	•	(8.2)	—	—	•	75.5	•
7e	C_7H_{15}	C_7H_{15}	•	38.1	•	50.8	•	64.6	•	80.8	•
7f	C_7H_{15}	C_9H_{19}	•	28.0	•	52.0	•	78.5	•	81.0	•
7g	C_9H_{19}	C_5H_{11}	•	36.1	•	—	—	—	•	77.5	•
7h	C_9H_{19}	C_7H_{15}	•	37.0	•	51.3	•	67.4	•	79.6	•
7i	C_9H_{19}	C_9H_{19}	•	45.6	•	54.7	•	79.8	•	80.8	•
18[6]	$C_6H_{13}O$	C_9H_{19}	•	47.9	•	91.5	—	—	•	109.6	•

Table 2 Transition temperatures for selected difluoroterphenyls (**19a**–**c** and **20**)[1,8]



Compound			Transition temperatures/°C								
No.	R	R′	Cryst		S_C		S_A		N		Iso
19a	C_5H_{11}	C_5H_{11}	•	81.0	•	115.5	•	131.5	•	142.0	•
19b	C_5H_{11}	C_7H_{15}	•	65.5	•	118.5	•	135.0	•	137.0	•
19c	C_7H_{15}	C_5H_{11}	•	56.0	•	105.5	•	131.0	•	136.0	•



20

Cryst 43.5 N 85.0 I

the nematic phase stability has been reduced by around 30 °C, but the smectic phase stability has been reduced by only 13 °C. However, the smectic C phase stability has been reduced by 40 °C, and combined with a reduction in melting point of only 20 °C results in a narrower smectic C temperature range. Generally, the very low melting points and reasonable smectic C phase thermal stabilities of compounds **7a**–**i** makes them ideally suited as components in ferroelectric mixtures.

Table 2 shows some difluoroterphenyls,[1] and it is most interesting to look at the influence of the additional fluoro substituent in the centre ring on liquid crystal behaviour (compare compounds **7a**, **7b** and **7d** with **19a**, **19b** and **19c** respectively). Melting points have been reduced by around 40 °C, which is quite surprising as previous views on fluoro substitution indicate that one fluoro, and possibly two, may reduce melting point significantly, but the high polarity from three fluoro substituents is usually expected to cause very high melting points. It is however, useful that melting points are so low since the all-important smectic C phase stability has been reduced by around 90 °C, although the trifluoroterphenyls are certainly far more influenced by chain lengths. Longer terminal chains (especially R′) are essential even for moderate smectic C phase stability. Nematic phase stability is less affected by the third inner-core fluoro substituent and is reduced by around 60 °C, showing the steric effect of the increased molecular breadth.

A comparison of compound **7a** with difluoroterphenyl **20**[8] shows the influence of the outer-edge fluoro substituent. Compound **20** supercools to −100 °C without the generation of a smectic C phase, yet the trifluoroterphenyl **7a** exhibits a monotropic smectic C phase at 20.3 °C despite the presence of an additional fluoro substituent. The additional fluoro substituent at the outer-edge position does not broaden the molecule, but its polar nature aids that lamellar attraction of the molecules dramatically enhancing smectic phase stability, but has little effect on the nematic phase stability which is similar for both compounds.

Compounds **17a**–**i** (Table 3) were prepared because the pattern of three fluoro substituents in the centre ring was expected to generate very low melting points, almost certainly lower than for the isomeric compounds shown in Table 1; hence it is very surprising that the melting points of compounds **17a**–**i** are considerably higher. It was always expected that compounds **17a**–**i** would have low liquid crystal phase stability, and probably not exhibit the smectic C phase, and this has been proved. However, the fluoro-substitution pattern shown by compounds **17a**–**i** is ideal for low viscosity and so the compounds would make ideal additives for ferroelectric mixtures. Since compounds **17a**–**i** are nematogens of high negative dielectric anisotropy they would also be useful as components in mixtures for vertically aligned nematic devices. Unlike those trifluoroterphenyls shown in Table 1, the nematic phase stabilities are remarkably independent of terminal chain length; this is quite unusual since longer terminal chains are expected to have reduced nematic phase stability.

The nematic phase stabilities of the difluoroterphenyls (**21a**–**d**, Table 4)[1] do vary with chain length in the expected manner, and the third fluoro substituent has reduced the values by around 40 to 50 °C. Taking account of substantial supercooling of compounds **17a–i** (Table 3), the third fluoro substituent has reduced the smectic C phase stability by at least 100 °C.

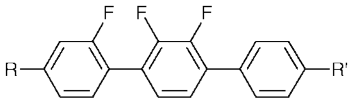
Conclusions

A wide range of materials have been synthesised with multiple fluoro substituents in strategic lateral positions in order to generate a large lateral dipole to provide a high dielectric biaxiality. Some interesting synthetic methods have been used including the development of selective palladium-catalysed cross-coupling reactions and selective low temperature lithiations to generate vital fluoro-substituted intermediates. It has been shown that highly polar materials with multiple lateral fluoro substituents can have low melting points and generate a reasonably high smectic C phase stability, which makes them suitable components in ferroelectric mixtures. These fluoro-substituted materials are of low viscosity and confer a high dielectric biaxiality on ferroelectric mixtures and a forthcoming paper by our collaborators at DERA (Malvern) will discuss the whole range of physical properties of the materials and their effect in ferroelectric mixtures (*e.g.*, dielectric biaxiality, viscosity and switching times). Additionally, those materials that are nematogenic will possibly be useful for vertically aligned nematic (VAN) devices where a negative dielectric anisotropy and a low viscosity are required.

Experimental

Confirmation of the structures of intermediates and products was obtained by ^{1}H and ^{13}C NMR spectroscopy (JEOL JNM-GX270 spectrometer), infrared spectroscopy (Perkin-Elmer 457 grating spectrophotometer) and mass spectrometry (Finnigan-MAT 1020 GC/MS spectrometer). Elemental analysis (Fisons EA1108 CHN) data were obtained for each final compound prepared (**7a–i** and **17a–i**). The progress of reactions was frequently monitored using a Chrompack 9001 capillary gas chromatograph fitted with a CP-SIL 5 CB 10 m × 0.25 mm, 0.12 µm column (Cat. No. 7700). 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-7 and IBM data station). The purities of intermediates were checked by GLC analysis (see above) and the purity of each final compound (**7a–i** and **17a–i**) was checked by HPLC analysis (Merck-Hitachi with Merck RP 18 column, Cat. No. 16 051) and was found to be >99.9% pure in each case.

Table 3 Transition temperatures for 4,4″-dialkyl-2,2′,3′-trifluoroterphenyls (**17a–i**)



Compound			Transition temperatures/°C				
No.	R	R′	Cryst		N		Iso
17a	C_5H_{11}	C_5H_{11}	•	62.4	•	71.1	•
17b	C_5H_{11}	C_7H_{15}	•	44.2	•	68.9	•
17c	C_5H_{11}	C_9H_{19}	•	50.5	•	69.1	•
17d	C_7H_{15}	C_5H_{11}	•	41.2	•	69.9	•
17e	C_7H_{15}	C_7H_{15}	•	56.4	•	69.5	•
17f	C_7H_{15}	C_9H_{19}	•	48.1	•	70.0	•
17g	C_9H_{19}	C_5H_{11}	•	50.4	•	69.2	•
17h	C_9H_{19}	C_7H_{15}	•	51.2	•	69.5	•
17i	C_9H_{19}	C_9H_{19}	•	61.0	•	70.7	•

The preparation of intermediates (**2a–c**, **3a–c**, **4a–c**, **5a–c**),[1] (**6**, **10a–c**)[8] and **16a–c**[11] have been reported previously. Tetrakis(triphenylphosphine)palladium(0) was prepared according to the literature procedure.[20] Compounds **1** and **8** were purchased from Aldrich.

2,2′,3-Trifluoro-4,4″-dipentylterphenyl 7a

Quantities: compound **5a** (0.97 g, 4.25 mmol); compound **6** (1.14 g, 3.54 mmol). The experimental procedure was as described in a previous publication.[6] The crude product was purified by column chromatography (silica gel; hexane) to give a colourless solid which was recrystallised from ethanol–ethyl acetate (5:1) to yield colourless crystals. Yield 0.49 g (43%); transitions (°C) Cryst 31.8 (S_C 20.3) N 81.5 Iso; δ_H (270 MHz; $CDCl_3$) 0.91 (3H, t), 0.92 (3H, t), 1.27–1.45 (8H, m), 1.66 (4H, 2 × quint), 2.66 (2H, t), 2.71 (2H, t), 7.01 (1H, ddd), 7.09 (1H, ddd), 7.28 (2H, d), 7.35–7.48 (3H, m), 7.53 (2H, d); MS *m*/*z* 424 (M^+); found C, 79.17%; H, 7.35%; $C_{28}H_{31}F_3$ requires: C, 79.21%; H, 7.36%.

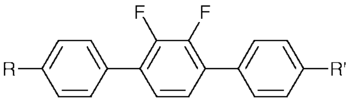
4′-Bromo-2,2′,3-trifluoro-4-pentylbiphenyl 9a

Quantities: compound **5a** (10.53 g, 0.046 mol); compound **8** (12.65 g, 0.042 mol). The experimental procedure was as described in a previous publication.[6] The crude product was purified by column chromatography (silica gel; hexane) and Kugelrohr distillation (160 °C at 0.1 mmHg) to give a colourless oil. Yield 8.72 g (58%); δ_H (270 MHz; $CDCl_3$) 0.91 (3H, t), 1.28–1.45 (4H, m), 1.65 (2H, quint), 2.69 (2H, t), 6.95–7.05 (2H, m), 7.25 (1H, dd), 7.32–7.40 (2H, m); MS *m*/*z* 358 (M^+), 356 (M^+).

4′-Bromo-2,2′,3-trifluoro-4-heptylbiphenyl 9b

Quantities: compound **5b** (11.01 g, 0.043 mol); compound **8** (11.74 g, 0.039 mol). The experimental procedure was as described for the preparation of compound **9a** to give a colourless oil. Yield 6.97 g (46%); δ_H (270 MHz; $CDCl_3$) 0.89 (3H, t), 1.20–1.44 (8H, m), 1.64 (2H, quint), 2.69 (2H, t), 6.95–7.05 (2H, m), 7.25 (1H, dd), 7.32–7.40 (2H, m); MS *m*/*z* 386 (M^+), 384 (M^+).

Table 4 Transition temperatures for selected difluoroterphenyls (**21a–c**)[1]



Compound			Transition temperatures/°C								
No.	R	R′	Cryst		S_C		S_A		N		Iso
21a	C_5H_{11}	C_5H_{11}	•	60.0	—	—	—	—	•	120.0	•
21b	C_5H_{11}	C_7H_{15}	•	36.5	•	(24.0)	—	—	•	111.5	•
21c	C_5H_{11}	C_9H_{19}	•	42.5	•	66.0	—	—	•	110.0	•
21d	C_7H_{15}	C_9H_{19}	•	49.0	•	77.0	•	93.0	•	108.5	•

4′-Bromo-2,2′,3-trifluoro-4-nonylbiphenyl 9c

Quantities: compound **5c** (11.36 g, 0.040 mol); compound **8** (10.93 g, 0.036 mol). The experimental procedure was as described for the preparation of compound **9a** to give a colourless oil. Yield 6.22 g (31%); δ_H (270 MHz; CDCl$_3$) 0.88 (3H, t), 1.18–1.44 (12H, m), 1.64 (2H, quint), 2.69 (2H, t), 6.95–7.05 (2H, m), 7.24 (1H, dd), 7.32–7.39 (2H, m); MS *m*/*z* 414 (M$^+$), 412 (M$^+$).

2,2′,3-Trifluoro-4″-heptyl-4-pentylterphenyl 7b

Quantities: compound **10b** (1.75 g, 7.97 mmol); compound **9a** (2.37 g, 6.64 mmol). The experimental procedure was as described for the preparation of compound **7a**. The crude product was purified by column chromatography (silica gel; hexane) to afford a colourless liquid which was further purified by Kugelrohr distillation (175 °C at 0.15 mmHg) in order to remove volatiles. The resultant smectic liquid crystal phase was again purified by column chromatography (silica gel; hexane) to afford a colourless smectic liquid crystal. Yield 1.54 g (54%); transitions (°C) Cryst ? S$_C$ 37.2 S$_A$ 51.7 N 75.0 Iso; δ_H (270 MHz; CDCl$_3$) 0.89 (3H, t), 0.92 (3H, t), 1.20–1.45 (12H, m), 1.66 (4H, 2 × quint), 2.65 (2H, t), 2.71 (2H, t), 7.01 (1H, ddd), 7.09 (1H, ddd), 7.27 (2H, d), 7.34–7.47 (3H, m), 7.53 (2H, d); MS *m*/*z* 452 (M$^+$); found C, 79.58%; H, 7.75%; C$_{30}$H$_{35}$F$_3$ requires: C, 79.61%; H, 7.79%.

2,2′,3-Trifluoro-4″-nonyl-4-pentylterphenyl 7c

Quantities: compound **10c** (1.86 g, 7.50 mmol); compound **9a** (2.23 g, 6.25 mmol). The experimental procedure was as described for the preparation of compound **7a**. The crude product was purified by column chromatography (silica gel; hexane) to give a colourless solid which was recrystallised from ethanol–ethyl acetate (4:1) to yield colourless crystals. Yield 1.80 g (60%); transitions (°C) Cryst 30.8 S$_C$ 49.2 S$_A$ 78.6 N 83.1 Iso; δ_H (270 MHz; CDCl$_3$) 0.88 (3H, t), 0.92 (3H, t), 1.19–1.45 (16H, m), 1.65 (4H, 2 × quint), 2.65 (2H, t), 2.70 (2H, t), 7.00 (1H, ddd), 7.09 (1H, ddd), 7.27 (2H, d), 7.34–7.47 (3H, m), 7.53 (2H, d); MS *m*/*z* 480 (M$^+$); found C, 79.91%; H, 8.16%; C$_{32}$H$_{39}$F$_3$ requires: C, 79.96%; H, 8.18%.

2,2′,3-Trifluoro-4-heptyl-4″-nonylterphenyl 7f

Quantities: compound **10c** (1.23 g, 4.96 mmol); compound **9b** (1.60 g, 4.16 mmol). The experimental procedure was as described for the preparation of compound **7a**. The crude product was purified by column chromatography (silica gel; hexane) to give a colourless solid which was recrystallised from ethanol to yield colourless crystals. Yield 1.23 g (58%); transitions (°C) Cryst 28.0 S$_C$ 52.0 S$_A$ 78.5 N 81.0 Iso; δ_H (270 MHz; CDCl$_3$) 0.89 (6H, 2 × t), 1.15–1.45 (20H, m), 1.65 (4H, 2 × quint), 2.65 (2H, t), 2.70 (2H, t), 7.01 (1H, ddd), 7.09 (1H, ddd), 7.27 (2H, d), 7.34–7.49 (3H, m), 7.53 (2H, d); MS *m*/*z* 508 (M$^+$); found C, 80.22%; H, 8.48%; C$_{34}$H$_{43}$F$_3$ requires: C, 80.28%; H, 8.52%.

2,2′,3-Trifluoro-4,4″-dinonylterphenyl 7i

Quantities: compound **10c** (1.39 g, 5.59 mmol); compound **9c** (1.93 g, 4.66 mmol). The experimental procedure was as described for the preparation of compound **7a**. The crude product was purified by column chromatography (silica gel; hexane) to give a colourless solid which was recrystallised from ethanol–ethyl acetate (5:1) to yield colourless crystals. Yield 1.84 g (74%); transitions (°C) Cryst 45.6 S$_C$ 54.7 S$_A$ 79.8 N 80.8 Iso; δ_H (270 MHz; CDCl$_3$) 0.88 (6H, 2 × t), 1.19–1.45 (24H, m), 1.65 (4H, 2 × quint), 2.65 (2H, t), 2.70 (2H, t), 7.00 (1H, ddd), 7.09 (1H, ddd), 7.27 (2H, d), 7.35–7.48 (3H, m), 7.53 (2H, d); MS *m*/*z* 536 (M$^+$); found C, 80.54%; H, 8.83%; C$_{36}$H$_{47}$F$_3$ requires: C, 80.56%; H, 8.83%.

1-(4-Pentylphenyl)-2,6,1-dioxaborinane 11a

A mixture of compound **10a** (16.90 g, 0.088 mol) and propane-1,3-diol (12.90 g, 0.170 mol) in hexane (150 ml) was stirred at room temperature for 16 h. The organic layer was decanted off from the aqueous propane-1,3-diol, dried (MgSO$_4$) and the solvent was removed *in vacuo* to yield a colourless oil. Yield 16.60 g (81%); δ_H (270 MHz; CDCl$_3$) 0.85 (3H, t), 1.25–1.40 (4H, m), 1.60 (2H, quint), 2.03 (2H, quint), 2.59 (2H, t), 4.14 (4H, 2 × t), 7.15 (2H, d), 7.67 (2H, d); MS *m*/*z* 232 (M$^+$).

1-(4-Heptylphenyl)-2,6,1-dioxaborinane 11b

Quantities: compound **10b** (17.38 g, 0.079 mol). The experimental procedure was as described for the preparation of compound **11a** to yield a colourless oil. Yield 25.85 g (99%); δ_H (270 MHz; CDCl$_3$) 0.87 (3H, t), 1.17–1.41 (8H, m), 1.60 (2H, quint), 2.03 (2H, quint), 2.60 (2H, t), 4.14 (4H, 2 × t), 7.16 (2H, d), 7.67 (2H, d); MS *m*/*z* 260 (M$^+$).

2,2′,3-Trifluoro-4-heptyl-4″-pentylterphenyl 7d

A stirred mixture of compound **11a** (0.83 g, 3.58 mmol), compound **9b** (1.15 g, 2.99 mmol), anhydrous potassium phosphate (0.95 g, 4.49 mmol) and tetrakis(triphenylphosphine)-palladium(0) (0.17 g, 0.15 mmol) in dry DMF (30 ml) under dry nitrogen was heated under reflux for 16 h (GLC analysis revealed a complete reaction) and the cooled mixture was poured into water. The product was extracted into ether, the ethereal extract was washed with brine, dried (MgSO$_4$), and the solvent was removed *in vacuo*. The crude product was purified by column chromatography (silica gel; hexane) to afford a colourless liquid which was further purified by Kugelrohr distillation (175 °C at 0.15 mmHg) in order to remove volatiles. The resultant nematic liquid crystal phase was again purified by column chromatography (silica gel; hexane) to afford a colourless nematic liquid crystal. Yield 1.11 g (82%); transitions (°C) Cryst 22.7 (S$_C$ 8.2) N 75.5 Iso; δ_H (270 MHz; CDCl$_3$) 0.89 (3H, t), 0.91 (3H, t), 1.21–1.45 (12H, m), 1.66 (4H, 2 × quint), 2.65 (2H, t), 2.70 (2H, t), 7.00 (1H, ddd), 7.09 (1H, ddd), 7.27 (2H, d), 7.35–7.48 (3H, m), 7.53 (2H, d); MS *m*/*z* 452 (M$^+$); found C, 79.60%; H, 7.76%; C$_{30}$H$_{35}$F$_3$ requires: C, 79.61%; H, 7.79%.

2,2′,3-Trifluoro-4,4″-diheptylterphenyl 7e

Quantities: compound **11b** (1.30 g, 3.38 mmol); compound **9b** (1.57 g, 5.21 mmol). The experimental procedure was as described for the preparation of compound **7d**. The crude product was purified by column chromatography (silica gel; hexane) to give a colourless solid which was recrystallised from ethanol–ethyl acetate (5:1) to yield colourless crystals. Yield 1.01 g (62%); transitions (°C) Cryst 38.1 S$_C$ 50.8 S$_A$ 64.6 N 80.8 Iso; δ_H (270 MHz; CDCl$_3$) 0.89 (6H, 2 × t), 1.20–1.45 (16H, m), 1.65 (4H, 2 × quint), 2.65 (2H, t), 2.70 (2H, t), 7.00 (1H, ddd), 7.09 (1H, ddd), 7.27 (2H, d), 7.35–7.48 (3H, m), 7.53 (2H, d); MS *m*/*z* 480 (M$^+$); found C, 79.94%; H, 8.17%; C$_{32}$H$_{39}$F$_3$ requires: C, 79.96%; H, 8.18%.

2,2′,3-Trifluoro-4-nonyl-4″-pentylterphenyl 7g

Quantities: compound **11a** (1.15 g, 4.94 mmol); compound **9c** (1.70 g, 4.12 mmol). The experimental procedure was as described for the preparation of compound **7d**. The crude product was purified by column chromatography (silica gel; hexane) to give a colourless solid which was recrystallised from ethanol–ethyl acetate (3:1) to yield colourless crystals. Yield 1.17 g (59%); transitions (°C) Cryst 36.1 N 77.5 Iso; δ_H (270 MHz; CDCl$_3$) 0.89 (3H, t), 0.91 (3H, t), 1.20–1.45 (16H, m), 1.66 (4H, 2 × quint), 2.65 (2H, t), 2.70 (2H, t), 7.00 (1H, ddd), 7.09 (1H, ddd), 7.27 (2H, d), 7.34–7.48 (3H, m), 7.53 (2H, d); MS *m*/*z* 480 (M$^+$); found C, 79.92%; H, 8.15%; C$_{32}$H$_{39}$F$_3$ requires: C, 79.96%; H, 8.18%.

2,2′,3-Trifluoro-4″-heptyl-4-nonylterphenyl 7h

Quantities: compound **11b** (1.51 g, 5.81 mmol); compound **9c** (2.00 g, 4.84 mmol). The experimental procedure was as described for the preparation of compound **7d**. The crude product was purified by column chromatography (silica gel; hexane) to give a colourless solid which was recrystallised from ethanol–ethyl acetate (5:1) to yield colourless crystals. Yield 1.55 g (63%); transitions (°C) Cryst 37.0 S_C 51.3 S_A 67.4 N 79.6 Iso; δ_H (270 MHz; $CDCl_3$) 0.88 (6H, 2 × t), 1.19–1.45 (20H, m), 1.65 (4H, 2 × quint), 2.65 (2H, t), 2.70 (2H, t), 7.00 (1H, ddd), 7.08 (1H, ddd), 7.27 (2H, d), 7.34–7.48 (3H, m), 7.53 (2H, d); MS *m*/*z* 508 (M^+); found C, 80.22%; H, 8.49%; $C_{34}H_{43}F_3$ requires: C, 80.28%; H, 8.52%.

2,2′,3′-Trifluoro-4,4″-dipentylterphenyl 17a

Quantities: compound **15a** (2.37 g, 7.79 mmol); compound **16a** (1.73 g, 7.08 mmol). The experimental procedure was as described for the preparation of compound **7a**. The crude product was purified by column chromatography (silica gel; hexane) to give a colourless solid which was recrystallised from ethanol to yield colourless crystals. Yield 1.42 g (47%); transitions (°C) Cryst 62.4 N 71.1 Iso; δ_H (270 MHz; $CDCl_3$) 0.91 (6H, 2 × t), 1.21–1.45 (8H, m), 1.67 (4H, 2 × quint), 2.66 (4H, 2 × t), 7.02 (1H, dd), 7.06 (1H, ddd), 7.13–7.36 (5H, m), 7.50 (2H, d); MS *m*/*z* 424 (M^+); found C, 79.19%; H, 7.33%; $C_{28}H_{31}F_3$ requires: C, 79.21%; H, 7.36%.

2,2′,3′-Trifluoro-4″-heptyl-4-pentylterphenyl 17b

Quantities: compound **15b** (2.65 g, 7.97 mmol); compound **16a** (1.63 g, 6.64 mmol). The experimental procedure was as described for the preparation of compound **7a**. The crude product was purified by column chromatography (silica gel; hexane) to give a colourless solid which was recrystallised from ethanol–ethyl acetate (5:1) to yield colourless crystals. Yield 1.48 g (49%); transitions (°C) Cryst 44.2 N 68.9 Iso; δ_H (270 MHz; $CDCl_3$) 0.89 (3H, t), 0.92 (3H, t), 1.21–1.45 (12H, m), 1.66 (4H, 2 × quint), 2.66 (4H, 2 × t), 7.02 (1H, dd), 7.06 (1H, ddd), 7.14–7.36 (5H, m), 7.50 (2H, d); MS *m*/*z* 452 (M^+); found C, 79.57%; H, 7.75%; $C_{30}H_{35}F_3$ requires: C, 79.61%; H, 7.79%.

2,2′,3′-Trifluoro-4″-nonyl-4-pentylterphenyl 17c

Quantities: compound **15c** (2.70 g, 7.50 mmol); compound **16a** (1.53 g, 6.25 mmol). The experimental procedure was as described for the preparation of compound **7a**. The crude product was purified by column chromatography (silica gel; hexane) to give a colourless solid which was recrystallised from ethanol–ethyl acetate (5:1) to yield colourless crystals. Yield 1.45 g (48%); transitions (°C) Cryst 50.5 N 69.1 Iso; δ_H (270 MHz; $CDCl_3$) 0.88 (3H, t), 0.92 (3H, t), 1.20–1.45 (16H, m), 1.66 (4H, 2 × quint), 2.66 (4H, 2 × t), 7.02 (1H, dd), 7.06 (1H, ddd), 7.13–7.37 (5H, m), 7.50 (2H, d); MS *m*/*z* 480 (M^+); found C, 79.90%; H, 8.14%; $C_{32}H_{39}F_3$ requires: C, 79.96%; H, 8.18%.

2,2′,3′-Trifluoro-4-heptyl-4″-pentylterphenyl 17d

Quantities: compound **15a** (2.42 g, 7.97 mmol); compound **16b** (1.81 g, 6.64 mmol). The experimental procedure was as described for the preparation of compound **7a**. The crude product was purified by column chromatography (silica gel; hexane) to give a colourless solid which was recrystallised from ethanol to yield colourless crystals. Yield 1.16 g (39%); transitions (°C) Cryst 41.2 N 69.9 Iso; δ_H (270 MHz; $CDCl_3$) 0.89 (3H, t), 0.91 (3H, t), 1.21–1.44 (12H, m), 1.66 (4H, 2 × quint), 2.65 (4H, 2 × t), 7.02 (1H, dd), 7.06 (1H, ddd), 7.14–7.36 (5H, m), 7.50 (2H, d); MS *m*/*z* 452 (M^+); found C, 79.59%; H, 7.76%; $C_{30}H_{35}F_3$ requires: C, 79.61%; H, 7.79%.

2,2′,3′-Trifluoro-4,4″-diheptylterphenyl 17e

Quantities: compound **15b** (2.49 g, 7.50 mmol); compound **16b** (1.71 g, 6.25 mmol). The experimental procedure was as described for the preparation of compound **7b**. The crude product was purified by column chromatography (silica gel; hexane) to give a colourless solid which was recrystallised from ethanol to yield colourless crystals. Yield 1.66 g (55%); transitions (°C) Cryst 56.4 N 69.5 Iso; δ_H (270 MHz; $CDCl_3$) 0.89 (6H, 2 × t), 1.21–1.44 (16H, m), 1.66 (4H, 2 × quint), 2.66 (4H, 2 × t), 7.02 (1H, dd), 7.06 (1H, ddd), 7.14–7.36 (5H, m), 7.50 (2H, d); MS *m*/*z* 480 (M^+); found C, 79.94%; H, 8.15%; $C_{32}H_{39}F_3$ requires: C, 79.96%; H, 8.18%.

2,2′,3′-Trifluoro-4-heptyl-4″-nonylterphenyl 17f

Quantities: compound **15c** (2.55 g, 7.09 mmol); compound **16b** (1.61 g, 5.91 mmol). The experimental procedure was as described for the preparation of compound **7a**. The crude product was purified by column chromatography (silica gel; hexane) to give a colourless solid which was recrystallised from ethanol to yield colourless crystals. Yield 1.63 g (54%); transitions (°C) Cryst 48.1 N 70.0 Iso; δ_H (270 MHz; $CDCl_3$) 0.90 (3H, t), 0.91 (3H, t), 1.22–1.45 (20H, m), 1.67 (4H, 2 × quint), 2.67 (4H, 2 × t), 7.03 (1H, dd), 7.07 (1H, ddd), 7.15–7.37 (5H, m), 7.52 (2H, d); MS *m*/*z* 508 (M^+); found C, 80.22%; H, 8.48%; $C_{34}H_{43}F_3$ requires: C, 80.28%; H, 8.52%.

2,2′,3′-Trifluoro-4-nonyl-4″-pentylterphenyl 17g

Quantities: compound **15a** (1.82 g, 6.00 mmol); compound **16c** (1.57 g, 5.21 mmol). The experimental procedure was as described for the preparation of compound **7a**. The crude product was purified by column chromatography (silica gel; hexane) to give a colourless solid which was recrystallised from ethanol–ethyl acetate (5:1) to yield colourless crystals. Yield 1.19 g (48%); transitions (°C) Cryst 50.4 N 69.2 Iso; δ_H (270 MHz; $CDCl_3$) 0.89 (3H, t), 0.92 (3H, t), 1.20–1.45 (16H, m), 1.66 (4H, 2 × quint), 2.66 (4H, 2 × t), 7.02 (1H, dd), 7.05 (1H, ddd), 7.13–7.36 (5H, m), 7.51 (2H, d); MS *m*/*z* 480 (M^+); found C, 79.93%; H, 8.14%; $C_{32}H_{39}F_3$ requires: C, 79.96%; H, 8.18%.

2,2′,3′-Trifluoro-4″-heptyl-4-nonylterphenyl 17h

Quantities: compound **15b** (2.35 g, 7.09 mmol); compound **16c** (1.78 g, 5.91 mmol). The experimental procedure was as described for the preparation of compound **7a**. The crude product was purified by column chromatography (silica gel; hexane) to give a colourless solid which was recrystallised from ethanol–ethyl acetate (5:1) to yield colourless crystals. Yield 2.18 g (73%); transitions (°C) Cryst 51.2 N 69.5 Iso; δ_H (270 MHz; $CDCl_3$) 0.89 (6H, 2 × t), 1.21–1.44 (20H, m), 1.66 (4H, 2 × quint), 2.66 (4H, 2 × t), 7.02 (1H, dd), 7.06 (1H, ddd), 7.14–7.36 (5H, m), 7.50 (2H, d); MS *m*/*z* 508 (M^+); found C, 80.28%; H, 8.50%; $C_{34}H_{43}F_3$ requires: C, 80.28%; H, 8.52%.

2,2′,3′-Trifluoro-4,4″-dinonylterphenyl 17i

Quantities: compound **15c** (2.42 g, 6.72 mmol); compound **16c** (1.69 g, 5.60 mmol). The experimental procedure was as described for the preparation of compound **7a**. The crude product was purified by column chromatography (silica gel; hexane) to give a colourless solid which was recrystallised from ethanol to yield colourless crystals. Yield 1.90 g (63%); transitions (°C) Cryst 61.0 N 70.7 Iso; δ_H (270 MHz; $CDCl_3$) 0.89 (6H, 2 × t), 1.19–1.44 (24H, m), 1.66 (4H, 2 × quint), 2.66 (4H, 2 × t), 7.02 (1H, dd), 7.05 (1H, ddd), 7.13–7.36 (5H, m), 7.50 (2H, d); MS *m*/*z* 536 (M^+); found C, 80.52%; H, 8.79%; $C_{36}H_{47}F_3$ requires: C, 80.56%; H, 8.83%.

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