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Novel liquid crystals with a bent molecular shape containing a 1,5-disubstituted 2,3,4-trifluorophenyl unit. Banana-shaped liquid crystals—synthesis and properties†‡

Michael Hird,* John W. Goodby, Neil Gough and Kenneth J. Toyne

Department of Chemistry, University of Hull, Hull, UK HU6 7RX.
E-mail: M.Hird@chem.hull.ac.uk

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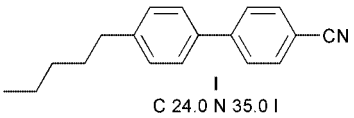
The synthesis, transition temperatures and chiral properties of a range of novel achiral and racemic liquid crystals with a bent molecular shape containing a 1,5-disubstituted 2,3,4-trifluorophenyl moiety are detailed in the context of the recently popular research topic of banana-shaped liquid crystals. The work represents a speculative extension of research into ferroelectric host materials with high dielectric biaxiality, and some interesting results are discussed. Notably, some achiral materials generate a columnar mesophase where the molecules are tilted within the columns, allowing the generation of chirality, other achiral materials exhibit a 'conventional' mesomorphism in the form of a smectic C phase, but an equal number of oppositely handed regions are generated. A racemic material generates an unidentified smectic phase, which exhibits chiral properties of single handedness despite the racemic nature.

Introduction

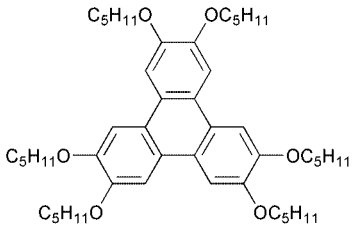
In many respects the molecular structures of liquid crystal molecules may be considered rather unadventurous; simple rod-like molecules (*e.g.*, compound **I**) generate calamitic liquid crystalline phases, disc-shaped molecules (*e.g.*, compound **II**) generate columnar liquid crystal phases, and simple amphiphilic molecules (*e.g.*, compound **III**) generate lyotropic liquid crystal phases. Compounds **I** and **II** are categorised as thermotropic liquid crystals, where the phases are generated by heating and cooling, and compound **III** is classed as a lyotropic liquid crystal, where the phases are generated by the action of a solvent, usually water, and are altered through changes in concentration and temperature.[1,2]

Of course, the complete picture is far more exciting, with a vast array of molecular combinations constituting a great many shapes, sizes and polarities of liquid crystalline compounds. The physical properties of even the most simple liquid crystal compound are truly remarkable; from the self-assembly of molecules in an ordered, yet fluid, liquid crystalline mesophase, through to the electrical, optical and visco-elastic properties. Who would possibly imagine that a molecule as plain and simple as compound **I** (5CB or K15)[3] could have been so significant in display device applications? When chirality is introduced into the molecular structure of liquid crystal compounds, a whole new range of chirality-related properties (a macroscopic helical arrangement of the constituent molecules, selective reflection of light, spontaneous polarisation, non-linear optical properties) can result depending on the particular mesophase exhibited.[4,5]

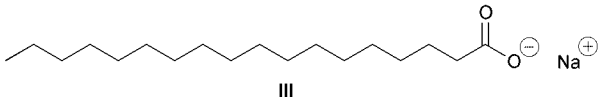
The potential use of liquid crystals in display device applications has fuelled a massive research effort throughout the world, from collaborations involving a wide range of scientific disciplines (*e.g.*, chemistry, physics engineering and mathematics).[2] In the search for improved properties, numerous liquid crystals have been synthesised and characterised which has significantly improved the understanding of structure–property relationships, and uncovered some more unusual physical properties. Additionally, of course, the vast importance of lyotropic liquid crystals in foods, cleansers and biological systems should not be overlooked.[6,7] As certain areas of liquid crystals have matured in a commercially successful manner (display devices and thermochromics) researchers have looked for other ways to exploit the remarkable properties of liquid crystals in areas such as ferroelectric and antiferroelectric devices, molecular electronics, and biological systems. With these more recent targeted applications comes the requirement for an ever more exacting combination of physical properties from the liquid crystal materials. Such a requirement necessitates that the molecular structures of the liquid crystals are ever more complex and



I
C 24.0 N 35.0 I



II
C 69.0 D_{ho} 122.0 I



III

†Basis of a presentation given at Materials Discussion No. 4, 11–14 September 2001, Grasmere, UK.
‡Electronic supplementary information (ESI) available: experimental details and spectroscopic data for compounds **4b**, **5b**, **8b**, **9b**, **14b**, **15b**, **21b**, **29**, **30**, **31**, **33**, **34**, **35**, **36** and **38**. See http://www.rsc.org/suppdata/jm/b1/b102988f/

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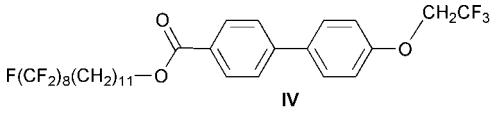
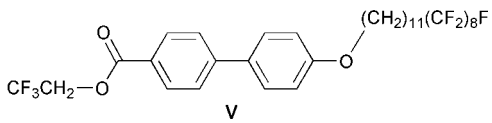
difficult to synthesise. In addition to the development of materials targeted towards applications, much fundamental research into liquid crystals has been carried out, particularly in the areas of chirality and unusual molecular architectures (*e.g.*, phasmidic, dendritic, T-shaped, wedge-shaped).[8,9]

One extremely intriguing area of recent research into liquid crystals is the generation of reduced symmetry mesophases from achiral materials, first reported in systems where the molecules are composed of alternating segments of polar and non-polar units (compounds **IV** and **V**).[10] Such alternating segments facilitate the molecular self-assembly in a polar asymmetric manner, and the mesophases generated were termed polyphilic. The bulk polarisation in the smectic C phase generated by these systems is parallel to the direction of the molecules and orthogonal to the layer planes, hence they are often called longitudinal ferroelectrics, and are particularly suitable for non-linear optical applications.

More recently, reduced symmetry mesophases have been found in a range of so-called banana-shaped achiral liquid crystals (*e.g.*, compound **VI**).[11–16] A great many analogous structures have been prepared, some with lateral substituents in the central aromatic ring, and although some are non-mesogenic, the vast majority of others exhibit the wide range of 'banana phases' commonly designated B_1 through to B_7.[16] Such banana phases are of different miscibility groups to the conventional liquid crystal phases exhibited by materials of calamitic structures. Many hypotheses have been presented to explain this unusual phenomenon of spontaneous polar ordering, overall it is thought that preferred conformers exist as handed entities (equal numbers of each handedness are always present) which result in areas of reduced symmetry. The banana-shaped molecules can pack in smectic layers and give C_{2v}, C_2, C_{1h} or C_1 symmetry which allow the possibility of ferroelectric, ferrielectric and antiferroelectric properties.

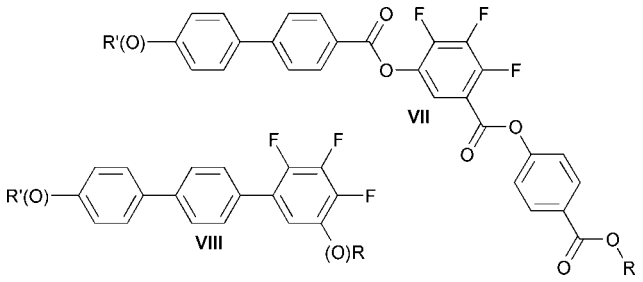


IV



V

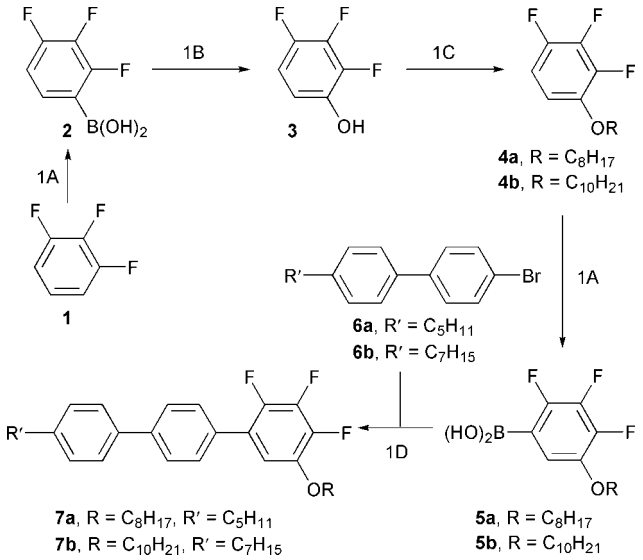
The novel research presented here did not set out to fit into the banana-shaped liquid crystals field, but was a fundamental research extension of research into high dielectric biaxiality ferroelectric host materials based on 1,2-difluorophenyl units.[17–22] The significant aspect was to include a 1,2,3-trifluorophenyl unit to generate higher lateral polarity than exhibited by the 1,2-difluorophenyl systems. However, such a molecular architecture must be bent in order to accommodate three fluoro substituents in a row (*e.g.*, structures **VII** and **VIII**).



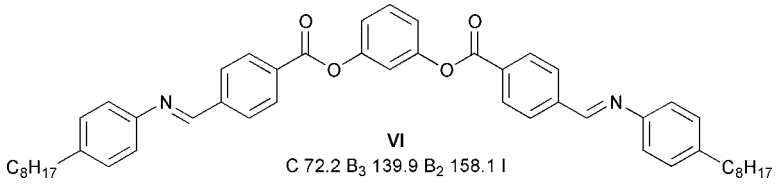
Synthesis

The synthetic routes to many of the intermediates are very similar to those employed for the synthesis of the high dielectric biaxiality ferroelectric host materials based on the 1,2-difluorophenyl moiety.[17,21,22] 1,2,3-Trifluorobenzene has two identical acidic protons which were sequentially exploited to introduce functional units and facilitate the synthesis of the final materials. Treatment of 1,2,3-trifluorobenzene (**1**) with *n*-butyllithium at −78 °C generated an aryllithium which was quenched with trimethyl borate to provide the boronic acid **2** after acid hydrolysis. Simple oxidation of boronic acid **2** provided a good yield of the phenol (**3**), which was *O*-alkylated to provide vital intermediates **4**. The remaining acidic proton of compounds **4** was exploited with *n*-butyllithium as described above to generate the functionalised boronic acids **5**. This time, however, the boronic acids were exploited in Suzuki coupling reactions,[23,24] which are invaluable in the synthesis of liquid crystals,[17,20–22,25] with the appropriate bromobiphenyls (**6**) to provide the final materials **7** in excellent overall yield (Scheme 1).

The introduction of alkyl chains can sometimes be a problem in highly functionalised aromatic units, but one truly excellent methodology, pioneered for the synthesis of ferroelectric host materials,[17] is illustrated in Scheme 2 for the generation of compounds **8**. The aryllithium of compound **1** is generated as described above, however, in this case it was quenched with an appropriate aldehyde to generate the benzylic alcohol, which was easily dehydrated with phosphorus(v) oxide to give the alkene, which was then hydrogenated, without isolation, using a palladium on carbon catalyst. The remaining acidic proton allowed the generation of the required arylboronic acids **9**,

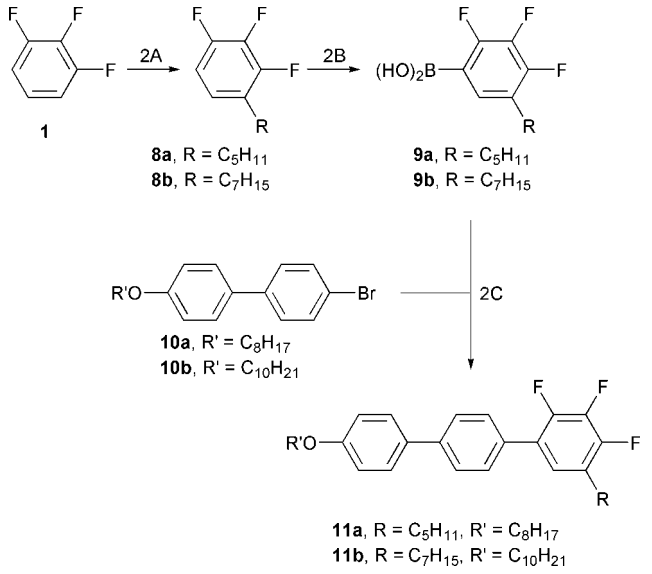


Scheme 1 *Reagents and conditions*: 1A: (i) *n*-BuLi; (ii) $(MeO)_3B$; (iii) HCl; 1B: H_2O_2, ether; 1C: RBr, NaH, DMF; 1D: $Pd(PPh_3)_4$, Na_2CO_3, DME, water.



VI

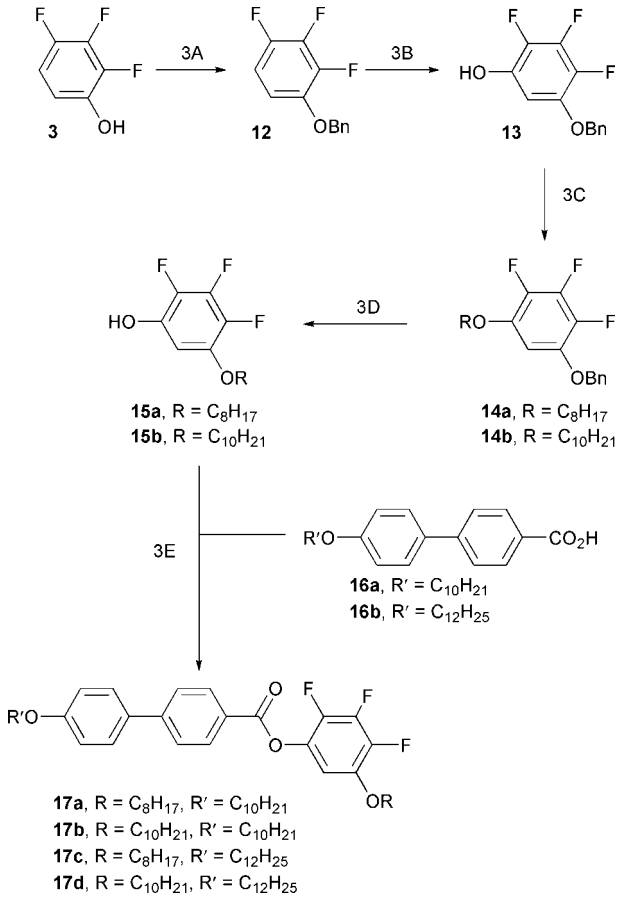
C 72.2 B_3 139.9 B_2 158.1 I



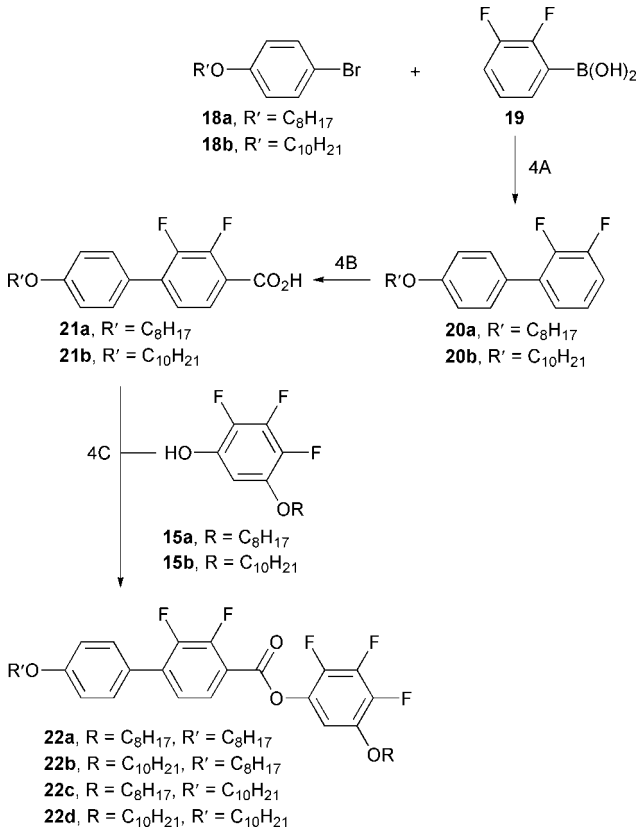
Scheme 2 *Reagents and conditions*: 2A: (i) *n*-BuLi; (ii) R″CHO; (iii) P_2O_5; (iv) H_2, Pd/C; 2B: (i) *n*-BuLi; (ii) $(MeO)_3B$; (iii) HCl; 2C: $Pd(PPh_3)_4$, Na_2CO_3, DME, water.

which were then coupled to the appropriate bromobiphenyls (**10**) to generate the final materials **11** (Scheme 2).

The preparation of esters based on the 1,2,3-trifluorophenyl moiety required the synthesis of phenols **15** (Scheme 3). These phenols could have been prepared from compounds **4** by oxidation of the boronic acids prepared through low-temperature lithiations; however, the benzyl-protected material was required for a wider range of materials (see Scheme 5), and so was prepared in high yield from phenol **3**. The



Scheme 3 *Reagents and conditions*: 3A: BnBr, Na_2CO_3, butanone; 3B: (i) *n*-BuLi; (ii) $(MeO)_3B$; (iii)AcOH, H_2O_2; 3C: RBr, K_2CO_3, acteone; 3D: 10% Pd/C, H_2, EtOAc, EtOH; 3E: DCC, DMAP.

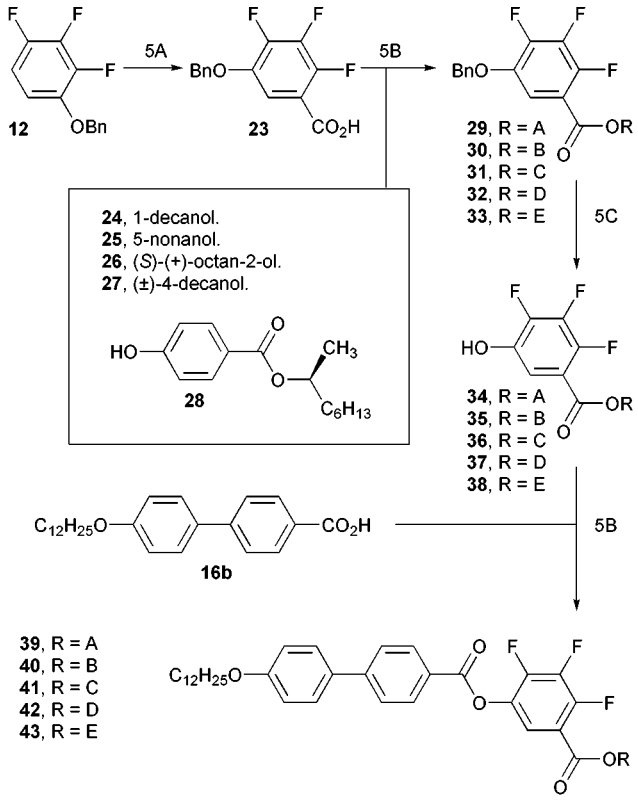


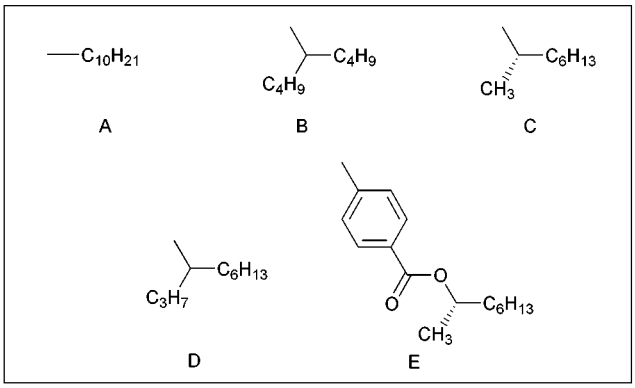
Scheme 4 *Reagents and conditions*: 4A: $Pd(PPh_3)_4$, Na_2CO_3, DME, water; 4B: (i) *n*-BuLi; (ii) CO_2; (iii) HCl; 4C: DCC, DMAP.

benzyl-protected material **12** was then involved in a low-temperature lithiation to generate the required phenol **13** in an identical manner to that already described (Scheme 1). *O*-Alkylations generated compounds **14**, which were then treated to catalytic hydrogenation to remove the benzyl protecting groups and generate phenols **15**. Phenols **15** were then esterified with standard biphenylcarboxylic acids **16** through convenient one-pot DCC–DMAP methodology to give high yields of final materials **17**.[26,27]

Scheme 4 shows a somewhat similar synthesis of final ester materials to those detailed in Scheme 3, however, fluoro-substituted biphenylcarboxylic acids were required. Compound **19** was involved in Suzuki couplings with aryl bromides **18** to provide the difluorobiphenyl moiety in compounds **20**, as reported previously. Exploitation of the acidic proton in compounds **20** with *n*-butyllithium and subsequent quenching with solid carbon dioxide generated the required acids **21** in good yield. DCC–DMAP reactions as discussed above provided the final ester materials (**22**) in excellent yield.

Scheme 5 considers the synthesis of a wide range of materials (**39**–**43**), but all are based on the same trifluorophenyl biphenylcarboxylate core unit seen in Schemes 3 and 4. However, here the terminal unit in the trifluorophenyl ring is an ester-linked moiety. This is where the benzyl-protected trifluorophenyl system **12** is essential, and lithiation to exploit the acidic proton allowed the synthesis of the carboxylic acid (**23**) through the use of low-temperature lithiation (see above). The carboxylic acid moiety was then functionalised with a variety of alcohols (**24**–**27**) and a more elaborate phenol (**28**) through the usual, highly efficient DCC–DMAP processes to give benzyl-protected terminal esters (**29**–**33**). Removal of the benzyl protecting group by catalytic hydrogenation give near-quantitative yields of the highly functionalised phenols **34**–**38**. Each of these phenols was then involved in a DCC–DAMP esterification with a standard biphenylcarboxylic acid (**16b**) to provide the desired final materials (**39**–**43**) in excellent yields.





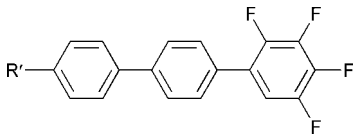
Scheme 5 *Reagents and conditions*: 5A: (i) *n*-BuLi; (ii) CO_2; (iii) HCl; 5B: DCC, DMAP; 5C: 10% Pd/C, H_2, EtOAc, EtOH.

Results and discussion

Some very interesting and unexpected results have been achieved through this fundamental research work, and at this time they cannot all be fully explained. Unlike more conventional liquid crystals, the final materials reported here all have a non-linear shape. The materials may be termed by some as possibly banana-shaped molecules, however, these systems are really hockey stick-shaped, and do not follow the usual pattern of symmetric bananas with the angular location in the centre of the molecule.

Compounds **7** and **11** (Table 1) have terphenyl cores without any linking groups, and so are quite rigid and the most hockey stick-shaped of all. Given the relatively short non-linear molecular structure compounds **7** and **11** may not be expected to generate mesophases. However, compounds **7a** and **7b** generate a mesophase which, by optical polarising microscopy, gives the appearance of a hexagonal columnar phase (see Fig. 1). Preliminary electrooptic investigations reveal that the molecules show ferroelectric switching between two states with equal numbers of oppositely switching regions, indicating a

Table 1 Transition temperatures (°C) for 2,3,4-trifluoroterphenyls (**7a**, **7b**, **11a**, **11b**)



Compound			Transition temperatures/°C				
No.	R	R′	Cr		Col_h		I
7a	$C_8H_{17}O$	C_5H_{11}	•	63.0	•	74.5	•
7b	$C_{10}H_{21}O$	C_7H_{15}	•	71.0	•	78.0	•
11a	C_5H_{11}	$C_8H_{17}O$	•	82.5	—	—	•
11b	C_7H_{15}	$C_{10}H_{21}O$	•	84.0	—	—	•

reduced symmetry mesophase, and perhaps suggesting that the molecules are tilted within the columns.[28] However, further work is required, and the phase should be designated as hexagonal columnar on the basis of the optical microscopy. It is thought that the columnar phase structure may arise through the formation of supramolecular aggregates which create a disc-shaped unit due to phenyl–fluorophenyl stacking of the molecules, something which is well established in many systems.[29,30] Compounds **11** are similar in shape to compounds **7**, but they are non-mesogenic because the melting points are too high.

The rather rigid molecular architectures of compounds **7** and **11** may well be restricting the conformations and thus preventing calamitic mesophases from being generated. Accordingly, materials with an ester-linkage (compounds **17**) were prepared in order to increase the rotation of the bent molecules and enhance the generation of conventional liquid crystalline phases.

As can be seen from Table 2, compounds **17** exhibit conventional mesomorphism in the form of the smectic C and the smectic A phases. However, closer examination through optical microscopy reveals the presence of reduced symmetry in the form of a helix with equal regions of opposite handedness present within the smectic C phase. On cooling at the transition temperature to the smectic C phase the focal-conic regions become lined, rather like transition bars; these lines quickly disappear on cooling, and the regions that were homeotropic in the smectic A phase give a schlieren texture typical of a smectic C phase. The schlieren texture appears to have different domains on the slight rotation of the analyser; the yellow coloured domain areas become blue on rotating the

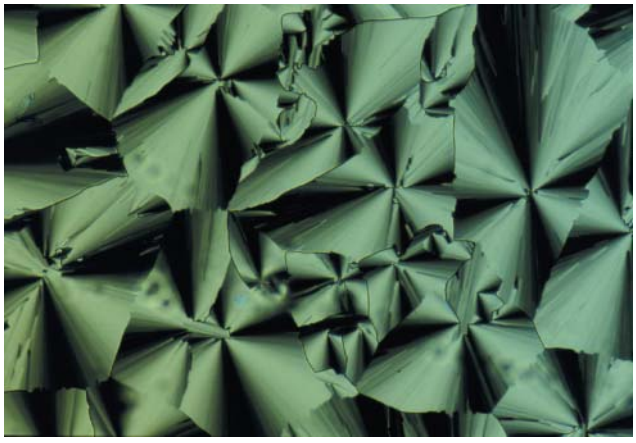
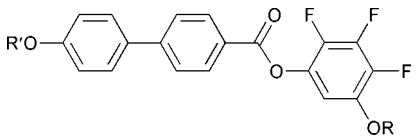


Fig. 1 A typical texture of the hexagonal columnar phase exhibited by compound **7b**.

Table 2 Transition temperatures (°C) for 2,3,4-trifluorophenyl biphenylcarboxylate esters (**17a–d**)



Compound			Transition temperatures/°C						
No.	R	R′	Cr		SmC		SmA		I
17a	C_8H_{17}	$C_{10}H_{21}$	•	77.5	•	(77.0)	•	85.0	•
17b	$C_{10}H_{21}$	$C_{10}H_{21}$	•	75.0	•	(71.0)	•	83.0	•
17c	C_8H_{17}	$C_{12}H_{25}$	•	68.5	•	79.0	•	83.0	•
17d	$C_{10}H_{21}$	$C_{12}H_{25}$	•	68.5	•	76.0	•	82.5	•

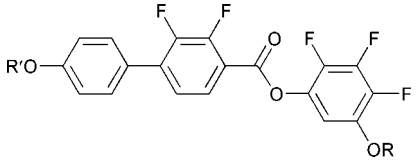
analyser clockwise, and become light yellow on anticlockwise rotation; an equal number of domains give the opposite effect. As the sample is cooled further into the smectic C phase the intensity of colour increases (as expected due to the increase in tilt angle) and the noticeability of the colour changes on rotating the analyser become far more intense.

At this point it should be mentioned that achiral banana-shaped systems that generate reduced symmetry mesophases normally consist of at least five aromatic rings, whereas compounds **17** are conventional three-ring structures that are more like hockey sticks than bananas, and hence would be expected to generate conventional mesomorphism rather than the so-called banana phases. The banana-shaped mesogens exhibit mesophases of reduced symmetry that are not analogous to conventional mesophases; they are the so-called banana phases, at present called B_1 to B_7, whereas compounds **17** exhibit conventional mesomorphism. The reduced symmetry regions in the smectic C phase of compounds **17** most likely arise because the conformationally flexible molecules can twist, and their unsymmetrical non-linear construction means that the twist is off-axis giving rise to two mirror-image orientations, which occur to equal extents. Recently, Watanabe[31] reported some achiral banana-shaped compounds that exhibited chiral smectic-like phases with chiral domains of opposite handedness, however, these phases were all unidentified in structure and not a conventional smectic C phase, whereas the optical textures of compounds **17** clearly show the smectic A and the smectic C phases. Electrooptic evaluation of compounds **17** reveals ferroelectric switching in opposite directions within the two different domain types which tends to support the optical microscopy in the phase identification as smectic C.

Fluoro substituents were introduced into the biphenylcarboxylate section of the esters (compounds **22**) in order to reduce melting points and generate a wider smectic C range, however, the smectic C phase has been eliminated (Table 3).

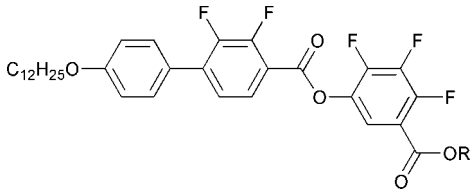
A range of compounds were prepared with an additional ester unit at the terminal position of the 2,3,4-trifluorophenyl moiety in order to determine the effect of enhanced conformational flexibility (Table 4). Except for the terminal ester linkage, compound **39** is identical to compound **17d**, and exhibits the same mesomorphism. However, the melting point of compound **39** is much lower, with a slightly lower reduction (17 °C) seen in the smectic C phase stability, but the additional ester linkage has enhanced the smectic A phase stability by 11 °C. As seen in compound **17d**, the smectic C phase of compound **39** has a reduced symmetry helical structure with equal regions of opposite handedness, as determined through optical microscopy and ferroelectric switching. Compounds with a branched terminal chain in linear analogues of compounds **40–43** tend to exhibit the smectic C alt phase (achiral or racemic) or the smectic C anti phase (chiral); hence it was thought worthwhile to prepare these bent-shaped compounds. Compound **40** is achiral and might be expected to generate the smectic C alt phase,[32] but despite a low melting point the branching in the chain is too severe to support any mesophases. Compound **41** possesses a chiral 1-methylheptyl chain, very commonly seen in antiferroelectric liquid crystals.[33] Fortunately, compound **41** has a very low melting point which allows liquid crystal phases to be generated. The branched chain has caused a 23.5 °C reduction in the smectic A phase stability (compared with compound **39**), and a monotropic smectic phase is generated at lower temperature which has been

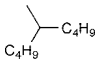
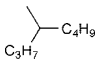
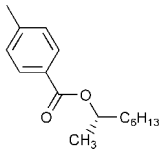
Table 3 Transition temperatures (°C) for 2,3,4-trifluorophenyl difluorobiphenylcarboxylate esters (**22a–d**)



Compound			Transition temperatures/°C						
No.	R	R′	Cr		SmC		SmA		I
22a	C_8H_{17}	C_8H_{17}	•	56.0	—	—	•	69.5	•
22b	$C_{10}H_{21}$	C_8H_{17}	•	67.0	—	—	•	70.0	•
22c	C_8H_{17}	$C_{10}H_{21}$	•	70.5	—	—	•	(69.0)	•
22d	$C_{10}H_{21}$	$C_{10}H_{21}$	•	57.5	—	—	•	70.0	•

Table 4 Transition temperatures (°C) for 2,3,4-trifluorophenyl biphenylcarboxylate esters with a range of ester-linked terminal units



Compound No.	R	Transition temperatures/°C
39		Cr 47.0 SmC 59.0 SmA 93.5 I
40		Cr 50.5 I
41		Cr 38.0 (SmX* 30.0) SmA* 70.0 I
42		Cr 38.0 SmX* 50.0 SmA 76.5 I
43		Cr 99.5 SmC*anti 137.5 SmC*ferri 141.0 SmC*ferro 166.0 SmA* 213.5 I

designated SmX*. By optical polarising microscopy, the SmX* phase is definitely helical (right handed), but the texture looks nothing like a conventional chiral smectic C (SmC*ferro) phase, quite possibly a chiral smectic C anti (SmC*anti), but more like smectic A with strong blue iridescence where the optically extinct homeotropic texture would be. Electrooptic switching reveals a ferroelectric-like behaviour, which would appear to rule out the antiferroelectric phase, but not necessarily. Certainly very interesting results, however, compound **42** is even more remarkable. Compound **42** is most certainly racemic (zero optical rotation for both compound **42** and the original (±)-decan-4-ol), yet it exhibits identical mesomorphic and electrooptical behaviour to the enantiomerically pure chiral compound **41**, including the reduced symmetry SmX* phase. The melting points of compounds **41** and **42** are identical, but surprisingly, in view of the much larger branch unit of compound **42**, the transition temperatures are higher; the smectic A phase stability is only slightly higher, but the SmX* phase stability is 20 °C higher. The larger branch unit has been shown to enhance the antiferroelectric phase stability in conventional linear systems,[34] so this finding could lead to the conclusion that the SmX* phase is in fact a smectic C antiferroelectric (SmC*anti) phase, or the higher transition temperatures could simply be due to some degree of space-filling in the bent molecular structure allowing a better packing. The SmX* phase has been examined for both compounds (**41** and **42**) by optical polarising microscopy (thin glass slides with and without cover-slips and free-standing films) and electro-optic switching, and is most certainly the same phase (confirmed by miscibility). Fig. 2 shows the optical texture of the SmX* phase of compound **42** using a microscope slide and cover-slip. The focal-conic areas are clearly seen, but they are not cracked as might be expected for the tilted smectic C phase, and where the homeotropic regions were in the smectic A phase the appearance is now brightly speckled (not a schlieren texture). Fig. 3 shows compound **42** as a free-standing film; here the region that was homeotropic in the smectic A phase is now strongly iridescent (blue) with mottled markings.

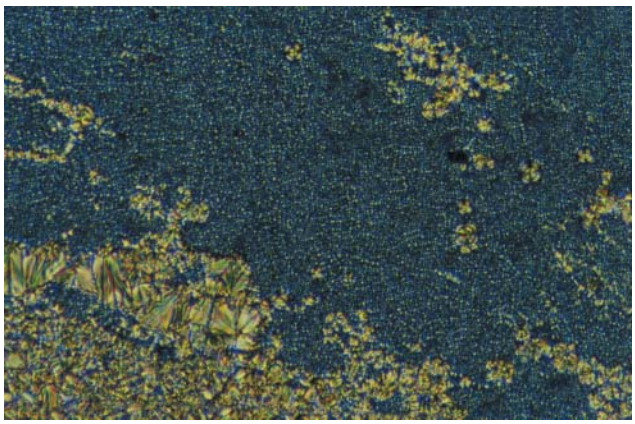


Fig. 2 The focal-conic and speckled textures exhibited by the SmX* phase of racemic compound **42** between a microscope slide and cover-slip.

The reduced symmetry of the SmX* phase in the racemic compound (**42**) can be explained in the same way as for compounds **17** (see above), but here only one handedness of reduced symmetry has been found, perhaps leading to the

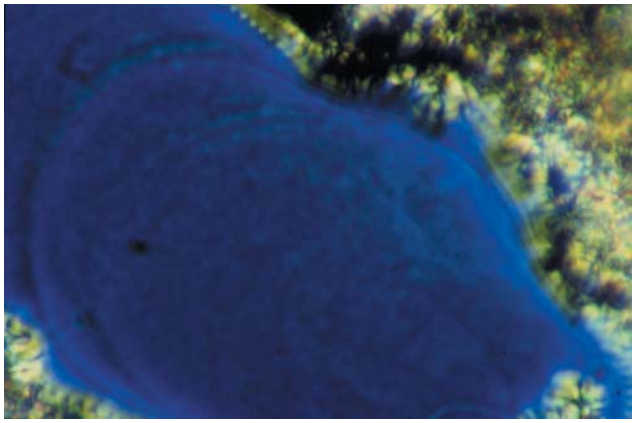
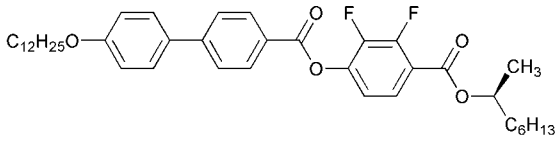


Fig. 3 A free-standing film showing the iridescent texture exhibited by the SmX* phase of racemic compound **42**.

conclusion that compound **42** is not racemic. However, the reduced symmetry in terms of optical rotation appears as strong as for the enantiomerically pure compound (**41**), so possibly there is the ever so slightest enantiomeric excess in the 'racemic' compound (**42**) which tips the balance so that the sample shows solely a right handed helix.

Compound **43** has an additional aromatic ring and an additional ester linkage when compared with compound **41**, which on the one hand exaggerates the bend to more like a banana-shape, perhaps reducing the tendency to generate liquid crystal phases, yet on the other hand the molecular length is much increased and there is more conformational flexibility, enhancing the generation of liquid crystal phases. As can be seen from Table 4, compound **43** exhibits liquid crystal phases to very high temperatures, much higher than the previously reported banana-shaped compounds, which have more aromatic rings in their structure.[16]

The mesophase morphology of compound **43** is identical to the analogous linear systems (*e.g.*, compound **IX**), but the transition temperatures are much higher showing that the additional ester-linked phenyl ring outweighs the molecular bend. It is interesting to compare compound **IX** with compound **41**, where the only differences in the structures are the extra fluoro substituent and the bend, which have caused a reduction in the smectic A phase stability by 40 °C and a change of mesophase morphology to the SmX* phase (see above).



IX

Cr 52.8 SmC*anti 94.0 SmC*ferri 95.2 SmC*ferro 99.5 SmA* 110.0 I

Summary

Some very interesting materials have been synthesised and evaluated. Where the core structure is conformationally rigid such as in terphenyls **7** and **11**, there is no scope for the generation of calamitic mesophases. However, the polar nature of the molecules facilitates self-assembly into disc-shaped entities, through phenyl–fluorophenyl stacking, which then pack in a columnar mesophase. The introduction of an ester linking group (compounds **17**) allows for much greater conformational flexibility which facilitates the generation of calamitic liquid crystalline phases. The subtle combination of a bent molecular structure, which can twist, allows for reduced symmetry in the smectic C phase (equal proportions of opposite handedness), despite the achiral molecular structure.

An unidentified reduced symmetry liquid crystalline phase (SmX*) was discovered in a non-racemic chiral compound (**41**). The SmX* phase has an iridescent optical texture and is obviously of reduced symmetry with a right-handed helical structure. Although electrooptic studies indicate that the phase is possibly ferroelectric, the optical texture does not support this finding. An analogous material (compound **42**) was prepared with a racemic terminal chain, however, despite the racemic nature an identical mesophase morphology was found, with the SmX* phase of reduced symmetry solely exhibiting one handedness (right handed helix).

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**, **7b**, **11a**, **11b**, **17a–d**, **22a–d**, **39–43**). 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**, **7b**, **11a**, **11b**, **17a–d**, **22a–d**, **39–43**) was checked by HPLC analysis (Merck-Hitachi with Merck RP 18 column, Cat. No. 16 051) and were found to be >99.9% pure in each case.

Compounds **2**, **3**, **6a**, **6b**, **10a**, **10b**, **18a**, **18b**, **19**, **20a** and **20b**,[17] and **16a**, **16b** and **28**,[27] were prepared as described previously. All other simple starting reagents and solvents are commercially available, and were used as supplied.

1,2,3-Trifluoro-4-octyloxybenzene (4a)

A solution of 1-bromooctane (3.10 g, 0.016 mol) in DMF (20 cm^3) was added to a stirred mixture of compound **3** (2.50 g, 0.017 mol), and sodium hydride (0.60 g, 0.020 mol, 80% in oil) in DMF (30 cm^3) under an atmosphere of dry nitrogen. The reaction mixture was stirred for 36 h at room temperature (GLC analysis revealed a complete reaction), washed with water, and the product was extracted into ether (twice). The combined ethereal extracts were washed with 5% sodium hydroxide (twice), washed with brine, dried ($MgSO_4$), and the solvent was removed *in vacuo*. The residue was purified by column chromatography [silica gel, hexane] to give a colourless liquid.

Yield 4.06 g (98%); δ_H (270 MHz; $CDCl_3$) 0.87 (3H, t), 1.32 (8H, m), 1.45 (2H, quintet), 1.79 (2H, quintet), 3.99 (2H, t), 6.64 (1H, m), 6.85 (1H, m); IR ν_{max}(KBr)/cm^{-1} 2930, 2860, 1630, 1510, 1265, 1085, and 1020 cm^{-1}; MS *m/z* 260(M^+).

2,3,4-Trifluoro-5-octyloxyphenylboronic acid (5a)

A solution of *n*-butyllithium (6.40 cm^3, 0.016 mol, 2.5 mol dm^{-3} in hexanes) was added dropwise to a stirred, cooled (−78 °C) solution of compound **4a** (4.06 g, 0.016 mol) in THF (60 cm^3) under dry nitrogen. The reaction mixture was stirred for 3 h at −78 °C, and trimethyl borate (3.33 g, 0.032 mol) added dropwise at −78 °C. The reaction mixture was allowed to warm to room temperature and hydrochloric acid (50 cm^3, 10%) was added. The reaction mixture was stirred

for 1 h, washed with water and the product was extracted into ether (twice). The combined ethereal extracts were washed with brine, dried ($MgSO_4$), and the was solvent removed *in vacuo* to yield a pale yellow solid.

Yield 4.74 g (100%); δ_H (270 MHz; $CDCl_3$) 0.81 (3H, t), 1.20 (10H, m), 1.74 (2H, quintet), 3.97 (2H, t), 6.78 (1H, ddd), no OH absorption observed; IR ν_{max}(KBr)/cm^{-1} 3500–3100, 2960, 2860, 1510, 1470, 1380, 1120, 1085, 1020, 880, 800, 705 cm^{-1}; MS *m*/*z* 304 (M^+).

2,3,4-Trifluro-5-octyloxy-4″-pentylterphenyl (7a)

A solution of compound **5a** (4.74 g, 0.016 mol) in MTBE (25 cm^3) was added dropwise to a stirred, warmed (35 °C) suspension of compound **6a** (3.39 g, 0.011 mol), $Pd(PPh_3)_4$ (0.38 g, 0.33 mmol), and aqueous sodium carbonate (11.0 cm^3, 2.0 mol dm^{-3}) in MTBE (40 cm^3) under dry nitrogen. The reaction mixture was heated under reflux for 6 h, cooled to room temperature and water was added. The product was extracted into ether (twice) and the combined ethereal extracts were washed with brine, and dried ($MgSO_4$). The solvent was removed *in vacuo* and the crude product was purified by column chromatography [silica gel, hexane–ethyl acetate (20 : 1)] to yield a colourless solid, which was recrystallised from ethanol to yield colourless crystals.

Yield 3.87 g (74%); transitions (°C) Cr 63.0 Col_h 74.5 I; δ_H (270 MHz; $CDCl_3$) 0.88 (3H, t), 0.91 (3H, t), 1.36 (12H, m), 1.47 (2H, quintet), 1.67 (2 H, quintet), 1.82 (2H, quintet), 2.66 (2H, t), 4.05 (2H, t), 6.79 (1H, ddd), 7.28 (2H, d), 7.54 (4H, d), 7.66 (2H, d); IR ν_{max}(KBr)/cm^{-1} 2930, 2860, 1540, 1500, 1475, 1400, 1375, 1260, 1230, 1105, 810, 700, 505; MS *m*/*z* 482 (M^+); found: C, 77.06%; H, 7.67%; $C_{31}H_{37}FO$ requires: C, 77.15%; H, 7.73%.

5-Decyloxy-2,3,4-trifluoro-4″-heptylterphenyl (7b)

Quantities: compound **5b** (5.15 g, 0.016 mol), compound **6b** (3.64 g, 0.011 mol), $Pd(PPh_3)_4$ (0.38 g, 0.33 mmol), and aqueous sodium carbonate (11.0 cm^3, 2.0 mol dm^{-3}). The experimental procedure was as described for the preparation of compound **7a**.

Yield 2.20 g (38%); transitions (°C) Cr 71.0 Col_h 78.0 I; δ_H (270 MHz; $CDCl_3$) 0.88 (3H, t), 0.91 (3H, t), 1.34 (20H, m), 1.44 (2H, quintet), 1.67 (2H, quintet), 1.82 (2H, quintet), 2.64 (2H, t), 4.00 (2H, t), 6.76 (1H, ddd), 7.30 (2H, d), 7.52 (4 H, d), 7.66 (2 H, d); IR ν_{max}(KBr)/cm^{-1} 2930, 2860, 1530, 1510, 1480, 1405, 1375, 1255, 1230, 1105, 810, 700, 505; MS *m*/*z* 538 (M^+); found: C, 77.95%; H, 8.40%; $C_{35}H_{45}F_3O$ requires: C, 78.03%; H, 8.42%.

1,2,3-Trifluoro-4-pentylbenzene (8a)

A solution of *n*-butyllithium (7.60 cm^3, 0.019 mol, 2.5 mol dm^{-3} in hexanes) was added dropwise to a stirred, cooled (−78 °C) solution of compound **1** (2.50 g, 0.019 mol) in THF (60 cm^3) under dry nitrogen. The reaction mixture was stirred at −78 °C for 3 h and a solution of pentanal (1.65 g, 0.019 mol) in THF (20 cm^3) was added dropwise. The reaction mixture was allowed to warm to room temperature and a solution of ammonium chloride (40 cm^3) was added. The reaction mixture was stirred for 1 h and the product was extracted into ether (twice). The combined ethereal extracts were washed with brine, dried ($MgSO_4$), and the solvent was removed *in vacuo*. The residue was dissolved in DCM (100 cm^3) and stirred over phosphorus(v) oxide (5.40 g, 0.038 mol) for 24 h. The reaction mixture was filtered, the DCM was removed *in vacuo*, and residue was dissolved in ethanol. Palladium on charcoal (0.02 g, 10%) was added and the suspension stirred under an atmosphere of hydrogen for 24 h. The reaction mixture was filtered and the solvent was removed *in vacuo* to yield a colourless oil.

Yield 3.68 g (96%); δ_H (270 MHz; $CDCl_3$) 0.90 (3H, t), 1.32 (4H, m), 1.58 (2H, quintet), 2.61 (2H, t), 6.85 (2H, m), IR ν_{max}(KBr)/cm^{-1} 2940, 2860, 1510, 1480, 1305, 1035, 810; MS *m*/*z* 202 (M^+).

2,3,4-Trifluoro-5-pentylphenylboronic acid (9a)

Quantities: compound **8a** (1.22 g, 6.00 mmol), *n*-butyllithium (2.40 cm^3, 6.00 mmol, 2.5 mol dm^{-3} in hexanes), and trimethyl borate (1.26 g, 12.00 mmol). The experimental procedure was as described for the preparation of compound **5a**.

Yield 1.40 g (94%); δ_H (270 MHz; $CDCl_3$) 0.89 (3H, t), 1.32 (4H, m), 1.59 (2H, quintet), 2.61 (2H, t), 4.45 (2H, br s), 7.38 (1H, ddd); IR ν_{max}(KBr)/cm^{-1} 3500–3100, 2940, 2870, 1620, 1470, 1355, 1220, 1080, 1040, 990, 900, 800, 750, 695, 625; MS *m*/*z* 246 (M^+).

2,3,4-Trifluoro-4″-octyloxy-5-pentylterphenyl (11a)

Quantities: compound **9a** (1.40 g, 5.70 mmol), compound **10a** (1.58 g, 4.40 mmol), $Pd(PPh_3)_4$ (0.15 g, 0.13 mmol), and aqueous sodium carbonate (4.40 cm^3, 2.0 mol dm^{-3}). The experimental procedure was as described for the preparation of compound **7a**.

Yield 1.61 g (76%); transitions (°C) Cr 82.5 I; δ_H (270 MHz; $CDCl_3$) 0.89 (6H, 2 × t), 1.31 (12H, m), 1.47 (2H, quintet), 1.63 (2H, quintet), 1.81 (2H, quintet), 2.67 (2H, t), 4.00 (2H, t), 7.00 (3H, m), 7.54 (2H, d), 7.56 (2H, d), 7.63 (2H, d); IR ν_{max}(KBr)/cm^{-1} 2930, 2865, 1735, 1540, 1495, 1470, 1420, 1400, 1250, 1210, 1175, 1110, 1050, 995, 890, 850, 820, 700, 505; MS *m*/*z* 482 (M^+); found: C, 77.12%; H, 7.70%; $C_{31}H_{37}F_3O$ requires: C, 77.15%; H, 7.73%.

4″-Decyloxy-2,3,4-trifluoro-5-heptylterphenyl (11b)

Quantities: compound **9b** (1.60 g, 5.84 mmol), compound **10b** (1.75 g, 4.50 mmol), $Pd(PPh_3)_4$ (0.15 g, 0.13 mmol), and aqueous sodium carbonate (4.40 cm^3, 2.0 mol dm^{-3}). The experimental procedure was as described for the preparation of compound **7a**.

Yield 1.65 g (68%); transitions (°C) Cr 84.0 I; δ_H (270 MHz; $CDCl_3$) 0.89 (6H, 2 × t), 1.31 (20H, m), 1.47 (2H, quintet), 1.63 (2H, quintet), 1.81 (2H, quintet), 2.67 (2H, t), 4.00 (2H, t), 7.00 (3H, m), 7.54 (2H, d), 7.56 (2H, d), 7.63 (2H, d); IR ν_{max}(KBr)/cm^{-1} 2930, 2865, 1735, 1540, 1495, 1470, 1420, 1400, 1250, 1210, 1175, 1110, 1050, 995, 890, 850, 820, 700, 505; MS *m*/*z* 538 (M^+); found: C, 77.91%; H, 8.38%; $C_{35}H_{45}F_3O$ requires: C, 78.03%; H, 8.42%.

1-Benzyloxy-2,3,4-trifluorobenzene (12)

A solution of compound **3** (13.64 g, 0.092 mol) in butanone (30 cm^3), was added dropwise to a warmed, stirred mixture of benzyl bromide (17.31 g, 0.101 mol), and sodium carbonate (19.50 g, 0.184 mol) in butanone (100 cm^3). The stirred reaction mixture was heated under reflux for 24 h (GLC analysis revealed a complete reaction), cooled to room temperature, washed with water, and the product was extracted into ether (twice). The combined ethereal extracts were washed with 5% sodium hydroxide, washed with brine, dried ($MgSO_4$), and the solvent was removed *in vacuo* to yield a pale yellow solid which was recrystallised from ethanol to give colourless crystals.

Yield 19.89 g (90%); δ_H (270 MHz; $CDCl_3$) 5.15 (2H, s), 6.64 (1H, m), and 6.85 (1H, m), 7.40 (5H, m); IR ν_{max}(KBr)/cm^{-1} 2930, 2860, 1630, 1510, 1265, 1085, 1020; MS *m*/*z* 238 (M^+).

5-Benzyloxy-2,3,4-trifluorophenol (13)

A solution of *n*-butyllithium (17.00 cm^3, 0.043 mol, 2.5 mol dm^{-3} in hexanes) was added dropwise to a stirred, cooled (−78 °C) solution compound **12** (10.00 g, 0.042 mol) in THF (60 cm^3) under dry nitrogen. The reaction mixture was

stirred for 3 h at −78 °C and trimethyl borate (8.74 g, 0.084 mol) added dropwise at −78 °C. The reaction mixture was allowed to warm to room temperature, acidified with glacial acetic acid (10.0 cm^3), and hydrogen peroxide (17.0 cm^3, 100 vol in 20.0 cm^3 of water) added dropwise. The reaction mixture was heated under reflux for 24 h, cooled to room temperature, washed with water, and the product was extracted into ether (twice). The combined ethereal extracts were washed with brine, dried ($MgSO_4$), and the solvent was removed *in vacuo* to yield a colourless solid which was recrystallised from ethanol to yield colourless crystals.

Yield 9.80g (93%); δ_H (270 MHz; $CDCl_3$) 5.00 (1H, br, s), 5.08 (2H, s), 6.46 (1H, ddd), 7.37 (5H, m); IR ν_{max}(KBr)/cm^{-1} 3415 (br), 1635, 1530, 1510, 1380, 1270, 1220, 1200, 1140, 1075, 995, 940, 825, 745, 695; MS *m*/*z* 254 (M^+).

1-Benzyloxy-2,3,4-trifluoro-5-octyloxybenzene (14a)

A suspension of compound **13** (3.00 g, 0.012 mol), 1-bromo-octane (2.28 g, 0.012 mol) and potassium carbonate (3.26 g, 0.024 mol) in acetone (60 cm^3) was heated under reflux for 24 h. The reaction mixture was cooled to room temperature, washed with water, and the product was extracted into ether (twice). The combined ethereal extracts were washed with 5% sodium hydroxide, dried ($MgSO_4$), and the solvent was removed *in vacuo* to yield a colourless oil.

Yield 4.15 g (96%); δ_H (270 MHz; $CDCl_3$) 0.88 (3H, t), 1.27 (10H, m), 1.74 (2H, quintet), 3.92 (2H, t) 5.10 (2H, s), 7.35 (1H, ddd), 7.39 (5H, m); IR ν_{max}(KBr)/cm^{-1} 2930, 2860, 1740, 1630, 1530, 1500, 1460, 1400, 1380, 1255, 1100, 1020, 950, 805, 750, 700; MS *m*/*z* 366 (M^+).

2,3,4-Trifluoro-5-octyloxyphenol (15a)

A mixture of compound **14a** (4.15 g, 0.011 mol), and 10% palladium on charcoal (0.50 g) in ethyl acetate–ethanol (100.0 cm^3, 2 : 1) was stirred under an atmosphere of hydrogen at room temperature and pressure for 24 h (TLC analysis revealed a complete reaction). The reaction mixture was filtered and the solvent was distilled off to leave a colourless liquid.

Yield 3.12 g (100%); δ_H (270 MHz; $CDCl_3$) 0.89 (3H, t), 1.23 (10H, m), 1.78 (2H, quintet), 3.95 (2H, t) 5.58 (1H, br s), 6.43 (1H, ddd); IR ν_{max}(KBr)/cm^{-1} 3500–3100, 2930, 2860, 1710, 1630, 1510, 1470, 1400, 1375, 1270, 1150, 1085, 990, 945, 825, 710, 560; MS *m*/*z* 276 (M^+).

2,3,4-Trifluoro-5-octyloxyphenyl 4′-decyloxybiphenyl-4-carboxylate (17a)

A solution of compound **15a** (0.41 g, 1.50 mmol), compound **16a** (0.53 g, 1.50 mmol), DCC (0.31 g, 1.50 mmol), and DMAP (0.02 g, 0.15 mmol) in DCM (50 cm^3) was stirred at room temperature for 24 h. The solvent was removed *in vacuo* and the residue was purified by column chromatography [silica gel, hexane–ethyl acetate (10 : 1)] to yield a colourless solid, which was recrystallised from ethanol to yield colourless crystals.

Yield 0.79 g (86%); transitions (°C) Cr 77.5 (SmC 77.0) SmA 85.0 I; δ_H (270 MHz; $CDCl_3$) 0.88 (6H, 2 × t), 1.31 (24H, m), 1.46 (4H, m), 3.99 (2H, t), 4.02 (H, t), 6.68 (1H, ddd), 7.01 (2H, d), 7.60 (2H, d), 7.70 (2H, d), 8.22 (2H, d); IR ν_{max}(KBr)/cm^{-1} 2930, 2860, 1745, 1605, 1525, 1505, 1475, 1380, 1285, 1260, 1195, 1145, 1090, 1050, 1015, 930, 830, 765, 720; MS *m*/*z* 612 (M^+); found: C, 72.47%; H, 7.69%; $C_{37}H_{47}F_3O_4$ requires: C, 72.52%; H, 7.73%.

5-Decyloxy-2,3,4-trifluorophenyl 4′-decyloxybiphenyl-4-carboxylate (17b)

Quantities: compound **15b** (0.46 g, 1.50 mmol), compound **16a** (0.53 g, 1.50 mmol), DCC (0.31 g, 1.50 mmol), and DMAP (0.02 g, 0.15 mmol). The experimental procedure was as described for the preparation of compound **17a**.

Yield 0.80 g (83%); transitions (°C) Cr 75.0 (SmC 71.0) SmA 83.0 I; δ_H (270 MHz; $CDCl_3$) 0.88 (6H, 2 × t), 1.31 (28H, m), 1.46 (4H, m), 4.00 (2H, t), 4.04 (2H, t), 6.69 (1H, ddd), 7.03 (2H, d), 7.62 (2H, d), 7.70 (2H, d), 8.22 (2H, d); IR ν_{max}(KBr)/cm^{-1} 2925, 2865, 1740, 1600, 1530, 1505, 1465, 1375, 1290, 1255, 1200, 1150, 1090, 1050, 1010, 930, 830, 765, 720; MS *m*/*z* 640 (M^+); found: C, 72.99%; H, 7.95%; $C_{39}H_{51}F_3O_4$ requires: C, 73.10%; H, 8.02%.

2,3,4-Trifluoro-5-octyloxyphenyl 4′-dodecyloxybiphenyl-4-carboxylate (17c)

Quantities: compound **15a** (0.41 g, 1.50 mmol), compound **16b** (0.57 g, 1.50 mmol), DCC (0.31 g, 1.50 mmol), and DMAP (0.02 g, 0.15 mmol). The experimental procedure was as described for the preparation of compound **17a**.

Yield 0.94 g (98%); transitions (°C) Cr 68.5 SmC 79.0 SmA 83.0 I; δ_H (270 MHz; $CDCl_3$) 0.88 (6H, 2 × t), 1.29 (28H, m), 1.44 (4H, m), 3.98 (2H, t), 4.04 (2H, t), 6.69 (1H, ddd), 7.06 (2H, d), 7.65 (2H, d), 7.72 (2H, d), 8.22 (2H, d); IR ν_{max}(KBr)/cm^{-1} 2925, 2850, 1730, 1610, 1520, 1510, 1480, 1380, 1285, 1260, 1195, 1145, 1090, 1050, 1015, 930, 830, 765, 720; MS *m*/*z* 640 (M^+); found: C, 73.04%; H, 8.00%; $C_{39}H_{51}F_3O_4$ requires: C, 73.10%; H, 8.02%.

5-Decyloxy-2,3,4-trifluorophenyl 4′-dodecyloxybiphenyl-4-carboxylate (17d)

Quantities: compound **15b** (0.46 g, 1.50 mmol), compound **16b** (0.57 g, 1.50 mmol), DCC (0.31 g, 1.50 mmol), and DMAP (0.02 g, 0.15 mmol). The experimental procedure was as described for the preparation of compound **17a**.

Yield 0.87 g (87%); transitions (°C) Cr 68.5 SmC 76.0 SmA 82.5 I; δ_H (270 MHz; $CDCl_3$) 0.90 (6H, 2 × t), 1.31 (32H, m), 1.46 (4H, m), 3.98 (2H, t), 4.04 (2H, t), 6.69 (1H, ddd), 7.01 (2H, d), 7.60 (2H, d), 7.70 (2H, d), 8.22 (2H, d); IR ν_{max}(KBr)/cm^{-1} 2935, 2855, 1730, 1610, 1525, 1500, 1470, 1370, 1285, 1255, 1210, 1150, 1090, 1050, 1010, 930, 830, 765, 720; MS *m*/*z* 668 (M^+); found: C, 73.58%; H, 8.21%; $C_{41}H_{55}F_3O_4$ requires: C, 73.62%; H, 8.29%.

2,3-Difluoro-4′-octyloxybiphenyl-4-carboxylic acid (21a)

A solution of *n*-butyllithium (4.00 cm^3, 10.0 mmol, 2.5 mol dm^{-3} in hexanes) was added dropwise to a stirred, cooled (−78 °C) solution of compound **20a** (3.18 g, 10.0 mmol) in THF (150 cm^3) under dry nitrogen. The reaction mixture was maintained at −78 °C for 3 h, poured onto solid carbon dioxide (excess), and allowed to warm to room temperature. The mixture was stirred with 10% hydrochloric acid for 1 h, washed with water, and the product was extracted into ether (twice). The combined ethereal extracts were washed with brine, dried ($MgSO_4$), and the solvent was removed *in vacuo* to yield a colourless solid which was recrystallised from ethanol to give colourless crystals.

Yield 3.24 g, (90%); δ_H (270 MHz; $CDCl_3$) 0.90 (3H, t), 1.31 (10H, m), 1.72 (2H, quintet), 4.00 (2H, t), 6.98 (2H, d), 7.29 (1H, ddd), 7.53 (2H, d), 7.81 (1H, ddd); IR ν_{max}(KBr)/cm^{-1} 3500–3100 broad, 2930, 2860, 2540, 1680, 1610, 1460, 1430, 1300, 1180, 1125, 950, 870, 820, 770, 705, 550, 490; MS *m*/*z* 362 (M^+).

2,3,4-Trifluoro-5-octyloxyphenyl 2,3-difluoro-4′-octyloxybiphenyl-4-carboxylate (22a)

Quantities: compound **15a** (0.41 g, 1.50 mmol), compound **20a** (0.49 g, 1.50 mmol), DCC (0.31 g, 1.50 mmol), and DMAP (0.02 g, 0.15 mmol). The experimental procedure was as described for the preparation of compound **17a**.

Yield 0.72 g (82%); transitions (°C) Cr 56.0 SmA 69.5 I; δ_H

(270 MHz; $CDCl_3$) 0.88 (6H, 2 × t), 1.31 (20H, m), 1.46 (4H, m), 3.99 (2H, t), 4.02 (2H, t), 6.80 (1H, ddd), 7.30 (1H, ddd), 7.60 (2H, d), 7.90 (2H, d), 8.21 (1H, ddd); IR ν_{max}(KBr)/cm^{-1} 2930, 2860, 1745, 1605, 1525, 1505, 1475, 1380, 1285, 1260, 1195, 1145, 1090, 1050, 1015, 930, 830, 765, 720; MS *m/z* 620 (M^+); found: C, 67.70%; H, 6.60%; $C_{35}H_{41}F_5O_4$ requires: C, 67.73%; H, 6.66%.

5-Decyloxy-2,3,4-trifluorophenyl 2,3-difluoro-4′-octyloxybiphenyl-4-carboxylate (22b)

Quantities: compound **15a** (0.37 g, 1.21 mmol), compound **21b** (0.46 g, 1.21 mmol), DCC (0.25 g, 1.21 mmol), and DMAP (0.01 g, 0.12 mmol). The experimental procedure was as described for the preparation of compound **17a**.

Yield 0.60 g (74%); transitions (°C) Cr 67.0 SmA 70.0 I; δ_H (270 MHz; $CDCl_3$) 0.88 (6H, 2 × t), 1.33 (24H, m), 1.46 (4H, m), 3.98 (2H, t), 4.02 (2H, t), 6.80 (1H, ddd), 7.31 (1H, ddd), 7.64 (2H, d), 7.89 (2H, d), 8.20 (1H, ddd); IR ν_{max}(KBr)/cm^{-1} 2930, 2860, 1730, 1620, 1525, 1505, 1460, 1390, 1285, 1245, 1180, 1145, 1085, 1050, 1010, 925, 830, 765, 720; MS *m/z* 648 (M^+); found: C, 68.44%; H, 6.93%; $C_{37}H_{45}F_5O_4$ requires: C, 68.50%; H, 6.99%.

2,3,4-Trifluoro-5-octyloxyphenyl 4′-decyloxy-2,3-difluorobiphenyl-4-carboxylate (22c)

Quantities: compound **15a** (0.41 g, 1.50 mmol), compound **21b** (0.53 g, 1.50 mmol), DCC (0.31 g, 1.50 mmol), and DMAP (0.02 g, 0.15 mmol). The experimental procedure was as described for the preparation of compound **17a**.

Yield 0.74 g (80%); transitions (°C) Cr 70.5 (SmA 69.0) I; δ_H (270 MHz: $CDCl_3$) 0.89 (6H, 2 × t), 1.31 (24H, m), 1.44 (4H, m), 3.96 (2H, t), 4.00 (2H, t), 6.78 (1H, ddd), 7.29 (1H, ddd), 7.62 (2H, d), 7.88 (2H, d) and 8.18 (1H, ddd); IR ν_{max}(KBr)/cm^{-1} 2925, 2855, 1740, 1610, 1520, 1500, 1465, 1385, 1290, 1255, 1190, 1155, 1090, 1050, 1015, 930, 830, 765, 720; MS *m/z* 648 (M^+); found: C, 68.42%; H, 6.99%; $C_{37}H_{45}F_5O_4$ requires: C, 68.5%; H, 6.99%.

5-Decyloxy-2,3,4-trifluorophenyl 4′-decyloxy-2,3-difluorobiphenyl-4-carboxylate (22d)

Quantities: compound **15b** (0.30 g, 1.00 mmol), compound **21b** (0.39 g, 1.00 mmol), DCC (0.21 g, 1.00 mmol), and DMAP (0.01 g, 0.10 mmol). The experimental procedure was as described for the preparation of compound **17a**.

Yield 0.49 g (71%); transitions (°C) Cr 57.5 SmA 70.0 I; δ_H (270 MHz; $CDCl_3$) 0.89 (6H, 2 × t), 1.31 (28H, m), 1.44 (4H, m), 3.96 (2H, t), 4.02 (2H, t), 6.82 (1H, ddd), 7.29 (1H, ddd), 7.66 (2H, d), 7.88 (2H, d), 8.19 (1H, ddd); IR ν_{max}(KBr)/cm^{-1} 2930, 2850, 1720, 1615, 1520, 1515, 1465, 1385, 1290, 1240, 1175, 1140, 1080, 1055, 1005, 930, 825, 760, 720; MS *m/z* 676 (M^+); found: C, 69.18%; H, 7.25%; $C_{39}H_{49}F_5O_4$ requires: C, 69.21%; H, 7.30%.

(±)-1-Propylheptyl 5-benzyloxy-2,3,4-trifluorobenzoate (32)

Quantities: compound **23** (0.71 g, 2.50 mmol), compound **27** (0.40 g, 2.50 mmol), DCC (0.52 g, 2.50 mmol), and DMAP (0.030 g, 0.250 mmol). The experimental procedure was as described for the preparation of compound **17a**.

Yield 0.52 g (98%); δ_H (270 MHz; $CDCl_3$) 0.92 (6H, 2 × t), 1.26 (10H, m), 1.90 (4H, m), 5.12 (1H quintet), 5.16 (2H, s), 7.40 (6H, m); IR ν_{max}(KBr)/cm^{-1} 2936, 2861, 2122, 1720, 1488, 1363, 1298, 1121, 1051; MS *m/z* 422 (M^+).

(±)-1-Propylheptyl 2,3,4-trifluoro-5-hydroxybenzoate (37)

Quantities: compound **32** (0.52 g, 1.23 mmol) and 10% palladium on charcoal (0.10 g). The experimental procedure was as described for the preparation of compound **15a**.

Yield 0.40 g (97%); δ_H (270 MHz; $CDCl_3$) 0.92 (6H, 2 × t), 1.26 (10H, m), 1.90 (4H, m), 5.12 (1H quintet), 5.21 (1H, br s), 7.32 (1H, ddd); IR ν_{max}(KBr)/cm^{-1} 3500–3100, 2936, 2861, 1720, 1488, 1363, 1298, 1121, 1051; MS *m/z* 332 (M^+).

Decyl 5-(4′-dodecyloxybiphenyl-4-ylcarbonyloxy)-2,3,4-fluorobenzoate (39)

Quantities: compound **34** (0.65 g, 1.97 mmol), compound **16b** (0.77 g, 1.97 mmol), DCC (0.41 g, 1.97 mmol), and DMAP (0.020 g, 0.20 mmol). The experimental procedure was as described for the preparation of compound **17a**.

Yield 0.95 g (68%); transitions (°C) Cr 47.0 SmC 59.0 SmA 93.5 I; δ_H (270 MHz; $CDCl_3$) 0.89 (6H, 2 × t), 1.29 (32H, m), 1.66 (2H, m), 1.71 (2H, quintet), 3.98 (2H, t), 4.20 (2H, t), 7.30 (1H, ddd), 7.42 (2H, d), 7.60 (2H, d), 7.80 (2H, d), 8.22 (2H, d); IR ν_{max}(KBr)/cm^{-1} 2930, 2857, 1741, 1715, 1610, 1523, 1461, 1377, 1251, 1180, 1147, 1092, 1049, 939, 813, 765, 738, 694, 541; MS *m/z* 696 (M^+); found: C, 72.33%; H, 7.90%; $C_{42}H_{55}F_3O_5$ requires: C, 72.39%; H, 7.96%.

1-Butylpentyl 5-(4′-dodecyloxybiphenyl-4-ylcarbonyloxy)-2,3,4-fluorobenzoate (40)

Quantities: compound **35** (0.61 g, 1.91 mmol), compound **16b** (0.75 g, 1.91 mmol), DCC (0.39 g, 1.91 mmol), and DMAP (0.020 g, 0.20 mmol). The experimental procedure was as described for the preparation of compound **17a**.

Yield 0.91 g (69%); transitions (°C) Cr 50.5 I; δ_H (270 MHz; $CDCl_3$) 0.89 (9H, 3 × t), 1.31 (26H, m), 1.63 (4H, m), 1.71 (2H, quintet), 4.00 (2H, t), 5.10 (1H, quintet), 7.30 (1H, ddd), 7.42 (2H, d), 7.65 (2H, d), 7.80 (2H, d), 8.22 (2H, d); IR ν_{max}(KBr)/cm^{-1} 2920, 2860, 1740, 1720, 1610, 1523, 1461, 1377, 1251, 1179, 1150, 1090, 1050, 940, 815, 765, 740, 695, 540; MS *m/z* 682 (M^+); found: C, 72.07%; H, 7.82%; $C_{41}H_{53}F_3O_5$ requires: C, 72.12%; H, 7.82%.

(*S*)-1-Methylheptyl 5-(4′-dodecyloxybiphenyl-4-ylcarbonyloxy)-2,3,4-fluorobenzoate (41)

Quantities: compound **36** (0.33 g, 1.10 mmol), compound **16b** (0.42 g, 1.10 mmol), DCC (0.23 g, 1.10 mmol), and DMAP (0.010 g, 0.110 mmol). The experimental procedure was as described for the preparation of compound **17a**.

Yield 0.40 g (36%); transitions (°C) Cr 38.0 (SmX* 30.0) SmA* 70.0 I; δ_H (270 MHz; $CDCl_3$) 0.88 (6H, 2 × t), 0.92 (3H, d), 1.29 (26H, m), 1.61 (2H, m), 1.71 (2H, quintet), 4.00 (2H, t), 5.10 (1H, sextet), 7.29 (1H, ddd), 7.43 (2H, d), 7.66 (2H, d), 7.81 (2H, d), 8.19 (2H, d); IR ν_{max}(KBr)/cm^{-1} 2922, 2860, 1730, 1715, 1620, 1520, 1465, 1380, 1249, 1180, 1145, 1080, 1045, 950, 820, 760, 740, 695, 540; MS *m/z* 668 (M^+); found: C, 71.77%; H, 7.67%; $C_{40}H_{51}F_3O_5$ requires: C, 71.83%; H, 7.69%.

(±)-1-Propylheptyl 5-(4′-dodecyloxybiphenyl-4-ylcarbonyloxy)-2,3,4-fluorobenzoate (42)

Quantities: compound **37** (0.95 g, 2.85 mmol), compound **16b** (1.10 g, 2.85 mmol), DCC (0.60 g, 2.85 mmol), and DMAP (0.030 g, 0.290 mmol). The experimental procedure was as described for the preparation of compound **17a**.

Yield 1.47 g (74%); transitions (°C) Cr 38.0 SmX* 50.0 SmA 76.5 I; δ_H (270 MHz; $CDCl_3$) 0.88 (9H, 3 × t), 1.31 (28H, m), 1.63 (4H, m), 1.70 (2H, quintet), 4.00 (2H, t), 5.05 (1H, sextet), 7.28 (1H, ddd), 7.40 (2H, d), 7.71 (2H, d), 7.78 (2H, d), 8.12 (2H, d); IR ν_{max}(KBr)/cm^{-1} 2920, 2850, 1725, 1715, 1610, 1525, 1460, 1385, 1250, 1175, 1150, 1075, 1050, 945, 820, 755, 740, 690, 540; MS *m/z* 696 (M^+); found: C, 72.34%; H, 7.91%; $C_{42}H_{55}F_3O_5$ requires: C, 72.39%; H, 7.96%.

(*S*)-1-Methylheptyl 4-[2,3,4-trifluoro-5-(4′-dodecyloxybiphenyl-4-ylcarbonyloxy)phenylcarbonyloxy]benzoate (43)

Quantities: compound **38** (0.39 g, 0.950 mmol), compound **16b** (0.36 g, 0.950 mmol), DCC (0.21 g, 0.950 mmol), and DMAP (0.010 g, 0.090 mmol). The experimental procedure was as described for the preparation of compound **17a**.

Yield 0.41 g (55%); transitions (°C) Cr 99.5 SmC*anti 137.5 SmC*ferri 141.0 SmC*ferro 166.0 SmA 213.5 I; δ_H (270 MHz; $CDCl_3$) 0.88 (6H, 2 × t), 0.92 (3H, d), 1.31 (26H, m), 1.63 (2H, m), 1.70 (2H, quintet), 4.00 (2H, t), 5.15 (1H, sextet), 7.20 (1H, ddd), 7.40 (4H, 2 × d), 7.70 (2H, d), 7.80 (2H, d), 8.22 (4H, 2 × d); IR ν_{max}(KBr)/cm^{-1} 2925, 2845, 1720, 1710, 1615, 1530, 1455, 1370, 1245, 1180, 1145, 1070, 1060, 940, 825, 760, 735, 695, 540; MS *m*/*z* 788 (M^+); found: C, 71.49%; H, 6.97%; $C_{47}H_{55}F_3O_7$ requires: C, 71.55%; H, 7.03%.

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