Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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Online publication date: 11 November 2010

To cite this Article Nagashima, Yutaka , Ichihashi, Tetsuya , Noguchi, Koji , Iwamoto, Masayuki , Aoki, Yoshio and Nohira, Hiroyuki(1997) 'The synthesis and mesomorphic properties of ferroelectric liquid crystals with a fluorinated asymmetric frame', Liquid Crystals, 23: 4, 537 — 546
To link to this Article: DOI: 10.1080/026782997208136
URL: http://dx.doi.org/10.1080/026782997208136

LIQUID CRYSTALS, 1997, VOL. 23, NO. 4, 537–546

The synthesis and mesomorphic properties of ferroelectric liquid crystals with a fluorinated asymmetric frame

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(*Received 25 April 1997; accepted 28 May 1997*)

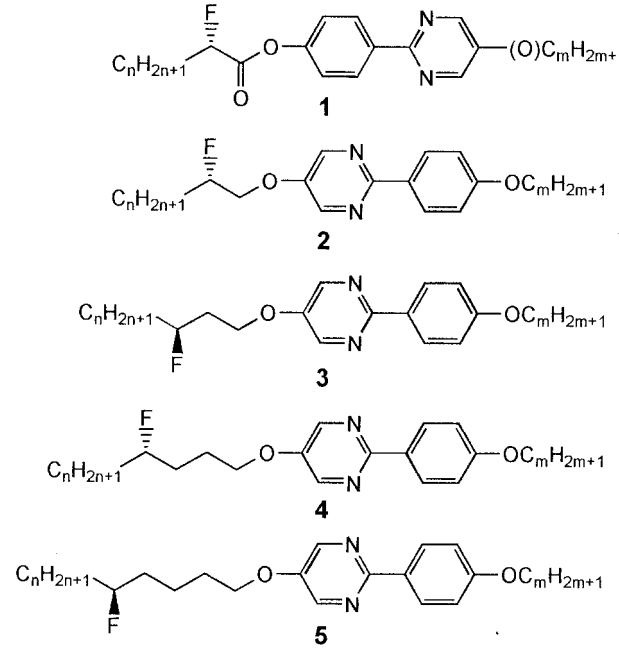
A novel series of ferroelectric liquid crystals with a fluorinated asymmetric frame were synthesized by utilizing optically active (*S*)-2-, (*S*)-3-, (*S*)-4- and (*S*)-5-fluoroalkanols prepared from corresponding (*R*)-1,2-epoxyalkanes. Their mesomorphic and physical properties, such as spontaneous polarization, optic tilt angle and response time, were investigated systematically in a series of homologous compounds having the chiral centre at different positions on tails of various lengths. All the compounds exhibited the chiral smectic C phase in a wide range of temperatures and were found to possess a fast response time in spite of the small magnitude of the spontaneous polarization.

1. Introduction

Ferroelectric liquid crystals (FLCs) have been an active field of investigation in recent years in the expectation of achieving practical devices for new-age flat panel displays [1]. The response time value is the most important property for application of FLCs in high speed display devices. The response time value is inversely proportional to the magnitude of the spontaneous polarization (P_S) [2]. Recently, a number of FLCs having large magnitude of P_S were designed and reported [3–6].

In recent years, we have investigated physical properties of FLCs having a fluorinated asymmetric frame using optically active fluoroalkanols and fluoroalkanoic acids [7–9]. We have reported that the FLCs derived from the (*S*)-2-fluoroalkanoic acids and (*S*)-2-fluoroalkanols (compounds **1** and **2** in Scheme 1) exhibited the chiral smectic C (SmC*) phase in a wide range of temperatures and a fast response time. The magnitude of the P_S of compound **1** having an ester linkage group was larger than that of compound **2** having an ester linkage group, while the response time of compound **2** was faster than that of compound **1**. It suggested that the viscosity of compound **1** was larger than that of compound **2**. It seems that compound **2** having the ether linkage group is more useful for the applications to high speed display devices than compound **1** having the ester linkage group.

The viscosity of FLCs increases with an increase in the magnitude of the P_S [10]. High viscosity of FLCs



Scheme 1. The structures of ferroelectric liquid crystals having a fluorinated asymmetric frame (**1**–**5**). m=6–12, n=4–8.

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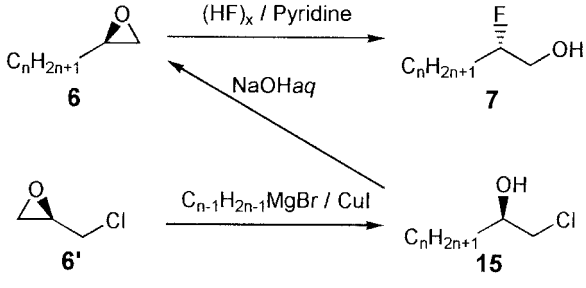
causes long response times because the response time value is inversely proportional to the viscosity. On the other hand, low viscosity of FLCs causes short response times. Therefore, we designed a novel FLC in order to decrease the viscosity. We synthesized such FLCs as the compounds **2**–**5** in Scheme 1, whose chiral centres were far away from the rigid core. We report the synthesis and mesomorphic properties of these FLC compounds.

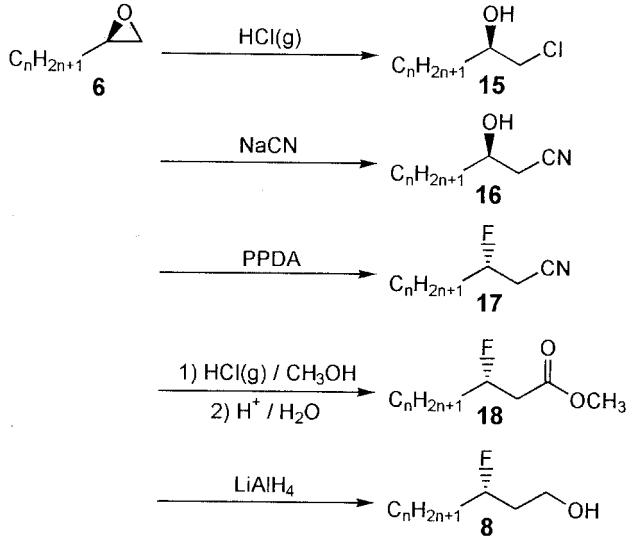
2. Synthesis

The syntheses of (*S*)-2-, (*S*)-3-, (*S*)-4- and (*S*)-5-fluoroalkanols (**7**–**10**) were carried out as described in Schemes 2–5. We have already reported that optically active (*S*)-2-fluoroalkanols (**7**) can be prepared from (*R*)-1,2-epoxyalkanes (**6**) with pyridinium poly(hydrogen fluoride) [7]. The optically active (*S*)-3-, (*S*)-4- and (*S*)-5-fluoroalkanols (**8**–**10**) were also prepared from (*R*)-1,2-epoxyalkanes (**6**). The fluoroalkanols (**7**–**10**) were also prepared from epichlorohydrin (**6′**) according to the reactions reported by Kasai and Sakaguchi [11].

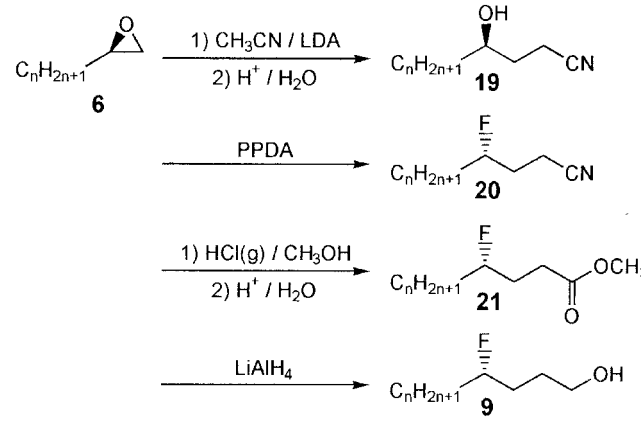
The absolute configurations of each fluoroalkanol



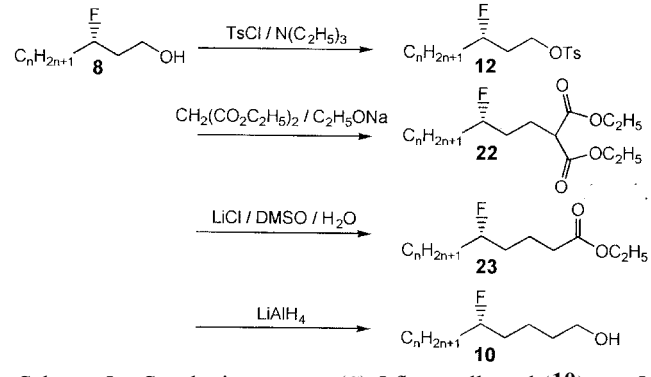
Scheme 2. Synthetic route to (*S*)-2-fluoroalkanol (**7**), $n=6$–8.



Scheme 3. Synthetic route to (*S*)-3-fluoroalkanol (**8**), $n=5$–7. PPDA: perfluoropropene–diethylamine complex.



Scheme 4. Synthetic route to (*S*)-4-fluoroalkanol (**9**), $n=6$. LDA: lithium diisopropylamide.



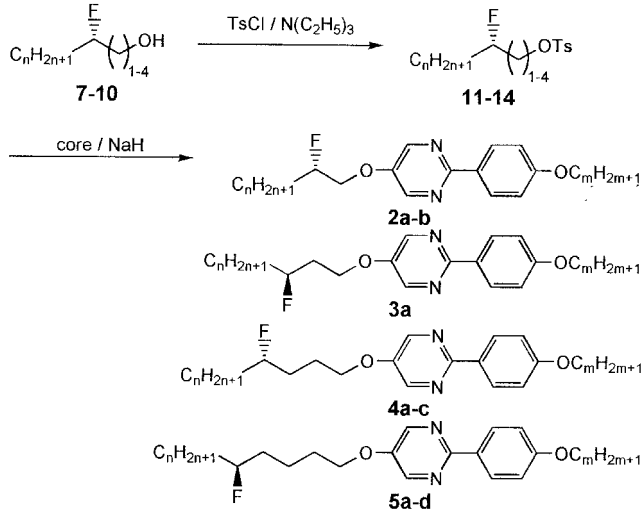
Scheme 5. Synthetic route to (*S*)-5-fluoroalkanol (**10**), $n=5$.

(**7**–**10**) were determined as follows; the reaction of (*R*)-1,2-epoxyalkanes (**6**) with pyridinium poly(hydrogen fluoride) afforded (*S*)-2-fluoroalkanols (**7**) with inversion of configuration [12]. The reaction of (*R*)-1,2-epoxyalkanes (**6**) with hydrogen chloride afforded (*R*)-1-chloro-2-alkanols (**15**) with retention of configuration [9, 11]. The reaction of (*R*)-3-hydroxyalkanitriles (**16**) with the perfluoropropene–diethylamine complex (PPDA; a novel fluorinating reagent) afforded (*S*)-3-fluoroalkanitrile (**17**) with inversion of the configuration (Scheme 2) [13, 14]. The reaction of (*R*)-1,2-epoxyalkanes (**6**) with cyanomethyllithium prepared from acetonitrile and lithium diisopropylamide (LDA) afforded (*R*)-4-hydroxyalkanitrile (**19**) with retention of the configuration [15]. The reaction of (*R*)-4-hydroxyalkanitriles (**19**) with PPDA afforded (*S*)-4-fluoroalkanitrile (**20**) with inversion of the configuration (Scheme 3). (*S*)-5-fluoroalkanols (**10**) were prepared from (*S*)-3-fluoroalkanols (**8**) (Scheme 4).

Optical purities of 2-fluoroalkanols (**7**) were determined by high performance liquid chromatography (HPLC) analysis after treatment of corresponding 2-fluoroalkanoic acids with optically active

1-(1-naphthyl)ethylamine as described in the previous paper [7]. Here, optical purities of all fluoroalkanols (**7**–**10**) were determined by HPLC analysis equipped with a chiral column (DAICEL CHIRALCEL OB-H) after conversion into corresponding fluoroalkyl tosylates (*p*-toluenesulphonates) (**11**–**14**) by treatment with tosyl chloride (*p*-toluenesulphonyl chloride). It was proved that all reactions proceeded without racemization.

The syntheses of FLCs were carried out as described in Scheme 6. Optically active (*S*)-2-, (*S*)-3-, (*S*)-4- and (*S*)-5-fluoroalkyl tosylates (**11**–**14**) were prepared from the corresponding alcohols (**7**–**10**). The products (**2a**–**5d**) were prepared from the corresponding fluoroalkyl tosylates (**11**–**14**) and 2-(4-alkyloxyphenyl)-5-hydroxypyrimidines, which were prepared by ordinary methods [16].



Scheme 6. Synthetic route to ferroelectric liquid crystals (**2**–**5**), m=6–12, n=5–8 core: 2-(4-alkyloxyphenyl)-5-hydroxypyrimidine.

3. Results and discussion

3.1. *Phase transition temperatures*

Phase sequences and transition temperatures of all the homologous liquid crystals are summarized in table 1. The phase sequences were determined by microscopic observation, and the transition temperatures were measured by differential scanning calorimetry (DSC) on cooling (5°C min^{-1}). All compounds exhibited a chiral smectic C phase (SmC*) in a wide range of temperatures. Compound **2a** derived from 2-fluoroalkanol (**7**) and compounds **4a–c** derived from 4-fluoroalkanol (**9**) exhibited the smectic A phase (SmA) above the SmC* phase, while compound **3a** derived from 3-fluoroalkanol (**8**) and compounds **5a–d** derived from 5-fluoroalkanol (**10**) exhibited only the SmC* phase. The crystallization temperature of compound **2a** was 13°C lower than that of compound **2b**. The crystallization temperature of compound **4b** was slightly (1°C) lower than that of compound **4a**. The crystallization temperature of compound **5c** was also 3°C lower than that of compound **5b**. The crystallization temperatures of these FLCs were dependent on the value of m, which was the length of the terminal chain, while they exhibited a much lower dependence on the value of n, which was the length of the chiral moiety. The clearing point of compound **2b** was 5°C higher than that of compound **2a**. The clearing point of compound **5c** was 3°C higher than that of compound **5b**. The clearing point of compound **4c** was equal to that of compounds **4a** and **4b**. The clearing point of these FLCs had little dependence on the values of m and n.

Table 1. Phase transition temperatures of FLCs **2a**–**5d**.

			Temperature[c]/°C							
Compound	m[a]	n[b]	Cr		SmC*		SmA		I	
2a	6	10	●	47	●	90	●	97	●	
2b	8	10	●	60	●	102			●	
3a	7	10	●	48	●	102			●	
4a	6	8	●	60	●	102	●	104	●	
4b	6	10	●	61	●	103	●	104	●	
4c	6	12	●	58	●	100	●	104	●	
5a	5	6	●	52	●	100			●	
5b	5	8	●	54	●	103			●	
5c	5	10	●	51	●	103			●	
5d	5	12	●	45	●	102			●	

[a] Length of the terminal chain.
[b] Length of the chiral moiety.
[c] Cr: crystallization temperature, SmC*: chiral smectic C phase, SmA: smectic A phase, I: isotropic liquid.

3.2. *Spontaneous polarization, tilt angle and response time*

Spontaneous polarization (P_S), tilt angle (θ) and response time (τ or τ_{10-90}) of all the compounds are summarized in table 2. These properties were measured with cells of 20 μm or 2 μm thickness coated by indium–tin oxide and rubbed polyimide. The magnitude of the P_S was measured by the triangular-wave method using 20-μm-gap cells under an applied voltage of $5\,V_{P-P}\,\mu m^{-1}$. The sign of the P_S was determined by observing the tilt angle direction with application of a sufficient d.c. field. Tilt angle was measured by microscopic observation using 2-μm-gap cells under an applied voltage of $5\,V\,\mu m^{-1}$. Response time (τ) was measured by the field reversal method [13]. The value of τ was measured with 20-μm-gap cells under an applied voltage of $5\,V_{P-P}\,\mu m^{-1}$. Optical response time (τ_{10-90}) was measured by observing the change of optical transmittance from 10 to 90 per cent using a digital oscilloscope. The value of τ_{10-90} was measured with 2-μm-gap cells under an applied voltage of $10\,V_{P-P}\,\mu m^{-1}$.

The compounds **2a–b** derived from (*S*)-2-fluoroalkanols (**7**) and the compounds **4a–c** derived from (*S*)-4-fluoroalkanols (**9**) possessed negative spontaneous polarization ($P_S(-)$). Compound **3a** derived from (*S*)-3-fluoroalkanols (**8**) and compounds **5a–d** derived from (*S*)-5-fluoroalkanols (**10**) possessed positive spontaneous polarization ($P_S(+)$). It was supported by the rules for cholesteric liquid crystals defined by Gray and McDonnell [18].

The magnitude of the P_S of the compound **4c** was smaller than that of compounds **4a** and **4b**. The magnitude of the P_S of compounds **5a–d** was in the order **5a** > **5b** > **5c** > **5d**. It seems that the magnitude of the P_S of these FLCs is inversely dependent on the value of *n*. Compared with **2b**, **3a**, **4b** and **5c**, in which the lengths of the chiral tail are equal, the magnitude of the P_S of compound **5c**, derived from (*S*)-5-fluoroalkanol (**10**), was smaller than that of the other compounds. It seems that the magnitude of the P_S of these FLCs is dependent on the length between the chiral centre and mesogenic core. The closer the chiral centre is to the core, the less freedom of movement it has due to steric hindrance with the rigid core. The magnitude of the P_S depends on the rotational freedom of the dipole at the chiral centre. On the other hand, the magnitude of the P_S of compound **3a** derived from (*S*)-3-fluoroalkanol (**8**) was smaller than that of compound **4b** derived from (*S*)-4-fluoroalkanol (**9**). It seems that the magnitude of P_S is induced by not only the dipole moment of the C–F bond at the chiral centre, but also that of the mesogenic core. Thus, the magnitude of P_S in this isomeric series was in the order **2b** > **4b** > **3a** > **5c**.

Compound **5d** possessed the smallest value of tilt angle (θ), and compound **3a** possessed the largest value. The θ of compound **5d** was slightly larger than that of the compound **3a**. It seems that the θ of these compounds have a small dependence on the chiral part and terminal chain.

Response time (τ) and optical response time (τ_{10-90}) are shown in table 2. The value of τ of some compounds, for example, compound **2a**, was not successfully observed, because the observed current curve was broad. Of the isomeric series **2b**, **3a**, **4b** and **5c**, compound **5c** had the smallest value of τ_{10-90}. In general, the response time was inversely proportional to the magnitude of P_S. In this case, however, compound **5c** possessed the smallest magnitude of P_S and shortest response time. The response time was generally proportional to the rotational viscosity. Therefore, it seems that the rotational

Table 2. Physical properties of the FLCs **2a–5d**.

Compound	m[a]	n[b]	P_s[c]/nC cm^{-2}	θ/°	τ[d]/μs	τ_{10-90}[e]/μs	$T(T_c-T)$[f]/°C
2a	6	10	−61·3	27·9		14·4	80(10)
2b	8	10	−66·3	27·7	18·6	78·5	82(20)
3a	7	10	+30·3	29·5	120·0	21·0	82(20)
4a	6	8	−75·9	27·0		46·8	82(20)
4b	6	10	−56·8	27·2	116·0	32·0	83(20)
4c	6	12	−49·3	26·9		52·0	80(20)
5a	5	6	+24·8	27·3	35·0	28·5	80(20)
5b	5	8	+22·2	25·5	93·0	33·0	83(20)
5c	5	10	+19·3	26·7		12·0	83(20)
5d	5	12	+18·5	24·0	104·0	36·0	82(20)

[a] Length of the terminal chain.
[b] Length of the chiral moiety.
[c] Measured by the triangular method.
[d] Measured by the field reversal method.
[e] Measured by observing the change of optical transmittance from 10 to 90 per cent.
[f] T: measurement temperature, T_c: Curie point.

viscosity of compound **5c** is very small. The rotational viscosity of these compounds may depend on the free rotation of the fluorine atom at the chiral centre, because the fluorine atom which is closer to the mesogenic core part is more hindered.

4. Summary

(1) Optically active (*S*)-2-, (*S*)-3-, (*S*)-4- and (*S*)-5-fluoroalkanols (**7**–**10**) were prepared from optically active (*R*)-1,2-epoxyalkanes (**6**), and FLCs (**2a–5d**) were synthesized from the corresponding fluoroalkanols.
(2) All compounds (**2a–5d**) exhibited the SmC* phase in a wide range of temperatures.
(3) The magnitude of P_S of all compounds **2a–5d** was not large, however, their response time (τ_{10-90}) was less than 100 μs.
(4) Compound **5c** possessed the smallest magnitude of P_S, however, it also possessed the shortest response time value, 10 μs.

5. Experimental

5.1. *Analyses*

The structures of intermediates and products were confirmed by ^{1}H, ^{13}C and ^{19}F NMR spectroscopy (JEOL PMX-60si, Bruker AC-200 and Bruker AM-400) and infrared spectroscopy (Perkin–Elmer FT-1640). Values of specific rotation, for example $[\alpha]_D$ value, were measured using a polarimeter (JASCO DIP-360 and JASCO DIP-370). Phase transition temperatures of the products were determined using a differential scanning calorimeter (SEIKO I&E DSC-20 and MAC Science DSC-3100). Phase sequences were identified using a polarizing microscope (Nikon OPTIPHOT2-POL) equipped with a thermal control system (Mettler FP-90/FP-82HT).

5.2. *Synthesis of (S)-2-fluoroalkanols*

5.2.1. (*S*)-2-*fluorodecanol* (**7**)

A solution of (*R*)-1,2-epoxydecane (**6**, from Japan Energy Co., Ltd., 0·816 g, 5·16 mmol) in 1·5 ml of dichloromethane was slowly added dropwise to a stirred solution of pyridinium poly(hydrogen fluoride) (HF, 70 per cent by weight, 2·0 ml) in dichloromethane (2·0 ml) in an Erlenmeyer flask made of polyethylene at ice–water temperature. The mixture was stirred vigorously for 12 h at room temperature. The mixture was carefully poured into 2·1 g of silica-gel suspended with a small amount of dichloromethane. The solvent was evaporated off, and the remaining mixture passed through a flash chromatography column (silica-gel: 10 g, eluent: hexane–hexane/ethyl acetate=10/1). The solvent was removed *in vacuo* and the crude product distilled under reduced pressure (110–125°C, 20 mmHg) to yield a white solid. Yield: 0·536 g (58·9 per cent). It contained a small amount of 1-fluoro-2-decanol (a few per cent by GC assay). It was not characterized because the mixtures were used for synthesis of compound **11** without further purification.

5.2.2. (*S*)-2-*fluorodecyl p-toluenesulphonate* (**11**)

The compound **7** (0·358 g, 2·03 mmol) was stirred with 1·5 ml of dry dichloromethane at ice–water temperature, *p*-toluenesulphonyl chloride (0·430 g, 2·26 mmol) was added and a solution of dry triethylamine (0·829 g, 8·19 mmol) in dichloromethane (1·5 ml) was added. The mixture was stirred for 12 h at room temperature. Three molar hydrochloric acid was added to the solution, and the organic layer was extracted with dichloromethane. The extract was washed with 1 M hydrochloric acid and dried with anhydrous magnesium sulphate. The concentration was purified by column chromatography (silica-gel: 30 g, eluent: hexane–hexane/benzene=1/2) to yield a colourless liquid. Yield: 0·460 g (68·5 per cent); ^{1}H NMR ($CDCl_3$): 0·88 (t, 3 H, CH_3), 1·20–1·64 (m, 14 H, CH_2), 2·45 (s, 3 H, CH_3Ph), 4·02–4·18 (m, 2 H, CH_2O), 4·44–4·79 (dm, 1 H, CHF, J=47 Hz), 7·35 (d, 2 H, Ph, J=8 Hz), 7·80 (d, 2 H, Ph, J=8 Hz); ^{13}C NMR ($CDCl_3$): 14·0 (CH_3), 21·6 (CH_3Ph), 22·6 (CH_2), 24·5 (d, CH_2, J=5 Hz), 29·0 (CH_2), 29·2 (CH_2), 29·2 (CH_2), 30·6 (CH_2), 31·0 (CH_2), 31·7 (CH_2), 70·6 (d, CH_2O, J=24 Hz), 90·5 (d, CHF, J=175 Hz), 127·9 (Ph), 129·8 (Ph), 132·7 (Ph), 145·0 (Ph); ^{19}F NMR ($CDCl_3$): −188·9 (dm, J=48 Hz); IR (Nujol): 2926, 2856, 1598, 1496, 1456, 1367, 1308, 1213, 1190, 1178, 1098, 1020, 981, 930, 880, 814, 792, 722, 706, 667, 556 cm^{-1}; $[\alpha]_D^{20}$+5·5°, $[\alpha]_{435}^{19}$+9·0° (*c*1·09, Et_2O).

5.3. *Synthesis of (S)-3-fluoroalkanols*

5.3.1. (*R*)-1-*chloro*-2-*nonanol* (**15**)

[Method A] hydrogen chloride gas made from 100 ml of concentrated hydrochloric acid dropped into 200 ml of concentrated sulphuric acid was bubbled into a stirred solution of (*R*)-1,2-epoxynonane (**6**, 2·862 g, 20·1 mmol) in dry diethylether (12 ml) at ice–water temperature. The mixture was stirred for 2 h at room temperature and carefully poured into distilled water (50 ml). The organic layer was extracted with diethylether. The extract was washed with distilled water and dried with anhydrous magnesium sulphate. The solvent was removed *in vacuo* to yield a colourless liquid. Yield: 13·541 g (98·5 per cent). It contained a small amount of 2-chloro-1-nonanol. [Method B] copper iodide(I) (2·998 g, 15·7 mmol) was vigorously suspended in 25 ml of dry diethylether at −78°C under a nitrogen atmosphere. The Grignard reagent made of magnesium (0·816 g, 33·6 mmol) and 1-bromohexane (5·008 g, 30·3 mmol) was added. A solution of (*R*)-epichlorohydrin (**6′**, 1·894 g,

20·5 mmol) in 10 ml of dry diethylether was added and stirred for 5 min.

A saturated aqueous ammonium chloride solution was added and allowed to warm up to room temperature. The organic layer was extracted with diethylether. The extract was washed with saturated aqueous sodium chloride solution and dried with anhydrous magnesium sulphate. The solvent was removed *in vacuo* to yield a colourless liquid. Yield: 3·565 g (97·1 per cent). It contained a small amount of 2-chloro-1-nonanol. It was not characterized because the mixtures were used for synthesis of compound **16** without further purification.

5.3.2. (*R*)-*3-hydroxydecanitrile* (**16**)

Sodium cyanide (1·970 g, 40·2 mmol) was suspended in 20 ml of dimethylsulphoxide at 50°C for 30 min. A solution of compound **15** (3·501 g, 19·6 mmol) in 10 ml of dimethylsulphoxide was added and stirred at 50°C for 8 h. Distilled water was added and the organic layer extracted with diethylether. The extract was washed with distilled water and dried with anhydrous magnesium sulphate. The solvent was removed *in vacuo*, and the crude product was distilled under reduced pressure (95–110°C, 2 mmHg) to yield a colourless liquid. Yield: 2·484 g (75·0 per cent); ^{1}H NMR ($CDCl_3$): 0·88 (t, 3 H, CH_3), 1·28–1·70 (m, 12 H, CH_2), 2·41–2·61 (m, 2 H, CH_2CN), 3·09–3·12 (m, 1 H, OH), 3·72–3·97 (m, 1 H, CH); ^{13}C NMR ($CDCl_3$): 13·9 (CH_3), 22·4 (CH_2), 25·2 (CH_2), 25·9 (CH_2), 29·0 (CH_2), 29·1 (CH_2), 31·6 (CH_2), 36·3 (CH_2), 67·4 (CHOH), 117·8 (CN); IR (Nujol): 3446, 2928, 2857, 2254, 1466, 1418, 1278, 1128, 1082, 670, 558 cm^{-1}; $[\alpha]_D^{23}$ + 5·0°, $[\alpha]_{435}^{24}$ + 6·1° (*c*1·05, Et_2O).

5.3.3. (*S*)-*3-fluorodecanitrile* (**17**)

A solution of perfluoropropene–diethylamine complex (from TCI Co., Ltd., 0·971 g, 32·8 mmol) in 15 ml of dry diethylether was dropwise to a stirred solution of compound **16** (2·502 g, 14·8 mmol) in dry diethylether (15 ml) at ice–water temperature under a nitrogen atmosphere. The mixture was stirred for 8 h at room temperature. Distilled water was added and the organic layer extracted with diethylether. The extract was washed with distilled water and dried with anhydrous magnesium sulphate. The solvent was evaporated off, and the remaining mixture purified by column chromatography (silica-gel: 140 g, eluent: hexane/ethyl acetate = 20/1) to yield a colourless liquid. Yield: 1·219 g (48·1 per cent); ^{1}H NMR ($CDCl_3$): 0·88 (t, 3 H, CH_3), 1·30–1·85 (m, 12 H, CH_2), 2·65–2·76 (m, 2 H, CH_2CN), 4·63–4·81 (dm, 1 H, CHF, J = 48 Hz); ^{13}C NMR ($CDCl_3$): 14·0 (CH_3), 22·5 (CH_2), 24·0 (d, CH_2CN, J = 26 Hz), 24·6 (CH_2), 24·6 (CH_2), 28·8 (CH_2), 31·6 (CH_2), 34·3 (d, CH_2, J = 20 Hz), 88·5 (d, CHF, J = 178 Hz), 116·0 (d, CN, J = 6 Hz); ^{19}F NMR ($CDCl_3$): −178·6 (dm, J = 48 Hz); IR (Nujol): 2930, 2858, 2255, 1674, 1467, 1379, 1360, 1229, 1126, 1077, 1046, 877, 840, 724 cm^{-1}; $[\alpha]_D^{23}$ −10·0°, $[\alpha]_{435}^{22}$ −23·1° (*c*1·05, Et_2O).

5.3.4. *Methyl* (*S*)-*3-fluorodecanoate* (**18**)

Hydrogen chloride gas made from 30 ml of concentrated hydrochloric acid dropped into 60 ml of concentrated sulphuric acid was bubbled into a stirred solution of compound **17** (1·035 g, 6·58 mmol) in 1·6 ml of dry methanol at ice–water temperature. The mixture was stirred for 8 h at room temperature. After addition of distilled water (1·3 ml), the mixture was stirred at 50°C for 3 h. Distilled water was added and the organic layer was extracted with diethylether. The extract was washed with saturated aqueous sodium carbonate solution and dried with anhydrous sodium sulphate. The solvent was removed *in vacuo* to yield a colourless liquid. Yield: 1·156 g (92·3 per cent); ^{1}H NMR ($CDCl_3$): 0·88 (t, 3 H, CH_3), 1·28–1·70 (m, 12 H, CH_2), 2·49–2·72 (m, 2 H, CH_2CO_2), 3·71 (s, 3 H, OCH_3), 4·74–5·11 (dm, 1 H, CHF, J = 48 Hz); ^{13}C NMR ($CDCl_3$): 14·0 (CH_3), 22·5 (CH_2), 24·4 (d, CH_2, J = 4 Hz), 29·0 (CH_2), 29·2 (CH_2), 31·7 (CH_2), 34·8 (d, CH_2, J = 21 Hz), 40·2 (d, CH_2, J = 24 Hz), 90·3 (d, CHF, J = 170 Hz), 170·6 (d, CO_2, J = 6 Hz); ^{19}F NMR ($CDCl_3$): −180·2 (dm, J = 48 Hz); IR (Nujol): 2926, 2857, 1745, 1464, 1438, 1398, 1372, 1262, 1198, 1168, 1129, 1071, 992, 886, 856, 723 cm^{-1}; $[\alpha]_D^{26}$ −9·0°, $[\alpha]_{435}^{23}$ −21·9° (*c*1·01, Et_2O).

5.3.5. (*S*)-*3-fluorodecanol* (**8**)

Lithium aluminium hydride (0·234 g, 6·17 mmol) was suspended in 2·5 ml of dry tetrahydrofuran at ice–water temperature under a nitrogen atmosphere. A solution of compound **18** (1·085 g, 5·70 mmol) in dry tetrahydrofuran (2·5 ml) was slowly added dropwise. The mixture was stirred for 1 h at room temperature.

A saturated solution of aqueous sodium sulphate was added until hydrogen gas was no longer generated and 3 M hydrochloric acid was added until dissolving the generated solid (lithium hydroxide). The organic layer was extracted with diethylether. The extract was washed with saturated aqueous sodium carbonate solution and dried with anhydrous magnesium sulphate. The solvent was removed *in vacuo* to yield a white solid. Yield: 0·872 g (86·8 per cent); ^{1}H NMR ($CDCl_3$): 0·88 (t, 3 H, CH_3), 1·28–1·91 (m, 14 H, CH_2), 2·21 (s, 1 H, OH), 3·79 (t, 2 H, CH_2O), 4·50–4·87 (dm, 1 H, CHF, J = 49 Hz); ^{13}C NMR ($CDCl_3$): 14·0 (CH_3), 22·6 (CH_2), 25·0 (d, CH_2, J = 5 Hz), 29·1 (CH_2), 29·3 (CH_2), 31·7 (CH_2), 35·3 (d, CH_2, J = 21 Hz), 37·8 (d, CH_2, J = 20 Hz), 59·2 (d, CH_2O, J = 4 Hz), 92·5 (d, CHF, J = 166 Hz); ^{19}F NMR ($CDCl_3$): −182·9 (dm, J = 49 Hz); IR (Nujol): 3271, 2916, 2850, 1674, 1616, 1524, 1470, 1445, 1398, 1382, 1358, 1305,

1252, 1239, 1247, 1206, 1145, 1130, 1105, 1081, 1066, 1038, 1012, 972, 944, 916, 862, 813, 778, 720, 578, 472 cm^{-1}; $[\alpha]_D^{19}$ +9·4°, $[\alpha]_{435}^{20}$ +15·3° (*c*1·02, Et_2O).

5.3.6. (*S*)-*3-fluorodecyl p-toluenesulphonate* (**12**)

The experimental procedure was as described for the preparation of compound **11**. Compound **8** (0·815 g, 4·62 mmol), *p*-toluenesulphonyl chloride (0·985 g, 5·17 mmol) and dry triethylamine (1·890 g, 18·7 mmol) were used to yield a colourless liquid. Yield: 1·362 g (89·2 per cent); ^{1}H NMR ($CDCl_3$): 0·88 (t, 3 H, CH_3), 1·26–1·99 (m, 14 H, CH_2), 2·43 (s, 3 H, CH_3Ph), 4·15 (t, 2 H, CH_2O), 4·35–4·71 (dm, 1 H, CHF, J = 48 Hz), 7·34 (d, 2 H, Ph, J = 8 Hz), 7·78 (d, 2 H, Ph, J = 7 Hz); ^{13}C NMR ($CDCl_3$): 14·0 (CH_3), 21·5 (CH_3Ph), 22·5 (CH_2), 24·8 (d, CH_2, J = 5 Hz), 29·0 (CH_2), 29·2 (CH_2), 31·6 (CH_2), 34·5 (d, CH_2, J = 19 Hz), 34·9 (d, CH_2, J = 18 Hz), 66·6 (d, CH_2O, J = 5 Hz), 90·2 (d, CHF, J = 168 Hz), 127·8 (Ph), 129·8 (Ph), 132·9 (Ph), 144·8 (Ph); ^{19}F NMR ($CDCl_3$): -184·7 (dm, J = 48 Hz); IR (Nujol): 2928, 2857, 1598, 1496, 1468, 1364, 1305, 1190, 1178, 1098, 1022, 974, 924, 837, 816, 763, 706, 690, 665, 586, 555 cm^{-1}; $[\alpha]_D^{19}$ +10·7°, $[\alpha]_{435}^{18}$ +17·8° (*c*1·00, Et_2O).

5.4. *Synthesis of* (*S*)-*4-fluoroalkanols*

5.4.1. (*R*)-*4-hydroxydecanitrile* (**19**)

Dry acetonitrile (0·266 g, 6·5 mmol) was added to a stirred solution of lithium diisopropylamide (from Aldrich Co., 1·5 M tetrahydrofuran solution, 4·3 ml, 6·5 mmol) at −78°C for 1 h under a nitrogen atmosphere. (*R*)-1,2-epoxyoctane (**6**, 0·833 g, 6·5 mmol) was added and the mixture stirred for 1 h.

A saturated aqueous sodium chloride solution was added and allowed to warm up to room temperature. The organic layer was extracted with diethylether. The extract was washed with 1 M hydrochloric acid and distilled water, and dried with anhydrous magnesium sulphate. The solvent was removed *in vacuo*, and the crude product distilled under reduced pressure (150°C, 4 mmHg) to yield a colourless liquid. Yield: 0·651 g (52·9 per cent); ^{1}H NMR ($CDCl_3$): 0·90 (t, 3 H, CH_3), 1·06–1·86 (m, 12 H, CH_2), 1·91 (s, 1 H, OH), 2·50 (t, 2 H, CH_2CN), 3·65–3·69 (m, 1 H, CHOH); IR (Nujol): 3421, 2929, 2857, 2247, 2192, 1762, 1684, 1458, 1377, 1189, 1129, 1088, 932 cm^{-1}; $[\alpha]_D^{26}$ −21·7°, $[\alpha]_{435}^{24}$ −42·3° (*c*2·10, Et_2O).

5.4.2. (*S*)-*4-fluorodecanitrile* (**20**)

The experimental procedure was as described for the preparation of compound **17**. Compound **19** (2·8 g, 16·6 mmol) and perfluoropropene–diethylamine complex (8·5 g, 39·8 mmol) were used to yield a colourless liquid. Yield: 1·59 g (55·9 per cent); ^{1}H NMR ($CDCl_3$): 0·89 (t, 3 H, CH_3), 1·22–2·03 (m, 12 H, CH_2), 2·50 (t, 2 H, CH_2CN), 4·34–4·78 (dm, 1 H, CHF, J = 49 Hz); IR (Nujol): 2933, 2360, 1484, 1456, 1371, 1071, 1039, 918, 854 cm^{-1}; $[\alpha]_D^{26}$ +16·4°, $[\alpha]_{435}^{24}$ +27·0° (*c*1·03, Et_2O).

5.4.3. *Methyl* (*S*)-*4-fluorodecanoate* (**21**)

The experimental procedure was as described for the preparation of compound **17**. Compound **19** (2·8 g, 16·6 mmol) and perfluoropropene–diethylamine complex (8·5 g, 39·8 mmol) were used to yield a colourless liquid. Yield: 1·59 g (55·9 per cent); ^{1}H NMR ($CDCl_3$): 0·89 (t, 3 H, CH_3), 1·22–2·03 (m, 12 H, CH_2), 2·50 (t, 2 H, CH_2CN), 4·34–4·78 (dm, 1 H, CHF, J = 49 Hz); IR (Nujol): 2933, 2360, 1484, 1456, 1371, 1071, 1039, 918, 854 cm^{-1}; $[\alpha]_D^{26}$ +16·4°, $[\alpha]_{435}^{24}$ +27·0° (*c*1·03, Et_2O).

5.4.4. *Methyl* (*S*)-*4-fluorodecanoate* (**21**)

The experimental procedure was as described for the preparation of compound **18**. Compound **20** (1·46 g, 8·5 mmol) and dry methanol (2·12 g, 66·2 mmol) were used to yield a colourless liquid. Yield: 1·47 g (84·8 per cent); specific rotation (*c*1·07, Et_2O): $[\alpha]_D^{26}$ +10·6°, $[\alpha]_{435}^{24}$ +16·4°; ^{1}H NMR ($CDCl_3$): 0·89 (t, 3 H, CH_3), 1·29–2·00 (m, 12 H, CH_2), 2·43–2·51 (m, 2 H, CH_2COO), 3·68 (s, 3 H, OCH_3), 4·32–5·19 (dm, 1 H, CHF, J = 46 Hz); IR (Nujol): 2934, 2860, 1744, 1540, 1438, 1354, 1175, 916, 724 cm^{-1}.

5.4.5. (*S*)-*4-fluorodecanol* (**9**)

The experimental procedure was as described for the preparation of compound **8**. Compound **21** (1·41 g, 6·9 mmol) and lithium aluminium hydride (0·262 g, 6·89 mmol) were used to yield a white solid. Yield: 1·00 g (84·2 per cent); specific rotation (*c*3·01, Et_2O): $[\alpha]_D^{26}$ −1·06°, $[\alpha]_{435}^{24}$ −1·72°; ^{1}H NMR ($CDCl_3$): 0·89 (t, 3 H, CH_3), 1·17–1·74 (m, 14 H, CH_2), 2·18 (s, 1 H, OH), 3·63–3·69 (m, 2 H, CH_2O), 4·36–4·71 (dm, 1 H, CHF, J = 50 Hz); IR (Nujol): 3319, 2934, 2856, 2364, 1638, 1458, 1376, 1060 cm^{-1}.

5.4.6. (*S*)-*4-fluorodecyl p-toluenesulphonate* (**13**)

The experimental procedure was as described for the preparation of compound **11**. Compound **9** (0·531 g, 3·0 mmol), *p*-toluenesulphonyl chloride (0·860 g, 4·5 mmol) and dry triethylamine (0·455 g, 4·5 mmol) were used to yield a colourless liquid. Yield: 0·851 g (85·4 per cent); ^{1}H NMR ($CDCl_3$): 0·89 (t, 3 H, CH_3), 1·28–1·81 (m, 14 H, CH_2), 2·45 (s, 3 H, CH_3Ph), 4·03–4·10 (m, 2 H, CH_2O), 4·22–4·60 (dm, 1 H, CHF, J = 48 Hz), 7·33–7·36 (d, 2 H, Ph, J = 6 Hz), 7·78–7·81 (d, 2 H, Ph, J = 6 Hz); IR (Nujol): 2928, 2860, 1922, 1598, 1495, 1466, 1363, 1177, 1098, 964, 816, 734, 665, 555 cm^{-1}; $[\alpha]_D^{26}$ +1·21°, $[\alpha]_{435}^{24}$ +2·25° (*c*7·09, Et_2O).

5.5. *Synthesis of (S)-5-fluoroalkanols*

5.5.1. *Diethyl 2-((S)-3-fluorooctyl)malonate* (**22**)

Sodium (0·337 g, 14·4 mmol) was dissolved in dry ethanol at 50°C under a nitrogen atmosphere. Diethyl malonate (2·337 g, 14·6 mmol) and (*S*)-3-fluorooctyl *p*-toluenesulphonate (**8**, 2·913 g, 9·63 mmol) were added to the solution. The mixture was stirred at 80°C for 2·5 h. Distilled water was added and the organic layer was extracted with diethylether. The extract was washed with distilled water and dried with anhydrous magnesium sulphate. The solvent was removed *in vacuo*, and the crude product distilled under reduced pressure (120–125°C, 4 mmHg) to yield a colourless liquid. Yield: 1·972 g (70·5 per cent); ^{1}H NMR ($CDCl_3$): 0·89 (t, 3 H, CH_3), 1·23–2·15 (m, 18 H, CH_2+CH_3), 3·35 (t, 1 H, CH), 4·20 (q, 4 H, OCH_2), 4·28–4·66 (dm, 1 H, CHF, J=49 Hz); ^{13}C NMR ($CDCl_3$): 13·9 (CH_3), 14·0 (CH_3), 22·4 (d, CH_2), 24·4 (d, CH_2, J=5 Hz), 24·6 (d, CH_2, J=5 Hz), 31·5 (CH_2), 32·6 (d, CH_2, J=21 Hz), 34·9 (d, CH_2, J=21 Hz), 51·6 (CH), 61·3 (OCH_2), 93·7 (d, CHF, J=168 Hz), 169·2 (CO); ^{19}F NMR ($CDCl_3$): −181·7 (dm, J=49 Hz); IR (Nujol): 2932, 2866, 1732, 1468, 1454, 1369, 1178, 1097, 1030, 968, 861, 820, 768, 728, 666, 596, 588, 556 cm^{-1}; $[\alpha]_D^{23}$+3·56°, $[\alpha]_{435}^{22}$+4·45° (*c*1·01, Et_2O).

5.5.2. *Ethyl (S)-5-fluorodecanoate* (**23**)

A solution of compound **22** (1·968 g, 6·78 mmol), distilled water (0·140 g, 7·77 mmol) and anhydrous lithium chloride (0·581 g, 13·71 mmol) in dimethylsulphoxide (10 ml) was stirred at 190°C for 4 h. Distilled water was added and the organic layer was extracted with diethylether. The extract was washed with saturated aqueous sodium chloride solution and dried with anhydrous magnesium sulphate. The solvent was removed *in vacuo* to yield a colourless liquid. Yield: 1·379 g (93·2 per cent); ^{1}H NMR ($CDCl_3$): 0·89 (t, 3 H, CH_3), 1·22–1·95 (m, 14 H, CH_2), 2·34 (t, 3 H, CH_3), 4·13 (q, 4 H, OCH_2), 4·27–4·65 (dm, 1 H, CHF, J=49 Hz); ^{13}C NMR ($CDCl_3$): 13·9 (CH_3), 14·1 (CH_3), 20·6 (d, CH_2, J=5 Hz), 22·4 (CH_2), 24·7 (d, CH_2, J=5 Hz), 31·6 (CH_2), 33·9 (CH_2), 34·4 (d, CH_2, J=21 Hz), 35·0 (d, CH_2, J=21 Hz), 61·3 (OCH_2), 93·9 (d, CHF, J=168 Hz), 173·3 (CO); ^{19}F NMR ($CDCl_3$): -181·3 (dm, J=49 Hz); IR (Nujol): 2936, 1734, 1458, 1374, 1351, 1300, 1251, 1170, 1120, 1098, 1034, 954, 857, 819, 728, 582 cm^{-1}; $[\alpha]_D^{27}$+0·91°, $[\alpha]_{435}^{25}$+0·55° (*c*1·08, Et_2O).

5.5.3. *(S)-5-fluorodecanol* (**10**)

The experimental procedure was as described for the preparation of compound **8**. Compound **23** (0·317 g, 1·45 mmol) and lithium aluminium hydride (0·058 g, 1·53 mmol) were used to yield a white solid. Yield: 0·249 g (97·2 per cent); ^{1}H NMR ($CDCl_3$): 0·90 (t, 3 H, CH_3), 1·24–1·68 (m, 14 H, CH_2), 1·89 (s, 1 H, OH), 3·64 (t, 2 H, CH_2OH), 4·38–4·56 (dm, 1 H, CHF, J=49 Hz); ^{13}C NMR ($CDCl_3$): 13·9 (CH_3), 21·4 (d, CH_2 J=5 Hz), 22·5 (CH_2), 24·7 (d, CH_2, J=5 Hz), 31·6 (CH_2), 32·5 (CH_2), 34·8 (d, CH_2, J=21 Hz), 35·1 (d, CH_2, J=20 Hz), 62·6 (CH_2OH), 94·4 (d, CHF, J=167 Hz); ^{19}F NMR ($CDCl_3$): -180·9 (dm, J=49 Hz); IR (Nujol): 3264, 2939, 2856, 1469, 1358, 1116, 1080, 1058, 1028, 1004, 968, 917, 860, 816, 778, 738 cm^{-1}; $[\alpha]_D^{24}$ −1·20°, $[\alpha]_{435}^{23}$ −2·34° (*c*1·88, Et_2O).

5.5.4. *(S)-5-fluorodecyl p-toluenesulphonate* (**14**)

The experimental procedure was as described for the preparation of compound **11**. Compound **10** (0·234 g, 1·33 mmol), *p*-toluenesulphonyl chloride (0·298 g, 1·56 mmol) and dry triethylamine (0·270 g, 2·67 mmol) were used to yield a colourless liquid. Yield: 0·386 g (88·0 per cent); ^{1}H NMR ($CDCl_3$): 0·89 (t, 3 H, CH_3), 1·29–1·70 (m, 14 H, CH_2), 2·45 (s, 3 H, CH_3Ph), 4·03 (t, 2 H, CH_2O), 4·31–4·49 (dm, 1 H, CHF, J=49 Hz), 7·35 (d, 2 H, Ph, J=8 Hz), 7·79 (d, 2 H, Ph, J=8 Hz); ^{13}C NMR ($CDCl_3$): 13·9 (CH_3), 21·1 (d, CH_3, J=5 Hz), 21·5 (CH_3Ph), 22·5 (CH_2), 24·7 (d, CH_2, J=4 Hz), 28·6 (CH_2), 31·6 (CH_2), 34·3 (d, CH_2, J=21 Hz), 35·0 (d, CH_2, J=21 Hz), 70·3 (CH_2O), 94·0 (d, CHF, J=167 Hz), 127·8 (Ph), 129·8 (Ph), 133·0 (Ph), 144·7 (Ph); ^{19}F NMR ($CDCl_3$): −181·3 (dm, J=49 Hz); IR (Nujol): 2933, 2870, 1598, 1496, 1458, 1364, 1190, 1177, 1098, 1019, 968, 936, 837, 836, 776, 732, 664, 579, 555 cm^{-1}; $[\alpha]_D^{28}$+0·44°, $[\alpha]_{435}^{25}$+0·08° (*c*1·83, Et_2O).

5.6. *Synthesis of ferroelectric liquid crystals*

5.6.1. *2-(4-Decyloxyphenyl)-5-((S)-2-fluorodecyloxy)-pyrimidine* (**2b**)

A solution of 2-(4-decyloxyphenyl)-5-hydroxypyrimidine (0·120 g, 0·37 mmol) in 1·5 ml of dry *N*, *N*-dimethylformamide was stirred under a nitrogen atmosphere. Sodium hydride (60 per cent by weight, 0·052 g, 1·30 mmol) and a solution of the compound **11** (0·120 g, 0·36 mmol) in dry *N*,*N*-dimethylformamide (1·5 ml) were added to a stirred solution. The mixture was stirred at 70°C for 8 h. Distilled water was added and the organic layer was extracted with diethylether. The extract was washed with saturated aqueous sodium chloride solution and dried with anhydrous magnesium sulphate. The solvent was removed *in vacuo*, and the residue was purified by silica-gel thin-layer chromatography (eluent: hexane–ethyl acetate=4/1). The crude product was recrystallized from the mixture of 1·5 ml hexane and 0·1 ml ethanol (99 v/v per cent) to yield a white solid. Yield: 0·105 g (59 per cent); ^{1}H NMR ($CDCl_3$): 0·88 (t, 3 H, CH_3), 0·90 (t, 3 H, CH_3), 1·28–1·95 (m, 30 H, CH_3), 4·00–4·06 (t+t, 4 H, CH_2O+CH_2O), 4·40–4·58 (dm, 1 H, CHF, J=50 Hz), 6·95 (d, 2 H, Ph, J=9 Hz), 8·28 (d,

2 H, Ph, J=9 Hz), 8·39 (s, 2 H, Py); ^{13}C NMR ($CDCl_3$): 13·9 (CH_3), 14·0 (CH_3), 21·8 (d, CH_2, J=4 Hz), 22·5 (CH_2), 22·6 (CH_2), 24·7 (d, CH_2, J=5 Hz), 25·8 (CH_2), 29·1 (CH_2), 29·3 (CH_2), 29·5 (CH_2), 31·6 (CH_2), 31·8 (CH_2), 34·8 (d, CH_2, J=21 Hz), 35·1 (d, CH_2, J=21 Hz), 35·8 (CH_2), 67·7 (CH_2O), 68·8 (CH_2O), 94·2 (d, CHF, J=168 Hz), 114·3 (Ar), 128·9 (Ar), 130·1 (Ar), 143·7 (Ar), 151·0 (Ar), 157·5 (Ar), 160·5 (Ar); ^{19}F NMR ($CDCl_3$): −180·9 (dm, J=50 Hz); IR (KBr): 2921, 2850, 1607, 1586, 1548, 1516, 1443, 1393, 1286, 1251, 1170, 1133, 1091, 1028, 914, 878, 842, 818, 789, 721, 646, 634, 625, 554, 532 cm^{-1}; $[\alpha]_D^{25}$+5·7°, $[\alpha]_{435}^{23}$+6·4° (*c*1·13, $CHCl_3$).

5.6.2. *2-(4-Decyloxyphenyl)-5-((S)-3-fluorodecyloxy)-pyrimidine* (**3 a**)

The experimental procedure was as described for the preparation of compound **2 b**. Compound **12** (0·116 g, 0·35 mmol), 2-(4-decyloxyphenyl)-5-hydroxypyrimidine (0·116 g, 0·35 mmol) and sodium hydride (60 per cent by weight, 0·051 g, 1·28 mmol) were used to yield a white solid. Yield: 0·121 g (71 per cent); ^{1}H NMR ($CDCl_3$): 0·88 (t, 3 H, CH_3), 0·89 (t, 3 H, CH_3), 1·28–1·95 (m, 30 H, CH_2), 4·00–4·06 (t+t, 4 H, CH_2O+CH_2O), 4·40–4·58 (dm, 1 H, CHF, J=50 Hz), 6·95 (d, 2 H, Ph, J=9 Hz), 8·28 (d, 2 H, Ph, J=9 Hz), 8·39 (s, 2 H, Py); ^{13}C NMR ($CDCl_3$): 13·9 (CH_3), 14·0 (CH_3), 21·8 (d, CH_2, J=4 Hz), 22·5 (CH_2), 22·6 (CH_2), 24·7 (d, CH_2, J=5 Hz), 25·8 (CH_2), 29·1 (CH_2), 29·3 (CH_2), 29·5 (CH_2), 31·6 (CH_2), 31·8 (CH_2), 34·8 (d, CH_2, J=21 Hz), 35·1 (d, CH_2, J=20 Hz), 35·8 (CH_2), 67·7 (CH_2O), 68·8 (CH_2O), 94·2 (d, CHF, J=168 Hz), 114·3 (Ar), 128·9 (Ar), 130·1 (Ar), 143·7 (Ar), 151·0 (Ar), 157·5 (Ar), 160·5 (Ar); ^{19}F NMR ($CDCl_3$): −180·9 (dm, J=50 Hz); IR (KBr): 2921, 2850, 1608, 1584, 1549, 1553, 1516, 1470, 1446, 1407, 1291, 1251, 1170, 1106, 1090, 1068, 1030, 920, 876, 866, 844, 819, 789, 719, 646, 632, 618, 563, 551, 500, 491 cm^{-1}; $[\alpha]_D^{24}$+1·06°, $[\alpha]_{435}^{22}$+1·58° (*c*1·15, $CHCl_3$).

5.6.3. *2-(4-Decyloxyphenyl)-5-((S)-4-fluorodecyloxy)-pyrimidine* (**4 b**)

The experimental procedure was as described for the preparation of compound **2 b**. Compound **13** (0·221 g, 0·70 mmol), 2-(4-decyloxyphenyl)-5-hydroxypyrimidine (0·295 g, 0·90 mmol) and sodium hydride (60 per cent by weight, 0·050 g, 1·25 mmol) were used to yield a white solid. Yield: 0·136 g (41 per cent); ^{1}H NMR ($CDCl_3$): 0·87 (t, 3 H, CH_3), 0·89 (t, 3 H, CH_3), 1·28–2·03 (m, 30 H, CH_2), 4·00–4·17 (t+t, 4 H, CH_2O+CH_2O), 4·47–4·63 (dm, 1 H, CHF, J=50 Hz), 6·97 (d, 2 H, Ph, J=9 Hz), 8·27 (d, 2 H, Ph, J=8 Hz), 8·41 (s, 2 H, Py); IR (KBr): 2925, 2856, 1608, 1582, 1543, 1508, 1468, 1439, 1394, 1278, 1249, 1169, 1016, 843, 790 cm^{-1}; $[\alpha]_D^{28}$+4·47°, $[\alpha]_{435}^{26}$+7·66° (*c*1·10, $CHCl_3$).

5.6.4. *2-(4-Decyloxyphenyl)-5-((S)-5-fluorodecyloxy)-pyrimidine* (**5 c**)

The experimental procedure was as described for the preparation of compound **2 b**. Compound **14** (0·116 g, 0·35 mmol), 2-(4-decyloxyphenyl)-5-hydroxypyrimidine (0·126 g, 0·38 mmol) and sodium hydride (60 per cent by weight, 0·066 g, 1·65 mmol) were used to yield a white solid. Yield: 0·115 g (62 per cent); ^{1}H NMR ($CDCl_3$): 0·88 (t, 3 H, CH_3), 0·90 (t, 3 H, CH_3), 1·26–1·83 (m, 30 H, CH_2), 4·00 (t, 2 H, CH_2O), 4·08 (t, 2 H, CH_2O), 4·42–4·59 (dm, 1 H, CHF, J=50 Hz), 6·96 (d, 2 H, Ph, J=9 Hz), 8·27 (d, 2 H, Ph, J=9 Hz), 8·40 (s, 2 H, Py); ^{13}C NMR ($CDCl_3$): 14·0 (CH_3), 14·1 (CH_3), 21·7 (d, CH_2, J=4 Hz), 22·5 (CH_2), 22·7 (CH_2), 24·8 (d, CH_2, J=5 Hz), 26·0 (CH_2), 29·0 (CH_2), 29·2 (CH_2), 29·3 (CH_2), 29·4 (CH_2), 29·5 (CH_2), 29·6 (CH_2), 31·6 (CH_2), 31·9 (CH_2), 34·8 (d, CH_2, J=21 Hz), 35·1 (d, CH_2, J=21 Hz), 35·8 (CH_2), 68·0 (CH_2O), 68·6 (CH_2O), 94·2 (d, CHF, J=168 Hz), 114·4 (Ar), 128·9 (Ar), 130·0 (Ar), 143·8 (Ar), 150·9 (Ar), 157·7 (Ar), 160·7 (Ar); ^{19}F NMR ($CDCl_3$): −181·2 (dm, J=50 Hz): IR (KBr): 2921, 2845, 1607, 1583, 1549, 1515, 1442, 1394, 1327, 1282, 1250, 1169, 1128, 1106, 1068, 1024, 1002, 913, 868, 840, 820, 789, 740, 721, 646, 616, 551 cm^{-1}; $[\alpha]_D^{24}$+1·65°, $[\alpha]_{435}^{22}$ −0·87° (*c*1·15, $CHCl_3$).

We express our thanks to Canon Inc. for their support and discussion of the physical measurements of mesomorphic properties.

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