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

Synthesis and physical properties of laterally fluoro substituted ferroelectric liquid crystals with a fluoro substituted chiral terminal chain

Riswoko Asep; Yoshio Aoki; Takuji Hirose; Hiroyuki Nohira

Online publication date: 06 August 2010

To cite this Article Asep, Riswoko , Aoki, Yoshio , Hirose, Takuji and Nohira, Hiroyuki(2001) 'Synthesis and physical properties of laterally fluoro substituted ferroelectric liquid crystals with a fluoro substituted chiral terminal chain', Liquid Crystals, 28: 5, 785 — 791
To link to this Article: DOI: 10.1080/02678290010025440
URL: http://dx.doi.org/10.1080/02678290010025440

LIQUID CRYSTALS, 2001, VOL. 28, NO. 5, 785–791

Synthesis and physical properties of laterally fluoro substituted ferroelectric liquid crystals with a fluoro substituted chiral terminal chain

RISWOKO ASEP*, YOSHIO AOKI, TAKUJI HIROSE
and HIROYUKI NOHIRA

Department of Applied Chemistry, Faculty of Engineering, Saitama University,
255 Shimo-Ohkubo, Urawa, Saitama 338-8570, Japan

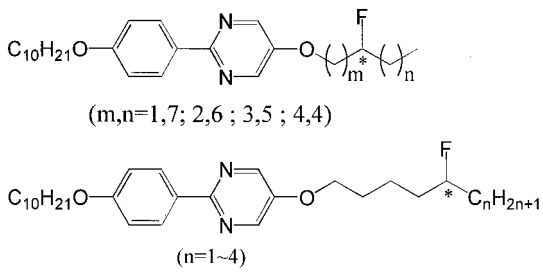
(*Received 24 August 2000; in final form 19 October 2000; accepted 13 November 2000*)

A new series of ferroelectric liquid crystals (FLCs) has been designed for active matrix displays based upon the chiral smectic C phase. The FLCs have been derived from optically active fluorinated alkanols and a laterally fluoro substituted biphenylyl-1,3-dioxan core. Their physical properties such as spontaneous polarization, current response time, and tilt angle have been determined. The FLC derived from 2-fluoro-octanol showed a very short current response time of 10 μs at $T_{Sm^*-N^*} - T = 10°C$, while another FLC with the same core derived from 5-fluoro-octanol gave a value of 150 μs.

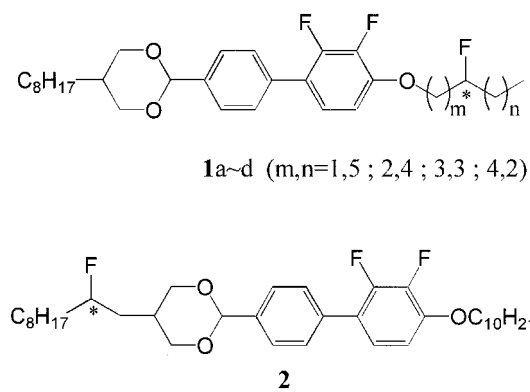
1. Introduction

FLCs have been actively studied for active matrix [1–5] and passive matrix display applications [6]. The inherent microsecond switching capability of the FLC electro-optical effect is a fascinating property which is applicable to flat panel displays [7]. To obtain an FLC with a short response time, many materials having the SmC* phase have been synthesized and characterized. However, the relationship between the molecular structure and the associated response time is very complicated. The influence of the position of a fluorinated chiral centre and of the alkyl chain length at the chiral centre on the response time has been previously studied for compounds with the phenylpyrimidinyl mesogenic core (scheme 1) [8, 9]. It was found that by introducing the fluoro substituent with the appropriate alkyl chain length at the chiral centre, the FLC showed a short response time.

Liquid crystal materials with a laterally fluorinated core, such as 2-(2,3-difluorobiphenyl-4′-yl)-1,3-dioxan, possess the phase sequence SmC–N [10]. We expected that by introduction of optically active fluorinated alkyl groups to this core, FLCs showing the phase sequence SmC*–N* and having a short response time could be obtained. However, for mesogens with their core, the influence of the fluorinated chiral tail on the response time has not yet been investigated. Here, we describe the physical properties, such as spontaneous polarization, current response time, and tilt angle, of the two types of FLC in scheme 2.



Scheme 1. The structures of pyrimidine-based ferroelectric liquid crystals with a fluorinated asymmetric structure.



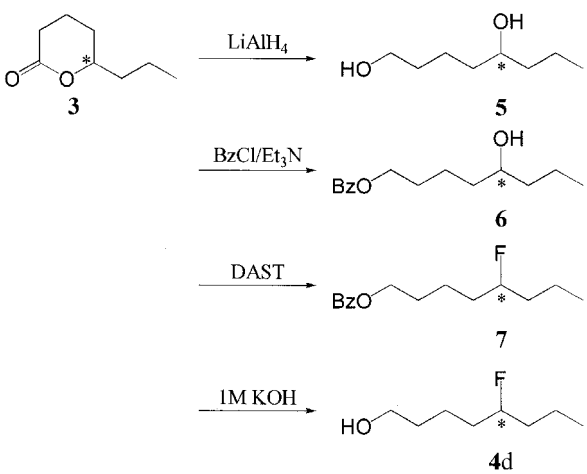
Scheme 2. The structures of the laterally fluoro substituted ferroelectric liquid crystals with a fluoro substituted chiral terminal chain **1a–d** and **2**.

*Author for correspondence; e-mail: asep@apc.saitama-u.ac.jp

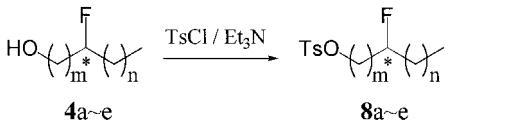
Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2001 Taylor & Francis Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290010025440

2. Synthesis

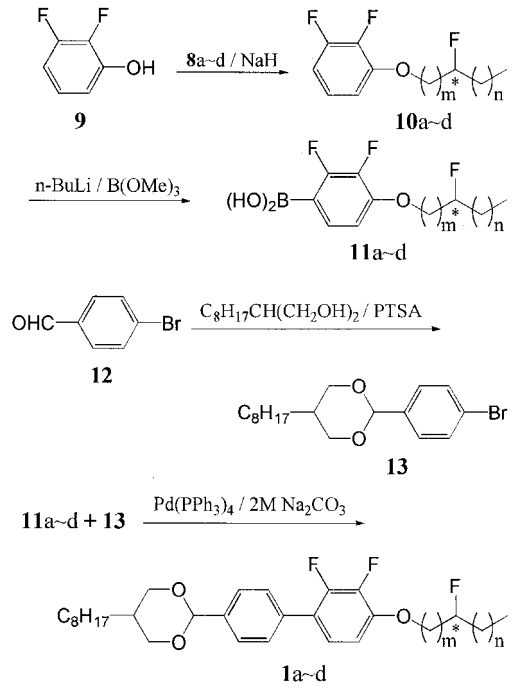
The required optically active fluorinated alkanols, except for a 5-fluoro-octanol, were prepared from the (*R*)-1,2-epoxyalkanes [8, 11]. Scheme 3 shows a synthetic procedure for optically active 5-fluoro-octanol using optically active δ-octanolactone **3** as starting material, obtained by optical resolution of its racemate [12]. The lactone was reduced to provide the diol **5**. After mono-benzoylation of **5**, the product **6** was fluorinated to give **7**. The compound **4d** was afforded by deprotection of **7**. The fluorinated alkanols **4a–e**—see scheme 4—were tosylated to give **8a–e** [8, 9, 11]. Etherification of **9** (scheme 5) with the tosylates **8a–d** yielded the products **10a–d**, which were then converted to the aryl boronic acids **11a–d**. The aryl bromide **13** was obtained by acetalization of **12** with 2-octyl-1,3-propandiol [10]. The reaction of the aryl boronic acids **11a–d** with **13** catalysed by $Pd(0)(PPh_3)_4$ afforded the FLCs **1a–d** in a good yield (scheme 5). Scheme 6 shows the synthetic route to compound **2**. The diol **15** was prepared by reduction of compound **14**, derived from the tosylate **8e** [8]. Optically active 2-(4-bromophenyl)-5-(2-fluorodecyl)-1,3-dioxan **16**, obtained from **12** and **15**, was reacted with **17** to give **2**.



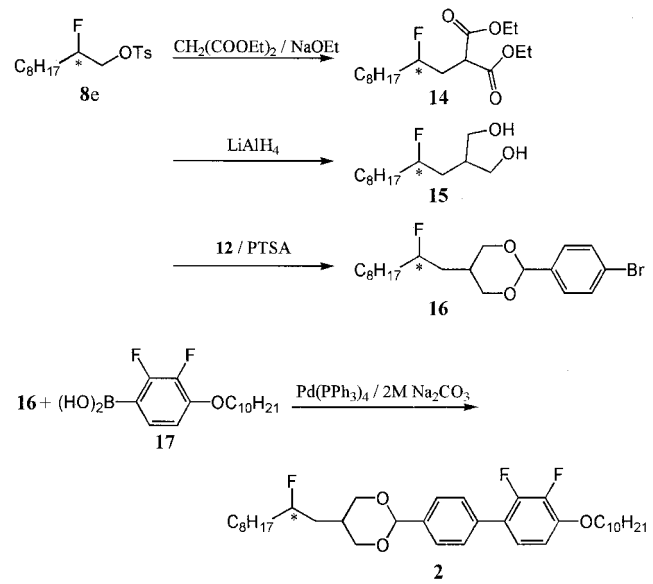
Scheme 3. Synthetic route to optically active 5-fluoro-octanol **4d**.



Scheme 4. Synthetic route for the optically active fluorinated alkyl tosylates **8a–e**.



Scheme 5. Synthetic route to ferroelectric liquid crystals **1a–d**.



Scheme 6. Synthetic route for ferroelectric liquid crystal **2**.

3. Results and discussion

3.1. *Phase transition temperatures*

As shown in the table, all of the compounds of type **1** showed the phase sequence SmC*–N*. The compound **2** with the chiral moiety at the dioxan ring exhibited additionally a SmA phase between the N* and SmC* phases, and an unidentified smectic phase below the SmC* phase. For compounds **1a–d**, it was found that

Table. Phase transition temperatures of compounds **1** and **2**

Compound	m[a]	n[b]	Temperature[c]/°C										
			Cr		SmX*		SmC*		SmA		N*		I
1a	1	5	•	39			•	103			•	115	•
1b	2	4	•	42			•	98			•	123	•
1c	3	3	•	27			•	94			•	111	•
1d	4	2	•	23			•	67			•	103	•
2			•	44	•	50	•	96	•	110	•	119	•

[a] Length of the alkyl chain of the chiral moiety (inner).
[b] Length of the alkyl chain of the chiral moiety (outer).
[c] Cr = crystallization temperature, SmX* = unidentified smectic phase, SmC* = chiral smectic C phase, SmA = smectic A phase, N* = chiral nematic phase, I = isotropic liquid.

the SmC* phase was stabilized when the chiral centre was located close to the 2,3-difluorobenzene ring. An odd–even effect was also found, and the liquid crystals with the chiral centre in the 2- (**1a**) and 4-position (**1c**) of the chain (even positions) have wider temperature ranges of the SmC* phase than those where it is in the 3- (**1b**) and 5-position (**1d**) (odd positions). However, the effect of the chiral centre position on the temperature range of the N* phase was found to be the opposite. Introduction of the chiral centre far away from the core has the effect that the clearing point ($T_{N\text{-}I}$) and the melting point ($T_{Cr\text{-}Sm}$) shift to lower temperatures. For the compound **2**, compared with the compound **1a**, the SmC* phase temperature range was decreased, and the SmA and the unidentified smectic phase were observed additionally. It might be that **2** is not preferred for forming the tilted smectic phase because **2** has the chiral tail attached to the dioxan ring.

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

Figure 1 shows the temperature dependence of the spontaneous polarization ($\mathbf{P}_s$). For the FLCs of type **1**, the compound with the chiral centre in the 2-position (**1a**) had a smaller $\mathbf{P}_s$ value than that with it in the 3-position (**1b**). The reverse tendency was found for the FLCs with a core consisting of the phenylpyrimidine ring (scheme 1). The closer the chiral centre is located to the phenylpyrimidinyl mesogenic core, the larger is the $\mathbf{P}_s$ value, due to the reduced rotational freedom of the chiral centre [8]. For the FLCs with the laterally fluorinated core, the directions of the dipole moments of the chiral centre and the core played an important role with regard to the magnitude of the $\mathbf{P}_s$ [13]. The odd–even effect was found and the compound with the chiral centre in the 4-position (**1c**) had a larger magnitude of $\mathbf{P}_s$ than that with the centre in the 3- (**1b**) and 5-position (**1d**). The compound **2** with the chiral tail attached to the dioxanyl ring without an ether linkage showed a larger $\mathbf{P}_s$ value than compound **1a**, due to the smaller rotational freedom of the dipole moment of the fluorinated chiral centre.

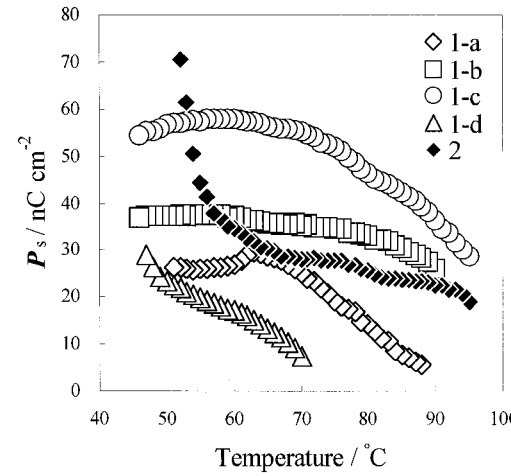


Figure 1. Temperature dependence of the spontaneous polarization ($\mathbf{P}_s$) of compounds **1a–d** and **2**.

As shown in figure 2, the response time also depended on the position of the chiral centre. The compounds with the chiral centre in the 2- (**1a**) and 4-position (**1c**) showed shorter response times than those with the centre in the 3- (**1b**) and 5-position (**1d**). The longest response time was observed for the FLC derived from 5-fluoro-octanol (**1d**), while the shortest was found for the product from 2-fluoro-octanol (**1a**). It is well known that the response time is inversely proportional to the magnitude of spontaneous polarization, and proportional to the viscosity [14]. Therefore, the very short response time achieved (about 10 μs at $T_{Sm^*\text{-}N^*} - T = 10$°C) for **1a** must be due to its low viscosity. For **1a**, considering the molecular structure and conformation, the extent of local fluorination within the molecular structure has been increased, and used to decrease the viscosity [15, 16].

The temperature dependences of the tilt angles are shown in figure 3. For the compounds of type **1**, the tilt

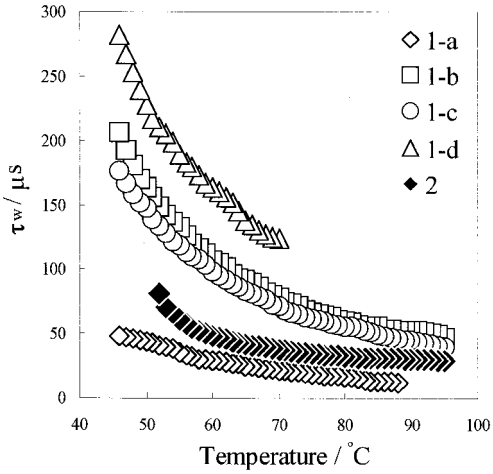


Figure 2. Temperature dependence of the current response time (τ_w) of compounds **1a–d** and **2**.

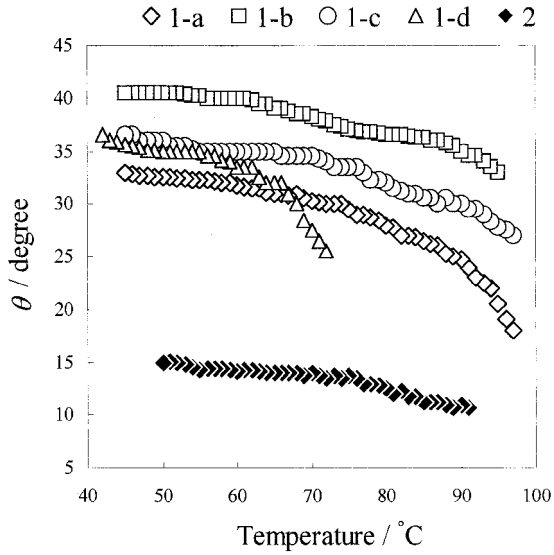


Figure 3. Temperature dependence of the tilt angle (θ) of compounds **1a–d** and **2**.

angles changed from around 20° to more than 30° at the first order SmC*–N* transition temperature ($T_{Sm^*\text{-}N^*}$). On the other hand, the tilt angle of **2** only changed from 10° to 15° over the phase transition SmC*–SmA.

4. Summary

A novel series of laterally fluorinated ferroelectric liquid crystals having a fluorinated alkyl chain (**1a–d** and **2**) have been prepared. Investigation of their mesomorphic properties showed that the mesogens of type **1** possessed the phase sequence SmC*–N*, while the mesogen **2** had the sequence SmX*–SmC*–SmA–N*. The ferroelectric properties, such as spontaneous polarization, response time, and tilt angle, were investigated systematically. It was found that the spontaneous polarization, response time, and tilt angle were dependent on the position of the fluorinated chiral centre. The liquid crystal materials **1a–d** showed an odd–even effect of the SmC* phase stability, the $\mathbf{P}_s$, and the response time. The shortest response time (of the order of 10 μs) was found for the compound **1a** derived from 2-fluorooctanol. The compounds of type **1** and **2** have a difference in tilting tendency due to the different order of their phase transitions.

5. Experimental

5.1. *Characterization*

The structures of the intermediates and products were confirmed by ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectroscopy (Bruker ARX400 and AM400), and infrared (IR) spectroscopy (Perkin-Elmer FT1640). Mesomorphic behaviour was investigated using differential scanning calorimetry (Mac Science DSC3100), and a Nikon Optiphot2-POL polarizing microscope equipped with a Mettler FP82HT hot stage and a Mettler FP90 thermal controller. The magnitude of the spontaneous polarization and the current response time were measured using the triangular-wave method and the field-reversal method, respectively, under a field of ± 10 $V_{p\text{-}p}$ in a 2 μm-thick cell.

5.2. *Synthesis*

5.2.1. *(R)-(−)-5-Hydroxy-1-octanol (**5**)*

To a suspension of lithium aluminium hydride ($LiAlH_4$) (0.11 g, 3 mmol) in THF, a solution of (*R*)-(+)-δ-octanolactone (265 mg, 1.9 mmol) [$[\alpha]_D^{25}$ + 42.0°, $[\alpha]_{435}^{23}$ + 84.3° (*c* 1.0, MeOH)], of optical purity 94% e.e. (determined using CHIRALCEL OB-H), in dry THF (2 ml) was slowly added. The mixture was stirred for 6 h at room temperature under a nitrogen atmosphere. Saturated aqueous sodium sulphate and 3M hydrochloric acid were added. The organic layer was shaken with diethyl ether, and dried over anhydrous magnesium sulphate. The residual crude product was distilled (135–150°C, 30 mm Hg) to yield a colourless liquid (240 mg, 1.6 mmol, 88%). $[\alpha]_D^{26}$ − 1.0°, $[\alpha]_{435}^{24}$ − 0.5° (*c* 1.0, MeOH). ^{1}H NMR ($CDCl_3$): 0.89–0.92 (t, 3H, CH_3), 1.29–1.61 (m, 10H, CH_2), 2.63 (m, 1H, OH), 3.58–3.59 (m, 1H, CHO), 3.61–3.64 (t, 2H, CH_2O). ^{13}C NMR ($CDCl_3$): 13.9 (CH_3), 21.7, 27.8, 32.4, 36.8, 37.2 (CH_2), 62.3 (CH_2OH), 71.6 (CHOH). IR (neat, cm^{-1}): 3355 (OH), 2932–2862 (CH_3, CH_2).

5.2.2. *(R)-(−)-5-Hydroxy-1-octyl benzoate (**6**)*

To a stirred solution of (*R*)-(−)-5-hydroxy-1-octanol (**5**) (56 mg, 0.38 mmol) and benzoyl chloride (54 mg, 0.38 mmol) in dry dichloromethane (1 ml), 1,4-diazabicyclo[2,2,2]octane (DABCO) (135 mg, 1.2 mmol) was

slowly added. The solution was then stirred at room temperature for 3 h under a nitrogen atmosphere. After adding diluted HCl solution, the organic layer was shaken with dichloromethane. The organic extract was washed with distilled water, and dried over anhydrous sodium sulphate. After concentration, the product was purified by thin layer chromatography (ethyl acetate : hexane = 1 : 5) to yield a light yellow liquid (87 mg, 0.35 mmol, 92%). $[\alpha]_D^{25}$ − 2.6°, $[\alpha]_{435}^{23}$ − 3.0° (*c* 1.1, MeOH). ^{1}H NMR ($CDCl_3$): 0.88–0.92 (t, 3H, CH_3), 1.31–1.81 (m, 10H, CH_2), 3.62 (m, 1H, CHO), 4.32–4.35 (t, 2H, CH_2O), 7.41–8.05 (m, 5H, C_6H_4). ^{13}C NMR ($CDCl_3$): 14.0 (CH_3), 22.2, 27.8, 28.8, 36.9, 37.2 (CH_2), 64.9 (CH_2OBzl), 71.7 (CHOH), 128.3–132.8 (Ph), 166.7 (C=O). IR (neat, cm^{-1}): 3411 (OH), 2932–2861 (CH_3, CH_2), 1720 (C=O).

5.2.3. *(S)-(+)-5-Fluoro-1-octyl benzoate (**7**)*

A solution of (diethylamino)sulphur trifluoride (DAST) (361 mg, 2.2 mmol) in dry dichloromethane (6 ml) was added to a stirred solution of (*R*)-(−)-5-hydroxy-1-octyl benzoate (**6**) (160 mg, 0.6 mmol) in dry dichloromethane (4 ml) at − 78°C under a nitrogen atmosphere. The mixture was stirred for 30 min at the same temperature. Saturated aqueous sodium sulphate was added, and the organic layer was shaken with dichloromethane. The extract was washed with distilled water and dried over anhydrous sodium sulphate. The solvent was evaporated off, and the remaining material purified by thin layer chromatography (ethyl acetate : hexane = 1 : 7) to yield a light yellow liquid (95 mg, 0.38 mmol, 59%). $[\alpha]_D^{24}$ + 0.9°, $[\alpha]_{435}^{23}$ + 0.7° (*c* 0.95, MeOH), optical purity 92% e.e. (determined using CHIRALCEL OB-H). ^{1}H NMR ($CDCl_3$): 0.88–0.92 (t, 3H, CH_3), 1.31–1.82 (m, 10H, CH_2), 4.32–4.35 (t, 2H, CH_2O), 4.40–4.57 (dm, 1H, CHF, $J_{H\text{-}F}$ = 49.45 Hz), 7.42–8.05 (m, 5H, C_6H_4). ^{13}C NMR ($CDCl_3$): 13.9 (CH_3), 21.8, 22.5, 28.6, 34.7, 34.9 (CH_2), 64.8 (CH_2OBzl), 93.4–95.1 (d, CHF, J = 166.8 Hz), 128.3–132.8 (Ph), 166.6 (C=O). ^{19}F NMR ($CDCl_3$): − 181.2 ∼ − 181.0 (m, CHF). IR (neat, cm^{-1}): 3063 (Ph), 2954–2870 (CH_3, CH_2), 1720 (C=O).

5.2.4. *(S)-(−)-5-Fluoro-1-octanol (**4d**)*

To a stirred solution of (*S*)-(+)-5-fluoro-1-octyl benzoate (**7**) (94 mg, 0.4 mmol) in methanol (3 ml), 1M potassium hydroxide (1 ml) was added. The mixture was stirred at room temperature overnight. The organic matter was extracted into diethyl ether, and the extract washed with 5 wt % aqueous sodium carbonate. The extract was then dried over anhydrous magnesium sulphate. The solvent was evaporated off to yield a colourless liquid (42 mg, 0.28 mmol, 77%). $[\alpha]_D^{27}$ − 1.8°, $[\alpha]_{435}^{24}$ − 2.2° (*c* 2.2, Et_2O). ^{1}H NMR ($CDCl_3$): 0.89–0.93 (t, 3H, CH_3), 1.32–1.62 (m, 10H, CH_2), 3.64–3.67 (t, 2H, CH_2O), 4.40–4.54 (dm, 1H, CHF, $J_{H\text{-}F}$ = 49 Hz). ^{13}C NMR ($CDCl_3$): 13.9 (CH_3), 21.4, 22.5, 32.5, 34.7, 34.9 (CH_2), 62.7 (CH_2OH), 93.6–95.2 (d, CHF, J = 166.9 Hz).

5.2.5. *(S)-(−)-5-Fluoro-1-octyl p-toluenesulphonate (**8d**)*

A solution of *p*-toluenesulphonyl chloride (64 mg, 0.34 mmol) and (*S*)-(−)-5-fluoro-1-octanol (42 mg, 0.28 mmol) in dry dichloromethane (1.5 ml) was stirred at 0°C. Dry triethylamine (120 mg, 1.2 mmol) was added. The mixture was stirred for 12 h at room temperature. To the mixture, 1M hydrochloric acid was then added, and the organic matter was extracted with dichloromethane. The extract was washed with dilute hydrochloric acid, and dried over anhydrous sodium sulphate. The concentrated mixture was purified by thin layer chromatography (ethyl acetate : hexane = 1 : 5) to yield a colourless liquid (56 mg, 0.19 mmol, 65%). $[\alpha]_D^{26}$ − 0.2°, $[\alpha]_{435}^{24}$ − 0.1° (*c* 2.8, Et_2O). ^{1}H NMR ($CDCl_3$): 0.88–0.92 (t, 3H, CH_3), 1.24–1.80 (m, 10H, CH_2), 2.47 (s, 3H, CH_3), 4.03 (t, 2H, CH_2O), 4.4–4.8 (dm, 1H, CHF, J = 80 Hz), 7.4–7.8 (dd, 4H, C_6H_4).

5.2.6. *(S)-(−)-1-(2-Fluoro-1-octyloxy)-2,3-difluorobenzene (**10a**)*

To a solution of 2,3-difluorophenol (414 mg, 3.18 mmol) and sodium hydride (NaH) (60 % wt, 381 mg, 9.52 mmol) in dry *N*,*N*-dimethylformamide (DMF) (2 ml), a solution of (*S*)-(+)-2-fluorooctyl *p*-toluenesulphonate (**8a**) [11] (0.8 g, 2.65 mmol) in dry DMF (1 ml) was added at 25°C under a nitrogen atmosphere. The mixture was heated for 10 h at 70°C. Distilled water was added, and the organic matter was extracted into diethyl ether. The extract was washed with distilled water and dried over anhydrous magnesium sulphate. After concentration, the product was purified by thin layer chromatography (ethyl acetate : hexane = 1 : 12) to yield a colourless liquid (300 mg, 1.15 mmol, 44%). $[\alpha]_D^{24}$ − 1.0° (*c* 1.4, $CHCl_3$). ^{1}H NMR ($CDCl_3$): 0.86–0.88 (t, 3H, CH_3), 1.23–1.81 (m, 10H, $5CH_2$), 4.08–4.17 (dd, 2H, CH_2O), 4.76–4.91 (dm, 1H, CHF, J = 42.4 Hz), 6.72–6.81, 6.93–6.98 (dm, 3H, $C_6H_3F_2$). ^{13}C NMR ($CDCl_3$): 13.9 (CH_3), 20.8, 24.8, 29.0, 31.3, 31.6 ($5CH_2$), 73.4 (CH_2O), 90.8–92.5 (d, CHF, J = 171.0 Hz), 109.6, 109.8, 110.5, 123.1, 140.3 ($C_6H_3F_2$). ^{19}F NMR ($CDCl_3$): − 137.8, − 159.5 ($C_6H_3F_2$), − 186.2 ∼ − 187.3 (m, CHF).

5.2.7. *(S)-(+)-2,3-Difluoro-4-(2-fluoro-octyloxy)-phenylboronic acid (**11a**)*

A solution of *n*-butyllithium (1.52 mol l^{-1} hexane) (1.5 ml) was added to a stirred solution of **10a** (400 mg, 1.5 mmol) in dry tetrahydrofuran (THF) (6 ml) at − 78°C under a nitrogen atmosphere. The mixture was stirred for 2 h at the same temperature. A solution of triisopropyl borate (620 mg, 3.3 ml) in dry THF (2 ml) was

cooled to 0°C, and added to the solution of **10a**. The mixture was stirred at room temperature overnight. To the mixture, 6M hydrochloric acid (2 ml) was added, and the mixture was stirred for a further 2 h. The organic material was extracted into diethyl ether, and the extract dried over anhydrous sodium sulphate. The solvent was evaporated off, and the remaining materials recrystallized from hexane to yield a white powder (245 mg, 0.81 mmol, 52%). ^{1}H NMR ($CDCl_3$): 0.85–0.89 (t, 3H, CH_3), 1.12–1.73 (m, 10H, $5CH_2$), 3.78–3.85 (dd, 2H, CH_2O), 4.38–4.50 (dm, 1H, CHF, J = 47.7 Hz), 6.43–6.46, 7.05–7.09 (dm, 2H, $C_6H_2F_2B(OH)_2$).

5.2.8. *(S)-(+)-2-[2,3-Difluoro-4-(2-fluoro-octyloxy)-biphenyl-4′-yl]-5-octyl-1,3-dioxan (**1a**)*

A mixed solution of tetrakis(triphenylphosphine)-palladium ($Pd(PPh_3)_4$) (20 mg, 0.012 mmol), 2-(4-bromophenyl)-5-octyl-1,3-dioxan (**13**) [10] (100 mg, 0.28 mmol), 2M aqueous sodium carbonate (0.5 ml), and (*S*)-(+)-2,3-difluoro-4-(2-fluoro-octyloxy)phenylboronic acid (**11a**) (110 mg, 0.36 mmol) in dry dimethoxyethane (DME) (4 ml) was stirred at 80°C for 40 h. To the mixture, 30% hydrogen peroxide was added slowly at room temperature. The organic layer was shaken with diethyl ether, and the extract dried over anhydrous magnesium sulphate. The solvent was evaporated from the extract, and the remaining product purified by thin layer chromatography twice (ethyl acetate : hexane = 1 : 12, and dichloromethane : hexane = 1 : 2) to yield a white powder. The powder was recrystallized from hexane (63 mg, 0.12 mmol, 43%). $[\alpha]_D^{23}$ + 1.5°, $[\alpha]_{435}^{24}$ + 2.3° (*c* 1.2, $CHCl_3$). ^{1}H NMR ($CDCl_3$): 0.87–0.89 (t, 6H, $2CH_3$), 1.12–1.13 (m, 2H, CH_2), 1.29–1.67 (m, 24H, $6CH_2$), 2.16–2.19 (m, 1H, CH), 3.52–3.57 (t, 2H, CH_2), 4.09–4.27 (dm, 4H, $2CH_2O$), 4.76–4.942 (dm, 1H, CHF, J = 48.7 Hz), 5.45 (s, 1H, CHO_2), 6.78–6.82, 7.05–7.09 (dm, 2H, $C_6H_2F_2$), 7.48–7.56 (m, 4H, C_6H_4). ^{13}C NMR ($CDCl_3$): 13.9, 14.1 ($2CH_3$), 22.5–34.9 ($13CH_2$), 69.4, 72.6 ($3CH_2O$), 90.9–92.8 (d, CHF, J = 191.2 Hz), 101.1, 109.6, 122.8, 122.9, 123.6, 126.2, 128.5, 128.6, 135.3, 135.7, 143.1, 147.6 ($C_{12}H_6F_2$). ^{19}F NMR ($CDCl_3$): − 142.1, − 159.3 ($C_6H_2F_2$), − 183.8– − 184.2 (m, CHF).

5.2.9. *(S)-(−)-2-(2,3-Difluoro-4-decyloxybiphenyl-4′-yl)-5-(2-fluorodecyl)-1,3-dioxan (**2**).*

This compound was synthesized by a similar preparative procedure to that used for compound **1a**. $[\alpha]_D^{24}$ − 1.75° (*c* 0.4, $CHCl_3$). ^{1}H NMR ($CDCl_3$): 0.87–0.89 (t, 6H, $2CH_3$), 1.21–1.83 (m, 30H, $15CH_2$), 1.79–1.87, (m, 2H, CH_2), 2.35–2.41 (m, 1H, CH), 3.57–3.64 (t, 2H, CH_2O), 4.05–4.08, 4.29–4.31 (dm, 4H, $2CH_2O$), 4.48–4.63 (dm, 1H, CHF, J = 49.2 Hz), 5.47 (s, 1H, CHO_2), 6.76–6.80, 7.05–7.09 (dm, 2H, $C_6H_2F_2$), 7.49–7.56 (dd, 4H, C_6H_4). ^{19}F NMR ($CDCl_3$): − 142.1, − 161.3 ($C_6H_2F_2$), − 180.5– − 180.9 (m, CHF).

5.2.10. *(S)-(−)-Ethyl 2-(2-fluorodecyl)malonate (**14**)*

To a solution of sodium ethoxide (NaOEt) (9 mmol) and diethyl malonate (1.5 g, 9.04 mmol) in dry benzene (1 ml), (*S*)-2-fluorodecyl tosylate [8] (2.7 g, 8.16 mmol) was added at 40°C. The mixture was heated at 90°C for 5 h, and water was then added to the dilute mixture at room temperature. The organic product was extracted with diethyl ether, and the extract dried over sodium sulphate. The solvent was evaporated off and the remaining product purified by column chromatography (silica gel, benzene) to yield a colourless liquid (0.77 g, 2.42 mmol, 30%). $[\alpha]_D^{23}$ − 26.5°, $[\alpha]_{435}^{22}$ − 53.9° (*c* 0.5, $CHCl_3$). ^{1}H NMR ($CDCl_3$): 0.86–0.89 (t, 3H, CH_3), 1.16–1.43 (m, 20H, $2CH_3$, $7CH_2$), 1.86–1.88 (m, 2H, CH_2), 2.11–2.18 (m, 1H, CH), 4.11–4.27 (m, 4H, $2CH_2O$), 4.41–4.60 (dm, 1H, CHF, J = 49.8 Hz). ^{13}C NMR ($CDCl_3$): 13.9, 14.0, 14.1 ($3CH_3$), 20.9, 22.6, 28.2–34.1 ($8CH_2$), 48.3 (CH), 61.2 ($2CH_2O$), 91.1–92.8 (d, CHF, J = 171.0 Hz), 168.2, 170.5 (2C=O).

5.2.11. *(S)-(−)-2-(2-Fluorodecyl)-1,3-propandiol (**15**)*

To a suspension of lithium aluminium hydride ($LiAlH_4$) (0.15 g, 3.1 mmol), a solution of (*S*)-(−)-**14** (500 mg, 1.6 mmol) in dry diethyl ether (5 ml) was slowly added. The mixture was stirred for 6 h at 50°C under a nitrogen atmosphere. Saturated aqueous sodium sulphate and 2M hydrochloric acid were added. The organic matter was extracted into diethyl ether, and dried over anhydrous magnesium sulphate. The crude residue was recrystallized from hexane to yield white crystals (230 mg, 0.98 mmol, 63%). $[\alpha]_D^{24}$ − 0.9° (*c* 0.9, $CHCl_3$). ^{1}H NMR ($CDCl_3$): 0.86–0.89 (t, 3H, CH_3), 1.23–1.43 (m, 14H, $7CH_2$), 1.79–1.87, (m, 2H, CH_2), 2.35–2.41 (m, 1H, CH), 3.87–3.90 (m, 4H, $2CH_2O$), 4.45–4.62 (dm, 1H, CHF, J = 49.5 *Hz*).

5.2.12. *(S)-2-(4-Bromophenyl)-5-(2-fluorodecyl)-1,3-dioxan (**16**)*

A mixture of *p*-bromobenzaldehyde (79 mg, 0.43 mmol), diol **15** (100 mg, 0.43 mmol), and *p*-toluenesulphonic acid in dry toluene was heated under reflux for 5 h. The cooled mixture was washed with 5 wt % aqueous sodium carbonate, and the solvent was evaporated. The remaining product was recrystallized from methanol twice to yield a white powder (53 mg, 0.13 mmol, 30%). ^{1}H NMR ($CDCl_3$): 0.86–0.89 (t, 3H, CH_3), 1.23–1.43 (m, 14H, $7CH_2$), 1.79–1.87 (m, 2H, CH_2), 2.35–2.41

(m, 1H, CH), 3.71–3.75, 4.10–4.13 (dt, 4H, $2CH_2O$), 4.46–4.63 (dm, 1H, CHF, $J = 49.6$ Hz), 5.35 (s, 1H, CHO_2), 7.49–7.56 (dd, 4H, C_6H_4).

References

[1] Hatano, T., Yamamoto, K., Takezoe, H., and Fukuda, A., 1986, *Jpn. J. appl. Phys*., **25,** 1762

[2] Jisaki, M., Nishimura, T., Park, B., Isozaki, T., Nito, K., and Kawasumi, K., 1999, in Proceedings of the Japanese Liquid Crystal Conference, p. 424.

[3] Asao, Y., Togano, T., Mori, H., Hanyu, Y., Katagiri, K., and Mizutani, H., 1999, in Proceedings of the Japanese Liquid Crystal Conference, p. 420.

[4] Yoshihara, T., Makino, T., and Inoue, H., 1999, in Proceedings of the Japanese Liquid Crystal Conference, p. 250.

[5] Nonaka, T., Li, J., Ogawa, A., Hornung, B., Schmidt, W., Wingen, R., and Dubal, H., 1999, *Liq. Cryst*., **26,** 1599.

[6] Schadt, M., 1994, *Liquid Crystals: Topics in Physical Chemistry*, Vol. 3, edited by H. Stegemeyer (Darmstadt: Steinkopff; New York: Springer), p. 215.

[7] Scheuble, B. S., 1989, *Kontakte*, **1,** 34.

[8] Nagashima, Y., Ichihashi, T., Koji, N., Iwamoto, M., Aoki, Y., and Nohira, H., 1997, *Liq. Cryst*., **23,** 537.

[9] Asep, R., Aoki, Y., Hirose, T., and Nohira, H., 1999, *Mol. Cryst. liq. Cryst*. (in the press).

[10] Dong, C. C., Goodby, J. W., Styring, P., and Chang, L. K. M., 1999, *J. mater. Chem*., **9,** 1669.

[11] Nakamura, S., and Nohira, H., 1990, *Mol. Cryst. liq. Cryst*., **185,** 199.

[12] Asep, R., Aoki, Y., and Nohira, H., 1999, in Proceedings of the 37th Synthetic Organic Chemistry Japan Symposium, p. 108.

[13] Loubser, C., and Goodby, J. W., 1995, *J. mater. Chem*., **5,** 1107.

[14] Goodby, J. W., Blinc, R., Clark, N. A., Lagerwall, S. T., Osipov, M. A., Pikin, S. A., Sakurai, T., Yoshino, K., and Zeks, B., 1991, *Ferroelecric Liquid Crystals* (Gordon & Breach), p. 409.

[15] Collings, P. J., and Hird, M., 1997, *Introduction to Liquid Crystals* (London: Taylor & Francis), p. 70.

[16] Guittard, F., Taffin de Givency, E., Geribaldi, S., and Cambon, A., 1999, *J. Fluorine Chem*., **100,** 85.