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Synthesis and properties of optically active α-trifluoromethylbenzyl derivatives for ferroelectric liquid crystals

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As new chiral dopants for ferroelectric liquid crystals (FLCs), some optically active α-trifluoromethylbenzyl derivatives were synthesized, utilizing optically active 3-(4-methoxyphenyl)-4,4,4-trifluorobutanoic acid. The magnitudes of the spontaneous polarizations (P_s) and the response times depended on the core structures and the type of linkage between the optically active and the core blocks. FLC mixtures containing the chiral dopants having an ether bond between the optically active block and the core blocks showed large P_s values compared with those having an ester linkage, while the response times were inversely proportional to the values of P_s.

1. Introduction

Recently a number of ferroelectric liquid crystals (FLCs) and chiral dopants for FLCs have been studied with great interest in connection with their application in flat panel display devices [1, 2]. Generally the FLC materials were made from achiral host liquid crystal mixtures, which have low viscosities and wide range smectic C (S_C) phases, and a chiral dopant having a large P_s. Many molecules have been designed, synthesized and investigated in order to obtain FLC materials showing the fastest response time. However the relationship between the molecular structures and their properties is very complicated. A FLC molecule and also a chiral dopant molecule contain an optically active part, a core part, and a terminal alkyl chain in their molecular frameworks. In particular, many optically active compounds which have a methyl [3–5], a fluoro [6–10], a trifluoromethyl [11–14], or a cyano [15, 16] group at the chiral centre have been synthesized. Some compounds have a γ- or δ-lactone structure or an oxazolidinone structure have also been synthesized as chiral dopants [17–21]. Although the optically active part is very important, the most important point for a FLC material showing a fast response time is the balance amongst the optically active part, the core part, and the terminal alkyl chain.

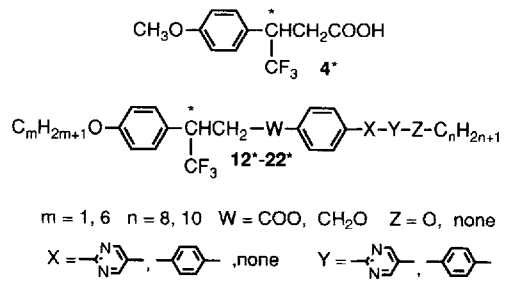
In this paper, we report the synthesis of a new optically active compound, 3-(4-methoxyphenyl)-4,4,4-trifluorobutanoic acid (**4***) and some chiral dopants derived from **4*** (see scheme 1) [22], and describe the effects of the structures of the chiral dopants on FLC properties, i.e. the magnitudes of P_s, the response times, the tilt angles and the phase transition temperatures.

2. Synthesis

2.1. *Synthesis of the optically active 3-(4-methoxyphenyl)-4,4,4-trifluorobutanoic acid* (4*)

The optically active key compound (**4***) was prepared by the following route (see scheme 2). 1,1,1-Trifluoro-4-methoxyacetophenone (**1**), prepared from the reaction of trifluoroacetic acid with 4-methoxyphenylmagnesium bromide, was converted into ethyl 3-(4-methoxyphenyl)-4,4,4-trifluorobut-2-enoate (**2**) by the treatment (step *b*) with the phosphonium salt in the presence of *n*-BuLi. The hydrogenation of **2** in the presence of palladium–carbon afforded ethyl 3-(4-methoxyphenyl)-4,4,4-tyrifluorobutanoate (**3**) which was hydrolyzed to give **4**.

The (+)- and (−)-optically active products, **4**, were prepared by disastereomeric salt formation, in good yield, using an optically active amine (*cis*-2-benzylamino-



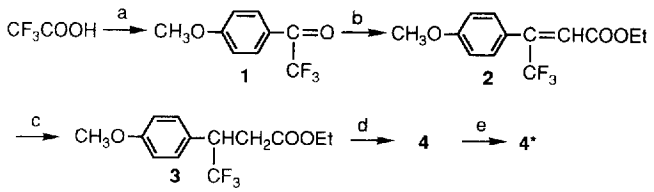
Scheme 1.

*Author for correspondence.

Table 1. Results on the optical resolution of racemic **4**.

Compound	Salt† $[\alpha]_D^{31}$‡	Salt† m.p./°C	Free acid $[\alpha]_D^{26}$§	O.P./ % ee‖	Yield¶/ per cent
(+)-**4**	+16·6	179–180	+44·9	>99	69
(−)-**4**	−16·8	179–180	−45·7	>99	67

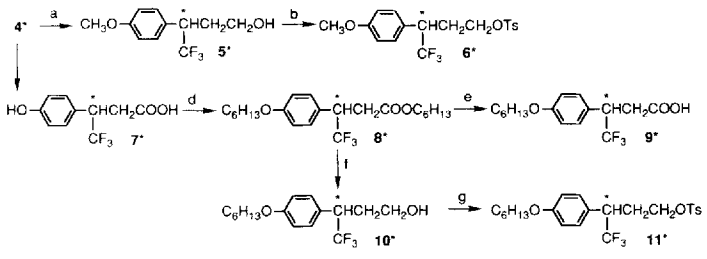
†(+)-(+)-salt and (−)-(−)-salt.
‡The solvent is methanol.
§The solvent is 99 per cent ethanol.
‖The optical purities of **4*** were determined on the ethyl ester using HPLC equipped with a chiral column, 'CHIRALCEL OB' (4·6 mm × 250 mm, carrier solvent hexane: 2-propanol = 99:1).
¶The yields were calculated based on half the amount of racemic **4**.



Scheme 2. (*a*) $CH_3OPhMgBr$, ether; (*b*) $[Ph_3PCH_2COOEt]Br$, *n*-BuLi, THF; (*c*) Pd-C, H_2, EtOH; (*d*) KOH, EtOH; (*e*) optical resolution.

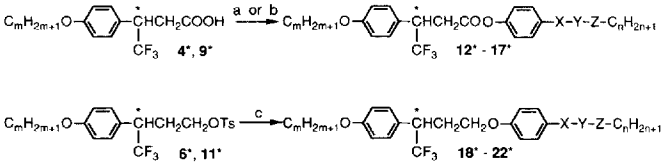
cyclohexylmethanol) as resolving agent. The salts were recrystallized two or three times from 95 per cent ethanol. The results and the properties of **4*** are shown in table 1.

The reduction of **4*** with lithium aluminium hydride gave 3-(4-methoxyphenyl)-4,4,4-trifluorobutanol (**5***) which was converted into 3-(4-methoxyphenyl)-4,4,4-trifluorobutyl tosylate (**6***). Demethylation of **4*** with hydrobromic acid afforded 3-(4-hydroxyphenyl)-4,4,4-trifluorobutanoic acid (**7***) which was alkylated and simultaneously esterified with 1-iodohexane to give hexyl 3-(4-hexyloxyphenyl)-4,4,4-trifluorobutanoate (**8***). Following hydrolysis of **8*** with potassium hydroxide, 3-(4-hexyloxyphenyl)-4,4,4-trifluorobutanoic acid (**9***) was obtained. 3-(4-Hexyloxyphenyl)-4,4,4-trifluorobutyl tosylate (**11***) was derived from **8*** in the same manner as **6*** (see scheme 3).



Scheme 3. (*a*) $LiAlH_4$, THF; (*b*) TsCl, DABCO, CH_2Cl_2; (*c*) HBr, AcOH; (*d*) $C_6H_{13}I$, NaH, DMF; (*e*) KOH, EtOH; (*f*) $LiAlH_4$, ether; (*g*) TsCl, DABCO, CH_2Cl_2.

The liquid crystal materials **12*** to **17*** were prepared by esterification of **4*** or **9*** with appropriate derivatives of phenol, while compounds **18*** to **22*** were obtained by treatment of **6*** or **11***, again with appropriate phenols (see scheme 4).



Scheme 4. (*a*) (1) $SOCl_2$, (2) core, DABCO, NaH, benzene; (*b*) DCC, core, CH_2Cl_2; (*c*) core, NaH, DMF.

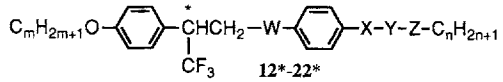
3. Results and discussion

None of the compounds synthesized showed the chiral smectic C (S_C^*) phase, but some did show the antiferroelectric liquid cyrstal (AFLC) phase [23, 24]. Details of the AFLC materials will be reported in a succeeding paper.

The FLC mixtures studied were prepared by adding 10 wt % of the chiral dopant to an achiral host liquid crystal mixtures [25]. The liquid crystal properties of these FLC mixtures, i.e. the phase transition temperatures, the P_s values, the response times and the tilt angles, are summarized in table 2.

For application in a FLC display (FLCD), the phase transition temperature between the smectic A(S_A) phase and the smectic C* (S_C^*) phase (T_c) is very important. The ester linked chiral dopants (**12***–**17***) had higher T_c values than the analogues ether linked materials (**18***–**22***), but the other phase transition temperatures, S_A–chiral nematic phase (N*) and N*–isotropic phase (I), did not depend on the linkage type in the chiral dopant. The phase transition temperatures of the chiral dopants having a three ring core (defined as the part of the structure derived from the phenolmoiety (**15***–**17***, **21***, **22***) were higher than those having a two ring core

Table 2. Electro-optical properties of FLC mixtures† at 25°C.



12*-22*

Compound	W	X‡	Y	Z	m	n	C⇌S$_C^*$⇌S$_A$⇌N*⇌I§				P_s‖/ nC cm^{-2}	τ_{10-90}¶/ μs	θ/deg
(−)-**12***	COO	Py	—	O	6	10	−6	56	64	74	+2·0	230	21
(−)-**13***	COO	Py	—	—	6	10	−5	51	57	72	+3·5	300	20
(+)-**14***	COO	Py	—	—	1	10	−4·5	52	59	72	−3·8	260	21
(+)-**15***	COO	Py	Ph	—	1	8	−6	57	70	79	−4·5	200	18
(+)-**16***	COO	Py	Ph	O	1	8	−8	60	73	82	−4·2	130	20
(+)-**17***	COO	Ph	Py	O	1	8	††	61	69	82	−3·6‡‡	150‡‡	22‡‡
(+)-**18***	CH_2O	Py	—	O	6	10	−7	49	63	73	−8·0	100	18
(+)-**19***	CH_2O	Py	—	—	6	10	−6	47	59	72	−7·5	92	22
(−)-**20***	CH_2O	Py	—	—	1	10	−6·5	46	59	70	+7·2	92	18
(−)-**21***	CH_2O	Py	Ph	—	1	8	−6·5	53	70	77	+9·6	82	19
(−)-**22***	CH_2O	Py	Ph	O	1	8	−7	56	72	80	+7·6	96	20

†FLC mixtures comprised of a chiral dopant (10 wt %) and the host liquid crystal (90 wt %).
‡Py indicates 2,5-pyrimidinyl and Ph indicates 1,4-phenyl.
§C indicates crystalline solid. S$_C^*$ indicates chiral smectic C phase. S$_A$ indicates smectic A phase. N* indicates chiral nematic phase. I indicates isotropic liquid.
‖The magnitude of P_s was measured by the triangular wave method.
¶The change of transmittance (from 10 to 90 per cent) of light was observed when a square wave of $\pm 5\,V\,\mu m^{-1}$ was applied.
‡‡The chiral dopant was deposited at 33°C. $T = 35°C$.

(**12***-**14***, **18***-**20***). On the other hand, for amalogues cores, the phase transition temperatures were not greatly affected by the length of the terminal alkyl chain.

The miscibility of **17*** with the host liquid crystal mixture was poor, but the other compounds were sufficiently miscible. It seemed that the core of **17***, namely the Ph-Ph-Py structure, gave rise to the poor miscibility with the host liquid crystal mixture.

The magnitude of P_s is a very important property for obtaining a rapid switching speed, and in the compounds under study here, the P_s value greatly depended on the type of linkage and the core structure. The temperature dependence of the P_s values of compounds **14***, **15***, **20*** and **21*** is shown in figure 1, and the order of the P_s values of these chiral dopants was found to be **14*** < **15*** < **20*** < **21***. The P_s values of the three ring core type were larger than those of the two ring core type, and it seems that the three ring core effectively fixes the dipole. At 25°C, the values of P_s of the chiral dopants with the ether linkage were about twice as large as those with the ester linkage, probably because the dipole of the trifluoromethyl moiety is offset by that of the carbonyl moiety. However, Sakaigawa and co-workers reported that the P_s values of $C_6H_{13}CH(CF_3)CH_2COOPh$-Py-$PhOC_8H_{17}$ ($P_s = 172\,nC\,cm^{-2}$, $T_c - T = 10°C$) were larger than those of $C_6H_{13}CH(CF_3)CH_2CH_2OPh$-Py-$PhOC_8H_{17}$ ($P_s = 127\,nC\,cm^{-2}$, $T_c - T = 10°C$) [14]. The former is similar to **16*** in structure, while the latter is similar to **22***. However, the P_s value of **22*** ($P_s = 7{\cdot}6\,nC\,cm^{-2}$, $T = 25°C$) was about twice as large as that of **16*** ($P_s = 4{\cdot}2\,nC\,cm^{-2}$, $T = 25°C$). This is the opposite order. In their ester type FLC material, the dopole of the trifluoromethyl group and that of the carbonyl moiety cooperatively enhance the magnitude of the P_s value. Therefore, the direction of the dipole of a trifluoromethyl group flanked by a phenyl moiety as in

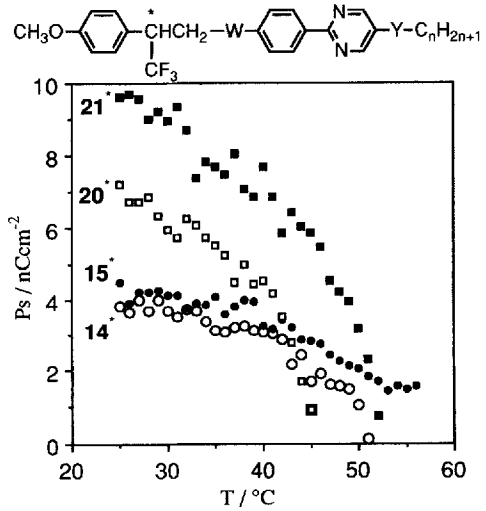


Figure 1. The relationship between the P_s value and temperature. **14***: W = COO, Y = non, $n = 10$. **15***: W = COO, Y = Ph, $n = 8$. **20***: $W = CH_2O$, Y = none, $n = 10$. **21***: $W = CH_2O$, Y = Ph, $n = 8$.

compound **16*** is probably changed by the steric effect of the phenyl moiety which is relatively bulky and rigid.

Saitoh and co-workers have reported on chiral dopants with a trifluoromethyl group at the chiral centre and the effect of the linkage between a core and the chiral moiety [13]. In their work, the P_s value of a chiral dopant containing -$COOCH(CF_3)C_6H_{13}$ was smaller than that of a dopant with a $CH_2OCH(CF_3)C_6H_{13}$ group. They also concluded that the alignment of the directions of the bond moments of the polar part and the trifluoromethyl group is important.

The phenyl moiety flanking the trifluoromethyl group probably plays important roles through (*a*) its steric effect and (*b*) its polarization effect. (*a*) It is well known that the closer the chiral centre is to the core, the larger is the P_s value, due to the steric effect of the core [2]. Also, LCs wherein the chiral centre was placed between two relatively inflexible moieties have been reported [26, 27], and as the chiral centre was strongly fixed, the rotation of the polarization of the trifluoromethyl group was hindered by the phenyl moiety. (*b*) Shiratori and co-workers have reported on the effect of the core structure on the magnitude of the polarization and concluded that introduction of a pyrimidine ring in the core part greatly increases the P_s value [11]. The polarization of the phenyl moiety by the trifluoromethyl group may therefore be important in the case of the chiral dopants **12***-**22***.

Although different host LCs were used, the magnitudes of the P_s values may be compared. A chiral dopant [11] having a S_C^* phase showed a P_s of over 400 nC cm^{-2} and a FLC mixture containing 11 wt % of the chiral dopant had a P_s of *c.* 6 nC cm^{-2} [11]. Arakawa and co-workers reported a FLC showing a P_s of over 300 nC cm^{-2}, and a FLC mixture containing 10 wt % of this FLC as the chiral dopant exhibited a P_s of *c.* 13 nC cm^{-2} [28]. For comparison, the FLC mixture containing 10 wt % of **21*** showed a P_s of *c.* 10 nC cm^{-2}, the chiral dopant **21*** effectively inducing the P_s in the achiral host liquid crystal mixture.

As FLC applications, especially for flat panel FLC displays, depend on a rapid switching speed, the response time of a FLC is a most important parameter. The temperature dependence of the response times of **14***, **15***, **20*** and **21*** is shown in figure 2, where the order of the response times of the chiral dopants is shown to be **21*** < **20*** < **15*** < **14***. This order of response times is the inverse of the order of the P_s values given above. At high temperatures, each chiral dopant showed short response times, and at low temperatures the chiral dopants with the ester linkage showed long response times (200–300 μs). The chiral dopants with the ether linkage type showed fast response times (under 100 μs) over a wide range of temperature.

Finally, the relationship between temperature and the tilt angle for **14***, **15***, **20*** asnd **21*** is shown in figure 3. The tilt angle of each of these chiral dopants at 25°C was about 20°, and a relationship between molecular structure of the chiral dopant and the tilt angle is not clear.

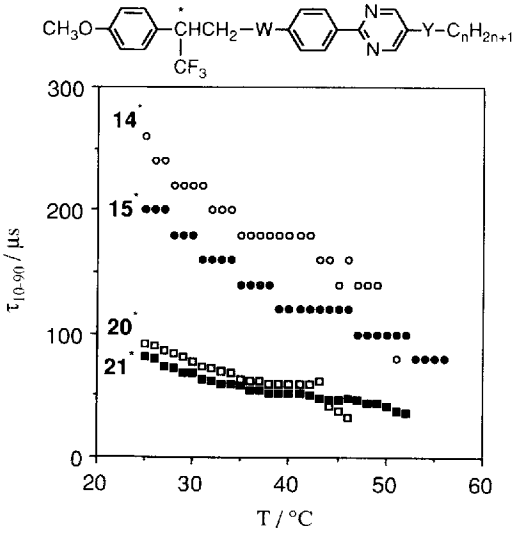


Figure 2. The relationship between response time (τ_{10-90}) and temperature; applied voltage = ± 5 V μm^{-1}. **14***: *W* = COO, *Y* = non, *n* = 10. **15***: *W* = COO, *Y* = Ph, *n* = 8. **20***: *W* = CH_2O, *Y* = none, *n* = 10. **21***: *W* = CH_2O, *Y* = Ph, *n* = 8.

4. Experimental

All compounds were characterized by ^{1}HNMR (JEOL JNM-PM60SI, JEOL FX-90Q and Bruker AM-

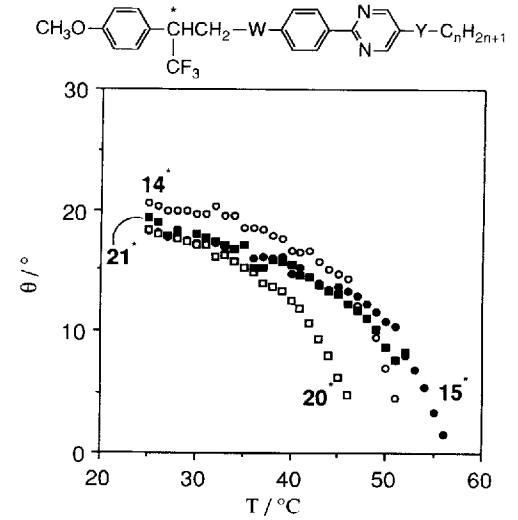


Figure 3. The relationship between the tilt angle and temperature. **14***: *W* = COO, *Y* = non, *n* = 10. **15***: *W* = COO, *Y* = Ph, *n* = 8. **20***: *W* = CH_2O, *Y* = none, *n* = 10. **21***: *W* = CH_2O, *Y* = Ph, *n* = 8.

400), IR (Perkin-Elmer FT1640) and MS (JEOL DX-303). Their specific rotations, i.e. $[\alpha]_D$ values, were determined using a JASCO DIP-360 or DIP-370. The purities of the products were measured by gas chromatography or high performance liquid chromatography (HPLC). Optical purities were also determined by HPLC (see table 1).

4.1.1. *1,1,1-Trifluoro-4-methoxyacetophenone* (**1**)

Under nitrogen, 4-bromoanisole (50·0 g, 267 mmol) was slowly added to a mixture of magnesium powder (7·80 g, 321 mmol) and dry ether (100 ml), and the rection mixture was heated with stirring for 2 h and then cooled in an ice bath. Trifluoroacetic acid (12·0 g, 105 mmol) was slowly added, and the reaction mixture was stirred for 12 h. Thereafter, 120 ml of 6 M hydrochloric acid and ether were added, and the phases were separated. The aqueous phase was shaken with ether, and the combined organic phases were washed with saturated aqueous sodium hydrogen carbonate and dried over sodium sulphate. Removal of the solvent and purification by reduced pressure distillation yielded 14·7 g (71·8 mmol, 66·6 per cent) of **1** as a light yellow liquid, b.p. 113°C/23 mmHg. IR (cm^{-1}, neat): 1703, 1603, 1572, 1515,, 1463, 1430, 1345, 1318, 1268, 1136, 1027, 941, 845, 769, 738, 649, 616, 532. MS $m/z=204$ (M^+). ^1H NMR (400 MHz, $CDCl_3$): δ 3·92 (s, 3 H, CH_3), 7·01 (d, 2 H, Ar), 8·06 (d, 2 H, Ar).

4.1.2. *Ethyl 3-(4-methoxyphenyl)-4,4,4-trifluorobut-2-enoate* (**2**)

Under nitrogen, after cooling to 0°C, a 1·65 M *n*-BuLi hexane solution (10·2 ml, 16·8 mmol) was slowly added to a dry THF solution of carboethoxytriphenylphosphonium bromide (7·20 g, 16·8 mmol), and the mixture stirred for 2 h at room temperature. An ether solution of 4-methoxy-1,1,1-trifluoroacetophenone (3·43 g, 16·8 mmol) was added, and the mixture was stirred for 24 h at room temperature. After evaporating the solvent, water and ether were added and stirred for a few minutes. The phases were separated, and the aqueous phase was shaken with ether; the combined organic phases were dried over sodium sulphate. Removal of the solvent and purification by reduced pressure distillation yielded 3·50 g (12·8 mmol, 76·0 per cent) of **2** as a yellow liquid. b.p. 125°C/10 mmHg. IR (cm^{-1}, neat): 1738, 1610, 1515, 1466, 1253, 1176, 1134, 1033, 834. MS $m/z=274$ (M^+). ^1H NMR (400 MHz, $CDCl_3$): δ 1·10 (t, 3 H, CH_3), 3·80 (s, 3 H, CH_3O), 4·06 (q, 2 H, OCH_2), 6·57 (s, 1 H, CH), 6·91 (d, 2 H, Ar), 7·23 (d, 2 H, Ar).

4.1.3. *Ethyl 3-(4-methoxyphenyl)-4,4,4-trifluorobutanoate* (**3**)

Under hydrogen, ethyl 3-(4-methoxyphenyl)-4,4,4-trifluorobut-2-enoate (7·74 g, 28·2 mmol), 5 per cent palladium carbon (1 g) and 99 per cent ethanol (30 ml) were stirred for 48 h at room temperature. The palladium carbon was filtered off, followed by removal of the solvent. Purification by reduced pressure distillation yielded 7·25 g (26·3 mmol, 93·0 per cent) of **3** as a colourless liquid, b.p. 98°C/2·5 mmHg. IR (cm^{-1}, neat): 1739, 1518, 1305, 1252, 1218, 1182, 1182, 1156, 1117, 1034, 830. MS $m/z=276$ (M^+). ^1H NMR (60 MHz, CCl_4): δ 1·1 (t, 3 H, CH_3), 2·7–2·9 (m, 2 H, CH_2), 3·7–4·2 (m, 6 H, CH_3O, $CHCF_3$, $COOCH_2$), 6·7 (d, 2 H, Ar), 7·1 (d, 2 H, Ar).

4.1.4. *3-(4-Methoxyphenyl)-4,4,4-trifluorobutanoic acid* (**4**)

Potassium hydroxide (6 g) dissolved in water (20 ml) was poured into a mixture of ethyl 3-(4-methoxyphenyl)-4,4,4-trifluorobutanoate (12·7 g, 46·0 mmol) and 99 per cent ethanol (20 ml). This mixture was heated under reflux with stirring for 3·5 h. After evaporating the ethanol, water and ether were added. Thereafter, the mixture was acidified with 6 M hydrochloric acid, and the phases were separated. The aqueous phase was shaken with ether, and the combined organic phases were washed with water and dried over sodium sulphate. Removal of the solvent yielded 11·4 g (46·0 mmol) of **4** as a white solid. IR (cm^{-1}, KBr): 1711, 1615, 1518, 1463, 1431, 1365, 1306, 1244, 1183, 1156, 1106, 1029, 969. MS $m/z=248$. ^1H NMR (400 MHz, DMSO-d_6): δ 2·76–2·96 (ddd, 2 H, CH_2), 3·79–3·88 (m, 4 H, CH_3O, $CHCF_3$), 6·88 (d, 2 H, Ar), 7·26 (d, 2 H Ar).

4.1.5. *Optically active 3-(4-methoxyphenyl)-4,4,4-trifluorobutanoic acid* (**4***)

The racemic 3-(4-methoxyphenyl)-4,4,4-trifluorobutanoic acid (**4**) (8·000 g, 32·26 mmol) and (+)-*cis*-2-benzylaminocyclohexylmethanol (*cis*-amine) (7·065 g, 32·26 mmol) were dissolved in 95 per cent ethanol (160 ml) with heating. After cooling to room temperature, the resulting, insoluble diastereomer salt was filtered off and recrystallized twice, from 100 ml of 95 per cent ethanol and then from 75 ml of 95 per cent ethanol. To be purified salt was added 1 M sodium hydroxide solution to liberate the *cis*-amine. After the amine had been extracted into ether, (+)-**4*** was liberated from the aqueous phase by acidifying with 6 M hydrochloric acid. (+)-**4*** was extracted into ether, and the organic phase was washed with dilute hydrochloric acid and water, and dried over sodium sulphate. Removal of the solvent yielded 2·442 g (9·847 mmol) of (+)-**4*** as a white solid. $[\alpha]_D^{26}=+44·9°$ (*c*. 1·24, 99 per cent EtOH).

The mother liquors were evaporated to give the salt of (−)-**4*** and the (+)-*cis*-amine. (−)-**4*** was liberated in a

similar manner. The (−)-**4*** (3·768 g, 15·19 mmol) so obtained and (−)-*cis*-amine (3·327 g, 15·19 mmol) were dissolved in 95 per cent ethanol (103 ml) with heating. In a similar manner to that given above, optically pure (−)-**4*** (2·355 g, 9·496 mmol) was obtained. $[\alpha]_D^{26} = -45{\cdot}7°$ (*c.* 1·56, 99 per cent EtOH).

4.1.6. *Ethyl 3-(4-methoxyphenyl)-4,4,4-trifluorobutanoate* (**3***)

In order to determine the optical purities of the 3-(4-methoxyphenyl)-4,4,4-trifluorobutanoic acids (**4***), their ethyl esters (**3***) were prepared from **4***.

(+)-**4*** (0·041 g, 0·65 mmol) and phosphoryl chloride (0·10 g, 0·65 mmol) were dissolved in 99 per cent ethanol (1 ml), and the mixture boiled for 2 h. After cooling to room temperature, water and ether were added, and the phases were separated. The aqueous phase was washed with ether, and the combined organic phases were washed with saturated aqueous sodium hydrogen carbonate, and dried over sodium sulphate. Removal of the solvent and purification by thin-layer chromatography (TLC) yielded (+)-**3***. In a similar manner, (−)-**3*** was also obtained.

The optical purities of **3*** were determined using HPLC with a chiral column, 'CHIRALCEL OB' (4·6 mm × 250 mm, carrier solvent hexane: 2-propanol = 99:1); the optical purities of both ethyl esters **3*** showed a 99 % ee.

4.1.7. *3-(4-Methoxyphenyl)-4,4,4-trifluorobutanol* (**5***)

Under nitrogen, (−)-3-(4-methoxyphenyl)-4,4,4-trifluorobutanoic acid (0·233 g, 0·94 mmol) dissolved in dry THF was poured into a mixture of lithium aluminium hydride (0·071 g, 1·9 mmol) and dry THF, and heated under reflux for 5 h. After cooling to room temperature, dilute hydrochloric acid and ether were added and the phases were separated. The aqueous phase was shaken with ether, and the combined organic phases were washed with saturated aqueous sodium hydrogen carbonate and dried over sodium sulphate. Removal of the solvent and purification by reduced pressure distillation yielded 0·202 g (0·863 mmol, 91·9 per cent) of **5*** as a colourless liquid, b.p. 135°C/7 mmHg. IR (cm^{-1}, neat): 1517, 1252, 1155, 1110, 1032, 828. MS $m/z = 234$. ^1H NMR (400 MHz, $CDCl_3$): δ 1·97–2·27 (m, 2 H, CH_2), 3·36–3·52 (m, 2 H, CH_2O), 3·65 (m, 1 H, $CHCF_3$), 3·60 (s, 3 H, CH_3O), 6·89 (d, 2 H, Ar), 7·22 (d, 2 H Ar). $[\alpha]_D^{27} = -58{\cdot}8°$ (*c.* 1·16, $CHCl_3$).

4.1.8. *3-(4-Methoxyphenyl)-4,4,4-trifluorobutyl tosylate* (**6***)

Under nitrogen, (−)-3-(4-methoxyphenyl)-4,4,4-trifluorobutanol (0·202 g, 0·863 mmol) dissolved in dry dichloromethane was poured into a mixture of tosyl chloride and dry dichloromethane at 0°C; a dry dichloromethane solution (1 ml) of 1,4-diazabicyclo[2.2.2]octane (0·101 g, 0·902 mmol) was added to the reaction mixture, followed by stirring for 12 h. Ether and water were added to the resulting mixture and the phases were separated. The organic phase was washed with dilute hydrochloric acid and saturated aqueous sodium hydrogen carbonate, and dried over sodium sulphate. Removal of the solvent and purification by preparative TLC yielded 0·276 g (0·711 mmol, 82·4 per cent) of **6*** as a colourless liquid. IR (cm^{-1}, neat): 1516, 1362, 1252, 1177, 1112, 1034, 996, 925, 909, 817, 783, 665, 555. ^1H NMR (60 HMz, $CDCl_3$); δ 2·0–2·4 (m, 5 H, CH_2, CH_3), 3·1–4·3 (m, 6 H, CH_3O, $CHCF_3$, CH_2O), 6·8 (d, 2 H, Ar), 7·0 (d, 2 H Ar), 7·3 (d, 2 H, Ar), 7·7 (d, 2 H Ar). $[\alpha]_D^{27} = -46{\cdot}5°$ (*c.* 1·23, $CHCl_3$).

4.1.9. *3-(4-Hydroxyphenyl)-4,4,4-trifluorobutanoic acid* (**7***)

(−)-3-(4-Methoxyphenyl)-4,4,4-trifluorobutanoic acid (0·350 g, 1·41 mmol) dissolved in 10 ml of acetic acid, and 47 per cent hydrobromic acid (2 ml) were mixed and boiled for 12 h. After cooling to room temperature, water and ether were added, and the phases were separated. The aqueous phase was shaken with ether, and the combined organic phases were washed with water and dried over sodium sulphate. Removal of the solvent and purification by reduced pressure distillation yielded 0·316 g (1·35 mmol, 95·7 per cent) of **7*** as a white, low melting solid, b.p. 150°C/0·5 mmHg. IR (cm^{-1}, neat): 1702, 1521, 1408, 1370, 1294, 1252, 1181, 1158, 1118, 974, 828, 723, 644. MS $m/z = 234$. ^1H NMR (60 MHz, DMSO-d_6): δ 2·7–2·8 (m, 2 H, CH_2), 3·7 (m, 1 H, $CHCF_3$), 6·6 (d, 2 H, Ar), 7·0 (d, 2 H, Ar). $[\alpha]_D^{29} = -48{\cdot}7°$ (*c.* 1·02, 99 per cent EtOH).

4.1.10. *Hexyl 3-(4-hexyloxyphenyl)-4,4,4-trifluorobutanoate* (**8***)

Under nitrogen, (−)-3-(4-hydroxyphenyl)-4,4,4-trifluorobutanoic acid (0·190 g, 0·811 mmol) dissolved in dry DMF (4 ml) was poured into a mixture of 60 per cent sodium hydride (0·097 g, 2·4 mmol) and dry DMF (3 ml), and stirred for a few minutes. A dry DMF (2 ml) solution of 1-iodohexane (0·516 g, 2·43 mmol) was added, and the resulting mixture was stirred for 1·25 hours at 80°C. After removing the solvent, ether and dilute hydrochloric acid were added, and the phases were separated. The aqueous phase was shaken with ether, and the combined organic phases were washed with saturated aqueous sodium sulphite and water and dried over sodium sulphate. Removal of the solvent and purification by preparative TLC yielded 0·275 g (0·684 mmol, 74·2 per cent) of **8*** as a colourless liquid. IR (cm^{-1}, neat): 1736, 1516, 1302, 1248, 1156, 1117, 967, 828. ^1H NMR (90 MHz,

$CDCl_3$): δ 0·9 (m, 6H, CH_3), 1·2–1·8 (m, 16H, CH_2) 2·8–3·0 (m, 2H, CH_2COO), 3·6–4·2 (m, 5H, CH_2O, $CHCF_3$, OCH_2), 6·9 (d, 2H, Ar), 7·2 (d, 2H Ar). $[\alpha]_D^{23} = -31·6°$ (*c.* 1·67, 99 per cent EtOH).

4.1.11. *3-(4-Hexyloxyphenyl)-4,4,4-trifluorobutanoic acid* (**9***)

Potassium hydroxide (0·09 g) dissolved in 1 ml of water was poured into a mixture of (−)-hexyl 3-(4-hexyloxyphenyl)-4,4,4-trifluorobutanoate (0·275 g, 0·684 mmol) and 99 per cent ethanol (2 ml). This mixture was boiled with stirring for 4 h. After evaporating the ethanol, water and ether were added, and the phases were separated. The organic phase was shaken with 1 M aqueous sodium hydroxide and after combining with the aqueous phase, the whole was acidified with 6 M hydrochloric acid. Ether was then added and the phases were separated. The aqueous phase was shaken with ether, and the combined organic phases were washed with water and dried over sodium sulphate. Removal of the solvent and purification by reduced pressure distillation yielded 0·189 g (0·594 mmol, 86·9 per cent) of **9*** as a white solid, b.p. 185°C/0·3 mmHg. IR (cm^{-1}, neat): 1718, 1516, 1305, 1250, 1181, 1161, 1118, 968, 827. ^1H NMR (60 MHz, $CDCl_3$); δ 0·88 (m, 3H, CH_3), 1·2–1·9 (m, 8H, CH_2), 2·8–2·9 (m, 2H, CH_2COO), 3·6–4·0 (m, 3H, CH_2O, $CHCF_3$), 6·7 (d, 2H, Ar), 7·1 (d, 2H Ar), 11·1 (s, 1H, COOH). $[\alpha]_D^{21} = -35·9°$ (*c.* 0·912, $CHCl_3$).

4.1.12. *3-(4-Hexyloxyphenyl)-4,4,4-trifluorobutanol* (**10***)

Under nitrogen, (+)-hexyl 3-(4-hexyloxyphenyl)-4,4,4-trifluorobutanoate (0·288 g, 0·716 mmol) dissolved in dry ether (4 ml) was poured into a mixture of lithium aluminium hydride (0·082 g, 2·2 mmol) and dry ether (2 ml), and boiled for 4 h. After cooling to room temperature, dilute hydrochloric acid and ether were added, and the phases were separated. The aqueous phase was shaken with ether, and the combined organic phases were washed with saturated aqueous sodium hydrogen carbonate and dried over sodium sulphate. Removal of the solvent and purification by reduced pressure distillation yielded 0·208 g (0·684 mmol, 95·5 per cent) of **10*** as a colourless liquid, b.p. 135°C/0·15 mmHg. IR (cm^{-1}, neat): 2934, 1614, 1515, 1470, 1369, 1248, 1180, 1157, 1110, 1060, 827. ^1H NMR (60 MHz, $CDCl_3$): δ 0·9 (m, 3H, CH_3), 1·2–2·3 (m, 10H, CH_2), 3·2–4·0 (m, 5H, CH_2O, $CHCF_3$), 6·8 (d, 2H, Ar), 7·1 (d, 2H Ar). $[\alpha]_D^{27} = +45·3°$ (*c.* 0·900, $CHCl_3$).

4.1.13. *3-(4-Hexyloxyphenyl)-4,4,4- trifluorobutyl tosylate* (**11***)

Under nitrogen, (+)-3-(4-hexyloxyphenyl)-4,4,4-trifluorobutanol (0·208 g, 0·684 mmol) dissolved in dry dichloromethane (2 ml) was poured into a mixture of tosyl chloride and dry dichloromethane (1 ml) at 0°C, and a dry dichloromethane solution (1 ml) of 1,4-diazabicyclo[2.2.2]octane (0·080 g, 0·71 mmol) was added to the reaction mixture, followed by stirring for 11·5 h. Ether and water were added to the resulting mixture and the phases were separated. The organic phase was washed with dilute hydrochloric acid and saturated aqueous sodium hydrogen carbonate and water, and dried over sodium sulphate. Removal of the solvent and purification by preparative TLC yielded 0·247 g (0·539 mmol, 78·8 per cent) of **11*** as a colourless liquid. IR (cm^{-1}, neat): 1515, 1363, 1248, 1179, 1114, 817, 554. ^1H NMR (90 MHz, $CDCl_3$): b 0·92 (t, 3H, CH_3), 1·2–2·4 (m, 13H, CH_2), 3·1–4·2 (m, 5H, CH_2O, $CHCF_3$), 6·8 (d, 2H, Ar), 7·1 (d, 2H Ar), 7·3 (d, 2H, Ar), 7·7 (d, 2H Ar). $[\alpha]_D^{23} = -40·5°$ (*c.* 0·878, $CHCl_3$).

4.1.14. *4-(5-Decyloxy-2-pyrimidinyl)phenyl 3-(4-hexyloxyphenyl)-4,4,4-trifluorobutanoate* (**12***)

A mixture of (−)-3-(4-hexyloxyphenyl)-4,4,4-trifluorobutanoic acid (0·090 g, 0·28 mmol) and 1 ml of thionyl chloride was heated at 90°C with stirring for 2 h to give the acid chloride. After the excess of thionyl chloride had been removed, 1 ml of dry benzene, a dry benzene solution (5 ml) of 4-(5-decyloxy-2-pyrimidinyl)phenol (0·093 g, 0·28 mmol) and a dry benzene solution (2 ml) of 1,4-diazabicyclo[2.2.2]octane (0·095 g, 0·85 mmol) were added to the acid chloride. The mixture was heated at 50°C with stirring for 2 h. After cooling to room temperature, 60 per cent sodium hydride (0·023 g, 0·58 mmol) was added, and the reaction mixture was boiled with stirring for 3 h. After cooling, dilute hydrochloric acid was added, and the product was extracted into benzene. The organic phase was washed with saturated aqueous sodium hydrogen carbonate and water, and dried over sodium sulphate. Removal of the solvent and purification by TLC yielded 0·126 g (0·201 mmol, 70·9 per cent) of **12*** as a white solid. IR (cm^{-1}, KBr): 1747, 1517, 1458, 1439, 1380, 1321, 1265, 1199, 1163, 1152, 1110, 1014, 964, 787. MS $m/z = 628$ (M^+). ^1H NMR (400 MHz, $CDCl_3$): δ 0·89 (m, 6H, CH_3), 1·28 (m, 20H, CH_2), 1·78 (m, 4H, CH_2), 3·07–3·29 (ddd, 2H, CH_2COO), 3·93–3·97 (m, 3H, CH_2OAr and $CHCF_3$), 4·07 (t, 2H, CH_2OAr), 6·90 (d, 2H, Ar), 6·93 (d, 2H, Ar), 7·29 (d, 2H, Ar), 8·30 (d, 2H, Ar), 8·40 (s, 2H, Ar). $[\alpha]_D^{25} = -76·1°$ (*c.* 0·414, $CHCl_3$).

4.1.15. *4-(5-Decyl-2-pyramidinyl)phenyl 3-(4-hexyloxyphenyl)-4,4,4-trifluorobutanoate* (**13***)

Under nitrogen, 4-*N*,*N*-dimethylaminopyridine (0·091 g, 0·16 mmol) was added to a mixture of (−)-3-(4-hexyloxyphenyl)-4,4,4,-trifluorobutanoic acid (0·099 g, 0·311 mmol) and 4-(5-decyl-2-pyrimidinyl)phenol

(0·098 g, 0·314 mmol) and dry dichloromethane (2 ml), and stirred for 30 min at room temperature. A dry dichloromethane solution (1 ml) of dicyclohexylcarbodiimide (0·192 g, 0·932 mmol) was added, and the reaction mixture was stirred for 3 h at room temperature. Ethyl acetate was added; the resulting mixture was filtered and the filtrate was evaporated. The purification by preparative TLC yielded 0·162 g (0·265 mmol, 85·0 per cent) of **13*** as a white solid. IR (cm^{-1}, KBr): 1764, 1616, 1516, 1430, 1302, 1248, 1197, 1162, 1143, 1116. MS $m/z=612$ (M^+). ^1H NMR (90 MHz, $CDCl_3$): δ 0·9 (m, 6 H, CH_3), 1·2–1·7 (m, 24 H, CH_2), 2·6 (t, 2 H, $ArCH_2$), 3·1–3·2 (m, 2 H, CH_2COO), 3·9–4·0 (m, 3 H, OCH_2 and $CHCF_3$), 6·9 (d, 2 H, Ar), 7·0 (d, 2 H, Ar), 7·3 (d, 2 H, Ar), 8·4 (d, 2 H, Ar), 8·6 (s, 2 H, Ar). $[\alpha]_D^{24}=-78·7°$ (*c.* 0·715, $CHCl_3$).

In a similar manner, compounds **14*–17*** were obtained.

4.1.16. *4-(5-Decyl-2-pyrimidinyl)phenyl 3-(4-methoxyphenyl-4,4,4-trifluorobutanoate* (**14***)

IR (cm^{-1}, KBr): 1763, 1518, 1430, 1306, 1264, 1199, 1162, 1152, 1110. MS $m/z=542$ (M^+). ^1H NMR (400 MHz, $CDCl_3$): δ 0·88 (t, 3 H, CH_3), 1·26 (m, 14 H, CH_2), 1·64 (m, 2 H, CH_2) 2·61 (t, 2 H, $ArCH_2$), 3·10–3·31 (ddd, 2 H, CH_2COO), 3·82 (5, 3 H, OCH_3), 3·98 (m, 1 H, $CHCF_3$), 6·93 (d, 2 H, Ar), 6·97 (d, 2 H, Ar), 7·33 (d, 2 H, Ar), 8·38 (d, 2 H, Ar), 8·59 (s, 2 H, Ar). $[\alpha]_D^{28}=+73·3°$ (*c.* 0·499, $CHCl_3$).

4.1.17. *4-[5-(4-Octylphenyl)-2-pyrimidinyl]phenyl 3-(4-methoxyphenyl)-4,4,4-trifluorobutanoate* (**15***)

IR (cm^{-1}, KBr): 1760, 1518, 1438, 1258, 1181, 1160, 1147, 1113, 834. MS $m/z=590$ (M^+). ^1H NMR (400 MHz, $CDCl_3$): δ 0·88 (t, 3 H, CH_3), 1·28 (m, 10 H, CH_2), 3·11–3·32 (ddd, 2 H, CH_2COO), 3·82 (s, 3 H, OCH_3) 3·99 (m, 1 H, $CHCF_3$), 6·93 (d, 2 H, Ar), 7·00 (d, 2 H, Ar), 7·33 (m, 4 H, Ar), 7·53 (d, 2 H, Ar), 8·45 (d, 2 H, Ar), 8·97 (s, 2 H, Ar). $[\alpha]_D^{32}=+95·1°$ (*c.* 0·572, $CHCl_3$).

4.1.18. *4-[5-(4-Octyloxyphenyl)-2-pyrimidinyl]phenyl 3-(4-methoxyphenyl)-4,4,4-trifluorobutanoate* (**16***)

IR (cm^{-1}, KBr): 1762, 1608, 1518, 1436, 1254, 1183, 1146, 1114, 1035, 963, 835. MS $m/z=606$ (M^+). ^1H NMR (400 MHz, $CDCl_3$): δ 0·89 (t, 3 H, CH_3), 1·29 (m, 10 H, CH_2), 1·80 (quintet, 2 H, CH_2), 3·09–3·31 (ddd, 2 H, CH_2COO), 3·79 (s, 3 H, OCH_3) 3·96–3·99 (m, 3 H, OCH_2 and $CHCF_3$), 6·92 (d, 2 H, Ar), 6·98 (d, 2 H, Ar), 7·00 (d, 2 H, Ar), 7·32 (d, 2 H, Ar), 7·50 (d, 2 H, Ar), 8·44 (d, 2 H, Ar), 8·92 (s, 2 H, Ar). $[\alpha]_D^{23}=+88·9°$ (*c.* 0·549, $CHCl_3$).

4.1.19. *4'-(5-Octyloxy-2-pyrimidinyl)biphenyl-4-yl 3-(4-methoxyphenyl)-4,4,4-trifluorobutanoate* (**17***)

IR (cm^{-1}, KBr) 1762, 1519, 1444, 1289, 1256, 1220, 1182, 1168, 1147, 1116, 1102, 788. MS $m/z=606$ (M^+). ^1H NMR (400 MHz, $CDCl_3$) δ 0·89 (t, 3 H, CH_3), 1·30 (m, 10 H, CH_2), 1·83 (quintet, 2 H, CH_2), 3·10–3·31 (ddd, 2 H, CH_2COO), 3·82 (s, 3 H, OCH_3) 3·99 (m, 1 H, $CHCF_3$), 4·10 (t, 2 H, OCH_2), 6·93 (d, 4 H, Ar), 7·33 (d, 2 H, Ar), 7·59 (d, 2 H, Ar), 7·63 (d, 2 H, Ar), 8·39 (d, 2 H, Ar), 8·46 (s, 2 H, Ar). $[\alpha]_D^{25}=+88·4°$ (*c.* 0·535, $CHCl_3$).

4.1.20. *5-Decyloxy-2-[4-{3-(4-hexyloxyphenyl)-4,4,4-trifluoro}butyloxy]phenylpyrimidine* (**18***)

Under nitrogen, 4-(5-decyloxy-2-pyrimidinyl)phenol (0·085 g, 0·26 mmol) dissolved in dry DMF (2 ml) was poured into a mixture of 60 per cent sodium hydride (0·013 g, 0·33 mmol) and dry DMF (1 ml), and stirred for a few minutes. A dry DMF solution (2 ml) of (+)-3-(4-hexyloxyphenyl)-4,4,4-trifluorobutyl tosylate (0·119 g, 0·260 mmol) was added, and the resulting mixture was stirred for 12 h a room temperature. After removing the solvent, ether and dilute hydrochloric acid were added, and the phases were separated. The aqueous phase was shaken with ether and the combined organic phases were washed with saturated aqueous sodium hydrogen carbonate and water, and dried over sodium sulphate. Removal of the solvent and purification by preparative TLC yielded 0·139 g (0·226 mmol, 87·1 per cent) of **18*** as a white solid. IR (cm^{-1}), KBr) 1514, 1427, 1326, 1301, 1242, 1160, 1111, 1067, 1040, 847, 828, 799. MS $m/z=614$ (M^+). ^1H NMR (400 MHz, $CDCl_3$) δ 0·88 (m, 6 H, CH_3), 1·27–1·44 (m, 20 H, CH_2), 1·76 (m, 4 H, CH_2), 2·15 2·54 (m, 2 H, CH_2), 3·57–3·73 (m, 2 H, $ArOCH_3$) 3·88–4·03 (m, 5 H, $ArOCH_2$ and $CHCF_3$), 6·84 (d, 2 H, Ar), 6·86 (d, 2 H, Ar), 7·18 (d, 2 H, Ar), 8·24 (d, 2 H, Ar), 8·38 (s, 2 H, Ar). $[\alpha]_D^{27}=+111°$ (*c.* 0·636, $CHCl_3$).

In a similar manner, **19*–22*** were obtained.

4.1.21. *5-Decyl-2-[4-{3-(4-hesyloxyphenyl)-4,4,4-trifluoro}butyloxy]phenylpyrimidine* (**19***)

IR (cm^{-1}, KBr) 1515, 1434, 1245, 1161, 1112, 1070, 1039, 884, 828, 791. MS $m/z=598$ (M^+). ^1H NMR (90 MHz, $CDCl_3$) δ 0·9 (m, 6 H, CH_3), 1·2–1·7 (m, 24 H, CH_2), 2·1–2·7 (m, 4 H, $ArCH_2$ and CH_2), 3·6–4·0 (m, 5 H, $ArOCH_2$ and $CHCF_3$), 6·8 (d, 2 H, Ar), 6·9 (d, 2 H, Ar), 7·3 (d, 2 H, Ar), 8·3 (d, 2 H, Ar), 8·6 (s, 2 H, Ar). $[\alpha]_D^{29}=+112°$ (*c.* 0·702, $CHCl_3$).

4.1.22. *5-Decyl-2-[4-{3-(4-methoxyphenyl)-4,4,4-trifluoro}butyloxy]phenylpyrimidine* (**20***)

IR (cm^{-1}, KBr) 1609, 1586, 1516, 1430, 1250, 1167, 1111, 1034, 799. MS $m/z=528$ (M^+). ^1H NMR (400 MHz, $CDCl_3$) δ 0·87 (t, 3 H, CH_3), 1·26 (m, 14 H,

CH_2), 1·63 (quintet, 2H, CH_2), 2·18–2·60 (m, 4H, CH_2), 3·58–3·79 (m, 5H, OCH_2 and OCH_3) 4·00 (m, 1H, $CHCF_3$), 6·86 (d, 2H, Ar), 6·89 (d, 2H, Ar), 7·22 (d, 2H, Ar), 8·32 (d, 2H, Ar), 8·56 (s, 2H, Ar). $[\alpha]_D^{22} = -127°$ (*c.* 1·29, $CHCl_3$).

4.1.23. *2-[4-{3-(4-Methoxyphenyl)-4,4,4-trifluoro} butyloxy]phenyl-5-(4-octylphenly)pyrimidine* (**21***)

IR (cm^{-1}, KBr) 1607, 1582, 1518, 1433, 1253, 1183, 1161, 1106, 1039, 823, 798. MS $m/z = 576$ (M^+). ^1H NMR (400 MHz, $CDCl_3$) δ 0·88 (t, 3H, CH_3), 1·27 (m, 10H, CH_2), 1·64 (quintet, 2H, CH_2), 2·18–2·57 (m, 2H, CH_2), 2·65 (t, 2H, $ArCH_2$), 3·62–3·79 (m, 5H, OCH_2 and OCH_3), 4·00 (m, 1H, $CHCF_3$), 6·87 (d, 2H, Ar), 6·90 (d, 2H, Ar), 7·23 (d, 2H, Ar), 7·30 (d, 2H, Ar), 7·51 (d, 2H, Ar), 8·39 d, 2H, Ar), 8·93 (s, 2H, Ar). $[\alpha]_D^{24} = -139°$ (*c.* 1·30, $CHCl_3$).

4.1.24. *2-[4-{3-(4-Methoxyphenyl)-4,4,4-trifluoro} butyloxy]phenyl-5-(4-octyloxyphenyl)pyrimidine* (**22***)

IR (cm^{-1}, KBr) 1608, 1583, 1517, 1435, 1288, 1251, 1182, 1166, 1111, 1036, 831. MS $m/z = 592$ (M^+). ^1H NMR (400 MHz, $CDCl_3$) δ 0·89 (t, 3H, CH_3), 1·29 (m, 8H, CH_2), 1·46 (quintet, 2H, CH_2), 1·80 (quintet, 2H, CH_2), 2·18–2·57 (m, 2H, CH_2), 3·59–3·79 (m, 5H, OCH_2 and OCH_3) 3·96–4·02 (m, 3H, OCH_2 and $CHCF_3$), 6·87 (d, 2H, Ar), 6·90 (d, 2H, Ar), 7·00 (d, 2H, Ar), 7·22 (d, 2H, Ar), 7·50 (d, 2H, Ar), 8·37 d, 2H, Ar), 8·89 (s, 2H, Ar). $[\alpha]_D^{23} = -131°$ (*c.* 0·548, $CHCl_3$).

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[25] The host liquid crystalline mixture consists of 2-(4-dodecycloxyphenyl)-5-hexylpyrimidine (20 wt %), 2-(4-nonyloxyphenyl)-5-octylpyrimidine (20 wt %), 2-(4-nonyloxyphenyl)-5-nonylpyrimidine (20 wt %), 2-(4-hexyloxyphenyl)-5-decylpyrimidine (20 wt %), 4-(5-undecyl-2-pyrimidinyl)phenyl 4-heptylcyclohexanecarboxylate (10 wt %), 4-(5-dodecyl-2-pyrimidinyl)phenyl 4-butylcyclohexanecarboxylate (10 wt %). The phase transition temperatures were

$$\underset{-2}{\overset{4}{C}} \rightleftharpoons \underset{64}{\overset{66}{S_C}} \rightleftharpoons \underset{68}{\overset{70}{S_A}} \rightleftharpoons \underset{80}{\overset{81}{N}} \rightleftharpoons I$$

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