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Some new α -fluoro esters incorporating a cyclohexane ring as chiral dopants for ferroelectric mixtures†

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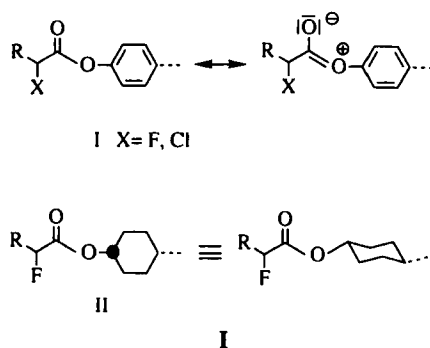
A wide variety of new, optically active α -fluoro esters incorporating a trans-1,4-disubstituted cyclohexane ring and several different core structures have been prepared. Several of these new materials exhibit an enantiotropic chiral smectic C mesophase at elevated temperatures, characterized by high spontaneous polarization, long pitch and low rotational viscosity. Furthermore, they possess exceptional thermal, chemical and photochemical stability. Thus these novel α -fluoro esters incorporating a cyclohexane ring are excellent chiral dopants for chiral smectic C mixtures for utilization in the surface stabilized ferroelectric liquid crystal display.

1. Introduction

Electrooptic display devices utilizing ferroelectric liquid crystals [1, 2] are in the process of being developed for commercial applications [3-5]. These display devices are characterized by exceptionally fast response times (μ s), high contrast, good viewing angle dependency and bistability [3-5]. The successful commercialization of these displays depends not only on the resolution of problems concerned with display device construction, stability and addressing [3-5], but also on the optimization of the ferroelectric mixtures used, which must exhibit a broad spectrum of narrowly defined physical properties [6-9]. A chiral smectic C mesophase in conjunction with a smectic A mesophase are usually regarded as essential [10, 11] over a wide temperature range (e.g. -30 to $+70^\circ\text{C}$). Additional requirements are a sufficiently large spontaneous polarization (P_s), a negative dielectric anisotropy ($\Delta\epsilon$), a small birefringence (Δn) and a low rotational viscosity (η) [6-11]. No single substance is able to satisfy all of these specifications simultaneously, thus mixtures of suitable components are required. Each component must, however, be chemically, thermally, photo and electrochemically stable.

The first mixtures designed for use in prototype surface stabilized ferroelectric liquid crystal displays [1, 2] consisted of a number of similar components, each of which exhibited a chiral smectic C mesophase [10-13]. Due to the difficulties of reconciling an acceptable chiral smectic C mesophase temperature range with a sufficiently high spontaneous polarization and short response times (the position of the optically active centre is decisive in all three cases) an alternative approach was developed [8, 14]. This involves doping an optically inactive base mixture with an optically active substance possessing a very large spontaneous polarization. This chiral dopant does not have to be liquid-crystalline. According to this new approach a wide variety of non-optically active components with a suitable spectrum of physical

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properties has been synthesized [14–22]. Equally a large number of optically active materials to be used as chiral dopants has been prepared [23–30]. The chiral dopant must also be chemically, thermally, photo and electrochemically stable, exhibit a high spontaneous polarization, low rotational viscosity, and induce a long helical pitch in the achiral base mixture without depressing the chiral smectic C mesophase transition temperature excessively. Almost all of the known chiral dopants synthesized so far fail to satisfy at least one of these requirements.

Initial studies of optically active esters formed from α -fluoro substituted aliphatic acids and variously substituted phenols indicated that good general results could be obtained using such systems as chiral dopants [31, 32]. In particular they exhibit a high spontaneous polarization comparable to that of previously synthesized [26, 27] α -chloroesters. All of these systems possess a strongly polarized chiral centre linked to an aromatic ring by a carboxylic group (see I, figure). As a common structural element it seems obvious that partial conjugation to the aromatic ring has an influence on the electron density of the chiral part, its conformational mobility and, therefore, on the large spontaneous polarization of these molecules. In order to investigate the importance of this conjugative effect on the spontaneous polarization and other physical properties, e.g. helical pitch, we decided to esterify the optically active α -fluoro substituted aliphatic acids with a variety of *trans*-4-substituted cyclohexanols. Their structures were designed to optimize the chiral smectic C tendencies of the resulting esters. As 4-alkoxy-2,3-difluorophenyl systems have been shown recently to promote smectic C character strongly and simultaneously to induce a significant negative dielectric anisotropy [15, 17, 20, 21], several core structures incorporating this moiety were designated for investigation. A second ring combination of interest was the 5-alkyl-2-phenylpyrimidine group, which is also known to induce smectic C character strongly in suitable structures [33–35]. The required optically active α -fluoro substituted aliphatic acids were prepared from the corresponding commercially available amino acids (i.e. D and L-norleucine and isoleucine) according to known methods [36]. The required 4-alkoxy-2,3-difluorobenzoic acids [15, 21], 5-alkyl-2-(4-hydroxyphenyl)pyrimidines [33, 34] and (*trans*-4-hydroxycyclohexyl)methyl tosylate [37] were synthesized according to literature methods. Other reaction intermediates used in the synthesis of the final products were either commercially available or are described in the Experimental Section.

2. Mesomorphic properties

The liquid crystal transition temperatures and enthalpies of fusion of the compounds (1–4) are collated in table 1. The compounds (1 and 2 where the

Table 1. Influence of the linking group Z between phenylpyrimidine and the cyclohexane unit on the transition temperatures and enthalpies of fusion.

No.	Z	Chirality	C	S_B	S_C^*	S_A	I	$\Delta H/\text{kJ mol}^{-1}$
1	-	S	● 48°C	● 116°C	-	● 145°C	●	19.3
2	CH ₂ CH ₂	S	● 32°C	● 108°C	-	● 126°C	●	21.0
3	OCH ₂	S	● 93°C	● 109°C	● 128°C	● 137°C	●	17.0
4	COO	R	● 103°C	-	-	● (95°C)	●	36.1

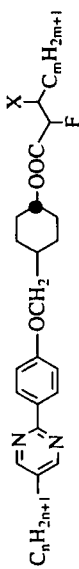
trans-1,4-disubstituted cyclohexane ring is connected to the benzene ring directly ($Z = -$) or by a dimethylene linking unit ($Z = \text{CH}_2\text{CH}_2$) exhibit similar liquid-crystalline morphology and transition temperatures. Both materials possess enantiotropic smectic mesophases (S_B and S_A) at relatively elevated temperatures and a reasonably low melting point ($C-S_B$). The compound (4) incorporating a second ester unit ($Z = \text{COO}$) is characterized by a monotropic smectic mesophase (S_A) and a high melting point ($C-I$). Only substance (3) containing a methylenoxy bridge ($Z = \text{OCH}_2$) exhibits a chiral smectic C mesophase as well as other smectic polymorphism (S_B and S_A mesophases). Although the melting point ($C-S_B$) is high, the enthalpy of fusion is moderately low, thus indicating acceptable solubility in basic, achiral smectic C mixtures [38].

Collated in table 2 are the liquid crystal transition temperatures and enthalpies of fusion of a homologous series ($n = 5-10$) of methylenoxy compounds (3, 5-9) containing one chiral centre ($X = \text{H}$) and two materials (10 and 11) incorporating a second chiral centre ($X = \text{CH}_3$). The melting points ($C-S_3$) and clearing points (S_A-I and N^*) of the substances (3, 5-9) are characterized by a striking stability. The deviations of the individual transition temperatures from the average values ($C-S_3 = 92^\circ\text{C}$ and $S_A-I/N^*-I = 136.5^\circ\text{C}$) are minimal ($\pm 6^\circ\text{C}$ and $\pm 2.5^\circ\text{C}$, respectively). The other transition temperatures ($S_3-S_C^*$ and $S_C^*-S_A$) increase moderately with increasing chain length ($n = 5-10$). However, the incremental increase for the chiral smectic C mesophase is greater than that for the, as yet, unidentified smectic mesophase (S_3). This results in a widening of the chiral smectic C mesophase temperature range with increasing chain length, by almost constant melting and clearing points. The presence of a smectic A mesophase above the smectic C mesophase is of advantage for electrooptic applications [38].

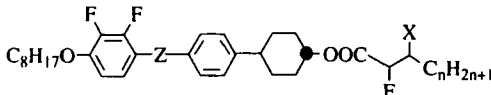
The two compounds (10 and 11) containing an additional optically active centre ($X = \text{CH}_3$) differ only in the sense of chirality (R and S) at the fluoro-substituted carbon atom. While the melting points ($C-S_C^*$) are identical, the other transition temperatures ($S_C^*-S_A$ and S_A-I) are only marginally different ($4-6^\circ\text{C}$). An important feature of the thermal data for these two substances is the absence of other observable smectic modifications. The melting point of the esters (10/11) is higher ($+15^\circ\text{C}$) than that of the ester (9). Thus the introduction of a second, optically active site of branching ($X = \text{CH}_3$) into the compound (9) to produce the compounds (10 and 11) results in only a small change ($\pm 2^\circ\text{C}$) in the observed temperature range of the chiral smectic C mesophase, although two other mesophases are totally suppressed.

A similar study of this effect is demonstrated in table 3 for two separate pairs of compounds (12 and 13 for $Z = -$; 14 and 15 for $Z = \text{COO}$) incorporating a

Table 2. Influence of the length of the side chain or of a second chiral centre on the transition temperatures and enthalpies of fusion.



No.	X	n	m	Chirality	C	S ₃	S ₃ [†]	S _A	N*	I	ΔH/kJ mol ⁻¹
5	H	5	3	S	●	92°C	●	103°C	●	136°C	-
6	H	6	3	S	●	93°C	●	109°C	●	134°C	21.4
7	H	7	3	S	●	87°C	●	105°C	●	138°C	18.9
8	H	8	3	S	●	90°C	●	106°C	●	136°C	20.7
9	H	9	3	S	●	98°C	●	108°C	●	138°C	18.3
10	CH ₃	9	2	2R/3S	●	113°C	●	-	●	-	20.9
11	CH ₃	9	2	2S/3S	●	113°C	●	-	●	-	13.2
3	H	10	3	S	●	93°C	●	109°C	●	137°C	17.0

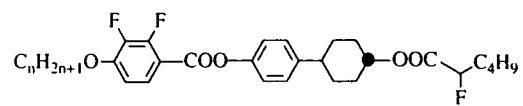
Table 3. Influence of the linking group *Z* or a second chiral centre on the transition temperatures.


No.	<i>Z</i>	<i>X</i>	<i>n</i>	Chirality	C	<i>S</i> _C [*]	<i>S</i> _A	<i>N</i> [*]	I		
12	-	H	3	<i>S</i>	●	33°C	-	●	134°C	-	●
13	-	CH ₃	2	2 <i>S</i> /3 <i>S</i>	●	48°C	-	●	123°C	-	●
14	COO	H	3	<i>S</i>	●	77°C	●	91°C	●	143°C	●
15	COO	CH ₃	2	2 <i>S</i> /3 <i>S</i>	●	45°C	●	101°C	●	126°C	●

2,3-difluoro substituted benzene ring in place of the pyrimidine ring. The directly bonded (*Z* = —) materials (**12** and **13**) exhibit an enantiotropic smectic A mesophase over a wide temperature range (75–100°C). Analogously to the corresponding pyrimidine compounds (**9** and **11**) the introduction of a second optically active centre (*X* = CH₃) leads to an increase in the melting point (15°C) and a decrease in the clearing point (11°C). Thus the smectic A mesophase temperature range is accordingly reduced (–25°C). The incorporation of an additional ester linking unit (*Z* = COO) in the compounds (**12** and **13**) to produce the compounds (**14** and **15**) gives rise to two new liquid-crystalline mesophases (*S*_C^{*} and *N*^{*}). The other liquid crystal transition temperatures are also increased in general. One consequence of these changes is the appearance of an enantiotropic chiral smectic C mesophase over a wide temperature range (56°C) for the ester (**15**) incorporating two chiral centres.

The liquid crystal transition temperatures and enthalpies of fusion of a homologous series (*n* = 1–12) of diesters (**14**, **16**–**25**) are recorded in table 4. The melting points (C–*S*_C^{*}, C–*S*_A, C–*N*^{*}) are remarkably consistent (±10°C), whereas the clearing points (*S*_A–I and *N*^{*}–I) decrease gradually with increasing chain length. The normal pattern of alternation is observed. However, the smectic A transition temperature

Table 4. Influence of the length of the side chain on the transition temperatures and enthalpies of fusion.



No.	<i>n</i>	Chirality	C	<i>S</i> _C [*]	<i>S</i> _A	<i>N</i> [*]	I	Δ <i>H</i> /kJ mol ⁻¹				
16	2	<i>R</i>	●	81°C	-	●	98°C	●	15.9			
17	3	<i>R</i>	●	90°C	-	●	114°C	●	21.8			
18	4	<i>R</i>	●	91°C	-	●	126°C	●	23.1			
19	5	<i>R</i>	●	92°C	-	●	132°C	●	23.0			
20	6	<i>R</i>	●	85°C	●	96°C	●	136°C	●	22.2		
21	7	<i>S</i>	●	82°C	●	93°C	●	140°C	●	21.1		
14	8	<i>S</i>	●	77°C	●	91°C	●	143°C	●	22.7		
22	9	<i>R</i>	●	74°C	●	87°C	●	145°C	●	39.4		
23	10	<i>S</i>	●	72°C	●	84°C	●	147°C	●	22.7		
24	11	<i>S</i>	●	78°C	(●	77°C)	●	-	-	147°C	●	47.4
25	12	<i>S</i>	●	73°C	●	74°C	●	-	-	147°C	●	-

rises first steeply and then smoothly with increasing chain length, thus systematically reducing the chiral nematic temperature range, until, for the longest chain lengths studied ($n = 11, 12$) the chiral nematic phase is totally displaced. A chiral smectic C mesophase is observed first at intermediate chain lengths ($n = 6$) and proceeds to decrease gradually with increasing chain length, finally becoming monotropic. The enantiotropic, chiral smectic C mesophase range remains moderate (11°C, on average) throughout. The enthalpies of fusion are neither remarkably high nor low (26.5 kJ mol⁻¹, on average).

3. Physical properties

The spontaneous polarization (P_s), pitch (P) and switching angle (Θ) of the diester (15) measured at various temperatures, either pure or in admixture (7 wt %) in a non-chiral smectic C mixture [38] consisting of phenylpyrimidines [33] and various esters [18–21] are collated in table 5. The directly measured value of the spontaneous polarization of the pure compound is very high ($P_s = 275$ nC cm⁻² at 45°C). It is remarkable that the extrapolated values for the spontaneous polarization determined from mixture experiments are very substantially lower ($P_s = 94$ nC cm⁻² at 25°C; this phenomenon has been described in detail elsewhere [38]). For the purpose of valid comparison all other measurements reported in this section have been carried out in the same liquid crystal solvent [38] at the same reduced temperature (15°C below the smectic C–smectic A transition) and at the same concentration (7 wt %).

Table 5. Spontaneous polarization and pitch of a selected α -fluoro ester with a broad S_C phase. P_s values in the liquid crystal solvent are extrapolated to 100 per cent.

Concentration	100%	7% in Sc 7 1007
P_s /nC cm ⁻² (45°C)	275	
(25°C)		94
($\Delta T = 15^\circ\text{C}$)	105	46
Switching angle/ $^\circ$	44 (77°C)	71 (25°C)
Pitch/ μm		27

The data collated in table 6 allow a valid comparison to be made between a fully aromatic system (type I) and the analogous cyclohexyl compound containing a trans-1,4-disubstituted cyclohexane ring in place of one of the two benzene rings (type II). As expected, the replacement of an aromatic ring by an aliphatic ring reduces the spontaneous polarization substantially (approximately 40 per cent). This value is still surprisingly high considering the total absence of conjugation exhibited by the corresponding aromatic materials. However, the observed switching time (τ) for the cyclohexane derivative is decidedly shorter (700 μs) than for the corresponding fully aromatic system (950 μs). This can only be attributed to a lower rotational viscosity and/or to a smaller tilt angle (ϑ) for the cyclohexane compound. The influence of the tilt angle can be estimated as follows: $P_s \propto \sin \vartheta$, $\eta_{\text{eff}} \propto \sin^2 \vartheta \rightarrow \tau \propto \eta_{\text{eff}}/P_s \propto \sin \vartheta$. Measured values for ϑ were (7 per cent in Sc 7 1007, 25°C): 24.5° for the biphenyl

Table 6. Comparison of spontaneous polarization (extrapolated to 100 per cent), switching time at, 25°C, helical pitch and tilt angle (at 25°C) of an aromatic (type I) and non-aromatic (type II) α -fluoro ester (τ : 10 $V_{pp}/\mu\text{m}$ square wave, time to maximum current). Mixture of 7 wt % in Sc 7 1007.

	$P_s/n\text{C cm}^{-2}$	$\tau/\mu\text{s}$	$\text{pC}^{-1}/\mu\text{m}^{-1}$	$\theta/^\circ$
	56	950	1.33	24.5
	35	700	0.66	22

derivative and 22° for the phenylcyclohexane derivative. The actual decrease of the switching time on going from phenyl (I) to cyclohexyl (II) is much stronger, indicating a substantially lower viscosity of the cyclohexane derivative. In addition the induced pitch is twice as large for the semiaromatic material (type II).

The values of the spontaneous polarization of a number of compounds incorporating one or two chiral centres are listed in table 7. The data in the table demonstrate the effect of an additional chiral centre next to the fluoro-substituted carbon atom in a variety of semiaromatic and fully aliphatic systems. Although the measurements in the usual matrix infer that the additional chiral centre induces a decrease in the observed spontaneous polarization for both epimers, there are some indications that in the pure compound the spontaneous polarization of the S/S epimers is increased [39]. Notable are the high values observed for the fully aliphatic bicyclohexane system shown in the table.

Table 7. Influence of an additional neighbouring chiral centre or of a combination of aromatic/non-aromatic α -fluoro ester on P_s (7 wt % in Sc 7 1007, extrapolated to 100 per cent).

R	[S]	[S/S]	[R/S]	
	$P_s/n\text{C cm}^{-2}$	43	36	25
	$P_s/n\text{C cm}^{-2}$	90	96	—
	$P_s/n\text{C cm}^{-2}$	112	97	—
	$P_s/n\text{C cm}^{-2}$	109	—	—

4. Conclusions

The α -fluoro esters incorporating a cyclohexane ring are eminently suitable chiral dopants for commercial ferroelectric mixtures designed for surface stabilized ferroelectric liquid crystal displays. Many of the esters exhibit an enantiotropic chiral smectic C mesophase. The spontaneous polarization is reduced by about 40 per cent compared to that of fully aromatic analogues. Considering the completely different electronic and steric situation created by the incorporation of an aliphatic ring, spontaneous polarization values up to 275 nC cm^{-2} are still surprisingly high. Shorter switching times compared to those of the corresponding fully aromatic compounds in the same mixture indicate an advantageously low rotational viscosity. All of the

compounds prepared exhibit very long helical pitches and so commercial mixtures for two micron thick surface stabilized ferroelectric liquid crystal cells can be prepared without pitch compensation. Additional properties not demonstrated here are relatively low optical anisotropies and good chemical stabilities [39].

5. Experimental

The liquid crystal transition temperatures of the compounds prepared and listed in table 1–6 were determined by optical microscopy using a Leitz Ortholux II POL-BK microscope in conjunction with a Mettler FP 82 heating stage and FP 80 control unit. All of the monotropic liquid crystal phases could be observed using a microscope and no virtual values (extrapolated) had to be determined. When necessary the Mettler stage could be cooled ($< -20^{\circ}\text{C}$) by allowing nitrogen gas, cooled by liquid nitrogen, to pass through the stage at a controlled rate. The liquid crystal transition temperatures and enthalpies were also determined using a Mettler DTA TA 2000.

The purity of the compounds was determined by thin layer chromatography, gas chromatography and DTA analysis. A Perkin–Elmer 8310 gas chromatograph and GP 100 graphics printer were used. 4 cm \times 8 cm precoated TLC plates, SiO₂ SIL G/UV₂₅₄, layer thickness 0.25 mm (Macheray-Nagel, Düren, Germany) were used.

The achiral liquid crystal solvent Sc 7 1007 is a mixture composed of four different alkoxyphenylalkylpyrimidines (49.6 wt %) and three different tricyclic phenyl benzoates incorporating a dimethylene linked cyclohexane ring (50.4 wt %).

trans-4-([4-(5-Pentyl-2-pyrimidinyl)phenoxy]methyl)cyclohexyl(R)-2-fluorohexanoate.

A solution of *trans-4-([4-(5-pentyl-2-pyrimidinyl)phenoxy]methyl)cyclohexanol* (0.11 g, 0.0031 mol), (*R*)-2-fluorohexanoic acid (0.04 g, 0.0031 mol), dicyclohexylcarbodiimide (0.08 g, 0.0037 mol), 4-(dimethylamino)pyridine (0.01 g) and anhydrous dichloromethane (30 cm³) was stirred at room temperature overnight. After filtration to remove the precipitated material, the filtrate was evaporated down under reduced pressure. The residue was purified by column chromatography on silica gel using a 4 : 1 toluene/ethyl acetate mixture as eluent followed by recrystallization from ethanol until the transition temperatures remained constant. The liquid crystal transition temperatures and enthalpy of fusion of this ester and other esters prepared using this general procedure are given in tables 1–4.

trans-4-([4-(5-Pentyl-2-pyrimidinyl)phenoxy]methyl)cyclohexanol. A mixture of 5-pentyl-2-(4-hydroxyphenyl)pyrimidine (0.4 g, 0.0018 mol), (*trans-4-hydroxycyclohexyl*)methyl tosylate [37] (0.5 g, 0.0017 mol), anhydrous potassium carbonate (1.0 g, 0.0070 mol) and anhydrous butanone (50 cm³) was refluxed overnight. The cooled reaction mixture was poured into water (500 cm³) and extracted with ether (3 \times 50 cm³). The combined organic layers were washed with saturated sodium chloride solution and dried over anhydrous magnesium sulphate. The solvent was removed under slightly reduced pressure and the resultant residue purified by column chromatography on silica gel with 4 : 1 toluene/ethyl acetate and subsequent crystallization from ethanol. This yielded the pure alcohol (yield 0.6 g, 98 per cent).

4-(trans-4-Hydroxycyclohexyl)phenyl 4-(dodecyloxy)-2,3-difluorobenzoate. A solution of 4-(dodecyloxy)-2,3-difluorobenzoic acid [15, 21] (0.34 g, 0.0010 mol), 4-(*trans-4-hydroxycyclohexyl*)phenol (0.19 g, 0.0010 mol), dicyclohexylcarbodiimide (0.24 g, 0.0012 mol), 4-(dimethylamino)pyridine (0.04 g) and anhydrous dichloromethane (50 cm³) was stirred at room temperature overnight. The reaction mixture was worked up and purified as described earlier to yield the pure alcohol (0.3 g, 59 per cent).

trans-4-Hydroxycyclohexyl 4-(5-decyl-2-pyrimidinyl)benzoate (yield 42 per cent) was prepared using the method described for 4-(*trans*-4-hydroxycyclohexyl)phenyl 4-(dodecyloxy)-2,3-difluorobenzoate.

4-(*trans*-4-Hydroxycyclohexyl)phenol. A solution of 4-(4-hydroxyphenyl)cyclohexanone (4.6 g, 0.0239 mol) and a 9 : 1 mixture of methanol/ether (40 cm³) was added dropwise to a freshly prepared mixture of sodium borohydride (0.9 g, 0.0239 mol) and a 9 : 1 mixture of methanol/ether (25 cm³) at 0°C and under a nitrogen atmosphere. After the addition was complete, the reaction mixture was stirred overnight at room temperature. At 25 per cent hydrochloric acid solution was added carefully to the reaction mixture, which was washed with dichloromethane (3 × 50 cm³). The combined organic layers were washed with water (2 × 500 cm³), dried over magnesium sulphate, filtered and evaporated down under reduced pressure. The residue was crystallized from ethanol (yield 4.0 g, 87 per cent).

trans-4-(2',3'-Difluoro-4'-(octyloxy)-4-biphenyl)cyclohexanol (yield 95 per cent) was prepared using the method described for 4-(*trans*-4-hydroxycyclohexyl)phenol.

(*S,S*)-2-Fluoro-3-methylpentanoic acid [36]. Anhydrous pyridine (88 cm³) was added dropwise to a solution of L-isoleucine (10.5 g, 0.08 mol) and a 70 per cent solution (200 cm³) of hydrogen fluoride in pyridine at -15°C and under a nitrogen atmosphere in a teflon apparatus. Sodium nitrite (8.2 g, 0.012 mol) was added portionwise to the reaction mixture at 0°C. After completion of the addition the reaction was stirred for 4 days at room temperature. The reaction mixture was poured into ice cold water (800 cm³) and extracted with ether (3 × 400 cm³). The combined organic layers were washed with brine (2 × 350 cm³), dried over anhydrous sodium sulphate, filtered and evaporated down under slightly reduced pressure. Distillation of the crude product gave the desired product (yield 2 g, 18.6 per cent; b.p. 55°C at 4.5 × 10⁻² mbar; $[\alpha]_D^{20} = -11.6^\circ$).

4-(2',3'-Difluoro-4-(octyloxy)-4-biphenyl)cyclohexanone. A solution of 2,3-difluoro-4-(octyloxy)phenyl boronic acid (0.6 g, 0.0022 mol), ethanol (1 cm³) and toluene (10 cm³) was added dropwise to a mixture of 4-(4-bromophenyl)cyclohexanone (0.5 g, 0.0020 mol), tetrakis-(triphenylphosphine)-palladium(0) (0.07 g, 0.06 mmol), toluene (20 cm³) and a 2M sodium carbonate solution (2 cm³) at room temperature. The reaction mixture was heated under gentle reflux for 6 hours and then allowed to cool. A 10 per cent hydrogen peroxide solution (0.5 cm³) was added to the reaction mixture, which was stirred for 30 min at room temperature, then poured into water (100 cm³) and extracted with ether (3 × 50 cm³). The combined organic layers were washed with saturated sodium metabisulphite solution (2 × 50 cm³) and brine (2 × 100 cm³), dried over anhydrous magnesium sulphate, filtered and evaporated down under slightly reduced pressure. The solid residue was recrystallized from ethanol to give the desired product (yield 0.3 g, 45 per cent; m.p. 66–67°C).

2,3-Difluoro-4-(octyloxy)phenyl boronic acid. A solution of 2,3-difluoro-4-(octyloxy)benzene (3.3 g, 0.0136 mol), 1.6M butyllithium solution in hexane (8.5 cm³, 0.0136 mol) and anhydrous tetrahydrofuran (50 cm³) was stirred at -78°C for 5 hours under a nitrogen atmosphere. A solution of trimethyl borate (1.6 cm³, 0.0136 mol) and anhydrous tetrahydrofuran (10 cm³) was added dropwise to the reaction mixture and left to stir for a further 30 min at -78°C, then heated under gentle reflux for a further 30 min. Concentrated hydrochloric acid (5 cm³) was added and the reaction mixture heated under gentle reflux for another 30 min, then poured into brine (100 cm³) and extracted with ether (3 × 100 cm³). The combined organic

layers were washed with brine ($2 \times 100 \text{ cm}^3$), dried over anhydrous magnesium sulphate, filtered and evaporated down to give the desired product (yield 1.5 g, 44 per cent), which was used in the next reaction without further purification.

4-(trans-4-Hydroxycyclohexyl)phenyl-imidoethyl ether hydrochloride. Hydrogen chloride gas was allowed to pass through a solution of 4-(trans-4-hydroxycyclohexyl)-benzotrile (5 g, 0.0249 mol), anhydrous ethanol (3.5 cm^3 , 0.0543 mol) and anhydrous toluene (50 cm^3) overnight and then evaporated down. Ether (50 cm^3) was added to the reaction mixture and the solid material separated off by filtration, washed with portions of ether, pressed dry and then dried under vacuum to give the desired product (yield 5.1 g, 72 per cent).

4-(trans-4-Hydroxycyclohexyl)phenyl-amidine hydrochloride. A 7 M ethanolic ammonia solution (10 cm^3 , 0.0689 mol) was added to a suspension of 4-(trans-4-hydroxycyclohexyl)phenyl-imidoethyl ether hydrochloride (5.1 g, 0.0180 mol) and anhydrous ethanol at room temperature under an atmosphere of nitrogen and left to stir overnight. The resultant clear solution was evaporated down and the residue taken up in ethanol (200 cm^3). Ether (200 cm^3) was added and the resultant precipitate separated off by filtration, washed with small portions of ether and then dried under vacuum to give the desired product (yield 3.2 g, 69 per cent).

trans-4-[4-(5-Decyl-2-pyrimidinyl)phenyl]cyclohexanol. A 5 per cent (mol. per cent) solution of sodium methoxide in methanol (15 cm^3) was added dropwise to a mixture of 2-(methoxymethylidene)-dodecanal (0.006 mol), 4-(trans-4-hydroxycyclohexyl)-phenyl-imidoethyl ether hydrochloride (1.5 g, 0.0046 mol) and anhydrous methanol (15 cm^3); during this addition the temperature was kept below 10°C . The reaction mixture was stirred at room temperature overnight. Concentrated hydrochloric acid was added (pH 4–5) and the inorganic material was filtered off. The filtrate was concentrated under reduced pressure, dichloromethane (100 cm^3) was added and the resultant solution washed with water ($2 \times 100 \text{ cm}^3$) and dried over anhydrous sodium sulphate. Column chromatography on silica gel using 4:1 toluene/ethyl acetate mixture as eluent and recrystallization from ethanol gave the desired product (yield 1.6 g, 69 per cent).

2-(Methoxymethylidene)-dodecanal. A mixture of 2-(decyl)malonaldehyde-tetramethylacetal [34] (1.8 g, 0.006 mol), 4-toluene-sulphonic acid-monohydrate (0.7 g, 0.004 mol) and water (0.2 cm^3) was heated at $70\text{--}80^\circ\text{C}$ for 1 hour. Sodium bicarbonate (0.1 g) was added to the cooled solution. The resultant mixture was stirred for 5 min and then filtered to remove the inorganic material; the residue was washed with small amounts of methanol. The filtered methanolic solution of the aldehyde was used immediately in the next reaction assuming a quantitative yield.

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