JOURNAL OF MATERIALS SCIENCE 30 (1995) 5199–5209

Synthesis and properties of trifluoromethylated chiral dopants for ferroelectric liquid crystals

M. TAKEDA
Kashima Oil Co. Ltd., R & D Department, 4 Touwada, Kamisumachi, Kashima-gun, Ibaraki, 314-02, Japan

T. KITAZUME, T. YAMAZAKI
Department of Bioengineering, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 226, Japan

M. KODEN
Functional Devices Laboratories, Sharp Corporation, Kashiwa, Chiba 277, Japan

The synthesis and specific properties of a new family of chiral dopants for ferroelectric liquid crystals, which are derived from a series of trifluorinated dihydrofuranones and tetrahydrofurans, are described. On the basis of the structural features of designed materials and the MOPAC-PM 3 calculations, a discussion of the response time–structure relationships is given. Optically active trifluoromethylated materials with a tetrahydrofuran tail unit were found to be superior chiral dopants for preparing ferroelectric liquid crystalline compositions.

1. Introduction

One objective of research in conductive liquid crystal design is to select ferroelectric liquid crystals with better response characteristics as well as being useful for preparing a large display [1–4]. In fact, new ferroelectric liquid crystals (FLCs) and chiral dopants for FLCs with quick response times and large spontaneous polarization have been reported [5–16]. Recently, an excellent chiral dopant including large spontaneous polarization has been produced by adding a compound with a cyclic chiral part containing a dipole to a non-chiral S_C host liquid crystal. It was elucidated that both the inhibition of the free rotation around the long axis by the steric hindrance and the fixation of the permanent dipole moment perpendicular to the molecular long axis were responsible for the above phenomenon [17–23]. Based on this hypothesis, chiral five-membered (γ-lactones [17–19], 1,3-dioxolan-2-one [20], and oxazolidine-2-one [21]) or six-membered rings (δ-lactones [22], 1,3-dioxanes and 1,3-dioxane-2-ones [23]) have been investigated. However, studies on the molecular design of chiral dopants for FLCs to derive the relation between response time and molecular structure have not been undertaken [24, 25].

A fundamental objective of ferroelectric liquid crystal design is to understand the relation between the physical properties and the molecular structure. It is possible to correlate specific properties of known FLCs and chiral dopants for FLCs with their structure and physical properties: (1) the rise time is dependent upon viscosity, (2) a large spontaneous polarization is induced by both the inhibition of free rotation around the long axis by the steric hindrance and the fixation of the permanent dipole moment perpendicular to the molecular long axis [5–25], and (3) FLCs and/or chiral dopants for FLCs with fluorine(s) or a trifluoromethyl group at their stereogenic centres, showing a larger spontaneous polarization and quick response time than the ones possessing a methyl group due to strong electronegativity of fluorine(s). In addition, we have observed that a fluoroalkyl group attached to the stereogenic centre may decrease the viscosity [4–8].

These above observations have led to the following cumulation in the design of a new family of chiral dopants for FLCs that (1) a fluoroalkyl group attached to the stereogenic centre may increase the polarization and decrease the viscosity, (2) the presence of a ring tail unit containing a carbonyl or ether group should be employed as the source of the dipole moment, and that (3) the presence of several stereogenic centres in a molecule is more effective.

In this paper, we describe work aimed at deriving a basic understanding of the relation between response time and molecular structure which could be applied to be new chiral dopants for FLCs with specific properties. The synthesis and some properties of a new family of ferroelectric liquid crystals designed upon the basis of the above considerations, are reported.

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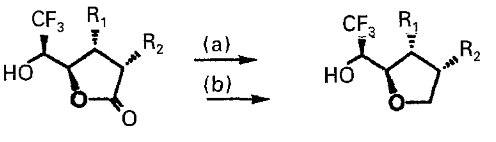
2. Results and discussion

2.1. Synthesis

The synthetic routes to a wide variety of chiral dopants for FLCs using by tail units **1** and **2**, which were designed upon the basis of the mentioned above, are shown in Scheme **I–III**. Recently, we exploited the synthetic route to access optically active 5-[1′-1′-hydroxy-2′,2′,2′-trifluoroethyl)]-3(or 4)-alkyldihydro-2 (3*H*)-*furanones* **1** ($R_1 = n\text{-}C_4H_9$, $R_2 = H$; $R_1 = H$, $R_2 = n\text{-}C_3H_9$) starting from silylated furan using enzymatic optical resolution as a key step [26–28]. To achieve the desired furans **2** as a chiral dopant for the FLCs tail unit, we carried out the reduction of optically active compounds **1** with $NaBH_4$.

Scheme I



1 **2**

(a) TBSCl, pyridine, CH_2Cl_2 ; $NaBH_4$, $BF_3\text{-}Et_2O$, THF, digyme, 1.5h reflux

(b) Bu_4NF, THF, MeOH

The next step in the synthetic strategy required the condensation of core structure groups and the fluorinated chiral tail unit **1** or **2**. For the present purpose, 4′-(alkoxy) biphenyl-4-carboxylic acid chlorides or 4′-chloromethyl-4-alkoxybiphenyl were condensed with the fluorinated chiral tail unit **1** or **2**. The products were purified by flash column chromatography on silica gel.

2.2. Ferroelectric liquid crystal properties

Because the prepared compounds were found not to behave as liquid crystals by themselves, FLCs were prepared by adding 2 wt % of these materials to the non-chiral host S_C liquid crystal which was prepared by blending several kinds of 2-(4-alkoxyphenyl)-5-alkylpyrimidines, and their phase behaviour is shown in Table I.

The phase sequences and phase transition temperatures of FLCs were determined with a polarizing microscope provided with temperature control units. Evaluation was done, after gradual cooling to ambient temperature, with a 2 μm thickness cell equipped with indium–tin oxide (ITO) electrodes covered with a polyimide-alignment layer treated by the parallel rubbing method [29], where a liquid crystal composition in the isotropic phase was injected.

The response time was determined by measuring the time required for the change of the strength of transmitted light from 0 to 50% under a crossed-Nicols when applying square wave voltage of ± 10 V at 30 °C. The tilt angle was determined as the half of the angle between two extinction positions obtained by applying d.c. voltage of ± 15 V at 30 °C. The spontaneous polarization was determined at the same temperature according to the triangular wave method [30]. It was found that the spontaneous polarization increases monotonically as a function of $T_{a.c.} - T$ without any irregularities. The synthetic materials **3**, **4**, **5**, **6** and **7** have not shown a ferroelectric liquid crystal phase. The results of the chiral dopants for FLCs are shown in Tables I and II.

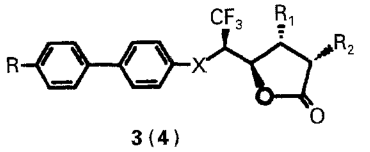
For the purpose of developing structure-physical properties relationships, these properties of several

TABLE I Physical properties of liquid crystals

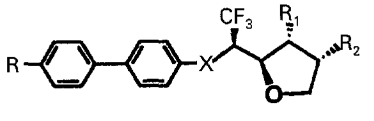
No	R_1	R_2	R	X	Transition temperature (°C)			Response time	Tilt angle (degree)	N* Pitch (μm)
					S_c^* S_A^x	N*	I	(ms)		
3a (1′*S*,5*S*)	H	H	$C_{10}H_{21}O$	CO_2	33	63	66	208	9	− 5
3b (1′*S*,5*R*)	H	H	$C_{10}H_{21}O$	CO_2	44	60	66	135	17	+ 8
3c (1′*R*,4*R*,5*R*)	C_4H_9	H	$C_{10}H_{21}O$	CO_2	42	62	67	408	15	+ 21
3d (1′*S*,4*S*,5*S*)	C_4H_9	H	$C_6H_{13}O$	CO_2	39	62	67	178	13	− 13
3e (1′*S*,3*R*,5*S*)	H	C_3H_7	$C_6H_{13}O$	CO_2	41	61	67	211	14	
3f (1′*S*,3*R*,5*S*)	H	C_3H_7	$C_{10}H_{21}O$	CH_2O	47	59	67	424	18	
4a (1′*S*,5*S*)	H	H	$C_{10}H_{21}O$	CH_2O	45	58	66	422	14	− 17
4b (1′*S*,5*R*)	H	H	$C_{10}H_{21}O$	CH_2O	41	61	67	206	14	− 13
5a (1′*R*,2*R*,3*R*)	C_4H_9	H	$C_6H_{13}O$	CO_2	43	61	67	122	16	− 34
5b (1′*R*,2*S*,3*S*)	C_4H_9	H	$C_6H_{13}O$	CO_2	43	61	67	152	19	− 9
6a (1′*R*,2*R*,3*R*)	C_4H_9	H	$C_6H_{13}O$	CH_2O	46	58	66	162	18	− 18
6b (1′*R*,2*S*,3*S*)	C_4H_9	H	$C_6H_{13}O$	CH_2O	45	59	67	156	17	> 100
7a (1′*S*,2*S*,4*R*)	H	C_3H_7	$C_6H_{13}O$	CO_2	41	63	67	174	13	+ 14
7b (1′*S*,2*R*,4*S*)	H	C_3H_7	$C_6H_{13}O$	CO_2	44	62	67	96	16	+ 13

Phase transition temperature of achiral Host LC: S_c 51 S_A 63 N 69 I (°C); Cell thickness: 2 μm; Response time: $V_{p-p} = 10\ V\,\mu m^{-1}$, 30 °C, 0 → 50% transmittance change.

FLCs were prepared by adding 2 wt % of the prepared chiral parts to the host S_c liquid crystal.

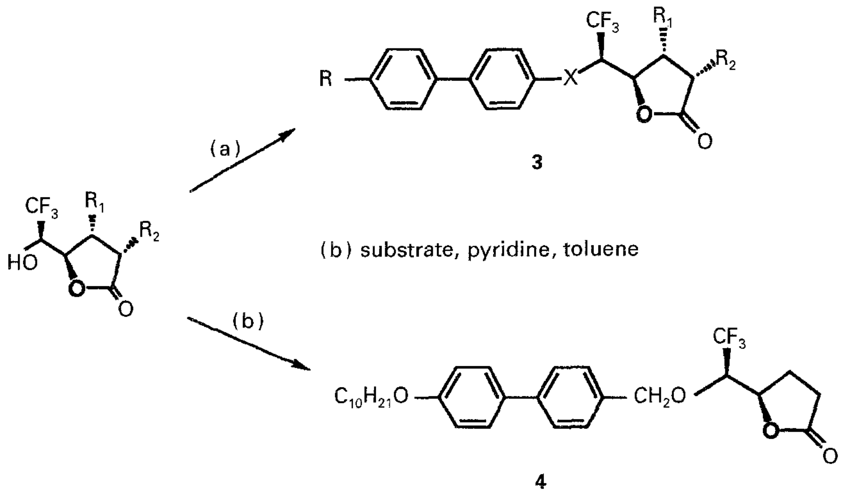


3 (4)



5 (6 or 7)

Scheme II



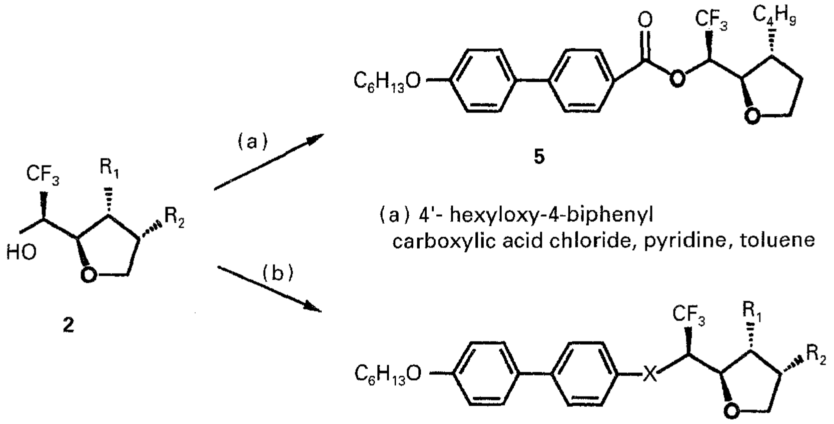
3

(b) substrate, pyridine, toluene

4

(b) NaH. THF. reflux, 20 min ;
4'-chloromethyl-4-decyloxybiphenyl,
THF, Me_2SO, RT, 30 min ; 60 °C, 24 h

Scheme III



2

5

(a) 4'- hexyloxy-4-biphenyl
carboxylic acid chloride, pyridine, toluene

6 ($R_1 = C_4H_9$; $R_2 = H$; $X = CH_2O$)

7 ($R_1 = H$; $R_2 = C_3H_7$; $X = CO_2$)

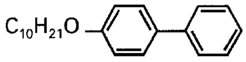
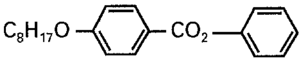
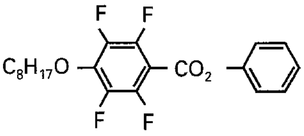
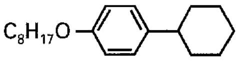
(b) NaH, THF, RT, 30 min ;
4'- chloromethyl-4-hexyloxybiphenyl,
THF, Me_2SO, RT
(b') 4'-hexyloxy-4-biphenyl
carboxylic acid chloride, pyridine, toluene

compounds with different core structure and the same chiral dihydrofuranose tail unit was compared, whose results were shown in Table II. The transition temperature from S_A to S_C of the host liquid crystal was not changed significantly and the apparent tilt angles were found to be relatively large. The response time of those compounds were measured as 280 to 410 μs.

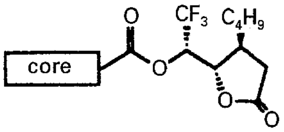
Meanwhile, it is found on the basis of the tabulated results in Table I that the response time of a tetrahydrofuran tail unit is generally quicker than that of a dihydrofuranone ring tail unit. Those of compounds (**5**, **6** and **7**) with tetrahydrofuran tail units are 100 to 180 μs, while those of the compounds (**3** and **4**) with a dihydrofuranone tail unit are 200–430 μs. Comparison of the response time of ester series (**3e**, **5a** and **5b**) (see Fig. 1) and methylene oxy series (**3f**, **6a** and **6b**) showed that the selection of the functional group was a very important factor in decreasing the response times. Furthermore, the response times of several FLCs with different molecular structures in the stereogenic centre and the alkyl chain length were compared, with results shown in Table I. The relationship between the configuration of stereogenic centre is an important factor for the response time. Those of compounds (**5a** and **7b**) are faster than those of compounds (**5b**, **6a**, **6b** and **7a**).

In the next stage to make clear the response time–structure relationships, we calculated the optimized structures by the PM3 calculations through multiconformer analysis [31] of dihydrofuranones and tetrahydrofurans.

TABLE II Physical properties of liquid crystals bearing various types of core structure

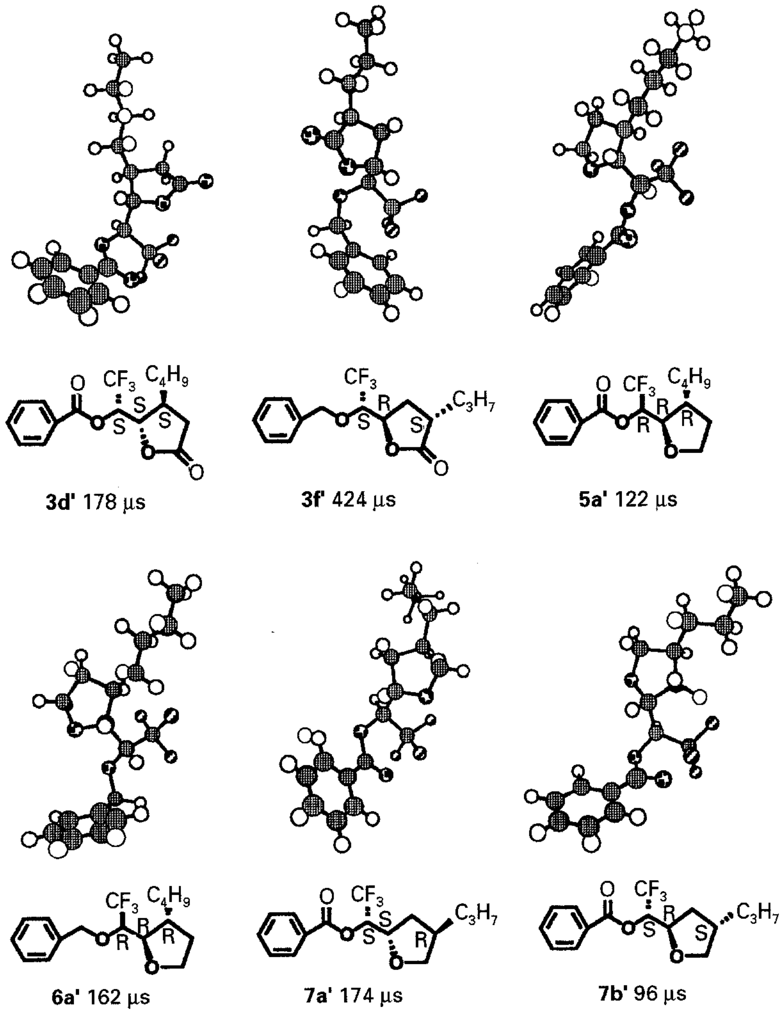
Core structure	Transition temperature (°C)			Response time (ms)	Tilte angle (degree)
	S_C S_A	N	I		
	42	62	67	408	15
	42	61	67	365	15
	44	60	67	282	17
	41	59	66	391	14

Response time: $V_{p-p} = 10\ V\ \mu m^{-1}$, 30 °C, 0 → 50% transmittance change



On the bases of the PM3 calculations shown in Fig. 1, the carbonyl group on the dihydrofuranone ring would not exhibit good polar orientation of the trifluoromethyl group (**3d**′ and **3f**′), however, the ester carbonyl group would exhibit good polar orientation of the trifluoromethyl group (**3d**′, **7a**′ and **7b**′).

The transition temperature from S_A to S_C of the host liquid crystal containing a dopant with a dihydrofuranose tail unit was lowered by a few degrees



3d' 178 μs **3f'** 424 μs **5a'** 122 μs

6a' 162 μs **7a'** 174 μs **7b'** 96 μs

Figure 1 Optimized structures by PM3 calculations.

compared with that of a tetrahydrofuran tail unit. The same trend was observed for the tilt angle, the former giving the smaller value. This difference might be elucidated by the alignment of the molecules themselves: thus, the latter ring derivatives contained much better linearity (Fig. 1).

The aforementioned features of the compounds depending upon the structure of chiral tail unit and the PM3 calculations are summarized as follows: (1) the compounds with a tetrahydrofuran tail unit exhibited faster response time than those of compounds with a dihydrofuranose tail unit, (2) the ester group with good polar orientation of the trifluoromethyl group, an important factor in decreasing the response time, is constructed by the relationship between the configuration of three stereogenic centres.

As described in this paper, optically active tetrahydrofurans with a trifluoromethyl group were found to be superior chiral dopants for preparing ferroelectric liquid crystalline compositions. Particularly, the FLC containing compound **7b** furnished the best result among all the materials prepared, with a response time as fast as 96 µs.

Appendix: Experimental procedure

General procedures

All commercially available reagents, 4′-(decyloxy)-4-biphenyl-carboxylic acid, 4′-chloromethyl-4-(decyloxy)biphenyl, 4-(octyloxy)tetrafluoro-benzoic acid and 4′-(octyloxy)phenyl-4-cyclohexylic acid were used without further purification. Ether and THF were distilled from sodium benzophenone under a nitrogen atmosphere immediately prior to use. CH_2Cl_2 was similarly distilled from calcium hydride. Infrared spectra were obtained by using a Jasco A-102 or a Jasco FT/IR-5000 spectrometer and KBr pellets. Nuclear magnetic resonance (NMR) spectra were recorded at 200 MHz or 500 MHz for ^1H NMR (internal Me_4Si) and at 470 MHz for ^{19}F NMR (internal C_6F_6) at 125 MHz for ^{13}C NMR in $CDCl_3$. Yields were those of isolated products. The optical purities were determined by ^1H or ^{19}F NMR and high pressure liquid chromatography (HPLC).

Hydrogenation of 2-Butenolides

To a suspension of 10% palladium on carbon (0.04 g) in anhydrous ethanol (20 ml) under H_2 was added the corresponding 2-butenolide (3.98 mmol), and the whole was stirred overnight. After removal of the catalyst and concentration of the filtrate, the crude product was chromatographed to yield the desired butyrolactone. (1′*S*,5*S*)-5-{1′-(1′*t*-butyl-dimethylsiloxy)-2′,2′,2′-trifluoro-ethyl]}-dihydro-2(3*H*)-furanone (**1a′**) [20]: $[\alpha]^{28}{}_D$ − 0.15° (*c* 1.09, MeOH), > 96% ee; ^1H NMR ($CDCl_3$): δ0.09 (3H, s), 0.11 (3 H, s), 0.87 (9 H, s), 2.1–2.6 (4 H, m), 4.35 (1 H, dq, $J_{H,H}$ = 1.83, 7.14 Hz), 4.72 (1 H, dt, $J_{H,H}$ = 1.76, 7.29 Hz); ^{13}C NMR ($CDCl_3$): δ − 5.84, − 5.25, 17.75, 20.13, 25.21, 28.01, 71.95 (q, *J* = 30.1 Hz), 77.64, 123.65 (q, *J* = 284.6 Hz), 176.41; ^{19}F NMR ($CDCl_3$): δ83.2 (d, $J_{F,H}$ = 8.1 Hz); i.r. (cm^{-1}): 1790 (C=O). (1′*S*,5*R*)-5-[1′-hydroxy-2′,2′,2′-trifluoroethyl]dihydro-2(3*H*)-furanone (**1b**) [20]: $[\alpha]^{18}{}_D$ − 55.24° (*c* 0.84, $CHCl_3$), > 98% ee; ^1H NMR ($CDCl_3$: δ 2.2–2.8 (4 H, m), 3.99 (1 H, dq, $J_{H,H}$ = 2.58, 7.29 Hz), 4.00 (1 H, br), 4.79 (1 H, ddd, $J_{H,H}$ = 2.61, 7.14, 7.14 Hz); ^{13}C NMR ($CDCl_3$): δ23.65, 27.63, 70.91 (q, *J* = 30.3 Hz), 76.62 (q, *J* = 2.2 Hz), 124.07 (q, *J* = 284.5 Hz), 177.69; ^{19}F NMR ($CDCl_3$): δ84.7 (d, $J_{F,H}$ = 6.9 Hz); i.r. (cm^{-1}): 1750 (C=O).

Preparation of (1′*S*,4*S*,5*S*)-5-[1′-hydroxy-2′,2′,2′-trifluoroethyl)]-4-butyldihydro-2(3H)-furanone (**1d′**).

(a) Michael Addition of Cuprate to 2-Butenolide.

Into the solution of CuI (1.0 g, 10 mmol) and tetrahydrofuran (10 ml), *n*-BuLi in hexane (1.6 M, 12.5 ml, 20 mmol) was added at − 78 °C under an atmosphere of nitrogen. The whole was stirred for 30 min at that temperature and the BF_3–Et_2O solution (2.8 g, 20 mmol) was added in the above solution. Into the above solution, (1′*S*,4*S*)-4-{1′-[1′-*t*-butyldimethylsiloxy)-2′,2′,2′-trifluoroethyl]}-2-buten-4-olide {$[\alpha]^{27}{}_D$ + 98.24° (*c* 1.00, MeOH), > 95% ee [20]} (1.5 g, 5 mmol) in tetrahydrofuran (2 ml) was added at − 78 °C and then the whole was stirred for 2 h at that temperature. The reaction was quenched with aqueous NH_4OH solution, and oily materials were extracted with ethyl acetate. The extract was washed with water, aqueous Na_2SO_3 and brine, and then the organic layer was dried over magnesium sulphate. On removal of the solvent, the crude compound (1′*S*,4*S*,5*S*)-5-{1′-[1′-*t*-butyldimethyl-siloxy)-2′,2′,2′-trifluoroethyl]}-4-butyldihydro-2(3H)-furanone (**1d′**) was isolated by column chromatography on silica gel by using a mixture of hexane-ethyl acetate in 86% yield; ^1H NMR ($CDCl_3$): δ0.11 (6 H, s), 0.88 (12 H, m), 1.20–1.70 (6 H, m), 2.19 (1 H, dd, $J_{H,H}$ = 6.3, 17.4 Hz), 2.30–2.60 (1 H, m), 2.71 (1 H, dd, $J_{H,H}$ = 9.0, 17.4 Hz), 3.98 (1 H, dq, $J_{H,H}$ = 2.7 Hz, $J_{H,F}$ = 6.3 Hz); ^{13}C NMR ($CDCl_3$): δ − 5.38 (q, *J* = 1.8 Hz), − 5.23 (s), 13.63, 22.27, 29.11, 33.57, 34.00, 36.09, 37.92 (s), 45.31 (s), 71.65 (q, *J* = 30.7 Hz), 82.25 (q, *J* = 1.7 Hz), 123.88 (q, *J* = 285.1 Hz), 175.93 (s); ^{19}F NMR ($CDCl_3$): δ89.8 (d, $J_{F,H}$ = 6.3 Hz); i.r. (cm^{-1}): 1790 (C=O).

(b) Desilylation.

Into a solution of the above compound (**1d′**) in tetrahydrofuran (3 ml) and methanol (2 ml), Bu_4NF (5 mmol % of furan) was added at room temperature. After 24 h of stirring at that temperature, the whole was quenched with water. Oily materials were extracted with diethyl ether, and the extract was washed with brine. On removal of the solvent, the title material was isolated by column chromatography on silica gel using a mixture of hexane-ethyl acetate; mp 58.0-58.5 °C, $[\alpha]^{21}{}_D$ (*c* 1.04, MeOH), >95% ee; ^1H NMR ($CDCl_3$): δ0.87 (3 H, t, $J_{H,H}$ = 6.7 Hz), 1.15–1.65 (6 H, m), 1.60–2.00 (1 H, br), 2.18 (1 H, dd, $J_{H,H}$ = 2.9, 17.4 Hz), 2.65–2.85 (1 H, m), 2.87 (1 H, dd, $J_{H,H}$ = 9.5, 17.5 Hz), 4.36 (1 H, dq, $J_{H,H}$ = 2.2 Hz, $J_{F,H}$ = 8.2 Hz), 4.45 (1 H, dd, $J_{H,H}$ = 2.2, 2.4 Hz);

^{13}C NMR ($CDCl_3$): δ 13.62 (s), Hz, 22.16, 28.60, 34.16, 34.81, 33.80 (q, J = 1.6 Hz), 70.67 (q, J = 30 Hz), 83.51 (q, J = 1.5 Hz), 123.89 (q, J = 283.7 Hz), 179.05 (s); ^{19}F NMR ($CDCl_3$): δ88.5 (d, $J_{F,H}$ = 8.2 Hz); i.r. (cm^{-1}): 3300 (OH), 1760 (C=O).

(1′*S*,3R,5*S*)-5-[1′-(1′-*t*-Butyldimethylsiloxy)-2′,2′,2′-trifluoroethyl)]-3-propyldihydro-2(3H)-furanone (**1e′**)

A 1 M solution of LHMDS [32] (1.2 equiv) in THF at − 78 °C was treated with (1′*S*,5*S*)-5-{1′-[1′-(*t*-butyldimethylsiloxy)-2′,2′,2′-trifluoroethyl]}dihydro-2(3*H*)-furanone (1 equiv), and the whole was stirred for 30 min, followed by the addition of propyl bromide (5 equiv) at the same temperature. The usual workup and purification by silica gel column chromatography afforded (1′*S*,3*R*,5*S*)-5-{1′-[1′-*t*-butyldimethyl-siloxy)-2′,2′,2′-trifluoroethyl]}-3-propyldihydro-2(3*H*)-furanone (**1e′**). ^{1}H NMR ($CDCl_3$): δ 0.12 (3 H, s), 0.13 (3 H, s), 0.9–1.10 (12 H, m), 1.21–1.74 (4 H, m), 2.01 (1 H, ddd, $J_{H,H}$ = 4.7, 8.2, 13.1 Hz), 2.6–2.8 (2 H, m), 4.30 (1 H, dq, $J_{H,H}$ = 1.8 Hz, $J_{H,F}$ = 7.1 Hz), 4.68 (1 H, ddd, $J_{H,H}$ = 1.8, 4.7, 7.5 Hz); ^{13}C NMR ($CDCl_3$): δ − 5.50 (q, J = 1.6 Hz), − 5.20 (s), 16.63, 21.47, 27.11, 34.30, 36.19, 38.02 (s), 45.45 (s), 71.41 (q, J = 30.5 Hz), 83.13 (q, J = 1.7 Hz), 124.13 (q, J = 285.4 Hz), 176.03 (s); ^{19}F NMR ($CDCl_3$): δ 82.6 (d, $J_{F,H}$ = 7.1 Hz); i.r. (cm^{-1}): 1780 (C=O).

(1′*R*,2*R*,3*R*)-2-[1′-(1-Hydroxy-2′,2′,2′-trifluoroethyl)]-3-butyltetrahydrofuran (**2c**)

(a) Reduction of (1′R,4R,5R)-5-{1′-[1′-(tert-butyldimethylsiloxy)-2′,2′,2′-trifluoroethyl]}-4-butyldihydro-2(3H)-furanone (1c′) [26–28].

Into a solution of $NaBH_4$ (0.11 g, 2.8 mmol) of a mixture solution of tetrahydrofuran (5 ml) and diglyme (5 ml) under an atmosphere of nitrogen, BF_3–Et_2O solution (5.3 ml, 42 mmol) was added at 0 °C. In the above solution, a solution of compound (1′*R*,4*R*,5*R*)-(**1c′**) (0.5 g, 1.4 mmol, > 95% ee) in tetrahydrofuran (3 ml) was added at 0 °C, and then the whole was stirred at that temperature. After 1 h of stirring, the whole was refluxed for 1 h, and then the reaction was quenched with water. Oily materials were extracted with diethyl ether, and the extract was washed with brine. On removal of the solvent, the corresponding furan derivative was isolated by column chromatography on silica gel using a mixture of hexane–ethyl acetate.

(b) Desilylation of tert-butyldimethylsilyl group.

Into a solution of the above furan derivative in tetrahydrofuran (3 ml) and methanol (2 ml), Bu_4NF (0.31 g, 1.2 mmol) was added at 0 °C. After 30 min of stirring at that temperature, the whole was stirred for four days at room temperature. After quenching with water, oily materials were extracted with diethyl ether, and the extract was washed with brine. On removal of the solvent, the title material was isolated by column chromatography on silica gel using a mixture of hexane–ethyl acetate in 79% yield; ^{1}H NMR ($CDCl_3$): δ 0.90 (3 H, t, $J_{H,H}$ = 6.5 Hz), 1.22–1.44 (5 H, m), 1.45–1.77 (2 H, m), 2.03–2.17 (1 H, m), 2.28–2.43 (1 H, m), 2.81 (1 H, d, $J_{H,H}$ = 5.6 Hz), 3.74–3.93 (3 H, m), 4.06 (1 H, ddq, $J_{H,H}$ = 4.7, 5.6 Hz, $J_{H,F}$ = 7.5 Hz): ^{19}F NMR ($CDCl_3$): δ 86.9 (d, $J_{F,H}$ = 7.4 Hz); i.r. (cm^{-1}): 3350 (OH). Analysis: Calculated for $C_{10}H_{17}O_2F_3$: C, 53.09; H, 7.57%. Found: C, 53.21; H, 7.84%; high-resolution mass calculated for $C_{10}H_{18}O_2F_3$ (M + 1) 227.1259, found 227.1270.

(1′*S*,2*R*,4*S*)-2-[1′-(1′-Hydroxy-2′,2′,2′-trifluoroethyl)]-4-propyltetrahydrofuran (**2e**)

In the above reaction, a mixture of (1′*S*,2*R*,4*S*)-5-{1-[1′-*t*-butyldimethylsiloxy)-2′,2′,2′-trifluoroethyl]}-3-propyldihydro-2(3*H*)-furanone (1.84 g, 5.39 mmol, > 96% ee), $NaBH_4$ (0.41 g, 10.8 mmol), BF_3–Et_2O (20.5 ml, 161 mmol), THF (13 ml) and diglyme (10 ml) were used, and then worked up similarly. On removal of the solvent, the isolated crude derivative was used in the next step without further purification.

Into a solution of the above crude furan derivative in THF (5 ml), Bu_4NF (5.5 ml, 5.5 mmol) was added at 0 °C and the whole was stirred for 1 h at that temperature. After 16 h of stirring at room temperature, the whole was worked up as usual. On removal of the solvent, the title material was isolated by column chromatography on silica gel: $[\alpha]^{25}_D$ − 19.8° (*c* 0.76, MeOH); ^{1}H NMR ($CDCl_3$): δ 0.89–0.95 (3 H, m), 1.18–1.40 (4 H, m), 1.73–1.83 (1 H, m), 1.99–2.09 (1 H, m), 2.20–2.29 (1 H, m), 3.00 (1 H, d, $J_{H,H}$ = 7.5 Hz), 3.47 (1 H, dd, $J_{H,H}$ = 7.5, 8.2 Hz), 3.72–3.81 (1 H, m), 4.04–4.10 (1 H, m), 4.12–4.24 (1 H, m); ^{13}C NMR ($CDCl_3$): δ 14.00 (s), 26.37 (s), 34.93 (s), 35.11, 38.71 (s), 71.93, 74.57, 74.77, 122.11; ^{19}F NMR ($CDCl_3$): δ 84.8 (d, $J_{F,H}$ = 7.1 Hz); i.r. (cm^{-1}): 3420 (OH). High-resolution mass calculated for $C_9H_{15}O_2F_3$ (M^+) 212.1025, found 212.1024.

(1′*S*,5*S*)-5-{1′-{1′-[4‴-(decyloxy)biphenyl-4″-carbonyloxy]-2′,2′,2′-trifluoroethyl}}-dihydro 2(3H)-furanone (**3a**)

Into a solution of 4′-(decyloxy)-4-biphenylcarboxylic acid chloride (0.99 g, 2.7 mmol) and 1′*S*,5*S*)-5-[1′-(1′-hydroxy-2′,2′,2′-trifluoroethyl)]-dihydro-2(3*H*)-furanone[20] (0.41 g, 2.2 mmol, > 95% ee) in toluene (5 ml), pyridine (2 ml) was added and the whole stirred for 14 h at room temperature. After quenching with 3 N HCl, oily materials were extracted with diethyl ether. The extract was washed by saturated $NaHCO_3$ (aq.) and brine. On removal of the solvent, the title material was isolated by column chromatography on silica gel. Recrystallization from ethanol gave liquid crystal (**3a**) in 83% yield; $[\alpha]^{25}_D$ − 70.0° ((*c* 1.07, $CHCl_3$), > 95% ee); ^{1}H NMR ($CDCl_3$): δ 0.89 (3 H, t, $J_{H,H}$ = 6.6 Hz), 1.22–1.57 (14 H, m), 1.76–1.87 (2 H, m), 2.40–2.71 (4 H, m), 4.01 (2 H, t, $J_{H,H}$ = 6.5 Hz), 4.96 (1 H, dt, $J_{H,H}$ = 4.0, 7.0 Hz), 5.94 (1 H, dq, $J_{H,H}$ =

4.0 Hz, $J_{H,F}$ = 7.0 Hz), 7.00 (2 H, d, $J_{H,H}$ = 8.8 Hz), 7.56 (2 H, d, $J_{H,H}$ = 8.8 Hz), 7.66 (2 H, d, $J_{H,H}$ = 8.5 Hz), 8.08 (2 H, d, $J_{H,H}$ = 8.5 Hz); ^{19}F NMR ($CDCl_3$): δ 88.6 (d, $J_{F,H}$ = 6.9 Hz); i.r. (cm^{-1}): 1800, 1745 (C=O). Analysis: Calculated for $C_{29}H_{35}O_5F_3$; C, 66.95; H, 6.78%. Found: C, 66.74; H, 6.91%; high-resolution mass calculated for $C_{29}H_{35}O_5F_3$ (M^+) 520.2437, found 520.2469.

(1′*S*,5*R*)-5-{1′-{1′-[4‴-(decyloxy)biphenyl-4″-carbonyloxy]-2′,2′,2′-trifluoroethyl}}dihydro-2(3H)-furanone (**3b**)

In the above reaction, 4′-(decyloxy)-biphenyl-4-carboxylic acid chloride (0.78 g, 2.1 mmol), (1′*S*,5*R*)-5-[1′-(1′-hydroxy-2′,2′,2′-trifluoro-ethyl)]dihydro-2(3*H*)-furanone[20] (0.32 g, 1.7 mmol) and pyridine (2 ml) in toluene (5 ml) were used, and worked up similarly. Liquid crystal (**3b**) was obtained in 24% yield; $[\alpha]^{27}_D$ − 31.5° ((*c* 1.01, $CHCl_3$), > 96% ee); ^{1}H NMR ($CDCl_3$): δ 0.89 (3 H, t, $J_{H,H}$ = 6.4 Hz), 1.20–1.59 (14 H, m), 1.76–1.87 (2 H, m), 2.09–2.27 (1 H, m), 2.43–2.60 (3 H, m), 4.01 (2 H, t, $J_{H,H}$ = 6.5 Hz), 5.01 (1 H, dt, $J_{H,H}$ = 3.5, 7.3 Hz), 5.71 (1 H, dq, $J_{H,H}$ = 3.5 Hz, $J_{H,F}$ = 6.7 Hz), 7.00 (2 H, d, $J_{H,H}$ = 8.7 Hz), 7.56 (2 H, d, $J_{H,H}$ = 8.7 Hz), 7.67 (2 H, d, $J_{H,H}$ = 8.4 Hz), 8.12 (2 H, d, $J_{H,H}$ = 8.5 Hz); ^{19}F NMR ($CDCl_3$): δ 88.8 (d, $J_{F,H}$ = 6.8 Hz); i.r. (cm^{-1}): 1780, 1740 (C=O). Analysis: Calculated for $C_{29}H_{35}O_5F_3$; C, 66.95; H, 6.78%. Found: C, 67.27; H, 6.49%; high-resolution mass calculated for $C_{29}H_{35}O_5F_3$ (M^+) 520.2437, found 520.2408.

(1′*R*,4*R*,5*R*)-5-{1′-{1′-[4‴-(decyloxy)biphenyl-4″-carbonyloxy]-2′,2′,2′-trifluoroethyl}}-4-butyldihydro-2(3H)-furanone (**3c**)

In the above reaction, (1′*R*,4*R*,5*R*)-5-[1′-(1′-hydroxy-2′,2′,2′-trifluoroethyl)]-4-butyldihydro-2(3*H*)-furanone (**1c**) [26] was used and worked up similarly, giving liquid crystal (**3c**) in 71% yield; $[\alpha]^{26}_D$ + 45.5° ((*c* 1.04, $CHCl_3$), > 95% ee); ^{1}H NMR ($CDCl_3$); δ 0.82–0.99 (6 H, m), 1.18–1.58 (20 H, m), 1.76–1.87 (2 H, m), 2.26 (1 H, dd, $J_{H,H}$ = 4.3, 17.2 Hz), 2.62–2.77 (1 H, m), 2.80 (2 H, dd, $J_{H,H}$ = 9.3, 17.3 Hz), 4.61 (1 H, d, $J_{H,H}$ = 4.3, 4.3 Hz), 5.82 (1 H, dq, $J_{H,H}$ = 4.7 Hz, $J_{H,F}$ = 6.8 Hz), 7.00 (2 H, d, $J_{H,H}$ = 8.8 Hz), 7.56 (2 H, d, $J_{H,H}$ = 8.7 Hz), 7.67 (2 H, d, $J_{H,H}$ = 8.4 Hz), 8.08 (2 H, d, $J_{H,H}$ = 8.4 Hz); ^{19}F NMR ($CDCl_3$): δ 89 (d, $J_{F,H}$ = 6.9 Hz); i.r. (cm^{-1}): 1790, 1740 (C=O). Analysis: Calculate for $C_{33}H_{43}O_5F_3$; C, 68.78; H, 7.52%. Found: C, 68.45; H, 7.83%; high-resolution mass calculated for $C_{33}H_{43}O_5F_3$ (M^+) 576.3063, found 576.3020.

(1′*S*,4*S*,5*S*)-5-{1′-{1′-[4‴-hexyloxy)biphenyl-4″-carbonyloxy]-2′,2′,2′-trifluoroethyl}}-4-butyldihydro-2(3H)-furanone (**3d**)

In the above reaction, (1′*S*,4*S*,5*S*)-5-[1′-(1′-hydroxy-2′,2′,2′-trifluoroethyl)]-4-butyldihydro-2(3*H*)-furanone (**1d**) (0.24 g, 1.0 mmol) was used and worked up similarly, giving liquid crystal **3d**) in 60% yield; $[\alpha]^{26}_D$ − 55.5° ((*c* 1.03, $CHCl_3$, > 96% ee)); ^{1}H NMR ($CDCl_3$): δ 0.85–0.95 (6 H, m), 1.23–1.59 (12 H, m), 1.77–1.88 (2 H, m), 2.26 (1 H, dd, $J_{H,H}$ = 4.4, 17.3 Hz), 2.62–2.75 (1 H, m), 2.80 (2 H, dd, $J_{H,H}$ = 9.3, 17.3 Hz), 4.01 (2 H, t, $J_{H,H}$ = 6.5 Hz), 4.61 (1 H, d, $J_{H,H}$ = 4.3, 4.4 Hz), 5.82 (1 H, dq, $J_{H,H}$ = 4.7 Hz, $J_{H,F}$ = 6.9 Hz), 7.00 (2 H, d, $J_{H,H}$ = 8.8 Hz), 7.57 (2 H, d, $J_{H,H}$ = 8.7 Hz), 7.67 (2 H, d, $J_{H,H}$ = 8.5 Hz), 8.08 (2 H, d, $J_{H,H}$ = 8.5 Hz); ^{19}F NMR ($CDCl_3$): δ 89 (d, $J_{F,H}$ = 6.9 Hz); i.r. (cm^{-1}): 1790 (C=O). Analysis: Calculated for $C_{29}H_{35}O_5F_3$; C, 66.91; H, 6.78%. Found: C, 67.14, H, 6.87%.

(1′*S*,3*R*,5*S*)-5-{1′-{1′-[4‴-(hexyloxy) biphenyl--4″-carbonyloxy]-2′,2′,2′-trifluoroethyl}}-3-propyldihydro-2(3H)-furanone (**3e**)

In the above reaction, (1′*S*,3*R*,5*S*)-5-[1′-(1′-hydroxy-2′,2′,2′-trifluoroethyl)]-3-propyldihydro-2(3*H*)-furanone (**1e**) (0.23 g, 1.0 mmol) was used and worked up similarly, giving liquid crystal (**3e**); $[\alpha]^{25}_D$ − 67.5° ((*c* 1.06, $CHCl_3$), > 95% ee); ^{1}H NMR ($CDCl_3$); δ 0.92 (3 H, t, $J_{H,H}$ = 7.2 Hz), 0.95 (3 H, t, $J_{H,H}$ = 7.0 Hz), 1.28–1.59 (9 H, m), 1.73–1.92 (3 H, m), 2.10–2.25 (1 H, m), 2.59–2.78 (2 H, m), 4.01 (2 H, t, $J_{H,H}$ = 6.6 Hz), 4.92–4.98 (1 H, m), 5.88 (1 H, dq, $J_{H,H}$ = 4.1 Hz, $J_{H,F}$ = 7.0 Hz), 7.00 (2 H, d, $J_{H,H}$ = 8.8 Hz), 7.56 (2 H, d, $J_{H,H}$ = 8.8 Hz), 7.66 (2 H, d, $J_{H,H}$ = 8.5 Hz), 8.08 (2 H, d, $J_{H,H}$ = 8.5 Hz); ^{19}F NMR ($CDCl_3$): δ 88.7 (d, $J_{F,H}$ = 7.0 Hz).

(1′*S*,3*R*,5*S*)-5-{1′-{{1′-[4‴-decyloxy) biphenyl-4″-methylenoxy]-2′,2′,2′-trifluoro-ethyl}}-3-propyldihydro-2(3H)-furanone (**3f**)

In the above reaction, (1′*S*,3*R*,5*S*)-5-[1′-(1′-hydroxy-2′,2′,2′-trifluoroethyl)]-3-propyldihydro-2(3*H*)-furanone (**1f**) (0.23 g, 1.0 mmol) was used and worked up similarly, giving liquid crystal (**3f**); $[\alpha]^{25}_D$ − 8.5° ((*c* 1.13, $CHCl_3$), > 96% ee); ^{1}H NMR ($CDCl_3$): δ 0.83–098 (6 H, m), 1.19–1.56 (17 H, m), 1.72–2.01 (4 H, m), 2.55–2.76 (2 H, m), 3.99 (2 H, t, $J_{H,H}$ = 6.5 Hz), 4.14 (1 H, dq, $J_{H,H}$ = 2.2, 7.2 Hz), 4.67 (1 H, d, $J_{H,H}$ = 10.8 Hz), 4.70–4.78 (1 H, m), 4.86 (1 H, d, $J_{H,H}$ = 10.8 Hz), 6.96 (2 H, d, $J_{H,H}$ = 8.8 Hz), 7.34 (2 H, d, $J_{H,H}$ = 8.2 Hz), 7.51 (2 H, d, $J_{H,H}$ = 8.7 Hz), 7.55 (2 H, d, $J_{H,H}$ = 8.2 Hz); ^{19}F NMR ($CDCl_3$): δ 89.1 (d, $J_{F,H}$ = 7.1 Hz).

(1′*S*,5*S*)-5-{1′-{1′-[4‴-(decyloxy)biphenyl-4⁗-methylenoxy]-2′,2′,2′-trifluoroethyl}}-dihydro-2(3H)-furanone (**4a**)

To a solution of NaH (1.8 mmol) in THF (3 ml), a solution of (1′*S*,5*S*)-5-[1′-(1′-hydroxy-2′,2′,2′-trifluoroethyl)]dihydro-2(3*H*)-furanone [26–28] (0.27 g, 1.5 mmol) in THF (3 ml) was added at 0 °C, and the whole was stirred for 30 min at that temperature. Into a mixture solution, a solution of 4′-chloro-methyl-4-

(decyloxy)-biphenyl (0.57 g, 1.6 mmol) in THF (3 ml) and Me$_2$SO (5 ml) was added at room temperature, and the whole was stirred for 20 h. After quenching with 1 N HCl, oily materials were extracted with diethyl ether, and the extract was washed with brine. On removal of the solvent, liquid crystal (**4a**) was isolated by column chromatography on silica gel in 40% yield; ^{1}H NMR (CDCl$_3$): δ 0.88 (3 H, t, $J_{H,H} = 6.4$ Hz), 1.19–1.53 (14 H, m), 1.75–1.86 (2 H, m), 2.18–2.31 (1 H, m), 2.41–2.64 (3H, m), 3.99 (2 H, t, $J_{H,H} = 6.6$ Hz), 4.19 (1 H, dq, $J_{H,H} = 2.1$ $J_{H,F} = 7.1$ Hz), 4.70 (1 H, d, $J_{H,H} = 10.8$ Hz), 4.77–4.82 (1 H, m), 4.87 (1 H, d, $J_{H,H} = 10.8$ Hz), 6.96 (2 H, d, $J_{H,H} = 8.7$ Hz), 7.35 (2 H, d $J_{H,H} = 8.1$ Hz), 7.51 (2 H, d, $J_{H,H} = 8.8$ Hz), 7.56 (2 H, d, $J_{H,H} = 8.1$ Hz) (1 H, m); ^{19}F NMR (CDCl$_3$): δ 89 (d, $J_{F,H} = 7.2$ Hz); i.r. (cm^{-1}): 1780 (C=O). Analysis: Calculated for $C_{29}H_{37}O_4F_3$; C, 68.76; H, 7.36%. Found: C, 68.45; H, 7.61%; high-resolution mass calculated for $C_{29}H_{37}O_4F_3$ (M$^+$) 506.2644, found 506.2672.

(1′*S*,5*R*)-5-{1′-{1′-[4‴-(decyloxy)biphenyl-4⁗-methylenoxy]-2′,2′,2′-trifluoroethyl}}-dihydro-2(3H)-furanone (**4b**)

In the above reaction, (1′*S*,5*R*)-5-[1′-(1′-hydroxy-2′,2′,2′-trifluoroethyl)]dihydro-2(3*H*)-furanone [26–28] (0.47 g, 2.6 mmol) and 4′-chloromethyl-4-(decyloxy)biphenyl (1.02 g, 2.8 mmol) were used, and then worked up similarly. Liquid crystal (**4b**) was isolated by column chromatography on silica gel in 9% yield; ^{1}H NMR (CDCl$_3$): δ 0.88 (3 H, t, $J_{H,H} = 6.4$ Hz), 1.18–1.54 (14 H, m), 1.74–1.85 (2 H, m), 2.18–2.29 (1 H, m), 2.39–2.69 (3 H, m), 3.99 (2 H, t, $J_{H,H} = 6.5$ Hz), 4.18 (1 H, dq, $J_{H,H} = 2.2$ Hz, $J_{H,F} = 7.1$ Hz), 4.69 (1 H, d, $J_{H,H} = 10.8$ H), 4.71–4.80 (1 H, m), 4.86 (1 H, d, $J_{H,H} = 10.8$ Hz), 6.96 (2 H, d, $J_{H,H} = 8.8$ Hz), 7.35 (2 H, d, $J_{H,H} = 8.2$ Hz), 7.51 (2 H, d, $J_{H,H} = 8.8$ Hz), 7.55 (2 H, d, $J_{H,H} = 8.2$ Hz); ^{19}F NMR (CDCl$_3$): δ 89 (d, $J_{F,H} = 7.2$ Hz); i.r. (cm^{-1}): 1780 (C=O); high-resolution mass calculated for $C_{29}H_{37}O_4F_3$ (M$^+$) 506.2644, found 506.2641.

(1′*S*,4*S*,5*S*)-5-{1′-{1′-[4‴-(decyloxy)biphenyl-4⁗-methylenoxy]-2′2′2′-trifluoroethyl}}-4-butyldihydro-2(3H)-furanone (**4c**)

To a solution of NaH (1.3 mmol) in THF (5 ml), a solution of (1′*S*,4*S*,5*S*)-5-[1′-(1′-hydroxy-2′,2′,2′-trifluoroethyl)]-4-butyldihydro-2(3*H*)-furanone (0.26 g, 1.1 mmol) in THF (3 ml) was added at 0 °C, and the whole was stirred for 30 min at that temperature. Into the mixture solution, a solution of 4′-chloromethyl-4-decyloxybiphenyl in THF (5 ml) and Me$_2$SO (10 ml) was added at 0 °C, and the whole was stirred for 30 min, and then was stirred for 24 h at 60 °C. After quenching with 1 N HCl, oily materials were extracted with diethyl ether, and the extract was washed with brine. On removal of the solvent, liquid crystal (**4c**) was isolated by column chromatography on silica gel in 39% yield; $[\alpha]^{26}$D −4.6° (c, 1.01, CHCl$_3$); ^{1}H NMR (CDCl$_3$); δ 0.80–0.98 (6 H, m), 1.14–1.60 (20 H, m) 1.74–1.86 (2 H, m), 2.13 (1 H, dd, $J_{H,H} = 2.5$, 17.2 Hz), 2.58–2.72 (1 H, m), 2.76 (1 H, dd, $J_{H,H} = 9.5$, 17.3 Hz), 3.98 (2 H, t, $J_{H,H} = 6.5$ Hz), 4.11 (1 H, dq, $J_{H,H} = 2.4$ Hz, $J_{H,F} = 7.2$ Hz), 4.42 (1 H, dd, $J_{H,H} = 2.4$, 2.4 Hz), 4.63 (1 H, d, $J_{H,H} = 10.7$ Hz), 4.85 (1 H, d, $J_{H,H} = 10.6$ Hz), 6.95 (2 H, d, $J_{H,H} = 8.8$ Hz), 7.33 (2 H, d, $J_{H,H} = 8.2$ Hz), 7.50 (2 H, d, $J_{H,H} = 8.8$ Hz), 7.55 (2 H, d, $J_{H,H} = 8.2$ Hz); ^{19}F NMR (CDCl$_3$): δ 88.9 (d, $J_{F,H} = 7.1$ Hz); i.r. (cm^{-1}): 1790 (C=O). Analysis: Calculated for $C_{33}H_{45}O_4F_3$; C, 70.49; H, 8.07%. Found: C, 70.85; H, 7.81%; high-resolution mass calculated for $C_{33}H_{45}O_4F_3$ (M$^+$) 562.3270, found 562.3268.

(1′*S*,4*S*,5*S*)-5-{1′-{1′-[4″-(4⁗-(octyloxy)phenyl-4‴-carbonyloxy)phenyl-1″-carbonyloxy]-2′,2′,2′-trifluoroethyl}}-4-butyldihydro-2(3H)-furanone (**4d**)

(a) Esterification.

A solution of 4-benzyloxybenzoic acid chloride (0.50 g, 2.0 mmol), (1′*S*,4*S*,5*S*)-5-[1′(1′-hydroxy-2′,2′,2′-trifluoroethyl)]-4-butyldihydro-2(3*H*)-furanone [26–28] (0.32 g, 1.7 mmol) and pyridine (2 ml) in toluene (5 ml) was stirred for 16 h at room temperature. After quenching with 3 N HCl, oily materials were extracted with diethyl ether. On removal of the solvent, the benzyl ether was isolated in 84% yield by column chromatography.

(b) Reduction.

The reduction of the above obtained ester with 10% Pd-C (0.1 g) in a solution of ethanol (5 ml) and toluene (5 ml) under an atmosphere of hydrogen, was carried out for 27 h at room temperature. After filtering the catalyst, the solvent was removed. The crude alcohol was isolated in 94% yield by column chromatography.

(c) Liquid crystal (4d).

To a solution on the above obtained crude alcohol (0.31 g, 1.0 mmol) and 4-octyloxybenzoic acid chloride (1.2 mmol) in toluene (5 ml), pyridine (2 ml) was added and then the whole was stirred for 15 h at room temperature. After quenching with 3 N HCl, oily materials were extracted with diethyl ether and the extract was washed with saturated NaHCO$_3$ and brine. On removal of the solvent, liquid crystal (**4d**) was isolated by column chromatography on silica. $[\alpha]^{24}$D −30.0° (*c* 1.00, CHCl$_3$); ^{1}H NMR (CDCl$_3$): δ 0.80–0.95 (6 H, m), 1.10–1.58 (16 H, m), 1.77–1.92 (2 H, m), 2.27 (1 H, dd, $J_{H,H} = 4.6$, 17.4 Hz), 2.58–2.72 (1 H, m), 2.79 (1 H, dd, $J_{H,H} = 9.3$, 17.4 Hz), 4.05 (2 H, t, $J_{H,H} = 6.5$ Hz), 4.60 (1 H, dd, $J_{H,H} = 4.4$, 4.5 Hz), 5.80 (1 H, dq, $J_{H,H} = 4.8$ Hz, $J_{H,F} = 6.8$ Hz), 6.99 (2 H, d, $J_{H,H} = 8.9$ Hz), 7.36 (2 H, d, $J_{H,H} = 8.8$ Hz), 8.10–8.17 (4 H, m); ^{19}F NMR (CDCl$_3$): δ 89.0 (d, $J_{H,F} = 6.8$ Hz); (i.r. (cm^{-1}): 1790, 1760, 1745 (C=O); high-resolution mass calculated for $C_{32}H_{39}O_7F_3$ (M$^+$) 592.2648, found 592.2610.

(1′*S*,4*S*,5*S*)-5-{1′-{1′-[4″-(4‴-(octyloxy)tetrafluorophenyl-4‴-carbonyloxy)phenyl-1″-carbonyloxy]-2′,2′,2′-trifluoroethyl}}-4-butyldihydro-2(3H)-furanone (**4e**)

In the above reaction, 4-(octyloxy)tetrafluorobenzoic acid chloride (1.2 mmol) and the above obtained crude alcohol (1.0 mmol were used, and worked up similarly to give liquid crystal (**4e**). $[\alpha]^{24}$D − 19.4° (*c* 1.05, $CHCl_3$); ^{1}H NMR ($CDCl_3$); δ 0.80–0.98 (6 H, m), 1.15–1.56 (16 H, m), 1.62–1.89 (2 H, m), 2.27 (1 H, dd, $J_{H,H}$ = 4.5, 17.3 Hz), 2.59–2.72 (1 H, m), 2.76 (1 H, dd, $J_{H,H}$ = 9.3, 17.3 Hz), 4.39 (2 H, t, $J_{H,H}$ = 6.5 Hz), 4.60 (1 H, dd, $J_{H,H}$ = 4.4, 4.4 Hz), 5.80 (1 H, dq, $J_{H,H}$ = 4.7 Hz, $J_{H,F}$ = 6.8 Hz), 7.41 (2 H, d, $J_{H,H}$ = 8.8 Hz). 8.15 (2 H, d, $J_{H,H}$ = 8.8 Hz); ^{19}F NMR ($CDCl_3$): δ 89.0 (d, $J_{F,H}$ = 6.8 Hz), 23.9 (2 F, m), 6.23 (2 F, m); i.r. (cm^{-1}): 1790, 1765, 1745 (C=O); high-resolution mass calculated for $C_{32}H_{35}O_7F_7$ (M^+) 664.2271, found 664.2279.

(1′*S*,4*S*,5*S*)-5-{1′-{1′-[4″-(4‴-(octyloxy) phenyl-4‴-cyclohexyl-1″-carbonyloxy]-2′,2′,2′-trifluoroethyl}}-4-butyldihydro-2(3H)-furanone (**4f**)

In the above reaction, 4′-(octyloxy)-phenyl-4-cyclohexylic acid chloride (1.2 mmol) and (1′*S*,4*S*,5*S*)-5-[1′-(1′-hydroxy-2′,2′,2′-trifluoroethyl)]-4-butyldihydro-2(3*H*)-furanone (**1d**) (1.0 mmol) were used, and worked up similarly to give liquid crystal (**4f**). $[\alpha]^{26}$D − 11.5° (*c* 1.04, $CHCl_3$): ^{1}H NMR ($CDCl_3$): δ 0.83–0.96 (6 H, m), 1.17–1.83 (22 H, m), 1.92–2.18 (2 H, m), 2.26 (1 H, dd, $J_{H,H}$ = 4.7, 7.8 Hz), 2.40–2.67 (3 H, m), 2.78 (1 H, dd, $J_{H,H}$ = 9.4, 17.7 Hz), 3.92 (2 H, t, $J_{H,H}$ = 6.5 Hz), 4.50 (1 H, dd, $J_{H,H}$ = 4.1, 4.2 Hz), 5.60 (1 H, dq, $J_{H,H}$ = 4.2 Hz, $J_{H,F}$ = 7.1 Hz), 6.83 (2 H, d, $J_{H,H}$ = 8.6 Hz), 7.09 (2 H,d, $J_{H,H}$ = 8.6 Hz); ^{19}F NMR ($CDCl_3$): δ 89.0 (d, $J_{F,H}$ = 7.0 Hz); i.r. (cm^{-1}): 1790, 1765, 1745 (C=O).

(1′*R*,2*R*,3*R*)-2-{1′-{1′-[4‴-(hexyloxy)biphenyl-4″-carboxy]-2′,2′,2′-trifluoroethyl}}-3-butyltetrahydrofuran (**5a**).

To a solution of (1′*R*,2*R*,3*R*)-2-([1′-(1′-hydroxy-2′,2′,2′-trifluoroethyl)]-3-butyltetrahydrofuran (**2c**) (0.34 g, 1.5 mmol) and 4′-(hexyloxy)-biphenyl-4-carboxylic acid chloride (0.57 g, 1.8 mmol) in toluene (5 ml), pyridine (1 ml) was added and the whole was stirred for 18 h at room temperature. After quenching with 3 N HCl, oily materials were extracted with diethyl ether and the extract was washed with saturated $NaHCO_3$ and brine. On removal of the solvent, liquid crystal (**5a**) was isolated in 70% yield by column chromatography on silica gel; $[\alpha]^{26}$D + 23.2° ((*c* 1.05, $CHCl_3$), > 96% ee); ^{1}H NMR ($CDCl_3$): δ 0.83 (3 H, t, $J_{H,H}$ = 6.9 Hz), 0.92 (3 H, t, $J_{H,H}$ = 7.3 Hz), 1.18–1.70 (14 H, m), 1.76–1.89 (2 H, m), 2.03–2.18 (1 H, m), 2.22–2.36 (1 H, m), 3.83–3.91 (2 H, m), 3.97–4.08 (1 H, m), 4.01 (2 H, t, $J_{H,H}$ = 6.5 Hz), 5.62 (3 H, dq, $J_{H,H}$ = 6.5 Hz, $J_{H,F}$ = 7.0 Hz), 6.99 (2 H, d, $J_{H,H}$ = 8.7 Hz), 7.57 (2 H, d, $J_{H,H}$ = 8.8 Hz), 7.66 (2 H, d, $J_{H,H}$ = 8.5 Hz), 8.11 (2 H, d, $J_{H,H}$ = 8.5 Hz); ^{13}C NMR (CDCl) δ 13.65, 13.97, 22.49, 25.66, 29.14, 30.21, 31.52, 32.36, 33.65, 41.23, 68.07, 68.23, 70.79 (d, *J* = 30.4 Hz), 80.66, 114.92, 123.29 (q, *J* = 282.2 Hz), 126.32, 126.57, 128.30, 130.52, 131.71, 146.27, 159.60, 164.50; ^{19}F NMR ($CDCl_3$): δ 88.8 (d, $J_{F,H}$ = 7.1 Hz); i.r. (cm^{-1}): 1740 (C=O). Analysis: Calculated for $C_{29}H_{37}O_4F_3$; C, 68.80; H, 7.37%. Found: C, 68.61; H, 7.09%.

(1′*R*,2*S*,3*S*)-2-{1′-{1′-[4‴-(hexyloxy)biphenyl-4″-carboxy]-2′,2′,2′-trifluoroethyl}}-3-butyltetrahydrofuran (**5b**)

In the above reaction, (1′*R*,2*S*,3*S*)-2-[1′-hydroxy-2′,2′,2′-trifluoroethyl)]-3-butyltetrahydrofuran (**2e**) (0.37 g, 1.6 mmol) was used, and worked up similarly, affording liquid crystal (**5b**) in 82% yield; $[\alpha]^{27}$D + 75.0° ((*c* 1.08, $CHCl_3$), > 95% ee); ^{1}H NMR ($CDCl_3$): δ 0.84–1.02 (6 H, m), 1.21–1.70 (13 H, m), 1.75–1.89 (2 H, m), 1.97–2.17 (2 H, m), 3.80–4.08 (3 H, m), 4.01 (2 H, t, $J_{H,H}$ = 6.5 Hz), 5.59 (3 H, dq, $J_{H,H}$ = 2.9 Hz, $J_{H,F}$ = 7.3 Hz), 6.99 (2 H, d, $J_{H,H}$ = 8.8 Hz), 7.56 (2 H, d, $J_{H,H}$ = 8.7 Hz), 7.66 (2 H, d, $J_{H,H}$ = 8.6 Hz), 8.16 (2 H, d, $J_{H,H}$ = 8.6 Hz); ^{13}C NMR (CDCl): δ 13.69, 13.97, 22.55, 22.61, 25.66, 29.15, 30.21, 31.53, 32.31, 32.53, 41.18, 68.06, 68.84, 80.36, 114.92, 123.42 (q, *J* = 283.1 Hz), 126.33, 126.57, 128.30 130.67, 131.75, 146.27, 159.58, 164.97; ^{19}F NMR ($CDCl_3$): δ 88 (d, $J_{F,H}$ = 7.3 Hz); i.r. (cm^{-1}): 1730 (C=O). Analysis: Calculated for $C_{29}H_{37}O_4F_3$; C, 68.80; H, 7.37%. Found: C, 68.57; H, 7.60%; high-resolution mass calculated for $C_{29}H_{37}O_4F_3$ (M^+) 506.2644, found 506.2641.

(1′*R*,2*R*,3*R*)-2-{1′-{1′-[4‴-(hexyloxy)biphenyl-4″-methylenoxy],2′,2′,2′-trifluoroethyl}}-3-butyltetrahydrofuran (**6a**)

To a solution of NaH (dry powder, 1.8 mmol) in THF (5 ml), a solution of (1′*R*,2*R*,3*R*)-2-[1′-(1′-hydroxy-2′,2′,2′-trifluoroethyl)]-3-butyl-tetrahydrofuran (**2c**) (0.34 g, 1.5 mmol) in THF (3 ml) was added at 0 °C under a nitrogen atmosphere and the whole was stirred for 30 min at that temperature. To the above solution, a solution of 4′-chloromethyl-4-(hexyloxy)biphenyl (0.55 g, 1.8 mmol) in THF (5 ml) and Me_2SO (5 ml) was added and the whole was stirred for five days at room temperature. After quenching with 1 N HCl, oily materials were extracted with diethyl ether, and the extract was washed with brine. On removal of the solvent, liquid crystal (**6a**) was isolated by column chromatography on silica gel in 93% yield; $[\alpha]^{28}$D − 11.8° ((*c* 1.08, $CHCl_3$), > 96% ee); ^{1}H NMR ($CDCl_3$): δ 0.80–0.99 (6 H, m), 1.18–1.65 (13 H, m), 1.76–1.88 (2 H, m), 1.98–2.16 (1 H, m), 2.27–2.42 (1 H, m), 3.78–3.95 (4 H, m), 3.99 (2 H, t, $J_{H,H}$ = 6.6 Hz), 4.68 (1 H, d, $J_{H,H}$ = 11.1 Hz), 4.86 (1 H, d, $J_{H,H}$ = 11.1 Hz), 6.96 (2 H, d, $J_{H,H}$ = 8.8 Hz), 7.38 (2 H, d, $J_{H,H}$ = 8.2 Hz), 7.51 (2 H, d, $J_{H,H}$ = 8.6 Hz), 7.54 (2 H, d, $J_{H,H}$ = 7.9 Hz); ^{13}C NMR (CDCl): δ 14.02, 22.63, 25.75, 29.26, 30.28, 31.61, 32.73, 33.77, 39.92, 68.05, 75.43, 79.22 (q, *J* = 27.5 Hz), 82.22, 114.77, 124.77 (q,

$J = 285$ Hz), 126.65, 128.01, 128.64, 131.57, 132.95, 135.28, 140.75, 158.85; ^{19}F NMR (CDCl$_3$): δ 88.9 (d, $J_{F,H} = 7.1$ Hz); i.r. (cm^{-1}): 1610, 1505. Analysis: Calculated for $C_{29}H_{39}O_3F_3$; C, 70.76; H, 7.99%. Found: C, 71.13; H, 8.24%.

(1′*R*,2*S*,3*S*)-2-{1′-{1′-[4‴-(hexyloxy)biphenyl-4″-methylenoxy)-2′,2′,2′-trifluoroethyl}}-3-butyltetrahydrofuran (**6b**)

In the above reaction, (1′*R*,2*S*,3*S*)-2-[1′-(1′-hydroxy-2′,2′,2′-trifluoroethyl)]-3-butyltetrahydrofuran (**2e**) (0.37 g, 1.6 mmol) was used, and worked up similarly, affording liquid crystal (**6b**) in 88% yield; $[\alpha]^{25}_D$ +44.7° ((*c* 1.03, CHCl$_3$), > 95% ee); ^{1}H NMR (CDCl$_3$): δ 0.79 (3 H, t $J_{H,H} = 6.8$ Hz), 0.91 (3 H, t, $J_{H,H} = 6.9$ Hz), 1.01–1.62 (13 H, m), 1.74–1.87 (2 H, m), 1.94–2.12 (2 H, m), 3.65–3.75 (2 H, m), 3.83–3.92 (2 H, m), 4.00 (2 H, t, $J_{H,H} = 6.6$ Hz), 4.63 (1 H, d, $J_{H,H} = 11.7$ Hz), 4.96 (1 H, d, $J_{H,H} = 11.7$ Hz), 6.97 (2 H, d, $J_{H,H} = 8.8$ Hz), 7.40 (2 H, d, $J_{H,H} = 8.2$ Hz), 7.51 (2 H, d, $J_{H,H} = 8.7$ Hz), 7.56 (2 H, d, $J_{H,H} = 8.3$ Hz); ^{13}C NMR (CDCl): δ 13.69, 13.99, 22.56, 22.71, 25.68, 29.19, 30.39, 31.54, 32.32, 32.40, 40.47, 68.03, 68.68, 74.28, 81.32, 114.75, 126.68, 127.96, 129.34, 132.74, 134.57, 141.00, 158.85; ^{19}F NMR (CDCl$_3$): δ 90.1 (d, $J_{F,H} = 7.1$ Hz); i.r. (cm^{-1}): 1610, 1505. Analysis: Calculated for $C_{29}H_{39}O_3F_3$; C, 70.76; H, 7.99%. Found: C, 70.53; H, 7.74%.

(1′*S*,2*S*,4*R*)-2-{1′-{1′-[4‴-(hexyloxy)biphenyl-4″-carbonyloxy)-2′,2′,2′-trifluoroethyl}-4-propyltetrahydrofuran (**7a**)

Into a solution of 4′-(hexyloxy)biphenyl-4-carboxylic acid chloride (0.31 g, 1.0 mmol) and (1′*S*,2*S*,4*R*)-2-[1′-(1′-hydroxy-2′,2′,2′-trifluoroethyl)]-4-propyl tetrahydrofuran (0.18 g, 0.8 mmol) in toluene (5 ml), pyridine (2 ml) was added and the whole stirred for 14 h at room temperature. After quenching with 3 N HCl, oily materials were extracted with diethyl ether. The extract was washed by saturated NaHCO$_3$ (aq) and brine. On removal of the solvent, the title material was isolated by column chromatography on silica gel. Recrystallization from ethanol gave liquid crystal (**7a**) in 41% yield; $[\alpha]^{26}_D$ − 42.2° ((*c* 0.79, CHCl$_3$), > 94% ee); ^{1}H NMR (CDCl$_3$): δ 0.81–0.97 (6 H, m), 1.20–1.57 (10 H, m), 1.65–1.79 (3 H, m), 2.18–2.33 (2 H, m) 3.38 (1 H, dd, $J_{H,H} = 6.8$, 8.3 Hz), 3.95–4.01 (1 H, m), 4.01 (2 H, t, $J_{H,H} = 6.6$ Hz), 4.45 (1 H dt, $J_{H,H} = 4.7$, 7.9 Hz), 5.71 (1 H, dq, $J_{H,H} = 4.7$ Hz, $J_{H,F} = 7.2$ Hz), 7.00 (2 H, d, $J_{H,H} = 8.8$ Hz), 7.57 (2 H, d, $J_{H,H} = 8.7$ Hz), 7.66 (2 H, d $J_{H,H} = 8.5$ Hz), 8.11 (2 H, d, $J_{H,H} = 8.4$ Hz); ^{13}C NMR (CDCl): δ 13.97, 14.04, 21.45, 22.55, 25.66, 29.14, 31.52, 33.26, 34.90, 38.68, 68.07, 70.54 (q, $J = 30.1$ Hz), 74.00, 75.17, 114.92, 123.19, (q, $J = 282.2$ Hz), 126.45, 126.57, 128.30, 130.74, 146.23, 159.59, 164.45; ^{19}F NMR (CDCl$_3$): δ 88.5 (d, $J_{F,H} = 7.2$ Hz); i.r. (cm^{-1}): 1740 (C=O). Analysis: Calculated for $C_{29}H_{35}O_5F_3$; C, 68.28; H, 7.16%. Found: C, 66.74; H, 6.91%.

(1′*S*,2*R*,4*S*)-2-{1′-{1′-[4‴-(hexyloxy)biphenyl-4″-carbonyloxy]-2′,2′,2′-trifluoroethyl}-4-propyltetrahydrofuran (**7b**)

In the above reaction, 4′-(hexyloxy)biphenyl-4-carboxylic acid chloride (0.34 g, 1.1 mmol) and (1′*S*,2*R*,4*S*)-2-[1′-(1′-hydroxy-2′,2′,2′-trifluoroethyl)]-4-propyl tetrahydrofuran (0.19 g, 0.9 mmol) were used, and then working up similarly. Liquid crystal (**7b**) was obtained in 50% yield; $[\alpha]^{25}_D$ − 64.4° ((*c* 1.02, CHCl$_3$), > 96% ee); ^{1}H NMR (CDCl$_3$): δ 0.82–1.01 (6 H, m), 1.22–1.56 (10 H, m), 1.73–1.83 (3 H, m), 1.97–2.33 (2 H, m), 3.45 (1 H, dd, $J_{H,H} = 6.6$, 8.3 Hz), 3.95–4.08 (1 H, m), 4.01 (2H, t, $J_{H,H} = 6.5$ Hz), 4.44 (1 H, dt, $J_{H,H} = 5.7$, 7.6 Hz), 5.52 (1 H, dq, $J_{H,H} = 5.4$ Hz, $J_{H,F} = 7.1$ Hz), 6.99 (2 H, d, $J_{H,H} = 8.7$ Hz), 7.56 (2 H, d, $J_{H,H} = 8.7$ Hz), 7.65 (2 H, d, $J_{H,H} = 8.4$ Hz), 8.15 (2 H, d, $J_{H,H} = 8.3$ Hz); ^{13}C NMR (CDCl): δ 13.98, 21.35, 22.55, 25.66, 29.15, 31.53, 34.67, 35.11, 38.62, 68.06, 71.34 (q, $J = 30.3$ Hz), 74.01, 74.63, 114.91, 123.22 (q, $J = 281.6$ Hz), 126.46, 126.53, 128.30, 130.63, 131.61, 146.16, 159.56, 164.94; ^{19}F NMR (CDCl$_3$): δ 89.1 (d, $J_{F,H} = 7.0$ Hz; i.r. (cm^{-1}): 1735 (C=O). High-resolution mass calculated for $C_{28}H_{35}O_4F_3$ (M$^+$) 492.2488, found 492.2474.

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Received 22 July 1994
and accepted 11 May 1995