cluding tables containing anisotropic thermal parameters, and final positional parameters, plot of the second order decay kinetics of *trans*-**1**, MNDO calculated stucture of *trans*-**1**, and the MM2(85) calculated structure of its Diels-Alder cycloadduct with cyclopentadiene, ^{1}H and ^{13}C NMR spectra of cyclopentadiene adduct **12**, table of MNDO calculated bond angles and bond lengths of *trans*-**1** and *trans*-cycloheptene, and the final calculated MNDO Z-matrices of *trans*-**1** and *trans*-1,4-disilacyclohept-2-ene (37 pages); observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

Design and Synthesis of New Fluorinated Ferroelectric Liquid Crystalline Polymers

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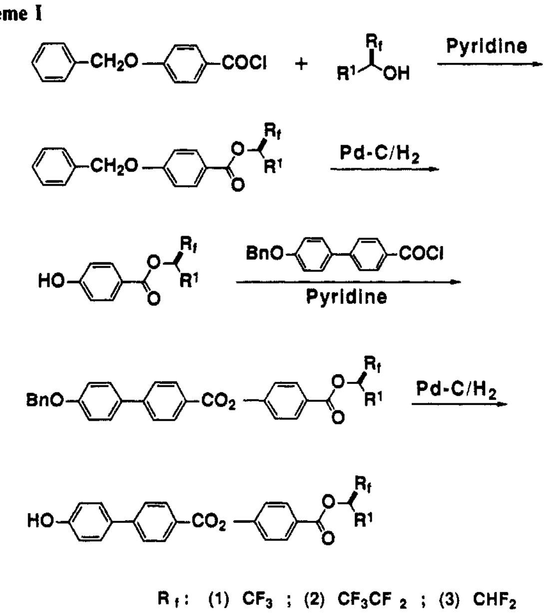
Abstract: The synthesis and specific properties of a new family of fluorinated ferroelectric liquid crystalline polymers of the general structure 1, are described. These materials exhibit quick response time (<10 ms) and large spontaneous polarization (40–70 nC/cm^2) (90 °C). A discussion of the response time-structure relationships is given. The response time becomes faster as the achiral chain connecting the mesogen to the polymer backbone and the chiral chain length becomes shorter. Especially, it is found that a trifluoromethyl group on the stereogenic center enhanced the response time.

Molecular recognition in ferroelectric liquid crystalline polymers is of fundamental importance to the understanding of differences in physical properties between racemic[2-6] and enantiomerically pure materials.[7] Recently, new ferroelectric liquid crystalline polymers with fast response times (3 ms) and large spontaneous polarizations (60 nC/cm^2) (85 °C) have been reported by Walba and Keller.[8] However, with the exception of the above report, studies on the molecular design of ferroelectric liquid crystalline polymers to give quick response times for switching and/or a large spontaneous polarizations have not been undertaken.[9-11] In fact, for ferroelectric liquid crystalline polymers, the minimum reported the response time is 100 ms, and the maximum reported spontaneous polarization P_s observed for liquid crystalline polymers is 6–8 nC/cm^2. In the case of these materials, naturally occurring 2-methylbutanol and 2-methylpentanol were used as the chiral tail groups.[9-14] Therefore, the challenge of preparing new ferroelectric liquid crystalline polymers with rapid response times, large spontaneous polarizations, and low viscosities remains.

We recently reported the possibility of tristable switching in a surface-stabilized ferroelectric liquid crystal display devices (SSFLCDs) of the Clark-Lagerwall type,[15] which had a fluoroalkyl group at the chiral center.[16,17] 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 ferroelectric liquid crystalline polymers with specific properties. The syntheses and some properties of a new family of ferroelectric liquid crystalline polymers possessing a fluoroalkylated chiral tail unit as a mesogenic pendant group are reported in the following.

Scheme I



Molecular Design Considerations

A fundamental objective of conductive polymer design is to select polymers with a quick response time, a large spontaneous polarization density, and a low orientation viscosity. It is possible to correlate specific properties of known ferroelectric liquid crystalline polymers with their structure and physical properties: (1) the response time (rise time) is temperature dependent, (2) the rise time is dependent upon viscosity (it increases with increasing molecular weights), and (3) the response time is dependent upon steric effects. The response time was, with introduction of an α-methyl groups, as in a methacrylic polymers, relative to an acrylic polymers.[18-23] In addition, we have observed

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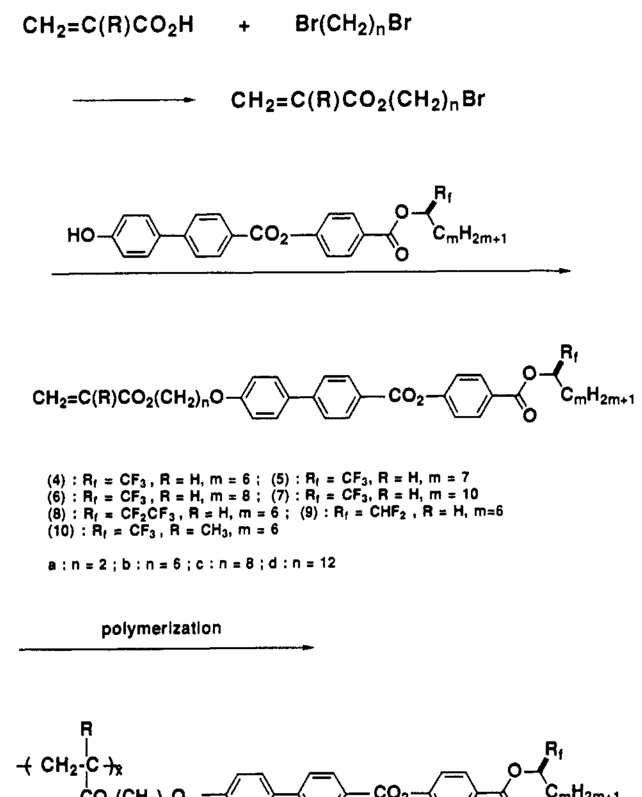
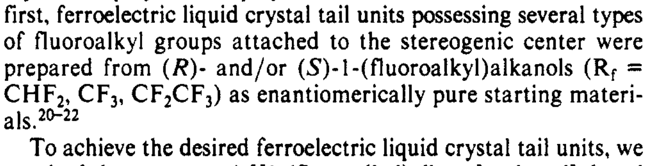
Scheme II



that a fluoroalkyl group attached to the stereogenic center may increase the polarization and decrease the viscosity.[16,24,25]

These early observations have led to the conclusion that (1) the presence of a fluoroalkylated tail unit should be employed as a mesogenic pendant group, (2) the molecular weight of conductive polymers should be less than 10^5, and that (3) an acrylic acid derived chain is more effective. Ferroelectric liquid crystalline polymers **1** were designed upon the basis of these considerations.



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Results and Discussion

Synthesis. A convenient synthetic route to ferroelectric liquid crystalline polymers employed is shown in Scheme I and II. At first, ferroelectric liquid crystal tail units possessing several types of fluoroalkyl groups attached to the stereogenic center were prepared from (*R*)- and/or (*S*)-1-(fluoroalkyl)alkanols (R_f = CHF_2, CF_3, CF_2CF_3) as enantiomerically pure starting materials.[20-22]

To achieve the desired ferroelectric liquid crystal tail units, we required the precursor 4-[[1-(fluoroalkyl)alkoxy]carbonyl]phenyl 4′-(benzyloxy)biphenyl-4-carboxylate. In the first step, 1-(fluoroalkyl)alkyl 4-(benzyloxy)benzoates were prepared by reaction of chiral 1-(fluoroalkyl)alkyl 4-hydroxybenzoate with *p*-(benzyloxy)benzoic acid chloride. Hydrogenolysis of the benzyl ether protecting group with H_2/10% Pd–C in ethanol under ultrasonic irradiation, was followed by coupling the resulting 1-(fluoroalkyl)alkyl 4-hydroxybenzoate and 4′-(benzyloxy)biphenyl-4-carboxylic acid chloride in dichloromethane. Debenzylation by the above mentioned catalytic hydrogenaton was required as the final step.

The next step in the synthetic strategy required the preparation of acrylic or methacrylic monomers which incorporated these fluorinated ferroelectric liquid crystal tail units. For the present purpose, a ω,ω′-alkyl dihalide and acrylic acid or methacrylic acid were condensed, to form a ω-halogenoalkyl esters. The resulting esters were converted to the target monomers incorporating the fluoroalkyl group at the stereogenic center of a mesogen pendant group by using the coupling reaction of the described FLC tail units.

Polymerization Reactions. The polymerization was carried out in the *n*-butyllithium–tetrahydrofuran system or in the azobisisobutyronitrile (AIBN–benzene system with ferroelectric liquid crystal monomers. The products were purified by flash column chromatography on silica gel. The samples were subjected to gel permeation chromatography (GPC) in tetrahydrofuran at 50° C. The results of the polymerization are shown in Table I.

Ferroelectric Liquid Crystalline Polymer Properties. The phase behavior of the new fluorinated ferroelectric liquid crystalline polymers is shown in Table I. Homogeneously aligned films of 2.5-μm thickness between conducting glass plates were prepared by a temperature gradient method.[26] The spontaneous polarization was measured by the triangular wave voltage method.[27] It was found that the spontaneous polarization increases monotonically as a function of $T_{AC} - T$ without any irregularities. Furthermore, the sign of spontaneous polarization P_s suggests the absolute configuration of the stereocenter. The plus signs in the table are for *R* enantiomers and/or (+) isomers and those for *S* enantiomers and/or (−) isomers have the minus sign. All the synthetic materials have the phase sequence of g ↔ S_mC^* ↔ S_mA ↔ Iso. The phase sequence was determined by a polarizing optical microscope with a hot stage (Mettler FP-82). The melting point was measured by a differential scanning calorimeter (Seiko DSC-20). The temperature range of the ordinary S_mC^* phase is rather narrow. Obviously, the obtained ferroelectric liquid crystalline polymers exhibit quick response time (<10 ms at 90 °C, 14 V/μm driving field) and large spontaneous polarization (40–70 nC/cm^2 at 90 °C).

For the purpose of developing structure–response time relationships, we varied the carbon chain length attached to the methylene group of acrylic skeletal chain and/or the mesogenic carbon chain length. As seen from the data shown in Table I, the response time decreases with the shorter carbon chain length in acrylic skeletal chain and as well in the chiral carbon chain. It is found on the basis of the tabulated results that a trifluoromethyl group attached to the asymmetic center, when compared to other fluoroalkyl groups such as difluoromethyl or pentafluoroethyl group, greatly decreased the response time. Furthermore, these results are consistent with the steric dependence of the response time as mentioned earlier.

Experimental Section

General Procedures. All commercially available reagents were used without further purification. Infrared spectra were obtained by using a JASCO A-102 spectrometer and KBr pellets. Nuclear magnetic resonance (NMR) spectra were recorded at 90 or 200 MHz for ^{1}H NMR and 56.5 MHz for ^{19}F NMR in $CDCl_3$ unless otherwise noted. ^{19}F chemical shifts are reported in parts per million (ppm) relative to trifluoroacetic acid (δ 0.00) as an external standard. The melting points were measured by a DSC (Seiko DSC-20), and the phase sequence was determined by a polarizing optical microscope with a hot stage (Mettler FP-82).

Ferroelectric Liquid Crystal Tail Unit. Typical Procedure. (*R*)-(+)-4-[[[1-(Trifluoromethyl)octyl]oxy]carbonyl]phenyl 4′-Hydroxybiphenyl-4-carboxylate (1a). (a) (*R*)-(+)-4-[[[1-(Trifluoromethyl)octyl]oxy]carbonyl]phenyl 4′-(Benzyloxy)biphenyl-4-carboxylate. A mixture of 4′-(benzyloxy)biphenyl-4-carboxylic acid (6.4 g, 20 mmol) and freshly dried thionyl chloride (50 mL) was refluxed for 1 h, and then the re-

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Table I. Physical Properties of Ferroelectric Liquid Crystal Polymers

Monomer No	Initiator	Polymer dispersity[a)] M_w	M_n	$D=M_w/M_n$	Phase sequence	Response[b)] time (m sec)	Ps[c)] (nC/cm^{-1})
(4a)	n-BuLi	37600	28900	1.30	g $\underset{16^{\circ}C}{\overset{23^{\circ}C}{\longleftrightarrow}}$ S_mC^* $\underset{44^{\circ}C}{\overset{57^{\circ}C}{\longleftrightarrow}}$ S_mA $\underset{109^{\circ}C}{\overset{115^{\circ}C}{\longleftrightarrow}}$ Iso	1.0	+71
	AIBN	48500	40700	1.19	g $\underset{18^{\circ}C}{\overset{25^{\circ}C}{\longleftrightarrow}}$ S_mC^* $\underset{54^{\circ}C}{\overset{66^{\circ}C}{\longleftrightarrow}}$ S_mA $\underset{123^{\circ}C}{\overset{127^{\circ}C}{\longleftrightarrow}}$ Iso	1.1	+70
	AIBN	44600	36100	1.24	g $\underset{17^{\circ}C}{\overset{23^{\circ}C}{\longleftrightarrow}}$ S_mC^* $\underset{58^{\circ}C}{\overset{61^{\circ}C}{\longleftrightarrow}}$ S_mA $\underset{117^{\circ}C}{\overset{122^{\circ}C}{\longleftrightarrow}}$ Iso	1.1	-70
(4b)	n-BuLi	47800	37400	1.28	g $\underset{19^{\circ}C}{\overset{26^{\circ}C}{\longleftrightarrow}}$ S_mC^* $\underset{55^{\circ}C}{\overset{65^{\circ}C}{\longleftrightarrow}}$ S_mA $\underset{132^{\circ}C}{\overset{141^{\circ}C}{\longleftrightarrow}}$ Iso	1.6	+68
	AIBN	51400	44700	1.15	g $\underset{25^{\circ}C}{\overset{33^{\circ}C}{\longleftrightarrow}}$ S_mC^* $\underset{59^{\circ}C}{\overset{71^{\circ}C}{\longleftrightarrow}}$ S_mA $\underset{136^{\circ}C}{\overset{147^{\circ}C}{\longleftrightarrow}}$ Iso	1.9	+69
	AIBN	42400	31700	1.33	g $\underset{17^{\circ}C}{\overset{23^{\circ}C}{\longleftrightarrow}}$ S_mC^* $\underset{47^{\circ}C}{\overset{59^{\circ}C}{\longleftrightarrow}}$ S_mA $\underset{119^{\circ}C}{\overset{132^{\circ}C}{\longleftrightarrow}}$ Iso	1.7	-67
(4c)	n-BuLi	51700	38200	1.35	g $\underset{16^{\circ}C}{\overset{22^{\circ}C}{\longleftrightarrow}}$ S_mC^* $\underset{53^{\circ}C}{\overset{68^{\circ}C}{\longleftrightarrow}}$ S_mA $\underset{125^{\circ}C}{\overset{141^{\circ}C}{\longleftrightarrow}}$ Iso	4.6	+60
	AIBN	52300	43600	1.20	g $\underset{17^{\circ}C}{\overset{25^{\circ}C}{\longleftrightarrow}}$ S_mC^* $\underset{50^{\circ}C}{\overset{59^{\circ}C}{\longleftrightarrow}}$ S_mA $\underset{135^{\circ}C}{\overset{146^{\circ}C}{\longleftrightarrow}}$ Iso	4.5	+61
	AIBN	48700	36300	1.34	g $\underset{15^{\circ}C}{\overset{21^{\circ}C}{\longleftrightarrow}}$ S_mC^* $\underset{45^{\circ}C}{\overset{54^{\circ}C}{\longleftrightarrow}}$ S_mA $\underset{121^{\circ}C}{\overset{134^{\circ}C}{\longleftrightarrow}}$ Iso	4.0	-58
(4d)	n-BuLi	49500	41100	1.20	g $\underset{18^{\circ}C}{\overset{27^{\circ}C}{\longleftrightarrow}}$ S_mC^* $\underset{37^{\circ}C}{\overset{50^{\circ}C}{\longleftrightarrow}}$ S_mA $\underset{128^{\circ}C}{\overset{141^{\circ}C}{\longleftrightarrow}}$ Iso	8.7	+50
	AIBN	54300	43800	1.24	g $\underset{19^{\circ}C}{\overset{30^{\circ}C}{\longleftrightarrow}}$ S_mC^* $\underset{56^{\circ}C}{\overset{69^{\circ}C}{\longleftrightarrow}}$ S_mA $\underset{148^{\circ}C}{\overset{159^{\circ}C}{\longleftrightarrow}}$ Iso	9.6	+53
	AIBN	56500	41400	1.36	g $\underset{24^{\circ}C}{\overset{32^{\circ}C}{\longleftrightarrow}}$ S_mC^* $\underset{59^{\circ}C}{\overset{70^{\circ}C}{\longleftrightarrow}}$ S_mA $\underset{151^{\circ}C}{\overset{164^{\circ}C}{\longleftrightarrow}}$ Iso	10.4	-48
(5c)	n-BuLi	55700	41800	1.33	g $\underset{13^{\circ}C}{\overset{21^{\circ}C}{\longleftrightarrow}}$ S_mC^* $\underset{57^{\circ}C}{\overset{65^{\circ}C}{\longleftrightarrow}}$ S_mA $\underset{122^{\circ}C}{\overset{145^{\circ}C}{\longleftrightarrow}}$ Iso	6.5	+55
	AIBN	56500	45500	1.24	g $\underset{19^{\circ}C}{\overset{26^{\circ}C}{\longleftrightarrow}}$ S_mC^* $\underset{56^{\circ}C}{\overset{69^{\circ}C}{\longleftrightarrow}}$ S_mA $\underset{129^{\circ}C}{\overset{144^{\circ}C}{\longleftrightarrow}}$ Iso	6.8	+54
(6c)	n-BuLi	56100	43700	1.28	g $\underset{18^{\circ}C}{\overset{27^{\circ}C}{\longleftrightarrow}}$ S_mC^* $\underset{64^{\circ}C}{\overset{72^{\circ}C}{\longleftrightarrow}}$ S_mA $\underset{145^{\circ}C}{\overset{154^{\circ}C}{\longleftrightarrow}}$ Iso	8.6	+51
	AIBN	55700	47100	1.18	g $\underset{24^{\circ}C}{\overset{30^{\circ}C}{\longleftrightarrow}}$ S_mC^* $\underset{65^{\circ}C}{\overset{75^{\circ}C}{\longleftrightarrow}}$ S_mA $\underset{147^{\circ}C}{\overset{157^{\circ}C}{\longleftrightarrow}}$ Iso	8.4	+52
(7c)	n-BuLi	60900	44300	1.38	g $\underset{30^{\circ}C}{\overset{37^{\circ}C}{\longleftrightarrow}}$ S_mC^* $\underset{58^{\circ}C}{\overset{72^{\circ}C}{\longleftrightarrow}}$ S_mA $\underset{147^{\circ}C}{\overset{161^{\circ}C}{\longleftrightarrow}}$ Iso	9.6	+53
	AIBN	63500	49800	1.28	g $\underset{28^{\circ}C}{\overset{40^{\circ}C}{\longleftrightarrow}}$ S_mC^* $\underset{64^{\circ}C}{\overset{77^{\circ}C}{\longleftrightarrow}}$ S_mA $\underset{145^{\circ}C}{\overset{164^{\circ}C}{\longleftrightarrow}}$ Iso	9.8	+52
(8a)	n-BuLi	35800	26500	1.35	g $\underset{14^{\circ}C}{\overset{21^{\circ}C}{\longleftrightarrow}}$ S_mC^* $\underset{40^{\circ}C}{\overset{54^{\circ}C}{\longleftrightarrow}}$ S_mA $\underset{102^{\circ}C}{\overset{115^{\circ}C}{\longleftrightarrow}}$ Iso	16.5	+38
	AIBN	37600	30100	1.25	g $\underset{19^{\circ}C}{\overset{27^{\circ}C}{\longleftrightarrow}}$ S_mC^* $\underset{51^{\circ}C}{\overset{65^{\circ}C}{\longleftrightarrow}}$ S_mA $\underset{117^{\circ}C}{\overset{124^{\circ}C}{\longleftrightarrow}}$ Iso	16.7	+40
	AIBN	33400	25700	1.30	g $\underset{15^{\circ}C}{\overset{20^{\circ}C}{\longleftrightarrow}}$ S_mC^* $\underset{39^{\circ}C}{\overset{52^{\circ}C}{\longleftrightarrow}}$ S_mA $\underset{77^{\circ}C}{\overset{109^{\circ}C}{\longleftrightarrow}}$ Iso	18.7	-34
(8b)	n-BuLi	41300	31400	1.32	g $\underset{15^{\circ}C}{\overset{24^{\circ}C}{\longleftrightarrow}}$ S_mC^* $\underset{64^{\circ}C}{\overset{71^{\circ}C}{\longleftrightarrow}}$ S_mA $\underset{144^{\circ}C}{\overset{153^{\circ}C}{\longleftrightarrow}}$ Iso	18.9	+37
	AIBN	42100	35700	1.18	g $\underset{29^{\circ}C}{\overset{36^{\circ}C}{\longleftrightarrow}}$ S_mC^* $\underset{65^{\circ}C}{\overset{78^{\circ}C}{\longleftrightarrow}}$ S_mA $\underset{147^{\circ}C}{\overset{155^{\circ}C}{\longleftrightarrow}}$ Iso	19.6	+35
	AIBN	39500	28900	1.37	g $\underset{16^{\circ}C}{\overset{23^{\circ}C}{\longleftrightarrow}}$ S_mC^* $\underset{53^{\circ}C}{\overset{64^{\circ}C}{\longleftrightarrow}}$ S_mA $\underset{120^{\circ}C}{\overset{139^{\circ}C}{\longleftrightarrow}}$ Iso	17.5	-38
(8c)	n-BuLi	49800	39400	1.26	g $\underset{29^{\circ}C}{\overset{38^{\circ}C}{\longleftrightarrow}}$ S_mC^* $\underset{61^{\circ}C}{\overset{73^{\circ}C}{\longleftrightarrow}}$ S_mA $\underset{134^{\circ}C}{\overset{147^{\circ}C}{\longleftrightarrow}}$ Iso	33.6	+25
	AIBN	51400	41800	1.23	g $\underset{27^{\circ}C}{\overset{41^{\circ}C}{\longleftrightarrow}}$ S_mC^* $\underset{65^{\circ}C}{\overset{75^{\circ}C}{\longleftrightarrow}}$ S_mA $\underset{138^{\circ}C}{\overset{150^{\circ}C}{\longleftrightarrow}}$ Iso	34.5	+24
	AIBN	46100	32700	1.41	g $\underset{19^{\circ}C}{\overset{34^{\circ}C}{\longleftrightarrow}}$ S_mC^* $\underset{53^{\circ}C}{\overset{64^{\circ}C}{\longleftrightarrow}}$ S_mA $\underset{118^{\circ}C}{\overset{134^{\circ}C}{\longleftrightarrow}}$ Iso	37.5	-21

Table I (Continued)

Monomer No	Initiator	Polymer dispersity[a] M_w	M_n	$D=M_w/M_n$	Phase sequence	Response[b] time (m sec)	Ps[c] (nC/cm^{-1})
(8d)	n-BuLi	53400	45700	1.17	g $\underset{28°C}{\overset{39°C}{\longleftrightarrow}}$ S_mC^* $\underset{67°C}{\overset{75°C}{\longleftrightarrow}}$ S_mA $\underset{135°C}{\overset{151°C}{\longleftrightarrow}}$ Iso	58.9	+21
	AIBN	56600	44400	1.28	g $\underset{31°C}{\overset{40°C}{\longleftrightarrow}}$ S_mC^* $\underset{69°C}{\overset{79°C}{\longleftrightarrow}}$ S_mA $\underset{157°C}{\overset{164°C}{\longleftrightarrow}}$ Iso	50.2	+20
	AIBN	60500	49300	1.23	g $\underset{33°C}{\overset{44°C}{\longleftrightarrow}}$ S_mC^* $\underset{70°C}{\overset{81°C}{\longleftrightarrow}}$ S_mA $\underset{156°C}{\overset{169°C}{\longleftrightarrow}}$ Iso	61.4	-18
(9a)	n-BuLi	50700	39800	1.38	g $\underset{14°C}{\overset{24°C}{\longleftrightarrow}}$ S_mC^* $\underset{47°C}{\overset{54°C}{\longleftrightarrow}}$ S_mA $\underset{110°C}{\overset{117°C}{\longleftrightarrow}}$ Iso	12.0	+49
	AIBN	51300	41400	1.24	g $\underset{16°C}{\overset{24°C}{\longleftrightarrow}}$ S_mC^* $\underset{57°C}{\overset{64°C}{\longleftrightarrow}}$ S_mA $\underset{121°C}{\overset{125°C}{\longleftrightarrow}}$ Iso	12.1	+51
	AIBN	47900	36490	1.32	g $\underset{15°C}{\overset{21°C}{\longleftrightarrow}}$ S_mC^* $\underset{44°C}{\overset{51°C}{\longleftrightarrow}}$ S_mA $\underset{91°C}{\overset{103°C}{\longleftrightarrow}}$ Iso	13.6	-50
(9b)	n-BuLi	54400	41900	1.30	g $\underset{19°C}{\overset{25°C}{\longleftrightarrow}}$ S_mC^* $\underset{56°C}{\overset{63°C}{\longleftrightarrow}}$ S_mA $\underset{127°C}{\overset{139°C}{\longleftrightarrow}}$ Iso	17.9	+43
	AIBN	55600	45300	1.23	g $\underset{27°C}{\overset{33°C}{\longleftrightarrow}}$ S_mC^* $\underset{57°C}{\overset{70°C}{\longleftrightarrow}}$ S_mA $\underset{132°C}{\overset{145°C}{\longleftrightarrow}}$ Iso	18.6	+39
	AIBN	60300	49000	1.23	g $\underset{31°C}{\overset{39°C}{\longleftrightarrow}}$ S_mC^* $\underset{63°C}{\overset{76°C}{\longleftrightarrow}}$ S_mA $\underset{148°C}{\overset{161°C}{\longleftrightarrow}}$ Iso	20.4	-37
(9c)	n-BuLi	58900	45100	1.31	g $\underset{17°C}{\overset{28°C}{\longleftrightarrow}}$ S_mC^* $\underset{52°C}{\overset{65°C}{\longleftrightarrow}}$ S_mA $\underset{131°C}{\overset{149°C}{\longleftrightarrow}}$ Iso	30.8	+24
	AIBN	59100	43500	1.36	g $\underset{24°C}{\overset{30°C}{\longleftrightarrow}}$ S_mC^* $\underset{58°C}{\overset{69°C}{\longleftrightarrow}}$ S_mA $\underset{141°C}{\overset{154°C}{\longleftrightarrow}}$ Iso	31.5	+25
	AIBN	53400	40300	1.33	g $\underset{16°C}{\overset{26°C}{\longleftrightarrow}}$ S_mC^* $\underset{46°C}{\overset{60°C}{\longleftrightarrow}}$ S_mA $\underset{109°C}{\overset{126°C}{\longleftrightarrow}}$ Iso	34.8	-21
(9d)	n-BuLi	59400	43600	1.36	g $\underset{21°C}{\overset{31°C}{\longleftrightarrow}}$ S_mC^* $\underset{53°C}{\overset{67°C}{\longleftrightarrow}}$ S_mA $\underset{134°C}{\overset{154°C}{\longleftrightarrow}}$ Iso	40.0	+28
	AIBN	63300	50500	1.25	g $\underset{23°C}{\overset{34°C}{\longleftrightarrow}}$ S_mC^* $\underset{61°C}{\overset{73°C}{\longleftrightarrow}}$ S_mA $\underset{146°C}{\overset{163°C}{\longleftrightarrow}}$ Iso	41.4	+27
	AIBN	52500	41400	1.27	g $\underset{18°C}{\overset{27°C}{\longleftrightarrow}}$ S_mC^* $\underset{51°C}{\overset{64°C}{\longleftrightarrow}}$ S_mA $\underset{124°C}{\overset{137°C}{\longleftrightarrow}}$ Iso	44.9	-25
(10a)	n-BuLi	40100	29800	1.35	g $\underset{15°C}{\overset{24°C}{\longleftrightarrow}}$ S_mC^* $\underset{55°C}{\overset{66°C}{\longleftrightarrow}}$ S_mA $\underset{123°C}{\overset{137°C}{\longleftrightarrow}}$ Iso	28.6	+24
	AIBN	54300	43700	1.24	g $\underset{15°C}{\overset{27°C}{\longleftrightarrow}}$ S_mC^* $\underset{57°C}{\overset{69°C}{\longleftrightarrow}}$ S_mA $\underset{136°C}{\overset{144°C}{\longleftrightarrow}}$ Iso	28.5	+24
(10b)	n-BuLi	53700	38800	1.38	g $\underset{15°C}{\overset{23°C}{\longleftrightarrow}}$ S_mC^* $\underset{64°C}{\overset{72°C}{\longleftrightarrow}}$ S_mA $\underset{132°C}{\overset{144°C}{\longleftrightarrow}}$ Iso	40.4	+17
	AIBN	61200	43500	1.40	g $\underset{17°C}{\overset{26°C}{\longleftrightarrow}}$ S_mC^* $\underset{63°C}{\overset{75°C}{\longleftrightarrow}}$ S_mA $\underset{134°C}{\overset{147°C}{\longleftrightarrow}}$ Iso	40.3	+18
(10c)	n-BuLi	57400	43500	1.32	g $\underset{15°C}{\overset{28°C}{\longleftrightarrow}}$ S_mC^* $\underset{65°C}{\overset{74°C}{\longleftrightarrow}}$ S_mA $\underset{146°C}{\overset{157°C}{\longleftrightarrow}}$ Iso	66.9	+13
	AIBN	68900	56500	1.21	g $\underset{25°C}{\overset{30°C}{\longleftrightarrow}}$ S_mC^* $\underset{67°C}{\overset{77°C}{\longleftrightarrow}}$ S_mA $\underset{153°C}{\overset{161°C}{\longleftrightarrow}}$ Iso	67.8	+13
(10d)	n-BuLi	62300	45500	1.37	g $\underset{30°C}{\overset{37°C}{\longleftrightarrow}}$ S_mC^* $\underset{62°C}{\overset{76°C}{\longleftrightarrow}}$ S_mA $\underset{151°C}{\overset{165°C}{\longleftrightarrow}}$ Iso	91.1	+10
	AIBN	82000	64400	1.27	g $\underset{28°C}{\overset{40°C}{\longleftrightarrow}}$ S_mC^* $\underset{67°C}{\overset{78°C}{\longleftrightarrow}}$ S_mA $\underset{153°C}{\overset{169°C}{\longleftrightarrow}}$ Iso	92.4	+11

[a] The analysis was done with Shimadzu LC-5A high-performance liquid chromatography using a Shodex GPC KF-803 column equipped a refractive index detector Shodex RI. The flow rate was 1.5 mL/min. [b] Response times were determined by observing the behavior of the transmitted light intensity (0 → 90%) in homogeneously aligned film of 2.5-μm thickness. Applied voltage is E = 14 V/μm for the transmitted light intensity. [c] Spontaneous polarization was measured by the triangular wave voltage method at 90 °C. The plus signs are for R enantiomers and/or (+) isomers and the minus signs are for S enantiomers and/or (−) isomers.

maining thionyl chloride was removed under dynamic vacuum at 90 °C. Into a mixture of the above obtained acid chloride and (R)-(+)-1-(trifluoromethyl)octyl p-hydroxybenzoate[16,28] (6.1 g, 20 mmol; $[\alpha]^{23}_{D}$ (MeOH) +56.53° (c 1.04), >96% ee) in dichloromethane (100 mL) under an atmosphere of nitrogen was added pyridine (5.0 mL) via syringe. after 3 days of stirring at room temperature, the mixture was quenched with 1 N HCl and then washed with brine. (R)-(+)-4-[[[1-(Trifluoromethyl)octyl]oxy]carbonyl]phenyl 4′-(benzyloxy)biphenyl-4-carboxylate was separated by column chromatography on silica gel with use of a mixture of hexane–ethyl acetate (3:1) in 64% yield: ^{19}F NMR δ −0.8 (d, J_{F-H} = 7.5 Hz); ^{1}H NMR δ 0.90–1.93 (13 H, m), 4.25 (OCH_2), 5.58 ($CHCF_3$, m), 7.00–8.25 ArH); IR (KBr) 1735 (C=O) cm^{-1}.

(b) Reduction. A flask containing (*R*)-(+)-4-[[[1-(trifluoromethyl)-octyl]oxy]carbonyl]phenyl 4'-(benzyloxy)biphenyl-4-carboxylate (5.9 g, 10 mmol) and 10% Pd-C (0.2 g) in ethanol (30 mL) was irradiated in the water bath of an ultrasonic laboratory cleaner for 5 h. Then, the solution was poured into 1 N HCl solution, and products were extracted with ethyl acetate. On removal of the solvent, (*R*)-(+)-4-[[[1-(trifluoromethyl)octyl]oxy]carbonyl]phenyl 4'-hydroxybiphenyl-4'-hydroxybiphenyl-4-carboxylate (**1a**) was purified by recrystallization from ethanol in 87% yield: mp 97-99 °C; $[\alpha]^{23}_D$ (MeOH) +46.96° (*c* 0.85), >96% ee; ^{19}F NMR δ -0.7 (d, J_{F-H} = 7.5 Hz); ^{1}H NMR δ 0.94-1.87 (13 H, m), 5.58 ($CHCF_3$, m), 6.50 (OH), 7.00-8.40 (ArH); IR (KBr) 3640 (OH), 1735 (C=0) cm^{-1}; high-resolution MS calcd for $C_{28}H_{27}O_5F_3$ 500.513, found 500.337. Anal. Found: C, 67.34; H, 5.61. Calcd for $C_{28}H_{27}O_5F_3$: C, 67.19; H, 5.44.

(*S*)-(-)-4-[[[1-(Trifluoromethyl)octyl]oxy]carbonyl]phenyl 4'-Hydroxybiphenyl-4-carboxylate. (a) (*S*)-(-)-4-[[[1-(Trifluoromethyl)-octyl]oxy]carbonyl]phenyl 4'-(Benzyloxy)biphenyl-4-carboxylate. A mixture of 4'-(benzyloxy)biphenyl-4-carboxylic acid (6.4 g, 20 mmol) and freshly dried thionyl chloride (50 mL) was refluxed for 1 h, and then the remaining thionyl chloride was removed under dynamic vacuum at 90 °C. Into a mixture of the above acid chloride and (*S*)-(-)-1-(trifluoromethyl)octyl *p*-hydroxybenzoate[16,28] (6.1 g, 20 mmol, $[\alpha]^{23}_D$ MeOH -56.57° (*c* 1.15), >96% ee) in dichloromethane (100 mL) under an atmosphere of nitrogen was added pyridine (5.0 mL) via syringe and then worked up as usual. (*S*)-(-)-4-[[[1-4-(Trifluoromethyl)octyl]oxy]-carbonyl]phenyl 4'-(benzyloxy)biphenyl-4-carboxylate was obtained in 64% yield: ^{19}F NMR δ -0.8 (d, J_{F-H} = 7.5 Hz); ^{1}H NMR δ 0.90-1.93 (13 H, m), 4.25 (OCH_2), 5.58 ($CHCF_3$, m), 7.00-8.25 (ArH); IR (KBr) 1735 (C=0) cm^{-1}.

(b) Reduction. A flask containing (*S*)-(-)-4-[[[1-(trifluoromethyl)-octyl]oxy]carbonyl]phenyl 4'-(benzyloxy)biphenyl-4-carboxylate (3.0 g, 5 mmol) and 10% Pd-C (0.1 g) in ethanol (15 mL) was irradiated in the water bath of an ultrasound laboratory cleaner for 3 h and then worked up as usual. (*S*)-(-)-4-[[[1-(Trifluoromethyl)octyl]oxy]carbonyl]phenyl 4'-hydroxybiphenyl-4-carboxylate was purified by recrystallization from ethanol in 83% yield: mp 97-99 °C; $[\alpha]^{23}_D$ (MeOH) -46.93° (*c* 0.92), >96% ee; ^{19}F NMR δ -0.7 (d, J_{F-H} = 7.5 Hz); ^{1}H NMR δ 0.94-1.87 (13 H, m), 5.58 ($CHCF_3$, m), 6.50 (OH), 7.00-8.40 (ArH); IR (KBr) 3640 (OH), 1735 (C=O) cm^{-1}; high-resolution MS calcd for $C_{28}H_{27}O_5F_3$ 500.513, found 500.671. Anal. Found: C, 66.95; H, 5.31. Calcd for $C_{28}H_{27}O_5F_3$: C, 67.19; H, 5.44.

(*R*)-(+)-4-[[[1-(Trifluoromethyl)nonyl]oxy]carbonyl]phenyl 4'-Hydroxybiphenyl-4-carboxylate (1b). (a) (*R*)-(+)-4-[[[1-(Trifluoromethyl)nonyl]oxy]carbonyl]phenyl 4'-(Benzyloxy)biphenyl-4-carboxylate. 4'-(Benzyloxy)biphenyl-4-carboxylic acid (6.4 g, 20 mmol), freshly dried thionyl chloride (50 mL), and (*R*)-(+)-1-(trifluoromethyl)nonyl-*p*-hydroxybenzoate (6.4 g, 20 mmol, $[\alpha]^{23}_D$ (MeOH) + 51.13° (*c* 1.08) >96% ee) were used. Yield 75%: ^{19}F NMR δ -0.7 (d, J_{F-H} = 7.5 Hz); ^{1}H NMR δ 0.92-1.97 (15 H, m), 4.27 (OCH_2), 5.56 ($CHCF_3$, m), 7.00-8.30 (ArH); IR (KBr) 1735 (C=O) cm^{-1}.

(b) Reduction. (*R*)-(+)-4-[[[1-(Trifluoromethyl)nonyl]oxy]-carbonyl]phenyl 4'-(benzyloxy)biphenyl-4-carboxylate (6.1 g, 10 mmol) and 10% Pd-C (0.2 g) in ethanol (30 mL) were irradiated and then worked up as usual. (*R*)-(+)-4-[[[1-(trifluoromethyl)nonyl]oxy]-carbonyl]phenyl 4'-hydroxybiphenyl-4-carboxylate (**1b**) was purified by recrystallization from ethanol in 83% yield: mp 101-102 °C; $[\alpha]^{23}_D$ (MeOH) +43.57° (*c* 0.85), >96% ee; ^{19}F NMR δ -0.7 (d, J_{F-H} = 7.5 Hz); ^{1}H NMR δ 0.91-1.90 (15 H, m), 5.57 ($CHCF_3$, m), 6.67 (OH), 7.06-8.29 (Ar H); IR (KBr) 3650 (OH), 1735 (C=O) cm^{-1}; high-resolution MS calcd for $C_{29}H_{29}O_5F_3$ 514.540, found 514.731. Anal. Found: C, 67.94; H, 5.46. Calcd for $C_{29}H_{29}O_5F_3$: C, 67.70; H, 5.68.

(*S*)-(-)-4-[[[1-(Trifluoromethyl)nonyl]oxy]carbonyl]phenyl 4'-Hydroxybiphenyl-4-carboxylate. (a) (*S*)-(-)-4-[[[1-(Trifluoromethyl)-nonyl]oxy]carbonyl]phenyl 4'-(Benzyloxy)biphenyl-4-carboxylate. 4'-(Benzyloxy)biphenyl-4-carboxylic acid (6.4 g, 20 mmol), thionyl chloride (50 mL), and (*S*)-(-)-(1-(trifluoromethyl)nonyl *p*-hydroxybenzoate (6.4 g, 20 mmol, $[\alpha]^{23}_D$ (MeOH) -51.09° (*c* 1.01), >96% ee) were used. Yield 73%.

(b) Reduction. (*S*)-(-)-4-[[[1-(Trifluoromethyl)nonyl]oxy]-carbonyl]phenyl 4'-(benzyloxy)biphenyl-4-carboxylate (3.1 g, 5 mmol) and 10% Pd-C (0.1 g) in ethanol (15 mL) were irradiated and then worked up similarly. (*S*)-(-)-4-[[[1-(Trifluoromethyl)nonyl]oxy]-carbonyl]phenyl 4'-hydroxybiphenyl-4-carboxylate was obtained in 87% yield: $[\alpha]^{23}_D$ (MeOH) -43.64° (*c* 0.72), >96% ee; high-resolution MS calcd for $C_{28}H_{27}O_5F_3$ 500.513, found 500.395. Anal. Found: C, 67.40; H, 5.27. Calcd for $C_{28}H_{27}O_5F_3$: C, 67.19; H, 5.44.

(*R*)-(+)-4-[[[1-(Trifluoromethyl)decyl]oxy]carbonyl]phenyl 4'-Hydroxybiphenyl-4-carboxylate (1c). (a) (*R*)-(+)-5-[[[1-(Trifluoromethyl)decyl]oxy]carbonyl]phenyl 4'-(Benzyloxy)biphenyl-4-carboxylate. 4'-(Benzyloxy)biphenyl-4-carboxylic acid (6.4 g, 20 mmol), thionyl chloride (50 mL), and (R)-(+)-1-(trifluoromethyl)decyl *p*-hydroxybenzoate (6.6 g, 20 mmol, $[\alpha]^{23}_D$ (MeOH) +50.51° (*c* 1.15), >97% ee) were used. Yield 69%: ^{19}F NMR δ -0.8 (d, J_{F-H} = 8.0 Hz); ^{1}H NMR δ 0.87-2.05 (17 H, m), 4.25 (OCH_2), 5.58 ($CHCF_3$, m), 7.10-8.35 (ArH); IR (KBr) 1735 (C=O) cm^{-1}.

(b) Reduction. (*R*)-(+)-4-[[[1-(Trifluoromethyl)decyl]oxy]-carbonyl]phenyl 4'-(benzyloxy)biphenyl-4-carboxylate (3.1 g, 5 mmol) and 10% Pd-C (0.1 g) in ethanol (15 mL) were irradiated and then worked up as usual. (*R*)-(+)-4-[[[1-(Trifluoromethyl)decyl]oxy]-carbonyl]phenyl 4'-hydroxybiphenyl-4-carboxylate (**1c**) was obtained in 81% yield: mp 104-106 °C; $[\alpha]^{23}_D$ (MeOH) +48.74° (*c* 0.83), >97% ee; ^{19}F NMR δ -0.8 (d, J_{F-H} = 8.0 Hz); ^{1}H NMR δ 0.89-2.14 (17 H, m), 5.59 ($CHCF_3$, m), 6.64 (OH), 7.14-8.45 (ArH); IR (KBr) 3650 (OH), 1735 (C=O) cm^{-1}; high-resolution MS calcd for $C_{30}H_{31}O_5F_3$ 528.567, found 528.396. Anal. Found: C, 68.41; H, 6.05. Calcd for $C_{30}H_{31}O_5F_3$: C, 68.17; H, 5.91.

(*S*)-(-)-4-[[[1-(Trifluoromethyl)decyl]oxy]carbonyl]phenyl 4'-Hydroxybiphenyl-4-carboxylate. (a) (*S*)-(-)-4-[[[1-(Trifluoromethyl)-decyl]oxy]carbonyl]phenyl 4'-(Benzyloxy)biphenyl-4-carboxylate. 4'-(Benzyloxy)biphenyl-4-carboxylic acid (6.4 g, 20 mmol), thionyl chloride (50 mL), and (*S*)-(-)-1-(trifluoromethyl) decyl *p*-hydroxybenzoate (6.6 g, 20 mmol, $[\alpha]^{24}_D$ (MeOH) -50.49° (*c* 1.04), >97% ee) were used. Yield 77%.

(b) Reduction. (*S*)-(-)-4-[[[1-(Trifluoromethyl)decyl]oxy]-carbonyl]phenyl 4'-(benzyloxy)biphenyl-4-carboxylate (3.1 g, 5 mmo) and 10% Pd-C (0.1 g) in ethanol (15 mL) were irradiated and then worked up as usual. (*S*)-(-)-4-[[[1-(Trifluoromethyl)decyl]oxy]-carbonyl]phenyl 4'-hydroxybiphenyl-4-carboxylate was obtained in 79% yield: $[\alpha]^{24}_D$ (MeOH) -48.91° (*c* 0.98), >97% ee; high-resolution MS calcd for $C_{30}H_{31}O_5F_3$ 528.567, found 528.396. Anal. Found: C, 68.41; H, 6.05. Calcd for $C_{30}H_{31}O_5F_3$: C, 68.17; H, 5.91.

(*R*)-(+)-4-[[[1-(Trifluoromethyl)undecyl]oxy]carbonyl]phenyl 4'-Hydroxybiphenyl-4-carboxylate (1d). (a) (*R*)-(+)-4-[[[1-(Trifluoromethyl)undecyl]oxy]carbonyl]phenyl 4'-(Benzyloxy)biphenyl-4-carboxylate. 4'-(Benzyloxy)biphenyl-4-carboxylic acid (6.4 g, 20 mmol), thionyl chloride (50 mL), and (*R*)-(+)-1-(trifluoromethyl)undecyl *p*-hydroxybenzoate (7.2 g, 20 mmol, $[\alpha]^{24}_D$ (MeOH) +52.04° (*c* 1.08), >97% ee) were used. Yield 75%: ^{19}F NMR δ -0.8 (d, J_{F-H} = 8.0 Hz); ^{1}H NMR δ 0.89-2.13 (21 H, m), 4.24 (OCH_2), 5.56 ($CHCF_3$, m), 7.00-8.40 (ArH); IR (KBr) 1735 (C=O) cm^{-1}.

(b) Reduction. (*R*)-(+)-4-[[[1-(Trifluoromethyl)undecyl]oxy]-carbonyl]phenyl 4'-(benzoyloxy)biphenyl-4-carboxylate (3.3 g, 5 mmol) and 10% Pd-C (0.1 g) in ethanol (15 mL) were irradiated and then worked up as usual. (*R*)-(+)-4-[[[1-(Trifluoromethyl)undecyl]oxy]-carbonyl]phenyl 4'-hydroxybiphenyl-4-carboxylate (**1d**) was obtained in 84% yield: mp 112-115 °C; $[\alpha]^{23}_D$ (MeOH) +49.07° (*c* 0.95), >97% ee; ^{19}F NMR δ -0.8 (d, J_{F-H} = 8.0 Hz); ^{1}H NMR δ 0.93-2.27 (21 H, m), 5.57 ($CHCF_3$, m), 6.62 (OH), 7.09-8.45 (ArH); IR (KBr) 3640 (OH), 1735 (C=O) cm^{-1}; high-resolution MS calcd for $C_{32}H_{35}O_5F_3$ 556.621, found 556.494. Anal. Found: C, 68.88; H, 6.51. Calcd for $C_{32}H_{35}O_5F_3$: C, 69.05; H, 6.34.

(*S*)-(-)-4-[[[1-(Trifluoromethyl)undecyl]oxy]carbonyl]phenyl 4'-Hydroxybiphenyl-4-carboxylate. (a) (*S*)-(-)-4-[[[1-(Trifluoromethyl)-undecyl]oxy]carbonyl]phenyl 4'-(Benzyloxy)biphenyl-4-carboxylate. 4'-(Benzyloxy)biphenyl-4-carboxylic acid (6.4 g, 20 mmol), thionyl chloride (50 mL), and (*S*)-(-)-1-(trifluoromethyl)undecyl *p*-hydroxybenzoate (7.2 g, 20 mmol, $[\alpha]^{24}_D$ (MeOH) -52.15° (*c* 1.01), >97% ee) were used. Yield 68%.

(b) Reduction. (*S*)-(-)-4-[[[1-(Trifluoromethyl)undecyl]oxy]-carbonyl]phenyl 4'-(benzyloxy)biphenyl-4-carboxylate (3.3 g, 5 mmol) and 10% Pd-C (0.1 g) in ethanol (15 mL) were irradiated and then worked up as usual. (*S*)-(-)-4-[[[1-(Trifluoromethyl)undecyl]oxy]-carbonyl]phenyl 4'-hydroxybiphenyl-4-carboxylate was obtained in 81% yield: $[\alpha]^{23}_D$ (MeOH) -49.13° (*c* 0.92) >97% ee; high-resolution MS calcd for $C_{32}H_{35}O_5F_3$ 556.621, found, 556.785. Anal. Found: C, 69.17; H, 6.49. Calcd for $C_{32}H_{35}O_5F_3$: C, 69.05; H, 6.34.

(+)-4-[[[1-(Pentafluoroethyl)octyl]oxy]carbonyl]phenyl 4'-Hydroxybiphenyl-4-carboxylate (2a). (a) (+)-4-[[[1-(Pentafluoroethyl)octyl]-oxy]carbonyl]phenyl 4'-(Benzyloxy)biphenyl-4-carboxylate. 4'-(Benzyloxy)biphenyl-4-carboxylic acid (3.2 g, 10 mmol), thionyl chloride (25 mL), and (+)-1-(pentafluoroethyl)octyl *p*-hydroxybenzoate[28] (3.5 g, 10 mmol, $[\alpha]^{24}_D$ (MeOH) + 47.82° (*c* 0.94), >96% ee) were used. (+)-4-[[[1-(Pentafluoroethyl)octyl]oxy]carbonyl]phenyl 4'-(benzyloxy)biphenyl-4-carboxylate was obtained in 68% yield: ^{19}F NMR δ 3.2 (CF_3, t, J_{F-F} = 1.5 Hz), 45.6 (CF_2, m); ^{1}H NMR δ 0.92-1.97 (13 H, m), 4.24 (OCH_2), 5.57 ($CHCF_3$, m), 7.09-8.10 (ArH); IR (KBr) 1730 (C=O) cm^{-1}.

(b) Reduction. (+)-4-[[[1-(Pentafluoroethyl)octyl]oxy]carbonyl]-phenyl 4'-(benzoyloxy)biphenyl-4-carboxylate (4.4 g, 10 mmol) and 10% Pd-C (0.2 g) in ethanol (20 mL) were irradiated and then worked up as usual. (+)-4-[[[1-(Pentafluoroethyl)octyl]oxy]carbonyl]phenyl 4'-hydroxybiphenyl-4-carboxylate (**2a**) was purified by recrystallization from ethanol in 74% yield: mp 104–106 °C; $[\alpha]^{23}_D$ (MeOH) +44.02° (*c* 0.98), >96% ee; ^{19}F NMR δ 2.7 (CF_3, t, J_{F-F} = 1.5 Hz), 44.8 (CF_2, m); ^{1}H NMR δ 0.89–1.91 (13 H, m), 5.60 ($CHCF_3$, m), 6.47 (OH), 7.00–8.20 (ArH); IR (KBr) 3660 (OH), 1730 (C=O) cm^{-1}; high-resolution MS calcd for $C_{29}H_{27}O_5F_5$ 550.520, found 550.731. Anal. Found: C, 63.44; H, 5.11. Calcd for $C_{29}H_{27}O_5F_5$: C, 63.27; H, 4.94.

(−)-4-[[[1-(Pentafluoroethyl)octyl]oxy]carbonyl]phenyl 4'-Hydroxybiphenyl-4-carboxylate. (a) (−)-4-[[[1-(Pentafluoroethyl)octyl]oxy]carbonyl]phenyl 4'-(Benzyloxy)biphenyl-4-carboxylate. 4'-(Benzyloxy)biphenyl-4-carboxylic acid (3.2 g, 10 mmol), thionyl chloride (25 mL), and (−)-1-(pentafluoroethyl)octyl *p*-hydroxybenzoate (3.5 g, 10 mmol, $[\alpha]^{24}_D$ (MeOH) −47.90° (*c* 1.17), >96% ee) were used. Yield 75%.

(b) Reduction. (−)-4-[[[1-(Pentafluoroethyl)octyl]oxy]carbonyl]phenyl 4'-(benzyloxy)biphenyl-4-carboxylate (2.2 g, 5 mmol) and 10% Pd–C (0.1 g) in ethanol (15 mL) were irradiated and then worked up similarly. (−)-4-[[[1-(Pentafluoroethyl)octyl]oxy]carbonyl]phenyl 4'-hydroxybiphenyl-4-carboxylate was purified by recrystallization from ethanol in 88% yield: $[\alpha]^{23}_D$ (MeOH) −44.17° (*c* 0.98), >96% ee; high-resolution MS calcd for $C_{29}H_{27}O_5F_5$ 550.520, found 550.396. Anal. Found: C, 62.98; H, 5.16. Calcd for $C_{29}H_{27}O_5F_5$: C, 63.27; H, 4.94.

(*R*)-(+)-4-[[[1-(Difluoromethyl)octyl]oxy]carbonyl]phenyl 4'-Hydroxybiphenyl-4-carboxylate (3a). (a) (*R*)-(+)-4-[[[1-(Difluoromethyl)octyl]oxy]carbonyl]phenyl 4'-(Benzyloxy)biphenyl-4-carboxylate. 4'-(Benzyloxy)biphenyl-4-carboxylic acid (3.2 g, 10 mmol), thionyl chloride (25 mL), and (*R*)-(+)-1-(difluoromethyl)octyl *p*-hydroxybenzoate[28] (2.9 g, 10 mmol, $[\alpha]^{24}_D$ (MeOH) +39.62° (*c* 1.24), >96% ee) were used. (*R*)-(+)-4-[[[1-(Difluoromethyl)octyl]oxy]carbonyl]phenyl 4'-(benzyloxy)biphenyl-4-carboxylate was obtained in 74% yield: ^{19}F NMR δ 50.2 (ddd, J_{F-F} = 281, $J_{FF,Hgem}$ = 54, $J_{F,Hvic}$ = 12.5 Hz), 53.0 (ddd, $J_{F,Hgem}$ = 54, $J_{F,Hvic}$ = 12.5 Hz); ^{1}H NMR δ 0.89–1.84 (13 H, m), 4.26 (OCH_2), 4.26 (OCH_2), 5.18 ($CHCHF_2$, m), 5.81 (CHF_2, ddd, $J_{H,Hvic}$ = 5.4 Hz), 7.10–8.20 (ArH); IR (KBr) 1730 (C=O) cm^{-1}.

(b) Reduction. (*R*)-(+)-4-[[[1-(Difluoromethyl)octyl]oxy]carbonyl]phenyl 4'-(benzyloxy)biphenyl-4-carboxylate (3.8 g, 10 mmol) and 10% Pd–C (0.2 g) in ethanol (20 mL) were irradiated and then worked up as usual. (*R*)-(+)-4-[[[1-(Difluoromethyl)octyl]oxy]carbonyl]phenyl] 4'-hydroxybiphenyl 4-carboxylate was purified by recrystallization from ethanol in 79% yield: mp 91–93 °C; $[\alpha]^{23}_D$ (MeOH) +33.18° (*c* 0.84), >96% ee; ^{19}F NMR δ 51.7 (ddd, J_{F-F} = 284, $J_{F,Hgem}$ = 55.6, $J_{F,Hvic}$ = 13 Hz), 54.3 (ddd, $J_{F,Hgem}$ = 54.5, $J_{F,Hvic}$ = 12 Hz); ^{1}H NMR δ 0.94–2.06 (13 H, m), 5.21 ($CHCHF_2$, m), 5.83 (CHF_2, ddd, $J_{H,Hvic}$ = 5.3 Hz), 6.50 (OH), 7.06–8.15 (ArH); IR (KBr) 3670 (OH), 1730 (C=O) cm^{-1}; high-resolution MS calcd for $C_{28}H_{28}O_5F_2$ 482.523, found 482.373. Anal. Found: C, 69.58; H, 5.61. Calcd for $C_{28}H_{28}O_5F_2$: C, 69.70; H, 5.85.

(*S*)-(−)-4-[[[1-(Difluoromethyl)octyl]oxy]carbonyl]phenyl 4'-Hydroxybiphenyl-4-carboxylate. 4'-(Benzyloxy)biphenyl-4-carboxylic acid (3.2 g, 10 mmol), thionyl chloride (25 mL), and (*S*)-(−)-1-(difluoromethyl)octyl *p*-hydroxybenzoate (2.9 g, 10 mmol, $[\alpha]^{24}_D$ (MeOH) −39.62° (*c* 1.17), >96% ee) were used. Yield 71%.

(b) Reduction. (*S*)-(−)-4-[[[1-(Difluoromethyl)octyl]oxy]carbonyl]phenyl 4'-(benzyloxy)biphenyl-4-carboxylate (1.9 g, 5 mmol) and 10% Pd–C (0.1 g) in ethanol (15 mL) were irradiated and then worked up similarly. (*S*)-(−)-4-[[[1-(Difluoromethyl)octyl]oxy]carbonyl]phenyl 4'-hydroxybiphenyl-4-carboxylate was purified by recrystallization from ethanol in 81% yield: $[\alpha]^{24}_D$ (MeOH) −33.26° (*c* 0.91) >96% ee); high-resolution MS calcd for $C_{28}H_{28}O_5F_2$ 482.523, found 482.647. Anal. Found: C, 69.93; H, 5.75. Calcd for $C_{28}H_{28}O_5F_2$: C, 69.70; H, 5.85.

Ferroelectric Liquid Crystalline Monomer. Typical Procedure. Ferroelectric Liquid Crystalline Monomer Possessing (*R*)-(+)-4-[[[1-(Trifluoromethyl)octyl]oxy]carbonyl]phenyl 4'-Hydroxybiphenyl-4-carboxylate (1a). Monomer 4a. (a) A suspension of (*R*)-(+)-4-[[[1-(trifluoromethyl)octyl]oxy]carbonyl]phenyl 4'-hydroxxybiphenyl-4-carboxylate [(*R*)-(+)-**1a**; 5.0 g, 10 mmol] and sodium hydroxide (0.26, 12 mmol) in tetrahydrofuran (20 mL) was stirred at room temperature. After 2 h of stirring, 2-bromoethyl acrylate (3.5 g, 20 mmol) in tetrahydrofuran (10 mL) was added, and then the whole was stirred at 50 °C. After 5 h of stirring, the mixture was poured into water, and then oily materials were extracted with ethyl acetate. On removal of the solvent, the resulting crude products were chromatographed on silica gel, giving ferroelectric liquid crystalline monomer **4a** as an oil in 85% yield: $[\alpha]^{23}_D$ (toluene) +14.31° (*c* 0.84); ^{19}F NMR δ −1.3 (d, $J_{F,H}$ = 6.0 Hz); ^{1}H NMR δ 0.84–2.17 (13 H, m), 4.21 (CH_2, t, $J_{R,H}$ = 2.5 Hz), 4.54 (CH_2, t), 5.19 ($CHCF_3$, m), 5.81–6.42 (3 H, m), 7.04–8.24 (ArH); IR (KBr) 1725 (C=O), 1615 (C=C) cm^{-1}; high-resolution MS calcd for $C_{33}H_{33}O_7F_3$ 598.614, found 598.253.

Monomer 4a. (b) (*S*)-(−)-4-[[[1-(Trifluoromethyl)octyl]oxy]carbonyl]phenyl 4'-hydroxybiphenyl-4-carboxylate [(*S*)-(−)-**1a**; 5.0 g, 10 mmol], sodium hydride (0.26 g, 12 mmol), and 2-bromoethyl acrylate (3.5 g, 20 mmol) in tetrahydrofuran (20 mL) were used. Yield 69%: $[\alpha]^{23}_D$ (toluene) −14.33° (*c* 0.91); high-resolution MS calcd for $C_{33}H_{33}O_7F_3$ 598.614, found 598.475.

Monomer 4b. (a) (*R*)-(+)-4-[[[1-(Trifluoromethyl)octyl]oxy]carbonyl]phenyl 4'-hydroxybiphenyl-4-carboxylate (**1a**; 5.0 g, 10 mmol), sodium hydride (0.26 g, 12 mmol), 6-bromohexyl acrylate (4.6 g, 20 mmol), and tetrahydrofuran (30 mL) were used. Yield 67%: $[\alpha]^{24}_D$ (toluene) +16.14° (*c* 0.81); ^{19}F NMR δ −1.1 (d, $J_{F,H}$ = 5.8 Hz); ^{1}H NMR δ 0.90–2.21 (21 H, m), 4.20 (CH_2, $J_{H,H}$ = 2.3 Hz), 4.51 (CH_2, t, $J_{H,H}$ = 2.4 Hz), 5.23 ($CHCF_3$, m), 5.86–6.43 (3 H, m), 7.10–8.25 (ArH); IR (KBr) 1725 (C=O), 1620 (C=C) cm^{-1}; high-resolution MS calcd for $C_{37}H_{41}O_7F_3$ 654.722, found 654.582.

Monomer 4b. (b) (*S*)-(−)-4-[[[1-(Trifluoromethyl)octyl]oxy]carbonyl]phenyl 4'-hydroxybiphenyl-4-carboxylate (**1a**; 5.0 g, 10 mmol), sodium hydride (0.26 g, 12 mmol), and 6-bromohexyl acrylate (4.6 g, 20 mmol) in tetrahydrofuran (30 mL) were used. Yield 71%: $[\alpha]^{23}_D$ (toluene) −16.09° (*c* 0.77); high-resolution MS calcd for $C_{37}H_{41}O_7F_3$ 654.722, found 654.499.

Monomer 4c. (a) (*R*)-(+)-4-[[[1-(Trifluoromethyl)octyl]oxy]carbonyl]phenyl 4'-hydroxybiphenyl-4-carboxylate[(*R*)-(+)-**1a**; 5.0 g, 10 mmol], sodium hydride (0.26 g, 12 mmol), 8-bromooctyl acrylate (5.2 g, 20 mmol), and tetrahydrofuran (30 mL) were used. Yield 69%: $[\alpha]^{24}_D$ (toluene) +12.17° (*c* 0.95); ^{19}F NMR δ −1.5 (d, $J_{F,H}$ = 5.0 Hz); ^{1}H NMR δ 0.90–2.14 (25 H, m), 4.18 (CH_2, $J_{H,H}$ = 2.1 Hz), 4.54 (CH_2, t, $J_{H,H}$ = 2.5 Hz), 5.18 ($CHCF_3$, m), 5.88–6.50 (3 H, m), 7.00–8.30 (ArH); IR (KBr) 1725 (C=O), 1625 (C=C) cm^{-1}; high-resolution MS calcd for $C_{39}H4_5O_7F_3$ 682.776, found 682.515.

Monomer 4c. (b) (*S*)-(−)--[[[1-(Trifluoromethyl)octyl]oxy]cabonyl]phenyl 4'-hydroxybiphenyl-4-carboxylate[(*S*)-(−)-**1a**; 5.0 g, 10 mmol], sodium hydride (0.26 g, 12 mmol), 8-bromooctyl acrylate (5.2 g, 20 mmol), and tetrahydrofuran (30 mL) were used. Yield 71%: $[\alpha]^{23}_D$ (toluene) −12.11° (*c* 0.94); high-resolution MS calcd for $C_{39}H_{45}O_7F_3$ 682.776, found 682.941.

Monomer 4d. (a) (*R*)-(+)-4-[[[1-(Trifluoromethyl)octyl]oxy]carbonyl]phenyl 4'-hydroxybiphenyl-4-carboxylate (**1a**; 5.0 g, 10 mmol), sodium hydride (0.26 g, 12 mmol), 12-bromoundecanyl acrylate (6.4 g, 20 mmol), and tetrahydrofuran (30 mL) were used. Yield 73%: $[\alpha]^{24}_D$ (toluene) +15.83° (*c* 0.93); ^{19}F NMR δ −1.2 (d, $J_{F,H}$ = 5.5 Hz); ^{1}H NMR δ 0.88–2.85 (33 H, m), 4.19 (CH_2, $J_{H,H}$ = 2.1 Hz), 4.52 (CH_2, t, $J_{H,H}$ = 2.4 Hz), 5.20 ($CHCF_3$, m), 5.84–6.45 (3 H, m), 7.09–8.17 (ArH); IR (KBr) 1725 (C=O), 1620 (C=C) cm^{-1}; high-resolution MS calcd for $C_{43}H_{53}O_7F_3$ 738.884, Found 738.704.

Monomer 4d. (b) (*S*)-(−)-4-[[[1-(Trifluoromethyl)octyl]oxy]carbonyl]phenyl 4'-hydroxybiphenyl-4-carboxylate (**1a**; 5.0 g, 10 mmol), sodium hydride (0.26 g, 12 mmol), and 12-bromoundecanyl acrylate (6.4 g, 20 mmol) in tetrahydrofuran (30 mL) were used. Yield 62%: $[\alpha]^{23}_D$ (toluene) −15.85° (*c* 0.86); high-resolution MS calcd for $C_{43}H_{53}O_7F_3$ 738.884, found 738.645.

Ferroelectric Liquid Crystalline Monomer Possessing (*R*)-(+)-4-[[[1-(Trifluoromethyl)nonyl]oxy]carbonyl]phenyl 4'-Hydroxybiphenyl-4-carboxylate (1b). Monomer 5c. (*R*)-(+)-4-[[[1-(Trifluoromethyl)nonyl]oxy]carbonyl]phenyl 4'-hydroxybiphenyl-4-[[[1-(Trifluoromethyl)nonyl]oxy]carbonyl]phenyl 4'-hydroxybiphenyl-4-carboxylate [(**1b**); 5.2 g, 10 mmol], sodium hydride (0.26 g, 12 mmol), 8-bromooctyl acrylate (5.2 g, 20 mmol), and tetrahydrofuran (20 mL) were used. Yield 76%: $[\alpha]^{24}_D$ (toluene) +18.04° (*c* 0.96); ^{19}F NMR δ −1.6 (d, $J_{F,H}$ = 6.0 Hz); ^{1}H NMR δ 0.94–2.45 (27 H,m), 4.24 (CH_2, t, $J_{H,H}$ = 2.2 Hz), 4.55 (CH_2, t), 5.24 ($CHCF_3$, m), 5.85–6.47 (3 H, m), 7.13–8.45 (ArH); IR (KBr) 1725 (C=O), 1620 (C=C) cm^{-1}; high-resolution MS calcd for $C_{40}H_{47}O_7F_3$ 696.803, found 696.638.

Ferroelectric Liquid Crystalline Monomer Possessing (*R*)-(+)-4-[[[1-(Trifluoromethyl)decyl]oxy]carbonyl]phenyl 4'-Hydroxybiphenyl-4-carboxylate (1c). Monomer 6c. (*R*)-(+)-4-[[[1-(Trifluoromethyl)decyl]oxy]carbonyl]phenyl 4'-hydroxybiphenyl-4-carboxylate [(**1c**); 5.3 g, 10 mmol], sodium hydride (0.26 g, 12 mmol), 8-bromooctyl acrylate (5.2 g, 20 mmol), and tetrahydrofuran (20 mL) were used. Yield 73%: $[\alpha]^{24}_D$ (toluene) +15.37° (*c* 0.98); ^{19}F NMR δ −1.5 (*d*, $J_{F,H}$ = 6.0 Hz); ^{1}H NMR δ 0.90–2.39 (29 H, m), 4.23 (CH_2, t, $J_{H,H}$ = 2.0 Hz), 4.51 (CH_2, t), 5.25 ($CHCF_3$, m), 5.83–6.51 (3 H, m), 7.01–8.40 (ArH); IR (KBr) 1725 (C=O), 1620 (C=C) cm^{-1}; high-resolution MS calcd for $C_{41}H_{49}O_7F_3$ 710.830, found 710.684.

Ferroelectric Liquid Crystalline Monomer Possessing (*R*)-(+)-4-[[[1-(Trifluoromethyl)undecyl]oxy]carbonyl]phenyl 4'-Hydroxybiphenyl-4-carboxylate (1d). Monomer 7c. (*R*)-(+)-4-[[[1-(trifluoromethyl)undecyl]oxy]carbonyl]phenyl 4'-hydroxybiphenyl-4-carboxylate [(**1c**); 5.6 g, 10 mmol], sodium hydride (0.26 g, 12 mmol), 8-bromooctyl acrylate (5.2 g, 20 mmol), and tetrahydrofuran (20 mL) were used. Yield 75%: $[\alpha]^{24}_D$ (toluene) +13.61° (*c* 1.03); ^{19}F NMR δ −1.5 (d, $J_{F,H}$ = 5.4 Hz); ^{1}H NMR δ 0.87–2.47 (29 H, m), 4.21 (CH_2, t, $J_{H,H}$ = 2.0 Hz), 4.48

(CH_2, t), 5.23 ($CHCF_3$, m), 5.84–6.47 (3 H, m), 7.00–8.35 (ArH); IR (KBr) 1725 (C=O), 1620 (C=C) cm^{-1}; high-resolution MS calcd for $C_{43}H_{53}O_7F_3$ 738.884, found 738.974.

Ferroelectric Liquid Crystalline Monomer Possessing (+)-4-[[[1-(Pentafluoroethyl)octyl]oxy]carbonyl]phenyl 4'-Hydroxybiphenyl-4-carboxylate (2a). Monomer 8a. (a) (+)-4-[[[1-(Pentafluoroethyl)-octyl]oxy]carbonyl]phenyl] 4'-hydroxybiphenyl-4-carboxylate (**2a**; 5.5 g, 10 mmol), sodium hydride (0.26 g, 12 mmol), 2-bromoethyl acrylate (3.5 g, 20 mmol), and tetrahydrofuran (30 mL) were used. Yield 63%: $[\alpha]^{24}_D$ (toluene) +21.04° (*c* 0.84); ^{19}F NMR δ 2.3 (CF_3, t, $J_{F,F}$ = 1.5 Hz), 45.4 (CF_2, m); ^1H NMR δ 0.87–2.35 (13 H, m), 4.21 (CH_2, $J_{H,H}$ = 2.6 Hz), 4.48 (CH_2, t, $J_{H,H}$ = 2.1 Hz), 5.23 ($CHCF_2$, m), 5.85–6.41 (3 H, m), 7.10–8.25 (ArH); IR (KBr) 1725 (C=O), 1620 (C=C) cm^{-1}; high-resolution MS calcd for $C_{34}H_{33}O_7F_5$ 648.621, found 648.844.

Monomer 8a. (b) (−)-4-[[[1-(Pentafluoroethyl)octyl]oxy]carbonyl]-phenyl 4'-hydroxybiphenyl-4-carboxylate (**2a**; 5.5 g, 10 mmol), sodium hydride (0.26 g, 12 mmol), and 2-bromoethyl acrylate (3.5 g, 20 mmol) in tetrahydrofuran (30 mL) were used. Yield 58%: $[\alpha]^{24}_D$ (toluene) −21.11° (*c* 0.87); high-resolution MS calcd for $C_{34}H_{33}O_7F_5$ 648.621, found 648.491.

Monomer 8b. (a) (+)-4-[[[1-(Pentafluoroethyl)octyl]oxy]carbonyl]-phenyl 4'-hydroxybiphenyl-4-carboxylate (**2a**; 5.5 g, 10 mmol), sodium hydride (0.26 g, 12 mmol), 6-bromohexyl acrylate (4.6 g, 20 mmol), and tetrahydrofuran (30 mL) were used. Yield 77%: $[\alpha]^{23}_D$ (toluene) +19.71° (*c* 0.97); ^{19}F NMR δ 2.4 (CF_3, t, $J_{F,F}$ = 2.0 Hz), 45.7 (CF_2, m); ^1H NMR δ 0.92–2.45 (21 H, m), 4.23 (CH_2, $J_{H,H}$ = 2.3 Hz), 4.53 (CH_2, t, $J_{H,H}$ = 2.1 Hz), 5.26 ($CHCF_2$, m), 5.81–6.44 (3 H, m), 7.04–8.27 (ArH); IR (KBr) 1725 (C=O), 1620 (C=C) cm^{-1}; high-resolution MS calcd for $C_{38}H_{41}O_7F_5$ 704.729, found 704.584.

Monomer 8b. (b) (−)-4-[[[1-(Pentafluoroethyl)octyl]oxy]carbonyl]-phenyl 4'-hydroxybiphenyl-4-carboxylate (**2a**; 5.5 g, 10 mmol), sodium hydride (0.26 g, 12 mmol), and 6-bromohexyl acrylate (4.6 g, 20 mmol) in tetrahydrofuran (30 mL) were used. Yield 71%: $[\alpha]^{23}_D$ (toluene) −19.67° (*c* 0.84); high-resolution MS calcd for $C_{38}H_{41}O_7F_5$ 704.729, found, 704.604.

Monomer 8c. (a) (+)-4-[[[1-(Pentafluoroethyl)octyl]oxy]carbonyl]-phenyl 4'-hydroxybiphenyl-4-carboxylate (**2a**; 5.5 g, 10 mmol), sodium hydride (0.26 g, 12 mmol), 8-bromooctyl acrylate (5.0 g, 20 mmol), and tetrahydrofuran (30 mL) were used. Yield 69%: $[\alpha]^{23}_D$ (toluene) +23.56° (*c* 0.98); ^{19}F NMR δ 2.5 (CF_3, t, $J_{F,F}$ = 2.1 Hz), 45.3 (CF_2, m); ^1H NMR δ 0.88–2.42 (25 H, m), 4.24 (CH_2, $J_{H,H}$ = 2.4 Hz), 4.50 (CH_2, t, $J_{H,H}$ = 2.3 Hz), 5.27 ($CHCF_2$, m), 5.82–6.46 (3 H, m), 7.00–8.25 (ArH); IR (KBr) 1725 (C=O), 1620 (C=C) cm^{-1}; high-resolution MS calcd for $C_{40}H_{45}O_7F_5$ 732.783, found 732.983.

Monomer 8c. (b) (−)-4-[[[1-(Pentafluoroethyl)octyl]oxy]carbonyl]-phenyl 4'-hydroxybiphenyl-4-carboxylate (**2a**; 5.5 g, 10 mmol), sodium hydride (0.26 g, 12 mmol), and 6-bromooctyl acrylate (5.0 g, 20 mmol) in tetrahydrofuran (30 mL) were used. Yield 53%: $[\alpha]^{23}_D$ (toluene) −23.47° (*c* 0.94); high-resolution MS calcd for $C_{40}H_{45}O_7F_5$ 732.783, found 732.549.

Monomer 8d. (a) (+)-4-[[[1-(Pentafluoroethyl)octyl]oxy]carbonyl]-phenyl 4'-hydroxybiphenyl-4-carboxylate (**2a**; 5.5 g, 10 mmol), sodium hydride (0.26 g, 12 mmol), 12-bromoundecanyl acrylate (6.4 g, 20 mmol), and tetrahydrofuran (30 mL) were used. Yield 80%: $[\alpha]^{24}_D$ (toluene) +23.57° (*c* 0.92); ^{19}F NMR δ 2.7 (CF_3, t, $J_{F,F}$ = 1.5 Hz), 45.2 (CF_2, m); ^1H NMR δ 0.91–2.92 (33 H, m), 4.24 (CH_2, $J_{H,H}$ = 2.4 Hz), 4.43 (CH_2, t, $J_{H,H}$ = 2.5 Hz), 5.25 ($CHCF_2$, m), 5.82–6.45 (3 H, m), 7.04–8.35 (ArH); IR (KBr) 1725 (C=O), 1615 (C=C) cm^{-1}; high-resolution MS calcd for $C_{44}H_{53}O_7F_5$ 788.891, found, 788.672.

Monomer 8d. (b) (−)-4-[[[1-(Pentafluoroethyl)octyl]oxy]carbonyl]-phenyl 4'-hydroxybiphenyl-4-carboxylate (**2a**; 5.5 g, 10 mmol), sodium hydride (0.26 g, 12 mmol), and 12-bromoundecanyl acrylate (6.4 g, 20 mmol) in tetrahydrofuran (30 mL) were used. Yield 64%: $[\alpha]^{24}_D$ (toluene) −23.60° (*c* 0.95); high-resolution MS calcd for $C_{44}H_{53}O_7F_5$ 788.891, found 788.741.

Ferroelectric Liquid Crystalline Monomer Possessing (*R*)-(+)-4-[[[1-(Difluoromethyl)octyl]oxy]carbonyl]phenyl 4'-Hydroxybiphenyl-4-carboxylate (3a). Monomer 9a. (a) (*R*)-(+)-4-[[[1-(Difluoromethyl)-octyl]oxy]carbonyl]phenyl 4'-hydroxybiphenyl-4-carboxylate (**3a**; 4.8 g, 10 mmol), sodium hydride (0.26 g, 12 mmol), 2-bromoethyl acrylate (3.5 g, 20 mmol), and tetrahydrofuran (30 mL) were used. Yield 65%: $[\alpha]^{23}_D$ (toluene) +17.34° (*c* 0.94); ^{19}F NMR δ 50.4 (ddd, J_{F-F} = 283, $J_{F,Hgem}$ = 54, $J_{F,Hvic}$ = 12 Hz), 53.4 (ddd, $J_{F,Hgem}$ = 53, $J_{F,Hvic}$ = 12.5 Hz); ^1H NMR δ 0.90–2.46 (13 H, m), 4.23 (CH_2, $J_{H,H}$ = 2.4 Hz), 4.47 (CH_2, t, $J_{H,H}$ = 2.3 Hz), 5.19 (CHCHF, m), 5.82 (CHF_2, ddd, $J_{H,Hvic}$ = 5.4 Hz), 5.85–6.39 (3 H, m), 7.15–8.35 (ArH); IR (KBr) 1725 (C=O), 1620 (C=C) cm^{-1}; high-resolution MS calcd for $C_{33}H_{34}O_7F_2$ 580.624, found 580.436.

Monomer 9a. (b) (*S*)-(−)-4-[[[1-(Difluoromethyl)octyl]oxy]-carbonyl]phenyl 4'-hydroxybiphenyl-4-carboxylate (**3a**; 4.8 g, 10 mmol), sodium hydride (0.26 g, 12 mmol), and 2-bromoethyl acrylate (3.5 g, 20 mmol) in tetrahydrofuran (30 mL) were used. Yield 68%: $[\alpha]^{23}_D$ (toluene) −17.29° (*c* 0.87); high-resolution MS calcd for $C_{33}H_{34}O_7F_2$ 580.624, found 580.528.

Monomer 9b. (a) (*R*)-(+)-4-[[[1-(Difluoromethyl)octyl]oxy]-carbonyl]phenyl 4'-hydroxybiphenyl-4-carboxylate (**3a**; 4.8 g, 10 mmol), sodium hydride (0.26 g, 12 mmol), 6-bromohexyl acrylate (4.6 g, 20 mmol), and tetrahydrofuran (30 mL) were used. Yield 73%: $[\alpha]^{23}_D$ (toluene) +18.02° (*c* 0.90); ^{19}F NMR δ 50.0 (ddd, J_{F-F} = 283, $J_{F,Hgem}$ = 54.2, $J_{F,Hvic}$ = 12.5 Hz), 53.2 (ddd, $J_{F,Hgem}$ = 54, $J_{F,Hvic}$ = 12.5 Hz); ^1H NMR δ 0.85–2.38 (21 H, m), 4.21 (CH_2, $J_{H,H}$ = 2.3 Hz), 4.44 (CH_2, t, $J_{H,H}$ = 2.1 Hz), 5.16 (CHCHF, m), 5.80 (CHF_2, ddd, $J_{H,Hvic}$ = 5.4 Hz), 5.83–6.41 (3 H, m), 7.07–8.29 (ArH); IR (KBr) 1725 (C=O), 1620 (C=C) cm^{-1}; high-resolution MS calcd for $C_{37}H_{42}O_7F_2$ 636.732, found 636.651.

Monomer 9b. (b) (*S*)-(−)-4-[[[1-(Difluoromethyl)octyl]oxy]-carbonyl]phenyl 4'-hydroxybiphenyl-4-carboxylate (**3a**; 4.8 g, 10 mmol), sodium hydride (0.26 g, 12 mmol), and 6-bromohexyl acrylate (4.6 g, 20 mmol) in tetrahydrofuran (30 mL) were used. Yield 58%: $[\alpha]^{24}_D$ (toluene) −18.14° (*c* 0.83); high-resolution MS calcd for $C_{37}H_{42}O_7F_2$ 636.732, found, 636.617.

Monomer 9c. (a) (*R*)-(+)-4-[[[1-(Difluoromethyl)octyl]oxy]-carbonyl]phenyl 4'-hydroxybiphenyl-4-carboxylate (**3a**; 4.8 g, 10 mmol), sodium hydride (0.26 g, 12 mmol), 8-bromooctyl acrylate (5.0 g, 20 mmol), and tetrahydrofuran (30 mL) were used. Yield 69%: $[\alpha]^{23}_D$ (toluene) +21.04° (*c* 0.84); ^{19}F NMR δ 50.3 (ddd, J_{F-F} = 283, $J_{F,Hgem}$ = 55, $J_{F,Hvic}$ = 13 Hz), 53.1 (ddd, $J_{F,Hgem}$ = 54, $J_{F,Hvic}$ = 13.5 Hz); ^1H NMR δ 0.93–2.50 (25 H, m), 4.22 (CH_2, $J_{H,H}$ = 2.1 Hz), 4.48 (CH_2, t, $J_{H,H}$ = 2.4 Hz), 5.15 (CHCHF, m), 5.81 (CHF_2, ddd, $J_{H,Hvic}$ = 5.1 Hz), 5.83–6.43 (3 H, m), 7.09–8.44 (ArH); IR (KBr) 1725 (C=O), 1620 (C=C) cm^{-1}; high-resolution MS calcd for $C_{39}H_{46}O_7F_2$ 664.786, found 664.584.

Monomer 9c. (b) (*S*)-(−)-4-[[[1-(Difluoromethyl)octyl]oxy]-carbonyl]phenyl 4'-hydroxybiphenyl-4-carboxylate (**3a**; 4.8 g, 10 mmol), sodium hydride (0.26 g, 12 mmol), and 8-bromooctyl acrylate (5.0 g, 20 mmol) in tetrahydrofuran (30 mL) were used. Yield 74%: $[\alpha]^{23}_D$ (toluene) −21.09° (*c* 0.88); high-resolution MS calcd for $C_{39}H_{46}O_7F_2$ 664.786, found 664.705.

Monomer 9d. (a) (*R*)-(+)-4-[[[1-(Difluoromethyl)octyl]oxy]-carbonyl]phenyl 4'-hydroxybiphenyl-4-carboxylate (3a; 4.8 g, 10 mmol), sodium hydride (0.26 g, 12 mmol), 12-bromoundecanyl acrylate (4.1 g, 20 mmol), and tetrahydrofuran (30 mL) were used. Yield 71%: $[\alpha]^{23}_D$ (toluene) +18.44° (*c* 0.94); ^{19}F NMR δ 50.1 (ddd, J_{F-F} = 283, $J_{F,Hgem}$ = 54.4, $J_{F,Hvic}$ = 12 Hz), 53.7 (ddd, $J_{F,Hgem}$ = 54, $J_{F,Hvic}$ = 12.5 Hz); ^1H NMR δ 0.85–2.97 (33 H, m), 4.21 (CH_2, $J_{H,H}$ = 2.4 Hz), 4.45 (CH_2, t, $J_{H,H}$ = 2.1 Hz), 5.17 (CHCHF, m), 5.81 (CHF_2 ddd, $J_{H,Hvic}$ = 5 Hz), 5.83–6.43 (3 H, m), 7.04–8.31 (Ar H); IR (KBr) 1725 (C=O), 1620 (C=C) cm^{-1}; high-resolution MS calcd for $C_{43}H_{54}O_7F_2$ 720.894, found 720.971.

Monomer 9d. (b) (*S*)-(−)-4-[[[1-(Difluoromethyl)octyl]oxy]-carbonyl]phenyl 4'-hydroxybiphenyl-4-carboxylate (**3a**; 4.8 g, 10 mmol), sodium hydride (0.26 g, 12 mmol), 12-bromoundecanyl acrylate (4.1 g, 20 mmol), and tetrahydrofuran (30 mL) were used. Yield 76%: $[\alpha]^{23}_D$ (toluene) −18.47° (*c* 0.91); high-resolution MS calcd for $C_{43}H_{54}O_7F_2$ 720.894, found 720.764.

Ferroelectric Liquid Crystalline Monomer Possessing (*R*)-(+)-4-[[[1-(Trifluoromethyl)octyl]oxy]carbonyl]phenyl 4'-Hydroxybiphenyl-4-carboxylate (1a). Monomer 10a. (*R*)-(+)-4-[[[1-(Trifluoromethyl)-octyl]oxy]carbonyl]phenyl 4'-hydroxybiphenyl-4-carboxylate (**1a**; 5.0 g, 10 mmol), sodium hydride (0.26 g, 12 mmol), 2-bromoethyl methacrylate (3.8 g, 20 mmol), and tetrahydrofuran (30 mL) were used. Yield 75%: $[\alpha]^{23}_D$ (toluene) +13.42° (*c* 0.78); ^{19}F NMR δ −1.5 (d, $J_{F,H}$ = 7.5 Hz); ^1H NMR δ 0.90–2.37 (16 H, m), 4.24 (CH_2, $J_{H,H}$ = 2.4 Hz), 4.45 (CH_2, t, $J_{H,H}$ = 2.1 Hz), 5.24 ($CHCF_3$, m) 5.75 (1 H, m), 6.36 (1 H, m), 7.15–8.30 (ArH); IR (KBr) 1725 (C=O), 1620 (C=C) cm^{-1}; high-resolution MS calcd for $C_{34}H_{36}O_7F_3$ 612.641, found 612.485.

Monomer 10b. (*R*)-(+)-4-[[[1-(Trifluoromethyl)octyl]oxy]-carbonyl]phenyl 4'-hydroxybiphenyl-4-carboxylate (**1a**; 5.0 g, 10 mmol), sodium hydride (0.26 g, 12 mmol), 6-bromohexyl methacrylate (4.9 g, 20 mmol), and tetrahydrofuran (30 mL) were used. Yield 63%: $[\alpha]^{24}_D$ (toluene) +15.93° (*c* 0.97); ^{19}F NMR δ −1.5 (d, $J_{F,H}$ = 7.0 Hz); ^1H NMR δ 0.93–2.47 (24, H, m), 4.25 (CH_2, $J_{H,H}$ = 2.5 Hz), 4.44 (CH_2, t, $J_{H,H}$ = 2.0 Hz), 5.21 ($CHCF_3$, m), 5.78 (1 H, m), 6.33 (1 H, m), 7.04–8.28 (ArH); IR (KBr) 1725 (C=O), 1620 (C=C) cm^{-1}; high-resolution MS calcd for $C_{38}H_{43}O_7F_3$ 668.749, found 668.581.

Monomer 10c. (*R*)-(+)-4-[[[1-(Trifluoromethyl)octyl]oxy]-carbonyl]phenyl 4'-hydroxybiphenyl-4-carboxylate (**1a**; 5.0 g, 10 mmol), sodium hydride (0.26 g, 12 mmol), 8-bromooctyl methacrylate (5.5 g, 20 mmol), and tetrahydrofuran (30 mL) were used. Yield 64%: $[\alpha]^{23}_D$ (toluene) +13.06° (*c* 0.95); ^{19}F NMR δ −1.7 (d, $J_{F,H}$ = 7.5 Hz); ^1H

NMR δ 0.87–2.48 (28 H, m), 4.25 (CH_2, $J_{H,H}$ = 2.5 Hz), 4.47 (CH_2, t, $J_{H,H}$ = 2.4 Hz), 5.25 ($CHCF_3$, m), 5.72 (1 H, m), 6.37 (1 H, m), 7.09–8.45 (ArH); IR (KBr) 1725 (C=O), 1620 (C=C) cm^{-1}; high-resolution MS calcd for $C_{40}H_{47}O_7F_3$ 696.803, found 696.674.

Monomer 10d. (*R*)-(+)-4-[[[1-(Trifluoromethyl)octyl]oxy]carbonyl]phenyl 4′-hydroxybiphenyl-4-carboxylate (**1a**; 5.0 g, 10 mmol), sodium hydride (0.26 g, 12 mmol), 12-bromoundecanyl methacrylate (6.7 g, 20 mmol), and tetrahydrofuran (30 mL) were used. Yield 78%: $[\alpha]^{23}{}_D$ (toluene) +15.43° (*c* 0.81); ^{19}F NMR δ −1.4 (d, $J_{F,H}$ = 7.5 Hz); ^1H NMR δ 0.89–2.91 (36 H, m), 4.23 (CH_2, $J_{H,H}$ = 2.5 Hz), 4.43 (CH_2, t, $J_{H,H}$ = 2.1 Hz) 5.23 ($CHCF_3$, m), 5.76 (1 H, m), 6.36 (1 H, m), 7.10–8.30 (ArH); IR (KBr) 1725 (C=O), 1620 (C=C) cm^{-1}; high-resolution MS calcd for $C_{44}H_{55}O_7F_3$ 752.911, found 752.750.

Ferroelectric Liquid Crystalline Polymer. Typical Procedures. (a) A solution of ferroelectric liquid crystalline monomer **4a** (6.0 g, 10 mmol) and azobisisobutyronitrile (0.4 g) in benzene (50 mL) was amplified under vacuum and then heated at 100 °C. After 24 h of heating at that temperature, the solvent was removed. The crude product was purified by column chromatography on silica, giving the corresponding polymer in 64% yield.

(b) Into a solution of ferroelectric liquid crystalline monomer **4a** (6.0 g, 10 mmol) in tetrahydrofuran (30 mL), *n*-butyllithium (0.6 mL, 1.0 mmol) in hexane was added with a syringe under an atmosphere of nitrogen at −78 °C. After 24 h of stirring at that temperature, the mixture was quenched with saturated NH_4Cl solution, and then precipitates were collected. The crude product was purified by column chromatography on silica gel, giving the corresponding polymer in a 58% yield.

Other polymerization reactions were carried out the same scale and manner.

Registry No. (*R*)-**1a**, 128054-69-3; (*S*)-**1a**, 128054-72-8; (*R*)-**1aa**, 128054-70-6; (*S*)-**1aa**, 128054-73-9; (*R*)-**1b**, 128054-75-1; (*S*)-**1b**, 128054-78-4; (*R*)-**1ba**, 128054-76-2; (*S*)-**1ba**, 128054-79-5; (*R*)-**1c**, 128054-81-9; (*S*)-**1c**, 128054-83-1; (*R*)-**1ca**, 128054-82-0; (*S*)-**1ca**, 128054-84-2; (*R*)-**1d**, 128083-46-5; (*S*)-**1d**, 128054-86-4; (*R*)-**1da**, 128083-47-6; (*S*)-**1da**, 128054-87-5; (*R*)-**2a**, 128054-89-7; (*S*)-**2a**, 128054-92-2; (*R*)-**2aa**, 128054-90-0; (*S*)-**2aa**, 128054-93-3; (*R*)-**3a**, 128054-95-5; (*S*)-**3a**, 128054-98-8; (*R*)-**3aa**, 128054-96-6; (*S*)-**3aa**, 128054-99-9; (*R*)-**4a**, 128055-01-6; (*S*)-**4a**, 128055-02-7; **4a** (homopolymer), 128055-34-5; (*R*)-**4b**, 128055-03-8; (*S*)-**4b**, 128055-04-9; **4b** (homopolymer), 128055-36-7; (*R*)-**4c**, 128055-05-0; (*S*)-**4c**, 128055-06-1; **4c** (homopolymer), 128055-38-9; (*R*)-**4d**, 128055-07-2; (*S*)-**4d**, 128055-08-3; **4d** (homopolymer), 128055-40-3; (*R*)-**5c**, 128055-09-4; **5c** (homopolymer), 128055-42-5; (*R*)-**6c**, 128055-10-7; **6c** (homopolymer), 128055-44-7; (*R*)-**7c**, 128055-11-8; **7c** (homopolymer), 128055-46-9; (*R*)-**8a**, 128055-12-9; (*S*)-**8a**, 128055-13-0; **8a** (homopolymer), 128055-48-1; (*R*)-**8b**, 128055-14-1; (*S*)-**8b**, 128055-15-2; **8b** (homopolymer), 128055-50-5; (*R*)-**8c**, 128055-16-3; (*S*)-**8c**, 128083-49-8; **8c** (homopolymer), 128055-52-7; (*R*)-**8d**, 128055-17-4; (*S*)-**8d**, 128055-18-5; **8d** (homopolymer), 128055-54-9; (*R*)-**9a**, 128055-19-6; (*S*)-**9a**, 128055-20-9; **9a** (homopolymer), 128055-56-1; (*R*)-**9b**, 128055-21-0; (*S*)-**9b**, 128055-22-1; **9b** (homopolymer), 128055-58-3; (*R*)-**9c**, 128055-23-2; (*S*)-**9c**, 128055-24-3; **9c** (homopolymer), 128055-60-7; (*R*)-**9d**, 128055-25-4; (*S*)-**9d**, 128055-26-5; **9d** (homopolymer), 128055-62-9; (*R*)-**10a**, 128083-50-1; **10a** (homopolymer), 128083-52-3; (*R*)-**10b**, 128055-27-6; **10b** (homopolymer), 128055-64-1; (*R*)-**10c**, 128055-29-8; **10c** (homopolymer), 128055-66-3; (*R*)-**10d**, 128055-31-2; **10d** (homopolymer), 128055-68-5; $PhCH_2(C_6H_4\text{-}p)CO_2H$, 128054-71-7; (*R*)-$HOC_6H_4\text{-}p\text{-}CO_2CH(CF_3)(CH_2)_6H$, 121170-47-6; (*S*)-$HOC_6H_4\text{-}p\text{-}CO_2CH(CF_3)(CH_2)_6H$, 128054-74-0; (*R*)-$HOC_6H_4\text{-}p\text{-}CO_2CH(CF_3)(CH_2)_7H$, 128054-77-3; (*S*)-$HOC_6H_4\text{-}p\text{-}CO_2CH(CF_3)(CH_2)_7H$, 128054-80-8; (*R*)-$HOC_6H_4\text{-}p\text{-}CO_2CH(CF_3)(CH_2)_8H$, 124689-86-7; (*S*)-$HOC_6H_4\text{-}p\text{-}CO_2CH(CF_3)(CH_2)_8H$, 128054-85-3; (*R*)-$HOC_6H_4\text{-}p\text{-}CO_2CH(CF_3)(CH_2)_9H$, 128083-48-7; (*S*)-$HOC_6H_4\text{-}p\text{-}CO_2CH(CF_3)(CH_2)_9H$, 128054-88-6; (*R*)-$HOC_6H_4\text{-}p\text{-}CO_2CH(CF_2CF_3)(CH_2)_6H$, 128054-91-1; (*S*)-$HOC_6H_4\text{-}p\text{-}CO_2CH(CF_2CF_3)(CH_2)_6H$, 128054-94-4; (*R*)-$HOC_6H_4\text{-}p\text{-}CO_2CH(CHCF_3)(CH_2)_6H$, 128054-97-7; (*S*)-$HOC_6H_4\text{-}p\text{-}CO_2CH(CHCF_3)(CH_2)_6H$, 128055-00-5; $H_2C{=}CHCO_2(CH_2)_2Br$, 4823-47-6; $H_2C{=}CHCO_2(CH_2)_6Br$, 112231-58-0; $H_2C{=}CHCO_2(CH_2)_8Br$, 123563-83-7; $H_2C{=}CHCO_2(CH_2)_{12}Br$, 112231-59-1; $H_2C{=}C(CH_3)CO_2(CH_2)_2Br$, 4513-56-8; $H_2C{=}C(CH_3)CO_2(CH_2)_6Br$, 128055-28-7; $H_2C{=}C(CH_3)CO_2(CH_2)_8Br$, 128055-30-1; $H_2C{=}C(CH_3)CO_2(CH_2)_{12}Br$, 128055-32-3.

Regiocontrol in Copper-Catalyzed Grignard Reactions with Allylic Substrates

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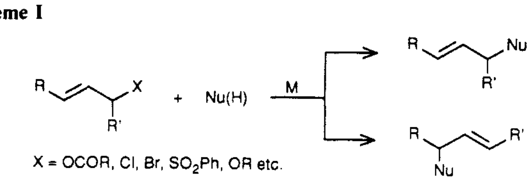
Abstract: The regiochemistry of copper-catalyzed reactions between Grignard reagents and allylic substrates has been studied. A dual regiocontrol was obtained in the Li_2CuCl_4-catalyzed Grignard reaction with primary allylic acetates. Reaction conditions that favor formation of an intermediate dialkylcuprate (fast addition of Grignard reagent, low temperature, low concentration of catalyst) gave α-substitution, whereas reaction conditions favoring formation of a monoalkylcopper intermediate (slow addition of Grignard reagent, increased temperature, increased concentration of catalyst) led to a γ-substitution. A remarkable solvent effect was observed for CuCN-catalyzed Grignard coupling with primary allylic acetates. In ether a highly γ-selective reaction took place, but in THF α-substitution predominated. Other allylic substrates such as allylic sulfones and allylic chlorides were also studied. The latter substrates showed a preference for γ-substitution, which is explained by their high reactivity.

Allylic compounds are important substrates in organic synthesis, and they have attracted a lot of mechanistic interest over the years, in particular with respect to nucleophilic displacement, i.e. S_N2 and S_N2'.[1] A number of studies dealing with the regio- and stereochemistry of nucleophilic substitution of allylic substrates have appeared.

Recently, transition metals have become popular tools for the activation of allylic substrates.[2] By coordination of the double bond to the metal, the reactivity of the allylic leaving group is considerably increased. Usually this leads to an intermediate σ- or π-allylmetal complex. A number of transition metals such as palladium,[3] nickel,[4] copper,[5] iron,[6] molybdenum,[7] and tungsten[8]

Scheme I



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