Ferroelectric Liquid Crystals Having Various Cores. Effect of Core Structure on Physical Properties

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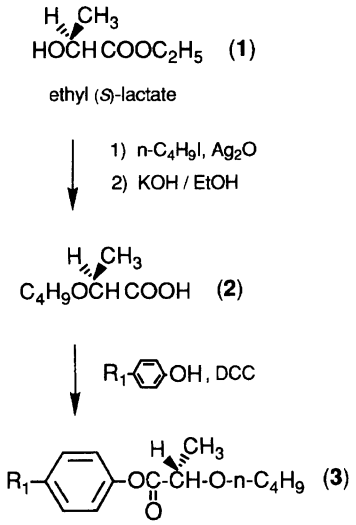
Ferroelectric liquid crystals (FLC's) having various cores were synthesized and the effect of the different core structures on the spontaneous polarization (P_s) values was investigated. The results indicate that the core structure has a great influence on the P_s value and introduction of a heterocycles such as pyrimidine and thiadiazole ring in the core increases the P_s value. Moreover, several compounds in this series are interesting as chiral dopants for FLC, because the mixtures containing them showed superior properties as FLC mixture.

Since the discovery of ferroelectricity in the chiral smectic C(Sc*) phase by R. Meyer[1] and the proposal of electrooptical devices using ferroelectric liquid crystals by Clark and Lagerwall in 1980,[2] extensive studies have been done on ferroelectric liquid crystal (FLC) materials and their applications.[3] One of the most important features of FLC is fast switching. To realize fast switching, the FLC materials needs to show large spontaneous polarization (P_s) and low rotational viscosity.[4] In order to obtain FLC with large P_s, the efforts have been mainly done on the synthesis of a new chiral part,[5] and little has been elucidated on the effect of the core structures. Therefore, we synthesized several ferroelectric liquid crystals having various cores and studied the effect of the core structure on the P_s value. Chiral 2-*n*-butoxypropionic acid derived from (*S*)-lactic acid was used as a chiral part because some FLC's derived from (*S*)-lactic acid were reported[6] and it is seems that (*S*)-lactic acid is useful as a chiral part of FLC. Moreover, we also investigated the abilities of these compounds as chiral dopants for FLC mixture.

Results and Discussion

The synthesis was carried out as outlined in Scheme 1. The secondary hydroxyl group of ethyl (*S*)-lactate was alkylated with n-butyl iodide in the presence of silver(I) oxide.[7] Alkaline hydrolysis followed by esterification with *p*-substituted phenol by using dicyclohexylcarbodiimide (DCC) as condensation reagent to afford final product, which was purified by column chromatography on silica gel using hexane and ether as the eluent followed by recrystallization from ethanol. Phase transition temperatures were measured with a polarizing microscope equipped with heating stage and a differential scanning calorimeter (DSC). Identity of the mesophases was confirmed by examining the texture of a thin sample sandwiched between glass slides.[8] Measurements of spontaneous polarization (P_s), response time (τ), and tilt angle (θ) were carried out on 2 μm thick cells.



Scheme 1. Synthesis route of compounds **3a**—**3k**.

Physical Properties of Compounds 3a—3k. The molecular structures of the compounds studied here are shown in Fig. 1. The optical purity of the compound is very important. So, we measured the enantiomeric excess of **3e** as a representative by HPLC with a chiral column and obtained e.e. of 99.7%. Other compounds are considered to have similar enantiomeric excesses because all reactions of *p*-substituted phenols with (*S*)-2-*n*-butoxypropionic acid were carried out by the same manner. The phase transition temperatures and P_s values of compounds **3a**—**3k** are listed in Table 1. The temperature dependencies of the P_s values of compounds **3c**—**3k** are shown in Fig. 2. All compounds which have three or four aromatic rings in the core (**3c**—**3k**) show enantiotropic chiral smectic C(Sc*) phase, in which compound **3h** having four aromatic rings shows the broadest Sc* range of 104 degrees. As shown in Table 1 and Fig. 2, the P_s values of these compounds (**3c**—**3k**) are so different from one another, though these compounds have the same chiral structure. It is clear that the core structure results in a drastic change of the P_s values. The relationship between core structure and P_s value will be summarized as follows: (1) Introduction of ester group in the core part decreases the P_s value. (2) Introduction of four aromatic rings in the core part decreases the P_s value. (3) Introduction of a heterocycles such as pyrimidine and thiadiazole ring in the core part increases the P_s value.

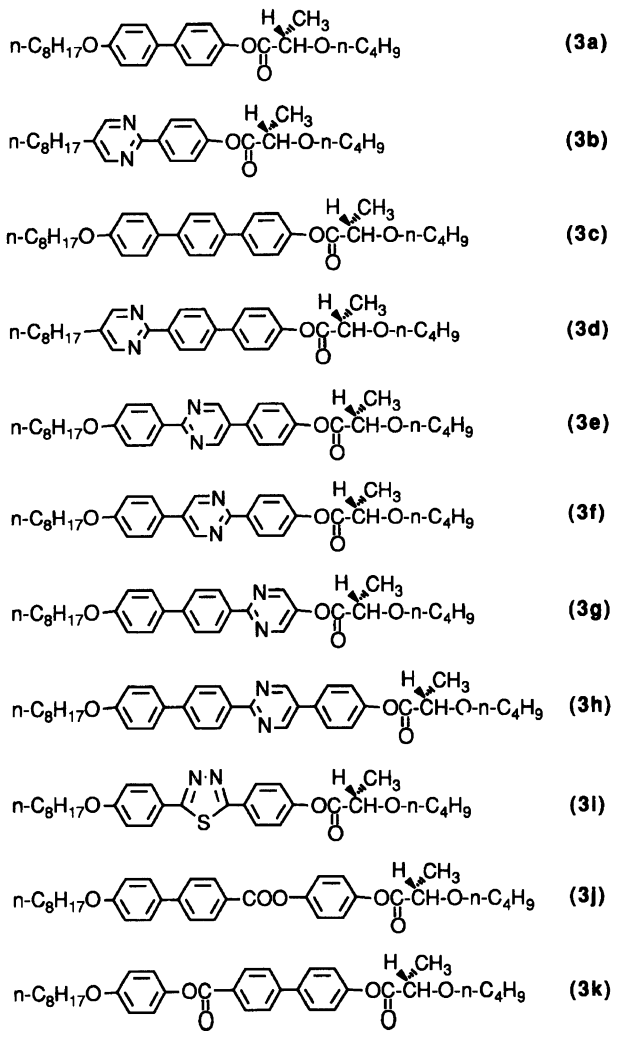


Fig. 1. The molecular structures of compounds **3a**—**3k**.

Compound **3e** showed the largest P_s of 215 nC cm^{-2}, in which pyrimidine ring seems to contribute to enhance the P_s value. What is the effect of pyrimidine ring? N. Shiratori reported that pyrimidine ring greatly contribute to promoting interaction between core parts of the molecules.[9] We guess the effect of pyrimidine ring is an electron delocalization, due to the planar structure of the 2-phenylpyrimidine skeleton. This would increase the polarizability and enhance the intermolecular attractive interaction, which leads to an increase in P_s value. Small P_s value of compound **3d** compared to that of the other pyrimidine compounds (**3e**, **3f**, and **3g**) is probably due to the lack of oxygen in achiral terminal chain,because the oxygen has a dipole moment perpendicular to the molecule which is known to increase the intermolecular attractive interaction.

Properties as Chiral Dopant for FLC. For practical use, the properties in achiral host liquid crystal mixtures are important. Therefore, we next investigated the ability as chiral dopants of these compounds. FLC mixtures were made by doping 5 wt% of compound to an achiral Sc host liquid crystal mixture being composed of 2-[4-(*n*-hexyloxy)phenyl]-5-*n*-nonylpyrimidine (33.3 wt%), 2-[4-(*n*-octyloxy)phenyl]-5-*n*-octylpyrimidine (33.3 wt%) and 2-[4-(*n*-decyloxy)phenyl]-5-*n*-octylpyrimidine (33.3 wt%). The physical properties of the resulting FLC mixtures are shown in Table 2. The P_s values of these FLC mixtures are smaller than the values expected from their own P_s values. For example, the FLC mixture containing 5 wt% of **3f** exhibited P_s of only 0.2 nC cm^{-2}, though compound **3f** showed maximum P_s value of 174 nC cm^{-2} by itself. We suppose the reason for this is that the free rotation of the chiral compound is promoted by diluting with the host liquid crystal mixture and this leads to decrease in the P_s values. The FLC mixtures of compounds **3b**,**3e**, and **3g** showed similar switching times of about 120—130 μs, though the P_s values of compounds **3e** and **3g** are 2 times larger than that of **3b**. As the response time (τ) can be represented by $\tau=\eta/(P_s\times E)$, where η is the rotational viscosity, P_s is the spontaneous polarization and E is the applied electric field,[4] above result suggests that the rotational viscosity of compound **3b** having 2-phenylpyrimidine as a core is lower than that of **3e** and **3g**. About the phase-transition temperature, the transition temperatures of the host liquid crystals were not so much affected by adding 5 wt% of two aromatic ring compounds **3a** and **3b**. The doping of three or four aromatic ring compound (**3c**—**3k**) tended to rise the transition temperatures of host liquid crystal mixture, but the transition temperature from a smectic A phase to a smectic C phase, T_{SA-SC}, dropped by doping of compound **3f** or **3j**. From the results shown in Table 2, compound **3e** and **3g** are considered most useful as chiral dopants for FLC, because the doping of these compounds induced large P_s's and suitable tilt angles (ca. 20 degrees) for an application in the birefringent mode and these FLC mixtures showed a short response times. Moreover, the Sc range of the host liquid crystal mixture was extended by doping of these compounds. In addition to above feature, good alignments was obtained.

We thus conclude that the core structure of the ferroelectric liquid crystal has a great influence on the P_s value and introduction of a heterocycles such as pyrimidine and thiadiazole ring in the core increases the P_s value. Moreover, several compounds in this series are interesting as chiral dopants for FLC, because the FLC mixtures containing them showed superior properties as mentioned above.

Experimental

IR and ^{1}H NMR were recorded on a Shimadzu IR-408 spectrometer and Varian EM-360 spectrometer, respectively, under standard conditions. Elemental analyses were carried out with a Perkin-Elmer 2400 CHN Elemental Analyzer. Final products were purified by column chromatography on silica gel followed by recrystallization from ethanol. Optical purity of compound **3e** was measured by HPLC

Table 1. Transition Temperatures and P_s Values of Compounds **3a**—**3k**

Compound	Phase transition temperature [a]/°C								P_s/nC cm^{-2}	
	Cr		Sx		Sc*		N*	I	$T_{AC-10°C}$ [b]	max.[c]
3a	·	87.7	—		—		—	·	—	—
3b	·	18.5	—		—		—	·	—	—
3c	·	148.5	—		·	167.0	· 195.5	·	+80	+117
3d	·	79.0	—		·	118.0	· 128.5	·	+41	+65
3e	·	88.0	—		·	148.0	—	·	+137	+215
3f	·	83.0	·	90.0	·	149.5	· 157.0	·	+83	+174
3g	·	133.8	—		·	137.5	—	·	+—[d]	+155
3h	·	150.0	·	164.0	·	267.5	—	·	+25	+75
3i	·	66.0	—		·	141.5	—	·	+45	+165
3j	·	76.5	·	93.0	·	135.0	· 169.5	·	+32	+95
3k	·	77.0	—		·	140.0	· 143.0	·	+45	+98

a) Cr: crystalline solid, Sx: unidentified smectic phase, Sc*: chiral smectic C phase, N*: chiral nematic phase, I: isotropic liquid phase. b) The value at a temperature 10°C below the upper limit of a Sc* phase. c) maximum value. d) P_s value was not measured because of crystallization.

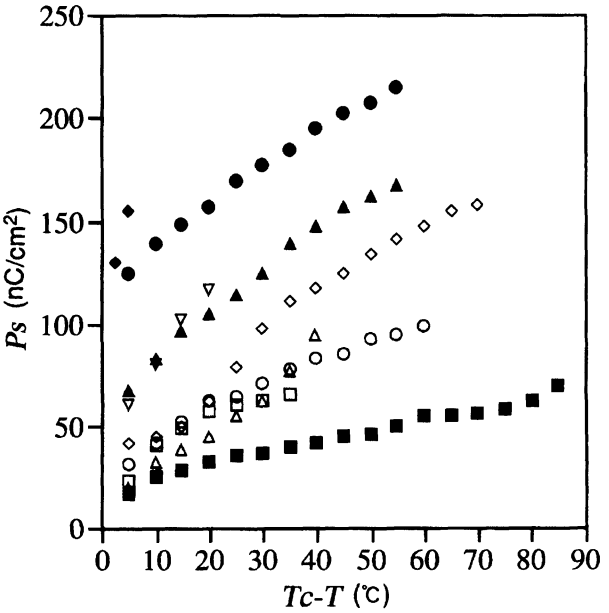


Fig. 2. Temperature dependence of the P_s value of **3c**(▽), **3d**(□), **3e**(●), **3f**(▲), **3g**(◆), **3h**(■), **3i**(◇), **3j**(△), and **3k**(○).

Table 2. Properties of Compounds **3a**—**3k** in Achiral Liquid Crystal Mixture[a]

Compound	P_s	τ	θ	Phase transition temp [b]/°C					
	nC cm^{-2}	μs	deg	Sc*		S_A		N*	I
3a	+0.6	200	15.0	·	54	· 61	·	64	·
3b	+0.7	125	14.5	·	54	· 62	·	64	·
3c	+0.8	210	16.4	·	56	· 70	·	75	·
3d	+0.5	250	14.0	·	54	· 68	·	70	·
3e	+1.6	120	18.5	·	56	· 65	·	77	·
3f	+0.2	410	10.5	·	47	· 60	·	75	·
3g	+1.4	130	19.5	·	61	· 66	·	69	·
3h	+0.1	260	15.3	·	58	· 69	·	73	·
3i	+0.2	320	16.5	·	56	· 65	·	68	·
3j	+—[c]	350	11.5	·	47	· 69	·	71	·
3k	+1.0	210	19.5	·	55	· 64	·	69	·
Host[d]	—	—	—	·	53[d]	· 60	·	65	·

a) Chiral compound was added 5 wt% to the host liquid crystal mixture. Measurments of P_s, τ, and θ were carried out at 25°C. b) Sc*: chiral smectic C phase, S_A: Smectic A phase, N*: chiral nematic phase, I: isotropic liquid phase. c) Very small (below detection limit). d) Consisted of 2-phenylpyrimidines. e) Sc phase.

with a chiral column; "CHIRALCEL OD' Produced by Daicel Chemical Industries, Ltd. Optical rotations were measured on a JASCO DIP 360 digital polarimeter. The phase transition temperatures were determined by using a Rigaku Denki DSC-8230 apparatus at a constant heating/cooling rate of 5°C min^{-1} and texture observations were made using a Nikon XTP-II polarizing microscope in conjunction with a Mettler FP-82 hot stage and FP-80 control unit. Test cells were made by filling the samples to 2 μm thick cells consisting of two indium-tin oxide (ITO) glass slides coated with polyimide rubbed in the same direction by capillary action at the temperature 20°C above a clearing point and were cooled at a rate of 5°C min^{-1} to a target temperature with a Mettler heating stage FP-82. The spontaneous polarization (P_s) was measured by the triangular wave method applying a triangular wave of 20 V_{p-p} μm^{-1}.[10] The sense of P_s was determined by the field reversal method by an optical observation of the director motion.[11] The response time (τ) was defined as the time difference between voltage reversal and a 90% change in optical transmission by applying a rectangular wave of 20 V_{p-p} μm^{-1}. The tilt angle (θ) was measured from the scale on the microscope turntable between the two extreme optical states, corresponding to the two polarities of a DC field applied across the sample cell. A typical procedure for the synthesis is described for **3a**. Other ester (**3b**—**3k**) was prepared according to the similar method as **3a**.

(*S*)-2-*n*-Butoxypropionic Acid (2). To a mixture of ethyl (*S*)-lactate ($[\alpha]^{14}$ −10° (neat), 16.4 g, 0.139 mol) and n-butyl iodide (51.0 g, 0.277 mol) was added freshly prepared silver(I) oxide (16.1 g, 0.07 mol) at room temperature for several portions. After stirring for 15 h, the reaction mixture was diluted with ether and silver(I) oxide was removed by filtration. The filtrate was evaporated in vacuo to leave an oil, which was purified by distillation under reduced pressure to afford ethyl (*S*)-2-butoxypropionate as an oil in 50% yield.

Bp 91.5—92.5°C (25 mmHg) (1 mmHg=133.322 Pa), [(lit,[12] bp 110°C (54 mmHg)]; ^{1}H NMR ($CDCl_3$) δ=0.88—0.97 (3H, m), 1.27 (3H, t, J=7 Hz), 1.40—1.48 (5H, m), 1.56—1.63 (2H, m), 3.93 (1H, q, J=7 Hz), 4.20 (2H, q, J=7 Hz); IR (neat) 2930, 2850, 1745, 1450, 1370, 1260, 1190 cm^{-1}; $[\alpha]_D^{25}$ − 73.5° (c 1.00, $CHCl_3$), [lit,[12] $[\alpha]_D^{25}$ −73°].

To a stirred solution of above ester (10.0 g, 57.4 mmol) in ethanol (50 ml) was added 5 M (1 M=1 mol dm^{-3}) KOH solution (11.5 ml, 57.5 mmol) dropwise at 3°C and the mixture was stirred further 2 h at 3°C. The reaction mixture was poured into 10% HCl and extracted twice with ether. The combined organic layer was washed several times with water, dried over anhydrous magnesium sulfate and concentrated in vacuo to afford (*S*)-2-*n*-butoxypropionic acid (**2**) as an oil (8.40 g, 99.5%). ^{1}H NMR ($CDCl_3$) δ=1.29 (3H, t, J=7 Hz), 1.35—1.64 (7H, m), 3.44—3.59 (2H, m), 3.94 (1H, q, J=7 Hz), 9.09 (1H, bs); IR (neat) 2940, 2850, 1729, 1450, 1370 cm^{-1};$[\alpha]_D^{25}$ −74.0° (c 1.00, $CHCl_3$), [lit,[12] $[\alpha]_D^{25}$ −74°].

4′-(*n*-Octyloxy)biphenyl-4-yl(*S*)-2-*n*-Butoxypropionate (3a). A solution of 4′-(*n*-octyloxy)biphenyl-4-ol (1.0 g, 3.35 mmol) and (*S*)-2-butoxypropionic acid (**2**, 0.60 g, 4.10 mmol) in dichloromethane (10 ml) was added dicyclohexylcarbodiimide (DCC, 1.10 g, 5.34 mmol) and catalytic amount of 4-(1-pyrrolidinyl)pyridine at room temperature and the resulting mixture was stirred at room temperature for 3 h. The reaction mixture was filtered and the filtrate was evaporated in vacuo. The resulting solid was purified by column chromatography on silica gel with hexane–ether as eluent, followed by recrystallization from ethanol to yield **3a** as plates (1.4 g, 97.9%). ^{1}H NMR ($CDCl_3$) δ=0.86—0.98 (6H, m), 1.29—1.84 (19H, m), 3.45—3.56 (1H, m), 3.66—3.77 (1H, m), 3.99 (2H, t, J=7 Hz), 4.20 (1H, q, J=7 Hz), 6.95 (2H, d, J=9 Hz), 7.14 (2H, d, J=9 Hz), 7.49 (2H, d, J=9 Hz), 7.54 (2H, d, J=9 Hz); IR (Nujol) 1750, 1600, 1490, 1210 cm^{-1}; $[\alpha]_D^{25}$ −35.4° (c 1.00, $CHCl_3$). Found: C, 75.81; H, 9.08%. Calcd for $C_{27}H_{38}O_4$: C, 76.01; H, 8.79%.

4-{5-(*n*-Octyl)pyrimidin-2-yl} phenyl (*S*)-2-*n*-Butoxypropionate (3b). ^{1}H NMR ($CDCl_3$) δ=0.85—0.98 (6H, m), 1.27—1.69 (19H, m), 2.62 (2H, t, J=7 Hz), 3.45—3.56 (1H, m), 3.66—3.77 (1H, m), 4.22 (1H, q, J=7 Hz), 7.22 (2H, d, J=9 Hz), 8.44 (2H, d, J=9 Hz), 8.61 (2H, s); IR (Neat) 1769, 1582, 1540, 1427, 1197, 1159, 1120 cm^{-1}; $[\alpha]_D^{25}$ −41.5° (c 1.05, $CHCl_3$). Found: C, 72.64; H, 9.01; N, 6.71%. Calcd for $C_{25}H_{36}N_2O_3$: C, 72.78; H, 8.79; N, 6.78%.

4″-(*n*-Octyloxy)-1,1′:4′,1″-terphenyl-4-yl (*S*)-2-*n*-Butoxypropionate (3c). ^{1}H NMR ($CDCl_3$) δ= 0.82—1.05 (6H, m), 1.20—1.90 (19H, m), 3.44—3.56 (1H, m), 3.65—3.77 (1H, m), 4.02(2H, t, J=7 Hz), 4.22 (1H, q, J=7 Hz), 6.96 (2H, d, J=9 Hz), 7.14 (2H, d, J=9 Hz), 7.54—7.64 (8H, m); IR (Nujol) 1750, 1600, 1500, 1210 cm^{-1}; $[\alpha]_D^{25}$ −30.8° (c 1.00, $CHCl_3$). Found: C, 78.61; H, 8.55%. Calcd for $C_{33}H_{42}O_4$: C, 78.84; H, 8.42%.

4′-{5-(*n*-Octyl)pyrimidin-2-yl} biphenyl-4-yl (*S*)-2-*n*-Butoxypropionate (3d). ^{1}H NMR ($CDCl_3$) δ= 0.85—0.98 (6H, m), 1.28—1.73 (19H, m), 2.63 (2H, t, J=7 Hz), 3.46—3.56 (1H, m), 3.66—3.77 (1H, m), 4.21 (1H, q, J=7 Hz), 7.20 (2H, d, J=9 Hz), 7.68 (2H, d, J=9 Hz), 7.69 (2H, d, J=9 Hz), 8.49 (2H, d, J=9 Hz), 8.64 (2H, s); IR (Nujol) 1764, 1115 cm^{-1}; $[\alpha]_D^{25}$ −35.9° (c 1.10, $CHCl_3$). Found: C, 76.35; H, 8.48; N, 5.76%. Calcd for $C_{31}H_{40}N_2O_3$: C, 76.19; H, 8.25; N, 5.73%.

4-[2-{4-(*n*-Octyloxy)phenyl}pyrimidin-5-yl]phenyl (*S*)-2-*n*-Butoxypropionate (3e). ^{1}H NMR ($CDCl_3$) δ=0.86—0.99 (6H, m), 1.26—1.86 (19H, m), 3.46—3.57 (1H, m), 3.67—3.77 (1H, m), 4.04 (2H, t, J=7 Hz), 4.22 (1H, q, J=7 Hz), 7.01 (2H, d, J=9 Hz), 7.26 (2H, d, J=9 Hz), 7.63 (2H, d, J=9 Hz), 8.42 (2H, d, J=9 Hz), 8.95 (2H, s); IR (Nujol) 1760, 1600, 1580, 1640, 1250 cm^{-1}; $[\alpha]_D^{25}$ −30.5° (c 1.00, $CHCl_3$). Found: C, 73.72; H, 8.21; N, 5.59%. Calcd for $C_{31}H_{40}N_2O_4$: C, 73.77; H, 7.98; N, 5.55%.

4-[5-{4-(*n*-Octyloxy)phenyl}pyrimidin-2-yl]phenyl (*S*)-2-*n*-Butoxypropionate (3f). ^{1}H NMR ($CDCl_3$) δ=0.86—0.98 (6H, m), 1.30—1.86 (19H, m), 3.46—3.57 (1H, m), 3.67—3.78 (1H, m), 4.00 (2H, t, J=7 Hz), 4.22 (1H, q, J=7 Hz), 7.04 (2H, d, J=9 Hz), 7.25 (2H, d, J=9 Hz), 7.55 (2H, d, J=9 Hz), 8.52 (2H, d, J=9 Hz), 8.97 (2H, s); IR (Nujol) 1750, 1600, 1580, 1510, 1430, 1280, 1240 cm^{-1}; $[\alpha]_D^{25}$ −33.1° (c 1.00, $CHCl_3$). Found: C, 74.06; H, 8.28; N, 5.61%. Calcd for $C_{31}H_{40}N_2O_3$: C, 73.77; H, 7.98; N, 5.55%.

2-{4′-(*n*-Octyloxy)biphenyl-4-yl}pyrimidin-5-yl (*S*)-2-*n*-Butoxypropionate (3g). ^{1}H NMR ($CDCl_3$) δ=0.89—1.00 (6H, m), 1.15—1.81 (19H, m), 3.44—3.59 (1H, m), 3.64—3.78(1H, m), 4.01 (2H, t, J=7 Hz), 4.26 (1H, q, J=7 Hz), 7.01 (2H, d, J=9 Hz), 7.60 (2H, d, J=9 Hz), 7.68 (2H, d, J=9 Hz), 8.45 (2H, d, J=9 Hz), 8.68 (2H, s); IR (Nujol) 1755, 1600, 1580, 1220, 1120 cm^{-1}; $[\alpha]_D^{25}$ −34.3° (c 1.01, $CHCl_3$). Found: C, 73.83; H, 7.82; N, 5.51%. Calcd for $C_{31}H_{40}N_2O_4$: C, 73.77; H, 7.98; N, 5.55%.

4-[2-{4′-(*n*-Octyloxy)biphenyl-4-yl}pyrimidin-5-yl]phenyl (*S*)-2-*n*-Butoxypropionate (3h). ^{1}H NMR ($CDCl_3$) δ=0.86—0.99 (6H, m), 1.30—1.85 (19H, m), 3.47—3.58 (1H, m), 3.66—3.77 (1H, m), 4.01 (2H, t, J=7 Hz), 4.22 (1H, q, J=7 Hz), 6.99 (2H, d, J=9 Hz), 7.27 (2H, d, J=9 Hz), δ=7.66—7.73 (6H, m), 8.53 (2H, d, J=9 Hz), 9.01 (2H, s); IR (Nujol) 1753, 1595, 1575, 1520, 1245, 1210 cm^{-1}; $[\alpha]_D^{25}$ −29.7° (c 1.07, $CHCl_3$). Found: C, 76.77; H, 7.83; N, 4.86%. Calcd for $C_{37}H_{44}N_2O_4$: C, 76.52; H, 7.63; N, 4.82%.

4-[2-{4-(*n*-Octyloxy)phenyl}-1,3,4-thiadiazol-5-yl]-phenyl (*S*)-2-*n*-Butoxypropionate (3i). ^{1}H NMR ($CDCl_3$) δ=0.90—1.05 (6H, m), 1.12—1.92 (19H, m), 3.46—3.57 (1H, m), 3.65—3.76 (1H, m), 4.03 (2H, t, J=7 Hz), 4.21 (1H, q, J=7 Hz), 6.97 (2H, d, J=9 Hz), 7.23 (2H, d, J=9 Hz), 7.92 (2H, d, J=9 Hz), 8.03 (2H, d, J=9 Hz); IR (Nujol) 1765, 1602, 1504, 1310, 1274, 1210, 1125 cm^{-1}; $[\alpha]_D^{25}$ −34.3° (c 1.02, $CHCl_3$). Found: C, 68.50; H,7.78; N, 5.54%. Calcd for $C_{29}H_{38}N_2O_4S$: C, 68.20; H, 7.49; N, 5.48; S, 6.27%.

4-{4′-(*n*-Octyloxy)biphenyl-4-carboxy}phenyl (*S*)-2-*n*-Butoxypropionate (3j). ^{1}H NMR ($CDCl_3$) δ= 0.86—1.05 (6H, m), 1.30—1.85 (19H, m), 3.45—3.55 (1H, m), 3.65—3.76 (1H, m), 4.02 (2H, t, J=7 Hz), 4.20 (1H, q, J=7 Hz), 7.00 (2H, d, J=9 Hz), 7.18 (2H, d, J=9 Hz), 7.27 (2H, d, J=9 Hz), 7.59 (2H, d, J=9 Hz), 7.70 (2H, d, J=9 Hz), 8.22 (2H, d, J=9 Hz); IR (Nujol) 1755, 1730, 1600, 1500, 1290, 1200, 1185 cm^{-1}; $[\alpha]_D^{25}$ −29.8° (c 1.07, $CHCl_3$). Found: C, 74.50; H,7.67%. Calcd for $C_{34}H_{42}O_6$: C, 74.69; H, 7.74%.

4′-{4-(*n*-Octyloxy)phenoxycarbony}biphenyl-4-yl-(*S*)-2-*n*-Butoxypropionate (3k). ^{1}H NMR ($CDCl_3$) δ=0.80—1.00 (6H, m), 1.15—1.85 (19H, m), 3.46—3.56 (1H, m), 3.67—3.77 (1H, m), 3.96 (2H, t, J=7 Hz), 4.22 (1H, q, J=7 Hz), 6.93 (2H, d, J=9 Hz), 7.13 (2H, d, J=9 Hz), 7.24 (2H, d, J=9 Hz), 7.64 (2H, d, J=9 Hz), 7.69 (2H, d, J=9 Hz), 8.26(2H, d, J=9 Hz); IR (Nujol) 1750, 1735, 1590,

1505, 1280, 1205, 1130 cm^{-1}; $[\alpha]_D^{25}$ $-30.5°$ (c 1.00, $CHCl_3$). Found: C, 74.49; H,7.85%. Calcd for $C_{34}H_{42}O_6$: C, 74.69; H, 7.74%.

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