Chiral self-sorting and the realization of ferroelectricity in the columnar liquid crystal phase of an optically inactive *N*,*N*'-diphenylurea derivative possessing six (±)-citronellyl groups

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Supporting Information

General. Thin layer chromatography (TLC) and column chromatography were performed using MERCK silica gel 60 GF TLC plates and Fuji-Silysia BM-200 silica gel.

^{1}H-NMR and ^{13}C-NMR spectra were measured by Bruker DPX-300 and AVANCE III-400M spectrometers. $CDCl_3$ was used as the solvent, and tetramethylsilane (TMS) was used as an internal standard. The chemical shifts are written with the d value, and the peak splits were indicated with abbreviations, s (singlet), d (doublet), t (triplet), q (quartet), quin (quintet), sext (sextet), sept (septet), m (multiplet), and br (broad) .

One-dimensional (1D-XRD) profiles were measured by a Rigaku RINT2200 diffractometer. Polarized light optical microscopy (POM) was performed by a Nikon ECLIPSE E400 POL microscope equipped with an INSTEC HCS400 hot-cool stage with crossed polarizer and analyzer. Differential scanning calorimetry (DSC) was measured by using a MAC-SCIENCE DSC 3100 S calorimeter.

Electroanalyses were measured using a Yokogawa FG110 function generator, a KEYENCE NR-2000 oscillograph, and an FLC electronics F10A amplifier. Second harmonic generation (SHG) was performed using a Continuum Minilite Q-switch Nd:YAG laser. The sample heated with an Omron E5CN-H ThermacNEO temperature controller, was polarized by an INSTEK AFG-3051 function generator, an FLC electronics F10A amplifier, and a Stanford Research Systems SR570 preamplifier. In the SHG and optoelectronic experiments, LC cells composed with two ITO-deposited glass plates (cell gap: 5 μm, ITO area: 1 cm ×1 cm) which are covered with a polyimide layer (anti-parallel homogeneous alignment) were purchased from E.H.C. Co., Ltd. The sample was heated to its isotropic liquid state and inserted between the electrodes by capillarity.

Circular dichroism (CD) spectra were measured by a JASCO J-820 spectroscopy. The sample was sandwiched between two quartz plates purchased from Daico MFG Co., Ltd.

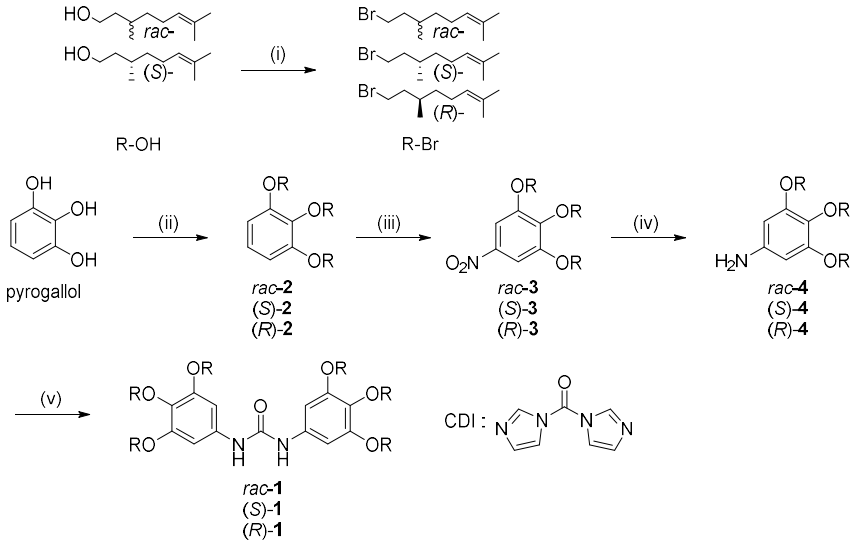

Figure S1. Synthesis of diphenylurea derivatives (*S*)-**1** and (*R*)-**1**, and *rac*-**1**; (i) PPh_3, CBr_4, CH_2Cl_2, 0 ºC to r.t.; (ii) RBr, K_2CO_3, DMF, 60 ºC; (iii) $NaNO_2$, HNO_3, CH_2Cl_2, 0 ºC to r.t.; (iv) iron powder, NH_4Cl, $EtOH/H_2O$ (= 10:1), 90 ºC, reflux; (v) CDI, CH_2Cl_2.

Synthesis of citronellyl bromide. Citronellol (1.72 g, 11.0 mmol), CBr_4 (3.65 g, 11.0 mmol), and CH_2Cl_2 (20 mL) were placed in a 100 mL recovery flask equipped with a $CaCl_2$ tube. The solution was stirred at 0 °C. To the reaction mixture were added PPh_3 (3.46 g, 13.2 mmol) slowly in small portions, and then it was stirred at 0 °C for 1 h and at room temperature for 3 h. After the reaction, the solution was concentrated by evaporation. The solid was dissolved in $CHCl_3$ (2 mL), and then the solution was dropped into *n*-hexane (150 mL) with stirring. The solution was filtered, and the filtrate was concentrated by evaporation. The product was purified by silica gel column chromatography eluting with *n*-hexane to give citronellyl bromide (1.86 g, 77.3%) as a colorless liquid.

(*S*)-citronellyl bromide was also prepared with the same procedure.

rac-Citronellyl bromide: colorless liquid; yield 77.3%; Rf = 0.49 (*n*-hexane); ^{1}H-NMR (300.22 MHz, $CDCl_3$): δ 0.90 (d, *J* = 6.4 Hz, 3H), 1.10-1.40 (m, 2H), 1.55-1.74 (m, 2H), 1.61 (s, 3H), 1.69 (s, 3H), 1.81-2.08 (m, 3H), 3.36-3.51 (m, 2H), 5.06-5.12 (m, 1H).

(*S*)-Citronellyl bromide: colorless liquid; yield 95.5%; Rf = 0.49 (*n*-hexane); ^{1}H-NMR (300.22 MHz, $CDCl_3$): δ 0.90 (d, *J* = 6.4 Hz, 3H), 1.12-1.40 (m, 2H), 1.54-1.76 (m, 2H), 1.61 (s, 3H), 1.69 (s, 3H), 1.82-2.08 (m, 3H), 3.36-3.51 (m, 2H), 5.06-5.11 (m, 1H).

Synthesis of *rac*-2. Potassium carbonate (2.16 g, 15.7 mmol) and dry DMF (11 mL) were placed in a 50 mL-three-necked round bottom flask under Ar atmosphere. The solution was stirred at 60 °C. To the solution were added pyrogallol (0.288 g, 2.28 mmol) and citronellyl bromide (2.00 g, 9.13 mmol) were added. The solution was stirred at 60 °C for 24 h. After cooling to room temperature, the solution was extracted with ethyl acetate (30 mL × 2), and the combined organic phase was washed with distilled water and brine. The organic phase was dried over $MgSO_4$ anhydrous. The solution was filtered, and the filtrate was concentrated by evaporation. The product was purified by silica gel column chromatography eluting with *n*-hexane-ethyl acetate (=20:1), alumina column chromatography eluting with *n*-hexane-ethyl acetate (=50:1) and then to give *rac*-**2** (0.805 g, 57.1%) as a colorless oil.

Compounds (*S*)-**2** and (*R*)-**2** were also prepared with the same procedure.

rac-**2**: colorless oil; yield 57.1%; Rf = 0.34 (*n*-hexane-ethyl acetate = 20:1); ^{1}H-NMR (300.22 MHz, $CDCl_3$): δ 0.94 (d, *J* = 6.5 Hz, 3H), 0.95 (d, *J* = 6.5 Hz, 6H), 1.13-1.45 (m, 6H), 1.52-1.74 (m, 6H), 1.58 (s, 9H), 1.66 (s, 9H), 1.81-2.05 (m, 9H), 3.91-4.06 (m, 6H), 5.07-5.12 (m, 3H), 6.54 (d, *J* = 8.4 Hz, 2H), 6.91 (t, *J* = 8.4 Hz, 1H); ^{13}C-NMR (100.63 MHz, $CDCl_3$): δ 17.65, 19.51, 25.54, 25.73, 29.61, 36.38, 37.29, 77.06, 77.38, 106.81, 123.18, 124.76, 131.19, 138.46, 153.45; IR (KBr) : 2952, 2909, 2868, 2722, 1739, 1669, 1598, 1461, 1382, 1295, 1248, 1176, 1094, 989 cm^{-1}; MS (ESI) calcd for $C_{36}H_{61}O_3$ $(M+H)^+$:541.4615, found 541.4616.

(*S*)-**2**: colorless oil; yield 93.3%; Rf = 0.38 (*n*-hexane-ethyl acetate = 20:1); ^{1}H-NMR (300.22 MHz, $CDCl_3$): δ 0.94 (d, *J* = 6.5 Hz, 3H), 0.95 (d, *J* = 6.5 Hz, 6H), 1.13-1.45 (m, 6H), 1.49-1.76 (m, 6H), 1.60 (s, 9H), 1.68 (s, 9H), 1.80-2.10 (m, 9H), 3.91-4.07 (m, 6H), 5.07-5.13 (m, 3H), 6.55 (d, *J* = 8.3 Hz, 2H), 6.92 (t, *J* = 8.4 Hz, 1H).

(*R*)-**2**: colorless oil; yield 92.1%; Rf = 0.31 (*n*-hexane-ethyl acetate = 30:1); ^{1}H-NMR (300.22 MHz, $CDCl_3$): δ 0.94 (d, *J* = 6. 6 Hz, 3H), 0.95 (d, *J* = 6.4 Hz, 6H), 1.12-1.45 (m, 6H), 1.48-1.74 (m, 6H), 1.60 (s, 9H), 1.68 (s, 9H), 1.80-2.08 (m, 9H), 3.91-4.06 (m, 6H), 5.06-5.14 (m, 3H), 6.55 (d, *J* = 8.4 Hz, 2H), 6.92 (t, *J* = 8.4 Hz, 1H).

Synthesis of *rac*-3. CH_2Cl_2 (20 mL) and *rac*-**2** (0.542 g, 1.00 mmol) were placed in a 100 mL recovery flask equipped with a $CaCl_2$ tube. The solution was stirred at room temperature for 15 min. To the solution was added HNO_3/SiO_2 (1.27 g, 5.00 mmol), and then the solution was stirred at room temperature for 1 h. The reaction mixture was filtered through Celite. The Celite was washed with ethyl acetate. The combined organic solutions were washed with distilled water and $NaHCO_3$ aq., and dried over $MgSO_4$ anhydrous. The solution was filtered, and the filtrate was concentrated by evaporation. The product was purified by silica gel column

chromatography eluting with *n*-hexane-ethyl acetate (= 20:1) to give *rac*-**3** (0.144 g, 24.5%) as a yellow oil.
rac-**3**: yellow oil; yield 24.5%; Rf = 0.28 (*n*-hexane-ethyl acetate = 20:1); ^{1}H-NMR (300.22 MHz, $CDCl_3$): δ 0.94 (d, *J* = 6.5 Hz, 3H), 0.95 (d, *J* = 6.5 Hz, 6H), 1.13-1.45 (m, 6H), 1.49-1.72 (m, 6H), 1.60 (s, 9H), 1.68 (s, 9H), 1.80-2.05 (m, 9H), 4.02-4.12 (m, 6H), 5.08-5.13 (m, 3H), 7.48 (s, 2H); ^{13}C-NMR (100.63 MHz, $CDCl_3$): δ17.63, 19.51, 25.52, 25.94, 29.61, 35.99, 37.17, 77.10, 106.75, 123.17, 124.74, 131.28, 138.40, 143.50, 153.11; IR (KBr) : 3100, 2931, 2908, 2865, 2732, 1617, 1525, 1435, 1379, 1339, 1215, 1174, 1124, 1048 cm^{-1}; MS (APCI) calcd for $C_{36}H_{60}NO_5$ $(M+H)^+$:586.4466, found 586.4460.

Synthesis of (*S*)-3. Compound (*S*)-**2** (1.93 g, 3.57 mmol), sodium nitrite (0.0356 g, 0.516 mmol), and CH_2Cl_2(40 mL) were placed in a 100 mL recovery flask equipped with a $CaCl_2$ tube. The solution was stirred and cooled to 0°C. To this, well-stirred suspension, 60% HNO_3(0.675 g, 10.7 mmol, 10% solution in CH_2Cl_2) was added dropwise. The mixture was stirred at room temperature for 1 h. The reaction mixture was extracted with CH_2Cl_2(30 mL × 2), and the combined organic phase was washed with distilled water and $NaHCO_3$ aq., and dried over $MgSO_4$ anhydrous. The solution was filtered, and the filtrate was concentrated by evaporation. The product was purified by silica gel column chromatography eluting with *n*-hexane-ethyl acetate (=20:1) to give (*S*)-**3** (0.5154 g, 24.6%) as a yellow oil.
Compound (*R*)-**3** was also prepared with the same procedure.
(*S*)-**3**: yellow oil; yield 24.6%; Rf = 0.24 (*n*-hexane-ethyl acetate = 30:1); ^{1}H-NMR (300.22 MHz, $CDCl_3$): δ 0.94 (d, *J* = 6.5 Hz, 3H), 0.95 (d, *J* = 6.5 Hz, 6H), 1.12-1.47 (m, 6H), 1.49-1.71 (m, 6H), 1.60 (s, 9H), 1.68 (s, 9H), 1.80-2.09 (m, 9H), 4.01-4.16 (m, 6H), 5.08-5.13 (m, 3H), 7.48 (s, 2H).
(*R*)-**3**: yellow oil; yield 16.7%; Rf = 0.23 (*n*-hexane-ethyl acetate = 20:1); ^{1}H-NMR (300.22 MHz, $CDCl_3$): δ 0.94 (d, *J* = 6.6 Hz, 3H), 0.95 (d, *J* = 6.6 Hz, 6H), 1.13-1.47 (m, 6H), 1.48-1.74 (m, 6H), 1.60 (s, 9H), 1.68 (s, 9H), 1.80-2.05 (m, 9H), 4.00-4.12 (m, 6H), 5.07-5.13 (m, 3H), 7.48 (s, 2H).

Synthesis of *rac*-4. Ammonium chloride (0.0708 g, 1.32 mmol), *rac*-**3** (0.222 g, 0.378 mmol), iron powder (0.212 g, 3.78 mmol), ethanol (20 mL), and distilled water (2 mL) were placed in a 100 mL two-necked eggplant flask equipped with a Dimroth and a $CaCl_2$ tube. The solution was stirred at 90 °C under reflux for 4 h. After cooling to room temperature, the solution was extracted with $CHCl_3$ (50 mL). The obtained $CHCl_3$ solution was washed with water and dried over $MgSO_4$ anhydrous. The solution was filtered, and the filtrate was concentrated by evaporation. The product was purified by silica gel column chromatography eluting with *n*-hexane-ethyl acetate (= 4:1) to give *rac*-**4** (0.270 g, 129%, contains solvents) as a colorless oil.
Compounds (*S*)-**4** and (*R*)-**4** were also prepared with the same procedure. These anilines obtained were used for the starting materials in the next step because they were highly reactive to oxygen and light to give dark brown polymerized products.
rac-**4**: colorless oil; yield 129%; Rf = 0.26 (*n*-hexane-ethyl acetate = 2:1); ^{1}H-NMR (300.22 MHz, $CDCl_3$): δ 0.94 (d, *J* = 6.5 Hz, 3H), 0.95 (d, *J* = 6.5 Hz, 6H), 1.13-1.45 (m, 6H), 1.49-1.74 (m, 6H), 1.60 (s, 9H), 1.68 (s, 9H), 1.80-2.08 (m, 9H), 3.48 (br, 2H), 3.83-3.98 (m, 6H), 5.08-5.13 (m, 3H), 5.92 (s, 2H).
(*S*)-**4**: colorless oil; yield 108% (contains solvents); Rf = 0.19 (*n*-hexane-ethyl acetate = 4:1); ^{1}H-NMR (300.22 MHz, $CDCl_3$): δ 0.94 (d, *J* = 6.6 Hz, 3H), 0.95 (d, *J* = 6.6 Hz, 6H), 1.11-1.47 (m, 6H), 1.49-1.75 (m, 6H), 1.60 (s, 9H), 1.68 (s, 9H), 1.78-2.09 (m, 9H), 3.48 (br, 2H), 3.83-3.98 (m, 6H), 5.07-5.13 (m, 3H), 5.92 (s, 2H).
(*R*)-**4**: colorless oil; yield 91.0%; Rf = 0.15 (*n*-hexane-ethyl acetate = 4:1); ^{1}H-NMR (300.22 MHz, $CDCl_3$): δ 0.94 (d, *J* = 6.5 Hz, 3H), 0.95 (d, *J* = 6.5 Hz, 6H), 1.11-1.45 (m, 6H), 1.49-1.72 (m, 6H), 1.60 (s, 9H), 1.68 (s, 9H), 1.80-2.06 (m, 9H), 3.48 (br, 2H), 3.83-3.98 (m, 6H), 5.08-5.13 (m, 3H), 5.92 (s, 2H).

Synthesis of *rac*-1. Compound *rac*-**4** (0.210 g, 0.378 mmol) and CH_2Cl_2 (12 mL) were placed in a

100 mL recovery flask wrapped with aluminum foil and equipped with a $CaCl_2$ tube. With stirring at room temperature, to the solution was added carbonyl diimidazole (0.0645 g, 0.398 mmol), and then it was stirred at room temperature for 21 h. The solution was concentrated by evaporation. The product was purified by silica gel column chromatography eluting with *n*-hexane-ethyl acetate (= 4:1) to give the desired product. The urea compound was further purified by recrystallization from methanol to give *rac*-**1** (0.0569 g, 26.5 %) as a liquid crystal. Compounds (*S*)-**1** and (*R*)-**1** were also prepared from (*S*)-**4** and (*R*)-**4** with the same procedure.
rac-**1**: liquid crystal; yield 26.5%; Rf = 0.20 (*n*-hexane-ethyl acetate = 4:1); ^{1}H-NMR (300.22 MHz, $CDCl_3$): δ 0.94 (d, *J* = 6.5 Hz, 6H), 0.95 (d, *J* = 6. 4 Hz, 12H), 1.14-1.45 (m, 12H), 1.49-1.73 (m, 12H), 1.60 (s, 18H), 1.67 (s, 18H), 1.80-2.05 (m, 18H), 3.91-4.00 (m, 12H), 5.07-5.12 (m, 6H), 6.26 (br, 2H), 6.57 (s, 4H); ^{13}C-NMR (100.63 MHz, $CDCl_3$): δ17.66, 19.49, 25.75, 36.29, 37.22, 77.02, 95.92, 124.68, 128.94, 131.09, 133.05, 147.19, 153.56; IR (KBr) : 3316, 3205, 2938, 2928, 2872, 2727, 1645, 1610, 1554, 1502, 1424, 1377, 1296, 1223, 1123, 996 cm^{-1}; MS (ESI) calcd for $C_{73}H_{121}N_2O_7$ $(M+H)^+$:1137.9168, found 1137.9198.
(*S*)-**1**: liquid crystal; yield 36.1%; Rf = 0.21 (*n*-hexane-ethyl acetate = 4:1); ^{1}H-NMR (300.22 MHz, $CDCl_3$): δ 0.94 (d, *J* = 6.5 Hz, 6H), 0.95 (d, *J* = 6.6 Hz, 12H), 1.14-1.43 (m, 12H), 1.48-1.74 (m, 12H), 1.60 (s, 18H), 1.67 (s, 18H), 1.79-2.07 (m, 18H), 3.89-4.02 (m, 12H), 5.08-5.13 (m, 6H), 6.26 (br, 2H), 6.56 (s, 4H); MS (APCI) calcd. for $C_{73}H_{121}N_2O_7$ $(M+H)^+$:1137.9168, found 1137.9172.
(*R*)-**1**: liquid crystal; yield 31.4%; Rf = 0.22 (*n*-hexane-ethyl acetate = 4:1); ^{1}H-NMR (300.22 MHz, $CDCl_3$): δ 0.94 (d, *J* = 6.5 Hz, 6H), 0.95 (d, *J* = 6.5 Hz, 12H), 1.13-1.45 (m, 12H), 1.48-1.72 (m, 12H), 1.60 (s, 18H), 1.68 (s, 18H), 1.80-2.05 (m, 18H), 3.91-4.01 (m, 12H), 5.08-5.13 (m, 6H), 6.28 (br, 2H), 6.56 (s, 4H); MS (APCI) calcd. for $C_{73}H_{121}N_2O_7$ $(M+H)^+$:1137.9168, found 1137.9172.

Reconstruction of relative electron density maps.
The relative electron density ρ(xy) for the columnar liquid crystal can be calculated by inverse Fourier transform of the structural factor F(hk) in the following equation.

$$\rho(xy) = \Sigma F(hk) \exp(2\pi i(hx+ky))$$

Here (hk) are the Miller Indices and x, y are the fractional coordinates of the unit cell. The structural factor F (hk) is a complex number whose amplitude is a square root of the integrated intensity I (hk) of XRD measurement and is expressed by the following equation.

$$F(hk) = |F(hk)| \exp(\pi i\Phi(hk)) = K\sqrt{I(hk)} \exp(\pi i\Phi(hk))$$

Here K is a proportionality constant including the volume of the unit cell, the area of the sample, and the intensity of the incident X-ray, etc., and Φ(hk) is the phase. For the purpose of obtaining relative electron density, the K was set to 1 to simplify the calculation. From the XRD experiments, we could obtain peak intensities related to the amplitude of the structural factor, but the phase could not be directly measured experimentally. However, in the case of a centrosymmetric structure, since ρ(xy) = ρ(-x-y) holds, the structural factor F(hk) is a real number and the phase Φ(hk) is limited to 0 or π. In this report, both the Col_r and Col_h phases of *rac*-**1** are centrosymmetric. Furthermore, due to the limited number of diffraction peaks observed, , all electron density maps were drawn with all phase combinations, and the correct phase combination was selected from them. The most appropriate phase combination was chosen to meet its chemical and physical characteristics such as molecular size, electron density distribution of functional groups, and molecular packing diagram.

Table S1. Indices, observed and calculated *d*-spacings, relative integrated intensities, and selected phases of *rac*-**1** in Col_r phase obtained from XRD measurement at 144°C.

(hkl)	$d_{obs.}$ (Å)	$d_{calc.}$ (Å)	intensity	phase
(200)	24.8	24.8	47.5	π
(110)	17.1	17.1	100	π
(400)	12.4	12.4	20.2	0
(600)	8.27	8.27	6.1	π
(420)	7.39	7.35	5.5	π
a=49.6 Å	*b*=18.3 Å	*c*=4.7 Å		

All the intensities were Lorentz-polarization and multiplicity corrected.

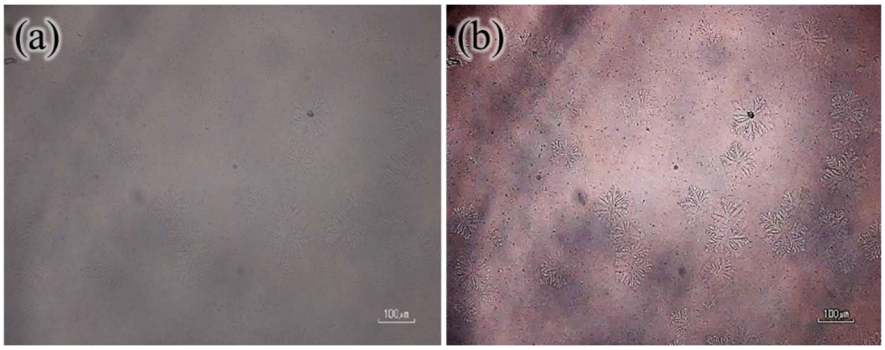

Figure S2. Dendric textures of *rac*-**1** Col_h; (a) microphotograph of Col_h at 151°C on cooling (without polarizers), and (b) microphotograph of (a), in which the contrast was modified for clarification.

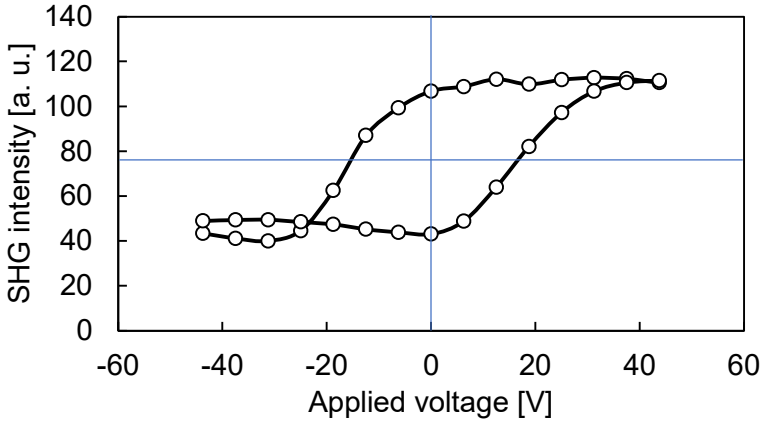

Figure S3. Plot of SHG intensity of *rac*-**1** at 134 °C against the applied voltage (voltage: 100 V_{pp}, frequency: 20 mHz, cell gap: 5 μm). Ec': ±18 V, coercive electric field (Ec): 3.6 V μm^{-1}

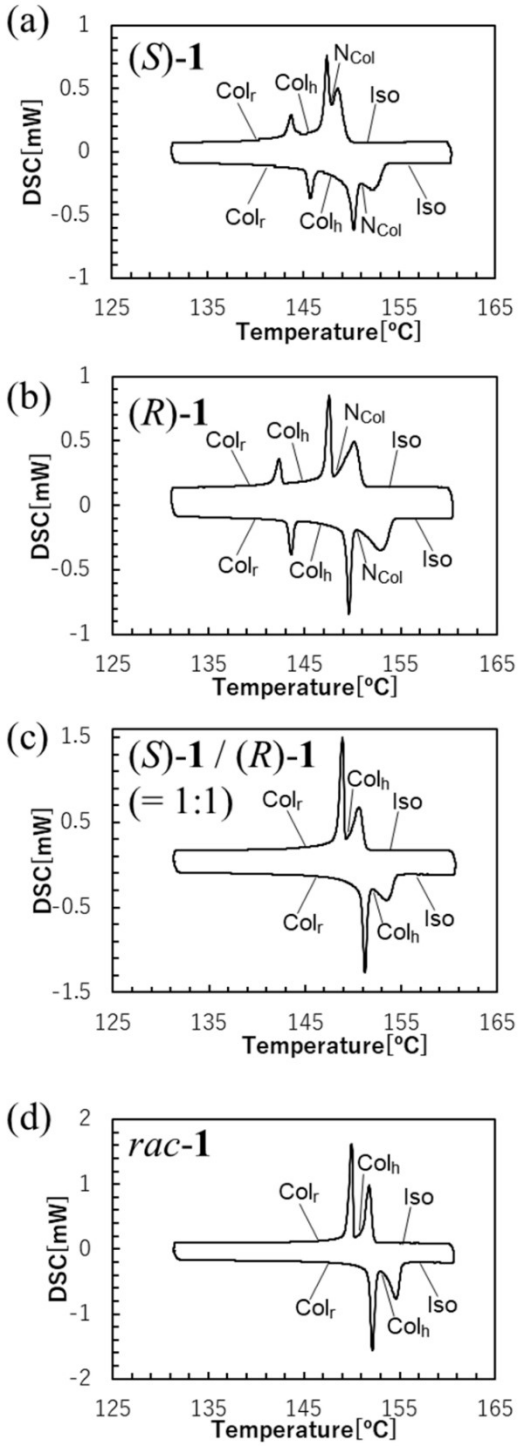

Figure S4. DSC tracs of **1**; (a) (*S*)-**1**, (b) (*R*)-**1**, (c) 1:1 mixture of (*S*)-**1** and (*R*)-**1**, and (d) *rac*-**1**.

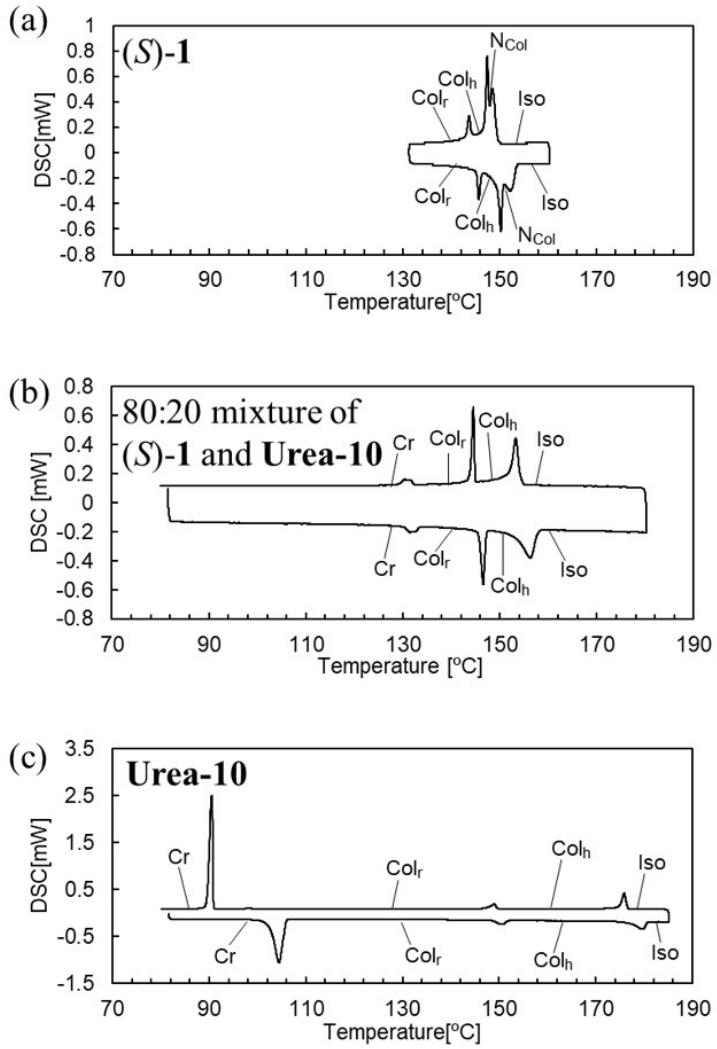

Figure S5. DSC tracs of **1** and **Urea-10**; (a) (*S*)-**1**, (b) 80:20 mixture of (*S*)-**1** and **Urea-10**, and (c) **Urea-10**.