

Synthesis of Enantiopure 1,8-Di(1-adamantyl)naphthalenes Stable at Ambient Temperatures

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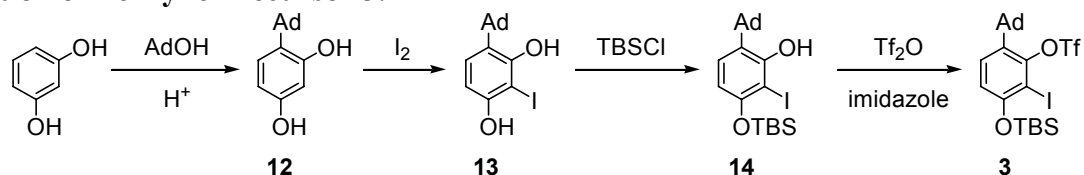
Supporting Informations

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General Methods. NMR spectra were measured at 600 MHz for ^1H and 150 MHz for ^{13}C by JEOL JNM-ECA600, and 400 MHz for ^1H and 100 MHz for ^{13}C by Varian 400-MR spectrometer. Chemical shifts of ^1H NMR were expressed in parts per million downfield from tetramethylsilane as the internal standard in CDCl_3 . Chemical shifts of ^{13}C NMR were expressed in parts per million downfield from CDCl_3 as an internal standard (δ 77.0) in CDCl_3 . Melting points were determined with a Yanaco micro melting point apparatus without correction. Elemental analyses were conducted with a Yanaco CHN CORDER MT-6. IR spectra were measured on a JASCO FT/IR-400 spectrophotometer. High performance liquid chromatography (HPLC) was performed on Agilent 1100 series system with Daicel Chiralcel[®] and Chiralpak[®] columns in hexane/isopropanol mixtures. Optical rotations were measured on a JASCO DIP-340 digital polarimeter. CD spectra were measured on a JASCO J-720 spectropolarimeter with PTC-423L Peltier type constant-temperature unit. High resolution mass spectra (HRMS) were performed on JEOL JMS-700 MStation spectrometer. X-ray diffraction data were recorded on Rigaku R-AxisIP and Bruker APEX-II CCD. For thin layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (silica gel 60 F₂₅₄) were used. The products were purified by flash column chromatography on silica gel 60N (KANTO, 40-50 μm).

Preparation of Benzyne Precursor 3.



4-(1-Adamantyl)-2-iodobenzene-1,3-diol 13

To a mixture of 4-(1-adamantyl)benzene-1,3-diol **12**^[1] (44 g, 180 mmol) and anhydrous sodium hydrogen carbonate (17 g, 200 mmol) in tetrahydrofuran (180 mL) and water (180 mL) was slowly added iodine (49 g, 190 mmol) in portions at 0 °C with vigorous stirring. Strong evolution of CO₂ occurred during the addition. The mixture was warmed to room temperature, and stirred for 30 min. The reaction was quenched by adding saturated aqueous sodium thiosulfate, and the organic materials were extracted with ethyl acetate. The combined organic layers were washed with saturated aqueous sodium thiosulfate, water, and brine, and dried over anhydrous magnesium sulfate. The solvents were

evaporated under reduced pressure, and the crude compound was recrystallized from hexane/toluene to give **13** (57g, 86%): colorless crystals. Mp 164-166 °C (dec). ¹H NMR (CDCl₃, 600 MHz) δ 1.71-1.82 (6H, m), 1.99-2.12 (9H, m), 5.10 (1H, s), 5.45 (1H, s), 6.51 (1H, d, *J* = 8.6 Hz), 7.07 (1H, d, *J* = 8.6 Hz). ¹³C NMR (CDCl₃, 150 MHz) δ 29.0, 36.8, 37.0, 40.6, 81.8, 106.4, 127.8, 129.5, 153.1, 153.3. IR (KBr) 3533, 3464, 2900, 2842, 1419, 1003, 795, 613 cm⁻¹. LRMS (EI) *m/z* 370 (M⁺, 100), 313 (M⁺ -57, 42), 276 (M⁺ -94, 16), 186 (M⁺ -184, 18). HRMS *m/z* calcd for C₁₆H₁₉IO₂: 370.0430, found: 370.0423. Anal. Calcd for C₁₆H₁₉IO₂: C, 51.91; H, 5.17. Found: C, 51.70; H, 5.17.

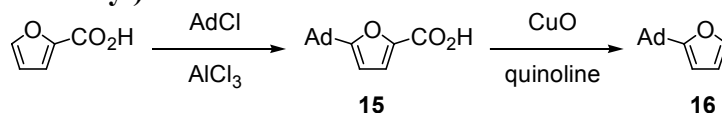
6-(1-Adamantyl)-3-(*t*-butyldimethylsilyloxy)-2-iodophenol 14

Under an argon atmosphere, a solution of **13** (37 g, 100 mmol), imidazole (15 g, 220 mmol), and *t*-butyldimethylsilyl chloride (16.6 g, 110 mmol) in *N,N*-dimethylformamide (52 mL) was stirred at room temperature for 1 h. The mixture was diluted with toluene, and cooled to 0 °C, to which saturated aqueous sodium hydrogen carbonate was added. The organic materials were extracted with toluene. The combined organic layers were washed with water and brine, and dried over anhydrous magnesium sulfate. The solvent was evaporated under reduced pressure, and the crude compound was recrystallized from methanol to give **14** (44.2 g, 91%): colorless crystals. Mp 125-126 °C. ¹H NMR (CDCl₃, 600 MHz) δ 0.27 (6H, s), 1.05 (9H, s), 1.71-1.80 (6H, m), 2.04-2.10 (9H, m), 5.64 (1H, s), 6.36 (1H, d, *J* = 8.6 Hz), 7.01 (1H, d, *J* = 8.6 Hz). ¹³C NMR (CDCl₃, 150 MHz) δ -4.1, 18.3, 25.8, 29.1, 36.8, 37.1, 40.6, 86.9, 109.2, 127.0, 129.7, 153.4, 154.0; LRMS (EI) *m/z* 484 (M⁺, 10), 427 (M⁺ -57, 100), 300 (M⁺ -184, 6), 135 (M⁺ -249, 6); HRMS *m/z* calcd for C₂₂H₃₃IO₂Si: 484.1294, found: 484.1297. IR (KBr) 3469, 2906, 2850, 1597, 1485, 1313, 1047, 839 cm⁻¹. Anal. Calcd for C₂₂H₃₃IO₂Si: C, 54.54; H, 6.87. Found: C, 54.41; H, 6.76.

6-(1-Adamantyl)-3-(*t*-butyldimethylsilyloxy)-2-iodophenyl trifluoromethanesulfonate 3

Under an argon atmosphere, a mixture of sodium hydride (60 % oil dispersion, 3.6 g, 90 mmol) in diethyl ether (18 mL) was cooled to 0 °C. To the suspension was slowly added **14** (29.1 g, 60 mmol) in diethyl ether (78 mL) at 0 °C with vigorous stirring. Strong evolution of H₂ occurred during the addition. The mixture was then heated at reflux for 30 min, and stirred at room temperature for 12 h. The mixture was cooled to 0 °C, to which trifluoromethanesulfonic anhydride (11.1 mL, 66 mmol) was added. The mixture was stirred for 30 min at room temperature, and the reaction was quenched by adding saturated aqueous sodium hydrogen carbonate at 0 °C. The organic materials were extracted with diethyl ether. The combined organic layers were washed with water and brine, and dried over anhydrous magnesium sulfate. The solvents were evaporated under reduced pressure, and the crude compound was recrystallized from methanol to give **3** (33.3 g, 90%): colorless crystals. Mp 97-99 °C. ¹H NMR (CDCl₃, 400 MHz) δ 0.29 (6H, s), 1.06 (9H, s), 1.70-1.81 (6H, br m), 1.79-2.11 (9H, br m), 6.80 (1H, d, *J* = 9.0 Hz), 7.45 (1H, d, *J* = 9.0 Hz). ¹³C NMR (100 MHz, CDCl₃) δ -4.1, 18.4, 25.8, 29.1, 36.4, 38.9, 42.3, 88.9, 117.4, 118.5(q, *J* = 321 Hz), 130.2, 138.3, 145.5, 155.2. LRMS (EI) *m/z* 616 (M⁺, 1), 559 (M⁺ -57, 100), 426 (M⁺ -190, 29), 407 (M⁺ -209, 10), 135 (M⁺ -481, 4). HRMS *m/z* calcd for C₂₃H₃₂F₃IO₄SSi: 616.0787, found 616.0792. IR (KBr) 2906, 2859, 1466, 1406, 1225, 1134, 1005, 804 cm⁻¹; Anal. Calcd for C₂₃H₃₂F₃IO₄SSi: C, 44.81; H, 5.23; F, 9.24; I, 20.58; S, 5.20. Found: C, 44.58; H, 5.25; F, 9.16; I, 20.39; S, 5.21.

Preparation of 2-(1-Adamantyl)furan 16



5-(1-Adamantyl)-2-furoic acid 15

Under an argon atmosphere, to 2-furoic acid (112.1 g, 1.00 mol) in methylene chloride (700 mL) was added aluminum chloride (266.7 g, 2.00 mol) in portions at the temperature below 10 °C. 1-Adamantyl chloride (170.7 g, 1.00 mol) in methylene chloride (300 mL) was added over 30 min. The mixture was allowed to warm to room temperature, and to stand at the temperature for 3 h. The mixture was carefully poured onto ice-water, and the organic materials were extracted with ethyl acetate. The combined organic layers were washed with water, and then with saturated aqueous potassium sodium tartrate until white precipitate disappeared. The organic layer was washed with brine, and dried over anhydrous magnesium sulfate. The solvents were evaporated under reduced pressure, and recrystallization (CHCl₃-hexane) gave **15** (159.7g, 65%): white powder. Mp 222-224 °C. ¹H NMR (CDCl₃, 400 MHz) δ 1.72-1.82 (6H, m), 1.92-2.02 (6H, m), 2.04-2.10 (3H, m), 6.12 (1H, d, *J* = 3.7 Hz), 7.25 (1H, d, *J* = 3.7 Hz), 11.72 (1H, br s). ¹³C NMR (CDCl₃, 100 MHz) δ 28.0, 35.1, 36.5, 40.7, 104.9, 121.4, 141.6, 163.8, 170.4. LRMS (EI) *m/z* 246 (M⁺, 100), 229 (M⁺-17, 2), 189 (M⁺-57, 50). HRMS *m/z* calcd for C₁₅H₁₈O₃: 246.1256, found: 246.1257. IR (KBr) 3300-2250, 2908, 2847, 1675 cm⁻¹. Anal. Calcd for C₁₅H₁₈O₃: C, 73.15; H, 7.37. Found: C, 73.05; H, 7.41.

2-(1-Adamantyl)furan 16

Under an argon atmosphere, a mixture of **15** (246.3 g, 1.00 mol), quinoline (740 mL), and copper (II) oxide (74.0 g) was stirred at 220 °C for 3 h. Strong evolution of CO₂ occurred during heating. The mixture was cooled to room temperature, and filtered through Celite pad to remove insoluble materials. The pad was washed with hexane. The filtrate was poured into saturated aqueous potassium hydrogen sulfate, and white precipitate generated was removed by filtration with Celite pad. The organic materials in the filtrate were extracted with hexane, and the combined organic layers were washed with saturated aqueous potassium hydrogen sulfate, water, and brine, and dried with anhydrous magnesium sulfate. The solvents were evaporated under reduced pressure, and silica gel column chromatography (hexane) gave **16** (172.5 g, 85%): colorless liquid. ¹H NMR (CDCl₃, 400 MHz) δ 1.70-1.80 (6H, m), 1.89-1.92 (6H, m), 2.01-2.06 (3H, m), 5.91 (1H, dd, *J* = 3.2, 0.9 Hz), 6.27 (1H, dd, *J* = 3.2, 1.8 Hz), 7.29 (1H, dd, *J* = 1.8, 0.9 Hz). ¹³C NMR (CDCl₃, 100 MHz) δ 28.2, 34.4, 36.7, 41.1, 101.2, 109.6, 140.3, 164.4. LRMS (EI) *m/z* 202 (M⁺, 100), 145 (M⁺-57, 86). HRMS *m/z* calcd for C₁₄H₁₈O: 202.1358, found: 202.1346; IR (KBr) 2905, 2850 cm⁻¹; Anal. Calcd for C₁₄H₁₈O: C, 83.12; H, 8.97. Found: C, 82.99; H, 8.96.

1,8-Di(1-adamantyl)-5-(*tert*-butyldimethylsilyloxy)-1,4-dihydro-1,4-epoxynaphthalene 4

Under an argon atmosphere, to a mixture of **3** (24.7 g, 40.0 mmol) and **16** (80.92 g, 400 mmol) at 40 °C was slowly added 1.0 M methyllithium in diethyl ether (80 mL, 80.0 mmol), and the mixture was stirred for 10 min at the temperature. The reaction was quenched by adding saturated aqueous ammonium chloride, and the organic materials were extracted with diethyl ether. The combined organic layers were washed with brine, and dried over anhydrous magnesium sulfate. The solvents were evaporated under reduced pressure, and silica gel column chromatography (hexane/toluene = 100/0 to 3/1) gave **4** (14.5 g, 67%) and unreacted **16** (71.7 g, 89 %): colorless crystals. Mp 193-194 °C (hexane). ¹H NMR (CDCl₃, 600 MHz) δ 0.17 (3H, s), 0.21 (3H, s), 1.00 (9H, s), 1.69-1.84 (12H, m), 1.93-1.96 (3H, m), 2.06-2.11 (9H, m), 2.23-2.26 (3H, m), 2.32-2.35 (3H, m), 5.76 (1H, d, *J* = 1.7 Hz), 6.41 (1H, d, *J* = 8.9 Hz), 6.89 (1H, dd, *J* = 5.5, 1.7 Hz), 6.94-6.96 (2H, m). ¹³C NMR (CDCl₃, 150 MHz) δ -4.2, -4.2, 18.1, 25.7, 28.8, 29.4, 36.6, 36.9, 38.0, 38.3, 39.0, 42.3, 76.1, 107.1, 115.9, 124.8,

140.5, 140.6, 141.2, 144.3, 146.1, 153.7. LRMS (EI) m/z 542 (M^+ , 40), 514 (M^+-28 , 27), 485 (M^+-57 , 11), 135 (M^+-407 , 100). HRMS m/z calcd for $C_{36}H_{50}O_2Si$: 542.3580, found: 542.3602. IR (KBr) 2906, 2847, 1616, 1487, 1294, 1134, 829 cm^{-1} ; Anal. Calcd for $C_{36}H_{50}O_2Si$: C, 79.65; H, 9.28. Found: C, 79.41; H, 9.36.

1,8-Di(1-adamantyl)-1,4-dihydro-5-methoxy-1,4-epoxynaphthalene 5

Under an argon atmosphere, to a mixture of **4** (13.4 g, 24.7 mmol), methyl iodide (3.1 mL, 49.5 mmol), and potassium carbonate (6.84 g, 49.5 mmol) in tetrahydrofuran (49.5 mL) was added 1.0 M tetrabutylammonium fluoride in tetrahydrofuran (27.2 mL, 27.2 mmol). The mixture was stirred for 30 min at room temperature, and then heated at reflux for 3 h. After cooled to room temperature, the reaction was quenched by adding saturated aqueous ammonium chloride, and the organic materials were extracted with toluene for three times. The combined organic layers were washed with water and brine, and dried over anhydrous magnesium sulfate. The solvents were evaporated under reduced pressure, and silica gel column chromatography (hexane/toluene = 1/2) gave **5** (10.7 g, 98%): colorless crystals. Mp 185-186 °C (hexane). 1H NMR ($CDCl_3$, 600 MHz) δ 1.69-1.84 (12H, m), 1.93-1.98 (3H, m), 2.06-2.12 (9H, m), 2.24-2.38 (6H, m), 3.78 (3H, s), 5.82-5.83 (1H, m), 6.55 (1H, d, $J = 8.9$ Hz), 6.92-6.94 (1H, m), 6.95-6.97 (1H, m), 7.07 (1H, d, $J = 8.9$ Hz). ^{13}C NMR ($CDCl_3$, 150 MHz) δ 28.8, 29.4, 36.5, 36.9, 38.0, 38.3, 39.0, 42.3, 55.3, 75.7, 107.1, 108.4, 125.2, 138.5, 140.7, 140.8, 144.6, 150.4, 153.8. LRMS (EI) m/z 442 (M^+ , 34), 414 (M^+-28 , 16), 290 (M^+-152 , 11), 135 (M^+-307 , 100). HRMS m/z calcd for $C_{31}H_{38}O_2$: 442.2872, found: 442.2862. IR (KBr) 2900, 2846, 1616, 1292, 1138, 1032 cm^{-1} . Anal. Calcd for $C_{31}H_{38}O_2$: C, 84.12; H, 8.65. Found: C, 84.15; H, 8.75.

4,5-Di(1-adamantyl)-8-methoxynaphthalen-1-ol *rac*-1

Under an argon atmosphere, to a solution of **5** (11.3 g, 25.5 mmol) in methylene chloride (51 mL) was added 2-bromopropionic acid (51 mL), and the mixture was stirred for 2 h at room temperature. Completion of the reaction was monitored by TLC, and the reaction mixture was poured into ice-water. Sodium hydrogen carbonate was slowly added at 0 °C to make the solution pH 8. Insoluble materials were removed by filtration through Celite pad, and the pad was washed with methylene chloride. The filtrate was extracted with methylene chloride. The combined organic layers were washed with water and brine, and dried over anhydrous magnesium sulfate. The solvents were evaporated under reduced pressure, and silica gel column chromatography (hexane/toluene = 1/2 to 1/3) gave *rac*-**1** (7.43 g, 66%): colorless amorphous solid. 1H NMR ($CDCl_3$, 600 MHz) δ 1.61-1.71 (18H, m), 1.95-1.98 (12H, m), 4.00 (3H, s), 6.61 (1H, d, $J = 8.2$ Hz), 6.71 (1H, d, $J = 8.2$ Hz), 7.38 (1H, d, $J = 8.2$ Hz), 7.43 (1H, d, $J = 8.2$ Hz), 9.19 (1H, s). ^{13}C NMR ($CDCl_3$, 150 MHz) δ 29.4, 36.8, 36.8, 41.4, 41.6, 44.0, 56.0, 102.3, 108.5, 117.8, 123.3, 125.6, 129.7, 140.0, 142.6, 152.0, 154.1. LRMS (EI) m/z 442 (M^+ , 49), 307 (M^+-135 , 100), 135 (M^+-307 , 27). HRMS m/z calcd for $C_{31}H_{38}O_2$: 442.2872, found: 442.2882. IR (KBr) 3398, 2900, 2844, 1610, 1448, 1257 cm^{-1} . Anal. Calcd for $C_{31}H_{38}O_2$: C, 84.12; H, 8.65. Found: C, 83.82; H, 8.62.

(1*S*)-(+)-Ketopinic acid esters of **1 (*M,S*)-**6** and (*P,S*)-**6****

Under an argon atmosphere, to a stirred solution of *rac*-**1** (5.08 g, 11.5 mmol) in tetrahydrofuran (34.5 mL) was added sodium hydride (60% oil dispersion, 0.688 g, 17.2 mmol) at room temperature. After stirring for 1 h, (1*S*)-7,7-dimethyl-2-oxobicyclo[2.2.1]heptane-1-carbonyl chloride (ketopinic acid chloride) (2.52 g, 12.6 mmol) was added, and the mixture was stirred for 1 h at room temperature. The reaction was quenched by adding saturated aqueous ammonium chloride, and the organic materials were extracted with diethyl ether. The combined organic layers were washed with brine, and dried over anhydrous magnesium sulfate. The solvents were evaporated under reduced pressure, and silica gel column chromatography (hexane/methylene chloride = 1/5) gave (*M,S*)-**6** (3.34 g, 48%) as

the first elution fraction, and (*P,S*)-**6** (3.26 g, 47%) as the second elution fraction. Alternatively, from the diastereomer mixture of **6**, (*P,S*)-**6** (45%, 99% de) was obtained by crystallization as a colorless crystal from dichloromethane. The other diastereomer (*M,S*)-**6** (40%, 99% de) was purified by recrystallization of remaining (*M,S*)-**6** dominant mixture from dichloromethane/hexane.

The de was determined on an OD-H column (hexane/isopropanol 9:1, flow 0.5 mL/min) with t_R 12.0 min for (*M,S*)-diastereomer, and t_R 20.2 min for (*P,S*)-diastereomer.

(*M,S*)-**6**: colorless crystals. Mp 180-184 °C. $[\alpha]_D^{23} +101.2$ (c 0.251, CHCl₃). ¹H NMR (CDCl₃, 600 MHz) δ 1.28 (3H, s), 1.29 (3H, s), 1.49-1.53 (1H, m), 1.56-1.71 (18H, m), 1.95-2.05 (14H, m), 2.11-2.18 (2H, m), 2.60-2.65 (2H, m), 3.83 (3H, s), 6.60 (1H, d, $J = 8.2$ Hz), 6.90 (1H, d, $J = 7.9$ Hz), 7.38 (1H, d, $J = 8.2$ Hz), 7.50 (1H, d, $J = 7.9$ Hz). ¹³C NMR (CDCl₃, 150 MHz) δ 19.9, 21.1, 26.6, 26.7, 29.4, 29.4, 36.8, 36.8, 41.4, 42.3, 43.9, 44.0, 44.0, 44.2, 49.2, 55.5, 67.7, 103.4, 117.2, 122.0, 123.4, 123.6, 129.4, 141.2, 143.8, 147.5, 153.5, 168.9, 210.5. LRMS (EI) m/z 606 (M^+ , 100), 471 ($M^+ - 135$, 35), 442 ($M^+ - 164$, 13), 165 ($M^+ - 441$, 88), 135 ($M^+ - 471$, 21). HRMS m/z calcd for C₄₁H₅₀O₄: 606.3709, found: 606.3711. IR (KBr) 2901, 2845, 1759, 1746 cm⁻¹. Anal. Calcd for C₄₁H₅₀O₄: C, 81.15; H, 8.30. Found: C, 80.95; H, 8.31.

(*P,S*)-**6**: colorless crystals. Mp 208-211 °C. $[\alpha]_D^{23} -86.6$ (c 0.251, CHCl₃). ¹H NMR (CDCl₃, 600 MHz) δ 1.26 (3H, s), 1.29 (3H, s), 1.48-1.53 (1H, m), 1.60-1.70 (18H, m), 1.91-2.05 (14H, br m), 2.11-2.18 (2H, m), 2.57-2.64 (2H, m), 3.83 (3H, s), 6.59 (1H, d, $J = 7.9$ Hz), 6.88 (1H, d, $J = 7.9$ Hz), 7.38 (1H, d, $J = 7.9$ Hz), 7.49 (1H, d, $J = 7.9$ Hz). ¹³C NMR (CDCl₃, 150 MHz) δ 19.9, 21.2, 26.6, 26.8, 29.4, 29.4, 36.7, 36.8, 41.4, 42.3, 43.9, 43.9, 44.0, 44.3, 49.3, 55.4, 67.7, 103.2, 117.1, 122.1, 123.4, 123.5, 129.4, 141.1, 143.8, 147.5, 153.5, 168.7, 210.4. LRMS (EI) m/z 606 (M^+ , 100), 471 ($M^+ - 135$, 35), 442 ($M^+ - 164$, 13), 165 ($M^+ - 441$, 74), 135 ($M^+ - 471$, 16). HRMS m/z calcd for C₄₁H₅₀O₄: 606.3709, found: 606.3700. IR (KBr) 2903, 2846, 1760, 1742, 1587, 1450 cm⁻¹. Anal. Calcd for C₄₁H₅₀O₄: C, 81.15; H, 8.30. Found: C, 80.85; H, 8.05.

(*P*)-4,5-Di(1-adamantyl)-1,8-dimethoxynaphthalene (*P*)-**7**

Under an argon atmosphere, to a solution of (*P,S*)-**6** (3.26 g, 5.38 mmol) in tetrahydrofuran (53.8 mL) was added 0.93 M diisobutylaluminum hydride in hexane (28.9 mL, 26.9 mmol) at -78 °C. After warmed to room temperature, the mixture was stirred for 2 h. The reaction was quenched by adding saturated aqueous potassium sodium tartrate at 0 °C, and the mixture was stirred for 1 h. The organic materials were extracted with ethyl acetate. The organic layer was washed with water and brine, and dried over sodium sulfate. The solvents were evaporated under reduced pressure, and silica gel chromatography (hexane/toluene = 1/2) gave (*P*)-**1** (2.35g, 99%, 99% ee, $[\alpha]_D^{24} +21.2$ (c 0.250, CHCl₃)). The ee of (*P*)-**1** was determined on an OD-H column (hexane/isopropanol 9:1, flow 0.5mL/min) with t_R (minor) 9.4 min, t_R (major) 10.6 min.

Under an argon atmosphere, to a solution of (*P*)-**1** in tetrahydrofuran (53.8 mL) was added sodium hydride (60% oil dispersion, 0.323 g, 8.07 mmol) at 0 °C, and the mixture was stirred for 1 h at room temperature. Dimethyl sulfate (1.0 mL, 10.8 mmol) was added, and the mixture was stirred at room temperature for 15 h. Then, 4 M aqueous sodium hydroxide was added, and the mixture was stirred overnight. The organic materials were extracted with methylene chloride. The combined organic layers were washed with saturated aqueous ammonium chloride, water and brine, and dried over anhydrous magnesium sulfate. The solvents were evaporated under reduced pressure, and silica gel column chromatography (toluene) gave (*P*)-**7** (2.33g, 96%, 99% ee): The ee of (*P*)-**7** was determined on an OD-H column (hexane/isopropanol 15:1, flow 0.5 mL/min) with t_R (minor) 9.3 min, t_R (major) 9.9 min. $[\alpha]_D^{23} -4.2$ (c 0.250, CHCl₃). colorless amorphous solid. ¹H NMR (CDCl₃, 400 MHz) δ 1.60-1.69 (18H, br m), 1.92-1.99 (12H, br m), 3.92 (6H, s), 6.63 (2H, d, $J = 8.0$ Hz), 7.37 (2H, d, $J = 8.0$ Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 29.4, 36.8, 41.3, 43.9, 56.4, 103.9, 120.6, 123.4, 130.4, 141.0, 154.7. LRMS (EI) m/z 456 (M^+ , 62), 322 ($M^+ - 134$, 100), 321 ($M^+ - 135$, 90), 135 ($M^+ - 321$, 24). HRMS m/z

calcd for C₃₂H₄₀O₂: 456.3028, found: 456.3040. IR (KBr) 2900, 2844, 1577, 1449, 1267, 782, 653 cm⁻¹. Anal. Calcd for C₃₂H₄₀O₂: C, 84.16; H, 8.83. Found: C, 84.18; H, 8.83.

(P)-4,5-Di(1-adamantyl)-1-benzyloxy-8-methoxynaphthalene (P)-17

Under an argon atmosphere, to a solution of (P)-1 (0.11 g, 0.25 mmol) in *N,N*-dimethylformamide (2 mL) was added sodium hydride (60% oil dispersion, 22 mg, 0.55 mmol) at 0 °C. The mixture was warmed to room temperature, and benzyl bromide (0.045 mL, 0.38 mmol) was added. After stirred at room temperature for 1.5 h, the reaction was quenched by adding of saturated aqueous ammonium chloride, and the organic materials were extracted with ethyl acetate. The combined organic layers were washed with water and brine, and dried over anhydrous magnesium sulfate. The solvents were evaporated under reduced pressure, and silica gel column chromatography (hexane/toluene = 3/1) gave (P)-17 (102.4 mg, 77%, 99% ee): The ee of (P)-17 was determined on an OD-H column (hexane/isopropanol 15:1, flow 0.5 mL/min) with *t*_R (minor) 8.2 min, *t*_R (major) 8.9 min. [α]_D²⁴ -77.0 (c 0.250, CHCl₃). White amorphous solid. ¹H NMR (CDCl₃, 400 MHz) δ 1.55-1.75 (18H, br m), 1.89-2.05 (12H, br m), 3.90 (3H, s), 5.14 (1H, d, *J* = 11.8 Hz), 5.15 (1H, d, *J* = 11.8 Hz), 6.64 (1H, d, *J* = 8.0 Hz), 6.74 (1H, d, *J* = 8.0 Hz), 7.31 (1H, td, *J* = 7.3, 1.9 Hz), 7.35-7.42 (4H, m), 7.56-7.60 (2H, m). ¹³C NMR (CDCl₃, 100 MHz) δ 29.4, 36.8, 41.3, 41.4, 44.0, 56.2, 71.8, 103.8, 106.6, 121.1, 123.4, 123.5, 127.1, 127.3, 128.2, 130.5, 138.0, 141.0, 141.8, 153.7, 154.9. LRMS (EI) *m/z* 532 (M⁺, 100), 441 (M⁺-91, 25), 397 (M⁺-135, 83), 305 (M⁺-227, 14), 135 (M⁺-397, 77). HRMS *m/z* calcd for C₃₈H₄₄O₂: 532.3341, found: 532.3336. IR (KBr) 2900, 2844, 1577, 1451, 1350, 1267, 1125, 1051 cm⁻¹. Anal. Calcd for C₃₈H₄₄O₂: C, 85.67; H, 8.32. Found: C, 85.52; H, 8.41.

(P)-4,5-Di(1-adamantyl)-8-methoxynaphthalen-1-yl acetate (P)-8

Under an argon atmosphere, to a solution of (P)-1 (0.11 g, 0.25 mmol) and 4-*N,N*-dimethylaminopyridine (6 mg, 0.05 mmol) in pyridine (5 mL) was added acetic anhydride (0.05 mL, 0.5 mmol) at room temperature. After stirred at room temperature for 30 min, the reaction was quenched by saturated aqueous sodium hydrogen carbonate, and organic materials were extracted with ether. The combined organic layers were washed with saturated aqueous potassium hydrogen sulfate, water and brine, and dried over anhydrous magnesium sulfate. The solvents were evaporated under reduced pressure, and silica gel column chromatography (hexane/ethyl acetate = 10/1 to 5/1) gave (P)-8 (84.6 mg, 70%, 98% ee): The ee of (P)-8 was determined on an OD-H column (hexane/isopropanol 9:1, flow 0.5 mL/min) with *t*_R (minor) 8.8 min, *t*_R (major) 10.0 min. [α]_D²² -49.3 (c 0.250, CHCl₃). Colorless microneedle. Mp 176-178 °C (hexane-ether). ¹H NMR (CDCl₃, 400 MHz) δ 1.60-1.72 (18H, br m), 1.90-2.00 (12H, br m), 2.31 (3H, s), 3.87 (3H, s), 6.61 (1H, d, *J* = 8.0 Hz), 6.84 (1H, d, *J* = 7.8 Hz), 7.40 (1H, d, *J* = 8.0 Hz), 7.50 (1H, d, *J* = 7.8 Hz). ¹³C NMR (CDCl₃, 100 MHz) δ 21.0, 29.3, 29.4, 36.7, 36.8, 41.5, 42.2, 43.9, 55.9, 103.7, 116.9, 121.6, 123.4, 123.6, 129.4, 141.6, 143.7, 147.4, 153.1, 170.2. LRMS (EI) *m/z* 484 (M⁺, 74), 442 (M⁺-42, 100), 349 (M⁺-135, 27), 307 (M⁺-177, 96), 135 (M⁺-349, 68). HRMS *m/z* calcd for C₃₃H₄₀O₃: 484.2977, found: 484.2966. IR (KBr) 2898, 2844, 1767, 1591, 1362, 1205, 1108 cm⁻¹. Anal. Calcd for C₃₃H₄₀O₃: C, 81.78; H, 8.32. Found: C, 81.92; H, 8.39.

(P)-4,5-Di(1-adamantyl)-2,7-dibromo-1,8-dimethoxynaphthalene (P)-9

Under an argon atmosphere, a mixture of (P)-7 (2.28 g, 4.98 mmol) and cyclohexene oxide (1.26 mL, 12.5 mmol) in methylene chloride (49.8 mL) was stirred with heating at reflux. Then portions of benzyltrimethylammonium tribromide^[2] (4.28 g, 11.0 mmol) in methylene chloride (24.9 mL) was slowly added over 10 min. After 5 min, the reaction was quenched by adding saturated aqueous sodium thiosulfate, and the organic materials were extracted with methylene chloride. The combined

organic layers were washed with water and brine, and dried over anhydrous magnesium sulfate. The solvents were evaporated under reduced pressure, and silica gel column chromatography (hexane/toluene = 2/1) gave (*P*)-**9** (2.00 g, 65%): $[\alpha]_{\text{D}}^{23} -16.6$ (c 0.250, CHCl₃). colorless crystals. Mp > 260 °C (toluene-hexane). ¹H NMR (CDCl₃, 400 MHz) δ 1.58-1.71 (18H, br m), 1.87-2.03 (12H, br m), 3.88 (6H, s), 7.56 (2H, s). ¹³C NMR (CDCl₃, 100 MHz) δ 29.2, 36.5, 42.2, 43.7, 62.2, 113.5, 126.2, 127.8, 128.8, 147.4, 149.1. LRMS (EI) *m/z* 614 (M⁺+2, 19), 612 (M⁺, 10), 135 (Ad⁺, 100). HRMS *m/z* calcd for C₃₂H₃₈Br₂O₂: 612.1239, found: 612.1254. IR (KBr) 2898, 2848, 1550, 1339, 1135, 1001 cm⁻¹. Anal. Calcd for C₃₂H₃₈Br₂O₂: C, 62.55; H, 6.23. Found: C, 62.33; H, 6.35.

(*P*)-4,5-Di(1-adamantyl)-1,8-dimethoxynaphthalene-2,7-dicarbaldehyde (*P*)-**10**

Under an argon atmosphere, to a solution of (*P*)-**9** (1.99 g, 3.23 mmol) in toluene (161 mL) was slowly added 1.56 M *n*-butyllithium in hexane (10.4 mL, 16.2 mmol) in portions at 0 °C. After 30 min, *N,N*-dimethylformamide (2.5 mL, 32.3 mmol) was added, and the mixture was stirred for 10 min at 0 °C. The reaction was quenched by adding saturated aqueous ammonium chloride, and the organic materials were extracted with toluene. The combined organic layers were washed with water and brine, and dried over anhydrous magnesium sulfate. The solvents were evaporated under reduced pressure, and silica gel column chromatography (toluene/ethyl acetate = 100/1) gave (*P*)-**10** (1.39 g, 84%, 99% ee): The ee of (*P*)-**10** was determined on an OD-H column (hexane/isopropanol 99:1, flow 0.3 mL/min) with *t*_R (major) 27.8 min, *t*_R (minor) 30.3 min. $[\alpha]_{\text{D}}^{22} -57.6$ (c 0.250, CHCl₃). yellow microneedle. Mp > 260 °C (ethyl acetate). ¹H NMR (CDCl₃, 400 MHz) δ 1.61-1.70 (18H, br m), 1.90-2.02 (12H, br m), 4.01 (6H, s), 7.95 (2H, s), 10.54 (2H, s). ¹³C NMR (CDCl₃, 100 MHz) δ 29.2, 36.4, 42.3, 43.7, 65.8, 121.9, 123.7, 124.6, 139.4, 147.5, 160.3, 189.7. LRMS (EI) *m/z* 512 (M⁺, 38), 377 (M⁺-135, 78), 135 (M⁺-377, 100). HRMS *m/z* calcd for C₃₄H₄₀O₄: 512.2927, found: 512.2918. IR (KBr) 2902, 2846, 1677, 1576, 1343, 1001 cm⁻¹. Anal. Calcd for C₃₄H₄₀O₄: C, 79.65; H, 7.86. Found: C, 79.39; H, 8.05.

Enantiomerization Barrier of 1,8-Di(adamantyl)naphthalenes Obtained by CD

Enantiomerization barriers of 1,8-di(1-adamantyl)naphthalene derivatives (*P,S*)-**6**, (*P*)-**7**, (*P*)-**8**, (*P*)-**9**, and (*P*)-**10** were obtained by CD. Sample solution was prepared in a quartz cell at room temperature. The sample cell was set into preheated Peltier type constant-temperature unit, and then immediately started to measure θ (deg) at 330 nm for (*P,S*)-**6**, (*P*)-**7**, (*P*)-**8**, and (*P*)-**9** and 370 nm for (*P*)-**10**. The CD intensity value θ (deg) was used after the Peltier unit indicated that the sample temperature reached to the setting temperature; setting temp./time-to-setting temp. were 90°C/35s, 95°C/50s, 100°C/65s, 105°C/105s, and 110°C/265s. The initial CD intensity θ_0 (deg) was estimated by extrapolation.

The enantiomerization rate constant k (s⁻¹) was obtained using following equations, where $[M]$, $[P]$, $[P]_0$ are concentration of (*M*)-enantiomer, (*P*)-enantiomer, and initial concentration of (*P*)-enantiomer, respectively. Rate constants of (*P*)-isomer and (*M*)-isomer were identical each other, and after a time long enough to reach equilibrium, θ (deg) should be zero.

Total concentration of (*P*) and (*M*) isomer is constant, and equal to $[P]_0$.

$$[M] = [P]_0 - [P] \quad (1)$$

From eq. (1), enantiomerization rate is obtained using eq. (2).

$$-\frac{d[P]}{dt} = k[P] - k[M] = k(2[P] - [P]_0) \quad (2)$$

The definite integral of eq. (2) gives eq.(3).

$$\ln \frac{2[P] - [P]_0}{[P]_0} = -2kt \quad (3)$$

Measured value θ has proportional to concentration, and therefore eq. (3) can be converted to eq. (4).

$$\ln \frac{\theta}{\theta_0} = -2kt \quad (4)$$

Rate constant k was obtained from the slope of the plot of time dependent $\ln(\theta/\theta_0)$ value. From k , Gibbs function of activation ΔG^\ddagger (kcal/mol) was obtained by eq. (5), where a statistical transmission factor κ was taken as 0.5 in the equation.^[3]

$$\Delta G^\ddagger = -RT \ln \frac{kh}{\kappa k_B T} \quad (5)$$

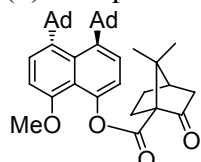
Activation parameters, ΔH^\ddagger (kcal/mol) and ΔS^\ddagger (cal/mol·K), were obtained by the Eyring plot. From the slope a of the Eyring plot, ΔH^\ddagger (kcal/mol) was obtained by eq. (6).

$$a = -\frac{\Delta H^\ddagger}{R} \quad (6)$$

From the y-axis intercept b of the Eyring plot, ΔS^\ddagger (cal/ mol·K) was obtained by eq. (7).

$$b = \ln \left(\frac{\kappa k_B}{h} \right) + \frac{\Delta S^\ddagger}{R} \quad (7)$$

(1) Ketopinic ester (*P,S*)-6



(*P,S*)-6

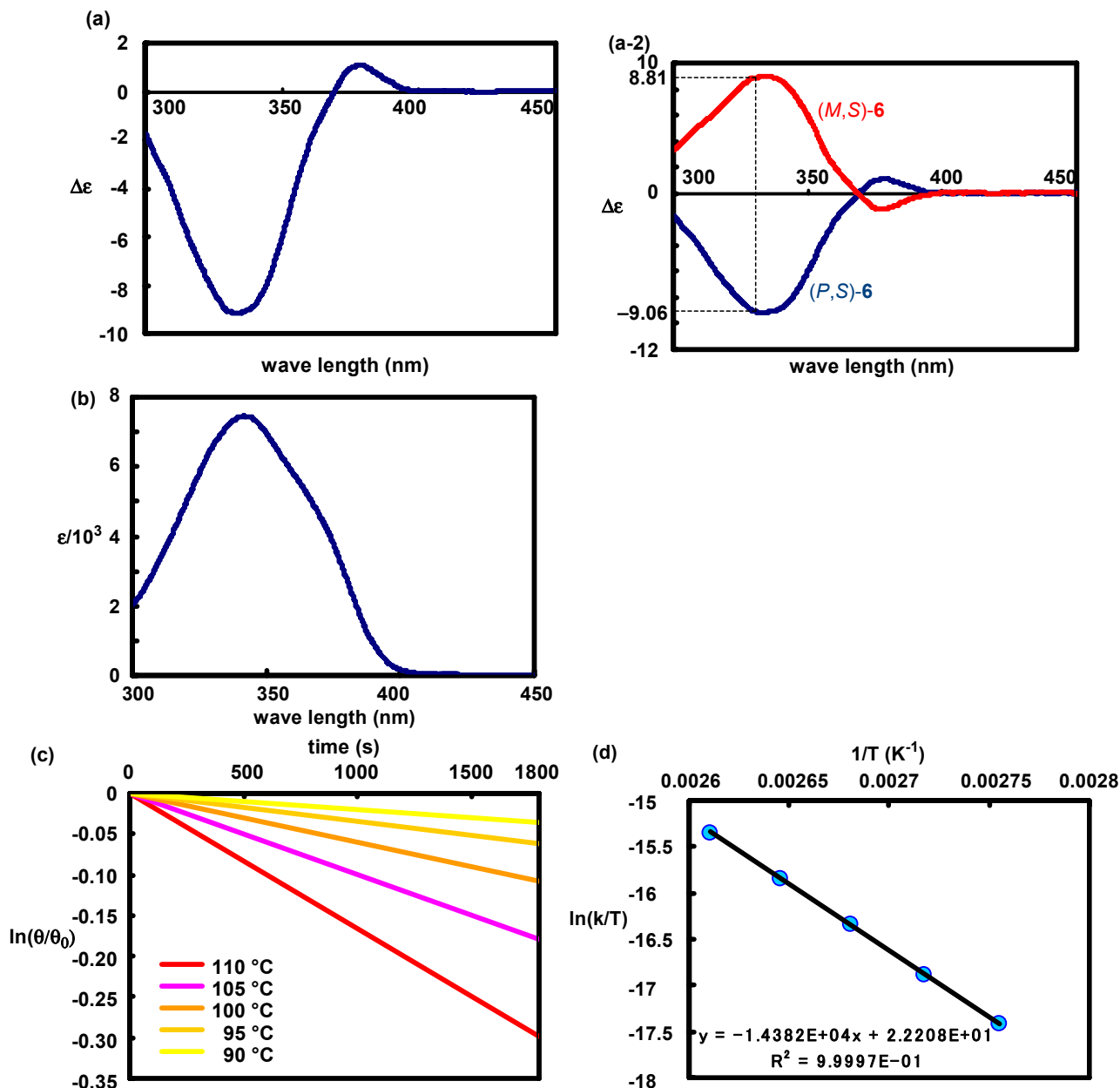
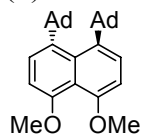


Figure S1. (a) CD spectra of (*P,S*)-6 (*o*-dichlorobenzene, 0.1 mM, 25 °C), (b) UV-vis spectra of (*P,S*)-6 (*o*-dichlorobenzene, 0.1 mM, 25 °C), (c) Reaction course obtained by θ at 330 nm of (*P,S*)-6 (*o*-dichlorobenzene, 0.1 mM) at each temperature, (d) The Eyring plots. The same experiments (c) and (d) were conducted twice to check reproducibility. For the estimation of enantiomerization barrier, (*P,S*)-6 and (*M,S*)-6 were assumed to have the same θ_0 and k values.

(2) Dimethyl ether (*P*)-7



(*P*)-7

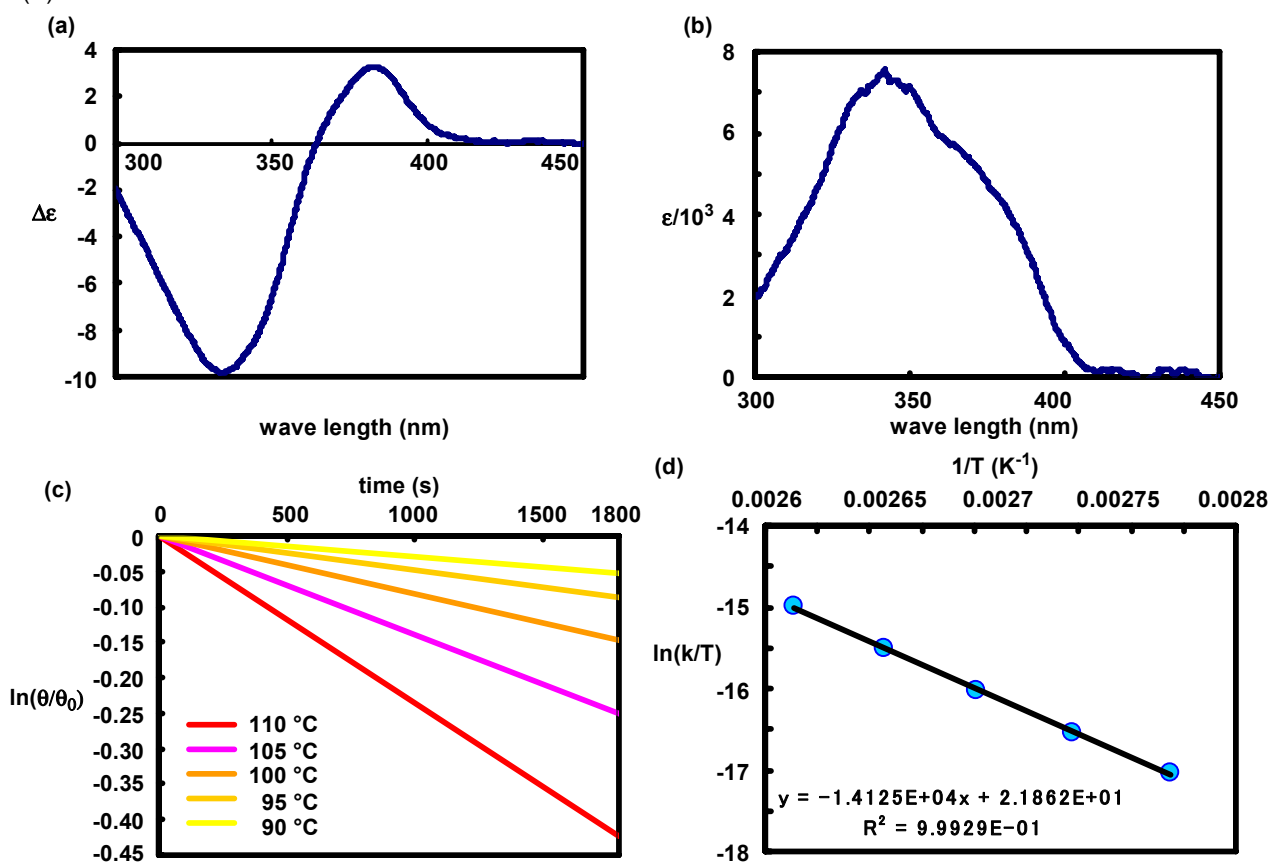


Figure S2. (a) CD spectra of (*P*)-7 (*o*-dichlorobenzene, 0.1 mM, 25 °C), (b) UV-vis spectra of (*P*)-7 (*o*-dichlorobenzene, 0.1 mM, 25 °C), (c) Reaction course obtained by θ at 330 nm of (*P*)-7 (*o*-dichlorobenzene, 0.1 mM) at each temperature, (d) The Eyring plots. The same experiments (c) and (d) were conducted twice to check reproducibility.

(3) benzyl methyl ether (*P*)-17

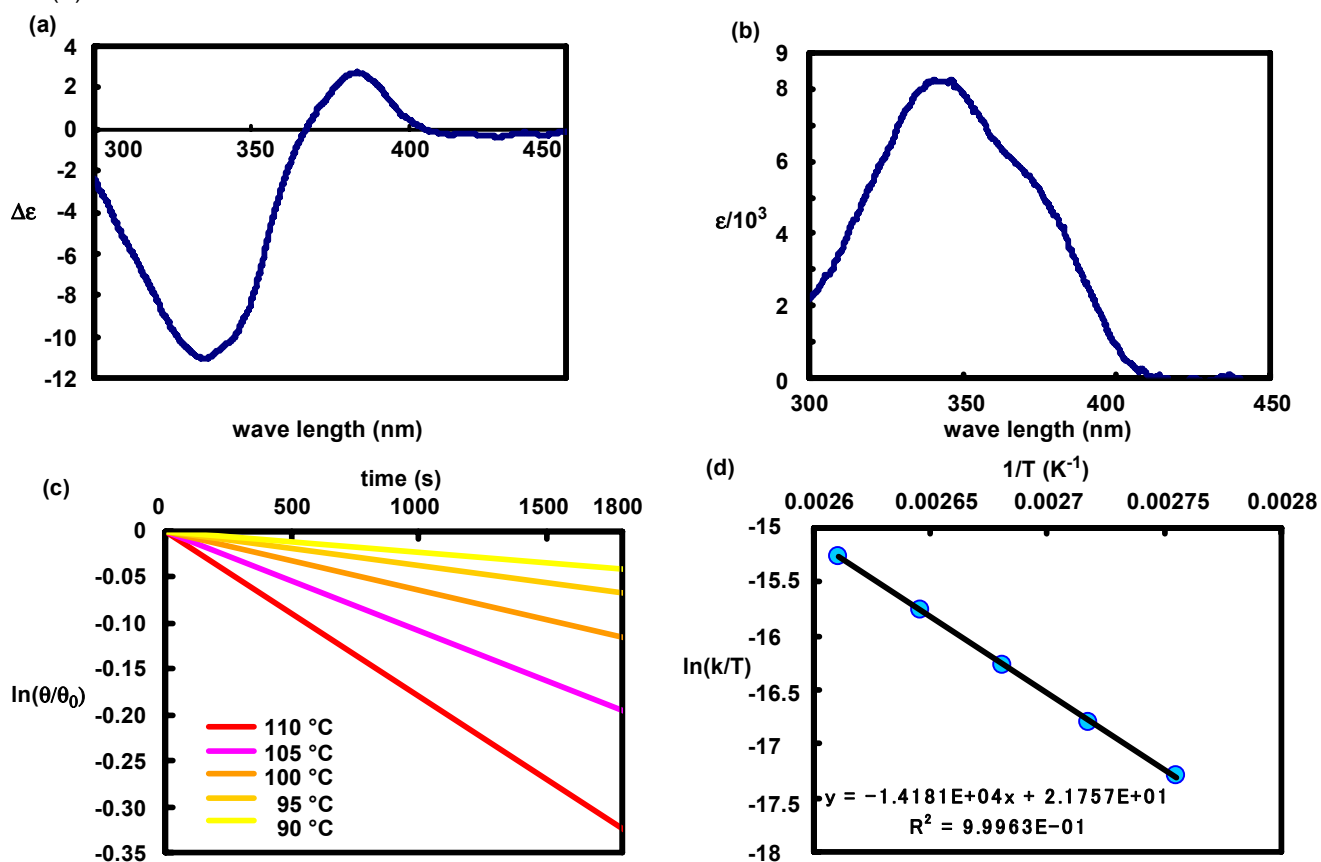
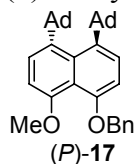
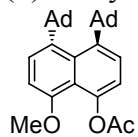


Figure S3. (a) CD spectra of (*P*)-17 (*o*-dichlorobenzene, 0.1 mM, 25 °C), (b) UV-vis spectra of (*P*)-17 (*o*-dichlorobenzene, 0.1 mM, 25 °C), (c) Reaction course obtained by θ at 330 nm of (*P*)-17 (*o*-dichlorobenzene, 0.1 mM) at each temperature, (d) The Eyring plots. The same experiments (c) and (d) were conducted twice to check reproducibility.

(4) Acetyl ester (*P*)-**8**



(*P*)-**8**

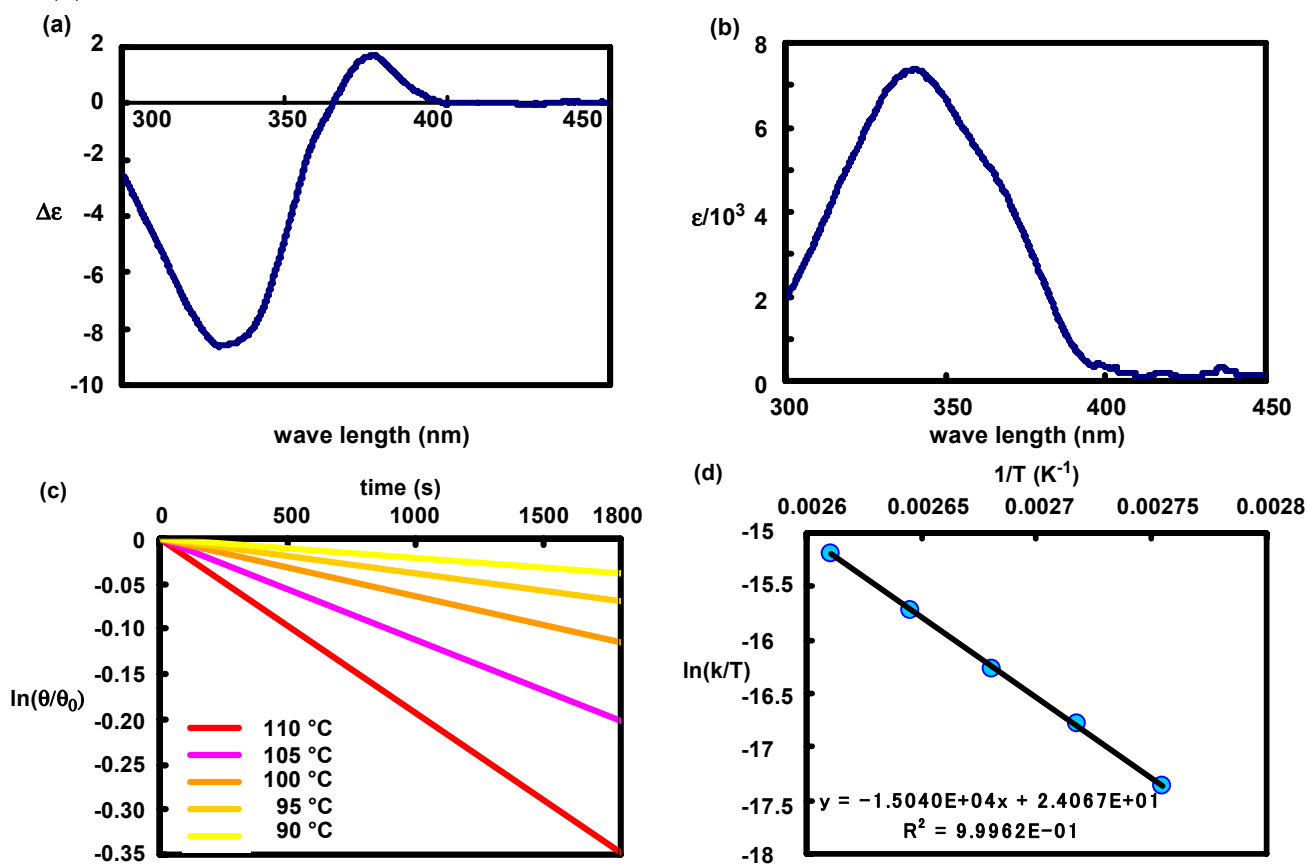


Figure S4. (a) CD spectra of (*P*)-**8** (*o*-benzene, 0.1 mM, 25 °C), (b) UV-vis spectra of (*P*)-**8** (*o*-dichlorobenzene, 0.1 mM, 25 °C), (c) Reaction course obtained by θ at 330 nm of (*P*)-**8** (*o*-dichlorobenzene, 0.1 mM) at each temperature, (d) The Eyring plots. The same experiments (c) and (d) were conducted twice to check reproducibility.

(5) 3,6-Dibromide (*P*)-9

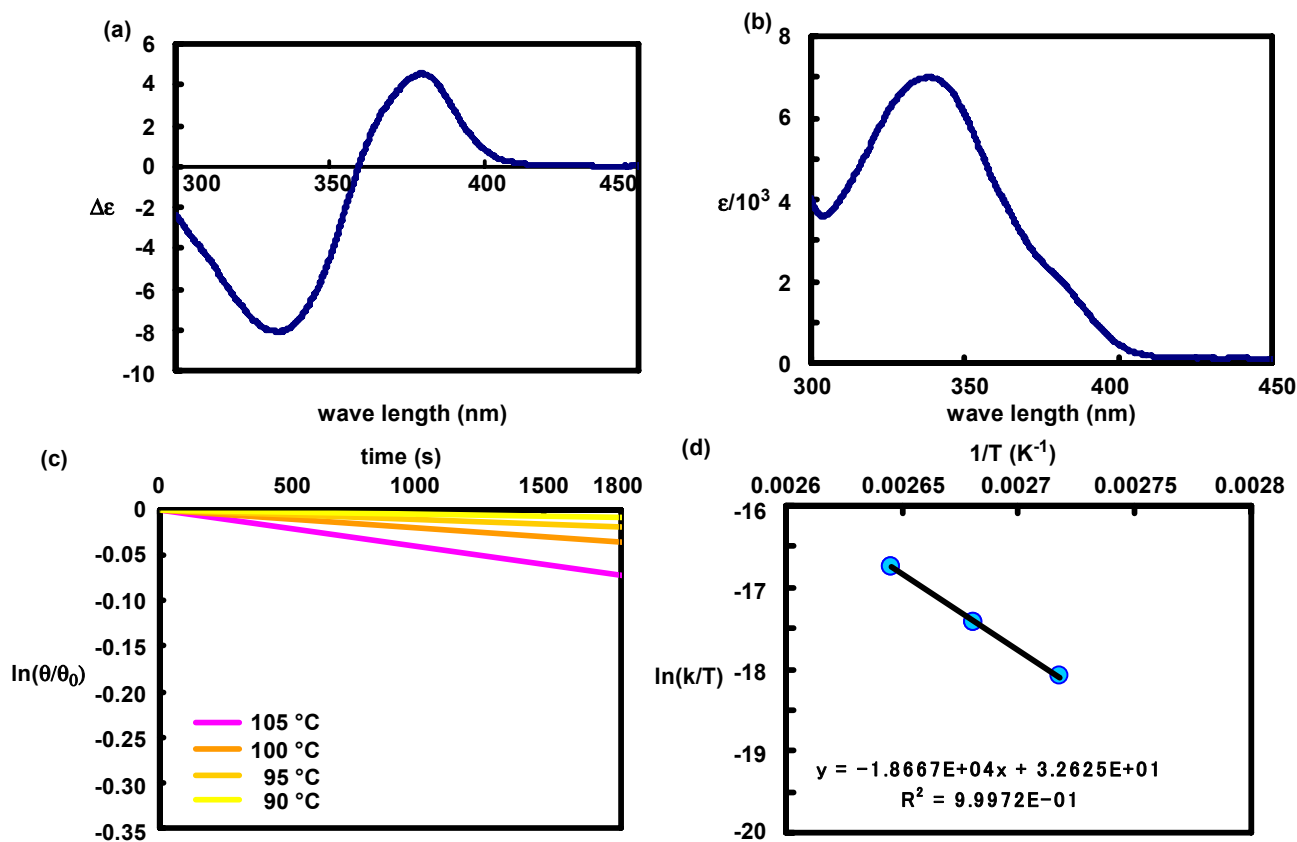
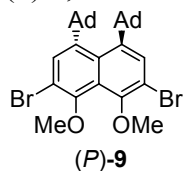


Figure S5. (a) CD spectra of (*P*)-9 (*o*-dichlorobenzene, 0.1 mM, 25 °C), (b) UV-vis spectra of (*P*)-9 (*o*-dichlorobenzene, 0.1 mM, 25 °C), (c-1) Reaction course obtained by θ at 330 nm of (*P*)-9 (*o*-dichlorobenzene, 0.1 mM) at each temperature, (d) The Eyring plots. The same experiments (c) and (d) were conducted twice to check reproducibility.

(6) 3,6-Dialdehyde (*P*)-10

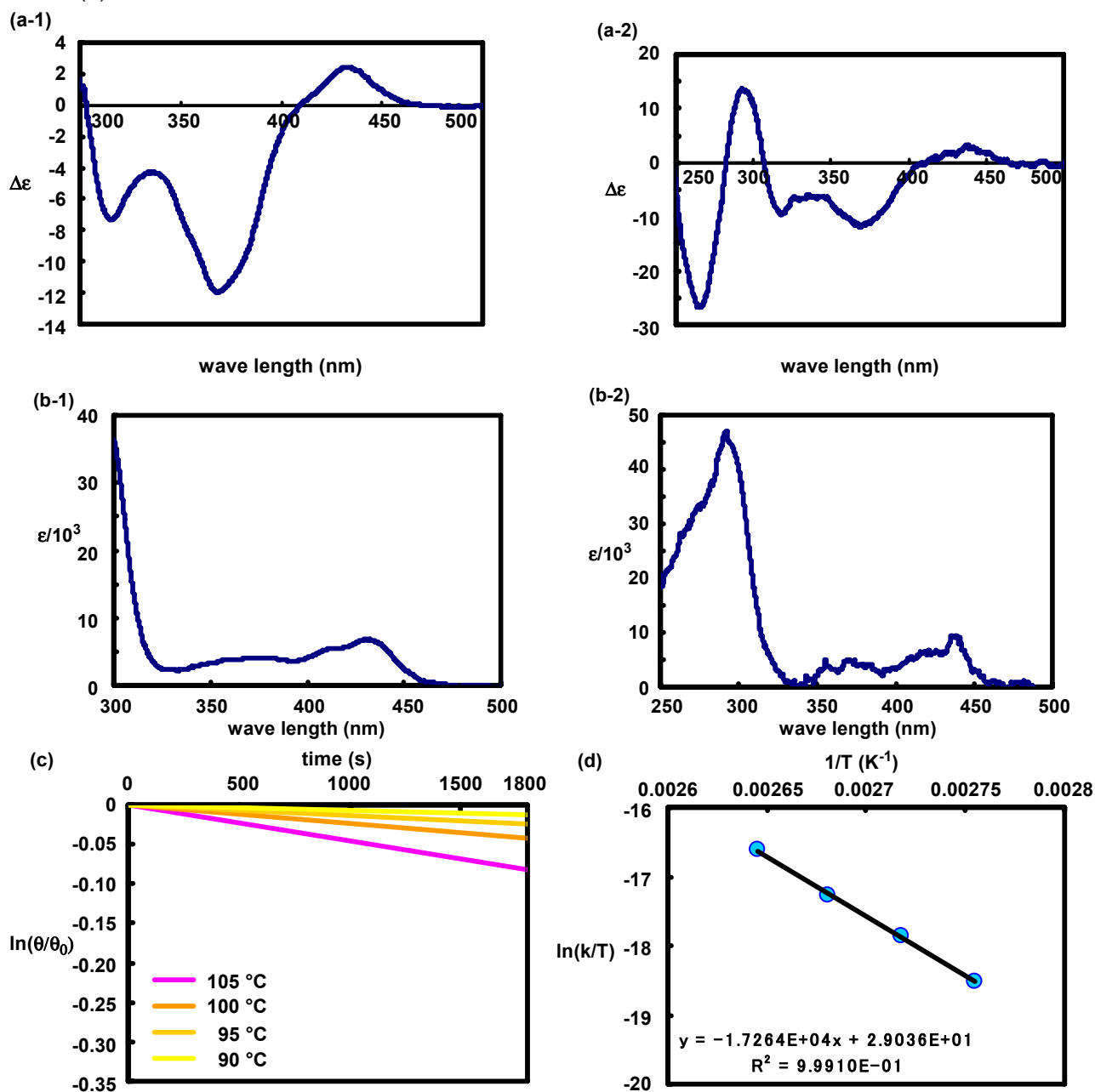
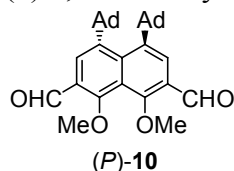


Figure S6. (a-1) CD spectra of (*P*)-10 (*o*-dichlorobenzene, 0.1 mM, 25 °C), (a-2) CD spectra of (*P*)-10 (CHCl_3 , 0.1 mM, 25 °C), (b-1) UV-vis spectra of (*P*)-10 (*o*-dichlorobenzene, 0.1 mM, 25 °C), (b-2) UV-vis spectra of (*P*)-10 (CHCl_3 , 0.1 mM, 25 °C), (c) Reaction course obtained by θ at 330 nm of (*P*)-10 (*o*-dichlorobenzene, 0.1 mM) at each temperature, (d) The Eyring plots. The same experiments (c) and (d) were conducted twice to check reproducibility.

Table S1. Summary of rate constant and activation energies

compound	R	temp. (K)	$k / 10^{-5}$ (s ⁻¹)	ΔG^\ddagger (kcal / mol)	E_a (kcal / mol)	ΔH^\ddagger (kcal / mol)	ΔS^\ddagger (cal / mol·K)
6	ketopinic	363	1.00	29.2	29.3	28.6	-1.7
		368	1.72	29.2			
		373	2.97	29.2			
		378	5.00	29.2			
		383	8.29	29.2			
6	ketopinic	363	0.96	29.2	27.8	27.0	-6.0
		368	1.69	29.2			
		373	2.83	29.2			
		378	4.64	29.3			
		383	6.45	29.4			
7	Me	363	1.20	29.0	29.5	28.7	-0.9
		368	1.97	29.1			
		373	3.75	29.0			
		378	5.40	29.1			
		383	10.4	29.0			
7	Me	363	1.47	28.9	28.8	28.0	-2.4
		368	2.42	28.9			
		373	4.07	29.0			
		378	6.98	29.0			
		383	11.7	29.0			
17	Bn	363	1.12	29.1	28.9	28.2	-2.6
		368	1.86	29.1			
		373	3.19	29.1			
		378	5.44	29.1			
		383	9.02	29.2			
17	Bn	363	1.11	29.1	29.7	29.0	-0.3
		368	1.99	29.1			
		373	3.45	29.1			
		378	5.89	29.1			
		383	9.53	29.1			

compound	R	temp. (K)	$k / 10^{-5}$ (s^{-1})	ΔG^\ddagger (kcal / mol)	E_a (kcal / mol)	ΔH^\ddagger (kcal / mol)	ΔS^\ddagger (cal / mol·K)
8	Ac	363	1.04	29.2	30.6	29.9	2.0
		368	1.90	29.1			
		373	3.19	29.1			
		378	5.60	29.1			
		383	9.66	29.1			
8	Ac	363	1.25	29.0	28.0	27.3	-4.8
		368	1.91	29.1			
		373	3.26	29.1			
		378	5.54	29.1			
		383	9.34	29.1			
9	3,6-Br	363	0.10	30.8	36.7	36.0	16.0
		368	0.53	30.1			
		373	1.01	30.0			
		378	2.00	29.9			
9	3,6-Br	363	0.21	30.3	37.8	37.1	19.0
		368	0.51	30.1			
		373	1.00	30.0			
		378	2.01	29.9			
10	3,6-CHO	363	0.33	30.0	36.1	34.3	11.9
		368	0.67	29.9			
		373	1.22	29.9			
		378	2.43	29.7			
10	3,6-CHO	363	0.33	30.0	35.0	35.4	14.9
		368	0.65	29.9			
		373	1.17	29.9			
		378	2.28	29.8			

Rate constant k was obtained by CD. Gibbs function of activation ΔG^\ddagger was calculated using k . The Arrhenius plot gave activation energy E_a , and the Eyring plot gave enthalpy of activation ΔH^\ddagger and entropy of activation ΔS^\ddagger .

X-ray crystal analysis^[4]

Selected data of (*P,S*)-**6**, (*P*)-**9**, and (*P*)-**11** are summarized in *Table S2-S5*. The numbering of atoms are based on the figure shown below. The absolute configuration of (*P*)-**9** was established by the Flack parameter (0.025(15)) using anomalous-dispersion effect.

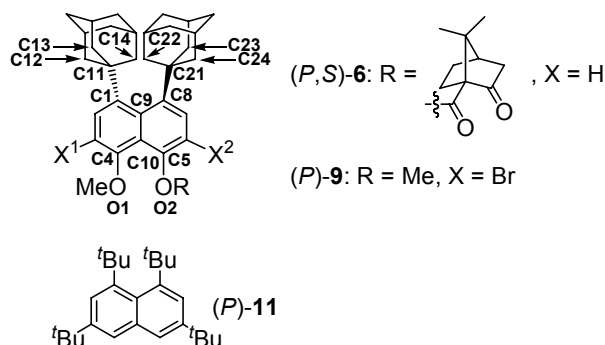


Table S2. Bond Length of (*P,S*)-**6**, (*P*)-**9**, and (*P*)-**11**

Bond	(<i>P,S</i>)- 6	(<i>P</i>)- 9	(<i>P</i>)- 11
C11-C12	1.567(3)	1.565(5)	1.539(4)
C21-C24	1.564(3)	1.565(5)	1.550(3)
C11-C13	1.546(3)	1.555(5)	1.528(4)
C21-C23	1.543(3)	1.555(5)	1.544(3)
C11-C14	1.537(3)	1.539(5)	1.536(4)
C21-C22	1.542(3)	1.539(5)	1.534(3)
C1-C11	1.556(3)	1.558(5)	1.558(3)
C8-C21	1.558(3)	1.558(5)	1.557(2)
C1-C9	1.457(3)	1.441(5)	1.454(2)
C8-C9	1.450(3)	1.441(5)	1.443(2)
C1-C2	1.375(3)	1.378(5)	1.377(2)
C8-C7	1.376(3)	1.378(5)	1.376(2)
C2-C3	1.401(3)	1.405(6)	1.417(2)
C7-C6	1.404(3)	1.405(6)	1.420(2)
C3-C4	1.363(3)	1.366(6)	1.362(2)
C6-C5	1.359(3)	1.366(6)	1.361(2)
C4-C10	1.445(3)	1.435(5)	1.415(2)
C5-C10	1.422(3)	1.435(5)	1.417(2)
C9-C10	1.445(3)	1.441(7)	1.433(2)
C4-O1	1.365(3)	1.370(5)	-
C5-O2	1.407(2)	1.370(5)	-
C3-Br1	-	1.894(4)	-

Table S3. Bond angles of (*P,S*)-**6**, (*P*)-**9**, and (*P*)-**11**

Angles	(<i>P,S</i>)- 6	(<i>P</i>)- 9	(<i>P</i>)- 11
C1-C11-C12	105.34(16)	104.0(3)	104.5(2)
C8-C21-C24	104.90(16)	104.0(3)	106.6(2)
C1-C11-C13	113.14(16)	113.4(3)	113.3(2)
C8-C21-C23	113.87(17)	113.4(3)	112.9(2)
C1-C11-C14	115.19(17)	116.4(3)	115.5(2)
C8-C21-C22	115.01(16)	116.4(3)	113.6(2)
C12-C11-C13	106.91(16)	107.2(3)	108.9(2)
C24-C21-C23	106.78(17)	107.2(3)	106.5(2)
C13-C11-C14	109.98(17)	109.3(3)	108.7(2)
C23-C21-C22	110.33(16)	109.3(3)	111.9(2)
C12-C11-C14	105.54(17)	105.6(3)	105.3(2)
C24-C21-C22	105.05(17)	105.6(3)	104.7(2)
C11-C1-C9	125.68(17)	124.6(3)	125.6(1)
C21-C8-C9	124.86(17)	124.6(3)	125.8(1)
C11-C1-C2	115.94(18)	114.7(3)	114.3(2)
C21-C8-C7	115.32(17)	114.7(3)	114.5(1)
C2-C1-C9	115.75(18)	117.6(4)	117.4(1)
C7-C8-C9	117.48(18)	117.6(4)	117.6(1)
C1-C2-C3	124.1(2)	121.6(4)	124.5(2)
C8-C7-C6	122.56(19)	121.6(4)	124.6(2)
C2-C3-C4	118.97(19)	120.4(4)	116.2(1)
C7-C6-C5	118.57(19)	120.4(4)	115.8(1)
C3-C4-C10	119.40(19)	119.2(4)	121.8(1)
C6-C5-C10	121.79(18)	119.2(4)	121.7(1)
C1-C9-C10	116.83(17)	116.8(2)	115.1(1)
C8-C9-C10	116.62(17)	116.8(2)	115.0(1)
C4-C10-C9	118.60(18)	118.5(3)	120.5(1)
C5-C10-C9	117.68(17)	118.5(3)	120.6(1)
C1-C9-C8	126.54(18)	126.5(5)	129.9(1)
C4-C10-C5	123.70(18)	123.0(5)	118.9(1)
C3-C4-O1	124.19(19)	119.6(4)	-
C6-C5-O2	115.75(18)	119.6(4)	-
C10-C4-O1	116.40(18)	121.0(4)	-
C10-C5-O2	122.42(18)	121.0(4)	-
C4-C3-Br1	-	121.7(3)	-
C2-C3-Br1	-	117.6(3)	-

Table S4. Torsion angles of (P,S)-6, (P)-9, and (P)-11

Angles	(P,S)-6	(P)-9	(P)-11
C9-C1-C11-C12	101.2(2)	100.1(4)	101.1
C9-C8-C21-C24	106.1(2)	100.1(4)	111.9
C9-C1-C11-C13	-142.3(2)	-143.8(3)	-140.4
C9-C8-C21-C23	-137.5(2)	-143.8(3)	-131.7
C9-C1-C11-C14	-14.6(3)	-15.6(5)	-14.1
C9-C8-C21-C24	-8.8(3)	-15.6(5)	-2.9
C2-C1-C11-C12	-59.5(2)	-59.2(4)	-51.9
C7-C8-C21-C24	-56.1(2)	-59.2(4)	-51.0
C2-C1-C11-C13	56.9(3)	56.9(4)	58.6
C7-C8-C21-C23	60.3(2)	56.9(4)	65.5
C2-C1-C11-C14	-175.4(2)	-174.9(3)	-175.1
C7-C8-C21-C22	-170.9(2)	-174.9(3)	-165.8
C11-C1-C9-C8	45.9(3)	47.5(3)	42.1
C21-C8-C9-C1	43.5(3)	47.5(3)	41.8
C10-C9-C1-C2	26.5(3)	26.3(4)	23.1
C10-C9-C8-C7	25.5(3)	26.3(4)	23.6
C1-C9-C10-C4	-23.2(3)	-23.9(2)	-19.3
C8-C9-C10-C5	-22.0(3)	-23.9(2)	-19.2
C9-C1-C2-C3	-10.3(3)	-10.1(5)	-11.4
C9-C8-C7-C6	-11.3(3)	-10.1(5)	-11.7
C1-C2-C3-C4	-10.6(4)	-9.6(6)	-5.8
C8-C7-C6-C5	-7.2(3)	-9.6(6)	-6.5
C2-C3-C4-C10	14.3(3)	12.0(6)	10.3
C7-C6-C5-C10	10.9(3)	12.0(6)	11.6
C3-C4-C10-C9	2.7(3)	5.0(4)	2.5
C6-C5-C10-C9	4.0(3)	5.0(4)	1.5
C1-C2-C3-Br1	-	176.3(3)	-
Br1-C3-C4-O1	-	-0.1(5)	-
Br1-C3-C4-C10	-	-174.1(2)	-
O1-C4-C10-C5	-	11.1(3)	-
O1-C4-C10-C9	-	-168.9(3)	-

Table S5. Deviations from mean plane (defined by carbons 2, 4, 5, 7, 9, and 10)

	(6) ^a	6	(9) ^a	9	11
C1	-0.357(2)	-0.346(3)	-0.357(4)	-0.340(4)	-0.29
C2	-0.110(2)	-0.079(1)	-0.132(3)	-0.098(2)	-0.07
C3	0.242(2)	0.282(3)	0.226(3)	0.260(5)	0.21
C4	0.141(2)	0.170(1)	0.172(4)	0.189(4)	0.13
C5	-0.161(2)	-0.164(1)	-0.172(4)	-0.189(4)	
C6	-0.202(2)	-0.225(3)	-0.226(3)	-0.260(5)	
C7	0.128(2)	0.095(1)	0.132(3)	0.098(2)	
C8	0.349(2)	0.327(3)	0.357(4)	0.340(4)	
C9	-0.010(2)	-0.011(2)	0.000(0)	0.000(0)	
C10	-0.20(2)	-0.012(2)	0.000(0)	0.000(0)	
C11	-1.330(3)	-1.324(4)	-1.377(4)	-1.358(4)	-1.22
C21	1.311(3)	1.280(4)	1.377(4)	1.358(4)	
O1	0.197(3)	0.234(3)	0.406(4)	0.424(4)	
O2	-0.217(3)	-0.213(3)	-0.406(4)	-0.424(4)	
Br1	-	-	0.615(4)	0.672(6)	

^a Deviations from C₁₀ mean plane defined by all naphthalene carbons.

Table S6. Selected parameters of chiral naphthalenes (*P,S*)-**6**, (*P*)-**9**, and (*P*)-**11**

	(<i>P,S</i>)- 6	(<i>P</i>)- 9	(<i>P</i>)- 11
Bond length, Å			
C1-C11	1.556	1.558	1.558
Bond angle, deg			
C11-C1-C9	125.7	124.6	125.6
C1-C9-C8	126.5	126.5	129.9
Torsion angle, deg			
C11-C1-C9-C8	45.9	47.5	42.1
C1-C9-C10-C4	-23.2	-23.9	-19.3
Deviation from naphthalene mean plane, Å			
C1	-0.346	-0.340	-0.29
C11	-1.324	-1.358	-1.22

Pyramidalization values

The pyramidalization values of C1, C8, C4 and C5 for (*P*)-**9** were calculated as following,

$$\chi(\text{C1}) = \tau(\text{C9-C1-C11-C2}) - 180 \text{ deg} = -20.6 \text{ deg};$$

$$\chi(\text{C8}) = \tau(\text{C7-C8-C21-C9}) + 360 \text{ deg} - 180 \text{ deg} = +20.6 \text{ deg};$$

$$\chi(\text{C4}) = \tau(\text{C3-C4-O1-C10}) + 360 \text{ deg} - 180 \text{ deg} = +6.1 \text{ deg};$$

$$\chi(\text{C5}) = \tau(\text{C10-C5-O2-C6}) - 180 \text{ deg} = -6.1 \text{ deg}.$$

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